$Sc(OTf)_3$ Catalyzed Dehydrogenative Reaction of Electron-rich (hetero)aryl Nucleophiles with 9-Aryl-fluoren-9-ols

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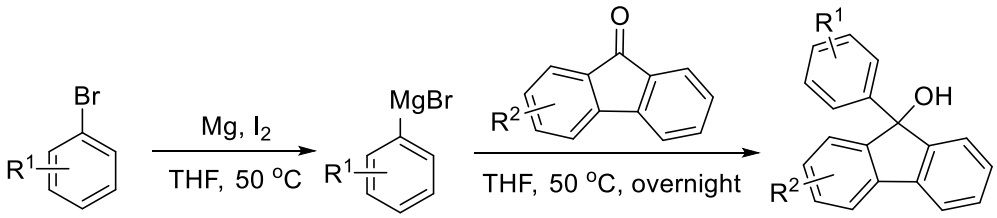
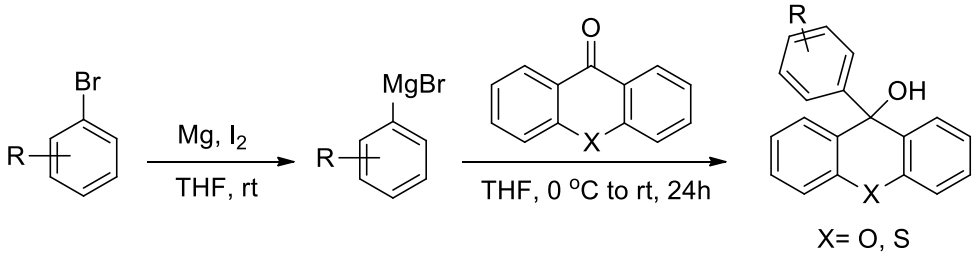
1. General Information

^{1}H NMR,^{13}C NMR and ^{19}F NMR spectra were recorded at 400 MHz, 100 MHz and 376 MHz respectively using tetramethylsilane as an internal reference. Chemical shifts (δ) and coupling constants (J) were expressed in parts per million and hertz, respectively. Melting points were uncorrected. High-resolution mass spectrometry (HRMS) was performed on an ESI-TOF spectrometer. Chemicals were commercially available and used without purification. Chromatography: Column chromatography was performed with silica gel (200-300 mesh ASTM). Emission spectra were recorded on a Shimadzu RF-530XPC luminescence spectrometer upon excitation at the absorption maxima in the degassed CH_2Cl_2 solvent after saturating with argon. Absorption spectra were measured with a Shimadzu UV-3150 spectrometer at 25 ºC. Differential scanning calorimetry (DSC) analyses were performed on a PerkinElmer DSC 8500. Thermogravimetric analyses (TGA) were conducted on a PerkinElmer TGA 8000.

2. Preparation of The Starting Materials



In an over-dried, argon purged round flask, the Grignard solution was prepared from magnesium turnings (15 mmol) reacting with bromobenzene (15 mmol) in anhydrous THF (30 mL). 9-fluorenone (5 mmol) was dissolved in anhydrous THF (15 mL) at room temperature and then added dropwise to Grignard solution. The reaction was allowed to stir overnight at 50 °C. After cooling to room temperature, the reaction was quenched by addition of saturated aqueous ammonium chloride (40 mL) and extracted with dichloromethane (3×40 mL). The combined organic layers were dried over anhydrous Na_2SO_4 and the solvent was evaporated under vacuum, the residue was purified by flash column chromatography on silica gel to give white solid 9-phenyl-fluoren-9-ol.[1]

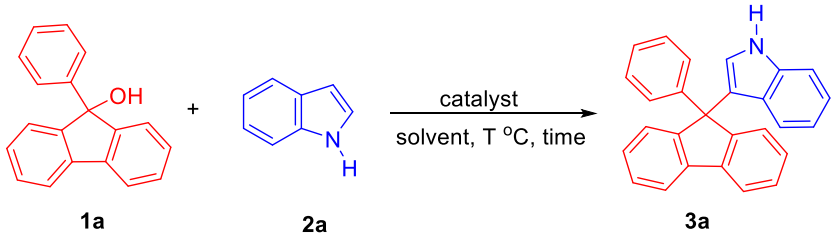


In an over-dried, argon purged round flask, the Grignard solution was prepared from magnesium turnings (15 mmol) reacting with bromobenzene (15 mmol) in anhydrous THF (30 mL). xanthenone (5 mmol) was dissolved in anhydrous THF (15 mL) at room temperature and then added quickly dropwise to Grignard solution which was chilled to 0 °C in an ice-water bath, over 20 min. The mixture was removed from the ice water bath to room temperature and stirred for 24h. After complication, the reaction was quenched by addition of saturated aqueous ammonium chloride (40 mL) and extracted with dichloromethane (3×40 mL). The combined organic layers were dried over anhydrous Na_2SO_4 and the solvent was evaporated under vacuum, the residue was purified by flash column chromatography on silica gel to give white solid xanthen-9-ol.[2]

3. Optimization of The Reaction Conditions

Initially, the recation of 9-phenyl-fluoren-9-ol **1a** and indole **2a** was carried out with 10 mol % $Sc(OTf)_3$ in dichloromethane (DCM) at 60 °C for 12 h (Table S1, entry 1). To our delight, the desired product **3a** was isolated in 97% yield. Then other rare earth Lewis acids were tested in this reaction system, and it was found that $Sc(OTf)_3$ was the most efficient in providing the desired product (Table S1, entries 2-7). Also, $AlCl_3$ and $FeCl_3$ were researched and produced **3a** in 88% and 79% yield respectively (Table S1, entries 8-9). Subsequently, optimization by variation of solvents and temperatures turned out to be futile (Table S1, entries 10-17). Gratifyingly, shortening the reaction time to only 4 h could still afford the product in 97% yield (Table S1, entries 18-20). Further investigation on the reaction conditions revealed that the ratio of **1a** to **2a** (1:1.2) led to a leap in the yield to 99% (Table S1, entry 21-22). Moreover, it was found that the yield remained intact when the catalyst amount was reduced to 2 mol % (Table S1, entry 23-24). Notably, using $BF_3.Et_2O$ or CF_3SO_3H system led to 33% and 9% yields, respectively.[3]

Table S1 Optimization of the reaction conditions [a]



1a 2a 3a

Entry	Catalyst (mol %)	Solvent	T (°C)	Time (h)	Yield[b] (%)
1	$Sc(OTf)_3$ (10)	DCM	60	12	97

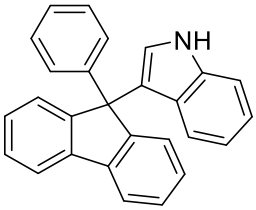
2	$Yb(OTf)_3$ (10)	DCM	60	12	74
3	$Y(OTf)_3$ (10)	DCM	60	12	53
4	$La(OTf)_3$ (10)	DCM	60	12	N.D.
5	$Yb(Pfb)_3$ (10)	DCM	60	12	N.D.
6	$Y(Pfb)_3$ (10)	DCM	60	12	N.D.
7	$Dy(Pfb)_3$ (10)	DCM	60	12	N.D.
8	$AlCl_3$ (10)	DCM	60	12	88
9	$FeCl_3$ (10)	DCM	60	12	79
10	$Sc(OTf)_3$ (10)	CH_3CN	60	12	96
11	$Sc(OTf)_3$ (10)	$CHCl_3$	60	12	94
12	$Sc(OTf)_3$ (10)	DMF	60	12	N.D.
13	$Sc(OTf)_3$ (10)	Toluene	60	12	91
14	$Sc(OTf)_3$ (10)	EtOH	60	12	N.D.
15	$Sc(OTf)_3$ (10)	DCM	80	12	96
16	$Sc(OTf)_3$ (10)	DCM	40	12	86
17	$Sc(OTf)_3$ (10)	DCM	25	12	30
18	$Sc(OTf)_3$ (10)	DCM	60	1	91
19	$Sc(OTf)_3$ (10)	DCM	60	3	95
20	$Sc(OTf)_3$ (10)	DCM	60	4	97
21[c]	$Sc(OTf)_3$ (10)	DCM	60	4	99
22[d]	$Sc(OTf)_3$ (10)	DCM	60	4	87
23[c]	$Sc(OTf)_3$ (2)	DCM	60	4	99
24[c]	$Sc(OTf)_3$ (1)	DCM	60	4	84

[a] Standard reaction conditions: **1a** (0.25 mmol), **2a** (0.25 mmol), Lewis acid (x mol %), and solvent (2 mL), at 60 °C. N.D. = Not Detected [b] Yield of isolated product. [c] **1a** (0.25 mmol), **2a** (0.3 mmol). [d] **1a** (0.25 mmol), **2a** (0.2 mmol)

4. General Procedure A

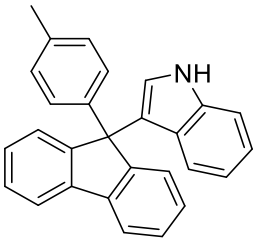
Substituted tertiary alcohols (0.25 mmol, 1 equiv), substituted indoles (0.3 mmol, 1.2 equiv), $Sc(OTf)_3$ (2 mol %), CH_2Cl_2 (2 mL) and a stir bar were added to a sealed tube. After being stirred at 60 °C for 4 h, the mixture was evaporated under vacuum. The desired product was isolated by silica gel column chromatography with an ethyl acetate /petroleum ether mixture as eluent.

3-(9-phenyl-9H-fluoren-9-yl)-1H-indole (3a)



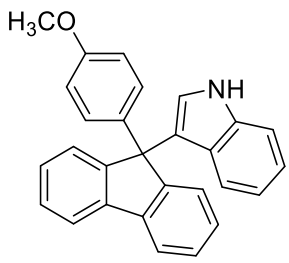
General procedure **A** was followed using 9-phenyl-fluoren-9-ol (64.58 mg, 0.25 mmol), indole (35.15 mg, 0.3 mmol) and $Sc(OTf)_3$ (2.46 mg, 0.005 mmol, 0.02 equiv) in CH_2Cl_2 (2 mL) at 60 ℃ for 4 h. Chromatography (ethyl acetate/ petroleum ether = 2:100) afforded **3a** (88.38 mg, 99% yield) as a white solid (mp 169-171 ℃). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.77 (d, *J* = 7.7 Hz, 3H), 7.54 (d, *J* = 7.6 Hz, 2H), 7.37–7.25 (m, 5H), 7.23–7.16 (m, 5H), 7.14–7.04 (m, 2H), 6.97–6.87 (m, 1H), 6.62 (d, *J* = 2.4 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 151.9, 144.4, 139.8, 137.2, 128.2, 127.6, 127.4, 126.6, 126.4, 125.7, 123.1, 121.9, 121.8, 120.6, 120.5, 120.1, 119.2, 111.3, 60.3; HRMS (ESI-TOF) m/z: $[M - H]^-$ Calcd for $C_{27}H_{18}N$ 356.1439; Found 356.1437.

3-(9-(p-tolyl)-9H-fluoren-9-yl)-1H-indole (3b)



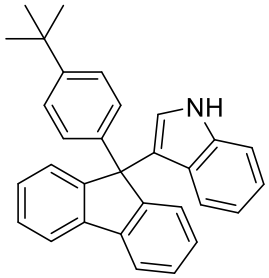
General procedure **A** was followed using 9-(p-tolyl)-9H-fluoren-9-ol (68.09 mg, 0.25 mmol), indole (35.15 mg, 0.3 mmol) and $Sc(OTf)_3$ (2.46 mg, 0.005 mmol, 0.02 equiv) in CH_2Cl_2 (2 mL) at 60 ℃ for 4 h. Chromatography (ethyl acetate: petroleum ether = 2:100) afforded **3b** (88.97 mg, 96% yield) as a white solid (mp 182-184 ℃). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.76 (d, *J* = 8.0 Hz, 3H), 7.53 (d, *J* = 7.6 Hz, 2H), 7.32 (t, *J* = 7.5 Hz, 2H), 7.26 (d, *J* = 8.2 Hz, 1H), 7.22–7.07 (m, 6H), 6.99 (d, *J* = 7.9 Hz, 2H), 6.92 (t, *J* = 7.7 Hz, 1H), 6.62 (s, 1H), 2.27 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 152.1, 141.4, 139.7, 137.2, 136.1, 129.0, 127.6, 127.5, 127.3, 126.5, 125.7, 123.1, 122.0, 121.8, 120.6, 120.0, 119.2, 111.3, 60.0, 21.1; HRMS (ESI-TOF) m/z: $[M - H]^-$ Calcd for $C_{28}H_{20}N$ 370.1596; Found 370.1597.

3-(9-(4-methoxyphenyl)-9H-fluoren-9-yl)-1H-indole (3c)



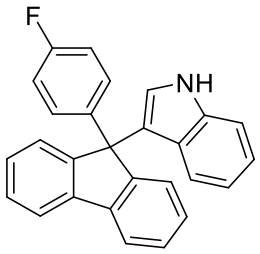
General procedure **A** was followed using 9-(4-methoxyphenyl)-9H-fluoren-9-ol (72.09 mg, 0.25 mmol), indole (35.15 mg, 0.3 mmol) and $Sc(OTf)_3$ (2.46 mg, 0.005 mmol, 0.02 equiv) in CH_2Cl_2 (2 mL) at 60 ℃ for 4 h. Chromatography (ethyl acetate: petroleum ether = 5:100) afforded **3c** (93.80 mg, 97%yield) as a white solid (mp 104-106 ℃). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.79–7.71 (m, 3H), 7.56–7.48 (m, 2H), 7.35–7.29 (m, 2H), 7.25–7.15 (m, 5H), 7.13–7.07 (m, 2H), 6.95–6.90 (m, 1H), 6.75–6.68 (m, 2H), 6.62-6.56 (m, 1H), 3.71 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 158.3, 152.2, 139.7, 137.2, 136.5, 128.7, 127.6, 127.3, 126.5, 125.6, 123.0, 122.0, 121.8, 120.7, 120.1, 119.2, 113.6, 111.3, 59.6, 55.2; HRMS (ESI-TOF) m/z: $[M - H]^-$ Calcd for $C_{28}H_{20}NO$ 386.1545; Found 386.1547.

3-(9-(4-(tert-butyl)phenyl)-9H-fluoren-9-yl)-1H-indole (3d)



General procedure **A** was followed using 9-(4-(tert-butyl)phenyl)-9H-fluoren-9-ol (78.61 mg, 0.25 mmol), indole (35.15 mg, 0.3 mmol) and $Sc(OTf)_3$ (2.46 mg, 0.005 mmol, 0.02 equiv) in CH_2Cl_2 (2 mL) at 60 ℃ for 4 h. Chromatography (ethyl acetate: petroleum ether = 2:100) afforded **3d** (93.85 mg, 91%yield) as a white solid (mp 103-105 ℃). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.70 (d, J = 7.7 Hz, 3H), 7.47 (d, J = 7.6 Hz, 2H), 7.26 (t, J = 7.6 Hz, 2H), 7.22–7.19 (m, 1H), 7.16–7.10 (m, 6H), 7.06–7.00 (m, 1H), 6.95–6.90 (m, 1H), 6.86–6.80 (m, 1H), 6.63–6.59 (m, 1H), 1.18 (t, J = 0.9 Hz, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 152.1, 149.3, 141.2, 139.8, 137.1, 127.5, 127.3, 127.2, 126.5, 125.9, 125.1, 123.2, 121.9, 121.8, 120.7, 120.0, 119.1, 111.3, 59.9, 34.4, 31.4. HRMS (ESI-TOF) m/z: $[M - H]^-$ Calcd for $C_{31}H_{26}N$ 412.2065; Found 412.2064.

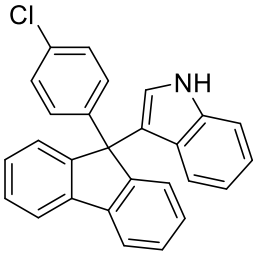
3-(9-(4-fluorophenyl)-9H-fluoren-9-yl)-1H-indole (3e)



General procedure **A** was followed using 9-(4-fluorophenyl)-9H-fluoren-9-ol (69.08 mg, 0.25 mmol), indole (35.15 mg, 0.3 mmol) and $Sc(OTf)_3$ (2.46 mg, 0.005 mmol, 0.02 equiv) in CH_2Cl_2 (2 mL) at 60 ℃ for 4 h. Chromatography (ethyl acetate: petroleum ether = 2:100) afforded **3e** (82.80 mg, 88% yield) as a white solid (mp 188-190 ℃).^{1}H NMR (400 MHz, $CDCl_3$) δ 7.78 (t, J = 7.4 Hz, 3H), 7.52 (d, J = 7.6 Hz, 2H), 7.34 (t, J = 7.5 Hz, 2H), 7.28 (d, J = 8.2 Hz, 1H), 7.24–7.06 (m, 6H), 6.95 (t, J =

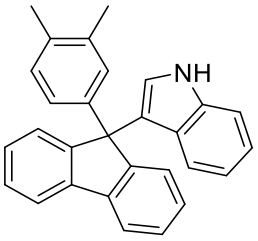
7.6 Hz, 1H), 6.91–6.82 (m, 2H), 6.61 (d, J = 2.5 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 163.0 (d, $J_{C\text{-}F}$ = 243.4 Hz), 151.8, 140.2, 139.7, 137.2, 129.2 (d, $J_{C\text{-}F}$ = 7.8 Hz), 127.7, 127.5, 126.3, 125.6, 123.0, 122.0 (d, $J_{C\text{-}F}$ = 13.2 Hz), 120.3, 120.2, 119.3, 115.1, 114.9, 111.4, 59.7; ^{19}F NMR (376 MHz, $CDCl_3$) δ -116.68; HRMS (ESI-TOF) m/z: $[M - H]^-$ Calcd for $C_{27}H_{17}NF$ 374.1345; Found 374.1346.

3-(9-(4-chlorophenyl)-9H-fluoren-9-yl)-1H-indole (3f)



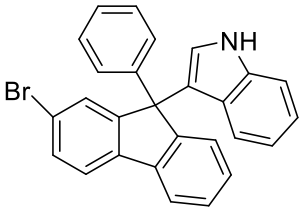
General procedure **A** was followed using 9-(4-chlorophenyl)-9H-fluoren-9-ol (73.19 mg, 0.25 mmol), indole (35.15 mg, 0.3 mmol) and $Sc(OTf)_3$ (2.46 mg, 0.005 mmol, 0.02 equiv) in CH_2Cl_2 (2 mL) at 60 ℃ for 4 h. Chromatography (ethyl acetate/ petroleum ether = 2:100) afforded **3f** (87.35 mg, 89% yield) as a white solid (mp 82-84 °C). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.78–7.67 (m, 3H), 7.44 (d, J = 7.6 Hz, 2H), 7.30–7.20 (m, 3H), 7.16–7.02 (m, 8H), 6.93–6.86 (m, 1H), 6.55 (d, J = 2.5 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 150.4, 142.0, 138.6, 136.2, 131.4, 128.0, 127.3, 126.7, 126.5, 125.2, 124.5, 122.0, 120.9, 120.7, 119.1, 118.9, 118.3, 110.4, 58.7; HRMS (ESI-TOF) m/z: $[M - H]^-$ Calcd for $C_{27}H_{17}NCl$ 390.1050; Found 390.1049.

3-(9-(3,4-dimethylphenyl)-9H-fluoren-9-yl)-1H-indole (3g)



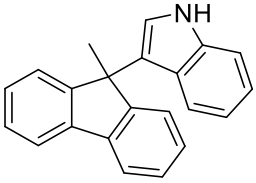
General procedure **A** was followed using 9-(3,4-dimethylphenyl)-9H-fluoren-9-ol (71.59 mg, 0.25 mmol), indole (35.15 mg, 0.3 mmol) and $Sc(OTf)_3$ (2.46 mg, 0.005 mmol, 0.02 equiv) in CH_2Cl_2 (2 mL) at 60 ℃ for 4 h. Chromatography (ethyl acetate: petroleum ether = 2:100) afforded **3g** (94.50 mg, 98% yield) as a white solid (mp 116-118 ℃).^{1}H NMR (400 MHz, $CDCl_3$) δ 7.76 (d, J = 7.2 Hz, 3H), 7.53 (d, J = 7.6 Hz, 2H), 7.32 (t, J = 7.5 Hz, 2H), 7.26–7.16 (m, 3H), 7.13–7.03 (m, 3H), 7.00–6.88 (m, 3H), 6.63 (t, J = 2.0 Hz, 1H), 2.18 (s, 3H), 2.09 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 152.2, 141.7, 139.7, 137.2, 136.3, 134.8, 129.5, 128.5, 127.6, 127.3, 126.6, 125.7, 125.3, 123.0, 122.0, 121.8, 120.8, 120.0, 119.1, 111.3, 60.0, 20.0, 19.4; HRMS (ESI-TOF) m/z: $[M - H]^-$ Calcd for $C_{29}H_{22}N$ 384.1752; Found 384.1753.

3-(2-bromo-9-phenyl-9H-fluoren-9-yl)-1H-indole (3h)



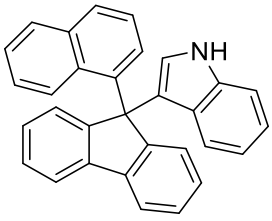
General procedure **A** was followed using 2-bromo-9-phenyl-9H-fluoren-9-ol (84.30 mg, 0.25 mmol), indole (35.15 mg, 0.3 mmol) and $Sc(OTf)_3$ (2.46 mg, 0.005 mmol, 0.02 equiv) in CH_2Cl_2 (2 mL) at 60 ℃ for 4 h. Chromatography (ethyl acetate/ petroleum ether = 3:100) afforded **3h** (62.07 mg, 57% yield) as a white solid (mp 97-99 ℃). ^{1}H NMR (400 MHz, DMSO-d_6) δ 10.99 (s, 1H), 8.10–7.87 (m, 2H), 7.64–7.54 (m, 2H), 7.49 (d, J = 7.6 Hz, 1H), 7.44–7.35 (m, 2H), 7.32–7.21 (m, 6H), 7.07–6.99 (m, 1H), 6.85–6.77 (m, 1H), 6.76–6.66 (m, 2H); ^{13}C NMR (100 MHz, DMSO-d_6) δ 159.0, 156.5, 148.9, 143.9, 143.3, 142.5, 135.8, 133.7, 133.4, 133.3, 132.9, 132.3, 132.1, 130.8, 130.6, 129.0, 127.7, 126.3, 126.0, 125.6, 125.5, 123.8, 122.8, 117.3, 65.2; HRMS (ESI-TOF) m/z: $[M - H]^-$ Calcd for $C_{27}H_{17}NBr$ 434.0544; Found 434.0545.

3-(9-methyl-9H-fluoren-9-yl)-1H-indole (3i)



General procedure **A** was followed using 9-methyl-9H-fluoren-9-ol (49.06 mg, 0.25 mmol), indole (35.15 mg, 0.3 mmol) and $Sc(OTf)_3$ (2.46 mg, 0.005 mmol, 0.02 equiv) in CH_2Cl_2 (2 mL) at 60 ℃ for 4 h. Chromatography (ethyl acetate/ petroleum ether = 2:100) afforded **3i** (55.50 mg, 75% yield) as a white solid (mp 180-182 ℃). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.95–7.76 (m, 3H), 7.38–7.30 (m, 3H), 7.24–7.14 (m, 5H), 6.97 (t, J = 7.6 Hz, 1H), 6.63 (t, J = 7.6 Hz, 1H), 6.30 (d, J = 8.1 Hz, 1H), 1.87 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 153.1, 139.6, 136.8, 127.6, 127.2, 125.6, 124.0, 121.8, 121.7, 120.2, 120.1, 120.0, 119.2, 110.8, 50.3, 26.7; HRMS (ESI-TOF) m/z: $[M - H]^-$ Calcd for $C_{22}H_{16}N$ 294.1283; Found 294.1281.

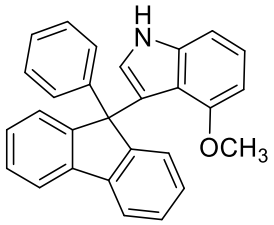
3-(9-(naphthalen-1-yl)-9H-fluoren-9-yl)-1H-indole (3j)



General procedure **A** was followed using 9-(naphthalen-1-yl)-9H-fluoren-9-ol (77.10 mg, 0.25 mmol), indole (35.15 mg, 0.3 mmol) and $Sc(OTf)_3$ (2.46 mg, 0.005 mmol, 0.02 equiv) in CH_2Cl_2 (2 mL) at 60 ℃ for 4 h. Chromatography (ethyl acetate/ petroleum ether = 2:100) afforded **3j** (96.67 mg, 95% yield) as a white solid (mp 120-

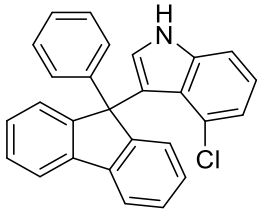
122 ℃). ^{1}H NMR (400 MHz, DMSO-d_6) δ 10.88 (s, 1H), 8.02 (d, J = 7.6 Hz, 2H), 7.93–7.46 (m, 5H), 7.42–7.14 (m, 9H), 7.06–6.96 (m, 2H), 6.86–6.77 (m, 1H), 6.50–6.28 (m, 1H); ^{13}C NMR (100 MHz, DMSO-d_6) δ 144.1, 142.6, 139.8, 134.1, 133.9, 133.7, 133.6, 133.6, 132.8, 132.7, 131.1, 130.3, 130.2 (2C), 130.1 (2C), 130.0 (2C), 126.3, 126.1 (2C), 125.1, 123.7, 117.3, 66.1; HRMS (ESI-TOF) m/z: [M - H]$^-$ Calcd for $C_{31}H_{20}N$ 406.1596; Found 406.1597.

4-methoxy-3-(9-phenyl-9H-fluoren-9-yl)-1H-indole (3k)



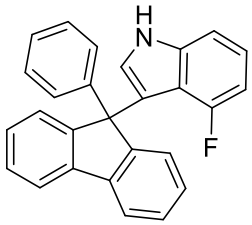
General procedure **A** was followed using 9-phenyl-9H-fluoren-9-ol (64.58 mg, 0.25 mmol), 4-methoxy-1H-indole (44.15 mg, 0.3 mmol) and $Sc(OTf)_3$ (2.46 mg, 0.005 mmol, 0.02 equiv) in CH_2Cl_2 (2 mL) at 60 ℃ for 4 h. Chromatography (ethyl acetate/ petroleum ether = 2:100) afforded **3k** (69.56 mg, 72% yield) as a white solid (mp 96-98 ℃). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.89–7.57 (m, 5H), 7.31 (t, J = 7.5 Hz, 2H), 7.24–7.06 (m, 8H), 6.91 (d, J = 8.1 Hz, 1H), 6.43 (d, J = 7.1 Hz, 2H), 3.24 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 153.6, 152.4, 147.6, 139.9, 139.2, 127.7, 127.6, 127.0, 126.7, 126.2, 125.4, 123.0, 122.3, 120.4, 119.8, 117.0, 104.5, 100.7, 60.7, 54.4; HRMS (ESI-TOF) m/z: [M - H]$^-$ Calcd for $C_{28}H_{20}NO$ 386.1545; Found 386.1543.

4-chloro-3-(9-phenyl-9H-fluoren-9-yl)-1H-indole (3l)



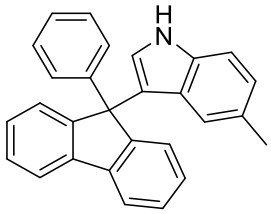
General procedure **A** was followed using 9-phenyl-9H-fluoren-9-ol (64.58 mg, 0.25 mmol), 4-chloro-1H-indole (45.48 mg, 0.3 mmol) and $Sc(OTf)_3$ (2.46 mg, 0.005 mmol, 0.02 equiv) in CH_2Cl_2 (2 mL) at 60 ℃ for 4 h. Chromatography (ethyl acetate/ petroleum ether = 2:100) afforded **3l** (95.91 mg, 98% yield) as a white solid (mp 258-260 ℃). ^{1}H NMR (400 MHz, DMSO-d_6) δ 11.32 (s, 1H), 7.92 (d, J = 7.5 Hz, 2H), 7.73–7.64 (m, 1H), 7.45–7.32 (m, 4H), 7.29 (t, J = 7.4 Hz, 2H), 7.22–6.97 (m, 7H), 6.71–6.60 (m, 1H); ^{13}C NMR (100 MHz, DMSO-d_6) δ 151.8, 147.2, 139.6, 139.1, 128.2, 127.7, 127.3, 126.3 (2C), 126.1, 125.6, 124.3, 122.6, 122.0, 121.2, 120.3, 117.7, 111.3, 60.3; HRMS (ESI-TOF) m/z: [M - H]$^-$ Calcd for $C_{27}H_{17}NCl$ 390.1050; Found 390.1051.

4-fluoro-3-(9-phenyl-9H-fluoren-9-yl)-1H-indole (3m)



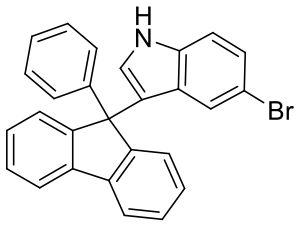
General procedure **A** was followed using 9-phenyl-9H-fluoren-9-ol (64.58 mg, 0.25 mmol), 4-fluoro-1H-indole (40.54 mg, 0.3 mmol) and $Sc(OTf)_3$ (2.46 mg, 0.005 mmol, 0.02 equiv) in CH_2Cl_2 (2 mL) at 60 ℃ for 4 h. Chromatography (ethyl acetate/ petroleum ether = 2:100) afforded **3m** (92.69 mg, 99% yield) as a white solid (mp 228-230 ℃). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.86–7.74 (m, 3H), 7.59 (d, J = 7.6 Hz, 2H), 7.34 (td, J = 7.5, 1.1 Hz, 2H), 7.26–7.22 (m, 2H), 7.21–7.14 (m, 5H), 7.10–7.05 (m, 2H), 6.73–6.66 (m, 1H), 6.52 (d, J = 2.6 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 156.0 (d, $J_{C\text{-}F}$ = 246.1 Hz), 151.8, 145.8 (d, $J_{C\text{-}F}$ = 3.4 Hz), 140.2 (d, $J_{C\text{-}F}$ = 11.1 Hz), 139.8, 128.1, 127.8, 127.4, 126.6, 126.3, 126.0 (d, $J_{C\text{-}F}$ = 5.4 Hz), 123.4, 122.9 (d, $J_{C\text{-}F}$ = 8.0 Hz), 120.1, 119.3 (d, $J_{C\text{-}F}$ = 4.0 Hz), 115.2 (d, $J_{C\text{-}F}$ = 19.5 Hz), 107.5 (d, $J_{C\text{-}F}$ = 3.6 Hz), 105.6 (d, $J_{C\text{-}F}$ = 21.4 Hz), 60.2; ^{19}F NMR (376 MHz, $CDCl_3$) δ -111.69; HRMS (ESI-TOF) m/z: $[M - H]^-$ Calcd for $C_{27}H_{17}NF$ 374.1345; Found 374.1347.

5-methyl-3-(9-phenyl-9H-fluoren-9-yl)-1H-indole (3n)



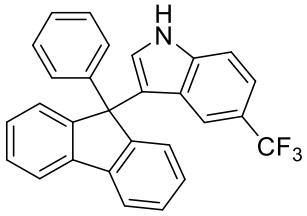
General procedure **A** was followed using 9-phenyl-9H-fluoren-9-ol (64.58 mg, 0.25 mmol), 5-methyl-1H-indole (39.35 mg, 0.3 mmol) and $Sc(OTf)_3$ (2.46 mg, 0.005 mmol, 0.02 equiv) in CH_2Cl_2 (2 mL) at 60 ℃ for 4 h. Chromatography (ethyl acetate/ petroleum ether = 1:100) afforded **3n** (87.15 mg, 94% yield) as a white solid (mp 137-139 ℃). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.80–7.67 (m, 3H), 7.56–7.51 (m, 2H), 7.34 (td, J = 7.5, 1.1 Hz, 2H), 7.29–7.22 (m, 3H), 7.21–7.17 (m, 5H), 6.98–6.93 (m, 1H), 6.85–6.81 (m, 1H), 6.61 (d, J = 2.5 Hz, 1H), 2.28 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 152.0, 144.4, 139.8, 135.6, 131.5, 130.8, 129.8, 128.2, 127.6, 127.3, 126.7, 126.6, 125.8, 123.5, 123.2, 121.6, 120.0, 111.0, 60.3, 21.7; HRMS (EI) Calcd for $C_{28}H_{21}N$ $[M]^+$ m/z: 371.1674; Found 371.1678.

5-bromo-3-(9-phenyl-9H-fluoren-9-yl)-1H-indole (3o)



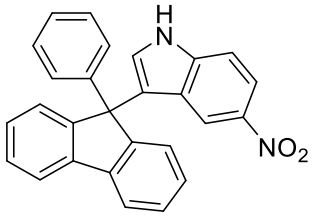
General procedure **A** was followed using 9-phenyl-9H-fluoren-9-ol (64.58 mg, 0.25 mmol), 5-bromo-1H-indole (58.81 mg, 0.3 mmol) and $Sc(OTf)_3$ (2.46 mg, 0.005 mmol, 0.02 equiv) in CH_2Cl_2 (2 mL) at 60 ℃ for 4 h. Chromatography (ethyl acetate/ petroleum ether = 2:100) afforded **3o** (99.15 mg, 91% yield) as a white solid (mp 220-222 ℃).^{1}H NMR (400 MHz, $CDCl_3$) δ 7.88–7.72 (m, 3H), 7.49 (d, *J* = 7.6 Hz, 2H), 7.35 (t, *J* = 7.6 Hz, 2H), 7.26–7.18 (m, 8H), 7.13 (d, *J* = 7.5 Hz, 2H), 6.63 (s, 1H);^{13}C NMR (100 MHz, $CDCl_3$) δ 151.5, 143.8, 139.7, 135.8, 128.4, 128.2, 127.7, 127.5, 127.4, 126.9, 125.6, 124.8, 124.3, 124.2, 120.4, 120.2, 112.7, 112.6, 60.1; HRMS (ESI-TOF) m/z: $[M - H]^-$ Calcd for $C_{27}H_{17}N^{81}Br$ 436.0524; Found 436.0526.

3-(9-phenyl-9H-fluoren-9-yl)-5-(trifluoromethyl)-1H-indole (3p)



General procedure **A** was followed using 9-phenyl-9H-fluoren-9-ol (64.58 mg, 0.25 mmol), 5-(trifluoromethyl)-1H-indole (55.54 mg, 0.3 mmol) and $Sc(OTf)_3$ (2.46 mg, 0.005 mmol, 0.02 equiv) in CH_2Cl_2 (2 mL) at 60 ℃ for 4 h. Chromatography (ethyl acetate/ petroleum ether = 2:100) afforded **3p** (105.63 mg, 99% yield) as a white solid (mp 249-251 ℃). ^{1}H NMR (400 MHz, DMSO-d_6) δ 11.44 (s, 1H), 8.00–7.95 (m, 2H), 7.55 (d, *J* = 8.5 Hz, 1H), 7.46 (d, *J* = 7.6 Hz, 2H), 7.44–7.39 (m, 2H), 7.32–7.26 (m, 8H), 6.96 (d, *J* = 2.5 Hz, 1H), 6.87 (s, 1H); ^{13}C NMR (100 MHz, DMSO-d_6) δ 151.1, 144.1, 139.2, 138.5, 128.3, 127.7, 127.6, 127.1, 126.8, 126.6 (q, $J_{C\text{-}F}$ = 269.5), 126.1, 125.4, 124.9, 120.5, 119.7, 119.3 (q, $J_{C\text{-}F}$ = 30.5), 117.5, 117.3, 112.7, 59.5. ^{19}F NMR (376 MHz, DMSO-d_6) δ -58.78; HRMS (ESI-TOF) m/z: $[M - H]^-$ Calcd for $C_{28}H_{17}NF_3$ 424.1313; Found 424.1312.

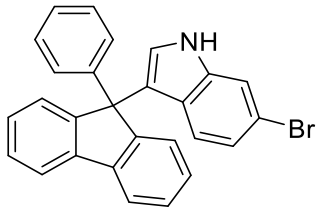
5-nitro-3-(9-phenyl-9H-fluoren-9-yl)-1H-indole(3q)



General procedure **A** was followed using 9-phenyl-9H-fluoren-9-ol (64.58 mg, 0.25 mmol), 5-nitro-1H-indole (48.64 mg, 0.3 mmol) and $Sc(OTf)_3$ (2.46 mg, 0.005 mmol, 0.02 equiv) in CH_2Cl_2 (2 mL) at 60 °C for 4 h. Chromatography (dichloromethane/ petroleum ether = 2:5) afforded **3q** (99.59 mg, 99% yield) as a yellow solid (mp 268-270 °C). ^{1}H NMR (400 MHz, DMSO-d_6) δ 11.73 (s, 1H), 7.99 (d, *J* = 7.5 Hz, 2H), 7.97–7.89 (m, 1H), 7.60–7.47 (m, 4H), 7.46–7.39 (m, 2H), 7.34–7.25 (m, 7H), 7.05 (d, *J* = 2.5 Hz, 1H); ^{13}C NMR (100 MHz, DMSO-d_6) δ 150.6, 143.9, 140.3, 140.1, 139.2, 128.5, 127.9, 127.8, 127.6, 127.1, 127.0, 125.4, 124.9, 121.4, 120.6,

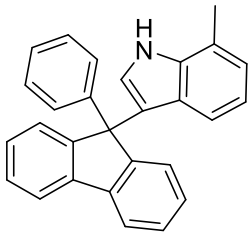
117.2, 116.4, 112.4, 59.4; HRMS (ESI-TOF) m/z: [M - H]$^-$ Calcd for $C_{27}H_{17}N_2O_2$ 401.1290; Found 401.1291

6-bromo-3-(9-phenyl-9H-fluoren-9-yl)-1H-indole (3r)



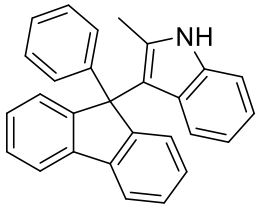
General procedure **A** was followed using 9-phenyl-9H-fluoren-9-ol (64.58 mg, 0.25 mmol), 6-bromo-1H-indole (58.81 mg, 0.3 mmol) and $Sc(OTf)_3$ (2.46 mg, 0.005 mmol, 0.02 equiv) in CH_2Cl_2 (2 mL) at 60 ℃ for 4 h. Chromatography (ethyl acetate/ petroleum ether = 2:100) afforded **3r** (100.18 mg, 92% yield) as a white solid (mp 221-223 ℃). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.77 (t, *J* = 7.6 Hz, 3H), 7.49 (d, *J* = 7.6 Hz, 2H), 7.43–7.31 (m, 3H), 7.25–7.15 (m, 7H), 7.02 (d, *J* = 8.6 Hz, 1H), 6.88 (d, *J* = 8.6 Hz, 1H), 6.60 (d, *J* = 2.4 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 151.5, 144.1, 139.7, 138.0, 128.3, 127.7, 127.6, 127.5, 126.8, 125.6, 125.4, 123.6, 123.0, 122.6, 120.9, 120.2, 115.5, 114.2, 60.1; HRMS (ESI-TOF) m/z: [M - H]$^-$ Calcd for $C_{27}H_{17}NBr$ 434.0544; Found 434.0542.

7-methyl-3-(9-phenyl-9H-fluoren-9-yl)-1H-indole (3s)



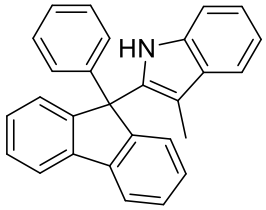
General procedure **A** was followed using 9-phenyl-9H-fluoren-9-ol (64.58 mg, 0.25 mmol), 7-methyl-1H-indole (39.35 mg, 0.3 mmol) and $Sc(OTf)_3$ (2.46 mg, 0.005 mmol, 0.02 equiv) in CH_2Cl_2 (2 mL) at 60 ℃ for 4 h. Chromatography (ethyl acetate/ petroleum ether = 1:100) afforded **3s** (91.72 mg, 99% yield) as a white solid (mp 65-67 ℃). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.80–7.67 (m, 3H), 7.56–7.52 (m, 2H), 7.34 (td, *J* = 7.5, 1.1 Hz, 2H), 7.30–7.26 (m, 2H), 7.24–7.16 (m, 5H), 6.95–6.90 (m, 2H), 6.89–6.83 (m, 1H), 6.64 (d, *J* = 2.5 Hz, 1H), 2.40 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 151.9, 144.4, 139.8, 136.8, 128.2, 127.6, 127.4, 126.6, 126.0, 125.7, 122.8, 122.4, 121.1, 120.4, 120.1, 119.8, 119.4, 60.3, 16.6; HRMS (ESI-TOF) m/z: [M - H]$^-$ Calcd for $C_{28}H_{20}N$ 370.1596; Found 370.1595.

2-methyl-3-(9-phenyl-9H-fluoren-9-yl)-1H-indole (3t)



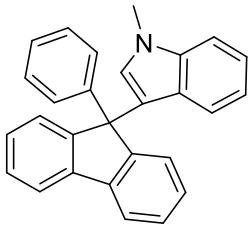
General procedure **A** was followed using 9-phenyl-9H-fluoren-9-ol (64.58 mg, 0.25 mmol), 2-methyl-1H-indole (39.35 mg, 0.3 mmol) and $Sc(OTf)_3$ (2.46 mg, 0.005 mmol, 0.02 equiv) in CH_2Cl_2 (2 mL) at 60 ℃ for 4 h. Chromatography (ethyl acetate/ petroleum ether = 1:100) afforded **3t** (60.10 mg, 65% yield) as a yellow solid (mp 182-184 ℃). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.76 (d, *J* = 7.5 Hz, 2H), 7.64 (s, 1H), 7.50 (d, *J* = 7.6 Hz, 2H), 7.39–7.28 (m, 4H), 7.25–7.16 (m, 6H), 7.01 (t, *J* = 7.5 Hz, 1H), 6.77 (t, *J* = 7.6 Hz, 1H), 6.65–6.24 (m, 1H), 1.40–1.23 (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 151.8, 145.6, 139.7, 135.2, 132.2, 128.4, 128.2, 127.6, 127.4, 127.3 126.5, 126.1, 121.4, 120.6, 120.0, 118.8, 113.8, 110.0, 60.5, 14.1; HRMS (ESI-TOF) m/z: $[M - H]^-$ Calcd for $C_{28}H_{20}N$ 370.1596; Found 370.1594.

3-methyl-2-(9-phenyl-9H-fluoren-9-yl)-1H-indole(3u)



General procedure **A** was followed using 9-phenyl-9H-fluoren-9-ol (64.58 mg, 0.25 mmol), 3-methyl-1H-indole (39.35 mg, 0.3 mmol) and $Sc(OTf)_3$ (2.46 mg, 0.005 mmol, 0.02 equiv) in CH_2Cl_2 (2 mL) at 60 °C for 4 h. Chromatography (ethyl acetate/ petroleum ether = 2:100) afforded **3u** (89.51 mg, 96% yield) as a yellow solid (mp 77-79 °C); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.77 (d, *J* = 7.5 Hz, 2H), 7.56–7.42 (m, 4H), 7.42–7.30 (m, 4H), 7.31–7.18 (m, 5H), 7.16–7.01 (m, 3H), 1.89 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 149.8, 143.6, 140.1, 135.8, 134.1, 130.4, 128.6, 128.1, 127.4, 127.2, 126.1, 121.6, 120.4, 119.2, 118.9, 118.3, 110.5, 108.8, 61.4, 10.4. HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{28}H_{22}N$ 372.1752; Found 372.1753.

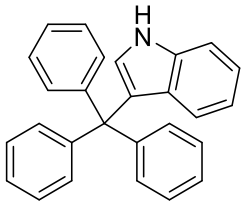
1-methyl-3-(9-phenyl-9H-fluoren-9-yl)-1H-indole (3v)



General procedure **A** was followed using 9-phenyl-9H-fluoren-9-ol (64.58 mg, 0.25 mmol), N-methyl-indole (39.35 mg, 0.3 mmol) and $Sc(OTf)_3$ (2.46 mg, 0.005 mmol, 0.02 equiv) in CH_2Cl_2 (2 mL) at 60 ℃ for 4 h. Chromatography (ethyl acetate/

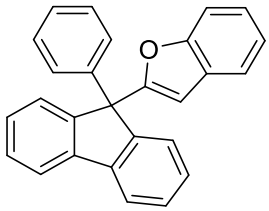
petroleum ether = 1:100) afforded **3v** (91.70 mg, 99% yield) as a white solid (mp 190-192 ℃). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.78 (d, *J* = 7.5 Hz, 2H), 7.55 (d, *J* = 7.6 Hz, 2H), 7.33 (q, *J* = 8.6 Hz, 3H), 7.28–7.12 (m, 8H), 7.07 (d, *J* = 8.1 Hz, 1H), 6.93 (t, *J* = 7.6 Hz, 1H), 6.50 (s, 1H), 3.60 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 152.1, 144.5, 139.7, 138.0, 128.2, 127.7, 127.6, 127.3, 126.9, 126.6, 125.7, 122.0, 121.4, 120.0, 118.8, 118.7, 109.4, 60.3, 32.6; HRMS (EI) Calcd for $C_{28}H_{21}N$ $[M]^+$ m/z: 371.1674; Found 371.1676.

3-trityl-1H-indole (3w)



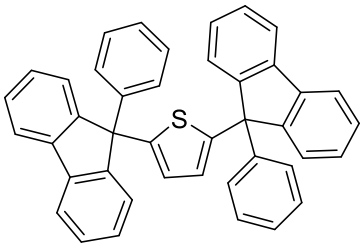
General procedure **A** was followed using triphenylmethanol (65.08 mg, 0.25 mmol), indole (35.15 mg, 0.3 mmol) and $Sc(OTf)_3$ (2.46 mg, 0.005 mmol, 0.02 equiv) in CH_2Cl_2 (2 mL) at 60 ℃ for 4 h. Chromatography (ethyl acetate/ petroleum ether = 1:100) afforded **3w** (79.38 mg, 88% yield) as a white solid (mp 207-209 ℃). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.87 (s, 1H), 7.29 (d, *J* = 8.2 Hz, 1H), 7.23–7.19 (m, 15H), 7.10–7.06 (m, 1H), 6.80–6.76 (m, 2H), 6.68–6.65 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 146.5, 137.0, 130.8, 127.8, 127.4, 126.0, 125.5, 123.9, 122.8, 121.7, 119.2, 110.9, 59.4; HRMS (ESI-TOF) m/z: $[M - H]^-$ Calcd for $C_{27}H_{20}N$ 358.1596; Found 358.1598.

2-(9-phenyl-9H-fluoren-9-yl)benzofuran (5a)



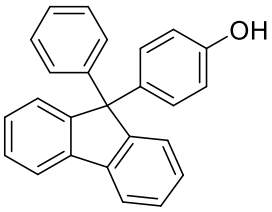
General procedure **A** was followed using 9-phenyl-9H-fluoren-9-ol (64.58 mg, 0.25 mmol), benzofuran (35.44 mg, 0.3 mmol) and $Sc(OTf)_3$ (2.46 mg, 0.005 mmol, 0.02 equiv) in CH_2Cl_2 (2 mL) at 60 ℃ for 4 h. Chromatography (ethyl acetate/ petroleum ether = 2:100) afforded **5a** (49.20 mg, 55% yield) as a white solid (mp 202-204 ℃). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.82–7.76 (m, 2H), 7.69–7.64 (m, 2H), 7.47–7.39 (m, 4H), 7.32 (td, *J* = 7.5, 1.2 Hz, 2H), 7.23–7.19 (m, 4H), 7.15 (td, *J* = 7.5, 1.1 Hz, 1H), 7.06–7.02 (m, 2H), 6.40 (d, *J* = 0.9 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 158.9, 155.7, 148.4, 143.0, 140.3, 128.5, 128.2, 128.1, 127.9, 127.2, 127.1, 126.4, 123.9, 122.7, 120.8, 120.3, 111.3, 105.1, 61.1; HRMS (EI) Calcd for $C_{27}H_{18}O$ $[M]^+$ m/z: 358.1358; Found 358.1355.

2,5-bis(9-phenyl-9H-fluoren-9-yl)thiophene (5b)



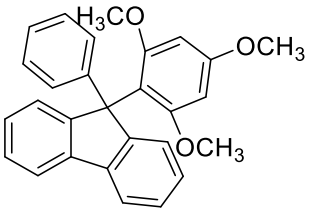
General procedure **A** was followed using 9-phenyl-9H-fluoren-9-ol (64.58 mg, 0.25 mmol), thiophene (25.24 mg, 0.3 mmol) and $Sc(OTf)_3$ (2.46 mg, 0.005 mmol, 0.02 equiv) in CH_2Cl_2 (2 mL) at 60 ℃ for 4 h. Chromatography (ethyl acetate/ petroleum ether = 1:100) afforded **5b** (59.08 mg, 84% yield) as a white solid (mp 254-256 ℃). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.77–7.67 (m, 4H), 7.48–7.41 (m, 4H), 7.34 (td, *J* = 7.5, 1.2 Hz, 4H), 7.27–7.22 (m, 4H), 7.20–7.08 (m, 10H), 6.59 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 150.9, 148.0, 145.6, 139.8, 128.1, 127.7, 127.6, 127.5, 126.9, 126.2, 125.6, 120.2, 62.3; HRMS (EI) Calcd for $C_{42}H_{28}S$ $[M]^+$ m/z: 564.1912; Found 564.1916. Spectral data match those previously reported.[4]

4-(9-phenyl-9H-fluoren-9-yl) phenol (5f)



General procedure **A** was followed using 9-phenyl-9H-fluoren-9-ol (64.58 mg, 0.25 mmol), phenol (28.23 mg, 0.3 mmol) and $Sc(OTf)_3$ (2.46 mg, 0.005 mmol, 0.02 equiv) in CH_2Cl_2 (2 mL) at 60 °C for 4 h. Chromatography (ethyl acetate/ petroleum ether = 4:100) afforded **5f** (66.80 mg, 71% yield) as a white solid (mp 185-187 °C); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.74 (d, *J* = 7.5 Hz, 2H), 7.46–7.12 (m, 12H), 7.10–7.01 (m, 2H), 6.69–6.61 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 154.3, 151.5, 146.1, 140.1, 138.1, 129.4, 128.2, 128.1, 127.7, 127.4, 126.6, 126.1, 120.2, 115.0, 64.8; HRMS (ESI-TOF) m/z: $[M - H]^-$ Calcd for $C_{25}H_{17}O$ 333.1279; Found 333.1278.

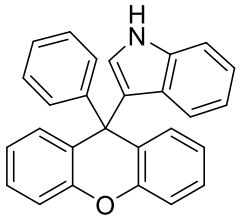
9-phenyl-9-(2,4,6-trimethoxyphenyl)-9H-fluorene (5g)



General procedure **A** was followed using 9-phenyl-9H-fluoren-9-ol (64.58 mg, 0.25 mmol), 1,3,5-trimethoxybenzene (50.46 mg, 0.3 mmol) and $Sc(OTf)_3$ (2.46 mg, 0.005 mmol, 0.02 equiv) in CH_2Cl_2 (2 mL) at 60 °C for 4 h. Chromatography (ethyl acetate/ petroleum ether = 2:100) afforded **5g** (101.40 mg, 99% yield) as a white solid (mp 150-152 °C); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.70 (d, *J* = 7.4 Hz, 2H), 7.50 (d, *J* =

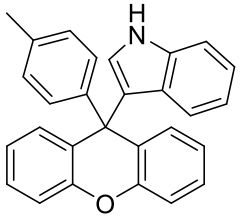
7.6 Hz, 2H), 7.28–7.24 (m, 2H), 7.21–7.13 (m, 2H), 7.11–6.98 (m, 5H), 6.09 (s, 2H), 3.77 (s, 3H), 3.18 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 160.2, 159.7, 152.2, 148.9, 139.5, 127.6, 127.0, 126.3, 125.7, 124.9, 124.4, 119.4, 114.5, 92.9, 61.2, 55.6, 55.2; HRMS (ESI-TOF) m/z: $[M + Na]^+$ Calcd for $C_{28}H_{24}NaO_3$ 431.1623; Found 431.1624.

3-(9-phenyl-9H-xanthen-9-yl)-1H-indole (7a)



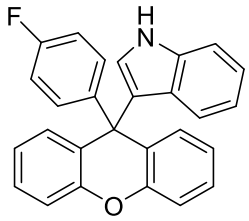
General procedure **A** was followed using 9-phenyl-9H-xanthen-9-ol (68.58 mg, 0.25 mmol), indole (35.15 mg, 0.3 mmol) and $Sc(OTf)_3$ (2.46 mg, 0.005 mmol, 0.02 equiv) in CH_2Cl_2 (2 mL) at 60 °C for 4 h. Chromatography (ethyl acetate/ petroleum ether = 4:100) afforded **7a** (88.85 mg, 95% yield) as a white solid (mp 249-251 °C). ^{1}H NMR (400 MHz, DMSO-d_6) δ 11.07 (s, 1H), 7.43–7.39 (m, 1H), 7.33–7.28 (m, 2H), 7.27–7.17 (m, 5H), 7.06–6.98 (m, 3H), 6.97–6.89 (m, 4H), 6.71–6.65 (m, 1H), 6.54 (d, J = 8.0 Hz, 1H), 6.48 (d, J = 2.5 Hz, 1H); ^{13}C NMR (100 MHz, DMSO-d_6) δ 151.8, 145.6, 137.4, 129.4, 128.7, 128.0, 127.9, 127.1, 126.4, 125.1, 123.1, 121.0, 120.7, 118.9, 118.4, 116.1, 111.8, 48.3; HRMS (ESI-TOF) m/z: $[M - H]^-$ Calcd for $C_{27}H_{18}NO$ 372.1388; Found 372.1390.

3-(9-(p-tolyl)-9H-xanthen-9-yl)-1H-indole (7b)



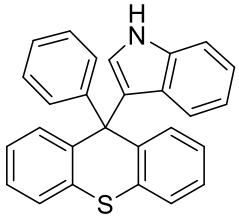
General procedure **A** was followed using 9-(p-tolyl)-9H-xanthen-9-ol (72.09 mg, 0.25 mmol), indole (35.15 mg, 0.3 mmol) and $Sc(OTf)_3$ (2.46 mg, 0.005 mmol, 0.02 equiv) in CH_2Cl_2 (2 mL) at 60 °C for 4 h. Chromatography (ethyl acetate/ petroleum ether = 4:100) afforded **7b** (95.13 mg, 98% yield) as a white solid (mp 298-300 °C). ^{1}H NMR (400 MHz, DMSO-d_6) δ 10.87 (s, 1H), 7.36 (d, J = 8.2 Hz, 1H), 7.24 (t, J = 7.2 Hz, 2H), 7.14 (d, J = 8.1 Hz, 2H), 7.02–6.90 (m, 7H), 6.78 (d, J = 7.9 Hz, 2H), 6.68–6.55 (m, 2H), 6.44 (d, J = 2.5 Hz, 1H), 2.23 (s, 3H); ^{13}C NMR (100 MHz, DMSO-d_6) δ 151.8, 142.6, 137.4, 135.2, 129.3, 128.9, 128.2, 127.9, 127.6, 127.0, 125.1, 122.6, 120.9, 120.8, 119.1, 118.1, 115.9, 111.5, 48.0, 20.4; HRMS (ESI-TOF) m/z: $[M - H]^-$ Calcd for $C_{28}H_{20}NO$ 386.1545; Found 386.1546.

3-(9-(4-fluorophenyl)-9H-xanthen-9-yl)-1H-indole (7c)



General procedure **A** was followed using 9-(4-fluorophenyl)-9H-xanthen-9-ol (73.08 mg, 0.25 mmol), indole (35.15 mg, 0.3 mmol) and $Sc(OTf)_3$ (2.46 mg, 0.005 mmol, 0.02 equiv) in CH_2Cl_2 (2 mL) at 60 °C for 4 h. Chromatography (ethyl acetate/ petroleum ether = 4:100) afforded **7c** (92.18 mg, 94% yield) as a white solid (mp 226-228 °C). ^{1}H NMR (400 MHz, DMSO-d_6) δ 11.12 (s, 1H), 7.42 (d, J = 8.2 Hz, 1H), 7.31 (t, J = 7.7 Hz, 2H), 7.24 (d, J = 8.1 Hz, 2H), 7.12–6.99 (m, 5H), 6.98–6.88 (m, 4H), 6.68 (t, J = 7.6 Hz, 1H), 6.59–6.48 (m, 2H); ^{13}C NMR (100 MHz, DMSO-d_6) δ 160.5 (d, $J_{C\text{-}F}$ = 242.2 Hz), 151.8, 141.7 (d, $J_{C\text{-}F}$ = 2.9 Hz), 137.5, 129.9 (d, $J_{C\text{-}F}$ = 7.9 Hz), 129.2, 128.6, 128.2, 127.0, 125.0, 123.2, 121.1, 120.7, 118.9, 118.5, 116.2, 114.7 (d, $J_{C\text{-}F}$ = 21.1 Hz), 111.8, 47.9; ^{19}F NMR (376 MHz, DMSO-d_6) δ -116.56; HRMS (ESI-TOF) m/z: $[M - H]^-$ Calcd for $C_{27}H_{17}NOF$ 390.1294; Found 390.1293.

3-(9-phenyl-9H-thioxanthen-9-yl)-1H-indole (7d)



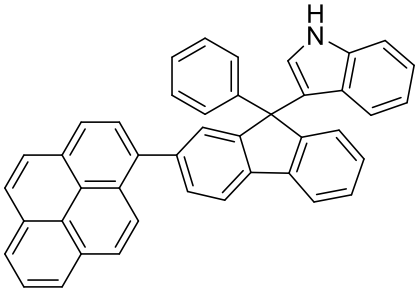
General procedure **A** was followed using 9-phenyl-9H-thioxanthen-9-ol (72.60 mg, 0.25 mmol), indole (35.15 mg, 0.3 mmol) and $Sc(OTf)_3$ (2.46 mg, 0.005 mmol, 0.02 equiv) in CH_2Cl_2 (2 mL) at 60 °C for 4 h. Chromatography (ethyl acetate/ petroleum ether = 4:100) afforded **7d** (89.60 mg, 92% yield) as a white solid (mp 230-232 °C). ^{1}H NMR (400 MHz, DMSO-d_6) δ 11.08 (s, 1H), 7.54–7.44 (m, 3H), 7.27 (t, J = 7.5 Hz, 2H), 7.18–7.10 (m, 4H), 7.06 (t, J = 7.6 Hz, 1H), 6.94 (d, J = 7.8 Hz, 2H), 6.73 (t, J = 7.5 Hz, 1H), 6.63–6.54 (m, 2H), 6.49 (d, J = 8.0 Hz, 1H), 6.15 (d, J = 2.4 Hz, 1H), 5.75 (d, J = 1.7 Hz, 1H); ^{13}C NMR (100 MHz, DMSO-d_6) δ 143.3, 139.5, 137.4, 132.6, 130.3, 128.4, 127.5, 126.9, 126.6, 126.3, 125.8, 125.7, 121.5, 121.2, 119.1, 118.5, 112.0, 55.3. HRMS (ESI-TOF) m/z: $[M - H]^-$ Calcd for $C_{27}H_{18}NS$ 388.1160; Found 388.1159.

5. Procedure B

2-bromo-9-phenyl-9H-fluoren-9-ol (1686.08 mg, 5.0 mmol), indole (702.90 mg, 6 mmol) and $Sc(OTf)_3$ (49.22 mg, 0.1 mmol, 0.02 equiv) in CH_2Cl_2 (15 mL) at 60 °C for 4 h. Chromatography (ethyl acetate/ petroleum ether = 3:100) afforded **3h** (809.51 mg, 37% yield) as a white solid. **3h** (0.5 mmol, 1 equiv), pyren-1-ylboronic acid (1.5 mmol, 3 equiv), $Pd(PPh_3)_4$ (0.05 mmol), aqueous Na_2CO_3 (2.0 M, 1 mL), ethanol (2 mL), and toluene (4 mL) and a stir bar were added to a sealed tube. After being stirred at 110 °C for 24 h, the mixture was evaporated under vacuum, and the product was extracted with

dichloromethane (3×40 mL). The combined organic layers were dried over anhydrous Na_2SO_4 and the solvent was removed by rotary evaporation. The target product was isolated by silica gel column chromatography with a dichloromethane/petroleum ether mixture as eluent.[4]

3-(9-phenyl-2-(pyren-1-yl)-9H-fluoren-9-yl)-1H-indole (8)



Product **8** was obtained by using **3h** (0.5 mmol, 1 equiv), pyren-1-ylboronic acid (1.5 mmol, 3 equiv), $Pd(PPh_3)_4$ (0.05 mmol), aqueous Na_2CO_3 (2.0 M, 1 mL), ethanol (2 mL), and toluene (4 mL) at 110 ℃ for 24 h, Chromatography (dichloromethane/petroleum ether = 25:100) afforded **8** (231.70 mg, 83% yield) yellowish white solid (mp 148-150 ℃). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.19–7.98 (m, 6H), 7.97–7.83 (m, 5H), 7.82–7.69 (m, 2H), 7.60 (t, *J* = 8.7 Hz, 2H), 7.43–7.33 (m, 3H), 7.28–7.19 (m, 5H), 7.13–7.03 (m, 2H), 6.86 (t, *J* = 7.6 Hz, 1H), 6.74 (d, *J* = 2.5 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 152.2, 152.1, 144.4, 140.3, 139.6, 138.9, 137.8, 137.2, 131.5, 131.0, 130.5, 130.1, 128.4, 128.3, 128.2, 127.8, 127.7, 127.6, 127.5, 127.4, 127.3, 127.2, 126.7, 126.4, 126.0, 125.9, 125.3, 125.1, 125.0, 124.9, 124.7, 124.6, 123.2, 121.9, 121.8, 120.6, 120.3, 120.1, 119.4, 111.3, 60.5; HRMS (ESI-TOF) m/z: $[M - H]^-$ Calcd for $C_{43}H_{26}N$ 556.2065; Found 556.2064.

6. Quantum Yields Measurements.[5]

The fluorescence quantum yields of substrates (**5a**, **5b**, **3p**, **3m**, **3e**, **3c**, **3a**, **3k**) were determined by comparing the integrated area of the corrected emission spectrum with the reference for 9,10-diphenylanthracene (Φ_F = 0.90, in cyclohexane). The fluorescence quantum yields of compound **8** was determined by comparing the integrated area of the corrected emission spectrum with the reference for quinine sulfate (Φ_F = 0.55 in 0.1 M H_2SO_4). The quantum yields of a sample was then calculated according to the following equation:

$$\Phi = \Phi' \times \frac{A'}{I'} \times \frac{I}{A} \times \frac{n^2}{n'^2}$$

where Φ is the fluorescence quantum yield of testing sample, *I* is the integrated emission intensity of testing sample, *n* is the refractive index (1.42 for dichloromethane, 1.43 for cyclohexane and 1.33 for water), *A* is the optical density. The superscript "′" refers to the referenced fluorescence dyes of known quantum yields.

7. References

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[2] D. T. Hogan and T. C. Sutherland, *J. Phys. Chem. Lett*., 2018, **9**, 2825.

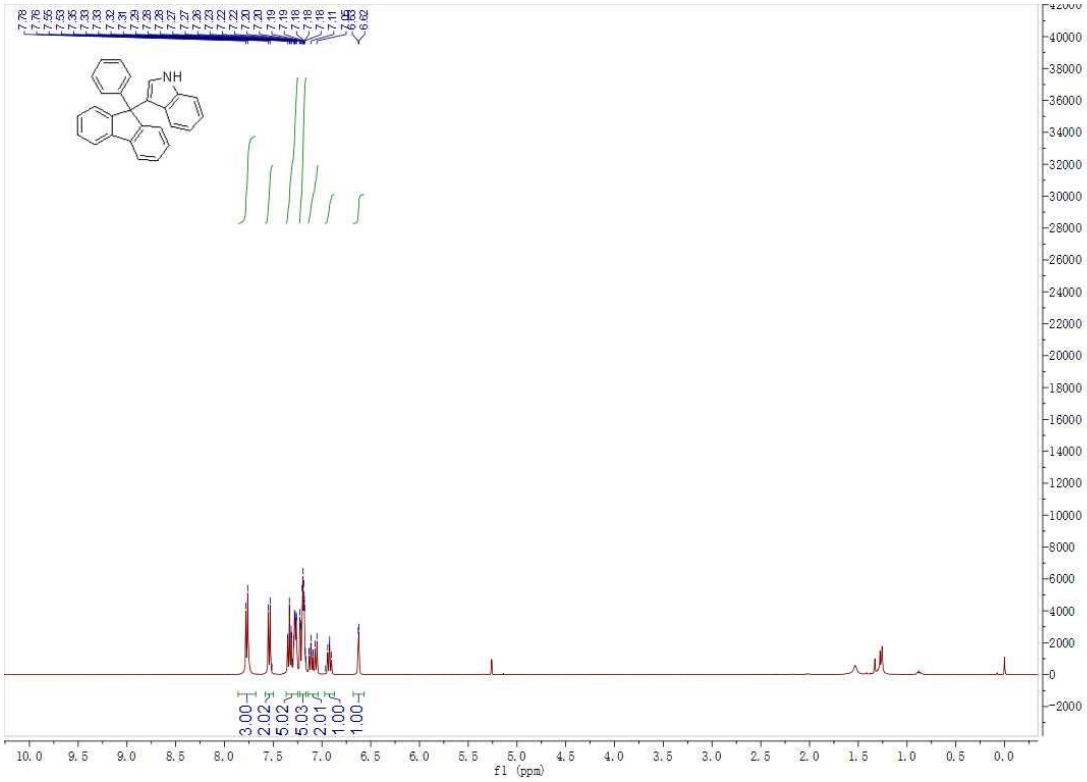
[3] (a) L. H. Xie, X. Y. Hou, Y. R. Hua, C. Tang, F. Liu, Q. L. Fan and W. Huang, *Org. Lett.,* 2006, **8**, 3701; (b) K.-T. Wong, Z.-J. Wang, Y.-Y. Chien and C.-L. Wang, *Org. Lett*., 2001, **3**, 2285.

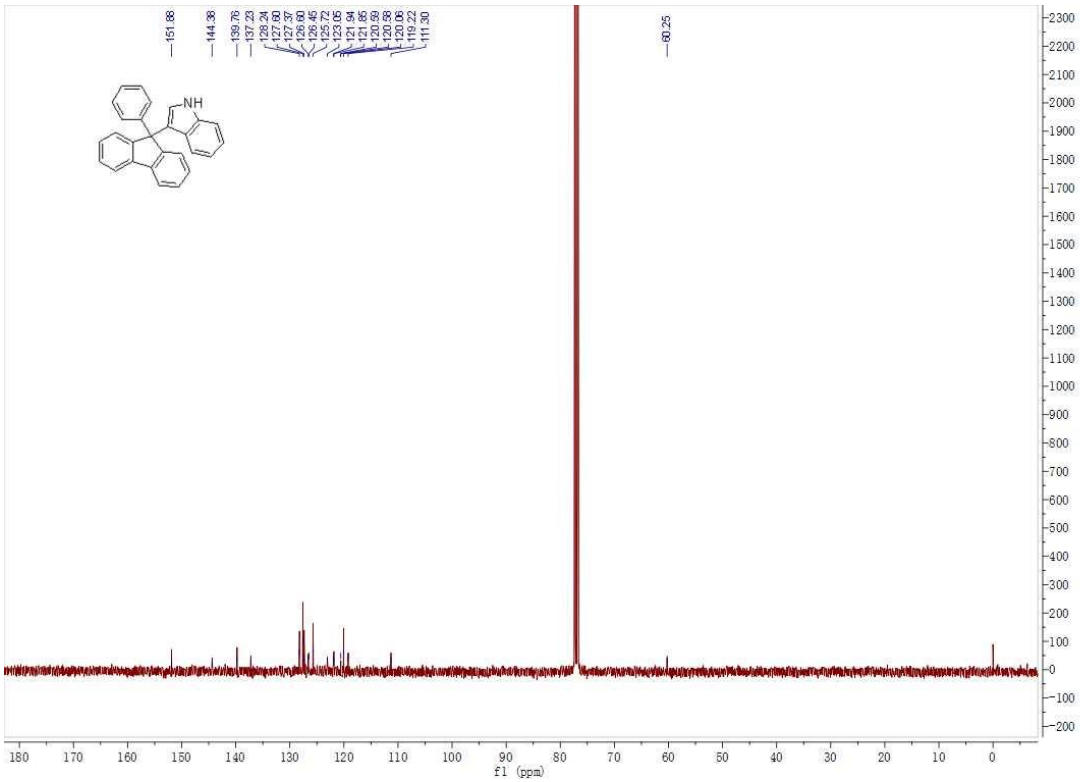
[4] Z. Peng, S. Tao, X. Zhang, J. Tang, C. S. Lee and S.-T. Lee, *J. Phys. Chem. C*., 2008, **112**, 2165.

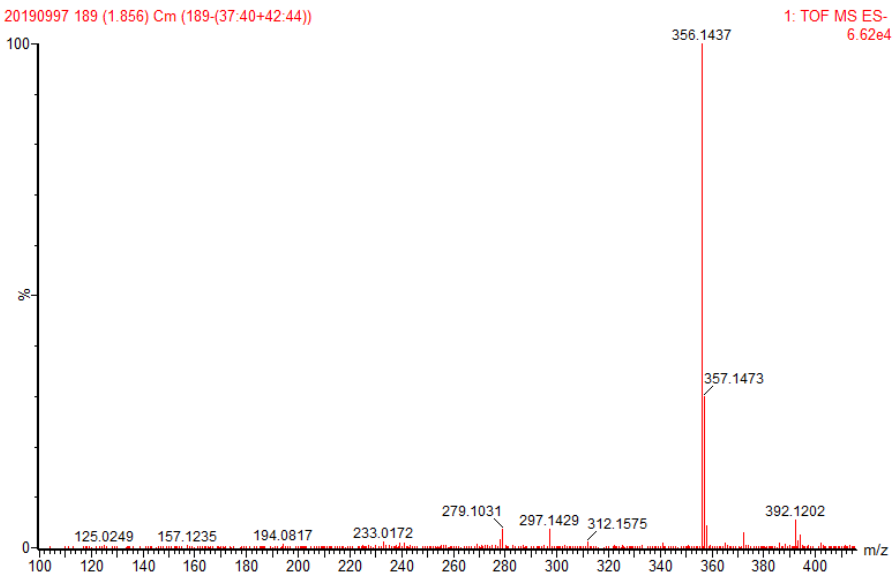
[5] (a) K. Jiang, S. Sun, L. Zhang, Y. Lu, A. Wu, C. Cai and H. Lin, *Angew. Chem. Int. Ed*., 2015, **54**, 5360; (b) D. F. Eaton, *Pure Appl. Chem*., 1988, **60**, 1107; (c) M. Grabolle, M. Spieles, V. Lesnyak, N.Gaponik, A. Eychmüller and U. Resch-Genger, *Anal. Chem*., 2009, **81**, 6285; (d) T. Karstens and K. Kobs, *J. Phys. Chem*., 1980, **84**, 1871.

Copies of ^{1}H NMR, ^{13}C NMR, ^{19}F NMR, HRMS

3a



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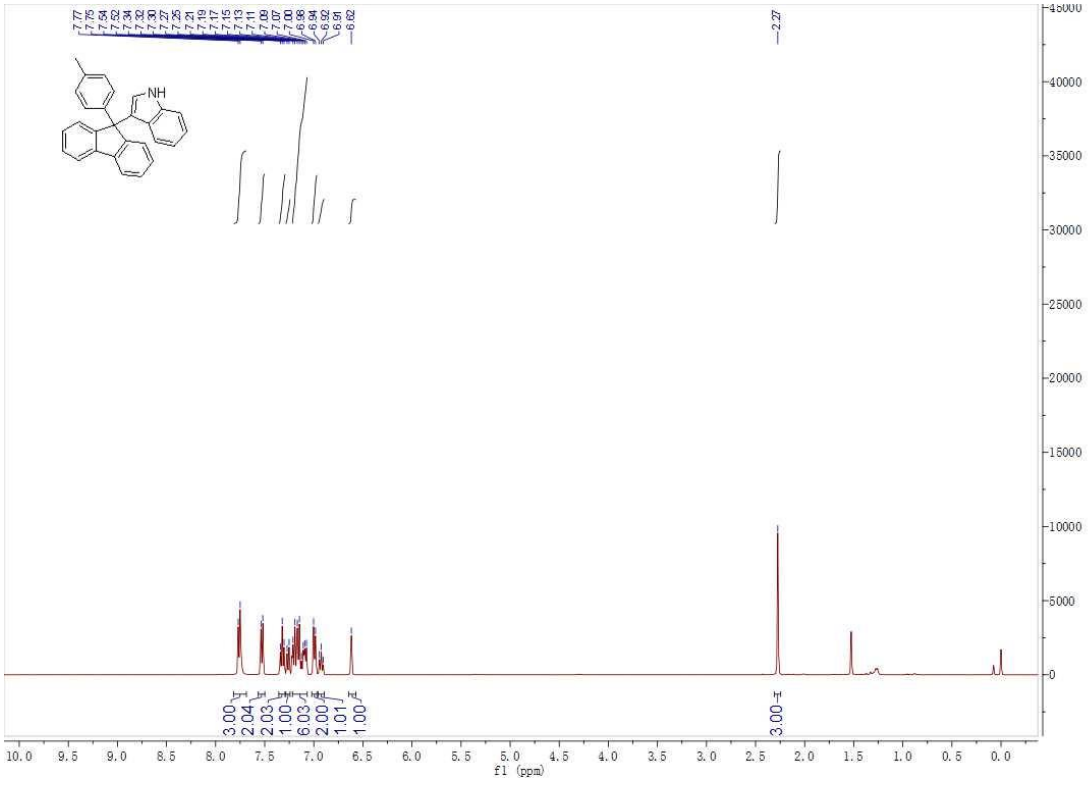
%
m/z

3b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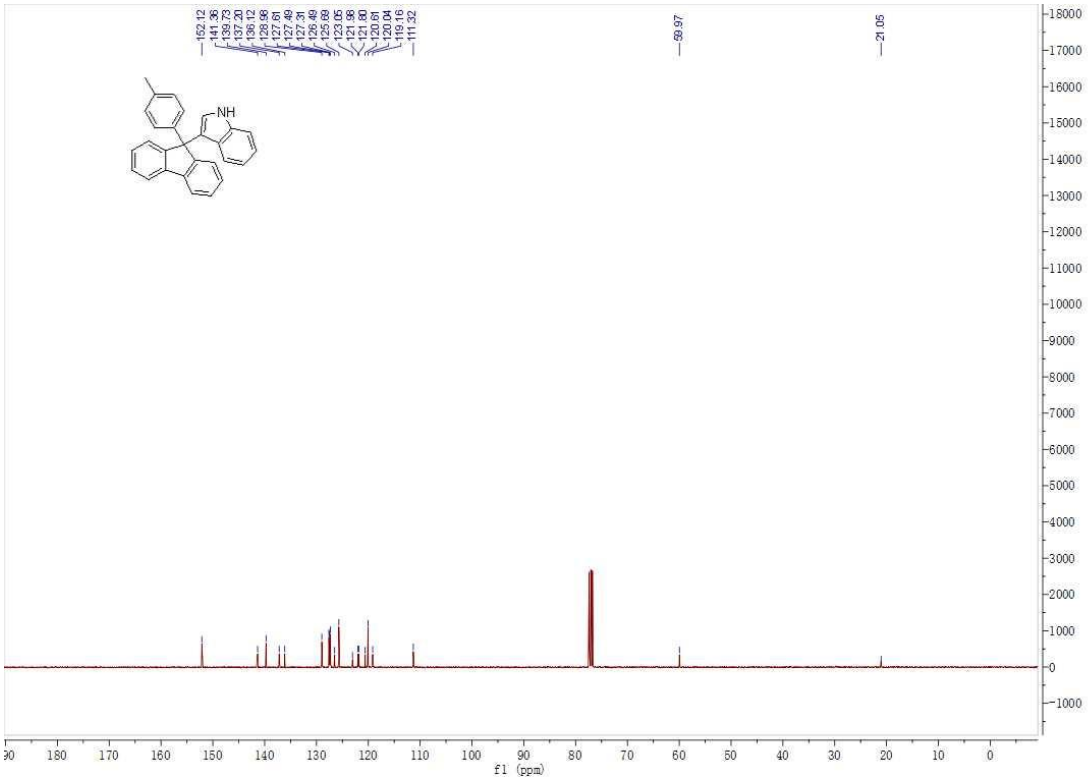
1.00
3.00
f1 (ppm)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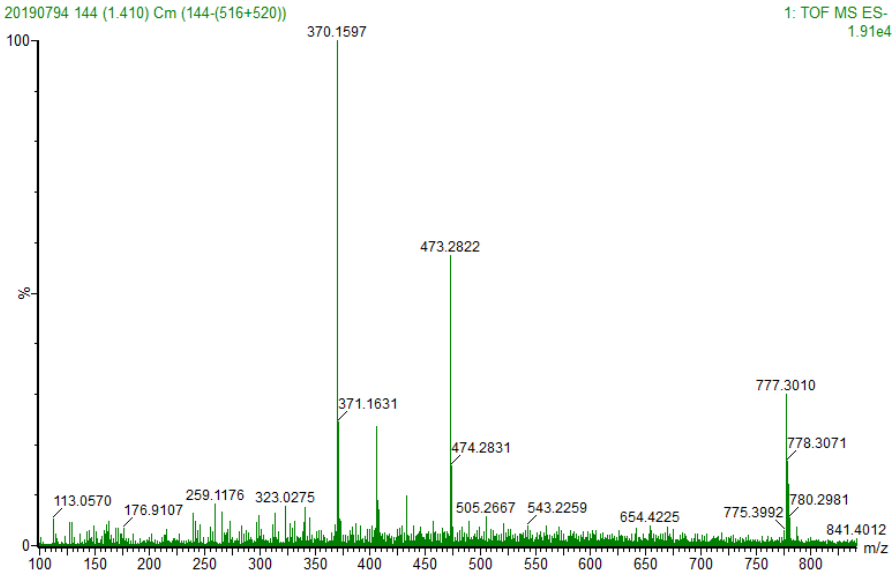
21.05
f1 (ppm)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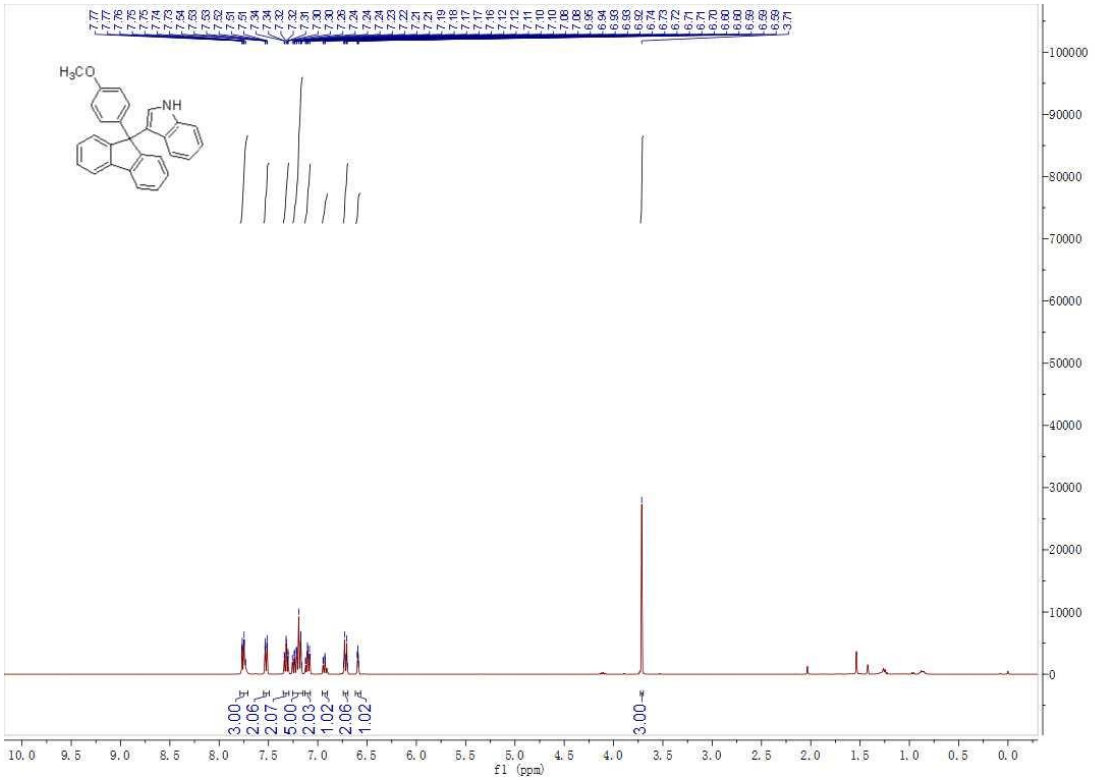
%
m/z

3c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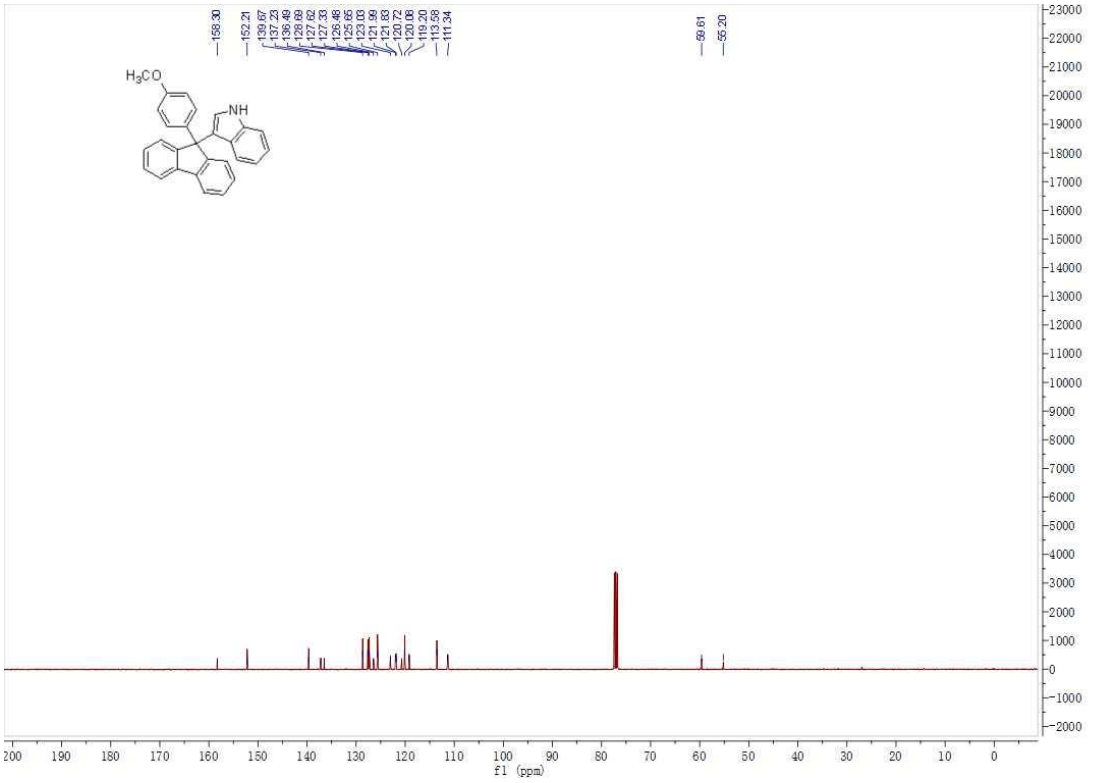
f1 (ppm)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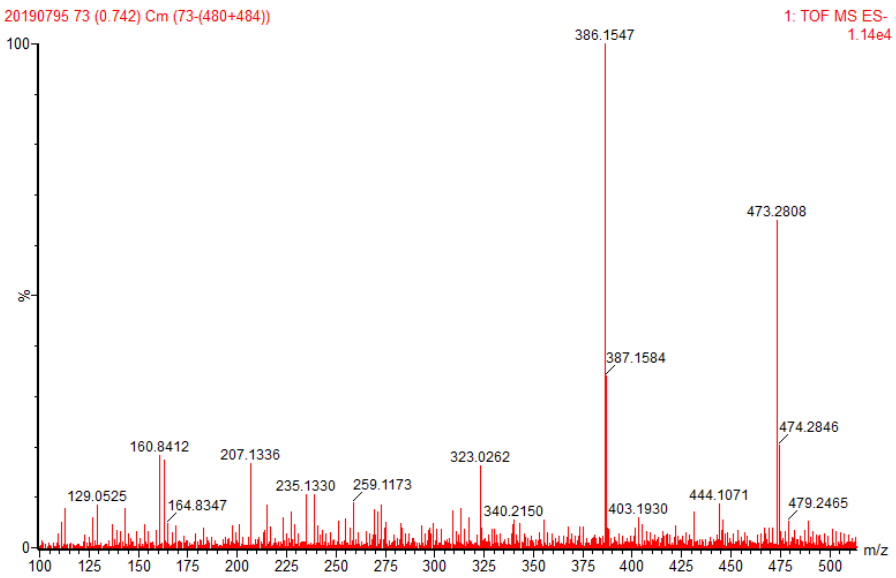
NH
f1 (ppm)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%
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m/z
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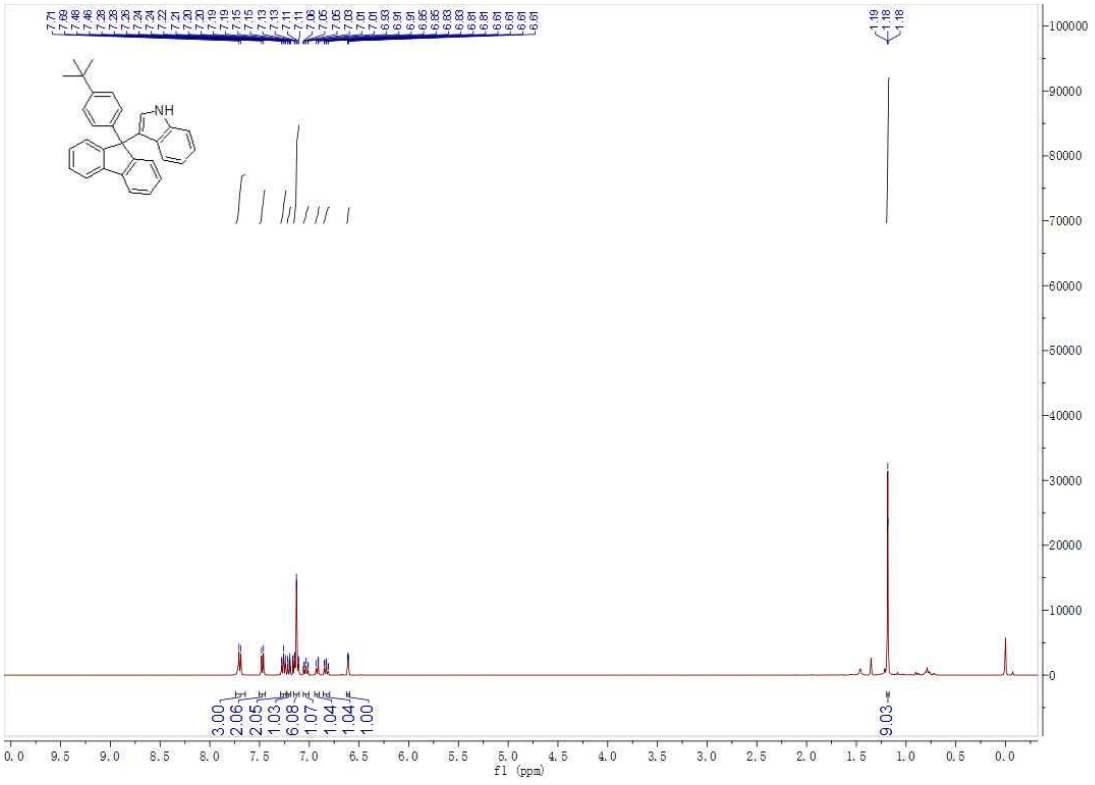
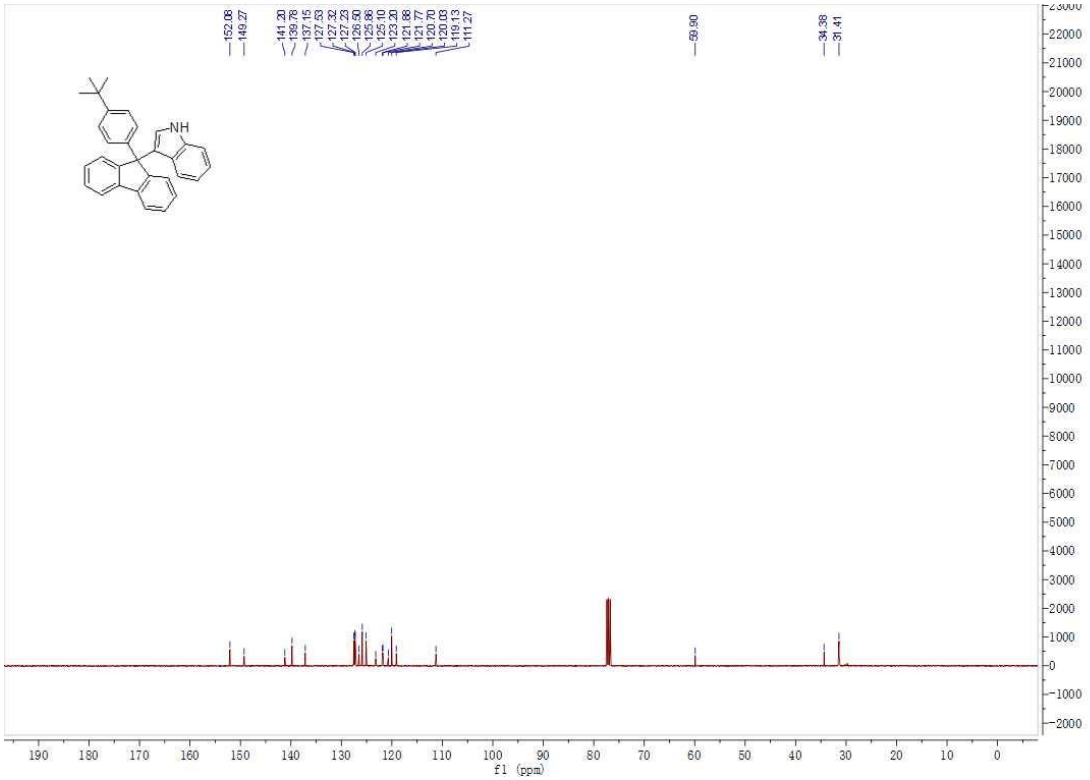
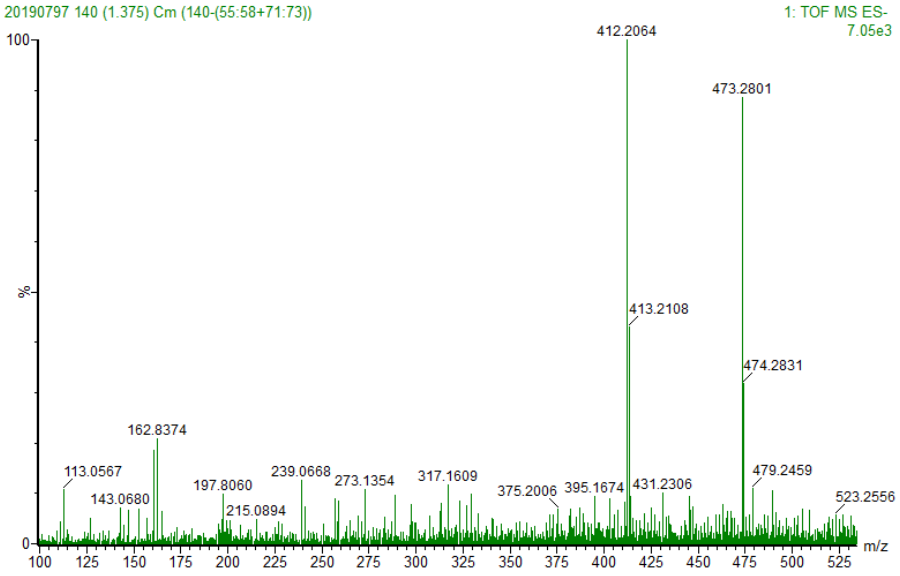
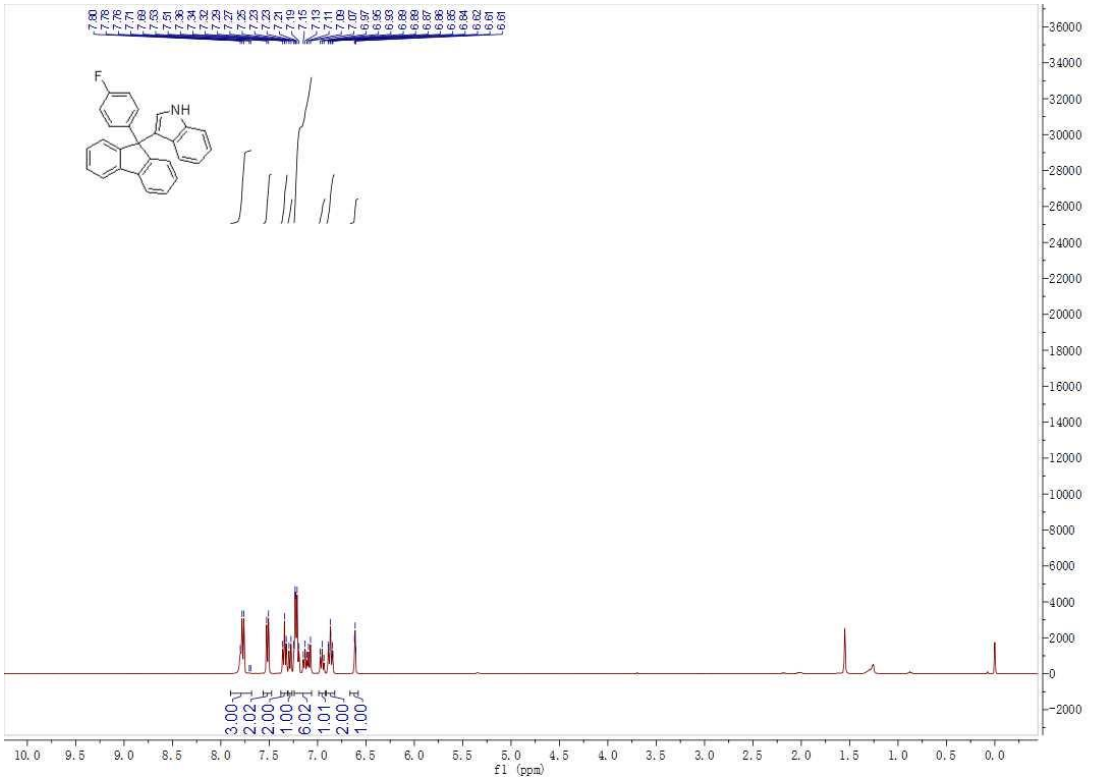
3d

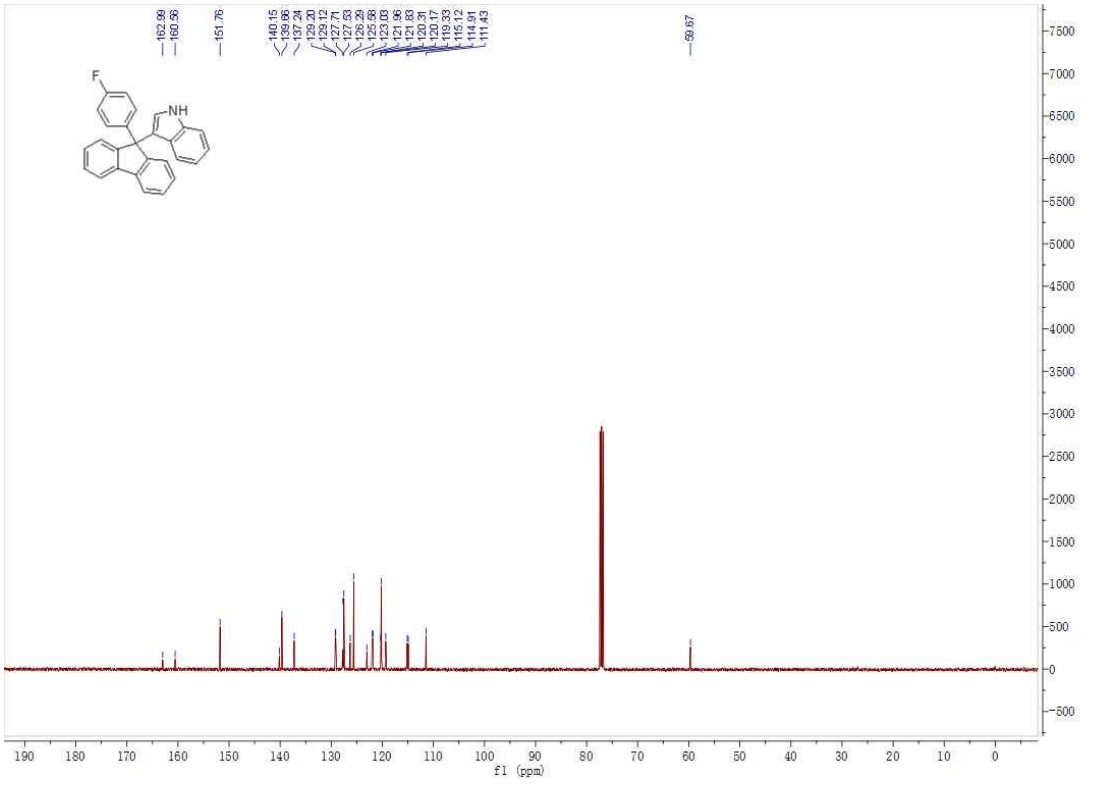

NH
7.71 7.69 7.48 7.46 7.28 7.26 7.24 7.22 7.21 7.20 7.19 7.19 7.15 7.15 7.13 7.11 7.11 7.06 7.05 7.05 7.03 7.01 7.01 6.93 6.91 6.91 6.85 6.85 6.83 6.83 6.81 6.81 6.61 6.61 6.61 6.61
1.19 1.18 1.18
3.00 2.06 2.05 1.03 6.08 1.07 1.04 1.04 1.00
9.03
f1 (ppm)

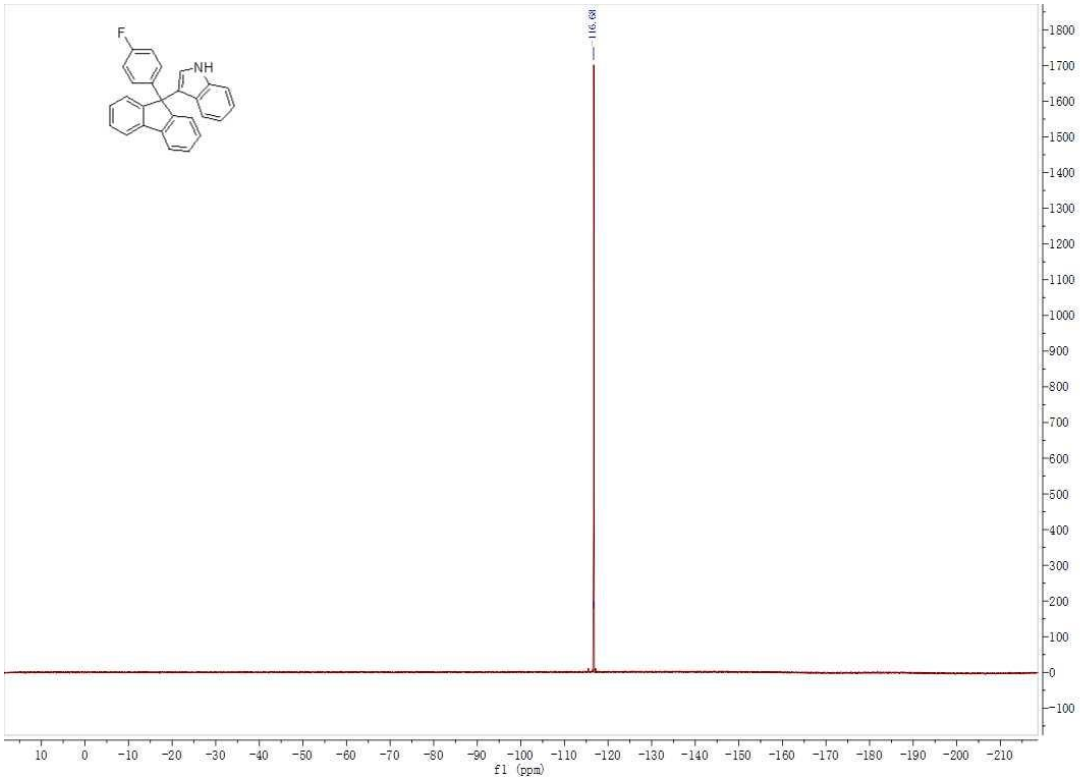

152.08
149.27
141.20
139.78
137.15
127.53
127.32
127.23
126.50
125.86
123.10
122.20
121.88
121.77
120.70
120.03
119.13
111.27
59.90
34.38
31.41
NH
f1 (ppm)

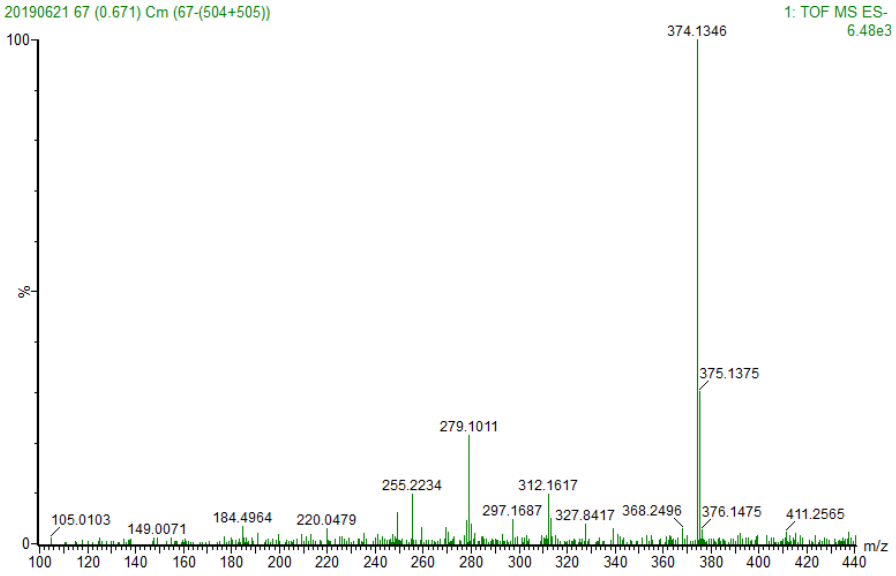

20190797 140 (1.375) Cm (140-(55:58+71:73))
1: TOF MS ES-
7.05e3
412.2064
473.2801
413.2108
474.2831
162.8374
113.0567
143.0680
197.8060
215.0894
239.0668
273.1354
317.1609
375.2006
395.1674
431.2306
479.2459
523.2556
%
m/z

3e

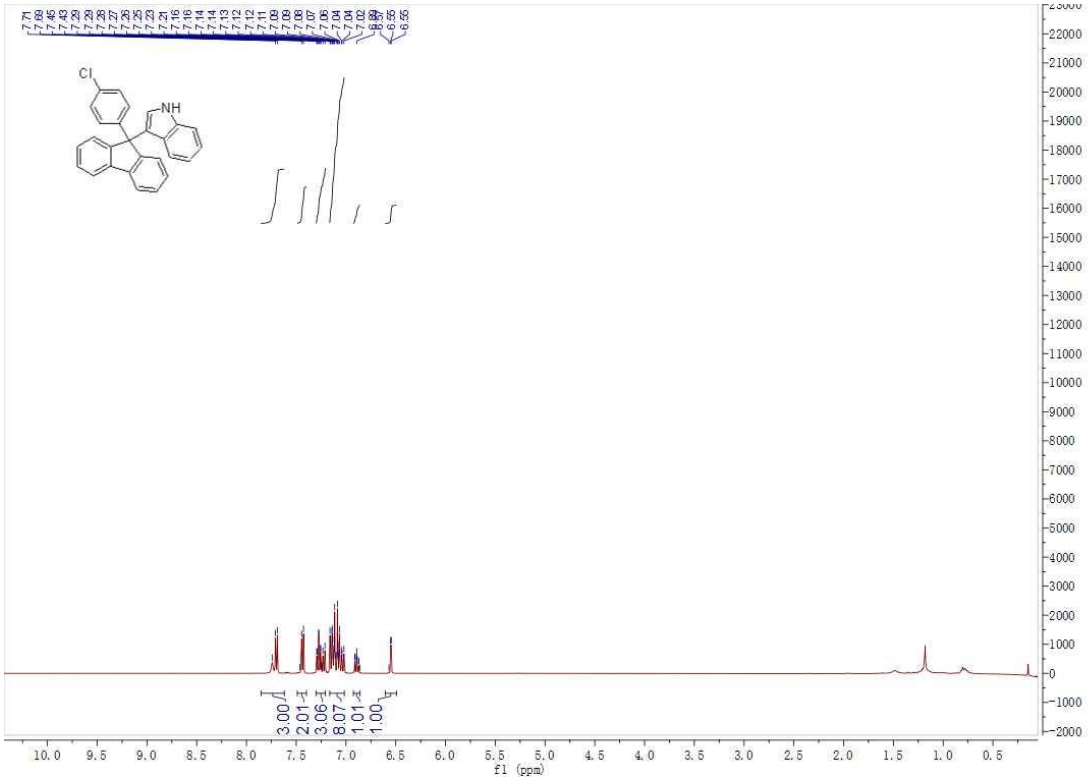

F
NH
3.00
2.02
2.00
1.00
6.02
1.01
2.00
1.00
f1 (ppm)

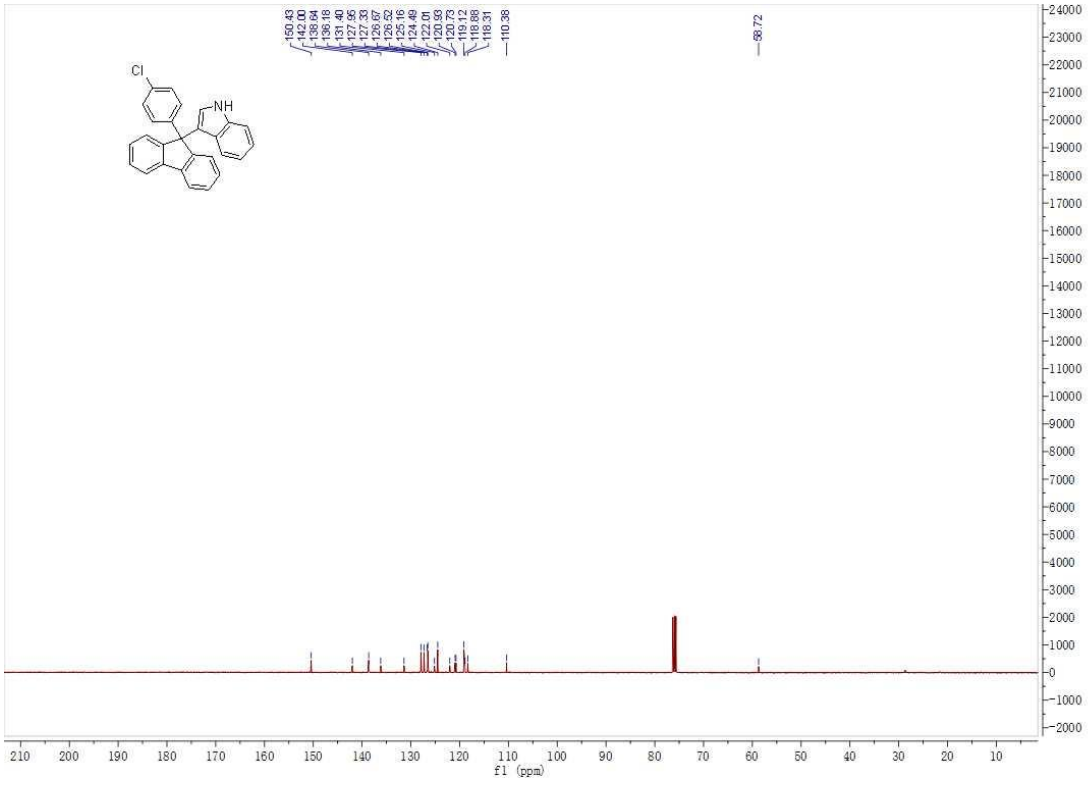

F
NH
162.99
160.56
151.76
140.15
139.66
137.24
129.20
129.12
127.71
127.53
126.29
125.66
123.03
121.96
121.83
120.71
120.17
119.33
115.12
114.91
111.43
59.67
f1 (ppm)

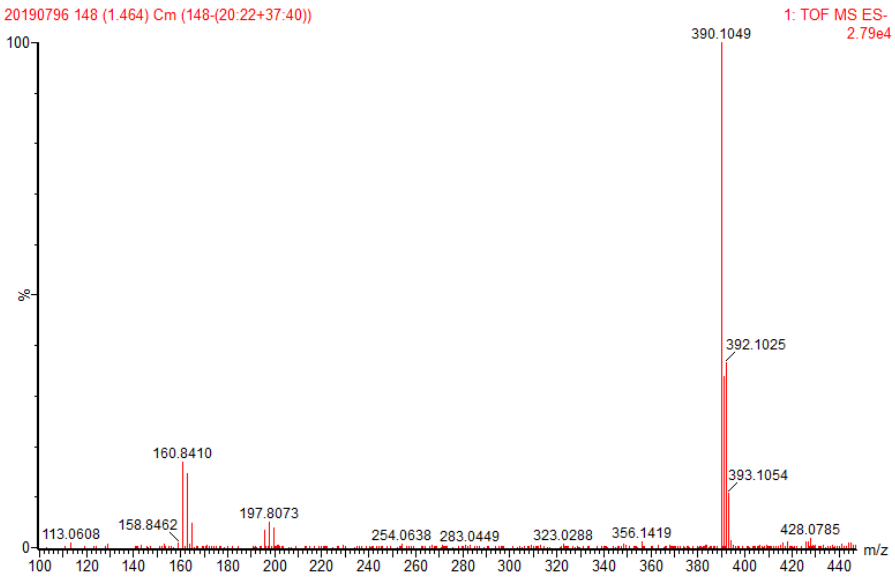

F
NH
-116.68
f1 (ppm)


20190621 67 (0.671) Cm (67-(504+505))
1: TOF MS ES-
6.48e3
374.1346
375.1375
279.1011
255.2234
312.1617
105.0103
149.0071
184.4964
220.0479
297.1687
327.8417
368.2496
376.1475
411.2565
%
m/z

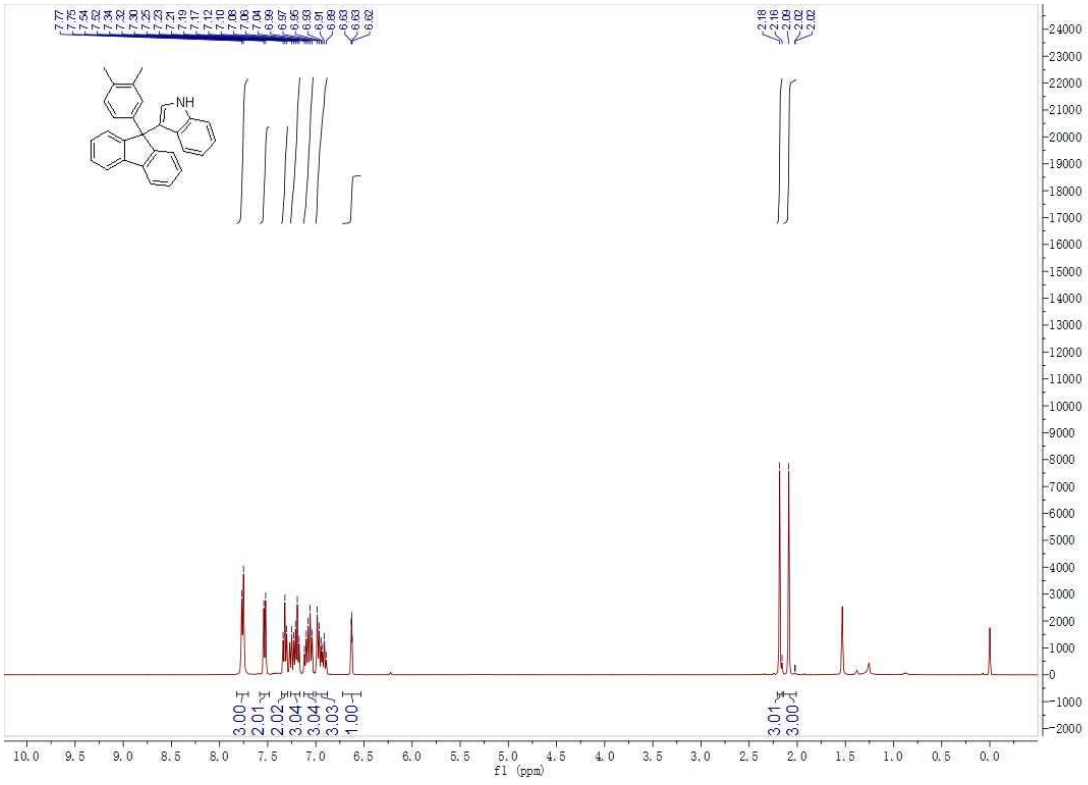
3f

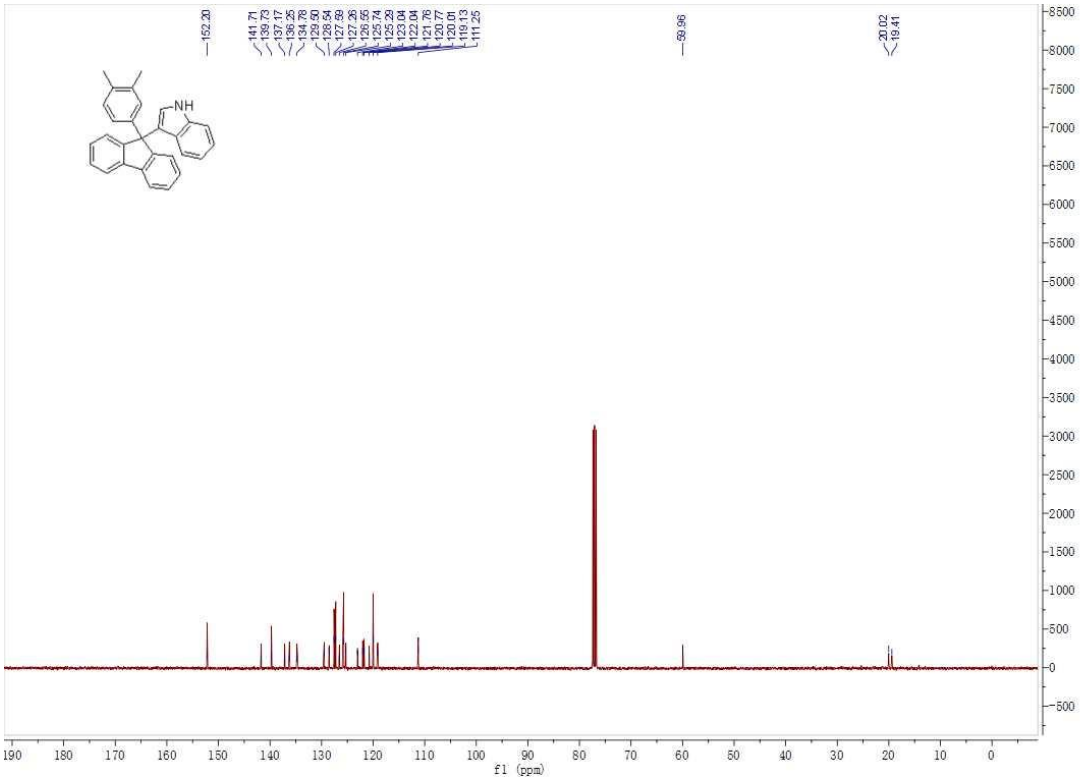

Cl
NH
3.00
2.01
3.06
8.07
1.01
1.00
f1 (ppm)

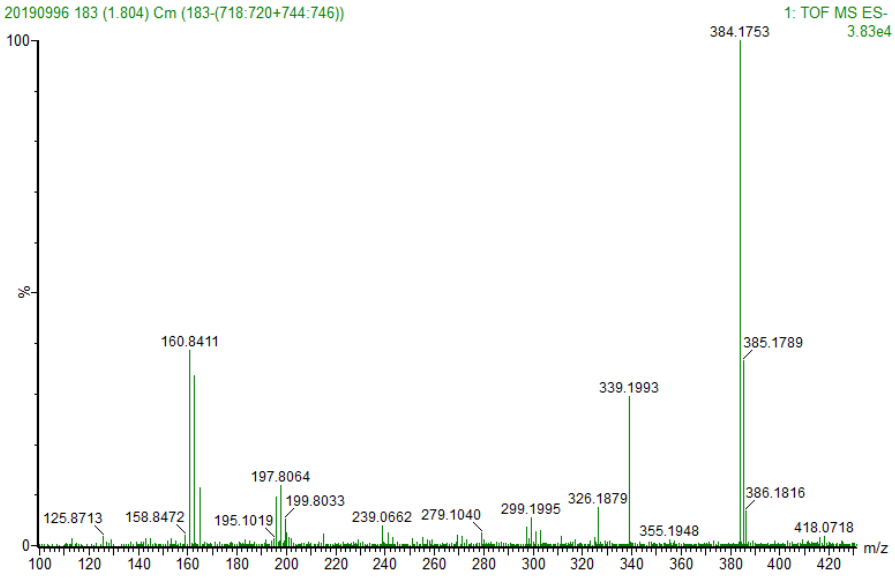

Cl
NH
f1 (ppm)


20190796 148 (1.464) Cm (148-(20:22+37:40))
1: TOF MS ES-
2.79e4
390.1049
392.1025
393.1054
160.8410
158.8462
197.8073
113.0608
254.0638
283.0449
323.0288
356.1419
428.0785
%
m/z

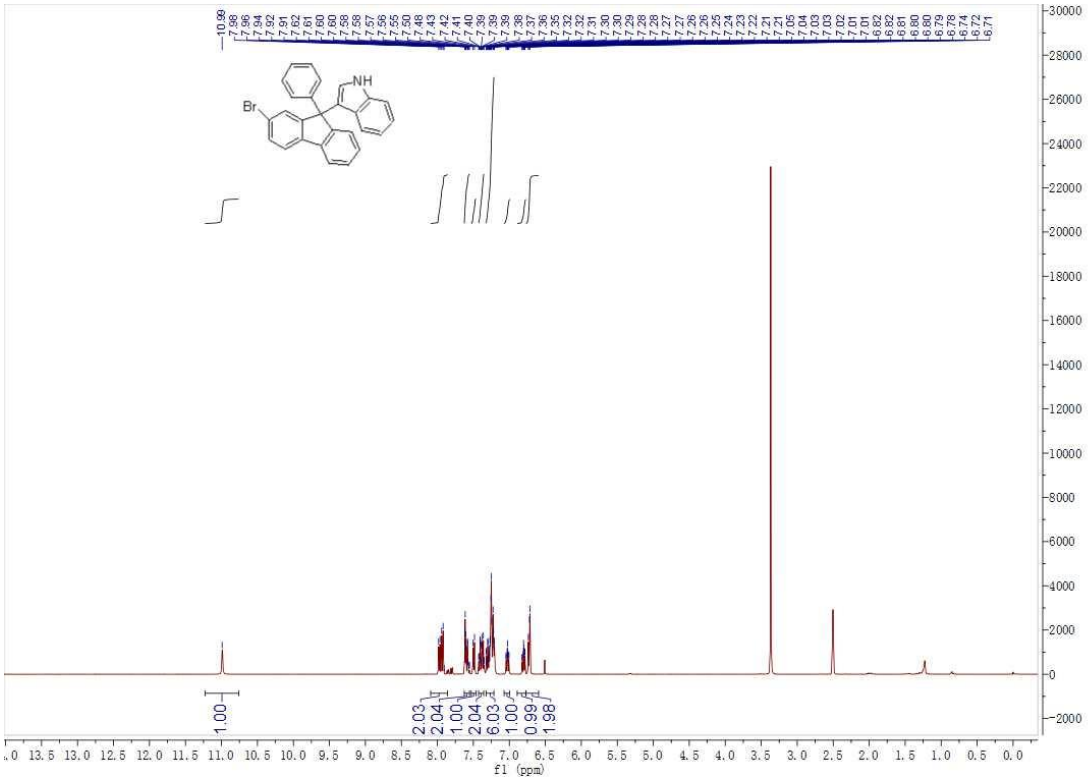
3g

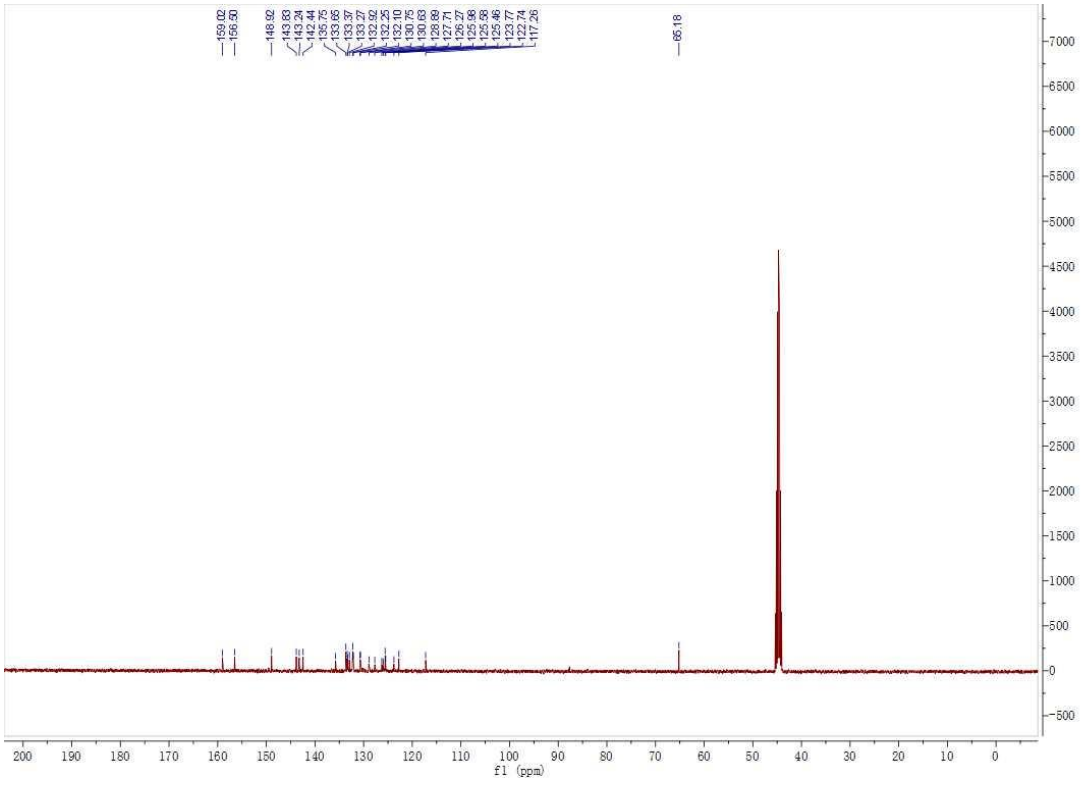

NH
f1 (ppm)

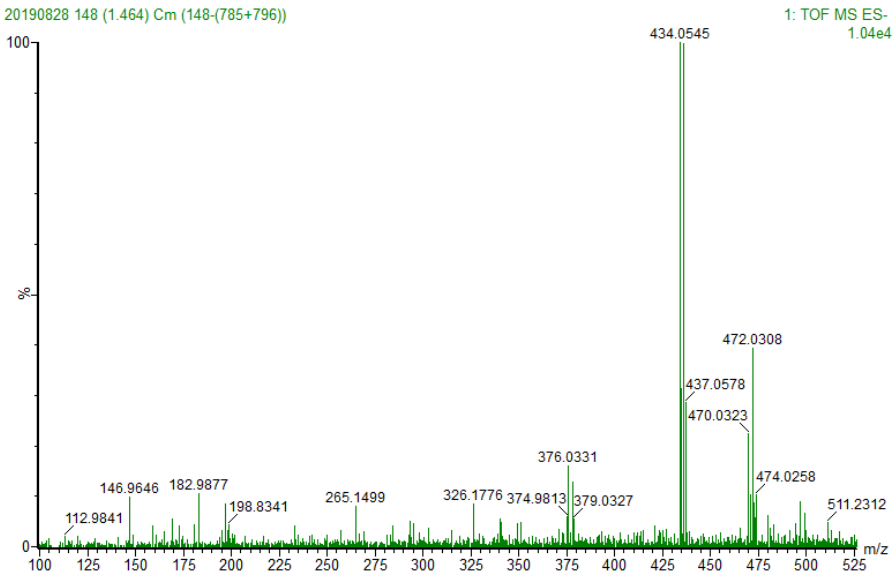

NH
152.20
141.71
139.73
137.17
136.25
134.78
129.50
128.54
69.96
20.02
19.41
f1 (ppm)


20190996 183 (1.804) Cm (183-(718:720+744:746))
1: TOF MS ES-
3.83e4
384.1753
385.1789
339.1993
160.8411
197.8064
199.8033
125.8713
158.8472
195.1019
239.0662
279.1040
299.1995
326.1879
355.1948
386.1816
418.0718
%
m/z

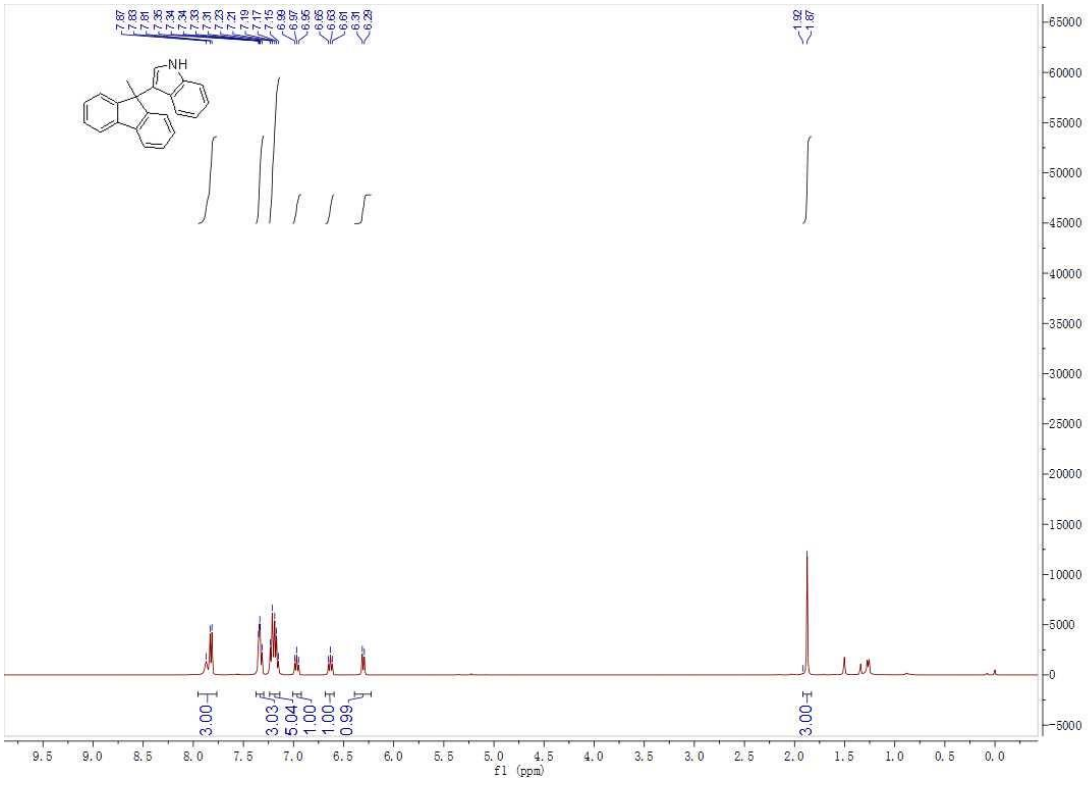
3h

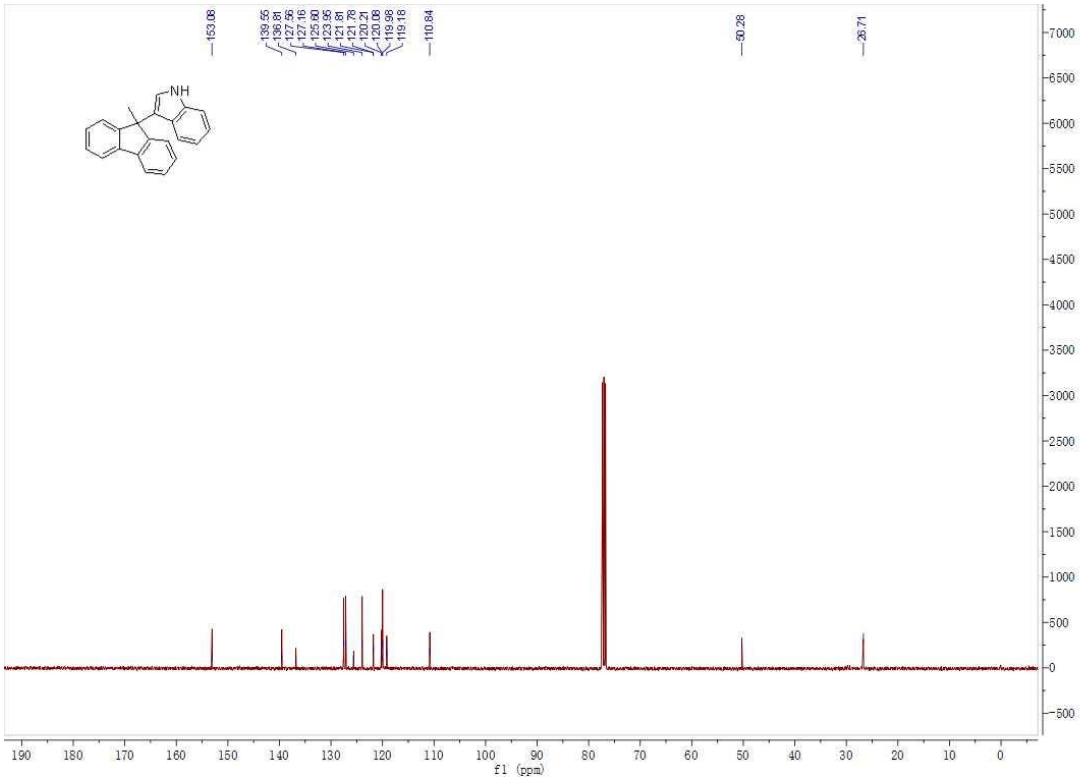

Br
NH
1.00
2.03
2.04
1.00
2.04
6.03
1.00
0.99
1.98
f1 (ppm)

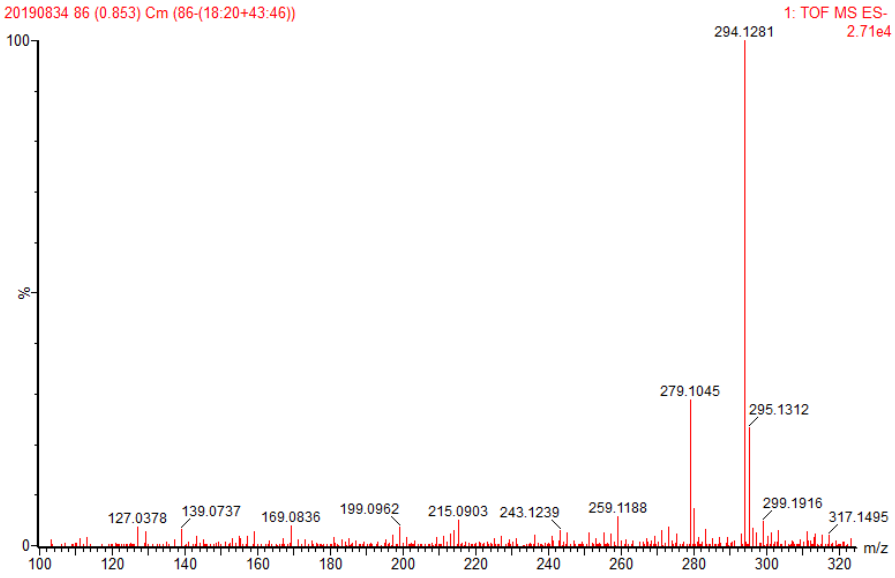

65.18
f1 (ppm)


20190828 148 (1.464) Cm (148-(785+796))
1: TOF MS ES-
1.04e4
100
%
0
434.0545
472.0308
437.0578
470.0323
376.0331
474.0258
146.9646
182.9877
198.8341
265.1499
326.1776
374.9813
379.0327
511.2312
112.9841
100 125 150 175 200 225 250 275 300 325 350 375 400 425 450 475 500 525
m/z

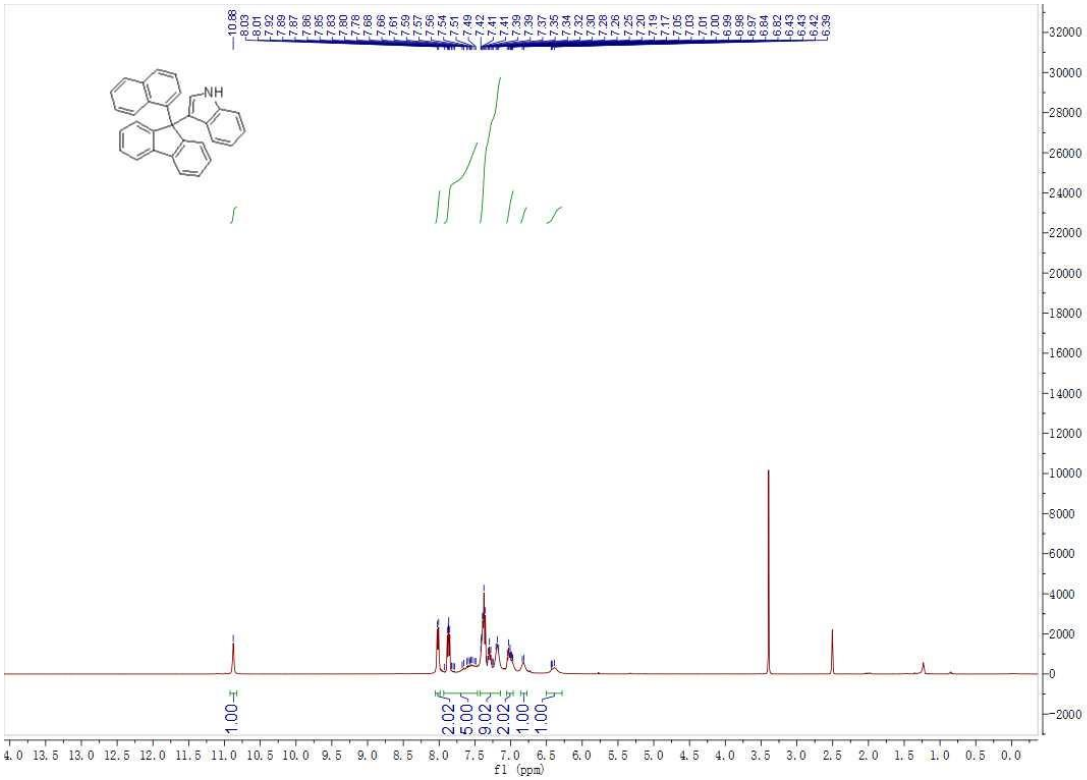
3i

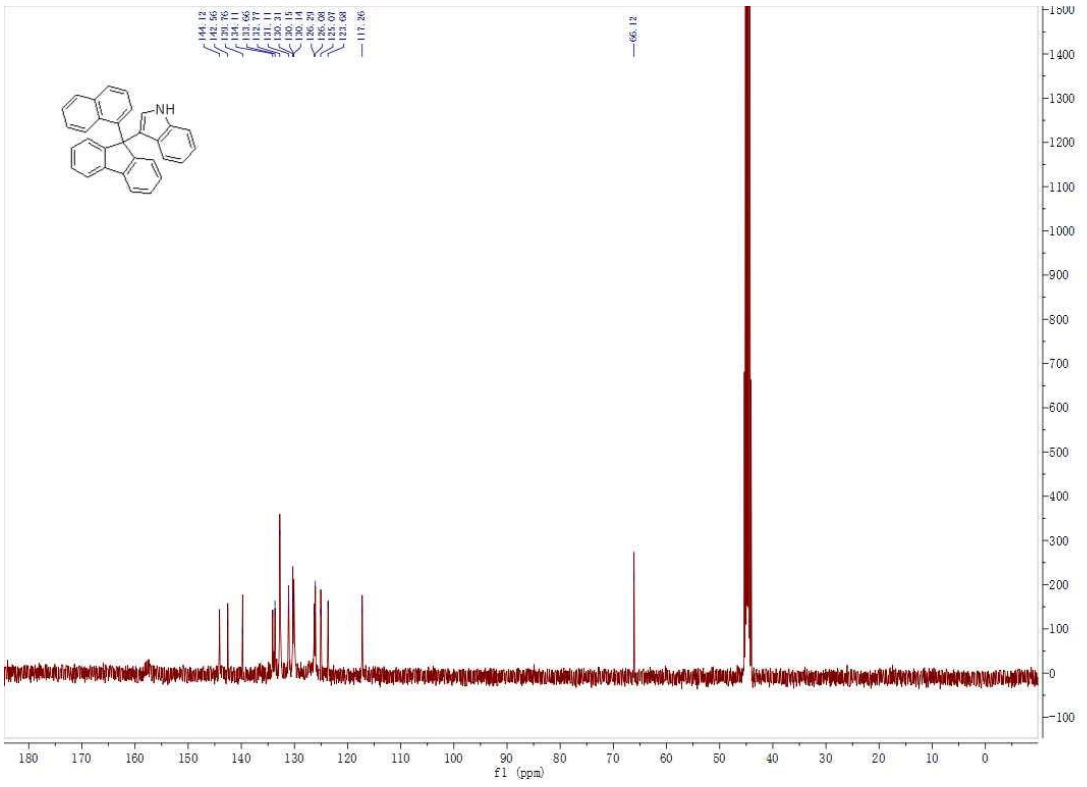

NH
7.87
7.83
7.81
7.35
7.34
7.34
7.33
7.31
7.23
7.21
7.19
7.17
7.15
6.99
6.97
6.95
6.65
6.63
6.61
6.31
6.29
1.92
1.87
3.00
3.03
5.04
1.00
1.00
0.99
3.00
f1 (ppm)

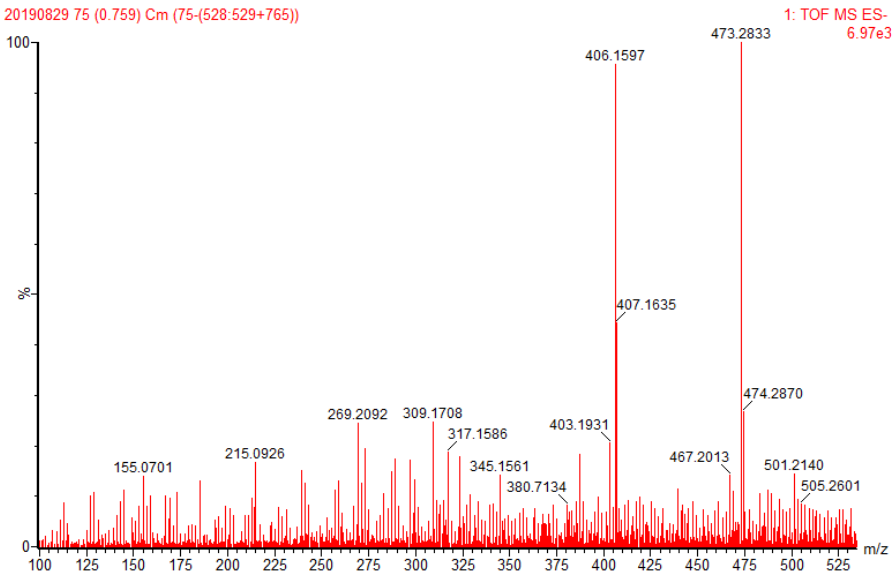

153.08
139.55
136.81
127.56
127.16
125.60
123.95
121.81
121.76
120.21
120.08
119.98
119.18
110.84
50.28
26.71
NH
f1 (ppm)


20190834 86 (0.853) Cm (86-(18:20+43:46))
1: TOF MS ES-
2.71e4
294.1281
279.1045
295.1312
299.1916
317.1495
127.0378
139.0737
169.0836
199.0962
215.0903
243.1239
259.1188
%
m/z

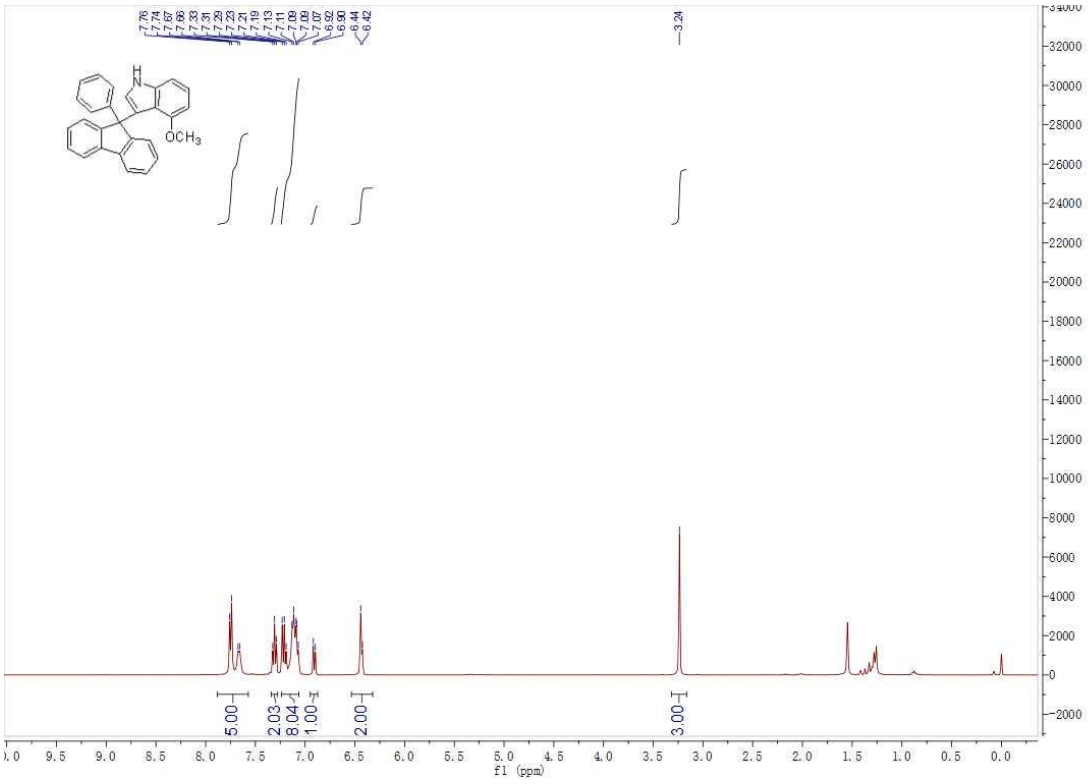
3j

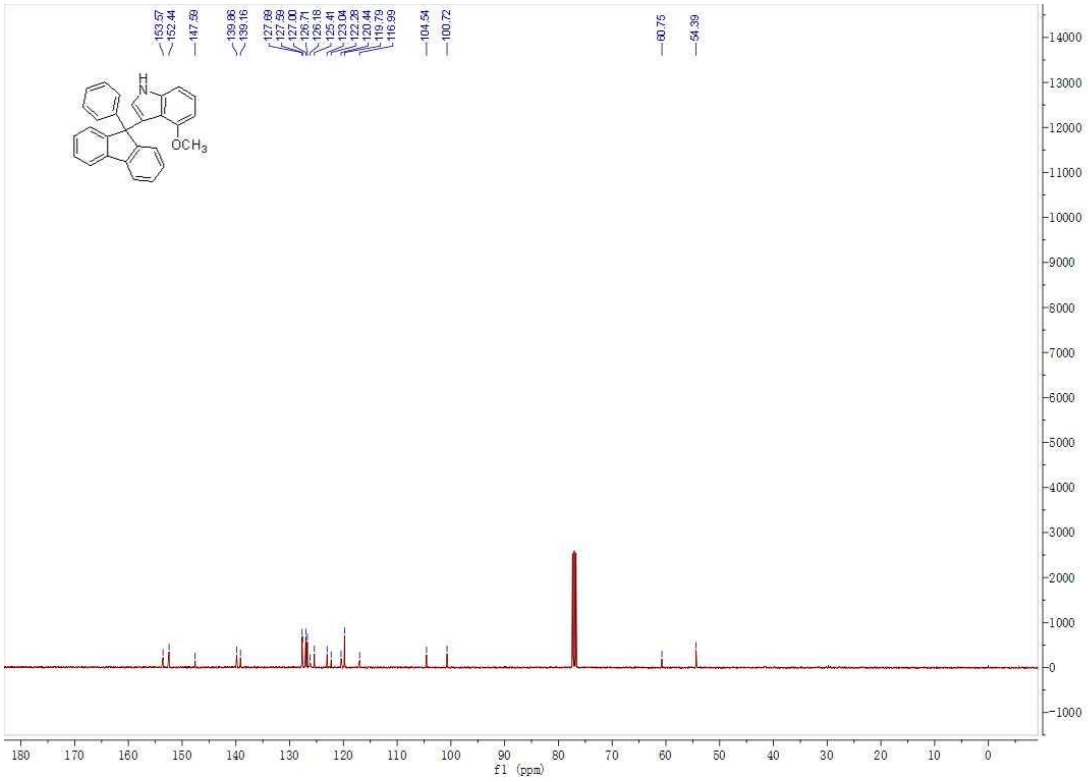

NH
10.88
8.03
8.01
7.92
7.89
7.87
7.86
7.85
7.83
7.80
7.78
7.66
7.61
7.59
7.57
7.56
7.54
7.51
7.49
7.42
7.41
7.39
7.37
7.35
7.34
7.32
7.30
7.28
7.26
7.25
7.20
7.19
7.17
7.05
7.03
7.01
7.00
6.99
6.98
6.97
6.84
6.82
6.43
6.43
6.42
6.39
1.00
2.02
5.00
9.02
2.02
1.00
1.00
f1 (ppm)

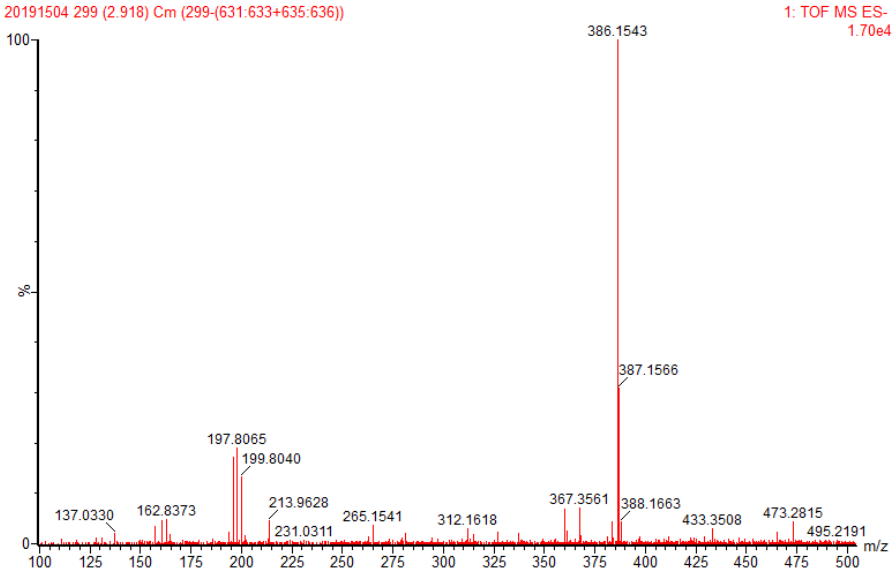

NH
144.12
142.95
139.36
134.11
133.66
132.77
131.11
130.31
130.15
130.14
126.39
126.08
125.07
123.68
117.26
66.12
f1 (ppm)


20190829 75 (0.759) Cm (75-(528:529+765))
1: TOF MS ES-
6.97e3
100
%
0
406.1597
473.2833
407.1635
474.2870
269.2092
309.1708
317.1586
403.1931
215.0926
155.0701
345.1561
467.2013
501.2140
380.7134
505.2601
m/z

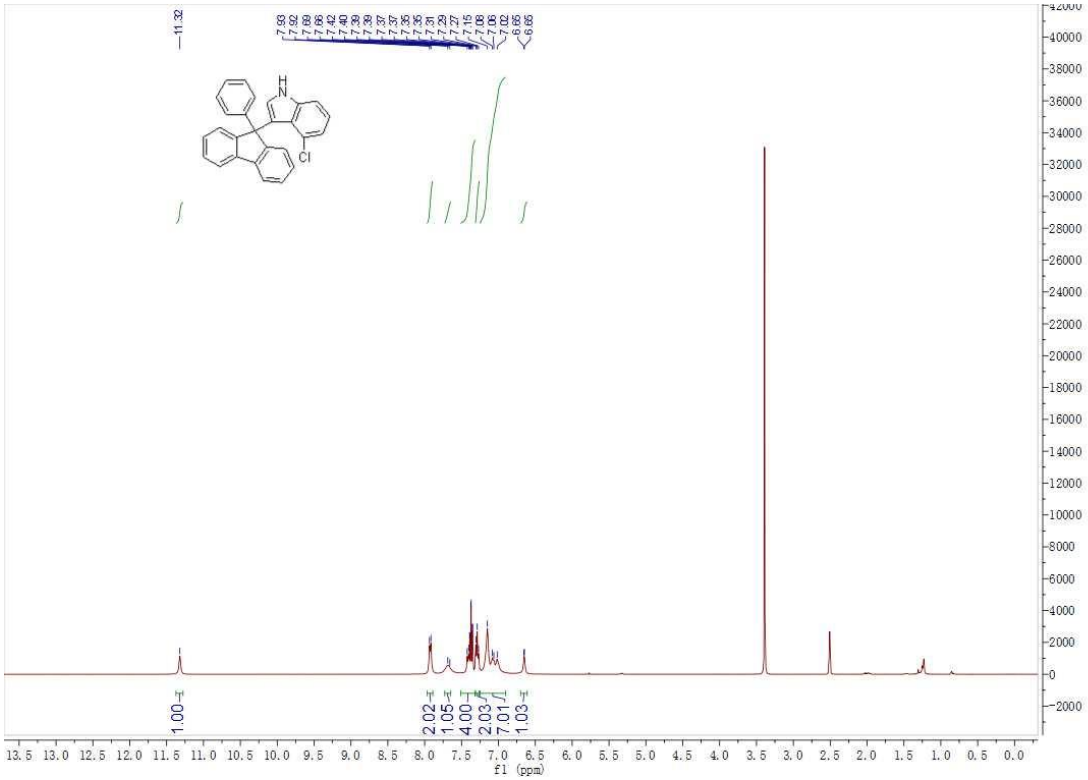
3k

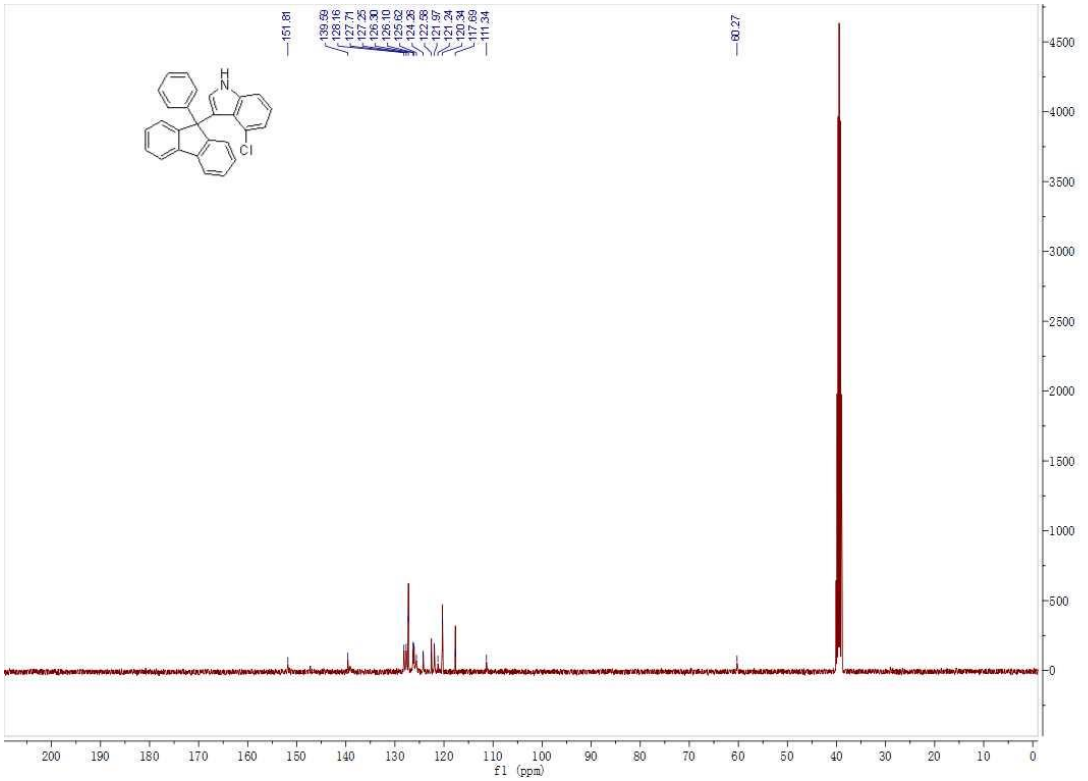

OCH3
5.00
2.03
8.04
1.00
2.00
3.00
f1 (ppm)

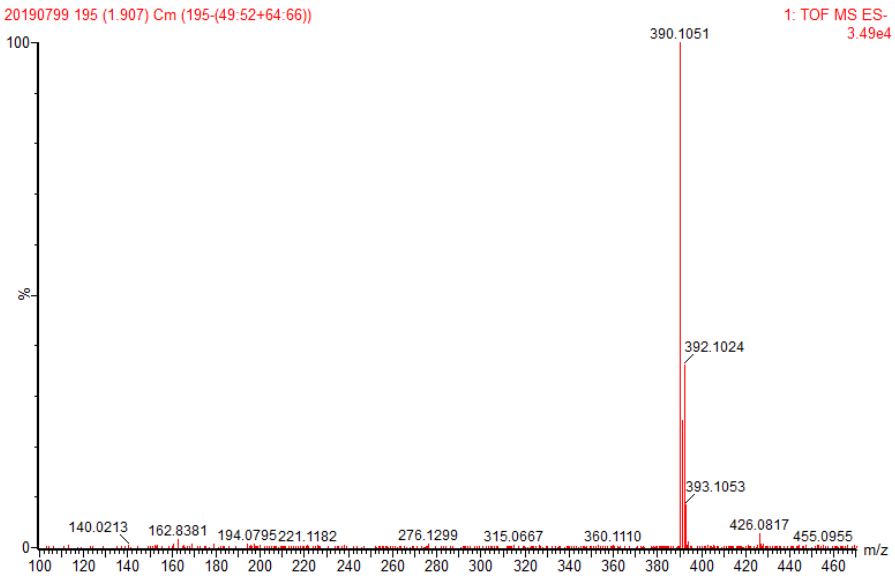

153.57
152.44
147.59
139.86
139.16
127.69
127.59
127.00
126.71
126.18
125.41
123.04
122.28
120.44
119.79
116.99
104.54
100.72
60.75
54.39
OCH3
H
14000
13000
12000
11000
10000
9000
8000
7000
6000
5000
4000
3000
2000
1000
0
-1000
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


20191504 299 (2.918) Cm (299-(631:633+635:636))
1: TOF MS ES-
1.70e4
100
%
0
386.1543
387.1566
197.8065
199.8040
213.9628
231.0311
137.0330
162.8373
265.1541
312.1618
367.3561
388.1663
433.3508
473.2815
495.2191
m/z
100 125 150 175 200 225 250 275 300 325 350 375 400 425 450 475 500

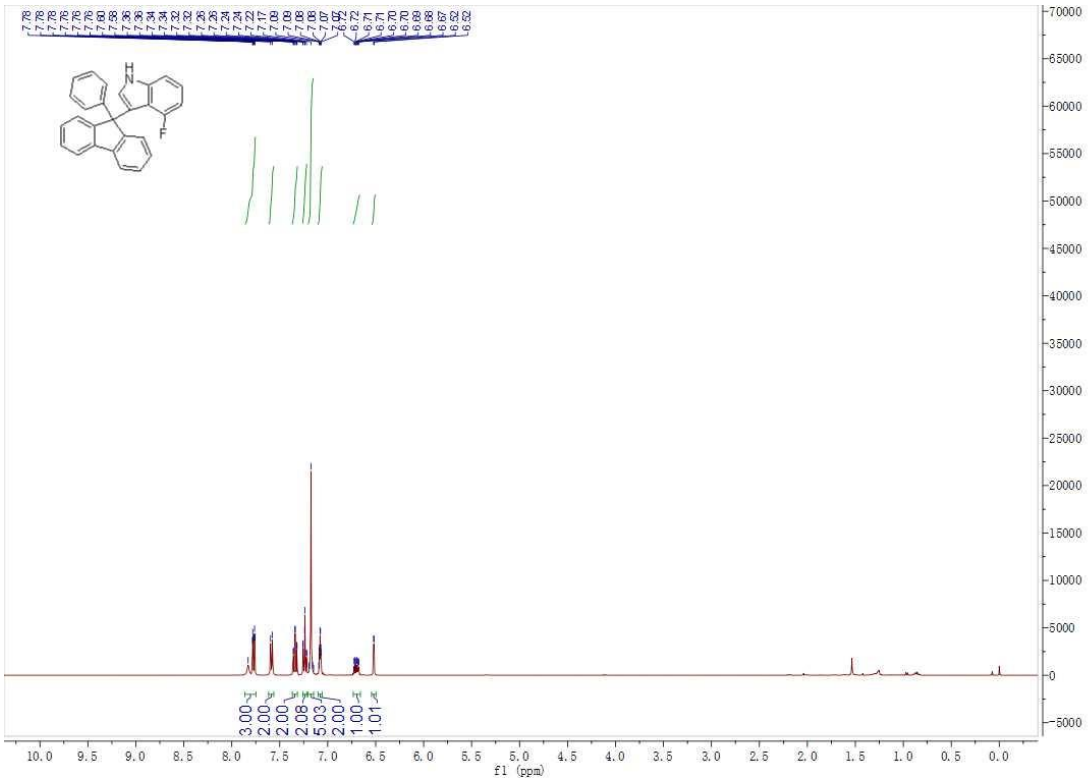
3l

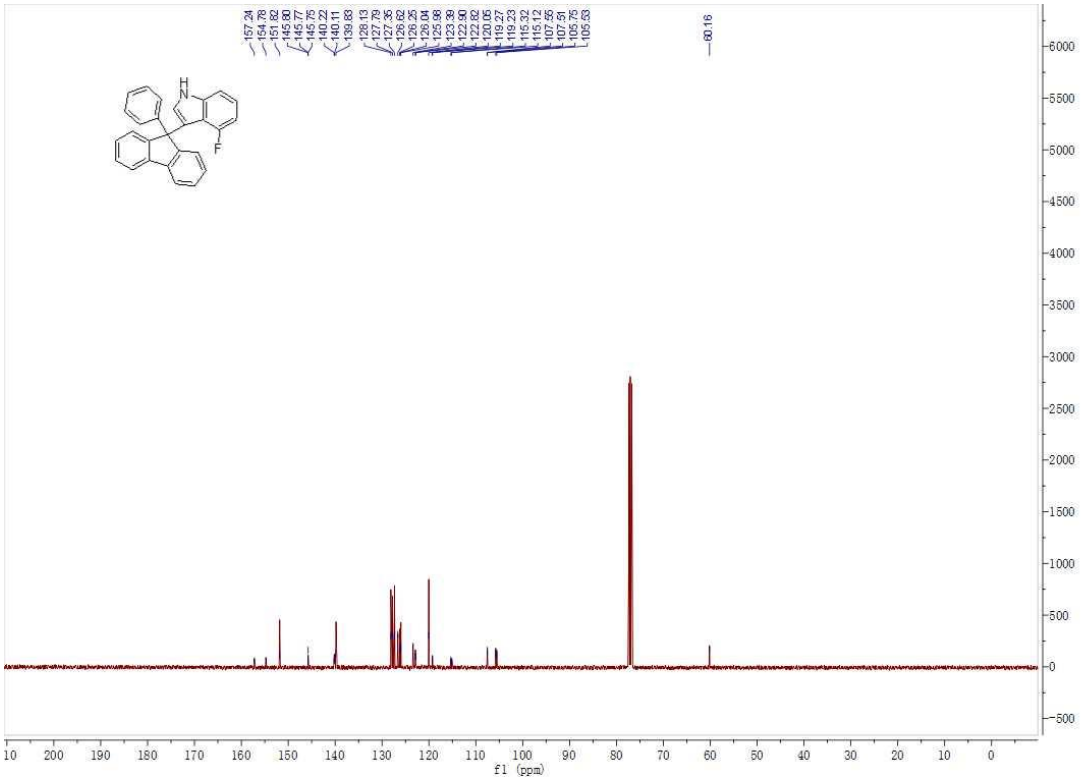

11.32
7.59
7.92
7.89
7.86
7.42
7.40
7.39
7.39
7.37
7.37
7.35
7.35
7.31
7.29
7.27
7.15
7.08
7.06
7.02
6.66
6.66
Cl
1.00
2.02
1.05
4.00
2.03
7.01
1.03
f1 (ppm)

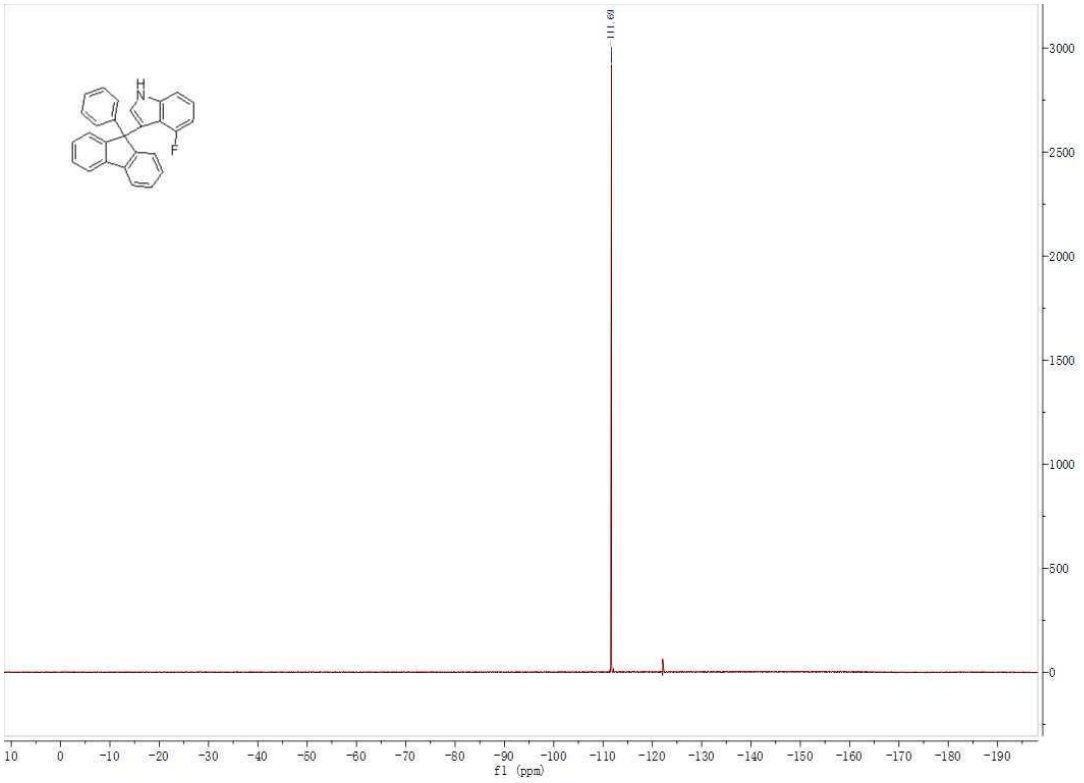

151.81
139.69
128.16
127.71
127.25
126.30
126.10
125.62
124.26
122.89
121.57
121.34
120.34
117.69
111.34
60.27
Cl
f1 (ppm)

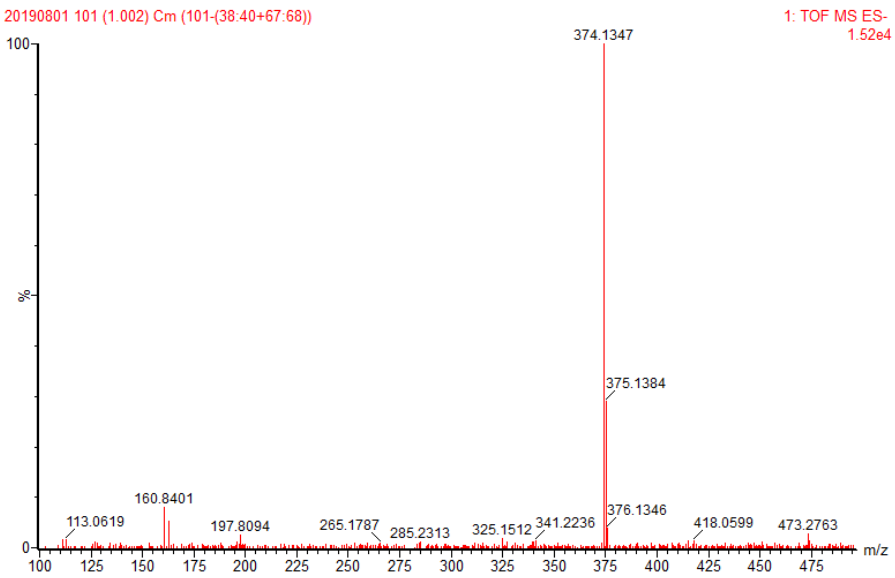

20190799 195 (1.907) Cm (195-(49:52+64:66))
1: TOF MS ES-
3.49e4
100
%
0
390.1051
392.1024
393.1053
426.0817
140.0213
162.8381
194.0795
221.1182
276.1299
315.0667
360.1110
455.0955
m/z
100 120 140 160 180 200 220 240 260 280 300 320 340 360 380 400 420 440 460

3m

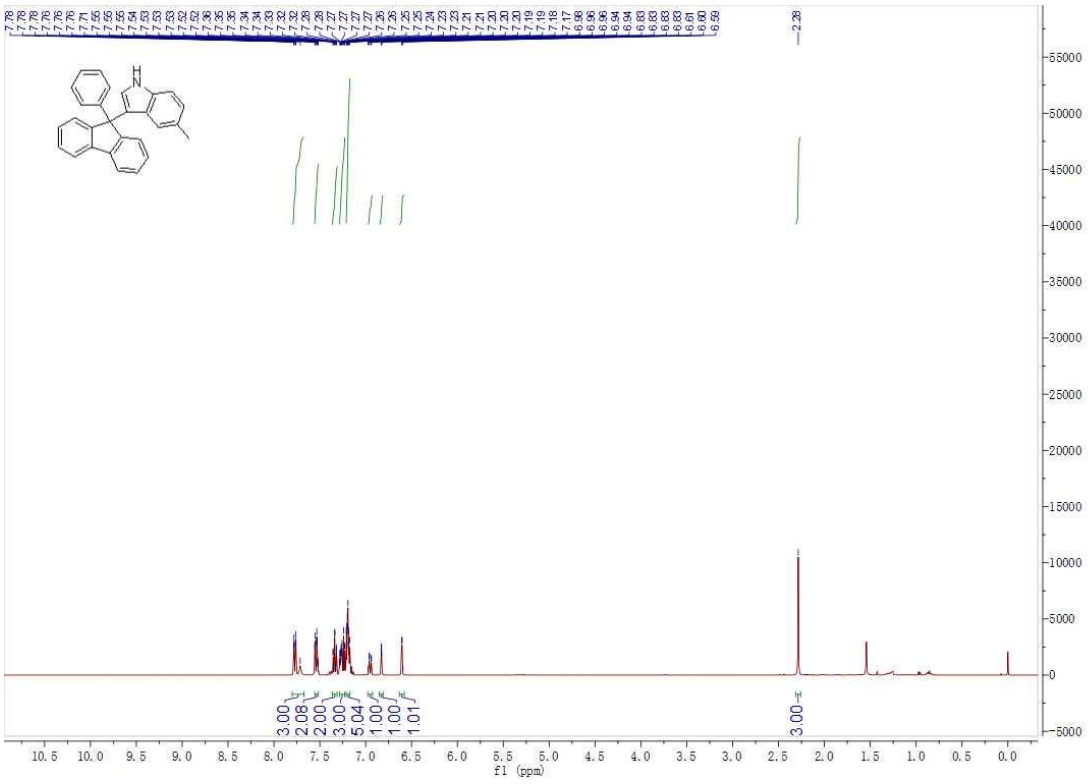

H
F
3.00
2.00
2.00
2.08
5.03
2.00
1.00
1.01
f1 (ppm)

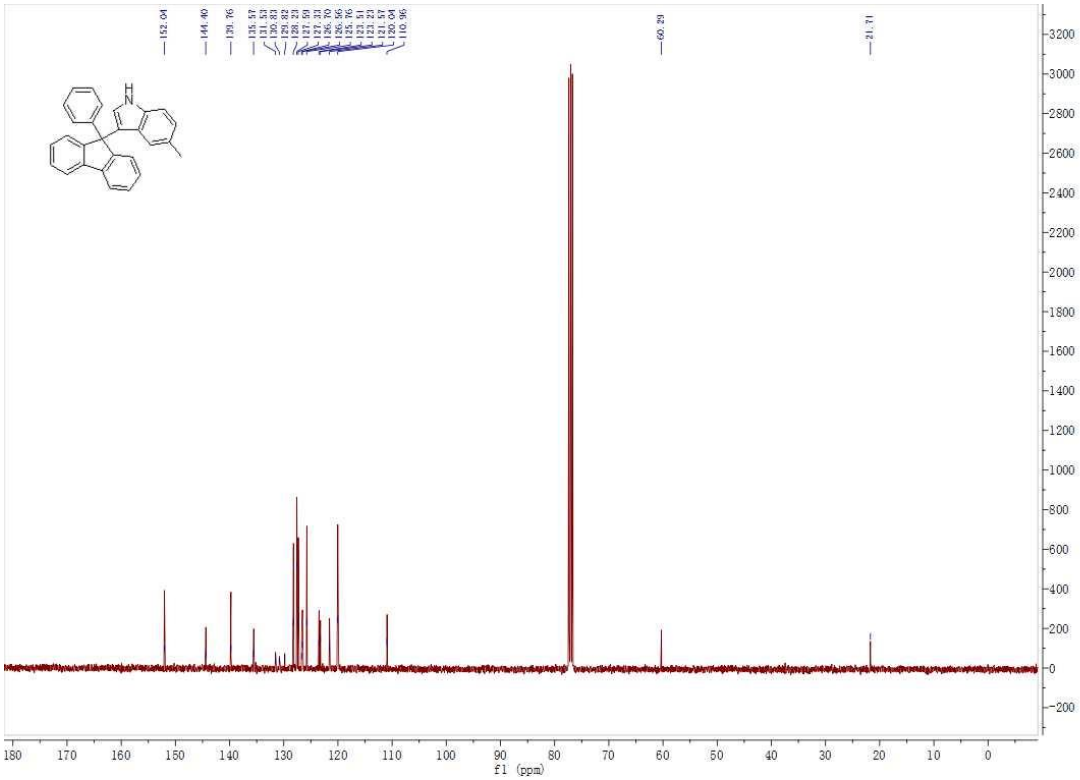

157.24
154.78
151.82
145.80
145.77
145.75
140.22
140.11
139.83
128.13
127.79
127.35
126.62
126.25
126.04
125.98
123.39
122.90
122.82
120.05
119.27
119.23
115.32
115.12
107.65
107.51
105.76
105.53
60.16
H
N
F
f1 (ppm)

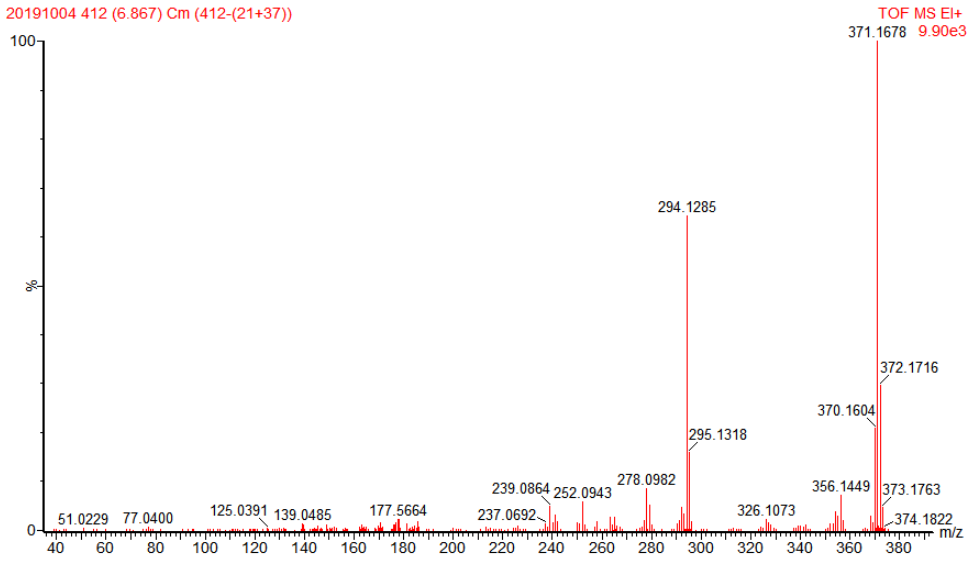

111.69
H
N
F
f1 (ppm)


20190801 101 (1.002) Cm (101-(38:40+67:68))
1: TOF MS ES-
1.52e4
374.1347
375.1384
160.8401
113.0619
197.8094
265.1787
285.2313
325.1512
341.2236
376.1346
418.0599
473.2763
%
m/z

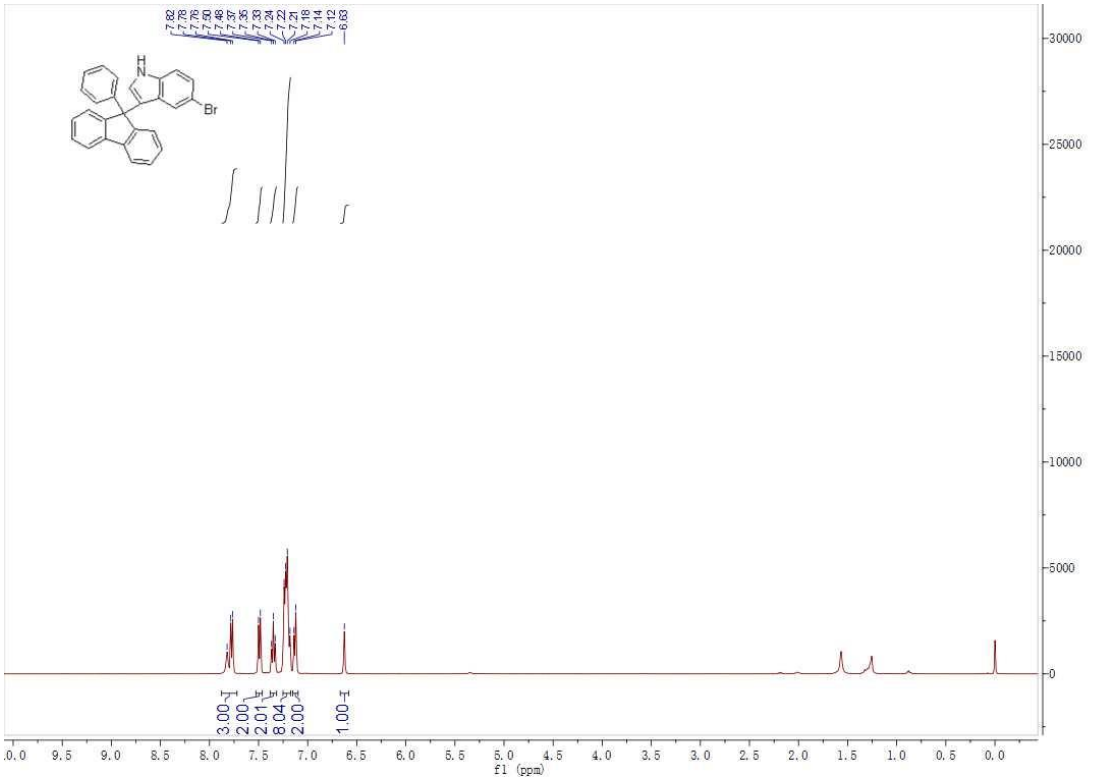
3n

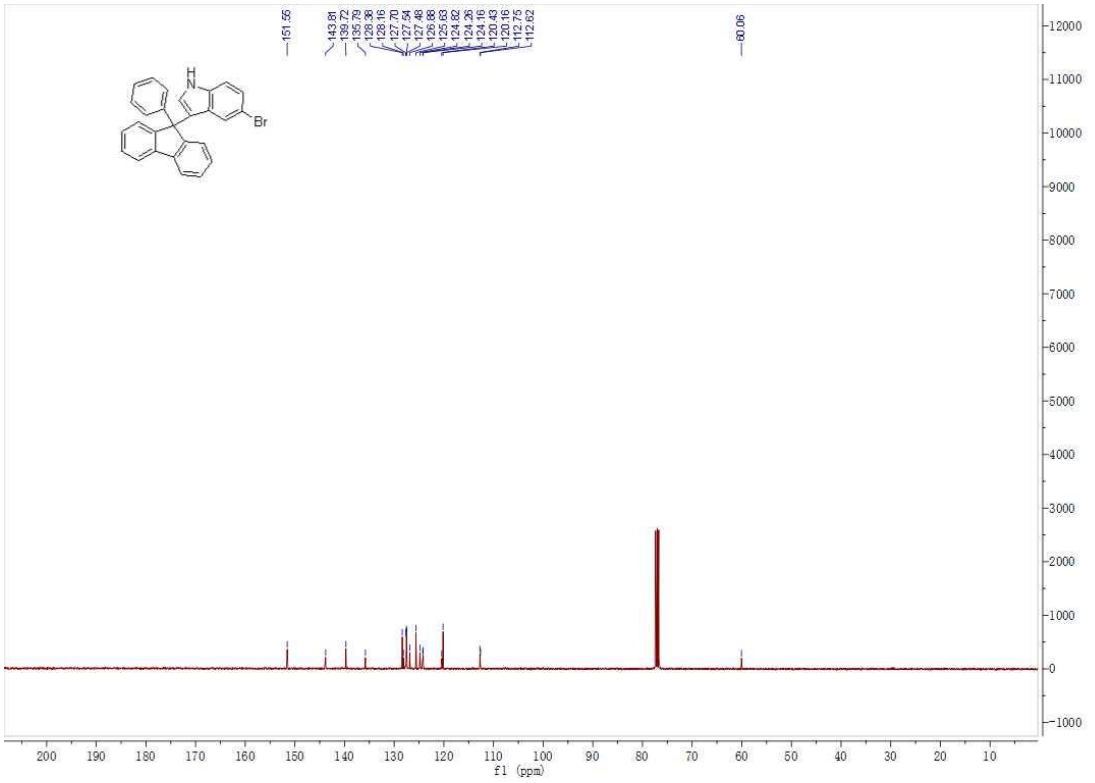

f1 (ppm)

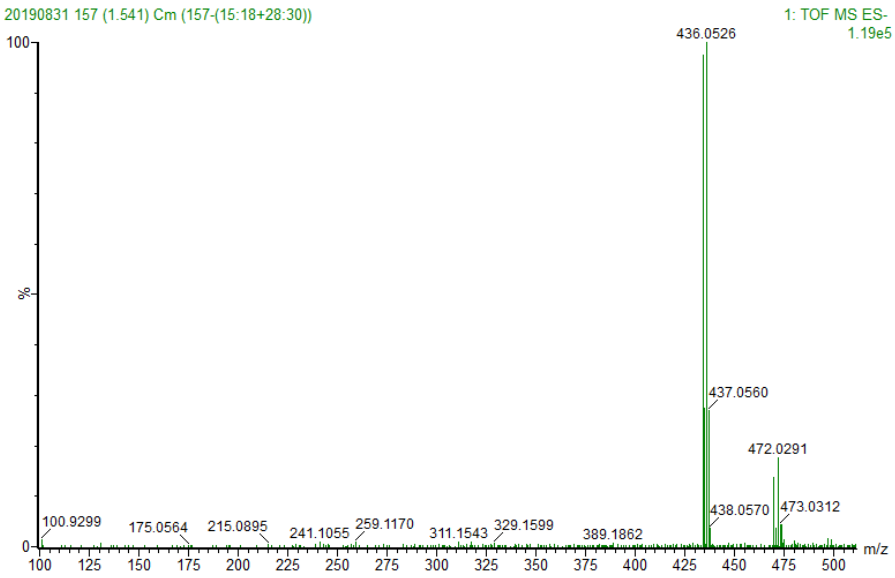

152.04
144.40
139.76
135.57
131.53
130.83
129.82
129.21
127.50
127.33
126.70
126.45
125.76
123.51
123.23
121.67
120.54
110.96
60.29
21.71
f1 (ppm)


20191004 412 (6.867) Cm (412-(21+37))
TOF MS EI+
371.1678 9.90e3
294.1285
372.1716
370.1604
295.1318
239.0864
252.0943
278.0982
356.1449
373.1763
51.0229
77.0400
125.0391
139.0485
177.5664
237.0692
326.1073
374.1822
%
m/z

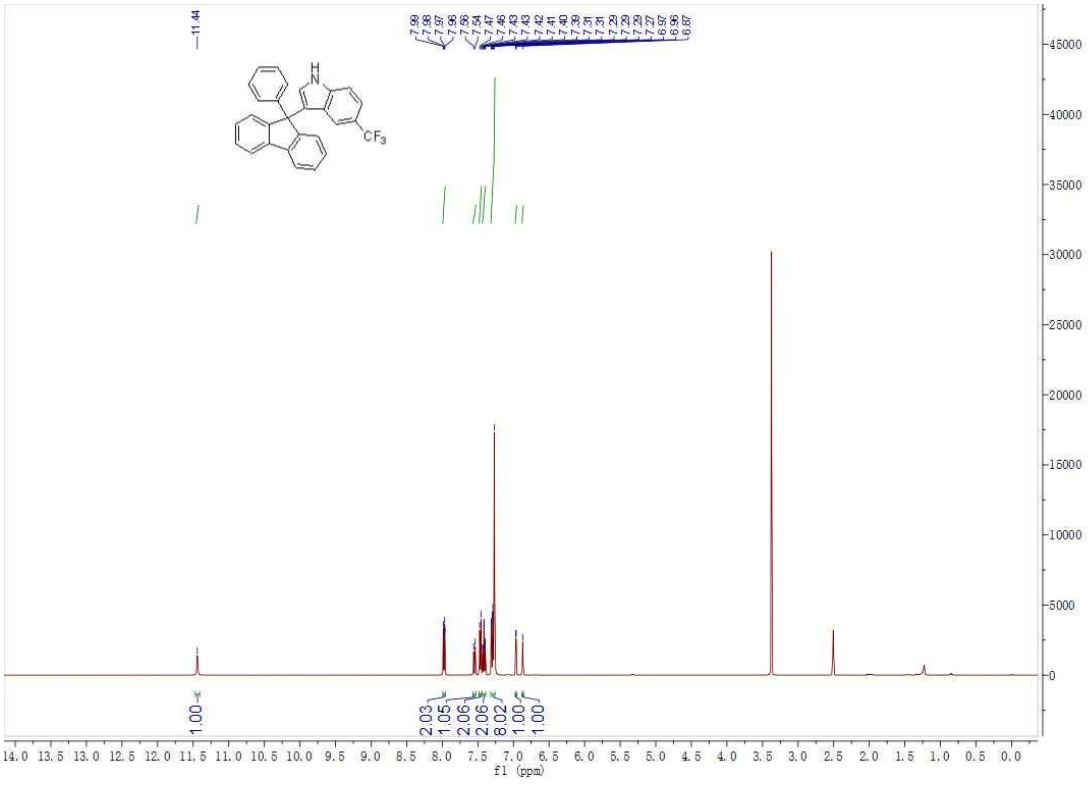
3o

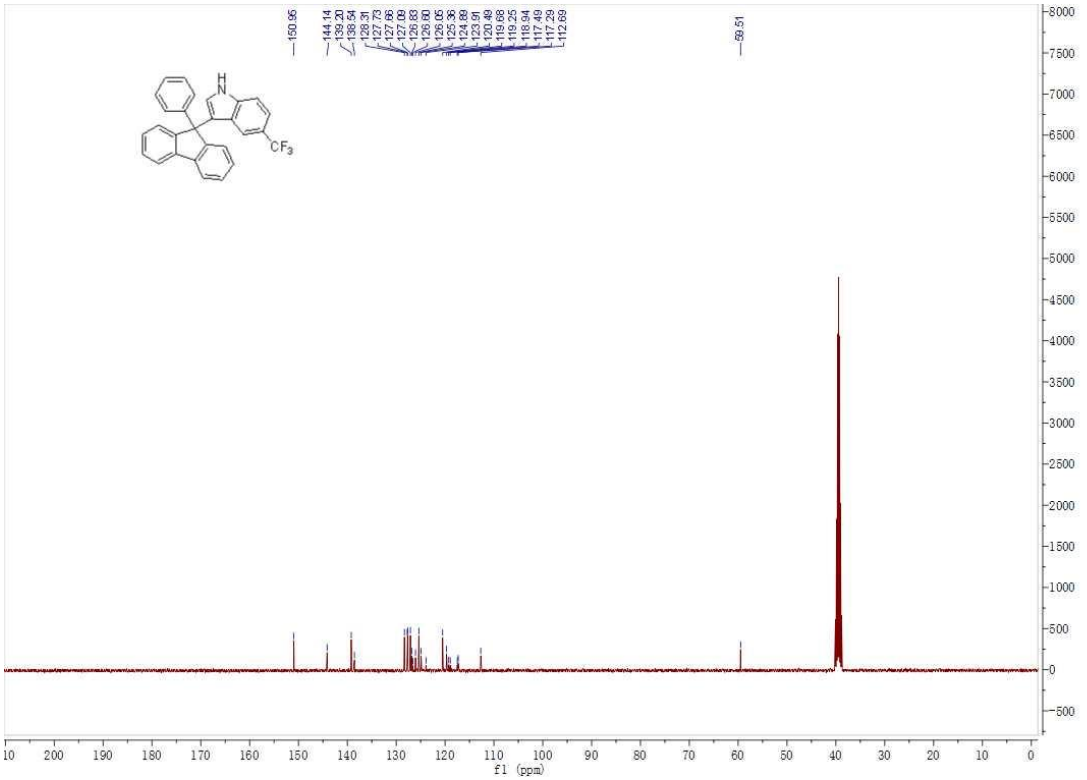

7.82
7.78
7.76
7.50
7.48
7.37
7.35
7.33
7.24
7.22
7.21
7.18
7.14
7.12
6.63
Br
3.00
2.00
2.01
8.04
2.00
1.00
f1 (ppm)

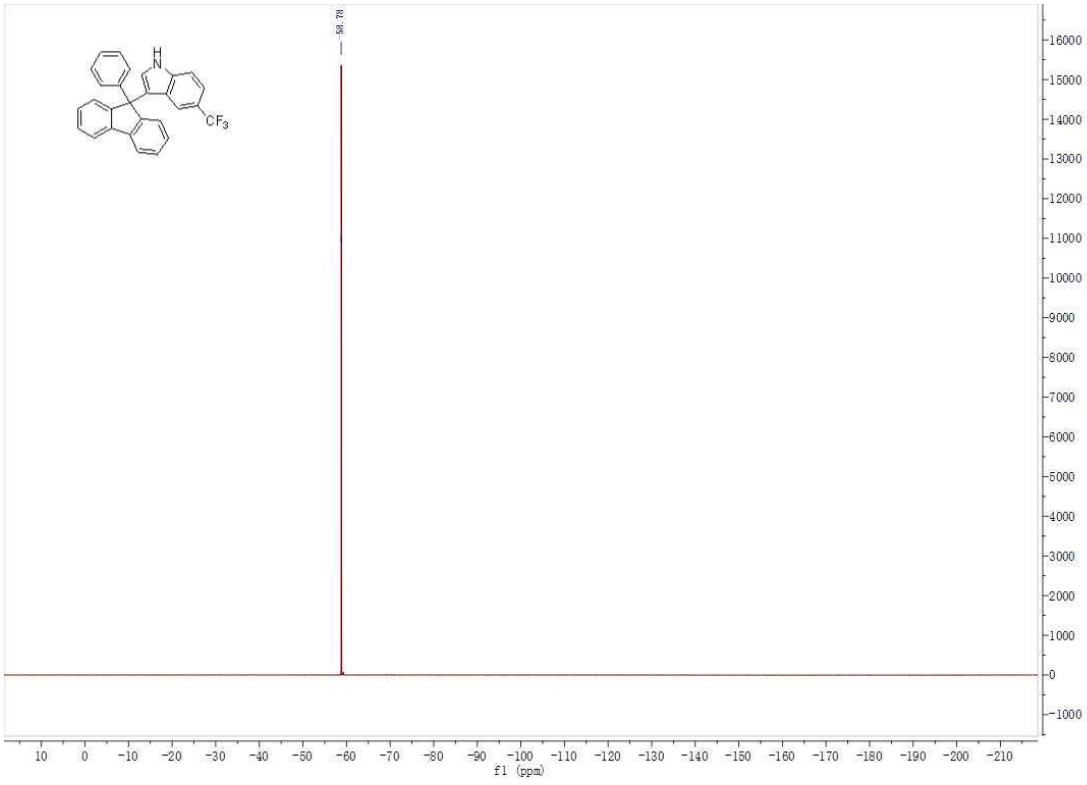

151.55
143.81
139.72
135.79
128.36
128.16
127.70
127.54
127.48
126.88
125.63
124.62
124.26
124.16
120.43
120.15
112.75
112.62
60.06
Br
f1 (ppm)

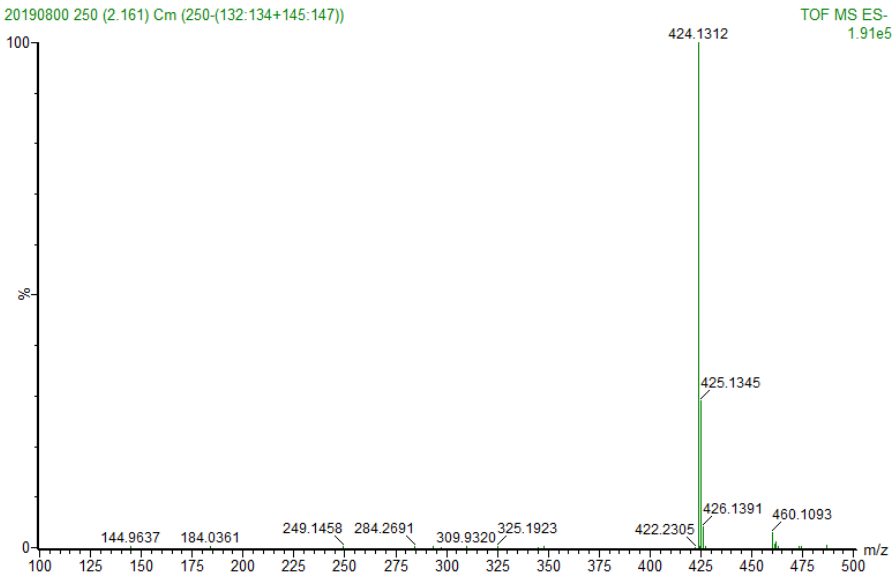

20190831 157 (1.541) Cm (157-(15:18+28:30))
1: TOF MS ES-
1.19e5
436.0526
437.0560
472.0291
438.0570
473.0312
100.9299
175.0564
215.0895
241.1055
259.1170
311.1543
329.1599
389.1862
%
m/z

3p

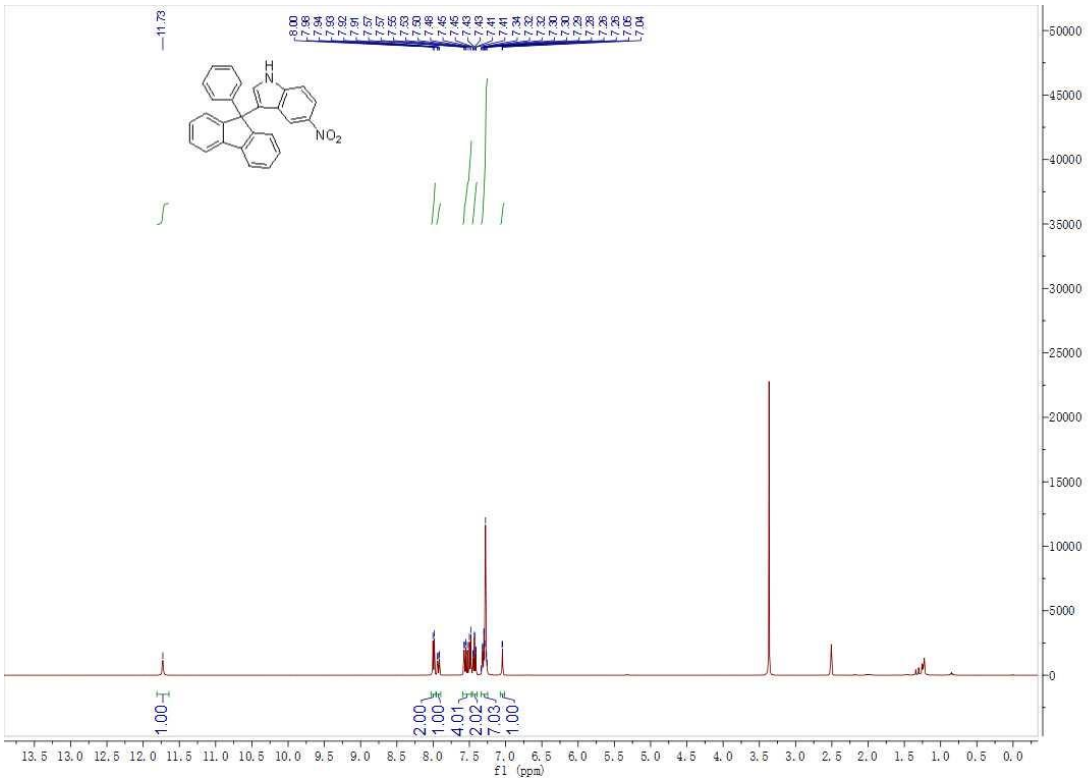

11.44
7.99
7.98
7.97
7.96
7.95
7.94
7.47
7.46
7.43
7.42
7.41
7.40
7.39
7.31
7.29
7.29
7.29
7.27
6.97
6.96
6.87
CF3
1.00
2.03
1.05
2.06
2.06
8.02
1.00
1.00
f1 (ppm)

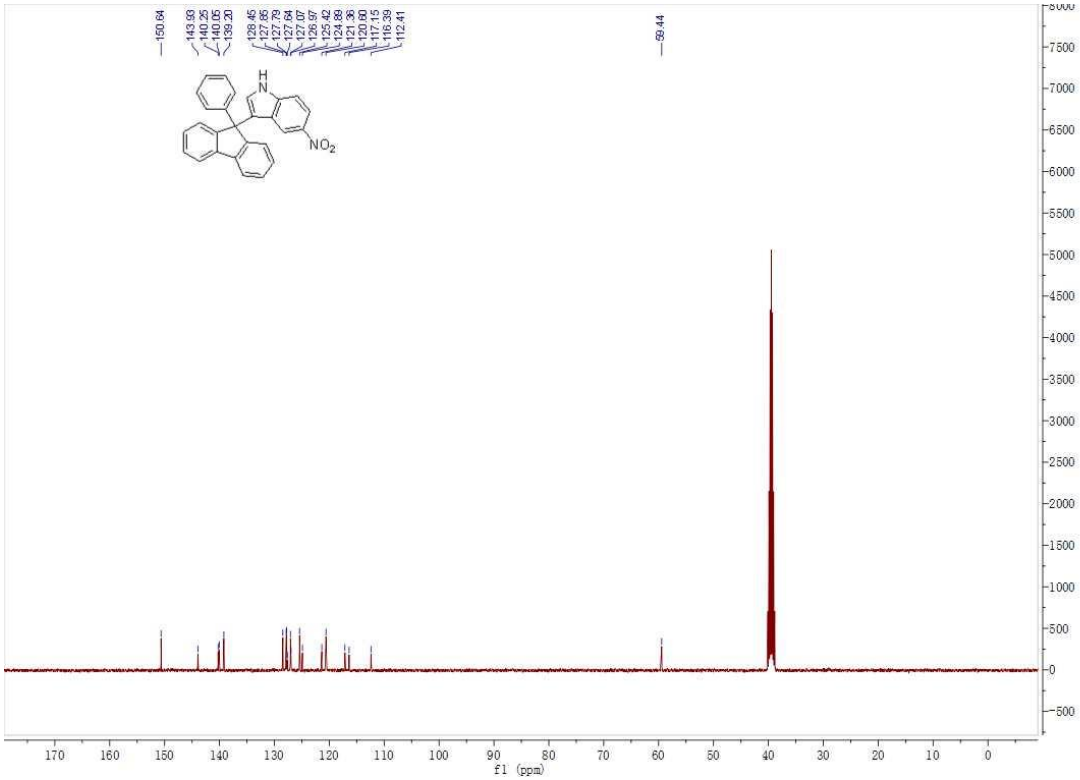

150.95
144.14
139.20
138.54
128.31
127.73
127.66
127.09
126.83
126.60
126.05
125.36
124.88
123.91
120.49
119.68
119.25
118.94
117.49
117.29
112.69
59.51
CF3
f1 (ppm)

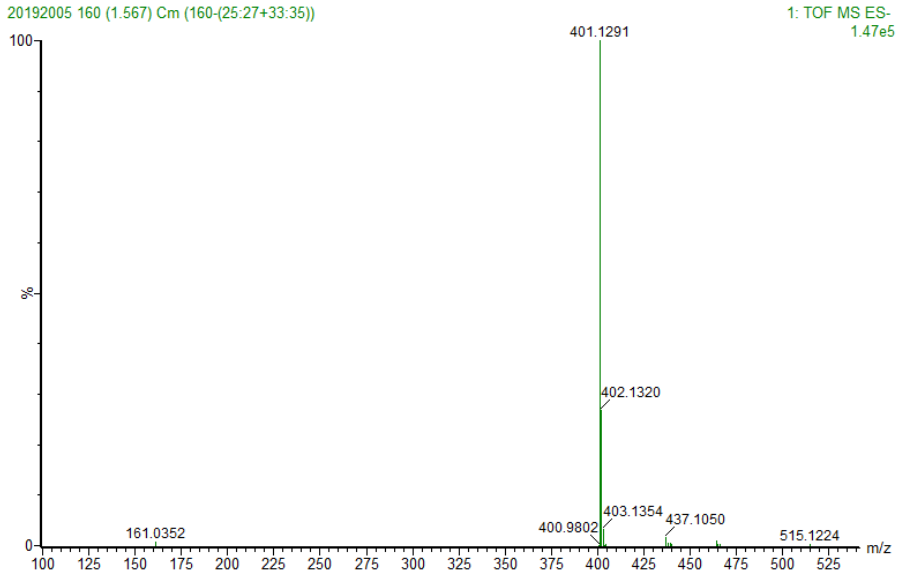

58.78
CF3
f1 (ppm)


20190800 250 (2.161) Cm (250-(132:134+145:147))
TOF MS ES-
1.91e5
424.1312
425.1345
426.1391
460.1093
422.2305
325.1923
309.9320
284.2691
249.1458
184.0361
144.9637
%
m/z

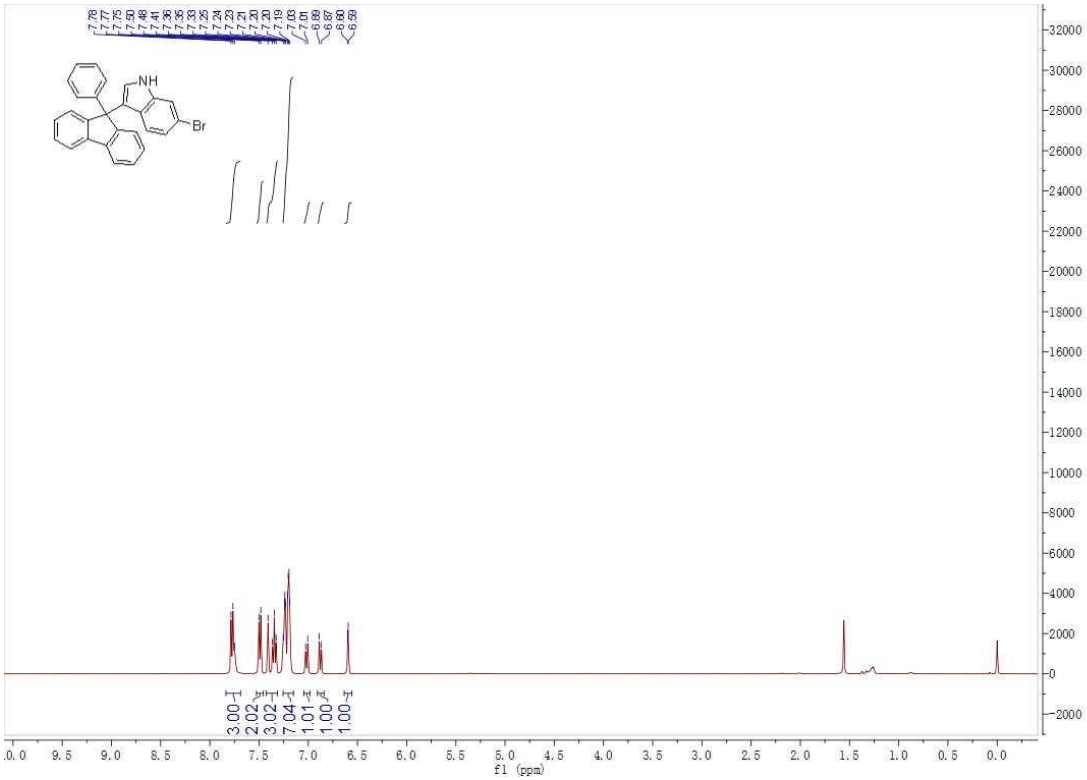
3q

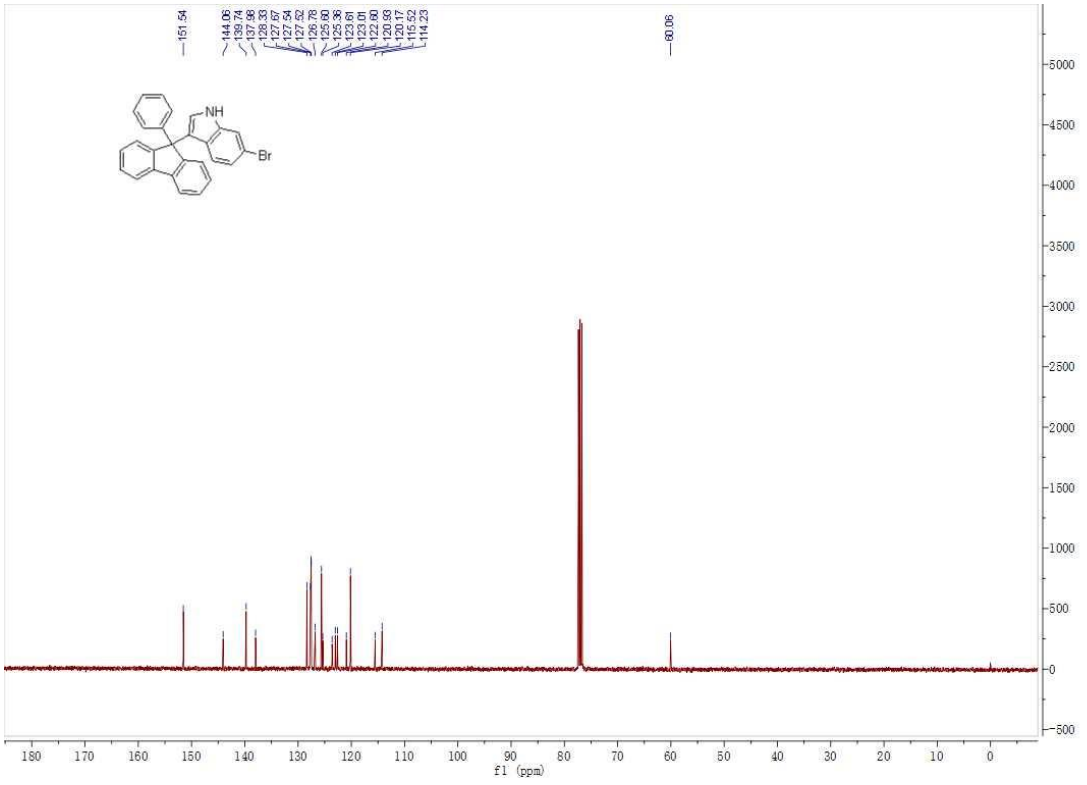

11.73
NH
NO2
f1 (ppm)

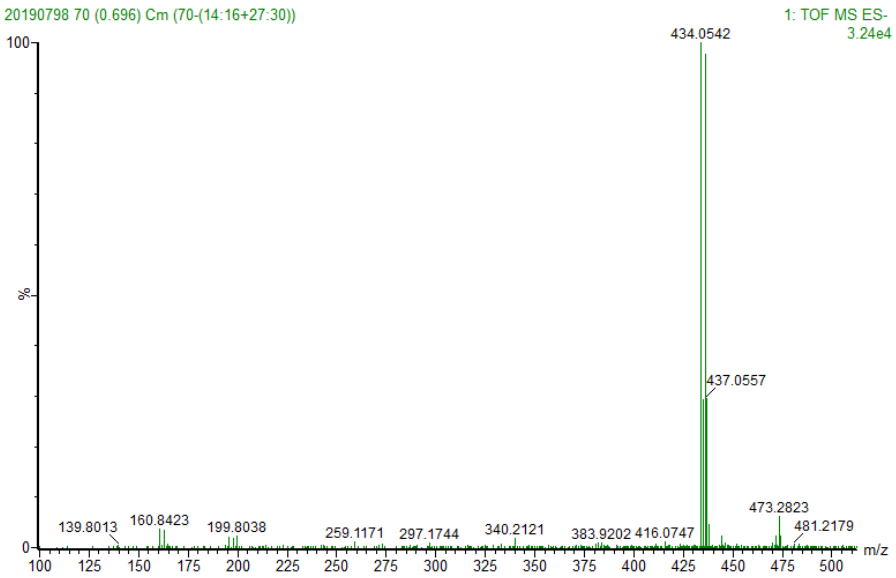

150.64
143.93
140.25
140.05
139.20
129.45
127.85
127.79
127.64
127.07
126.97
125.42
124.89
124.38
120.60
117.15
116.39
112.41
59.44
NO2
H
N
f1 (ppm)


20192005 160 (1.567) Cm (160-(25:27+33:35))
1: TOF MS ES-
1.47e5
401.1291
402.1320
403.1354
437.1050
515.1224
400.9802
161.0352
%
m/z

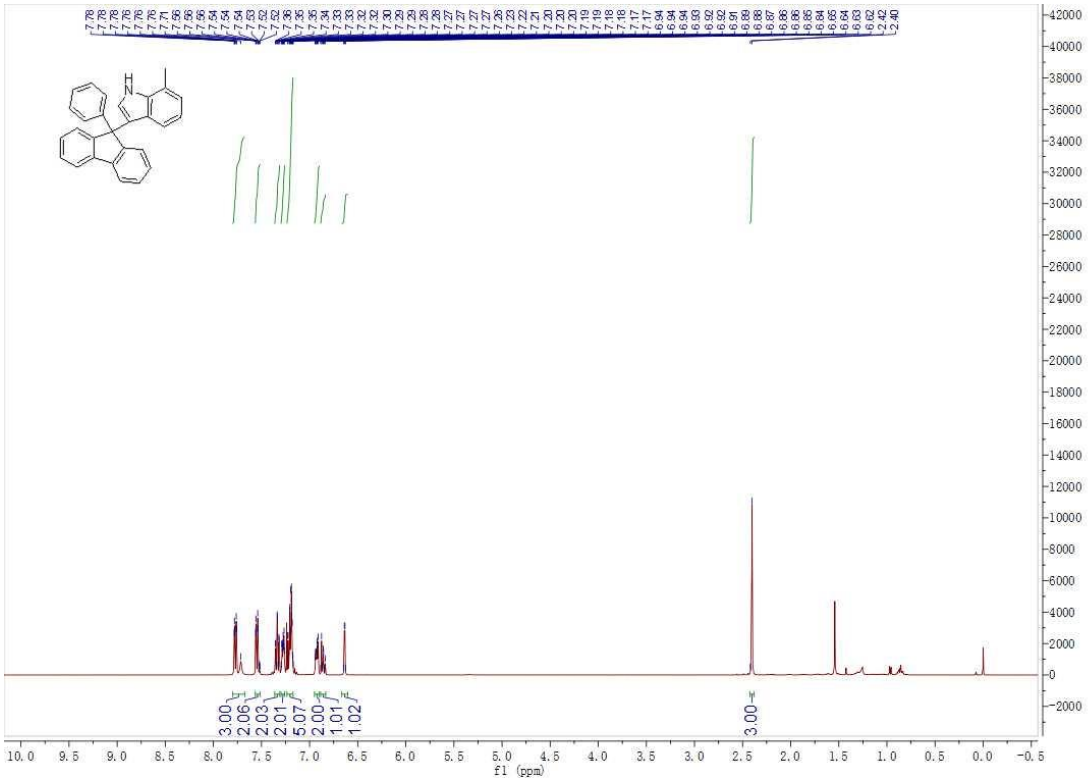
3r

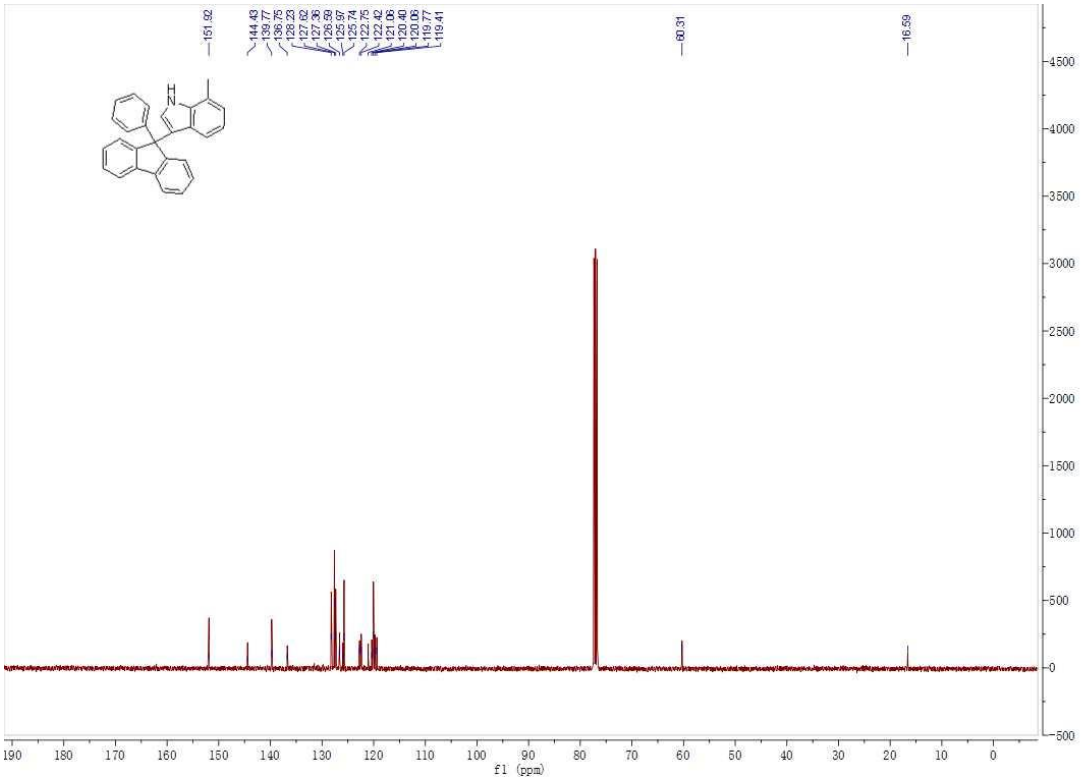

NH
Br
f1 (ppm)

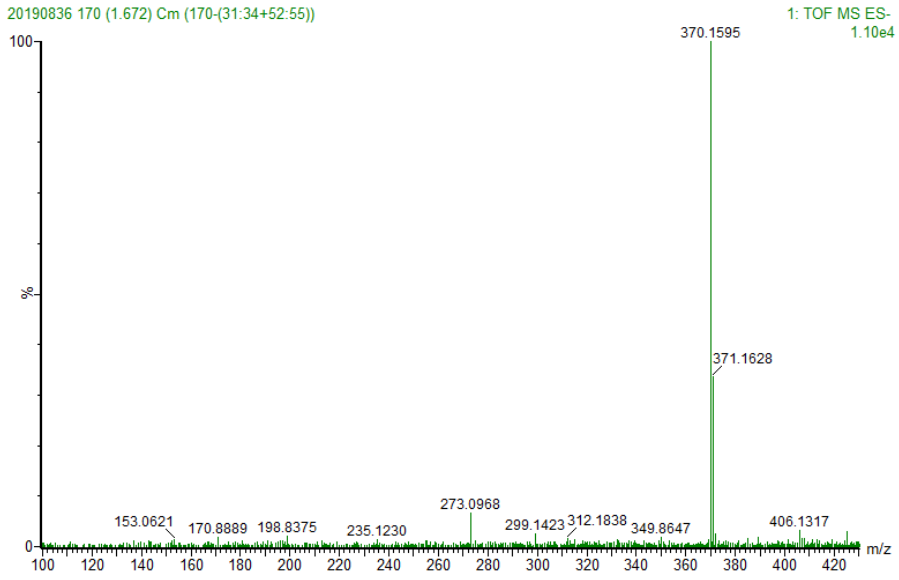

NH
Br
f1 (ppm)


20190798 70 (0.696) Cm (70-(14:16+27:30))
1: TOF MS ES-
3.24e4
100
%
0
434.0542
437.0557
473.2823
481.2179
139.8013
160.8423
199.8038
259.1171
297.1744
340.2121
383.9202
416.0747
m/z
100 125 150 175 200 225 250 275 300 325 350 375 400 425 450 475 500

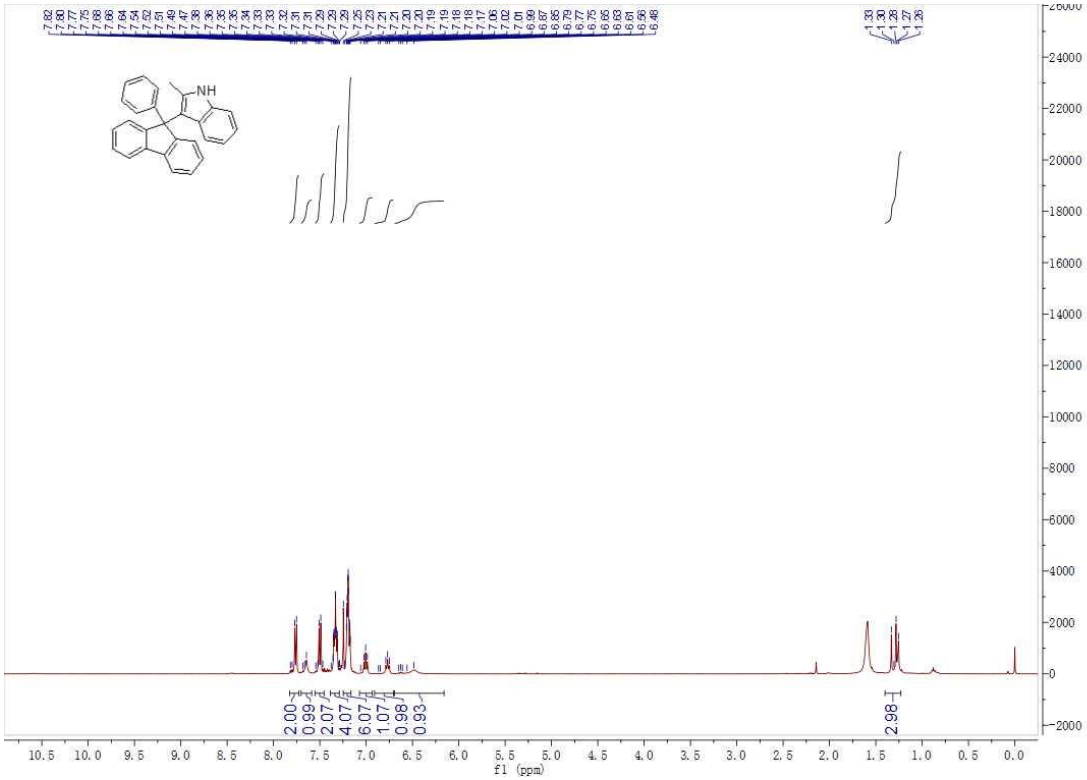
3s

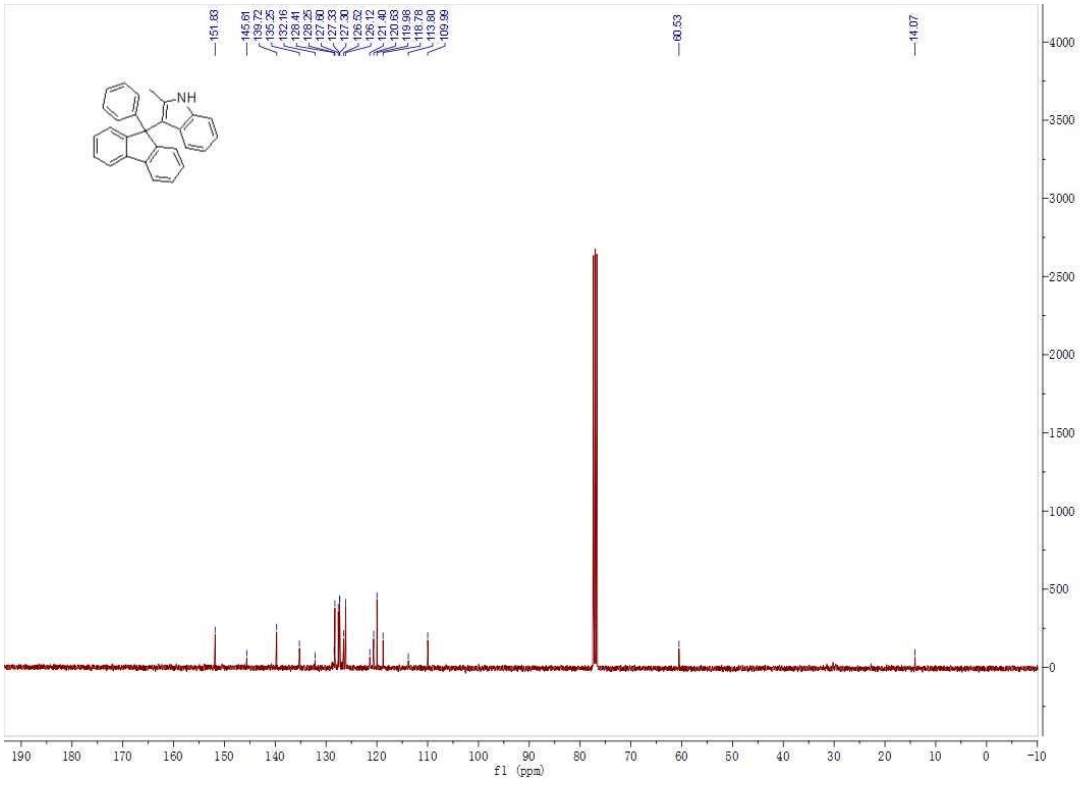

3.00
2.06
2.03
2.01
5.07
2.00
1.01
1.02
3.00
f1 (ppm)

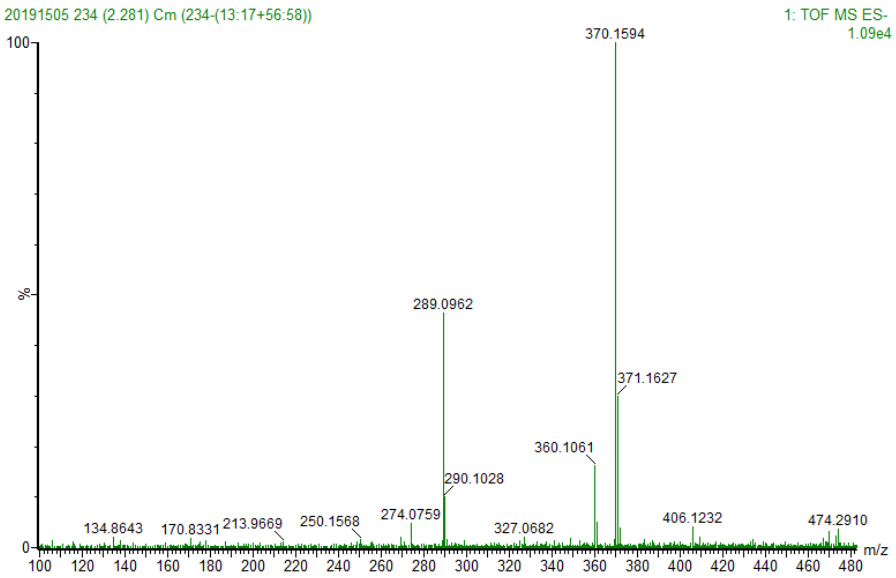

151.92
144.43
139.77
136.75
128.23
127.62
127.36
126.59
125.97
125.74
122.75
122.42
121.06
120.40
120.06
119.77
119.41
60.31
16.59
f1 (ppm)


20190836 170 (1.672) Cm (170-(31:34+52:55))
1: TOF MS ES-
1.10e4
370.1595
371.1628
273.0968
153.0621
170.8889
198.8375
235.1230
299.1423
312.1838
349.8647
406.1317
%
m/z

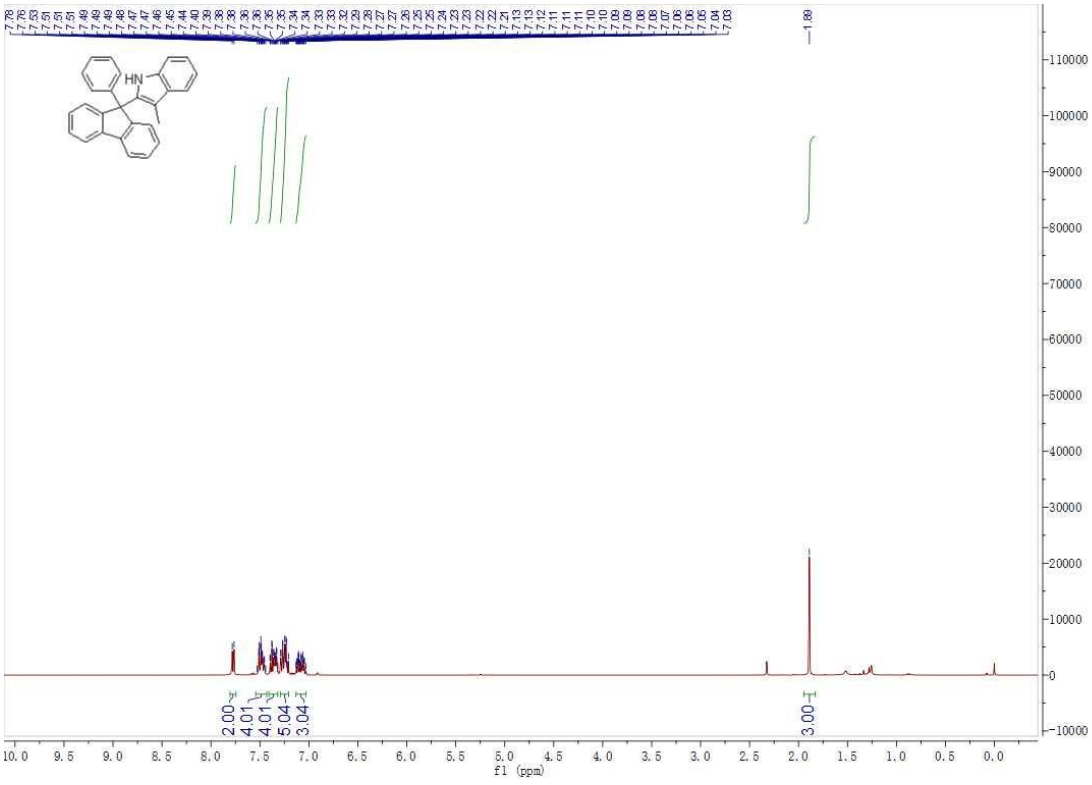
3t

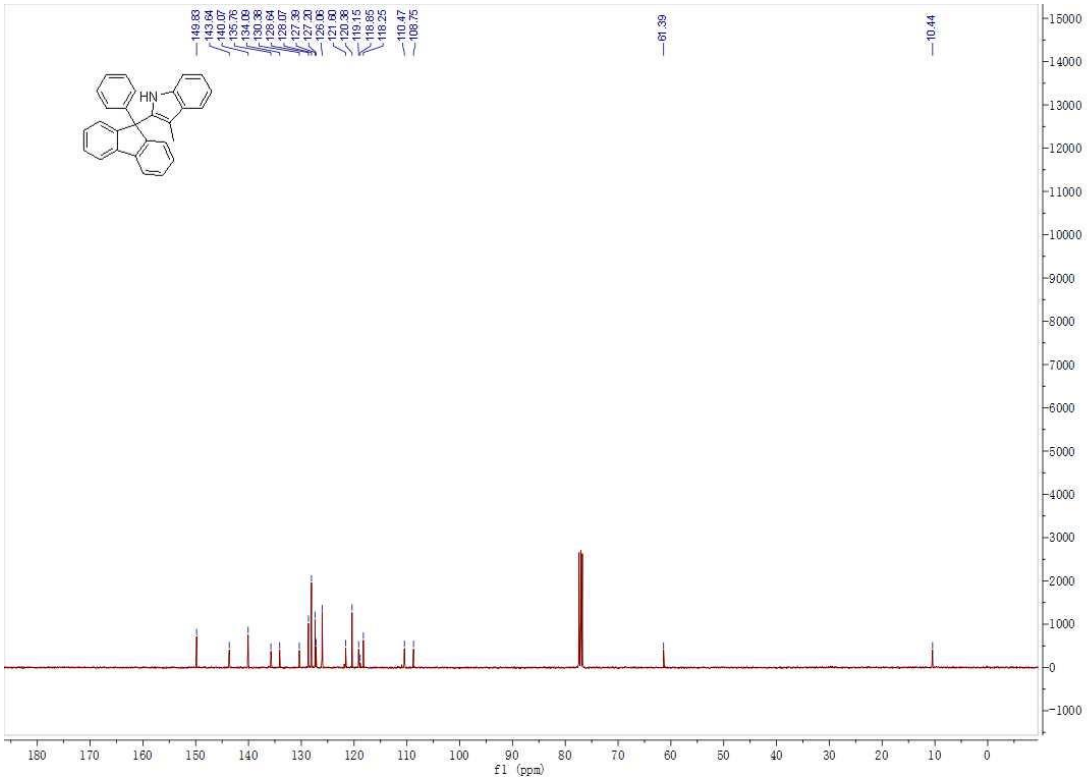

NH
2.00
0.99
2.07
4.07
6.07
1.07
0.98
0.93
2.98
f1 (ppm)

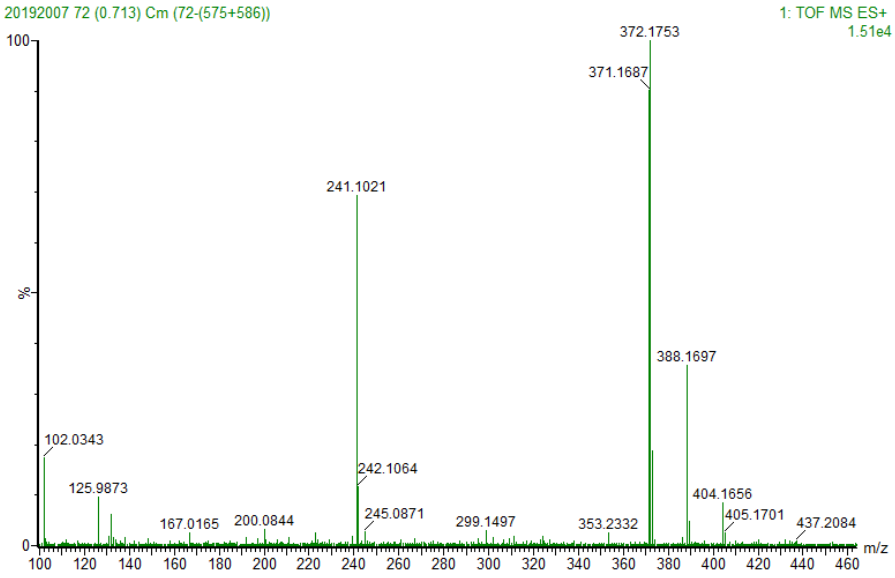

151.83
145.61
139.72
135.25
132.16
129.44
128.25
127.60
127.33
127.30
126.52
126.12
121.40
120.03
119.98
118.78
113.80
109.99
80.53
14.07
NH
f1 (ppm)


20191505 234 (2.281) Cm (234-(13:17+56:58))
1: TOF MS ES-
1.09e4
370.1594
289.0962
371.1627
360.1061
290.1028
134.8643
170.8331
213.9669
250.1568
274.0759
327.0682
406.1232
474.2910
m/z

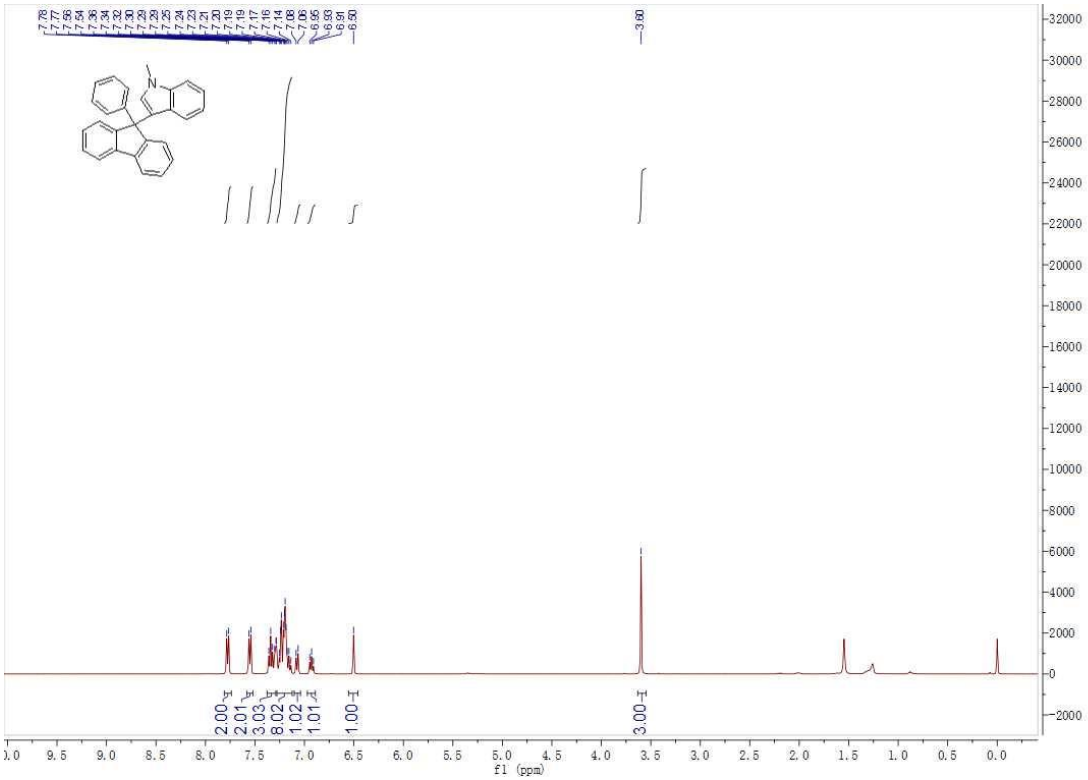
3u

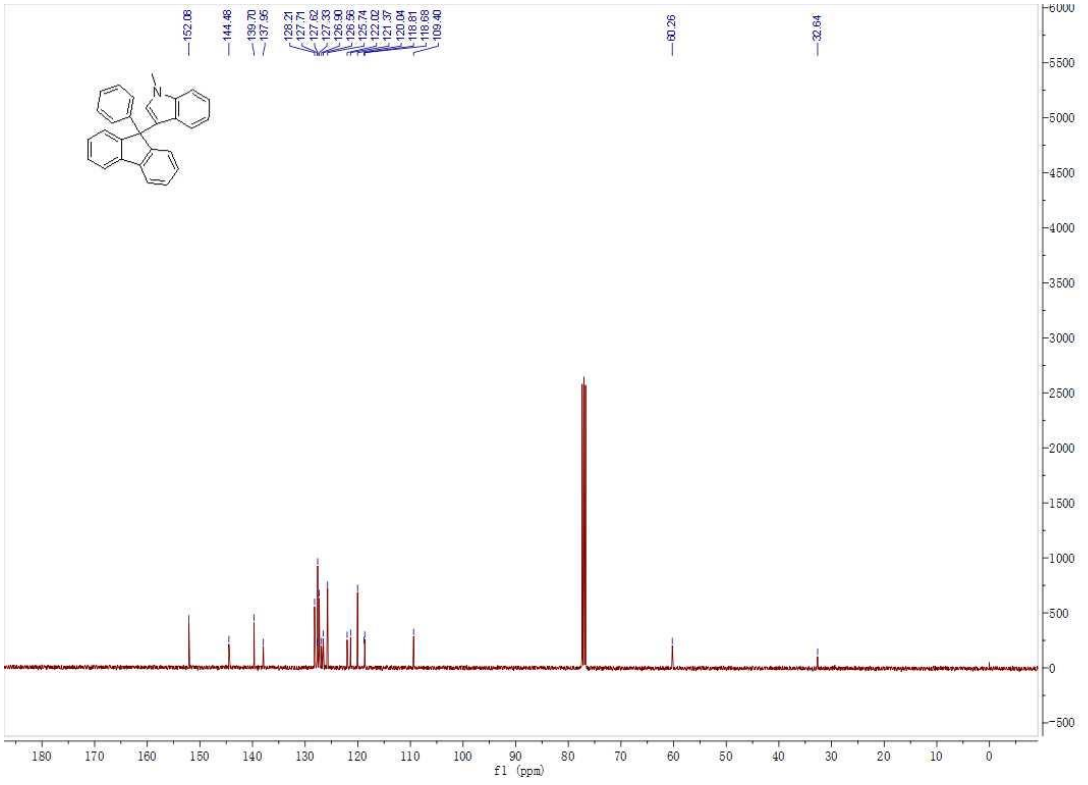

HN
2.00
4.01
4.01
5.04
3.04
3.00
f1 (ppm)

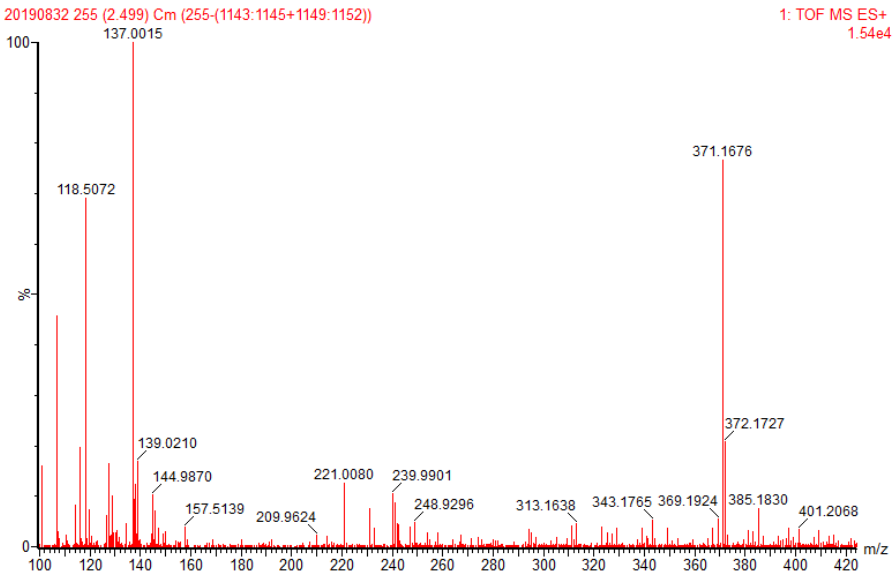

149.83
143.64
140.07
135.76
134.09
130.38
128.64
125.07
127.20
126.06
121.60
120.38
119.15
118.85
118.25
110.47
108.75
61.39
10.44
HN
f1 (ppm)


20192007 72 (0.713) Cm (72-(575+586))
1: TOF MS ES+
1.51e4
372.1753
371.1687
241.1021
388.1697
102.0343
242.1064
125.9873
404.1656
405.1701
437.2084
167.0165
200.0844
245.0871
299.1497
353.2332
%
m/z

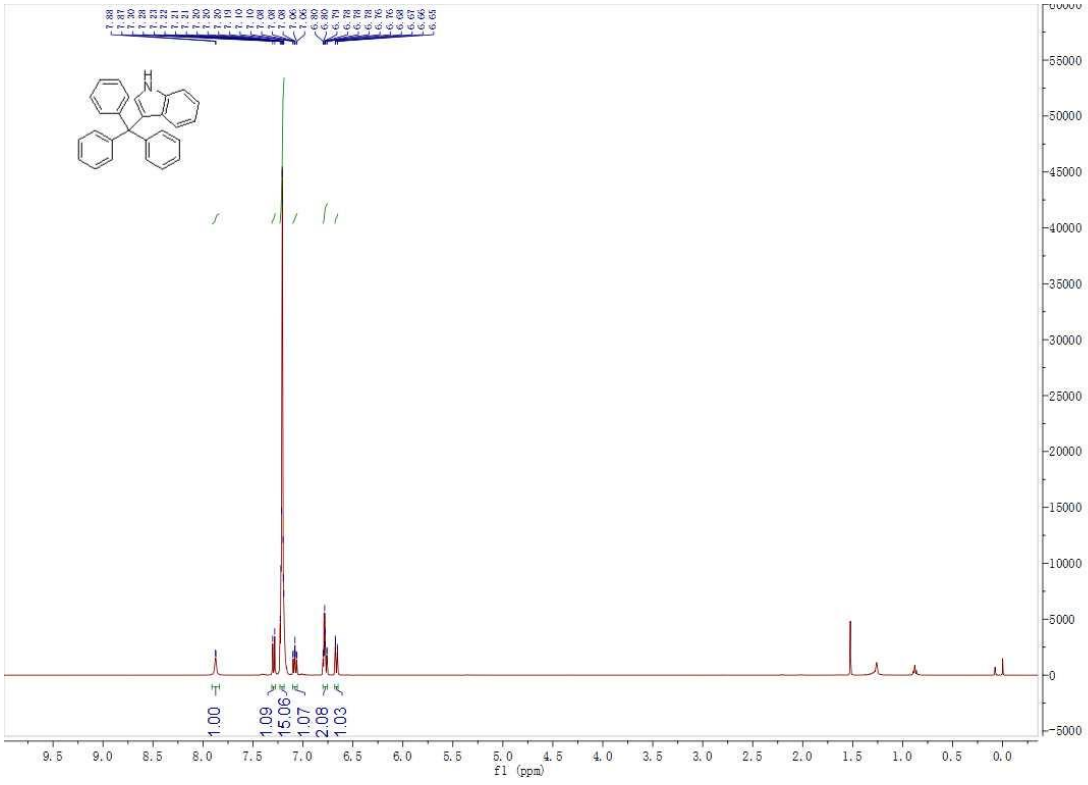
3v

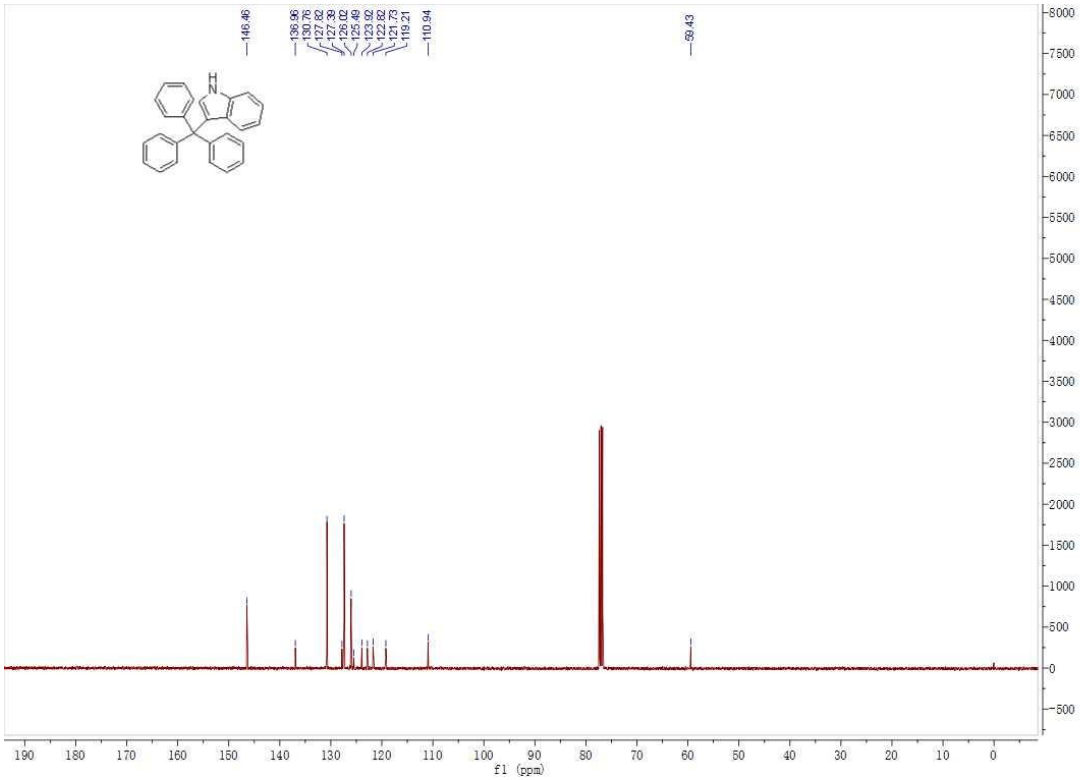

7.78
7.77
7.55
7.54
7.36
7.34
7.32
7.30
7.29
7.25
7.24
7.23
7.21
7.20
7.19
7.17
7.16
7.14
7.08
7.06
6.95
6.93
6.91
6.90
3.60
2.00
2.01
3.03
8.02
1.02
1.01
1.00
3.00
f1 (ppm)

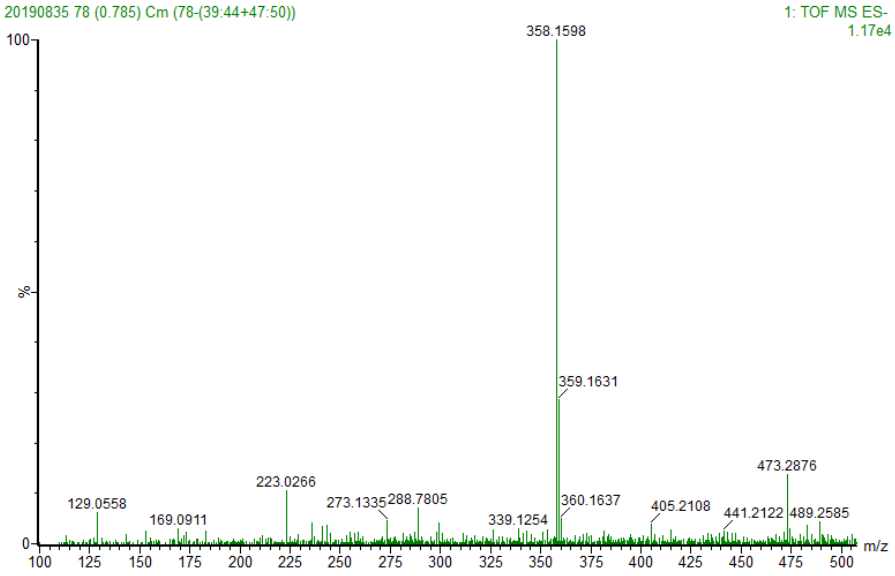

152.08
144.48
139.70
137.95
128.21
127.71
127.62
127.33
126.90
126.56
125.74
122.02
121.37
120.04
118.81
118.68
109.40
60.26
32.64
f1 (ppm)


20190832 255 (2.499) Cm (255-(1143:1145+1149:1152))
1: TOF MS ES+
1.54e4
137.0015
371.1676
118.5072
372.1727
139.0210
144.9870
221.0080
239.9901
157.5139
209.9624
248.9296
313.1638
343.1765
369.1924
385.1830
401.2068
%
m/z

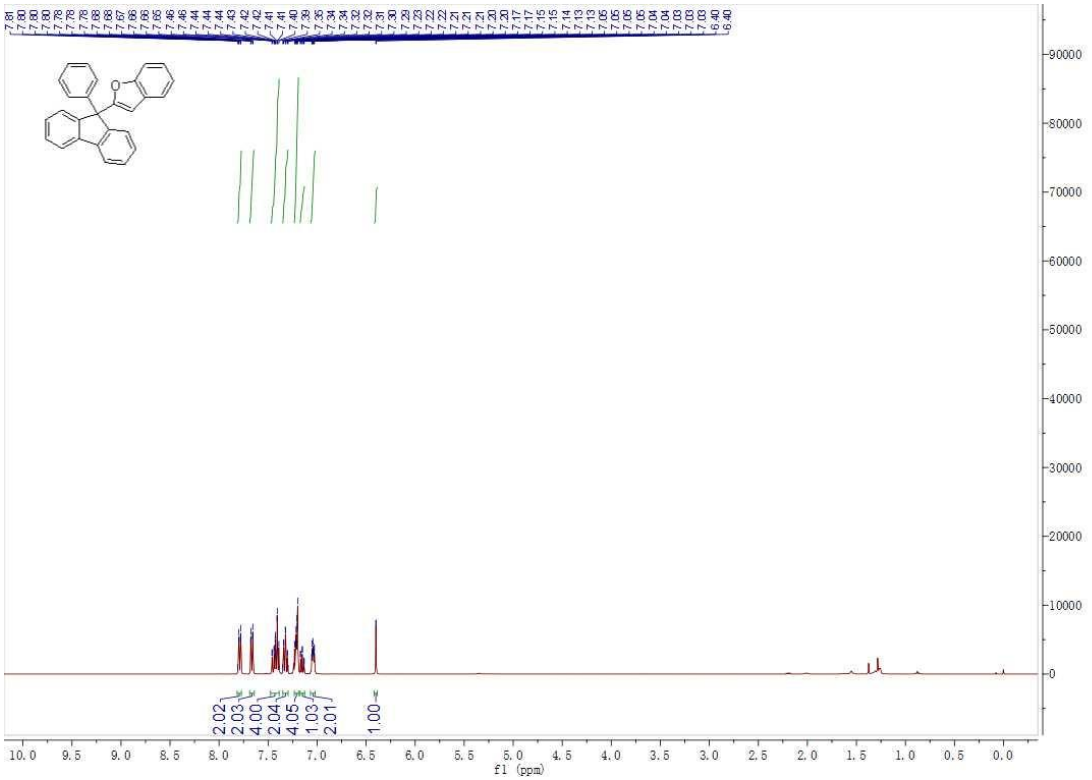
3w

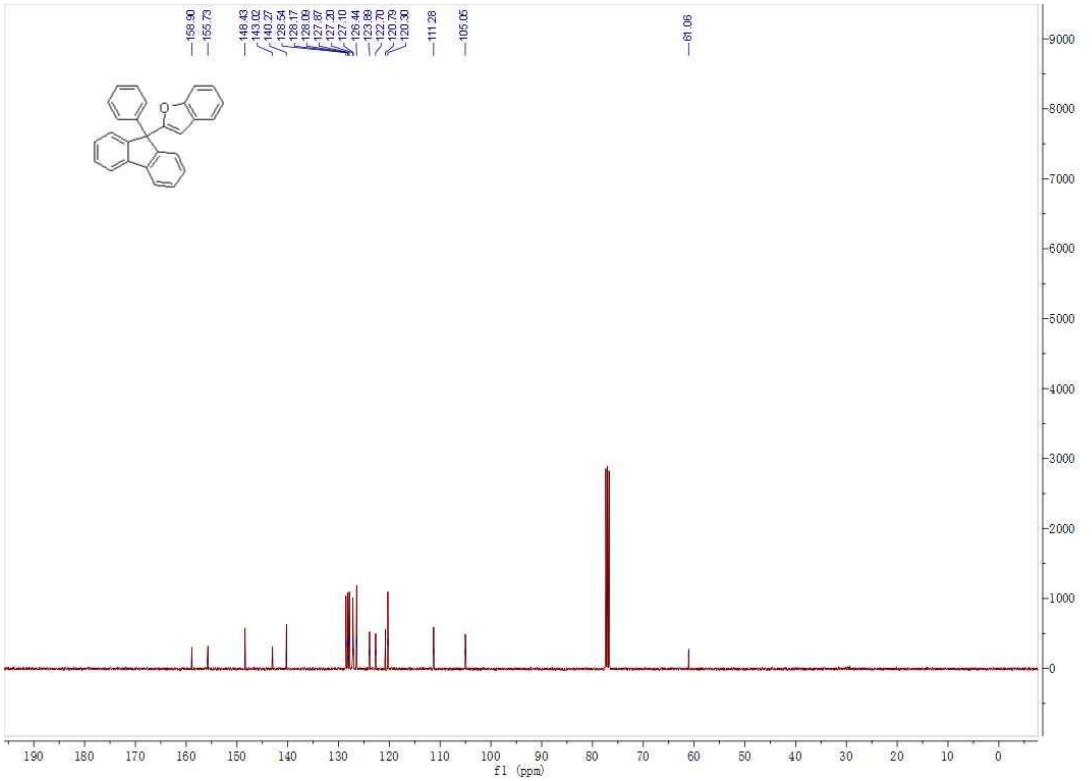

1.00
1.09
15.06
1.07
2.08
1.03
f1 (ppm)

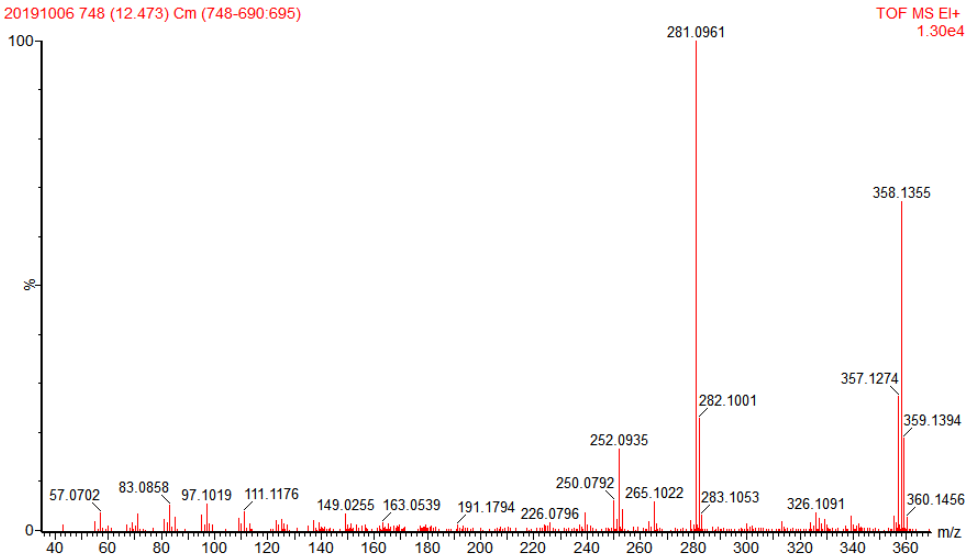

146.46
138.96
130.76
127.82
127.39
126.02
125.49
123.92
122.82
121.73
119.21
110.94
59.43
f1 (ppm)


20190835 78 (0.785) Cm (78-(39:44+47:50))
1: TOF MS ES-
1.17e4
358.1598
359.1631
473.2876
223.0266
129.0558
169.0911
273.1335
288.7805
339.1254
360.1637
405.2108
441.2122
489.2585
%
m/z

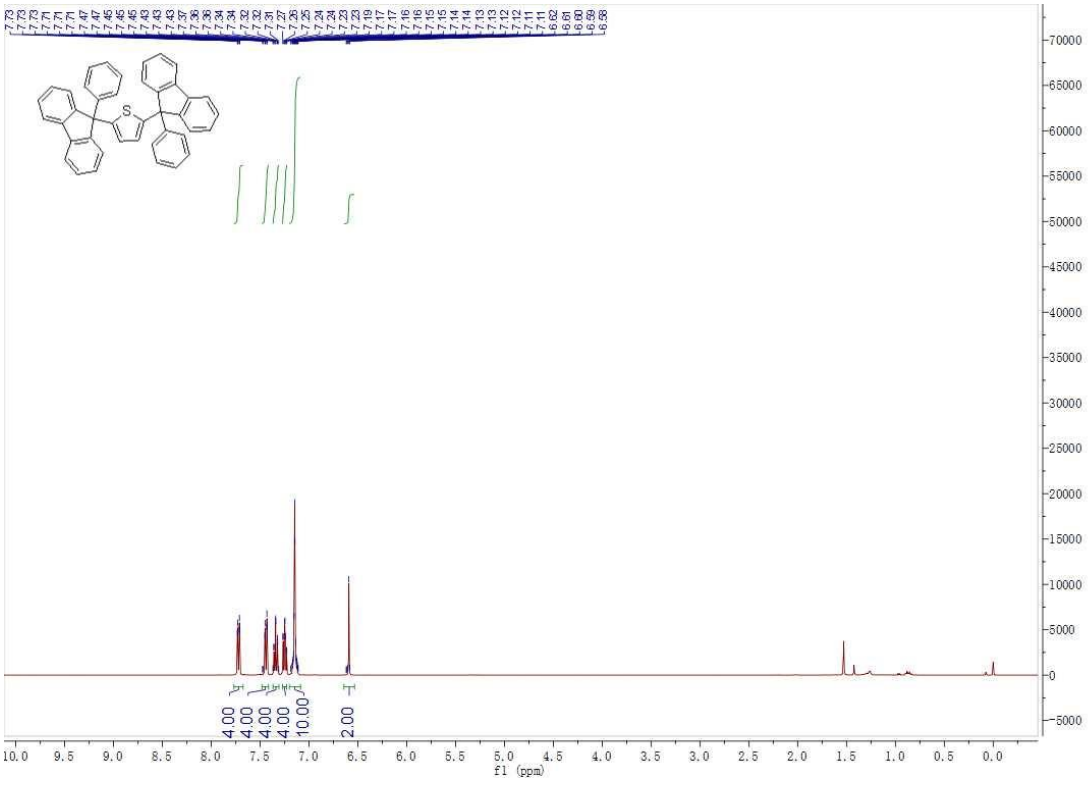
5a

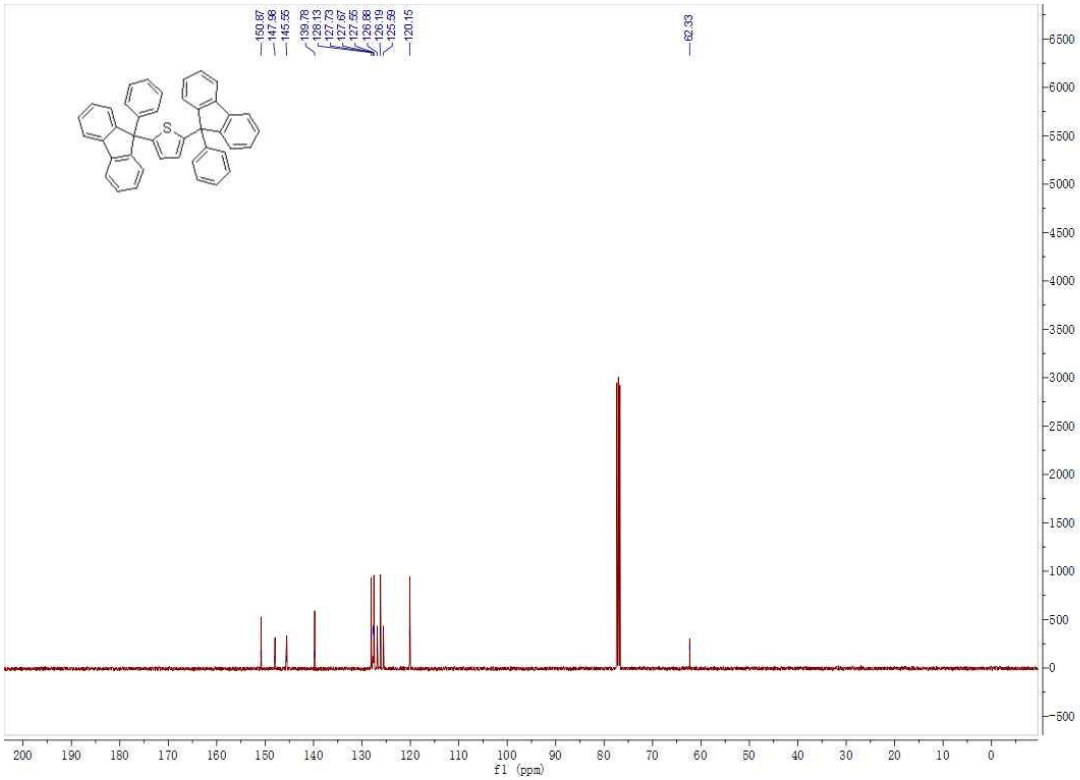

2.02
2.03
4.00
2.04
4.05
1.03
2.01
1.00
f1 (ppm)

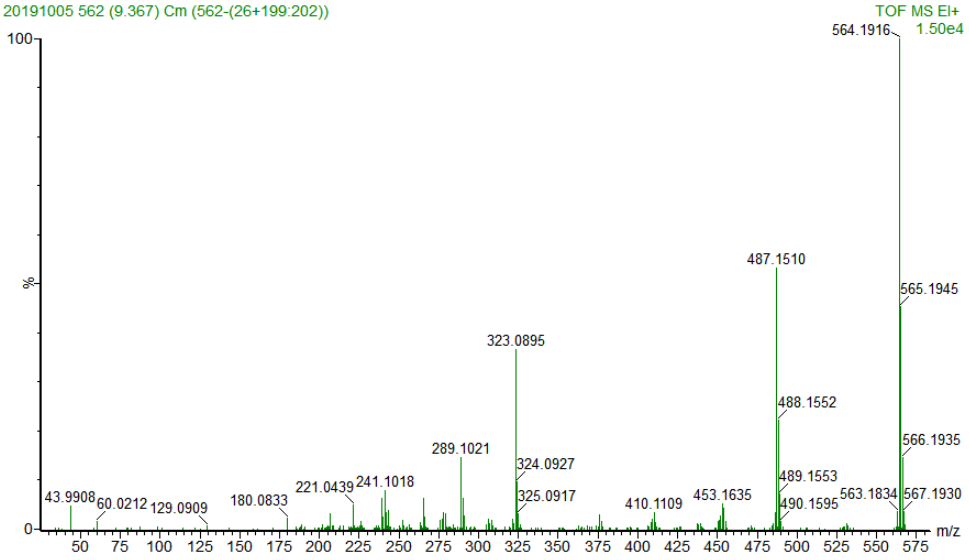

158.90
155.73
148.43
143.02
140.27
128.54
128.17
128.09
127.87
127.20
127.10
126.44
123.86
123.70
120.79
120.30
111.28
105.06
61.06
f1 (ppm)


20191006 748 (12.473) Cm (748-690:695)
TOF MS EI+
1.30e4
100
%
0
281.0961
358.1355
357.1274
282.1001
359.1394
252.0935
250.0792
265.1022
283.1053
326.1091
360.1456
57.0702
83.0858
97.1019
111.1176
149.0255
163.0539
191.1794
226.0796
m/z
40
60
80
100
120
140
160
180
200
220
240
260
280
300
320
340
360

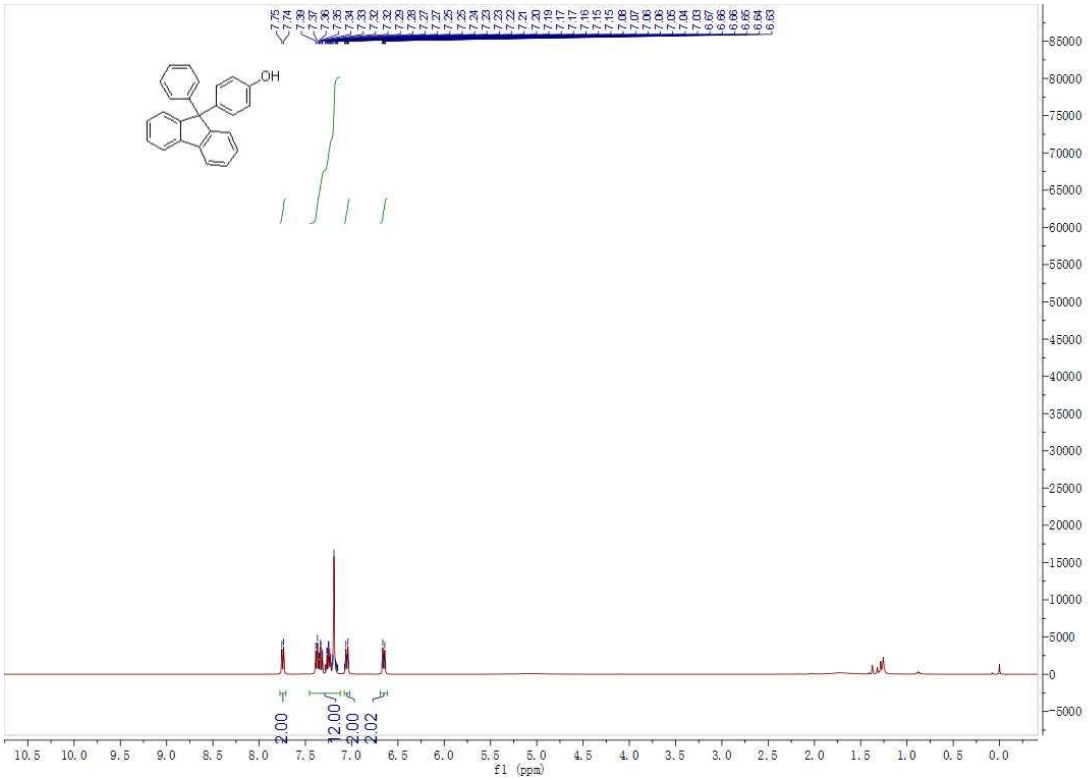
5b

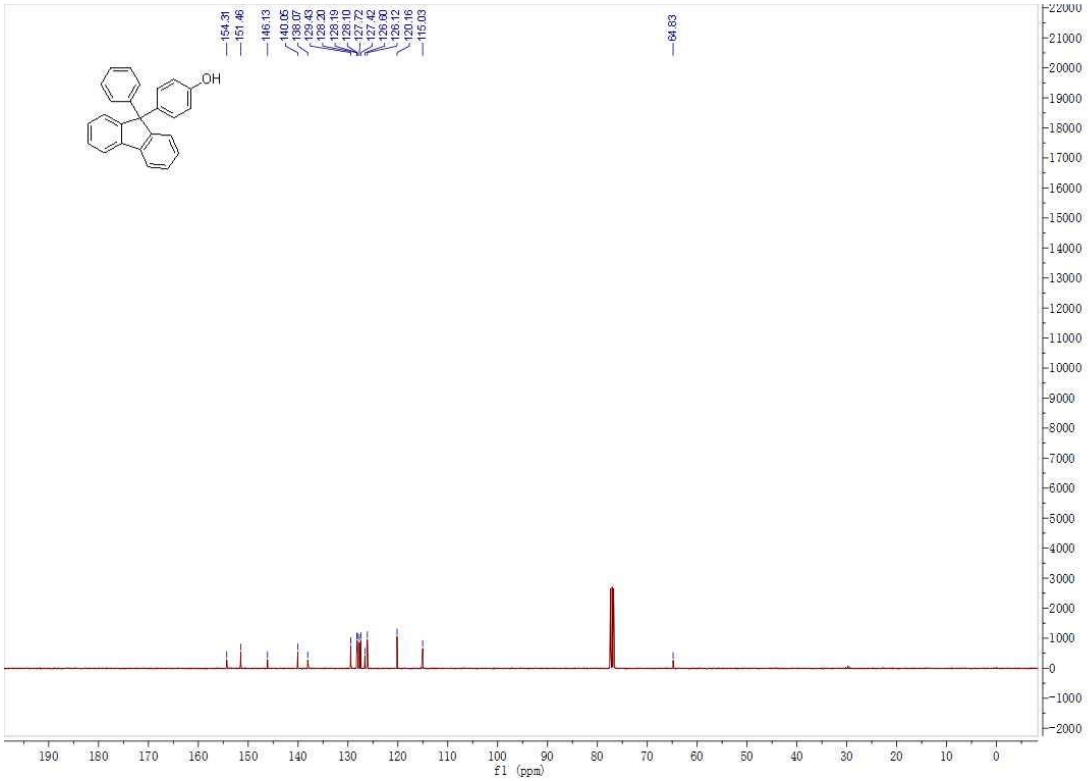

4.00
4.00
4.00
10.00
2.00
f1 (ppm)

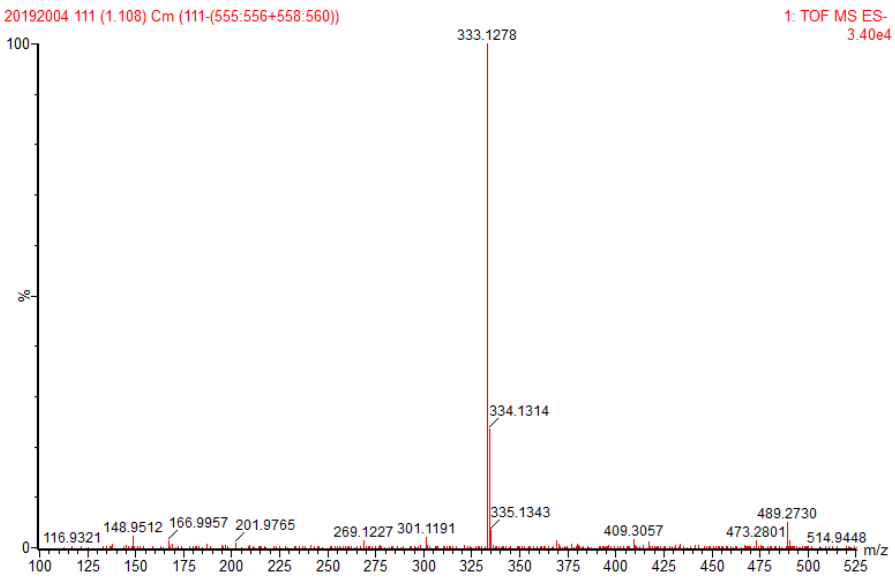

150.87
147.98
145.55
139.76
128.13
127.73
127.67
127.55
126.88
126.19
125.59
120.15
62.33
f1 (ppm)


20191005 562 (9.367) Cm (562-(26+199:202))
TOF MS EI+
1.50e4
564.1916
487.1510
565.1945
323.0895
488.1552
566.1935
289.1021
324.0927
489.1553
325.0917
563.1834
567.1930
43.9908
60.0212
129.0909
180.0833
221.0439
241.1018
410.1109
453.1635
490.1595
%
m/z

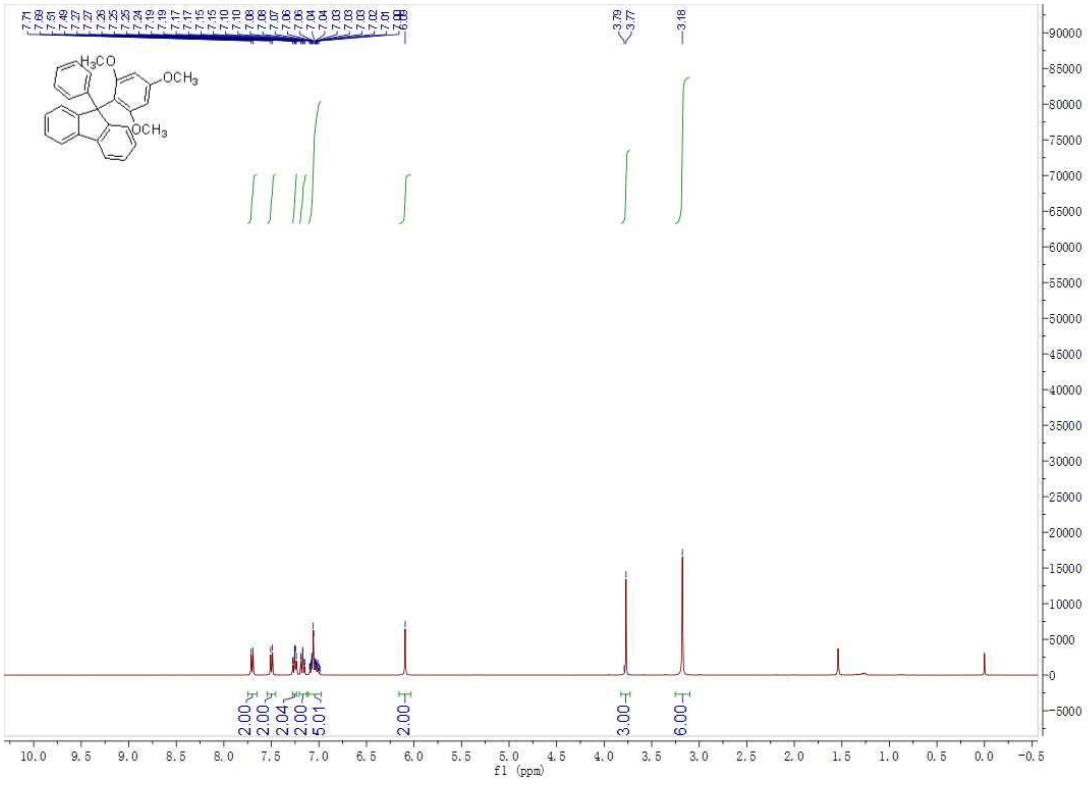
5f

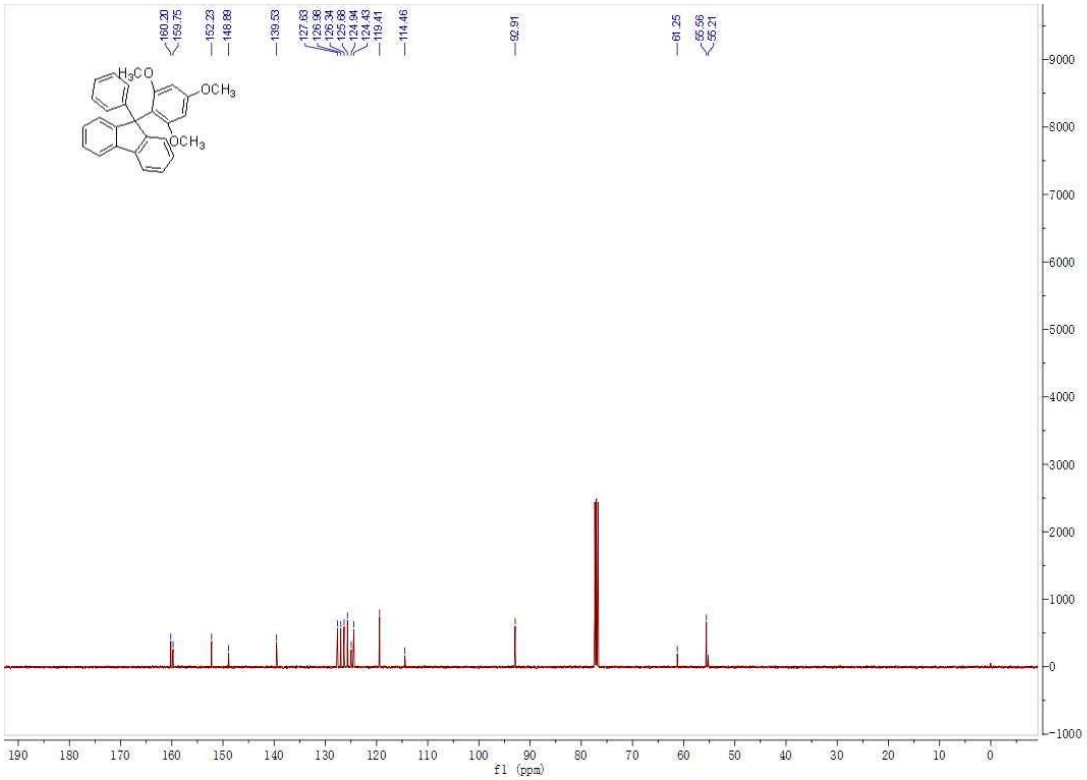

OH
7.75
7.74
7.39
7.37
7.36
7.35
7.34
7.33
7.32
7.29
7.28
7.27
7.25
7.24
7.23
7.22
7.21
7.20
7.19
7.17
7.16
7.15
7.08
7.07
7.06
7.05
7.04
7.03
6.67
6.66
6.65
6.64
6.63
2.00
1.00
2.00
2.02
f1 (ppm)

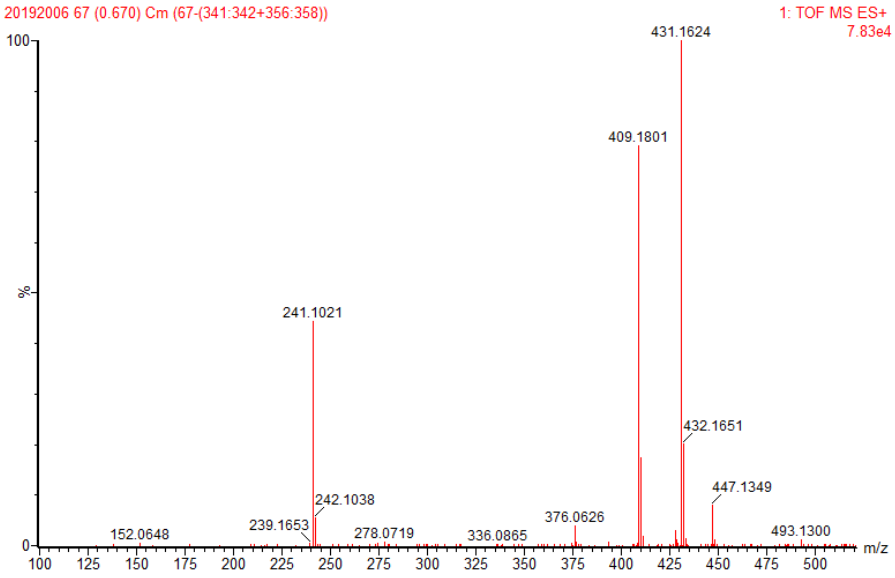

OH
154.31
151.46
146.13
140.05
139.07
139.43
128.20
128.19
128.10
127.72
127.42
126.60
126.12
120.16
115.03
64.83
f1 (ppm)


20192004 111 (1.108) Cm (111-(555:556+558:560))
1: TOF MS ES-
3.40e4
333.1278
334.1314
335.1343
116.9321
148.9512
166.9957
201.9765
269.1227
301.1191
409.3057
473.2801
489.2730
514.9448
m/z

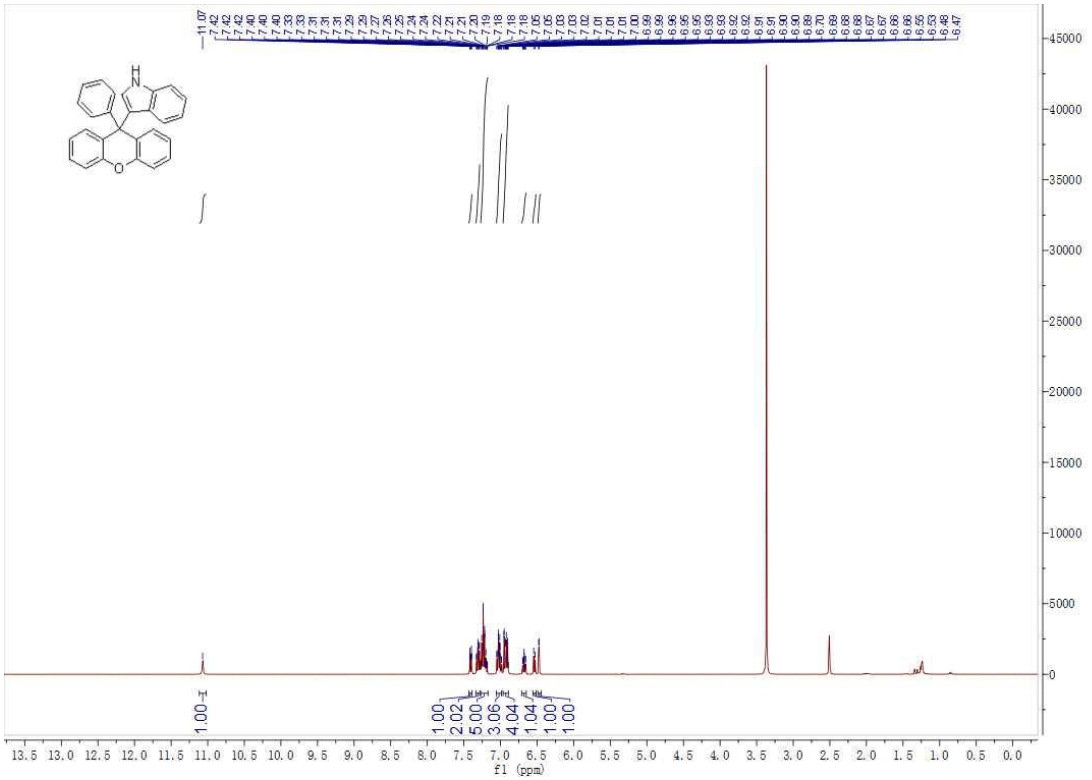
5g

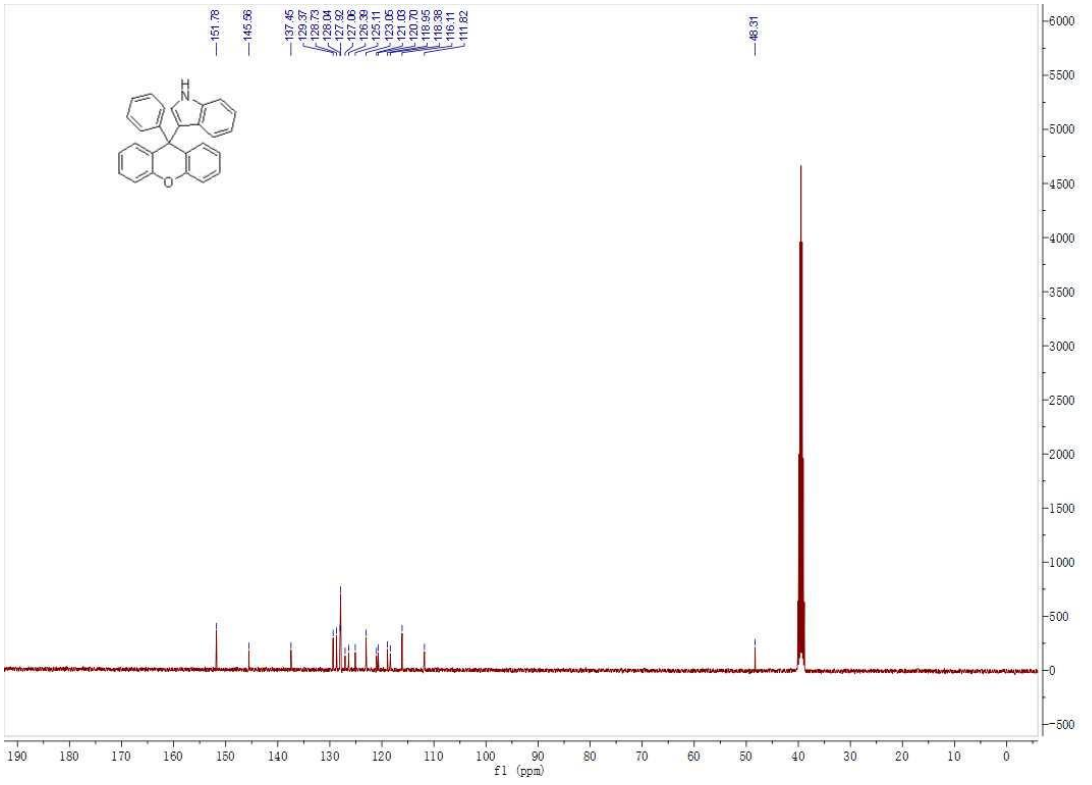

H3CO
OCH3
OCH3
3.79
3.77
3.18
2.00
2.00
2.04
2.00
5.01
2.00
3.00
6.00
f1 (ppm)

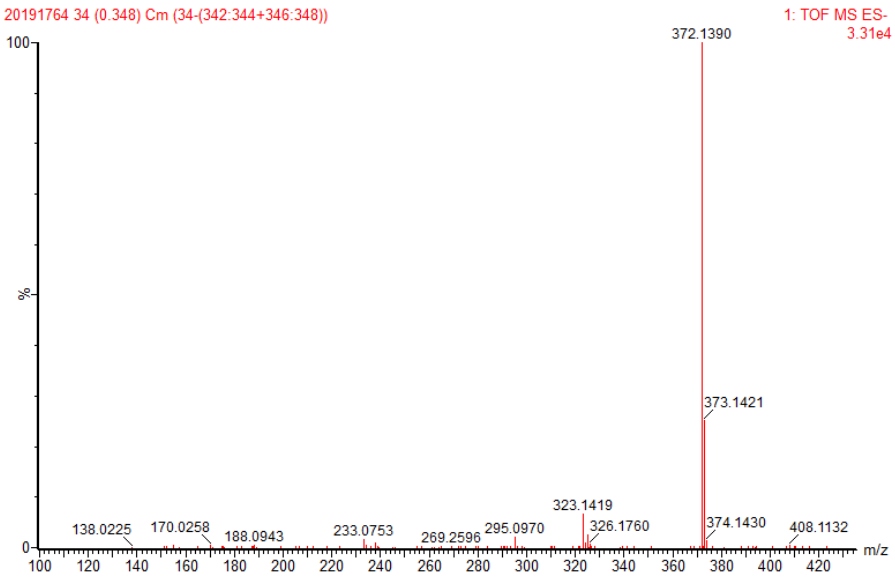

160.20
159.75
152.23
146.89
139.53
127.63
126.98
126.34
125.68
124.94
124.43
119.41
114.46
92.91
61.25
55.56
55.21
H3CO
OCH3
OCH3
f1 (ppm)


20192006 67 (0.670) Cm (67-(341:342+356:358))
1: TOF MS ES+
7.83e4
431.1624
409.1801
241.1021
432.1651
447.1349
242.1038
376.0626
239.1653
278.0719
336.0865
493.1300
152.0648
%
m/z

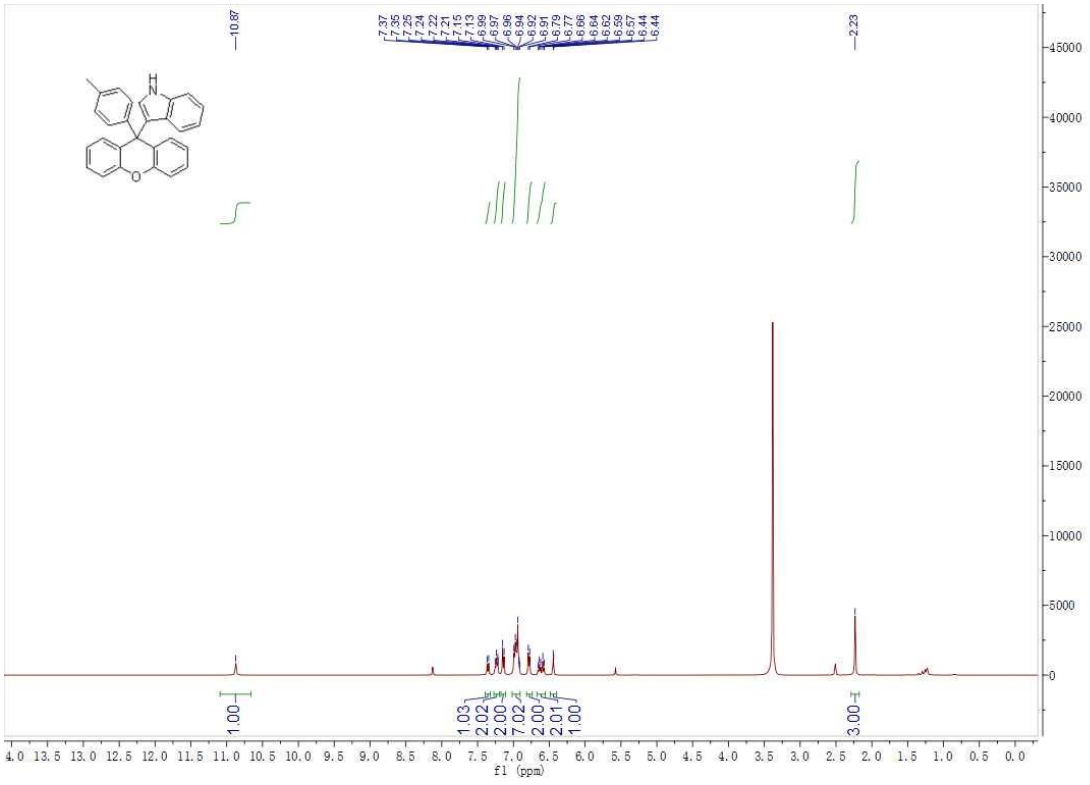
7a

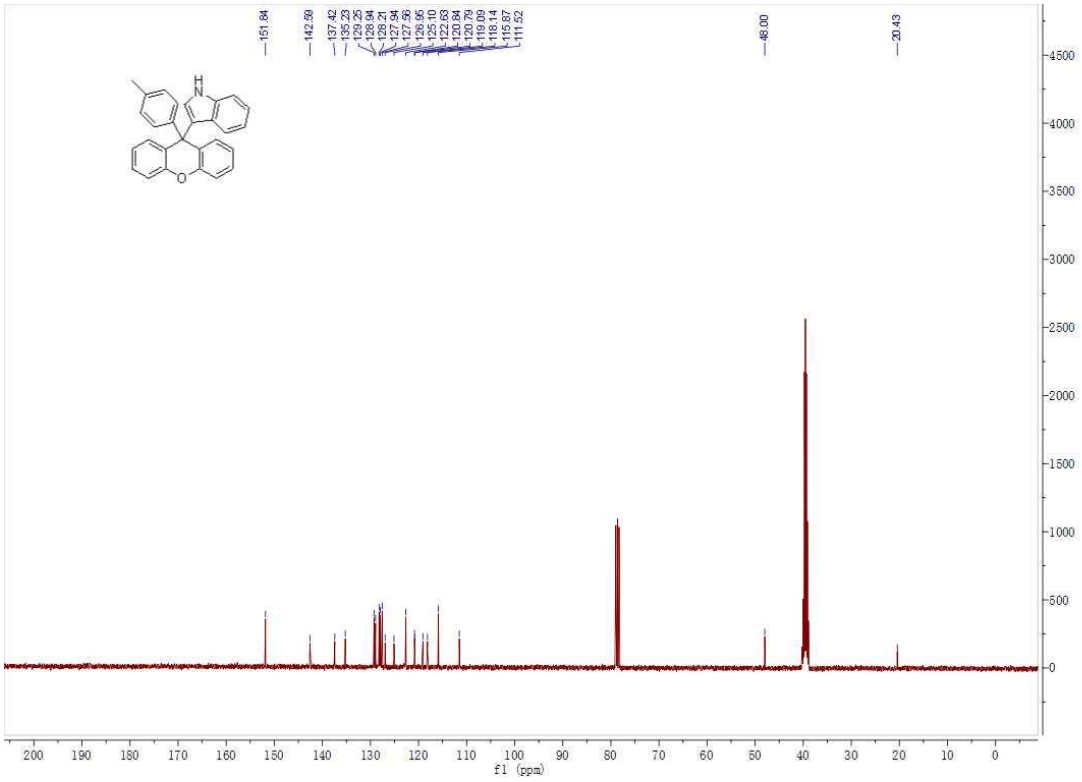


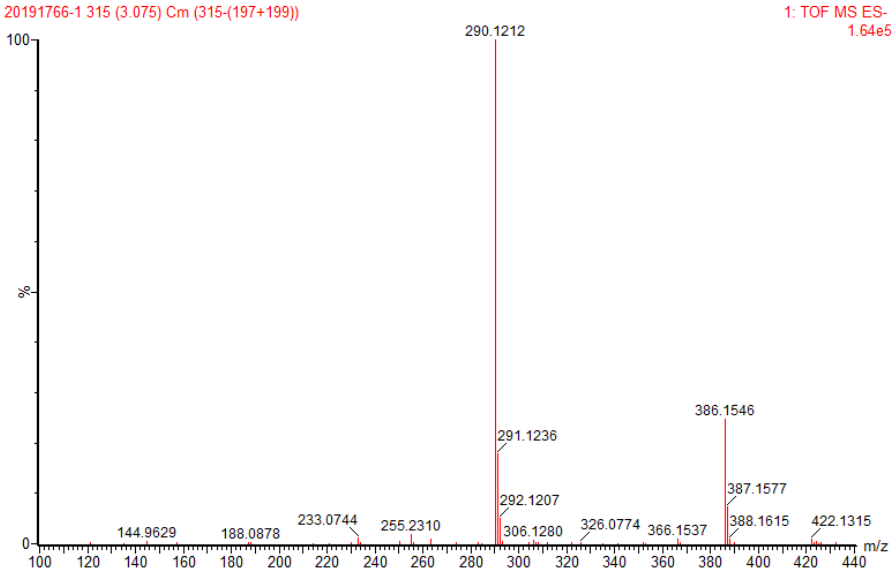



20191764 34 (0.348) Cm (34-(342:344+346:348))
1: TOF MS ES-
3.31e4
372.1390
373.1421
323.1419
326.1760
374.1430
408.1132
138.0225
170.0258
188.0943
233.0753
269.2596
295.0970
%
m/z

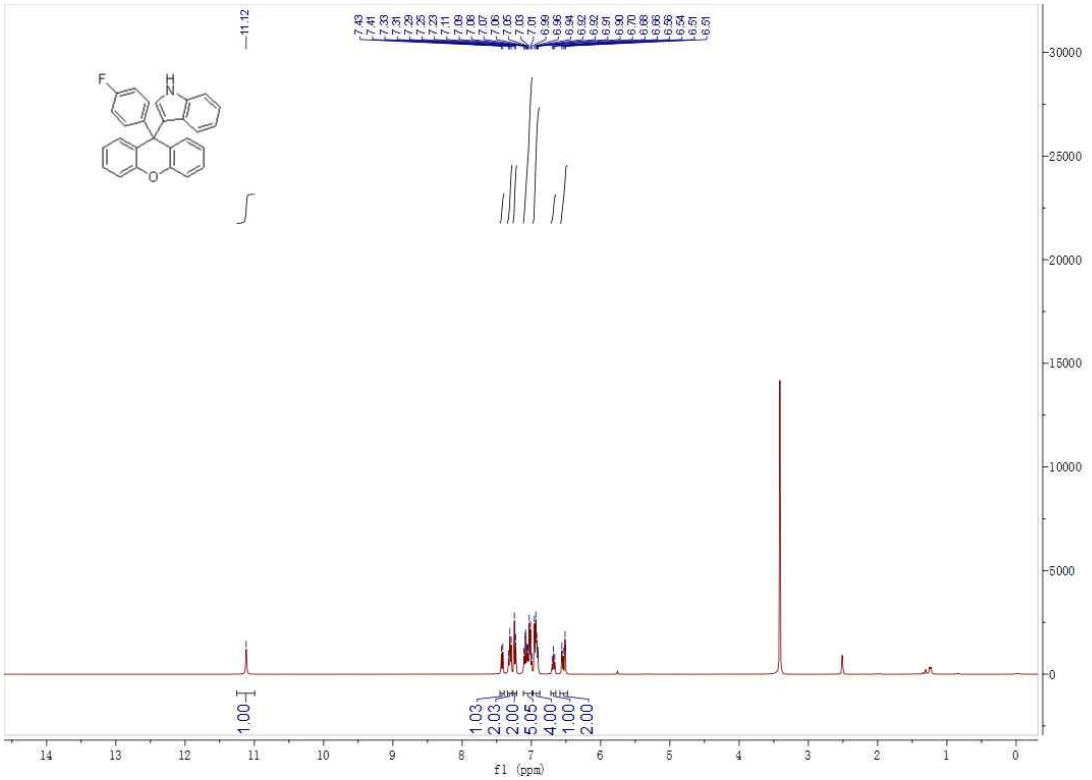
7b

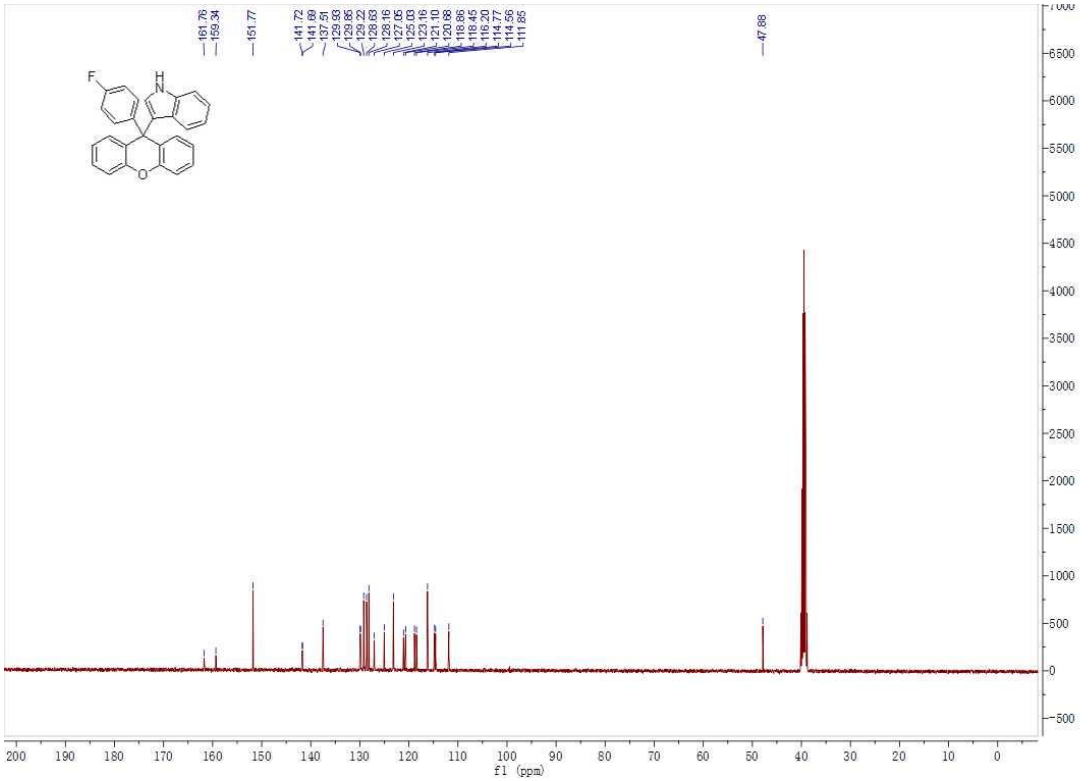

10.87
2.23
1.00
1.03
2.02
2.00
7.02
2.00
2.01
1.00
3.00
f1 (ppm)

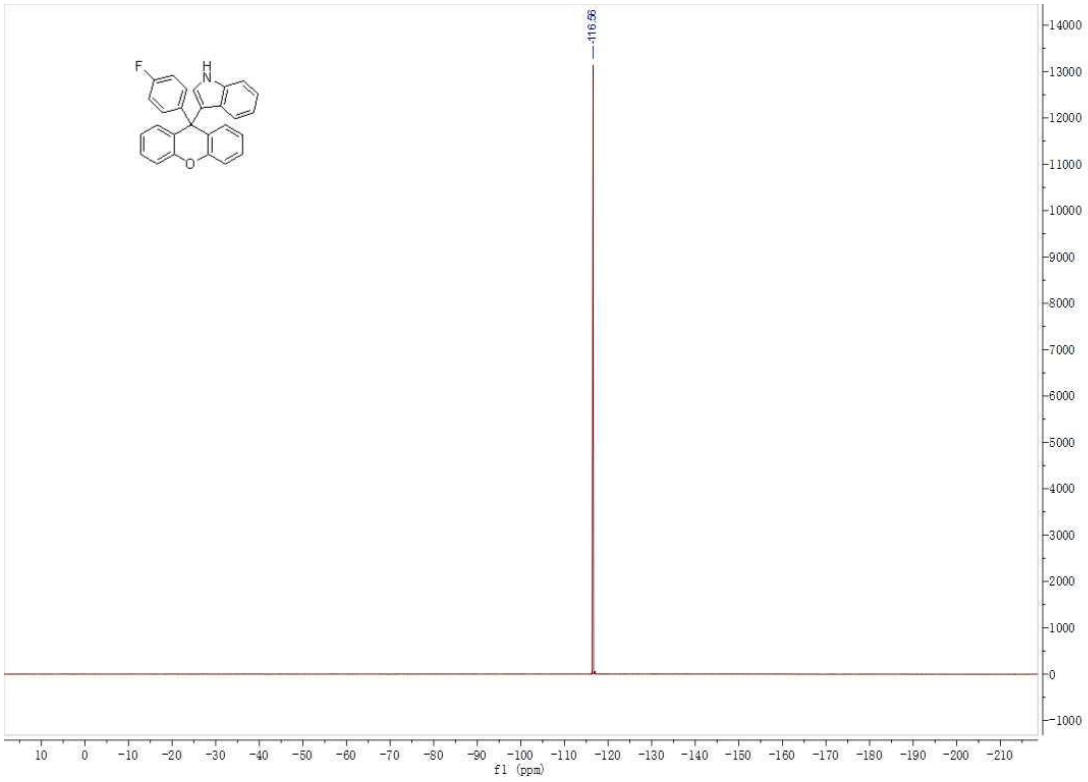

151.84
142.59
137.42
135.23
129.25
128.94
128.21
127.94
127.36
126.96
125.10
122.63
120.84
120.79
119.09
118.14
115.67
111.52
48.00
30.43
H
N
O
f1 (ppm)

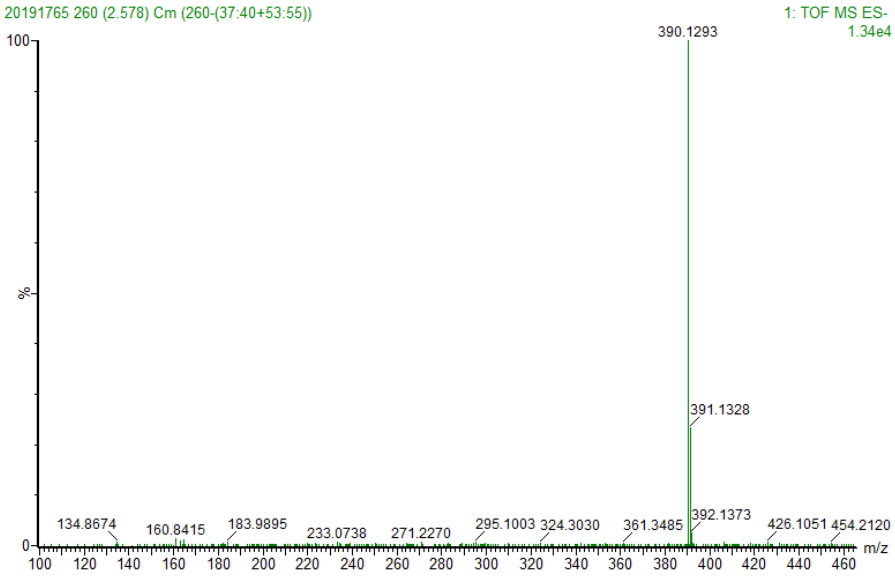

20191766-1 315 (3.075) Cm (315-(197+199))
1: TOF MS ES-
1.64e5
290.1212
291.1236
292.1207
386.1546
387.1577
388.1615
422.1315
144.9629
188.0878
233.0744
255.2310
306.1280
326.0774
366.1537
%
m/z

7c

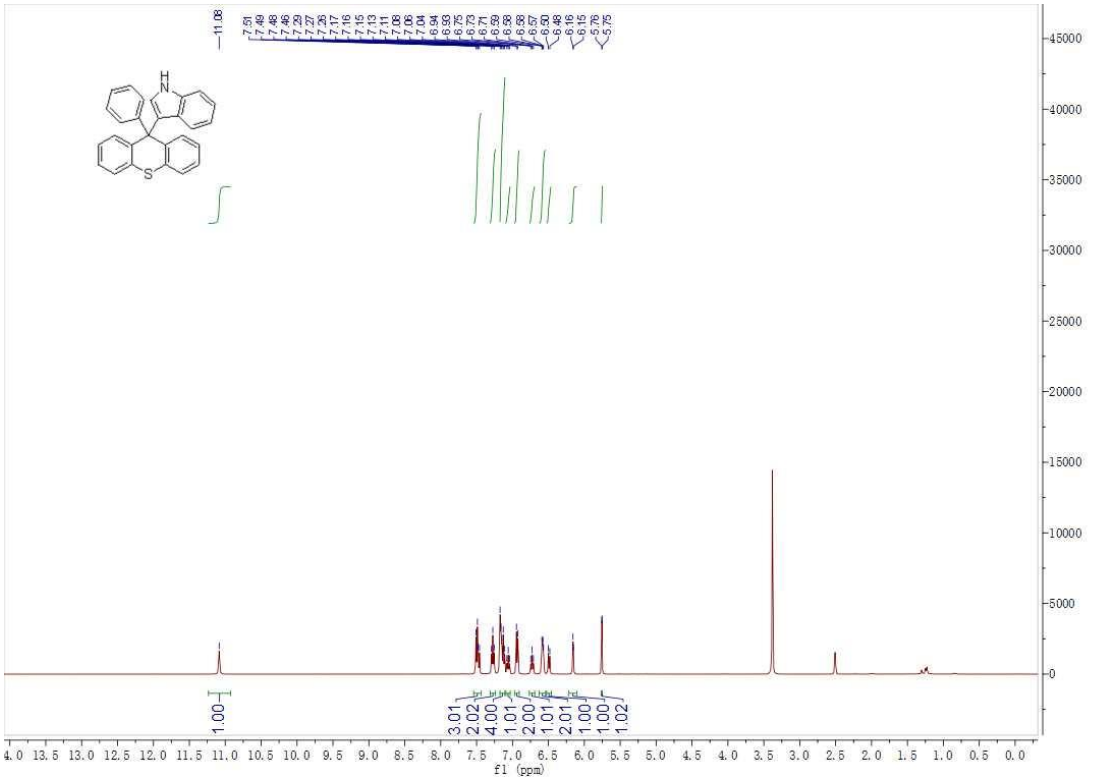

11.12
7.43
7.41
7.33
7.31
7.29
7.25
7.23
7.11
7.09
7.08
7.07
7.06
7.05
7.03
7.01
6.99
6.96
6.94
6.92
6.91
6.90
6.70
6.68
6.66
6.56
6.54
6.51
6.51
1.00
1.03
2.03
2.00
5.05
4.00
1.00
2.00
f1 (ppm)

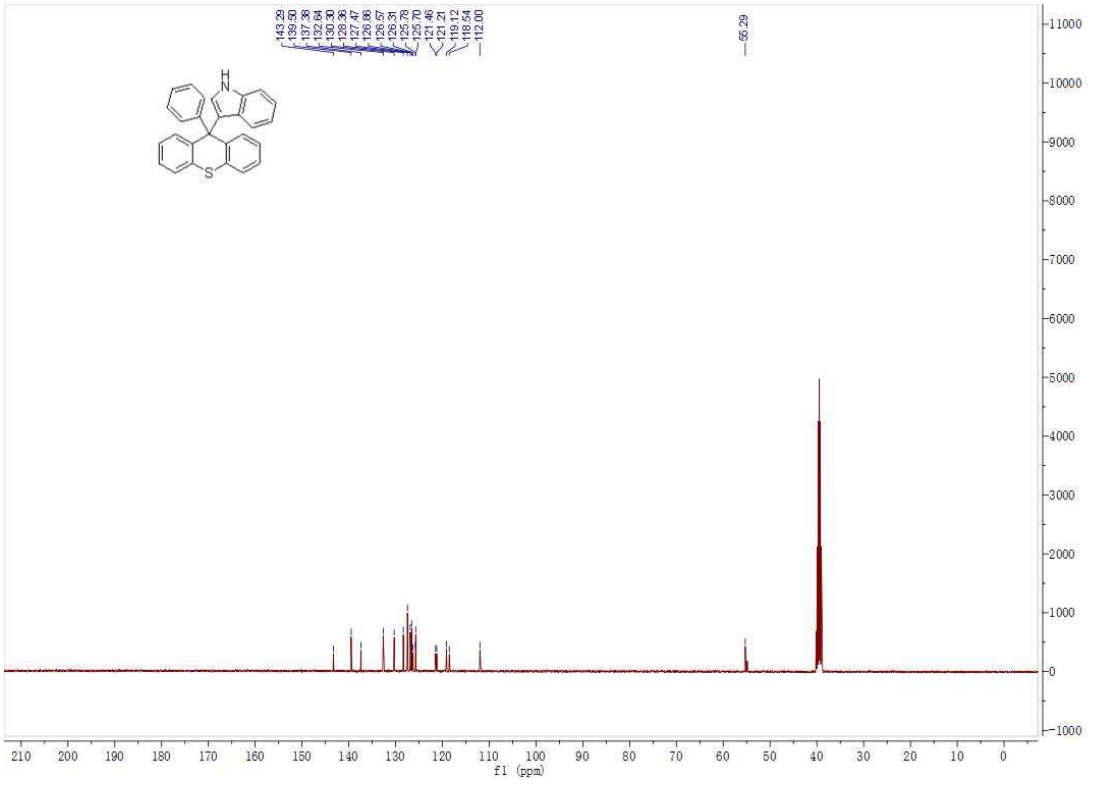

161.76
159.34
151.77
141.72
141.69
137.61
129.93
129.86
129.22
128.63
128.16
127.05
125.03
123.16
123.10
120.88
118.86
118.45
116.20
114.77
114.56
111.85
47.88
f1 (ppm)

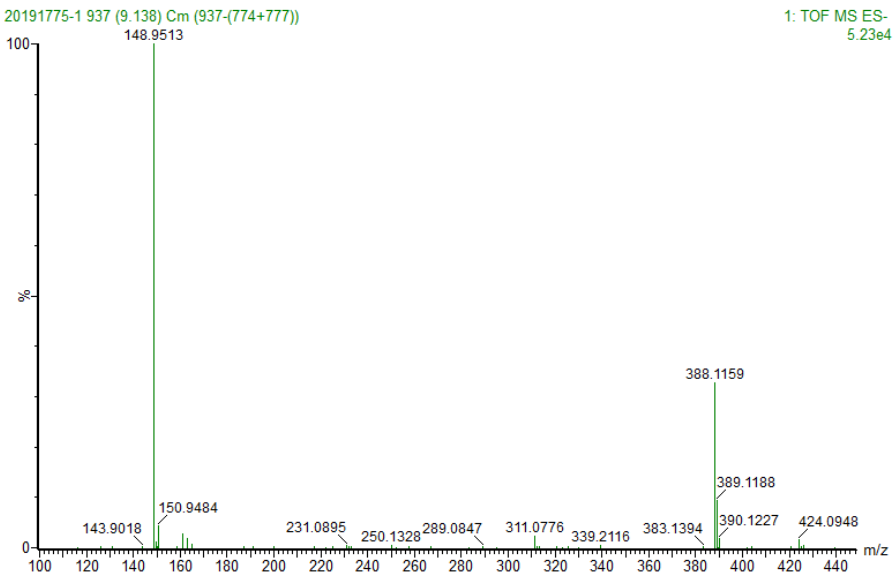

F
H
N
O
-116.66
14000
13000
12000
11000
10000
9000
8000
7000
6000
5000
4000
3000
2000
1000
0
-1000
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)


20191765 260 (2.578) Cm (260-(37:40+53:55))
1: TOF MS ES-
1.34e4
100
%
0
390.1293
391.1328
392.1373
134.8674
160.8415
183.9895
233.0738
271.2270
295.1003
324.3030
361.3485
426.1051
454.2120
m/z
100 120 140 160 180 200 220 240 260 280 300 320 340 360 380 400 420 440 460

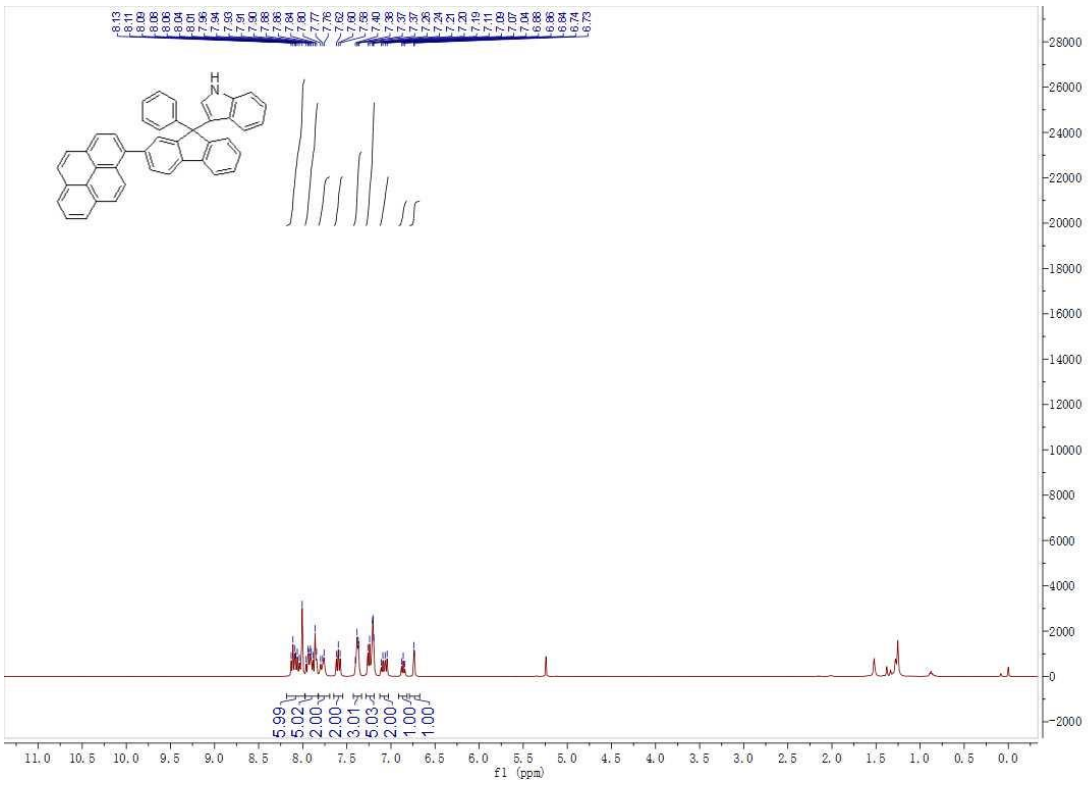
7d

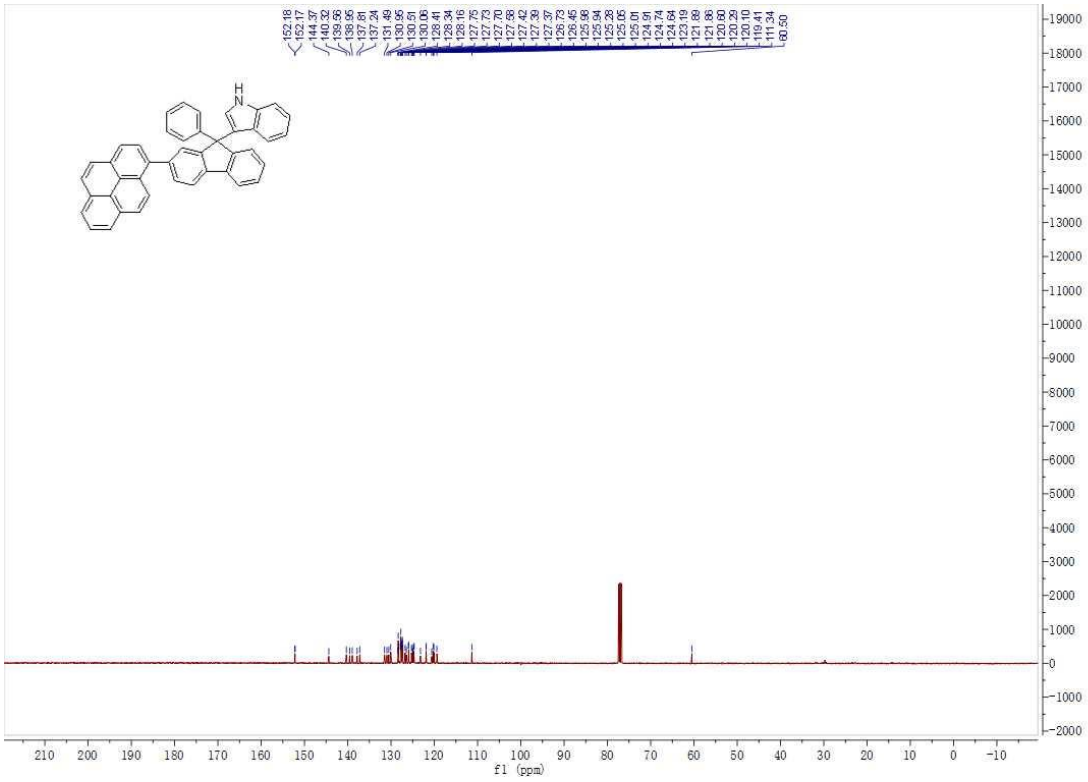

11.08
7.51
7.49
7.48
7.46
7.29
7.27
7.26
7.17
7.16
7.15
7.13
7.11
7.08
7.06
7.04
6.94
6.93
6.75
6.73
6.71
6.59
6.58
6.56
6.55
6.50
6.48
6.16
6.15
5.76
5.75
1.00
3.01
2.02
4.00
1.01
2.00
1.01
2.01
1.00
1.00
1.02
f1 (ppm)

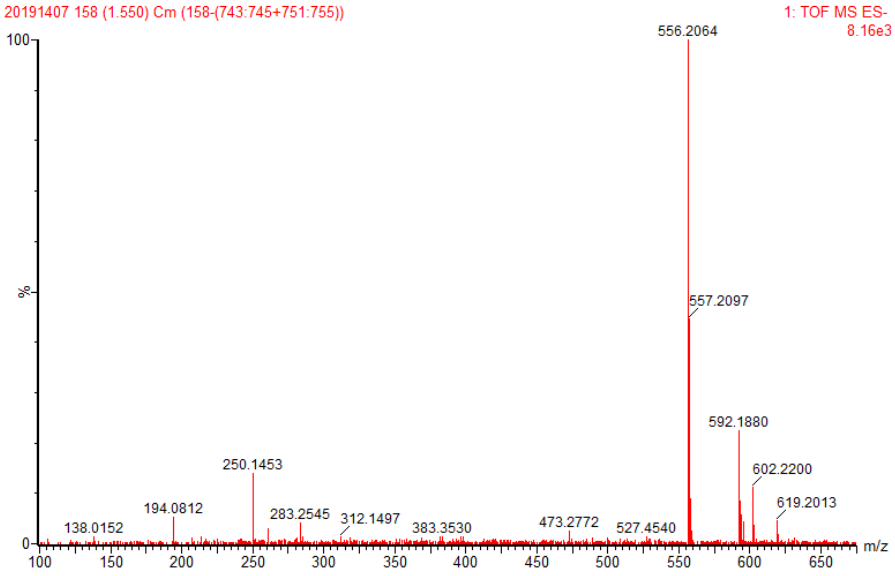

143.29
139.50
137.38
132.64
130.30
128.36
127.47
126.88
126.57
126.31
125.78
125.70
121.46
121.21
119.12
118.54
112.00
55.29
f1 (ppm)


20191775-1 937 (9.138) Cm (937-(774+777))
1: TOF MS ES-
5.23e4
148.9513
388.1159
389.1188
150.9484
390.1227
424.0948
143.9018
231.0895
250.1328
289.0847
311.0776
339.2116
383.1394
%
m/z

8


f1 (ppm)


152.18
152.17
144.37
140.92
138.95
137.81
137.24
131.49
130.95
130.51
130.06
129.41
128.34
128.16
127.75
127.73
127.70
127.58
127.42
127.39
127.37
126.73
126.45
125.98
125.94
125.38
125.05
125.01
124.91
124.74
124.64
123.19
121.89
121.86
120.60
120.29
120.10
116.47
111.34
60.50
f1 (ppm)


20191407 158 (1.550) Cm (158-(743:745+751:755))
1: TOF MS ES-
8.16e3
556.2064
557.2097
592.1880
602.2200
619.2013
250.1453
194.0812
283.2545
312.1497
383.3530
473.2772
527.4540
138.0152
%
m/z

DSC and TGA curves

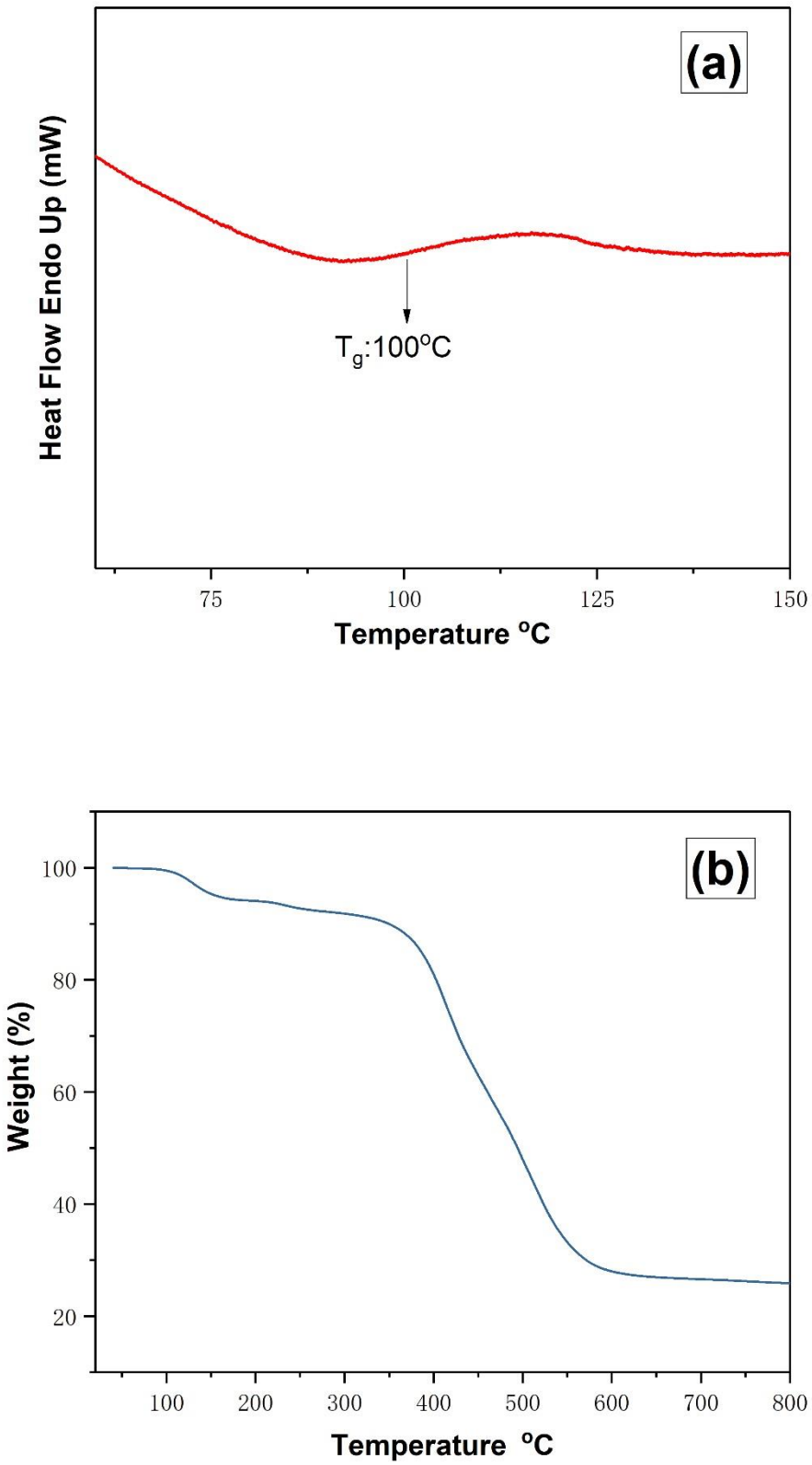


Figure S1: (a) DSC curve of product **8** and (b) TGA curve of product **8**

UV and PL Spectra of Pyrene and Product 8

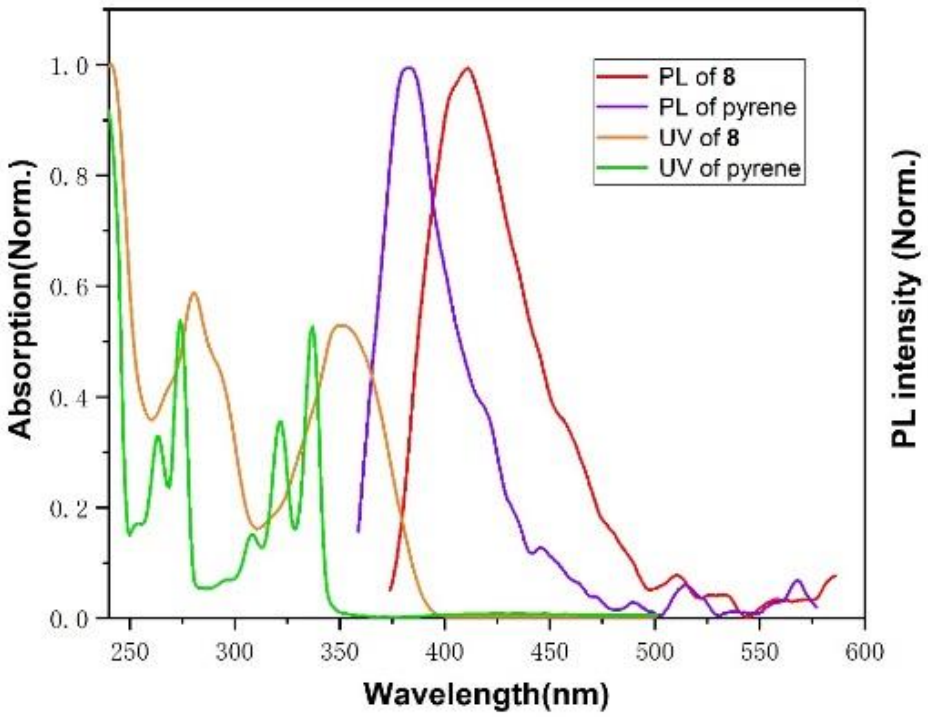


Figure S2 UV and PL spectra of pyrene and product **8** in CH_2Cl_2 solution