

# An Efficient Stereoselective Synthesis of *cis*-2,6-Disubstituted Tetrahydropyrans via Gold-catalyzed Meyer–Schuster Rearrangement/Hydration/*oxa*-Michael Addition Sequence

## Supporting Information

Nobuyoshi Morita \*, Daichi Yamashita, Yoshimitsu Hashimoto and Osamu Tamura \*

*Department of Pharmacy, Showa Pharmaceutical University, 3-3165 Higashi-Tamagawagakuen, Machida 194-8543, Tokyo, Japan;*

*\*Correspondence: morita@ac.shoyaku.ac.jp (N.M.); tamura@ac.shoyaku.ac.jp (O.T.);  
Tel.: +81-42-721-1579 (N.M.)*

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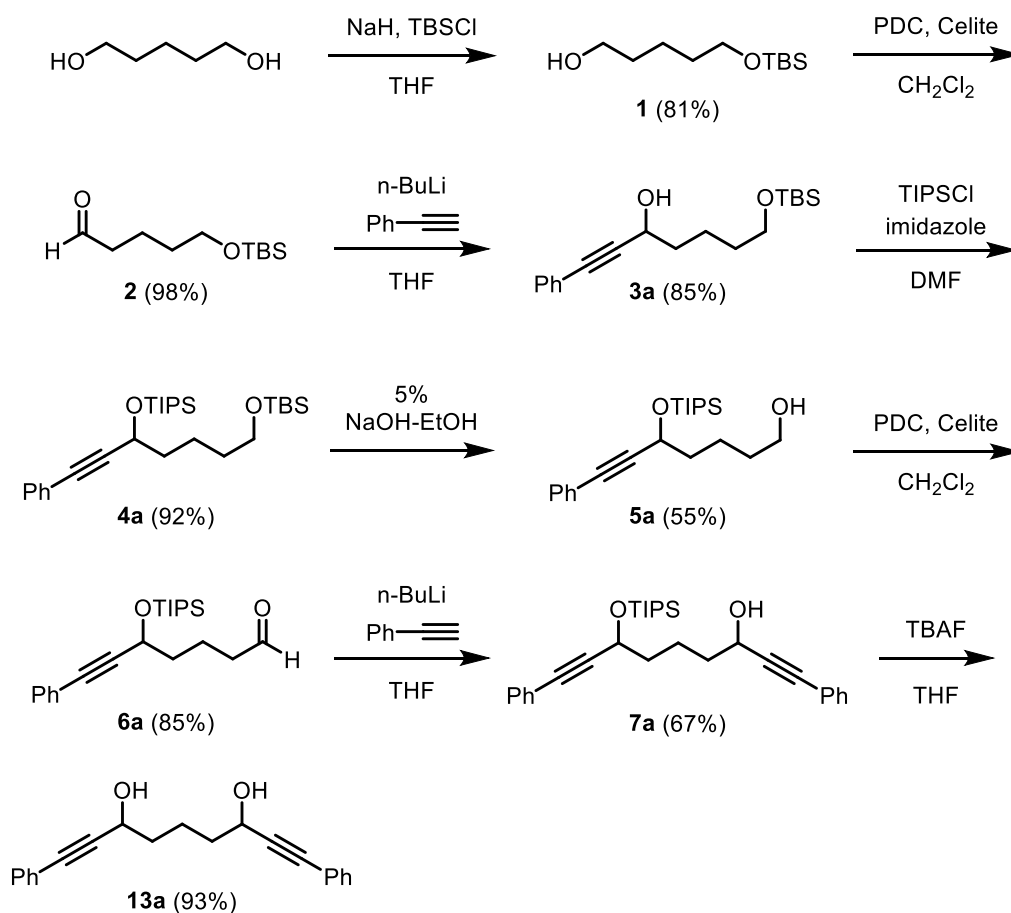
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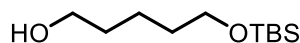
## General Information

$^1\text{H}$  and  $^{13}\text{C}$  NMR spectra were recorded with a JEOL JNM-AL300 (Japan Electron Optics Laboratory Co., Ltd., Tokyo, Japan) or BRUKER AV-300 spectrometer (Bruker, Billerica, MA, USA) at room temperature, with tetramethylsilane as an internal standard ( $\text{CDCl}_3$  solution). Chemical shifts were recorded in ppm and coupling constants ( $J$ ) in Hz. Infrared (IR) spectra were recorded with a Shimadzu FTIR-8200A spectrometer (Shimadzu Corporation, Kyoto, Japan). Mass spectra were recorded on JEOL JMS-700 spectrometers (Japan Electron Optics Laboratory Co., Ltd., Tokyo, Japan). Merck silica gel 60 (1.09385) (Merck, Darmstadt, Germany) and Merck silica gel 60 F254 (Merck, Darmstadt, Germany) were used for column chromatography and thin-layer chromatography (TLC), respectively.

## Synthesis of bis-propargylic alcohols **13a**

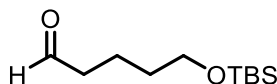


### 5-[(*tert*-Butyldimethylsilyl)oxy]pentan-1-ol (1)



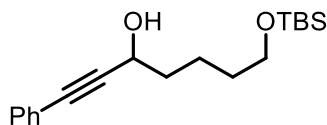
A solution of 1,5-pentanediol (3.00 g, 28.8 mmol) in THF (20 mL) was added at 0 °C to a suspension of NaH (0.829 g, 34.6 mmol) in THF (100 mL). The reaction mixture was stirring at 0 °C for 1 h and TBSCl (4.77 g, 31.7 mmol) was added to the reaction mixture. Reaction mixture was stirred at room temperature for 24 h and was poured into saturated NH<sub>4</sub>Cl solution and extracted with Et<sub>2</sub>O. The combined organic phases were washed with brine and dried with Na<sub>2</sub>SO<sub>4</sub>, the solvent was removed by rotary evaporation, and the crude product was purified by column chromatography (hexane:AcOEt = 4:1) on silica gel to afford the product **1** (5.12 g, 81%) as a colorless oil. <sup>1</sup>H-NMR (300 MHz, CDCl<sub>3</sub>) δ 3.65 (2H, t, *J* = 6.6 Hz), 3.62 (2H, t, *J* = 6.3 Hz), 1.64 (1H, brs), 1.62–1.55 (4H, m), 1.46–1.38 (2H, m), 0.90 (9H, s), 0.05 (6H, s); <sup>13</sup>C-NMR (75 MHz, CDCl<sub>3</sub>) δ 63.1, 62.9, 32.5, 32.4, 25.9, 22.0, 18.3, -5.3.

### 5-[(*tert*-Butyldimethylsilyl)oxy]pentanal (2)



To a solution of PDC (26.4 g, 70.2 mmol) and celite (26.4 g) in CH<sub>2</sub>Cl<sub>2</sub> (450 mL) was added a solution of 5-[(*tert*-butyldimethylsilyl)oxy]pentan-1-ol (**1**) (5.12 g, 23.4 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (20 mL) at room temperature. The reaction mixture was stirring at reflux for 3.5 h. PDC and celite was removed by filtration and the filtrate was removed by rotary evaporation. The crude product was purified by column chromatography (hexane:AcOEt = 10:1) on silica gel to afford the product **2** (4.96 g, 98%) as a colorless oil. <sup>1</sup>H-NMR (300 MHz, CDCl<sub>3</sub>) δ 9.77 (1H, t, *J* = 1.8 Hz), 3.63 (2H, t, *J* = 6.0 Hz), 2.46 (2H, td, *J* = 7.2, 1.8 Hz), 1.76–1.67 (2H, m), 1.60–1.53 (2H, m), 0.89 (9H, s), 0.05 (6H, s); <sup>13</sup>C-NMR (75 MHz, CDCl<sub>3</sub>) δ 202.7, 62.6, 43.6, 32.1, 25.9, 18.6, 18.3, -5.4.

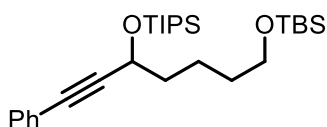
### 7-[(*tert*-Butyldimethylsilyl)oxy]-1-phenylhept-1-yn-3-ol (3a)



To a solution of ethynylbenzene (5.03 mL, 45.8 mmol) in THF (80 mL) was added *n*-BuLi (1.58 mol/L in hexane, 29.0 mL, 45.8 mmol) at -78 °C under argon. The reaction mixture was stirred at -78 °C for 30 min and a solution of **2** (4.96 g, 22.9 mmol) in THF (50 mL) was added to the reaction mixture at -78 °C. The reaction mixture was stirred at -78 °C for 2 h and was poured into saturated NH<sub>4</sub>Cl solution and extracted with Et<sub>2</sub>O. The combined organic phases were washed with brine and dried with Na<sub>2</sub>SO<sub>4</sub>, the solvent was removed by rotary evaporation, and the crude product was purified by column chromatography (hexane:AcOEt = 7:1) on silica gel to afford the product **3a** (6.17 g, 85%) as a colorless oil.

<sup>1</sup>H-NMR (300 MHz, CDCl<sub>3</sub>) δ 7.45–7.39 (2H, m), 7.35–7.28 (3H, m), 4.61 (1H, t, *J* = 6.6 Hz), 3.65 (2H, t, *J* = 6.3 Hz), 1.86–1.79 (2H, m), 1.60–1.54 (4H, m), 0.88 (9H, s), 0.04 (6H, s); <sup>13</sup>C-NMR (75 MHz, CDCl<sub>3</sub>) δ 131.7, 128.3, 128.2, 122.7, 90.1, 84.9, 63.0, 37.6, 32.4, 25.9, 21.6, 18.3, -5.3 (overlapped).

#### 7-[(*tert*-Butyldimethylsilyl)oxy]-3-[(triisopropylsilyl)oxy]-1-phenylhept-1-yn (4a)

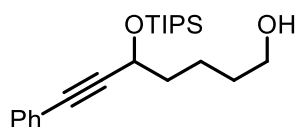


Imidazole (1.28 g, 18.8 mmol) and TIPSCl (2.02 mL, 9.42 mmol) were added to a solution of compound **3a** (2.00 g, 6.28 mmol) in DMF (45 mL) at 0 °C. The reaction mixture was stirred at room temperature for 48 h and was poured into H<sub>2</sub>O and extracted with Et<sub>2</sub>O. The combined organic phases were washed with brine and dried with Na<sub>2</sub>SO<sub>4</sub>, the solvent was removed by rotary evaporation, and the crude product was purified by column chromatography (hexane:AcOEt = 40:1) on silica gel to afford the product **4a** (2.75 g, 92%) as a colorless oil.

<sup>1</sup>H-NMR (300 MHz, CDCl<sub>3</sub>) δ 7.41–7.38 (2H, m), 7.31–7.26 (3H, m), 4.69 (1H, t, *J* = 6.3 Hz), 3.66–3.62 (2H, m), 1.81–1.77 (2H, m), 1.60–1.57 (4H, m), 1.19–1.14 (3H, m), 1.12 (18H, d, *J*

= 6.3 Hz), 0.89 (9H, s), 0.05 (6H, s);  $^{13}\text{C}$ -NMR (75 MHz,  $\text{CDCl}_3$ )  $\delta$  131.5, 128.2, 128.0, 123.3, 91.3, 84.0, 63.5, 63.1, 38.8, 32.7, 26.0, 21.6, 18.09, 18.07, 12.3, -5.3.

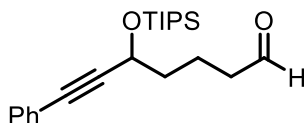
#### 7-Phenyl-5-[(triisopropylsilyl)oxy]hept-6-yn-1-ol (5a)



Compound **4a** (1.00 g, 2.11 mmol) was added to a solution of NaOH (1.09 g) in EtOH (20.6 g) at room temperature. The reaction mixture was stirred at reflux for 4.5 h and was poured into  $\text{H}_2\text{O}$  and extracted with  $\text{CH}_2\text{Cl}_2$ . The combined organic phases were washed with brine and dried with  $\text{Na}_2\text{SO}_4$ , the solvent was removed by rotary evaporation, and the crude product was purified by column chromatography (hexane:AcOEt = 6:1) on silica gel to afford the product **5a** (0.416 g, 55%) as a colorless oil.

$^1\text{H}$ -NMR (300 MHz,  $\text{CDCl}_3$ )  $\delta$  7.41–7.40 (2H, m), 7.31–7.26 (3H, m), 4.71 (1H, t,  $J$  = 6.0 Hz), 3.69 (2H, t,  $J$  = 5.7 Hz), 1.86–1.79 (2H, m), 1.64–1.58 (5H, m), 1.24–1.16 (3H, m), 1.12 (18H, d,  $J$  = 6.3 Hz);  $^{13}\text{C}$ -NMR (75 MHz,  $\text{CDCl}_3$ )  $\delta$  131.4, 128.2, 128.0, 123.1, 91.1, 84.1, 63.3, 62.9, 38.6, 32.5, 21.3, 18.1, 12.3.

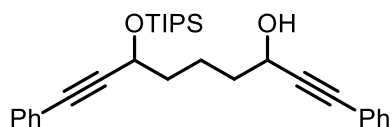
#### 7-Phenyl-5-[(triisopropylsilyl)oxy]hept-6-ynal (6a)



According to the synthesis of compound **2**, treatment of **5a** (0.490 g, 1.36 mmol) with PDC (1.53 g, 4.08 mmol) and celite (1.53 g) afforded the product **6a** (0.413 g, 85%) as a colorless oil (hexane:AcOEt = 10:1).

$^1\text{H}$ -NMR (300 MHz,  $\text{CDCl}_3$ )  $\delta$  9.80 (1H, t,  $J$  = 1.5 Hz), 7.41–7.38 (2H, m), 7.31–7.26 (3H, m), 4.74 (1H, t,  $J$  = 5.7 Hz), 2.53 (1H, td,  $J$  = 7.2, 1.5 Hz), 2.46 (1H, t,  $J$  = 6.9 Hz), 1.95–1.82 (4H, m), 1.22–1.17 (3H, m), 1.12 (18H, d,  $J$  = 6.0 Hz);  $^{13}\text{C}$ -NMR (75 MHz,  $\text{CDCl}_3$ )  $\delta$  202.5, 131.4, 128.24, 128.21, 123.0, 90.6, 84.4, 63.0, 43.6, 38.0, 20.3, 18.0, 12.3.

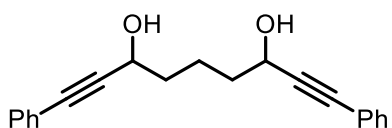
### 1,9-Diphenyl-7-[(triisopropylsilyl)oxy]nona-1,8-diyn-3-ol (7a)



According to the synthesis of compound **3a**, treatment of **6a** (1.78 g, 4.96 mmol) with ethynylbenzene (1.09 mL, 9.92 mmol), and *n*-BuLi (1.60 mol/L in hexane, 6.20 mL, 9.92 mmol) afforded the product **7a** (1.53 g, 67%) in colorless oil (hexane:AcOEt = 10:1).

$^1\text{H-NMR}$  (300 MHz,  $\text{CDCl}_3$ )  $\delta$  7.41–7.36 (4H, m), 7.33–7.27 (6H, m), 4.74 (1H, t,  $J$  = 5.4 Hz), 4.65 (1H, br s), 1.85–1.76 (6H, m), 1.60 (1H, br s), 1.19–1.14 (3H, m), 1.11 (18H, d,  $J$  = 5.7 Hz);  $^{13}\text{C-NMR}$  (75 MHz,  $\text{CDCl}_3$ )  $\delta$  131.8, 131.7, 131.5, 128.6, 128.2, 128.0, 123.1, 122.6, 91.0, 90.0, 85.0, 84.2, 63.3, 62.9, 38.4, 37.6, 20.9, 18.0, 12.3.

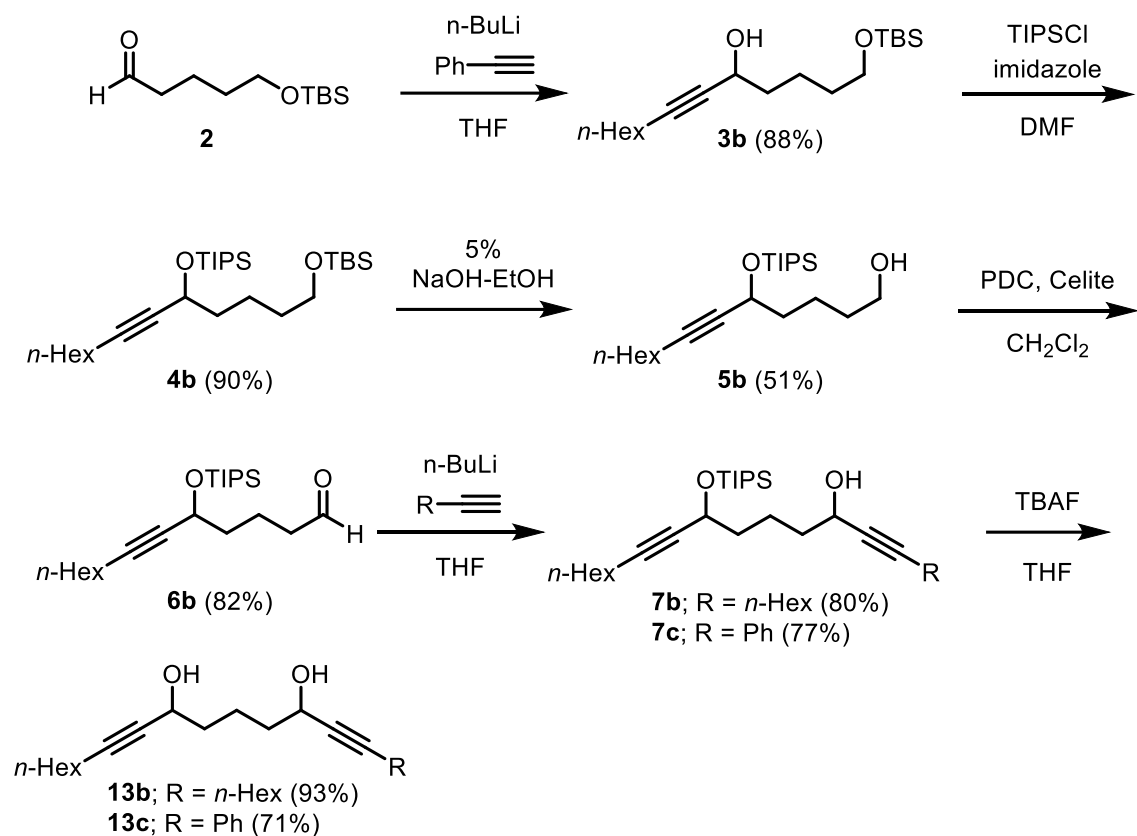
### 1,9-Diphenylnona-1,8-diyne-3,7-diol (13a)



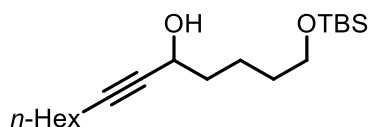
TBAF (1 mol/L in tetrahydrofuran, 1.82 mL, 1.82 mmol) was added to a solution of **7a** (0.700 g, 1.52 mmol) in THF (25 mL) at 0 °C. The reaction mixture was stirred at room temperature for 1.5 h and was poured into saturated  $\text{NH}_4\text{Cl}$  aq. and extracted with  $\text{Et}_2\text{O}$ . The combined organic phases were washed with brine and dried with  $\text{Na}_2\text{SO}_4$ , the solvent was removed by rotary evaporation, and the crude product was purified by column chromatography (hexane: $\text{Et}_2\text{O}$  = 3:2) on silica gel to afford the product **8a** (0.428 g, 93%) as a colorless oil.

IR (KBr) 3319, 3055, 2947, 2864, 2228, 1599, 1489, 1443, 1026, 756, 691  $\text{cm}^{-1}$ ;  $^1\text{H-NMR}$  (300 MHz,  $\text{CDCl}_3$ )  $\delta$  7.42–7.40 (4H, m), 7.31–7.26 (6H, m), 4.65 (2H, t,  $J$  = 6.0 Hz), 2.07 (2H, br s), 1.90–1.79 (6H, m);  $^{13}\text{C-NMR}$  (75 MHz,  $\text{CDCl}_3$ )  $\delta$  131.7, 128.4, 128.3, 122.5, 89.8, 85.1, 62.8, 37.3, 21.0; HRMS (EI)  $m/z$  calcd for  $\text{C}_{21}\text{H}_{20}\text{O}_2$   $[\text{M}]^+$  304.1463, found 304.1452.

## Synthesis of bis-propargylic alcohols **13b** and **13c**



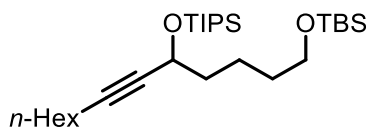
### 1-[(*tert*-Butyldimethylsilyl)oxy]tridec-6-yn-5-ol (**3b**)



According to the synthesis of compound **3a**, treatment of **2** (3.00 g, 13.9 mmol) with 1-octyne (4.08 mL, 27.8 mmol) afforded the product **3b** (4.02 g, 88%) in colorless oil (hexane:AcOEt = 10:1).

$^1\text{H-NMR}$  (300 MHz,  $\text{CDCl}_3$ )  $\delta$  4.36 (1H, t,  $J$  = 6.5 Hz), 3.62 (2H, t,  $J$  = 6.3 Hz), 2.20 (2H, td,  $J$  = 6.9, 1.8 Hz), 1.72–1.24 (14H, m), 0.89 (3H, t,  $J$  = 5.6 Hz), 0.90 (9H, s), 0.05 (6H, s);  $^{13}\text{C-NMR}$  (75 MHz,  $\text{CDCl}_3$ )  $\delta$  85.6, 81.2, 63.1, 62.8, 38.0, 32.4, 31.3, 28.6, 28.5, 26.0, 22.5, 21.6, 18.7, 18.3, 14.0, -5.3.

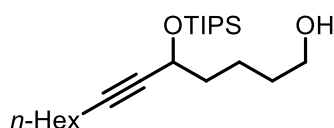
**1-[(*tert*-Butyldimethylsilyl)oxy]-5-[(triisopropylsilyl)oxy]tridec-6-yn (4b)**



According to the synthesis of compound **4a**, treatment of **3b** (4.00 g, 12.2 mmol) afforded the product **4b** (5.33 g, 90%) in colorless oil (hexane:AcOEt = 40:1).

$^1\text{H-NMR}$  (300 MHz,  $\text{CDCl}_3$ )  $\delta$  4.47–4.41 (1H, m), 3.61 (2H, t,  $J$  = 6.0 Hz), 2.17 (2H, td,  $J$  = 7.2, 1.8 Hz), 1.70–1.63 (3H, m), 1.54–1.28 (11H, m), 1.17–1.11 (3H, m), 1.08 (18H, d,  $J$  = 4.8 Hz), 0.91–0.86 (12H, m), 0.04 (6H, s);  $^{13}\text{C-NMR}$  (75 MHz,  $\text{CDCl}_3$ )  $\delta$  84.4, 82.0, 63.22, 63.21, 39.1, 32.7, 31.4, 28.6, 28.6, 26.0, 22.6, 21.6, 18.7, 18.1, 18.0, 14.1, 12.3, -5.3.

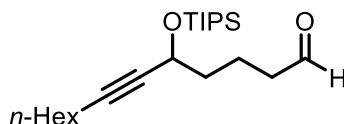
**5-[(Triisopropylsilyl)oxy]tridec-6-yn-1-ol (5b)**



According to the synthesis of compound **5a**, treatment of **4b** (1.00 g, 2.07 mmol) afforded the product **5b** (0.389 g, 51%) in colorless oil (hexane:AcOEt = 10:1).

$^1\text{H-NMR}$  (300 MHz,  $\text{CDCl}_3$ )  $\delta$  4.48–4.44 (1H, m), 3.66 (2H, q,  $J$  = 5.7 Hz), 2.18 (2H, td,  $J$  = 6.9, 1.8 Hz), 1.73–1.61 (4H, m), 1.52–1.27 (11H, m), 1.16–1.14 (3H, m), 1.09 (18H, d,  $J$  = 4.8 Hz), 0.89 (3H, t,  $J$  = 6.6 Hz);  $^{13}\text{C-NMR}$  (75 MHz,  $\text{CDCl}_3$ )  $\delta$  84.6, 81.8, 63.1, 62.9, 38.8, 32.5, 31.4, 28.57, 28.53, 22.6, 21.2, 18.7, 18.0, 14.0, 12.3; HRMS (FAB)  $m/z$  calcd for  $\text{C}_{22}\text{H}_{45}\text{O}_2\text{Si}$   $[\text{M} + \text{H}]^+$  369.3189, found 369.3180.

**5-[(Triisopropylsilyl)oxy]tridec-6-ynal (6b)**

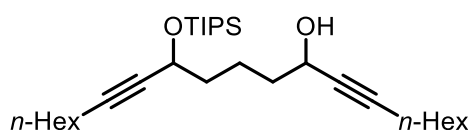


According to the synthesis of compound **6a**, treatment of **5b** (2.26 g, 6.13 mmol) afforded the product **6b** (1.84 g, 82%) in colorless oil (hexane:AcOEt = 12:1).



$^1\text{H-NMR}$  (300 MHz,  $\text{CDCl}_3$ )  $\delta$  9.78 (1H, t,  $J = 1.2$  Hz), 4.51–4.48 (1H, m), 2.48 (2H, td,  $J = 6.9, 1.2$  Hz), 2.17 (2H, td,  $J = 6.3, 1.2$  Hz), 1.86–1.78 (2H, m), 1.75–1.66 (3H, m), 1.50–1.32 (7H, m), 1.16–1.11 (3H, m), 1.08 (18H, d,  $J = 4.5$  Hz), 0.89 (3H, t,  $J = 7.2$  Hz);  $^{13}\text{C-NMR}$  (75 MHz,  $\text{CDCl}_3$ )  $\delta$  202.7, 85.0, 81.4, 62.8, 43.6, 38.3, 31.4, 28.5, 22.6, 18.7, 18.05, 18.03, 17.8, 14.0, 12.3.

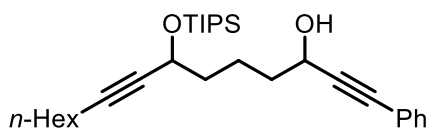
### 13-[(Triisopropylsilyl)oxy]henicosa-7,14-diyn-9-ol (**7b**)



According to the synthesis of compound **7a**, treatment of **6b** (1.24 g, 3.38 mmol) with 1-octyne (0.993 mL, 6.76 mmol) afforded the product **7b** (1.29 g, 80%) in colorless oil (hexane:AcOEt = 20:1).

$^1\text{H-NMR}$  (300 MHz,  $\text{CDCl}_3$ )  $\delta$  4.48–4.44 (1H, m), 4.37–4.35 (1H, m), 2.22–2.15 (4H, m), 1.70–1.63 (6H, m), 1.54 (6H, m), 1.39–1.27 (11H, m), 1.17–1.11 (3H, m), 1.09 (18H, d,  $J = 4.8$  Hz), 0.89 (6H, t,  $J = 6.6$  Hz);  $^{13}\text{C-NMR}$  (75 MHz,  $\text{CDCl}_3$ )  $\delta$  85.6, 84.6, 81.8, 81.1, 63.1, 62.7, 38.8, 38.0, 31.4, 31.3, 28.6, 28.6, 28.5, 22.6, 22.5, 20.9, 18.68, 18.67, 18.1, 18.0, 14.03, 14.02, 12.3.

### 1-Phenyl-7-[(triisopropylsilyl)oxy]pentadeca-1,8-diyn-3-ol (**7c**)

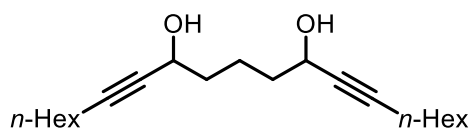


According to the synthesis of compound **7a**, treatment of **6b** (0.600 g, 1.64 mmol) with ethynylbenzene (0.360 mL, 3.28 mmol) afforded the product **7c** (0.592 g, 77%) in colorless oil (hexane:AcOEt = 20:1).

$^1\text{H-NMR}$  (300 MHz,  $\text{CDCl}_3$ )  $\delta$  7.43–7.41 (2H, m), 7.31–7.26 (3H, m), 4.61 (1H, t,  $J = 6.3$  Hz), 4.49 (1H, br s), 2.16 (2H, t,  $J = 6.6$  Hz), 1.87–1.81 (2H, m), 1.73–1.66 (7H, m), 1.51–1.40 (3H,

m), 1.37–1.30 (3H, m), 1.16–1.11 (3H, m), 1.08 (18H, d,  $J = 4.8$  Hz), 0.88 (3H, t,  $J = 6.9$  Hz);  $^{13}\text{C}$ -NMR (75 MHz,  $\text{CDCl}_3$ )  $\delta$  131.6, 128.3, 128.2, 122.7, 90.1, 84.9, 84.7, 81.7, 63.1, 62.9, 38.7, 37.6, 31.3, 28.6, 22.5, 20.9, 18.7, 18.0, 14.0, 12.3 (overlapped); HRMS (FAB)  $m/z$  calcd for  $\text{C}_{30}\text{H}_{49}\text{O}_2\text{Si}$   $[\text{M} + \text{H}]^+$  469.3502, found 469.3494.

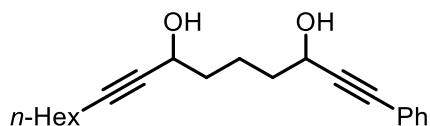
### Henicosa-7,14-diyne-9,13-diol (**13b**)



According to the synthesis of compound **13a**, treatment of **7b** (0.500 g, 1.05 mmol) afforded the product **13b** (0.309 g, 92%) in colorless oil (hexane:Et<sub>2</sub>O = 3:2).

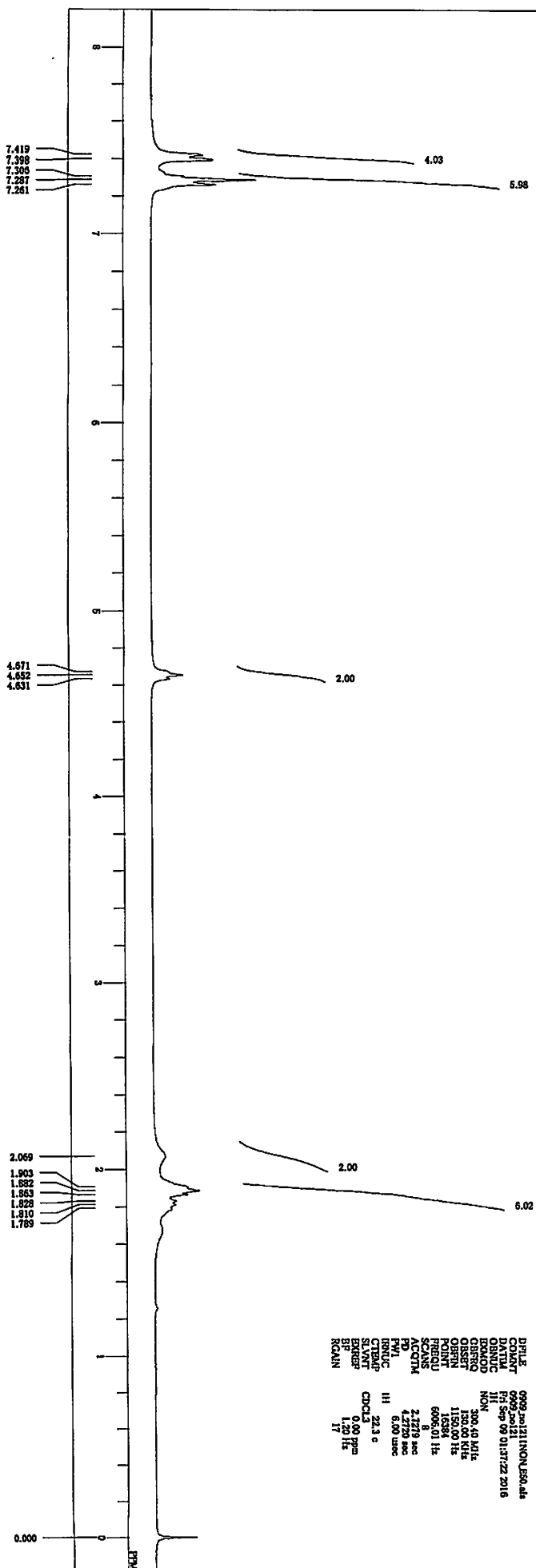
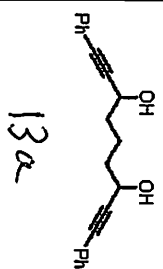
IR (KBr) 3362, 2928, 2856, 2233, 1464, 1082, 1022  $\text{cm}^{-1}$ ;  $^1\text{H}$ -NMR (300 MHz,  $\text{CDCl}_3$ )  $\delta$  4.37 (4H, br s), 2.20 (2H, td,  $J = 7.1, 1.8$  Hz), 1.74–1.68 (3H, m), 1.65–1.59 (5H, m), 1.53–1.48 (3H, m), 1.40–1.27 (13H, m), 0.89 (6H, t,  $J = 6.6$  Hz);  $^{13}\text{C}$ -NMR (75 MHz,  $\text{CDCl}_3$ )  $\delta$  85.6, 81.1, 62.4, 37.7, 31.3, 28.6, 28.5, 22.5, 21.0, 18.6, 14.0; HRMS (FAB)  $m/z$  calcd for  $\text{C}_{21}\text{H}_{37}\text{O}_2$   $[\text{M} + \text{H}]^+$  321.2794, found 321.2740.

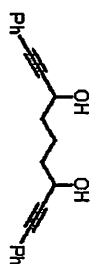
### 1-Phenylpentadeca-1,8-diyne-3,7-diol (**13c**)



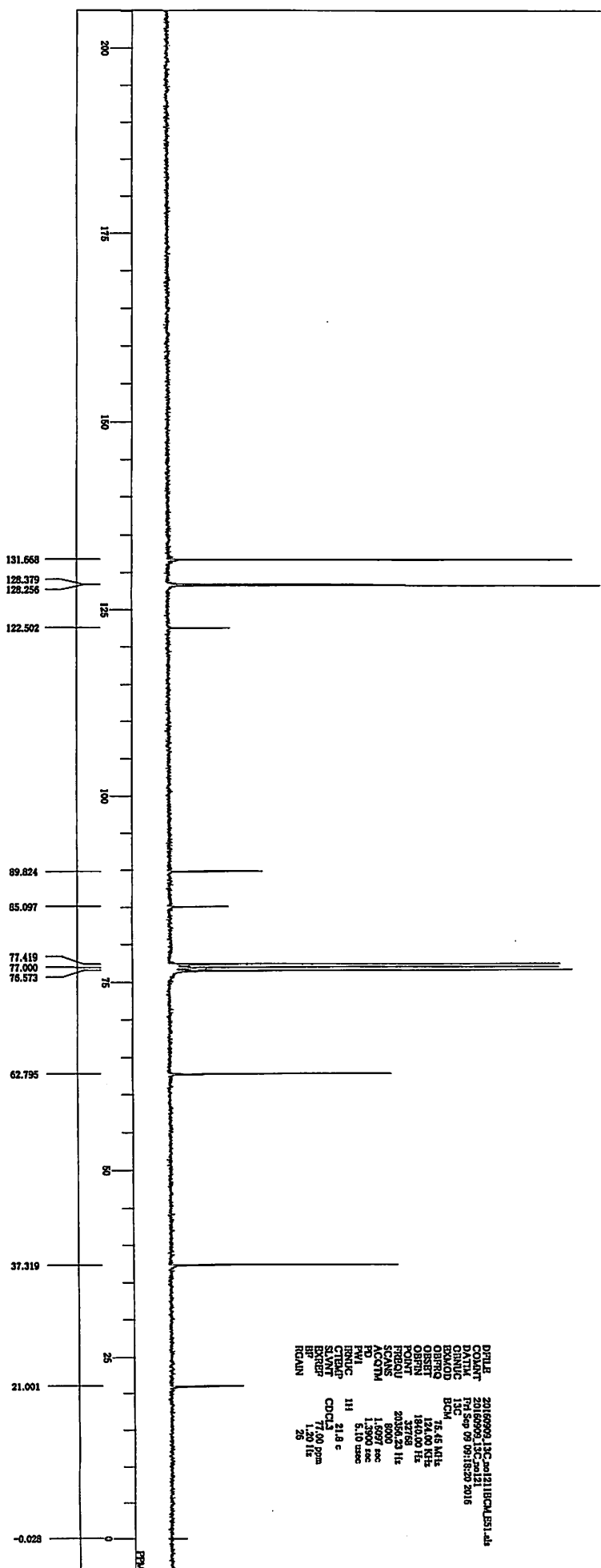
According to the synthesis of compound **13a**, treatment of **7c** (0.200 g, 0.427 mmol) afforded the product **13c** (0.0946 g, 71%) in colorless oil (hexane:Et<sub>2</sub>O = 1:1).

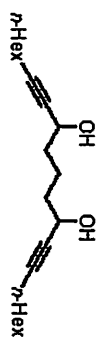
IR (KBr) 3354, 3082, 2932, 2860, 2233, 1599, 1490, 1026  $\text{cm}^{-1}$ ;  $^1\text{H}$ -NMR (300 MHz,  $\text{CDCl}_3$ )  $\delta$  7.45–7.41 (2H, m), 7.32–7.26 (3H, m), 4.62 (1H, t,  $J = 6.0$  Hz), 4.40–4.38 (1H, m), 2.19 (2H, td,  $J = 7.0, 0.9$  Hz), 2.07 (1H, br s), 1.88–1.82 (3H, m), 1.79–1.69 (4H, m), 1.53–1.44 (2H, m), 1.38–1.27 (6H, m), 0.88 (3H, t,  $J = 7.5$  Hz);  $^{13}\text{C}$ -NMR (75 MHz,  $\text{CDCl}_3$ )  $\delta$  131.6, 128.23, 128.16, 122.6, 90.0, 85.6, 84.8, 81.0, 62.6, 62.4, 37.5, 37.3, 31.2, 28.6, 28.5, 22.4, 20.9, 18.6, 14.0; HRMS (EI)  $m/z$  calcd for  $\text{C}_{21}\text{H}_{28}\text{O}_2$   $[\text{M}]^+$  312.2089, found 312.2076.



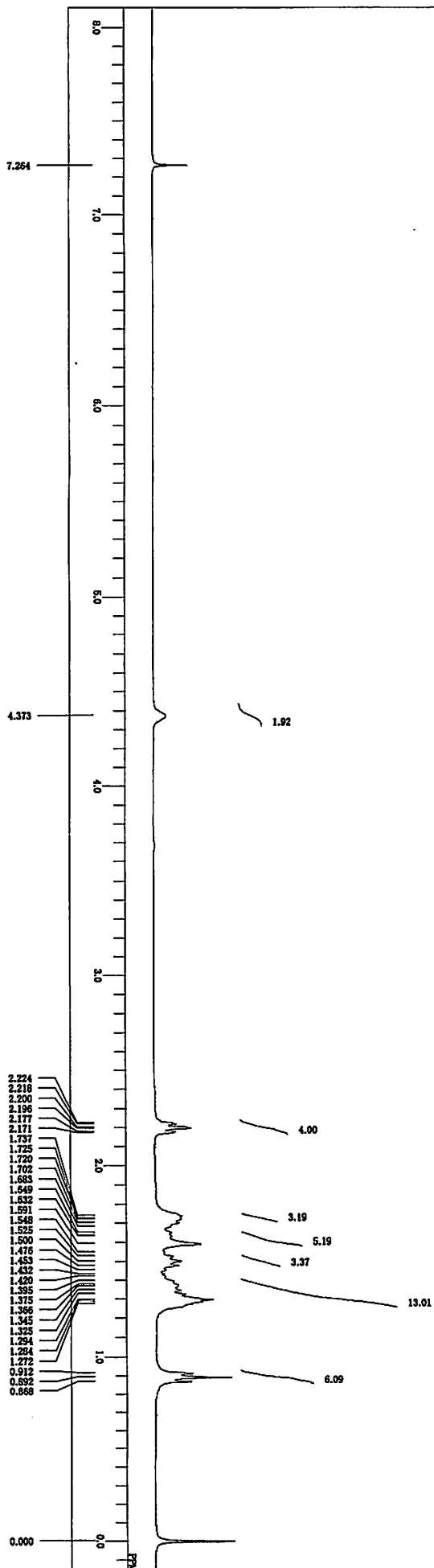


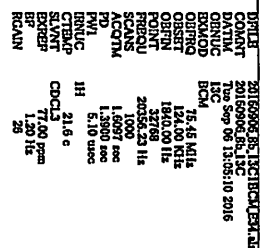
13a

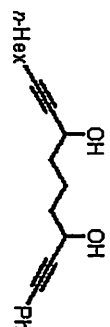




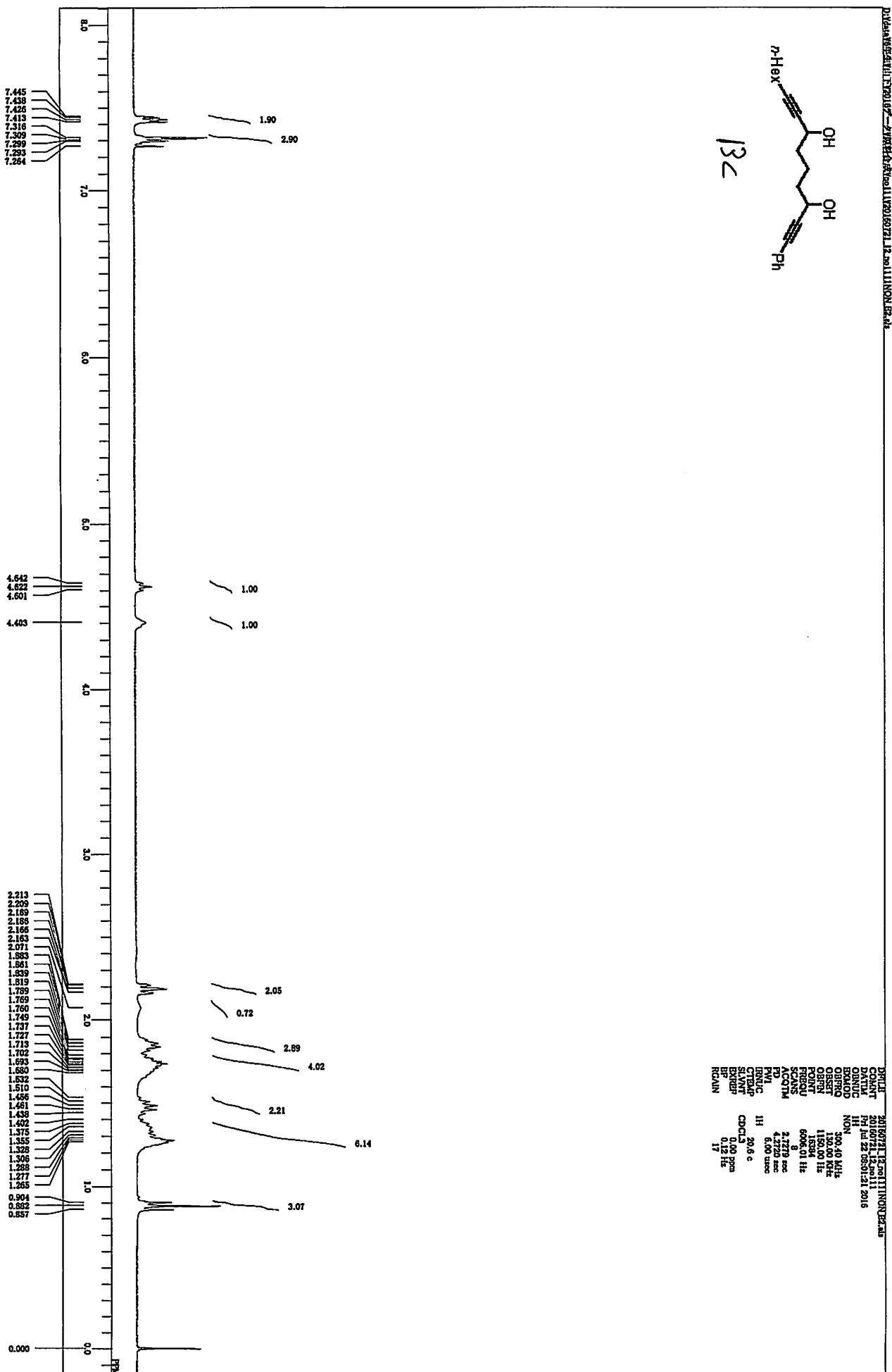
136

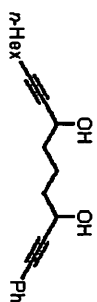
[illegible]



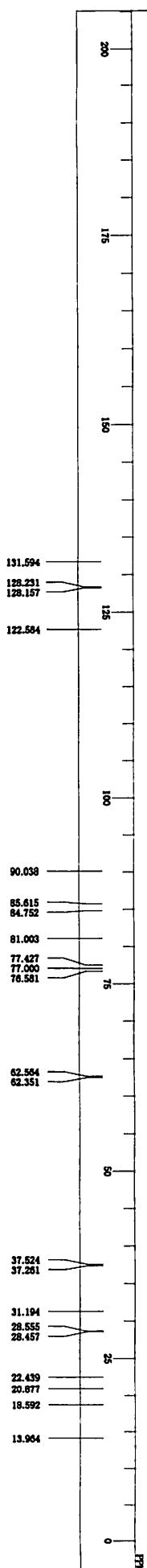


13c



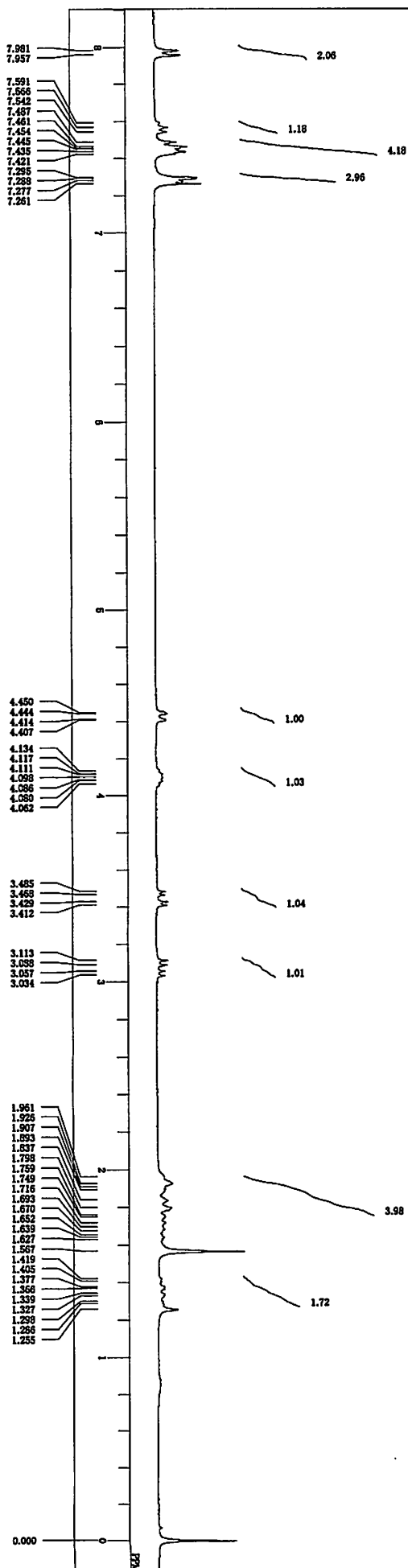
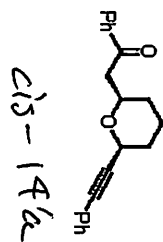


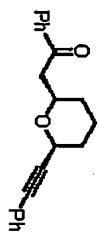
13C



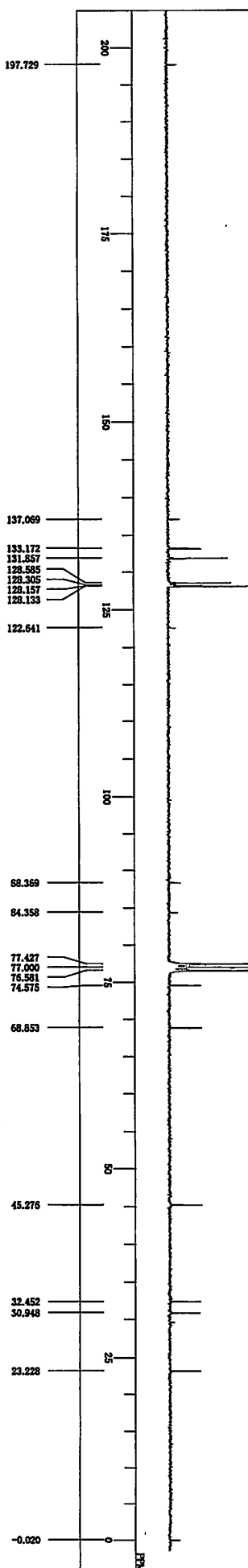
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COUNT 20160623\_d1HexPh\_13C  
DATE/TIME Thu Jun 23 20:38:01 2016  
PROC 13C  
INSTRUM spect  
PULPROG zgpg30  
PROBHD 5mm QNP1H  
P1 12.00  
PC 1.5000  
PD 1.0000  
SFO 500  
AQ 1.6697  
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C-826 -826.00  
C-82



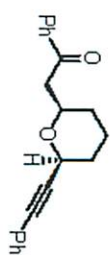
[illegible]



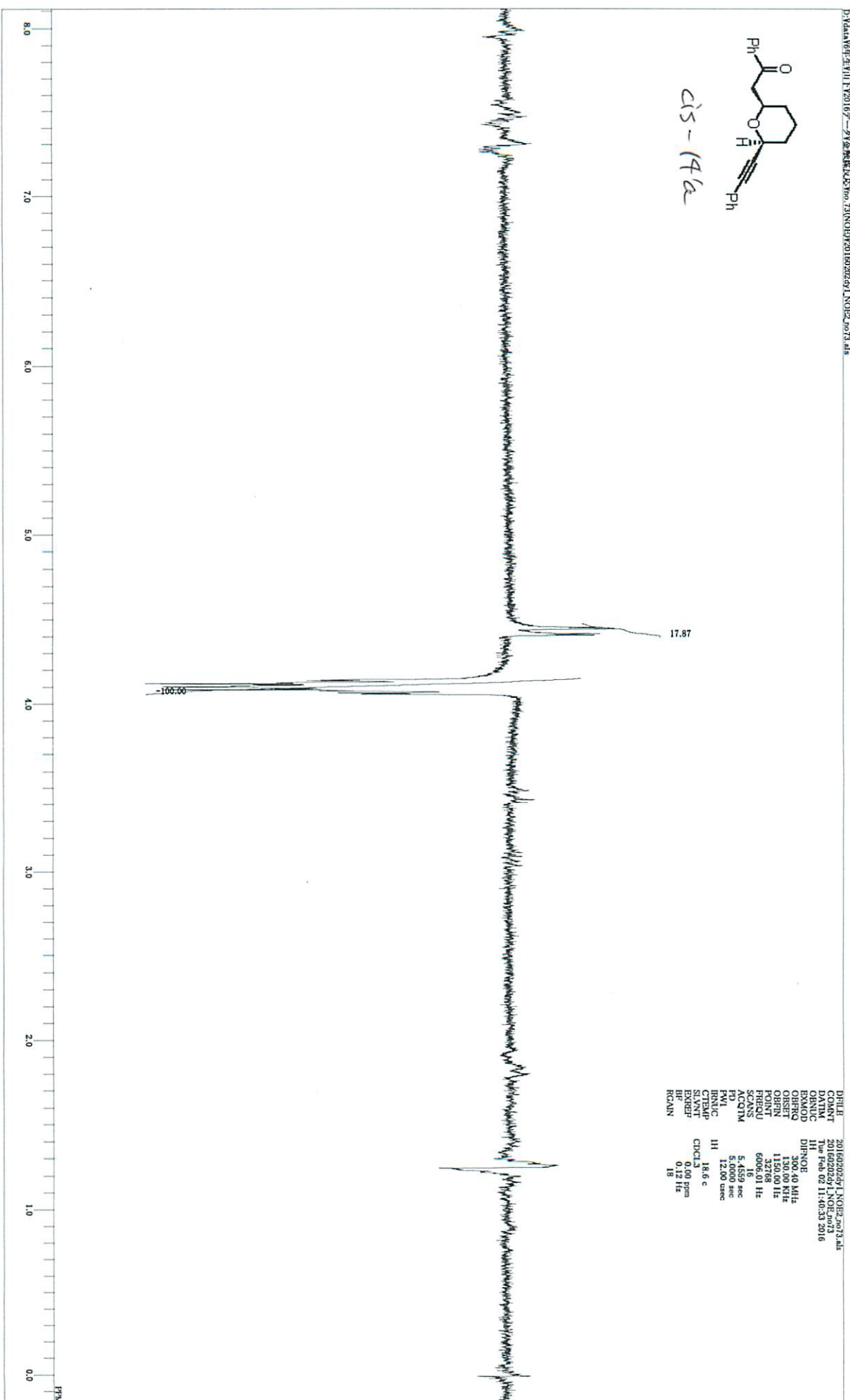
2/5-14a



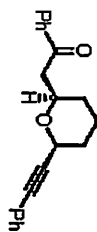
DEAL	20160809ZUL3433313CUL3433313EAL
COUNT	20160809ZUL3433313CUL3433313EAL
ROUTING	13C
BOND	REDA
OBERRO	75.15 Moltz
OBST	184.00 Hz
POINT	32769
FREQAU	20555.23 Hz
ACTION	1.13800 sec
PD	1.3800 sec
PW1	5.10 usec
CRUC	III
CHOC3	21.5 c
SLANT	CD3C3
EXREP	77.00 ppm
RF	1.20 Hz
REQUN	25



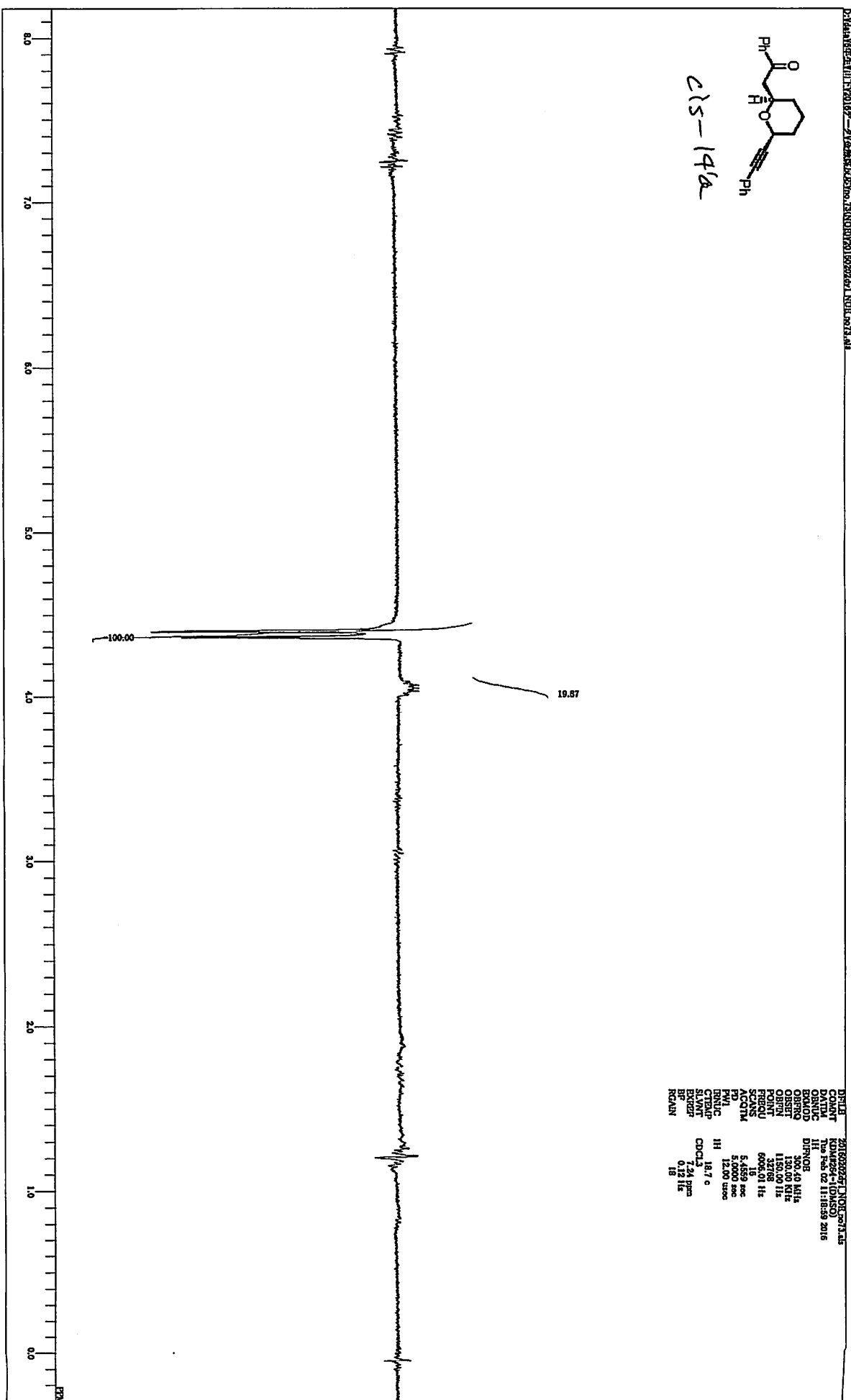
cis-14a



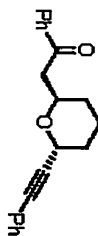
KDM#264-1(DMSO)



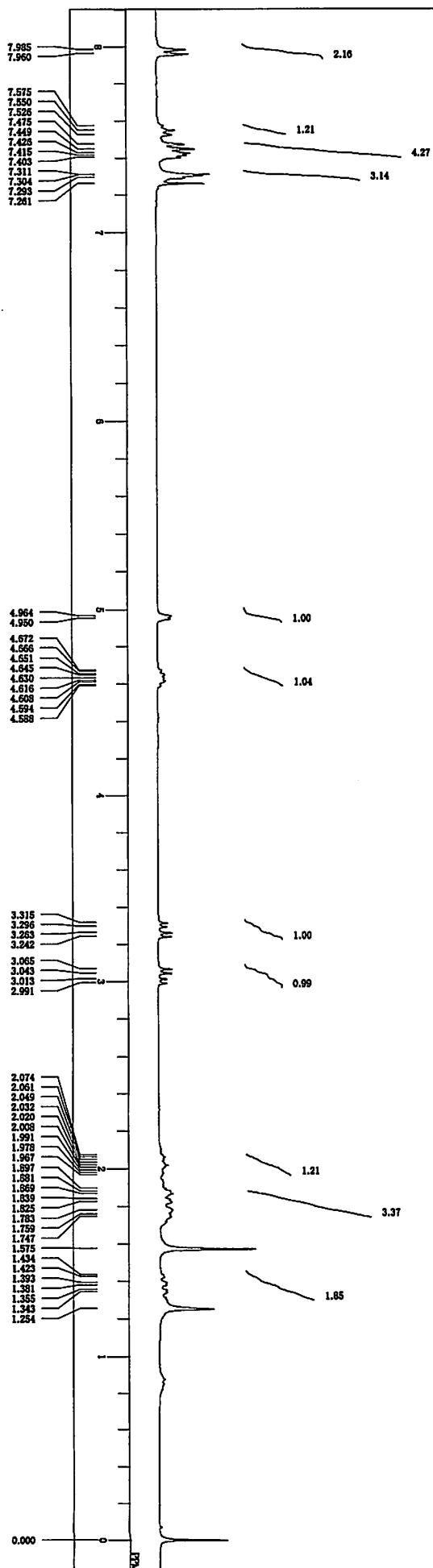
C15-14a



FILE 201602021.DMSO-14a  
 CONT KDM#264-1(DMSO)  
 DATE 7th Feb 02 11:18:59 2016  
 INSTR DPMOR  
 OBSER 1H  
 PULPROG zgpg30  
 OBSER 1H  
 POINT 32708 Hz  
 FREQ 600.135 MHz  
 SCANS 16  
 ACQTM 5.4559 sec  
 PD 12.00 usec  
 P1 12.00 usec  
 FWHM 18.7 c  
 CTBAP 0.00  
 SLYNT 0.00  
 EXPT 0.00  
 RFLAN 16

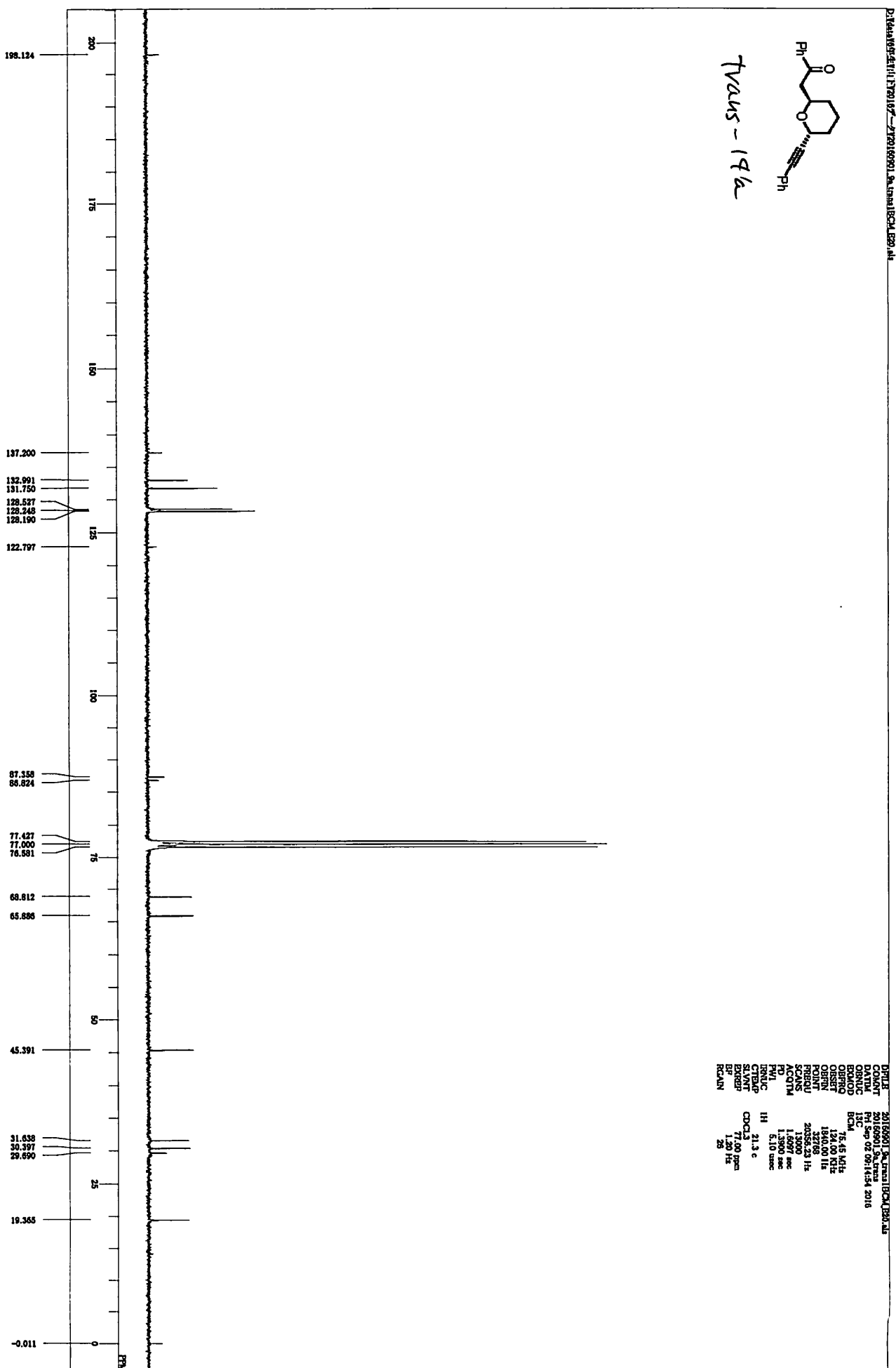
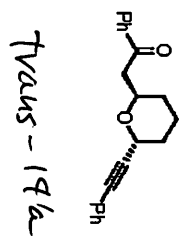


trans-14a



20160731\_trans.no73.NMR.H16.F3  
 CONT 20160731\_trans.no73  
 DATE 24 Jul 20 14:56:27 2016  
 ORIGIN NMR  
 ORIGIN 300.40 MHz  
 ORIGIN 130.00 MHz  
 ORIGIN 100.624 MHz  
 ORIGIN 600.00 MHz  
 SCANS 8  
 ACQTM 2.7279 sec  
 PD 4.2720 sec  
 T1 6.00 sec  
 T1ALC 20.5 c  
 CTBKP CHCl3  
 SLYNT 0.00 ppm  
 BKBP 1.20 Hz  
 RGAIN 21

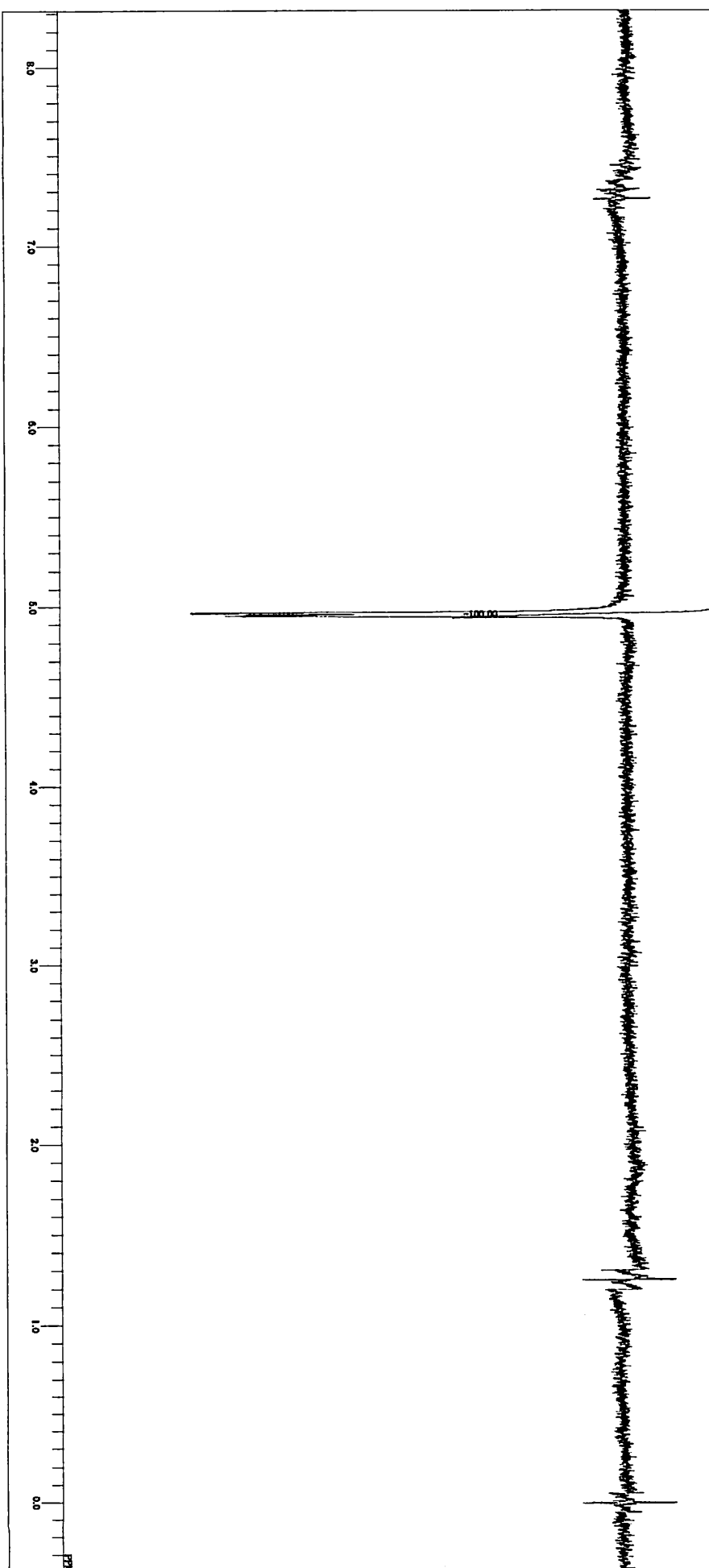
20160901\_9a\_trans



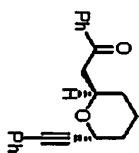
DATA: 20160901\_9a\_trans18C4\_1820.ms  
 DATE: 20160901 09:14:54 2016  
 INSTR: 1H  
 NAME: 19a  
 OBSID: 124.00 MHz  
 OBSID: 1840.00 Hz  
 POINT: 2.0000 Hz  
 POINT: 20.0000 Hz  
 SCANS: 13000  
 ACQTM: 1.6097 sec  
 PD: 1.3900 sec  
 FWHM: 5.10 sec  
 T1RHO: 21.3 s  
 CTDP: 77.00 ppm  
 SLEW: 1.00 Hz  
 EXPR: 1.00 Hz  
 RCAN: 28

O=C(Cc1ccccc1)C2=CC=CC=C2

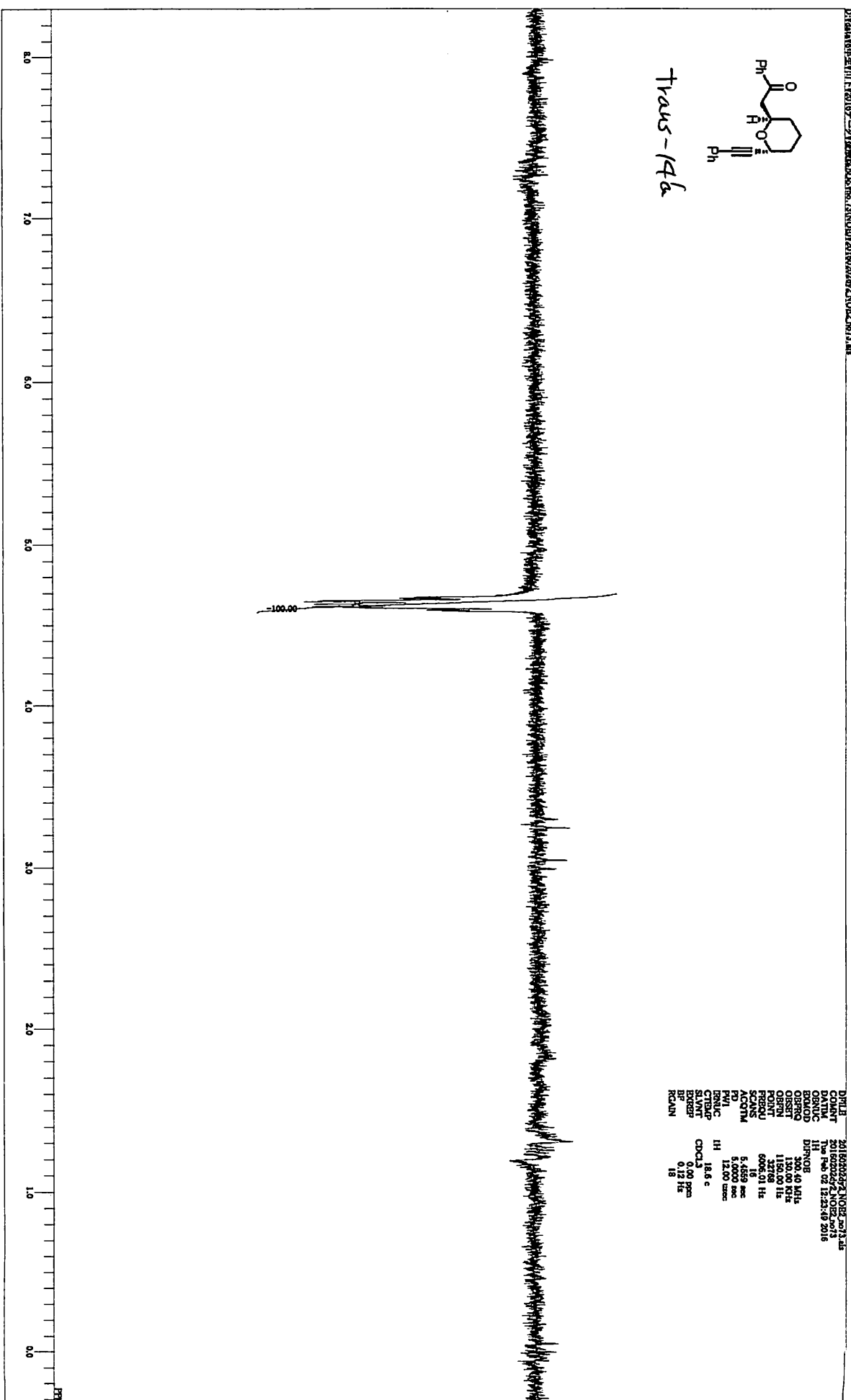
trans-14a



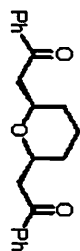
DRILE	20160629ZJNOHJ0073
COMANT	20160629ZJNOHJ0073
DATUM	The Feb 02 12:03:32 2016
ORNUC	IH
BEADOD	DIPNO 40 Mph
ORNUC	130.00 KHz
ORNUC	1156.00 Hz
ORNUC	32738
ORNUC	6006.01 Hz
ORNUC	18
ORNUC	5.65589 sec
ORNUC	5.65589 sec
ORNUC	12.00 sec
ORNUC	18.5 s
ORNUC	0.00 ppm
ORNUC	0.12 Hz
ORNUC	18



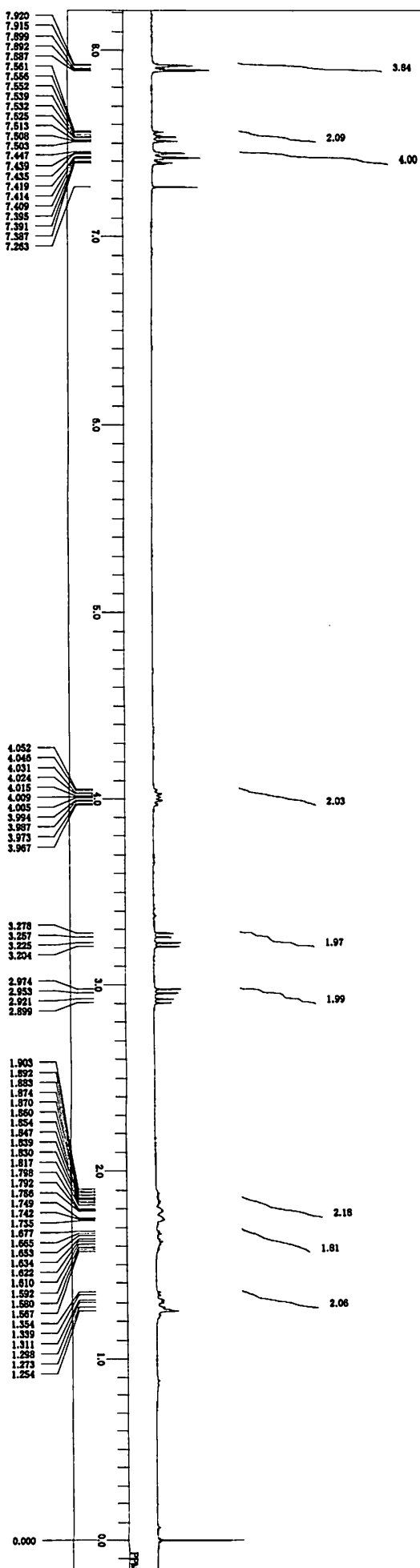
Trans-14a



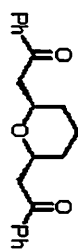




14a

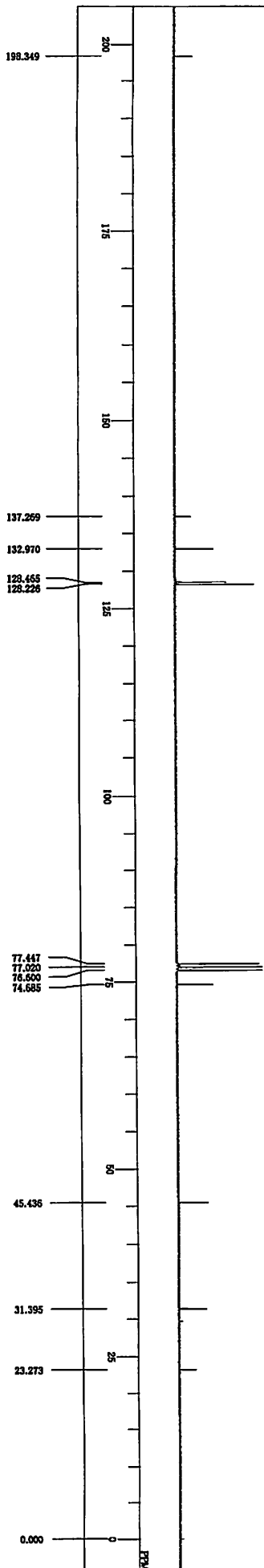
[illegible]

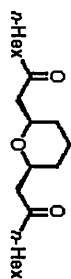
D:\MSDCHEM\1720187-2\4654\20160218e.4654.no79\BPA.BRO.d18



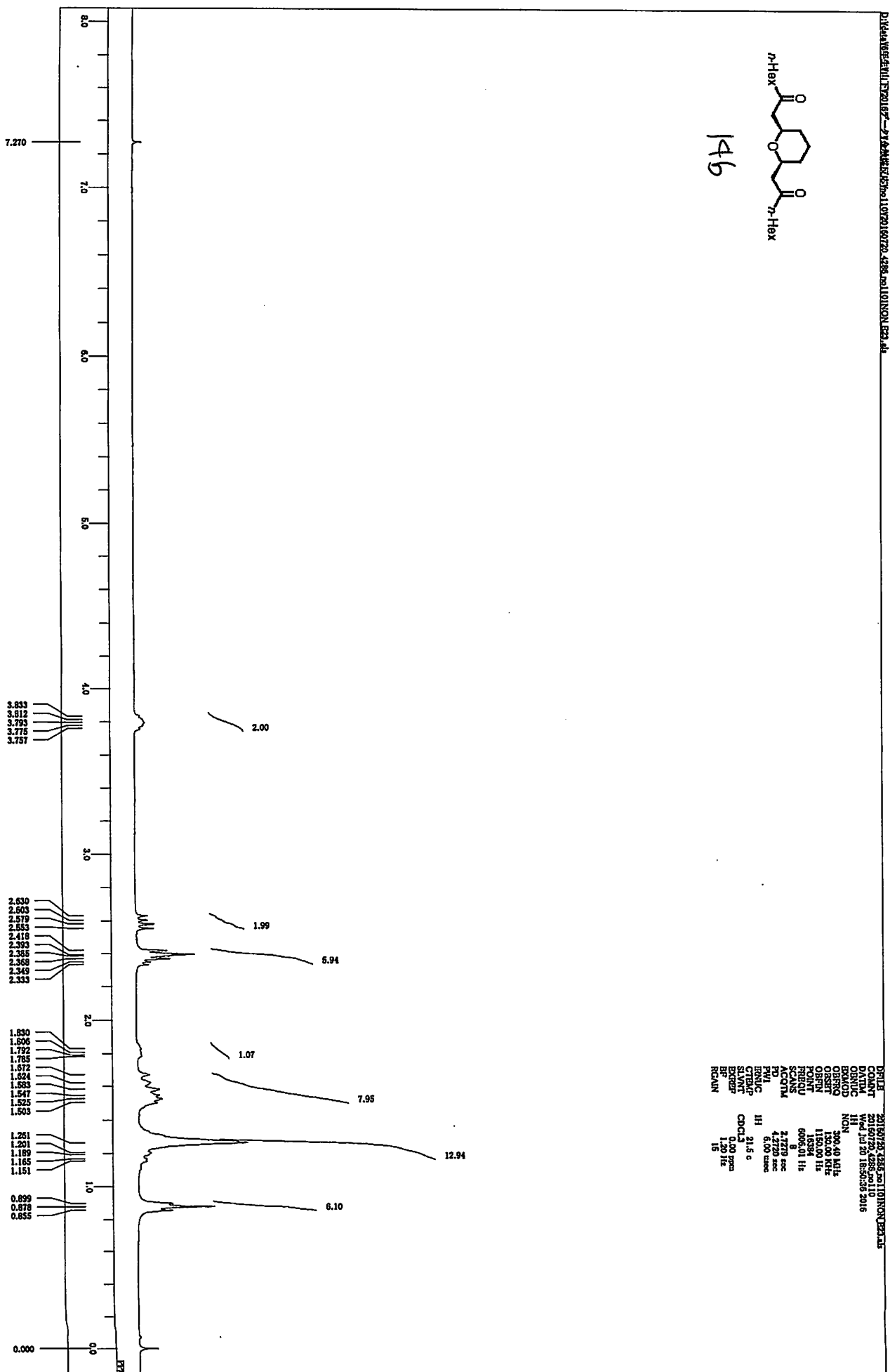
K4a

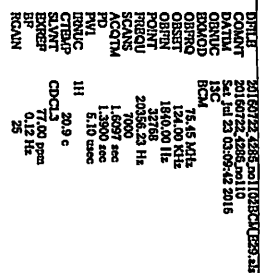
FILE 20160218e.4654.no79\BPA.BRO.d18  
 COUNT 20160218e.4654.no79  
 DATA 19 Feb 19 06:57:20 2016  
 NAME K4a  
 CNAME BPA  
 BRNCD BPA  
 OBSERD 75.45 KHz  
 ORIGIN 124.00 KHz  
 FREQ 1840.00 Hz  
 FREQ2 3240.00 Hz  
 FREQ3 20356.23 Hz  
 SCANS 7000  
 ACQTM 1.697 sec  
 PUL 1.500 sec  
 PM 5.10 sec  
 ENLUC 19.9 c  
 CTRAP 19.9 c  
 SAMP CHCL3  
 SOLVENT CDCl3  
 BR 0.12 Hz  
 RCALN 25

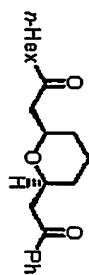




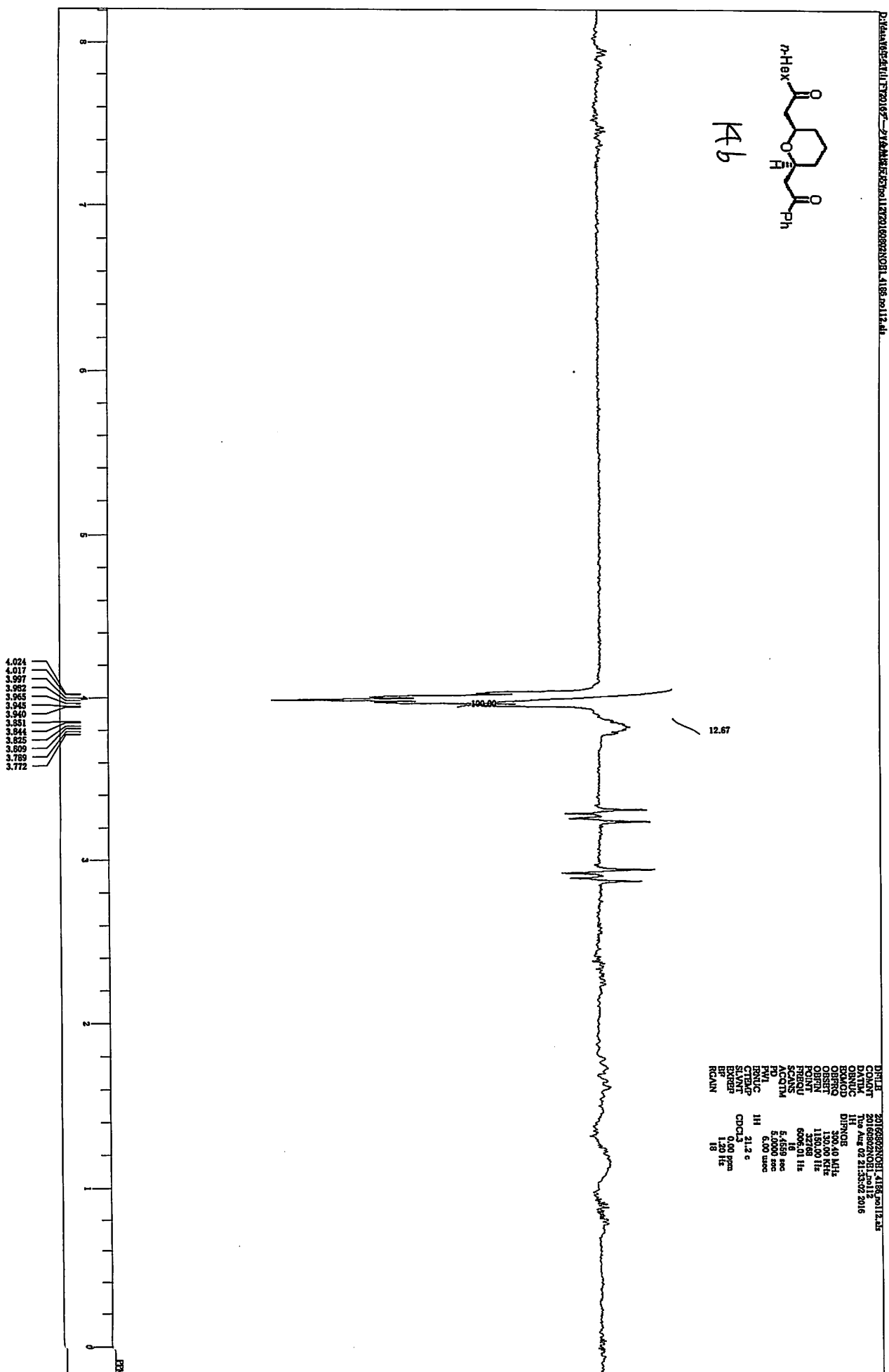
146



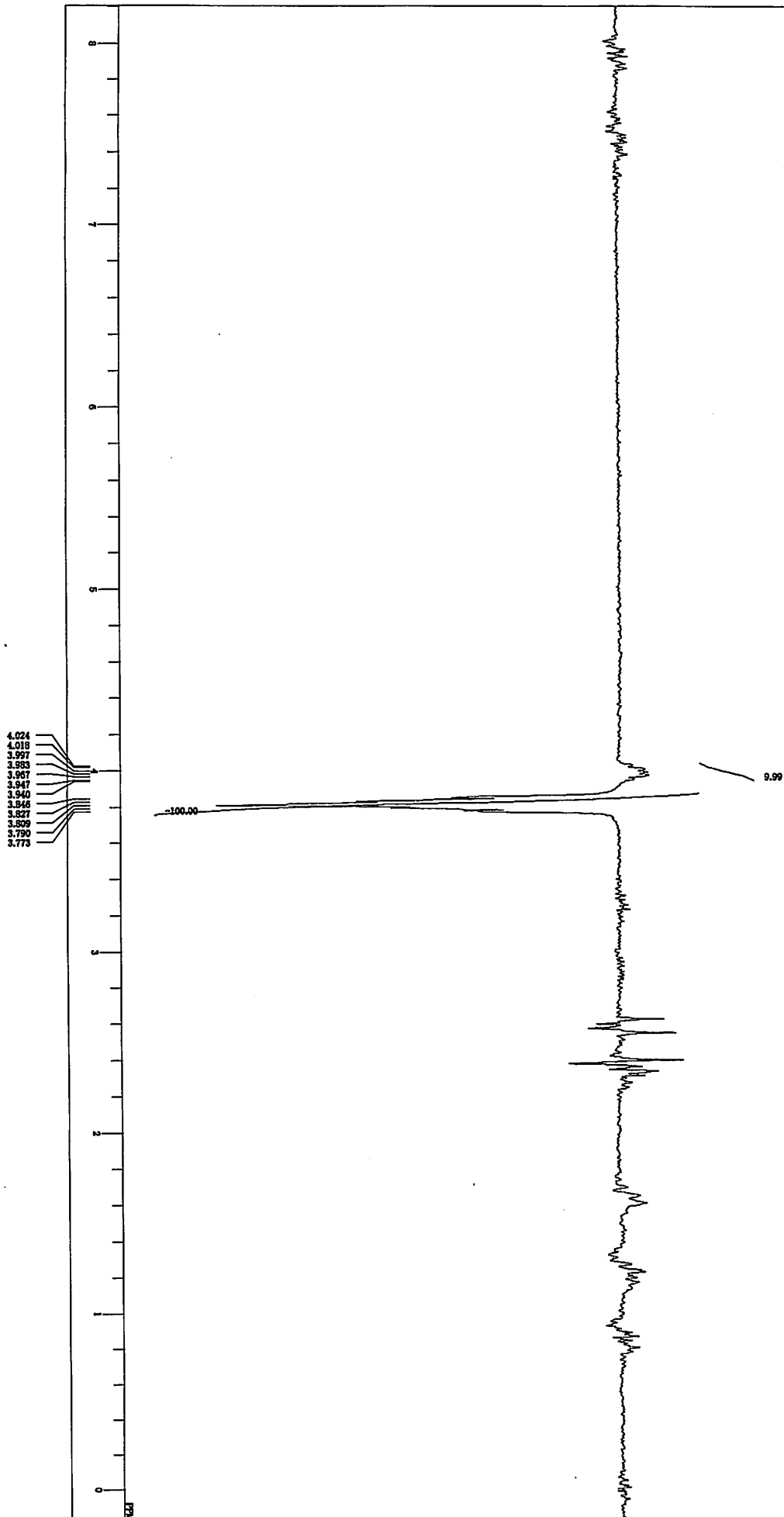
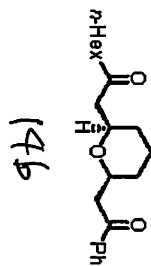




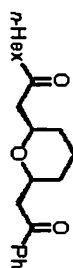
Kb



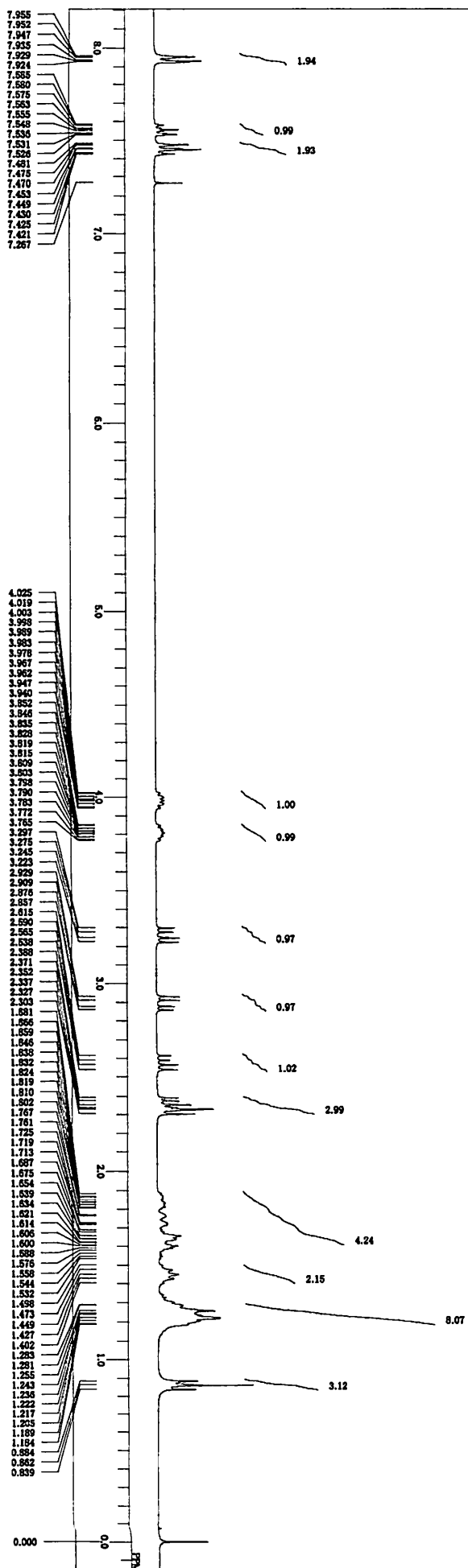
D:\MSD\MSD\4111720107-216444\FID\20160802NOE2\_4188.no112.ms



FILE 20160802NOE2\_4188.ms (16.25  
 CONT 20160802NOE2.no112  
 DATA 17 Aug 02 21:56:08 2016  
 NAME  
 DIRNOE  
 300.40 MHz  
 PULPROG zgpg30  
 OBSERV 130.00 kHz  
 ORIGIN 130.00 Hz  
 F2 - 130.00  
 FREQ 600.01 Hz  
 SCANS 16  
 ACQTM 5.4559 sec  
 PD 5.000 sec  
 P1 6.00 sec  
 INFLC 20.0 s  
 CTBAP 120 Hz  
 SLEW 120 Hz  
 BR 18  
 RCALN



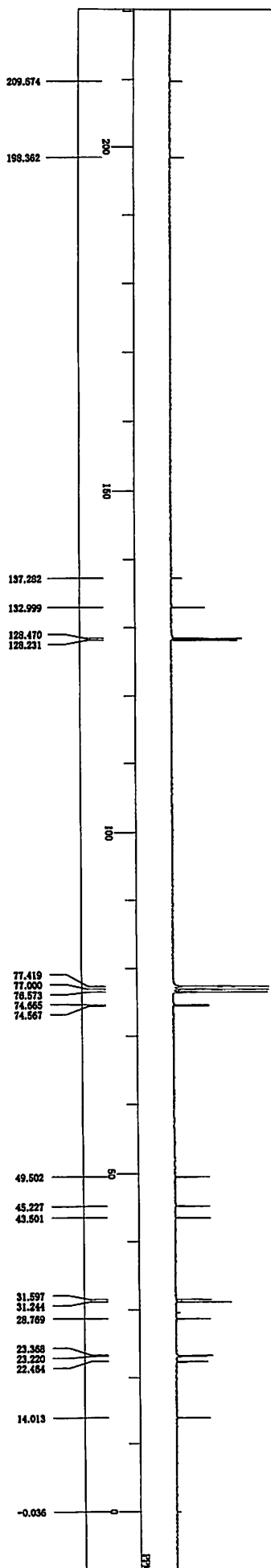
14c



NAME: 20160728recolumn.2132.no112  
 COUNT: 20160728recolumn.2132.no112  
 DATE: Thu Jul 28 18:32:44 2016  
 NAME: 14c  
 CONCENT: 100.00 MHz  
 OBSERVE: 130.00 MHz  
 PULPROG: zgpg30  
 SCANS: 60000 Hz  
 ACOU: 2.7779 sec  
 FID: 4.3720 sec  
 T1: 6.00 sec  
 T2: 21.2 sec  
 CDCL3: 0.00 ppm  
 EXPT: 0.12 Hz  
 F2: 18

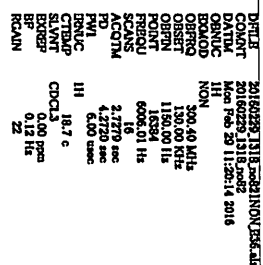


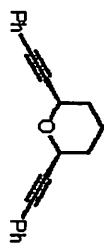
142



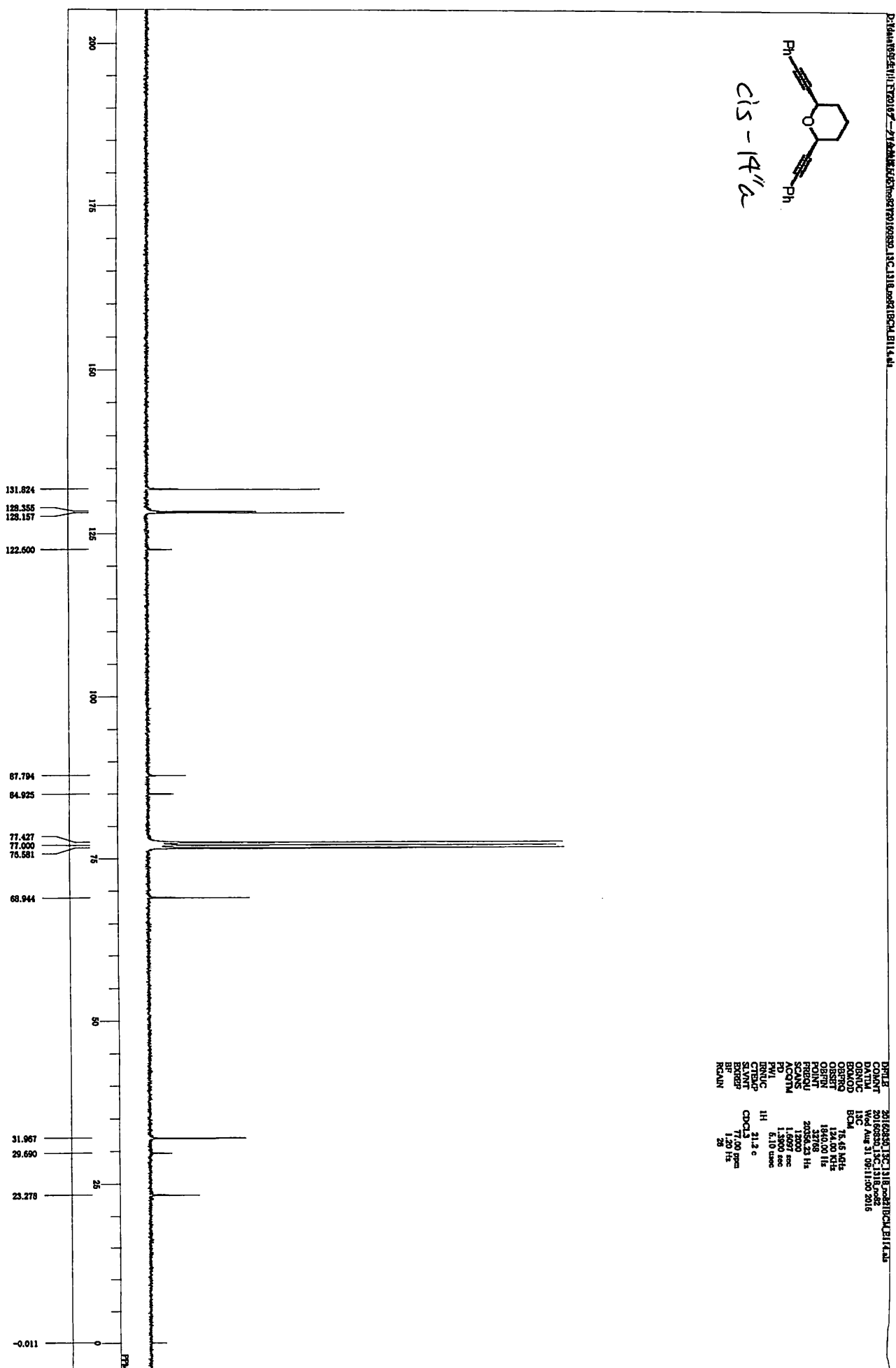
DRUG	20180801	4186	us	123828	CDL	21	21
COAST	20100801	2188	us	1112	CDL	21	21
CONV	20100801	4186	us	123828	CDL	21	21
CONV	13C	4186	us	633338	2016		
BROWD							
OBSPRO							
OBSPRO							
OBSPRO							
POINT							
POINT							
POINT							
ACOMMS							
ACOMMS							
PD							
PV1							
FINANC							
FINANC							
FINANC							
SLAVANT							
EXEMP							
BP							
ROCAN							

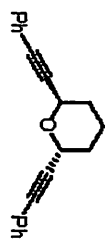




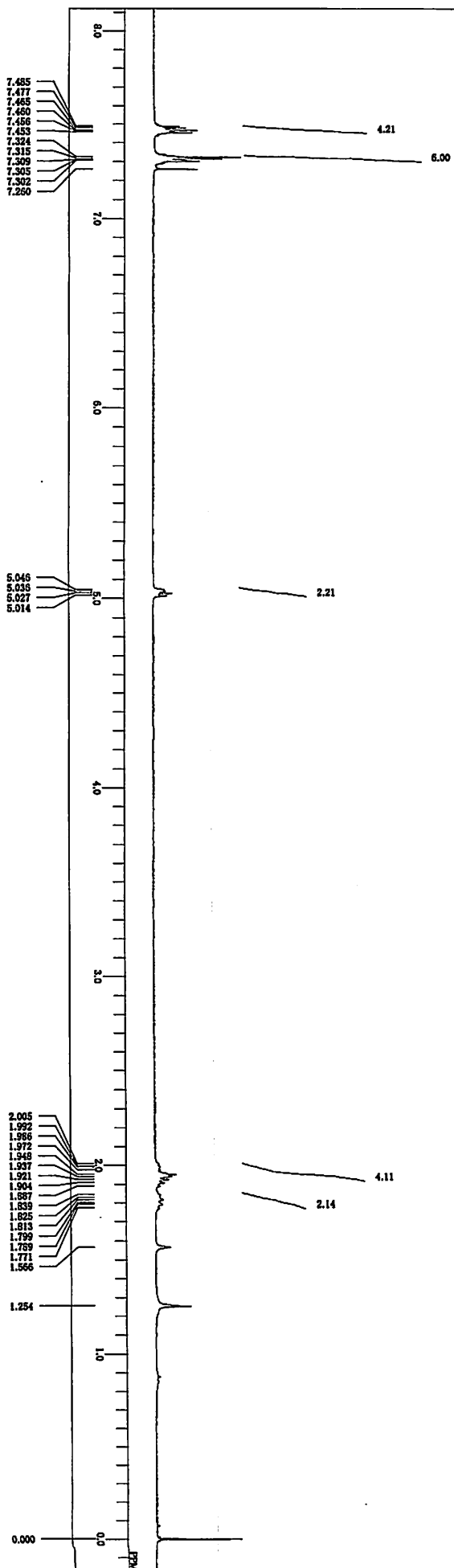


cis-14''a

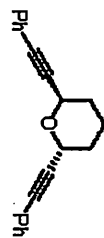




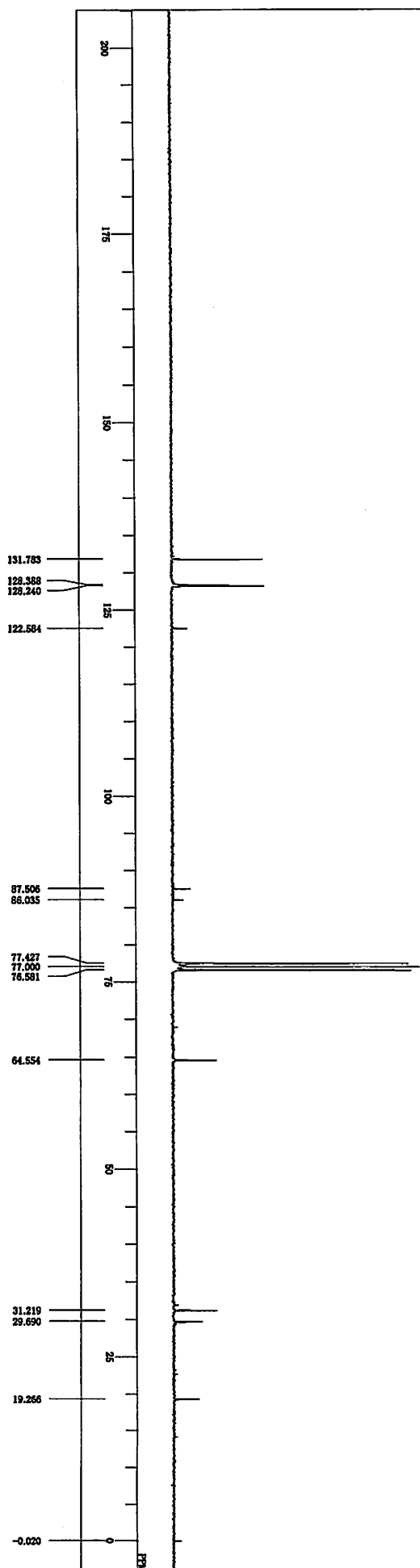
trans-14'a

[illegible]

20151216dy



Trans-14" a

[illegible]

[ Elemental Composition ]

Data : Yakukagaku-Yamashita-106

Date : 06-Aug-2016 11:20

Page: 1

Sample: no71

Note : -

Inlet : Reserv.

Ion Mode : EI+

RT : 1.04 min

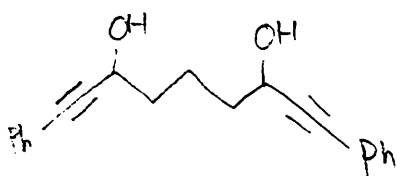
Scan#: 32

Elements : C 40/0, H 60/0, O 3/0

Mass Tolerance : 1000ppm, 3mmu if m/z < 3, 5mmu if m/z > 5

Unsaturation (U.S.) : -0.5 - 30.0

Observed m/z	Int%	Err[ppm / mmu]	U.S.	Composition
<u>304.1452</u>	<u>9.2</u>	<u>-3.8 / -1.2</u>	12.0	C 21 H 20 O 2
303.1402	19.1	+5.5 / +1.7	12.5	C 21 H 19 O 2



13a

[ Elemental Composition ]

Data : Yakukagaku-Yamashita-083

Date : 29-Jun-2016 15:22

Page:

Sample: 9b-no102

Note : CH<sub>2</sub>Cl<sub>2</sub> + NBA

Inlet : Direct

Ion Mode : FAB+

RT : 0.50 min

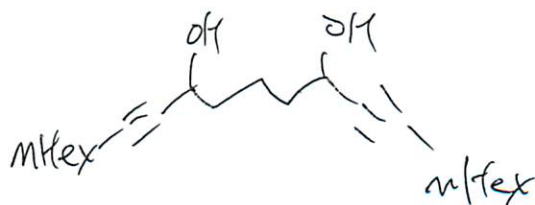
Scan#: 3

Elements : C 40/0, H 100/0, O 2/2

Mass Tolerance : 1000ppm, 10mmu if m/z < 10, 20mmu if m/z > 20

Unsaturation (U.S.) : -0.5 - 20.0

Observed m/z	Int%	Err[ppm / mmu]	U.S.	Composition
321.2740	6.1	-16.8 / -5.4	3.5	C 21 H 37 O 2



136

## [ Elemental Composition ]

Data : Yakukagaku-Yamashita-107

Date : 06-Aug-2016 11:28

Sample: n0111

Note : -

Inlet : Reserv.

Ion Mode : EI+

RT : 0.90 min

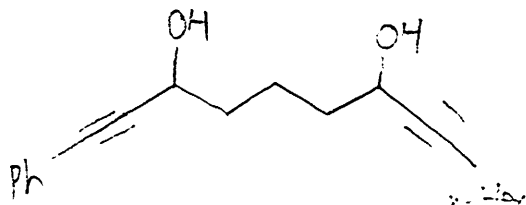
Scan#: 28

Elements : C 40/0, H 60/0, O 3/0

Mass Tolerance : 1000ppm, 3mmu if m/z &lt; 3, 10mmu if m/z &gt; 10

Unsaturation (U.S.) : -0.5 - 30.0

Observed m/z	Int%	Err[ppm / mmu]	U.S. Composition
312.2076	11.5	-4.2 / -1.3	8.0 C 21 H 28 O 2



13c

[ Elemental Composition ]

Data : Yakukagaku-Yamashita-034

Date : 06-Sep-2016 15:30

Page: 1

Sample: 9a-cis

Note : DH2Cl2 + NBA

Inlet : Direct

Ion Mode : FAB+

RT : 0.67 min

Scan#: 3

Elements : C 50/0, H 100/0, O 2/2

Mass Tolerance : 1000ppm, 3mmu if m/z < 3, 5mmu if m/z > 5

Unsaturation (U.S.) : -0.5 - 20.0

Observed m/z	Int%	Err[ppm / mmu]	U.S. Composition
305.1538	100.0	-1.1 / -0.3	11.5 C 21 H 21 O 2



cis-14a



[ Elemental Composition ]

Data : Yakukagaku-Yamashita-032

Date : 06-Sep-2016 15:17

Page: 1

Sample: 9a-trans

Note : DH2Cl2 + NBA

Inlet : Direct

Ion Mode : FAB+

RT : 1.34 min

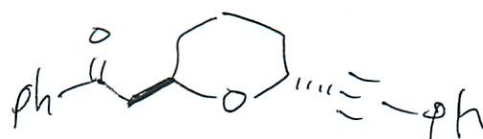
Scan#: 5

Elements : C 50/0, H 100/0, O 2/2

Mass Tolerance : 1000ppm, 3mmu if m/z < 3, 5mmu if m/z > 5

Unsaturation (U.S.) : -0.5 - 20.0

Observed m/z	Int%	Err[ppm / mmu]	U.S.	Composition
305.1536	100.0	-1.8 / -0.6	11.5	C 21 H 21 O 2



trans-14a

[ Elemental Composition ]

Data : Yakukagaku-Yamashita-030

Date : 16-Feb-2016 11:28

Page: 1

Sample: 0216-no79

Note : -

Inlet : Direct

Ion Mode : EI+

RT : 1.55 min

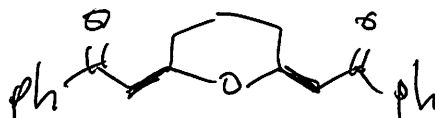
Scan#: 32

Elements : C 40/0, H 49/0, N 0/0, O 3/3, S 0/0

Mass Tolerance : 1000ppm, 3mmu if m/z < 3, 5mmu if m/z > 5

Unsaturation (U.S.) : -0.5 - 20.0

Observed m/z	Int%	Err[ppm / mmu]	U.S.	Composition
322.1570	6.4	+0.2 / +0.1	11.0	C 21 H 22 O 3



14a

[ Elemental Composition ]

Data : Yakukagaku-Yamashita-099

Date : 05-Aug-2016 14:05

Page: 1

Sample: no110

Note : -

Inlet : Reserv.

Ion Mode : EI+

RT : 0.27 min

Scan#: 9

Elements : C 40/0, H 60/0, O 3/0

Mass Tolerance : 1000ppm, 3mmu if m/z < 3, 5mmu if m/z > 5

Unsaturation (U.S.) : -0.5 - 30.0

Observed m/z	Int%	Err[ppm / mmu]	U.S.	Composition
338.2812	56.6	-2.6 / -0.9	3.0	C 21 H 38 O 3



146

[ Elemental Composition ]

Data : Yakukagaku-Yamashita-102

Date : 05-Aug-2016 14:30

Page: 1

Sample: n0112

Note : -

Inlet : Reserv.

Ion Mode : EI+

RT : 0.97 min

Scan#: 30

Elements : C 40/0, H 60/0, O 3/0

Mass Tolerance : 1000ppm, 3mmu if m/z < 3, 5mmu if m/z > 5

Unsaturation (U.S.) : -0.5 - 30.0

Observed m/z	Int%	Err[ppm / mmu]	U.S.	Composition
330.2202	100.0	+2.0 / +0.7	7.0	C 21 H 30 O 3



KE