Supporting Information

Synthesis of Chiral N-Heterocyclic Carbene Ligands with Rigid Backbones and Application to the Palladium-Catalyzed Enantioselective Intramolecular α-Arylation of Amides

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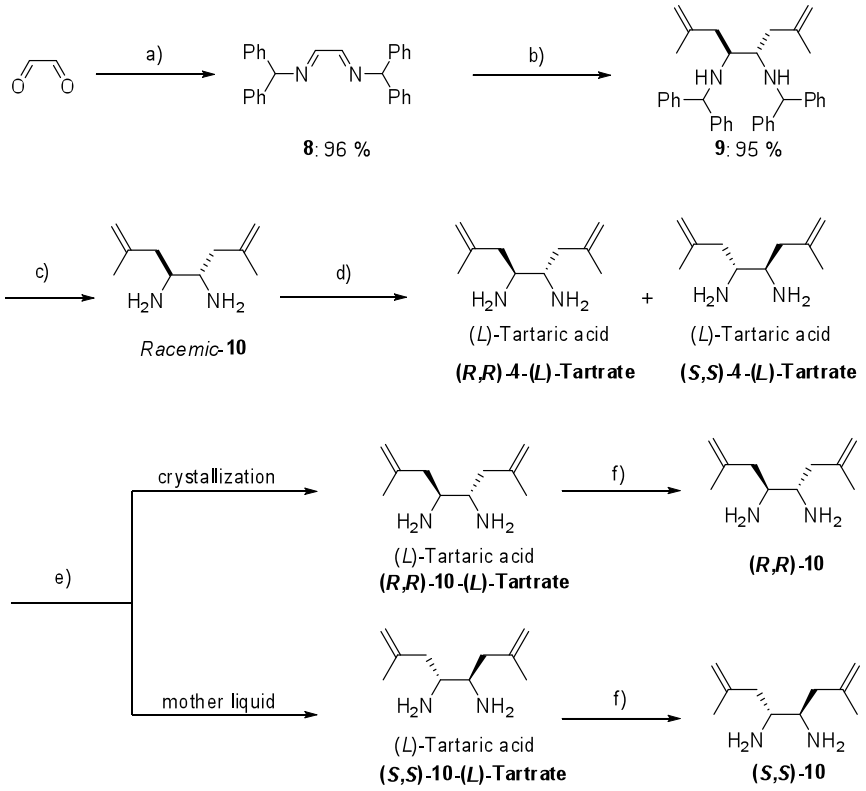
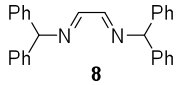
General. NMR spectra were recorded on a Varian Gemini 2000 (^{1}H at 300 MHz and ^{13}C at 75 MHz), or Varian Mercury-400 spectrometers. Unless otherwise noted, $CDCl_3$ was used as a solvent. Chemical Shifts are recorded in δ ppm referenced to a residual $CDCl_3$ (δ = 7.26 for ^{1}H, δ = 77.0 for ^{13}C). High-resolution mass spectra were recorded on Applied Biosystems Voyager Elite or JEOL JMS-HX110A spectrometer. Infrared spectra were recorded on a SHIMADZU FT-IR 8100. Optical rotation was measured by a JASCO P-1020 polarimeter. HPLC analysis was performed by 4.6 × 250 mm column. Column chromatography was performed with silica gel 60 N (Kanto). Preparative thin-layer chromatography was performed with Silica gel 60 PF_{254} (Merck). Gel permeation chromatography (GPC) was carried out with Japan Analytical Industry LC-908 or LC-9204 equipped with JAIGEL-1H.

Materials. Amides **14**[1,2,3] and TMEDA·$PdMe_2$[4] were prepared by the reported procedures. **14a**,[1] **14c**,[1] **14e**,[2] and **14g**[1] are known compounds. Toluene and hexane were dried over sodium benzophenone ketyl. Chlorobenzene and 1,2-dichloroethane were dried over CaH_2. Unless otherwise noted, all chemicals and anhydrous solvents were obtained from commercial suppliers.

Synthesis of Chiral Diamines (*R*,*R*)-10 and (*S*,*S*)-10



Diimine 8

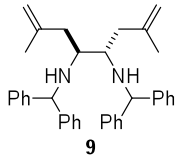


8

To a stirred solution of aminodiphenylmethane (25 g, 137 mmol) in hexane (60 mL) at room temperature was added glyoxal (40 wt.% solution in water, 7.8 mL, 68 mmol). After being stirred at room temperature overnight, the white precipitate generated was collected by filtration, washed with hexane and then dried under vacuum to give dimine **8** as a white solid (25.2 g, 65 mmol, 96% yield).

^{1}H NMR δ 8.23 (s, 2H), 7.33 (d, J = 4.4 Hz, 16H), 7.22-7.30 (m, 4H), 5.60 (s, 2H); ^{13}C NMR δ 162.1, 142.6, 128.6, 127.6, 127.3, 78.1; IR (KBr) 1628, 1492, 1448, 748, 696 cm^{-1}; HRMS (ESI): Calcd for $C_{28}H_{25}N_2$ ([M+H]$^+$): 389.2012. Found m/z 389.2005.

9

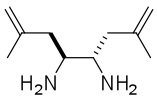


9

To a stirred solution of **8** (23.2 g, 64 mmol) in THF (240 mL) at -78 ˚C was added dropwise the 2-methylallylmagnesium choloride (1.0 M in THF, 192mL, 192 mmol). The mixture was allowed to increase gradually to room temperature and stirred for 10 hours. The reaction was quenched with water, the aq. layer was extracted with $CHCl_3$, and the combined organic layers were dried over $MgSO_4$ and concentrated to give diamine **9** as brown oil (30.4 g, 60.8 mmol, 95% yield) which was pure enough for next step.

^{1}H NMR δ 7.16-7.40 (m, 20H), 4.76 (s, 2H), 4.65 (s, 2H), 4.42 (s, 2H), 2.77 (t, J = 6.0 Hz, 2H), 2.46 (dd, J = 13.2, 4.8 Hz, 2H), 2.04 (dd, J = 13.6, 8.0 Hz, 2H), 1.62 (br, 2H), 1.45 (s, 6H); ^{13}C NMR δ 144.6, 144.5, 144.1, 128.4, 128.2, 127.8, 127.4, 126.9, 126.8, 112.8, 64.6, 53.3, 38.7, 21.9; IR (neat) 1642, 1599, 1492, 1451, 893, 745, 699 cm^{-1}; HRMS(ESI): Calcd for $C_{36}H_{41}N_2$ ([M+H]$^+$): 501.3264. Found m/z 501.3250.

Chiral Diamines (*R*,*R*)-10 and (*S*,*S*)-10

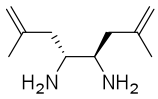


Racemic-**10**

Racemic-**10**: To **9** (30.0 g, 60 mmol) at room temperature was added Et_3SiH (28.6 mL, 180 mmol) and TFA (60 mL) subsequently. The mixture was stirred at 60 ˚C for 6 hours. The reaction was cooled with ice bath and quenched with aq. NaOH (6 M, 150 mL, 900 mmol). The aq. layer was extracted with $CHCl_3$, and the combined organic layers were dried over Na_2SO_4 and concentrated to brown oil containing *racemic*-**4** which was used for next step without further purification.

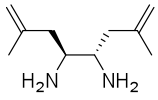
(R,R)-**10**:[5] To the mixture containing *Racemic*-**10** that was obtained from last step was added (*L*)-tartaric acid (9.0 g, 60 mmol) and ethanol (300 mL). The mixture was refluxed for 2 hours. The salt of (*L*)-tartaric acid and *Racemic*-**10** was collected by suction filtration. To the solid was added ethanol 300 ml and water 100 mL. The mixture was refluxed for 2 hours and cooled to room temperature gradually. The (*R,R*)-**10**-(*L*)-tartrate was precipitated as white solid while (*S,S*)-**10**-(*L*)-tartrate remained in the mother liquid. To the white solid was added aq. NaOH (6 M, 5 mL, 30 mmol) and stirred for 5 minutes. The mixture was extracted with Et_2O (30 mL × 2), and the combined organic layers were dried over Na_2SO_4 and concentrated to afford chiral diamine (*R,R*)-**10** (1.86 g, 11 mmol, 37% yield) as colorless liquid.

(R,R)-**10**:



(R,R)-10

^{1}H NMR δ 4.80-4.86 (m, 2H), 4.73-4.79 (m, 2H), 2.72-2.82 (m, 2H), 2.20 (dd, *J* = 13.5, 2.7 Hz, 2H), 1.96-2.08 (m, 2H), 1.72 (s, 6H), 1.28 (br, 4H); ^{13}C NMR δ 143.2, 112.9, 52.3, 43.7, 22.1; IR (neat) 3373, 2932, 1648, 1445, 1375, 890 cm^{-1}; HRMS(ESI): Calcd for $C_{10}H_{21}N_2$ ($[M+H]^+$): 169.1699. Found m/z 169.1699; $[\alpha]_D^{25}$ = -23.0 (*c* = 1.0 in $CHCl_3$).

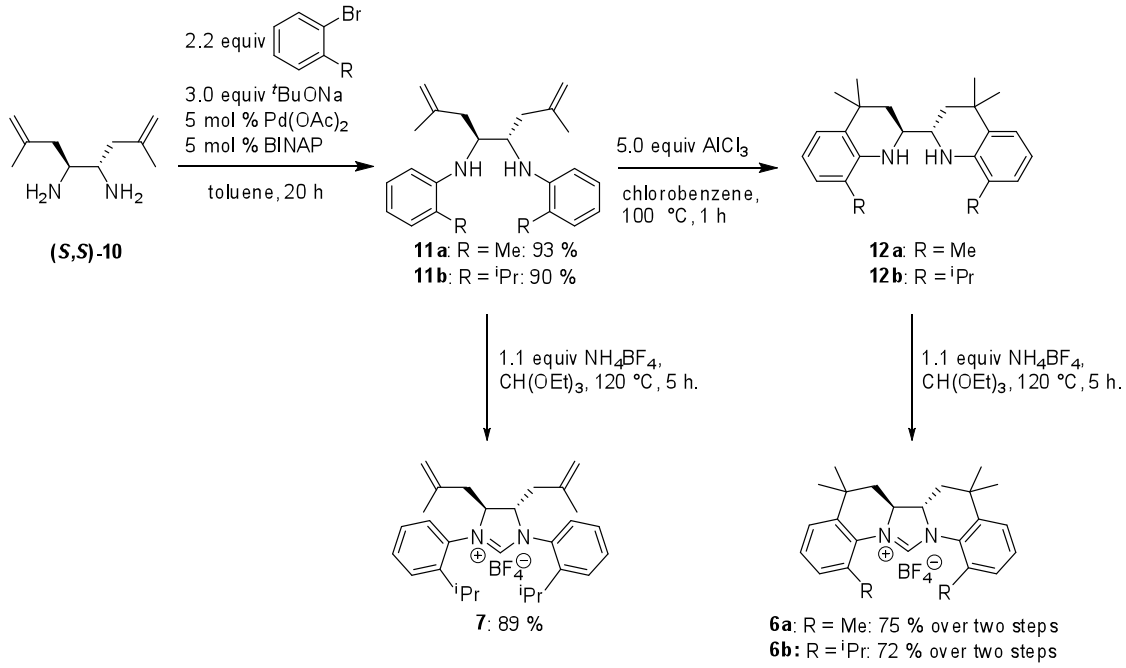


(S,S)-10

(S,S)-**10**: To the mother liquid was added aq. NaOH (6 M, 20 mL, 120 mmol) and stirred for 5 minutes. The mixture was extracted with Et_2O (30 mL × 2), and the

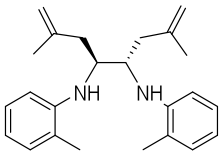
combined organic layers were dried over Na_2SO_4 to afford enantioenriched *(S,S)*-**10** as colorless liquid. The enantioenriched (*S,S*)-**10** was further purified by the complexation with (*D*)-tartaric acid: To the enantioenriched *(S,S)*-**10** was added (*D*)-tartaric acid (2.25 g, 15 mmol), ethanol (210 mL) and water (70 mL). The mixture was refluxed for 2 hours and then cooled to room temperature gradually. (*S,S*)-**10**-(*D*)-Tartrate was precipitated as white solid. To the white solid of (*S,S*)-**10**-(*D*)-Tartrate was added aq. NaOH (6 M, 5 mL, 30 mmol) and stirred for 5 minutes. The mixture was extracted with Et_2O (15 ml × 2), and the combined organic layers were dried over Na_2SO_4 and concentrated to afford chiral diamine (*S,S*)-**10** (1.76 g, 10.5 mmol, 35% yield) as colorless liquid. $[\alpha]_D^{25}$ = +23.0 (*c* = 1.0 in $CHCl_3$).

Synthesis of the Chiral Carbene Precursors 6a, 6b and 7



General procedure for synthesis of chiral diamines 11:[6] To a dried Schlenk tube were added $Pd(OAc)_2$ (22.4 mg, 0.1 mmol, 5 mol %), *racemic*-BINAP (62.3 mg, 0.1 mmol, 5 mol %), ^{t}BuONa (576 mg, 6.0 mmol, 3.0 equiv), (*S,S*)-**10** (336 mg, 2.0 mmol, 1.0 equiv), 2-alkyl bromobenzene (4.4 mmol, 2.2 equiv), and toluene (4 mL). The mixture was stirred at 100 ˚C for 20 hours. After cooling to room temperature, volatiles were removed under vacuum and the residue was purified by flash chromatography (f.c.) (hexane/ether 100/3) to give diamine **11a** (647 mg, 93% yield) and **11b** (728 mg, 90% yield).

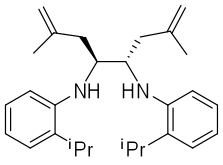
11a



11a

^{1}H NMR δ 7.18 (t, *J* = 8.0 Hz, 2H), 7.11 (d, *J* = 7.2 Hz, 2H), 6.81 (d, *J* = 8.0 Hz, 2H), 6.71 (t, *J* = 7.2 Hz, 2H), 4.89 (d, *J* = 1.2 Hz, 2H), 4.85 (d, *J* = 0.4 Hz, 2H), 4.00 (psedo t, *J* = 7.2 Hz, 2H), 3.55 (s, 2H), 2.49 (dd, *J* = 14, 6.4 Hz, 2H), 2.34 (dd, *J* = 14, 7.2 Hz, 2H), 2.18 (s, 6H), 1.74 (s, 6H); ^{13}C NMR δ 145.8, 143.1, 130.4, 127.3, 122.2, 116.9, 113.0, 110.1, 52.6, 41.0, 22.3, 17.5; IR (KBr) 3421, 1607, 1586, 1513, 1316, 1263, 1124, 1055, 904, 746 cm^{-1}; HRMS(ESI): Calcd for $C_{24}H_{33}N_2$ ([M+H]$^+$): 349.2638. Found m/z 349.2642; $[\alpha]_D^{25}$ = +20.0 (*c* = 1.0 in $CHCl_3$); HPLC [Daicel Chiralcel OD-H, hexane/*i*-PrOH = 98/2, flow rate = 1.0 mL/min, λ = 254 nm): *t*1 = 6.0 min (minor), *t*2 = 6.6 min (major), ee: > 99%].

11b



11b

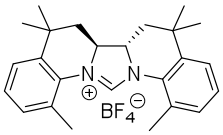
^{1}H NMR δ 7.10-7.22 (m, 4H), 6.81 (d, *J* = 8.0 Hz, 2H), 6.76 (t, *J* = 7.6 Hz, 2H), 4.87 (s, 2H), 4.82 (s, 2H), 3.98 (d, *J* = 5.6 Hz, 2H), 3.73 (s, 2H), 2.88 (sept, *J* = 6.8 Hz, 2H), 2.40 (dd, *J* = 14, 7.2 Hz, 2H), 2.32 (dd, *J* = 14, 7.2 Hz, 2H), 1.72 (s, 6H), 1.31 (d, *J* = 6.8 Hz, 6H), 1.26 (d, *J* = 6.8 Hz, 6H); ^{13}C NMR δ 144.5, 143.2, 132.6, 126.9, 125.3, 117.4, 113.1, 111.0, 52.3, 40.9, 27.5, 22.5, 22.4, 22.2; IR (neat) 2963, 1604, 1583, 1504, 1451, 1311, 1256, 1041, 891, 744 cm^{-1}; HRMS(ESI): Calcd for $C_{28}H_{41}N_2$ ([M+H]$^+$): 405.3264. Found m/z 405.3246; $[\alpha]_D^{25}$ = +27.7 (*c* = 1.0 in $CHCl_3$).

General procedure for synthesis of chiral cyclic diamines 12: To a dried Schlenk tube were added **5** (1 mmol), chlorobenzene (40 mL) and $AlCl_3$ (665 mg, 5 mmol). The mixture was stirred at 100 ˚C for 1 hour. After cooling to 0 ˚C, to the mixture was added aq. NaOH (6 M, 5 mL, 30 mmol) and stirred for 20 minutes. The mixture was extracted with Et_2O (30 mL × 3), the combined organic layers were dried over Na_2SO_4. The volatiles were removed under vacuum, and the residue was purified by

flash chromatography (f.c.) (hexane/ether 100/3) to give diamine **12** which were used without characterization.

General procedure for synthesis of chiral imidazolidiniums 6 and 7: To a dried Schlenk tube were added the diamines **11b** (1 mmol) or **12** (obtained from last step), $CH(OEt)_3$ (2 ml), and NH_4BF_4 (1.2 mmol). The mixture was stirred at 120 ˚C for 5 hours. After cooling to room temperature, the volatiles were removed under vacuum, and the residue was purified by flash chromatography (f.c.) (DMC/CH_3OH 10/1) to give chiral imidazolidiniums **6a** (350 mg, 75 % yield over two steps), **6b** (361 mg, 72 % yield over two steps) and **7** (447 mg, 89 % yield).

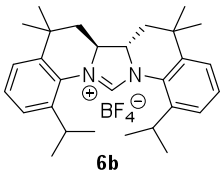
6a



6a

^{1}H NMR δ 8.39 (s, 1H), 7.20-7.40 (m, 4H), 7.14 (d, J = 7.2 Hz, 2H), 4.34 (d, J = 12.6 Hz, 2H), 2.42 (s, 6H), 2.16-2.38 (m, 4H), 1.47 (s, 6H), 1.39 (s, 6H); ^{13}C NMR δ 150.3, 139.4, 130.2, 129.7, 129.1, 128.1, 126.0, 62.2, 42.6, 34.2, 32.2, 30.9, 19.2; IR (KBr) 2969, 1607, 1577, 1453, 1303, 1257, 1058, 790, 749 cm^{-1}; HRMS(ESI): Calcd for $C_{25}H_{31}N_2$ ($[M\text{-}BF_4]^+$): 359.2482. Found m/z 359.2479; $[\alpha]_D^{25}$ = -96.5 (c = 0.2 in $CHCl_3$).

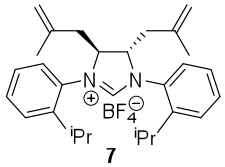
6b



6b

^{1}H NMR δ 7.85 (s, 1H), 7.20-7.42 (m, 6H), 4.47 (d, J = 14.4 Hz, 2H), 2.94 (sept, J = 6.6 Hz, 2H), 2.20-2.43 (m, 4H), 1.50 (s, 6H), 1.43 (s, 6H), 1.32 (d, J = 6.6 Hz, 6H), 1.27 (d, J = 6.9 Hz, 6H); ^{13}C NMR δ 151.1, 140.0, 139.7, 128.7, 128.2, 126.0, 125.6, 62.7, 42.4, 34.6, 32.4, 30.9, 27.4, 24.7, 24.2; IR (KBr) 2960, 1609, 1581, 1438, 1300, 1255, 1050, 752 cm^{-1}; HRMS(APCI): Calcd for $C_{29}H_{39}N_2$ ($[M\text{-}BF_4]^+$): 415.3108. Found m/z 415.3088; $[\alpha]_D^{25}$ = -59.0 (c = 0.6 in $CHCl_3$)

7

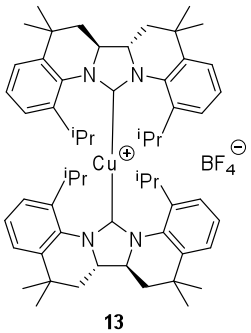


7

^{1}H NMR δ 8.21 (s, 1H), 7.55 (dd, *J* = 8.0, 0.8 Hz, 2H), 7.41-7.51 (m, 4H), 7.30-7.37 (m, 2H), 4.99 (t, *J* = 1.6 Hz, 2H), 4.91 (s, 2H), 4.48-4.56 (m, 2H), 3.11 (sept, *J* = 6.8 Hz, 2H), 2.60 (dd, *J* = 13.2, 11.2 Hz, 2H), 2.42 (dd, *J* = 13.2, 2.8 Hz, 2H), 1.59 (s, 6H), 1.37 (d, *J* = 6.8 Hz, 6H), 1.32 (d, *J* = 6.8 Hz, 6H); ^{13}C NMR δ 156.8, 144.9, 138.4, 131.1, 130.5, 128.8, 127.9, 127.4, 117.3, 66.2, 40.2, 28.4, 24.4, 24.0, 21.5; IR (KBr) 2971, 1637, 1491, 1448, 1253, 1050, 920, 763 cm^{-1}; HRMS(APCI): Calcd for $C_{29}H_{39}N_2$ ([M-BF_4]$^+$): 415.3108. Found m/z 415.3087. $[\alpha]_D^{25}$ = -227 (*c* = 0.6 in $CHCl_3$).

Synthesis of chiral NHC-copper complex 13: To a dried schlenk tube were added **6b** (0.1 mmol, 50 mg), ^{t}BuONa (0.1 mmol, 9.6 mg), CuCl (0.1 mmol, 9.9 mg), and THF (2 mL). The mixture was stirred at room temprature for 3 hours. The volatiles were removed under vacuum, and the residue was purified by preparative thin layer chromatography on silica gel (DCM/EtOH 10/1) to give **13** (16.2 mg, 33% yield). A single crystal suitable for an X-ray structural analysis was obtained by recrystallization from $CHCl_3$/hexane

13



13

^{1}H NMR δ 7.19 (dd, *J* = 8.0, 1.2 Hz, 4H), 7.03 (t, *J* = 8.0 Hz, 4H), 6.42 (dd, *J* = 8.0, 1.2 Hz, 4H), 3.81 (t, *J* = 7.6 Hz, 4H), 3.70 (sept, *J* = 6.8 Hz, 4H), 3.70 (sept, *J* = 6.8 Hz, 4H), 1.90 (d, *J* = 6.4 Hz, 8H), 1.47 (s, 12H), 1.29 (s, 12H), 0.92 (d, *J* = 6.8 Hz, 12H), 0.89 (d, *J* = 6.4 Hz, 12H); ^{13}C NMR δ 200.5, 139.7, 139.5, 133.0, 128.0, 124.6, 123.8, 62.7, 43.1, 34.6, 33.9, 30.2, 29.0, 26.1, 20.8; IR (KBr) 2963, 1441, 1405, 1388, 1299, 1052, 749 cm^{-1}; HRMS(ESI): Calcd for $C_{58}H_{76}CuN_4$ ([M-BF_4]$^+$): 891.5361. Found m/z 891.5344; $[\alpha]_D^{25}$ = -462.4 (*c* = 0.1 in $CHCl_3$).

The single crystal was mounted on a plastic loop. Data were collected on Rigaku/MSC Saturn CCD diffractometer with confocal monochromated Mo KR radiation (λ = 0.7107 Å) and processed using the CrystalClear program (Rigaku). The structure was solved by a direct method and refined by full matrix least-squares refinement cycles on F2 for all data using the SHELX-97. Details of crystal and data collection parameters are shown in ***Table S1–S5***.

Table S1. Crystal data and structure refinement

Identification code	1
Empirical formula	C60 H78 B Cl6 Cu F4 N4
Formula weight	1218.31
Temperature	296(2) K
Wavelength	0.71075 A
Crystal system, space group	P212121
Unit cell dimensions	a = 11.9578(3) A alpha = 90 deg. b = 16.9032(4) A beta = 90 deg. c = 31.2535(9) A gamma = 90 deg.
Volume	6317.1(3) A^3
Z, Calculated density	4, 1.281 Mg/m^3
Absorption coefficient	0.651 mm^-1
F(000)	2552
Crystal size	0.10 x 0.10 x 0.10 mm
Theta range for data collection	3.02 to 27.49 deg.
Limiting indices	-13<=h<=15, -21<=k<=21, -40<=l<=40
Reflections collected / unique	59307 / 14109 [R(int) = 0.0292]
Completeness to theta = 27.49	98.2 %
Max. and min. transmission	0.9378 and 0.9378
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	14109 / 0 / 701
Goodness-of-fit on F^2	1.065
Final R indices [I>2sigma(I)]	R1 = 0.0536, wR2 = 0.1539
R indices (all data)	R1 = 0.0638, wR2 = 0.1641
Absolute structure parameter	0.020(11)
Largest diff. peak and hole	0.613 and -0.493 e.A^-3

Table S2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (A^2 x 10^3) for 1. U(eq) is defined as one third of the trace of the orthogonalized Uij tensor.

	x	y	z	U(eq)
Cu(1)	6921(1)	68(1)	1515(1)	40(1)
C(19)	7313(2)	210(2)	921(1)	40(1)
N(1)	6636(2)	383(1)	591(1)	44(1)
N(2)	5900(2)	352(1)	2359(1)	38(1)
Cl(1)	3311(2)	820(1)	-1037(1)	143(1)
C(24)	4690(3)	346(2)	839(1)	51(1)
C(25)	6576(2)	-95(2)	2113(1)	39(1)
N(3)	8357(2)	123(2)	763(1)	48(1)
C(27)	7760(2)	-165(2)	3017(1)	50(1)
C(28)	6730(2)	-529(2)	2821(1)	43(1)
N(4)	6994(2)	-667(1)	2365(1)	41(1)
C(30)	5042(2)	886(2)	2205(1)	42(1)
C(31)	5707(2)	-10(2)	2783(1)	42(1)
C(32)	5560(2)	744(2)	629(1)	46(1)
Cl(4)	7810(3)	-2173(1)	-730(1)	202(2)
C(34)	3948(2)	728(2)	2333(1)	48(1)
C(35)	3619(2)	71(2)	2645(1)	53(1)
C(36)	4467(3)	2032(2)	1819(1)	64(1)
C(37)	4785(3)	-529(2)	947(1)	58(1)
C(38)	4626(2)	-467(2)	2752(1)	49(1)
C(39)	5337(3)	1560(2)	1965(1)	51(1)
C(40)	9709(3)	-939(2)	797(1)	65(1)
C(41)	9699(3)	92(3)	1356(1)	61(1)
Cl(5)	7320(5)	-1859(2)	-1578(1)	247(2)
C(43)	5415(3)	1489(2)	438(1)	54(1)
C(44)	7884(3)	-1206(2)	2283(1)	49(1)
C(45)	3114(3)	1235(2)	2179(1)	66(1)
C(46)	6726(4)	-1849(2)	1690(1)	64(1)
C(47)	4398(4)	1873(3)	511(1)	70(1)
Cl(2)	2910(3)	-796(1)	-815(1)	181(1)
C(49)	3360(3)	1854(2)	1922(1)	72(1)
C(50)	6280(4)	1863(2)	137(1)	63(1)

C(51)	8778(3)	-718(2)	2991(1)	57(1)
C(52)	6548(3)	1825(2)	1911(1)	56(1)
C(53)	9257(3)	-250(2)	981(1)	51(1)
C(54)	3567(3)	1514(3)	747(1)	75(1)
C(55)	7815(3)	-1749(2)	1945(1)	62(1)
C(56)	3693(3)	758(3)	896(1)	66(1)
C(57)	8402(4)	-772(2)	169(1)	71(1)
C(58)	9425(4)	-1200(3)	343(1)	79(1)
C(59)	10558(4)	-1310(3)	1034(2)	90(1)
C(60)	2703(3)	-454(3)	2459(2)	76(1)
C(61)	8762(3)	-1218(2)	2584(1)	61(1)
C(62)	9850(3)	-212(3)	3011(2)	84(1)
C(63)	7288(3)	538(2)	193(1)	52(1)
C(64)	7399(3)	1423(2)	156(1)	62(1)
C(65)	5797(5)	1795(3)	-321(1)	82(1)
B(1)	9268(5)	557(4)	-949(1)	80(1)
C(67)	3197(3)	448(3)	3063(1)	73(1)
C(68)	8703(5)	-2274(3)	1892(2)	93(2)
C(69)	9393(3)	931(2)	1482(1)	66(1)
C(70)	8749(4)	-1271(3)	3381(1)	73(1)
C(71)	8366(3)	105(2)	289(1)	57(1)
C(72)	10912(4)	-1038(3)	1419(2)	89(1)
C(73)	5890(6)	-2313(3)	1954(2)	103(2)
Cl(6)	6091(3)	-1174(2)	-941(2)	271(3)
C(75)	9197(6)	-2105(3)	334(2)	107(2)
F(1)	9805(5)	692(3)	-599(1)	167(2)
C(77)	6763(5)	2299(3)	1502(2)	102(2)
C(78)	4059(5)	-755(4)	1328(2)	102(2)
C(79)	9608(4)	-1758(3)	2517(2)	89(1)
C(80)	6873(4)	2275(3)	2319(2)	94(2)
C(81)	10510(4)	-326(3)	1575(2)	85(1)
C(82)	6465(5)	2737(2)	243(2)	93(2)
C(83)	9590(5)	-2272(4)	2167(2)	102(2)
C(84)	10142(6)	1485(4)	1220(2)	118(2)
C(85)	4560(7)	-1013(3)	551(2)	110(2)
C(86)	2630(5)	161(3)	-690(2)	89(1)
C(87)	6911(7)	-2175(4)	1239(2)	115(2)
F(2)	9199(6)	1108(3)	-1248(2)	178(2)

F(3)	8225(4)	293(4)	-818(2)	173(2)
F(4)	9484(10)	-98(5)	-1157(2)	256(4)
C(91)	10431(5)	-1016(5)	56(2)	123(2)
C(92)	9517(5)	1103(4)	1958(2)	103(2)
C(94)	7365(7)	-1470(4)	-1083(2)	128(3)
Cl(3)	2997(2)	381(1)	-163(1)	121(1)

Table S3. Bond lengths [A] and angles [deg]

Cu(1)-C(19)	1.929(3)
Cu(1)-C(25)	1.934(2)
C(19)-N(1)	1.344(3)
C(19)-N(3)	1.350(4)
N(1)-C(32)	1.428(4)
N(1)-C(63)	1.490(3)
N(2)-C(25)	1.348(3)
N(2)-C(30)	1.447(3)
N(2)-C(31)	1.480(3)
Cl(1)-C(86)	1.756(6)
C(24)-C(56)	1.392(5
C(24)-C(32)	1.402(5)
C(24)-C(37)	1.521(5)
C(25)-N(4)	1.344(3)
N(3)-C(53)	1.422(4)
N(3)-C(71)	1.480(4)
C(27)-C(28)	1.506(4)
C(27)-C(51)	1.537(4)
C(28)-N(4)	1.478(3)
C(28)-C(31)	1.510(4)
N(4)-C(44)	1.424(4)
C(30)-C(34)	1.394(4)
C(30)-C(39)	1.410(4)
C(31)-C(38)	1.508(4)
C(32)-C(43)	1.404(4)
Cl(4)-C(94)	1.707(7)
C(34)-C(45)	1.401(4)

C(34)-C(35)	1.528(5)
C(35)-C(60)	1.524(5)
C(35)-C(67)	1.539(5)
C(35)-C(38)	1.545(4)
C(36)-C(39)	1.389(5)
C(36)-C(49)	1.395(6)
C(37)-C(85)	1.506(6)
C(37)-C(78)	1.522(6)
C(39)-C(52)	1.524(5)
C(40)-C(59)	1.406(6)
C(40)-C(53)	1.406(5)
C(40)-C(58)	1.525(6)
C(41)-C(81)	1.380(6)
C(41)-C(53)	1.409(5)
C(41)-C(69)	1.517(6)
Cl(5)-C(94)	1.682(8)
C(43)-C(47)	1.397(5)
C(43)-C(50)	1.537(5
C(44)-C(55)	1.403(5)
C(44)-C(61)	1.409(5)
C(45)-C(49)	1.352(6)
C(46)-C(73)	1.514(7)
C(46)-C(87)	1.530(6)
C(46)-C(55)	1.535(6)
C(47)-C(54)	1.378(6)
Cl(2)-C(86)	1.698(6)
C(50)-C(82)	1.531(6)
C(50)-C(64)	1.532(5)
C(50)-C(65)	1.547(6)
C(51)-C(61)	1.528(6)
C(51)-C(70)	1.536(5)
C(51)-C(62)	1.541(5)
C(52)-C(77)	1.531(5)
C(52)-C(80)	1.534(6)
C(54)-C(56)	1.369(7)
C(55)-C(68)	1.394(6)
C(57)-C(58)	1.521(6)
C(57)-C(71)	1.529(5)

C(58)-C(91)	1.532(8)
C(58)-C(75)	1.553(8)
C(59)-C(72)	1.354(8)
C(61)-C(79)	1.379(5)
C(63)-C(64)	1.506(5)
C(63)-C(71)	1.512(5)
B(1)-F(1)	1.288(6)
B(1)-F(4)	1.310(9)
B(1)-F(2)	1.323(7)
B(1)-F(3)	1.387(7)
C(68)-C(83)	1.364(8)
C(69)-C(92)	1.521(6)
C(69)-C(84)	1.534(6)
C(72)-C(81)	1.385(8)
Cl(6)-C(94)	1.664(10)
C(79)-C(83)	1.397(8)
C(86)-Cl(3)	1.743(5)
C(19)-Cu(1)-C(25)	177.98(11)
N(1)-C(19)-N(3)	107.5(2)
N(1)-C(19)-Cu(1)	128.2(2)
N(3)-C(19)-Cu(1)	124.26(19)
C(19)-N(1)-C(32)	124.9(2)
C(19)-N(1)-C(63)	111.2(2)
C(32)-N(1)-C(63)	117.8(2)
C(25)-N(2)-C(30)	125.9(2)
C(25)-N(2)-C(31)	111.9(2)
C(30)-N(2)-C(31)	116.4(2)
C(56)-C(24)-C(32)	117.1(3)
C(56)-C(24)-C(37)	121.4(3)
C(32)-C(24)-C(37)	121.0(3)
N(4)-C(25)-N(2)	107.0(2)
N(4)-C(25)-Cu(1)	126.19(19)
N(2)-C(25)-Cu(1)	126.83(19)
C(19)-N(3)-C(53)	125.0(2)
C(19)-N(3)-C(71)	112.0(2)
C(53)-N(3)-C(71)	117.7(2)
C(28)-C(27)-C(51)	112.2(3)
N(4)-C(28)-C(27)	106.4(2)

N(4)-C(28)-C(31)	100.9(2)
C(27)-C(28)-C(31)	117.2(3)
C(25)-N(4)-C(44)	129.2(2)
C(25)-N(4)-C(28)	111.9(2)
C(44)-N(4)-C(28)	115.7(2)
C(34)-C(30)-C(39)	122.8(3)
C(34)-C(30)-N(2)	116.8(2)
C(39)-C(30)-N(2)	120.2(3)
N(2)-C(31)-C(38)	106.7(2)
N(2)-C(31)-C(28)	100.60(19)
C(38)-C(31)-C(28)	113.7(2)
C(24)-C(32)-C(43)	122.4(3)
C(24)-C(32)-N(1)	120.2(3)
C(43)-C(32)-N(1)	117.3(3)
C(30)-C(34)-C(45)	116.9(3)
C(30)-C(34)-C(35)	124.3(2)
C(45)-C(34)-C(35)	118.8(3)
C(60)-C(35)-C(34)	111.4(3)
C(60)-C(35)-C(67)	109.2(3)
C(34)-C(35)-C(67)	109.0(3)
C(60)-C(35)-C(38)	107.5(3)
C(34)-C(35)-C(38)	111.4(2)
C(67)-C(35)-C(38)	108.3(3)
C(39)-C(36)-C(49)	120.8(3)
C(85)-C(37)-C(24)	109.4(3)
C(85)-C(37)-C(78)	113.8(4)
C(24)-C(37)-C(78)	112.0(4)
C(31)-C(38)-C(35)	112.4(3)
C(36)-C(39)-C(30)	116.9(3)
C(36)-C(39)-C(52)	120.4(3)
C(30)-C(39)-C(52)	122.2(3)
C(59)-C(40)-C(53)	115.5(4)
C(59)-C(40)-C(58)	121.6(4)
C(53)-C(40)-C(58)	122.4(3)
C(81)-C(41)-C(53)	117.7(4)
C(81)-C(41)-C(69)	121.2(4)
C(53)-C(41)-C(69)	120.7(3)
C(47)-C(43)-C(32)	117.2(3)

C(47)-C(43)-C(50)	119.6(3)
C(32)-C(43)-C(50)	123.1(3)
C(55)-C(44)-C(61)	122.5(3)
C(55)-C(44)-N(4)	120.6(3)
C(61)-C(44)-N(4)	116.6(3)
C(49)-C(45)-C(34)	121.6(4)
C(73)-C(46)-C(87)	114.2(5)
C(73)-C(46)-C(55)	109.6(3)
C(87)-C(46)-C(55)	113.3(4)
C(54)-C(47)-C(43)	120.6(4)
C(45)-C(49)-C(36)	120.7(3)
C(82)-C(50)-C(64)	109.5(4)
C(82)-C(50)-C(43)	111.2(4)
C(64)-C(50)-C(43)	111.3(3)
C(82)-C(50)-C(65)	109.1(4)
C(64)-C(50)-C(65)	109.1(3)
C(43)-C(50)-C(65)	106.6(3)
C(61)-C(51)-C(70)	108.8(3)
C(61)-C(51)-C(27)	111.7(3)
C(70)-C(51)-C(27)	108.1(3)
C(61)-C(51)-C(62)	110.6(3)
C(70)-C(51)-C(62)	108.9(3)
C(27)-C(51)-C(62)	108.6(3)
C(39)-C(52)-C(77)	113.9(4)
C(39)-C(52)-C(80)	107.1(3)
C(77)-C(52)-C(80)	113.0(4)
C(40)-C(53)-C(41)	122.4(3)
C(40)-C(53)-N(3)	117.5(3)
C(41)-C(53)-N(3)	120.0(3)
C(56)-C(54)-C(47)	120.9(4)
C(68)-C(55)-C(44)	117.4(4)
C(68)-C(55)-C(46)	121.0(4)
C(44)-C(55)-C(46)	120.9(3)
C(54)-C(56)-C(24)	121.2(4)
C(58)-C(57)-C(71)	113.3(4)
C(57)-C(58)-C(40)	111.9(3)
C(57)-C(58)-C(91)	109.0(4)
C(40)-C(58)-C(91)	108.1(5)

C(57)-C(58)-C(75)	108.7(5)
C(40)-C(58)-C(75)	109.9(4)
C(91)-C(58)-C(75)	109.1(5)
C(72)-C(59)-C(40)	122.9(5)
C(79)-C(61)-C(44)	117.0(4)
C(79)-C(61)-C(51)	119.0(3)
C(44)-C(61)-C(51)	123.8(3)
N(1)-C(63)-C(64)	106.5(3)
N(1)-C(63)-C(71)	101.3(2)
C(64)-C(63)-C(71)	115.0(3)
C(63)-C(64)-C(50)	114.1(3)
F(1)-B(1)-F(4)	118.2(7)
F(1)-B(1)-F(2)	120.5(6)
F(4)-B(1)-F(2)	104.8(5)
F(1)-B(1)-F(3)	104.8(5)
F(4)-B(1)-F(3)	93.0(7)
F(2)-B(1)-F(3)	112.3(6)
C(83)-C(68)-C(55)	121.1(4)
C(41)-C(69)-C(92)	114.3(4)
C(41)-C(69)-C(84)	106.9(4)
C(92)-C(69)-C(84)	110.4(4)
N(3)-C(71)-C(63)	100.5(2)
N(3)-C(71)-C(57)	105.4(3)
C(63)-C(71)-C(57)	116.4(3)
C(59)-C(72)-C(81)	119.9(4)
C(61)-C(79)-C(83)	121.3(4)
C(41)-C(81)-C(72)	121.0(5)
C(68)-C(83)-C(79)	120.4(4)
Cl(2)-C(86)-Cl(3)	111.8(3)
Cl(2)-C(86)-Cl(1)	111.7(3)
Cl(3)-C(86)-Cl(1)	109.4(3)
Cl(6)-C(94)-Cl(5)	109.5(5)
Cl(6)-C(94)-Cl(4)	108.8(5)
Cl(5)-C(94)-Cl(4)	109.4(5)

Symmetry transformations used to generate equivalent atoms:

Table S4. Anisotropic displacement parameters (A^2 x 10^3) The anisotropic displacement factor exponent takes the form: -2 pi^2 [h^2 a*^2 U11 + ... + 2 h k a* b* U12]

	U11	U22	U33	U23	U13	U12
Cu(1)	45(1)	44(1)	32(1)	4(1)	0(1)	1(1)
C(19)	43(1)	43(1)	35(1)	5(1)	-2(1)	1(1)
N(1)	51(1)	48(1)	32(1)	6(1)	0(1)	3(1)
N(2)	37(1)	43(1)	34(1)	5(1)	0(1)	4(1)
Cl(1)	184(2)	154(2)	90(1)	-6(1)	16(1)	-48(2)
C(24)	50(2)	61(2)	42(1)	4(1)	-5(1)	-4(1)
C(25)	40(1)	40(1)	36(1)	4(1)	-3(1)	-2(1)
N(3)	48(1)	60(1)	37(1)	4(1)	2(1)	4(1)
C(27)	44(1)	62(2)	42(1)	3(1)	-7(1)	1(1)
C(28)	44(1)	54(1)	33(1)	6(1)	-1(1)	5(1)
N(4)	45(1)	44(1)	34(1)	3(1)	-1(1)	6(1)
C(30)	45(1)	45(1)	36(1)	0(1)	-4(1)	6(1)
C(31)	41(1)	52(1)	34(1)	4(1)	1(1)	0(1)
C(32)	47(1)	51(2)	41(1)	2(1)	-8(1)	4(1)
Cl(4)	275(3)	107(1)	223(3)	10(1)	-157(3)	-20(2)
C(34)	43(1)	54(2)	47(2)	1(1)	-6(1)	9(1)
C(35)	39(1)	67(2)	55(2)	6(2)	3(1)	4(2)
C(36)	74(2)	54(2)	64(2)	9(2)	-8(2)	14(2)
C(37)	60(2)	57(2)	57(2)	12(1)	-11(2)	-12(2)
C(38)	42(1)	58(2)	47(1)	11(1)	1(1)	-3(1)
C(39)	64(2)	42(1)	45(1)	3(1)	-5(1)	6(1)
C(40)	59(2)	70(2)	65(2)	1(2)	8(2)	18(2)
C(41)	43(1)	80(2)	60(2)	2(2)	-8(1)	-6(2)
Cl(5)	476(7)	124(2)	139(2)	8(1)	-59(3)	-94(3)
C(43)	65(2)	53(2)	44(2)	7(1)	-5(1)	6(2)
C(44)	49(2)	53(2)	46(1)	6(1)	3(1)	15(1)
C(45)	47(2)	78(2)	72(2)	5(2)	-9(2)	19(2)
C(46)	100(3)	42(1)	49(2)	-3(1)	-8(2)	10(2)
C(47)	75(2)	68(2)	68(2)	12(2)	-8(2)	19(2)
Cl(2)	273(3)	100(1)	169(2)	-46(1)	-30(2)	28(2)

C(49)	69(2)	65(2)	82(3)	9(2)	-21(2)	24(2)
C(50)	83(2)	54(2)	53(2)	15(1)	1(2)	4(2)
C(51)	42(1)	73(2)	56(2)	11(2)	-6(1)	6(2)
C(52)	65(2)	41(1)	63(2)	1(1)	7(2)	0(1)
C(53)	43(1)	60(2)	51(2)	5(1)	4(1)	6(1)
C(54)	58(2)	94(3)	72(2)	4(2)	-2(2)	22(2)
C(55)	75(2)	55(2)	54(2)	5(1)	6(2)	21(2)
C(56)	45(2)	92(3)	62(2)	8(2)	-2(1)	2(2)
C(57)	90(3)	76(2)	47(2)	-10(2)	4(2)	23(2)
C(58)	90(3)	87(3)	60(2)	-6(2)	3(2)	36(2)
C(59)	69(2)	91(3)	108(4)	11(3)	0(2)	32(3)
C(60)	43(2)	93(3)	91(3)	13(2)	-5(2)	-9(2)
C(61)	50(2)	74(2)	59(2)	11(2)	-3(1)	16(2)
C(62)	43(2)	116(4)	93(3)	18(3)	-11(2)	-5(2)
C(63)	62(2)	63(2)	30(1)	8(1)	5(1)	-1(2)
C(64)	68(2)	69(2)	48(2)	15(2)	4(2)	-5(2)
C(65)	99(3)	90(3)	57(2)	24(2)	-9(2)	9(3)
B(1)	79(3)	113(4)	48(2)	-7(2)	-5(2)	-16(3)
C(67)	65(2)	94(3)	60(2)	5(2)	13(2)	16(2)
C(68)	122(4)	79(3)	77(3)	-9(2)	15(3)	43(3)
C(69)	53(2)	78(2)	67(2)	-4(2)	-2(2)	-15(2)
C(70)	68(2)	87(3)	65(2)	17(2)	-15(2)	8(2)
C(71)	64(2)	70(2)	38(1)	1(1)	7(1)	8(2)
C(72)	67(2)	108(4)	94(3)	12(3)	-23(2)	13(2)
C(73)	128(5)	82(3)	98(4)	25(3)	-22(3)	-24(3)
Cl(6)	145(2)	190(3)	477(8)	125(4)	46(3)	11(2)
C(75)	147(5)	79(3)	93(3)	-20(3)	-19(3)	40(4)
F(1)	203(5)	205(5)	94(2)	19(3)	-57(3)	-82(4)
C(77)	106(4)	93(3)	108(4)	52(3)	24(3)	4(3)
C(78)	91(3)	106(4)	109(4)	48(3)	13(3)	-23(3)
C(79)	76(3)	99(3)	90(3)	3(3)	-10(2)	46(3)
C(80)	76(3)	100(3)	106(4)	-43(3)	8(3)	-21(3)
C(81)	64(2)	101(3)	89(3)	7(3)	-25(2)	1(2)
C(82)	121(4)	53(2)	104(4)	22(2)	13(3)	-3(2)
C(83)	94(3)	109(4)	102(4)	0(3)	5(3)	61(3)
C(84)	133(5)	90(4)	131(5)	1(3)	39(4)	-41(4)
C(85)	184(6)	60(2)	85(3)	-3(2)	-44(4)	-11(3)
C(86)	92(3)	96(3)	78(3)	-8(2)	-12(2)	-2(3)

C(87)	158(6)	110(4)	77(3)	-41(3)	-11(4)	39(4)
F(2)	253(6)	171(4)	110(3)	55(3)	-20(3)	-66(4)
F(3)	138(3)	220(5)	162(4)	23(4)	17(3)	-43(4)
F(4)	380(11)	221(7)	166(5)	-73(5)	49(6)	15(8)
C(91)	119(4)	160(6)	89(4)	9(4)	37(3)	69(5)
C(92)	81(3)	152(5)	76(3)	-24(3)	-26(2)	2(3)
C(94)	166(7)	93(4)	123(5)	18(3)	-57(5)	-44(4)
Cl(3)	170(2)	116(1)	76(1)	-7(1)	-31(1)	8(1)

—

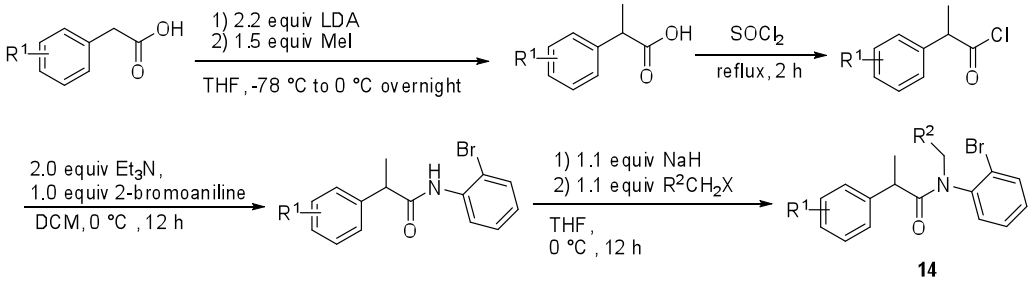
Table S5. Hydrogen coordinates (x 10^4) and isotropic displacement parameters (A^2 x 10^3).

	x	y	z	U(eq)
H(63)	7611	-40	3315	59
H(64)	7930	326	2870	59
H(71)	6545	-1028	2964	52
H(72)	5680	389	3011	51
H(3)	4624	2472	1650	77
H(75)	5563	-627	1029	70
H(65)	4487	-733	3022	59
H(66)	4699	-868	2532	59
H(4)	2374	1144	2255	79
H(76)	6411	-1317	1655	77
H(5)	4281	2376	399	84
H(6)	2786	2164	1812	86
H(77)	7012	1347	1898	67
H(7)	2911	1789	805	90
H(8)	3102	515	1038	80
H(67)	7734	-1029	278	85
H(68)	8394	-819	-140	85
H(9)	10892	-1762	923	108
H(57)	2972	-705	2204	113
H(58)	2060	-137	2393	113
H(59)	2501	-851	2665	113

H(60)	9834	112	3263	126
H(61)	9891	119	2762	126
H(62)	10491	-553	3021	126
H(73)	6914	315	-58	62
H(69)	7824	1545	-99	74
H(70)	7820	1617	400	74
H(15)	6276	2070	-518	123
H(16)	5063	2025	-328	123
H(17)	5752	1248	-401	123
H(18)	2933	40	3252	109
H(19)	2598	807	3000	109
H(20)	3798	730	3198	109
H(10)	8691	-2631	1666	111
H(78)	8613	1026	1401	79
H(21)	9356	-1641	3363	110
H(22)	8053	-1554	3385	110
H(23)	8820	-965	3638	110
H(74)	9013	389	174	68
H(11)	11424	-1329	1578	107
H(24)	5149	-2216	1848	154
H(25)	5936	-2150	2248	154
H(26)	6055	-2868	1933	154
H(27)	8527	-2218	491	160
H(28)	9816	-2379	462	160
H(29)	9109	-2276	43	160
H(30)	6344	2073	1270	153
H(31)	7546	2284	1435	153
H(32)	6535	2838	1545	153
H(33)	3286	-676	1257	153
H(34)	4252	-430	1569	153
H(35)	4181	-1301	1398	153
H(12)	10203	-1781	2708	106
H(36)	6466	2764	2331	141
H(37)	7661	2384	2315	141
H(38)	6696	1959	2565	141
H(13)	10790	-125	1830	102
H(39)	7017	2954	53	139
H(40)	6720	2786	533	139

H(41)	5775	3021	210	139
H(14)	10186	-2615	2121	122
H(42)	10885	1480	1336	177
H(43)	9847	2013	1232	177
H(44)	10161	1309	928	177
H(45)	4896	-1526	582	164
H(46)	4874	-751	307	16
H(47)	3768	-1071	513	164
H(1)	1822	243	-720	107
H(48)	7322	-2661	1255	173
H(49)	7326	-1797	1073	173
H(50)	6200	-2269	1105	173
H(51)	10271	-1180	-232	184
H(52)	11075	-1296	159	184
H(53)	10576	-458	61	184
H(54)	8928	846	2112	155
H(55)	9476	1664	2004	155
H(56)	10227	910	2056	155
H(2)	7879	-1019	-1079	153

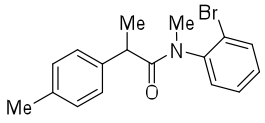
Synthesis of Amides **14**[1,2,3]



The 2-methyl-arylacetic acid derivatives the acids were prepared according to literature.[7] The acid (1.0 eq.) was refluxed with 2.0 eq. $SOCl_2$ for 2 hours. After evaporation of excess $SOCl_2$, the resulting acyl chloride was diluted with CH_2Cl_2. Then the mixture was cooled to 0 ˚C before the addition of 2.0 eq. NEt_3 and 1.0 eq. arylamine. The mixture was allowed to increase to room temperature stirred for 12 hours. The *N*-H amide was purified by flash chromatography. The amide in THF was dropped to a suspension of 1.1 eq. NaH in THF at 0 ˚C and the micxture was

stirred for 1 h at room temperature, followed by the addition of 1.1 eq. MeI or benzylbromide at 0 ˚C. Stirring was continued for 12 h at room temperature. The product was purified by flash chromatography to give **14**.

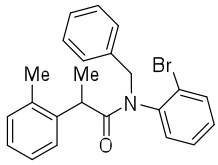
14b



14b

70% yield. ^{1}H NMR δ 7.69 (d, *J* = 7.6 Hz, 0.70H), 7.59 (d, *J* = 8.0 Hz, 0.27H), 7.39-7.46 (m, 0.26H), 7.35 (dd, *J* = 8.0, 1.6 Hz, 0.29H), 7.11-7.31 (m, 2.03H), 7.00 (d, *J* = 8.0 Hz, 1.97H), 6.92 (d, *J* = 8.0 Hz, 0.55H), 6.85 (d, *J* = 8.0 Hz, 1.50H), 6.75 (dd, *J* = 7.6, 1.6 Hz, 0.76H), 3.48 (q, *J* = 6.8 Hz, 0.28H), 3.30 (q, *J* = 6.8 Hz, 0.82H), 3.18 (s, 0.80H), 3.16 (s, 2.30H), 2.25-2.32 (m, 3.00H), 1.36-1.46 (m, 3.13H); ^{13}C NMR δ 174.1, 173.9, 142.6, 142.3, 138.6, 137.6, 136.20, 136.19, 134.0, 133.5, 130.9, 130.0, 129.7, 129.6, 129.0, 128.8, 128.6, 128.4, 127.9, 127.3, 124.1, 123.6, 43.5, 42.7, 36.10, 36.06, 21.00, 20.97, 20.63, 20.59; IR (KBr) 1654, 1513, 1477, 1379, 1283, 1254, 1124, 1050, 828, 772, 730 cm^{-1}; HRMS(ESI): Calcd for $C_{17}H_{19}BrNO$ ([M+H]$^{+}$): 332.0645. Found m/z 332.0649.

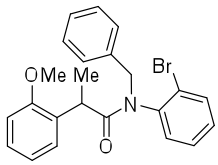
14d



14d

79% yield. ^{1}H NMR δ 7.63-7.69 (m, 0.81H), 7.45-7.51 (m, 0.28H), 7.37 (d, *J* = 7.6 Hz, 0.91H), 7.00-7.26 (m, 7.68H), 6.93 (d, *J* = 7.2 Hz, 0.14H), 6.74-6.89 (m, 1.71H), 5.75-5.84 (m, 0.95H), 5.68 (d, *J* = 14.4 Hz, 0.84H), 3.93 (dd, *J* = 14.4, 1.2 Hz, 1.01 H), 3.76-3.84 (m, 0.15H), 3.47-3.56 (m, 0.88H), 1.30-1.50 (m, 6.00H); ^{13}C NMR δ 173.8, 173.7, 140.3, 140.0, 139.9, 138.8, 137.1, 137.0, 135.0, 134.8, 134.0, 133.2, 132.2, 132.1, 130.0, 129.8, 129.4, 129.3, 129.0, 128.25, 128.16, 127.9, 127.6, 127.4, 127.3, 126.5, 126.4, 126.3, 126.2, 124.4, 124.2, 51.6, 51.2, 40.5, 39.1, 20.1, 19.2, 18.2, 18.1; IR (neat) 1667, 1475, 1389, 1270, 1245, 1205, 1030, 762, 727, 699 cm^{-1}; HRMS(ESI): Calcd for $C_{23}H_{23}BrNO$ ([M+H]$^{+}$): 408.0958. Found m/z 408.0956.

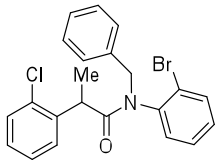
14f



14f

85% yield. ^{1}H NMR δ 7.65 (dd, *J* = 8.0, 0.8 Hz, 0.76H), 7.46-7.52 (m, 0.38H), 7.33 (dd, *J* = 7.6, 1.6 Hz, 0.80H), 7.04-7.27 (m, 7.15H), 6.76-6.93 (m, 2.01H), 6.63 (d, *J* = 8.0 Hz, 0.20H), 6.57 (d, *J* = 8.4 Hz, 0.79H), 6.00 (dd, *J* = 7.6, 1.2 Hz, 0.77H), 5.74 (d, *J* = 14.4 Hz, 0.21H), 5.67 (d, *J* = 14.4 Hz, 0.82H), 4.14 (q, *J* = 7.2 Hz, 0.23H), 3.82-3.99 (m, 1.86H), 1.33-1.38 (m, 3.00H); ^{13}C NMR δ 174.5, 155.6, 140.1, 137.3, 133.4, 133.1, 132.2, 132.0, 130.2, 129.3, 129.1, 129.0, 128.8, 128.2, 128.1, 127.62, 127.59, 127.3, 127.20, 127.18, 124.2, 120.7, 120.5, 109.6, 109.4, 54.6, 51.6, 51.2, 36.6, 34.5, 19.8, 18.7; IR (neat) 1661, 1493, 1475, 1390, 1246, 1030, 754, 727 cm^{-1}; HRMS(ESI): Calcd for $C_{23}H_{23}BrNO_2$ ([M+H]$^{+}$): 424.0907. Found m/z 424.0902.

14h



14h

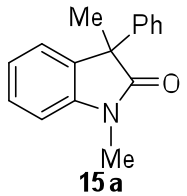
83% yield. ^{1}H NMR δ 7.63-7.70 (m, 0.90H), 7.45-7.54 (m, 0.93H), 7.02-7.29 (m, 9.00H), 6.79-6.87 (m, 1.09H), 5.86 (dd, *J* = 7.6, 1.6 Hz, 0.76H), 5.76 (d, *J* = 14.0 Hz, 0.24H), 5.66 (d, *J* = 14.4 Hz, 0.80H), 4.15 (q, *J* = 6.8 Hz, 0.22H), 3.84-4.01 (m, 1.76H), 1.34-1.42 (m, 3.00H); ^{13}C NMR δ 173.2, 139.55, 139.48, 137.0, 134.1, 133.5, 133.4, 132.0, 131.6, 129.6, 129.4, 129.3, 129.1, 128.9, 128.3, 128.2, 128.1, 127.84, 127.77, 127.5, 127.4, 127.2, 127.0, 124.1, 51.8, 51.4, 40.9, 39.2, 20.0, 18.9; IR (neat) 1667, 1475, 1394, 1270, 1032, 753, 726 cm^{-1}; HRMS(ESI): Calcd for $C_{22}H_{20}BrClNO$ ([M+H]$^{+}$): 428.0411. Found m/z 428.0407.

Catalytic asymmetric intramolecular α-arylation reactions

General procedure: In an N_2-filled glove-box, TMEDA·$PdMe_2$ (2.5 mg, 0.01 mmol, 5 mol %), **6b** (5.0 mg, 0.01 mmol, 5 mol %), ^{t}BuONa (29 mg, 0.3 mmol, 1.5 equiv), amide **14a** (63.6mg, 0.2 mmol, 1.0 equiv), and toluene (2 mL), were added to an oven-dried Schlenk tube containing a stirrer bar. The tube was sealed and taken out of

the glove box. After being heated at 50 ˚C for 20 h, the reaction mixture was cooled to room temperature. The solvent were evaporated under vacuum and the residue was purified by preparative thin layer chromatography (hexane/ethyl acetate 5:1) on silica gel to give **15a** (47.1 mg, 0.199 mmol, 99% yield).

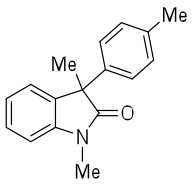
15a



15a

^{1}H NMR δ 7.17-7.35 (m, 7H), 7.09 (td, *J* = 7.6, 0.8 Hz, 1H), 6.91 (d, *J* = 8.0 Hz, 1H), 3.24 (s, 3H), 1.79 (s, 3H); ^{13}C NMR δ 179.4, 143.2, 140.7, 134.7, 128.5, 128.0, 127.1, 126.6, 124.1, 122.7, 108.2, 52.1, 26.4, 23.7; HPLC [(Daicel Chiralcel OD-H, hexane/*i*-PrOH = 95/5, flow rate = 1.0 mL/min, λ = 254 nm): *t*1 = 14.2 min (major), *t*2 = 16.9 min (minor) ee = 86%].

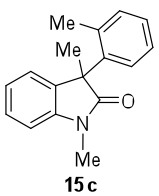
15b



15b

^{1}H NMR δ 7.33 (t, *J* = 7.6 Hz, 1H), 7.16-7.25 (m, 3H), 7.07-7.15 (m, 3H), 6.92 (d, *J* = 8.0 Hz, 1H), 3.25 (s, 3H), 2.31 (s, 3H), 1.79 (s, 3H); ^{13}C NMR δ 179.5, 143.2, 137.8, 136.8, 134.9, 129.2, 128.0, 126.4, 124.1, 122.7, 108.2, 51.8, 26.4, 23.7, 20.9; [(Daicel Chiralcel AD-H, hexane/*i*-PrOH = 95/5, flow rate = 1.0 mL/min, λ = 254 nm): *t*1 = 14.4 min (major), *t*2 = 18.7 min (minor) ee = 84%].

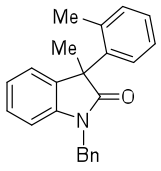
15c



15c

^{1}H NMR δ 7.63-7.70 (m, 1H), 7.25-7.34 (m, 2H), 7.20 (td, *J* = 7.6, 1.2 Hz, 1H), 7.04 (d, *J* = 7.2 Hz, 1H), 6.99 (td, *J* = 7.6, 1.2 Hz, 1H), 6.92 (d, *J* = 7.6 Hz, 1H), 6.83-6.89 (m, 1H), 3.33 (s, 3H), 1.78 (s, 3H), 1.62 (s, 3H); ^{13}C NMR δ 180.0, 142.9, 137.8, 136.8, 135.0, 131.6, 127.7, 127.6, 127.4, 126.0, 122.9, 122.8, 108.0, 52.3, 26.4, 25.7, 19.1; [(Daicel Chiralcel OD-H, hexane/*i*-PrOH = 98/2, flow rate = 1.0 mL/min, λ = 254 nm): *t*1 = 20.7 min (major), *t*2 = 32.3 min (minor) ee = 96%].

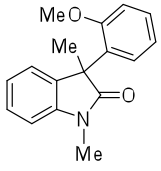
15d



15 d

^{1}H NMR δ 7.68 (d, *J* = 7.6 Hz, 1H), 7.39-7.45 (m, 2H), 7.25-7.39 (m, 4H), 7.15-7.25 (m, 2H), 7.04 (d, *J* = 7.6 Hz, 1H), 6.96 (t, *J* = 7.6 Hz, 1H), 6.82-6.92 (m, 2H), 5.24 (d, *J* = 15.2 Hz, 1H), 4.80 (d, *J* = 15.6 Hz, 1H), 1.84 (s, 3H), 1.61 (s, 3H); ^{13}C NMR δ 180.0, 142.1, 137.7, 137.0, 136.1, 135.2, 131.7, 128.8, 127.81, 127.78, 127.75, 127.69, 127.6, 126.0, 122.97, 122.96, 109.1, 52.5, 44.1, 26.3, 19.5; IR (neat) 1714, 1611, 1486, 1464, 1343, 1173, 752, 745 cm^{-1}; HRMS(ESI): Calcd for $C_{23}H_{22}NO$ ($[M+H]^+$): 328.1696. Found m/z 328.1704; $[\alpha]_D^{25}$ = +76.1 (*c* = 2.3 in $CHCl_3$). [(Daicel Chiralcel OD-H, hexane/*i*-PrOH = 98/2, flow rate = 1.0 mL/min, λ = 254 nm): *t*1 = 20.9 min (major), *t*2 = 31.0 min (minor) ee = 98%].

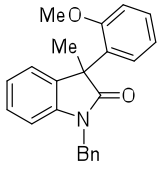
15e



15 e

^{1}H NMR δ 7.59 (dd, *J* = 8.0, 1.6 Hz, 1H), 7.25-7.30 (m, 2H), 7.05 (td, *J* = 7.6, 1.2 Hz, 1H), 6.93 (td, *J* = 7.6, 1.2 Hz, 1H), 6.83-6.92 (m, 2H), 6.76 (dd, *J* = 8.0, 1.2 Hz, 1H), 3.41 (s, 3H), 3.32 (s, 3H), 1.71 (s, 3H); ^{13}C NMR δ 181.0, 156.9, 143.5, 135.6, 129.7, 128.7, 127.5, 127.2, 122.13, 122.10, 120.8, 112.0, 107.3, 55.8, 49.8, 26.3, 23.3. [(Daicel Chiralcel OD-H, hexane/*i*-PrOH = 90/10, flow rate = 1.0 mL/min, λ = 254 nm): *t*1 = 11.9 min (major), *t*2 = 26.3 min (minor) ee = 92%].

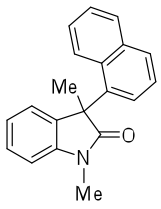
15f



15f

^{1}H NMR δ 7.63 (dd, *J* = 7.6, 1.6 Hz, 1H), 7.44-7.52 (m, 2H), 7.25-7.40 (m, 4H), 7.13 (td, *J* = 8.0, 1.6 Hz, 1H), 7.07 (td, *J* = 7.6, 1.2 Hz, 1H), 6.90 (td, *J* = 7.6, 1.2 Hz, 1H), 6.80-6.87 (m, 2H), 6.76 (td, *J* = 8.0, 1.2 Hz, 1H), 5.01 (s, 2H), 3.22 (s, 3H), 1.77 (s, 3H); ^{13}C NMR δ 180.6, 157.0, 142.5, 136.6, 135.9, 129.3, 128.8, 128.6, 127.9, 127.7, 127.4, 127.1, 122.10, 122.07, 120.7, 111.8, 108.3, 55.4, 49.9, 44.0, 24.0; IR (KBr) 1710, 1611, 1470, 1341, 1174, 1081, 912, 883, 750 cm^{-1}; HRMS(ESI): Calcd for $C_{23}H_{22}NO_2$ ([M+H]$^+$): 344.1645. Found m/z 344.1652; $[\alpha]_D^{25}$ = +76.1 (*c* = 2.3 in $CHCl_3$). [(Daicel Chiralcel OD-H, hexane/*i*-PrOH = 90/10, flow rate = 1.0 mL/min, λ = 254 nm): *t*1 = 12.8 min (major), *t*2 = 19.9 min (minor) ee = 94%].

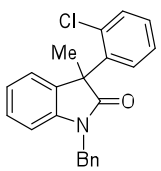
15g



15g

^{1}H NMR δ 7.76-7.94 (m, 3H), 7.56 (t, *J* = 7.6 Hz, 1H), 7.28-7.40 (m, 2H), 7.13-7.24 (m, 1H), 7.06 (d, *J* = 8.0 Hz, 1H), 6.88-6.99 (m, 2H), 6.80-6.88 (m, 1H), 3.45 (s, 3H), 1.92 (s, 3H); ^{13}C NMR δ 180.4, 142.2, 136.7, 135.1, 134.3, 131.3, 129.1, 129.0, 127.9, 126.2, 125.2, 125.0, 123.4, 123.0, 122.8, 108.6, 52.4, 26.8, 26.7. [(Daicel Chiralcel AD-H, hexane/*i*-PrOH = 95/5, flow rate = 1.0 mL/min, λ = 254 nm): *t*1 = 17.0 min (major), *t*2 = 32.9 min (minor) ee = 97%].

15h



15h

^{1}H NMR δ 7.72-7.78 (m, 1H), 7.23-7.48 (m, 8H), 7.18 (td, *J* = 7.6, 1.2 Hz, 1H), 6.95 (td, *J* = 7.2, 1.2 Hz, 1H), 6.80-6.87 (m, 2H), 5.22 (d, *J* = 15.2 Hz, 1H), 4.82 (d, *J* = 15.6 Hz, 1H), 1.84 (s, 3H); ^{13}C NMR δ 179.2, 142.8, 137.5, 136.0, 134.4, 134.0, 130.7, 129.3, 129.0, 128.6, 127.8, 127.7, 127.6, 126.8, 122.6, 122.3, 109.1, 52.3, 44.3, 25.7; IR (KBr) 1720, 1611, 1480, 1341, 1174, 1081, 750 cm^{-1}; HRMS(ESI): Calcd for $C_{22}H_{19}ONCl$ ([M+H]$^{+}$): 348.1150. Found m/z 348.1155.; $[\alpha]_D^{25}$ = +80.0 (*c* = 0.5 in $CHCl_3$). [(Daicel Chiralcel OD-H, hexane/*i*-PrOH = 90/10, flow rate = 1.0 mL/min, λ = 254 nm): *t*1 = 12.8 min (major), *t*2 = 19.0 min (minor) ee = 97%].

References

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4. A. M.Taylor, R. A. Altman, S. L. Buchwald, *J. Am. Chem. Soc.* **2009**, *131*, 9900.
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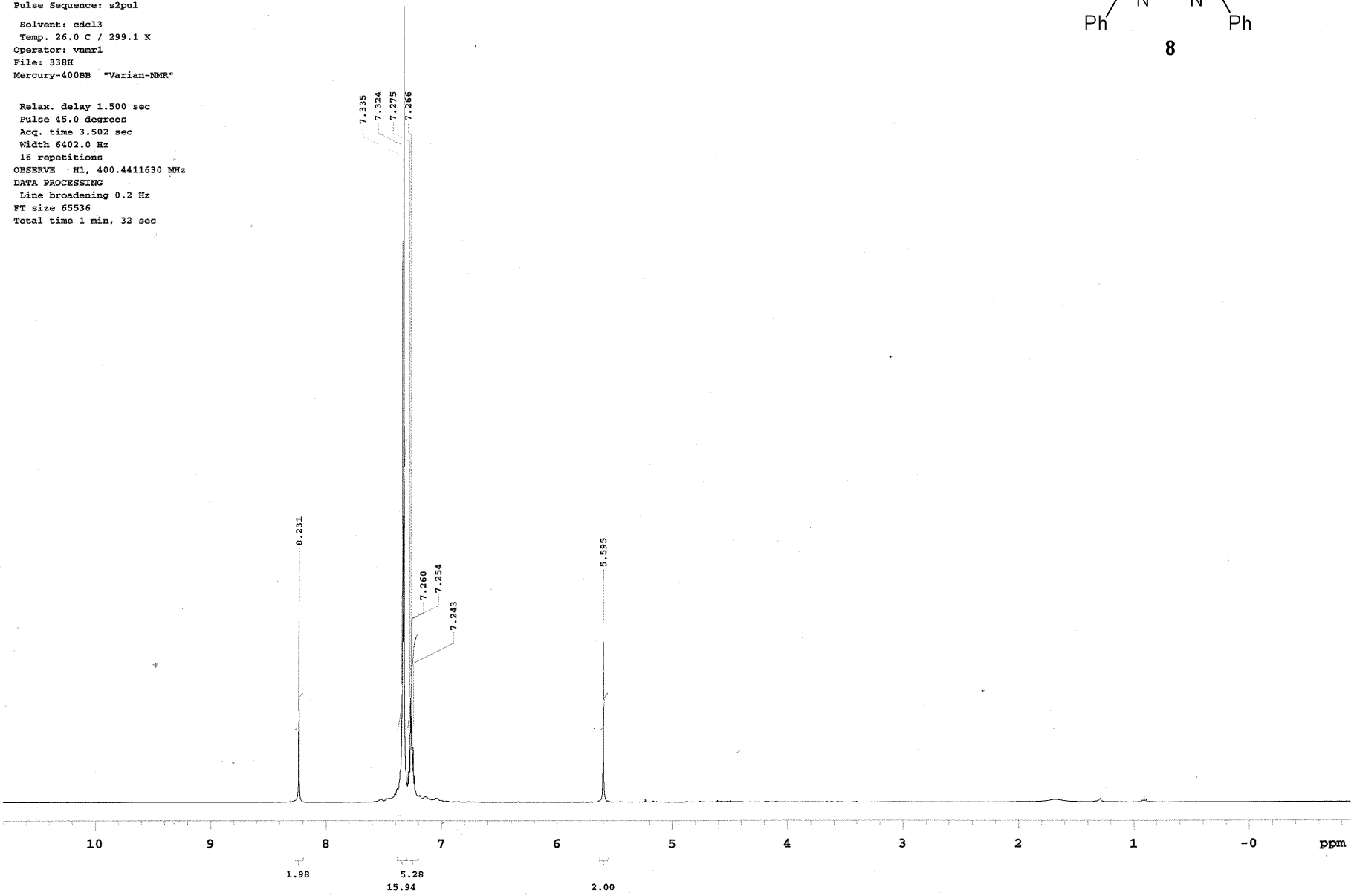
338H

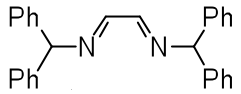
File: home/vnmr1/vnmrsys/data/murakami_lab/LIULT/338H.fid

Pulse Sequence: s2pul

Solvent: cdcl3
Temp. 26.0 C / 299.1 K
Operator: vnmr1
File: 338H
Mercury-400BB "Varian-NMR"

Relax. delay 1.500 sec
Pulse 45.0 degrees
Acq. time 3.502 sec
Width 6402.0 Hz
16 repetitions
OBSERVE H1, 400.4411630 MHz
DATA PROCESSING
Line broadening 0.2 Hz
FT size 65536
Total time 1 min, 32 sec





8

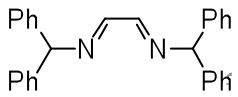
338C

File: home/vnmr1/vnmrsys/data/murakami_lab/LIULT/338c.fid

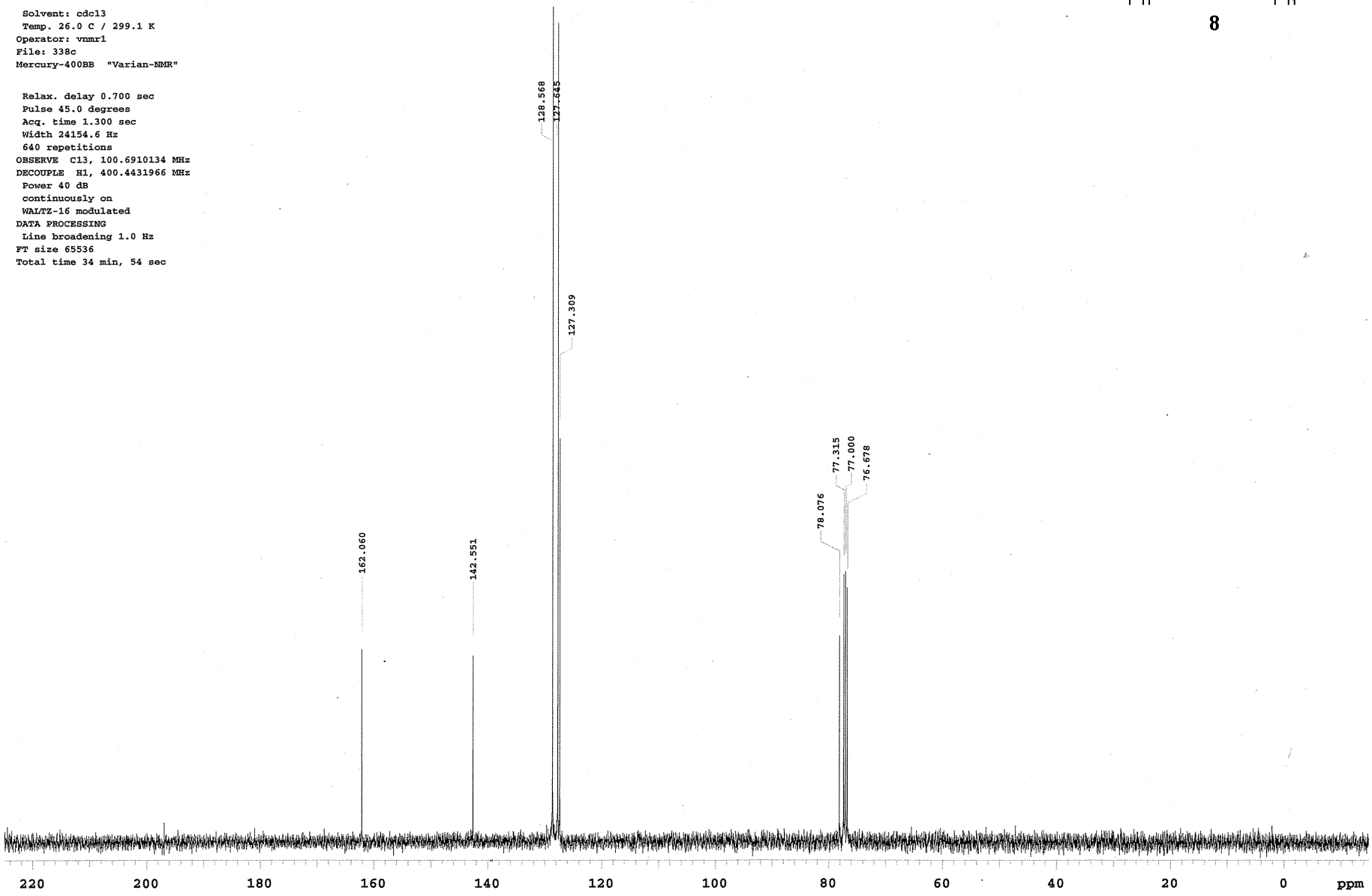
Pulse Sequence: s2pul

Solvent: cdcl3
Temp. 26.0 C / 299.1 K
Operator: vnmr1
File: 338c
Mercury-400BB "Varian-NMR"

Relax. delay 0.700 sec
Pulse 45.0 degrees
Acq. time 1.300 sec
Width 24154.6 Hz
640 repetitions
OBSERVE C13, 100.6910134 MHz
DECOUPLE H1, 400.4431966 MHz
Power 40 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 1.0 Hz
FT size 65536
Total time 34 min, 54 sec



8



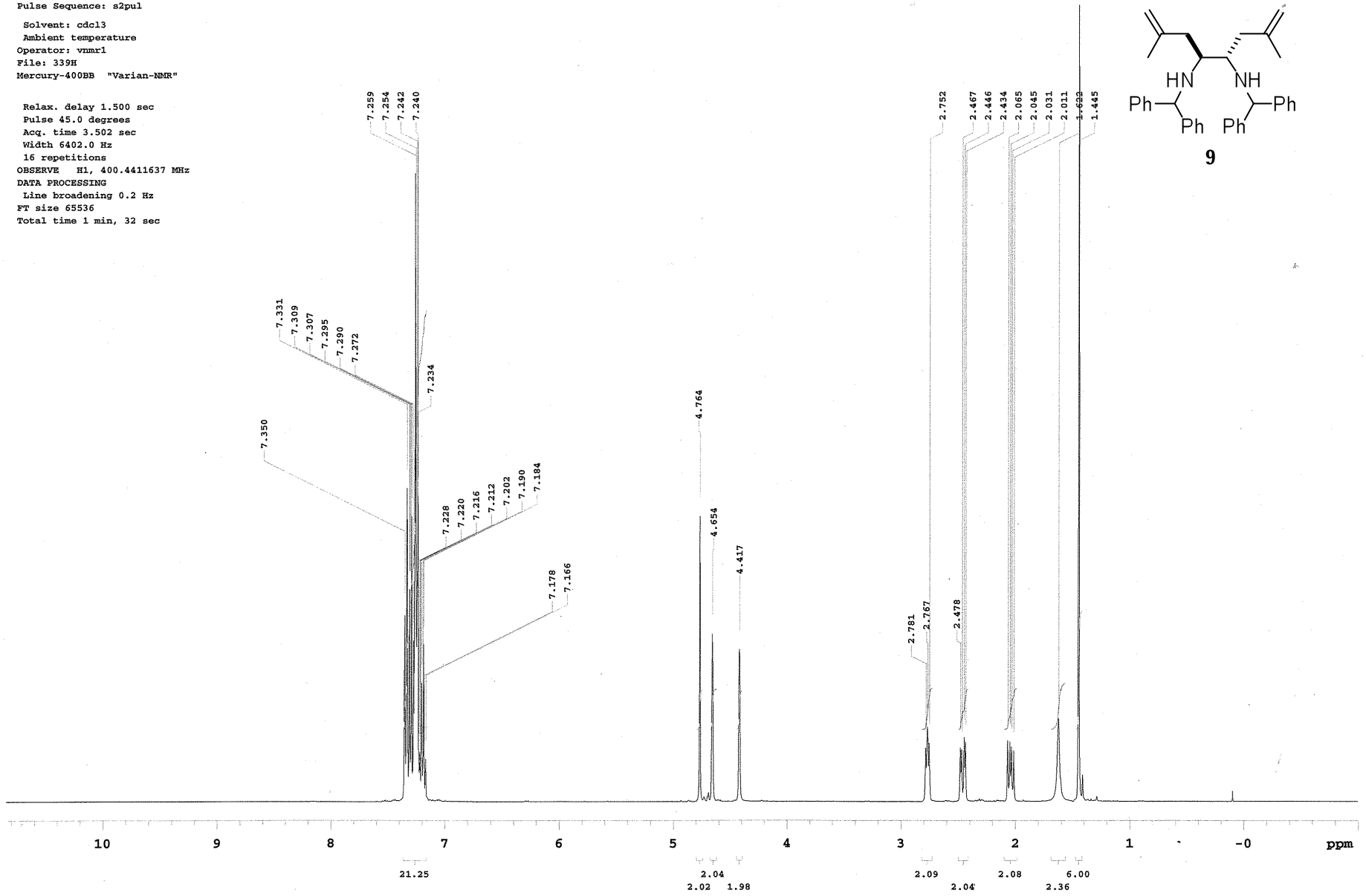
339h

File: home/vnmr1/vnmrsys/data/murakami_lab/LIULT/339H.fid

Pulse Sequence: s2pul

Solvent: cdcl3
Ambient temperature
Operator: vnmr1
File: 339H
Mercury-400BB "Varian-NMR"

Relax. delay 1.500 sec
Pulse 45.0 degrees
Acq. time 3.502 sec
Width 6402.0 Hz
16 repetitions
OBSERVE H1, 400.4411637 MHz
DATA PROCESSING
Line broadening 0.2 Hz
FT size 65536
Total time 1 min, 32 sec



9

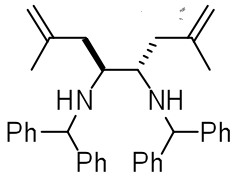
339c

File: home/vnmr1/vnmrsys/data/murakami_lab/LIULT/339c.fid

Pulse Sequence: s2pul

Solvent: cdcl3
Ambient temperature
Operator: vnmr1
File: 339c
Mercury-400BB "Varian-NMR"

Relax. delay 0.700 sec
Pulse 45.0 degrees
Acq. time 1.300 sec
Width 24154.6 Hz
512 repetitions
OBSERVE C13, 100.6910157 MHz
DECOUPLE H1, 400.4431966 MHz
Power 40 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 1.0 Hz
FT size 65536
Total time 17 min, 51 sec



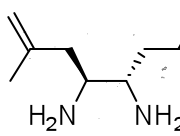
9

STANDARD 1H OBSERVE

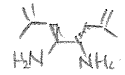
Pulse Sequence: s2pul

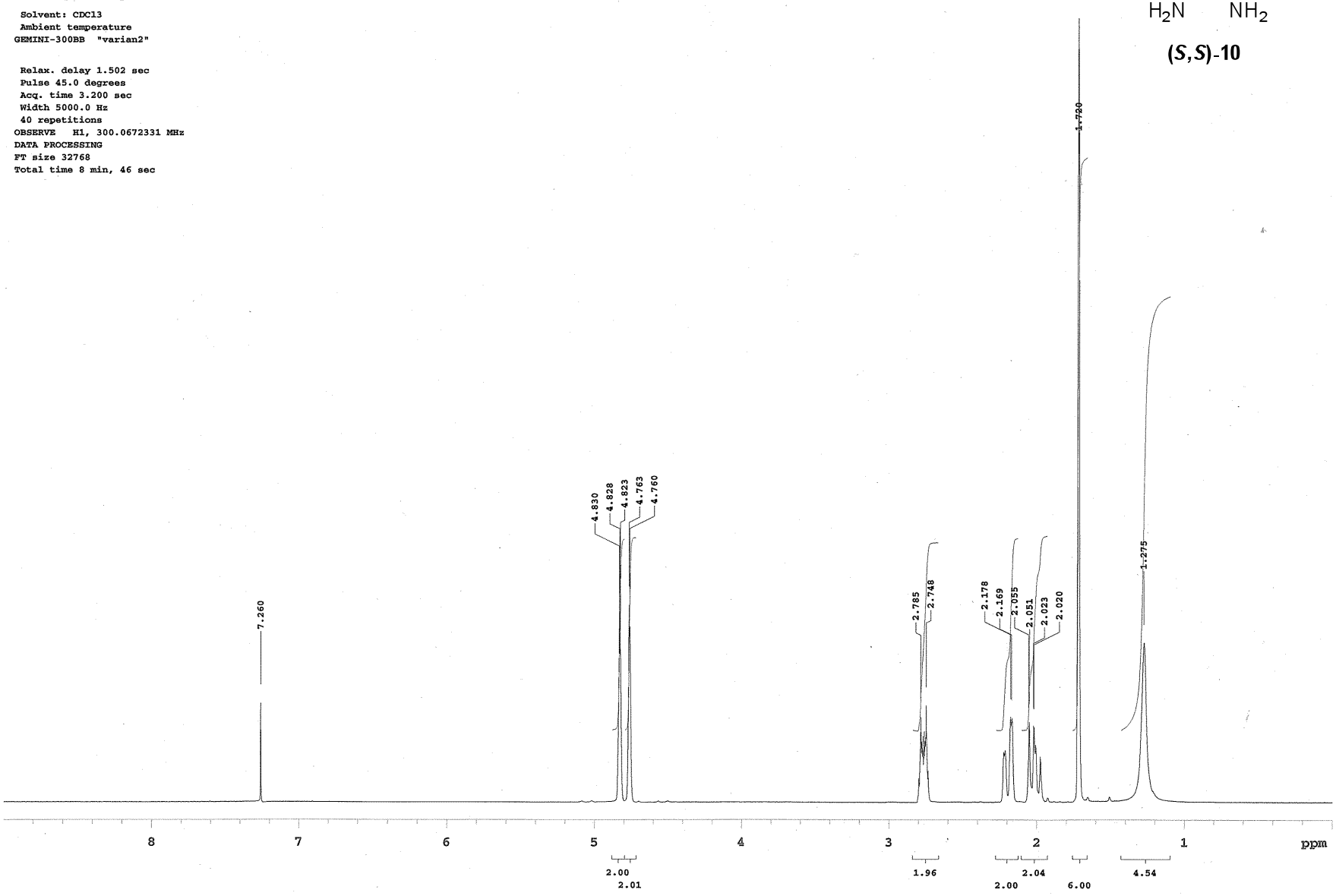
Solvent: CDCl3
Ambient temperature
GEMINI-300BB "varian2"

Relax. delay 1.502 sec
Pulse 45.0 degrees
Acq. time 3.200 sec
Width 5000.0 Hz
40 repetitions
OBSERVE H1, 300.0672331 MHz
DATA PROCESSING
FT size 32768
Total time 8 min, 46 sec



(*S*,*S*)-10

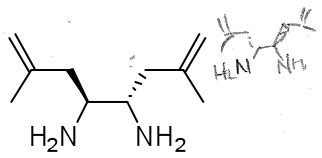




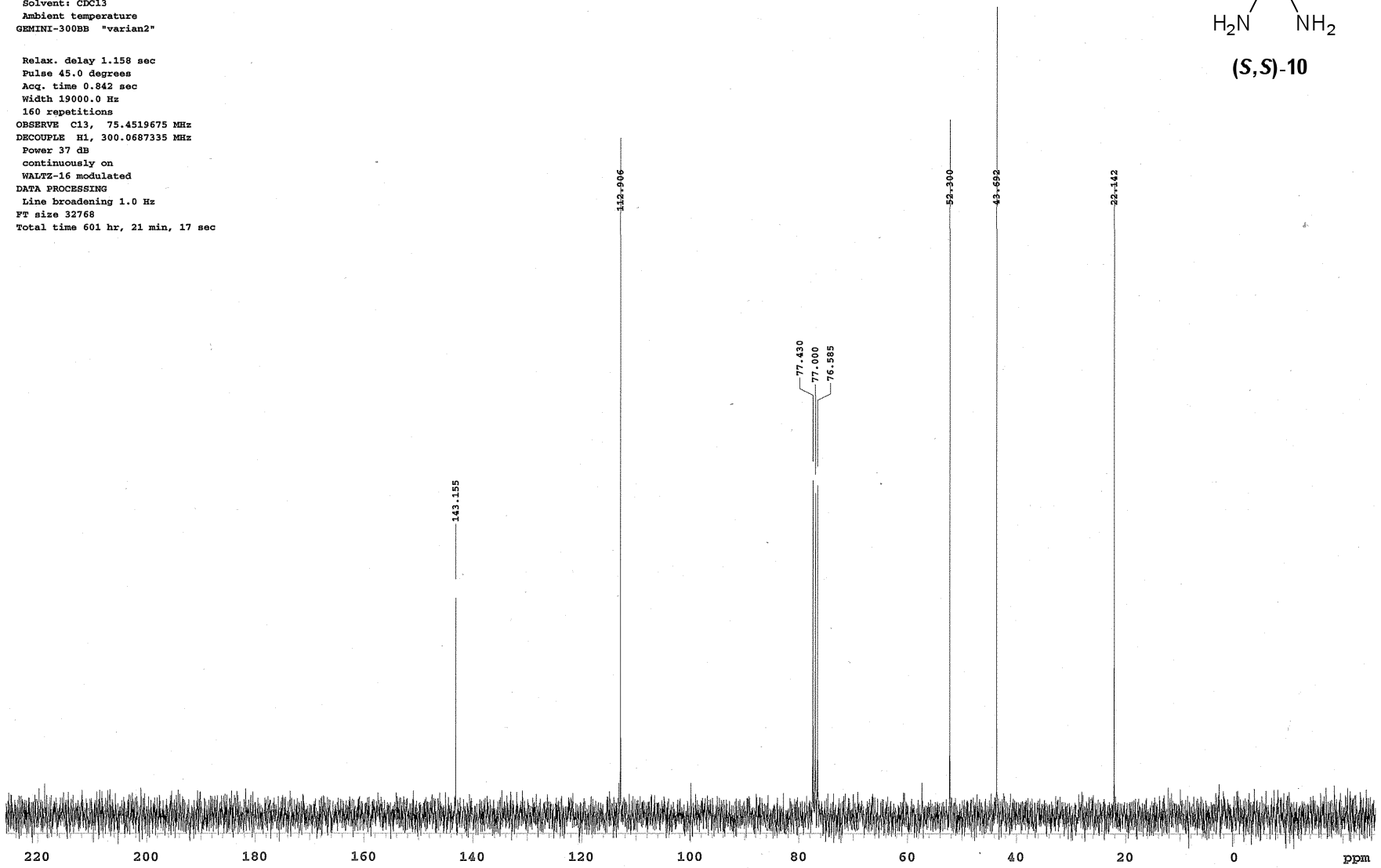
13C OBSERVE

Pulse Sequence: s2pul
Solvent: CDCl3
Ambient temperature
GEMINI-300BB "varian2"

Relax. delay 1.158 sec
Pulse 45.0 degrees
Acq. time 0.842 sec
Width 19000.0 Hz
160 repetitions
OBSERVE C13, 75.4519675 MHz
DECOUPLE H1, 300.0687335 MHz
Power 37 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 1.0 Hz
FT size 32768
Total time 601 hr, 21 min, 17 sec



(*S*,*S*)-10



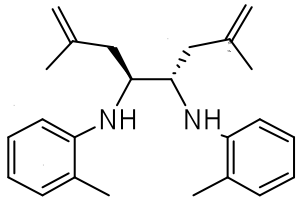
336H

File: home/vnmr1/vnmrsys/data/murakami_lab/LIULT/336H.fid

Pulse Sequence: s2pul

Solvent: cdcl3
Temp. 26.0 C / 299.1 K
Operator: vnmr1
File: 336H
Mercury-400BB "Varian-NMR"

Relax. delay 1.500 sec
Pulse 45.0 degrees
Acq. time 3.502 sec
Width 6402.0 Hz
16 repetitions
OBSERVE H1, 400.4411626 MHz
DATA PROCESSING
Line broadening 0.2 Hz
FT size 65536
Total time 1 min, 32 sec



11a

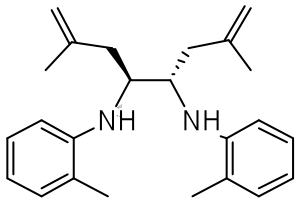
336C

File: home/vnmr1/vnmrsys/data/murakami_lab/LIULT/336c.fid

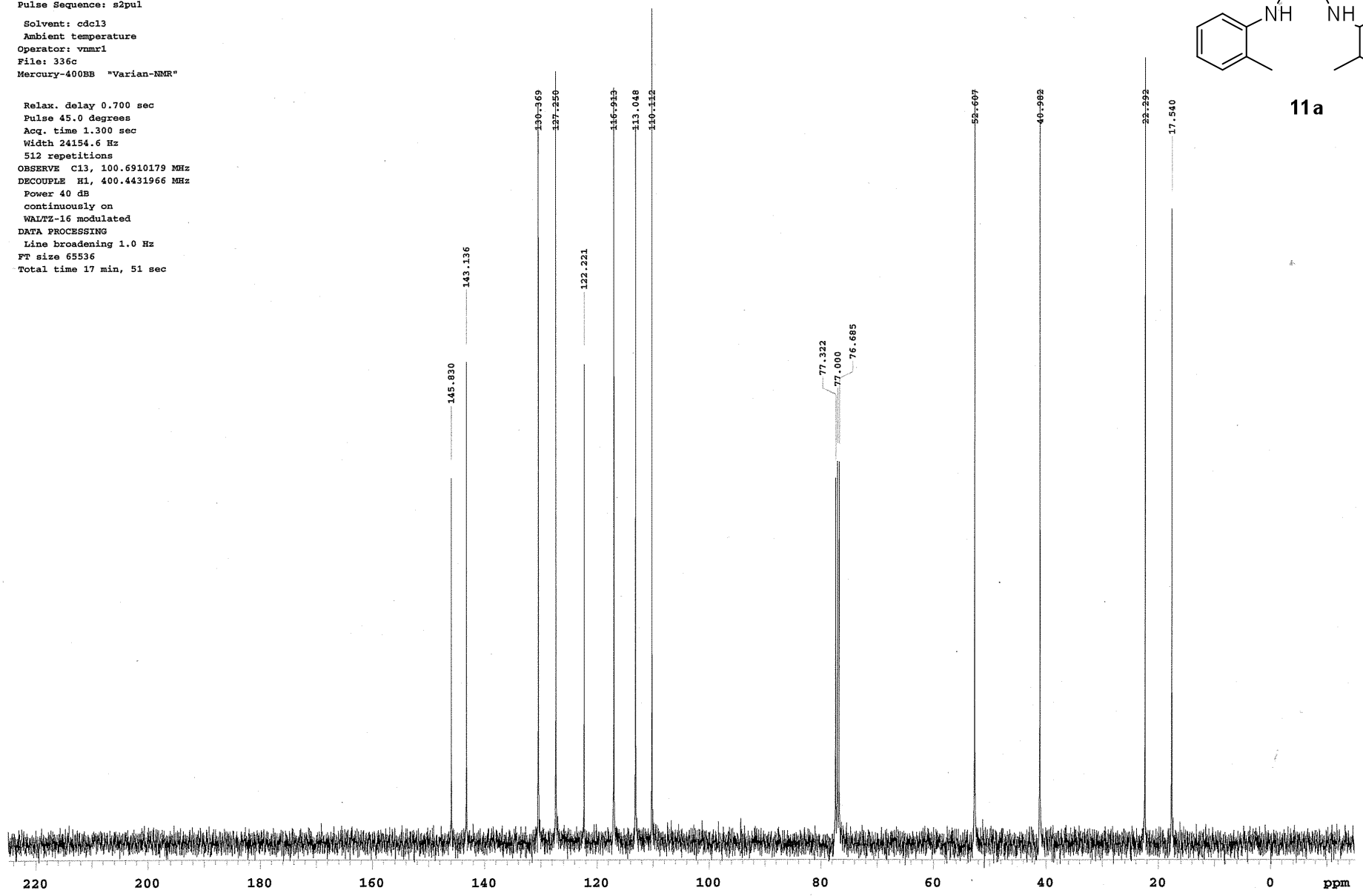
Pulse Sequence: s2pul

Solvent: cdcl3
Ambient temperature
Operator: vnmr1
File: 336c
Mercury-400BB "Varian-NMR"

Relax. delay 0.700 sec
Pulse 45.0 degrees
Acq. time 1.300 sec
Width 24154.6 Hz
512 repetitions
OBSERVE C13, 100.6910179 MHz
DECOUPLE H1, 400.4431966 MHz
Power 40 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 1.0 Hz
FT size 65536
Total time 17 min, 51 sec



11a



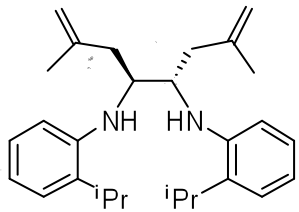
264h

File: xp

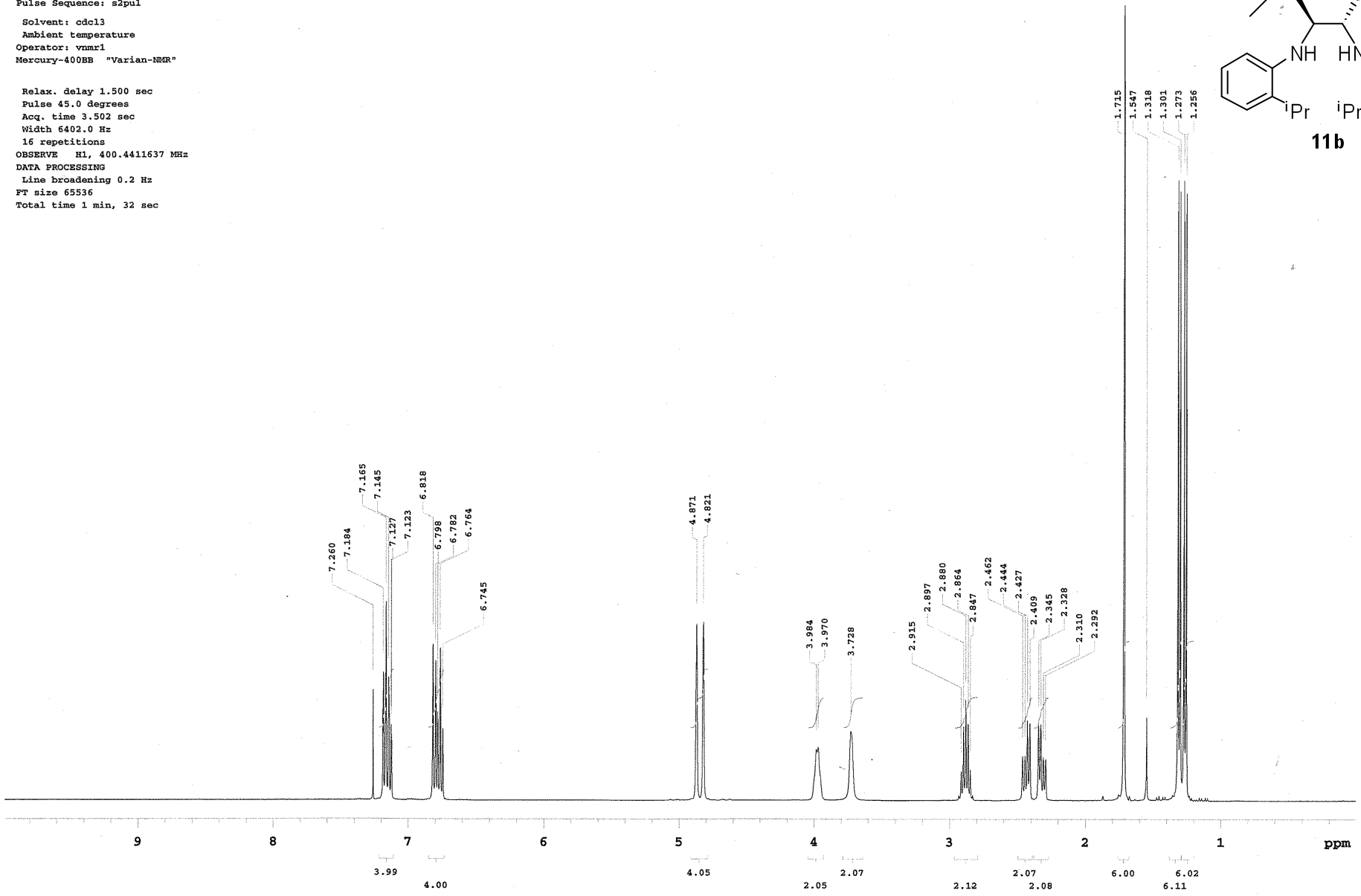
Pulse Sequence: s2pul

Solvent: cdcl3
Ambient temperature
Operator: vnmr1
Mercury-400BB "Varian-NMR"

Relax. delay 1.500 sec
Pulse 45.0 degrees
Acq. time 3.502 sec
Width 6402.0 Hz
16 repetitions
OBSERVE H1, 400.4411637 MHz
DATA PROCESSING
Line broadening 0.2 Hz
FT size 65536
Total time 1 min, 32 sec



11b



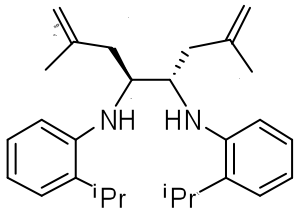
264c

File: xp

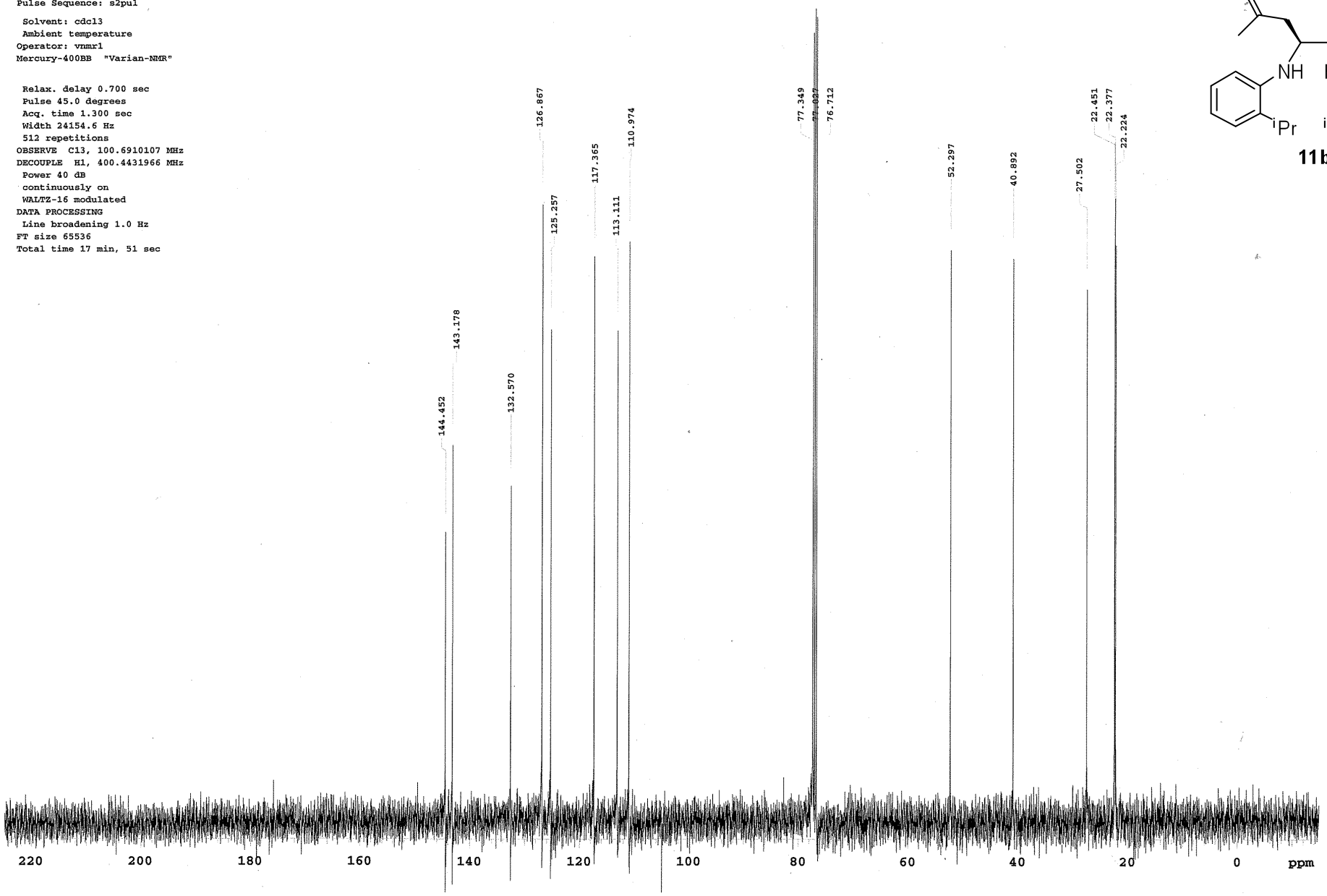
Pulse Sequence: s2pul

Solvent: cdcl3
Ambient temperature
Operator: vnmr1
Mercury-400BB "Varian-NMR"

Relax. delay 0.700 sec
Pulse 45.0 degrees
Acq. time 1.300 sec
Width 24154.6 Hz
512 repetitions
OBSERVE C13, 100.6910107 MHz
DECOUPLE H1, 400.4431966 MHz
Power 40 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 1.0 Hz
FT size 65536
Total time 17 min, 51 sec



11b

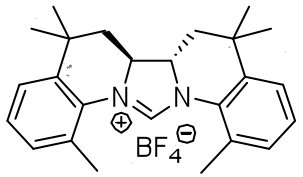


STANDARD 1H OBSERVE

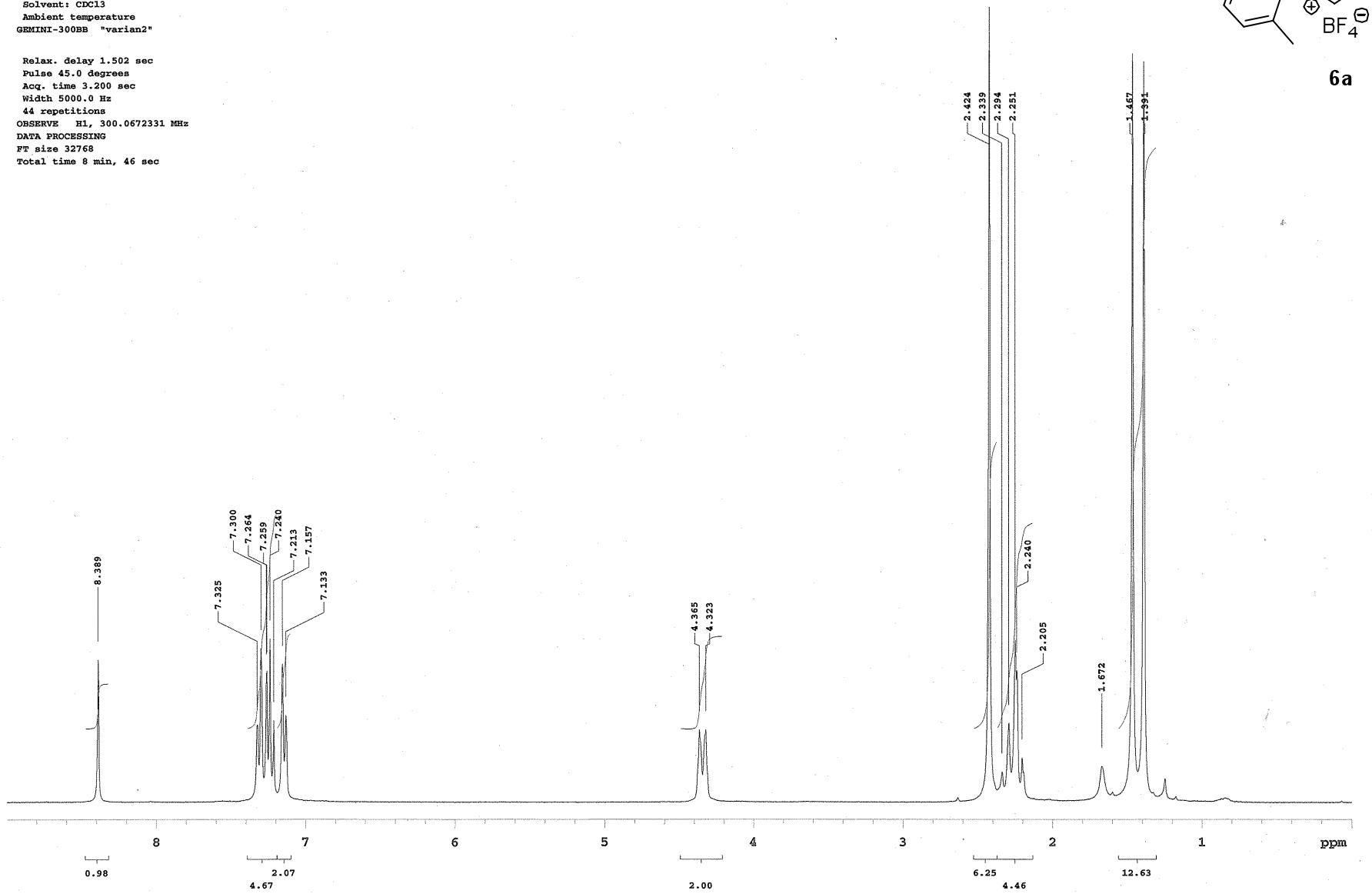
Pulse Sequence: s2pul

Solvent: CDCl3
Ambient temperature
GEMINI-300BB "varian2"

Relax. delay 1.502 sec
Pulse 45.0 degrees
Acq. time 3.200 sec
Width 5000.0 Hz
44 repetitions
OBSERVE H1, 300.0672331 MHz
DATA PROCESSING
FT size 32768
Total time 8 min, 46 sec



6a

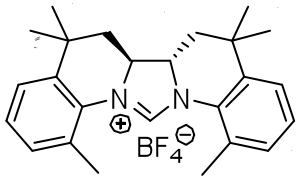


13C OBSERVE

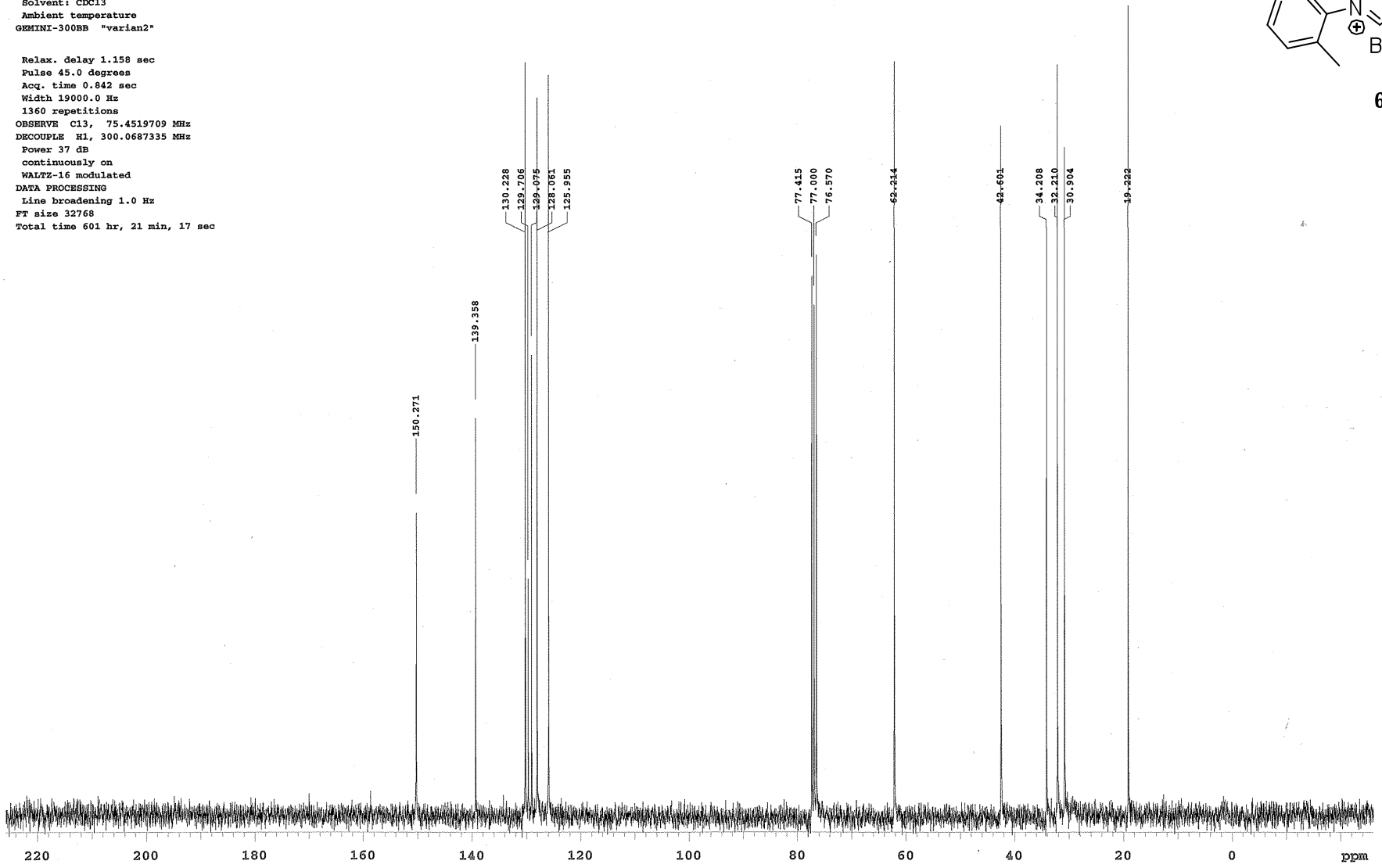
Pulse Sequence: s2pul

Solvent: CDCl3
Ambient temperature
GEMINI-300BB "varian2"

Relax. delay 1.158 sec
Pulse 45.0 degrees
Acq. time 0.842 sec
Width 19000.0 Hz
1360 repetitions
OBSERVE C13, 75.4519709 MHz
DECOUPLE H1, 300.0687335 MHz
Power 37 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 1.0 Hz
FT size 32768
Total time 601 hr, 21 min, 17 sec



6a

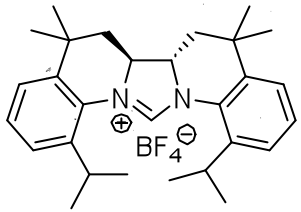


STANDARD 1H OBSERVE

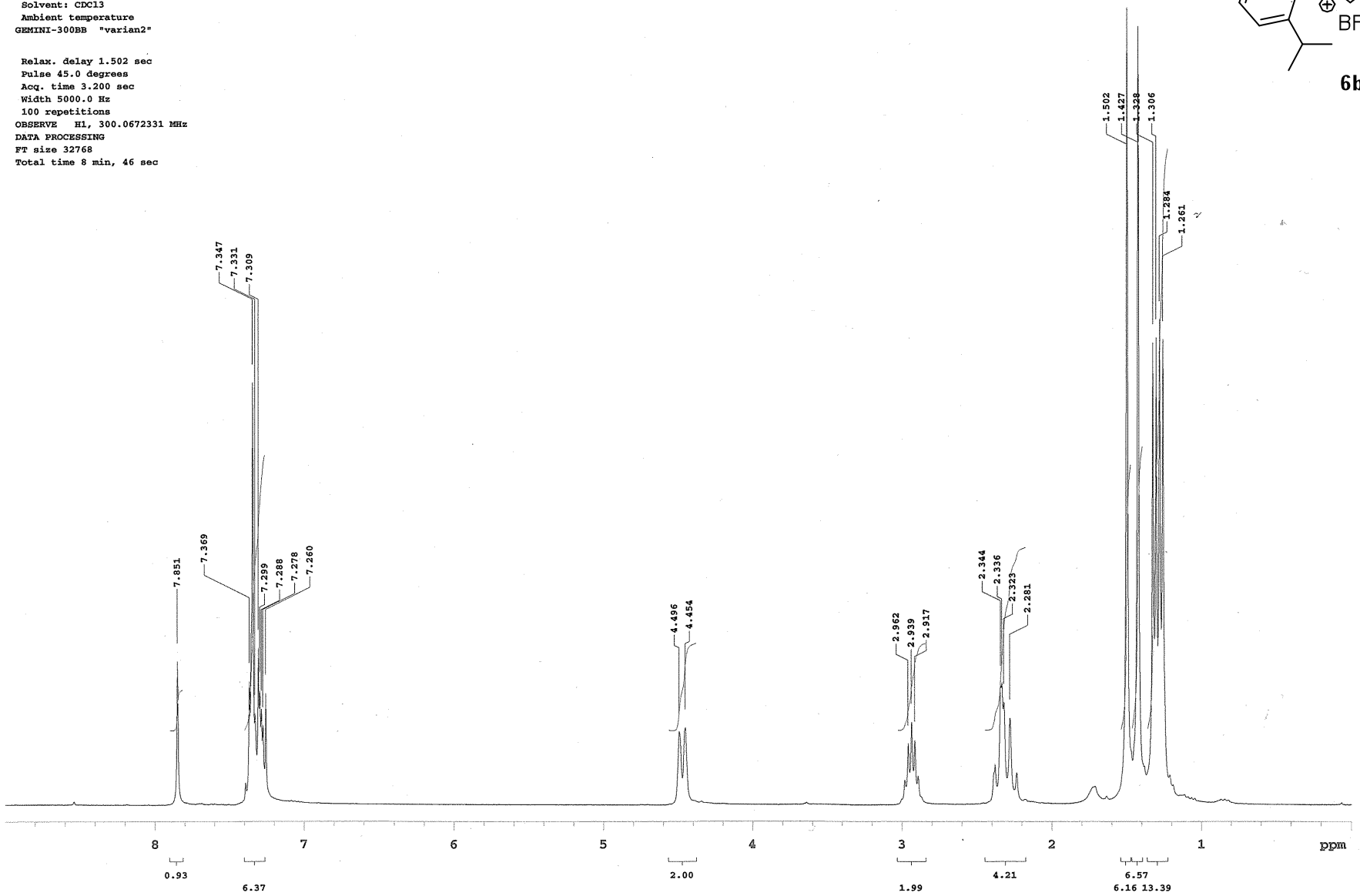
Pulse Sequence: s2pul

Solvent: CDCl3
Ambient temperature
GEMINI-300BB "varian2"

Relax. delay 1.502 sec
Pulse 45.0 degrees
Acq. time 3.200 sec
Width 5000.0 Hz
100 repetitions
OBSERVE H1, 300.0672331 MHz
DATA PROCESSING
FT size 32768
Total time 8 min, 46 sec



6b

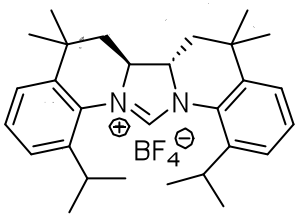


13C OBSERVE

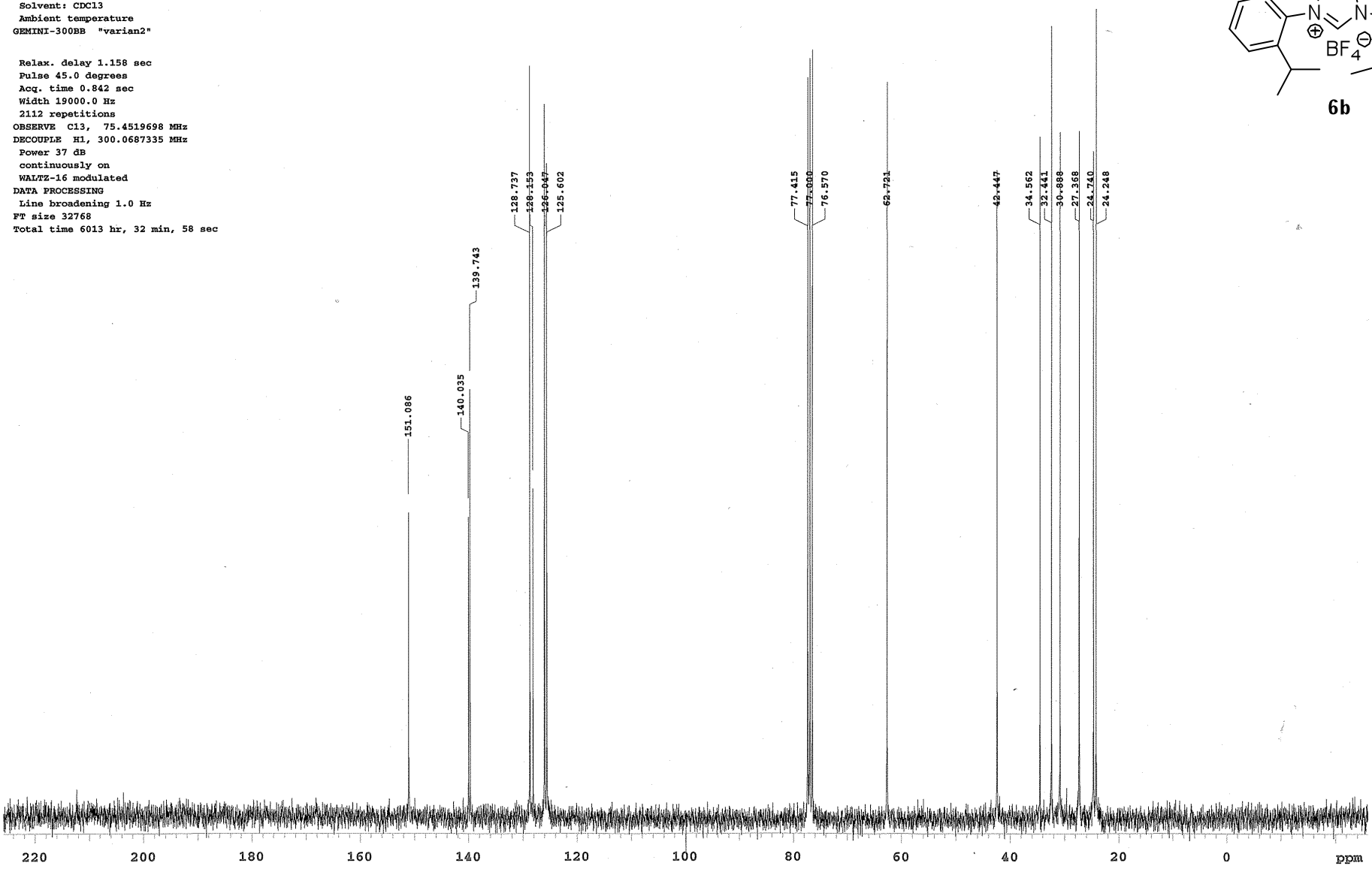
Pulse Sequence: s2pul

Solvent: CDCl3
Ambient temperature
GEMINI-300BB "varian2"

Relax. delay 1.158 sec
Pulse 45.0 degrees
Acq. time 0.842 sec
Width 19000.0 Hz
2112 repetitions
OBSERVE C13, 75.4519698 MHz
DECOUPLE H1, 300.0687335 MHz
Power 37 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 1.0 Hz
FT size 32768
Total time 6013 hr, 32 min, 58 sec



6b



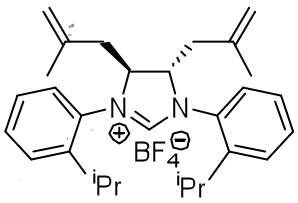
282H

File: home/vnmr1/vnmrsys/data/murakami_lab/LIULT/282h2.fid

Pulse Sequence: s2pul

Solvent: cdcl3
Ambient temperature
Operator: vnmr1
File: 282h2
Mercury-400BB "Varian-NMR"

Relax. delay 1.500 sec
Pulse 45.0 degrees
Acq. time 3.502 sec
Width 6402.0 Hz
16 repetitions
OBSERVE H1, 400.4411637 MHz
DATA PROCESSING
Line broadening 0.2 Hz
FT size 65536
Total time 1 min, 32 sec



7

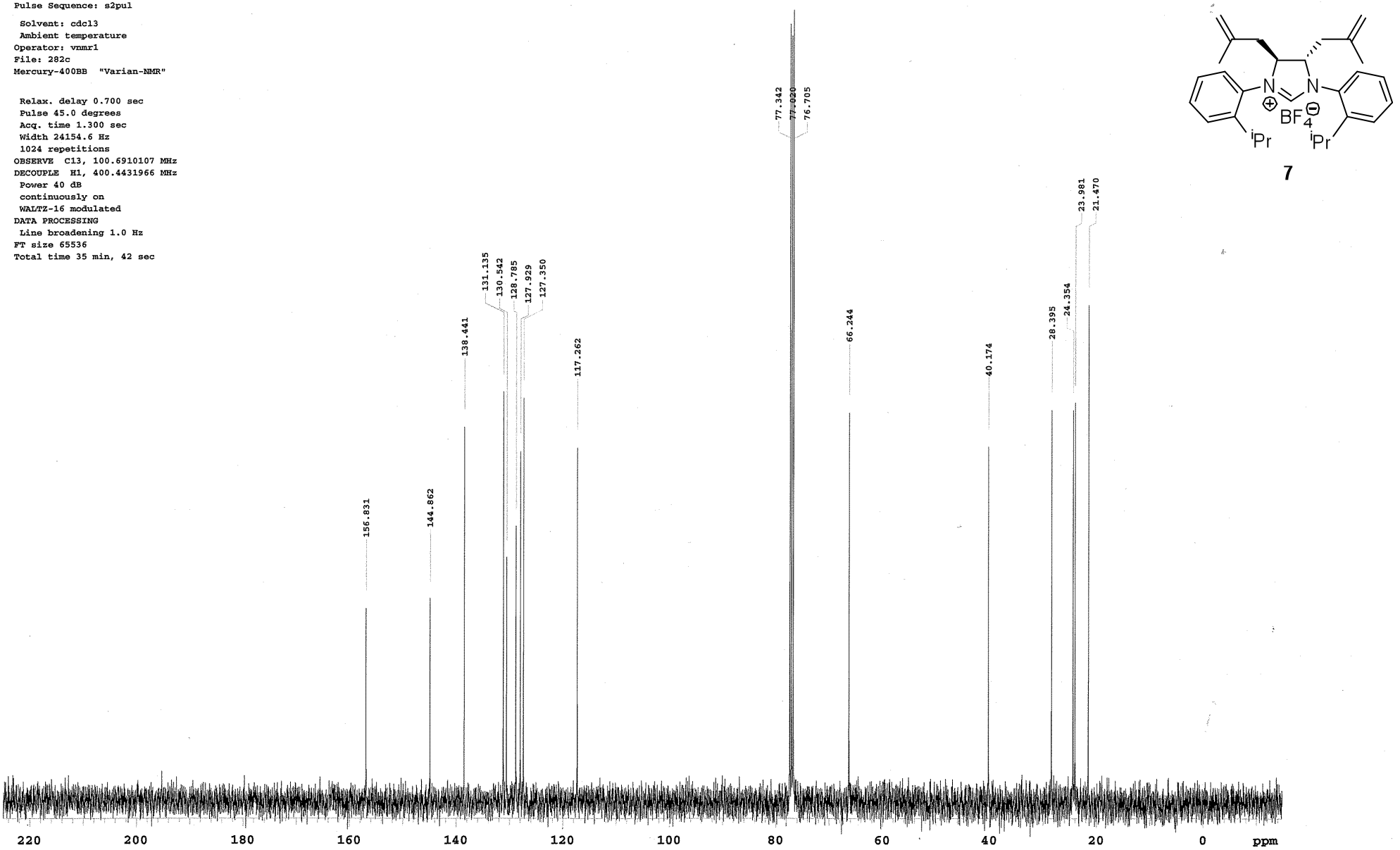
282h

File: home/vnmr1/vnmrsys/data/murakami_lab/LIULT/282c.fid

Pulse Sequence: s2pul

Solvent: cdcl3
Ambient temperature
Operator: vnmr1
File: 282c
Mercury-400BB "Varian-NMR"

Relax. delay 0.700 sec
Pulse 45.0 degrees
Acq. time 1.300 sec
Width 24154.6 Hz
1024 repetitions
OBSERVE C13, 100.6910107 MHz
DECOUPLE H1, 400.4431966 MHz
Power 40 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 1.0 Hz
FT size 65536
Total time 35 min, 42 sec



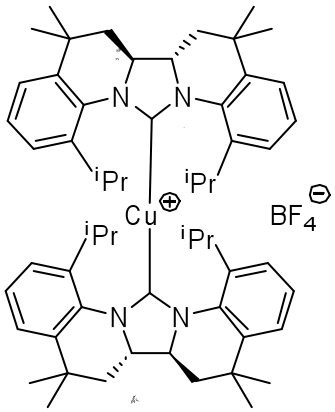
7

File: home/vnmr1/vnmrsys/data/murakami_lab/LIULT/DiPrCuH.fid

Pulse Sequence: s2pul

Solvent: cdcl3
Ambient temperature
Operator: vnmr1
File: DiPrCuH
Mercury-400BB "Varian-NMR"

Relax. delay 1.500 sec
Pulse 45.0 degrees
Acq. time 3.502 sec
Width 6402.0 Hz
16 repetitions
OBSERVE H1, 400.4411632 MHz
DATA PROCESSING
Line broadening 0.2 Hz
FT size 65536
Total time 1 min, 32 sec



13

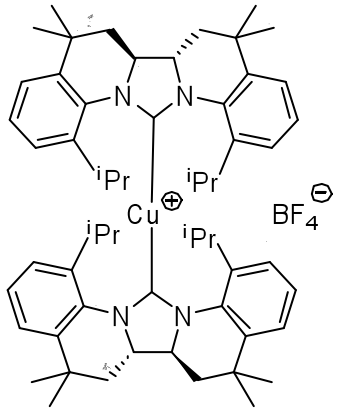
288p2c

File: home/vnmr1/vnmrsys/data/murakami_lab/LIULT/288p2c.fid

Pulse Sequence: s2pul

Solvent: cdcl3
Ambient temperature
Operator: vnmr1
File: 288p2c
Mercury-400BB "Varian-NMR"

Relax. delay 0.700 sec
Pulse 45.0 degrees
Acq. time 1.300 sec
Width 24154.6 Hz
1024 repetitions
OBSERVE C13, 100.6910134 MHz
DECOUPLE H1, 400.4431966 MHz
Power 40 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 1.0 Hz
FT size 65536
Total time 35 min, 42 sec



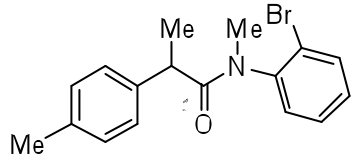
13

File: home/vnmr1/vnmrsys/data/murakami_lab/LIULT/402hgpc2.fid

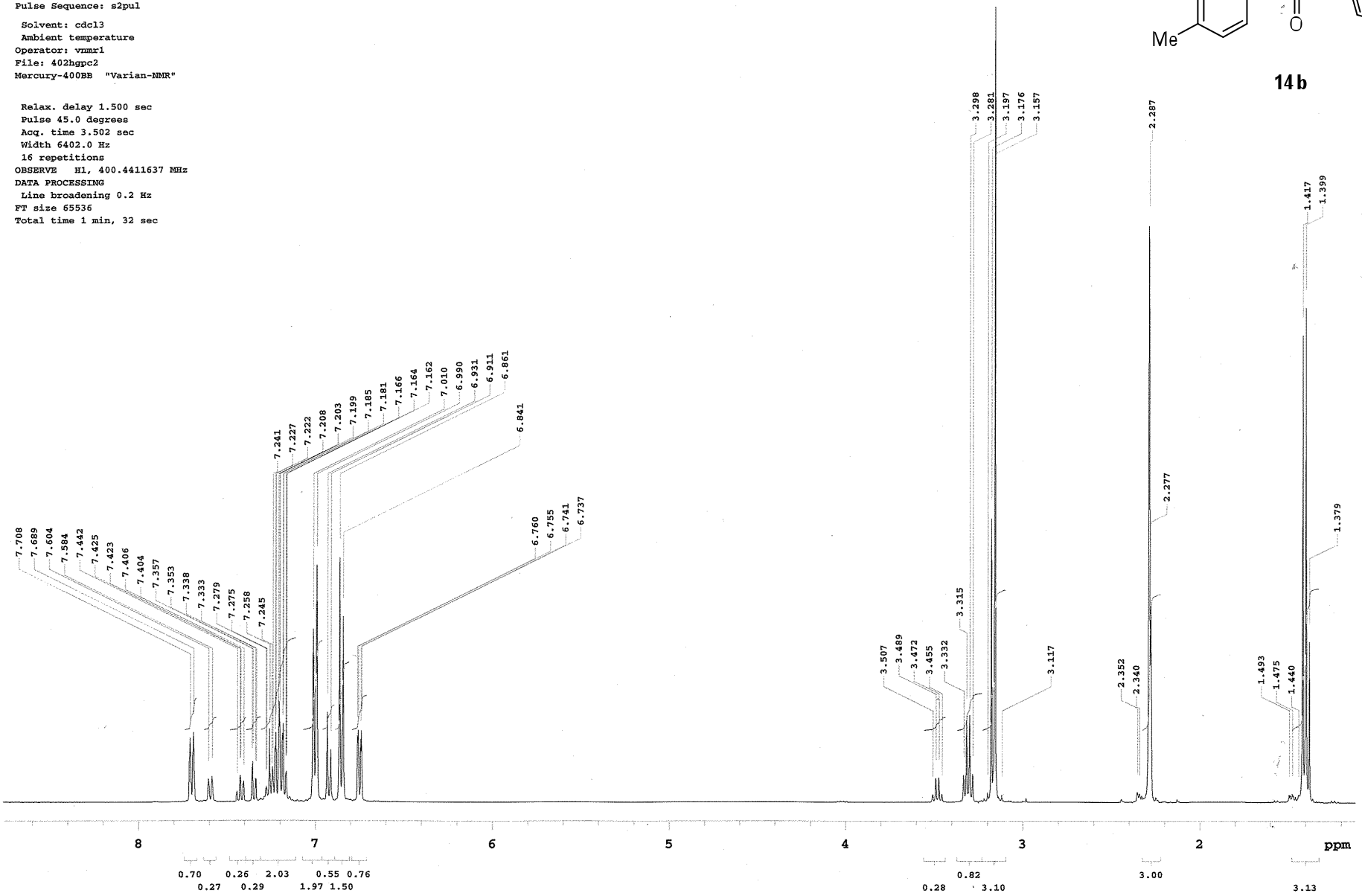
Pulse Sequence: s2pul

Solvent: cdcl3
Ambient temperature
Operator: vnmr1
File: 402hgpc2
Mercury-400BB "Varian-NMR"

Relax. delay 1.500 sec
Pulse 45.0 degrees
Acq. time 3.502 sec
Width 6402.0 Hz
16 repetitions
OBSERVE H1, 400.4411637 MHz
DATA PROCESSING
Line broadening 0.2 Hz
FT size 65536
Total time 1 min, 32 sec



14b



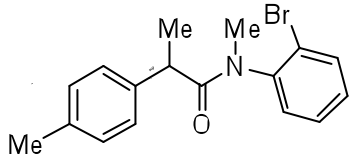
402c

File: home/vnmr1/vnmrsys/data/murakami_lab/LIULT/402c.fid

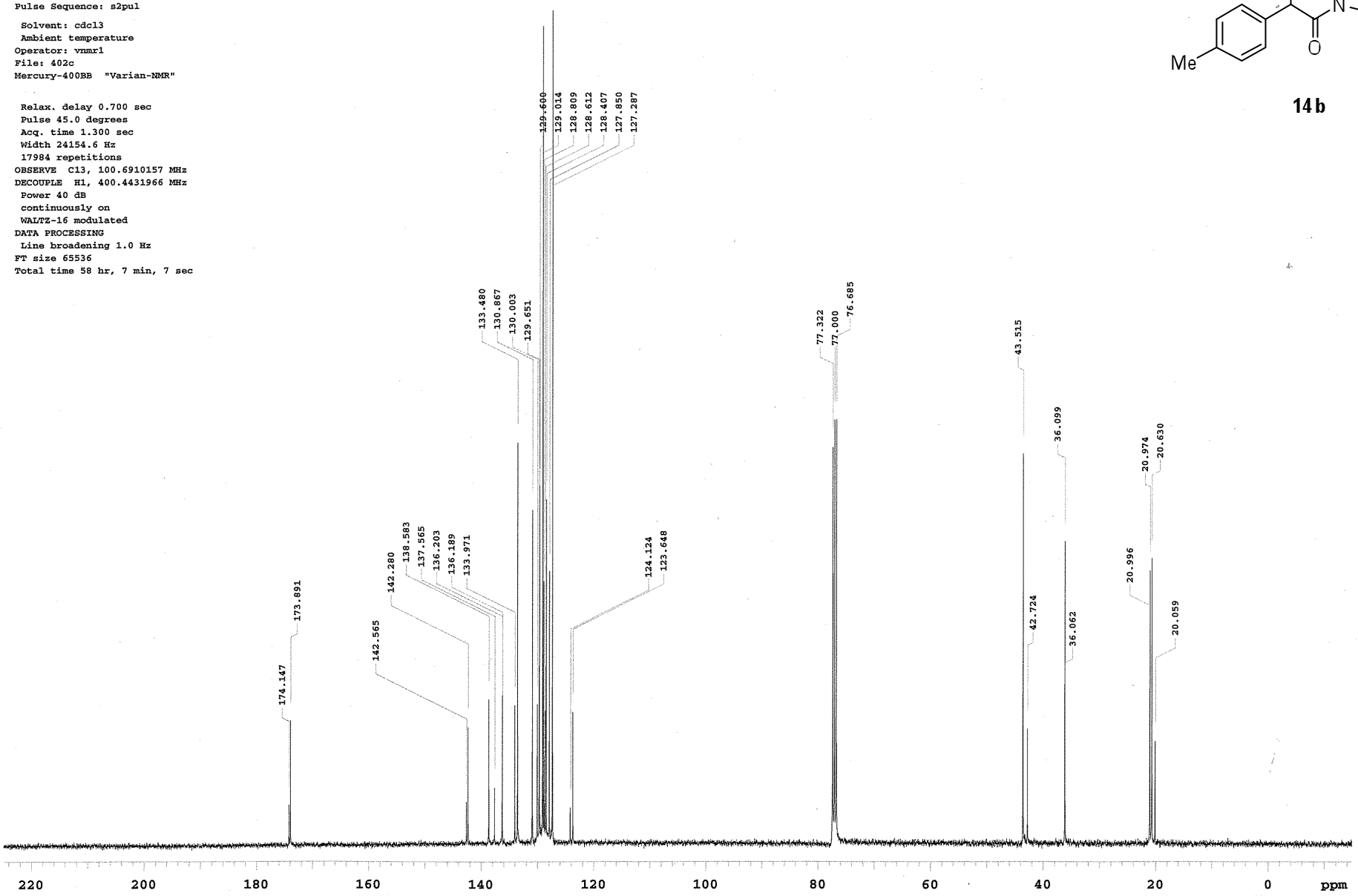
Pulse Sequence: s2pul

Solvent: cdcl3
Ambient temperature
Operator: vnmr1
File: 402c
Mercury-400BB "Varian-NMR"

Relax. delay 0.700 sec
Pulse 45.0 degrees
Acq. time 1.300 sec
Width 24154.6 Hz
17984 repetitions
OBSERVE C13, 100.6910157 MHz
DECOUPLE H1, 400.4431966 MHz
Power 40 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 1.0 Hz
FT size 65536
Total time 58 hr, 7 min, 7 sec



14b



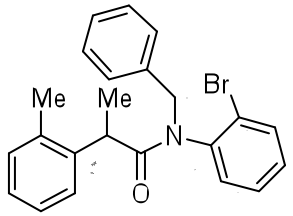
345h

File: home/vnmr1/vnmrsys/data/murakami_lab/LIULT/278c2.fid

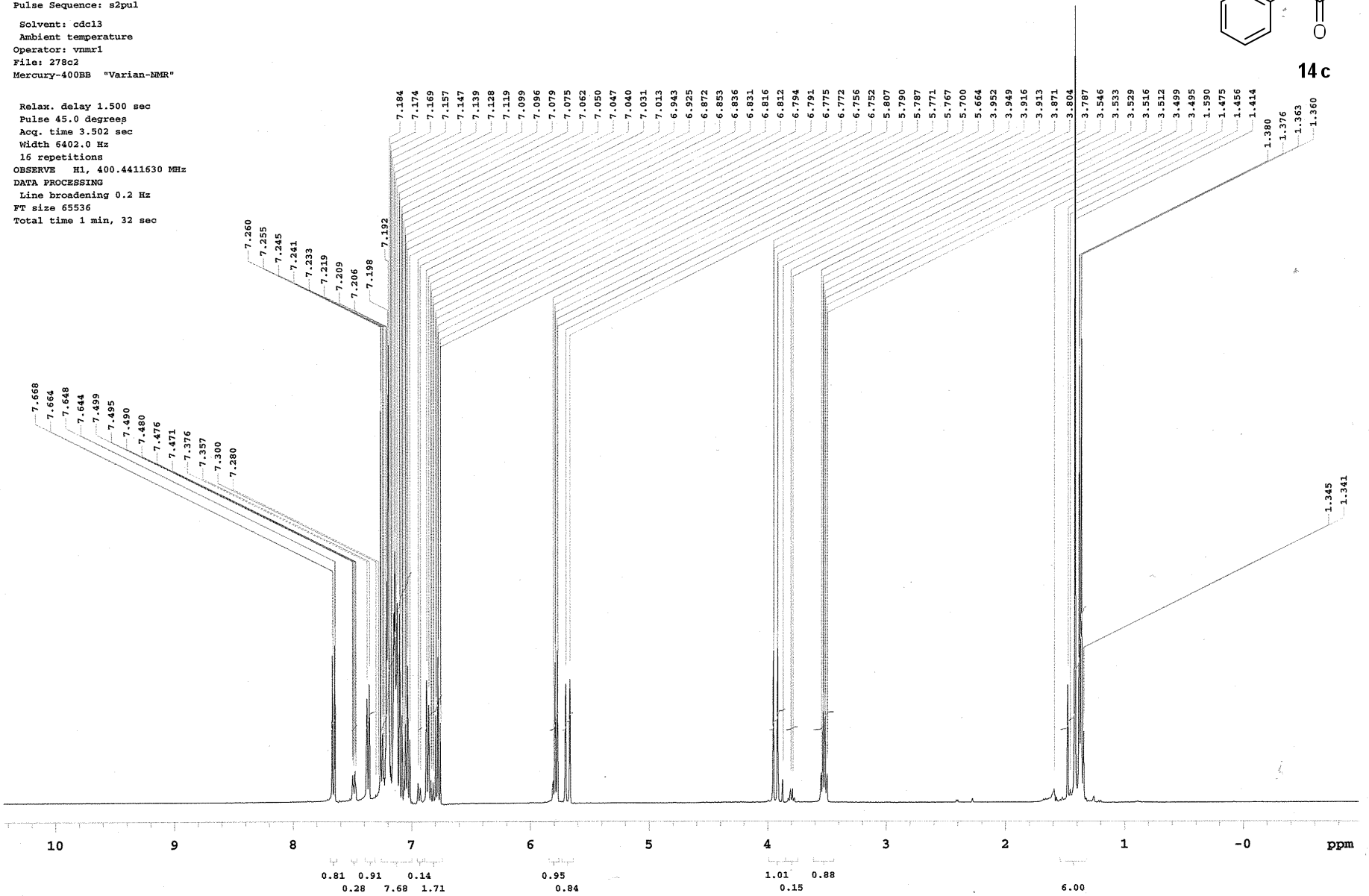
Pulse Sequence: s2pul

Solvent: cdcl3
Ambient temperature
Operator: vnmr1
File: 278c2
Mercury-400BB "Varian-NMR"

Relax. delay 1.500 sec
Pulse 45.0 degrees
Acq. time 3.502 sec
Width 6402.0 Hz
16 repetitions
OBSERVE H1, 400.4411630 MHz
DATA PROCESSING
Line broadening 0.2 Hz
FT size 65536
Total time 1 min, 32 sec



14c

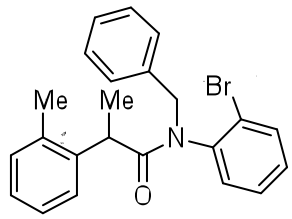


File: xp

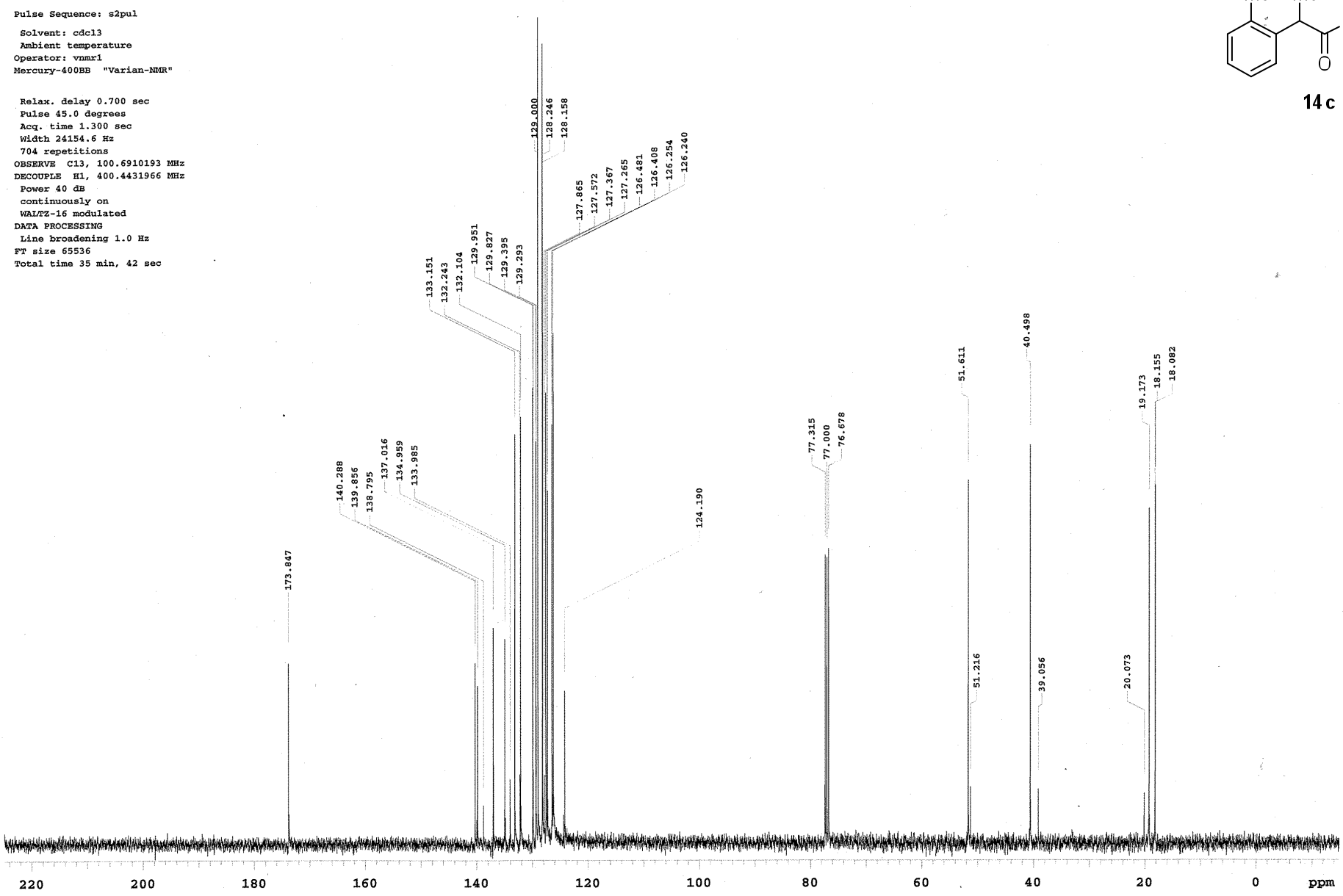
Pulse Sequence: s2pul

Solvent: cdcl3
Ambient temperature
Operator: vnmr1
Mercury-400BB "Varian-NMR"

Relax. delay 0.700 sec
Pulse 45.0 degrees
Acq. time 1.300 sec
Width 24154.6 Hz
704 repetitions
OBSERVE C13, 100.6910193 MHz
DECOUPLE H1, 400.4431966 MHz
Power 40 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 1.0 Hz
FT size 65536
Total time 35 min, 42 sec



14c



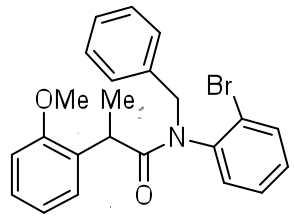
306H

File: xp

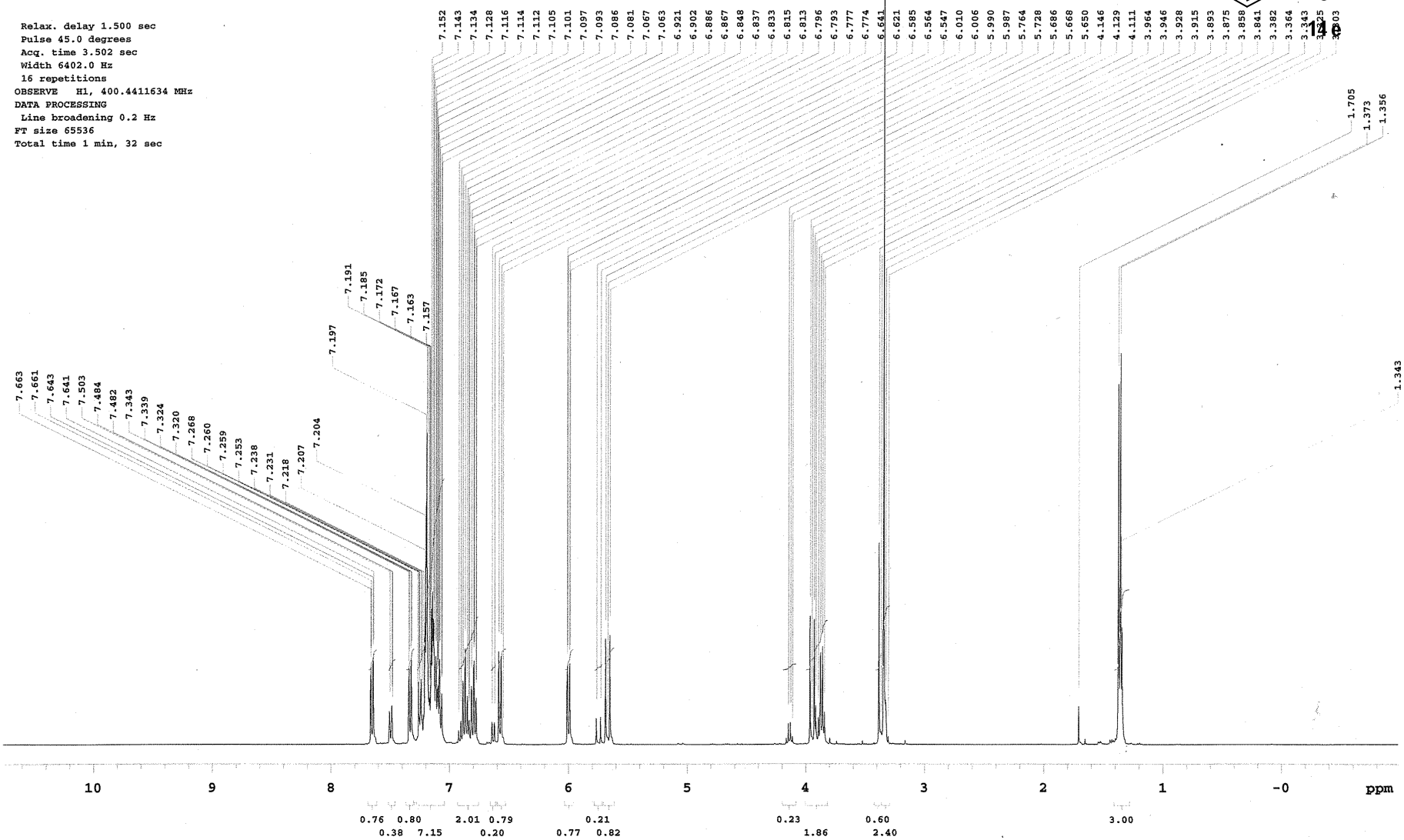
Pulse Sequence: s2pul

Solvent: cdcl3
Ambient temperature
Operator: vnmr1
Mercury-400BB "Varian-NMR"

Relax. delay 1.500 sec
Pulse 45.0 degrees
Acq. time 3.502 sec
Width 6402.0 Hz
16 repetitions
OBSERVE H1, 400.4411634 MHz
DATA PROCESSING
Line broadening 0.2 Hz
FT size 65536
Total time 1 min, 32 sec



14e



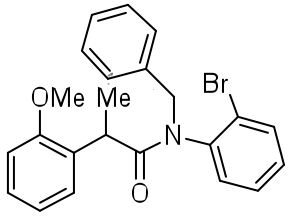
306C

File: xp

Pulse Sequence: s2pul

Solvent: cdcl3
Ambient temperature
Operator: vmmr1
Mercury-400BB "Varian-NMR"

Relax. delay 0.700 sec
Pulse 45.0 degrees
Acq. time 1.300 sec
Width 24154.6 Hz
384 repetitions
OBSERVE C13, 100.6910157 MHz
DECOUPLE H1, 400.4431966 MHz
Power 40 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 1.0 Hz
FT size 65536
Total time 35 min, 42 sec



14e

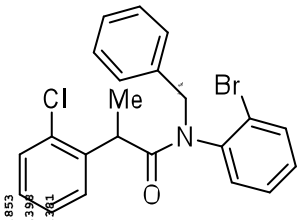
345
278H cl

345
File: home/vnmr1/vnmrsys/data/murakami_lab/LIULT/278h.fid

Pulse Sequence: s2pul

Solvent: cdcl3
Ambient temperature
Operator: vnmr1
File: 278h
Mercury-400BB "Varian-NMR"

Relax. delay 1.500 sec
Pulse 45.0 degrees
Acq. time 3.502 sec
Width 6402.0 Hz
16 repetitions
OBSERVE H1, 400.4411630 MHz
DATA PROCESSING
Line broadening 0.2 Hz
FT size 65536
Total time 1 min, 32 sec



14h

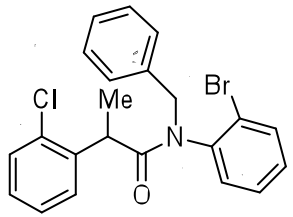
278g

File: home/vnmr1/vnmrsys/data/murakami_lab/LIULT/278c.fid

Pulse Sequence: s2pul

Solvent: cdcl3
Ambient temperature
Operator: vnmr1
File: 278c
Mercury-400BB "Varian-NMR"

Relax. delay 0.700 sec
Pulse 45.0 degrees
Acq. time 1.300 sec
Width 24154.6 Hz
512 repetitions
OBSERVE C13, 100.6910142 MHz
DECOUPLE H1, 400.4431966 MHz
Power 40 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 1.0 Hz
FT size 65536
Total time 17 min, 51 sec



14h

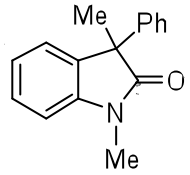
343H

File: home/vnmr1/vnmrsys/data/murakami_1ab/LIULT/343h.fid

Pulse Sequence: s2pul

Solvent: cdcl3
Ambient temperature
Operator: vnmr1
File: 343h
Mercury-400BB "Varian-NMR"

Relax. delay 1.500 sec
Pulse 45.0 degrees
Acq. time 3.502 sec
Width 6402.0 Hz
16 repetitions
OBSERVE H1, 400.4411692 MHz
DATA PROCESSING
Line broadening 0.2 Hz
FT size 65536
Total time 1 min, 32 sec



15a

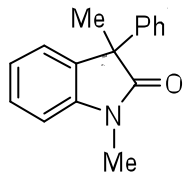
343C

File: home/vnmr1/vnmrsys/data/murakami_lab/LIULT/343c.fid

Pulse Sequence: s2pul

Solvent: cdcl3
Ambient temperature
Operator: vnmr1
File: 343c
Mercury-400BB "Varian-NMR"

Relax. delay 0.700 sec
Pulse 45.0 degrees
Acq. time 1.300 sec
Width 24154.6 Hz
1024 repetitions
OBSERVE C13, 100.6910193 MHz
DECOUPLE H1, 400.4431966 MHz
Power 40 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 1.0 Hz
FT size 65536
Total time 35 min, 42 sec



15a

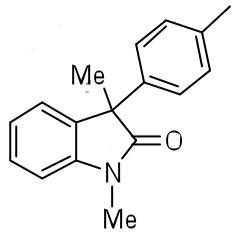
405H

File: xp

Pulse Sequence: s2pul

Solvent: cdcl3
Ambient temperature
Operator: vnmr1
Mercury-400BB "Varian-NMR"

Relax. delay 1.500 sec
Pulse 45.0 degrees
Acq. time 3.502 sec
Width 6402.0 Hz
16 repetitions
OBSERVE H1, 400.4411634 MHz
DATA PROCESSING
Line broadening 0.2 Hz
FT size 65536
Total time 1 min, 32 sec



15b

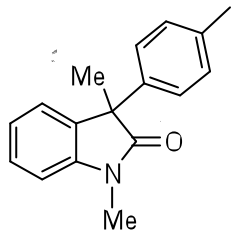
405H

File: xp

Pulse Sequence: s2pul

Solvent: cdcl3
Ambient temperature
Operator: vnmr1
Mercury-400BB "Varian-NMR"

Relax. delay 0.700 sec
Pulse 45.0 degrees
Acq. time 1.300 sec
Width 24154.6 Hz
960 repetitions
OBSERVE C13, 100.6910186 MHz
DECOUPLE H1, 400.4431966 MHz
Power 40 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 1.0 Hz
FT size 65536
Total time 34 min, 54 sec



15b

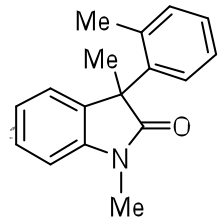
279H

File: home/vnmr1/vnmrsys/data/murakami_lab/LIULT/279h.fid

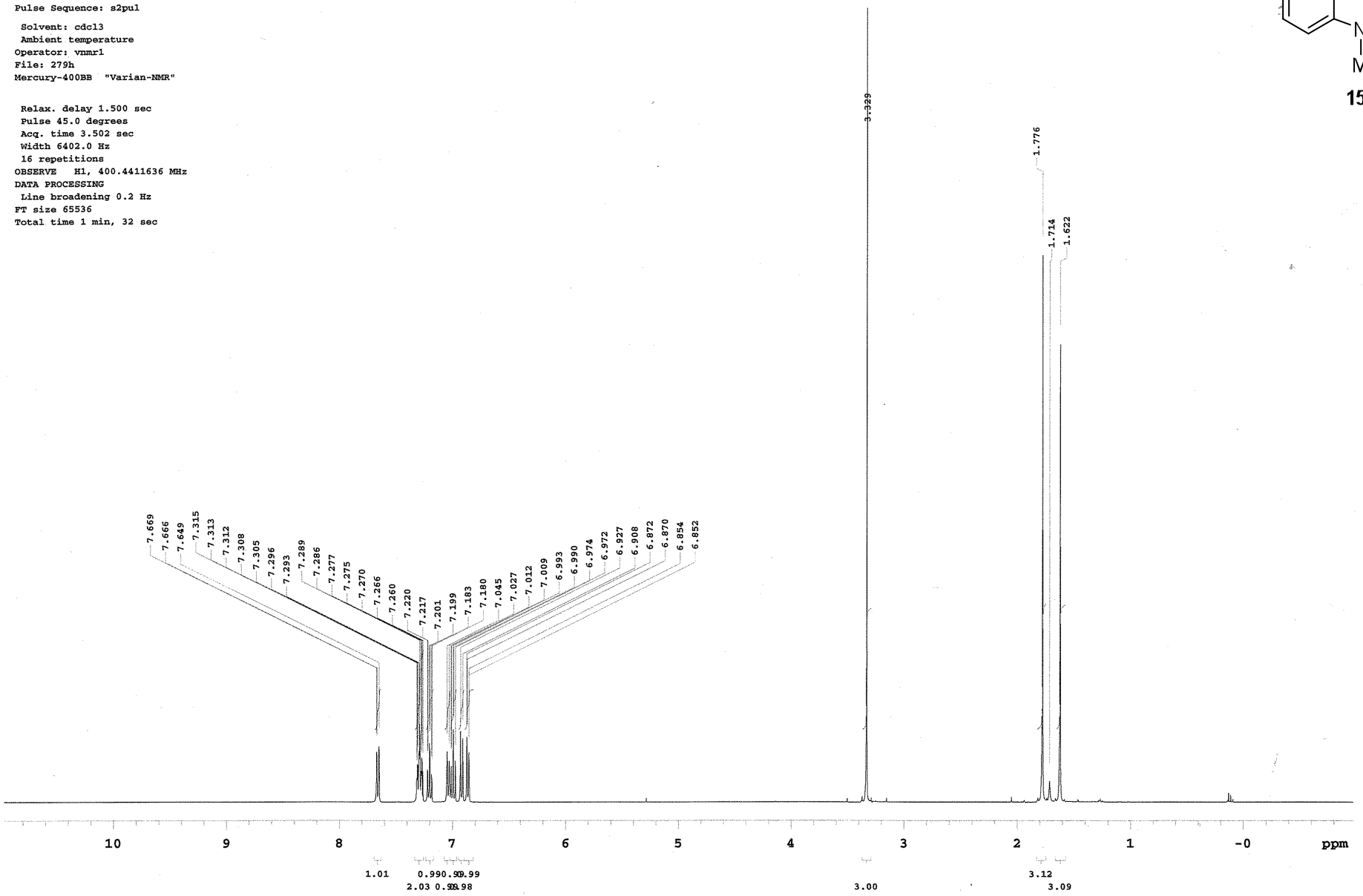
Pulse Sequence: s2pul

Solvent: cdcl3
Ambient temperature
Operator: vnmr1
File: 279h
Mercury-400BB "Varian-NMR"

Relax. delay 1.500 sec
Pulse 45.0 degrees
Acq. time 3.502 sec
Width 6402.0 Hz
16 repetitions
OBSERVE H1, 400.4411636 MHz
DATA PROCESSING
Line broadening 0.2 Hz
FT size 65536
Total time 1 min, 32 sec



15c



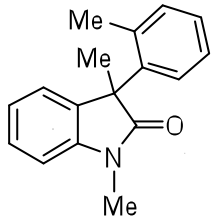
279GPCC

File: home/vnmr1/vnmrsys/data/murakami_lab/LIULT/279GPCC.fid

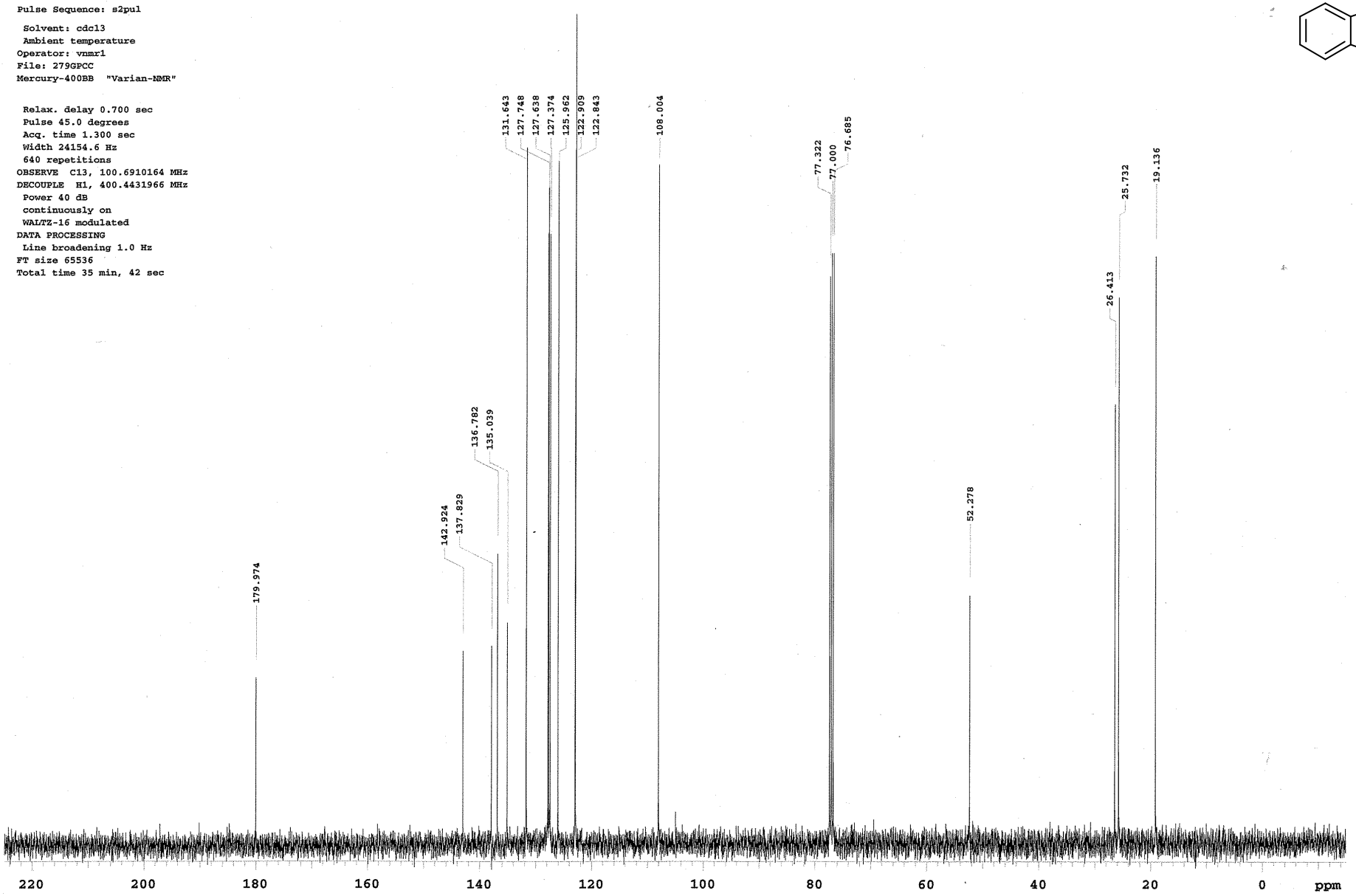
Pulse Sequence: s2pul

Solvent: cdcl3
Ambient temperature
Operator: vnmr1
File: 279GPCC
Mercury-400BB "Varian-NMR"

Relax. delay 0.700 sec
Pulse 45.0 degrees
Acq. time 1.300 sec
Width 24154.6 Hz
640 repetitions
OBSERVE C13, 100.6910164 MHz
DECOUPLE H1, 400.4431966 MHz
Power 40 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 1.0 Hz
FT size 65536
Total time 35 min, 42 sec



15c



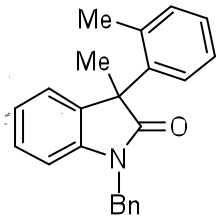
280h

File: home/vnmr1/vnmrsys/data/murakami_lab/LIULT/280h.fid

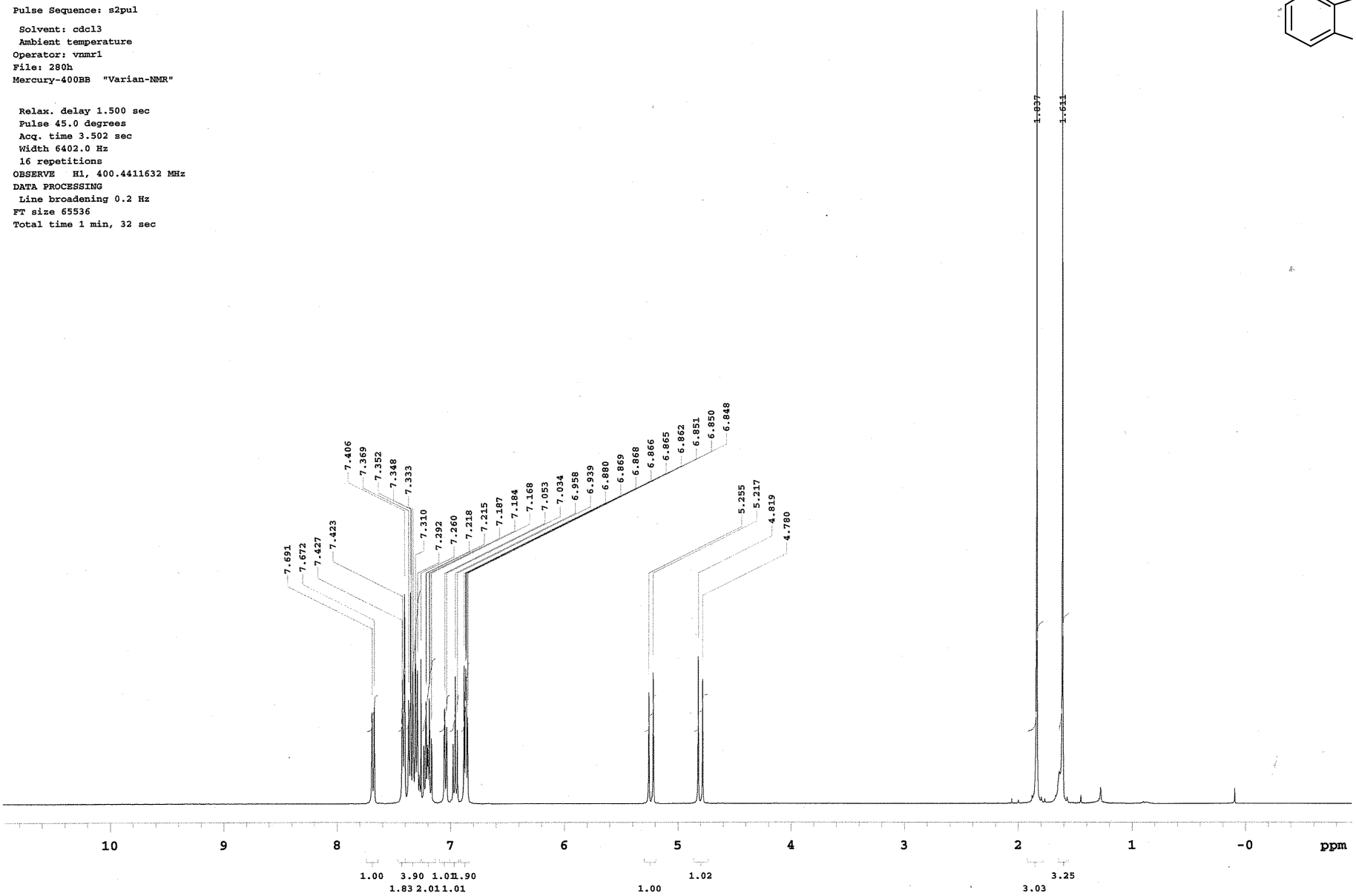
Pulse Sequence: s2pul

Solvent: cdcl3
Ambient temperature
Operator: vnmr1
File: 280h
Mercury-400BB "Varian-NMR"

Relax. delay 1.500 sec
Pulse 45.0 degrees
Acq. time 3.502 sec
Width 6402.0 Hz
16 repetitions
OBSERVE H1, 400.4411632 MHz
DATA PROCESSING
Line broadening 0.2 Hz
FT size 65536
Total time 1 min, 32 sec



15 d



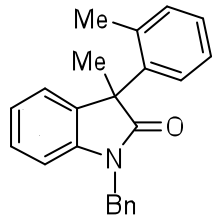
280c

File: home/vnmr1/vnmrsys/data/murakami_lab/LIULT/280c.fid

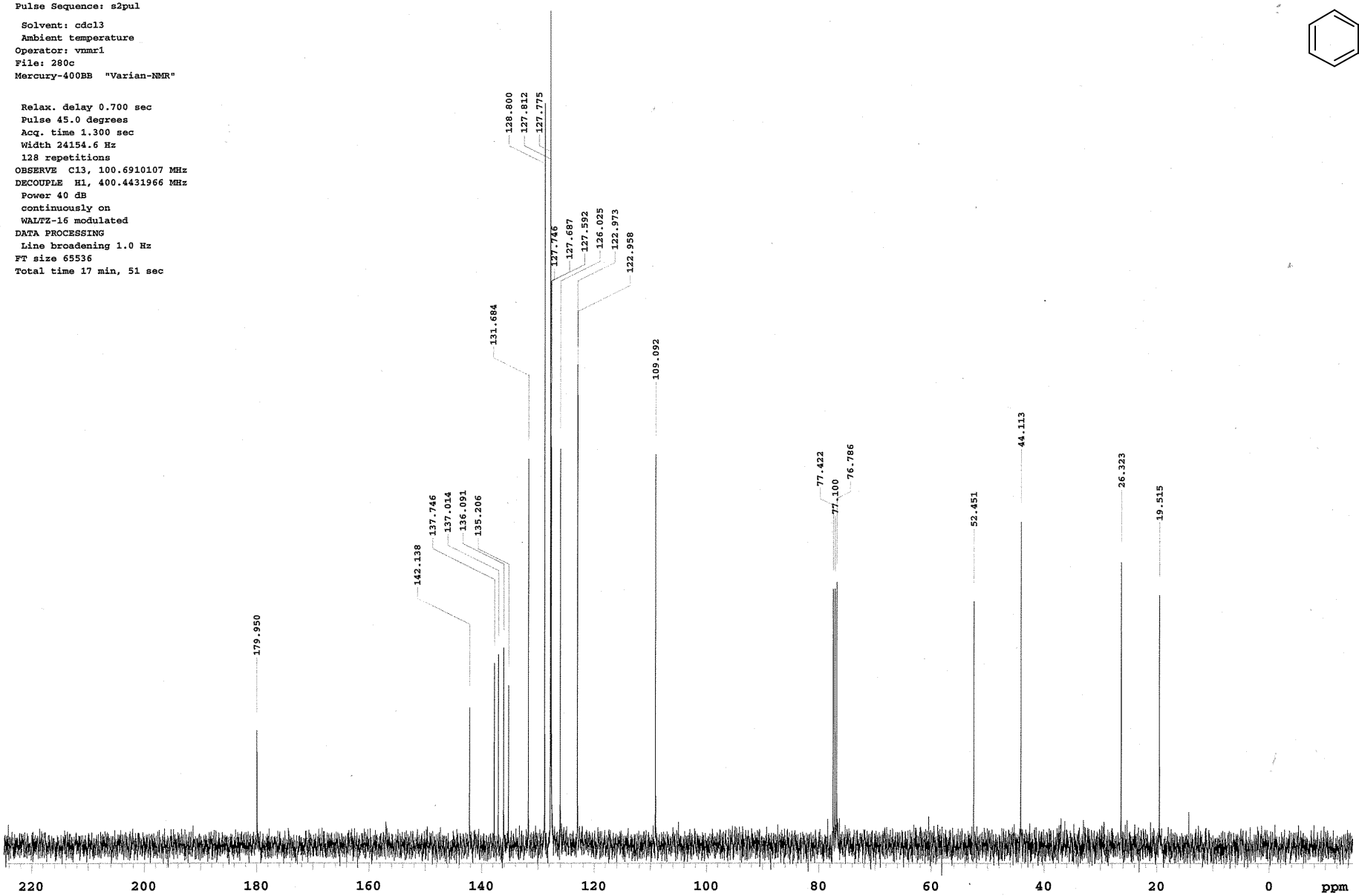
Pulse Sequence: s2pul

Solvent: cdcl3
Ambient temperature
Operator: vnmr1
File: 280c
Mercury-400BB "Varian-NMR"

Relax. delay 0.700 sec
Pulse 45.0 degrees
Acq. time 1.300 sec
Width 24154.6 Hz
128 repetitions
OBSERVE C13, 100.6910107 MHz
DECOUPLE H1, 400.4431966 MHz
Power 40 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 1.0 Hz
FT size 65536
Total time 17 min, 51 sec



15d



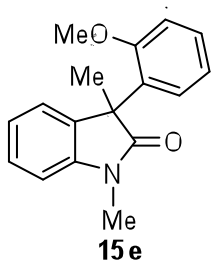
309H

File: home/vnmr1/vnmrsys/data/murakami_lab/LIULT/309H2.fid

Pulse Sequence: s2pul

Solvent: cdcl3
Ambient temperature
Operator: vnmr1
File: 309H2
Mercury-400BB "Varian-NMR"

Relax. delay 1.500 sec
Pulse 45.0 degrees
Acq. time 3.502 sec
Width 6402.0 Hz
16 repetitions
OBSERVE H1, 400.4411630 MHz
DATA PROCESSING
Line broadening 0.2 Hz
FT size 65536
Total time 1 min, 32 sec



15e

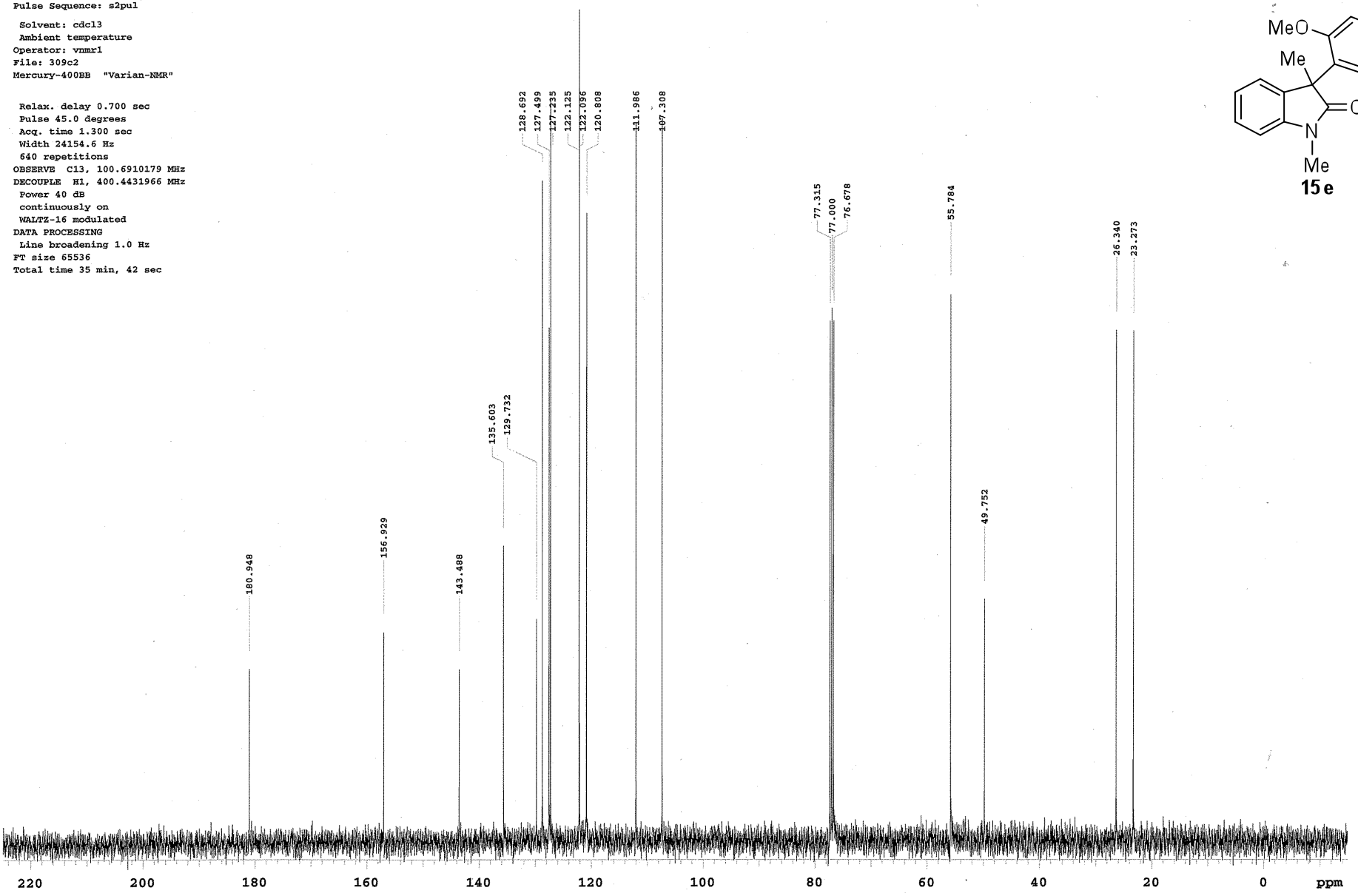
309H

File: home/vnmr1/vnmrsys/data/murakami_lab/LIULT/309c2.fid

Pulse Sequence: s2pul

Solvent: cdcl3
Ambient temperature
Operator: vnmr1
File: 309c2
Mercury-400BB "Varian-NMR"

Relax. delay 0.700 sec
Pulse 45.0 degrees
Acq. time 1.300 sec
Width 24154.6 Hz
640 repetitions
OBSERVE C13, 100.6910179 MHz
DECOUPLE H1, 400.4431966 MHz
Power 40 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 1.0 Hz
FT size 65536
Total time 35 min, 42 sec



15e

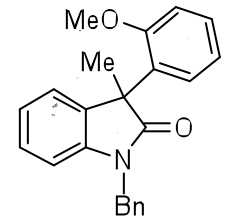
310H

File: home/vnmr1/vnmrsys/data/murakami_lab/LIULT/310H2.fid

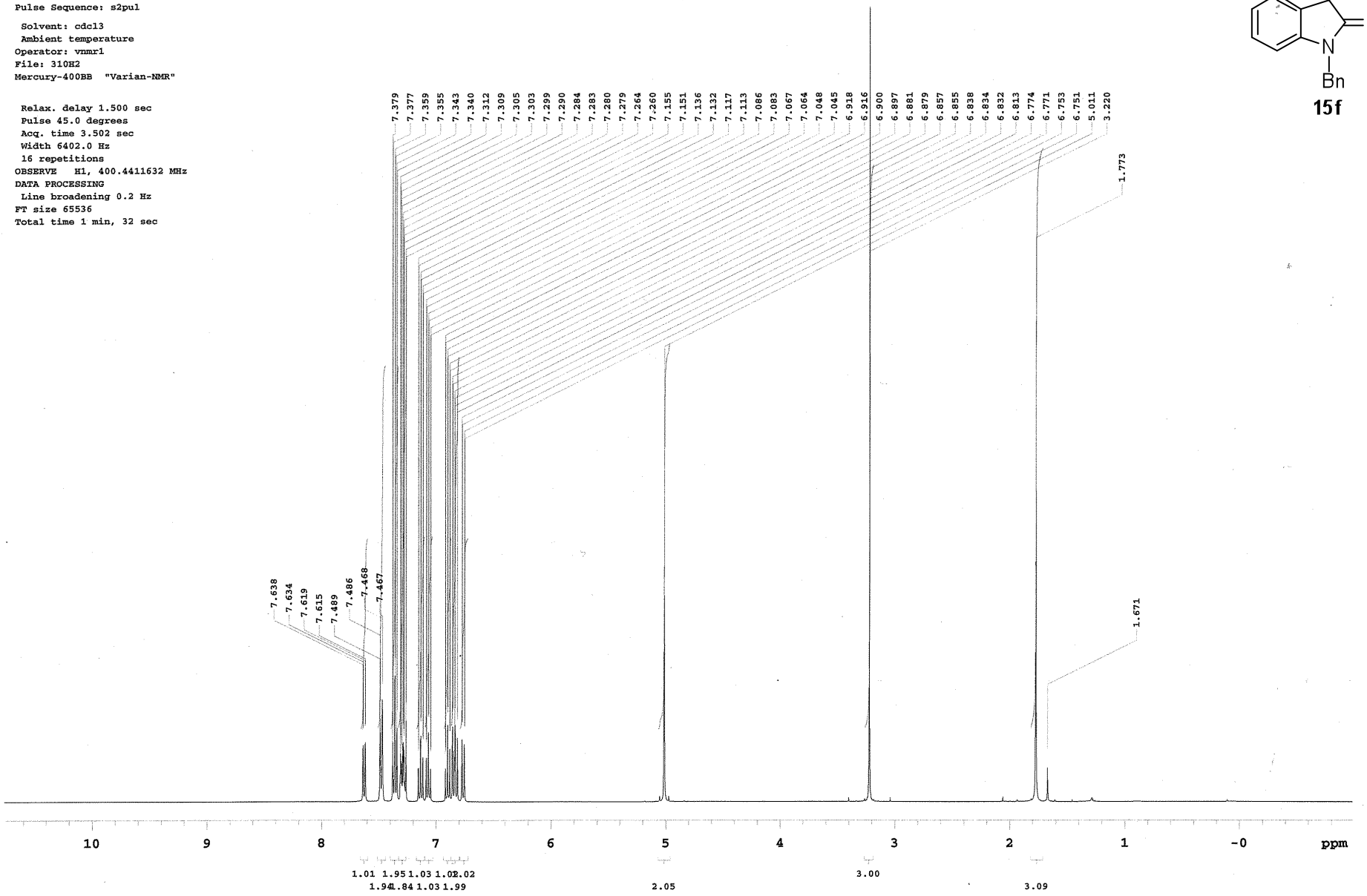
Pulse Sequence: s2pul

Solvent: cdcl3
Ambient temperature
Operator: vnmr1
File: 310H2
Mercury-400BB "Varian-NMR"

Relax. delay 1.500 sec
Pulse 45.0 degrees
Acq. time 3.502 sec
Width 6402.0 Hz
16 repetitions
OBSERVE H1, 400.4411632 MHz
DATA PROCESSING
Line broadening 0.2 Hz
FT size 65536
Total time 1 min, 32 sec



15f



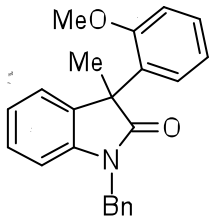
310H

File: home/vnmr1/vnmrsys/data/murakami_lab/LIULT/310Hc.fid

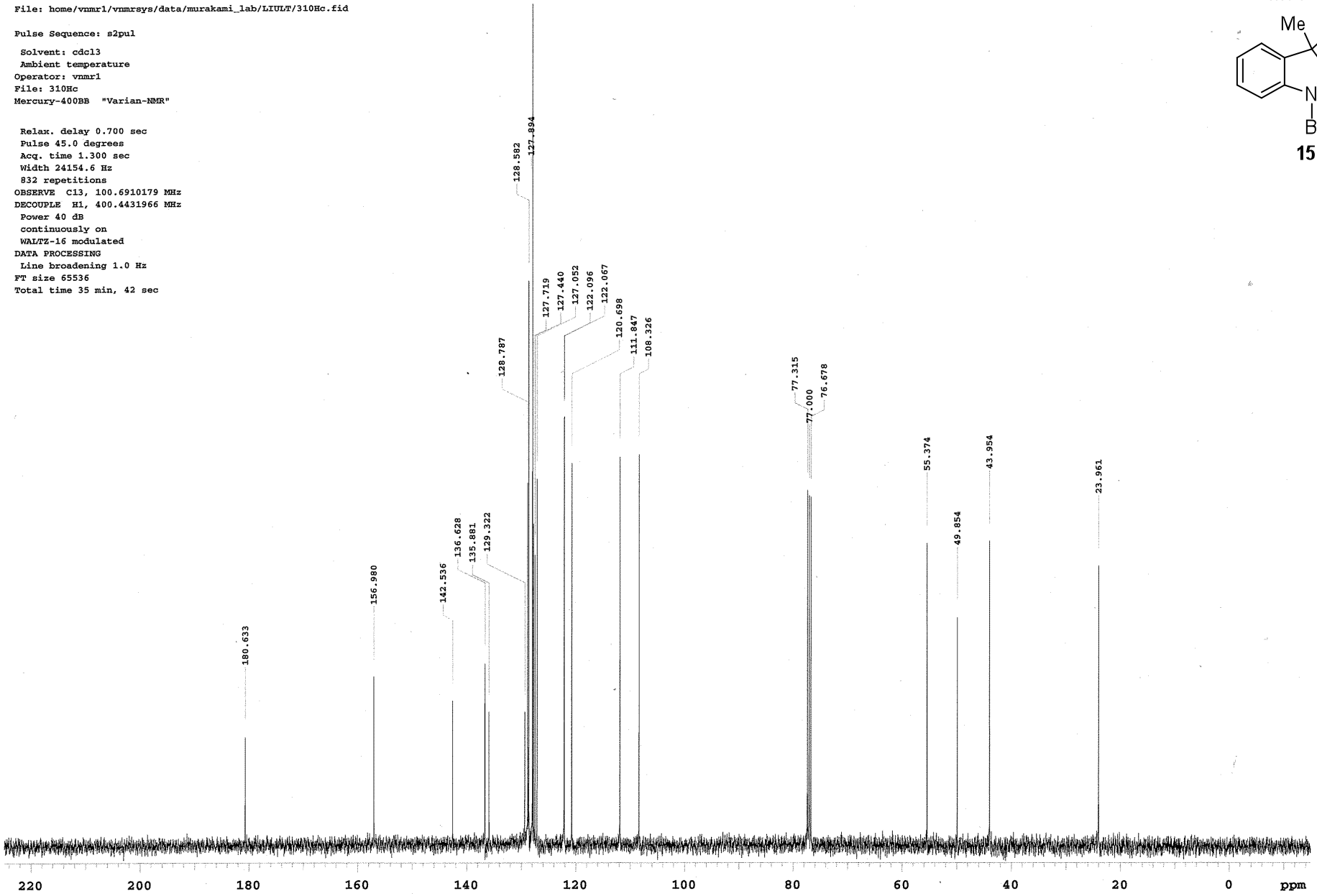
Pulse Sequence: s2pul

Solvent: cdcl3
Ambient temperature
Operator: vnmr1
File: 310Hc
Mercury-400BB "Varian-NMR"

Relax. delay 0.700 sec
Pulse 45.0 degrees
Acq. time 1.300 sec
Width 24154.6 Hz
832 repetitions
OBSERVE C13, 100.6910179 MHz
DECOUPLE H1, 400.4431966 MHz
Power 40 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 1.0 Hz
FT size 65536
Total time 35 min, 42 sec



15f



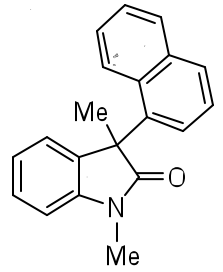
328H

File: home/vnmr1/vnmrsys/data/murakami_lab/LIULT/328h2.fid

Pulse Sequence: s2pul

Solvent: cdcl3
Temp. 26.0 C / 299.1 K
Operator: vnmr1
File: 328h2
Mercury-400BB "Varian-NMR"

Relax. delay 1.500 sec
Pulse 45.0 degrees
Acq. time 3.502 sec
Width 6402.0 Hz
16 repetitions
OBSERVE H1, 400.4411628 MHz
DATA PROCESSING
Line broadening 0.2 Hz
FT size 65536
Total time 1 min, 32 sec



15g

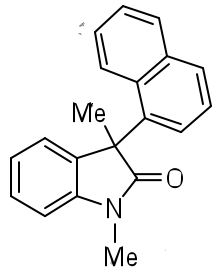
328C

File: home/vnmr1/vnmrsys/data/murakami_lab/LIULT/328c2.fid

Pulse Sequence: s2pul

Solvent: cdcl3
Temp. 26.0 C / 299.1 K
Operator: vnmr1
File: 328c2
Mercury-400BB "Varian-NMR"

Relax. delay 0.700 sec
Pulse 45.0 degrees
Acq. time 1.300 sec
Width 24154.6 Hz
1000 repetitions
OBSERVE C13, 100.6910193 MHz
DECOUPLE H1, 400.4431966 MHz
Power 40 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 1.0 Hz
FT size 65536
Total time 34 min, 54 sec



15g

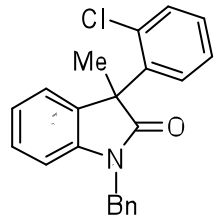
348H

File: home/vnmr1/vnmrsys/data/murakami_lab/LIULT/348h2.fid

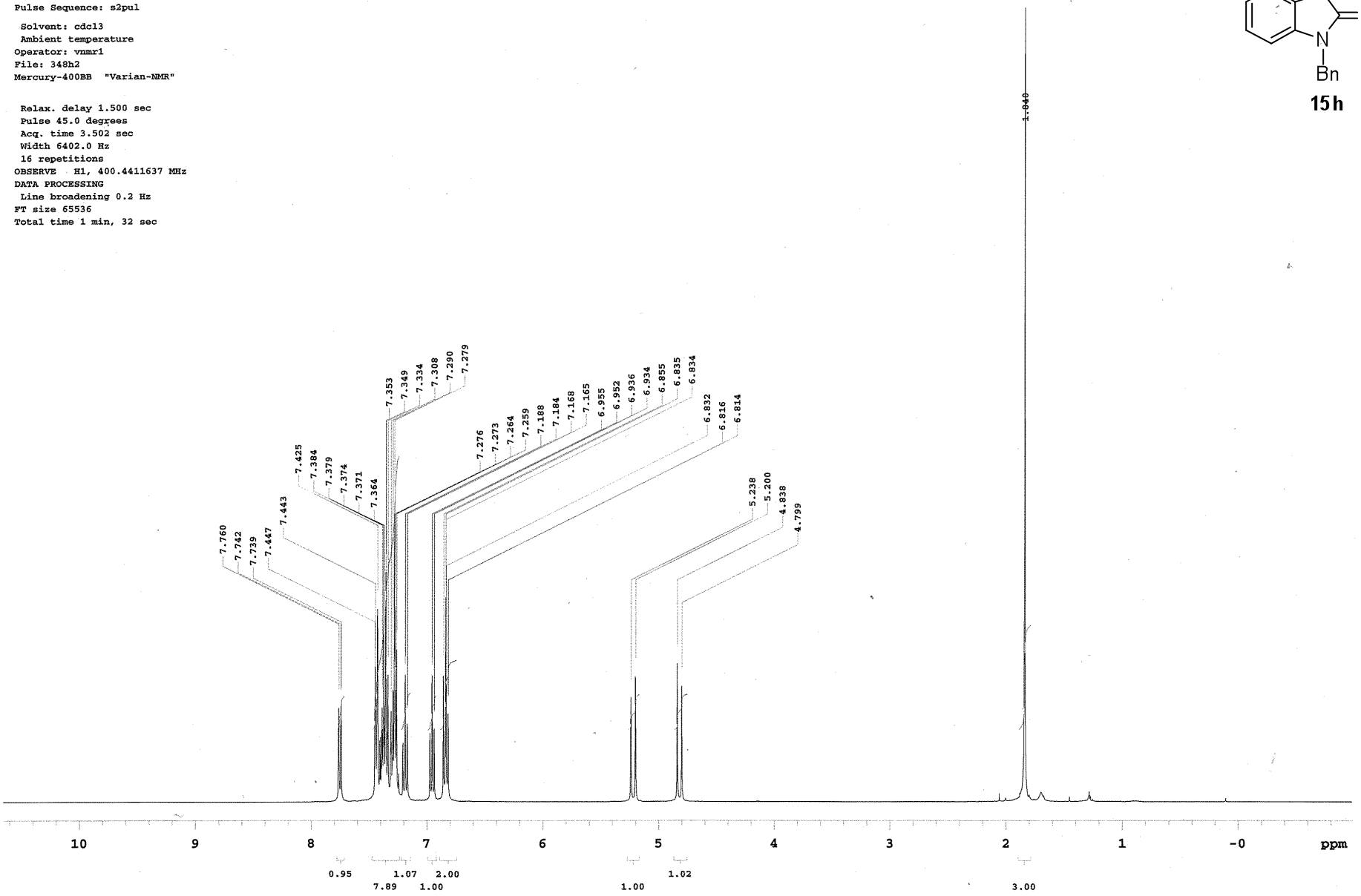
Pulse Sequence: s2pul

Solvent: cdcl3
Ambient temperature
Operator: vnmr1
File: 348h2
Mercury-400BB "Varian-NMR"

Relax. delay 1.500 sec
Pulse 45.0 degrees
Acq. time 3.502 sec
Width 6402.0 Hz
16 repetitions
OBSERVE H1, 400.4411637 MHz
DATA PROCESSING
Line broadening 0.2 Hz
FT size 65536
Total time 1 min, 32 sec



15h



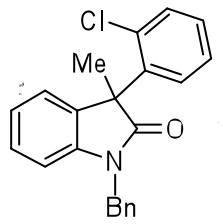
348C

File: home/vnmr1/vnmrsys/data/murakami_lab/LIULT/348c.fid

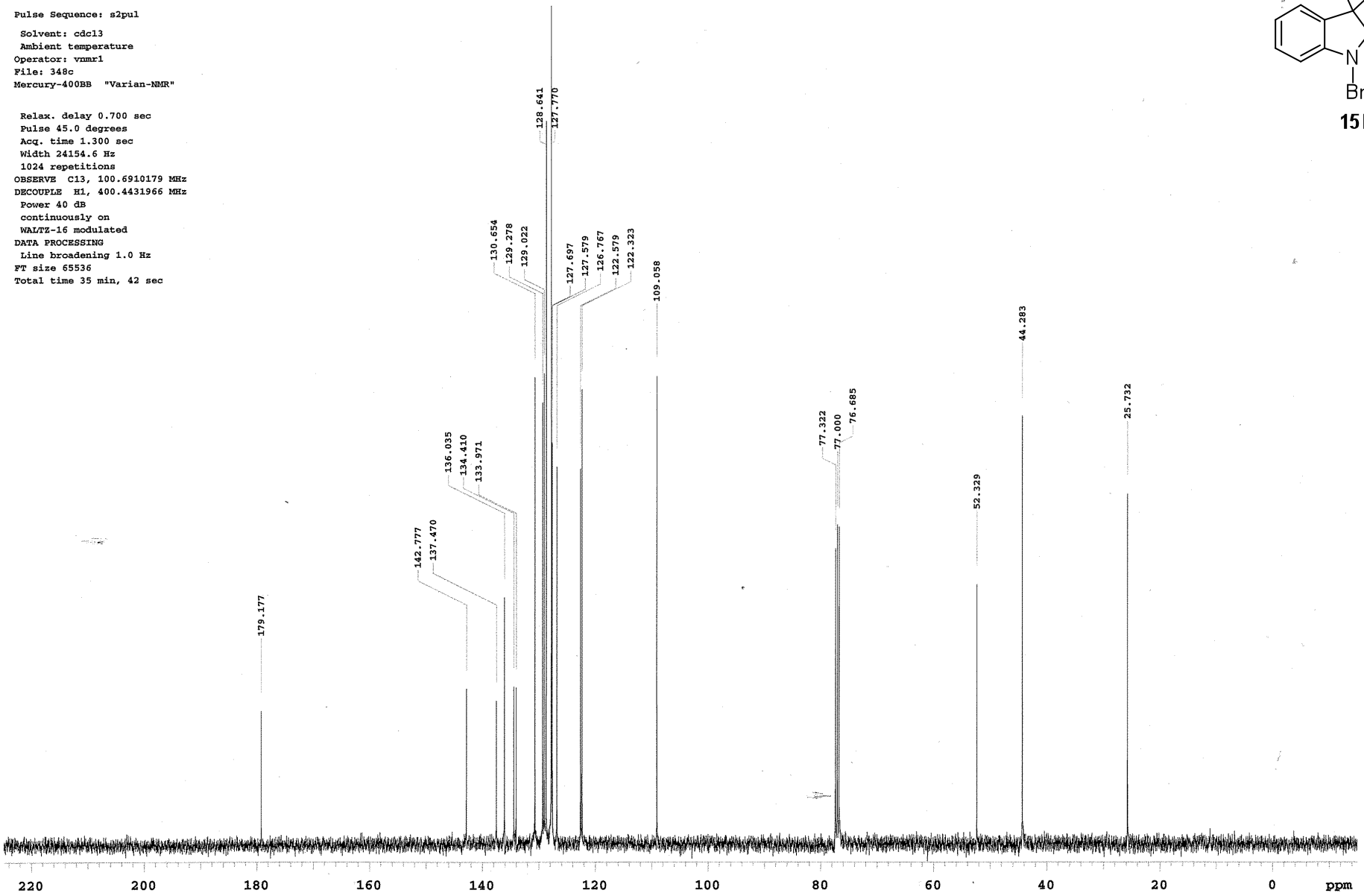
Pulse Sequence: s2pul

Solvent: cdcl3
Ambient temperature
Operator: vnmr1
File: 348c
Mercury-400BB "Varian-NMR"

Relax. delay 0.700 sec
Pulse 45.0 degrees
Acq. time 1.300 sec
Width 24154.6 Hz
1024 repetitions
OBSERVE C13, 100.6910179 MHz
DECOUPLE H1, 400.4431966 MHz
Power 40 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 1.0 Hz
FT size 65536
Total time 35 min, 42 sec

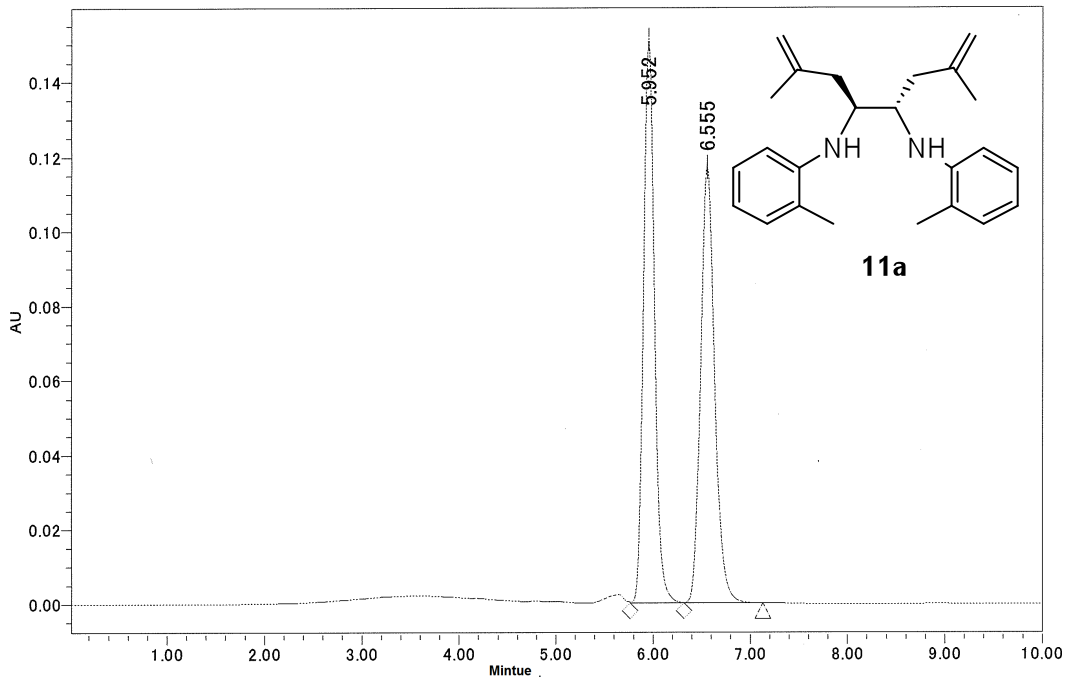


15h



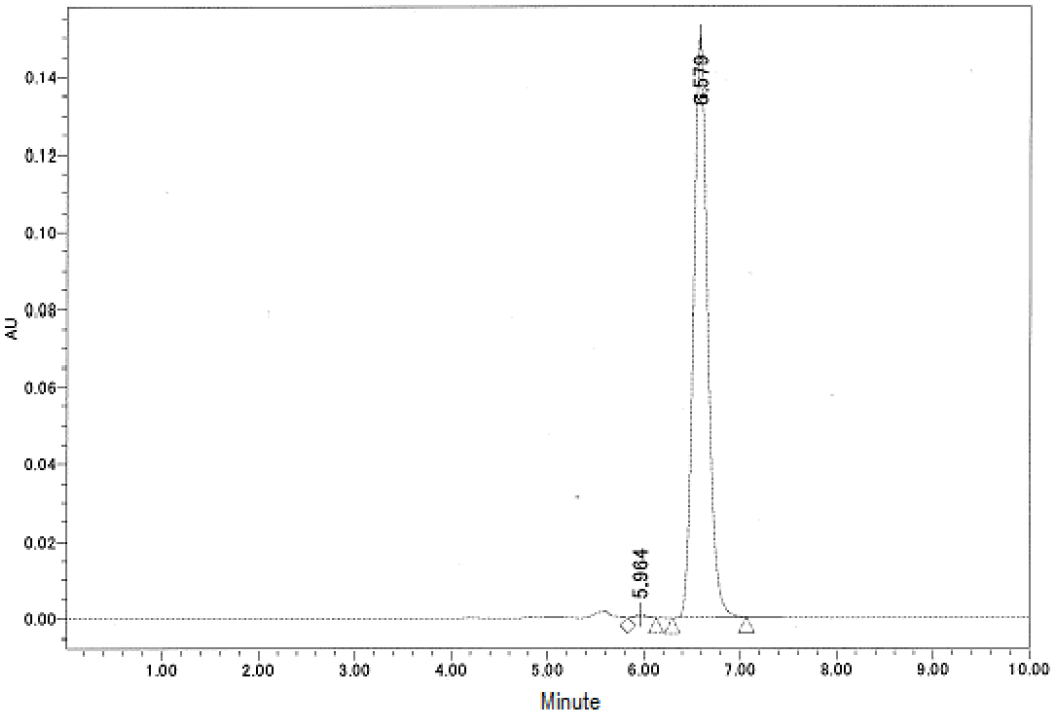
11a (*Scheme 1*)

Racemic mixture



Peak	Name	Retention time (min)	Area(μVs)	Height(μV)	Concentration	Unit
1		5.952	1184965	151503		
2		6.555	1191661	117588		

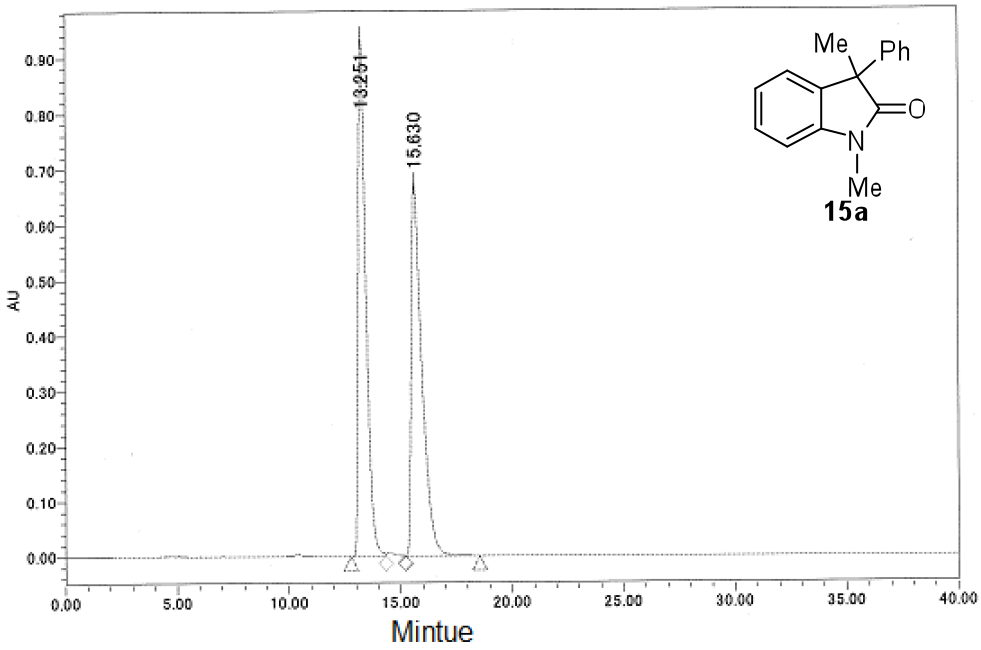
Enantioenriched mixture



Peak	Name	Retention time (min)	Area(μVs)	Height(μV)	Concentration	Unit
1		5.964	6094	746		
2		6.579	1552260	150570		

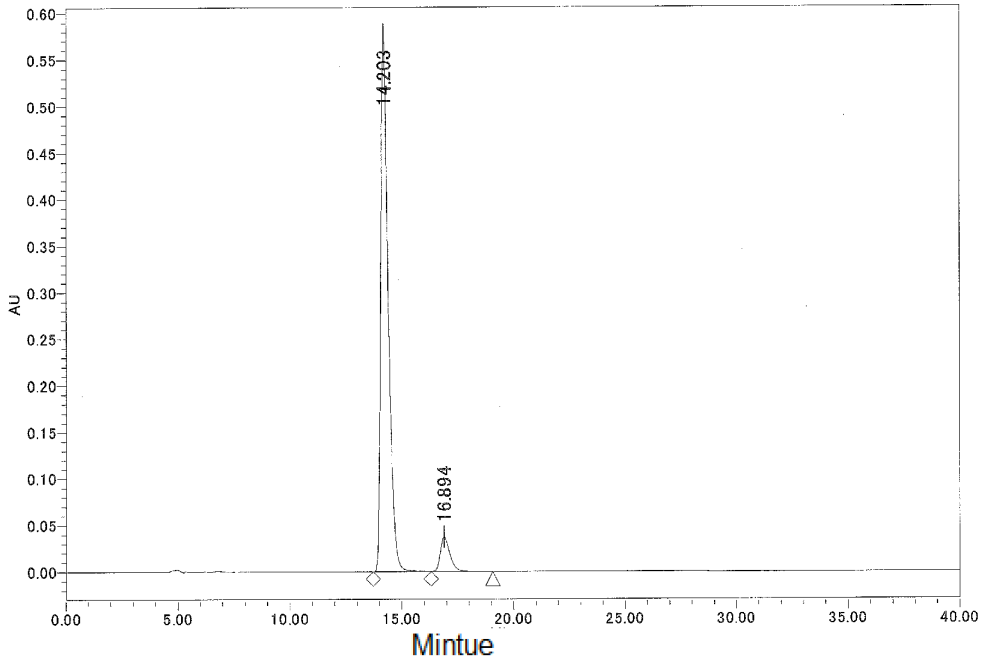
15a (*Table 1, Entry 2*)

Racemic mixture



Peak	Name	Retention time (min)	Area(μVs)	Height(μV)	Concentration	Unit
1		13.251	22473207	936667		
2		15.630	22384682	673280		

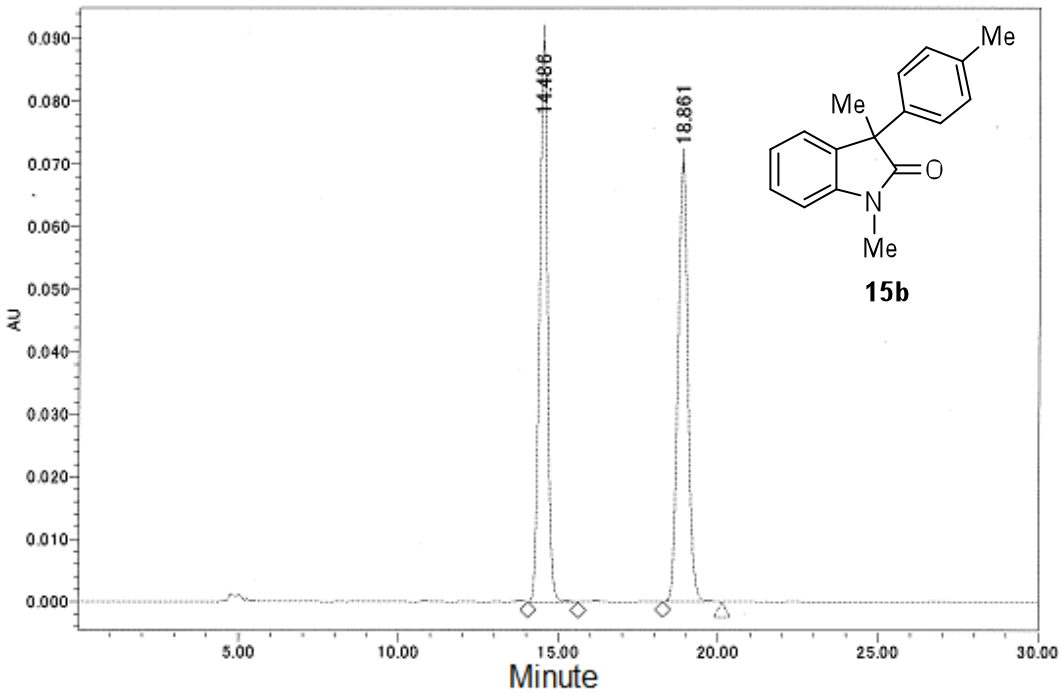
Enantioenriched mixture



Peak	Name	Retention time (min)	Area(μVs)	Height(μV)	Concentration	Unit
1		14.203	13588741	577111		
2		16.894	1117848	37342		

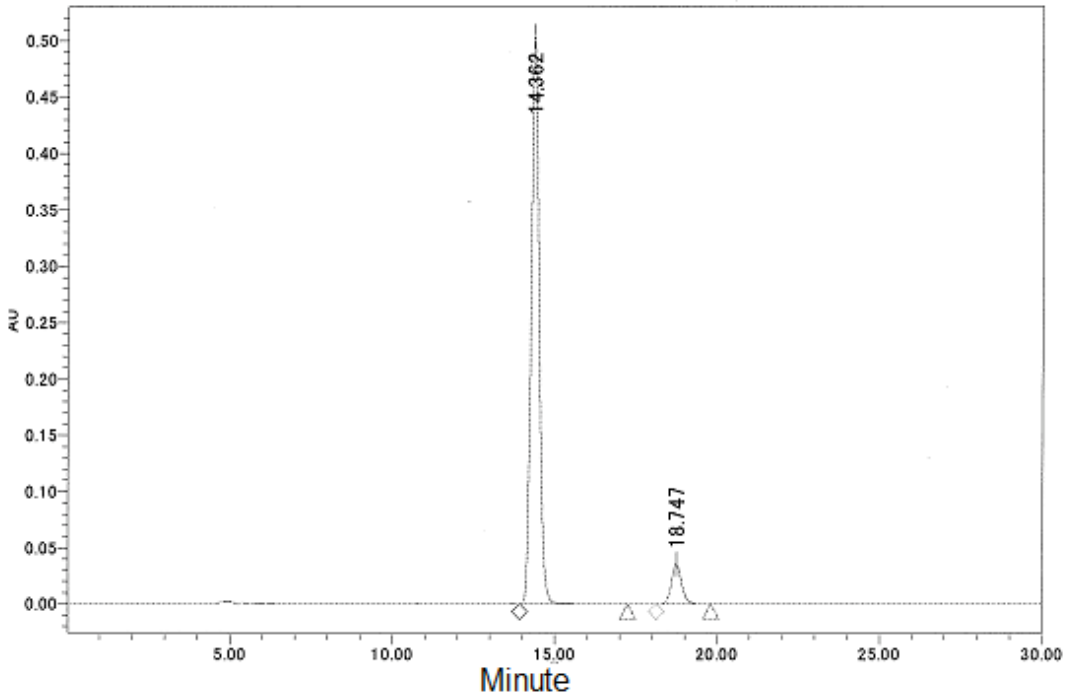
15b (*Table 2, Entry 1*)

Racemic mixture



Peak	Name	Retention time (min)	Area(μVs)	Height(μV)	Concentration	Unit
1		14.486	1559454	90370		
2		18.861	1551572	70554		

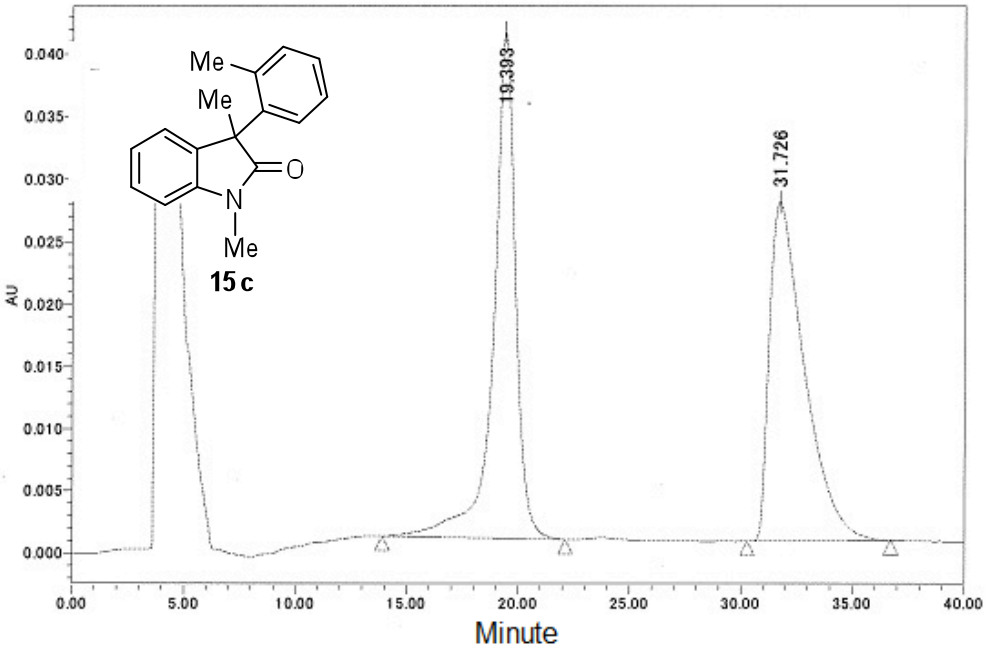
Enantioenriched mixture



Peak	Name	Retention time (min)	Area(μVs)	Height(μV)	Concentration	Unit
1		14.362	8730586	504828		
2		18.747	773872	35409		

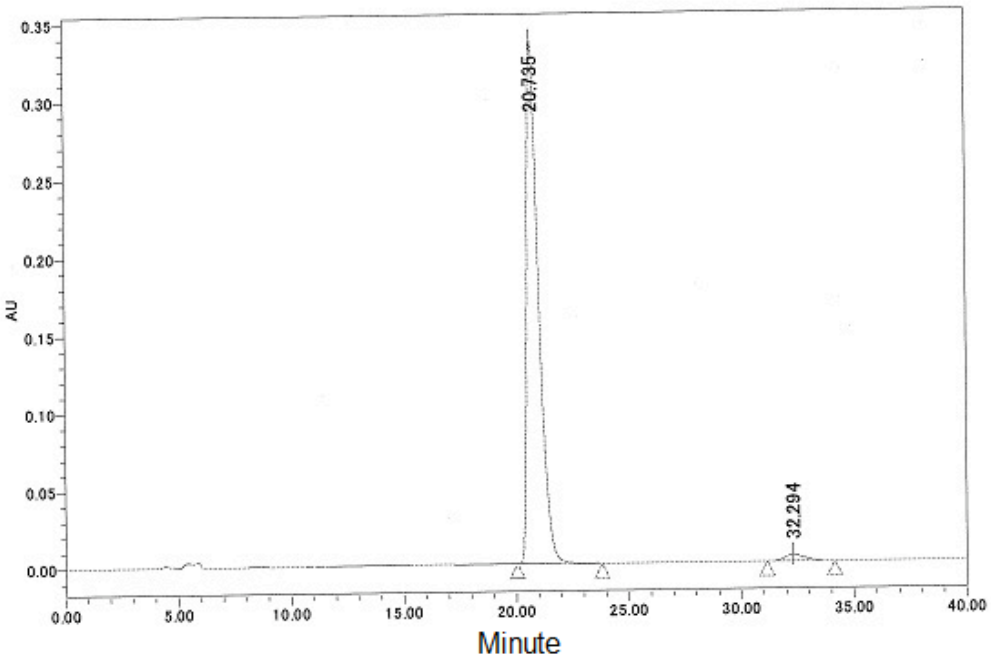
15c (*Table 2, Entry 2*)

Racemic mixture



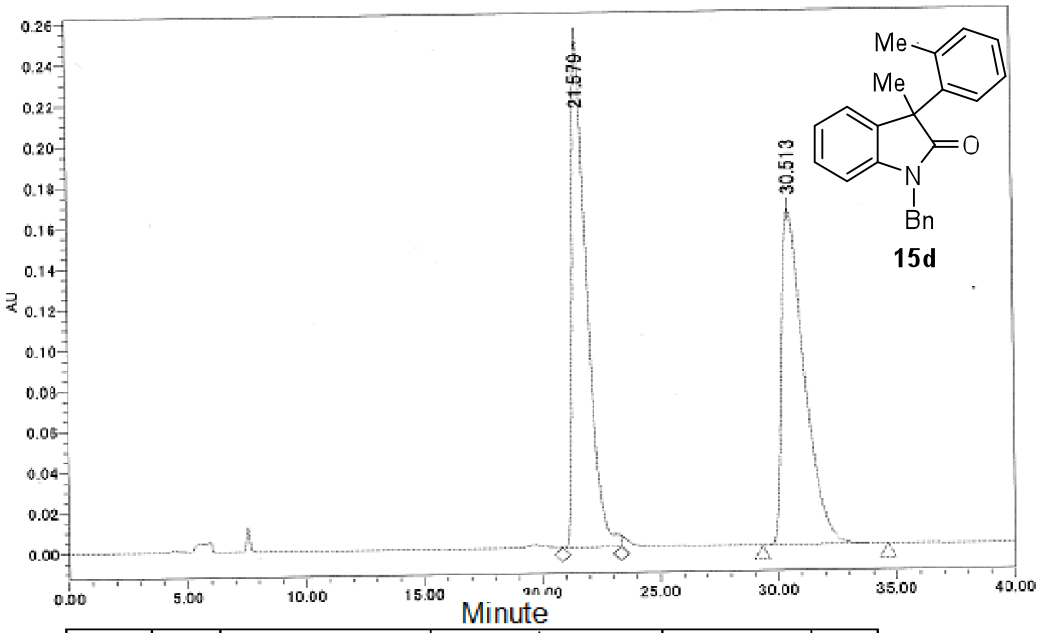
Peak	Name	Retention time (min)	Area(μVs)	Height(μV)	Concentration	Unit
1		19.393	2927475	40596		
2		31.726	2984283	27218		

Enantioenriched mixture



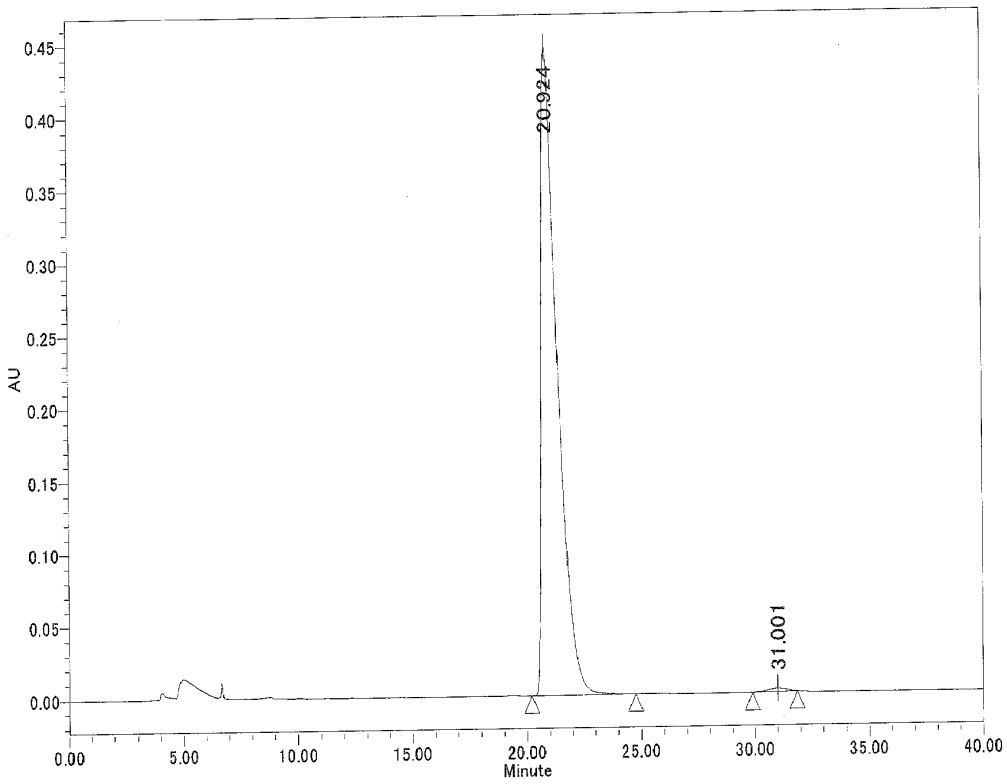
Peak	Name	Retention time (min)	Area(μVs)	Height(μV)	Concentration	Unit
1		20.735	12333929	338542		
2		32.294	267580	4444		

15d (*Table 2, Entry 3*)
Racemic mixture



Peak	Name	Retention time (min)	Area(μVs)	Height(μV)	Concentration	Unit
1		21.579	11100604	249910		
2		30.513	11016467	164881		

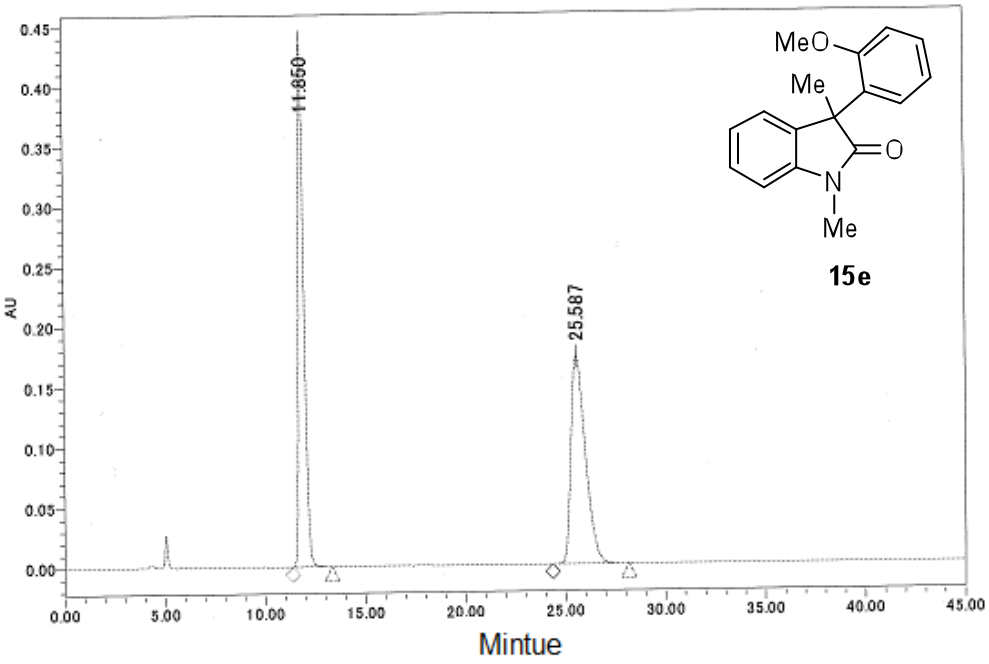
Enantioenriched mixture



Peak	Name	Retention time (min)	Area(μVs)	Height(μV)	Concentration	Unit
1		20.924	21735230	445835		
2		31.001	126662	2291		

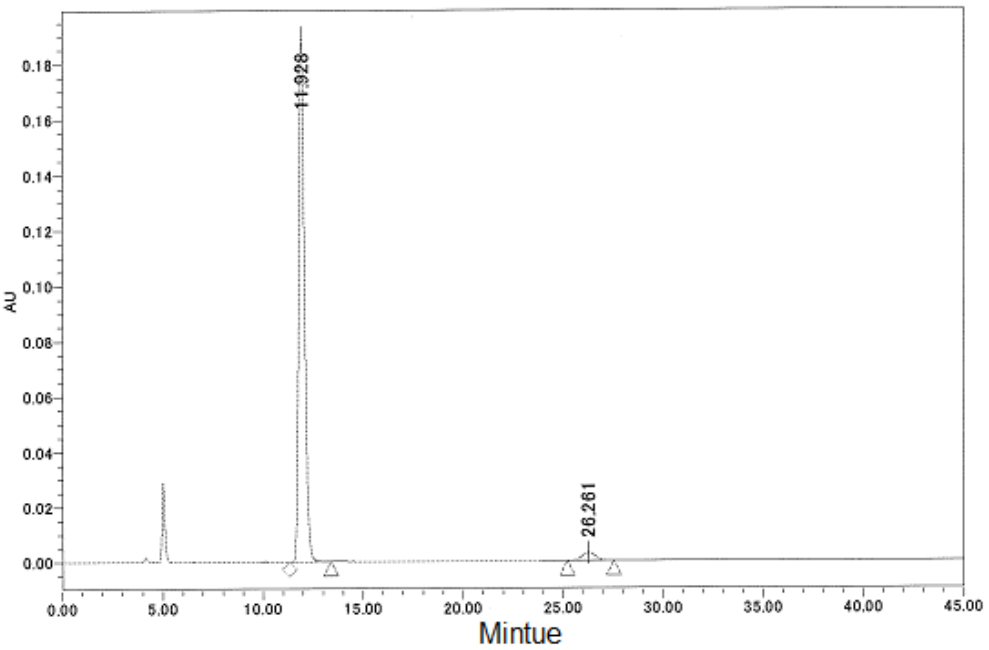
15e (*Table 2, Entry 4*)

Racemic mixture



Peak	Name	Retention time (min)	Area(μVs)	Height(μV)	Concentration	Unit
1		11.850	8615792	436682		
2		25.587	8634107	172084		

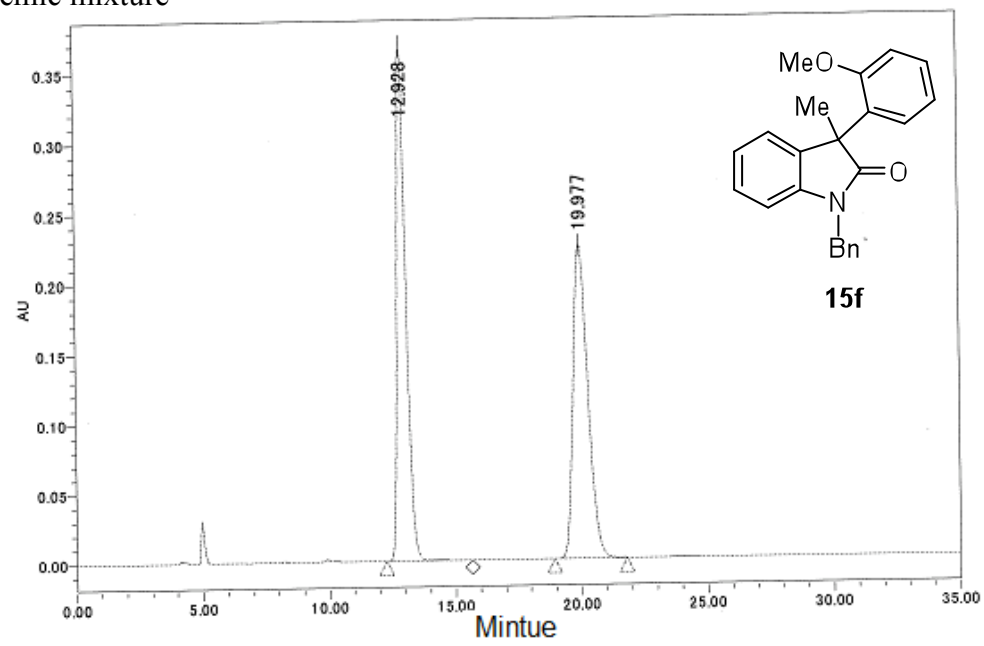
Enantioenriched mixture



Peak	Name	Retention time (min)	Area(μVs)	Height(μV)	Concentration	Unit
1		11.928	3185736	189861		
2		26.261	139968	2933		

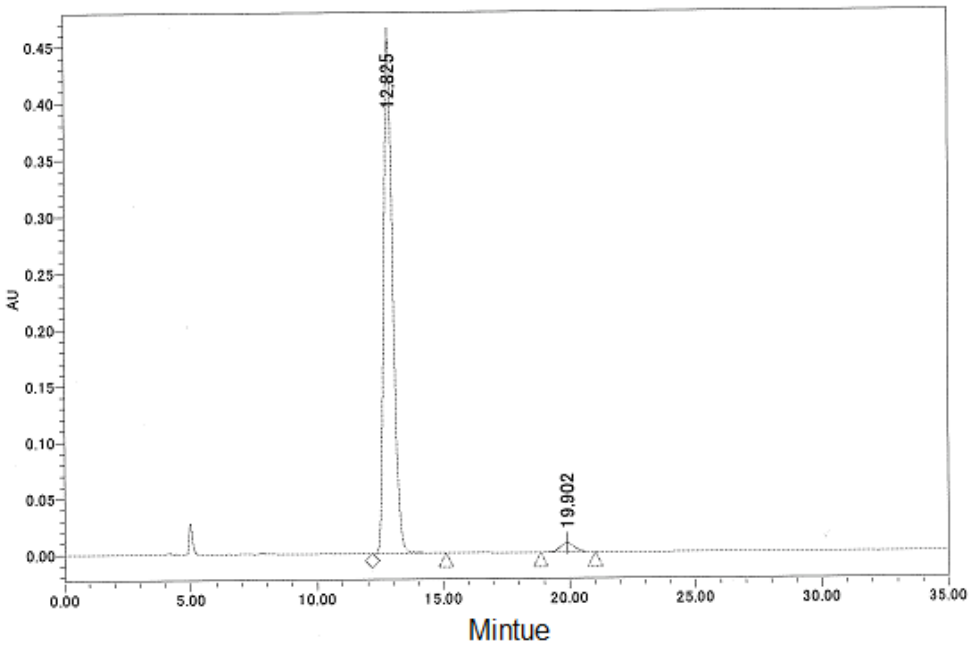
15f (*Table 2, Entry 5*)

Racemic mixture



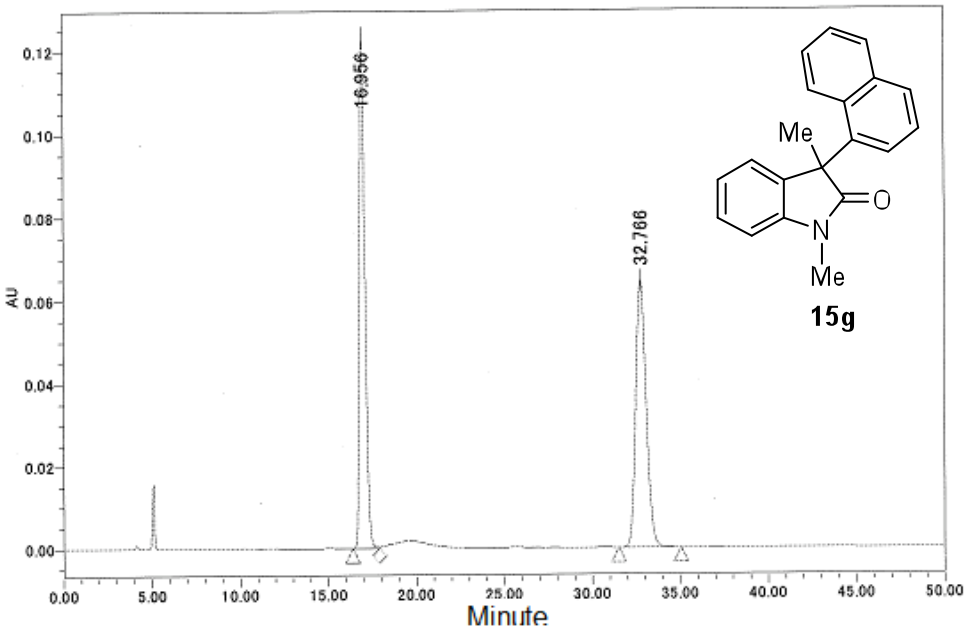
Peak	Name	Retention time (min)	Area(μVs)	Height(μV)	Concentration	Unit
1		12.928	9239697	367914		
2		19.997	9137331	224183		

Enantioenriched mixture



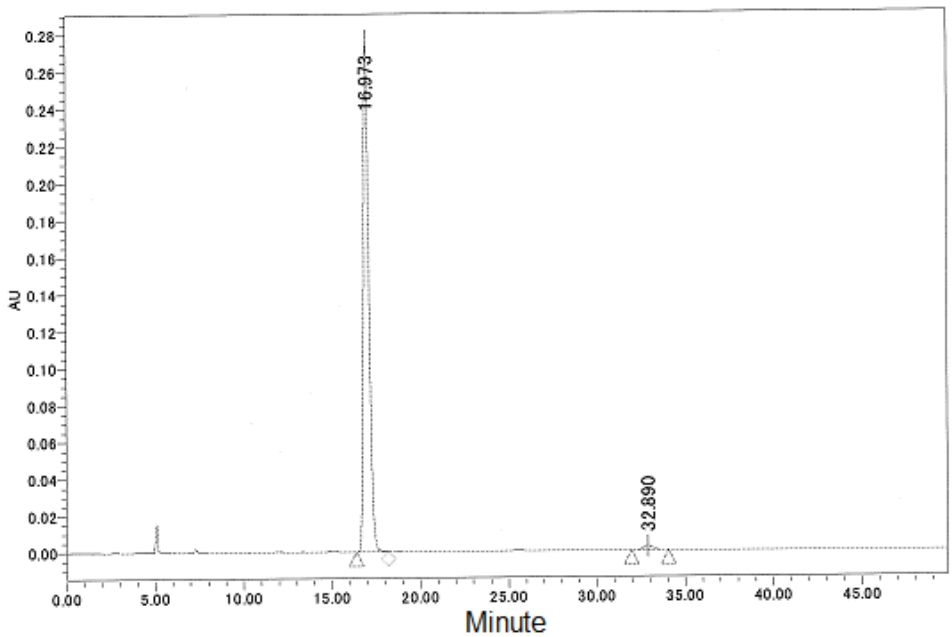
Peak	Name	Retention time (min)	Area(μVs)	Height(μV)	Concentration	Unit
1		12.825	11375981	456863		
2		19.902	325717	8207		

15g (*Table 2, Entry 6*)
Racemic mixture



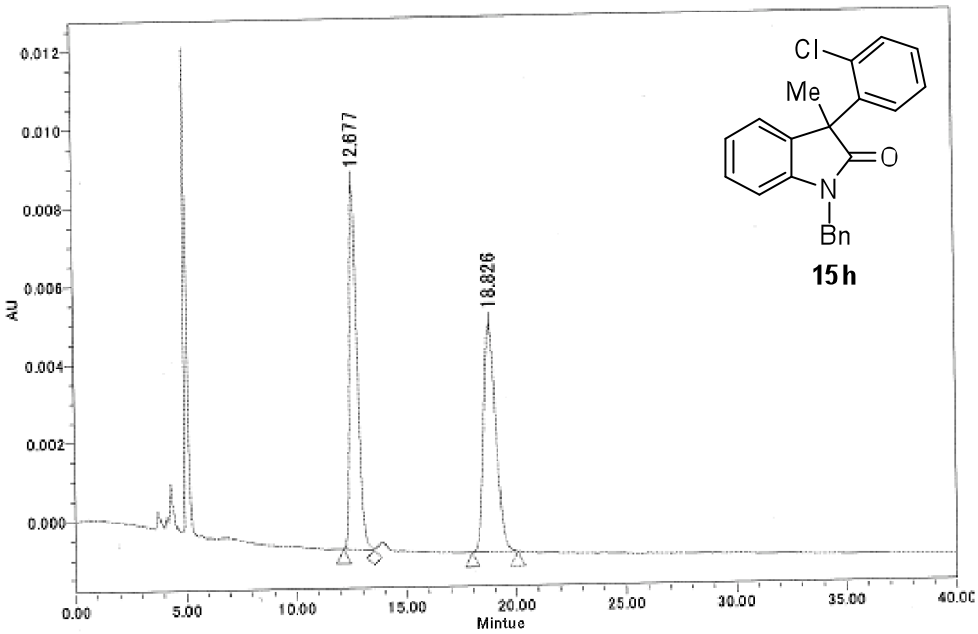
Peak	Name	Retention time (min)	Area(μVs)	Height(μV)	Concentration	Unit
1		16.956	2654469	123404		
2		32.766	2658435	64571		

Enantioenriched mixture



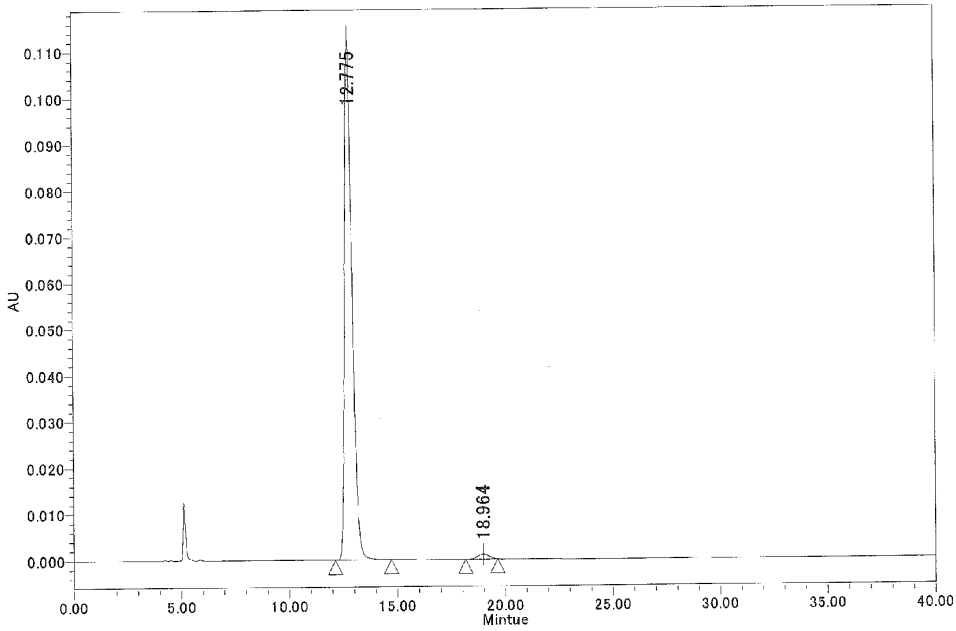
Peak	Name	Retention time (min)	Area(μVs)	Height(μV)	Concentration	Unit
1		16.973	6006481	276994		
2		32.890	98352	2418		

15h (*Table 2, Entry 7*)
Racemic mixture



Peak	Name	Retention time (min)	Area(μVs)	Height(μV)	Concentration	Unit
1		12.677	225279	9390		
2		18.826	223666	5837		

Enantioenriched mixture



Peak	Name	Retention time (min)	Area(μVs)	Height(μV)	Concentration	Unit
1		12.775	2707132	113382		
2		18.964	40841	1116		