Supplementary Information

Catalytic asymmetric Diels-Alder reactions involving aryl vinyl ketones

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General Information

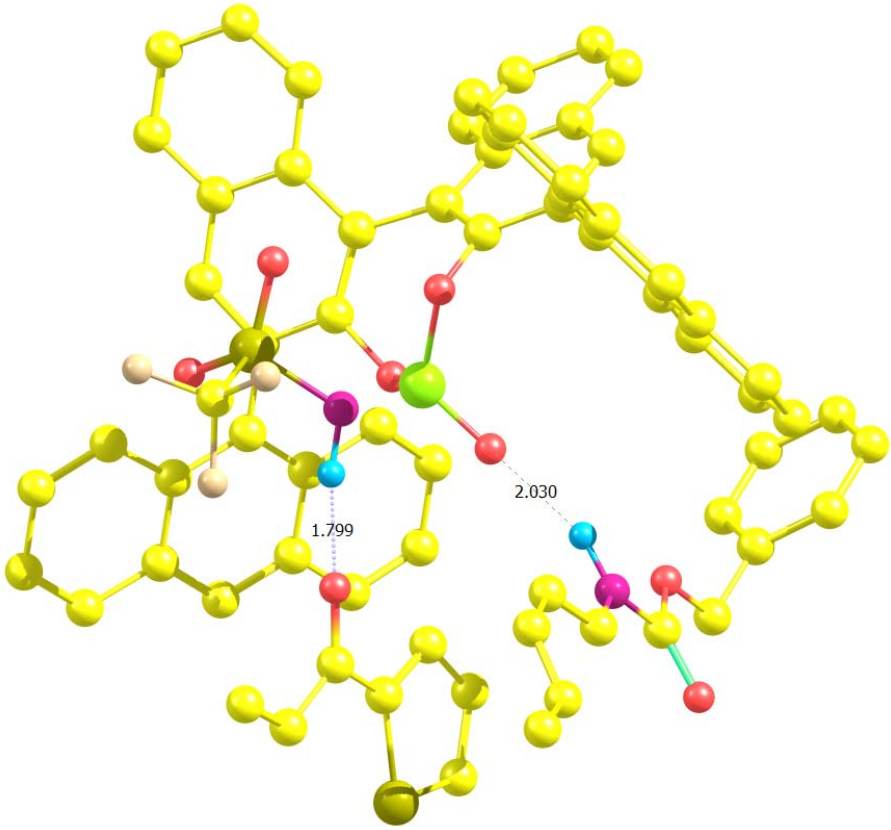
All glassware for reactions using anhydrous solvents were dried under high vacuum (< 0.1 torr) using a heat gun. General Schlenk techniques were applied for addition and transfer operations.

Commercial reagents and solvents were purchased from Acros, Alfa Aesar, J&K Scientific Ltd., Sinopharm Chemical Reagent Co. or Beijing Chemical Works, and used as received unless otherwise noted. Toluene, THF or Et_2O was distilled over sodium benzophenone ketyl under N_2. CH_2Cl_2, $CHCl_3$, CCl_4 or CH_3CN was distilled over CaH_2 under N_2. CH_3OH was distilled over Mg flakes. $B(OEt)_3$ was distilled over Na ribbons prior to use. Silica gel products were purchased from Qingdao Haiyang Chemical Co.. Thin-layer chromatography was performed on precoated silica gel (0.2-0.25 mm thick) plates with fluorescent indicator 254 nm. The plate was visualized with 254 nm UV lamp, PMA or $KMnO_4$ stain. Column chromatography was performed on 200-300 mesh silica gel.

^1H NMR and ^{13}C NMR spectra were recorded on a Bruker Avance 400 spectrometer at 400 MHz and 100 MHz respectively. Chemical shifts of ^1H NMR and ^{13}C NMR were referred to TMS (δ =0) and chloroform (δ = 77.0) respectively. The following abbreviations were used to denote the multiplicity of each peak: s (singlet), d (doublet), t (triplet), q (quartet), dd (doublet of doublets), dt (doublet of triplets), br (broad signal), m (multiplet). IR spectra were recorded on a Nicolet AVATAR 360 FT-IR spectrometer. The sample was prepared as a thin-film on a NaCl disc. MS spectra were obtained on a Waters Quattro Micro triple quadrupole mass spectrometer. HPLC was performed at room temperature using a Shimazu LC-20AT solvent delivery unit equipped with a SPD-20A UV/VIS detector. A Daicel Chiralcel OD-H, OJ-H or Chiralpak AD-H column (0.46 cm Φ × 25 cm) without guard column was used. Specific rotation was measured on a Perkin-Elmer 343 Polarimeter using the 589 nm D-line of sodium lamp and a quartz cell with 10 cm path length. X-ray diffraction experiment was conducted on a Rigaku Saturn 724 diffractometer using Mo Kα radiation in ICCAS, Beijing, China.

***Ab initio* density functional theory (DFT) calculations**[1]

The density functional theory (DFT) method was used to optimize stationary structures of the complex of catalyst **4g** with benzyl (1*E*,3*E*)-1,3-pentadienylcarbamate (**1a)** and 2-thiophenyl vinyl ketone. The B3LYP functional and 6-31G* basis set were employed for structural optimizations. In the present work, all *ab initio* calculations were performed using Gaussian program packages.



The schematic minimum of "catalyst-reactants" complex with hydrogen bond in Å. Some hydrogen atoms are omitted for clarity.

The cartesian coordinates of optimized "catalyst-reactants" complex

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6	-2.272340000	-3.685103000	1.587610000
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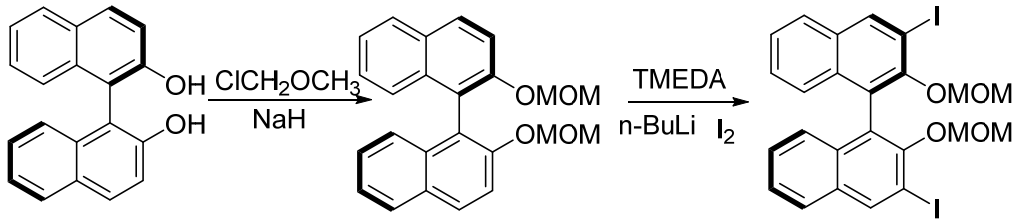


(*R*)-2,2'–Bis(methoxymethoxy)-1,1'-binaphthyl[2]

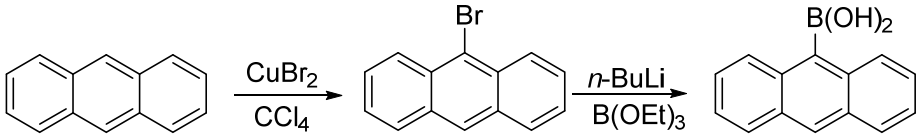
Note: Chloromethyl methyl ether was used as received.

Under a N_2 atmosphere, NaH (prewashed with hexanes, 3.5 g, 146 mmol, 2.2 equiv.) was suspended in anhydrous THF (200 mL) cooled at 0°C. A solution of (*R*)-BINOL (19 g, 66.4 mmol) in THF (100 mL) was added dropwise through an addition funnel. After the addition was complete, the mixture was stirred at 0°C for 1 h. Then it was allowed to warm to r.t. and stirred at r.t. for 15 min. A clear solution was obtained. It was again cooled to 0°C. Chloromethyl methyl ether (11.08 mL, 146 mmol, 2.2 equiv.) was slowly added via syringe. After completion of the addition, the mixture was warmed to r.t. and stirred overnight. TLC indicated small amount of mono-protected BINOL was present. Additional NaH (2.25 g, 94 mmol, 1.4 equiv.) was added slowly at r.t. and the mixture stirred at r.t. for ca. 0.5 h. Chloromethyl methyl ether (5 mL, 66 mmol, 1 equiv.) was slowly added via syringe. After the reaction was complete, saturated aqueous NH_4Cl (100 mL) was added. The aqueous layer was extracted with AcOEt (2 × 50 mL). The organic layers were combined, dried over anhydrous Na_2SO_4 and concentrated to give the final product as an off-white solid (24.7 g, 99% yield). R_f = 0.33 (hexanes/AcOEt = 5/1).

(*R*)-3,3'-Diiodo-2,2'-bis(methoxymethoxy)-1,1'-binaphthyl[3]

n-BuLi (2.5 M in hexanes, 16 mL, 40 mmol, 2.5 equiv.) was added to a solution of (*R*)-2,2'-bis(methoxymethoxy)-1,1'-binaphthyl (6 g, 16 mmol) in anhydrous Et_2O (120 mL) at r.t.. The mixture was stirred at r.t. for 3 h and cooled to 0°C. Anhydrous THF (32 mL) was added. After 10 min, a solution of iodine (12 g, 48 mmol, 3 equiv.) in THF (20 mL) was added dropwise. The mixture was allowed to warm to r.t. over 4 h. Saturated aqueous $Na_2S_2O_3$ (100 mL) was added to remove excessive iodine. The aqueous mixture was extracted with AcOEt (2 × 50 mL). The combined organic layers were washed with saturated aqueous $Na_2S_2O_3$ (100 mL), dried over Na_2SO_4 and

concentrated. The crude product (11.45 g) was purified by silica gel column chromatography (hexanes/AcOEt = 20/1 to 10/1). The product was obtained as a yellow solid (6.5 g, 65% yield). R_f = 0.55 (hexanes/AcOEt = 5:1).



9-Bromoanthracene[4]

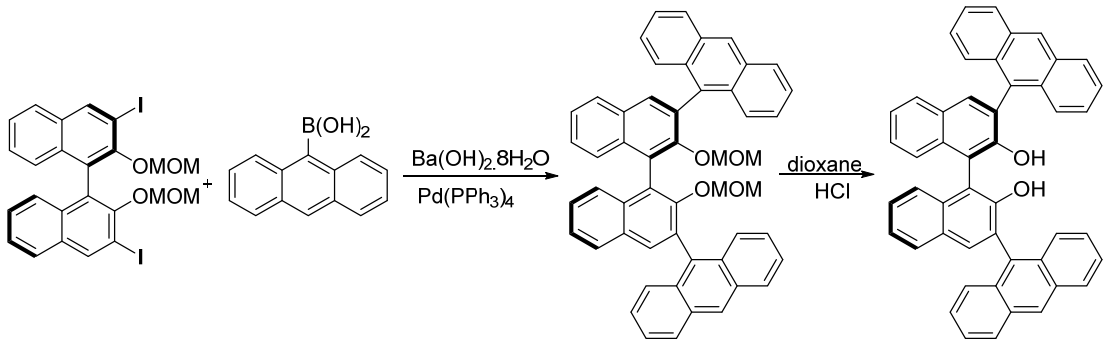
Note: CCl_4 was distilled over CaH_2. Wet CCl_4 led to a very poor yield.

A one-necked round bottom flask was charged with anthracene (93% purity, 28.5 g, 149 mmol), $CuBr_2$ (67.0 g, 300 mmol, 2 equiv.) and anhydrous CCl_4 (500 mL). The flask was fitted with a reflux condenser, which was connected to an HBr absorption apparatus. The reaction mixture was refluxed for 16 h at 90°C. After cooling to room temperature, CuBr was filtered off. The filtrate was filtered through an alumina column, and the column was eluted with CCl_4 (4 × 100 mL). The eluents were concentrated to give the crude product as a yellow solid (35.15 g, 100% yield). Recrystallization in hot EtOH gave crystalline product with very nice purity. But for our synthesis, this was not necessary.

9-Anthraceneboronic acid[5]

To a 500 mL three-necked flask 9-bromoanthracene (12.5 g, 48 mmol) and anhydrous THF (150 mL) were added. The solution was cooled to -78°C. *n*-BuLi (40 mL, 96 mmol, 2 equiv.) was added at -78°C. The reaction mixture was stirred for 0.5 h at -78°C and then $B(OEt)_3$ (16.5 mL, 96 mmol, 2 equiv.) was added. After completion of the addition, the reaction mixture was allowed to warm to room temperature and stirred for 12 h. 2 N HCl (100 mL) was added to quench the reaction. The mixture was stirred for 30 min. The aqueous layer was extracted with AcOEt (2 × 40 mL). The combined organic layers were dried over anhydrous Na_2SO_4 and concentrated. TLC (hexanes) indicated anthracene was included in the crude product. The residue was treated with hexanes (100 mL) and the mixture refluxed for 1 h and cooled to r.t.. The solution containing anthracene was filtered off to leave pure 9-anthraceneboronic acid as a light yellow solid (9.7 g, 90% yield). R_f = 0.33

(hexanes/AcOEt = 3:1)



(*R*)-3,3'-Di(9-anthryl)-2,2'-bis(methoxymethoxy)-1,1'-binaphthyl[6]

A single neck round bottom flask (250 mL) was charged with (*R*)-3,3'-diiodo-2,2'-bis(methoxymethoxy)-1,1'-binaphthyl (6.5 g, 10.38 mmol), $Ba(OH)_2 \cdot 8H_2O$ (9.82 g, 31.14 mmol, 3 equiv.), dioxane (100 mL) and H_2O (33 mL). N_2 gas was bubbled through the mixture for 30 min before 9-anthraceneboronic acid (6.9 g, 31.14 mmol, 3 equiv.) and $Pd(PPh_3)_4$ (1.15 g, 1 mmol) were added. The reaction mixture was then refluxed for 24 h under N_2. It was cooled to room temperature and concentrated to remove dioxane. Then 1 N HCl (50 mL) and CH_2Cl_2 (50 mL) were added and the mixture stirred for 10 min. The organic layer was washed with 1 N HCl (2 × 50 mL), brine (100 mL), dried over anhydrous Na_2SO_4 and concentrated. TLC (hexanes) indicated anthracene was included in the crude product. The crude product was refluxed in hexanes (150 mL) for 2 h. After cooling to r.t., the hexanes solution containing anthracene was filtered off to leave the product as a yellow solid (7.99 g, 100% yield). R_f = 0.3 (hexanes/ethyl acetate = 10/1).

(*R*)-3,3′-Di(9-anthryl)-2,2′-bis(methoxymethoxy)-1,1′-binaphthol[6]

To a single neck 250 mL round bottom flask were added (*R*)-3,3'-dianthryl-2,2'-bis(methoxymethoxy)-1,1'-binaphthyl (7.54 g, 10.38 mmol), 12 N HCl (10 mL) and dioxane (100 mL). The mixture was heated at 60°C for 12 h. It was cooled to room temperature and concentrated to remove dioxane. The residue was dissolved in CH_2Cl_2 (50 mL) and dried with anhydrous Na_2SO_4. To the CH_2Cl_2 filtrate was added suitable amount of acetone and the precipitated solids were collected by filtration.

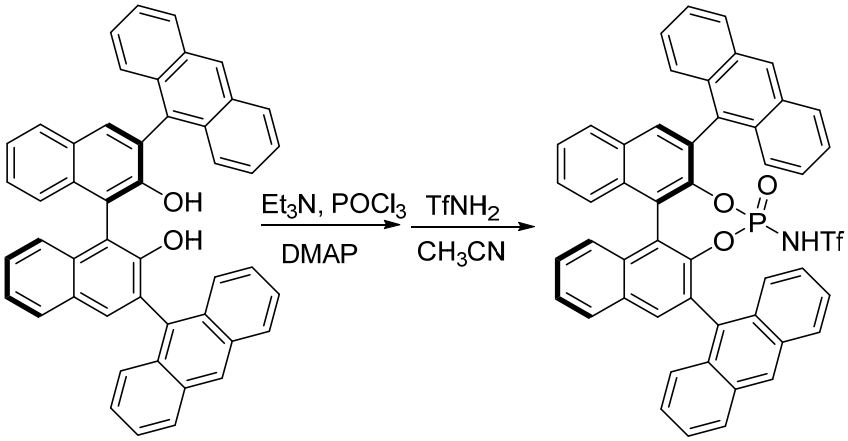
Further crops of the product was obtained in the following way: The filtrate was

concentrated and the residue treated with hot hexanes to remove anthracene. The product was once again dissolved in CH_2Cl_2 and precipitated with acetone.

Totally 5.6 g of the product was obtained as an off-white solid (84.5 % yield). R_f = 0.14 (hexanes/AcOEt = 10/1).

Synthesis of Chiral *N*-Triflyl Phosphoramide (cat. 4g)[7]

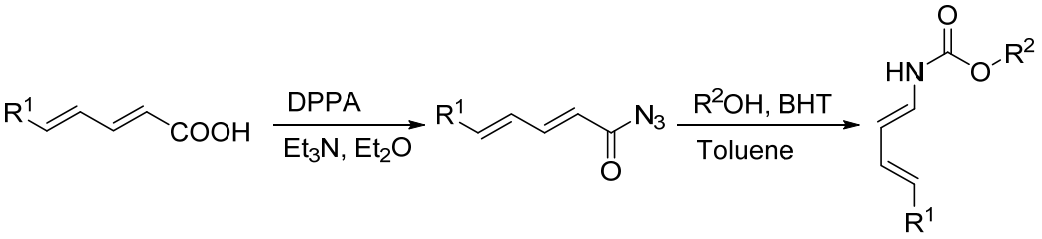
*Note: Chiral N-triflyl phosphoramide (**cat. 4a-4f**) was similarly prepared from the corresponding 3,3'-disubstitutued BINOL.*



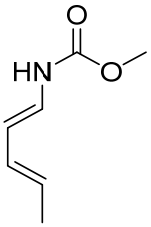
To a solution of (*R*)-3,3'-dianthryl-2,2'-bis(methoxymethoxy)-1,1'-binaphthol (3 g, 4.7 mmol) in anhydrous CH_2Cl_2 (60 mL) were added Et_3N (4.68 mL, 33 mmol), DMAP (1.14 g, 9.36 mmol) and $POCl_3$ (522 μL, 5.61 mmol) at 0°C. After stirring for 1 h at room temperature, anhydrous CH_3CN (78 mL) and $TfNH_2$ (1.4 g, 9.36 mmol) were added. The mixture was refluxed for 12 h at 100°C (oil bath) and cooled to r.t.. H_2O (50 mL) and CH_2Cl_2 (50 mL) were added and the mixture washed successively with saturated $NaHCO_3$ (100 mL), 6 N HCl (2 × 50 mL), dried over anhydrous Na_2SO_4, and concentrated. The residue was washed with small amount of CH_2Cl_2 to give very pure product as a light yellow solid (1.65 g). The CH_2Cl_2 filtrate was concentrated and the residue chromatographed on silica gel using 1:1 hexanes/ethyl acetate as eluent to give another crop of product (1.92 g).

The above product was dissolved in CH_2Cl_2, and the solution washed with 6 N HCl, dried over anhydrous Na_2SO_4 and concentrated. Totally 3.3 g of the phosphoramide was obtained in 85% yield.

General Procedure for The Synthesis of 1,3-Dienylcarbamte[8,9]



Methyl (1*E*,3*E*)-1,3-pentadienylcarbamate (1c)

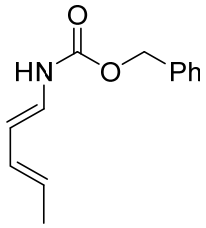


Sorbic acid was dissolved in anhydrous Et_2O (80 mL) under N_2 atmosphere. The solution was cooled to 0°C and dry Et_3N (11 mL, 79 mmol, 1.1 equiv.) was added. After 5 min, diphenylphosphoryl azide (DPPA) (17.2 mL, 80.4 mmol, 1.1 equiv.) was added and the reaction mixture was allowed to warm to room temperature. After 1 h, saturated aqueous $NaHCO_3$ (80 mL) and Et_2O (80 mL) were added to quench the reaction. The organic layer was separated and the aqueous layer extracted with Et_2O (3 × 50 mL). The combined organic layers were dried over anhydrous Na_2SO_4 and concentrated in vacuum. The brown oil was passed through a short column of silica gel (hexanes/ethyl acetate = 10: 1) to afford crude sorboyl azide as a bright yellow oil (12.85 g), which was used immediately in the next step without characterization.

In a three-necked 250 mL round bottom flask 3,5-di-tert-butyl-4-hydroxytoluene (BHT, 66.1 mg, 0.3 mmol, 0.004 equiv.), anhydrous methanol (3.03 mL, 75 mmol, 1.05 equiv.) and anhydrous toluene (80 mL) were heated under vigorous reflux. Crude sorboyl azide (12.85 g) in anhydrous toluene (30 mL) was added via an addition funnel over 30 min. The reaction mixture was heated under reflux for 30 min, then concentrated in vacuum. The residue was cooled to room temperature and the desired carbamate precipitated as white solids. They were collected by filtration. The filtrate was chromatographed on silica gel using hexanes/ethyl acetate (10/1 to 5/1) as eluent to give another crop of white solids. Totally 7.6 g of product was obtained in 76% yield. m.p. 98-100°C, R_f = 0.23 (hexanes/ethyl acetate = 10/1). ^{1}H NMR (400 MHz,

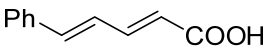
$CDCl_3$) δ 6.61 (m, 1H, CH=CH), 6.40 (br s, 1H, NH), 5.97 (m, 1H, CH=CH), 5.65 (m, 1H, CH=CH), 5.50 (dq, *J* = 14.8, 6.6 Hz, 1H, C**H**CH_3), 3.73 (s, 3H, CH_3O), 1.73 (d, *J* = 6.6 Hz，3H, CHC**H**$_3$); ^{13}C NMR (100 MHz, $CDCl_3$) δ 154.2, 128.7, 125.7, 124.5, 111.9, 52.6, 18.2; IR (cm^{-1}): 3281, 3007, 2953, 1697, 1665, 1537, 1327, 1274, 1051, 975; MS (ESI): calculated for $C_7H_{11}NO_2$ $[M+H]^+$ 142.1, found 142.0.

Benzyl (1*E*,3*E*)-1,3-pentadienylcarbamate (1a)



1a was prepared from benzyl alcohol similarly to **1c**. White solid (100% yield), m.p. 88-90°C, R_f = 0.28 (hexanes/ethyl acetate = 10/1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.36 (m, 5H, ArH), 6.61 (m, 1H, CH=CH), 6.38-6.35 (m, 1H, NH), 5.96 (m, 1H, CH=CH), 5.63 (m, 1H, CH=CH), 5.50 (dq, *J* = 15.0, 6.7 Hz, 1H, C**H**CH_3), 5.14 (s, 2H, C**H**$_2$Ph), 1.73 (d, *J* = 6.6 Hz, 3H, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$) δ 153.5, 136.0, 128.6, 128.3, 128.2, 125.7, 124.3, 112.0, 67.2, 18.1; IR (cm^{-1}): 3304, 3034, 2959, 1699, 1663, 1637, 1528, 1453, 1325, 1269, 1230, 1061, 973, 925, 734, 694; MS (ESI): calculated for $C_{13}H_{15}NO_2$ $[M+H]^+$ 218.1, found 218.1.

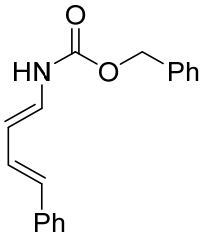
(2*E*,4*E*)-5-Phenyl-2,4-pentadienoic acid



To a 250 mL round bottom flask malonic acid (24.97 g, 0.24 mol, 1.2 equiv.) and pyridine (32.4 mL, 0.4 mol, 2 equiv.) were added. The mixture was stirred to give a clear solution. Cinnamaldehyde (25.2 mL, 0.2 mol) was added and the reaction mixture was refluxed overnight. After cooling to r.t., the reaction mixture was poured into a mixture of ice (150 g) and concentrated H_2SO_4 (22 mL) slowly. Pale yellow solids precipitated. Concentrated H_2SO_4 (3 mL) was added until pH=1. The yellow solids were collected by filtration and dissolved in ethyl acetate (300 mL). The organic layer was washed with water (200 mL) to remove excess malonic acid, dried over anhydrous Na_2SO_4 and concentrated in vacuum. The crude product was washed

with CH_2Cl_2 to give a white solid (16.7 g, 48% yield). R_f = 0.27 (hexanes/ethyl acetate = 2/1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.55 (dd, *J* = 9.8, 15.3 Hz, 1H, CH=CH), 7.49 (d, *J* = 7.2 Hz, 2H, ArH), 7.39-7.31 (m, 3H, ArH), 6.99-6.87 (m, 2H, CH=CH), 6.01 (d, *J* = 15.2 Hz, 1H, CH=CH).

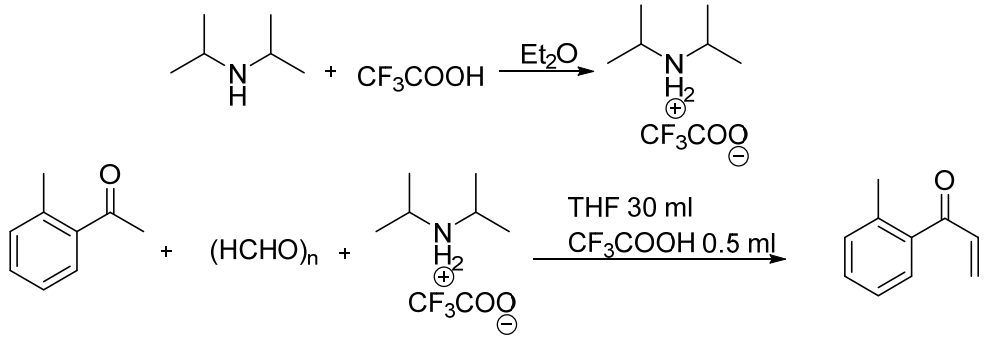
Benzyl (1*E*,3*E*)-4-phenyl-1,3-butadienylcarbamate (1b)



1b was prepared from benzyl alcohol and (2*E*,4*E*)-5-phenyl-2,4-pentadienoic acid similarly to **1c**. White solid (54% yield), m.p. 120-122°C, R_f = 0.25 (hexanes/ethyl acetate = 10/1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37-7.25 (m, 9H, ArH), 7.17 (t, *J* = 7.2 Hz, 1H, ArH), 6.86 (m, 1H, CH=CH), 6.75-6.69 (m, 1H, CH=CH), 6.56 (m, 1H, NH), 6.38 (d, *J* = 15.6 Hz, 1H, CH=CH), 5.84 (m, 1H, CH=CH), 5.17 (s, 2H, C**H**$_2$Ph); ^{13}C NMR (100 MHz, $CDCl_3$) δ 153.5, 137.8, 136.0, 129.0, 128.83, 128.80, 128.7, 128.5, 127.3, 127.1, 126.9, 126.1, 112.3, 67.7; IR (cm^{-1}): 3314, 3024, 1696, 1648, 1619, 1594, 1521, 1446, 1340, 1292, 1259, 1225, 1052, 972, 770, 747, 735, 693; MS (ESI): calculated for $C_{18}H_{17}NO_2$ $[M+H]^+$ 280.1, found 280.0.

General Procedure for The Synthesis of Vinyl Ketone

*Note: Except **2e**, vinyl ketones **2c-2l** were prepared according to the reported method.* [10] **2c**, **2g-2l** are known compounds.



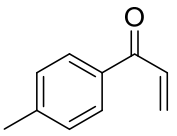
2-Methylphenyl vinyl ketone (2d)

Trifluoroacetic acid (15.3 mL, 0.2 mol) was added dropwise to a stirred mixture of diisopropylamine (28.2 mL, 0.2 mol) in Et_2O (150 mL) at 0°C. The reaction

mixture was stirred at 0°C for an additional 5 min. The formed crystals were filtered, washed with Et_2O and dried under vacuum. Diisopropylammonium trifluoroacetate was obtained as a white solid (41.7 g, 97% yield).

To a mixture of 2-methylacetophenone (3.95 mL, 30 mmol), paraformaldehyde (1.8 g, 60 mmol, 2 equiv.) and anhydrous THF (30 mL) were added diisopropylammonium trifluoroacetate (6.5 g, 30 mmol, 1 equiv.) and trifluoroacetic acid (0.5 mL, 6 mmol, 0.2 equiv.). The reaction mixture was stirred open to the atmosphere at reflux overnight. A clear solution was obtained. It was cooled to room temperature and a second batch of paraformaldehyde (1.8 g, 60 mmol, 2 equiv.) and diisopropylammonium trifluoroacetate (6.5 g, 30 mmol, 1 equiv.) were added. The reaction mixture was refluxed for an additional 8 h open to the atmosphere. The reaction mixture was cooled down and the solvent was removed under reduced pressure. The residue was dissolved in Et_2O (30 mL) and washed with 1 N HCl (50 mL), brine (50 mL), 1 N NaOH (50 mL), dried over anhydrous Na_2SO_4 and concentrated under vacuum. The resulting yellow oil was chromatographed on silica gel using hexanes/ethyl acetate (30/1 to 5/1) to get a light yellow oil (3.79 g, yield 86%). R_f = 0.3 (hexanes/ethyl acetate = 20/1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.44 (d, *J* = 7.8 Hz, 1H, ArH), 7.38 (t, *J* = 1.2 Hz, 1H, ArH), 7.26-7.22 (m, 2H, ArH), 6.78 (dd, *J* = 10.6, 17.4 Hz, 1H, CH_2=C**H**), 6.14 (dd, *J* = 1.3, 17.4 Hz, 1H, C**H**$_2$=CH), 6.00 (dd, *J* = 1.2, 10.6 Hz, 1H, C**H**$_2$=CH), 2.42 (s, 3H, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$) δ 196.8, 138.0, 137.5, 136.7, 131.5, 131.4, 130.9, 128.6, 125.5, 20.4; IR (cm^{-1}): 3062, 3015, 2972, 2923, 1674, 1662, 1606, 1401, 1295, 1269, 1227, 985, 961, 750; MS (ESI): calculated for $C_{10}H_{10}O$ $[M+H]^+$ 147.1, found 146.8.

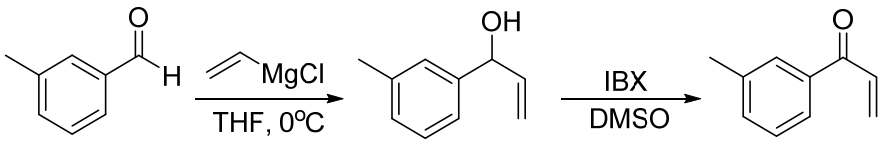
4-Methylphenyl vinyl ketone (2f)



A light yellow oil (40% yield). R_f = 0.43 (hexanes/ethyl acetate = 20/1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.86 (d, *J* = 8.2 Hz, 2H, ArH), 7.28 (d, *J* = 8.5 Hz, 2H, ArH), 7.16 (dd, *J* = 10.5, 17.1 Hz, 1H, CH_2=C**H**), 6.43 (dd, *J* = 1.7, 17.1 Hz, 1H, C**H**$_2$=CH), 5.90 (dd, *J* =

1.7, 10.5 Hz, 1H, C**H**$_2$=CH), 2.42 (s, 3H, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$) δ 190.1, 143.9, 134.8, 132.3, 129.5, 129.4, 128.9, 21.6; IR (cm^{-1}): 3029, 2975, 2918, 1668, 1605, 1571, 1409, 1398, 1291, 1236, 1181, 1001, 981, 770; MS (ESI): calculated for $C_{10}H_{10}O$ $[M+H]^+$ 147.1, found 147.0.

3-Methylphenyl vinyl ketone (2e)[11]



A 2.0 M solution of vinylmagnesium chloride (27 mL, 54 mmol, 1.2 equiv) in anhydrous THF was added via an addition funnel to a solution of 3-methylbenzaldehyde (45 mmol, 5.3 mL) in THF (120 mL) at 0°C over 1 h. Upon complete addition, the reaction solution was warmed to room temperature and stirred for 6 h, then quenched with saturated aqueous NH_4Cl (50 mL), stirred for 20 min, and extracted with diethyl ether (3 × 30 mL). The combined organic layers were washed with brine (50 mL), dried over anhydrous Na_2SO_4 and concentrated under reduced pressure. The crude product was purified by column chromatography using hexanes/ethyl acetate (20/1) as eluent to give a yellow oil.

The above allylic alcohol was dissolved in DMSO (20 mL) and 2-iodoxybenzoic acid (IBX) (15.1 g, 54 mmol, 1.2 equiv.) was added in three portions over 10 min at room temperature. The reaction mixture was stirred for 6 h at room temperature. Then water (50 mL) and diethyl ether (30 mL) were added. The biphasic mixture was filtered through a pad of Celite. The plug was rinsed with diethyl ether (40 mL). The organic layer was separated. The aqueous layer was extracted with diethyl ether (2 × 30 mL). The combined organic layers were washed with water (2 ×50 mL), dried over anhydrous Na_2SO_4 and concentrated under reduced pressure. The crude product was purified by column chromatography using hexanes/ethyl acetate (v/v = 20/1) as eluent to give a light yellow oil (3.99 g, 61% yield). R_f = 0.47 (hexanes/ethyl acetate = 10/1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.76-7.72 (m, 2H, ArH), 7.42-7.33 (m, 2H, ArH), 7.15 (dd, *J* = 10.6, 17.1 Hz, 1H, CH_2=C**H**), 6.42 (dd, *J* = 1.7, 17.1 Hz, 1H, C**H**$_2$=CH), 5.90 (dd, *J* =

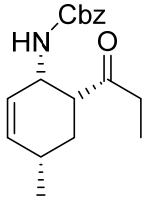
1.7, 10.5 Hz, 1H, C**H**$_2$=CH), 2.41 (s, 3H, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$) δ 191.1, 138.6, 137.4, 133.9, 132.6, 130.0, 129.3, 128.6, 126.0, 21.5; IR (cm^{-1}): 3024, 2915, 2858, 1670, 1610, 1583, 1402, 1258, 1185, 1168, 980, 761; MS (ESI): calculated for $C_{10}H_{10}O$ $[M+H]^+$ 147.1, found 146.8.

General Procedure for Catalytic Asymmetric Diels-Alder Reaction

A dry 50 mL Schlenk tube was charged with 4Å MS (500 mg), **cat. 4g** (83 mg, 0.1 mmol) and anhydrous $CHCl_3$ (5 mL). The reaction mixture was cooled to -60°C. 1 mmol of vinyl ketone was added. Then the carbamate (2 mmol) in anhydrous $CHCl_3$ (5 mL) was added via syringe pump over 5 h. The reaction was quenched with saturated aq. $NaHCO_3$ (10 mL) after 24 h. The aqueous layer was extracted with $CHCl_3$ (2 × 15 mL). The combined organic layers were washed with brine, dried over anhydrous Na_2SO_4 and concentrated. The crude product was purified by silica gel chromatography.

Note: All racemic DA products were prepared in ca. 30% yield according to the above general procedure using 10 mol% p-TsOH·H_2O instead of the chiral N-triflyl phosphoramide as the catalyst.

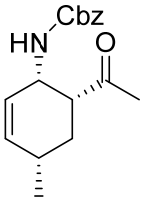
Benzyl (1*S*,4*S*,6*R*)-4-methyl-6-propionyl-2-cyclohexen-1-ylcarbamate (3a)



Colorless oil (72% yield), ee = 97%, R_f = 0.25 (5:1 hexanes/AcOEt). $[\alpha]_D^{23}$ = + 112 (*c* 0.680, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.36-7.29 (m, 5H, ArH), 5.70 (m, 2H, C**H**=C**H**), 5.04 (m, 2H, C**H**$_2$Ph), 4.74-4.65 (m, 2H, C**H**NH and N**H**), 2.84-2.78 (m, 2H, C**H**CO and one of C**H**$_2$CO), 2.39 (dq, *J* = 18.0, 7.2 Hz, 1H, one of CH_2CO), 2.14 (m, 1H, C**H**CH_3), 1.82-1.78 (m, 1H, $CH_3CHC\mathbf{H}_2$), 1.25-1.19 (m, 1H, $CH_3CHC\mathbf{H}_2$), 1.02 (d, *J* = 4.6 Hz, 3H, CHC**H**$_3$), 1.00 (t, *J* = 4.7 Hz, 3H, $COCH_2C\mathbf{H}_3$); ^{13}C NMR (100 MHz, $CDCl_3$) δ 211.8, 155.8, 137.3, 136.5, 128.6, 128.2, 128.1, 125.2, 66.9, 50.4, 46.1, 35.0, 30.8, 27.9, 21.3, 7.7; IR (cm^{-1}): 3324, 3018, 2956, 2872, 1712, 1521,

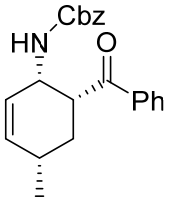
1455, 1330, 1234, 1072, 1005, 737, 697; MS (ESI): calculated for $C_{18}H_{23}NO_3$ $[M+H]^+$ 302.2, found 302.0; The enantiomeric ratio was determined by HPLC analysis, HPLC (Daicel OD-H column, *n*-hexane: *i*-PrOH = 97: 3, Flow rate = 1 mL/min, λ = 254 nm.), t_{minor} = 10.6 min, t_{major} = 11.2 min.

Benzyl (1*S*,4*S*,6*R*)-6-acetyl-4-methyl-2-cyclohexen-1-ylcarbamate (3b)



White solid (66% yield), m.p. 90-91°C, ee = 80%, R_f = 0.25 (5:1 hexanes/AcOEt). $[\alpha]_D^{23}$ = + 109 (*c* 2.20, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.35-7.32 (m, 5H, ArH), 5.70 (m, 2H, C**H**=C**H**), 5.10-4.99 (m, 2H, C**H**$_2$Ph), 4.73-4.65 (m, 2H, N**H** and NHC**H**), 2.82-2.79 (m, 1H, CHCO), 2.26 (s, 3H, $COCH_3$), 2.17-2.11 (m, 1H, CH_3C**H**), 1.88-1.85 (m, 1H, CH_3CHC**H**$_2$), 1.15 (dd, *J* = 13.1, 24.8 Hz, 1H, CH_3CHC**H**$_2$), 1.01 (d, *J* = 7.1 Hz, 3H, CHC**H**$_3$) ; ^{13}C NMR (100 MHz, $CDCl_3$) δ 209.3, 155.8, 137.4, 136.4, 128.6, 128.3, 128.1, 125.2, 67.0, 51.5, 45.9, 30.8, 29.2, 27.8, 21.2; IR (cm^{-1}): 3329, 3021, 2956, 2866, 1708, 1522, 1454, 1329, 1235, 1071, 1011, 752, 697; MS (ESI): calculated for $C_{17}H_{21}NO_3$ $[M+H]^+$ 288.2, found 288.0. The enantiomeric ratio was determined by HPLC analysis, HPLC (Daicel AD-H column, *n*-hexane: *i*-PrOH = 97: 3, Flow rate = 1 mL/min, λ = 254 nm.), t_{major} = 21.3 min, t_{minor} = 30.6 min.

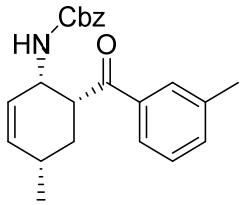
Benzyl (1*S*,4*S*,6*R*)-6-benzoyl-4-methyl-2-cyclohexen-1-ylcarbamate (3c)



Colorless oil (70% yield), ee = 94%, R_f = 0.2 (5:1 hexanes/AcOEt). $[\alpha]_D^{23}$ = + 188 (*c* 0.775, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.90 (d, *J* = 8.0 Hz, 2H, ArH), 7.55 (t, *J* = 7.1 Hz, 1H, ArH), 7.44 (t, *J* = 7.6 Hz, 2H, ArH), 7.33-7.25 (m, 5H, ArH), 5.75-5.73 (m, 2H, C**H**=C**H**), 4.92 (s, 2H, C**H**$_2$Ph), 4.83-4.81 (m, 1H, NH), 4.66-4.64 (m, 1H, C**H**NH), 3.76-3.73 (m, 1H, CHCO), 2.31-2.26 (m, 1H, C**H**CH_3), 1.92-1.89 (m, 1H, C**H**$_2$$CHCH_3$), 1.48 (dd, *J* = 12.6, 24.5 Hz, 1H, C**H**$_2$$CHCH_3$), 1.06 (d, *J* = 7.1

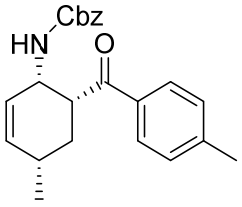
Hz, 3H, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$) δ 201.3, 155.4, 136.86, 136.84, 136.6, 133.2, 128.8, 128.6, 128.2, 128.1, 128.0, 125.6, 66.7, 46.8, 45.8, 30.8, 28.8, 21.3; IR (cm^{-1}): 3336, 3026, 2955, 2872, 1719, 1678, 1499, 1448, 1333, 1279, 1215, 1065, 1010, 774, 736, 695; MS (ESI): calculated for $C_{22}H_{23}NO_3$ $[M+H]^+$ 350.2, found 350.0; The enantiomeric ratio was determined by HPLC analysis, HPLC (Daicel OD-H column, *n*-hexane: *i*-PrOH = 97: 3, Flow rate = 1 mL/min, λ = 254 nm.), t_{minor} = 30.6 min, t_{major} = 38.8 min.

Benzyl (1*S*,4*S*,6*R*)-6-(3-methylbenzoyl)-4-methyl-2-cyclohexen-1-ylcarbamate (3e)



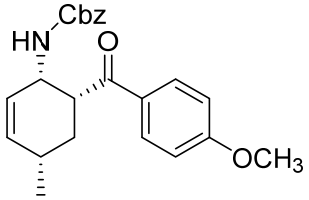
Colorless oil (43% yield, 43% 3-Methylphenyl vinyl ketone was recovered), ee = 91%, R_f = 0.36 (5:1 hexanes/AcOEt). $[\alpha]_D^{23}$ = + 164 (*c* 0.905, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$) δ 7.71 (s, 2H, ArH), 7.35-7.27 (m, 7H, ArH), 5.81-5.73 (m, 2H, C**H**=C**H**), 4.93 (s, 2H, C**H**$_2$Ph), 4.85-4.83 (m, 1H, NH), 4.65-4.63 (m, 1H, C**H**NH), 3.76-3.73 (m, 1H, CHCO), 2.40 (s, 3H, C**H**$_3$Ph), 2.28 (m, 1H, C**H**CH_3), 1.91-1.87 (m, 1H, CH_3CHC**H**$_2$), 1.47 (dd, *J* = 12.7, 24.4 Hz, 1H, CH_3CHC**H**$_2$), 1.06 (d, *J* = 7.1 Hz, 3H, C**H**$_3$CH); ^{13}C NMR (100 MHz, $CDCl_3$) δ 201.3, 155.3, 138.3, 136.8, 136.6, 133.9, 128.6, 128.5, 128.4, 127.9, 127.8, 125.6, 125.4, 66.5, 46.7, 45.7, 30.7, 28.8, 21.4, 21.2; IR (cm^{-1}): 3337, 3026, 2955, 2923, 2870, 1720, 1678, 1602, 1585, 1498, 1454, 1334, 1281, 1232, 1066, 1011, 774, 740, 697; MS (ESI): calculated for $C_{23}H_{25}NO_3$ $[M+H]^+$ 364.2, found 364.0; The enantiomeric ratio was determined by HPLC analysis, HPLC (Daicel AD-H column, *n*-hexane: *i*-PrOH = 95: 5, Flow rate = 1 mL/min, λ = 254 nm.), t_{major} = 26.8 min, t_{minor} = 46.0 min.

Benzyl (1*S*,4*S*,6*R*)-6-(4'-methylbenzoyl)-4-methyl-2-cyclohexen-1-ylcarbamate (3f)



Colorless oil (80% yield), ee = 97%, R_f = 0.34 (5:1 hexanes/AcOEt). $[\alpha]_D^{23}$ = + 193 (*c* 0.580, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$) δ 7.82 (d, *J* = 8.1 Hz, 2H, ArH), 7.35-7.23 (m, 7H, ArH), 5.77-5.73 (m, 2H, C**H**=C**H**), 4.93-4.85 (m, 3H, PhC**H**$_2$ and NH), 4.65 (m, 1H, C**H**NH), 3.75-3.72 (m, 1H, CHCO), 2.40 (s, 3H, C**H**$_3$Ph), 2.27 (m, 1H, C**H**CH_3), 1.90-1.87 (m, 1H, CH_3CHC**H**$_2$), 1.48 (dd, *J* = 12.6, 24.6 Hz, 1H, CH_3CHC**H**$_2$), 1.06 (d, *J* = 7.0 Hz, 3H, CHC**H**$_3$); ^{13}C NMR (100 MHz, $CDCl_3$) δ 200.9, 155.5, 144.0, 136.8, 136.7, 134.3, 129.5, 128.6, 128.4, 128.1, 128.0, 125.7, 66.7, 46.9, 45.7, 30.9, 28.9, 21.9, 21.3; IR (cm^{-1}): 3335, 3026, 2955, 2869, 1720, 1675, 1607, 1498, 1454, 1333, 1280, 1221, 1066, 1011, 744, 692; MS (ESI): calculated for $C_{23}H_{25}NO_3$ $[M+H]^+$ 364.2, found 364.0; The enantiomeric ratio was determined by HPLC analysis, HPLC (Daicel OJ-H column, *n*-hexane: *i*-PrOH = 90: 10, Flow rate = 1 mL/min, λ = 254 nm.), t_{minor} = 9.3 min, t_{major} = 15.8 min.

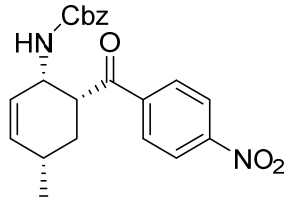
Benzyl (1*S*,4*S*,6*R*)-6-(4-methoxybenzoyl)-4-methyl-2-cyclohexen-1-ylcarbamate (3g)



White solid (80% yield), m.p. 109-110°C, ee = 99%, R_f = 0.17 (5:1 hexanes/AcOEt). $[\alpha]_D^{23}$ = + 197 (*c* 0.650, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$) δ 7.90 (d, *J* = 8.68 Hz, 2H, ArH), 7.33-7.26 (m, 5H, ArH), 6.91 (d, *J* = 8.6 Hz, 2H, ArH), 5.77-5.73 (m, 2H, C**H**=C**H**), 4.93-4.85 (m, 3H, NH and PhC**H**$_2$), 4.63-4.62 (m, 1H, C**H**NH), 3.86 (s, 3H, CH_3O), 3.71-3.68 (m, 1H, CHCO), 2.26 (m, 1H, C**H**CH_3), 1.88-1.85 (m, 1H, CH_3CHC**H**$_2$), 1.47 (dd, *J* = 12.4, 24.6 Hz, 1H, CH_3CHC**H**$_2$), 1.06 (d, *J* = 7.0 Hz, 3H, C**H**$_3$CH); ^{13}C NMR (100 MHz, $CDCl_3$) δ 199.7, 163.6, 155.5, 136.8, 136.7, 130.5, 129.8, 128.5, 128.1, 128.0, 125.8, 114.0, 66.6, 55.5, 47.0, 45.4, 30.9, 29.0, 21.3; IR (cm^{-1}): 3341, 3026, 2955, 2861, 1718, 1669, 1600, 1509, 1455, 1259, 1217, 1167, 1066, 1026, 847, 741,

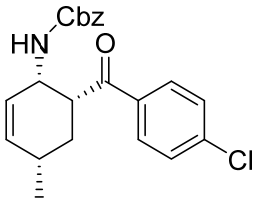
695; MS (ESI): calculated for $C_{23}H_{25}NO_4$ $[M+H]^+$ 380.2, found 379.9; The enantiomeric ratio was determined by HPLC analysis, HPLC (Daicel AD-H column, *n*-hexane: *i*-PrOH = 90: 10, Flow rate = 1 mL/min, λ = 254 nm.), t_{minor} = 36.0 min, t_{major} = 44.5 min.

Benzyl (1*S*,4*S*,6*R*)-6-(4-nitrobenzoyl)-4-methyl-2-cyclohexen-1-ylcarbamate (3h)



White solid (37% yield, 45% 4-nitrophenyl vinyl ketone was recovered), m.p. 118-119°C, ee = 99%, R_f = 0.2 (5:1 hexanes/AcOEt). $[\alpha]_D^{23}$ = + 205 (*c* 0.260, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.25 (d, *J* = 8.6 Hz, 2H, ArH), 7.97 (d, *J* = 8.7 Hz, 2H, ArH), 7.34 (m, 3H, ArH), 7.25 (m, 2H, ArH), 5.81-5.70 (m, 2H, C**H**=C**H**), 4.92-4.85 (m, 2H, C**H**$_2$Ph), 4.74-4.64 (m, 2H, N**H** and NHC**H**), 3.72-3.68 (m, 1H, COCH), 2.29 (m, 1H, CH_3C**H**), 1.93-1.90 (m, 1H, CH_3CHC**H**$_2$), 1.47 (dd, *J* = 12.8, 24.7 Hz, 1H, CH_3CHC**H**$_2$), 1.09 (d, *J* = 7.1 Hz, 3H, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$) δ 199.7, 155.3, 150.2, 141.6, 137.7, 136.4, 129.1, 128.6, 128.3, 128.1, 124.9, 124.0, 66.9, 47.1, 46.7, 30.8, 28.4, 21.2; IR (cm^{-1}): 3352, 3026, 2956, 2872, 1718, 1687, 1524, 1454, 1346, 1319, 1231, 1066, 1011, 859, 697; MS (ESI): calculated for $C_{22}H_{22}N_2O_5$ $[M+H]^+$ 395.2, found 395.0. The enantiomeric ratio was determined by HPLC analysis, HPLC (Daicel AD-H column, *n*-hexane: *i*-PrOH = 85: 15, Flow rate = 1 mL/min, λ = 254 nm.), t_{minor} = 21.6 min, t_{major} = 49.0 min.

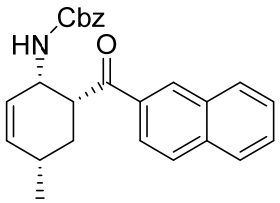
Benzyl (1*S*,4*S*,6*R*)-6-(4-chlorobenzoyl)-4-methyl-2-cyclohexen-1-ylcarbamate (3i)



White solid (60% yield, 16.2% 4-chlorophenyl vinyl ketone was recovered), m.p. 90-92°C, ee = 96%, R_f = 0.33 (5:1 hexanes/AcOEt). $[\alpha]_D^{23}$ = + 212 (*c* 0.480, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.82 (d, *J* = 8.5 Hz, 2H, ArH), 7.40 (d, *J* = 8.4 Hz, 2H, ArH), 7.34-7.30 (m, 3H, ArH), 7.25 (m, 2H, ArH), 5.75 (m, 2H, CH=CH), 4.92 (s, 2H,

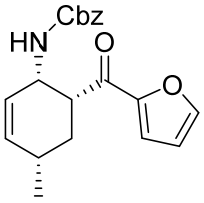
C**H**$_2$Ph), 4.77 (d, *J* = 9.2 Hz, 1H, NH), 4.63 (m, 1H, NHC**H**), 3.69-3.66 (m, 1H, CHCO), 2.26 (m, 1H, C**H**CH$_3$), 1.89-1.86 (m, 1H, CH$_3$CHC**H**$_2$), 1.46 (dd, *J* = 12.8, 24.6 Hz, 1H, CH$_3$CHC**H**$_2$), 1.06 (d, *J* = 7.1 Hz, 3H, CH$_3$); ^{13}C NMR (100 MHz, CDCl$_3$) δ 200.0, 155.4, 139.5, 137.2, 136.6, 135.2, 129.6, 129.1, 128.6, 128.2, 128.1, 125.4, 66.8, 46.8, 46.1, 30.8, 28.7, 21.3; IR (cm^{-1}): 3336, 2955, 1718, 1680, 1588, 1499, 1454, 1400, 1334, 1277, 1233, 1215, 1091, 1067, 1011, 803, 700; MS (ESI): calculated for $C_{22}H_{22}ClNO_3$ $[M+H]^+$ 384.1, found 383.9; The enantiomeric ratio was determined by HPLC analysis, HPLC (Daicel AD-H column, *n*-hexane: *i*-PrOH = 90: 10, Flow rate = 1 mL/min, λ = 254 nm.), t_{minor} = 19.5 min, t_{major} = 25.2 min.

Benzyl (1*S*,4*S*,6*R*)-4-methyl-6-(2-naphthoyl)-2-cyclohexen-1-ylcarbamate (3j)



White solid (69% yield), m.p. 124-125°C, ee = 85%, R_f = 0.36 (5:1 hexanes/AcOEt). $[\alpha]_D^{23}$ = + 231 (*c* 1.06, CHCl$_3$); ^{1}H NMR (400 MHz, CDCl$_3$) δ 8.45 (s, 1H, ArH), 7.96 (d, *J* = 7.8 Hz, 2H, ArH), 7.89-7.85 (m, 2H, ArH), 7.60-7.52 (m, 2H, ArH), 7.33-7.24 (m, 5H, ArH), 5.84 (m, 2H, C**H**=C**H**), 4.90 (s, 3H, C**H**$_2$Ph and NH), 4.73 (m, 1H, NHC**H**), 3.94-3.91 (m, 1H, COCH), 2.33 (m, 1H, CH$_3$C**H**), 1.96-1.93 (m, 1H, CH$_3$CHC**H**$_2$), 1.60-1.51 (m, 1H, CH$_3$CHC**H**$_2$), 1.09 (d, *J* = 7.0 Hz, 3H, CH$_3$); ^{13}C NMR (100 MHz, CDCl$_3$) δ 201.2, 155.5, 136.9, 136.7, 135.8, 134.2, 132.8, 129.8, 128.8, 128.6, 128.5, 128.1, 128.05, 128.0, 126.8, 125.7, 124.2, 66.7, 47.1, 45.9, 30.9, 29.0, 21.3; IR (cm^{-1}): 3336, 3029, 2954, 2866, 1718, 1673, 1499, 1454, 1332, 1231, 1065, 793, 752, 695; MS (ESI): calculated for $C_{26}H_{25}NO_3$ $[M+H]^+$ 400.2, found 400.0; The enantiomeric ratio was determined by HPLC analysis, HPLC (Daicel AD-H column, *n*-hexane: *i*-PrOH = 90: 10, Flow rate = 1 mL/min, λ = 254 nm.) t_{major} = 29.9 min, t_{minor} = 44.0 min.

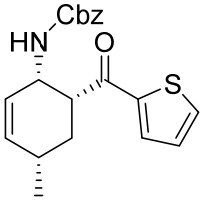
Benzyl (1*S*,4*S*,6*R*)-6-(2-furoyl)-4-methyl-2-cyclohexen-1-ylcarbamate (3k)



White solid (60% yield), m.p. 150-151°C, ee = 99.4%, R_f = 0.17 (5:1 hexanes/AcOEt). $[\alpha]_D^{23}$ = + 214 (*c* 0.560, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$) δ 7.59 (s, 1H, one of furan), 7.34-7.26 (m, 5H, ArH), 7.18 (d, *J* = 3.5Hz, 1H, one of furan), 6.53 (d, *J* = 1.52 Hz, 1H, one of furan), 5.75 (m, 2H, C**H**=C**H**), 5.00-4.90 (m, 2H, C**H**$_2$Ph), 4.83-4.76 (m, 2H, C**H**NH and N**H**), 3.57-3.53 (m, 1H, CHCO), 2.25-2.24 (m, 1H, C**H**CH_3), 1.87-1.84 (m, 1H, C**H**$_2$$CHCH_3$), 1.44 (dd, *J* = 12.8, 24.7 Hz, 1H, C**H**$_2$$CHCH_3$), 1.06 (d, *J* = 7.1 Hz, 3H, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$) δ 189.8, 155.5, 152.9, 146.4, 137.0, 136.6, 128.6, 128.11, 128.06, 125.5, 117.0, 66.8, 46.8, 46.6, 30.8, 27.9, 21.3; IR (cm^{-1}): 3409, 3127, 2942, 1716, 1706, 1659, 1506, 1470, 1240, 1220, 1069, 1041, 784, 746, 728, 695; MS (ESI): calculated for $C_{20}H_{21}NO_4$ $[M+H]^+$ 340.2, found 340.0; The enantiomeric ratio was determined by HPLC analysis, HPLC (Daicel AD-H column, *n*-hexane: *i*-PrOH = 90: 10, Flow rate = 1 mL/min, λ = 254 nm.), t_{major} = 22.0 min, t_{minor} = 34.8 min.

Benzyl (1*S*,4*S*,6*R*)-4-methyl-6-(2-thienoyl)-2-cyclohexen-1-ylcarbamate (3l)

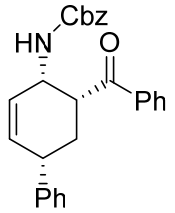
*Note: The absolute configuration was confirmed by XRD analysis. All other DA products (**3a-3q**) were assumed by analogy to have the same configuration.*



White solid (97% yield), m.p. 62-63°C, ee = 99%, R_f = 0.3 (5:1 hexanes/AcOEt). $[\alpha]_D^{23}$ = + 186 (*c* 0.410, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$) δ 7.75 (d, *J* = 3.5 Hz, 1H, one of thiophene), 7.63 (d, *J* = 2.8 Hz, 1H, one of thiophene), 7.35-7.28 (m, 5H, ArH), 7.13 (t, *J* = 4.3 Hz, 1H, one of thiophene), 5.81-5.74 (m, 2H, C**H**=C**H**), 4.96 (s, 2H, C**H**$_2$Ph), 4.90-4.87 (m, 1H, NH), 4.71-4.69 (m, 1H, NHC**H**), 3.59-3.56 (m, 1H, CHCO), 2.29 (m, 1H, CH_3C**H**), 1.90-1.88 (m, 1H, CH_3CHCH_2), 1.49 (dd, *J* = 12.9, 24.5 Hz, 1H, CH_3CHCH_2), 1.06 (d, *J* = 7.1 Hz, 3H, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$) δ 192.5, 154.4,

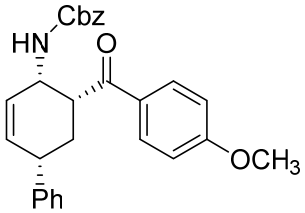
143.0, 135.7, 135.5, 132.7, 130.7, 127.4, 127.1, 126.9, 126.8, 124.4, 65.6, 46.3, 46.1, 29.6, 27.6, 20.1; IR (cm^{-1}): 3336, 3024, 2955, 2869, 1718, 1655, 1517, 1499, 1414, 1232, 1067, 1008, 787, 731, 697; MS (ESI): calculated for $C_{20}H_{21}NO_3S$ $[M+H]^+$ 356.1, found 355.9; The enantiomeric ratio was determined by HPLC analysis, HPLC (Daicel AD-H column, *n*-hexane: *i*-PrOH = 90: 10, Flow rate = 1 mL/min, λ = 254 nm.) t_{major} = 25.9 min, t_{minor} = 35.9 min.

Benzyl (1*S*,4*S*,6*R*)-6-benzoyl-4-phenyl-2-cyclohexen-1-ylcarbamate (3m)



White solid (66% yield), m.p. 120-122°C, ee = 97%, R_f = 0.28 (5:1 hexanes/AcOEt). $[\alpha]_D^{23}$ = + 92.6 (*c* 0.365, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$) δ 7.89 (d, *J* = 7.1 Hz, 2H, ArH), 7.56-7.17 (m, 13H, ArH), 5.99 (m, 2H, C**H**=C**H**), 4.95 (m, 3H, NH and C**H**$_2$Ph), 4.76 (m, 1H, C**H**NH), 3.93-3.90 (m, 1H, CHCO), 3.46 (m, 1H, PhC**H**), 2.14-2.11 (m, 1H, PhCHC**H**$_2$), 1.86 (dd, *J* = 12.5, 24.8 Hz, 1H, PhCHC**H**$_2$); ^{13}C NMR (100 MHz, $CDCl_3$) δ 200.9, 155.5, 144.4, 136.7, 136.6, 134.2, 133.3, 128.8, 128.6, 128.3, 128.2, 128.1, 127.6, 127.4, 126.9, 66.8, 46.7, 45.9, 42.4, 29.9; IR (cm^{-1}): 3324, 3027, 2942, 1719, 1676, 1597, 1496, 1448, 1335, 1279, 1233, 1053, 982, 758, 697; MS (ESI): calculated for $C_{27}H_{25}NO_3$ $[M+H]^+$ 412.2, found 411.9; The enantiomeric ratio was determined by HPLC analysis, HPLC (Daicel AD-H column, *n*-hexane: *i*-PrOH = 90: 10, Flow rate = 1 mL/min, λ = 254 nm.), t_{major} = 28.2 min, t_{minor} = 40.5 min.

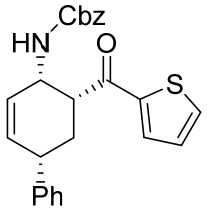
Benzyl (1*S*,4*S*,6*R*)-6-(4-methoxybenzoyl)-4-phenyl-2-cyclohexen-1-ylcarbamate (3n)



White solid (77% yield), m.p. 150-152°C, ee = 99.3%, R_f = 0.19 (5:1 hexanes/AcOEt).

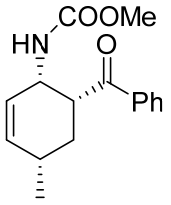
$[\alpha]_D^{23}$ = + 90.0 (*c* 0.685, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$) δ 7.90 (d, *J* = 8.7 Hz, 2H, ArH), 7.31-7.17 (m, 10H, ArH), 6.92 (d, *J* = 8.4 Hz, 2H, ArH), 6.00-5.95 (m, 2H, C**H**=C**H**), 4.99-4.92 (m, 3H, NH and C**H**$_2$Ph), 4.73 (m, 1H, NHC**H**), 3.87 (m, 4H, CHCO and CH_3O), 3.45 (m, 1H, C**H**Ph), 2.10-2.07 (m, 1H, PhCHC**H**$_2$), 1.85 (dd, *J* = 12.6, 25.0 Hz, 1H, PhCHC**H**$_2$); ^{13}C NMR (100 MHz, $CDCl_3$) δ 199.2, 163.7, 155.6, 144.5, 136.6, 134.2, 130.5, 129.7, 128.8, 128.6, 128.13, 128.09, 127.6, 127.4, 126.8, 114.0, 66.8, 55.6, 46.8, 45.4, 42.5, 30.0; IR (cm^{-1}): 3334, 3026, 2937, 1715, 1669, 1599, 1510, 1453, 1312, 1259, 1213, 1172, 1027, 757, 700; MS (ESI): calculated for $C_{28}H_{27}NO_4$ $[M+H]^+$, 442.2, found 441.9; The enantiomeric ratio was determined by HPLC analysis, HPLC (Daicel AD-H column, *n*-hexane: *i*-PrOH = 80: 20, Flow rate = 1 mL/min, λ = 254 nm.), t_{minor} = 24.7 min, t_{major} = 28.4 min.

Benzyl (1*S*,4*S*,6*R*)-4-phenyl-6-(2-thienoyl)-2-cyclohexen-1-ylcarbamate (3o)



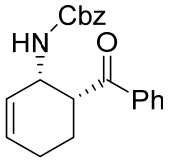
White solid (94% yield), m.p. 139-140°C, ee = 99.2%, R_f = 0.2 (5:1 hexanes/AcOEt). $[\alpha]_D^{23}$ = + 139 (*c* 0.535, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$) δ 7.60 (d, *J* = 3.2 Hz, 1H, one of thiophene), 7.18 (d, *J* = 4.7 Hz, 1H, one of thiophene), 7.30 (m, 5H, ArH), 7.17 (t, *J* = 7.4 Hz, 1H, one of thiophene), 5.98 (m, 2H, C**H**=C**H**), 5.00 (m, 3H, C**H**$_2$Ph and NH), 4.83-4.75 (m, 1H, C**H**NH), 3.77-3.73 (m, 1H, CHCO), 3.46-3.45 (m, 1H, C**H**Ph), 2.12-2.10 (m, 1H, C**H**$_2$CHPh), 1.87 (dd, *J* = 12.7, 25.6 Hz, 1H, C**H**$_2$CHPh); ^{13}C NMR (100 MHz, $CDCl_3$) δ 193.2, 155.6, 144.3, 143.9, 136.6, 134.3, 134.1, 131.9, 128.8, 128.6, 128.3, 128.2, 128.1, 127.5, 127.2, 126.9, 66.9, 47.4, 47.1, 42.4, 29.8; IR (cm^{-1}): 3324, 3056, 3027, 2940, 1718, 1655, 1497, 1452, 1414, 1333,1280, 1232, 1055, 729, 699; MS (ESI): calculated for $C_{25}H_{23}NO_3S$ $[M+H]^+$ 418.2, found 417.9; The enantiomeric ratio was determined by HPLC analysis, HPLC (Daicel AD-H column, *n*-hexane: *i*-PrOH = 85: 15, Flow rate = 1 mL/min, λ = 254 nm.), t_{major} = 19.0 min, t_{minor} = 39.4 min.

Methyl (1*S*,4*S*,6*R*)-6-benzoyl-4-methyl-2-cyclohexen-1-ylcarbamate (3p)



White solid (66% yield), m.p. 88-90°C, ee = 94%, R_f = 0.2 (5:1 hexanes/AcOEt). $[\alpha]_D^{23}$ = + 188 (*c* 0.570, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.94 (d, *J* = 7.4 Hz, 2H, ArH), 7.56 (t, *J* = 7.3 Hz, 1H, ArH), 7.47 (t, *J* = 7.6 Hz, 2H, ArH), 5.78 (m, 2H, C**H**=C**H**), 4.77 (m, 1H, NH), 4.62 (m, 1H, C**H**NH), 3.75 (ddd, *J* = 6.8, 4.2, 2.4 Hz, 1H, CHCO), 3.50 (s, 3H, COOC**H**$_3$), 2.28 (m, 1H, C**H**CH_3), 1.92-1.88 (m, 1H, C**H**$_2$$CHCH_3$), 1.49 (dd, *J* = 12.7, 24.4 Hz, 1H, C**H**$_2$$CHCH_3$), 1.08 (d, *J* = 7.1 Hz, 3H, CHC**H**$_3$); ^{13}C NMR (100 MHz, $CDCl_3$) δ 201.4, 156.1, 136.8, 136.7, 133.2, 128.8, 128.2, 125.7, 52.2, 46.8, 45.8, 30.8, 28.8, 21.3; IR (cm^{-1}): 3347, 3021, 2954, 1719, 1679, 1508, 1448, 1336, 1279, 1238, 1072, 1012, 778, 750, 728, 696; MS (ESI): calculated for $C_{16}H_{19}NO_3$ $[M+H]^+$, 274.1, found 274.0. The enantiomeric ratio was determined by HPLC analysis, HPLC (Daicel OD-H column, *n*-hexane: *i*-PrOH = 97: 3, Flow rate = 1 mL/min, λ = 254 nm.), t_{minor} = 22.6 min, t_{major} = 27.5 min.

Benzyl (1*S*,6*R*)-6-benzoyl-2-cyclohexen-1-ylcarbamate (3q)



Colorless oil (40% yield), ee = 76%, R_f = 0.2 (5:1 hexanes/AcOEt). $[\alpha]_D^{23}$ = + 109 (*c* 0.310, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.91 (d, *J* = 8.0 Hz, 2H, ArH), 7.56 (t, *J* = 7.2 Hz, 1H, ArH), 7.45 (t, *J* = 7.6 Hz, 2H, ArH), 7.31-7.26 (m, 5H, ArH), 5.84-5.81 (m, 1H, C**H**=CH), 5.75-5.72 (m, 1H, CH=C**H**), 5.25 (m, 1H, NH), 5.00 (m, 2H, C**H**$_2$Ph), 4.69 (m, 1H, C**H**NH), 3.90-3.88 (m, 1H, C**H**CO), 2.00 (m, 4H, C**H**$_2$C**H**$_2$); ^{13}C NMR (100 MHz, $CDCl_3$) δ 201.3, 155.8, 136.6, 130.4, 133.2, 129.0, 128.8, 128.6, 128.3, 128.09, 128.06, 127.7, 66.7, 47.6, 45.5, 23.1, 22.9; IR (cm^{-1}): 3422, 3336, 3029, 2940, 1720, 1679, 1596, 1498, 1448, 1327, 1235, 1055, 1019, 732, 696; MS (ESI): calculated for $C_{21}H_{21}NO_3$ $[M+H]^+$ 336.2, found 336.0. The

enantiomeric ratio was determined by HPLC analysis, HPLC (Daicel AD-H column, *n*-hexane: *i*-PrOH = 90: 10, Flow rate = 1 mL/min, λ = 254 nm.) t_{major} = 21.3 min, t_{minor} = 27.9 min.

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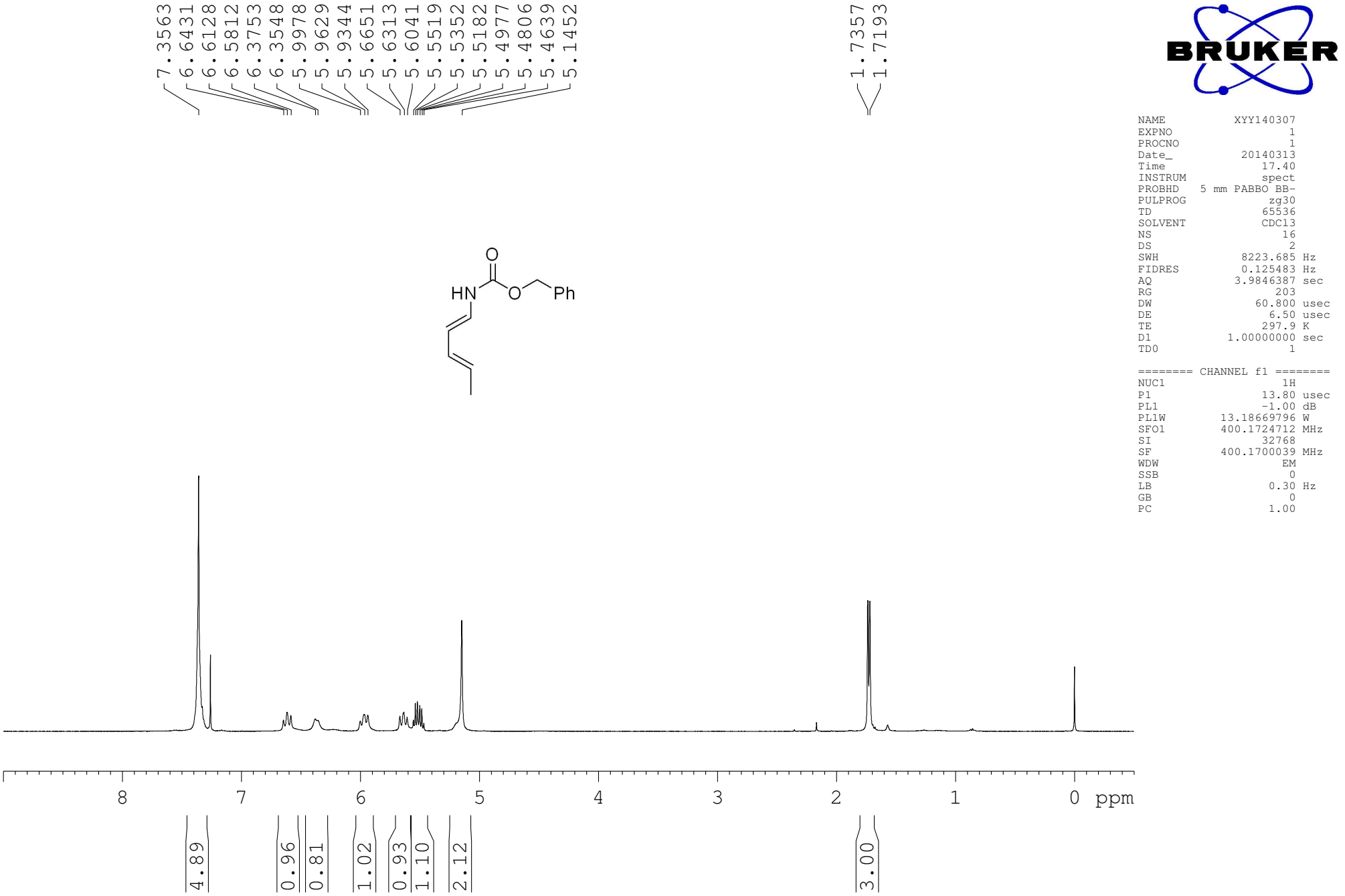
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6.6431
6.6128
6.5812
6.3753
6.3548
5.9978
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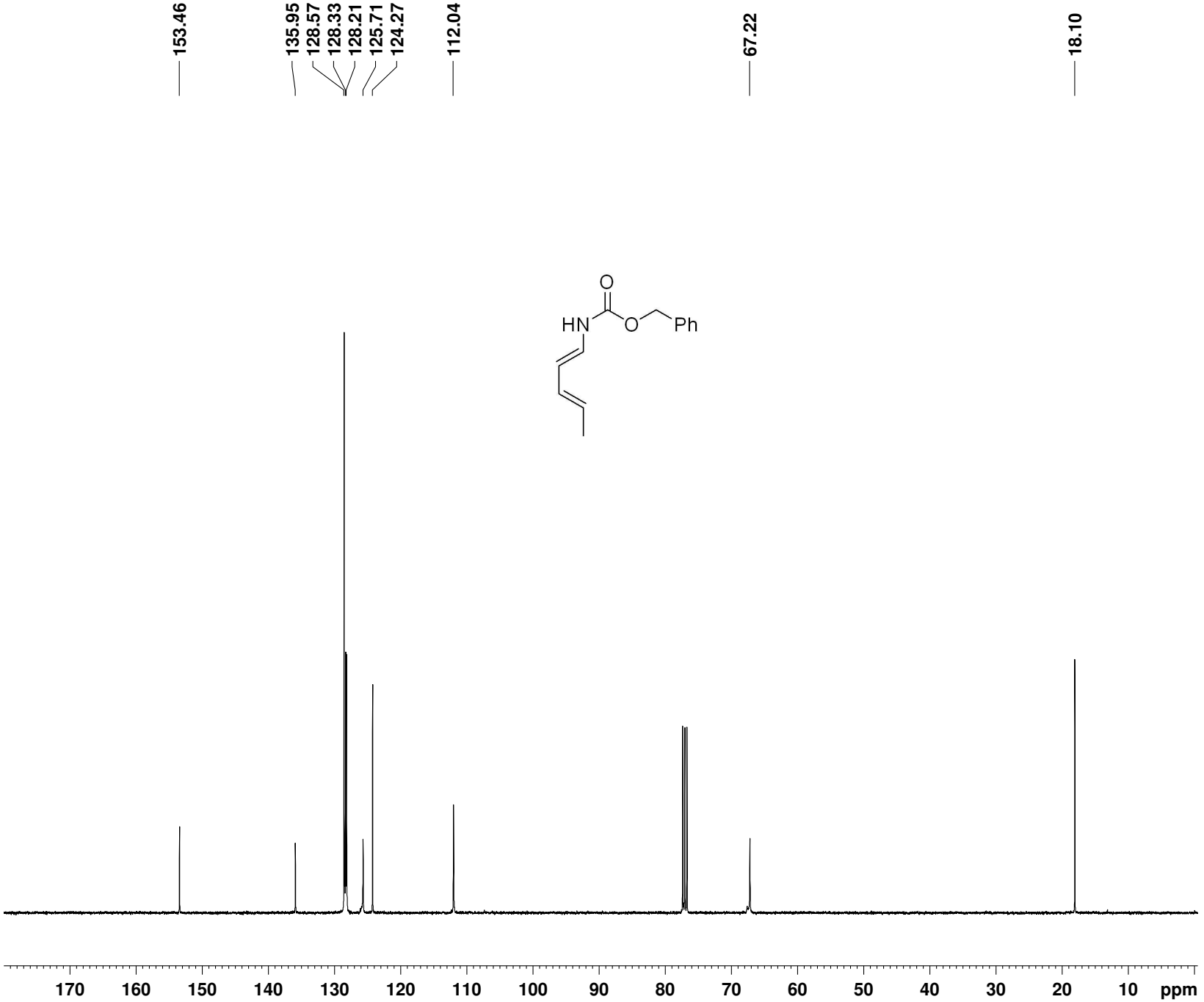
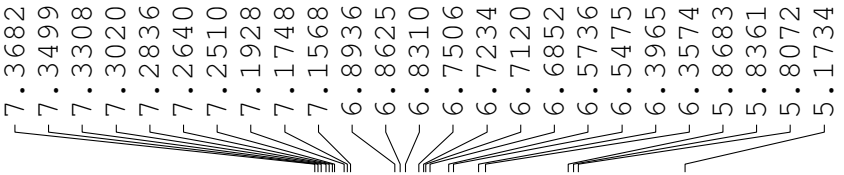
5.9344
5.6651
5.6313
5.6041
5.5519
5.5352
5.5182
5.4977
5.4806
5.4639
5.1452
1.7357
1.7193
HN
O
O
Ph
NAME XYY140307
EXPNO 1
PROCNO 1
Date_ 20140313
Time 17.40
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 16
DS 2
SWH 8223.685 Hz
FIDRES 0.125483 Hz
AQ 3.9846387 sec
RG 203
DW 60.800 usec
DE 6.50 usec
TE 297.9 K
D1 1.00000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 1H
P1 13.80 usec
PL1 -1.00 dB
PL1W 13.18669796 W
SFO1 400.1724712 MHz
SI 32768
SF 400.1700039 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00
8
7
6
5
4
3
2
1
0 ppm
4.89
0.96
0.81
1.02
0.93
1.10
2.12
3.00

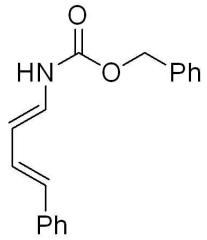



```
NAME          XYY140307-C13
EXPNO                     1
PROCNO                    1
Date_              20140313
Time                  21.36
INSTRUM               spect
PROBHD    5 mm PABBO BB-
PULPROG            zgpg30
TD                    65536
SOLVENT               CDC13
NS                     1024
DS                        4
SWH             24038.461 Hz
FIDRES           0.366798 Hz
AQ               1.3631988 sec
RG                      203
DW                 20.800 usec
DE                  6.50 usec
TE                  296.9 K
D1              2.00000000 sec
D11             0.03000000 sec
TD0                       1

======== CHANNEL f1 ========
NUC1                    13C
P1                   8.50 usec
PL1                 -2.00 dB
PL1W          57.32743073 W
SFO1         100.6328888 MHz

======== CHANNEL f2 ========
CPDPRG2           waltz16
NUC2                    1H
PCPD2               80.00 usec
PL2                 -1.00 dB
PL12                14.26 dB
PL13                14.46 dB
PL2W          13.18669796 W
PL12W          0.39276794 W
PL13W          0.37509048 W
SFO2         400.1716007 MHz
SI                  32768
SF           100.6228270 MHz
WDW                    EM
SSB                     0
LB                   1.00 Hz
GB                      0
PC                   1.40
```






```
NAME          LMK130927-1
EXPNO                   1
PROCNO                  1
Date_            20130929
Time                15.34
INSTRUM             spect
PROBHD    5 mm PABBO BB-
PULPROG              zg30
TD                  65536
SOLVENT             CDCl3
NS                     16
DS                      2
SWH              8223.685 Hz
FIDRES           0.125483 Hz
AQ               3.9846387 sec
RG                    203
DW                 60.800 usec
DE                  6.50 usec
TE                 297.7 K
D1              1.00000000 sec
TD0                     1

======== CHANNEL f1 ========
NUC1                   1H
P1                  13.80 usec
PL1                 -1.00 dB
PL1W          13.18669796 W
SFO1          400.1724712 MHz
SI                  32768
SF            400.1700074 MHz
WDW                    EM
SSB                     0
LB                  0.30 Hz
GB                      0
PC                   1.00
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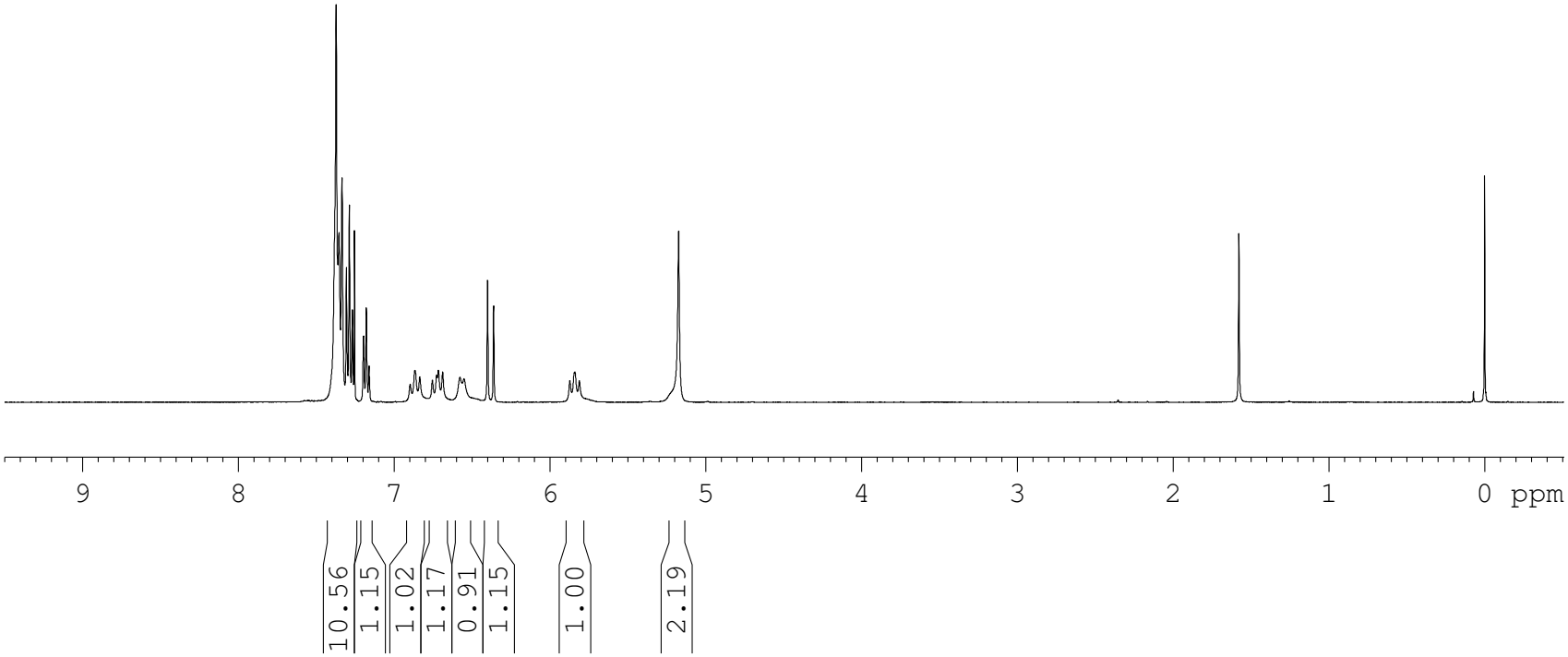
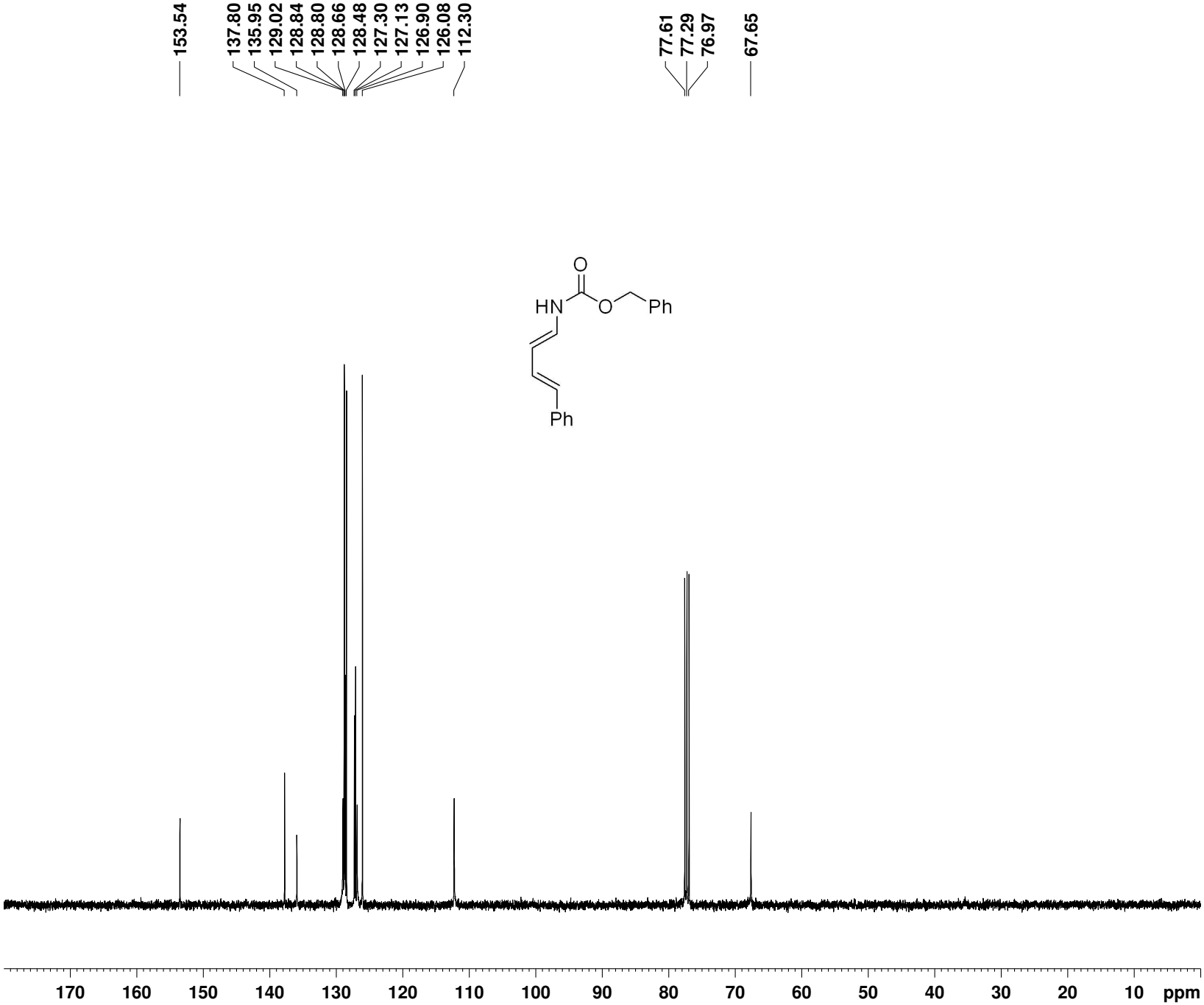
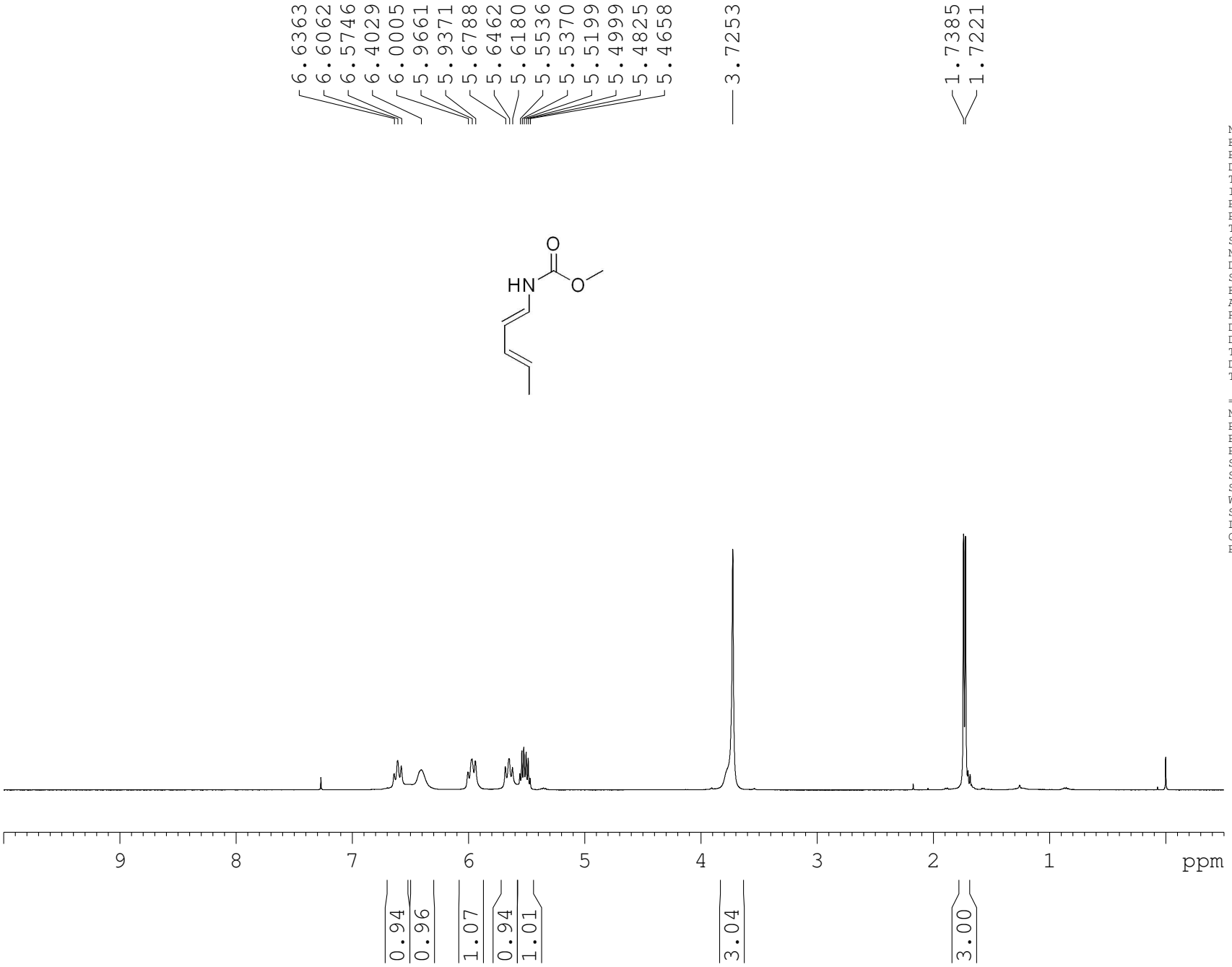




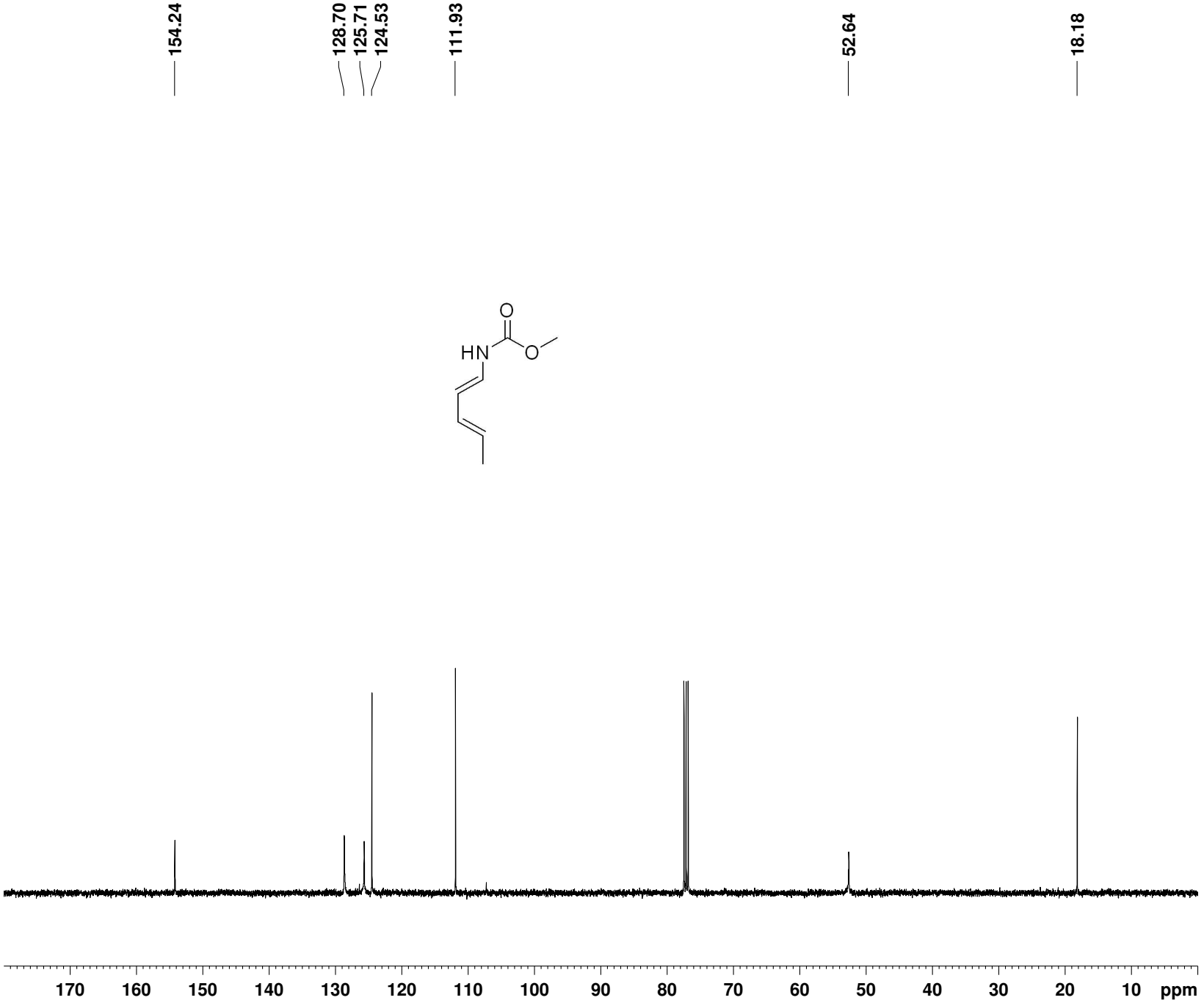
BRUKER

NAME	LMK130927-C13
EXPNO	1
PROCNO	1
Date_	20140228
Time	22.22
INSTRUM	spect
PROBHD	5 mm PABBO BB-
PULPROG	zgpg30
TD	65536
SOLVENT	CDCl3
NS	101
DS	4
SWH	24038.461 Hz
FIDRES	0.366798 Hz
AQ	1.3631988 sec
RG	203
DW	20.800 usec
DE	6.50 usec
TE	293.7 K
D1	2.00000000 sec
D11	0.03000000 sec
TD0	1
======== CHANNEL f1 ========	
NUC1	13C
P1	8.50 usec
PL1	-2.00 dB
PL1W	57.32743073 W
SFO1	100.6328888 MHz
======== CHANNEL f2 ========	
CPDPRG2	waltz16
NUC2	1H
PCPD2	80.00 usec
PL2	-1.00 dB
PL12	14.26 dB
PL13	14.46 dB
PL2W	13.18669796 W
PL12W	0.39276794 W
PL13W	0.37509048 W
SFO2	400.1716007 MHz
SI	32768
SF	100.6228110 MHz
WDW	EM
SSB	0
LB	1.00 Hz
GB	0
PC	1.40



BRUKER

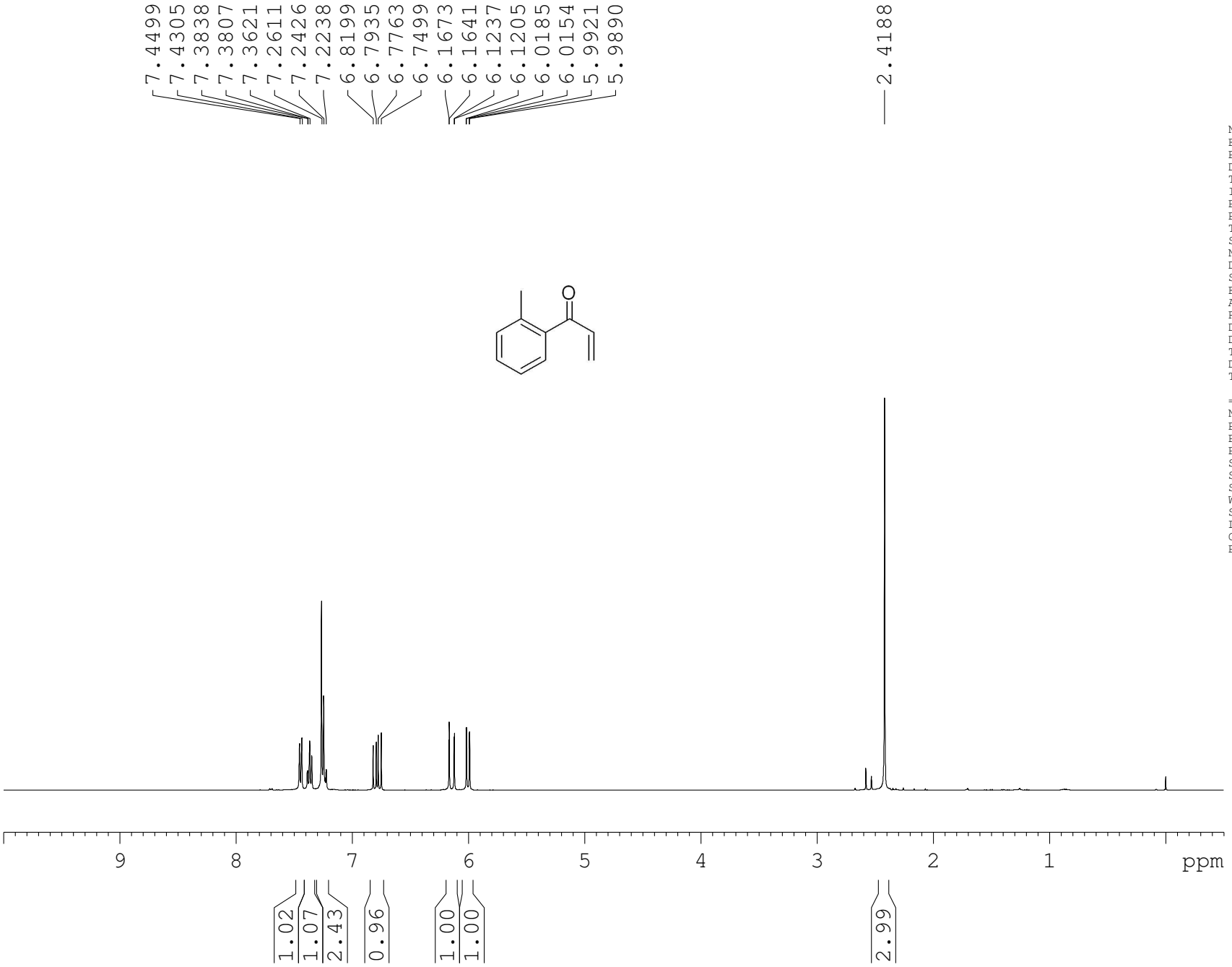
NAME	XYH130624-2
EXPNO	1
PROCNO	1
Date_	20140314
Time	19.20
INSTRUM	spect
PROBHD	5 mm PABBO BB-
PULPROG	zg30
TD	65536
SOLVENT	CDCl3
NS	16
DS	2
SWH	8223.685 Hz
FIDRES	0.125483 Hz
AQ	3.9846387 sec
RG	144
DW	60.800 usec
DE	6.50 usec
TE	298.0 K
D1	1.00000000 sec
TD0	1
======== CHANNEL f1 ========	
NUC1	1H
P1	13.80 usec
PL1	-1.00 dB
PL1W	13.18669796 W
SFO1	400.1724712 MHz
SI	32768
SF	400.1700002 MHz
WDW	EM
SSB	0
LB	0.30 Hz
GB	0
PC	1.00




```
NAME          XYH130624-C13-2
EXPNO                       1
PROCNO                      1
Date_                20140315
Time                    17.17
INSTRUM                 spect
PROBHD    5 mm PABBO BB-
PULPROG                 zgpg30
TD                       65536
SOLVENT                  CDCl3
NS                         156
DS                           4
SWH                 24038.461 Hz
FIDRES               0.366798 Hz
AQ                   1.3631988 sec
RG                         203
DW                      20.800 usec
DE                       6.50 usec
TE                      300.8 K
D1                  2.00000000 sec
D11                 0.03000000 sec
TD0                          1

======== CHANNEL f1 ========
NUC1                       13C
P1                       8.50 usec
PL1                     -2.00 dB
PL1W               57.32743073 W
SFO1              100.6328888 MHz

======== CHANNEL f2 ========
CPDPRG2                waltz16
NUC2                       1H
PCPD2                   80.00 usec
PL2                     -1.00 dB
PL12                    14.26 dB
PL13                    14.46 dB
PL2W               13.18669796 W
PL12W               0.39276794 W
PL13W               0.37509048 W
SFO2              400.1716007 MHz
SI                       32768
SF                100.6228110 MHz
WDW                         EM
SSB                          0
LB                        1.00 Hz
GB                           0
PC                        1.40
```

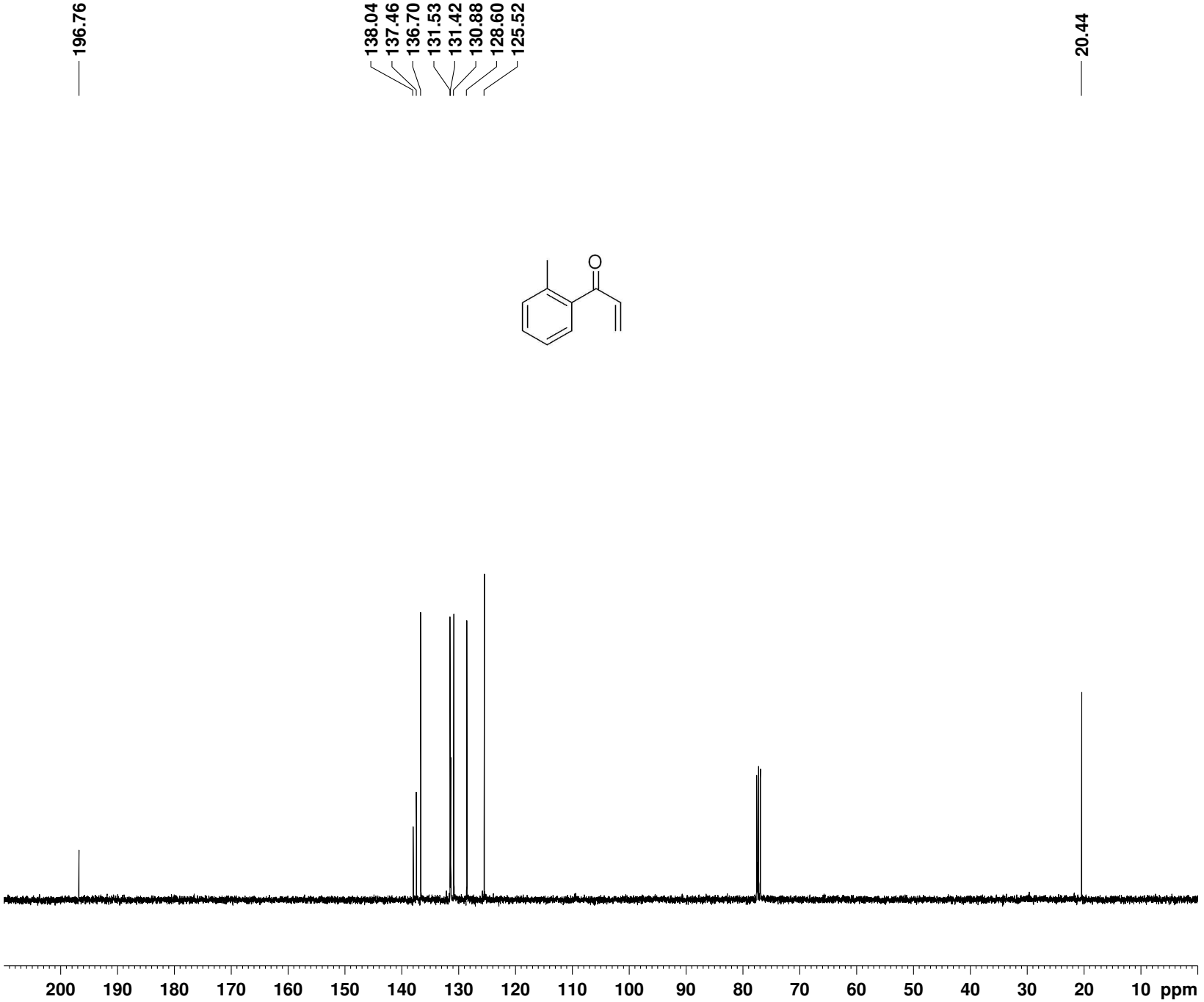


BRUKER

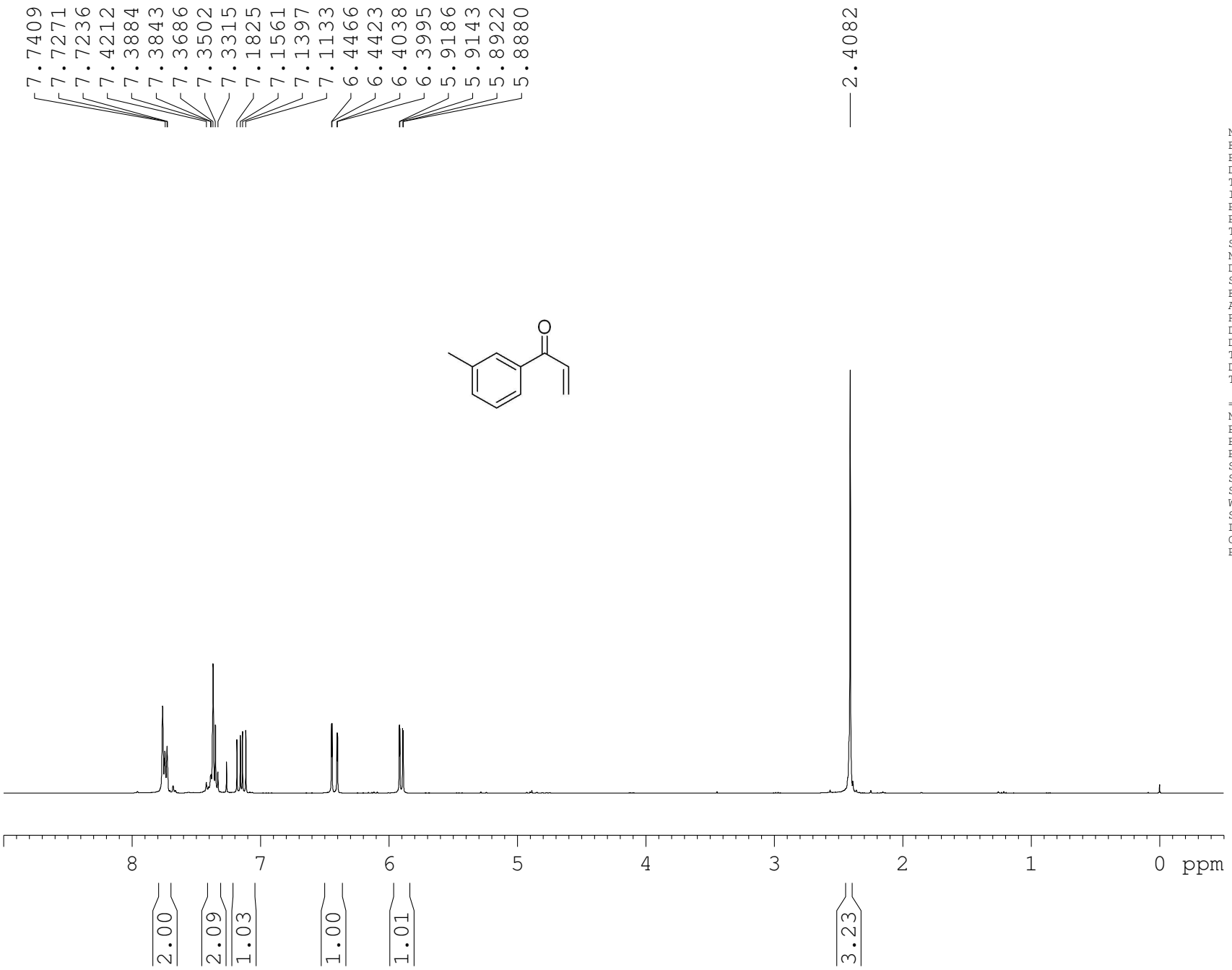
NAME	LMK140226-1
EXPNO	1
PROCNO	1
Date_	20140228
Time	9.14
INSTRUM	spect
PROBHD	5 mm PABBO BB-
PULPROG	zg30
TD	65536
SOLVENT	CDCl3
NS	16
DS	2
SWH	8223.685 Hz
FIDRES	0.125483 Hz
AQ	3.9846387 sec
RG	90.5
DW	60.800 usec
DE	6.50 usec
TE	292.9 K
D1	1.00000000 sec
TD0	1

======== CHANNEL f1 ========

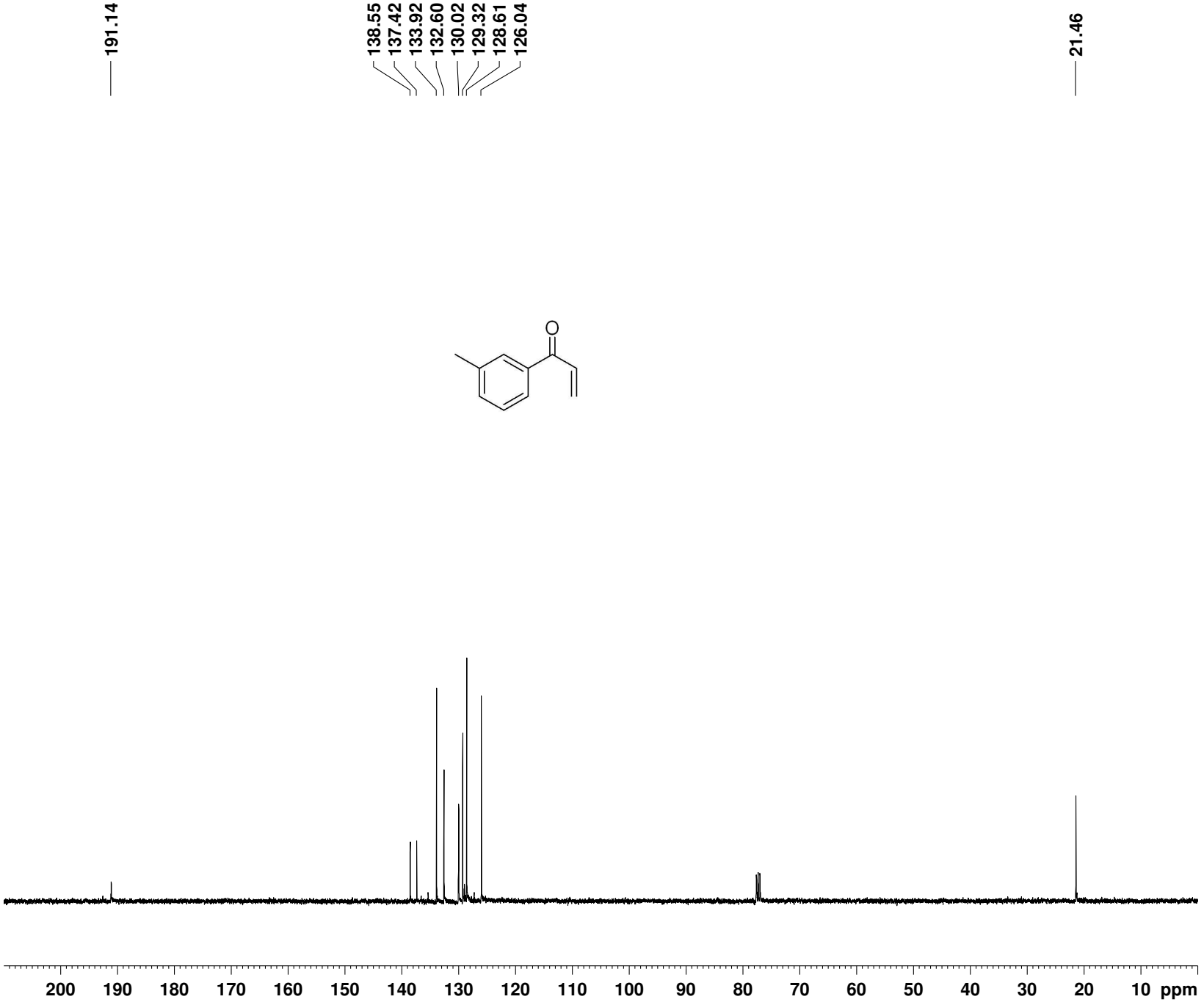
NUC1	1H
P1	13.80 usec
PL1	-1.00 dB
PL1W	13.18669796 W
SFO1	400.1724712 MHz
SI	32768
SF	400.1700024 MHz
WDW	EM
SSB	0
LB	0.30 Hz
GB	0
PC	1.00



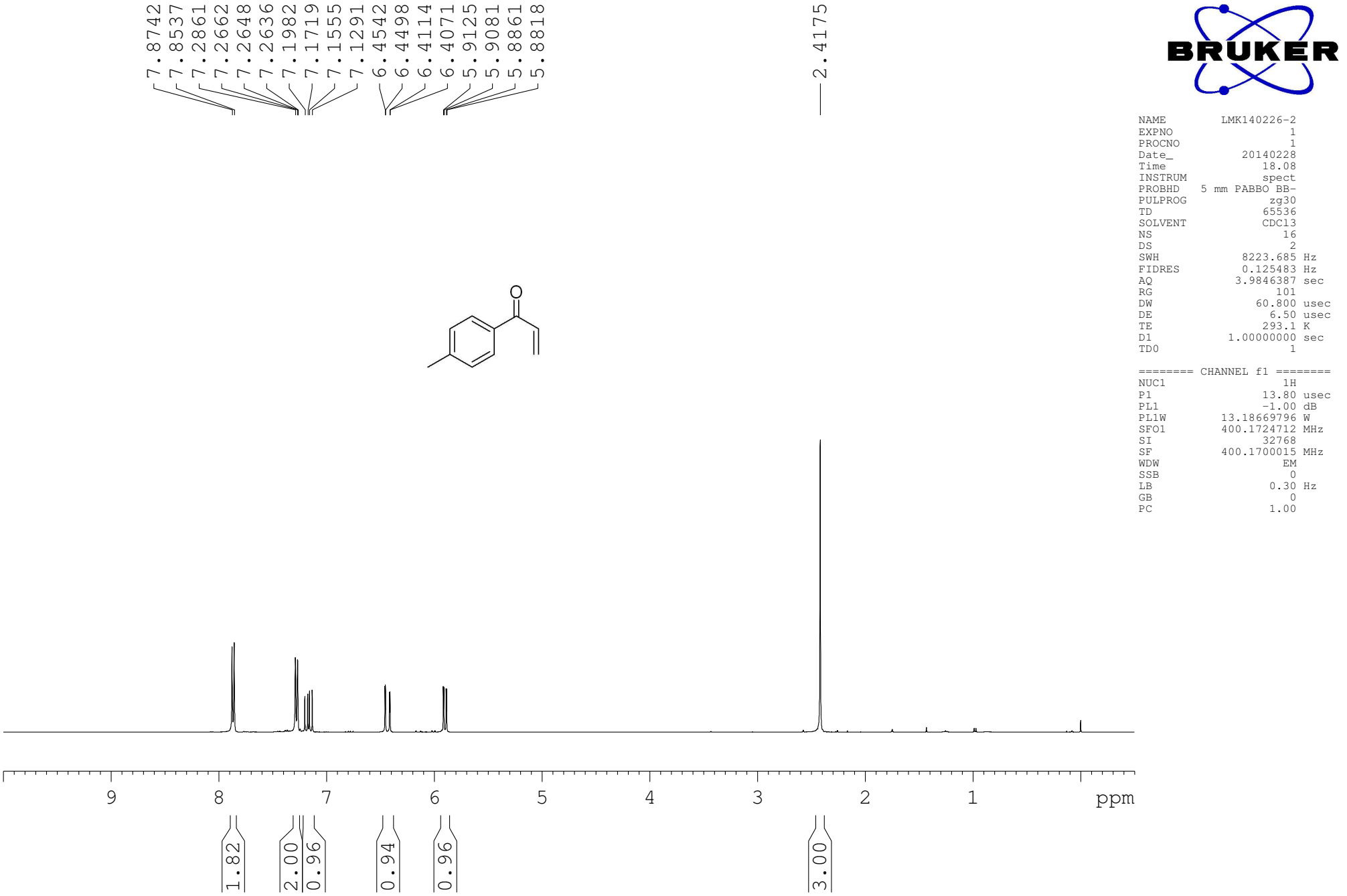
NAME	LMK140226-1-C13
EXPNO	1
PROCNO	1
Date_	20140307
Time	20.23
INSTRUM	spect
PROBHD	5 mm PABBO BB-
PULPROG	zgpg30
TD	65536
SOLVENT	CDCl3
NS	34
DS	4
SWH	24038.461 Hz
FIDRES	0.366798 Hz
AQ	1.3631988 sec
RG	203
DW	20.800 usec
DE	6.50 usec
TE	294.6 K
D1	2.00000000 sec
D11	0.03000000 sec
TD0	1
======== CHANNEL f1 ========	
NUC1	13C
P1	8.50 usec
PL1	-2.00 dB
PL1W	57.32743073 W
SFO1	100.6328888 MHz
======== CHANNEL f2 ========	
CPDPRG2	waltz16
NUC2	1H
PCPD2	80.00 usec
PL2	-1.00 dB
PL12	14.26 dB
PL13	14.46 dB
PL2W	13.18669796 W
PL12W	0.39276794 W
PL13W	0.37509048 W
SFO2	400.1716007 MHz
SI	32768
SF	100.6228110 MHz
WDW	EM
SSB	0
LB	1.00 Hz
GB	0
PC	1.40



NAME	LMK140303-3
EXPNO	1
PROCNO	1
Date_	20140305
Time	13.10
INSTRUM	spect
PROBHD	5 mm PABBO BB-
PULPROG	zg30
TD	65536
SOLVENT	CDCl3
NS	16
DS	2
SWH	8223.685 Hz
FIDRES	0.125483 Hz
AQ	3.9846387 sec
RG	40.3
DW	60.800 usec
DE	6.50 usec
TE	295.3 K
D1	1.00000000 sec
TD0	1
======== CHANNEL f1 ========	
NUC1	1H
P1	13.80 usec
PL1	-1.00 dB
PL1W	13.18669796 W
SFO1	400.1724712 MHz
SI	32768
SF	400.1700010 MHz
WDW	EM
SSB	0
LB	0.30 Hz
GB	0
PC	1.00

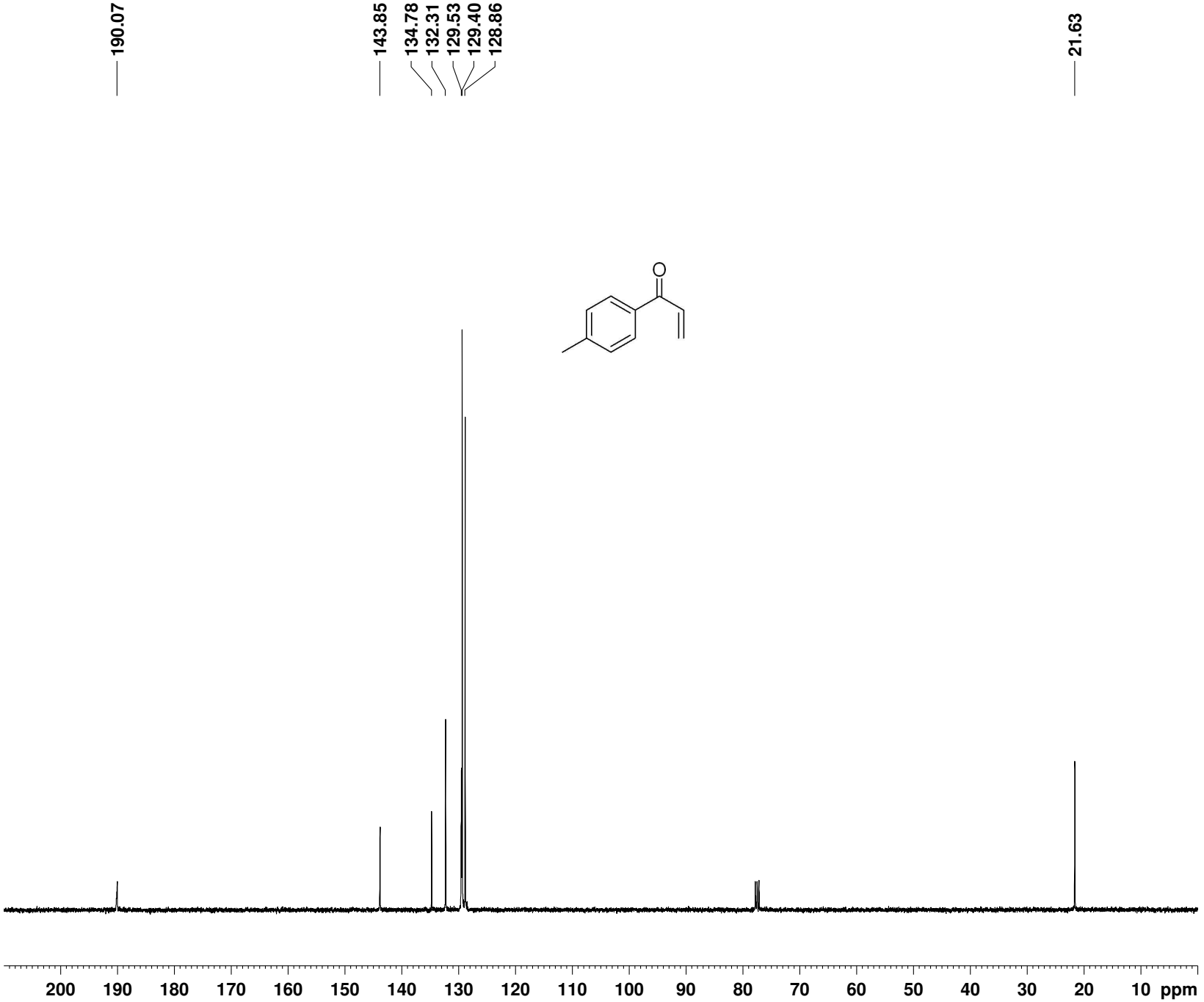


NAME	LMK140303-3-C13
EXPNO	1
PROCNO	1
Date_	20140307
Time	20.29
INSTRUM	spect
PROBHD	5 mm PABBO BB-
PULPROG	zgpg30
TD	65536
SOLVENT	CDCl3
NS	28
DS	4
SWH	24038.461 Hz
FIDRES	0.366798 Hz
AQ	1.3631988 sec
RG	203
DW	20.800 usec
DE	6.50 usec
TE	294.6 K
D1	2.00000000 sec
D11	0.03000000 sec
TD0	1
======== CHANNEL f1 ========	
NUC1	13C
P1	8.50 usec
PL1	-2.00 dB
PL1W	57.32743073 W
SFO1	100.6328888 MHz
======== CHANNEL f2 ========	
CPDPRG2	waltz16
NUC2	1H
PCPD2	80.00 usec
PL2	-1.00 dB
PL12	14.26 dB
PL13	14.46 dB
PL2W	13.18669796 W
PL12W	0.39276794 W
PL13W	0.37509048 W
SFO2	400.1716007 MHz
SI	32768
SF	100.6228110 MHz
WDW	EM
SSB	0
LB	1.00 Hz
GB	0
PC	1.40



BRUKER

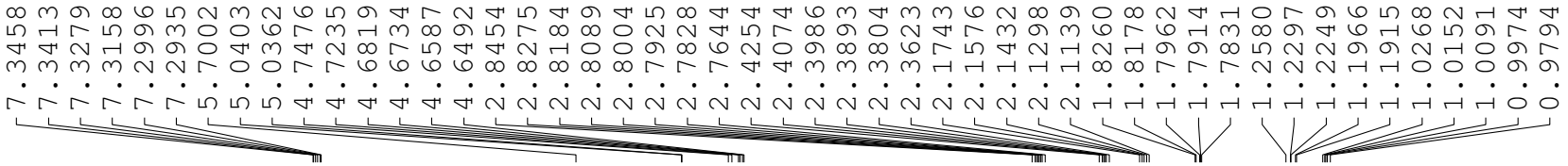
NAME	LMK140226-2
EXPNO	1
PROCNO	1
Date_	20140228
Time	18.08
INSTRUM	spect
PROBHD	5 mm PABBO BB-
PULPROG	zg30
TD	65536
SOLVENT	CDCl3
NS	16
DS	2
SWH	8223.685 Hz
FIDRES	0.125483 Hz
AQ	3.9846387 sec
RG	101
DW	60.800 usec
DE	6.50 usec
TE	293.1 K
D1	1.00000000 sec
TD0	1
======== CHANNEL f1 ========	
NUC1	1H
P1	13.80 usec
PL1	-1.00 dB
PL1W	13.18669796 W
SFO1	400.1724712 MHz
SI	32768
SF	400.1700015 MHz
WDW	EM
SSB	0
LB	0.30 Hz
GB	0
PC	1.00

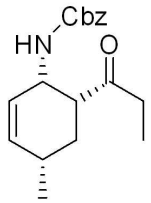



```
NAME      LMK140226-2-C13
EXPNO                  1
PROCNO                 1
Date_           20140307
Time               20.36
INSTRUM            spect
PROBHD   5 mm PABBO BB-
PULPROG          zgpg30
TD                65536
SOLVENT            CDC13
NS                    37
DS                     4
SWH           24038.461 Hz
FIDRES         0.366798 Hz
AQ             1.3631988 sec
RG                   203
DW                20.800 usec
DE                 6.50 usec
TE                294.5 K
D1            2.00000000 sec
D11           0.03000000 sec
TD0                    1

======== CHANNEL f1 ========
NUC1                 13C
P1                  8.50 usec
PL1                -2.00 dB
PL1W        57.32743073 W
SFO1       100.6328888 MHz

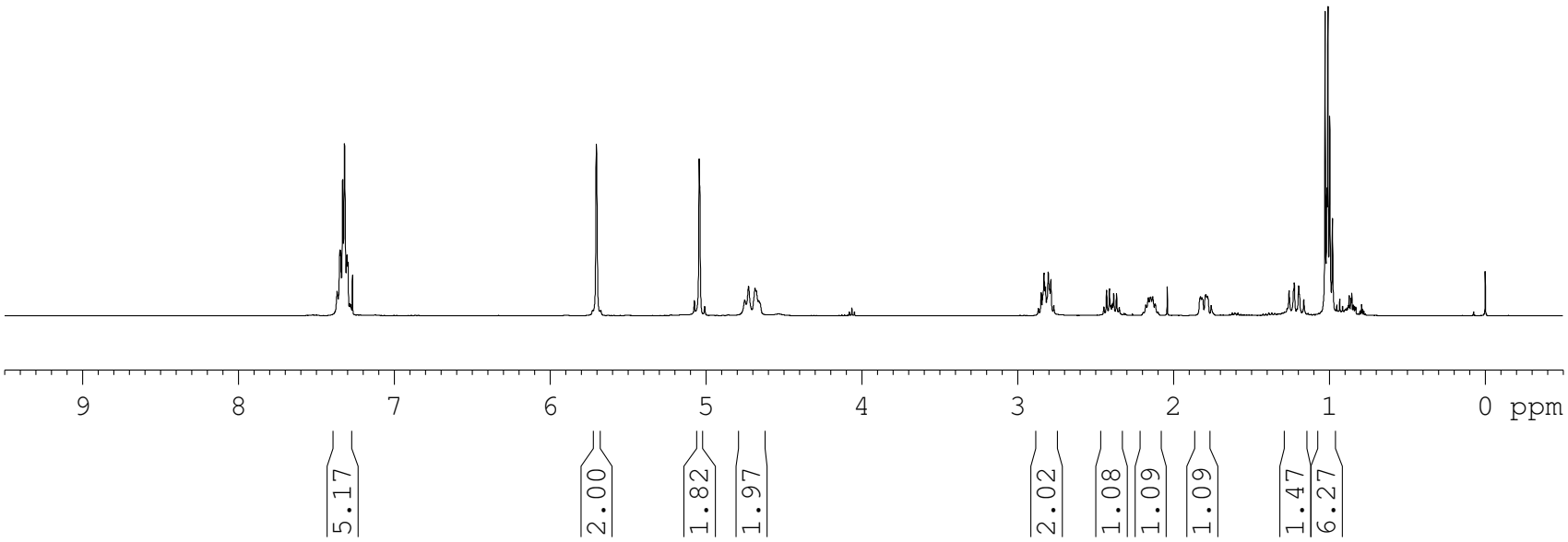
======== CHANNEL f2 ========
CPDPRG2          waltz16
NUC2                 1H
PCPD2              80.00 usec
PL2                -1.00 dB
PL12               14.26 dB
PL13               14.46 dB
PL2W        13.18669796 W
PL12W        0.39276794 W
PL13W        0.37509048 W
SFO2       400.1716007 MHz
SI                 32768
SF         100.6228110 MHz
WDW                   EM
SSB                    0
LB                  1.00 Hz
GB                     0
PC                  1.40
```

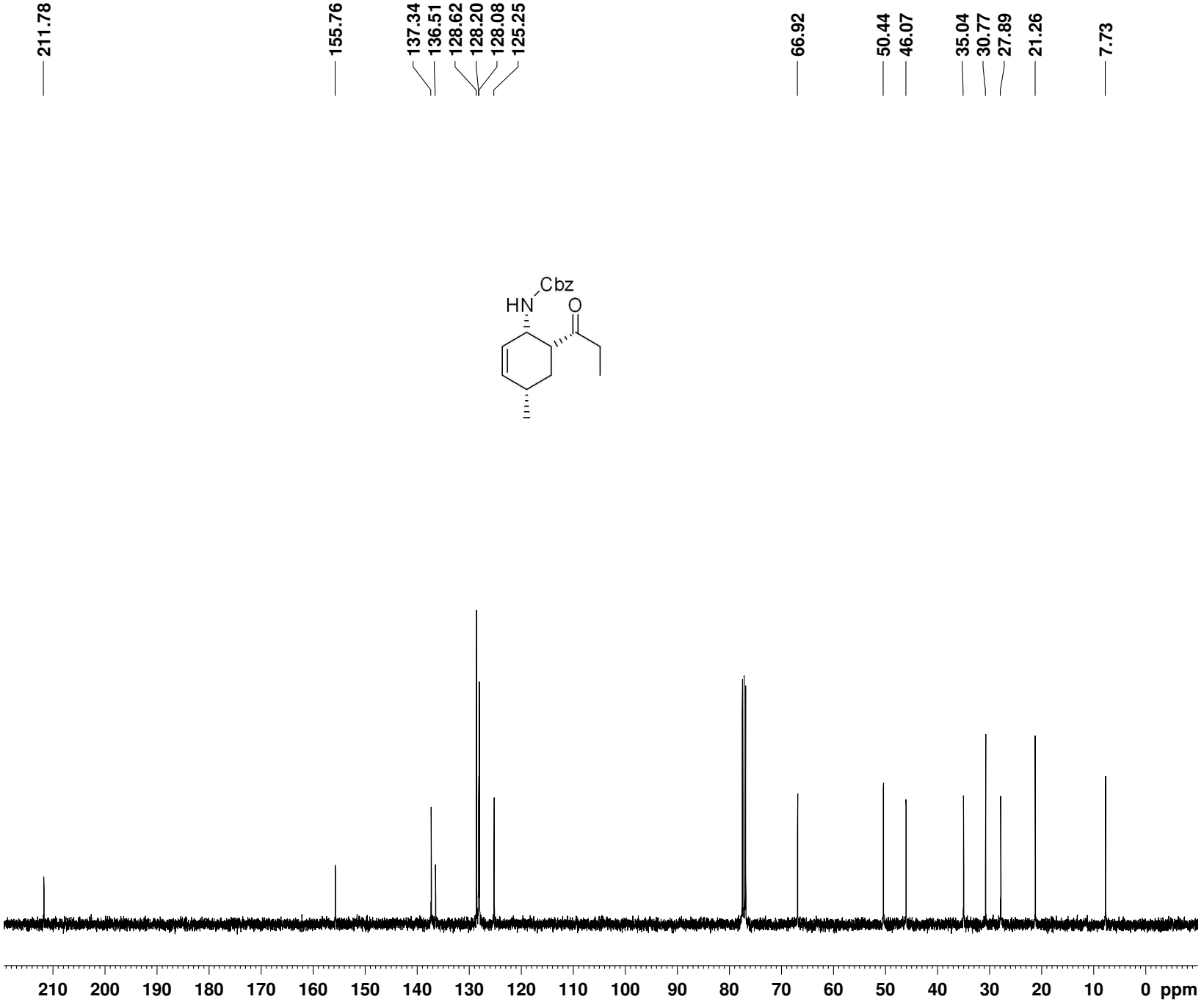


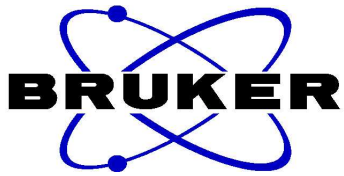



```
NAME          LMK131124-2
EXPNO                   1
PROCNO                  1
Date_            20131125
Time                17.40
INSTRUM             spect
PROBHD    5 mm PABBO BB-
PULPROG              zg30
TD                  65536
SOLVENT             CDCl3
NS                     16
DS                      2
SWH              8223.685 Hz
FIDRES           0.125483 Hz
AQ               3.9846387 sec
RG                   71.8
DW                60.800 usec
DE                 6.50 usec
TE                294.7 K
D1             1.00000000 sec
TD0                     1

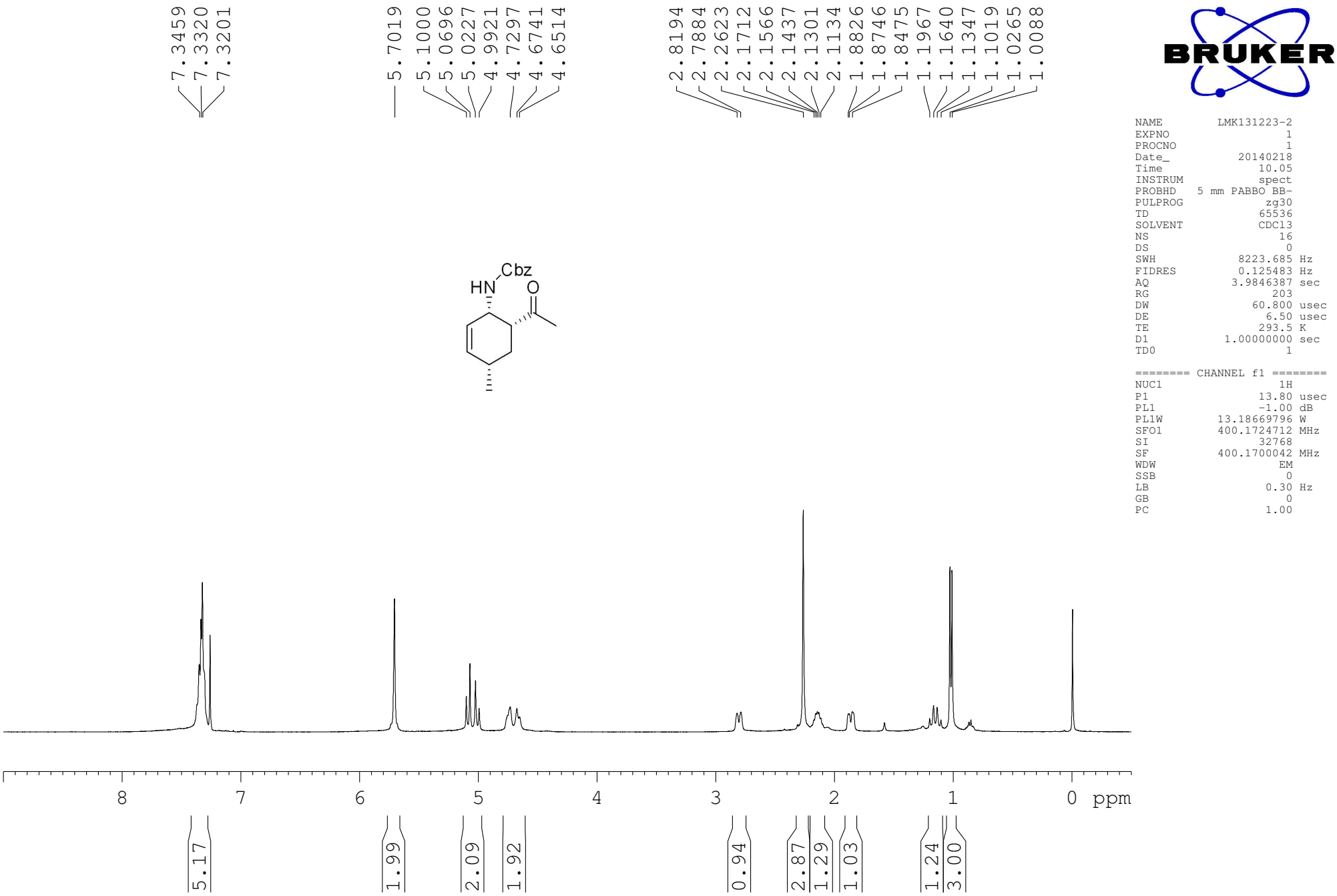
======== CHANNEL f1 ========
NUC1                   1H
P1                  13.80 usec
PL1                 -1.00 dB
PL1W          13.18669796 W
SFO1          400.1724712 MHz
SI                  32768
SF            400.1700008 MHz
WDW                    EM
SSB                     0
LB                   0.30 Hz
GB                      0
PC                   1.00
```



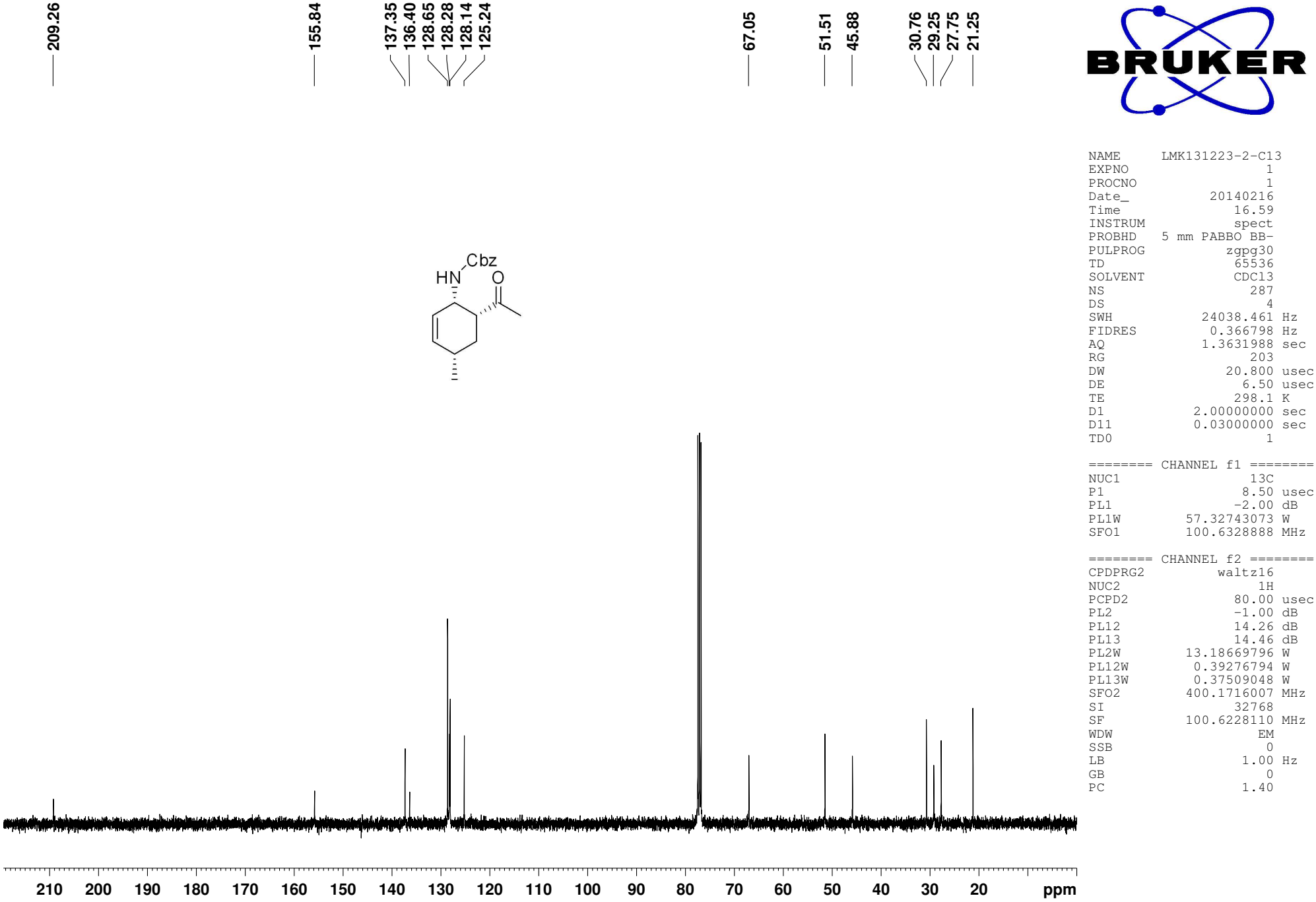




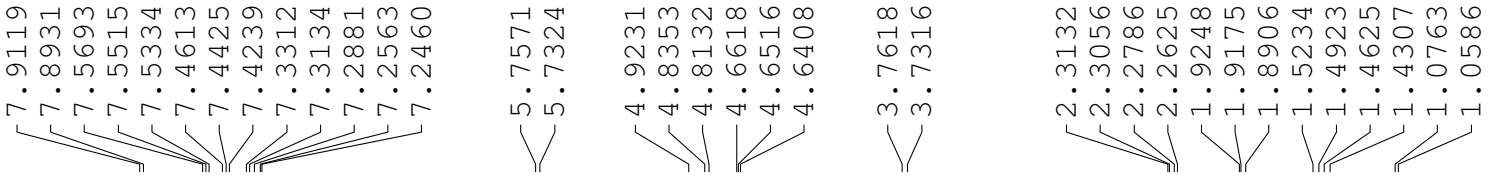
NAME	LMK131124-2-C13
EXPNO	1
PROCNO	1
Date_	20140216
Time	18.45
INSTRUM	spect
PROBHD	5 mm PABBO BB-
PULPROG	zgpg30
TD	65536
SOLVENT	CDCl3
NS	93
DS	4
SWH	24038.461 Hz
FIDRES	0.366798 Hz
AQ	1.3631988 sec
RG	203
DW	20.800 usec
DE	6.50 usec
TE	296.7 K
D1	2.00000000 sec
D11	0.03000000 sec
TD0	1
======== CHANNEL f1 ========	
NUC1	13C
P1	8.50 usec
PL1	-2.00 dB
PL1W	57.32743073 W
SFO1	100.6328888 MHz
======== CHANNEL f2 ========	
CPDPRG2	waltz16
NUC2	1H
PCPD2	80.00 usec
PL2	-1.00 dB
PL12	14.26 dB
PL13	14.46 dB
PL2W	13.18669796 W
PL12W	0.39276794 W
PL13W	0.37509048 W
SFO2	400.1716007 MHz
SI	32768
SF	100.6228110 MHz
WDW	EM
SSB	0
LB	1.00 Hz
GB	0
PC	1.40

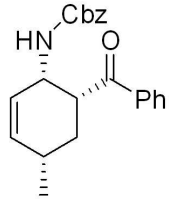


NAME	LMK131223-2
EXPNO	1
PROCNO	1
Date_	20140218
Time	10.05
INSTRUM	spect
PROBHD	5 mm PABBO BB-
PULPROG	zg30
TD	65536
SOLVENT	CDCl3
NS	16
DS	0
SWH	8223.685 Hz
FIDRES	0.125483 Hz
AQ	3.9846387 sec
RG	203
DW	60.800 usec
DE	6.50 usec
TE	293.5 K
D1	1.00000000 sec
TD0	1
======== CHANNEL f1 ========	
NUC1	1H
P1	13.80 usec
PL1	-1.00 dB
PL1W	13.18669796 W
SFO1	400.1724712 MHz
SI	32768
SF	400.1700042 MHz
WDW	EM
SSB	0
LB	0.30 Hz
GB	0
PC	1.00



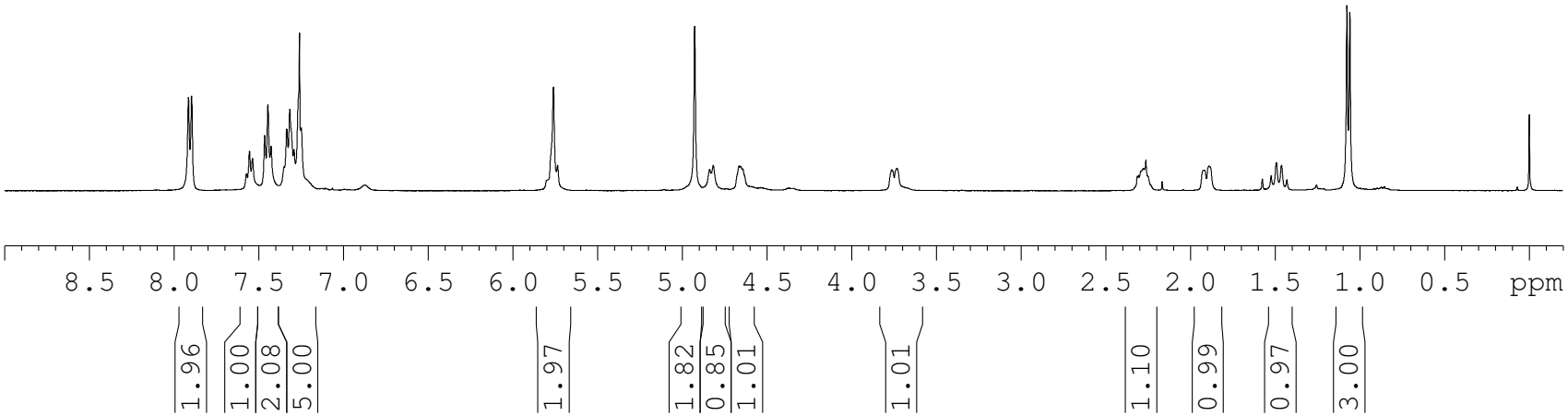
NAME	LMK131223-2-C13
EXPNO	1
PROCNO	1
Date_	20140216
Time	16.59
INSTRUM	spect
PROBHD	5 mm PABBO BB-
PULPROG	zgpg30
TD	65536
SOLVENT	CDC13
NS	287
DS	4
SWH	24038.461 Hz
FIDRES	0.366798 Hz
AQ	1.3631988 sec
RG	203
DW	20.800 usec
DE	6.50 usec
TE	298.1 K
D1	2.00000000 sec
D11	0.03000000 sec
TD0	1
======== CHANNEL f1 ========	
NUC1	13C
P1	8.50 usec
PL1	-2.00 dB
PL1W	57.32743073 W
SFO1	100.6328888 MHz
======== CHANNEL f2 ========	
CPDPRG2	waltz16
NUC2	1H
PCPD2	80.00 usec
PL2	-1.00 dB
PL12	14.26 dB
PL13	14.46 dB
PL2W	13.18669796 W
PL12W	0.39276794 W
PL13W	0.37509048 W
SFO2	400.1716007 MHz
SI	32768
SF	100.6228110 MHz
WDW	EM
SSB	0
LB	1.00 Hz
GB	0
PC	1.40

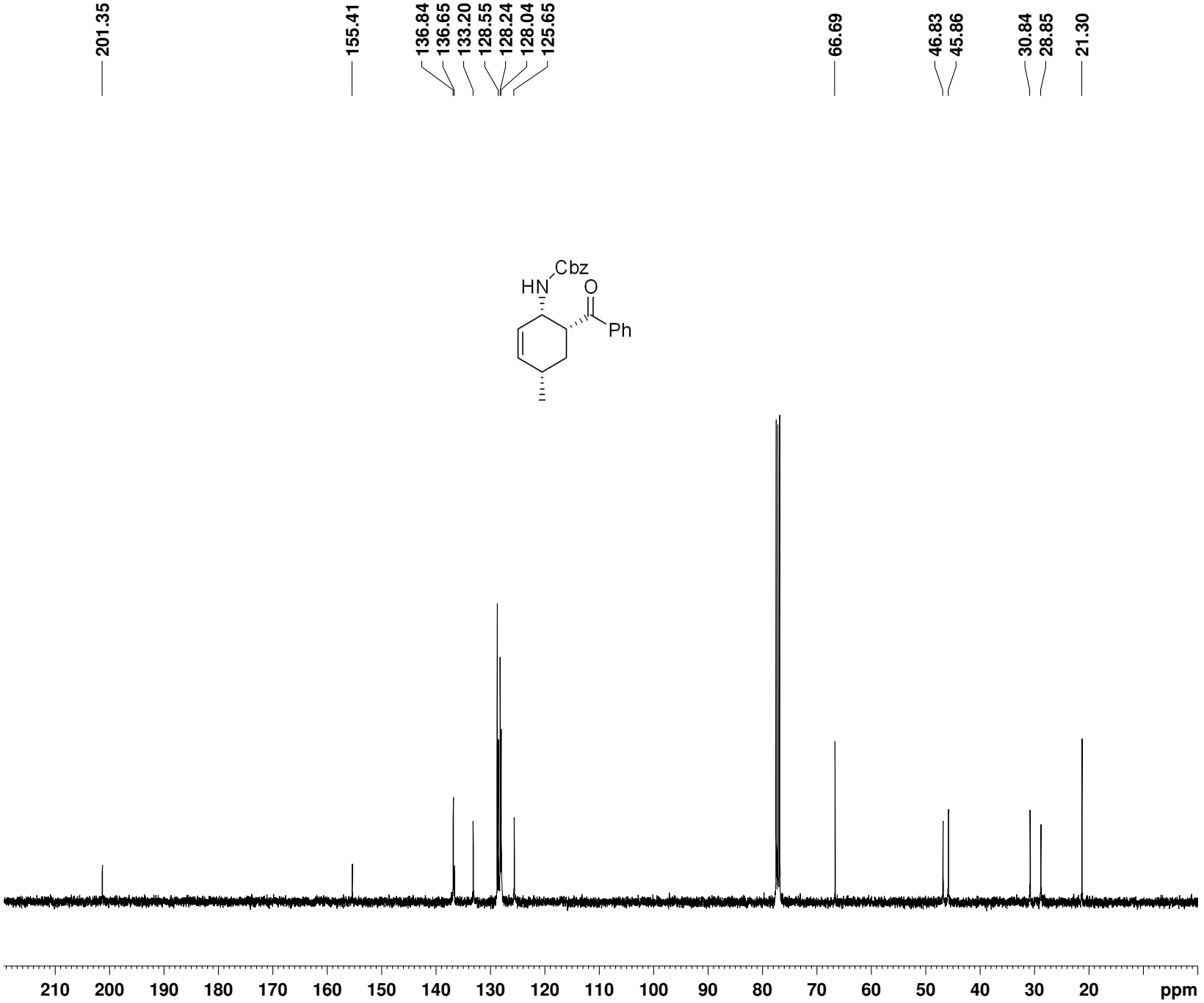




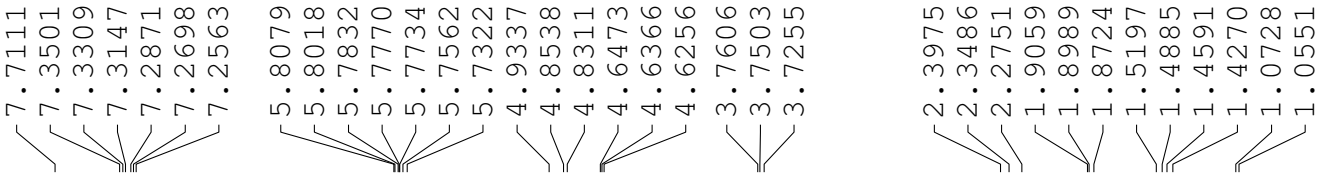

```
NAME          LMK131210-X
EXPNO                   1
PROCNO                  1
Date_            20140314
Time                11.44
INSTRUM             spect
PROBHD    5 mm PABBO BB-
PULPROG              zg30
TD                  65536
SOLVENT             CDCl3
NS                     16
DS                      2
SWH              8223.685 Hz
FIDRES           0.125483 Hz
AQ               3.9846387 sec
RG                    161
DW                 60.800 usec
DE                  6.50 usec
TE                 297.7 K
D1              1.00000000 sec
TD0                     1

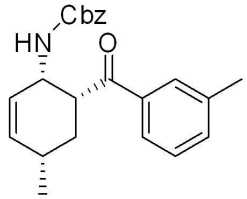
======== CHANNEL f1 ========
NUC1                   1H
P1                  13.80 usec
PL1                 -1.00 dB
PL1W          13.18669796 W
SFO1          400.1724712 MHz
SI                  32768
SF            400.1700042 MHz
WDW                    EM
SSB                     0
LB                  0.30 Hz
GB                      0
PC                   1.00
```





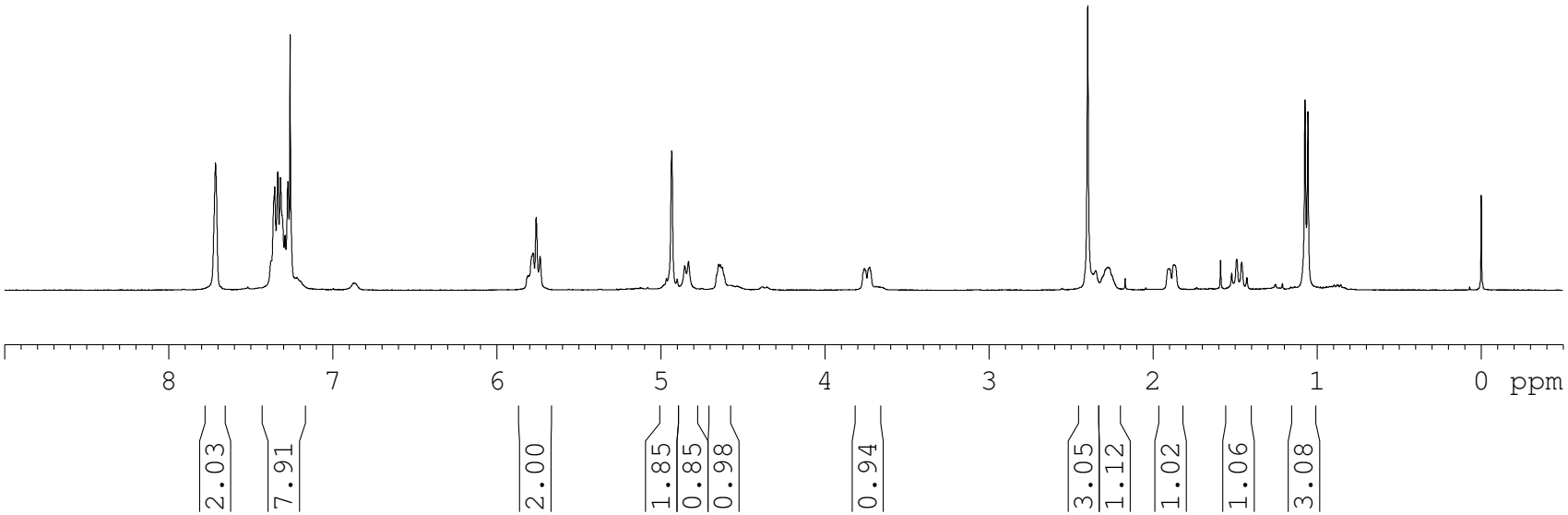
NAME	LMK1311210-C13
EXPNO	1
PROCNO	1
Date_	20140216
Time	18.55
INSTRUM	spect
PROBHD	5 mm PABBO BB-
PULPROG	zgpg30
TD	65536
SOLVENT	CDC13
NS	355
DS	4
SWH	24038.461 Hz
FIDRES	0.366798 Hz
AQ	1.3631988 sec
RG	203
DW	20.800 usec
DE	6.50 usec
TE	296.5 K
D1	2.00000000 sec
D11	0.03000000 sec
TD0	1
======== CHANNEL f1 ========	
NUC1	13C
P1	8.50 usec
PL1	-2.00 dB
PL1W	57.32743073 W
SFO1	100.6328888 MHz
======== CHANNEL f2 ========	
CPDPRG2	waltz16
NUC2	1H
PCPD2	80.00 usec
PL2	-1.00 dB
PL12	14.26 dB
PL13	14.46 dB
PL2W	13.18669796 W
PL12W	0.39276794 W
PL13W	0.37509048 W
SFO2	400.1716007 MHz
SI	32768
SF	100.6228110 MHz
WDW	EM
SSB	0
LB	1.00 Hz
GB	0
PC	1.40

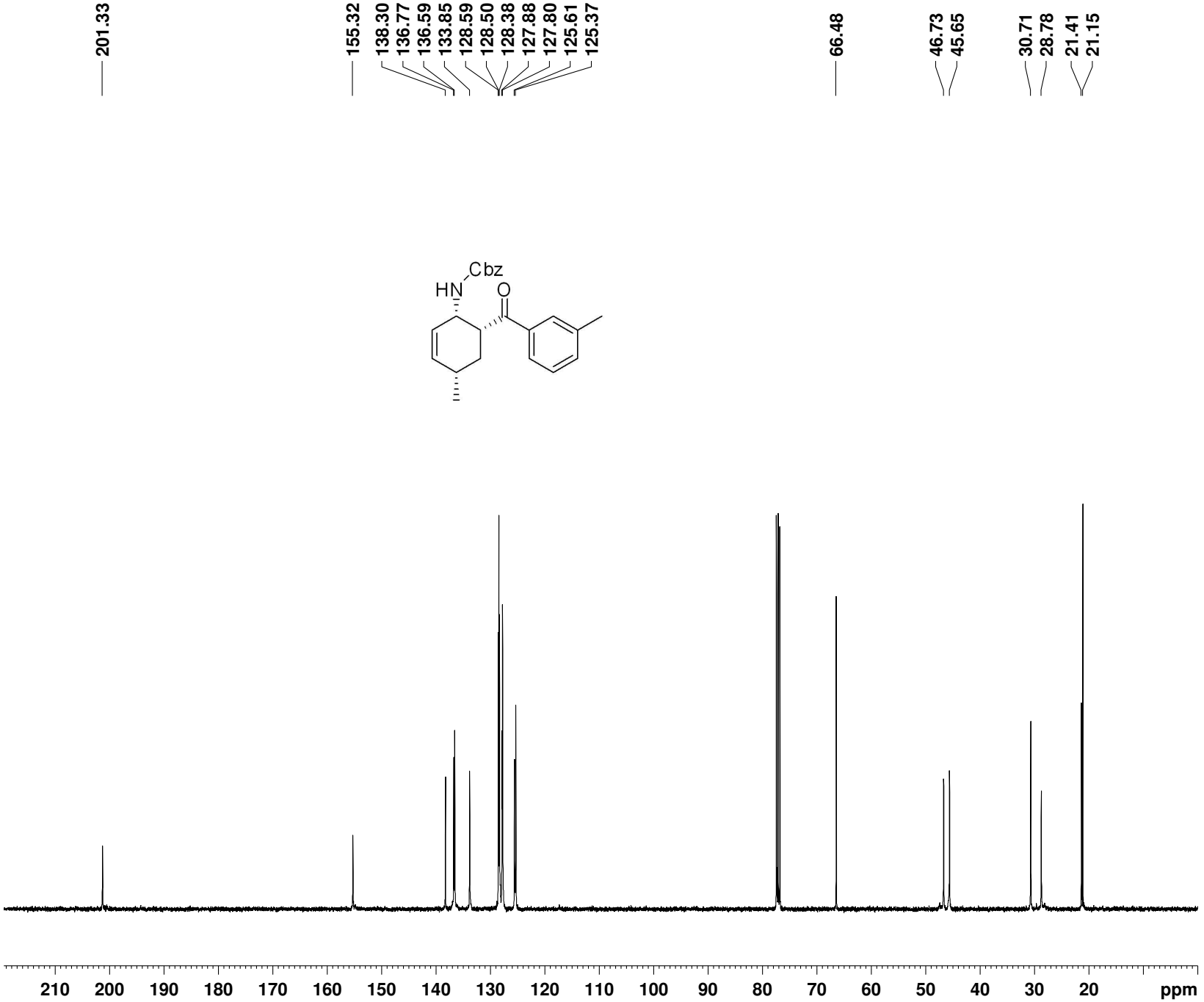




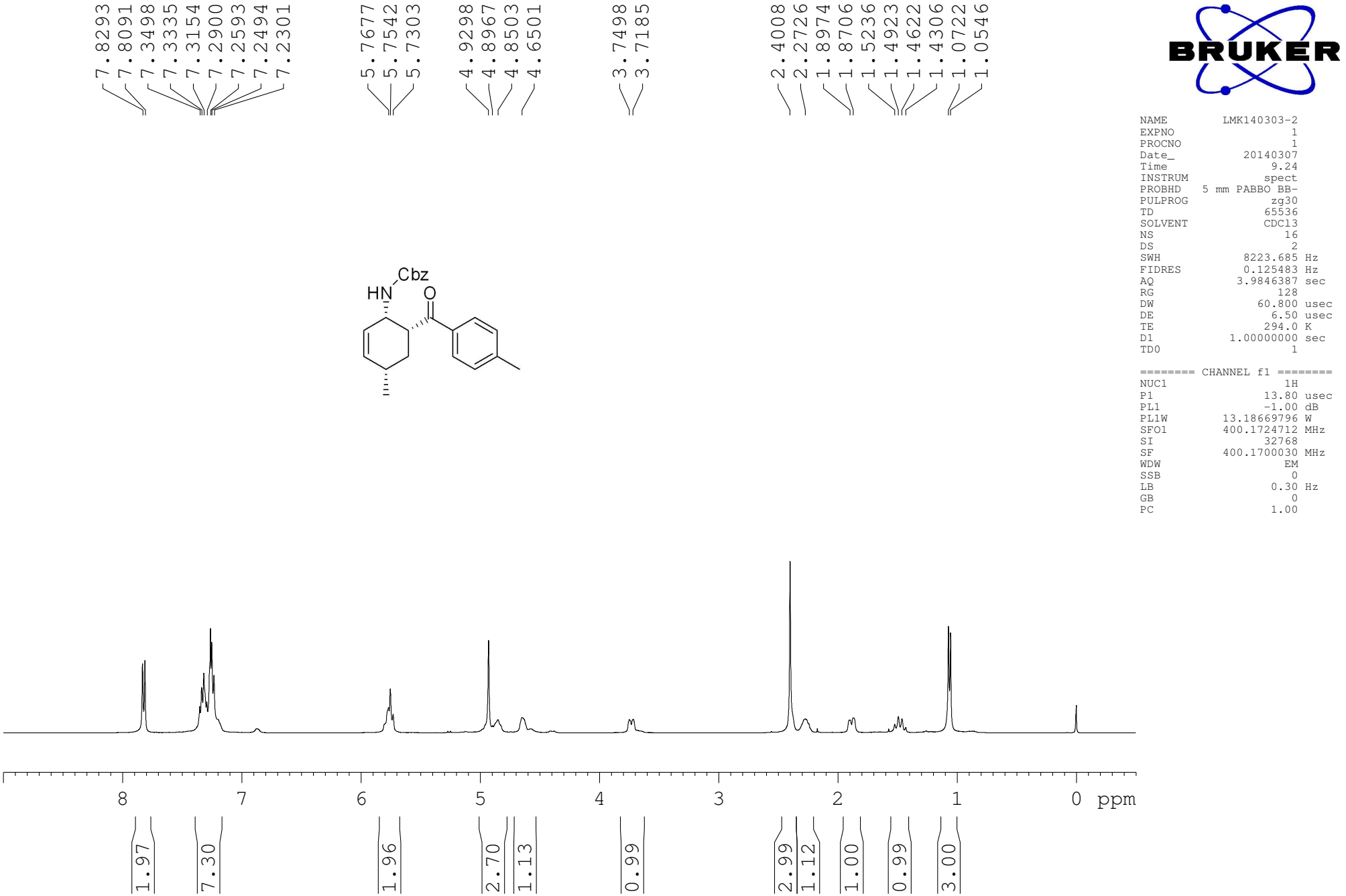

```
NAME          LMK140306-2
EXPNO                   1
PROCNO                  1
Date_            20140307
Time                20.13
INSTRUM             spect
PROBHD    5 mm PABBO BB-
PULPROG              zg30
TD                  65536
SOLVENT             CDCl3
NS                     16
DS                      0
SWH              8223.685 Hz
FIDRES           0.125483 Hz
AQ               3.9846387 sec
RG                    144
DW                 60.800 usec
DE                  6.50 usec
TE                 294.6 K
D1              1.00000000 sec
TD0                     1

======== CHANNEL f1 ========
NUC1                   1H
P1                  13.80 usec
PL1                 -1.00 dB
PL1W          13.18669796 W
SFO1          400.1724712 MHz
SI                  32768
SF            400.1700042 MHz
WDW                    EM
SSB                     0
LB                   0.30 Hz
GB                      0
PC                   1.00
```





NAME	LMK140310-2-C13
EXPNO	1
PROCNO	1
Date_	20140314
Time	14.16
INSTRUM	spect
PROBHD	5 mm PABBO BB-
PULPROG	zgpg30
TD	65536
SOLVENT	CDCl3
NS	717
DS	4
SWH	24038.461 Hz
FIDRES	0.366798 Hz
AQ	1.3631988 sec
RG	203
DW	20.800 usec
DE	6.50 usec
TE	301.6 K
D1	2.00000000 sec
D11	0.03000000 sec
TD0	1
======== CHANNEL f1 ========	
NUC1	13C
P1	8.50 usec
PL1	-2.00 dB
PL1W	57.32743073 W
SFO1	100.6328888 MHz
======== CHANNEL f2 ========	
CPDPRG2	waltz16
NUC2	1H
PCPD2	80.00 usec
PL2	-1.00 dB
PL12	14.26 dB
PL13	14.46 dB
PL2W	13.18669796 W
PL12W	0.39276794 W
PL13W	0.37509048 W
SFO2	400.1716007 MHz
SI	32768
SF	100.6228270 MHz
WDW	EM
SSB	0
LB	1.00 Hz
GB	0
PC	1.40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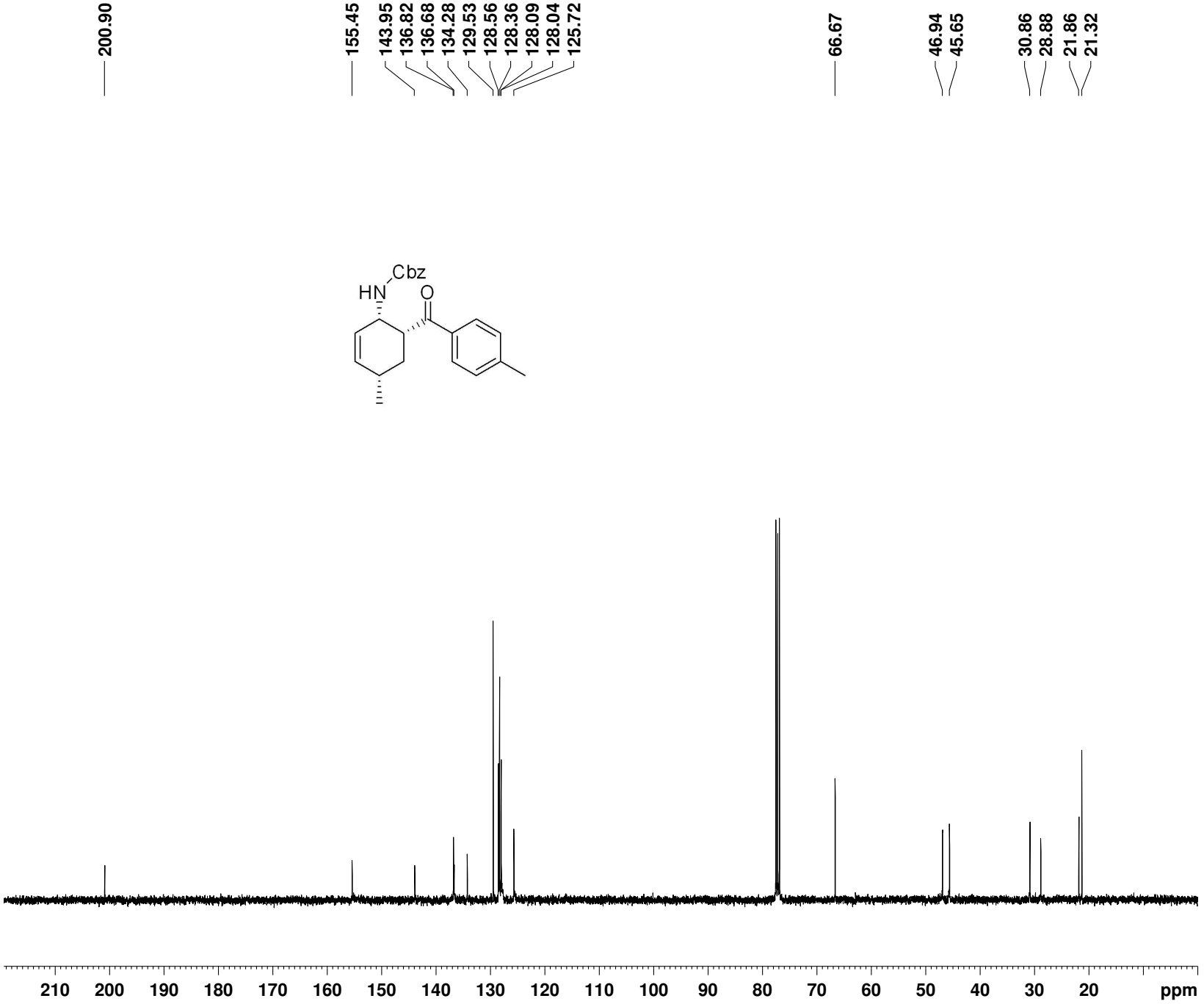
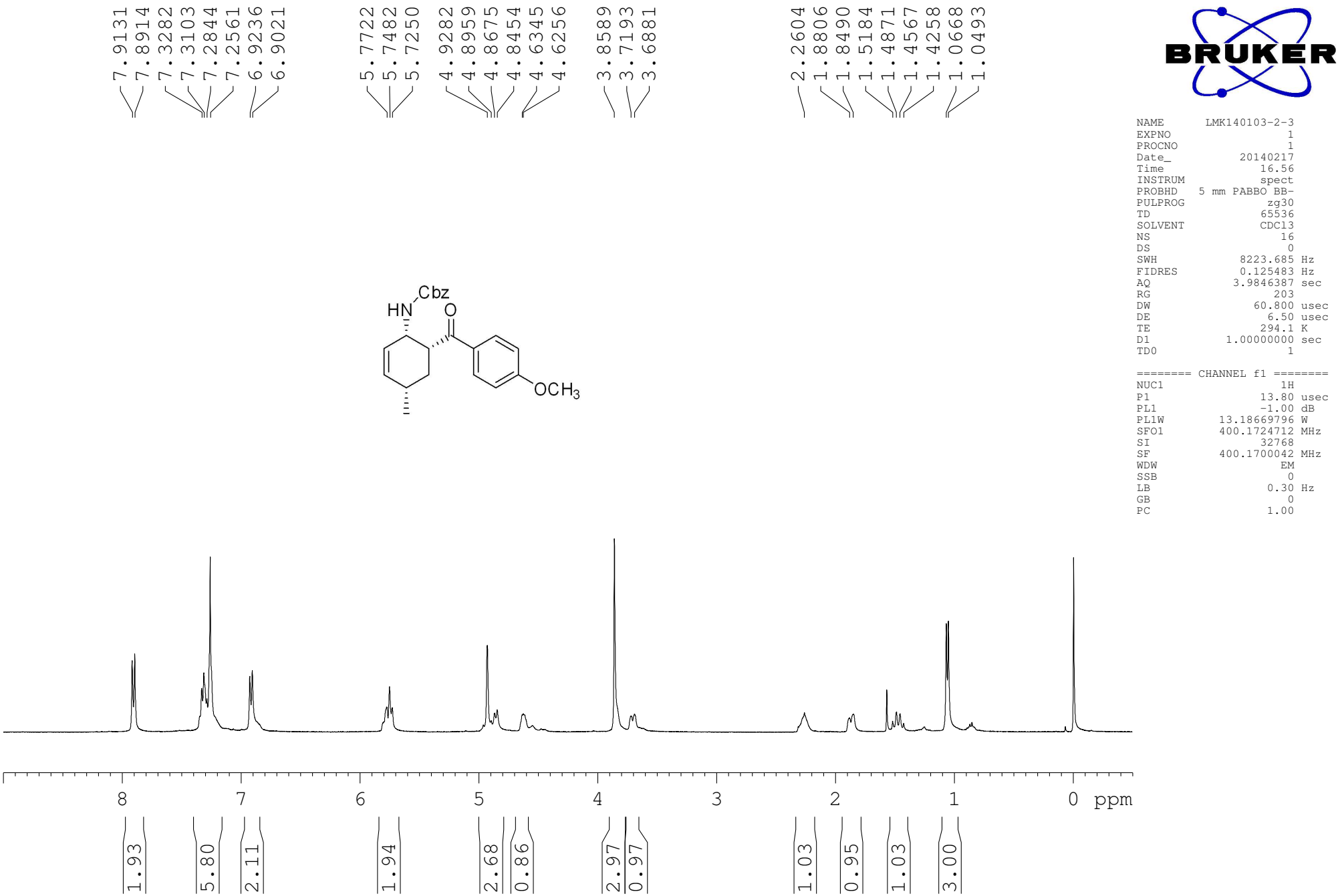
7.3498
7.3335
7.3154
7.2900
7.2593
7.2494
7.2301
5.7677
5.7542
5.7303
4.9298
4.8967
4.8503
4.6501
3.7498
3.7185
2.4008
2.2726
1.8974
1.8706
1.5236
1.4923
1.4622
1.4306
1.0722
1.0546
Cbz
HN
O
NAME LMK140303-2
EXPNO 1
PROCNO 1
Date_ 20140307
Time 9.24
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 16
DS 2
SWH 8223.685 Hz
FIDRES 0.125483 Hz
AQ 3.9846387 sec
RG 128
DW 60.800 usec
DE 6.50 usec
TE 294.0 K
D1 1.00000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 1H
P1 13.80 usec
PL1 -1.00 dB
PL1W 13.18669796 W
SFO1 400.1724712 MHz
SI 32768
SF 400.1700030 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00
8
7
6
5
4
3
2
1
0 ppm
1.97
7.30
1.96
2.70
1.13
0.99
2.99
1.12
1.00
0.99
3.00



NAME	LMK140303-2-C13
EXPNO	1
PROCNO	1
Date_	20140307
Time	20.42
INSTRUM	spect
PROBHD	5 mm PABBO BB-
PULPROG	zgpg30
TD	65536
SOLVENT	CDCl3
NS	119
DS	4
SWH	24038.461 Hz
FIDRES	0.366798 Hz
AQ	1.3631988 sec
RG	203
DW	20.800 usec
DE	6.50 usec
TE	294.5 K
D1	2.00000000 sec
D11	0.03000000 sec
TD0	1
======== CHANNEL f1 ========	
NUC1	13C
P1	8.50 usec
PL1	-2.00 dB
PL1W	57.32743073 W
SFO1	100.6328888 MHz
======== CHANNEL f2 ========	
CPDPRG2	waltz16
NUC2	1H
PCPD2	80.00 usec
PL2	-1.00 dB
PL12	14.26 dB
PL13	14.46 dB
PL2W	13.18669796 W
PL12W	0.39276794 W
PL13W	0.37509048 W
SFO2	400.1716007 MHz
SI	32768
SF	100.6228110 MHz
WDW	EM
SSB	0
LB	1.00 Hz
GB	0
PC	1.40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7.2561
6.9236
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5.7722
5.7482
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4.9282
4.8959
4.8675
4.8454
4.6345
4.6256
3.8589
3.7193
3.6881
2.2604
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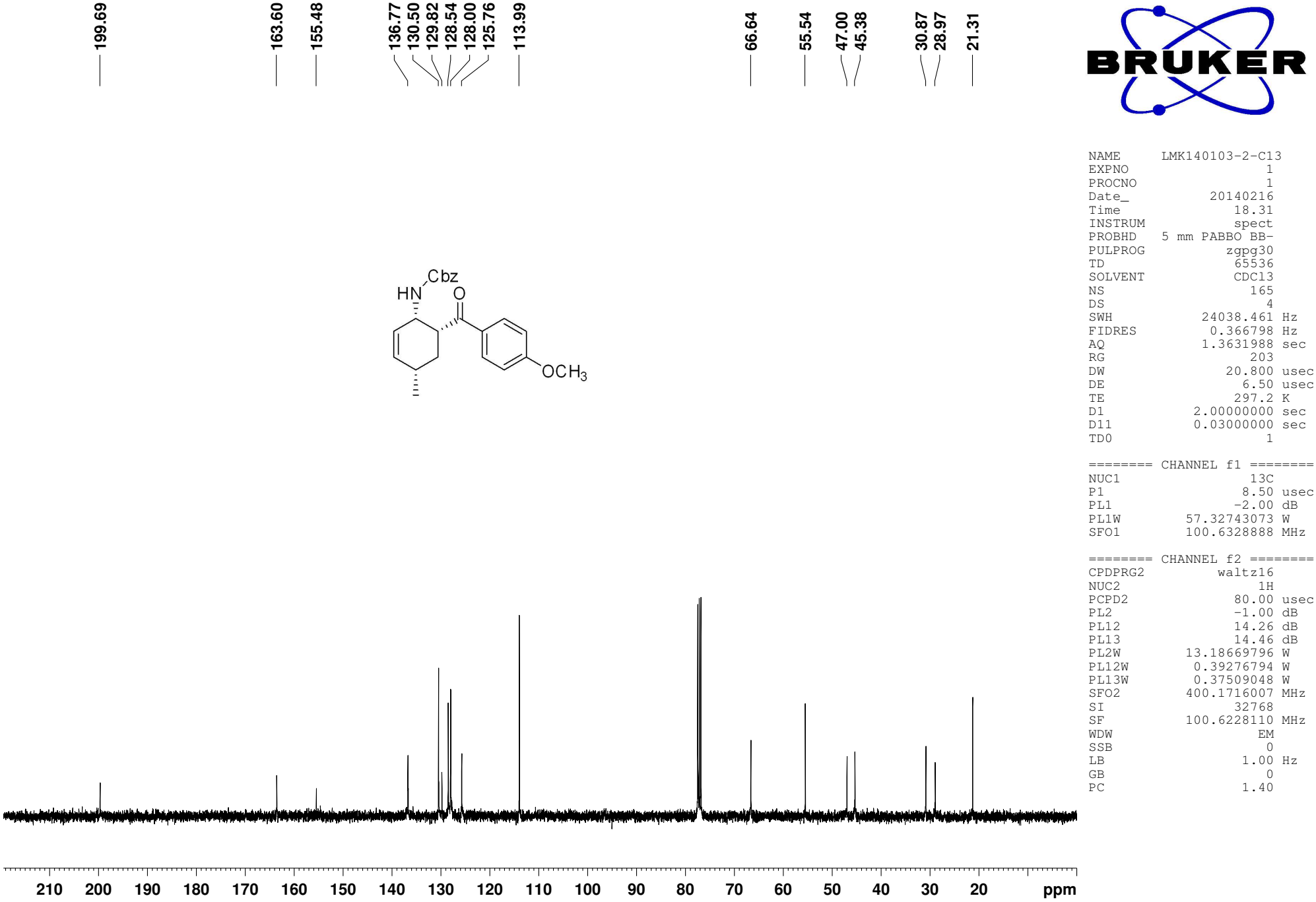
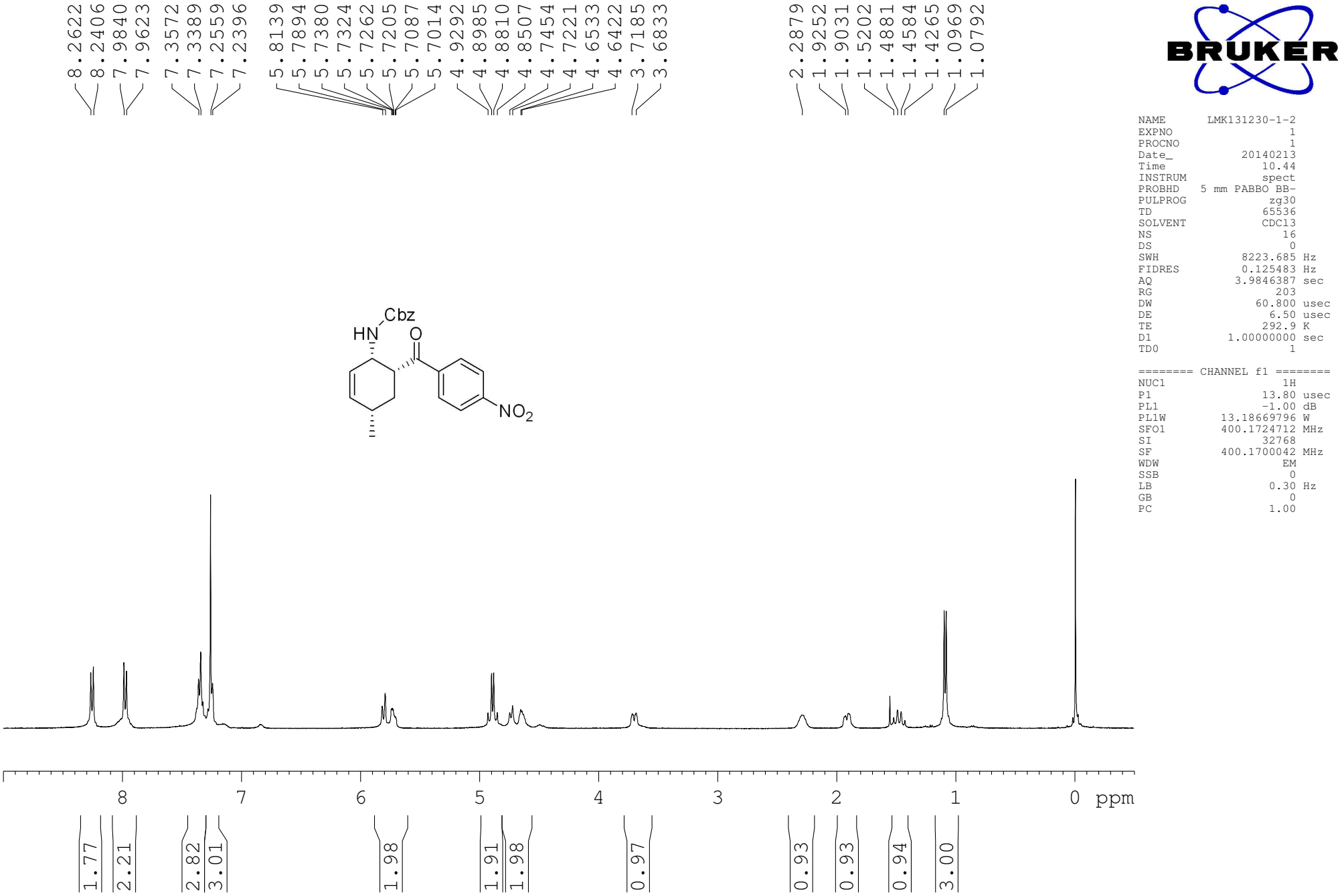
1.4871
1.4567
1.4258
1.0668
1.0493
Cbz
HN
O
OCH3
NAME LMK140103-2-3
EXPNO 1
PROCNO 1
Date_ 20140217
Time 16.56
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 16
DS 0
SWH 8223.685 Hz
FIDRES 0.125483 Hz
AQ 3.9846387 sec
RG 203
DW 60.800 usec
DE 6.50 usec
TE 294.1 K
D1 1.00000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 1H
P1 13.80 usec
PL1 -1.00 dB
PL1W 13.18669796 W
SFO1 400.1724712 MHz
SI 32768
SF 400.1700042 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00
8
7
6
5
4
3
2
1
0 ppm
1.93
5.80
2.11
1.94
2.68
0.86
2.97
0.97
1.03
0.95
1.03
3.00

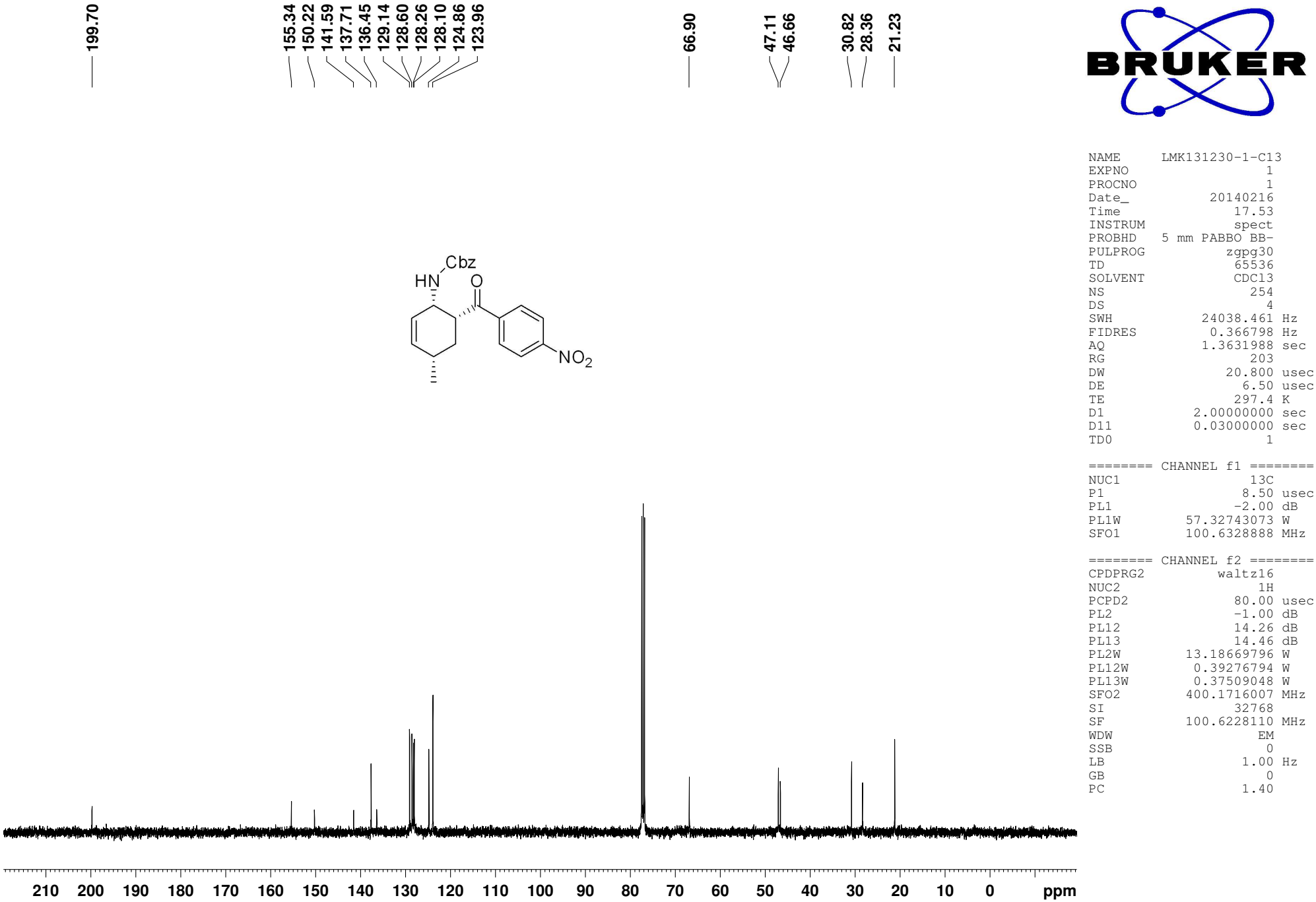


NAME	LMK140103-2-C13
EXPNO	1
PROCNO	1
Date_	20140216
Time	18.31
INSTRUM	spect
PROBHD	5 mm PABBO BB-
PULPROG	zgpg30
TD	65536
SOLVENT	CDCl3
NS	165
DS	4
SWH	24038.461 Hz
FIDRES	0.366798 Hz
AQ	1.3631988 sec
RG	203
DW	20.800 usec
DE	6.50 usec
TE	297.2 K
D1	2.00000000 sec
D11	0.03000000 sec
TD0	1
======== CHANNEL f1 ========	
NUC1	13C
P1	8.50 usec
PL1	-2.00 dB
PL1W	57.32743073 W
SFO1	100.6328888 MHz
======== CHANNEL f2 ========	
CPDPRG2	waltz16
NUC2	1H
PCPD2	80.00 usec
PL2	-1.00 dB
PL12	14.26 dB
PL13	14.46 dB
PL2W	13.18669796 W
PL12W	0.39276794 W
PL13W	0.37509048 W
SFO2	400.1716007 MHz
SI	32768
SF	100.6228110 MHz
WDW	EM
SSB	0
LB	1.00 Hz
GB	0
PC	1.40

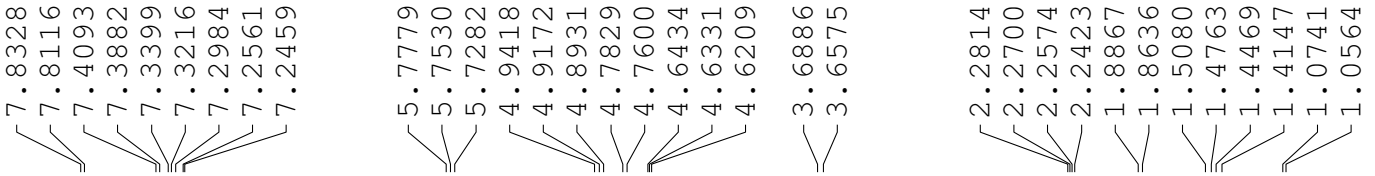


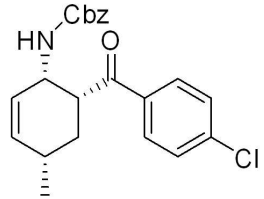

```
NAME       LMK131230-1-2
EXPNO                  1
PROCNO                 1
Date_           20140213
Time               10.44
INSTRUM            spect
PROBHD   5 mm PABBO BB-
PULPROG             zg30
TD                 65536
SOLVENT            CDCl3
NS                    16
DS                     0
SWH             8223.685 Hz
FIDRES          0.125483 Hz
AQ             3.9846387 sec
RG                   203
DW                60.800 usec
DE                 6.50 usec
TE                292.9 K
D1           1.00000000 sec
TD0                    1

======== CHANNEL f1 ========
NUC1                  1H
P1                 13.80 usec
PL1                -1.00 dB
PL1W         13.18669796 W
SFO1         400.1724712 MHz
SI                 32768
SF           400.1700042 MHz
WDW                   EM
SSB                    0
LB                 0.30 Hz
GB                     0
PC                  1.00
```



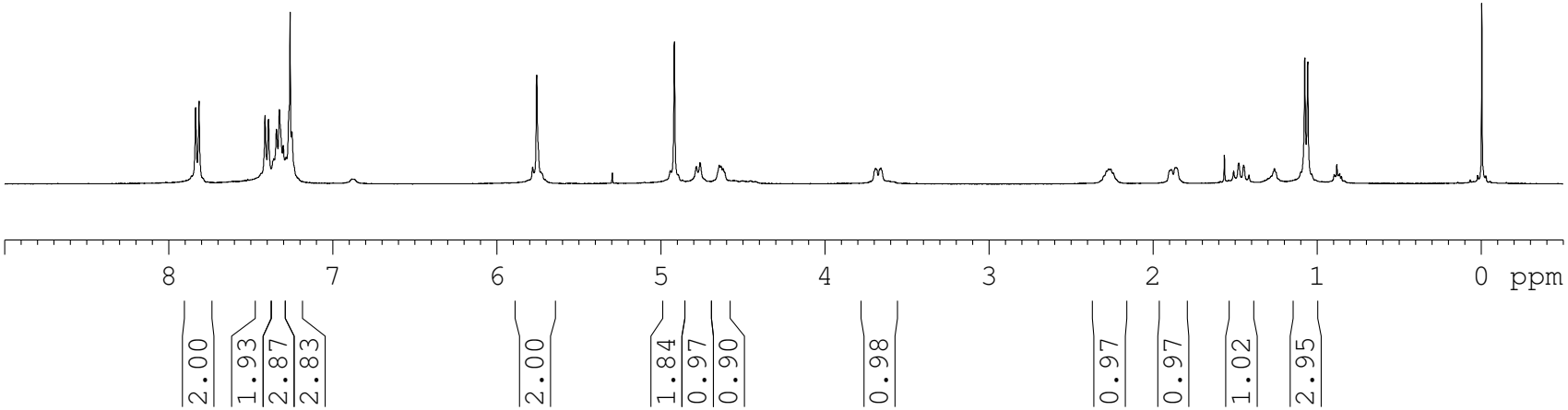
NAME	LMK131230-1-C13
EXPNO	1
PROCNO	1
Date_	20140216
Time	17.53
INSTRUM	spect
PROBHD	5 mm PABBO BB-
PULPROG	zgpg30
TD	65536
SOLVENT	CDCl3
NS	254
DS	4
SWH	24038.461 Hz
FIDRES	0.366798 Hz
AQ	1.3631988 sec
RG	203
DW	20.800 usec
DE	6.50 usec
TE	297.4 K
D1	2.00000000 sec
D11	0.03000000 sec
TD0	1
======== CHANNEL f1 ========	
NUC1	13C
P1	8.50 usec
PL1	-2.00 dB
PL1W	57.32743073 W
SFO1	100.6328888 MHz
======== CHANNEL f2 ========	
CPDPRG2	waltz16
NUC2	1H
PCPD2	80.00 usec
PL2	-1.00 dB
PL12	14.26 dB
PL13	14.46 dB
PL2W	13.18669796 W
PL12W	0.39276794 W
PL13W	0.37509048 W
SFO2	400.1716007 MHz
SI	32768
SF	100.6228110 MHz
WDW	EM
SSB	0
LB	1.00 Hz
GB	0
PC	1.40

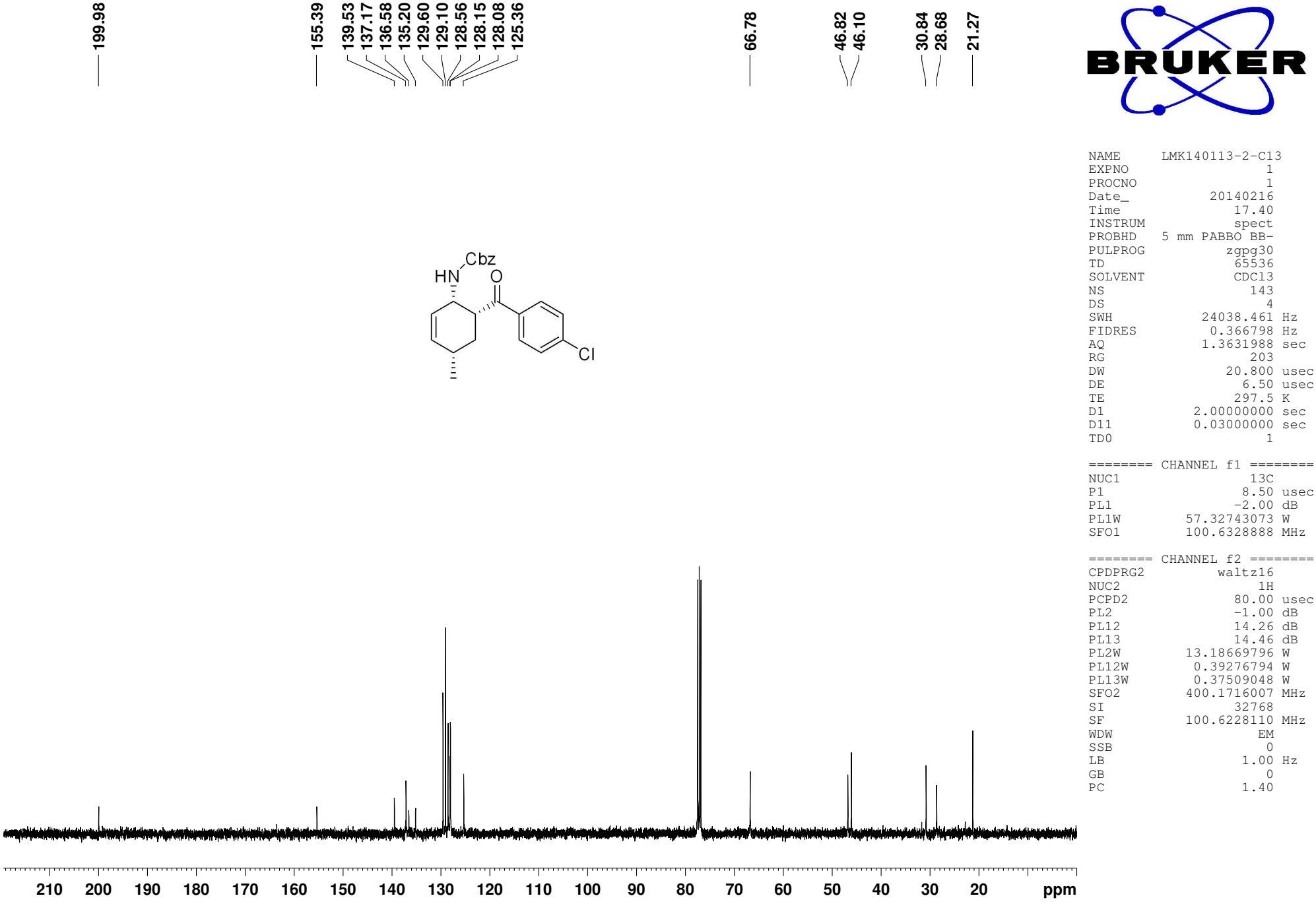




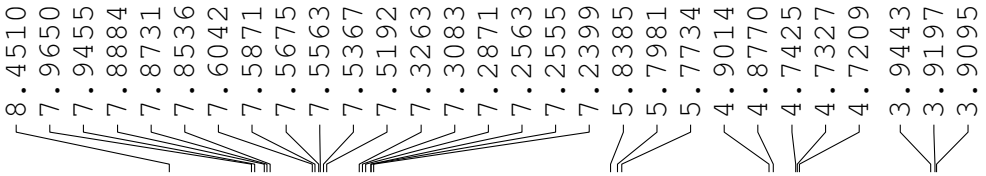

```
NAME        LMK140113-2-2
EXPNO                   1
PROCNO                  1
Date_            20140213
Time                10.37
INSTRUM             spect
PROBHD    5 mm PABBO BB-
PULPROG              zg30
TD                  65536
SOLVENT             CDCl3
NS                     16
DS                      0
SWH              8223.685 Hz
FIDRES           0.125483 Hz
AQ               3.9846387 sec
RG                    203
DW                 60.800 usec
DE                  6.50 usec
TE                 293.0 K
D1              1.00000000 sec
TD0                     1

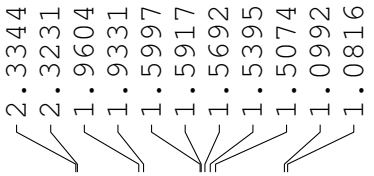
======== CHANNEL f1 ========
NUC1                   1H
P1                  13.80 usec
PL1                 -1.00 dB
PL1W          13.18669796 W
SFO1          400.1724712 MHz
SI                  32768
SF            400.1700042 MHz
WDW                    EM
SSB                     0
LB                   0.30 Hz
GB                      0
PC                   1.00
```

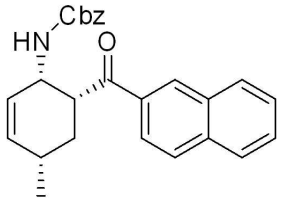




NAME	LMK140113-2-C13
EXPNO	1
PROCNO	1
Date_	20140216
Time	17.40
INSTRUM	spect
PROBHD	5 mm PABBO BB-
PULPROG	zgpg30
TD	65536
SOLVENT	CDCl3
NS	143
DS	4
SWH	24038.461 Hz
FIDRES	0.366798 Hz
AQ	1.3631988 sec
RG	203
DW	20.800 usec
DE	6.50 usec
TE	297.5 K
D1	2.00000000 sec
D11	0.03000000 sec
TD0	1
======== CHANNEL f1 ========	
NUC1	13C
P1	8.50 usec
PL1	-2.00 dB
PL1W	57.32743073 W
SFO1	100.6328888 MHz
======== CHANNEL f2 ========	
CPDPRG2	waltz16
NUC2	1H
PCPD2	80.00 usec
PL2	-1.00 dB
PL12	14.26 dB
PL13	14.46 dB
PL2W	13.18669796 W
PL12W	0.39276794 W
PL13W	0.37509048 W
SFO2	400.1716007 MHz
SI	32768
SF	100.6228110 MHz
WDW	EM
SSB	0
LB	1.00 Hz
GB	0
PC	1.40

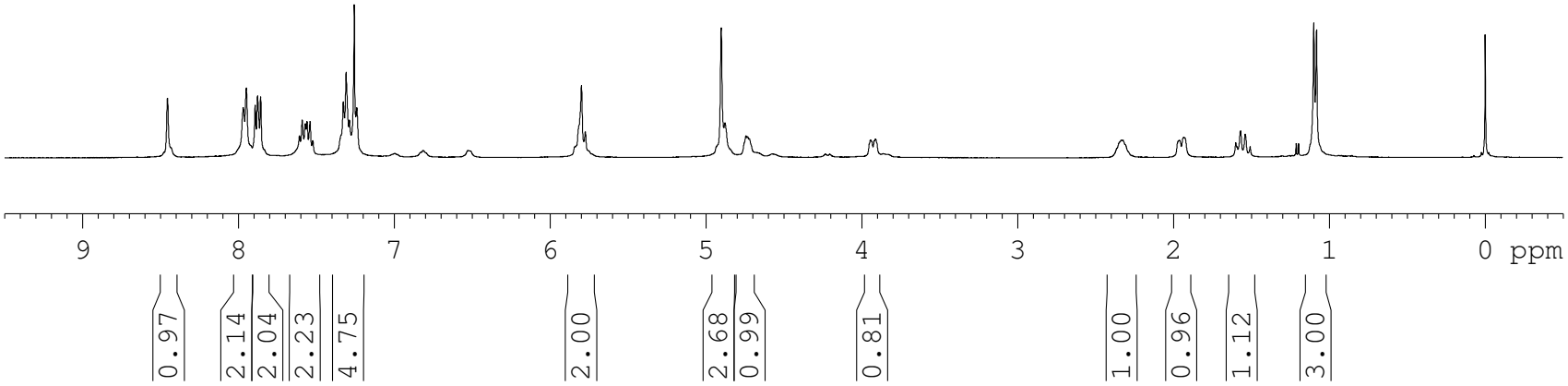


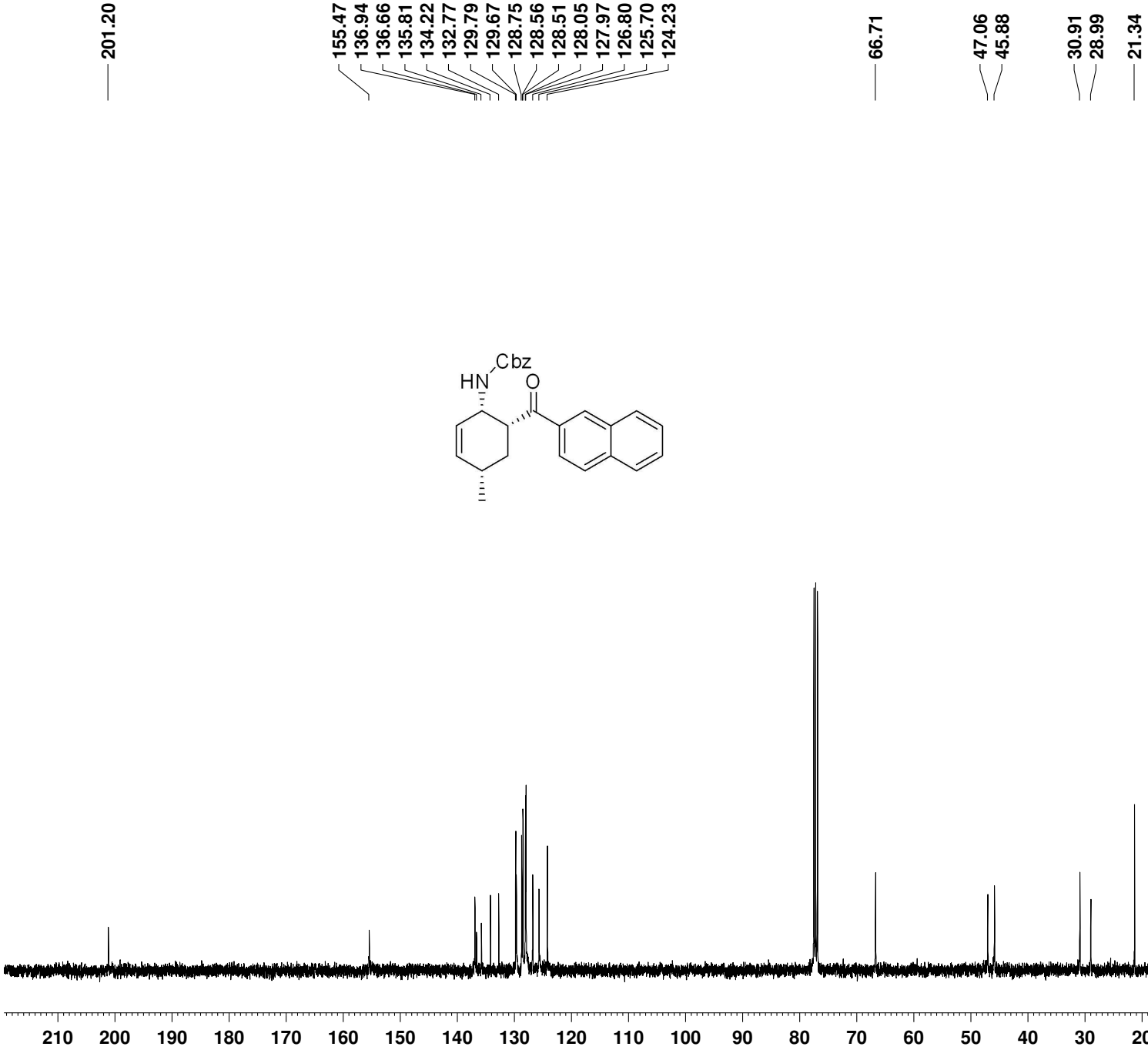




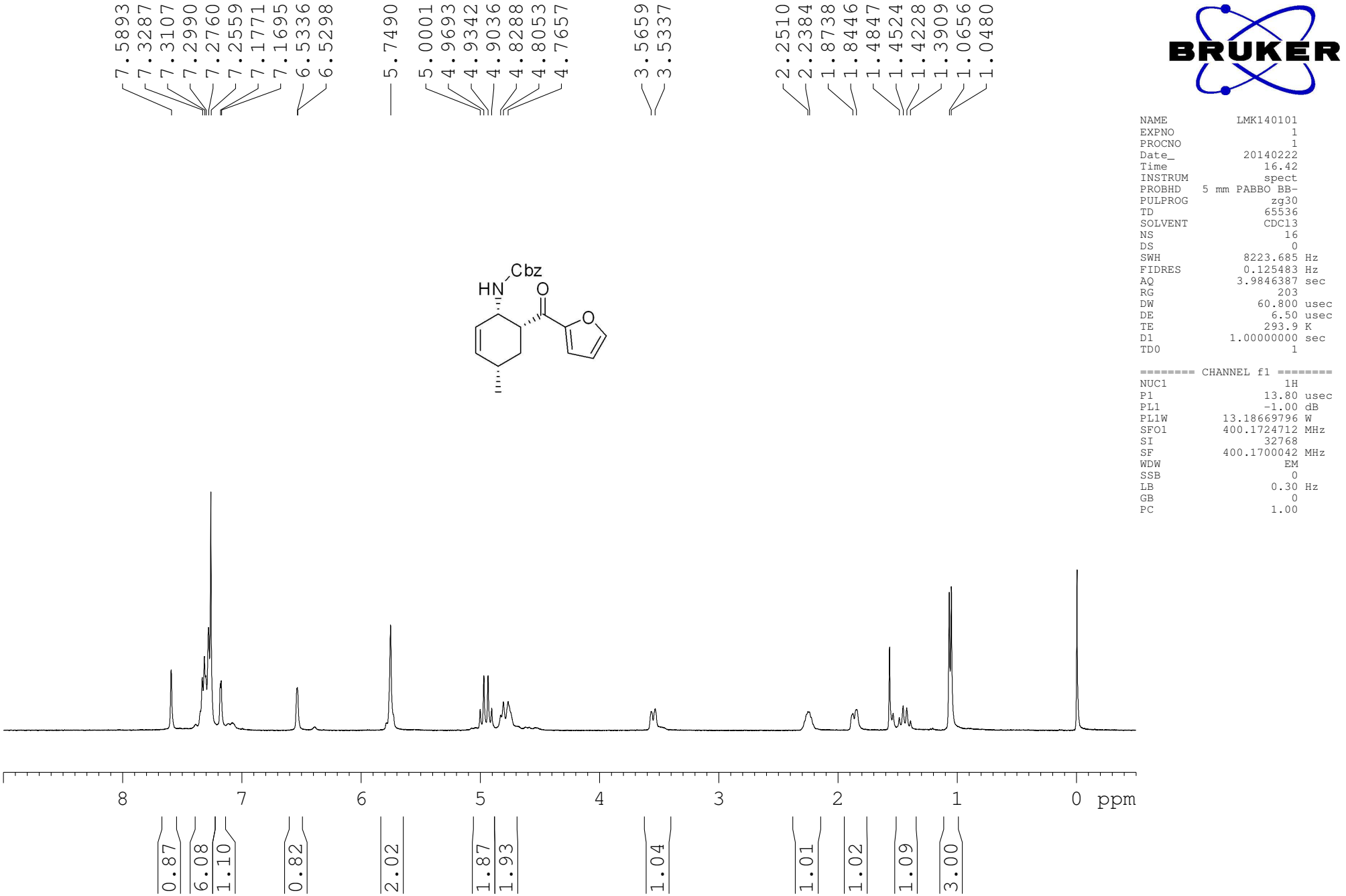

```
NAME       LMK140110-1-2
EXPNO                 1
PROCNO                1
Date_          20140213
Time              11.00
INSTRUM           spect
PROBHD   5 mm PABBO BB-
PULPROG            zg30
TD                65536
SOLVENT           CDCl3
NS                   16
DS                    0
SWH            8223.685 Hz
FIDRES        0.125483 Hz
AQ            3.9846387 sec
RG                  161
DW               60.800 usec
DE                6.50 usec
TE               292.9 K
D1            1.00000000 sec
TD0                   1

======== CHANNEL f1 ========
NUC1                  1H
P1                13.80 usec
PL1               -1.00 dB
PL1W         13.18669796 W
SFO1         400.1724712 MHz
SI                 32768
SF           400.1700042 MHz
WDW                   EM
SSB                   0
LB                0.30 Hz
GB                    0
PC                 1.00
```





NAME	LMK140110-1-C13
EXPNO	1
PROCNO	1
Date_	20140216
Time	17.24
INSTRUM	spect
PROBHD	5 mm PABBO BB-
PULPROG	zgpg30
TD	65536
SOLVENT	CDCl3
NS	187
DS	4
SWH	24038.461 Hz
FIDRES	0.366798 Hz
AQ	1.3631988 sec
RG	203
DW	20.800 usec
DE	6.50 usec
TE	298.0 K
D1	2.00000000 sec
D11	0.03000000 sec
TD0	1
======== CHANNEL f1 ========	
NUC1	13C
P1	8.50 usec
PL1	-2.00 dB
PL1W	57.32743073 W
SFO1	100.6328888 MHz
======== CHANNEL f2 ========	
CPDPRG2	waltz16
NUC2	1H
PCPD2	80.00 usec
PL2	-1.00 dB
PL12	14.26 dB
PL13	14.46 dB
PL2W	13.18669796 W
PL12W	0.39276794 W
PL13W	0.37509048 W
SFO2	400.1716007 MHz
SI	32768
SF	100.6228110 MHz
WDW	EM
SSB	0
LB	1.00 Hz
GB	0
PC	1.40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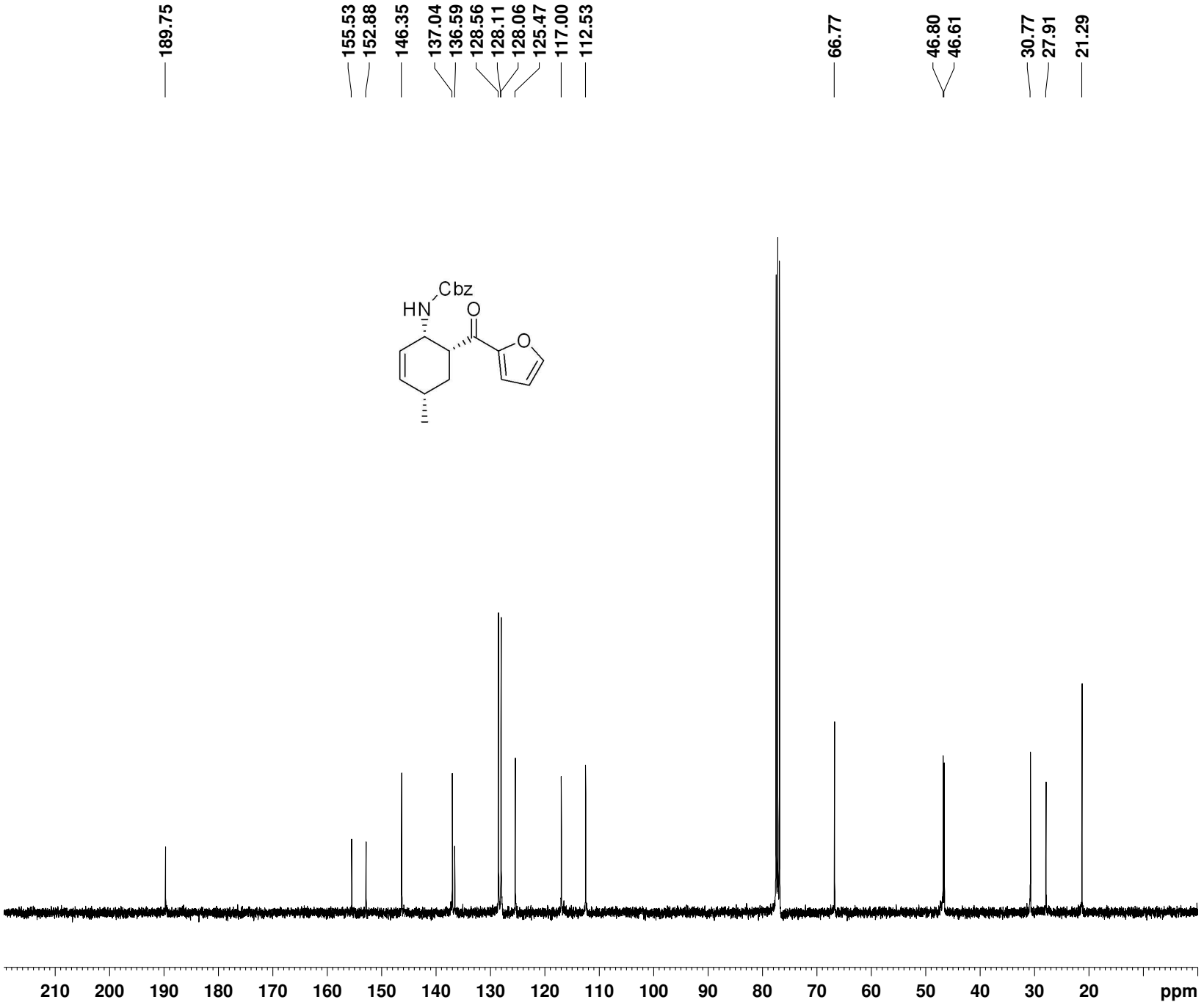
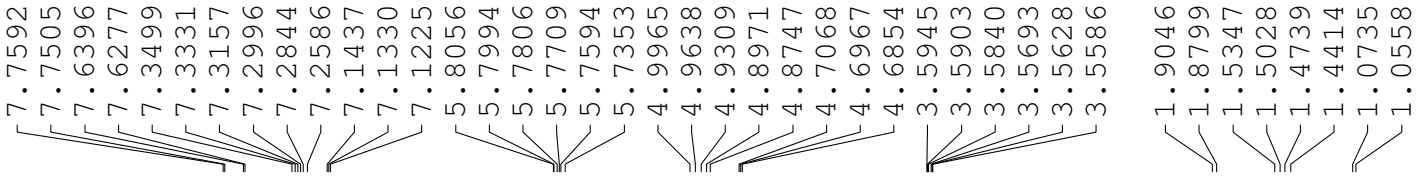
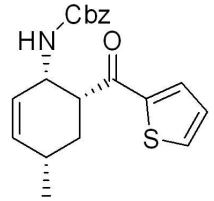
7.3287
7.3107
7.2990
7.2760
7.2559
7.1771
7.1695
6.5336
6.5298
5.7490
5.0001
4.9693
4.9342
4.9036
4.8288
4.8053
4.7657
3.5659
3.5337
2.2510
2.2384
1.8738
1.8446
1.4847
1.4524
1.4228
1.3909
1.0656
1.0480
Cbz
HN
O
O
NAME LMK140101
EXPNO 1
PROCNO 1
Date_ 20140222
Time 16.42
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 16
DS 0
SWH 8223.685 Hz
FIDRES 0.125483 Hz
AQ 3.9846387 sec
RG 203
DW 60.800 usec
DE 6.50 usec
TE 293.9 K
D1 1.00000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 1H
P1 13.80 usec
PL1 -1.00 dB
PL1W 13.18669796 W
SFO1 400.1724712 MHz
SI 32768
SF 400.1700042 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00
8
7
6
5
4
3
2
1
0 ppm
0.87
6.08
1.10
0.82
2.02
1.87
1.93
1.04
1.01
1.02
1.09
3.00



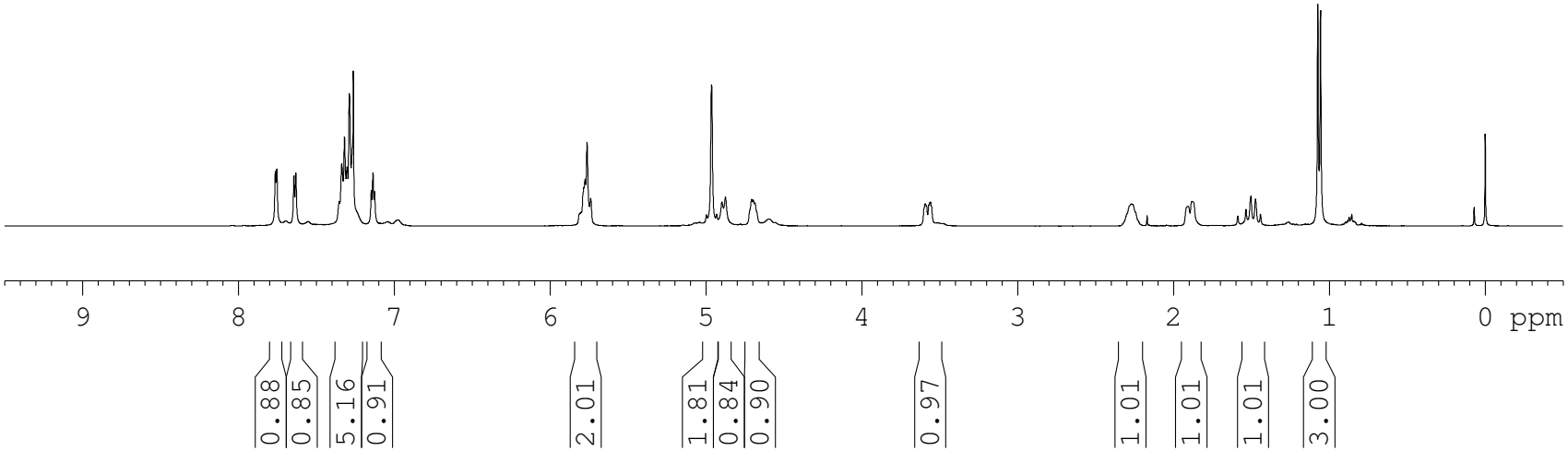
NAME	LMK140101-C13
EXPNO	1
PROCNO	1
Date_	20140222
Time	19.30
INSTRUM	spect
PROBHD	5 mm PABBO BB-
PULPROG	zgpg30
TD	65536
SOLVENT	CDCl3
NS	472
DS	4
SWH	24038.461 Hz
FIDRES	0.366798 Hz
AQ	1.3631988 sec
RG	203
DW	20.800 usec
DE	6.50 usec
TE	293.3 K
D1	2.00000000 sec
D11	0.03000000 sec
TD0	1
======== CHANNEL f1 ========	
NUC1	13C
P1	8.50 usec
PL1	-2.00 dB
PL1W	57.32743073 W
SFO1	100.6328888 MHz
======== CHANNEL f2 ========	
CPDPRG2	waltz16
NUC2	1H
PCPD2	80.00 usec
PL2	-1.00 dB
PL12	14.26 dB
PL13	14.46 dB
PL2W	13.18669796 W
PL12W	0.39276794 W
PL13W	0.37509048 W
SFO2	400.1716007 MHz
SI	32768
SF	100.6228110 MHz
WDW	EM
SSB	0
LB	1.00 Hz
GB	0
PC	1.40

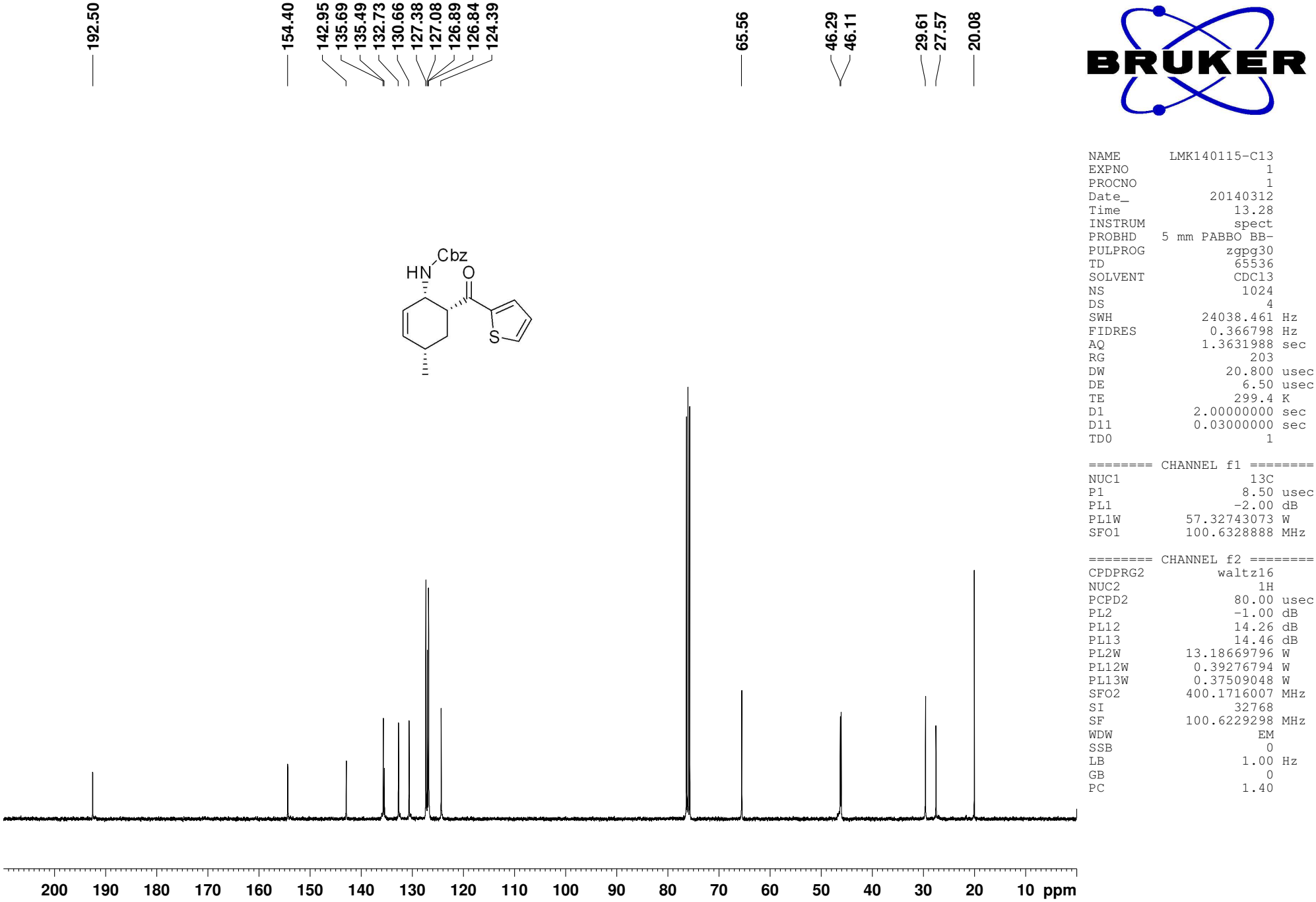




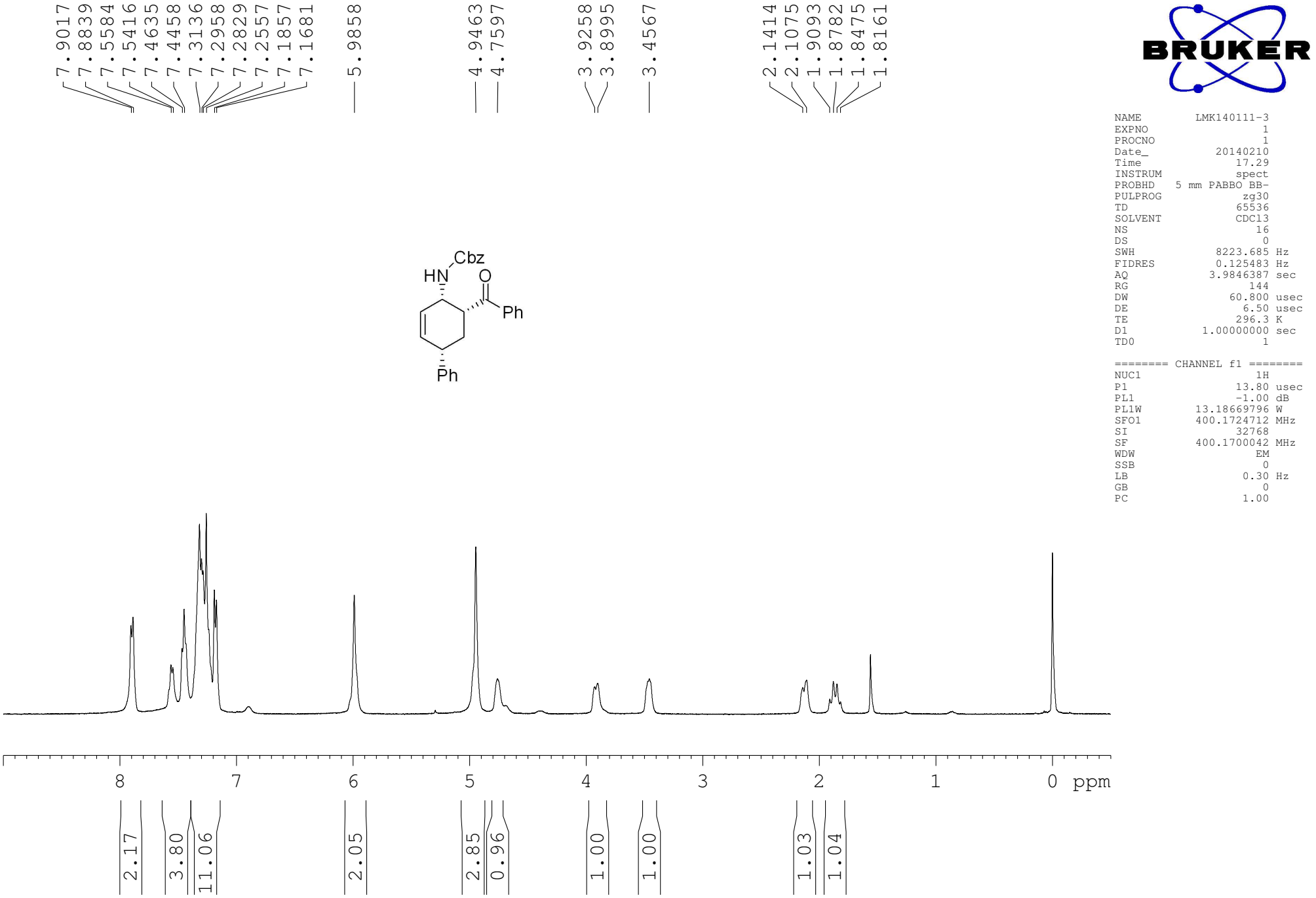

```
NAME        LMK140116-1-2
EXPNO                   1
PROCNO                  1
Date_            20140312
Time                10.04
INSTRUM             spect
PROBHD    5 mm PABBO BB-
PULPROG              zg30
TD                  65536
SOLVENT             CDCl3
NS                     16
DS                      2
SWH              8223.685 Hz
FIDRES           0.125483 Hz
AQ               3.9846387 sec
RG                    181
DW                 60.800 usec
DE                  6.50 usec
TE                 296.1 K
D1              1.00000000 sec
TD0                     1

======== CHANNEL f1 ========
NUC1                   1H
P1                  13.80 usec
PL1                 -1.00 dB
PL1W          13.18669796 W
SFO1          400.1724712 MHz
SI                  32768
SF            400.1700034 MHz
WDW                    EM
SSB                     0
LB                   0.30 Hz
GB                      0
PC                   1.00
```





NAME	LMK140115-C13
EXPNO	1
PROCNO	1
Date_	20140312
Time	13.28
INSTRUM	spect
PROBHD	5 mm PABBO BB-
PULPROG	zgpg30
TD	65536
SOLVENT	CDC13
NS	1024
DS	4
SWH	24038.461 Hz
FIDRES	0.366798 Hz
AQ	1.3631988 sec
RG	203
DW	20.800 usec
DE	6.50 usec
TE	299.4 K
D1	2.00000000 sec
D11	0.03000000 sec
TD0	1
======== CHANNEL f1 ========	
NUC1	13C
P1	8.50 usec
PL1	-2.00 dB
PL1W	57.32743073 W
SFO1	100.6328888 MHz
======== CHANNEL f2 ========	
CPDPRG2	waltz16
NUC2	1H
PCPD2	80.00 usec
PL2	-1.00 dB
PL12	14.26 dB
PL13	14.46 dB
PL2W	13.18669796 W
PL12W	0.39276794 W
PL13W	0.37509048 W
SFO2	400.1716007 MHz
SI	32768
SF	100.6229298 MHz
WDW	EM
SSB	0
LB	1.00 Hz
GB	0
PC	1.40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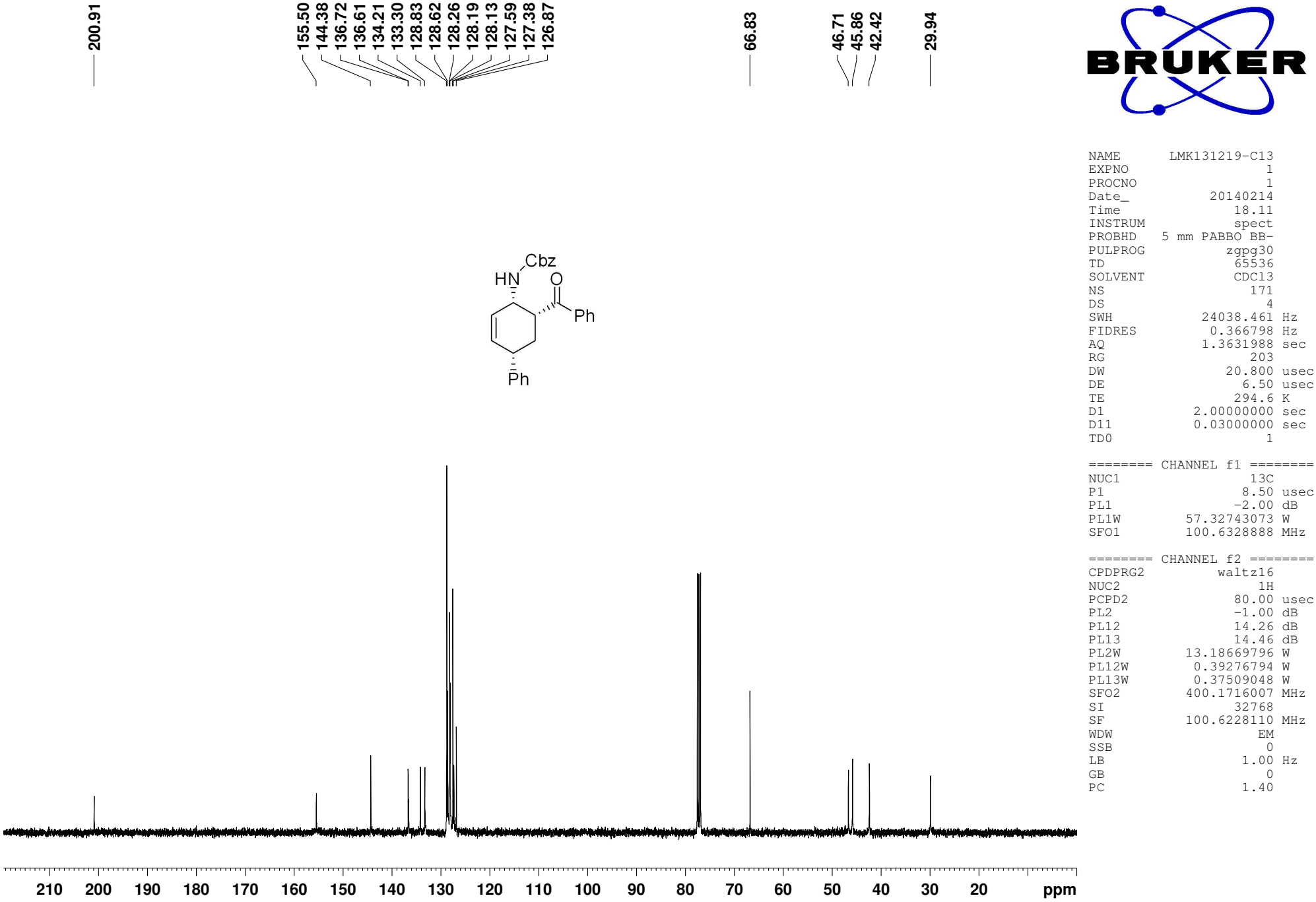
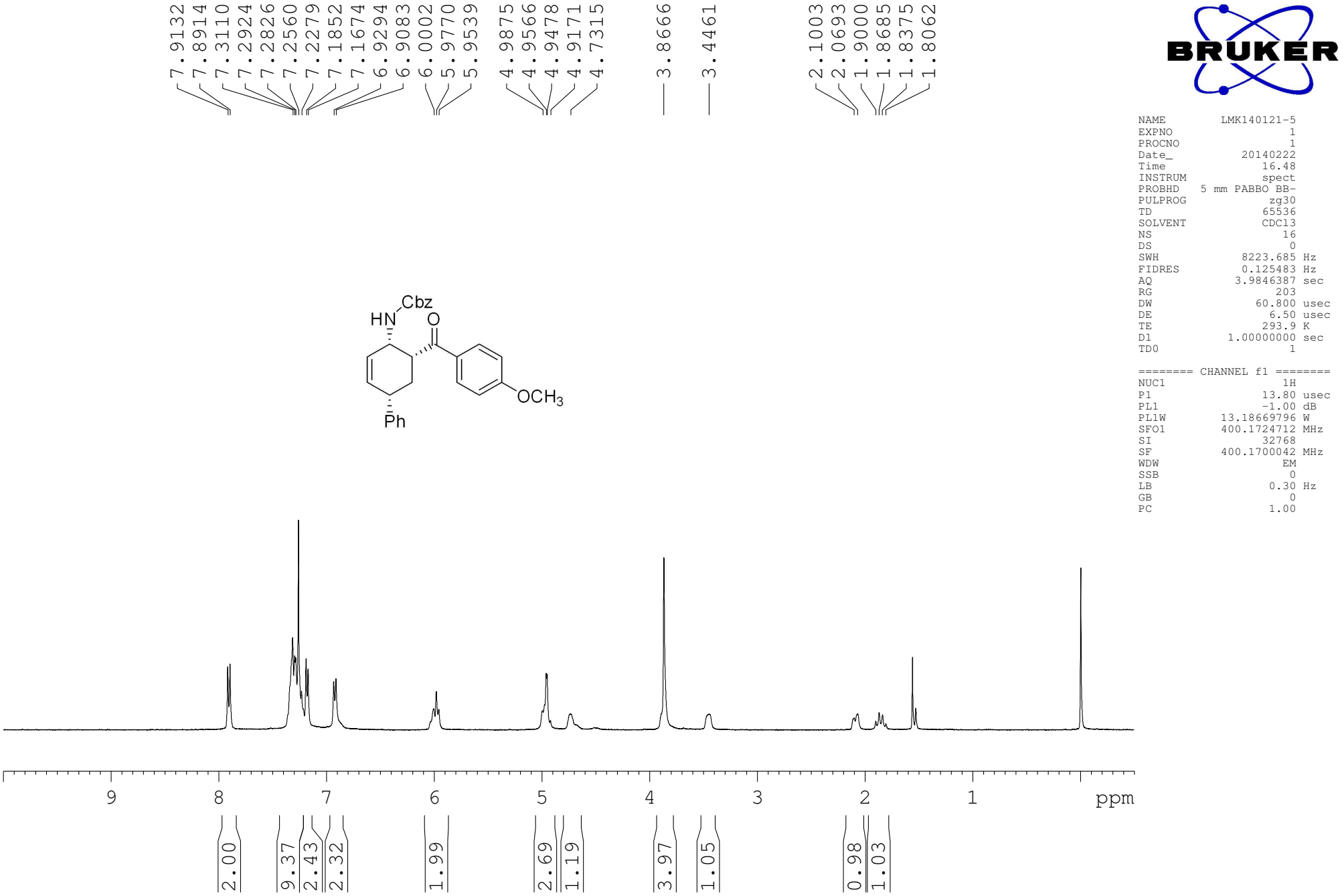
7.5416
7.4635
7.4458
7.3136
7.2958
7.2829
7.2557
7.1857
7.1681
5.9858
4.9463
4.7597
3.9258
3.8995
3.4567
2.1414
2.1075
1.9093
1.8782
1.8475
1.8161
Cbz
HN
O
Ph
Ph
NAME LMK140111-3
EXPNO 1
PROCNO 1
Date_ 20140210
Time 17.29
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 16
DS 0
SWH 8223.685 Hz
FIDRES 0.125483 Hz
AQ 3.9846387 sec
RG 144
DW 60.800 usec
DE 6.50 usec
TE 296.3 K
D1 1.00000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 1H
P1 13.80 usec
PL1 -1.00 dB
PL1W 13.18669796 W
SFO1 400.1724712 MHz
SI 32768
SF 400.1700042 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00
8
7
6
5
4
3
2
1
0
ppm
2.17
3.80
11.06
2.05
2.85
0.96
1.00
1.00
1.03
1.04




```
NAME          LMK131219-C13
EXPNO                     1
PROCNO                    1
Date_              20140214
Time                 18.11
INSTRUM              spect
PROBHD    5 mm PABBO BB-
PULPROG           zgpg30
TD                  65536
SOLVENT             CDC13
NS                    171
DS                      4
SWH           24038.461 Hz
FIDRES         0.366798 Hz
AQ             1.3631988 sec
RG                    203
DW                20.800 usec
DE                 6.50 usec
TE                294.6 K
D1            2.00000000 sec
D11           0.03000000 sec
TD0                     1

======== CHANNEL f1 ========
NUC1                  13C
P1                  8.50 usec
PL1                -2.00 dB
PL1W         57.32743073 W
SFO1        100.6328888 MHz

======== CHANNEL f2 ========
CPDPRG2           waltz16
NUC2                  1H
PCPD2              80.00 usec
PL2                -1.00 dB
PL12               14.26 dB
PL13               14.46 dB
PL2W         13.18669796 W
PL12W         0.39276794 W
PL13W         0.37509048 W
SFO2        400.1716007 MHz
SI                 32768
SF          100.6228110 MHz
WDW                   EM
SSB                    0
LB                  1.00 Hz
GB                     0
PC                  1.40
```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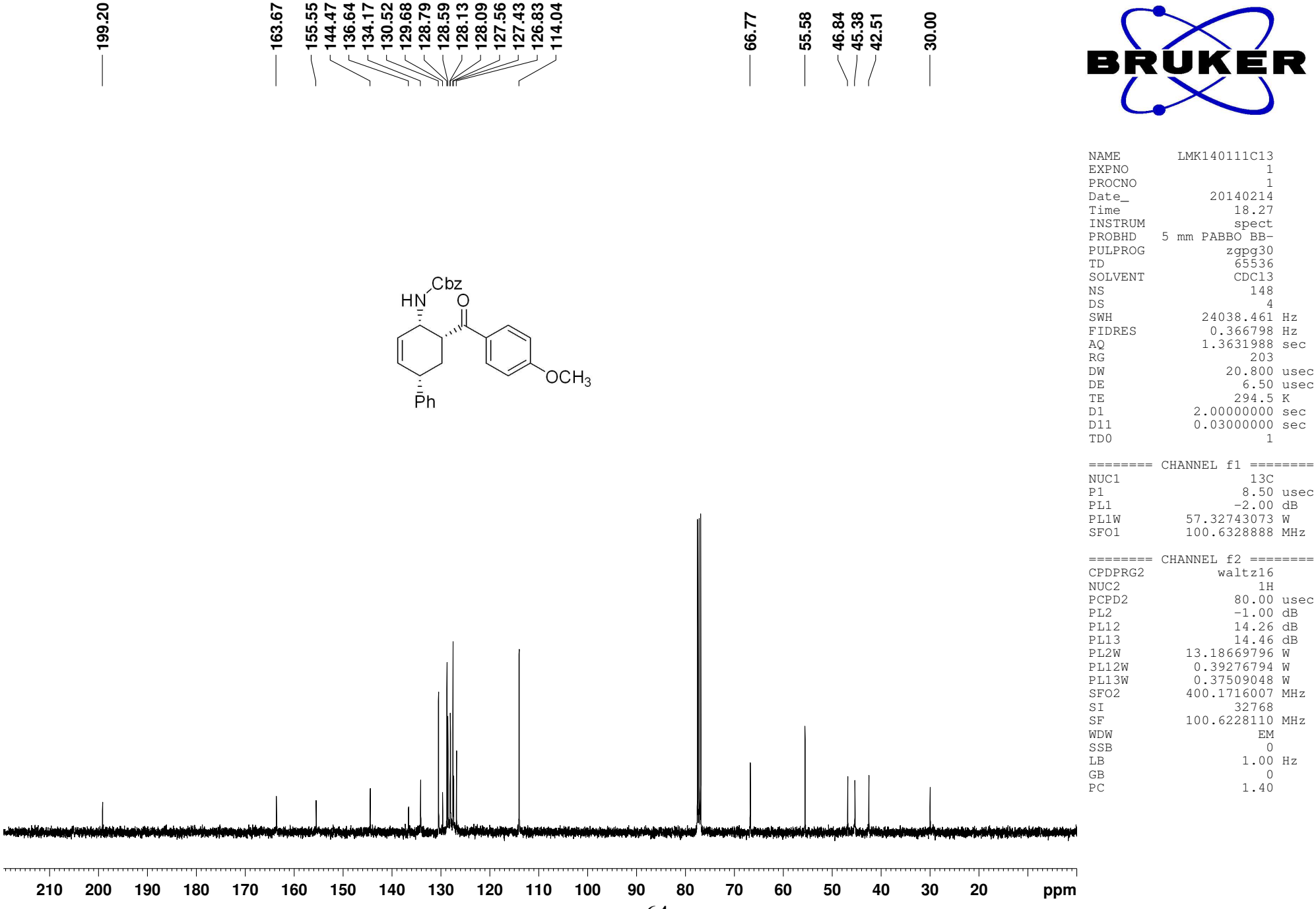
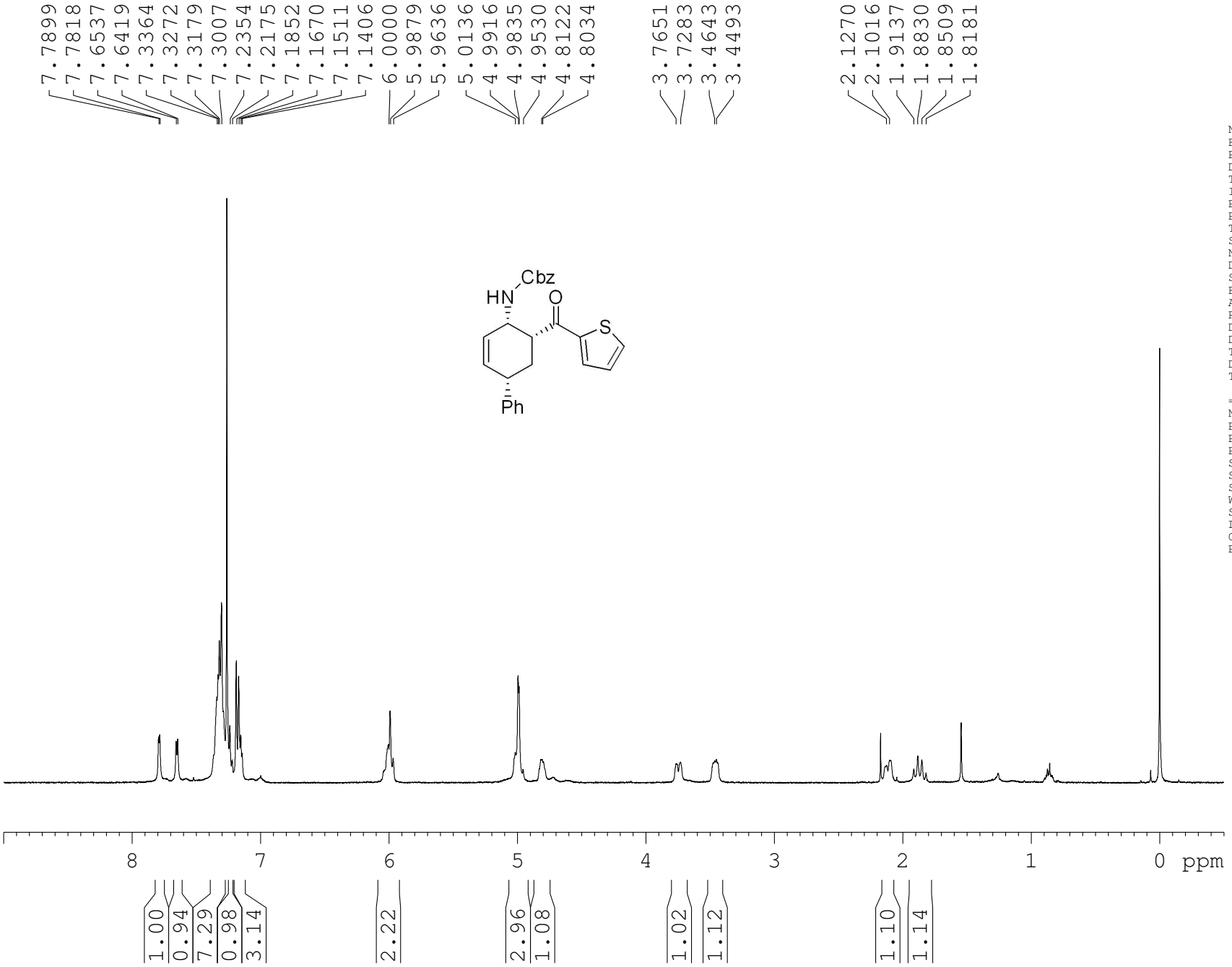
7.2826
7.2560
7.2279
7.1852
7.1674
6.9294
6.9083
6.0002
5.9770
5.9539
4.9875
4.9566
4.9478
4.9171
4.7315
3.8666
3.4461
2.1003
2.0693
1.9000
1.8685
1.8375
1.8062
Cbz
HN
O
OCH3
Ph
NAME LMK140121-5
EXPNO 1
PROCNO 1
Date_ 20140222
Time 16.48
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 16
DS 0
SWH 8223.685 Hz
FIDRES 0.125483 Hz
AQ 3.9846387 sec
RG 203
DW 60.800 usec
DE 6.50 usec
TE 293.9 K
D1 1.00000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 1H
P1 13.80 usec
PL1 -1.00 dB
PL1W 13.18669796 W
SFO1 400.1724712 MHz
SI 32768
SF 400.1700042 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00
9
8
7
6
5
4
3
2
1
ppm
2.00
9.37
2.43
2.32
1.99
2.69
1.19
3.97
1.05
0.98
1.03

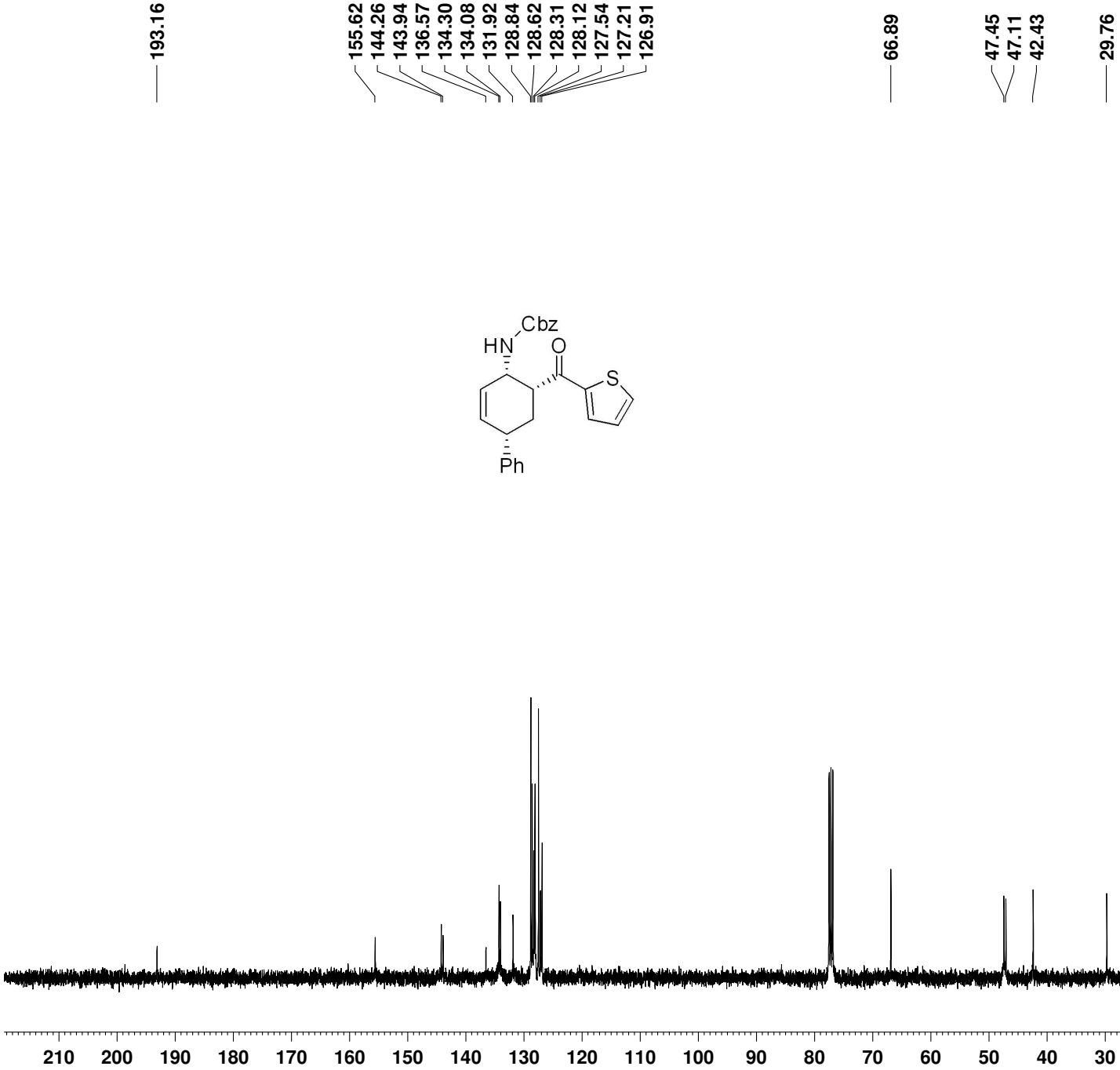


NAME	LMK140111C13
EXPNO	1
PROCNO	1
Date_	20140214
Time	18.27
INSTRUM	spect
PROBHD	5 mm PABBO BB-
PULPROG	zgpg30
TD	65536
SOLVENT	CDC13
NS	148
DS	4
SWH	24038.461 Hz
FIDRES	0.366798 Hz
AQ	1.3631988 sec
RG	203
DW	20.800 usec
DE	6.50 usec
TE	294.5 K
D1	2.00000000 sec
D11	0.03000000 sec
TD0	1
======== CHANNEL f1 ========	
NUC1	13C
P1	8.50 usec
PL1	-2.00 dB
PL1W	57.32743073 W
SFO1	100.6328888 MHz
======== CHANNEL f2 ========	
CPDPRG2	waltz16
NUC2	1H
PCPD2	80.00 usec
PL2	-1.00 dB
PL12	14.26 dB
PL13	14.46 dB
PL2W	13.18669796 W
PL12W	0.39276794 W
PL13W	0.37509048 W
SFO2	400.1716007 MHz
SI	32768
SF	100.6228110 MHz
WDW	EM
SSB	0
LB	1.00 Hz
GB	0
PC	1.40



BRUKER

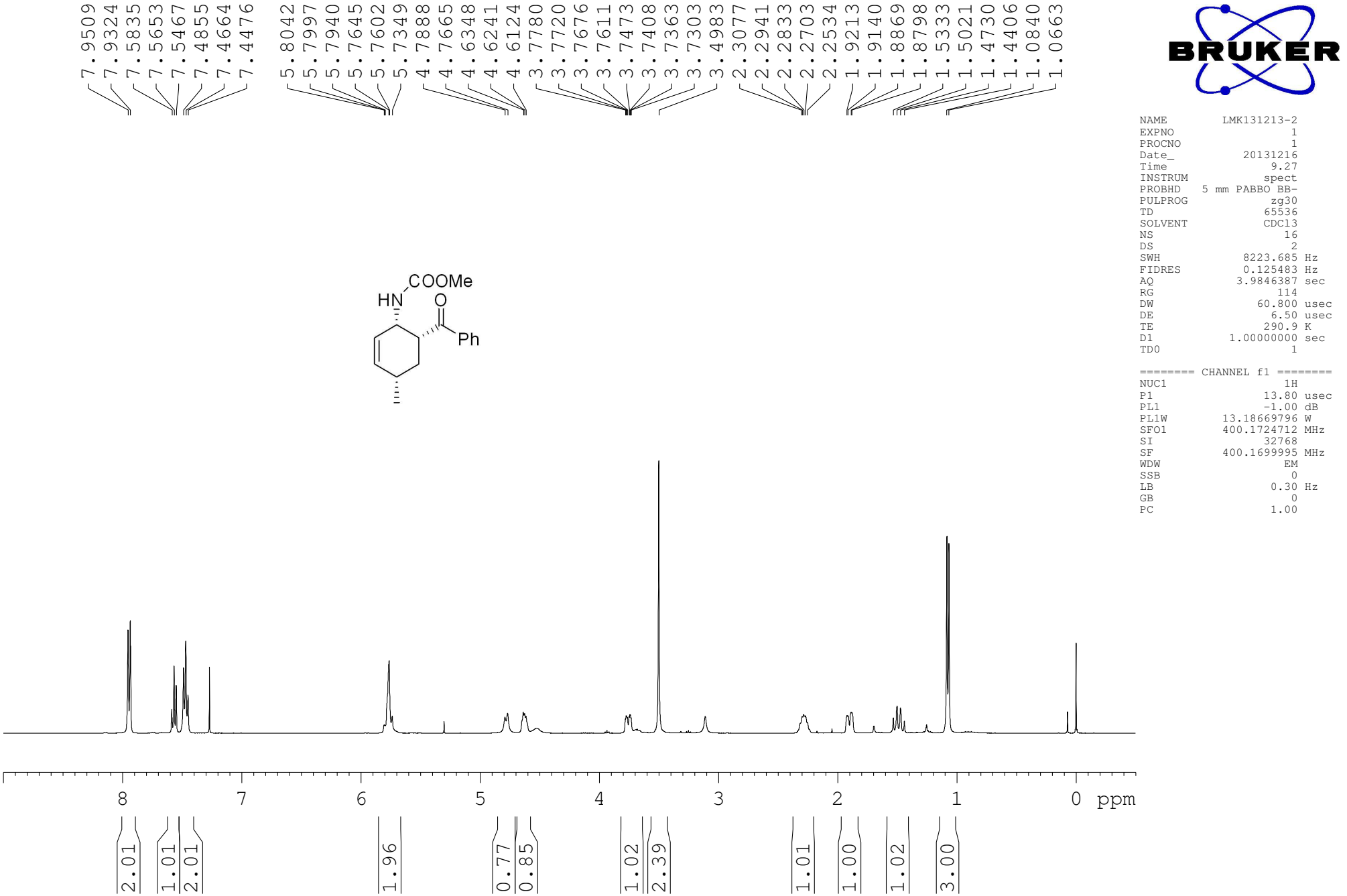
NAME	LMK140121-1-3
EXPNO	1
PROCNO	1
Date_	20140312
Time	10.10
INSTRUM	spect
PROBHD	5 mm PABBO BB-
PULPROG	zg30
TD	65536
SOLVENT	CDCl3
NS	16
DS	2
SWH	8223.685 Hz
FIDRES	0.125483 Hz
AQ	3.9846387 sec
RG	203
DW	60.800 usec
DE	6.50 usec
TE	296.1 K
D1	1.00000000 sec
TD0	1
======== CHANNEL f1 ========	
NUC1	1H
P1	13.80 usec
PL1	-1.00 dB
PL1W	13.18669796 W
SFO1	400.1724712 MHz
SI	32768
SF	400.1700031 MHz
WDW	EM
SSB	0
LB	0.30 Hz
GB	0
PC	1.00



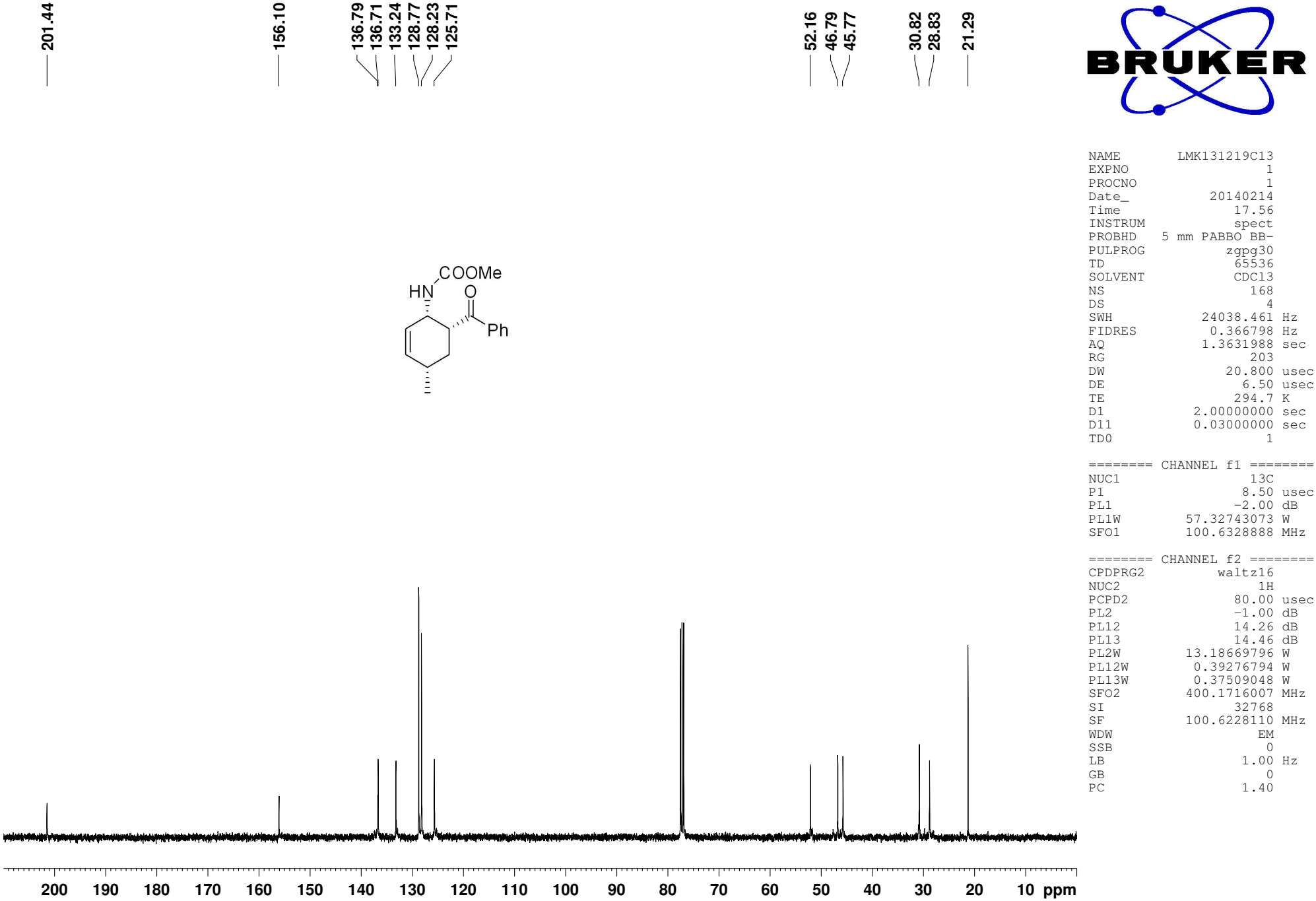

```
NAME      LMK140121-1-C13
EXPNO                  1
PROCNO                 1
Date_           20140216
Time               18.14
INSTRUM            spect
PROBHD   5 mm PABBO BB-
PULPROG          zgpg30
TD                65536
SOLVENT           CDCl3
NS                  163
DS                    4
SWH           24038.461 Hz
FIDRES         0.366798 Hz
AQ             1.3631988 sec
RG                  203
DW                20.800 usec
DE                 6.50 usec
TE                297.1 K
D1           2.00000000 sec
D11          0.03000000 sec
TD0                    1

======== CHANNEL f1 ========
NUC1                13C
P1                 8.50 usec
PL1               -2.00 dB
PL1W        57.32743073 W
SFO1       100.6328888 MHz

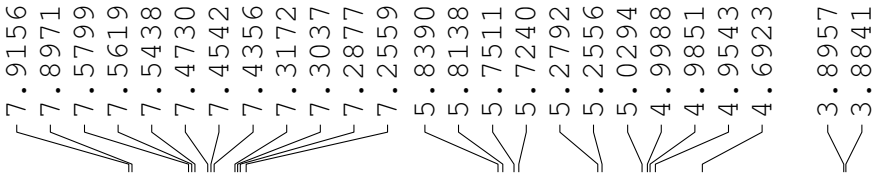
======== CHANNEL f2 ========
CPDPRG2         waltz16
NUC2                1H
PCPD2              80.00 usec
PL2                -1.00 dB
PL12               14.26 dB
PL13               14.46 dB
PL2W        13.18669796 W
PL12W        0.39276794 W
PL13W        0.37509048 W
SFO2       400.1716007 MHz
SI                 32768
SF         100.6228110 MHz
WDW                EM
SSB                 0
LB                1.00 Hz
GB                  0
PC                1.40
```

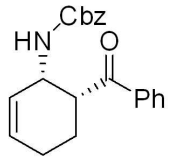


NAME	LMK131213-2
EXPNO	1
PROCNO	1
Date_	20131216
Time	9.27
INSTRUM	spect
PROBHD	5 mm PABBO BB-
PULPROG	zg30
TD	65536
SOLVENT	CDCl3
NS	16
DS	2
SWH	8223.685 Hz
FIDRES	0.125483 Hz
AQ	3.9846387 sec
RG	114
DW	60.800 usec
DE	6.50 usec
TE	290.9 K
D1	1.00000000 sec
TD0	1
======== CHANNEL f1 ========	
NUC1	1H
P1	13.80 usec
PL1	-1.00 dB
PL1W	13.18669796 W
SFO1	400.1724712 MHz
SI	32768
SF	400.1699995 MHz
WDW	EM
SSB	0
LB	0.30 Hz
GB	0
PC	1.00

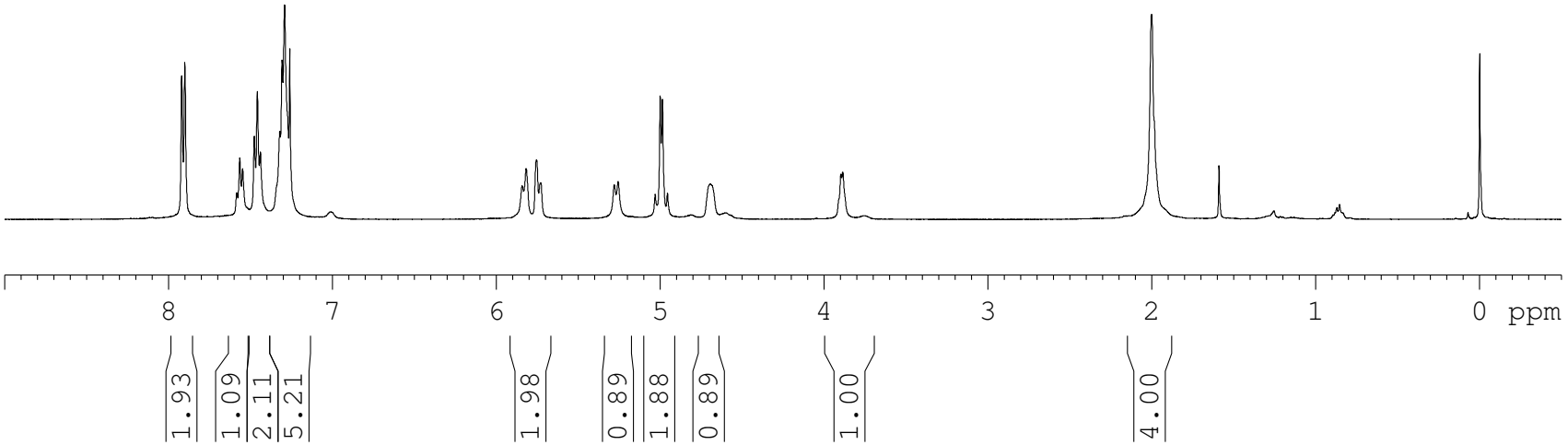


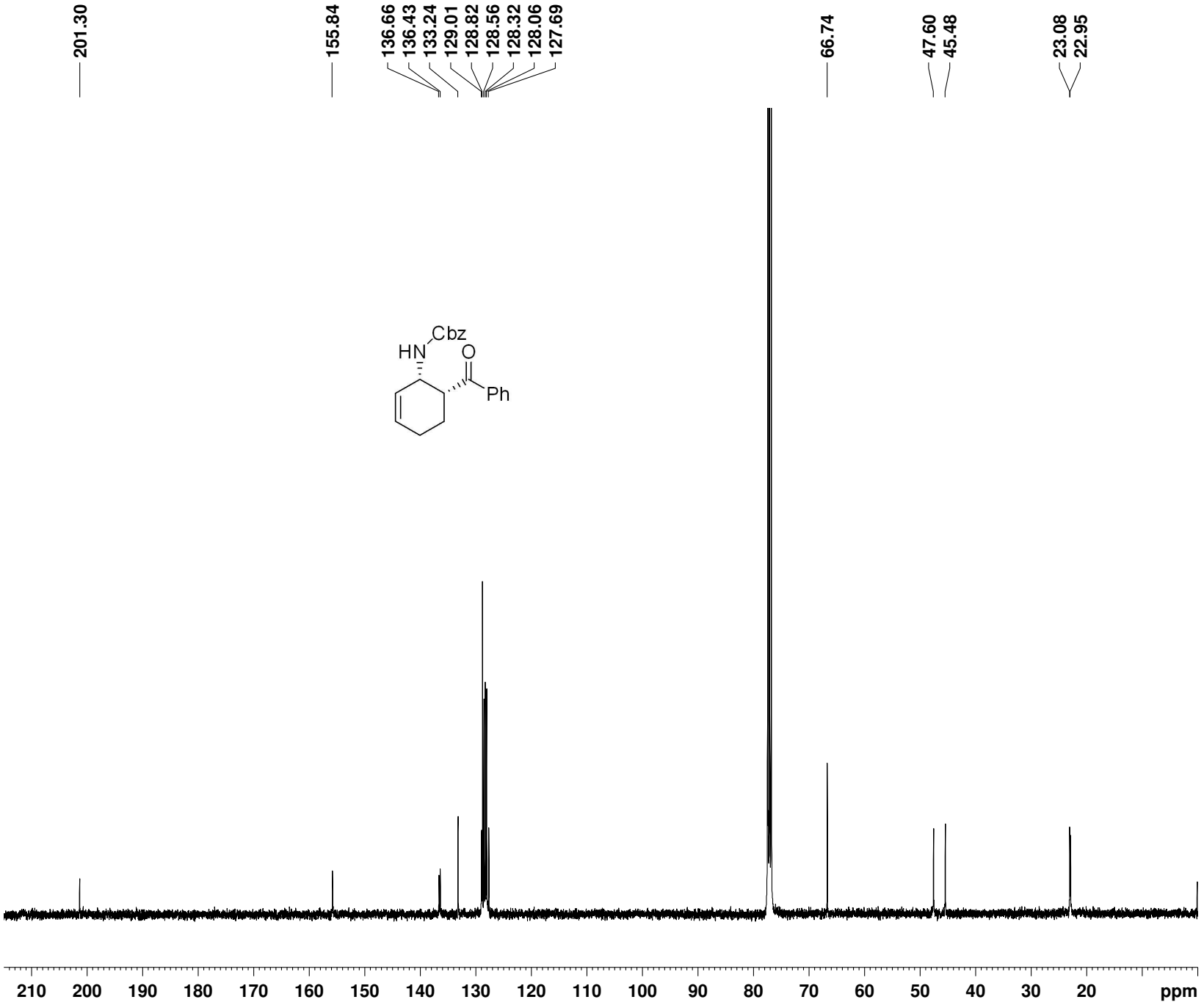
NAME	LMK131219C13
EXPNO	1
PROCNO	1
Date_	20140214
Time	17.56
INSTRUM	spect
PROBHD	5 mm PABBO BB-
PULPROG	zgpg30
TD	65536
SOLVENT	CDC13
NS	168
DS	4
SWH	24038.461 Hz
FIDRES	0.366798 Hz
AQ	1.3631988 sec
RG	203
DW	20.800 usec
DE	6.50 usec
TE	294.7 K
D1	2.00000000 sec
D11	0.03000000 sec
TD0	1
======== CHANNEL f1 ========	
NUC1	13C
P1	8.50 usec
PL1	-2.00 dB
PL1W	57.32743073 W
SFO1	100.6328888 MHz
======== CHANNEL f2 ========	
CPDPRG2	waltz16
NUC2	1H
PCPD2	80.00 usec
PL2	-1.00 dB
PL12	14.26 dB
PL13	14.46 dB
PL2W	13.18669796 W
PL12W	0.39276794 W
PL13W	0.37509048 W
SFO2	400.1716007 MHz
SI	32768
SF	100.6228110 MHz
WDW	EM
SSB	0
LB	1.00 Hz
GB	0
PC	1.40





NAME	LMK131213-1
EXPNO	1
PROCNO	1
Date_	20140217
Time	15.56
INSTRUM	spect
PROBHD	5 mm PABBO BB-
PULPROG	zg30
TD	65536
SOLVENT	CDCl3
NS	16
DS	0
SWH	8223.685 Hz
FIDRES	0.125483 Hz
AQ	3.9846387 sec
RG	203
DW	60.800 usec
DE	6.50 usec
TE	294.3 K
D1	1.00000000 sec
TD0	1
======== CHANNEL f1 ========	
NUC1	1H
P1	13.80 usec
PL1	-1.00 dB
PL1W	13.18669796 W
SFO1	400.1724712 MHz
SI	32768
SF	400.1700042 MHz
WDW	EM
SSB	0
LB	0.30 Hz
GB	0
PC	1.00





NAME	LMK131213-1-C13
EXPNO	1
PROCNO	1
Date_	20140216
Time	19.21
INSTRUM	spect
PROBHD	5 mm PABBO BB-
PULPROG	zgpg30
TD	65536
SOLVENT	CDC13
NS	5000
DS	4
SWH	24038.461 Hz
FIDRES	0.366798 Hz
AQ	1.3631988 sec
RG	203
DW	20.800 usec
DE	6.50 usec
TE	296.4 K
D1	2.00000000 sec
D11	0.03000000 sec
TD0	1
======== CHANNEL f1 ========	
NUC1	13C
P1	8.50 usec
PL1	-2.00 dB
PL1W	57.32743073 W
SFO1	100.6328888 MHz
======== CHANNEL f2 ========	
CPDPRG2	waltz16
NUC2	1H
PCPD2	80.00 usec
PL2	-1.00 dB
PL12	14.26 dB
PL13	14.46 dB
PL2W	13.18669796 W
PL12W	0.39276794 W
PL13W	0.37509048 W
SFO2	400.1716007 MHz
SI	32768
SF	100.6228110 MHz
WDW	EM
SSB	0
LB	1.00 Hz
GB	0
PC	1.40

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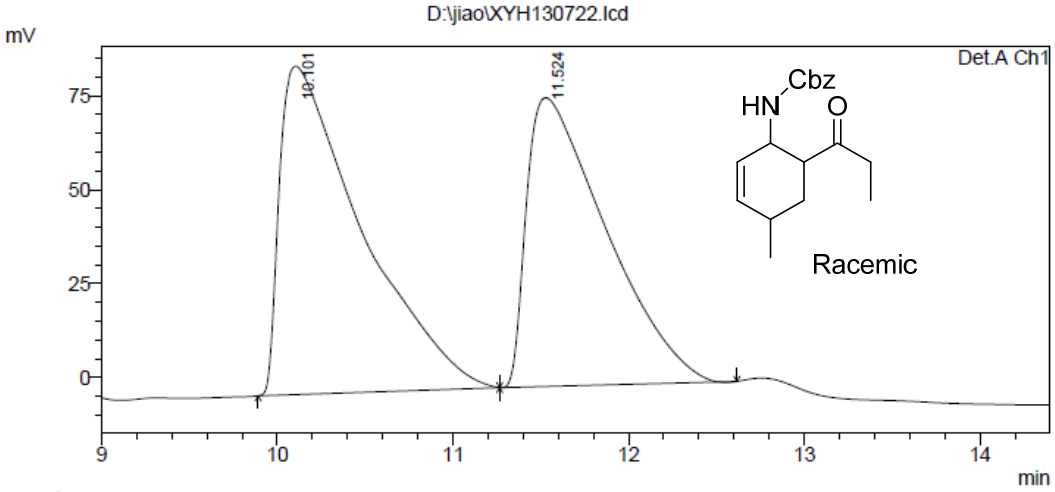

PeakTable

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	10.101	2814397	87407	53.855	53.204
2	11.524	2411504	76878	46.145	46.796
Total		5225900	164285	100.000	100.000

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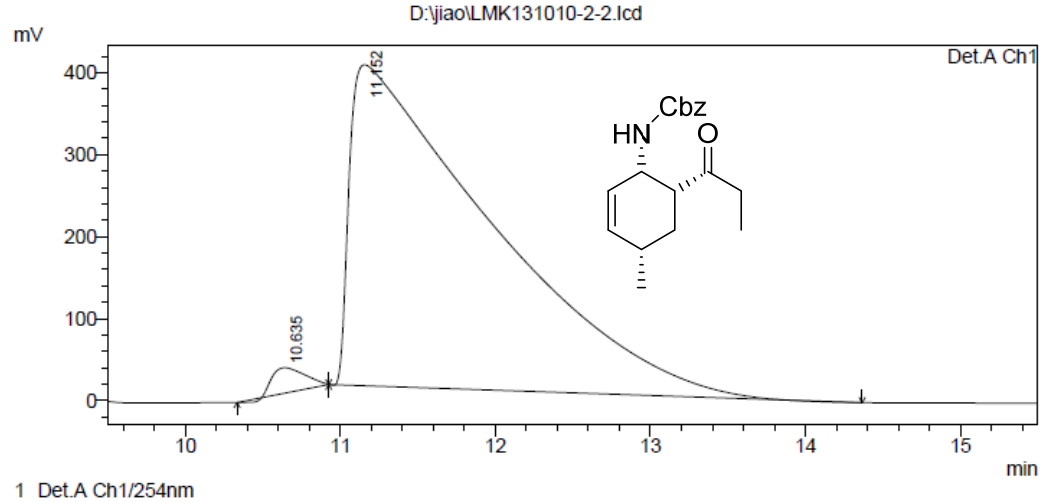
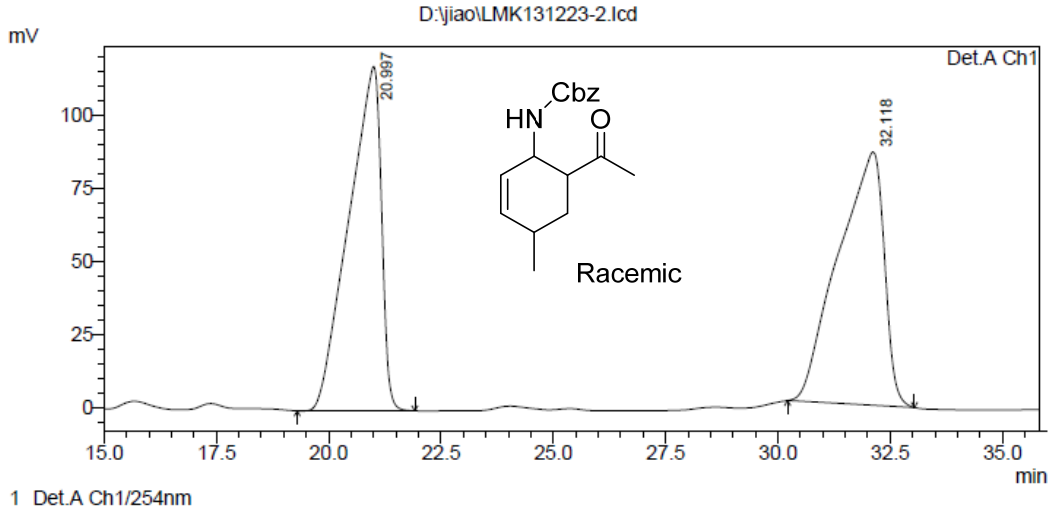


PeakTable

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	10.635	441668	31182	1.754	7.381
2	11.152	24743277	391286	98.246	92.619
Total		25184945	422468	100.000	100.000

<Chromatogram>



1 Det.A Ch1/254nm

PeakTable

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	20.997	5915084	117571	49.057	57.620
2	32.118	6142592	86474	50.943	42.380
Total		12057676	204045	100.000	100.000

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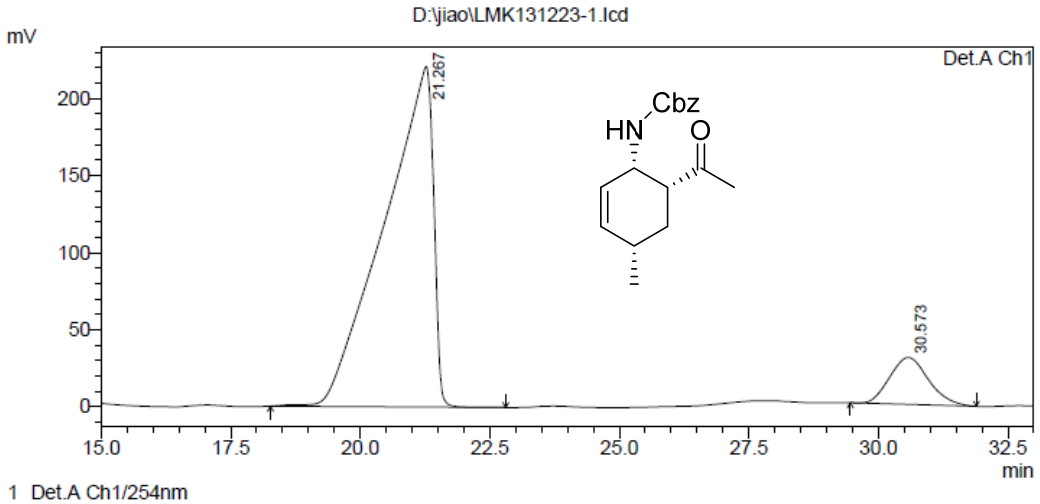

1 Det.A Ch1/254nm

PeakTable

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	21.267	14592053	220842	90.202	87.895
2	30.573	1585116	30415	9.798	12.105
Total		16177169	251257	100.000	100.000

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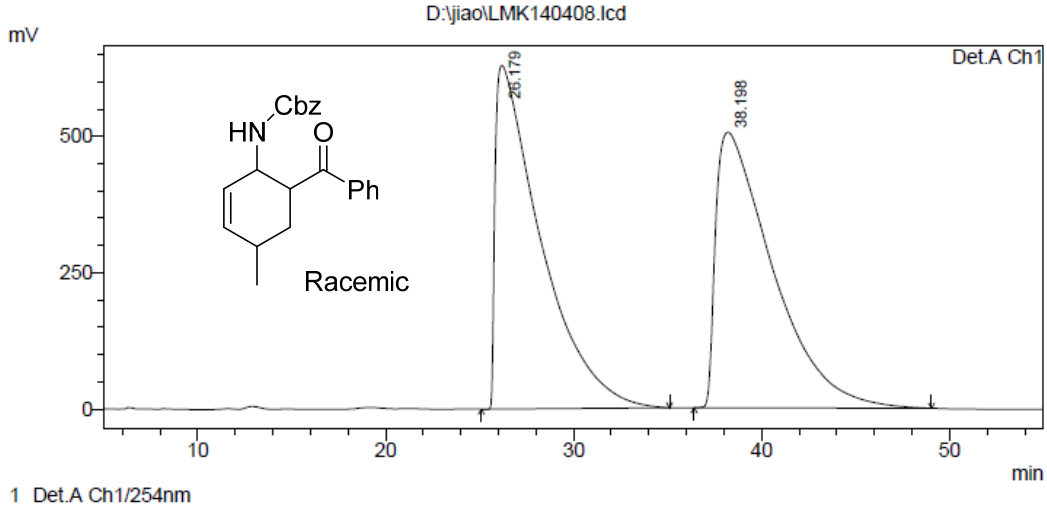

1 Det.A Ch1/254nm

PeakTable

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	26.179	105917095	629226	49.927	55.500
2	38.198	106227853	504519	50.073	44.500
Total		212144949	1133745	100.000	100.000

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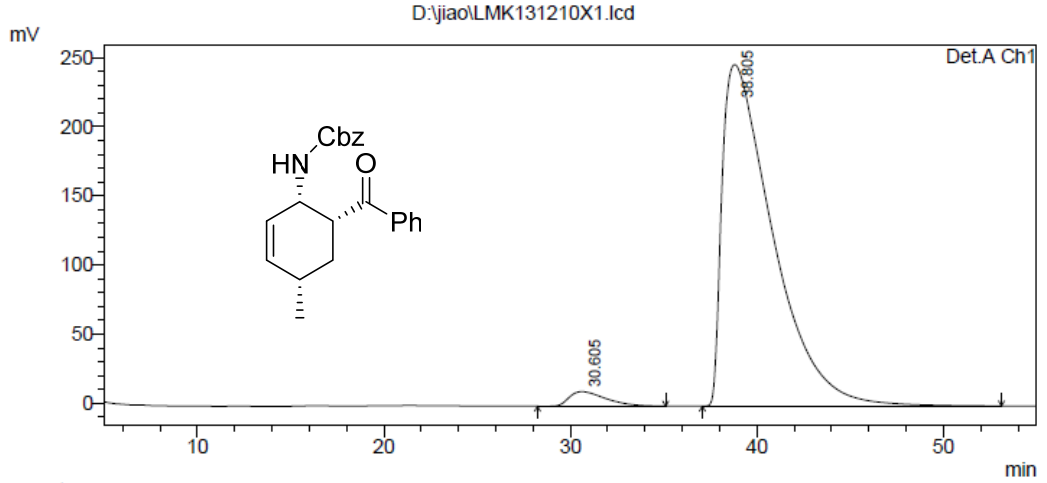


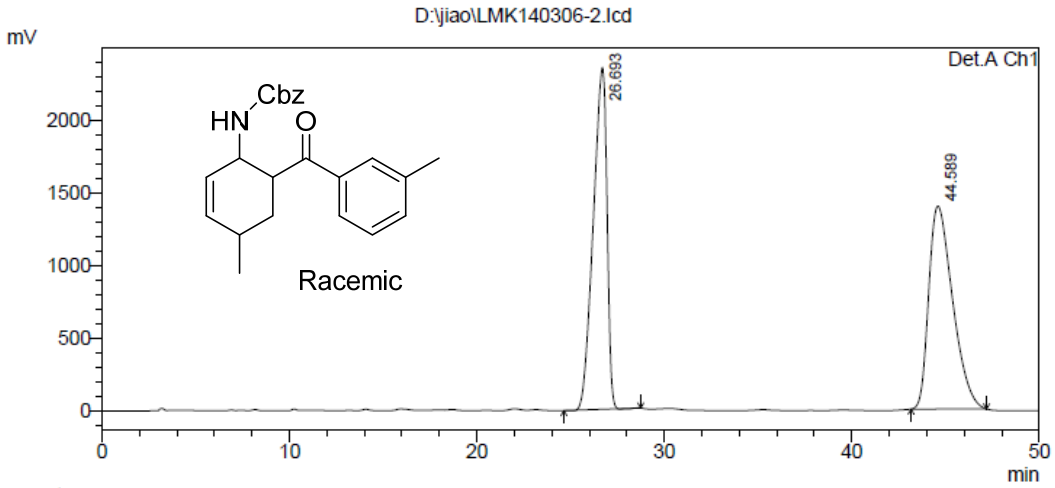
1 Det.A Ch1/254nm

PeakTable

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	30.605	1440817	10529	2.992	4.091
2	38.805	46721712	246854	97.008	95.909
Total		48162529	257383	100.000	100.000

<Chromatogram>



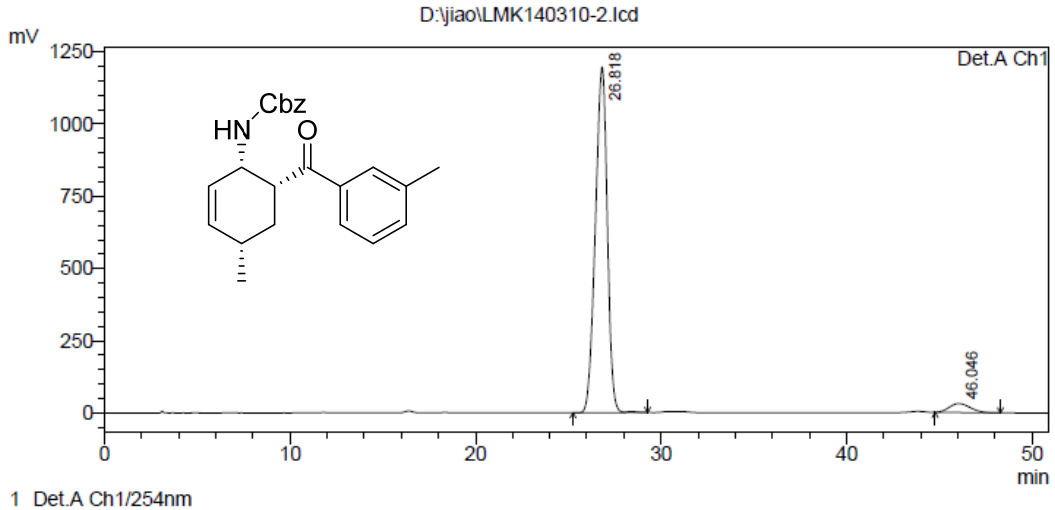
1 Det.A Ch1/254nm

PeakTable

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	26.693	119607568	2354621	49.120	62.742
2	44.589	123895329	1398241	50.880	37.258
Total		243502898	3752862	100.000	100.000

<Chromatogram>



1 Det.A Ch1/254nm

PeakTable

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	26.818	53543190	1196068	95.585	97.459
2	46.046	2473348	31185	4.415	2.541
Total		56016538	1227253	100.000	100.000

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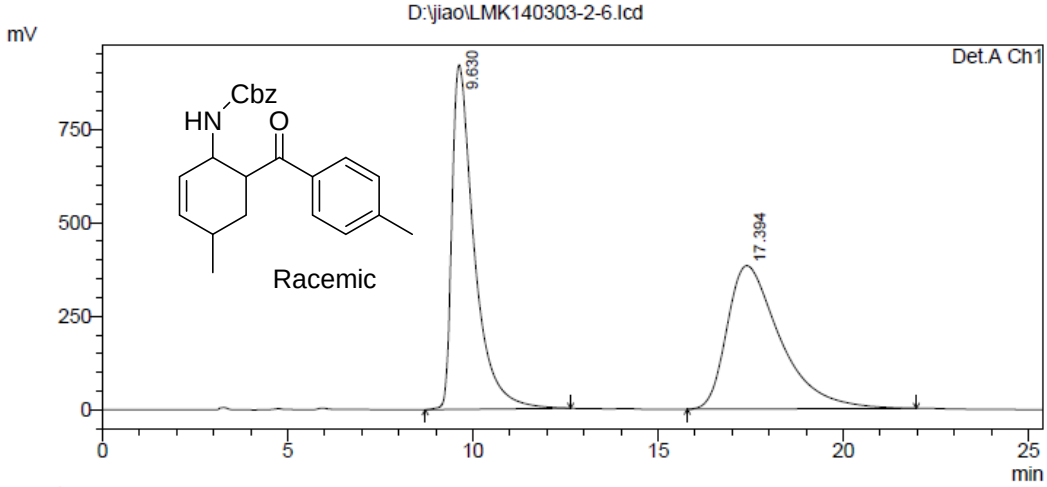

1 Det.A Ch1/254nm

PeakTable

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	9.630	38436006	920485	50.093	70.632
2	17.394	38293150	382729	49.907	29.368
Total		76729156	1303214	100.000	100.000

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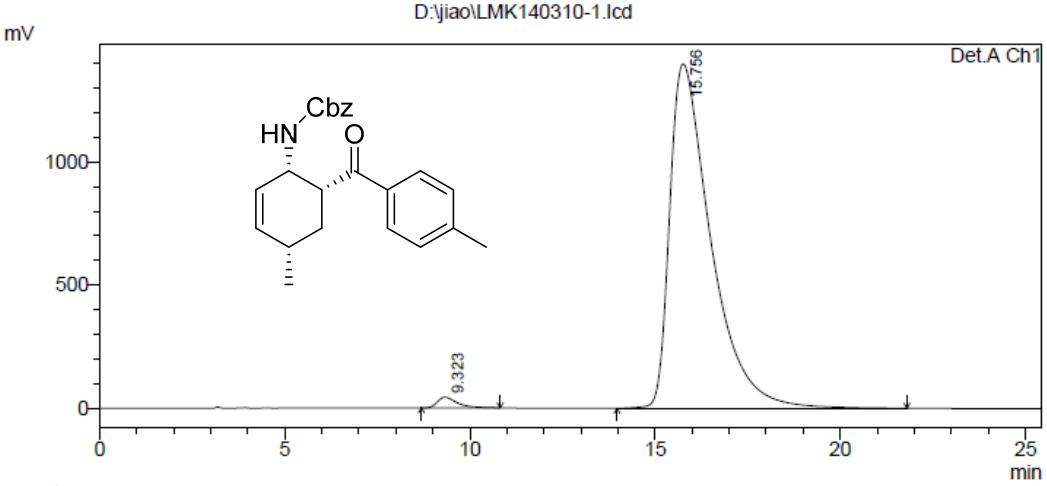


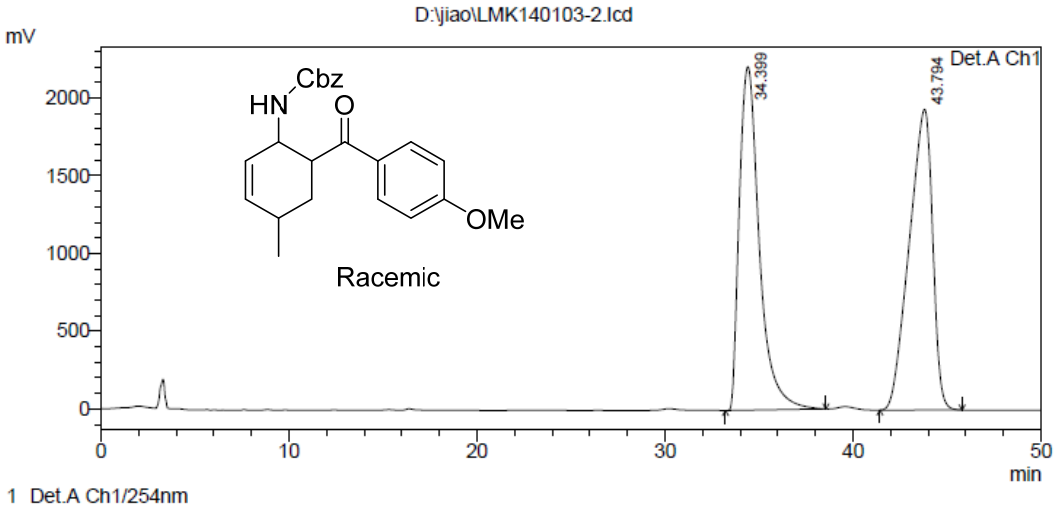
1 Det.A Ch1/254nm

PeakTable

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	9.323	1603996	43261	1.461	3.000
2	15.756	108176405	1398548	98.539	97.000
Total		109780400	1441809	100.000	100.000

<Chromatogram>



1 Det.A Ch1/254nm

PeakTable

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	34.399	163044241	2207439	49.385	53.319
2	43.794	167104866	1932634	50.615	46.681
Total		330149107	4140074	100.000	100.000

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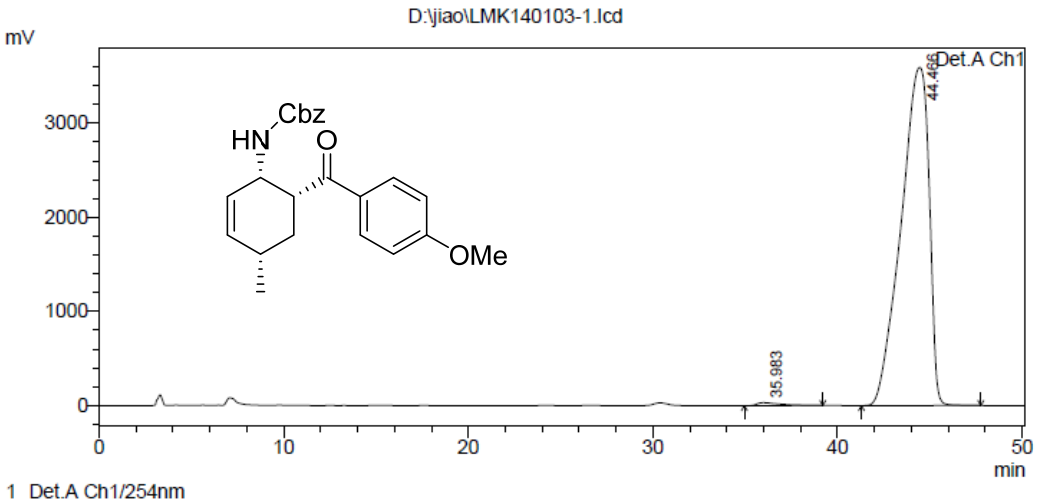

1 Det.A Ch1/254nm

PeakTable

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	35.983	2734852	31529	0.714	0.870
2	44.466	380086813	3591474	99.286	99.130
Total		382821666	3623003	100.000	100.000

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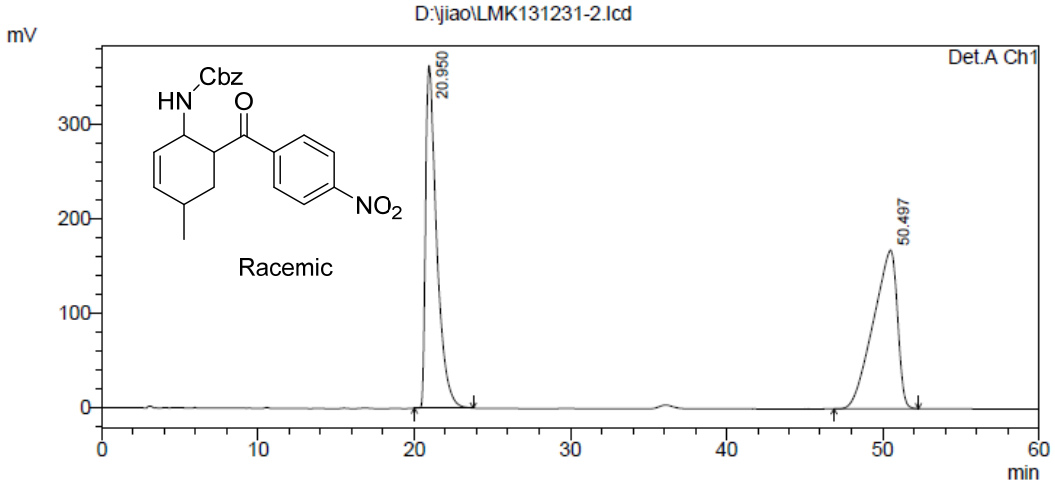


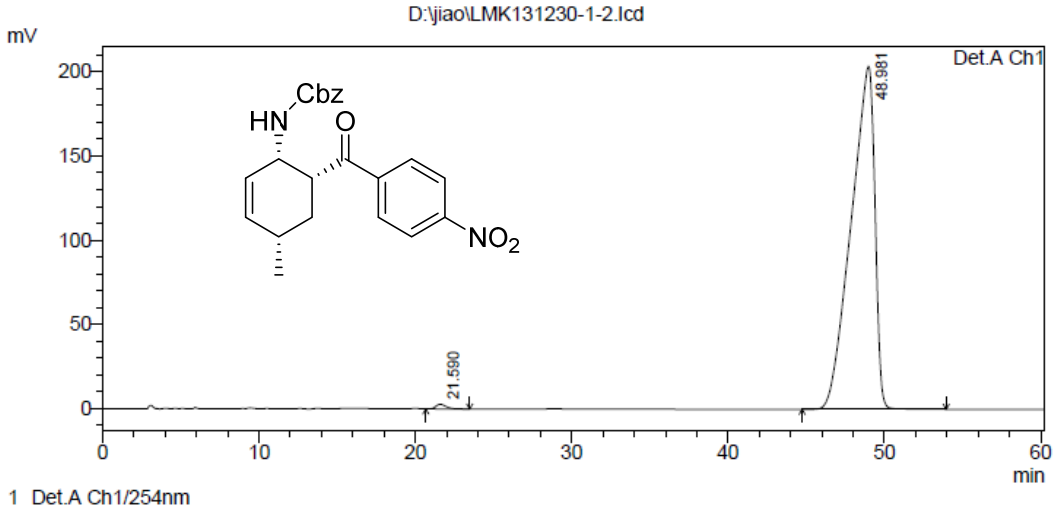
1 Det.A Ch1/254nm

PeakTable

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	20.950	17913335	362005	49.858	68.359
2	50.497	18015384	167558	50.142	31.641
Total		35928719	529563	100.000	100.000

<Chromatogram>



1 Det.A Ch1/254nm

PeakTable

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	21.590	129236	2782	0.598	1.348
2	48.981	21473285	203611	99.402	98.652
Total		21602521	206394	100.000	100.000

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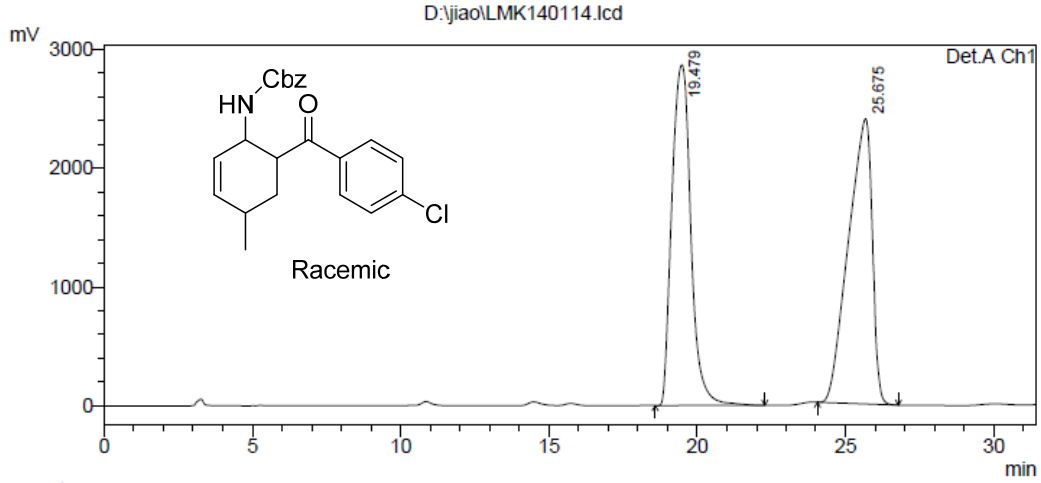

1 Det.A Ch1/254nm

PeakTable

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	19.479	127752073	2864220	48.913	54.448
2	25.675	133430176	2396289	51.087	45.552
Total		261182250	5260509	100.000	100.000

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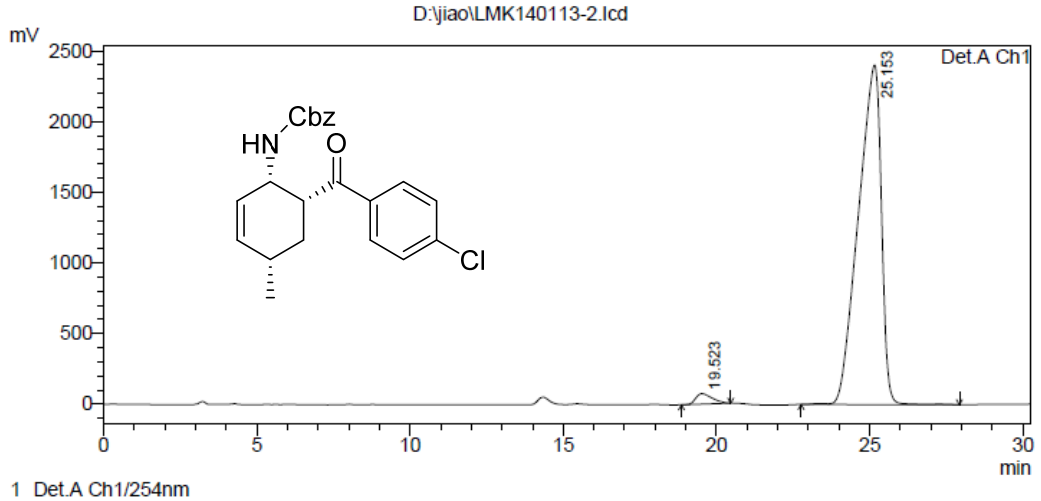

1 Det.A Ch1/254nm

PeakTable

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	19.523	2784337	74323	2.175	3.001
2	25.153	125216347	2402430	97.825	96.999
Total		128000684	2476753	100.000	100.000

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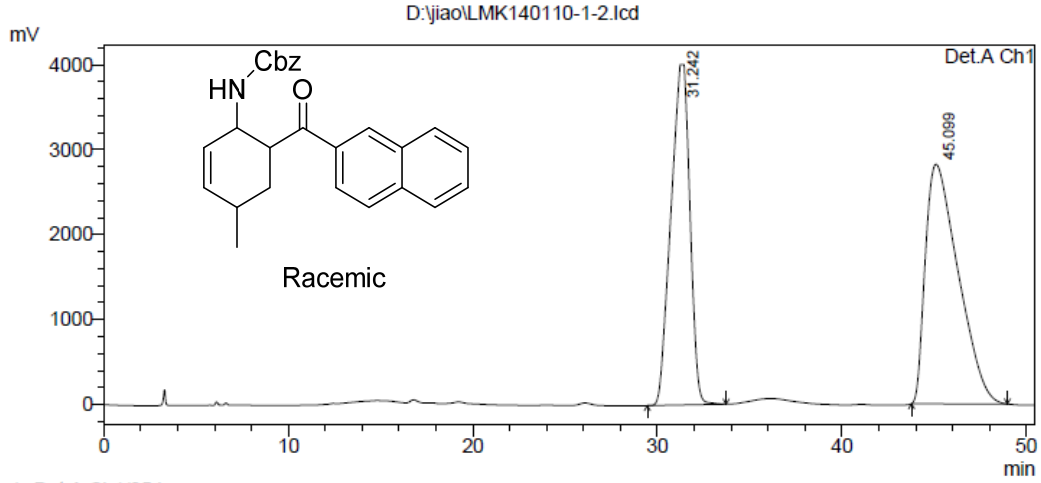

1 Det.A Ch1/254nm

PeakTable

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	31.242	286835080	4004365	45.104	58.694
2	45.099	349108678	2818049	54.896	41.306
Total		635943758	6822414	100.000	100.000

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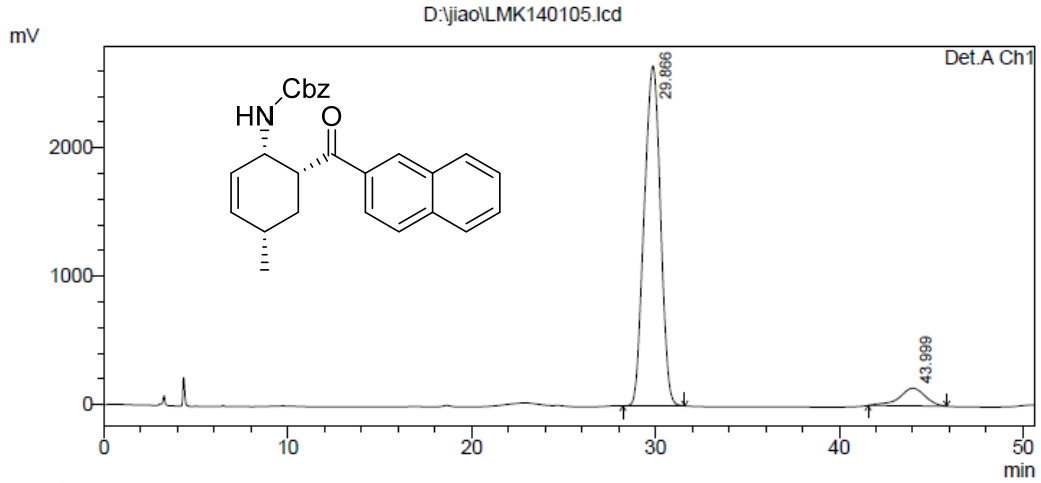

1 Det.A Ch1/254nm

PeakTable

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	29.866	162575162	2646310	92.342	95.064
2	43.999	13482976	137407	7.658	4.936
Total		176058138	2783716	100.000	100.000

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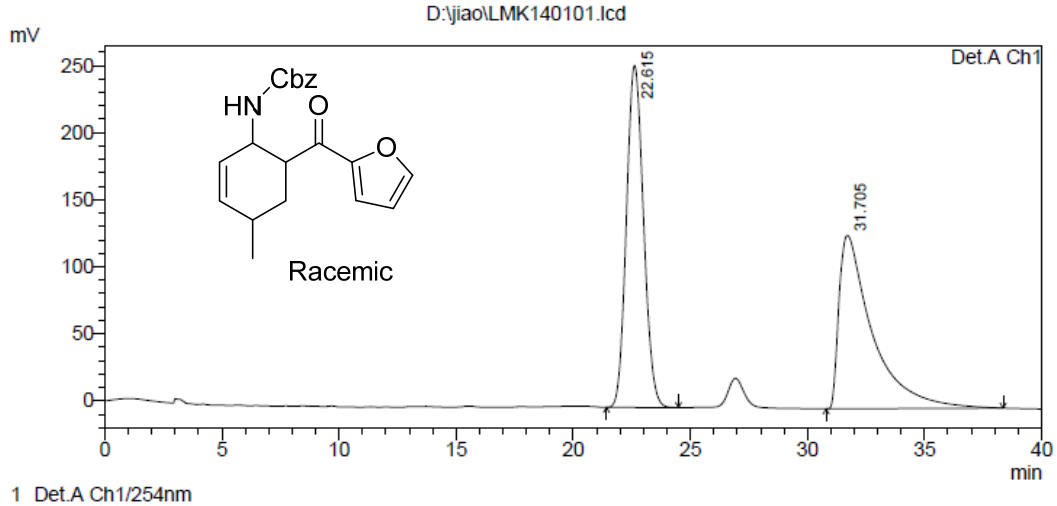

1 Det.A Ch1/254nm

PeakTable

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	22.615	12958795	254916	50.260	66.347
2	31.705	12824878	129299	49.740	33.653
Total		25783673	384214	100.000	100.000

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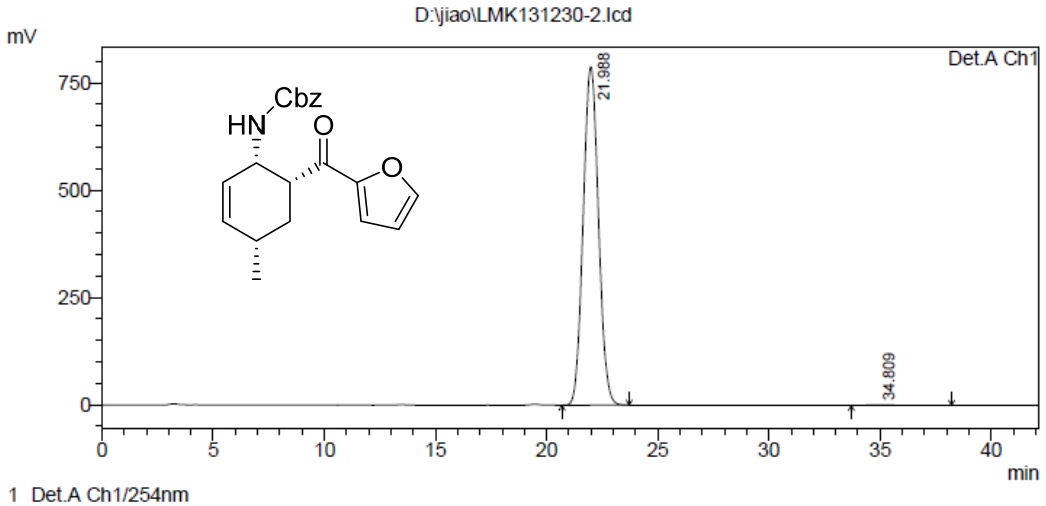

1 Det.A Ch1/254nm

PeakTable

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	21.988	37658276	787745	99.710	99.871
2	34.809	109601	1015	0.290	0.129
Total		37767877	788759	100.000	100.000

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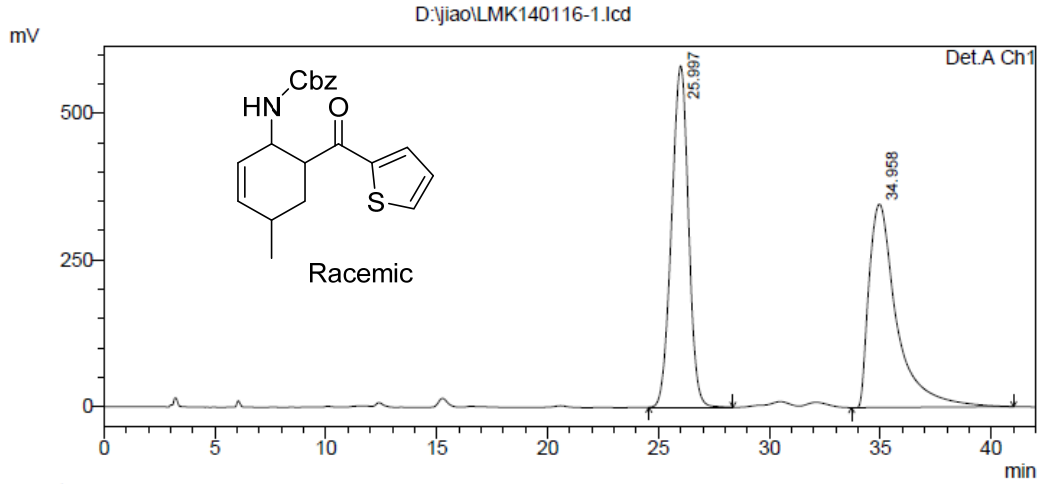

1 Det.A Ch1/254nm

PeakTable

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	25.997	30858766	581506	50.569	62.665
2	34.958	30163978	346454	49.431	37.335
Total		61022744	927960	100.000	100.000

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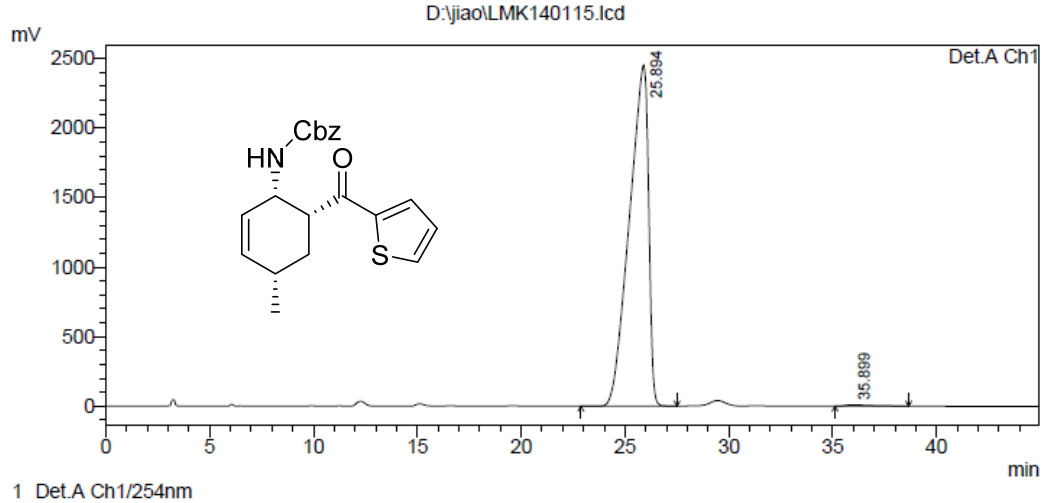

1 Det.A Ch1/254nm

PeakTable

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	25.894	157280323	2455286	99.460	99.631
2	35.899	854056	9087	0.540	0.369
Total		158134380	2464373	100.000	100.000

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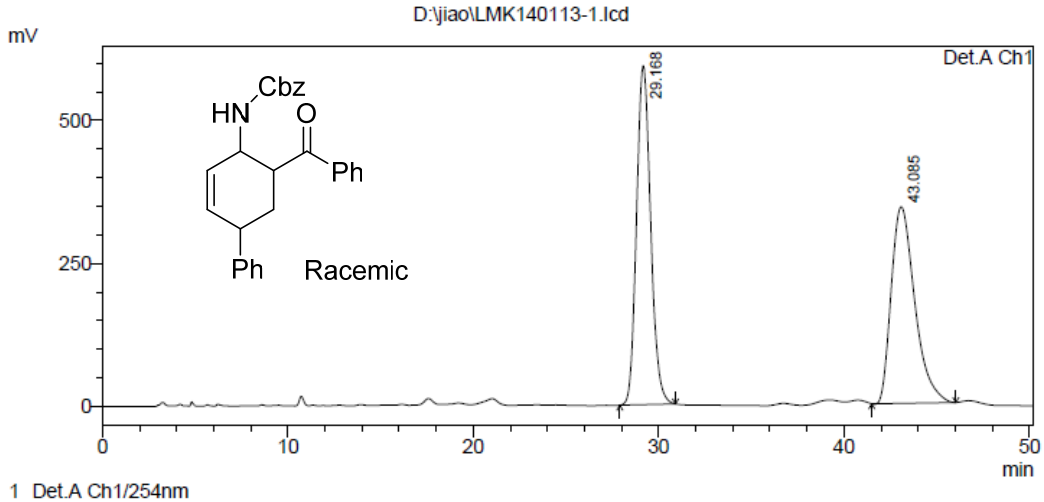

1 Det.A Ch1/254nm

PeakTable

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	29.168	31376108	592452	50.809	63.301
2	43.085	30376460	343480	49.191	36.699
Total		61752567	935932	100.000	100.000

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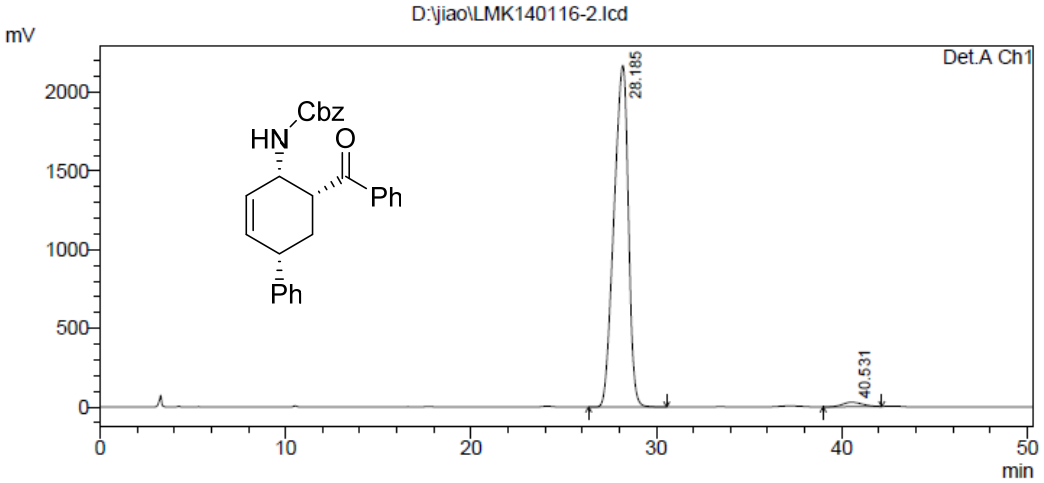

1 Det.A Ch1/254nm

PeakTable

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	28.185	117106130	2170348	98.229	98.692
2	40.531	2111829	28757	1.771	1.308
Total		119217959	2199105	100.000	100.000

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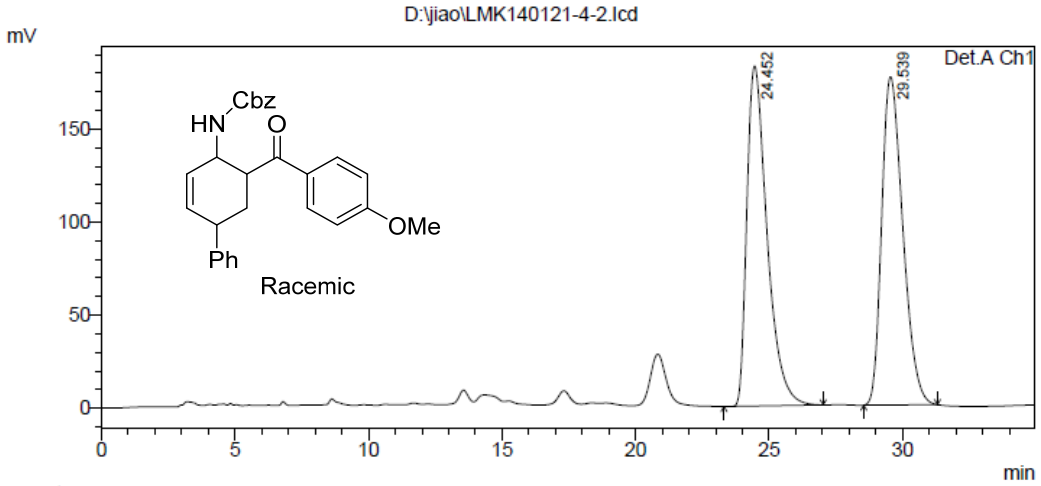

1 Det.A Ch1/254nm

PeakTable

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	24.452	9605122	182722	49.721	50.878
2	29.539	9712836	176414	50.279	49.122
Total		19317957	359136	100.000	100.000

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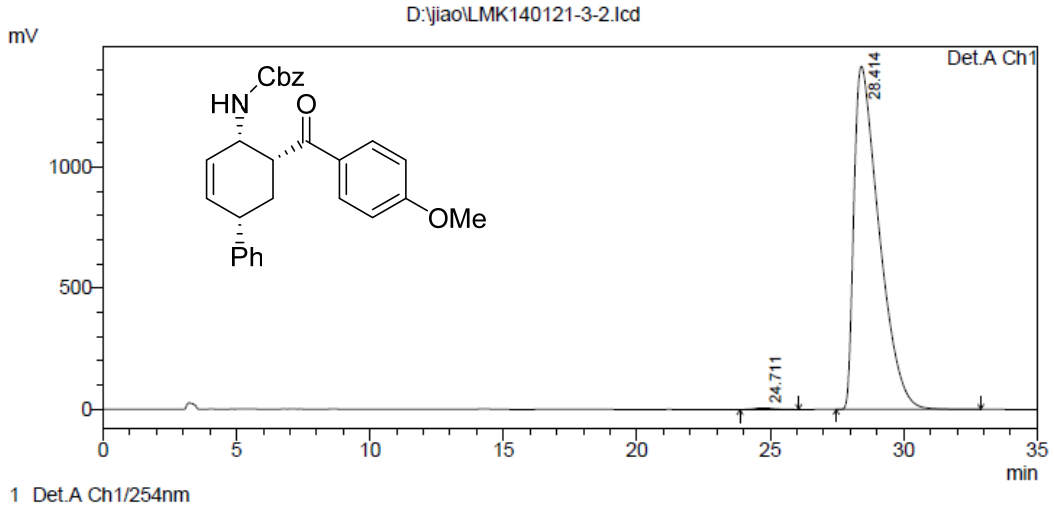

1 Det.A Ch1/254nm

PeakTable

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	24.711	312310	6094	0.335	0.428
2	28.414	92870080	1418053	99.665	99.572
Total		93182390	1424147	100.000	100.000

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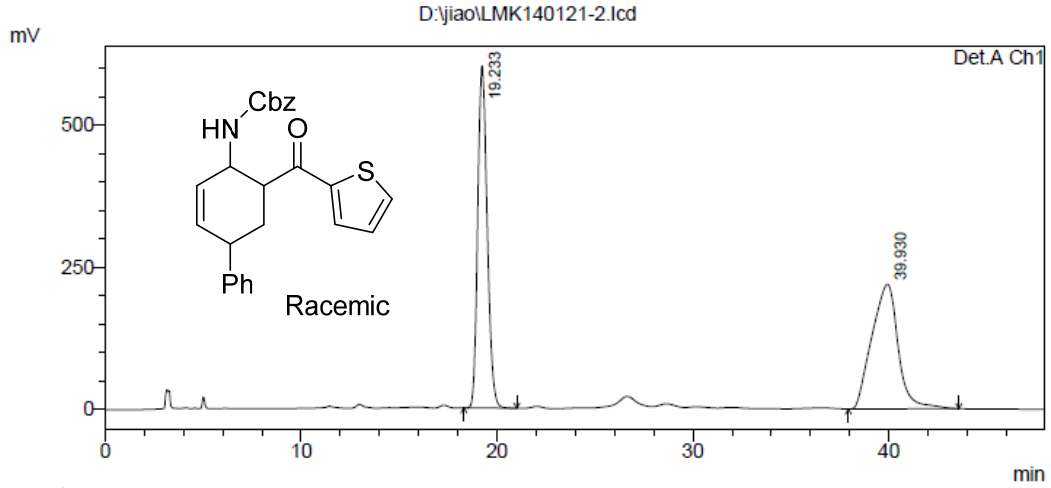

1 Det.A Ch1/254nm

PeakTable

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	19.233	20290858	601534	49.729	73.297
2	39.930	20512203	219141	50.271	26.703
Total		40803061	820675	100.000	100.000

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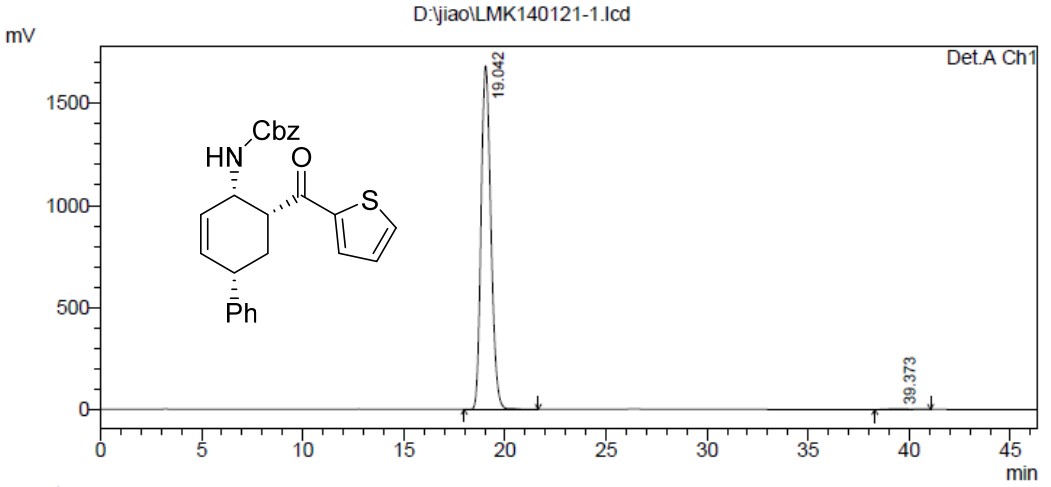

1 Det.A Ch1/254nm

PeakTable

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	19.042	56990886	1684413	99.599	99.818
2	39.373	229428	3071	0.401	0.182
Total		57220314	1687484	100.000	100.000

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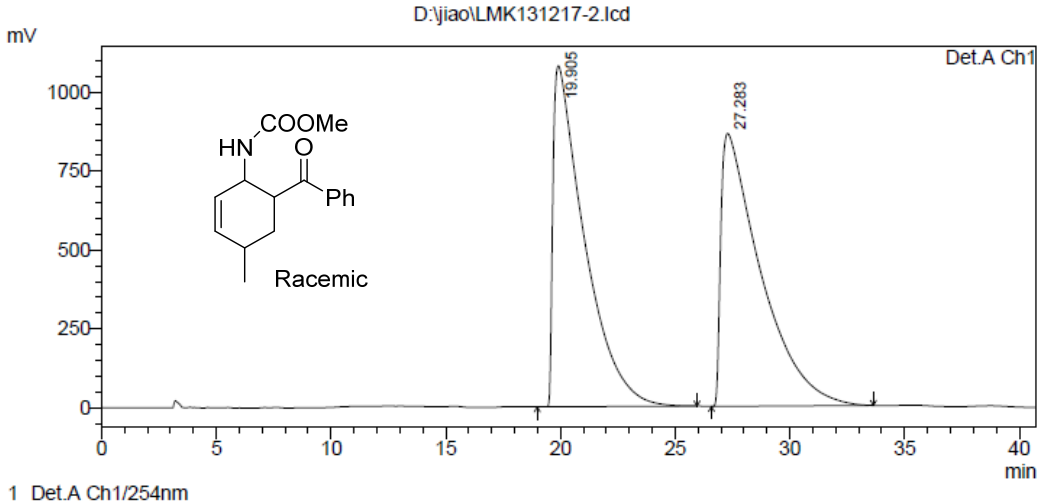

1 Det.A Ch1/254nm

PeakTable

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	19.905	102644035	1081903	49.575	55.542
2	27.283	104405954	865986	50.425	44.458
Total		207049989	1947889	100.000	100.000

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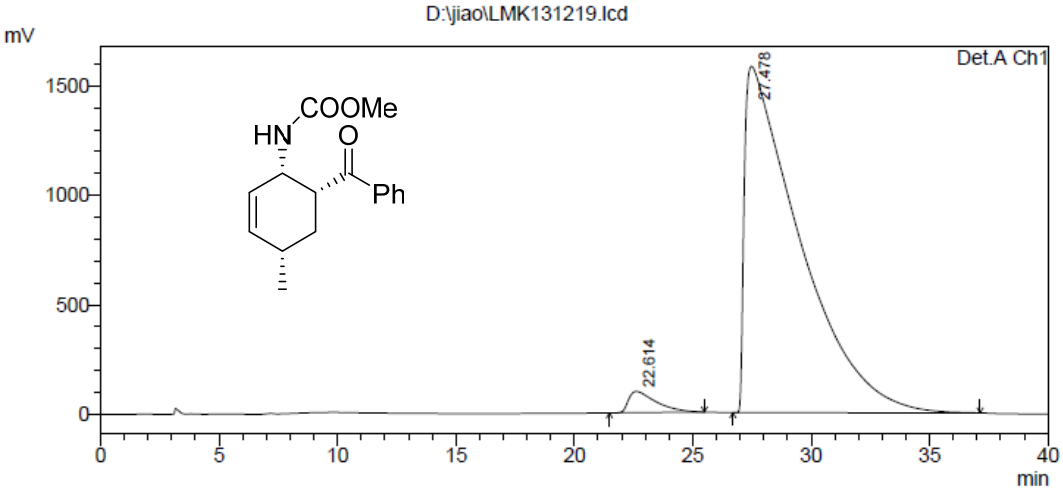


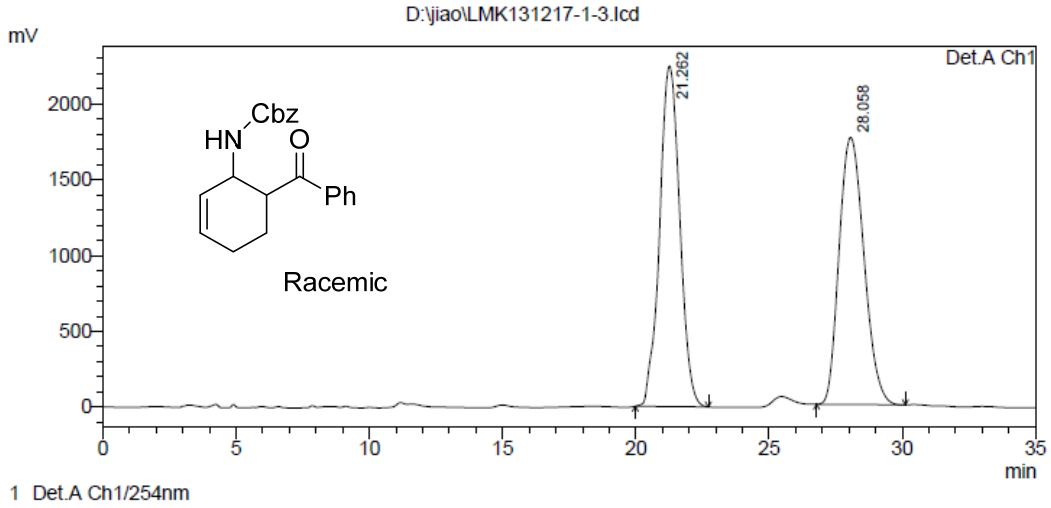
1 Det.A Ch1/254nm

PeakTable

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	22.614	7846188	97165	2.964	5.786
2	27.478	256914358	1582161	97.036	94.214
Total		264760546	1679326	100.000	100.000

<Chromatogram>



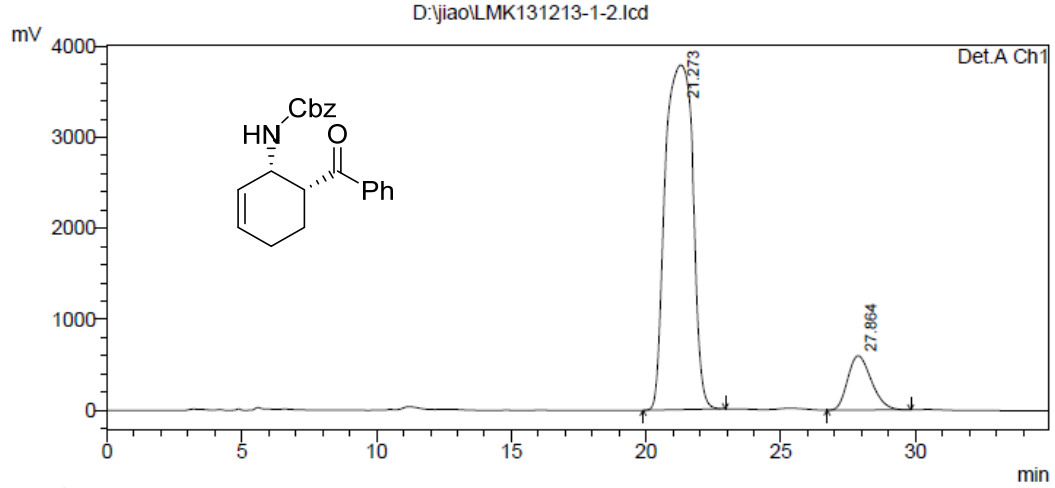
1 Det.A Ch1/254nm

PeakTable

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	21.262	118415770	2248839	50.844	56.050
2	28.058	114482814	1763374	49.156	43.950
Total		232898585	4012213	100.000	100.000

<Chromatogram>



1 Det.A Ch1/254nm

PeakTable

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	21.273	270583278	3786814	88.185	86.415
2	27.864	36252349	595301	11.815	13.585
Total		306835628	4382115	100.000	100.000