Electronic Supplementary Material (ESI) for ChemComm.

Rhodium-Catalyzed Diastereo- and Enantioselective Cyclopropanation of *α*-Boryl Styrenes

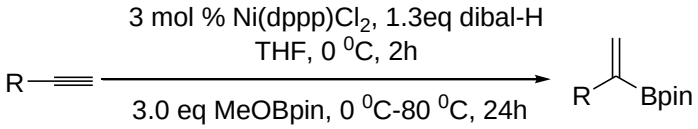
Supporting Information

Contents:

General.

All of the reagents were purchased from Acros, Sigma-Aldrich, AlfaAesar, Aladdin, Accela. or Adamas, and they were used as received. All of the solvents were distilled using the classic method before use. The reactions were monitored by thin-layer chromatography (TLC) on 2.5 × 10 cm, 250 μm analytical plates coated with silica gel 60 F254, and they were purchased from Qingdao Haiyang Chemical Co. Ltd. The thin-layer chromatography plates were visualized by exposure to the ultraviolet light (UV, 254 nm) or Phosphomolybdic acid. Purification of the synthetic compounds by the flash column chromatography employed the neutral silica gel (200-300 mesh or 300-400 mesh), which was purchased from Qingdao Haiyang Chemical Co. Ltd. The ^{1}H, ^{13}C and ^{19}F NMR spectra were recorded on a Bruker 400 MHz spectrometer, and the tetramethylsilane (δ = 0) was used as an internal standard, and $CDCl_3$ (δ = 7.26) for ^{1}H NMR (400 MHz) and $CDCl_3$ (δ = 77.16) for ^{13}C NMR (100 MHz). NMR multiplicities are abbreviated as follows: s = singlet, d = doublet, t = triplet, qui = quint, m = multiplet. The ^{13}C NMR were obtained with an APT technology [methyl and methine (down), methylene and quaternary carbon (up)]. The ^{11}B NMR spectra were recorded on Bruker AX-400 MHz instruments and spectral data were reported in ppm. The eantiomeric excess was determined with Daicel chiral columns on Shimadzu HPLC (Model: LC20AT). Optical rotation was measured by the AUTOPOL IV. The IR spectra were recorded on a Perkein Elmer with a potassium bromide crystal optic rectangle. High-resolution mass spectra (HRMS) were measured on an LTQ Orbitrap XL Domain35A (Thermo Fisher) spectrometer, and the electrospray ionization (ESI) was used as the ion source. X-ray diffraction data were collected on Agilent SuperNova Eos diffractometer.

Preparation of α-boryl styrenes 2



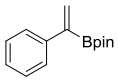
Representative preparation for α-boryl stryenes via Hoveyda's procedure[1]:

In an inert gas atmosphere, Ni (dppp)Cl_2 (81mg, 0.15 mmol, 0.03eq) was placed in a 100mL flask with a constant pressure dropping funnel and reflux condenser. Added tetrahydrofuran (THF, 10 mL) via syringe, and then dibal–H (6.5 mL, 6.5 mmol, 1.3eq) was added dropwise at 22 ℃. The resulting black solution was cooled to 0 ℃ (ice bath), and then phenylacetylene (510 mg, 5 mmol, 1eq) was slowly added dropwise over five minutes. Stirred for another 2 hours and the reaction system was cooled to 0 ℃ with the 2-methoxy-4,4,5,5-tetramethyl-1,3,2-dioxaborane (2.6 g, 15mmol, 3eq) added dropwise to the reaction solution. The resulting solution was heated to 80 ℃ and stirred for 24 hours. Then the reaction was quenched by adding water (15.0 mL) dropwise at 0 ℃ (ice bath). The mixture was allowed to warm to 22 ℃, stirred for an additional hour, and then washed with ether acetate (25.0 mL × 3). The combined organic layers were dried over anhydrous $MgSO_4$ and concentrated under vacuum. After chromatography the desired product was obtained as a yellow oil (0.82 g, 3.55 mmol, 71% yield). Further purification by vacuum distillation get white solid product **2a**, and the phase state was different from the literature's description.

Reference:

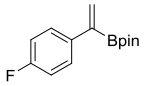
[1] F. Gao, A. H. Hoveyda, *J. Am. Chem. Soc.,* 2010, ***132***, 10961.

4,4,5,5-tetramethyl-2-(1-phenylvinyl)-1,3,2-dioxaborolane (2a)



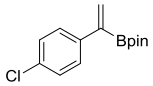
^{1}H NMR (400 MHz , $CDCl_3$) δ 7.48 (d, *J* = 7.6 Hz, 2H), 7.32 (t, *J* = 7.2 Hz, 2H), 7.24 (t, *J* = 7.6 Hz, 1H), 6.07 (t, *J* = 4.8 Hz, 2H), 1.32 (s, 12H) ppm. **^{13}C NMR** (100 MHz, $CDCl_3$) δ 141.5, 131.1, 128.5, 128.3, 128.1, 127.3, 127.2, 83.9 (2C), 25.0 (4C) ppm [Note: the carbon attached to boron was not observed due to quadrupole broadening caused by the ^{11}B nucleus]. **IR** $\tilde{\nu}$ (cm^{-1}) 1307, 1145, 887, 850. **M. P.** 44.0 – 45.8 °C. **Yield =** 71%.

2-(1-(4-fluorophenyl)vinyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (2b)



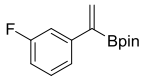
The compound is prepared as described in general procedure and is the light yellow solid. **^{1}H NMR** (400 MHz , $CDCl_3$) δ 7.47 – 7.43 （m, 2H）, 7.02 – 6.97 (m, 2H), 6.04 (s, 2H), 1.32 (s, 12H) ppm. **^{13}C NMR** (100 MHz, $CDCl_3$) δ 162.3 (d, *J* = 245 Hz), 137.5 (d, *J* = 3 Hz), 130.9, 128.9 (d, *J* = 8 Hz, 2C), 115.1 (d, *J* = 8 Hz, 2C), 84.0 (2C), 24.9 (4C) ppm [Note: the carbon attached to boron was not observed due to quadrupole broadening caused by the ^{11}B nucleus]. **^{19}F NMR** (376 MHz, $CDCl_3$) δ -116.11 ppm. **ESI-HR** calcd for $C_{14}H_{18}BFO_2H^+$ ($[M+H]^+$) 249.14567, found 249.14487. **IR** $\tilde{\nu}$ (cm^{-1}) 1317, 1145, 888, 851. **M. P.** 43.2 – 44.1 °C. **Yield =** 80%.

2-(1-(4-chlorophenyl)vinyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (2c)



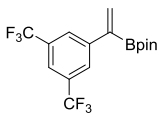
The compound is prepared as described in general procedure and is the light yellow solid. **^{1}H NMR** (400 MHz , $CDCl_3$) δ 7.41 (d, *J* = 8.4 Hz, 2H), 7.27 (d, *J* = 8.4 Hz, 2H), 6.07 (s, 2H), 1.32 (s, 12H) ppm. **^{13}C NMR** (100 MHz, $CDCl_3$) δ 140.0, 133.0, 131.5, 128.7 (2C), 128.4 (2C), 84.1 (2C), 24.9 (4C) ppm [Note: the carbon attached to boron was not observed due to quadrupole broadening caused by the ^{11}B nucleus]. **ESI-HR** calcd for $C_{14}H_{18}BClO_2H^+$ ($[M+H]^+$) 265.11611, found 265.11502. **IR** $\tilde{\nu}$ (cm^{-1}) 1318, 1145, 888, 851. **M. P.** 52.3 – 52.5 °C. **Yield =** 71%.

2-(1-(3-fluorophenyl)vinyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (2d).



The compound is prepared as described in the general procedure, and is the colorless oil. **^{1}H NMR** (400 MHz , $CDCl_3$) δ 7.28 – 7.25 (m, 2H), 7.23 – 7.19 (m, 1H), 6.96 – 6.91 (m, 1H)，6.10 (s, 2H)，1.32 (s, 12H) ppm. **^{13}C NMR** (100 MHz, $CDCl_3$) δ 164.2, 132.1, 129.7(d, *J* = 8 Hz), 123.0 (d, *J* = 2 Hz), 114.3(d, *J* = 21 Hz), 113.9(d, *J* = 22 Hz), 84.1 (2C), 25.0 (4C) ppm [Note: the carbon attached to boron was not observed due to quadrupole broadening caused by the ^{11}B nucleus]. **^{19}F NMR** (376 MHz, $CDCl_3$) δ -114.03 ppm. **ESI-HR** calcd for $C_{14}H_{18}BFO_2H^+$ ($[M+H]^+$) 249.14567, found 249.14459. **IR** $\tilde{\nu}$ (cm^{-1}) 1317, 1143, 868, 851. **Yield =** 67%.

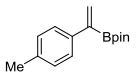
2-(1-(3,5-bis(trifluoromethyl)phenyl)vinyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (2e)



The compound is prepared as described in the general procedure, and is the

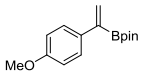
yellow oil. **^{1}H NMR** (400 MHz , $CDCl_3$) δ 7.92 (s, 2H), 7.75 (s, 1H), 6.25 (d, *J* = 2.4 Hz, 1H), 6.19 (d, *J* = 2.0 Hz, 1H), 1.32(s, 12H) ppm. **^{13}C NMR** (100 MHz, $CDCl_3$) δ 143.5, 134.2 (2C), 131.5 (dd, *J* = 33 Hz, 2C), 127.6 (d, *J* = 3 Hz, 2C), 125.0, 120.8 (qui , *J* = 3.8 Hz), 84.5 (2C), 25.0 (4C) ppm [Note: the carbon attached to boron was not observed due to quadrupole broadening caused by the ^{11}B nucleus]. **^{19}F NMR** (376 MHz, $CDCl_3$) δ -62.91 ppm. **ESI-HR** calcd for $C_{16}H_{17}BF_6O_2H^+$ ($[M+H]^+$) 367.12986, found 367.13028. **IR** ṽ (cm^{-1}) 1324, 1135, 806, 847. **Yield =** 68%.

4,4,5,5-tetramethyl-2-(1-(p-tolyl)vinyl)-1,3,2-dioxaborolane (2f)



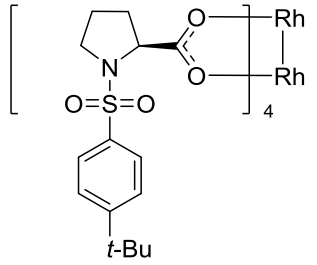
The compound is prepared as described in the general procedure. **^{1}H NMR** (400 MHz , $CDCl_3$) δ 7.37 (d, *J* = 8.0 Hz, 2H), 7.12 (d, *J* = 8.0 Hz, 2H), 6.04 (d, *J* = 2.4 Hz, 1H), 6.04 (d, *J*=2.4 Hz, 1H), 2.33 (s, 3H), 1.32 (s, 12H) ppm. **^{13}C NMR** (100 MHz, $CDCl_3$) δ 138.7, 136.8, 130.2, 129.0 (2C), 127.2 (2C), 83.9 (2C), 24.9 (4C), 21.3 ppm. [Note: the carbon attached to boron was not observed due to quadrupole broadening caused by the ^{11}B nucleus]. **ESI-HR** calcd for $C_{15}H_{21}BO_2H^+$ ($[M+H]^+$) 245.17074, found 245.16991. **IR** ṽ (cm^{-1}) 1307, 1144, 889, 852. **M. P.** 63.8 – 64.1 °C. **Yield =** 62%.

2-(1-(4-methoxyphenyl)vinyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (2g)

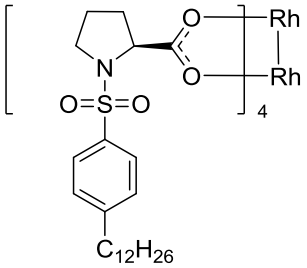


^{1}H NMR (400 MHz , $CDCl_3$) δ 7.45 (dd, *J* = 2.4, 4.4 Hz, 2H), 6.86 (dd, *J* = 2.4, 4.4 Hz, 2H), 6.01 (d, *J* = 2.8 Hz, 1H), 5.96 (d, *J* = 2.8 Hz, 1H), 3.80 (s, 3H), 1.32 (s, 12H) ppm. **^{13}C NMR** (100 MHz, $CDCl_3$) δ 159.0, 134.1, 129.2, 128.4 (2C), 113.8 (2C), 83.9 (2C), 55.4, 24.8 (4C) ppm [Note: the carbon attached to boron was not observed due to quadrupole broadening caused by the ^{11}B nucleus]. **ESI-HR** calcd for $C_{15}H_{21}BO_3H^+$ ($[M+H]^+$) 261.16565, found 261.16449. **IR** ṽ (cm^{-1}) 1303, 1145, 889, 852. **M. P.** 44.9 – 46.1 °C. **Yield =** 72%.

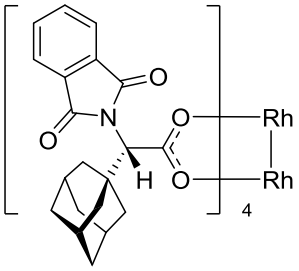
The Structures of Rh Catalyst



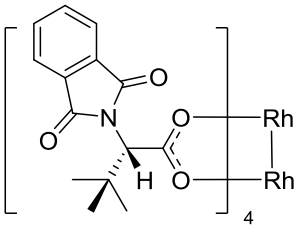
Rh_2(*S*-TBSP)$_4$



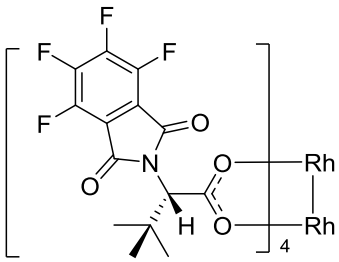
Rh_2(*S*-DOSP)$_4$



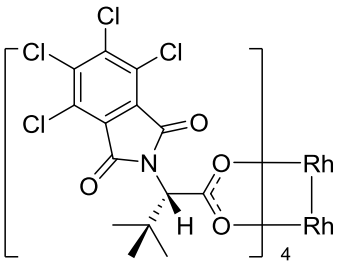
Rh_2(*S*-PTAD)$_4$



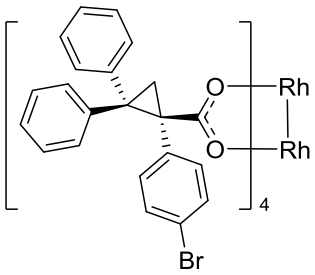
Rh_2(*S*-PTTL)$_4$



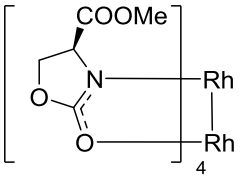
Rh_2(*S*-TFPTTL)$_4$



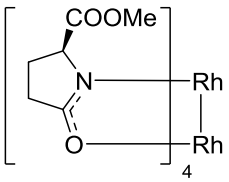
Rh_2(*S*-TCPTTL)$_4$



Rh_2(*S*-BTPCP)$_4$



Rh_2(4*S*-MEOX)$_4$



Rh_2(5*S*-MEPY)$_4$

Figure SI-1 The Structures of Rh Catalyst

The X-ray crystal structure of 3ba

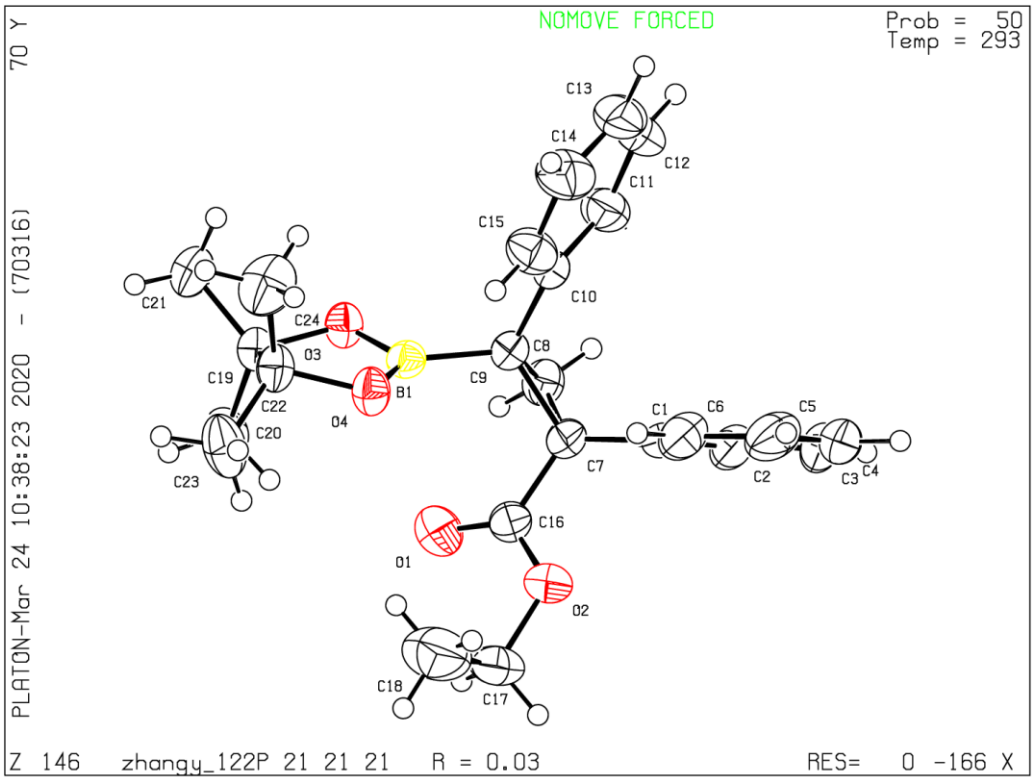


Figure SI-2 The X-ray crystal structure of 3ba

Single crystals of $C_{24}H_{29}BO_4$ were obtained from recrystallization of 3ba in methylene chloride. A suitable crystal was selected and intensity data were collected on a SuperNova (Dual,Cu at zero, Eos) diffractometer. The crystal was kept at 292.55(14) K during data collection. Using Olex2 [2], the structure was solved with the ShelXS [3] structure solution program using Direct Methods and refined with the ShelXL [4] refinement package using Least Squares minimisation.

REFERENCES:

[2]. Dolomanov, O. V., Bourhis, L. J., Gildea, R.J, Howard, J. A. K., Puschmann, H. *J. Appl. Cryst.*, **2009**, *42*, 339.

[3]. Sheldrick, G. M., *Acta Cryst.*, **2008**, *A64*, 112.

[4]. Sheldrick, G. M. *Acta Cryst.*, **2015**, *C71*, 3.

Crystal structure determination of 3ba

Crystal Data for $C_{24}H_{29}BO_4$ (M = 392.28 g/mol): orthorhombic, space group $P2_12_12_1$ (no. 19), a = 6.48035(14) Å, b = 17.3087 (3) Å, c = 19.7454(4) Å, V = 2214.77(8) Å^3, Z = 4, T = 292.55 (14) K, μ (CuK α) = 0.620 mm^{-1}, *Dcalc* = 1.176 g/cm^3, 6999 reflections measured (10.32° ≤ 2Θ ≤ 133.08°), 3762 unique (R_{int} = 0.0198, R_{sigma} = 0.0287) which were used in all calculations. The final R_1 was 0.0344 (> 2sigma(I)) and wR_2 was 0.0893 (all data).

Table 1 Crystal data and structure refinement for 3ba.

Identification code	3ba
Empirical formula	$C_{24}H_{29}BO_4$
Formula weight	392.28

Temperature/K	292.55(14)
Crystal system	orthorhombic
Space group	$P2_12_12_1$
a/Å	6.48035(14)
b/Å	17.3087(3)
c/Å	19.7454(4)
α/°	90.00
β/°	90.00
γ/°	90.00
Volume/$Å^3$	2214.77(8)
Z	4
$\rho_{calc}g/cm^3$	1.176
μ/mm^{-1}	0.620
F(000)	840.0
Crystal size/mm^3	0.21 × 0.15 × 0.14
Radiation	CuKα (λ = 1.54184)
2Θ range for data collection/°	10.32 to 133.08
Index ranges	$-7 \leq h \leq 4$, $-20 \leq k \leq 20$, $-23 \leq l \leq 17$
Reflections collected	6999
Independent reflections	3762 [R_{int} = 0.0198, R_{sigma} = 0.0287]
Data/restraints/parameters	3762/0/267
Goodness-of-fit on F^2	1.048
Final R indexes [I>=2σ (I)]	R_1 = 0.0344, wR_2 = 0.0874
Final R indexes [all data]	R_1 = 0.0367, wR_2 = 0.0893
Largest diff. peak/hole / e $Å^{-3}$	0.14/-0.12
Flack parameter	-0.14(17)

Table 2 Fractional Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Parameters ($Å^2 \times 10^3$) for 3ba. U_{eq} is defined as 1/3 of of the trace of the orthogonalised U_{IJ} tensor.

Atom	***x***	***y***	***z***	**U(eq)**
O1	-928(3)	-4591.9(8)	-6918.8(6)	69.4(4)
O2	521(2)	-5289.6(7)	-7746.5(6)	60.3(3)
O3	-1268.9(16)	-2656.0(6)	-6768.5(5)	39.3(2)
O4	1769.4(16)	-3177.4(6)	-7123.4(5)	42.7(3)
C1	-1468(3)	-4520.0(8)	-8778.4(8)	41.7(3)
C2	-3208(3)	-4833.1(9)	-9078.2(10)	53.8(4)

C3	-3165(4)	-5093.4(12)	-9742.8(11)	72.9(7)
C4	-1383(5)	-5046.1(11)	-10112.2(10)	74.3(7)
C5	365(5)	-4752.6(11)	-9819.5(11)	73.1(7)
C6	333(3)	-4491.6(10)	-9151.0(9)	57.6(5)
C7	-1568(2)	-4232.2(8)	-8061.1(8)	40.2(3)
C8	-3416(2)	-3765.3(9)	-7841.9(8)	43.8(3)
C9	-1400(2)	-3347.8(8)	-7913.9(7)	36.1(3)
C10	-1059(3)	-2802.6(8)	-8496.2(7)	37.9(3)
C11	-2660(3)	-2522.3(11)	-8886.9(10)	56.1(4)
C12	-2288(4)	-1991.3(12)	-9400.1(11)	69.2(6)
C13	-342(4)	-1736.5(11)	-9528.4(10)	69.8(6)
C14	1281(4)	-1997.9(12)	-9137.4(10)	67.4(5)
C15	921(3)	-2532.3(11)	-8625.9(9)	53.5(4)
C16	-646(3)	-4716.3(9)	-7510.0(8)	46.6(4)
C17	1581(4)	-5776.3(10)	-7246.7(12)	70.1(6)
C18	3593(4)	-5444.0(16)	-7061.7(15)	97.4(9)
C19	153(2)	-2549.8(9)	-6203.0(7)	38.0(3)
C20	-400(3)	-3161(1)	-5680.9(8)	52.3(4)
C21	-167(3)	-1746.8(10)	-5918.1(9)	56.1(4)
C22	2308(2)	-2696.0(9)	-6539.5(8)	41.8(3)
C23	3839(3)	-3130.9(14)	-6109.4(9)	64.2(5)
C24	3283(3)	-1968.0(13)	-6829.7(12)	72.2(6)
B1	-272(3)	-3083.2(9)	-7245.2(8)	35.3(3)

Table 3 Anisotropic Displacement Parameters ($Å^2 \times 10^3$) for 3ba. The Anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U_{11}+2hka^*b^*U_{12}+\cdots]$.

Atom	$\mathbf{U_{11}}$	$\mathbf{U_{22}}$	$\mathbf{U_{33}}$	$\mathbf{U_{23}}$	$\mathbf{U_{13}}$	$\mathbf{U_{12}}$
O1	100.9(11)	64.0(8)	43.2(7)	5.4(6)	-2.0(7)	3.3(8)
O2	85.1(9)	41.5(6)	54.3(7)	5.4(5)	-12.1(7)	10.6(6)
O3	35.0(5)	46.4(6)	36.5(5)	-6.2(4)	-1.7(4)	0.6(4)
O4	38.8(5)	53.2(6)	36.2(5)	-9.0(5)	-0.6(4)	3.5(5)
C1	55.8(9)	27.2(6)	42.1(8)	0.2(6)	-5.5(7)	2.1(6)
C2	60.6(11)	40.5(8)	60.3(10)	-11.5(8)	-13.9(9)	4.2(8)
C3	101.5(19)	51.7(11)	65.6(13)	-21.0(9)	-35.0(13)	15.7(11)
C4	132(2)	46.7(10)	44.3(10)	-8.1(8)	-14.0(13)	15.7(13)
C5	112.4(19)	47(1)	59.8(11)	-3.6(9)	26.3(12)	0.6(11)
C6	70.6(12)	44.1(8)	58.3(10)	-7.2(8)	8.9(9)	-4.7(8)

C7	47.2(8)	32.7(7)	40.8(8)	-1.2(6)	-2.9(7)	-5.6(6)
C8	40.9(8)	45.7(8)	44.8(8)	-4.1(7)	0.6(7)	-5.9(7)
C9	39.3(7)	32.8(7)	36.1(7)	-2.5(6)	-1.2(6)	-1.1(6)
C10	48.3(8)	31.1(6)	34.2(7)	-4.8(6)	-2.9(6)	2.0(6)
C11	59(1)	48.6(8)	60.8(11)	8.9(8)	-16.0(9)	-2.6(8)
C12	89.9(15)	59.2(11)	58.5(12)	18.4(10)	-20.9(11)	3.7(11)
C13	109.3(18)	51.8(10)	48.3(10)	14.0(8)	7.0(11)	3.7(11)
C14	73.2(13)	65.5(11)	63.5(12)	16.4(10)	17.9(10)	-3.4(11)
C15	51.7(9)	58.0(9)	50.8(10)	9.1(8)	5.4(8)	3.9(8)
C16	60.9(10)	35.5(7)	43.4(9)	4.5(6)	-5.8(7)	-12.3(7)
C17	92.5(15)	43.4(9)	74.3(13)	16.6(9)	-21.8(12)	-0.2(10)
C18	92.1(18)	79.2(15)	121(2)	26.1(15)	-32.6(17)	-4.2(14)
C19	38.6(7)	41.6(7)	33.8(7)	-4.5(6)	-2.0(6)	-2.2(6)
C20	55.1(9)	61.1(10)	40.7(8)	4.3(8)	2.7(7)	-7.9(9)
C21	66.9(12)	50.8(9)	50.6(9)	-14.2(8)	1.2(9)	2.4(8)
C22	38.9(7)	48.7(8)	37.8(8)	-6.7(7)	-1.7(6)	-6.3(6)
C23	43.0(9)	101.0(15)	48.8(10)	-10.8(10)	-9.2(8)	12.8(10)
C24	64.4(12)	72.4(13)	79.9(13)	-3.8(11)	17.2(11)	-29.1(11)
B1	39.2(8)	31.8(7)	35.0(8)	1.3(6)	2.0(7)	-3.5(6)

Table 4 Bond Lengths for 3ba.

Atom	**Atom**	**Length/Å**	**Atom**	**Atom**	**Length/Å**
O1	C16	1.201(2)	C7	C16	1.498(2)
O2	C16	1.332(2)	C8	C9	1.500(2)
O2	C17	1.468(2)	C9	C10	1.504(2)
O3	C19	1.4594(17)	C9	B1	1.577(2)
O3	B1	1.3604(19)	C10	C11	1.381(2)
O4	C22	1.4648(17)	C10	C15	1.390(2)
O4	B1	1.354(2)	C11	C12	1.389(3)
C1	C2	1.384(2)	C12	C13	1.360(3)
C1	C6	1.380(3)	C13	C14	1.381(3)
C1	C7	1.503(2)	C14	C15	1.389(3)
C2	C3	1.388(3)	C17	C18	1.471(4)
C3	C4	1.368(4)	C19	C20	1.520(2)
C4	C5	1.369(4)	C19	C21	1.514(2)
C5	C6	1.395(3)	C19	C22	1.567(2)
C7	C8	1.508(2)	C22	C23	1.507(2)

C7	C9	1.5618(19)	C22	C24	1.522(3)		

Table 5 Bond Angles for 3ba.

Atom	**Atom**	**Atom**	**Angle/°**	**Atom**	**Atom**	**Atom**	**Angle/°**
C16	O2	C17	117.22(15)	C15	C10	C9	119.20(14)
B1	O3	C19	107.33(11)	C10	C11	C12	120.61(19)
B1	O4	C22	107.70(12)	C13	C12	C11	120.79(19)
C2	C1	C7	119.85(16)	C12	C13	C14	119.72(18)
C6	C1	C2	118.35(16)	C13	C14	C15	119.8(2)
C6	C1	C7	121.80(15)	C14	C15	C10	120.85(18)
C1	C2	C3	121.0(2)	O1	C16	O2	124.11(17)
C4	C3	C2	120.1(2)	O1	C16	C7	123.01(17)
C3	C4	C5	119.69(18)	O2	C16	C7	112.87(14)
C4	C5	C6	120.5(2)	O2	C17	C18	110.93(18)
C1	C6	C5	120.4(2)	O3	C19	C20	106.41(12)
C1	C7	C8	118.84(13)	O3	C19	C21	108.26(13)
C1	C7	C9	119.82(12)	O3	C19	C22	102.59(10)
C8	C7	C9	58.46(10)	C20	C19	C22	112.66(13)
C16	C7	C1	118.81(13)	C21	C19	C20	110.78(13)
C16	C7	C8	114.10(14)	C21	C19	C22	115.34(14)
C16	C7	C9	112.66(12)	O4	C22	C19	102.32(11)
C9	C8	C7	62.56(10)	O4	C22	C23	108.43(14)
C7	C9	B1	118.20(12)	O4	C22	C24	105.88(14)
C8	C9	C7	58.98(10)	C23	C22	C19	115.35(14)
C8	C9	C10	120.19(13)	C23	C22	C24	110.64(17)
C8	C9	B1	117.67(13)	C24	C22	C19	113.34(15)
C10	C9	C7	118.89(12)	O3	B1	C9	121.12(13)
C10	C9	B1	112.93(11)	O4	B1	O3	113.99(13)
C11	C10	C9	122.49(15)	O4	B1	C9	124.51(14)
C11	C10	C15	118.21(15)				

Table 6 Torsion Angles for 3ba.

A	**B**	**C**	**D**	**Angle/°**	**A**	**B**	**C**	**D**	**Angle/°**
O3	C19	C22	O4	-24.04(14)	C9	C7	C16	O1	44.1(2)
O3	C19	C22	C23	-141.52(15)	C9	C7	C16	O2	-135.47(14)
O3	C19	C22	C24	89.49(16)	C9	C10	C11	C12	176.97(17)

C1	C2	C3	C4	0.3(3)	C9	C10	C15	C14	-176.72(16)
C1	C7	C8	C9	-109.15(15)	C10	C9	B1	O3	94.10(16)
C1	C7	C9	C8	107.49(17)	C10	C9	B1	O4	-78.38(18)
C1	C7	C9	C10	-2.3(2)	C10	C11	C12	C13	0.0(3)
C1	C7	C9	B1	-145.50(15)	C11	C10	C15	C14	-0.4(3)
C1	C7	C16	O1	-168.28(17)	C11	C12	C13	C14	-1.1(3)
C1	C7	C16	O2	12.2(2)	C12	C13	C14	C15	1.4(3)
C2	C1	C6	C5	1.9(3)	C13	C14	C15	C10	-0.7(3)
C2	C1	C7	C8	-43.11(19)	C15	C10	C11	C12	0.7(3)
C2	C1	C7	C9	-111.24(17)	C16	O2	C17	C18	-87.3(3)
C2	C1	C7	C16	103.48(18)	C16	C7	C8	C9	102.75(14)
C2	C3	C4	C5	1.1(3)	C16	C7	C9	C8	-105.24(15)
C3	C4	C5	C6	-0.9(3)	C16	C7	C9	C10	144.98(15)
C4	C5	C6	C1	-0.6(3)	C16	C7	C9	B1	1.8(2)
C6	C1	C2	C3	-1.7(2)	C17	O2	C16	O1	-2.5(3)
C6	C1	C7	C8	137.73(16)	C17	O2	C16	C7	177.09(16)
C6	C1	C7	C9	69.6(2)	C19	O3	B1	O4	-10.11(17)
C6	C1	C7	C16	-75.7(2)	C19	O3	B1	C9	176.67(12)
C7	C1	C2	C3	179.11(16)	C20	C19	C22	O4	89.97(14)
C7	C1	C6	C5	-178.99(16)	C20	C19	C22	C23	-27.52(19)
C7	C8	C9	C10	107.60(14)	C20	C19	C22	C24	-156.50(15)
C7	C8	C9	B1	-107.90(14)	C21	C19	C22	O4	-141.49(13)
C7	C9	C10	C11	84.44(19)	C21	C19	C22	C23	101.03(18)
C7	C9	C10	C15	-99.36(17)	C21	C19	C22	C24	-27.96(19)
C7	C9	B1	O3	-120.60(15)	C22	O4	B1	O3	-6.76(17)
C7	C9	B1	O4	66.9(2)	C22	O4	B1	C9	166.19(13)
C8	C7	C9	C10	-109.78(16)	B1	O3	C19	C20	-97.45(14)
C8	C7	C9	B1	107.00(15)	B1	O3	C19	C21	143.43(14)
C8	C7	C16	O1	-20.2(2)	B1	O3	C19	C22	21.05(14)
C8	C7	C16	O2	160.27(13)	B1	O4	C22	C19	19.13(15)
C8	C9	C10	C11	15.5(2)	B1	O4	C22	C23	141.45(14)
C8	C9	C10	C15	-168.27(14)	B1	O4	C22	C24	-99.80(16)
C8	C9	B1	O3	-52.88(19)	B1	C9	C10	C11	-130.52(16)
C8	C9	B1	O4	134.65(15)	B1	C9	C10	C15	45.68(19)

Table 7 Hydrogen Atom Coordinates ($Å \times 10^4$) and Isotropic Displacement Parameters ($Å^2 \times 10^3$) for 3ba.

Atom	***x***	***y***	***z***	**U(eq)**
H2	-4425	-4869	-8830	65
H3	-4349	-5300	-9937	87
H4	-1359	-5213	-10560	89
H5	1582	-4727	-10068	88
H6	1531	-4297	-8955	69
H8A	-4473	-3663	-8178	53
H8B	-3936	-3849	-7387	53
H11	-4001	-2691	-8806	67
H12	-3382	-1808	-9659	83
H13	-105	-1388	-9878	84
H14	2610	-1817	-9216	81
H15	2020	-2712	-8367	64
H17A	1782	-6289	-7433	84
H17B	731	-5824	-6844	84
H18A	4449	-5412	-7457	146
H18B	4248	-5767	-6730	146
H18C	3394	-4936	-6877	146
H20A	-1792	-3082	-5530	78
H20B	523	-3123	-5302	78
H2oC	-279	-3664	-5881	78
H21A	10	-1372	-6272	84
H21B	822	-1653	-5566	84
H21C	-1536	-1706	-5736	84
H23A	3325	-3641	-6021	96
H23B	4034	-2863	-5688	96
H23C	5132	-3165	-6344	96
H24A	4409	-2107	-7121	108
H24B	3786	-1651	-6467	108
H24C	2269	-1687	-7084	108

DFT Study

Details of DFT calculations

We have performed a DFT mechanistic study using Gaussian 09. The structures of Rh-carbene were optimized and characterized to be energy minima at the B3LYP/BSI level in the gas phase, where BSI denotes a basis set 6-31G (d) for atoms H, C, N, and O, SDD for atom Rh.

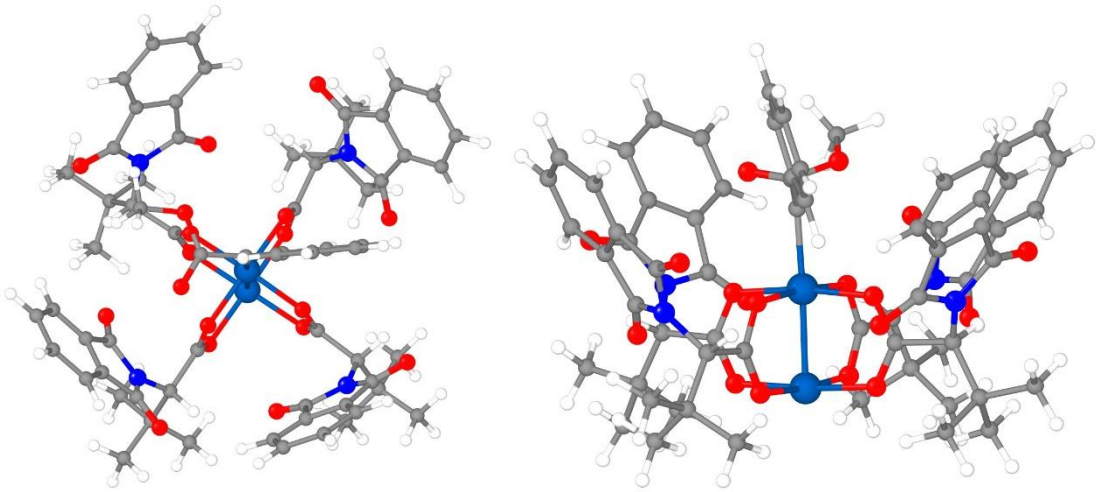


Figure SI-3 The Top view of Rh-carbenoid and the side view of Rh-carbenoid

Rh-carbenoid:

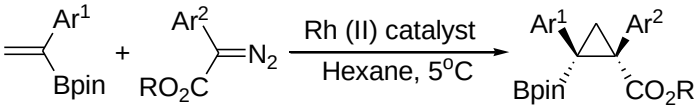
Rh	0.03543400	0.07072400	-0.08970800
Rh	0.07644800	-0.00689300	-2.55783200
N	-4.51231200	1.51534900	-0.33301400
N	2.20283000	4.17458700	-0.35063900
N	4.34090400	-1.76059200	-0.08088800
N	-1.91225900	-4.19902400	-0.17580000
O	-1.99193000	0.51176100	-0.25254700
O	-1.94550900	0.40352900	-2.51438200
O	-3.17846100	3.38215000	-0.77202000
O	-5.91739900	0.01787100	0.78107100
O	0.52747500	2.06899300	-0.27329700
O	0.53598200	2.01615500	-2.53783200
O	3.58410700	2.42054100	-1.01904300
O	1.15830000	5.77626000	0.98652300
O	2.03775400	-0.39833700	-0.19606200
O	2.08718400	-0.44929900	-2.45994500
O	2.79693000	-3.43244900	-0.60541500
O	5.79151700	-0.40283600	1.14456700
O	-0.40865800	-1.94406500	-0.13933400
O	-0.34695700	-2.02588800	-2.40379900
O	-0.84602800	-5.64477900	1.31432300
O	-3.37715500	-2.59670200	-1.02271500
C	-2.53700000	0.52888600	-1.40819100
C	-4.07815200	0.61013600	-1.40142000
H	-4.38030700	-0.38289800	-1.04714500
C	-4.81557900	0.83704800	-2.76948500
C	-4.60004300	-0.40569300	-3.66284400
H	-5.19507600	-0.30165600	-4.57824500
H	-4.92084600	-1.32191200	-3.15391900
H	-3.55277400	-0.52361600	-3.94439100

C	-4.35340400	2.10266600	-3.51762000
H	-4.91369400	2.19088500	-4.45676800
H	-3.28880300	2.05944100	-3.75827000
H	-4.53360800	3.01146200	-2.93576000
C	-6.33012600	0.95138000	-2.48536800
H	-6.87564600	0.99155800	-3.43492100
H	-6.57666200	1.86214800	-1.92817000
H	-6.70353900	0.09216800	-1.91707400
C	-4.02772900	2.81447600	-0.11180600
C	-4.74953500	3.32153200	1.09325700
C	-4.70265800	4.56411700	1.70929900
H	-4.07209900	5.35746000	1.31904000
C	-5.50678500	4.75224000	2.84202500
H	-5.50203600	5.71278400	3.34959900
C	-6.32199900	3.72185600	3.32931000
H	-6.93437200	3.89822700	4.20909800
C	-6.36292700	2.47172400	2.69692300
H	-6.99385800	1.66782800	3.06315400
C	-5.56612600	2.29838100	1.57441300
C	-5.40021600	1.11470800	0.68135200
C	0.71046700	2.58537500	-1.42787000
C	1.14796800	4.06869000	-1.36744200
H	0.29836400	4.59149700	-0.91042400
C	1.45166700	4.81417700	-2.70769000
C	0.14838400	4.88045900	-3.53448500
H	0.31465000	5.48730200	-4.43234100
H	-0.66289300	5.34932000	-2.96309200
H	-0.18244600	3.88853700	-3.84884000
C	1.87206400	6.25904400	-2.35913500
H	1.99142400	6.83922700	-3.28127000
H	2.82885900	6.28576500	-1.82633700
H	1.12422700	6.76163500	-1.73526900
C	2.56795800	4.15733100	-3.54177600
H	2.72299300	4.73964600	-4.45868100
H	2.31044800	3.13429800	-3.82335300
H	3.51736900	4.13046400	-2.99884700
C	3.27695200	3.27752200	-0.21182900
C	3.91818400	3.59445100	1.09419800
C	5.01056000	3.00695900	1.71788100
H	5.53181900	2.16588800	1.27095000
C	5.38392300	3.52398900	2.96643000
H	6.23125500	3.09092500	3.49035500
C	4.68073900	4.58391000	3.55461900
H	4.99867300	4.96170300	4.52254000

C	3.56900900	5.15573400	2.92086000
H	3.00778600	5.96698300	3.37423200
C	3.20517000	4.63870900	1.68585000
C	2.06065400	4.98419800	0.79469200
C	2.61803000	-0.55798900	-1.32021200
C	4.13037000	-0.83772300	-1.20119500
H	4.53939700	0.11375300	-0.84180100
C	4.92944600	-1.20377500	-2.49842100
C	4.92231800	0.01825800	-3.44405500
H	5.56906100	-0.18421200	-4.30638200
H	5.30436000	0.91346600	-2.93940000
H	3.91867700	0.23883600	-3.81146300
C	4.37772700	-2.43812400	-3.23695100
H	4.98338900	-2.62466300	-4.13279600
H	3.34188900	-2.28796500	-3.54913500
H	4.41683700	-3.33687400	-2.61450800
C	6.39405700	-1.47795300	-2.09086200
H	7.00249900	-1.62672400	-2.99026500
H	6.48450000	-2.38223500	-1.47902400
H	6.82202100	-0.64188000	-1.52613300
C	5.13792300	-1.42296500	1.02795700
C	5.01156400	-2.55850200	1.98581600
C	5.62516300	-2.77249400	3.21099200
H	6.32711900	-2.05097400	3.61734300
C	5.30145200	-3.95123500	3.89648600
H	5.76331300	-4.15665300	4.85826200
C	4.39097600	-4.87216600	3.36123400
H	4.16155300	-5.77809300	3.91551800
C	3.77459100	-4.64407300	2.12320400
H	3.06570600	-5.34927900	1.69963100
C	4.10457200	-3.47451100	1.45413600
C	3.62927200	-2.95151200	0.14111000
C	-0.50373500	-2.54093700	-1.26422300
C	-0.80199000	-4.05187000	-1.12800400
H	0.06523300	-4.45134800	-0.58883400
C	-0.95115300	-4.90604200	-2.42930900
C	0.38898100	-4.86960200	-3.19720100
H	0.34605700	-5.57010400	-4.03974600
H	1.22545900	-5.16820300	-2.55393200
H	0.60267500	-3.87374300	-3.58977800
C	-2.09639800	-4.43485000	-3.34491300
H	-3.06616400	-4.48819600	-2.84051000
H	-2.14410500	-5.08451300	-4.22779500
H	-1.94565000	-3.40699100	-3.68090700

C	-1.21929600	-6.36777200	-2.00692600
H	-2.18738500	-6.47644700	-1.50556900
H	-0.44403100	-6.74446400	-1.33034100
H	-1.23565800	-7.00832400	-2.89608300
C	-1.79910900	-4.95383700	1.00613400
C	-3.04817800	-4.69640700	1.78026100
C	-3.47702600	-5.21603800	2.99349800
H	-2.89123700	-5.96291200	3.52089600
C	-4.69207200	-4.73805500	3.50392700
H	-5.06380600	-5.12195500	4.44997100
C	-5.43272500	-3.76603300	2.81834400
H	-6.36353300	-3.40566600	3.24712300
C	-4.99311600	-3.24660700	1.59230000
H	-5.54578000	-2.47271500	1.06872600
C	-3.79657600	-3.74077700	1.09166400
C	-3.06913000	-3.40096900	-0.16292900
C	0.08167900	0.13252300	1.92049400
C	-0.23134800	1.23904400	2.77862300
C	0.16515500	1.24814700	4.14704700
C	-0.94533900	2.36187900	2.27945500
C	-0.12118500	2.33090800	4.96277400
H	0.73001100	0.41106200	4.54383700
C	-1.24159600	3.43541900	3.11036000
H	-1.26341800	2.36482000	1.24621000
C	-0.82720200	3.42549900	4.44524400
H	0.20102500	2.33095700	6.00004500
H	-1.78785000	4.28596900	2.71629300
H	-1.05251000	4.27335800	5.08700000
C	0.65055300	-1.07484000	2.57665100
O	1.84569200	-1.22344900	2.75213900
O	-0.29477300	-1.95387200	2.93954200
C	0.18557300	-3.18803300	3.51328900
H	-0.70815200	-3.71594200	3.84329000
H	0.71172500	-3.77345200	2.75749800
H	0.85229700	-2.98398700	4.35471300

Preparation of Cyclopropylboronates 3

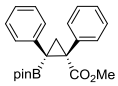


General procedure:

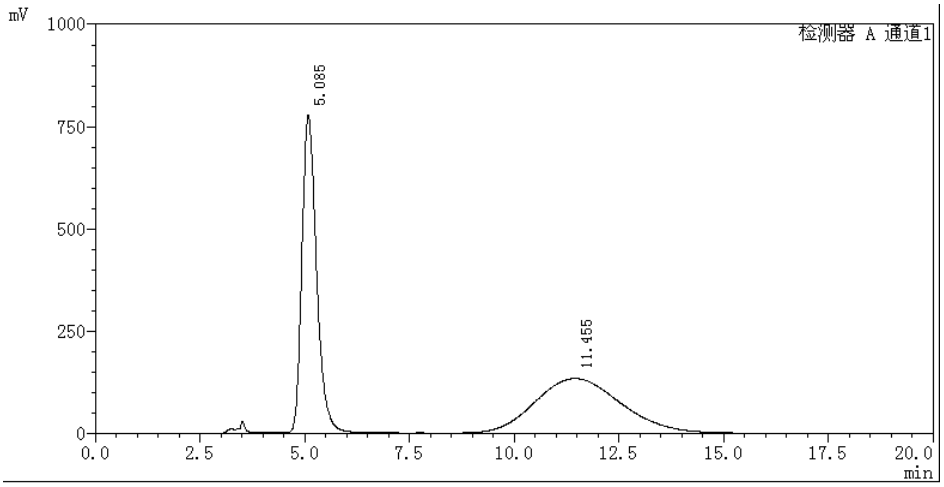
In an inert gas atmosphere, Rh (II) catalyst (0.2 mol % eq) was added into α-borylstyrenes **2** (2 eq) and hexane (3 mL) at 5 ^{o}C. Stirred for 30 min and then α-diazoarylacetates **1**(0.5 mmol) diluted in n-hexane (13 mL) was added dropwise over a period of 1h. The mixture was reacted for additional 30 min and the pure chiral cyclopropylborates **3** was obtained by flash chromatography.

It should be noted that the solution of α-diazoarylacetates **1** in hexane should be very slowly added into the mixture of α-borylstyrenes **2** and the dirhodium catalyst in all cases, otherwise some by-products would be formed, resulting in moderate yield.

Methyl (1*S*,2*R*)-1,2-diphenyl–2-(4,4,5,5–tetramethyl-1,3,2-dioxaborolan-2-yl) cyclopropane-1-carboxylate (3aa)



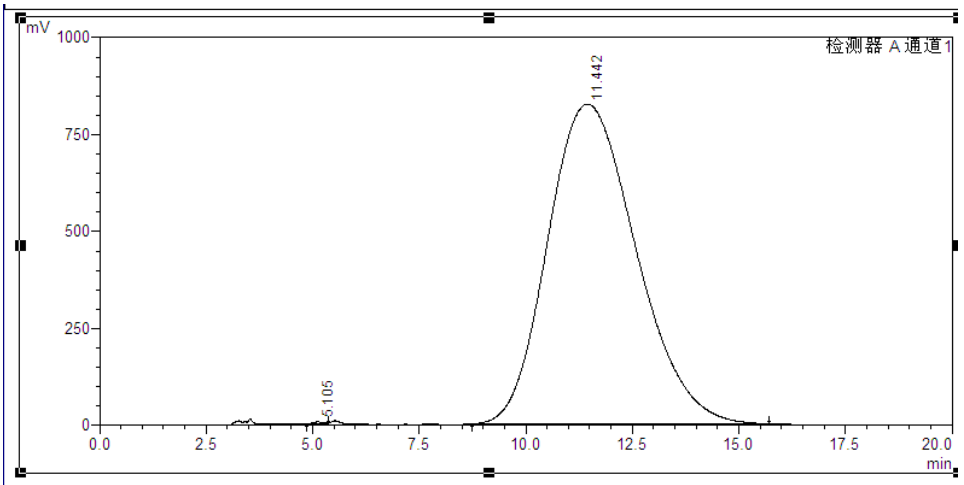
White solid, 99% ee (Daicel OJ-H 0.46*25 cm, *n*-Hexane : *i*-PrOH 97 : 3, 1 mL/min, 35 °C, 4.2 Mpa, t_R (minor) = 5.105 min, t_R (major) = 11.442 min); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.20 – 7.17 (m, 2H), 7.15 – 7.12 (m, 2H), 7.07 – 6.99 (m, 5H), 6.97 – 6.92 (m, 1H), 3.68 (s, 3H), 2.18 (d, *J* = 4.4 Hz, 1H), 2.09 (d, *J* = 4.4 Hz, 1H), 1.25 (s, 6H), 1.24 (s, 6H) ppm. **^{13}C NMR** (100 MHz, $CDCl_3$) δ 175.2, 137.4, 135.1, 131.5 (2C), 130.1 (2C), 127.6 (2C), 127.4 (2C), 126.8, 126.0, 83.8 (2C), 52.9, 40.3, 25.0 (2C), 24.3 (2C), 21.9 ppm [Note: the carbon attached to boron was not observed due to quadrupole broadening caused by the ^{11}B nucleus]. **^{11}B NMR** (128 MHz, $CDCl_3$) δ 30.36. **ESI-HR** calcd for $C_{23}H_{27}BO_4Na^+$ ($[M+Na]^+$) 401.18946, found 401.18979. **IR** ṽ (cm^{-1}) 1709, 1326, 1145. **M. P.** 112.0 – 112.1 °C. **Yield=** 87%. $[\alpha]_D^{20}$ = 16.1 (*c* = 1, MeOH) for a 99% ee sample. $[\alpha]_D^{20}$ = -9 (*c* = 1, CH_2Cl_2) for a 99% ee sample.



峰表

检测器 A Ch1 230nm

峰#	保留时间	面积	高度	面积 %	高度 %
1	5.085	18899584	776441	50.018	85.402
2	11.455	18885933	132721	49.982	14.598
总计		37785516	909162	100.000	100.000

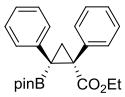


峰表

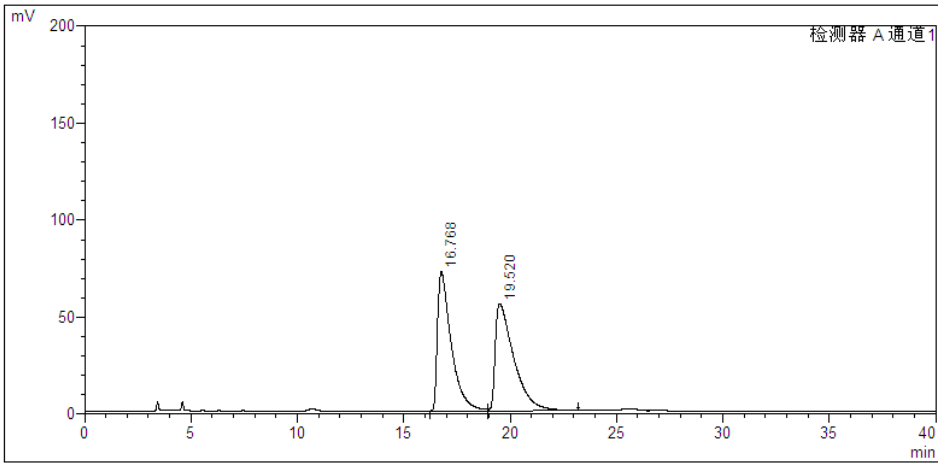
检测器 A Ch1 230nm

峰#	保留时间	面积	高度	面积 %	高度 %
1	5.105	124757	6153	0.105	0.740
2	11.442	119136258	825305	99.895	99.260
总计		119261015	831459	100.000	100.000

Ethyl (1*S*,2*R*)-1, 2-diphenyl–2-(4,4,5,5–tetramethyl-1,3,2-dioxaborolan-2-yl)cyclopropane-1-carboxylate (3ba)



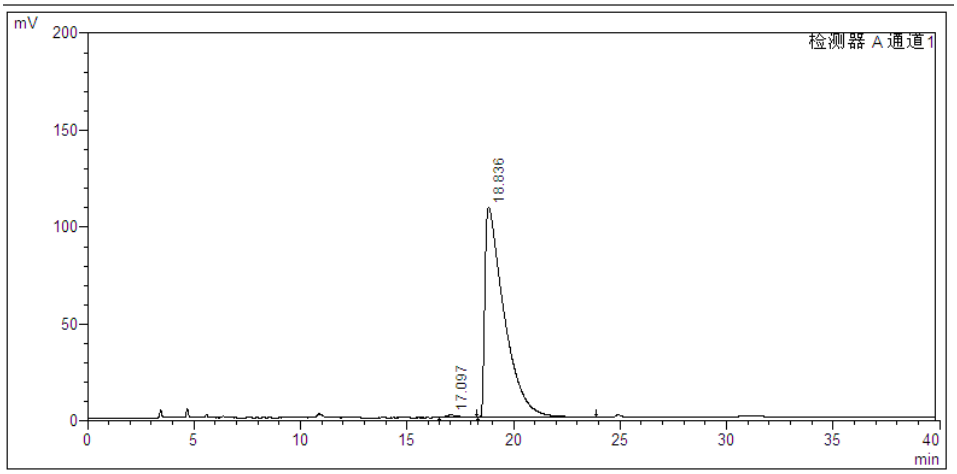
Electronic Supplementary Information (ESI) available: CCDC 1992721 contains the supplementary crystallographic data for this paper. For ESI and crystallographic data in CIF. White solid, 98% ee (Daicel OD-H 0.46*25 cm, *n*-Hexane : *i*-PrOH 99.9 : 0.1, 1 mL/min, 35 °C, 3.6 Mpa, t_R (minor) = 17.097 min, t_R (major) = 18.836 min); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.18 (d, *J* = 7.6 Hz, 2H), 7.12 (d, *J* = 8 Hz, 2H), 7.04 – 6.91 (m, 6H), 4.27 – 4.19 (m, 1H), 4.09 – 4.01 (m, 1H), 2.16 (d, *J* = 4.0 Hz, 1H), 2.07 (d, *J* = 4.0 Hz, 1H), 1.25 (s, 6H), 1.23 (s, 6H), 1.84 (t, *J* = 7.2 Hz, 3H) ppm. **^{13}C NMR** (100 MHz, $CDCl_3$) δ 174.8, 137.6, 135.1, 131.4 (2C), 130.1 (2C), 127.5 (2C), 127.3 (2C), 126.6, 125.9, 83.7 (2C), 61.6, 40.5, 25.0 (2C), 24.8 (2C), 21.8, 14.3 ppm [Note: the carbon attached to boron was not observed due to quadrupole broadening caused by the ^{11}B nucleus]. **ESI-HR** calcd for $C_{24}H_{29}BO_4Na^+$ ($[M+Na]^+$) 415.20511, found 415.20502. **IR** ν̃ (cm^{-1}) 1706, 1302, 1145. **M. P.** 139.3 – 139.5 °C. **Yield =** 90%. $[\alpha]_D^{20}$ = 26.0 (*c* = 1, MeOH) for a 98% ee sample.



峰表

检测器 A Ch1 230nm

峰#	保留时间	面积	高度	面积 %	高度 %
1	16.768	3230546	71534	49.293	56.459
2	19.520	3323265	55167	50.707	43.541
总计		6553811	126702	100.000	100.000

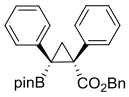


峰表

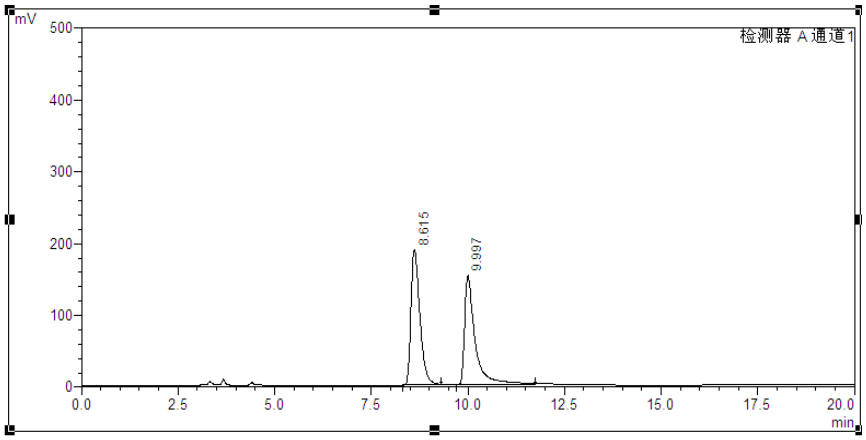
检测器 A Ch1 230nm

峰#	保留时间	面积	高度	面积 %	高度 %
1	17.097	57824	1304	0.835	1.188
2	18.836	6865632	108439	99.165	98.812
总计		6923456	109742	100.000	100.000

Benzyl (1*S*,2*R*)-1,2-diphenyl-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl) cyclopropane-1-carboxylate (3ca)



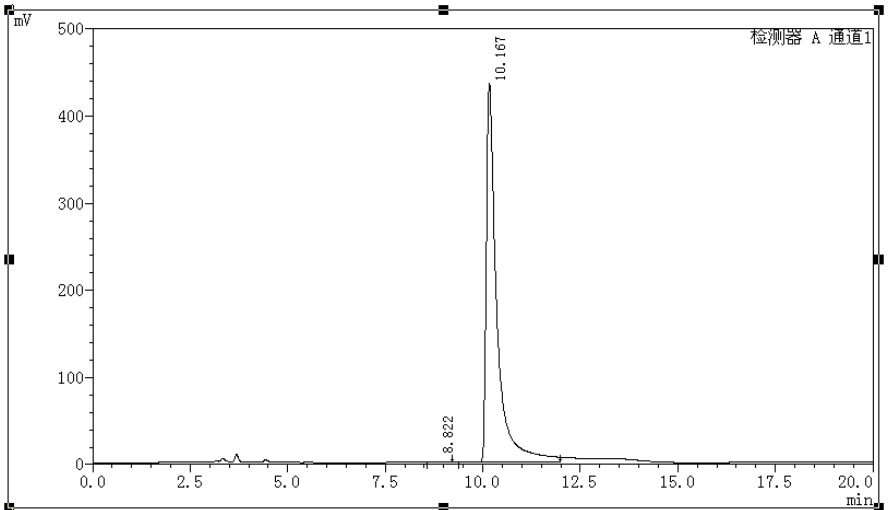
White solid, 99% ee (Daicel OD-H 0.46*25 cm, *n*-Hexane : *i*-PrOH 99.6 : 0.4, 1 mL/min, 35 °C, 3.9 Mpa, t_R (minor) = 8.822 min, t_R (major) =10.167 min); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.32 – 7.24 (m, 3H), 7.21 – 7.19 (m, 4H), 7.15 – 7.12 (m, 2H), 7.06 – 7.00 (m, 5H), 6.98 – 6.93 (m, 1H), 5.28 (d, *J* = 13.2 Hz, 1H), 5.03 (d, *J* = 13.2 Hz, 1H), 2.21 (d, *J* = 4.4 Hz, 1H), 2.12 (d, *J* = 4.4 Hz, 1H), 1.23 (s, 6H), 1.20 (s, 6H) ppm. **^{13}C NMR** (100 MHz, $CDCl_3$) δ 174.6, 137.5, 136.3, 134.9, 131.5 (2C), 130.1 (2C), 128.5 (2C), 127.8, 127.6 (2C), 127.3 (4C), 126.7, 126.0, 83.8 (2C), 66.9, 40.5, 25.0 (2C), 24.8 (2C), 22.0 ppm [Note: the carbon attached to boron was not observed due to quadrupole broadening caused by the ^{11}B nucleus]. **ESI-HR** calcd for $C_{29}H_{31}BO_4Na^+$ ([M+Na]$^+$) 477.22076, found 477.22070. **IR** ṽ (cm^{-1}) 1710, 1303, 1146. **M. P.** 102.3 – 102.9 °C. **Yield** = 96%. $[\alpha]_D^{20}$ = 15.8 (*c* = 1, MeOH) for a 99% ee sample.



峰表

检测器 A Ch1 230nm

峰#	保留时间	面积	高度	面积 %	高度 %
1	8.615	3025085	188233	50.556	55.228
2	9.997	2958491	152594	49.444	44.772
总计		5983576	340828	100.000	100.000

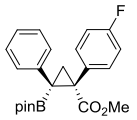


峰表

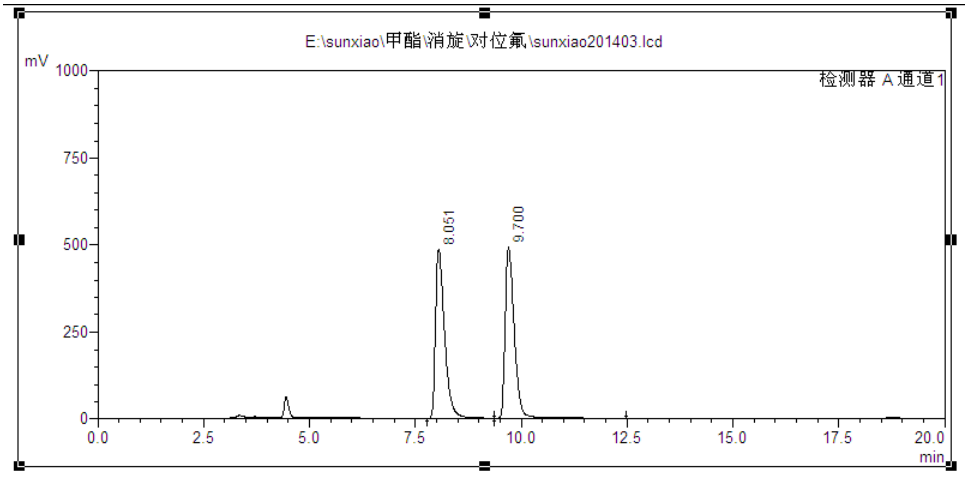
检测器 A Ch1 230nm

峰#	保留时间	面积	高度	面积 %	高度 %
1	8.822	12619	696	0.153	0.160
2	10.167	8244372	435130	99.847	99.840
总计		8256991	435826	100.000	100.000

Methyl (1*S*,2*R*)-1-(4-fluorophenyl)-2-phenyl-2-(4,4,5,5-tetramethyl-1,3,2- dioxaborolan-2-yl) cyclopropane-1-carboxylate (3da)



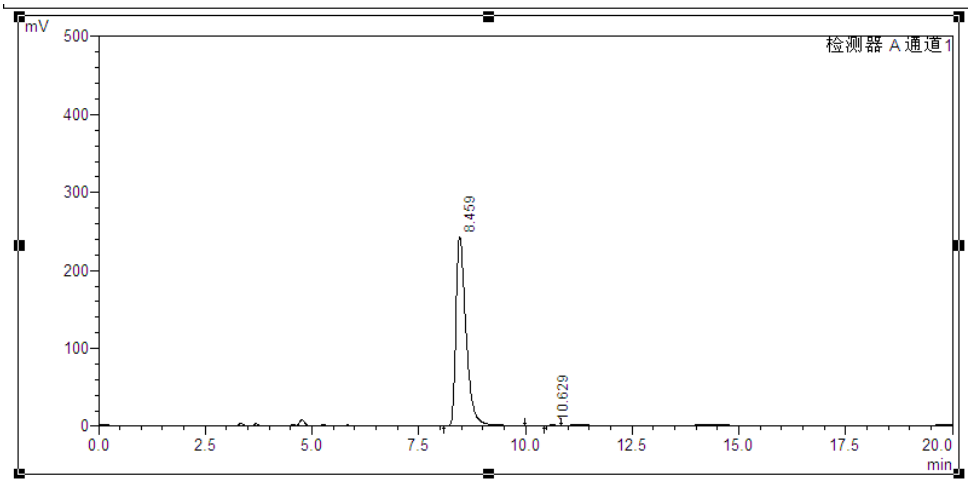
White solid, 99% ee (Daicel OD-H 0.46*25 cm, *n*-Hexane : *i*-PrOH 99.7 : 0.3, 1 mL/min, 35 °C, 3.9 Mpa, t_R (major) = 8.459 min, t_R (minor) =10.629 min); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.18 – 7.16 (m, 2H), 7.12 – 7.07(m, 2H), 7.06 – 7.02 (m, 2H), 6.99 – 6.95 (m, 1H), 6.75 – 6.70 (m, 2H), 3.67 (s, 3H), 2.13 (d, *J* = 4.4 Hz, 1H), 2.11 (d, *J* = 4.4 Hz, 1H), 1.25 (s, 6H), 1.23 (s, 6H) ppm. **^{13}C NMR** (100 MHz, $CDCl_3$) δ 174.9, 161.6 (F-C, *J* = 244 Hz), 137.2, 133.1 (F-C-C-C, *J* = 8 Hz, 2 C), 131.0 (F-C-C-C-C, *J* = 4 Hz), 130.0 (2C), 127.8 (2C), 126.2, 114.3 (F-C-C, *J* = 22 Hz, 2 C), 83.9, 52.8, 39.5, 25.0 (2C), 24.8 (2C), 22.0 ppm [Note: the carbon attached to boron was not observed due to quadrupole broadening caused by the ^{11}B nucleus]. **^{19}F NMR** (376 MHz, $CDCl_3$) δ -115.61 ppm. **ESI-HR** calcd for $C_{23}H_{26}BFO_4Na^+$ ($[M+Na]^+$) 418.18367, found 418.18307. **IR** ṽ (cm^{-1}) 1709, 1327, 1142. **M. P.** 138.5 – 138.7 °C. **Yield =** 95%. $[\alpha]_D^{20}$ = 6.0 (*c* = 1.1, MeOH) for a 99% ee sample.



峰表

检测器 A Ch1 230nm

峰#	保留时间	面积	高度	面积 %	高度 %
1	8.051	7266748	484750	49.418	49.696
2	9.700	7437938	490679	50.582	50.304
总计		14704686	975429	100.000	100.000

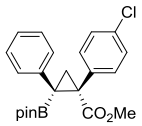


峰表

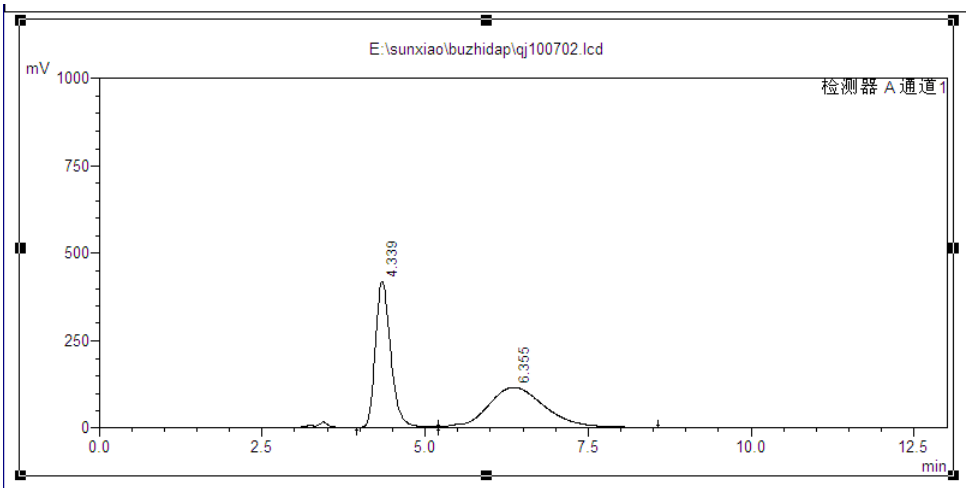
检测器 A Ch1 230nm

峰#	保留时间	面积	高度	面积 %	高度 %
1	8.459	3972374	241949	99.811	99.754
2	10.629	7503	598	0.189	0.246
总计		3979877	242546	100.000	100.000

Methyl (1*S*,2*R*)-1-(4–chlorophenyl)-2–phenyl–2-(4,4,5,5–tetramethyl–1,3,2- dioxaborolan –2-yl)cyclopropane-1-carboxylate (3ea)



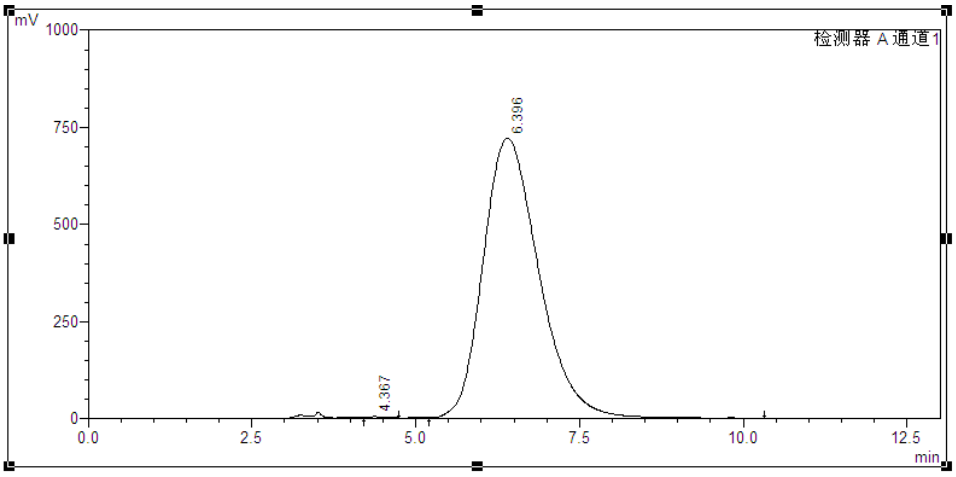
White solid, 99% ee (Daicel OJ-H 0.46*25 cm, *n*-Hexane : *i*-PrOH 97 : 3, 1 mL/min, 35 °C, 4.2 Mpa, t_R (minor) = 4.367 min, t_R (major) = 6.396 min); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.17 (d, *J* = 7.2 Hz, 2H), 7.08 – 6.96 (m, 7H), 3.67 (s, 3H), 2.12 (d, *J* = 4.4 Hz, 1H), 2.10 (d, *J* = 4.4 Hz, 1H), 1.25 (s, 6H), 1.23 (s, 6H) ppm. **^{13}C NMR** (100 MHz, $CDCl_3$) δ 174.7, 137.1, 133.8, 132.9 (2C), 132.6, 129.9 (2C), 127.8 (2C), 127.7 (2C), 126.3, 83.9 (2C), 52.9, 39.6, 25.0 (2C), 24.8 (2C), 22.0 ppm [Note: the carbon attached to boron was not observed due to quadrupole broadening caused by the ^{11}B nucleus]. **ESI-HR** calcd for $C_{23}H_{26}BClO_4Na^+$ ($[M+Na]^+$) 434.15412, found 434.15353. **IR** ṽ (cm^{-1}) 1715, 1310, 1145. **M. P.** 144.5 – 144.7 °C. **Yield =** 84%. $[\alpha]_D^{20}$ = 16.7 (*c* = 1.24, MeOH) for a 99% ee sample.



峰表

检测器 A Ch1 230nm

峰#	保留时间	面积	高度	面积 %	高度 %
1	4.339	6805063	418015	49.763	78.502
2	6.355	6869947	114477	50.237	21.498
总计		13675009	532492	100.000	100.000

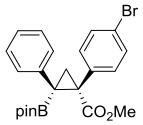


峰表

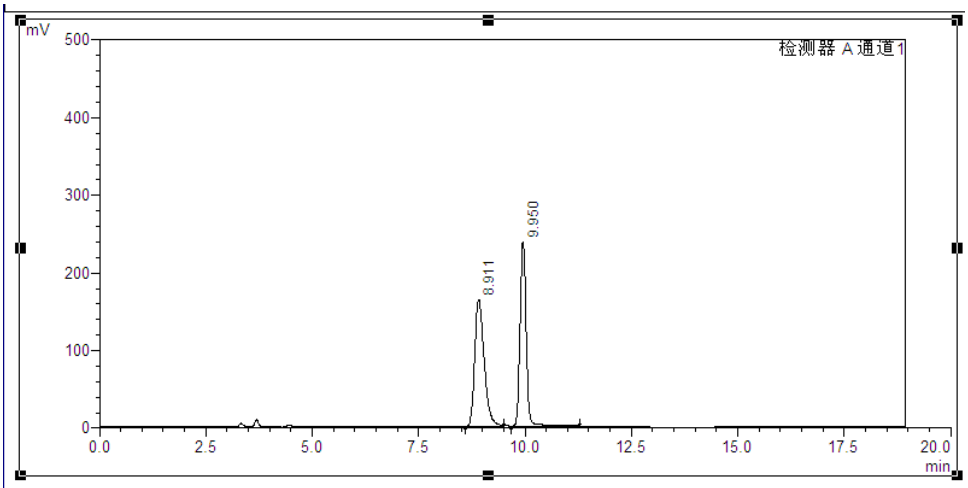
检测器 A Ch1 230nm

峰#	保留时间	面积	高度	面积 %	高度 %
1	4.367	124540	5573	0.289	0.767
2	6.396	42925760	721007	99.711	99.233
总计		43050300	726580	100.000	100.000

Methyl (1*S*, 2*R*)–1-(4-bromophenyl)-2- phenyl-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl) cyclopropane-1-carboxylate (3fa)



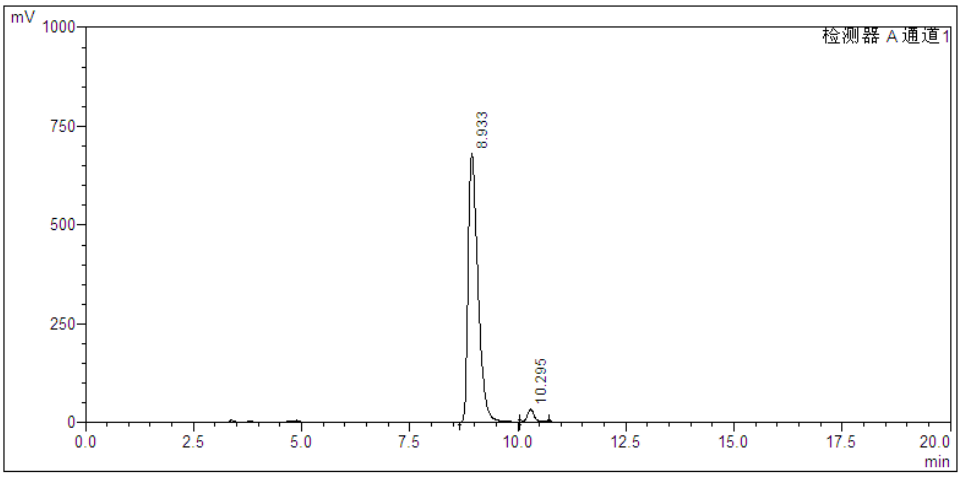
White solid, 94% ee (Daicel OD-H 0.46*25 cm, *n*-Hexane : *i*-PrOH 99.7 : 0.3, 1 mL/min, 35 °C, 3.9 Mpa, t_R (minor) = 10.295 min, t_R (major) = 8.933 min); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.19 – 7.16 (m, 4H), 7.07 – 6.97 (m, 5H), 3.67 (s, 3H), 2.12 (d, *J* = 4.8 Hz, 1H), 2.10 (d, *J* = 4.8 Hz, 1H), 1.25 (s, 6H), 1.23 (s, 6H) ppm. **^{13}C NMR** (100 MHz, $CDCl_3$) δ 174.6, 137.0, 134.4, 133.2 (2C), 130.6 (2C), 129.9 (2C), 127.9 (2C), 126.3, 120.9, 83.9 (2C), 52.9, 39.6, 25.0 (2C), 24.7 (2C), 21.9 ppm [Note: the carbon attached to boron was not observed due to quadrupole broadening caused by the ^{11}B nucleus]. **ESI-HR** calcd for $C_{23}H_{26}BBrO_4Na^+$ ([M+Na]$^+$) 479.09997, found 479.09915. **IR** ṽ (cm^{-1}) 1715, 1309, 1145. **M. P.** 167.6 – 168.3 °C . **Yield =** 89%. $[\alpha]_D^{20}$ = 17.8 (*c* = 0.37, MeOH) for a 94% ee sample.



峰表

检测器 A Ch1 230nm

峰#	保留时间	面积	高度	面积 %	高度 %
1	8.911	2565450	163856	50.979	40.802
2	9.950	2466879	237731	49.021	59.198
总计		5032329	401587	100.000	100.000

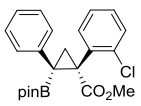


峰表

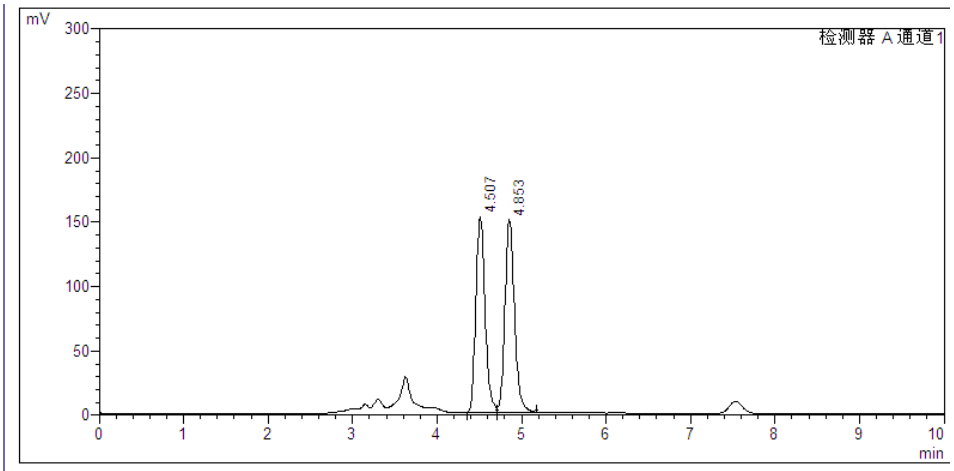
检测器 A Ch1 230nm

峰#	保留时间	面积	高度	面积 %	高度 %
1	8.933	10735678	678516	96.760	95.462
2	10.295	359534	32254	3.240	4.538
总计		11095212	710770	100.000	100.000

Methyl (1*S*, 2*R*) -1-(2-chlorophenyl)-2-phenyl-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl) cyclopropane-1-carboxylate (3ga)



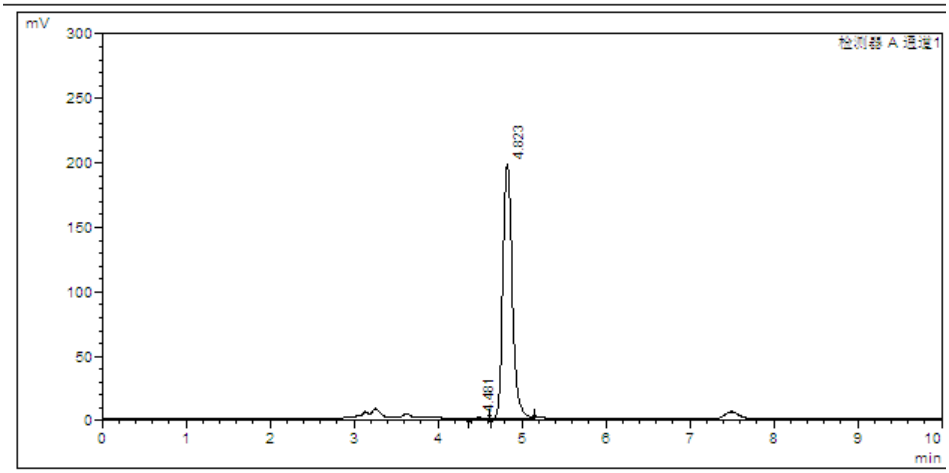
White solid, 99% ee (Daicel AD-H 0.46*25 cm, *n*-Hexane : *i*-PrOH 98 : 2, 1 mL/min, 35 °C, 3.2 Mpa, t_R (minor) = 4.481 min, t_R (major) = 4.823 min); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.19 (d, *J* = 7.2 Hz, 2H), 7.15 – 7.13 (m, 1H), 7.05 (t, *J* = 7.2 Hz, 2H), 7.01 – 6.93 (m, 4H), 3.68 (s, 3H), 2.14 (d, *J* = 4.4 Hz, 1H), 2.10 (d, *J* = 4.4 Hz, 1H), 1.26 (s, 6H), 1.23 (s, 6H) ppm. **^{13}C NMR** (100 MHz, $CDCl_3$) δ 174.5, 137.3, 136.9, 133.2, 131.8, 129.9 (2C), 129.7, 128.6, 127.8 (2C), 127.0, 126.3, 84.0 (2C), 52.9, 39.8, 25.0 (2C), 24.8 (2C), 21.9 ppm [Note: the carbon attached to boron was not observed due to quadrupole broadening caused by the ^{11}B nucleus]. **ESI-HR** calcd for $C_{23}H_{26}BClO_4Na^+$ ($[M+Na]^+$) 435.15049, found 435.15012. **IR** ṽ (cm^{-1}) 1718, 1311, 1147. **M. P.** 128.1 – 129.3 °C . **Yield =** 85%. $[\alpha]_D^{20}$ = 86.7 (*c* = 0.98, MeOH) for a 99% ee sample.



峰表

检测器 A Ch1 230nm

峰#	保留时间	面积	高度	面积 %	高度 %
1	4.507	1159699	152085	49.615	50.321
2	4.853	1177702	150144	50.385	49.679
总计		2337401	302229	100.000	100.000

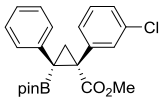


峰表

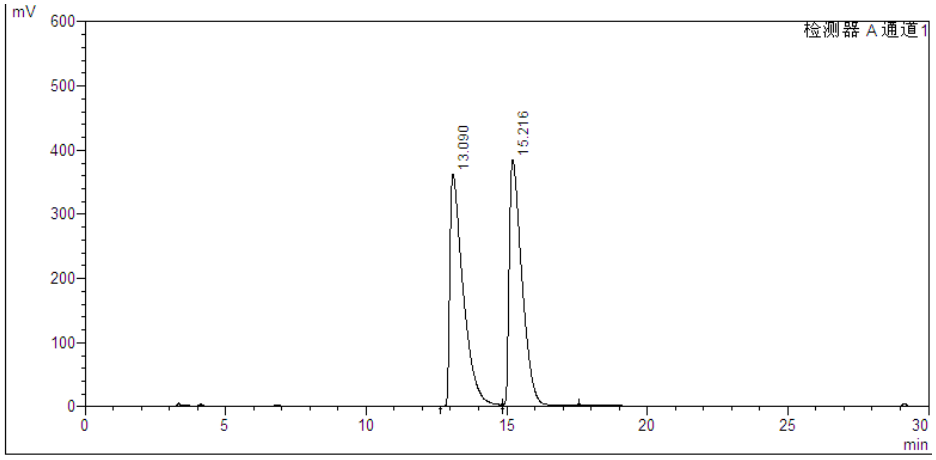
检测器 A Ch1 230nm

峰#	保留时间	面积	高度	面积 %	高度 %
1	4.481	3320	461	0.217	0.234
2	4.823	1524858	196840	99.783	99.766
总计		1528179	197301	100.000	100.000

Methyl (1*S*, 2*R*)-1 -(3-chlorophenyl)-2-phenyl-2-(4,4,5,5-tetramethyl-1, 3, 2- dioxaborolan- 2-yl) cyclopropane-1-carboxylate (3ha)



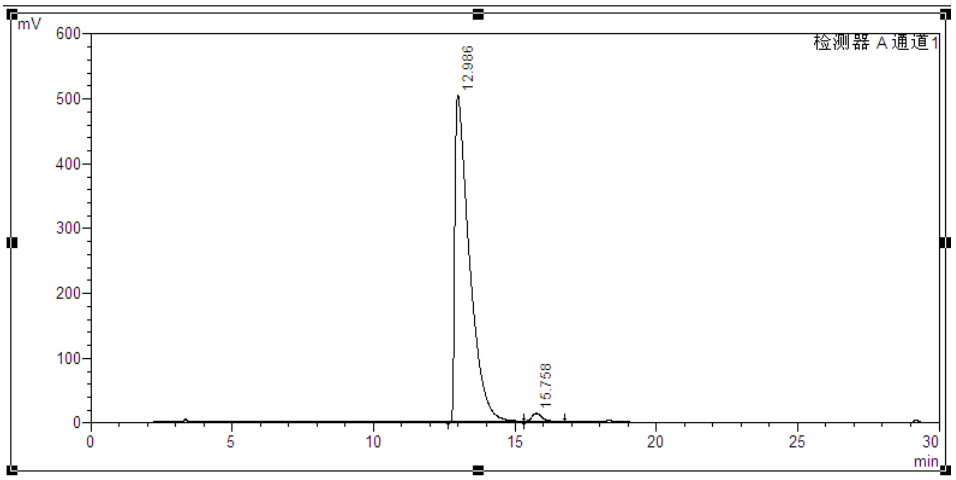
White solid, 96% ee (Daicel OD-H 0.46*25 cm, *n*-Hexane : *i*-PrOH 99.8 : 0.2, 1 mL/min, 35 °C, 4.0 Mpa, t_R (minor) = 15.758 min, t_R (major) = 12.986 min); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.34 – 7.32 (m, 2H), 7.17 (d, *J* = 8.0 Hz, 1H), 7.04 – 6.90 (m, 6H), 3.67 (s, 3H), 2.22 (d, *J* = 4.4 Hz, 1H), 2.04 (d, *J* = 4.4 Hz, 1H), 1.27 (s, 6H), 1.25 (s, 6H) ppm. **^{13}C NMR** (100 MHz, $CDCl_3$) δ 174.7, 137.2, 137.0, 134.0, 129.8 (2C), 129.4, 128.3 (2C), 127.5, 126.2, 125.9, 83.7 (2C), 53.0, 25.1 (2C), 24.8 (2C)ppm [Note: the carbon attached to boron was not observed due to quadrupole broadening caused by the ^{11}B nucleus]. **ESI-HR** calcd for $C_{23}H_{26}BClO_4H^+$ ($[M+H]^+$) 413.16854, found 413.16669. **IR** ν̃ (cm^{-1}) 1715, 1309, 1146. **M. P.** 140.1 – 140.7 °C. **Yield =** 88%. $[\alpha]_D^{20}$ = 16.0 (*c* = 1, MeOH) for a 96% ee sample.



峰表

检测器 A Ch1 230nm

峰#	保留时间	面积	高度	面积 %	高度 %
1	13.090	11912143	361732	49.725	48.502
2	15.216	12043753	384076	50.275	51.498
总计		23955896	745807	100.000	100.000

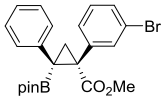


峰表

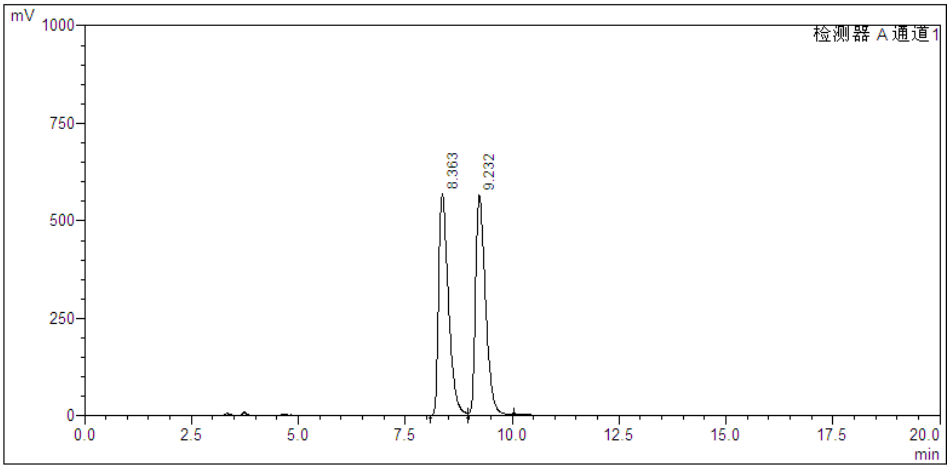
检测器 A Ch1 230nm

峰#	保留时间	面积	高度	面积 %	高度 %
1	12.986	18096346	504711	97.969	97.476
2	15.758	375207	13070	2.031	2.524
总计		18471553	517781	100.000	100.000

Methyl (1*S*,2*R*)-1-(3-bromophenyl)-2-phenyl-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl) cyclopropane-1-carboxylate (3ia)



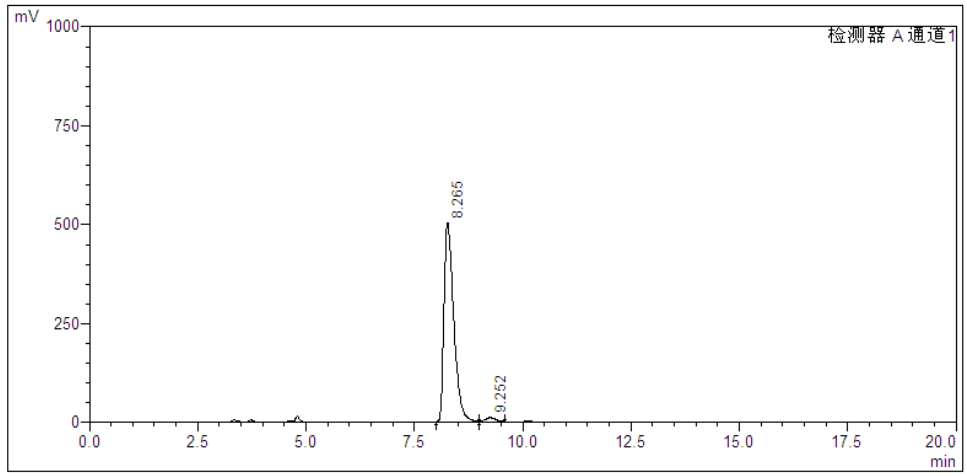
White solid, 96% ee (Daicel OD-H 0.46*25 cm, *n*-Hexane : *i*-PrOH 99.7 : 0.3, 1 mL/min, 35 °C, 3.9 Mpa, t_R (minor) = 9.252 min, t_R (major) = 8.265 min); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.30 (t, *J* = 1.6 Hz, 1H), 7.20 – 7.17 (m, 2H), 7.14 – 7.12 (m, 1H), 7.08 – 7.03 (m, 3H), 7.00 – 6.96 (m, 1H), 6.90 (t, *J* = 8.0 Hz, 1H), 3.68 (s, 3H), 2.14 (d, *J* = 4.8 Hz, 1H), 2.10 (d, *J* = 4.8 Hz, 1H), 1.25 (s, 6H), 1.23 (s, 6H) ppm. **^{13}C NMR** (100 MHz, $CDCl_3$) δ 174.5, 137.6, 136.9, 134.7, 130.2, 129.9 (3C), 128.9, 127.8 (2C), 126.3, 121.4, 84.0 (2C), 53.0, 39.7, 25.0 (2C), 24.8 (2C), 21.9 ppm [Note: the carbon attached to boron was not observed due to quadrupole broadening caused by the ^{11}B nucleus]. **^{11}B NMR** (128 MHz, $CDCl_3$) δ 30.36. **ESI-HR** calcd for $C_{23}H_{25}BCl_2O_4Na^+$ ($[M+Na]^+$) 469.11152, found 469.11148. **IR** ṽ (cm^{-1}) 1718, 1309, 1145. **M. P.** 133.5 – 133.9 °C. **Yield=** 96%. $[\alpha]_D^{20}$ = 9.2 (*c* = 1, MeOH) for a 96% ee sample.



峰表

检测器 A Ch1 230nm

峰#	保留时间	面积	高度	面积 %	高度 %
1	8.363	9059523	567920	49.673	50.196
2	9.232	9178654	563488	50.327	49.804
总计		18238177	1131408	100.000	100.000

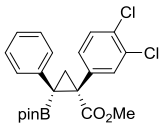


峰表

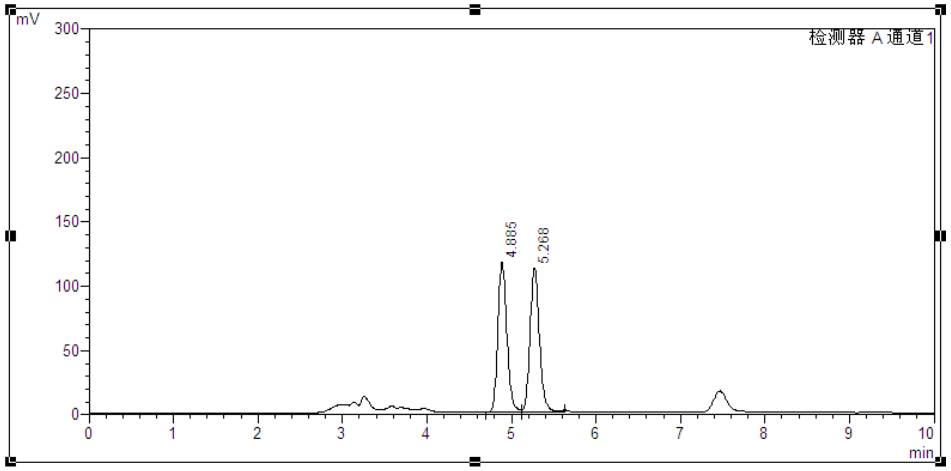
检测器 A Ch1 230nm

峰#	保留时间	面积	高度	面积 %	高度 %
1	8.265	7896582	503406	97.738	97.967
2	9.252	182738	10445	2.262	2.033
总计		8079319	513851	100.000	100.000

Methyl(1*S*,2*R*)-1-(3,4-dichlorophenyl)-2-phenyl-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl) cyclopropane-1-carboxylate (3ja)



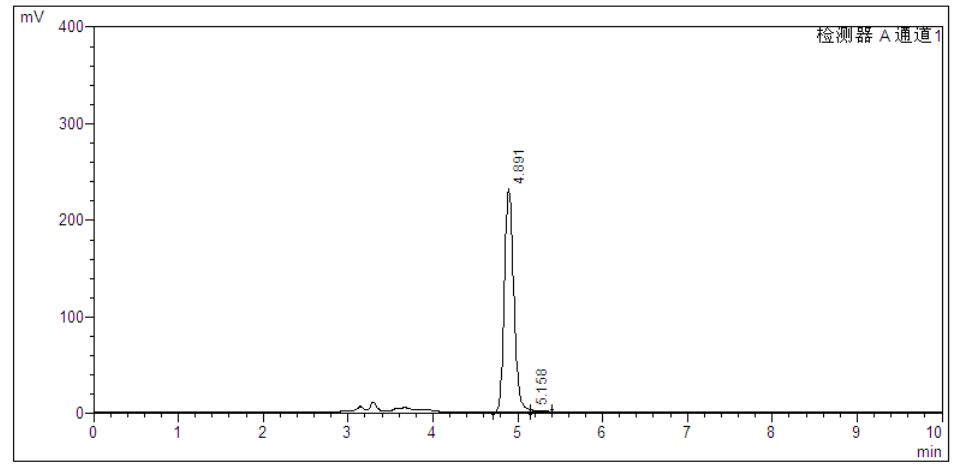
White solid, 98% ee (Daicel AD-H 0.46*25 cm, *n*-Hexane : *i*-PrOH 98 : 2, 1 mL/min, 35 °C, 3.2 Mpa, t_R (minor) = 5.158 min, t_R (major) = 4.891 min); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.23 (d, *J* = 2 Hz, 1H), 7.20 – 7.17 (m, 2H), 7.11 – 7.06 (m, 3H), 7.02 – 6.95 (m, 2H), 3.68(s, 3H), 2.12 (d, *J* = 4.4 Hz, 1H), 2.10 (d, *J* = 4.4 Hz, 1H), 1.25 (s, 6H), 1.23 (s, 6H) ppm. **^{13}C NMR** (100 MHz, $CDCl_3$) δ 174.1, 136.7, 135.7, 133.5, 131.4, 131.0, 130.9, 129.8 (2C), 129.3, 128.0, 126.6 (2C), 84.0 (2C), 53.0, 39.2, 25.0 (2C), 24.7 (2C), 22.0 ppm [Note: the carbon attached to boron was not observed due to quadrupole broadening caused by the ^{11}B nucleus]. **ESI-HR** calcd for $C_{23}H_{26}BBrO_4Na^+$ ($[M+Na]^+$) 479.09997, found 479.09854. **IR** ṽ (cm^{-1}) 1714, 1311, 1146. **M. P.** 124.3 – 124.5 °C. **Yield=** 85%. $[\alpha]_D^{20}$ = 19.0 (*c* = 1, MeOH) for a 98% ee sample.



峰表

检测器 A Ch1 230nm

峰#	保留时间	面积	高度	面积 %	高度 %
1	4.885	862548	116812	49.665	51.002
2	5.268	874169	112220	50.335	48.998
总计		1736717	229032	100.000	100.000

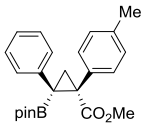


峰表

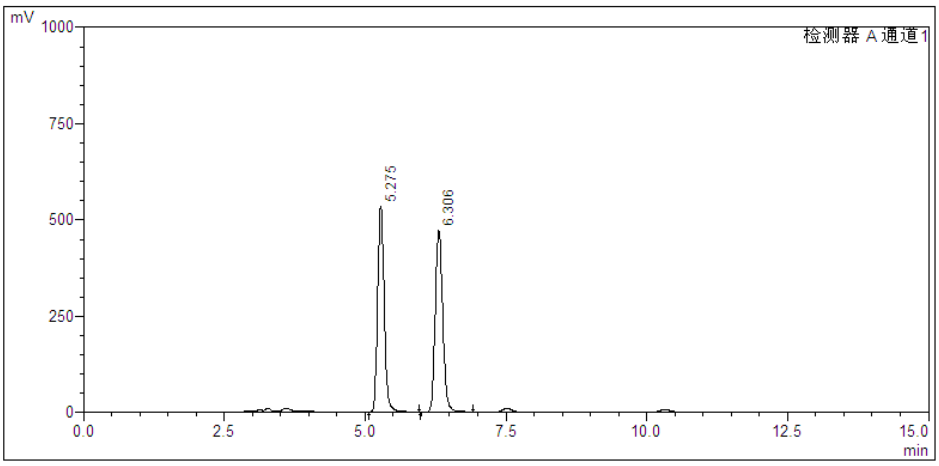
检测器 A Ch1 230nm

峰#	保留时间	面积	高度	面积 %	高度 %
1	4.891	1769421	231309	98.976	99.092
2	5.158	18311	2121	1.024	0.908
总计		1787733	233429	100.000	100.000

Methyl (1*S*,2*R*)-2-phenyl-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-1-(p-tolyl) cyclopropane-1-carboxylate (3ka)



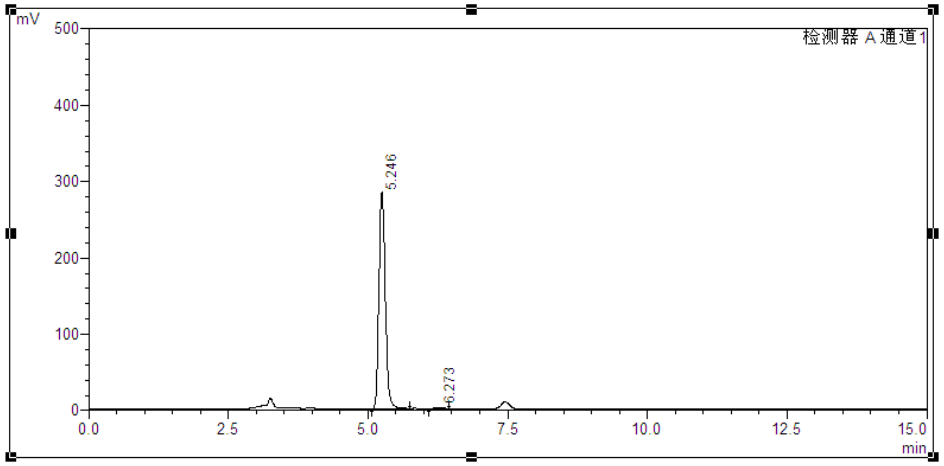
White solid, 98% ee (Daicel AD-H 0.46*25 cm, *n*-Hexane : *i*-PrOH 98 : 2, 1 mL/min, 35 °C, 3.2 Mpa, t_R (minor) = 6.273 min, t_R (major) = 5.246 min); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.20 – 7.18 (m, 2H), 7.06 – 7.01 (m, 4H), 6.97 – 6.93 (m, 1H), 6.85 (d, *J* = 8.0 Hz, 2H), 3.67 (s, 3H), 2.16 (s, 3H), 2.13 (d, *J* = 4.4 Hz, 1H), 2.07 (d, *J* = 4.4 Hz, 1H), 1.24 (s, 6H), 1.23 (s, 6H) ppm. **^{13}C NMR** (100 MHz, $CDCl_3$) δ 175.5, 137.6, 136.3, 132.0, 131.3 (2C), 130.1 (2C), 128.2 (2C), 127.6 (2C), 126.0, 83.7 (2C), 52.9, 40.0, 25.0 (2C), 24.8 (2C), 22.1, 21.2 ppm [Note: the carbon attached to boron was not observed due to quadrupole broadening caused by the ^{11}B nucleus]. **ESI-HR** calcd for $C_{24}H_{29}BO_4Na^+$ ($[M+Na]^+$) 415.20511, found 415.20514. **IR** ṽ (cm^{-1}) 1712, 1305, 1146. **M. P.** 127.3 – 128.1 °C. **Yield =** 96%. $[\alpha]_D^{20}$ = 16.8 (*c* = 1.2, MeOH) for a 98% ee sample.



峰表

检测器 A Ch1 230nm

峰#	保留时间	面积	高度	面积 %	高度 %
1	5.275	4303084	533344	49.968	53.032
2	6.306	4308583	472355	50.032	46.968
总计		8611667	1005699	100.000	100.000

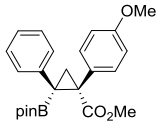


峰表

检测器 A Ch1 230nm

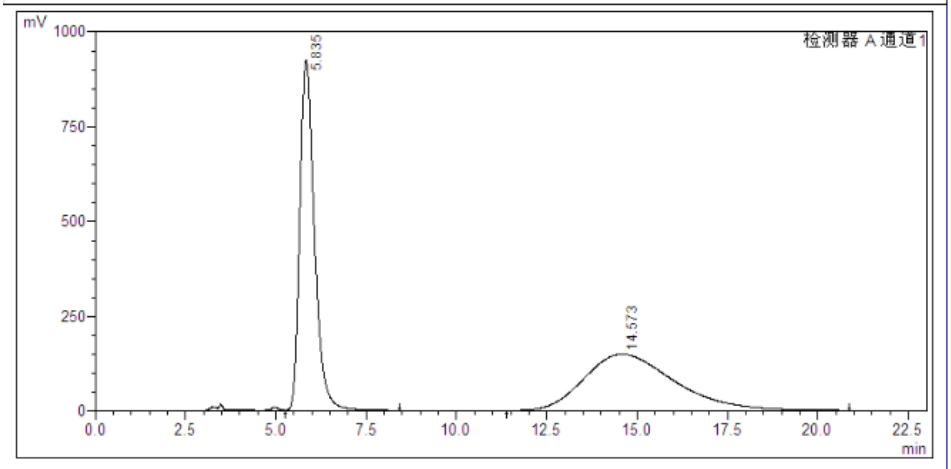
峰#	保留时间	面积	高度	面积 %	高度 %
1	5.246	2242780	284918	99.011	99.355
2	6.273	22399	1851	0.989	0.645
总计		2265179	286769	100.000	100.000

Methyl(1*S*,2*R*)-1-(4-methoxyphenyl)-2-phenyl-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl) cyclopropane-1-carboxylate (3la)



White solid, 99% ee (Daicel OJ-H 0.46*25 cm, *n*-Hexane : *i*-PrOH 97 : 3, 1 mL/min, 35 °C, 4.2 Mpa, t_R (minor) = 5.857 min, t_R (major) = 14.277 min); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.18 (d, *J* = 7.2 Hz, 2H), 7.05 – 7.00 (m, 4H), 6.94 – 6.92 (t, *J* = 7.2 Hz, 1H), 6.55 (d, *J* = 8.8 Hz, 2H), 3.63 (s, 3H), 3.58 (s, 3H), 2.10 (d, *J* = 4.0 Hz, 1H), 2.07 (d, *J* = 4.0Hz, 1H), 1.24 (s, 6H), 1.22 (s, 6H) ppm. **^{13}C NMR** (100 MHz, $CDCl_3$) δ 175.3, 158.1, 137.5, 132.4 (2C), 129.9 (2C), 127.5 (2C), 127.1, 125.9, 112.7 (2C), 83.6 (2C), 54.9, 52.66, 39.5, 24.9 (2C), 24.7 (2C), 22.0 ppm [Note: the carbon attached to boron was not observed due to quadrupole broadening caused by the ^{11}B nucleus]. **ESI-HR** calcd for $C_{24}H_{29}BO_5Na^+$ ($[M+Na]^+$) 431.20003, found 431.20090. **IR** ṽ (cm^{-1}) 1712, 1307, 1146. **M. P.** 136.7-136.8 °C. **Yield =** 99%. $[\alpha]_D^{20}$ = 6.3 (*c* = 0.67, MeOH) for a 99% ee sample.

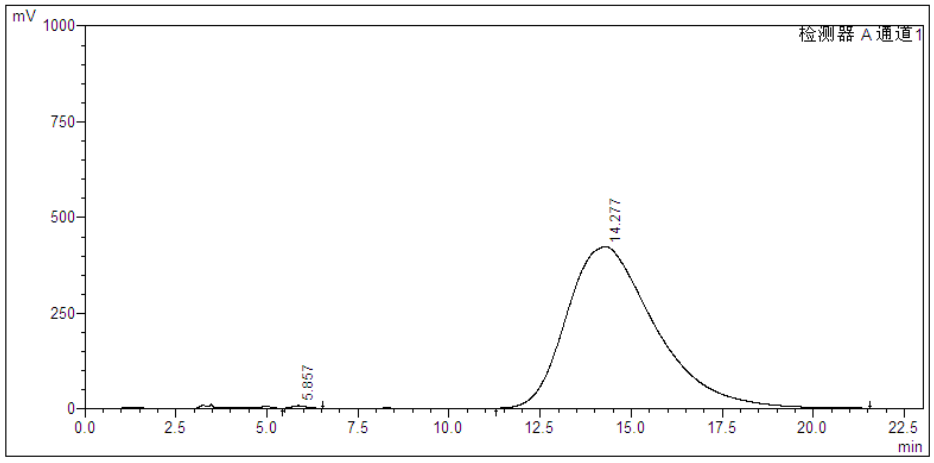
<色谱图>



峰表

检测器 A Ch1 230nm

峰#	保留时间	面积	高度	面积 %	高度 %
1	5.835	26032071	923270	50.229	86.177
2	14.573	25794873	148100	49.771	13.823
总计		51826944	1071370	100.000	100.000

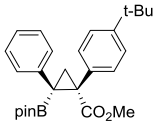


峰表

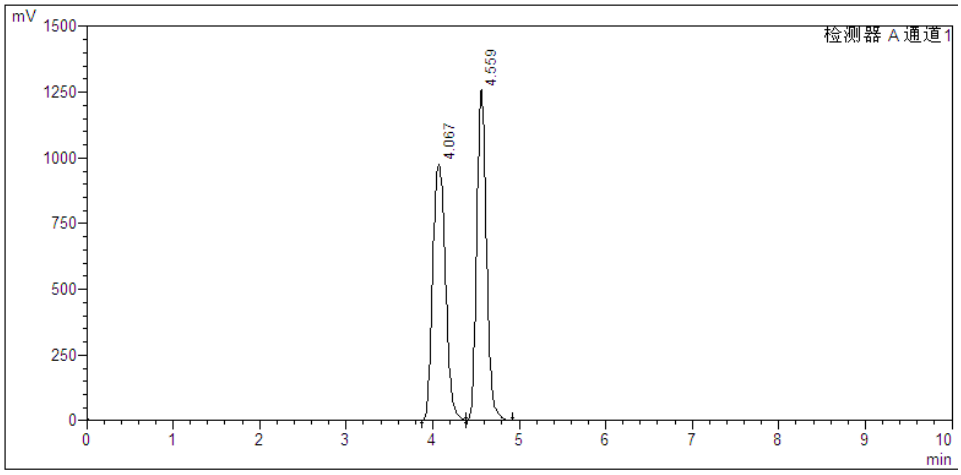
检测器 A Ch1 230nm

峰#	保留时间	面积	高度	面积 %	高度 %
1	5.857	250297	7771	0.347	1.802
2	14.277	71877655	423479	99.653	98.198
总计		72127952	431251	100.000	100.000

Methyl(1*S*,2*R*)-1-(4-(tert-butyl)phenyl)-2-phenyl-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl) cyclopropane-1–carboxylate (3ma)



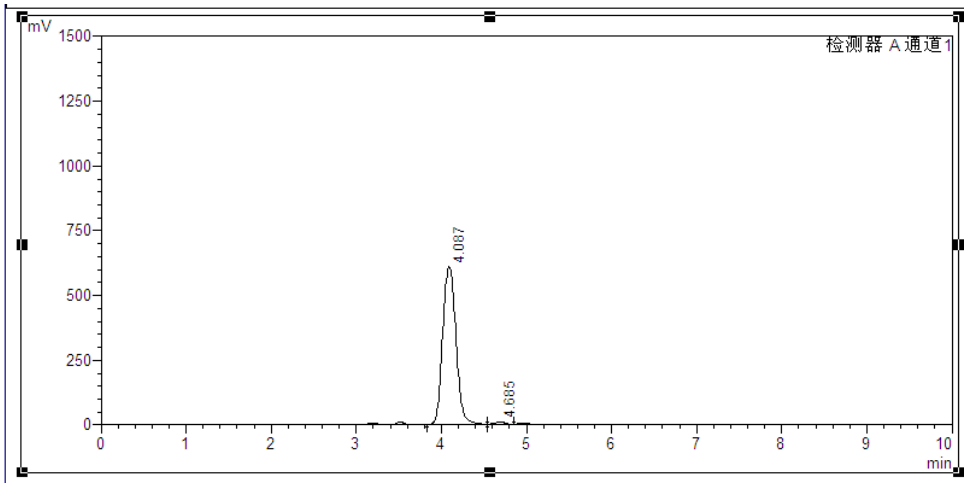
White solid, 97% ee (Daicel AD-H 0.46*25 cm, *n*-Hexane : *i*-PrOH 98 : 2, 1 mL/ min, 35 ^{o}C, 3.4 Mpa, t_R (minor) = 4.685 min, t_R (major) = 4.087 min); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.16 – 7.14 (m, 2H), 7.04 – 6.96 (m, 6H), 6.93 – 6.90 (m, 1H), 3.68 (s, 3H), 2.14 (d, *J* = 4.4 Hz, 1H), 2.07 (d, *J* = 4.4 Hz, 1H), 1.31 (s, 6H), 1.30 (s, 6H), 1.23(s, 9H) ppm. **^{13}C NMR** (100 MHz, $CDCl_3$) δ 175.4, 149.4, 137.6, 131.8, 130.9 (2C), 130.1 (2C), 127.5 (2C), 125.8, 124.3 (2C), 83.8 (2C), 52.8, 39.9, 34.4, 31.3 (3C), 25.0 (2C), 24.8 (2C), 22.0 ppm [Note: the carbon attached to boron was not observed due to quadrupole broadening caused by the ^{11}B nucleus]. **ESI-HR** calcd for $C_{27}H_{35}BO_4Na^+$ ([M+Na]$^+$) 457.25206, found 457.25232. **IR** ṽ (cm^{-1}) 1710, 1324, 1144. **M. P.** 159.6 – 160.3 ^{o}C. **Yield =** 87%. $[\alpha]_D^{20}$ = 13.9 (*c* = 1, MeOH) for a 97% ee sample.



峰表

检测器 A Ch1 230nm

峰#	保留时间	面积	高度	面积 %	高度 %
1	4.067	10190979	979912	50.403	43.694
2	4.559	10028087	1262776	49.597	56.306
总计		20219066	2242688	100.000	100.000

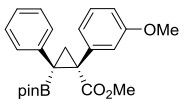


峰表

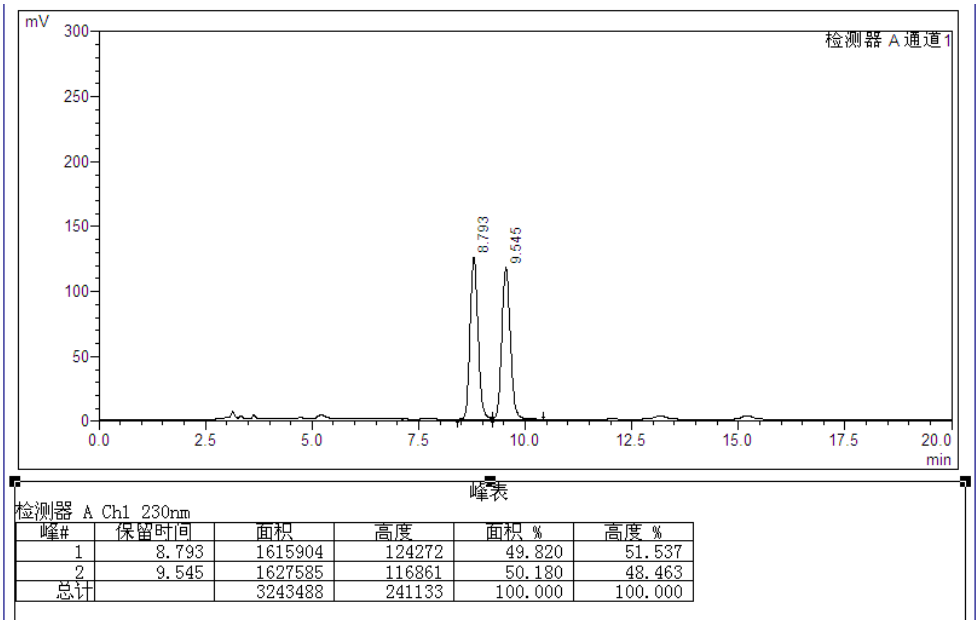
检测器 A Ch1 230nm

峰#	保留时间	面积	高度	面积 %	高度 %
1	4.087	6656096	610187	98.516	98.330
2	4.685	100265	10364	1.484	1.670
总计		6756361	620551	100.000	100.000

Methyl (1*S*, 2*R*)-1-(3-methoxyphenyl)-2-phenyl-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl) cyclopropane-1-carboxylate (3na)



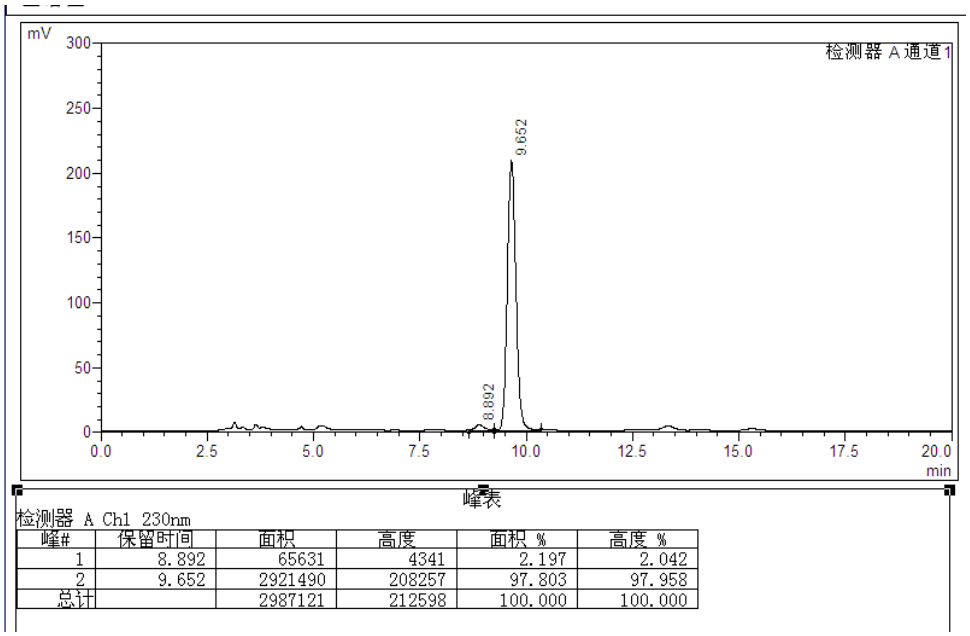
White solid, 96% ee (Daicel AD-H 0.46*25 cm, *n*-Hexane : *i*-PrOH 99 : 1, 1 mL/ min, 35 ^{o}C, 3.3 Mpa, t_R (minor) = 8.892 min, t_R (major) = 9.662 min); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.22 – 7.19 (m, 2H), 7.05 – 7.02 (m, 2H), 6.98 – 6.94 (m, 2H), 6.76 – 6.73 (m, 1H), 6.64 (t, *J* = 2.4 Hz, 1H), 6.58 – 6.55 (m, 1H), 3.68 (s, 3H), 3.64 (s, 3H), 2.14 (d, *J* = 4.4 Hz, 1H), 2.07 (d, *J* = 4.4 Hz, 1H), 1.26 (s, 6H), 1.24 (s, 6H) ppm. **^{13}C NMR** (100 MHz, $CDCl_3$) δ 175.1, 158.7, 137.4, 136.7, 130.0 (2C), 128.3, 127.6 (2C), 126.1, 124.1, 117.2, 112.8, 83.9 (2C), 55.3, 52.9, 40.4, 25.0 (2C), 24.8 (2C), 22.1 ppm [Note: the carbon attached to boron was not observed due to quadrupole broadening caused by the ^{11}B nucleus]. **ESI-HR** calcd for $C_{24}H_{29}BO_5Na^+$ ([M+Na]$^+$) 431.20003, found 431.20041. **IR** ṽ (cm^{-1}) 1712, 1309, 1146. **M. P.** 126.0 – 126.4 ^{o}C. **Yield =** 97%. $[\alpha]_D^{20}$ = 32.1 (*c* = 1.1, MeOH) for a 96% ee sample.



峰表

检测器 A Ch1 230nm

峰#	保留时间	面积	高度	面积 %	高度 %
1	8.793	1615904	124272	49.820	51.537
2	9.545	1627585	116861	50.180	48.463
总计		3243488	241133	100.000	100.000

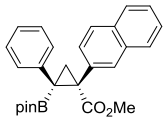


峰表

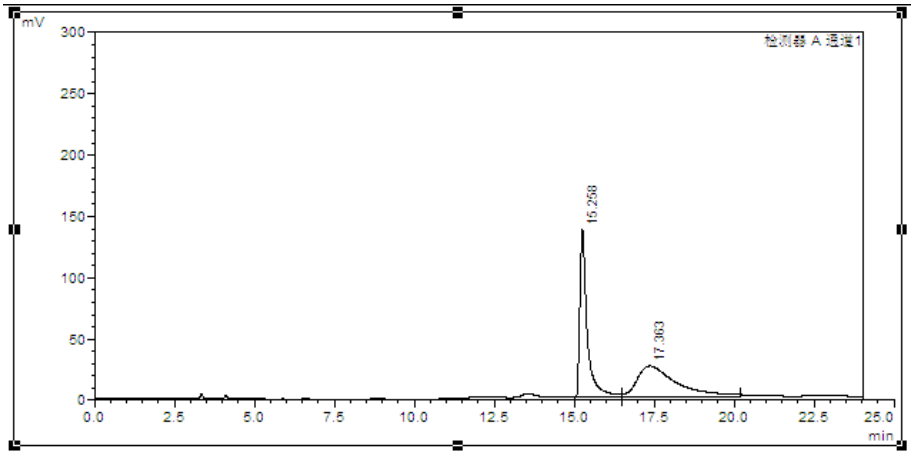
检测器 A Ch1 230nm

峰#	保留时间	面积	高度	面积 %	高度 %
1	8.892	65631	4341	2.197	2.042
2	9.652	2921490	208257	97.803	97.958
总计		2987121	212598	100.000	100.000

Methyl (1*S*,2*R*)-1-(naphthalen-2-yl)-2-phenyl-2-(4,4,5,5-tetramethyl-1,3,2- dioxaborolan-2-yl) cyclopropane -1-carboxylate (3oa)



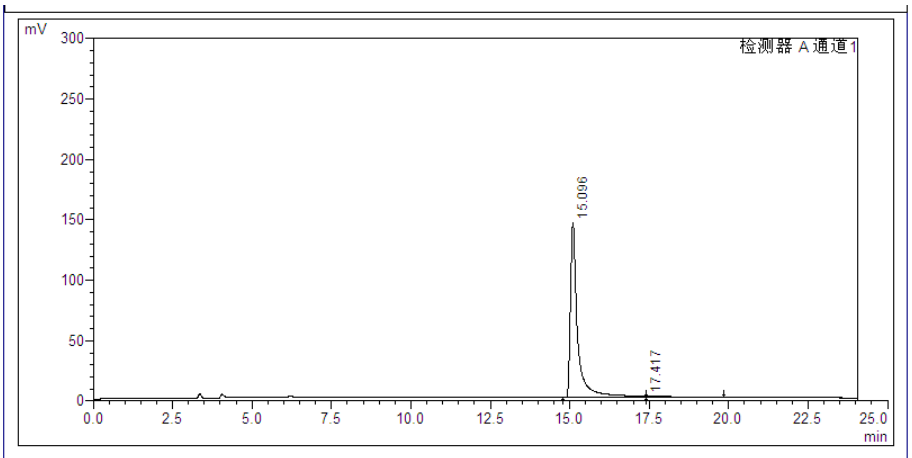
White solid, 96% ee (Daicel OD-H 0.46*25 cm, *n*-Hexane : *i*-PrOH 99.8 : 0.2, 1 mL/ min, 35 ^{o}C, 3.9 Mpa, t_R (minor) = 17.417 min, t_R (major) = 15.096 min); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.66 – 7.63 (m, 2H), 7.55 (d, *J* = 1.2 Hz, 1H), 7.51 (d, *J* =8.4 Hz, 1H), 7.37 – 7.31 (m, 3H), 7.26 – 7.23 (m, 2H), 6.98 – 6.94 (m, 2H), 6.88 – 6.84 (m, 1H), 3.66 (s, 3H), 2.30 (d, *J* = 4.4 Hz, 1H), 2.18 (d, *J* = 4.4 Hz, 1H), 1.27 (s, 6H), 1.25 (s, 6H) ppm. **^{13}C NMR** (100 MHz, $CDCl_3$) δ 175.3, 137.2, 133.0, 132.9, 132.4, 130.2 (2C), 130.1, 129.8, 127.9, 127.7 (2C), 127.5, 126.7, 126.1, 125.7, 125.6, 83.9 (2C), 52.9, 40.4, 25.0 (2C), 24.8 (2C), 22.2 ppm [Note: the carbon attached to boron was not observed due to quadrupole broadening caused by the ^{11}B nucleus]. **ESI-HR** calcd for $C_{27}H_{29}BO_4Na^+$ ([M+Na]$^+$) 451.20511, found 451.20541. **IR** ṽ (cm^{-1}) 1711, 1373, 1146. **M. P.** 135.0 – 146.9 ^{o}C. **Yield =** 83%. $[\alpha]_D^{20}$ = -33.3 (*c* = 0.67, MeOH) for a 96% ee sample.



峰表

检测器 A Ch1 230nm

峰#	保留时间	面积	高度	面积 %	高度 %
1	15.258	2210774	137070	49.384	84.275
2	17.363	2265902	25575	50.616	15.725
总计		4476676	162645	100.000	100.000

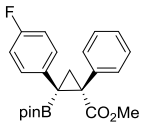


峰表

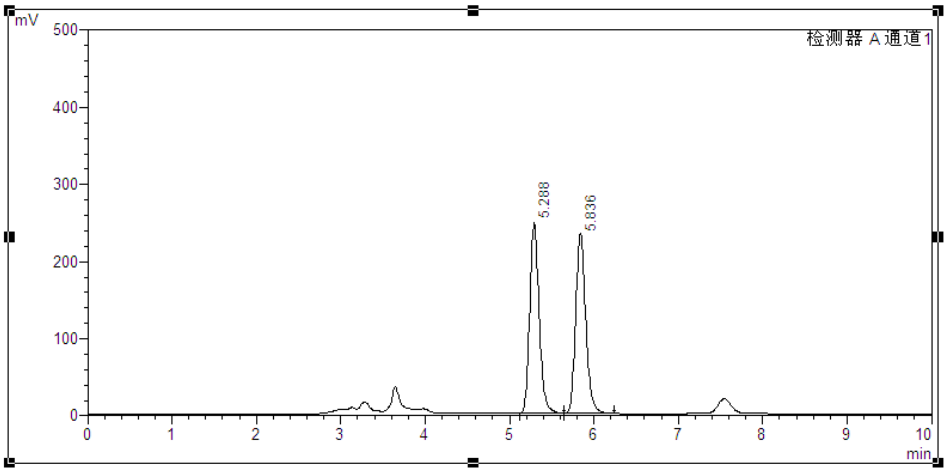
检测器 A Ch1 230nm

峰#	保留时间	面积	高度	面积 %	高度 %
1	15.096	2280910	144627	97.802	99.472
2	17.417	51272	767	2.198	0.528
总计		2332182	145394	100.000	100.000

Methyl (1*S*, 2*R*)-2-(4-fluorophenyl)-1-phenyl-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl) cyclopropane-1-carboxylate (3ab)



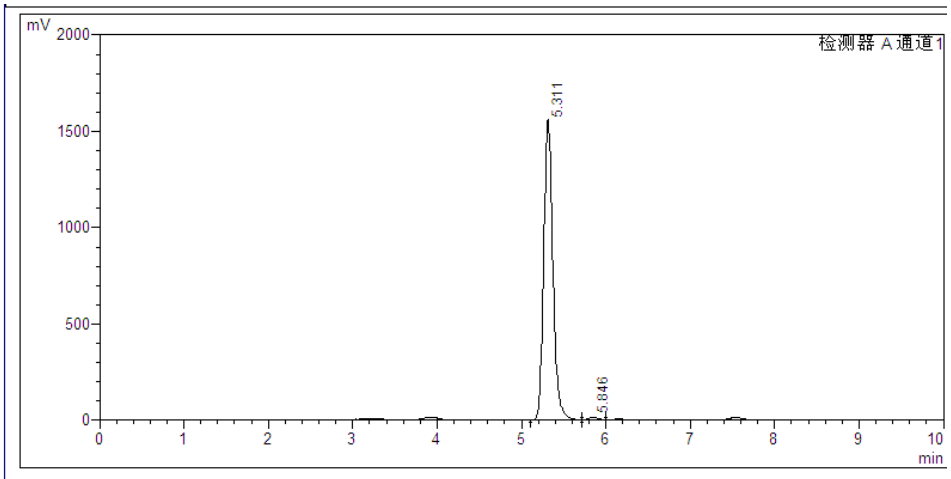
White solid, 98% ee (Daicel AD- H 0.46*25 cm, *n*- Hexane : *i*- PrOH 98: 2, 1 mL/ min, 35 ^{o}C, 3.2 Mpa, t_R (minor) = 5.846 min, t_R (major) = 5.311 min); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.17 – 7.01 (m, 7H), 6.73 – 6.67 (m, 2H), 3.68 (s, 3H), 2.12 (d, *J* = 4.4 Hz, 1H), 2.08 (d, *J* = 4.4 Hz, 1H), 1.24 (s, 6H), 1.23 (s, 6H) ppm. **^{13}C NMR** (100 MHz, $CDCl_3$) δ 175.1, 162.3 (F-C, *J* = 244 Hz), 134.9, 133.3(F-C-C-C-C, *J* = 3 Hz), 131.5(F-C-C-C, *J* = 8 Hz, 2C), 131.4 (2C), 127.6 (2C), 127.0, 114.5(F-C-C, *J* = 21 Hz, 2C), 83.9 (2C), 52.9, 40.3, 25.0 (2C), 24.8 (2C), 22.1 ppm [Note: the carbon attached to boron was not observed due to quadrupole broadening caused by the ^{11}B nucleus]. **^{19}F NMR** (376 MHz, $CDCl_3$) δ -117.02 ppm. **^{11}B NMR** (128 MHz, $CDCl_3$) δ 30.08. **ESI-HR** calcd for $C_{23}H_{26}BFO_4Na^+$ ($[M+Na]^+$) 419.18004, found 419.18079. **IR** $\tilde{\nu}$ (cm^{-1}) 1712, 1321, 1145. **M. P.** 150.0 – 151.2 ^{o}C. **Yield =** 91%. $[\alpha]_D^{20}$ = 10.3 (*c* = 1, MeOH) for a 98% ee sample.



峰表

检测器 A Ch1 230nm

峰#	保留时间	面积	高度	面积 %	高度 %
1	5.288	1928695	246904	49.911	51.470
2	5.836	1935557	232803	50.089	48.530
总计		3864252	479706	100.000	100.000

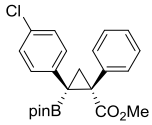


峰表

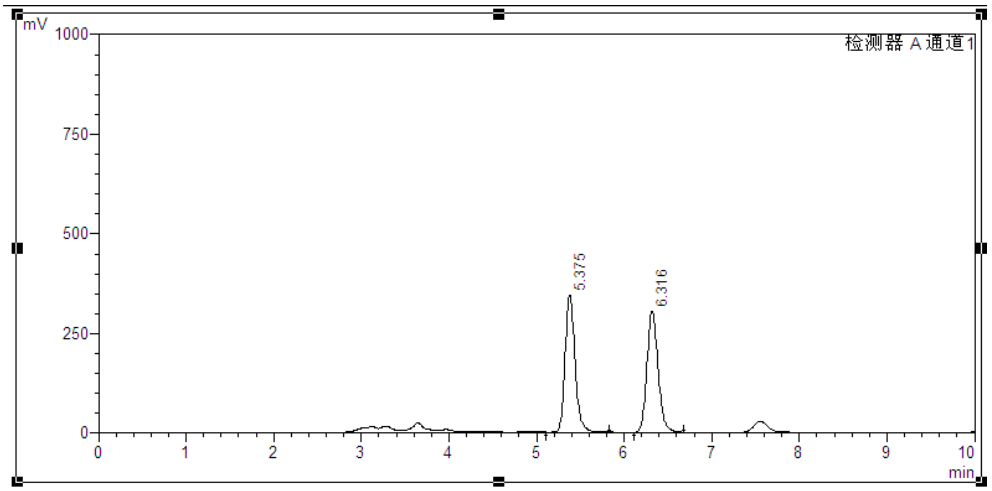
检测器 A Ch1 230nm

峰#	保留时间	面积	高度	面积 %	高度 %
1	5.311	11863346	1557628	99.014	99.075
2	5.846	118083	14544	0.986	0.925
总计		11981429	1572172	100.000	100.000

Methyl (1*S*, 2*R*)-2-(4-chlorophenyl)-1-phenyl-2-(4,4,5,5-tetramethyl-1,3,2- dioxaborolan-2-yl) cyclopropane-1-carboxylate (3ac)



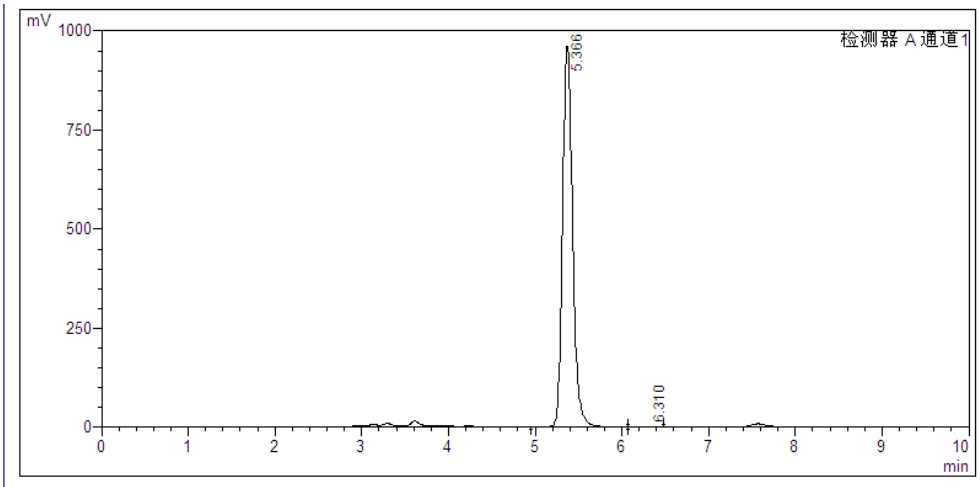
White solid, 99% ee (Daicel AD-H 0.46*25 cm, *n*-Hexane : *i*-PrOH 98 : 2, 1 mL/ min, 35 °C, 3.2 Mpa, t_R (minor) = 6.310 min, t_R (major) = 5.366 min); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.13 – 7.05 (m, 7H), 7.00 – 6.97 (m, 2H), 3.67 (s, 3H), 2.12 (d, *J* = 4.4 Hz, 1H), 2.08 (d, *J* = 4.4 Hz, 1H), 1.24 (s, 6H), 1.23 (s, 6H) ppm. **^{13}C NMR** (100 MHz, $CDCl_3$) δ 175.1, 136.3, 134.7, 131.8, 131.4 (2C), 131.3 (2C), 127.8 (2C), 127.6 (2C), 127.1, 84.0 (2C), 53.0, 40.4, 25.0 (2C), 24.8 (2C), 22.0 ppm [Note: the carbon attached to boron was not observed due to quadrupole broadening caused by the ^{11}B nucleus]. **ESI-HR** calcd for $C_{23}H_{26}BClO_4Na^+$ ($[M+Na]^+$) 435.15049, found 435.15002. IR ṽ (cm^{-1}) 1712, 1320, 1146. **M. P.** 157.4 – 158.0 °C. **Yield =** 95%. $[\alpha]_D^{20}$ = 8.6 (*c* = 1, MeOH) for a 99% ee sample.



峰表

检测器 A Ch1 230nm

峰#	保留时间	面积	高度	面积 %	高度 %
1	5.375	2759908	345169	50.276	53.051
2	6.316	2729654	305463	49.724	46.949
总计		5489562	650632	100.000	100.000

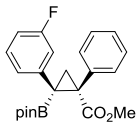


峰表

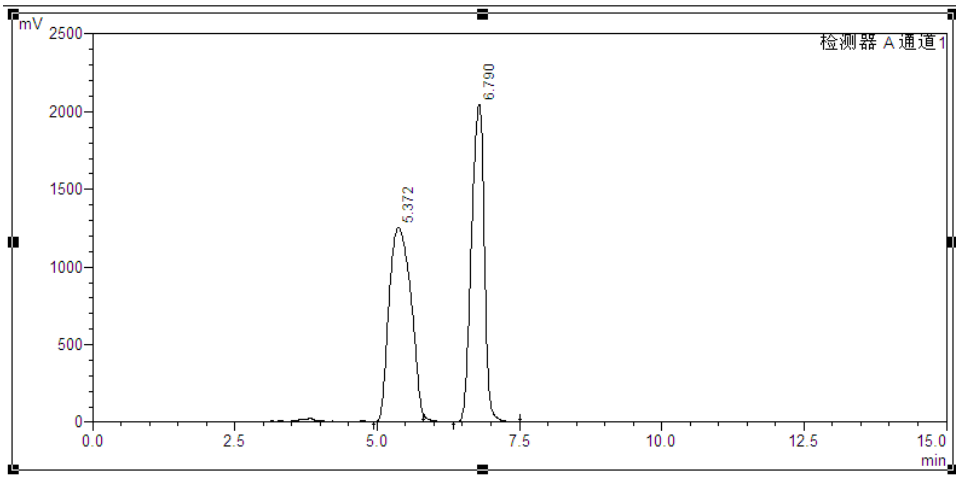
检测器 A Ch1 230nm

峰#	保留时间	面积	高度	面积 %	高度 %
1	5.366	7715164	960341	99.887	99.884
2	6.310	8725	1116	0.113	0.116
总计		7723889	961457	100.000	100.000

Methyl (1*S*,2*R*)-2-(3-fluorophenyl)-1-phenyl-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl) cyclopropane-1-carboxylate (3ad)



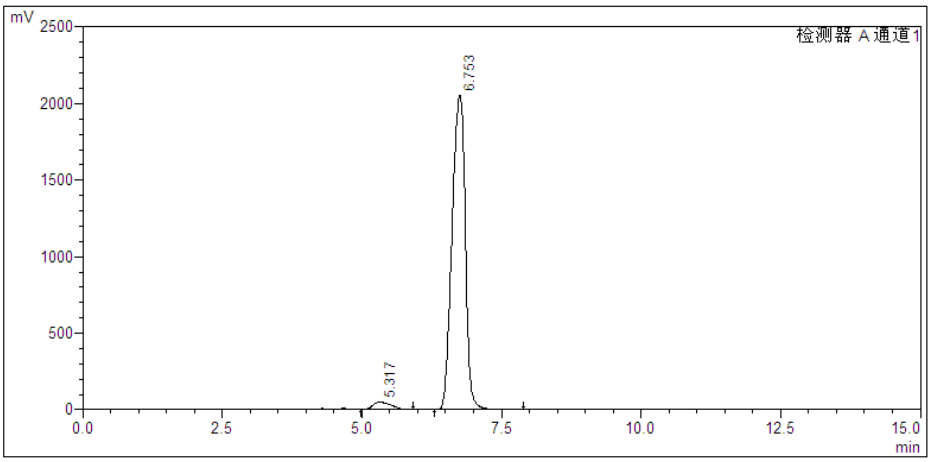
White solid, 94% ee (Daicel AD-H 0.46*25 cm, *n*-Hexane : *i*-PrOH 99: 1, 1 mL/ min, 35 °C, 3.2 Mpa, t_R (minor) = 5.371 min, t_R (major) = 6.753 min); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.14 – 7.02 (m, 5H), 7.00 – 6.92 (m, 3H), 6.67 – 6.62 (m, 1H), 3.68 (s, 3H), 2.14 (d, *J* = 4.4 Hz, 1H), 2.09 (d, *J* = 4.4 Hz, 1H), 1.26 (s, 6H), 1.25 (s, 6H) ppm. **^{13}C NMR** (100 MHz, $CDCl_3$) δ 175.0, 162.4 (d, *J* = 243 Hz), 140.4(d, *J* = 7 Hz), 134.7, 131.3 (2C), 128.9(d, *J* = 8 Hz), 127.6 (2C), 127.0, 125.6 (d, *J* = 3 Hz), 117.0 (d, *J* = 21 Hz), 113.0 (d, *J* = 21 Hz), 84.0 (2C), 53.0, 40.6, 25.0 (2C), 24.8 (2C), 21.9 ppm [Note: the carbon attached to boron was not observed due to quadrupole broadening caused by the ^{11}B nucleus]. **^{19}F NMR** (376 MHz, $CDCl_3$) δ -114.58 ppm. **ESI-HR** calcd for $C_{23}H_{26}BFO_4Na^+$ ($[M+Na]^+$) 419.18004, found 439.18005. **IR** ṽ (cm^{-1}) 1712, 1323, 1142. **M. P.** 146.4 – 146.4 °C. **Yield =** 82%. $[\alpha]_D^{20}$ = 9.8 (*c* = 1.3, MeOH) for a 94% ee sample.



峰表

检测器 A Ch1 230nm

峰#	保留时间	面积	高度	面积 %	高度 %
1	5.372	33489215	1252383	51.233	37.974
2	6.790	31877900	2045649	48.767	62.026
总计		65367116	3298032	100.000	100.000

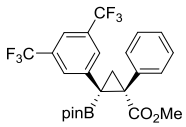


峰表

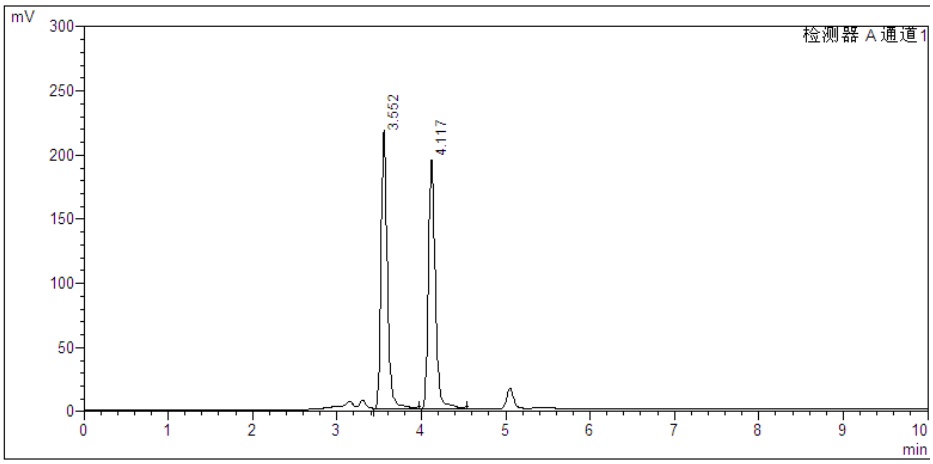
检测器 A Ch1 230nm

峰#	保留时间	面积	高度	面积 %	高度 %
1	5.317	1041580	46757	2.993	2.228
2	6.753	33759475	2051859	97.007	97.772
总计		34801055	2098616	100.000	100.000

Methyl (1S, 2R)-2-(3,5-bis(trifluoromethyl)phenyl)-1-phenyl-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl) cyclopropane-1-carboxylate (3ae)



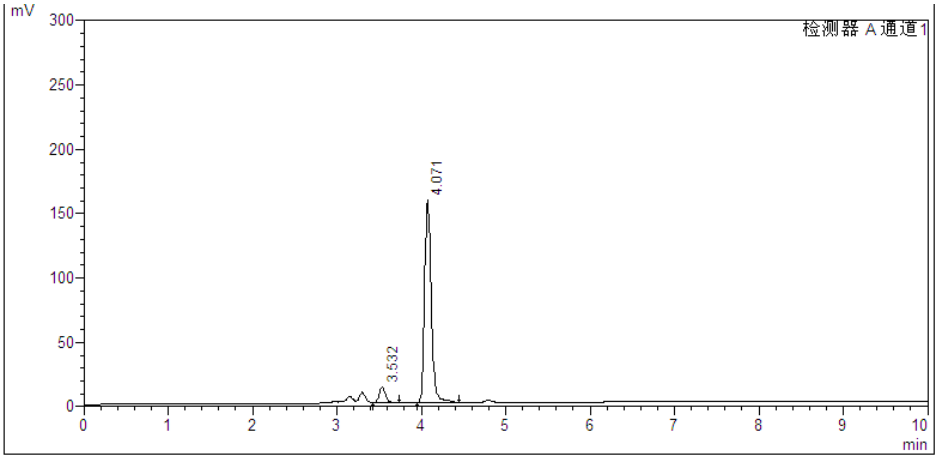
Colorless oil, 86% ee (Daicel AD-H 0.46*25 cm, *n*-Hexane : *i*-PrOH 99: 1, 1 mL/ min, 35 ^{o}C, 3.3 Mpa, t_R (minor) = 3.532 min, t_R (major) = 4.071 min); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.53 (s, 2H), 7.44 (s, 1H), 7.10 – 7.00 (m, 5H), 3.71 (s, 3H), 2.23 (d, *J* = 4.8 Hz, 1H), 2.17 (d, *J* = 4.8 Hz, 1H), 1.27 (s, 6H), 1.25 (s, 6H) ppm. **^{13}C NMR** (100 MHz, $CDCl_3$) δ 174.7, 140.9, 133.8, 131.0 (2C), 130.6 (F-C-C, *J* = 33 Hz, 2C), 130.3 (broad peak), 127.9 (2C), 127.5, 123.4 (F-C, *J* = 271 Hz, 2C), 119.8 (F-C-C-C, *J* = 4 Hz), 84.4 (2C), 53.2, 41.1, 25.1 (2C), 24.6 (2C), 21.8 ppm [Note: the carbon attached to boron was not observed due to quadrupole broadening caused by the ^{11}B nucleus]. **^{19}F NMR** (376 MHz, $CDCl_3$) δ -63.10 ppm. **ESI-HR** calcd for $C_{25}H_{25}BF_6O_4Na^+$ ($[M+Na]^+$) 537.16423, found 537.16553; **IR** ṽ (cm^{-1}) 1716, 1320, 1136; **Yield =** 75%. $[\alpha]_D^{20}$ = 32.0 (*c* = 0.5, MeOH) for a 86% ee sample.



峰表

检测器 A Ch1 230nm

峰#	保留时间	面积	高度	面积 %	高度 %
1	3.552	1133781	216935	50.490	52.820
2	4.117	1111792	193767	49.510	47.180
总计		2245573	410702	100.000	100.000

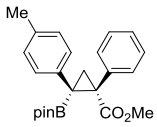


峰表

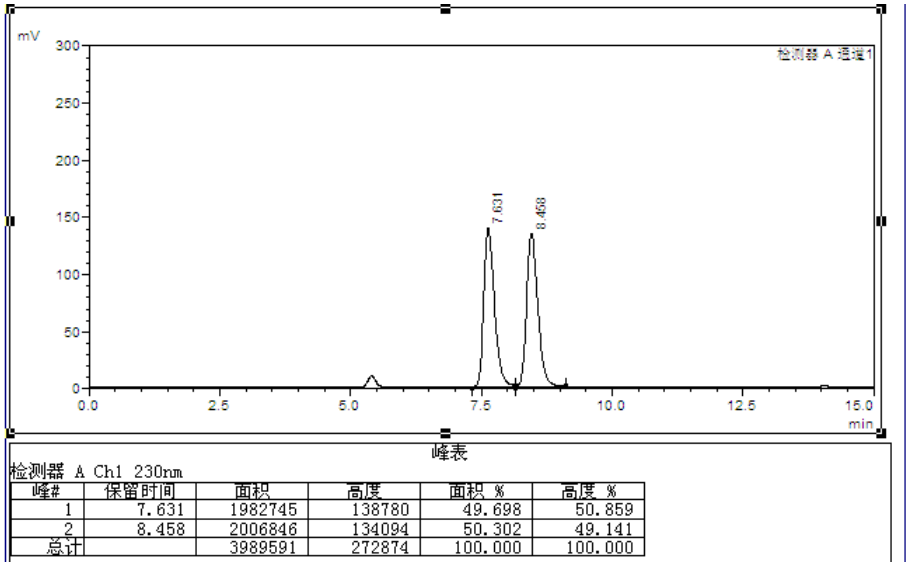
检测器 A Ch1 230nm

峰#	保留时间	面积	高度	面积 %	高度 %
1	3.532	63490	12260	6.801	7.234
2	4.071	870042	157210	93.199	92.766
总计		933532	169470	100.000	100.000

Methyl(1*S*,2*R*)-1-phenyl-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-2-(p-tolyl)cyclopropane-1-carboxylate (3af)



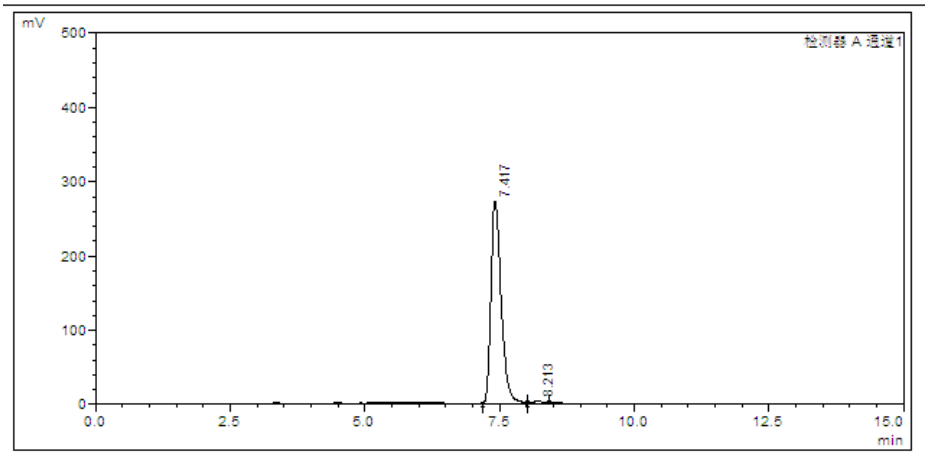
White solid, 98% ee (Daicel OD-H 0.46*25 cm, *n*- Hexane : *i*- PrOH 99.5: 0.5, 1 mL/ min, 35 ^{o}C, 3.9 Mpa, t_R (minor) = 8.213 min, t_R (major) = 7.417 min); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.15 – 7.12 (m, 2H), 7.08 – 7.00 (m, 5H), 6.83 – 6.81(m, 2H), 3.66 (s, 3H), 2.14 – 2.13(m, 4H), 2.08 – 2.07(m,1H), 1.25 (s, 6H), 1.23 (s, 6H) ppm. **^{13}C NMR** (100 MHz, $CDCl_3$) δ 175.3, 135.4, 135.3, 134.2, 131.6 (2C), 129.8 (2C), 128.4 (2C), 127.4 (2C), 126.8, 83.8 (2C), 52.8, 40.2, 25.0 (2C), 24.8 (2C), 22.0, 21.1 ppm [Note: the carbon attached to boron was not observed due to quadrupole broadening caused by the ^{11}B nucleus]. **M. P.** 124.0 – 124.2 ^{o}C. **Yield** = 91%.



峰表

检测器 A Ch1 230nm

峰#	保留时间	面积	高度	面积 %	高度 %
1	7.631	1982745	138780	49.698	50.859
2	8.458	2006846	134094	50.302	49.141
总计		3989591	272874	100.000	100.000

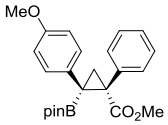


峰表

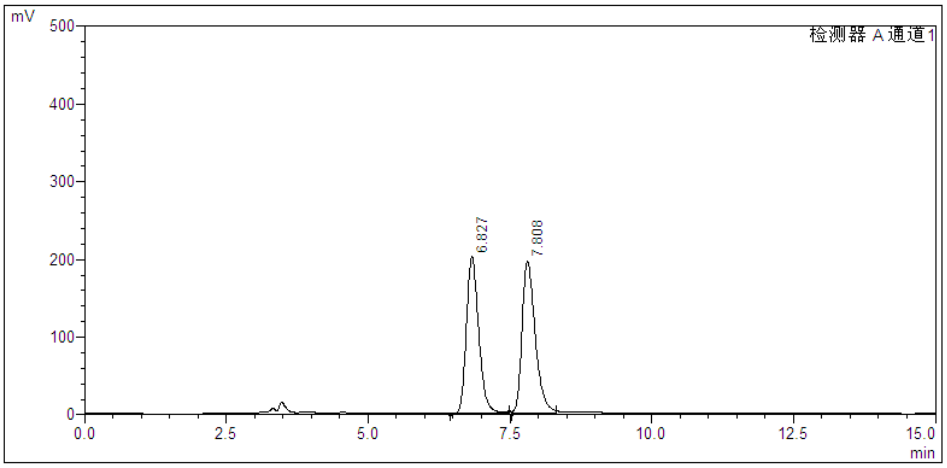
检测器 A Ch1 230nm

峰#	保留时间	面积	高度	面积 %	高度 %
1	7.417	3592084	272341	98.968	99.131
2	8.213	37447	2388	1.032	0.869
总计		3629530	274729	100.000	100.000

Methyl (1*S*,2*R*)-2-(4-methoxyphenyl)-1-phenyl-2-(4,4,5,5-tetramethyl-1,3,2- dioxaborolan-2 -yl) cyclopropane-1-carboxylate (3ag)



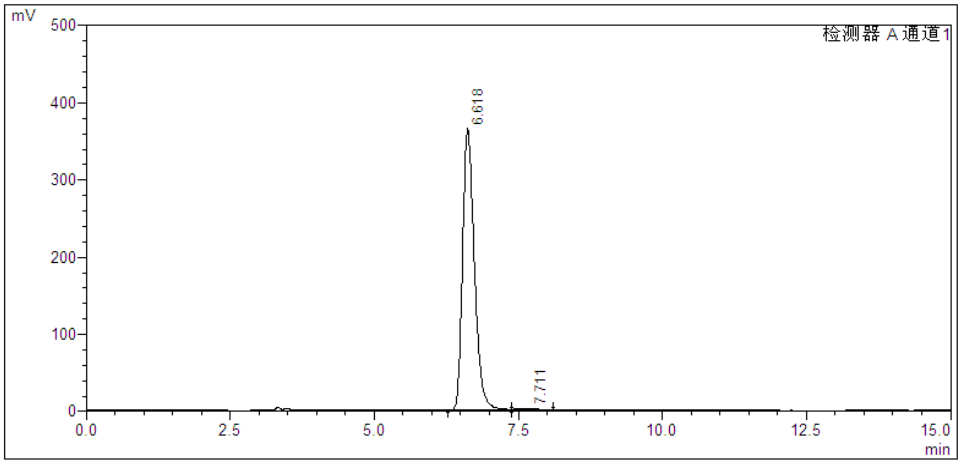
White solid, 98% ee (Daicel OD-H 0.46*25 cm, *n*-Hexane : *i*-PrOH 99: 1, 1 mL/ min, 35 °C, 3.9 Mpa, t_R (minor) = 7.711 min, t_R (major) = 6.618 min); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.14 – 7.00 (m, 7H), 6.57 – 6.55 (m, 2H), 3.66 (s, 3H), 3.65 (s, 3H), 2.11 (d, *J* = 4.4 Hz, 1H), 2.07 (d, *J* = 4.4 Hz, 1H), 1.25 (s, 6H), 1.23 (s, 6H) ppm. **^{13}C NMR** (100 MHz, $CDCl_3$) δ 175.3, 157.8, 135.2, 131.6 (2C), 131.0 (2C), 129.4, 127.4 (2C), 126.8, 113.0 (2C), 83.8 (2C), 55.1, 52.8, 40.2, 25.0 (2C), 24.8 (2C), 22.2 ppm [Note: the carbon attached to boron was not observed due to quadrupole broadening caused by the ^{11}B nucleus]. **ESI-HR** calcd for $C_{24}H_{29}BO_5Na^+$ ($[M+Na]^+$) 431.20003, found 431.19904. **IR** ṽ (cm^{-1}) 1711, 1320, 1303, 1146. **M. P.** 141.9 – 144.3 °C. **Yield =** 85%. $[\alpha]_D^{20}$ = 14.1 (*c* = 1.48, MeOH) for a 98% ee sample.



峰表

检测器 A Ch1 230nm

峰#	保留时间	面积	高度	面积 %	高度 %
1	6.827	3076159	201827	49.017	50.779
2	7.808	3199595	195635	50.983	49.221
总计		6275754	397463	100.000	100.000



峰表

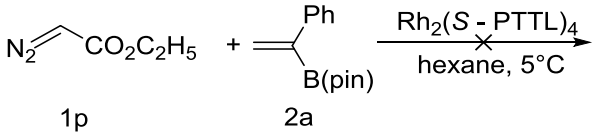
检测器 A Ch1 230nm

峰#	保留时间	面积	高度	面积 %	高度 %
1	6.618	5208965	364541	99.060	99.512
2	7.711	49431	1788	0.940	0.488
总计		5258397	366329	100.000	100.000

Attempts at other substrates

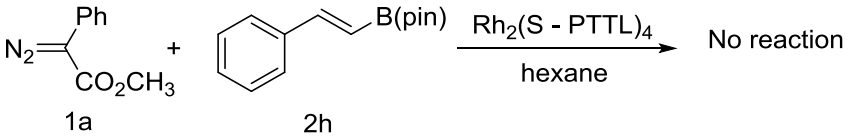
The β-boryl styrene, a 1,2-disubstituted alkene, was also examined for the reaction with phenyldiazoacetate 1a, and it failed to give any desired product, indicating that only the terminal alkene was suitable for the conversion. Asymmetric cyclopropanation of the 2-boryl-1-octene with phenyldiazoacetate **1a** gave very trace cyclopropylboronate in the presence of Rh_2(*S*-PTTL)$_4$. Further, the attempt to cyclopropanation of α-boryl styrene **2a** with ethyl diazoacetate also encountered a failure. The two experiments indicated that both the two Ar groups (one in alkene, and the other in the diazo compound) were essential for the reaction

1.The cyclopropanation of α-boryl styrene **2a** with ethyl diazoacetate **1p**



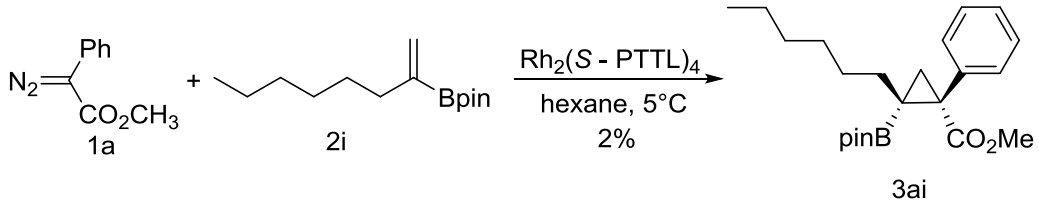
In an inert gas atmosphere, Rh_2(*S*-PTTL)$_4$ (1 mg, 0.2 mol % eq) was added into α-borylstyrenes **2a** (230 mg, 1 mmol, 2 eq) and hexane (3 mL) at 5 ^{o}C. Stirred for 30 min and then α-diazoarylacetates **1p** (57 mg, 0.5 mmol, 1 eq) diluted in n-hexane (13 mL) was added dropwise over a period of 1h. The mixture was reacted for additional 30 min and the pure chiral cyclopropylborates was obtained by flash chromatography.

2. The reaction of phenyldiazoacetate **1a** with the β-boryl styrene 2h



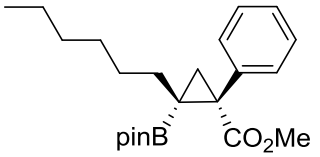
In an inert gas atmosphere, Rh_2(*S*-PTTL)$_4$ (1 mg, 0.2 mol % eq) was added into α-borylstyrenes **2h** (230 mg, 1 mmol, 2 eq) and hexane (3 mL) at 5 ^{o}C. Stirred for 30 min and then α-diazoarylacetates **1a** (88 mg, 0.5 mmol, 1eq) diluted in n-hexane (13 mL) was added dropwise over a period of 1h. The mixture was reacted for additional 30 min and the pure chiral cyclopropylborates was obtained by flash chromatography.

3.The reaction of phenyldiazoacetate **1a** with the 2-boryl-1-octene 2i



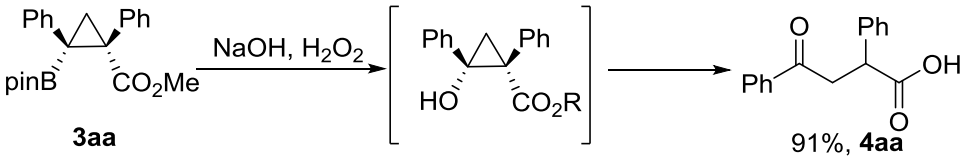
In an inert gas atmosphere, Rh_2(*S*-PTTL)$_4$ (1 mg, 0.2 mol % eq) was added into α-borylstyrenes **2** (238 mg, 1 mmol, 2 eq) and hexane (3 mL) at 5 ^{o}C. Stirred for 30 min and then α-diazoarylacetates **1a** (88 mg, 0.5 mmol, 1eq) diluted in n-hexane (13 mL) was added dropwise over a period of 1h. The mixture was reacted for additional 30 min and the pure chiral cyclopropylborates was obtained by flash chromatography.

methyl(1S,2S)-2-hexyl-1-phenyl-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl) cyclopropane-1 - carboxylate



Colorless oil, **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.43 – 7.15 (m, 5H), 3.58 (s, 3H), 1.77 (d, *J* = 3.7 Hz, 1H), 1.55 (ddd, *J* = 13.8, 11.0, 4.4 Hz, 1H), 1.33 – 1.29 (m, 1H), 1.32 (s, 6H), 1.31 (s, 6H), 1.24 – 1.02 (m, 8H), 0.81 (t, *J* = 7.1 Hz, 3H), 0.21 (ddd, *J* = 13.3, 11.3, 5.9 Hz, 1H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 175.5, 136.7, 131.6 (2C), 127.9 (2C), 127.1, 83.5 (2C), 52.6, 38.5, 38.5, 31.9, 29.6, 28.9, 25.3 (2C), 25.2 (2C), 24.9, 22.6, 14.2.

Preparation of 1,4-dicarbonyl compounds

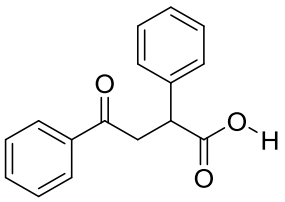


3aa 91%, **4aa**

3aa (378mg, 1mmol) was dissolved in THF (6ml), cooled to 0℃ then 3M NaOH (4ml) was added, dropwise followed by 2.1ml 35% H_2O_2 solution in H_2O (2ml). After the treatment, the reaction system was concentrated first, and then Add 1M HCl to adjust Ph = 12 – 13, extract the aqueous phase with CH_2Cl_2, combine the organic phases and dry over Na_2SO_4 to obtain the product 4aa (205, 0.81 mmol, 91%).

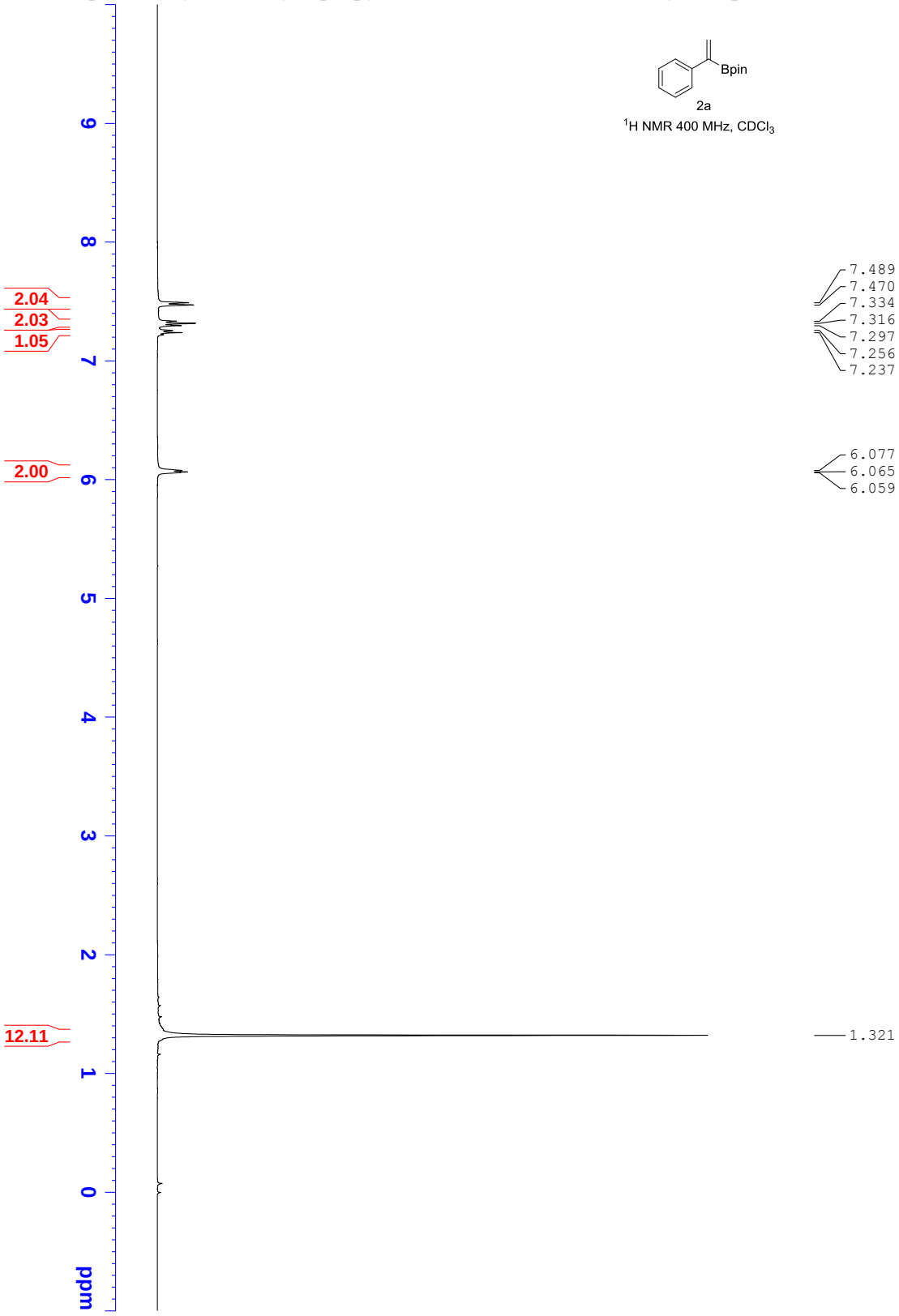
General procedure:

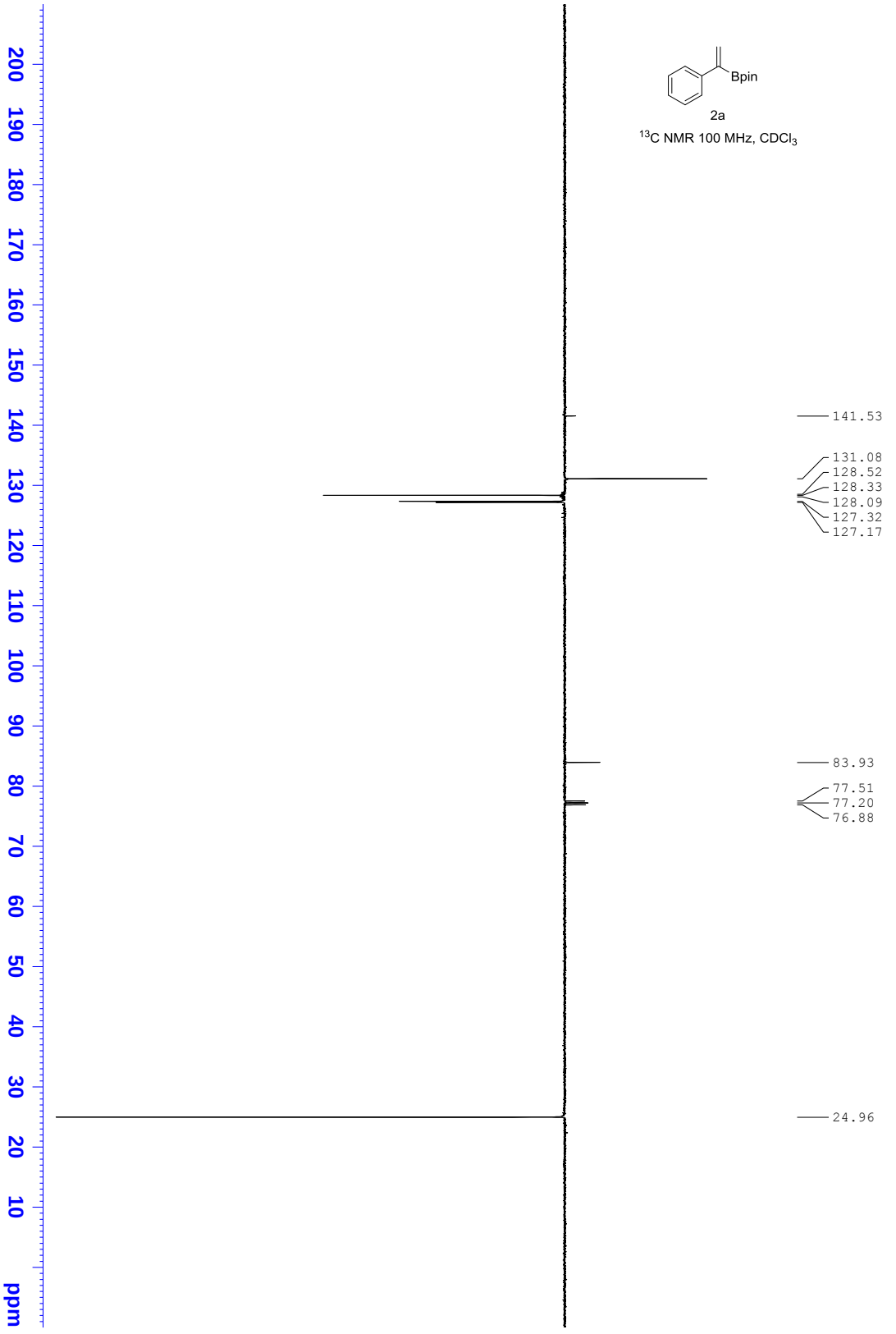
4-oxo-2,4-diphenylbutanoic acid (4aa)

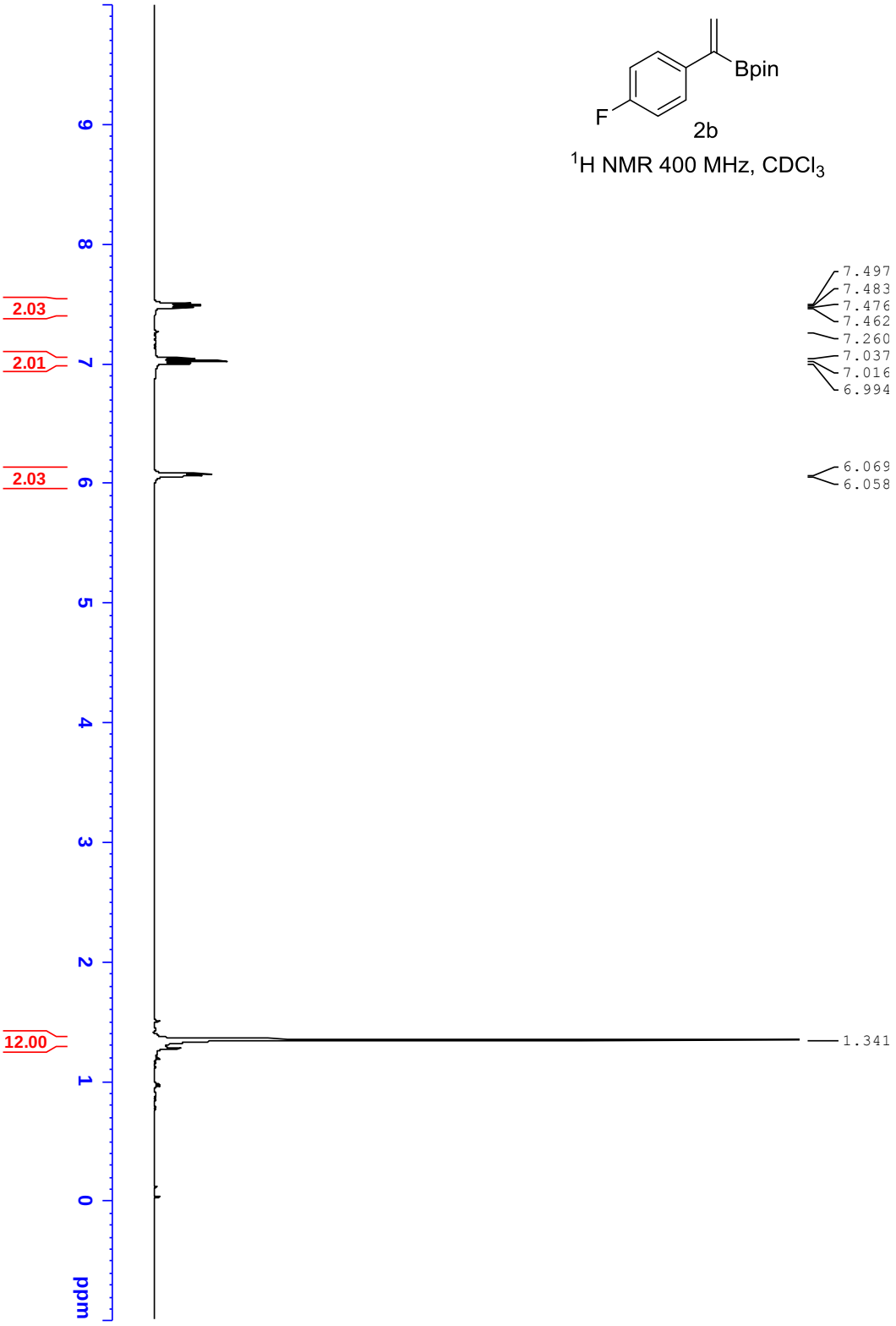


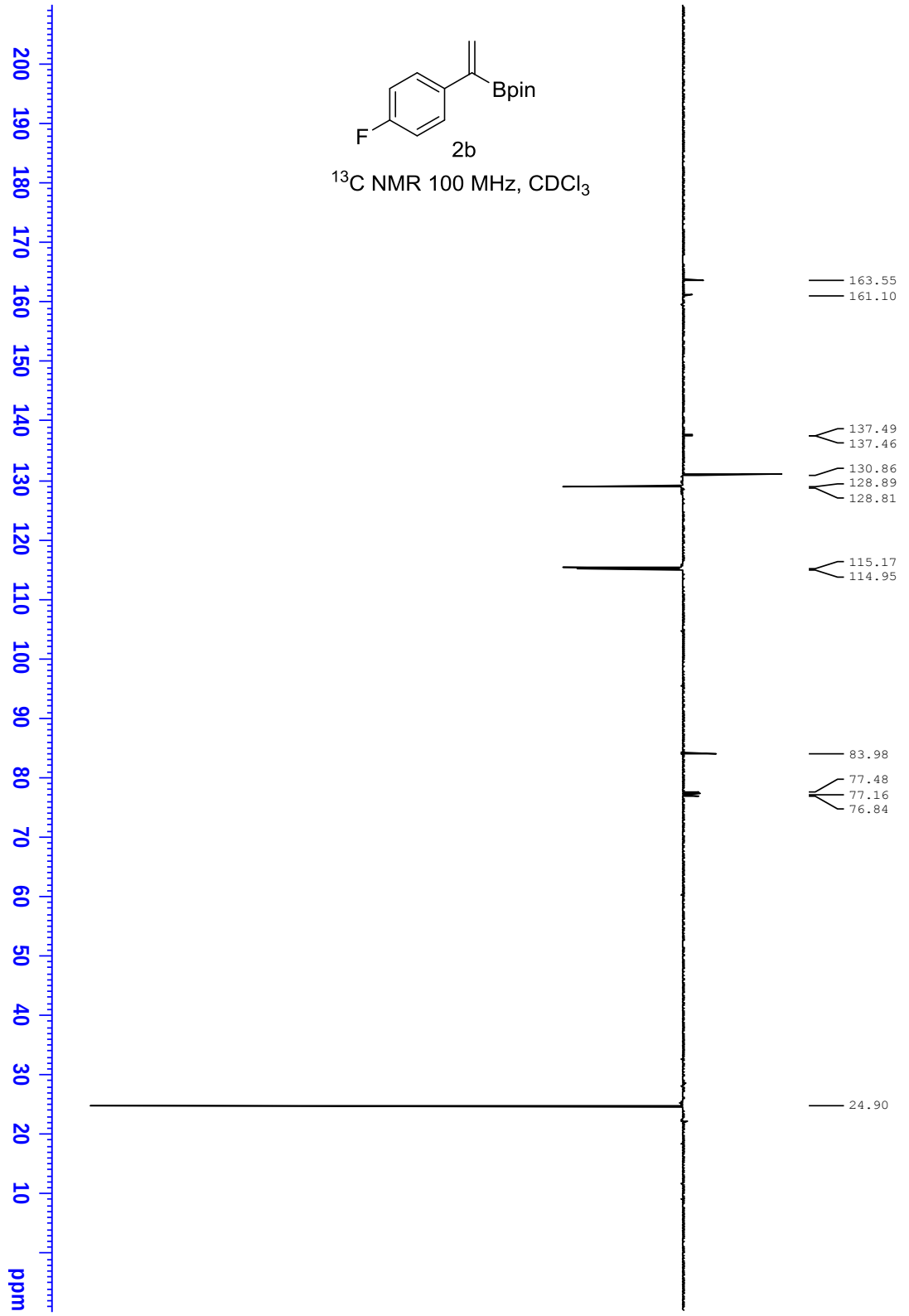
White solid, **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.96 (d, *J* = 7.7 Hz, 1H), 7.56 (t, *J* = 7.4 Hz, 1H), 7.45 (t, *J* = 7.6 Hz, 1H), 7.42 – 7.27 (m, 3H), 4.32 (dd, *J* = 10.1, 4.2 Hz, 1H), 3.91 (dd, *J* = 18.1, 10.1 Hz, 1H), 3.29 (dd, *J* = 18.1, 4.2 Hz, 1H) ppm. **^{13}C NMR** (101 MHz, $CDCl_3$) δ 197.5, 179.1, 137.8, 136.4, 133.5, 129.1 (2C), 128.7 (2C), 128.2 (2C), 128.1 (2C), 127.9, 46.4, 42.4 ppm. **ESI-HR** calcd for $C_{16}H_{14}O_3H^+$ ($[M+H]^+$) 255.10156, found 255.10150. **IR** ν (cm^{-1}) 1708, 1684. **M. P.** 152.4 – 152.5 ^{o}C. **Yield =** 91%.

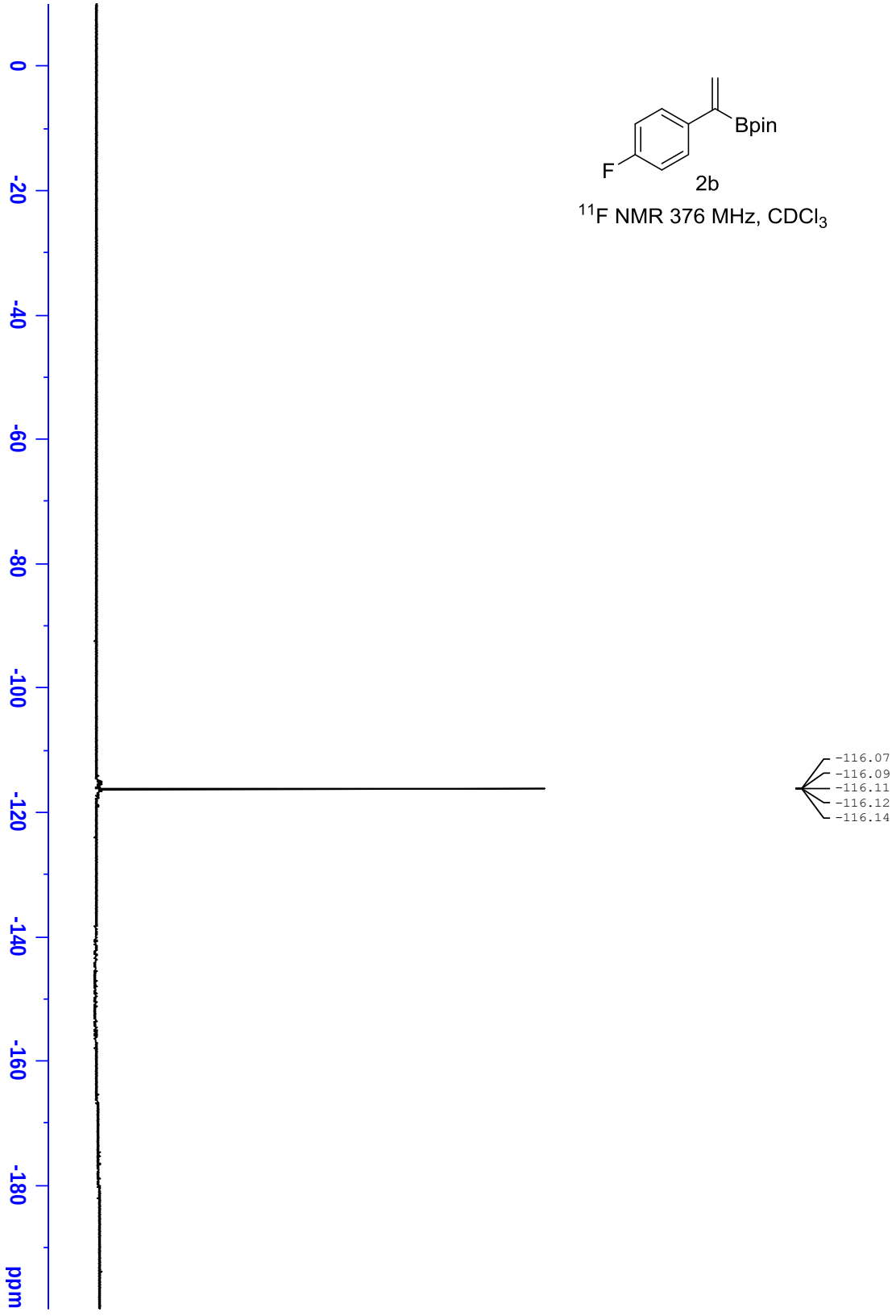
NMR Copies of stryenes 2, Cyclopropylboronates 3 and 1,4-dicarbonyl compounds 4aa.




Bpin
2a
^{13}C NMR 100 MHz, $CDCl_3$
141.53
131.08
128.52
128.33
128.09
127.32
127.17
83.93
77.51
77.20
76.88
24.96
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

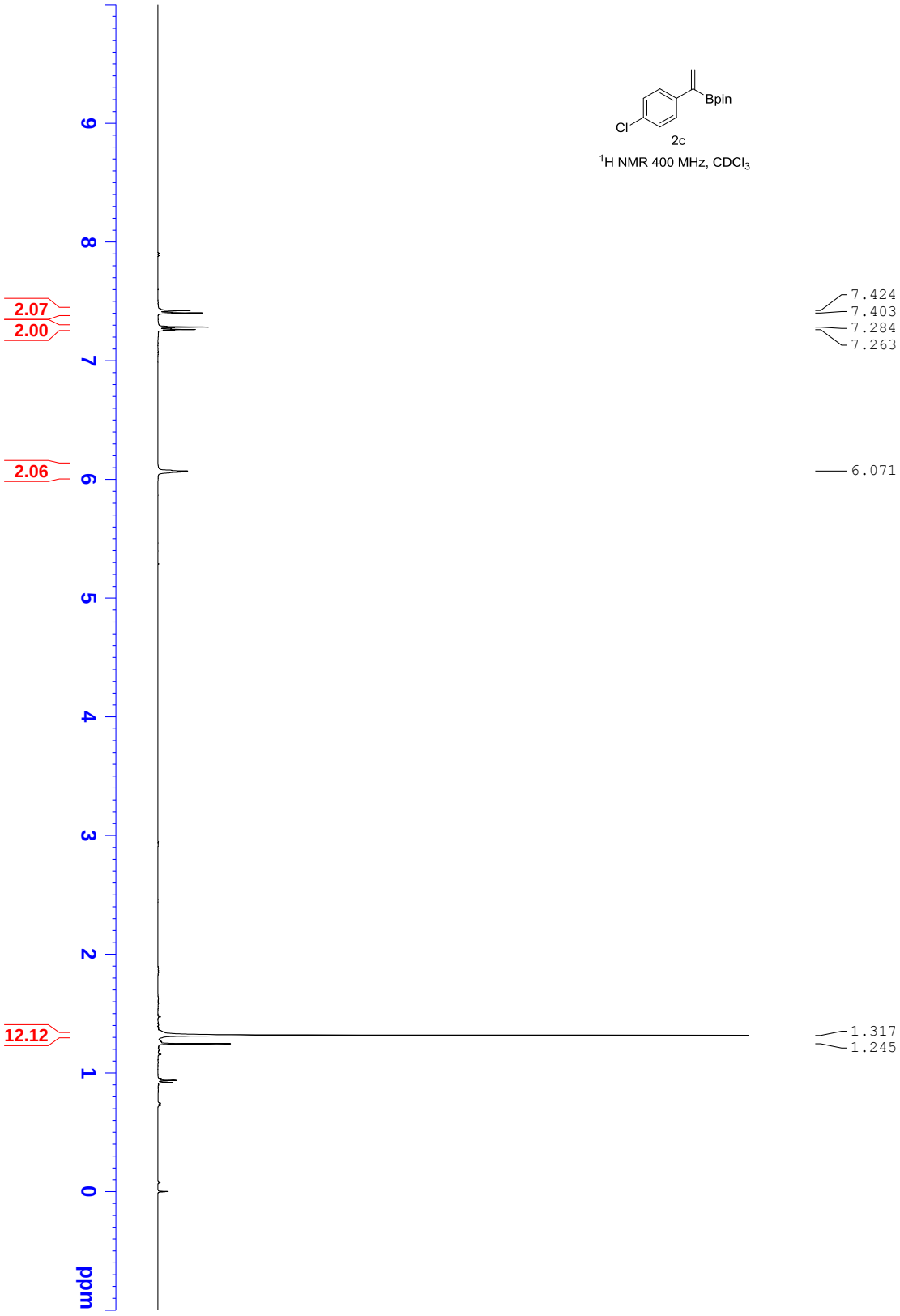

Bpin
F
2b
^{1}H NMR 400 MHz, $CDCl_3$
7.497
7.483
7.476
7.462
7.260
7.037
7.016
6.994
6.069
6.058
1.341
2.03
2.01
2.03
12.00
9
8
7
6
5
4
3
2
1
0
ppm

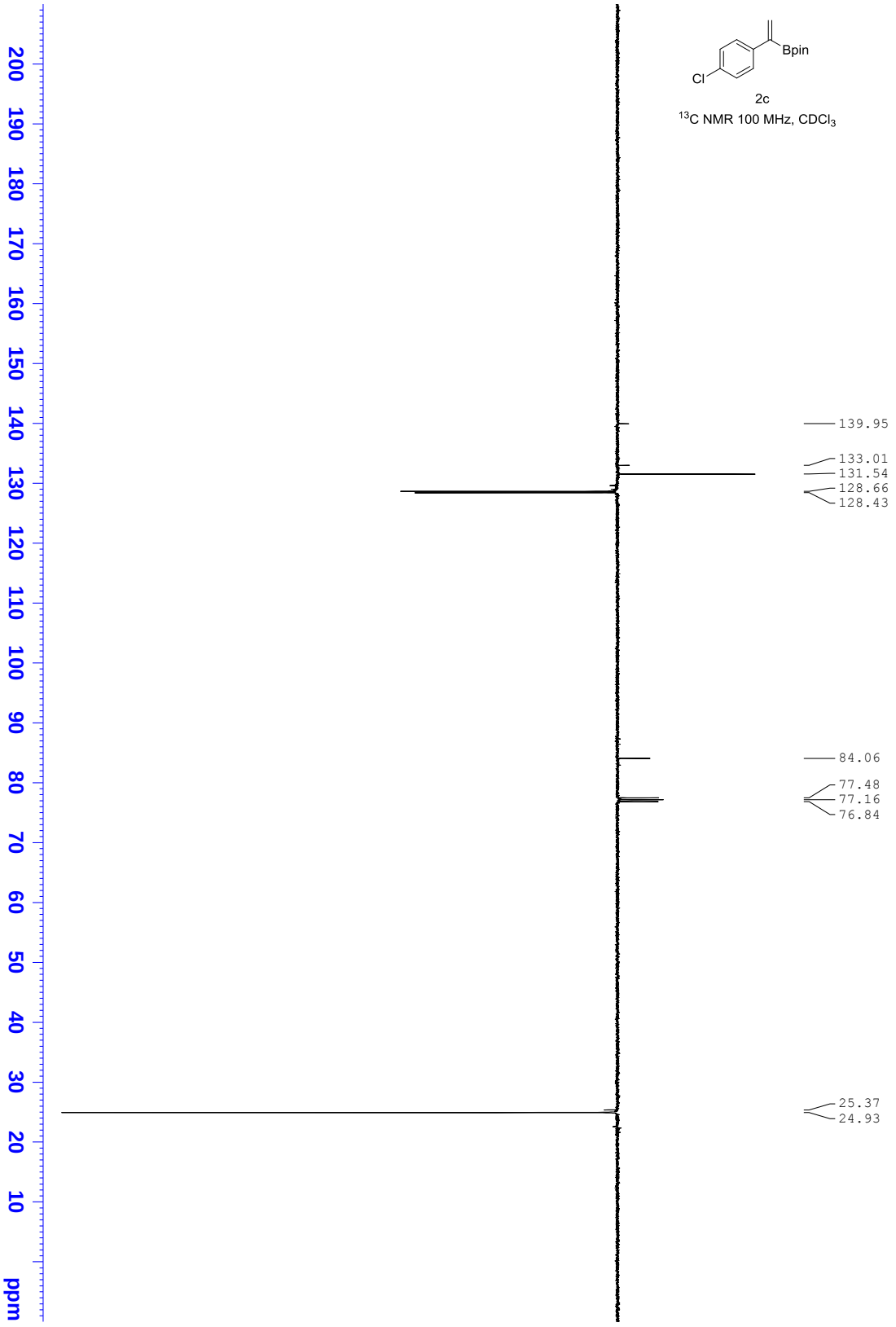

Bpin
F
2b
^{13}C NMR 100 MHz, $CDCl_3$
163.55
161.10
137.49
137.46
130.86
128.89
128.81
115.17
114.95
83.98
77.48
77.16
76.84
24.90
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm

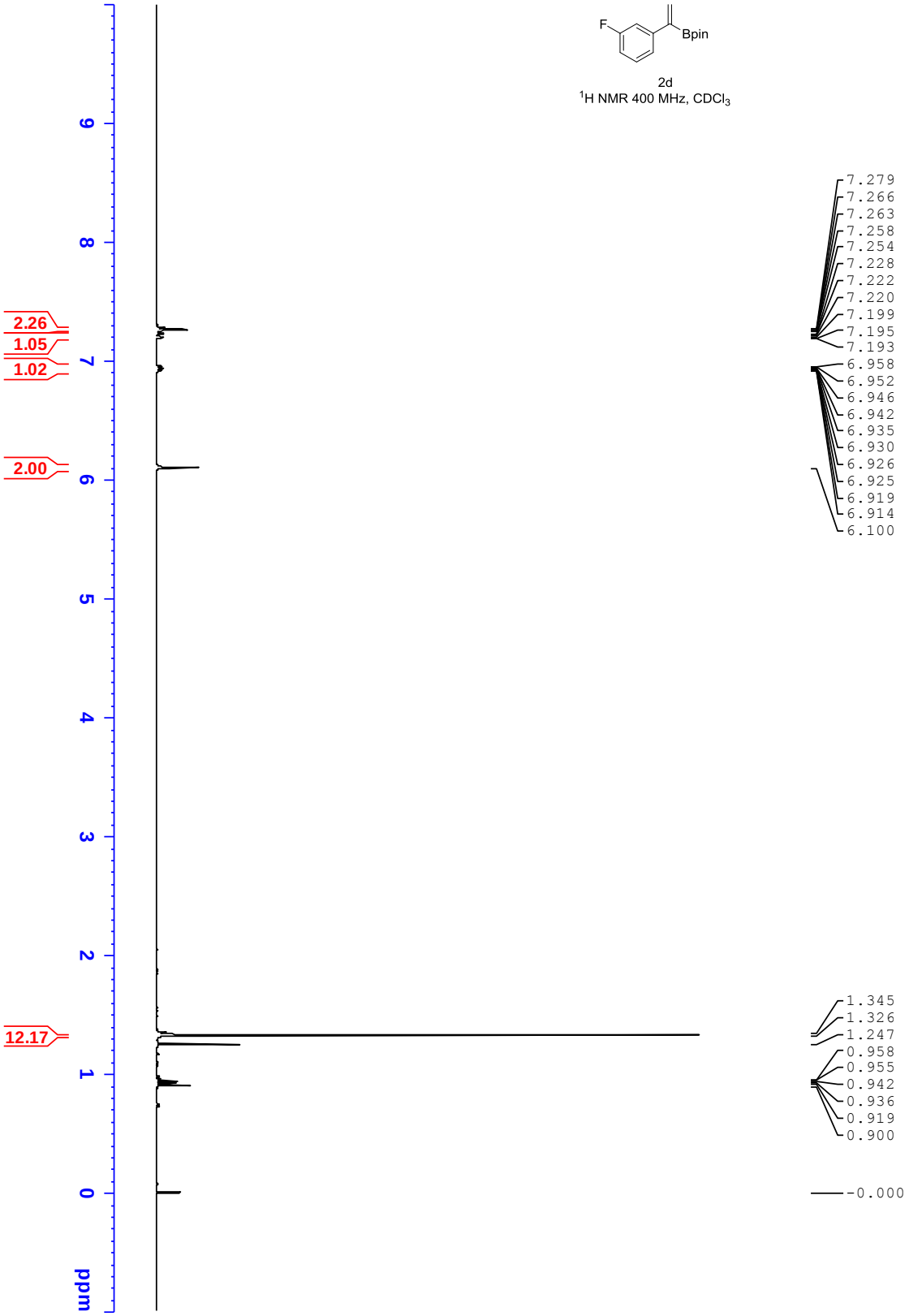


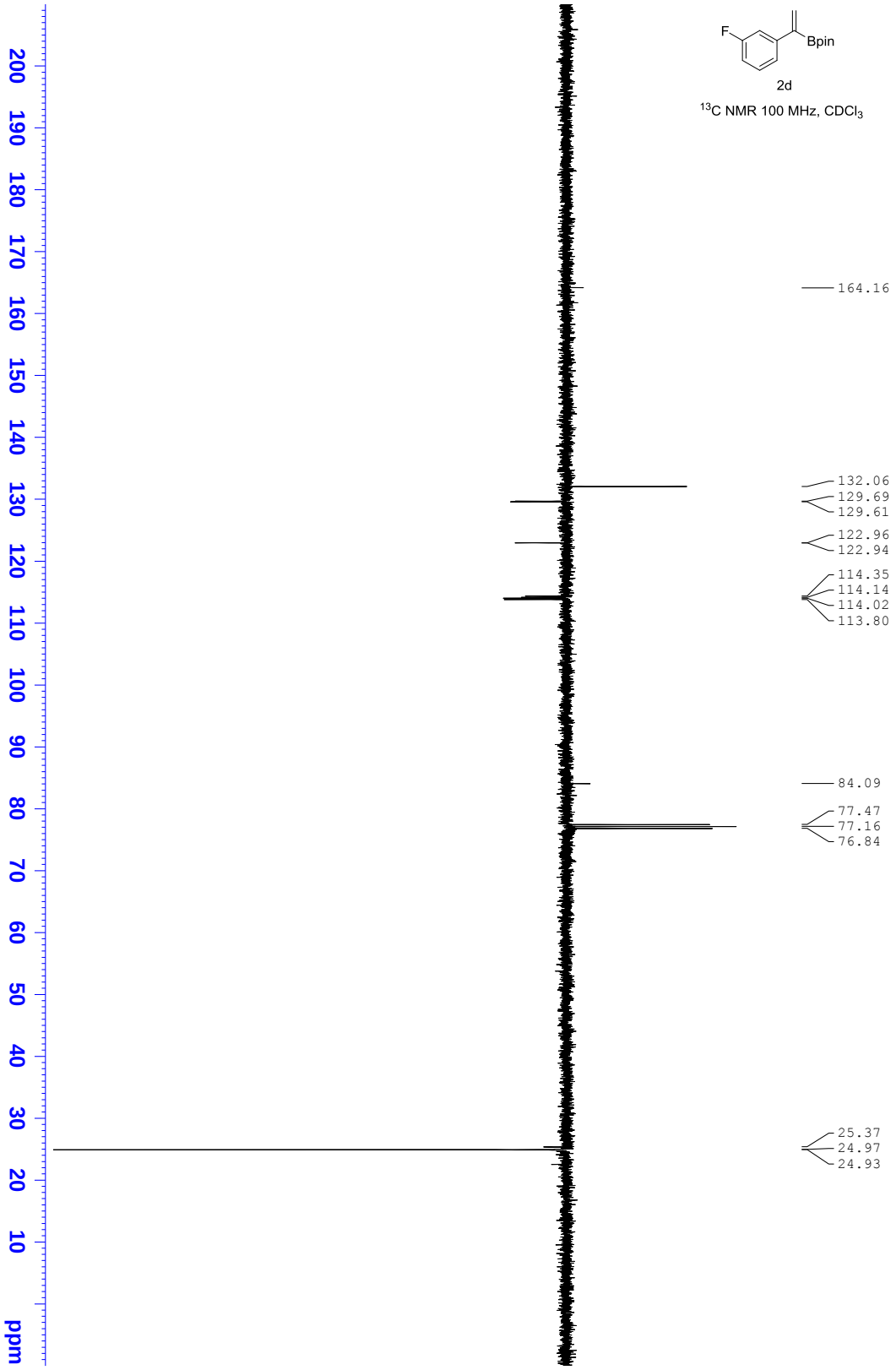
2b

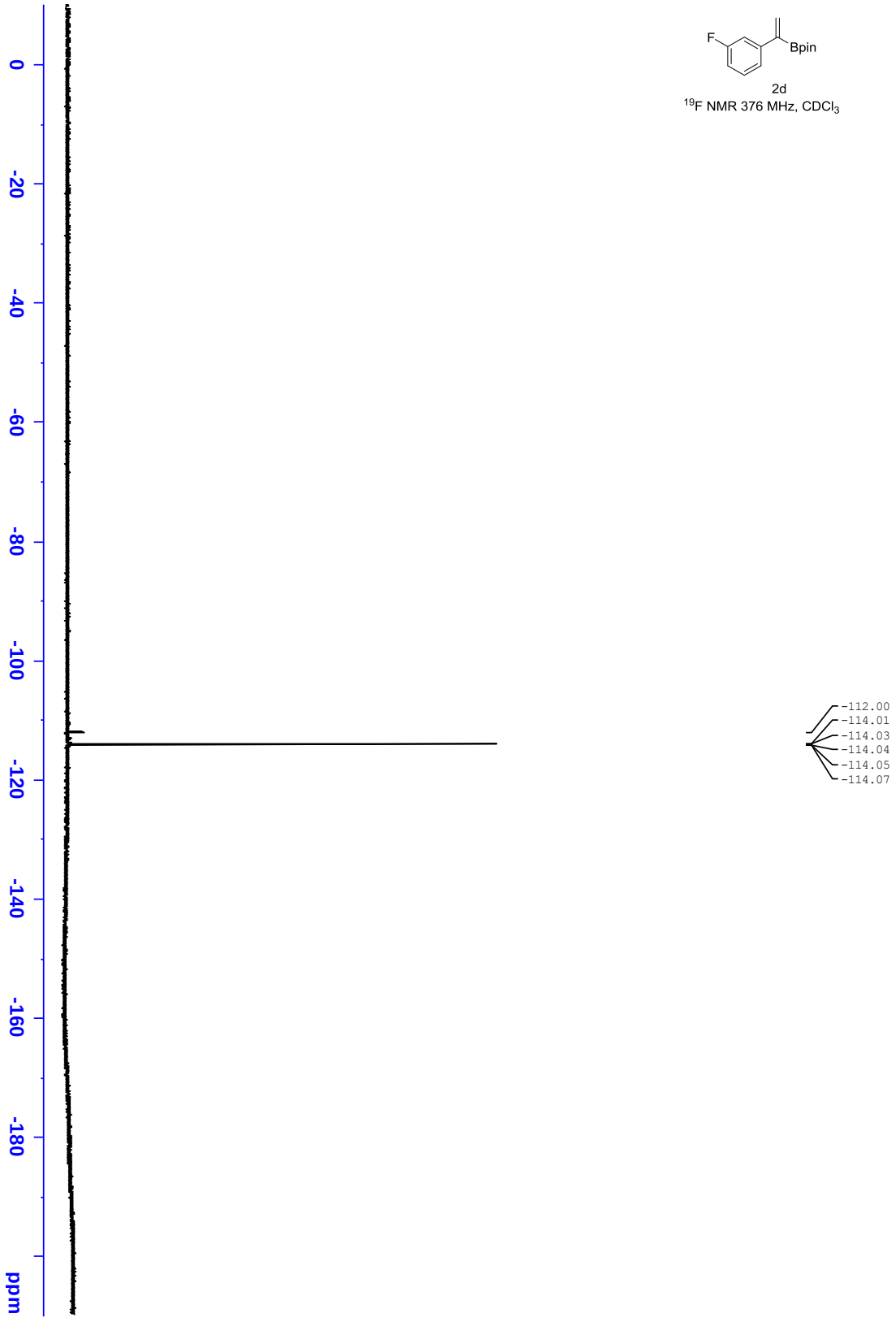
^{11}F NMR 376 MHz, $CDCl_3$

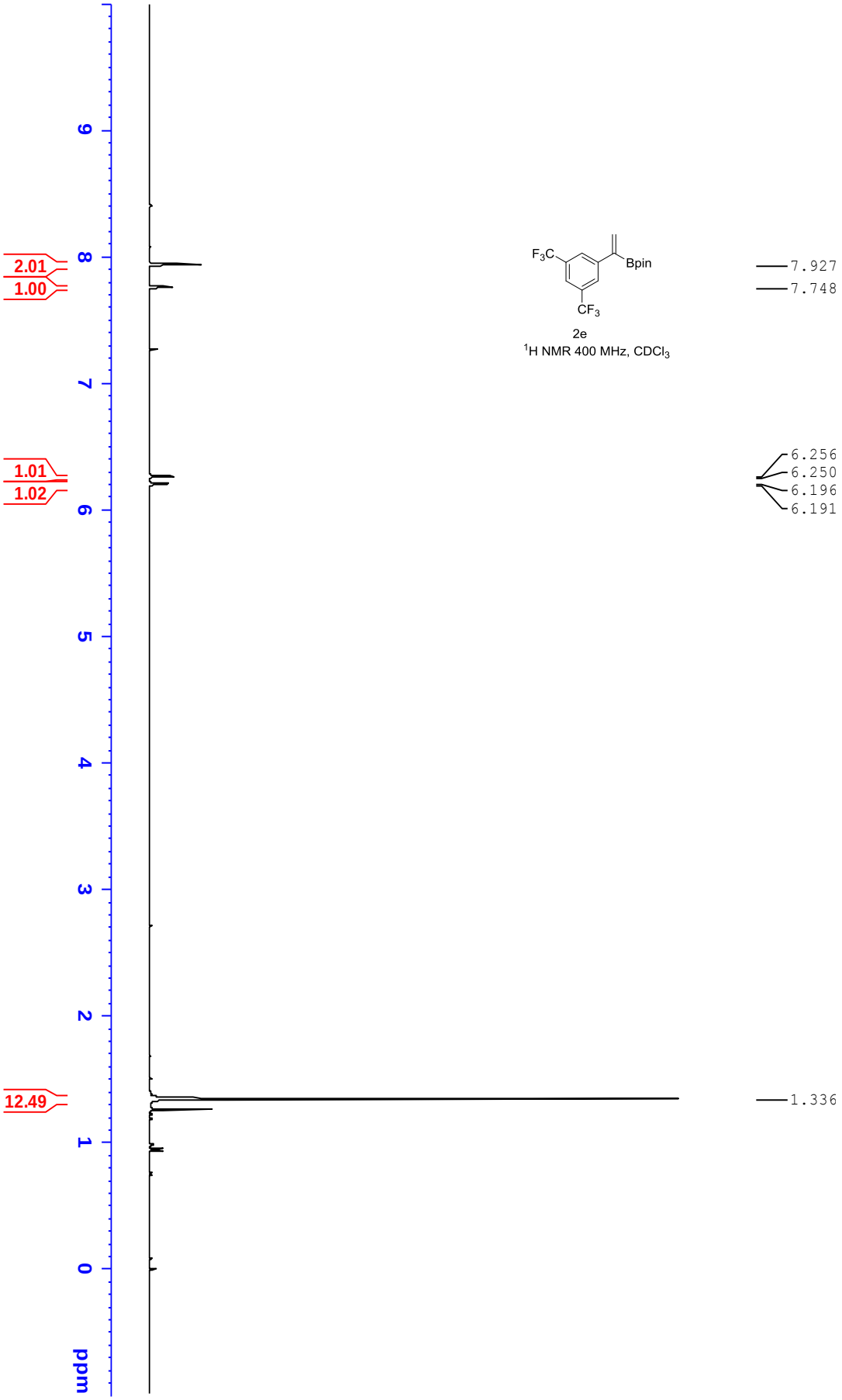

Bpin
Cl
2c
^{1}H NMR 400 MHz, $CDCl_3$
2.07
2.00
2.06
12.12
7.424
7.403
7.284
7.263
6.071
1.317
1.245
ppm

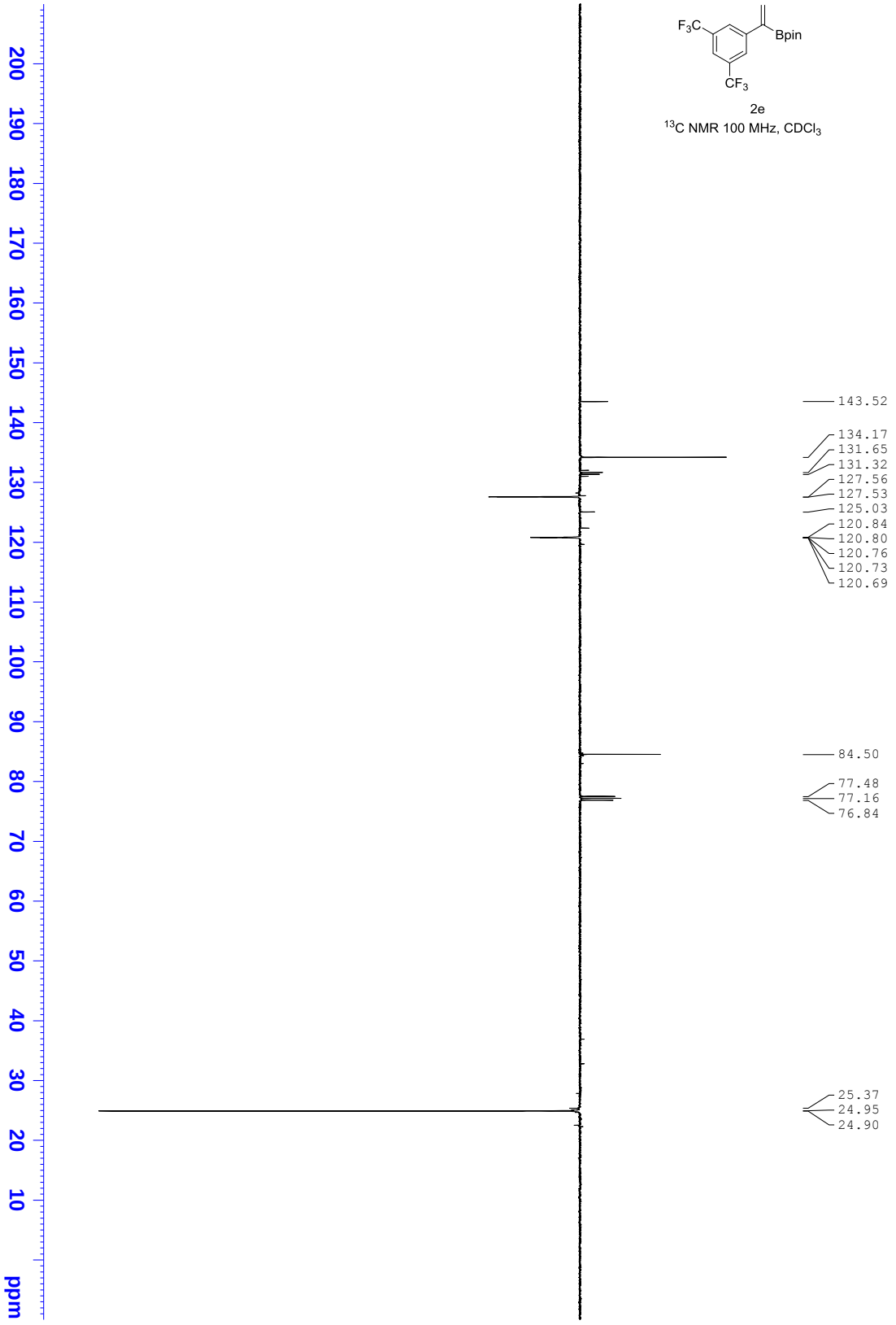

Bpin
Cl
2c
^{13}C NMR 100 MHz, $CDCl_3$
139.95
133.01
131.54
128.66
128.43
84.06
77.48
77.16
76.84
25.37
24.93
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

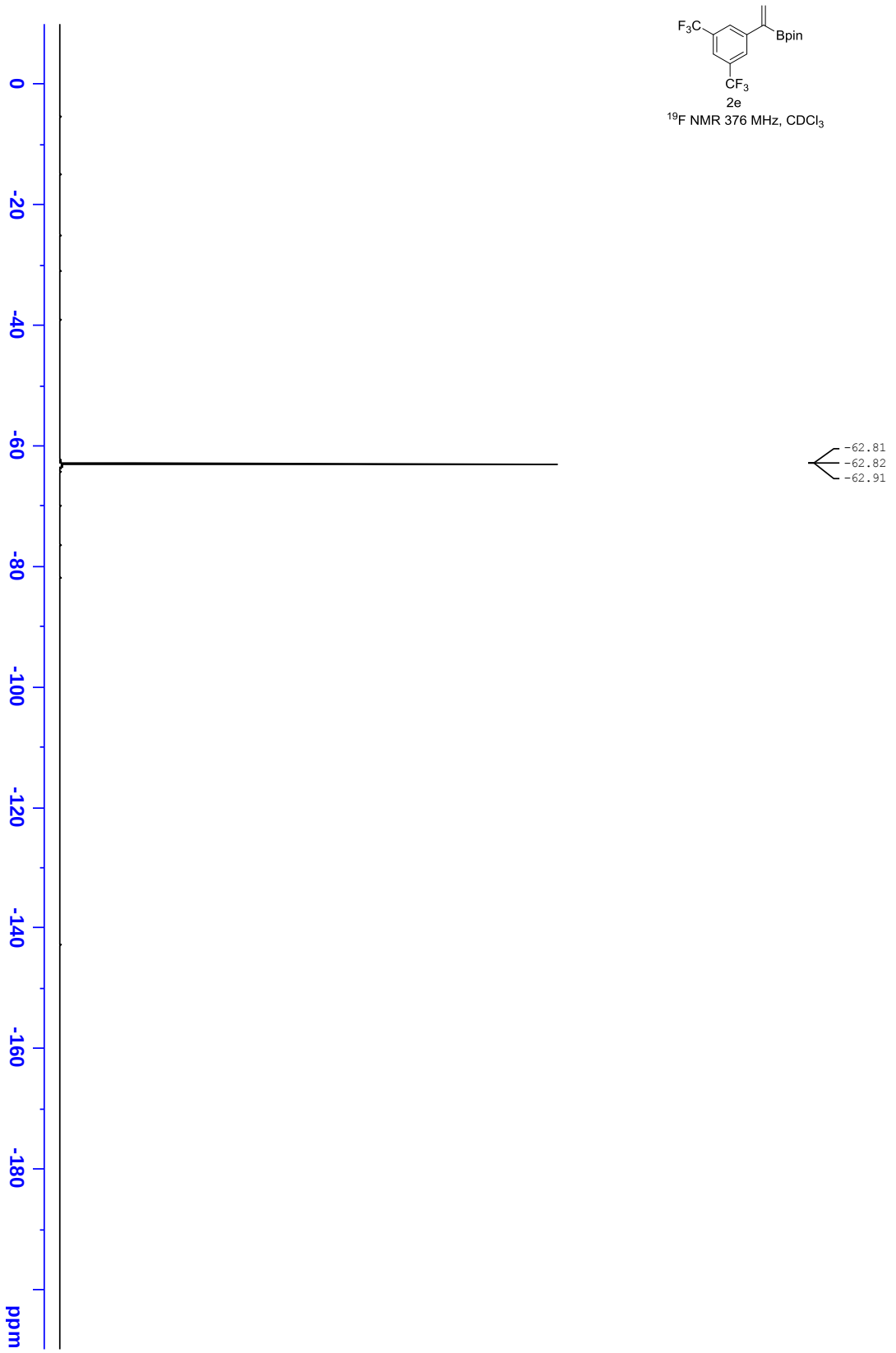

F
Bpin
2d
1H NMR 400 MHz, CDCl3
7.279
7.266
7.263
7.258
7.254
7.228
7.222
7.220
7.199
7.195
7.193
6.958
6.952
6.946
6.942
6.935
6.930
6.926
6.925
6.919
6.914
6.100
1.345
1.326
1.247
0.958
0.955
0.942
0.936
0.919
0.900
-0.000
2.26
1.05
1.02
2.00
12.17
ppm

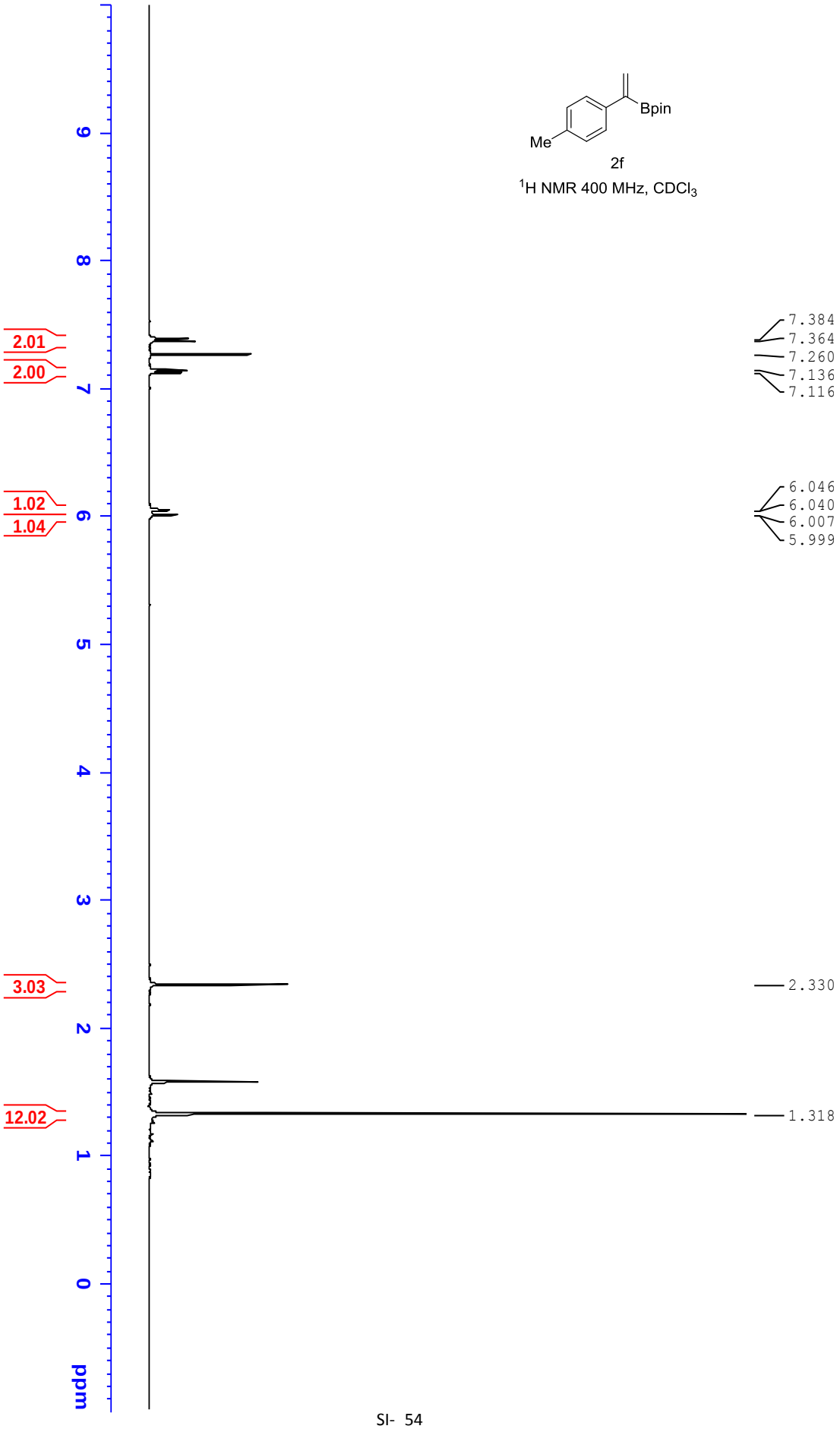

F
Bpin
2d
^{13}C NMR 100 MHz, $CDCl_3$
164.16
132.06
129.69
129.61
122.96
122.94
114.35
114.14
114.02
113.80
84.09
77.47
77.16
76.84
25.37
24.97
24.93
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

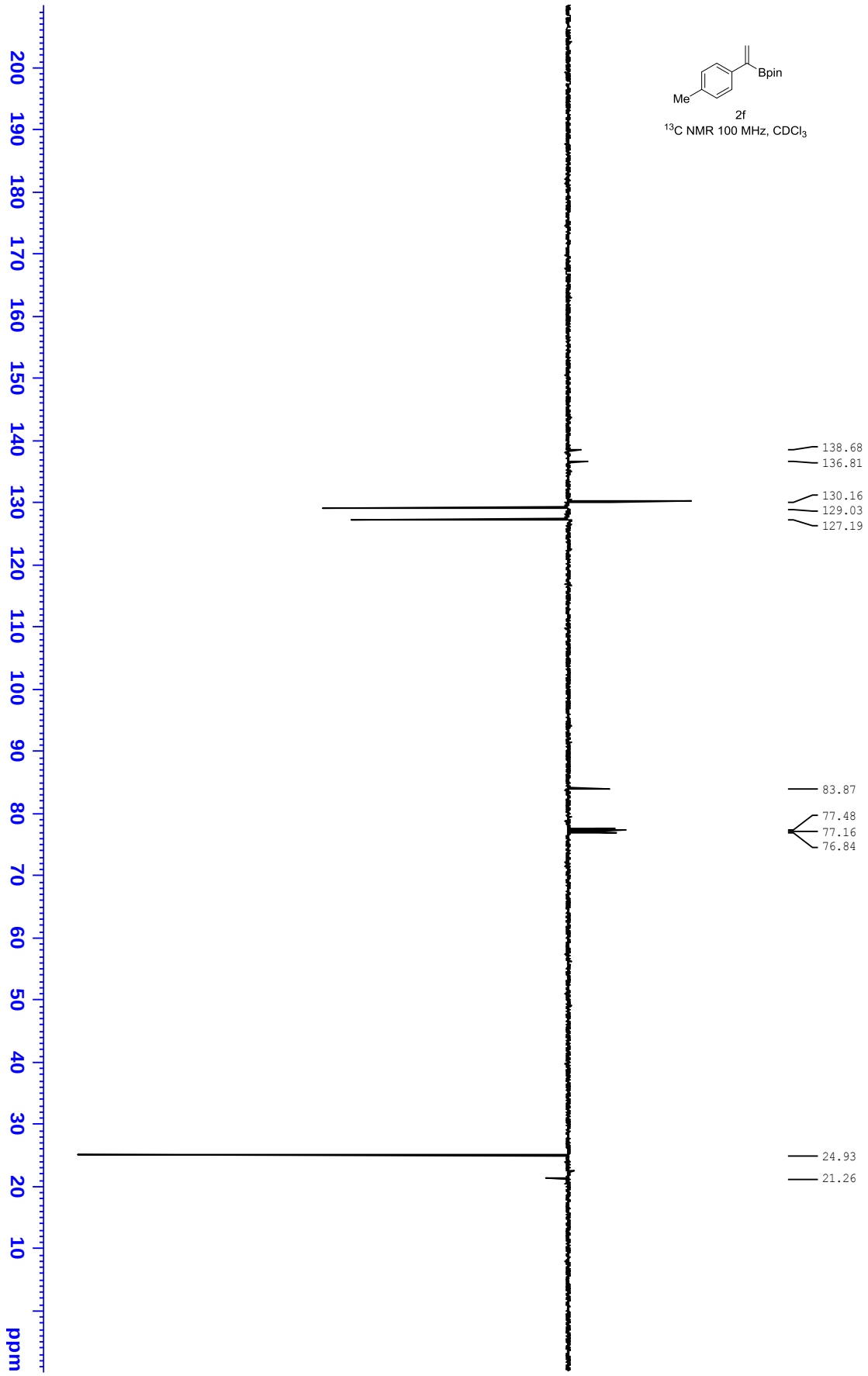

F
Bpin
2d
^{19}F NMR 376 MHz, $CDCl_3$
0
-20
-40
-60
-80
-100
-120
-140
-160
-180
ppm
-112.00
-114.01
-114.03
-114.04
-114.05
-114.07

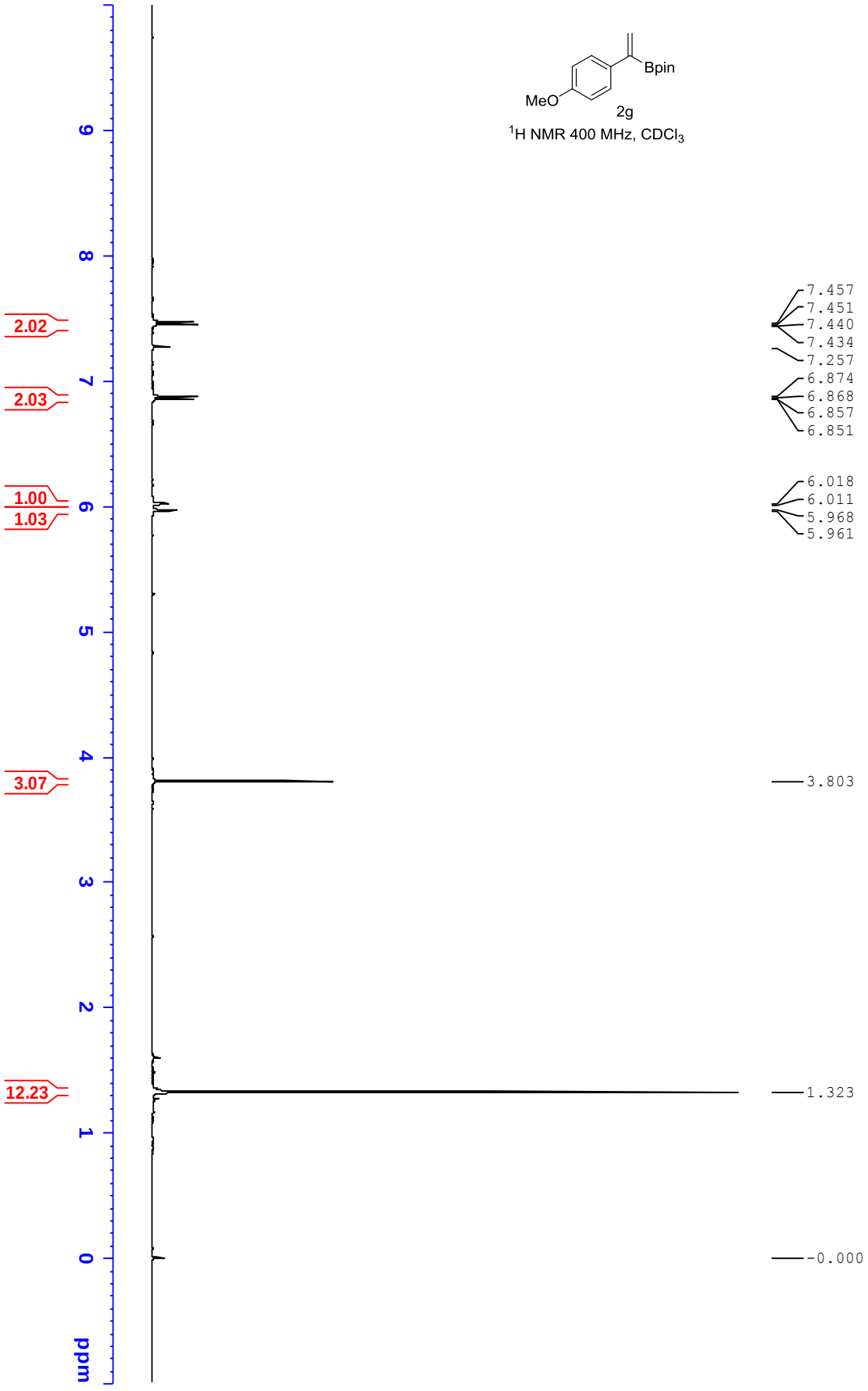

F3C
Bpin
CF3
2e
1H NMR 400 MHz, CDCl3
7.927
7.748
6.256
6.250
6.196
6.191
1.336
2.01
1.00
1.01
1.02
12.49
9
8
7
6
5
4
3
2
1
0
ppm

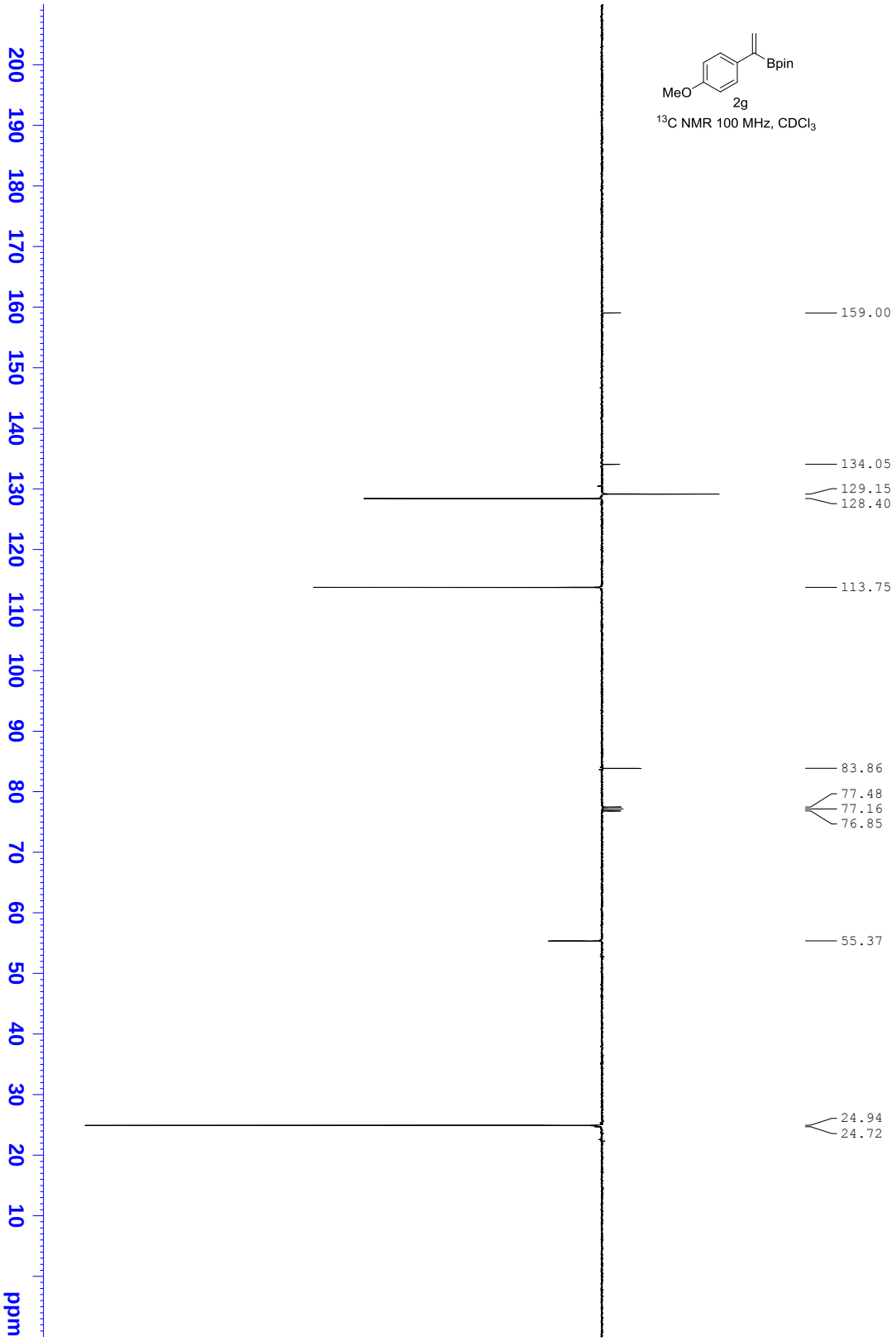

F3C
Bpin
CF3
2e
13C NMR 100 MHz, CDCl3
143.52
134.17
131.65
131.32
127.56
127.53
125.03
120.84
120.80
120.76
120.73
120.69
84.50
77.48
77.16
76.84
25.37
24.95
24.90
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

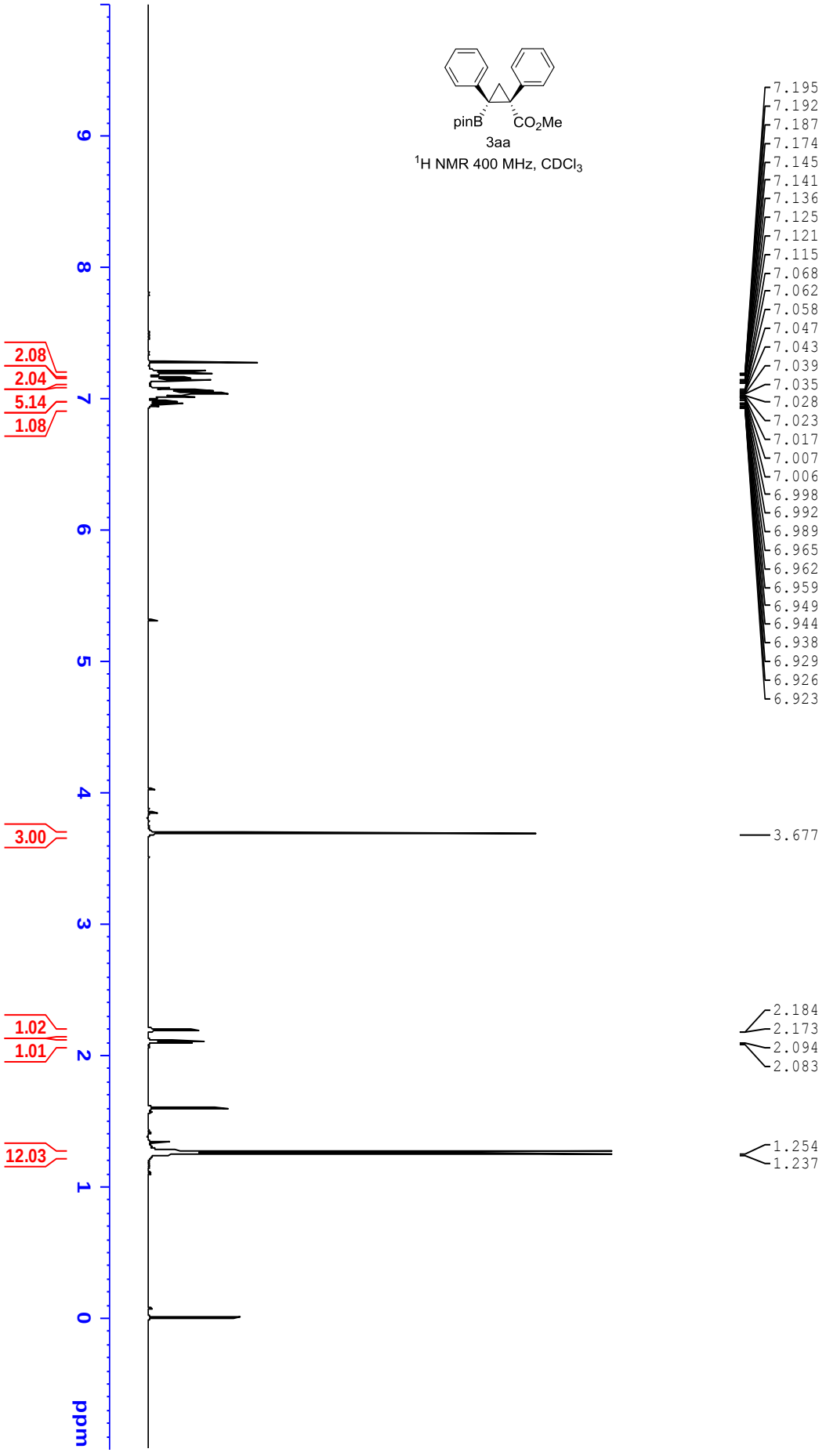

F3C
Bpin
CF3
2e
19F NMR 376 MHz, CDCl3
-62.81
-62.82
-62.91
0
-20
-40
-60
-80
-100
-120
-140
-160
-180
ppm

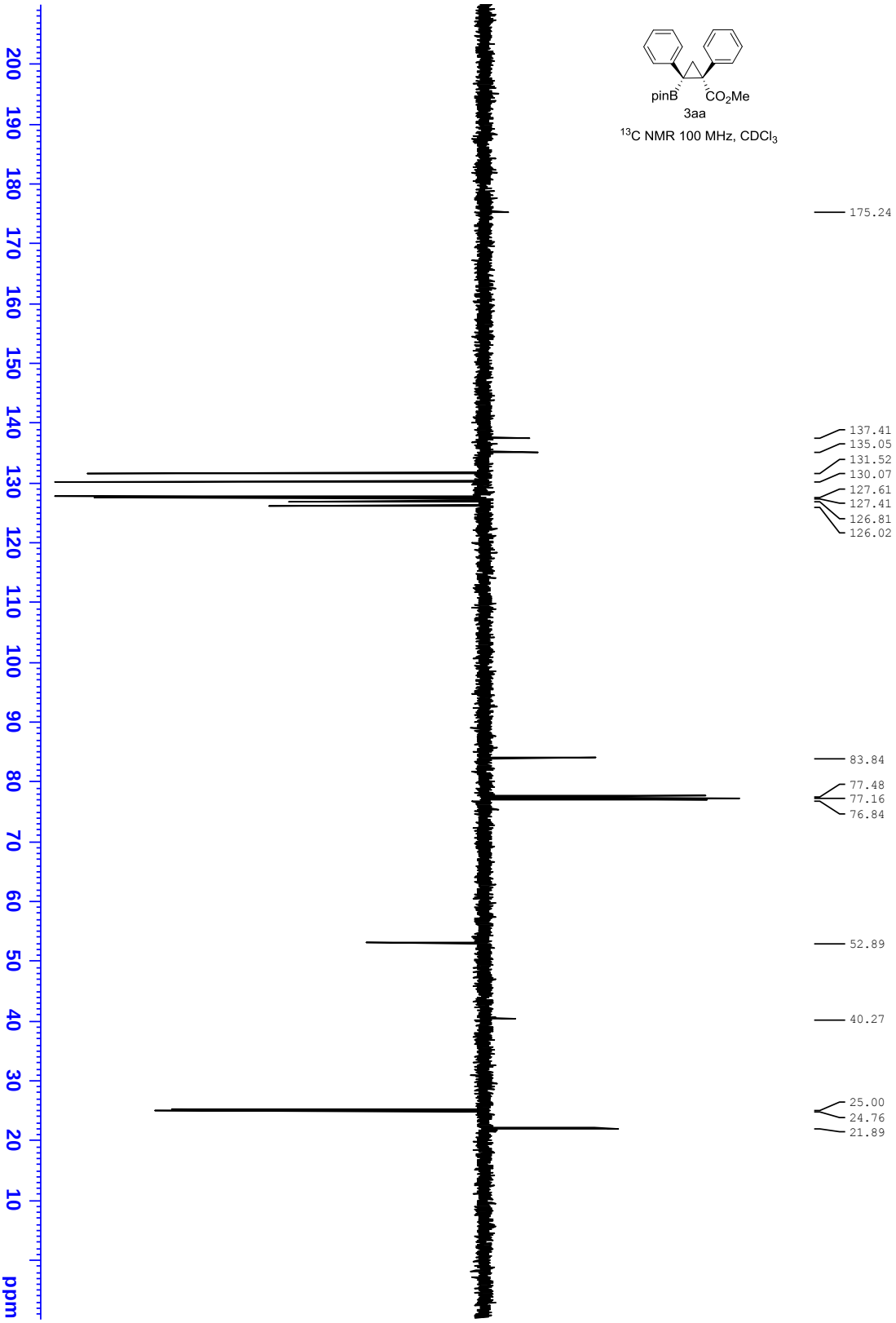

Bpin
Me
2f
^{1}H NMR 400 MHz, $CDCl_3$
7.384
7.364
7.260
7.136
7.116
6.046
6.040
6.007
5.999
2.330
1.318
2.01
2.00
1.02
1.04
3.03
12.02
ppm


Bpin
Me
2f
13C NMR 100 MHz, CDCl3
138.68
136.81
130.16
129.03
127.19
83.87
77.48
77.16
76.84
24.93
21.26
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

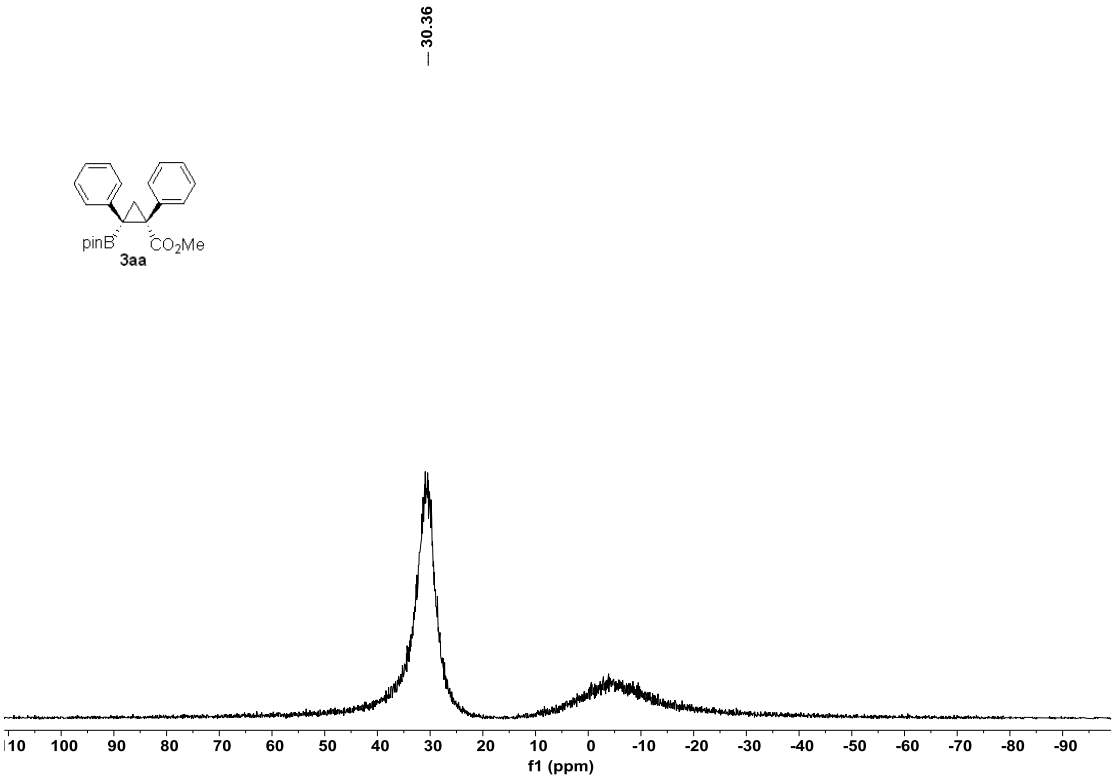

Bpin
MeO
2g
^{1}H NMR 400 MHz, $CDCl_3$
7.457
7.451
7.440
7.434
7.257
6.874
6.868
6.857
6.851
6.018
6.011
5.968
5.961
3.803
1.323
-0.000
2.02
2.03
1.00
1.03
3.07
12.23
ppm

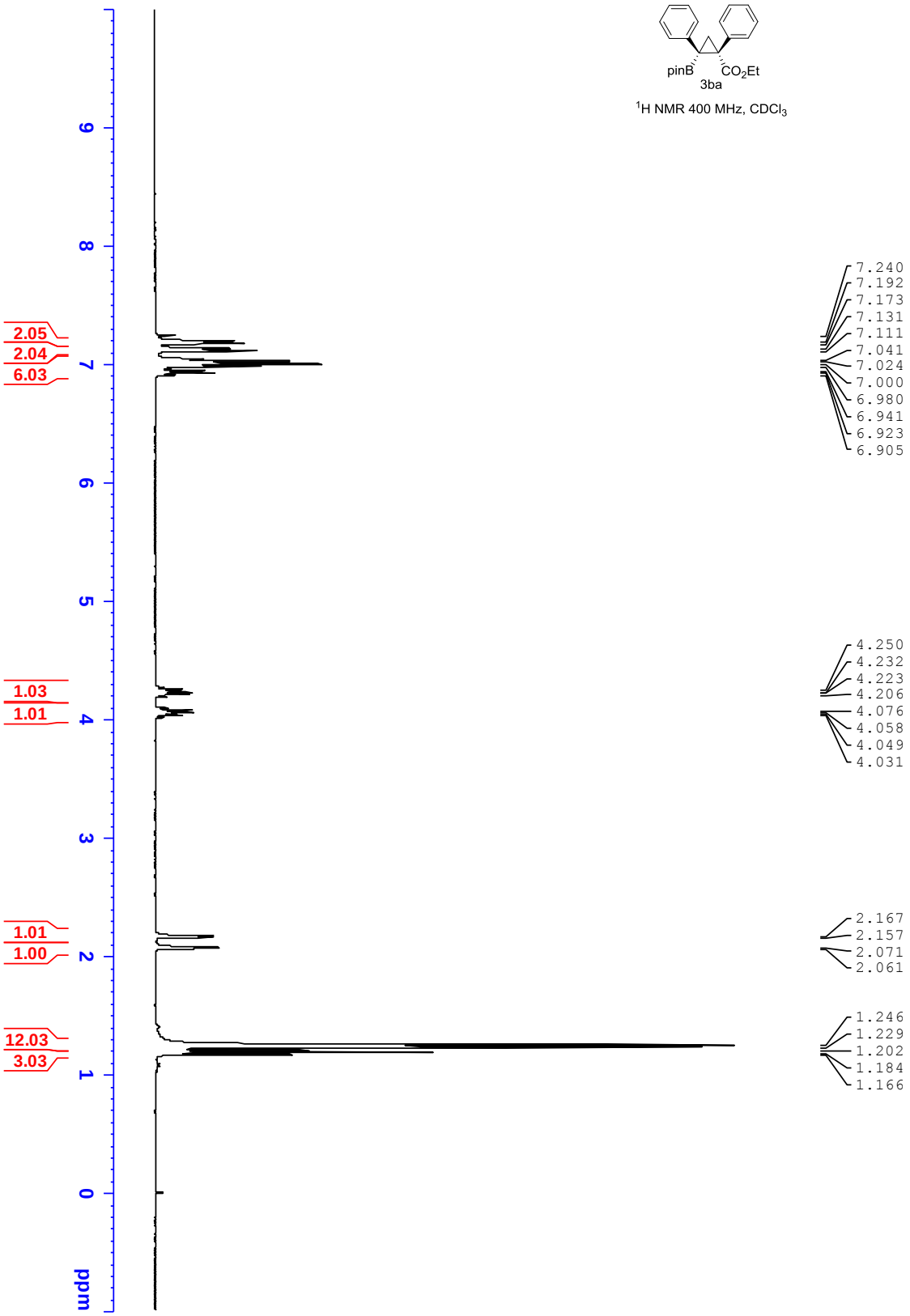

Bpin
MeO
2g
^{13}C NMR 100 MHz, $CDCl_3$
159.00
134.05
129.15
128.40
113.75
83.86
77.48
77.16
76.85
55.37
24.94
24.72
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

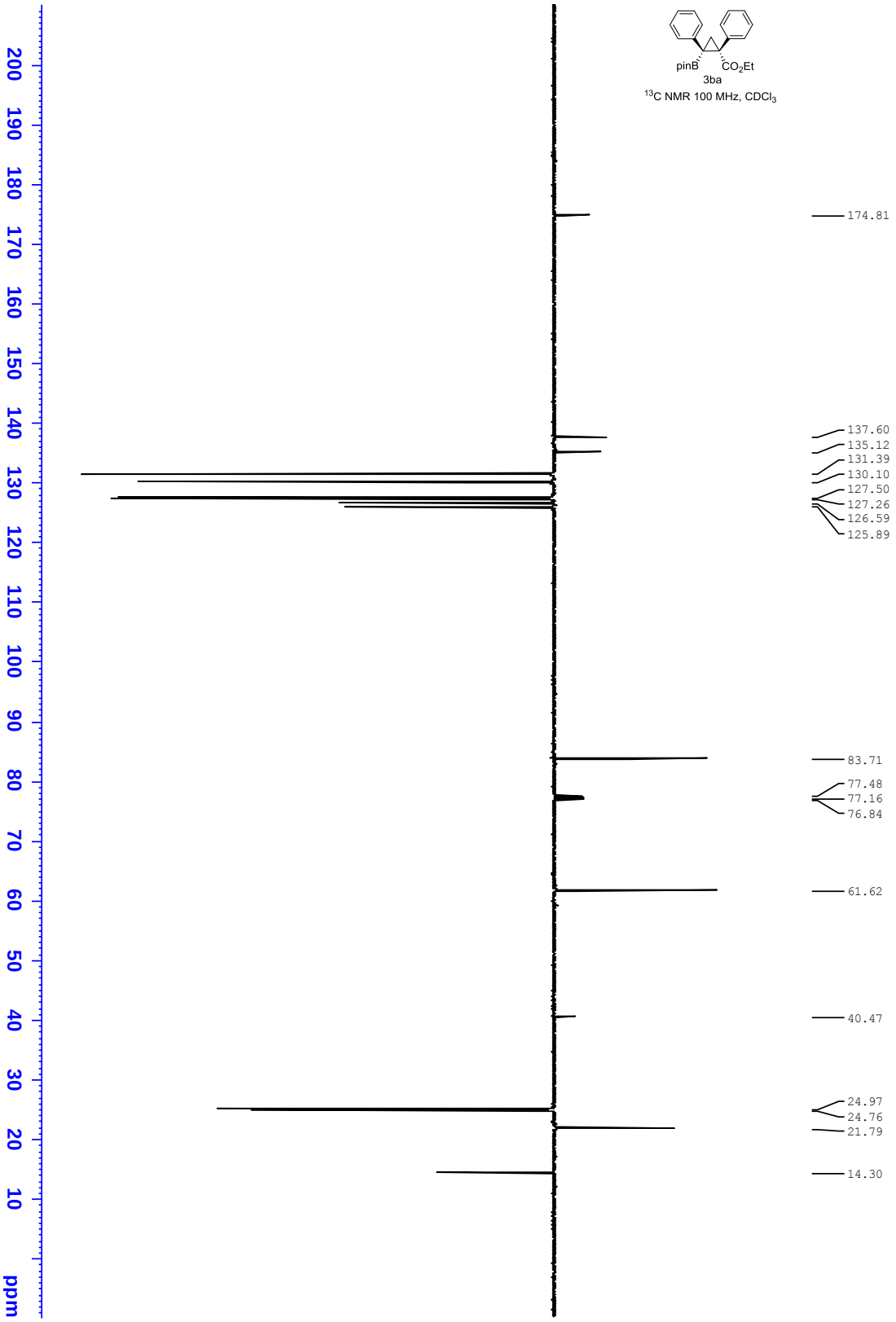

pinB
CO2Me
3aa
1H NMR 400 MHz, CDCl3
7.195
7.192
7.187
7.174
7.145
7.141
7.136
7.125
7.121
7.115
7.068
7.062
7.058
7.047
7.043
7.039
7.035
7.028
7.023
7.017
7.007
7.006
6.998
6.992
6.989
6.965
6.962
6.959
6.949
6.944
6.938
6.929
6.926
6.923
3.677
2.184
2.173
2.094
2.083
1.254
1.237
2.08
2.04
5.14
1.08
3.00
1.02
1.01
12.03
ppm

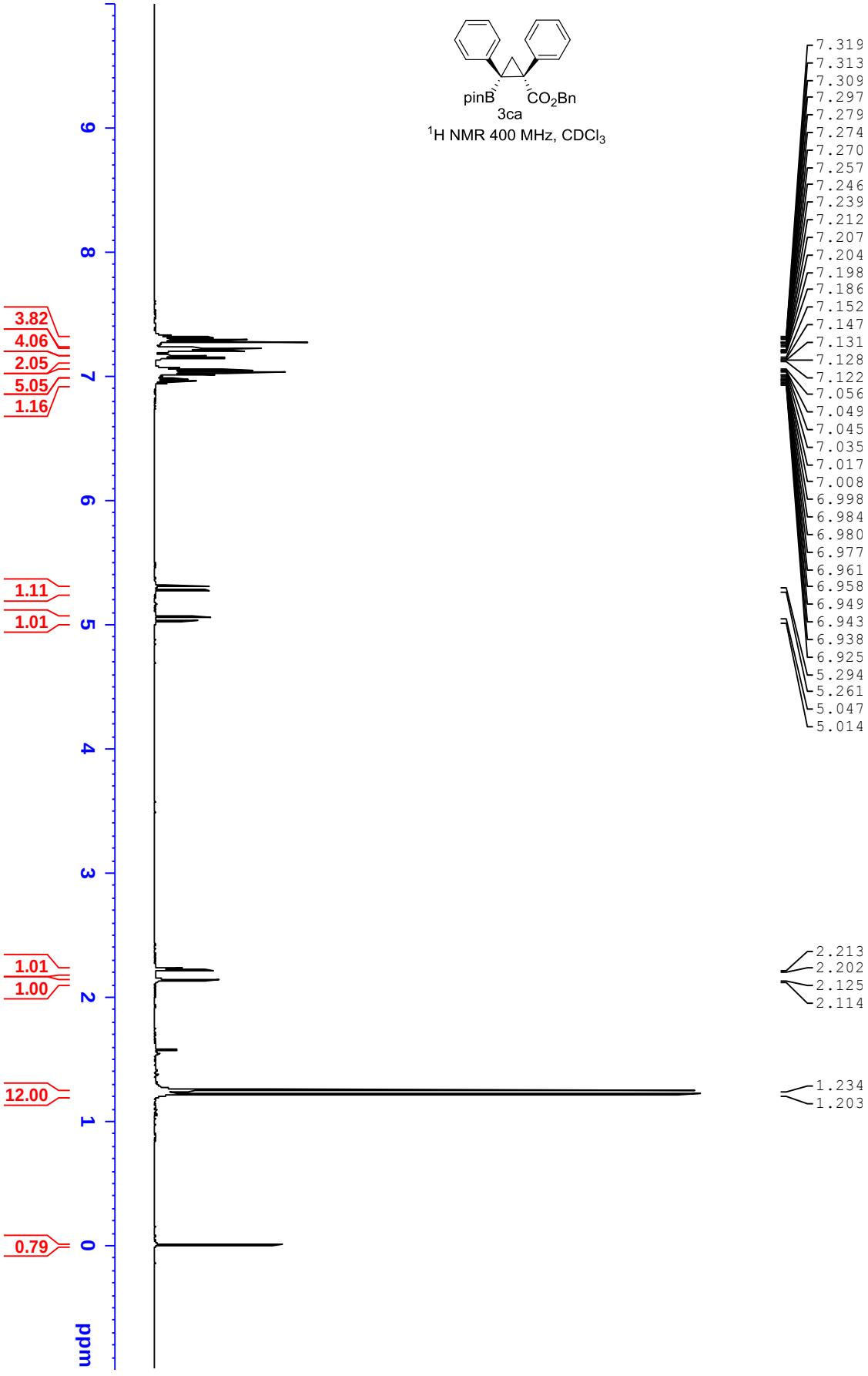

pinB
CO2Me
3aa
13C NMR 100 MHz, CDCl3
175.24
137.41
135.05
131.52
130.07
127.61
127.41
126.81
126.02
83.84
77.48
77.16
76.84
52.89
40.27
25.00
24.76
21.89
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

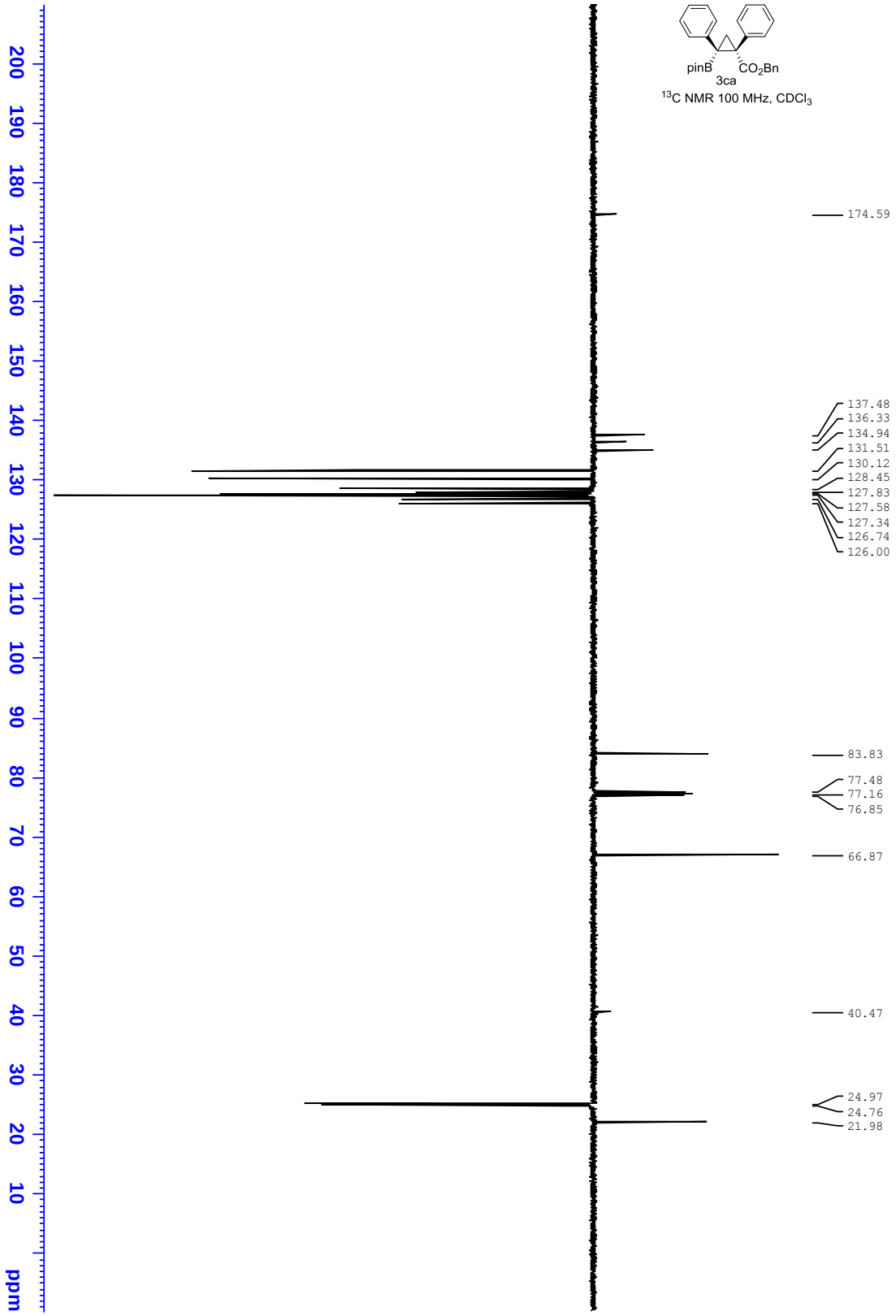
3aa ^{11}B NMR (128 MHz, $CDCl_3$)

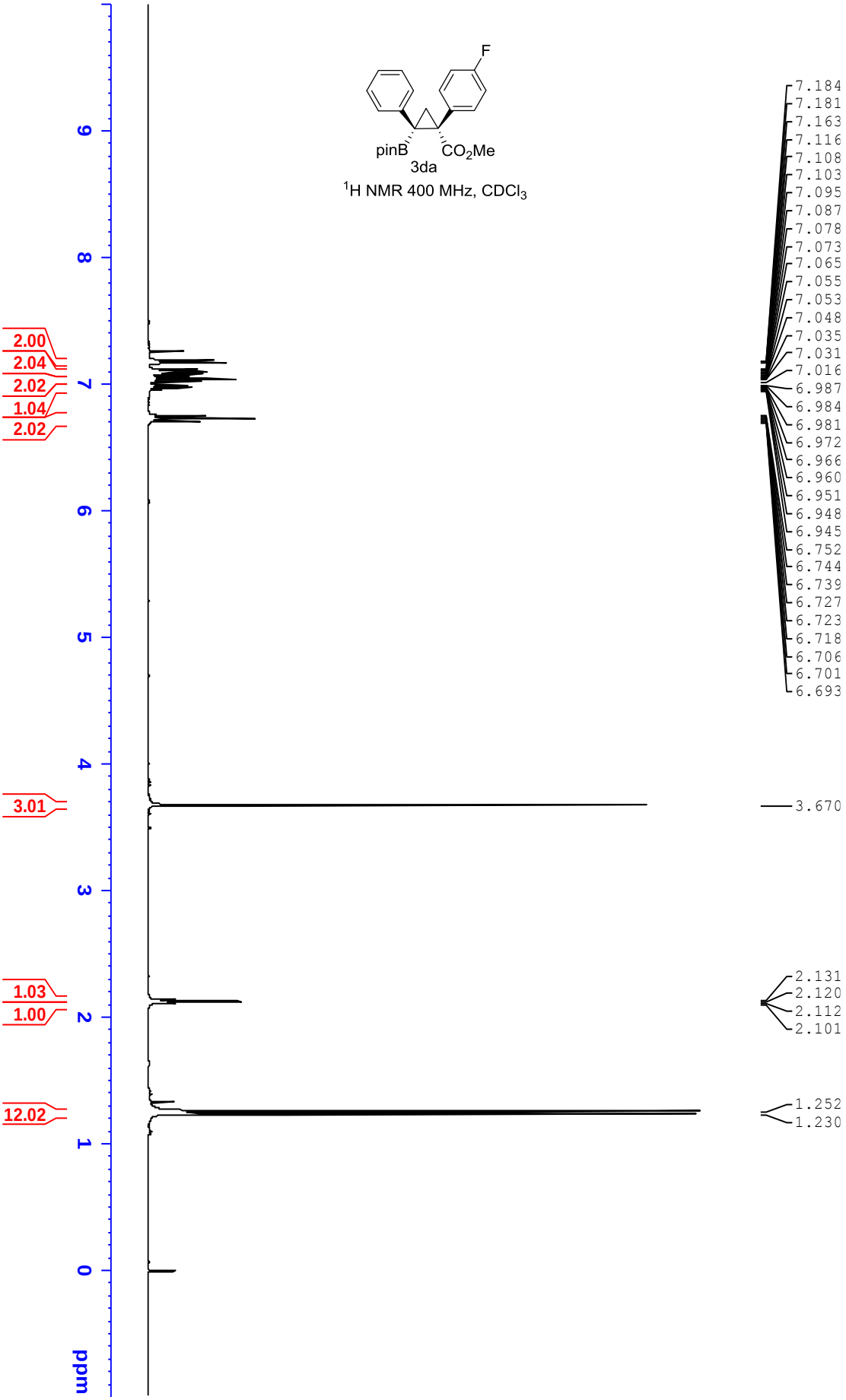


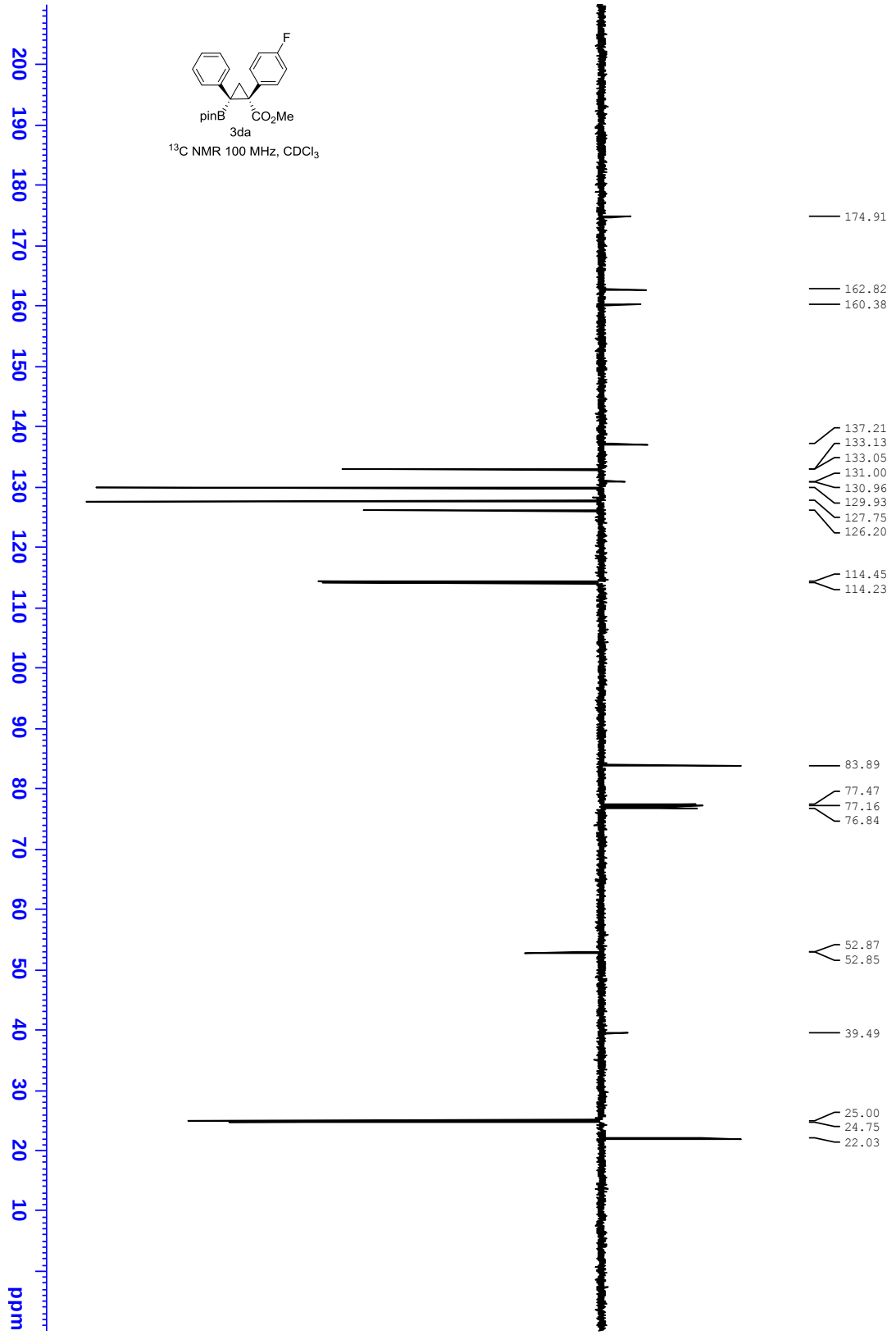

pinB
CO2Et
3ba
1H NMR 400 MHz, CDCl3
7.240
7.192
7.173
7.131
7.111
7.041
7.024
7.000
6.980
6.941
6.923
6.905
4.250
4.232
4.223
4.206
4.076
4.058
4.049
4.031
2.167
2.157
2.071
2.061
1.246
1.229
1.202
1.184
1.166
2.05
2.04
6.03
1.03
1.01
1.01
1.00
12.03
3.03
ppm

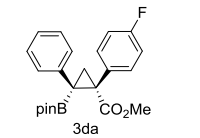

pinB
CO2Et
3ba
13C NMR 100 MHz, CDCl3
174.81
137.60
135.12
131.39
130.10
127.50
127.26
126.59
125.89
83.71
77.48
77.16
76.84
61.62
40.47
24.97
24.76
21.79
14.30
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm


pinB
CO2Bn
3ca
1H NMR 400 MHz, CDCl3
7.319
7.313
7.309
7.297
7.279
7.274
7.270
7.257
7.246
7.239
7.212
7.207
7.204
7.198
7.186
7.152
7.147
7.131
7.128
7.122
7.056
7.049
7.045
7.035
7.017
7.008
6.998
6.984
6.980
6.977
6.961
6.958
6.949
6.943
6.938
6.925
5.294
5.261
5.047
5.014
2.213
2.202
2.125
2.114
1.234
1.203
3.82
4.06
2.05
5.05
1.16
1.11
1.01
1.01
1.00
12.00
0.79
ppm


pinB
CO2Bn
3ca
13C NMR 100 MHz, CDCl3
174.59
137.48
136.33
134.94
131.51
130.12
128.45
127.83
127.58
127.34
126.74
126.00
83.83
77.48
77.16
76.85
66.87
40.47
24.97
24.76
21.98
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

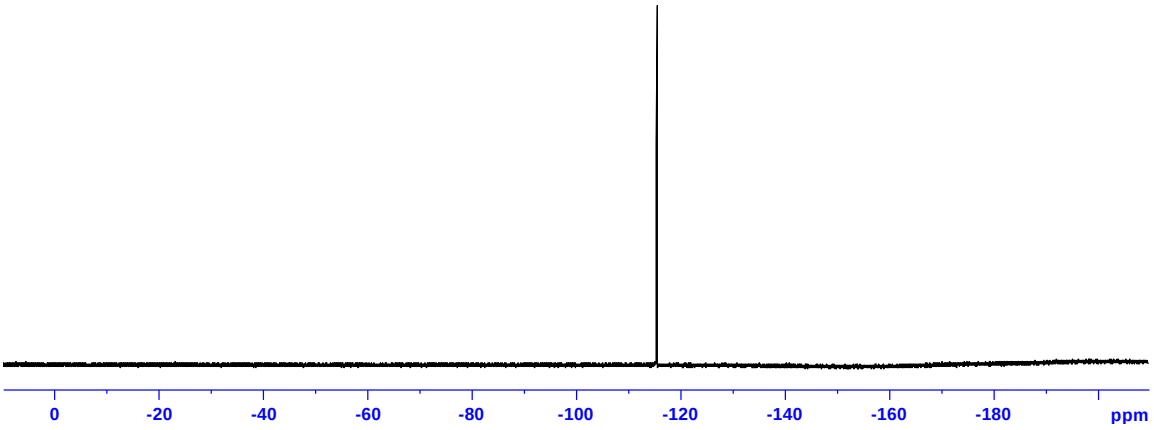

F
pinB
CO2Me
3da
1H NMR 400 MHz, CDCl3
7.184
7.181
7.163
7.116
7.108
7.103
7.095
7.087
7.078
7.073
7.065
7.055
7.053
7.048
7.035
7.031
7.016
6.987
6.984
6.981
6.972
6.966
6.960
6.951
6.948
6.945
6.752
6.744
6.739
6.727
6.723
6.718
6.706
6.701
6.693
3.670
2.131
2.120
2.112
2.101
1.252
1.230
2.00
2.04
2.02
1.04
2.02
3.01
1.03
1.00
12.02
ppm

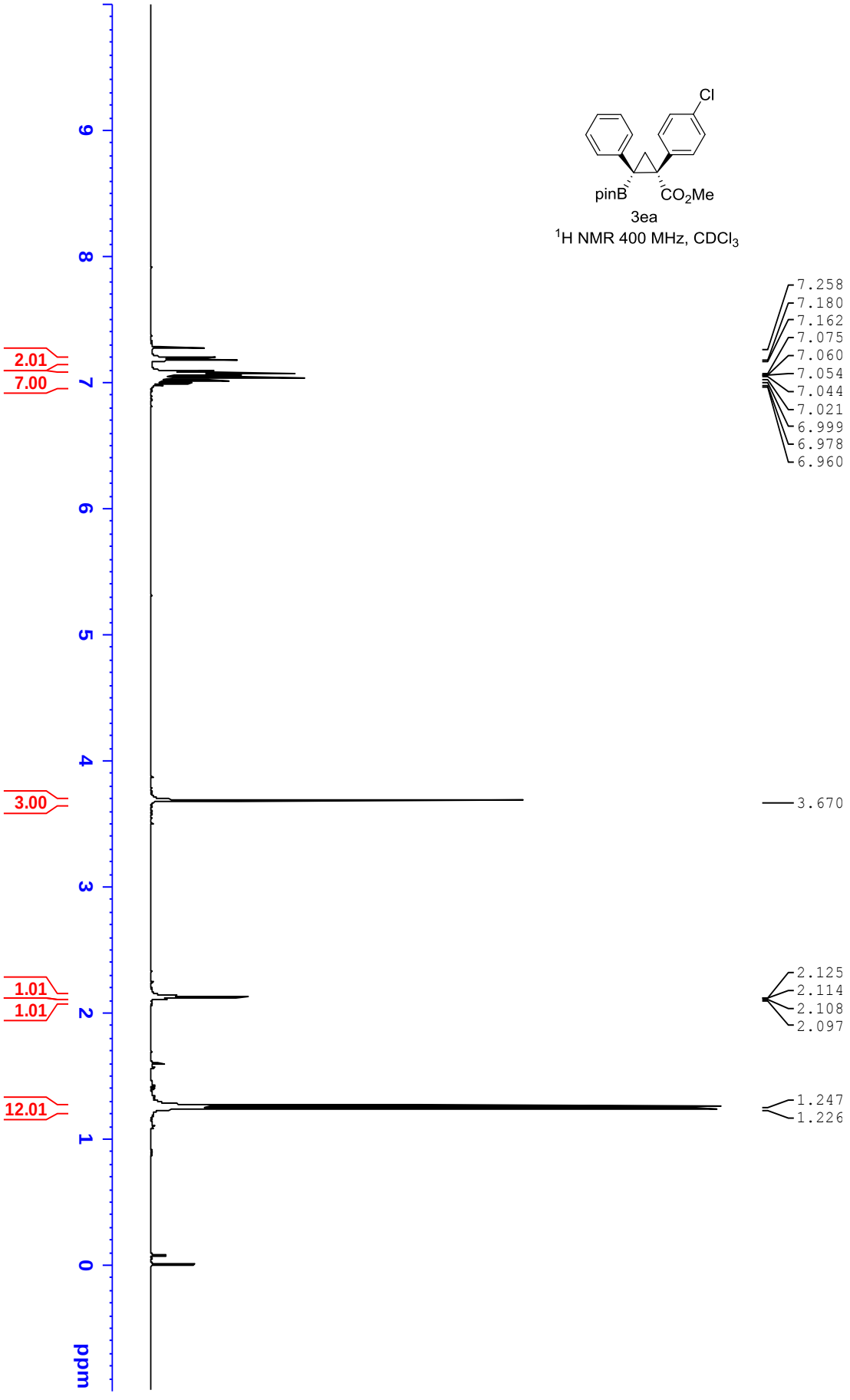

F
pinB
CO2Me
3da
13C NMR 100 MHz, CDCl3
174.91
162.82
160.38
137.21
133.13
133.05
131.00
130.96
129.93
127.75
126.20
114.45
114.23
83.89
77.47
77.16
76.84
52.87
52.85
39.49
25.00
24.75
22.03
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

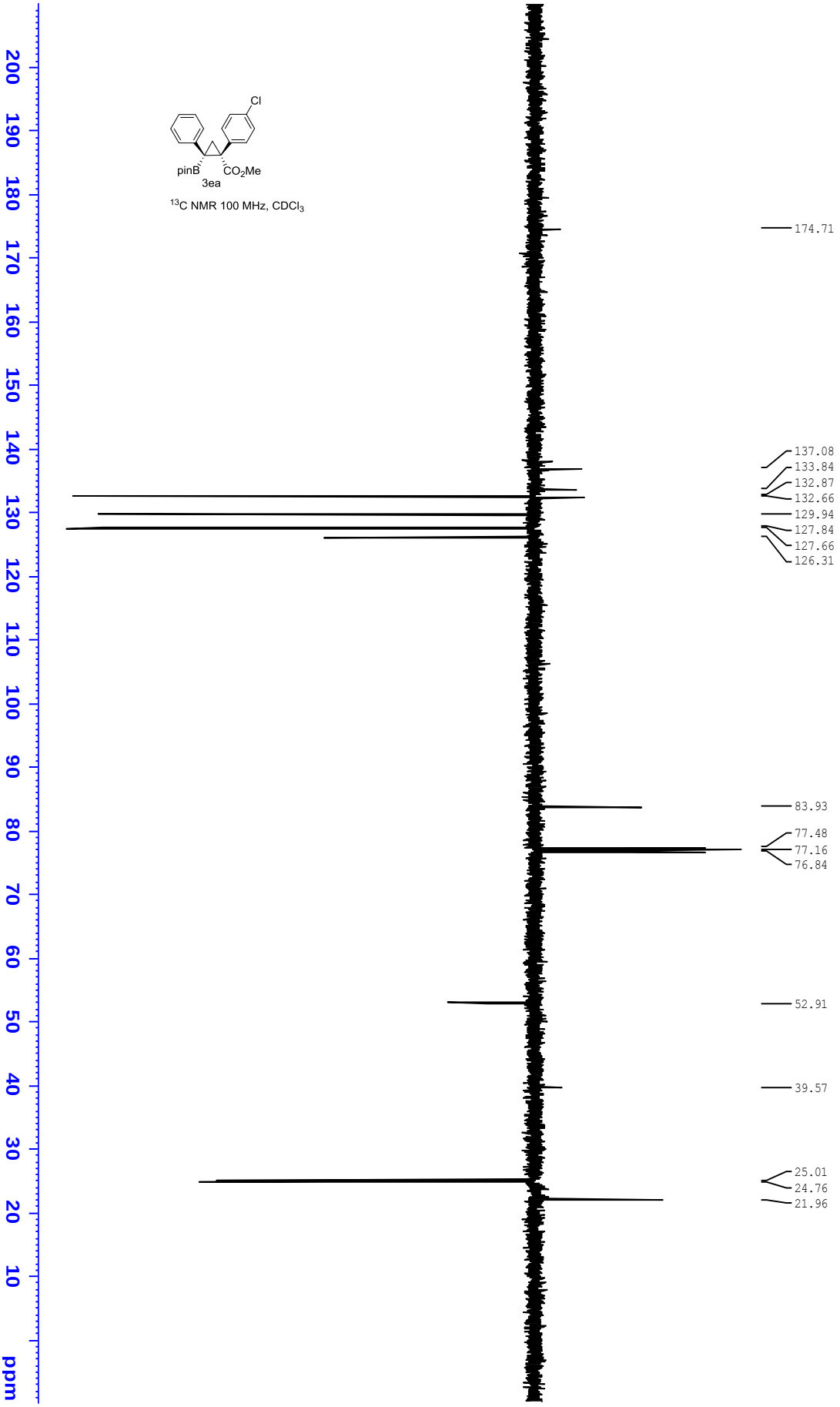


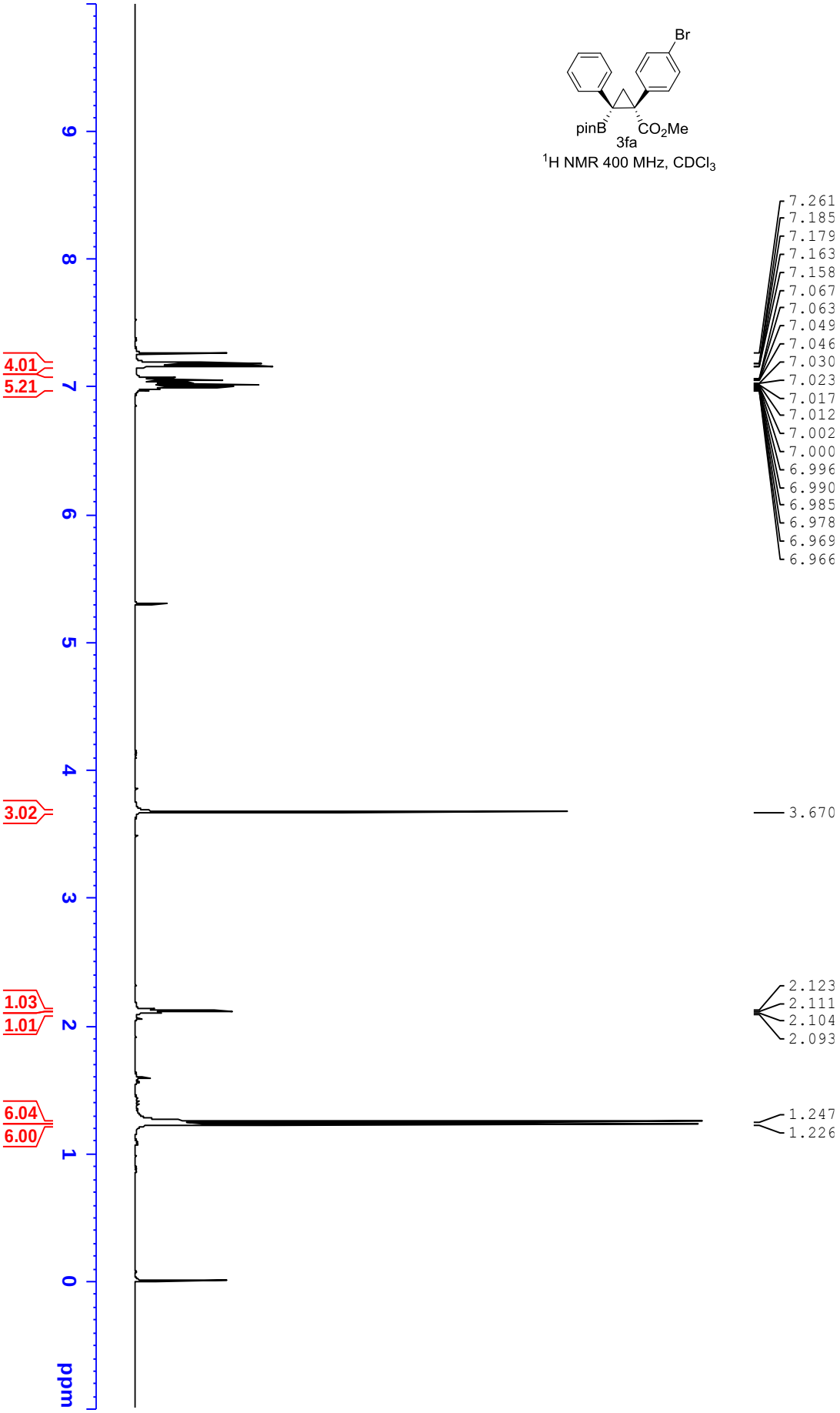
3da

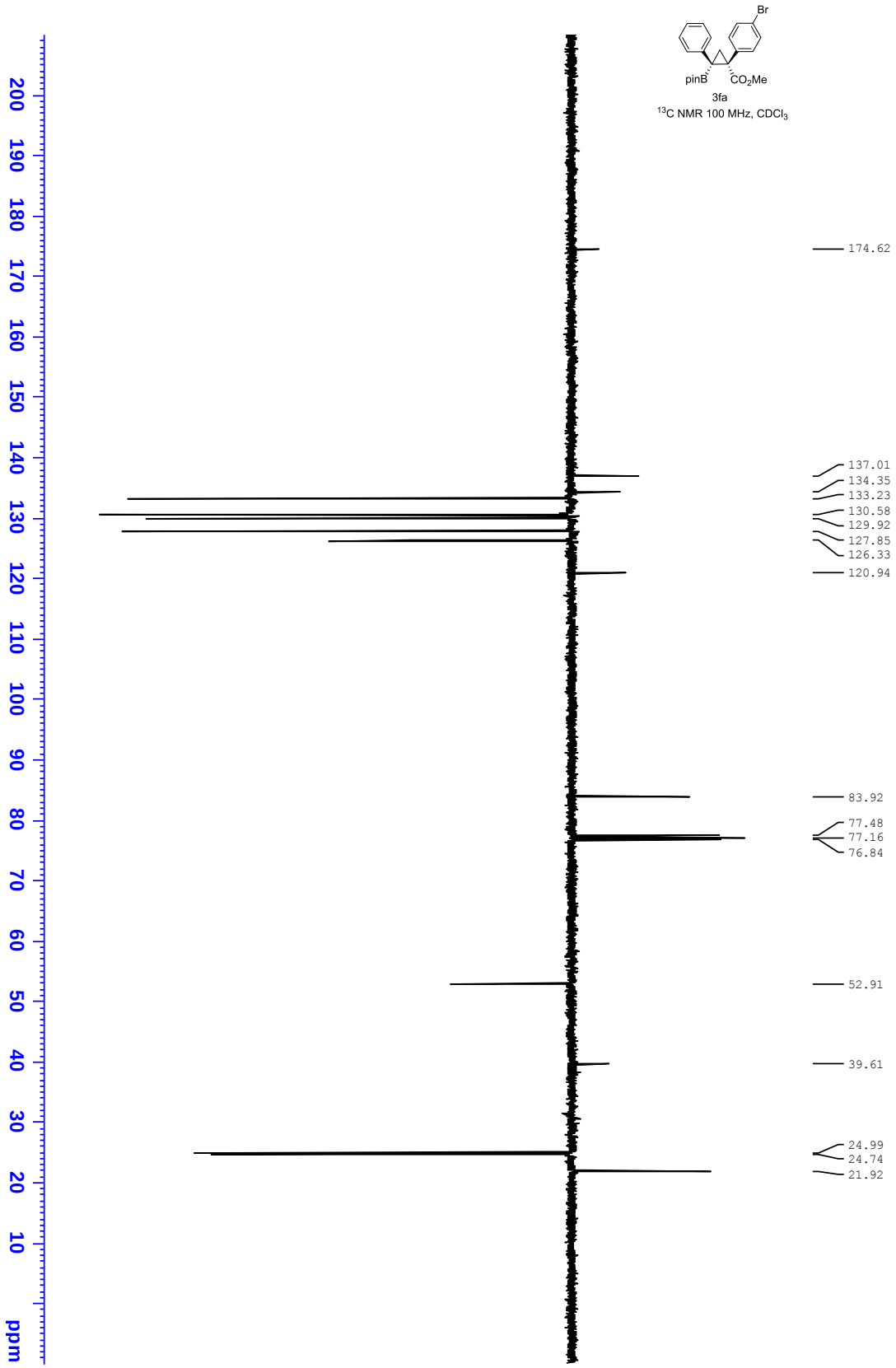
^{19}F NMR (376 MHz, $CDCl_3$)

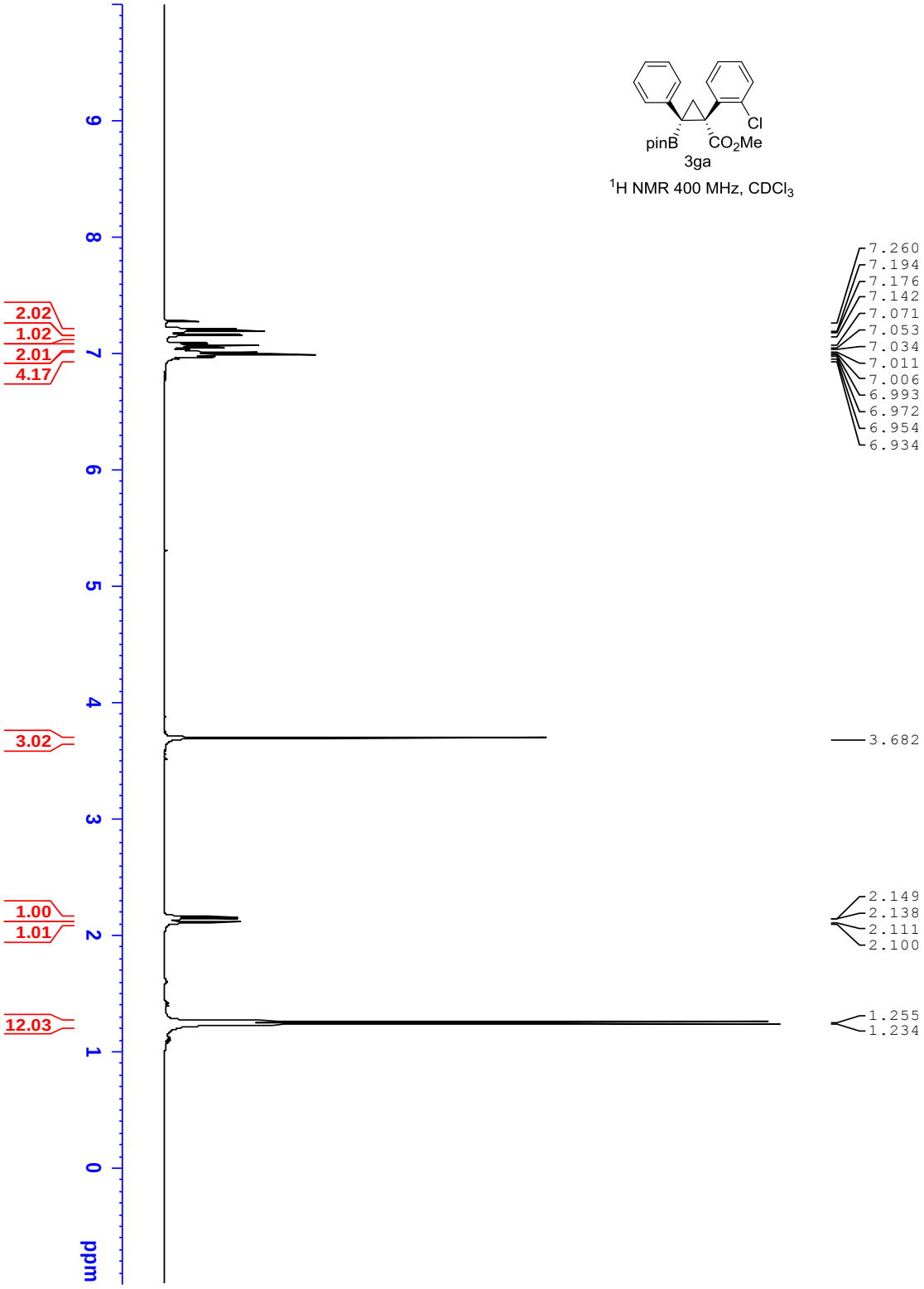


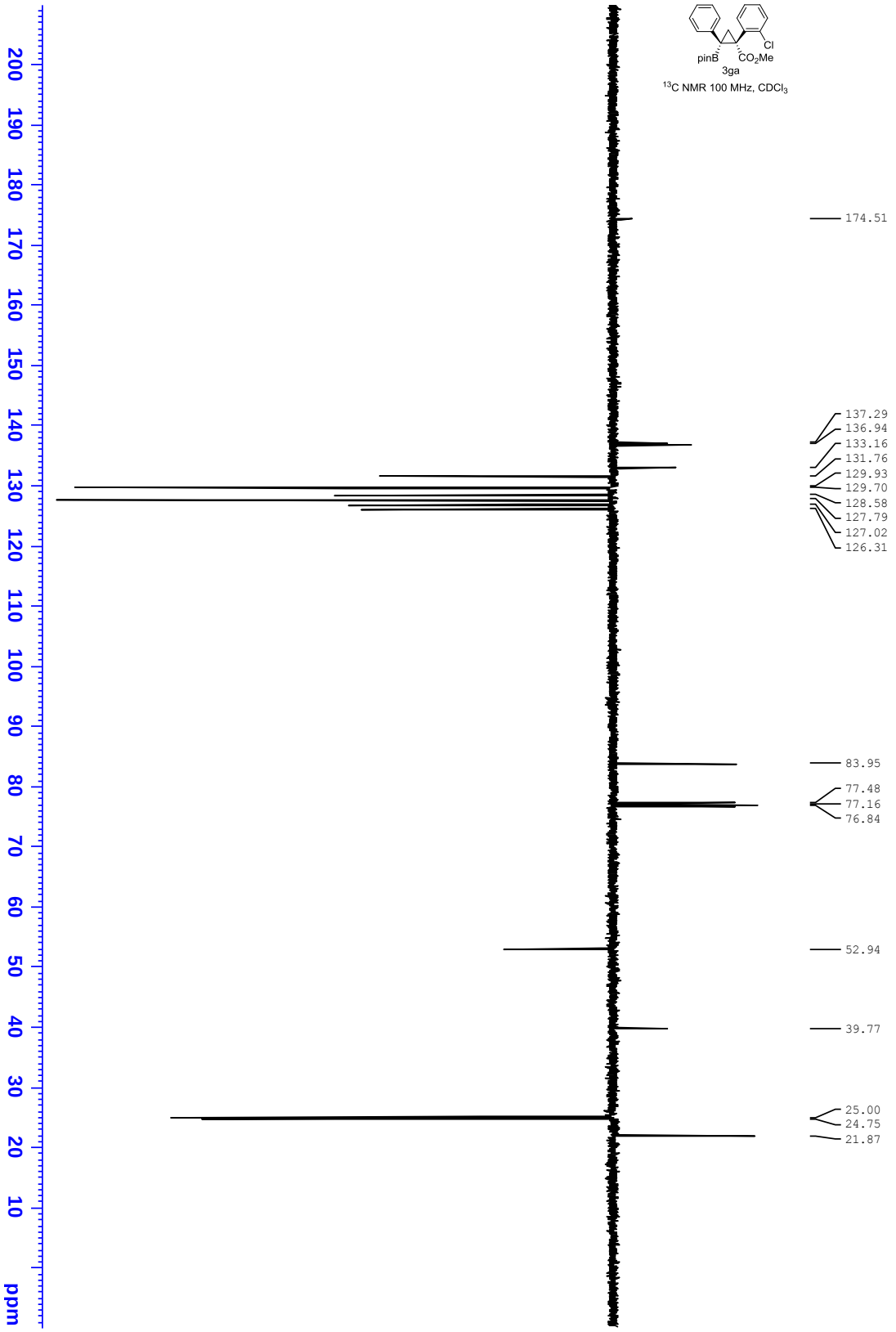

Cl
pinB
CO2Me
3ea
1H NMR 400 MHz, CDCl3
7.258
7.180
7.162
7.075
7.060
7.054
7.044
7.021
6.999
6.978
6.960
3.670
2.125
2.114
2.108
2.097
1.247
1.226
2.01
7.00
3.00
1.01
1.01
12.01
ppm

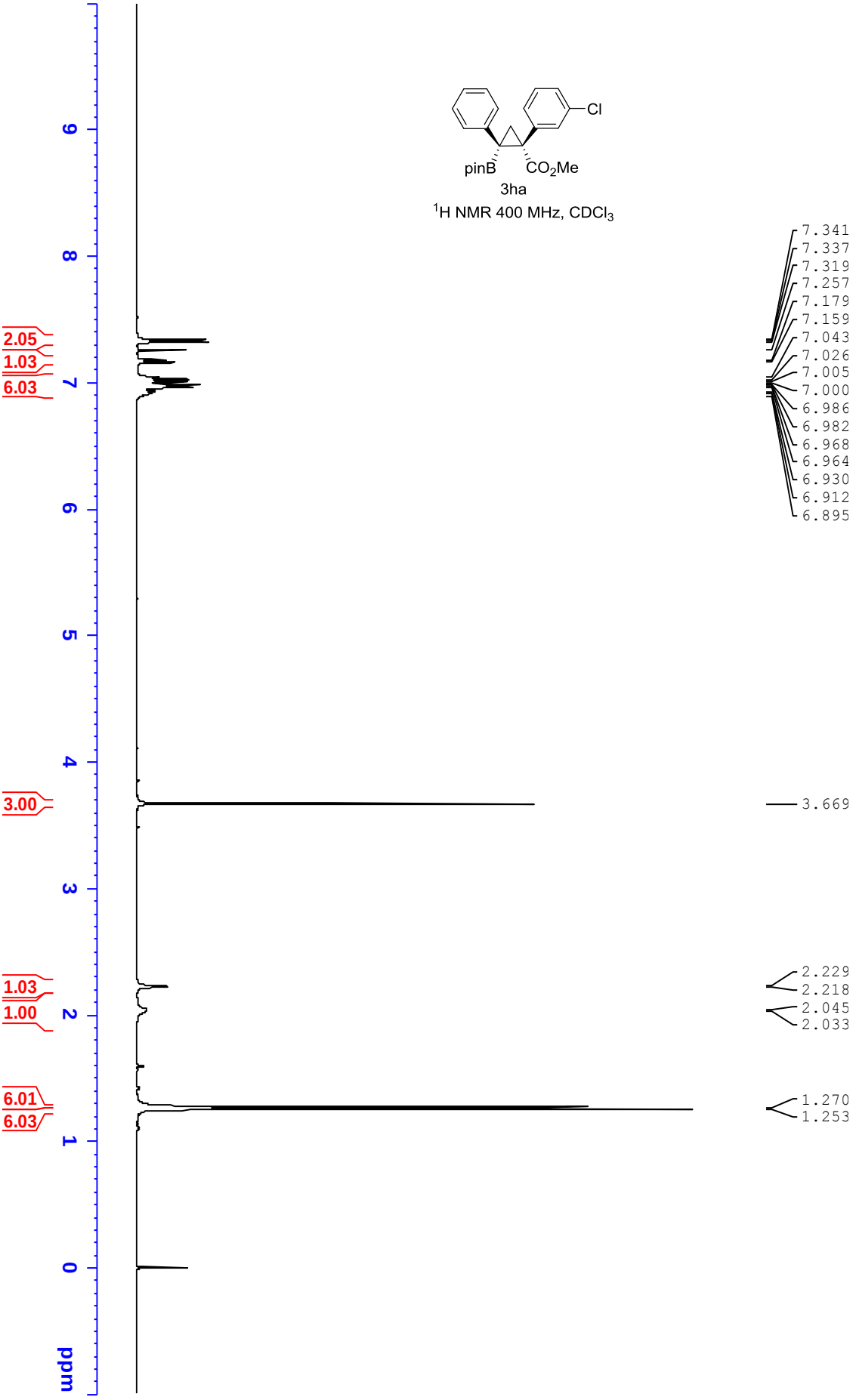

Cl
pinB
CO2Me
3ea
13C NMR 100 MHz, CDCl3
174.71
137.08
133.84
132.87
132.66
129.94
127.84
127.66
126.31
83.93
77.48
77.16
76.84
52.91
39.57
25.01
24.76
21.96
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

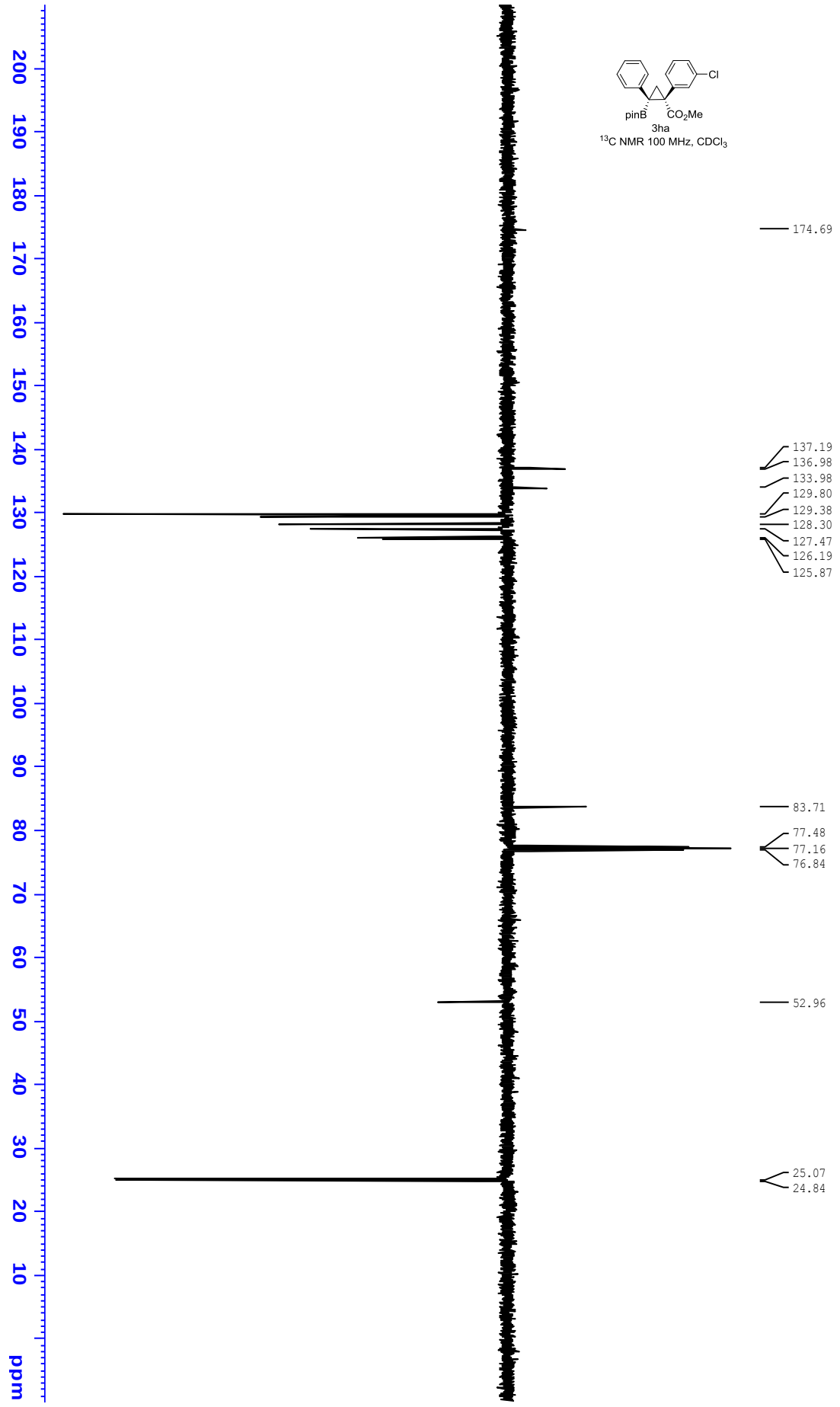

Br
pinB
CO2Me
3fa
1H NMR 400 MHz, CDCl3
7.261
7.185
7.179
7.163
7.158
7.067
7.063
7.049
7.046
7.030
7.023
7.017
7.012
7.002
7.000
6.996
6.990
6.985
6.978
6.969
6.966
3.670
2.123
2.111
2.104
2.093
1.247
1.226
4.01
5.21
3.02
1.03
1.01
6.04
6.00
ppm

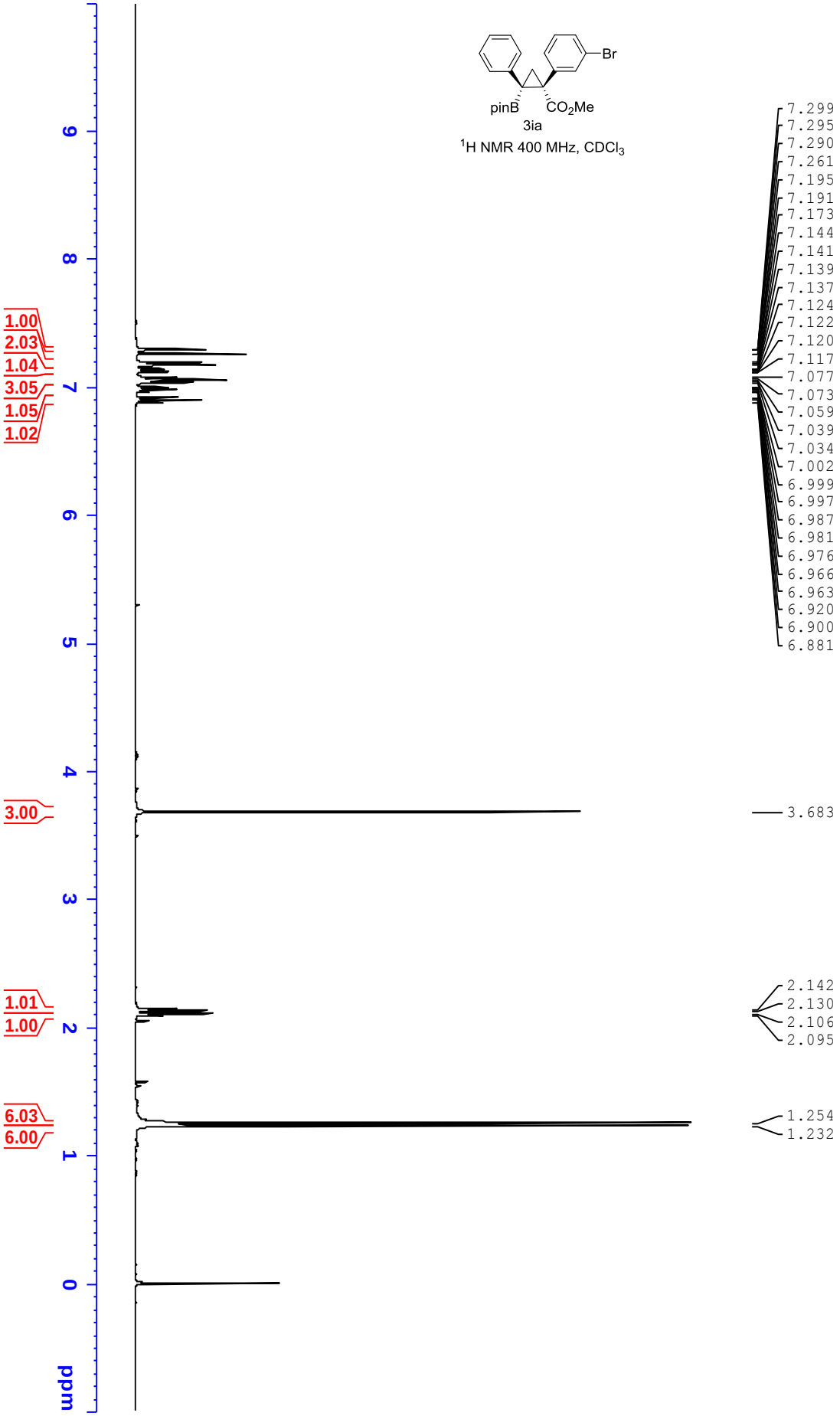

Br
pinB
CO2Me
3fa
13C NMR 100 MHz, CDCl3
174.62
137.01
134.35
133.23
130.58
129.92
127.85
126.33
120.94
83.92
77.48
77.16
76.84
52.91
39.61
24.99
24.74
21.92
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

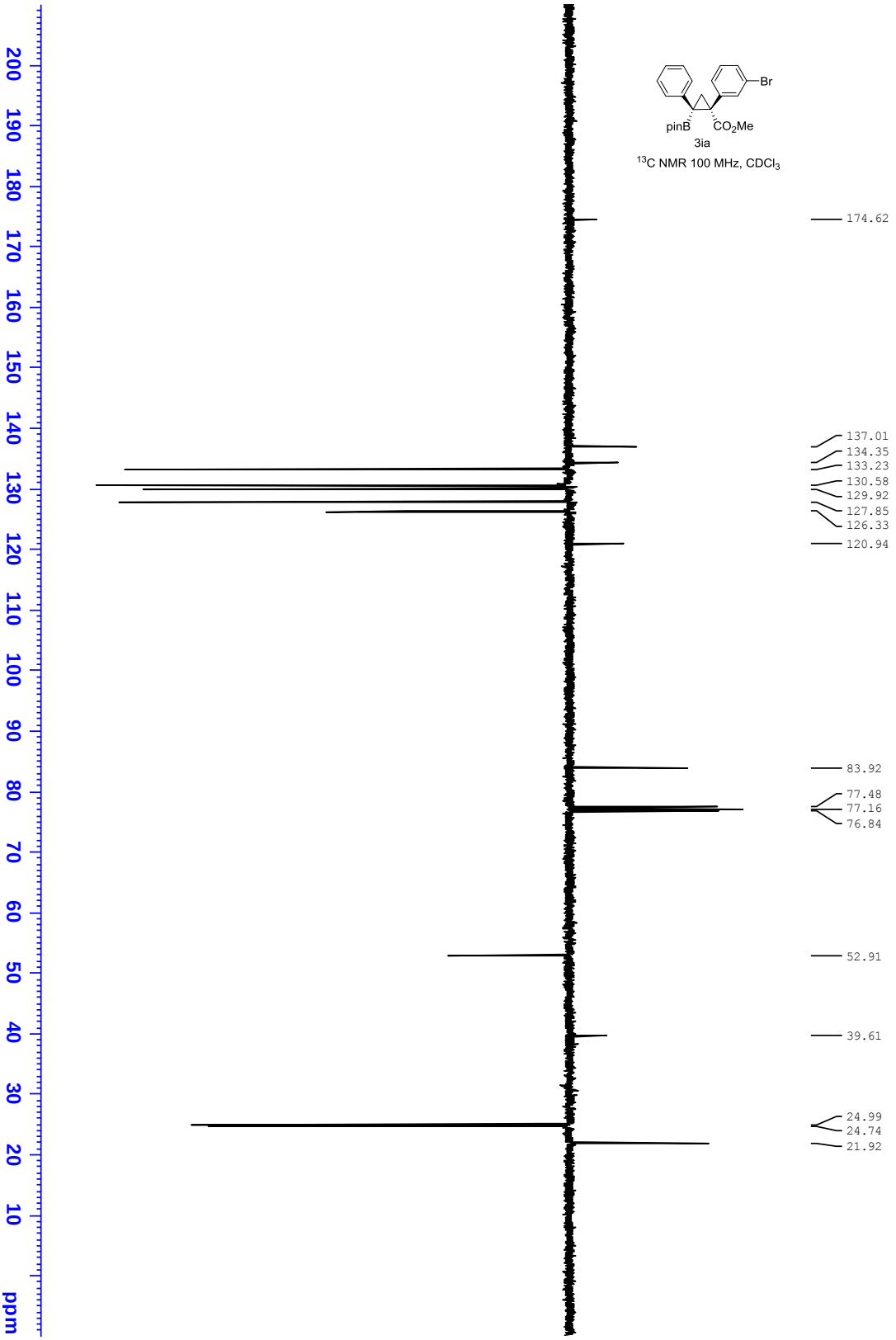

Cl
pinB
CO2Me
3ga
1H NMR 400 MHz, CDCl3
7.260
7.194
7.176
7.142
7.071
7.053
7.034
7.011
7.006
6.993
6.972
6.954
6.934
3.682
2.149
2.138
2.111
2.100
1.255
1.234
2.02
1.02
2.01
4.17
3.02
1.00
1.01
12.03
ppm


Cl
pinB
CO2Me
3ga
13C NMR 100 MHz, CDCl3
174.51
137.29
136.94
133.16
131.76
129.93
129.70
128.58
127.79
127.02
126.31
83.95
77.48
77.16
76.84
52.94
39.77
25.00
24.75
21.87
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

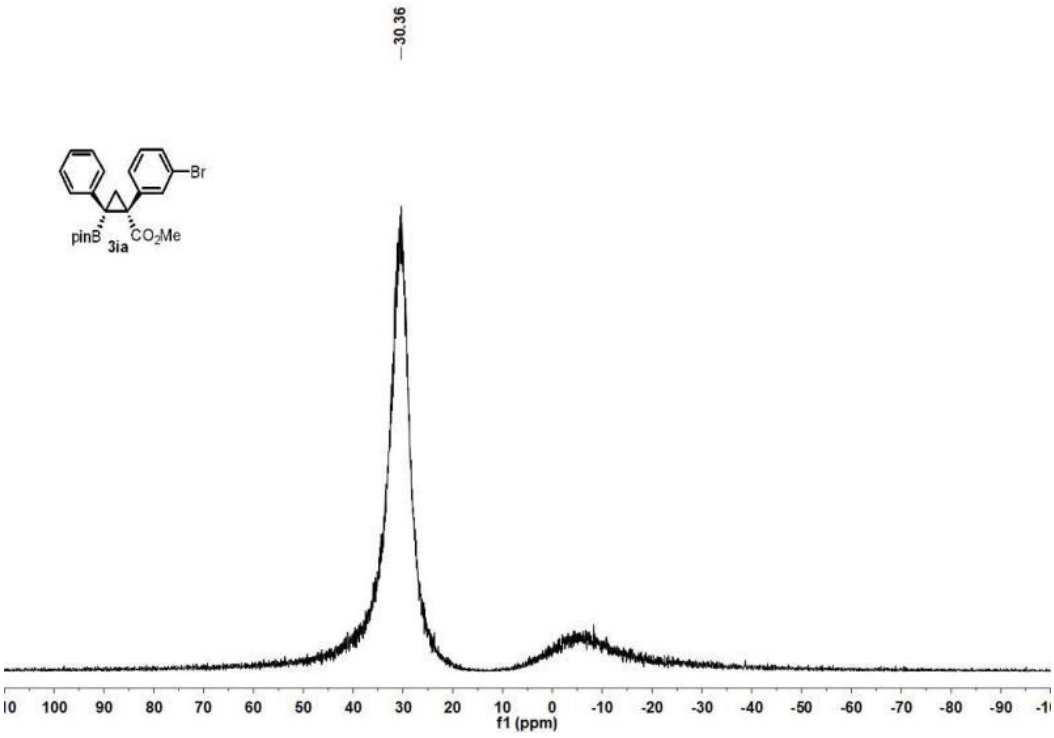

Cl
pinB
CO2Me
3ha
1H NMR 400 MHz, CDCl3
7.341
7.337
7.319
7.257
7.179
7.159
7.043
7.026
7.005
7.000
6.986
6.982
6.968
6.964
6.930
6.912
6.895
3.669
2.229
2.218
2.045
2.033
1.270
1.253
2.05
1.03
6.03
3.00
1.03
1.00
6.01
6.03
ppm

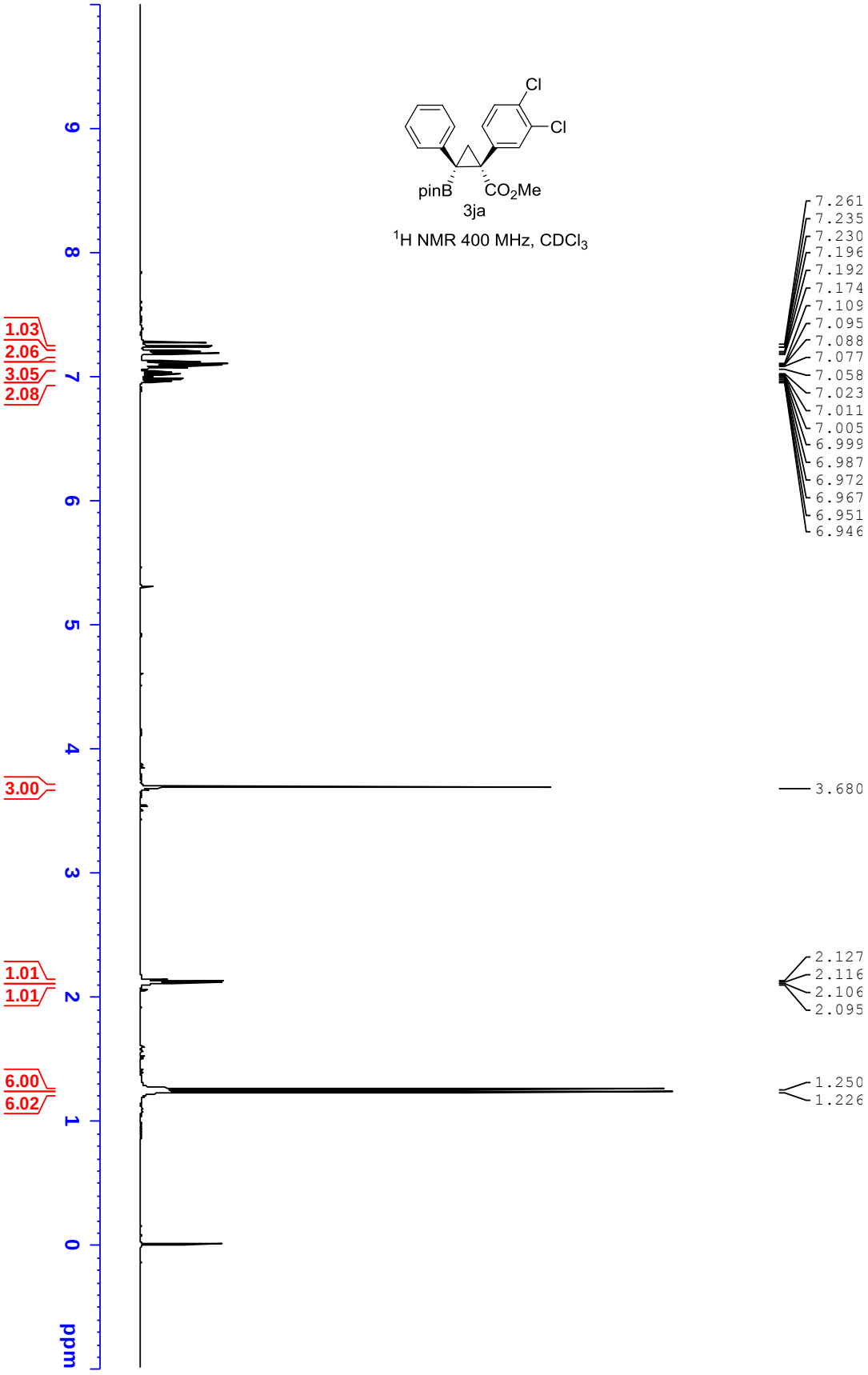

Cl
pinB
CO2Me
3ha
13C NMR 100 MHz, CDCl3
174.69
137.19
136.98
133.98
129.80
129.38
128.30
127.47
126.19
125.87
83.71
77.48
77.16
76.84
52.96
25.07
24.84
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

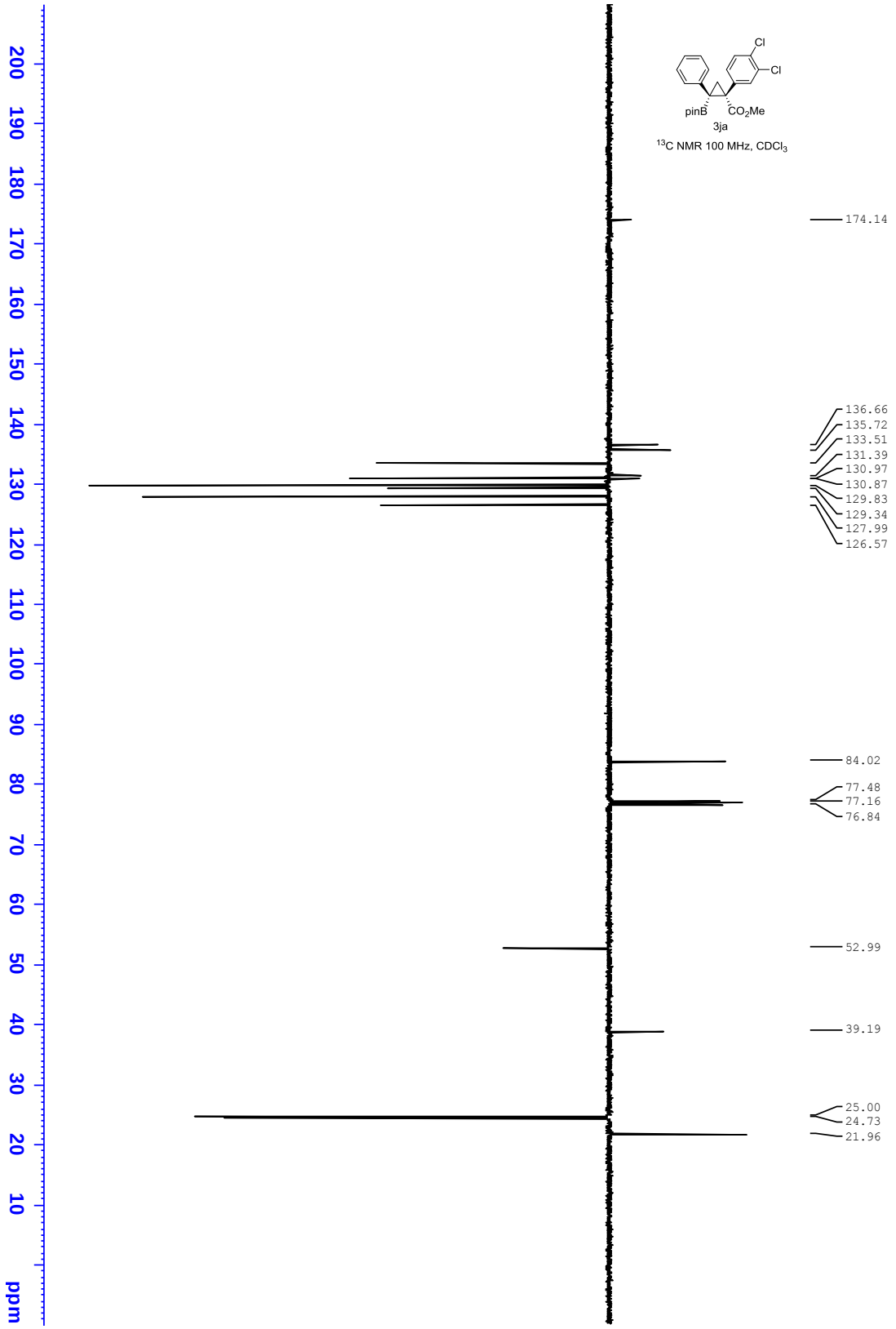

Br
pinB
CO2Me
3ia
1H NMR 400 MHz, CDCl3
7.299
7.295
7.290
7.261
7.195
7.191
7.173
7.144
7.141
7.139
7.137
7.124
7.122
7.120
7.117
7.077
7.073
7.059
7.039
7.034
7.002
6.999
6.997
6.987
6.981
6.976
6.966
6.963
6.920
6.900
6.881
3.683
2.142
2.130
2.106
2.095
1.254
1.232
1.00
2.03
1.04
3.05
1.05
1.02
3.00
1.01
1.00
6.03
6.00
9
8
7
6
5
4
3
2
1
0
ppm

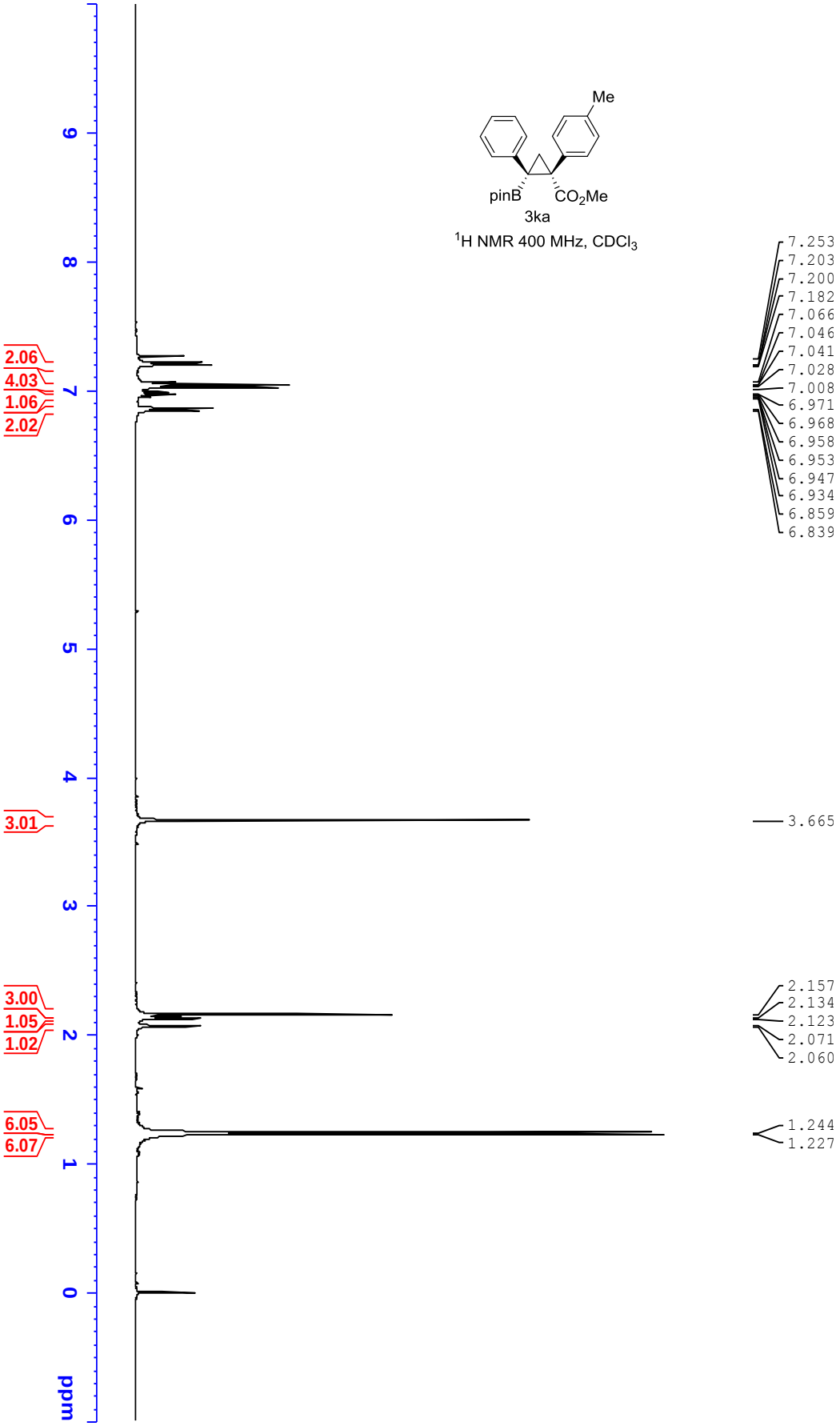

Br
pinB
CO2Me
3ia
13C NMR 100 MHz, CDCl3
174.62
137.01
134.35
133.23
130.58
129.92
127.85
126.33
120.94
83.92
77.48
77.16
76.84
52.91
39.61
24.99
24.74
21.92
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

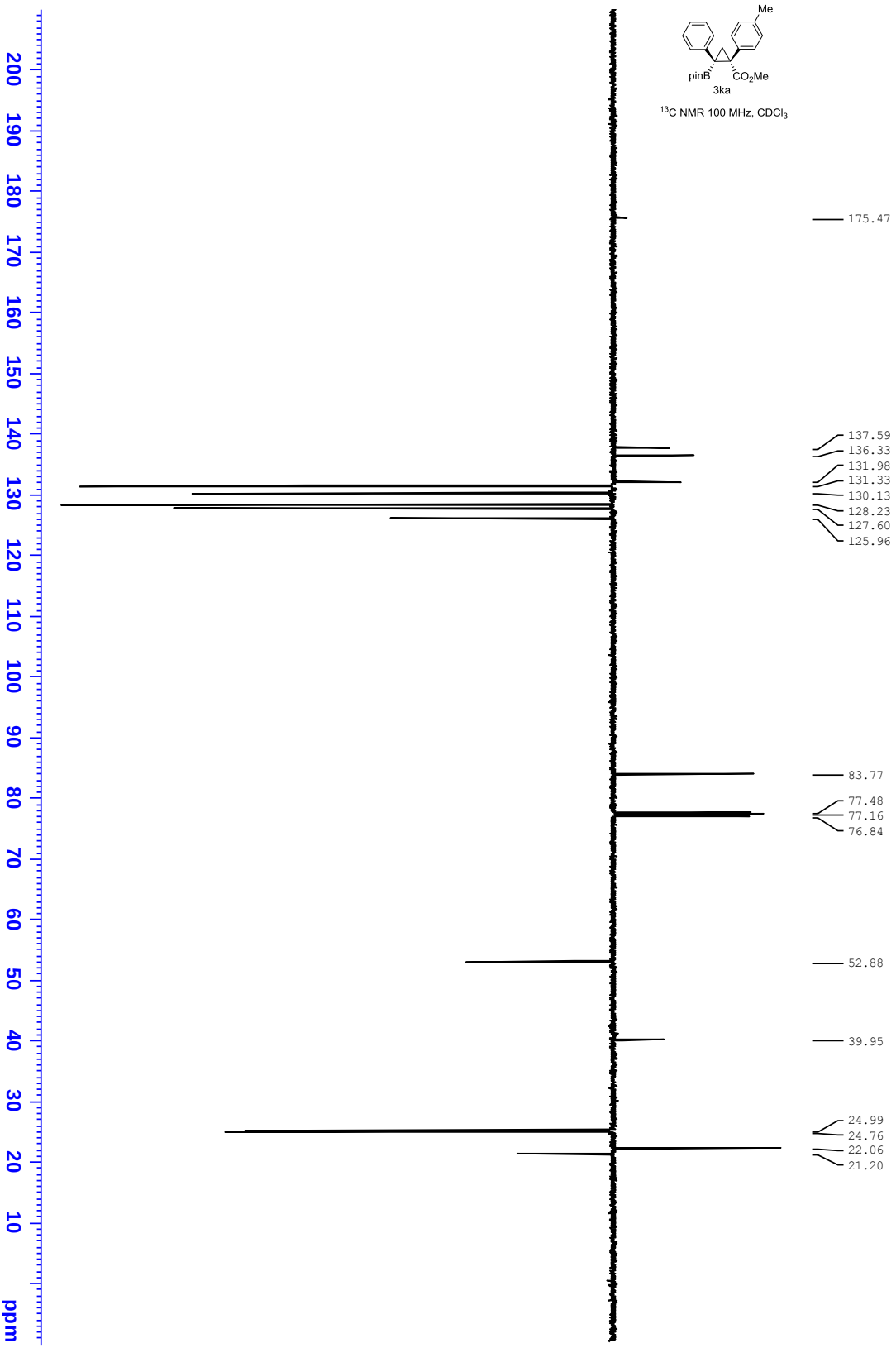
3ia ^{11}B NMR (128 MHz, $CDCl_3$)

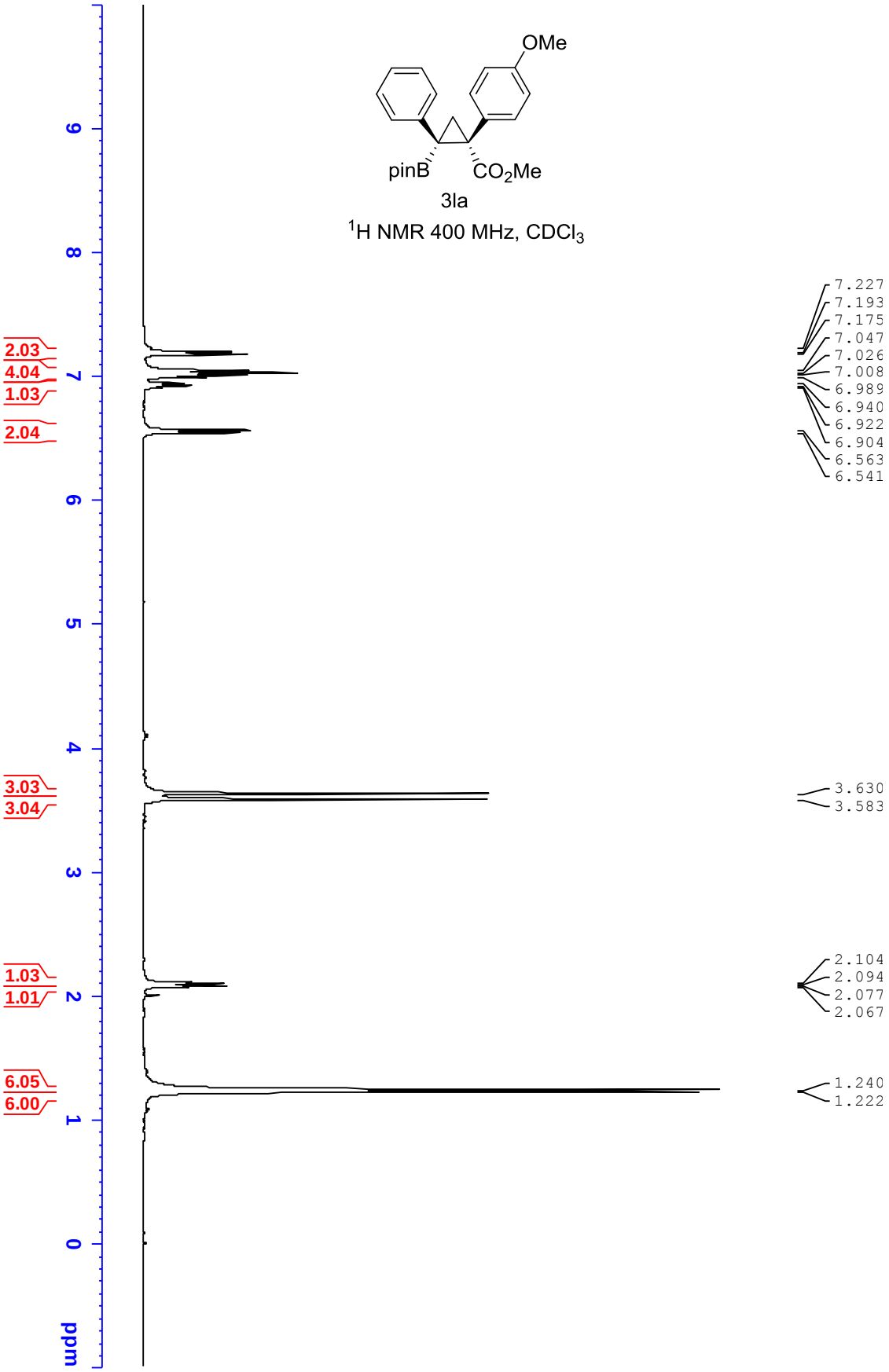


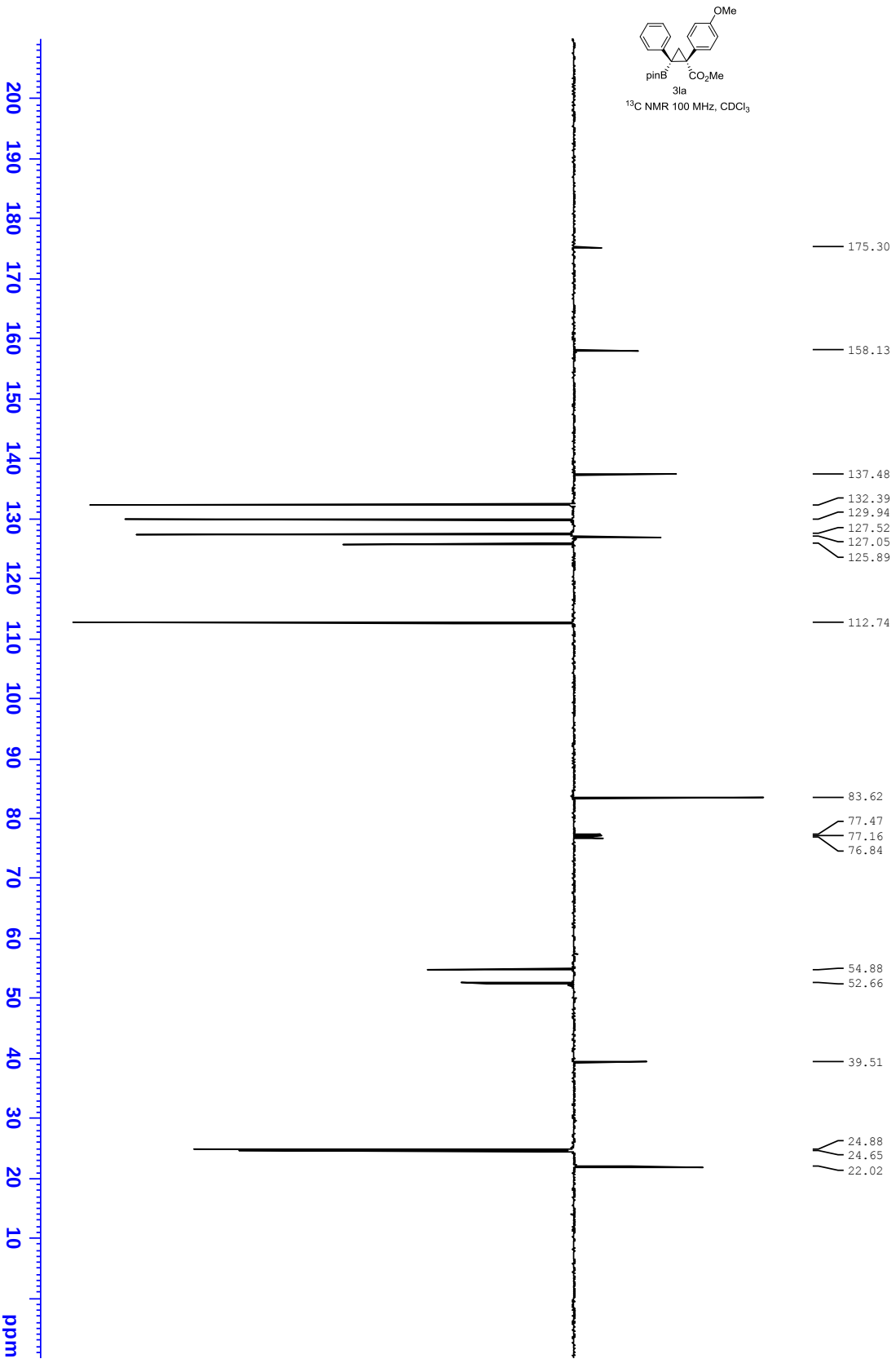

Cl
Cl
pinB
CO2Me
3ja
1H NMR 400 MHz, CDCl3
7.261
7.235
7.230
7.196
7.192
7.174
7.109
7.095
7.088
7.077
7.058
7.023
7.011
7.005
6.999
6.987
6.972
6.967
6.951
6.946
3.680
2.127
2.116
2.106
2.095
1.250
1.226
1.03
2.06
3.05
2.08
3.00
1.01
1.01
6.00
6.02
ppm

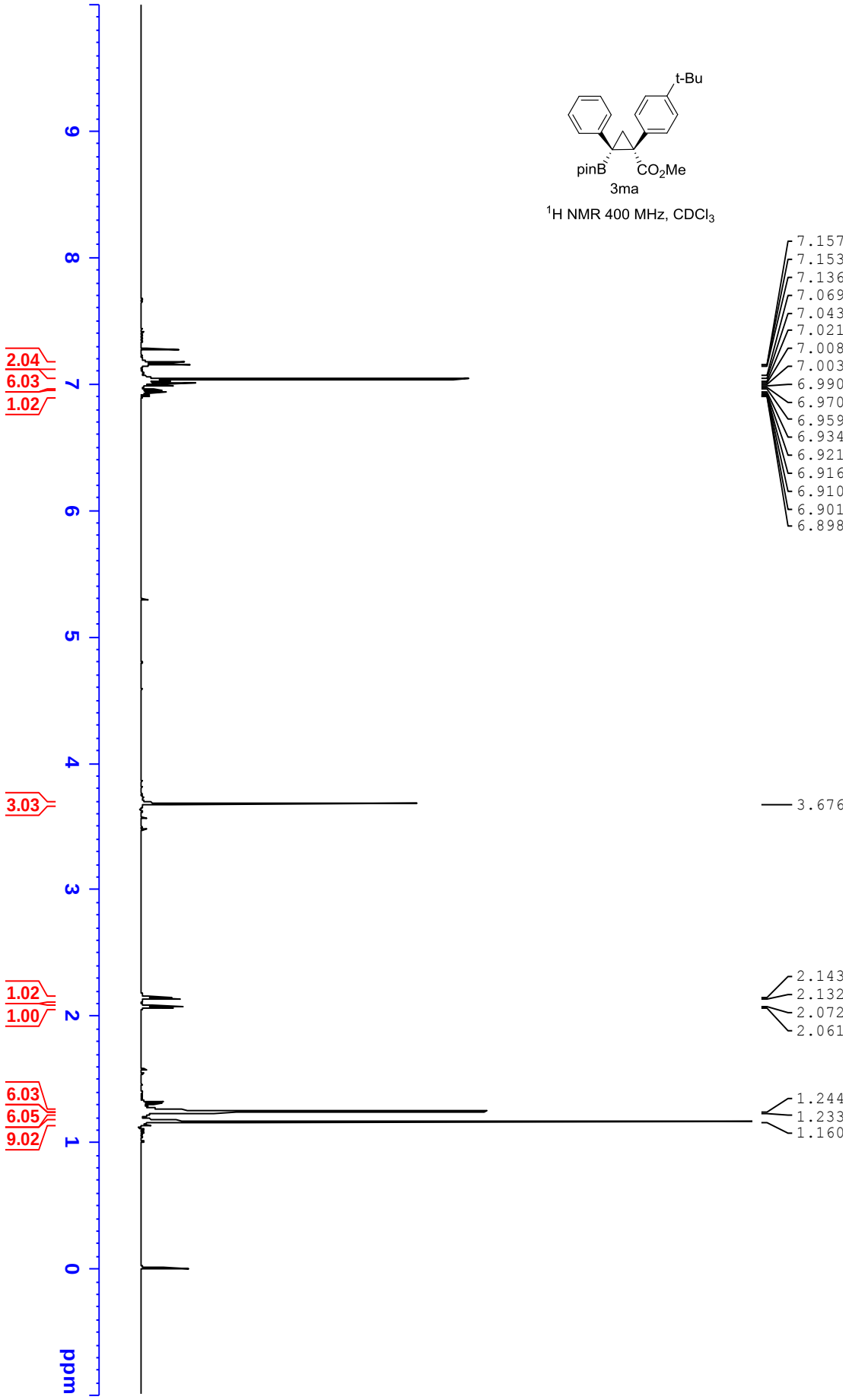

Cl
Cl
pinB
CO2Me
3ja
13C NMR 100 MHz, CDCl3
174.14
136.66
135.72
133.51
131.39
130.97
130.87
129.83
129.34
127.99
126.57
84.02
77.48
77.16
76.84
52.99
39.19
25.00
24.73
21.96
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

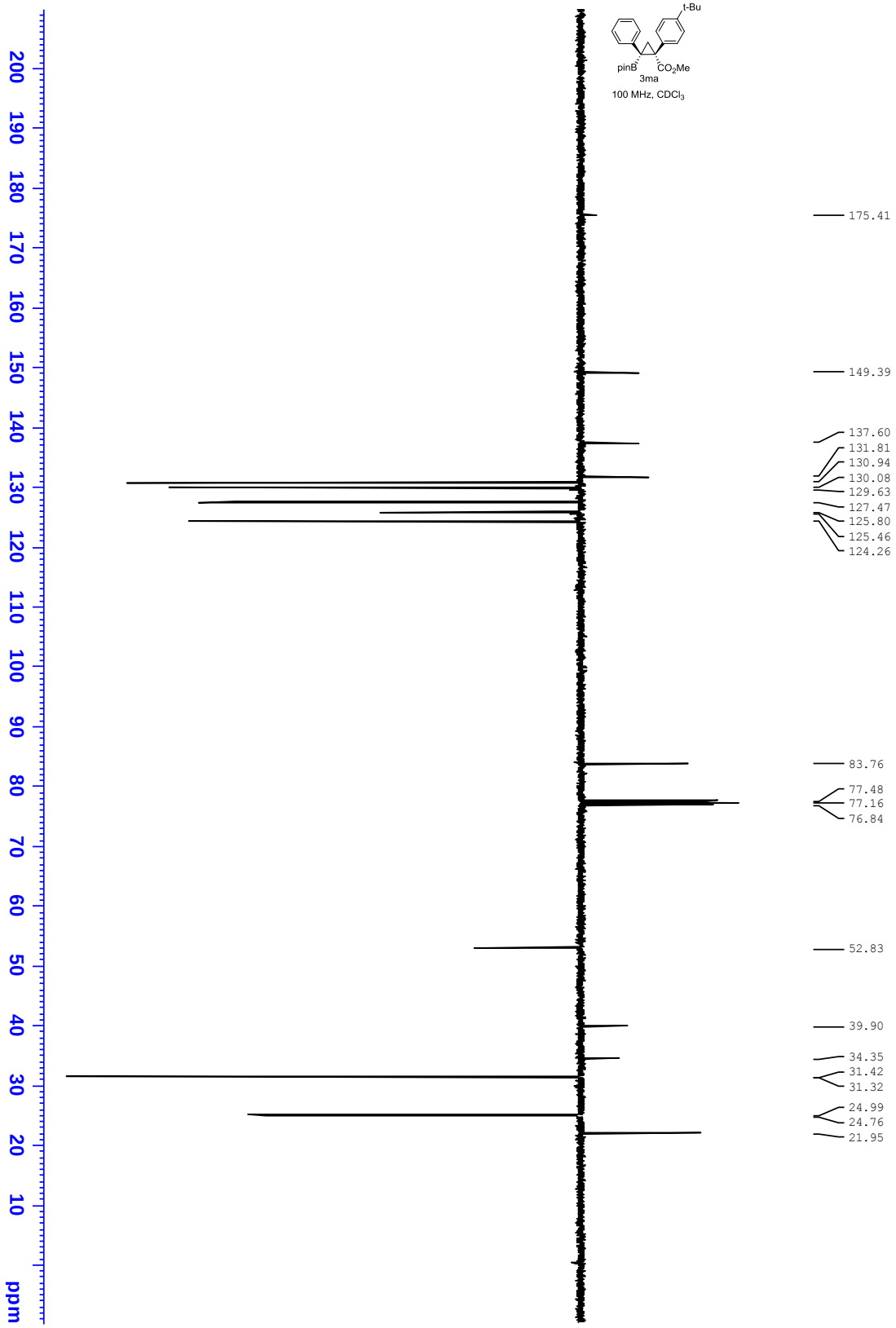

Me
pinB
CO2Me
3ka
1H NMR 400 MHz, CDCl3
7.253
7.203
7.200
7.182
7.066
7.046
7.041
7.028
7.008
6.971
6.968
6.958
6.953
6.947
6.934
6.859
6.839
3.665
2.157
2.134
2.123
2.071
2.060
1.244
1.227
2.06
4.03
1.06
2.02
3.01
3.00
1.05
1.02
6.05
6.07
ppm

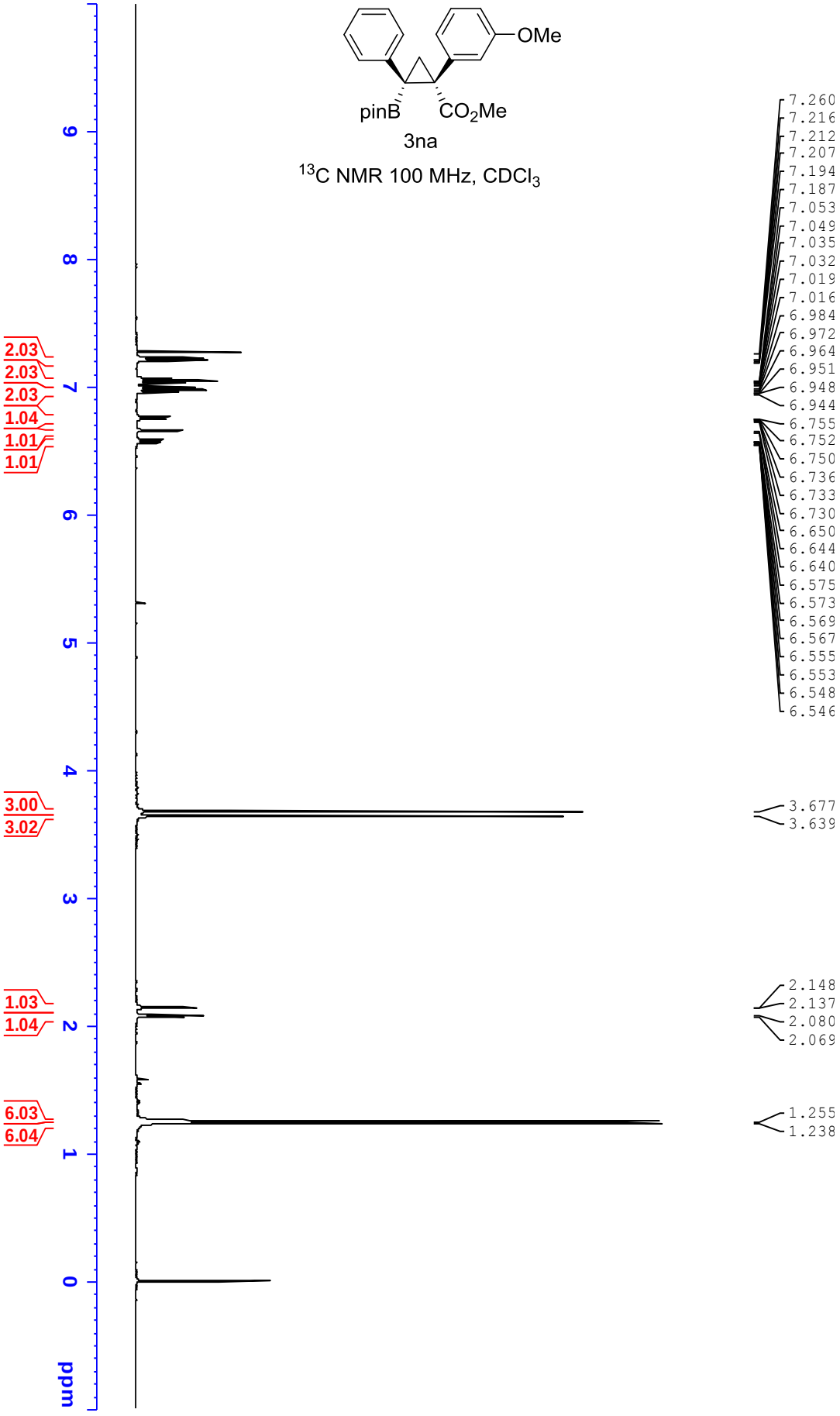

Me
pinB
CO2Me
3ka
13C NMR 100 MHz, CDCl3
175.47
137.59
136.33
131.98
131.33
130.13
128.23
127.60
125.96
83.77
77.48
77.16
76.84
52.88
39.95
24.99
24.76
22.06
21.20
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

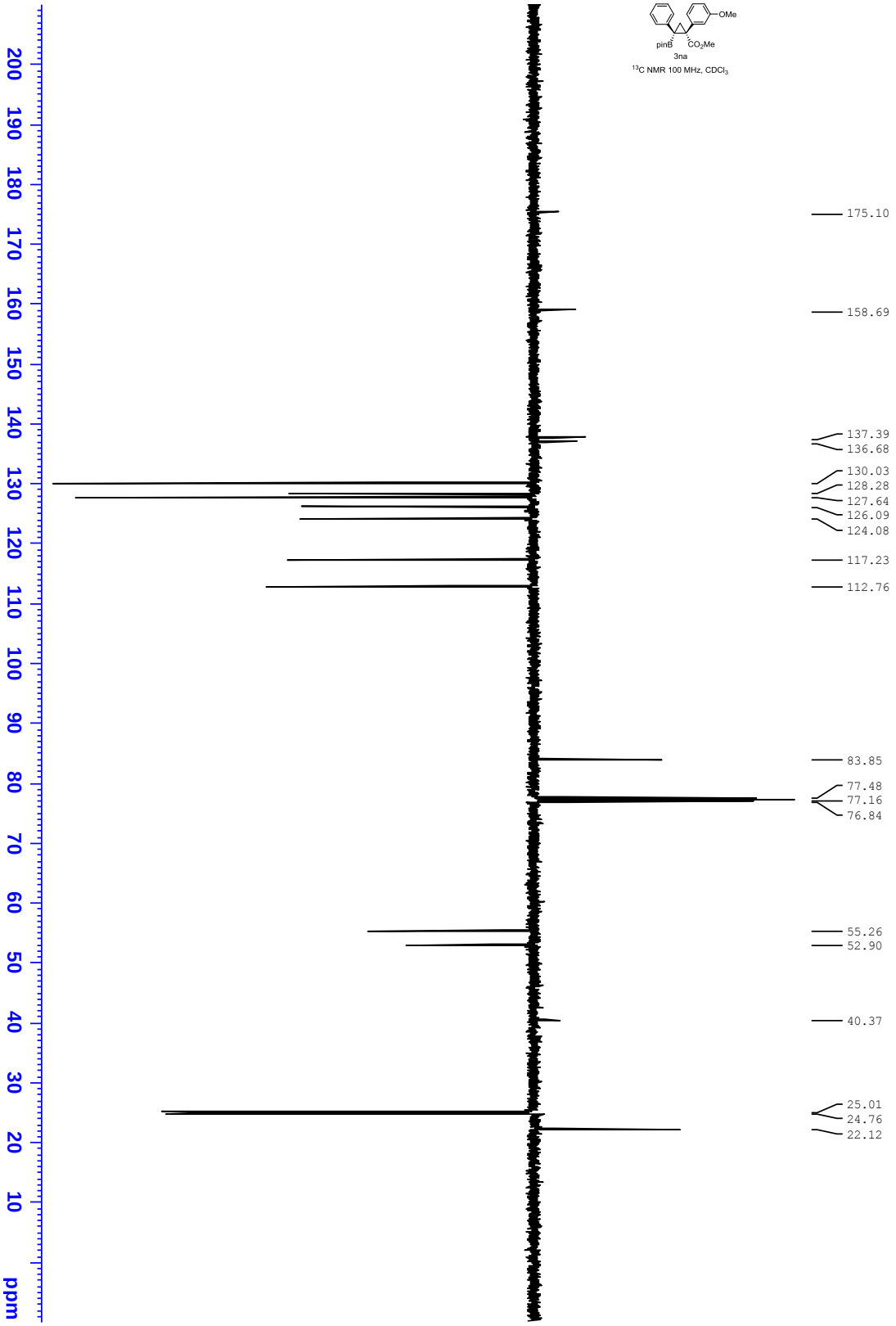

OMe
pinB
CO2Me
3la
1H NMR 400 MHz, CDCl3
7.227
7.193
7.175
7.047
7.026
7.008
6.989
6.940
6.922
6.904
6.563
6.541
3.630
3.583
2.104
2.094
2.077
2.067
1.240
1.222
2.03
4.04
1.03
2.04
3.03
3.04
1.03
1.01
6.05
6.00
ppm

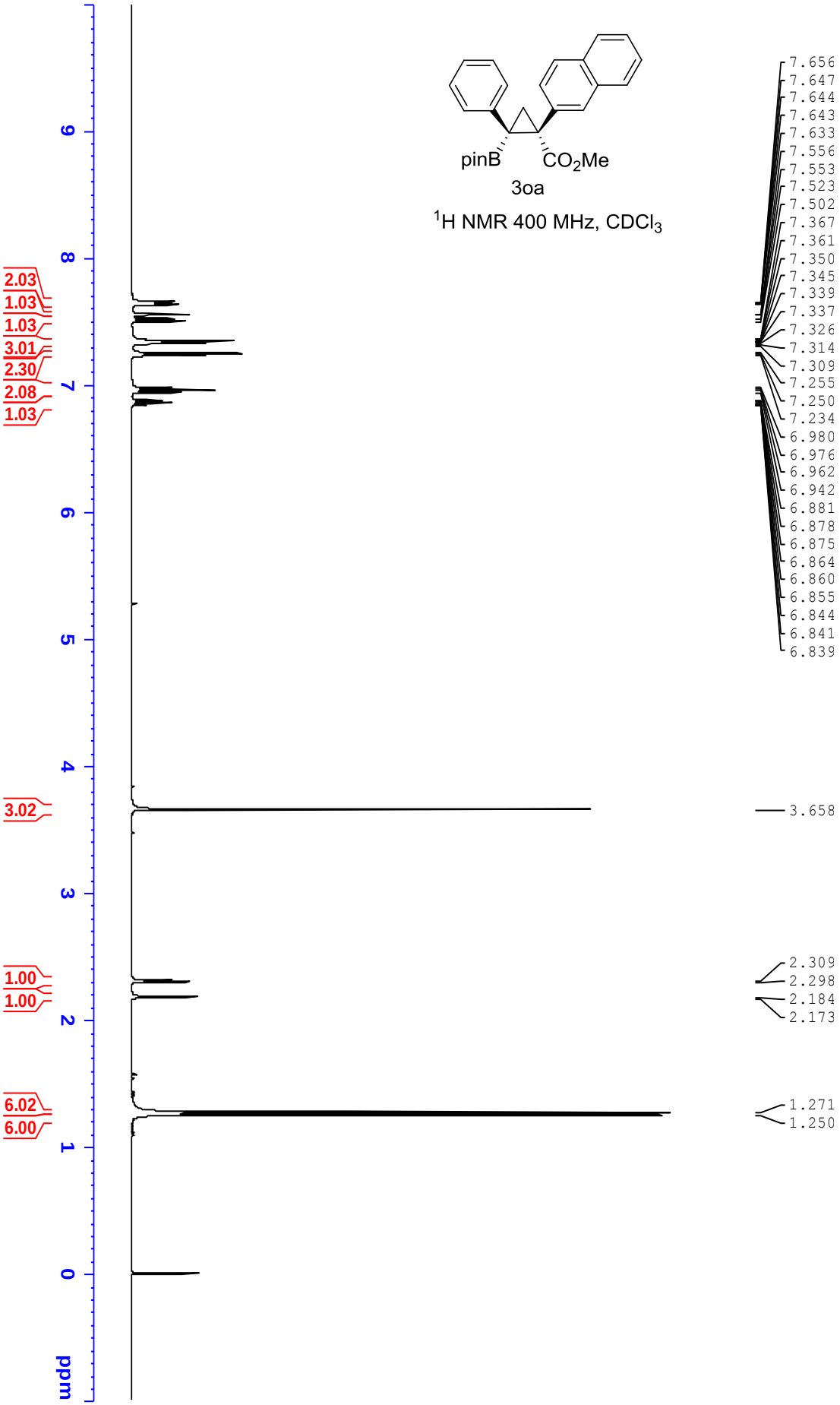

OMe
pinB
CO2Me
3la
13C NMR 100 MHz, CDCl3
175.30
158.13
137.48
132.39
129.94
127.52
127.05
125.89
112.74
83.62
77.47
77.16
76.84
54.88
52.66
39.51
24.88
24.65
22.02
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

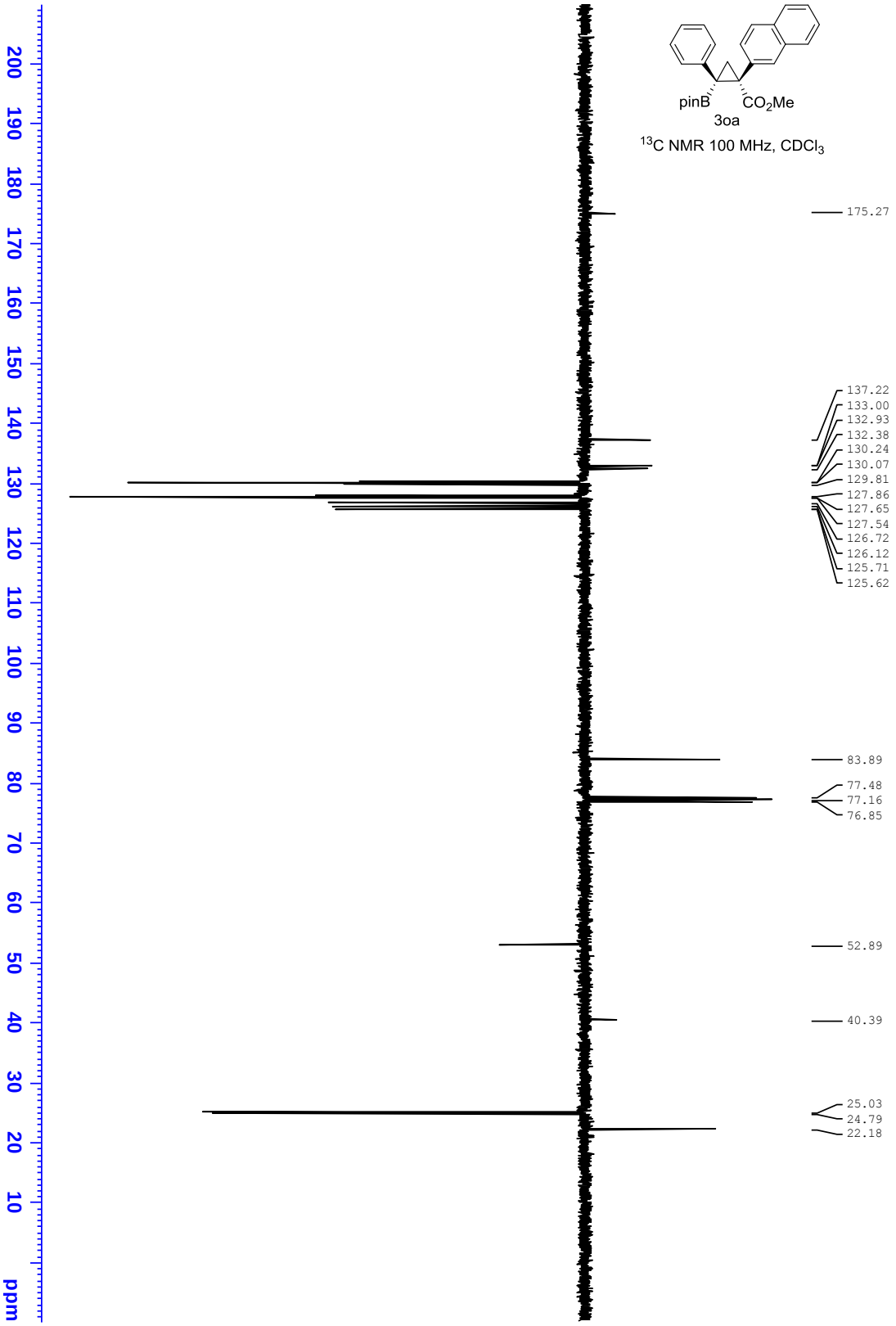

t-Bu
pinB
CO2Me
3ma
1H NMR 400 MHz, CDCl3
7.157
7.153
7.136
7.069
7.043
7.021
7.008
7.003
6.990
6.970
6.959
6.934
6.921
6.916
6.910
6.901
6.898
3.676
2.143
2.132
2.072
2.061
1.244
1.233
1.160
2.04
6.03
1.02
3.03
1.02
1.00
6.03
6.05
9.02
ppm

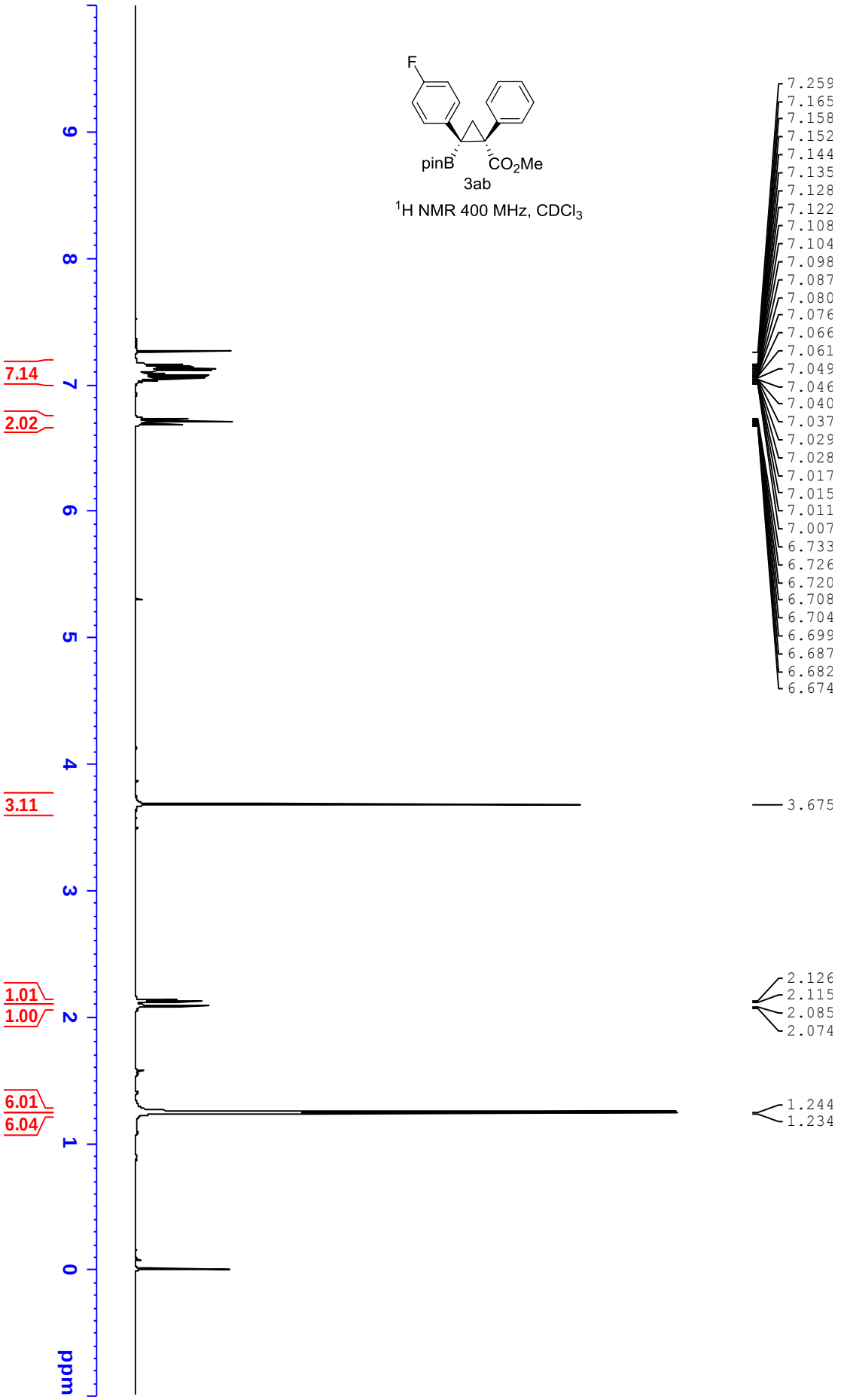

t-Bu
pinB
CO2Me
3ma
100 MHz, CDCl3
175.41
149.39
137.60
131.81
130.94
130.08
129.63
127.47
125.80
125.46
124.26
83.76
77.48
77.16
76.84
52.83
39.90
34.35
31.42
31.32
24.99
24.76
21.95
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

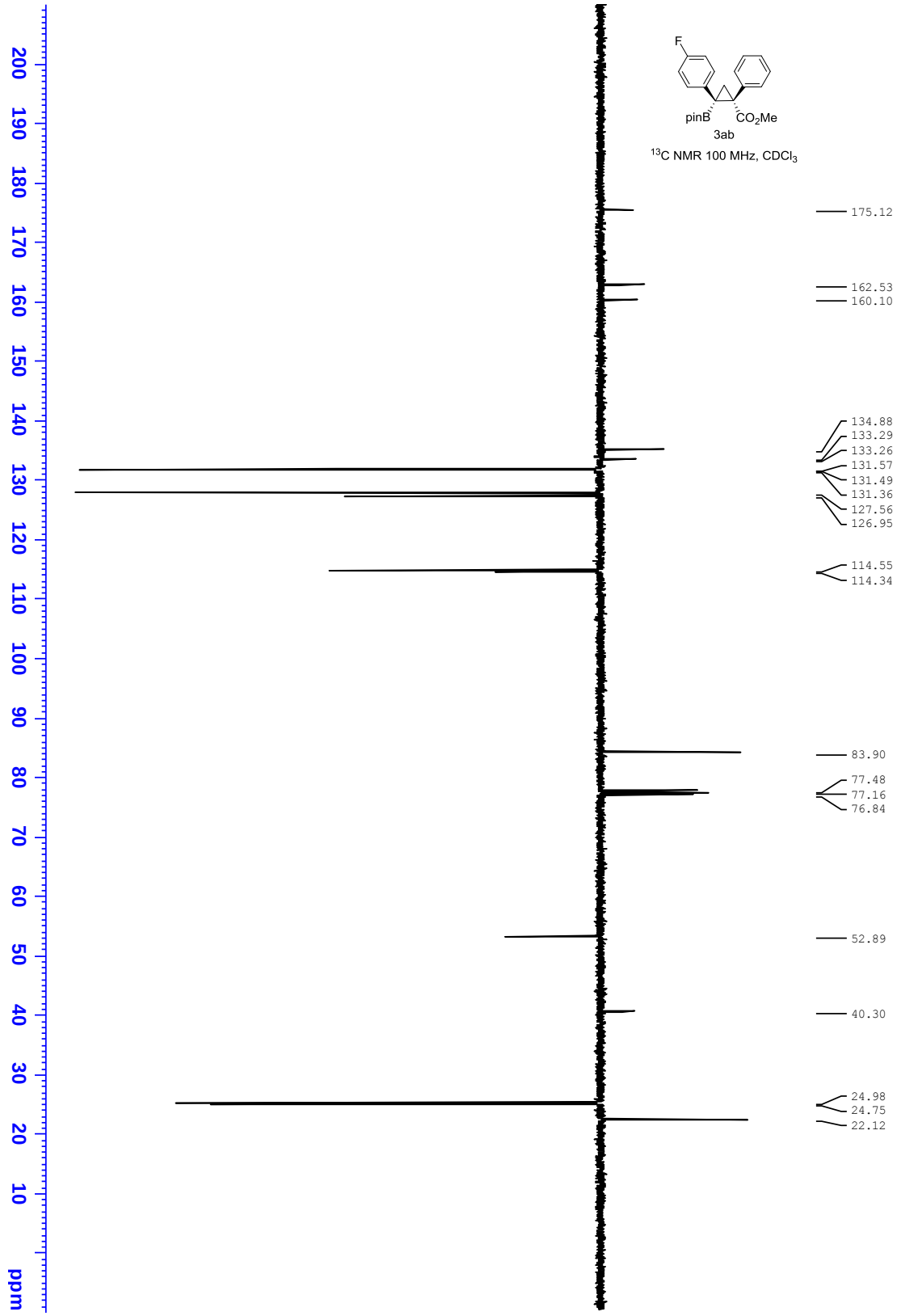

OMe
pinB
CO2Me
3na
13C NMR 100 MHz, CDCl3
7.260
7.216
7.212
7.207
7.194
7.187
7.053
7.049
7.035
7.032
7.019
7.016
6.984
6.972
6.964
6.951
6.948
6.944
6.755
6.752
6.750
6.736
6.733
6.730
6.650
6.644
6.640
6.575
6.573
6.569
6.567
6.555
6.553
6.548
6.546
3.677
3.639
2.148
2.137
2.080
2.069
1.255
1.238
2.03
2.03
2.03
1.04
1.01
1.01
3.00
3.02
1.03
1.04
6.03
6.04
ppm

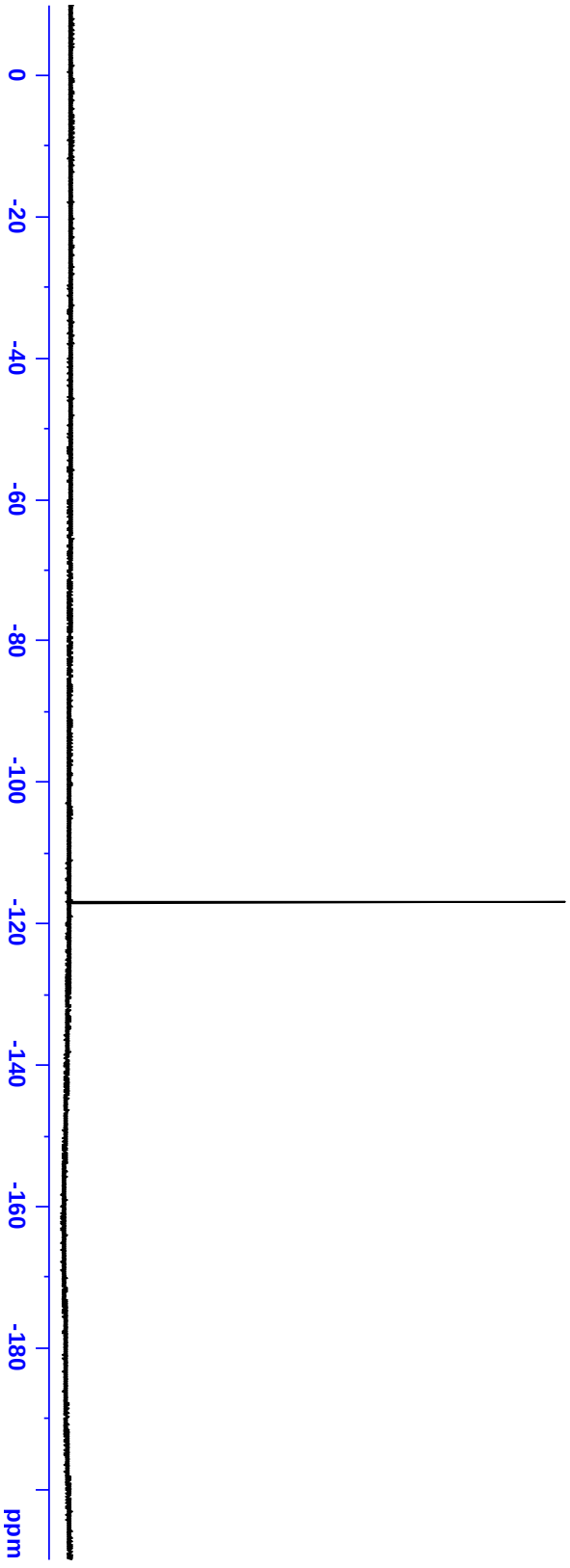

OMe
pinB
CO2Me
3na
13C NMR 100 MHz, CDCl3
175.10
158.69
137.39
136.68
130.03
128.28
127.64
126.09
124.08
117.23
112.76
83.85
77.48
77.16
76.84
55.26
52.90
40.37
25.01
24.76
22.12
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

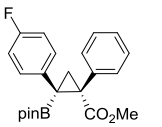

pinB
CO2Me
3oa
1H NMR 400 MHz, CDCl3
7.656
7.647
7.644
7.643
7.633
7.556
7.553
7.523
7.502
7.367
7.361
7.350
7.345
7.339
7.337
7.326
7.314
7.309
7.255
7.250
7.234
6.980
6.976
6.962
6.942
6.881
6.878
6.875
6.864
6.860
6.855
6.844
6.841
6.839
3.658
2.309
2.298
2.184
2.173
1.271
1.250
2.03
1.03
1.03
3.01
2.30
2.08
1.03
3.02
1.00
1.00
6.02
6.00
ppm


pinB
CO2Me
3oa
13C NMR 100 MHz, CDCl3
175.27
137.22
133.00
132.93
132.38
130.24
130.07
129.81
127.86
127.65
127.54
126.72
126.12
125.71
125.62
83.89
77.48
77.16
76.85
52.89
40.39
25.03
24.79
22.18
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm


F
pinB
CO2Me
3ab
1H NMR 400 MHz, CDCl3
7.259
7.165
7.158
7.152
7.144
7.135
7.128
7.122
7.108
7.104
7.098
7.087
7.080
7.076
7.066
7.061
7.049
7.046
7.040
7.037
7.029
7.028
7.017
7.015
7.011
7.007
6.733
6.726
6.720
6.708
6.704
6.699
6.687
6.682
6.674
3.675
2.126
2.115
2.085
2.074
1.244
1.234
7.14
2.02
3.11
1.01
1.00
6.01
6.04
ppm


F
pinB
CO2Me
3ab
13C NMR 100 MHz, CDCl3
175.12
162.53
160.10
134.88
133.29
133.26
131.57
131.49
131.36
127.56
126.95
114.55
114.34
83.90
77.48
77.16
76.84
52.89
40.30
24.98
24.75
22.12
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm



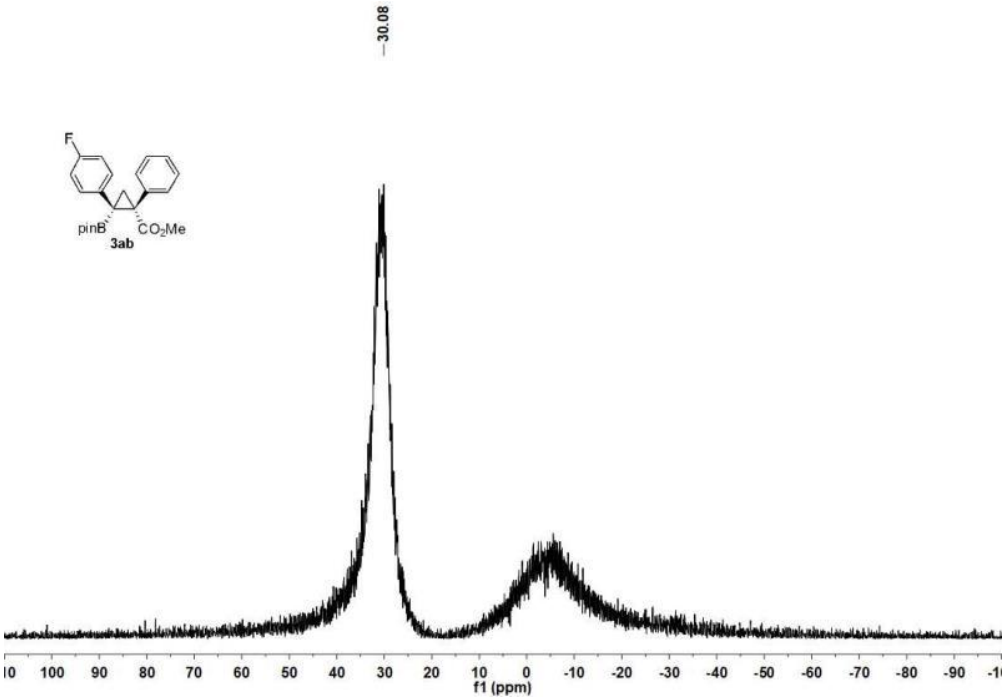


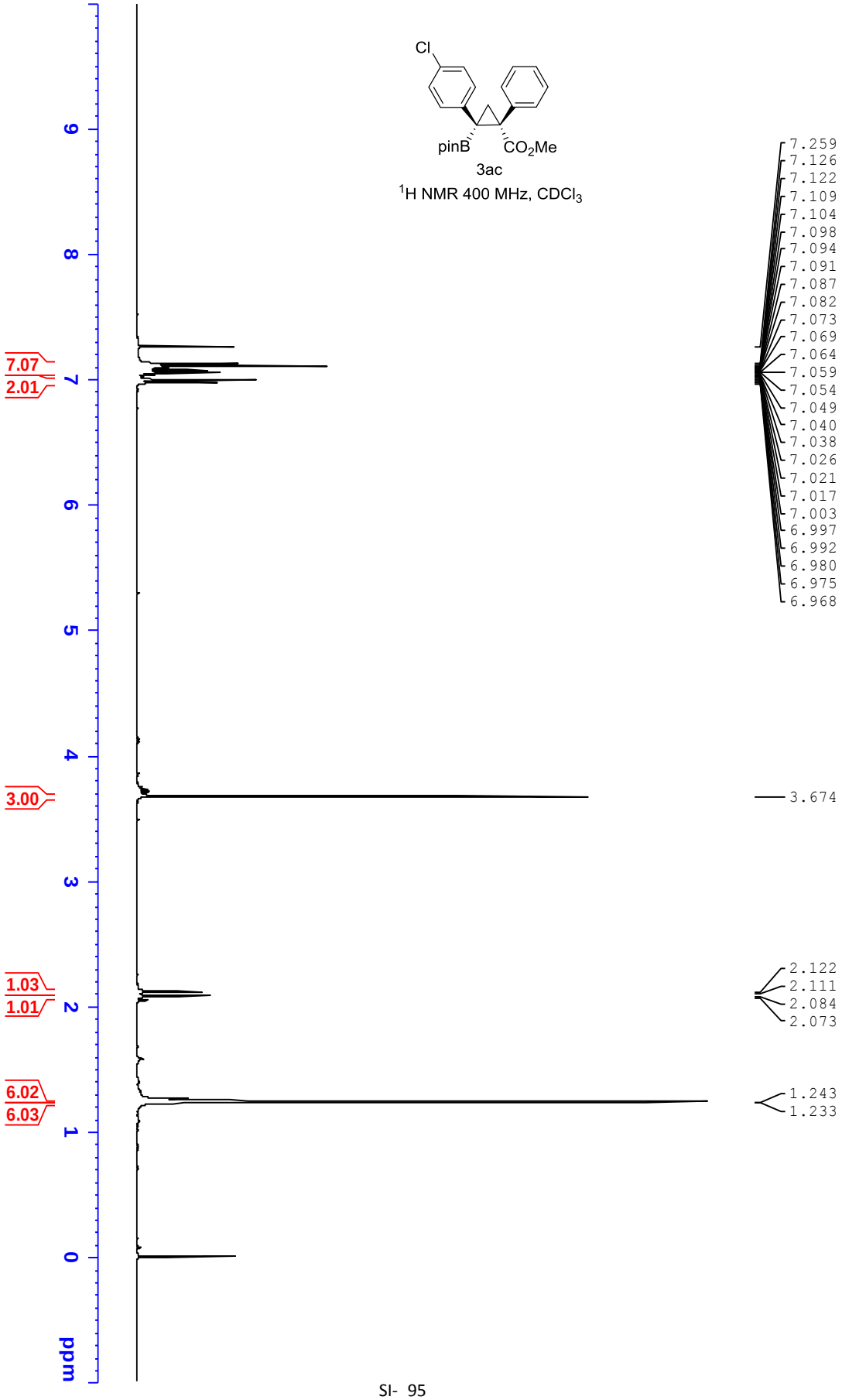
3ab

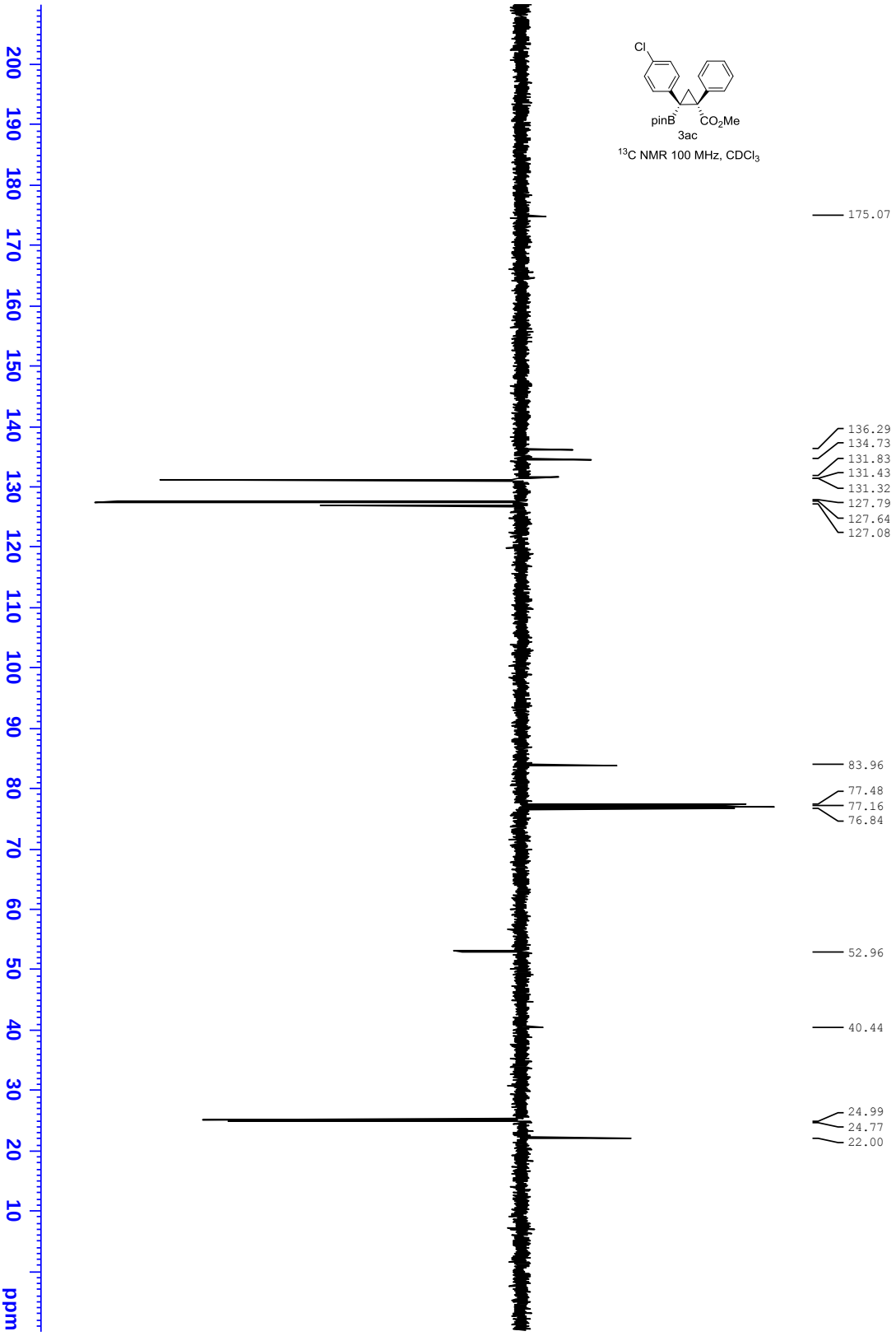
^{19}F NMR 376 MHz, $CDCl_3$

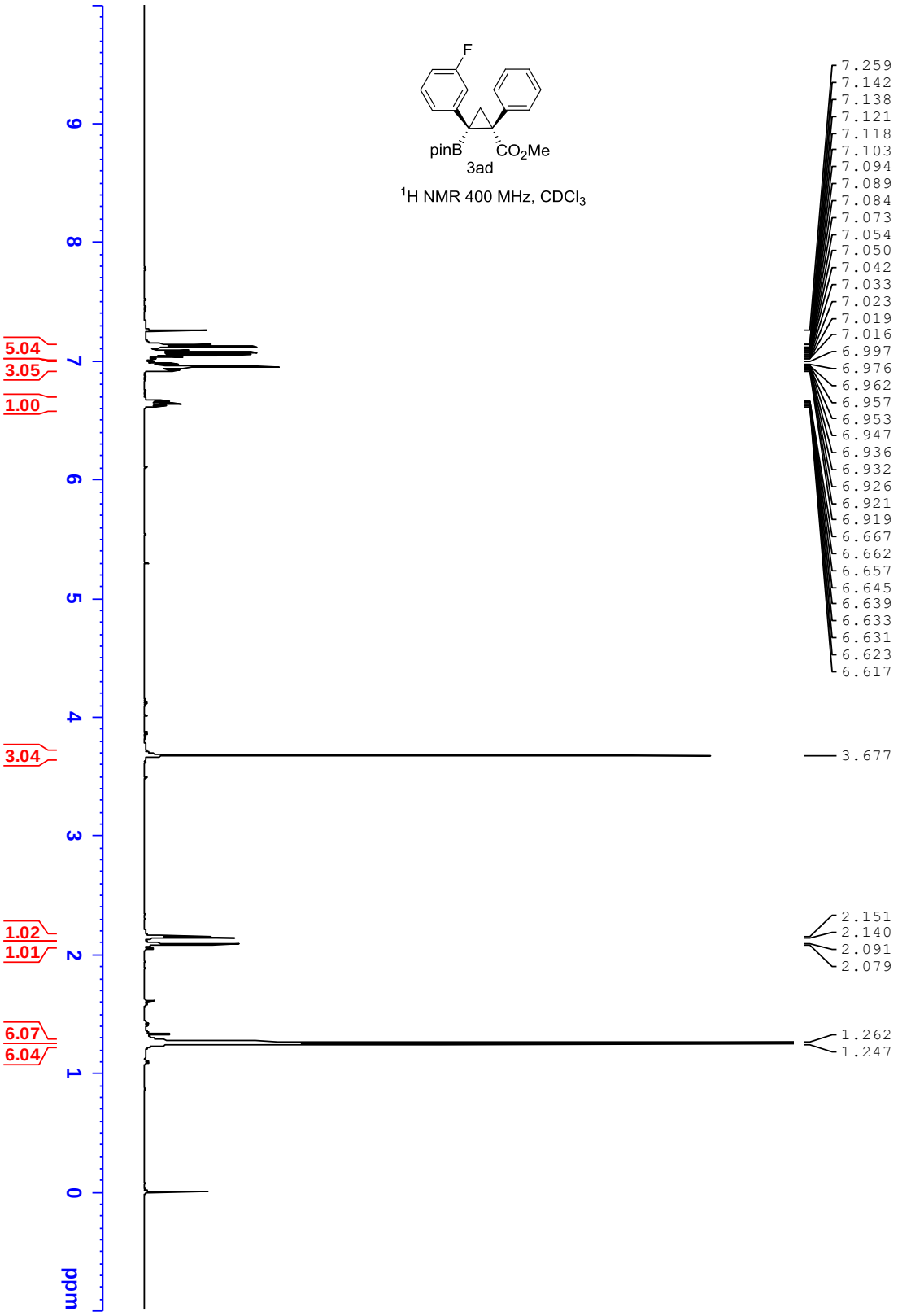
-116.99
-117.00
-117.01
-117.02
-117.04
-117.05
-117.06

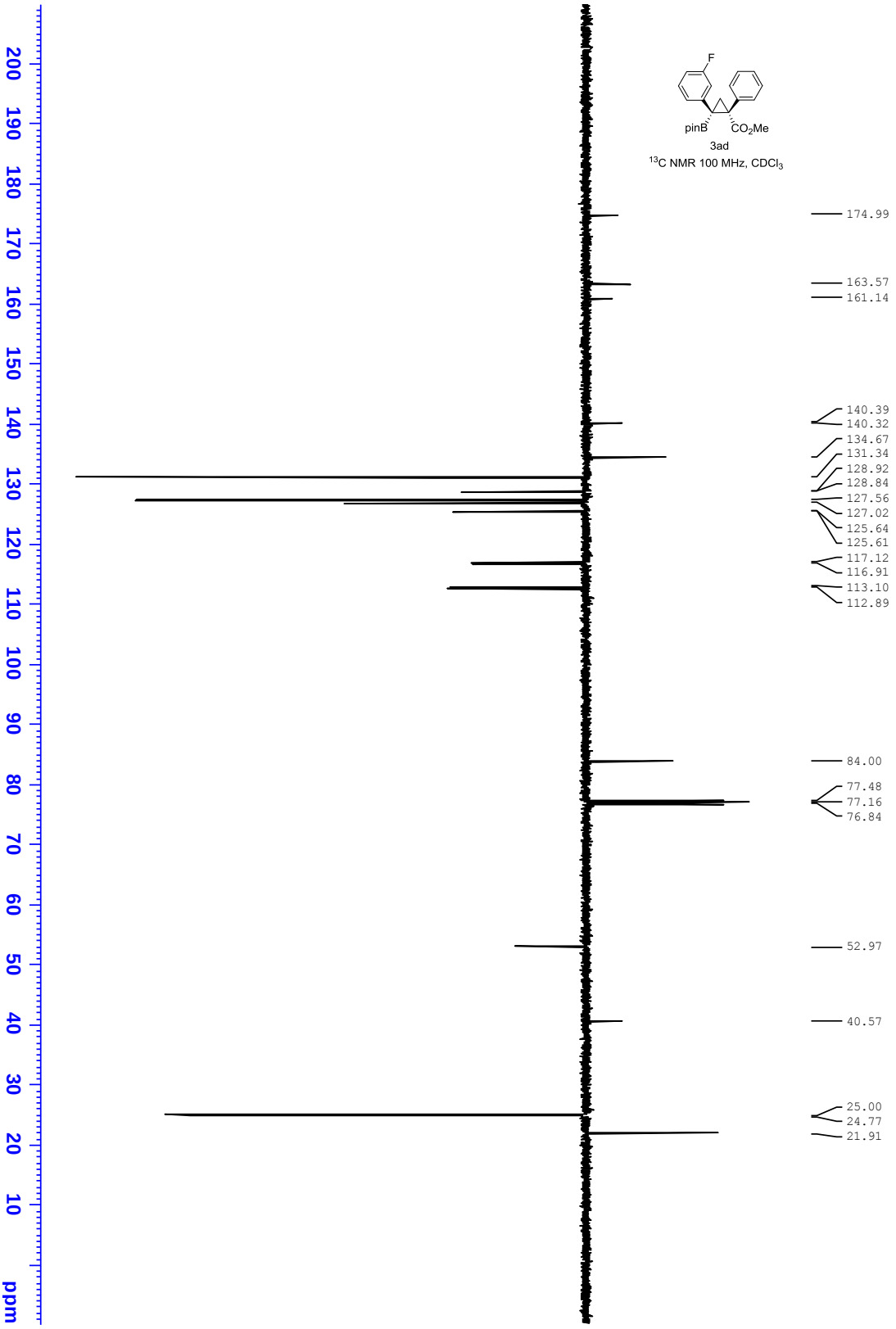
3ab ^{11}B NMR (128 MHz, $CDCl_3$)

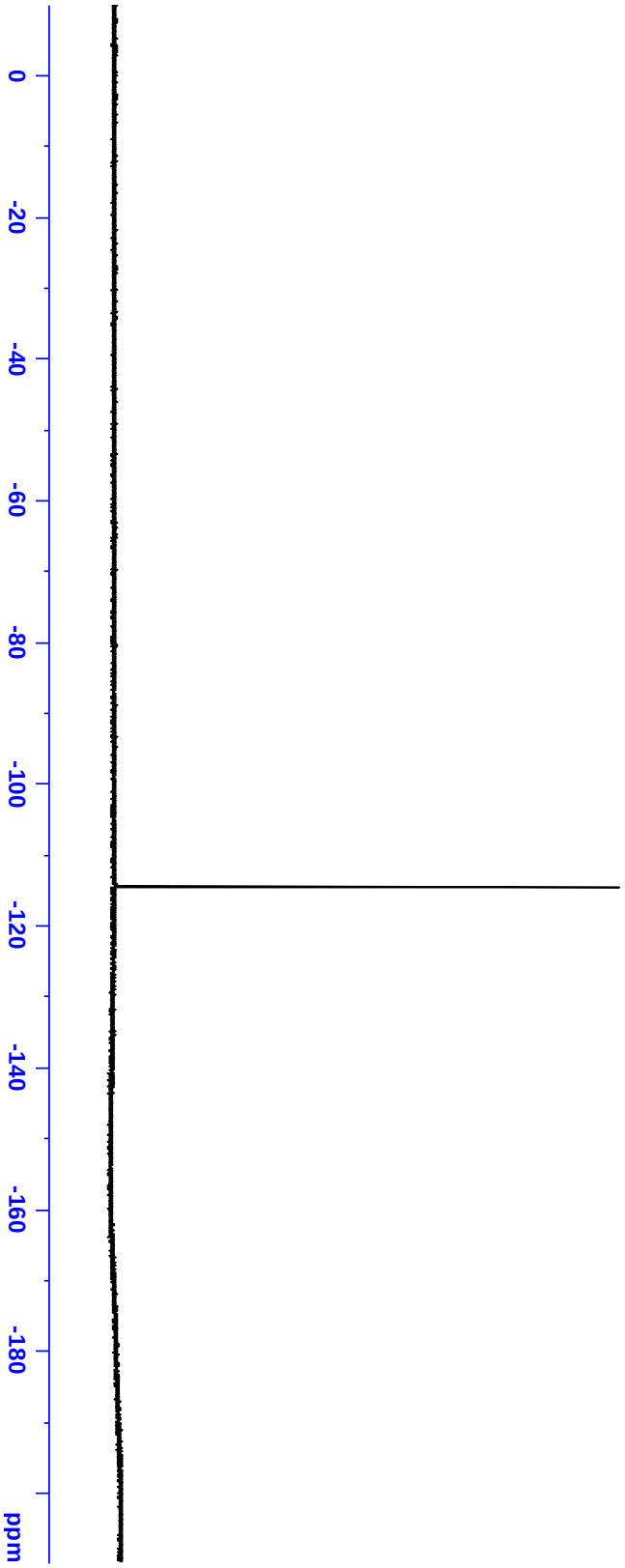


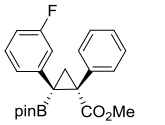

Cl
pinB
CO2Me
3ac
1H NMR 400 MHz, CDCl3
7.259
7.126
7.122
7.109
7.104
7.098
7.094
7.091
7.087
7.082
7.073
7.069
7.064
7.059
7.054
7.049
7.040
7.038
7.026
7.021
7.017
7.003
6.997
6.992
6.980
6.975
6.968
3.674
2.122
2.111
2.084
2.073
1.243
1.233
7.07
2.01
3.00
1.03
1.01
6.02
6.03
ppm


Cl
pinB
CO2Me
3ac
13C NMR 100 MHz, CDCl3
175.07
136.29
134.73
131.83
131.43
131.32
127.79
127.64
127.08
83.96
77.48
77.16
76.84
52.96
40.44
24.99
24.77
22.00
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm


F
pinB
CO2Me
3ad
1H NMR 400 MHz, CDCl3
7.259
7.142
7.138
7.121
7.118
7.103
7.094
7.089
7.084
7.073
7.054
7.050
7.042
7.033
7.023
7.019
7.016
6.997
6.976
6.962
6.957
6.953
6.947
6.936
6.932
6.926
6.921
6.919
6.667
6.662
6.657
6.645
6.639
6.633
6.631
6.623
6.617
3.677
2.151
2.140
2.091
2.079
1.262
1.247
5.04
3.05
1.00
3.04
1.02
1.01
6.07
6.04
ppm


F
pinB
CO2Me
3ad
13C NMR 100 MHz, CDCl3
174.99
163.57
161.14
140.39
140.32
134.67
131.34
128.92
128.84
127.56
127.02
125.64
125.61
117.12
116.91
113.10
112.89
84.00
77.48
77.16
76.84
52.97
40.57
25.00
24.77
21.91
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

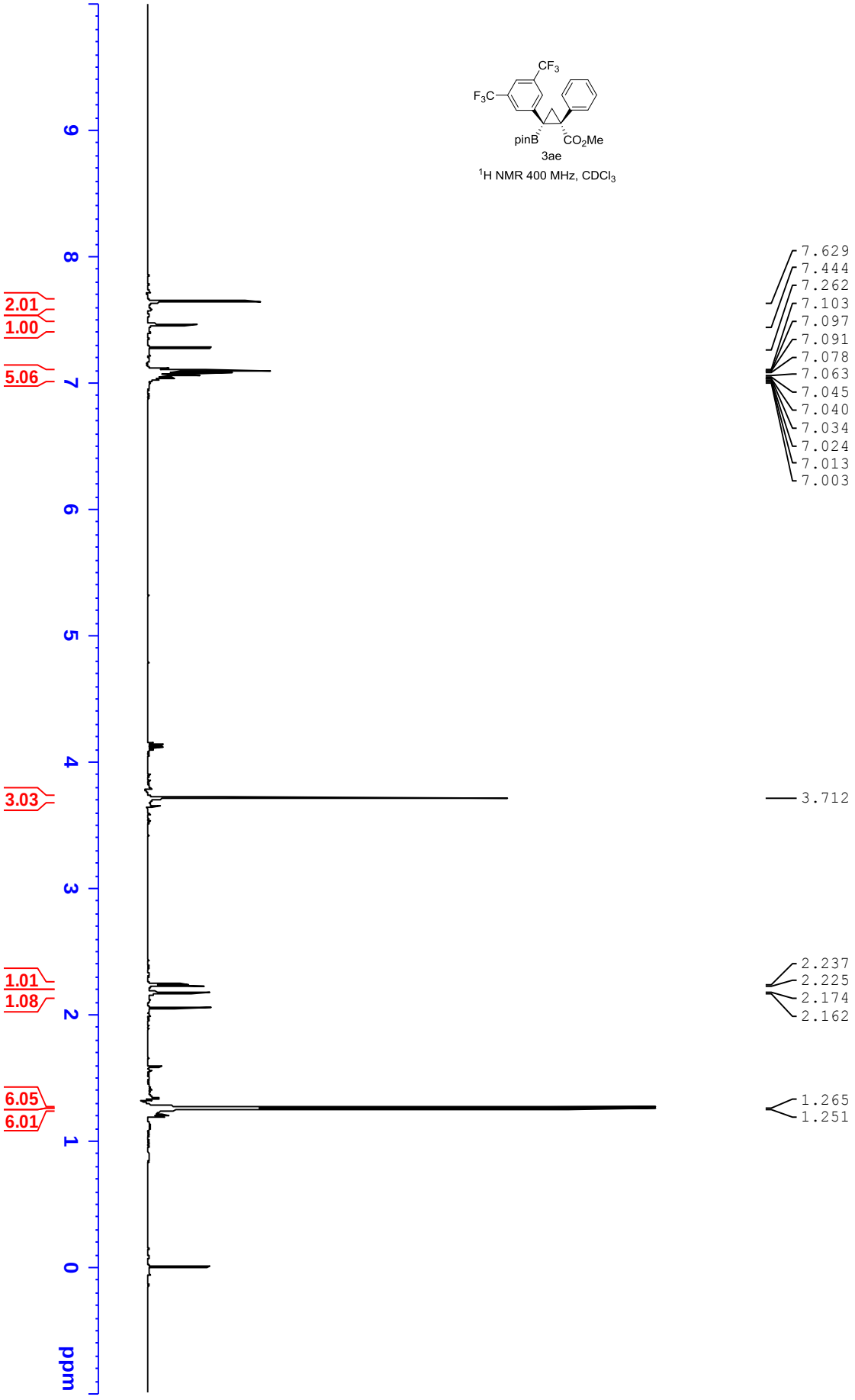


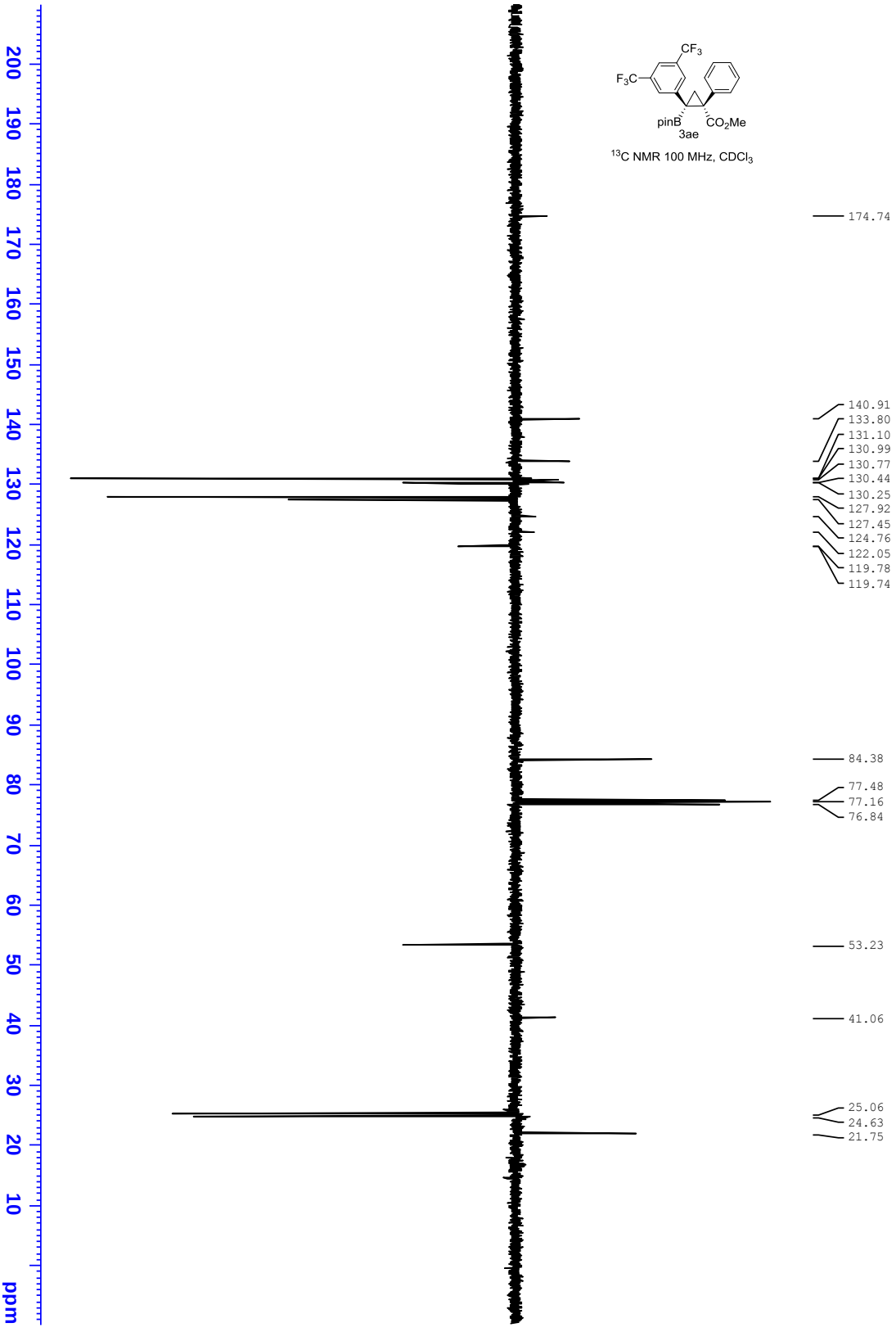


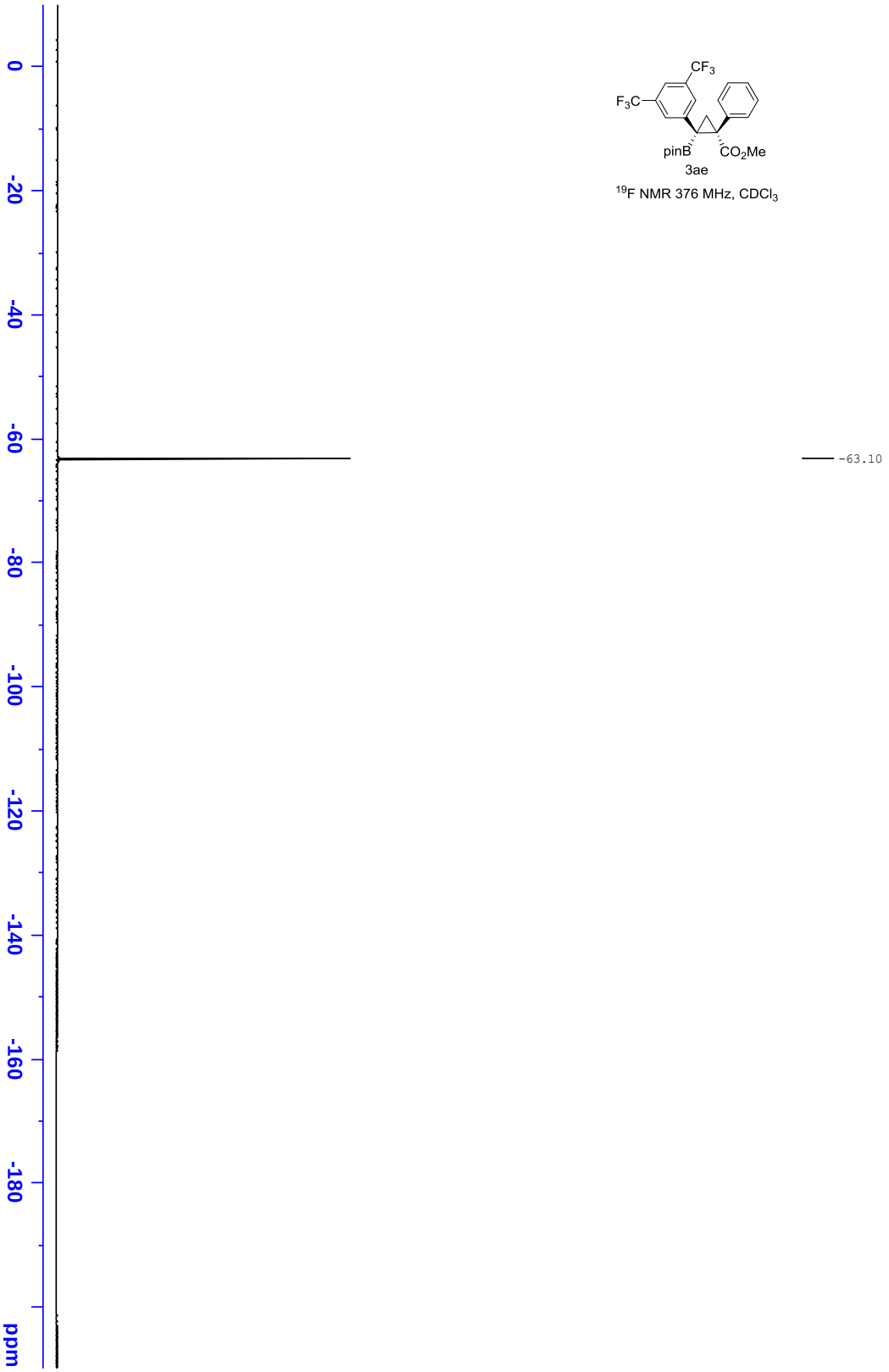
3ad

^{19}F NMR 376 MHz, $CDCl_3$

-114.55
-114.58
-114.59
-114.61

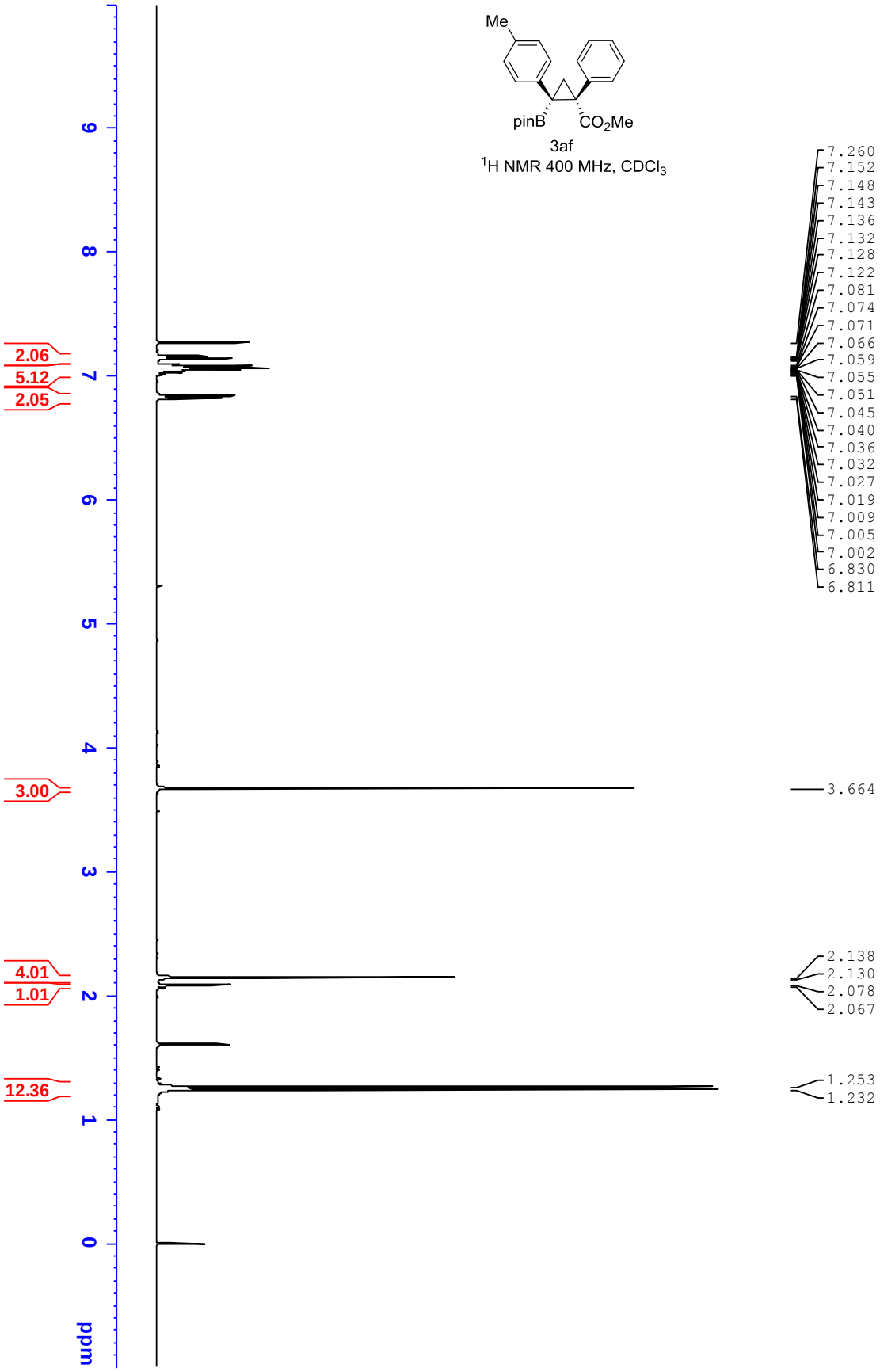

CF3
F3C
pinB
CO2Me
3ae
1H NMR 400 MHz, CDCl3
7.629
7.444
7.262
7.103
7.097
7.091
7.078
7.063
7.045
7.040
7.034
7.024
7.013
7.003
3.712
2.237
2.225
2.174
2.162
1.265
1.251
2.01
1.00
5.06
3.03
1.01
1.08
6.05
6.01
ppm

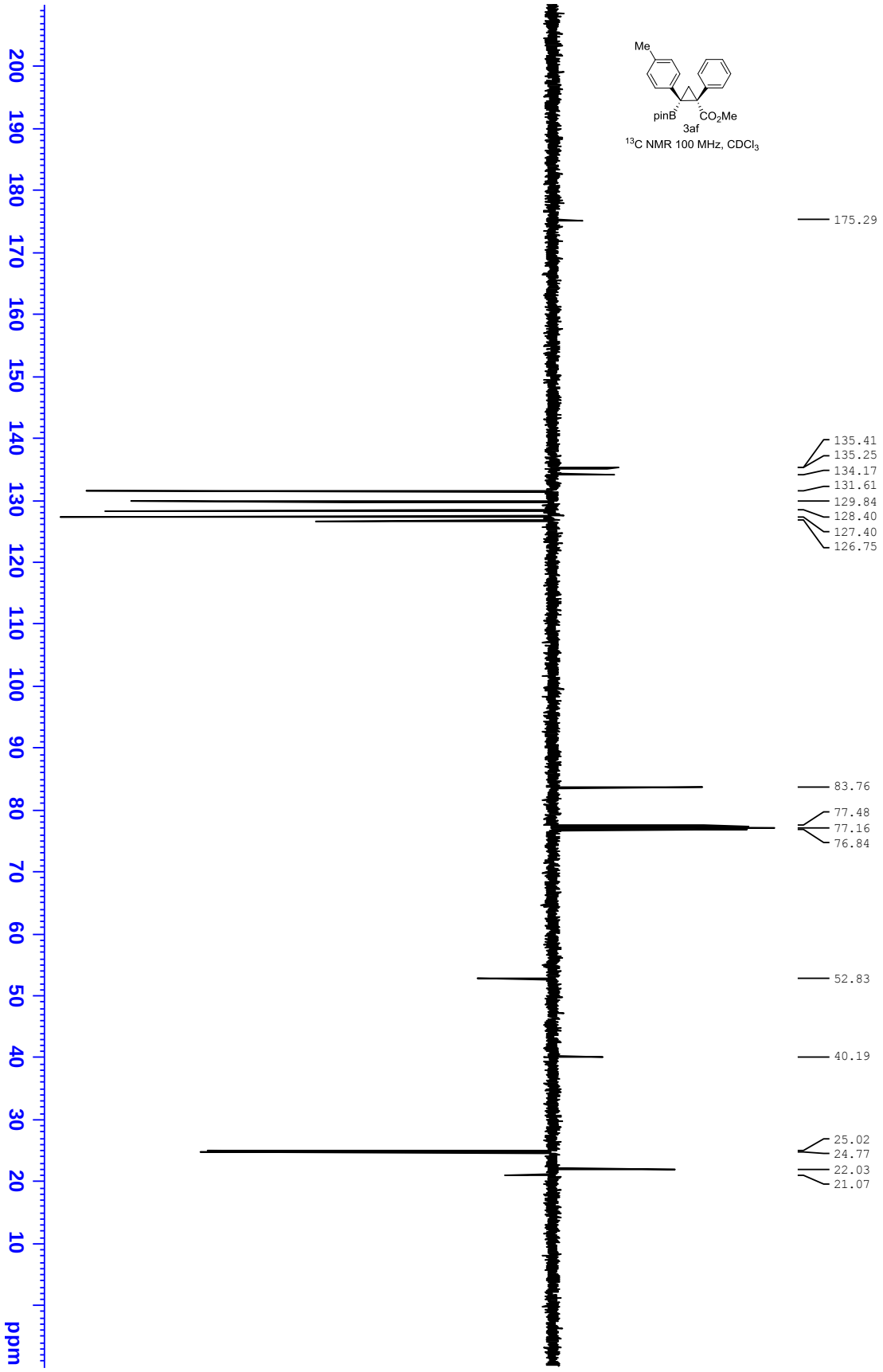

CF3
F3C
pinB
CO2Me
3ae
13C NMR 100 MHz, CDCl3
174.74
140.91
133.80
131.10
130.99
130.77
130.44
130.25
127.92
127.45
124.76
122.05
119.78
119.74
84.38
77.48
77.16
76.84
53.23
41.06
25.06
24.63
21.75
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

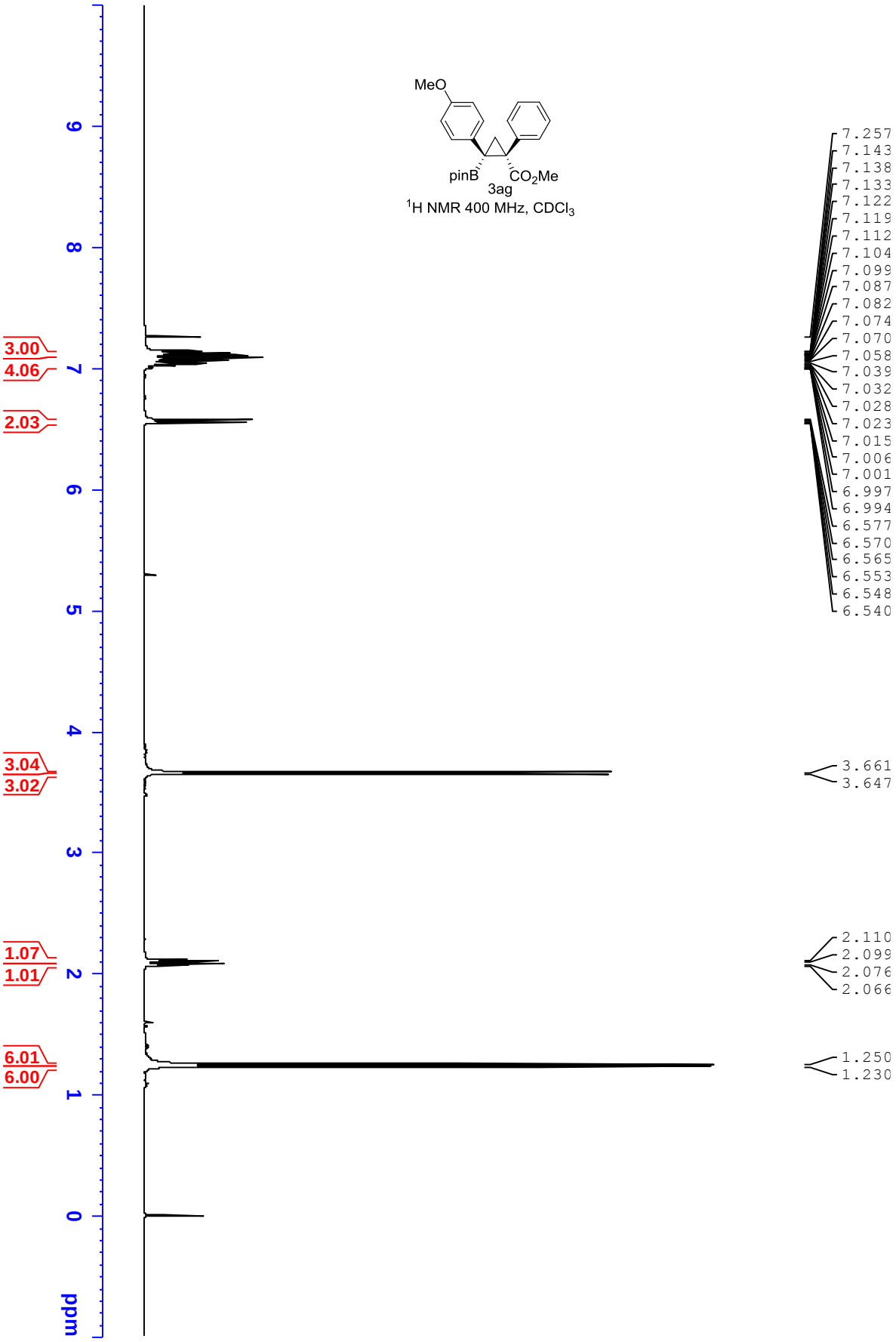


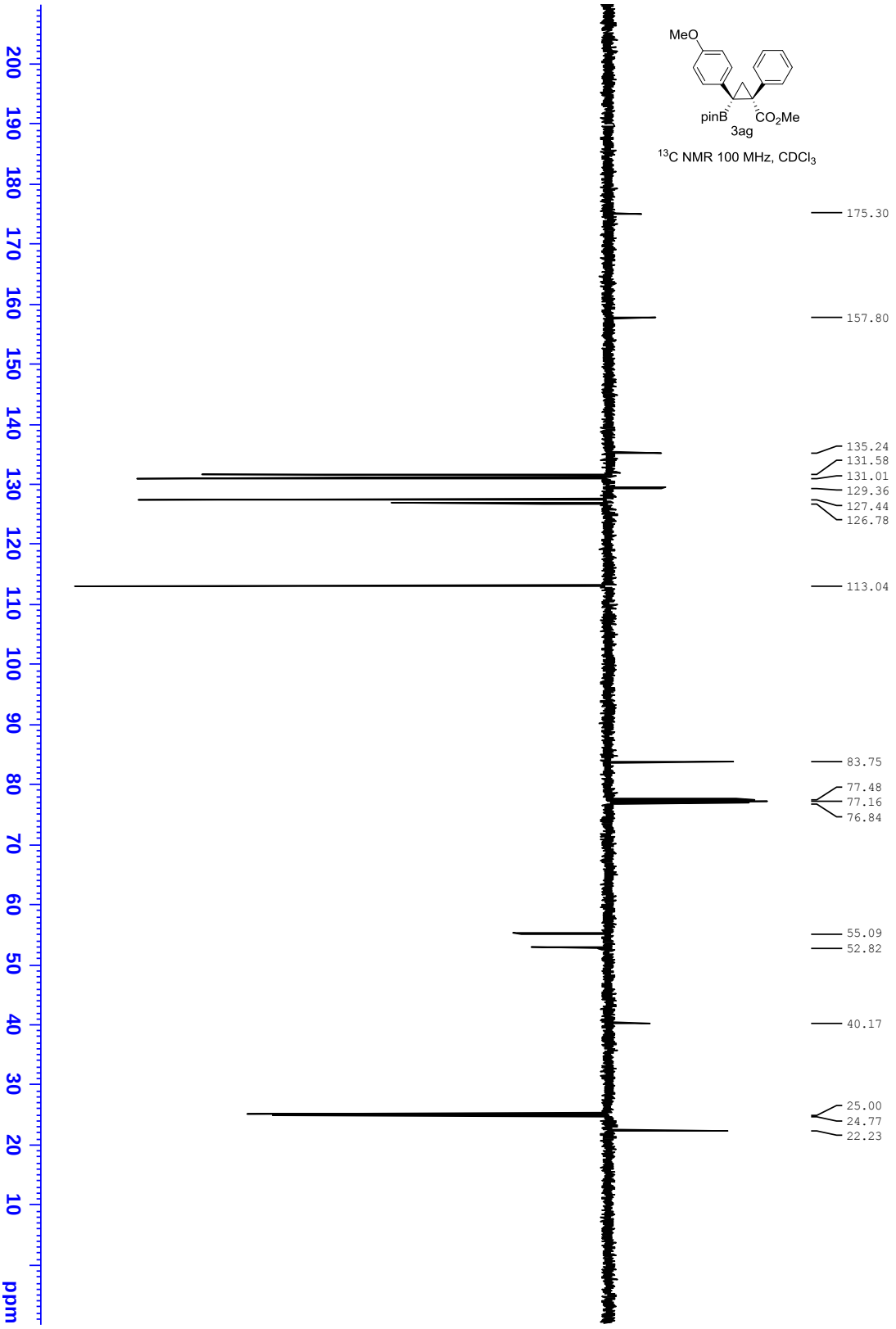
3ae

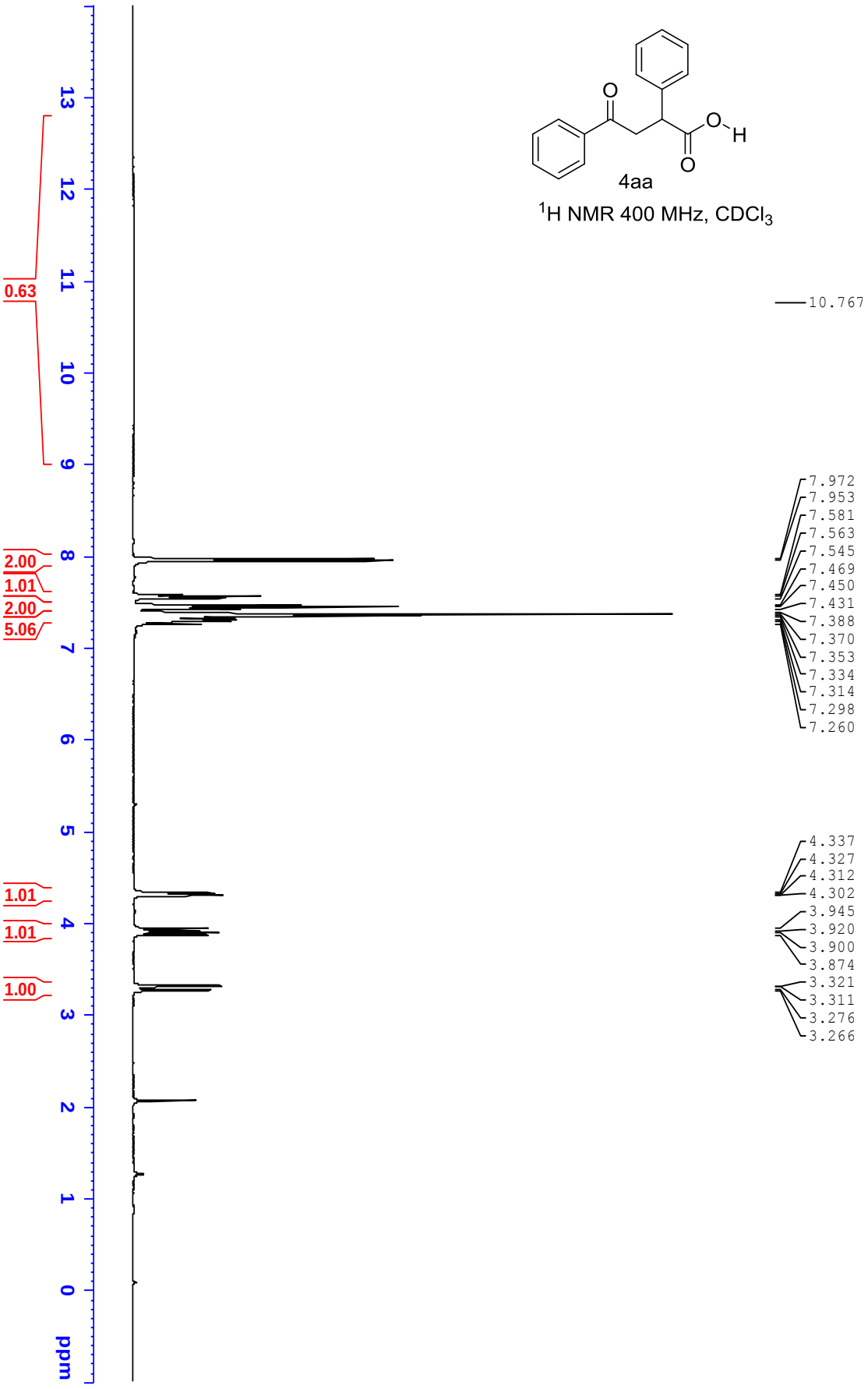
^{19}F NMR 376 MHz, $CDCl_3$

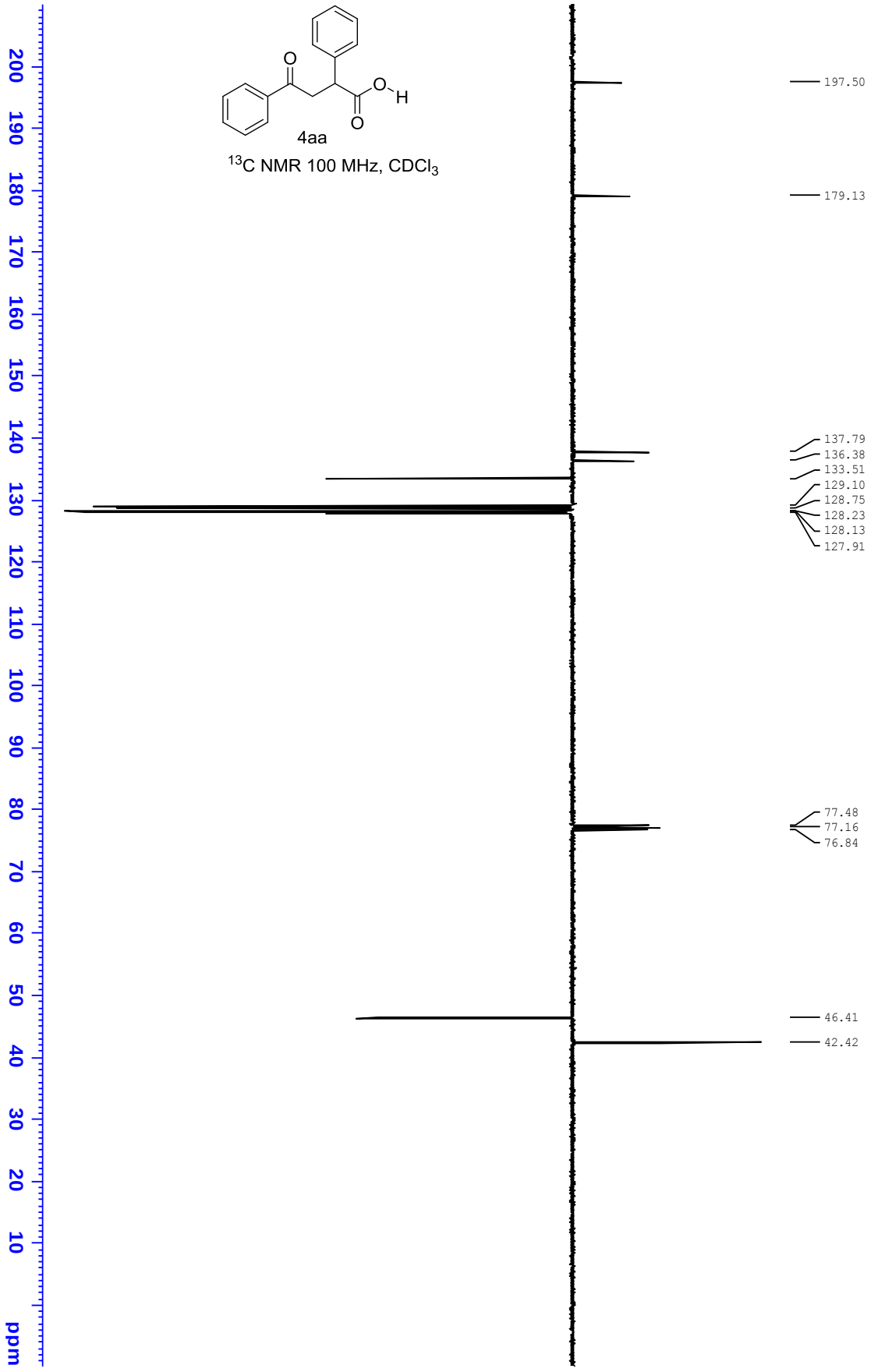

Me
pinB
CO2Me
3af
1H NMR 400 MHz, CDCl3
7.260
7.152
7.148
7.143
7.136
7.132
7.128
7.122
7.081
7.074
7.071
7.066
7.059
7.055
7.051
7.045
7.040
7.036
7.032
7.027
7.019
7.009
7.005
7.002
6.830
6.811
3.664
2.138
2.130
2.078
2.067
1.253
1.232
2.06
5.12
2.05
3.00
4.01
1.01
12.36
ppm

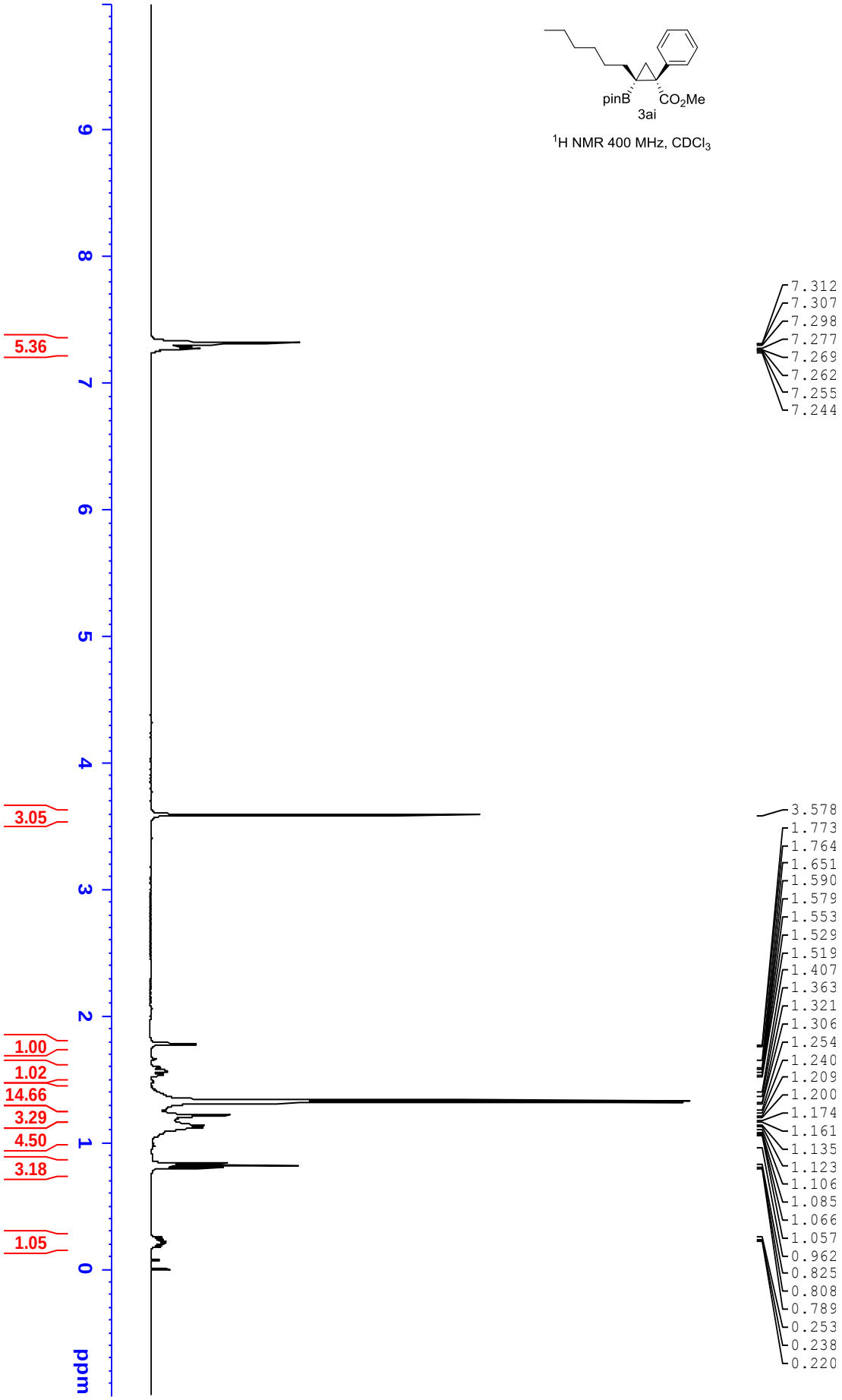

Me
pinB
CO2Me
3af
13C NMR 100 MHz, CDCl3
175.29
135.41
135.25
134.17
131.61
129.84
128.40
127.40
126.75
83.76
77.48
77.16
76.84
52.83
40.19
25.02
24.77
22.03
21.07
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

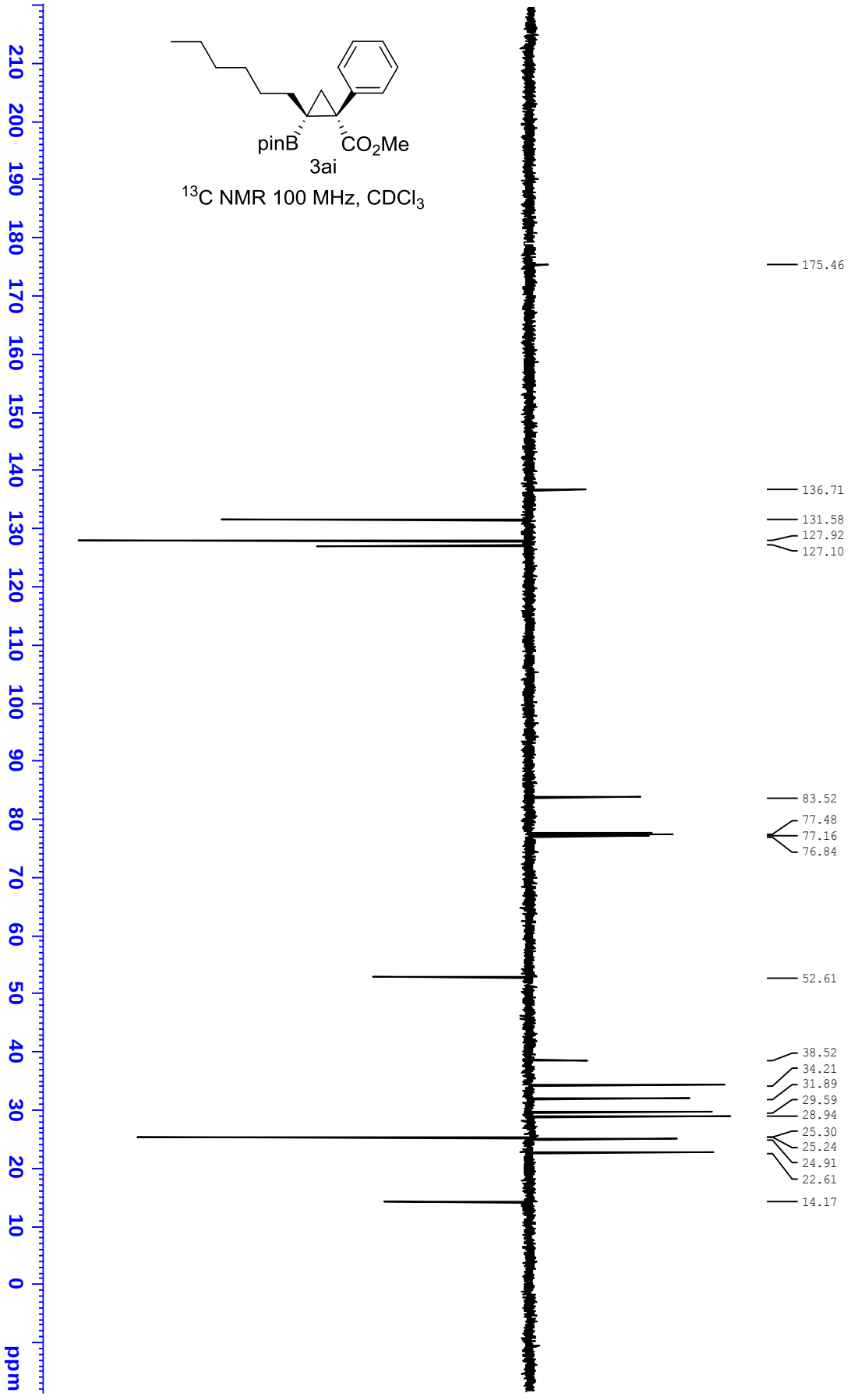

MeO
pinB
CO2Me
3ag
1H NMR 400 MHz, CDCl3
7.257
7.143
7.138
7.133
7.122
7.119
7.112
7.104
7.099
7.087
7.082
7.074
7.070
7.058
7.039
7.032
7.028
7.023
7.015
7.006
7.001
6.997
6.994
6.577
6.570
6.565
6.553
6.548
6.540
3.661
3.647
2.110
2.099
2.076
2.066
1.250
1.230
3.00
4.06
2.03
3.04
3.02
1.07
1.01
6.01
6.00
ppm


MeO
pinB
CO2Me
3ag
13C NMR 100 MHz, CDCl3
175.30
157.80
135.24
131.58
131.01
129.36
127.44
126.78
113.04
83.75
77.48
77.16
76.84
55.09
52.82
40.17
25.00
24.77
22.23
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm


4aa
^{1}H NMR 400 MHz, $CDCl_3$
10.767
7.972
7.953
7.581
7.563
7.545
7.469
7.450
7.431
7.388
7.370
7.353
7.334
7.314
7.298
7.260
4.337
4.327
4.312
4.302
3.945
3.920
3.900
3.874
3.321
3.311
3.276
3.266
0.63
2.00
1.01
2.00
5.06
1.01
1.01
1.00
ppm


O
O
O
H
4aa
^{13}C NMR 100 MHz, $CDCl_3$
197.50
179.13
137.79
136.38
133.51
129.10
128.75
128.23
128.13
127.91
77.48
77.16
76.84
46.41
42.42
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm


pinB
CO2Me
3ai
1H NMR 400 MHz, CDCl3
7.312
7.307
7.298
7.277
7.269
7.262
7.255
7.244
3.578
1.773
1.764
1.651
1.590
1.579
1.553
1.529
1.519
1.407
1.363
1.321
1.306
1.254
1.240
1.209
1.200
1.174
1.161
1.135
1.123
1.106
1.085
1.066
1.057
0.962
0.825
0.808
0.789
0.253
0.238
0.220
5.36
3.05
1.00
1.02
14.66
3.29
4.50
3.18
1.05
ppm


pinB
CO2Me
3ai
13C NMR 100 MHz, CDCl3
175.46
136.71
131.58
127.92
127.10
83.52
77.48
77.16
76.84
52.61
38.52
34.21
31.89
29.59
28.94
25.30
25.24
24.91
22.61
14.17
210
200
190
180
170
160
150
140
130
120
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100
90
80
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20
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ppm