

Supporting Information

Design and synthesis of scopoletin sulfonate derivatives as potential insecticidal agents

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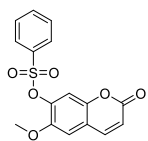
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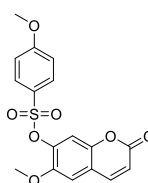
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Characterization of products 8-11.

6-methoxy-2-oxo-2H-chromen-7-yl-benzenesulfonate (4a).

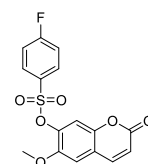


White solid; yield 74.2%; mp:201-203 °C; ^1H NMR (500 MHz, CDCl_3) δ 7.91 (d, J = 8.6 Hz, 2H), 7.71 (t, J = 7.5 Hz, 1H), 7.62 (d, J = 9.6 Hz, 1H), 7.56 (t, J = 7.9 Hz, 2H), 7.09 (s, 1H), 6.89 (s, 1H), 6.42 (d, J = 9.6 Hz, 1H), 3.66 (s, 3H); ^{13}C NMR (125 MHz, CDCl_3) δ 160.13, 149.12, 147.78, 142.42, 140.92, 135.94, 134.45, 129.11, 128.51, 117.80, 117.28, 112.83, 109.87, 56.26; HRMS (ESI): calcd for $\text{C}_{16}\text{H}_{13}\text{O}_6\text{S}$ ($[\text{M}+\text{H}]^+$), 333.0427, found, 333.0424.



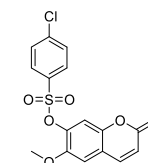
6-methoxy-2-oxo-2H-chromen-7-yl-4-methoxybenzenesulfonate (4b).

White solid; yield 77.5%; mp:180-183 °C; ^1H NMR (500 MHz, CDCl_3) δ 7.74 (d, J = 9.0 Hz, 2H), 7.54 (d, J = 9.6 Hz, 1H), 6.98 (s, 1H), 6.92 (d, J = 9.0 Hz, 2H), 6.82 (s, 1H), 6.33 (d, J = 9.6 Hz, 1H), 3.82 (s, 3H), 3.64 (s, 3H); ^{13}C NMR (125 MHz, CDCl_3) δ 164.36, 160.26, 149.23, 147.74, 142.54, 141.06, 130.84, 126.99, 117.66, 117.14, 114.31, 112.69, 109.86, 56.35, 55.82; HRMS (ESI): calcd for $\text{C}_{17}\text{H}_{15}\text{O}_7\text{S}$ ($[\text{M}+\text{H}]^+$), 363.0533, found, 363.0535.



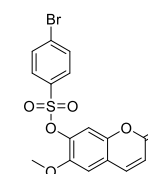
6-methoxy-2-oxo-2H-chromen-7-yl-4-fluorobenzenesulfonate (4c).

Yellow solid; yield 66.9%; mp:173-175 °C; ^1H NMR (500 MHz, $\text{DMSO}-d_6$) δ 8.03 – 7.92 (m, 3H), 7.52 (t, J = 8.8 Hz, 2H), 7.43 (s, 1H), 7.30 (s, 1H), 6.53 (d, J = 9.6 Hz, 1H), 3.55 (s, 3H); ^{13}C NMR (125 MHz, $\text{DMSO}-d_6$) δ 165.31 (d, J = 252.9 Hz), 160.06, 148.52, 147.50, 143.88, 139.82, 132.24 (d, J = 10.4 Hz), 131.21 (d, J = 3.2 Hz), 118.78, 117.44, 117.36 (d, J = 21.5 Hz), 112.70, 111.70, 56.53; HRMS (ESI): calcd for $\text{C}_{16}\text{H}_{12}\text{FO}_6\text{S}$ ($[\text{M}+\text{H}]^+$), 351.0333, found, 351.0337.



6-methoxy-2-oxo-2H-chromen-7-yl-4-chlorobenzenesulfonate (4d).

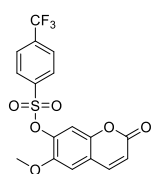
White solid; yield 66.9%; mp:164-165 °C; ^1H NMR (500 MHz, CDCl_3) δ 7.76 (d, J = 8.7 Hz, 2H), 7.56 (d, J = 9.6 Hz, 1H), 7.45 (d, J = 8.7 Hz, 2H), 7.08 (s, 1H), 6.83 (s, 1H), 6.35 (d, J = 9.6 Hz, 1H), 3.59 (s, 3H); ^{13}C NMR (125 MHz, CDCl_3) δ 160.08, 148.81, 147.71, 142.47, 141.27, 140.50, 134.19, 129.96, 129.41, 117.98, 117.37, 112.86, 109.94, 56.19; HRMS (ESI): calcd for $\text{C}_{16}\text{H}_{12}\text{ClO}_6\text{S}$ ($[\text{M}+\text{H}]^+$), 367.0037, found, 367.0038.



6-methoxy-2-oxo-2H-chromen-7-yl-4-bromobenzenesulfonate (4e).

Yellow solid; yield 82.3%; mp:188-190 °C; ^1H NMR (500 MHz, CDCl_3) δ 7.76 (s, 2H), 7.70 (d, J = 8.6 Hz, 2H), 7.63 (d, J = 9.6 Hz, 1H), 7.16 (s, 1H), 6.90 (s, 1H), 6.44 (d, J = 9.6 Hz, 1H), 3.67 (s, 3H); ^{13}C NMR (125 MHz, CDCl_3) δ 160.01, 148.88, 147.81, 142.32, 140.63, 134.91, 132.41,

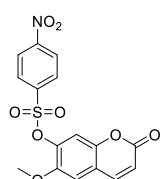
129.97, 129.85, 117.95, 117.45, 112.91, 109.93, 56.23; HRMS (ESI): calcd for $C_{16}H_{12}BrO_6S$ ($[M+H]^+$), 412.9512 found, 412.9510.



6-methoxy-2-oxo-2H-chromen-7-yl-4-(trifluoromethyl)-benzenesulfonate (4f). White solid;

yield 81.5%; mp:169-171 °C; ^1H NMR (500 MHz, $CDCl_3$) δ 8.06 (d, J = 8.2 Hz, 2H), 7.84 (d, J = 8.3 Hz, 2H), 7.62 (d, J = 9.6 Hz, 1H), 7.21 (s, 1H), 6.89 (s, 1H), 6.45 (d, J = 9.6 Hz, 1H), 3.62 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 159.91, 148.71, 147.85, 142.22, 140.44, 139.58,

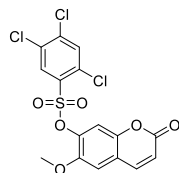
135.98(q, J = 34.5 Hz), 129.12, 126.18(q, J = 3.59 Hz), 123.12 (q, J = 274.8 Hz), 118.08, 117.61, 113.07, 109.87, 56.09; HRMS (ESI): calcd for $C_{17}H_{12}F_3O_6S$ ($[M+H]^+$), 401.0301, found, 401.0300.



6-methoxy-2-oxo-2H-chromen-7-yl-4-nitrobenzenesulfonate (4g).

Yellow solid; yield 68.3%; mp:178-181 °C; ^1H NMR (500 MHz, $DMSO-d_6$) δ 8.46 (d, J = 8.9 Hz, 2H), 8.16 (d, J = 8.9 Hz, 2H), 8.00 (d, J = 9.6 Hz, 1H), 7.45 (s, 1H), 7.39 (s, 1H), 6.55 (d, J = 9.6 Hz, 1H), 3.52 (s, 3H); ^{13}C NMR (125 MHz, $DMSO-d_6$) δ 160.00, 151.56, 148.38, 147.55,

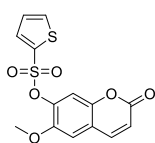
143.82, 140.56, 139.68, 130.52, 125.18, 119.03, 117.58, 112.75, 111.90, 56.55; HRMS (ESI): calcd for $C_{16}H_{12}NO_8S$ ($[M+H]^+$), 378.0278, found, 378.0277.



6-methoxy-2-oxo-2H-chromen-7-yl-2,4,5-trichlorobenzenesulfonate (4h). White solid; yield

66.1%; mp:186-188 °C; ^1H NMR (500 MHz, $CDCl_3$) δ 7.97 (s, 1H), 7.69 (s, 1H), 7.56 (d, J = 9.6 Hz, 1H), 7.08 (s, 1H), 6.88 (s, 1H), 6.37 (d, J = 9.6 Hz, 1H), 3.66 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 159.95, 148.79, 147.79, 142.29, 140.50, 139.67, 134.09, 133.33, 132.81, 132.32,

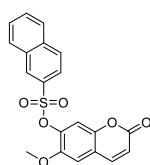
131.83, 118.21, 117.65, 113.00, 110.13, 56.36; HRMS (ESI): calcd for $C_{16}H_9Cl_3O_6S$ ($[M+H]^+$), 436.9229, found, 436.9228.



6-methoxy-2-oxo-2H-chromen-7-yl-thiophene-2-sulfonate (4i).

White solid; yield 81.2%; mp:188-189 °C; ^1H NMR (500 MHz, $DMSO-d_6$) δ 8.26 (d, J = 4.9 Hz, 1H), 8.00 (d, J = 9.6 Hz, 1H), 7.83 (d, J = 3.8 Hz, 1H), 7.45 (s, 1H), 7.34 – 7.28 (m, 1H), 7.23 (s,

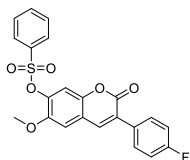
1H), 6.54 (d, J = 9.6 Hz, 1H), 3.64 (s, 3H); ^{13}C NMR (125 MHz, $DMSO-d_6$) δ 160.03, 148.80, 147.40, 143.82, 139.90, 137.88, 137.14, 133.72, 128.77, 118.79, 117.41, 112.44, 111.63, 56.68; HRMS (ESI): calcd for $C_{14}H_{11}O_6S_2$ ($[M+H]^+$), 338.9991, found, 338.9995.



6-methoxy-2-oxo-2H-chromen-7-yl-naphthalene-2-sulfonate (4j).

White solid; yield 57.2%; mp:164-166 °C; ^1H NMR (500 MHz, $CDCl_3$) δ 8.42 (s, 1H), 8.04 – 7.85 (m, 4H), 7.65 (m, J = 24.7, 15.8, 8.5 Hz, 3H), 7.14 (s, 1H), 6.85 (s, 1H), 6.38 (d, J = 9.5 Hz,

1H), 3.52 (s, 3H); ¹³C NMR (125 MHz, CDCl₃) δ 160.13, 149.02, 147.74, 142.49, 140.90, 135.53, 132.66, 131.73, 130.44, 129.83, 129.43, 129.36, 128.03, 127.99, 122.91, 117.81, 117.17, 112.81, 109.93, 56.14; HRMS (ESI): calcd for C₂₀H₁₅O₆S ([M+H]⁺), 383.0584, found, 383.0586.



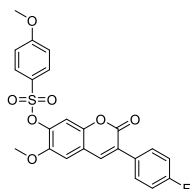
3-(4-fluorophenyl)-6-methoxy-2-oxo-2H-chromen-7-yl-benzenesulfonate (5a). White solid;

yield 88.4%; mp:129-130 °C; ¹H NMR (500 MHz, DMSO-*d*₆) δ 8.15 (s, 1H), 7.87 (dd, *J* =

11.2, 10.3 Hz, 3H), 7.75 (dd, *J* = 10.6, 3.6 Hz, 2H), 7.69 (t, *J* = 7.8 Hz, 2H), 7.43 (s, 1H), 7.32

(t, *J* = 8.8 Hz, 2H), 7.27 (s, 1H), 3.53 (s, 3H); ¹³C NMR (125 MHz, DMSO-*d*₆) δ 162.79(d, *J* = 248.6 Hz), 159.86, 148.74, 146.92, 140.08, 139.84, 135.61, 135.13, 131.33(d, *J* = 3.16 Hz), 131.19(d, *J* = 9.06 Hz), 130.05, 128.80, 126.93, 119.36, 115.72(d, *J* = 21.3 Hz), 112.17, 111.58, 56.51; HRMS (ESI): calcd for C₂₂H₁₆FO₆S ([M+H]⁺), 427.0646, found, 427.0649.

3-(4-fluorophenyl)-6-methoxy-2-oxo-2H-chromen-7-yl-4-methoxybenzenesulfonate (5b).



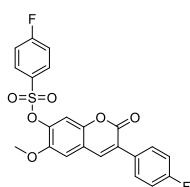
White solid; yield 74.4%; mp:148-150 °C; ¹H NMR (500 MHz, CDCl₃) δ 7.81 (d, *J* = 7.5 Hz,

2H), 7.70 (s, 1H), 7.65 (dd, *J* = 7.1, 5.5 Hz, 2H), 7.14 – 7.06 (m, 3H), 7.00 – 6.96 (m, 3H),

3.90 (s, 3H), 3.70 (s, 3H); ¹³C NMR (125 MHz, CDCl₃) δ 164.40, 163.16 (d, *J* = 251.4

Hz), 160.11, 149.31, 147.08, 140.74, 138.82, 130.88 (d, *J* = 7.8 Hz), 130.83, 130.44 (d, *J* = 3.5

Hz), 127.53, 126.88, 118.47, 115.53 (d, *J* = 21.7 Hz), 114.33, 112.22, 109.86, 56.30, 55.84; HRMS (ESI): calcd for C₂₃H₁₈FO₇S ([M+H]⁺), 457.0751, found, 457.0756.



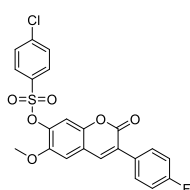
3-(4-fluorophenyl)-6-methoxy-2-oxo-2H-chromen-7-yl 4-fluorobenzenesulfonate (5c).

Yellow solid; yield 84.1%; mp:155-157 °C; ¹H NMR (500 MHz, DMSO-*d*₆) δ 8.17 (s, 1H),

7.97 (dd, *J* = 8.8, 5.0 Hz, 2H), 7.76 (dd, *J* = 8.7, 5.6 Hz, 2H), 7.53 (t, *J* = 8.8 Hz, 2H), 7.44 (s,

1H), 7.32 (dd, *J* = 14.5, 5.3 Hz, 3H), 3.56 (s, 3H); ¹³C NMR (125 MHz, DMSO-*d*₆) δ 166.18

(d, *J* = 260.1 Hz), 162.8 (d, *J* = 247.1 Hz), 159.85, 148.62, 146.96, 140.07, 139.70, 132.26 (d, *J* = 10.18 Hz), 131.39 (d, *J* = 3.2 Hz), 131.32 (d, *J* = 3.2 Hz), 131.19 (d, *J* = 8.75 Hz), 126.98, 119.46, 117.28 (d, *J* = 22.6 Hz), 115.72(d, *J* = 21.65 Hz), 112.37, 111.59, 56.51; HRMS (ESI): calcd for C₂₂H₁₅F₂O₆S ([M+H]⁺), 445.0556, found, 445.0556.



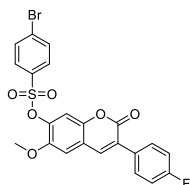
3-(4-fluorophenyl)-6-methoxy-2-oxo-2H-chromen-7-yl-4-chlorobenzenesulfonate (5d).

White solid; yield 88.4%; mp:137-140 °C; ¹H NMR (500 MHz, CDCl₃) δ 7.85 (d, *J* = 8.5 Hz,

2H), 7.70 (s, 1H), 7.67 (dd, *J* = 8.4, 5.5 Hz, 2H), 7.54 (d, *J* = 8.5 Hz, 2H), 7.18 (s, 1H), 7.14 (t,

J = 8.6 Hz, 2H), 6.95 (s, 1H), 3.69 (s, 3H); ¹³C NMR (125 MHz, CDCl₃) δ 163.27 (d, *J* =

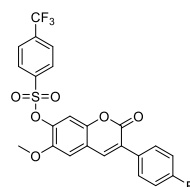
246.7 Hz), 159.97, 149.06, 147.18, 141.31, 140.39, 138.50, 134.30, 130.44 (d, $J = 8.5$ Hz), 130.35 (d, $J = 3.4$ Hz), 129.98, 129.44, 128.01, 118.72, 115.62 (d, $J = 21.9$ Hz), 112.52, 109.75, 56.23; HRMS (ESI): calcd for $C_{22}H_{15}ClFO_6S$ ($[M+H]^+$), 461.0256, found, 461.0258.



3-(4-fluorophenyl)-6-methoxy-2-oxo-2H-chromen-7-yl-4-bromobenzenesulfonate (5e).

Yellow solid; yield 63.1%; mp:142-146 °C; ^1H NMR (500 MHz, $CDCl_3$) δ 7.77 (d, $J = 8.5$ Hz, 2H), 7.74 – 7.69 (m, 3H), 7.67 (dd, $J = 8.5, 5.5$ Hz, 2H), 7.18 (s, 1H), 7.13 (t, $J = 8.6$ Hz, 2H), 6.95 (s, 1H), 3.69 (s, 3H). (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 163.21(d, $J = 249.4$ Hz),

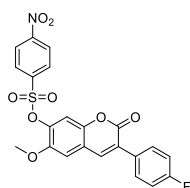
159.97, 149.04, 147.17, 140.36, 138.51, 134.84, 132.44, 130.44 (d, $J = 8.6$ Hz), 130.35 (d, $J = 3.5$ Hz), 129.99, 129.90, 128.01, 118.73, 115.62 (d, $J = 21.8$ Hz), 112.52, 109.75, 56.23; HRMS (ESI): calcd for $C_{22}H_{15}BrFO_6S$ ($[M+H]^+$), 506.9731, found, 506.9730.



3-(4-fluorophenyl)-6-methoxy-2-oxo-2H-chromen-7-yl-(trifluoromethyl)-benzenesulfonate (5f).

White solid; yield 78.4%; mp:156-160 °C; ^1H NMR (500 MHz, $DMSO-d_6$) δ 8.17 (s, 1H), 8.11 (d, $J = 8.3$ Hz, 2H), 8.07 (d, $J = 8.4$ Hz, 2H), 7.79 – 7.73 (m, 2H), 7.44 (d, $J = 3.4$ Hz,

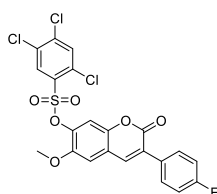
2H), 7.32 (t, $J = 8.8$ Hz, 2H), 3.48 (s, 3H); ^{13}C NMR (125 MHz, $DMSO-d_6$) δ 162.75 (d, $J = 245.2$ Hz), 159.82, 148.43, 147.00, 140.00, 139.52, 139.12, 134.83 (q, $J = 32.4$ Hz), 131.29 (d, $J = 3.1$ Hz), 131.19 (d, $J = 8.4$ Hz), 129.93, 127.19 (q, $J = 3.47$ Hz), 127.09, 123.71 (q, $J = 274.1$ Hz), 119.65, 115.73 (d, $J = 21.4$ Hz), 112.57, 111.60, 56.33; HRMS (ESI): calcd for $C_{23}H_{15}F_4O_6S$ ($[M+H]^+$), 495.0519, found, 495.0518.



3-(4-fluorophenyl)-6-methoxy-2-oxo-2H-chromen-7-yl-4-nitrobenzenesulfonate (5g).

White solid; yield 77.9%; mp:150-151 °C; ^1H NMR (500 MHz, $DMSO-d_6$) δ 8.46 (d, $J = 8.8$ Hz, 2H), 8.17 (d, $J = 9.0$ Hz, 3H), 7.75 (dd, $J = 8.6, 5.6$ Hz, 2H), 7.45 (d, $J = 12.3$ Hz, 2H), 7.32 (t, $J = 8.8$ Hz, 2H), 3.53 (s, 3H); ^{13}C NMR (125 MHz, $DMSO-d_6$) δ 162.82 (d, $J = 245.6$

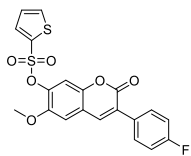
Hz), 159.83, 151.57, 148.47, 147.00, 140.49, 140.01, 139.50, 131.29 (d, $J = 3.3$ Hz), 131.20 (d, $J = 8.5$ Hz), 130.56, 127.13, 125.21, 119.72, 115.75 (d, $J = 21.6$ Hz), 112.47, 111.74, 56.50; HRMS (ESI): calcd for $C_{22}H_{15}FNO_8S$ ($[M+H]^+$), 472.0496, found, 472.0496.



3-(4-fluorophenyl)-6-methoxy-2-oxo-2H-chromen-7-yl-2,4,5-trichlorobenzenesulfonate (5h).

White solid; yield 68.7%; mp:197-199 °C; ^1H NMR (500 MHz, $CDCl_3$) δ 8.05 (s, 1H), 7.76 (s, 1H), 7.71 (s, 1H), 7.67 (dd, $J = 8.6, 5.4$ Hz, 2H), 7.17 (s, 1H), 7.13 (t, $J = 8.6$ Hz, 2H),

7.00 (s, 1H), 3.74 (s, 3H); ^{13}C NMR (125 MHz, CDCl_3) δ 163.25 (d, J = 250.4 Hz), 159.87, 148.95, 147.15, 140.24, 139.69, 138.42, 134.07, 133.35, 132.83, 132.33, 131.83, 130.45 (d, J = 8.5 Hz), 130.28 (d, J = 3.5 Hz), 128.18, 118.99, 115.62 (d, J = 21.4 Hz), 112.58, 110.04, 56.38; HRMS (ESI): calcd for $\text{C}_{22}\text{H}_{13}\text{Cl}_3\text{FO}_6\text{S}$ ($[\text{M}+\text{H}]^+$), 530.9448, found, 530.9448.

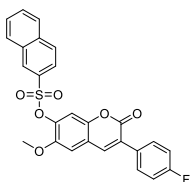


3-(4-fluorophenyl)-6-methoxy-2-oxo-2H-chromen-7-yl-thiophene-2-sulfonate (5i). White

solid; yield 76.1%; mp:135-136 °C; ^1H NMR (500 MHz, $\text{DMSO}-d_6$) δ 8.25 (d, J = 4.9 Hz, 1H),

8.17 (s, 1H), 7.82 (d, J = 3.7 Hz, 1H), 7.79 – 7.72 (m, 2H), 7.48 (s, 1H), 7.31 (dd, J = 19.6, 11.0

Hz, 4H), 3.63 (s, 3H); ^{13}C NMR (125 MHz, $\text{DMSO}-d_6$) δ 162.71 (d, J = 246.5 Hz), 159.87, 148.93, 146.89, 140.07, 139.78, 137.98, 137.21, 133.67, 131.26 (d, J = 3.3 Hz), 131.21 (d, J = 8.7 Hz), 128.84, 127.04, 119.51, 115.72 (d, J = 21.7 Hz), 112.14, 111.60, 56.70; HRMS (ESI): calcd for $\text{C}_{20}\text{H}_{14}\text{FO}_6\text{S}_2$ ($[\text{M}+\text{H}]^+$), 433.0210, found, 433.0212.



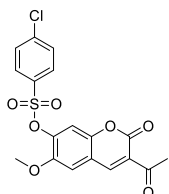
3-(4-fluorophenyl)-6-methoxy-2-oxo-2H-chromen-7-yl-naphthalene-2-sulfonate (5j). White

solid; yield 78.8%; mp:140-142 °C; ^1H NMR (500 MHz, CDCl_3) δ 8.45 (s, 1H), 8.01 (d, J =

8.7 Hz, 1H), 7.96 (d, J = 8.4 Hz, 2H), 7.91 (d, J = 8.7 Hz, 1H), 7.73 – 7.70 (m, 1H), 7.69 – 7.62

(m, 4H), 7.13 (dd, J = 17.4, 8.8 Hz, 3H), 6.90 (s, 1H), 3.58 (s, 3H); ^{13}C NMR (125 MHz,

CDCl_3) δ 163.19 (d, J = 250.7 Hz), 160.06, 149.27, 147.17, 140.75, 135.56, 132.68, 131.76, 130.48 (d, J = 7.05 Hz), 130.44, 130.41, 130.38, 129.83, 129.49, 129.41, 128.00, 128.06, 127.80, 122.95, 118.55, 115.59 (d, J = 21.2 Hz), 112.46, 109.70, 56.19; HRMS (ESI): calcd for $\text{C}_{26}\text{H}_{18}\text{FO}_6\text{S}$ ($[\text{M}+\text{H}]^+$), 477.0802, found, 477.0800.



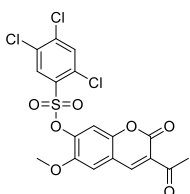
3-acetyl-6-methoxy-2-oxo-2H-chromen-7-yl-4-chlorobenzenesulfonate (6d).

White solid; yield 66.2 %; mp:130-133 °C; ^1H NMR (500 MHz, CDCl_3) δ 8.35 (s, 1H), 7.75 (d,

J = 8.5 Hz, 2H), 7.47 (d, J = 8.5 Hz, 2H), 7.40 (s, 1H), 6.73 (s, 1H), 3.63 (s, 3H), 2.62 (s, 3H);

^{13}C NMR (125 MHz, CDCl_3) δ 194.93, 158.94, 157.11, 155.85, 146.93, 141.36, 135.48, 134.12,

129.99, 129.42, 124.51, 122.03, 111.21, 100.54, 56.48, 30.52; HRMS (ESI): calcd for $\text{C}_{18}\text{H}_{14}\text{ClO}_7\text{S}$ ($[\text{M}+\text{H}]^+$), 409.0143, found, 409.0148.



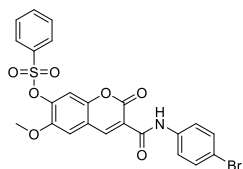
3-acetyl-6-methoxy-2-oxo-2H-chromen-7-yl-2,4,5-trichlorobenzenesulfonate (6h). White

solid; yield 78.3 %; mp:124-128 °C; ^1H NMR (500 MHz, CDCl_3) δ 8.35 (s, 1H), 7.98 (s, 1H),

7.69 (s, 1H), 7.39 (s, 1H), 6.78 (s, 1H), 3.71 (s, 3H), 2.63 (s, 3H); ^{13}C NMR (125 MHz, CDCl_3)

δ 194.89, 158.87, 156.97, 155.97, 146.84, 139.74, 135.47, 133.97, 133.31, 132.82, 132.37,

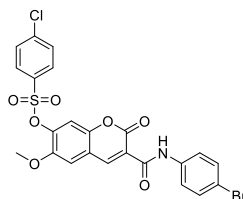
131.89, 124.53, 122.16, 111.28, 100.74, 56.58, 30.52; HRMS (ESI): calcd for $\text{C}_{18}\text{H}_{12}\text{Cl}_3\text{O}_7\text{S}$ ($[\text{M}+\text{H}]^+$), 478.9335, found, 478.9334.



3-((4-bromophenyl)carbamoyl)-6-methoxy-2-oxo-2H-chromen-7-yl benzenesulfonate

(7a). Yellow solid; yield 66.2 %; mp:200-203 °C; ^1H NMR (500 MHz, $\text{DMSO-}d_6$) δ 10.75

(s, 1H), 8.86 (s, 1H), 7.98 – 7.89 (m, 3H), 7.77 (d, J = 2.26 Hz, 2H), 7.76 (d, J = 2.33 Hz, 2H), 7.74 (s, 1H), 7.63 (d, J = 8.8 Hz, 2H), 7.48 (s, 1H), 3.60 (s, 3H); ^{13}C NMR (125 MHz, $\text{DMSO-}d_6$) δ 160.45, 165.38, 149.20, 148.14, 146.95, 141.74, 137.69, 135.73, 135.06, 132.31, 130.12, 128.78, 122.42, 120.81, 118.36, 116.56, 112.99, 112.58, 56.70; HRMS (ESI): calcd for $\text{C}_{23}\text{H}_{16}\text{BrNO}_7\text{SNa}$ ($[\text{M}+\text{Na}]^+$), 531.9884, found, 531.9882.



3-((4-bromophenyl)carbamoyl)-6-methoxy-2-oxo-2H-chromen-7-yl-4-chlorobenzenesulfonate (7d).

Yellow solid; yield 65.1 %; mp:220-225°C; ^1H NMR (500 MHz, $\text{DMSO-}d_6$) δ

10.82 (s, 1H), 8.91 (s, 1H), 7.88 – 7.85 (m, 2H), 7.65 – 7.63 (m, 2H), 7.57 – 7.54 (m, 2H), 7.51 – 7.48 (m, 2H), 7.34 (s, 1H), 7.10 (s, 1H), 3.72 (s, 3H); ^{13}C NMR (125 MHz, $\text{DMSO-}d_6$) δ 160.40, 149.07, 148.21, 146.95, 141.55, 140.80, 137.72, 133.91, 132.32, 130.76, 130.28, 129.14, 122.42, 120.90, 118.53, 116.56, 113.09, 112.80, 56.37; HRMS (ESI): calcd for $\text{C}_{23}\text{H}_{15}\text{BrClNO}_7\text{SNa}$ ($[\text{M}+\text{Na}]^+$), 587.9312, found, 587.9312.

^1H NMR, ^{13}C NMR, HRMS data of title compounds 8-11

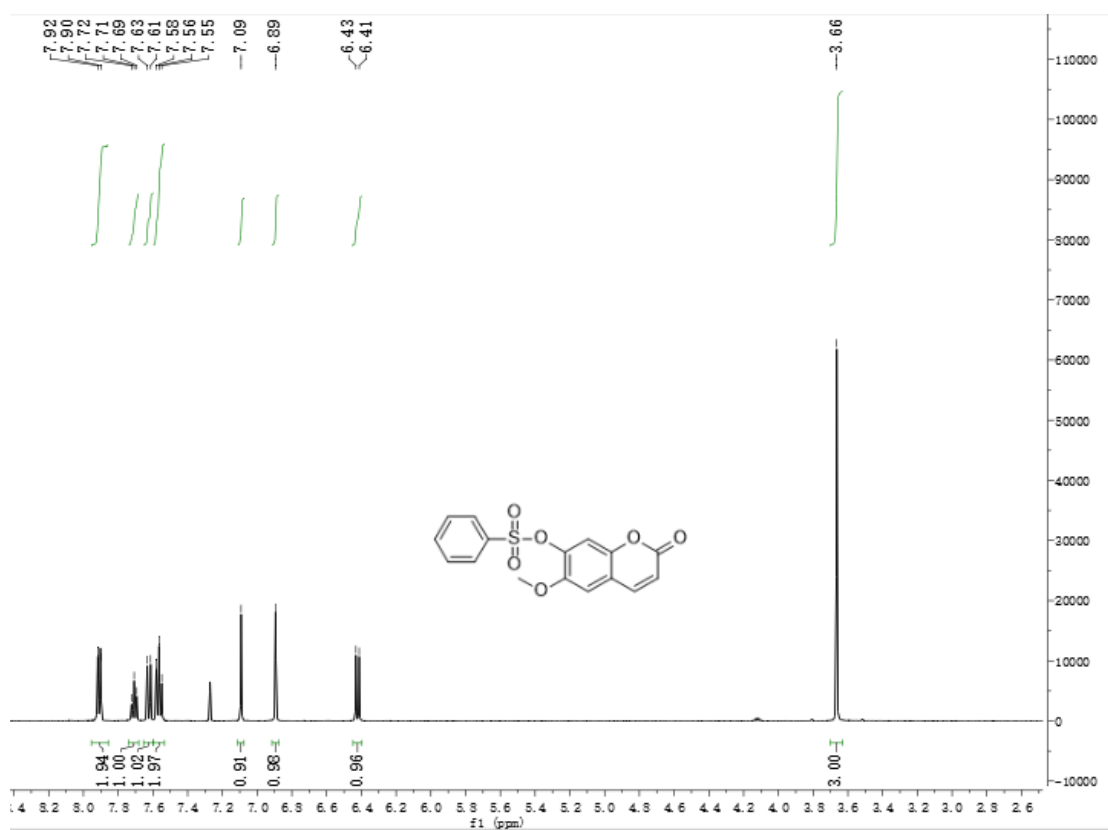


Figure S1 ^1H NMR of 4a

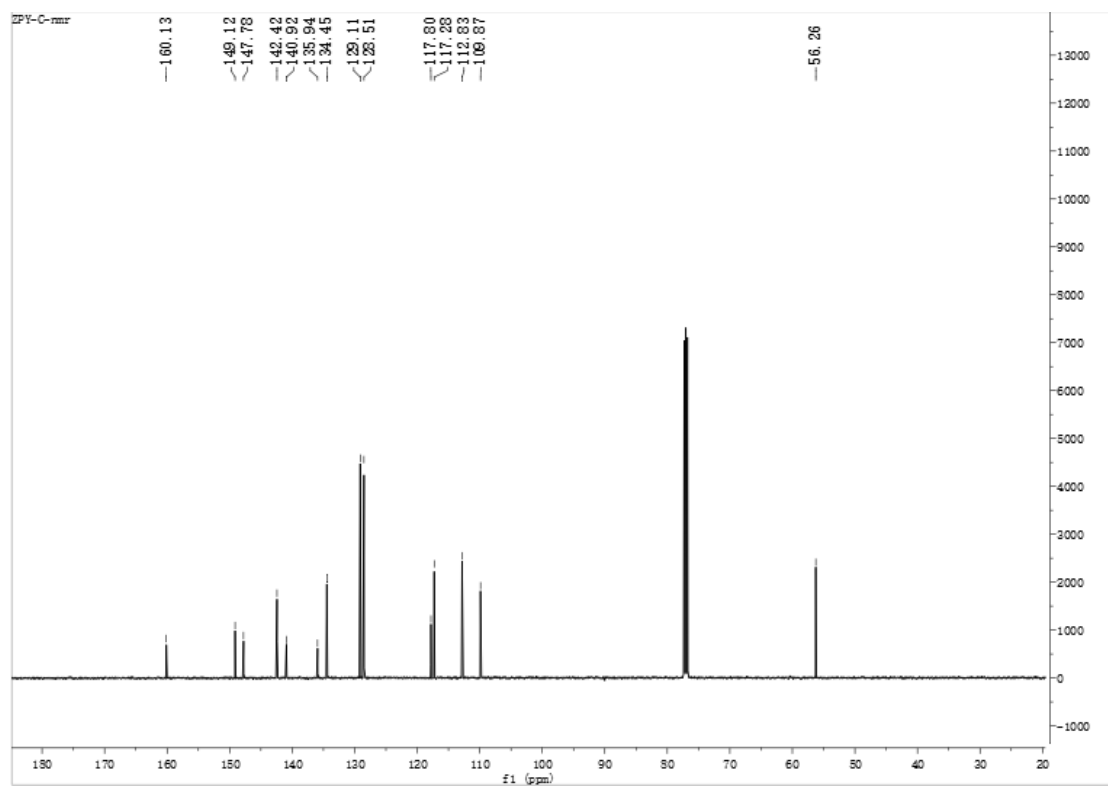


Figure S2 ^{13}C NMR of 4a

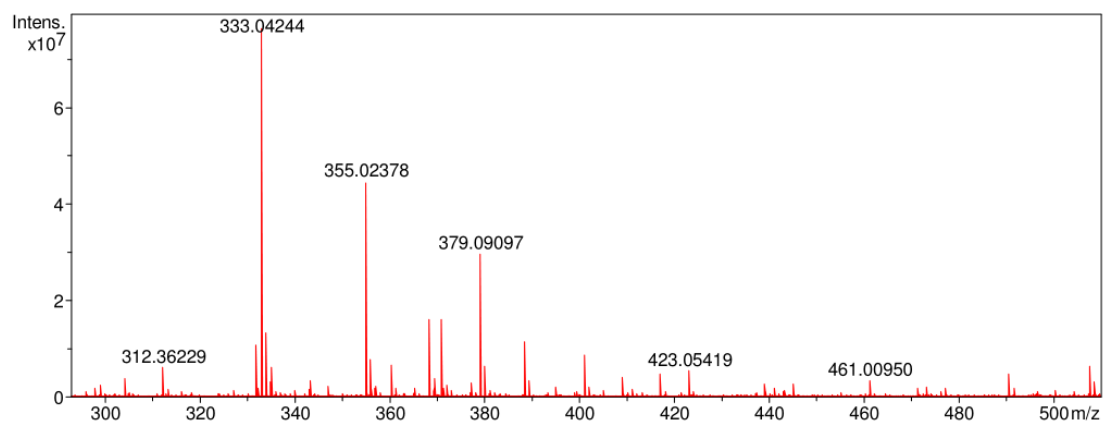


Figure S3 HRMS of 8a

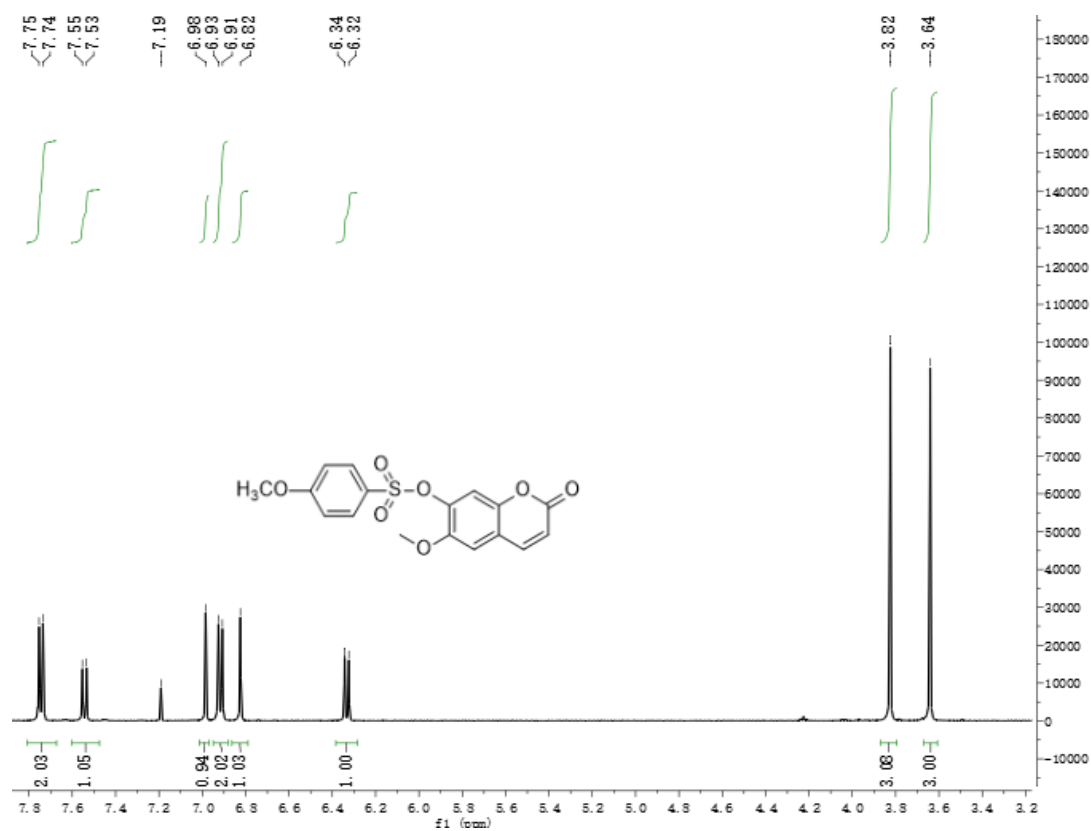


Figure S4 ¹H NMR of 8b

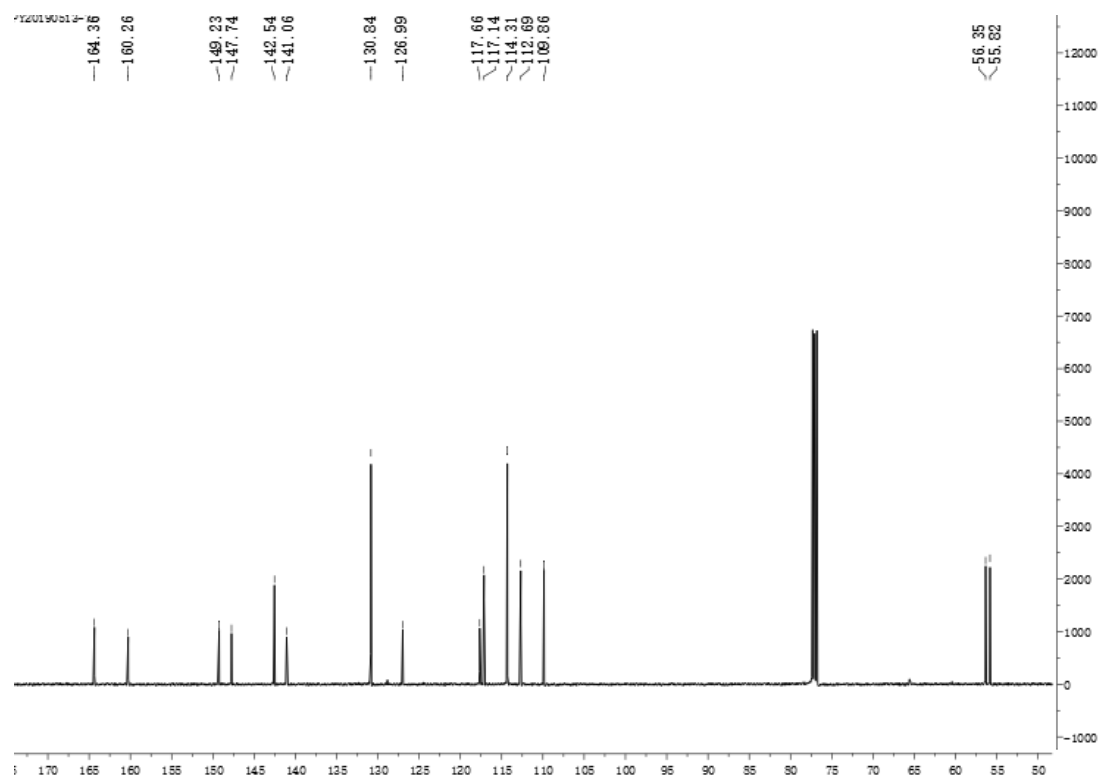


Figure S5 ^{13}C NMR of 8b

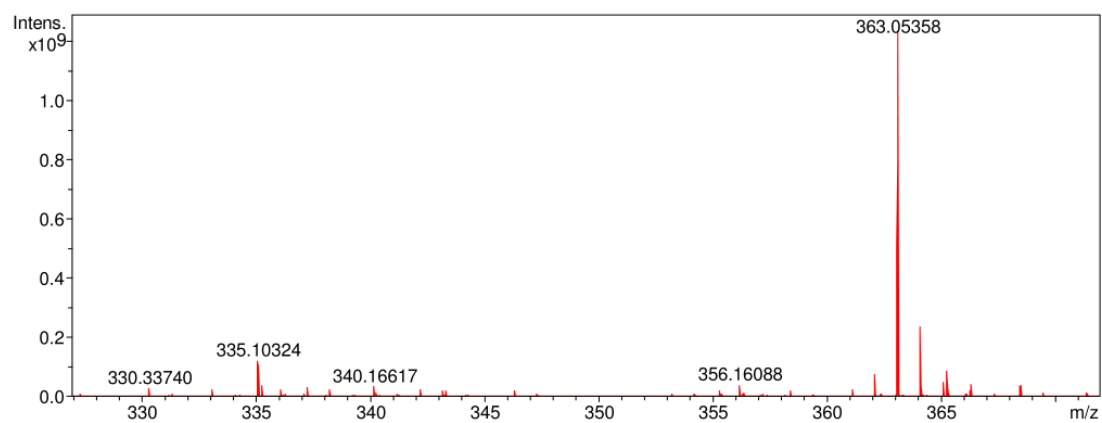


Figure S6 HRMS of 8b

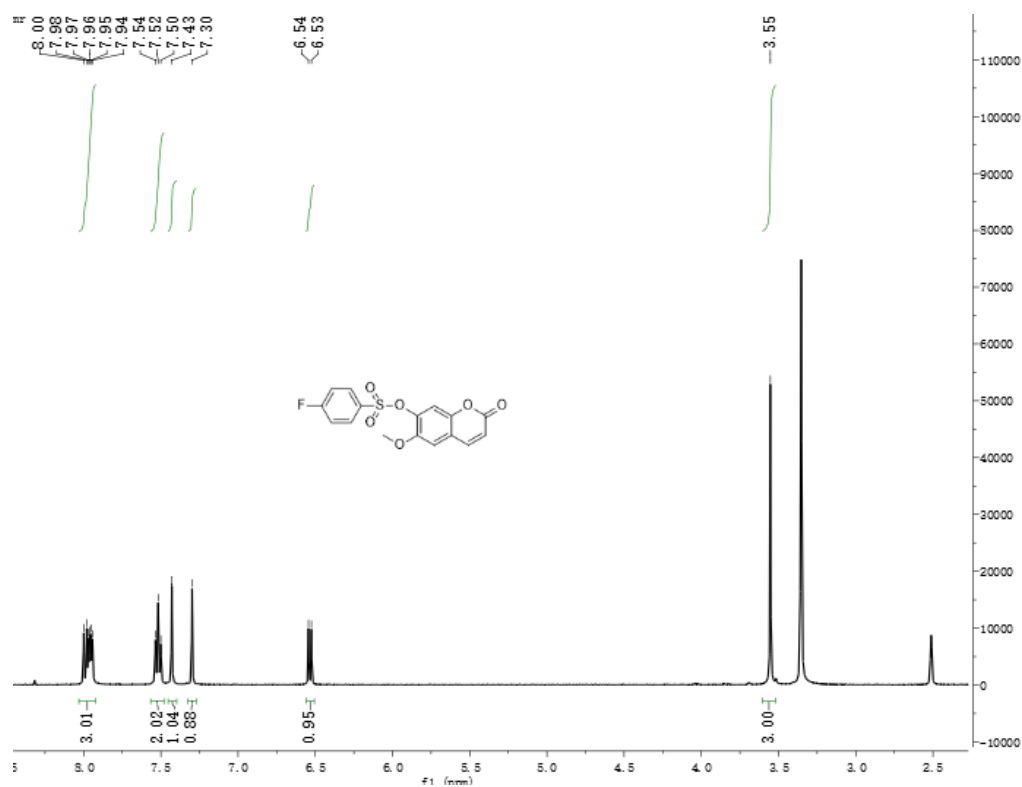


Figure S7 ^1H NMR of 8c

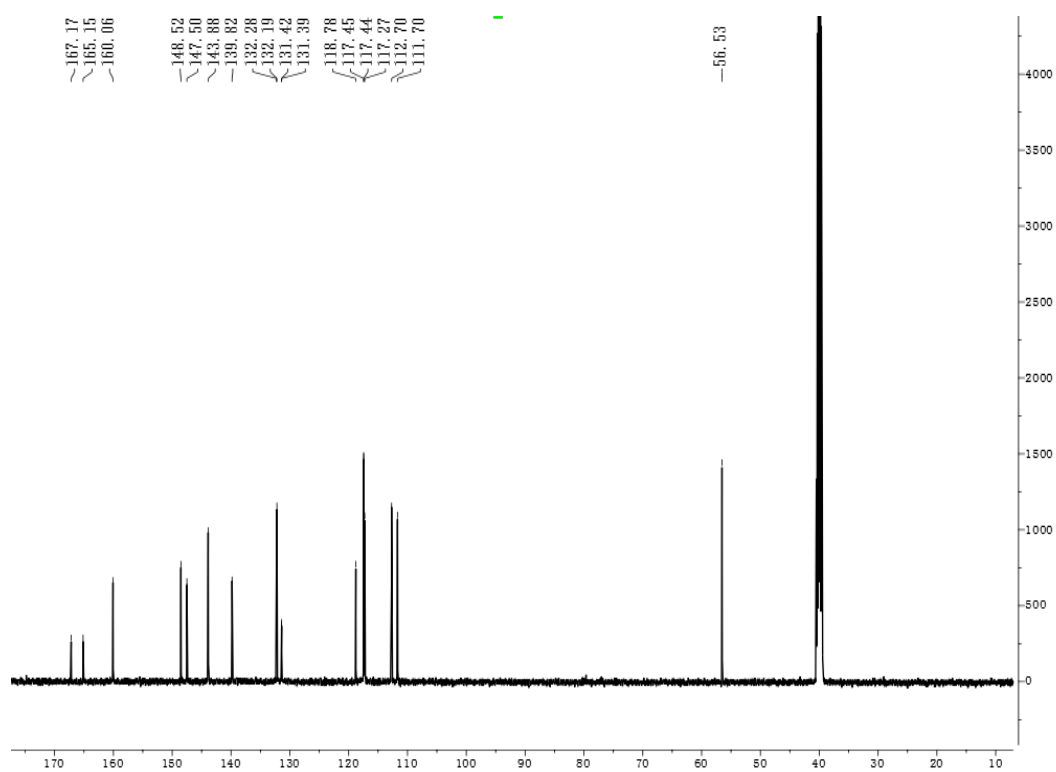


Figure S8 ^{13}C NMR of 8c

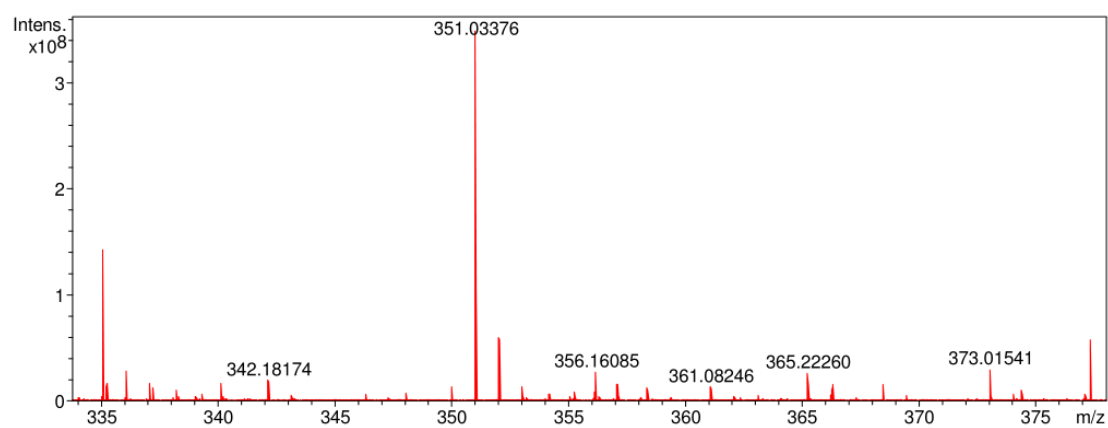


Figure S9 HRMS of 8c

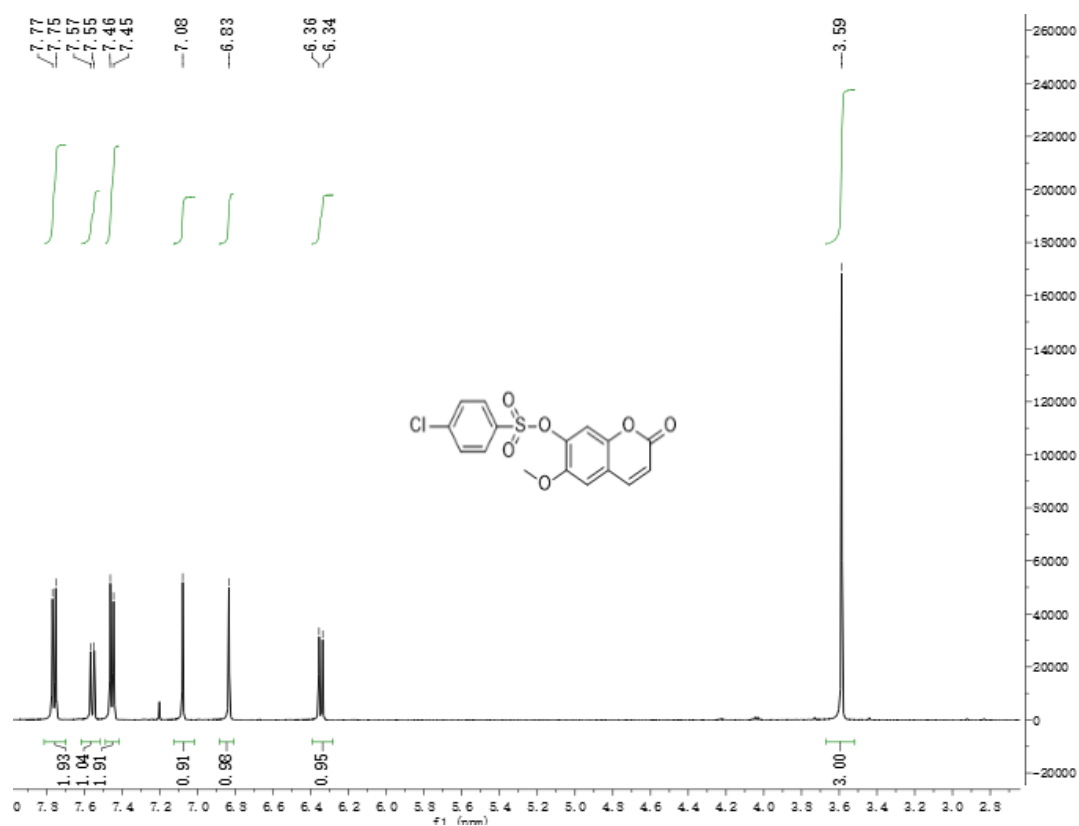


Figure S10 ¹H NMR of 8d

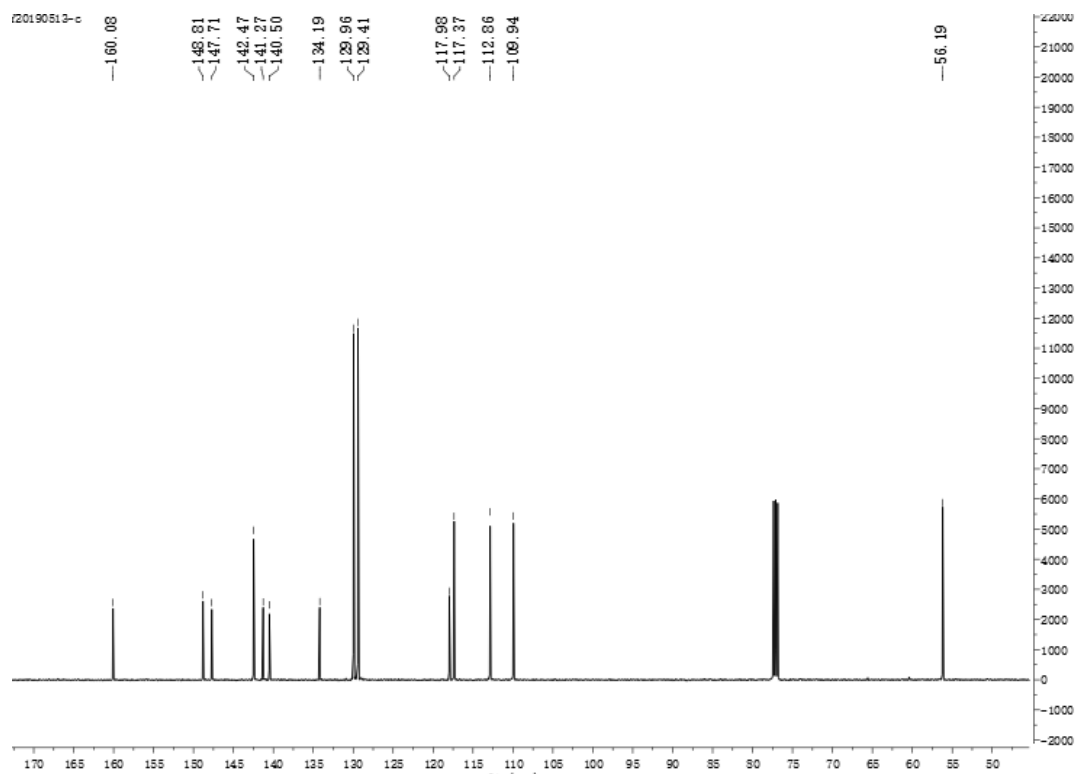


Figure S11 ¹³C NMR of 8d

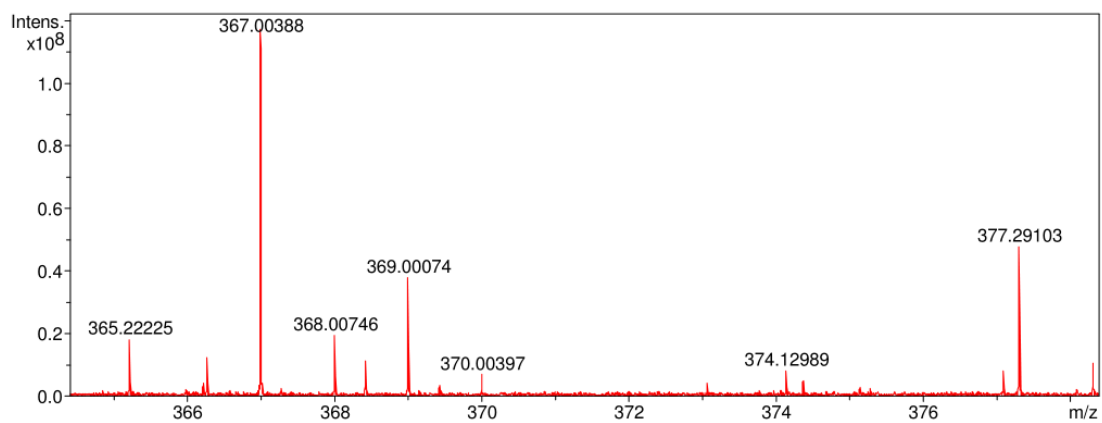


Figure S12 HRMS of 8d

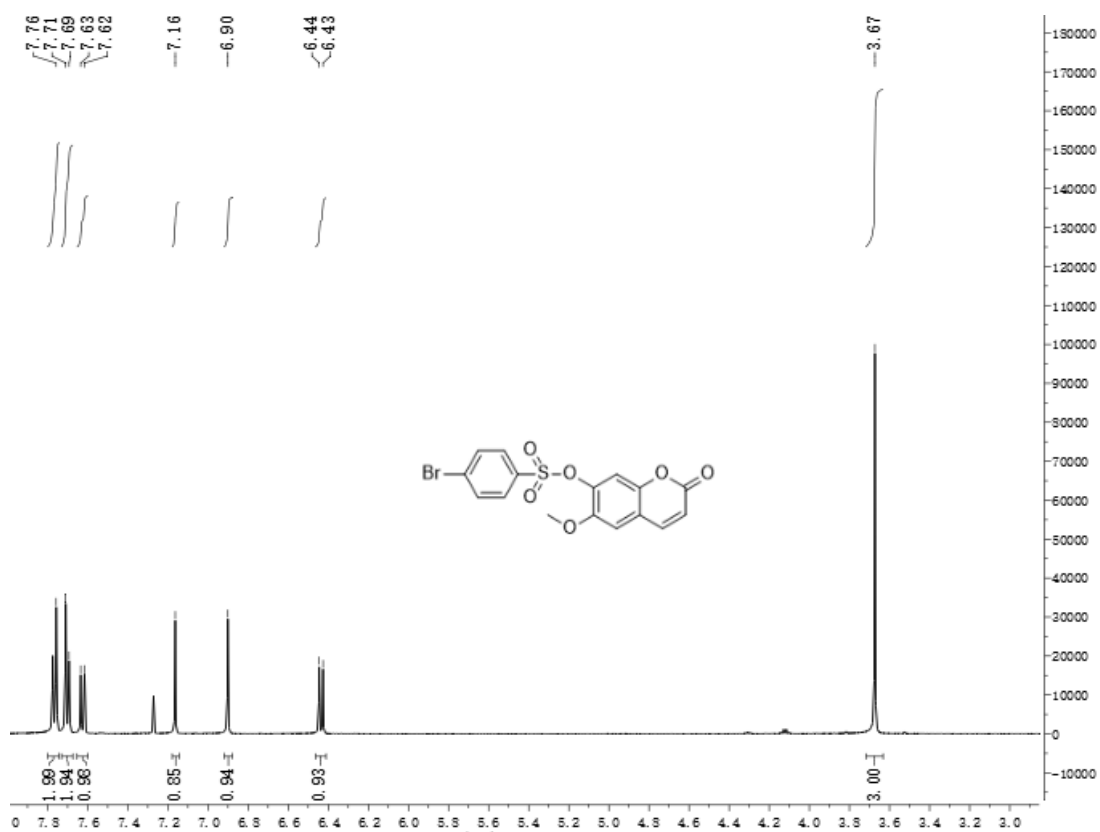


Figure S13 ^1H NMR of 8e

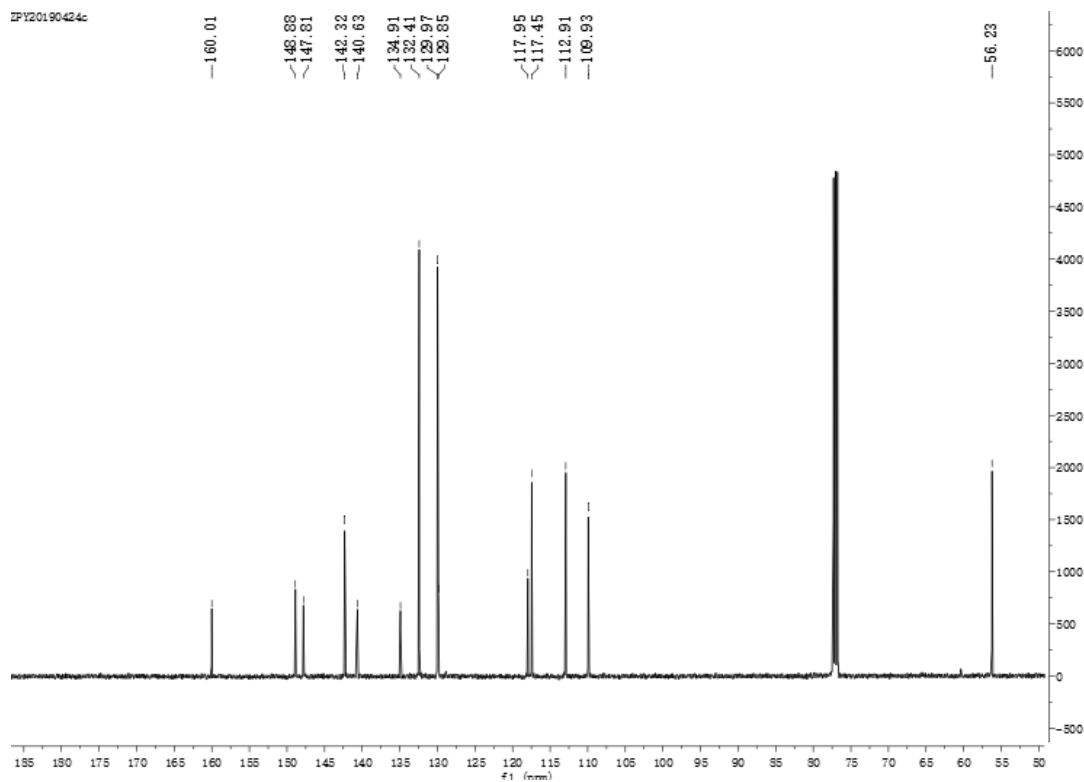


Figure S14 ^{13}C NMR of 8e

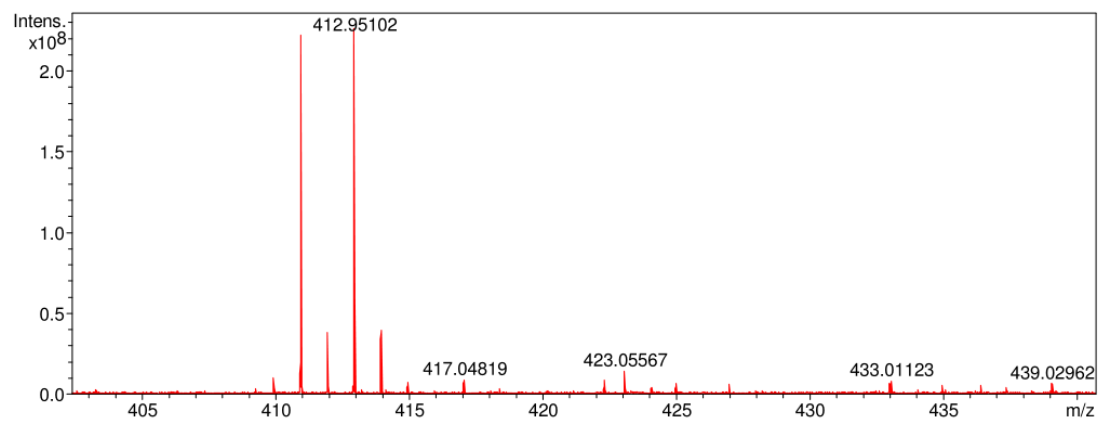


Figure S15 HRMS of 8e

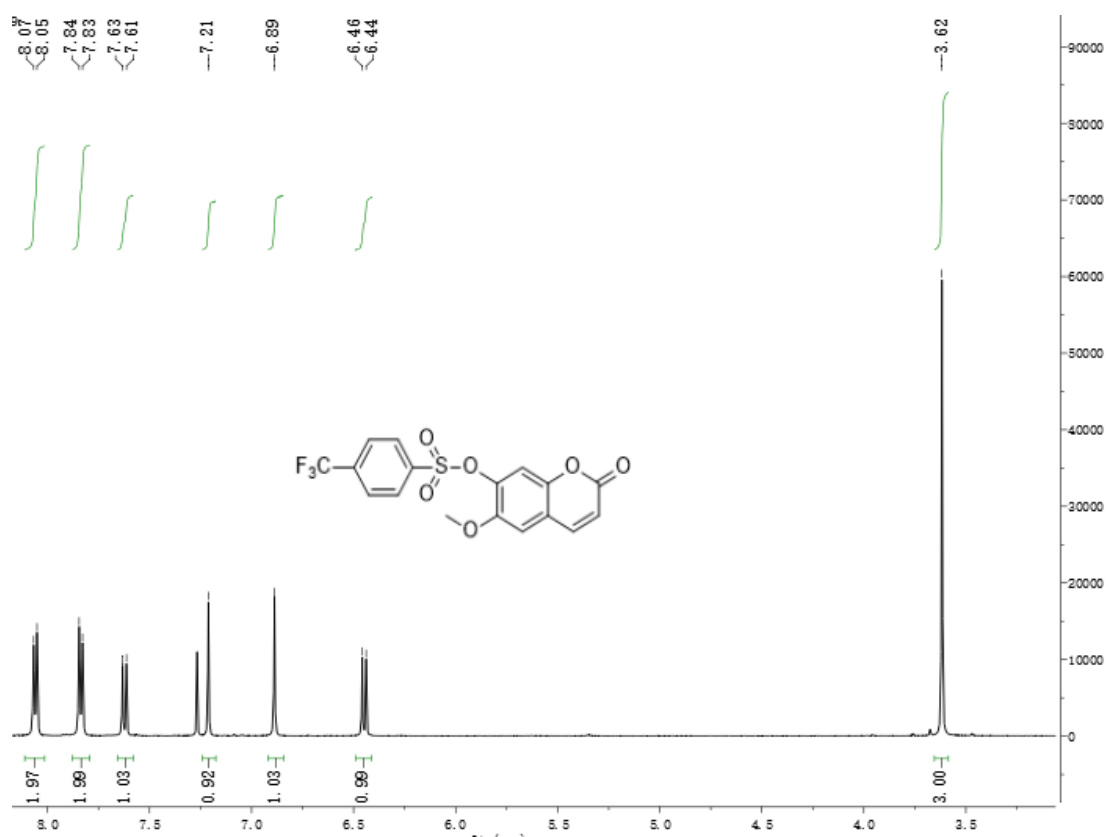


Figure S16 ^1H NMR of 8f

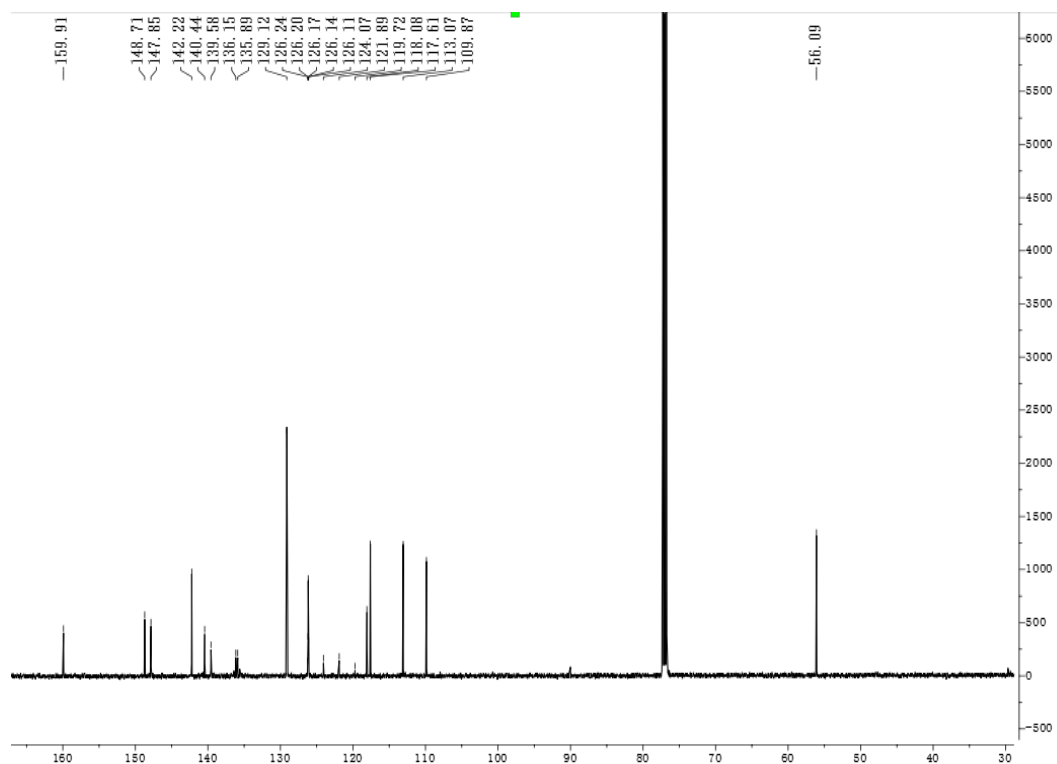


Figure S17 ^{13}C NMR of 8f

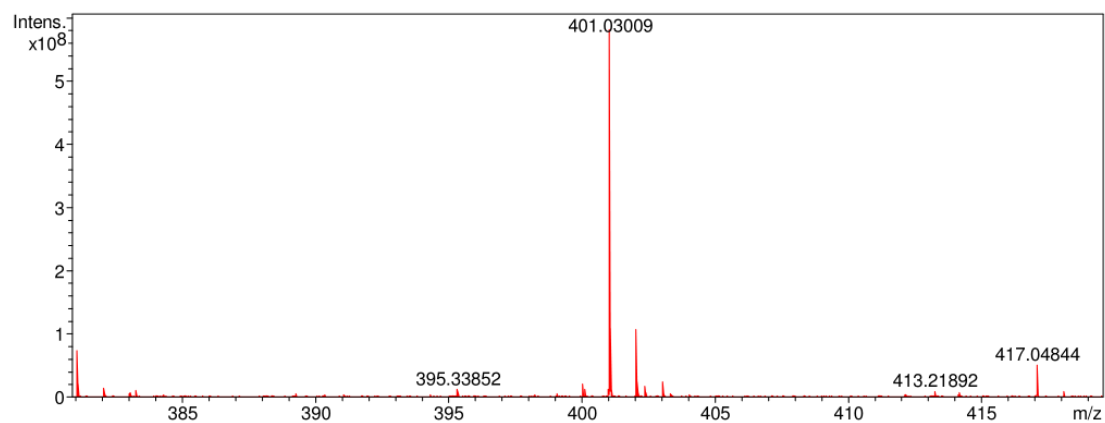


Figure S18 HRMS of 8f

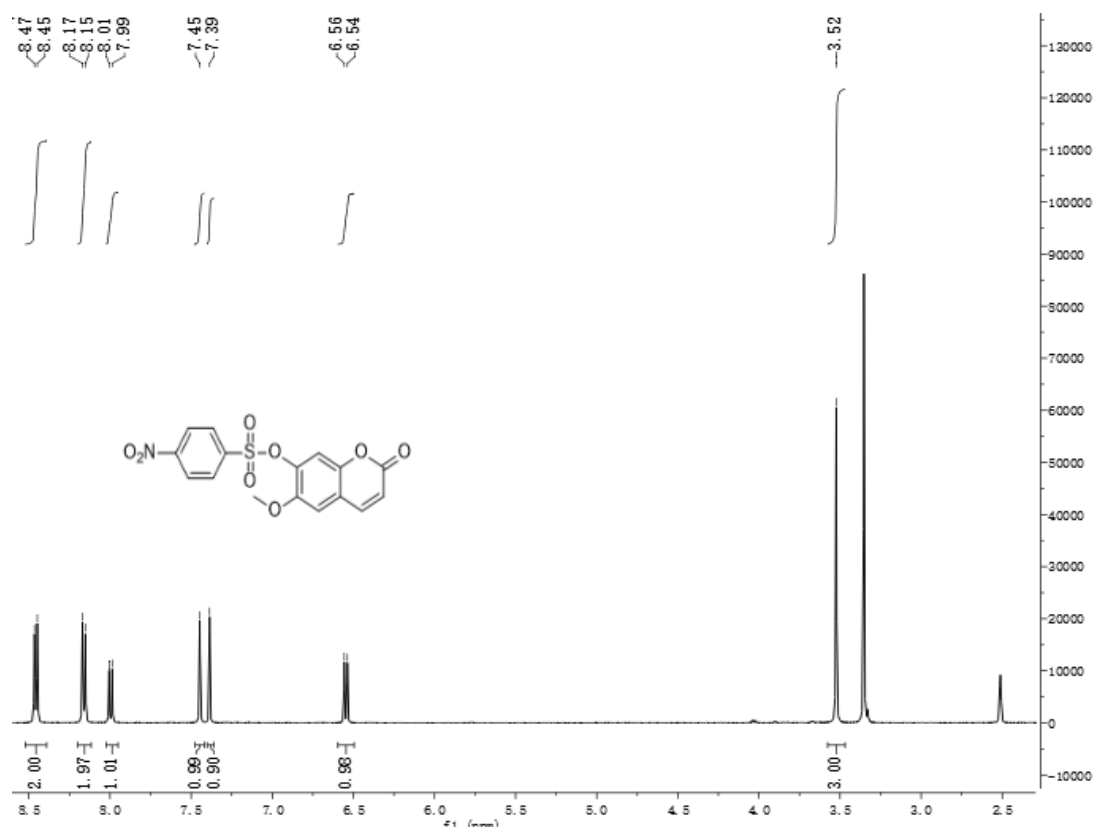


Figure S19 ^1H NMR of 8g

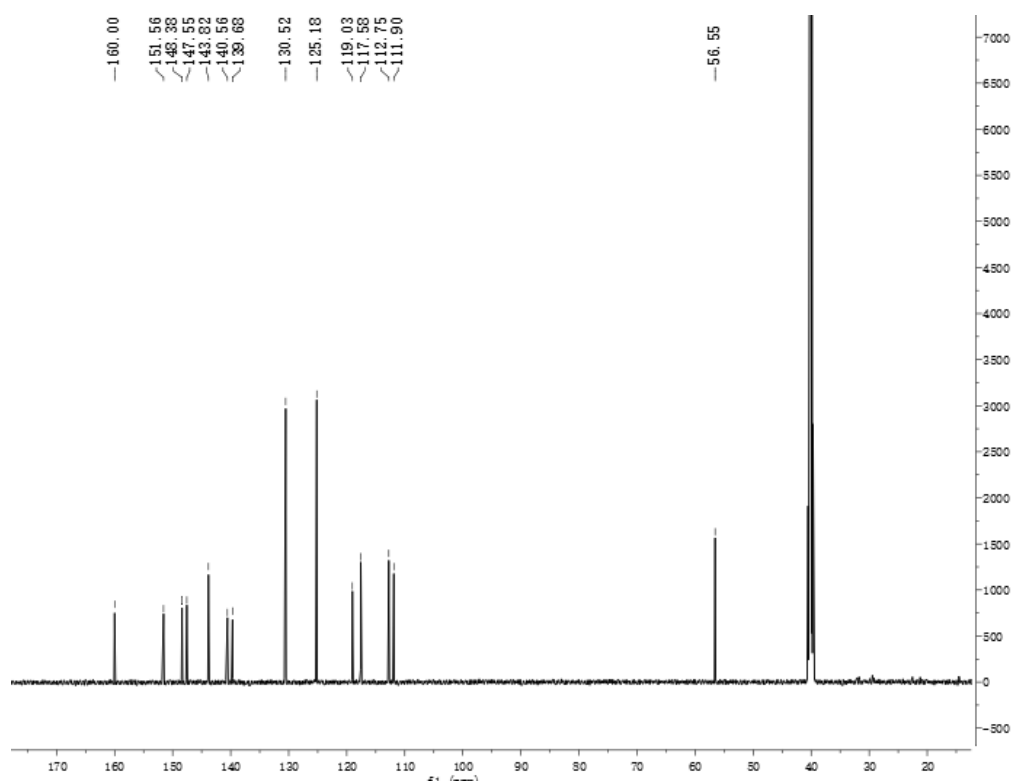


Figure S20 ^{13}C NMR of 8g

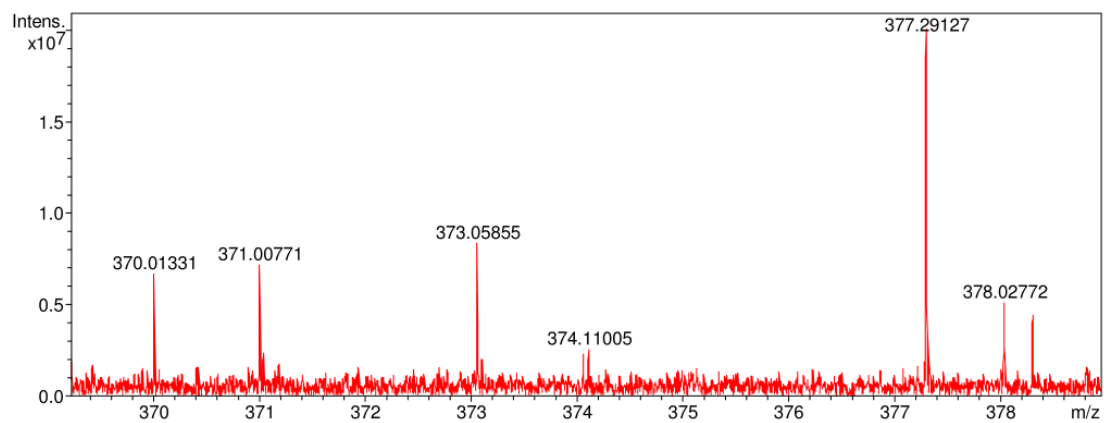


Figure S21 HRMS of 8g

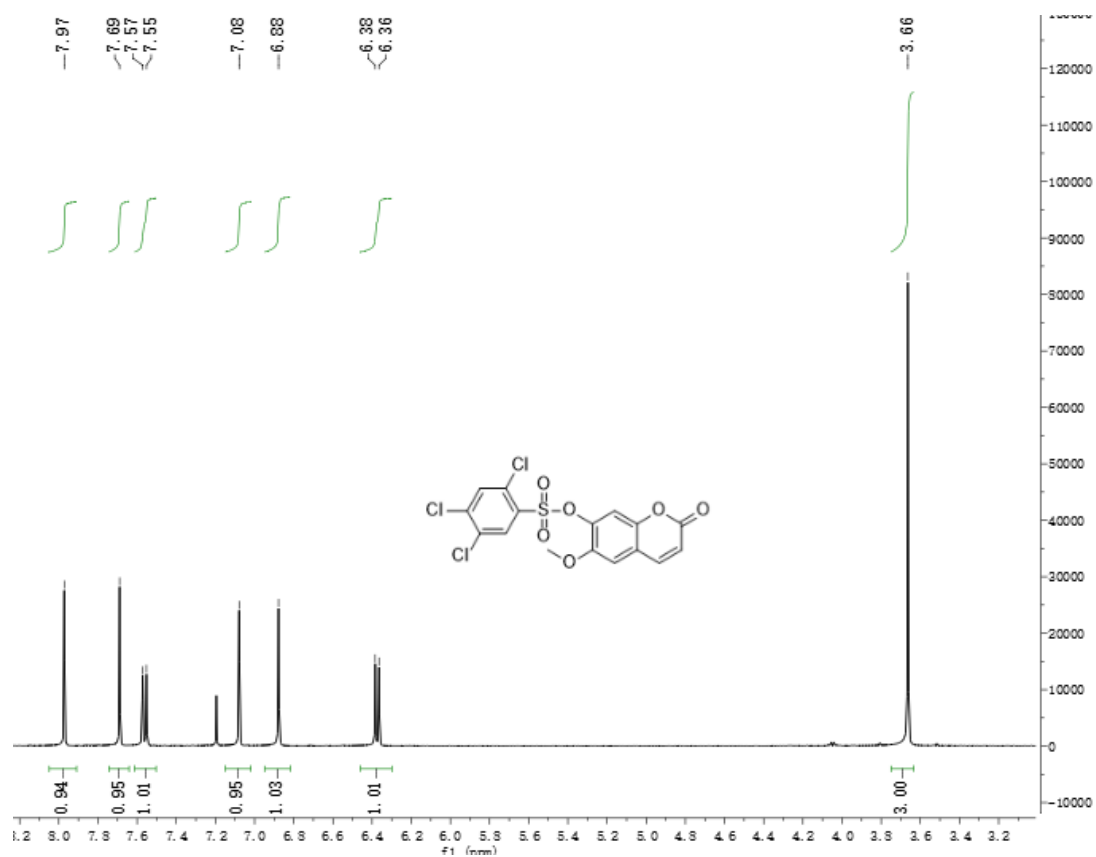


Figure S22 ^1H NMR of 8h

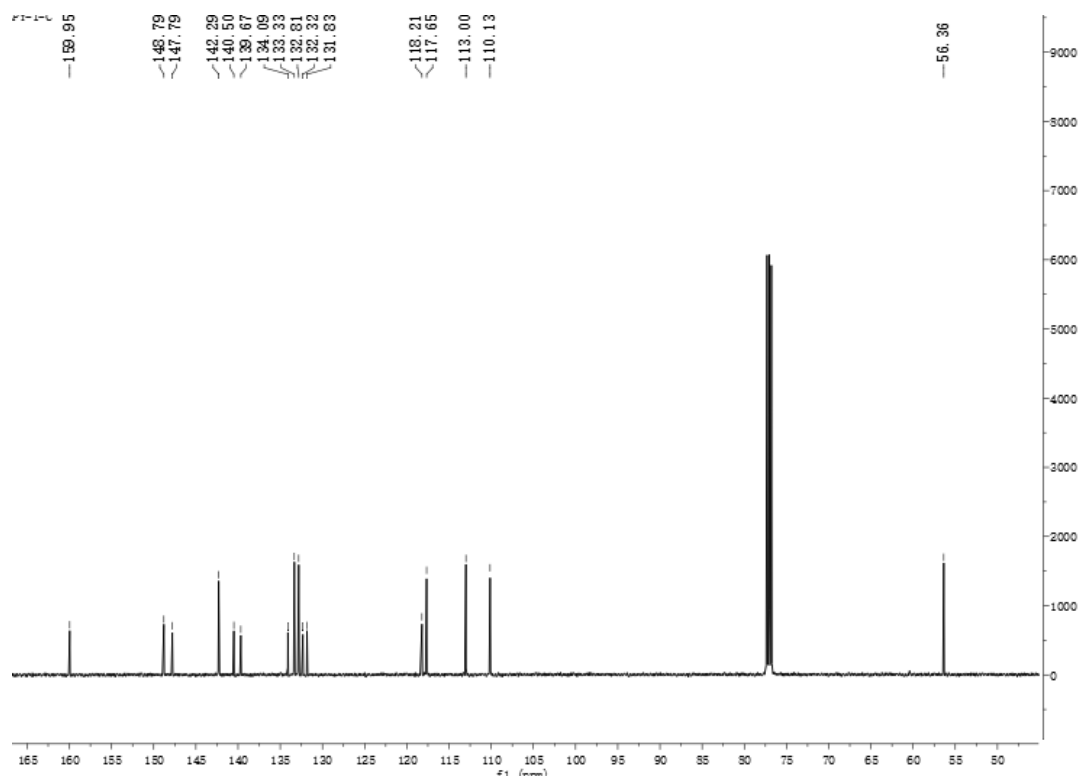


Figure S23 ¹³C NMR of 8h

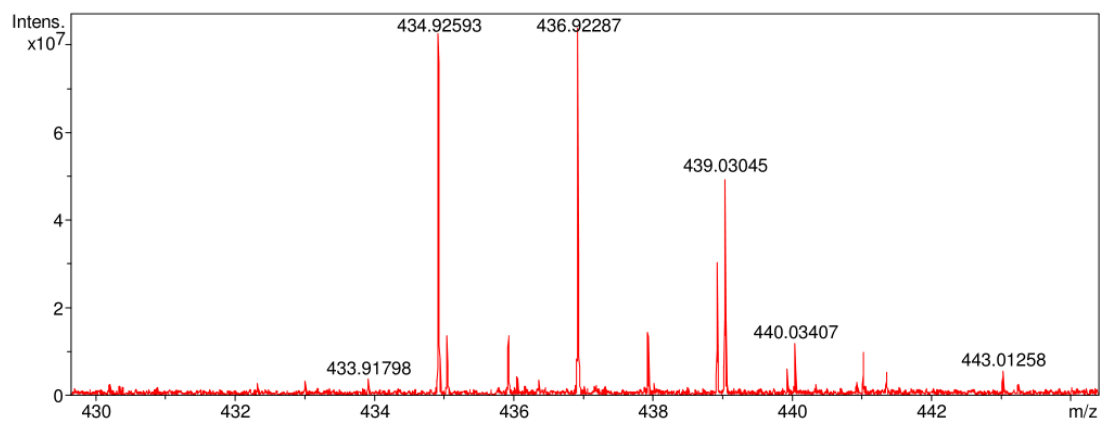


Figure S24 HRMS of 8h

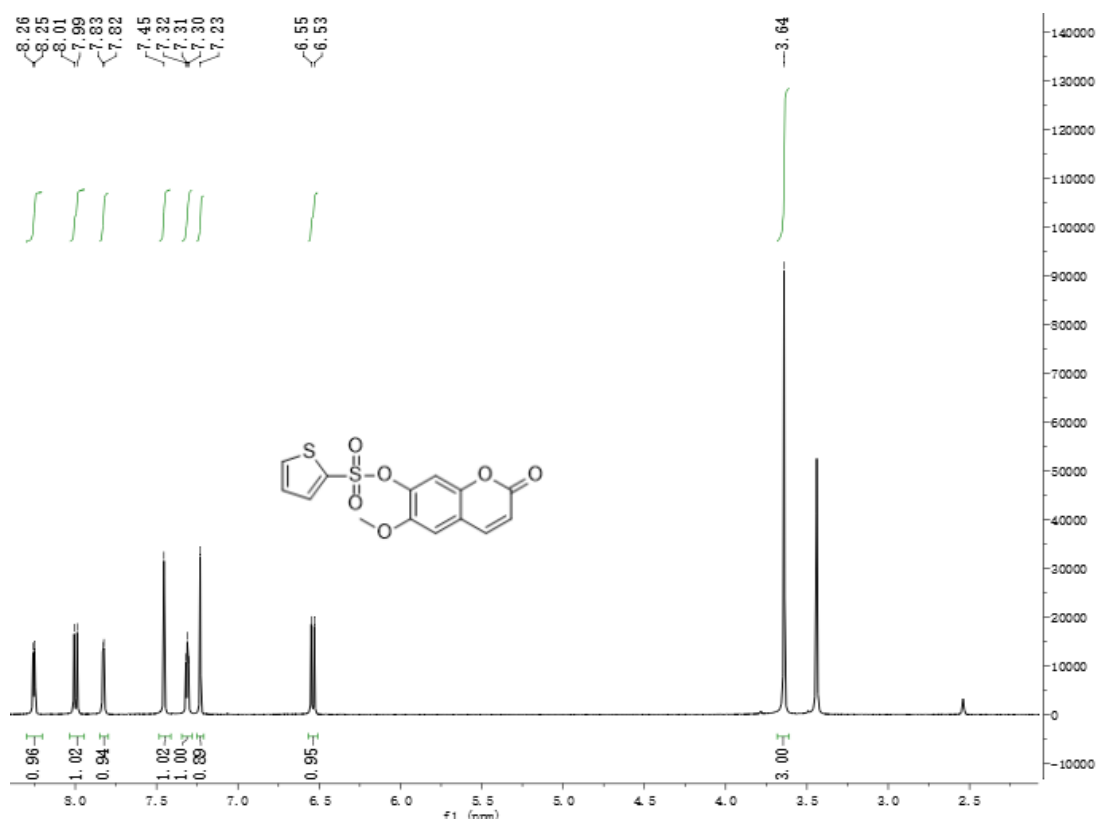


Figure S25 ^1H NMR of 8i

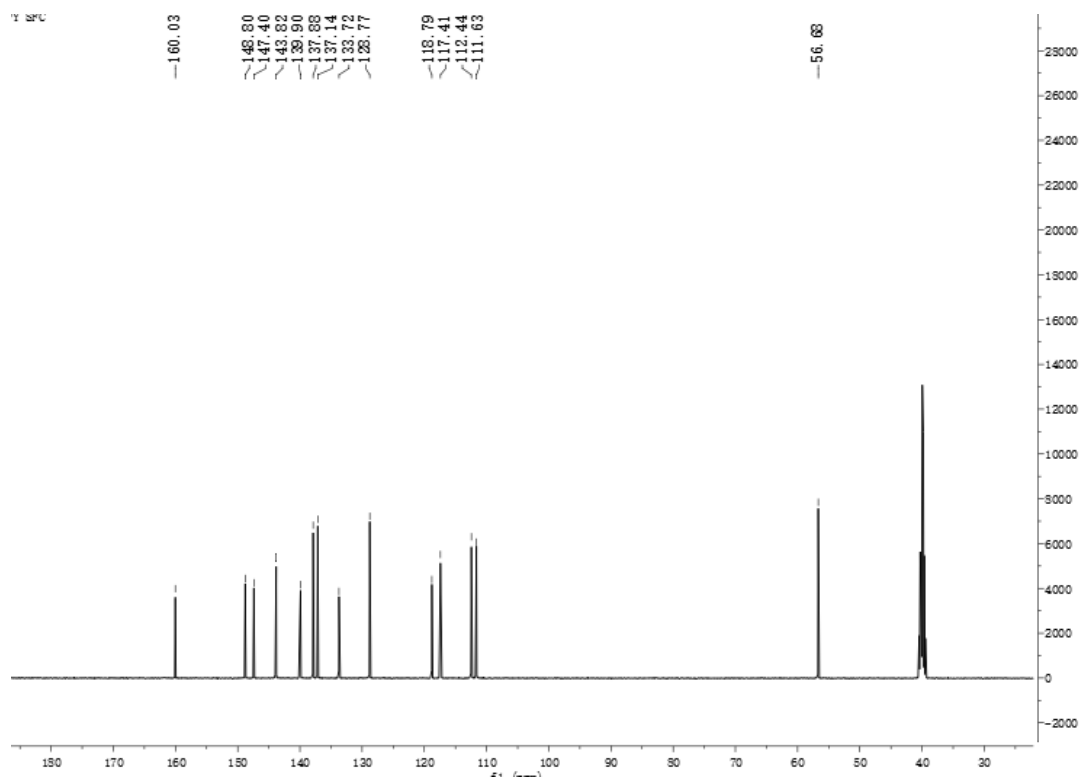


Figure S26 ^{13}C NMR of 8i

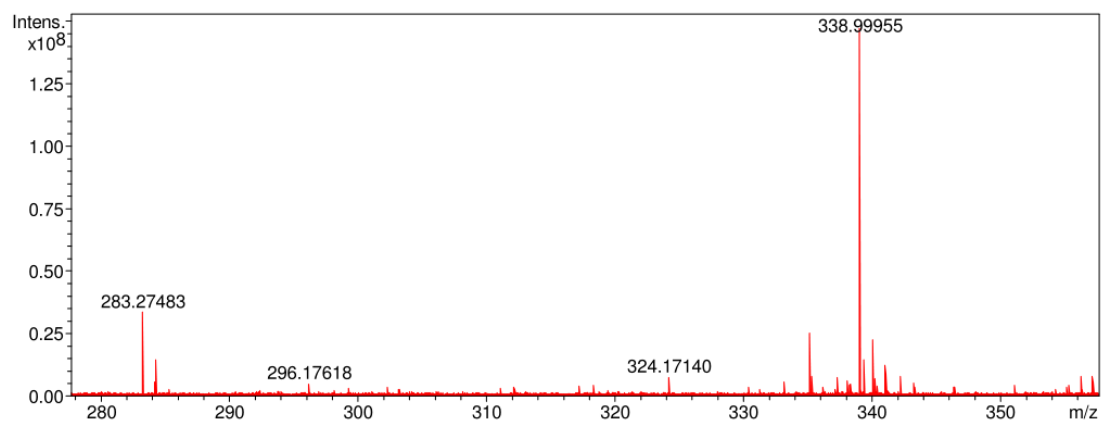


Figure S27 HRMS of 8i



Figure S28 ¹H NMR of 8j

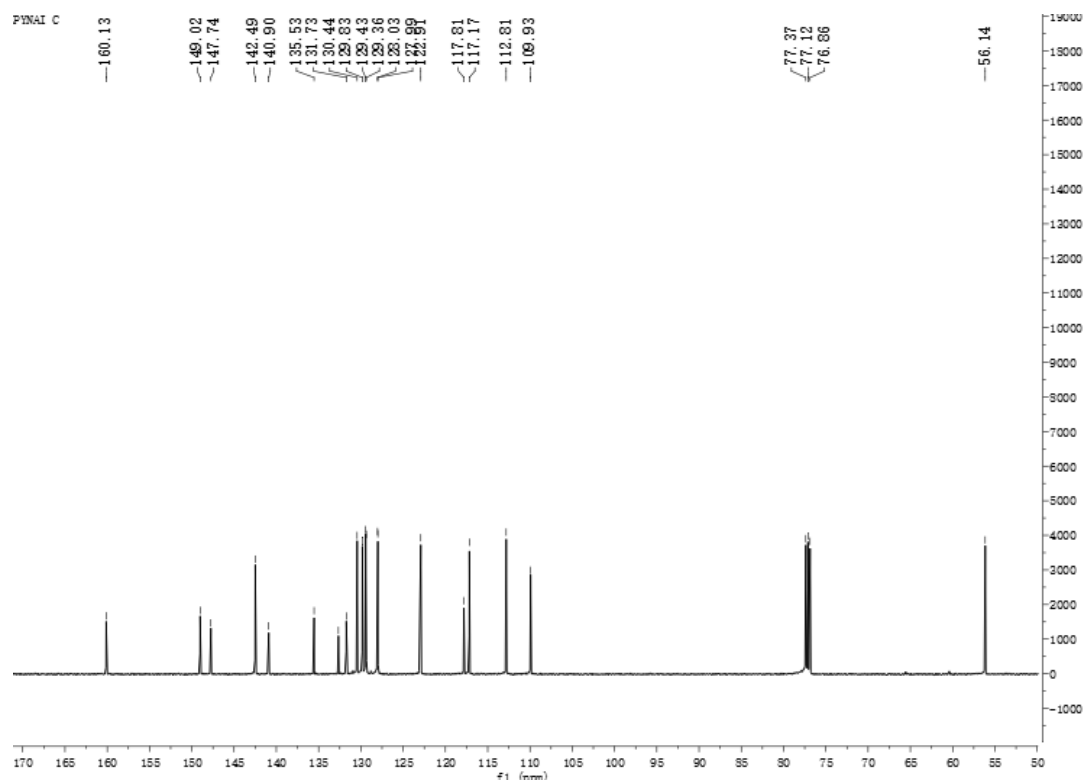


Figure S29 ^{13}C NMR of 8j

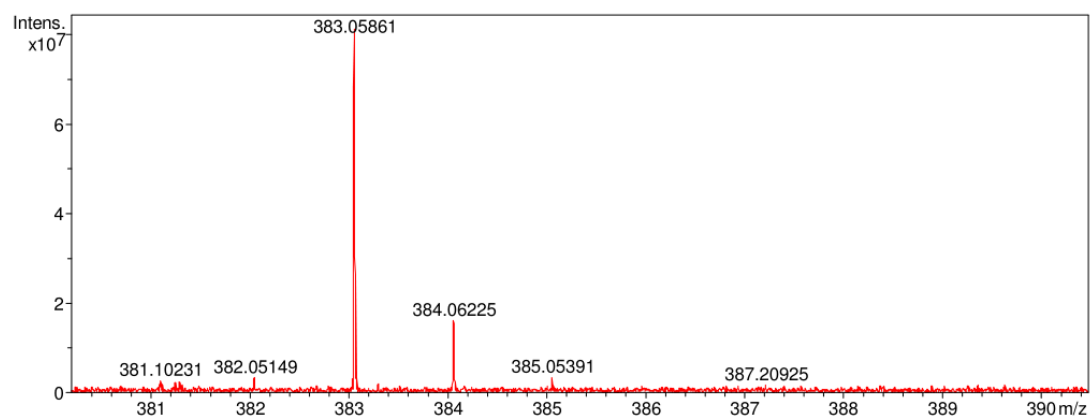


Figure S30 HRMS of 8j

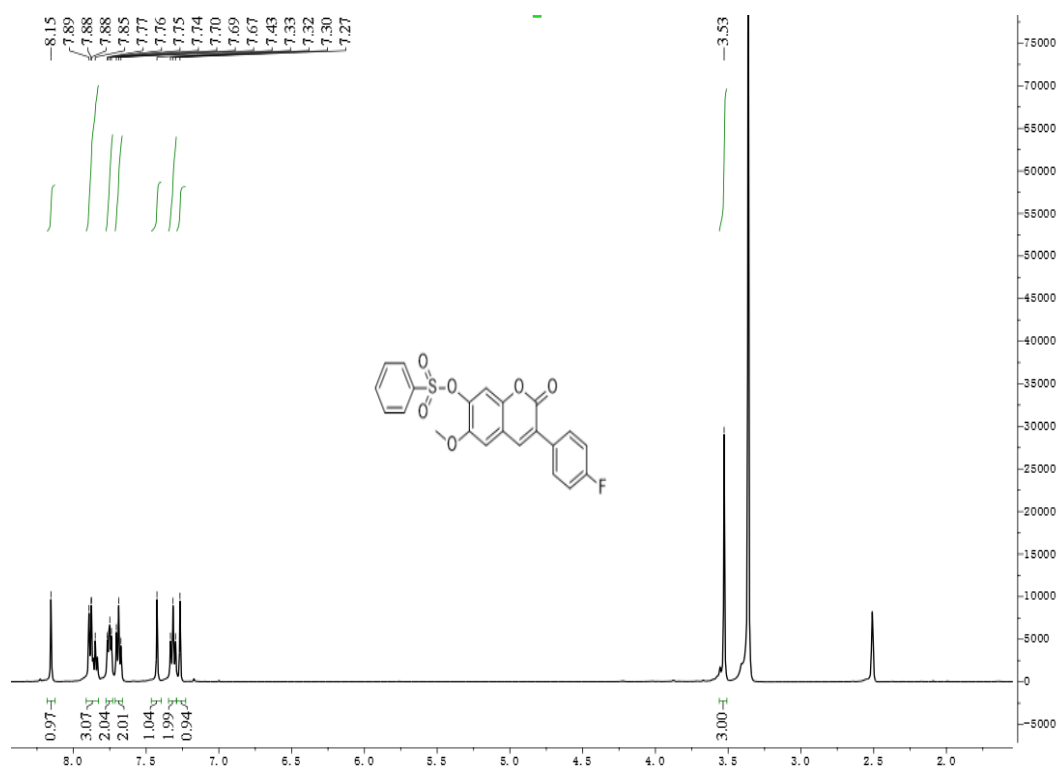


Figure S31 ^1H NMR of 9a

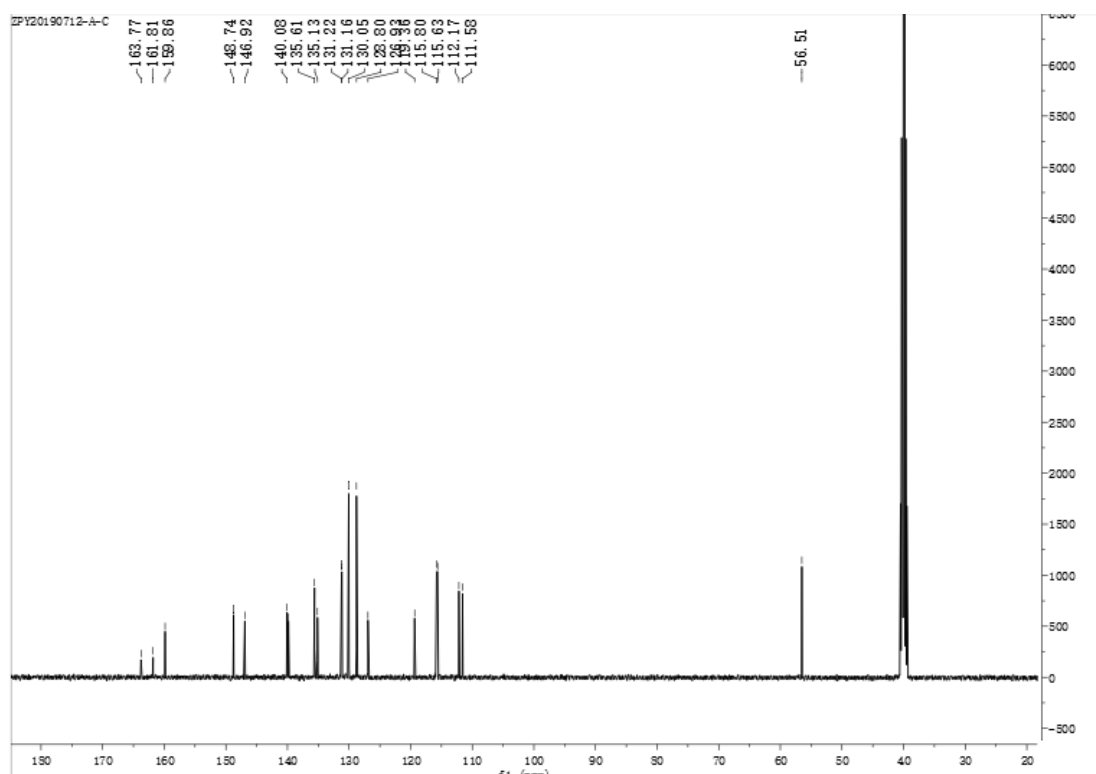


Figure S32 ^{13}C NMR of 9a

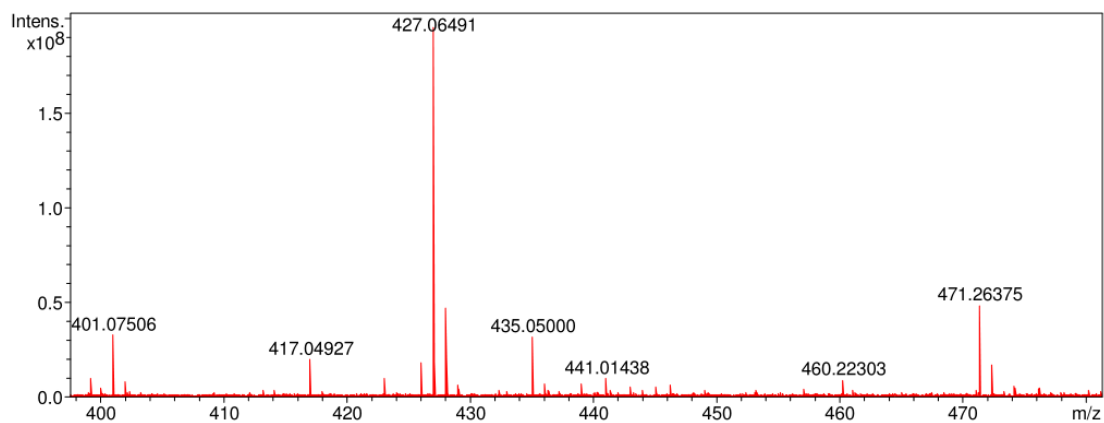


Figure S33 HRMS of 9a

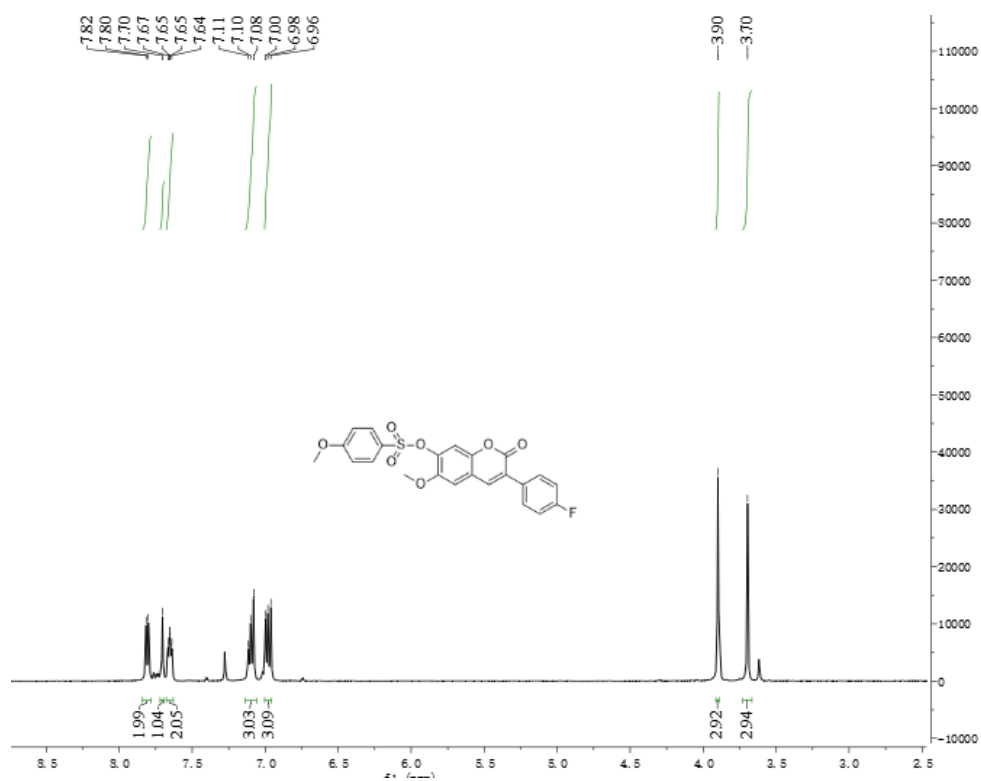


Figure S34 ¹H NMR of 9b

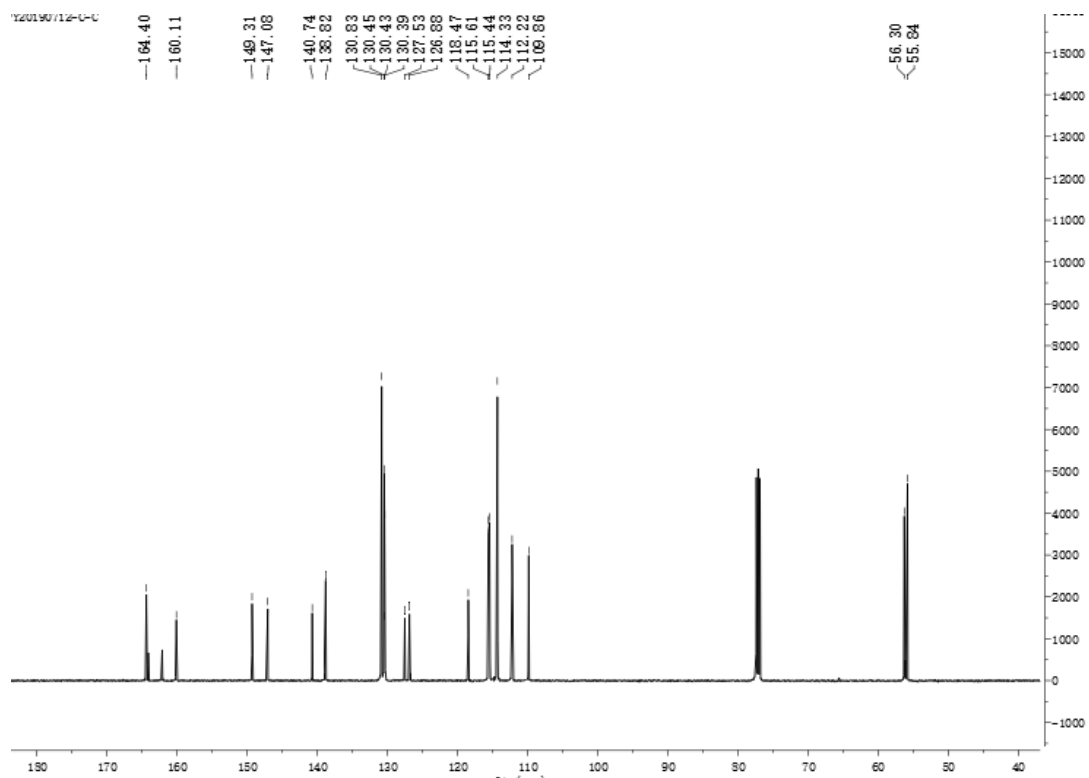


Figure S35 ¹³C NMR of 9b

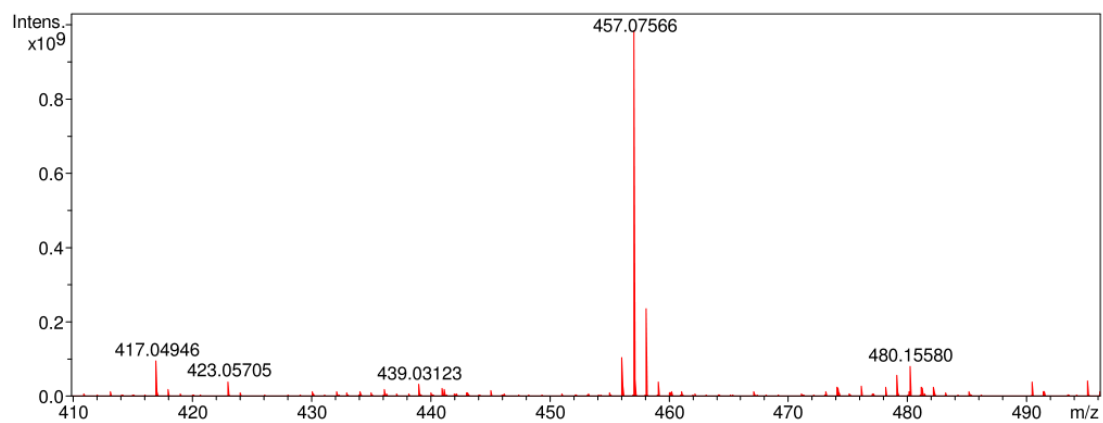


Figure S36 HRMS of 9b

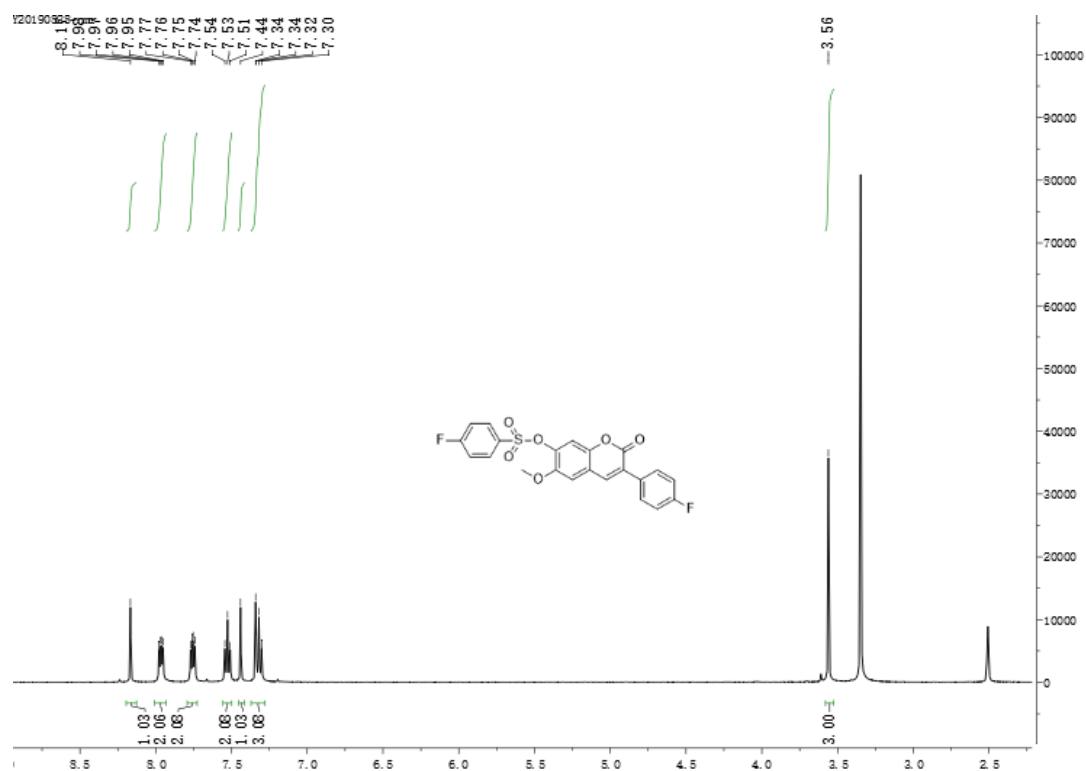


Figure S37 ¹H NMR of 9c

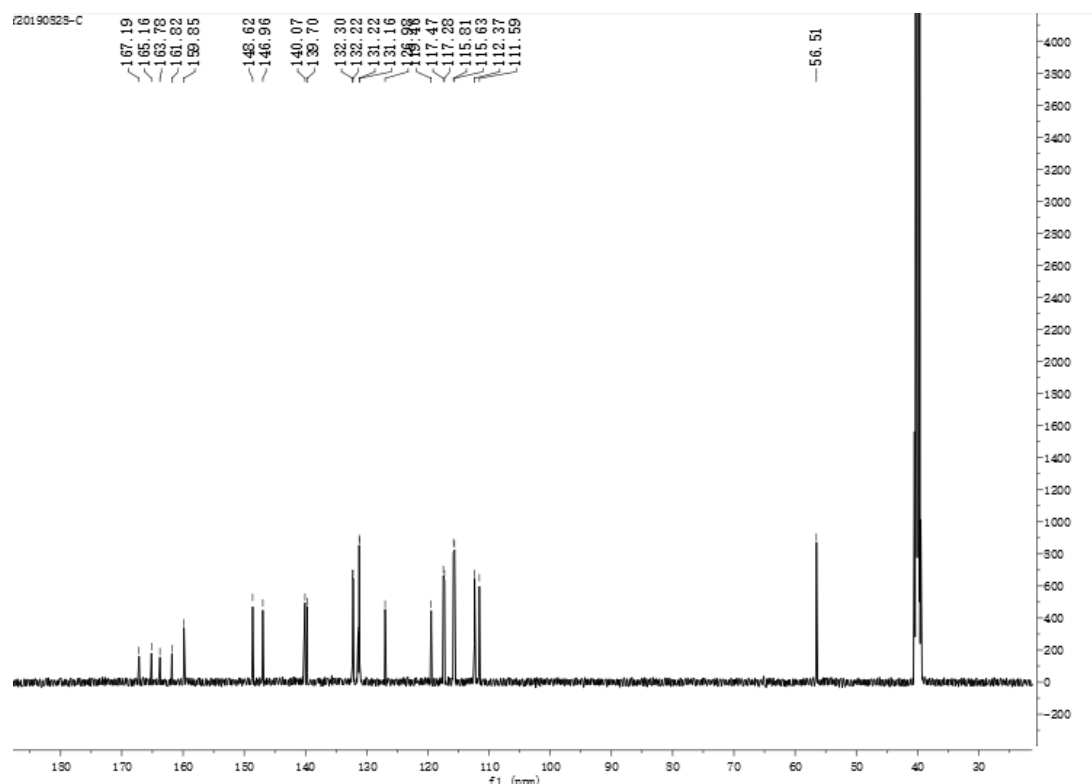


Figure S38 ¹³C NMR of 9c

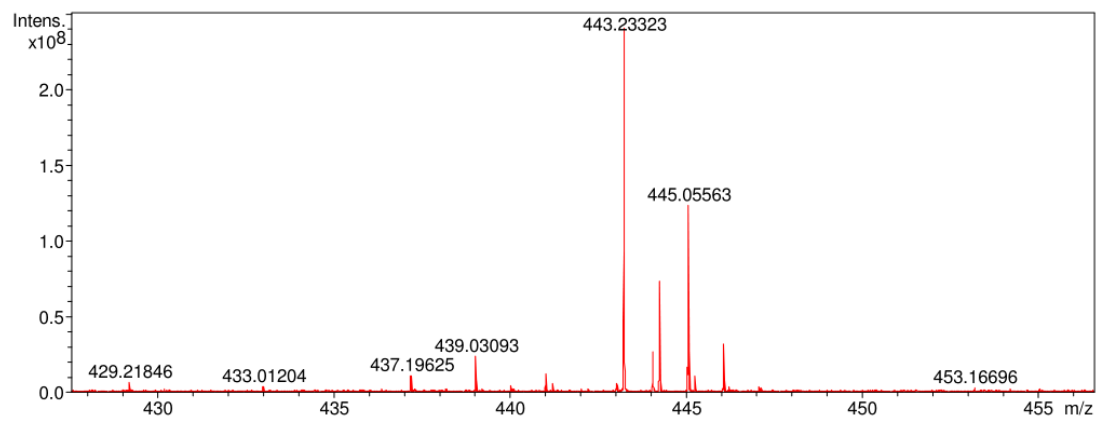


Figure S39 HRMS of 9c

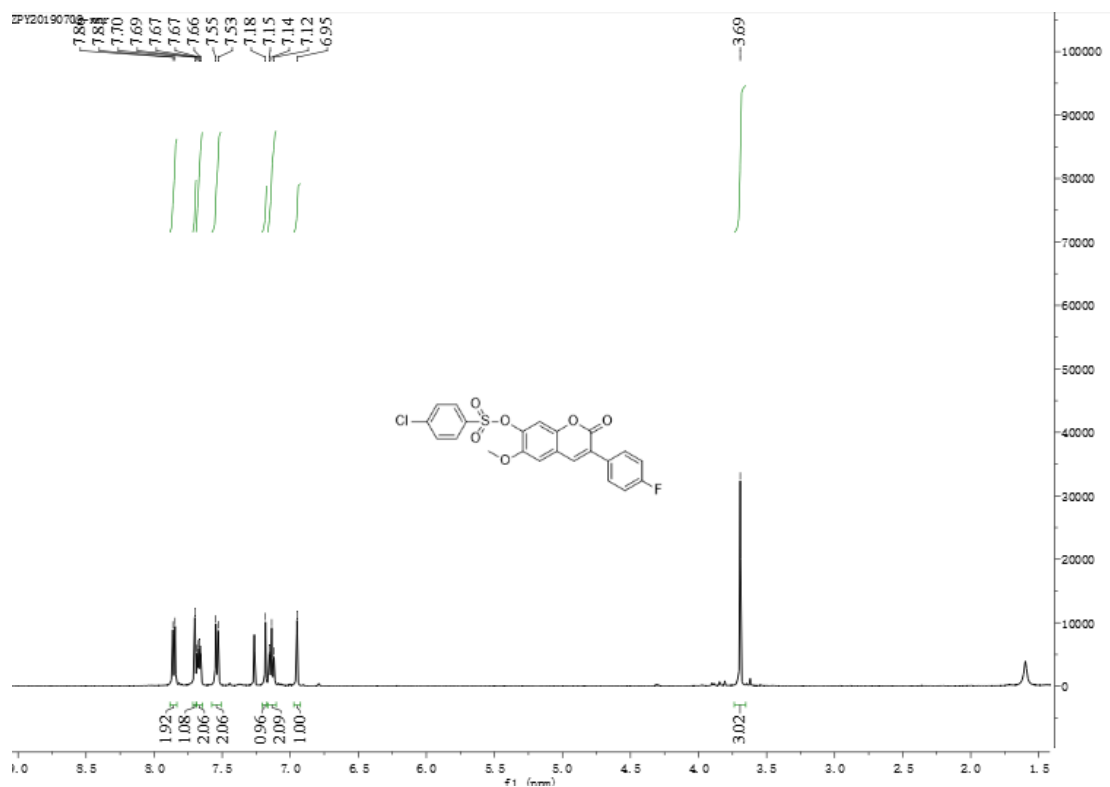


Figure S40 ^1H NMR of 9d

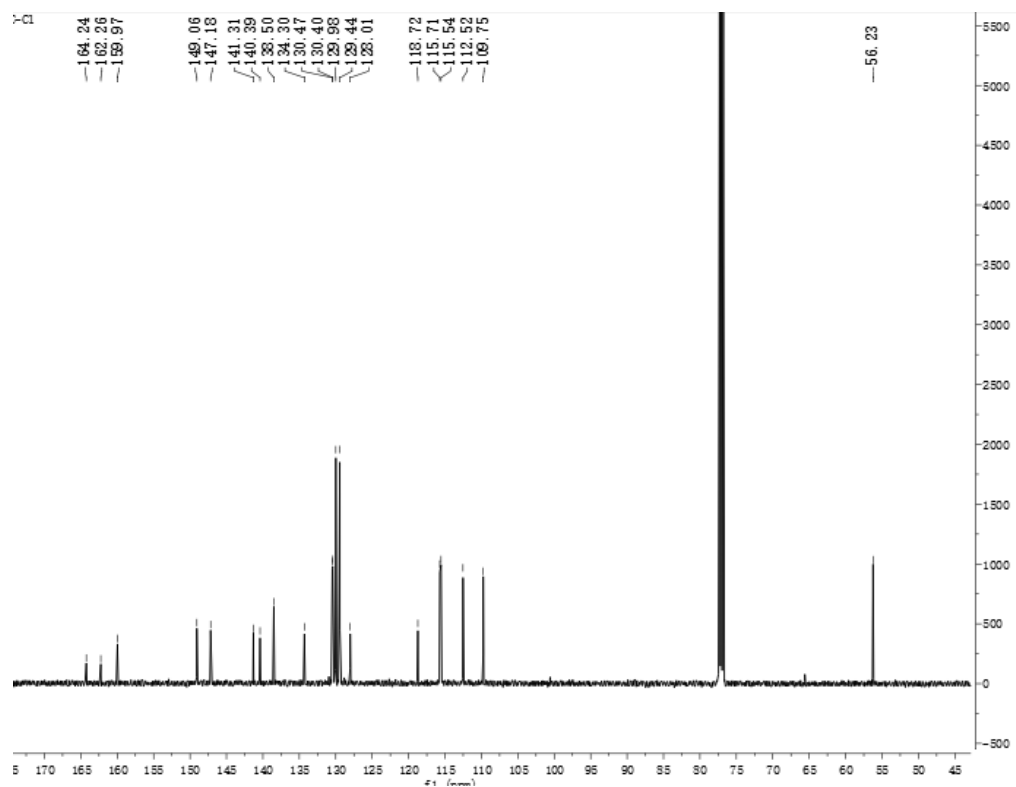


Figure S41 ^{13}C NMR of 9d

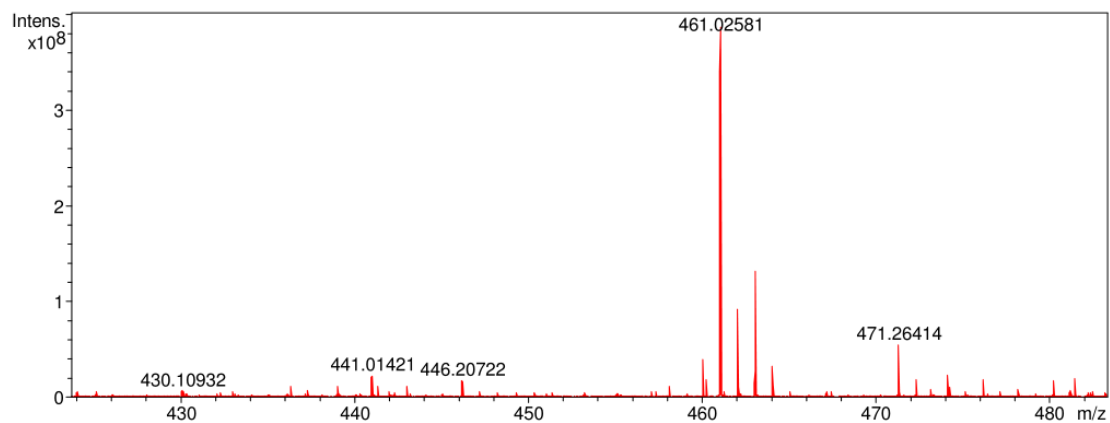


Figure S42 HRMS of 9d

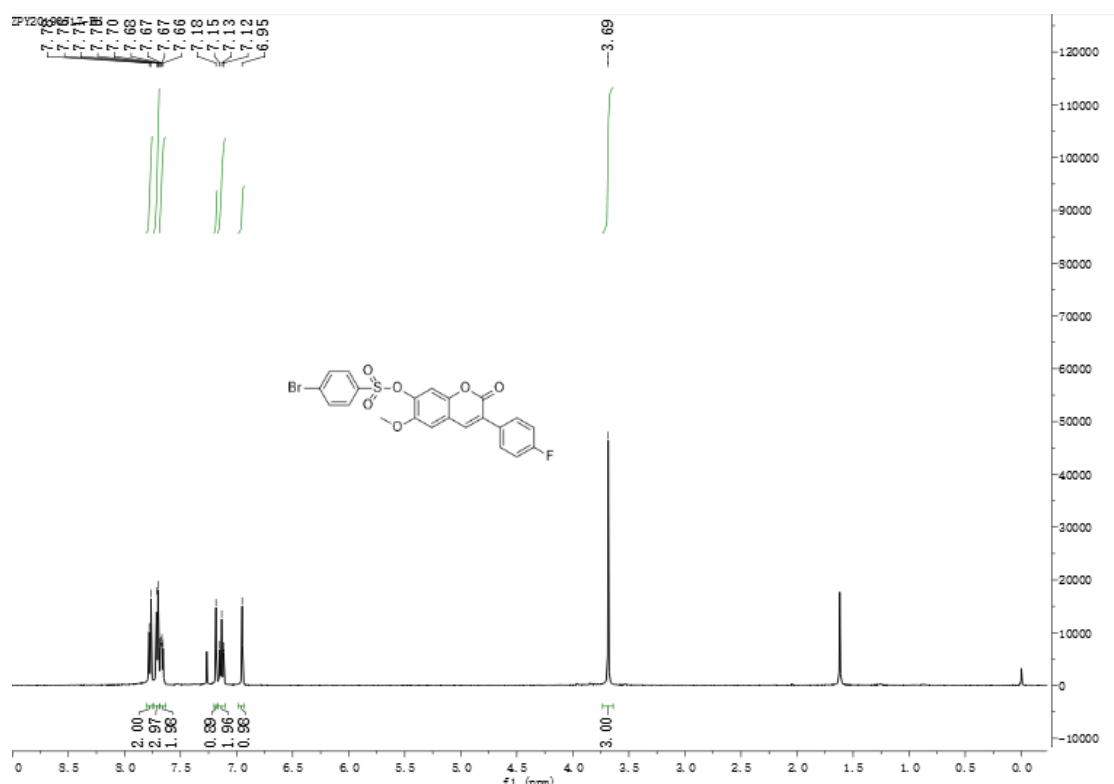


Figure S43 ¹H NMR of 9e

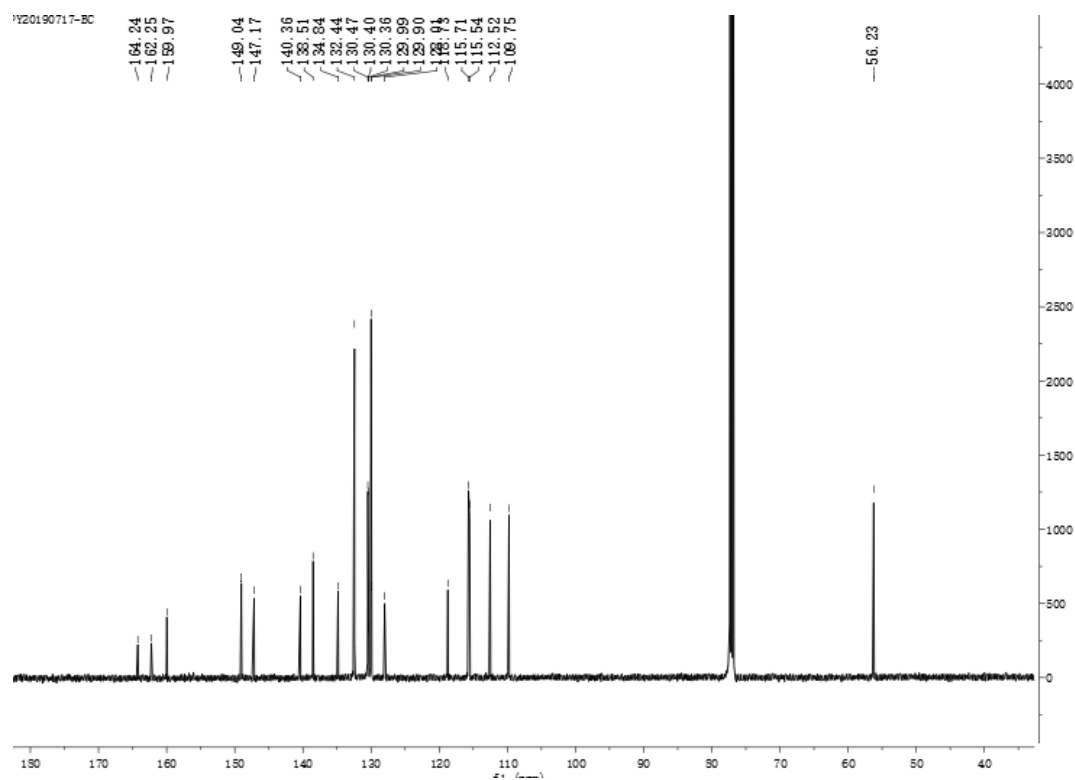


Figure S44 ¹³C NMR of 9e

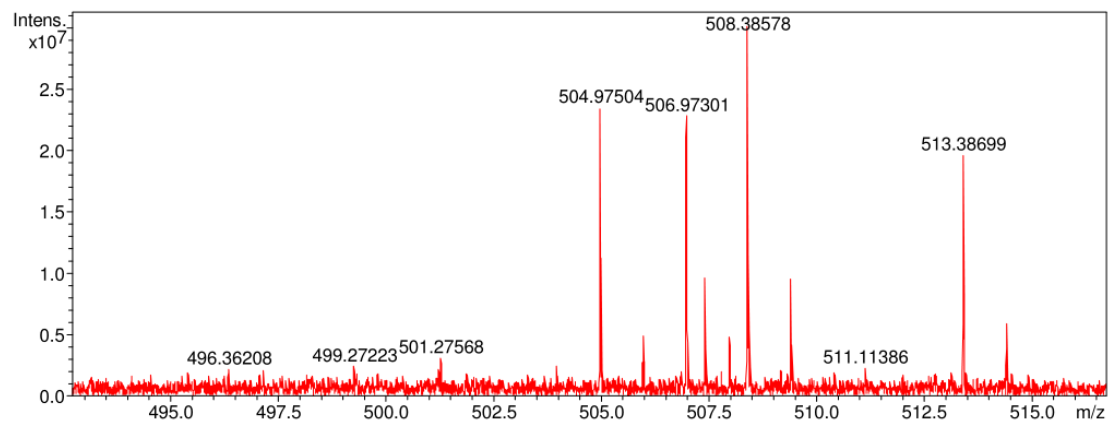


Figure S45 HRMS of 9e

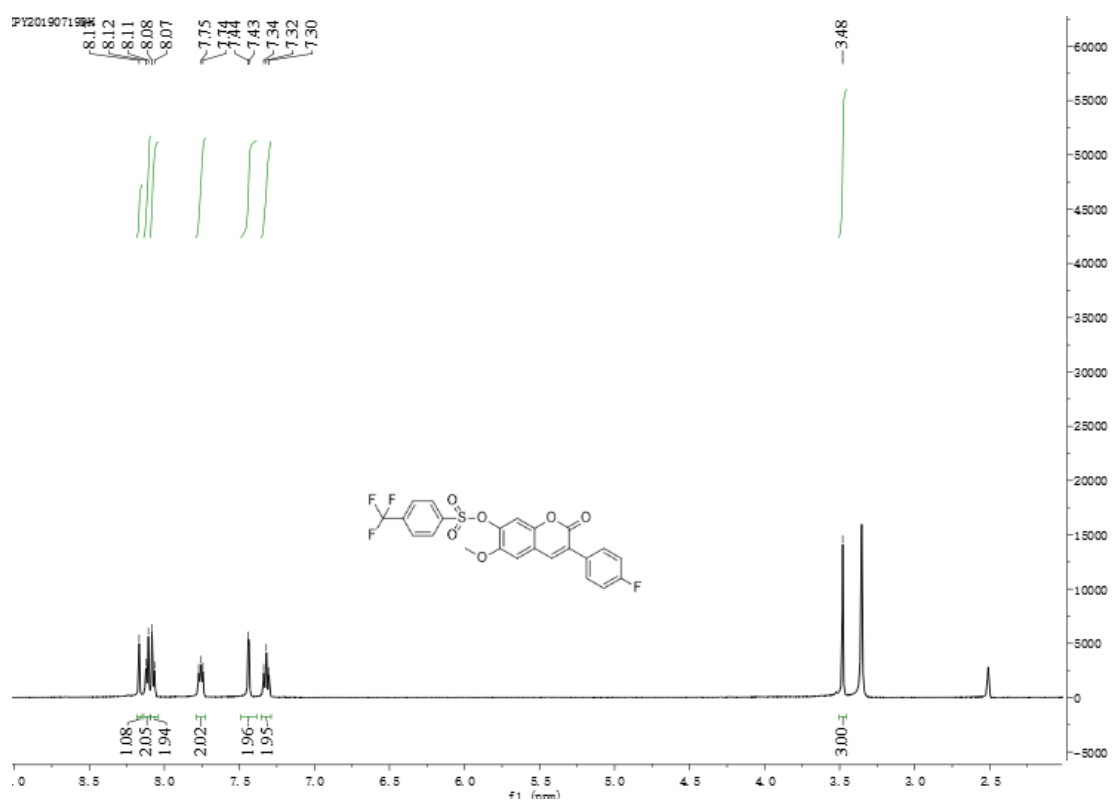


Figure S46 ^1H NMR of 9f

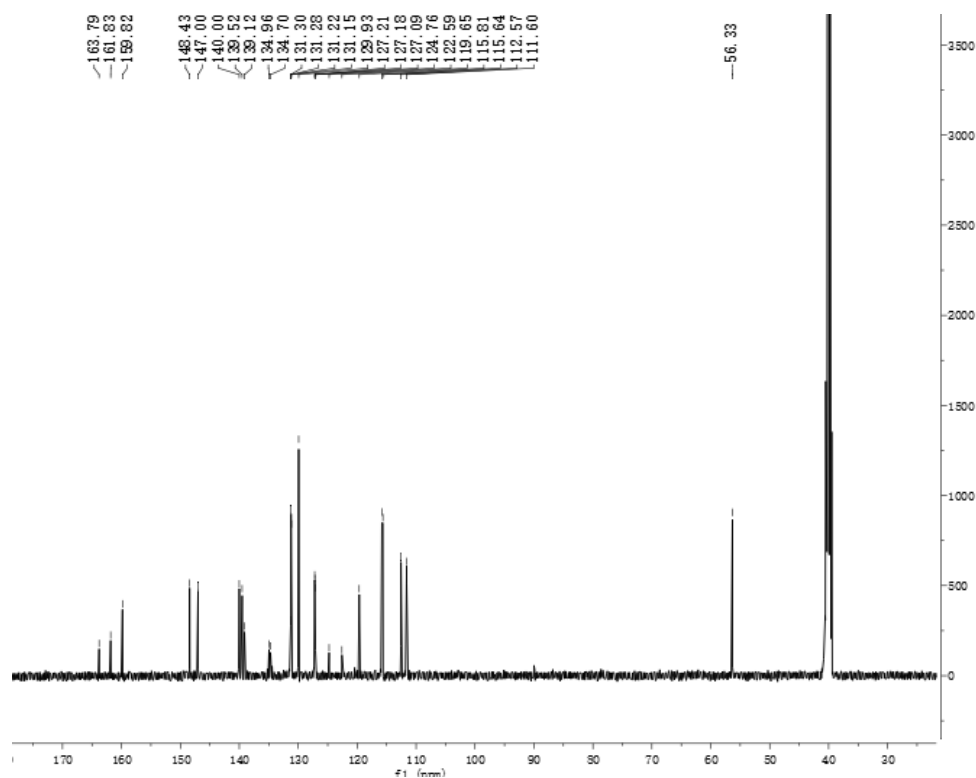


Figure S47 ^{13}C NMR of 9f

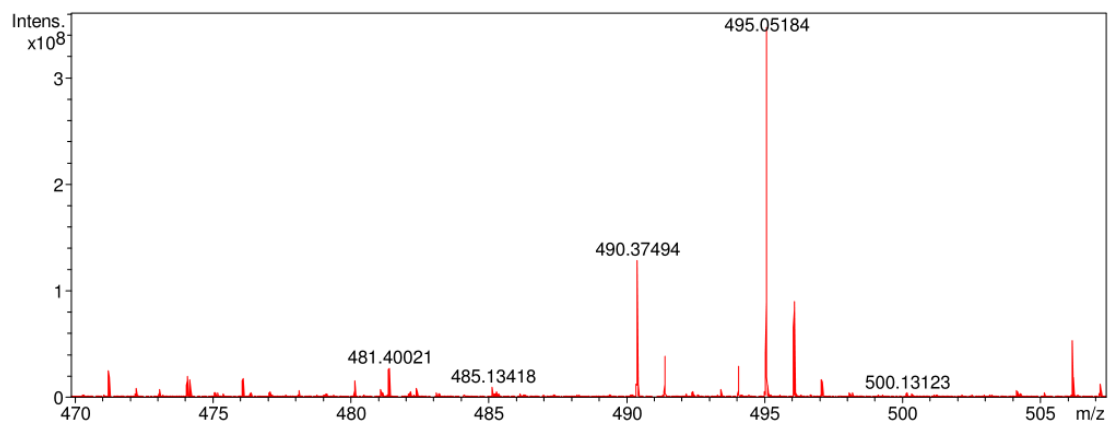


Figure S48 HRMS of 9f

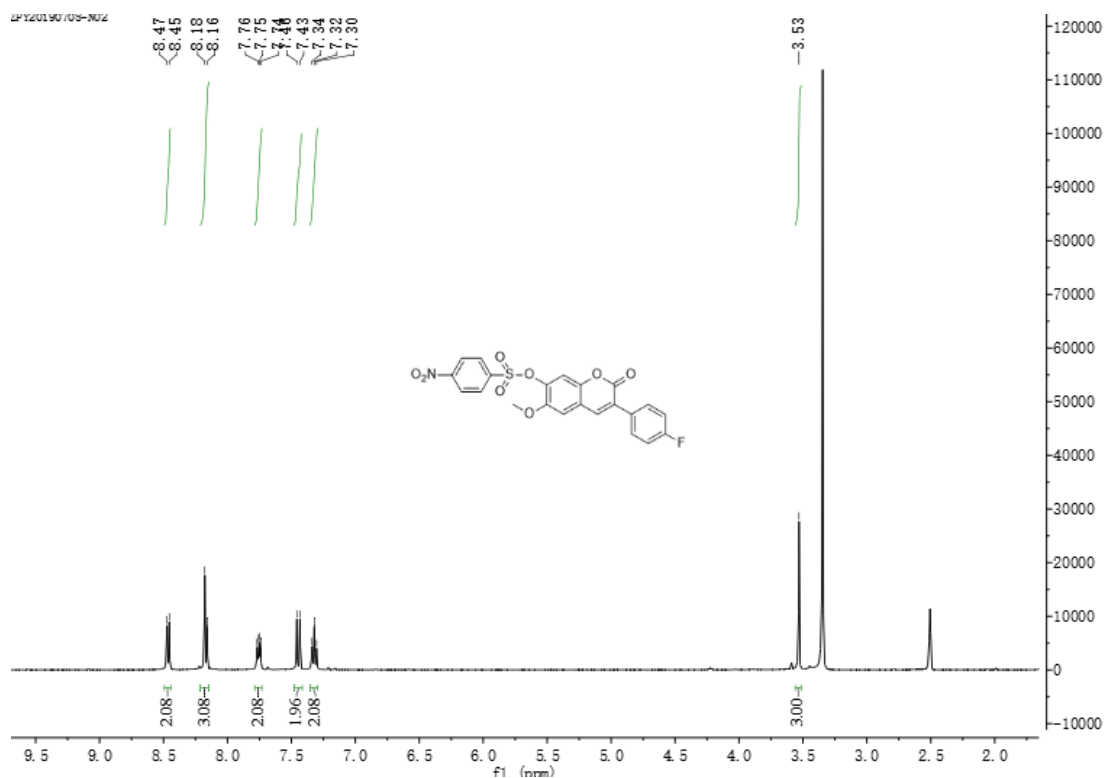


Figure S49 ^1H NMR of 9g

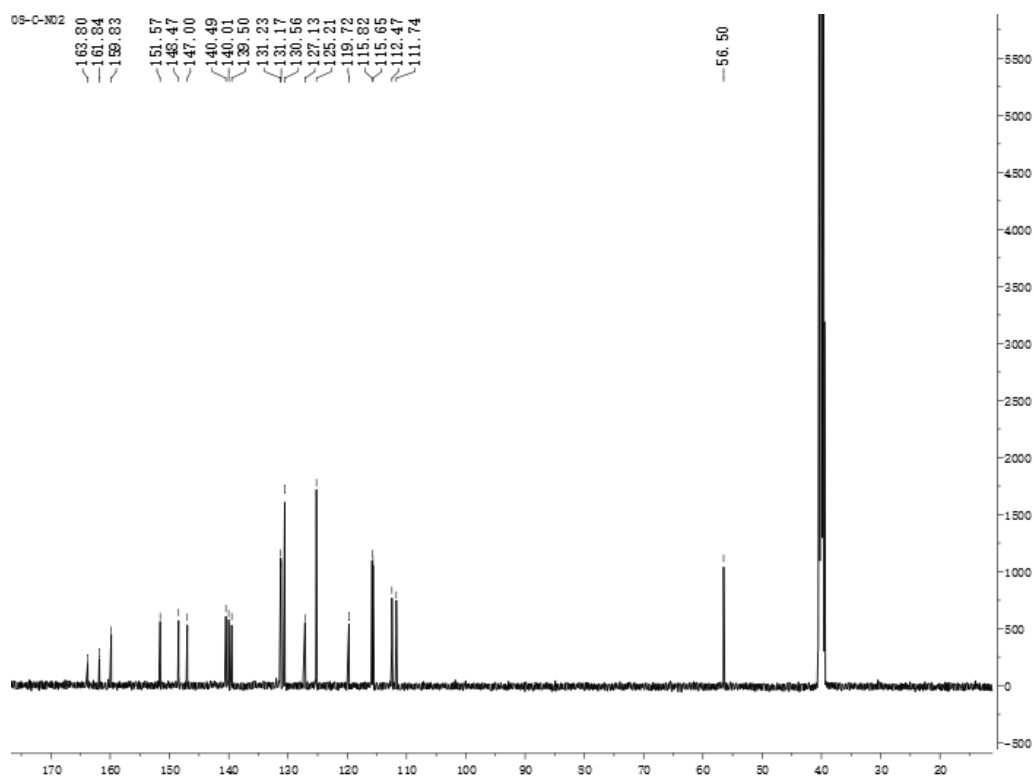


Figure S50 ^{13}C NMR of 9g

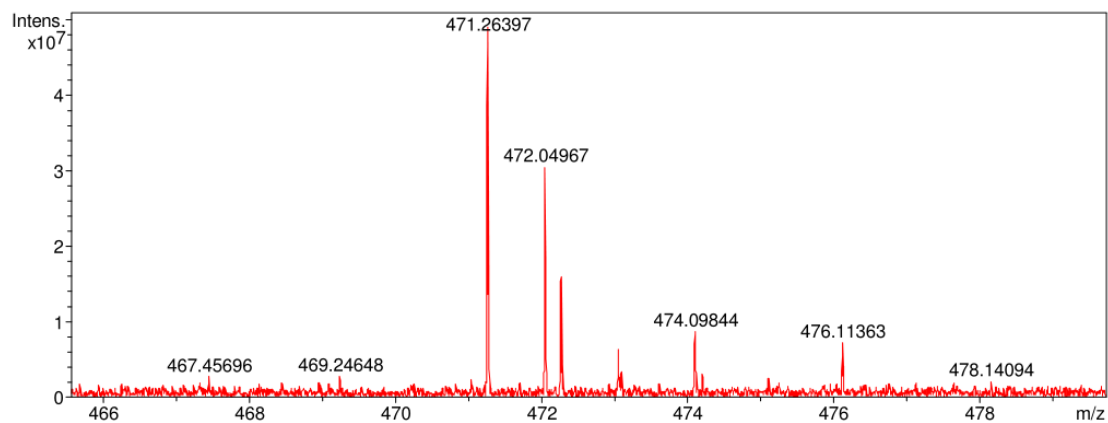


Figure S51 HRMS of 9g

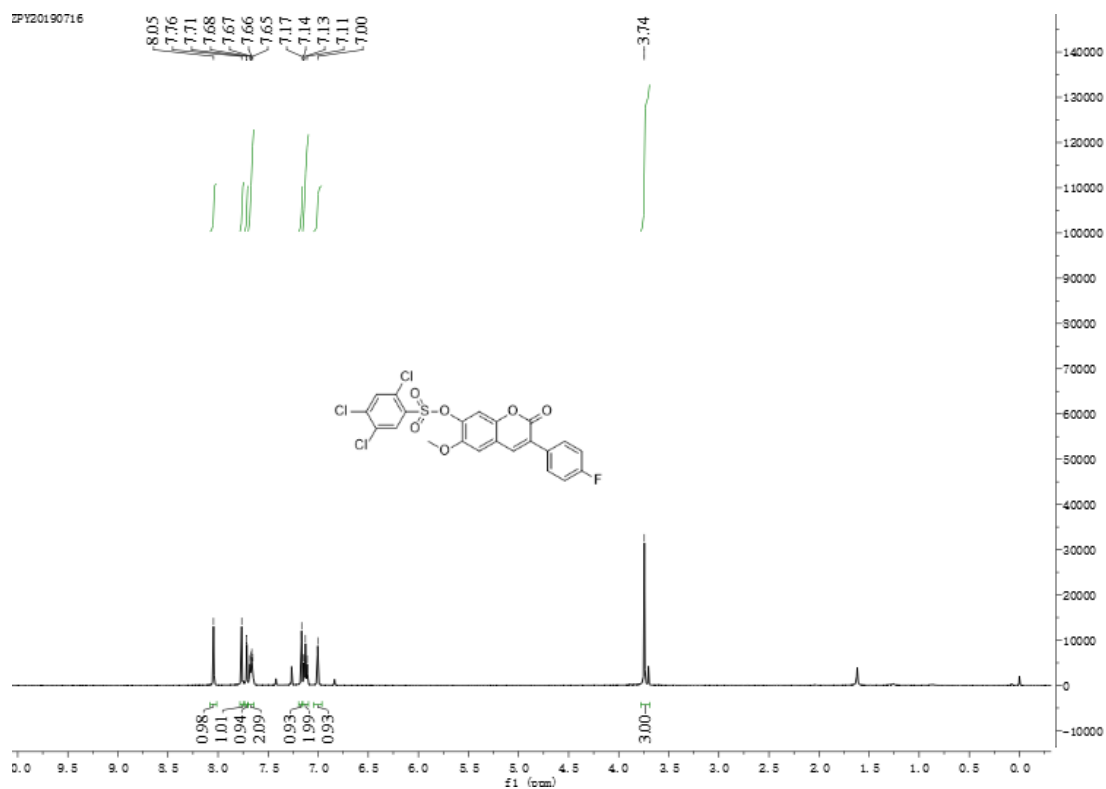


Figure S52 ¹H NMR of 9h

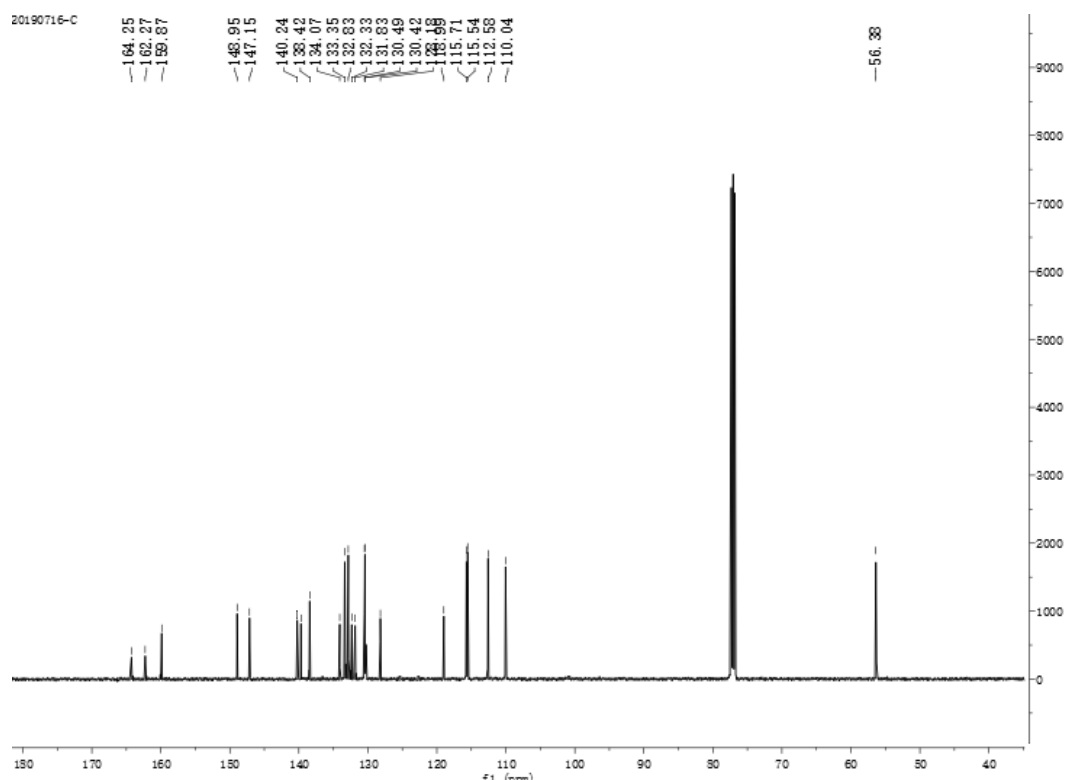


Figure S53 ^{13}C NMR of 9h

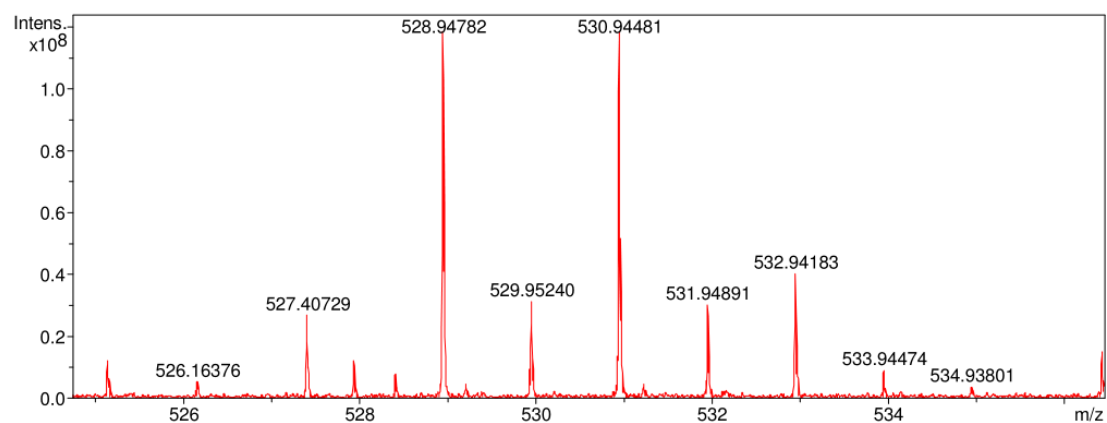


Figure S54 HRMS of 9h

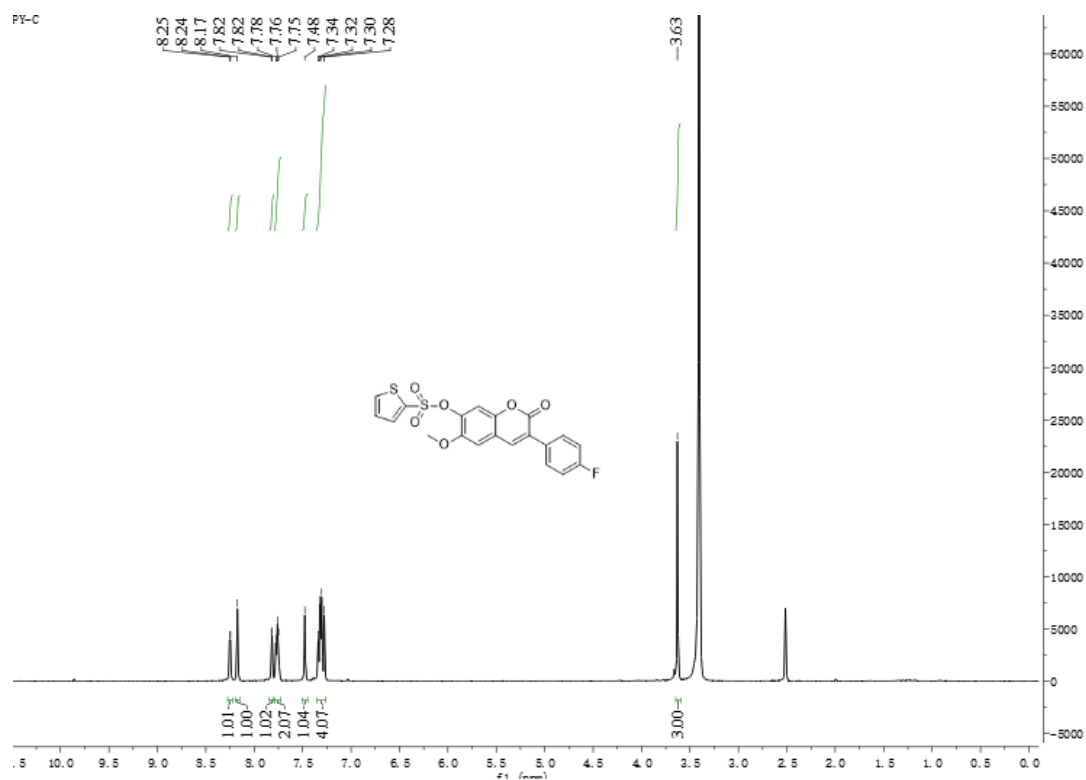


Figure S55 ^1H NMR of 9i

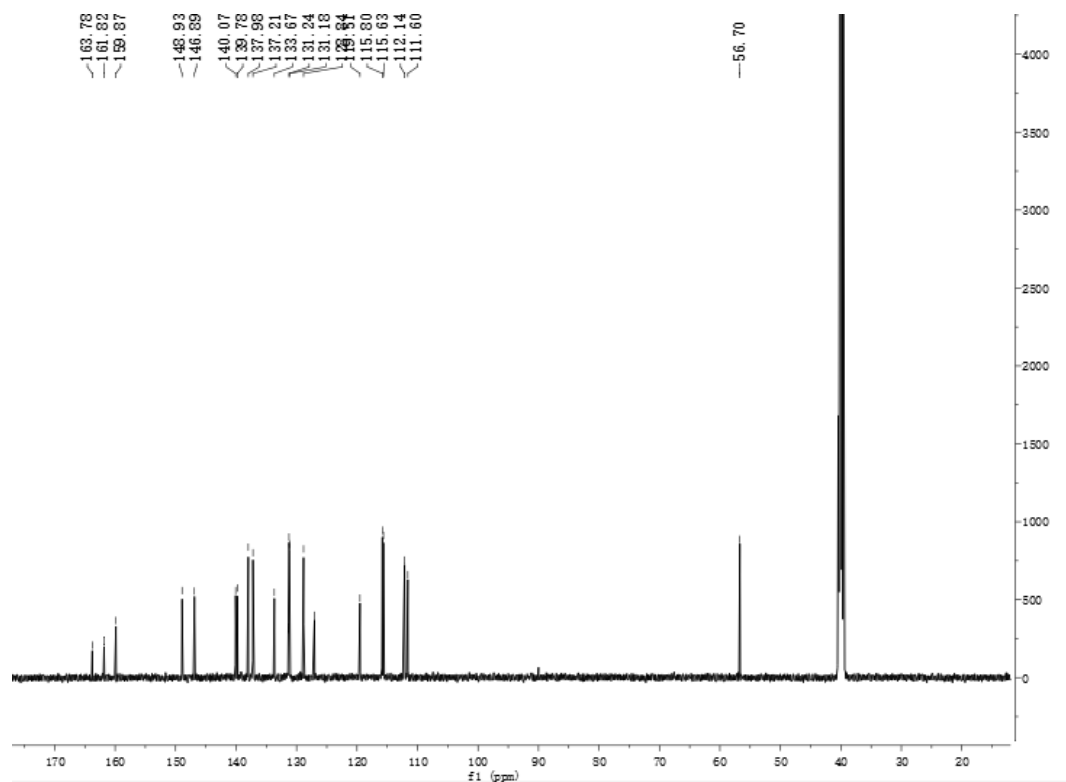


Figure S56 ^{13}C NMR of 9i

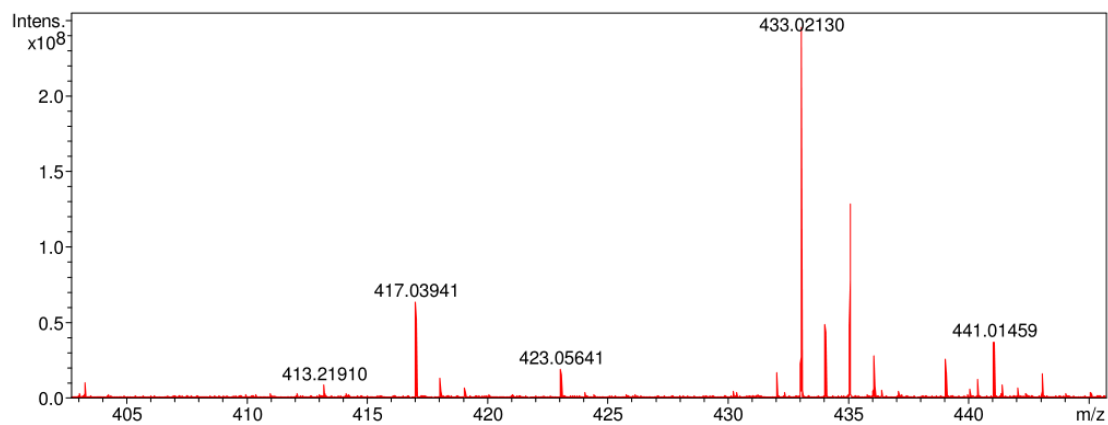


Figure S57 HRMS of 9i

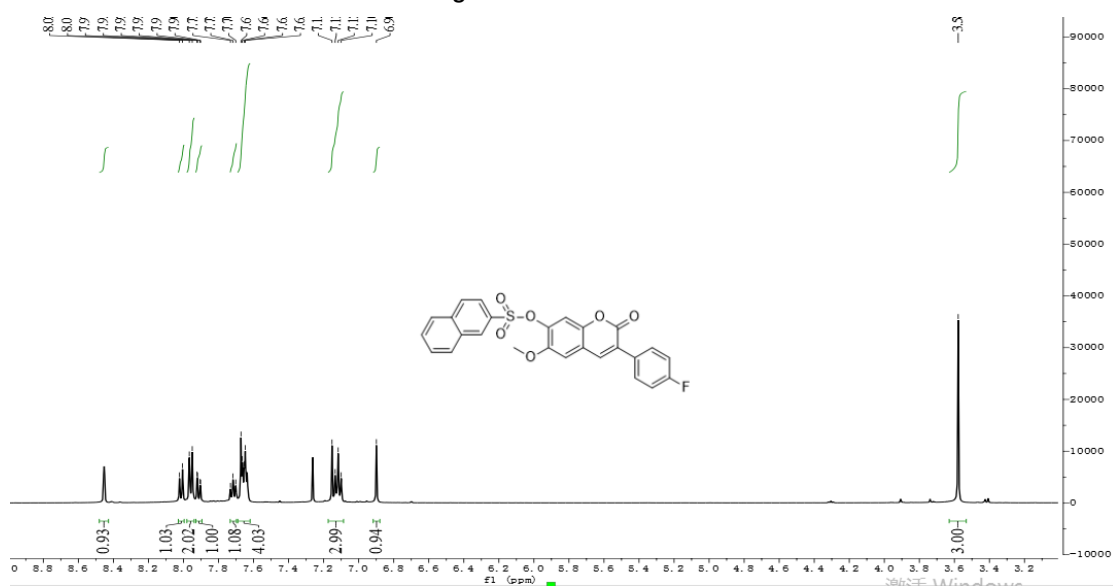


Figure S58 ^1H NMR of 9j

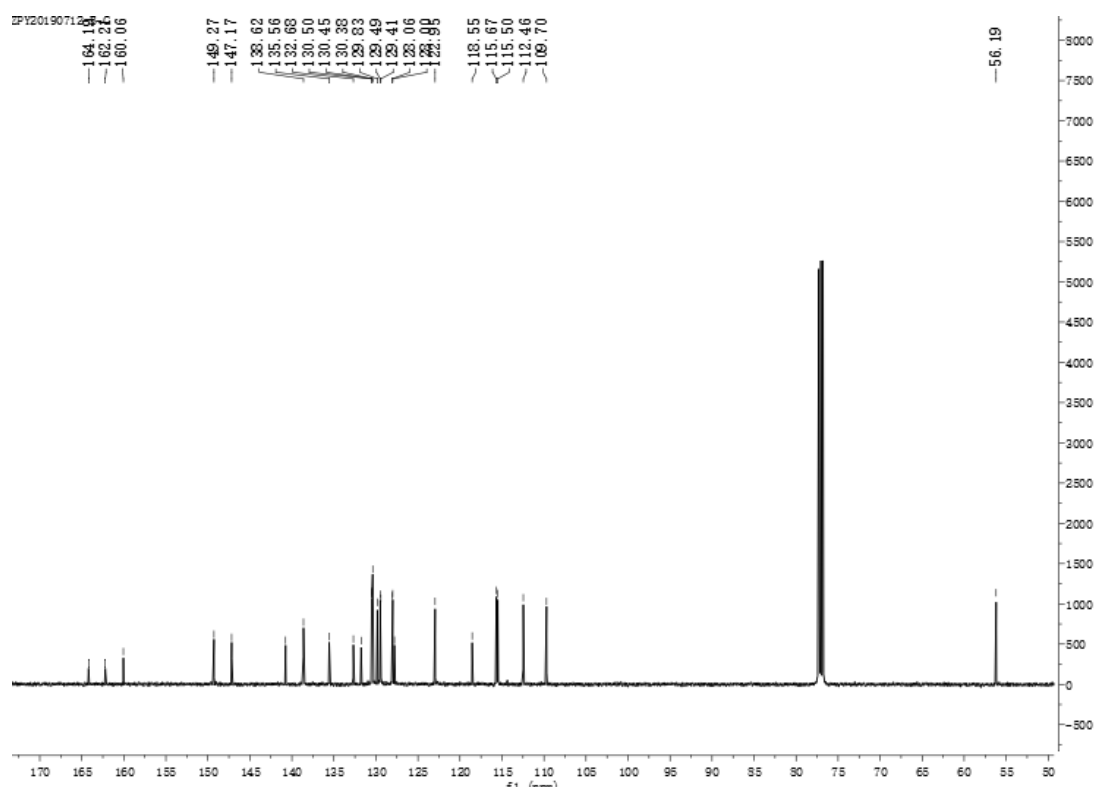


Figure S59 ^{13}C NMR of 9j

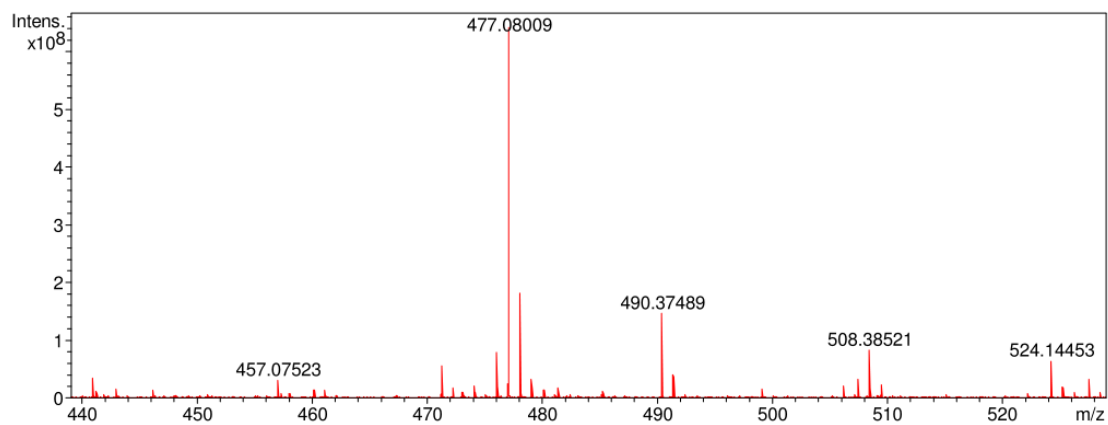


Figure S60 HRMS of 9j

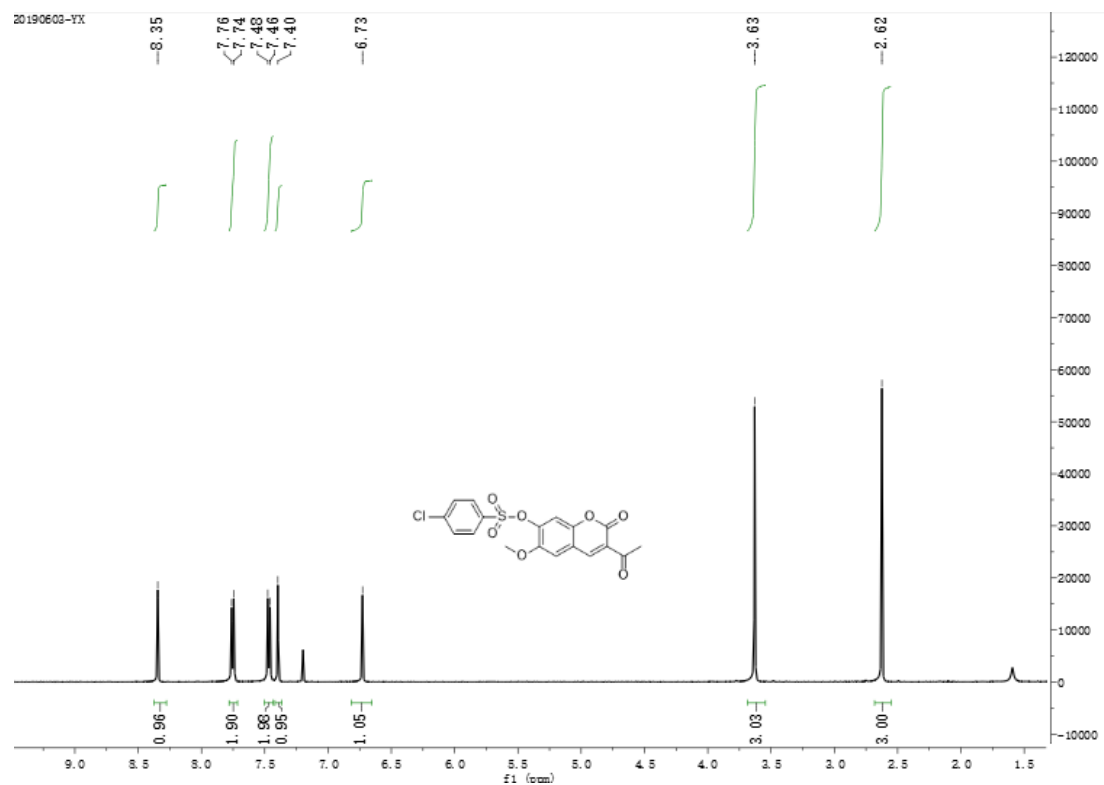


Figure S61 ^1H NMR of 10d

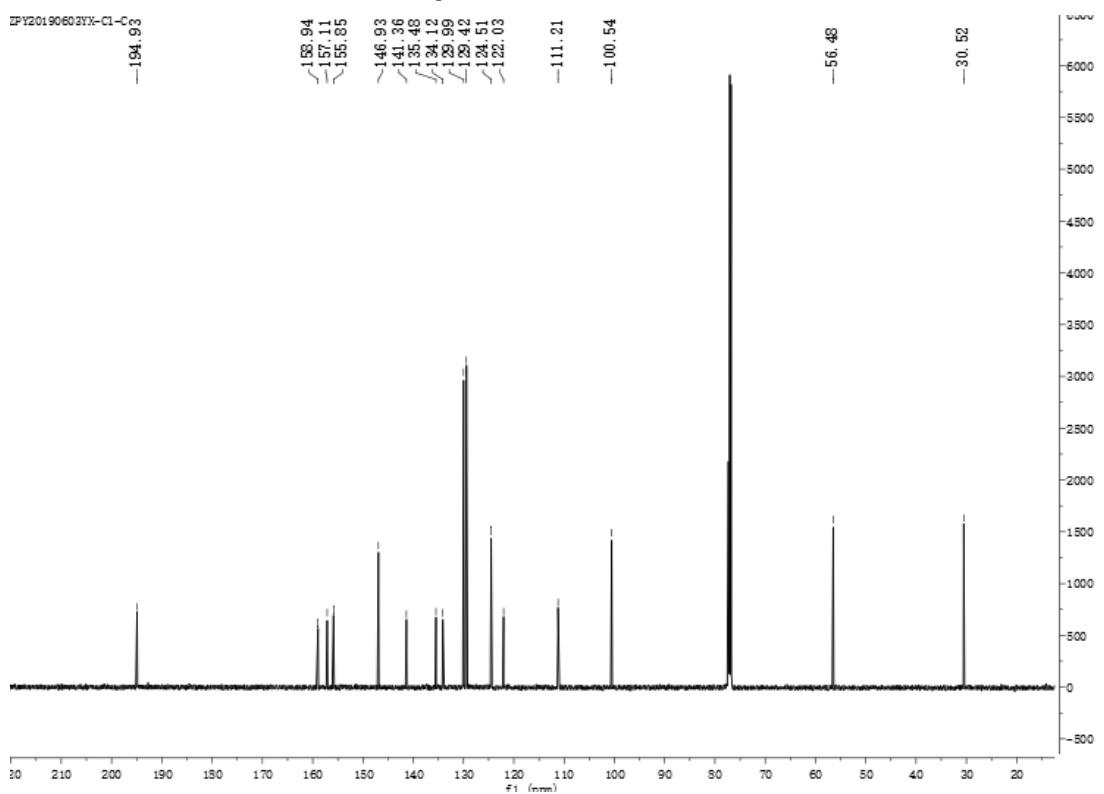


Figure S62 ^{13}C NMR of 10d

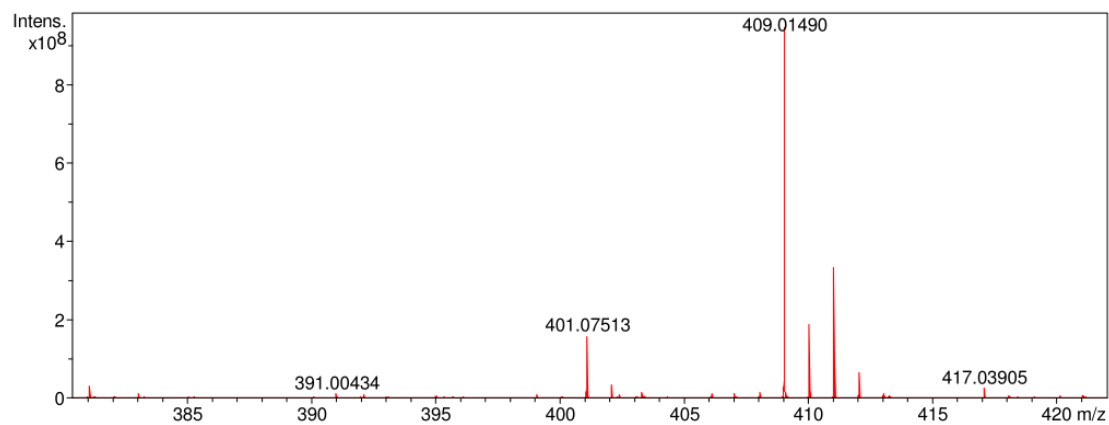


Figure S63 HRMS of 10d

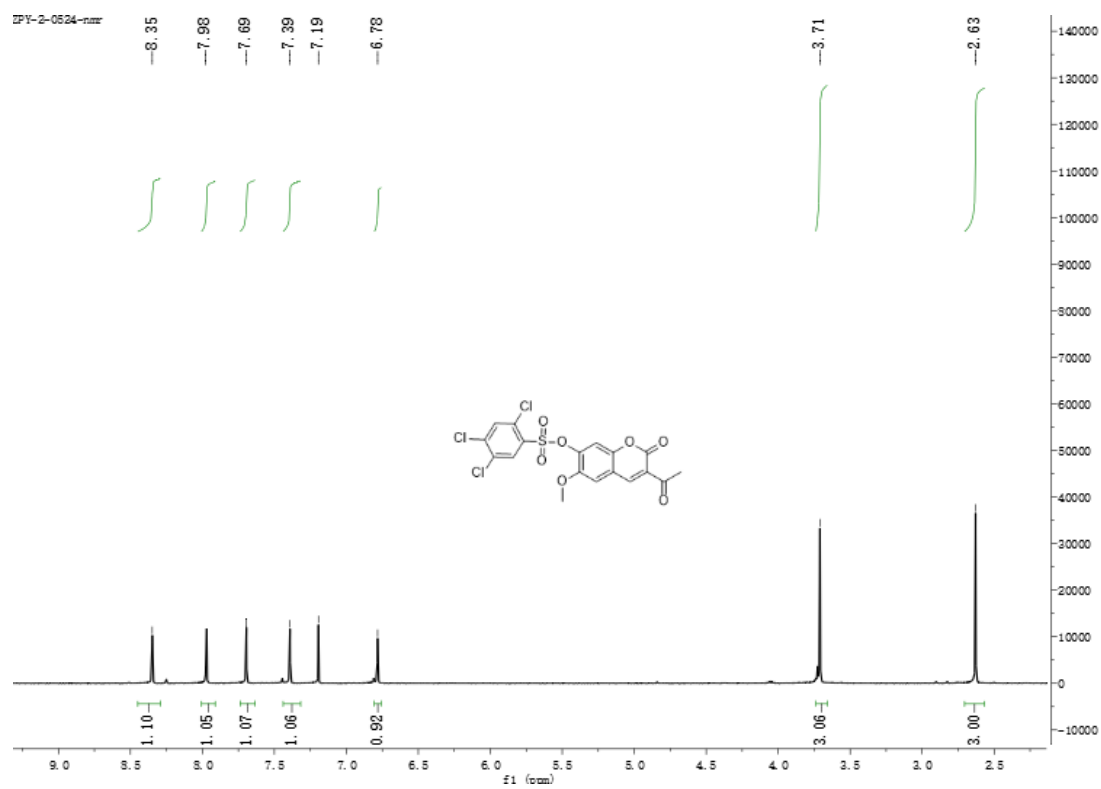


Figure S64 ^1H NMR of 10h

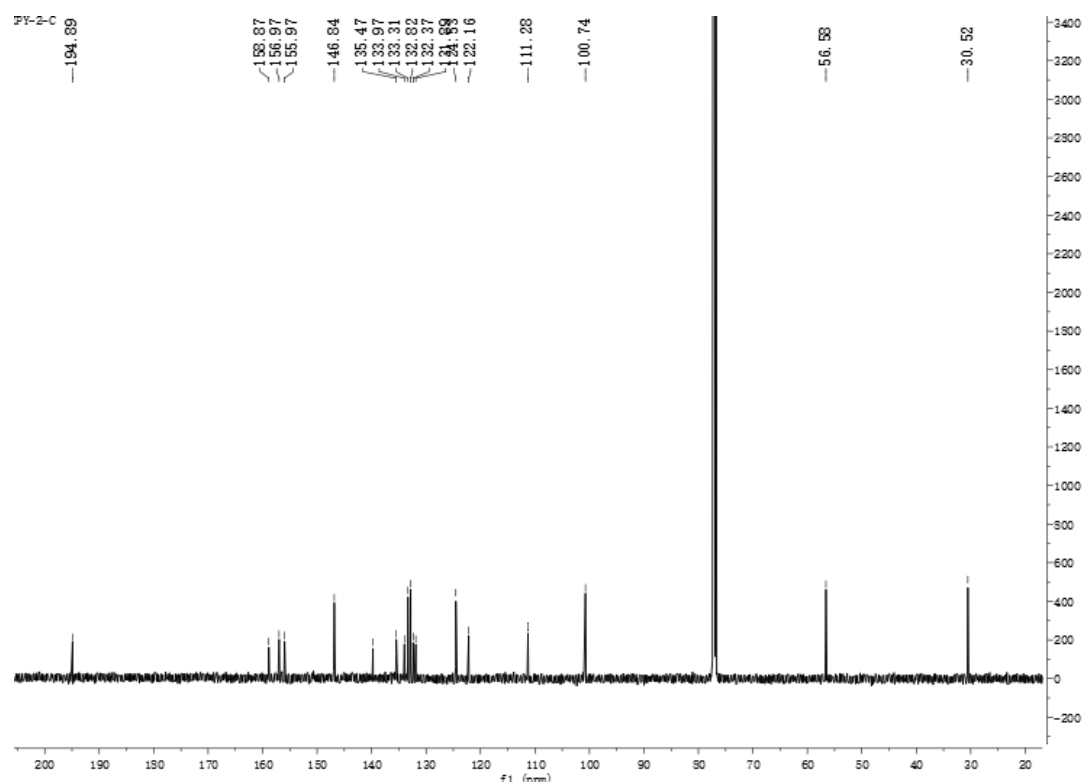


Figure S65 ¹³C NMR of 10h

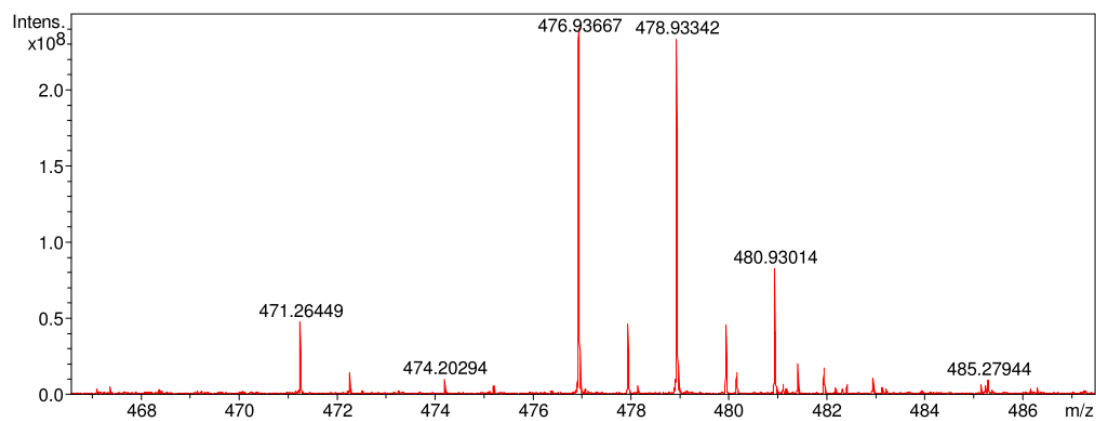


Figure S66 HRMS of 10h

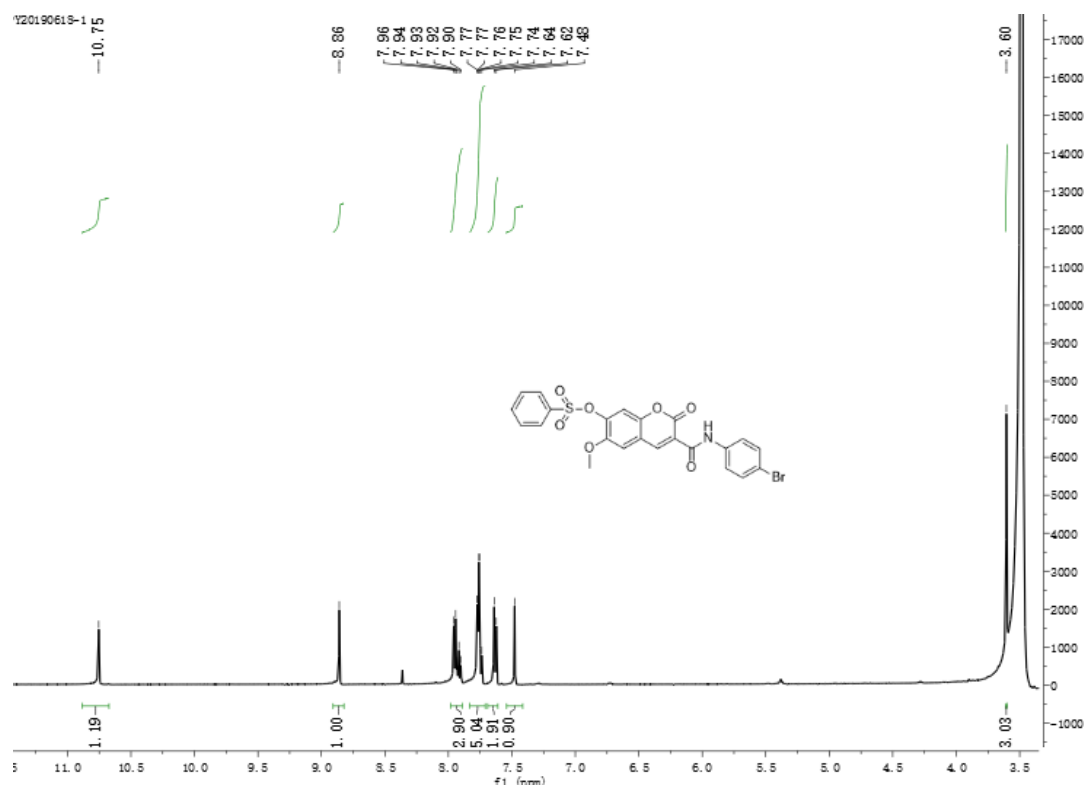


Figure S67 ¹H NMR of 11a

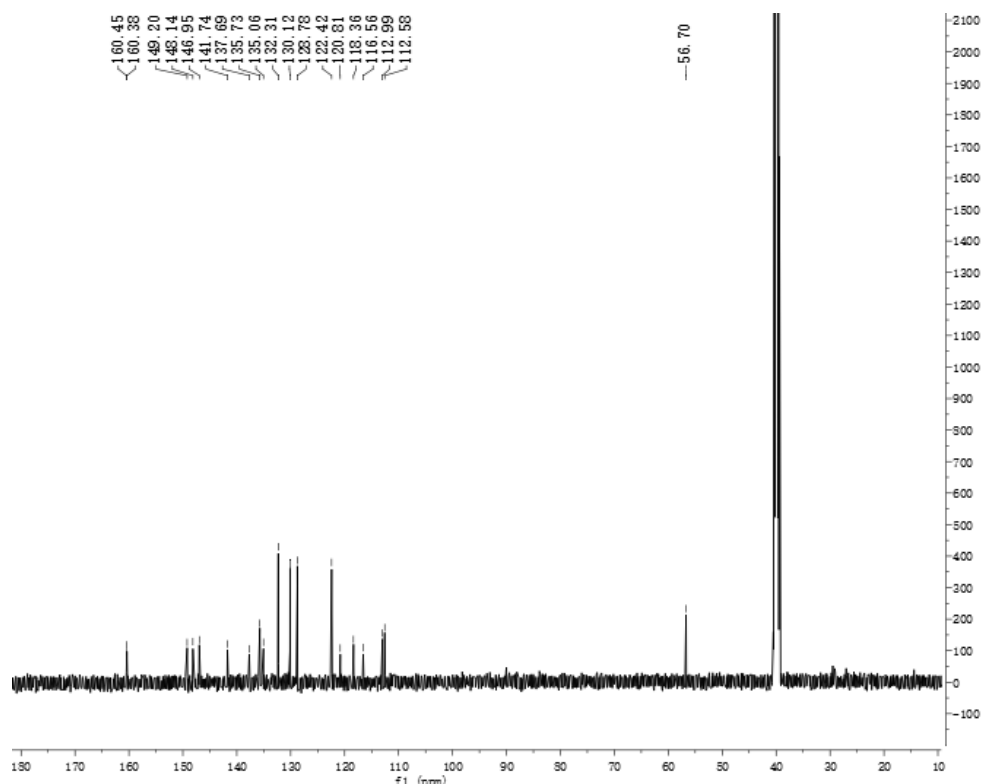


Figure S68 ¹³C NMR of 11a

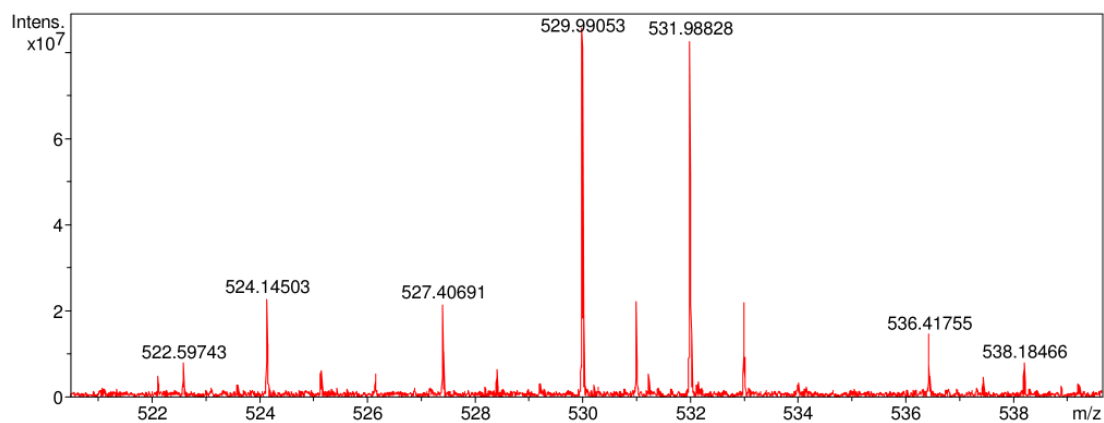


Figure S69 HRMS of 11a

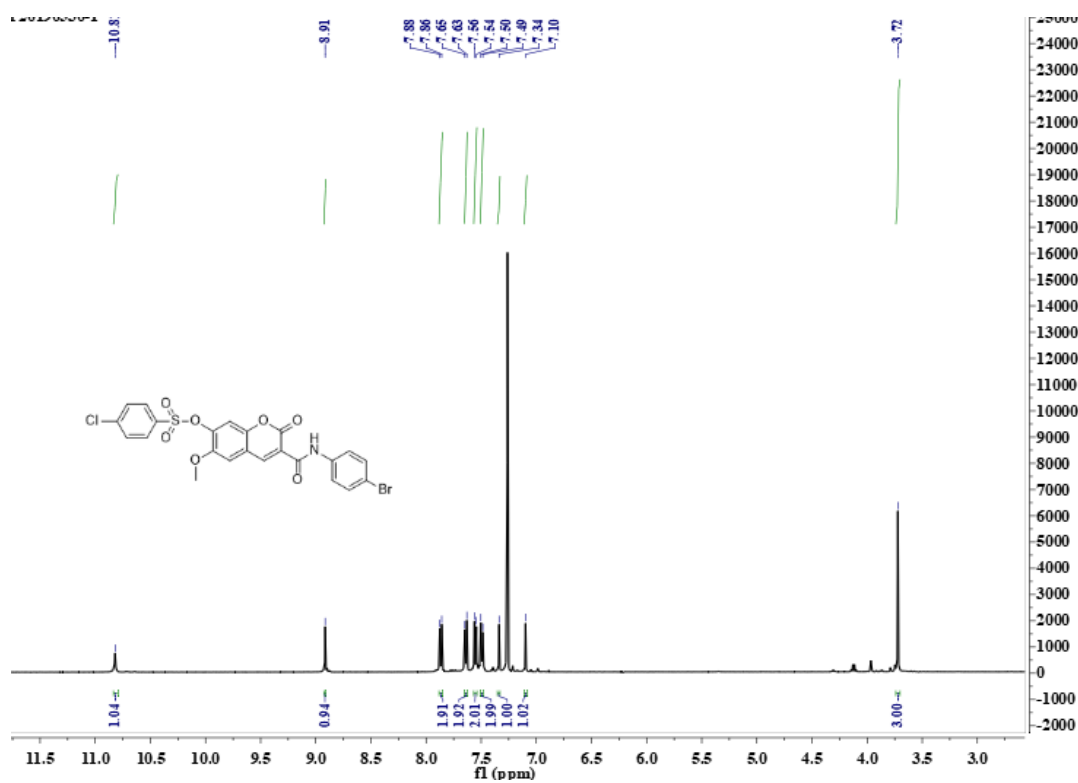


Figure S70 ¹H NMR of 11d

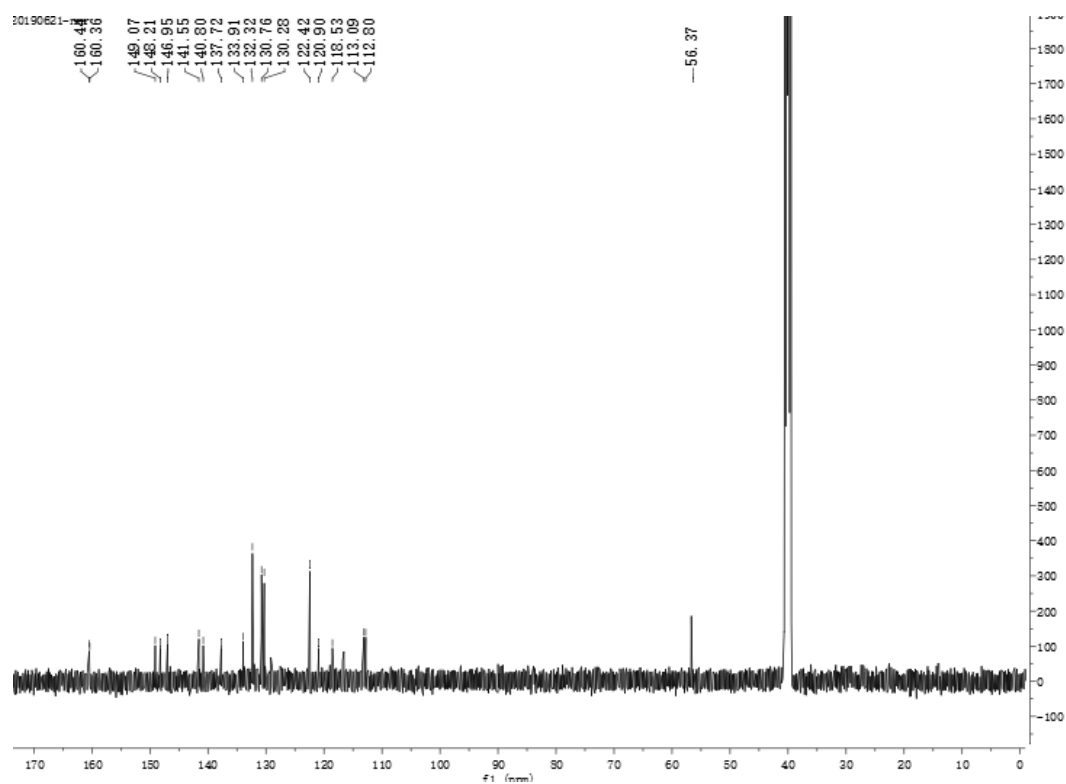


Figure S71 ^{13}C NMR of 11d

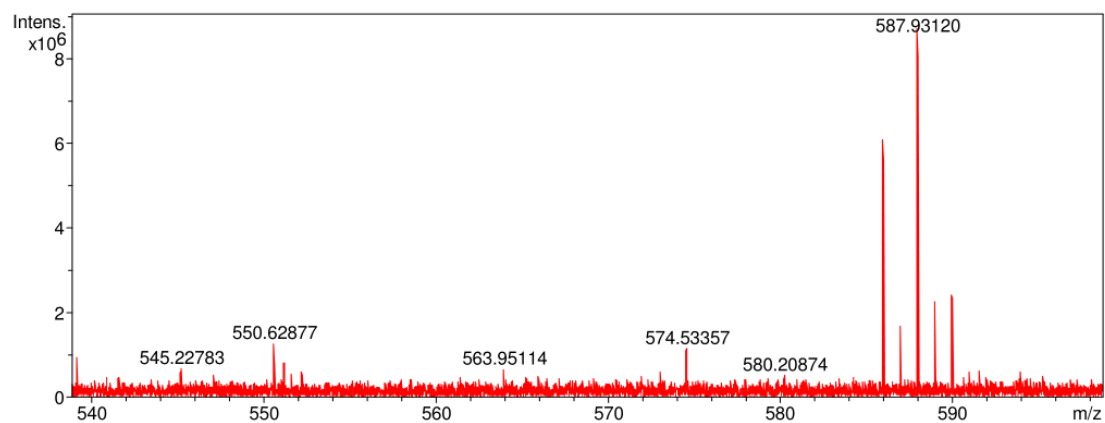


Figure S72 HRMS of 11d

Table S1. Acaricidal activities (LC₅₀, mg/mL, 72 h), AChE inhibitions (IC₅₀, µg/mL) of title compounds and their physicochemical properties

Compd.	LC ₅₀ (95% CI)	Slope±SE	X ²	IC ₅₀ values	MW ^a	clog <i>P</i> ^a	TPSA ^a
4	0.144 (0.0523-0.445)	0.23±0.080	0.213	105.98±21.87	192.2	1.35	55.76
4a	0.448 (0.223-0.861)	0.62±0.21	0.625	143.31±9.14	333.0	2.47	78.90
4b	0.209 (0.0325-0.377)	0.12±0.060	1.916	110.22±11.32	363.1	2.70	88.13
4c	0.318 (0.192-0.519)	0.75±0.16	0.855	126.91±29.39	351.0	2.62	78.90
4d	0.529 (0.298-0.966)	0.75±0.22	2.466	81.57±12.35	367.0	3.19	78.9
4e	0.636 (0.354-2.188)	0.67±0.16	2.645	141.15±14.41	413.0	3.34	78.90
4f	0.441 (0.215-0.930)	0.53±0.14	1.644	168.01±28.07	401.0	3.36	78.90
4g	0.183 (0.114-0.325)	0.49±0.090	0.955	133.10±8.44	378.0	2.22	130.71
4h	0.832 (0.348-2.025)	0.60±0.33	3.122	183.58±11.26	436.9	4.20	78.90
4i	0.489 (0.261-0.873)	0.71±0.25	0.659	146.02±17.18	339.0	2.15	78.90
4j	0.0930 (0.0566-0.178)	0.42±0.13	0.213	56.75±2.10	383.1	3.65	78.90
5	0.116 (0.0645-0.236)	0.37±0.15	0.315	93.09±15.61	286.1	3.59	55.76
5a	0.0570 (0.0489-0.0923)	0.75±0.19	2.448	40.60±4.16	427.1	4.71	78.90
5b	0.338 (0.174-0.687)	0.50±0.13	0.525	153.43±15.44	457.1	4.94	88.13
5c	0.0940 (0.0756-0.147)	0.82±0.42	1.222	85.52±11.20	445.1	4.86	78.90
5d	0.0990 (0.0752-0.143)	0.47±0.26	0.316	68.86±8.32	461.0	5.43	78.90
5e	0.0800 (0.0551-0.112)	0.81±0.38	0.415	71.12±14.10	509.0	5.58	78.90
5f	0.104 (0.0654-0.162)	0.57±0.17	0.266	119.64±15.70	495.1	5.60	78.90
5g	0.0680 (0.0447-0.119)	0.59±0.12	0.919	123.18±24.77	472.0	4.46	130.71
5h	0.0960 (0.0645-0.145)	0.66±0.22	0.626	104.83±15.43	530.9	6.43	78.90
5i	0.0730 (0.0526-0.124)	0.59±0.24	0.318	110.46±7.82	433.0	4.39	78.90
5j	0.0200 (0.0145-0.0421)	0.61±0.16	0.615	54.83±6.39	477.1	5.89	78.90
6	0.0810 (0.0563-0.131)	0.58±0.28	0.429	92.59±16.84	243.2	0.84	72.83
6d	0.159 (0.0933-0.262)	0.54±0.14	0.327	145.00±11.20	409.0	3.65	95.97
6h	0.107 (0.0752-0.161)	0.67±0.33	0.518	131.15±17.52	478.9	2.65	95.97
7	0.0820 (0.0544-0.126)	0.68±0.14	1.216	76.88±1.59	390.2	2.82	84.86
7a	0.117 (0.0852-0.181)	0.63±0.16	0.589	117.40±7.08	532.0	4.22	108.00
7d	0.0890 (0.0645-0.133)	0.68±0.22	0.978	98.17±7.61	587.9	4.93	108.00
Cyetyprafen	0.0150 (0.0126-0.0384)	0.49±0.19	0.325	14.06±10.20	393.2	5.15	65.69

^a These values were extracted from ChemBioDraw Ultra12.0; MW: molecular weight; clog *P*: partition coefficient; TPSA: topological polar surface area.

Table S2. Lethal activities of title compounds to *Artemia* (LC₅₀, mg/mL)

Compd.	6 h			12 h		
	LC ₅₀ (95% CI)	Slope±SE	X ²	LC ₅₀ (95% CI)	Slope±SE	X ²
4	0.0272 (0.0143-0.0481)	0.83±0.19	0.992	0.0142 (0.00825-0.0261)	1.29±0.15	2.923
4a	0.0475 (0.0284-0.0773)	1.14±0.26	2.195	0.0291 (0.0175-0.0486)	1.04±0.22	1.832
4b	0.0386 (0.0231-0.0660)	1.08±0.14	0.771	0.0182 (0.0112-0.0328)	1.29±0.26	2.215
4c	0.0915 (0.0591-0.141)	1.95±0.22	2.555	0.0563 (0.0381-0.0823)	0.28±0.020	1.342
4d	0.0336 (0.0221-0.0495)	1.30±0.16	1.958	0.0160 (0.00925-0.0281)	1.36±0.050	2.391
4e	0.157 (0.0714-0.351)	1.62±0.33	2.955	0.0898 (0.0521-0.153)	1.59±0.10	8.615
4f	0.109 (0.0682-0.173)	2.01±0.36	2.061	0.0756 (0.0481-0.118)	1.45±0.11	0.416
4g	0.0467 (0.0321-0.0664)	1.72±0.12	4.324	0.0256 (0.0184-0.0336)	2.26±0.24	1.747
4h	0.131 (0.0712-0.243)	1.87±0.23	1.577	0.125 (0.0616-0.254)	1.43±0.030	2.148
4i	0.0765 (0.0451-0.129)	1.32±0.14	0.956	0.0451 (0.0315-0.0654)	1.39±0.23	3.214
4j	0.0136 (0.00515-0.0345)	0.95±0.03 0	0.235	0.00936 (0.00323-0.0227)	1.37±0.15	1.763
5	0.0525 (0.0326-0.0841)	1.02±0.11	1.468	0.0325 (0.0224-0.0436)	1.34±0.13	3.411
5a	0.0958 (0.0564-0.159)	1.86±0.12	1.722	0.0558 (0.0399-0.0765)	1.98±0.25	5.715
5b	0.0945 (0.0561-0.157)	1.55±0.13	1.471	0.0362 (0.0283-0.0475)	1.65±0.27	7.428
5c	0.0947 (0.0514-0.176)	1.45±0.22	2.895	0.0486 (0.0295-0.0781)	1.10±0.17	1.645
5d	0.0728 (0.0373-0.139)	0.98±0.15	1.589	0.0337 (0.0233-0.0473)	1.33±0.090	2.314
5e	0.114 (0.0687-0.179)	1.92±0.22	0.960	0.0795 (0.0526-0.121)	1.65±0.12	0.636
5f	0.0715 (0.0431-0.118)	1.34±0.13	1.533	0.0399 (0.0237-0.0685)	0.89±0.16	0.0690
5g	0.0866 (0.0572-0.129)	1.96±0.16	1.217	0.0536 (0.0399-0.0715)	1.87±0.33	1.157
5h	0.106 (0.0581-0.195)	1.66±0.18	0.134	0.0576 (0.0401-0.0823)	1.77±0.22	3.085
5i	0.0998 (0.0611-0.161)	1.94±0.19	2.018	0.0567 (0.0393-0.0794)	1.70±0.05	5.344
5j	0.0779 (0.0534-0.114)	1.99±0.36	2.455	0.0297 (0.0201-0.0423)	1.33±0.12	2.625
6	0.0565 (0.0327-0.0976)	1.02±0.12	1.223	0.0356 (0.0173-0.0527)	0.88±0.090	1.669
6d	0.0455 (0.0244-0.0823)	0.80±0.22	0.192	0.0279 (0.0142-0.0545)	0.88±0.16	1.388
6h	0.0485 (0.0301-0.0776)	1.04±0.36	1.394	0.0339 (0.0214-0.0526)	0.99±0.24	2.156
7	0.0523 (0.0331-0.0773)	1.24±0.06 0	2.198	0.0323 (0.0201-0.0463)	1.10±0.040	1.271
7a	0.0576 (0.0245-0.139)	0.65±0.11	1.587	0.0336 (0.0188-0.0519)	0.95±0.15	0.652
7d	0.0542 (0.0381-0.0762)	1.66±0.32	2.074	0.0394 (0.0327-0.0466)	2.98±0.36	5.325
Cyetryrafen	0.0117 (0.00935-0.0141)	2.05±0.39	3.791	0.00613 (0.00508-0.00727)	1.24±0.20	2.156

Table S3. The molecular docking scores of compound **4j** and the acetylcholinesterase

Name	Pose	Grid Score (kcal/mol)	Grid_vdw ^a (kcal/mol)	Grid_es ^b (kcal/mol)	Internal energy repulsive (kcal/mol)	Cluster Size
4j	1	-64.654701	-60.91954	-3.735158	4.798172	4
4j	2	-64.482681	-62.427189	-2.055494	6.316545	2
4j	3	-64.171875	-64.39386	0.221982	6.168889	3

^a vdw: van der Waals interaction. ^b es: electrostatic interaction.

Table S4. The molecular docking scores of compound **5a** and the acetylcholinesterase

Name	Pose	Grid Score (kcal/mol)	Grid_vdw ^a (kcal/mol)	Grid_es ^b (kcal/mol)	Internal energy repulsive (kcal/mol)	Cluster Size
5a	1	-65.409058	-64.687553	-0.721504	5.695736	8
5a	2	-63.488708	-57.522991	-5.965718	11.793267	1

^a vdw: van der Waals interaction. ^b es: electrostatic interaction.

Table S5. The molecular docking scores of compound **5j** and the acetylcholinesterase

Name	Pose	Grid Score (kcal/mol)	Grid_vdw ^a (kcal/mol)	Grid_es ^b (kcal/mol)	Internal energy repulsive (kcal/mol)	Cluster Size
5j	1	-72.95015	-72.541328	-0.40882	8.8318	5
5j	2	-69.114731	-68.981514	-0.133219	8.012092	3
5j	3	-67.184402	-64.211487	-2.972916	11.853454	1

^a vdw: van der Waals interaction. ^b es: electrostatic interaction.