# Crystal structure determination

**Table S1.** Crystal and structure refinement data of **1a-3a** and **3b**

| Complex | **1a** | **2a** | **3a** | **3b** |
|---|---|---|---|---|
| Empirical fomula | $C_{10}H_{11}BrO_3$ | $C_{12}H_{13}N_3O_3$ | $C_{11}H_{11}N_3O_3$ | $C_{12}H_{13}N_3O_4$ |
| Fomula weight | 259.10 | 247.25 | 233.23 | 263.25 |
| Temperature (K) | 296(2) | 296(2) | 296(2) | 296(2) |
| Wavelength (Å) | 0.71073 | 0.71073 | 0.71073 | 0.71073 |
| Crystal system | Monoclinic | Monoclinic | Monoclinic | Orthorhombic |
| Space group | $P2_1/n$ | $P2_1$ | $P2_1$ | $Pca2_1$ |
| $a$ (Å) | 4.7745(6) | 8.8786(15) | 4.5923(7) | 17.8859(17) |
| $b$ (Å) | 18.454(3) | 4.4485(8) | 19.343(3) | 4.0963(5) |
| $c$ (Å) | 12.3429(17) | 15.455(3) | 6.4024(10) | 17.4011(17) |
| $\alpha$ (°) | 90 | 90 | 90 | 90 |
| $\beta$ (°) | 99.501(2) | 107.779(2) | 93.168(2) | 90 |
| $\gamma$ (°) | 90 | 90 | 90 | 90 |
| V (Å$^3$) | 1072.6(2) | 597.58(18) | 567.85(15) | 1274.9(2) |
| Z | 4 | 2 | 2 | 4 |
| Dc (g cm$^{-3}$) | 1.604 | 1.374 | 1.364 | 1.372 |
| $\mu$ (mm$^{-1}$) | 3.811 | 1.033 | 0.102 | 0.105 |
| F(000) | 520 | 260 | 244 | 552 |
| Crystal size (mm) | 0.18 x 0.13 x 0.12 | 0.20 x 0.15 x 0.13 | 0.21 x 0.16 x 0.13 | 0.23 x 0.17 x 0.14 |
| $\Theta$ range for date | 2.77-22.65 | 2.453-25.495 | 3.187-25.498 | 4.188-25.482 |
| Reflections collected | 8187 | 4646 | 4385 | 2828 |
| Independent reflection | 1996 [R(int) = 0.0274] | 2210 [R(int) = 0.0181] | 2096 [R(int) = 0.0154] | 1730 [R(int) = 0.0181] |
| Goodness-of-fit on $F^2$ | 1.026 | 1.038 | 1.083 | 1.011 |
| Final $R$ indices[$I > 2\sigma(I)$][a] | $R_1$= 0.0323,$wR_2$= 0.0788 | $R_1$= 0.0283, $wR_2$= 0.0742 | $R_1$= 0.0307, $wR_2$= 0.0685 | $R_1$= 0.0364, $wR_2$= 0.0739 |
| $R$ indices(all data)a | $R_1$=0.0497, $wR_2$= 0.0874 | $R_1$= 0.0315, $wR_2$= 0.0766 | $R_1$= 0.0398, $wR_2$= 0.0727 | $R_1$= 0.0441, $wR_2$= 0.0782 |

[a] $R_1 = \Sigma \| F_o | - | F_c \| / \Sigma | F_o |$ ; [b] $wR_2 = [\Sigma w(F_o^2 - F_c^2)_2 / \Sigma w(F_o^2)^2]^{1/2}$

**Table S2.** Selected bond lengths (Å) and bond angles (°) of **1a**-**3a** and **3b**

| **Bond** | **Bond** | **Angle** | **Bond** | **Angle** | **Bond** |
|---|---|---|---|---|---|
| | | | **1a** | | |
| C(1)-O(3) | 1.364(3) | O(3)-C(1)-C(2 | 125.0(2) | C(5)-C(6)-C(1) | 120.6(3) |
| C(1)-C(2) | 1.382(4) | O(3)-C(1)-C(6 | 115.4(2) | O(1)-C(7)-O(2) | 122.5(3) |
| C(1)-C(6) | 1.389(4) | C(2)-C(1)-C(6 | 119.6(2) | O(1)-C(7)-C(4) | 124.5(3) |
| C(2)-C(3) | 1.377(4) | C(3)-C(2)-C(1 | 119.5(3) | O(2)-C(7)-C(4) | 113.0(2) |
| C(4)-C(5) | 1.385(4) | C(2)-C(3)-C(4 | 121.3(2) | O(3)-C(9)-C(10 | 108.2(2) |
| C(3)-C(4) | 1.389(4) | C(3)-C(4)-C(5 | 118.8(2) | C(9)-C(10)-Br(1 | 111.6(2) |
| C(4)-C(7) | 1.478(4) | C(3)-C(4)-C(7 | 118.6(2) | C(7)-O(2)-C(8) | 116.9(3) |

| | | | | | |
|---|---|---|---|---|---|
| C(5)-C(6) | 1.371(4) | C(5)-C(4)-C(7 | 122.6(2) | C(1)-O(3)-C(9) | 117.4(2) |
| C(7)-O(1) | 1.201(3) | C(6)-C(5)-C(4 | 120.2(3) | | |
| C(7)-O(2) | 1.328(3) | | | | |
| C(8)-O(2) | 1.441(4) | | | | |
| C(9)-O(3) | 1.427(3) | | | | |
| C(9)-C(10) | 1.489(4) | | | | |
| C(10)-Br(1) | 1.942(3) | | | | |

**2a**

| | | | | | |
|---|---|---|---|---|---|
| C(1)-C(2) | 1.375(3) | C(2)-C(1)-C(6 | 120.57(18) | O(2)-C(7)-C(6) | 112.10(17) |
| C(1)-C(6) | 1.394(3) | C(1)-C(2)-C(3 | 120.22(18) | O(3)-C(9)-C(10 | 107.93(15) |
| C(2)-C(3) | 1.383(3) | O(3)-C(3)-C(2 | 116.20(16) | N(1)-C(10)-C(9 | 112.61(19) |
| C(3)-O(3) | 1.368(2) | O(3)-C(3)-C(4 | 123.78(17) | N(2)-C(11)-N(3 | 115.4(2) |
| C(3)-C(4) | 1.389(3) | C(2)-C(3)-C(4 | 120.02(19) | N(3)-C(12)-N(1 | 111.52(18) |
| C(4)-C(5) | 1.379(3) | C(5)-C(4)-C(3 | 119.09(17) | C(12)-N(1)-N(2 | 109.06(17) |
| C(5)-C(6) | 1.383(3) | C(4)-C(5)-C(6 | 121.70(17) | C(12)-N(1)-C(1 | 130.05(17) |
| C(6)-C(7) | 1.473(3) | C(5)-C(6)-C(1 | 118.39(18) | N(2)-N(1)-C(10 | 120.89(15) |
| C(7)-O(1) | 1.202(2) | C(5)-C(6)-C(7 | 122.59(17) | C(11)-N(2)-N(1 | 102.15(16) |
| C(7)-O(2) | 1.349(2) | C(1)-C(6)-C(7 | 119.02(17) | C(12)-N(3)-C(1 | 101.82(18) |
| C(8)-O(2) | 1.445(3) | O(1)-C(7)-O( | 122.4(2) | C(7)-O(2)-C(8) | 116.23(17) |
| C(9)-O(3) | 1.430(2) | O(1)-C(7)-C(6 | 125.48(18) | C(3)-O(3)-C(9) | 117.43(14) |
| C(9)-C(10) | 1.503(3) | | | | |
| C(10)-N(1) | 1.453(3) | | | | |
| C(11)-N(2) | 1.316(3) | | | | |
| C(11)-N(3) | 1.337(3) | | | | |
| C(12)-N(3) | 1.312(3) | | | | |
| C(12)-N(1) | 1.321(3) | | | | |
| N(1)-N(2) | 1.347(2) | | | | |

**3a**

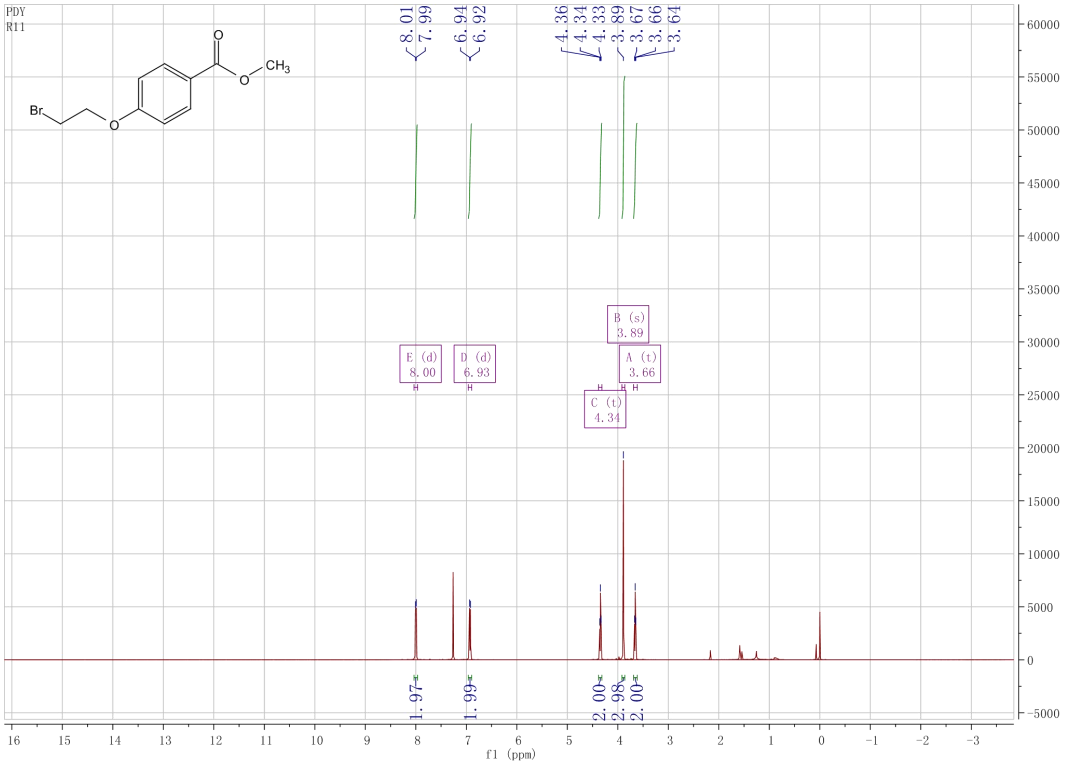
| | | | | | |
|---|---|---|---|---|---|
| C(1)-C(2) | 1.363(4) | C(2)-C(1)-C(6 | 121.1(2) | O(2)-C(7)-C(6) | 114.4(2) |
| C(1)-C(6) | 1.388(4) | C(1)-C(2)-C(3 | 120.1(2) | O(3)-C(8)-C(9) | 106.2(2) |
| C(2)-C(3) | 1.371(3) | O(3)-C(3)-C(2 | 115.0(2) | N(1)-C(9)-C(8) | 111.8(2) |
| C(3)-O(3) | 1.363(3) | O(3)-C(3)-C(4 | 124.9(2) | N(1)-C(10)-N(3 | 110.7(2) |
| C(3)-C(4) | 1.381(3) | C(2)-C(3)-C(4 | 120.1(3) | N(2)-C(11)-N(3 | 114.5(2) |
| C(4)-C(5) | 1.374(4) | C(5)-C(4)-C(3 | 119.1(2) | C(10)-N(1)-N(2 | 109.4(2) |
| C(5)-C(6) | 1.378(4) | C(4)-C(5)-C(6 | 121.6(2) | C(10)-N(1)-C(9 | 129.8(2) |
| C(6)-C(7) | 1.478(4) | C(5)-C(6)-C(1 | 117.9(3) | N(2)-N(1)-C(9) | 120.7(2) |
| C(7)-O(1) | 1.211(3) | C(5)-C(6)-C(7 | 119.6(2) | C(11)-N(2)-N(1 | 102.7(2) |
| C(7)-O(2) | 1.314(3) | C(1)-C(6)-C(7 | 122.5(2) | C(10)-N(3)-C(1 | 102.7(3) |
| C(8)-O(3) | 1.418(3) | O(1)-C(7)-O( | 122.2(3) | C(3)-O(3)-C(8) | 118.7(2) |
| C(8)-C(9) | 1.500(4) | O(1)-C(7)-C(6 | 123.4(3) | | |
| C(9)-N(1) | 1.455(3) | | | | |
| C(10)-N(1) | 1.310(3) | | | | |

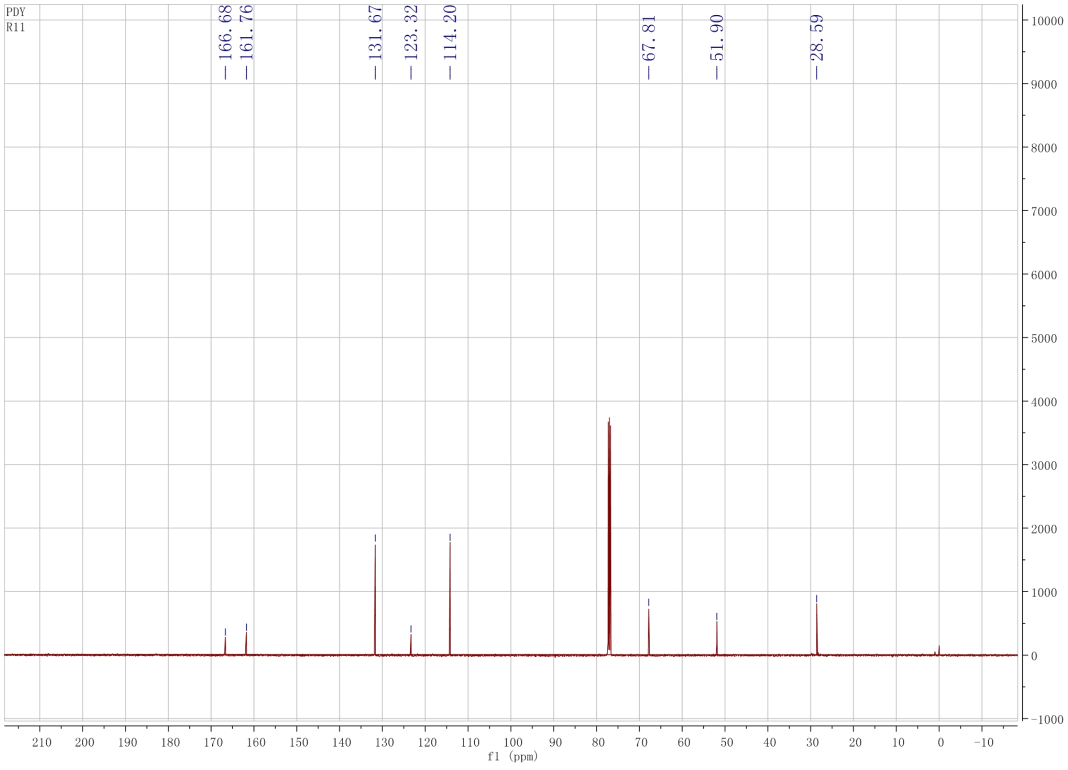
| | | | | | |
|---|---|---|---|---|---|
| C(10)-N(3) | 1.313(4) | | | | |
| C(11)-N(2) | 1.307(4) | | | | |
| C(11)-N(3) | 1.334(4) | | | | |
| N(1)-N(2) | 1.343(3) | | | | |
| | | **3b** | | | |
| C(1)-O(1) | 1.207(3) | O(1)-C(1)-O( | 122.7(3) | C(7)-C(6)-C(5) | 118.9(3) |
| C(1)-O(2) | 1.324(4) | O(1)-C(1)-C(2 | 123.7(3) | C(6)-C(7)-C(2) | 120.9(3) |
| C(1)-C(2) | 1.479(4) | O(2)-C(1)-C(2 | 113.5(3) | O(3)-C(9)-C(10 | 106.1(3) |
| C(2)-C(3) | 1.380(4) | C(3)-C(2)-C(7 | 119.6(3) | N(1)-C(10)-C(9 | 113.5(2) |
| C(2)-C(7) | 1.395(4) | C(3)-C(2)-C(1 | 122.8(3) | C(12)-N(2)-N(1 | 102.4(3) |
| C(3)-C(4) | 1.386(4) | C(7)-C(2)-C(1 | 117.6(3) | C(11)-N(3)-C(1 | 102.3(3) |
| C(4)-C(5) | 1.374(4) | C(2)-C(3)-C(4 | 120.0(3) | C(11)-N(1)-N(2 | 109.3(3) |
| C(5)-O(3) | 1.370(3) | C(5)-C(4)-C(3 | 120.3(3) | C(11)-N(1)-C(1 | 130.5(3) |
| C(5)-C(6) | 1.401(4) | O(3)-C(5)-C(4 | 125.1(3) | N(2)-N(1)-C(10 | 120.2(2) |
| C(6)-O(4) | 1.365(4) | O(3)-C(5)-C(6 | 114.5(3) | N(3)-C(11)-N(1 | 111.1(3) |
| C(6)-C(7) | 1.374(4) | C(4)-C(5)-C(6 | 120.4(3) | N(2)-C(12)-N(3 | 115.0(3) |
| C(8)-O(4) | 1.431(3) | O(4)-C(6)-C(7 | 125.3(3) | C(5)-O(3)-C(9) | 117.9(2) |
| C(9)-O(3) | 1.441(3) | O(4)-C(6)-C(5 | 115.7(3) | C(6)-O(4)-C(8) | 117.1(2) |
| C(9)-C(10) | 1.501(4) | | | | |
| C(10)-N(1) | 1.463(4) | | | | |
| N(2)-C(12) | 1.317(4) | | | | |
| N(2)-N(1) | 1.349(3) | | | | |
| N(3)-C(11) | 1.313(5) | | | | |
| N(3)-C(12) | 1.346(4) | | | | |
| N(1)-C(11) | 1.327(4) | | | | |

2.3.1. Crystal structure of compoud **1a**

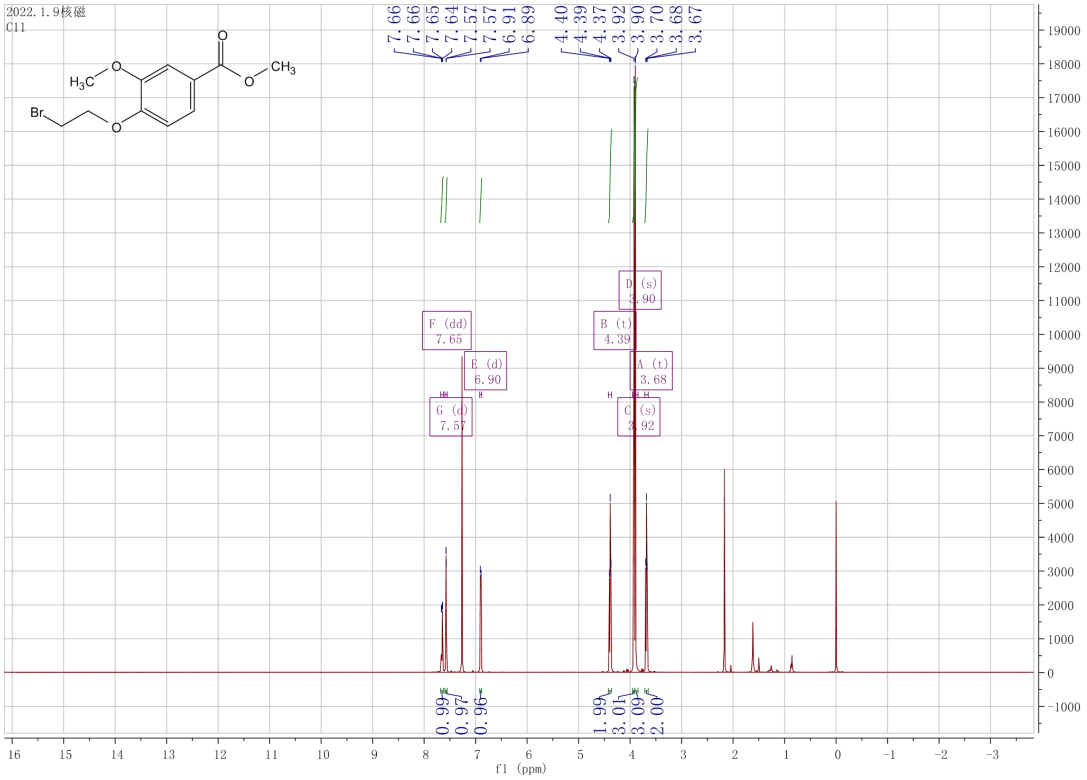
# NMR

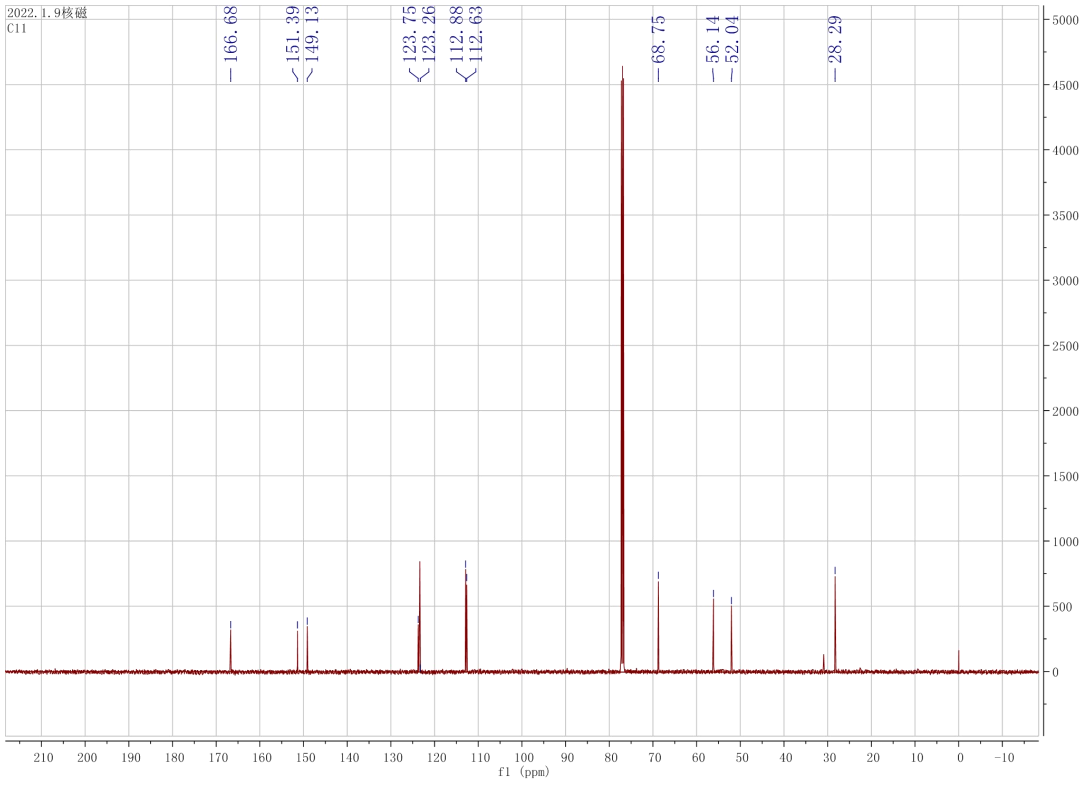
1a


PDY
R11
Br
O
O
CH3
8.01
7.99
6.94
6.92
4.36
4.34
4.33
3.89
3.67
3.66
3.64
E (d)
8.00
D (d)
6.93
B (s)
3.89
A (t)
3.66
C (t)
4.34
1.97
1.99
2.00
2.98
2.00
f1 (ppm)

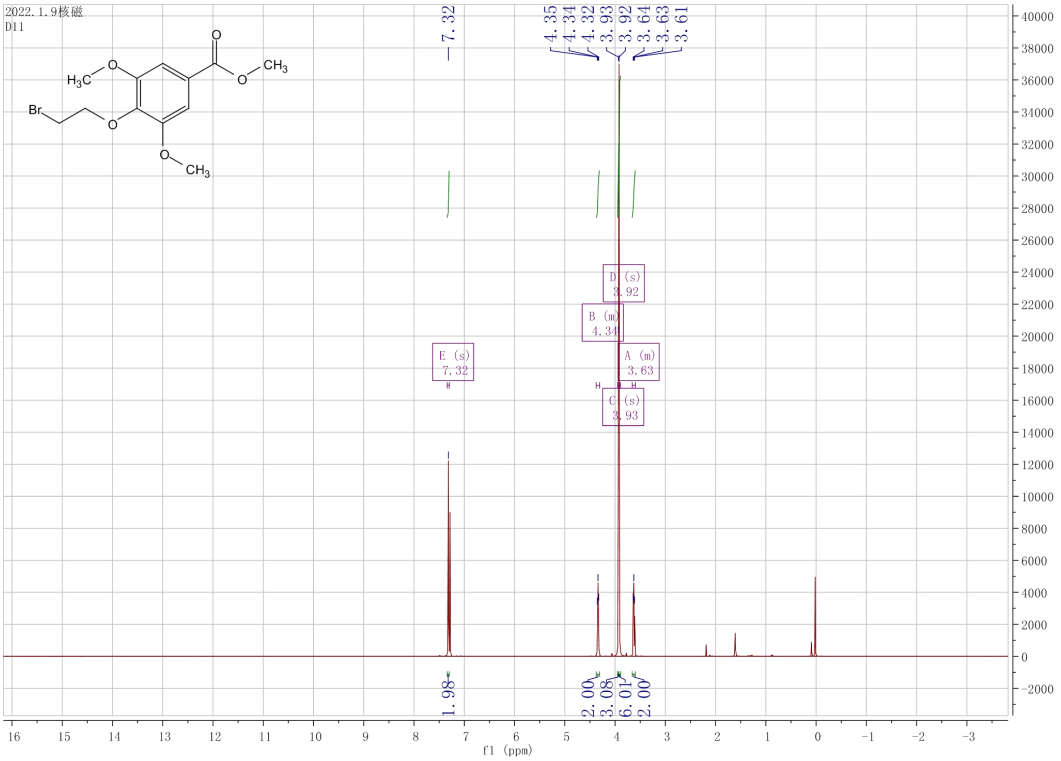

PDY
R11
166.68
161.76
131.67
123.32
114.20
67.81
51.90
28.59
f1 (ppm)

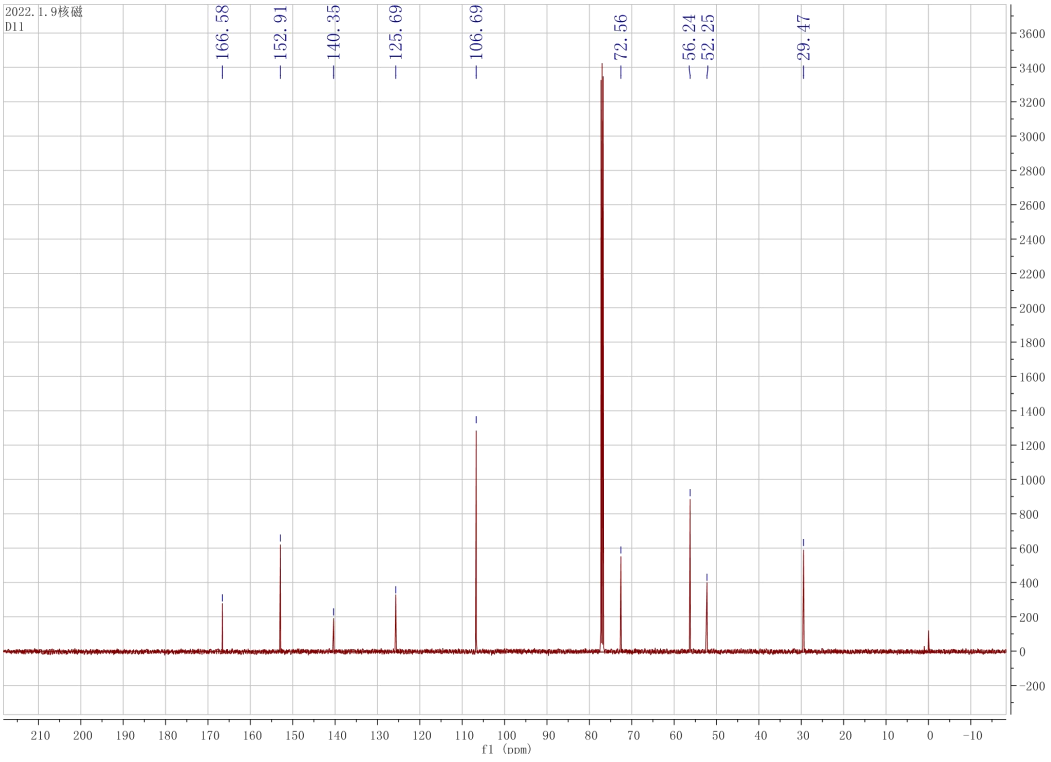
1b


2022.1.9核磁
C11
7.66
7.66
7.65
7.64
7.57
7.57
6.91
6.89
4.40
4.39
4.37
3.92
3.90
3.70
3.68
3.67
D (s)
3.90
F (dd)
7.65
B (t)
4.39
E (d)
6.90
A (t)
3.68
G (d)
7.57
C (s)
3.92
0.99
0.97
0.96
1.99
3.01
3.09
2.00
f1 (ppm)

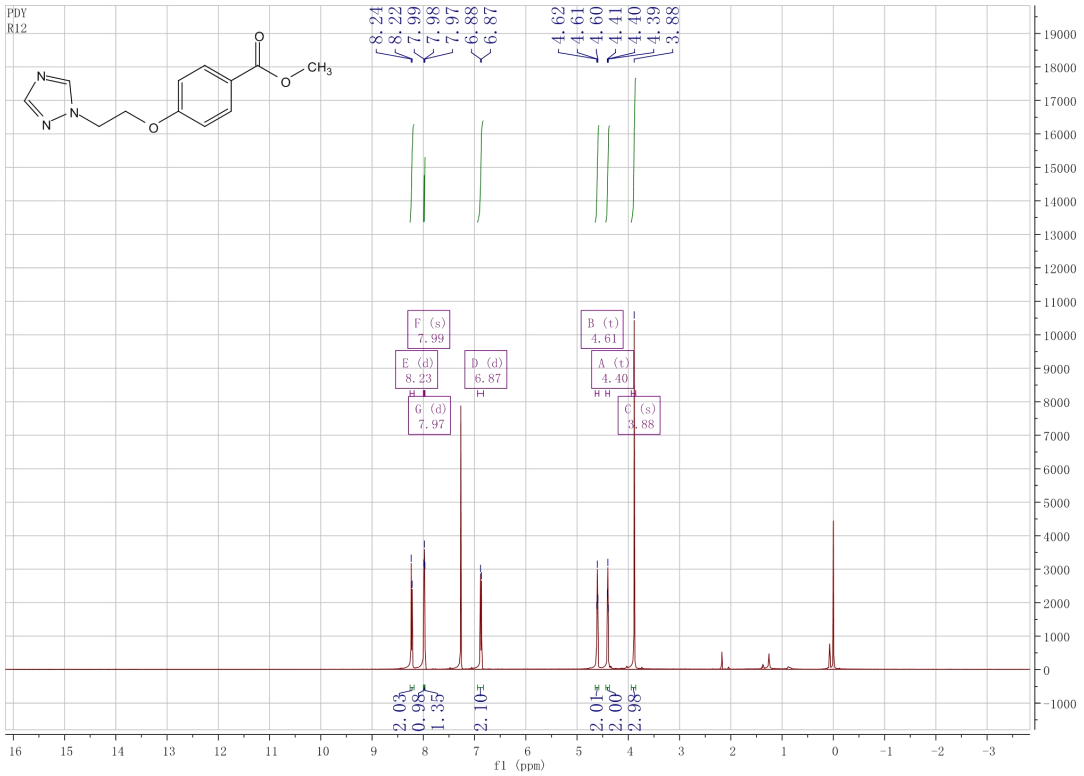

2022.1.9核磁
C11
166.68
151.39
149.13
123.75
123.26
112.88
112.63
68.75
56.14
52.04
28.29
f1 (ppm)

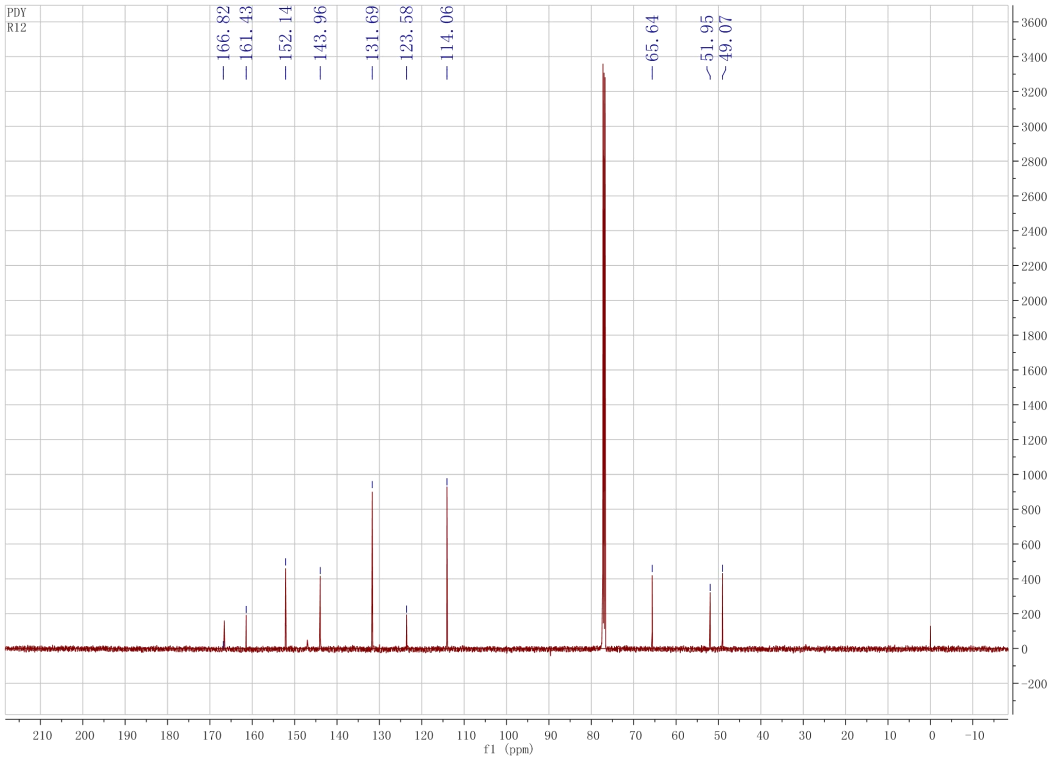
1c


2022.1.9核磁
D11
7.32
4.35
4.34
4.32
3.93
3.92
3.64
3.63
3.61
D (s) 3.92
B (m) 4.34
A (m) 3.63
E (s) 7.32
G (s) 3.93
1.98
2.00
3.08
6.01
2.00
f1 (ppm)

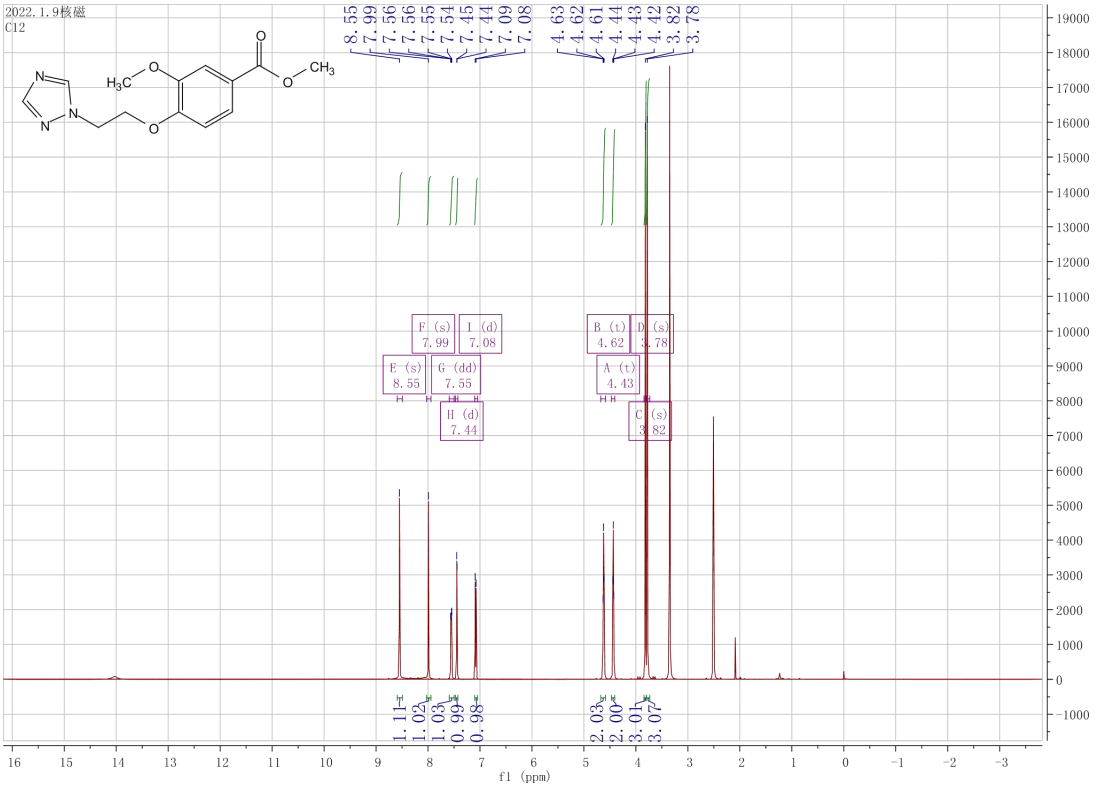

2022.1.9核磁
D11
166.58
152.91
140.35
125.69
106.69
72.56
56.24
52.25
29.47
f1 (ppm)

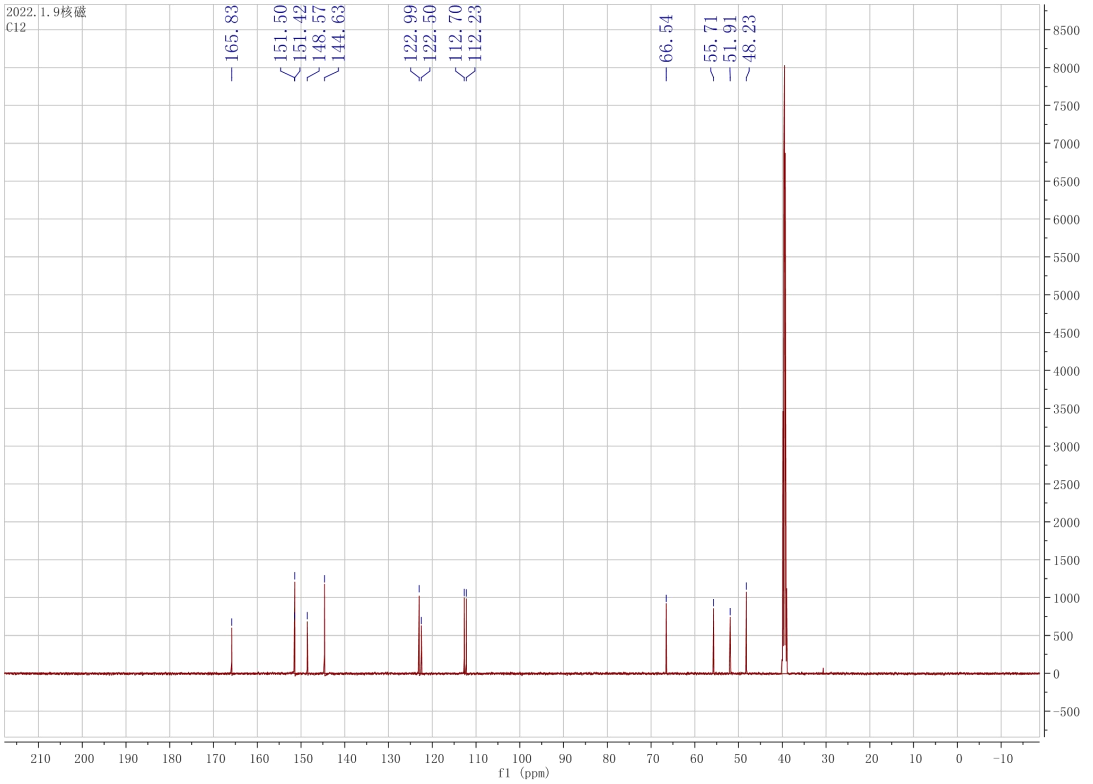
2a


PDY
R12
8.24
8.22
7.99
7.98
7.97
6.88
6.87
4.62
4.61
4.60
4.41
4.40
4.39
3.88
F (s) 7.99
E (d) 8.23
D (d) 6.87
G (d) 7.97
B (t) 4.61
A (t) 4.40
C (s) 3.88
2.03
0.98
1.35
2.10
2.01
2.00
2.98
f1 (ppm)

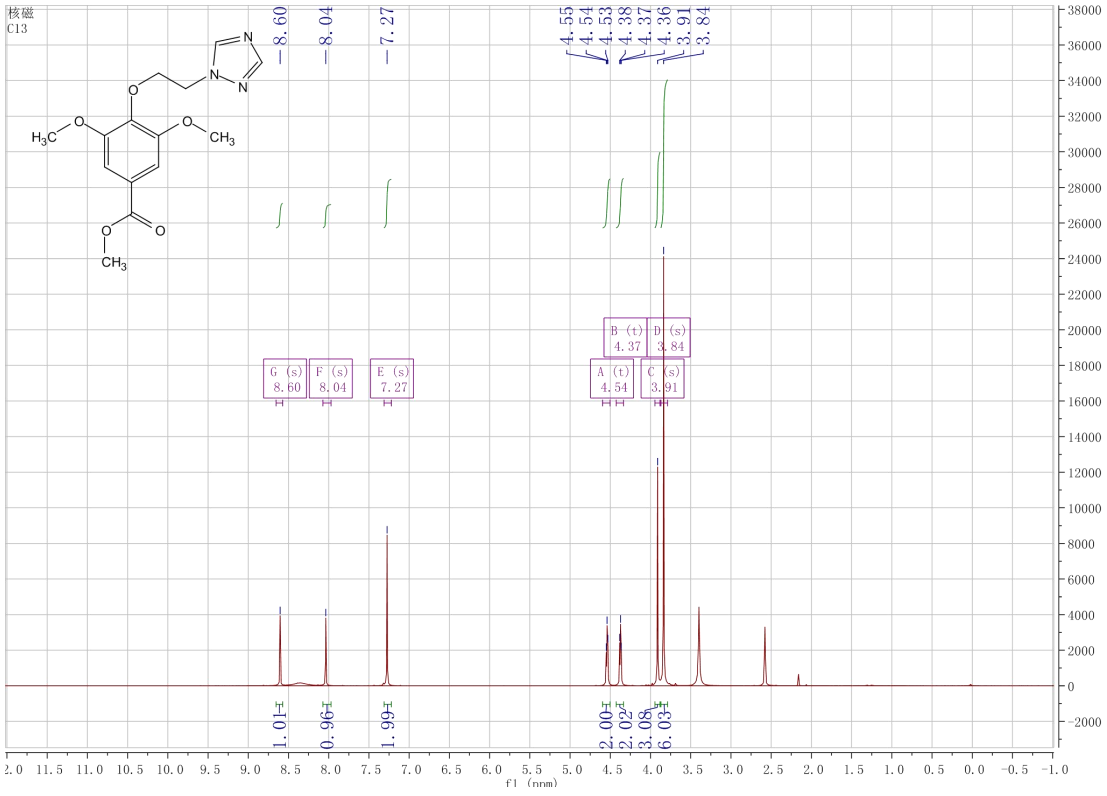

PDY
R12
166.82
161.43
152.14
143.96
131.69
123.58
114.06
65.64
51.95
49.07
f1 (ppm)

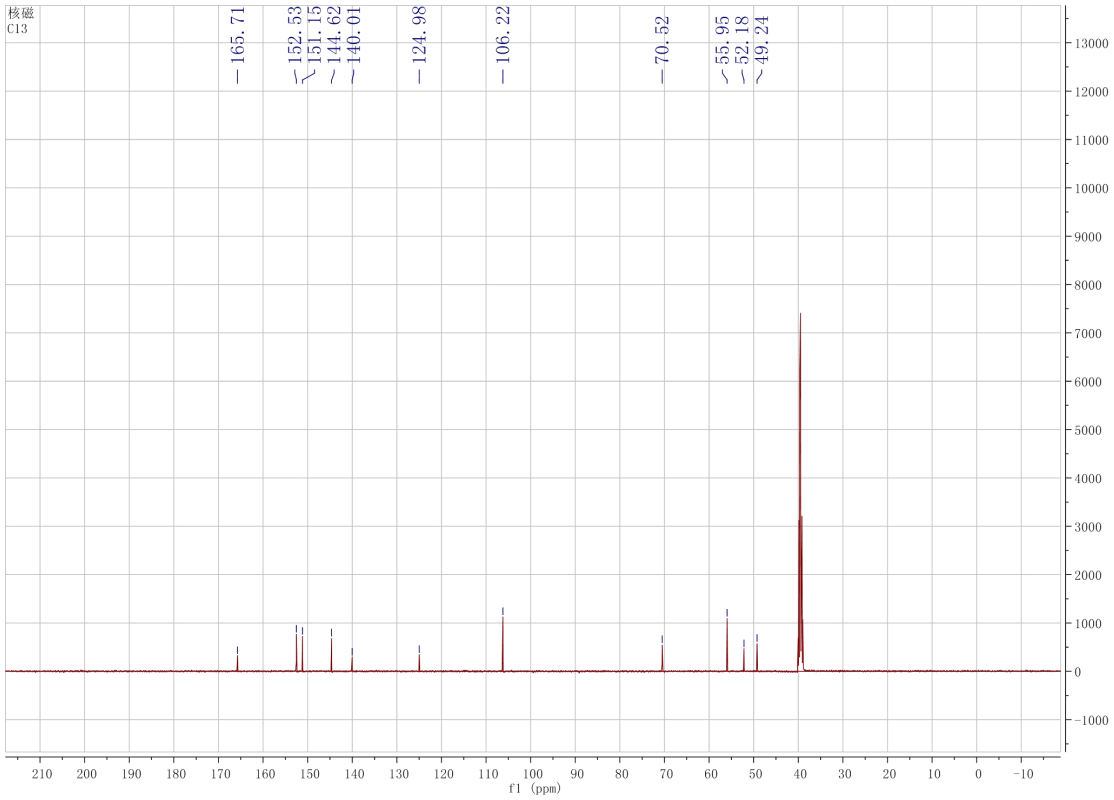
2b


2022.1.9核磁
C12
8.55
7.99
7.56
7.55
7.54
7.45
7.44
7.09
7.08
4.63
4.62
4.61
4.44
4.43
4.42
3.82
3.78
F (s) 7.99
I (d) 7.08
B (t) 4.62
D (s) 3.78
E (s) 8.55
G (dd) 7.55
A (t) 4.43
H (d) 7.44
C (s) 3.82
1.11
1.02
1.03
0.99
0.98
2.03
2.00
3.01
3.07
f1 (ppm)

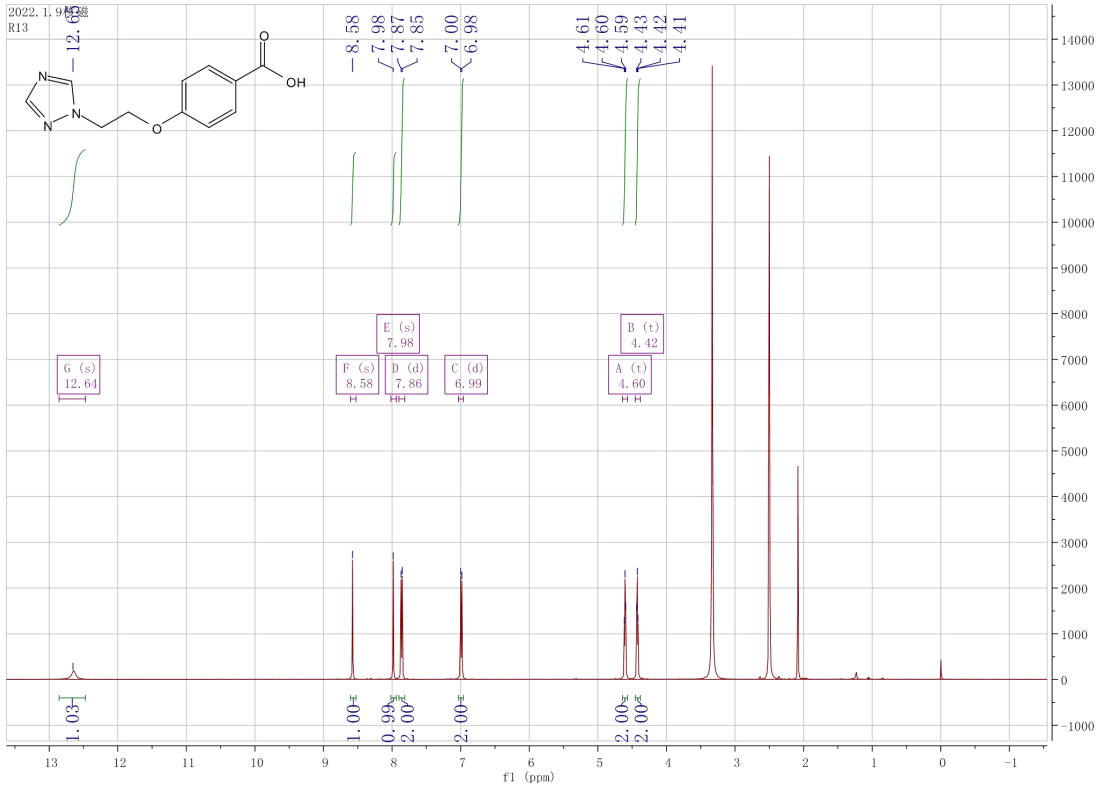

2022.1.9核磁
C12
165.83
151.50
151.42
148.57
144.63
122.99
122.50
112.70
112.23
66.54
55.71
51.91
48.23
f1 (ppm)

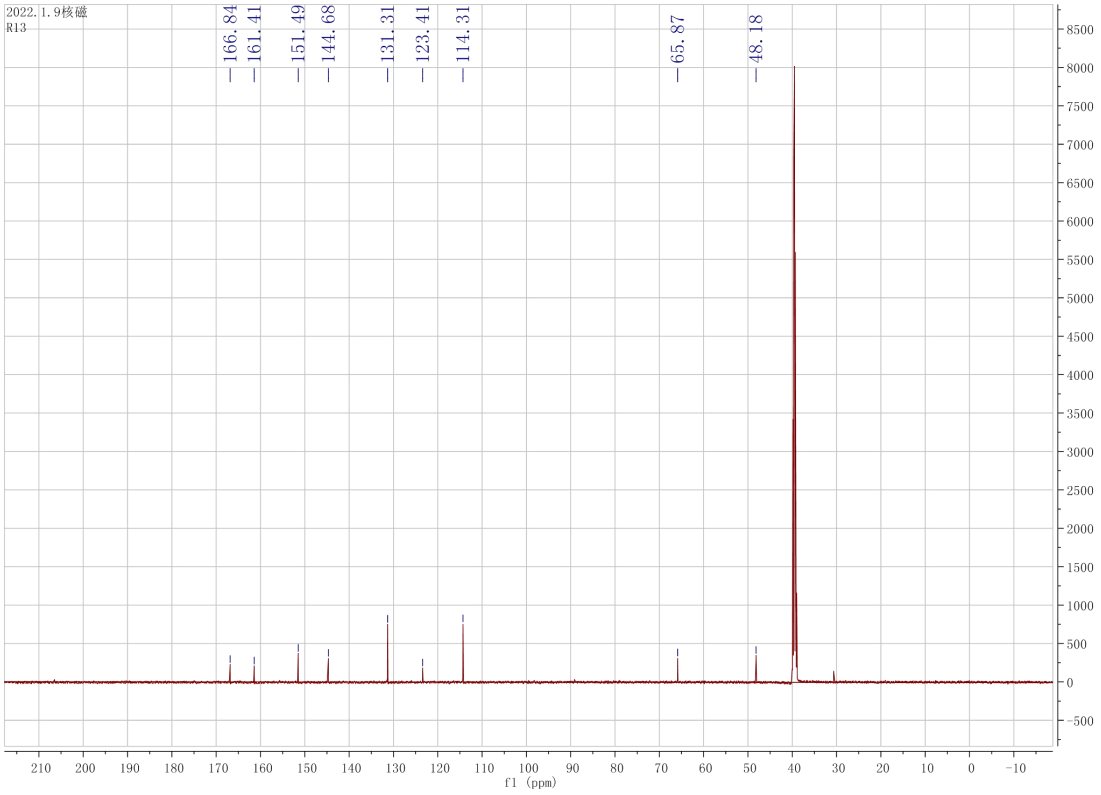
2c


核磁
C13
8.60
8.04
7.27
4.55
4.54
4.53
4.38
4.37
4.36
3.91
3.84
G (s) 8.60
F (s) 8.04
E (s) 7.27
B (t) 4.37
D (s) 3.84
A (t) 4.54
C (s) 3.91
1.01
0.96
1.99
2.00
2.02
3.08
6.03
f1 (ppm)

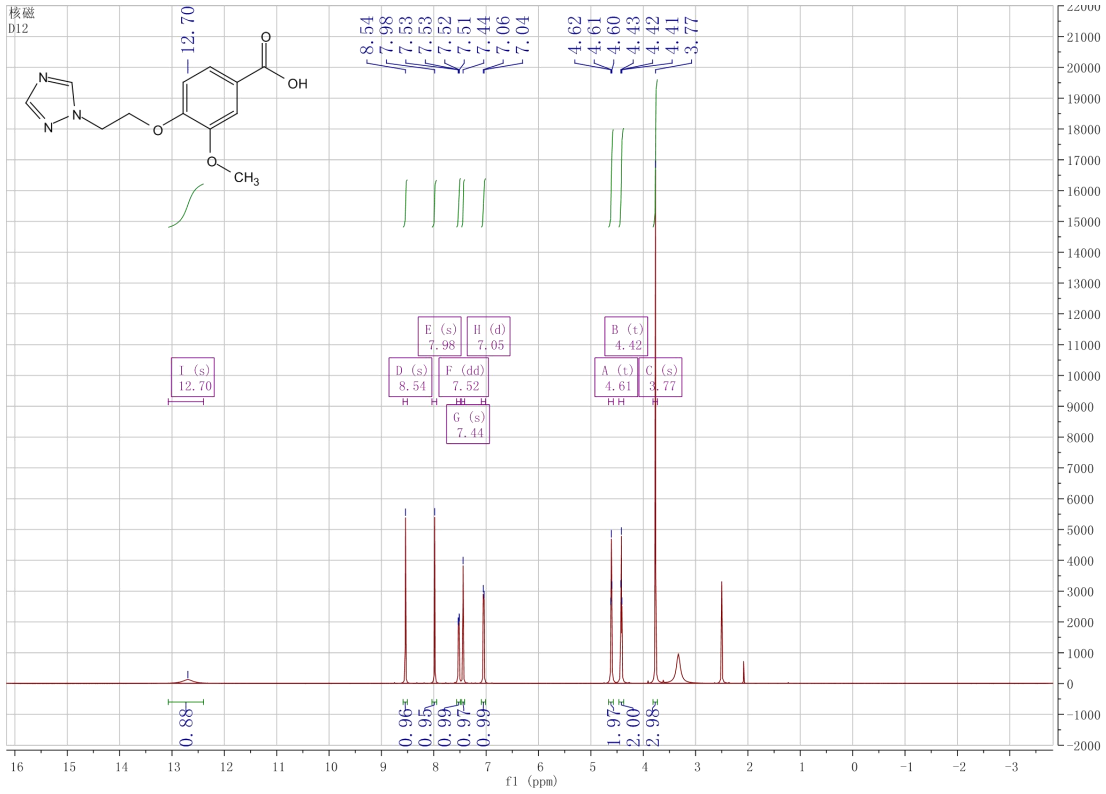

核磁
C13
165.71
152.53
151.15
144.62
140.01
124.98
106.22
70.52
55.95
52.18
49.24
f1 (ppm)

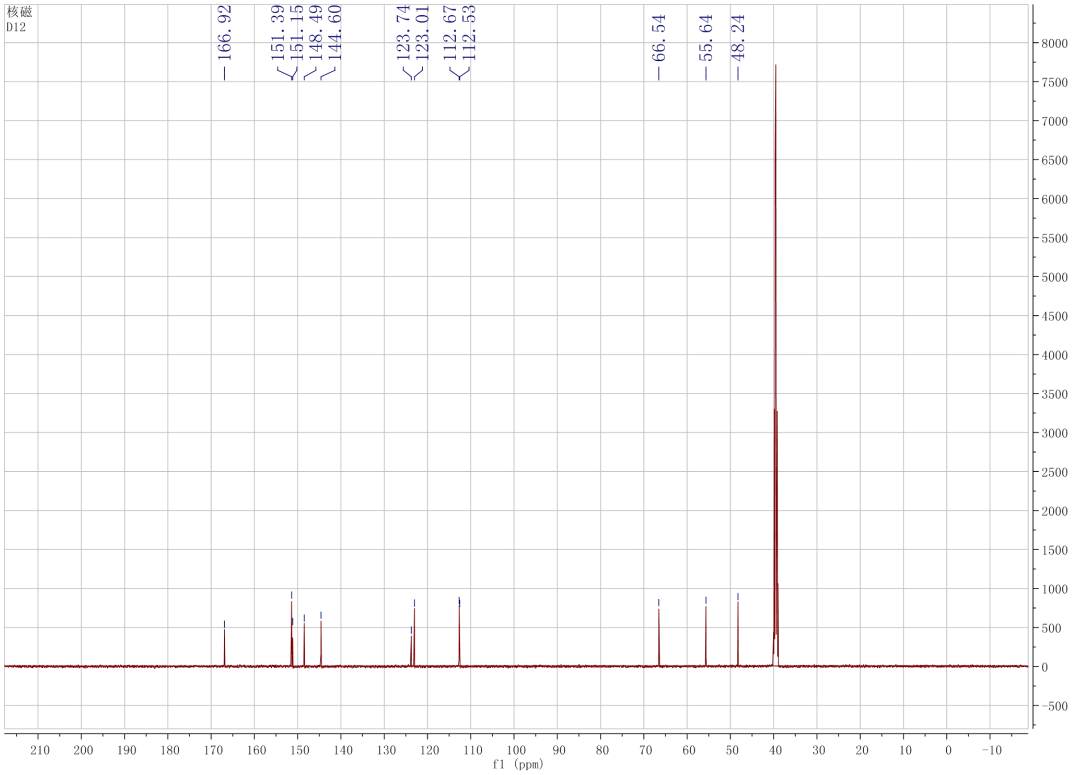
3a


2022.1.9核磁
R13
12.64
8.58
7.98
7.87
7.85
7.00
6.98
4.61
4.60
4.59
4.43
4.42
4.41
OH
O
N
N
N
G (s) 12.64
E (s) 7.98
F (s) 8.58
D (d) 7.86
C (d) 6.99
B (t) 4.42
A (t) 4.60
1.03
1.00
0.99
2.00
2.00
2.00
2.00
f1 (ppm)

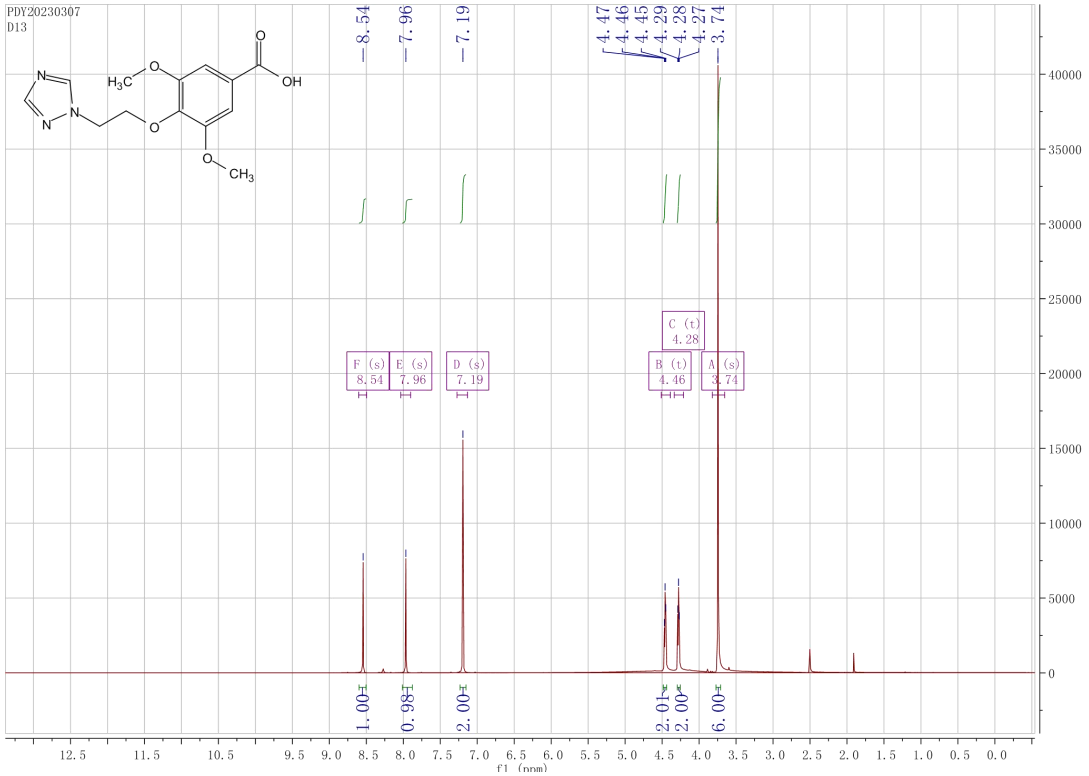

2022.1.9核磁
R13
166.84
161.41
151.49
144.68
131.31
123.41
114.31
65.87
48.18
f1 (ppm)

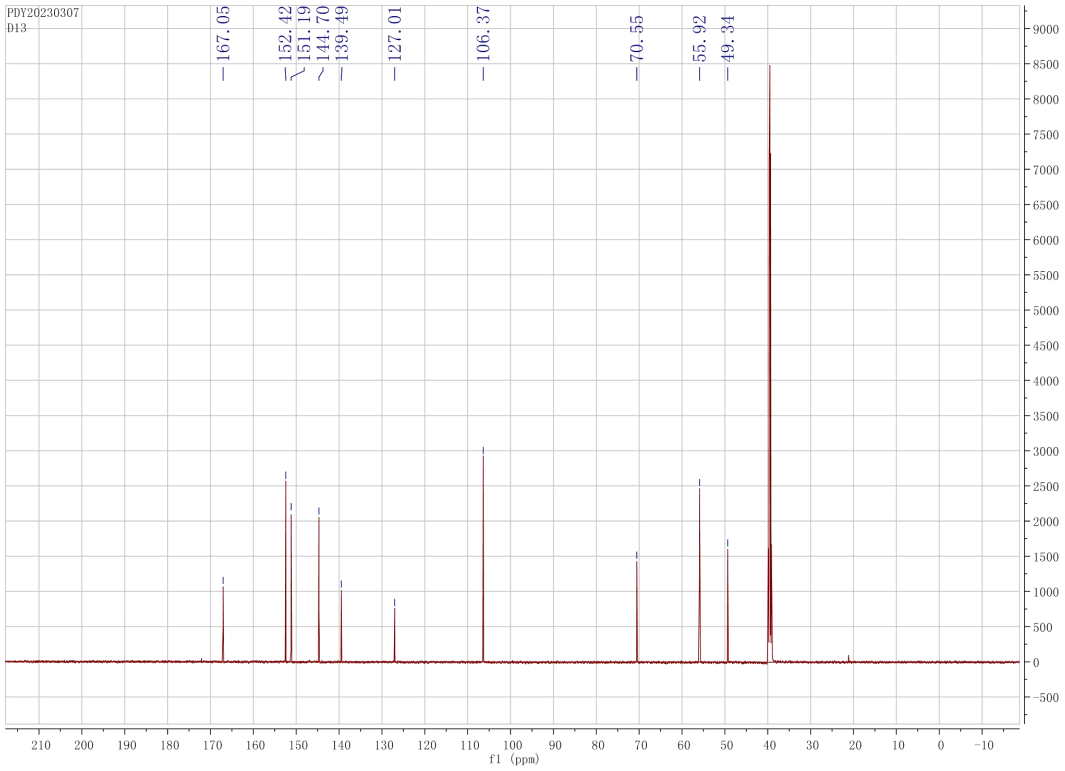
3b


核磁
D12
12.70
8.54
7.98
7.53
7.53
7.52
7.51
7.44
7.06
7.04
4.62
4.61
4.60
4.43
4.42
4.41
3.77
OH
O
N
N
N
O
O
CH3
I (s) 12.70
D (s) 8.54
E (s) 7.98
F (dd) 7.52
G (s) 7.44
H (d) 7.05
A (t) 4.61
B (t) 4.42
C (s) 3.77
0.88
0.96
0.95
0.99
0.97
0.99
1.97
2.00
2.98
f1 (ppm)


核磁
D12
166.92
151.39
151.15
148.49
144.60
123.74
123.01
112.67
112.53
66.54
55.64
48.24
f1 (ppm)

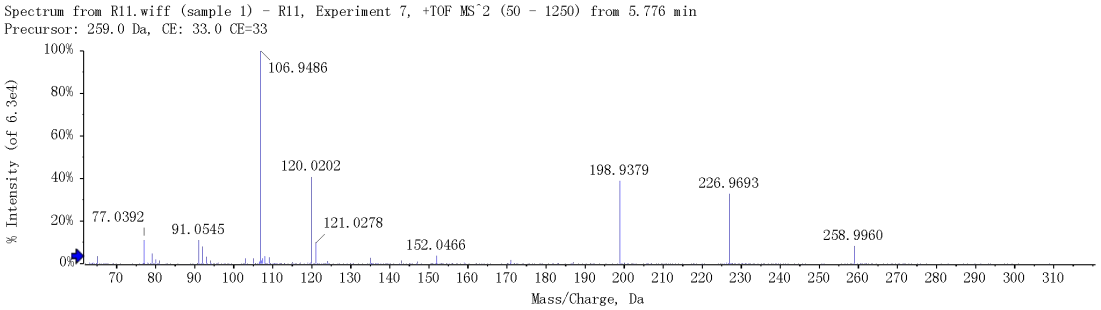
3c


PDY20230307
D13
8.54
7.96
7.19
4.47
4.46
4.45
4.29
4.28
4.27
3.74
F (s) 8.54
E (s) 7.96
D (s) 7.19
C (t) 4.28
B (t) 4.46
A (s) 3.74
1.00
0.98
2.00
2.01
2.00
6.00
f1 (ppm)

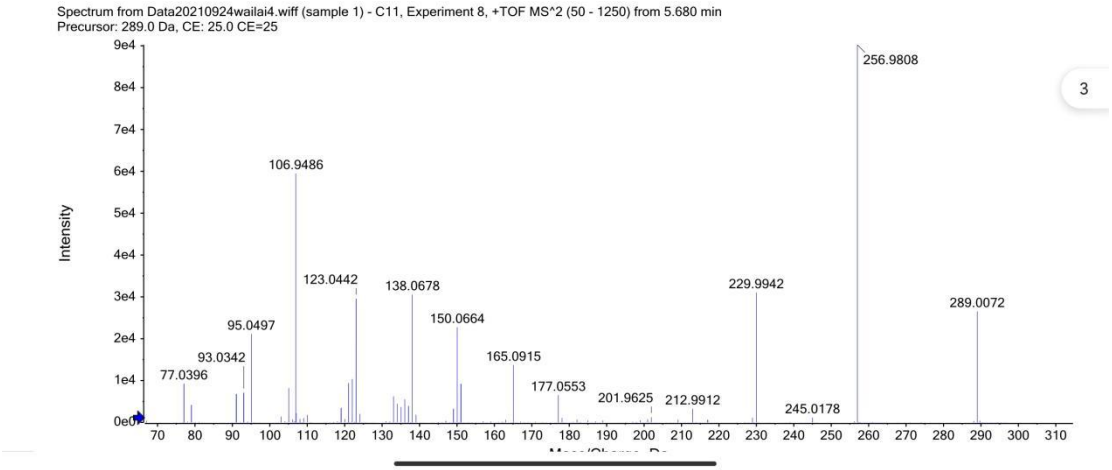

PDY20230307
D13
167.05
152.42
151.19
144.70
139.49
127.01
106.37
70.55
55.92
49.34
f1 (ppm)

HRMS

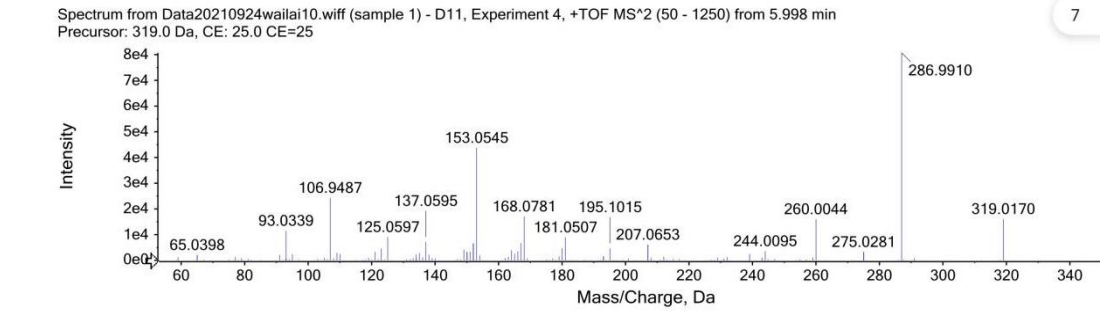
The mass spectrum of 1a:



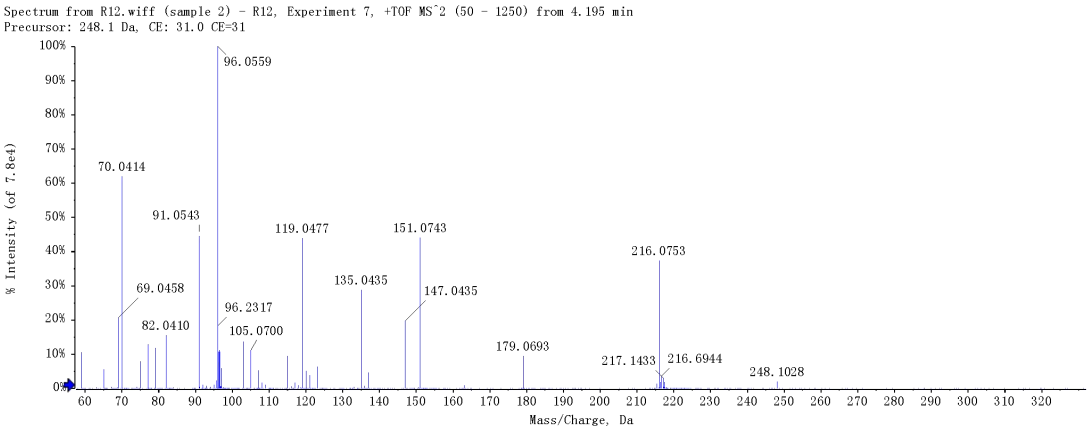

The mass spectrum of 1b:



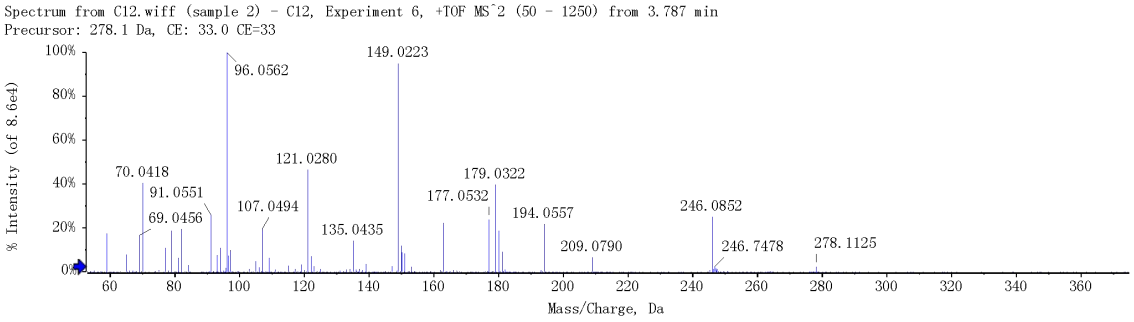

The mass spectrum of 1c:



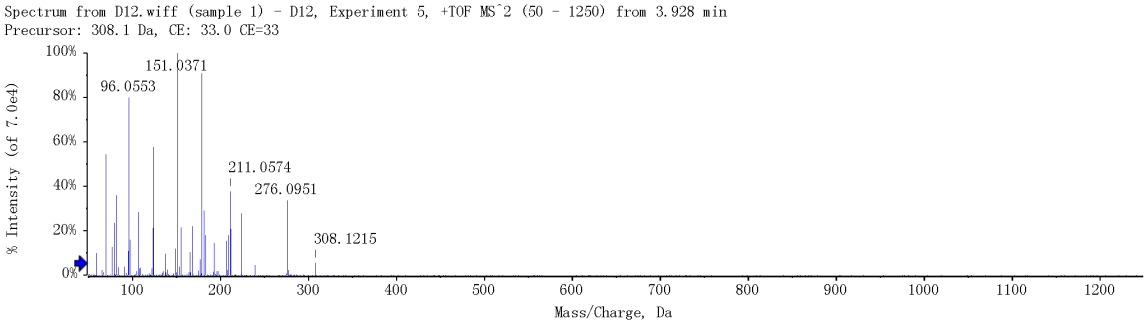

The mass spectrum of 2a:



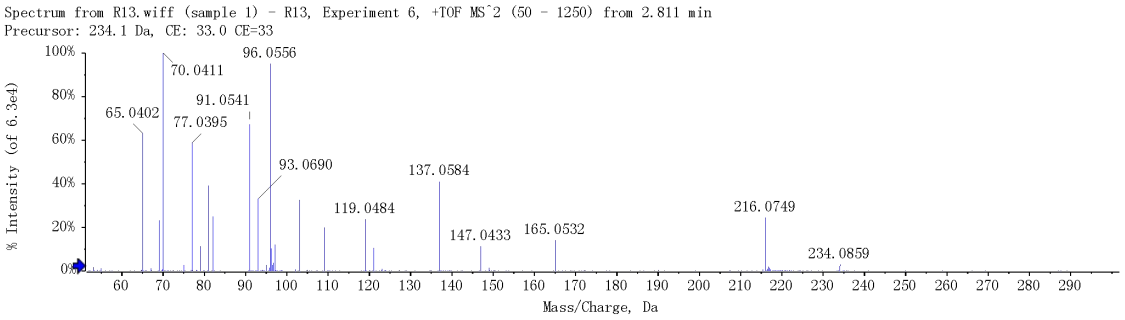

The mass spectrum of 2b:



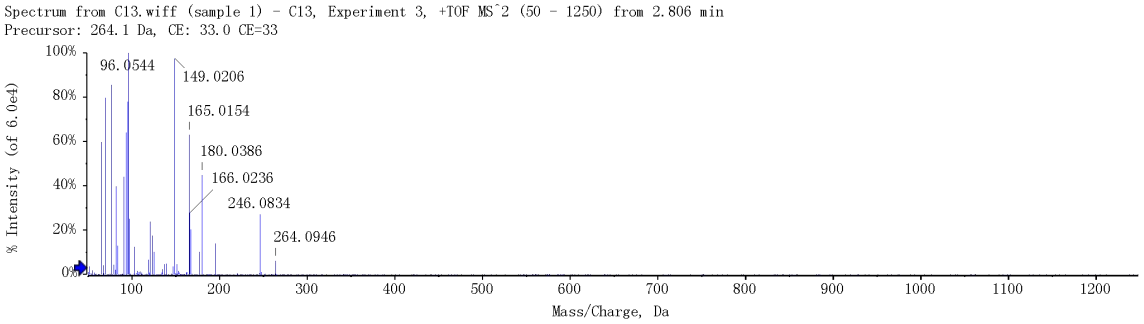

The mass spectrum of 2c:




The mass spectrum of 3a:




The mass spectrum of 3b:




## The mass spectrum of 3c:

