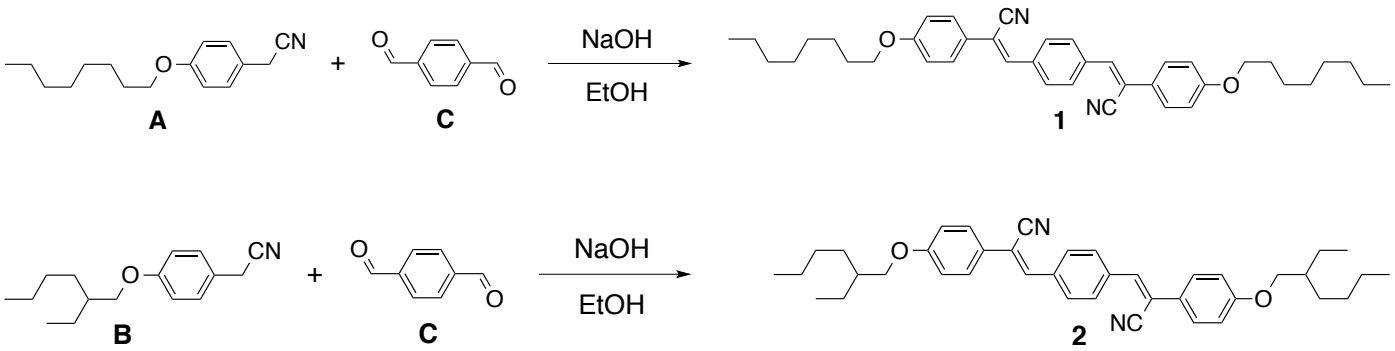
Experimental

Synthetic Procedure

*Synthesis of **1** and **2** via Condensation of p-Terephthalaldehyde with Alcoxyphenyl acetonitrile*

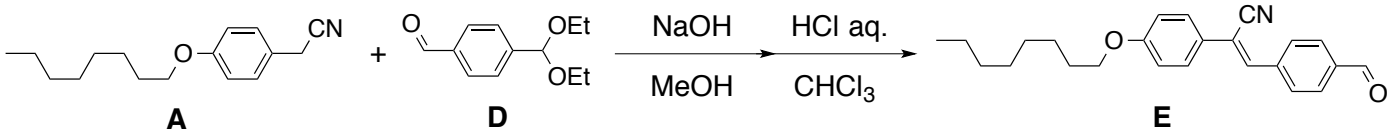


To a mixture of alcoxyphenylacetonitrile (245 mg, 1.0 mmol) and *p*-terephthalaldehyde (77 mg, 0.50 mmol) in ethanol (5 mL), sodium methoxide in methanol (1.0 M, 5 mL) was added and stirred for 10 min at room temperature under air. The reaction mixture was diluted with a large amount of methanol (100 mL), and then filtered to remove solid. The solid was washed with an ethanol (10 mL), and dried under vacuum to give as a powder.

Yellow-colored solid **1**: Yield: Quant. (293 mg). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.95 (Ar-*H*, s, 4H), 7.62 (Ar-*H*, d, J = 9.2, 4H), 7.42 (Vinylene-*H*, s, 2H), 6.96 (Ar-*H*, d, J = 8.8, 4H), 4.00 (O-C*H*$_2$-CH$_2$-CH$_2$-[CH$_2$]$_4$-CH$_3$, t, J = 6.4, 4H), 1.82 (O-CH$_2$-C*H*$_2$-CH$_2$-[CH$_2$]$_4$-CH$_3$, m, 4H), 1.78 (O-CH$_2$-CH$_2$-C*H*$_2$-[CH$_2$]$_4$-CH$_3$, m, 4H), 1.3 (O-CH$_2$-CH$_2$-CH$_2$-[C*H*$_2$]$_4$-CH$_3$, m, 8H), 0.88 (O-CH$_2$-CH$_2$-CH$_2$-[CH$_2$]$_4$-C*H*$_3$, t, J = 7.2, 6H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 160.5, 138.5, 135.6, 129.6, 127.6, 126.6, 118.1, 115.2, 112.5, 68.4, 32.0, 29.5, 29.4, 29.3, 26.1, 22.8, 14.2. HRMS (ESI) m/z: calcd for $C_{40}H_{48}N_2O_2$ $[M]^+$, 588.3710; found, 588.3698.

Yellow-colored solid **2**: Yield: Quant. (295 mg). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.95 (Ar-*H*, s, 4H), 7.62 (Ar-*H*, d, J = 8.8, 4H), 7.42 (Vinylene-*H*, s, 2H), 6.97 (Ar-*H*, d, J = 9.2, 4H), 3.89 (O-C*H*$_2$-CH[CH$_2$-CH$_3$]-CH$_2$-[CH$_2$]$_2$-CH$_3$, d, J = 3.2, 4H), 1.76 (O-CH$_2$-C*H*[CH$_2$-CH$_3$]-CH$_2$-[CH$_2$]$_2$-CH$_3$, m, 2H), 1.75 (O-CH$_2$-CH[C*H*$_2$-CH$_3$]-C*H*$_2$-[CH$_2$]$_2$-CH$_3$ m, 8H), 1.40 (O-CH$_2$-CH[CH$_2$-CH$_3$]-CH$_2$-[C*H*$_2$]$_2$-CH$_3$ m, 10H), 0.88 (O-CH$_2$-CH[CH$_2$-C*H*$_3$]-CH$_2$-[CH$_2$]$_2$-C*H*$_3$, m, 12H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 160.7, 160.5, 138.5$_0$, 138.4$_7$, 135.6, 129.6, 127.6, 126.6$_3$, 126.5$_8$, 118.1, 115.2, 112.5$_0$, 112.4$_7$, 70.9, 68.4, 39.5, 31.9, 30.6, 29.5, 29.4, 29.3, 29.2, 26.1, 24.0, 23.2, 22.8, 14.2$_4$, 14.2$_2$, 11.2. HRMS (ESI) m/z: calcd for $C_{40}H_{48}N_2O_2$ $[M]^+$, 588.3710; found, 588.3718.

*Synthesis of **E***

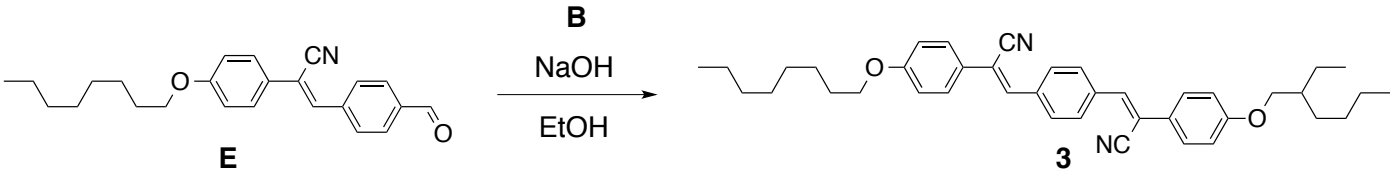


To a mixture of 4-octyoxyphenylacetonitrile (2.45 g, 10 mmol) and terepthalaldehyde mono(diethyl acetal) (2.08 g, 10 mmol) in methanol (10 mL), sodium methoxide in methanol (1 M, 10 mL) was added and stirred for 10 min at room temperature under air. The reaction mixture was diluted with methanol (30 mL), and then

filtered to remove yellow solid. The filtrate was poured into a large amount of water (100 mL). The solid was collected by filtration, and then washed with a small amount of methanol (5 mL). The solid was dissolved in chloroform (30 mL). To the solution, concentrated HCl solution (10 mL) was added and stirred by refax conditions. Chloroform phase was extracted, evaporated, and dried under vacuum to give as a powder.

Yellow-colored solid **E**: Yield: 93% (3.36 g). ^{1}H NMR (400 MHz, $CDCl_3$): δ 10.04 (Aldehyde, s, 1H), 7.97 (Ar-*H*, dd, *J* = 4.8, *J* = 4.8, 4H), 7.62 (Ar-*H*, d, *J* = 9.2, 2H), 7.42 (Vinylene-*H*, s, 1H), 6.96 (Ar-*H*, d, *J* = 8.8, 4H), 4.00 (O-C*H*$_2$-CH$_2$-CH$_2$-[CH$_2$]$_4$-CH$_3$, t, *J* = 6.4, 4H), 1.82 (O-CH$_2$-C*H*$_2$-CH$_2$-[CH$_2$]$_4$-CH$_3$, m, 4H), 1.78 (O-CH$_2$-CH$_2$-C*H*$_2$-[CH$_2$]$_4$-CH$_3$, m, 4H), 1.3 (O-CH$_2$-CH$_2$-CH$_2$-[C*H*$_2$]$_4$-CH$_3$, m, 8H), 0.88 (O-CH$_2$-CH$_2$-CH$_2$-[CH$_2$]$_4$-C*H*$_3$, t, *J* = 7.2, 6H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 191.4, 160.8, 139.7, 137.8, 136.8, 130.2, 129.6, 127.7, 126.2, 117.7, 115.2, 114.5, 68.4, 32.0, 29.4, 29.3, 29.2, 26.1, 22.8, 14.2. HRMS (ESI) m/z: calcd for $C_{24}H_{27}NO_2$ $[M]^+$, 361.2040; found, 361.2036.

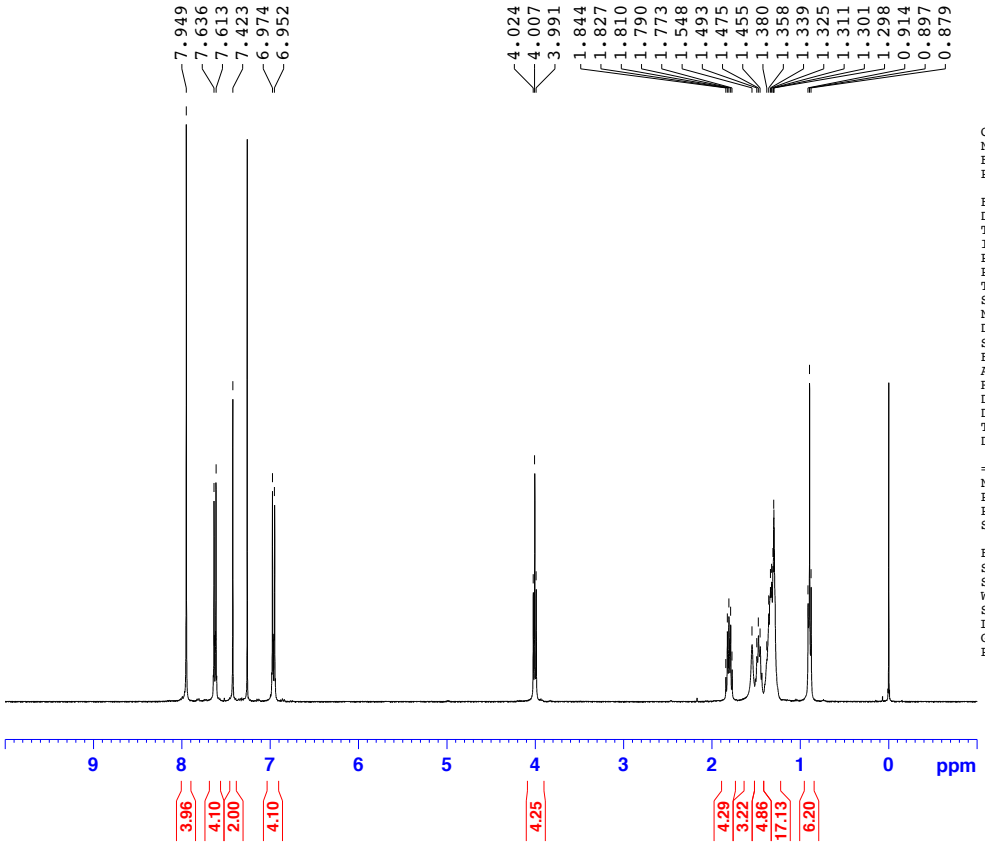
Synthesis of ***3***



To a mixture of **E** (361 mg, 1.0 mmol) and **B** (245 mg, 1.0 mmol) in ethanol (10 mL), sodium methoxide in methanol (1 M, 5 mL) was added and stirred for 10 min at room temperature under air. The reaction mixture was diluted with ethanol (10 mL), and then filtered to remove solid. The solid was washed with an ethanol (10 mL) and a large amount of methanol (100 mL), and dried under vacuum to give as a powder.

Yellow-colored solid **3**: Yield: Quant. (588 mg). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.95 (Ar-*H*, s, 4H), 7.62 (Ar-*H*, d, *J* = 8.2, 4H), 7.42 (Vinylene-*H*, s, 2H), 6.96 (Ar-*H*, d, *J* = 3.2, 2H), 6.96 (Ar-*H*, d, *J* = 2.8, 2H), 4.00 (O-C*H*$_2$-CH$_2$-CH$_2$-[CH$_2$]$_4$-CH$_3$, t, *J* = 6.8, 2H), 3.89 (O-C*H*$_2$-CH[CH$_2$-CH$_3$]-CH$_2$-[CH$_2$]$_2$-CH$_3$, d, *J* = 5.6, 2H), 1.81 (O-CH$_2$-C*H*$_2$-CH$_2$-[CH$_2$]$_4$-CH$_3$ and O-CH$_2$-C*H*[CH$_2$-CH$_3$]-CH$_2$-[CH$_2$]$_2$-CH$_3$, m, 3H), 1.78 (O-CH$_2$-CH$_2$-C*H*$_2$-[CH$_2$]$_4$-CH$_3$ and O-CH$_2$-CH[C*H*$_2$-CH$_3$]-C*H*$_2$-[CH$_2$]$_2$-CH$_3$ m, 6H), 1.35 (O-CH$_2$-CH$_2$-CH$_2$-[C*H*$_2$]$_4$-CH$_3$ and O-CH$_2$-CH[CH$_2$-CH$_3$]-CH$_2$-[C*H*$_2$]$_2$-CH$_3$ m, 10H), 0.88 (O-CH$_2$-CH$_2$-CH$_2$-[CH$_2$]$_4$-C*H*$_3$ and O-CH$_2$-CH[CH$_2$-C*H*$_3$]-CH$_2$-[CH$_2$]$_2$-C*H*$_3$ t, *J* = 7.2, 9H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 160.7, 138.4, 135.5, 129.6, 127.5, 126.6, 118.1, 115.2, 112.5, 112.5, 70.9, 39.5, 30.6, 29.2, 24.0, 23.2, 14.2, 11.2. HRMS (ESI) m/z: calcd for $C_{40}H_{48}N_2O_2$ $[M]^+$, 588.3710; found, 588.3707.

1

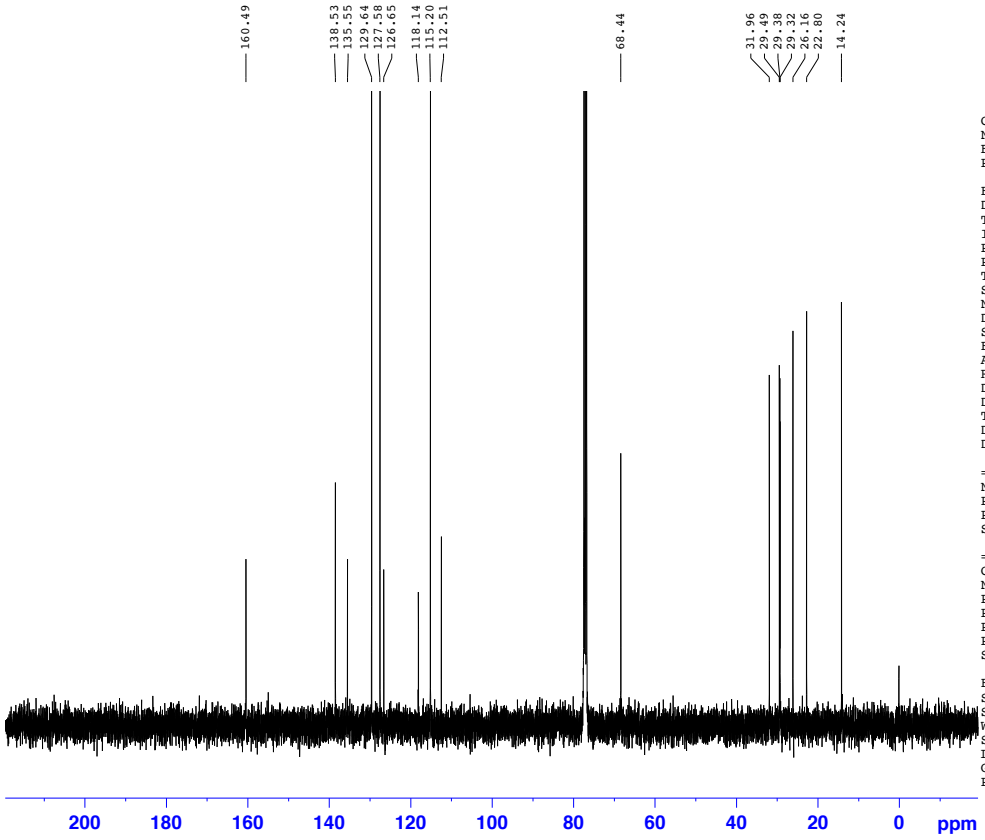


Current Data Parameters
NAME HAY hayashi_a 1H
EXPNO 10
PROCNO 1

F2 - Acquisition Parameters
Date_ 20210123
Time 5.42
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 8
DS 2
SWH 8223.685 Hz
FIDRES 0.125483 Hz
AQ 3.9846387 sec
RG 98.17
DW 60.800 usec
DE 6.50 usec
TE 299.8 K
D1 1.00000000 sec

======== CHANNEL f1 ========
NUC1 1H
P1 15.00 usec
PLW1 8.39999962 W
SFO1 400.1324710 MHz

F2 - Processing parameters
SI 65536
SF 400.1300099 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00



Current Data Parameters
NAME HAY hayashi_a 13C
EXPNO 10
PROCNO 1

F2 - Acquisition Parameters
Date_ 20210123
Time 6.42
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 1024
DS 4
SWH 24038.461 Hz
FIDRES 0.366798 Hz
AQ 1.3631988 sec
RG 194.19
DW 20.800 usec
DE 6.50 usec
TE 299.8 K
D1 2.00000000 sec
D11 0.03000000 sec

======== CHANNEL f1 ========
NUC1 13C
P1 10.00 usec
PLW1 82.00000000 W
SFO1 100.6228293 MHz

======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 80.00 usec
PLW2 8.39999962 W
PLW12 0.29530999 W
PLW13 0.29530999 W
SFO2 400.1316005 MHz

F2 - Processing parameters
SI 32768
SF 100.6127541 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40

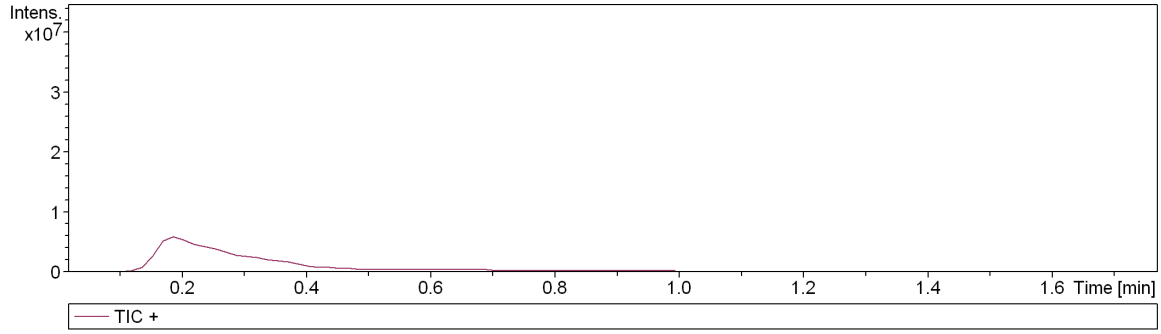
Display Report

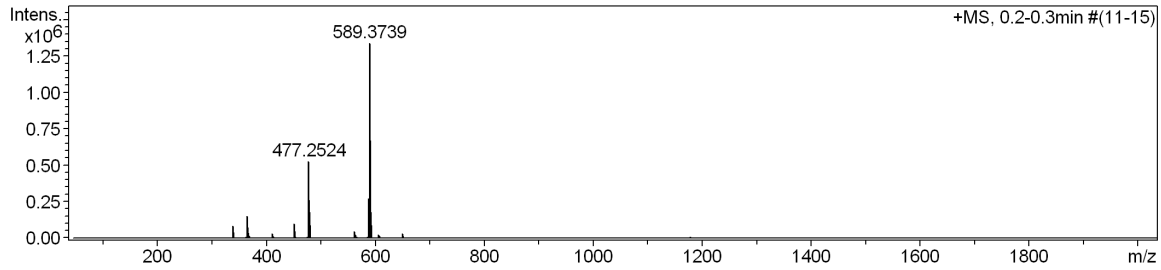
Analysis Info

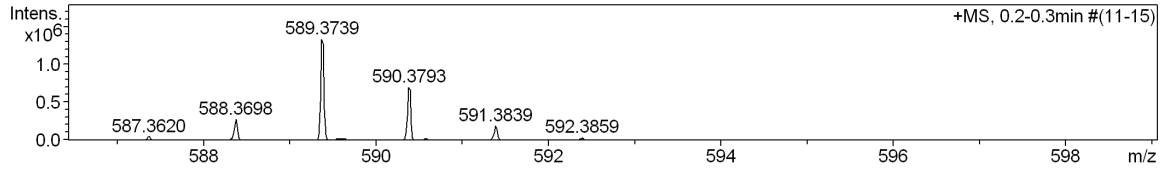
Analysis Name	D:\Data\Members\hayashi\1\RH9.d	Acquisition Date	4/27/2018 2:18:49 PM
Method	apci_pos_wide.m	Operator	bruker
Sample Name		Instrument / Ser#	micrOTOF 10387
Comment			

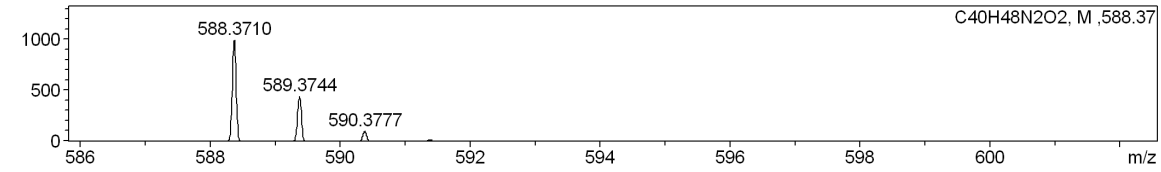
Acquisition Parameter

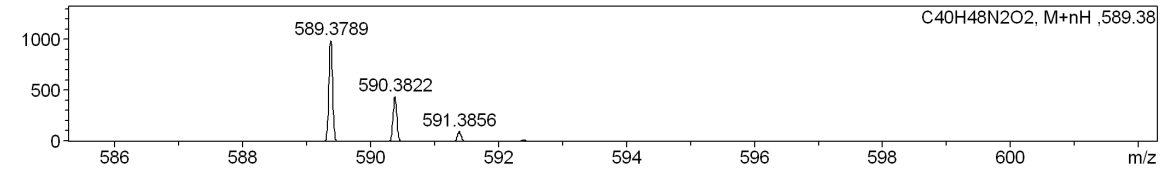
Source Type	APCI	Ion Polarity	Positive	Set Nebulizer	1.6 Bar
Focus	Active			Set Dry Heater	200 °C
Scan Begin	50 m/z	Set Capillary	4000 V	Set Dry Gas	3.0 l/min
Scan End	3000 m/z	Set End Plate Offset	-500 V	Set Divert Valve	Waste



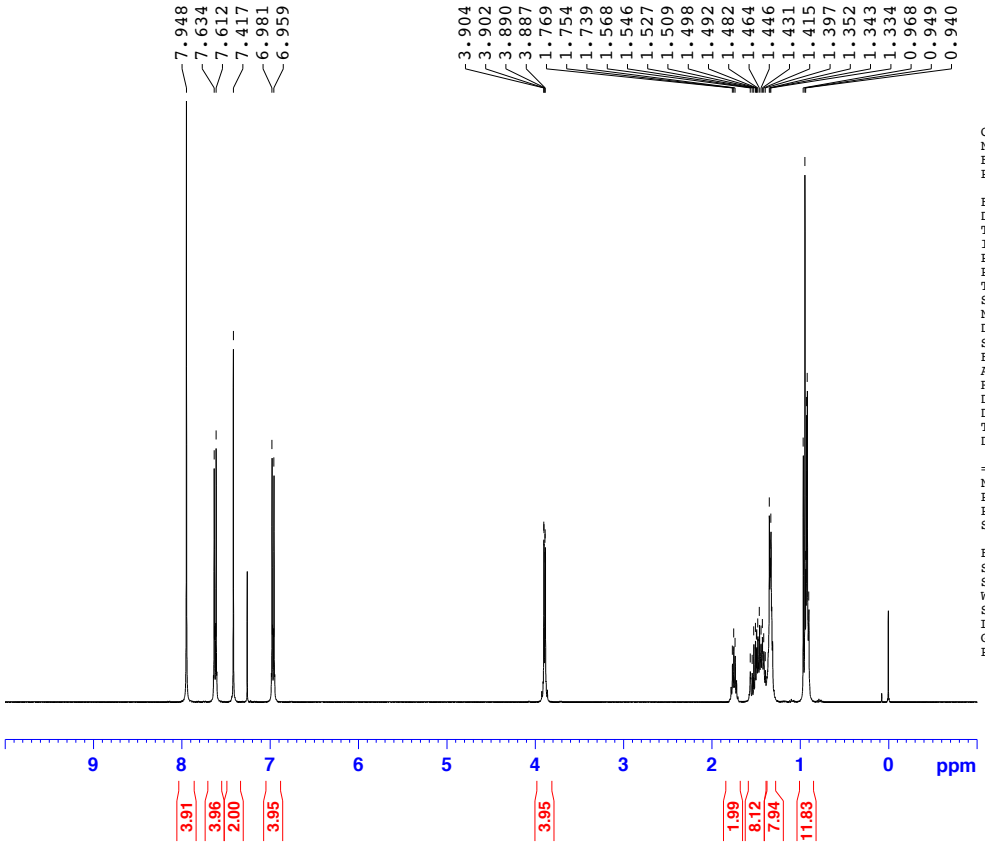








2

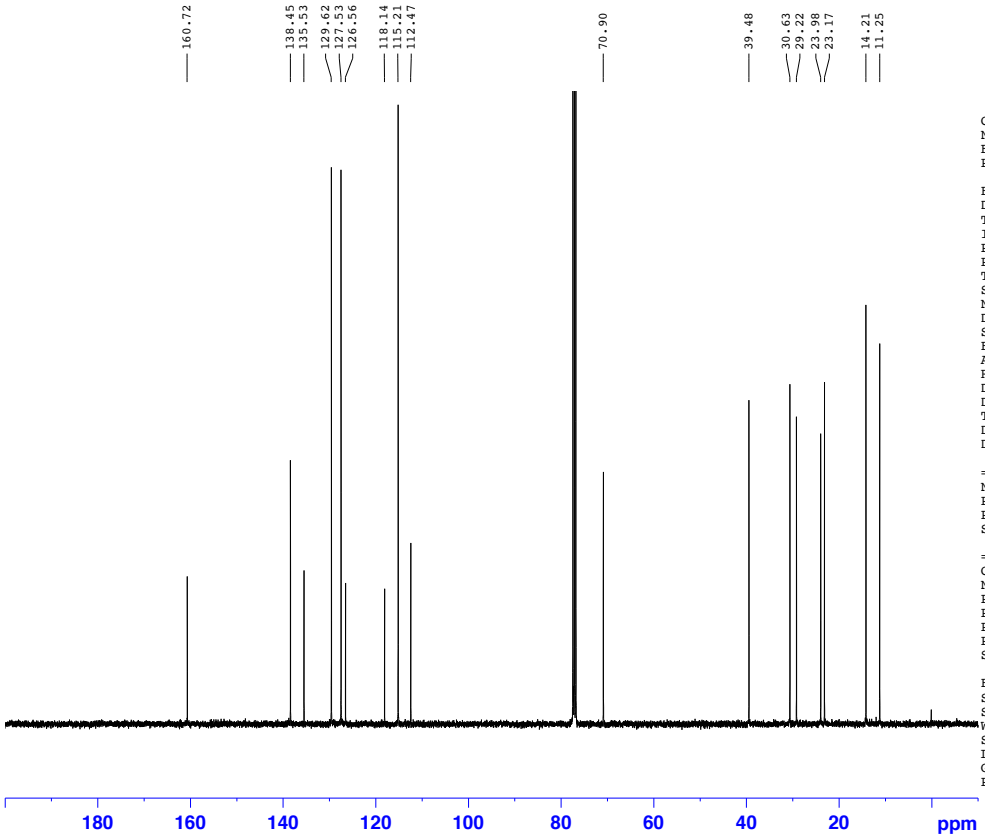


Current Data Parameters
NAME HAY hayashi_c 1H
EXPNO 10
PROCNO 1

F2 - Acquisition Parameters
Date_ 20210123
Time 4.33
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 8
DS 2
SWH 8223.685 Hz
FIDRES 0.125483 Hz
AQ 3.9846387 sec
RG 31.29
DW 60.800 usec
DE 6.50 usec
TE 299.8 K
D1 1.00000000 sec

======== CHANNEL f1 ========
NUC1 1H
P1 15.00 usec
PLW1 8.39999962 W
SFO1 400.1324710 MHz

F2 - Processing parameters
SI 65536
SF 400.1300098 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00



Current Data Parameters
NAME HAY hayashi_c 13C
EXPNO 10
PROCNO 1

F2 - Acquisition Parameters
Date_ 20210123
Time 5.36
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 1024
DS 4
SWH 24038.461 Hz
FIDRES 0.366798 Hz
AQ 1.3631988 sec
RG 194.19
DW 20.800 usec
DE 6.50 usec
TE 299.8 K
D1 2.00000000 sec
D11 0.03000000 sec

======== CHANNEL f1 ========
NUC1 13C
P1 10.00 usec
PLW1 82.00000000 W
SFO1 100.6228293 MHz

======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 80.00 usec
PLW2 8.39999962 W
PLW12 0.29530999 W
PLW13 0.29530999 W
SFO2 400.1316005 MHz

F2 - Processing parameters
SI 32768
SF 100.6127563 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40

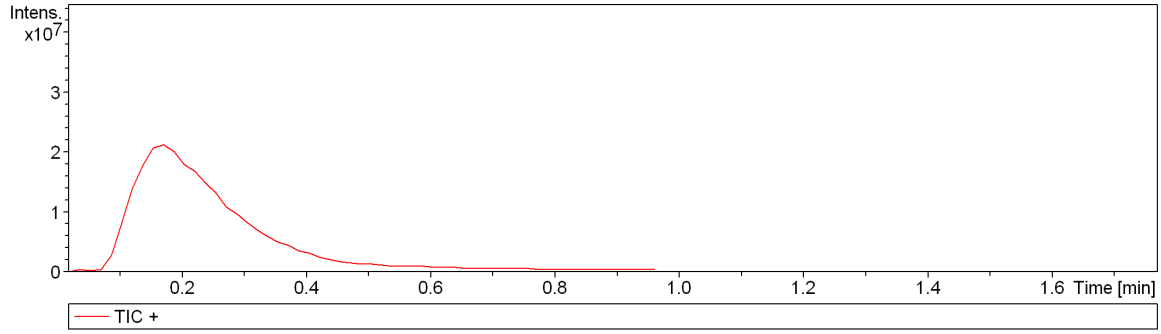
Display Report

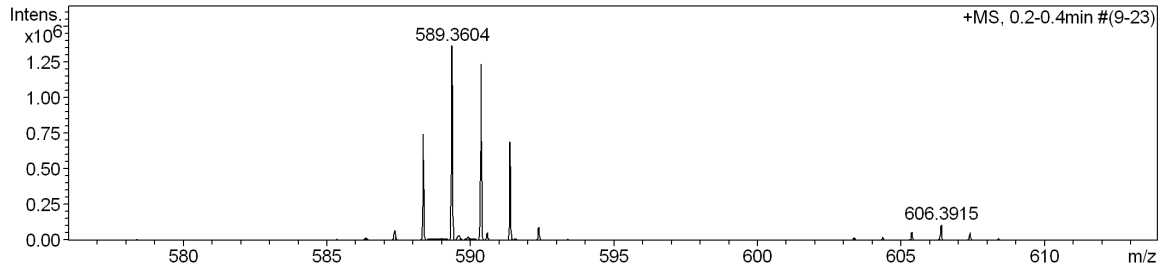
Analysis Info

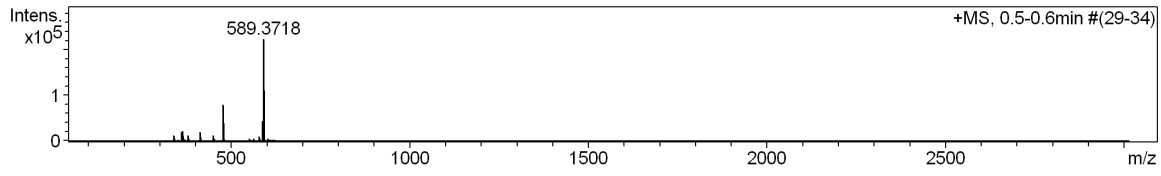
Analysis Name	D:\Data\Members\hayashi\1\RH6a.d	Acquisition Date	4/27/2018 3:46:09 PM
Method	apci_pos_wide.m	Operator	bruker
Sample Name		Instrument / Ser#	micrOTOF 10387
Comment			

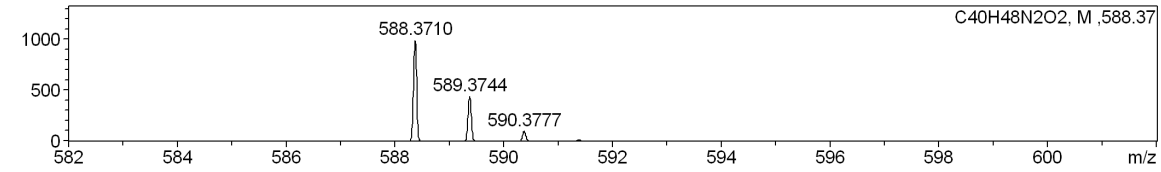
Acquisition Parameter

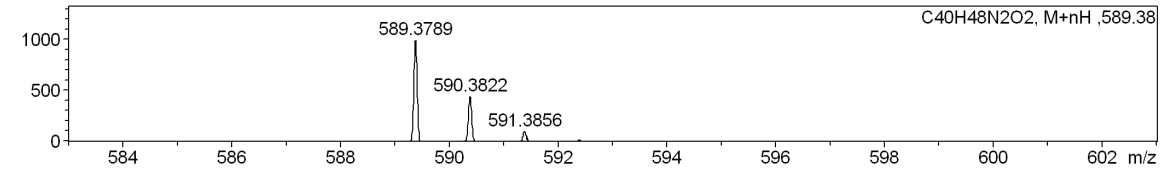
Source Type	APCI	Ion Polarity	Positive	Set Nebulizer	1.6 Bar
Focus	Active			Set Dry Heater	200 °C
Scan Begin	50 m/z	Set Capillary	4000 V	Set Dry Gas	3.0 l/min
Scan End	3000 m/z	Set End Plate Offset	-500 V	Set Divert Valve	Waste



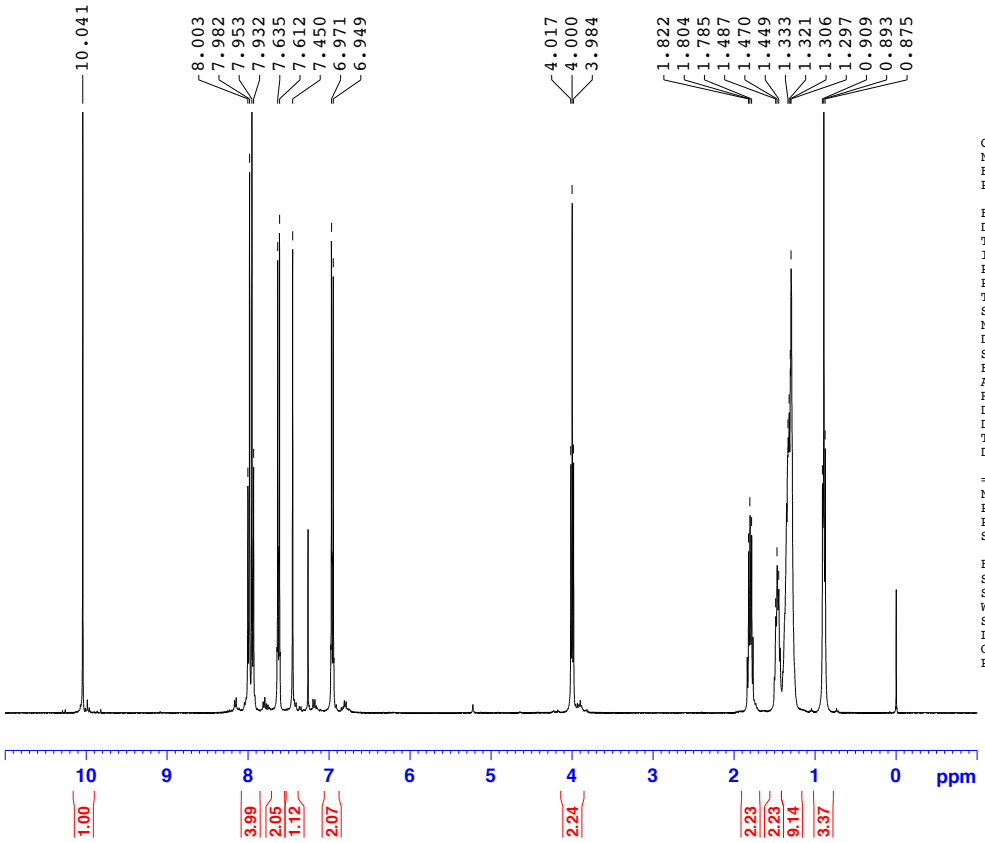








E

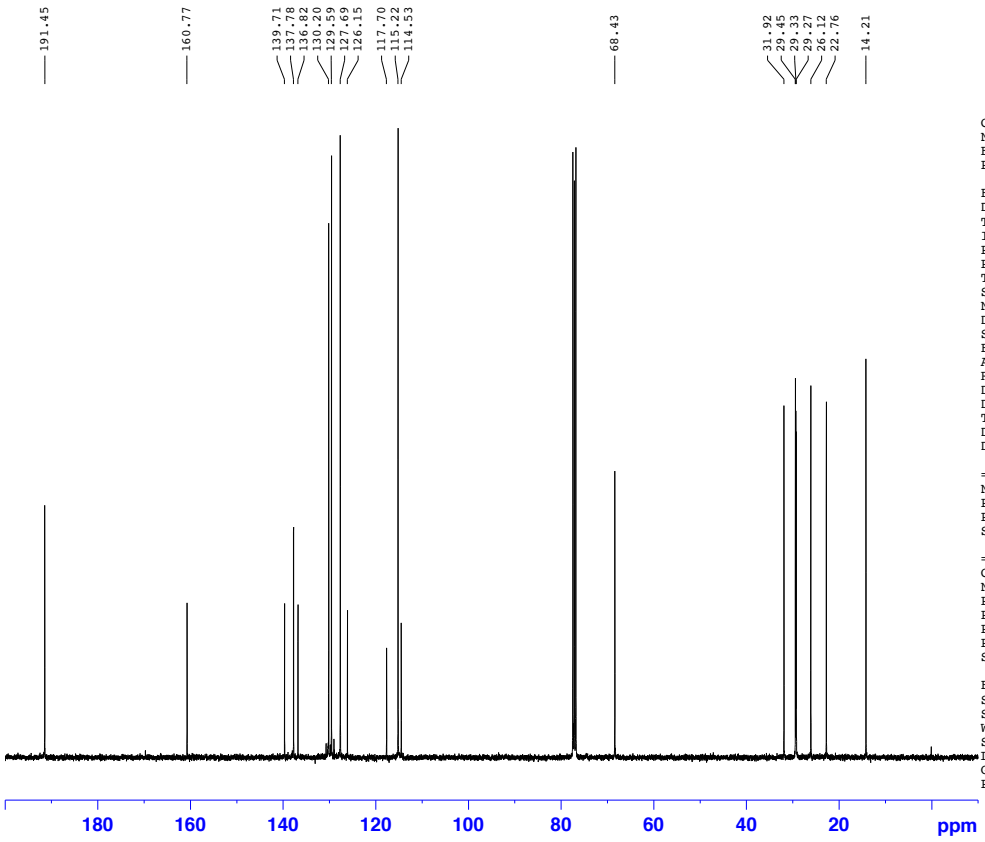



```
Current Data Parameters
NAME      HAY hayashi_d 1H
EXPNO                 10
PROCNO                 1

F2 - Acquisition Parameters
Date_           20210126
Time                1.34
INSTRUM            spect
PROBHD   5 mm PABBO BB-
PULPROG             zg30
TD                 65536
SOLVENT            CDCl3
NS                     8
DS                     2
SWH             8223.685 Hz
FIDRES          0.125483 Hz
AQ              3.9846387 sec
RG                 31.29
DW                60.800 usec
DE                 6.50 usec
TE                299.8 K
D1            1.00000000 sec

======== CHANNEL f1 ========
NUC1                  1H
P1                15.00 usec
PLW1         8.39999962 W
SFO1         400.1324710 MHz

F2 - Processing parameters
SI                 65536
SF           400.1300097 MHz
WDW                   EM
SSB       0
LB                0.30 Hz
GB        0
PC                1.00
```




```
Current Data Parameters
NAME      HAY hayashi_d 13C
EXPNO                 10
PROCNO                 1

F2 - Acquisition Parameters
Date_           20210126
Time                2.37
INSTRUM            spect
PROBHD   5 mm PABBO BB-
PULPROG          zgpg30
TD                 65536
SOLVENT            CDCl3
NS                  1024
DS                     4
SWH            24038.461 Hz
FIDRES          0.366798 Hz
AQ              1.3631988 sec
RG                194.19
DW                20.800 usec
DE                 6.50 usec
TE                299.8 K
D1            2.00000000 sec
D11           0.03000000 sec

======== CHANNEL f1 ========
NUC1                 13C
P1                10.00 usec
PLW1         82.00000000 W
SFO1         100.6228293 MHz

======== CHANNEL f2 ========
CPDPRG2          waltz16
NUC2                  1H
PCPD2             80.00 usec
PLW2         8.39999962 W
PLW12        0.29530999 W
PLW13        0.29530999 W
SFO2         400.1316005 MHz

F2 - Processing parameters
SI                 32768
SF           100.6127582 MHz
WDW                   EM
SSB       0
LB                1.00 Hz
GB        0
PC                1.40
```

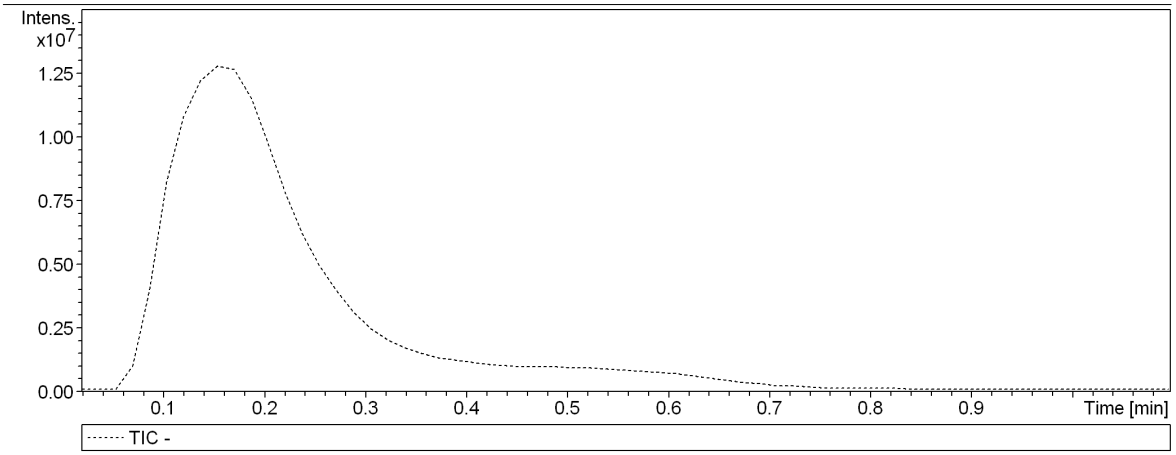
Display Report

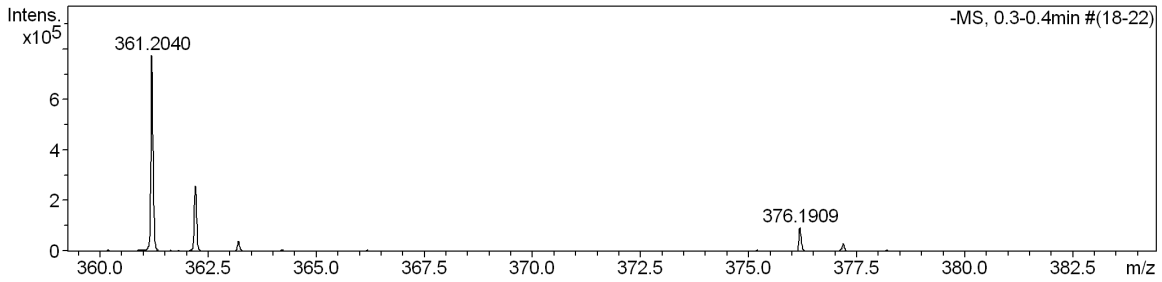
Analysis Info

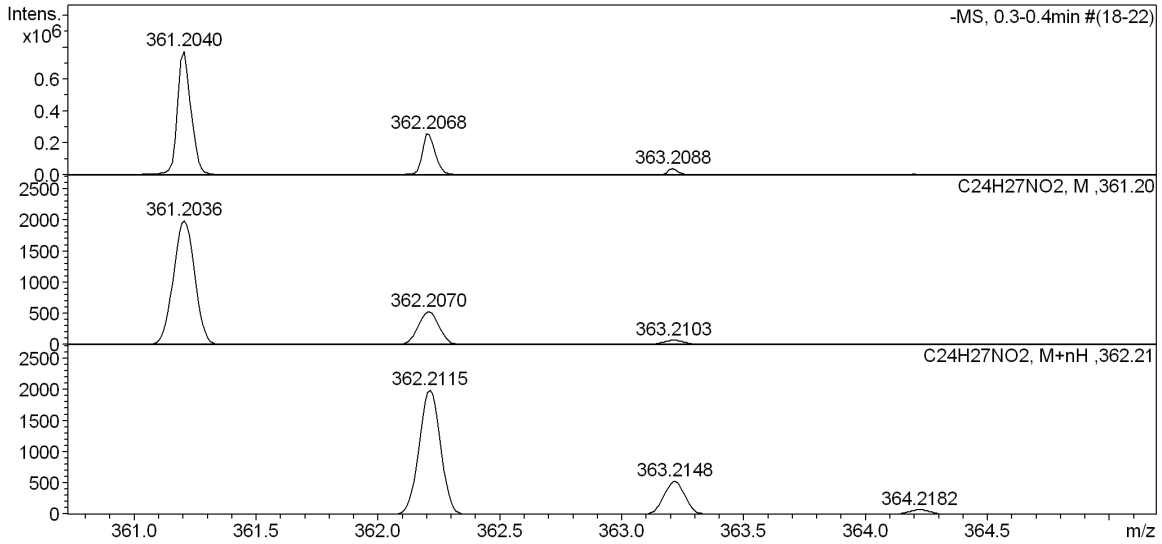
Analysis Name	D:\Data\Members\hayashi\20170417\SHA-1919.d	Acquisition Date	4/17/2017 4:02:45 PM
Method	dir_apci_neg_low.m	Operator	BDAL@DE
Sample Name		Instrument / Ser#	micrOTOF 10387
Comment			

Acquisition Parameter

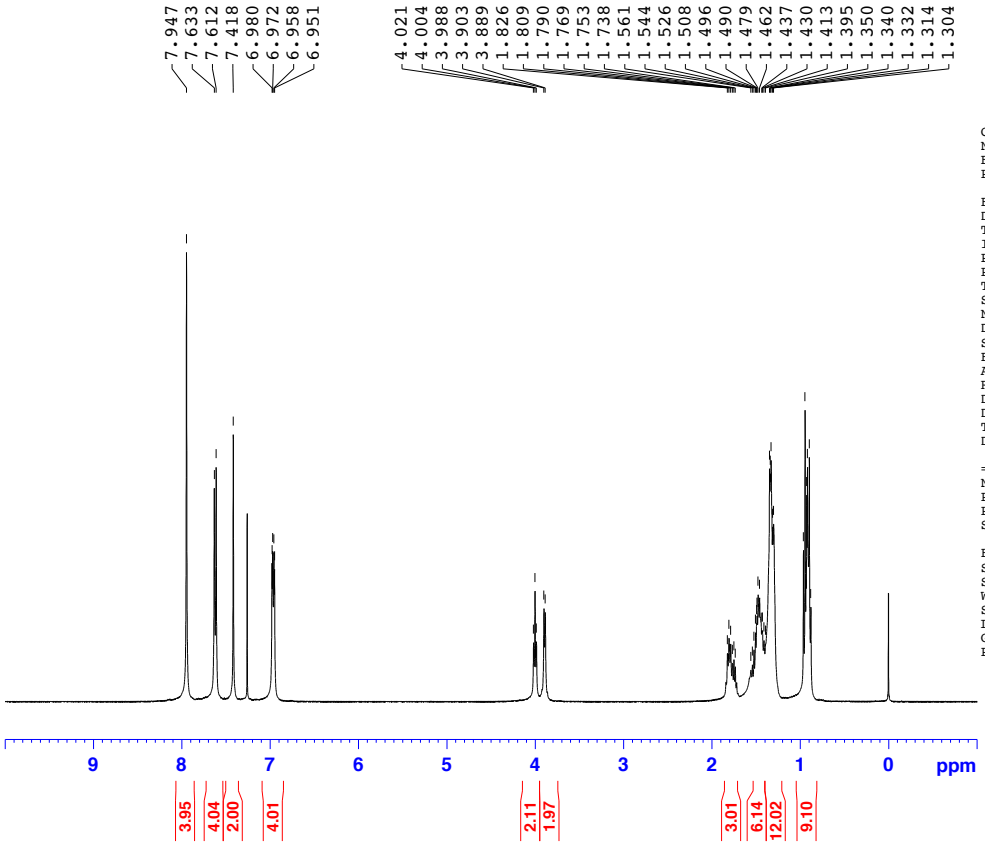
Source Type	APCI	Ion Polarity	Negative	Set Nebulizer	2.0 Bar
Focus	Not active			Set Dry Heater	200 °C
Scan Begin	50 m/z	Set Capillary	3500 V	Set Dry Gas	3.5 l/min
Scan End	3000 m/z	Set End Plate Offset	-500 V	Set Divert Valve	Waste







3

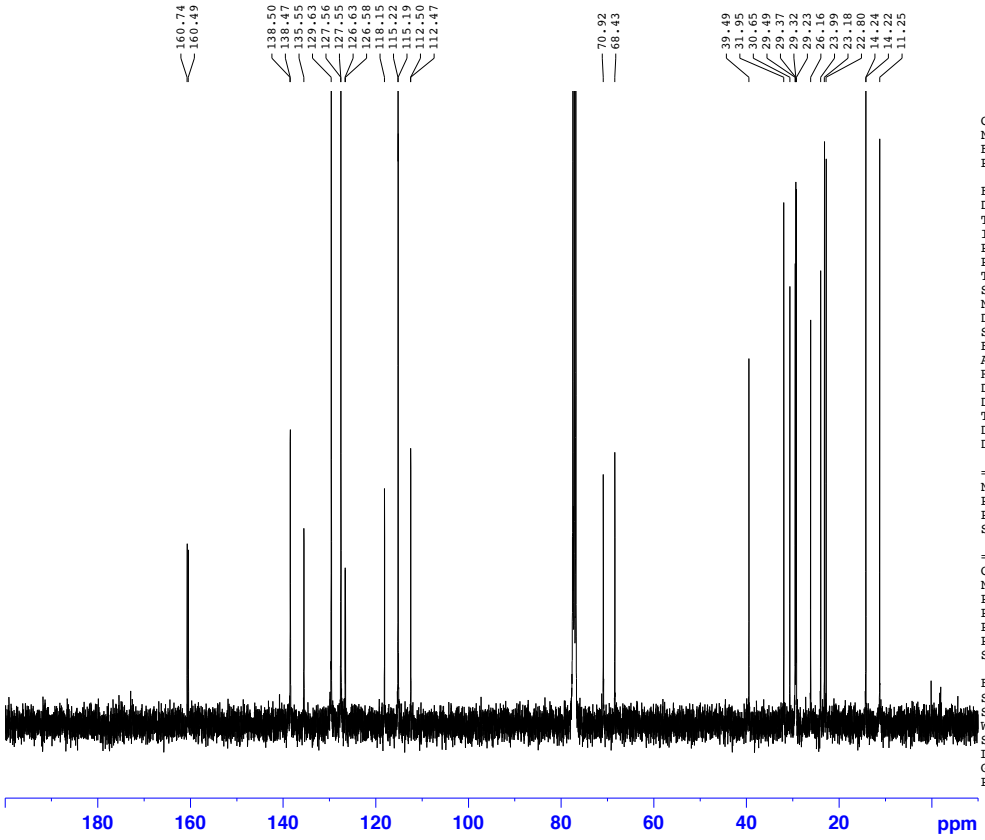


```
Current Data Parameters
NAME      HAY hayashi_b 1H
EXPNO                 10
PROCNO                 1

F2 - Acquisition Parameters
Date_           20210123
Time                6.46
INSTRUM            spect
PROBHD   5 mm PABBO BB-
PULPROG             zg30
TD                 65536
SOLVENT            CDCl3
NS                     8
DS                     2
SWH             8223.685 Hz
FIDRES          0.125483 Hz
AQ             3.9846387 sec
RG                 56.92
DW                60.800 usec
DE                 6.50 usec
TE                299.8 K
D1           1.00000000 sec

======== CHANNEL f1 ========
NUC1                  1H
P1                15.00 usec
PLW1         8.39999962 W
SFO1         400.1324710 MHz

F2 - Processing parameters
SI                 65536
SF          400.1300097 MHz
WDW                   EM
SSB       0
LB                0.30 Hz
GB        0
PC                1.00
```



```
Current Data Parameters
NAME      HAY hayashi_b 13C
EXPNO                 10
PROCNO                 1

F2 - Acquisition Parameters
Date_           20210123
Time                7.46
INSTRUM            spect
PROBHD   5 mm PABBO BB-
PULPROG          zgpg30
TD                 65536
SOLVENT            CDCl3
NS                  1024
DS                     4
SWH            24038.461 Hz
FIDRES          0.366798 Hz
AQ             1.3631988 sec
RG                194.19
DW                20.800 usec
DE                 6.50 usec
TE                299.8 K
D1           2.00000000 sec
D11          0.03000000 sec

======== CHANNEL f1 ========
NUC1                 13C
P1                10.00 usec
PLW1        82.00000000 W
SFO1         100.6228293 MHz

======== CHANNEL f2 ========
CPDPRG2          waltz16
NUC2                  1H
PCPD2             80.00 usec
PLW2         8.39999962 W
PLW12        0.29530999 W
PLW13        0.29530999 W
SFO2         400.1316005 MHz

F2 - Processing parameters
SI                 32768
SF          100.6127549 MHz
WDW                   EM
SSB       0
LB                1.00 Hz
GB        0
PC                1.40
```

Display Report

Analysis Info

Analysis Name	D:\Data\Members\hayashi\1\RH-7a.d	Acquisition Date	4/27/2018 2:06:23 PM
Method	apci_pos_wide.m	Operator	bruker
Sample Name		Instrument / Ser#	micrOTOF 10387
Comment			

Acquisition Parameter

Source Type	APCI	Ion Polarity	Positive	Set Nebulizer	1.6 Bar
Focus	Active			Set Dry Heater	200 °C
Scan Begin	50 m/z	Set Capillary	4000 V	Set Dry Gas	3.0 l/min
Scan End	3000 m/z	Set End Plate Offset	-500 V	Set Divert Valve	Waste