

Supporting Information

Rhodium(II)-catalyzed synthesis of tetracyclic 3,4-fused indoles and dihydroindoles

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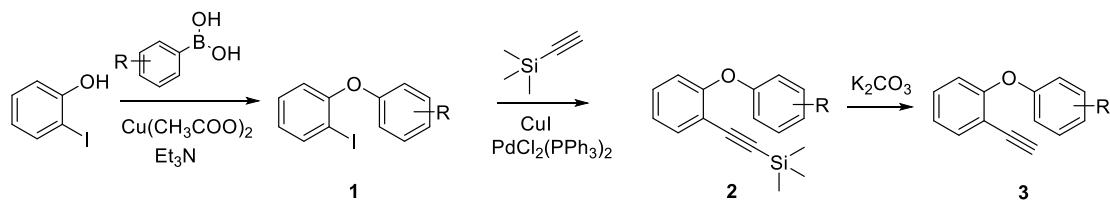
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General methods

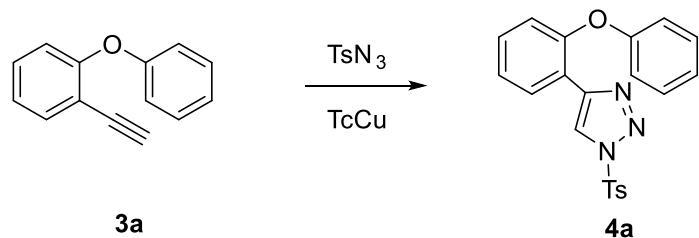
All flash column chromatography was performed using 300-400 mesh silica gel. ¹H NMR (400 MHz) and ¹³C NMR (100 MHz) spectra were carried out on a Bruker AV-400 Nuclear Magnetic Resonance spectrometer. The high-resolution MS spectra were measured on an electron ionization mass spectrometer (Q-TOF, Agilent). The fluorescence spectrum was recorded on a fluorescence spectrophotometer (Hitachi, F-7000).

Preparation of 1-ethynyl-2-phenoxybenzene

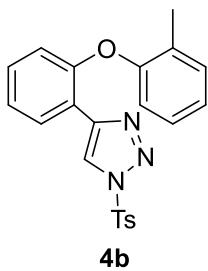


Compounds **1-3** were prepared following the method reported by Tietze.¹

NMR and HRMS data of compound **4**

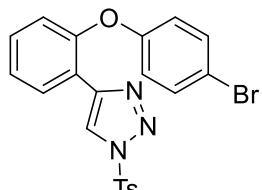


4a: 77% yield. ¹H NMR (400 MHz, DMSO-*d*₆) δ 8.83 (s, 1H), 8.17 (d, *J* = 7.8 Hz, 1H), 8.03(d, *J* = 8.04 Hz, 2H), 7.53 (d, *J* = 8.1 Hz, 2H), 7.46-7.38 (m, 3H), 7.30 (t, *J* = 7.7 Hz, 1H), 7.20 (t, *J* = 7.4 Hz, 1H), 7.10 (d, *J* = 8.0 Hz, 2H), 6.99 (d, *J* = 8.2 Hz, 1H), 2.42 (s, 3H). ¹³C NMR (100 MHz, DMSO-*d*₆) δ 155.60, 153.15, 147.74, 141.98, 132.14, 130.83, 130.62, 130.16, 128.35, 128.27, 124.07, 123.88, 122.86, 119.87, 118.89, 118.53, 21.23. HRMS-ESI (m/z): [M+H]⁺ calcd. for C₂₁H₁₇N₃O₃S⁺ 392.1069, found 392.1053.



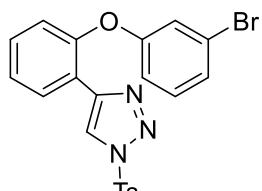
4b

4b: yield 60%. ^1H NMR (400 MHz, DMSO-*d*₆) δ 8.84 (d, *J* = 1.4 Hz, 1H), 8.14 (dd, *J* = 7.7, 1.8 Hz, 1H), 8.02 (dd, *J* = 8.3, 1.6 Hz, 2H), 7.49 (d, *J* = 7.9 Hz, 2H), 7.37 – 7.27 (m, 2H), 7.24 – 7.09 (m, 3H), 6.90 (d, *J* = 8.0 Hz, 1H), 6.65 (d, *J* = 8.3 Hz, 1H), 2.37 (s, 3H), 2.11 (s, 3H). ^{13}C NMR (101 MHz, DMSO-*d*₆) δ 154.43, 153.52, 148.33, 142.68, 132.78, 132.25, 131.40, 131.09, 129.91, 128.90, 128.71, 128.19, 125.40, 123.54, 123.23, 120.45, 118.95, 116.73, 21.80, 16.25. HRMS-ESI (m/z): [M+H]⁺ calcd. for C₂₂H₁₉N₃O₃S⁺ 406.1225, found 406.1223.



4c

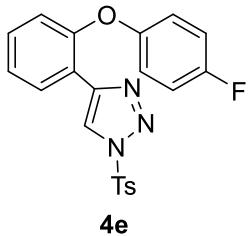
4c: yield 54%. ^1H NMR (400 MHz, DMSO-*d*₆) δ 8.86 (s, 1H), 8.15 (dd, *J* = 7.8, 1.8 Hz, 1H), 8.05-7.97 (m, 2H), 7.58-7.50 (m, 5H), 7.47 (ddd, *J* = 8.4, 7.4, 1.8 Hz, 1H), 7.34 (td, *J* = 7.5, 1.2 Hz, 1H), 7.07 (dd, *J* = 8.3, 1.2 Hz, 1H), 7.02-6.95 (m, 2H), 2.42 (s, 3H). ^{13}C NMR (100 MHz, DMSO-*d*₆) δ 155.33, 152.41, 147.74, 141.89, 132.82, 132.21, 130.94, 128.56, 128.31, 127.27, 124.93, 123.17, 120.53, 120.37, 119.62, 115.38, 21.34. HRMS-ESI (m/z): [M+H]⁺ calcd. for C₂₁H₁₆BrN₃O₃S⁺ 470.0174, found 469.9129.



4d

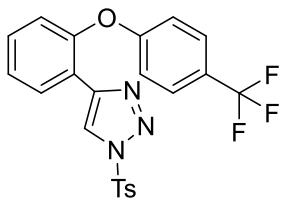
4d: yield 58%. ^1H NMR (400 MHz, DMSO-*d*₆) δ 8.89 (s, 1H), 8.15 (dd, *J* = 7.9, 1.8

Hz, 1H), 7.99 (d, $J = 8.5$ Hz, 2H), 7.49 (d, $J = 8.3$ Hz, 2H), 7.45 (td, $J = 7.7, 1.6$ Hz, 1H), 7.40-7.29 (m, 3H), 7.29 (t, $J = 2.0$ Hz, 1H), 7.10-7.05 (m, 1H), 7.03 (dt, $J = 7.2, 2.2$ Hz, 1H), 2.42 (s, 3H). ^{13}C NMR (100 MHz, DMSO- d_6) δ 156.75, 152.36, 147.75, 141.96, 132.24, 131.85, 130.86, 128.95, 128.63, 128.24, 126.65, 124.85, 123.13, 122.32, 121.21, 120.36, 119.57, 117.38, 21.24. HRMS-ESI (m/z): [M+H]⁺ calcd. for C₂₁H₁₆BrN₃O₃S⁺ 470.0174, found 470.0175.



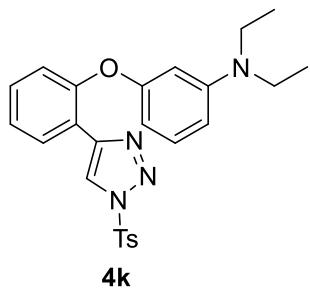
4e

4e: yield 92%. ^1H NMR (400 MHz, DMSO- d_6) δ 8.88 (s, 1H), 8.15 (dd, $J_{\text{HH}} = 7.6, 1.6$ Hz, 1H), 8.04 (d, $J_{\text{HH}} = 8.4$ Hz, 2H), 7.53 (d, $J_{\text{HH}} = 8.4$ Hz, 2H), 7.41 (td, $J_{\text{HH}} = 9.2, 2.0$ Hz, 1H), 7.28-7.21 (m, 3H), 7.12 (dd, $J_{\text{HH}} = 9.2, J_{\text{HF}} = 4.4$ Hz, 2H), 6.93 (d, $J_{\text{HH}} = 8.4$, 1H). ^{13}C NMR (100 MHz, DMSO- d_6) δ 158.46 (d, $J_{\text{CF}} = 238.6$ Hz), 153.64, 151.54, 147.75, 141.99, 132.17, 130.82, 130.63, 128.38, 128.30, 123.88, 122.92, 120.73 (d, $J_{\text{CF}} = 8.3$ Hz), 119.49, 118.10, 116.66 (d, $J_{\text{CF}} = 23.4$ Hz), 21.23. HRMS-ESI (m/z): [M+H]⁺ calcd. for C₂₁H₁₆FN₃O₃S⁺ 410.0975, found 410.0969.

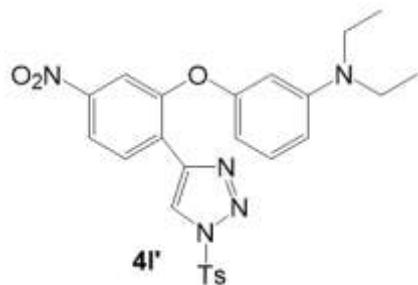


4f

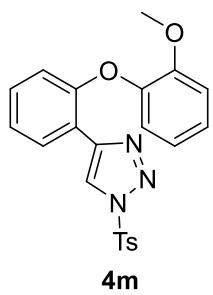
4f: yield 81%. ^1H NMR (400 MHz, DMSO- d_6) δ 8.20 (d, $J_{\text{HH}} = 7.5$ Hz, 1H), 8.07 (s, 1H), 7.72 (d, $J_{\text{HH}} = 8.4$ Hz, 2H), 7.53-7.46 (m, 3H), 7.41 (t, $J_{\text{HH}} = 7.4$ Hz, 1H), 7.21 (d, $J_{\text{HH}} = 8.0$ Hz, 1H), 7.13 (m, 4H), 2.30 (s, 3H). ^{13}C NMR (100 MHz, DMSO- d_6) δ 159.96, 150.89, 137.99, 129.92, 128.73, 128.16, 127.45 (q, $J_{\text{CF}} = 3.5$ Hz), 125.78, 125.49, 124.22 (q, $J_{\text{CF}} = 270.2$ Hz), 123.14 (q, $J_{\text{CF}} = 32.4$ Hz), 123.12, 121.59, 117.09, 20.74. HRMS-ESI (m/z): [M+H]⁺ calcd. for C₂₂H₁₆F₃N₃O₃S⁺ 460.0943, found 460.0939.



4k: yield 54%. ^1H NMR (400 MHz, DMSO-*d*₆) δ 8.80 (s, 1H), 8.20 (dd, *J* = 7.7, 1.6 Hz, 1H), 7.99 (d, *J* = 8.0 Hz, 2H), 7.51 (d, *J* = 8.2 Hz, 2H), 7.42 (t, *J* = 8.7 Hz, 1H), 7.27 (t, *J* = 7.5 Hz, 1H), 7.13 (t, *J* = 8.2 Hz, 1H), 7.02 (d, *J* = 8.2 Hz, 1H), 6.48 (dd, *J* = 8.5, 2.4 Hz, 1H), 6.36 (s, 1H), 6.12 (dd, *J* = 8.0, 2.1 Hz, 1H), 3.30 (q, *J* = 7.0 Hz, 4H), 2.41 (s, 3H), 1.06 (t, *J* = 7.0 Hz, 6H). ^{13}C NMR (100 MHz, DMSO-*d*₆) δ 157.34, 153.87, 149.62, 148.22, 142.52, 132.67, 131.31, 130.93, 128.74, 128.50, 124.21, 123.31, 120.16, 119.38, 107.75, 104.81, 102.10, 44.19, 21.73, 12.76. HRMS-ESI (m/z): [M+H]⁺ calcd. for C₂₅H₂₆N₄O₃S⁺ 463.1804, found 463.1803.



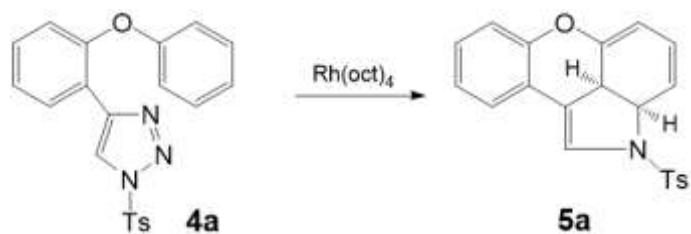
4l': yield 50%. ^1H NMR (400 MHz, CDCl₃) δ 8.80 (s, 1H), 8.59 (d, *J* = 8.7 Hz, 1H), 8.05 (d, *J* = 8.2 Hz, 2H), 8.01 (dd, *J* = 8.7, 2.3 Hz, 1H), 7.77 (d, *J* = 2.3 Hz, 1H), 7.42 (d, *J* = 8.1 Hz, 2H), 7.28 (t, *J* = 8.2 Hz, 2H), 6.62 (dd, *J* = 8.5, 2.5 Hz, 1H), 6.42 (s, 1H), 6.33 (dd, *J* = 7.9, 2.2 Hz, 1H), 3.40 (q, *J* = 7.1 Hz, 4H), 2.48 (s, 3H), 1.22 (t, *J* = 7.1 Hz, 6H). ^{13}C NMR (100 MHz, CDCl₃) δ 155.47, 155.28, 149.91, 148.36, 147.51, 140.83, 132.94, 131.00, 130.50, 128.86, 128.58, 125.16, 123.74, 117.39, 111.59, 109.04, 106.28, 103.24, 44.49, 21.88, 12.51. HRMS-ESI (m/z): [M+H]⁺ calcd. for C₂₅H₂₅N₅O₅S⁺ 508.1655, found 508.1653.



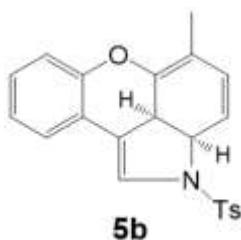
4m

4m: yield 56%. ^1H NMR (400 MHz, DMSO- d_6) δ 8.87 (s, 1H), 8.17 (dd, J = 7.8, 1.7 Hz, 1H), 8.08-8.03 (m, 2H), 7.54 (d, J = 8.2 Hz, 2H), 7.35 (ddd, J = 8.3, 7.3, 1.8 Hz, 1H), 7.27-7.18 (m, 3H), 7.08 (dd, J = 7.7, 1.3 Hz, 1H), 6.99 (ddd, J = 7.9, 6.2, 2.6 Hz, 1H), 6.77 (dd, J = 8.3, 1.0 Hz, 1H), 3.78 (s, 3H), 2.42 (s, 3H). ^{13}C NMR (100 MHz, DMSO- d_6) δ 154.03, 150.89, 147.81, 143.03, 142.13, 132.23, 130.84, 130.34, 128.34, 127.84, 125.84, 122.94, 122.64, 121.14, 121.04, 118.14, 116.24, 113.44, 55.74, 21.24. HRMS-ESI (m/z): [M+H] $^+$ calcd. for $\text{C}_{22}\text{H}_{19}\text{N}_3\text{O}_4\text{S}^+$ 422.1175, found 422.1186.

NMR and HRMS data of compound 5



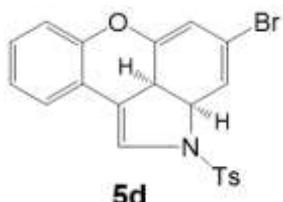
5a: 72% yield. ^1H NMR (400 MHz, DMSO-*d*₆) δ 7.82 (d, *J* = 8.2 Hz, 2H), 7.49 (d, *J* = 8.0 Hz, 3H), 7.21-7.17 (m, 2H), 7.00-6.92 (m, 2H), 6.00 (t, *J* = 6.5 Hz, 1H), 5.52 (dd, *J* = 9.7, 4.4, Hz, 1H), 5.41 (dd, *J* = 6.4, 1.6 Hz, 1H), 5.10 (dd, *J* = 15.3, 3.8 Hz, 1H), 4.20(d, *J* = 15.6 Hz, 1H), 2.42(s, 1H). ^{13}C NMR (100 MHz, DMSO-*d*₆) δ 151.36, 148.18, 144.14, 132.46, 129.99, 129.25, 127.45, 127.08, 126.00, 124.89, 122.10, 118.90, 117.38, 116.16, 115.93, 98.24, 59.32, 21.02. HRMS-ESI (m/z): [M+H]⁺ calcd. for C₂₁H₁₈NO₃S⁺ 364.1007, found 364.1008.



5b: yield 70%. ^1H NMR (400 MHz, DMSO- d_6) δ 7.76 (d, J = 8.2 Hz, 2H), 7.41 (d, J = 8.0 Hz, 3H), 7.16 – 7.11 (m, 1H), 7.10 (d, J = 2.6 Hz, 1H), 6.90 (t, J = 7.7 Hz, 2H), 5.84 (d, J = 9.8 Hz, 1H), 5.45 (dd, J = 9.6, 4.4 Hz, 1H), 4.97 (dd, J = 15.2, 4.4 Hz, 1H), 3.99 (dq, J = 14.0, 2.5 Hz, 1H), 2.35 (s, 3H), 1.63 (d, J = 2.3 Hz, 3H). ^{13}C NMR (101 MHz, DMSO- d_6) δ 152.24, 144.68, 142.27, 133.01, 130.55, 130.50, 129.74, 128.02, 126.74, 126.54, 122.39, 119.59, 117.84, 117.57, 116.58, 106.03, 60.00, 40.97, 21.58, 13.56. HRMS-ESI (m/z): [M+H] $^+$ calcd. for $\text{C}_{22}\text{H}_{20}\text{NO}_3\text{S}^+$ 378.1158, found 378.1163.



5c: yield 85%. ^1H NMR (400 MHz, DMSO- d_6) δ 7.80 (d, J = 8.0 Hz, 2H), 7.59 (d, J = 7.8 Hz, 1H), 7.39 (d, J = 8.2 Hz, 2H), 7.30-7.15 (m, 2H), 7.03-6.93 (m, 2H), 6.45 (d, J = 7.0 Hz, 1H), 5.51-5.37 (m, 2H), 3.59 (dd, J = 14.0, 2.6 Hz, 1H), 2.35 (s, 3H). ^{13}C NMR (100 MHz, DMSO- d_6) δ 152.91, 147.56, 144.22, 132.26, 130.07, 129.63, 128.10, 127.11, 126.57, 125.85, 122.36, 121.43, 117.17, 116.30, 116.05, 101.23, 65.43, 43.47, 21.09. HRMS-ESI (m/z): [M+H] $^+$ calcd. for $\text{C}_{21}\text{H}_{17}\text{BrNO}_3\text{S}^+$ 442.0113, 444.0092, found 442.0109, 444.0090.



5d: yield 92%. ^1H NMR (400 MHz, DMSO- d_6) δ 7.79 (d, J = 8.1 Hz, 2H), 7.48 (dd, J = 7.1, 4.4 Hz, 4H), 7.27-7.19 (m, 2H), 7.04-6.94 (m, 2H), 5.86 (d, J = 5.0 Hz, 1H),

5.60 (d, $J = 1.7$ Hz, 1H), 5.04 (dd, $J = 15.2, 5.0$ Hz, 1H), 4.29 (dd, $J = 14.9, 2.9$ Hz, 1H), 2.42 (s, 3H). ^{13}C NMR (100 MHz, DMSO- d_6) δ 151.01, 150.11, 144.42, 132.31, 130.22, 129.51, 128.02, 127.61, 126.13, 122.72, 119.82, 118.5, 117.34, 116.01, 114.72, 102.73, 59.77, 39.94, 21.01. HRMS-ESI (m/z): [M+H]⁺ calcd. for C₂₁H₁₇BrNO₃S⁺ 442.0113, 444.0113, found 442.0102, 444.0083.



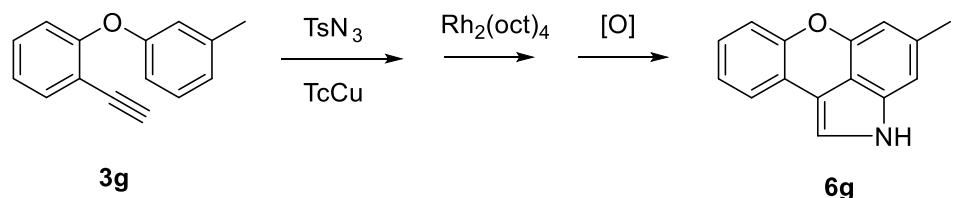
5e: yield 84%. ^1H NMR (400 MHz, DMSO- d_6) δ 7.88 (d, $J_{\text{HH}} = 8.4$ Hz, 2H), 7.55 (dd, $J_{\text{HH}} = 8.0, 1.6$ Hz, 1H), 7.51 (d, $J_{\text{HH}} = 8.4$, 2H), 7.32 (td, $J_{\text{HH}} = 8.4, 1.6$ Hz, 1H), 7.09 (td, $J_{\text{HH}} = 8.4, 0.8$ Hz, 1H), 7.05 (d, $J_{\text{HH}} = 2.4$, Hz, 1H), 7.02 (d, $J_{\text{HH}} = 8.4$ Hz, 1H), 5.75 (dd, $J_{\text{HH}} = 7.2$ Hz, $J_{\text{HF}} = 12.4$ Hz, 1H), 5.44 (d, $J_{\text{HH}} = 7.6$, Hz, 1H), 5.27 (dd, $J_{\text{HH}} = 14.8$ Hz, $J_{\text{HF}} = 2.8$ Hz, 1H), 4.04 (d, $J_{\text{HH}} = 14.4$, Hz, 1H), 2.43 (s, 3H). ^{13}C NMR (100 MHz, DMSO- d_6) δ 152.74 (d, $J_{\text{CF}} = 266.1$ Hz), 146.01, 145.59, 145.54, 133.35, 130.96, 130.87, 128.96, 127.13, 127.02, 123.28, 120.88, 117.32, 117.06, 103.89 (d, $J_{\text{CF}} = 23.5$ Hz), 99.26 (d, $J_{\text{CF}} = 6.2$ Hz), 60.20 (d, $J_{\text{CF}} = 25.6$ Hz), 45.03 (d, $J_{\text{CF}} = 7.6$ Hz), 27.62. HRMS-ESI (m/z): [M+H]⁺ calcd. for C₂₁H₁₇FNO₃S⁺ 382.0913, found 382.0912.



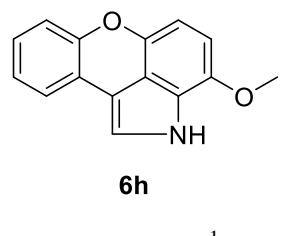
5f: yield 86%. ^1H NMR (400 MHz, DMSO- d_6) δ 7.79 (d, $J_{\text{HH}} = 7.9$ Hz, 2H), 7.59 (d, $J_{\text{HH}} = 7.5$ Hz, 1H), 7.39 (d, $J_{\text{HH}} = 7.9$ Hz, 3H), 7.28-7.21 (m, 2H), 7.05-6.99 (m, 2H), 6.79 (d, $J_{\text{HH}} = 6.7$ Hz, 1H), 5.64 (d, $J_{\text{HH}} = 7.0$ Hz, 1H), 5.56 (d, $J_{\text{HH}} = 14.1$ Hz, 1H), 3.90 (d, $J_{\text{HH}} = 14.0$ Hz, 1H), 2.36 (s, 3H). ^{13}C NMR (100 MHz, DMSO- d_6) δ 152.18, 151.91, 144.31, 131.73, 130.20, 130.07 (q, $J_{\text{CF}} = 49.2$ Hz), 129.71, 128.06, 127.47, 126.78, 126.54, 123.55 (q, $J_{\text{CF}} = 270.9$ Hz) 122.75, 120.61, 116.50 (q, $J_{\text{CF}} = 14.4$ Hz),

116.16, 115.97, 98.54, 58.29, 42.72, 21.00. HRMS-ESI (m/z): [M+H]⁺ calcd. for C₂₂H₁₇F₃NO₃S⁺ 432.0881, found 432.0935.

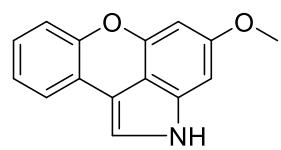
NMR and HRMS data of compound 6



6g: 60% yield. ¹H NMR (400 MHz, DMSO-*d*₆) δ 8.17(dd, *J* = 7.9, 1.7 Hz, 1H), 8.05(d, *J* = 8.1 Hz, 1H), 7.85(ddd, *J* = 8.7, 7.1, 1.8 Hz, 1H), 7.62(dd, *J* = 8.4, 1.0 Hz, 1H), 7.49-7.41 (m, 2H), 7.27(dd, *J* = 8.2, 1.5 Hz, 1H), 2.47(s, 3H). ¹³C NMR (100 MHz, DMSO-*d*₆) δ 175.66, 155.66, 155.56, 146.66, 135.36, 125.96, 125.76, 125.76, 124.56, 124.26, 121.16, 118.96, 118.16, 117.76, 21.46. HRMS-ESI (m/z): [M+H]⁺ calcd. for C₁₅H₁₂NO⁺ calcd. for 222.0919, found 222.0914.

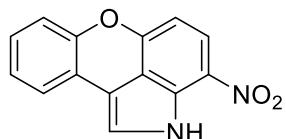


6h: yield 65%. ¹H NMR (400 MHz, DMSO-*d*₆) δ 8.19 (dd, *J* = 8.0, 1.7 Hz, 1H), 7.85 (td, *J* = 8.6, 1.8 Hz, 1H), 7.64-7.61 (m, 2H), 7.54 (d, *J* = 3.1 Hz, 1H), 7.47-7.44 (m, 2H), 3.87 (s, 3H). ¹³C NMR (100 MHz, DMSO-*d*₆) δ 176.22, 156.16, 155.96, 150.74, 135.79, 126.39, 125.13, 124.65, 121.95, 120.94, 120.25, 118.62, 106.18, 56.19. HRMS-ESI (m/z): [M+H]⁺ calcd. for C₁₅H₁₂NO₂⁺ calcd. for 238.0868, found 238.0867.



6i: yield 63%. ¹H NMR (400 MHz, DMSO-*d*₆) δ 8.15 (dd, *J* = 7.9, 1.7 Hz, 1H), 8.07 (d, *J* = 8.8 Hz, 1H), 7.82 (ddd, *J* = 8.7, 7.1, 1.8 Hz, 1H), 7.58 (dd, *J* = 8.5, 1.0 Hz, 1H),

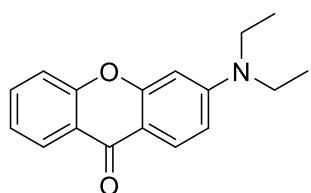
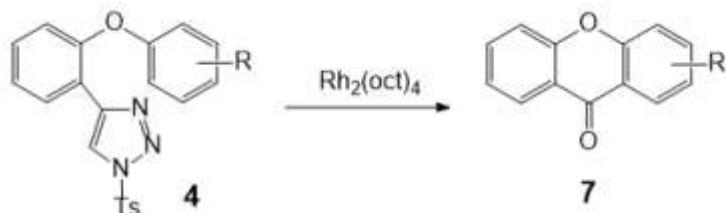
7.45 (ddd, $J = 8.0, 7.1, 1.1$ Hz, 1H), 7.10 (d, $J = 2.4$ Hz, 1H), 7.02 (dd, $J = 8.9, 2.4$ Hz, 1H), 3.92 (s, 3H). ^{13}C NMR (100 MHz, DMSO- d_6) δ 174.81, 164.91, 157.51, 155.51, 134.91, 127.51, 125.81, 124.21, 121.11, 117.81, 114.91, 113.61, 100.51, 56.11. HRMS-ESI (m/z): [M+H] $^+$ calcd. for C₁₅H₁₂NO₂ $^+$ calcd. for 238.0868, found 238.0864.



6j

6j: yield 73%. ^1H NMR (400 MHz, DMSO- d_6) δ 8.36 (d, $J = 8.0$ Hz, 2H), 7.94 (d, $J = 8.0$ Hz, 2H), 7.51 (t, $J = 7.6$ Hz, 1H), 7.42 (d, $J = 7.5$ Hz, 1H), 7.09-6.86 (m, 2H). ^{13}C NMR (100 MHz, DMSO- d_6) δ 196.04, 157.27, 149.45, 142.83, 134.23, 131.68, 131.47, 130.71, 130.20, 128.62, 123.82, 123.62, 119.33, 116.89. HRMS-ESI (m/z): [M+H] $^+$ calcd. for C₁₄H₈N₂O₃ $^+$ 253.0613, found 253.0611.

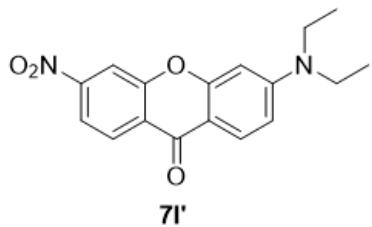
NMR and HRMS data of compound 7



7k

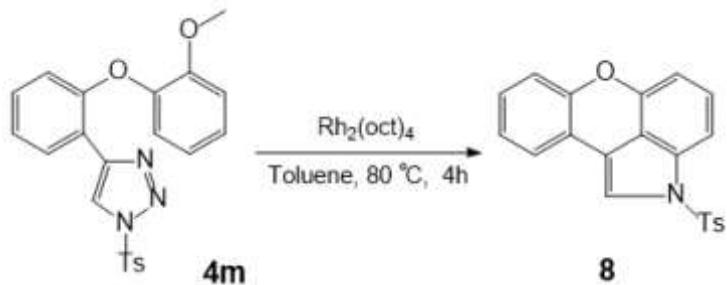
7k: yield 75%. ^1H NMR (400 MHz, DMSO- d_6) δ 8.11 (dd, $J = 7.9, 1.7$ Hz, 1H), 7.93 (d, $J = 9.1$ Hz, 1H), 7.75 (td, $J = 8.6, 1.8$ Hz, 1H), 7.53 (d, $J = 8.3$ Hz, 1H), 7.41 (t, $J = 7.7$ Hz, 1H), 6.83 (dd, $J = 9.12, 2.3$ Hz, 1H), 6.57 (d, $J = 2.4$ Hz, 1H), 3.47 (q, $J = 7.0$ Hz, 2H).

Hz, 4H), 1.15 (t, J = 7.0 Hz, 6H). ^{13}C NMR (100 MHz, DMSO- d_6) δ 197.21, 174.23, 158.49, 155.93, 153.12, 134.58, 127.91, 126.14, 124.14, 122.08, 117.95, 110.55, 110.24, 96.20, 44.62, 12.77. HRMS-ESI (m/z): [M+H] $^+$ calcd. for C₁₇H₁₈NO₂ $^+$ 268.1332, found 268.1339.



7l': yield 80%. ^1H NMR (400 MHz, CDCl₃) δ 8.38 (d, J = 8.7 Hz, 1H), 8.19 (d, J = 2.1 Hz, 1H), 8.10 – 7.99 (m, 2H), 6.68 (dd, J = 9.2, 2.5 Hz, 1H), 6.45 (d, J = 2.5 Hz, 1H), 3.43 (q, J = 7.1 Hz, 4H), 1.21 (t, J = 7.1 Hz, 7H). ^{13}C NMR (100 MHz, CDCl₃) δ 172.74, 157.98, 154.52, 152.43, 149.48, 128.72, 127.41, 127.17, 125.46, 116.55, 112.48, 110.13, 109.30, 95.04, 43.97, 11.46. HRMS-ESI (m/z): [M+H] $^+$ calcd. for C₁₇H₁₇N₂O₄ $^+$ 313.1183, found: 313.1189.

NMR and HRMS data of compound 8



8: yield 78%. ^1H NMR (400 MHz, DMSO- d_6) δ 7.90 – 7.87 (m, 2H), 7.81 – 7.79 (m, 2H), 7.42 – 7.39 (m, 3H), 7.33 – 7.28 (m, 2H), 7.21 – 7.16 (m, 2H), 6.80 (d, J = 8.0 Hz, 1H), 2.32 (s, 3H), 1.21 (t, J = 7.1 Hz, 7H). ^{13}C NMR (100 MHz, DMSO- d_6) δ 152.25, 147.42, 145.57, 134.40, 134.00, 130.30, 129.99, 128.18, 126.54, 125.64, 124.33, 119.41, 117.76, 116.89, 114.96, 113.49, 107.38, 105.84, 20.99. HRMS-ESI (m/z): [M+H] $^+$ calcd. for C₂₁H₁₆NO₃S $^+$ 362.0845, found: 362.0844.

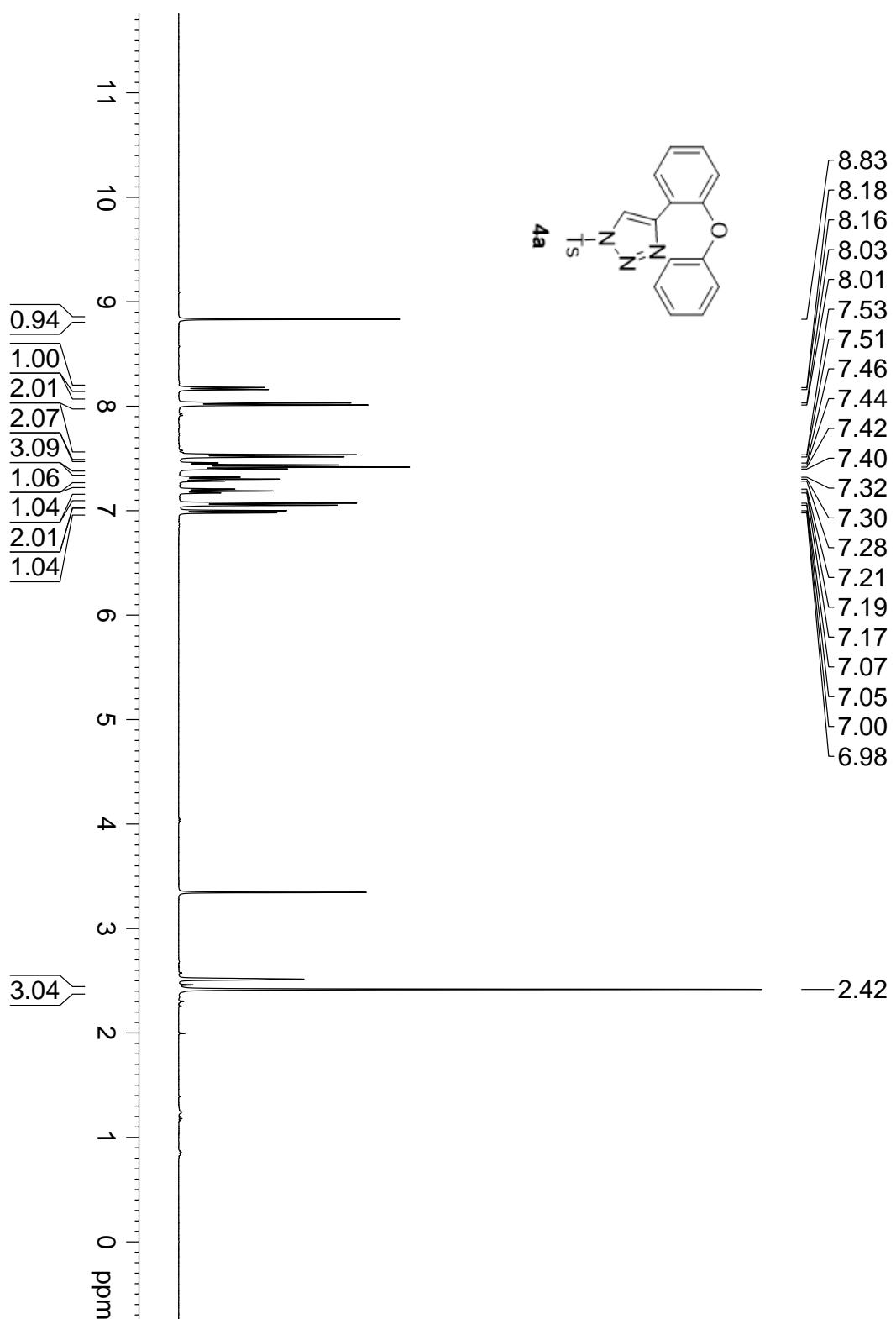
Reference

1. Tietze L F, Dr. M. Alexander Dufert, Hungerland T, et al. Synthesis and Photochemical Investigations of Tetrasubstituted Alkenes as Molecular Switches-The Effect of Substituents. *Chemistry*, 2011, 17(30):8452-8461.
2. Crosby G A, Demas J N. Measurement of photoluminescence quantum yields. Review. *Journal of Physical Chemistry*, 1971, 75(8):991-1024.

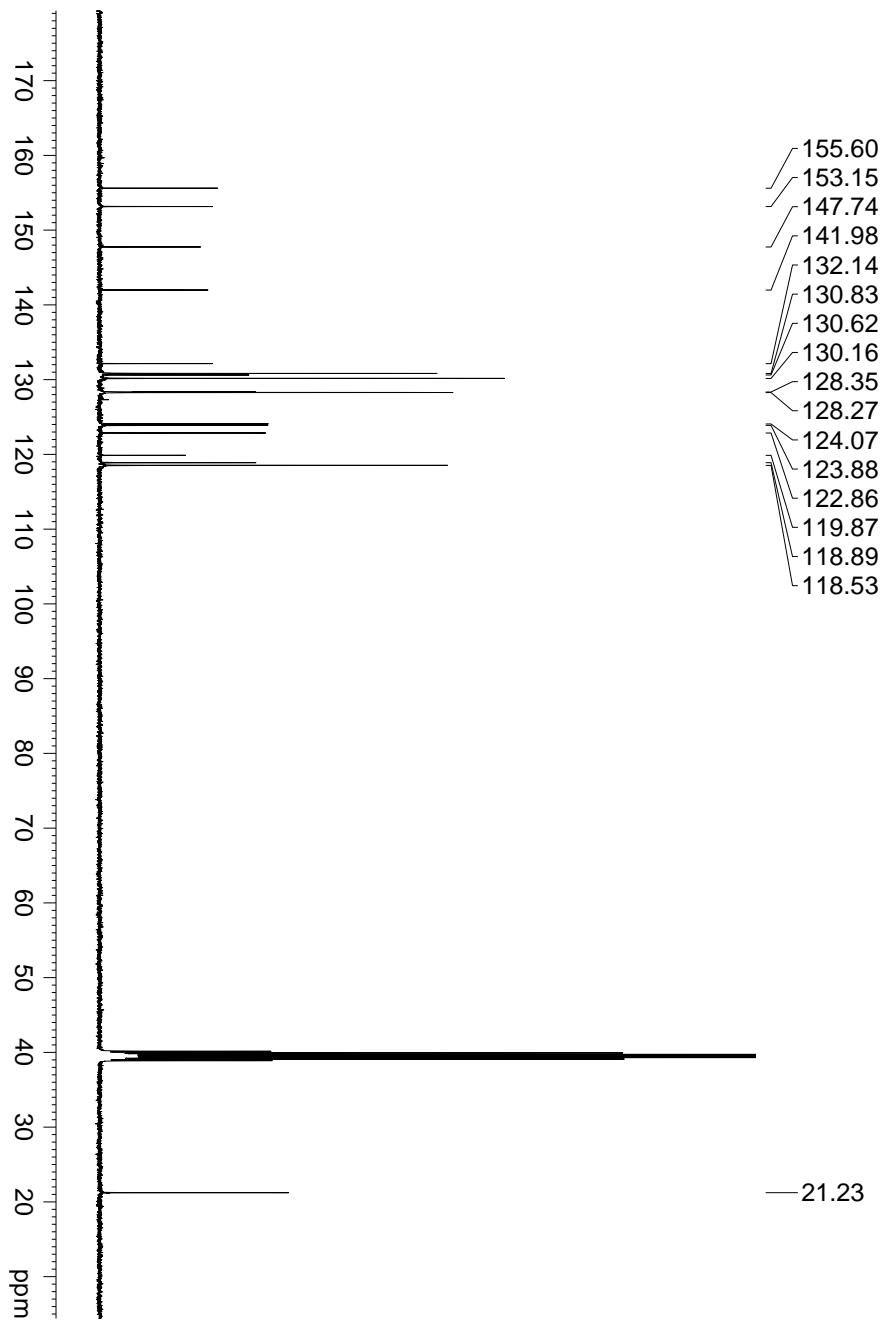
¹H NMR and ¹³C NMR spectra of **4**

Compound **4a**

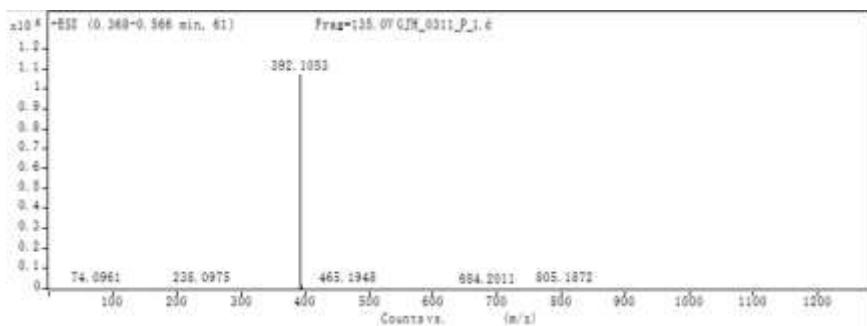
¹H NMR



¹³C NMR

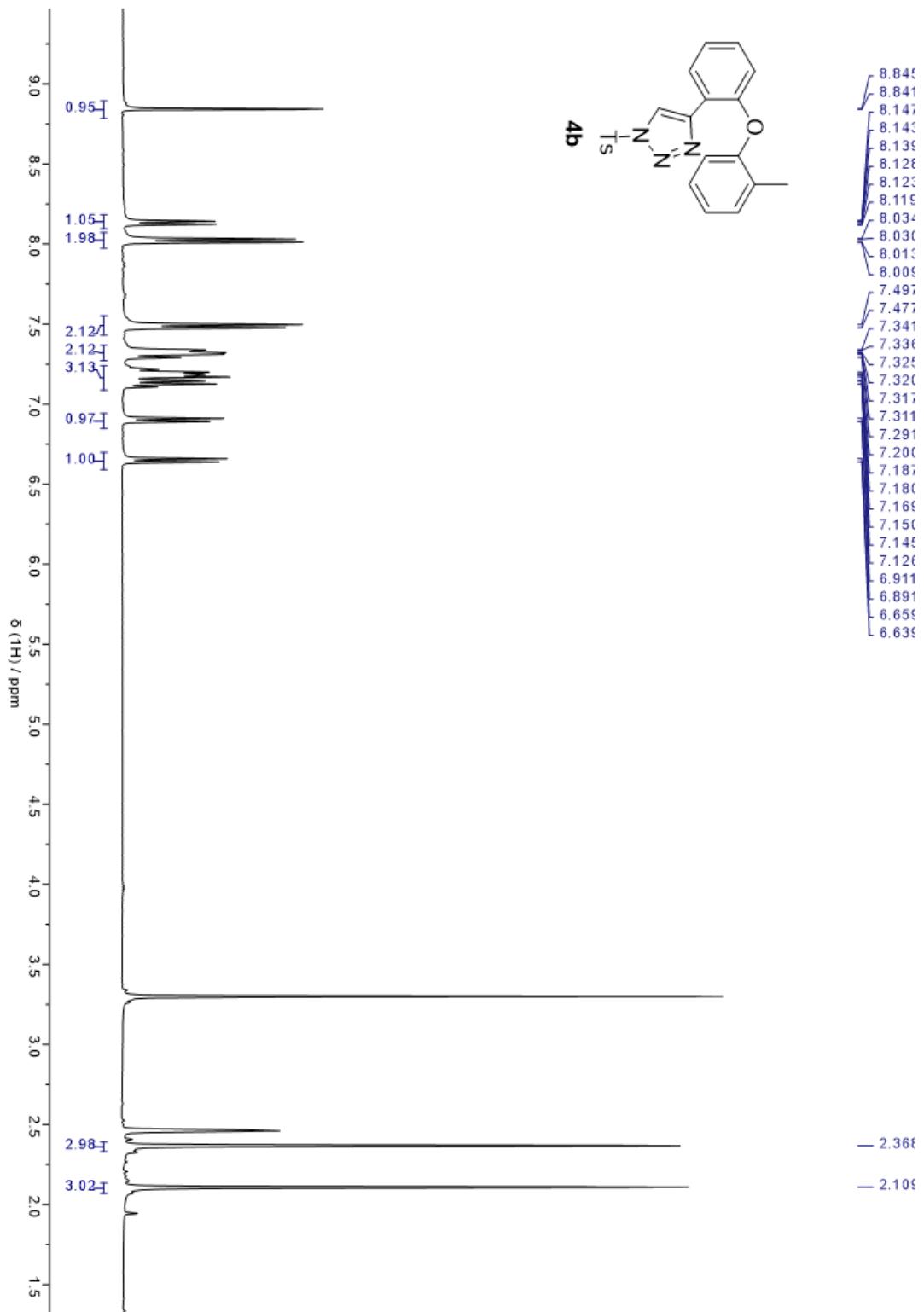


HRMS

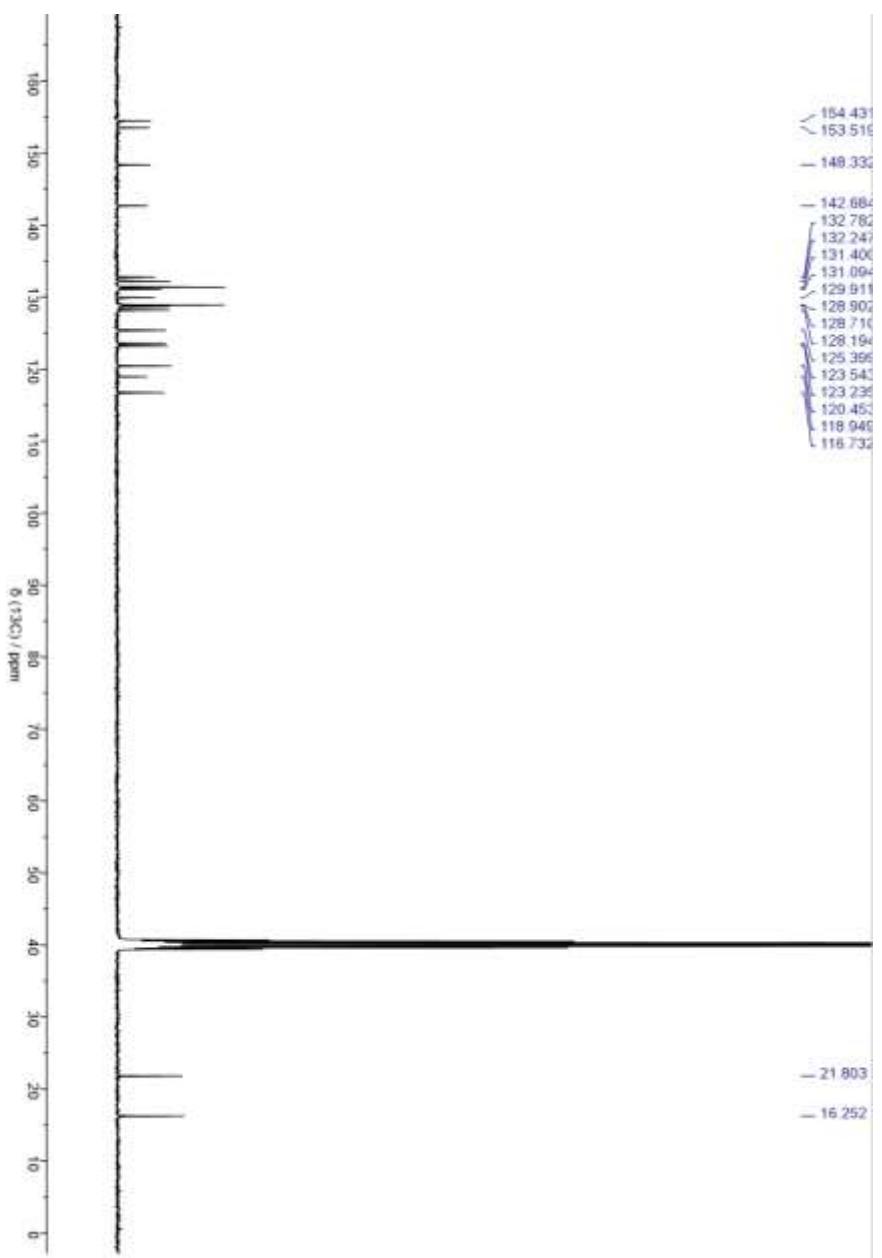


Compound **4b**

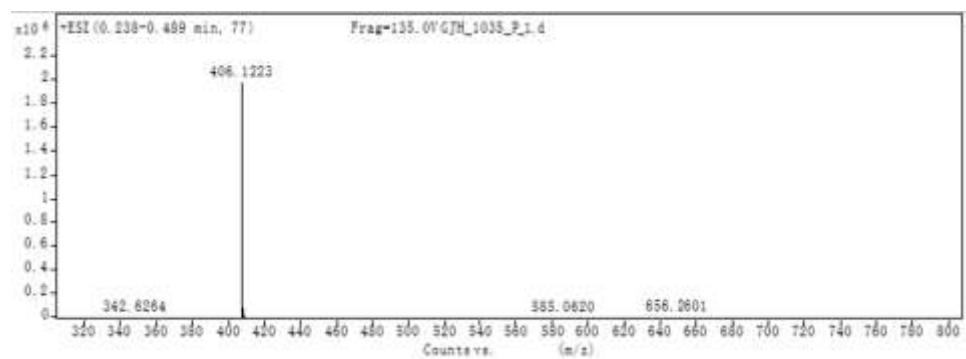
¹H NMR



¹³C NMR

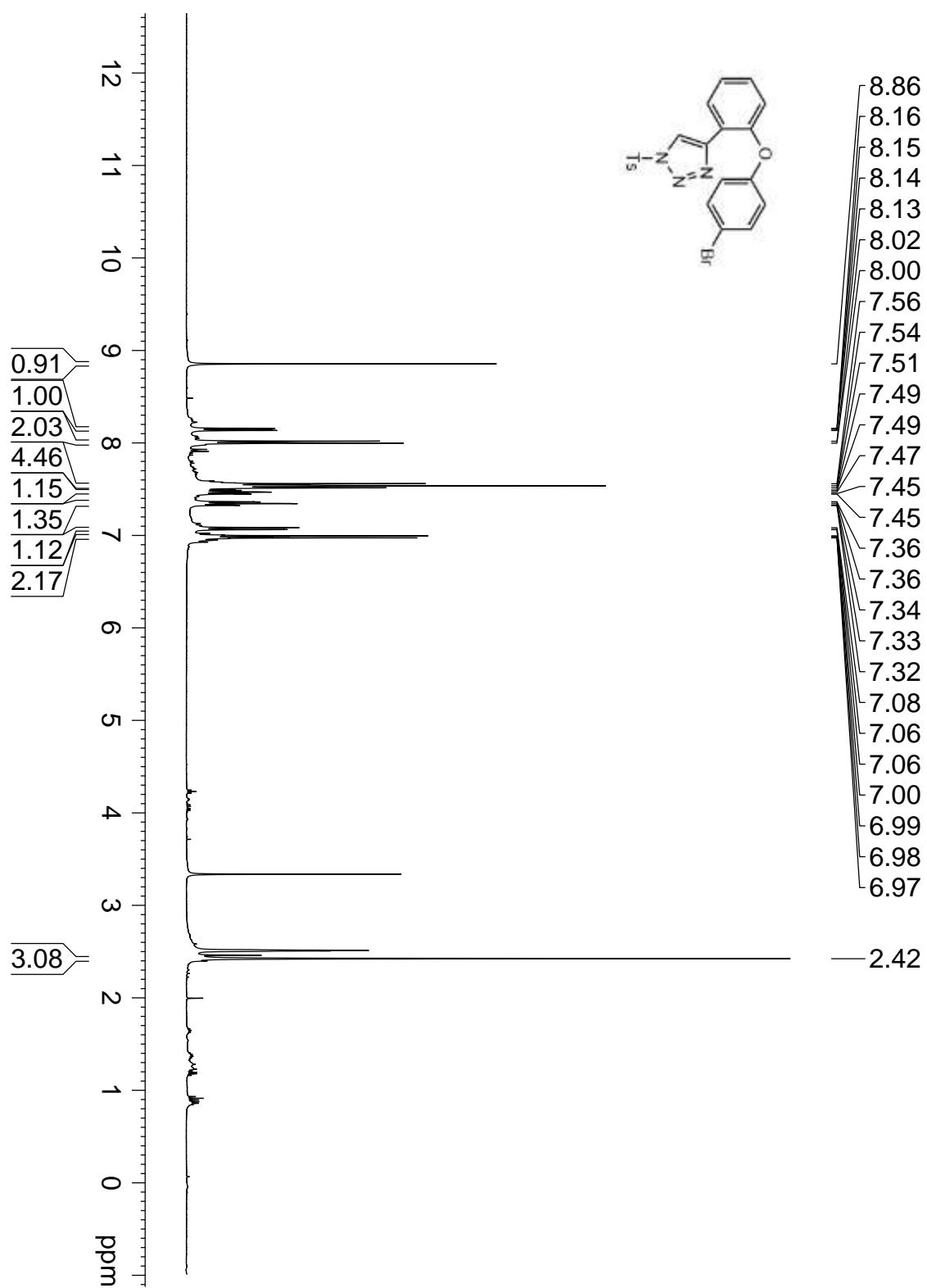


HRMS

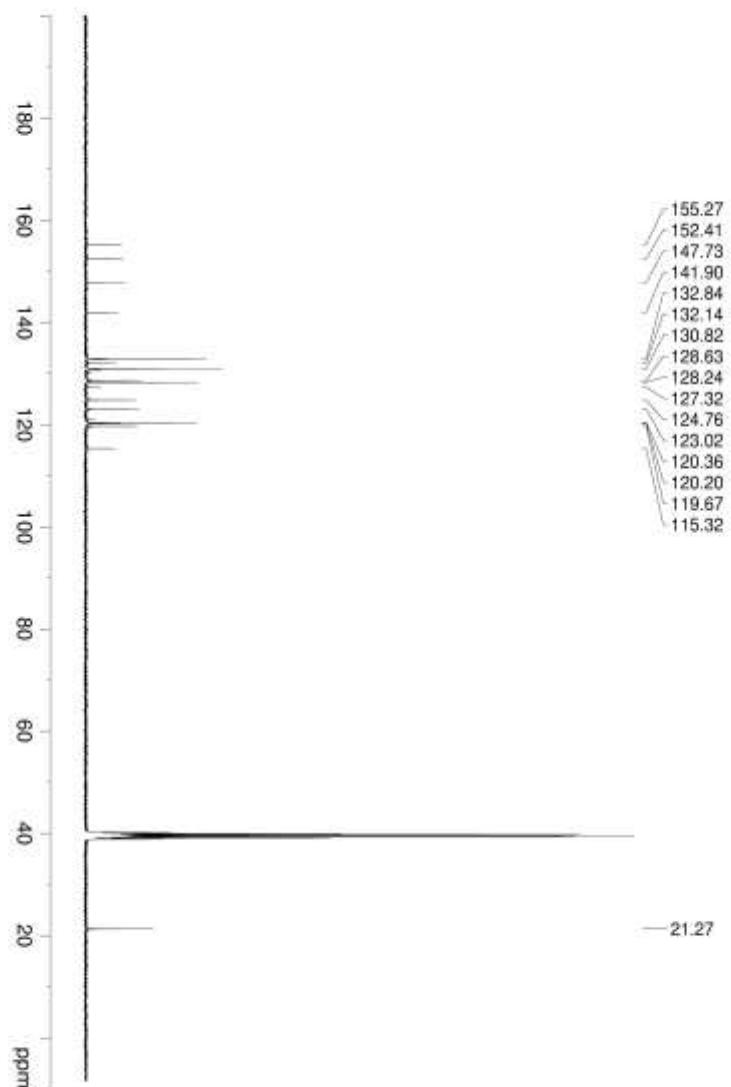


Compound **4c**

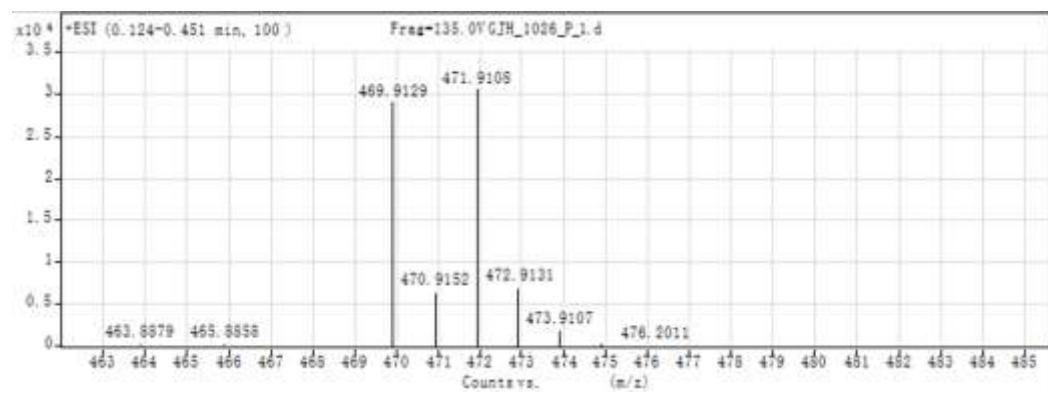
¹H NMR



¹³C NMR

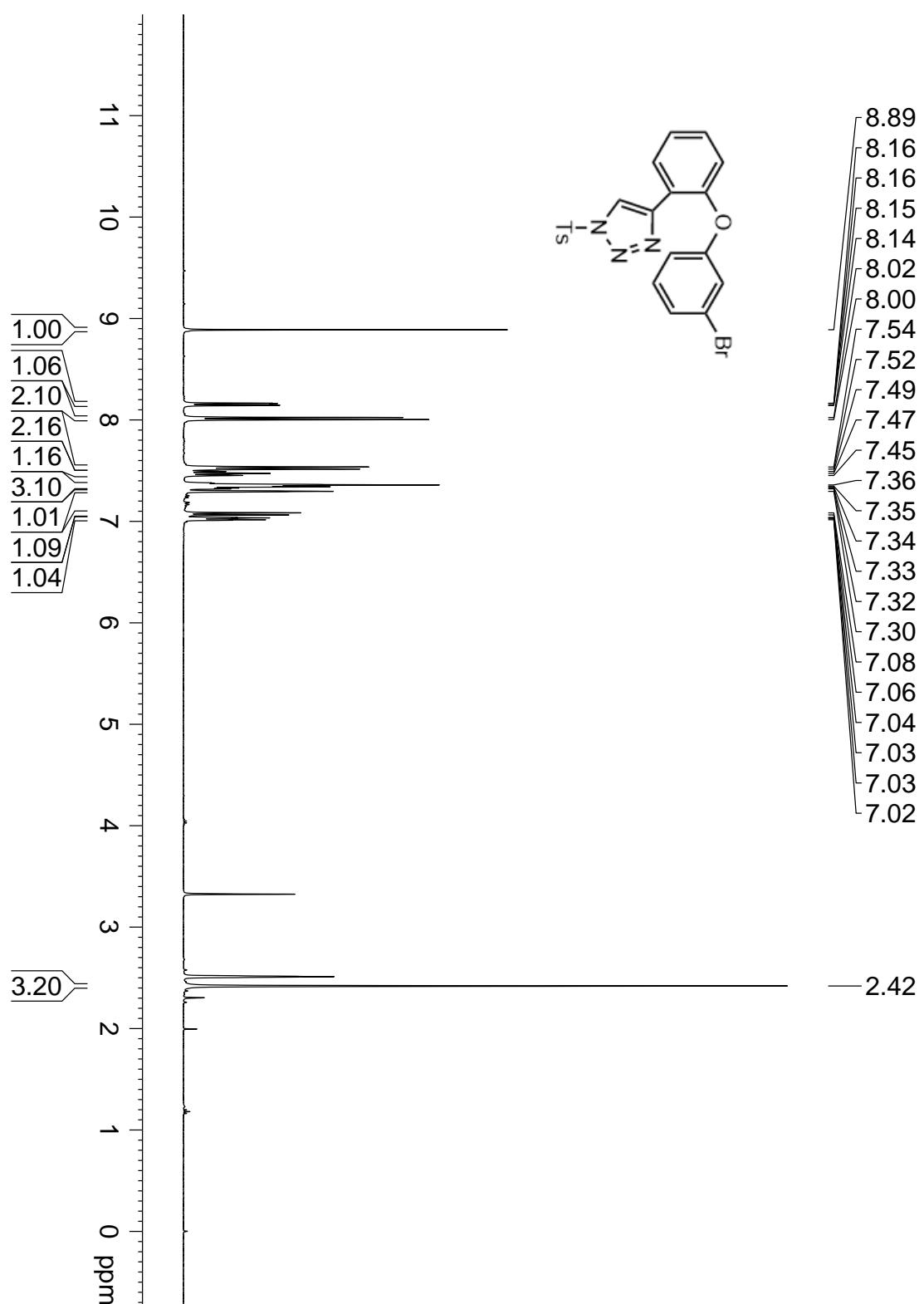


HRMS

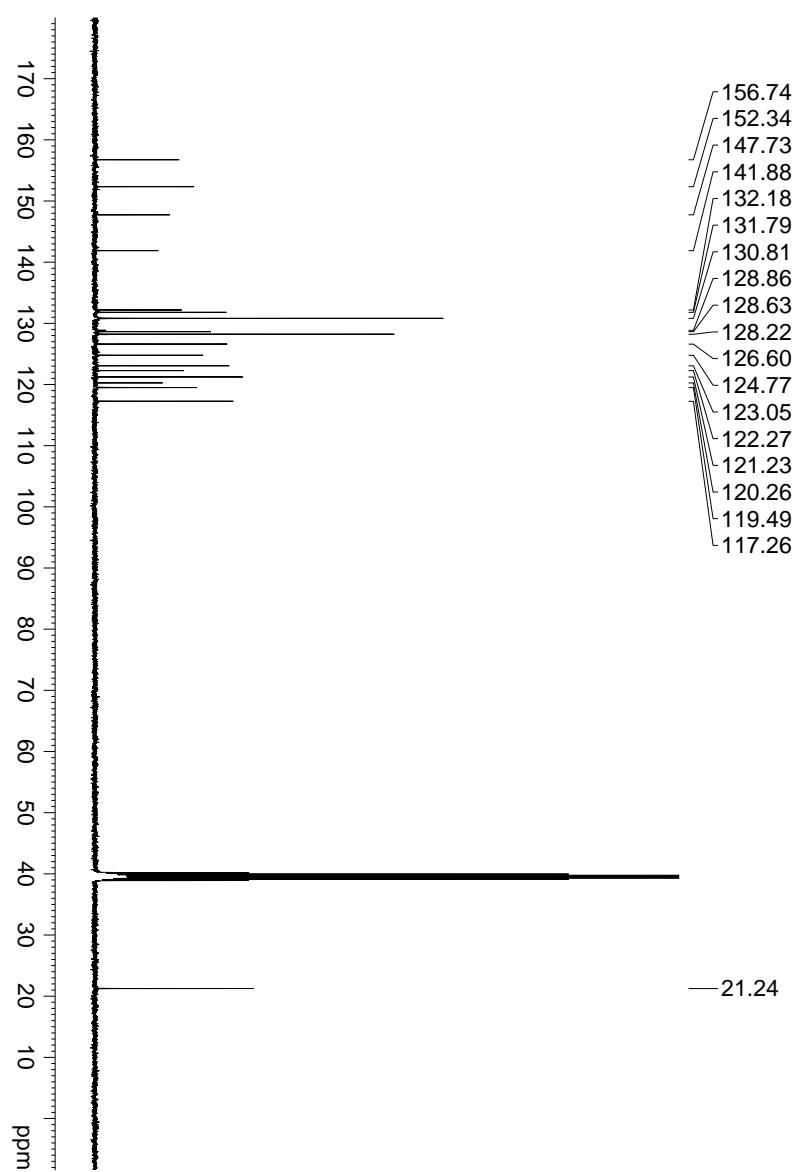


Compound **4d**

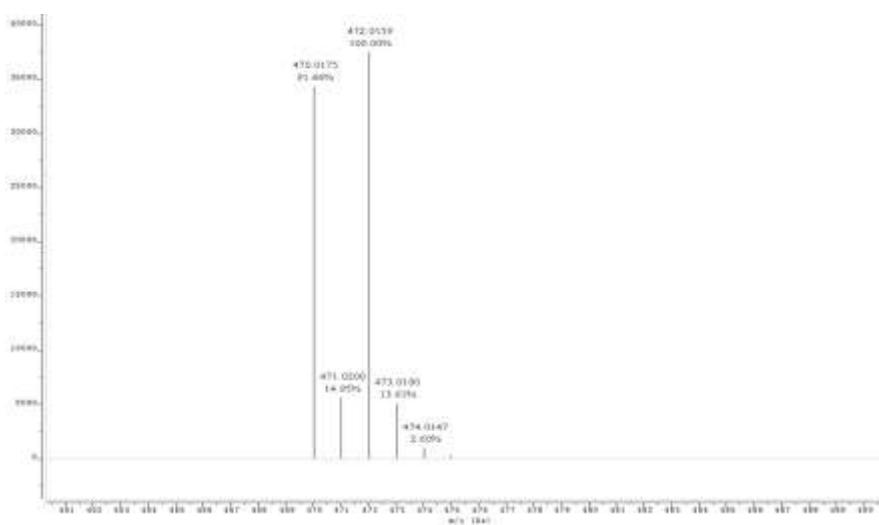
¹H NMR



¹³C NMR

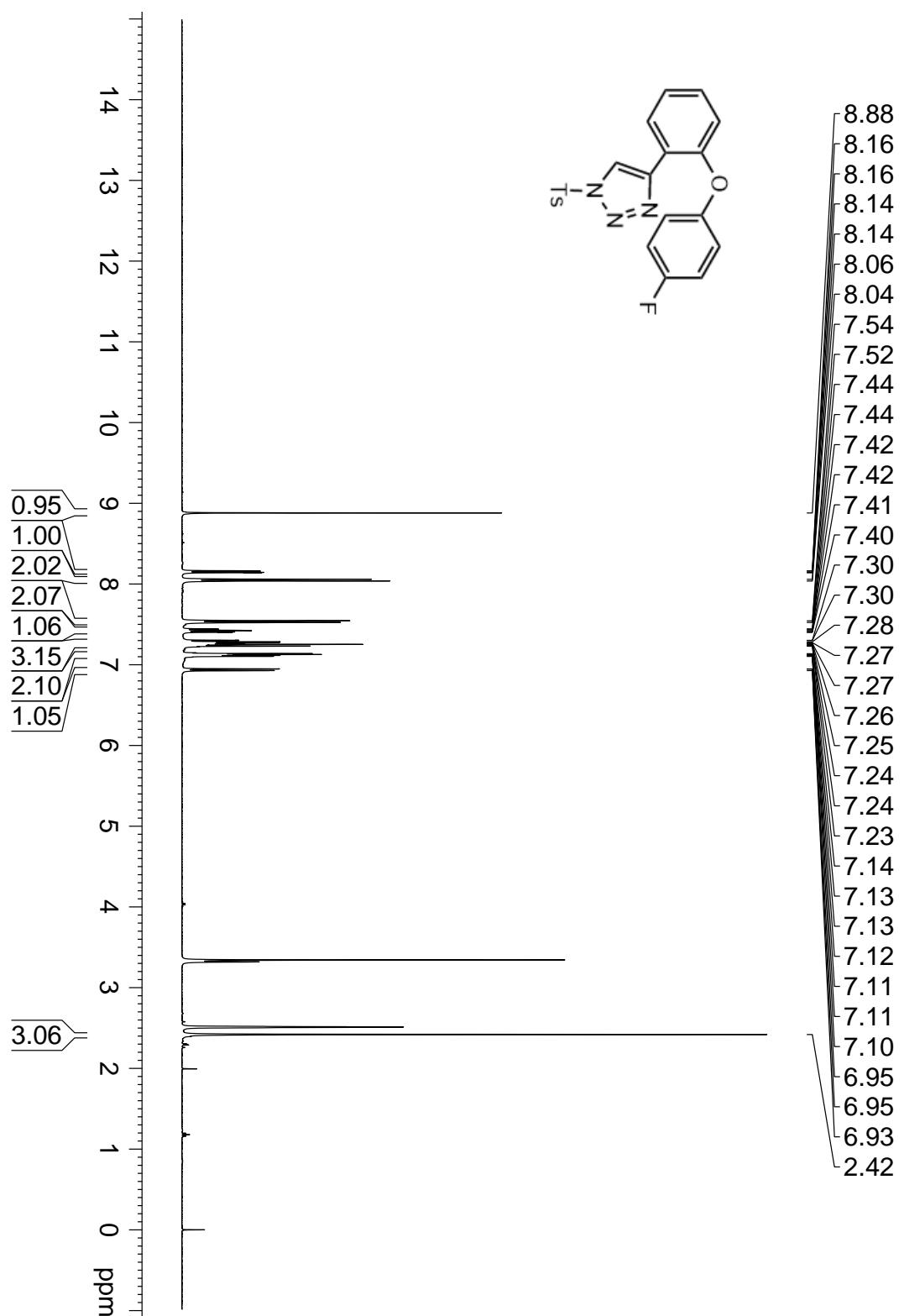


HRMS

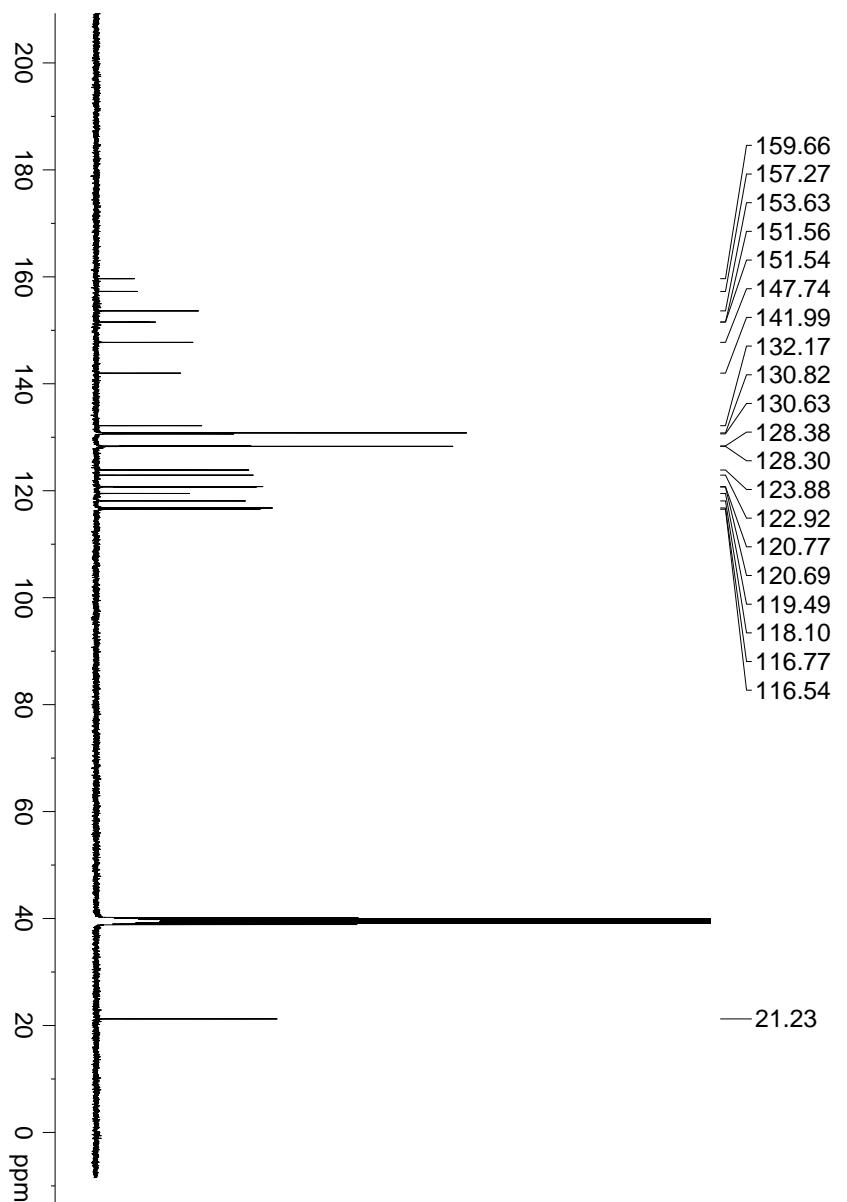


Compound **4e**

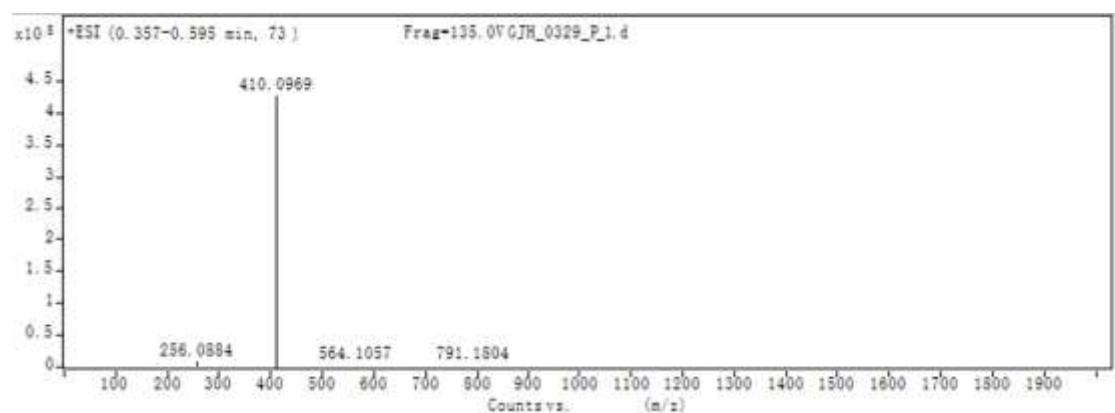
¹H NMR



¹³C NMR

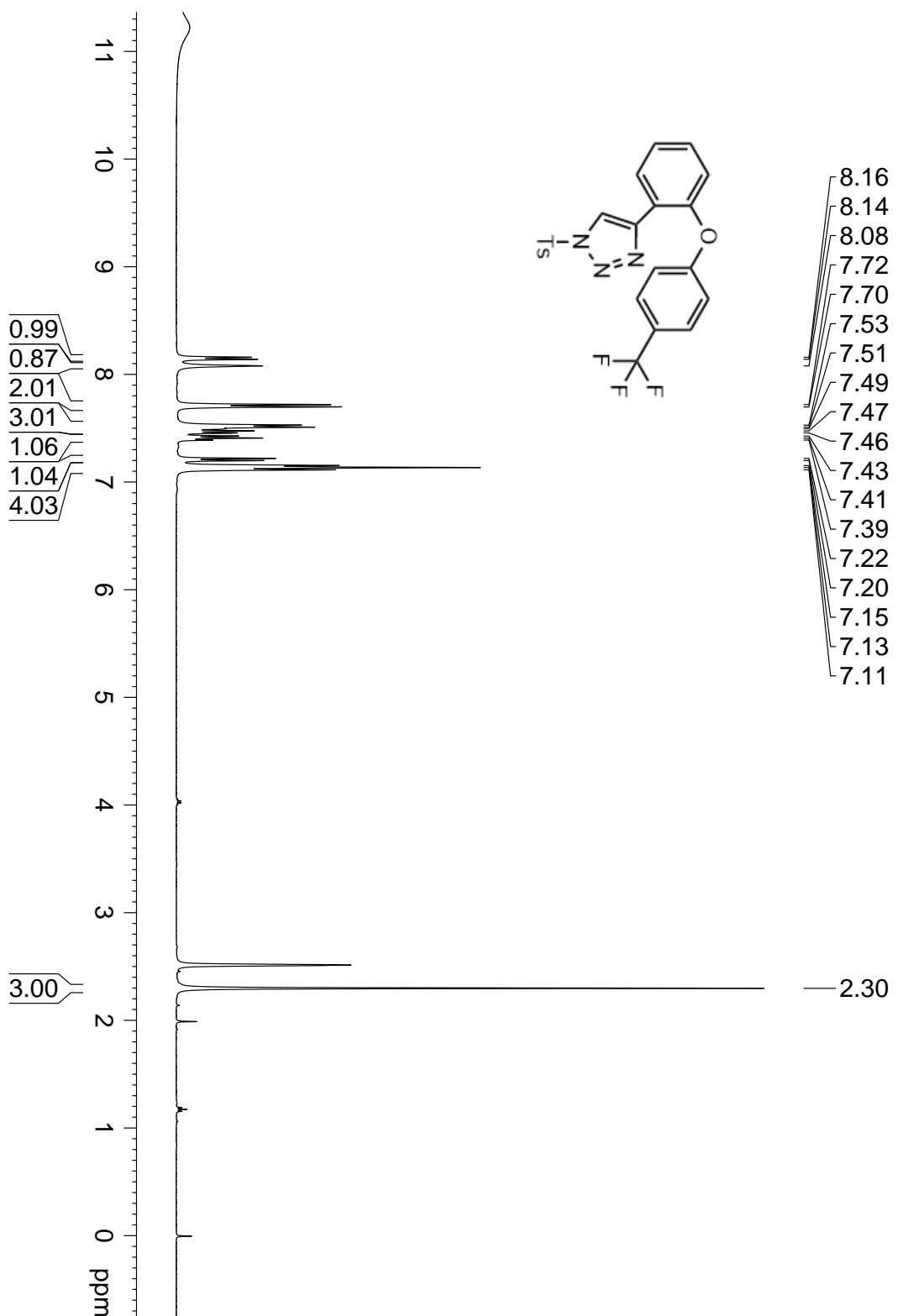


HRMS

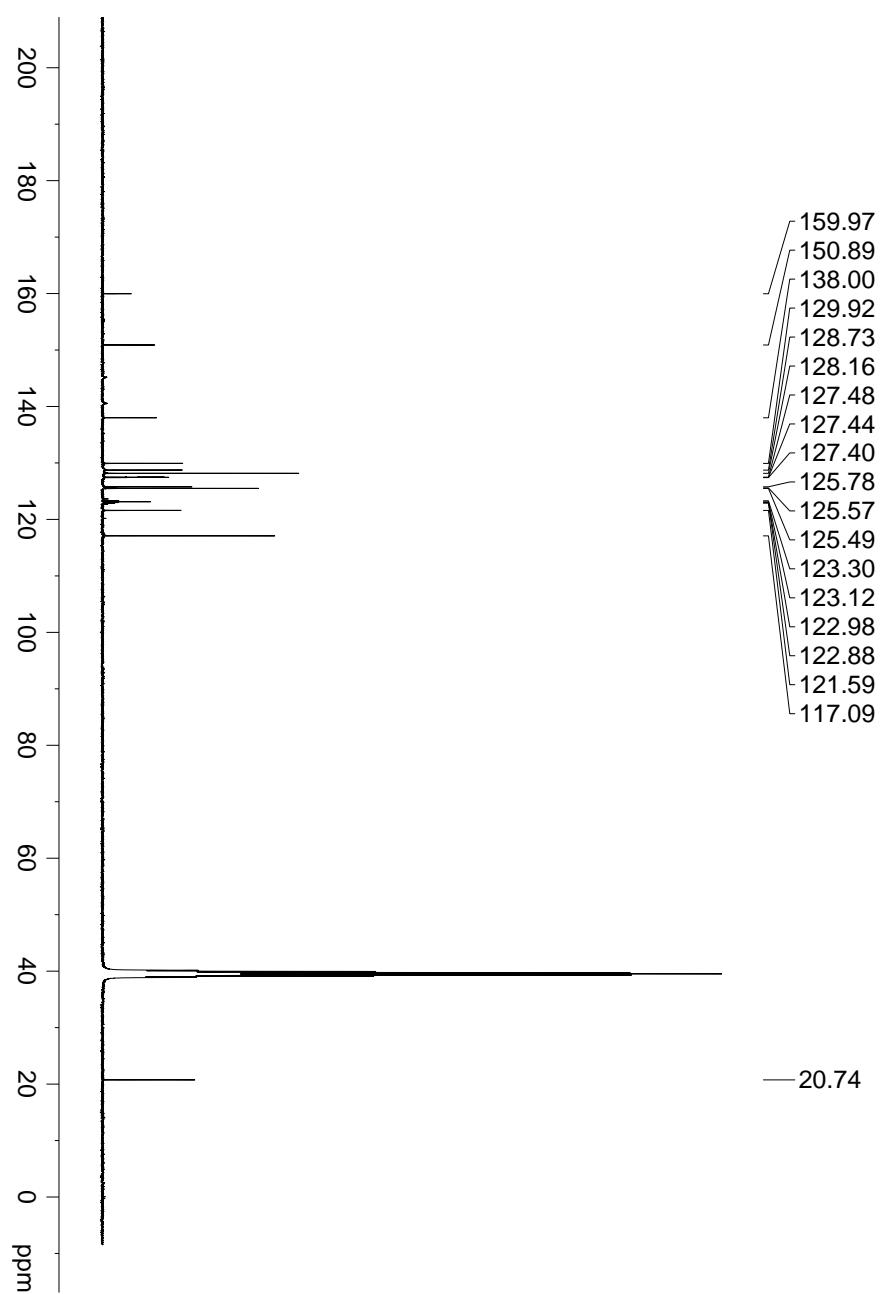


Compound 4f

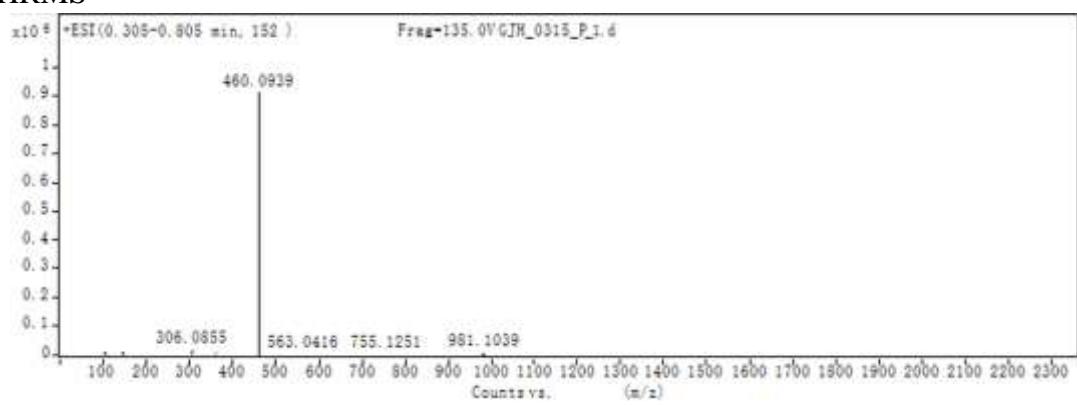
¹H NMR



¹³C NMR

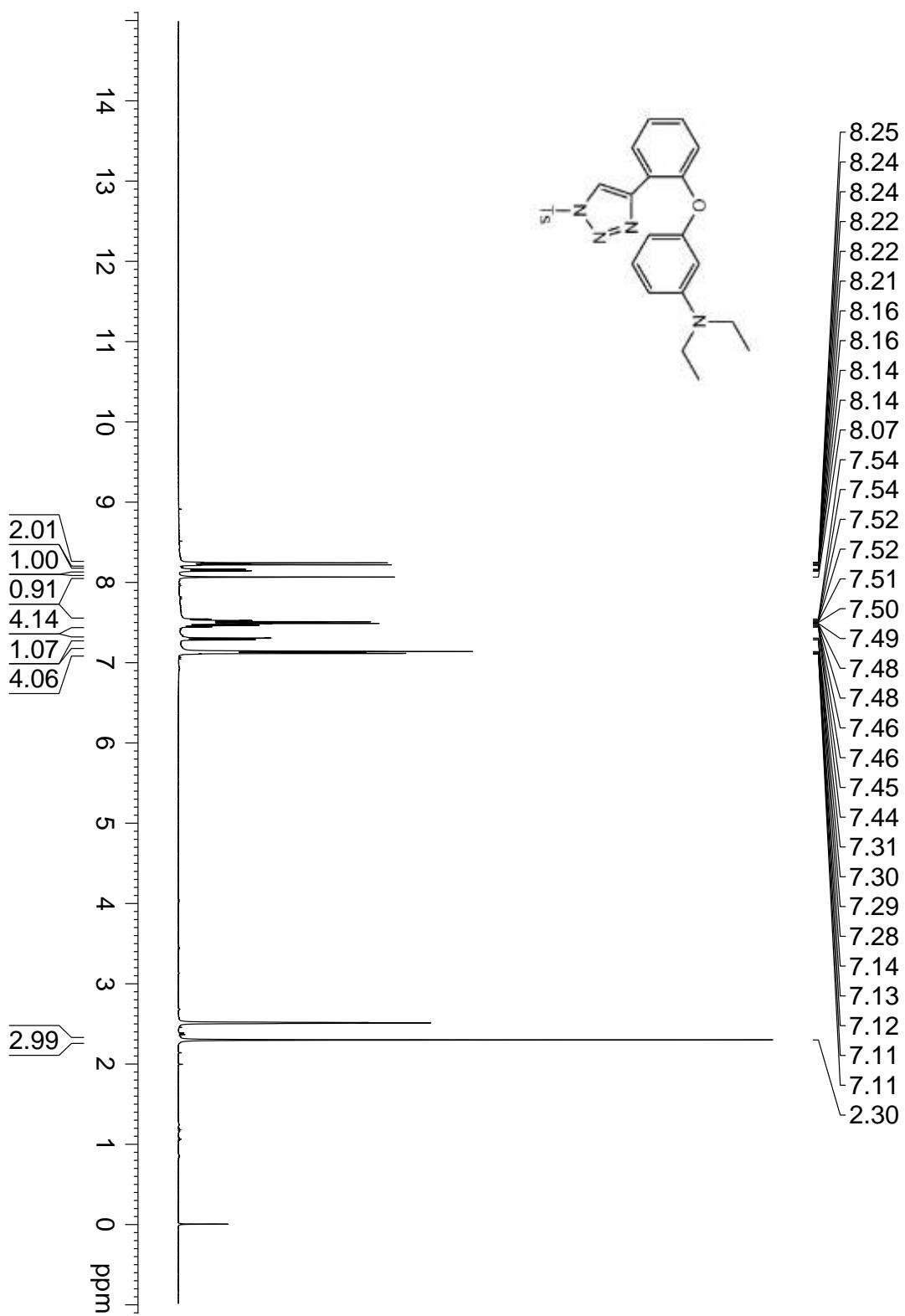


HRMS

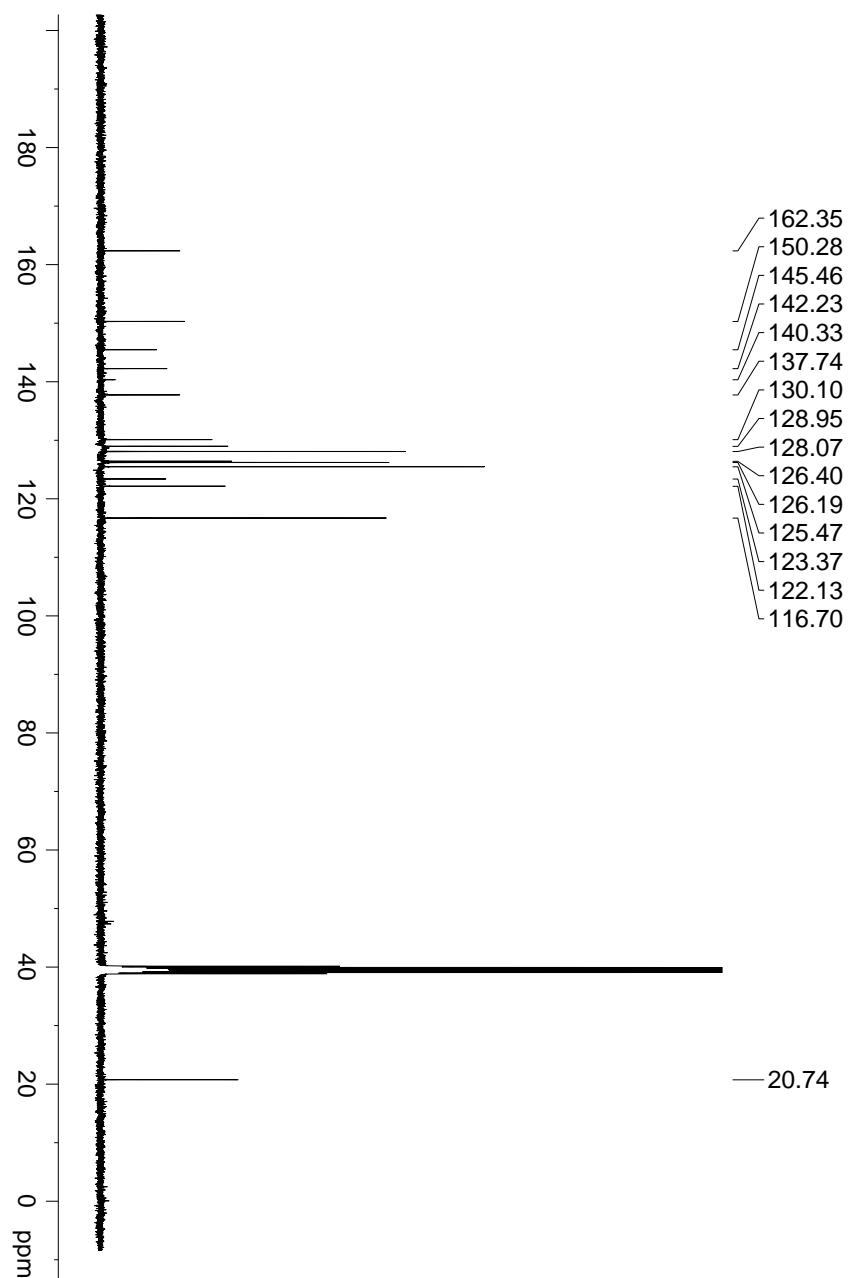


Compound **4k**

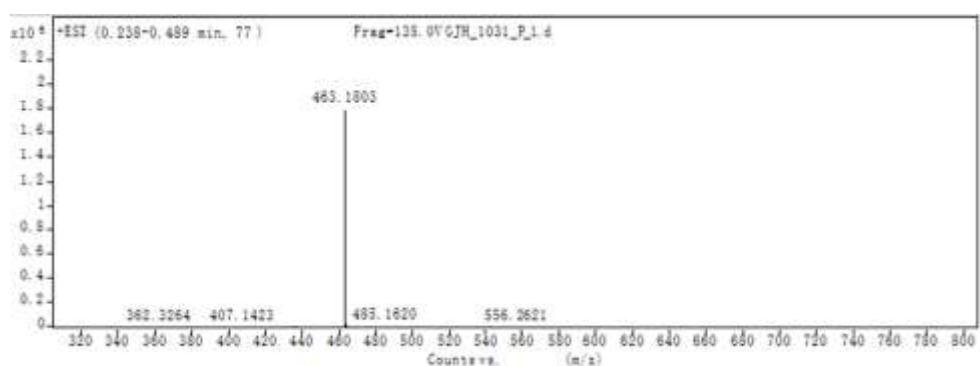
¹H NMR



¹³C NMR

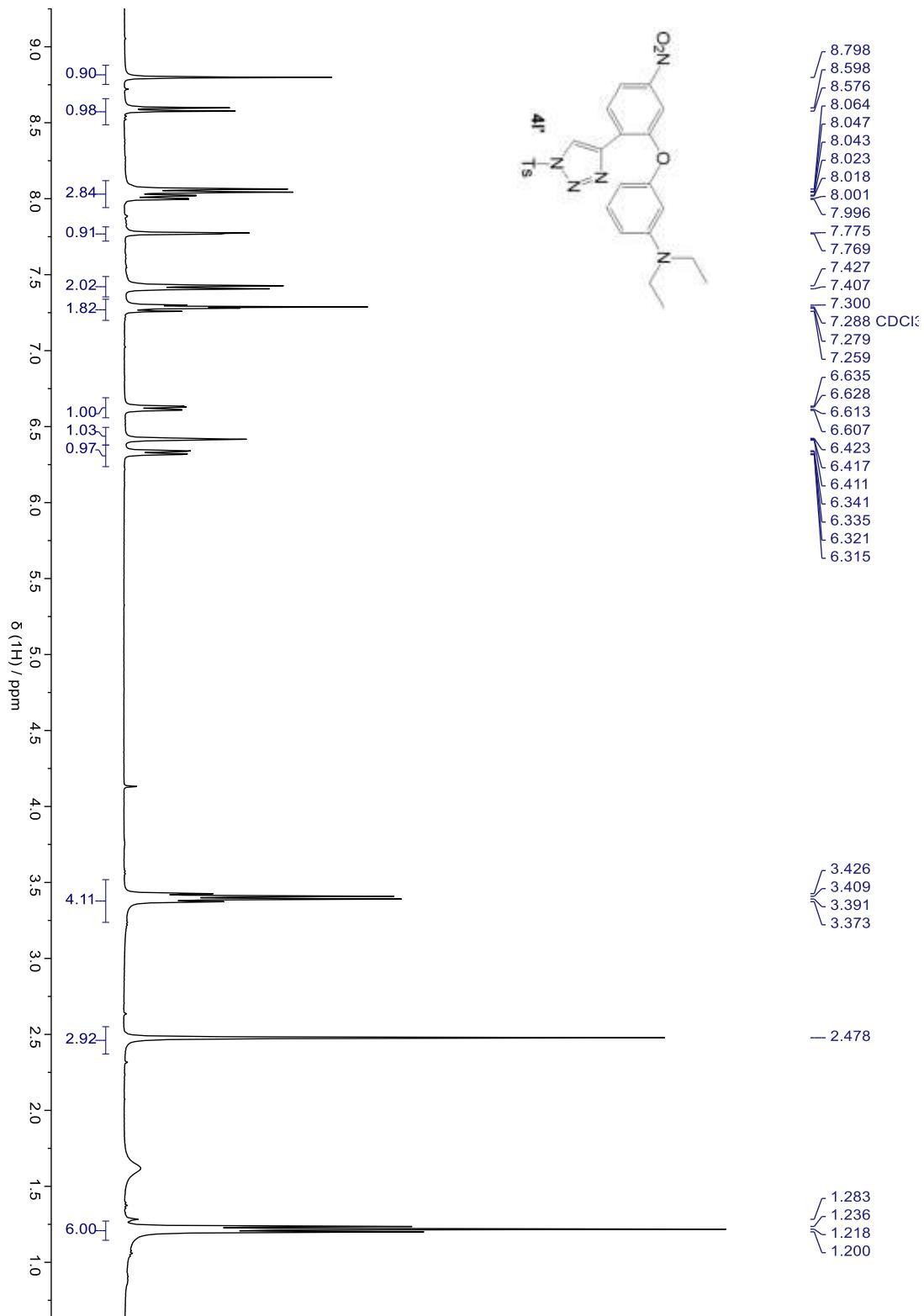


HRMS

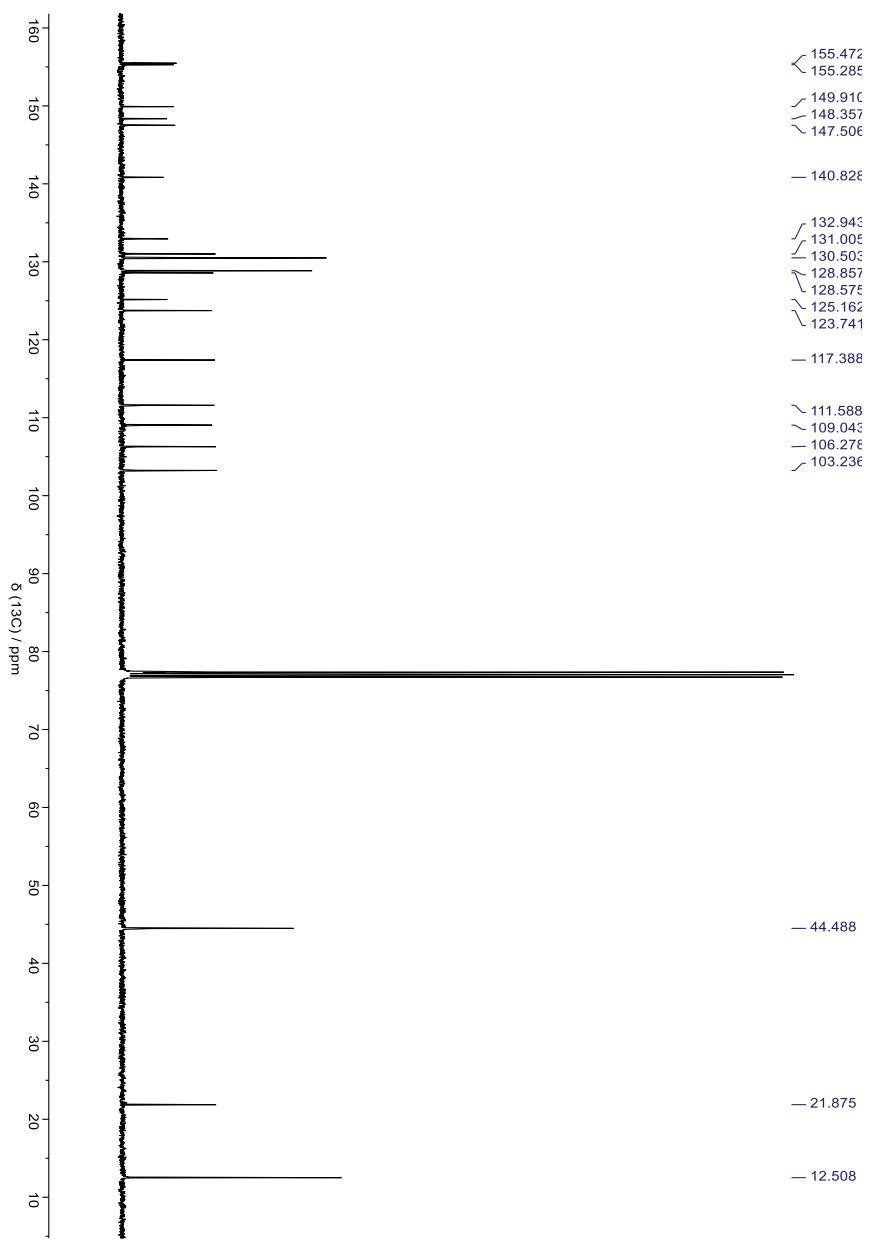


Compound 4l'

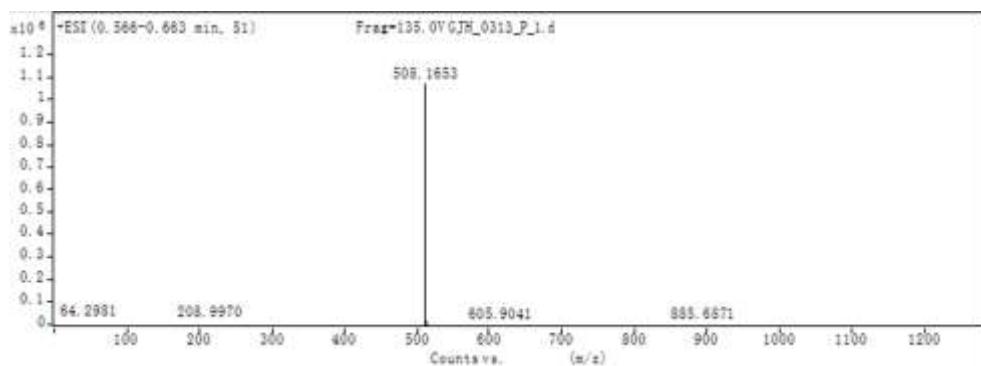
^1H NMR



¹³C NMR

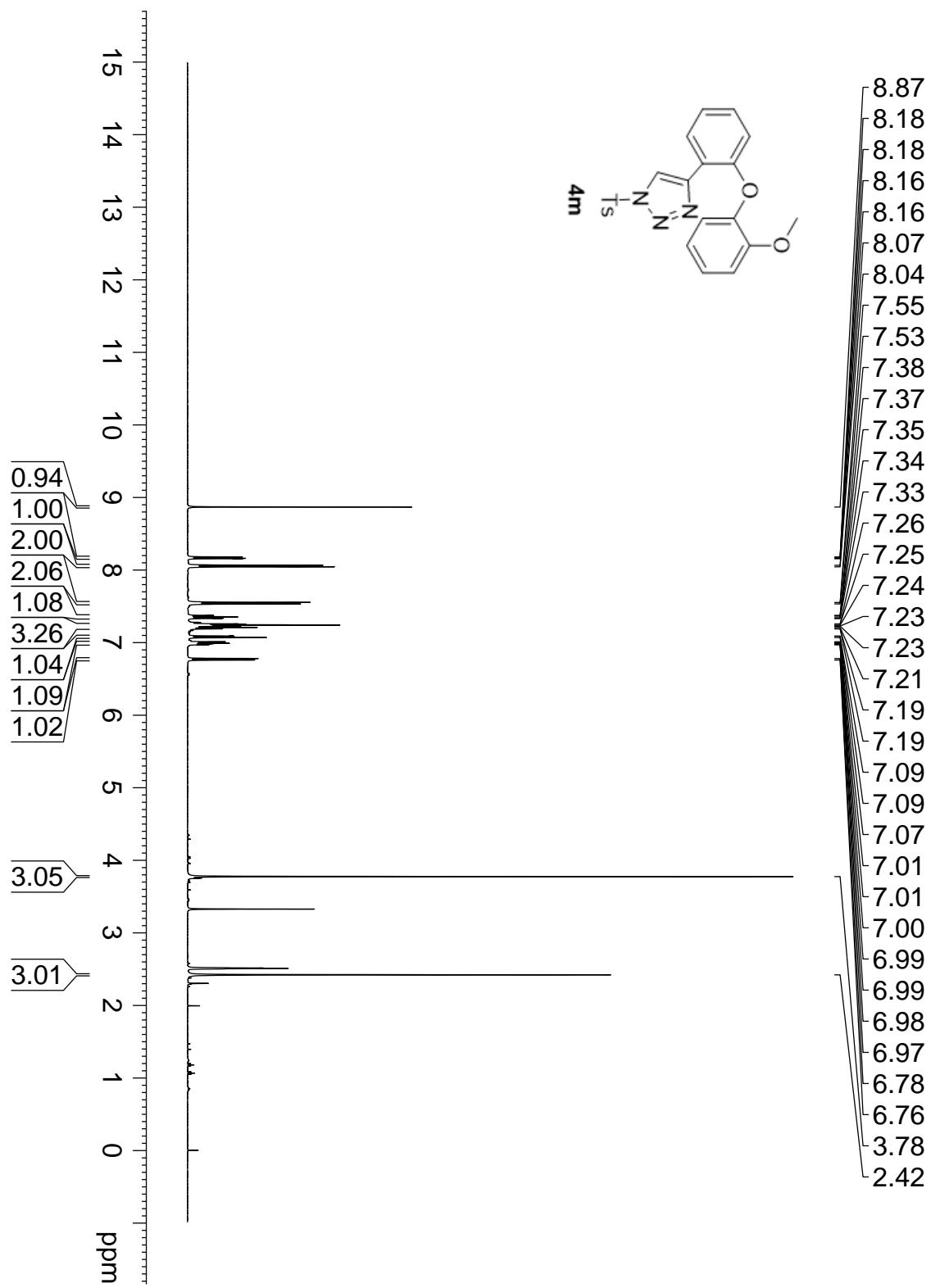


HRMS

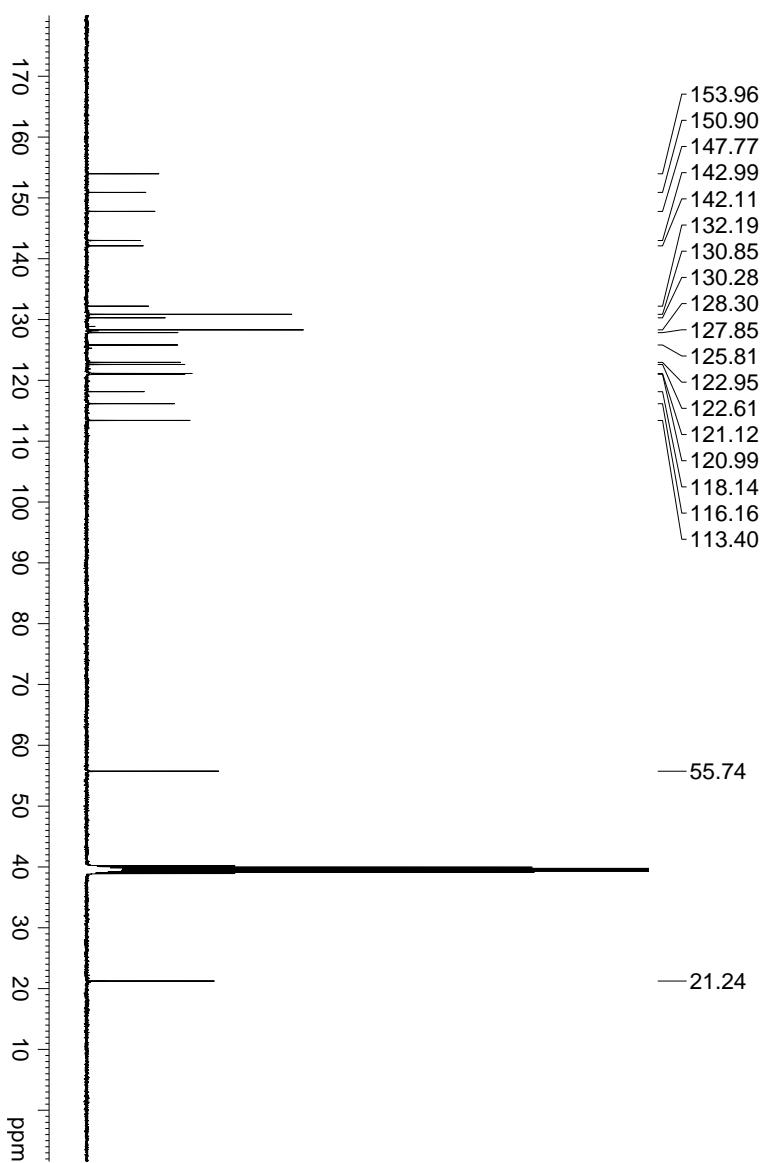


Compound **4m**

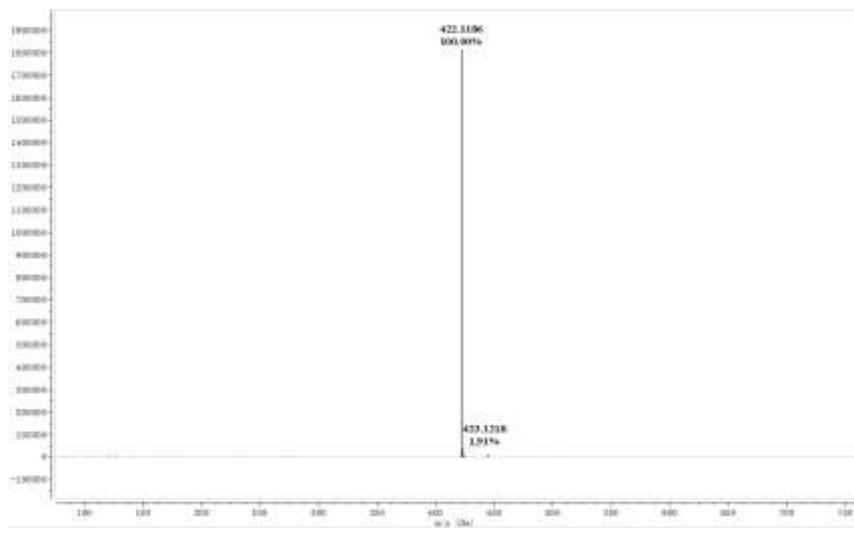
^1H NMR



¹³C NMR



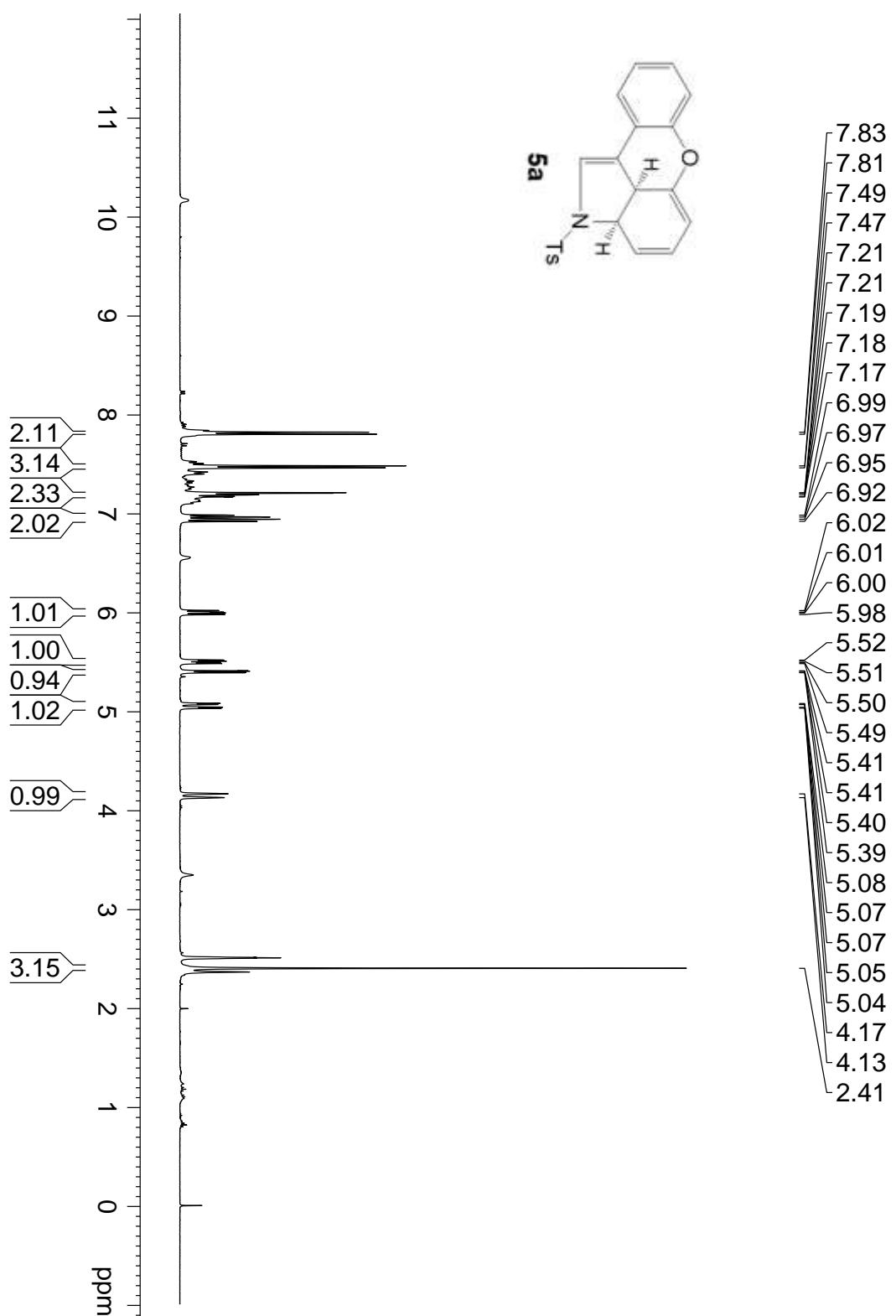
HRMS



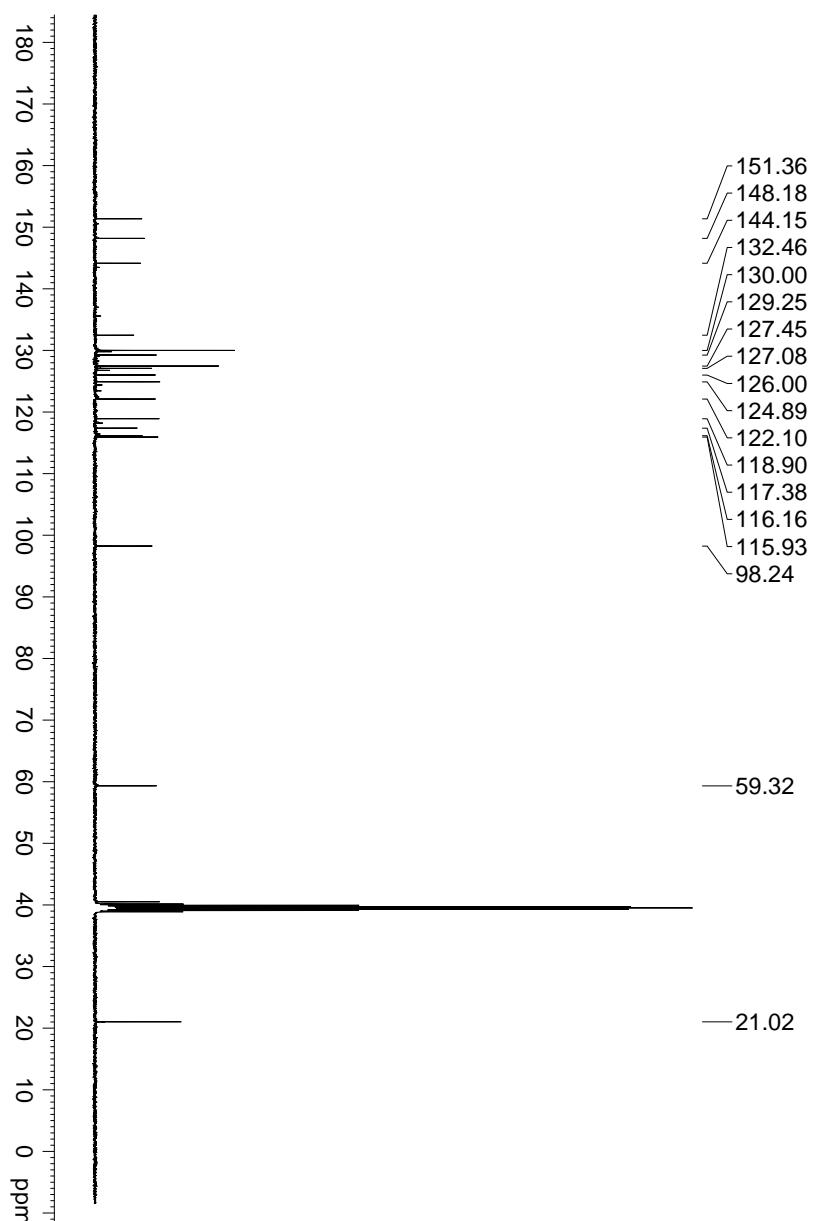
¹H NMR, ¹³C NMR and HRMS spectra of 5-8

Compound 5a

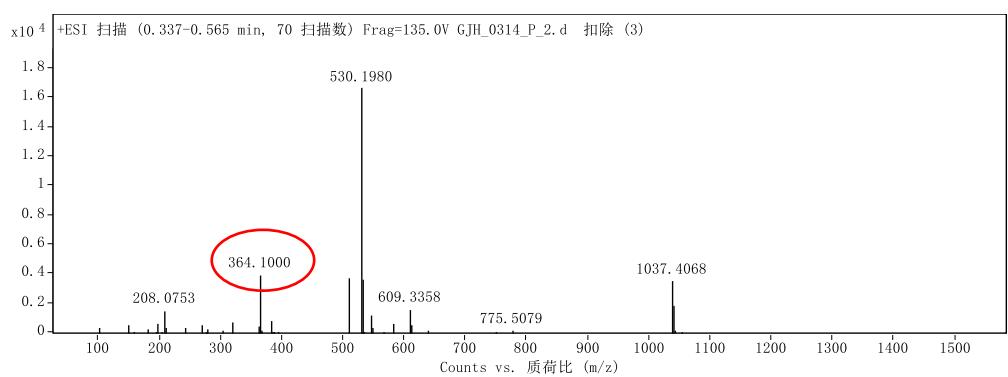
¹H NMR



¹³C NMR

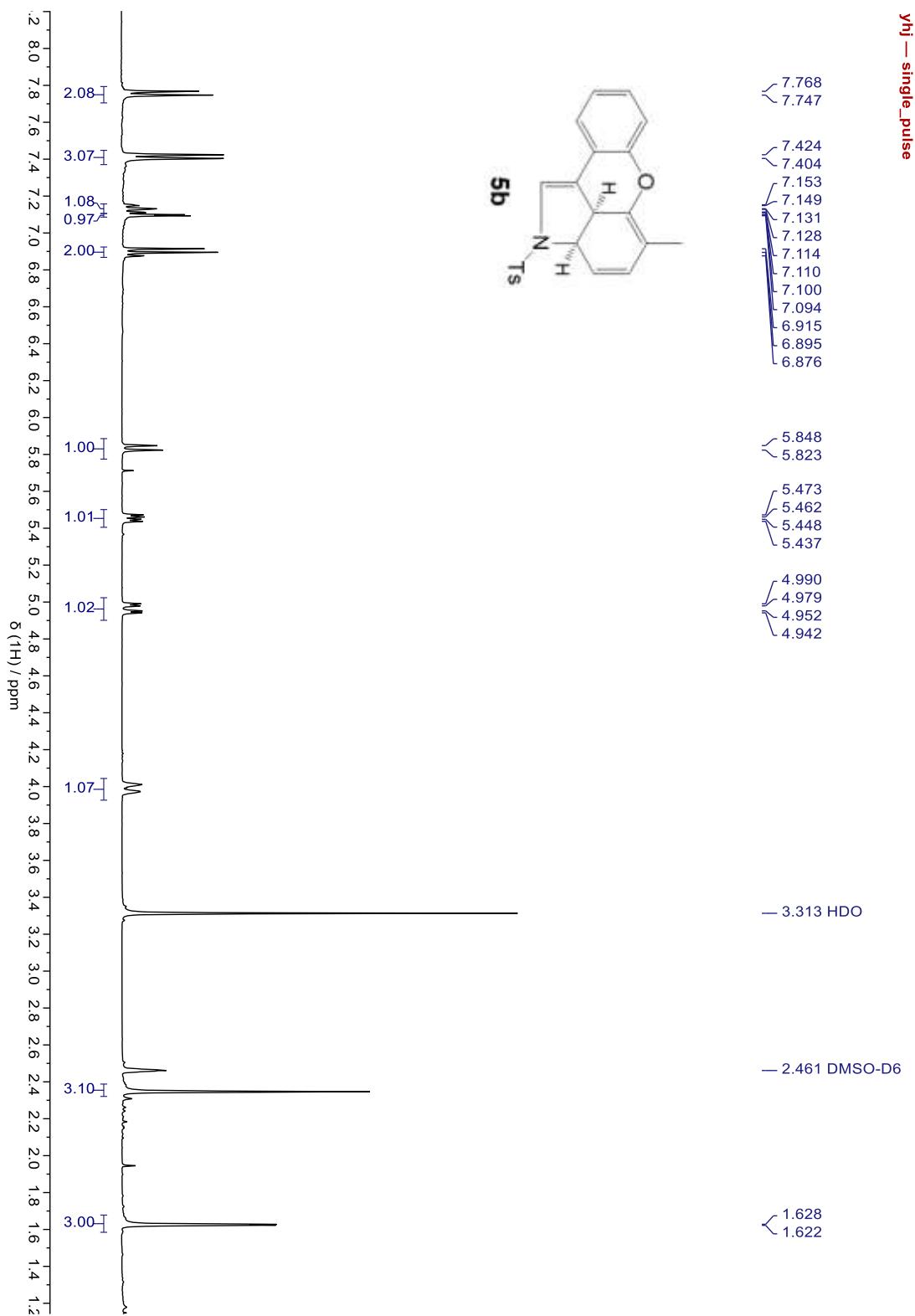


HRMS

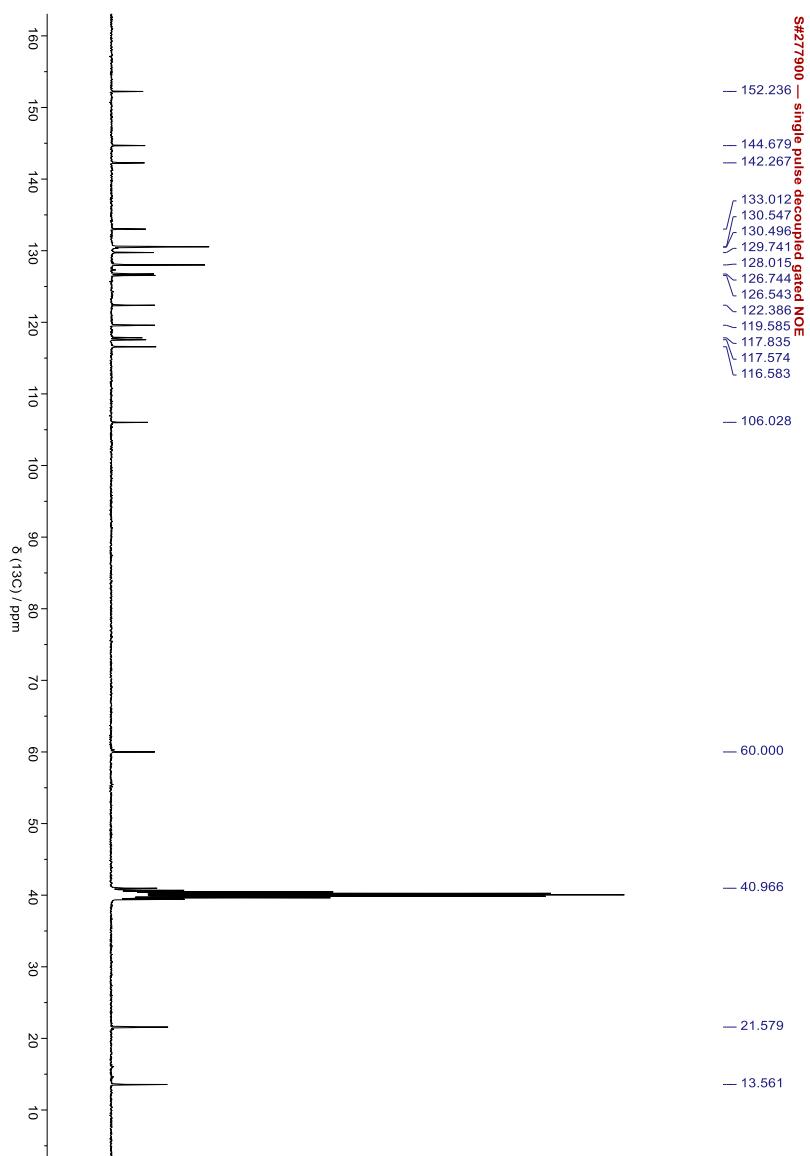


Compound **5b**

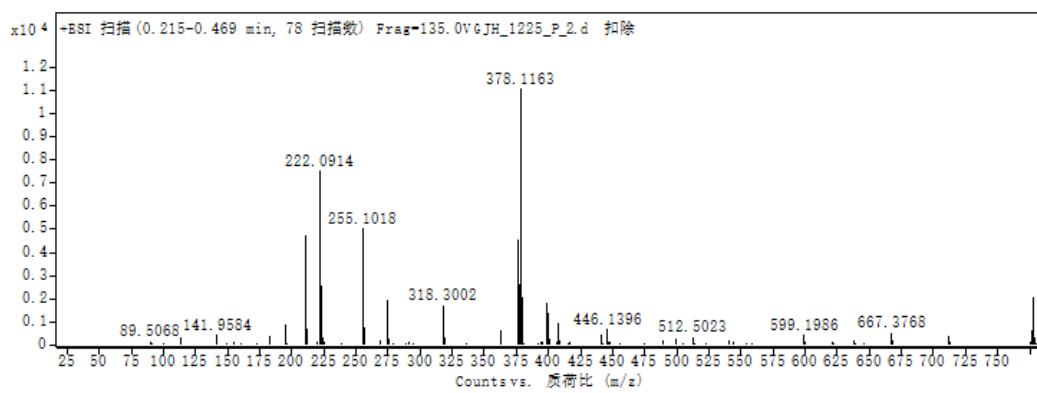
¹H NMR



¹³C NMR

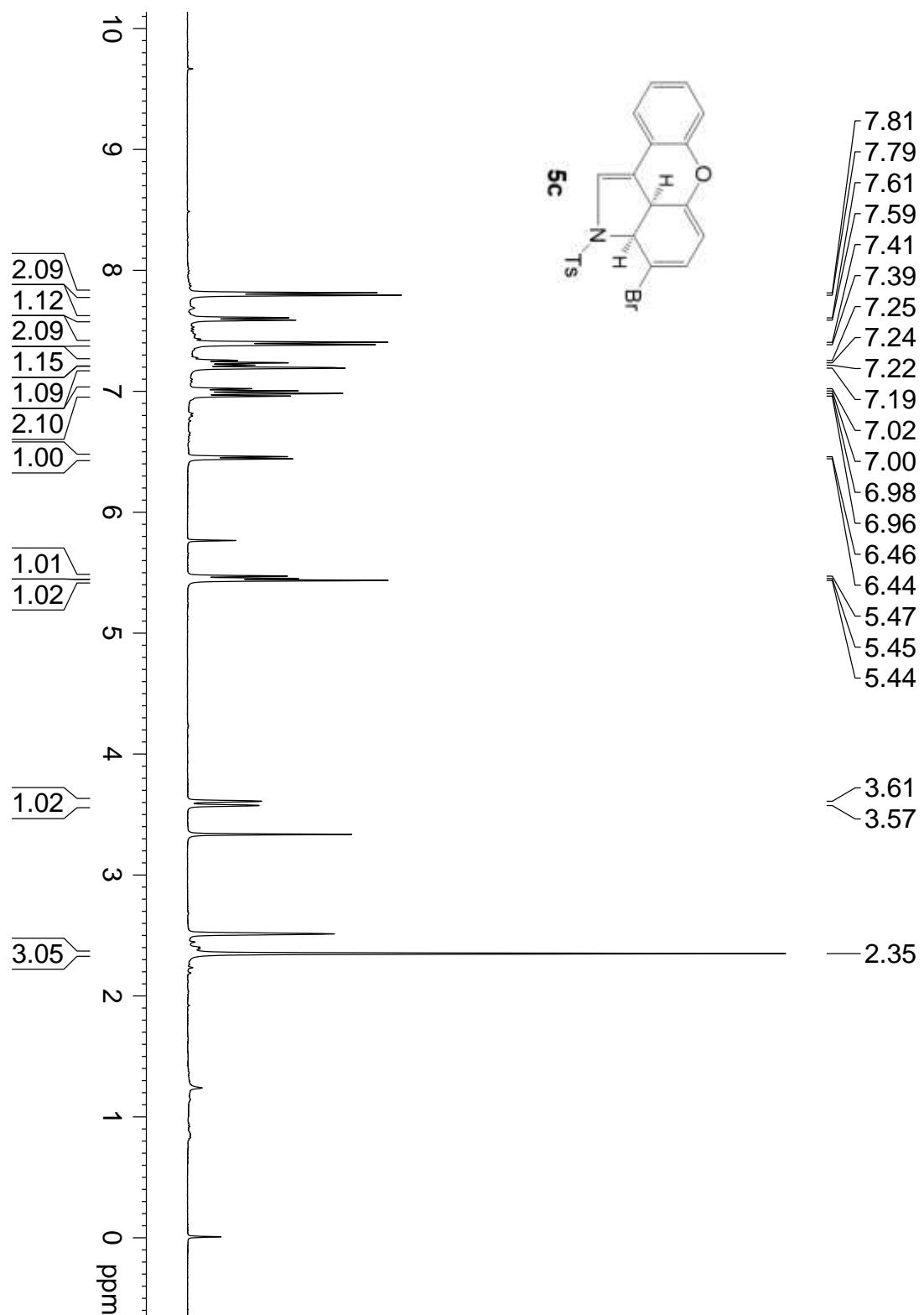


HRMS

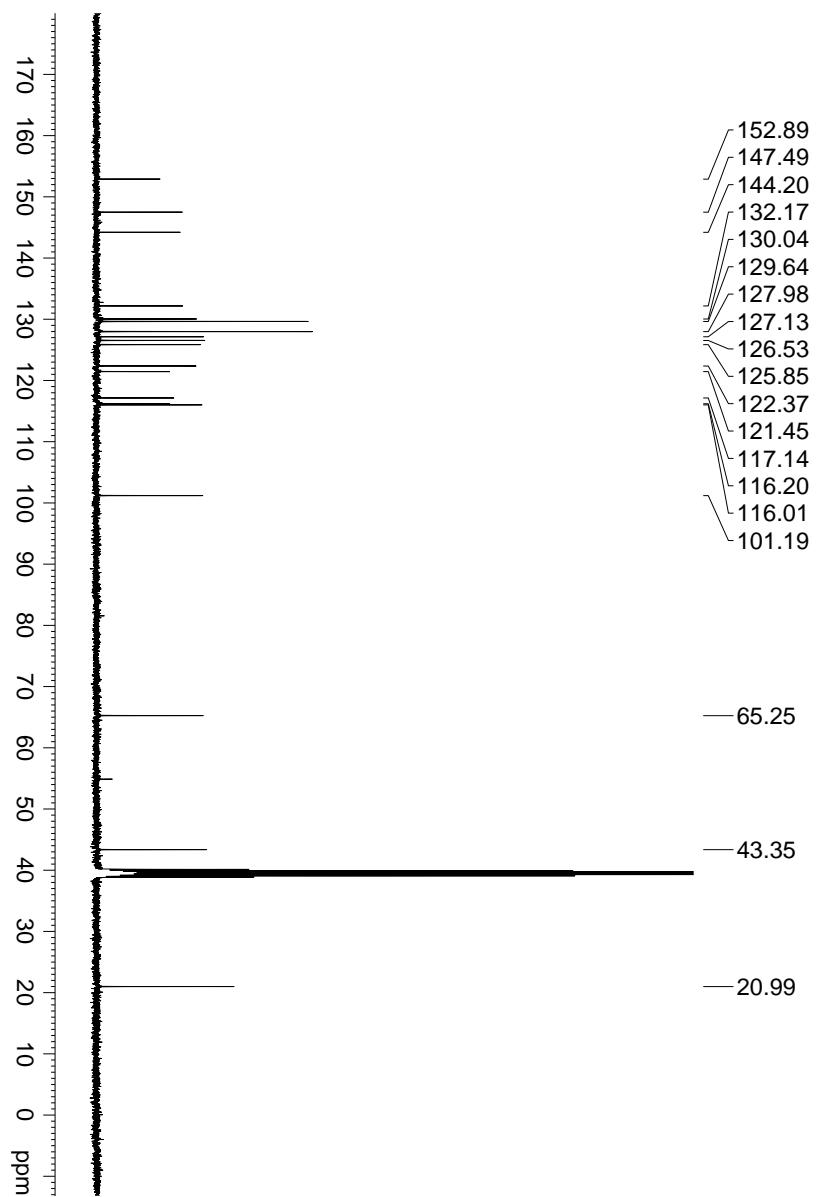


Compound **5c**

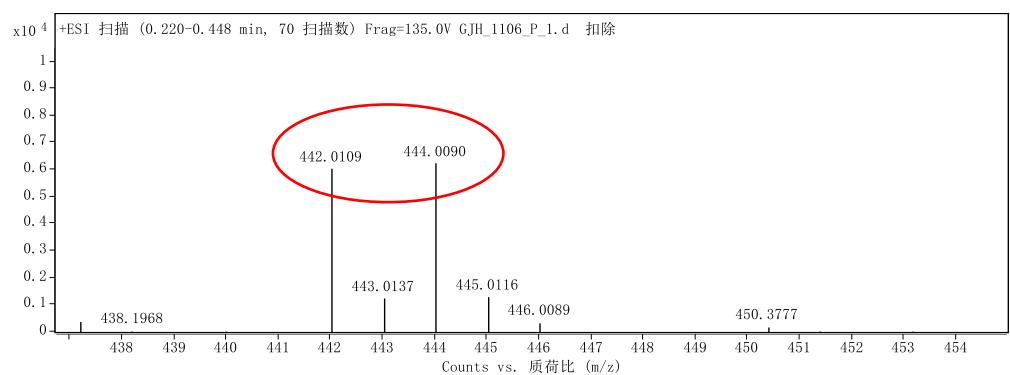
¹H NMR



¹³C NMR

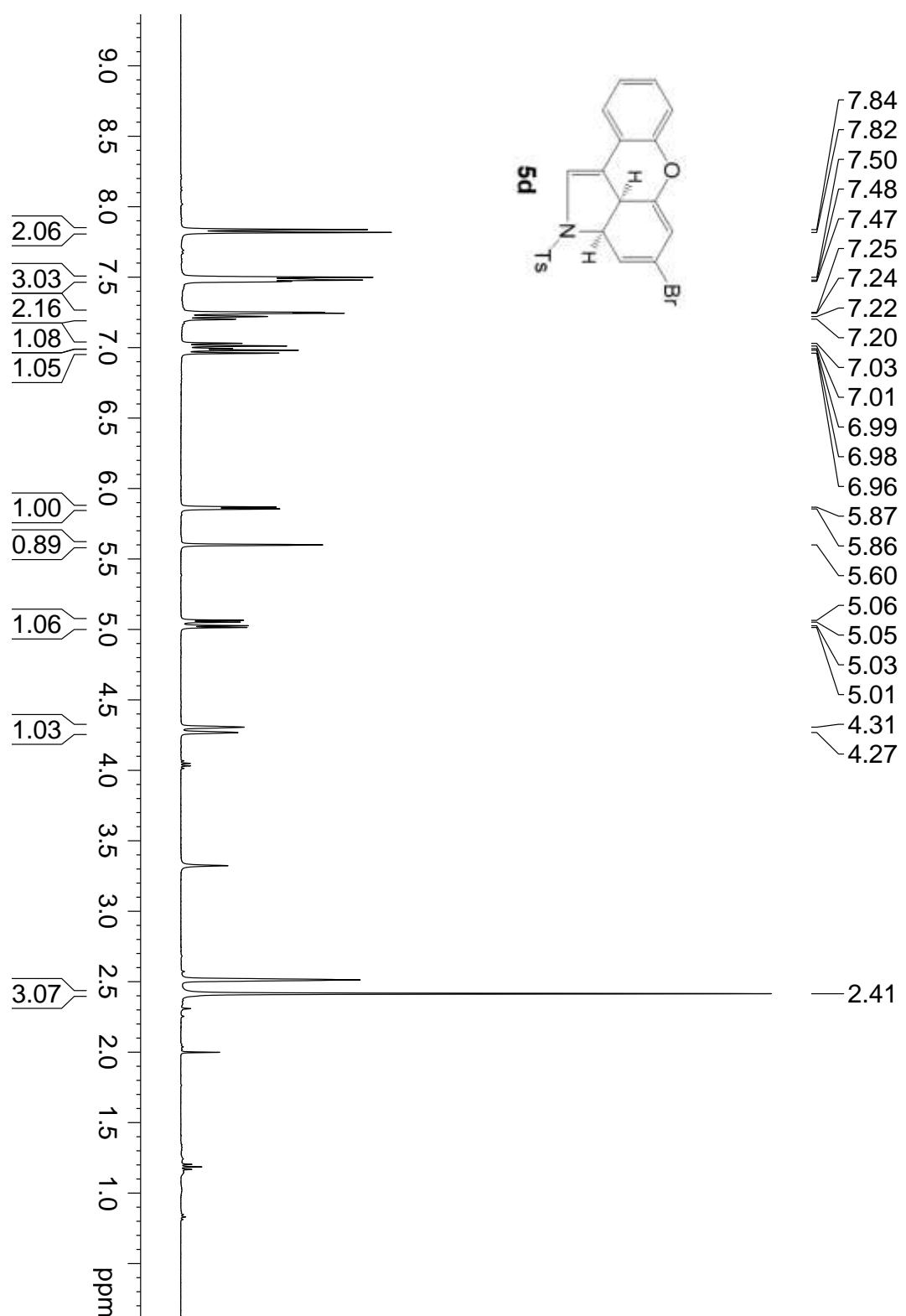


HRMS

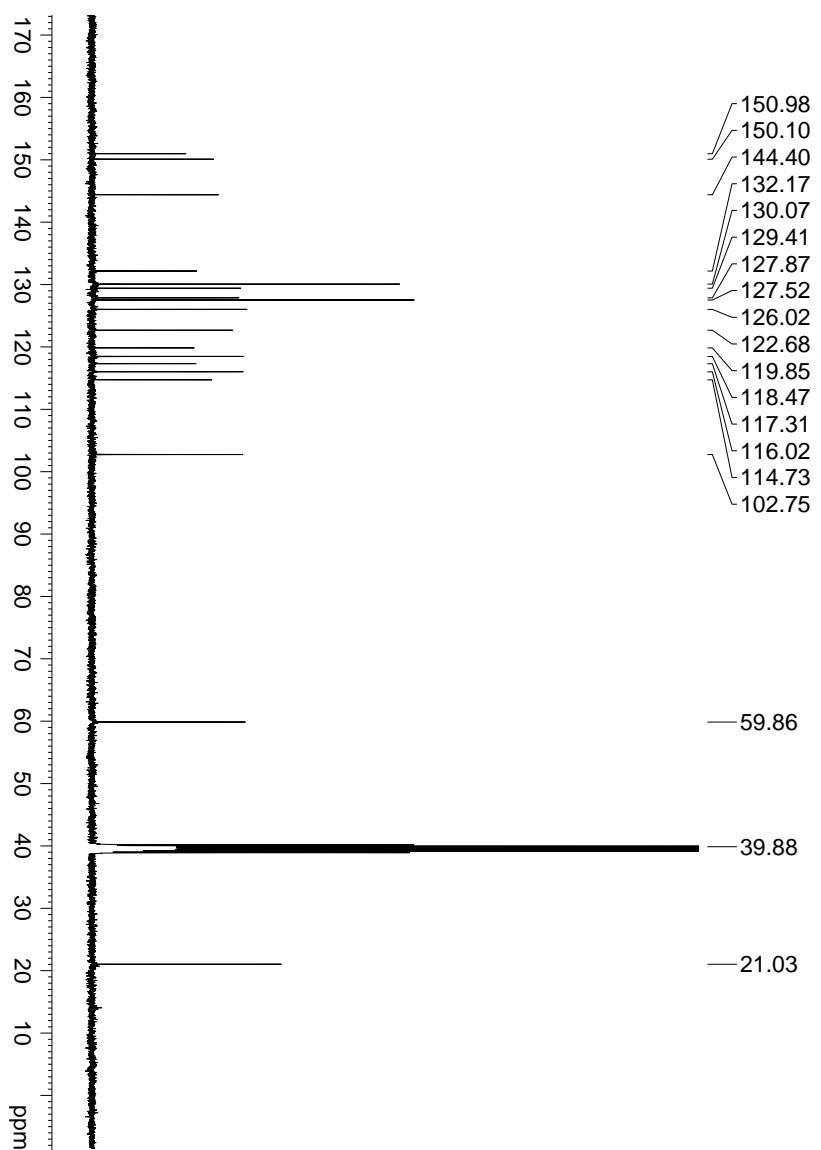


Compound **5d**

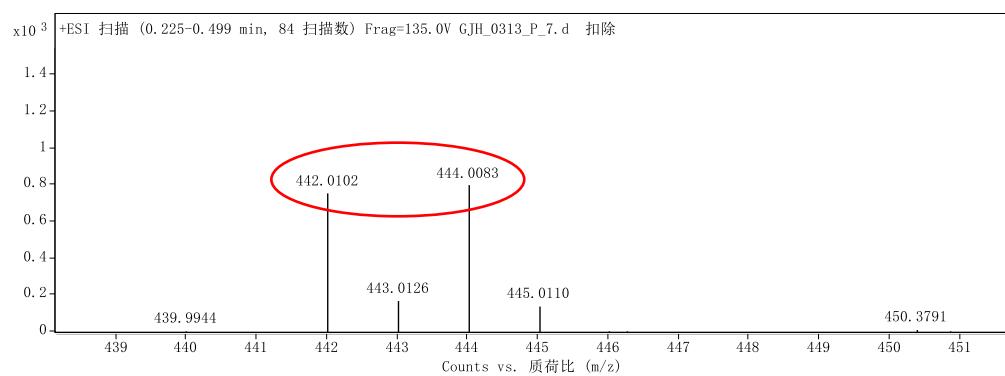
¹H NMR



¹³C NMR

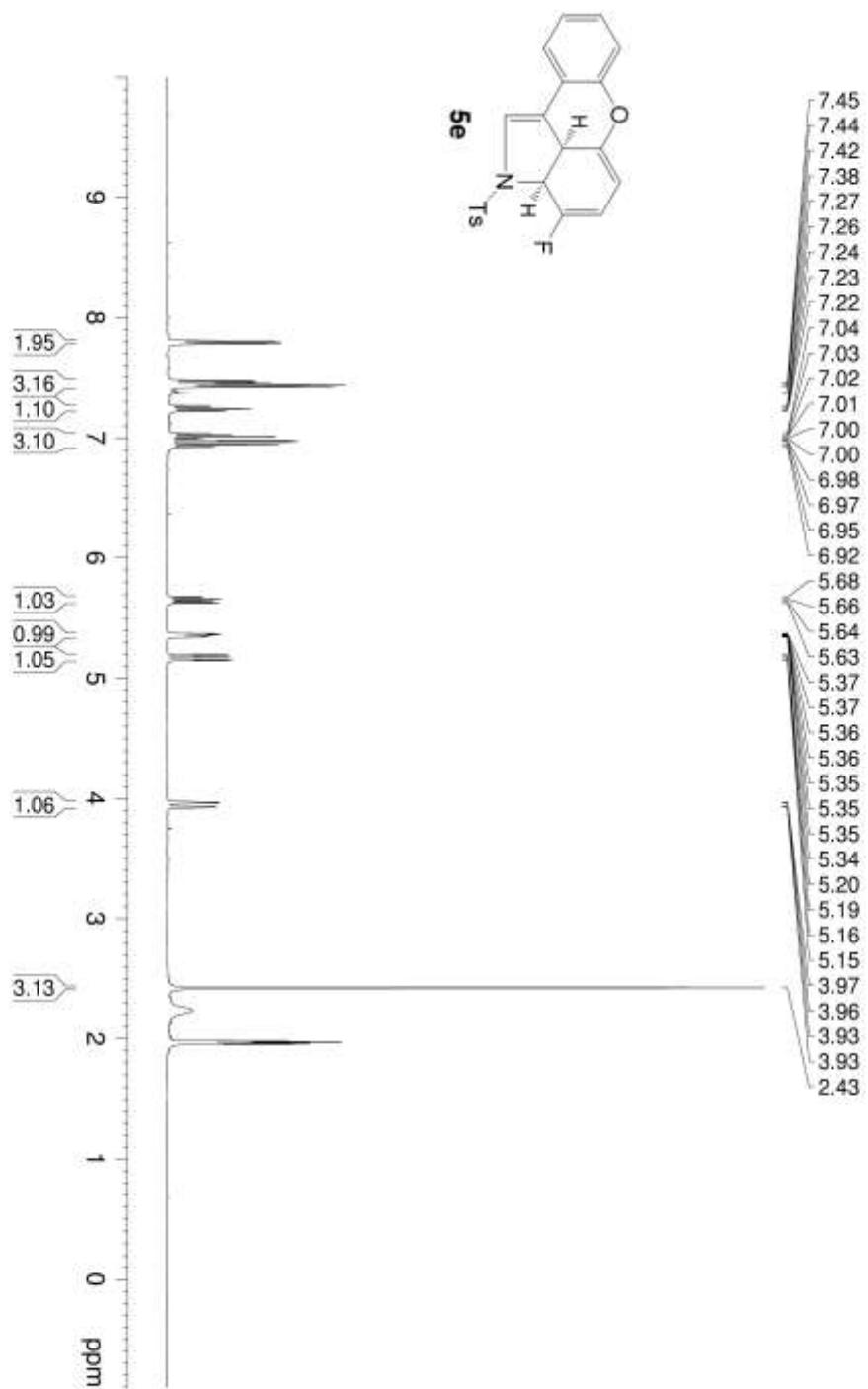


HRMS

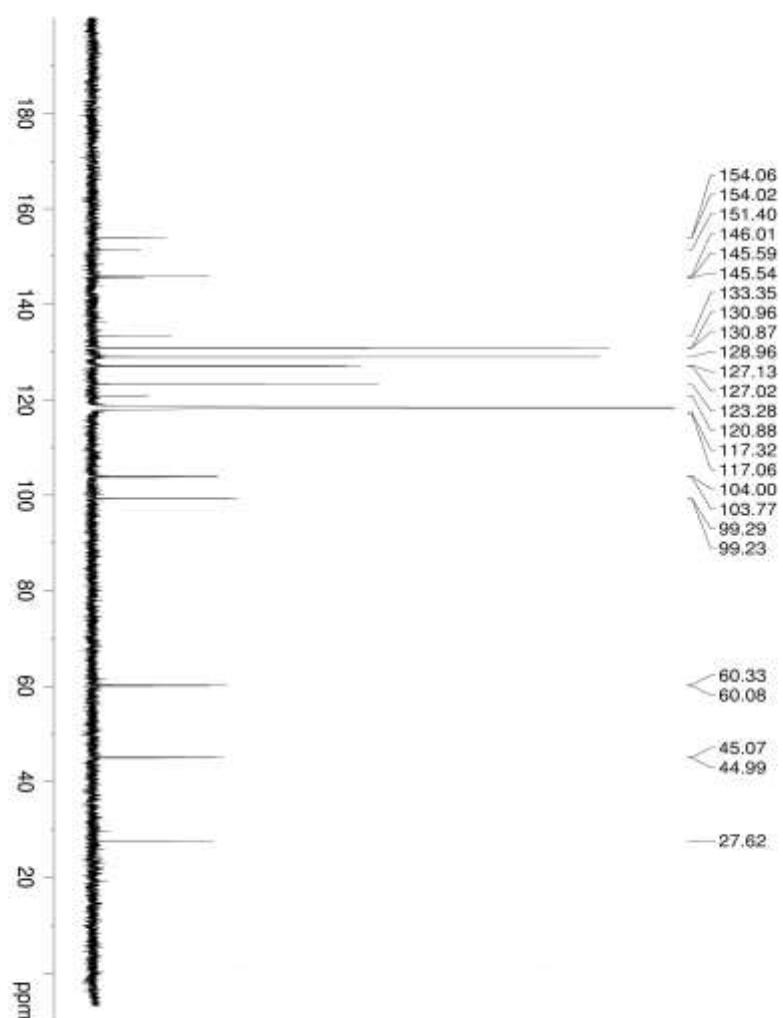


Compound **5e**

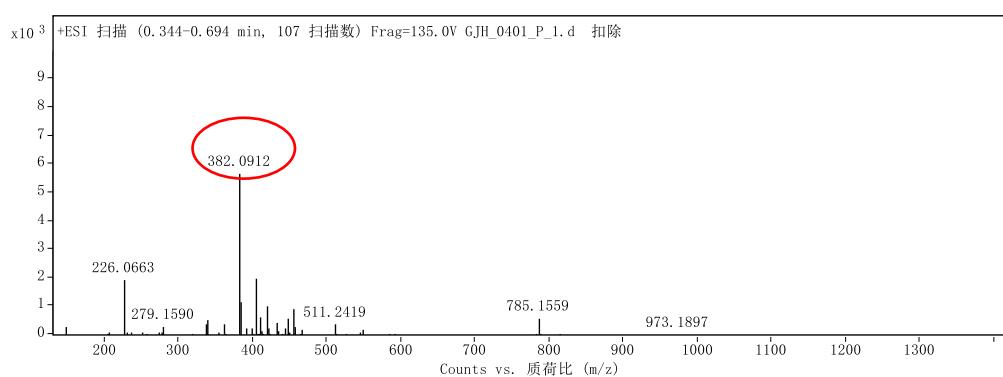
¹H NMR



¹³C NMR

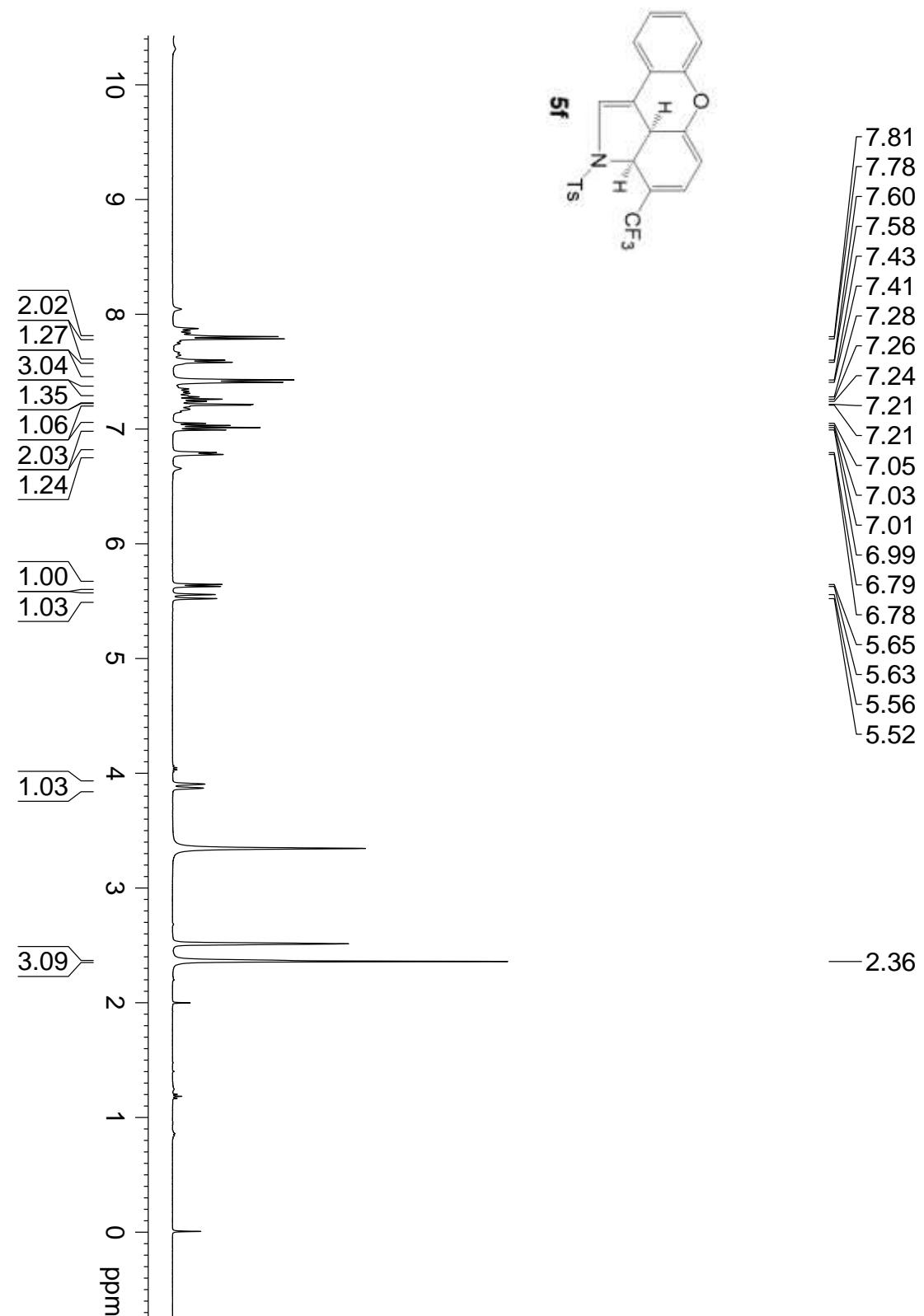


HRMS

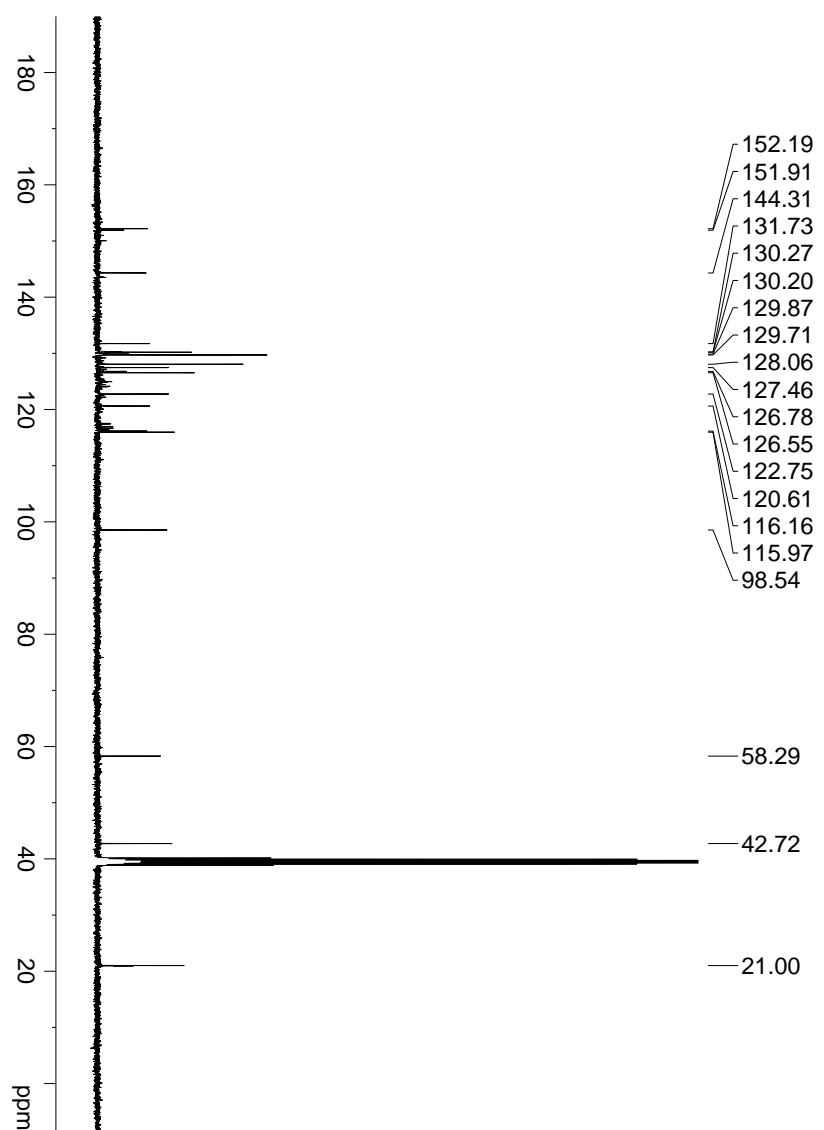


Compound **5f**

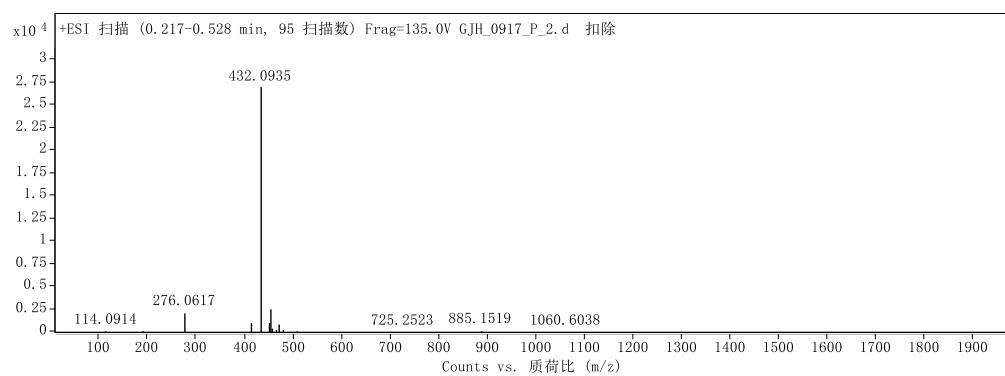
¹H NMR



¹³C NMR

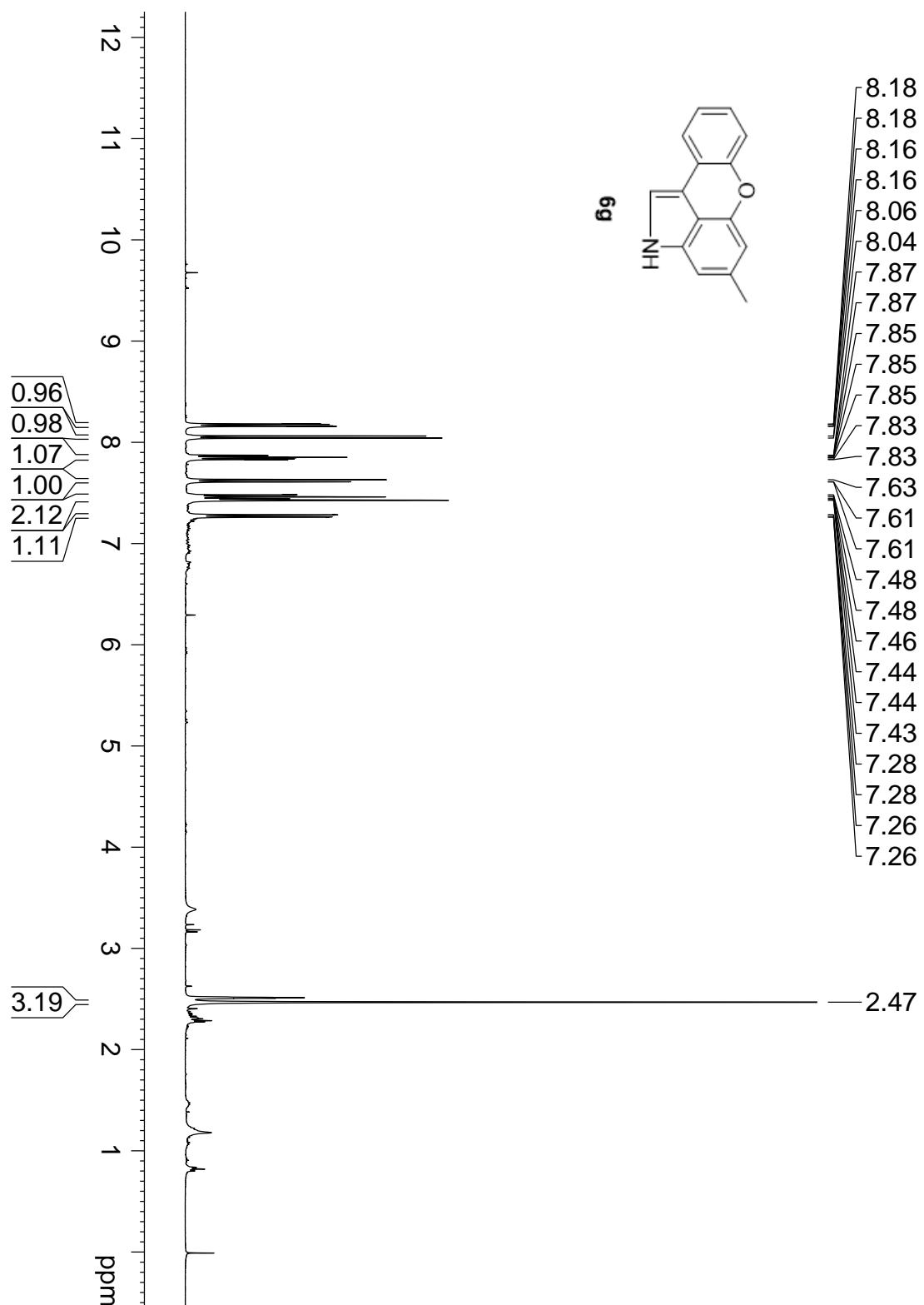


HRMS

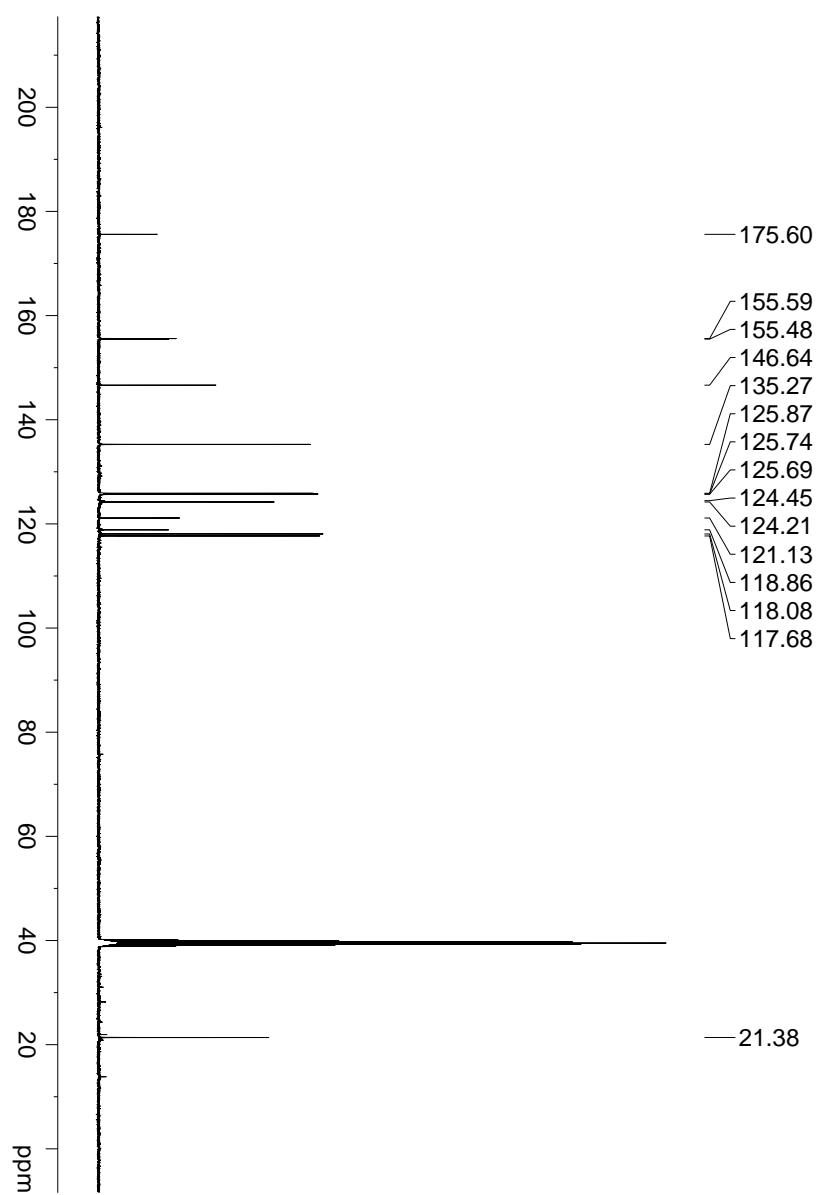


Compound **6g**

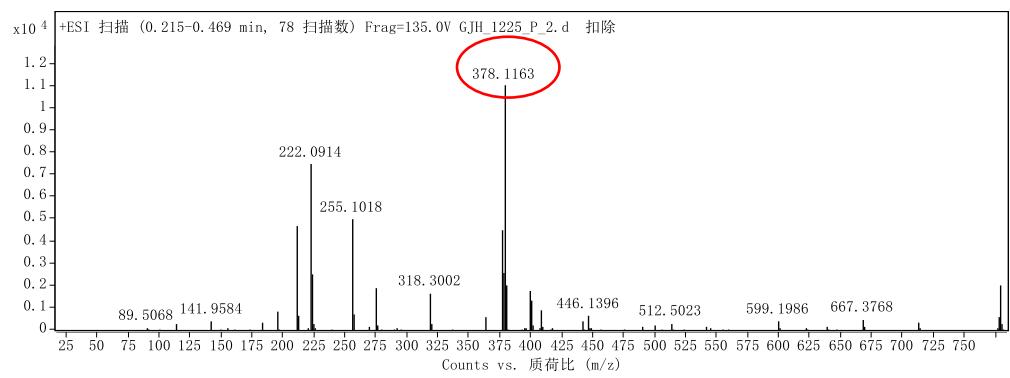
¹H NMR



¹³C NMR

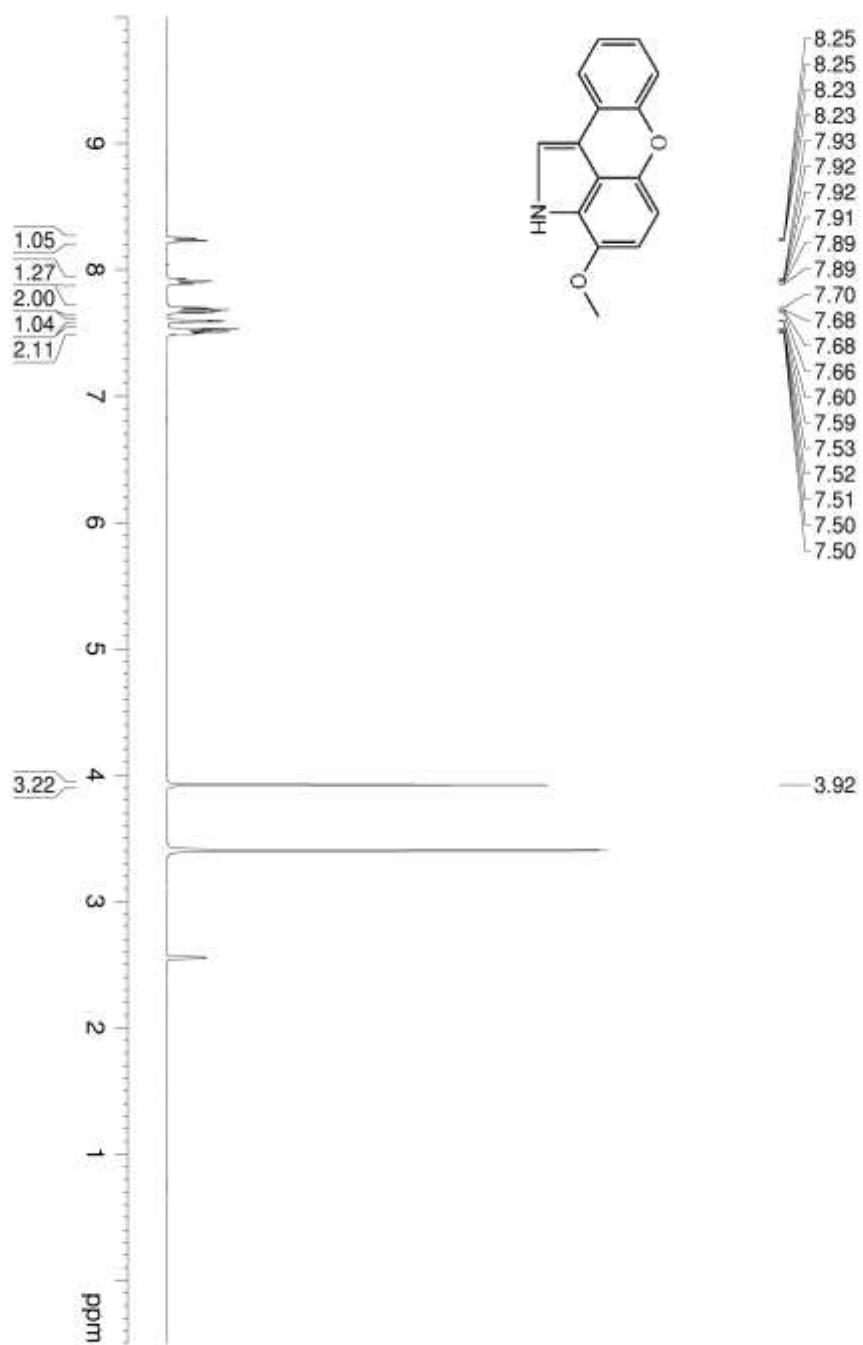


HRMS

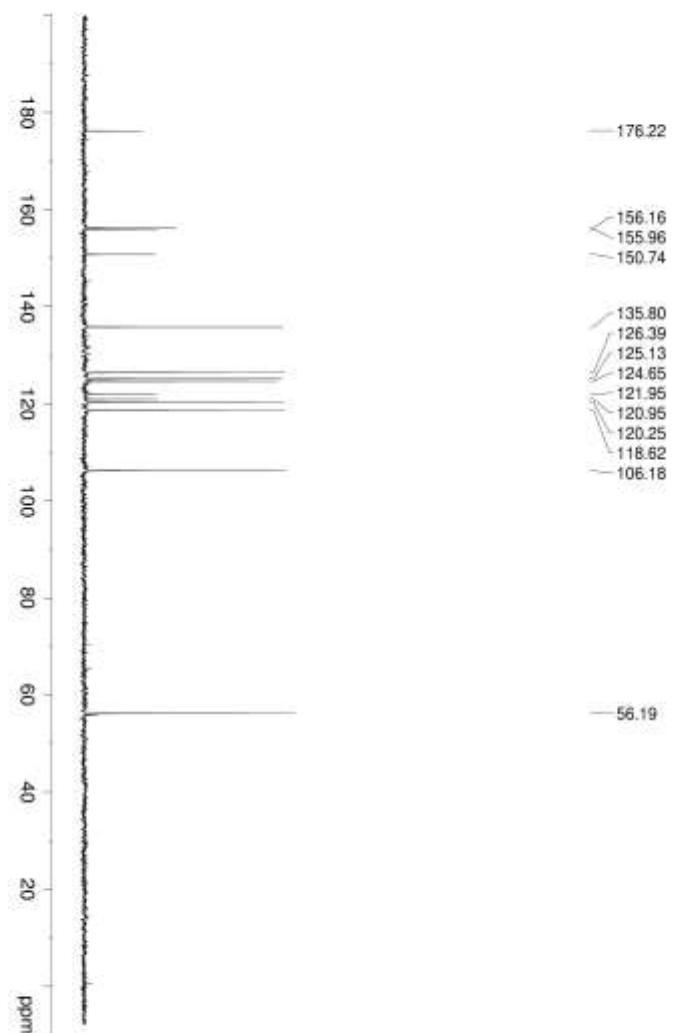


Compound **6h**

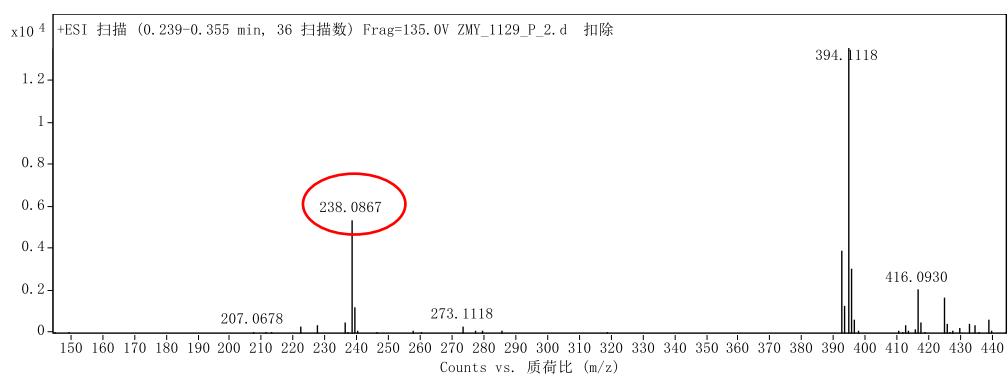
¹H NMR



¹³C NMR

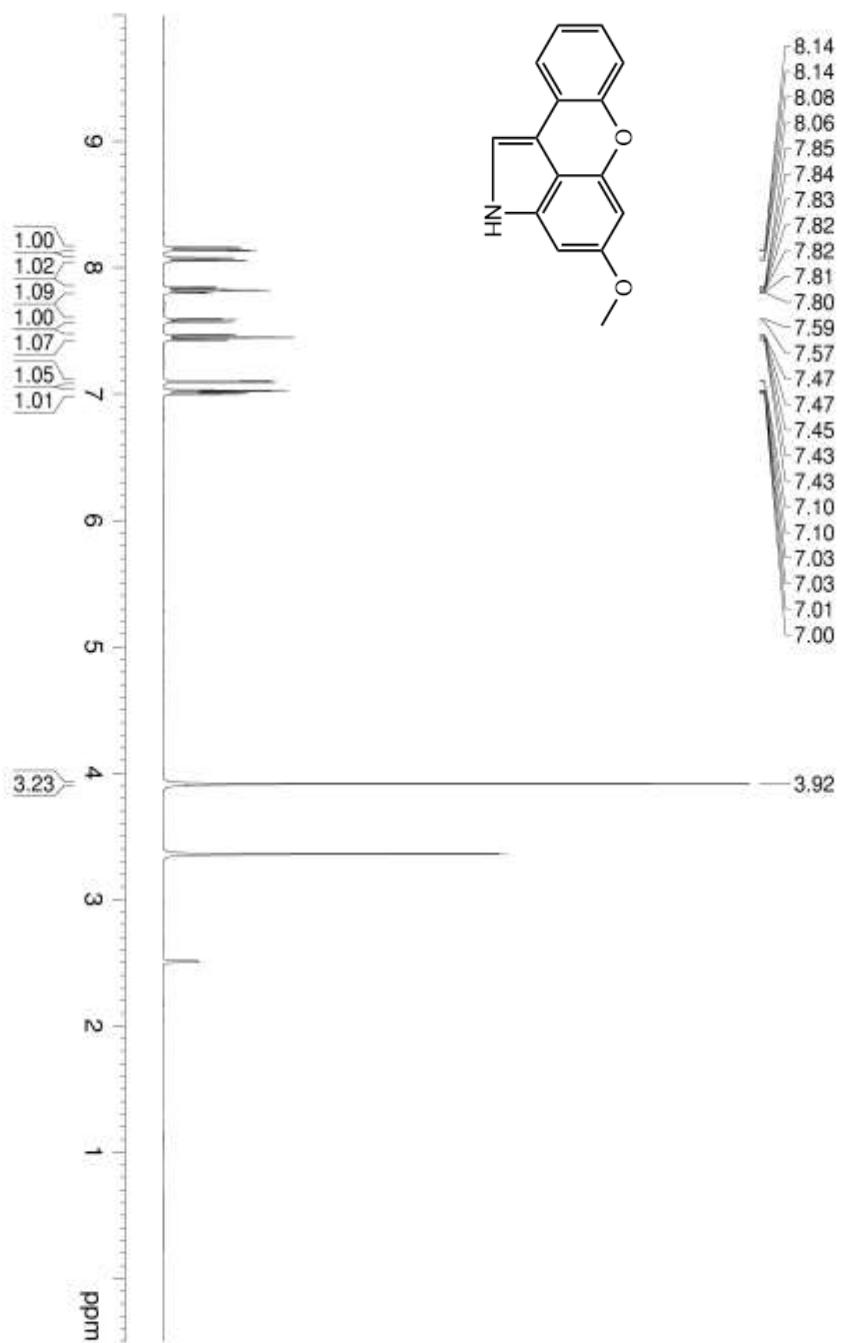


HRMS

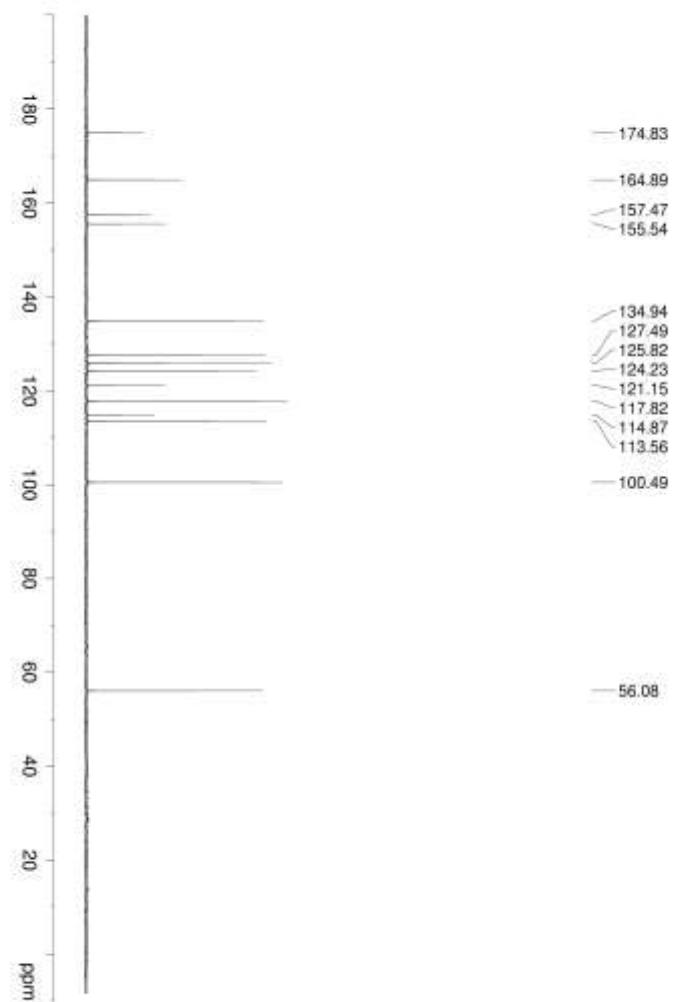


Compound **6i**

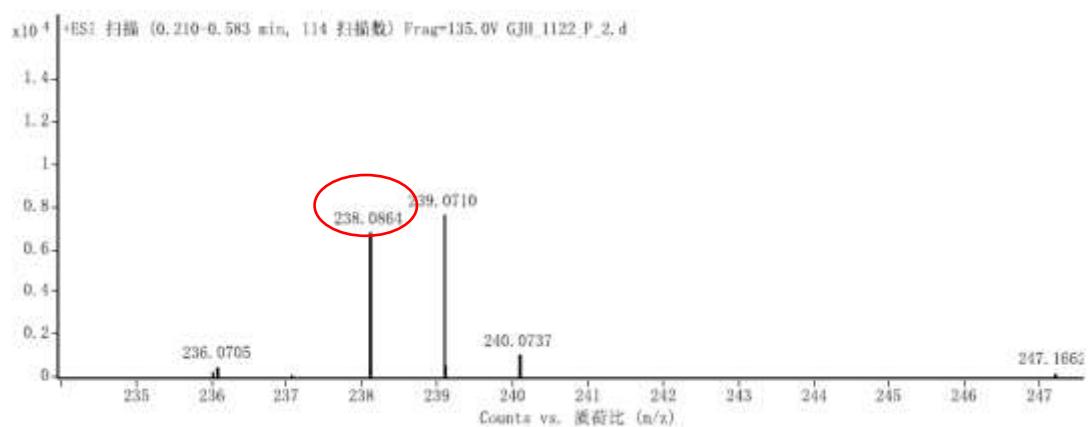
¹H NMR



¹³C NMR

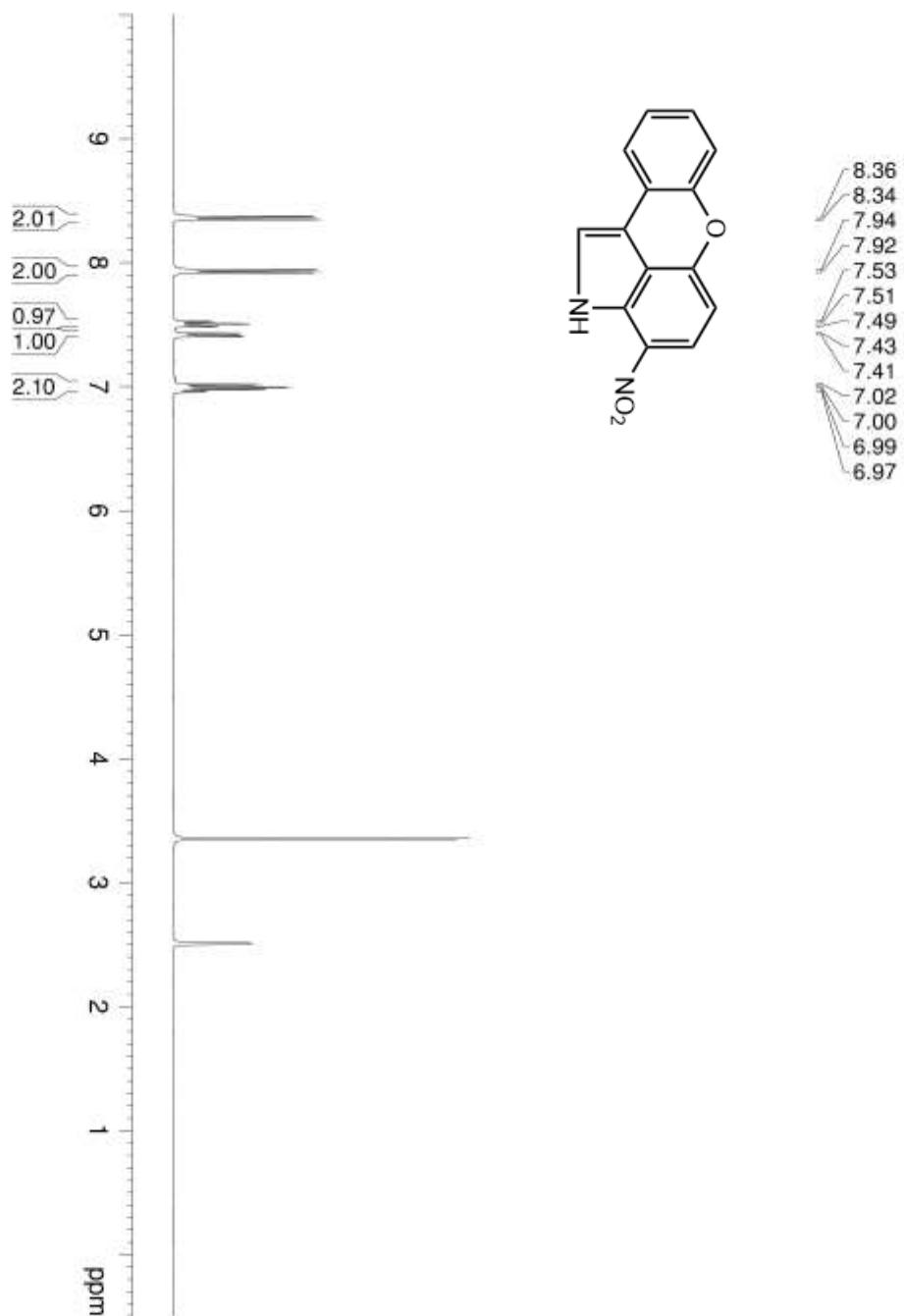


HRMS

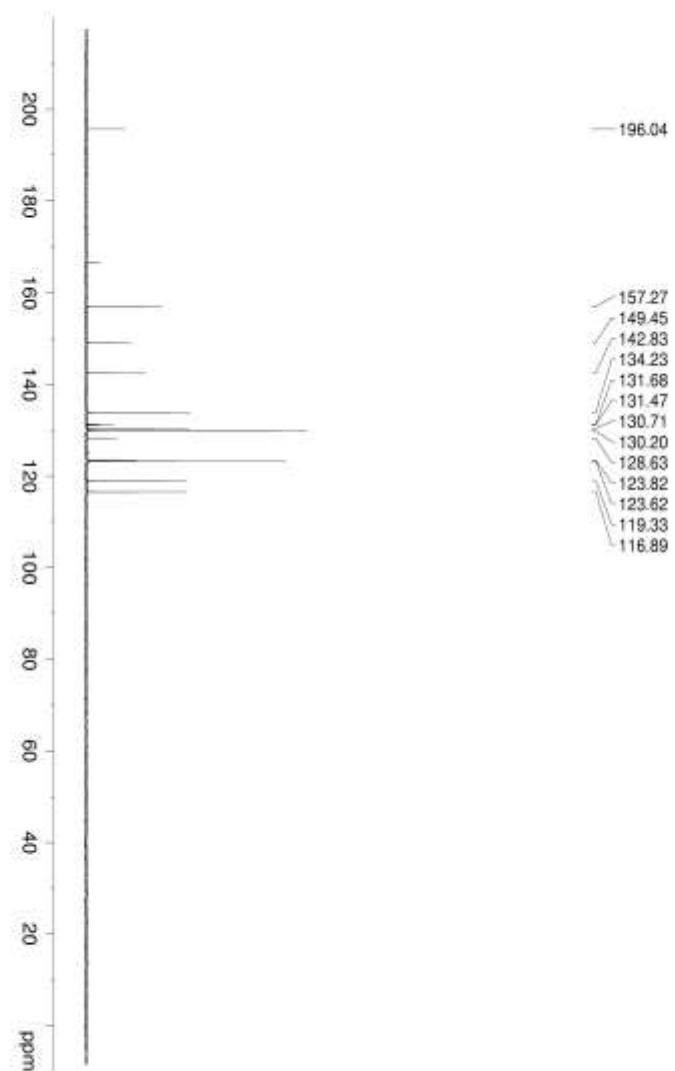


Compound **6j**

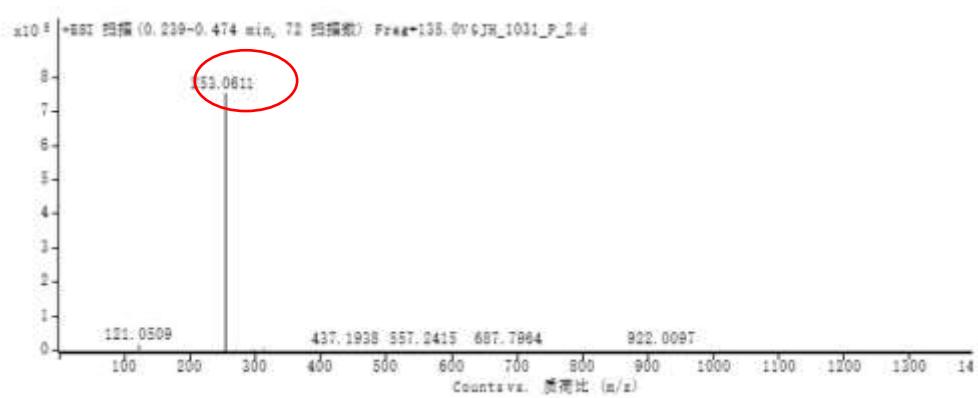
¹H NMR



¹³C NMR

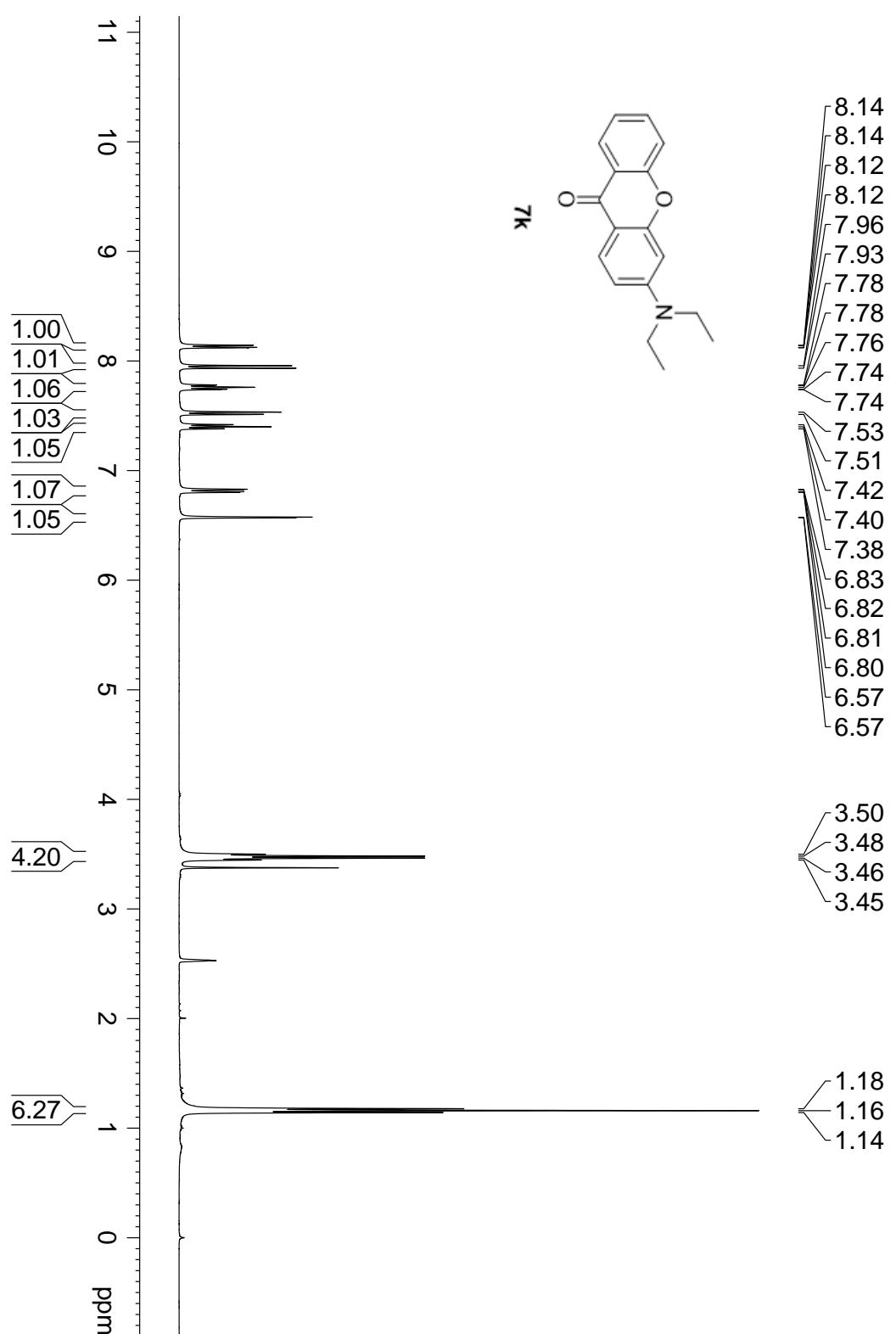


HRMS

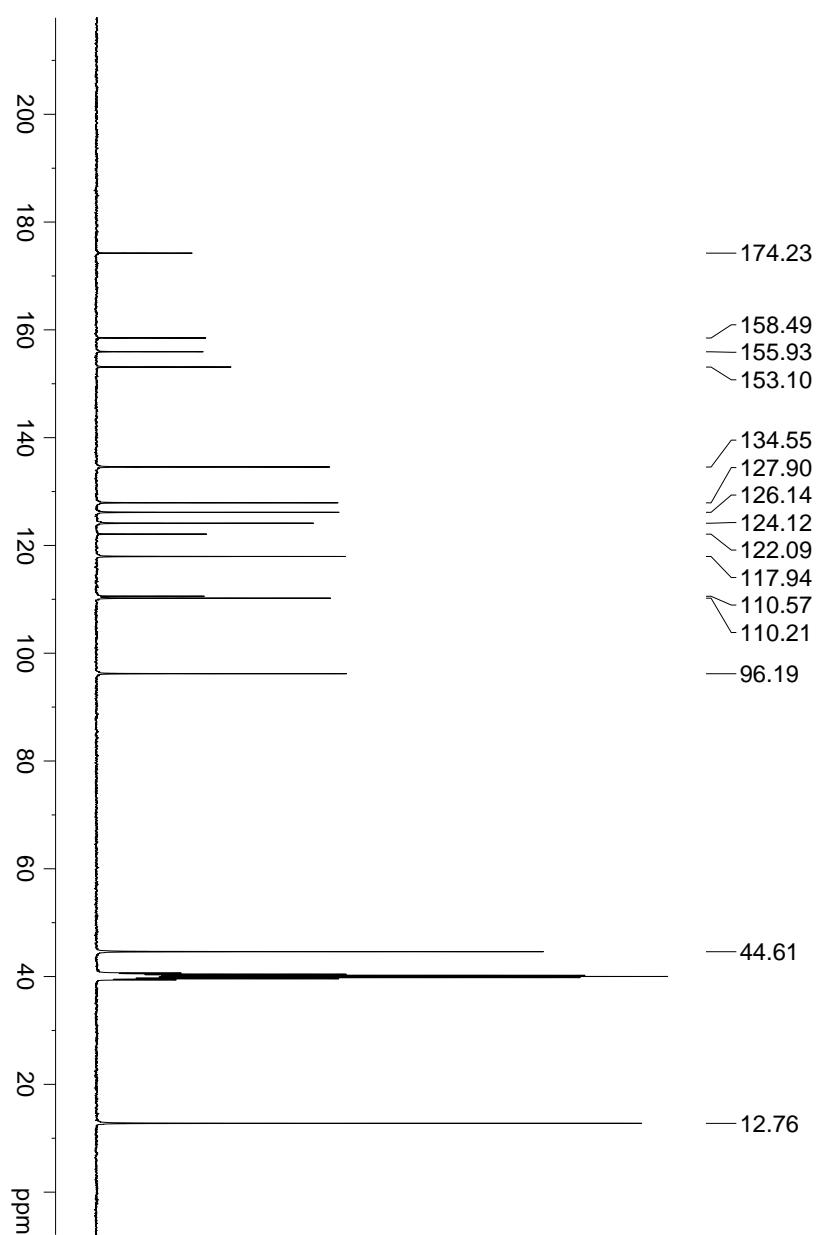


Compound 7k

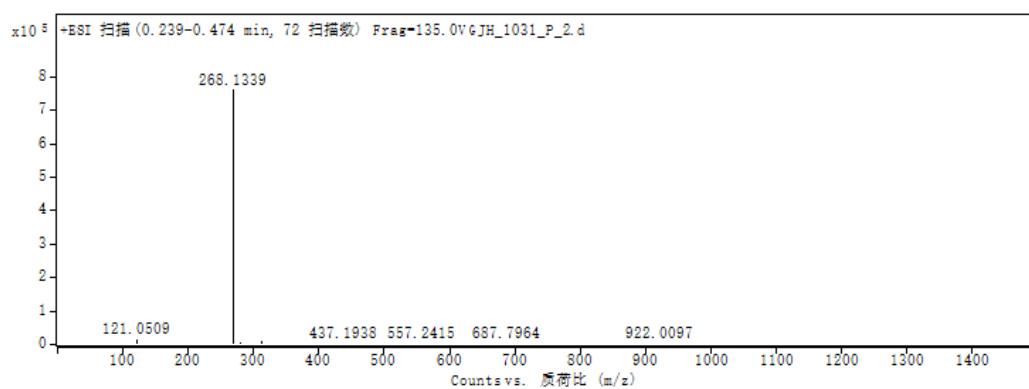
¹H NMR



¹³C NMR

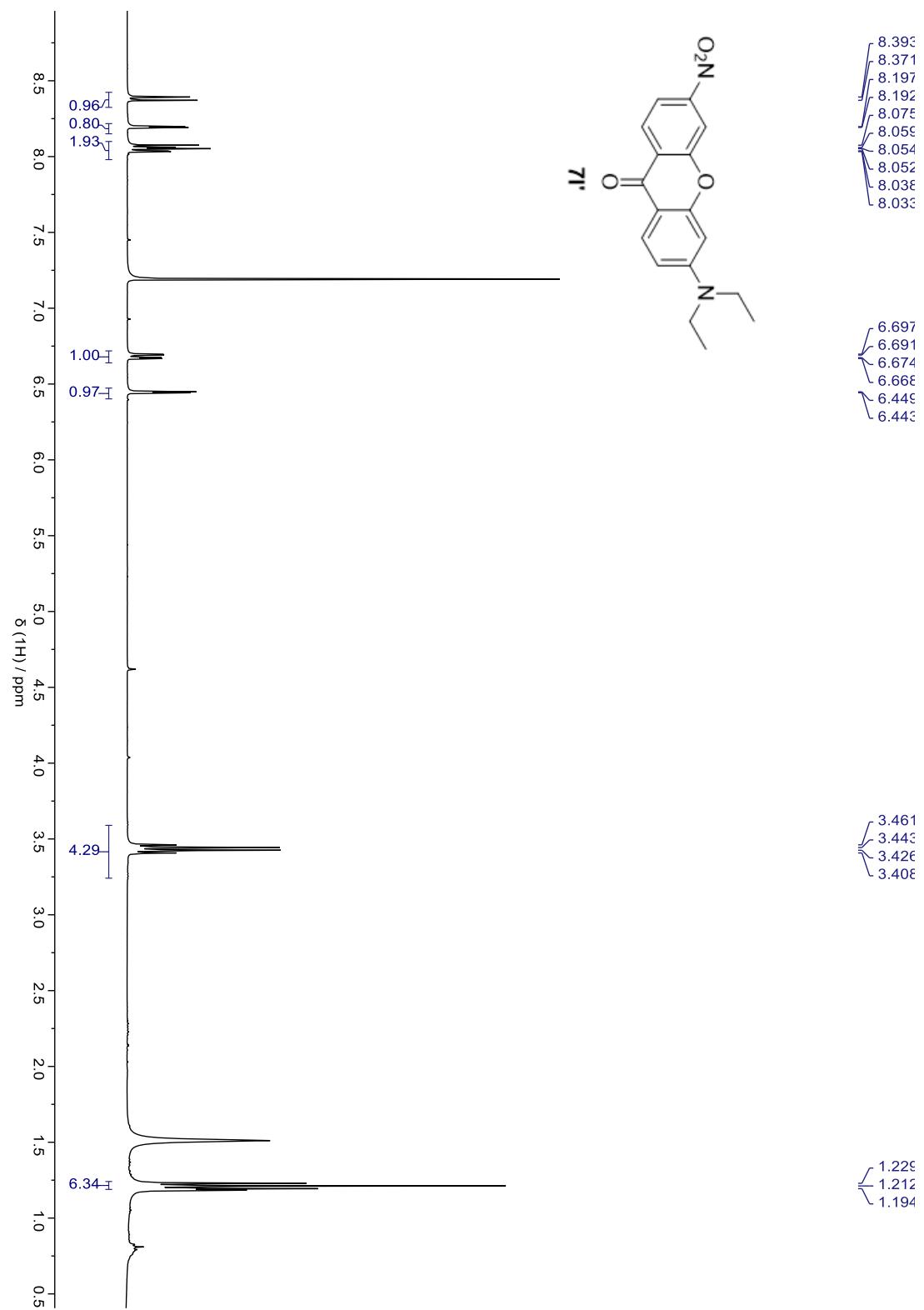


HRMS

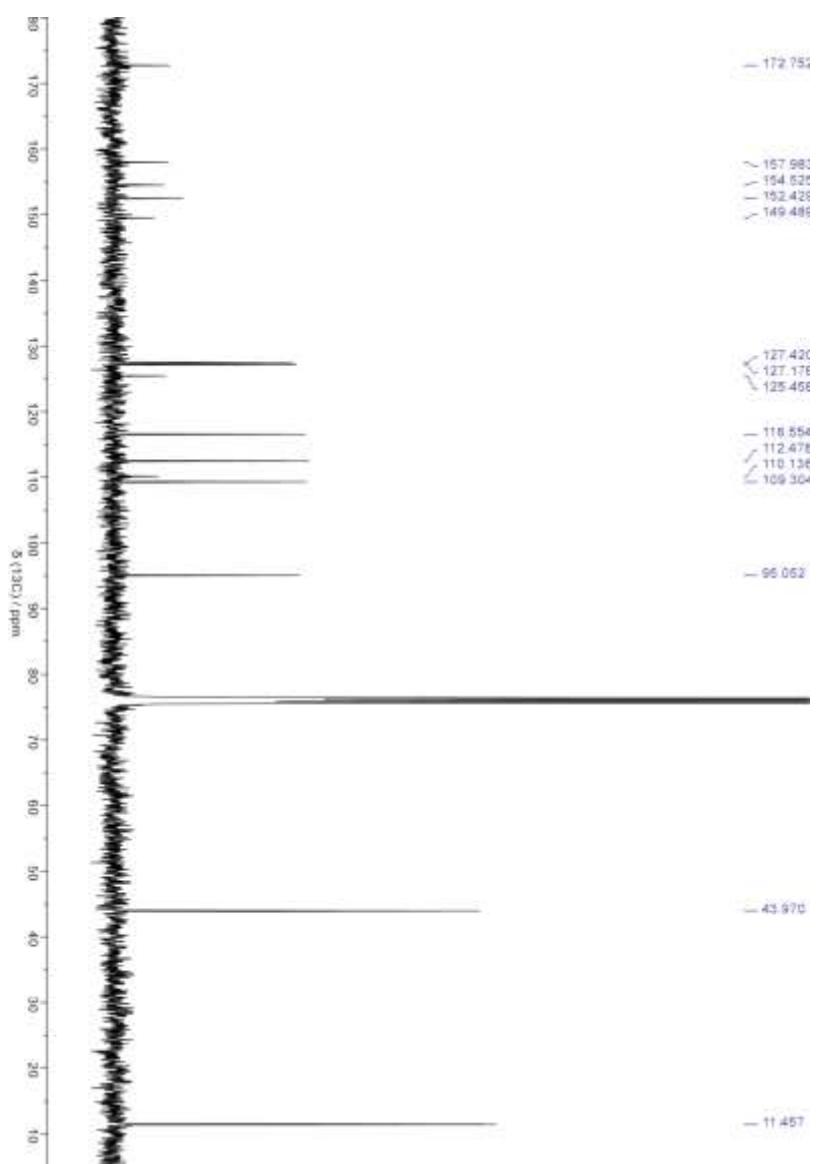


Compound 7l'

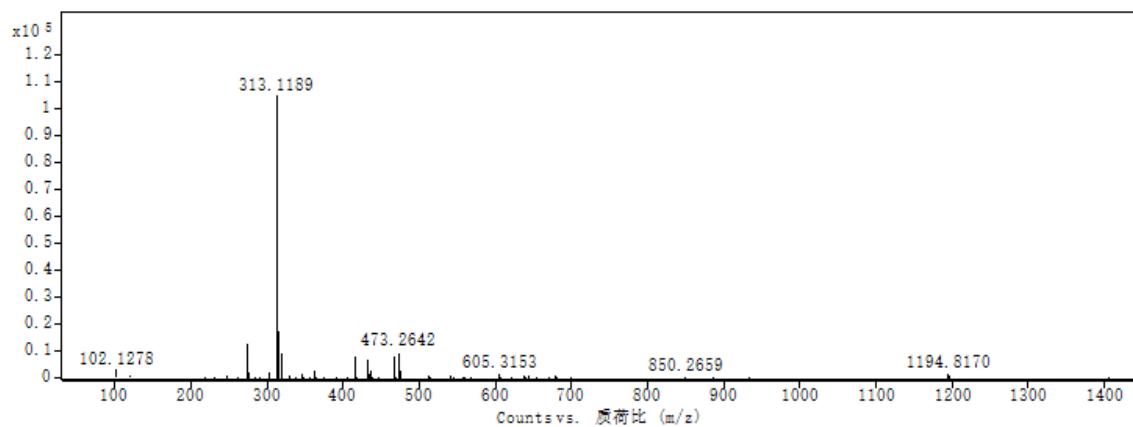
¹H NMR



¹³C NMR

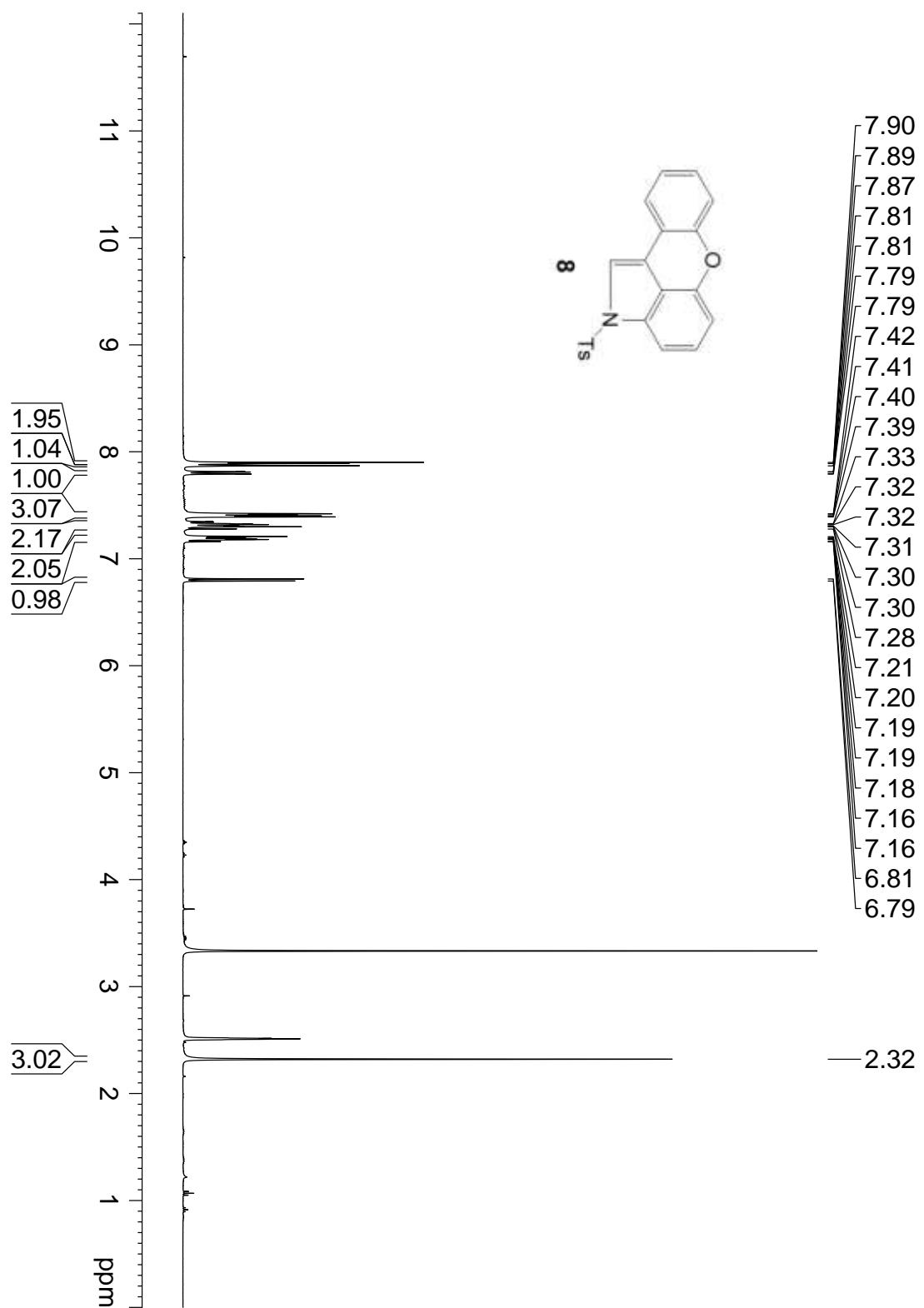


HRMS

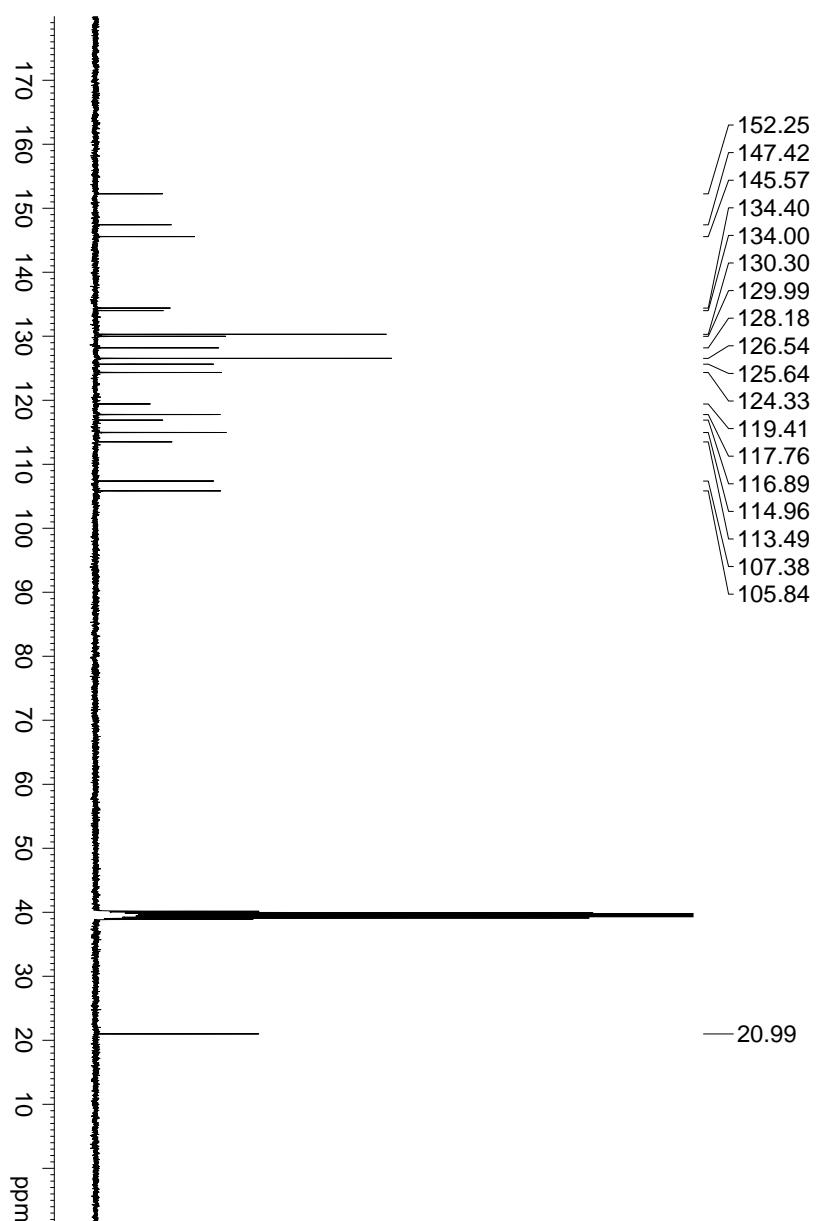


Compound 8

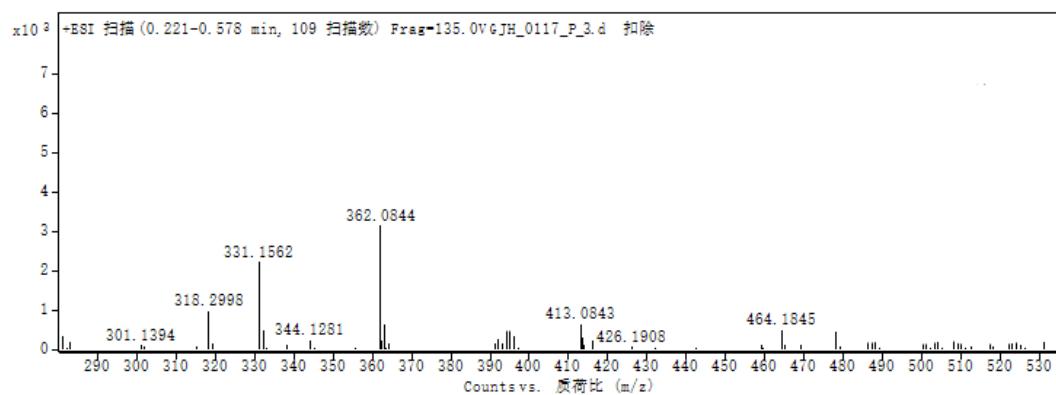
¹H NMR



¹³C NMR



HRMS



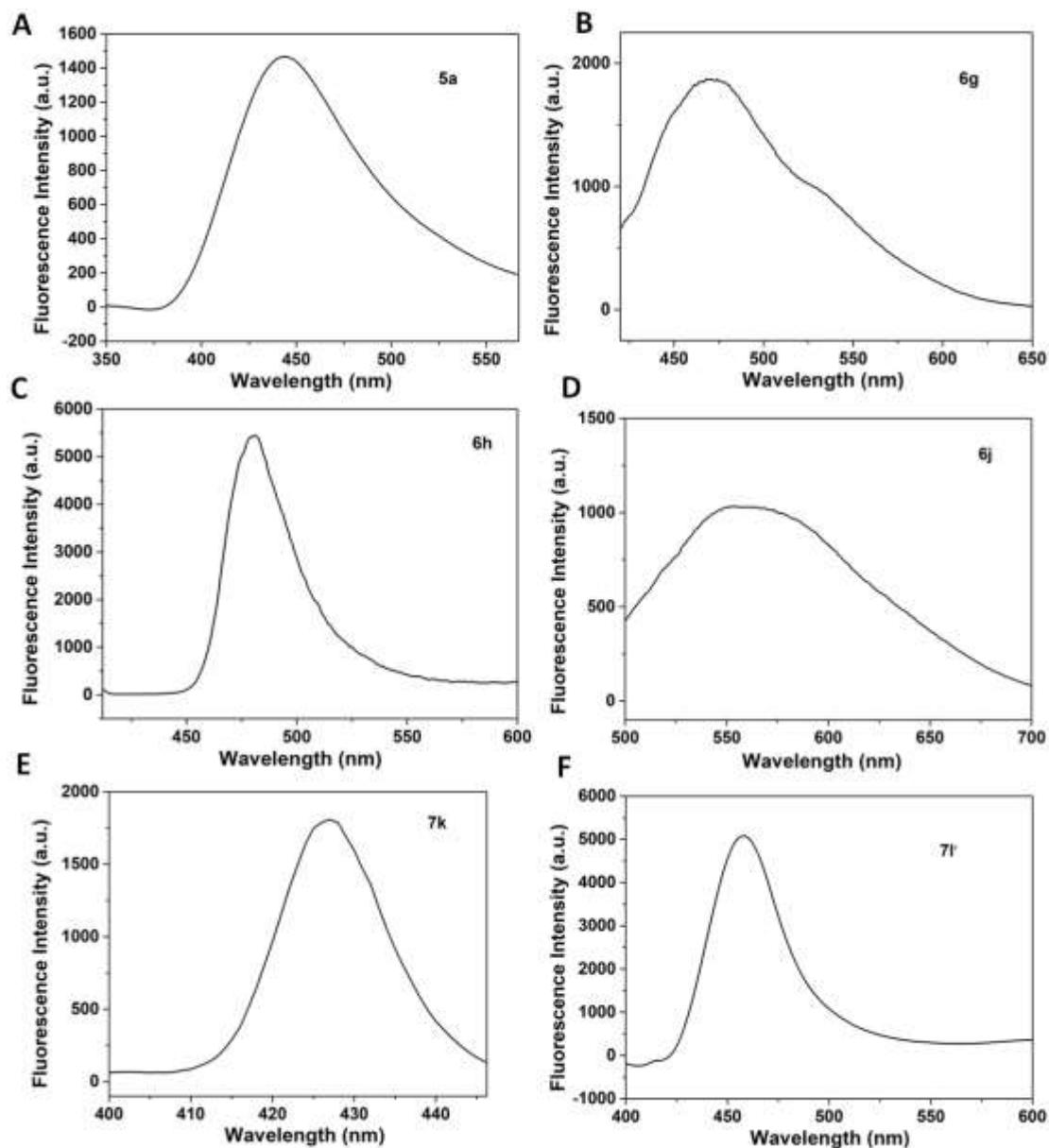


Figure S1. The fluorescence spectra of compounds. (A) **5a**; (B) **6g**; (C) **6h**; (D) **6j**; (E) **7k**; (F) **7l'**.