Electronic Supplementary Information (ESI)

Straightforward intra/intermolecular cyclization to AIE-active cyclic TPE: Selective discriminating for benzaldehyde and as temperature sensor

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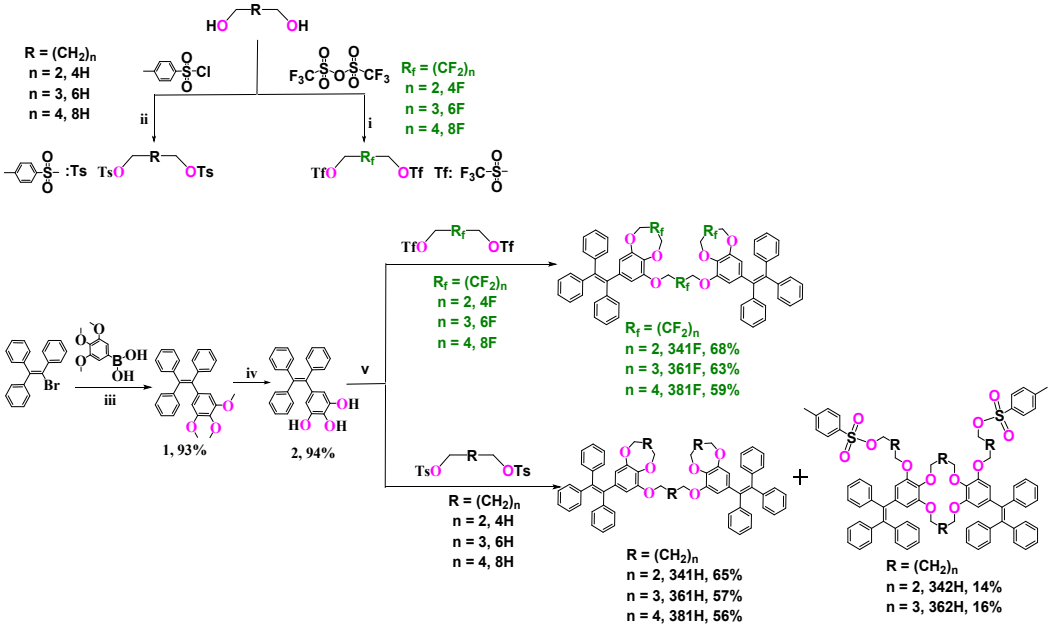
General experimental details and materials

Materials and Charaterization: All the reagents and solvents were commercially available and used as received. ^{1}H and ^{19}F were recorded on a 600 MHz nuclear magnetic resonance spectrometer operating at 376 MHz, chemical shifts were reported relative to Me_4Si for ^{1}H and CCl_3F for ^{19}F. The solvent was either $CDCl_3$ unless otherwise specified. Thermogravimetric analysis (TGA) measurements worked at a heating rate of 10 ºC min^{-1} with a Netzsch TG-209F3 (Germany) apparatus. Differential scaning calorimetry (DSC) was performed at a scan rate of 10 ºC min^{-1} on a Shimadzu TA-60WS (Japan) instrument. UV/Vis spectra were recorded with a Shimadzu UV-2700 (Japan) instrument. Fluorescence spectra were recorded with a Hitachi LTD spectrophotometer F-4600. Fluorescence quantum yields were determined with a Hamamatsu C11347 Quantaurus-QY absolute fluorescence quantum yield spectrometerFluorescence quantum yields were determined with a Hamamatsu C11347 Quantaurus-QY absolute fluorescence quantum yield spectrometer. Fluorescence lifetime measurements were executed by Edinburgh FLS920 spectrofluorometer. Steady-state photoluminescence spectra were obtained using Acton SP2750 spectrometer CCD (SPEC-10, Princeton) and local heating plant. X-ray diffraction (XRD) measurement was conducted on a Bruker D8 Advance X-ray diffractometer. Single crystal structures were collected on a Bruker Smart Apex II diffractometer with graphite-monochromated Mo Kα radiation (λ = 0.71073 Å) at 296(2) K. The data reduction, multi-scan absorption corrections, solution and refinement were performed with the programs APEX II1 and SHELXL-2014/72. Anisotropic thermal parameters were used to refine all non-H atoms. The hydrogen atoms for C-H were placed in idealized positions. The ground-state geometries were optimized by density functional theory (DFT) method with the B3LYP hybrid functional at the basis set level of 6-31G (d) in the gas state.

Synthesis and characterization

The polyfluoroalkyldiols, were reacted with trifluoromethanesulfonic anhydride to give trifluoromethanesulfonate esters,[1] **4F**, **6F** and **8F**. Alkyl methyl *p*-toluenesulfonate, **4H**, **6H** and **8H**, were prepared by the reaction of corresponding alkyldiols with *p*-toluenesulfonyl chloride. As depicted in **Scheme 1**, (2-(3,5-dimethoxyphenyl)ethene-1,1,2-triyl)tribenzene, **1**, was obtained by Suzuki cross-coupling reaction in 93% yield, whereafter, it was transformed into the corresponding phenol **2** in 94% yield. Two kinds of polyfluoroalkyl or alkyl linked cyclic TPE with two TPE cores (**341F**, **361F**, **381F**, **341H**, **342H**, **361H**, **362H** and **381H**) were simultaneously obtained in 14%-68% yield *via* the reaction of **2** with trifluoromethanesulfonate esters (**4F**, **6F** and **8F**)[2] or alkyl methyl p-toluenesulfonate (**4H**, **6H** and **8H**)[2] respectively.



i: pyridine, DCM, 0 °C~rt, 12 h; ii: triethylamine, DCM, 0 °C~rt, 12 h; iii: 0.01% mol $Pd(PPh_3)_4$, K_2CO_3, TBAB, CH_2ClCH_2Cl, 92 °C, 12 h; iv: BBr_3, DCM, 0 °C, 10 h; v: K_2CO_3, CH_3CN, 92 °C, 48 h.

Scheme S1. Synthesis of novel TPE-based cyclic TPE.

Trifluoromethanesulfonic anhydride (12.5 mL, 74.04 mmol) was reacted respectively

with 2,2,3,3-tetrafluoro-1,4-butanediol (4.0000 g, 24.68 mmol), 2,2,3,3,4,4-hexafluoro-1,5-pentanediol (5.2386 g, 24.68 mmol) and 2,2,3,3,4,4,5,5-octafluoro-1,6-hexanediol (6.4667 g, 24.68 mmol) in dichloromethane (75 mL) and pyridine (5 mL) to get the corresponding compounds, 2,2,3,3-tetrafluorobutane-1,4-diyl bis(trifluoromethanesulfonate), **4F**, 2,2,3,3,4,4-hexafluoropentane-1,5-diyl bis(trifluoromethanesulfonate), **6F** and 2,2,3,3,4,4,5,5-octafluorohexane-1,6-diyl bis(trifluoromethanesulfonate), **8F**. Then the mixture was stirred at 0 ºC~rt for 12 h under nitrogen. The solution was added 50 mL dichloromethane and washed with water, brine and dried with anhydrous sodium sulfate. The solvent was removed under vacuum and the crude product was purified by column chromatography (petroleum/EtOAc = 3/1) to give the target products.

P-toluenesulfonyl chloride (11.4390 g, 60 mmol) was reacted respectively with 1,4-butanediol (1.84 mL, 20 mmol), 1,5-pentanediol (2.08 mL, 20 mmol) and 1,6-hexanediol (2.3634g, 20 mmol) in dichloromethane (100 mL) and triethylamine (15 mL) to give butane-1,4-diyl bis(4-methylbenzenesulfonate), **4H**, pentane-1,5-diyl bis(4-methylbenzenesulfonate), **6H** and hexane-1,6-diyl bis(4-methylbenzenesulfonate), **8H**. Then the mixture was stirred at 0 ºC~rt for 12 h. The solution was added 25 mL dichloromethane and washed with water, brine and dried with anhydrous sodium sulfate. The solvent was removed under vacuum and the crude product was purified by column chromatography (petroleum/EtOAc = 5/1) to give the target products.

2,2,3,3-tetrafluorobutane-1,4-diyl bis(trifluoromethanesulfonate) (**4F**): ^{1}H NMR (600 MHz, $CDCl_3$) δ (ppm): 5.06–4.60 (m, 4H). ^{19}F NMR (565 MHz, $CDCl_3$) δ (ppm): -73.96 (s, 4F), -120.37–120.47 (m, 4F).

2,2,3,3,4,4-hexafluoropentane-1,5-diyl bis(trifluoromethanesulfonate) (**6F**): ^{1}H NMR (600 MHz, DMSO-d_6) δ (ppm): 4.77 (t, J = 12.7 Hz, 4H). ^{19}F NMR (565 MHz, DMSO-d_6) δ (ppm): -74.67 (s, 6F), -120.29 (s, 4F), -124.99 (s, 2F).

2,2,3,3,4,4,5,5-octafluorohexane-1,6-diyl bis(trifluoromethanesulfonate) (**8F**): ^{1}H NMR (600 MHz, $CDCl_3$) δ (ppm): 4.83 (t, J = 12.1 Hz, 4H). ^{19}F NMR (565 MHz, $CDCl_3$) δ (ppm): -73.95 (s, 4F), -119.74 (s, 4F), -122.97 (s, 4F).

Butane-1,4-diyl bis(4-methylbenzenesulfonate) (**4H**): ^{1}H NMR (600 MHz, $CDCl_3$) δ (ppm): 7.78 (d, *J* = 8.2 Hz, 4H), 7.37 (d, *J* = 8.1 Hz, 4H), 4.01 (t, *J* = 5.3 Hz, 4H), 2.48 (s, 6H), 1.77 – 1.69 (m, 4H).

Pentane-1,5-diyl bis(4-methylbenzenesulfonate) (**6H**): ^{1}H NMR (600 MHz, $CDCl_3$) δ (ppm): 7.79 (d, *J* = 8.3 Hz, 4H), 7.37 (d, *J* = 8.0 Hz, 4H), 3.99 (t, *J* = 6.3 Hz, 4H), 2.48 (s, 6H), 1.65 – 1.60 (m, 4H), 1.40 – 1.36 (m, 2H).

Hexane-1,6-diyl bis(4-methylbenzenesulfonate) (**8H**): ^{1}H NMR (400 MHz, DMSO-d_6) δ (ppm): 7.76 (d, *J* = 8.2 Hz, 4H), 7.46 (d, *J* = 7.9 Hz, 4H), 3.94 (t, *J* = 6.2 Hz, 4H), 2.40 (s, 6H), 1.46 (s, 4H), 1.12 (d, *J* = 19.7 Hz, 4H).

Synthesis of (2-(3,4,5-trimethoxyphenyl)ethene-1,1,2-triyl)tribenzene **(1)**

White solid, Yield: 93%. bromotriphenylethylene (3.3524 g, 10 mmol), 3,4,5-trimethylphenylboronic acid (2.6952 g, 15 mmol), tetrabutylammonium bromide (0.3224 g, 1 mmol) were dissolved in CH_2ClCH_2Cl (60 mL), adding K_2CO_3 (2.764 g, 20 mmol) dissolved in water (18 mL) and $Pd(PPh_3)_4$ (0.1155 g, 0.1 mmol) under nitrogen. The solution was stirred for 12 h at 92 ºC. After removing of the solvent under vacuum, the residue was diluted with CH_2Cl_2 (100 mL), washed with water and dried with anhydrous sodium sulfate. The crude product was purified by column chromatography (PE/EtOAc = 15/1) to obtain the product **1** (3.9263 g, 93%) , white solid. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.18–7.00 (m, 15H), 6.24 (s, 2H), 3.89 (d, *J* = 1.3 Hz, 3H), 3.83 (s, 3H), 3.52 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 152.35, 144.20, 143.68, 143.21, 140.90, 140.83, 138.79, 136.82, 131.42, 131.32, 130.96, 127.85, 127.67, 127.64, 126.59, 126.45, 126.42, 109.17, 60.89, 55.90. HRMS (ESI) m/z: $C_{29}H_{26}O_3$ for $[M+H^+]$ calculated 423.1952, found 423.1955.

Synthesis of 5-(1,2,2-triphenylvinyl)benzene-1,2,3-triol **(2)**

White solid, Yield: 94 %. The compound **1** (10 mmol) was dissolved in 100 mL dichloromethane at 0 ºC and then BBr_3 (6.01 mL, 10 mmol/mL) was added dropwise under nitrogen without water. The solution was stirred for 10 h. Water was added dropwise to quench the reaction. Dilute the solution with dichloromethane, washed with water and dried with anhydrous sodium sulfate. The crude product was purified by column chromatography (PE/EtOAc = 3/1) to get the product **2** (3.5721g, 94%) ,

white solid. ^{1}H NMR (600 MHz, DMSO) δ 8.60 (s, 2H), 8.03 (s, 1H), 7.20–6.90 (m, 15H), 5.95 (s, 2H), ^{13}C NMR (151 MHz, DMSO) δ 145.86, 144.32, 144.25, 141.59, 139.13, 134.03, 132.56, 131.30, 131.11, 130.96, 128.19, 126.70, 126.64, 110.44. HRMS (ESI) m/z: $C_{26}H_{20}O_3$ for [M+H$^+$] calculated 381.1483, found 381.1485.

Synthesis of **341F**, **361F**, **381F**, **341H**, **342H**, **361H**, **362H** and **381H**: 5-(1,2,2-triphenylvinyl)benzene-1,2,3-triol **(2)** (0.3801 g, 1 mmol) was reacted with the corresponding alkyl chain in dry acetonitrile (30 mL) and K_2CO_3 (0.2764 g, 6 mmol) to give **341F**, **361F**, **381F**, **341H**, **342H, 361H, 362H** and **381H**. Then the mixture was stirred at 92 ºC for 48 h under nitrogen. The solution was added 50 mL dichloromethane and washed with water, brine and dried with anhydrous sodium sulfate. The solvent was removed by vacuum and the crude product was purified by column chromatography (petroleum/EtOAc = 20/1) to give the target products.

10,10'-((2,2,3,3-tetrafluorobutane-1,4-diyl)bis(oxy))bis(3,3,4,4-tetrafluoro-8-(1,2,2-triphenylvinyl)-2,3,4,5-tetrahydrobenzo[*b*][1,4]dioxocine) (**341F**): White solid, m.p: 204 ℃, yield: 68%. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.21–7.09 (m, 18H), 7.06–7.00 (m, 12H), 6.46 (t, *J* = 2.7 Hz, 2H), 6.38 (t, *J* = 2.8 Hz, 2H), 4.40–4.33 (m, 8H), 4.04 (t, *J* = 13.0 Hz, 4H). ^{19}F NMR (565 MHz, $CDCl_3$) δ -120.15 (s, 4F), -120.62 (s, 4F), -121.42 (s, 4F). ^{13}C NMR (151 MHz, $CDCl_3$) δ 149.90, 143.54, 142.96, 142.43, 142.16, 140.82, 139.23, 137.39, 131.23, 131.17, 131.03, 128.04, 127.94, 127.76, 126.94, 126.86, 126.79, 118.78, 116.71, 115.02, 114.03, 70.38, 70.19, 66.36. HRMS (ESI) m/z: $C_{64}H_{46}F_{12}O_6$ for [M+Na$^+$] calculated 1161.2995, found 1161.2986.

11,11'-((2,2,3,3,4,4-hexafluoropentane-1,5-diyl)bis(oxy))bis(3,3,4,4,5,5-hexafluoro-9-(1,2,2-triphenylvinyl)-3,4,5,6-tetrahydro-2*H*-benzo[*b*][1,4]dioxonine) (**361F**): White solid, m.p: 143 ℃, yield: 63%. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.22–7.13 (m, 18H), 7.09–7.03 (m, 12H), 6.46 (d, *J* = 1.4 Hz, 2H), 6.42 (s, 2H), 4.48 (t, *J* = 12.0 Hz, 4H), 4.26 (t, *J* = 11.4 Hz, 4H), 4.08 (t, *J* = 12.5 Hz, 4H). ^{19}F NMR (565 MHz, $CDCl_3$) δ -114.47 (s, 3F), -116.37 (s, 3F), -118.28 (s, 3F), -119.67 (s, 3F), -120.34 (s, 3F), -123.50 (s, 3F). ^{13}C NMR (151 MHz, $CDCl_3$) δ 150.45, 149.89, 143.66, 142.83, 142.50, 142.23, 141.08, 139.12, 137.45, 131.27, 131.15, 131.04, 128.14, 128.03, 127.82, 127.11, 126.98, 126.91, 117.20, 116.47, 114.76, 114.29, 112.56, 71.05, 69.91, 66.48.

HRMS (ESI) m/z: $C_{67}H_{46}F_{18}O_6$ for [M+NH_4^+] calculated 1306.3351, found 1307.3367.

12,12'-((2,2,3,3,4,4,5,5-octafluorohexane-1,6-diyl)bis(oxy))bis(3,3,4,4,5,5,6,6-octafluoro-10-(1,2,2-triphenylvinyl)-2,3,4,5,6,7-hexahydrobenzo[*b*][1,4]dioxecine) (**381F**): White solid, m.p: 81 ℃, yield: 59%. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.23–7.02 (m, 30H), 6.48 (d, *J* = 1.8 Hz, 2H), 6.38 (d, *J* = 1.7 Hz, 2H), 4.65 (t, *J* = 11.5 Hz, 4H), 4.45 (t, *J* = 11.0 Hz, 4H), 4.02 (t, *J* = 12.4 Hz, 4H). ^{19}F NMR (565 MHz, $CDCl_3$) δ -116.44 (s, 6F), -117.45 (s, 6F), -119.98 (s, 6F), -125.29 (s, 6F). ^{13}C NMR (151 MHz, $CDCl_3$) δ 149.82, 149.69, 143.59, 142.86, 142.32, 140.93, 139.17, 137.18, 131.22, 131.12, 131.01, 128.05, 127.98, 127.76, 127.00, 126.91, 126.83, 118.34, 117.12, 116.45, 115.41, 114.75, 113.16, 71.49, 70.04, 66.15. HRMS (ESI) m/z: $C_{70}H_{46}F_{24}O_6$ for [M+NH_4^+] calculated 1456.3249, found 1456.3263.

1,4-bis((9-(1,2,2-triphenylvinyl)-2,3,4,5-tetrahydrobenzo[*b*][1,4]dioxocin-7-yl)oxy)butane (**341H**): White solid, m.p: 241 ℃, yield: 65%. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.04–6.90 (m, 30H), 6.19 (d, *J* = 1.9 Hz, 2H), 6.17 (d, *J* = 1.9 Hz, 2H), 4.12 (s, 4H), 4.03 (s, 4H), 3.51 (s, 4H), 1.72 (s, 8H), 1.57 (s, 4H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 151.43, 150.81, 144.14, 143.65, 143.20, 140.65, 140.59, 138.49, 137.70, 131.32, 131.07, 127.72, 127.62, 126.49, 126.35, 117.66, 111.61, 72.81, 72.66, 68.35, 27.63, 26.64, 25.62. HRMS (ESI) m/z: $C_{64}H_{58}O_6$ for [M+H^+] calculated 923.4306, found 923.4298.

((3,12-bis(1,2,2-triphenylvinyl)-6,7,8,9,16,17,18,19-octahydrodibenzo[*b*,*j*][1,4,9,12]tetraoxacyclohexadecine-1,14-diyl)bis(oxy))bis(butane-4,1-diyl) bis(4-methylbenzenesulfonate) (**342H**): White solid, m.p: 91 ℃, yield: 14%. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.83–7.80 (m, 4H), 7.36 (d, *J* = 8.3 Hz, 4H), 7.13–7.01 (m, 30H), 6.29 (d, *J* = 2.1 Hz, 2H), 6.22 (d, *J* = 2.1 Hz, 2H), 4.18 (s, 4H), 4.13 (s, 4H), 4.09–4.06 (m, 4H), 3.58–3.55 (m, 4H), 2.47 (s, 6H), 1.81 (s, 8H), 1.77–1.74 (m, 4H), 1.64–1.61 (m, 4H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 151.17, 150.82, 144.75, 144.15, 143.60, 143.15, 140.65, 140.56, 138.50, 137.79, 133.20, 131.30, 131.08, 129.87, 127.90, 127.63, 126.52, 126.39, 117.86, 111.86, 72.79, 70.27, 67.91, 27.60, 26.61, 25.79, 25.06, 21.67. HRMS (ESI) m/z: $C_{82}H_{80}O_{12}S_2$ for [M+Na^+] calculated 1343.4983, found 1343.4966.

1,5-bis((10-(1,2,2-triphenylvinyl)-3,4,5,6-tetrahydro-2*H*-benzo[*b*][1,4]dioxonin-8-yl)oxy)pentane (**361H**): White solid, m.p: 165 ℃, yield: 57%. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.14–7.01 (m, 30H), 6.29 (d, *J* = 2.0 Hz, 2H), 6.26 (d, *J* = 2.0 Hz, 2H), 4.14 (dd, *J* = 11.1, 5.8 Hz, 8H), 3.57 (t, *J* = 6.6 Hz, 4H), 1.82–1.71 (m, 12H), 1.64–1.55 (m, 6H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 151.93, 151.92, 144.18, 143.71, 143.26, 140.73, 140.54, 139.80, 138.40, 131.36, 131.08, 127.74, 127.61, 126.46, 126.33, 117.68, 111.73, 75.07, 73.29, 68.55, 29.45, 29.29, 28.67, 24.30, 22.40. HRMS (ESI) m/z: $C_{67}H_{64}O_6$ for [M+H$^+$] calculated 965.4776, found 965.4767.

((3,13-bis(1,2,2-triphenylvinyl)-7,8,9,10,18,19,20,21-octahydro-6*H*,17*H*-dibenzo[*b*,*k*][1,4,10,13]tetraoxacyclooctadecine-1,15-diyl)bis(oxy))bis(pentane-5,1-diyl) bis(4-methylbenzenesulfonate) (**362H**): White solid, m.p: 156 ℃, yield: 16%. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.81 (d, *J* = 8.3 Hz, 4H), 7.36 (d, *J* = 8.0 Hz, 4H), 7.14–7.01 (m, 30H), 6.29 (d, *J* = 2.0 Hz, 2H), 6.24 (d, *J* = 2.0 Hz, 2H), 4.15–4.10 (m, 8H), 4.04 (t, *J* = 6.5 Hz, 4H), 3.54 (t, *J* = 6.4 Hz, 4H), 2.46 (s, 6H), 1.83–1.76 (m, 8H), 1.76–1.72 (m, 4H), 1.66 (dd, *J* = 14.8, 6.9 Hz, 4H), 1.55 (dd, *J* = 14.6, 6.8 Hz, 4H), 1.44–1.37 (m, 4H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 151.94, 151.74, 144.72, 144.16, 143.68, 143.23, 140.66, 140.57, 139.82, 138.40, 133.20, 131.34, 131.08, 129.86, 127.89, 127.73, 127.61, 126.47, 126.32, 117.79, 111.77, 75.08, 73.32, 70.38, 68.26, 29.41, 29.25, 28.51, 28.28, 24.28, 21.98, 21.66. HRMS (MALDI) m/z: $C_{86}H_{88}O_{812}S_2$ for [M+NH_4^+] calculated 1394.6061, found 1394.6057.

1,6-bis((11-(1,2,2-triphenylvinyl)-2,3,4,5,6,7-hexahydrobenzo[*b*][1,4]dioxecin-9-yl)oxy)hexane (**381H**): White solid, m.p: 163 ℃, yield: 56%. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.10–7.00 (m, 30H), 6.32 (d, *J* = 1.4 Hz, 2H), 6.23 (s, 2H), 4.04–4.00 (m, 4H), 3.89–3.87 (m, 4H), 3.60 (t, *J* = 6.5 Hz, 4H), 1.81 (d, *J* = 5.7 Hz, 4H), 1.57 (d, *J* = 22.8 Hz, 8H), 1.46–1.39 (m, 8H), 1.33 (s, 4H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 152.71, 152.52, 144.26, 143.67, 143.11, 140.92, 140.61, 138.98, 137.83, 131.37, 131.05, 127.72, 127.59, 126.52, 126.37, 114.90, 111.53, 72.20, 71.87, 68.67, 29.02, 26.50, 26.38, 25.72, 25.19, 23.03. HRMS (ESI) m/z: $C_{70}H_{70}O_6$ for [M+Na^+] calculated 1029.5065, found 1029.5052.

Absoption and photoluminescence (PL) spectra of cyclic TPE in tetrahydrofuran/water mixtures with different water fractions

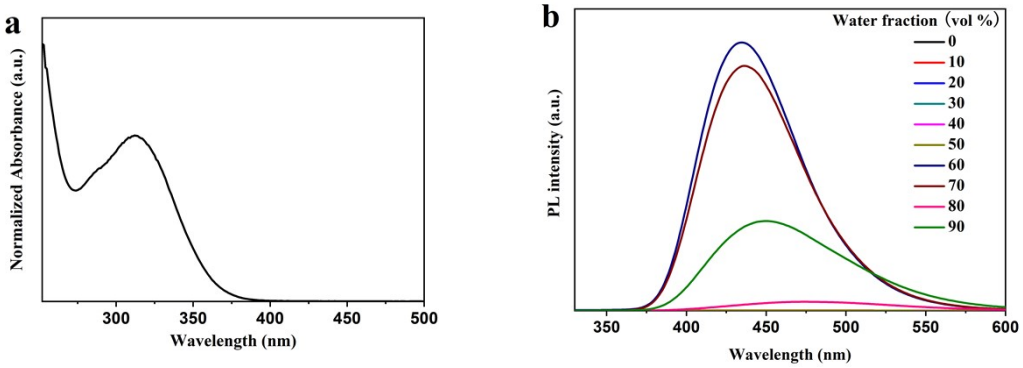


Fig. S1 (a) Absorption spectrum of **341F** in THF solution and (b) PL intensity spectra of **341F** in tetrahydrofuran/water mixtures with different water fractions.

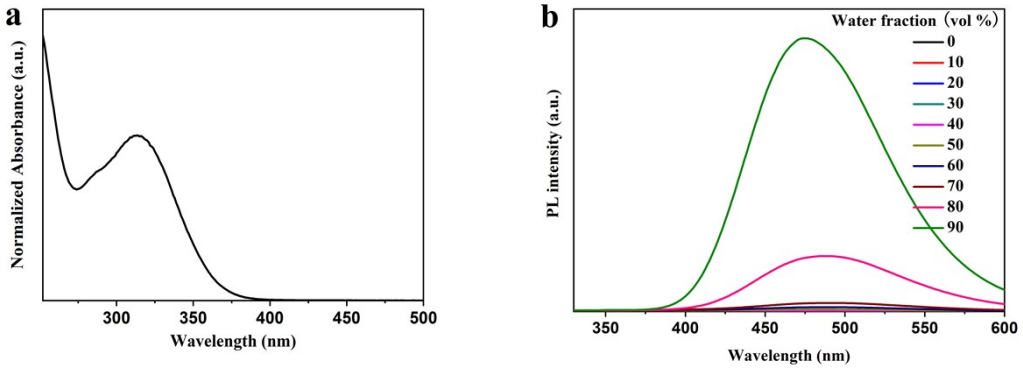


Fig. S2 (a) Absorption spectrum of **361F** in THF solution and (b) PL intensity spectra of **361F** in tetrahydrofuran/water mixtures with different water fractions.

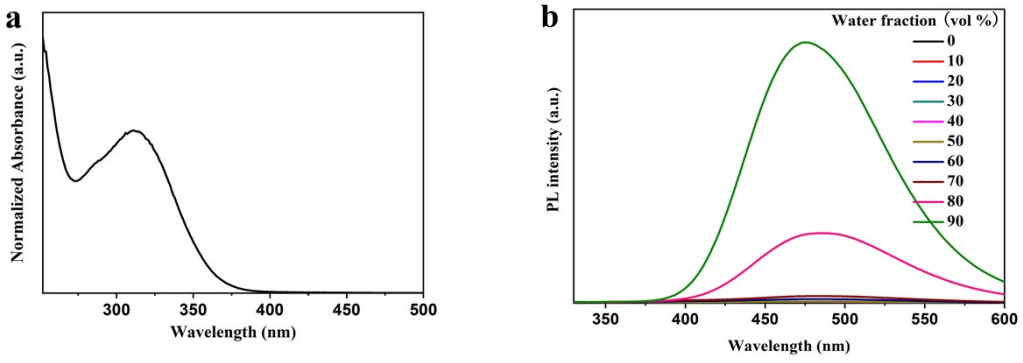


Fig. S3 (a) Absorption spectrum of **381F** in THF solution and (b) PL intensity spectra of **381F** in tetrahydrofuran/water mixtures with different water fractions.

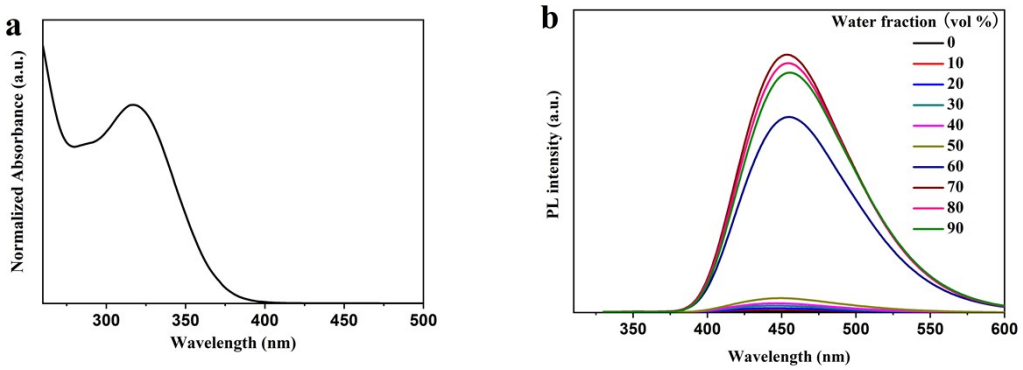


Fig. S4 (a) Absorption spectrum of **341H** in THF solution and (b) PL intensity spectra of **341H** in tetrahydrofuran/water mixtures with different water fractions.

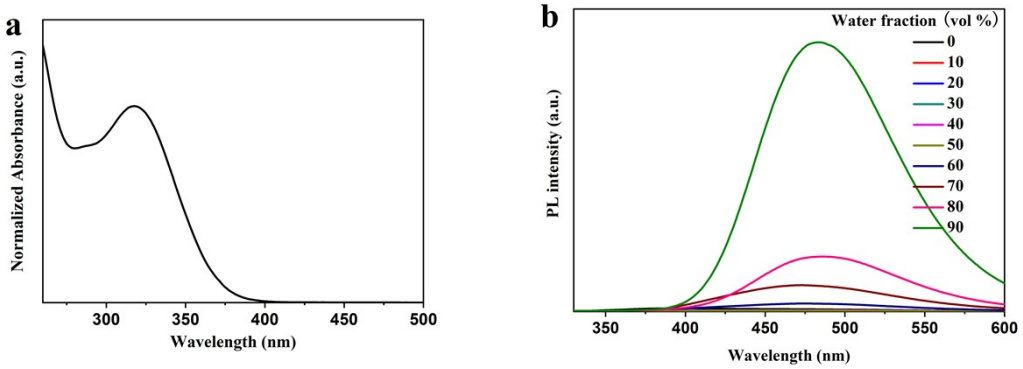


Fig. S5 (a) Absorption spectrum of **361H** in THF solution and (b) PL intensity spectra of **361H** in tetrahydrofuran/water mixtures with different water fractions.

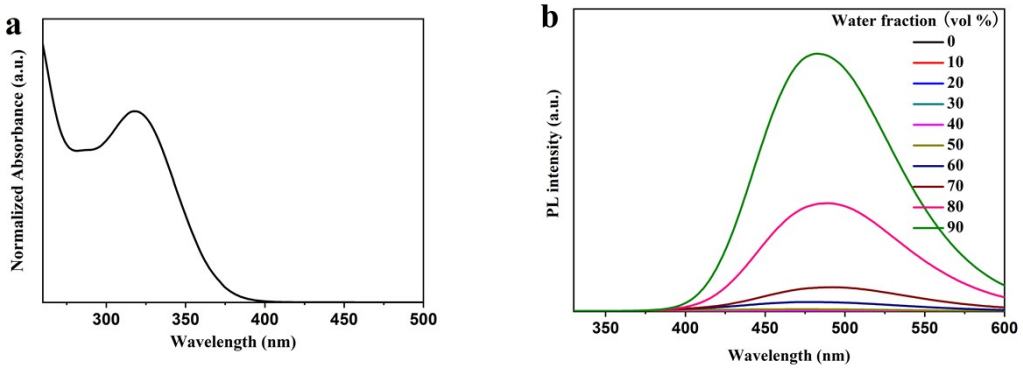


Fig. S6 (a) Absorption spectrum of **381H** in THF solution and (b) PL intensity spectra of **381H** in tetrahydrofuran/water mixtures with different water fractions.

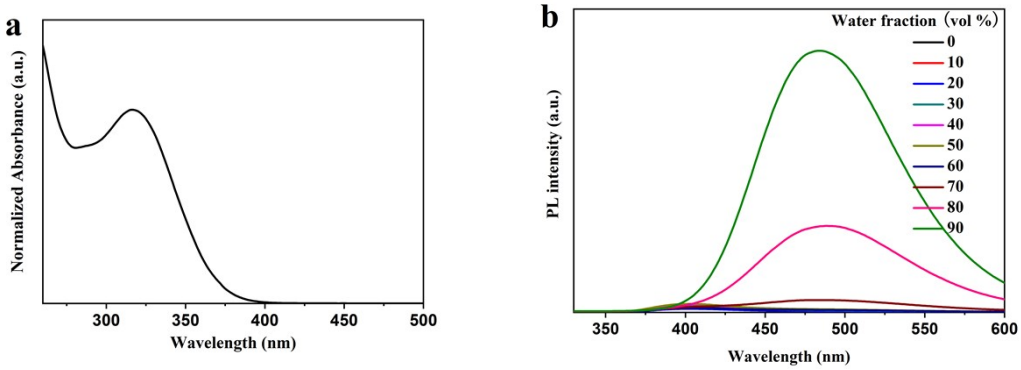


Fig. S7 (a) Absorption spectrum of **342H** in THF solution and (b) PL intensity spectra of **342H** in tetrahydrofuran/water mixtures with different water fractions.

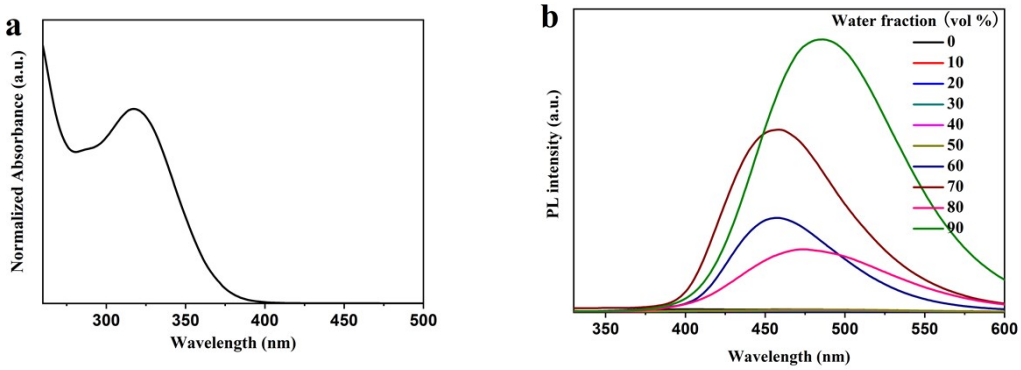


Fig. S8 (a) Absorption spectrum of **362H** in THF solution and (b) PL intensity spectra of **362H** in tetrahydrofuran/water mixtures with different water fractions.

The normalized PL spectra of cyclic TPE in solid state in mortar

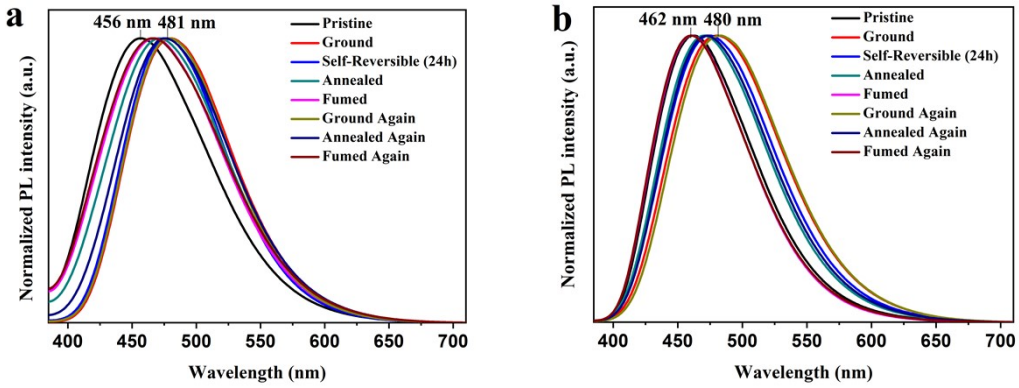


Fig. S9 Normalized PL spectra of (a) **341F** and (b) **341H** excited at 365 nm.

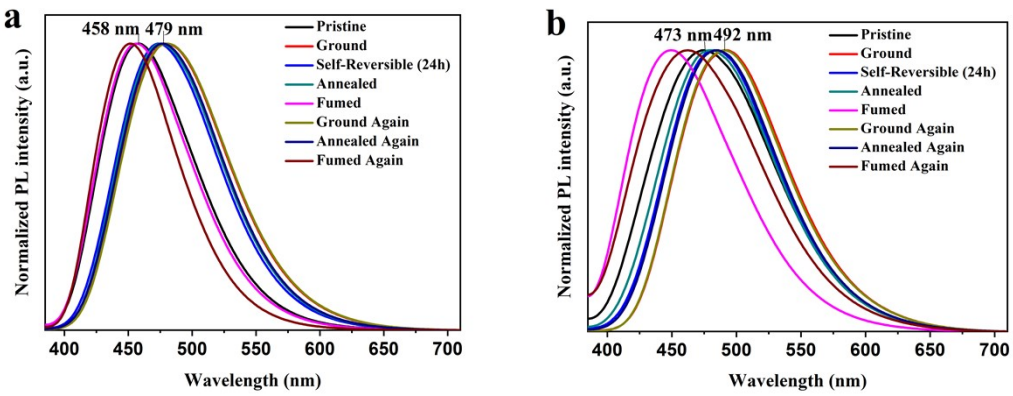


Fig. S10 Normalized PL spectra of (a) **361F** and (b) **361H** excited at 365 nm.

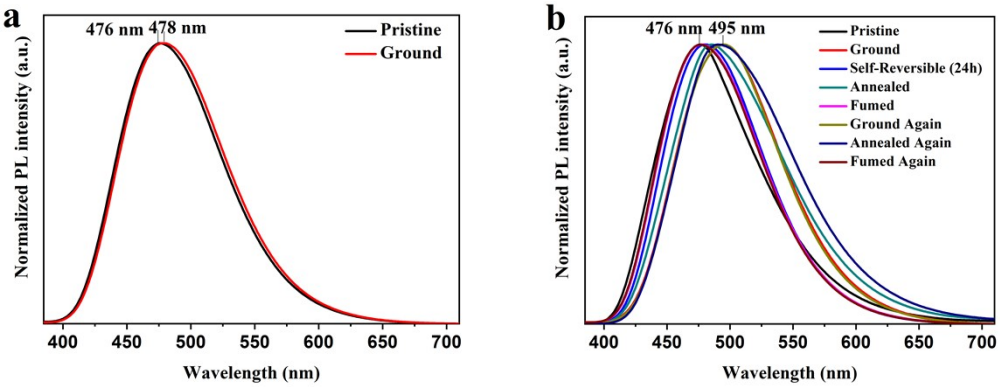


Fig. S11 Normalized PL spectra of (a) **381F** and (b) **381H** excited at 365 nm.

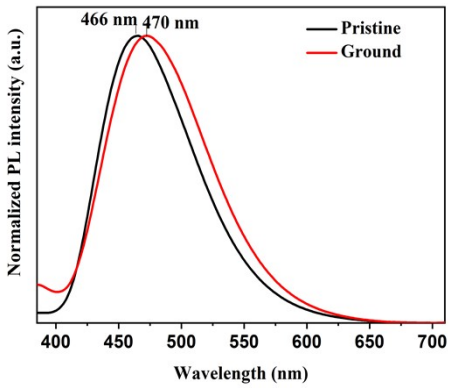


Fig. S12 Normalized PL spectra of **362H** excited at 365 nm.

Powder X-ray diffraction (PXRD) of cyclic TPE

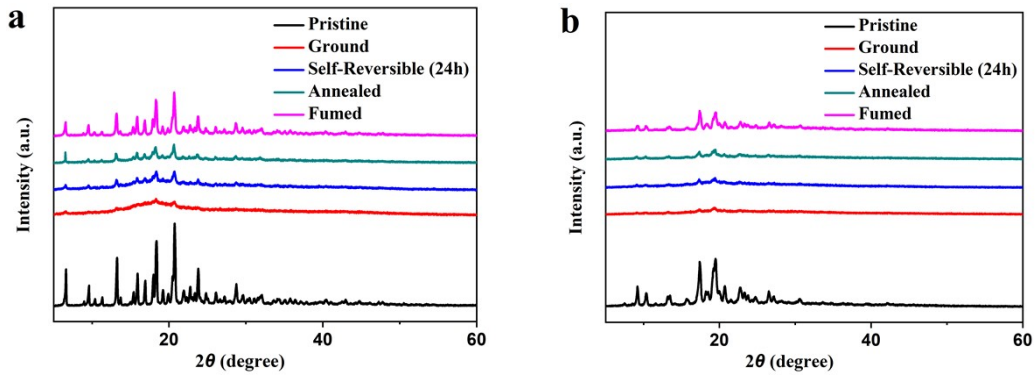


Fig. S13 PXRD patterns of (a) **341F** and (b) **341H**.

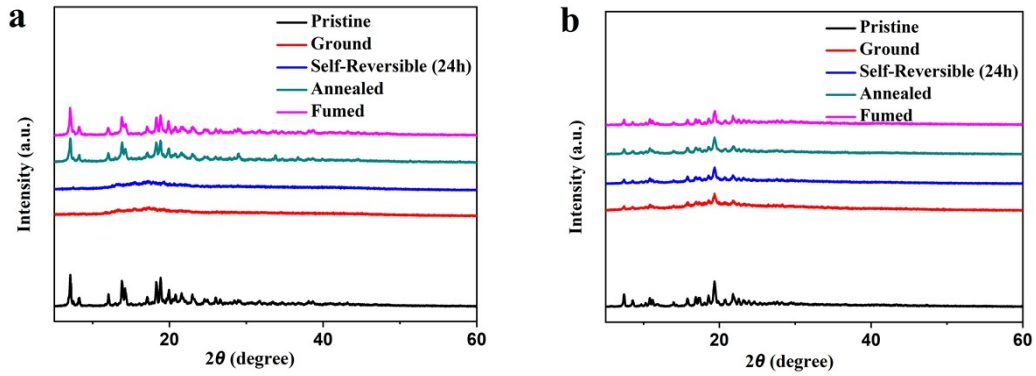


Fig. S14 PXRD patterns of (a) **361F** and (b) **361H**.

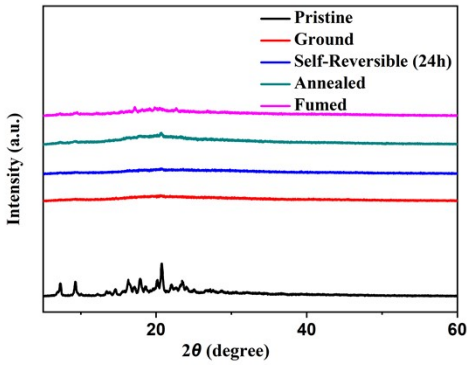


Fig. S15 PXRD patterns of **381H**.

Differential scanning calorimeter (DSC) and Thermogravimetric analysis (TGA) curves of cyclic TPE

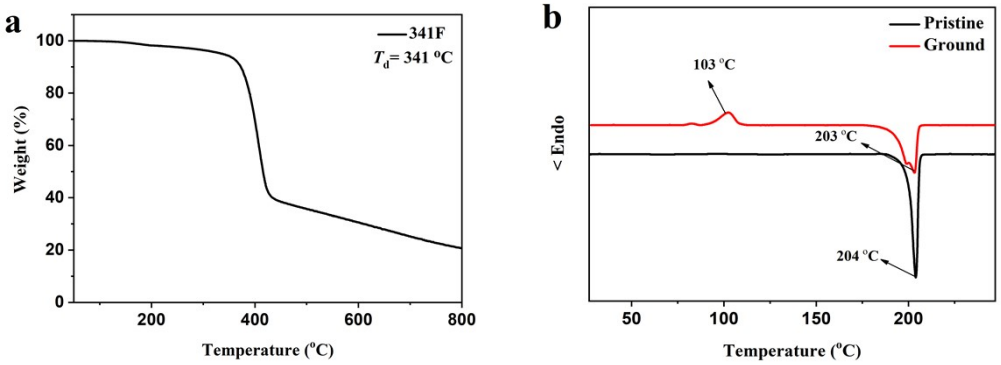


Fig. S16 (a) TGA and (b) DSC curves of **341F**.

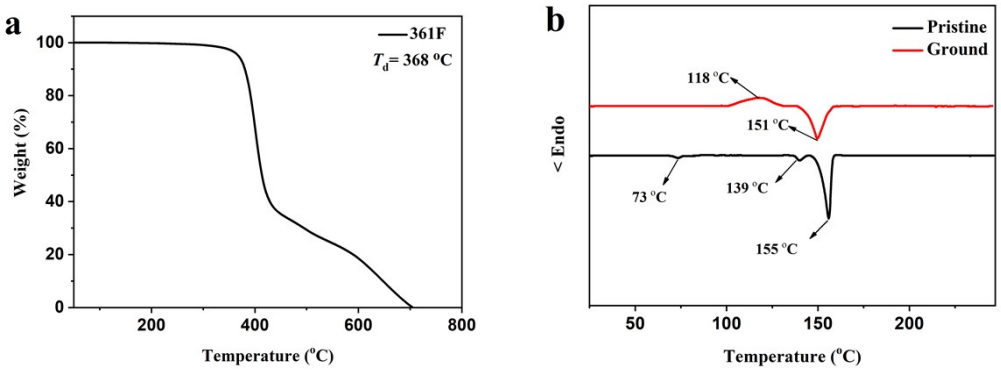


Fig. S17 (a) TGA and (b) DSC curves of **361F**.

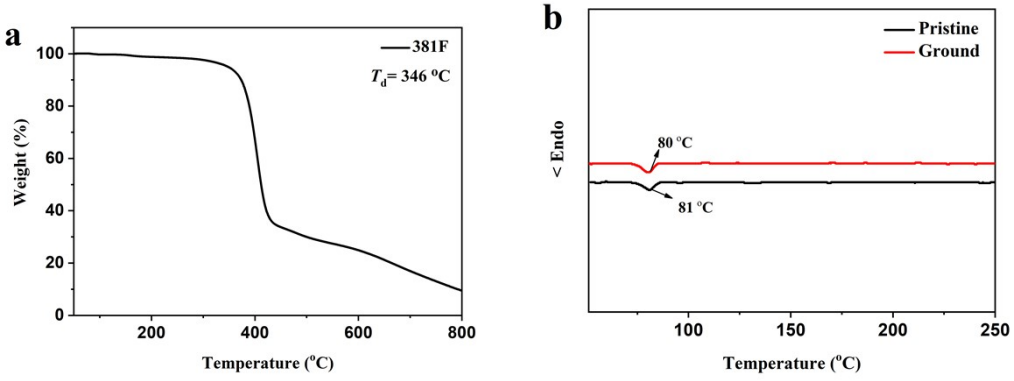


Fig. S18 (a) TGA and (b) DSC curves of **381F**.

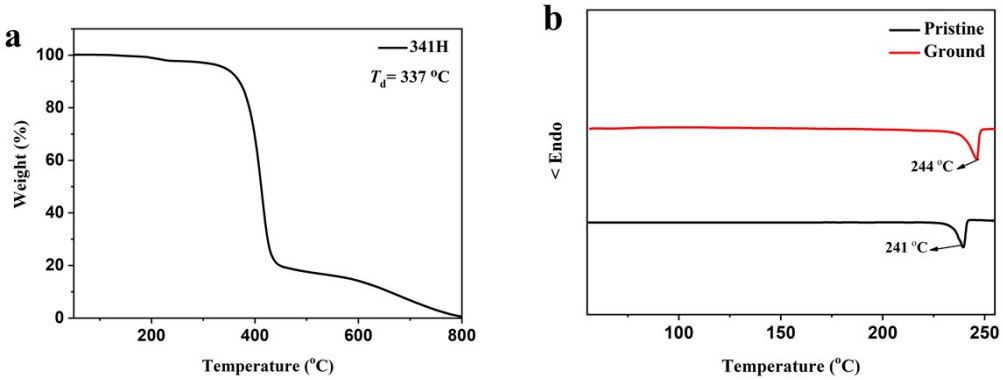


Fig. S19 (a) TGA and (b) DSC curves of **341H**.

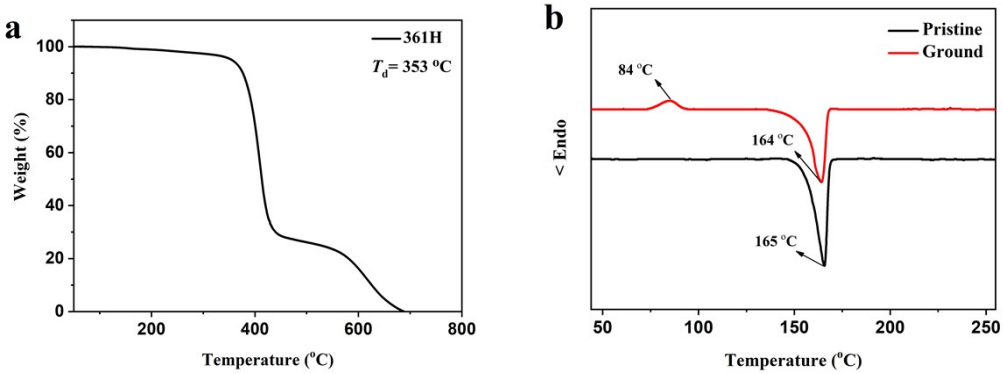


Fig. S20 (a) TGA and (b) DSC curves of **361H**.

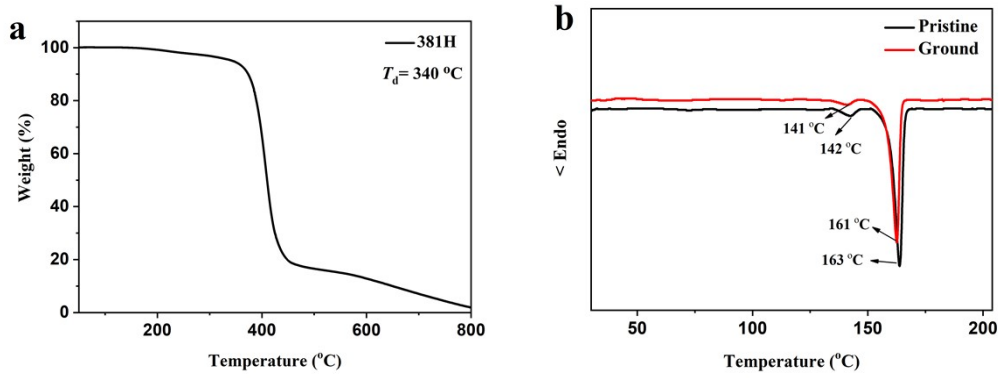


Fig. S21 (a) TGA and (b) DSC curves of **381H**.

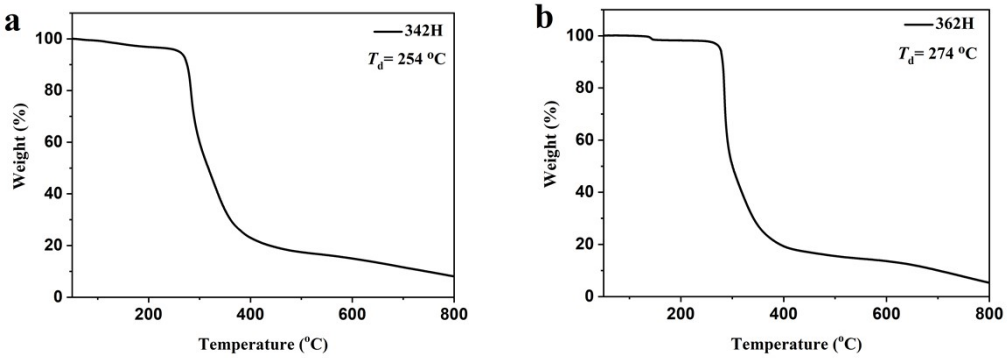


Fig. S22 TGA curves of (a) **342H** and (b) **362H**, respectively.

Single crystal structure and molecular packing of 341F and 381F

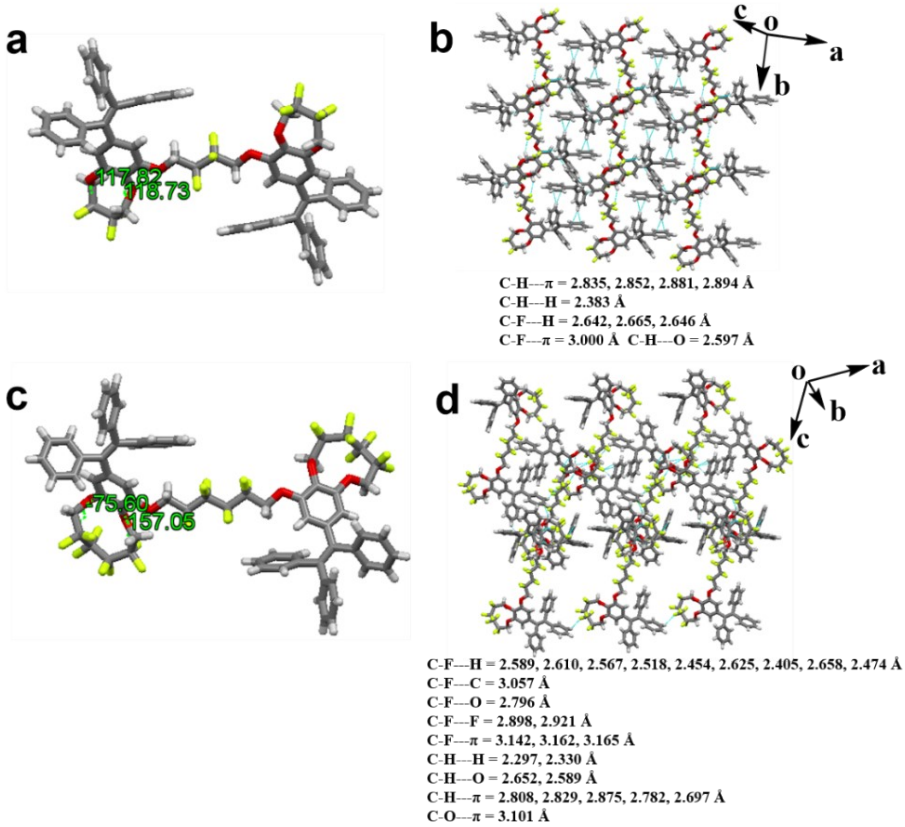


Fig. S23 Single crystal structure (a) **341F** and (c) **381F** and molecular packing of (b) **341F** and (d) **381F**.

Theoretical calculations of cyclic TPE

To further understand the electronic structure of cyclic TPE, the geometry

optimization was carried out by density functional theory (DFT) method at B3LYP/6-31G (d) leve[5] in the gas state.

Table S1. Geometrical parameters of the cyclic TPE calculated by Gaussian09

Compounds	Energy [a.u.]	E_{HOMO} [eV]	E_{LUMO} [eV]	ΔE_H [eV]
341F	-4115.825181	-0.199	-0.055	0.144
361F	-4829.157156	-0.205	-0.057	0.148
381F	-5542.478896	-0.206	-0.070	0.136
341H	-2925.005655	-0.182	-0.042	0.140
342H	-4872.262366	-0.193	0.058	0.135
361H	-3042.938489	-0.189	-0.042	0.147
362H	-5029.538063	-0.194	-0.050	0.144
381H	-3160.881355	-0.190	-0.044	0.146

The cyclic TPE compounds calculated at B3LYP/6-31G (d) level based on the geometry optimization.

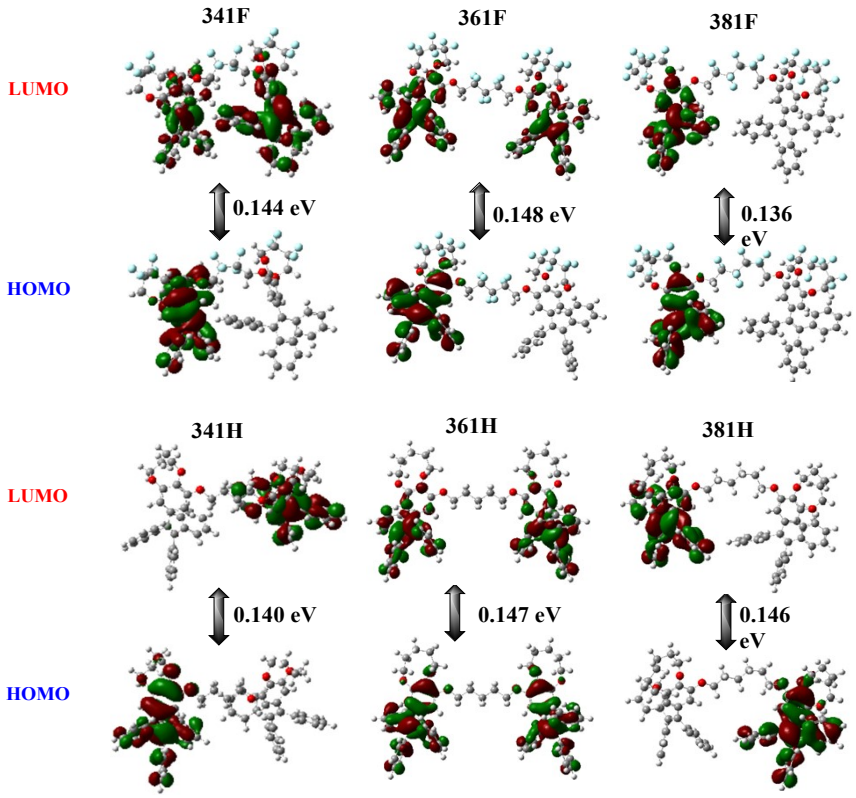


Fig. S24 Molecular orbital amplitude plots of HOMO and LUMO energy levels of cyclic TPE calculated at B3LYP/6-31G (d) level based on the geometry optimization.

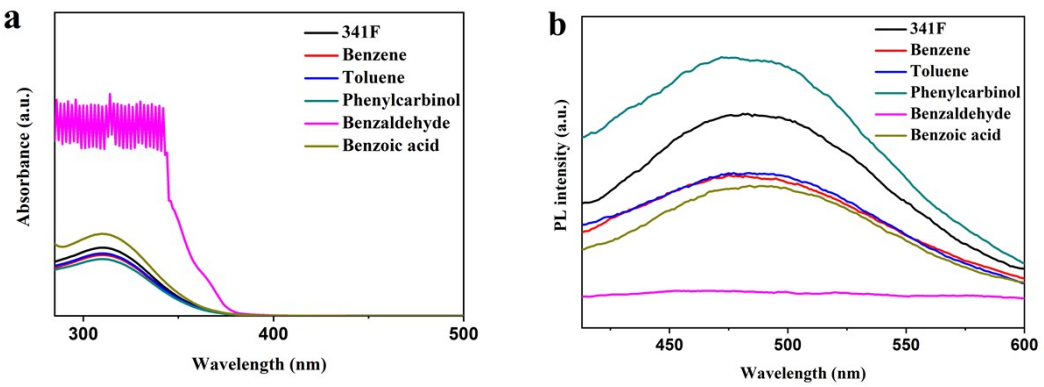


Fig. S25 (a) Absorption spectrum and (b) PL intensity spectra of benzene derivates in **341F** solution (1×10^{-4} M, benzene derivates: **341F** solution = 1:100 (v/v)).

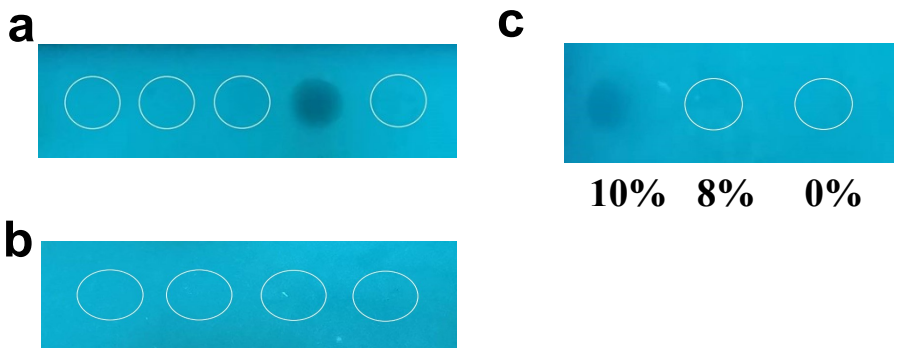


Fig. S26 The film of **341F** with solvent from left to right: a) benzene, toluene, phenylcarbinol, benzaldehyde, benzoic acid (these compounds are dissolved in ethyl acetate in 2 mg/mL), b) acetonitrile, acetic acid, ethanol, ethyl acetate, c) benzaldehyde fraction in benzene/ethyl acetate (v/v).

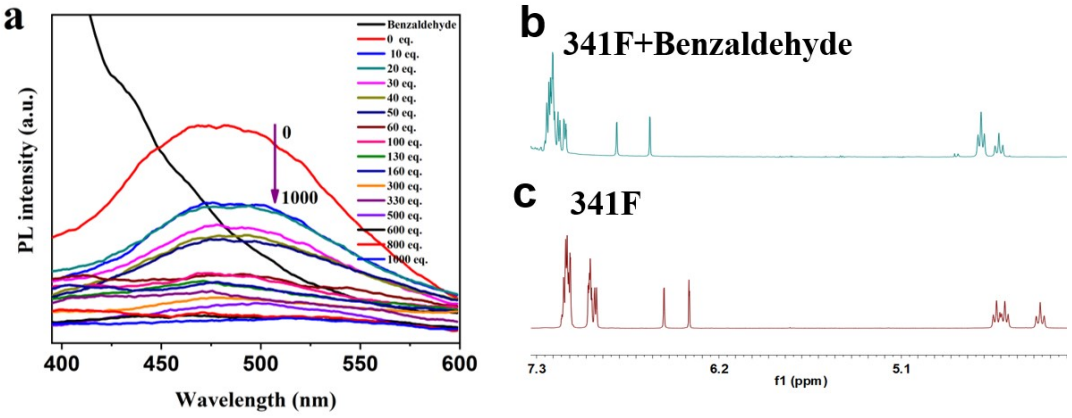


Fig. S27 (a) PL intensity spectra of the **341F** solution (1×10^{-4} M) upon adding molar equivalent of benzaldehyde from 10 to 1000, the partial ^{1}H NMR spectra of (b) a mixture of **341F** and benzaldehyde (mol ratio, **341F** : benzaldehyde = 1 : 100) and (c) pure **341F** (DMSO-d^{6}, 600 MHz).

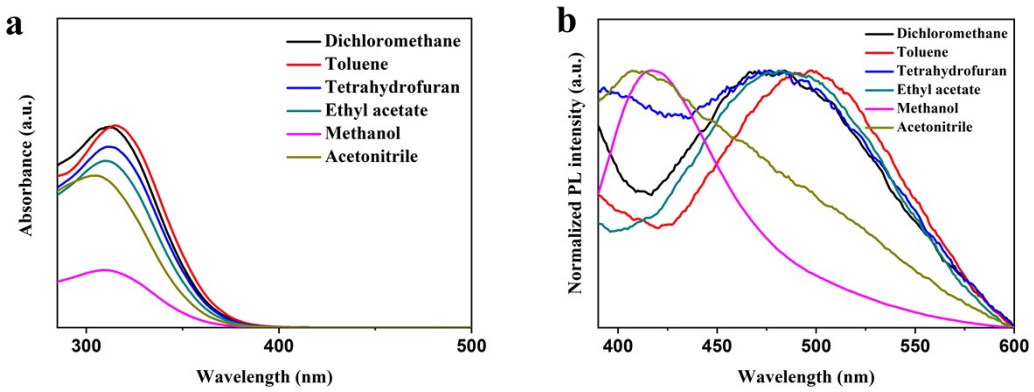
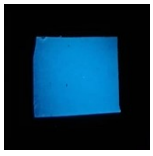
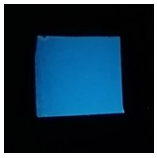
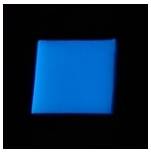
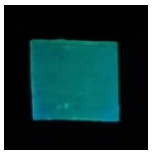
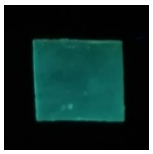
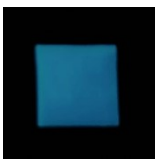
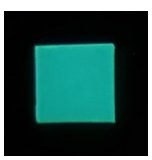
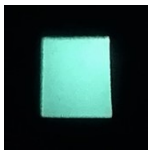
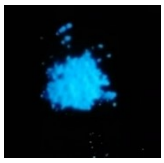
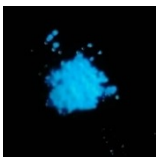
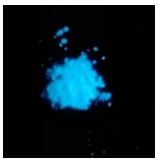
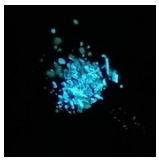
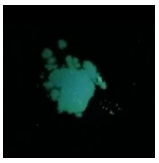
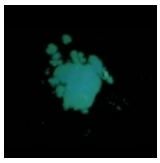


Fig. S28 (a) Absorption spectrum and (b) Normalized PL intensity spectra of **341F** in different solvents (1×10^{-4} M).

The PL spectra of cyclic TPE PDMS film and 361F solid powder with different temperature

Table S2. A variety of the cyclic TPE PDMS film and **361F** solid powder with different temperature excited at 365 nm.

	30 °C	70 °C	100 °C	120 °C	140 °C	160 °C	180 °C
341F PDMS film							
341H PDMS film							
361F PDMS film							
361H PDMS film							
381F PDMS film							

381H PDMS film							
361F solid powder							

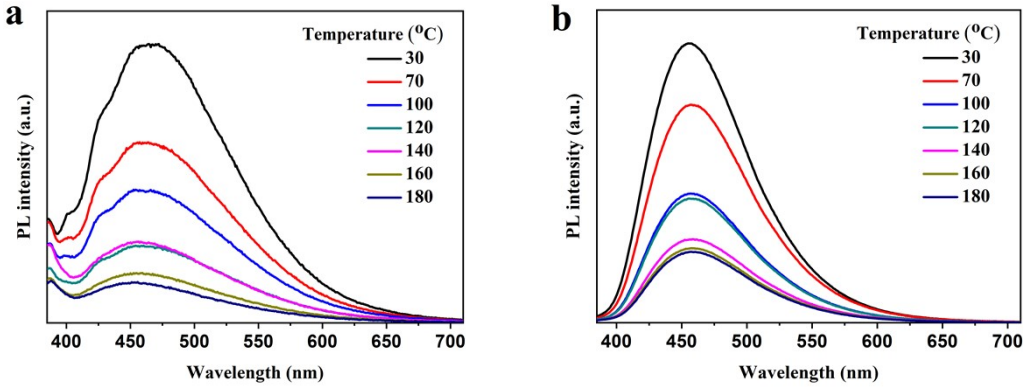


Fig. S29 The PL spectra of (a) **341F** and (b) **341H** PDMS film excited at 365 nm.

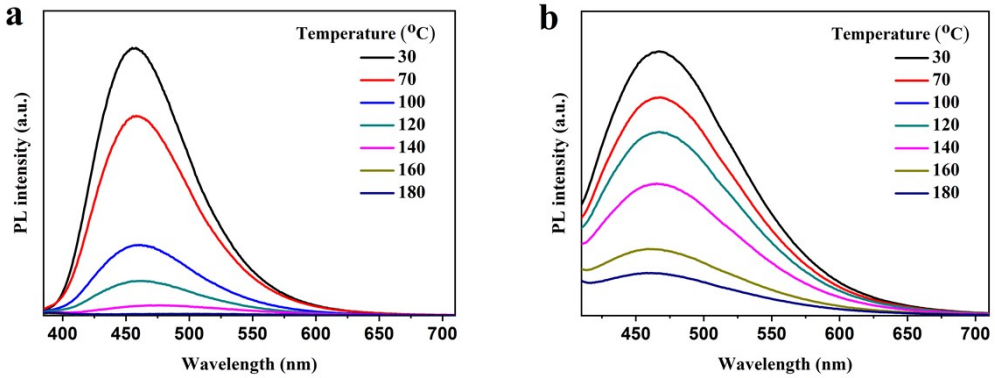


Fig. S30 The PL spectra of (a) **361F** and (b) **361H** PDMS film excited at 365 nm.

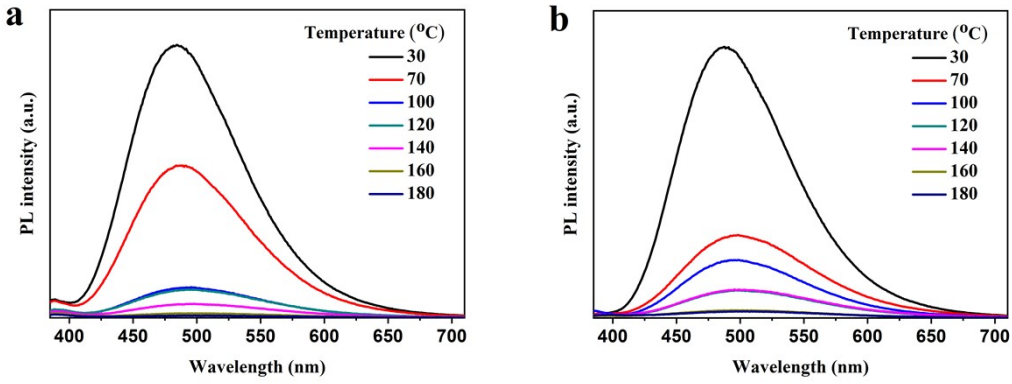


Fig. S31 The PL spectra of (a) **381F** and (b) **381H** PDMS film excited at 365 nm.

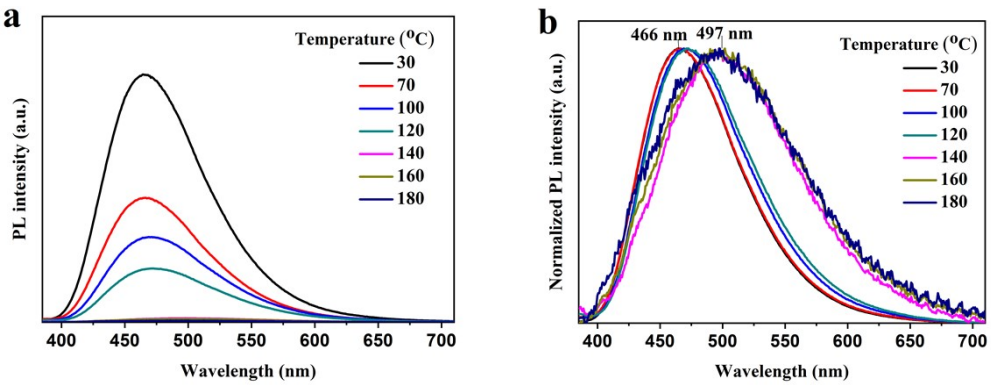


Fig. S32 (a) The PL spectra and (b) normalized PL spectra of pure original **361F** solid excited at 365 nm.

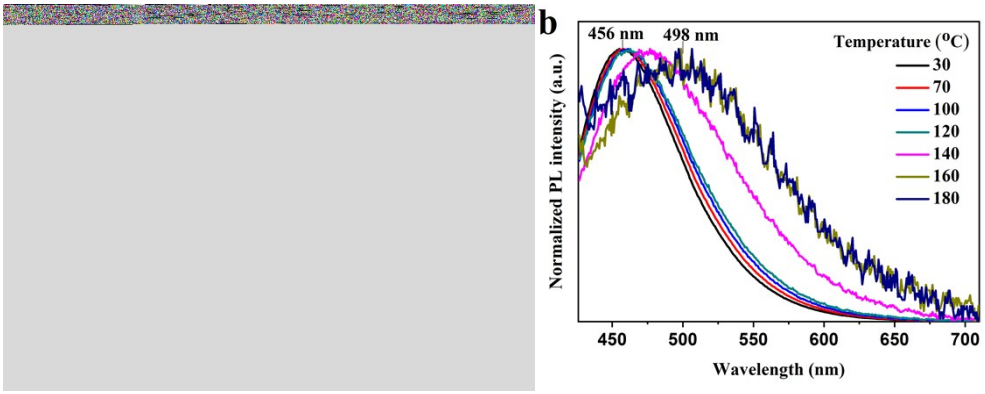


Fig. S33 (a) The PL spectra and (b) normalized PL spectra of **361F** PDMS film excited at 365 nm.

Crystal data and structure refinement of 341F and 381F

Table S3. Crystal data and structure refinement for **341F** (CCDC 2213002)**.**

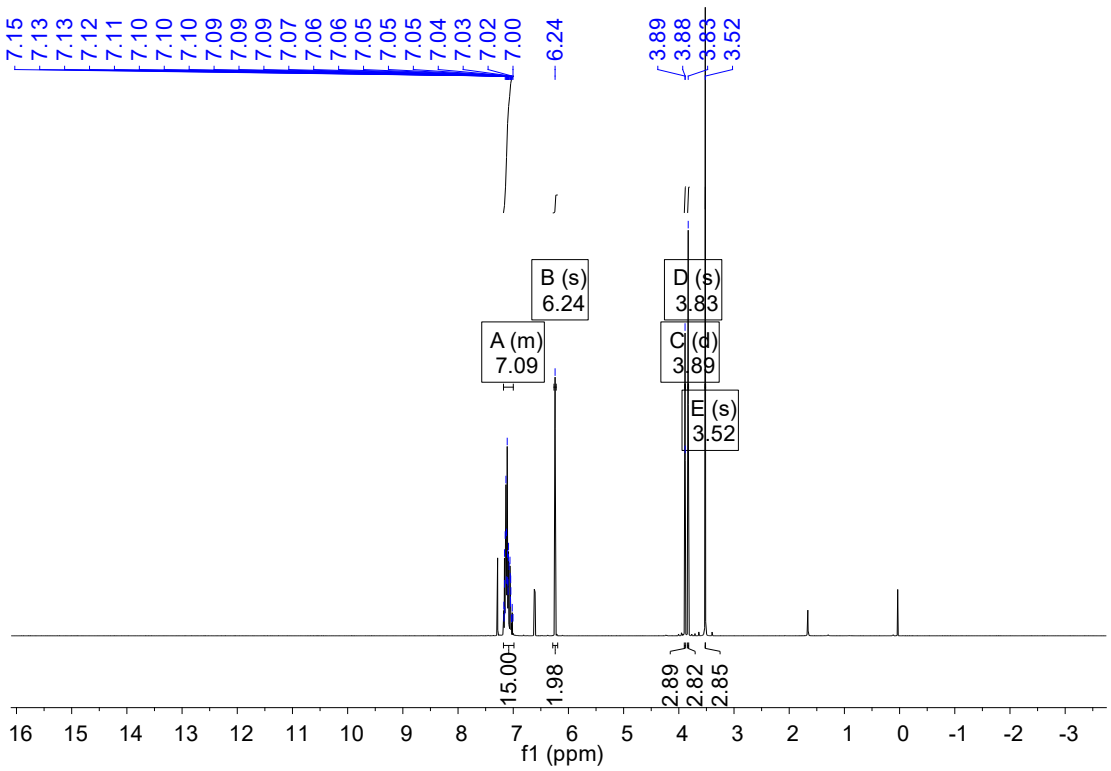
complex	**341F**
empirical formula	$C_{64}H_{46}F_{12}O_6$
formula weight	1139.01
T (K)	213(2)
crystal system	Monoclinic
space group	*P -21/n*
a (Å)	13.6474(8)
b (Å)	12.6815(7)
c (Å)	15.7895 (11)
a (deg)	90°
β(deg)	102.355(2)°
γ(deg)	90°

V (Å ^{3})	2669.4(3)
Z	2
D calcd (Mg/m3)	1.417
μ/mm^{-1}	0.118
F (000)	1172
GOF	1.053
R1 [I > 2σ(I)] [a]	0.0363
ωR_2 (all data) [b]	0.0910
Data/restraints/parameters	5204 / 0 / 370
CCDC number	2213002

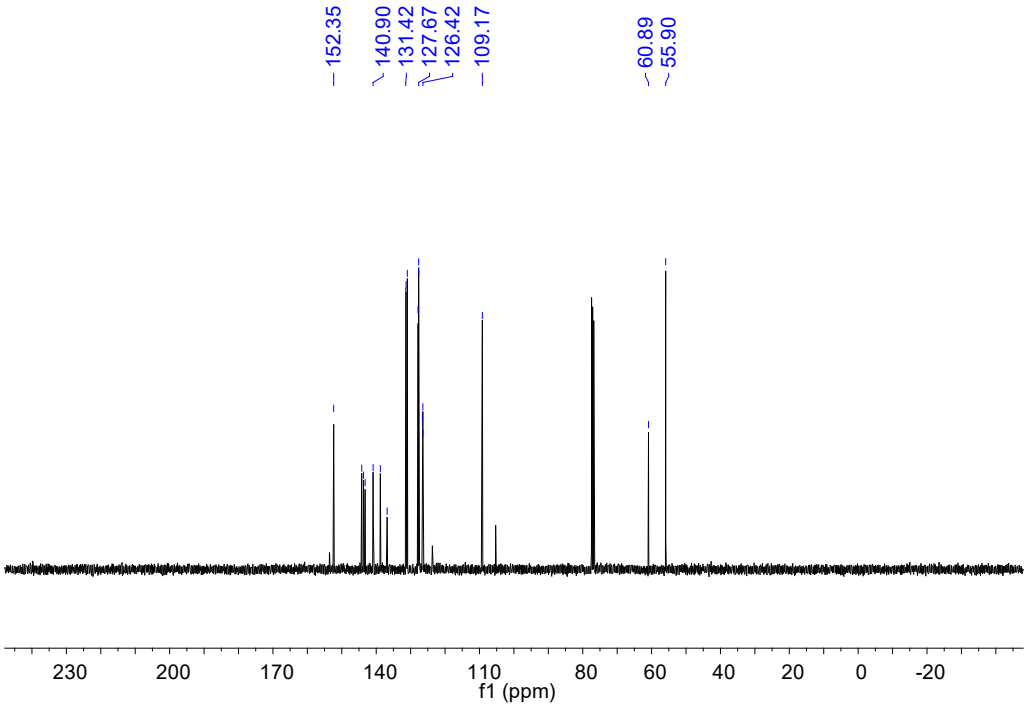
Table S4. Crystal data and structure refinement for **381F** (CCDC 2213003)**.**

complex	**381F**
empirical formula	$C_{70}H_{46}F_{24}O_6$
formula weight	1439.07
T (K)	213(2) K
crystal system	Monoclinic
space group	*C c*
a (Å)	29.274(3)
b (Å)	9.8162(8)
c (Å)	25.246(2)
a (deg)	90°
β(deg)	122.082(2)°
γ(deg)	90°
V (Å ^{3})	61.468(9)
Z	4
D calcd (Mg/m3)	1.555
μ/mm^{-1}	0.147
F (000)	2920
GOF	1.082
R1 [I > 2σ(I)] [a]	0.0469
ωR_2 (all data) [b]	0.1182
Data/restraints/parameters	11058 / 2 / 901
CCDC number	2213003

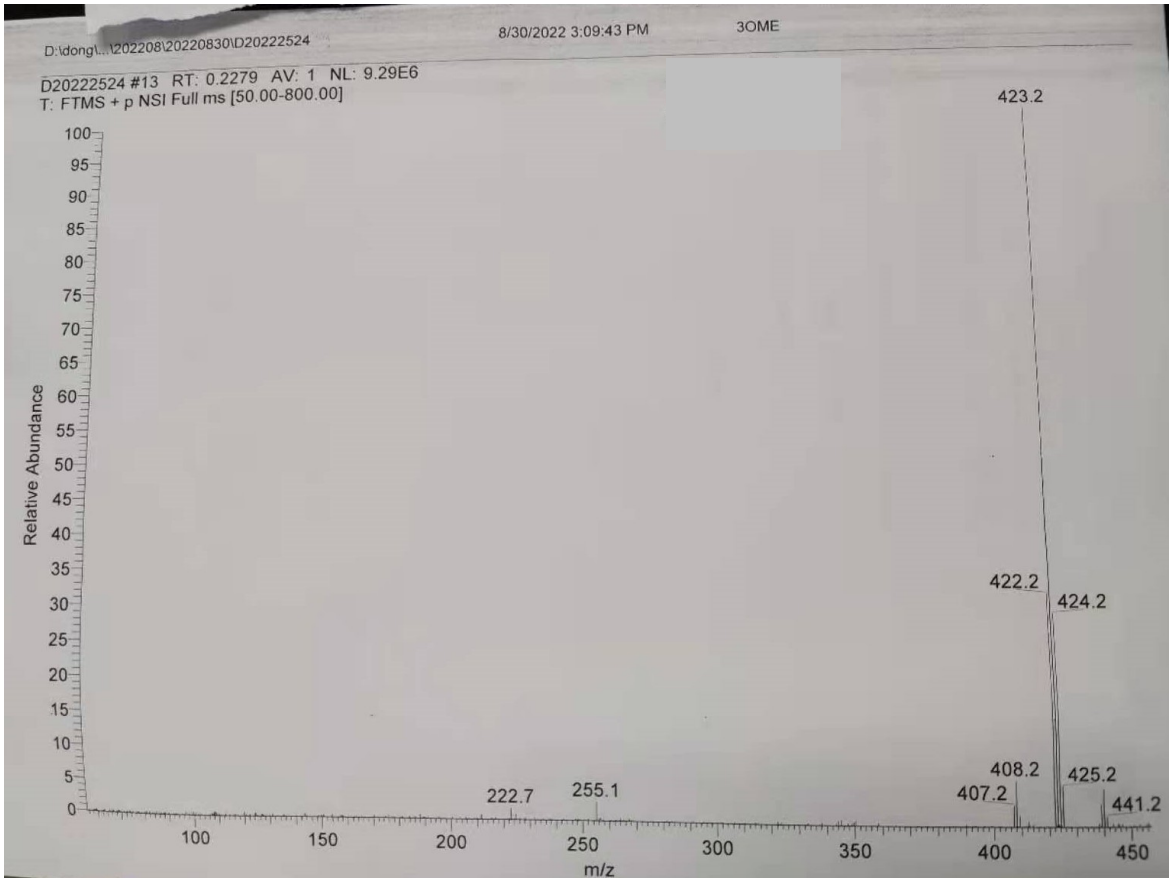
The NMR spectrum and Mass spectrum HRMS of cyclic TPE compounds



^{1}H-NMR spectrum of compound **1** ($CDCl_3$, 600MHz)



^{13}C-NMR spectrum of compound **1** ($CDCl_3$, 600MHz)



Mass spectrum of compound **1**

National Center for Organic Mass Spectrometry in Shanghai
Shanghai Institute of Organic Chemistry
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High Resolution MS DATA REPORT

Instrument: Thermo Fisher Scientific LTQ FTICR-MS

Card Serial Number : D20222525

Sample Serial Number: 3OME

Operator : DONG Date: 2022/08/30

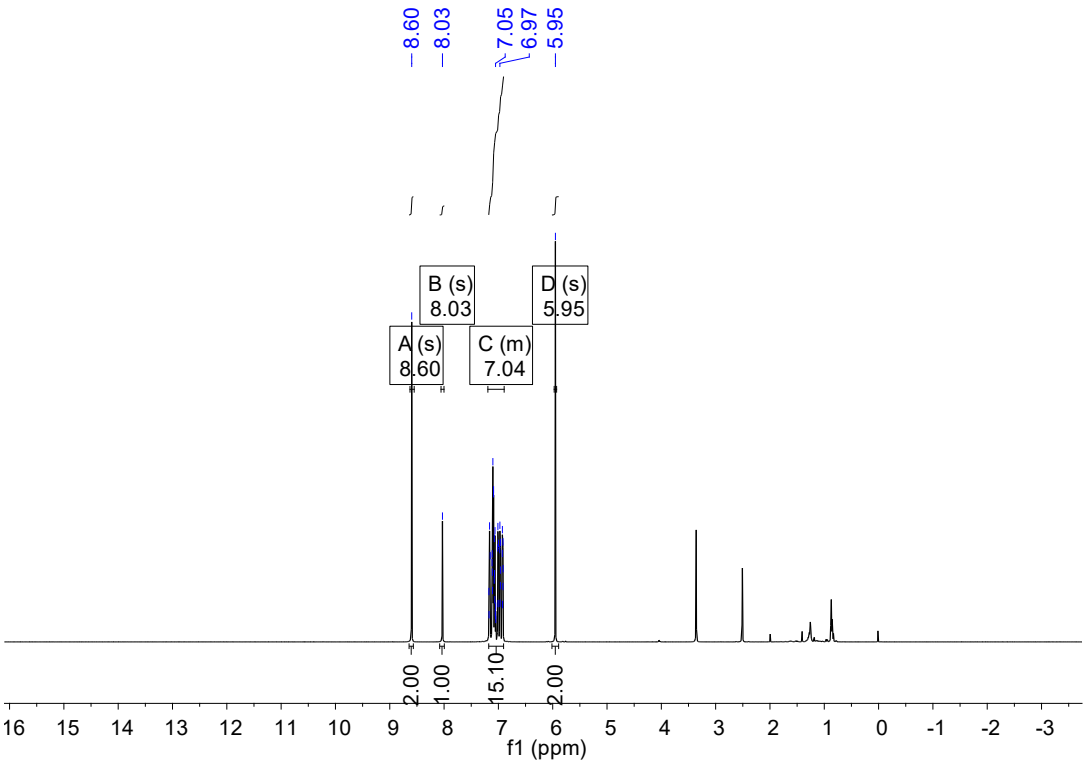
Operation Mode: DART POSITIVE

Elemental composition search on mass 423.1952

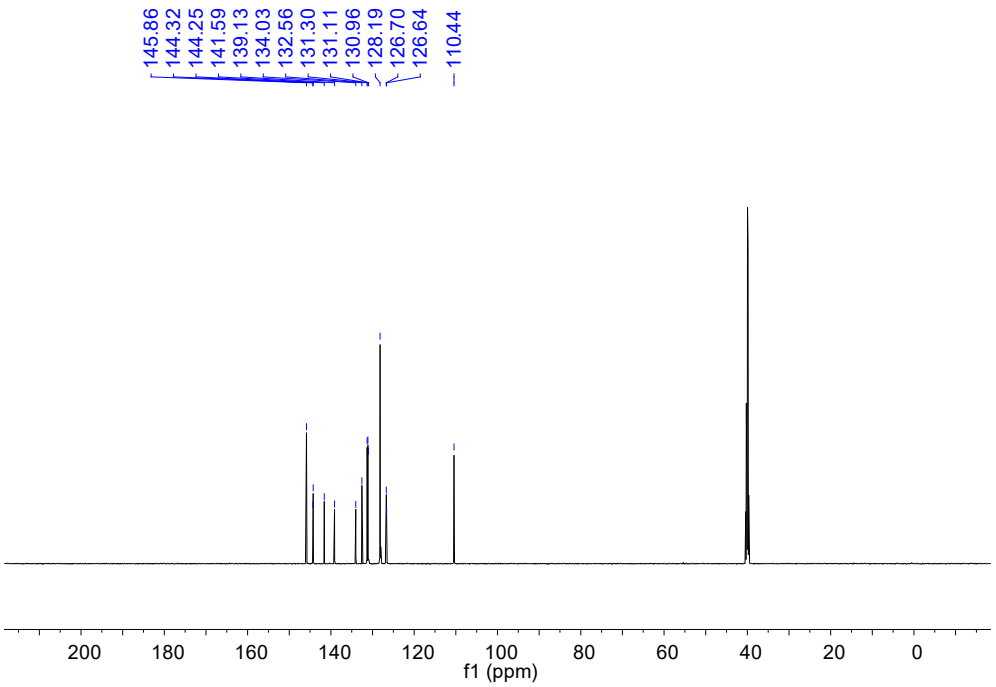
m/z= 418.1952-428.1952

m/z	Theo. Mass	Delta (ppm)	RDB equiv.	Composition
423.1952	423.1953	-0.15	13.0	$C_{24}H_{26}O_3N_3F$
	423.1953	-0.24	5.5	$C_{21}H_{28}O_3F_5$
	423.1955	-0.62	16.5	$C_{29}H_{27}O_3$
	423.1942	2.46	9.5	$C_{24}H_{27}O_2F_4$
	423.1941	2.56	17.0	$C_{27}H_{25}O_2N_3$
	423.1964	-2.85	9.0	$C_{21}H_{27}O_4N_3F_2$
	423.1940	2.93	6.0	$C_{19}H_{26}O_2N_3F_5$
	423.1966	-3.32	12.5	$C_{26}H_{28}O_4F$
	423.1930	5.16	13.5	$C_{27}H_{26}OF_3$
	423.1976	-5.55	5.0	$C_{18}H_{28}O_5N_3F_3$

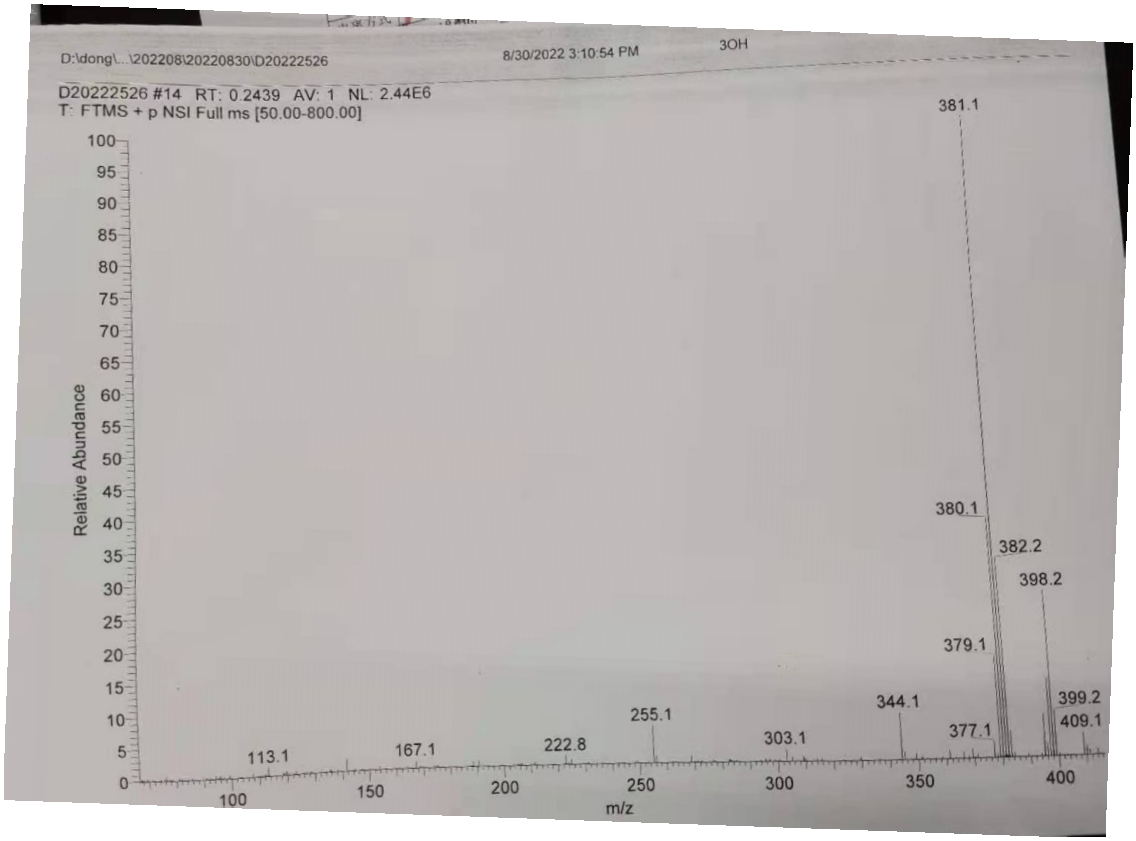
HRMS of compound **1**



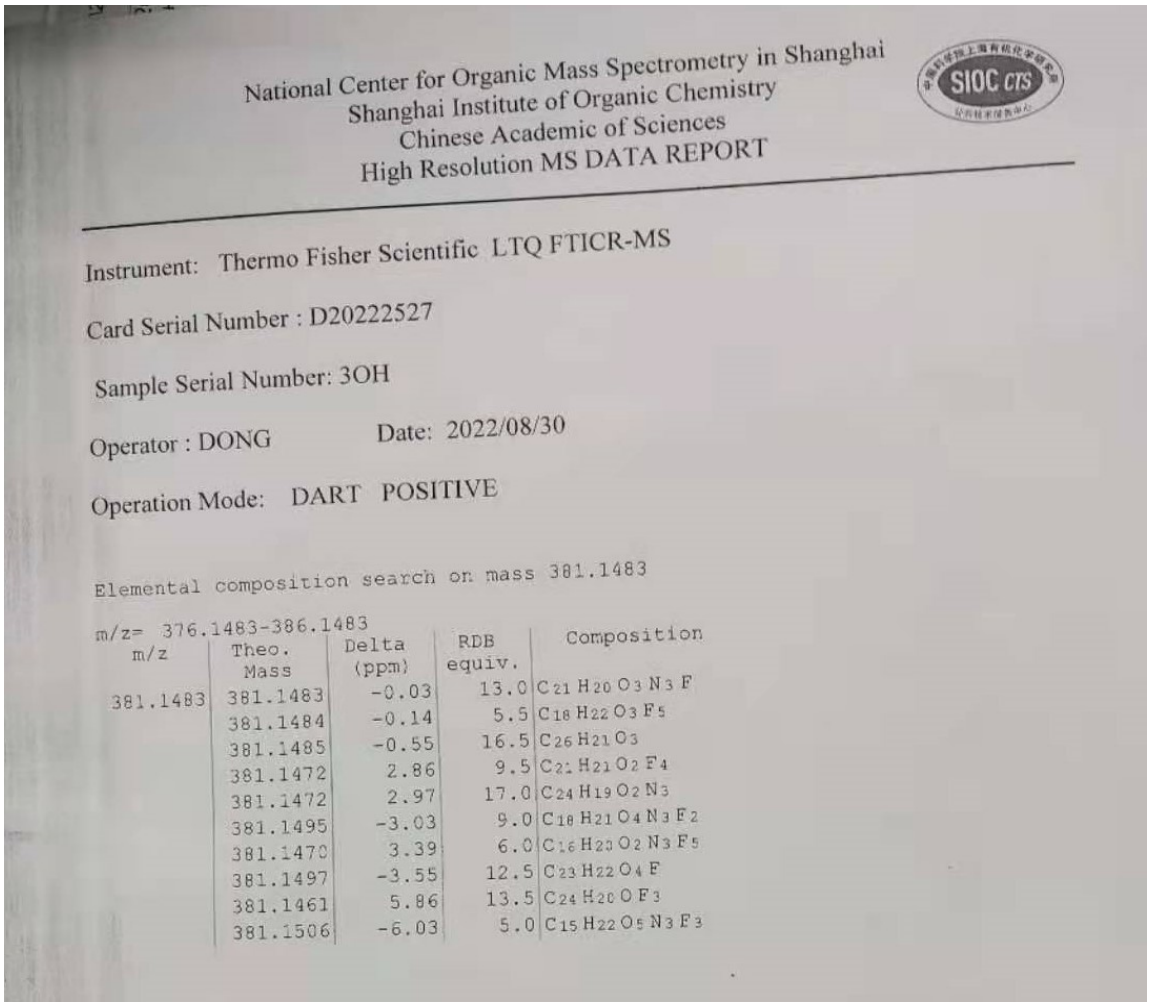
[1]H-NMR spectrum of compound **2** (DMSO, 600MHz)



[13]C-NMR spectrum of compound **2** (DMSO, 600MHz)



Mass spectrum of compound **2**



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

Instrument: Thermo Fisher Scientific LTQ FTICR-MS

Card Serial Number : D20222527

Sample Serial Number: 3OH

Operator : DONG Date: 2022/08/30

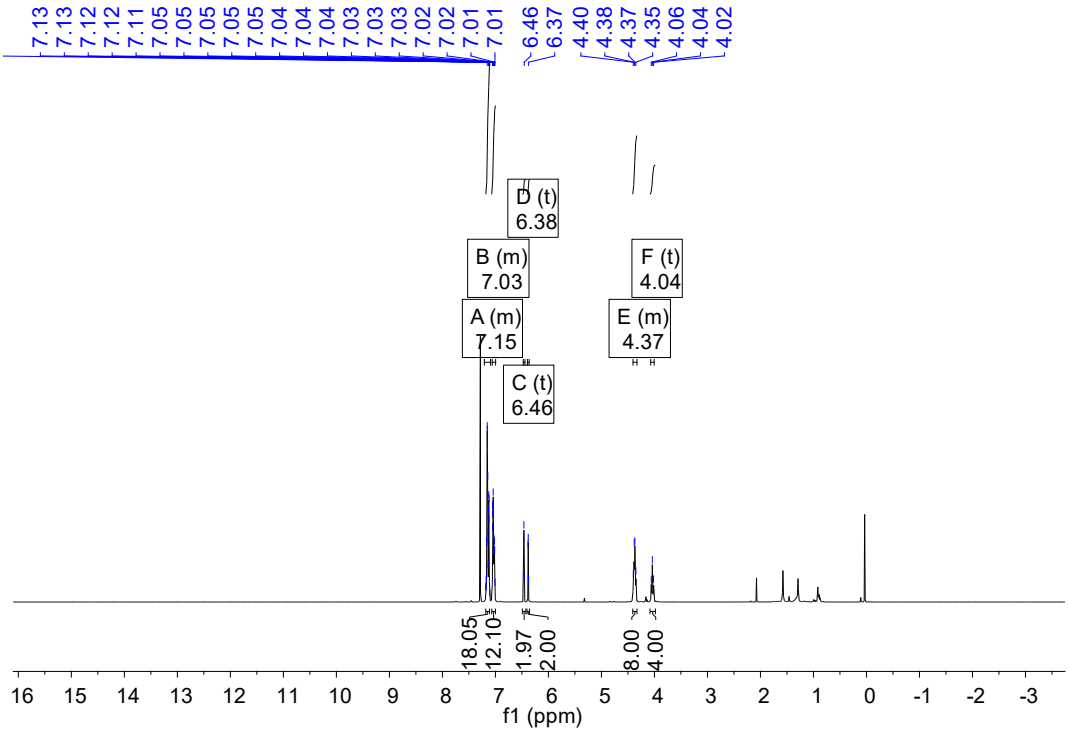
Operation Mode: DART POSITIVE

Elemental composition search on mass 381.1483

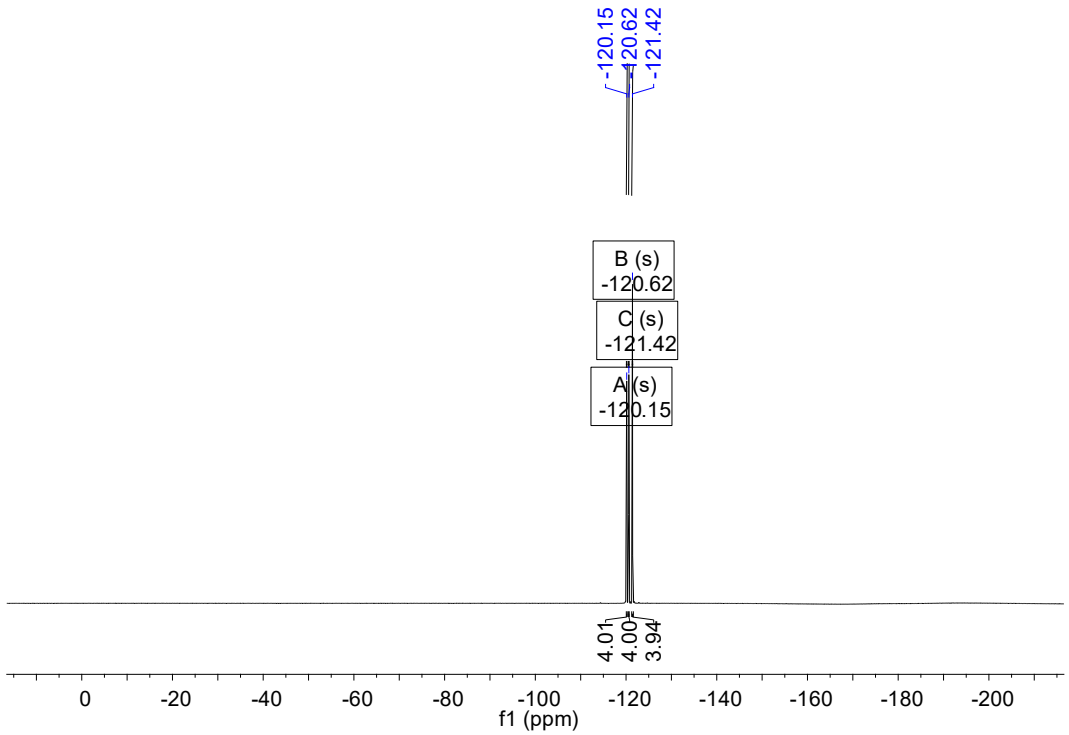
m/z= 376.1483-386.1483

m/z	Theo. Mass	Delta (ppm)	RDB equiv.	Composition
381.1483	381.1483	-0.03	13.0	$C_{21}H_{20}O_3N_3F$
	381.1484	-0.14	5.5	$C_{18}H_{22}O_3F_5$
	381.1485	-0.55	16.5	$C_{26}H_{21}O_3$
	381.1472	2.86	9.5	$C_{21}H_{21}O_2F_4$
	381.1472	2.97	17.0	$C_{24}H_{19}O_2N_3$
	381.1495	-3.03	9.0	$C_{18}H_{21}O_4N_3F_2$
	381.1470	3.39	6.0	$C_{16}H_{23}O_2N_3F_5$
	381.1497	-3.55	12.5	$C_{23}H_{22}O_4F$
	381.1461	5.86	13.5	$C_{24}H_{20}OF_3$
	381.1506	-6.03	5.0	$C_{15}H_{22}O_5N_3F_3$

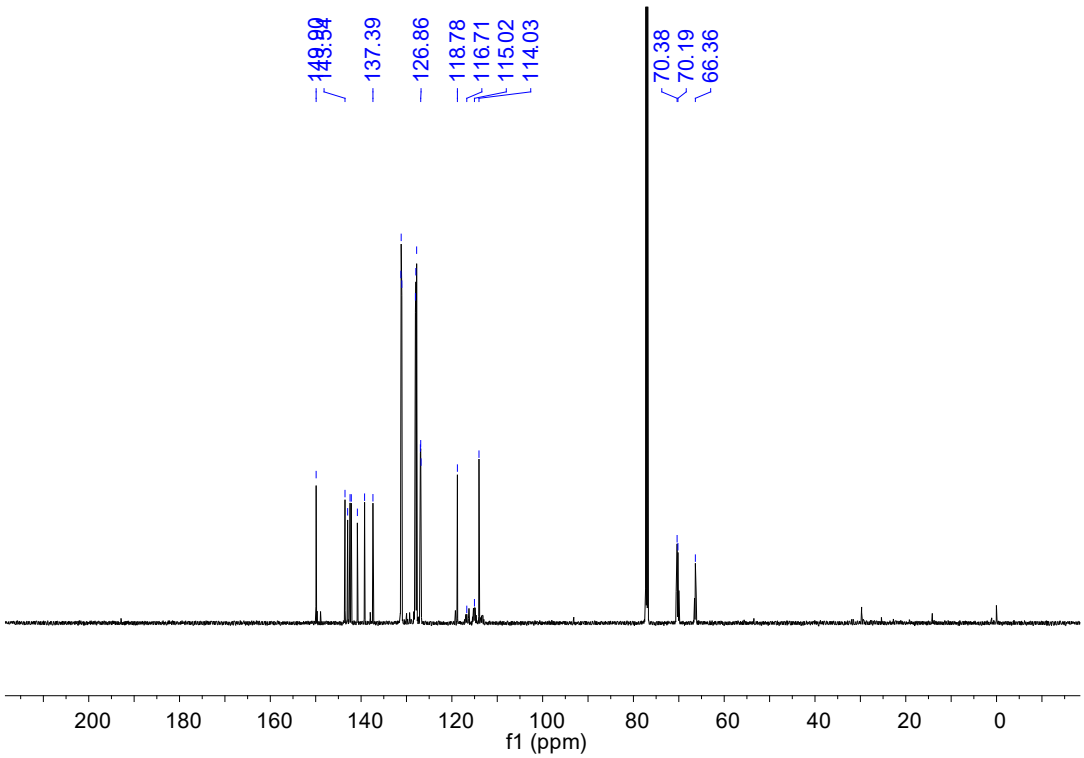
HRMS of compound **2**



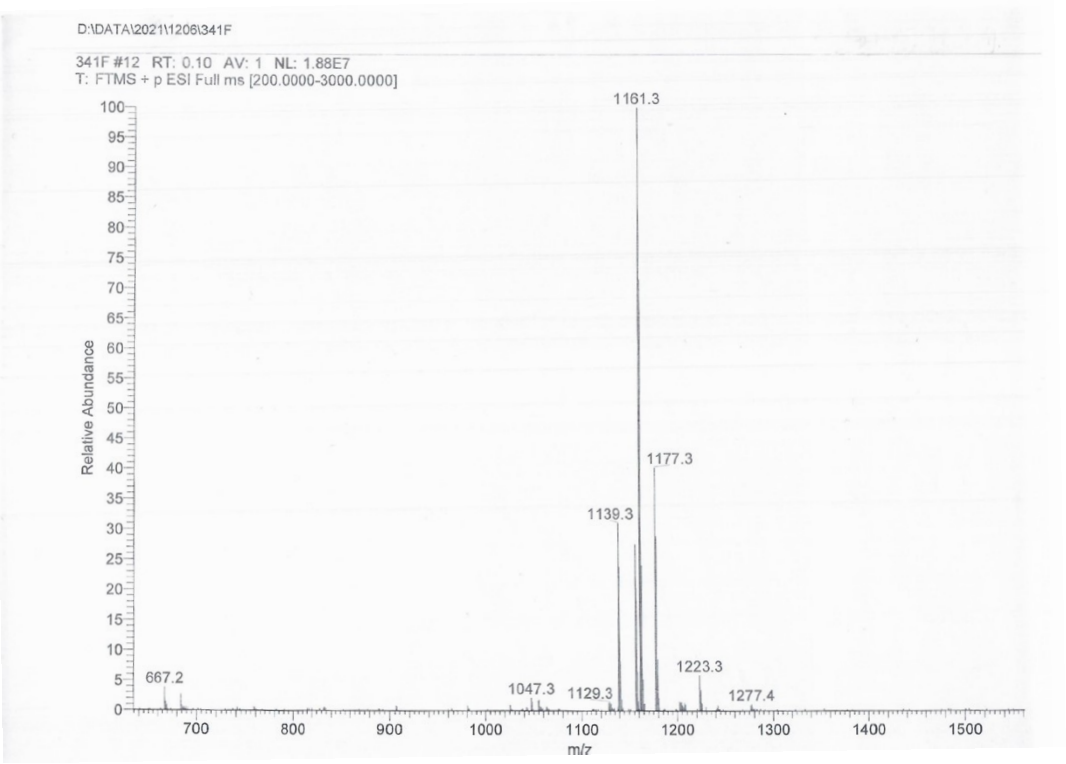
^{1}H-NMR spectrum of compound **341F** ($CDCl_3$, 600MHz)



^{19}F-NMR spectrum of compound **341F** ($CDCl_3$, 600MHz)



^{13}C-NMR spectrum of compound **341F** ($CDCl_3$, 600MHz)



Mass spectrum of compound **341F**

National Center for Organic Mass Spectrometry in Shanghai
Shanghai Institute of Organic Chemistry
Chinese Academic of Sciences
High Resolution ESI-MS REPORT

Instrument: Thermo Scientific Q Exactive HF Orbitrap-FTMS

Card Serial Number: E213079

Sample Serial Number: 341F

Operator: Songw Date: 2021/12/06

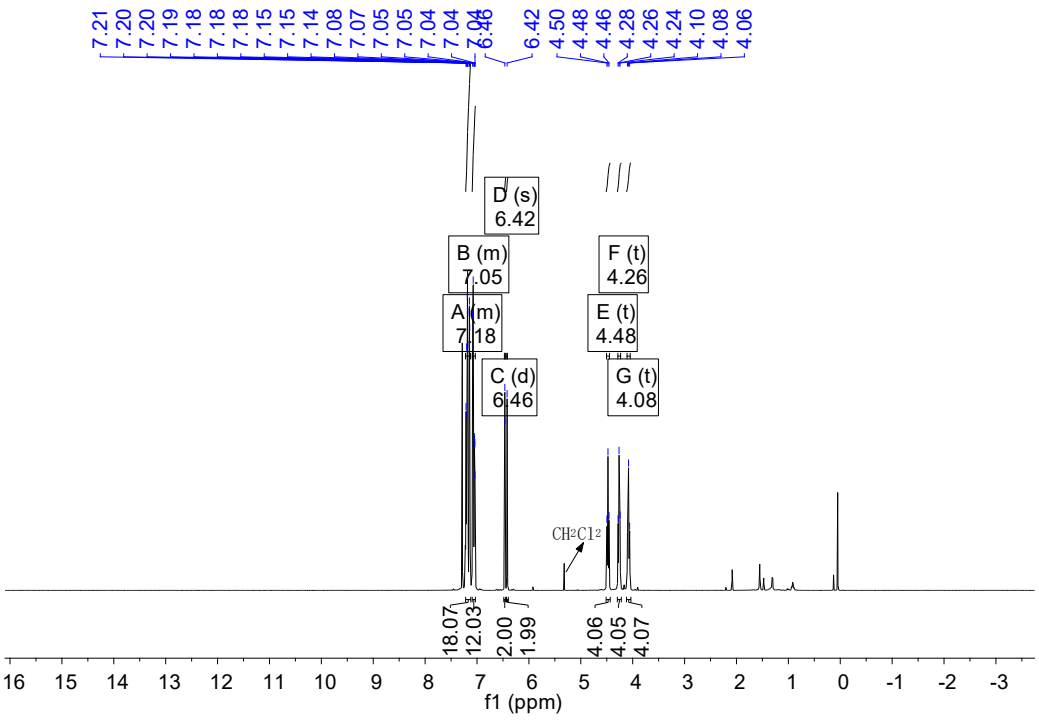
Operation Mode: ESI Positive Ion Mode

Elemental composition search on mass 1161.2986

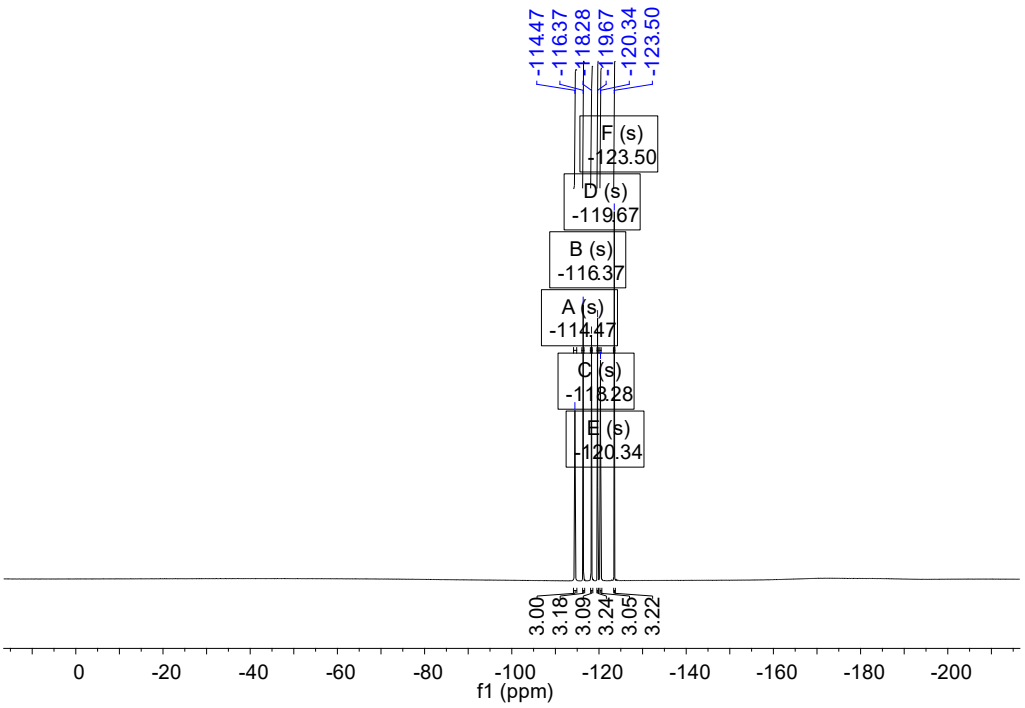
m/z= 1156.2986-1166.2986

m/z	Theo. Mass	Delta (ppm)	RDB equiv.	Composition
1161.2986	1161.2995	-0.79	35.5	$C_{64}H_{46}O_6F_{12}Na$

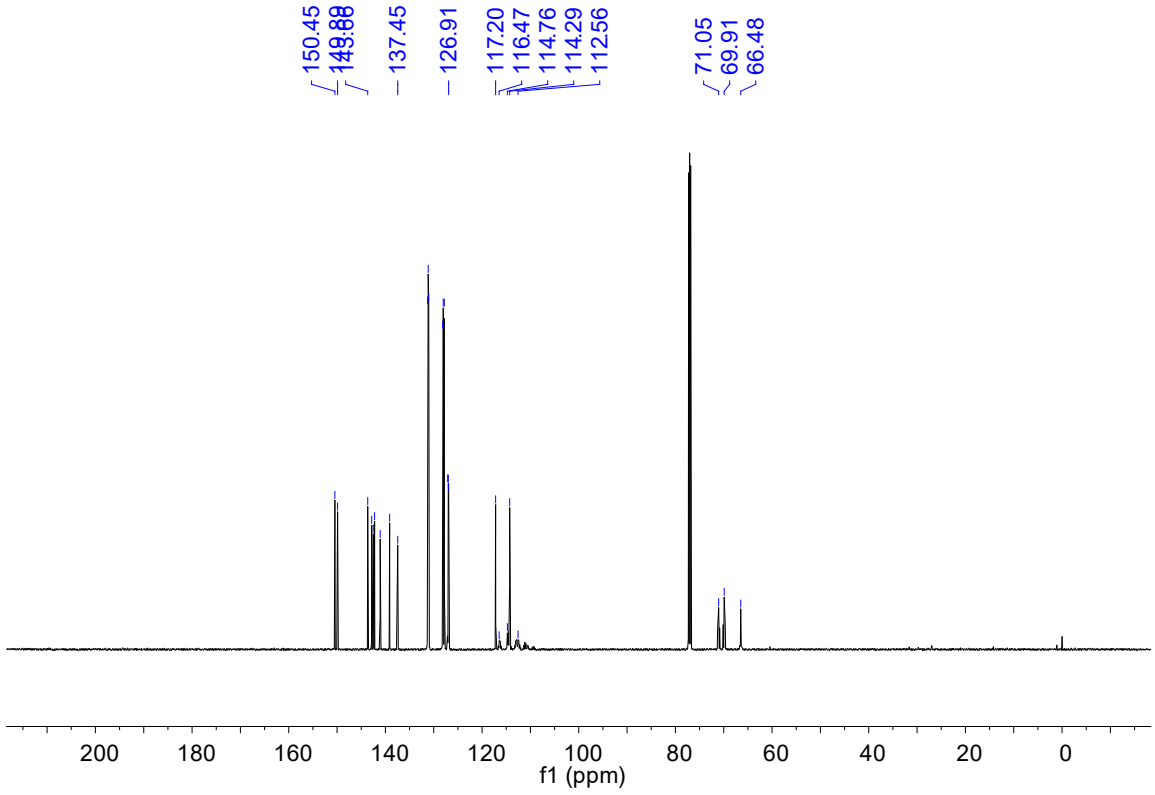
HRMS of compound **341F**



^{1}H-NMR spectrum of compound **361F** ($CDCl_3$, 600MHz)



^{19}F-NMR spectrum of compound **361F** ($CDCl_3$, 600MHz)



^{13}C-NMR spectrum of compound **361F** ($CDCl_3$, 600MHz)

National Center for Organic Mass Spectrometry in Shanghai
Shanghai Institute of Organic Chemistry
Chinese Academic of Sciences
High Resolution AP-MALDI REPORT

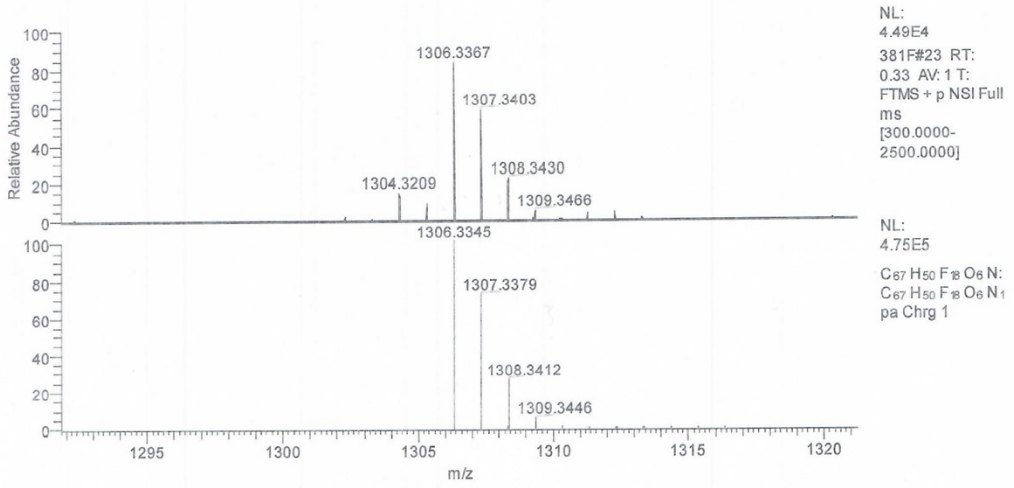
Instrument: Thermo Scientific Q Exactive HF Orbitrap-FTMS

Card Serial Number: EW2021123108

Sample Serial Number: 381F

Operator: WHY Date: 2021/12/31

Operation Mode: AP-MALDI Positive Ion Mode

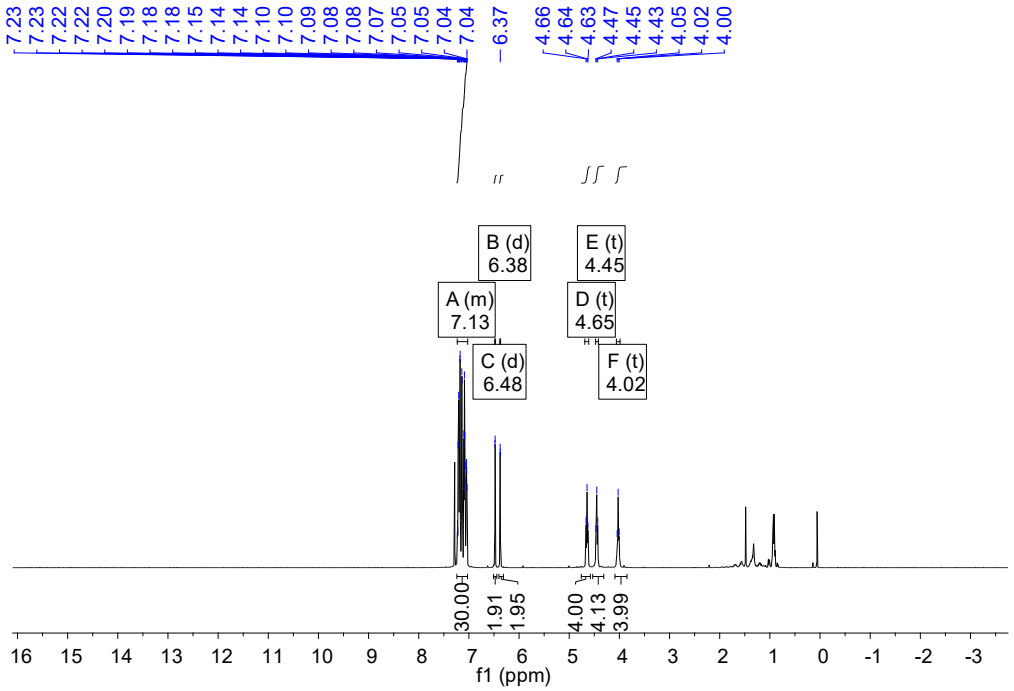


Elemental composition search on mass 1306.3367

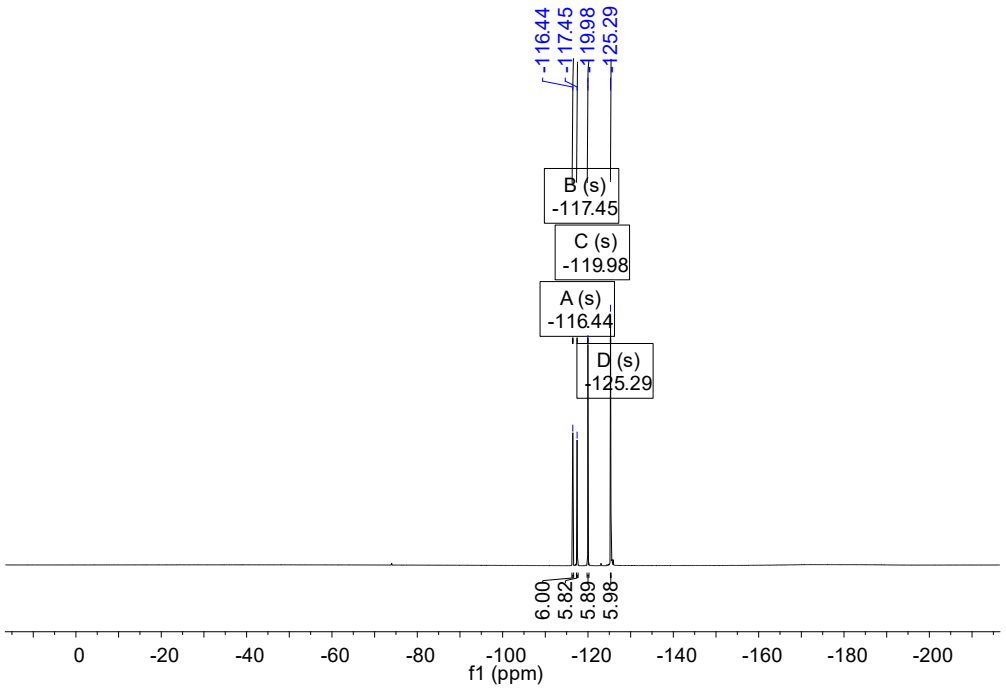
m/z= 1301.3367-1311.3367

m/z	Theo. Mass	Delta (ppm)	RDB equiv.	Composition
1306.3367	1306.3369	-0.17	35.0	$C_{65}H_{49}ON_6ClF_{18}$
	1306.3351	1.22	34.5	$C_{67}H_{50}O_6NF_{18}$

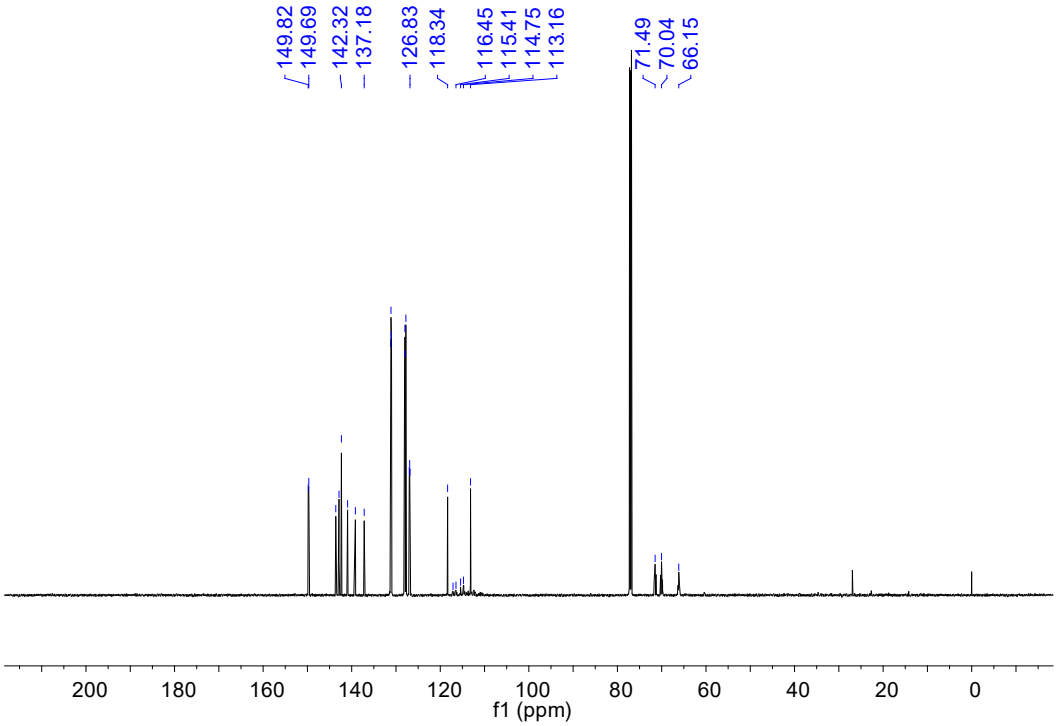
HRMS of compound **361F**



^{1}H-NMR spectrum of compound **381F** ($CDCl_3$, 600MHz)



^{19}F-NMR spectrum of compound **381F** ($CDCl_3$, 600MHz)



^{13}C-NMR spectrum of compound **381F** ($CDCl_3$, 600MHz)

National Center for Organic Mass Spectrometry in Shanghai
Shanghai Institute of Organic Chemistry
Chinese Academic of Sciences
High Resolution AP-MALDI REPORT

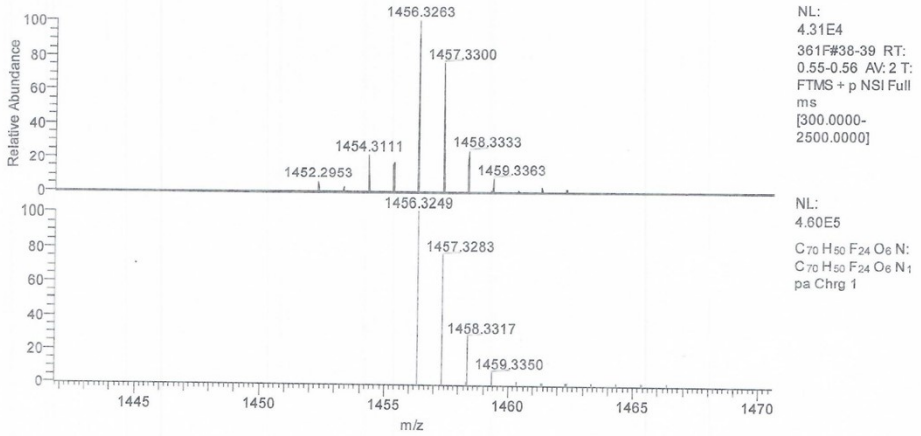
Instrument: Thermo Scientific Q Exactive HF Orbitrap-FTMS

Card Serial Number: EW2021123106

Sample Serial Number: 361F

Operator: WHY Date: 2021/12/31

Operation Mode: AP-MALDI Positive Ion Mode

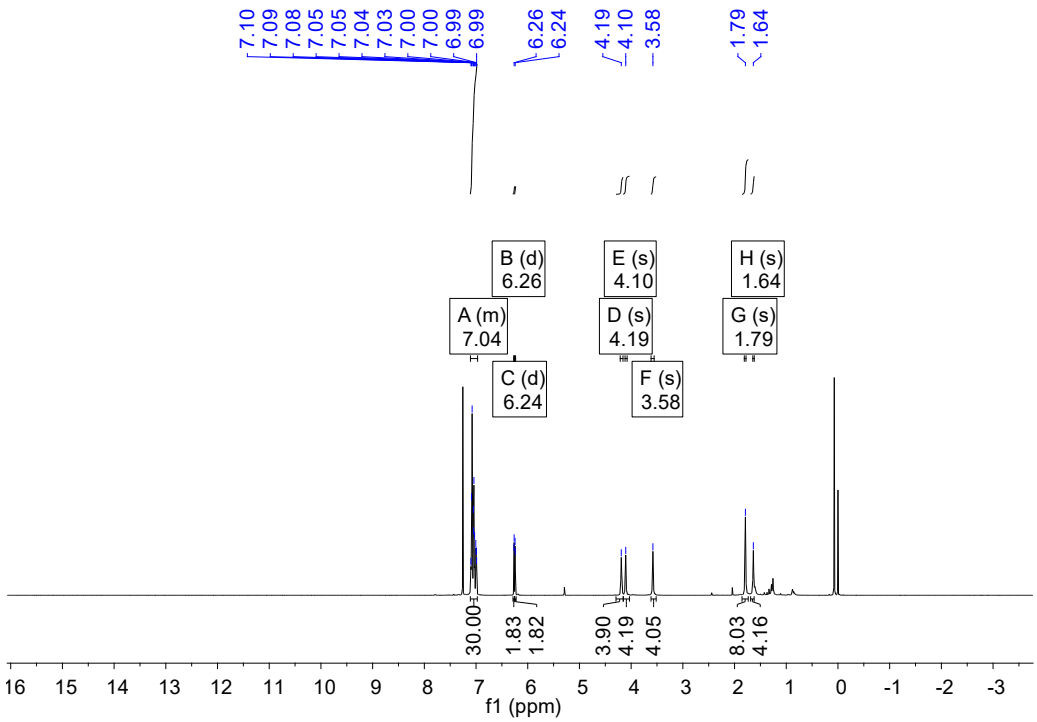


Elemental composition search on mass 1456.3263

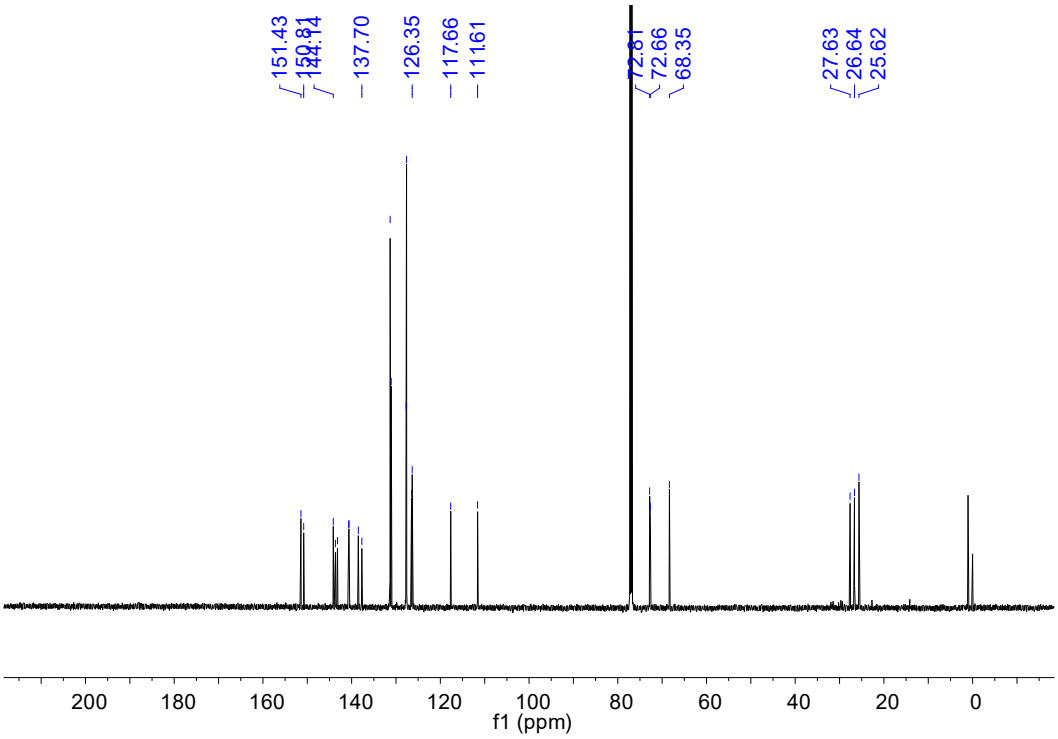
m/z= 1451.3263-1461.3263

m/z	Theo. Mass	Delta (ppm)	RDB equiv.	Composition
1456.3263	1456.3249	0.93	34.5	$C_{70}H_{50}O_6NF_{24}$

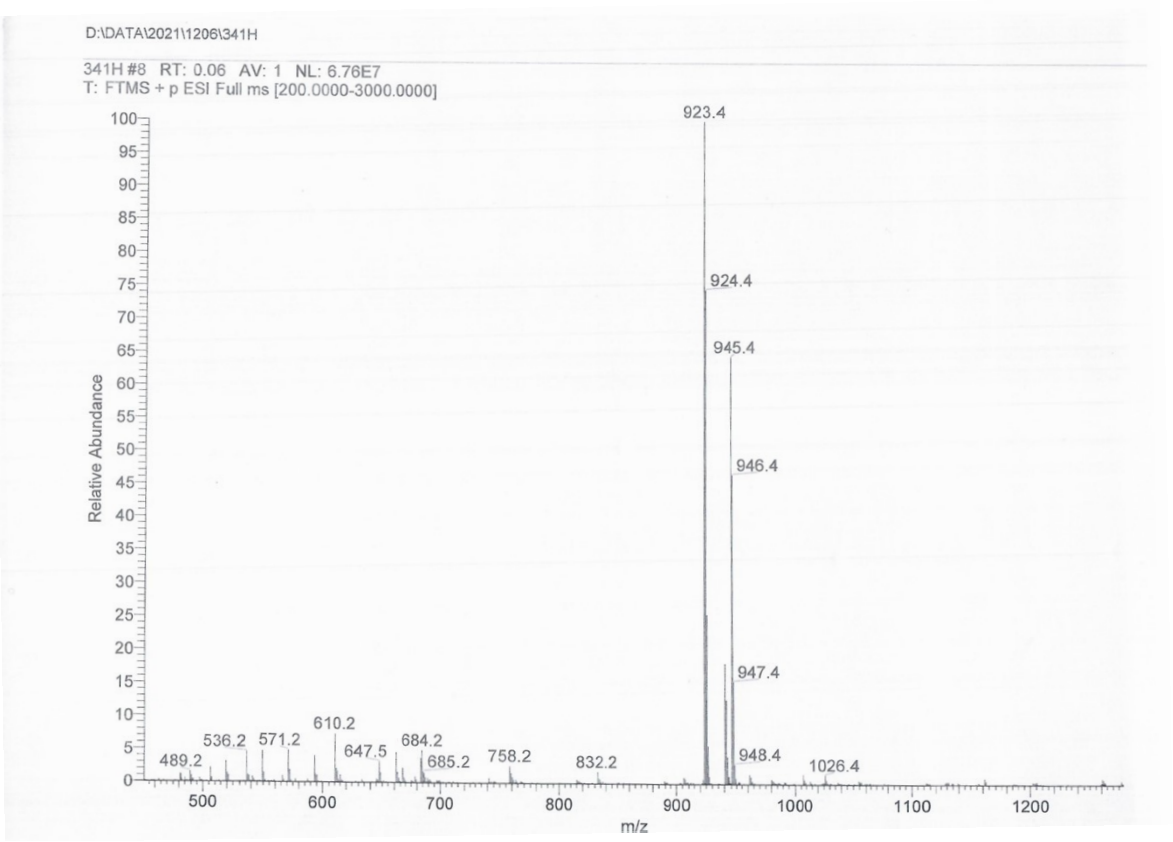
HRMS of compound **381F**



^{1}H-NMR spectrum of compound **341H** ($CDCl_3$, 600MHz)



^{13}C-NMR spectrum of compound **341H** ($CDCl_3$, 600MHz)



Mass spectrum of compound **341H**

National Center for Organic Mass Spectrometry in Shanghai
Shanghai Institute of Organic Chemistry
Chinese Academic of Sciences
High Resolution ESI-MS REPORT

Instrument: Thermo Scientific Q Exactive HF Orbitrap-FTMS

Card Serial Number: E213080

Sample Serial Number: 341H

Operator: Songw Date: 2021/12/06

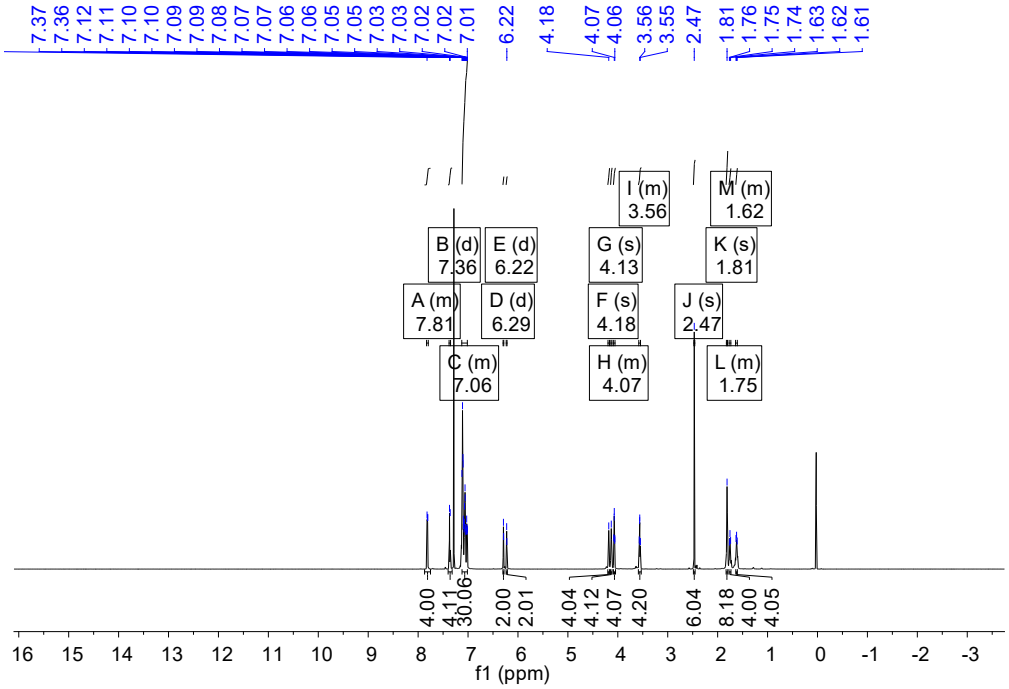
Operation Mode: ESI Positive Ion Mode

Elemental composition search on mass 923.4298

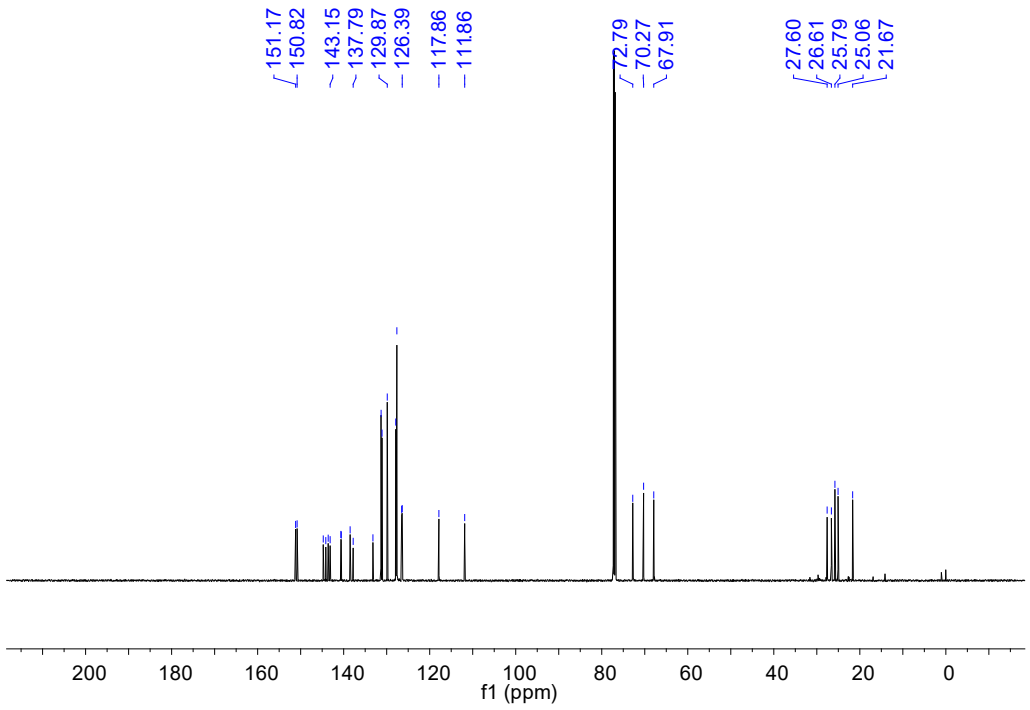
m/z= 918.4298-928.4298

m/z	Theo. Mass	Delta (ppm)	RDB equiv.	Composition
923.4298	923.4306	-0.87	35.5	$C_{64}H_{59}O_6$

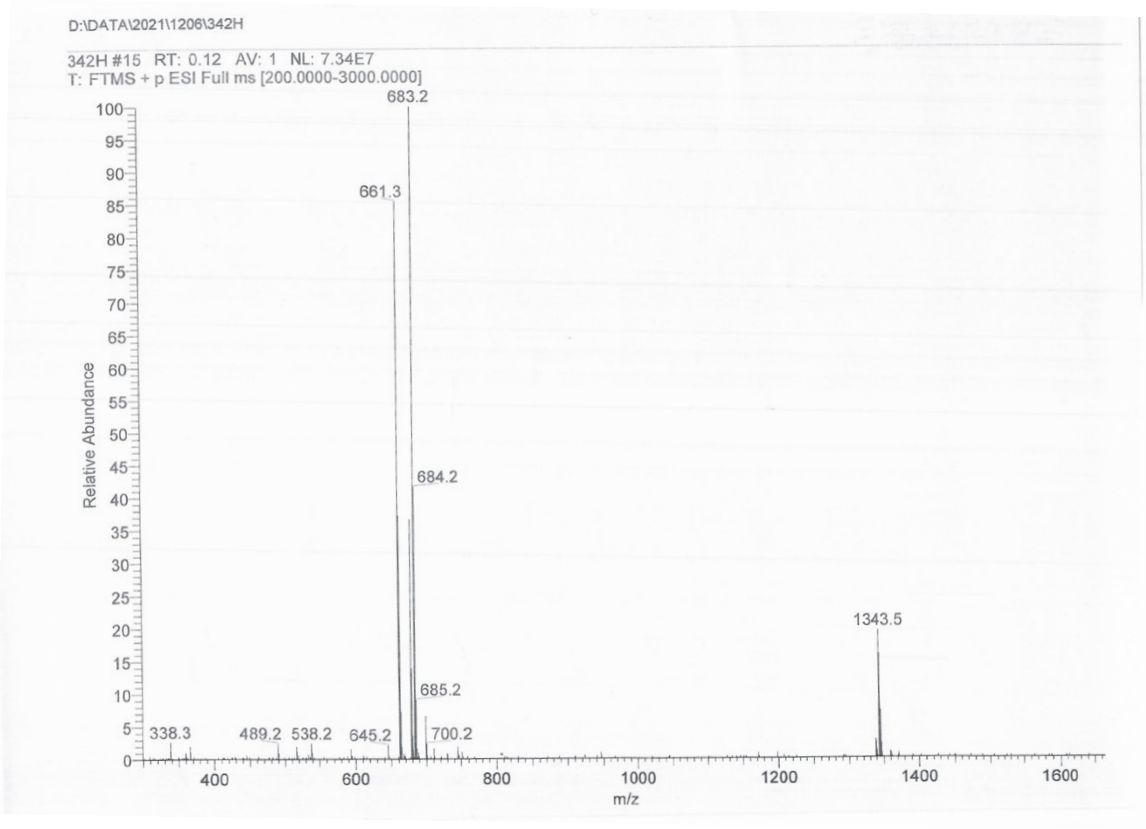
HRMS of compound **341H**



^{1}H-NMR spectrum of compound **342H** ($CDCl_3$, 600MHz)



^{13}C-NMR spectrum of compound **342H** ($CDCl_3$, 600MHz)



Mass spectrum of compound **342H**

National Center for Organic Mass Spectrometry in Shanghai
Shanghai Institute of Organic Chemistry
Chinese Academic of Sciences
High Resolution ESI-MS REPORT

Instrument: Thermo Scientific Q Exactive HF Orbitrap-FTMS

Card Serial Number: E213081

Sample Serial Number: 342H

Operator: Songw Date: 2021/12/06

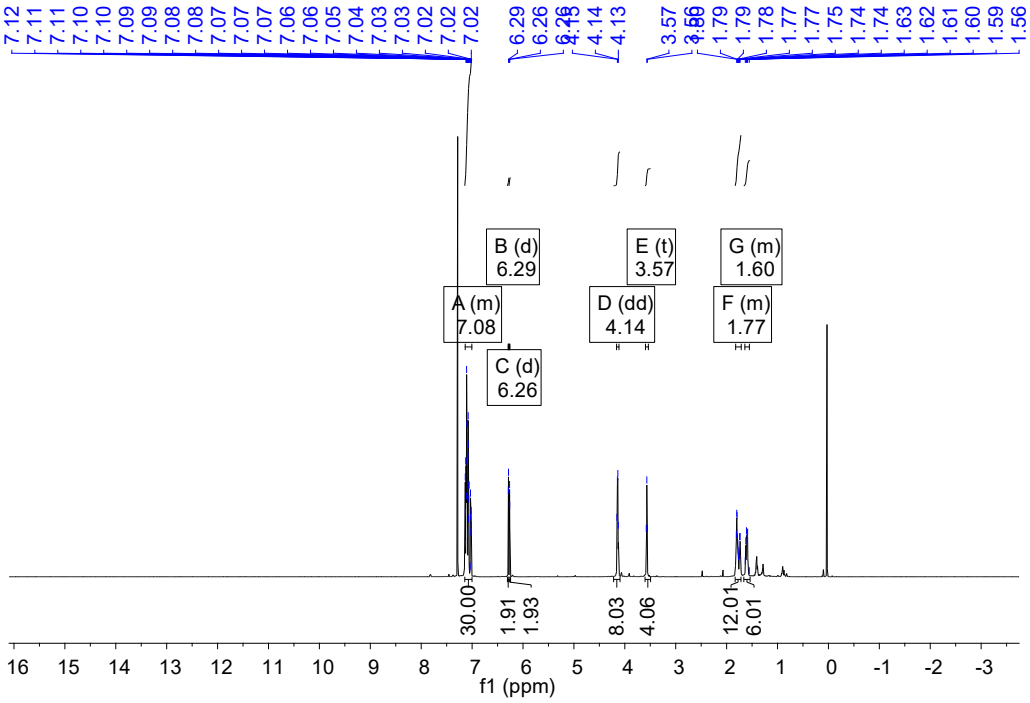
Operation Mode: ESI Positive Ion Mode

Elemental composition search on mass 1343.4966

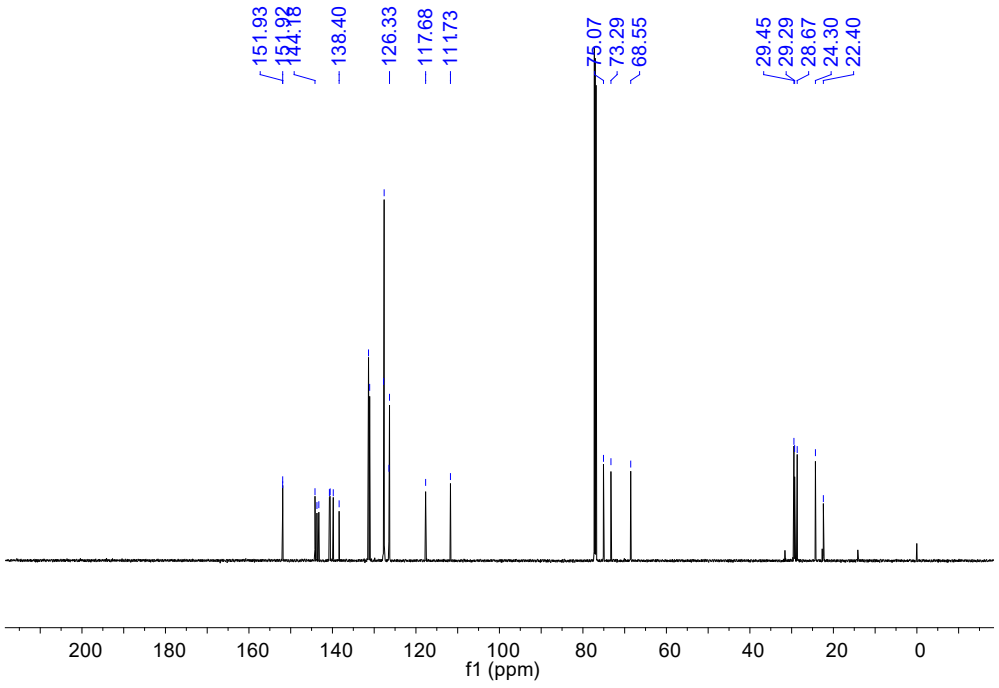
m/z= 1338.4966-1348.4966

m/z	Theo. Mass	Delta (ppm)	RDB equiv.	Composition
1343.4966	1343.4983	-1.31	42.5	$C_{82}H_{80}O_{12}NaS_2$

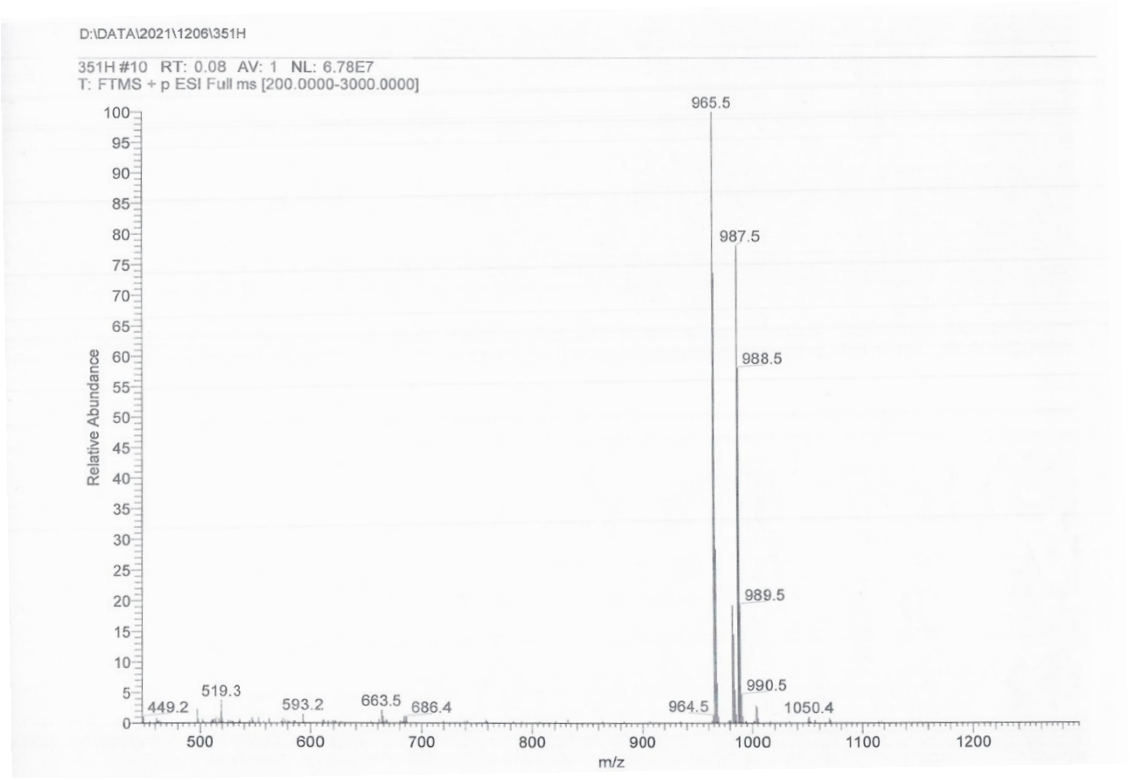
HRMS of compound **342H**



^{1}H-NMR spectrum of compound **361H** ($CDCl_3$, 600MHz)



^{13}C-NMR spectrum of compound **361H** ($CDCl_3$, 600MHz)



Mass spectrum of compound **361H**

National Center for Organic Mass Spectrometry in Shanghai
Shanghai Institute of Organic Chemistry
Chinese Academic of Sciences
High Resolution ESI-MS REPORT

Instrument: Thermo Scientific Q Exactive HF Orbitrap-FTMS

Card Serial Number: E213082

Sample Serial Number: 351H

Operator: Songw Date: 2021/12/06

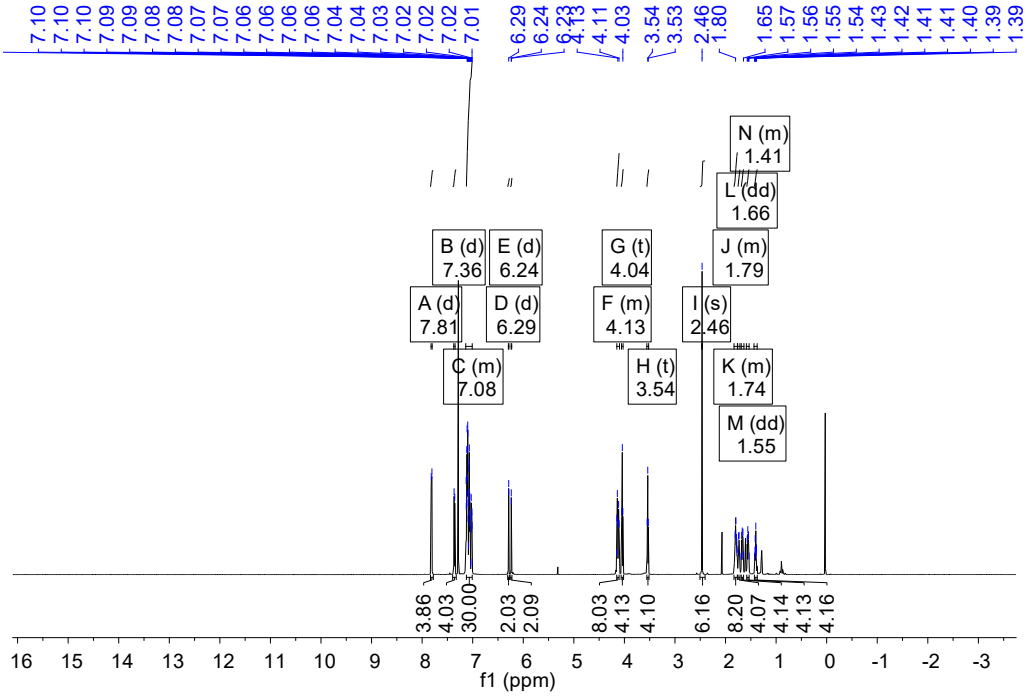
Operation Mode: ESI Positive Ion Mode

Elemental composition search on mass 965.4767

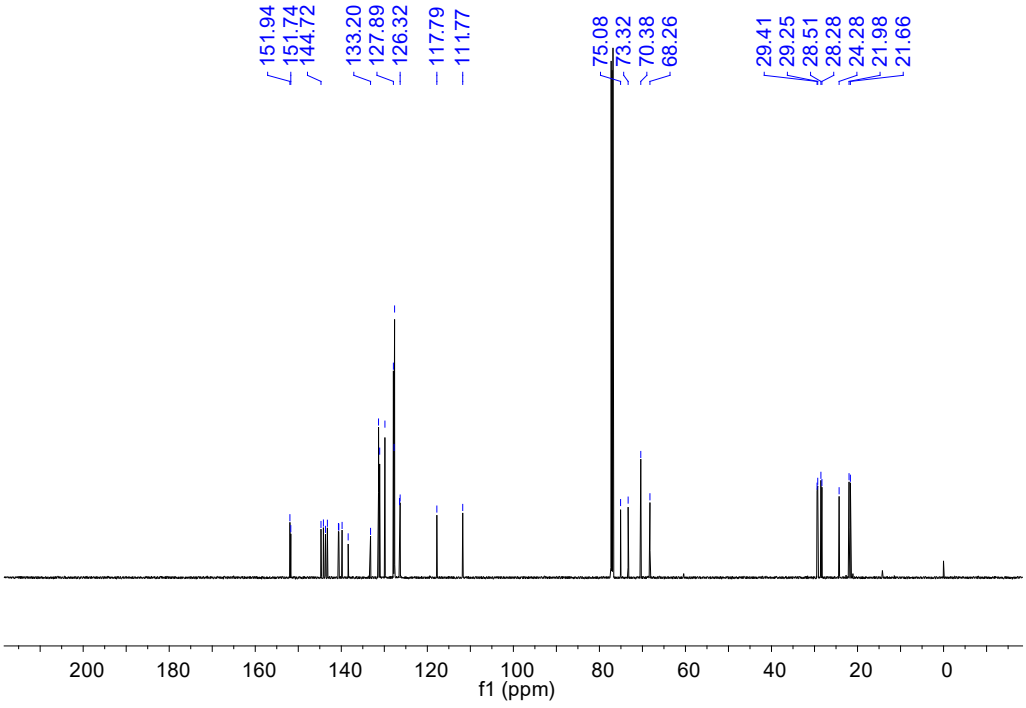
m/z= 960.4767-970.4767

m/z	Theo. Mass	Delta (ppm)	RDB equiv.	Composition
965.4767	965.4776	-0.92	35.5	$C_{67}H_{65}O_6$
	965.4778	-1.20	37.0	$C_{68}H_{64}O_3NNa$
	965.4752	1.57	32.5	$C_{65}H_{66}O_6Na$

HRMS of compound **361H**



^{1}H-NMR spectrum of compound **362H** ($CDCl_3$, 600MHz)



^{13}C-NMR spectrum of compound **362H** ($CDCl_3$, 600MHz)

National Center for Organic Mass Spectrometry in Shanghai
Shanghai Institute of Organic Chemistry
Chinese Academic of Sciences
High Resolution AP-MALDI REPORT

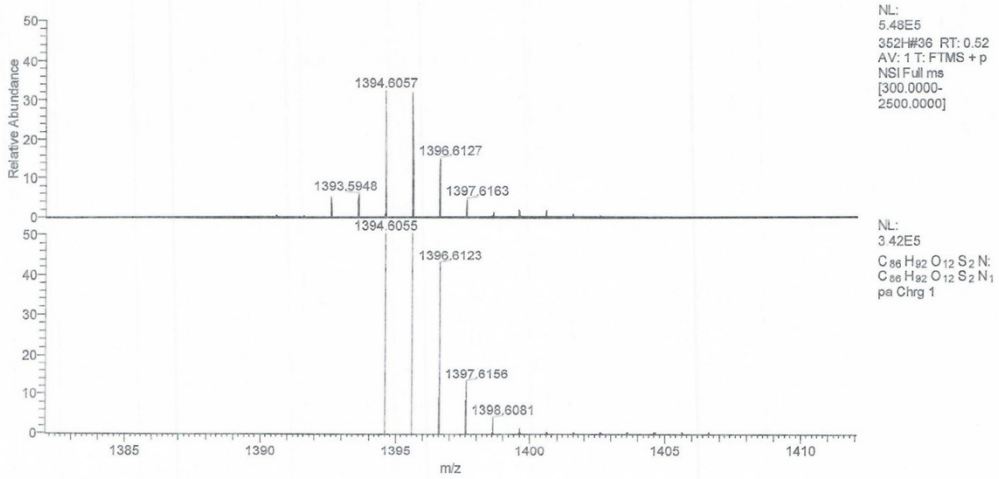
Instrument: Thermo Scientific Q Exactive HF Orbitrap-FTMS

Card Serial Number: EW2021123107

Sample Serial Number: 352H

Operator: WHY Date: 2021/12/31

Operation Mode: AP-MALDI Positive Ion Mode

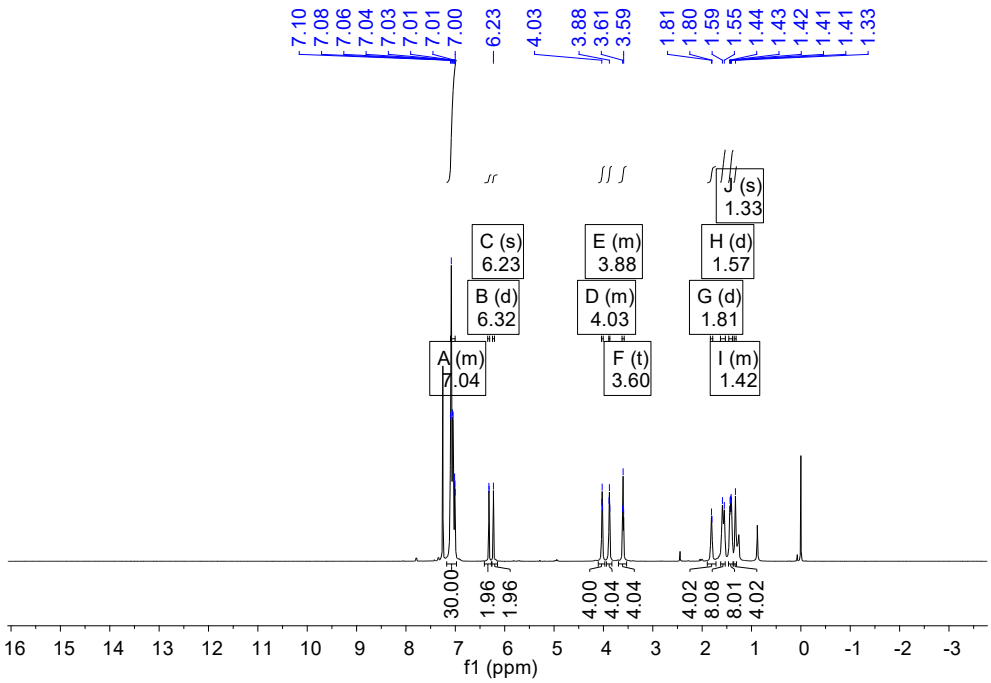


Elemental composition search on mass 1394.6057

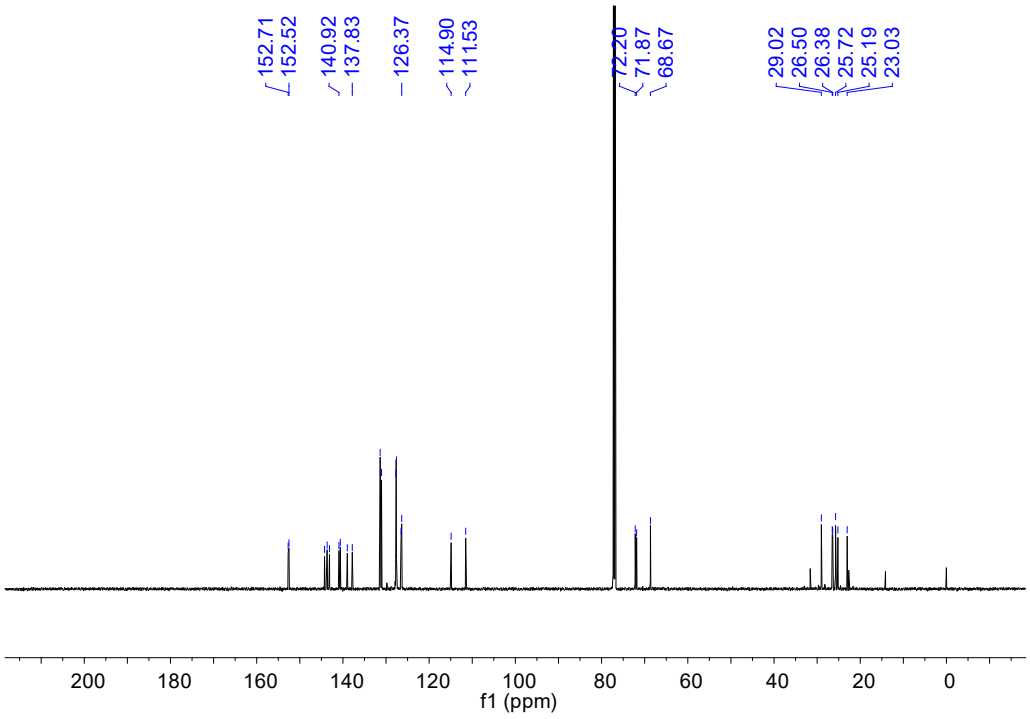
m/z= 1389.6057-1399.6057

m/z	Theo. Mass	Delta (ppm)	RDB equiv.	Composition
1394.6057	1394.6061	-0.27	41.5	$C_{86}H_{92}O_{12}NS_2$

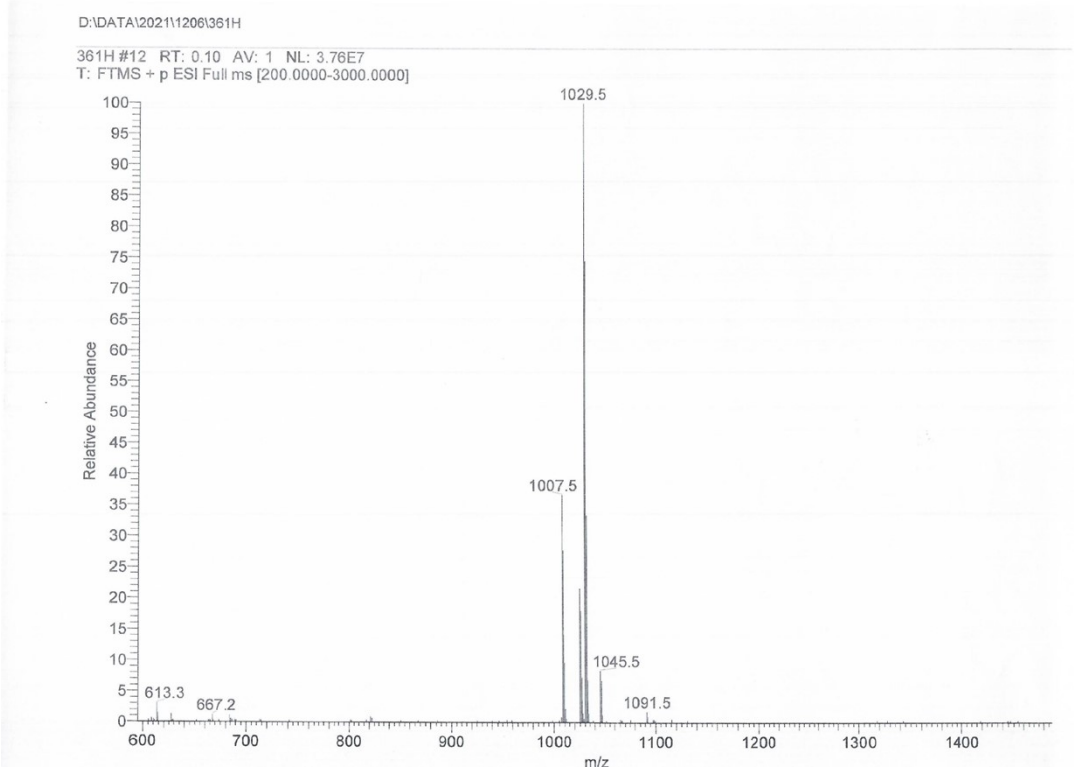
HRMS of compound **362H**



[1]H-NMR spectrum of compound **381H** ($CDCl_3$, 600MHz)



[13]C-NMR spectrum of compound **381H** ($CDCl_3$, 600MHz)



Mass spectrum of compound **381H**

National Center for Organic Mass Spectrometry in Shanghai
Shanghai Institute of Organic Chemistry
Chinese Academic of Sciences
High Resolution ESI-MS REPORT

Instrument: Thermo Scientific Q Exactive HF Orbitrap-FTMS

Card Serial Number: E213084

Sample Serial Number: 361H

Operator: Songw Date: 2021/12/06

Operation Mode: ESI Positive Ion Mode

Elemental composition search on mass 1029.5052

m/z= 1024.5052-1034.5052

m/z	Theo. Mass	Delta (ppm)	RDB equiv.	Composition
1029.5052	1029.5065	-1.18	35.5	$C_{70}H_{70}O_6Na$

HRMS of compound **381H**

References

1. X. Bu, D. Zhu, T. Liu, Y. Li, S. Cai, H. Wang and Z. Zeng, *Dyes Pigm.*, 2017, **145**, 324-330.
2. M. Zhang, J. Guo, T. Liu, Z. He, M. Irfan, Z. Zhao and Z. Zeng, *J. Mater. Chem. C*, 2020, **8**, 14919-14924.