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## Supporting Information

# *E*-Selective *N*-Heterocyclic Carbene-Catalyzed Reaction of Aldehydes and Butadienoates: Effect of Water and Chloroform as the Proton Shuttle

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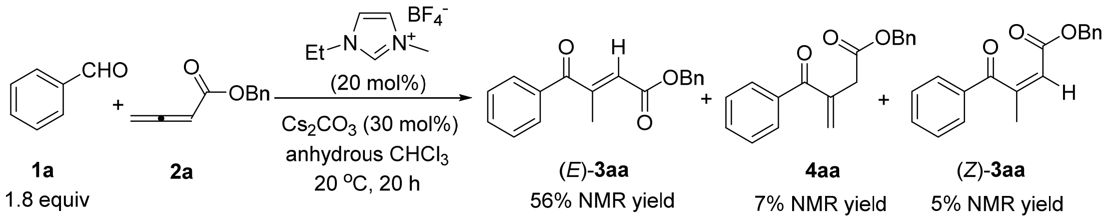
**General information**: $^1$H and $^{13}$C NMR spectra were recorded with a Bruker AM 300 MHz spectrometer. IR spectra were recorded with a Perkin–Elmer 983G instrument. Elemental analyses were measured with a Carlo-Erba EA1110 elementary analysis instrument. Mass spectrometry was performed with an HP 5989A system. High-resolution mass spectrometry was determined with a Finnigan MAT 8430 or Bruker APEXIII instrument. 1-Ethyl-3-methylimidazolium tetrafluoroborate was purchased from Aladdin. $Cs_2CO_3$ was purchased from Energy Chemical. Commercial $CHCl_3$ was purchased from Sinopharm Chemical Reagent Co., Ltd and used as received. Anhydrous $CHCl_3$ and $CDCl_3$ were distilled from $CaH_2$ under $N_2$ before use. Anhydrous THF was distilled from Na wire using benzophenone as indicator under $N_2$ before use. All liquid aldehydes were freshly distilled before use. Unless otherwise indicated, chemicals and solvents were purchased from commercial suppliers. The commercial petroleum ether (bp. 60~90 $^{o}$C) was redistilled to collect the fraction of bp. in the range of 60~90 $^{o}$C.

Allenoates **2a**~**2c** were prepared according to reported literatures.[1]

## 1. Preparation of authentic products: benzyl 3-methyl-4-oxo-4-phenylbut-2(*E*)-enoate ((*E*)-3aa) (mdk-11-058-1), benzyl 3-methylene-4-oxo-4-phenylbutanoate (4aa) (mdk-11-058-2), and benzyl 3-methyl-4-oxo-4-phenylbut-2(*Z*)-enoate ((*Z*)-3aa) (mdk-11-058-3)



**1a** 1.8 equiv

**2a**

(*E*)-**3aa**
56% NMR yield
52% isolated yield
(*E*)-**3aa**/(*Z*)-**3aa** = 97/3 by NMR analysis of the crude product

**4aa**
7% NMR yield
6% isolated yield

(*Z*)-**3aa**
5% NMR yield
5% isolated yield
purity = 97%

To a dry Schlenk flask was added $Cs_2CO_3$ (0.0978 g, 0.3 mmol) in a glove box. Then 1-ethyl-3-methylimidazolium tetrafluoroborate (0.0405 g, 0.2 mmol) and anhydrous $CHCl_3$ (5 mL) were added sequentially under $N_2$. The resulting mixture was stirred at 20 °C. After 10 min, **1a** (0.1912 g, 1.8 mmol), $CHCl_3$ (2.5 mL), **2a** (0.1749 g, 1 mmol), and $CHCl_3$ (2.5 mL) were added sequentially. The resulting mixture was stirred at 20 °C. After 20 h, the reaction was complete as monitored by TLC. Filtration through a short column of silica gel (eluent: ethyl acetate (20 mL × 3)), evaporation, and column chromatography on silica gel (petroleum ether/ethyl ether = 30/1 (450 mL × 5)) afforded (*E*)-**3aa** (0.1456 g, 52%), **4aa** (0.0163 g, 6%), and (*Z*)-**3aa** (0.0140 g, 5%, purity = 97%) (the ratio of (*E*)-**3aa**/(*Z*)-**3aa** was 92/8 and 7% of **4aa** was formed by NMR analysis of the crude product) (in the order of polarity in silica gel column).

(*E*)-**3aa**, the less polar isomer, liquid: $^1$H NMR (300 MHz, $CDCl_3$) δ 7.81-7.73 (m, 2H, ArH), 7.60-7.51 (m, 1H, ArH), 7.48-7.39 (m, 2H, ArH), 7.39-7.26 (m, 5H, ArH), 6.20

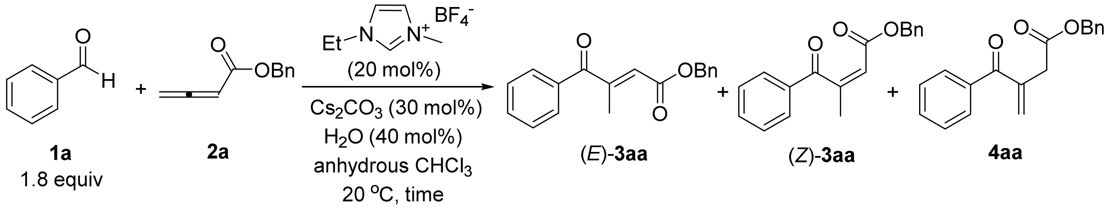
(q, *J* = 1.5 Hz, 1H, =CH), 5.20 (s, 2H, $CH_2$), 2.44 (d, *J* = 1.5 Hz, 3H, $CH_3$); $^{13}$C NMR (75 MHz, $CDCl_3$) δ 197.6, 165.4, 152.4, 135.6, 135.4, 133.0, 129.6, 128.5, 128.4, 128.3, 124.9, 66.4, 15.5; IR (neat) ν ($cm^{-1}$) 3064, 3034, 2955, 1723, 1663, 1596, 1579, 1498, 1448, 1381, 1352, 1316, 1267, 1190, 1138, 1075, 1037, 1023, 1002; MS (70 ev, EI) m/z (%) 280 ($M^+$, 1.90), 91 (100); HRMS calcd for $C_{18}H_{16}O_3$ ($M^+$): 280.1099, found: 280.1098.

**4aa**, the second polar isomer, liquid: $^1$H NMR (300 MHz, $CDCl_3$) δ 7.82-7.74 (m, 2H, ArH), 7.58-7.49 (m, 1H, ArH), 7.47-7.39 (m, 2H, ArH), 7.37-7.28 (m, 5H, ArH), 5.99 (s, 1H, one proton from =$CH_2$), 5.78 (s, 1H, one proton from =$CH_2$), 5.12 (s, 2H, $CH_2$), 3.61 (s, 2H, $CH_2$); $^{13}$C NMR (75 MHz, $CDCl_3$) δ 196.9, 170.7, 141.1, 137.2, 135.5, 132.3, 129.7, 128.9, 128.5, 128.3, 128.25, 128.16, 66.8, 38.1; IR (neat) ν ($cm^{-1}$) 3064, 3033, 2957, 1737, 1658, 1598, 1577, 1498, 1448, 1425, 1398, 1378, 1322, 1259, 1217, 1163, 1077, 1028; MS (ESI) *m/z* (%) 303 ($[M + Na]^+$), 281 ($[M + H]^+$); HRMS calcd. for $C_{18}H_{17}O_3$ ($[M + H]^+$): 281.1172, found: 281.1175.

(*Z*)-**3aa**, the more polar isomer, liquid: $^1$H NMR (300 MHz, $CDCl_3$) δ 7.92-7.83 (m, 2H, ArH), 7.61-7.54 (m, 1H, ArH), 7.50-7.40 (m, 2H, ArH), 7.31-7.24 (m, 3H, ArH), 7.19-7.10 (m, 2H, ArH), 6.06 (q, *J* = 1.5 Hz, 1H, =CH), 4.97 (s, 2H, $CH_2$), 2.14 (d, *J* = 1.5 Hz, 3H, $CH_3$); $^{13}$C NMR (75 MHz, $CDCl_3$) δ 198.1, 164.5, 155.6, 135.2, 134.3, 133.6, 128.8, 128.7, 128.4, 128.3, 128.2, 119.2, 66.5, 21.8; IR (neat) ν ($cm^{-1}$) 3064, 3033, 2950, 1716, 1675, 1644, 1598, 1584, 1498, 1450, 1379, 1350, 1310, 1264, 1232, 1196, 1173, 1129, 1026, 1002; MS (ESI) *m/z* (%) 303 ($[M + Na]^+$), 281 ($[M + H]^+$); HRMS calcd. for $C_{18}H_{17}O_3$ ($[M + H]^+$): 281.1172, found: 281.1179.

## 2. Mechanistic studies

### (1) The reaction profile as monitored by $^{1}$H NMR analysis (mdk-11-103)



To a dry Schlenk flask was added $Cs_2CO_3$ (0.0977 g, 0.3 mmol) in a glove box. Then 1-ethyl-3-methylimidazolium tetrafluoroborate (0.0406 g, 0.2 mmol) and anhydrous $CHCl_3$ (5 mL) were added sequentially under $N_2$. The resulting mixture was stirred at 20 $^{o}$C. After 10 min, **1a** (0.1906 g, 1.8 mmol), $CHCl_3$ (2.5 mL), **2a** (0.1740 g, 1 mmol), $CHCl_3$ (2.5 mL), $H_2O$ (7.2 μL, d = 1 g/mL, 0.0072 g, 0.4 mmol) and 1,3,5-trimethylbenezene (42 μL, internal standard) were added sequentially. The resulting mixture was stirred at 20 $^{o}$C. Then each time 0.2 mL of reaction mixture was taken by a syringe and submitted to $^{1}$H NMR analysis at 0.5 h, 1 h, 1.5 h, 2 h, 2.5 h, 3 h, 3.5 h, 4 h, 5 h, 6 h, 7 h, 8 h, 9 h, and 19 h.

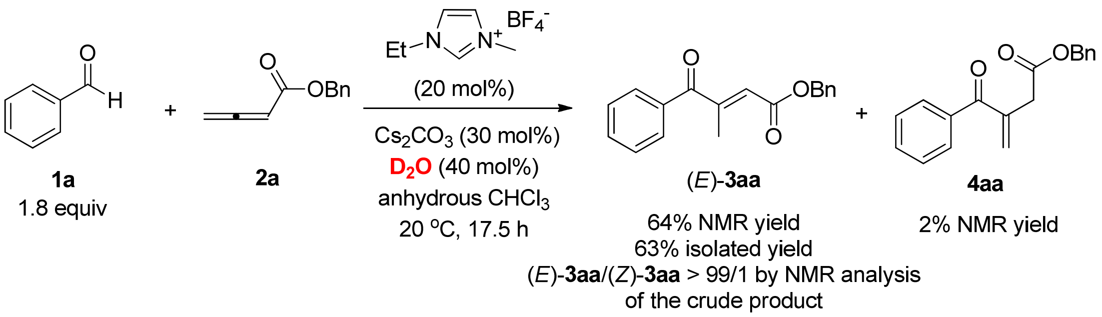
Table S1. The reaction profile

| Entry | time (h) | Yield[a] (%) |  |  | Recovery of **2a**[a] (%) |
|---|---|---|---|---|---|
|  |  | (*E*)-**3aa** | (*Z*)-**3aa** | **4aa** |  |
| 1 | 0.5 | 12 | 0 | 0 | 67 |
| 2 | 1 | 23 | 0 | 0 | 54 |
| 3 | 1.5 | 32 | 0 | 0 | 43 |
| 4 | 2 | 39 | 0 | 0 | 36 |
| 5 | 2.5 | 44 | 0 | 0 | 28 |
| 6 | 3 | 48 | 0 | 0 | 24 |
| 7 | 3.5 | 51 | 0 | 0 | 19 |
| 8 | 4 | 55 | 0 | 0 | 16 |
| 9 | 5 | 58 | 0 | 0 | 12 |
| 10 | 6 | 60 | 0 | 0 | 9 |
| 11 | 7 | 62 | 0 | 0 | 7 |
| 12 | 8 | 61 | 0 | 0.5 | 6 |
| 13 | 9 | 62 | 0 | 1 | 4 |
| 14 | 19 | 63 | 0.1 | 2 | 1 |

[a] Determined by NMR using 1,3,5-trimethylbenzene as the internal standard.

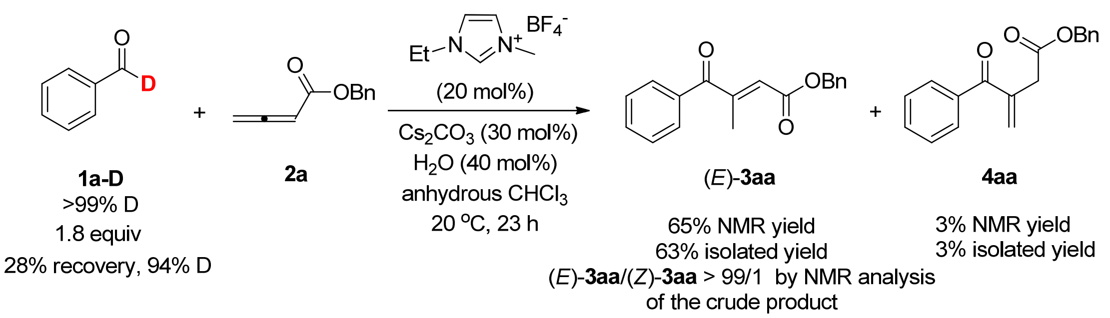
## (2) Isotopic labeling experiments

**(2.1)** The reaction of **1a** and **2a** using $D_2O$ instead of $H_2O$ (mdk-11-079)



**Typical Procedure I**: To a dry Schlenk flask was added $Cs_2CO_3$ (0.0980 g, 0.3 mmol) in a glove box. Then 1-ethyl-3-methylimidazolium tetrafluoroborate (0.0408 g, 0.2 mmol) and anhydrous $CHCl_3$ (5 mL) were added sequentially under $N_2$. The resulting mixture was stirred at 20 $^{o}$C. After 10 min, **1a** (0.1914 g, 1.8 mmol), anhydrous $CHCl_3$ (2.5 mL), **2a** (0.1745 g, 1 mmol), anhydrous $CHCl_3$ (2.5 mL), and $D_2O$ (7.2 μL, d = 1.107 g/mL, 0.0080 g, 0.4 mmol) were added sequentially. The resulting mixture was stirred at 20 $^{o}$C. After 17.5 h, the reaction was complete as monitored by TLC. Filtration through a short column of silica gel (eluent: ethyl acetate (20 mL × 3)), evaporation, and column chromatography on silica gel (petroleum ether/ethyl acetate = 40/1 (400 mL) to 20/1 (420 mL)) afforded (*E*)-**3aa** (0.1780 g, 63%) (The ratio of (*E*)-**3aa**/(*Z*)-**3aa** was >99/1 and 2% of **4aa** was detected by NMR analysis of the crude product) as a liquid: $^{1}$H NMR (300 MHz, $CDCl_3$) δ 7.81-7.73 (m, 2H, ArH), 7.61-7.53 (m, 1H, ArH), 7.49-7.41 (m, 2H, ArH), 7.40-7.27 (m, 5H, ArH), 6.20 (q, *J* = 1.5 Hz, 1H, =CH), 5.21 (s, 2H, $CH_2$), 2.44 (d, *J* = 1.5 Hz, 3H, $CH_3$); $^{13}$C NMR (75 MHz, $CDCl_3$) δ 197.7, 165.5, 152.5, 135.7, 135.4, 133.1, 129.6, 128.53, 128.48, 128.3, 124.9, 66.4, 15.5.

**(2.2)** The reaction of **1a-D** and **2a** in anhydrous $CHCl_3$ (mdk-11-086)



**1a-D**
>99% D
1.8 equiv
28% recovery, 94% D

**2a**

(*E*)-**3aa**
65% NMR yield
63% isolated yield

**4aa**
3% NMR yield
3% isolated yield

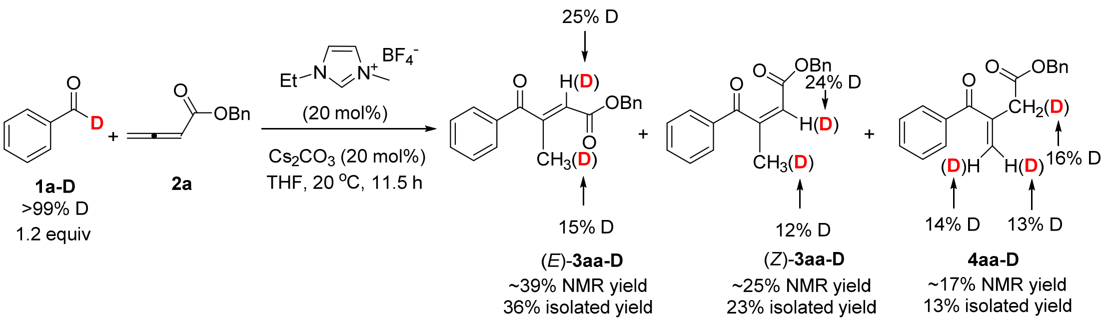
(*E*)-**3aa**/(*Z*)-**3aa** > 99/1 by NMR analysis of the crude product

Following **Typical Procedure I**, the reaction of $Cs_2CO_3$ (0.0980 g, 0.3 mmol), 1-ethyl-3-methylimidazolium tetrafluoroborate (0.0408 g, 0.2 mmol)/anhydrous $CHCl_3$ (5 mL), **1a-D**[2] (0.1927 g, 1.8 mmol)/anhydrous $CHCl_3$ (2.5 mL), **2a** (0.1743 g, 1 mmol)/anhydrous $CHCl_3$ (2.5 mL), and $H_2O$ (7.2 μL, d = 1.000 g/mL, 0.0072 g, 0.4 mmol) at 20 °C for 23 h afforded (*E*)-**3aa** (0.1776 g, 63%) and **4aa** (0.0081 g, 3%) (petroleum ether/ethyl ether = 30/1 (450 mL × 3) to 20/1 (200 mL)) (The ratio of (*E*)-**3aa**/(*Z*)-**3aa** was >99/1 and 3% of **4aa** was detected by NMR analysis of the crude product).

(*E*)-**3aa**, liquid: $^1$H NMR (300 MHz, $CDCl_3$) δ 7.81-7.73 (m, 2H, ArH), 7.61-7.52 (m, 1H, ArH), 7.49-7.41 (m, 2H, ArH), 7.40-7.26 (m, 5H, ArH), 6.20 (q, $J$ = 1.4 Hz, 1H, =CH), 5.21 (s, 2H, $CH_2$), 2.44 (d, $J$ = 1.5 Hz, 3H, $CH_3$); $^{13}$C NMR (75 MHz, $CDCl_3$) δ 197.7, 165.5, 152.5, 135.7, 135.4, 133.1, 129.6, 128.53, 128.45, 128.3, 124.9, 66.4, 15.5.

**4aa**, liquid: $^1$H NMR (300 MHz, $CDCl_3$) δ 7.81-7.72 (m, 2H, ArH), 7.58-7.50 (m, 1H, ArH), 7.46-7.38 (m, 2H, ArH), 7.36-7.28 (m, 5H, ArH), 5.99 (s, 1H, one proton from =$CH_2$), 5.78 (s, 1H, one proton from =$CH_2$), 5.12 (s, 2H, $CH_2$), 3.61 (s, 2H, $CH_2$); $^{13}$C NMR (75 MHz, $CDCl_3$) δ 196.9, 170.7, 141.2, 137.2, 135.5, 132.3, 129.7, 128.9, 128.5, 128.31, 128.26, 128.2, 66.8, 38.1.

**(2.3)** The reaction of **1a-D** and **2a** in anhydrous THF (mdk-11-107)



To a dry Schlenk flask was added $Cs_2CO_3$ (0.0262 g, 0.08 mmol) in a glove box. Then 1-ethyl-3-methylimidazolium tetrafluoroborate (0.0160 g, 0.08 mmol) and THF

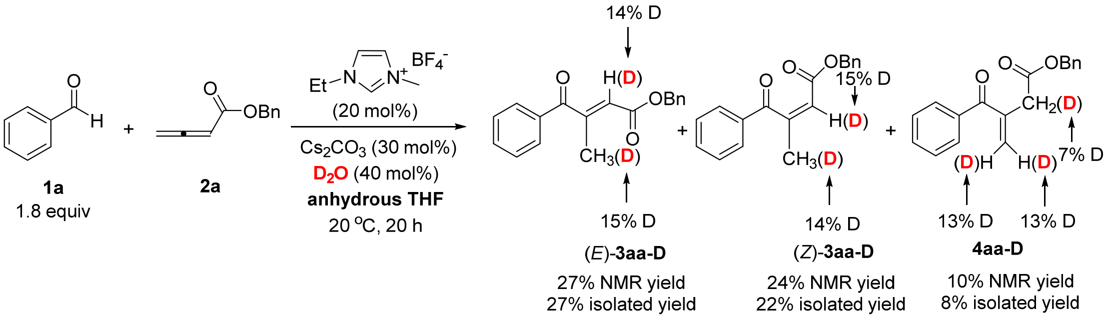
(2 mL) were added sequentially under $N_2$. The resulting mixture was stirred at 20 °C. After 10 min, **1a-D** (0.0516 g, 0.48 mmol), THF (1 mL), **2a** (0.0694 g, 0.4 mmol), and THF (1 mL) were added sequentially. The resulting mixture was stirred at 20 °C. After 11.5 h, the reaction was complete as monitored by TLC. Filtration through a short column of silica gel (eluent: ethyl acetate (15 mL × 3)), evaporation, and column chromatography on silica gel (petroleum ether/ethyl ether = 40/1 (400 mL × 3) to 30/1 (400 mL) to 20/1 (400 mL)) afforded (*E*)-**3aa-D** (0.0409 g, 36%), **4aa-D** (0.0142 g, 13%), and (*Z*)-**3aa-D** (0.0260 g, 23%) (The ratio of *E*/*Z* was ~61/39 and ~17% of **4aa-D** was detected by NMR analysis of the crude product) (in the order of polarity in silica gel column).

(*E*)-**3aa-D**, the least isomer, liquid: $^1$H NMR (300 MHz, $CDCl_3$) δ 7.82-7.73 (m, 2H, ArH), 7.62-7.53 (m, 1H, ArH), 7.51-7.41 (m, 2H, ArH), 7.41-7.27 (m, 5H, ArH), 5.21 (s, 2H, $CH_2$); the following signals is discernible for (*E*)-**3aa**: δ 6.23-6.17 (m, 0.75H, =CH), 2.49-2.35 (m, 1.61H, $CH_3$).

**4aa-D**, the second polar isomer, liquid: $^1$H NMR (300 MHz, $CDCl_3$) δ 7.81-7.73 (m, 2H, ArH), 7.58-7.49 (m, 1H, ArH), 7.46-7.38 (m, 2H, ArH), 7.38-7.27 (m, 5H, ArH), 5.12 (s, 2H, $CH_2$); the following signals is discernible for **4aa**: δ 6.01-5.95 (m, 0.87H, one proton from $=CH_2$), 5.79-5.74 (m, 0.86H, one proton from $=CH_2$), 3.64-3.55 (m, 1.68H, $CH_2$); IR (neat) ν (cm$^{-1}$) 3063, 3033, 2950, 1716, 1675, 1642, 1598, 1583, 1498, 1449, 1379, 1350, 1316, 1262, 1195, 1172, 1128, 1026, 1002; MS (ESI) *m/z* (%) 303 ([M + Na]$^+$), 281 ([M + H]$^+$); HRMS calcd. for $C_{18}H_{17}O_3$ ([M + H]$^+$): 281.1172, found: 281.1175. For detailed MS and HRMS spectra, please see attached copies.

(*Z*)-**3aa-D**, the most polar isomer, liquid: $^1$H NMR (300 MHz, $CDCl_3$) δ 7.91-7.82 (m, 2H, ArH), 7.61-7.53 (m, 1H, ArH), 7.49-7.39 (m, 2H, ArH), 7.32-7.21 (m, 3H, ArH), 7.19-7.09 (m, 2H, ArH), 4.96 (s, 2H, $CH_2$); the following signals is discernible for (*Z*)-**3aa**: δ 6.09-6.03 (m, 0.76H, =CH), 2.18-2.08 (m, 2.64H, $CH_3$); IR (neat) ν (cm$^{-1}$) 3088, 3064, 3033, 2955, 1737, 1658, 1598, 1498, 1447, 1400, 1378, 1321, 1259, 1215, 1163, 1077, 1028; MS (ESI) *m/z* (%) 303 ([M + Na]$^+$), 281 ([M + H]$^+$); HRMS calcd. for $C_{18}H_{17}O_3$ ([M + H]$^+$): 281.1172, found: 281.1172. For detailed MS and HRMS spectra, please see attached copies.

(**2.4**) The reaction of **1a** and **2a** using $D_2O$ instead of $H_2O$ in anhydrous THF (hx-16-162)



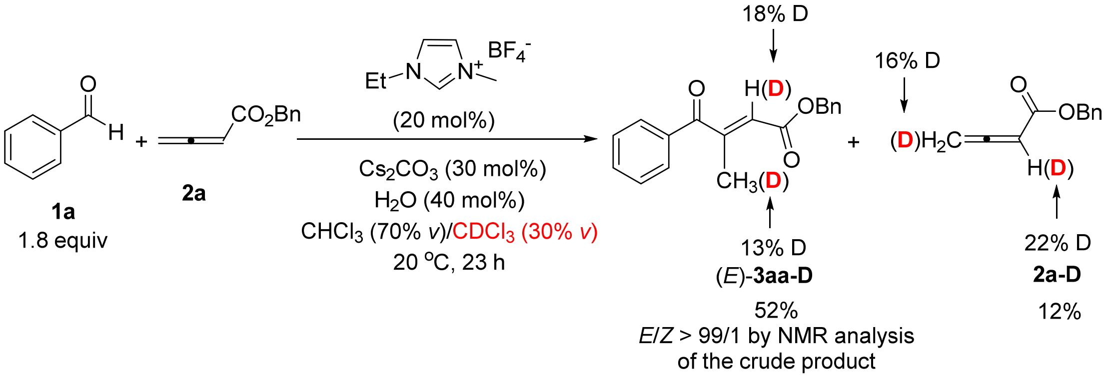
Following **Typical Procedure I**, the reaction of $Cs_2CO_3$ (0.0980 g, 0.3 mmol), 1-ethyl-3-methylimidazolium tetrafluoroborate (0.0398 g, 0.2 mmol)/anhydrous THF (5 mL), benzaldehyde **1a** (0.1910 g, 1.8 mmol)/anhydrous THF (2.5 mL), **2a** (0.1745 g, 1 mmol)/anhydrous THF (2.5 mL), and $D_2O$ (7.2 μL, d = 1.107 g/mL, 0.0079 g, 0.4 mmol) at 20 °C for 20 h afforded (*E*)-**3aa-D** (0.0756 g, 27%), **4aa-D** (0.0224 g, 8%), and (*Z*)-**3aa-D** (0.0616 g, 22%) (The ratio of *E*/*Z* was ~53/47 and ~10% of **4aa-D** was detected by NMR analysis of the crude product) (in the order of polarity in silica gel column) after chromatography on silica gel (eluent: petroleum ether (60-90 °C)/ethyl ether = 40/1 (1500 mL) to 30/1 (500 mL) to 10/1 (300 mL)).

(*E*)-**3aa-D**, the least polar isomer, liquid: $^1$H NMR (300 MHz, $CDCl_3$) δ 7.84-7.73 (m, 2H, ArH), 7.62-7.53 (m, 1H, ArH), 7.50-7.41 (m, 2H, ArH), 7.40-7.27 (m, 5H, ArH), 5.21 (s, 2H, $CH_2$); the following signals is discernible for (*E*)-**3aa**: δ 6.24-6.15 (m, 0.86H, =CH), 2.49-2.35 (m, 2.55H, $CH_3$).

**4aa-D**, the second polar isomer, liquid: $^1$H NMR (300 MHz, $CDCl_3$) δ 7.82-7.72 (m, 2H, ArH), 7.58-7.49 (m, 1H, ArH), 7.46-7.37 (m, 2H, ArH), 7.37-7.26 (m, 5H, ArH), 5.12 (s, 2H, $CH_2$); the following signals is discernible for **4aa**: δ 6.03-5.95 (m, 0.87H, one proton from =$CH_2$), 5.82-5.73 (m, 0.87H, one proton from =$CH_2$), 3.64-3.55 (m, 1.86H, $CH_2$).

(*Z*)-**3aa-D**, the most polar isomer, liquid: $^1$H NMR (300 MHz, $CDCl_3$) δ 7.92-7.85 (m, 2H, ArH), 7.63-7.53 (m, 1H, ArH), 7.49-7.38 (m, 2H, ArH), 7.35-7.23 (m, 3H, ArH), 7.19-7.09 (m, 2H, ArH), 4.96 (s, 2H, $CH_2$); the following signals is discernible for (*Z*)-**3aa**: δ 6.12-6.01 (m, 0.85H, =CH), 2.18-2.08 (m, 2.57H, $CH_3$).

**(2.5)** The reaction of **1a** and **2a** in a mixed anhydrous solvent of $CHCl_3$ (70% *v*)/$CDCl_3$ (30% *v*). (hx-16-144)

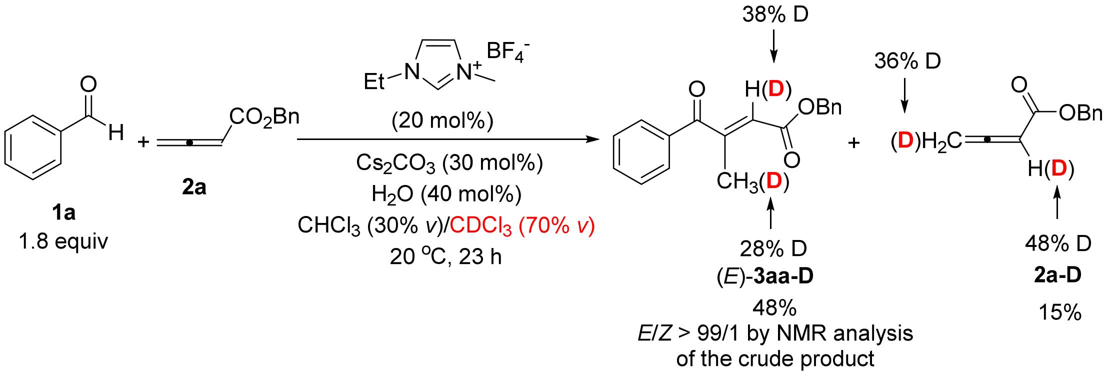


Following **Typical Procedure I**, the reaction of $Cs_2CO_3$ (0.0490 g, 0.15 mmol), 1-ethyl-3-methylimidazolium tetrafluoroborate (0.0197 g, 0.10 mmol), benzaldehyde **1a** (0.0961 g, 0.9 mmol), **2a** (0.0869 g, 0.5 mmol), and $H_2O$ (3.6 µL, d = 1.000 g/mL, 0.0036 g, 0.2 mmol) in a mixed anhydrous solvent of $CHCl_3$ (3.5 mL)/$CDCl_3$ (1.5 mL) at 20 °C for 23 h afforded **2a-D** (0.0101 g, 12%) and (*E*)-**3aa-D** (0.0735 g, 52%) (petroleum ether (60-90 °C)/ethyl acetate = 50/1 (500 mL)) (the ratio of *E*/*Z* was >99/1 by NMR analysis of the crude product) (in the order of polarity in silica gel column).

**2a-D**, liquid: $^1H$ NMR (300 MHz, $CDCl_3$) δ 7.43-7.28 (m, 5H, ArH), 5.20 (s, 2H, $CH_2$); the following signals is discernible for **2a**: δ 5.72-5.65 (m, 0.78H, =CH), 5.27-5.21 (m, 1.68H, =$CH_2$).

(*E*)-**3aa-D**, liquid: $^1H$ NMR (300 MHz, $CDCl_3$) δ 7.83-7.72 (m, 2H, ArH), 7.62-7.52 (m, 1H, ArH), 7.49-7.41 (m, 2H, ArH), 7.40-7.27 (m, 5H, ArH), 5.21 (s, 2H, $CH_2$); the following signals is discernible for (*E*)-**3aa**: δ 6.25-6.15 (m, 0.82H, =CH), 2.49-2.36 (m, 2.62H, $CH_3$).

**(2.6)** The reaction of **1a** and **2a** in a mixed anhydrous solvent of $CHCl_3$ (30% *v*)/$CDCl_3$ (70% *v*). (hx-16-145)

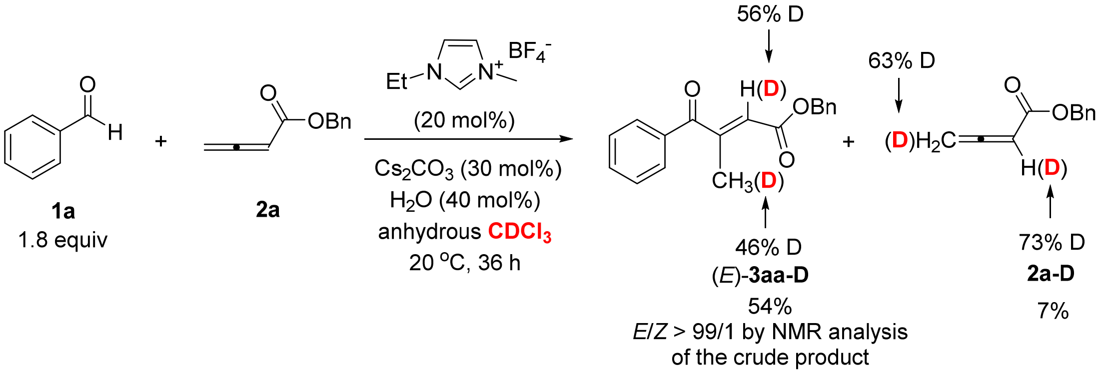


Following **Typical Procedure I**, the reaction of $Cs_2CO_3$ (0.0492 g, 0.15 mmol), 1-ethyl-3-methylimidazolium tetrafluoroborate (0.0196 g, 0.10 mmol), benzaldehyde **1a** (0.0959 g, 0.9 mmol), **2a** (0.0868 g, 0.5 mmol), and $H_2O$ (3.6 μL, d = 1.000 g/mL, 0.0036 g, 0.2 mmol) in a mixed anhydrous solvent of $CHCl_3$ (1.5 mL)/$CDCl_3$ (3.5 mL) at 20 $^{o}$C for 23 h afforded **2a-D** (0.0134 g, 15%) and (*E*)-**3aa-D** (0.0680 g, 48%) (petroleum ether (60-90 $^{o}$C)/ethyl acetate = 50/1 (500 mL)) (the ratio of *E*/*Z* was >99/1 by NMR analysis of the crude product) (in the order of polarity in silica gel column).

**2a-D**, liquid: $^1$H NMR (300 MHz, $CDCl_3$) δ 7.42-7.28 (m, 5H, ArH), 5.20 (s, 2H, $CH_2$); the following signals is discernible for **2a**: δ 5.72-5.65 (m, 0.52H, =CH), 5.27-5.21 (m, 1.29H, =$CH_2$).

(*E*)-**3aa-D**, liquid: $^1$H NMR (300 MHz, $CDCl_3$) δ 7.83-7.72 (m, 2H, ArH), 7.62-7.51 (m, 1H, ArH), 7.49-7.41 (m, 2H, ArH), 7.40-7.27 (m, 5H, ArH), 5.21 (s, 2H, $CH_2$); the following signals is discernible for (*E*)-**3aa**: δ 6.23-6.16 (m, 0.62H, =CH), 2.48-2.36 (m, 2.16H, $CH_3$).

**(2.7)** The reaction of **1a** and **2a** in anhydrous $CDCl_3$. (mdk-11-089)



Following **Typical Procedure I**, the reaction of $Cs_2CO_3$ (0.0390 g, 0.12 mmol), 1-ethyl-3-methylimidazolium tetrafluoroborate (0.0164 g, 0.08 mmol)/anhydrous

$CDCl_3$ (2 mL), benzaldehyde **1a** (0.0759 g, 0.72 mmol)/anhydrous $CDCl_3$ (1 mL), **2a** (0.0698 g, 0.4 mmol)/anhydrous $CDCl_3$ (1 mL), and $H_2O$ (2.9 μL, d = 1.000 g/mL, 0.0029 g, 0.16 mmol) at 20 °C for 36 h afforded **2a-D** (0.0048 g, 7%) and (*E*)-**3aa-D** (0.0611 g, 54%) (petroleum ether/ethyl acetate = 50/1 (400 mL × 2)) (the ratio of *E*/*Z* was >99/1 by NMR analysis of the crude product) (in the order of polarity in silica gel column).

**2a-D**, liquid: $^1$H NMR (300 MHz, $CDCl_3$) δ 7.43-7.28 (m, 5H, ArH), 5.20 (s, 2H, $CH_2$); the following signals is discernible for **2a**: δ 5.72-5.67 (m, 0.27H, =CH), 5.27-5.21 (m, 0.74H, $=CH_2$); IR (neat) ν ($cm^{-1}$) 3090, 3066, 3033, 2955, 2892, 2308, 2263, 2215, 1927, 1722, 1715, 1587, 1498, 1456, 1386, 1379, 1356, 1318, 1294, 1258, 1216, 1173, 1081, 1016; MS (ESI) *m/z* (%) 200 ($[M(D_3) + Na]^+$), 199 ($[M(D_2) + Na]^+$), 198 ($[M(D) + Na]^+$), 197 ($[M + Na]^+$), 178 ($[M(D_3) + H]^+$), 177 ($[M(D_2) + H]^+$), 176 ($[M(D) + H]^+$), 175 ($[M + H]^+$); HRMS calcd. for $C_{11}H_8D_3O_2$ ($[M(D)_3 + H]^+$): 178.0942, found: 178.0935, $C_{11}H_9D_2O2$ ($[M(D)_2 + H]^+$): 177.0879, found: 177.0876, $C_{11}H_{10}DO_2$ ($[M(D) + H]^+$): 176.0816, found: 176.0811, $C_{11}H_{11}O_2$ ($[M + H]^+$): 175.0754, found: 175.0754.

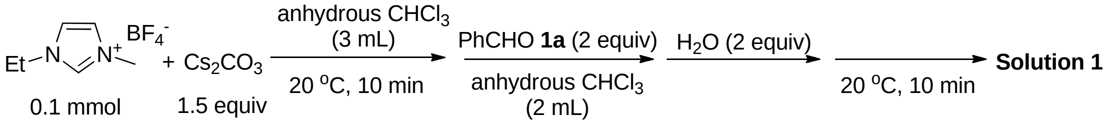
(*E*)-**3aa-D**, liquid: $^1$H NMR (300 MHz, $CDCl_3$) δ 7.82-7.71 (m, 2H, ArH), 7.61-7.53 (m, 1H, ArH), 7.49-7.40 (m, 2H, ArH), 7.40-7.27 (m, 5H, ArH), 5.21 (s, 2H, $CH_2$); the following signals is discernible for (*E*)-**3aa**: δ 6.23-6.16 (m, 0.44H, =CH), 2.47-2.36 (m, 1.61H, $CH_3$); IR (neat) ν ($cm^{-1}$) 3064, 3034, 2954, 1722, 1662, 1597, 1580, 1498, 1448, 1377, 1352, 1318, 1265, 1231, 1180, 1025, 1002; MS (ESI) *m/z* (%) 307 ($[M(D_4) + Na]^+$), 306 ($[M(D_3) + Na]^+$), 305 ($[M(D_2) + Na]^+$), 304 ($[M(D) + Na]^+$), 303 ([M + Na]$^+$), 302 ([M(D$_4$) + NH$_4$]$^+$), 301 ([M(D$_3$) + NH$_4$]$^+$), 300 ([M(D$_2$) + NH$_4$]$^+$), 299 ([M(D) + NH$_4$]$^+$), 298 ([M + NH$_4$]$^+$), 285 ([M(D$_4$) + H]$^+$), 284 ([M(D$_3$) + H]$^+$), 283 ([M(D$_2$) + H]$^+$), 282 ([M(D) + H]$^+$), 281 ([M + H]$^+$); HRMS calcd. for $C_{18}H_{13}D_4O_3$ ([M(D)$_4$ + H]$^+$): 285.1423, found: 285.1418, $C_{18}H_{14}D_3O_3$ ([M(D)$_3$ + H]$^+$): 284.1361, found: 284.1361, $C_{18}H_{15}D_2O_3$ ([M(D)$_2$ + H]$^+$): 283.1298, found: 283.1294, $C_{18}H_{16}DO_3$ ([M(D) + H]$^+$): 282.1235, found: 282.1237, $C_{18}H_{17}O_3$ ([M + H]$^+$): 281.1172, found: 281.1175.

### (3) SAESI-MS experiments

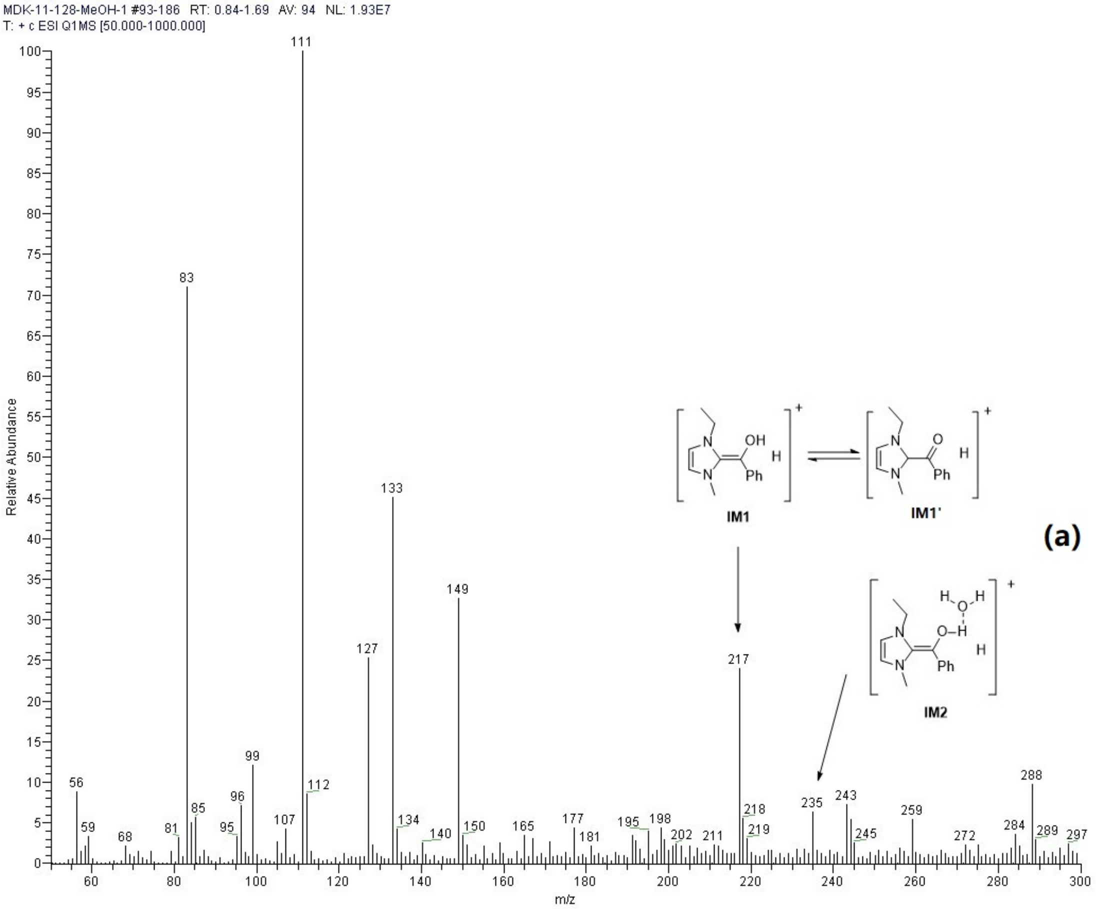
SAESI-MS spectra were recorded on a Finnigan TSQ (Thermo Finnigan, Quantum Access TM) triple-quadrupole mass spectrometer equipped with a home-made SAESI ion source in positive mode. The basic SAESI conditions were: vacuum, $2.8\times10^{-6}$ torr; spray voltage, 3000 V; capillary temperature, 275°C; sheath gas pressure of two sprayers, 2 arb. units; the collision energy of CID, 25 eV. Data acquisition and analysis were done with the Xcalibur (version 2.0, Thermoquest Finnigan) software package.

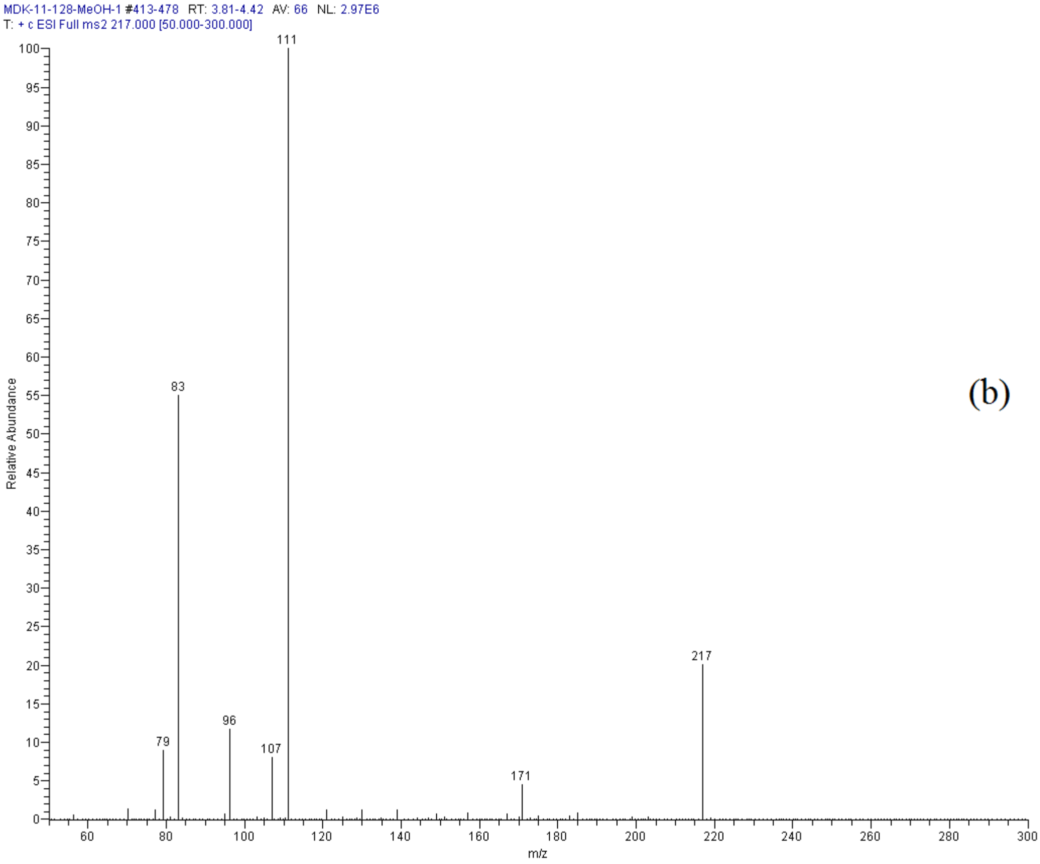
The reaction solutions were injected by a 500-μL air-tight syringe with a speed at 5 μL/min to SAESI-MS. The assisted solvent of MeOH or anhydrous acetonitrile was injected by another 500-μL air-tight syringe with a speed at 5 μL/min to SAESI-MS.

### (3.1) SAESI-MS experiments in anhydrous CHCl$_3$ after 10 min (mdk-11-128)



**Typical Procedure II**: To a dry Schlenk tube was added $Cs_2CO_3$ (0.0490 g, 0.15 mmol) in a glove box. Then 1-ethyl-3-methylimidazolium tetrafluoroborate (0.0203 g, 0.1 mmol) and anhydrous $CHCl_3$ (3 mL) were added sequentially under Ar atmosphere. The resulting mixture was stirred at 20 $^oC$. After 10 min, **1a** (20.3 μL, d = 1.044 g/mL, 0.0212 g, 0.2 mmol), anhydrous $CHCl_3$ (2 mL), and $H_2O$ (3.6 μL, d = 1.000 g/mL, 0.0036 g, 0.2 mmol) were added sequentially. The resulting mixture was stirred at 20 $^oC$. After 10 min, the reaction **solution 1** was submitted to SAESI-MS analysis.




MDK-11-128-MeOH-1 #413-478 RT: 3.81-4.42 AV: 66 NL: 2.97E6
T: + c ESI Full ms2 217.000 [50.000-300.000]
Relative Abundance
m/z
(b)
111
83
79
96
107
171
217
0
5
10
15
20
25
30
35
40
45
50
55
60
65
70
75
80
85
90
95
100
60
80
100
120
140
160
180
200
220
240
260
280
300

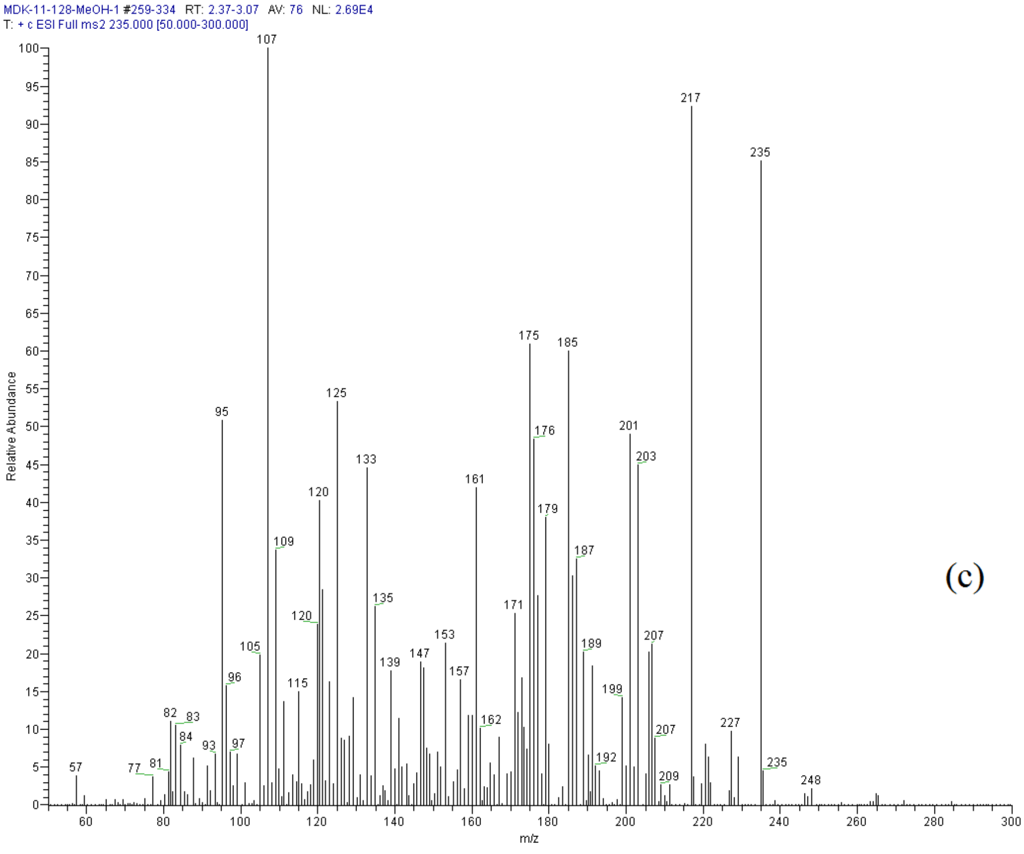
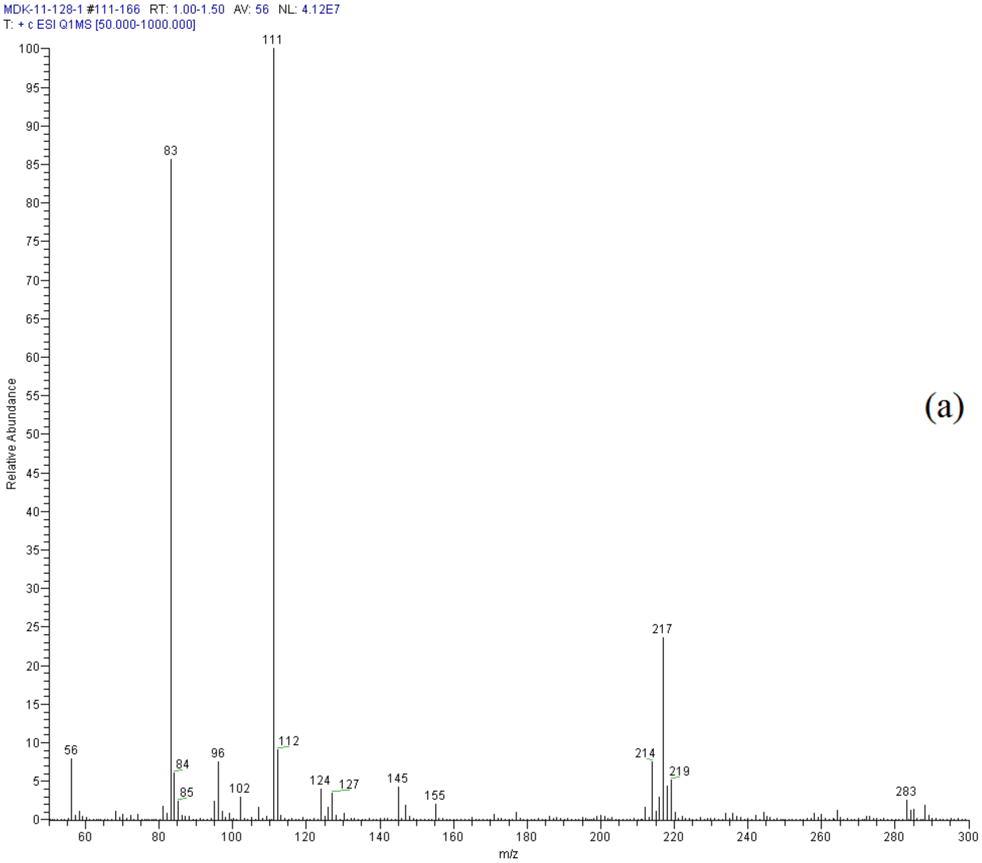

MDK-11-128-MeOH-1 #259-334 RT: 2.37-3.07 AV: 76 NL: 2.69E4
T: + c ESI Full ms2 235.000 [50.000-300.000]
Relative Abundance
m/z
(c)
107
217
235
175
185
125
95
176
201
203
133
161
120
179
109
187
135
171
120
153
105
189
139
147
157
207
96
115
199
82
83
162
227
84
93
97
207
192
81
77
57
235
209
248
0
5
10
15
20
25
30
35
40
45
50
55
60
65
70
75
80
85
90
95
100
60
80
100
120
140
160
180
200
220
240
260
280
300

Figure S1. (a) SAESI-MS spectrum of the reaction **solution 1** using MeOH as the assisted solvent. (b) The SAESI-MS/MS spectra of the ion at *m/z* 217. (c) The SAESI-MS/MS spectra of the ion at *m/z* 235.

**Table S2. Signal intensities of the target ions in Figure S1**

| *m/z* | Intensity |
|---|---|
| 217 | 4620347.8 |
| 218 | 1059949.9 |
| 235 | 1220695.5 |



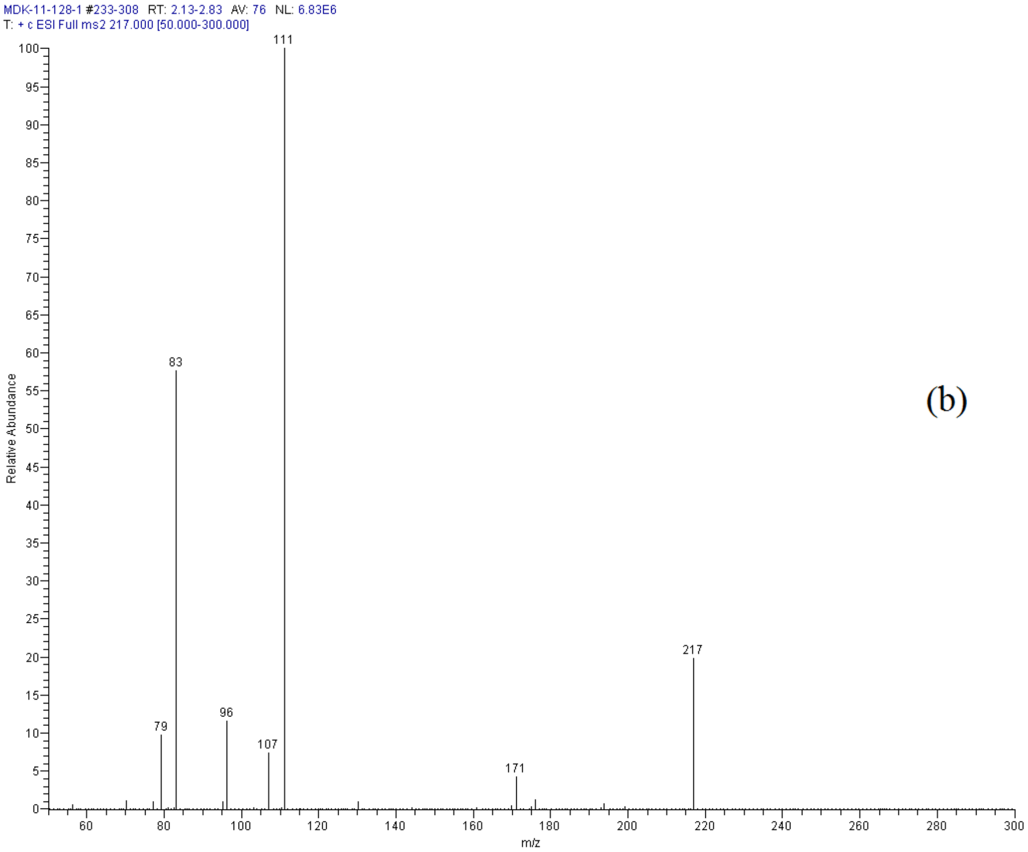
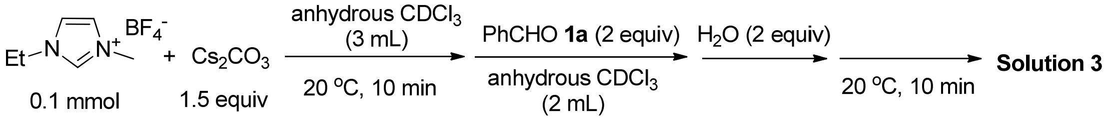


Figure S2. (a) SAESI-MS spectrum of the reaction **solution 1** using anhydrous acetonitrile as the assisted solvent. (b) The SAESI-MS/MS spectra of the ion at *m/z* 217.

**Table S3. Signal intensities of the target ions in Figure S2**

| *m/z* | Intensity |
|---|---|
| 217 | 9740060.5 |
| 218 | 1782792.5 |
| 219 | 2152750.9 |

## (3.2) SAESI-MS experiments in $CDCl_3$ after 10 min (mdk-11-121)



Following **Typical Procedure II**, the reaction of $Cs_2CO_3$ (0.0486 g, 0.15 mmol), 1-ethyl-3-methylimidazolium tetrafluoroborate (0.0202 g, 0.1 mmol)/anhydrous $CDCl_3$ (3 mL), **1a** (0.0213 g, 0.2 mmol)/anhydrous $CDCl_3$ (2 mL), and $H_2O$ (3.6 µL, d = 1.000 g/mL, 0.0036 g, 0.2 mmol) at 20 °C for 10 min afforded **solution 3**. Then the reaction **solution 3** was submitted to SAESI-MS analysis.

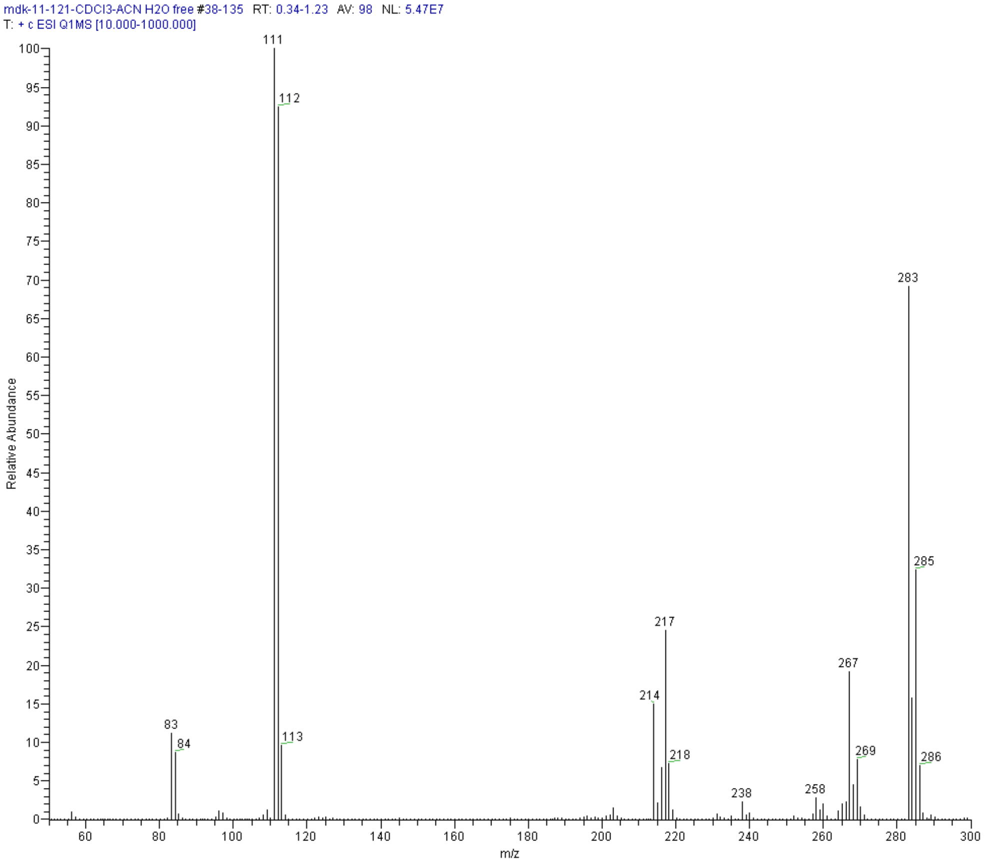
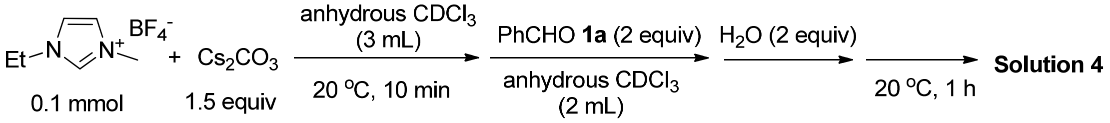


Figure S3. (a) SAESI-MS spectrum of the reaction **solution 3** using anhydrous acetonitrile as the assisted solvent.

**Table S4. Signal intensities of the target ions in Figure S3**

| *m/z* | Intensity |
|---|---|
| 217 | 13404158.6 |
| 218 | 3948675.6 |

## (3.3) SAESI-MS experiments in $CDCl_3$ after 1 h (mdk-11-123)



Following **Typical Procedure II**, the reaction of $Cs_2CO_3$ (0.0490 g, 0.15 mmol), 1-ethyl-3-methylimidazolium tetrafluoroborate (0.0202 g, 0.1 mmol)/anhydrous

$CDCl_3$ (3 mL), **1a** (0.0210 g, 0.2 mmol)/anhydrous $CDCl_3$ (2 mL), and $H_2O$ (3.6 μL, d = 1.000 g/mL, 0.0036 g, 0.2 mmol) at 20 °C for 1 h afforded **solution 4**. Then the reaction **solution 4** was submitted to SAESI-MS analysis.

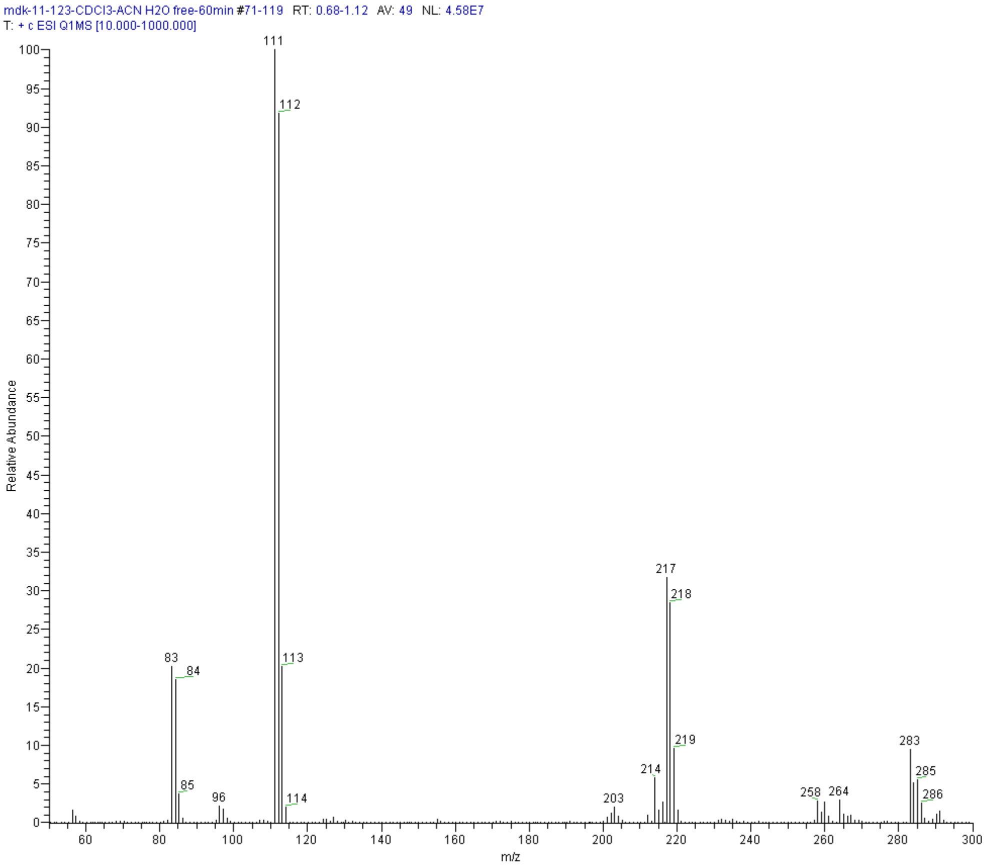
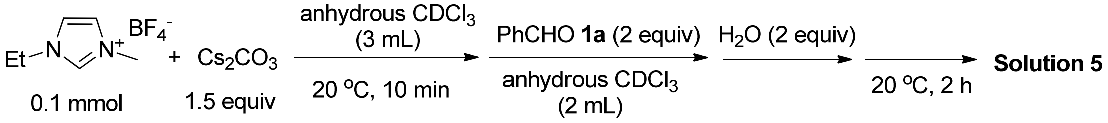


Figure S4. SAESI-MS spectrum of the reaction **solution 4** using anhydrous acetonitrile as the assisted solvent.

**Table S5. Signal intensities of the target ions in Figure S4**

| *m/z* | Intensity |
|---|---|
| 217 | 14555928.5 |
| 218 | 13012113.7 |
| 219 | 4381850.3 |

## (3.4) SAESI-MS experiments in $CDCl_3$ after 2 h (mdk-11-124)



Following **Typical Procedure II**, the reaction of $Cs_2CO_3$ (0.0485 g, 0.15 mmol), 1-ethyl-3-methylimidazolium tetrafluoroborate (0.0203 g, 0.1 mmol)/anhydrous $CDCl_3$ (3 mL), **1a** (20.3 μL, d = 1.044 g/mL, 0.0212 g, 0.2 mmol)/anhydrous $CDCl_3$ (2 mL), and $H_2O$ (3.6 μL, d = 1.000 g/mL, 0.0036 g, 0.2 mmol) at 20 °C for 2 h afforded **solution 5**. Then the reaction **solution 5** was submitted to SAESI-MS analysis.

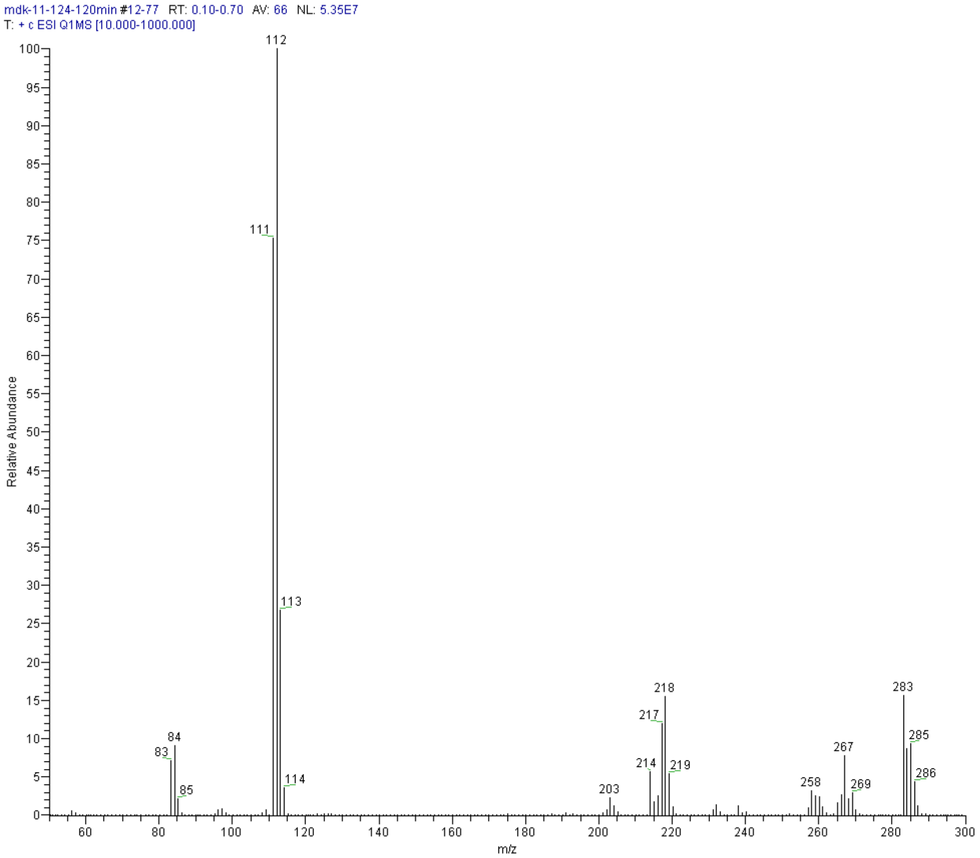
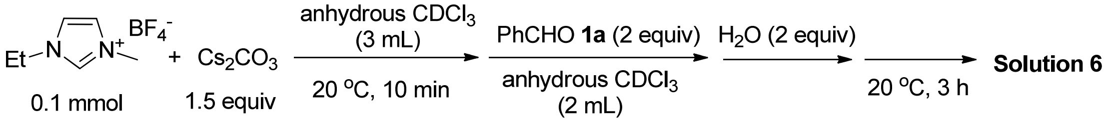


Figure S5. SAESI-MS spectrum of the reaction **solution 5** using anhydrous acetonitrile as the assisted solvent.

**Table S6. Signal intensities of the target ions in Figure S5**

| *m/z* | Intensity |
|---|---|
| 217 | 6390120.8 |
| 218 | 8300253.3 |
| 219 | 2914590.8 |

### (3.5) SAESI-MS experiments in $CDCl_3$ after 3 h (mdk-11-125)



Following **Typical Procedure II**, the reaction of $Cs_2CO_3$ (0.0492 g, 0.15 mmol), 1-ethyl-3-methylimidazolium tetrafluoroborate (0.0203 g, 0.1 mmol)/anhydrous $CDCl_3$ (3 mL), **1a** (20.3 μL, d = 1.044 g/mL, 0.0212 g, 0.2 mmol)/anhydrous $CDCl_3$ (2 mL), and $H_2O$ (3.6 μL, d = 1.000 g/mL, 0.0036 g, 0.2 mmol) at 20 °C for 3 h afforded **solution 6**. Then the reaction **solution 6** was submitted to SAESI-MS analysis.

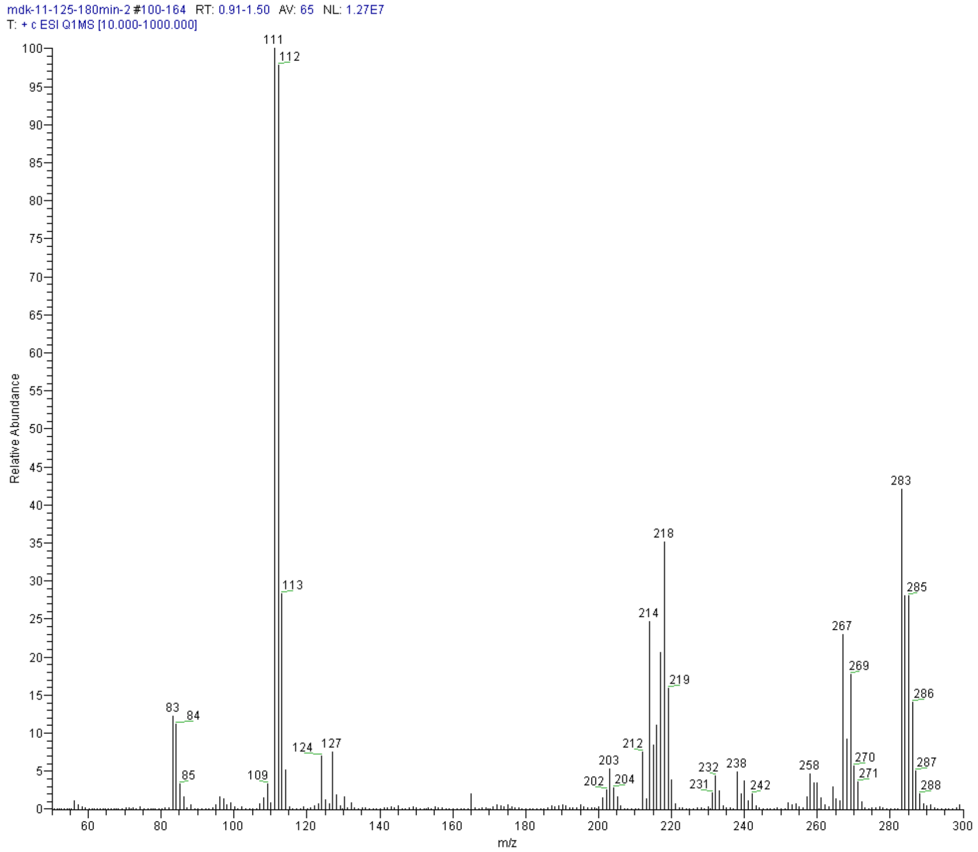
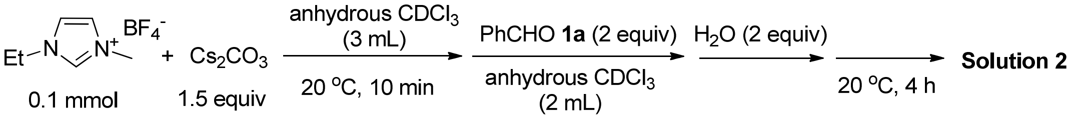


Figure S6. SAESI-MS spectrum of the reaction **solution 6** using anhydrous acetonitrile as the assisted solvent.

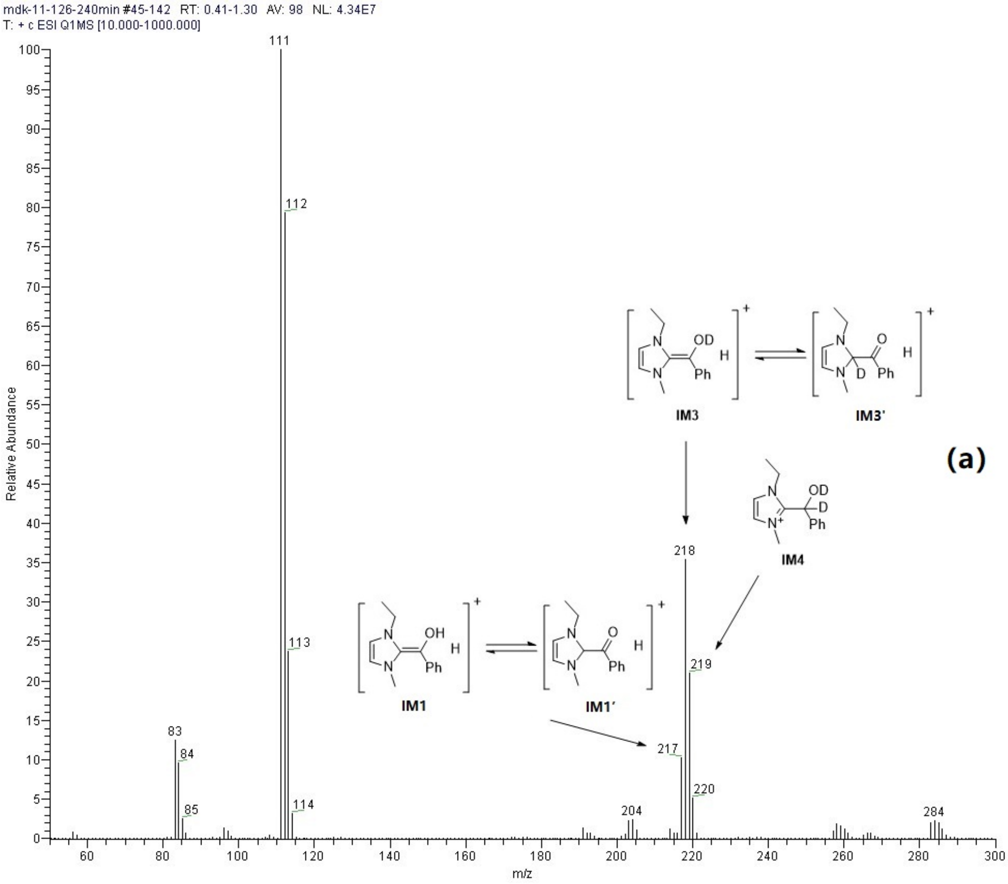
**Table S7. Signal intensities of the target ions in Figure S6**

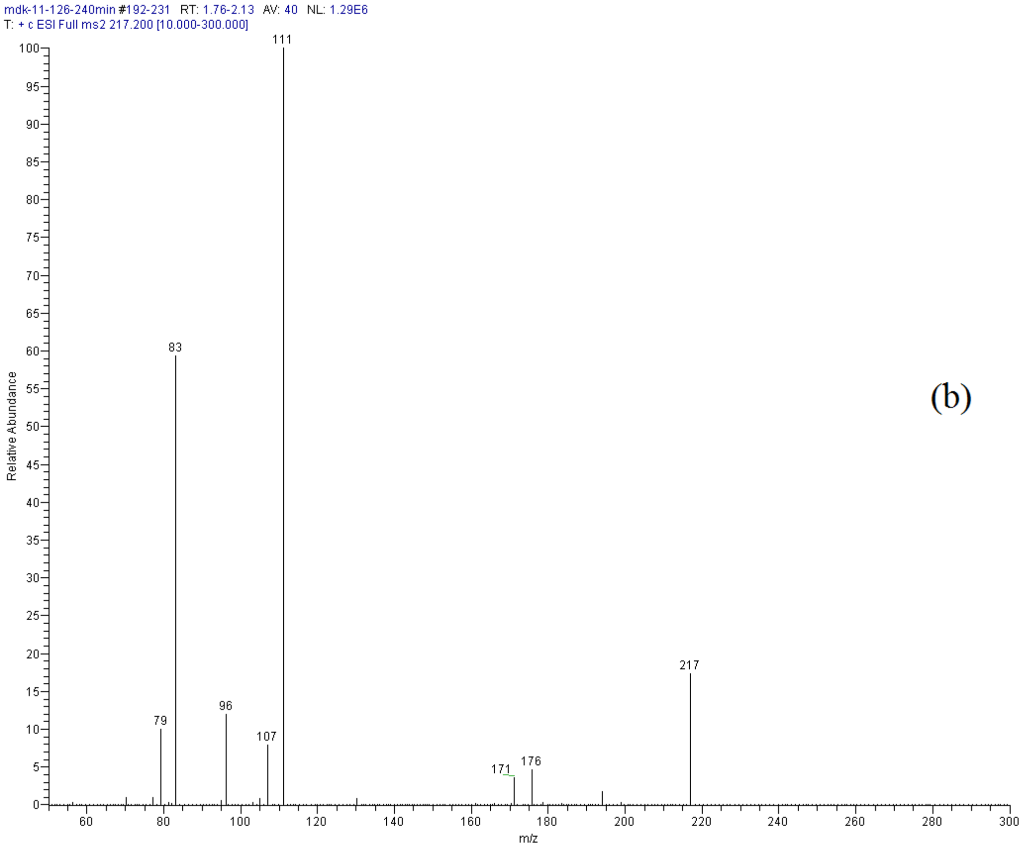
| *m/z* | Intensity |
|---|---|
| 217 | 2627898.1 |
| 218 | 4468922.0 |
| 219 | 2015608.7 |

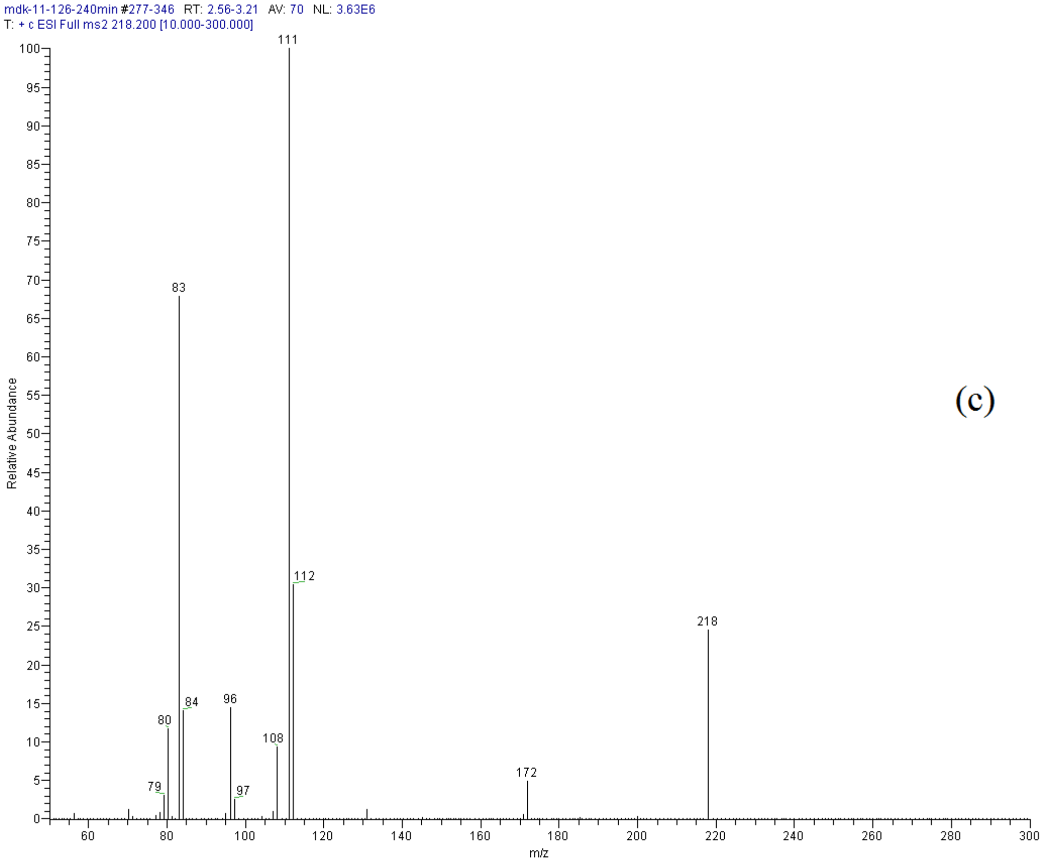
## (3.6) SAESI-MS experiments in $CDCl_3$ after 4 h (mdk-11-126)



Following **Typical Procedure II**, the reaction of $Cs_2CO_3$ (0.0491 g, 0.15 mmol), 1-ethyl-3-methylimidazolium tetrafluoroborate (0.0203 g, 0.1 mmol)/anhydrous $CDCl_3$ (3 mL), **1a** (20.3 μL, d = 1.044 g/mL, 0.0212 g, 0.2 mmol)/anhydrous $CDCl_3$ (2 mL), and $H_2O$ (3.6 μL, d = 1.000 g/mL, 0.0036 g, 0.2 mmol) at 20 °C for 4 h afforded **solution 2**. Then the reaction **solution 2** was submitted to SAESI-MS analysis.


mdk-11-126-240min #45-142 RT: 0.41-1.30 AV: 98 NL: 4.34E7
T: + c ESI Q1MS [10.000-1000.000]
Relative Abundance
m/z
111
112
113
114
83
84
85
204
217
218
219
220
284
IM3
IM3'
IM4
IM1
IM1′
OD
D
H
Ph
OH
O
N
(a)


mdk-11-126-240min #192-231 RT: 1.76-2.13 AV: 40 NL: 1.29E6
T: + c ESI Full ms2 217.200 [10.000-300.000]
Relative Abundance
m/z
111
83
79
96
107
171
176
217
(b)


mdk-11-126-240min #277-346 RT: 2.56-3.21 AV: 70 NL: 3.63E6
T: + c ESI Full ms2 218.200 [10.000-300.000]
111
83
112
218
84
80
96
108
79
97
172
Relative Abundance
m/z
(c)

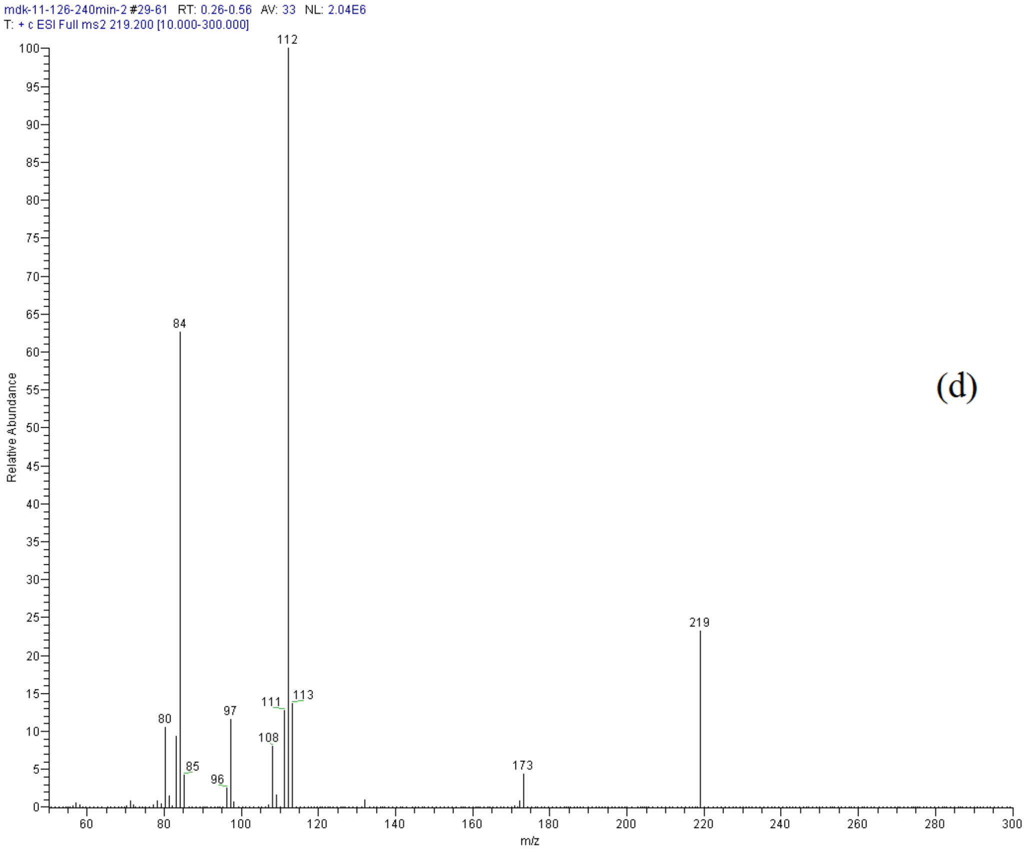
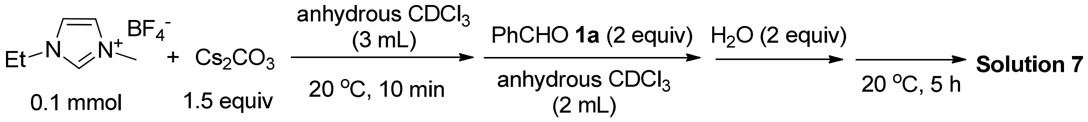

mdk-11-126-240min-2 #29-61 RT: 0.26-0.56 AV: 33 NL: 2.04E6
T: + c ESI Full ms2 219.200 [10.000-300.000]
112
84
219
80
97
111
113
108
85
96
173
Relative Abundance
m/z
(d)

Figure S7. (a) SAESI-MS spectrum of the reaction **solution 2** using anhydrous acetonitrile as the assisted solvent. (b) The SAESI-MS/MS spectra of the ion at *m/z* 217. (c) The SAESI-MS/MS spectra of the ion at *m/z* 218. (d) The SAESI-MS/MS spectra of the ion at *m/z* 219.

**Table S8. Signal intensities of the target ions in Figure S7**

| *m/z* | Intensity |
|---|---|
| 217 | 4462860.3 |
| 218 | 15348270.8 |
| 219 | 9134749.2 |

### (3.7) SAESI-MS experiments in $CDCl_3$ after 5 h (mdk-11-127)



Following **Typical Procedure II**, the reaction of $Cs_2CO_3$ (0.0485 g, 0.15 mmol), 1-ethyl-3-methylimidazolium tetrafluoroborate (0.0202 g, 0.1 mmol)/anhydrous $CDCl_3$ (3 mL), **1a** (20.3 μL, d = 1.044 g/mL, 0.0212 g, 0.2 mmol)/anhydrous $CDCl_3$ (2 mL), and $H_2O$ (3.6 μL, d = 1.000 g/mL, 0.0036 g, 0.2 mmol) at 20 °C for 5 h afforded **solution 7**. Then the reaction **solution 7** was submitted to SAESI-MS analysis.

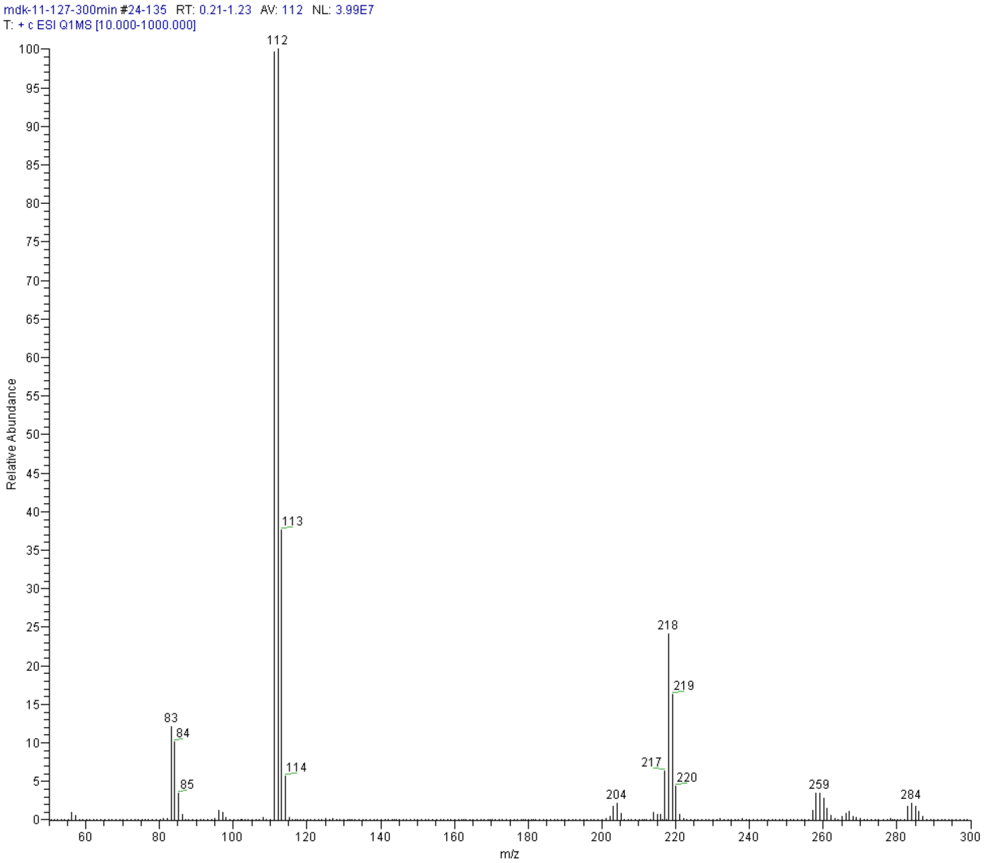


Figure S8. SAESI-MS spectrum of the reaction **solution 7** using anhydrous acetonitrile as the assisted solvent.

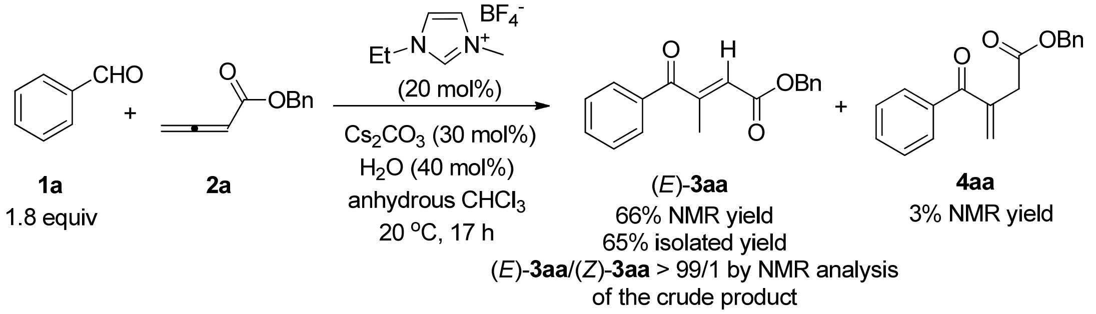
**Table S9. Signal intensities of the target ions in Figure S8**

| *m/z* | Intensity |
|---|---|
| 217 | 2550729.0 |
| 218 | 9619641.8 |
| 219 | 6516477.7 |

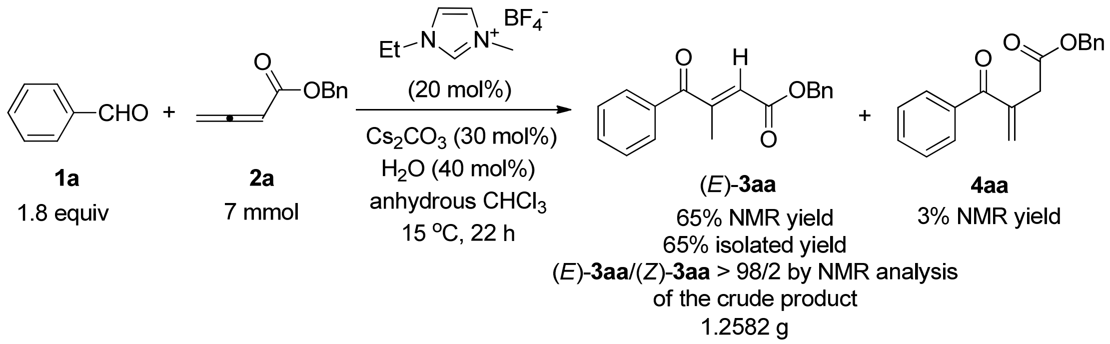
## 3. Highly stereoselective preparation of (*E*)-4-oxo-2-butenoates (*E*)-3aa-(*E*)-3la

The following compounds were prepared according to **Typical Procedure I**.

### (1) Benzyl 3-methyl-4-oxo-4-phenylbut-2(*E*)-enoate ((*E*)-3aa) (mdk-10-189-1, mdk-11-082)

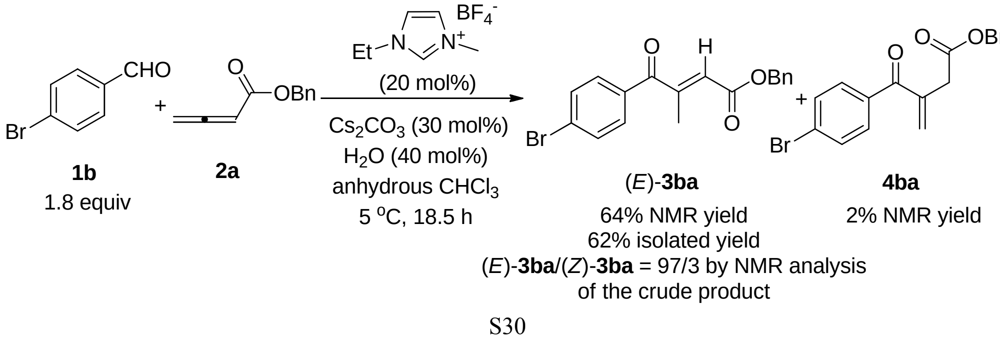


Following **Typical Procedure I**, the reaction of $Cs_2CO_3$ (0.0976 g, 0.3 mmol), 1-ethyl-3-methylimidazolium tetrafluoroborate (0.0404 g, 0.2 mmol)/anhydrous $CHCl_3$ (5 mL), **1a** (0.1917 g, 1.8 mmol)/anhydrous $CHCl_3$ (2.5 mL), **2a** (0.1741 g, 1 mmol)/anhydrous $CHCl_3$ (2.5 mL), and $H_2O$ (7.2 μL, d = 1.000 g/mL, 0.0072 g, 0.4 mmol) at 20 °C for 17 h afforded (*E*)-**3aa** (0.1812 g, 65%) (petroleum ether/ethyl acetate = 40/1 (400 mL) to 30/1 (400 mL) to 20/1 (300 mL)) (the ratio of (*E*)-**3aa**/(*Z*)-**3aa** was > 99/1 and 3% of **4aa** was formed by NMR analysis of the crude product) as a liquid: $^1$H NMR (300 MHz, $CDCl_3$) δ 7.81-7.74 (m, 2H, ArH), 7.61-7.54 (m, 1H, ArH), 7.49-7.41 (m, 2H, ArH), 7.40-7.28 (m, 5H, ArH), 6.20 (q, *J* = 1.4 Hz, 1H, =CH), 5.21 (s, 2H, $CH_2$), 2.44 (d, *J* = 1.5 Hz, 3H, $CH_3$); $^{13}$C NMR (75 MHz, $CDCl_3$) δ 197.8, 165.5, 152.5, 135.7, 135.4, 133.1, 129.7, 128.55, 128.49, 128.3, 125.0, 66.4, 15.5.



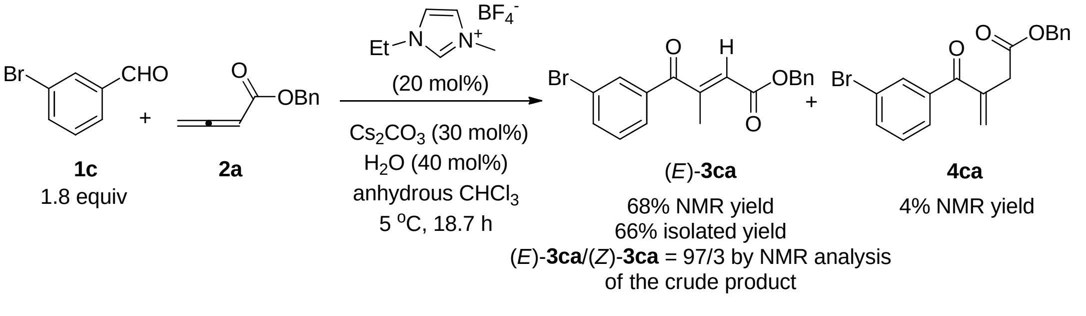
**Gram scale reaction:** Following **Typical Procedure I**, the reaction of $Cs_2CO_3$ (0.6849 g, 2.1 mmol), 1-ethyl-3-methylimidazolium tetrafluoroborate (0.2826 g, 1.4 mmol)/anhydrous $CHCl_3$ (35 mL), benzaldehyde **1a** (1.3373 g, 12.6 mmol)/anhydrous $CHCl_3$ (17.5 mL), **2a** (1.2193 g, 7 mmol)/anhydrous $CHCl_3$ (17.5 mL), and $H_2O$ (50.5 μL, d = 1.000 g/mL, 0.0505 g, 2.8 mmol) at 15 °C for 22 h afforded (*E*)-**3aa** (1.2582 g, 64%) (petroleum ether/ethyl acetate = 40/1 (400 mL × 3) to 30/1 (420 mL)) (the ratio of (*E*)-**3aa**/(*Z*)-**3aa** was >99/1 and 3% of **4aa** was formed by NMR analysis of the crude product) as a liquid: $^1$H NMR (300 MHz, $CDCl_3$) δ 7.81-7.74 (m, 2H, ArH), 7.61-7.53 (m, 1H, ArH), 7.49-7.41 (m, 2H, ArH), 7.40-7.29 (m, 5H, ArH), 6.20 (q, *J* = 1.5 Hz, 1H, =CH), 5.21 (s, 2H, $CH_2$), 2.44 (d, *J* = 1.5 Hz, 3H, $CH_3$); $^{13}$C NMR (75 MHz, $CDCl_3$) δ 197.8, 165.5, 152.5, 135.7, 135.5, 133.1, 129.7, 128.6, 128.5, 128.4, 125.0, 66.5, 15.6.

### (2) Benzyl 4-(4-bromophenyl)-3-methyl-4-oxobut-2(*E*)-enoate ((*E*)-3ba) (mdk-11-006)



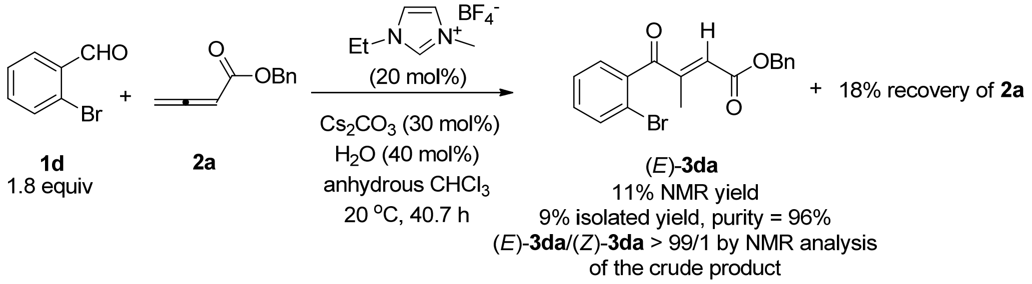
The reaction of $Cs_2CO_3$ (0.0982 g, 0.3 mmol), 1-ethyl-3-methylimidazolium tetrafluoroborate (0.0403 g, 0.2 mmol)/anhydrous $CHCl_3$ (5 mL), 4-bromobenzaldehyde **1b** (0.3399 g, 1.8 mmol)/anhydrous $CHCl_3$ (2.5 mL), **2a** (0.1738 g, 1 mmol)/anhydrous $CHCl_3$ (2.5 mL), and $H_2O$ (7.2 μL, d = 1.000 g/mL, 0.0072 g, 0.4 mmol) at 5 °C for 18.5 h afforded (*E*)-**3ba** (0.2227 g, 62%) (petroleum ether/ethyl acetate = 50/1 (400 mL) to 20/1 (300 mL)) (the ratio of (*E*)-**3ba**/(*Z*)-**3ba** was 97/3 and 2% of **4ba** was formed by NMR analysis of the crude product) as a liquid: $^1$H NMR (300 MHz, $CDCl_3$) δ 7.69-7.55 (m, 4H, ArH), 7.42-7.28 (m, 5H, ArH), 6.17 (q, *J* = 1.6 Hz, 1H, =CH), 5.21 (s, 2H, $CH_2$), 2.42 (d, *J* = 1.5 Hz, 3H, $CH_3$); $^{13}$C NMR (75 MHz, $CDCl_3$) δ 196.6, 165.3, 151.9, 135.3, 134.4, 131.8, 131.1, 128.5, 128.4, 128.3, 125.3, 66.5, 15.4; IR (neat) ν (cm$^{-1}$) 3065, 3033, 2954, 1723, 1667, 1584, 1567, 1497, 1481, 1455, 1396, 1384, 1351, 1304, 1263, 1190, 1137, 1110, 1069, 1028, 1010; MS (70 ev, EI) m/z (%) 360 ($M^+$($^{81}$Br), 0.61), 358($M^+$($^{79}$Br), 0.60), 91 (100); Elemental analysis calcd (%) for $C_{18}H_{15}BrO_3$: C, 60.18, H, 4.21; Found: C, 60.13; H, 4.31.

### (3) Benzyl 4-(3-bromophenyl)-3-methyl-4-oxobut-2(*E*)-enoate ((*E*)-3ca) (mdk-11-035-1)



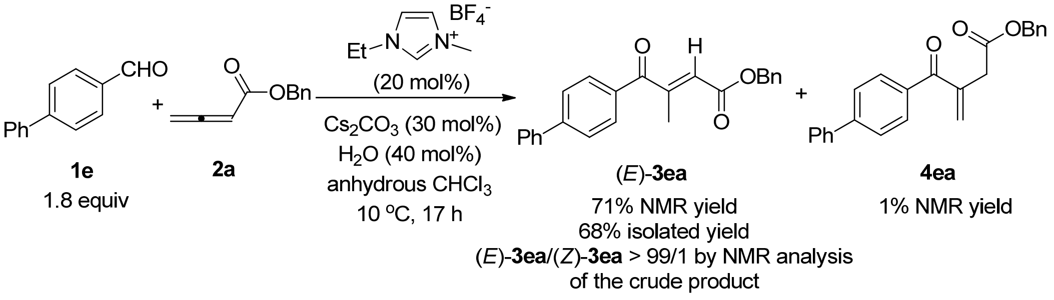
The reaction of $Cs_2CO_3$ (0.0978 g, 0.3 mmol), 1-ethyl-3-methylimidazolium tetrafluoroborate (0.0399 g, 0.2 mmol)/anhydrous $CHCl_3$ (5 mL), 3-bromobenzaldehyde **1c** (0.3334 g, 1.8 mmol)/anhydrous $CHCl_3$ (2.5 mL), **2a** (0.1735 g, 1 mmol)/anhydrous $CHCl_3$ (2.5 mL), and $H_2O$ (7.2 μL, d = 1.000 g/mL, 0.0072 g, 0.4 mmol) at 5 °C for 18.7 h afforded (*E*)-**3ca** (0.2368 g, 66%) (petroleum ether/ethyl acetate = 40/1 (400 mL) to 20/1 (420 mL)) (the ratio of (*E*)-**3ca**/(*Z*)-**3ca** was 97/3 and 4% of **4ca** was formed by NMR analysis of the crude product) as a liquid: $^1H$ NMR (300 MHz, $CDCl_3$) δ 7.90 (t, *J* = 1.8 Hz, 1H, ArH), 7.73-7.63 (m, 2H, ArH), 7.43-7.28 (m, 6H, ArH), 6.20 (q, *J* = 1.5 Hz, 1H, =CH), 5.21 (s, 2H, $CH_2$), 2.42 (d, *J* = 1.5 Hz, 3H, $CH_3$); $^{13}C$ NMR (75 MHz, $CDCl_3$) δ 196.3, 165.3, 151.7, 137.7, 135.9, 135.3, 132.3, 130.0, 128.6, 128.4, 128.1, 125.8, 122.8, 66.6, 15.4; IR (neat) ν ($cm^{-1}$) 3089, 3065, 3033, 2954, 2889, 1723, 1667, 1639, 1587, 1565, 1498, 1455, 1418, 1382, 1352, 1256, 1190, 1139, 1069, 1029; MS (70 ev, EI) m/z (%) 360 ($M^+$($^{81}$Br), 0.69), 358 ($M^+$($^{79}$Br), 0.70), 91 (100); Elemental analysis calcd (%) for $C_{18}H_{15}BrO_3$: C, 60.18, H, 4.21; Found: C, 60.08; H, 4.37.

### (4) Benzyl 4-(2-bromophenyl)-3-methyl-4-oxobut-2(*E*)-enoate ((*E*)-3da) (mdk-11-036)



The reaction of $Cs_2CO_3$ (0.0975 g, 0.3 mmol), 1-ethyl-3-methylimidazolium tetrafluoroborate (0.0406 g, 0.2 mmol)/anhydrous $CHCl_3$ (5 mL), 2-bromobenzaldehyde **1d** (0.3334 g, 1.8 mmol)/anhydrous $CHCl_3$ (2.5 mL), **2a** (0.1746 g, 1 mmol)/anhydrous $CHCl_3$ (2.5 mL), and $H_2O$ (7.2 μL, d = 1.000 g/mL, 0.0072 g, 0.4 mmol) at 20 °C for 40.7 h afforded (*E*)-**3da** (0.0332 g, 9%, purity = 96%) (petroleum ether/ethyl acetate = 40/1 (400 mL × 2)) (the ratio of (*E*)-**3da**/(*Z*)-**3da** was > 99/1 and 18% recovery of 2**a** was obtained by NMR analysis of the crude product) as a liquid: $^1$H NMR (300 MHz, $CDCl_3$) δ 7.62-7.55 (m, 1H, ArH), 7.45-7.24 (m, 8H, ArH), 6.20 (q, *J* = 1.5 Hz, 1H, =CH), 5.18 (s, 2H, $CH_2$), 2.41 (d, *J* = 1.5 Hz, 3H, $CH_3$); $^{13}$C NMR (75 MHz, $CDCl_3$) δ 198.1, 165.6, 150.9, 139.8, 135.2, 133.2, 131.5, 129.4, 129.0, 128.6, 128.54, 158.52, 127.3, 119.5, 66.8, 13.4; IR (neat) ν (cm$^{-1}$) 3065, 3033, 2955, 1723, 1675, 1640, 1587, 1561, 1497, 1465, 1456, 1430, 1378, 1351, 1281, 1246, 1191, 1145, 1135, 1080, 1056, 1026; MS (ESI) *m/z* (%) 378 (M($^{81}$Br) + $NH_4^+$), 376 (M($^{79}$Br) + $NH_4^+$), 361 (M($^{81}$Br) + $H^+$), 359 (M($^{79}$Br) + $H^+$); HRMS calcd. for $C_{18}H_{16}BrO_3$ [M($^{79}$Br) + $H^+$]: 359.0277, found: 359.0280.

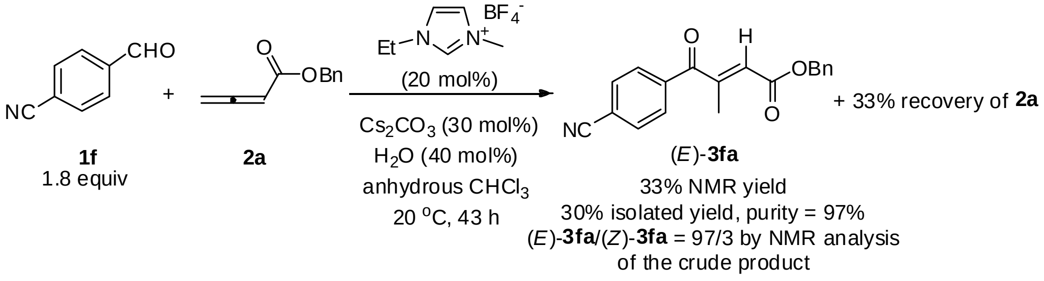
### (5) Benzyl 4-([1,1'-biphenyl]-4-yl)-3-methyl-4-oxobut-2(*E*)-enoate ((*E*)-3ea) (mdk-11-057)



The reaction of $Cs_2CO_3$ (0.0976 g, 0.3 mmol), 1-ethyl-3-methylimidazolium tetrafluoroborate (0.0402 g, 0.2 mmol)/anhydrous $CHCl_3$ (5 mL), 4-phenylbenzaldehyde **1e** (0.3345 g, 1.8 mmol)/anhydrous $CHCl_3$ (2.5 mL), **2a**

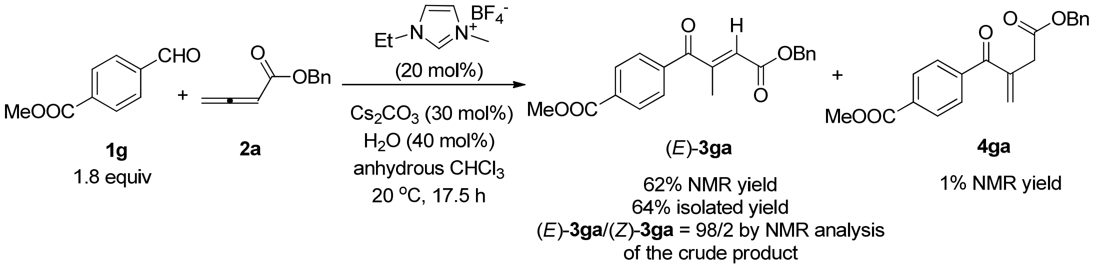
(0.1748 g, 1 mmol)/anhydrous $CHCl_3$ (2.5 mL), and $H_2O$ (7.2 μL, d = 1.000 g/mL, 0.0072 g, 0.4 mmol) at 10 $^{o}$C for 17 h afforded (*E*)-**3ea** (0.2427 g, 68%) (petroleum ether/ethyl acetate = 40/1 (440 mL × 2) to 20/1 (420 mL × 2)) (the ratio of (*E*)-**3ea**/(*Z*)-**3ea** was > 99/1 and 1% of **4ea** was formed by NMR analysis of the crude product) as a solid: m. p. 64~66 °C (*n*-hexane/$Et_2O$); $^{1}$H NMR (300 MHz, $CDCl_3$) δ 7.92-7.83 (m, 2H, ArH), 7.72-7.65 (m, 2H, ArH), 7.65-7.58 (m, 2H, ArH), 7.52-7.29 (m, 8H, ArH), 6.24 (q, *J* = 1.5 Hz, 1H, =CH), 5.22 (s, 2H, $CH_2$), 2.47 (d, *J* = 1.5 Hz, 3H, $CH_3$); $^{13}$C NMR (75 MHz, $CDCl_3$) δ 197.3, 165.5, 152.7, 145.9, 139.6, 135.5, 134.3, 130.3, 128.9, 128.6, 128.4, 128.3, 127.22, 127.16, 124.6, 66.5, 15.7; IR (neat) ν (cm$^{-1}$) 3063, 3032, 2954, 2890, 1951, 1723, 1660, 1602, 1558, 1498, 1486, 1455, 1449, 1404, 1381, 1351, 1312, 1266, 1189, 1137, 1077, 1030, 1007; MS (70 ev, EI) m/z (%) 356 (M$^{+}$, 19.71), 91 (100); Elemental analysis calcd (%) for $C_{24}H_{20}O_3$: C, 80.88, H, 5.66; Found: C, 80.59; H, 5.64.

### **(6) Benzyl 4-(4-cyanophenyl)-3-methyl-4-oxobut-2(*E*)-enoate ((*E*)-3fa) ((zwl-cf-1-127))**



The reaction of $Cs_2CO_3$ (0.0978 g, 0.3 mmol), 1-ethyl-3-methylimidazolium tetrafluoroborate (0.0401 g, 0.2 mmol)/anhydrous $CHCl_3$ (5 mL), 4-cyanobenzaldehyde **1f** (0.2408 g, 1.8 mmol)/anhydrous $CHCl_3$ (2.5 mL), **2a** (0.1741 g, 1 mmol)/anhydrous $CHCl_3$ (2.5 mL), and $H_2O$ (7.2 μL, d = 1.000 g/mL, 0.0072 g, 0.4 mmol) at 20 °C for 43 h afforded (*E*)-**3fa** (0.0946 g, 30%, purity = 97%) (petroleum ether/ethyl acetate = 40/1 (1.6 L) to 20/1 (800 mL)) (the ratio of (*E*)-**3fa**/(*Z*)-**3fa** was 97/3 and 33% recovery of **2a** was obtained by NMR analysis of the crude product) as a liquid: $^1$H NMR (300 MHz, $CDCl_3$) δ 7.87-7.80 (m, 2H, ArH), 7.80-7.71 (m, 2H, ArH), 7.42-7.30 (m, 5H, ArH), 6.20 (d, *J* = 1.2 Hz, 1H, =CH), 5.22 (s, 2H, $CH_2$), 2.43 (d, *J* = 0.8 Hz, 3H, $CH_3$); $^{13}$C NMR (75 MHz, $CDCl_3$) δ 196.2, 165.1, 150.9, 139.5, 135.2, 132.3, 129.8, 128.6, 128.5, 128.4, 127.1, 117.7, 116.2, 66.7, 15.0; IR (neat) ν (cm$^{-1}$) 3091, 3065, 3035, 2956, 2231, 1723, 1668, 1639, 1606, 1587, 1564, 1498, 1455, 1404, 1383, 1353, 1310, 1290, 1264, 1192, 1138, 1115, 1081, 1029, 1017, 1002; MS (70 ev, EI) m/z (%) 305 ($M^+$, 0.48), 91 (100); Elemental analysis calcd (%) for $C_{19}H_{15}NO_3$: C, 74.74, H, 4.95; Found: C, 74.61; H, 5.03.

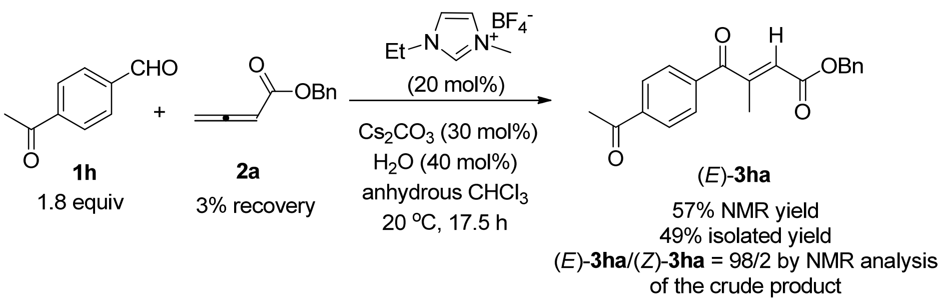
### (7) Benzyl 4-(4-methoxycarbonylphenyl)-3-methyl-4-oxobut-2(*E*)-enoate ((*E*)-3ga) (mdk-10-184)



The reaction of $Cs_2CO_3$ (0.0978 g, 0.3 mmol), 1-ethyl-3-methylimidazolium tetrafluoroborate (0.0406 g, 0.2 mmol)/anhydrous $CHCl_3$ (5 mL), methyl 4-formylbenzoate **1g** (0.3016 g, 1.8 mmol)/anhydrous $CHCl_3$ (2.5 mL), **2a** (0.1738 g, 1 mmol)/anhydrous $CHCl_3$ (2.5 mL), and $H_2O$ (7.2 μL, d = 1.000 g/mL, 0.0072 g, 0.4 mmol) at 20 °C for 17.5 h afforded (*E*)-**3ga** (0.2170 g, 64%) (petroleum ether/ethyl acetate = 30/1 (420 mL × 2 + 300 mL)) (the ratio of (*E*)-**3ga**/(*Z*)-**3ga** was 98/2 and 1%

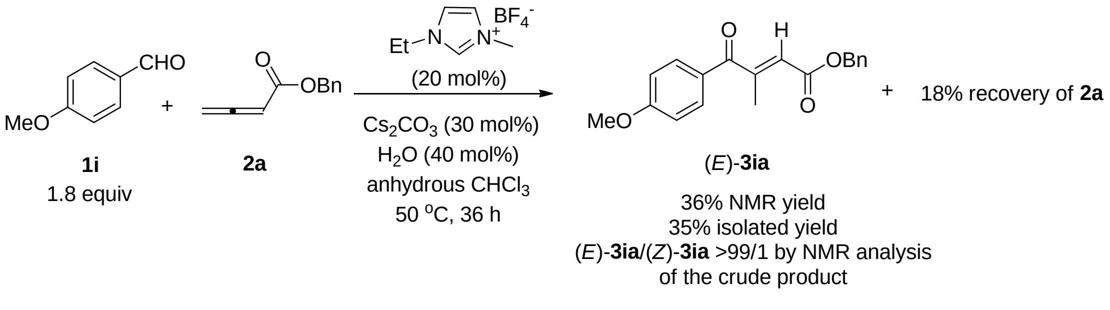
of **4ga** was formed by NMR analysis of the crude product) as a solid; m.p. 68~70 °C (*n*-hexane/DCM): $^{1}$H NMR (300 MHz, $CDCl_3$) δ 8.16-8.08 (m, 2H, ArH), 7.84-7.75 (m, 2H, ArH), 7.40-7.28 (m, 5H, ArH), 6.22 (q, *J* = 1.5 Hz, 1H, =CH), 5.21 (s, 2H, $CH_2$), 3.95 (s, 3H, $OCH_3$), 2.44 (d, *J* = 1.5 Hz, 3H, $CH_3$); $^{13}$C NMR (75 MHz, $CDCl_3$) δ 197.2, 166.0, 165.3, 151.6, 139.5, 135.3, 133.7, 129.6, 129.4, 128.6, 128.4, 126.4, 66.6, 52.4, 15.1; IR (neat) ν (cm$^{-1}$) 3065, 3034, 3004, 1727, 1667, 1639, 1587, 1571, 1500, 1455, 1436, 1406, 1382, 1353, 1282, 1265, 1191, 1139, 1107, 1029, 1017; MS (70 ev, EI) m/z (%) 338 (M$^{+}$, 1.60), 232 (100); Elemental analysis calcd (%) for $C_{20}H_{18}O_5$: C, 70.99, H, 5.36; Found: C, 70.88; H, 5.44.

### (8) Benzyl 4-(4-acetylphenyl)-3-methyl-4-oxobut-2(*E*)-enoate ((*E*)-3ha) (mdk-11-043)



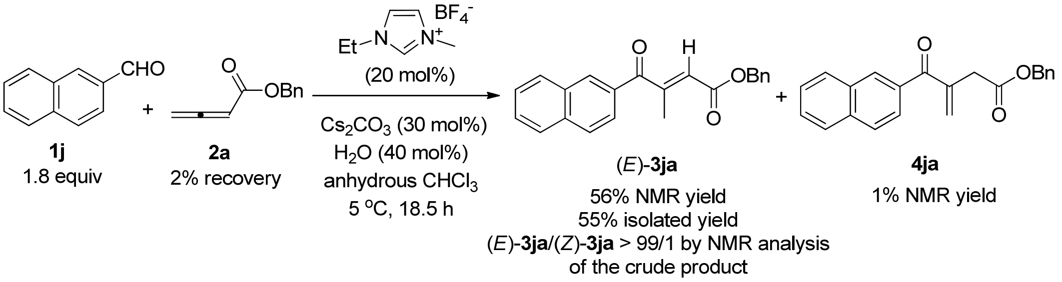
The reaction of $Cs_2CO_3$ (0.0979 g, 0.3 mmol), 1-ethyl-3-methylimidazolium tetrafluoroborate (0.0407 g, 0.2 mmol)/anhydrous $CHCl_3$ (5 mL), 4-acetylbenzaldehyde **1h** (0.2664 g, 1.8 mmol)/anhydrous $CHCl_3$ (2.5 mL), **2a** (0.1747 g, 1 mmol)/anhydrous $CHCl_3$ (2.5 mL), and $H_2O$ (7.2 μL, d = 1.000 g/mL, 0.0072 g, 0.4 mmol) at 20 °C for 17.5 h afforded (*E*)-**3ha** (DCM (300 mL), afforded pure (*E*)-**3ha** (0.0238 g) and impure (*E*)-**3ha** (0.1108 g), the impure part was recrystallized in *n*-hexane/DCM, afforded pure (*E*)-**3ha** (0.1024 g), the mother liquid was evaporated and recrystallized in *n*-hexane/DCM again, afforded pure (*E*)-**3ha** (0.0319 g), combined weight: 0.0238 g + 0.1024 g + 0.0319 g = 0.1581 g, 49%) (the ratio of (*E*)-**3ha**/(*Z*)-**3ha** was 98/2 by NMR analysis of the crude product) as a solid; m.p. 83~85 °C (*n*-hexane/DCM): $^1$H NMR (300 MHz, $CDCl_3$) δ 8.07-7.98 (m, 2H, ArH), 7.86-7.79 (m, 2H, ArH), 7.42-7.29 (m, 5H, ArH), 6.22 (q, $J$ = 1.4 Hz, 1H, =CH), 5.21 (s, 2H, $CH_2$), 2.65 (s, 3H, $CH_3$), 2.44 (d, $J$ = 1.5 Hz, 3H, $CH_3$); $^{13}$C NMR (75 MHz, $CDCl_3$) δ 197.2, 197.1, 165.3, 151.6, 139.9, 139.5, 135.3, 129.7, 128.6, 128.4, 128.3, 126.5, 66.6, 26.8, 15.1; IR (KBr) ν (cm$^{-1}$) 3092, 3066, 3037, 3011, 2935, 2879, 1720, 1683, 1656, 1637, 1499, 1452, 1403, 1389, 1353, 1306, 1272, 1261, 1249, 1200, 1158, 1142, 1118, 1074, 1040, 1030, 1000; MS (70 ev, EI) m/z (%) 322 ($M^+$, 1.27), 91 (100); Elemental analysis calcd (%) for $C_{20}H_{18}O_4$: C, 74.52, H, 5.63; Found: C, 74.12; H, 5.89.

### (9) Benzyl 4-(4-methoxyphenyl)-3-methyl-4-oxobut-2(*E*)-enoate ((*E*)-3ia) (mdk-11-096)



The reaction of $Cs_2CO_3$ (0.0976 g, 0.3 mmol), 1-ethyl-3-methylimidazolium tetrafluoroborate (0.0403 g, 0.2 mmol)/anhydrous $CHCl_3$ (5 mL), 4-methoxybenzaldehyde **1i** (0.2455 g, 1.8 mmol)/anhydrous $CHCl_3$ (2.5 mL), **2a** (0.1742 g, 1 mmol)/anhydrous $CHCl_3$ (2.5 mL), and $H_2O$ (7.2 μL, d = 1.000 g/mL, 0.0072 g, 0.4 mmol) at 50 °C for 36 h afforded (*E*)-**3ia** (0.1081 g, 35%) (petroleum ether/ethyl acetate = 30/1 (420 mL + 300 mL)) (the ratio of (*E*)-**3ia**/(*Z*)-**3ia** was >99/1 and 18% recovery of **2a** was obtained by NMR analysis of the crude product) as a liquid: $^1$H NMR (300 MHz, CDCl$_3$) δ 7.86-7.77 (m, 2H, ArH), 7.42-7.28 (m, 5H, ArH), 6.97-6.90 (m, 2H, ArH), 6.13 (q, *J* = 1.6 Hz, 1H, =CH), 5.21 (s, 2H, CH$_2$), 3.87 (s, 3H, OCH$_3$), 2.43 (d, *J* = 1.5 Hz, 3H, CH$_3$); $^{13}$C NMR (75 MHz, CDCl$_3$) δ 196.4, 165.6, 163.8, 153.4, 135.6, 132.2, 128.6, 128.3, 128.1, 123.0, 113.8, 66.3, 55.5, 16.0; IR (neat) ν (cm$^{-1}$) 3065, 3034, 3008, 2956, 2840, 1722, 1657, 1652, 1599, 1574, 1508, 1456, 1442, 1421, 1381, 1351, 1313, 1258, 1192, 1136, 1027; MS (70 ev, EI) m/z (%) 310 (M$^+$, 9.53), 135 (100); HRMS calcd for $C_{19}H_{18}O_4$ (M$^+$): 310.1205, found: 310.1202.

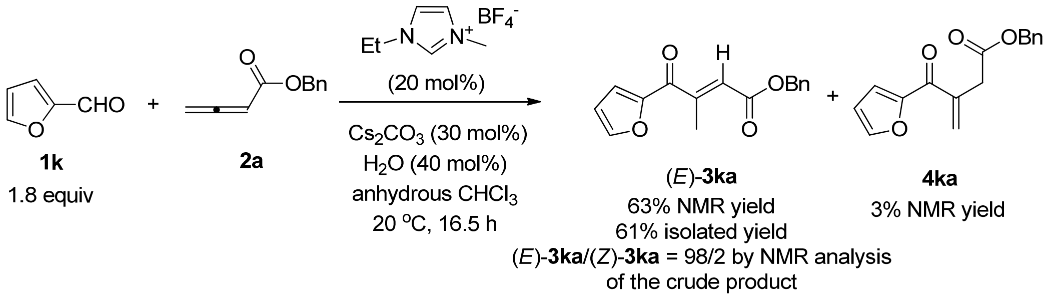
### (10) Benzyl 3-methyl-4-(naphthalen-2-yl)-4-oxobut-2(*E*)-enoate ((*E*)-3ja) (mdk-11-049)



The reaction of Cs$_2$CO$_3$ (0.0975 g, 0.3 mmol), 1-ethyl-3-methylimidazolium tetrafluoroborate (0.0400 g, 0.2 mmol)/anhydrous CHCl$_3$ (5 mL), 2-naphthaldehyde **1j** (0.2866 g, 1.8 mmol)/anhydrous CHCl$_3$ (2.5 mL), **2a** (0.1746 g, 1 mmol)/anhydrous CHCl$_3$ (2.5 mL), and H$_2$O (7.2 μL, d = 1.000 g/mL, 0.0072 g, 0.4 mmol) at 5 °C for 18.5 h afforded (*E*)-**3ja** (0.1810 g, 55%) (petroleum ether/ethyl acetate = 50/1 (400 mL × 3)) (the ratio of (*E*)-**3ja**/(*Z*)-**3ja** was >99/1 and 1% of **4ja** was formed by NMR analysis of the crude product) as a liquid: $^1$H NMR (300 MHz,

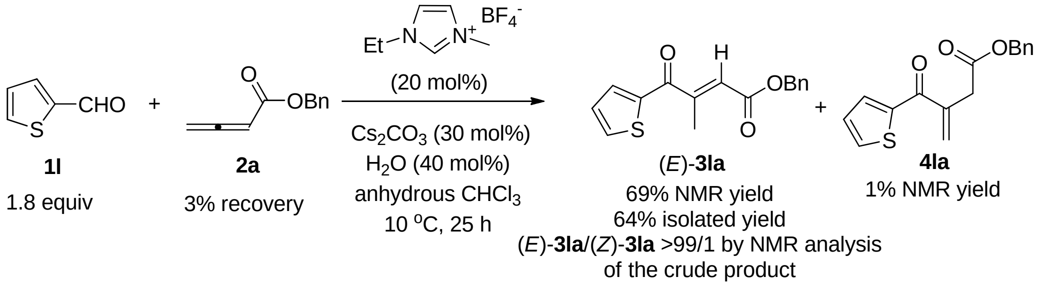
$CDCl_3$) δ 8.27 (d, *J* = 0.6 Hz, 1H, ArH), 7.96-7.82 (m, 4H, ArH), 7.64-7.50 (m, 2H, ArH), 7.41-7.27 (m, 5H, ArH), 6.26 (q, *J* = 1.5 Hz, 1H, =CH), 5.22 (s, 2H, $CH_2$), 2.51 (d, *J* = 1.5 Hz, 3H, $CH_3$); $^{13}C$ NMR (75 MHz, $CDCl_3$) δ 197.7, 165.6, 152.9, 135.5, 135.4, 132.9, 132.1, 131.8, 129.5, 128.7, 128.6, 128.5, 128.3, 127.8, 126.9, 124.9, 124.6, 66.5, 15.8; IR (neat) ν ($cm^{-1}$) 3060, 3034, 2954, 1722, 1659, 1626, 1596, 1498, 1465, 1456, 1436, 1383, 1352, 1283, 1233, 1202, 1183, 1140, 1117, 1028; MS (70 ev, EI) m/z (%) 330 ($M^+$, 6.49), 91 (100); HRMS calcd for $C_{22}H_{18}O_3$ ($M^+$): 330.1256, found: 330.1256.

### (11) Benzyl 4-(furan-2-yl)-3-methyl-4-oxobut-2(*E*)-enoate ((*E*)-3ka) (mdk-11-071-1)



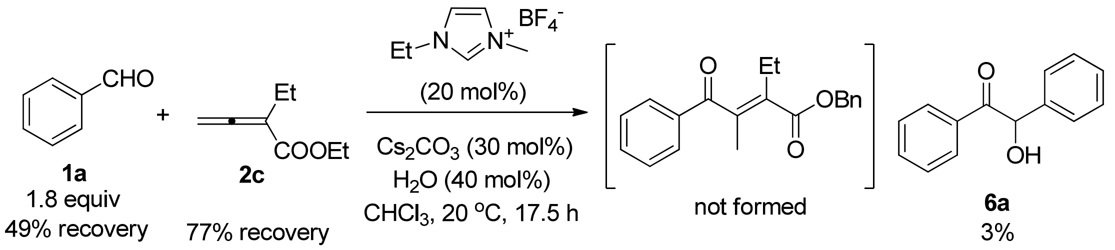
The reaction of $Cs_2CO_3$ (0.0978 g, 0.3 mmol), 1-ethyl-3-methylimidazolium tetrafluoroborate (0.0400 g, 0.2 mmol)/anhydrous $CHCl_3$ (5 mL), furan-2-carbaldehyde **1k** (0.1728 g, 1.8 mmol)/anhydrous $CHCl_3$ (2.5 mL), **2a** (0.1736 g, 1 mmol)/anhydrous $CHCl_3$ (2.5 mL), and $H_2O$ (7.2 μL, d = 1.000 g/mL, 0.0072 g, 0.4 mmol) at 20 °C for 16.5 h afforded (*E*)-**3ka** (0.1631 g, 61%) ((petroleum ether/ethyl acetate = 30/1 (450 mL × 2) to 20/1 (420 mL) to 10/1 (400 mL + 330 mL)) (the ratio of (*E*)-**3ka**/(*Z*)-**3ka** was 98/2 and 3% of **4ka** was formed by NMR analysis of the crude product) as a liquid: $^1H$ NMR (300 MHz, $CDCl_3$) δ 7.70-7.65 (m, 1H, ArH), 7.44-7.29 (m, 5H, ArH), 7.21 (dd, $J_1$ = 3.6 Hz, $J_2$ = 0.6 Hz, 1H, ArH), 6.56 (dd, $J_1$ = 3.6 Hz, $J_2$ = 1.8 Hz, 1H, ArH), 6.49 (q, $J$ = 1.5 Hz, 1H, =CH), 5.23 (s, 2H, $CH_2$), 2.42 (d, $J$ = 1.5 Hz, 3H, $CH_3$); $^{13}$C NMR (75 MHz, $CDCl_3$) δ 183.8, 165.4, 151.5, 150.8, 147.9, 135.4, 128.5, 128.3, 124.3, 121.0, 112.3, 66.5, 15.2; IR (neat) ν ($cm^{-1}$) 3134, 3091, 3065, 3034, 2955, 1722, 1651, 1561, 1498, 1463, 1385, 1352, 1294, 1285, 1201, 1143, 1083, 1039, 1027; MS (70 ev, EI) m/z (%) 270 ($M^+$, 1.03), 91 (100); HRMS calcd. for $C_{16}H_{14}O_4$ ($M^+$): 270.0892, found: 270.0894.

### (12) Benzyl 3-methyl-4-oxo-4-(thiophen-2-yl)but-2(*E*)-enoate ((*E*)-3la) (mdk-11-076)



The reaction of $Cs_2CO_3$ (0.0975 g, 0.3 mmol), 1-ethyl-3-methylimidazolium tetrafluoroborate (0.0403 g, 0.2 mmol)/anhydrous $CHCl_3$ (5 mL), thiophene-2-carbaldehyde **1l** (0.2025 g, 1.8 mmol)/anhydrous $CHCl_3$ (2.5 mL), **2a** (0.1740 g, 1 mmol)/anhydrous $CHCl_3$ (2.5 mL), and $H_2O$ (7.2 μL, d = 1.000 g/mL, 0.0072 g, 0.4 mmol) at 10 °C for 25 h afforded (*E*)-**3la** (0.1828 g, 64%) ((petroleum ether/ethyl acetate = 40/1 (400 mL × 2)) (the ratio of (*E*)-**3la**/(*Z*)-**3la** was >99/1 and 1% of **4la** was formed by NMR analysis of the crude product) as a liquid: $^1$H NMR (300 MHz, $CDCl_3$) δ 7.71 (dd, $J_1$ = 5.0 Hz, $J_2$ = 1.1 Hz, 1H, ArH), 7.64 (dd, $J_1$ = 3.8 Hz, $J_2$ = 1.1 Hz, 1H, ArH), 7.43-7.29 (m, 5H, ArH), 7.13 (dd, $J_1$ = 5.0 Hz, $J_2$ = 4.1 Hz, 1H, ArH), 6.36 (q, $J$ = 1.5 Hz, 1H, =CH), 5.22 (s, 2H, $CH_2$), 2.44 (d, $J$ = 1.5 Hz, 3H, $CH_3$); $^{13}C$ NMR (75 MHz, $CDCl_3$) δ 189.3, 165.4, 152.5, 141.9, 135.4, 135.3, 134.8, 128.5, 128.31, 128.28, 128.1, 123.4, 66.4, 15.7; IR (neat) ν ($cm^{-1}$) 3091, 3033, 2953, 1722, 1636, 1513, 1498, 1455, 1412, 1383, 1356, 1278, 1189, 1134, 1081, 1055, 1025; MS (70 ev, EI) *m/z* (%) 286 ($M^+$, 1.82), 91 (100); HRMS calcd. for $C_{16}H_{14}O_3S$ ($M^+$): 286.0664, found: 286.0666.

**(13) 2-Hydroxy-1,2-diphenylethanone (6a) (mdk-11-102)**



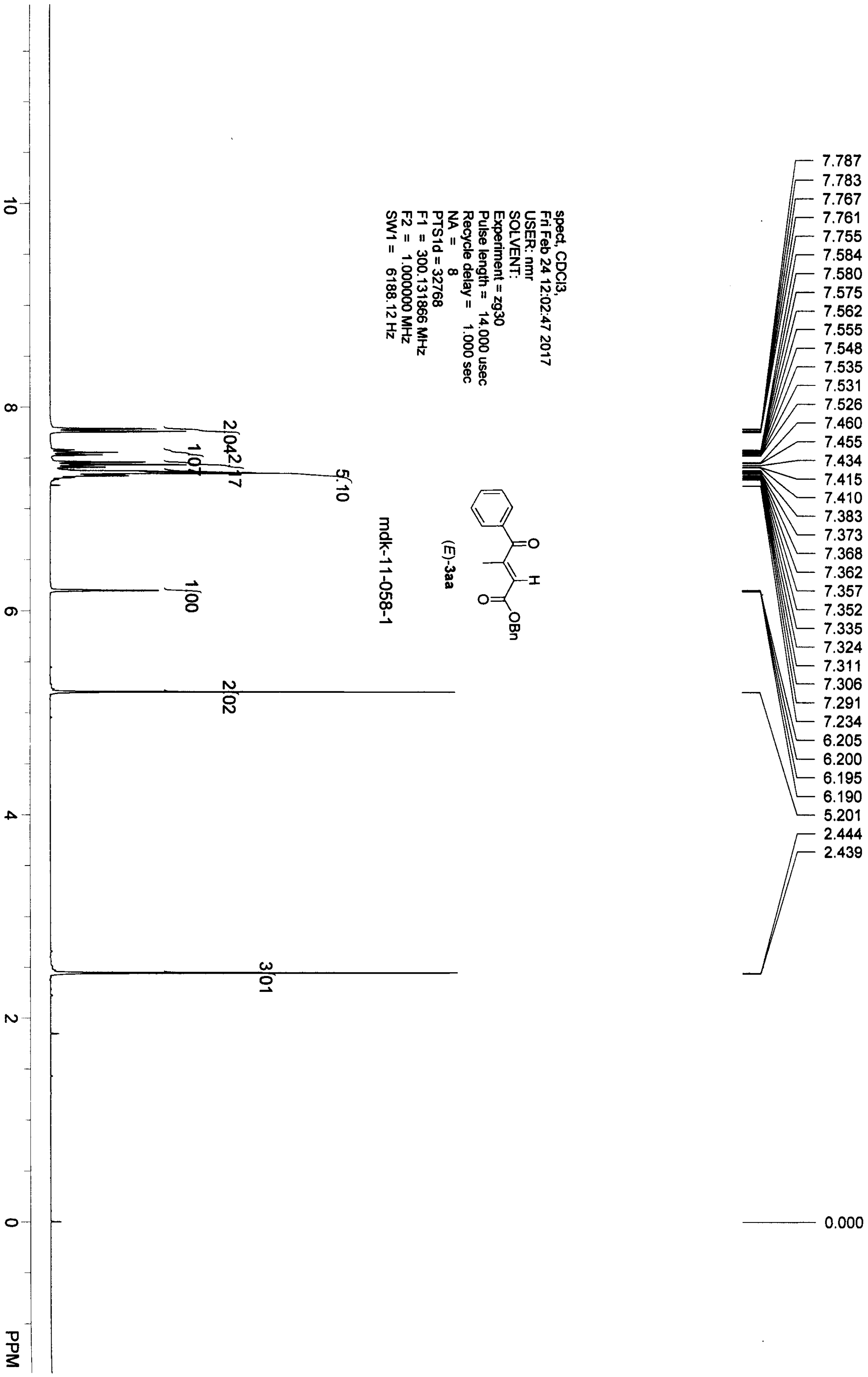
The reaction of $Cs_2CO_3$ (0.0975 g, 0.3 mmol), 1-ethyl-3-methylimidazolium tetrafluoroborate (0.0401 g, 0.2 mmol)/anhydrous $CHCl_3$ (5 mL), benzaldehyde **1a** (0.1906 g, 1.8 mmol)/anhydrous $CHCl_3$ (2.5 mL), **2c** (0.1405 g, 1 mmol)/anhydrous $CHCl_3$ (2.5 mL), and $H_2O$ (7.2 μL, d = 1.000 g/mL, 0.0072 g, 0.4 mmol) at 20 °C for 17.5 h afforded **6a**[1] (0.0063 g, 3%) ((petroleum ether/ethyl acetate = 6/1 (420 mL)) (49% recovery of **1a** and 77% recovery of **2c** were obtained by NMR analysis of the crude product) as a solid; m.p. 129~131 °C (*n*-hexane/DCM) (lit.[1a] 132~133 °C): $^1H$ NMR (300 MHz, $CDCl_3$) δ 7.96-7.86 (m, 2H, ArH), 7.58-7.47 (m, 1H, ArH), 7.44-7.22 (m, 7H, ArH), 5.96 (d, $J$ = 6.0 Hz, 1H, CH), 4.57 (d, $J$ = 6.3 Hz, 1H, OH); $^{13}C$ NMR (75 MHz, $CDCl_3$) δ 198.9, 139.0, 133.9, 133.4, 129.1, 128.7, 128.6, 127.8, 76.2; IR (neat) ν ($cm^{-1}$) 3416, 3381, 3084, 3060, 3029, 2933, 1679, 1596, 1577, 1561, 1491, 1450, 1389, 1343, 1318, 1307, 1263, 1207, 1180, 1093, 1069, 1028, 1004; MS

(EI) *m/z* (%) 212 ($M^+$, 1.01), 105 (100).

## References:

(1) L. Rout, A. M. Harned, *Chem. Eur. J.*, 2009, **15**, 12926.

(2) H. Yuan, W. Yoo, H. Miyamura, S. Kobayashi, *J. Am. Chem. Soc.*, 2012, **134**, 13970.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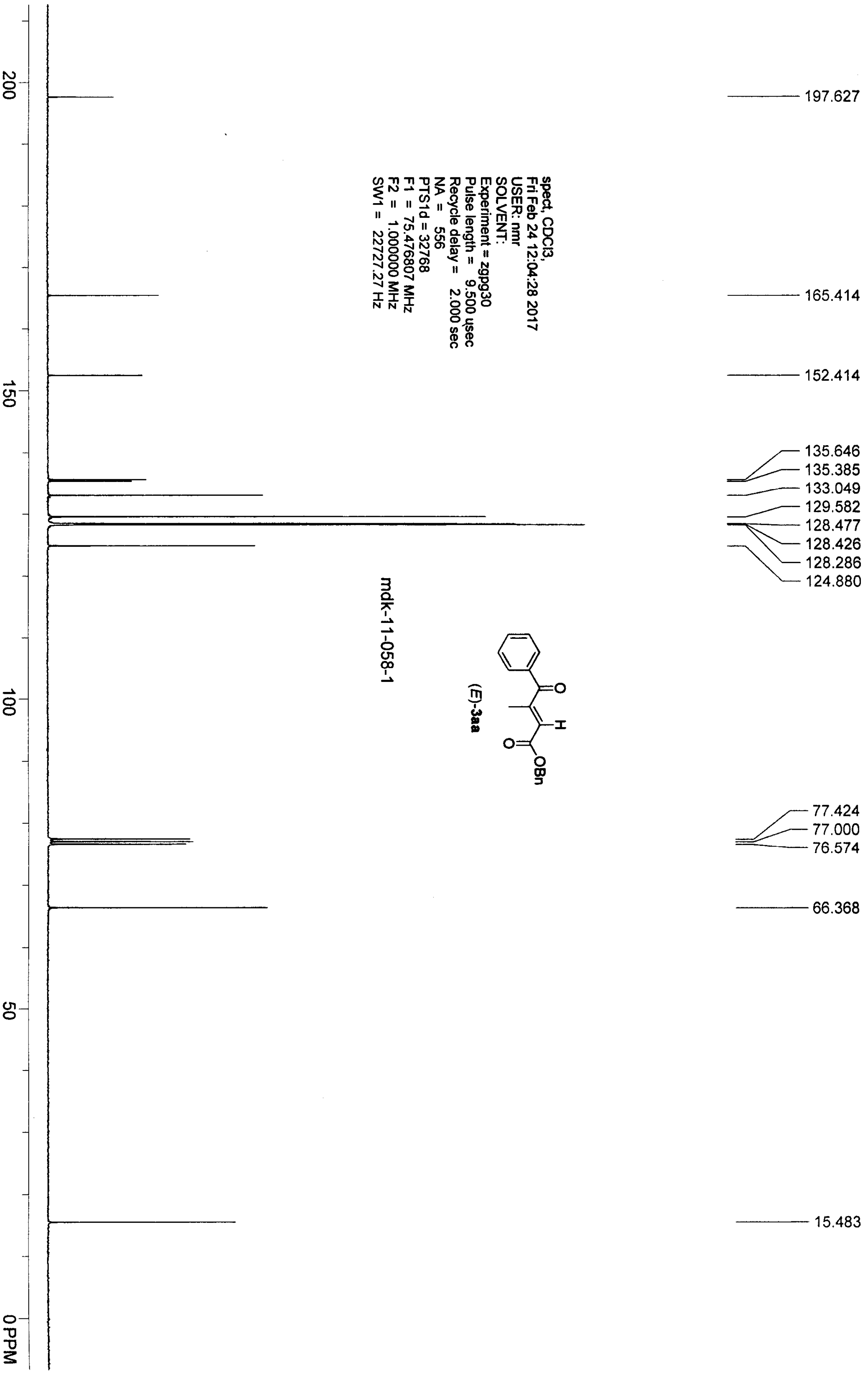
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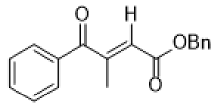

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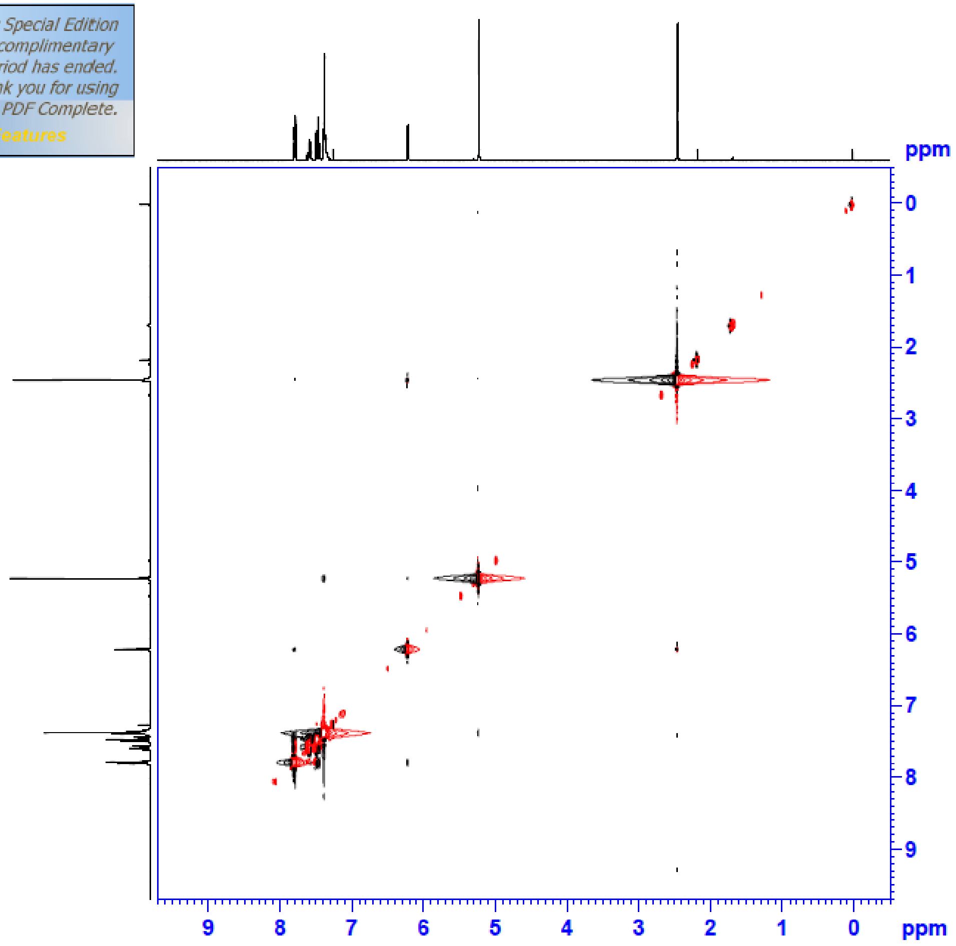

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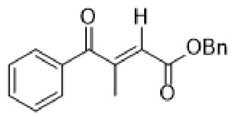

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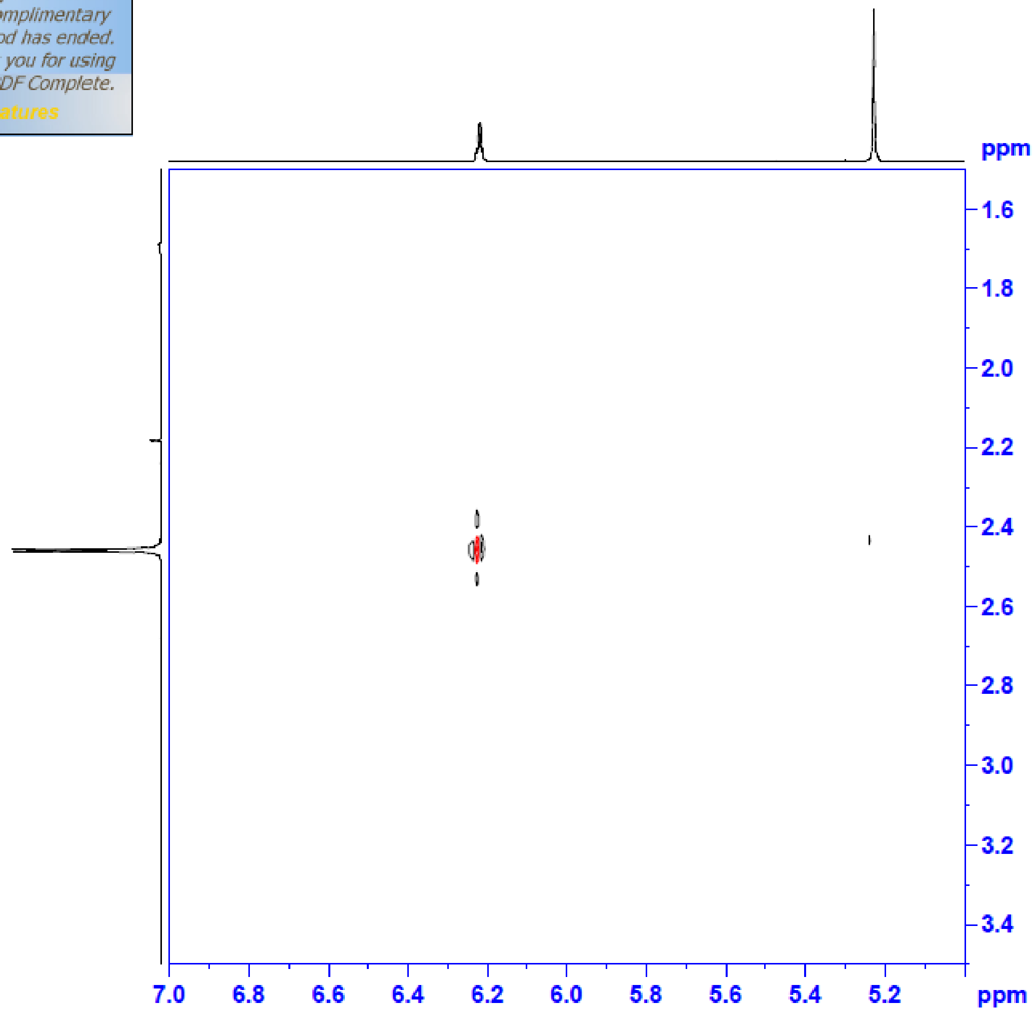

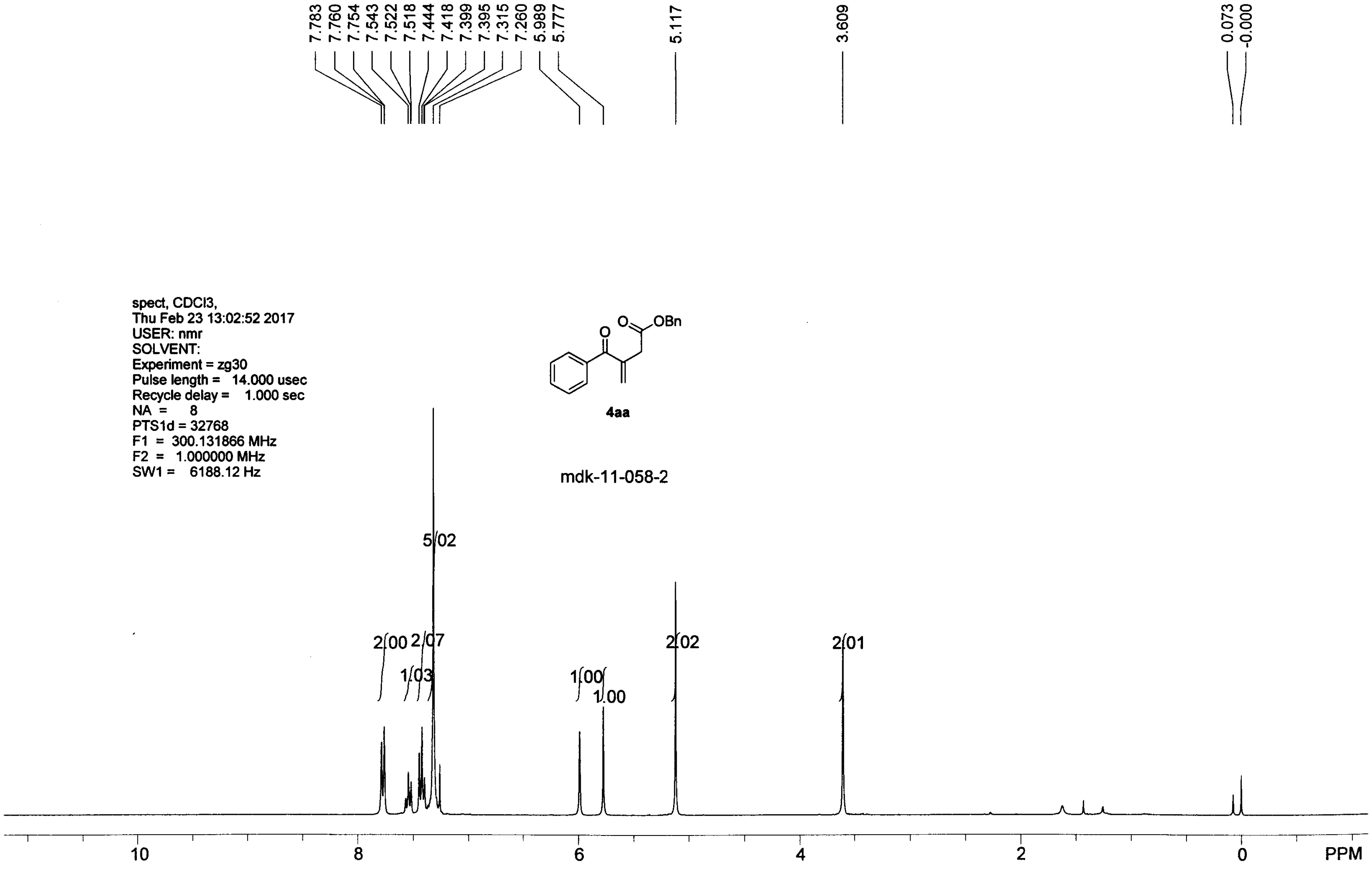
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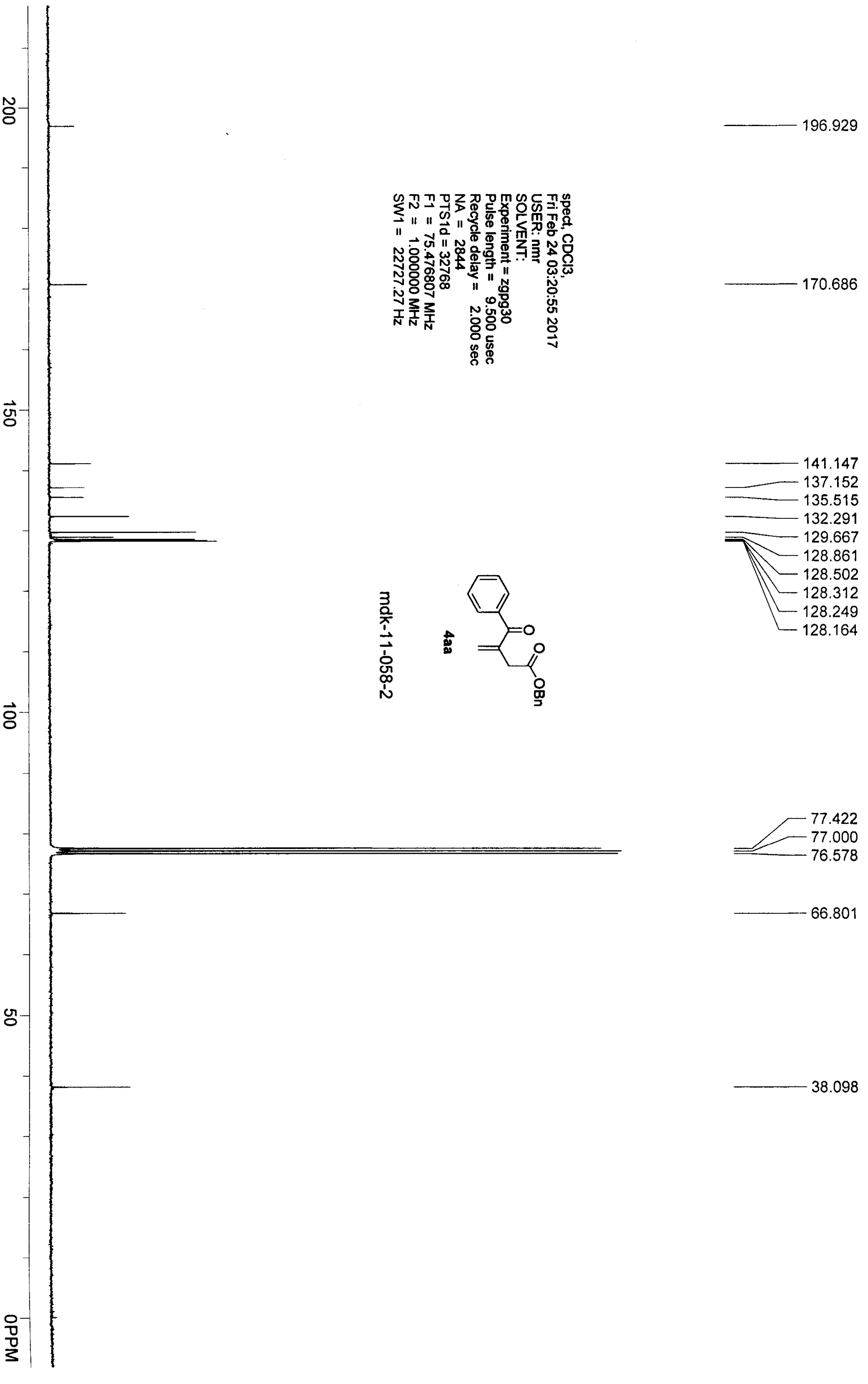
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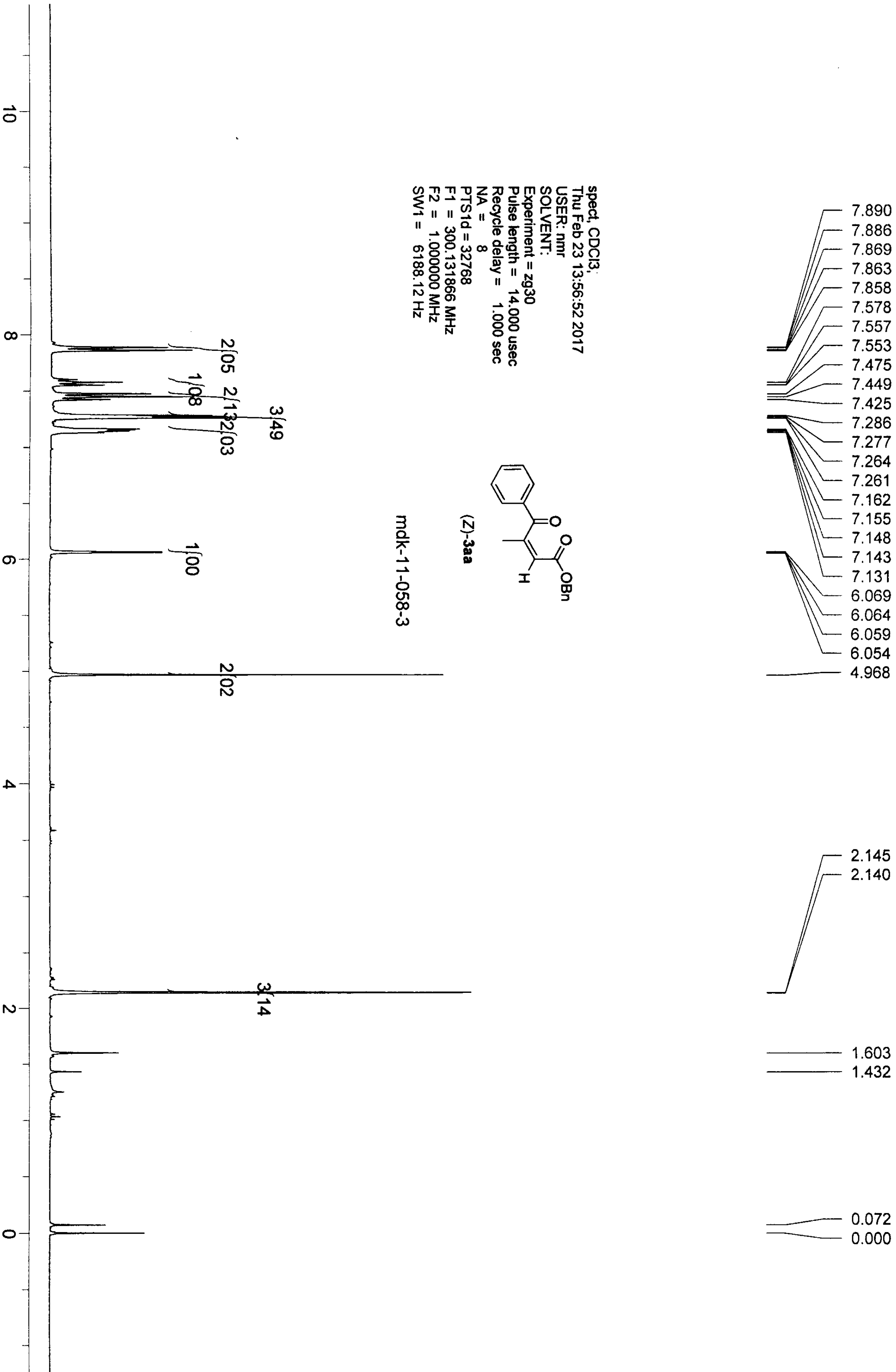
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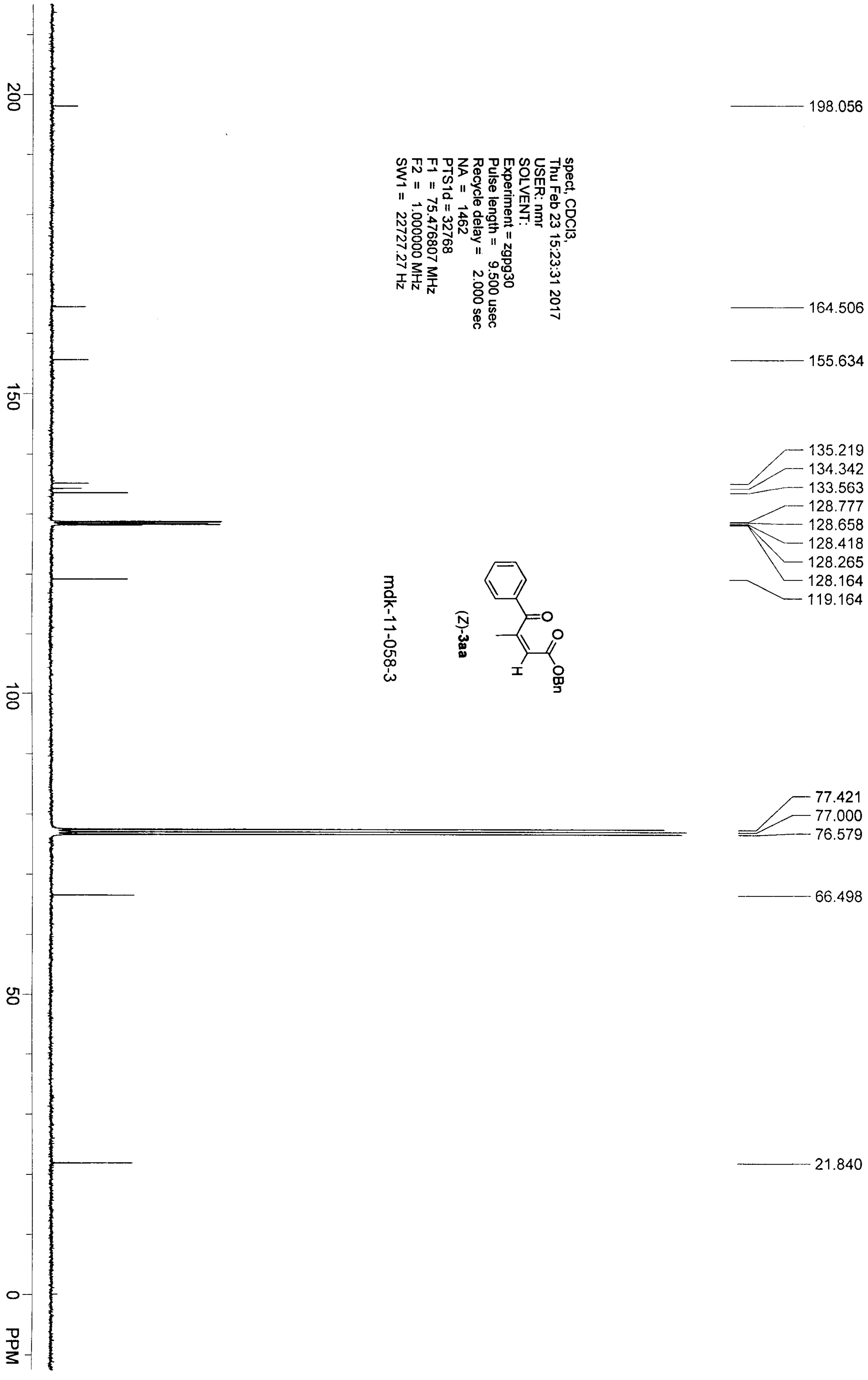
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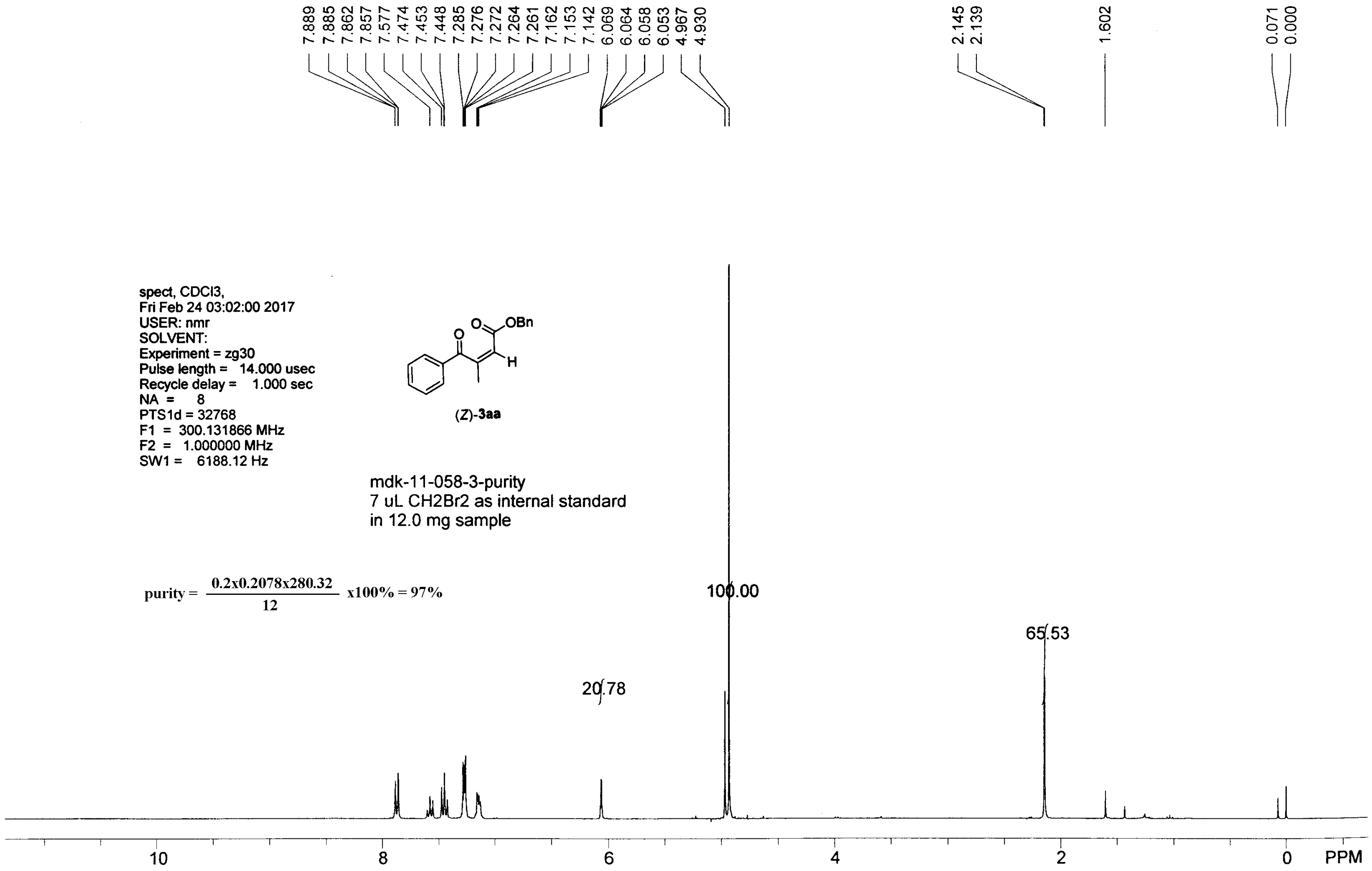

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(*Z*)-**3aa**

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7 uL CH2Br2 as internal standard
in 12.0 mg sample

$$\text{purity} = \frac{0.2\text{x}0.2078\text{x}280.32}{12}\ \text{x}100\% = 97\%$$

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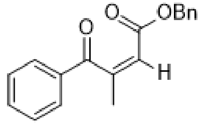

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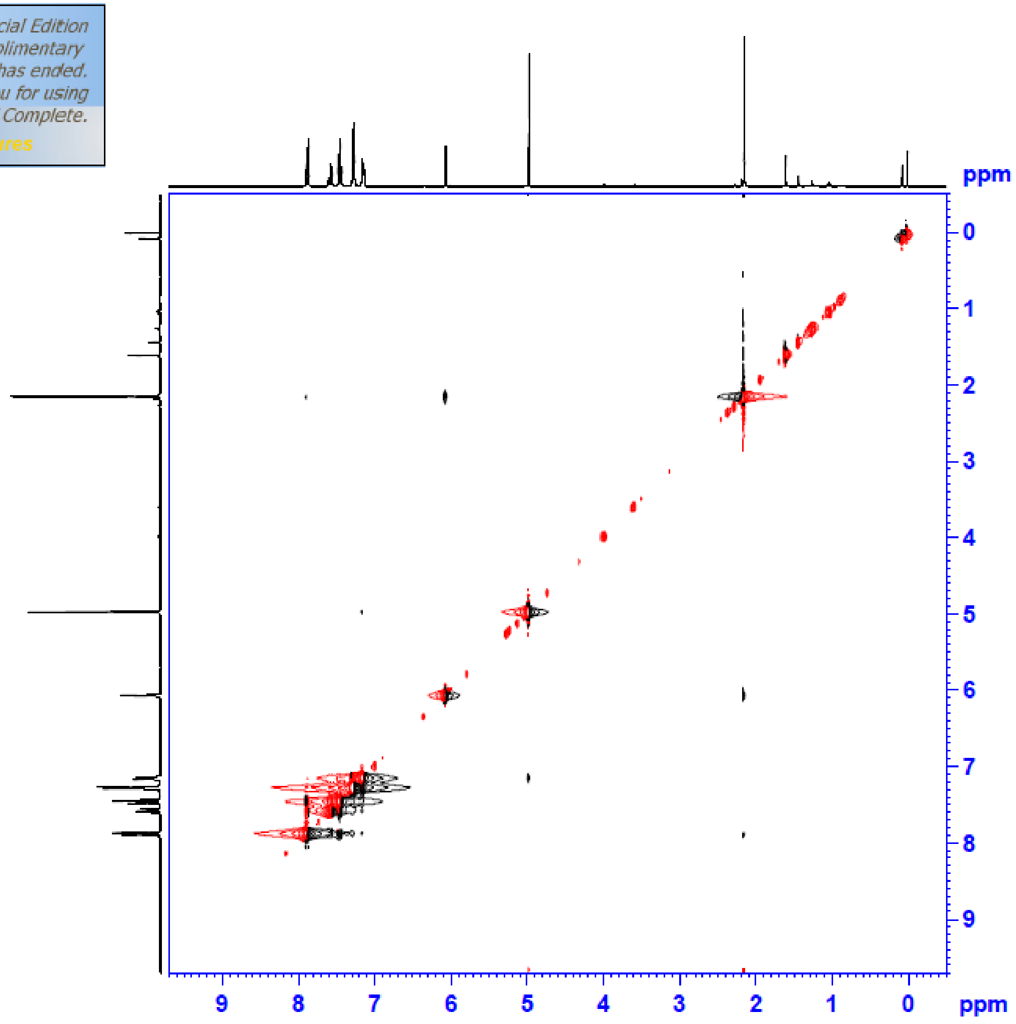

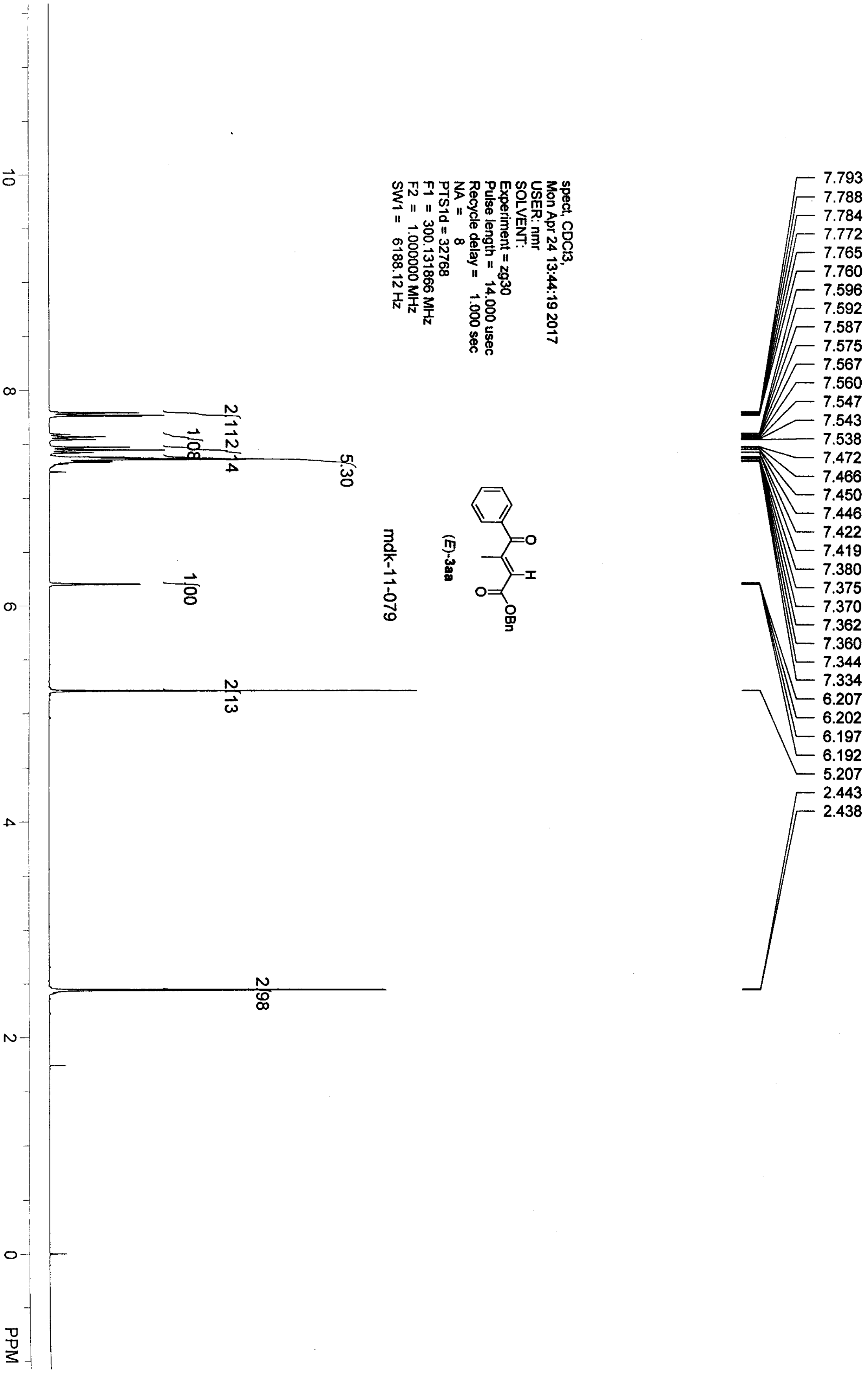
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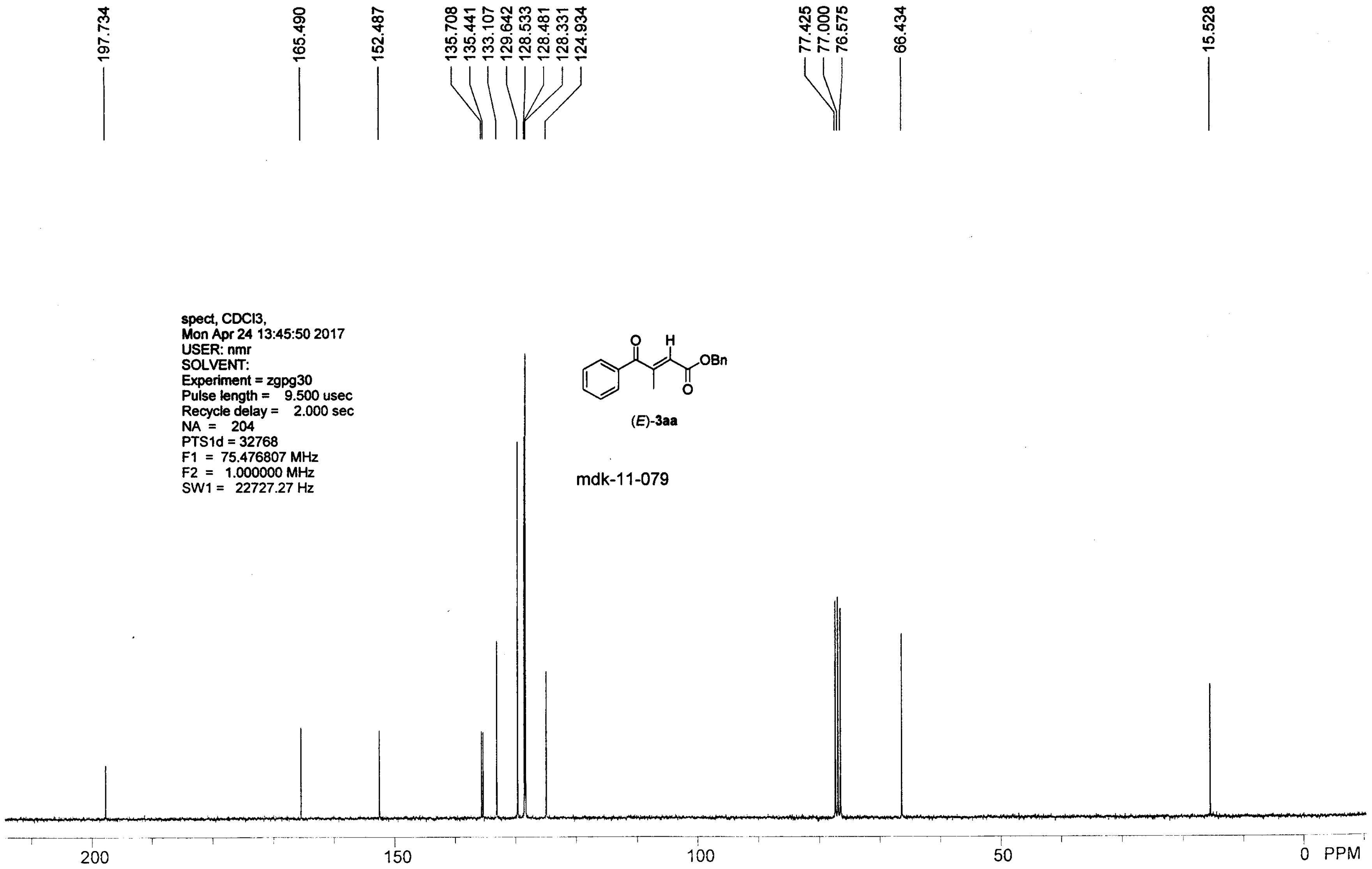
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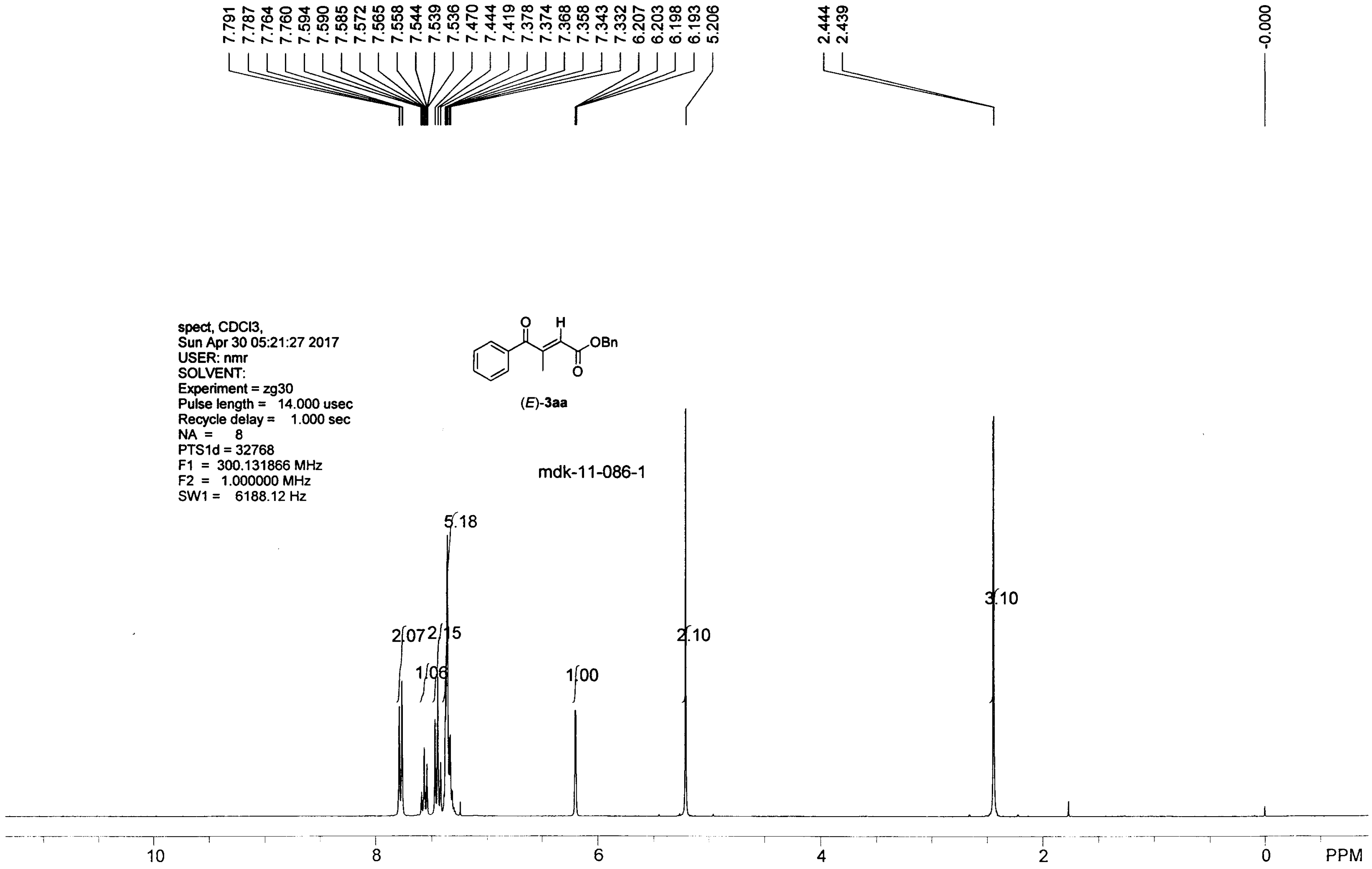
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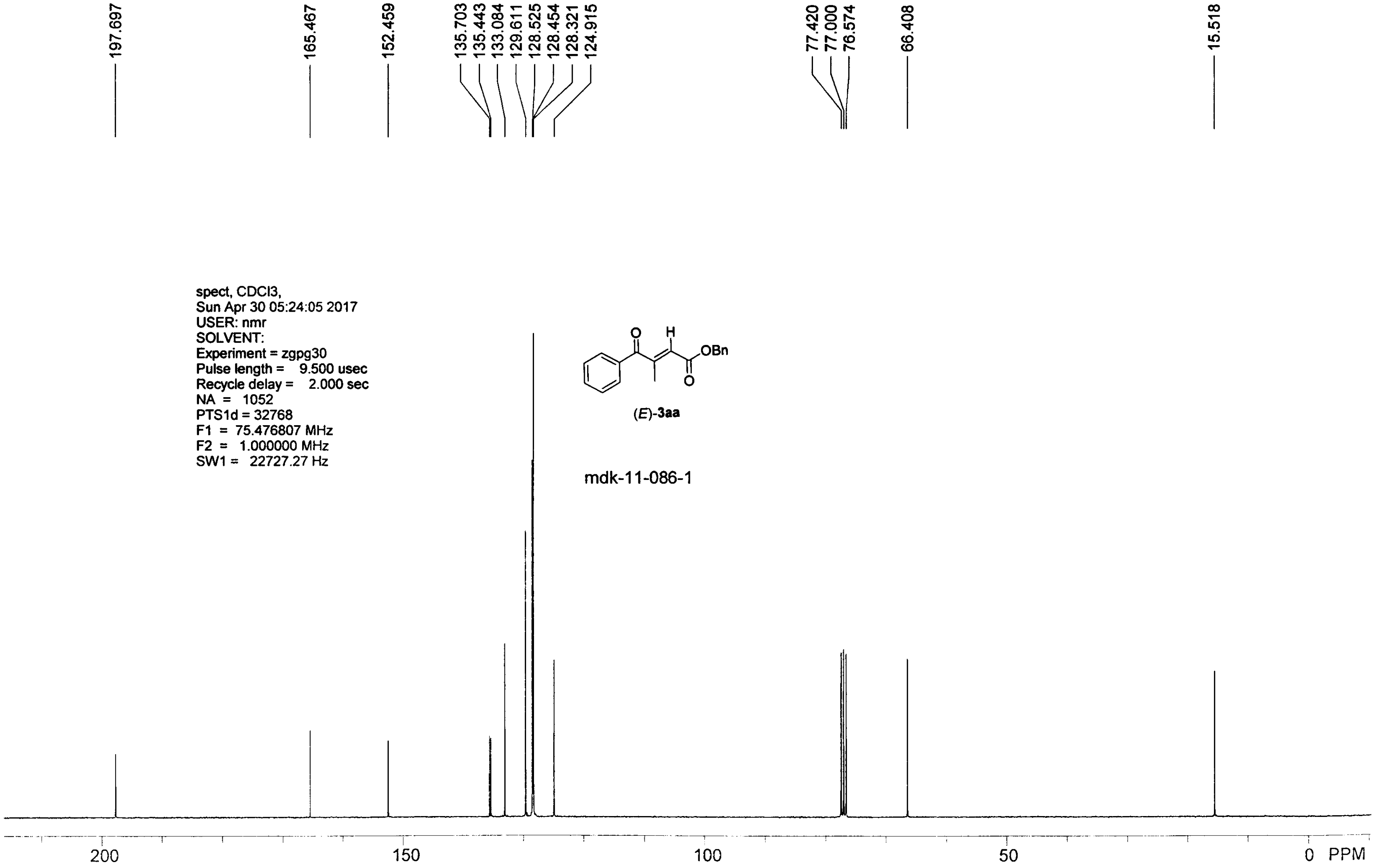
(*E*)-**3aa**



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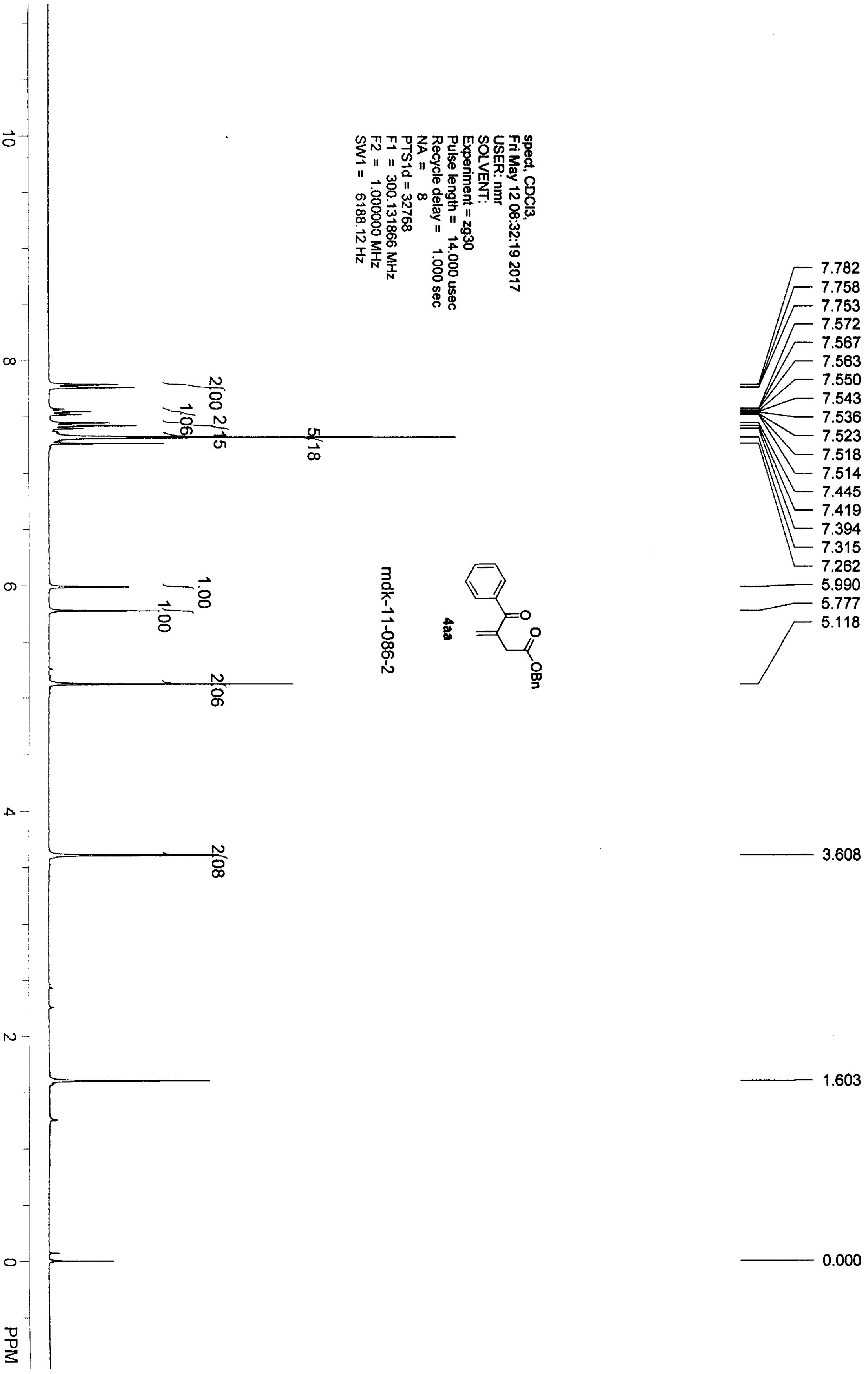
mdk-11-086-1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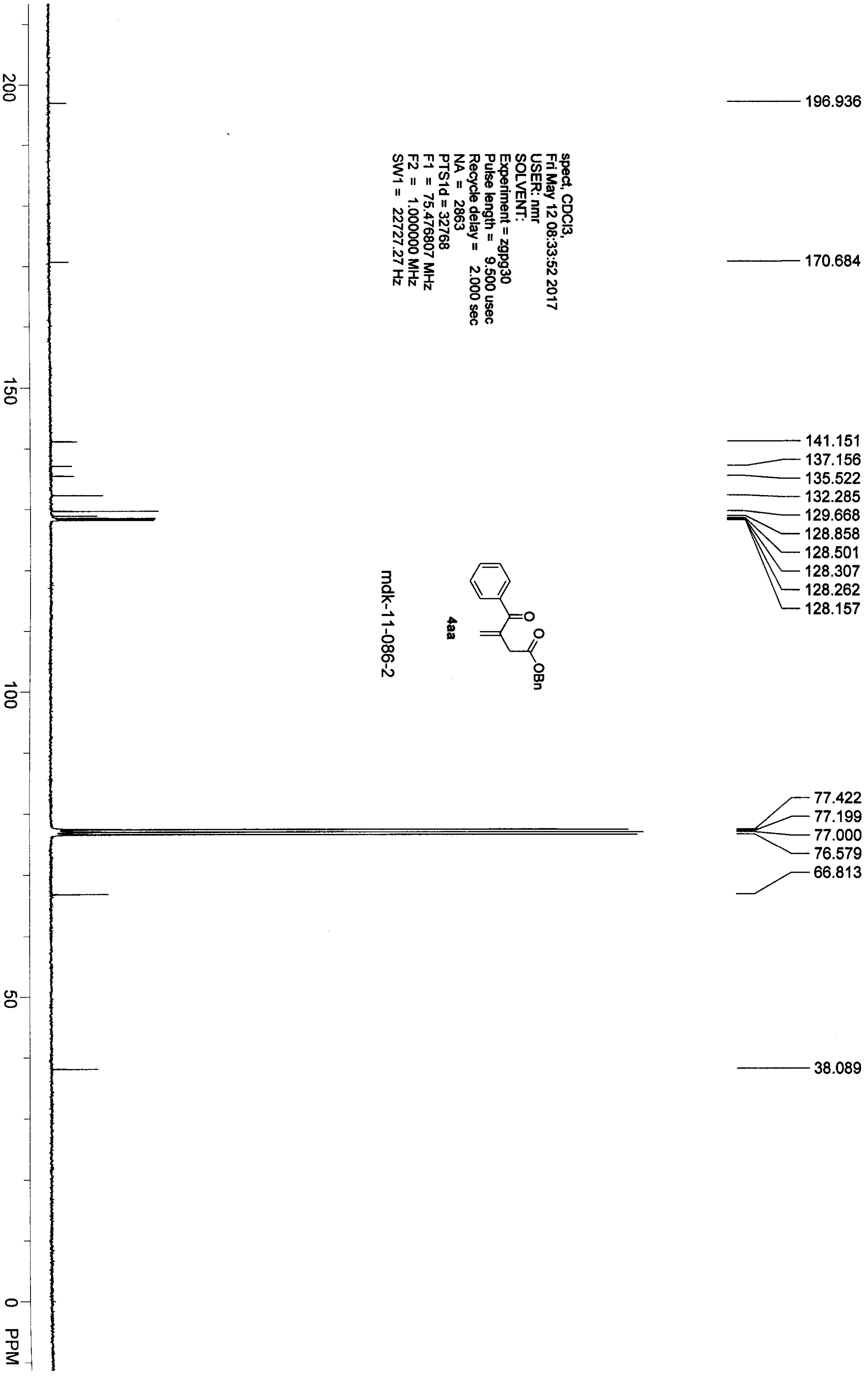
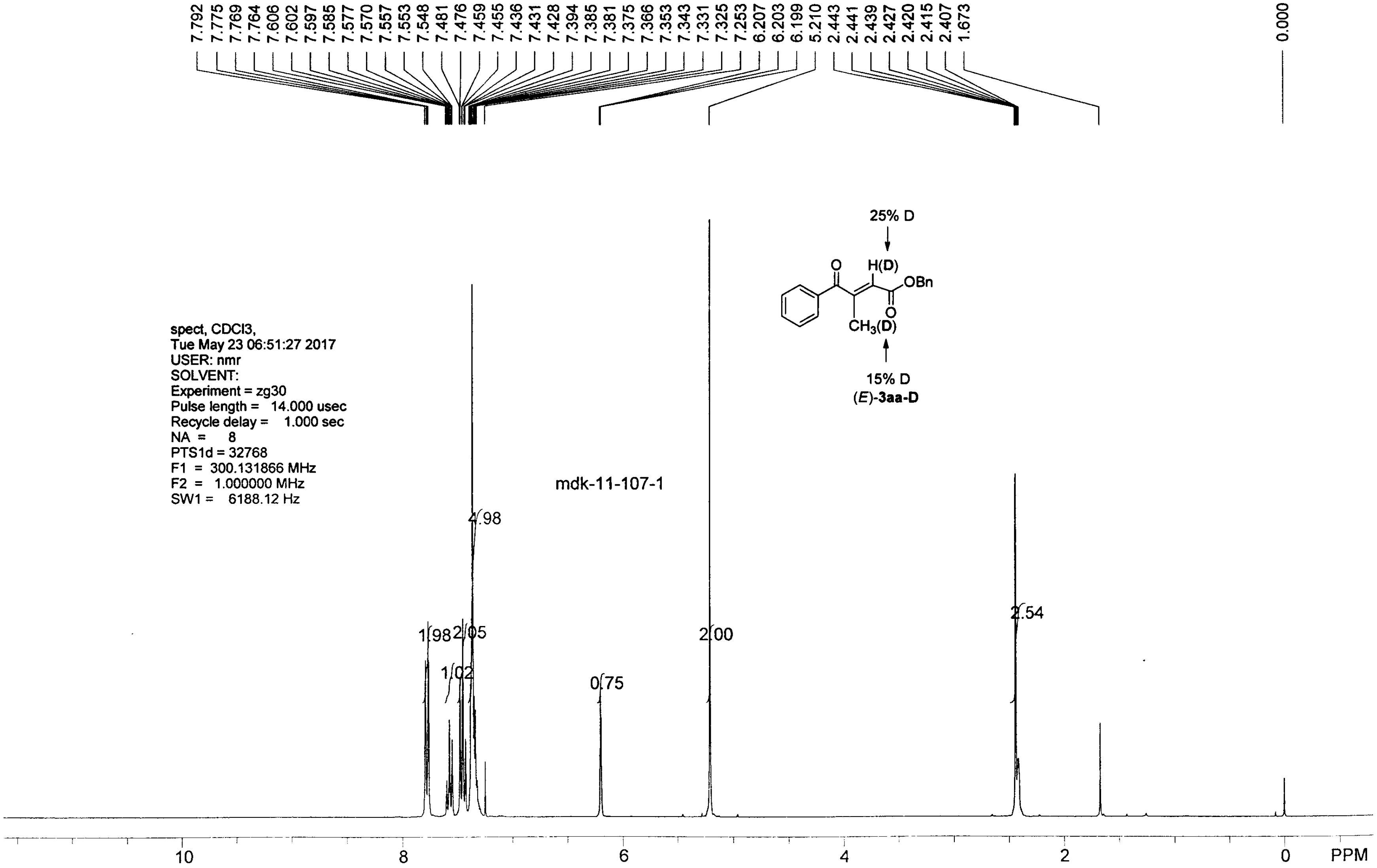
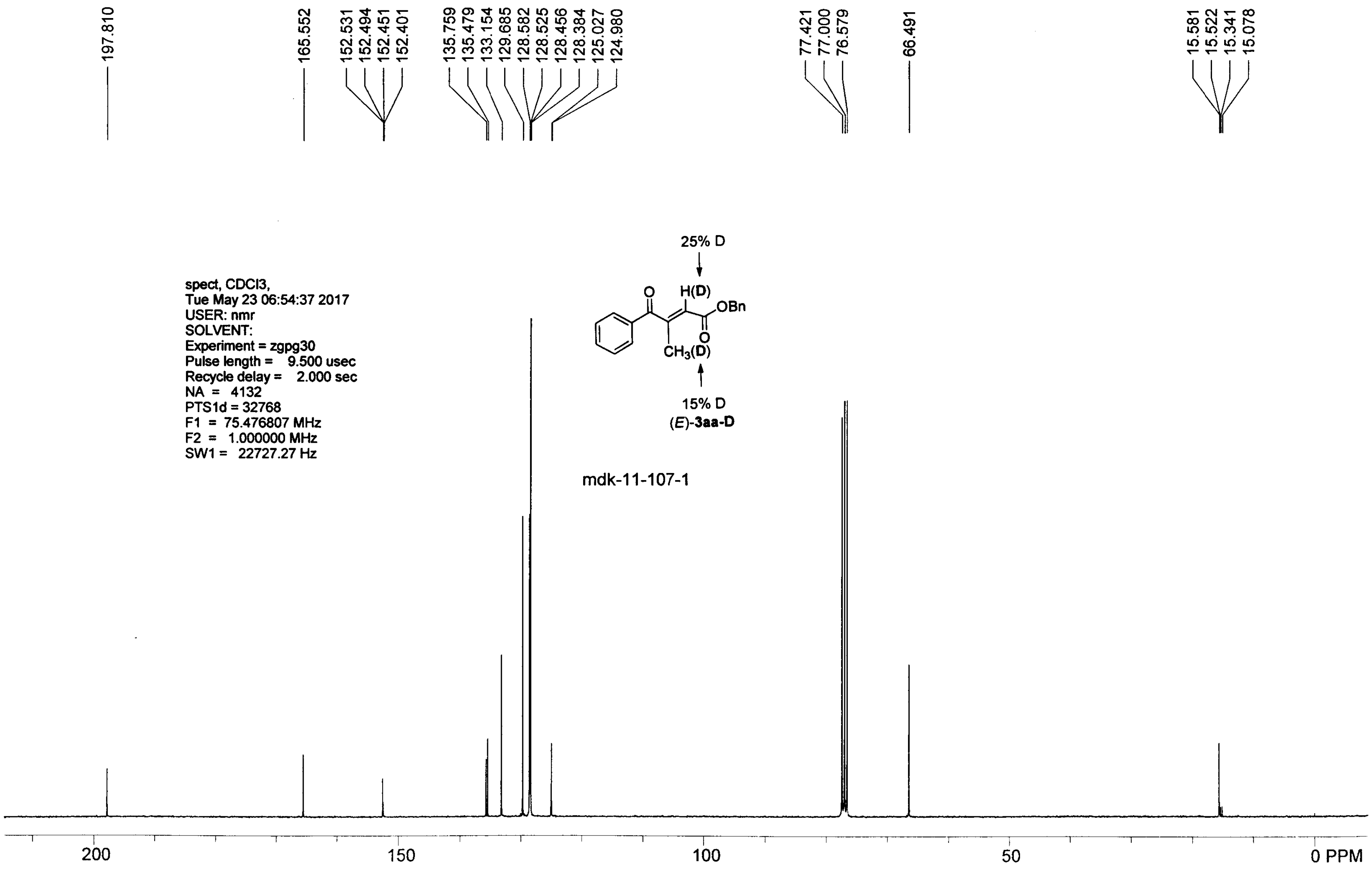
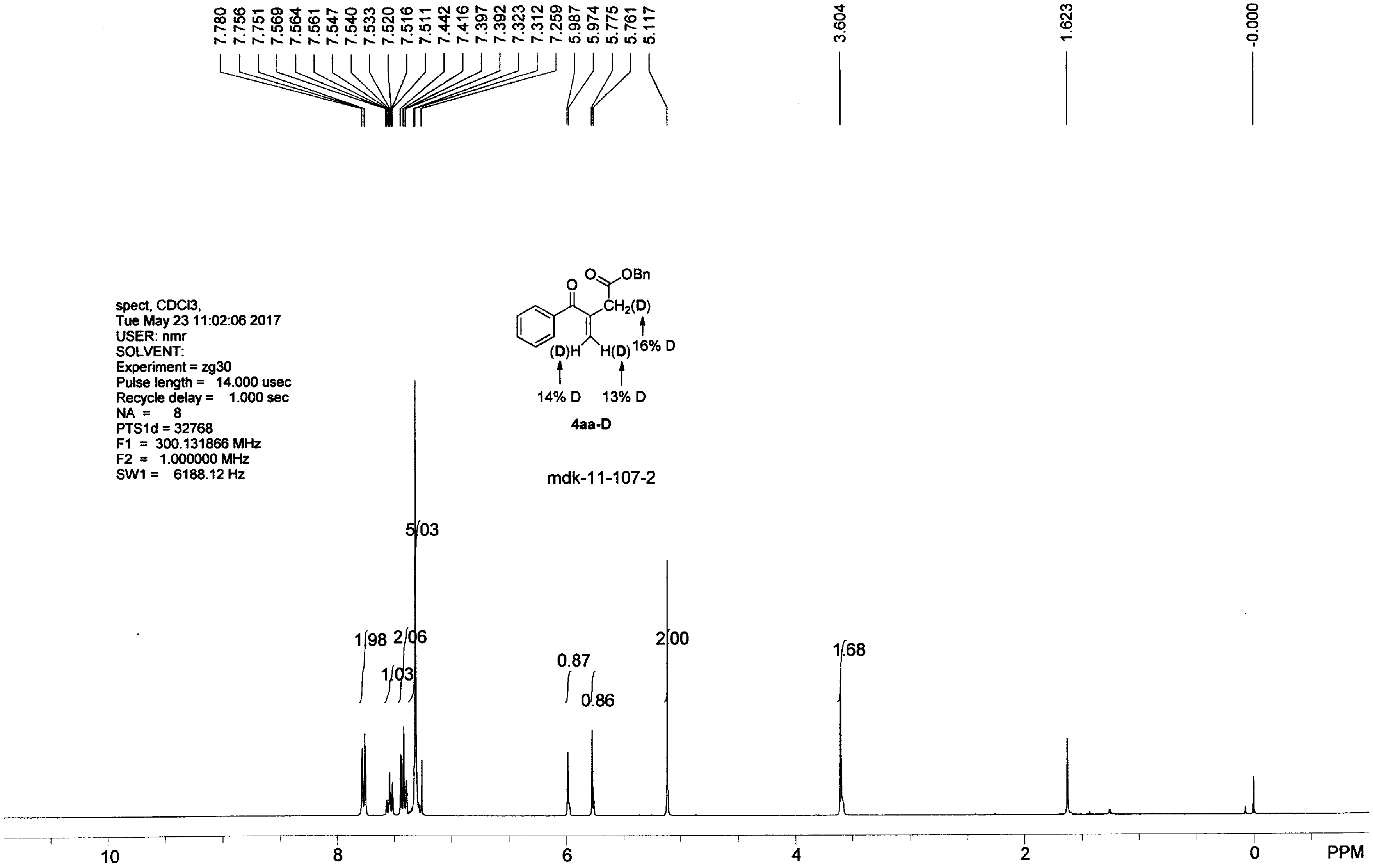
7.563
7.550
7.543
7.536
7.523
7.518
7.514
7.445
7.419
7.394
7.315
7.262
5.990
5.777
5.118
3.608
1.603
0.000
2.00
2.15
1.06
5.18
1.00
1.00
2.06
2.08
10
8
6
4
2
0
PPM

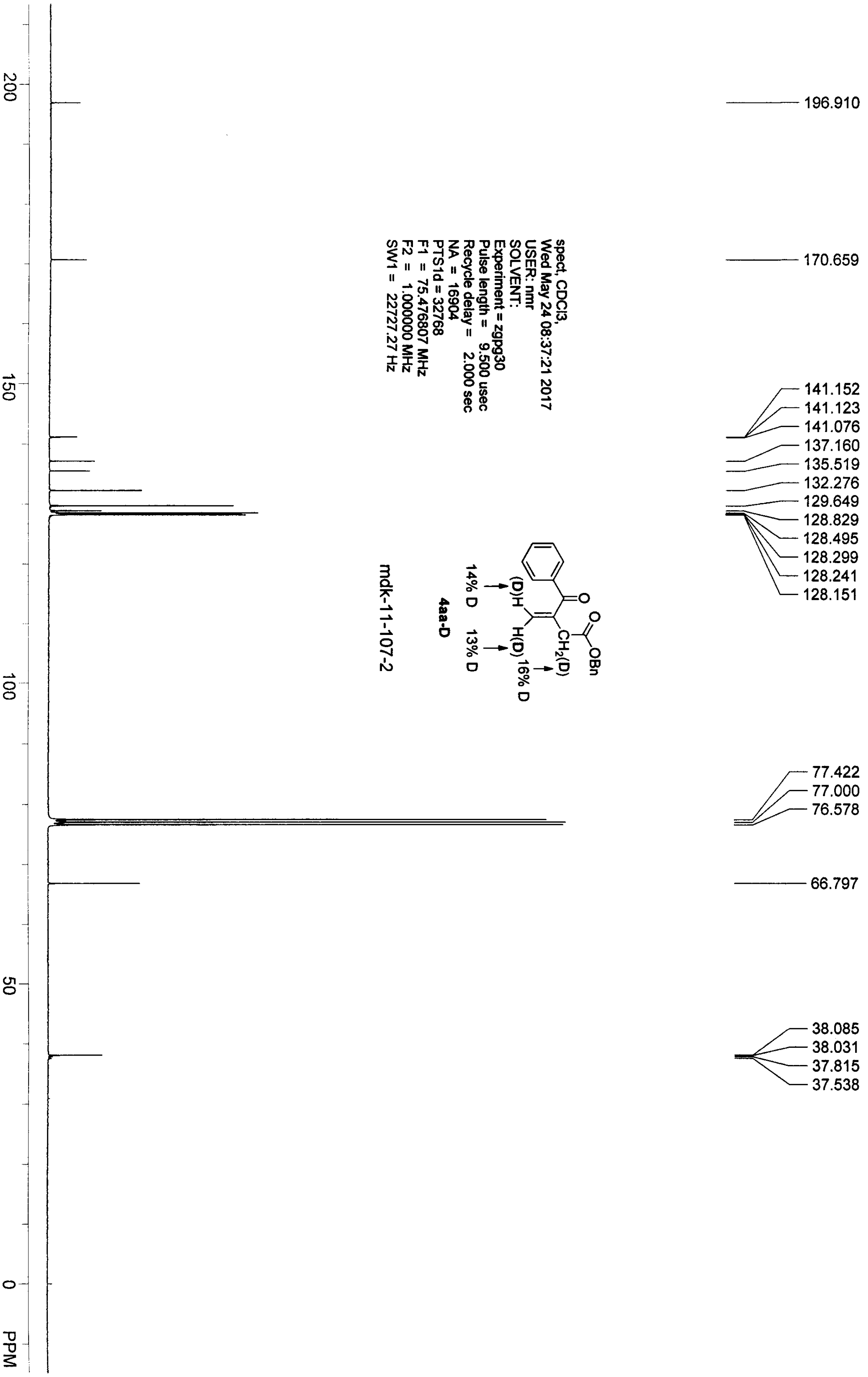

spect, CDCl3,
Fri May 12 08:33:52 2017
USER: nmr
SOLVENT:
Experiment = zgpg30
Pulse length = 9.500 usec
Recycle delay = 2.000 sec
NA = 2863
PTS1d = 32768
F1 = 75.476807 MHz
F2 = 1.000000 MHz
SW1 = 22727.27 Hz
4aa
OBn
mdk-11-086-2
196.936
170.684
141.151
137.156
135.522
132.285
129.668
128.858
128.501
128.307
128.262
128.157
77.422
77.199
77.000
76.579
66.813
38.089
200
150
100
50
0
PPM


7.792
7.775
7.769
7.764
7.606
7.602
7.597
7.585
7.577
7.570
7.557
7.553
7.548
7.481
7.476
7.459
7.455
7.436
7.431
7.428
7.394
7.385
7.381
7.375
7.366
7.353
7.343
7.331
7.325
7.253
6.207
6.203
6.199
5.210
2.443
2.441
2.439
2.427
2.420
2.415
2.407
1.673
0.000
spect, CDCl3,
Tue May 23 06:51:27 2017
USER: nmr
SOLVENT:
Experiment = zg30
Pulse length = 14.000 usec
Recycle delay = 1.000 sec
NA = 8
PTS1d = 32768
F1 = 300.131866 MHz
F2 = 1.000000 MHz
SW1 = 6188.12 Hz
mdk-11-107-1
25% D
O
H(D)
OBn
O
CH3(D)
15% D
(E)-3aa-D
4.98
1.98
2.05
1.02
0.75
2.00
2.54
10
8
6
4
2
0
PPM



spect, CDCl3,
Tue May 23 06:54:37 2017
USER: nmr
SOLVENT:
Experiment = zgpg30
Pulse length = 9.500 usec
Recycle delay = 2.000 sec
NA = 4132
PTS1d = 32768
F1 = 75.476807 MHz
F2 = 1.000000 MHz
SW1 = 22727.27 Hz

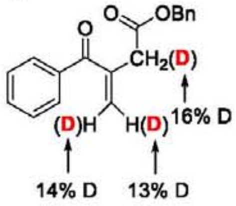

7.780
7.756
7.751
7.569
7.564
7.561
7.547
7.540
7.533
7.520
7.516
7.511
7.442
7.416
7.397
7.392
7.323
7.312
7.259
5.987
5.974
5.775
5.761
5.117
3.604
1.623
-0.000
spect, CDCl3,
Tue May 23 11:02:06 2017
USER: nmr
SOLVENT:
Experiment = zg30
Pulse length = 14.000 usec
Recycle delay = 1.000 sec
NA = 8
PTS1d = 32768
F1 = 300.131866 MHz
F2 = 1.000000 MHz
SW1 = 6188.12 Hz
O
O
OBn
CH₂(D)
(D)H
H(D)
16% D
14% D
13% D
4aa-D
mdk-11-107-2
5.03
1.98
2.06
1.03
0.87
0.86
2.00
1.68
10
8
6
4
2
0
PPM


spect, CDCl3,
Wed May 24 08:37:21 2017
USER: nmr
SOLVENT:
Experiment = zgpg30
Pulse length = 9.500 usec
Recycle delay = 2.000 sec
NA = 16904
PTS1d = 32768
F1 = 75.476807 MHz
F2 = 1.000000 MHz
SW1 = 22727.27 Hz
O
O
OBn
CH2(D)
16% D
(D)H
H(D)
14% D
13% D
4aa-D
mdk-11-107-2
196.910
170.659
141.152
141.123
141.076
137.160
135.519
132.276
129.649
128.829
128.495
128.299
128.241
128.151
77.422
77.000
76.578
66.797
38.085
38.031
37.815
37.538
200
150
100
50
0
PPM

National Center for Organic Mass Spectrometry in Shanghai
Shanghai Institute of Organic Chemistry
Chinese Academic of Sciences
MS DATA REPORT

Instrument: Agilent UHD Accurate Mass Q-TOF LC-MS

Sample Serial Number: mdk-11-107-2

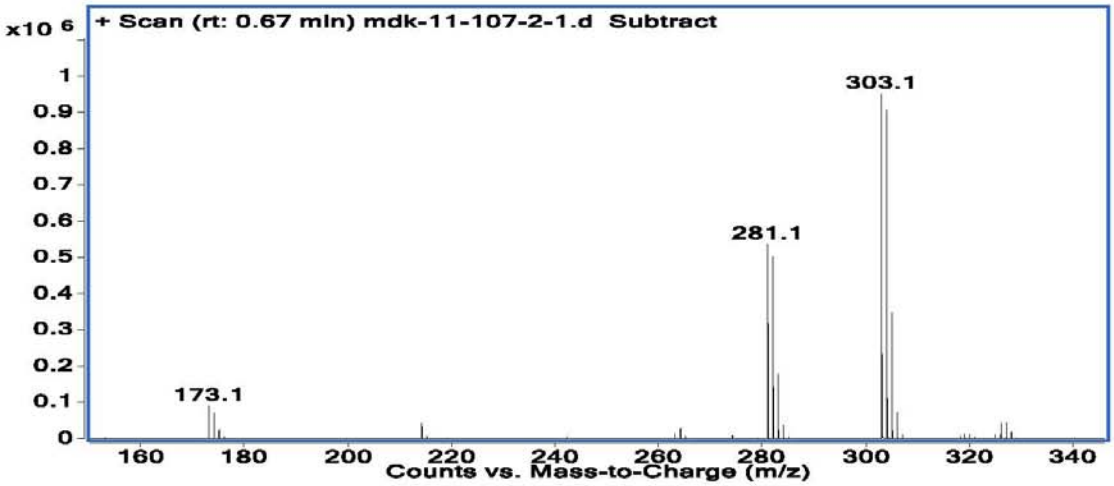


**4aa-D**

Operator: Wang, Jiawei

Date: 2018/05/22

Operation Mode: ESI-Positive



National Center for Organic Mass Spectrometry in Shanghai
Shanghai Institute of Organic Chemistry
Chinese Academic of Sciences
HIGH RESOLUTION MS REPORT

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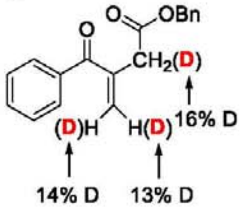
Instrument: Agilent UHD Accurate Mass Q-TOF LC-MS

Sample Serial Number: mdk-11-107-2



**4aa-D**

Operator: Wang, Jiawei

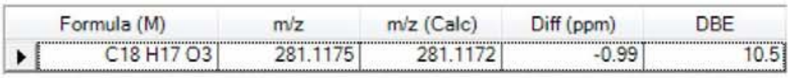
Date: 2018/05/22

Operation Mode: ESI-Positive

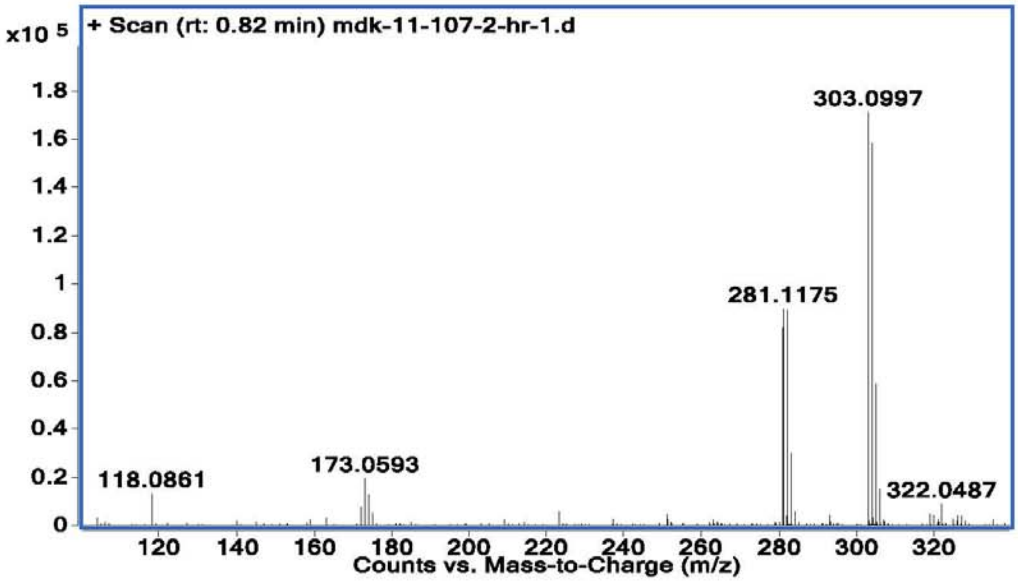
Single Mass Analysis

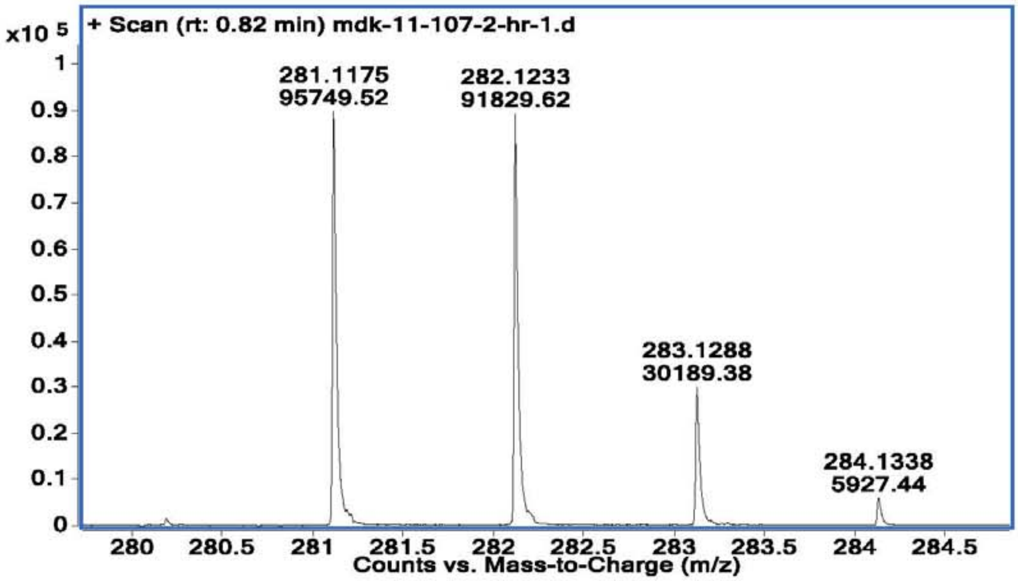
Tolerance = 5.0 ppm / DBE: min = 0, max = 50.0

C: 0-80; H: 0-100; O: 0-10; Na: 0-1; D: 0-5

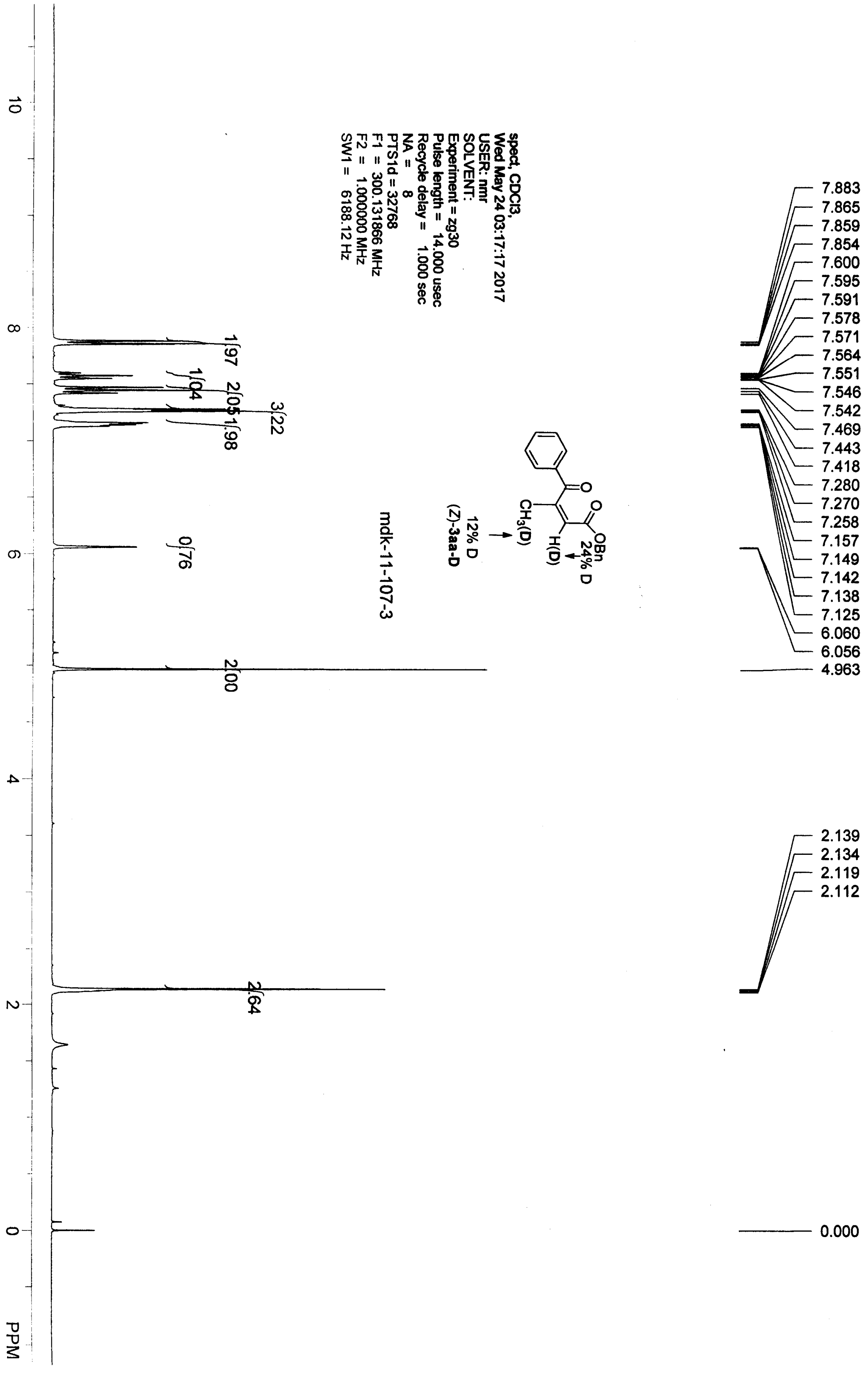


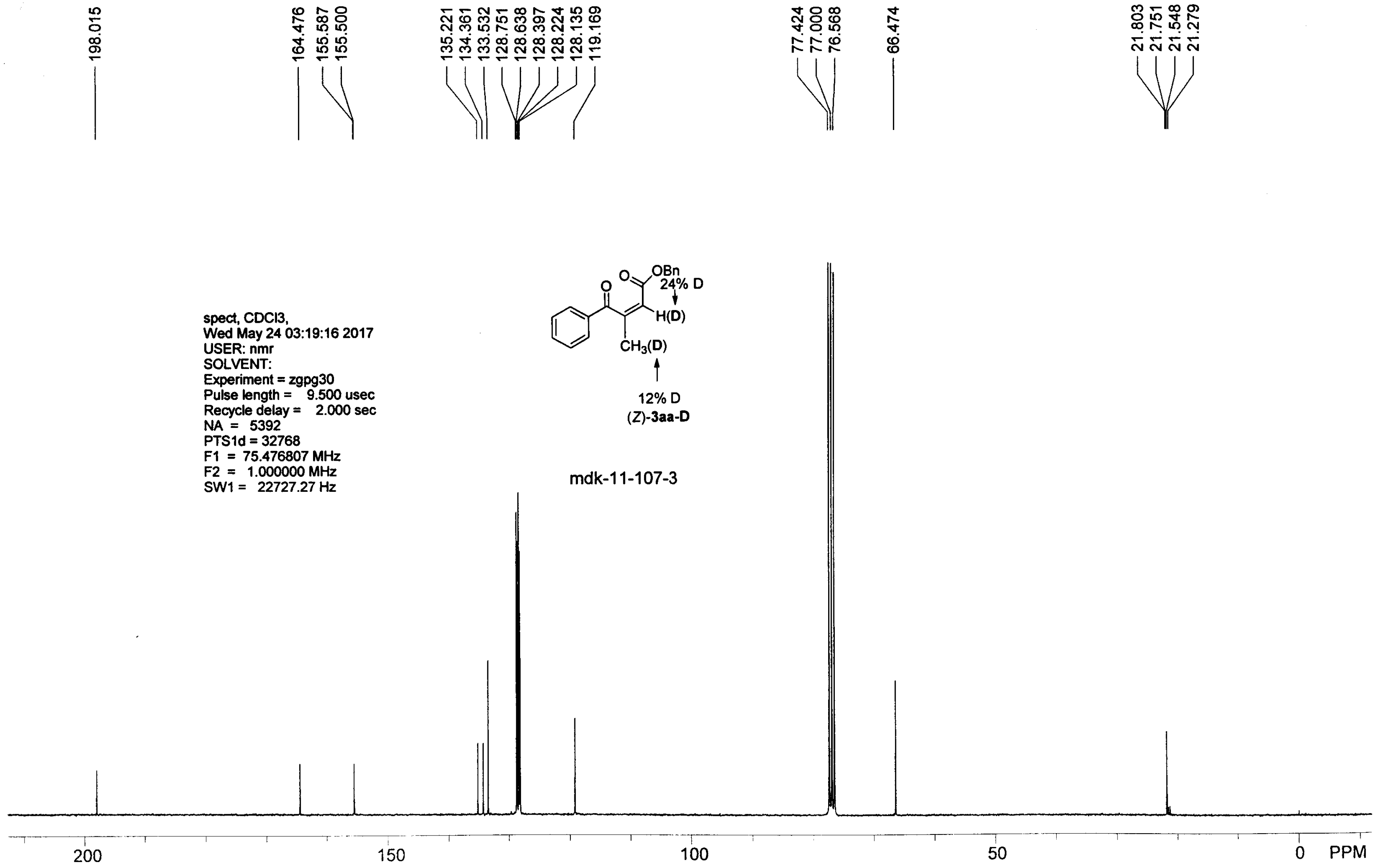
| Formula (M) | m/z | m/z (Calc) | Diff (ppm) | DBE |
|---|---|---|---|---|
| C18 H17 O3 | 281.1175 | 281.1172 | -0.99 | 10.5 |





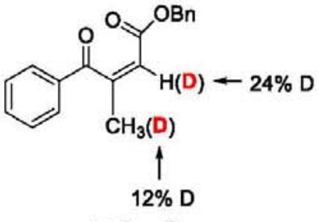
**Reference ions: *m/z* 118.0861 (calc.118.0863`); *m/z* 322.0487 (calc.322.0481)**


spect, CDCl3,
Wed May 24 03:17:17 2017
USER: nmr
SOLVENT:
Experiment = zg30
Pulse length = 14.000 usec
Recycle delay = 1.000 sec
NA = 8
PTS1d = 32768
F1 = 300.131866 MHz
F2 = 1.000000 MHz
SW1 = 6188.12 Hz
O
OBn
O
24% D
H(D)
CH3(D)
12% D
(Z)-3aa-D
mdk-11-107-3
7.883
7.865
7.859
7.854
7.600
7.595
7.591
7.578
7.571
7.564
7.551
7.546
7.542
7.469
7.443
7.418
7.280
7.270
7.258
7.157
7.149
7.142
7.138
7.125
6.060
6.056
4.963
2.139
2.134
2.119
2.112
0.000
1.97
1.04
2.05
3.22
1.98
0.76
2.00
2.64
10
8
6
4
2
0
PPM


198.015
164.476
155.587
155.500
135.221
134.361
133.532
128.751
128.638
128.397
128.224
128.135
119.169
77.424
77.000
76.568
66.474
21.803
21.751
21.548
21.279
spect, CDCl3,
Wed May 24 03:19:16 2017
USER: nmr
SOLVENT:
Experiment = zgpg30
Pulse length = 9.500 usec
Recycle delay = 2.000 sec
NA = 5392
PTS1d = 32768
F1 = 75.476807 MHz
F2 = 1.000000 MHz
SW1 = 22727.27 Hz
O
O
OBn
24% D
H(D)
CH3(D)
12% D
(Z)-3aa-D
mdk-11-107-3
200
150
100
50
0
PPM

Instrument: Agilent UHD Accurate Mass Q-TOF LC-MS

Sample Serial Number: mdk-11-107-3

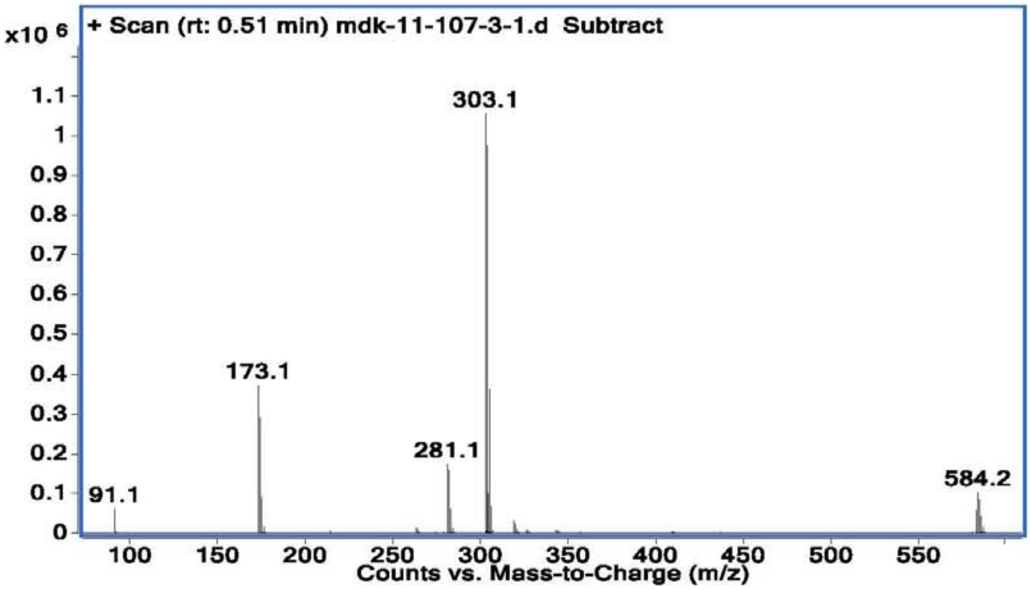


(*Z*)-**3aa-D**

Operator: Wang, Jiawei

Date: 2018/05/22

Operation Mode: ESI-Positive

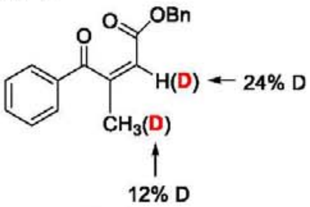


National Center for Organic Mass Spectrometry in Shanghai
Shanghai Institute of Organic Chemistry
Chinese Academic of Sciences

## HIGH RESOLUTION MS REPORT

Instrument: Agilent UHD Accurate Mass Q-TOF LC-MS

Sample Serial Number: mdk-11-107-3



**(*Z*)-3aa-D**

Operator: Wang, Jiawei

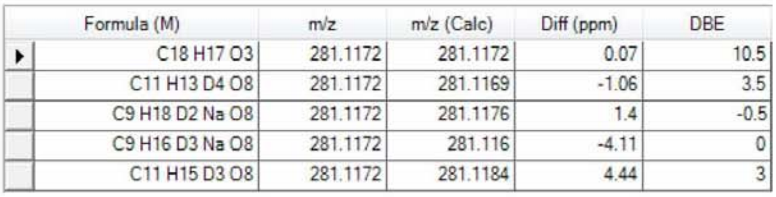
Date: 2018/05/22

Operation Mode: ESI-Positive

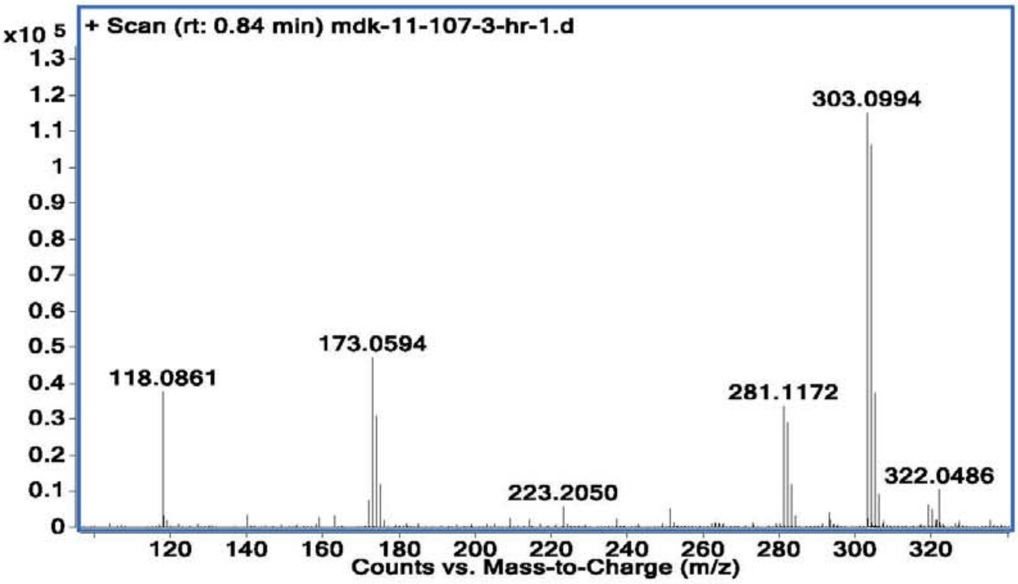
Single Mass Analysis

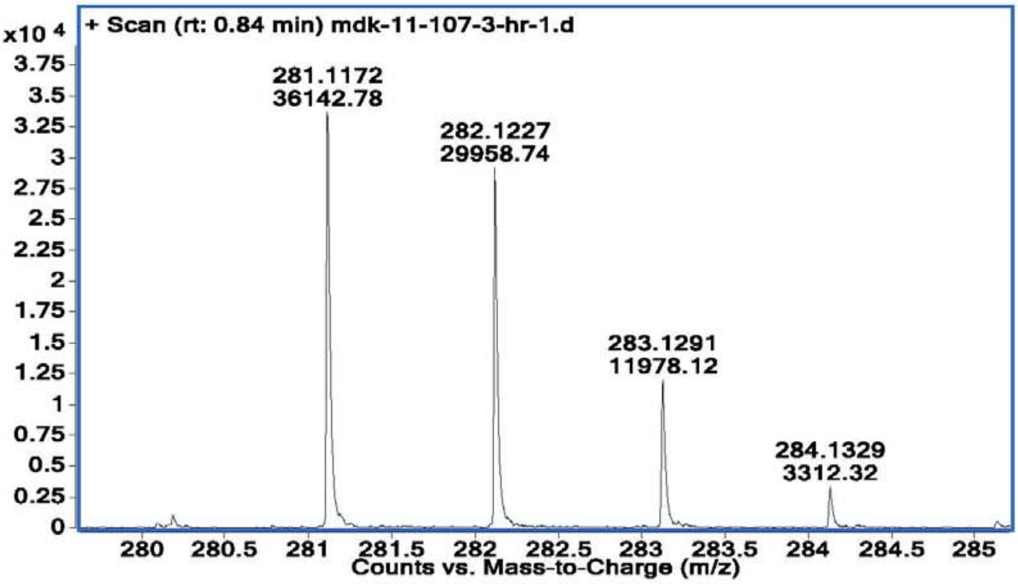
Tolerance = 5.0 ppm / DBE: min = 0, max = 50.0

C: 0-80; H: 0-100; O: 0-10; Na: 0-1; D: 0-5

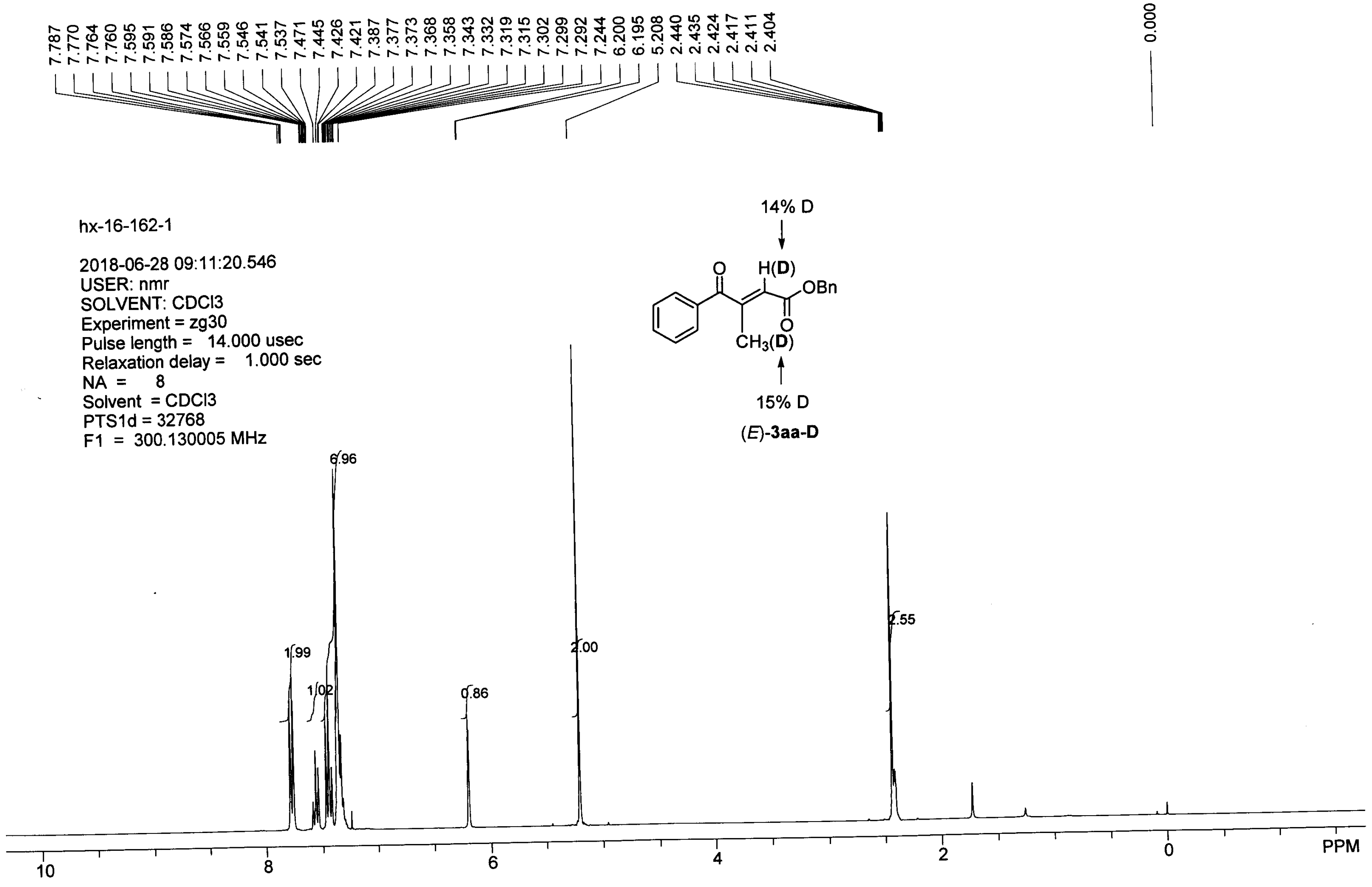


| Formula (M) | m/z | m/z (Calc) | Diff (ppm) | DBE |
|---|---|---|---|---|
| C18 H17 O3 | 281.1172 | 281.1172 | 0.07 | 10.5 |
| C11 H13 D4 O8 | 281.1172 | 281.1169 | -1.06 | 3.5 |
| C9 H18 D2 Na O8 | 281.1172 | 281.1176 | 1.4 | -0.5 |
| C9 H16 D3 Na O8 | 281.1172 | 281.116 | -4.11 | 0 |
| C11 H15 D3 O8 | 281.1172 | 281.1184 | 4.44 | 3 |

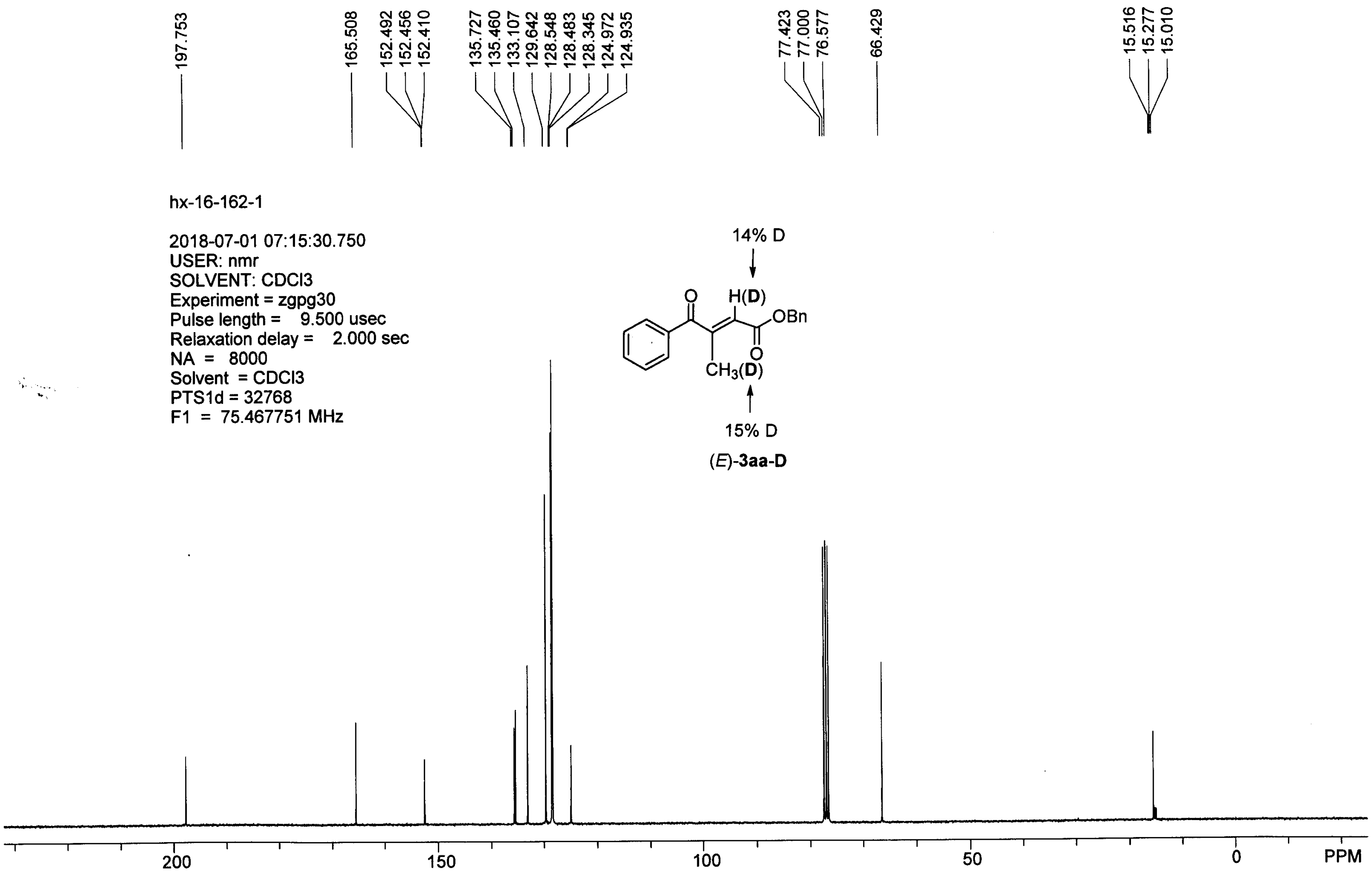




**Reference ions:** *m/z* 118.0861 (calc.118.0863); *m/z* 322.0486 (calc.322.0481)


7.787
7.770
7.764
7.760
7.595
7.591
7.586
7.574
7.566
7.559
7.546
7.541
7.537
7.471
7.445
7.426
7.421
7.387
7.377
7.373
7.368
7.358
7.343
7.332
7.319
7.315
7.302
7.299
7.292
7.244
6.200
6.195
5.208
2.440
2.435
2.424
2.417
2.411
2.404
0.000
hx-16-162-1
2018-06-28 09:11:20.546
USER: nmr
SOLVENT: CDCl3
Experiment = zg30
Pulse length = 14.000 usec
Relaxation delay = 1.000 sec
NA = 8
Solvent = CDCl3
PTS1d = 32768
F1 = 300.130005 MHz
14% D
15% D
H(D)
CH3(D)
OBn
O
1.99
1.02
6.96
0.86
2.00
2.55
10
8
6
4
2
0
PPM

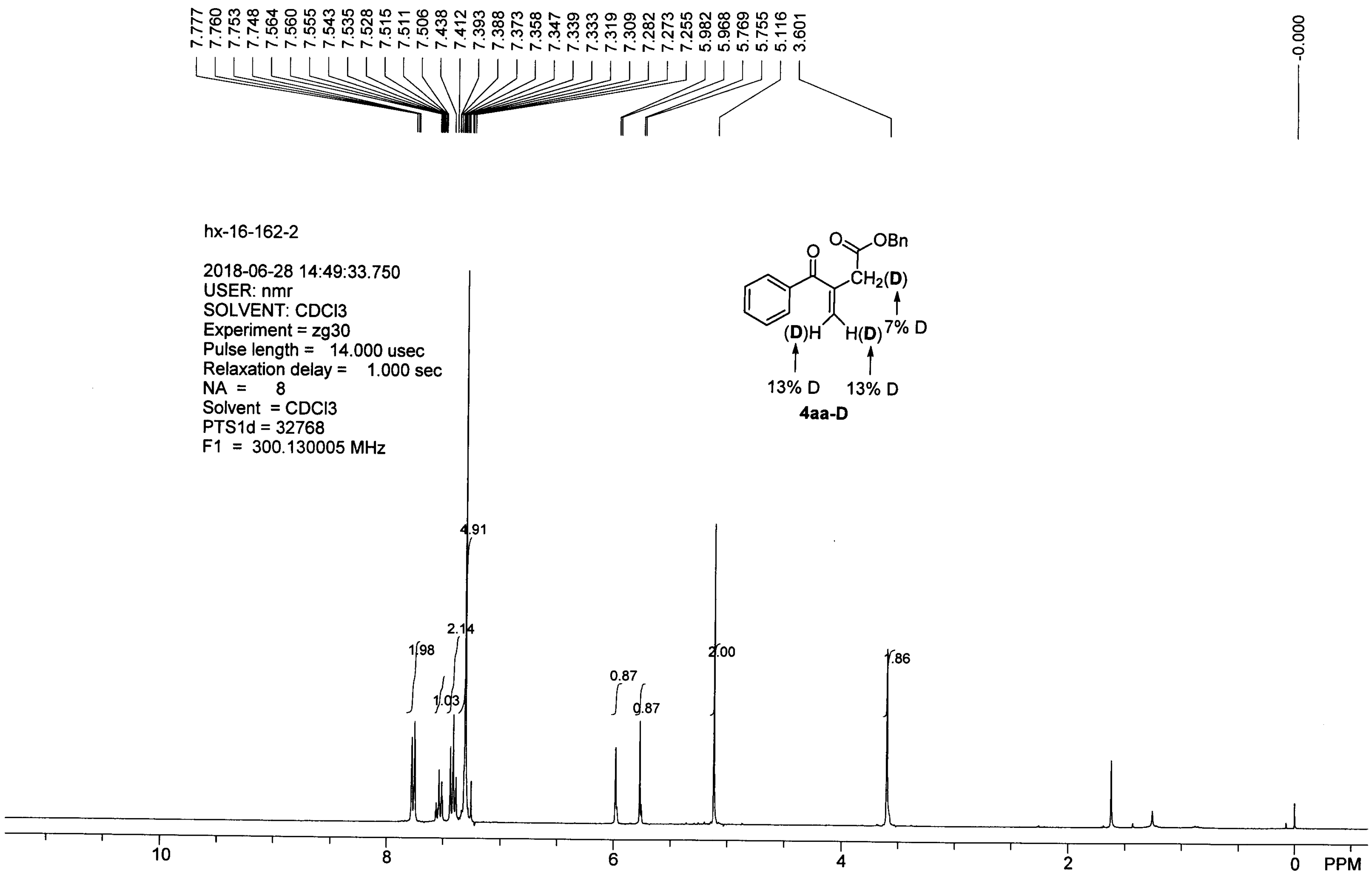
(*E*)-**3aa-D**



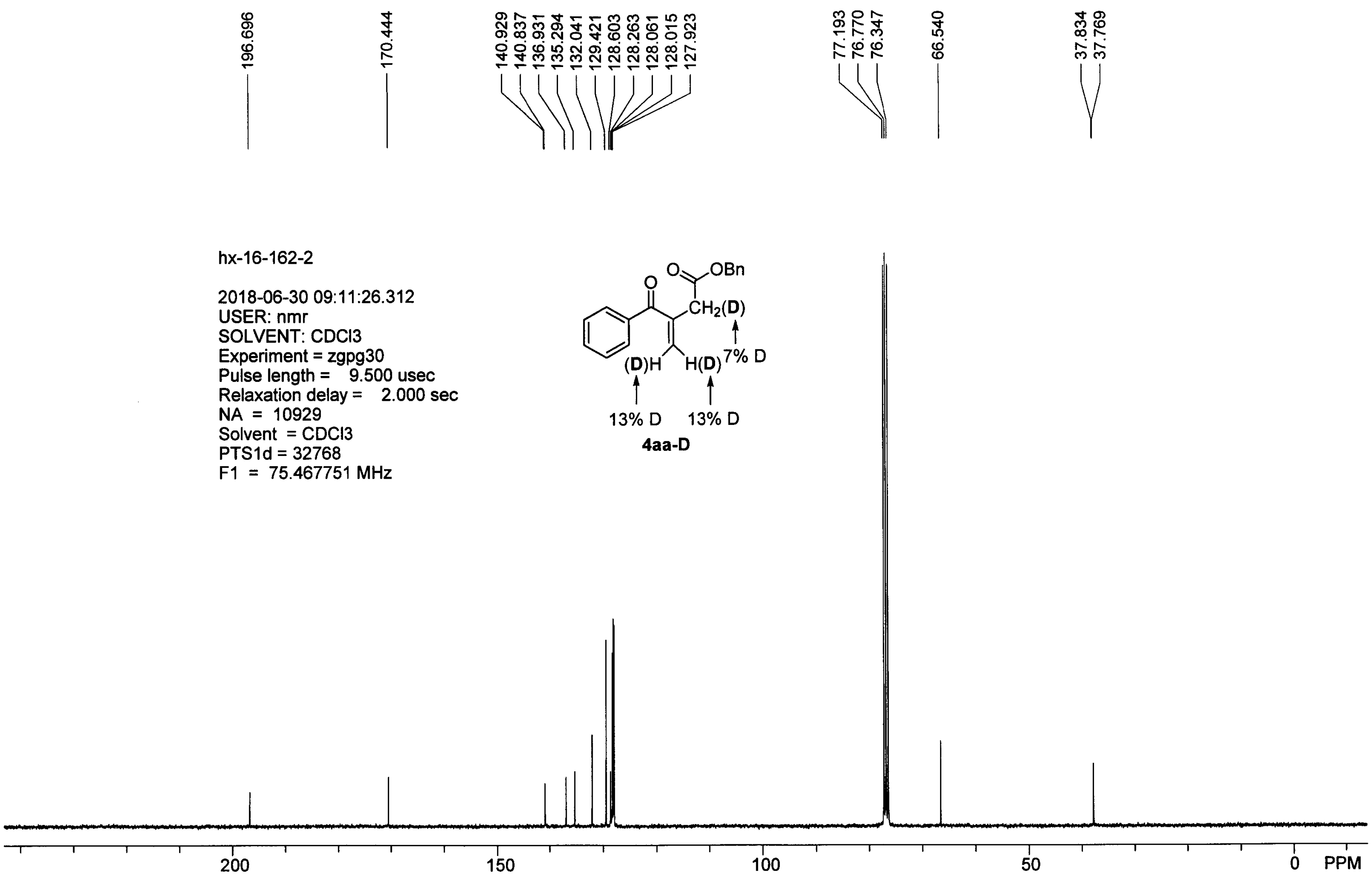
hx-16-162-1

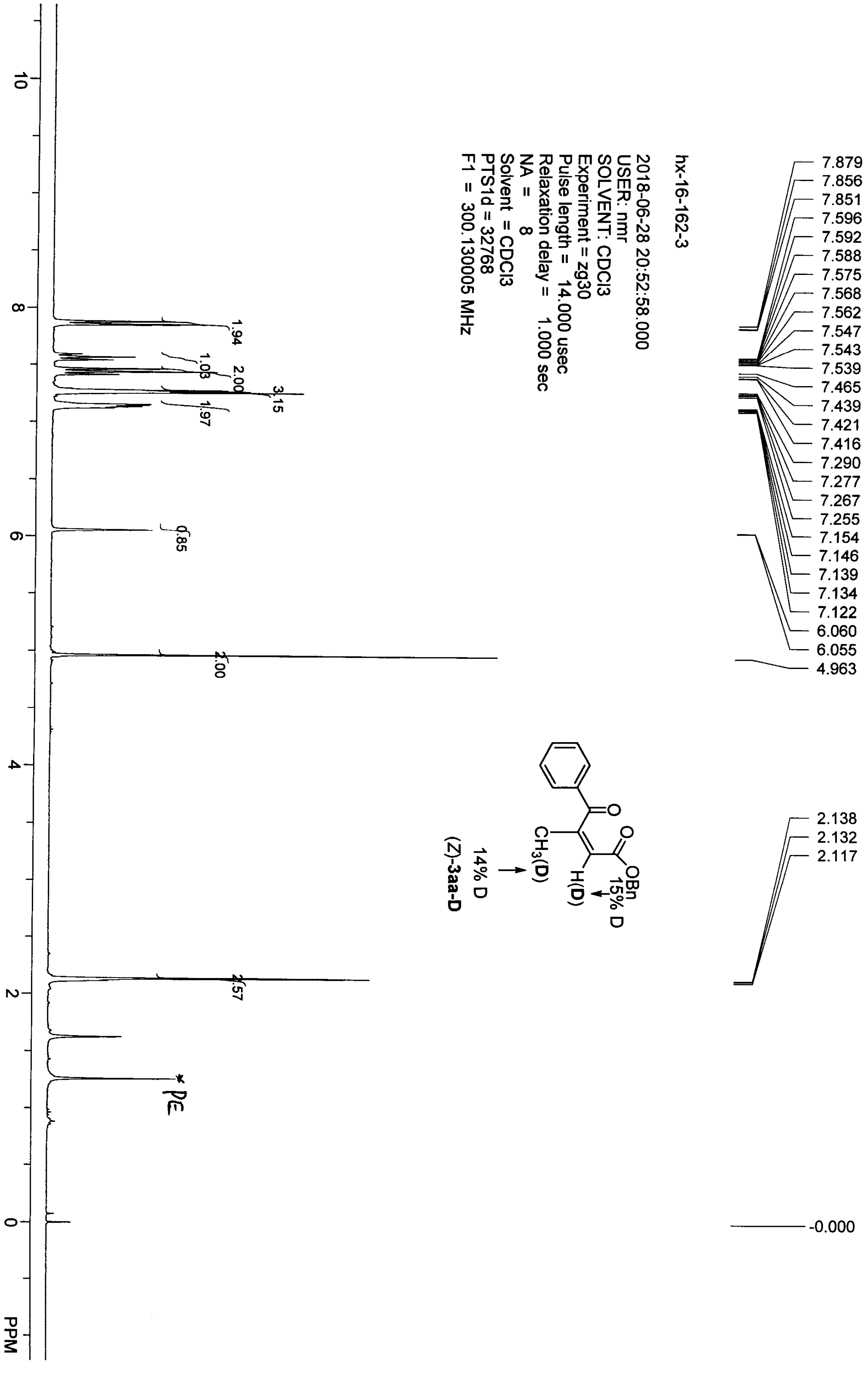
2018-07-01 07:15:30.750
USER: nmr
SOLVENT: CDCl3
Experiment = zgpg30
Pulse length = 9.500 usec
Relaxation delay = 2.000 sec
NA = 8000
Solvent = CDCl3
PTS1d = 32768
F1 = 75.467751 MHz

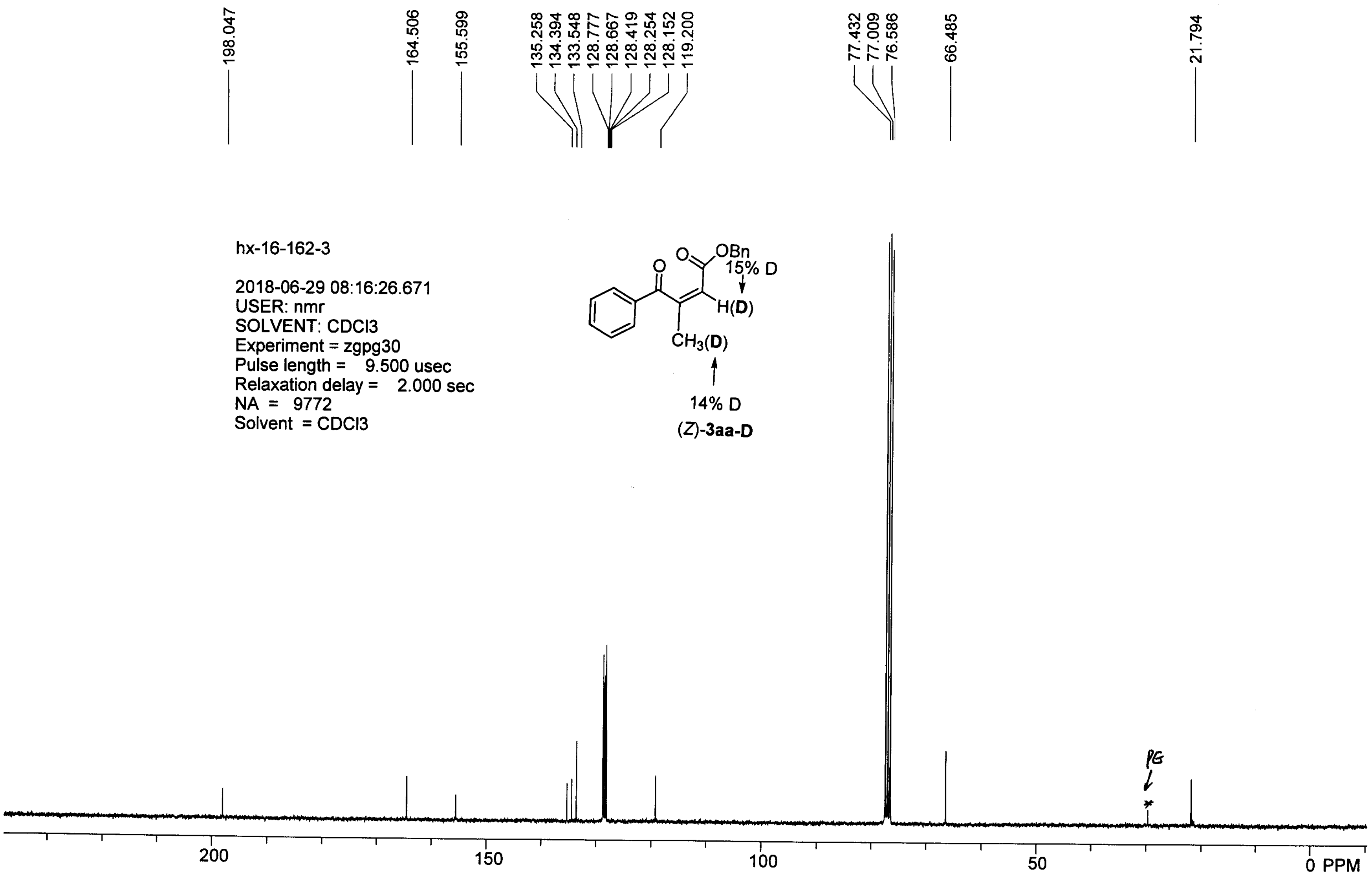
(*E*)-**3aa-D**

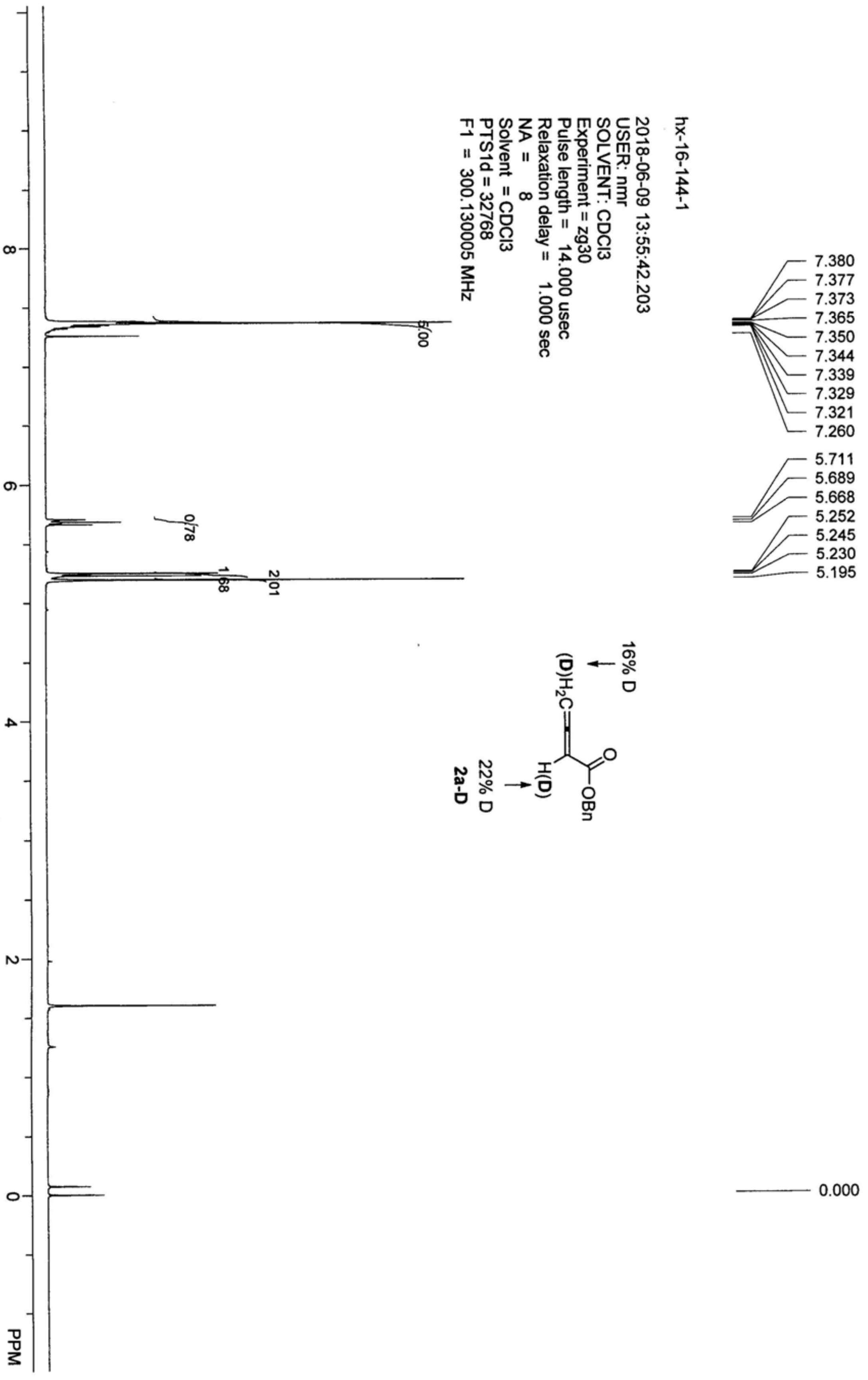

7.777
7.760
7.753
7.748
7.564
7.560
7.555
7.543
7.535
7.528
7.515
7.511
7.506
7.438
7.412
7.393
7.388
7.373
7.358
7.347
7.339
7.333
7.319
7.309
7.282
7.273
7.255
5.982
5.968
5.769
5.755
5.116
3.601
-0.000
hx-16-162-2
2018-06-28 14:49:33.750
USER: nmr
SOLVENT: CDCl3
Experiment = zg30
Pulse length = 14.000 usec
Relaxation delay = 1.000 sec
NA = 8
Solvent = CDCl3
PTS1d = 32768
F1 = 300.130005 MHz
O
O
OBn
CH2(D)
7% D
(D)H
H(D)
13% D
13% D
1.98
1.03
2.14
4.91
0.87
0.87
2.00
1.86
10
8
6
4
2
0
PPM

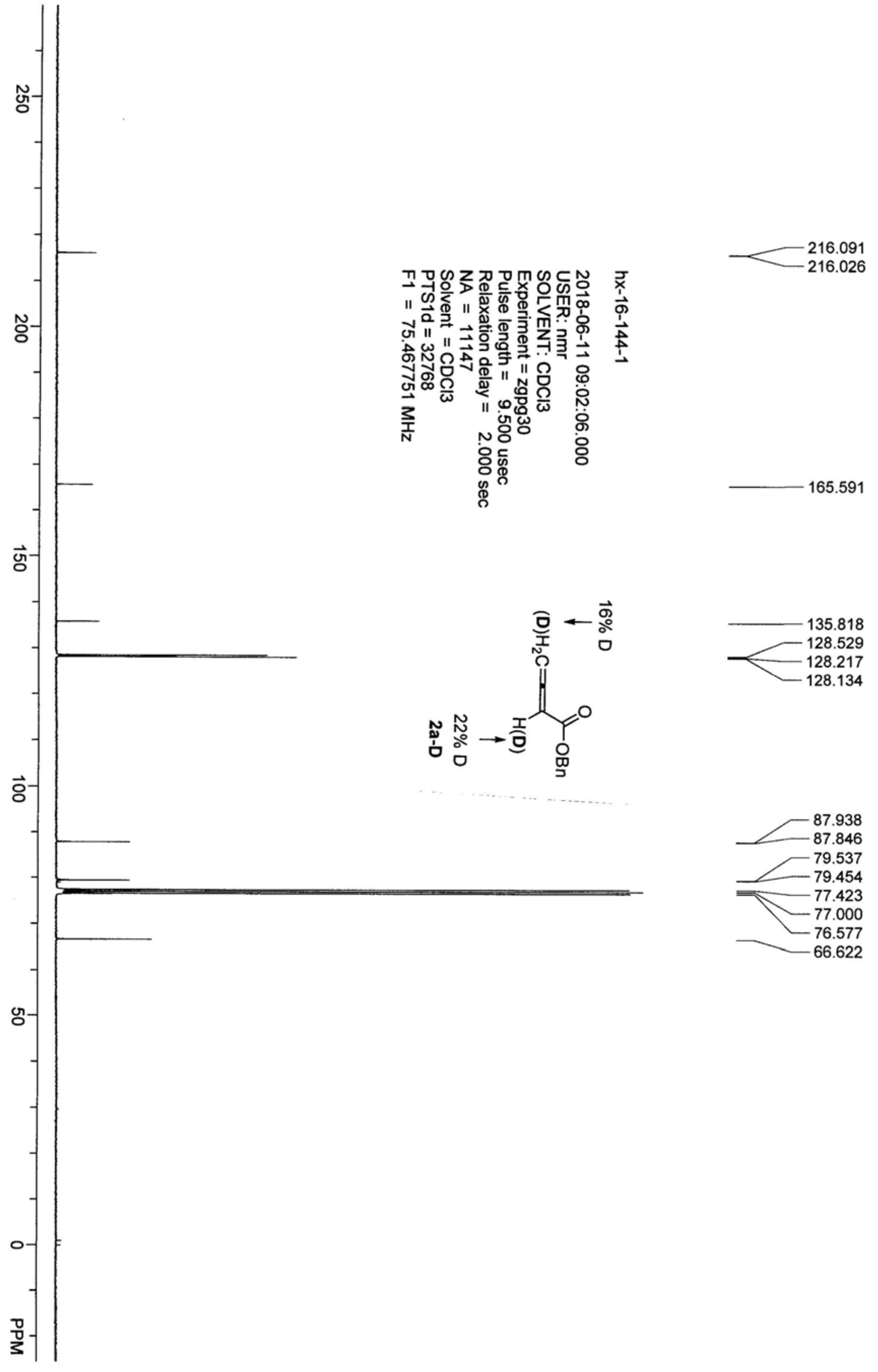
**4aa-D**

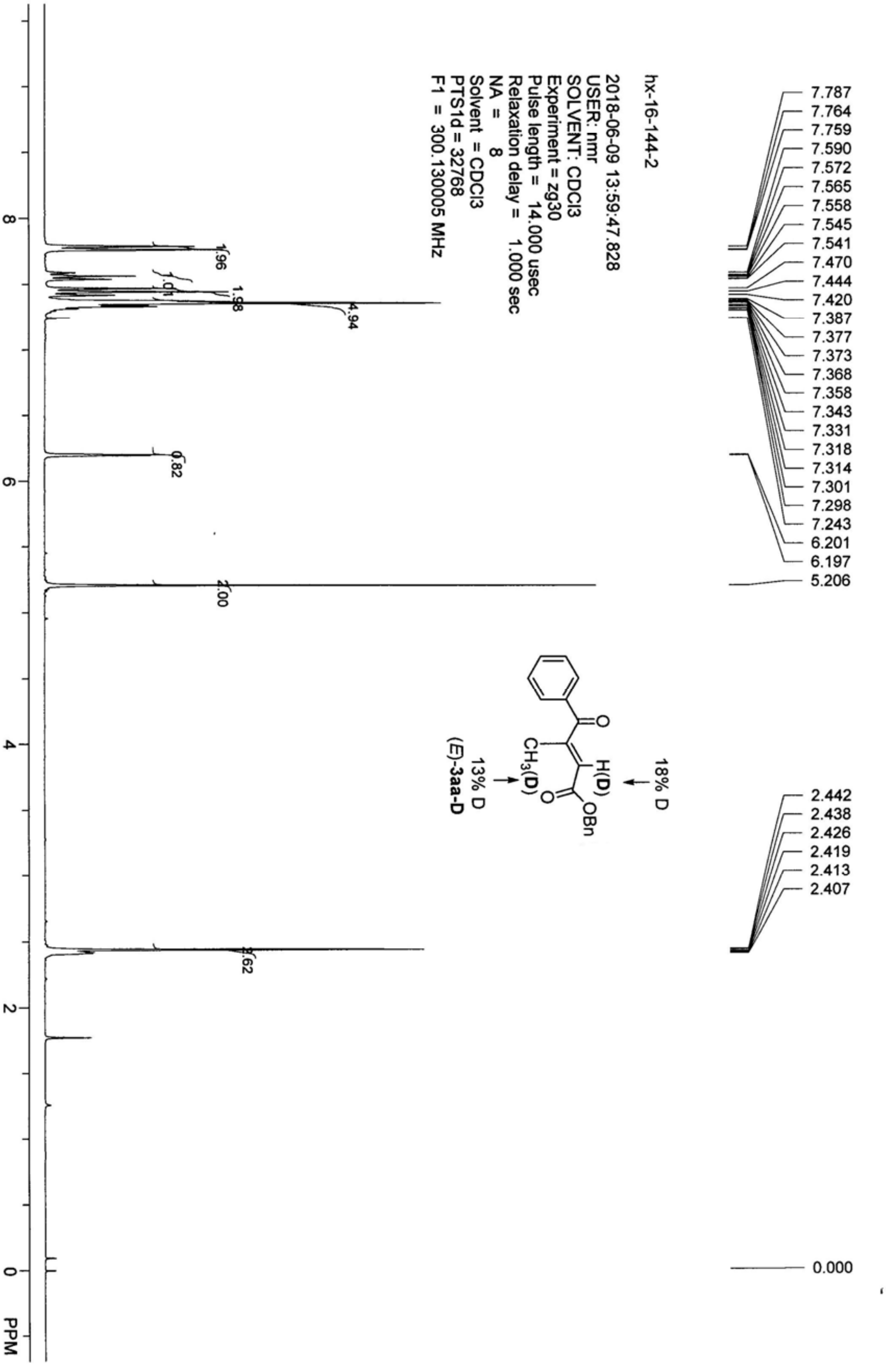

196.696
170.444
140.929
140.837
136.931
135.294
132.041
129.421
128.603
128.263
128.061
128.015
127.923
77.193
76.770
76.347
66.540
37.834
37.769
hx-16-162-2
2018-06-30 09:11:26.312
USER: nmr
SOLVENT: CDCl3
Experiment = zgpg30
Pulse length = 9.500 usec
Relaxation delay = 2.000 sec
NA = 10929
Solvent = CDCl3
PTS1d = 32768
F1 = 75.467751 MHz
O
O
OBn
CH2(D)
7% D
(D)H
H(D)
13% D
13% D
4aa-D
200
150
100
50
0
PPM

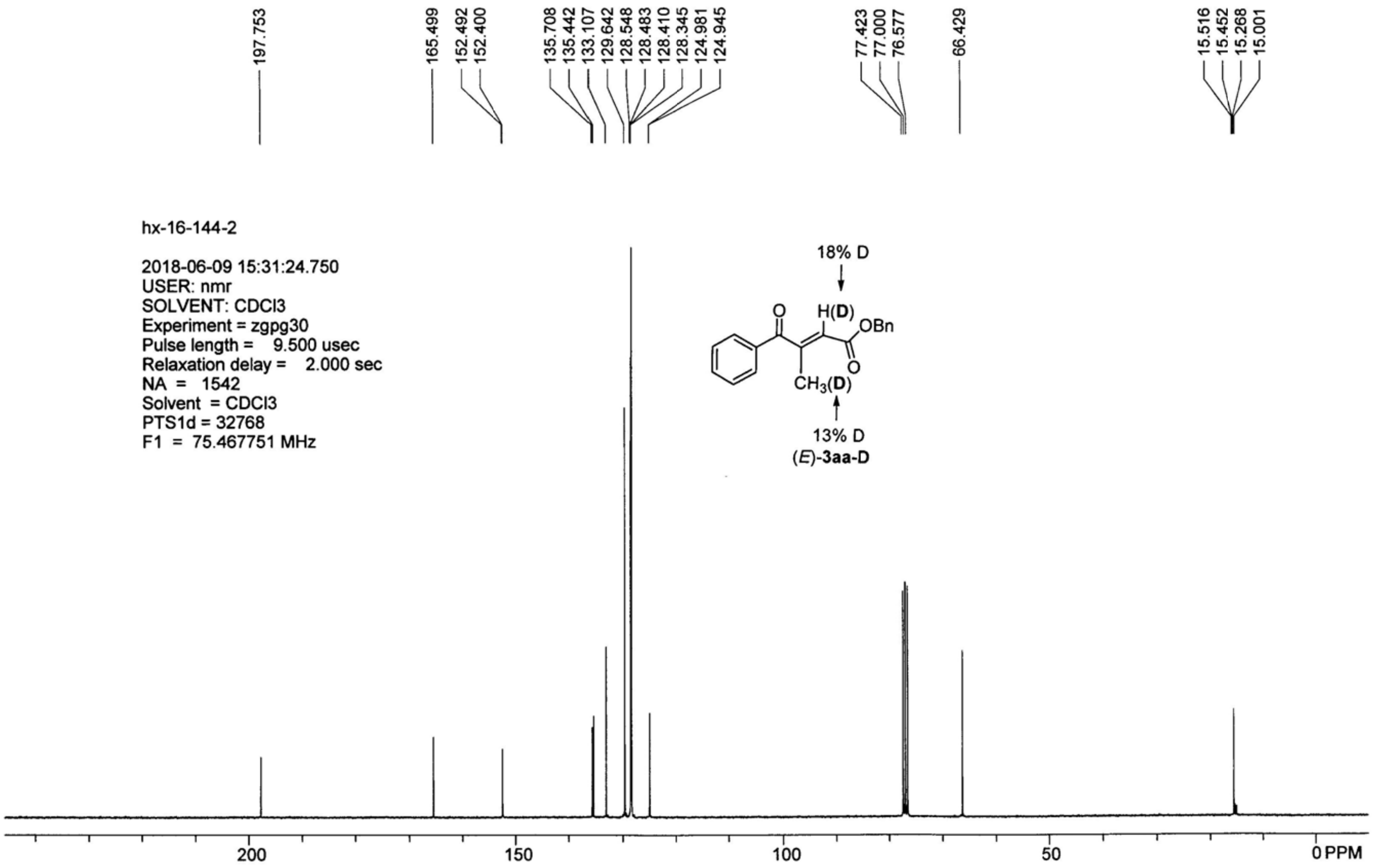

hx-16-162-3
2018-06-28 20:52:58.000
USER: nmr
SOLVENT: CDCl3
Experiment = zg30
Pulse length = 14.000 usec
Relaxation delay = 1.000 sec
NA = 8
Solvent = CDCl3
PTS1d = 32768
F1 = 300.130005 MHz
7.879
7.856
7.851
7.596
7.592
7.588
7.575
7.568
7.562
7.547
7.543
7.539
7.465
7.439
7.421
7.416
7.290
7.277
7.267
7.255
7.154
7.146
7.139
7.134
7.122
6.060
6.055
4.963
2.138
2.132
2.117
-0.000
1.94
1.03
2.00
3.15
1.97
0.85
2.00
2.57
*PE
10
8
6
4
2
0
PPM
OBn
15% D
H(D)
CH3(D)
14% D
(Z)-3aa-D

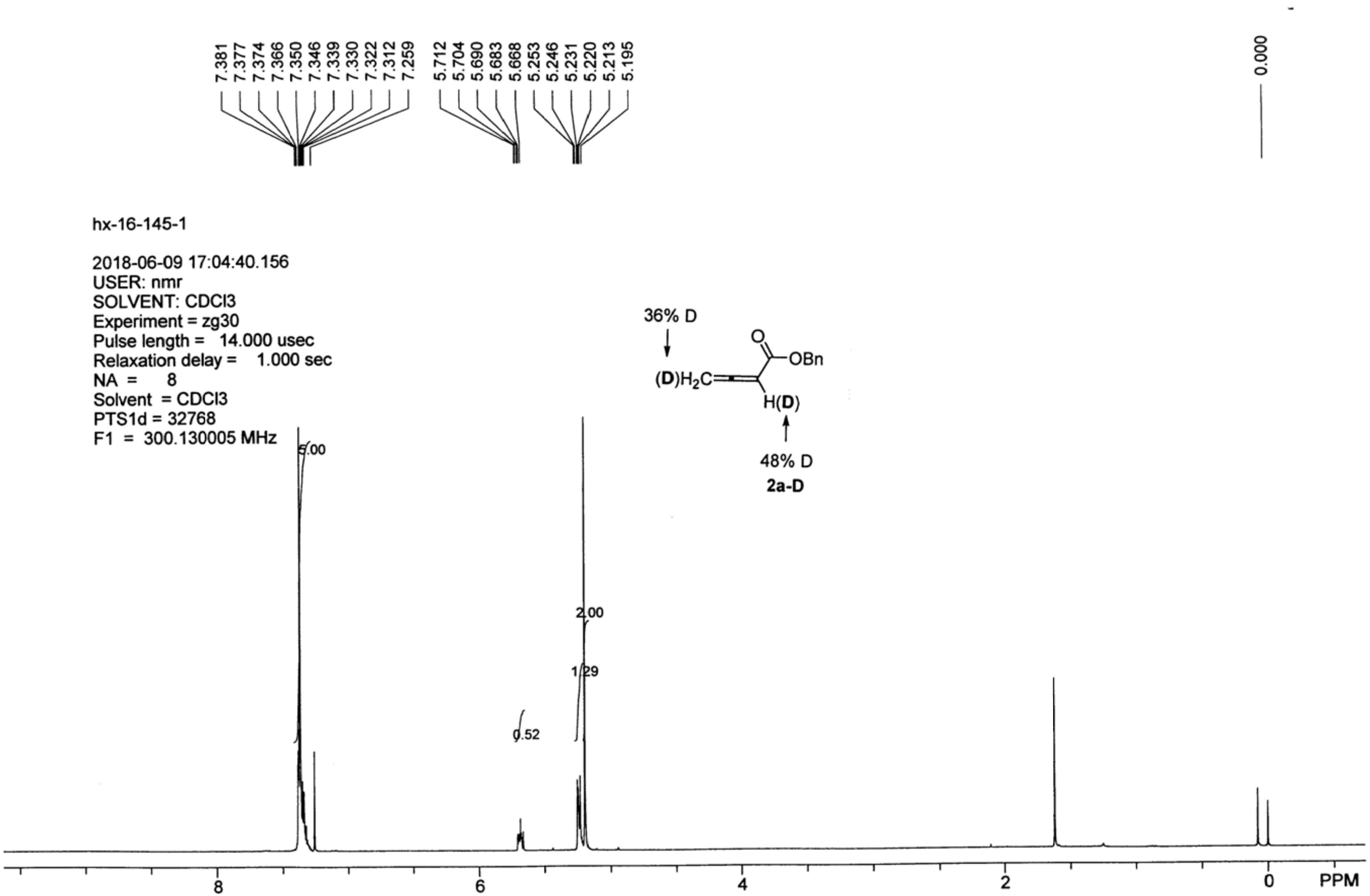

198.047
164.506
155.599
135.258
134.394
133.548
128.777
128.667
128.419
128.254
128.152
119.200
77.432
77.009
76.586
66.485
21.794
hx-16-162-3
2018-06-29 08:16:26.671
USER: nmr
SOLVENT: CDCl3
Experiment = zgpg30
Pulse length = 9.500 usec
Relaxation delay = 2.000 sec
NA = 9772
Solvent = CDCl3
O
O
OBn
15% D
H(D)
CH3(D)
14% D
(Z)-3aa-D
PG
*
200
150
100
50
0 PPM

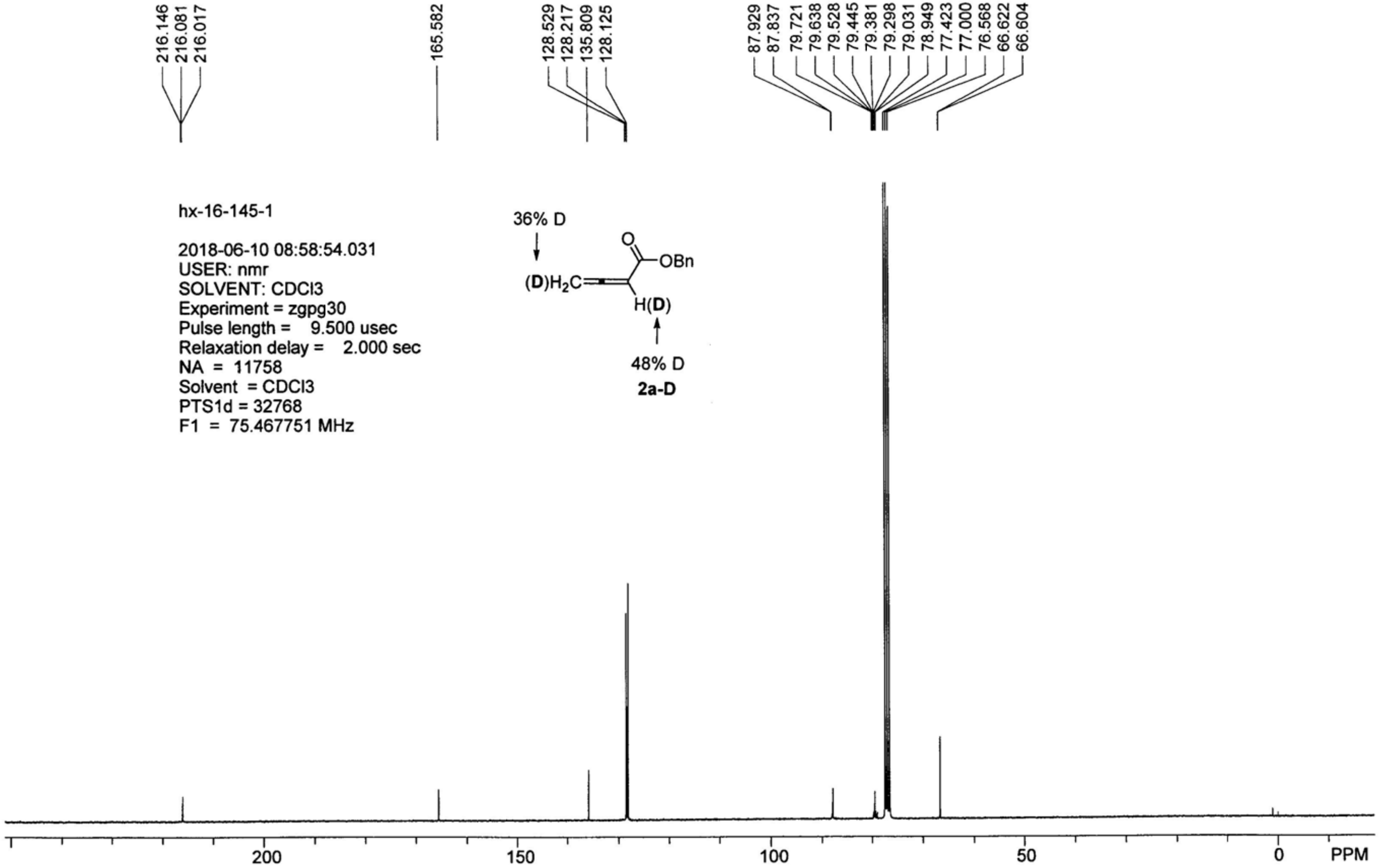

hx-16-144-1
2018-06-09 13:55:42.203
USER: nmr
SOLVENT: CDCl3
Experiment = zg30
Pulse length = 14.000 usec
Relaxation delay = 1.000 sec
NA = 8
Solvent = CDCl3
PTS1d = 32768
F1 = 300.130005 MHz
7.380
7.377
7.373
7.365
7.350
7.344
7.339
7.329
7.321
7.260
5.711
5.689
5.668
5.252
5.245
5.230
5.195
0.000
5.00
0.78
1.68
2.01
16% D
(D)H2C
OBn
H(D)
22% D
2a-D
8
6
4
2
0
PPM

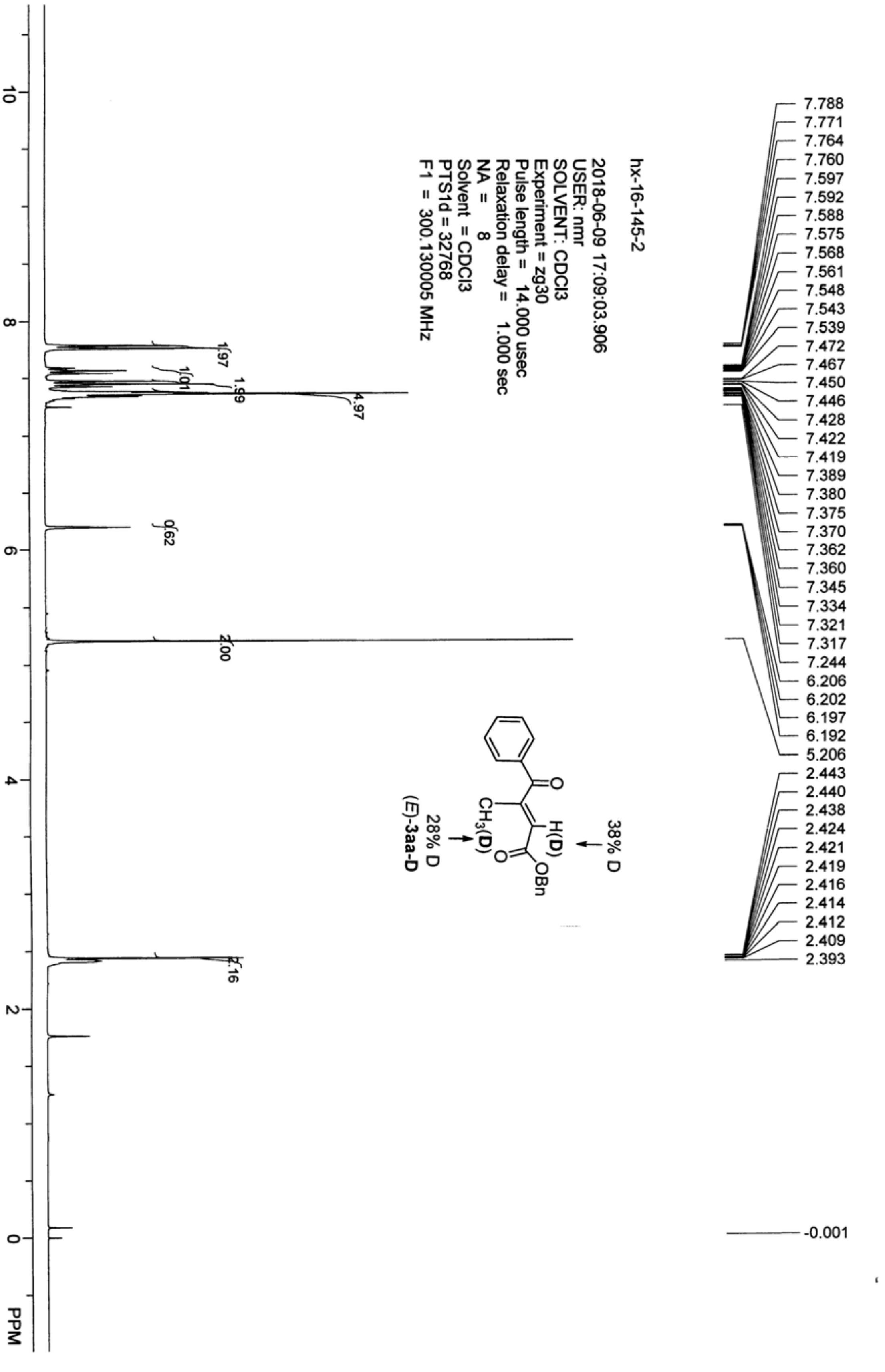

hx-16-144-1
2018-06-11 09:02:06.000
USER: nmr
SOLVENT: CDCl3
Experiment = zgpg30
Pulse length = 9.500 usec
Relaxation delay = 2.000 sec
NA = 11147
Solvent = CDCl3
PTS1d = 32768
F1 = 75.467751 MHz
16% D
(D)H2C
O
OBn
H(D)
22% D
2a-D
216.091
216.026
165.591
135.818
128.529
128.217
128.134
87.938
87.846
79.537
79.454
77.423
77.000
76.577
66.622
250
200
150
100
50
0
PPM

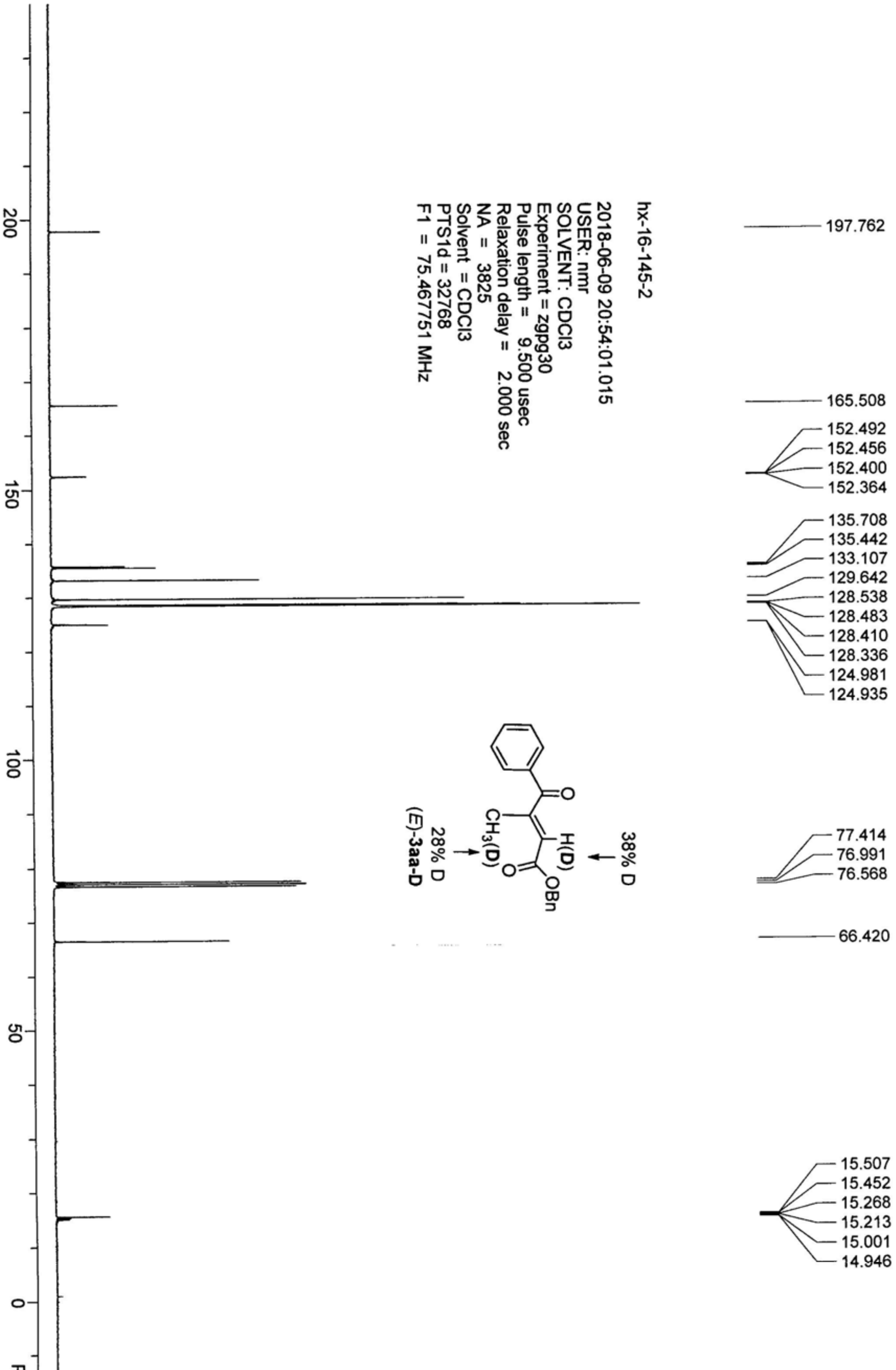

hx-16-144-2
2018-06-09 13:59:47.828
USER: nmr
SOLVENT: CDCl3
Experiment = zg30
Pulse length = 14.000 usec
Relaxation delay = 1.000 sec
NA = 8
Solvent = CDCl3
PTS1d = 32768
F1 = 300.130005 MHz
7.787
7.764
7.759
7.590
7.572
7.565
7.558
7.545
7.541
7.470
7.444
7.420
7.387
7.377
7.373
7.368
7.358
7.343
7.331
7.318
7.314
7.301
7.298
7.243
6.201
6.197
5.206
2.442
2.438
2.426
2.419
2.413
2.407
0.000
1.96
1.01
1.98
4.94
0.82
2.00
2.62
18% D
H(D)
OBn
O
O
CH3(D)
13% D
(E)-3aa-D
8
6
4
2
0
PPM

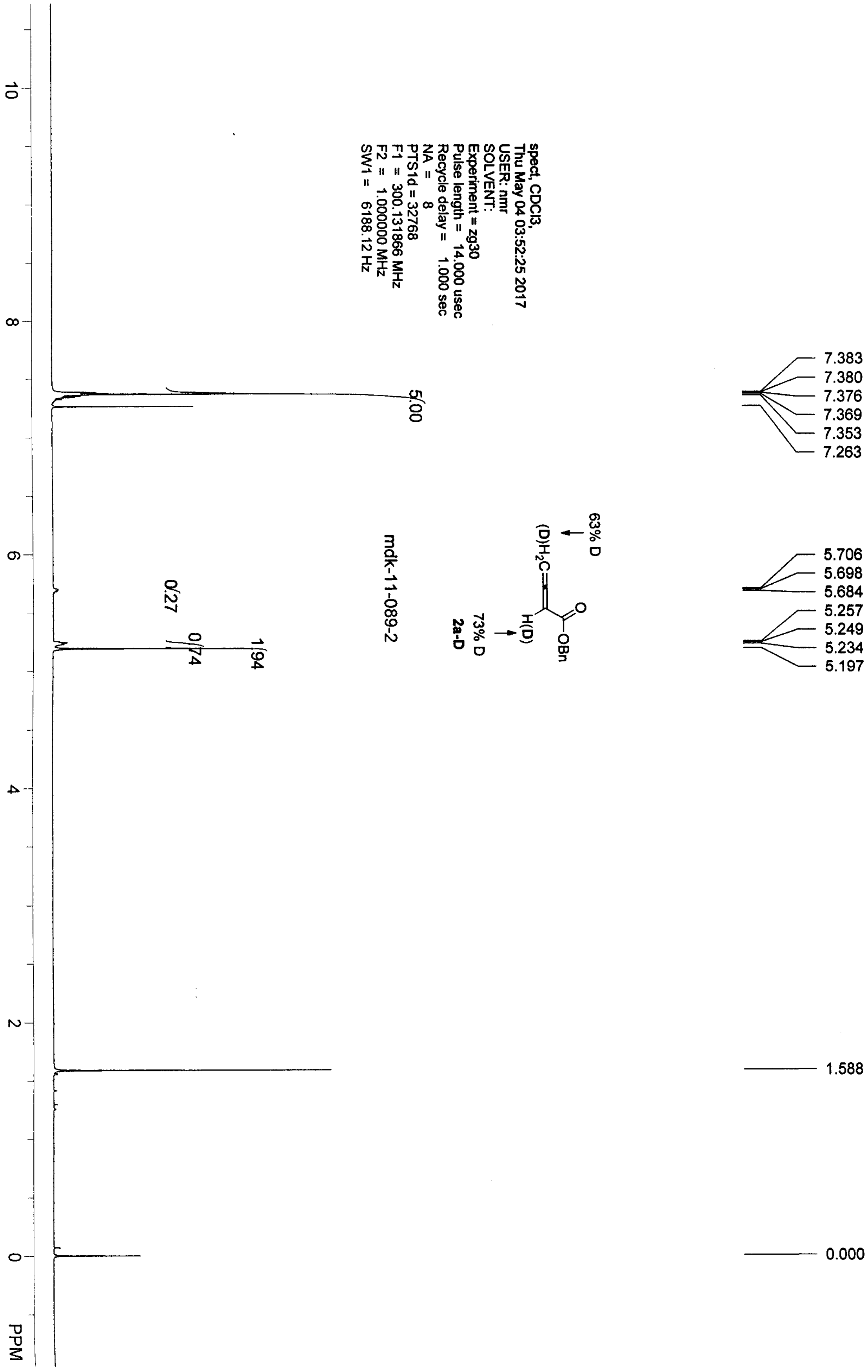

197.753
165.499
152.492
152.400
135.708
135.442
133.107
129.642
128.548
128.483
128.410
128.345
124.981
124.945
77.423
77.000
76.577
66.429
15.516
15.452
15.268
15.001
hx-16-144-2
2018-06-09 15:31:24.750
USER: nmr
SOLVENT: CDCl3
Experiment = zgpg30
Pulse length = 9.500 usec
Relaxation delay = 2.000 sec
NA = 1542
Solvent = CDCl3
PTS1d = 32768
F1 = 75.467751 MHz
18% D
H(D)
OBn
O
O
CH3(D)
13% D
(E)-3aa-D
200
150
100
50
0 PPM


7.381
7.377
7.374
7.366
7.350
7.346
7.339
7.330
7.322
7.312
7.259
5.712
5.704
5.690
5.683
5.668
5.253
5.246
5.231
5.220
5.213
5.195
0.000
hx-16-145-1
2018-06-09 17:04:40.156
USER: nmr
SOLVENT: CDCl3
Experiment = zg30
Pulse length = 14.000 usec
Relaxation delay = 1.000 sec
NA = 8
Solvent = CDCl3
PTS1d = 32768
F1 = 300.130005 MHz
36% D
(D)H2C
O
OBn
H(D)
48% D
2a-D
5.00
0.52
1.29
2.00
8
6
4
2
0
PPM


216.146
216.081
216.017
165.582
128.529
128.217
135.809
128.125
87.929
87.837
79.721
79.638
79.528
79.445
79.381
79.298
79.031
78.949
77.423
77.000
76.568
66.622
66.604
hx-16-145-1
2018-06-10 08:58:54.031
USER: nmr
SOLVENT: CDCl3
Experiment = zgpg30
Pulse length = 9.500 usec
Relaxation delay = 2.000 sec
NA = 11758
Solvent = CDCl3
PTS1d = 32768
F1 = 75.467751 MHz
36% D
(D)H2C
O
OBn
H(D)
48% D
2a-D
200
150
100
50
0
PPM

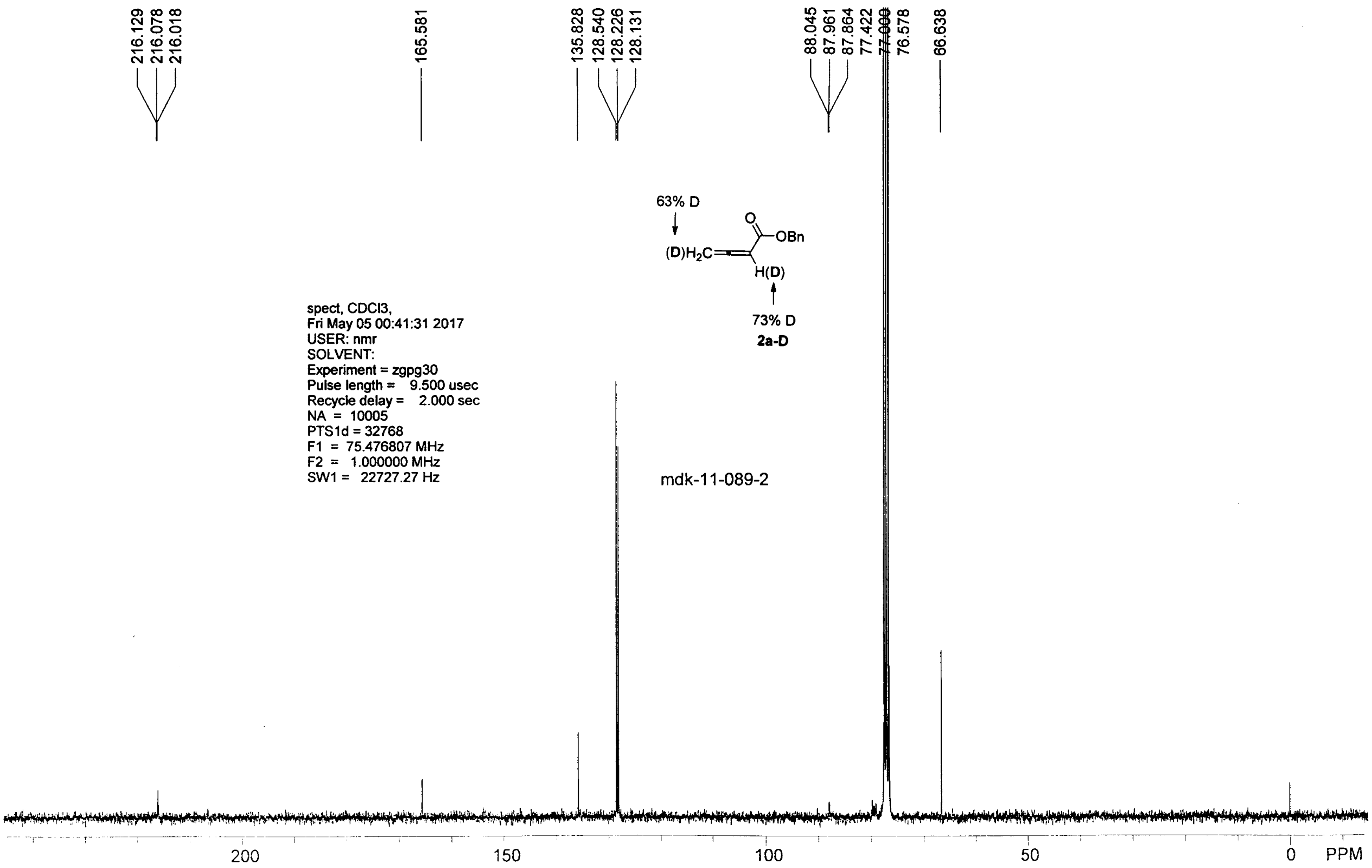

hx-16-145-2
2018-06-09 17:09:03.906
USER: nmr
SOLVENT: CDCl3
Experiment = zg30
Pulse length = 14.000 usec
Relaxation delay = 1.000 sec
NA = 8
Solvent = CDCl3
PTS1d = 32768
F1 = 300.130005 MHz
7.788
7.771
7.764
7.760
7.597
7.592
7.588
7.575
7.568
7.561
7.548
7.543
7.539
7.472
7.467
7.450
7.446
7.428
7.422
7.419
7.389
7.380
7.375
7.370
7.362
7.360
7.345
7.334
7.321
7.317
7.244
6.206
6.202
6.197
6.192
5.206
2.443
2.440
2.438
2.424
2.421
2.419
2.416
2.414
2.412
2.409
2.393
-0.001
38% D
H(D)
OBn
O
O
CH3(D)
28% D
(E)-3aa-D
1.97
1.01
1.99
4.97
0.62
2.00
2.16
10
8
6
4
2
0
PPM

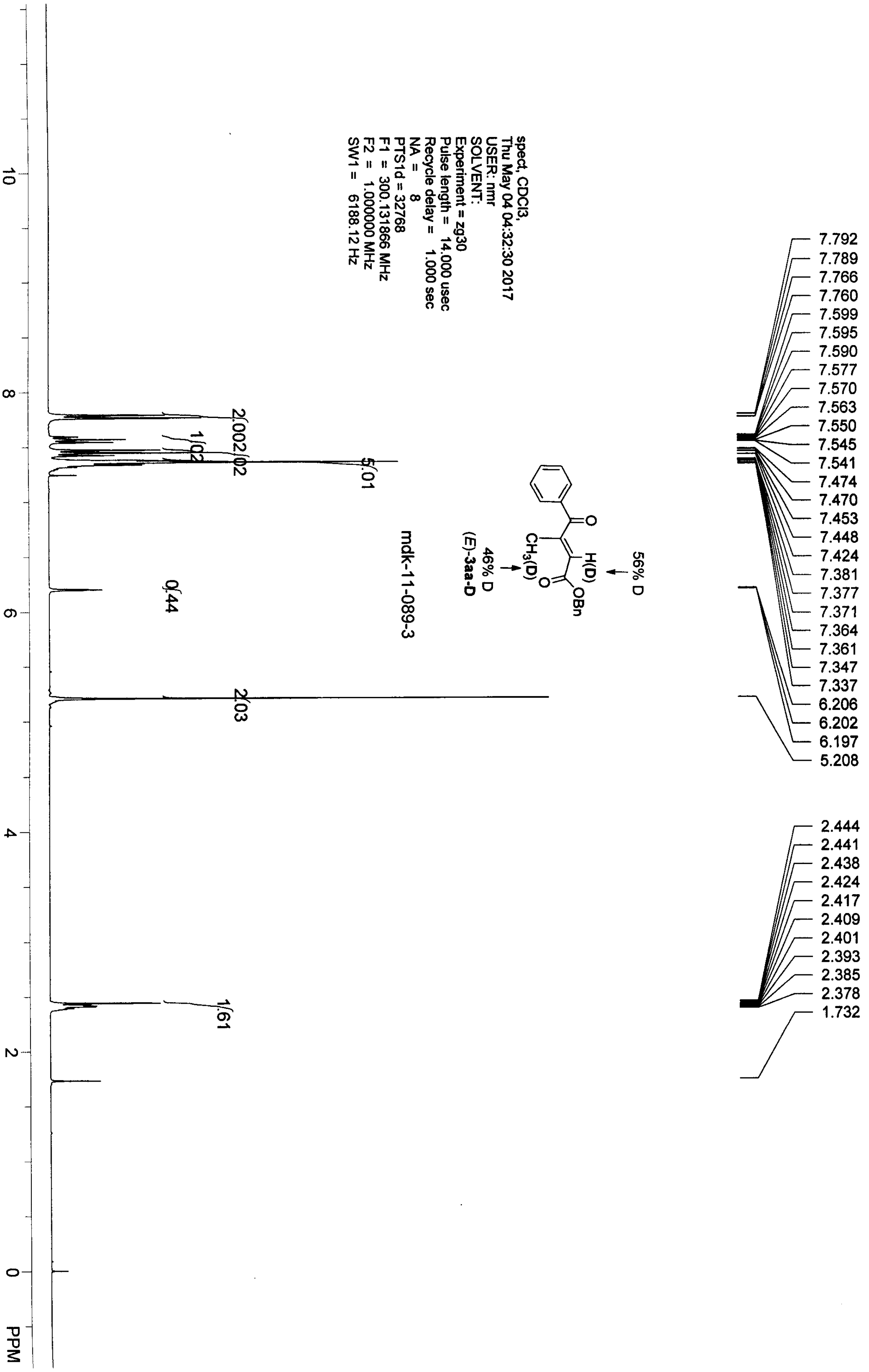

hx-16-145-2
2018-06-09 20:54:01.015
USER: nmr
SOLVENT: CDCl3
Experiment = zgpg30
Pulse length = 9.500 usec
Relaxation delay = 2.000 sec
NA = 3825
Solvent = CDCl3
PTS1d = 32768
F1 = 75.467751 MHz
197.762
165.508
152.492
152.456
152.400
152.364
135.708
135.442
133.107
129.642
128.538
128.483
128.410
128.336
124.981
124.935
77.414
76.991
76.568
66.420
15.507
15.452
15.268
15.213
15.001
14.946
38% D
H(D)
OBn
O
O
CH3(D)
28% D
(E)-3aa-D
200
150
100
50
0
PPM

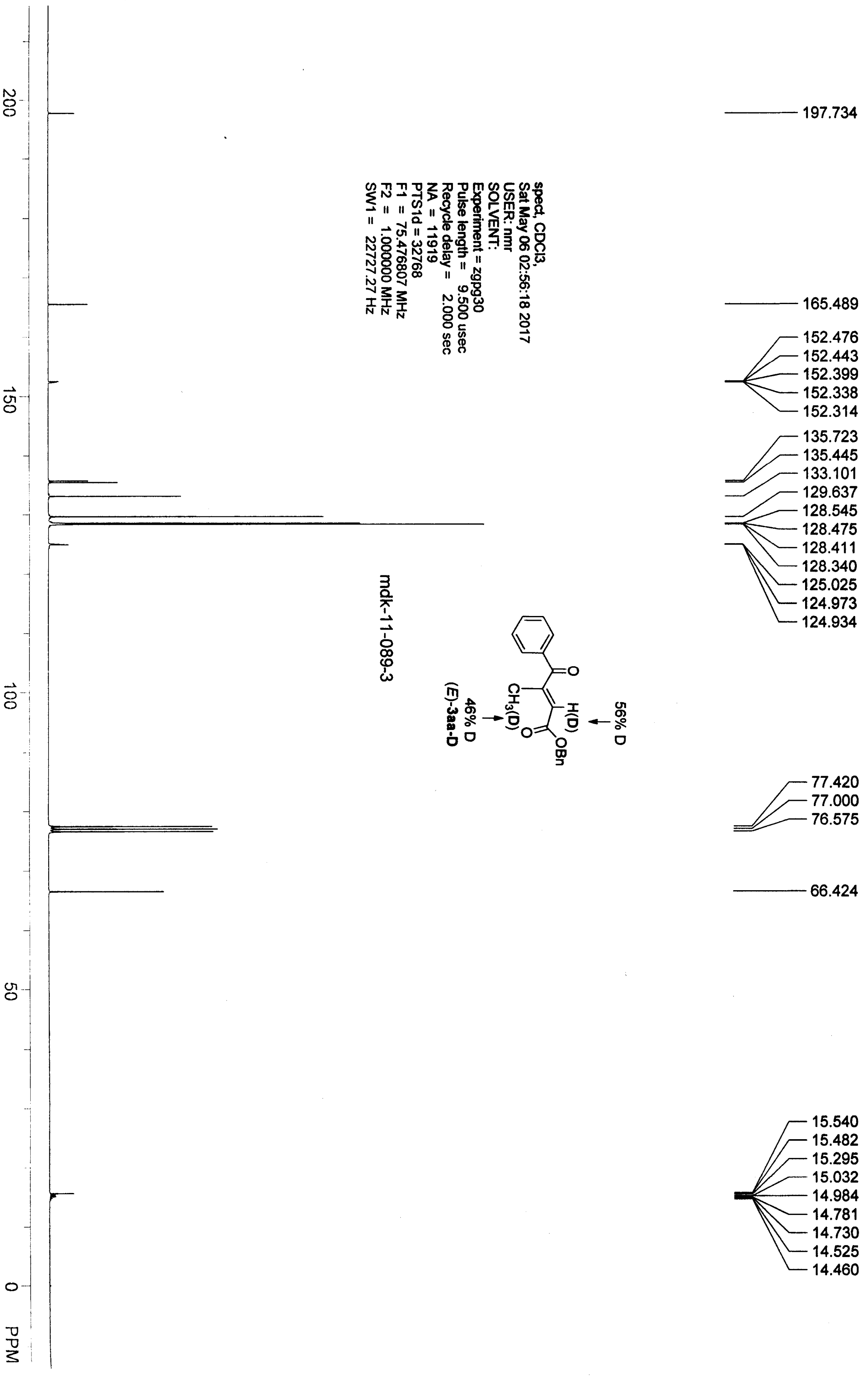

spect, CDCl3,
Thu May 04 03:52:25 2017
USER: nmr
SOLVENT:
Experiment = zg30
Pulse length = 14.000 usec
Recycle delay = 1.000 sec
NA = 8
PTS1d = 32768
F1 = 300.131866 MHz
F2 = 1.000000 MHz
SW1 = 6188.12 Hz

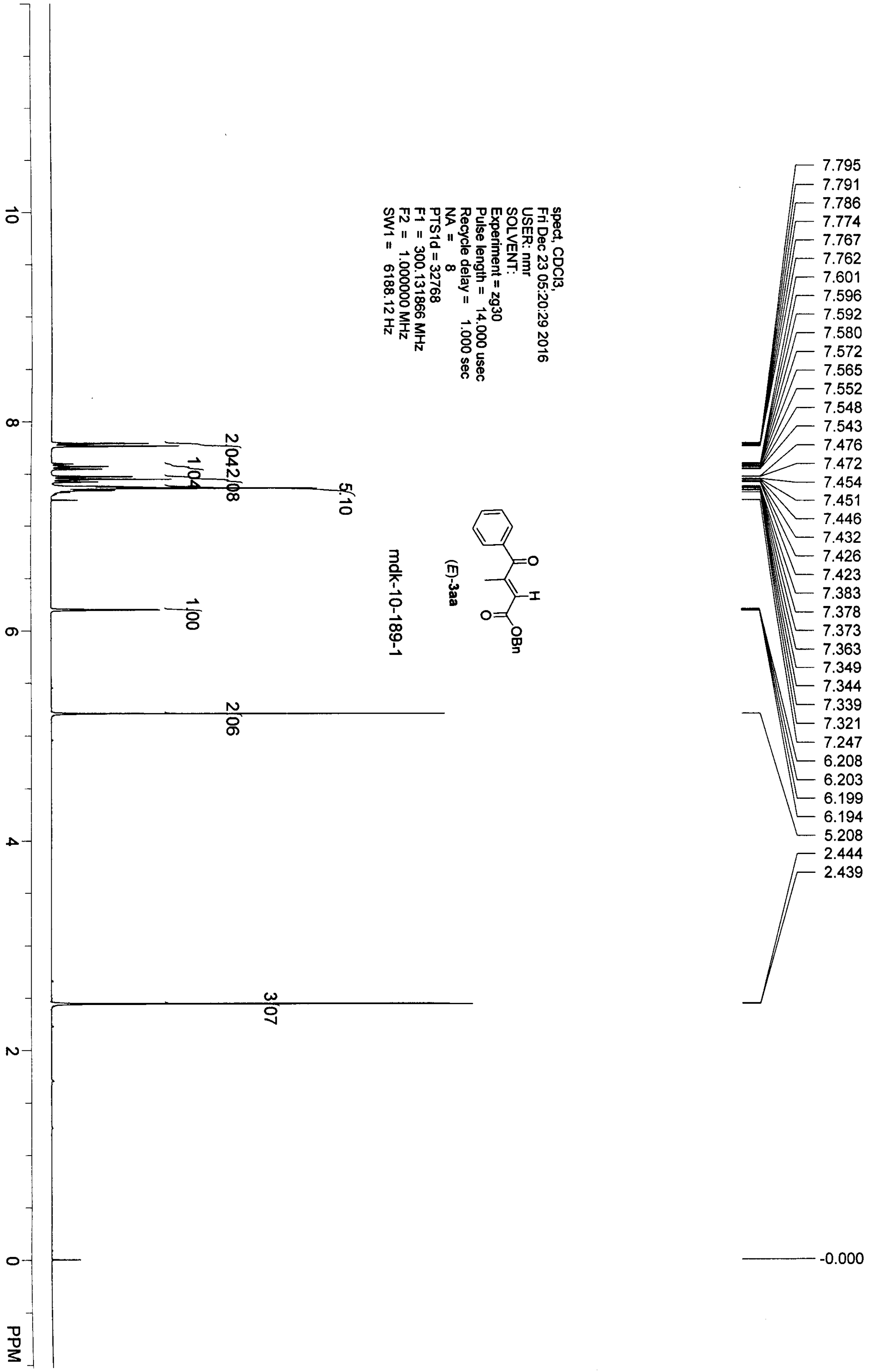
mdk-11-089-2

**2a-D**

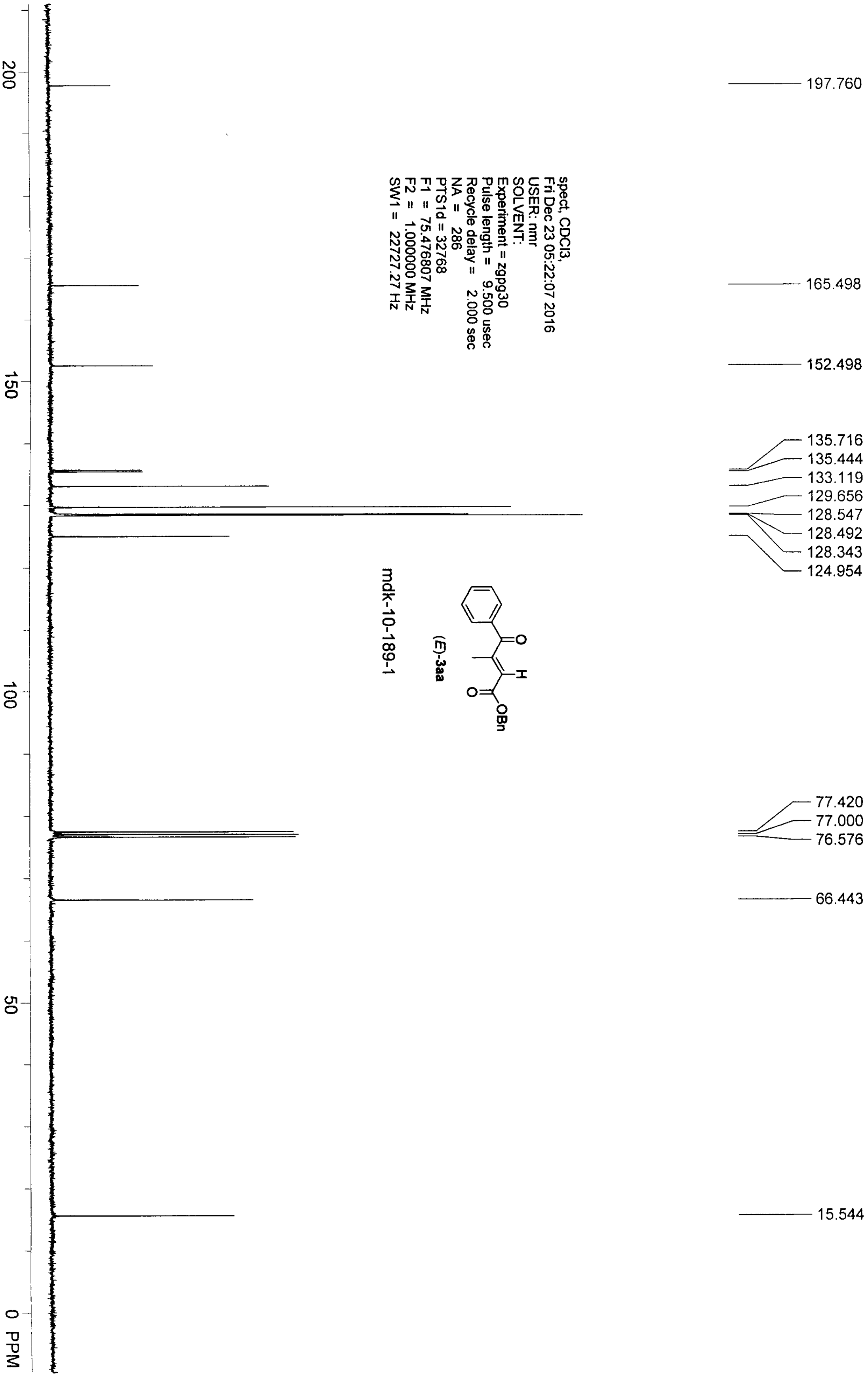

216.129
216.078
216.018
165.581
135.828
128.540
128.226
128.131
88.045
87.961
87.864
77.422
77.000
76.578
66.638
63% D
(D)H$_2$C
O
OBn
H(D)
73% D
2a-D
spect, CDCl3,
Fri May 05 00:41:31 2017
USER: nmr
SOLVENT:
Experiment = zgpg30
Pulse length = 9.500 usec
Recycle delay = 2.000 sec
NA = 10005
PTS1d = 32768
F1 = 75.476807 MHz
F2 = 1.000000 MHz
SW1 = 22727.27 Hz
mdk-11-089-2
200
150
100
50
0
PPM

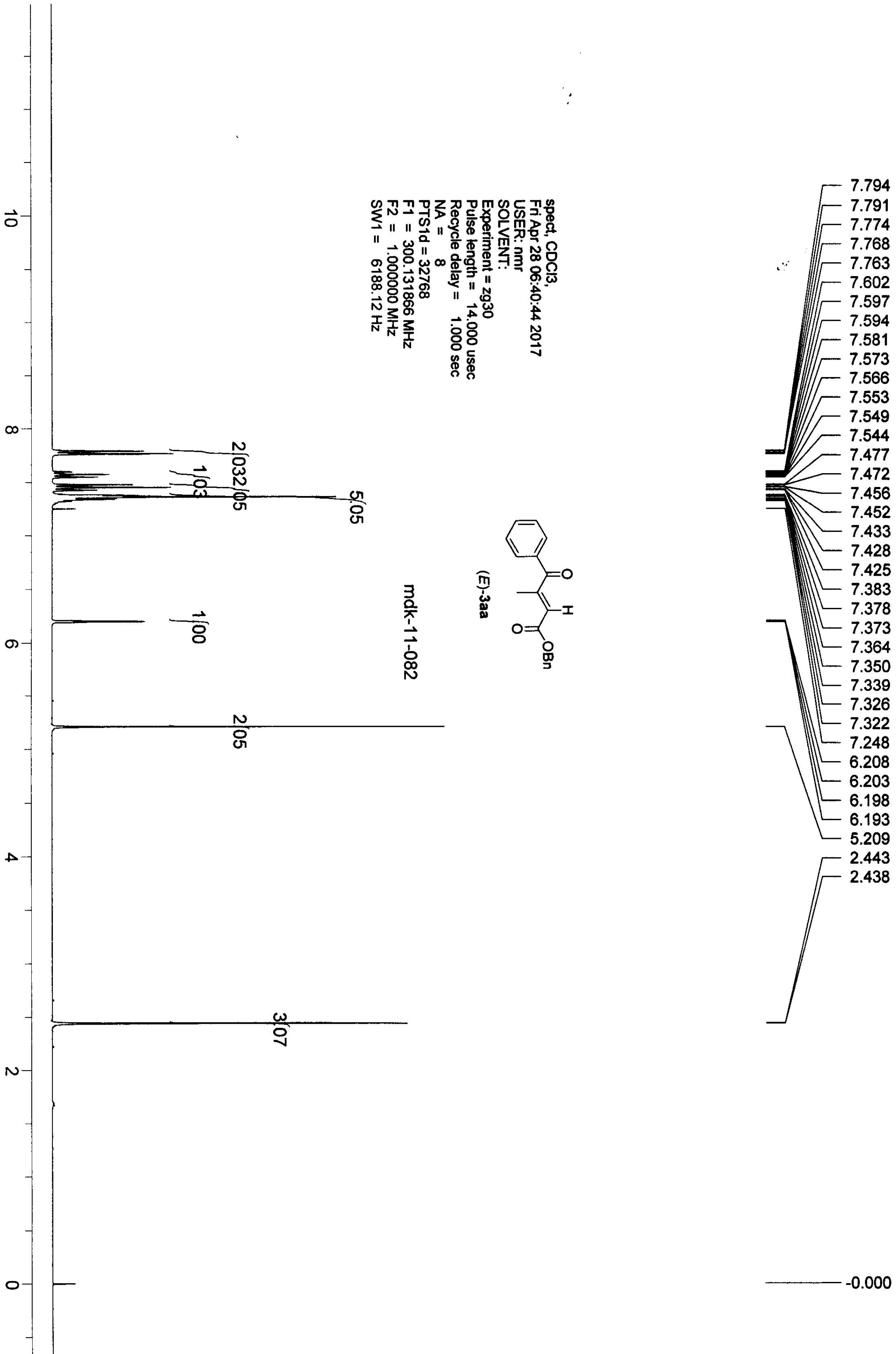

spect, CDCl3,
Thu May 04 04:32:30 2017
USER: nmr
SOLVENT:
Experiment = zg30
Pulse length = 14.000 usec
Recycle delay = 1.000 sec
NA = 8
PTS1d = 32768
F1 = 300.131866 MHz
F2 = 1.000000 MHz
SW1 = 6188.12 Hz
56% D
H(D)
OBn
O
O
CH3(D)
46% D
(E)-3aa-D
mdk-11-089-3
7.792
7.789
7.766
7.760
7.599
7.595
7.590
7.577
7.570
7.563
7.550
7.545
7.541
7.474
7.470
7.453
7.448
7.424
7.381
7.377
7.371
7.364
7.361
7.347
7.337
6.206
6.202
6.197
5.208
2.444
2.441
2.438
2.424
2.417
2.409
2.401
2.393
2.385
2.378
1.732
2.00
1.02
2.02
5.01
0.44
2.03
1.61
10
8
6
4
2
0
PPM

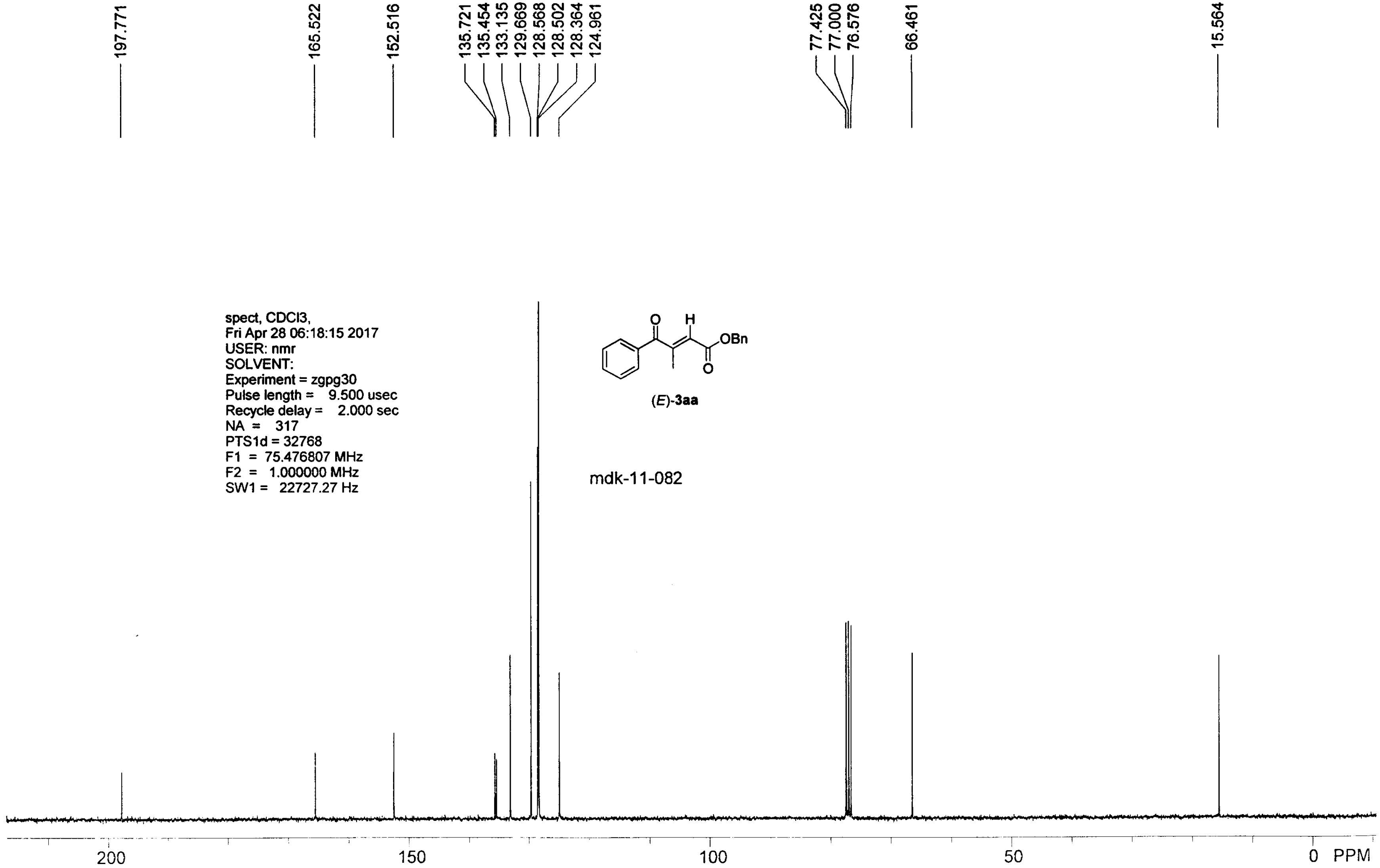

spect, CDCl3,
Sat May 06 02:56:18 2017
USER: nmr
SOLVENT:
Experiment = zgpg30
Pulse length = 9.500 usec
Recycle delay = 2.000 sec
NA = 11919
PTS1d = 32768
F1 = 75.476807 MHz
F2 = 1.000000 MHz
SW1 = 22727.27 Hz
mdk-11-089-3
56% D
H(D)
OBn
O
CH3(D)
46% D
(E)-3aa-D
197.734
165.489
152.476
152.443
152.399
152.338
152.314
135.723
135.445
133.101
129.637
128.545
128.475
128.411
128.340
125.025
124.973
124.934
77.420
77.000
76.575
66.424
15.540
15.482
15.295
15.032
14.984
14.781
14.730
14.525
14.460
200
150
100
50
0
PPM


(E)-3aa

spect, CDCl3,
Fri Dec 23 05:20:29 2016
USER: nmr
SOLVENT:
Experiment = zg30
Pulse length = 14.000 usec
Recycle delay = 1.000 sec
NA = 8
PTS1d = 32768
F1 = 300.131866 MHz
F2 = 1.000000 MHz
SW1 = 6188.12 Hz
mdk-10-189-1
O
H
O
OBn
2.04
1.04
2.08
5.10
1.00
2.06
3.07
10
8
6
4
2
0
PPM
7.795
7.791
7.786
7.774
7.767
7.762
7.601
7.596
7.592
7.580
7.572
7.565
7.552
7.548
7.543
7.476
7.472
7.454
7.451
7.446
7.432
7.426
7.423
7.383
7.378
7.373
7.363
7.349
7.344
7.339
7.321
7.247
6.208
6.203
6.199
6.194
5.208
2.444
2.439
-0.000


spect, CDCl3,
Fri Dec 23 05:22:07 2016
USER: nmr
SOLVENT:
Experiment = zgpg30
Pulse length = 9.500 usec
Recycle delay = 2.000 sec
NA = 286
PTS1d = 32768
F1 = 75.476807 MHz
F2 = 1.000000 MHz
SW1 = 22727.27 Hz
O
H
O
OBn
(E)-3aa
mdk-10-189-1
197.760
165.498
152.498
135.716
135.444
133.119
129.656
128.547
128.492
128.343
124.954
77.420
77.000
76.576
66.443
15.544
200
150
100
50
0 PPM

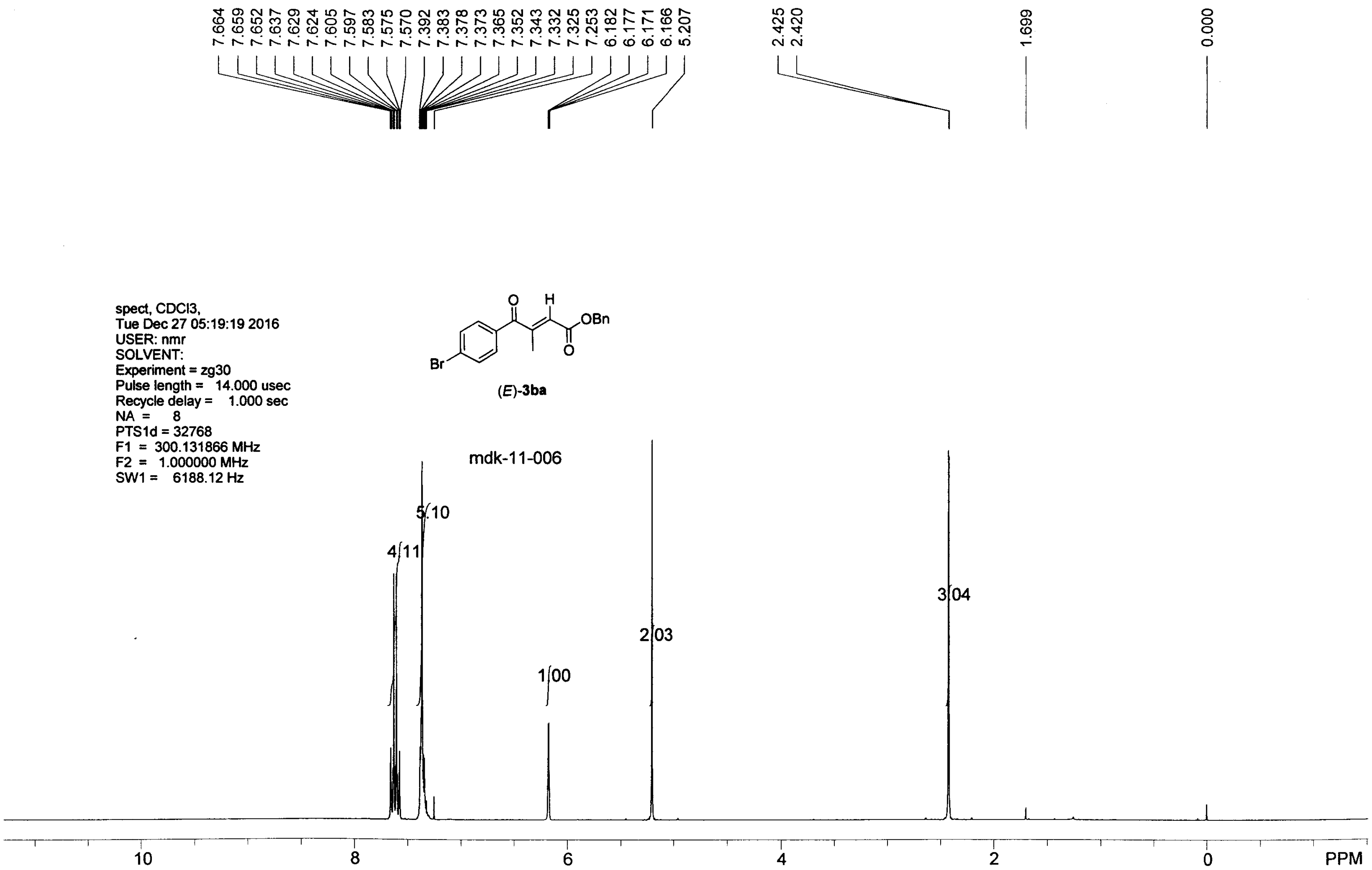

spect, CDCl3,
Fri Apr 28 06:40:44 2017
USER: nmr
SOLVENT:
Experiment = zg30
Pulse length = 14.000 usec
Recycle delay = 1.000 sec
NA = 8
PTS1d = 32768
F1 = 300.131866 MHz
F2 = 1.000000 MHz
SW1 = 6188.12 Hz
(E)-3aa
mdk-11-082
O
H
O
OBn
2.03
2.05
1.03
5.05
1.00
2.05
3.07
10
8
6
4
2
0
PPM
7.794
7.791
7.774
7.768
7.763
7.602
7.597
7.594
7.581
7.573
7.566
7.553
7.549
7.544
7.477
7.472
7.456
7.452
7.433
7.428
7.425
7.383
7.378
7.373
7.364
7.350
7.339
7.326
7.322
7.248
6.208
6.203
6.198
6.193
5.209
2.443
2.438
-0.000



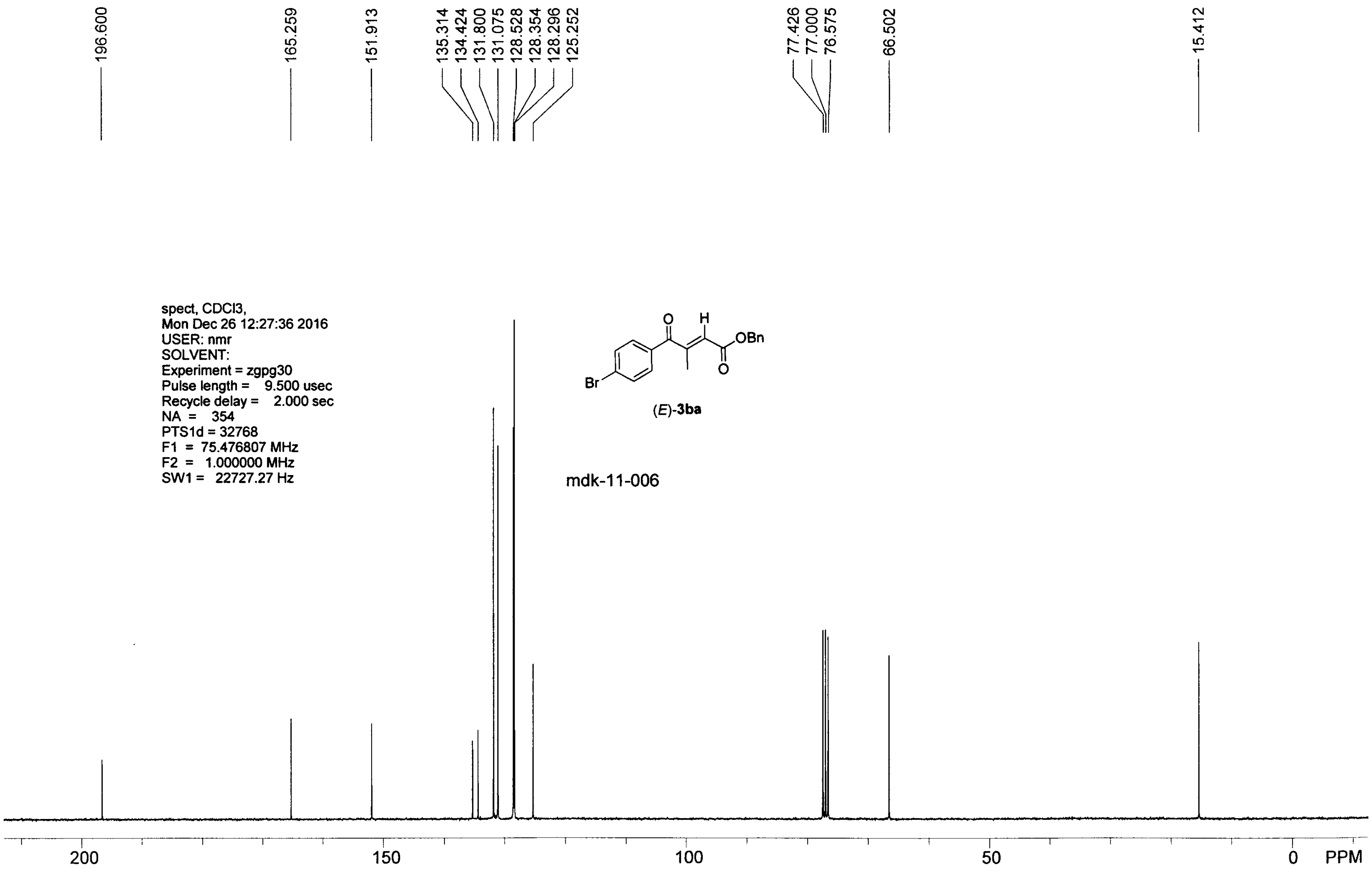
spect, CDCl3,
Fri Apr 28 06:18:15 2017
USER: nmr
SOLVENT:
Experiment = zgpg30
Pulse length = 9.500 usec
Recycle delay = 2.000 sec
NA = 317
PTS1d = 32768
F1 = 75.476807 MHz
F2 = 1.000000 MHz
SW1 = 22727.27 Hz

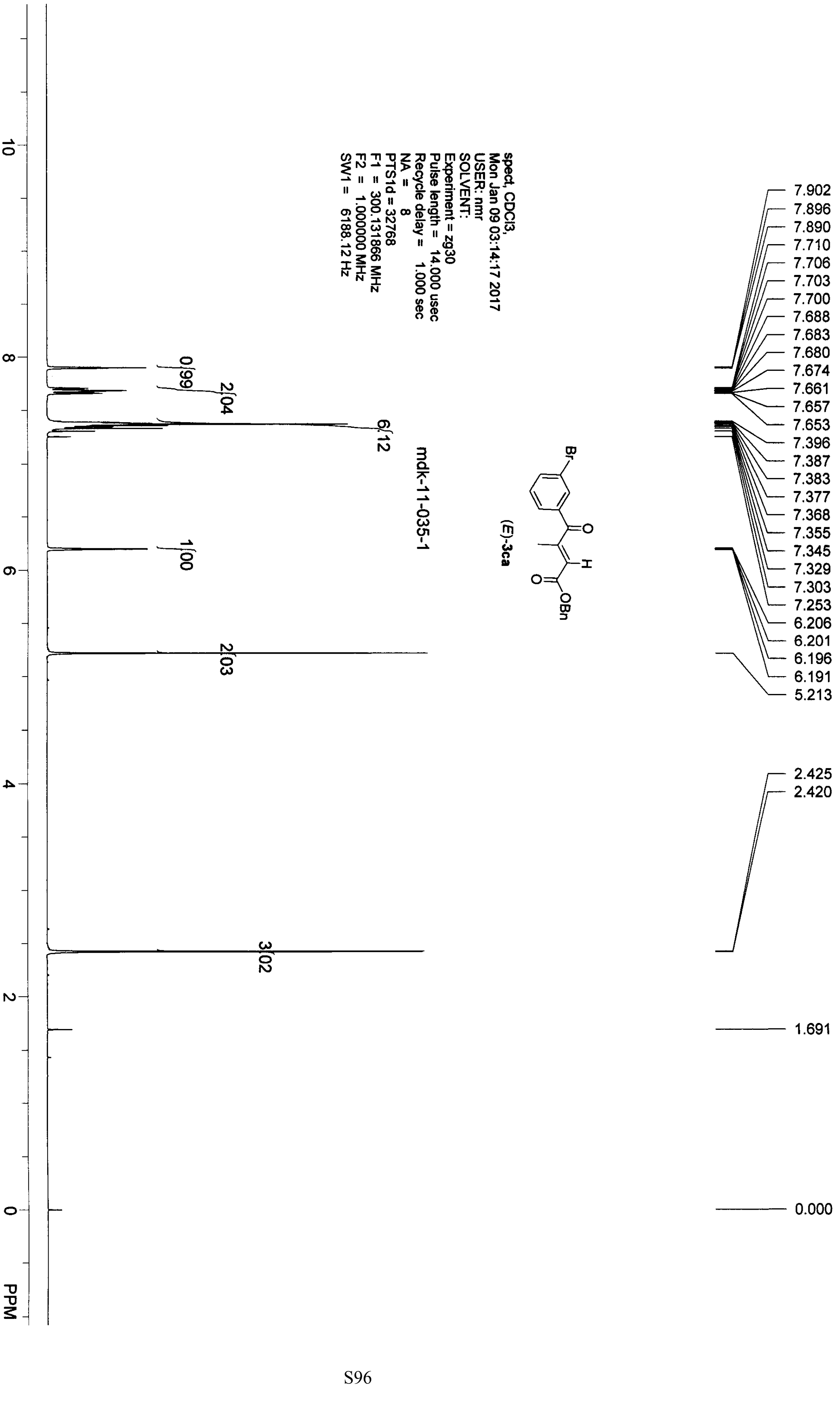
(*E*)-**3aa**

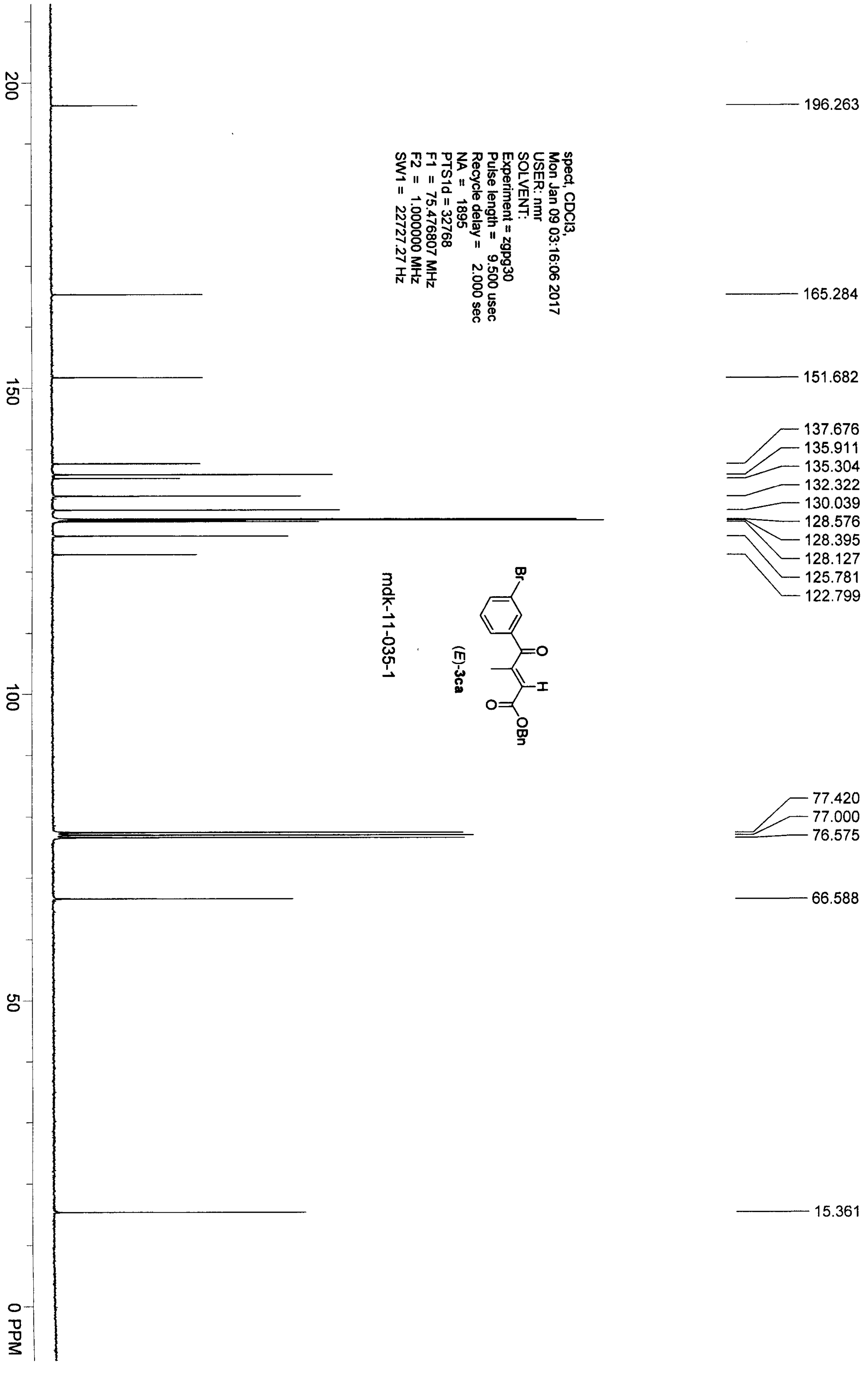
mdk-11-082

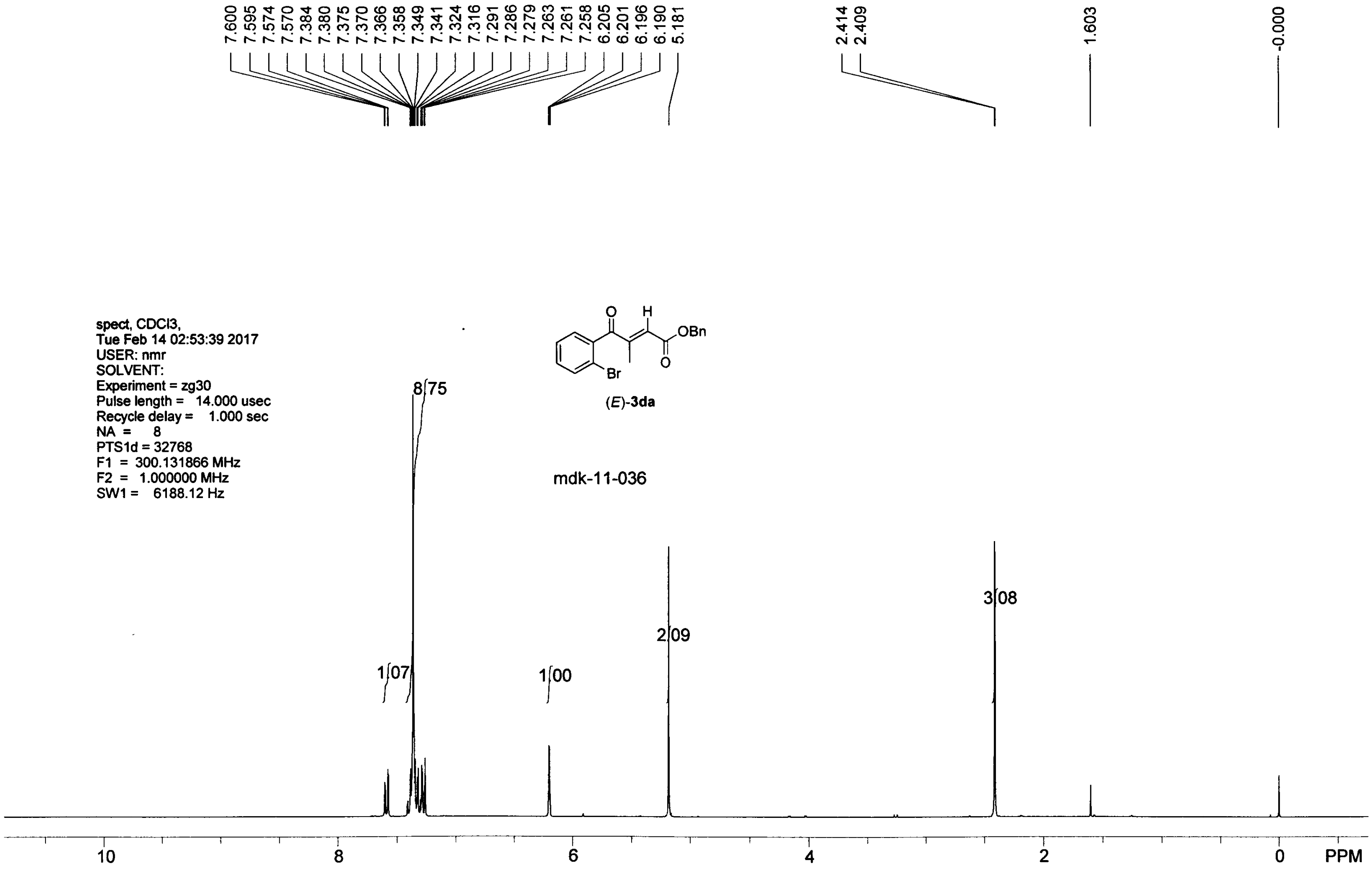

7.664
7.659
7.652
7.637
7.629
7.624
7.605
7.597
7.583
7.575
7.570
7.392
7.383
7.378
7.373
7.365
7.352
7.343
7.332
7.325
7.253
6.182
6.177
6.171
6.166
5.207
2.425
2.420
1.699
0.000
spect, CDCl3,
Tue Dec 27 05:19:19 2016
USER: nmr
SOLVENT:
Experiment = zg30
Pulse length = 14.000 usec
Recycle delay = 1.000 sec
NA = 8
PTS1d = 32768
F1 = 300.131866 MHz
F2 = 1.000000 MHz
SW1 = 6188.12 Hz
O
H
OBn
O
Br
mdk-11-006
4.11
5.10
1.00
2.03
3.04
10
8
6
4
2
0
PPM

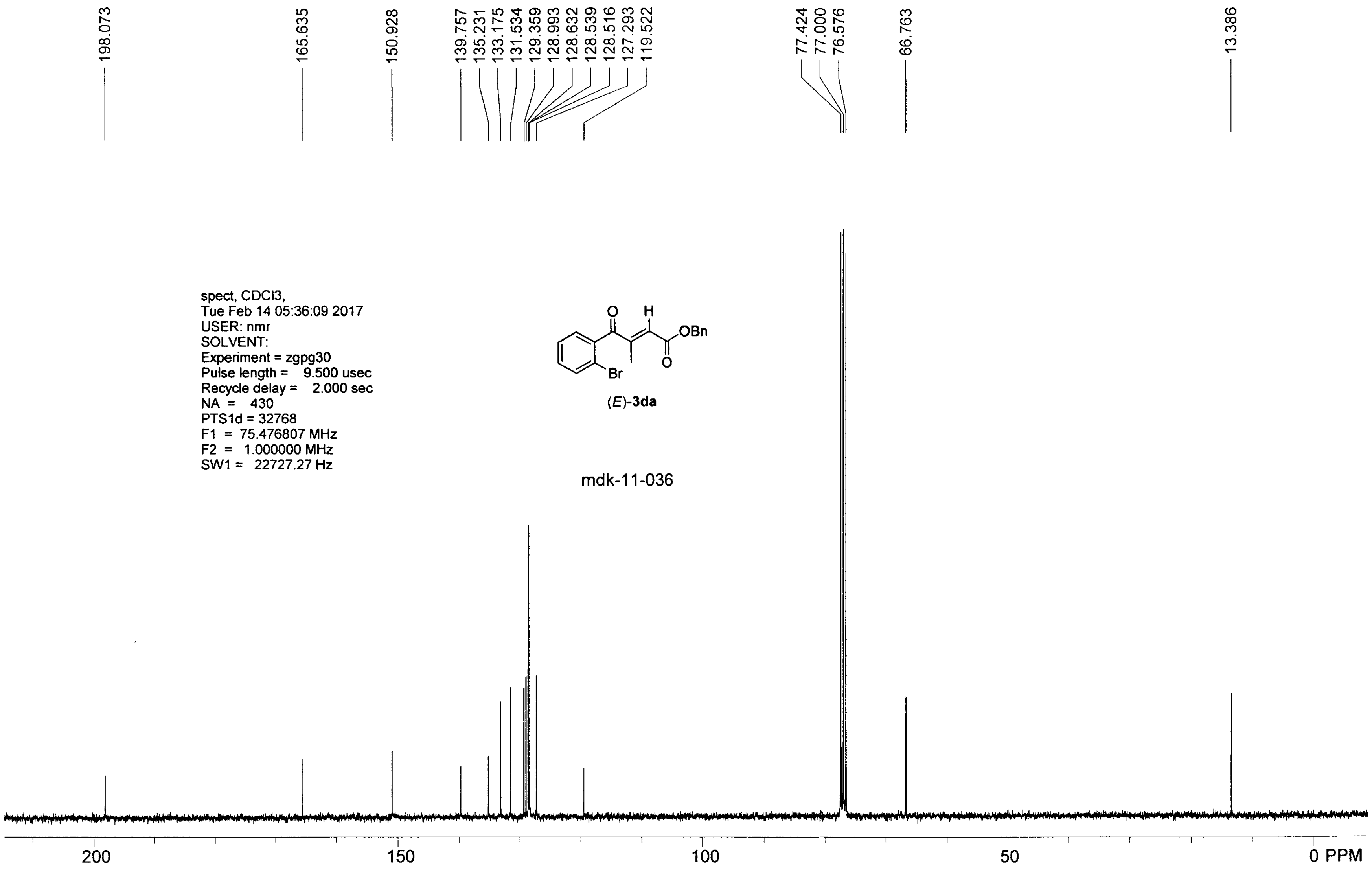
(*E*)-**3ba**

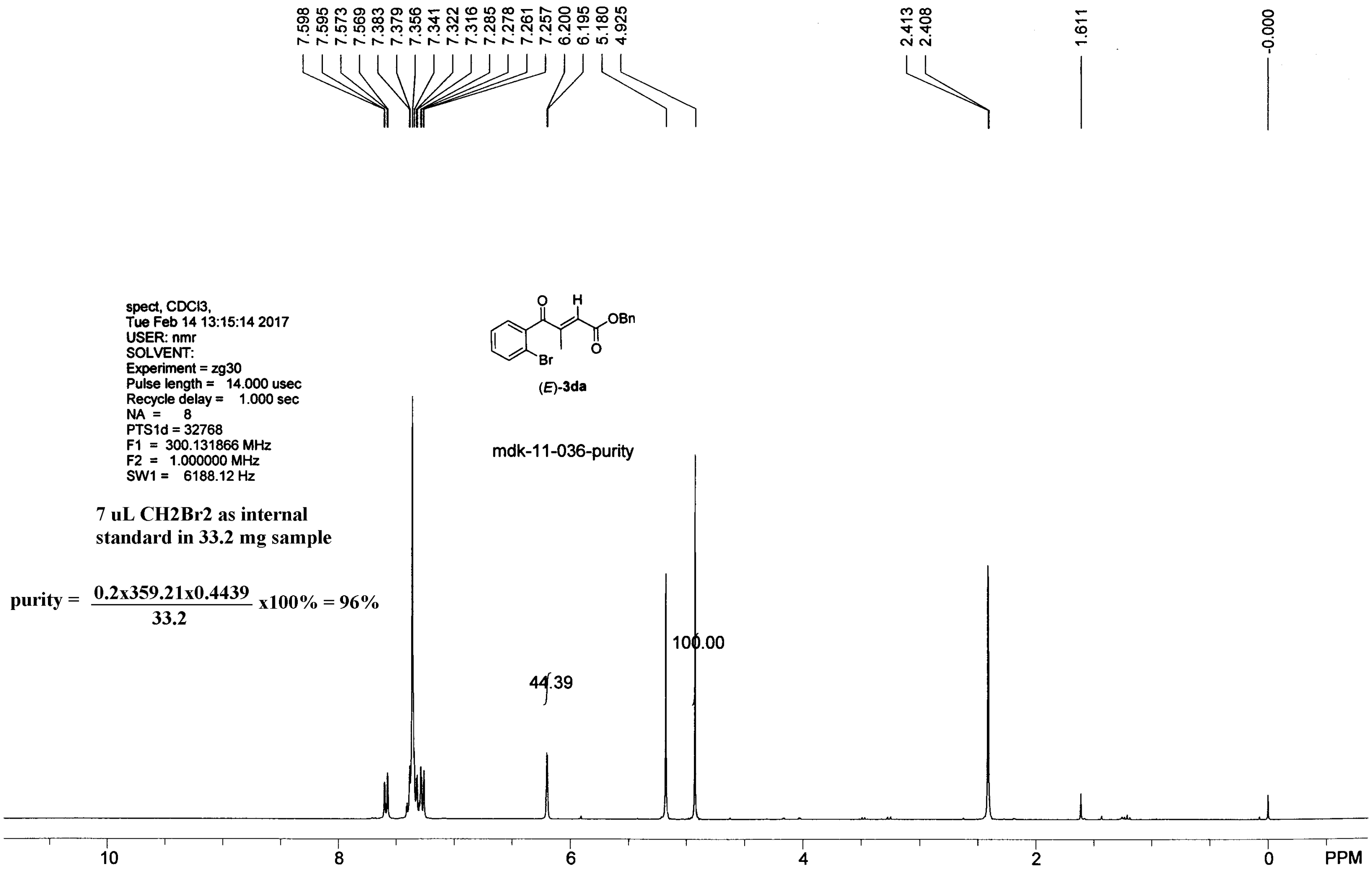

196.600
165.259
151.913
135.314
134.424
131.800
131.075
128.528
128.354
128.296
125.252
77.426
77.000
76.575
66.502
15.412
spect, CDCl3,
Mon Dec 26 12:27:36 2016
USER: nmr
SOLVENT:
Experiment = zgpg30
Pulse length = 9.500 usec
Recycle delay = 2.000 sec
NA = 354
PTS1d = 32768
F1 = 75.476807 MHz
F2 = 1.000000 MHz
SW1 = 22727.27 Hz
O
H
OBn
O
Br
(*E*)-**3ba**
mdk-11-006
200
150
100
50
0
PPM


```
spect, CDCl3,
Mon Jan 09 03:14:17 2017
USER: nmr
SOLVENT:
Experiment = zg30
Pulse length =  14.000 usec
Recycle delay =  1.000 sec
NA =  8
PTS1d = 32768
F1 = 300.131866 MHz
F2 =  1.000000 MHz
SW1 =  6188.12 Hz
```


spect, CDCl3,
Mon Jan 09 03:16:06 2017
USER: nmr
SOLVENT:
Experiment = zgpg30
Pulse length = 9.500 usec
Recycle delay = 2.000 sec
NA = 1895
PTS1d = 32768
F1 = 75.476807 MHz
F2 = 1.000000 MHz
SW1 = 22727.27 Hz
Br
O
H
OBn
O
(E)-3ca
mdk-11-035-1
196.263
165.284
151.682
137.676
135.911
135.304
132.322
130.039
128.576
128.395
128.127
125.781
122.799
77.420
77.000
76.575
66.588
15.361
200
150
100
50
0 PPM


7.600
7.595
7.574
7.570
7.384
7.380
7.375
7.370
7.366
7.358
7.349
7.341
7.324
7.316
7.291
7.286
7.279
7.263
7.261
7.258
6.205
6.201
6.196
6.190
5.181
2.414
2.409
1.603
-0.000
spect, CDCl3,
Tue Feb 14 02:53:39 2017
USER: nmr
SOLVENT:
Experiment = zg30
Pulse length = 14.000 usec
Recycle delay = 1.000 sec
NA = 8
PTS1d = 32768
F1 = 300.131866 MHz
F2 = 1.000000 MHz
SW1 = 6188.12 Hz
O
H
OBn
Br
O
(E)-3da
mdk-11-036
8.75
1.07
1.00
2.09
3.08
10
8
6
4
2
0
PPM


198.073
165.635
150.928
139.757
135.231
133.175
131.534
129.359
128.993
128.632
128.539
128.516
127.293
119.522
77.424
77.000
76.576
66.763
13.386
spect, CDCl3,
Tue Feb 14 05:36:09 2017
USER: nmr
SOLVENT:
Experiment = zgpg30
Pulse length = 9.500 usec
Recycle delay = 2.000 sec
NA = 430
PTS1d = 32768
F1 = 75.476807 MHz
F2 = 1.000000 MHz
SW1 = 22727.27 Hz
O
H
OBn
O
Br
(*E*)-**3da**
mdk-11-036
200
150
100
50
0 PPM



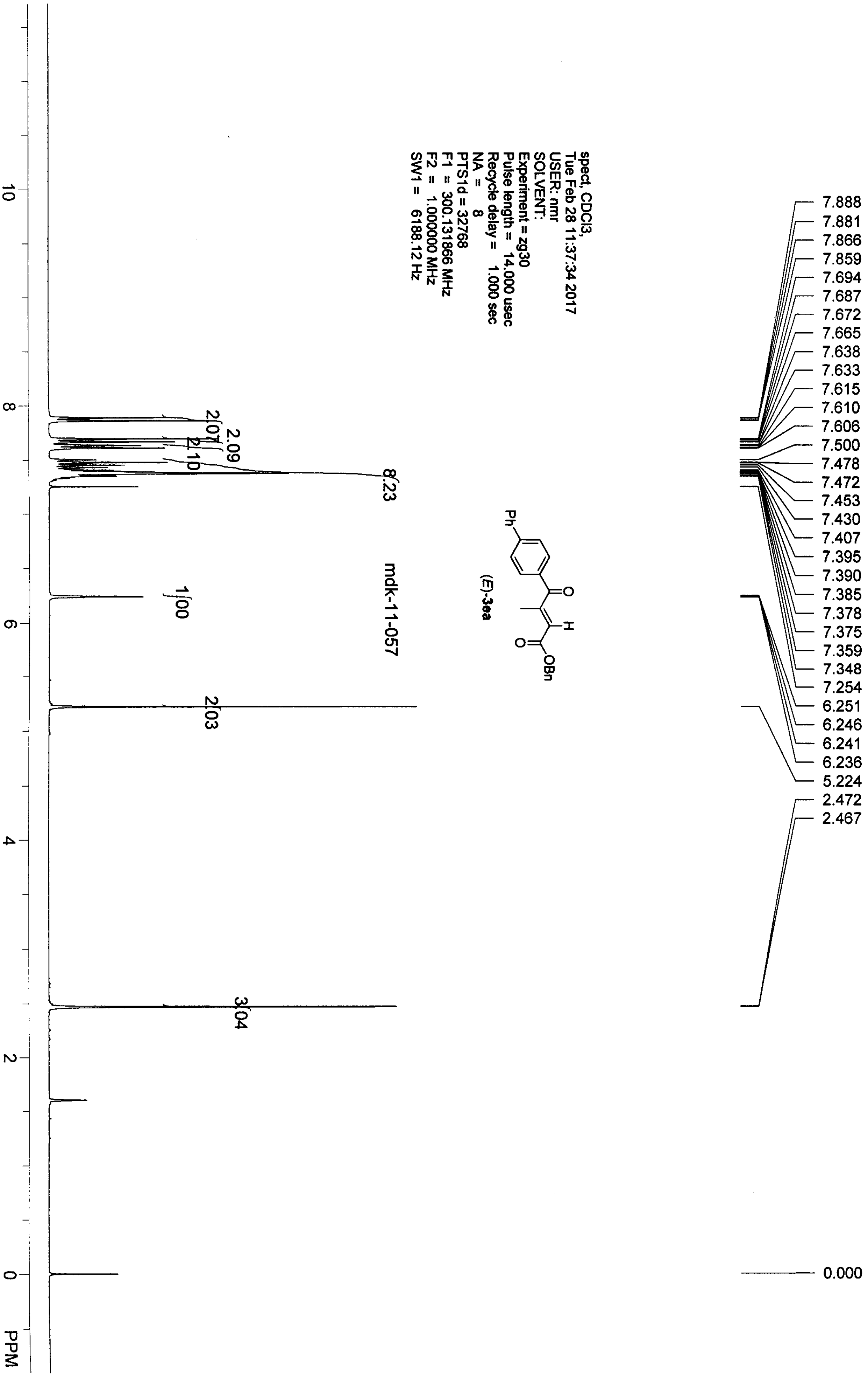
(*E*)-**3da**

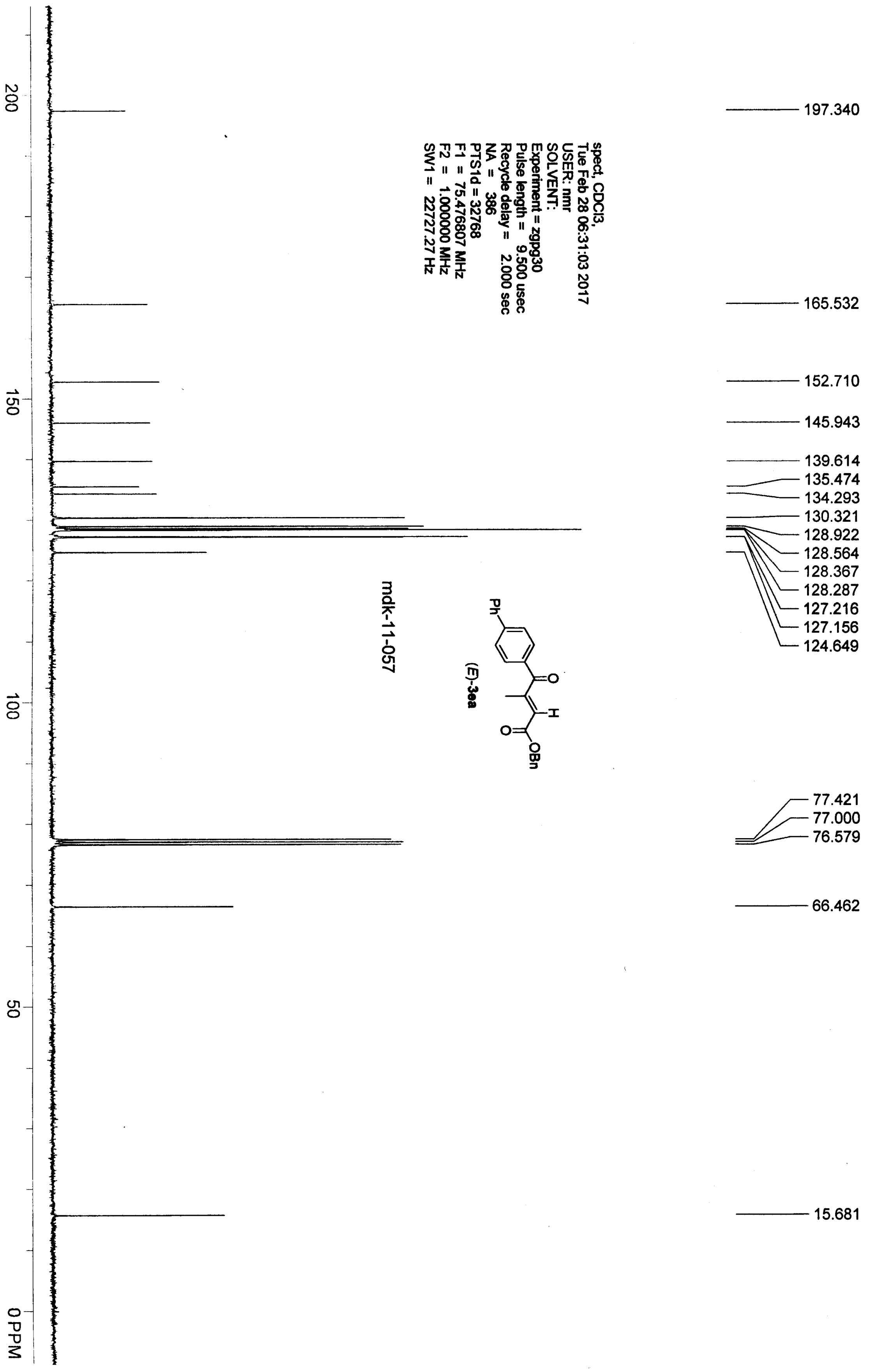
mdk-11-036-purity

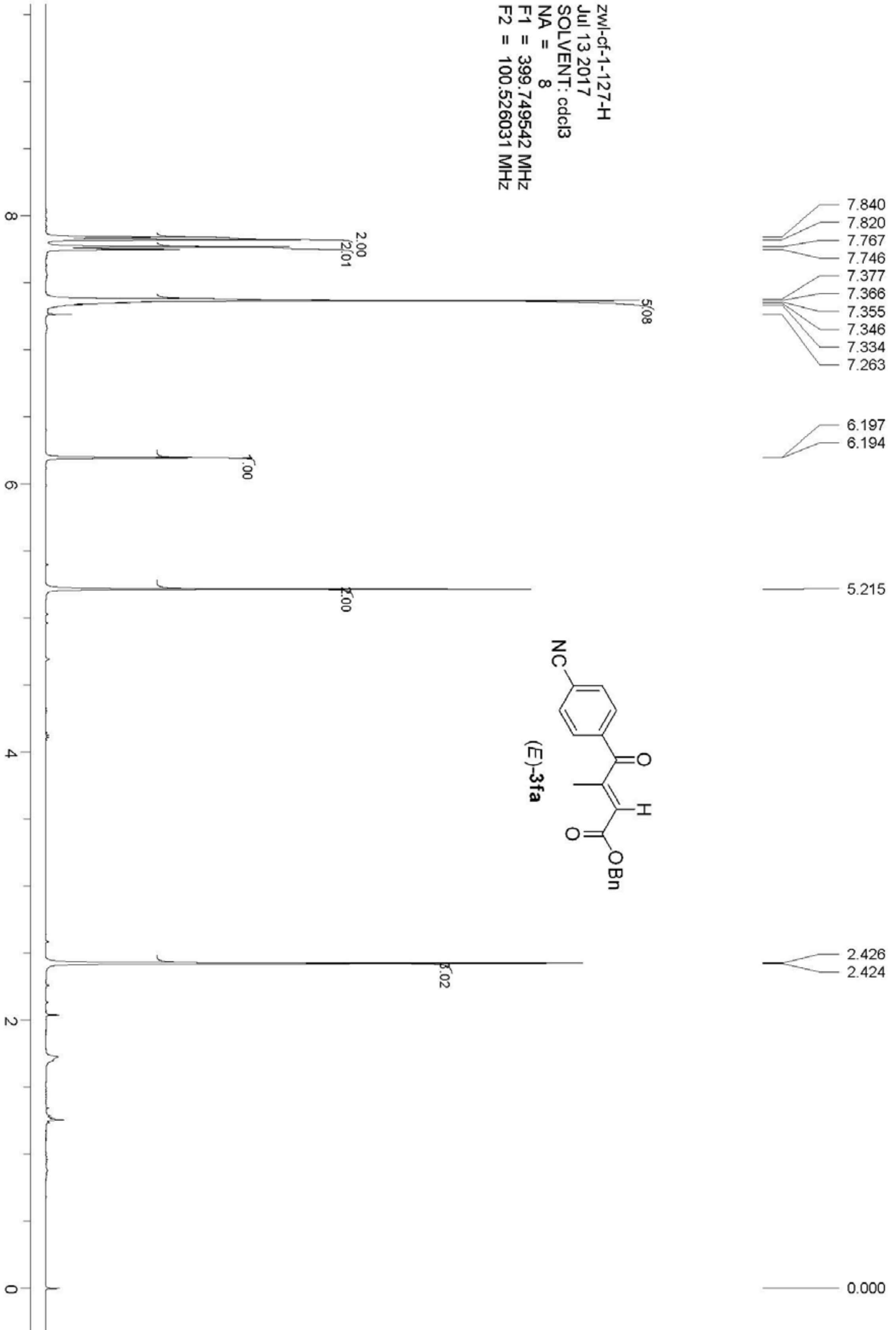
spect, CDCl3,
Tue Feb 14 13:15:14 2017
USER: nmr
SOLVENT:
Experiment = zg30
Pulse length = 14.000 usec
Recycle delay = 1.000 sec
NA = 8
PTS1d = 32768
F1 = 300.131866 MHz
F2 = 1.000000 MHz
SW1 = 6188.12 Hz

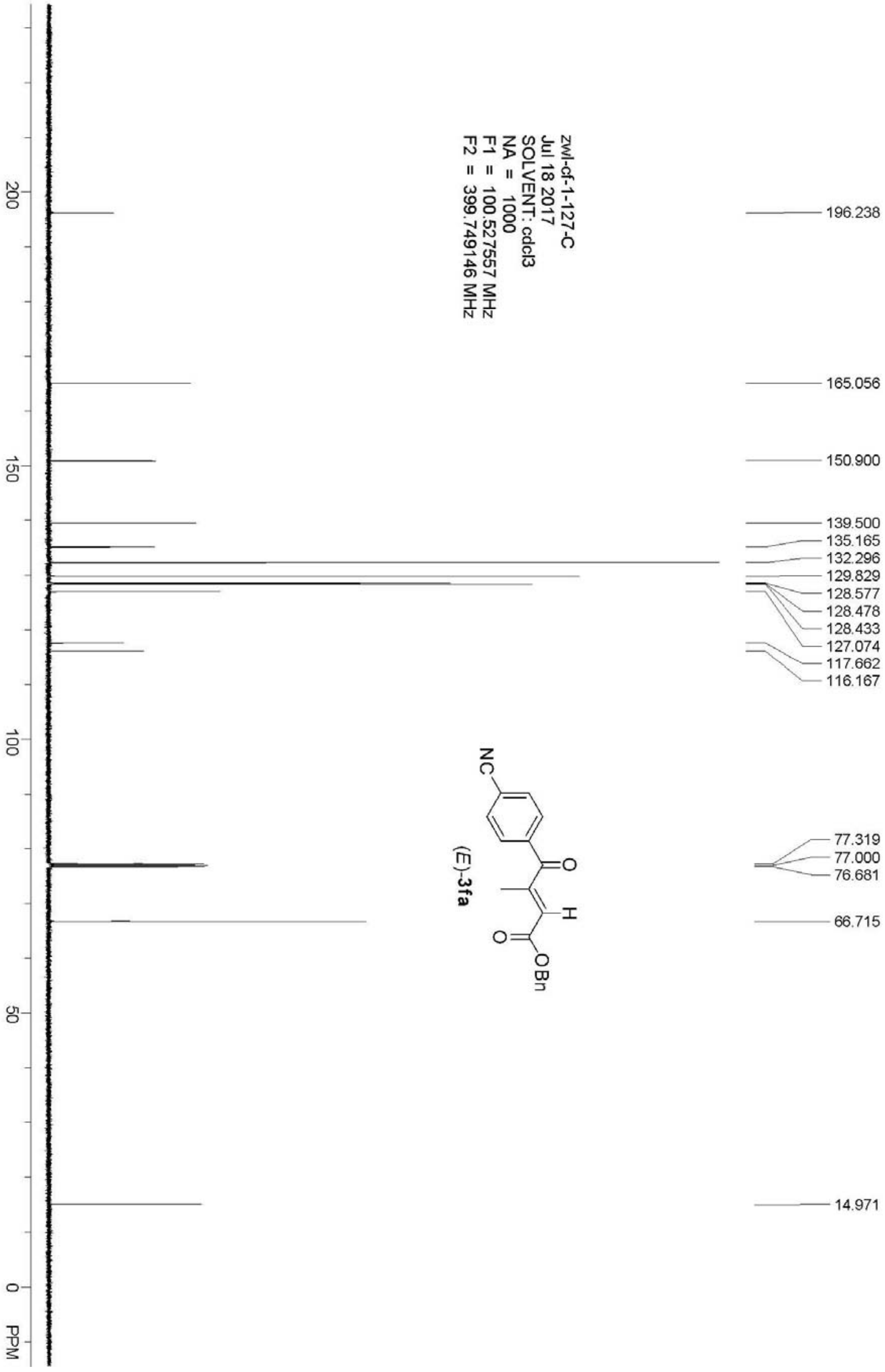
**7 uL CH2Br2 as internal standard in 33.2 mg sample**

$$\text{purity} = \frac{0.2\text{x}359.21\text{x}0.4439}{33.2}\text{x}100\% = 96\%$$

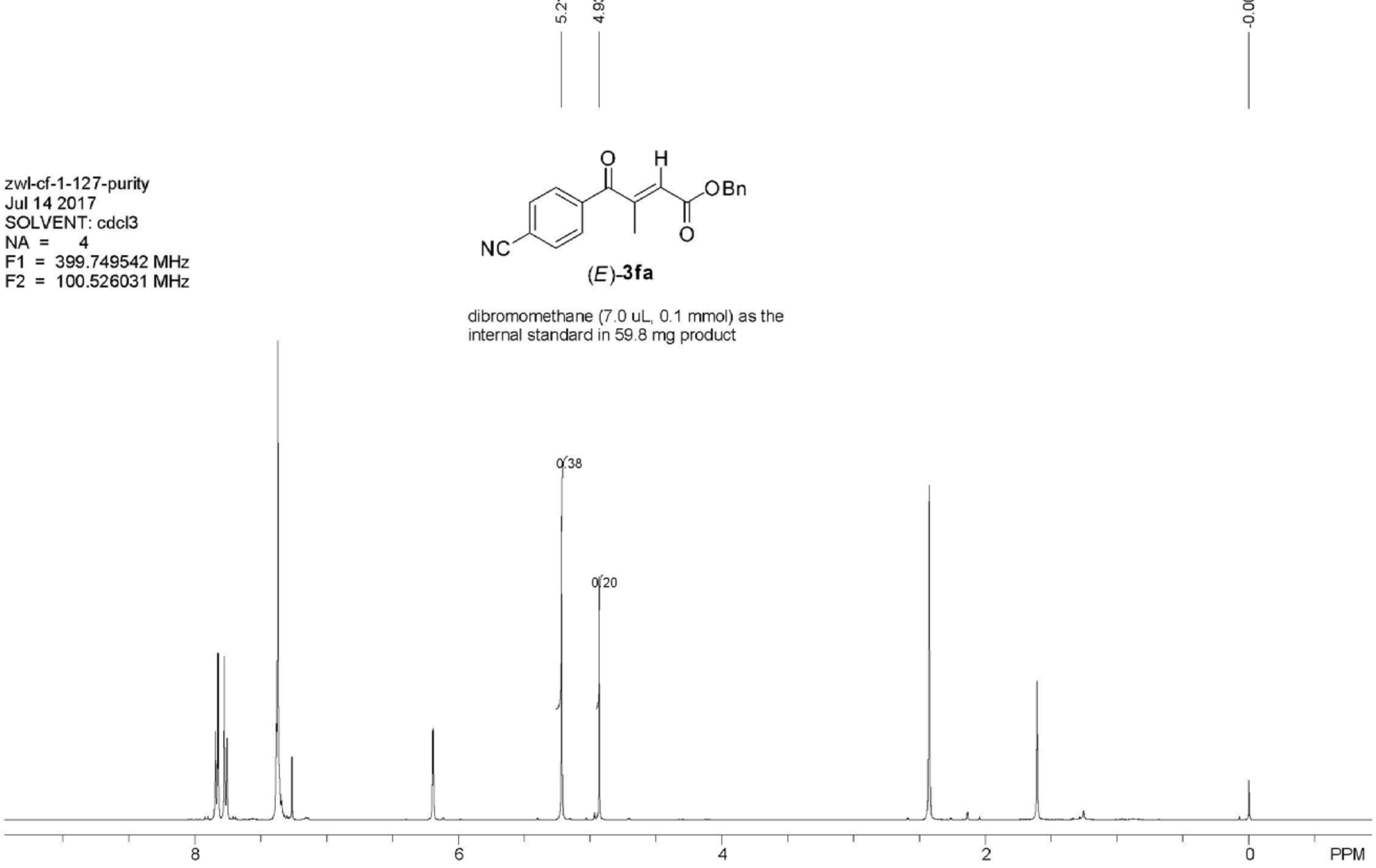

spect, CDCl3,
Tue Feb 28 11:37:34 2017
USER: nmr
SOLVENT:
Experiment = zg30
Pulse length = 14.000 usec
Recycle delay = 1.000 sec
NA = 8
PTS1d = 32768
F1 = 300.131866 MHz
F2 = 1.000000 MHz
SW1 = 6188.12 Hz
mdk-11-057
Ph
O
H
O
OBn
(E)-3ea
7.888
7.881
7.866
7.859
7.694
7.687
7.672
7.665
7.638
7.633
7.615
7.610
7.606
7.500
7.478
7.472
7.453
7.430
7.407
7.395
7.390
7.385
7.378
7.375
7.359
7.348
7.254
6.251
6.246
6.241
6.236
5.224
2.472
2.467
0.000
2.07
2.09
2.10
8.23
1.00
2.03
3.04
10
8
6
4
2
0
PPM


spect, CDCl3,
Tue Feb 28 06:31:03 2017
USER: nmr
SOLVENT:
Experiment = zgpg30
Pulse length = 9.500 usec
Recycle delay = 2.000 sec
NA = 386
PTS1d = 32768
F1 = 75.476807 MHz
F2 = 1.000000 MHz
SW1 = 22727.27 Hz
197.340
165.532
152.710
145.943
139.614
135.474
134.293
130.321
128.922
128.564
128.367
128.287
127.216
127.156
124.649
77.421
77.000
76.579
66.462
15.681
Ph
O
H
O
OBn
(E)-3ea
mdk-11-057
200
150
100
50
0 PPM


zwl-cf-1-127-H
Jul 13 2017
SOLVENT: cdcl3
NA = 8
F1 = 399.749542 MHz
F2 = 100.526031 MHz
7.840
7.820
7.767
7.746
7.377
7.366
7.355
7.346
7.334
7.263
6.197
6.194
5.215
2.426
2.424
0.000
2.00
2.01
5.08
1.00
2.00
3.02
NC
O
H
O
OBn
(E)-3fa
8
6
4
2
0
PPM


zwl-cf-1-127-C
Jul 18 2017
SOLVENT: cdcl3
NA = 1000
F1 = 100.527557 MHz
F2 = 399.749146 MHz
196.238
165.056
150.900
139.500
135.165
132.296
129.829
128.577
128.478
128.433
127.074
117.662
116.167
77.319
77.000
76.681
66.715
14.971
NC
O
H
O
OBn
200
150
100
50
0
PPM

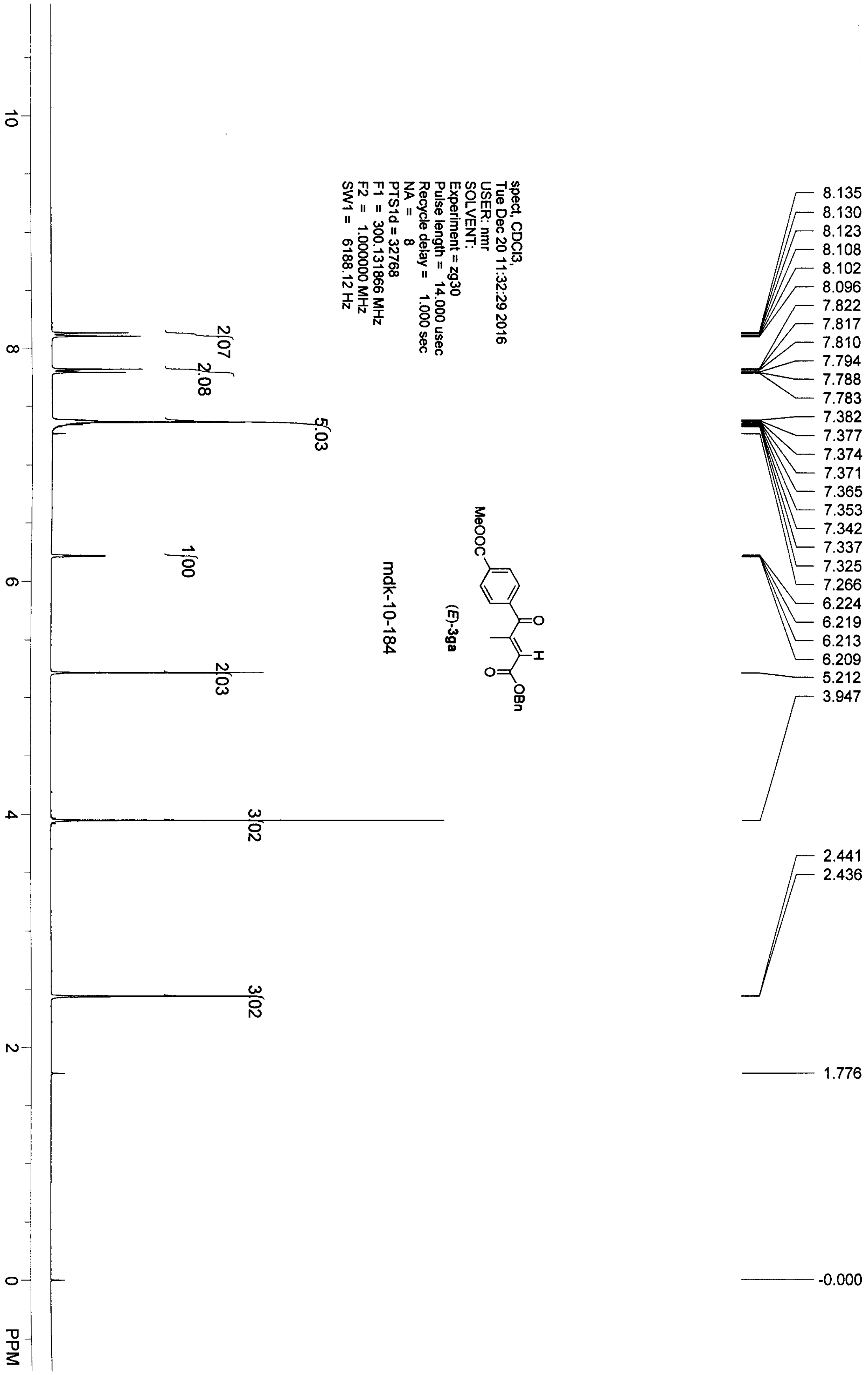
(E)-3fa

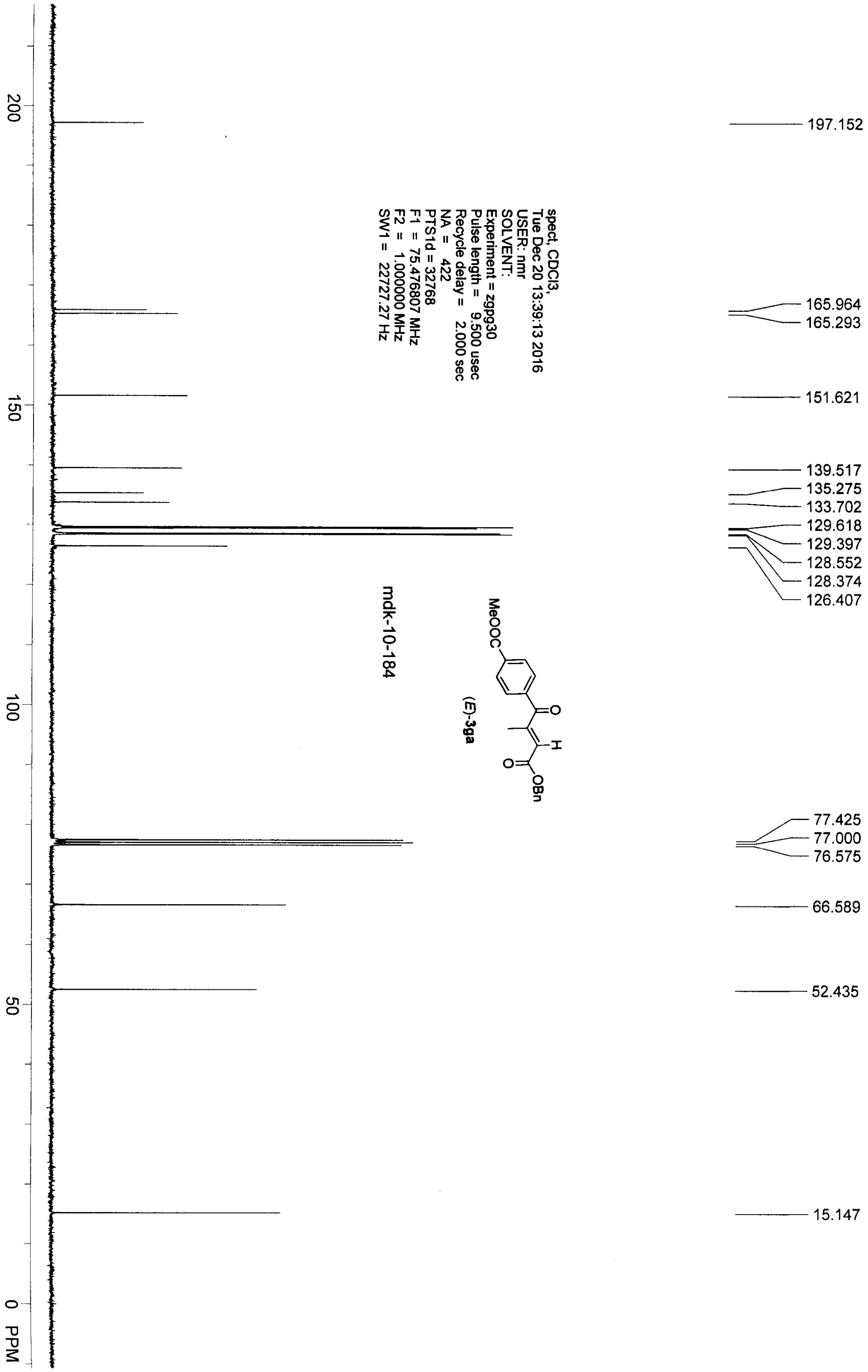


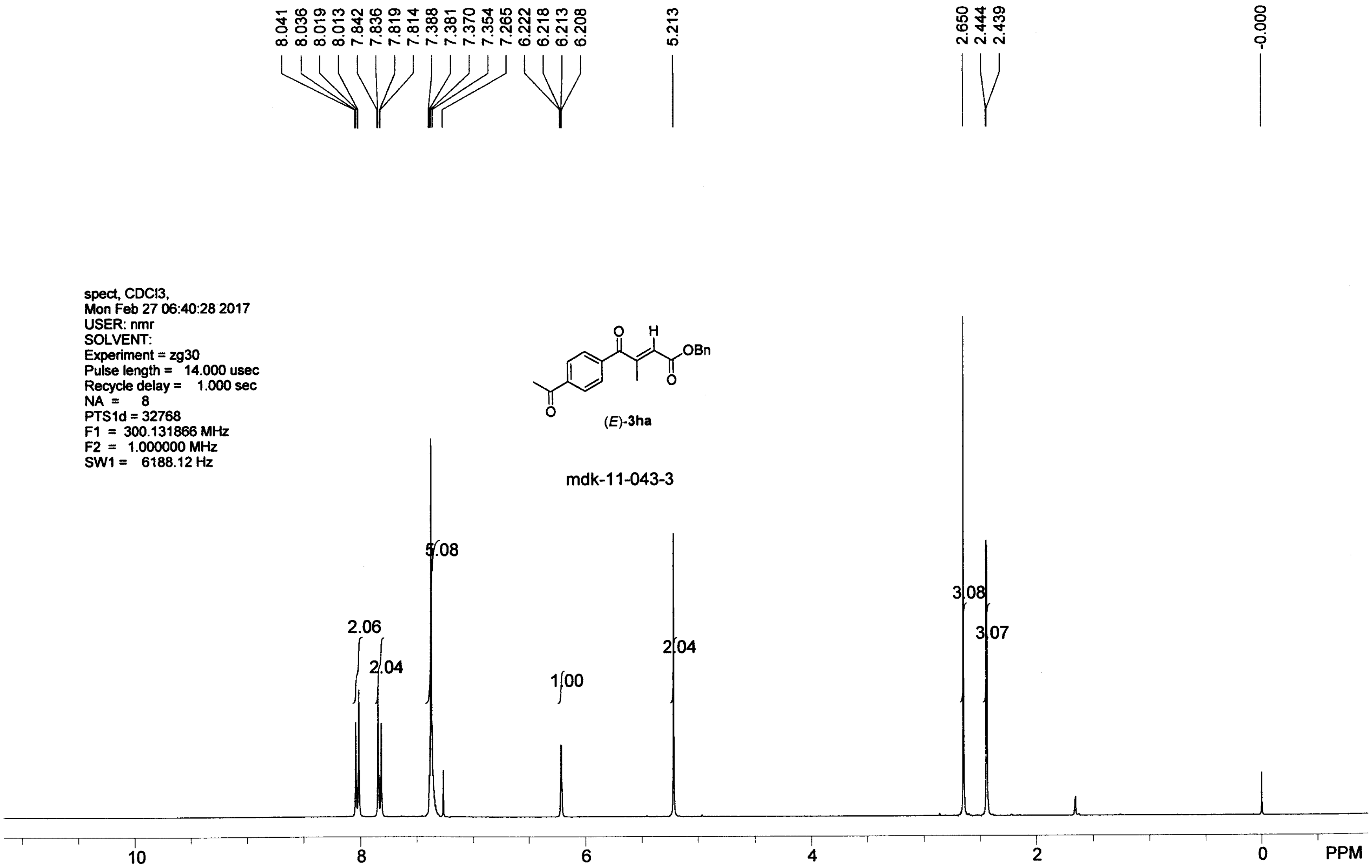
zwl-cf-1-127-purity
Jul 14 2017
SOLVENT: cdcl3
NA = 4
F1 = 399.749542 MHz
F2 = 100.526031 MHz

(*E*)-**3fa**

dibromomethane (7.0 uL, 0.1 mmol) as the
internal standard in 59.8 mg product


spect, CDCl3,
Tue Dec 20 11:32:29 2016
USER: nmr
SOLVENT:
Experiment = zg30
Pulse length = 14.000 usec
Recycle delay = 1.000 sec
NA = 8
PTS1d = 32768
F1 = 300.131866 MHz
F2 = 1.000000 MHz
SW1 = 6188.12 Hz
MeOOC
O
H
OBn
O
(E)-3ga
mdk-10-184
8.135
8.130
8.123
8.108
8.102
8.096
7.822
7.817
7.810
7.794
7.788
7.783
7.382
7.377
7.374
7.371
7.365
7.353
7.342
7.337
7.325
7.266
6.224
6.219
6.213
6.209
5.212
3.947
2.441
2.436
1.776
-0.000
2.07
2.08
5.03
1.00
2.03
3.02
3.02
10
8
6
4
2
0
PPM

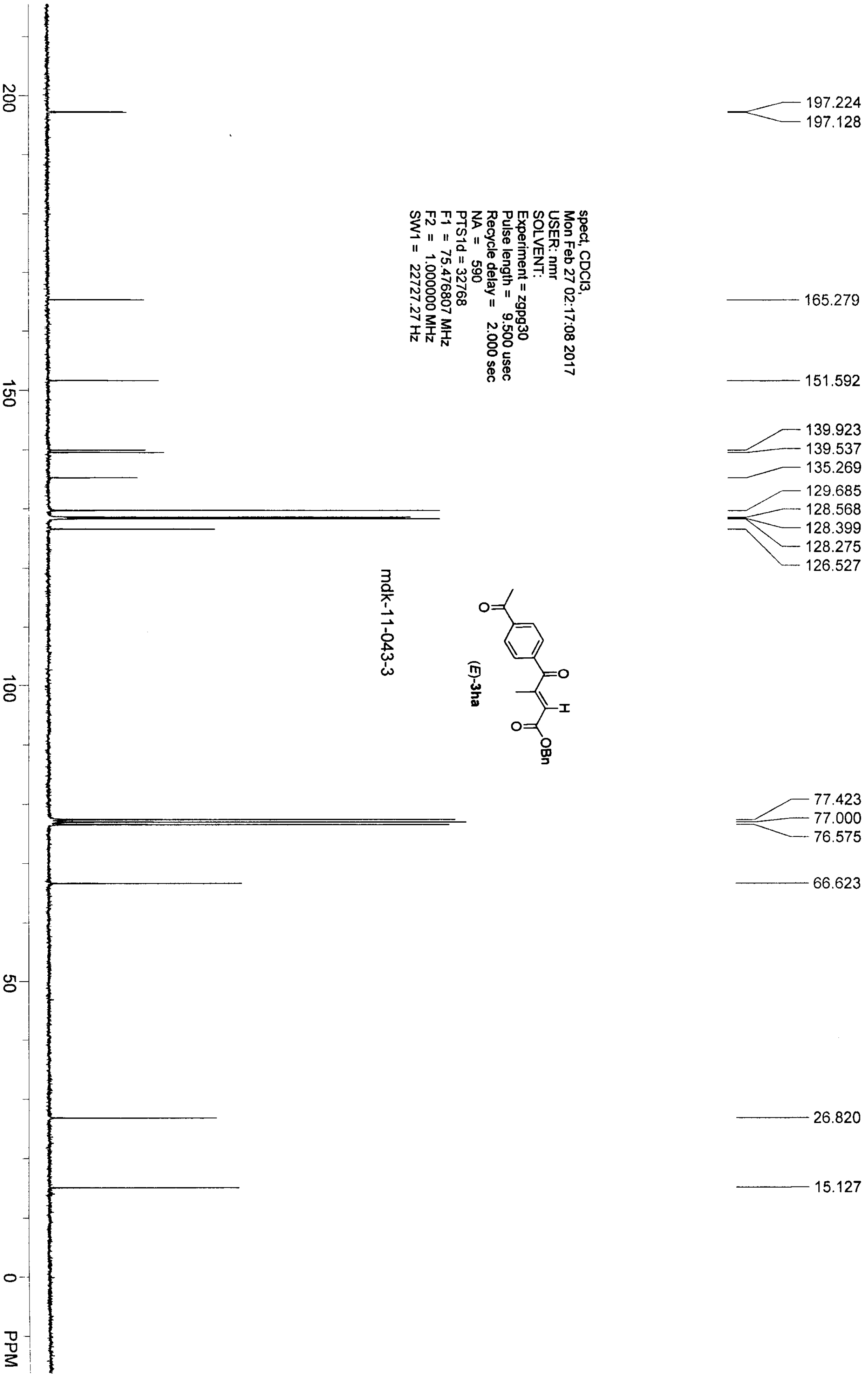
197.152
165.964
165.293
151.621
139.517
135.275
133.702
129.618
129.397
128.552
128.374
126.407
77.425
77.000
76.575
66.589
52.435
15.147
spect, CDCl3,
Tue Dec 20 13:39:13 2016
USER: nmr
SOLVENT:
Experiment = zgpg30
Pulse length = 9.500 usec
Recycle delay = 2.000 sec
NA = 422
PTS1d = 32768
F1 = 75.476807 MHz
F2 = 1.000000 MHz
SW1 = 22727.27 Hz
MeOOC
O
H
O
OBn
(E)-3ga
mdk-10-184
200
150
100
50
0 PPM

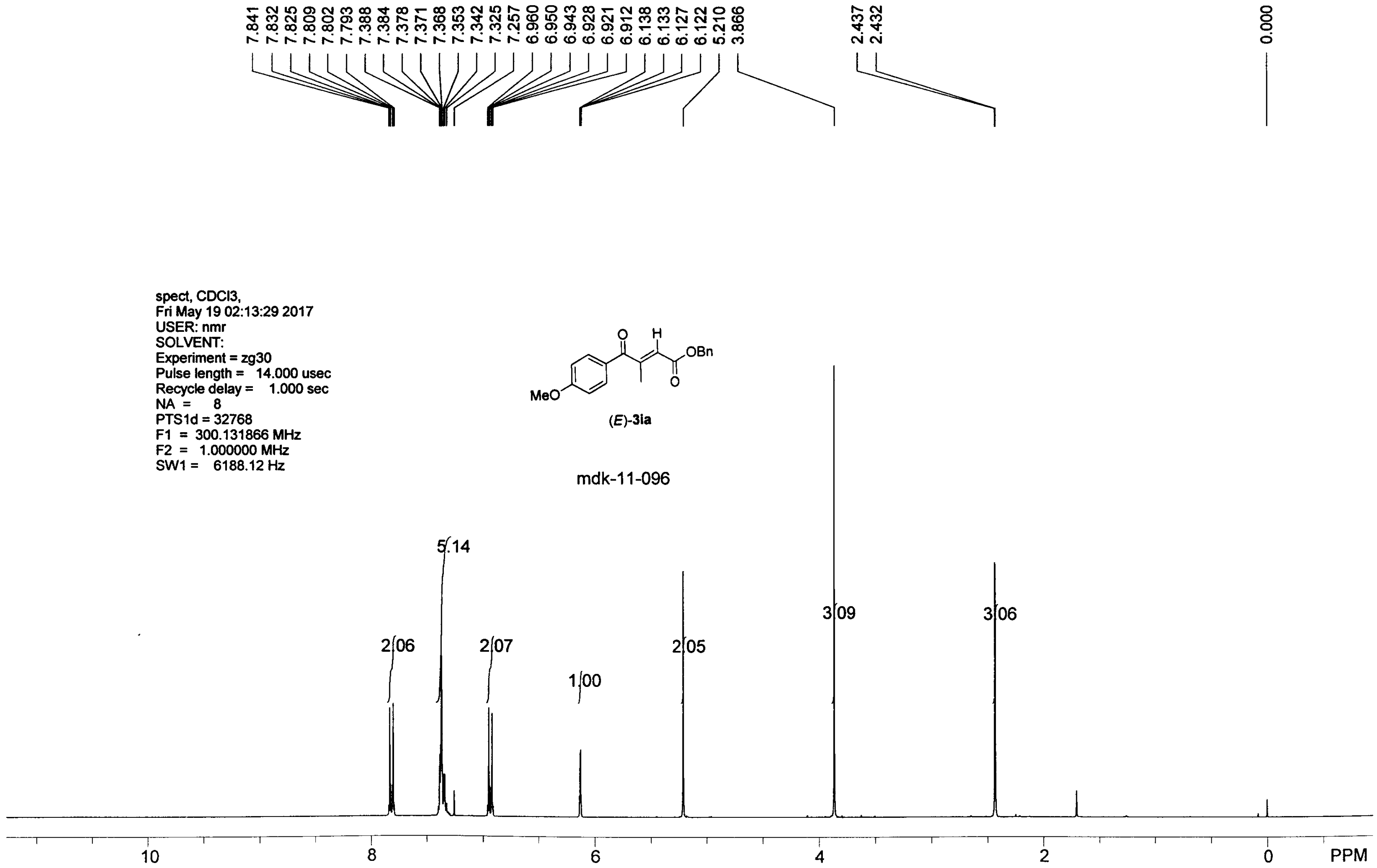


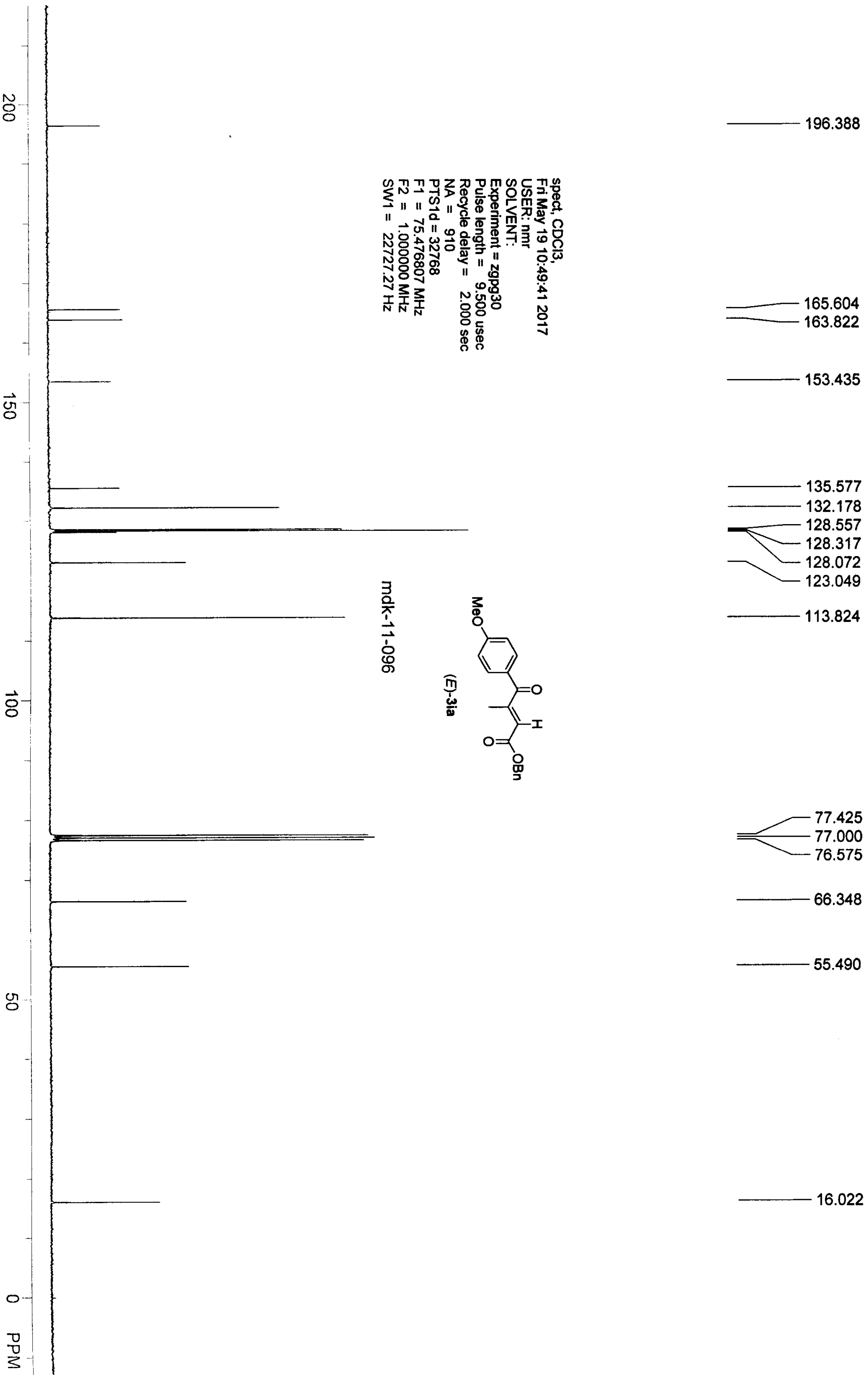
spect, CDCl3,
Mon Feb 27 06:40:28 2017
USER: nmr
SOLVENT:
Experiment = zg30
Pulse length = 14.000 usec
Recycle delay = 1.000 sec
NA = 8
PTS1d = 32768
F1 = 300.131866 MHz
F2 = 1.000000 MHz
SW1 = 6188.12 Hz

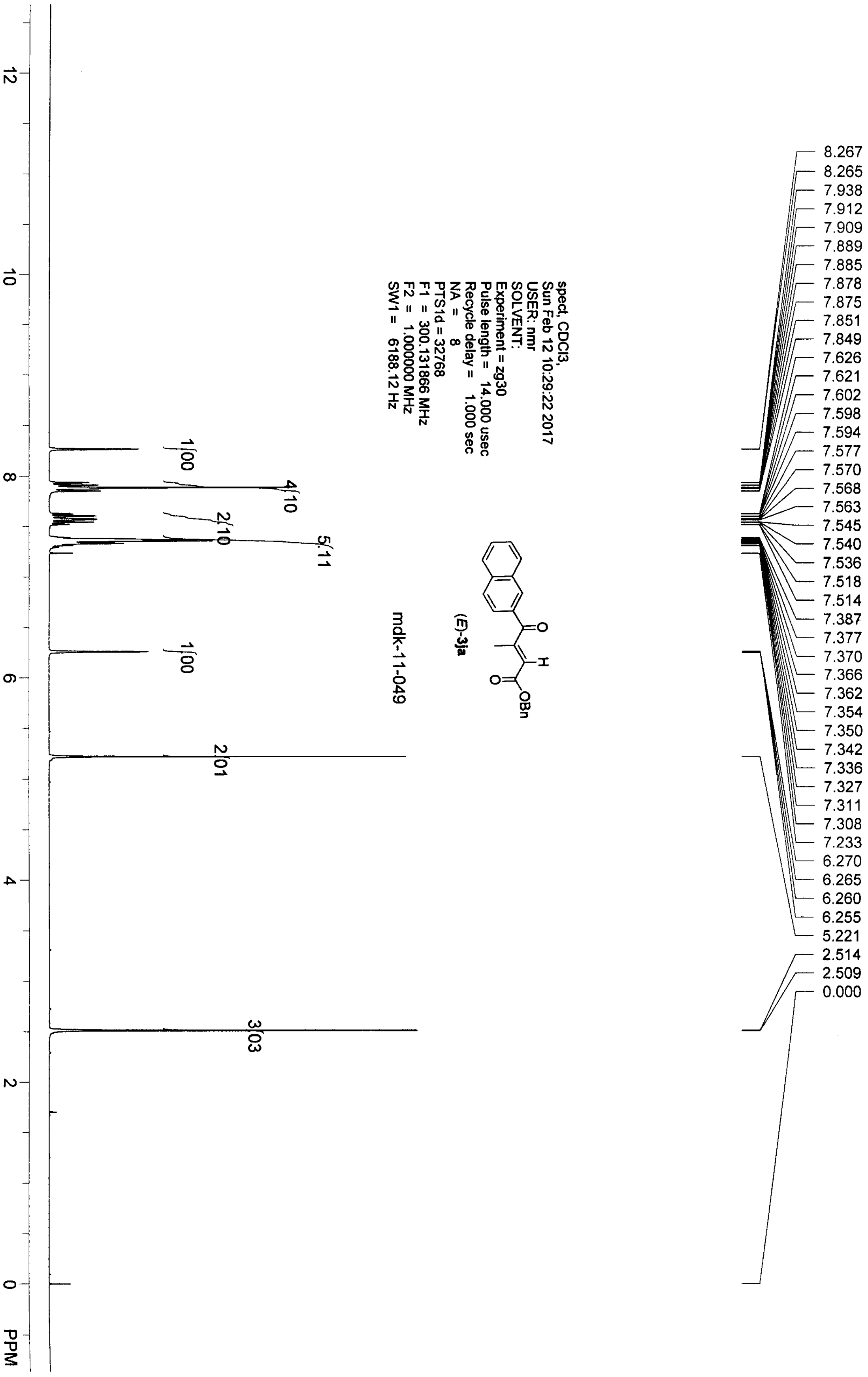
(*E*)-**3ha**

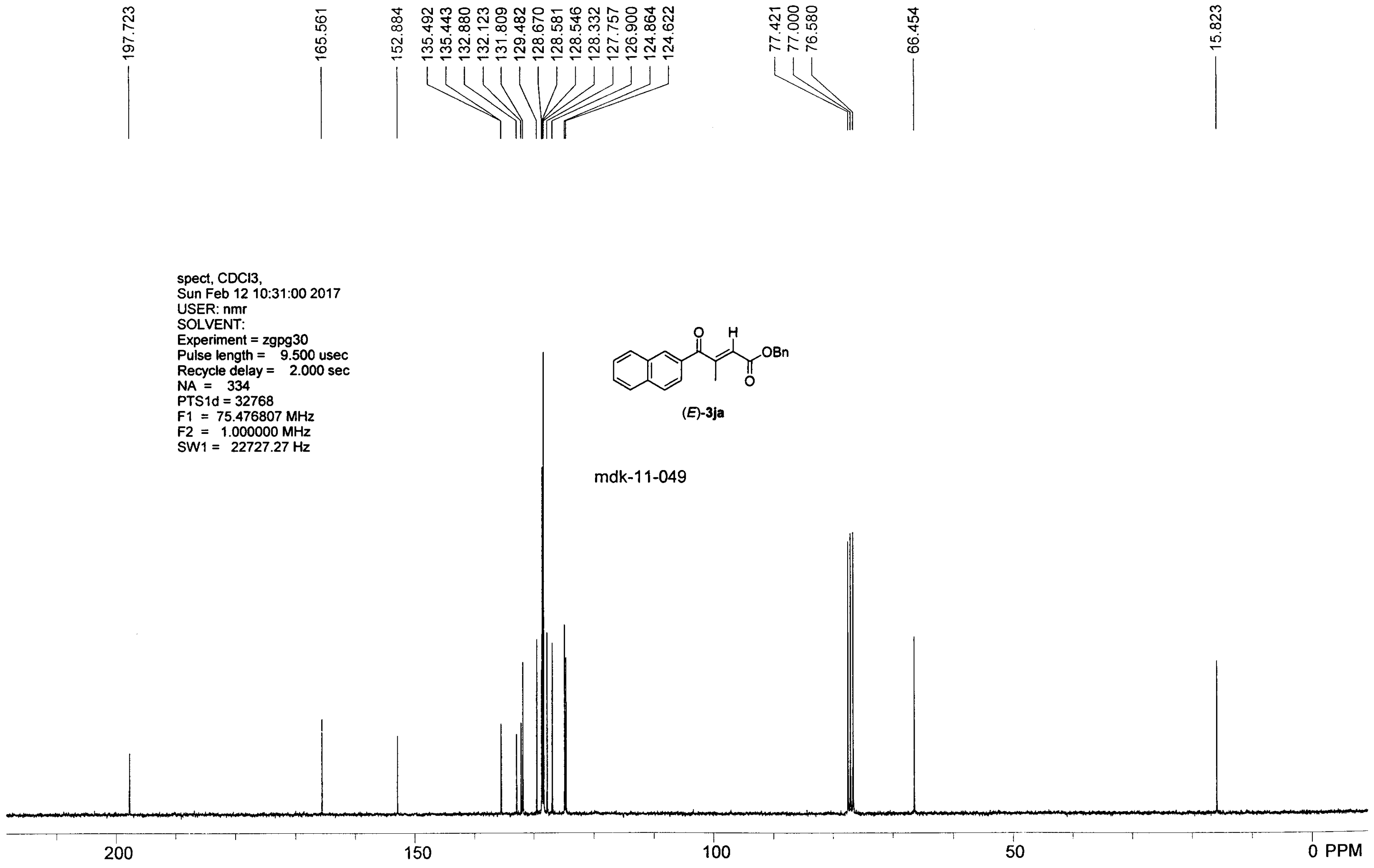
mdk-11-043-3


spect, CDCl3,
Mon Feb 27 02:17:08 2017
USER: nmr
SOLVENT:
Experiment = zgpg30
Pulse length = 9.500 usec
Recycle delay = 2.000 sec
NA = 590
PTS1d = 32768
F1 = 75.476807 MHz
F2 = 1.000000 MHz
SW1 = 22727.27 Hz
mdk-11-043-3
(E)-3ha
O
O
H
O
OBn
197.224
197.128
165.279
151.592
139.923
139.537
135.269
129.685
128.568
128.399
128.275
126.527
77.423
77.000
76.575
66.623
26.820
15.127
200
150
100
50
0
PPM


spect, CDCl3,
Fri May 19 02:13:29 2017
USER: nmr
SOLVENT:
Experiment = zg30
Pulse length = 14.000 usec
Recycle delay = 1.000 sec
NA = 8
PTS1d = 32768
F1 = 300.131866 MHz
F2 = 1.000000 MHz
SW1 = 6188.12 Hz
MeO
O
H
OBn
O
(E)-3ia
mdk-11-096
7.841
7.832
7.825
7.809
7.802
7.793
7.388
7.384
7.378
7.371
7.368
7.353
7.342
7.325
7.257
6.960
6.950
6.943
6.928
6.921
6.912
6.138
6.133
6.127
6.122
5.210
3.866
2.437
2.432
0.000
2.06
5.14
2.07
1.00
2.05
3.09
3.06
10
8
6
4
2
0
PPM

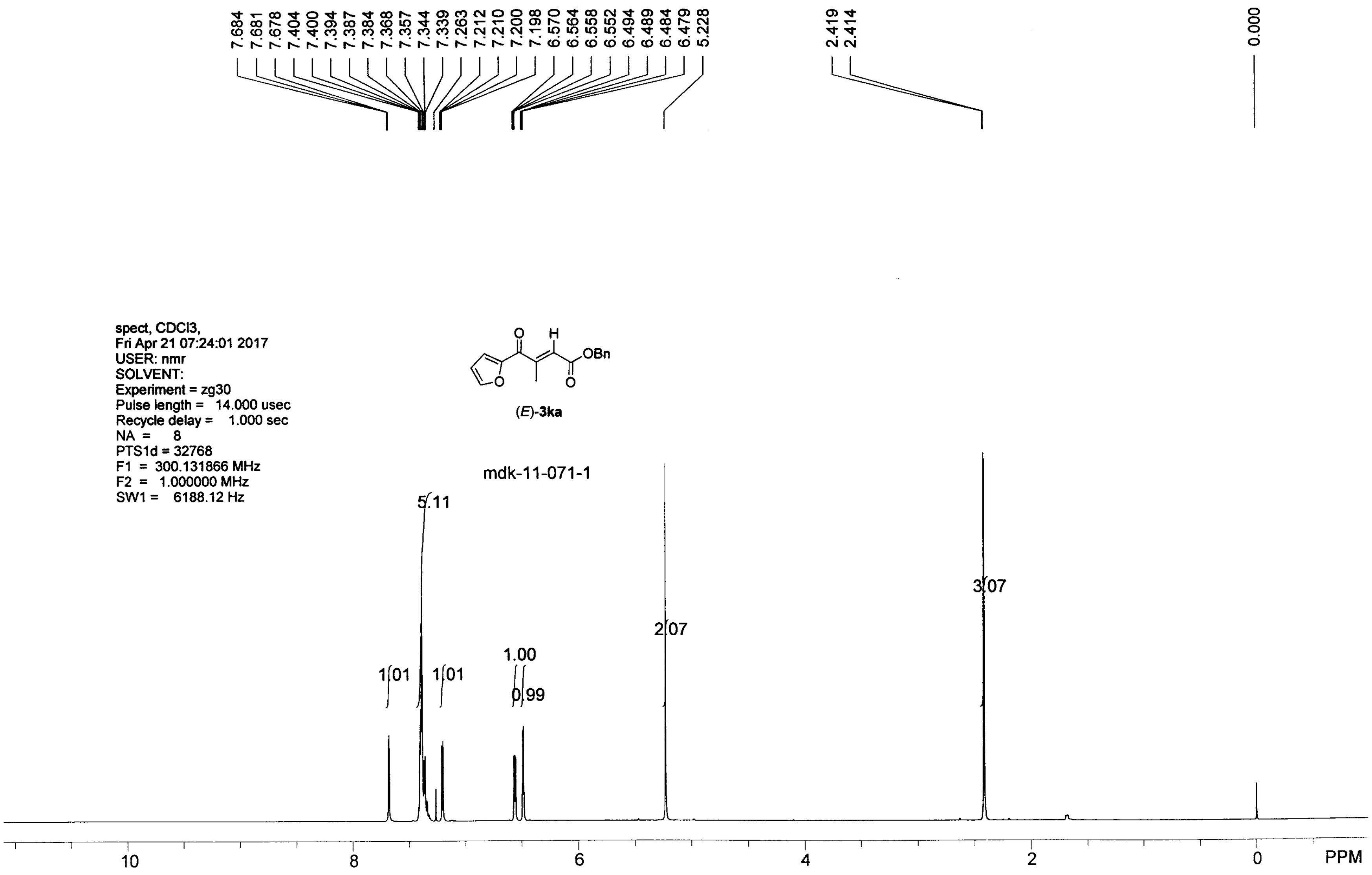

spect, CDCl3,
Fri May 19 10:49:41 2017
USER: nmr
SOLVENT:
Experiment = zgpg30
Pulse length = 9.500 usec
Recycle delay = 2.000 sec
NA = 910
PTS1d = 32768
F1 = 75.476807 MHz
F2 = 1.000000 MHz
SW1 = 22727.27 Hz
mdk-11-096
MeO
O
H
OBn
O
(E)-3ia
196.388
165.604
163.822
153.435
135.577
132.178
128.557
128.317
128.072
123.049
113.824
77.425
77.000
76.575
66.348
55.490
16.022
200
150
100
50
0
PPM


spect, CDCl3,
Sun Feb 12 10:29:22 2017
USER: nmr
SOLVENT:
Experiment = zg30
Pulse length = 14.000 usec
Recycle delay = 1.000 sec
NA = 8
PTS1d = 32768
F1 = 300.131866 MHz
F2 = 1.000000 MHz
SW1 = 6188.12 Hz
O
H
OBn
O
(E)-3ja
mdk-11-049
8.267
8.265
7.938
7.912
7.909
7.889
7.885
7.878
7.875
7.851
7.849
7.626
7.621
7.602
7.598
7.594
7.577
7.570
7.568
7.563
7.545
7.540
7.536
7.518
7.514
7.387
7.377
7.370
7.366
7.362
7.354
7.350
7.342
7.336
7.327
7.311
7.308
7.233
6.270
6.265
6.260
6.255
5.221
2.514
2.509
0.000
1.00
4.10
2.10
5.11
1.00
2.01
3.03
12
10
8
6
4
2
0
PPM



(*E*)-**3ja**

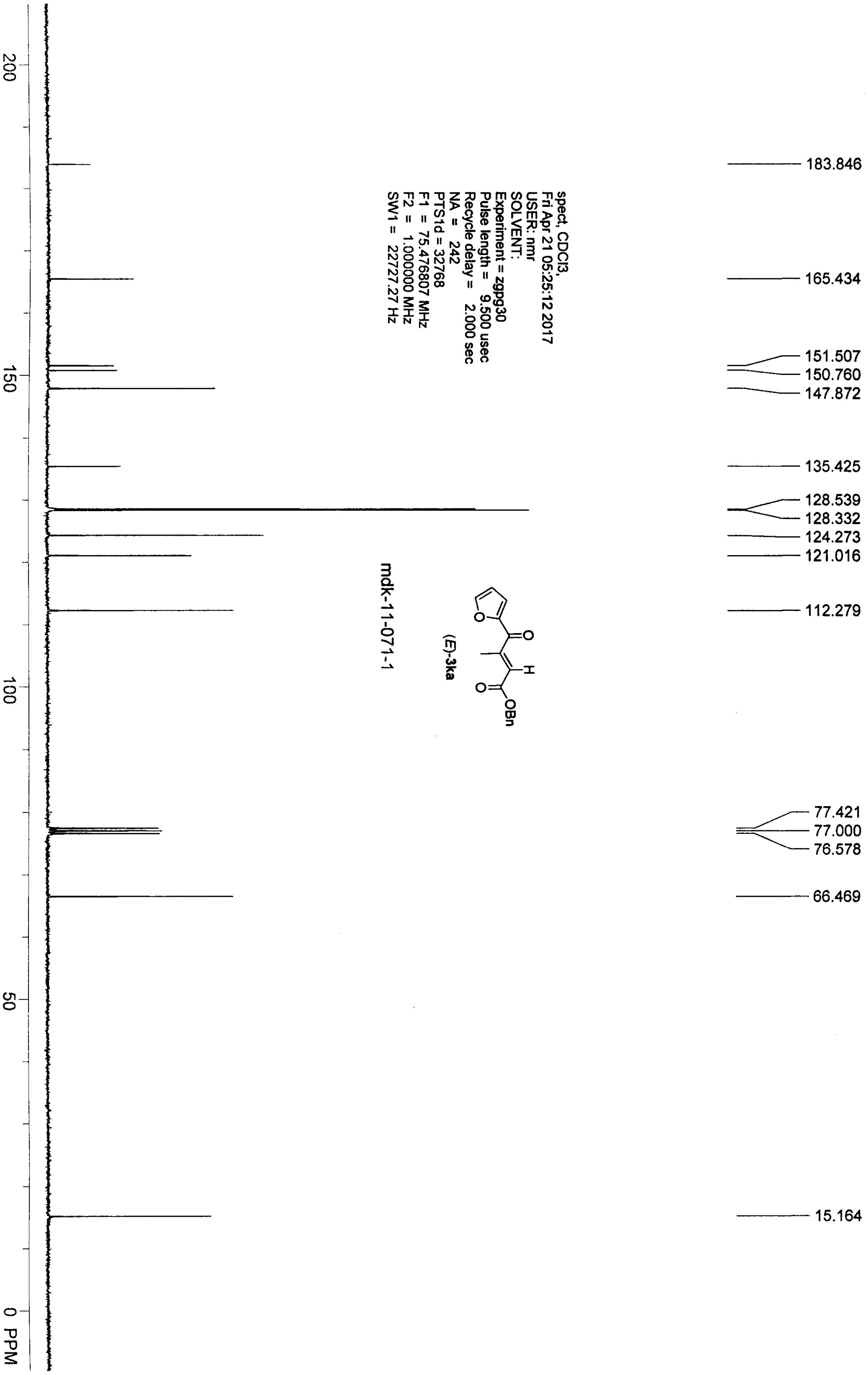
mdk-11-049

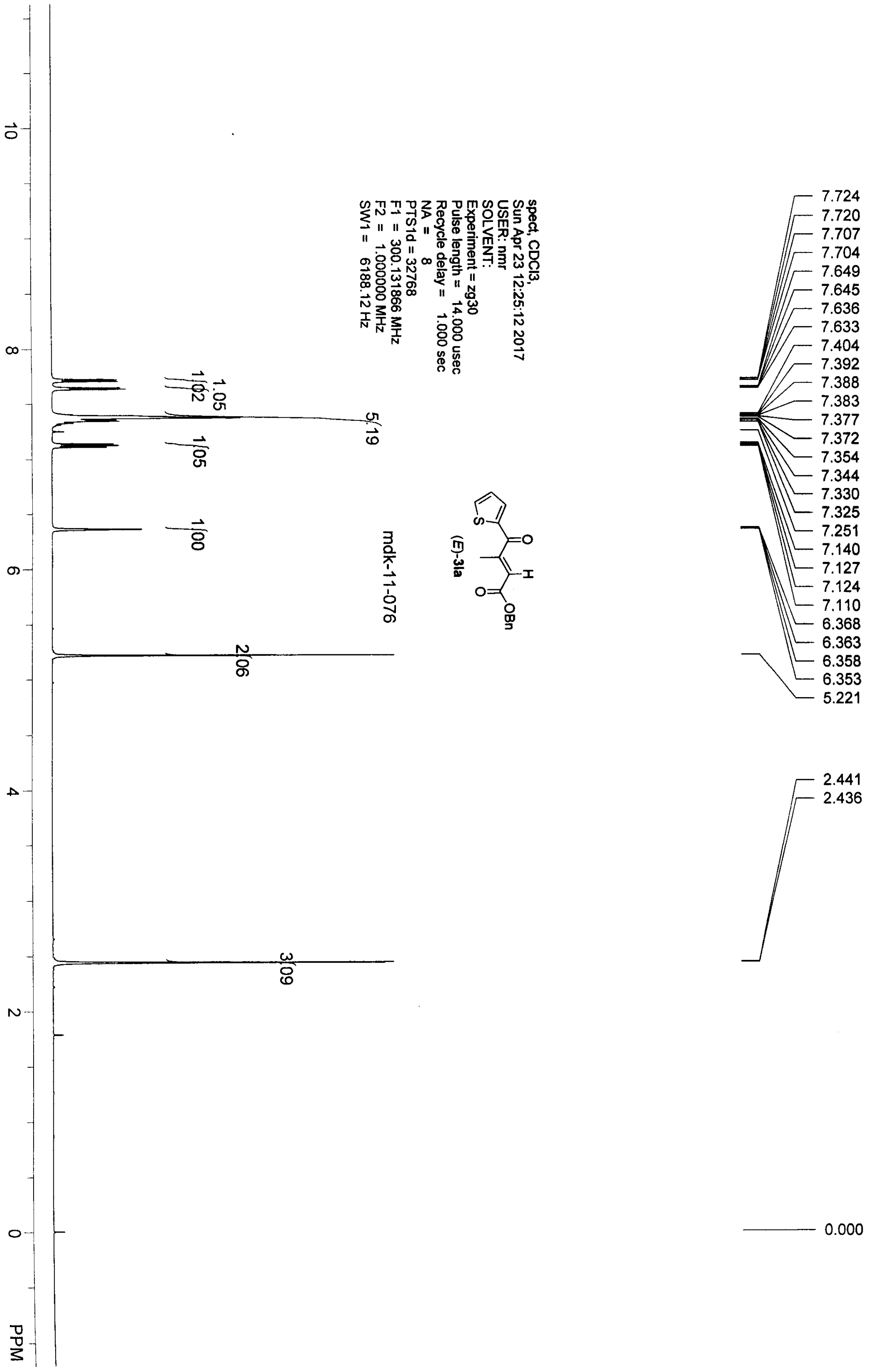


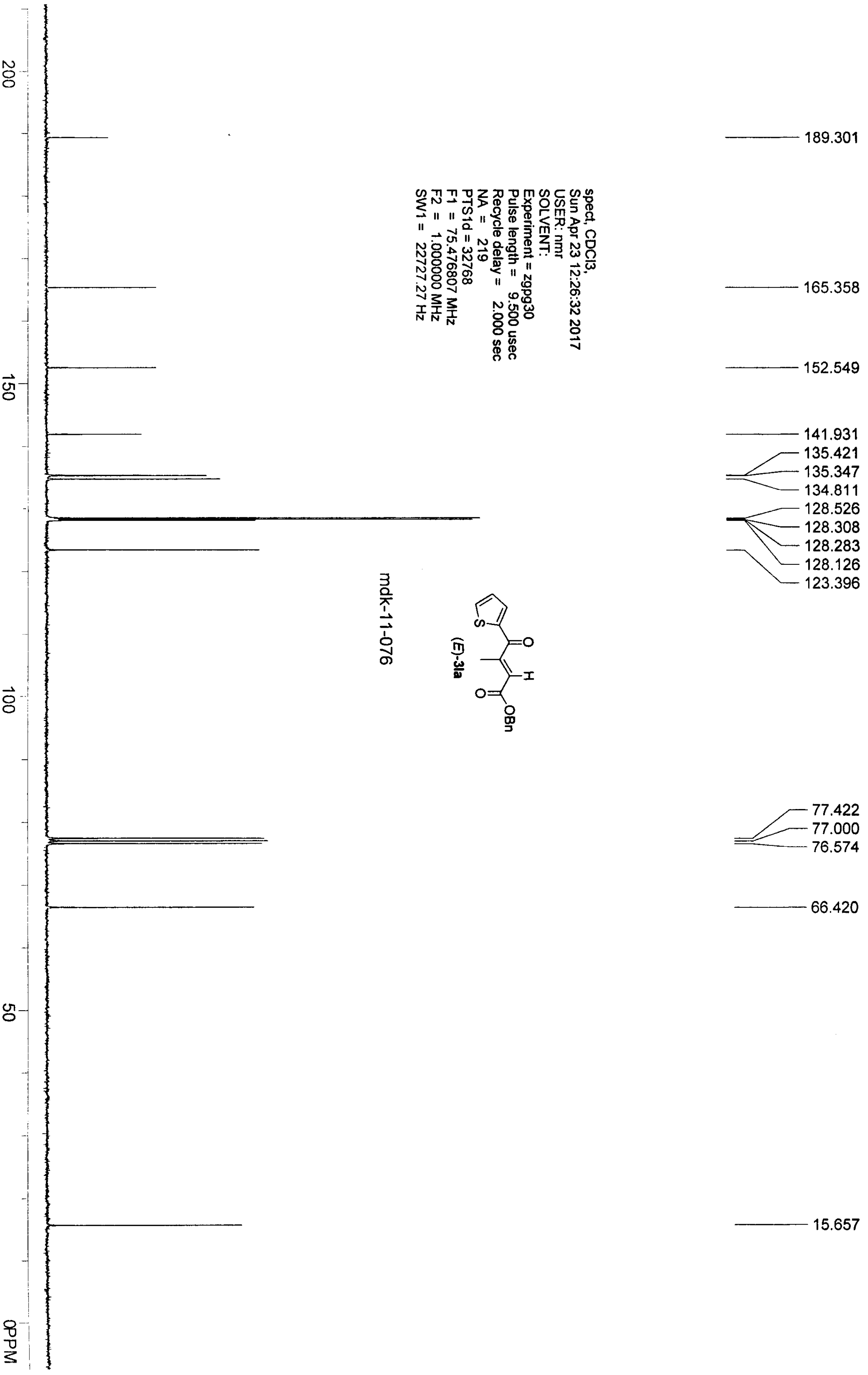
spect, CDCl3,
Fri Apr 21 07:24:01 2017
USER: nmr
SOLVENT:
Experiment = zg30
Pulse length = 14.000 usec
Recycle delay = 1.000 sec
NA = 8
PTS1d = 32768
F1 = 300.131866 MHz
F2 = 1.000000 MHz
SW1 = 6188.12 Hz

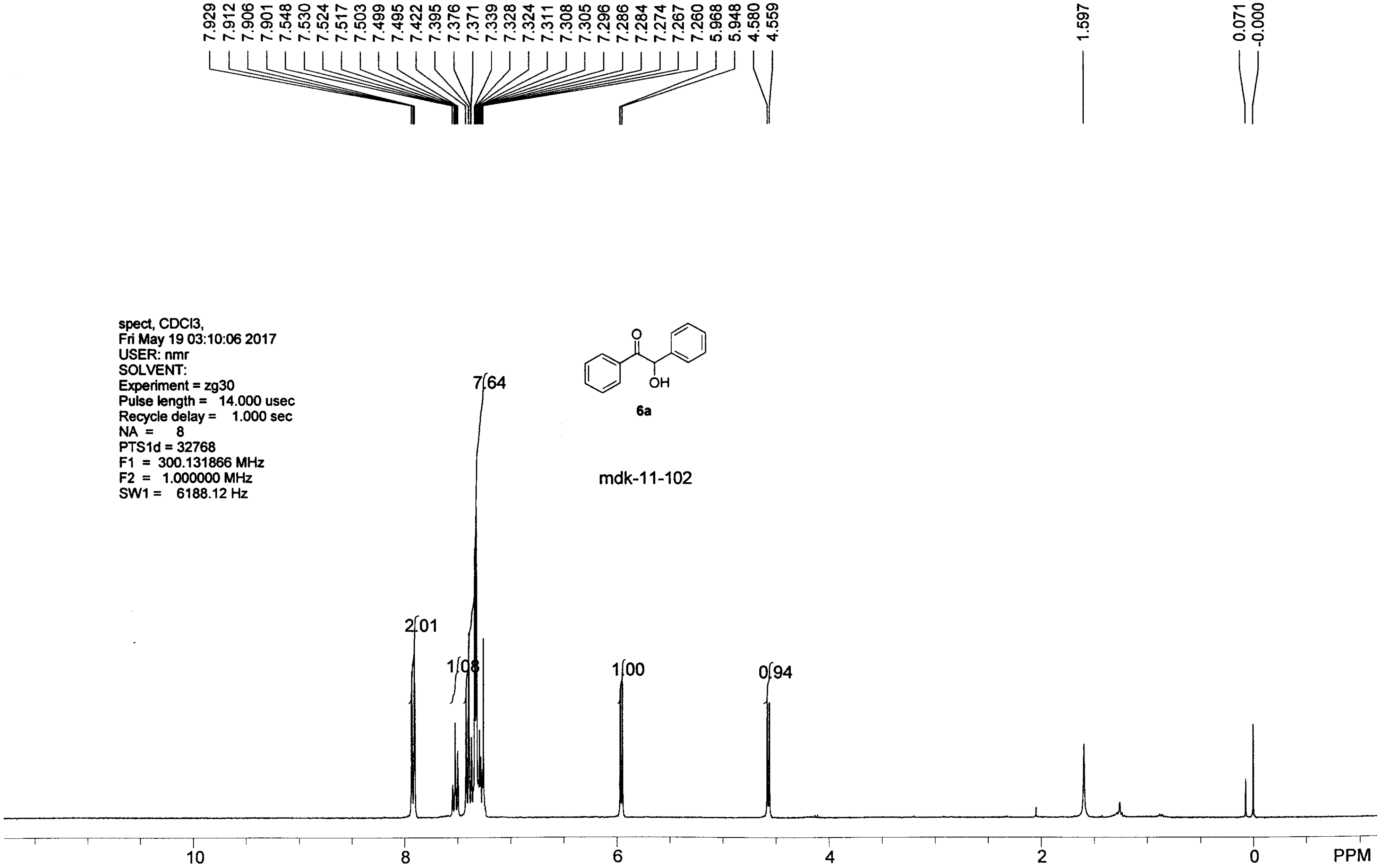
(*E*)-**3ka**

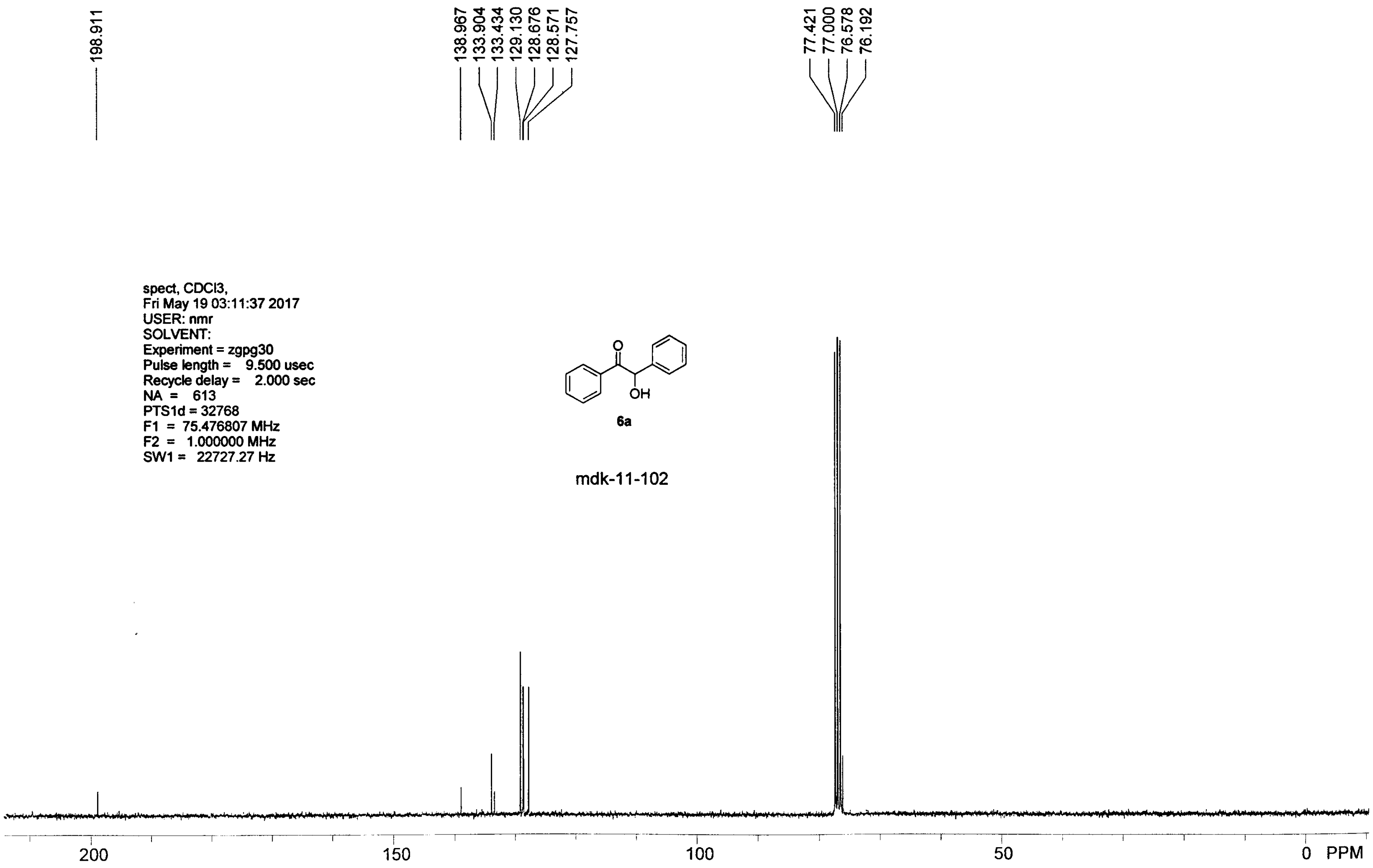
mdk-11-071-1


spect, CDCl3,
Fri Apr 21 05:25:12 2017
USER: nmr
SOLVENT:
Experiment = zgpg30
Pulse length = 9.500 usec
Recycle delay = 2.000 sec
NA = 242
PTS1d = 32768
F1 = 75.476807 MHz
F2 = 1.000000 MHz
SW1 = 22727.27 Hz
(E)-3ka
mdk-11-071-1
O
H
OBn
183.846
165.434
151.507
150.760
147.872
135.425
128.539
128.332
124.273
121.016
112.279
77.421
77.000
76.578
66.469
15.164
200
150
100
50
0 PPM


spect, CDCl3,
Sun Apr 23 12:25:12 2017
USER: nmr
SOLVENT:
Experiment = zg30
Pulse length = 14.000 usec
Recycle delay = 1.000 sec
NA = 8
PTS1d = 32768
F1 = 300.131866 MHz
F2 = 1.000000 MHz
SW1 = 6188.12 Hz
mdk-11-076
(E)-3la
O
H
OBn
S
7.724
7.720
7.707
7.704
7.649
7.645
7.636
7.633
7.404
7.392
7.388
7.383
7.377
7.372
7.354
7.344
7.330
7.325
7.251
7.140
7.127
7.124
7.110
6.368
6.363
6.358
6.353
5.221
2.441
2.436
0.000
1.05
1.02
5.19
1.05
1.00
2.06
3.09
10
8
6
4
2
0
PPM


spect, CDCl3,
Sun Apr 23 12:26:32 2017
USER: nmr
SOLVENT:
Experiment = zgpg30
Pulse length = 9.500 usec
Recycle delay = 2.000 sec
NA = 219
PTS1d = 32768
F1 = 75.476807 MHz
F2 = 1.000000 MHz
SW1 = 22727.27 Hz
189.301
165.358
152.549
141.931
135.421
135.347
134.811
128.526
128.308
128.283
128.126
123.396
77.422
77.000
76.574
66.420
15.657
O
H
OBn
O
S
(E)-3la
mdk-11-076
200
150
100
50
0PPM


7.929
7.912
7.906
7.901
7.548
7.530
7.524
7.517
7.503
7.499
7.495
7.422
7.395
7.376
7.371
7.339
7.328
7.324
7.311
7.308
7.305
7.296
7.286
7.284
7.274
7.267
7.260
5.968
5.948
4.580
4.559
1.597
0.071
-0.000
spect, CDCl3,
Fri May 19 03:10:06 2017
USER: nmr
SOLVENT:
Experiment = zg30
Pulse length = 14.000 usec
Recycle delay = 1.000 sec
NA = 8
PTS1d = 32768
F1 = 300.131866 MHz
F2 = 1.000000 MHz
SW1 = 6188.12 Hz
O
OH
6a
mdk-11-102
2.01
1.08
7.64
1.00
0.94
10
8
6
4
2
0
PPM


198.911
138.967
133.904
133.434
129.130
128.676
128.571
127.757
77.421
77.000
76.578
76.192
spect, CDCl3,
Fri May 19 03:11:37 2017
USER: nmr
SOLVENT:
Experiment = zgpg30
Pulse length = 9.500 usec
Recycle delay = 2.000 sec
NA = 613
PTS1d = 32768
F1 = 75.476807 MHz
F2 = 1.000000 MHz
SW1 = 22727.27 Hz
O
OH
6a
mdk-11-102
200
150
100
50
0 PPM