Supporting Information

A new class of unique quinoidal-like imidazoliumyl tetrazinides: Synthesis, structure and mechanism

Yanxue Geng, Weijun Sun, Weixu Zhang, Mengyao Li, Guo Wang, Jianchun Wang*

Department of Chemistry, Capital Normal University, Beijing 100048, P. R. China.E-mail: cnuwjc@cnu.edu.cn

Table of Contents

Experimental Section

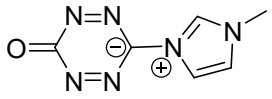
Most materials and reagents were purchased from commercial suppliers and used without further purification. Compound **1** was prepared according to the literature [1,2]. Anhydrous tetrahydrofuran was first dried by molecular sieve overnight, and then refluxed with potassium and benzophenone to dark blue. ^{1}H and ^{13}C NMR spectra were mainly recorded on 600 MHz Varian VNMRS Spectrometer (Some samples were completed on Bruker AVANCE 400/700 MHZ during the epidemic.), using D_2O or DMSO-d_6 as solvent. High-resolution mass spectroscopy (HRMS) was performed on a Bruker APEXIIFT-ICR mass spectrometer. Melting points were measured on a WRS-1B micro-melting point apparatus (YiCe, Shanghai).

Synthesis of imidazoliumyl tetrazinide

A general method was used to synthesize **3a-3z**, **3aa-3ak** and we provide the method for synthesis of **3a**. In a three-neck flask, 3,6-dichlorotetrazine (90mg, 0.6mmol) was dissolved in THF (20mL). The mixture was stirred for 10 min at temperature of fluxing. Then 1-methylimidazole (57μL, 0.8mmol) was added slowly, a red solid was precipitated immediately. The slurry was stirred at 60°C for 3 hr. After filtration and washing with THF, the red solid was chromatographed on silicon gel column, and the second orange band was collected, when eluent was ethyl acetate and methanol ($V_{ethyl\ acetate}/V_{methanol}$=2:1). After all the solvents were evaporated, a red solid (83mg, 87%) was obtained.

Gram-scale preparation of **3a**. At room temperature, in a three-neck flask, 3,6-dichlorotetrazine (1324.2mg，9mmol) was dissolved in THF (300.0mL). The mixture was stirred for 10 min at temperature of fluxing. Then 1-methylimidazole (450ul，10.8mmol) was added slowly, a red solid was precipitated immediately. The slurry was stirred at 60°C for 3 hr. After filtration and washing with THF, the red solid was chromatographed on silicon gel column, and the second orange band was collected, when eluent was ethyl acetate and methanol ($V_{ethyl\ acetate}/V_{methanol}$=2:1). After all the solvents were evaporated, a red solid (757.5mg, 47%) was obtained.

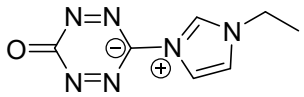
3-(1-methyl-1*H*-imidazol-3-ium-3-yl)-6-oxo-3,6-dihydro-1,2,4,5-tetrazin-3-ide (3a)



83mg red solid, yield: 87%. Mp: 259.7-260.1°C. HRMS (ESI) *m/z* calculated for $C_6H_7N_6O[M+H]^+$, 179.0676; found 179.0681. ^{1}H NMR (600 MHz, DMSO-d_6, ppm) δ 9.87 (s, 1H), 8.29 (s, 1H), 7.92 (s, 1H), 3.96 (s, 3H); ^{13}C NMR (151 MHz, DMSO-d_6, ppm) δ 165.55, 148.94, 134.18, 124.85, 118.79, 36.63. IR: (cm^{-1})=3426, 3416, 3117, 1629, 1594, 1552, 1433, 1399, 1251, 1093, 1042, 969, 878, 836, 809, 773, 643, 569.

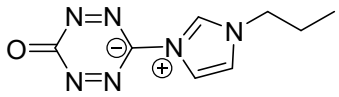
[1] M. D. Helm, A. Plant and J. P. Harrity, *Org Biomol Chem*, 2006, **4**, 4278-4280.
[2] J. Zhu, J. Hiltz, R. B. Lennox, R. Schirrmacher, *Chem. Commun.,* 2013, **49**, 10275—10277.

3-(1-ethyl-1*H*-imidazol-3-ium-3-yl)-6-oxo-3,6-dihydro-1,2,4,5-tetrazin-3-ide (3b)



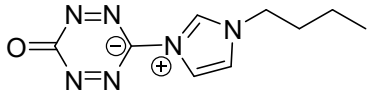
80mg red solid, yield: 70%. Mp: 201.0-202.7°C. HRMS (ESI) *m/z* calculated for $C_7H_9N_6O$ $[M+H]^+$, 193.0832; found 193.0831. ^{1}H NMR (600 MHz, DMSO-d_6, ppm) δ 9.93 (t, *J* = 1.7 Hz, 1H), 8.30 (t, *J* = 1.9 Hz, 1H), 8.04 (t, *J* = 1.9 Hz, 1H), 4.32 (q, *J* = 7.3 Hz, 2H), 1.49 (t, *J* = 7.3 Hz, 3H); ^{13}C NMR (151 MHz, DMSO-d_6, ppm) δ 165.67, 149.02, 133.44, 123.38, 119.01, 45.24, 15.51. IR: (cm^{-1})=3379, 3141, 3042, 2980, 1639, 1574, 1547, 1462, 1401, 1226, 1156, 1088, 1049, 970, 893, 790, 715, 632, 585.

6-oxo-3-(1-propyl-1*H*-imidazol-3-ium-3-yl)-3,6-dihydro-1,2,4,5-tetrazin-3-ide (3c)



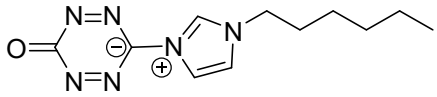
80mg crimson solid, yield: 65%. Mp: 232.3-233.0°C. HRMS (ESI) *m/z* calculated for $C_8H_{11}N_6O$ $[M+H]^+$, 207.0989; found 207.0988. ^{1}H NMR (600 MHz, DMSO-d_6, ppm) δ 9.99 (t, *J* = 1.6 Hz, 1H), 8.32 (t, *J* = 1.9 Hz, 1H), 8.07 (t, *J* = 1.8 Hz, 1H), 4.27 (t, *J* = 7.1 Hz, 2H), 1.89 (h, *J* = 7.2 Hz, 2H), 0.88 (t, *J* = 7.4 Hz, 3H); ^{13}C NMR (151 MHz, DMSO-d_6, ppm) δ 165.65, 149.02, 133.69, 123.70, 119.03, 51.22, 23.19, 10.83.

3-(1-butyl-1*H*-imidazol-3-ium-3-yl)-6-oxo-3,6-dihydro-1,2,4,5-tetrazin-3-ide (3d)



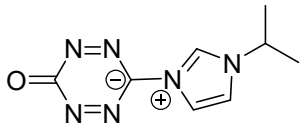
86mg crimson solid, yield: 65%. Mp: 224.3-226.4°C. HRMS (ESI) *m/z* calculated for $C_9H_{13}N_6O$ $[M+H]^+$, 221.1145; found 221.1141. ^{1}H NMR (600 MHz, DMSO-d_6, ppm) δ 9.98 (t, *J* = 1.7 Hz, 1H), 8.32 (t, *J* = 1.9 Hz, 1H), 8.06 (t, *J* = 1.9 Hz, 1H), 4.30 (t, *J* = 7.2 Hz, 2H), 1.88 – 1.82 (m, 2H), 1.33 – 1.26 (m, 2H), 0.91 (t, *J* = 7.4 Hz, 3H); ^{13}C NMR (151 MHz, DMSO-d_6, ppm) δ 165.66, 149.02, 133.67, 123.67, 119.04, 49.50, 31.67, 19.20, 13.72.

3-(1-hexyl-1*H*-imidazol-3-ium-3-yl)-6-oxo-3,6-dihydro-1,2,4,5-tetrazin-3-ide (3e)



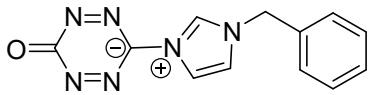
113mg crimson solid, yield: 76%. Mp: 223.4.3-226.3°C. HRMS (ESI) *m/z* calculated for $C_{11}H_{17}N_6O$ $[M+H]^+$, 249.1458; found 249.1461. ^{1}H NMR (600 MHz, DMSO-d_6, ppm) δ 9.99 (d, *J* = 2.6 Hz, 1H), 8.32 (t, *J* = 1.9 Hz, 1H), 8.07 (t, *J* = 2.3 Hz, 1H), 4.30 (t, *J* = 7.3 Hz, 2H), 1.87 (p, *J* = 7.1 Hz, 2H), 1.29 – 1.26 (m, 6H), 0.86 (m, 3H); ^{13}C NMR (151 MHz, DMSO-d_6, ppm δ 165.63 , 149.01 , 133.67 , 123.68 , 119.03 , 49.77 , 30.97 , 29.65 , 25.55 , 22.29 , 14.26.

3-(1-isopropyl-1*H*-imidazol-3-ium-3-yl)-6-oxo-3,6-dihydro-1,2,4,5-tetrazin-3-ide (3f)



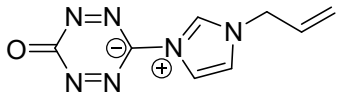
97mg amaranth solid, yield: 79%. Mp: 229.8-231.8°C. HRMS (ESI) *m/z* calculated for $C_8H_{11}N_6O$ $[M+H]^+$, 207.0989; found 207.0991. ^{1}H NMR (600 MHz, DMSO-d_6, ppm) δ 9.98 (d, *J* = 2.2 Hz, 1H), 8.33 (d, *J* = 1.9 Hz, 1H), 8.18 (t, *J* = 1.9 Hz, 1H), 4.82 (p, *J* = 6.7 Hz, 1H), 1.55 (d, *J* = 6.7 Hz, 6H); ^{13}C NMR (151 MHz, DMSO-d_6, ppm) δ 165.63 , 149.02 , 132.60 , 121.74 , 119.23 , 53.45 , 22.65.

3-(1-benzyl-1*H*-imidazol-3-ium-3-yl)-6-oxo-3,6-dihydro-1,2,4,5-tetrazin-3-ide (3g)



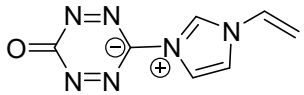
96mg amaranth solid, yield: 63%. Mp:164.0-166.4°C. HRMS (ESI) *m/z* calculated for $C_{12}H_{11}N_6O$ $[M+H]^+$, 255.0989; found 255.0985. ^{1}H NMR (600 MHz, DMSO-d_6, ppm) δ 10.14 (s, 1H), 8.32 (s, 1H), 8.02 (s, 1H), 7.52 (d, *J* = 7.4 Hz, 2H), 7.41 (dt, *J* = 23.7, 7.4 Hz, 3H), 5.54 (s, 2H); ^{13}C NMR (151 MHz, DMSO-d_6, ppm) δ 165.58, 148.98, 135.08, 133.79, 129.40, 129.23, 128.84, 123.56, 119.46, 52.77.

3-(1-allyl-1*H*-imidazol-3-ium-3-yl)-6-oxo-3,6-dihydro-1,2,4,5-tetrazin-3-ide (3h)



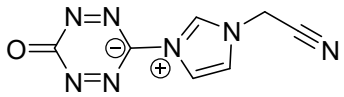
87mg amaranth solid, yield: 75%. Mp: 219.7-220.3°C. HRMS (ESI) *m/z* calculated for $C_8H_9N_6O$ $[M+H]^+$, 205.0832; found 205.0831.^{1}H NMR (600 MHz, DMSO-d_6, ppm) δ 9.98 (d, *J* = 1.7 Hz, 1H), 8.33 (t, *J* = 1.9 Hz, 1H), 7.99 (t, *J* = 1.9 Hz, 1H), 6.15 -6.08 (m, 1H), 5.40 – 5.35 (m, 2H), 4.99 (dd, *J* = 6.0, 1.5 Hz, 2H); ^{13}C NMR (151 MHz, DMSO-d_6, ppm) δ 165.64, 149.01, 133.77, 132.03, 123.69, 120.85, 119.19, 51.67. IR: (cm^{-1})=3426, 3180, 3137, 3095, 2978, 1967, 1619, 1593, 1542, 1448, 1429, 1404, 1371, 1276, 1247, 1219, 1091, 1043, 1018, 980, 946, 838, 760, 748, 628, 569.

6-oxo-3-(1-vinyl-1*H*-imidazol-3-ium-3-yl)-3,6-dihydro-1,2,4,5-tetrazin-3-ide (3i)



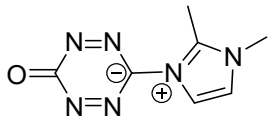
68mg amaranth solid, yield: 64%. Mp: 169.7-175.5°C. HRMS (ESI) *m/z* calculated for $C_7H_7N_6O$ $[M+H]^+$, 191.0676; found 191.0676. ^{1}H NMR (600 MHz, DMSO-d_6, ppm) δ 10.29 (t, *J* = 1.7 Hz, 1H), 8.50 (t, *J* = 2.0 Hz, 1H), 8.46 (t, *J* = 2.0 Hz, 1H), 7.44 (dd, *J* = 15.7, 8.8 Hz, 1H), 6.20 (dd, *J* = 15.7, 2.5 Hz, 1H), 5.51 (dd, *J* = 8.8, 2.5 Hz, 1H); ^{13}C NMR (151 MHz, DMSO-d_6, ppm) δ 165.56, 148.80, 132.54, 129.18, 120.28, 119.66, 110.04.

3-(1-(cyanomethyl)-1*H*-imidazol-3-ium-3-yl)-6-oxo-3,6-dihydro-1,2,4,5-tetrazin-3-ide (3j)



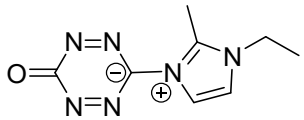
79mg amaranth solid, yield: 65%. Mp: 239.1-244.2°C. HRMS (ESI) *m/z* calculated for $C_7H_6N_7O$ $[M+H]^+$ m/z, 204.0628; found 204.0627. ^{1}H NMR (600 MHz, DMSO-d_6, ppm) δ 10.09 (d, J = 1.8 Hz, 1H), 8.39 (t, J = 1.9 Hz, 1H), 8.18 (t, J = 1.9 Hz, 1H), 5.74 (s, 2H); ^{13}C NMR (151 MHz, DMSO-d_6, ppm) δ 165.57, 148.88, 134.91, 123.89, 119.56, 114.95, 37.68.

3-(1,2-dimethyl-1*H*-imidazol-3-ium-3-yl)-6-oxo-3,6-dihydro-1,2,4,5-tetrazin-3-ide (3k)



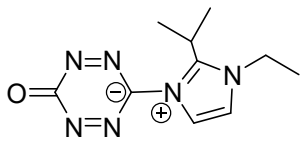
89mg orange red solid, yield: 78%. Mp:169.8-171.2°C. HRMS (ESI) *m/z* calculated for $C_7H_8N_6O$ $[M+H]^+$, 193.0832; found 193.0831. ^{1}H NMR (600 MHz, DMSO-d_6, ppm) δ 8.07 (d, J = 2.2 Hz, 1H), 7.87 (d, J = 2.2 Hz, 1H), 3.87 (s, 3H), 2.69 (s, 3H); ^{13}C NMR (151 MHz, DMSO-d_6, ppm) δ 164.36, 150.07, 145.07, 123.41, 120.41, 35.54, 11.28.

3-(1-ethyl-2-methyl-1*H*-imidazol-3-ium-3-yl)-6-oxo-3,6-dihydro-1,2,4,5-tetrazin-3-ide (3l)



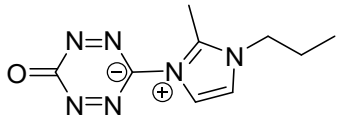
74mg amaranth solid, yield: 60%. Mp: 221.6-223.8°C. HRMS (ESI) *m/z* calculated for $C_8H_{11}N_6O$ $[M+H]^+$, 207.0989; found 207.0985. ^{1}H NMR (600 MHz, DMSO-d_6, ppm) δ 8.11 (d, J = 2.2 Hz, 1H), 7.92 (d, J = 2.2 Hz, 1H), 4.25 (q, J = 7.3 Hz, 2H), 2.73 (s, 3H), 1.43 (t, J = 7.3 Hz, 3H). ^{13}C NMR (151 MHz, DMSO-d_6, ppm) δ 164.31, 150.03, 144.38, 121.70, 120.98, 43.72, 14.91, 11.14. IR: (cm^{-1})=3426, 3098, 3071, 2975, 1957, 1591, 1520, 1463, 1438, 1398, 1298, 1263, 1173, 1126, 1060, 981, 818, 702, 682, 597, 537.

3-(1-ethyl-2-isopropyl-1*H*-imidazol-3-ium-3-yl)-6-oxo-3,6-dihydro-1,2,4,5-tetrazin-3-ide (3m)



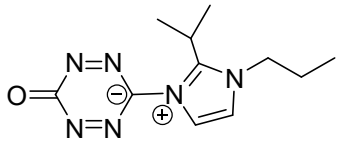
81mg amaranth solid, yield: 58%. Mp: 204.3-206.8°C. HRMS (ESI) *m/z* calculated for $C_{10}H_{15}N_6O$ $[M+H]^+$, 235.1302; found 235.1297. ^{1}H NMR (600 MHz, DMSO-d_6, ppm) δ 8.10 (d, J = 2.2 Hz, 1H), 7.98 (d, J = 2.2 Hz, 1H), 4.34 (q, J = 7.3 Hz, 2H), 3.64 (hept, J = 7.1 Hz, 1H), 1.48 (t, J = 7.3 Hz, 3H), 1.21 (d, J = 7.1 Hz, 6H); ^{13}C NMR (151 MHz, DMSO-d_6, ppm) δ 163.90, 150.30, 150.22, 123.23, 122.20, 44.04, 25.51, 19.63, 15.60.

3-(2-methyl-1-propyl-1*H*-imidazol-3-ium-3-yl)-6-oxo-3,6-dihydro-1,2,4,5-tetrazin-3-ide (3n)



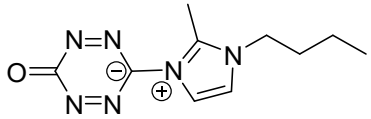
60mg amaranth solid, yield: 45%. Mp: 222.0-223.4°C. HRMS (ESI) *m/z* calculated for $C_9H_{13}N_6O$ $[M+H]^+$, 221.1145; found 221.1142. ^{1}H NMR (600 MHz, DMSO-d_6, ppm) δ 8.13 (t, *J* = 2.1 Hz, 1H), 7.94 (d, *J* = 2.2 Hz, 1H), 4.20 (td, *J* = 7.5, 2.6 Hz, 2H), 2.73 (d, *J* = 2.6 Hz, 3H), 1.83 (dd, *J* = 7.3, 2.6 Hz, 2H), 0.94 – 0.91 (m, 3H); ^{13}C NMR (151 MHz, DMSO-d_6, ppm) δ 164.33, 150.06, 144.55, 122.35, 120.87, 49.77, 22.74, 11.28, 10.97. IR: (cm^{-1})=3406, 3129, 3049, 2972, 2879, 1956, 1583, 1522, 1433, 1394, 1306, 1263, 1240, 1175, 1059, 979, 836, 817, 786, 707, 595, 543.

3-(2-isopropyl-1-propyl-1*H*-imidazol-3-ium-3-yl)-6-oxo-3,6-dihydro-1,2,4,5-tetrazin-3-ide (3o)



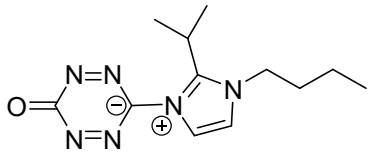
74mg amaranth solid, yield: 50%. Mp: 238.6-240.7°C. HRMS (ESI) *m/z* calculated for $C_{11}H_{17}N_6O$ $[M+H]^+$, 249.1458; found 249.1454. ^{1}H NMR (600 MHz, DMSO-d_6, ppm) δ 8.11 (d, *J* = 2.1 Hz, 1H), 7.98 (d, *J* = 2.2 Hz, 1H), 4.27-4.24 (m, 2H), 3.69- 3.64 (m, 1H), 1.91-1.84 (m, 2H), 1.19 (d, *J* = 7.1 Hz, 6H), 0.96 (t, *J* = 7.4 Hz, 3H); ^{13}C NMR (151 MHz, DMSO-d_6, ppm) δ 163.87, 150.55, 150.23, 123.31, 122.62, 49.98, 25.44, 23.36, 19.75, 10.97. IR: (cm^{-1})=3425, 3100, 2975, 2878, 1964, 1712, 1638, 1595, 1509, 1449, 1402, 1365, 1259, 1236, 1191, 1176, 1044, 979, 801, 732, 578, 556.

3-(1-butyl-2-methyl-1H-imidazol-3-ium-3-yl)-6-oxo-3,6-dihydro-1,2,4,5-tetrazin-3-ide (3p)



88mg amaranth solid, yield: 63%. Mp: 202.0-204.7°C. HRMS (ESI) *m/z* calculated for $C_{10}H_{15}N_6O$ $[M+H]^+$, 235.1302; found 235.1297. ^{1}H NMR (600 MHz, DMSO-d_6, ppm) δ 8.12 (dd, *J* = 2.3, 0.9 Hz, 1H), 7.92 (dd, *J* = 2.3, 0.9 Hz, 1H), 4.22 (t, *J* = 7.4 Hz, 2H), 2.73 (d, *J* = 0.9 Hz, 3H), 1.82-1.76 (m, 2H), 1.35 (h, *J* = 7.4 Hz, 2H), 0.93 (td, *J* =7.3, 1.0 Hz, 3H); ^{13}C NMR (151 MHz, DMSO-d_6, ppm) δ 164.29, 150.04, 144.51, 122.29, 120.89, 48.21, 31.27, 19.45, 13.85, 11.27.

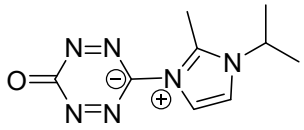
3-(1-butyl-2-isopropyl-1*H*-imidazol-3-ium-3-yl)-6-oxo-3,6-dihydro-1,2,4,5-tetrazin-3-ide (3q)



83mg amaranth solid, yield: 53%. Mp: 236.6-239.0°C. HRMS (ESI) *m/z* calculated for $C_{12}H_{19}N_6O$

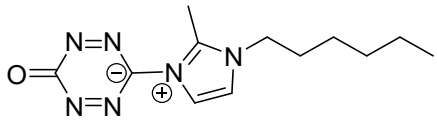
[M+H]$^+$, 263.1615; found 263.1610. ^{1}H NMR (600 MHz, DMSO-d_6, ppm) δ 8.13-8.09 (m, 1H), 7.99 (s, 1H), 4.28 (t, J = 7.5 Hz, 2H), 3.66 (p, J = 7.1 Hz, 1H), 1.83 (t, J = 7.7 Hz, 2H), 1.38 (q, J = 7.6 Hz, 2H), 1.18 (d, J = 7.1 Hz, 6H), 0.94 (t, J =7.3 Hz, 3H). ^{13}C NMR (151 MHz, DMSO-d_6, ppm) δ 163.87, 150.49, 150.23, 123.31, 122.62, 48.49, 31.95, 25.46, 19.75, 19.52, 13.91.

3-(1-isopropyl-2-methyl-1*H*-imidazol-3-ium-3-yl)-6-oxo-3,6-dihydro-1,2,4,5-tetrazin-3-ide (3r)



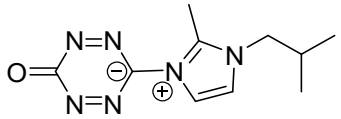
63mg amaranth solid, yield:48%. Mp: 232.5-235.1°C. HRMS (ESI) *m/z* calculated for $C_9H_{12}N_6O$ [M+H]$^+$ m/z: 221.1145，found 221.1143.^{1}H NMR (600 MHz, DMSO-d_6, ppm) δ 8.16 (s, 1H), 8.08 (s, 1H), 4.77 (p, J = 6.8 Hz, 1H), 2.74 (s, 3H), 1.50 (d, J = 6.7 Hz, 6H). ^{13}C NMR (151 MHz, DMSO-d_6, ppm) δ 164.28, 149.99, 143.88, 121.60, 118.79, 51.04, 22.21, 11.19.

3-(1-hexyl-2-methyl-1*H*-imidazol-3-ium-3-yl)-6-oxo-3,6-dihydro-1,2,4,5-tetrazin-3-ide (3s)



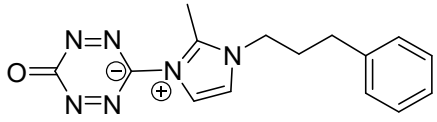
82mg amaranth solid, yield: 52%. Mp: 208.4-210.9°C. HRMS (ESI) *m/z* calculated for $C_{12}H_{19}N_6O$ [M+H]$^+$, 263.1615; found 263.1611. ^{1}H NMR (600 MHz, DMSO-d_6, ppm) δ 8.12 (d, J =2.2 Hz, 1H), 7.96 (d, J =2.2 Hz, 1H), 4.23 (t, J =7.5 Hz, 2H), 2.73 (s, 3H), 1.80 (p, J = 7.4 Hz, 2H), 1.33-1.27 (m, 6H), 0.88-0.84 (m, 3H); ^{13}C NMR (151 MHz, DMSO-d_6, ppm) δ 164.38, 150.08, 144.49, 122.35, 120.85, 48.42, 31.11, 29.25, 25.76, 22.36, 14.28, 11.29. IR: (cm^{-1})=3426, 3113, 2932, 2860, 1958, 1714, 1589, 1520, 1471, 1399, 1263, 1230, 1058, 984, 837, 817, 583.

3-(1-isobutyl-2-methyl-1*H*-imidazol-3-ium-3-yl)-6-oxo-3,6-dihydro-1,2,4,5-tetrazin-3-ide (3t)



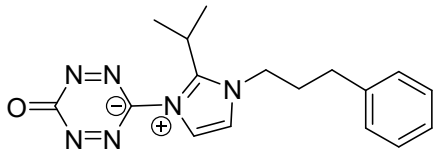
93mg amaranth solid, yield: 66%. Mp: 224.5-227.6°C. HRMS (ESI) *m/z* calculated for $C_{10}H_{15}N_6O$ [M+H]$^+$, 235.1302; found 235.1301. ^{1}H NMR (600 MHz, DMSO-d_6, ppm) δ 8.15 (d, J = 2.2 Hz, 1H), 7.90 (d, J = 2.3 Hz, 1H), 4.08 (d, J = 7.5 Hz, 2H), 2.74 (s, 3H), 2.15 (dt, J = 13.8, 6.9 Hz, 1H), 0.93 (d, J = 6.6 Hz, 6H); ^{13}C NMR (151 MHz, DMSO-d_6, ppm) δ 164.30, 150.07, 144.71, 122.80, 120.82, 54.91, 28.82, 19.62, 11.49.

3-(2-methyl-1-(3-phenylpropyl)-1*H*-imidazol-3-ium-3-yl)-6-oxo-3,6-dihydro-1,2,4,5-tetrazin-3-ide (3u)



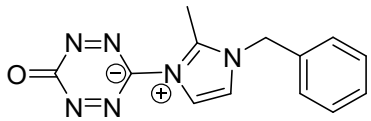
110mg amaranth solid, yield: 62%. Mp: 204.1-206.3°C. HRMS (ESI) *m/z* calculated for $C_{15}H_{15}N_6O$ $[M-H]^-$, 295.1313; found 295.1312. ^1H NMR (600 MHz, DMSO-d_6, ppm) δ 8.11 (d, *J* = 2.0 Hz, 1H), 7.99 (d, *J* = 2.2 Hz, 1H), 7.29 (t, *J* = 7.5 Hz, 2H), 7.26 – 7.23 (m, 2H), 7.21 – 7.17 (m, 1H), 4.28 (t, *J* = 7.4 Hz, 2H), 2.71 (s, 3H), 2.68 (dd, *J* = 9.3, 6.6 Hz, 2H), 2.18 – 2.12 (m, 2H); ^{13}C NMR (151 MHz, DMSO-d_6, ppm) δ 164.39, 150.11, 144.59, 141.01, 128.84, 128.82, 128.66, 128.64, 126.51, 122.31, 120.86, 48.17, 32.15, 30.69, 11.37.

3-(2-isopropyl-1-(3-phenylpropyl)-1*H*-imidazol-3-ium-3-yl)-6-oxo-3,6-dihydro-1,2,4,5-tetrazin-3-ide (3v)



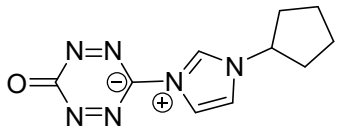
91mg amaranth solid, yield: 47%. Mp: 232.1-234.2°C. HRMS (ESI) *m/z* calculated for $C_{17}H_{21}N_6O$ $[M-H]^-$, 323.1626; found 323.1627. ^1H NMR (600 MHz, DMSO-d_6, ppm) δ 8.11-8.10 (m, 1H), 8.05 (t, *J* = 1.7 Hz, 1H), 7.30 (d, *J* = 7.4 Hz, 2H), 7.27 (d, *J* = 7.4 Hz, 2H), 7.23 – 7.19 (m, 1H), 4.32 (t, *J* = 7.7 Hz, 2H), 3.61 (p, *J* = 7.1 Hz, 1H), 2.74 – 2.70 (m, 2H), 2.19 (td, *J* = 7.4, 3.7 Hz, 2H), 1.15 (d, *J* = 7.1 Hz, 6H); ^{13}C NMR (151 MHz, DMSO-d_6, ppm) δ 163.92, 150.47, 150.25, 140.96, 128.86, 128.72, 126.57, 123.26, 122.64, 48.28, 32.15, 31.43, 25.46, 19.66.

3-(1-benzyl-2-methyl-1*H*-imidazol-3-ium-3-yl)-6-oxo-3,6-dihydro-1,2,4,5-tetrazin-3-ide (3w)



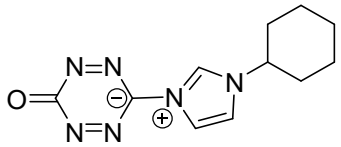
96mg red solid, yield: 63%. Mp: 254.7-257.4°C. HRMS (ESI) *m/z* calculated for $C_{13}H_{13}N_6O$ $[M+H]^+$, 269.1145; found 269.1150. ^1H NMR (600 MHz, DMSO-d_6, ppm) δ 8.16 (d, *J* = 2.2 Hz, 1H), 7.99 (dd, *J* = 4.7, 2.4 Hz, 1H), 7.46-7.34 (m, 5H), 5.56 (t, *J* = 2.7 Hz, 2H), 2.75 (s, 3H). ^{13}C NMR (151 MHz, DMSO-d_6, ppm) δ 164.36, 150.08, 144.82, 134.57, 129.50, 129.07, 128.43, 122.70, 121.11, 51.49, 11.68. IR: (cm^{-1})=3424, 3100, 3058, 1958, 1587, 1519, 1457, 1412, 1355, 1311, 1287, 1265, 1222, 1199, 1139, 1060, 1025, 982, 839, 816, 732, 644, 588.

3-(1-cyclopentyl-1*H*-imidazol-3-ium-3-yl)-6-oxo-3,6-dihydro-1,2,4,5-tetrazin-3-ide (3x)



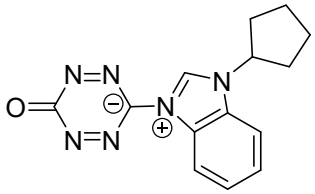
91.42mg purple solid, yield: 66%. Mp:197.9-199.9°C. HRMS (ESI) m/z calculated for $C_{10}H_{12}N_6O[M+H]^+$ m/z: 233.1145, found 233.1151. ^1H NMR(600MHz, DMSO-d_6): δ9.95(t, *J*=1.7Hz, 1H), 8.35(t, *J*=1.9Hz, 1H), 8.10(t, *J*=1.9Hz, 1H), 4.89(p, *J*=7.4Hz, 1H)，2.28–2.21(m, 2H), 2.01-1.95(m, 2H), 1.85(tdd, *J*=11.6, 8.5, 5.0Hz, 2H), 1.72-1.64(m, 2H). ^{13}C NMR(151MHz, DMSO-d6): δ165.15, 148.58, 132.59, 121.87, 119.00, 61.15, 32.55, 23.28.

3-(1-cyclohexyl-1*H*-imidazol-3-ium-3-yl)-6-oxo-3,6-dihydro-1,2,4,5-tetrazin-3-ide (3y)



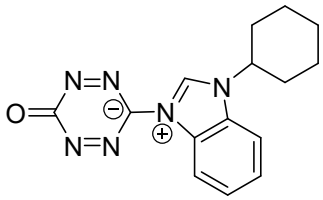
92mg purple solid, yield: 62%. Mp:139.5-140.1°C. HRMS (ESI) m/z calculated for $C_{11}H_{14}N_6O$ $[M+H]^+$ m/z: 247.1302, found 247.1308. ^{1}H NMR(600MHz，DMSO-d_6): δ9.93(t, *J*=1.7Hz, 1H), 8.34(t, *J*=1.9Hz, 1H), 8.11(t, *J*=1.9Hz, 1H), 4.43(tt, *J*=11.9, 3.9Hz, 1H), 2.15-2.08(m, 2H), 1.90-1.77(m, 4H), 1.72-1.64(m, 1H), 1.44-1.34(m, 2H), 1.23(qt, *J*=13.0, 3.6Hz, 1H). ^{13}C NMR(151MHz, DMSO-d_6): δ165.12, 148.56, 132.14, 121.56, 118.71, 59.40, 32.25, 24.64, 24.29.

3-(1-cyclopentyl-1*H*-benzo[*d*]imidazol-3-ium-3-yl)-6-oxo-3,6-dihydro-1,2,4,5-tetrazin-3-ide (3z)



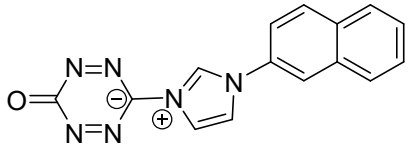
123mg purple solid, yield:73%. Mp:249.7-250.1°C. HRMS (ESI) m/z calculated for $C_{14}H_{14}N_6O$ $[M+H]^+$m/z: 283.1302, found 283.1309. ^{1}HNMR(600MHz, DMSO-d_6): δ10.35(s, 1H), 8.36–8.32(m, 1H)，8.19(ddd, *J*=6.3, 4.3, 2.6Hz，1H)，7.79-7.74(m, 2H), 5.27(p, *J*=7.4Hz, 1H), 2.41-2.34(m, 2H)，2.23-2.16(m, 2H), 1.94(tdd, *J*=11.5, 8.3, 5.8Hz, 2H), 1.80-1.71(m, 2H). ^{13}CNMR(151MHz，DMSO-d_6):δ164.51, 149.58, 138.55, 131.34, 129.35, 127.66, 126.91, 116.02, 114.27, 59.37, 31.46, 23.53.

3-(1-cyclohexyl-1*H*-benzo[*d*]imidazol-3-ium-3-yl)-6-oxo-3,6-dihydro-1,2,4,5-tetrazin-3-ide (3aa)



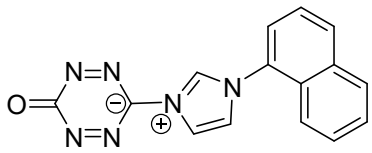
56.8mg purple solid, yield:43%. Mp:191.3-191.6°C. HRMS (ESI) m/z calculated for $C_{15}H_{16}N_6O$ $[M+H]^+$ m/z: 297.1458, found 297.1455. ^{1}H NMR (600MHz, DMSO-d_6)：δ10.41(s, 1H), 8.38-8.34(m, 1H), 8.32-8.28(m, 1H), 7.78-7.73(m, 2H), 4.87(tt, *J*=12.1, 3.8Hz, 1H), 2.26-2.19(m, 2H), 2.05(qd, *J*=12.4, 3.6Hz, 2H), 1.91(dt, *J*=13.9, 3.4Hz, 2H), 1.74(dt, *J*=13.0, 3.5Hz, 1H), 1.55(qt, *J*=13.2, 3.5Hz, 2H), 1.37-1.27(m, 1H). ^{13}C NMR (151MHz，DMSO-d_6):δ164.55, 149.67, 138.56, 130.88, 129.03, 127.66, 126.85, 116.10, 114.20, 57.58, 31.67, 24.83, 24.47.

3-(1-(naphthalen-2-yl)-1*H*-imidazol-3-ium-3-yl)-6-oxo-3,6-dihydro-1,2,4,5-tetrazin-3-ide (3ab)



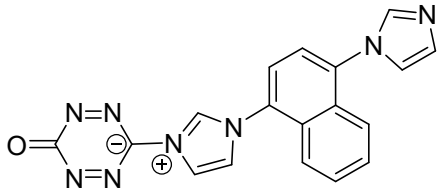
120.7mg purple solid, yield:69%. Mp:261.9-262.2°C. HRMS (ESI) m/z calculated for $C_{15}H_{10}N_6O$ $[M+H]^+$ m/z: 291.0989, found 291.0992. ^1H NMR(600MHz, DMSO-d_6):δ10.62(t, *J*=1.7Hz, 1H), 8.67(t, *J*=2.0Hz, 1H), 8.64(t, *J*=1.9Hz, 1H), 8.58(d, *J*=2.3Hz, 1H), 8.24(d, *J*=8.9Hz, 1H), 8.11-8.04(m, 3H), 7.72-7.67(m, 2H). ^{13}C NMR(151MHz, DMSO-d6):δ165.17, 148.61, 132.81, 132.56, 132.16, 132.03, 130.14, 128.33, 127.96, 127.83, 127.75, 122.28, 120.84, 119.90, 119.55.

3-(1-(naphthalen-1-yl)-1*H*-imidazol-3-ium-3-yl)-6-oxo-3,6-dihydro-1,2,4,5-tetrazin-3-ide (3ac)



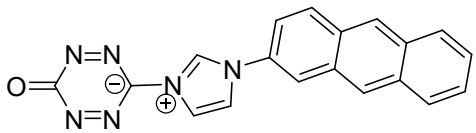
129mg purple solid, yield:74%. Mp:294.5-294.7°C. HRMS (ESI) m/z calculated for $C_{15}H_{10}N_6O$ $[M+H]^+$ m/z: 291.0989, found 291.0989. ^1H NMR(600MHz, DMSO-d_6):δ10.42(t, *J*=1.6Hz, 1H), 8.67(t, *J*=1.8Hz, 1H), 8.40(t, *J*=1.9Hz, 1H), 8.28(d, *J*=8.3Hz, 1H), 8.19(dd, *J*=7.7, 1.5Hz, 1H), 7.96(dd, *J*=7.3, 1.1Hz, 1H), 7.79-7.68(m, 4H). ^{13}C NMR(151MHz, DMSO-d_6):δ165.05, 148.62, 134.80, 133.58, 131.20, 131.15, 128.44, 128.39, 127.85, 127.49, 125.58, 125.44, 125.18, 121.68, 118.98.

3-(1-(4-(1*H*-imidazol-1-yl)naphthalen-1-yl)-1*H*-imidazol-3-ium-3-yl)-6-oxo-3,6-dihydro-1,2,4,5-tetrazin-3-ide (3ad)



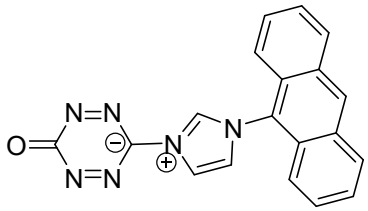
90mg purple solid, yield:51%. Mp:207.1-207.9°C. HRMS (ESI) m/z calculated for $C_{18}H_{12}N_8O$ $[M+H]^+$m/z: 357.1207, found 357.1200. ^1H NMR(600MHz, DMSO-d_6): δ10.49(t, *J*=1.6Hz, 1H), 8.72(t, *J*=1.9Hz, 1H), 8.43(t, *J*=1.9Hz, 1H), 8.13-8.09(m, 2H), 7.91-7.88(m, 2H), 7.84-7.80(m, 2H), 7.73-7.70(m, 1H), 7.67(t, *J*=1.3Hz, 1H), 7.29(t, *J*=1.1Hz, 1H). ^{13}C NMR(151MHz, DMSO-d_6):δ165.12, 148.63, 138.56, 136.17, 135.02, 131.62, 129.45, 129.25, 129.19, 129.19, 128.81, 125.66, 125.27, 123.44, 122.82, 122.64, 122.12, 119.11.

3-(1-(anthracen-2-yl)-1*H*-imidazol-3-ium-3-yl)-6-oxo-3,6-dihydro-1,2,4,5-tetrazin-3-ide (3ae)



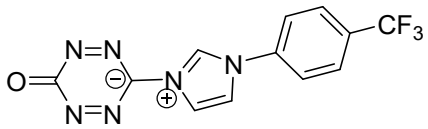
65mg purple solid, yield:47.74%. Mp:202.9-203.2°C. HRMS (ESI) m/z calculated for $C_{19}H_{12}N_6O$ $[M+H]^+$m/z: 341.1145, found 341.1148. ^1H NMR(600MHz，DMSO-d_6): δ10.67(t, *J*=1.7Hz, 1H), 8.78–8.71(m, 4H), 8.66(t, J=1.9Hz, 1H), 8.41(d, J=9.1Hz, 1H), 8.19(ddd, *J*=24.4, 6.1, 3.2Hz, 2H)，8.05(dd，*J*=9.1, 2.3Hz, 1H), 7.62(dt, *J*=6.6, 3.3Hz, 2H). ^{13}C NMR(151MHz , DMSO-d_6): δ165.02, 148.54, 132.17, 132.04, 132.02, 131.57, 130.75, 130.24, 129.97, 128.24, 128.15, 127.23, 126.77, 126.61, 126.60, 122.19, 120.92, 119.70, 119.56.

3-(1-(anthracen-9-yl)-1*H*-imidazol-3-ium-3-yl)-6-oxo-3,6-dihydro-1,2,4,5-tetrazin-3-ide (3af)



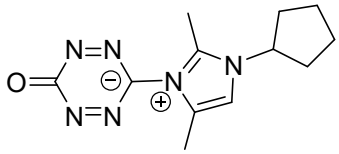
78.3mg purple solid, yield:54%. Mp:294.5-294.7°C. HRMS (ESI) m/z calculated for $C_{19}H_{12}N_6O$ $[M-H]^-$ m/z: 339.1000, found 339.1004. ^1H NMR(600MHz，DMSO-d_6): δ10.56(t, *J*=1.6Hz, 1H), 9.07(s, 1H), 8.85(t, *J*=1.9Hz, 1H), 8.43(t, *J*=1.9Hz, 1H), 8.34(dt, *J*=6.6, 2.7Hz, 2H), 7.71(td, *J*=7.2, 6.4, 3.9Hz, 6H). ^{13}C NMR(151MHz, DMSO-d_6): δ165.22, 148.81, 135.81, 130.64, 130.61, 128.84, 128.62, 127.43, 126.44, 126.40, 125.74, 121.61, 119.66.

6-oxo-3-(1-(4-(trifluoromethyl)phenyl)-1*H*-imidazol-3-ium-3-yl)-3,6-dihydro-1,2,4,5-tetrazin-3-ide (3ag)



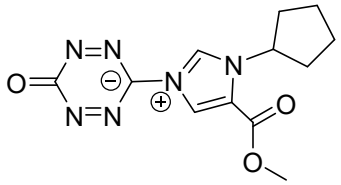
32mg purple solid, yield:42%. Mp:248.7-249.1°C. HRMS (ESI) m/z calculated for $C_{12}H_7F_3N_6O$ $[M+H]^+$ m/z: 309.0706, found 309.0705. ^1H NMR(600MHz, DMSO-d_6): δ10.64(d, *J*=1.7Hz, 1H), 8.66–8.59(m, 2H), 8.20(d, *J*=8.3Hz, 2H), 8.09(d, *J*=8.4Hz, 2H). ^{13}C NMR(151MHz, DMSO-d_6): δ165.02, 148.48, 137.74, 137.73, 132.68, 127.31, 127.29, 127.27, 127.24, 123.36, 122.18, 119.62.

3-(1-cyclopentyl-2,4-dimethyl-1*H*-imidazol-3-ium-3-yl)-6-oxo-3,6-dihydro-1,2,4,5-tetrazin-3-ide (3ah)



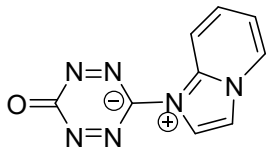
184.6mg, purple solid, yield:70.9%. Mp:261.1-261.7°C HRMS (ESI) m/z calculated for $C_{12}H_{16}N_6O$ $[M+H]^+$ m/z: 261.1459，found 261.1458. ^1H NMR (400 MHz, DMSO-d_6):δ 7.83 (s, 1H), 4.88 – 4.83 (m, 1H), 2.18 (s, 3H), 1.92 – 1.81 (m, 5H), 1.69 (s, 3H). ^{13}C NMR (176 MHz, DMSO-d_6):δ 165.09, 150.26, 140.83, 132.63, 129.19, 128.08, 127.36, 116.56, 114.29, 34.08.

3-(1-cyclopentyl-5-(methoxycarbonyl)-1*H*-imidazol-3-ium-3-yl)-6-oxo-3,6-dihydro-1,2,4,5-tetrazin-3-ide (3ai)



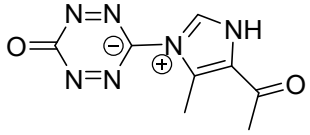
200.6mg, purple solid, yield: 69.2%. Mp:242.2-243.1 °C. HRMS (ESI) m/z calculated for $C_{12}H_{14}N_6O_3$ $[M+H]^+$ m/z: 290.1201, found 291.1198. ^{1}H NMR (400 MHz, DMSO-d_6):δ 10.12 (d, J = 2.3 Hz, 1H), 8.89 (d, J = 1.6 Hz, 1H), 5.41 (p, J = 7.3 Hz, 1H), 3.93 (s, 3H), 2.28 – 2.21 (m, 2H), 2.12 – 2.05 (m, 2H), 1.90 – 1.83 (m, 2H), 1.71 – 1.64 (m, 2H).^{13}C NMR (176 MHz, DMSO-d_6):δ 165.31, 158.24, 148.91, 135.76, 125.29, 124.82, 61.63, 53.55, 33.29, 23.80.

3-(imidazo[1,2-α]pyridin-1-ium-1-yl)-6-oxo-3,6-dihydro-1,2,4,5-tetrazin-3-ide (3aj)



79.1mg, purple solid, yield:61.7%. Mp:284.1-284.4 °C. HRMS (ESI) m/z calculated for $C_9H_6N_6O$ $[M+H]^+$ m/z: 215.0676, found 215.0675. ^{1}H NMR (400 MHz, DMSO-d_6):δ 9.03 (d, J = 6.7 Hz, 1H), 8.77 (s, 1H), 8.61 – 8.50 (m, 2H), 8.19 – 8.12 (m, 1H), 7.68 (t, J = 6.9 Hz, 1H). ^{13}C NMR (151 MHz, DMSO-d_6):δ 165.04, 150.38, 137.47, 136.16, 130.92, 122.69, 118.81, 116.91, 114.25.

3-(5-acetyl-4-methyl-1H-imidazol-3-ium-3-yl)-6-oxo-3,6-dihydro-1,2,4,5-tetrazin-3-ide (3ak)



93.1mg, purple solid, yield:44.9%. Mp:236.1-237.2 °C. HRMS (ESI) m/z calculated for $C_7H_6N_6O_2$ $[M+H]^+$ m/z: 207.0630, found 207.0628. ^{1}H NMR (400 MHz, DMSO-d_6):δ 9.89 (s, 1H), 8.16 (s, 1H), 2.54 (s, 3H). ^{13}C NMR (151 MHz, DMSO-d_6):δ 186.89, 164.90, 150.19, 137.97, 137.69, 136.70, 10.27.

Figure and scheme

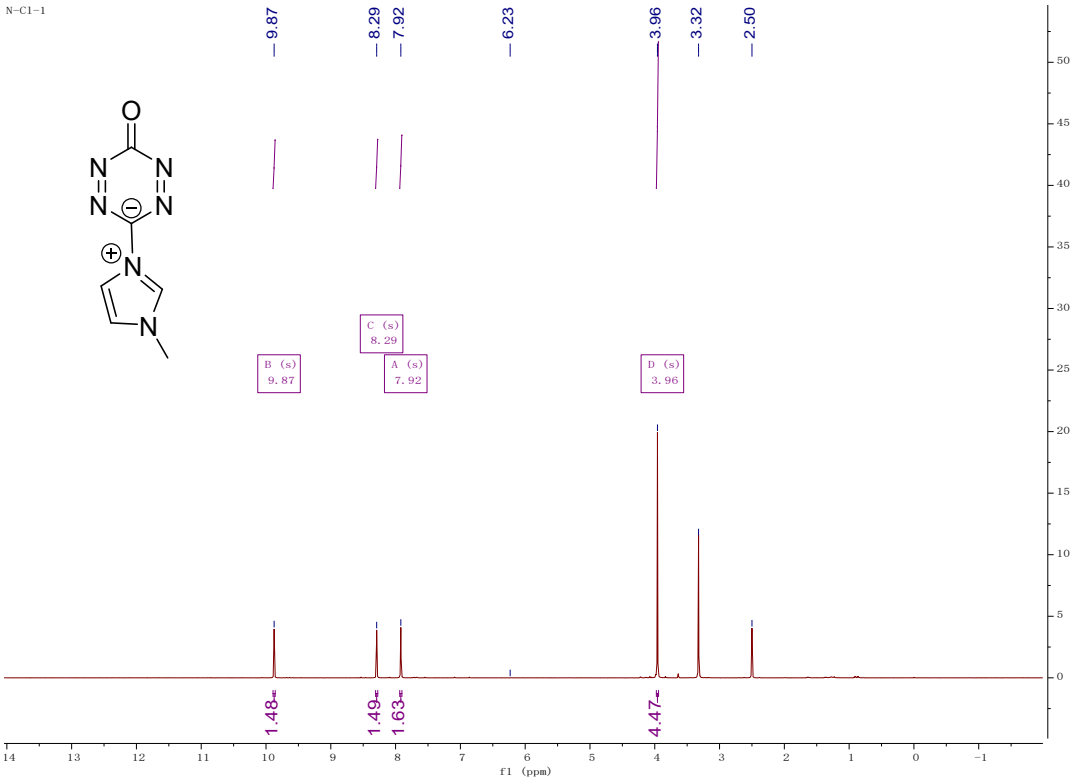


Figure S1. ^{1}H-NMR spectra of 3a in DMSO-d_6

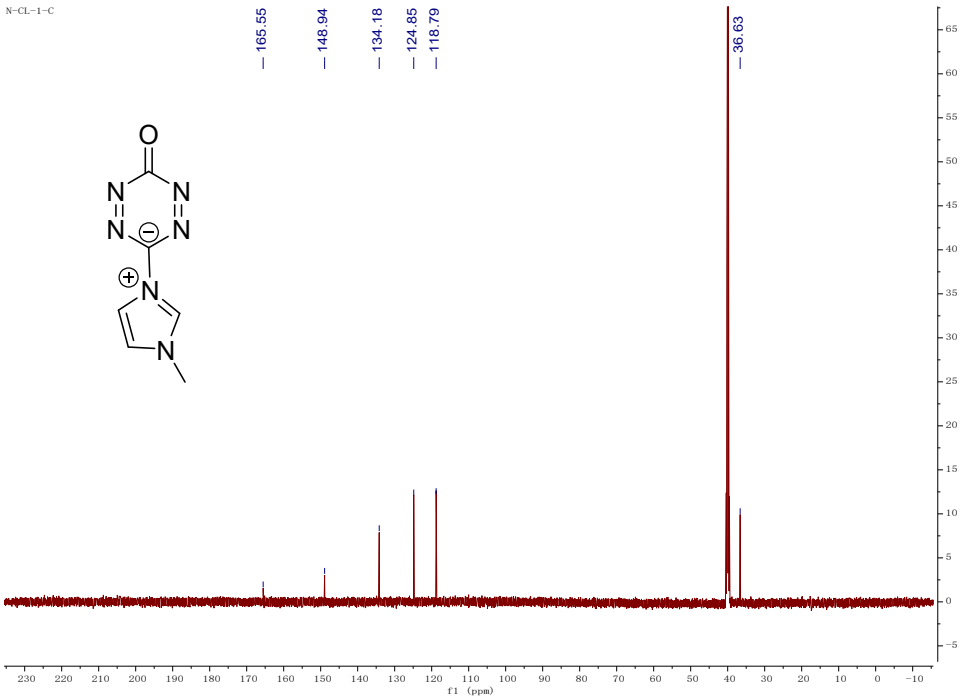


Figure S2. ^{13}C-NMR spectra of 3a in DMSO-d_6

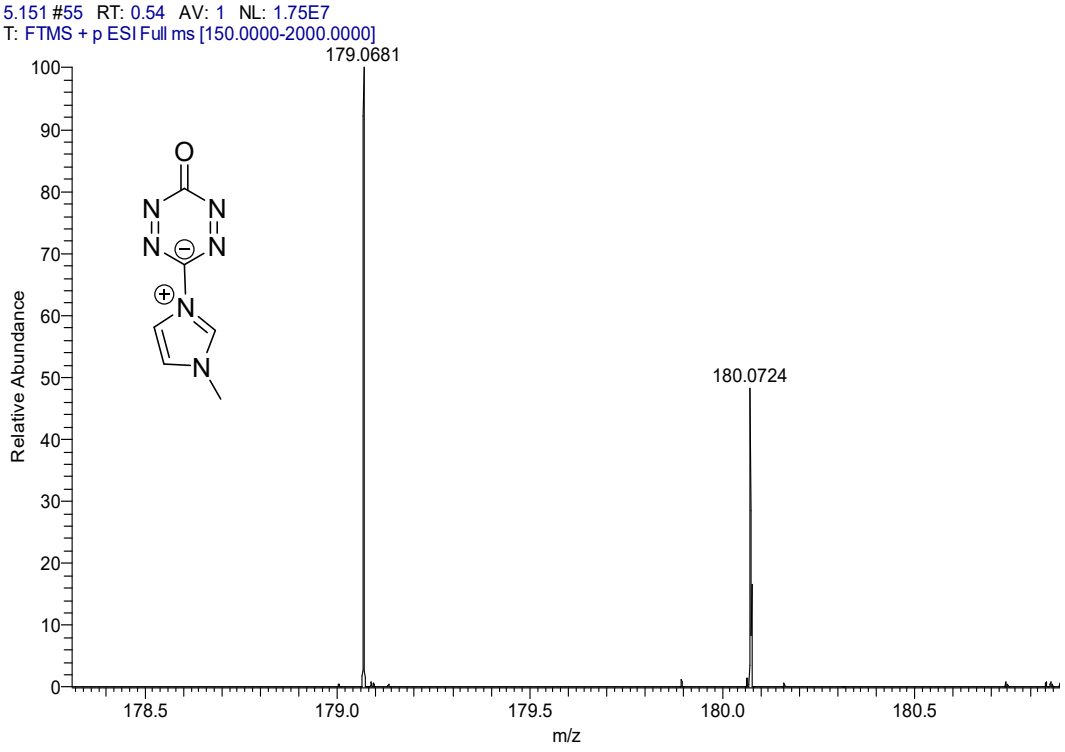


Figure S3. HRMS spectra of 3a in DMSO-d_6

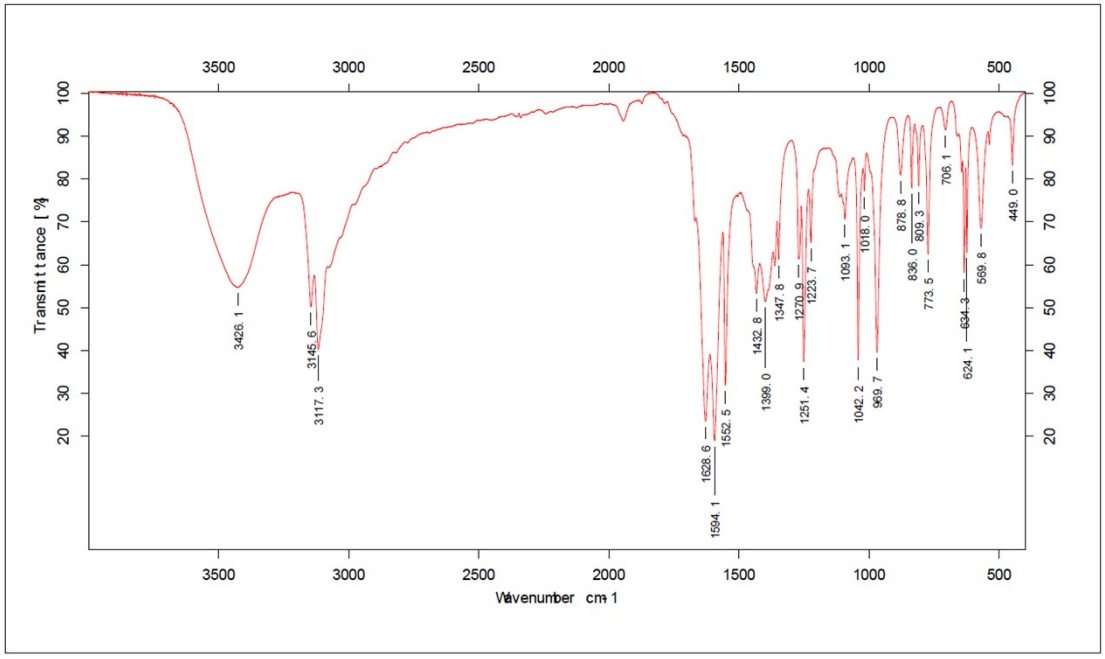


Figure S4. IR spectra of 3a

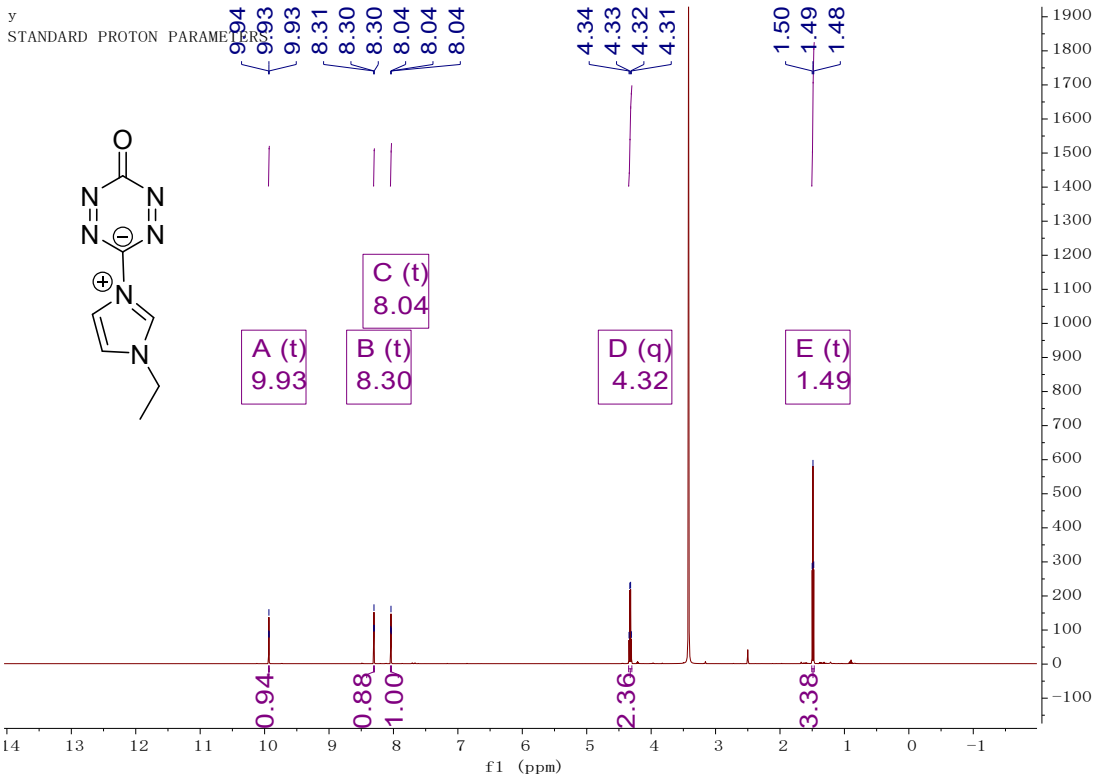


Figure S5. ^{1}H-NMR spectra of 3b in DMSO-d_6

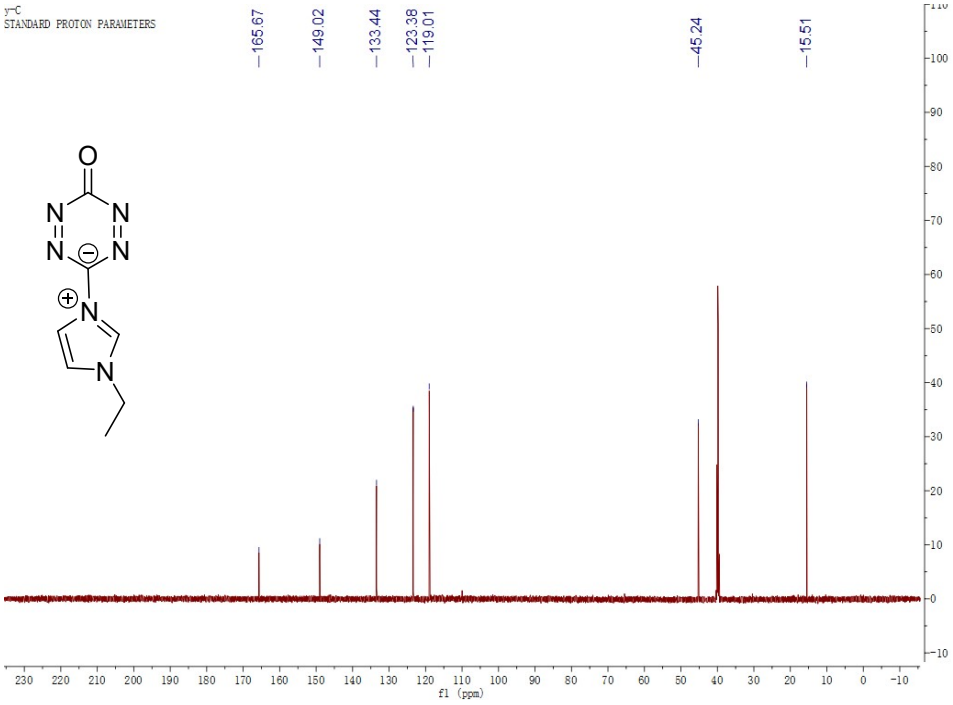


Figure S6. ^{13}C-NMR spectra of 3b in DMSO-d_6

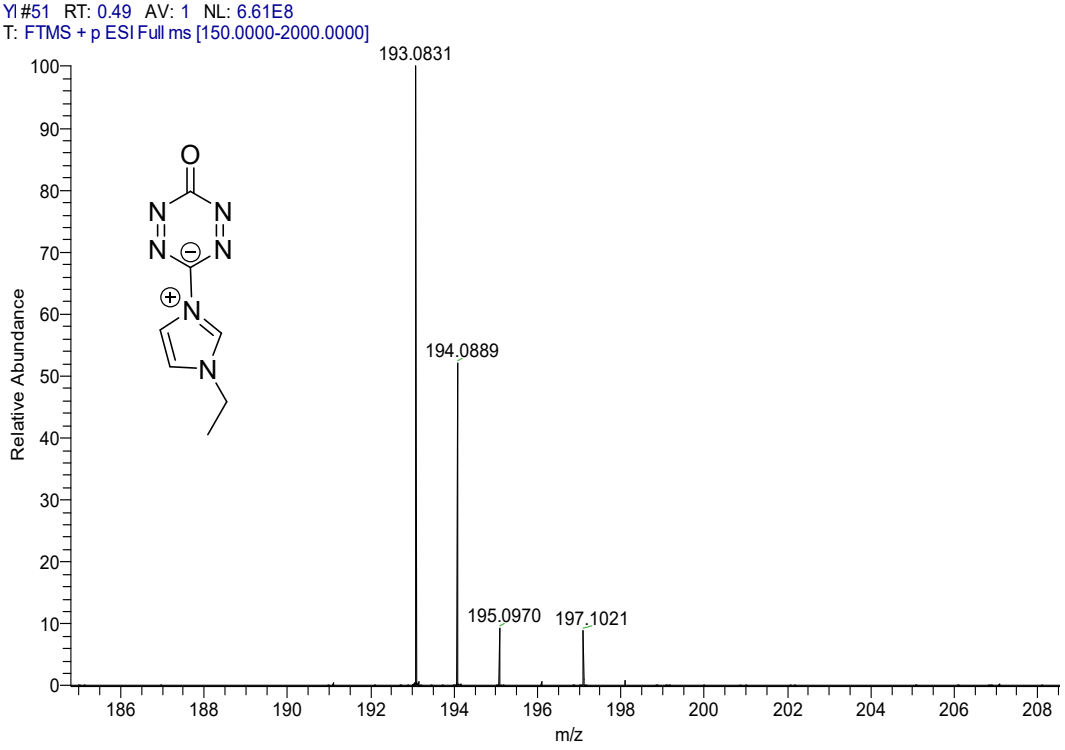


Figure S7. HRMS spectra of 3b in DMSO-d_6

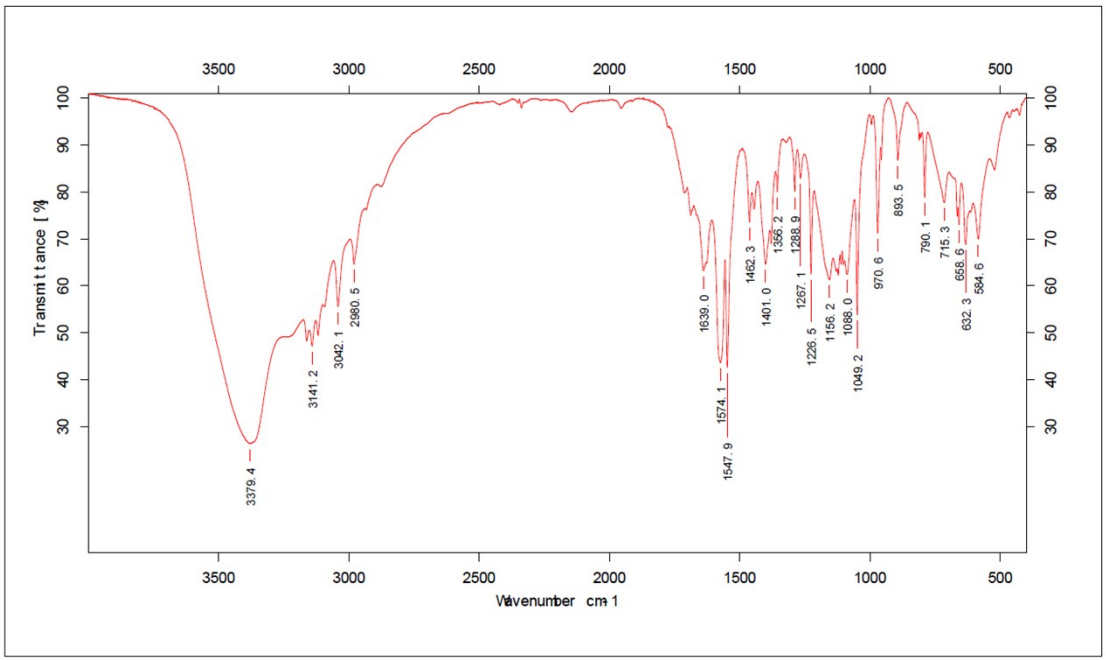


Figure S8. IR spectra of 3b

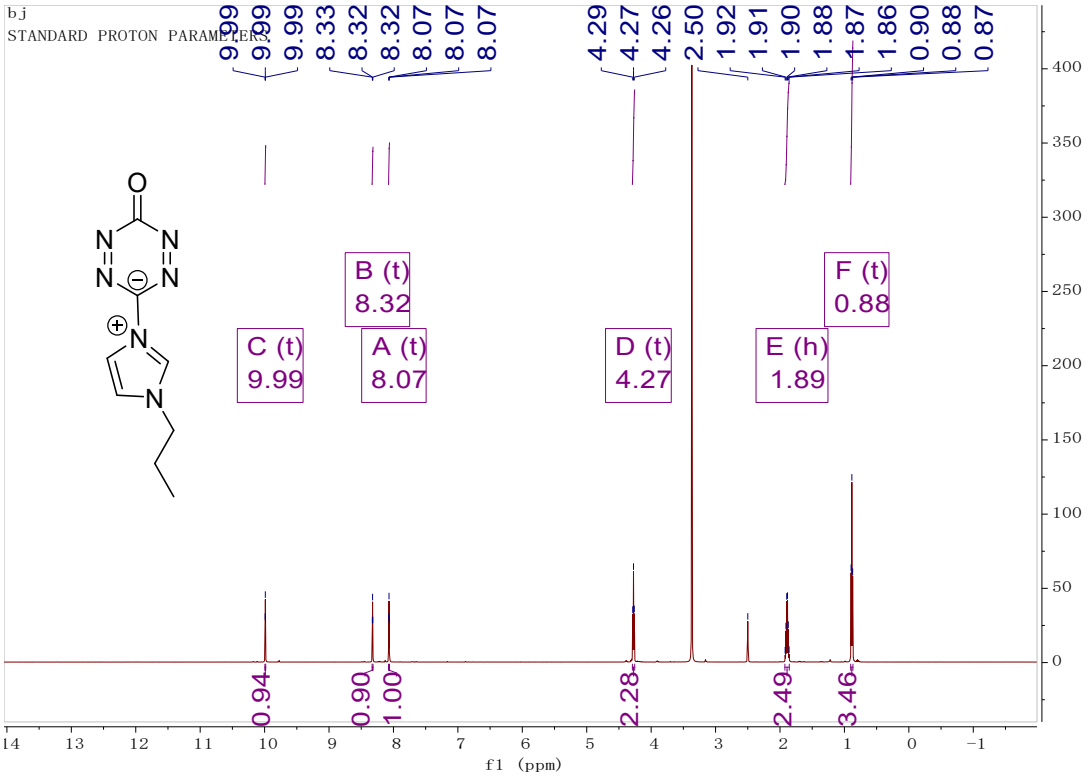


Figure S9. ^{1}H-NMR spectra of 3c in DMSO-d_6

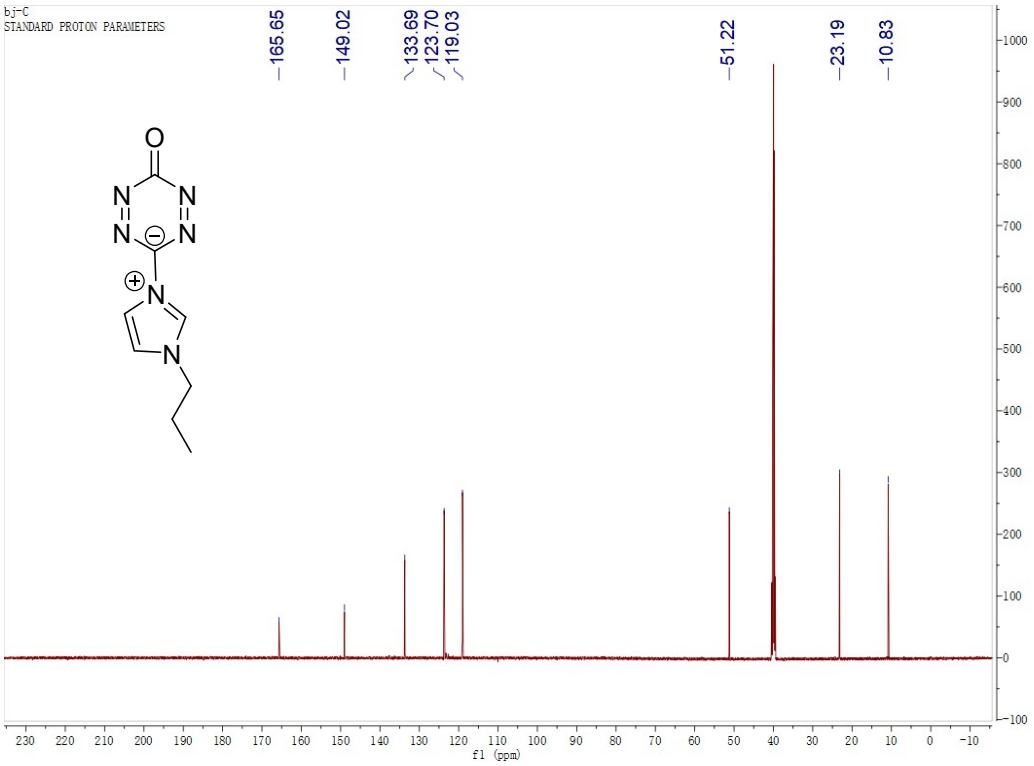


Figure S10. ^{13}C-NMR spectra of 3c in DMSO-d_6

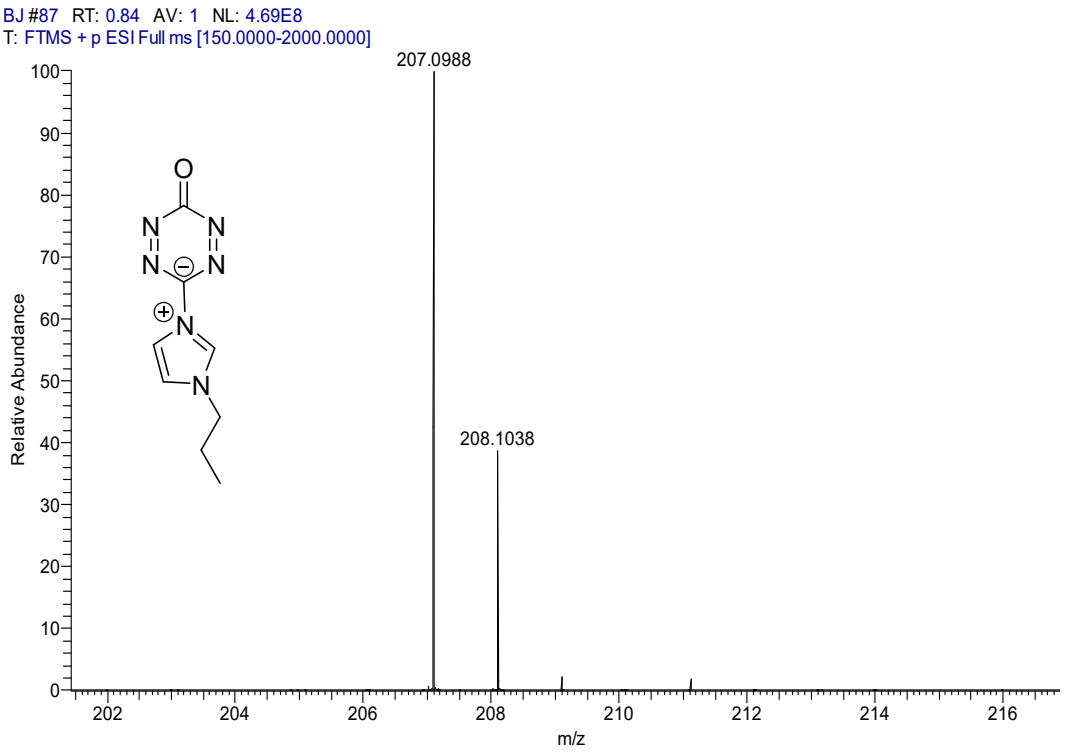


Figure S11. HRMS spectra of 3c in DMSO-d_6

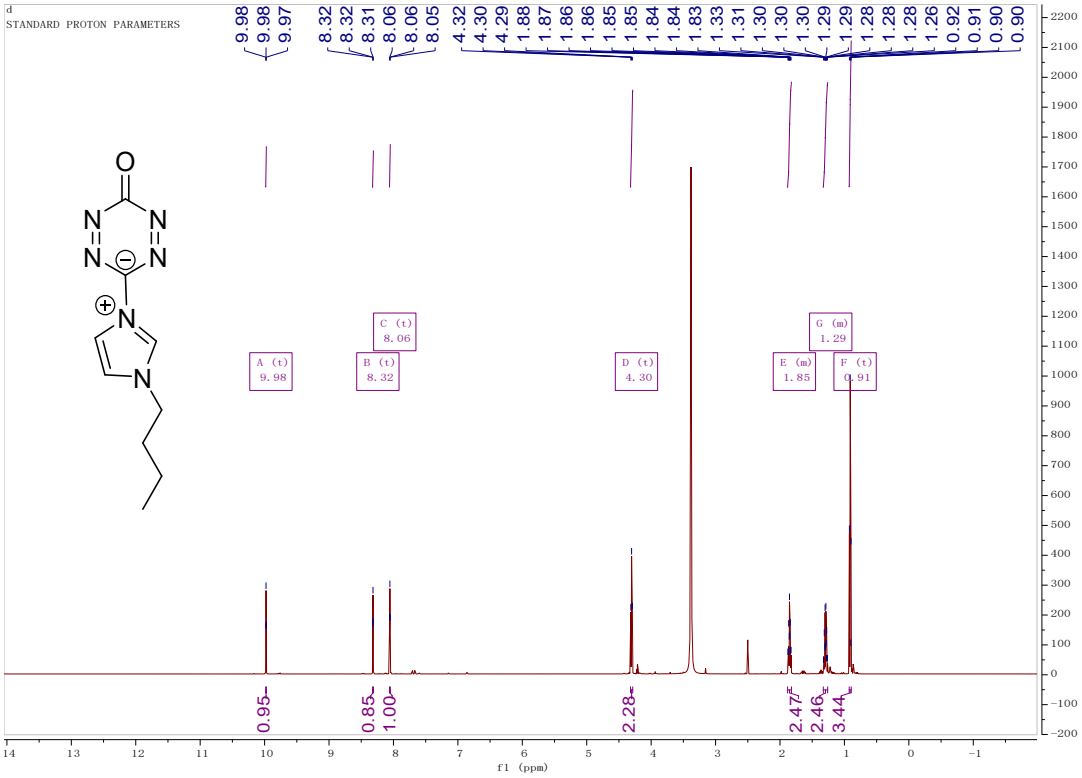


Figure S12. ^{1}H-NMR spectra of 3d in DMSO-d_6

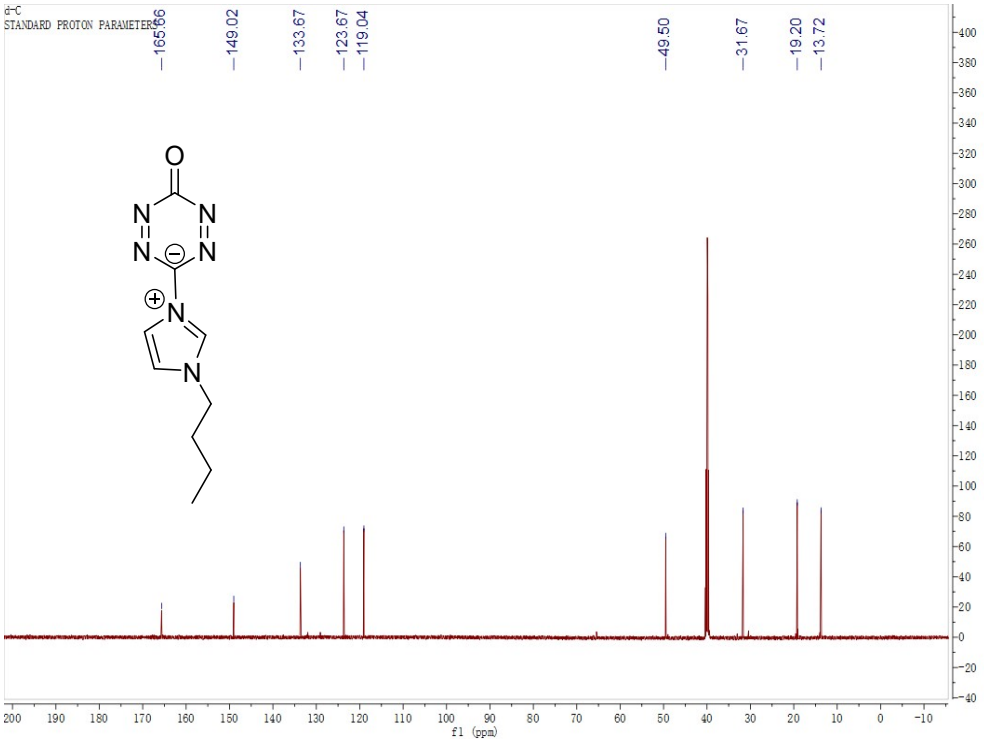


Figure S13. ^{13}C-NMR spectra of 3d in DMSO-d_6

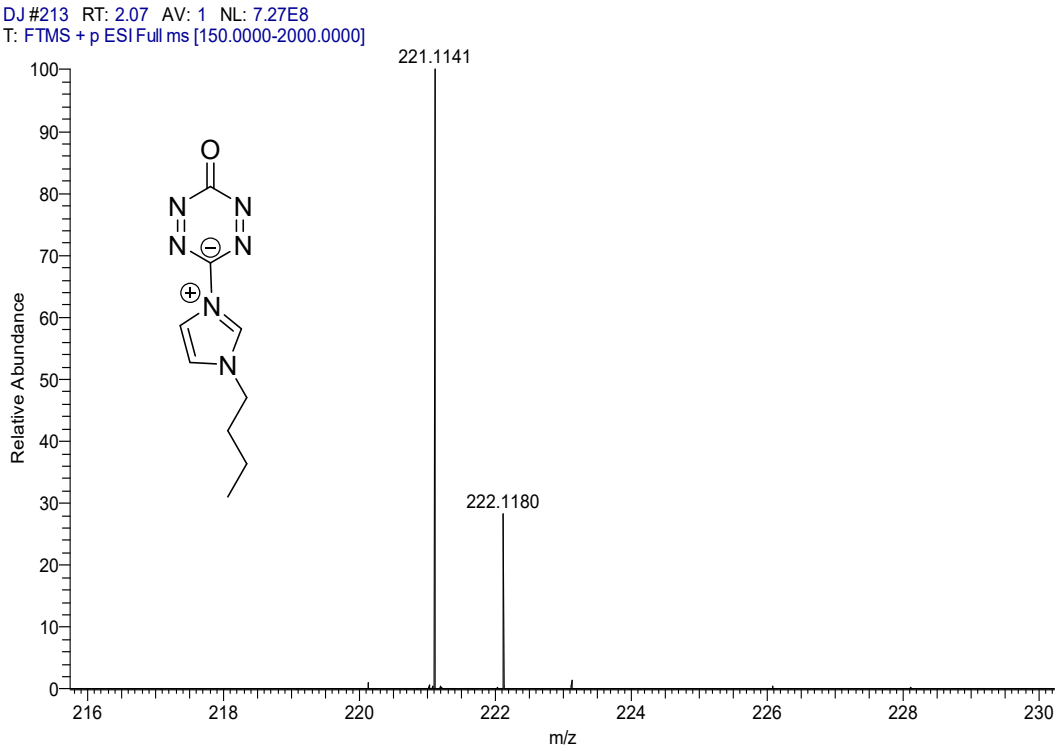


Figure S14. HRMS spectra of 3d in DMSO-d_6

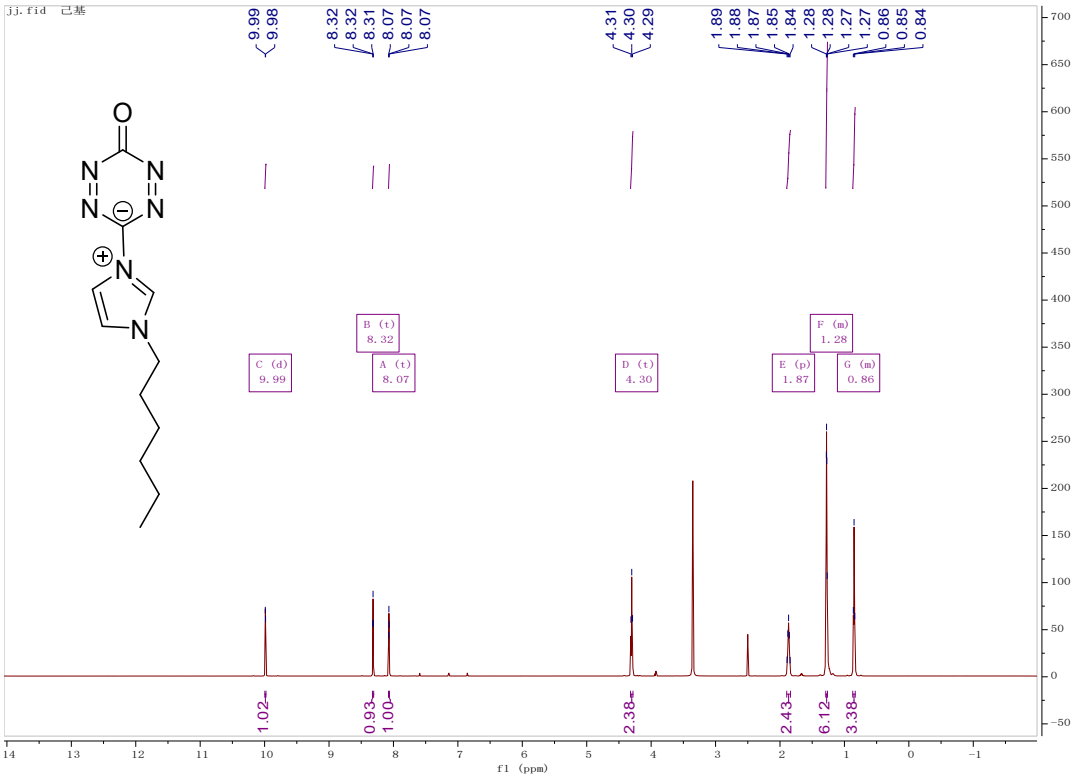


Figure S15. ^{1}H-NMR spectra of 3e in DMSO-d_6

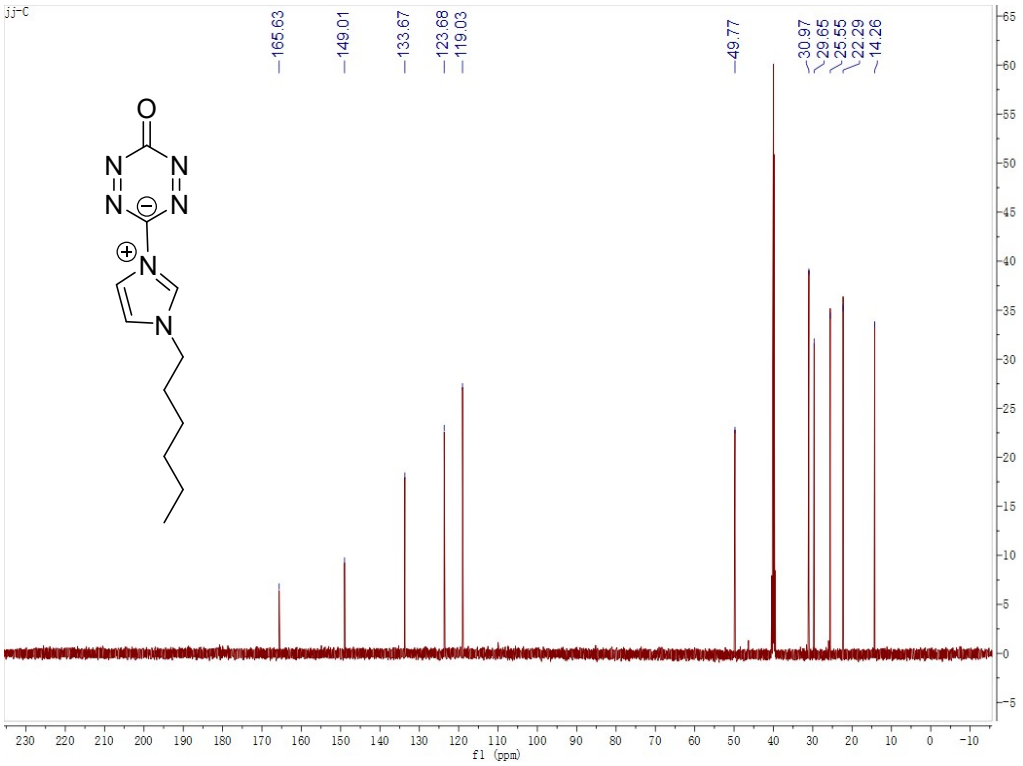


Figure S16. ^{13}C-NMR spectra of 3e in DMSO-d_6

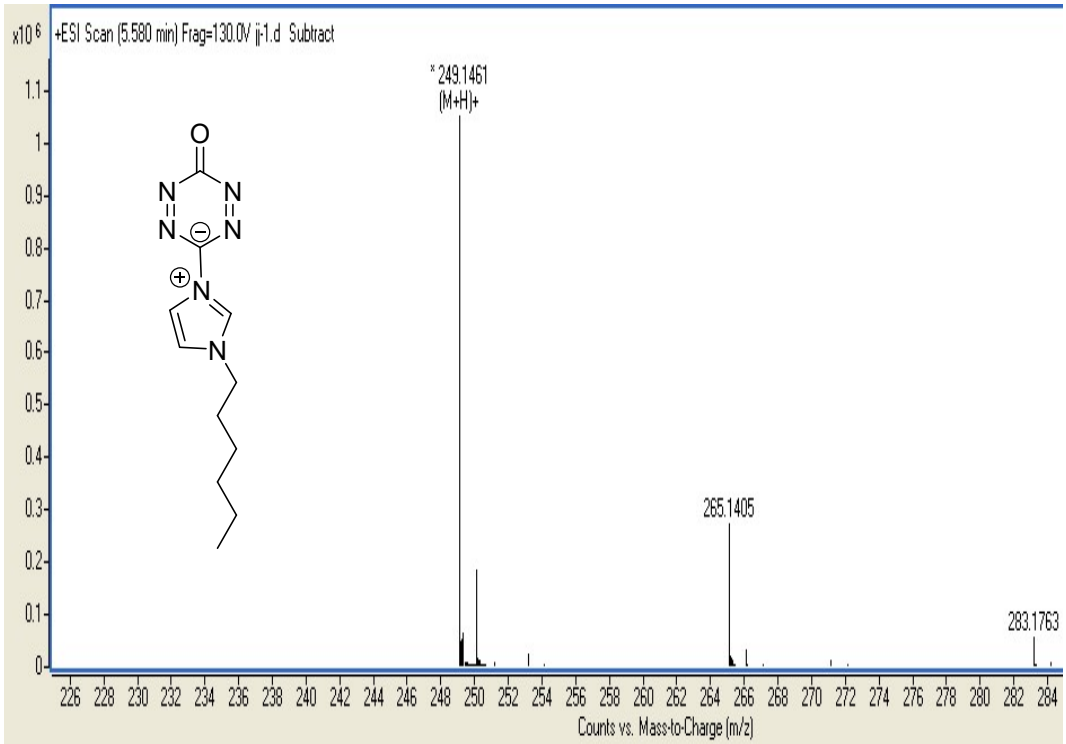


Figure S17. HRMS spectra of 3e in DMSO-d_6

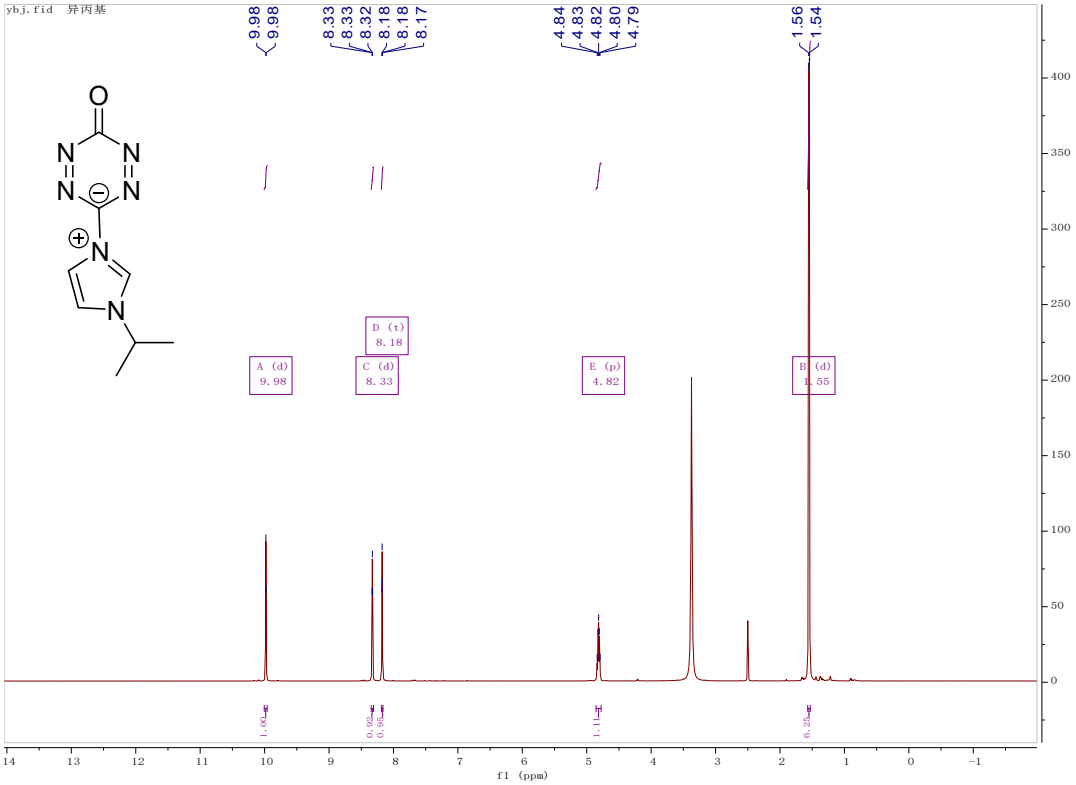


Figure S18. ^{1}H-NMR spectra of 3f in DMSO-d_6

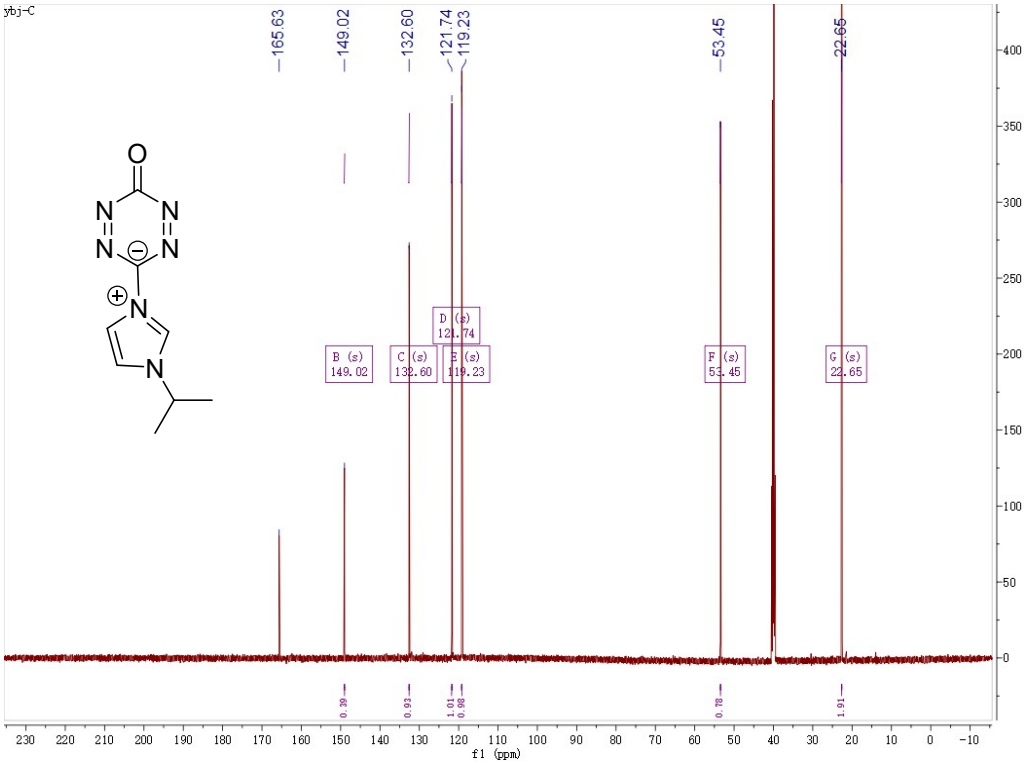


Figure S19. ^{13}C-NMR spectra of 3f in DMSO-d_6

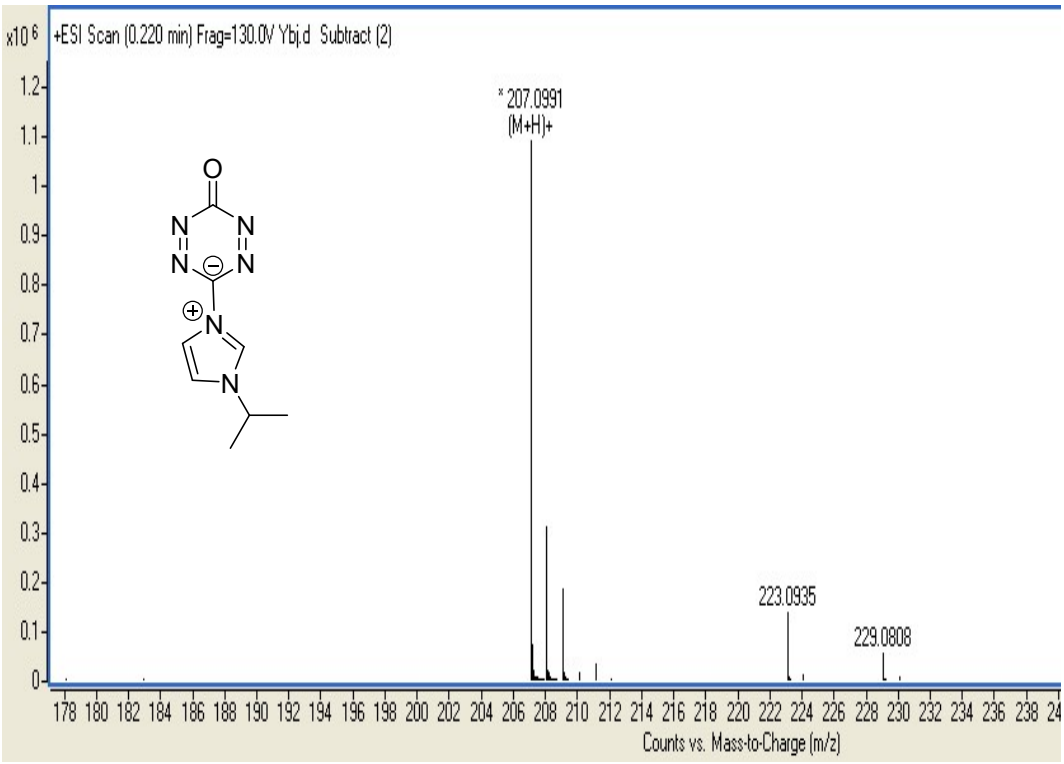


Figure S20. HRMS spectra of 3f in DMSO-d_6

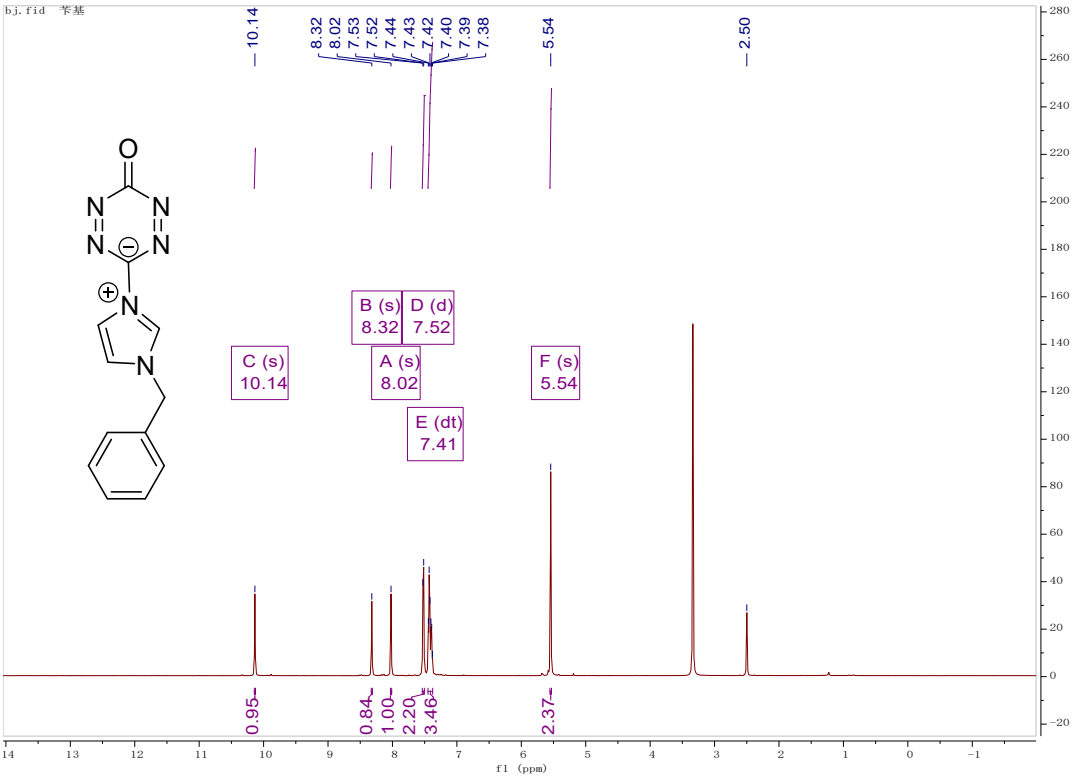


Figure S21. ^{1}H-NMR spectra of 3g in DMSO-d_6

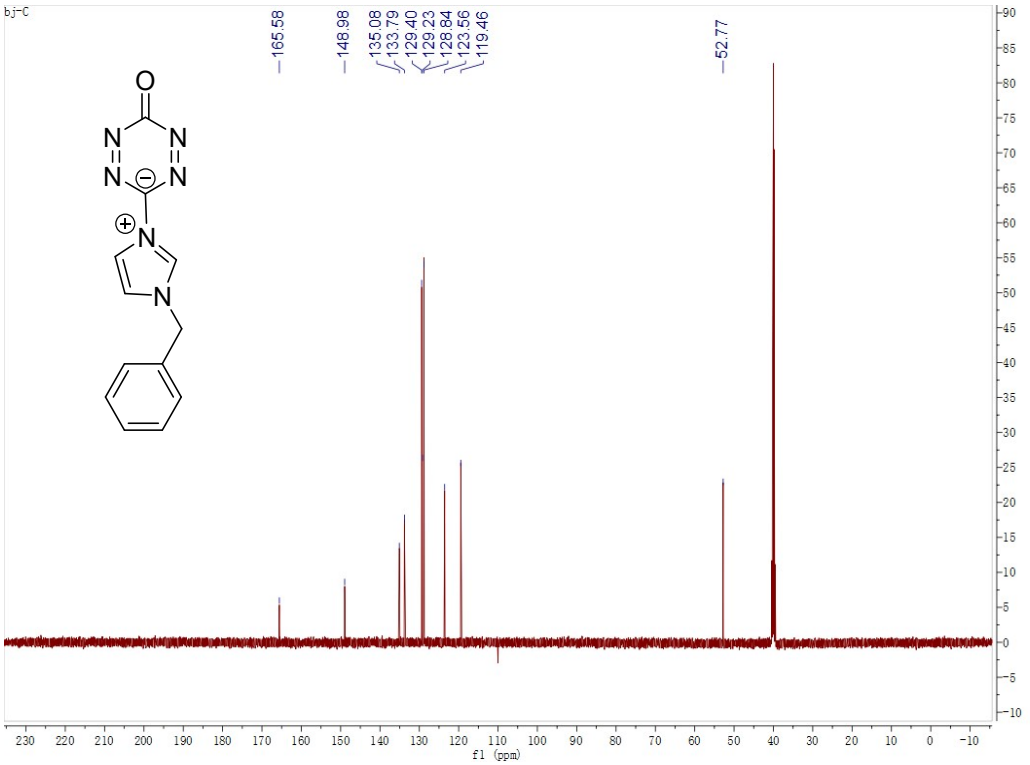


Figure S22. ^{13}C-NMR spectra of 3g in DMSO-d_6

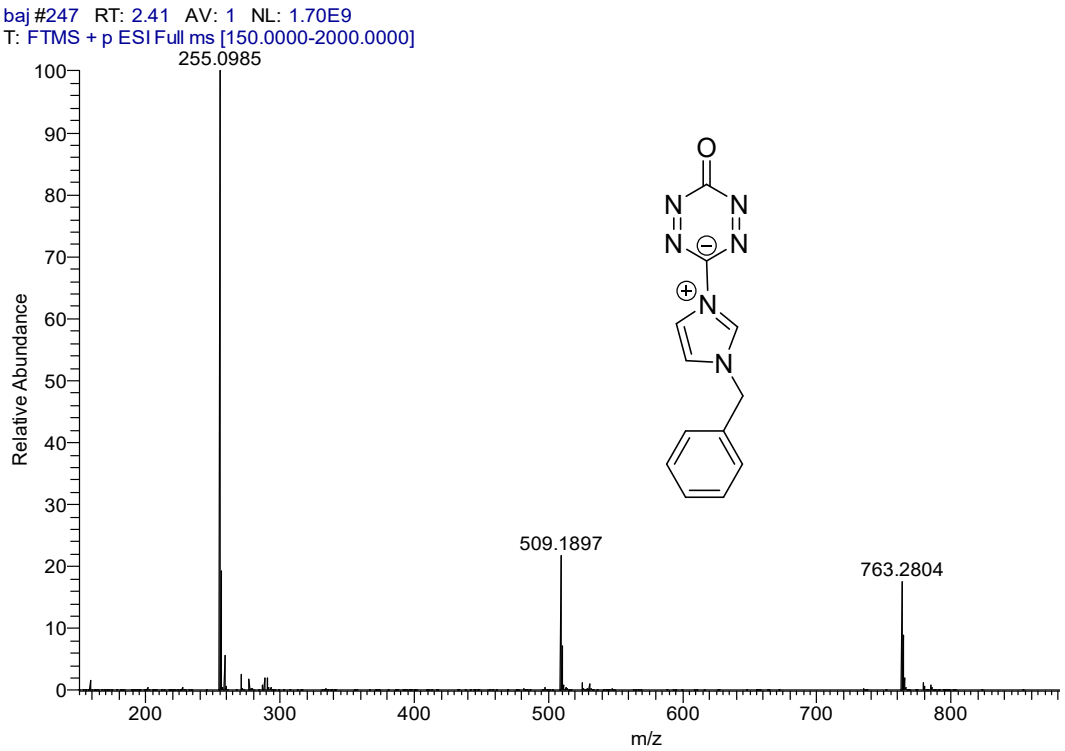


Figure S23. HRMS spectra of 3g in DMSO-d_6

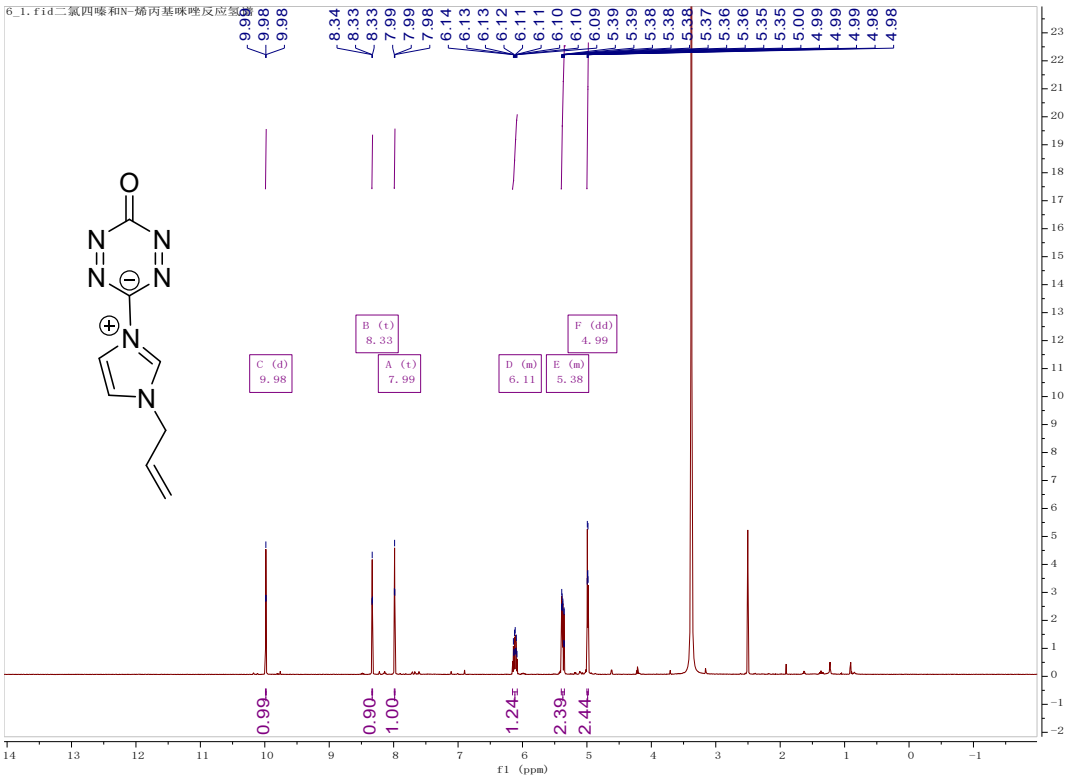


Figure S24. ^{1}H-NMR spectra of 3h in DMSO-d_6

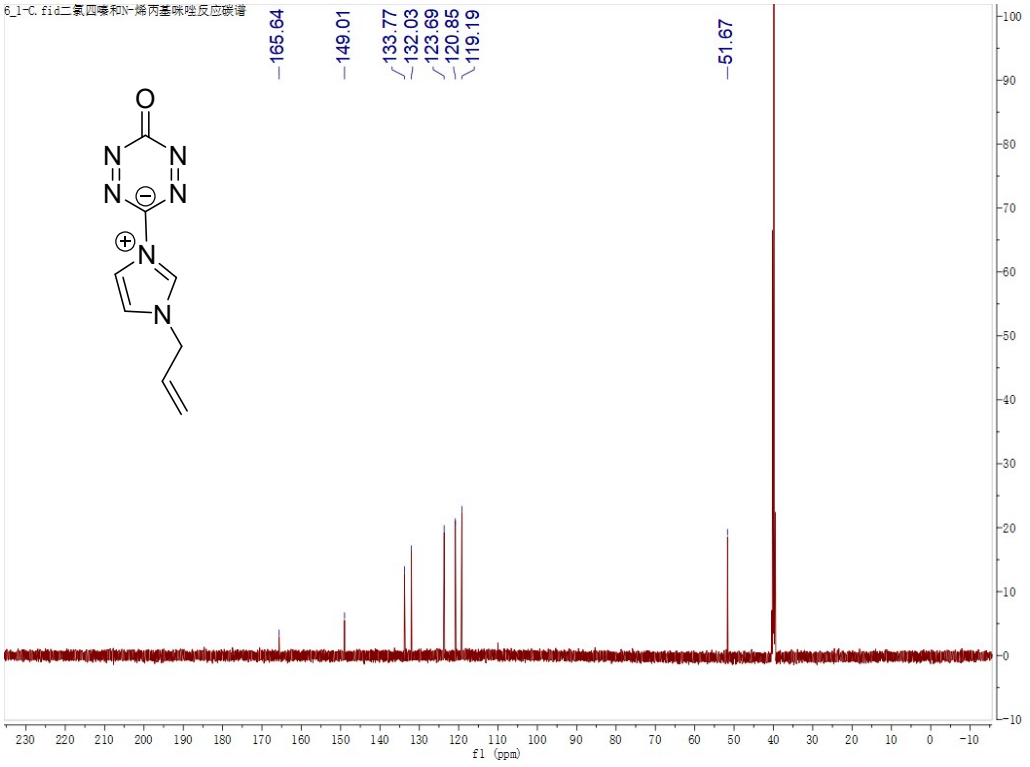


Figure S25. ^{13}C-NMR spectra of 3h in DMSO-d_6

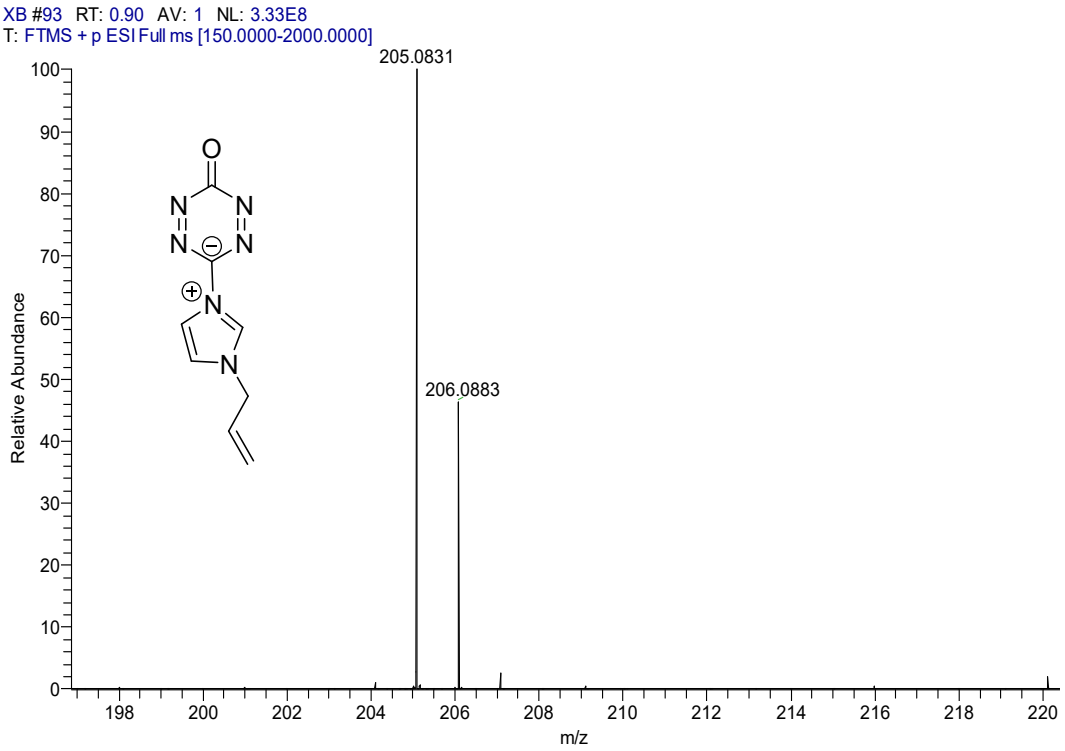


Figure S26. HRMS spectra of 3h in DMSO-d_6

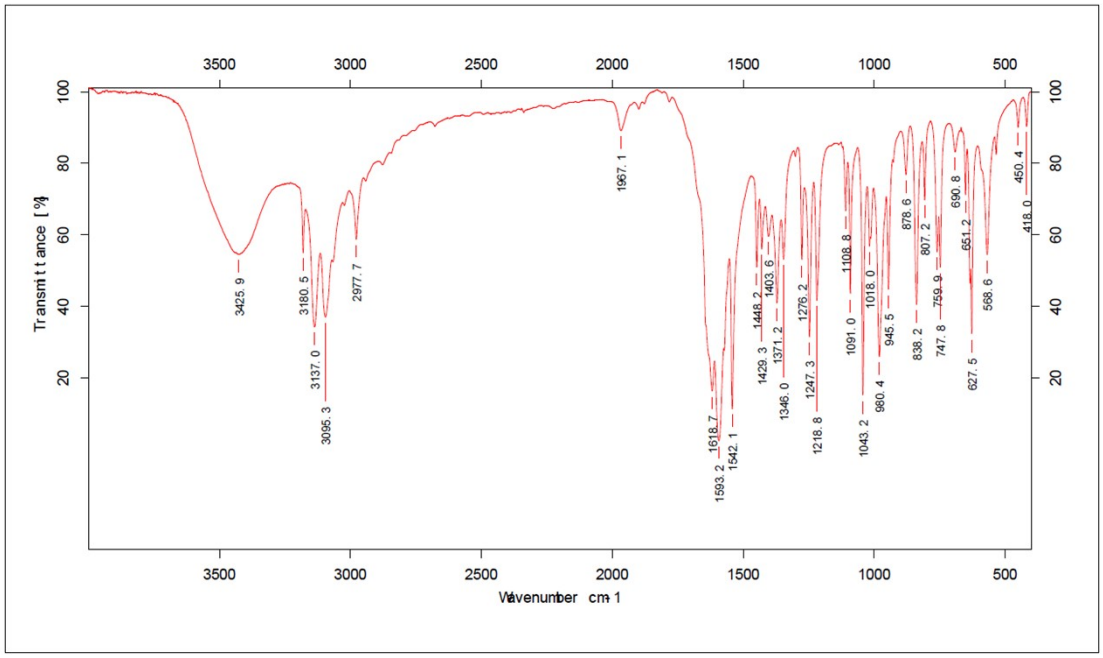


Figure S27. IR spectra of 3h

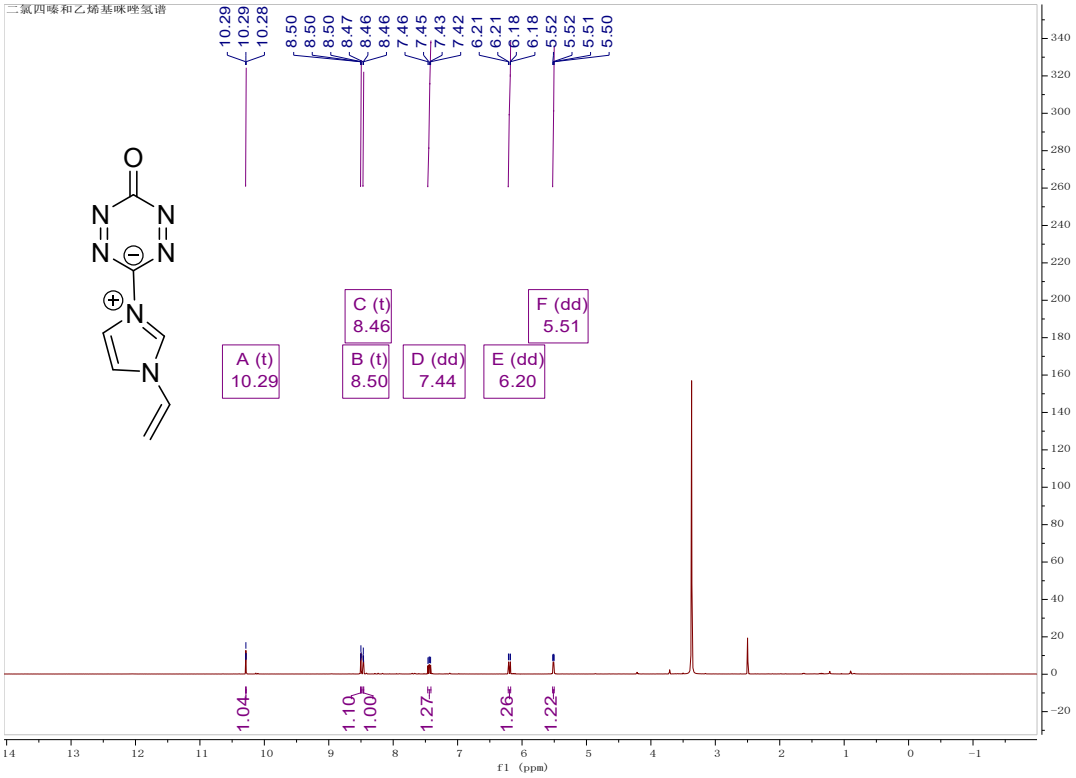


Figure S28. ^{1}H-NMR spectra of 3i in DMSO-d_6

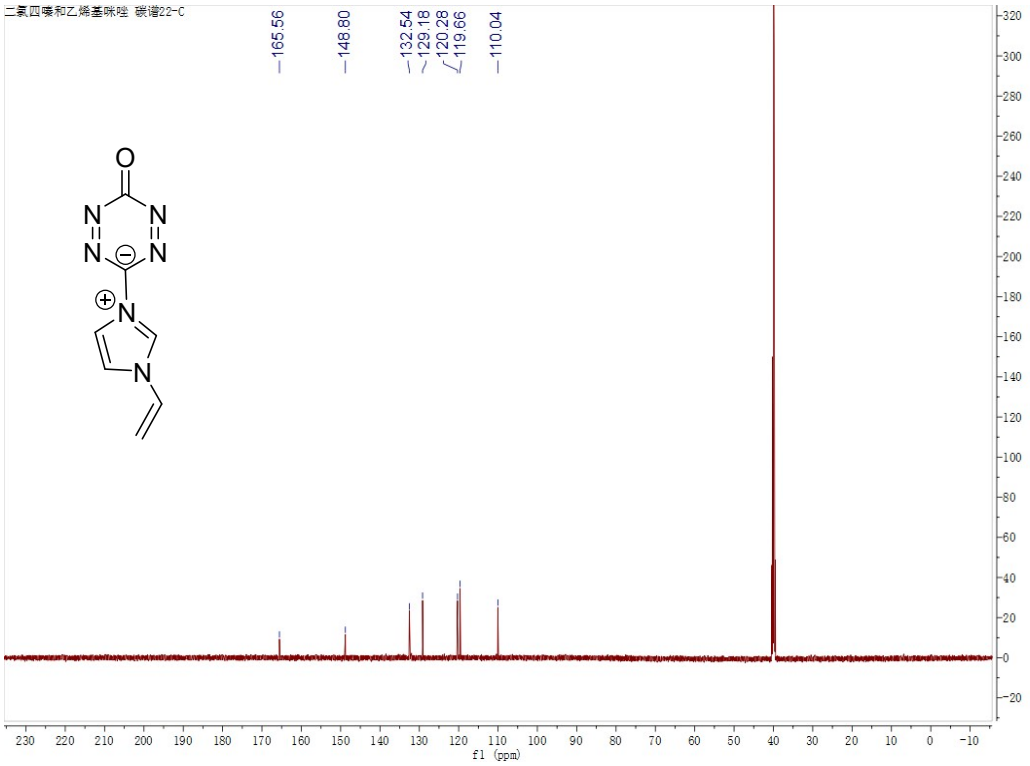


Figure S29. ^{13}C-NMR spectra of 3i in DMSO-d_6

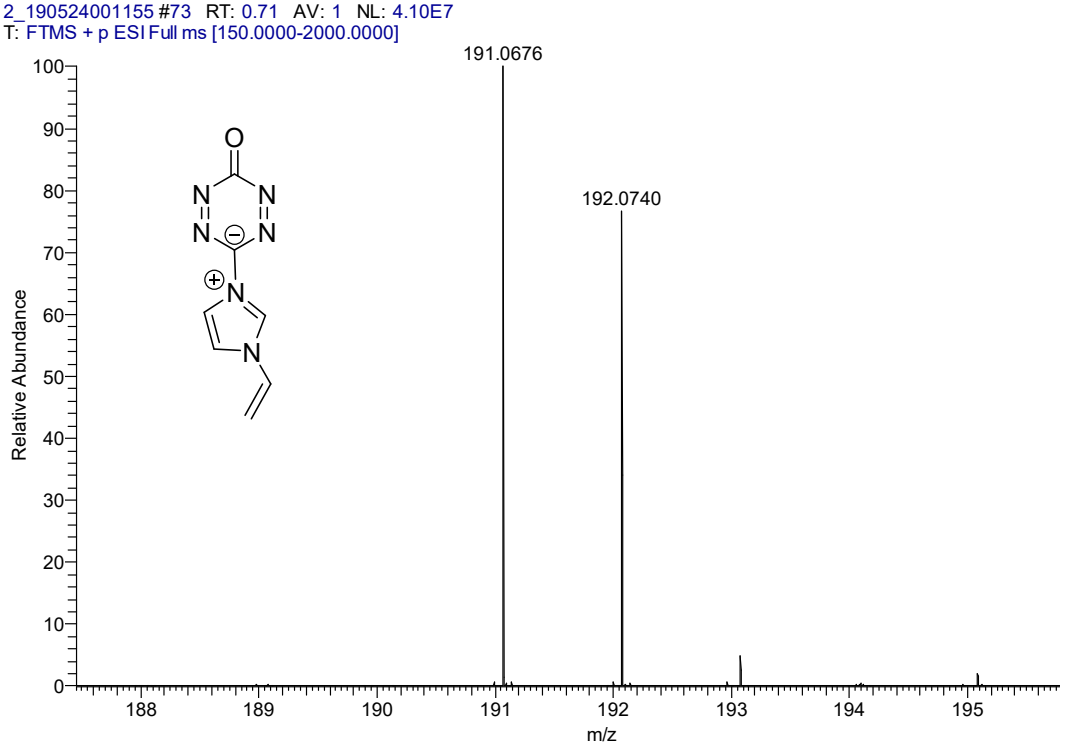


Figure S30. HRMS spectra of 3i in DMSO-d_6

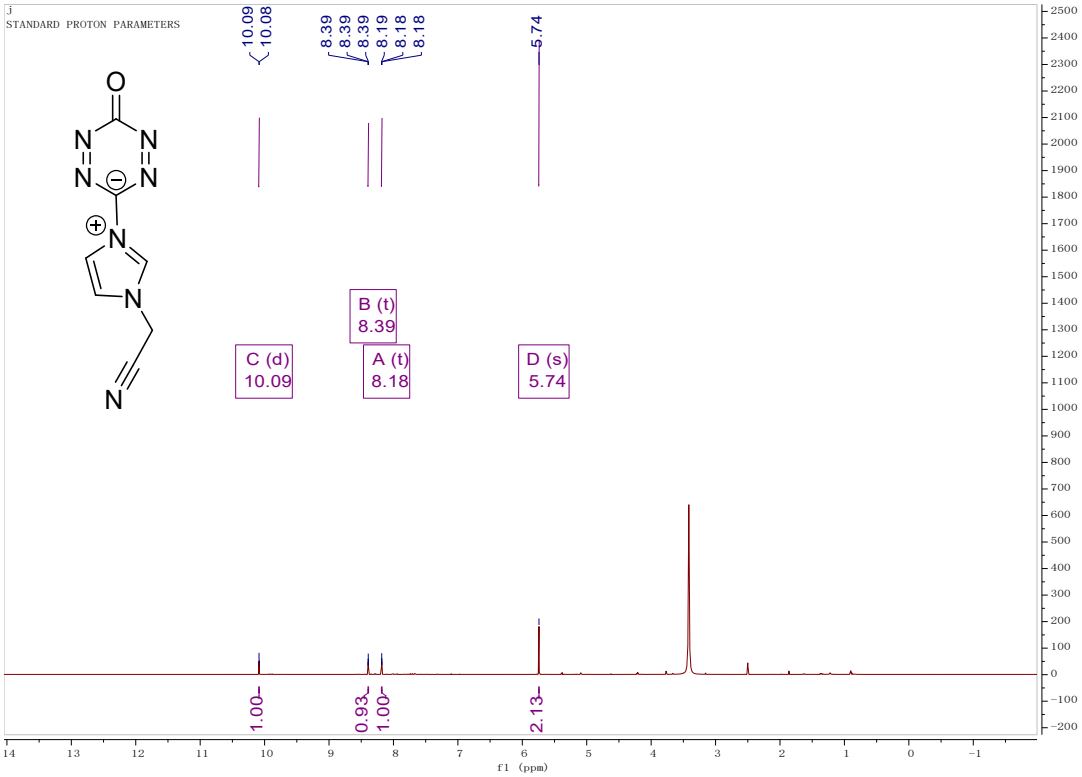


Figure S31. ^{1}H-NMR spectra of 3j in DMSO-d_6

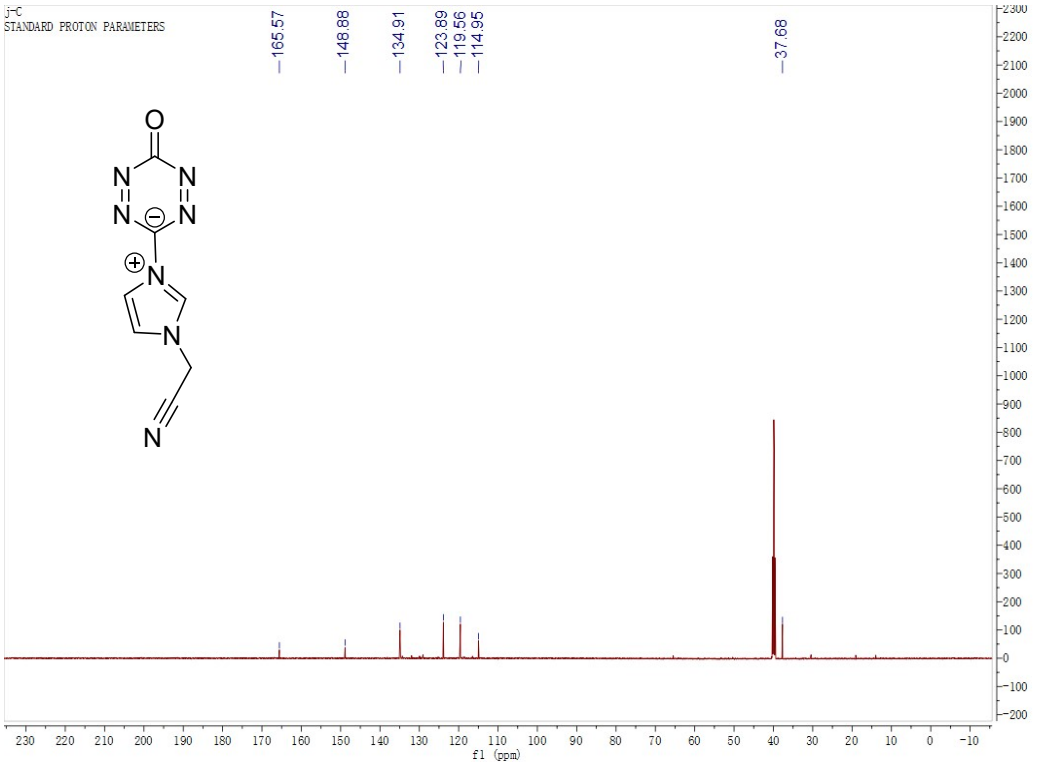


Figure S32. ^{13}C-NMR spectra of 3j in DMSO-d_6

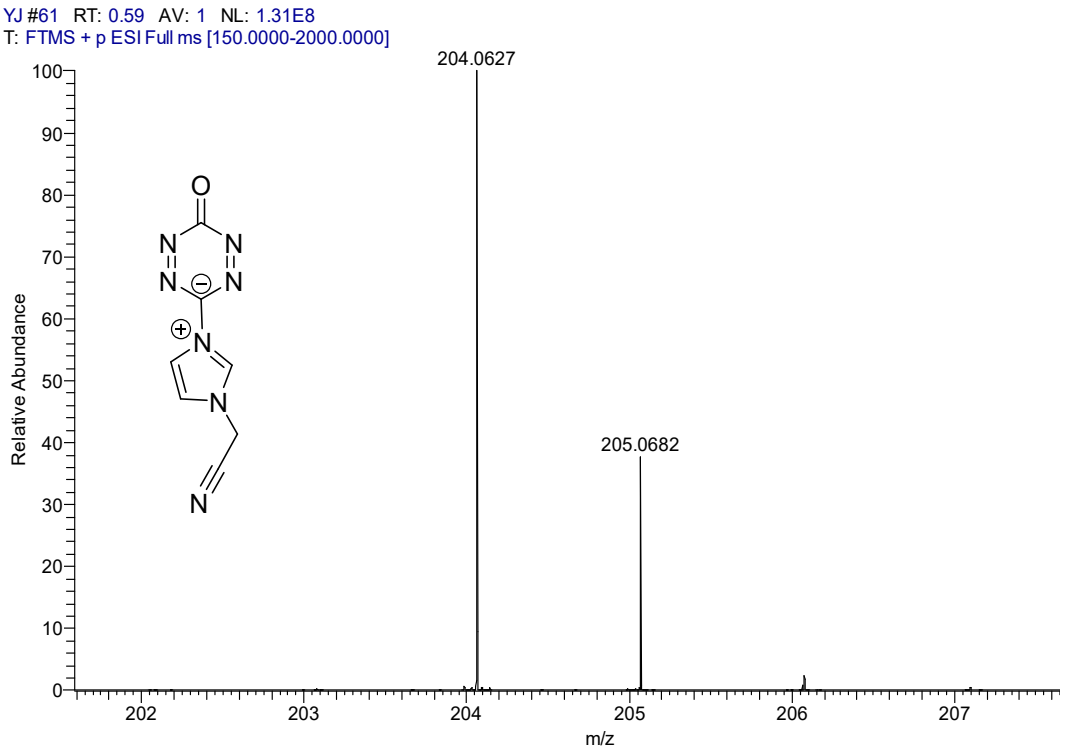


Figure S33. HRMS spectra of 3j in DMSO-d_6

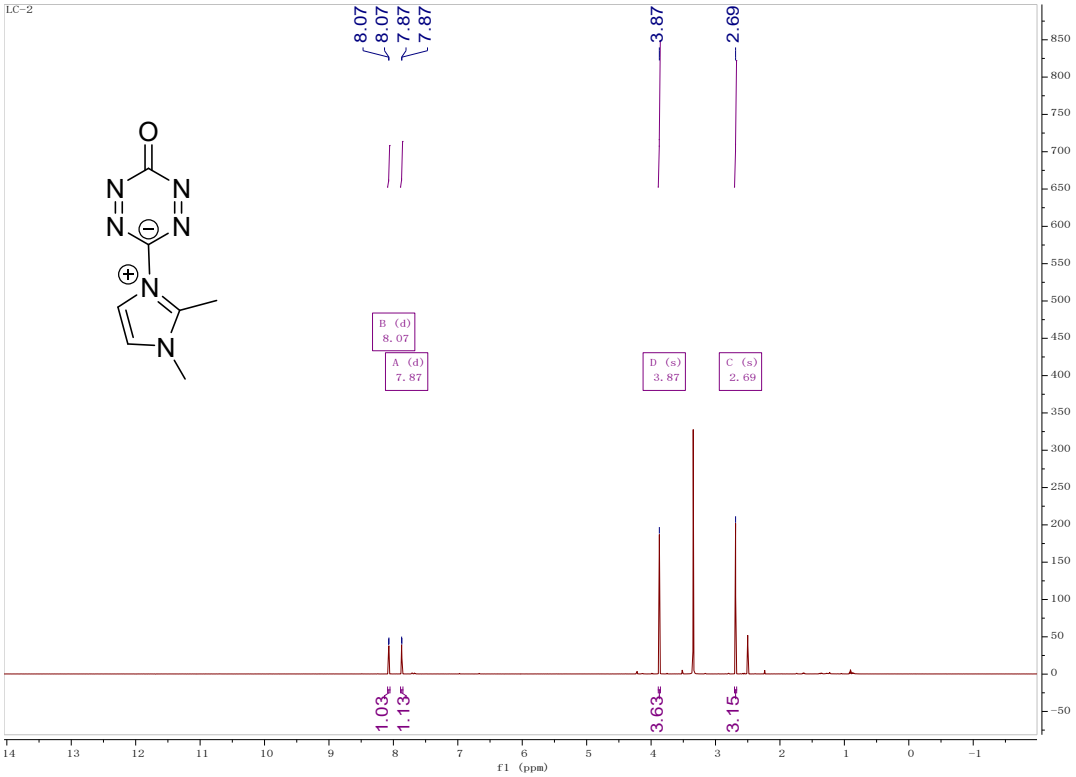


Figure S34. ^{1}H-NMR spectra of 3k in DMSO-d_6

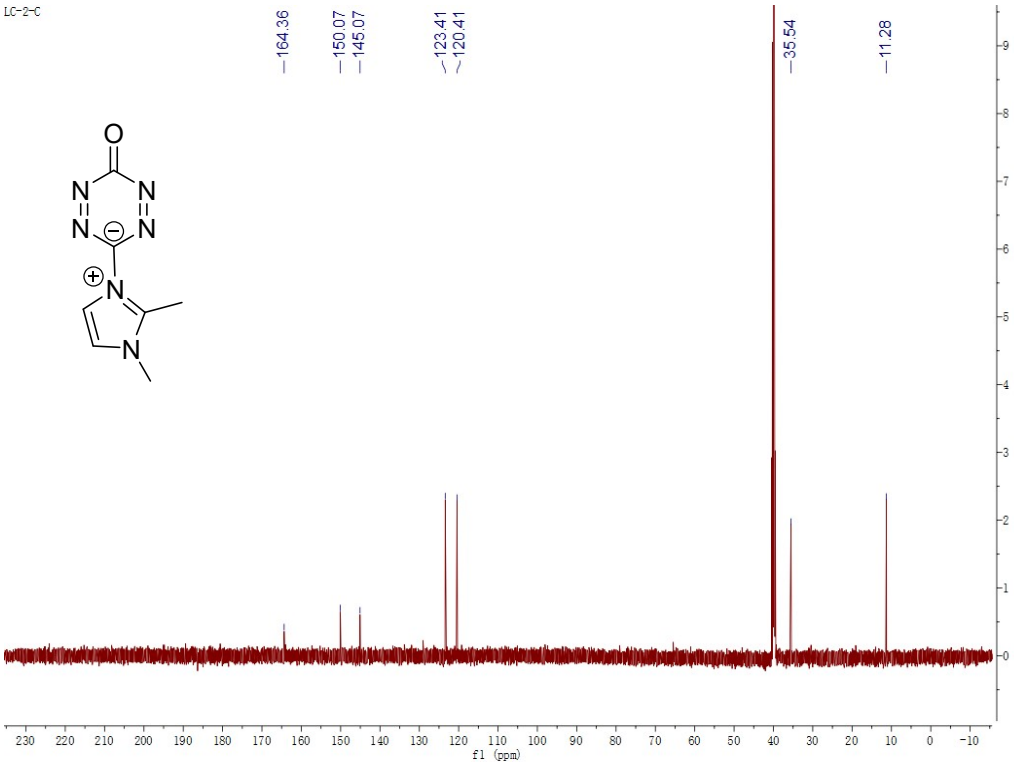


Figure S35. ^{13}C-NMR spectra of 3k in DMSO-d_6

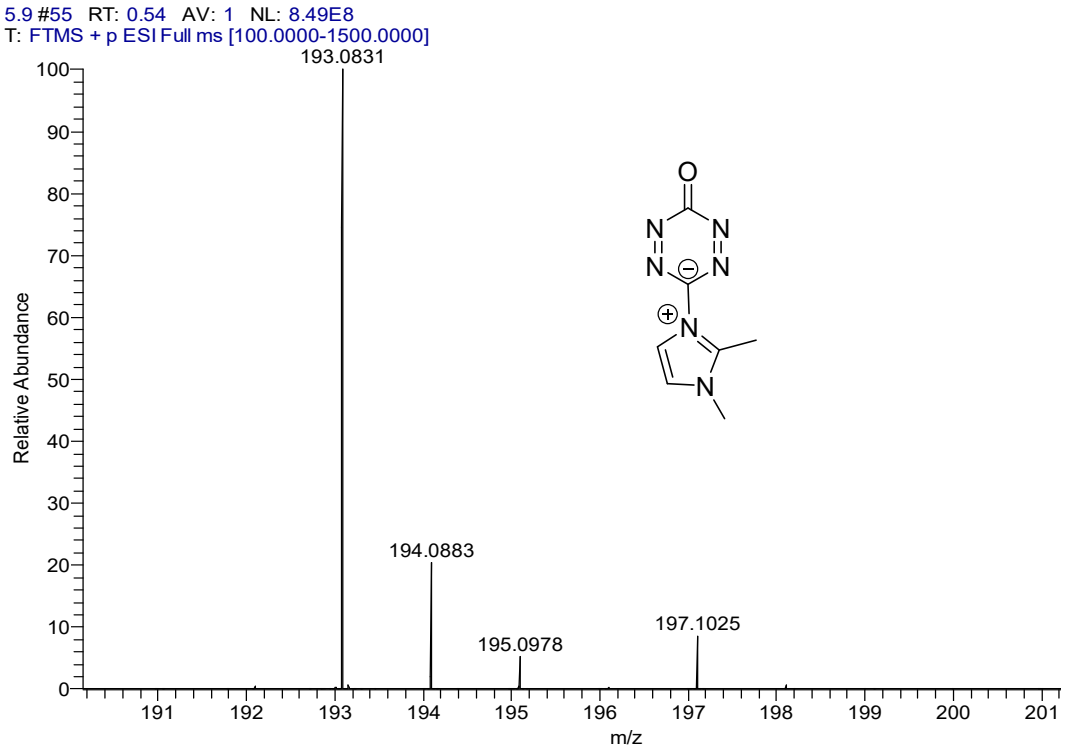


Figure S36. HRMS spectra of 3k in DMSO-d_6

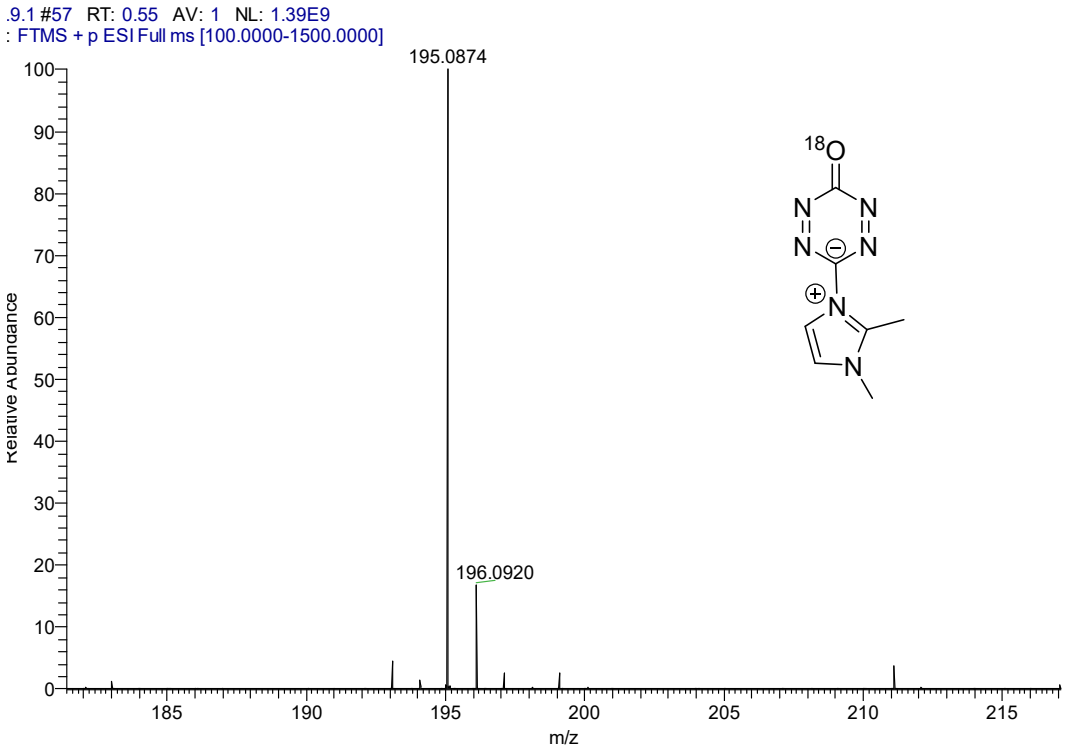


Figure S37. HRMS spectra of 3k-^{18}O in DMSO-d_6

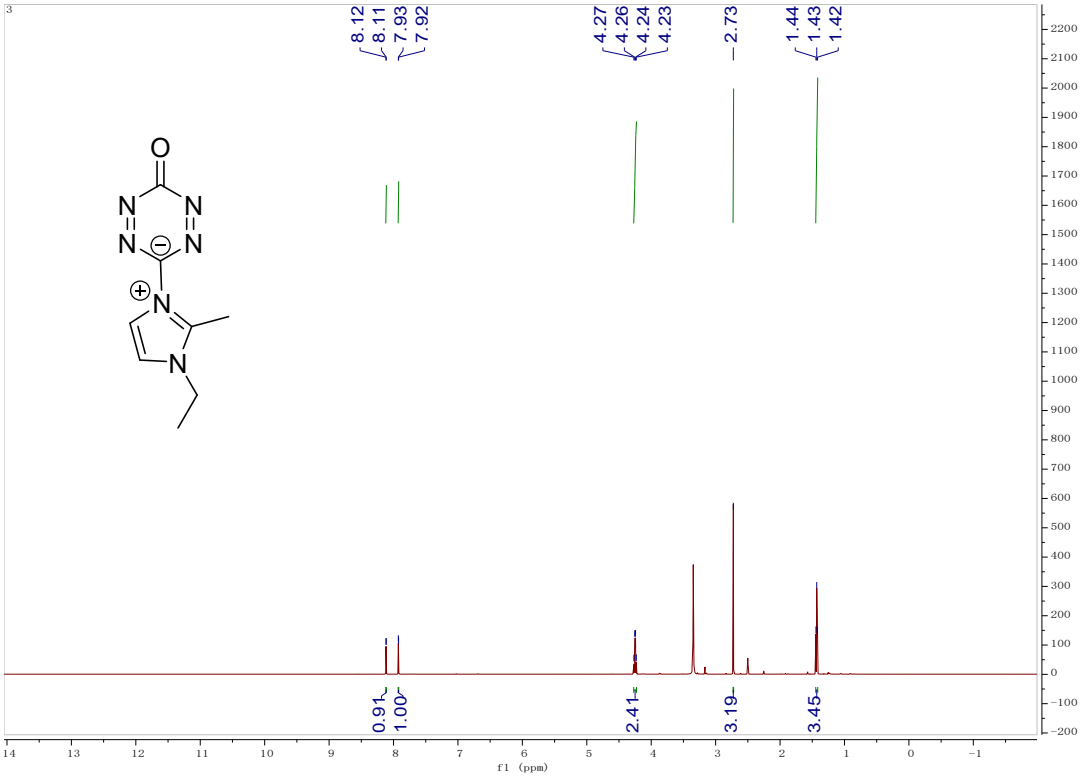


Figure S38. ^{1}H-NMR spectra of 3l in DMSO-d_6

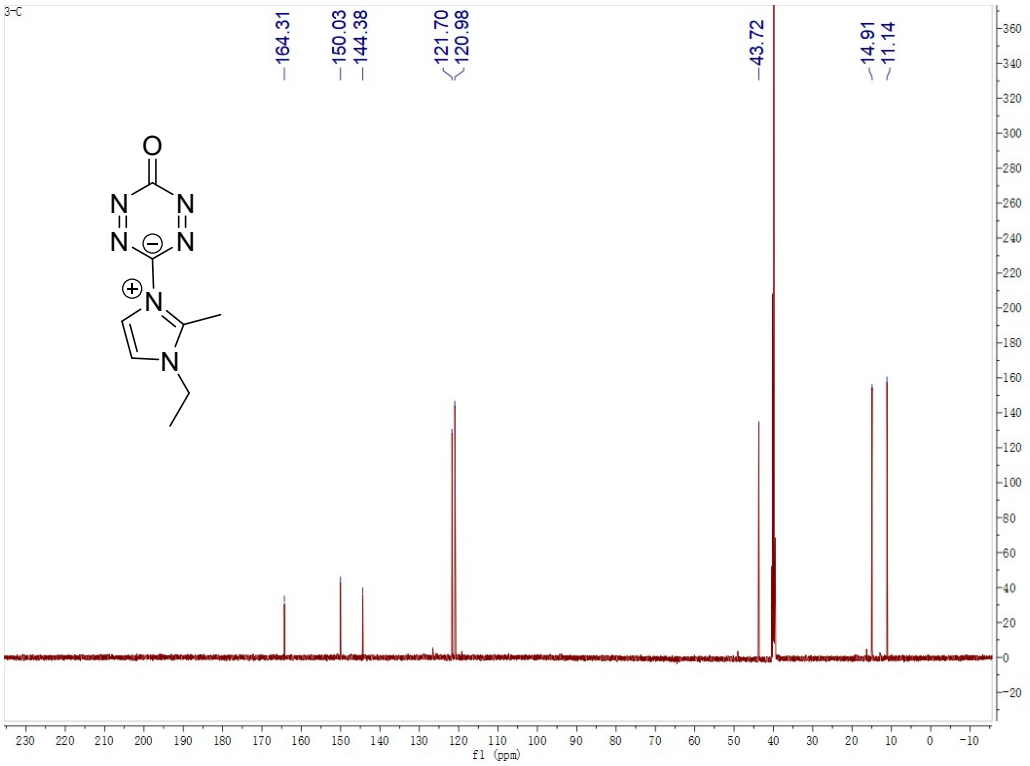


Figure S39. ^{13}C-NMR spectra of 3l in DMSO-d_6

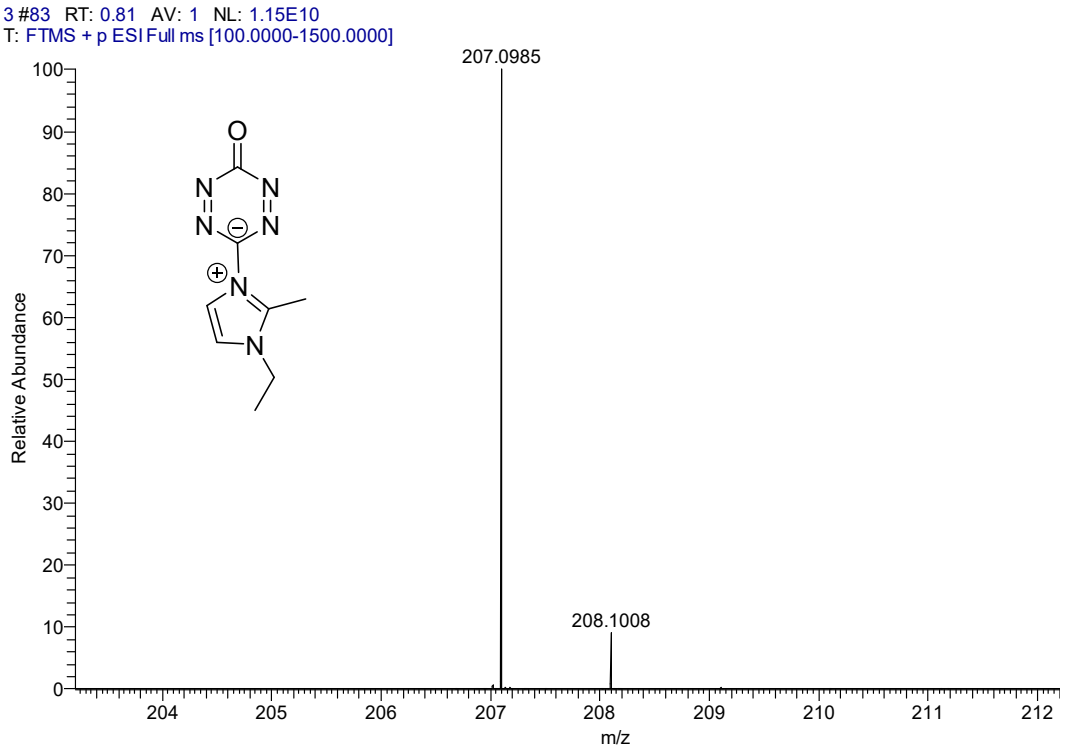


Figure S40. HRMS spectra of 3l in DMSO-d_6

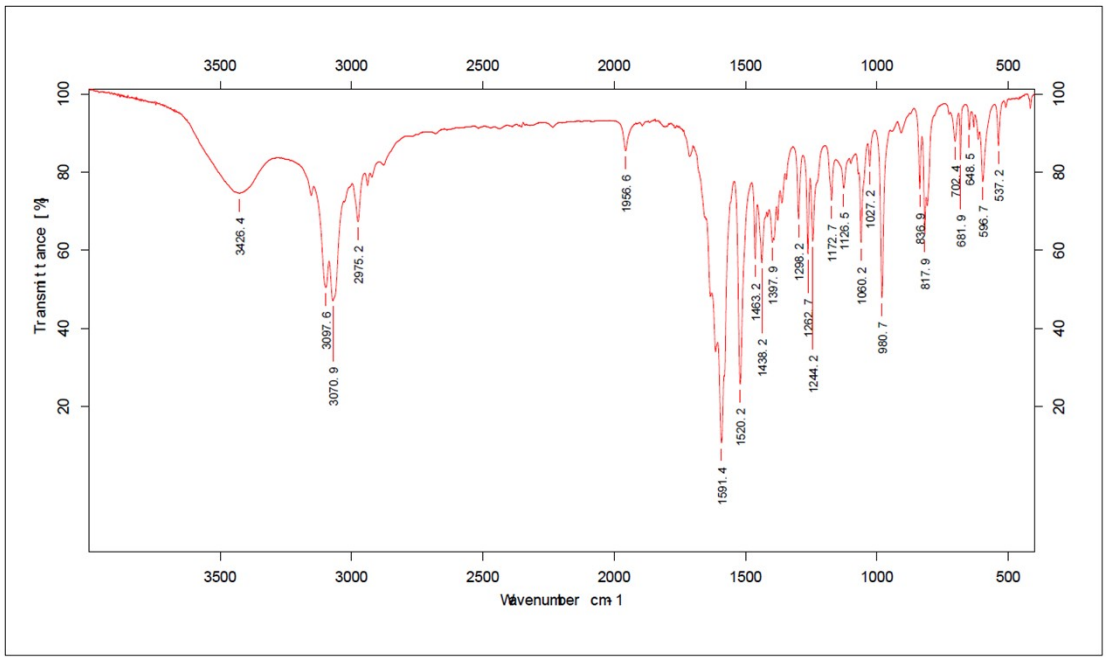


Figure S41. IR spectra of 3l

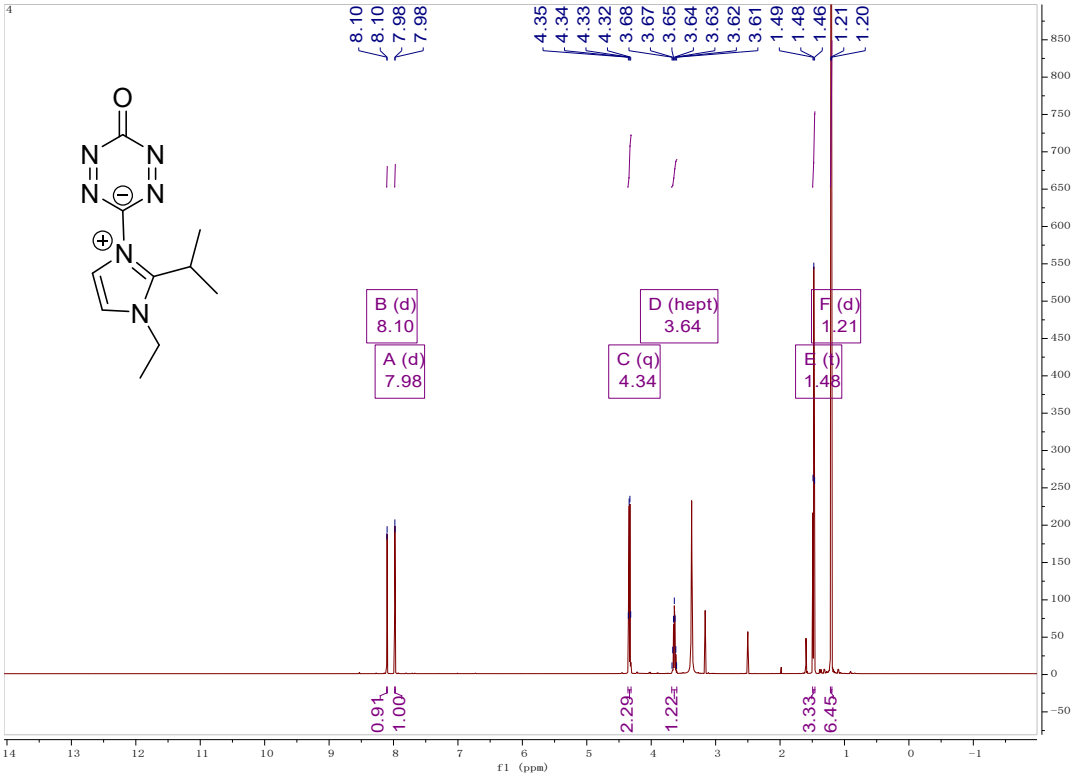


Figure S42. ^{1}H-NMR spectra of 3m in DMSO-d_6

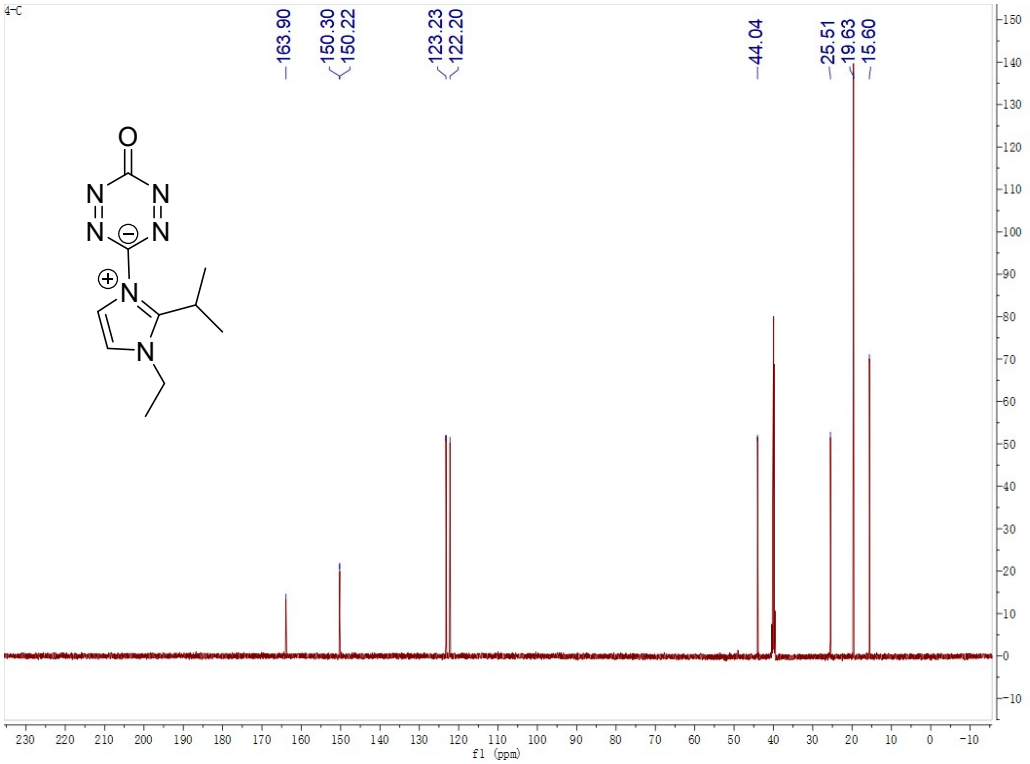


Figure S43. ^{13}C-NMR spectra of 3m in DMSO-d_6

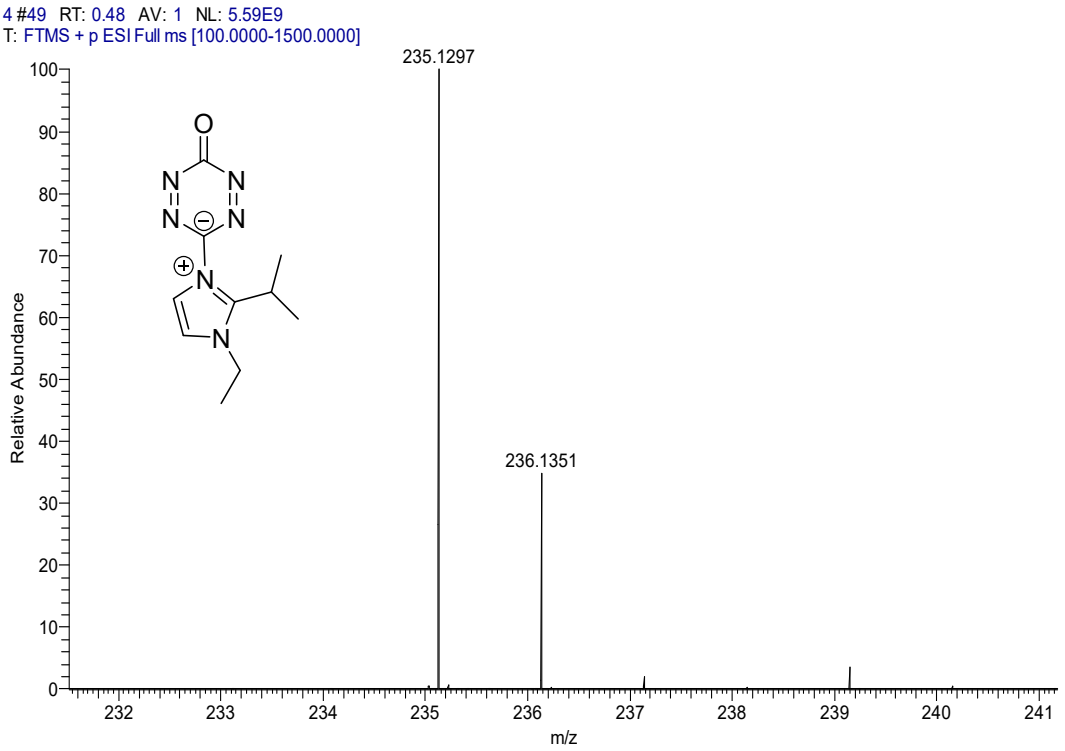


Figure S44. HRMS spectra of 3m in DMSO-d_6

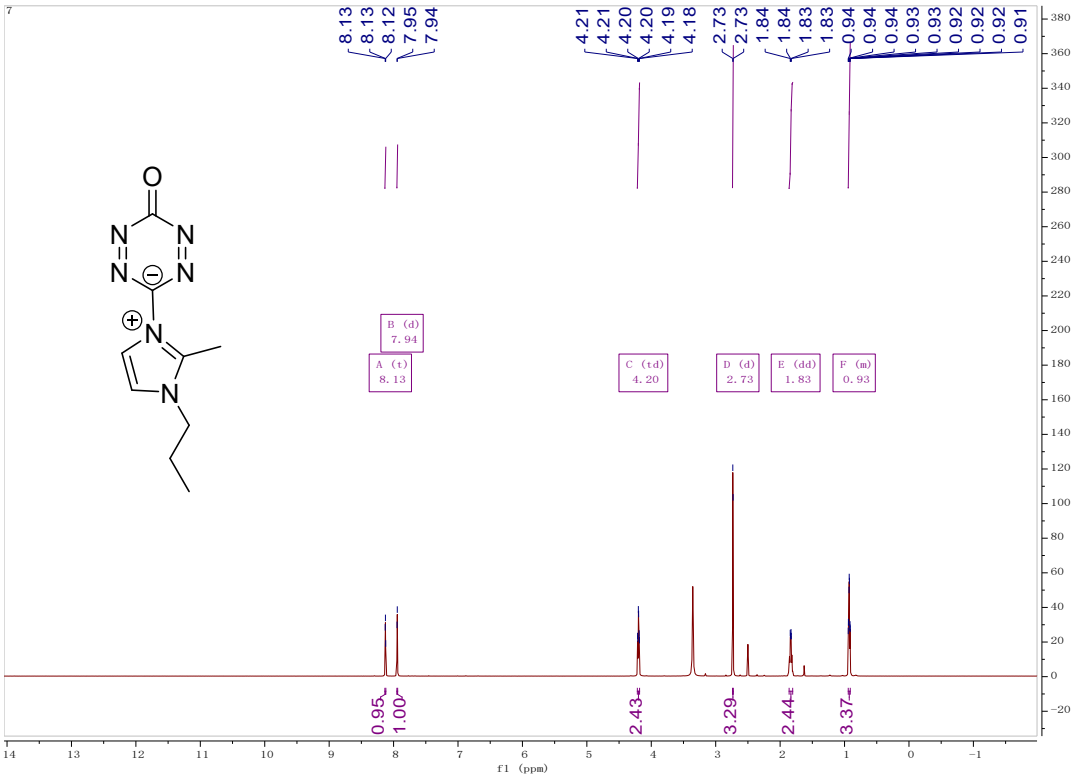


Figure S45. ^{1}H-NMR spectra of 3n in DMSO-d_6

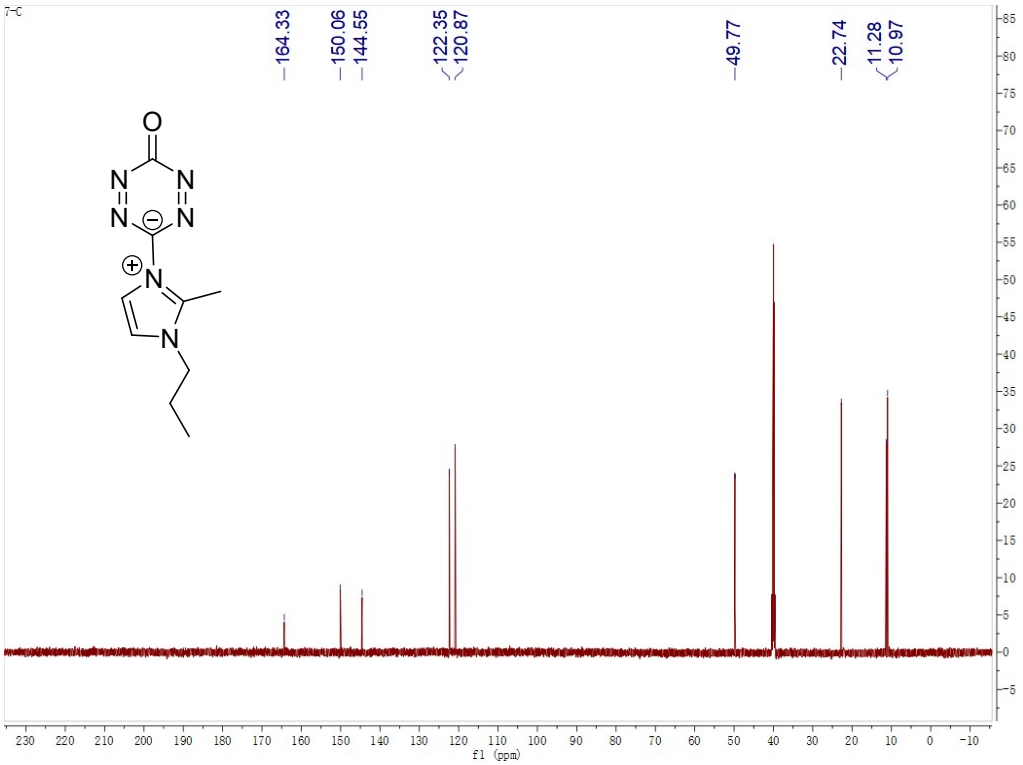


Figure S46. ^{13}C-NMR spectra of 3n in DMSO-d_6

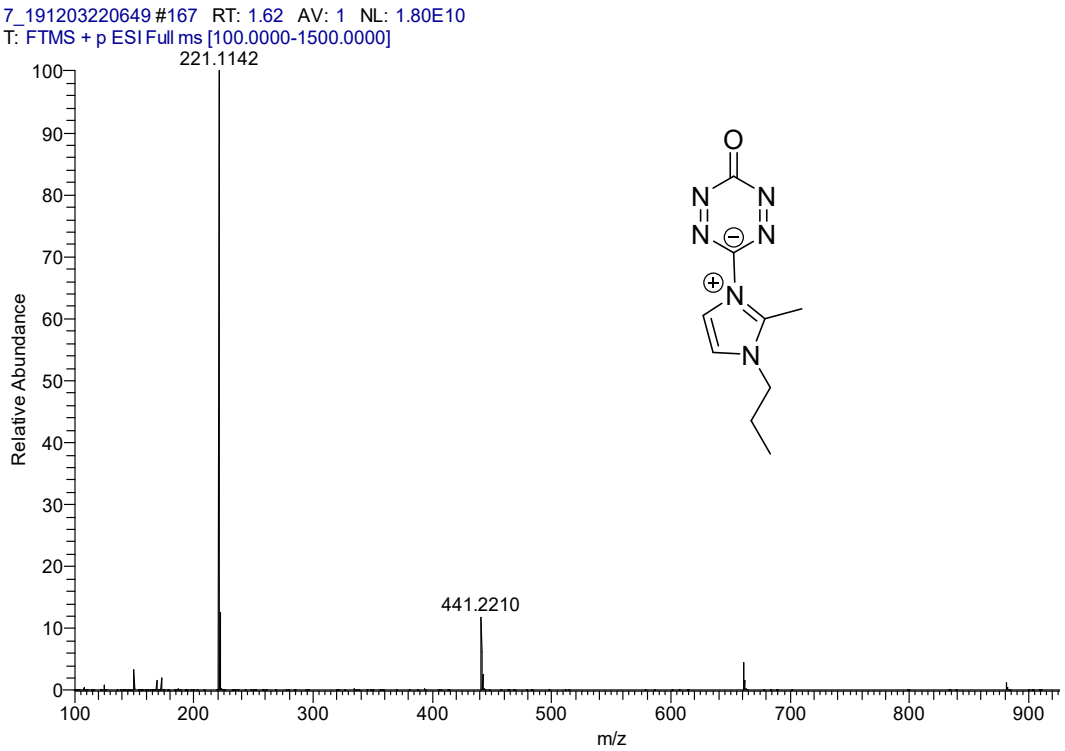


Figure S47. HRMS spectra of 3n in DMSO-d_6

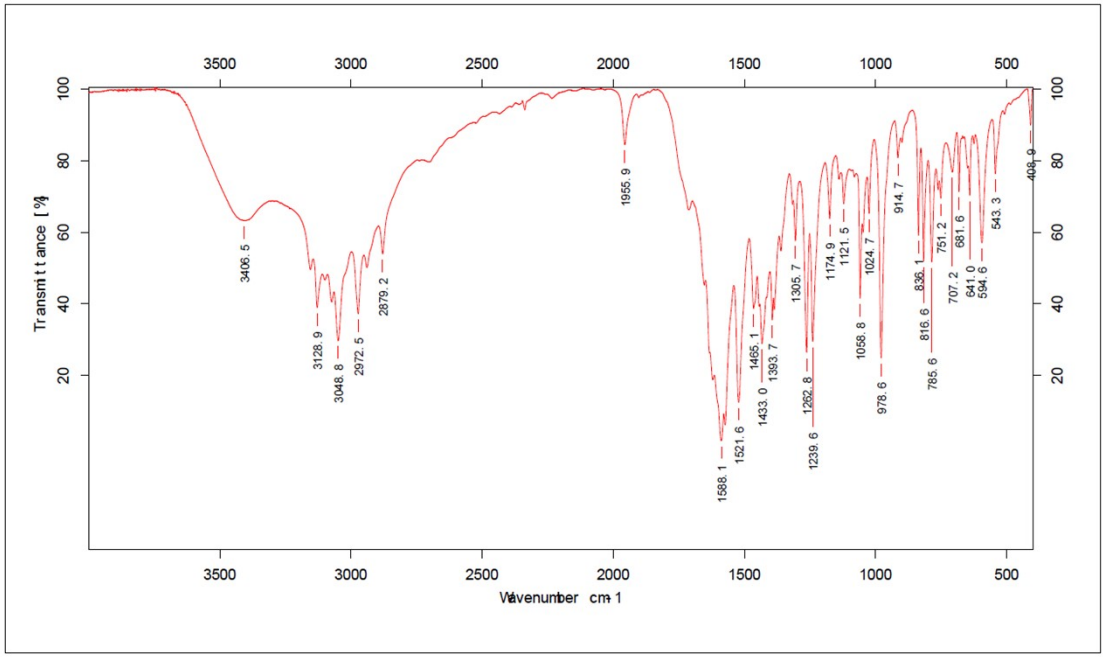


Figure S48. IR spectra of 3n

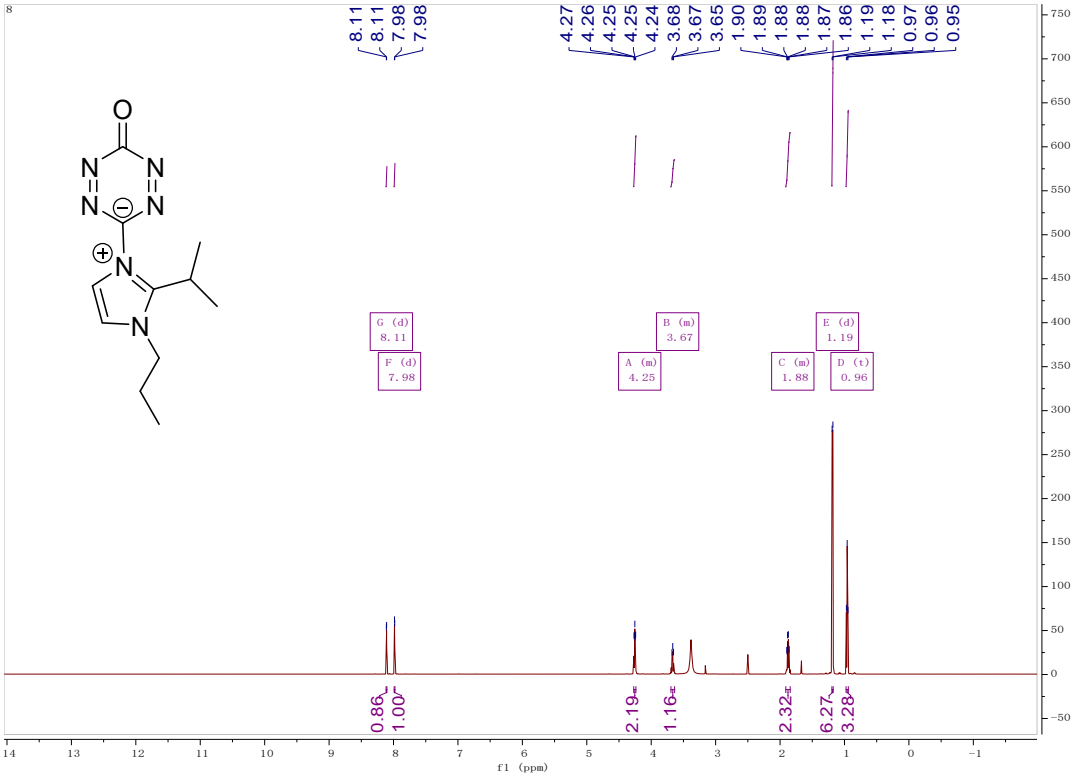


Figure S49. ^{1}H-NMR spectra of 3o in DMSO-d_6

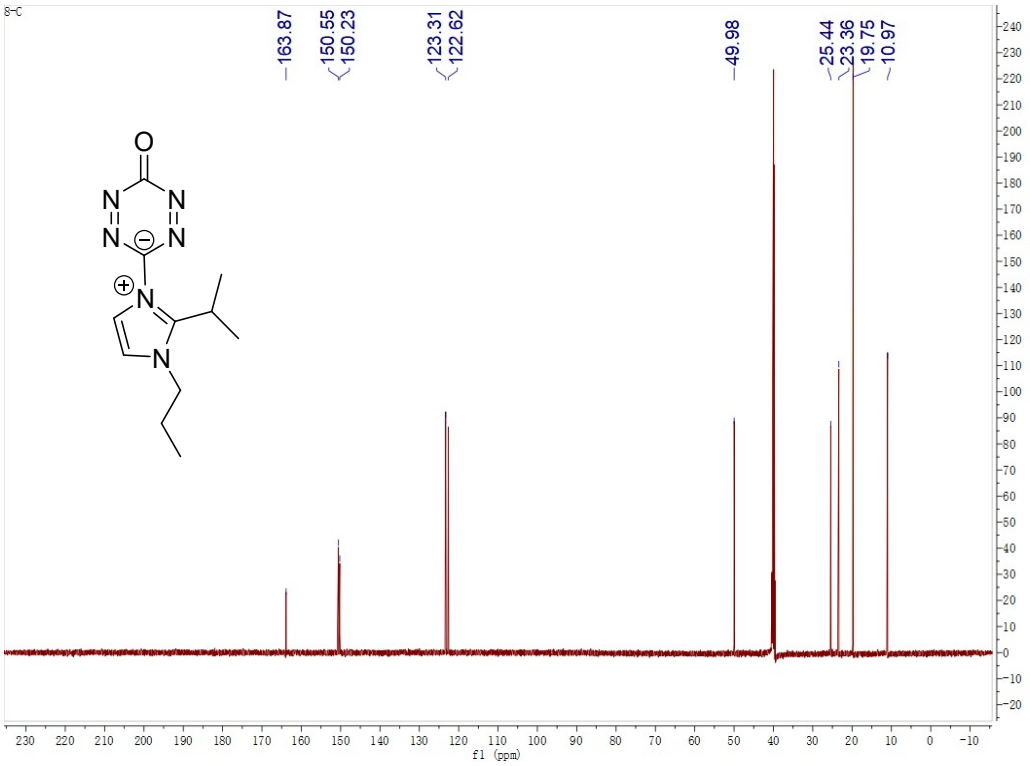


Figure S50. ^{13}C-NMR spectra of 3o in DMSO-d_6

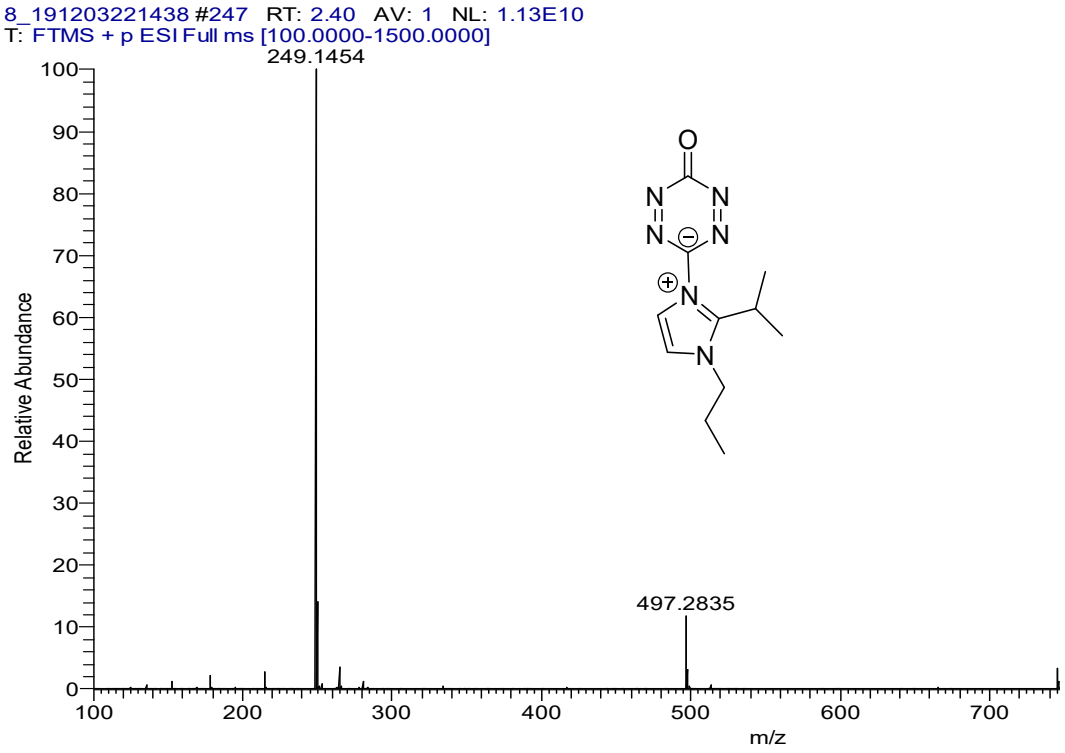


Figure S51. HRMS spectra of 3o in DMSO-d_6

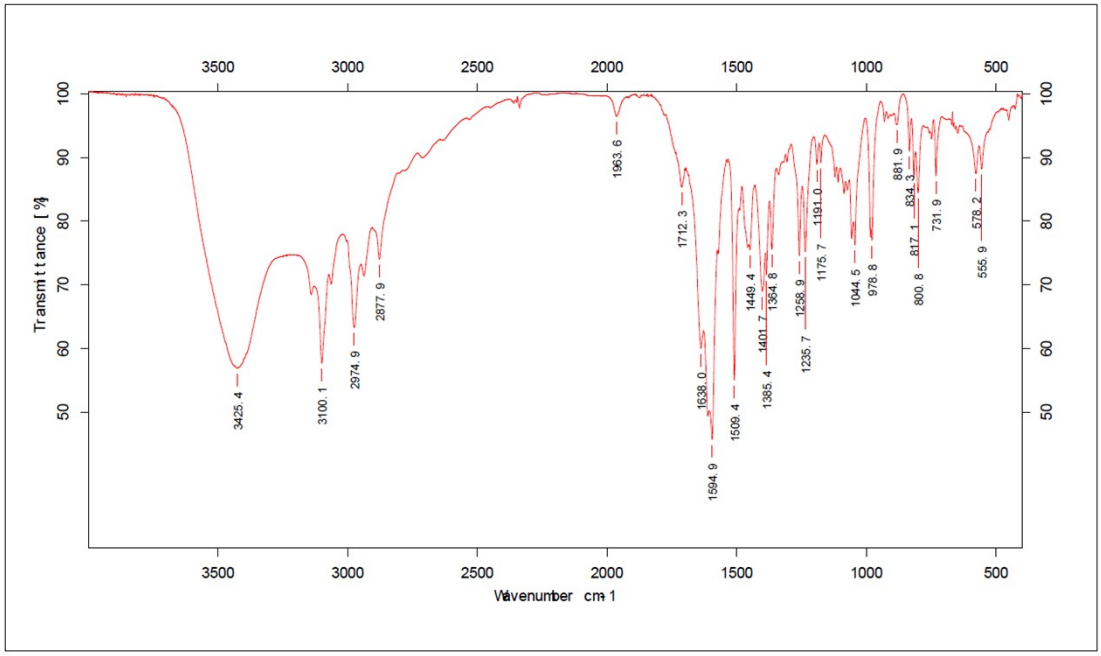


Figure S52. IR spectra of 3o

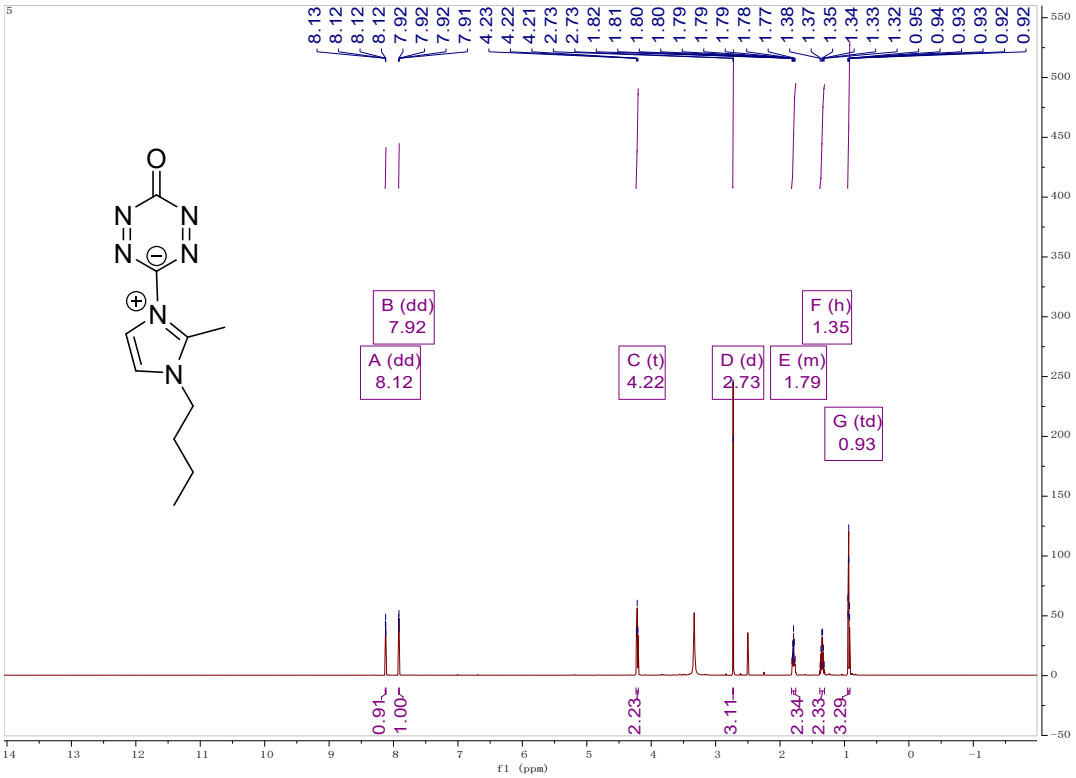


Figure S53. ^{1}H-NMR spectra of 3p in DMSO-d_6

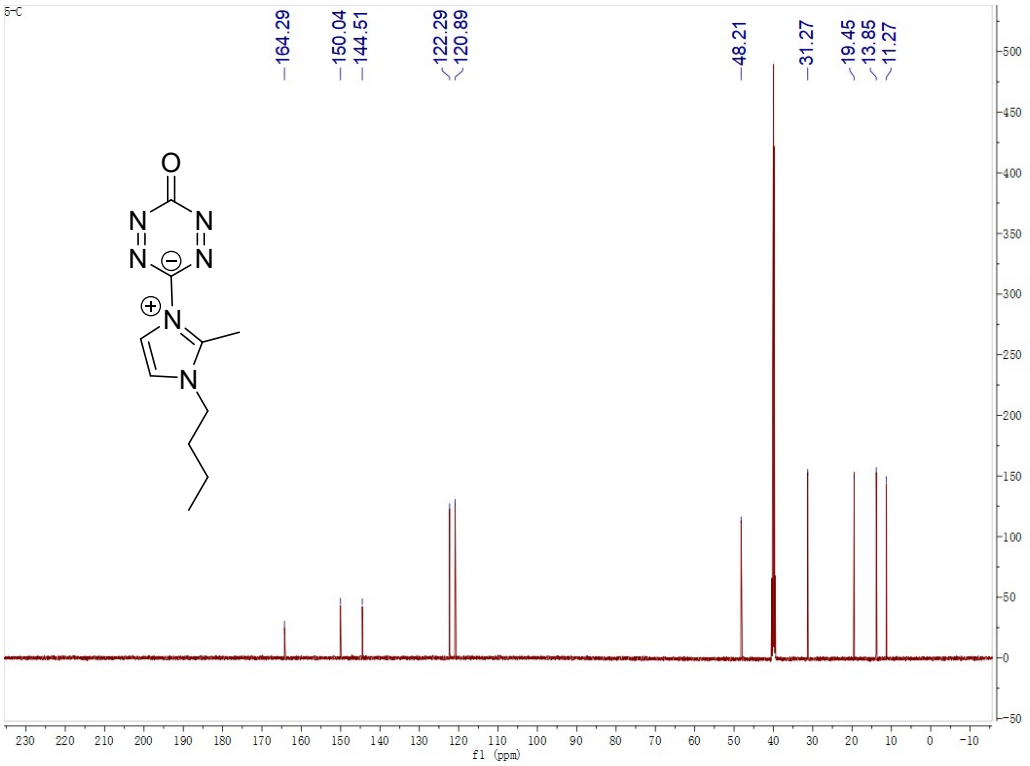


Figure S54. ^{13}C-NMR spectra of 3p in DMSO-d_6

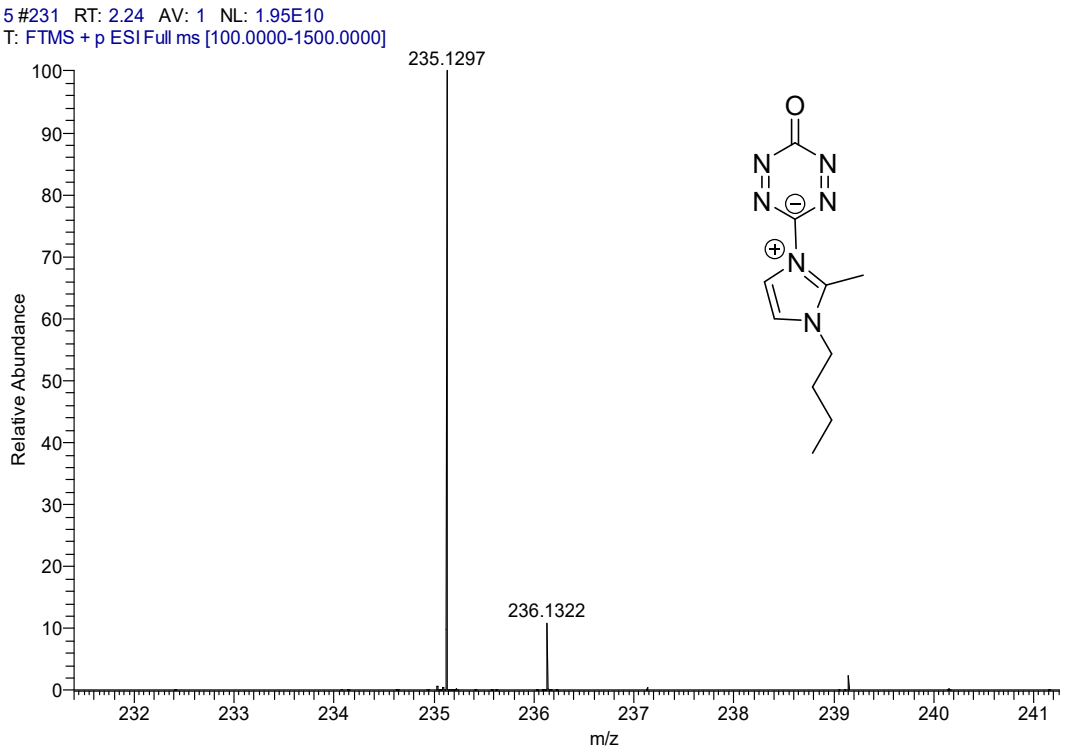


Figure S55. HRMS spectra of 3p in DMSO-d_6

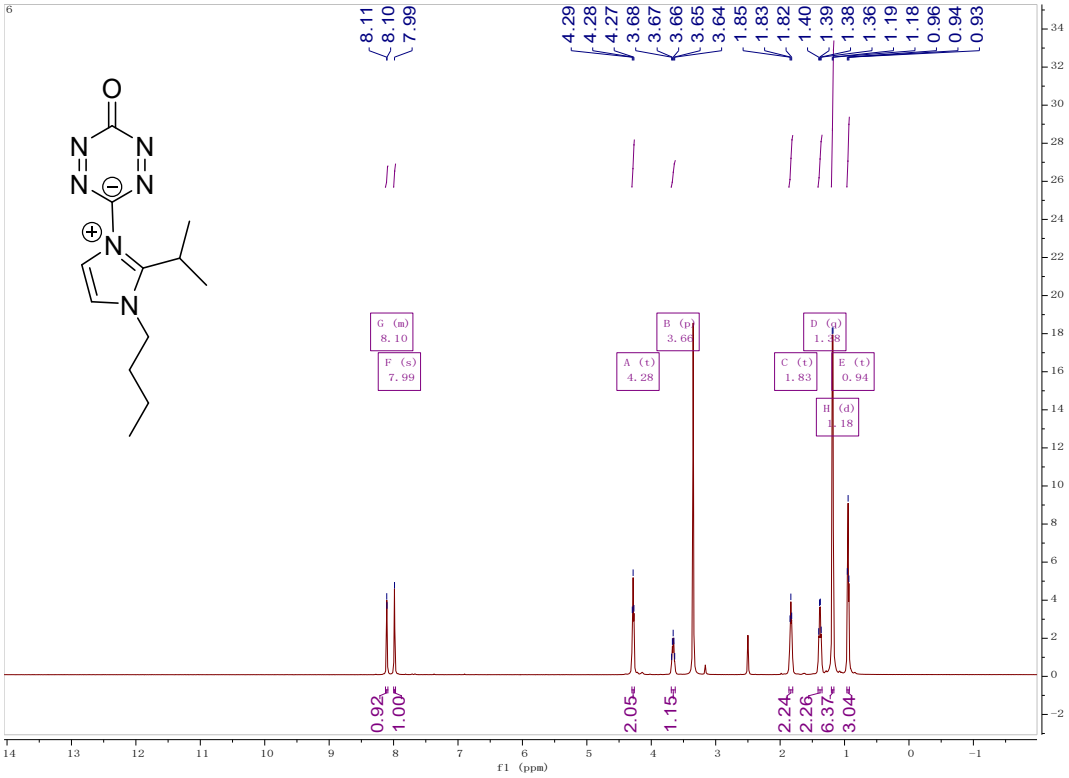


Figure S56. ^{1}H-NMR spectra of 3q in DMSO-d_6

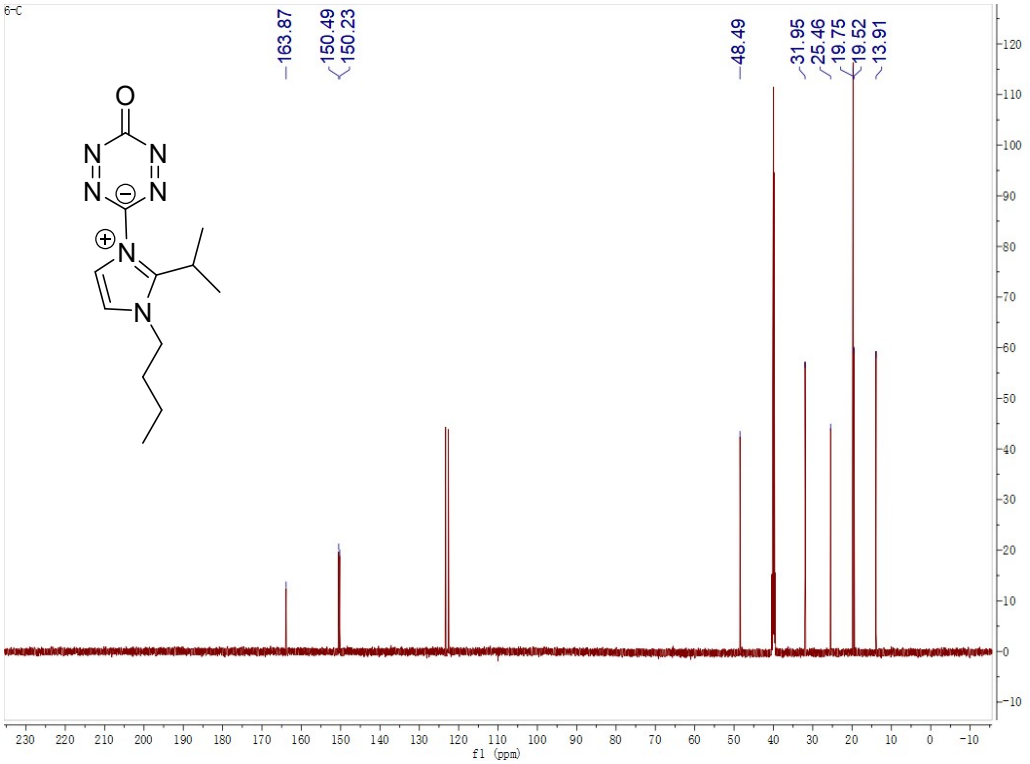


Figure S57. ^{13}C-NMR spectra of 3q in DMSO-d_6

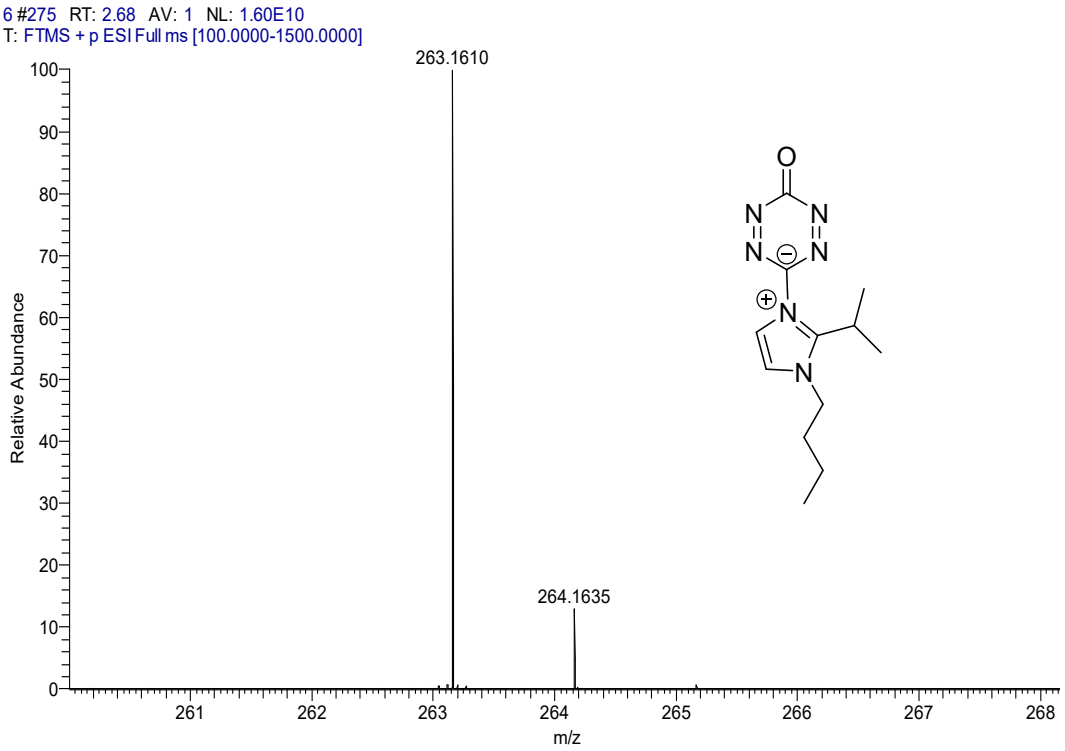


Figure S58. HRMS spectra of 3q in DMSO-d_6

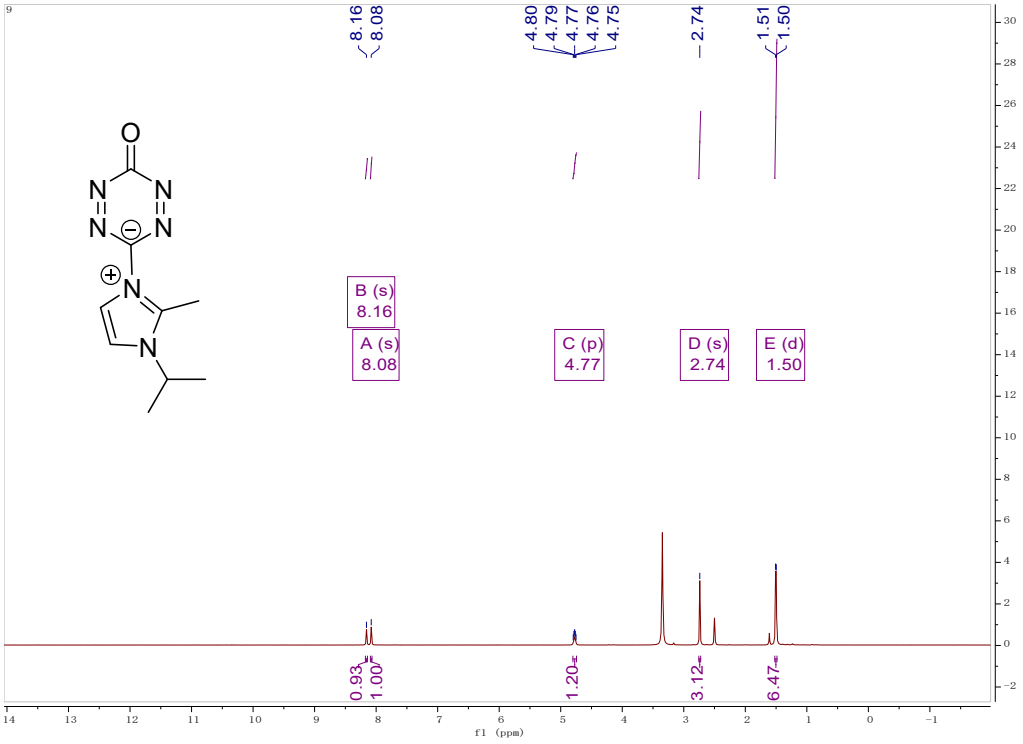


Figure S59. ^{1}H-NMR spectra of 3r in DMSO-d_6

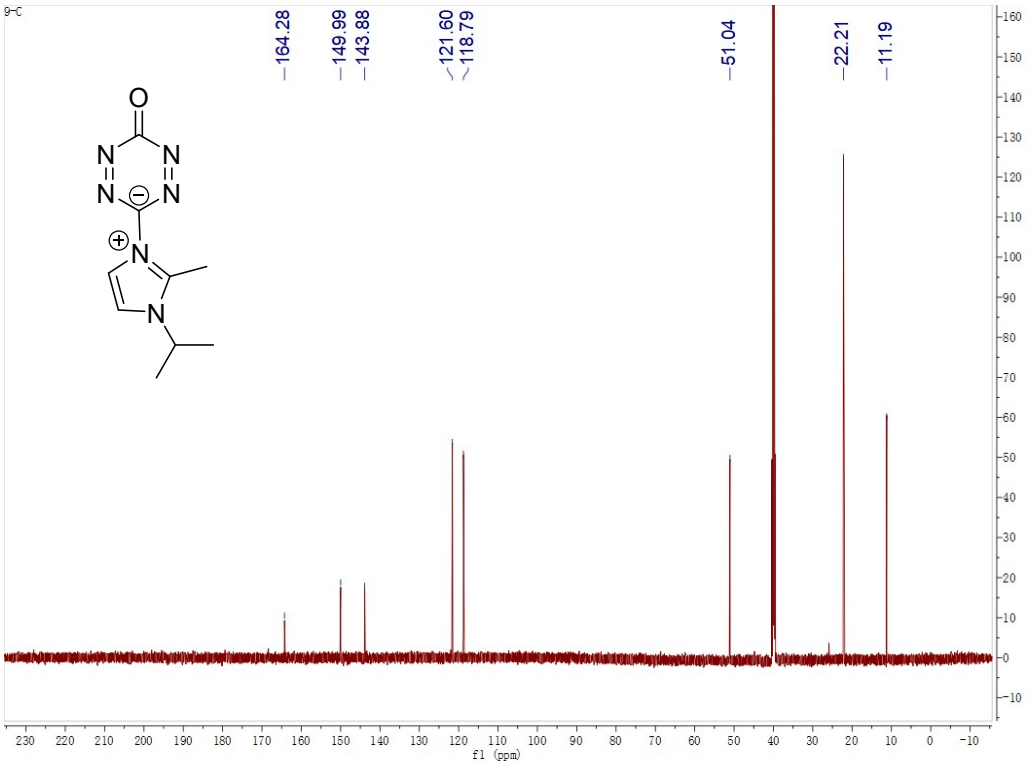


Figure S60. ^{13}C-NMR spectra of 3r in DMSO-d_6

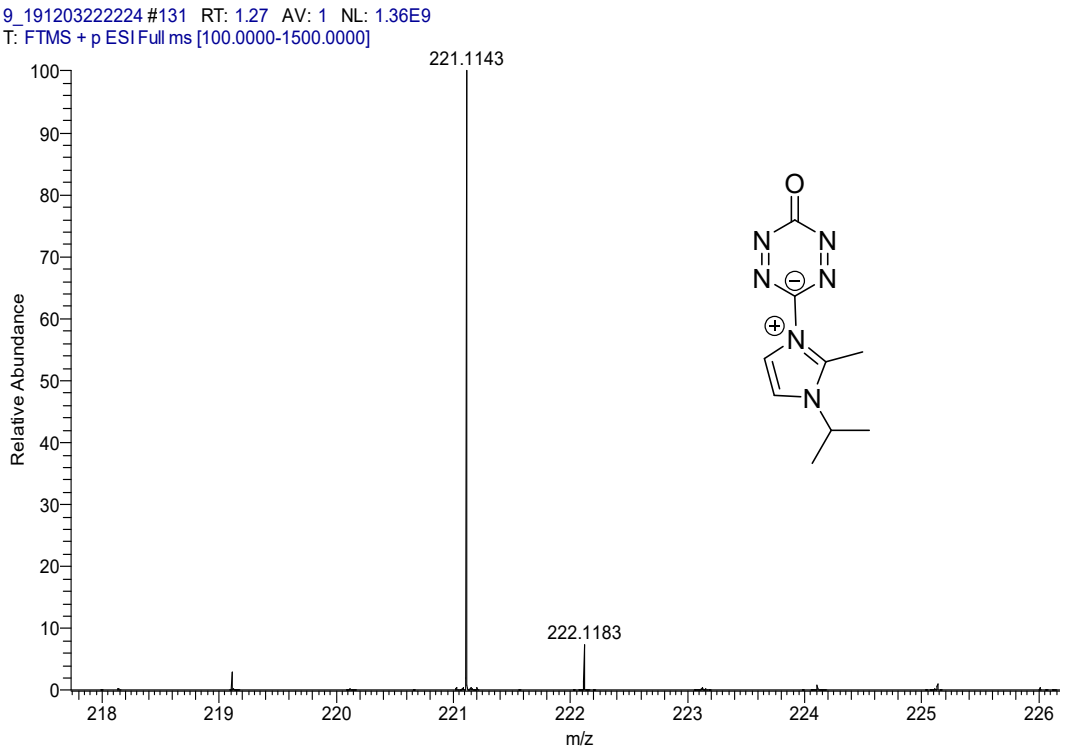


Figure S61. HRMS spectra of 3r in DMSO-d_6

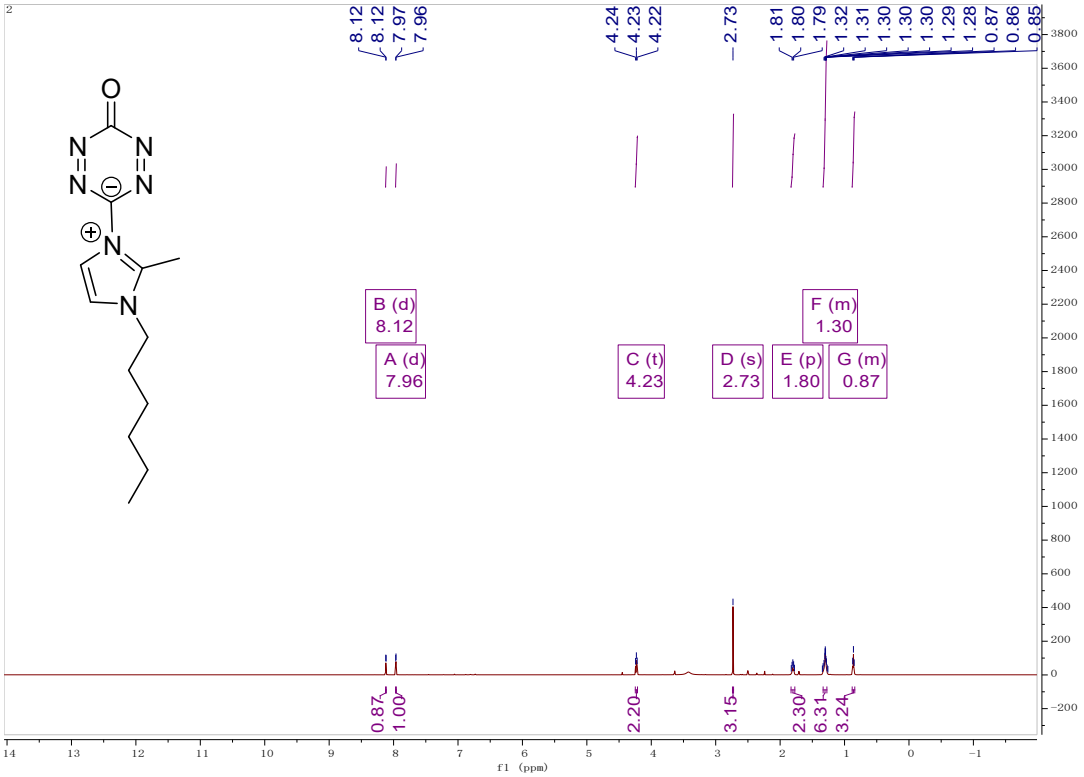


Figure S62. ^{1}H-NMR spectra of 3s in DMSO-d_6

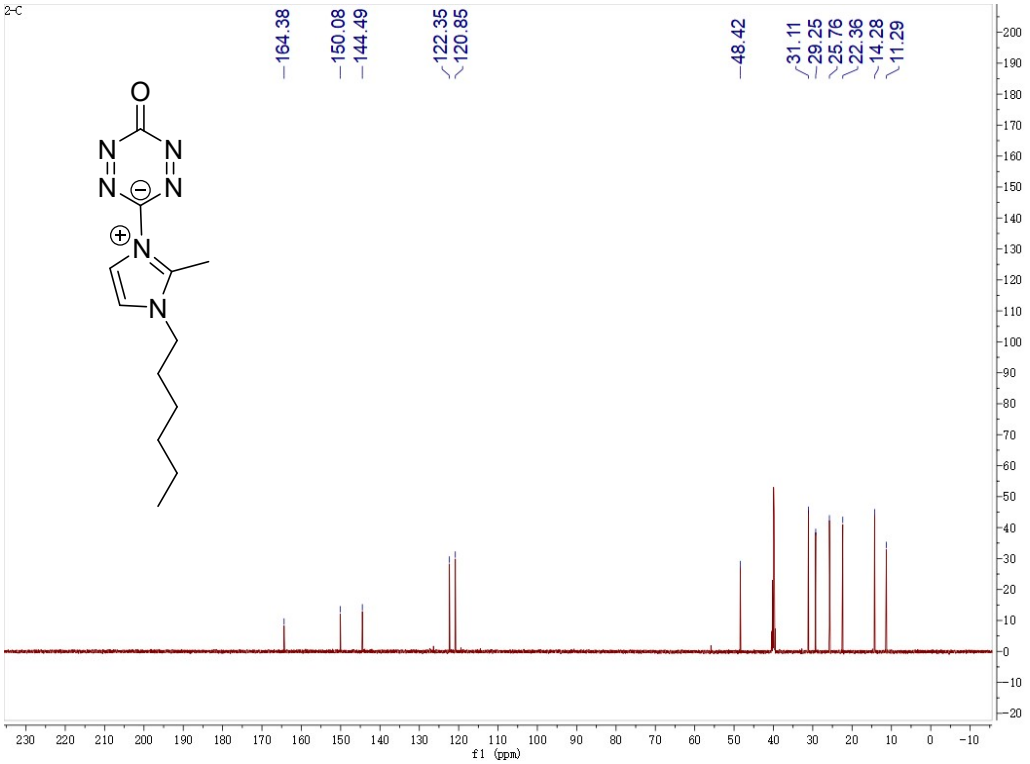


Figure S63. ^{13}C-NMR spectra of 3s in DMSO-d_6

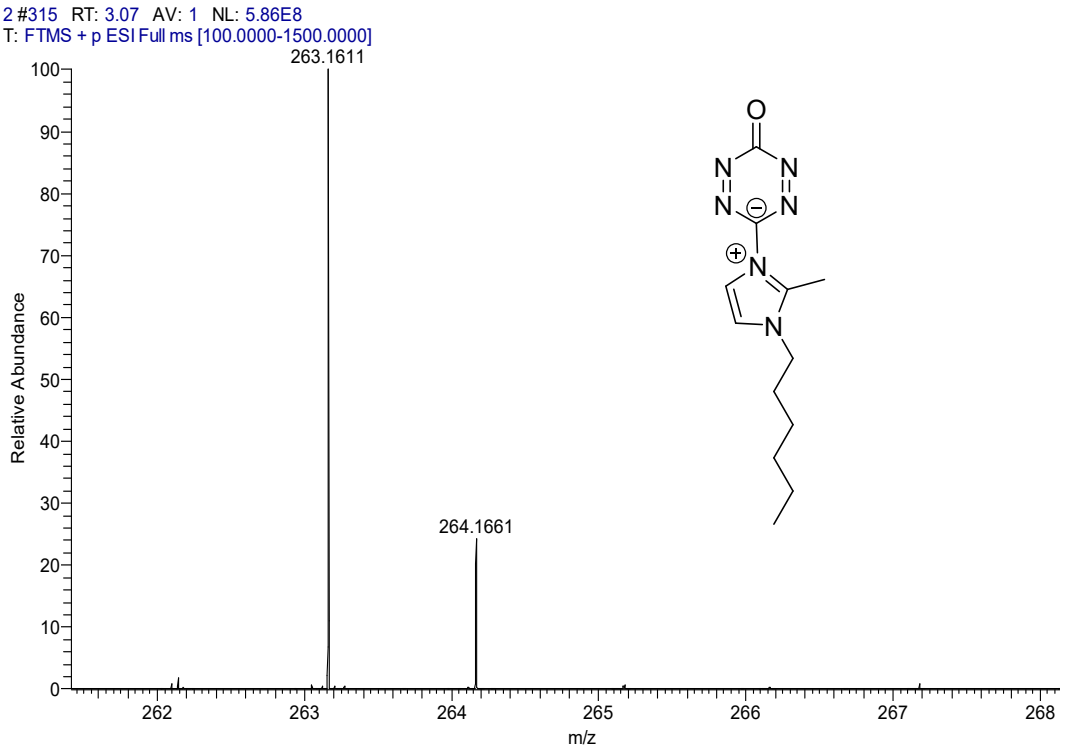


Figure S64. HRMS spectra of 3s in DMSO-d_6

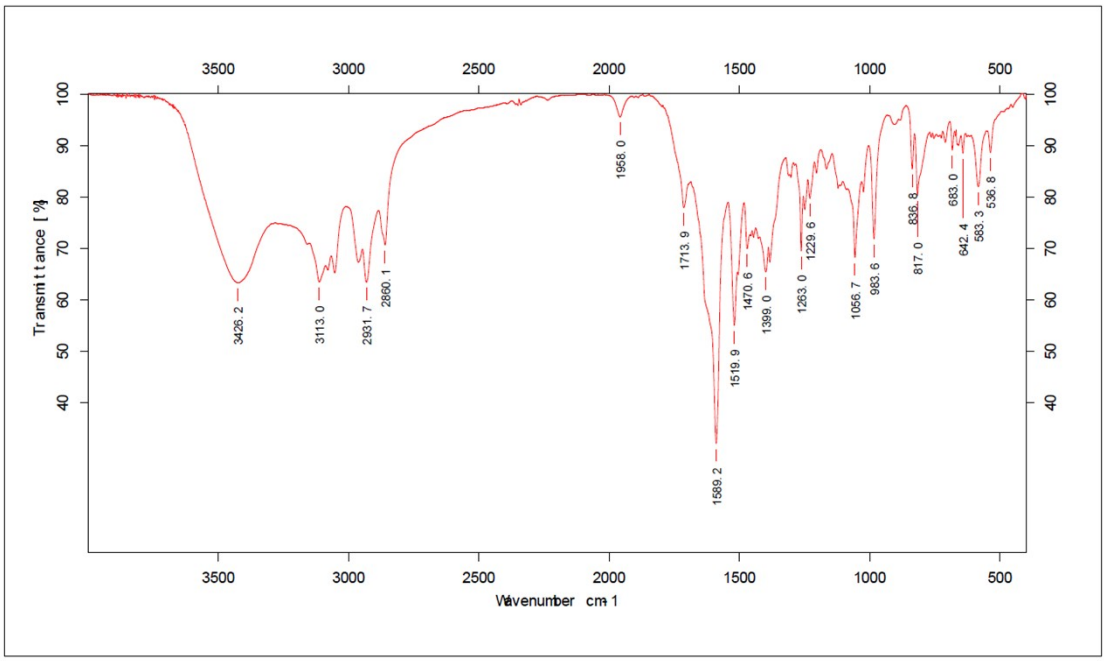


Figure S65. IR spectra of 3s

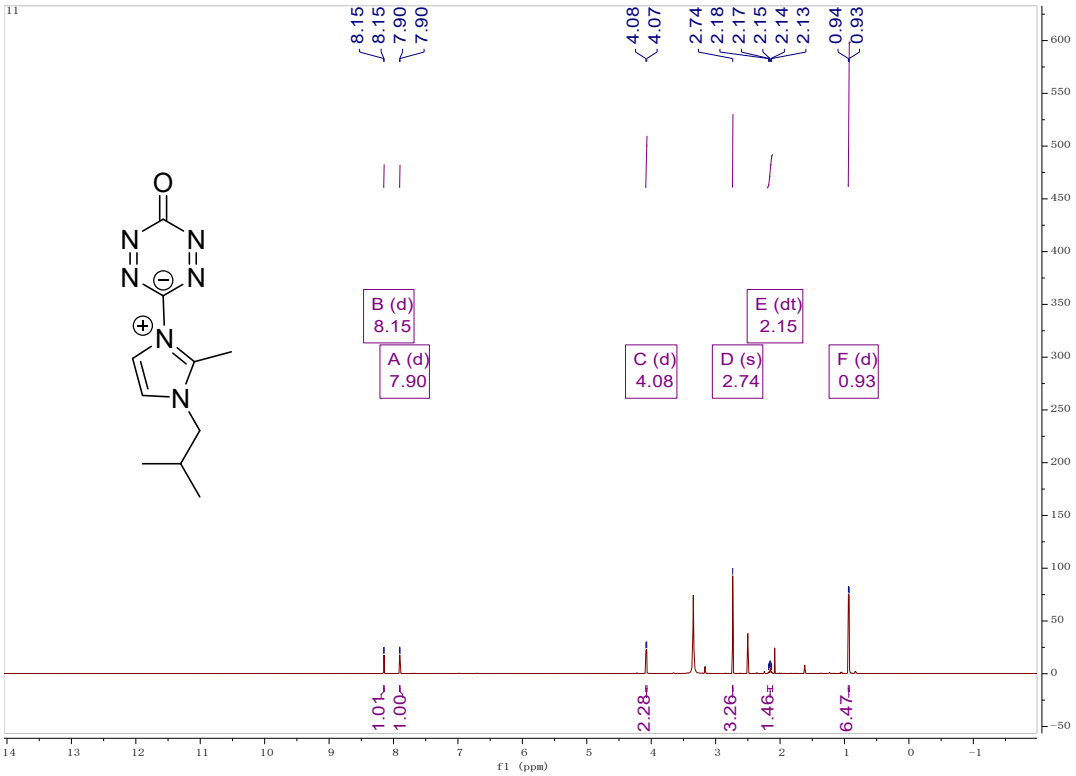


Figure S66. ^{1}H-NMR spectra of 3t in DMSO-d_6

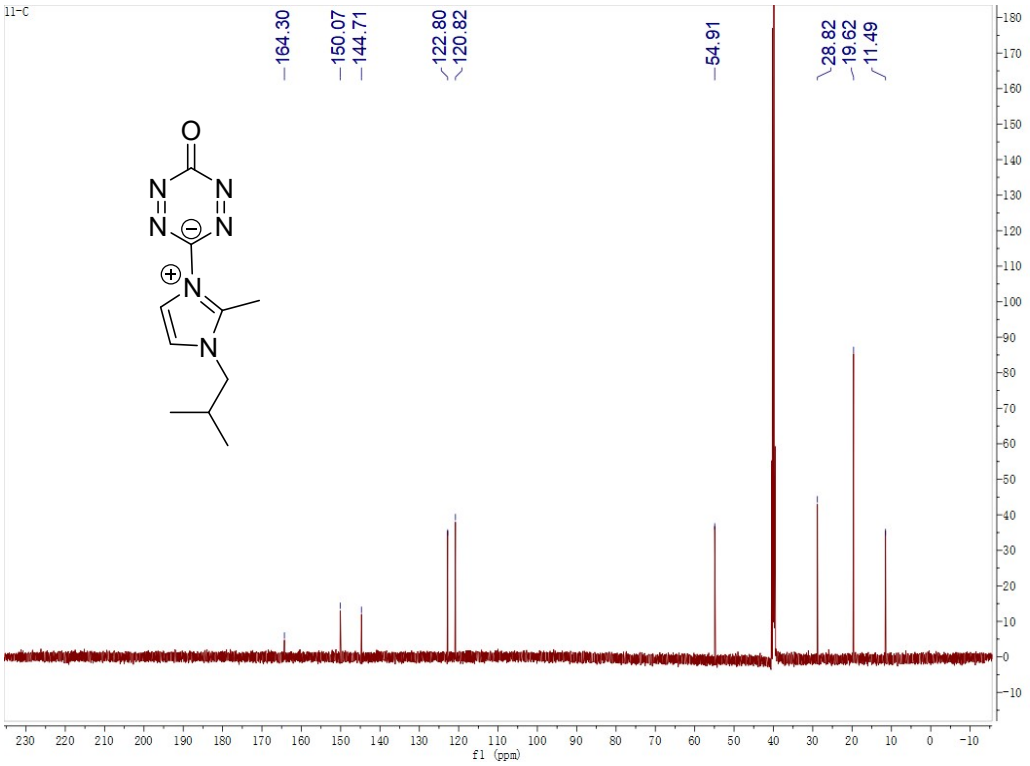


Figure S67. ^{13}C-NMR spectra of 3t in DMSO-d_6

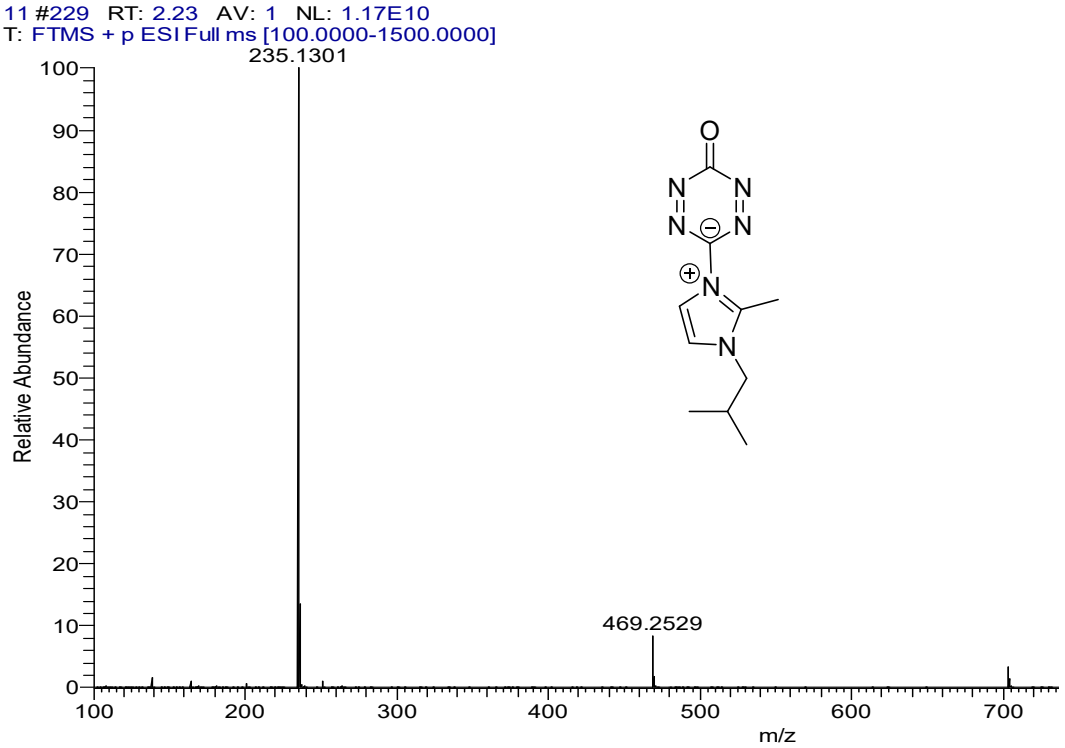


Figure S68. HRMS spectra of 3t in DMSO-d_6

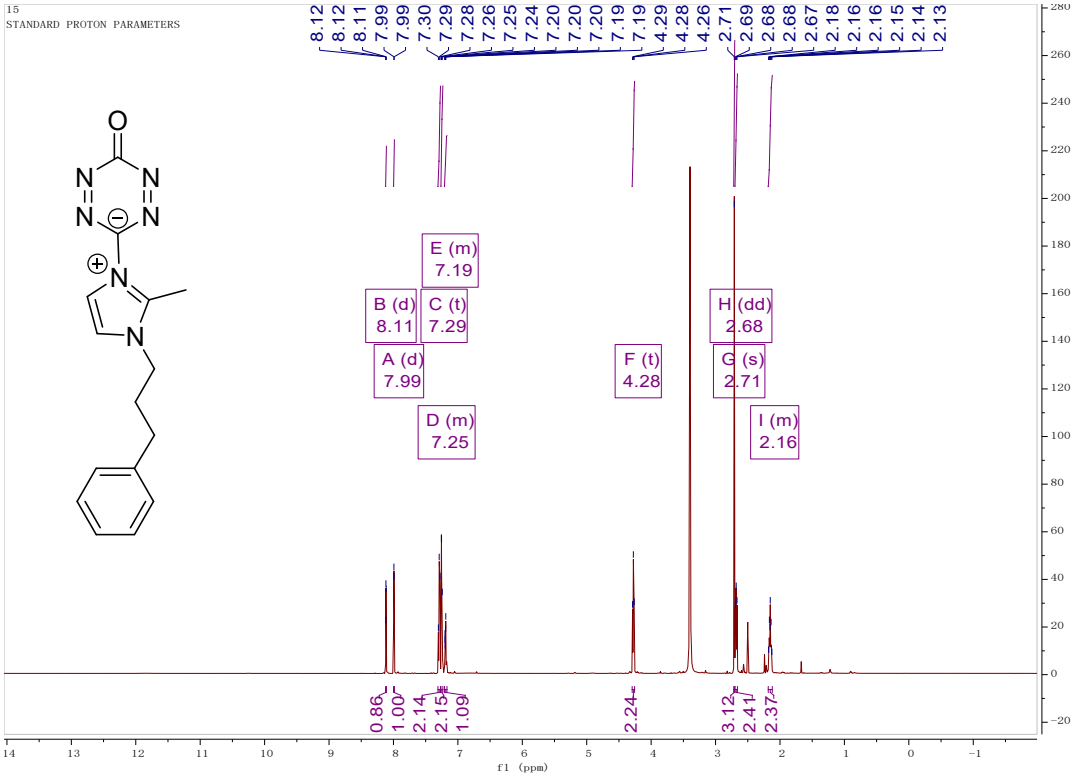


Figure S69. ^{1}H-NMR spectra of 3u in DMSO-d_6

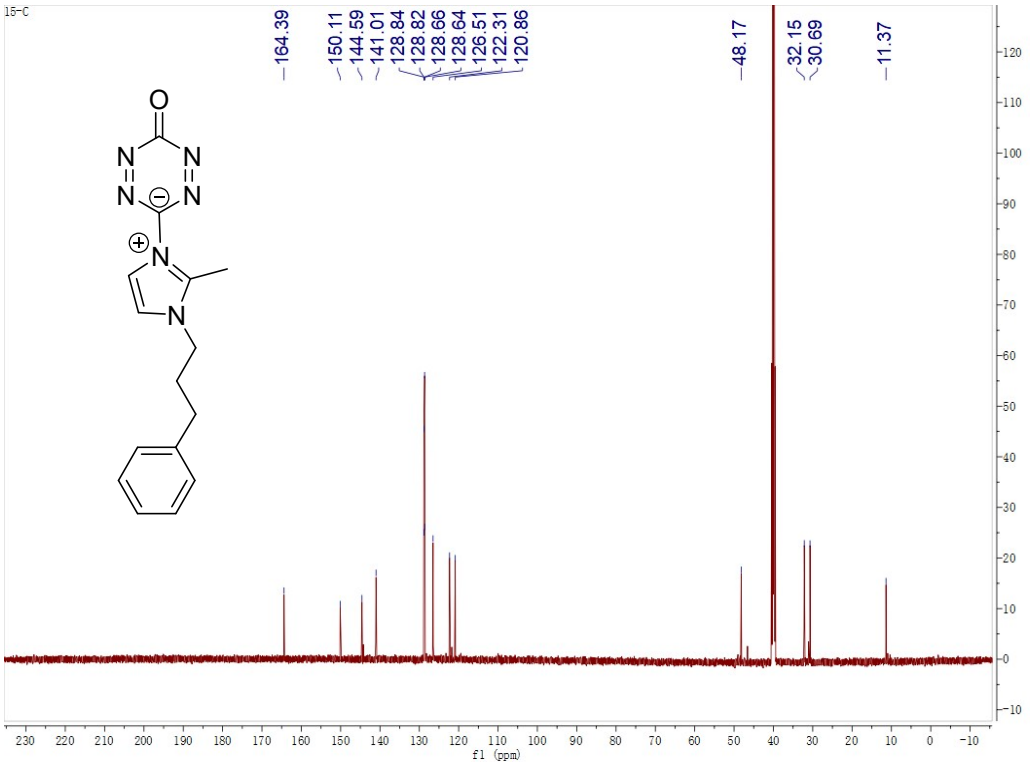


Figure S70. ^{13}C-NMR spectra of 3u in DMSO-d_6

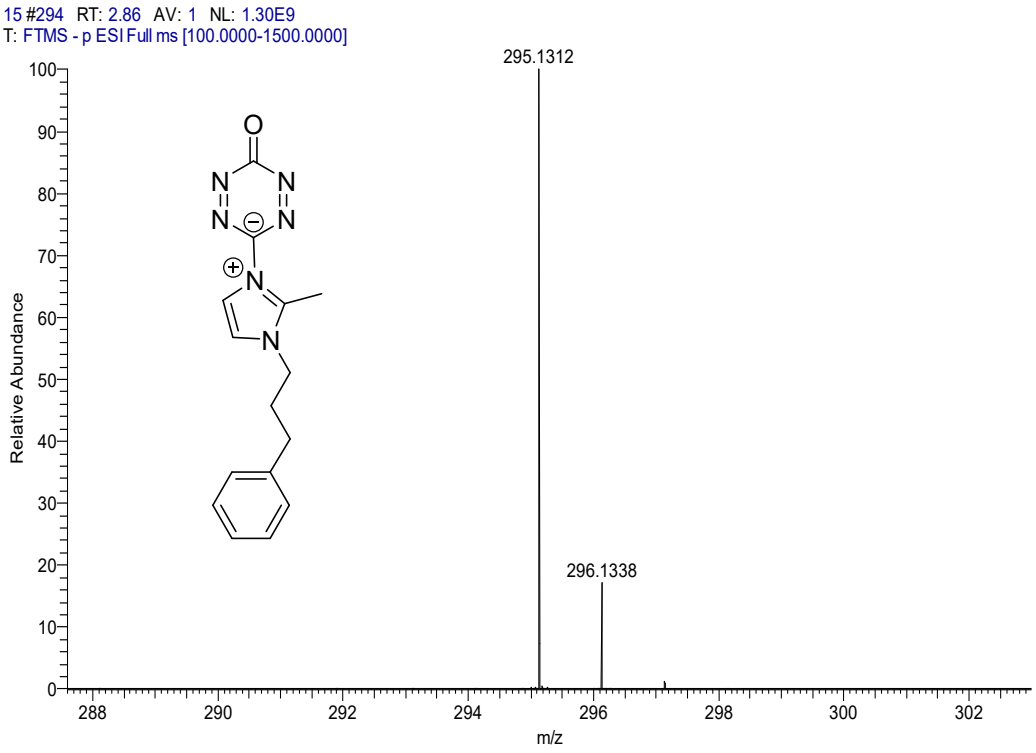


Figure S71. HRMS spectra of 3u in DMSO-d_6

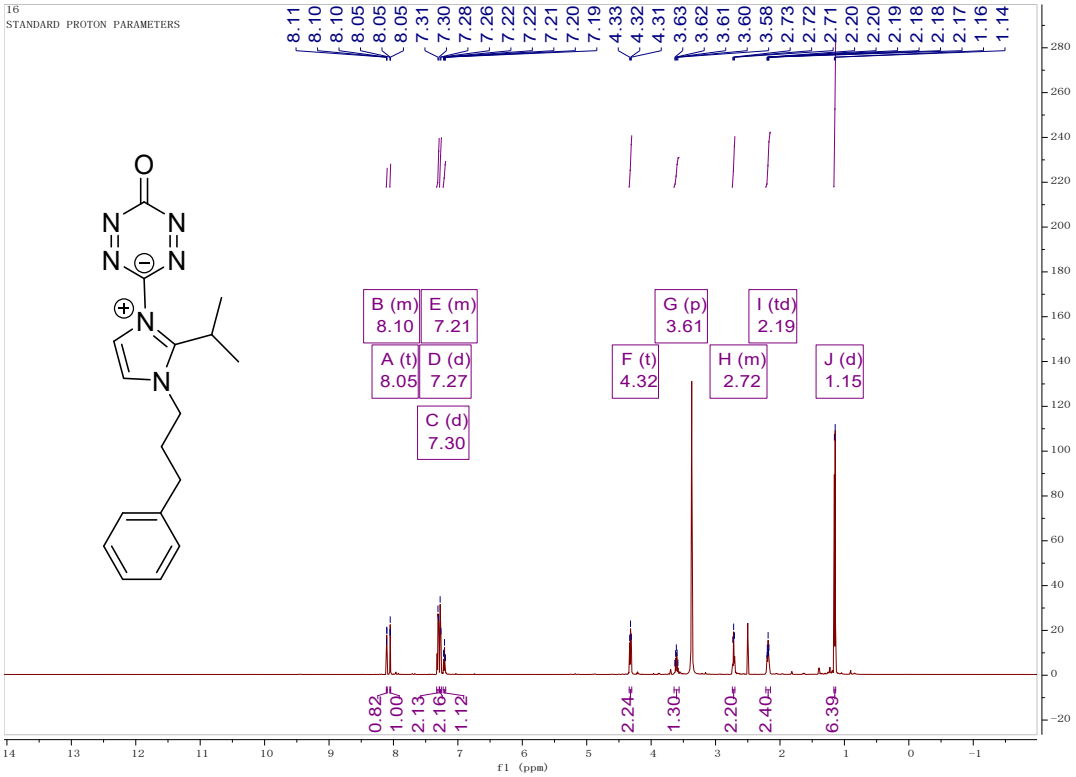


Figure S72. ^{1}H-NMR spectra of 3v in DMSO-d_6

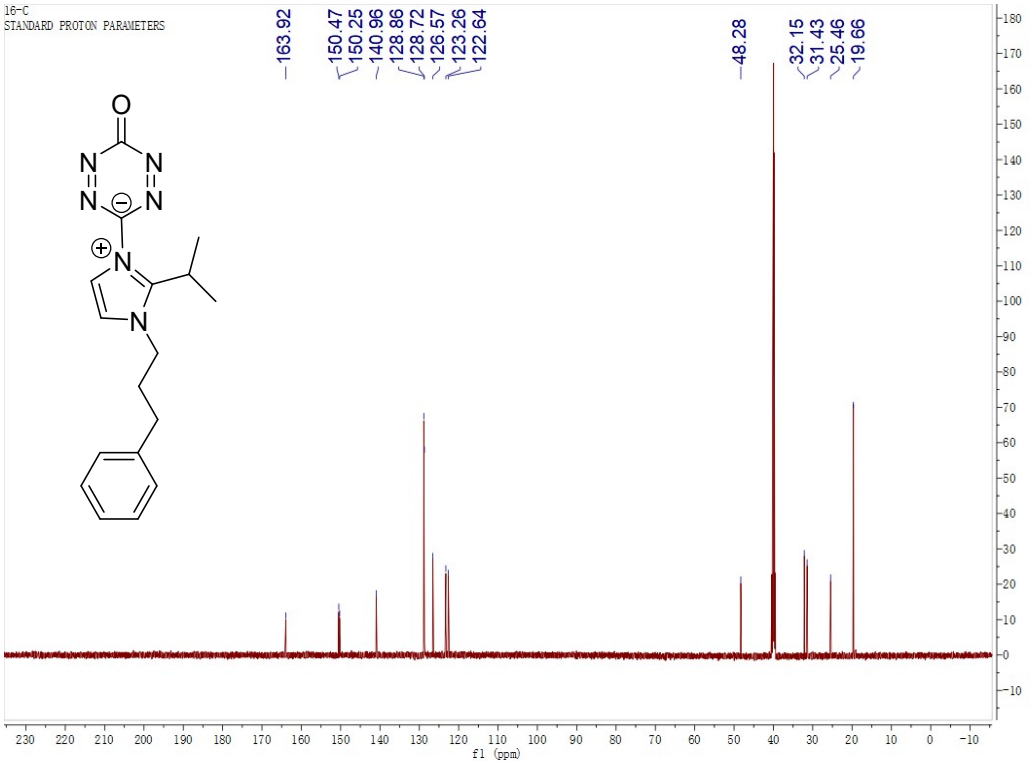


Figure S73. ^{13}C-NMR spectra of 3v in DMSO-d_6

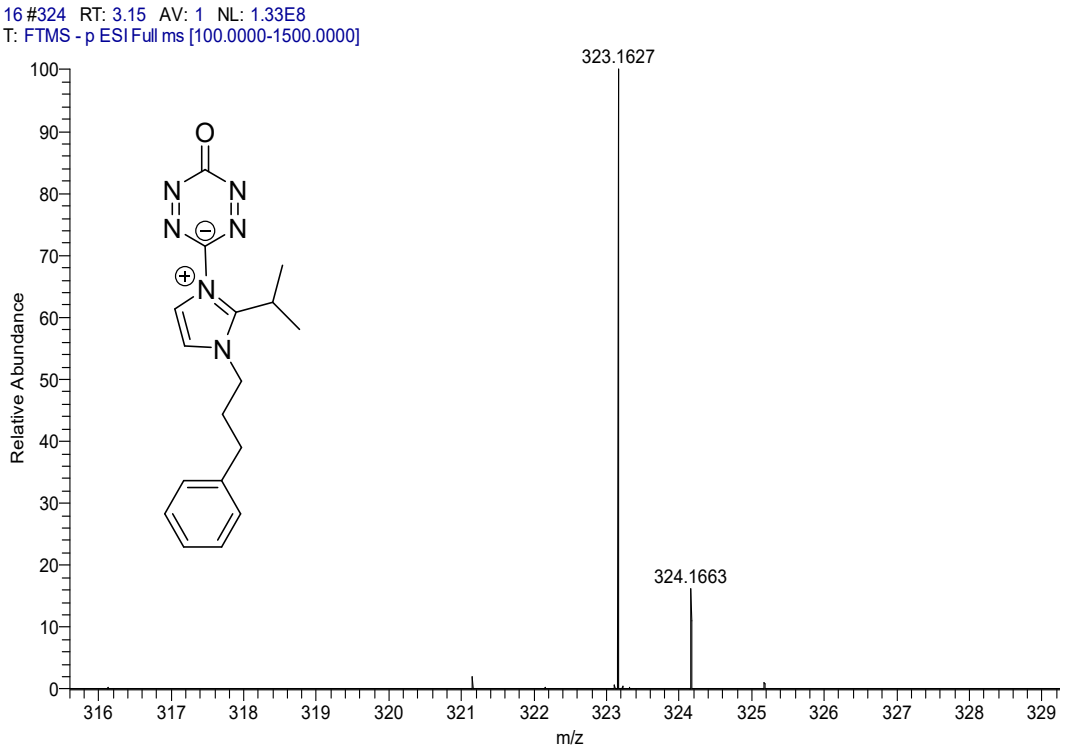


Figure S74. HRMS spectra of 3v in DMSO-d_6

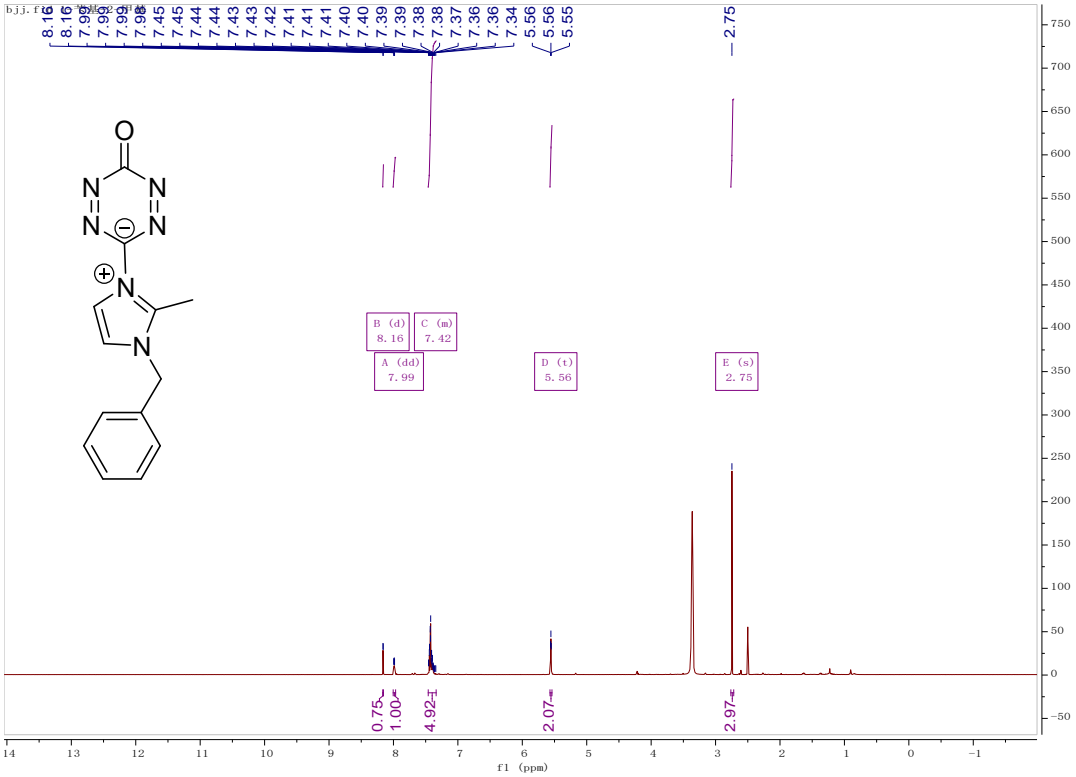


Figure S75. ^{1}H-NMR spectra of 3w in DMSO-d_6

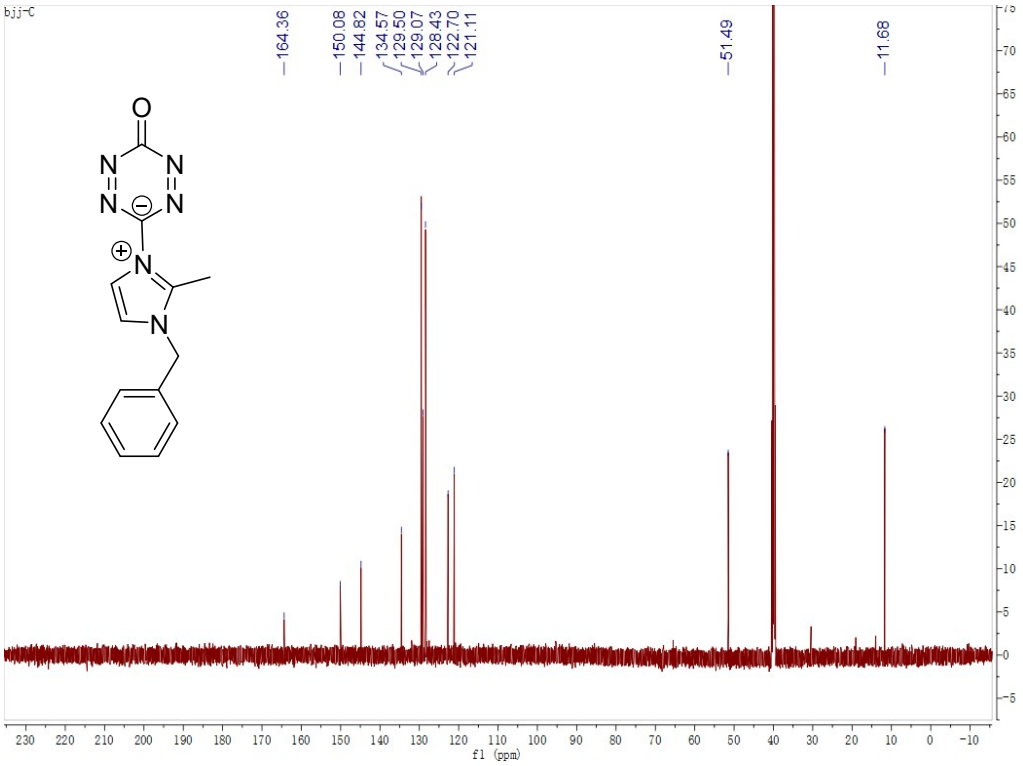


Figure S76. ^{13}C-NMR spectra of 3w in DMSO-d_6

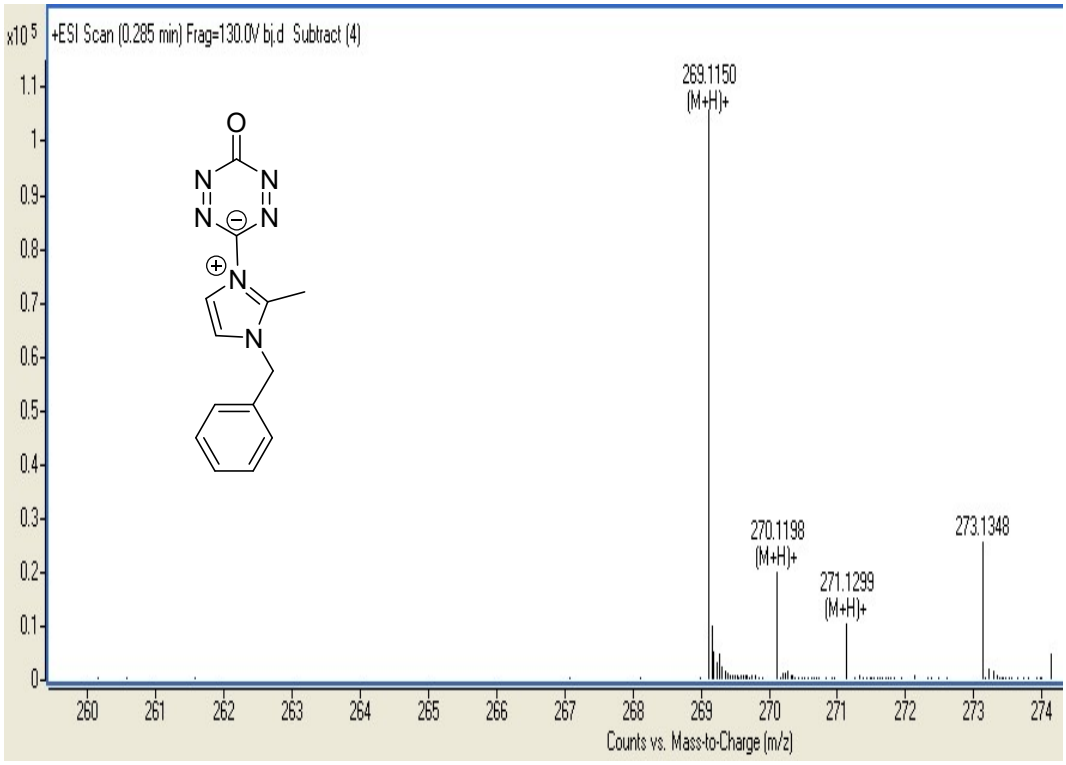


Figure S77. HRMS spectra of 3w in DMSO-d_6

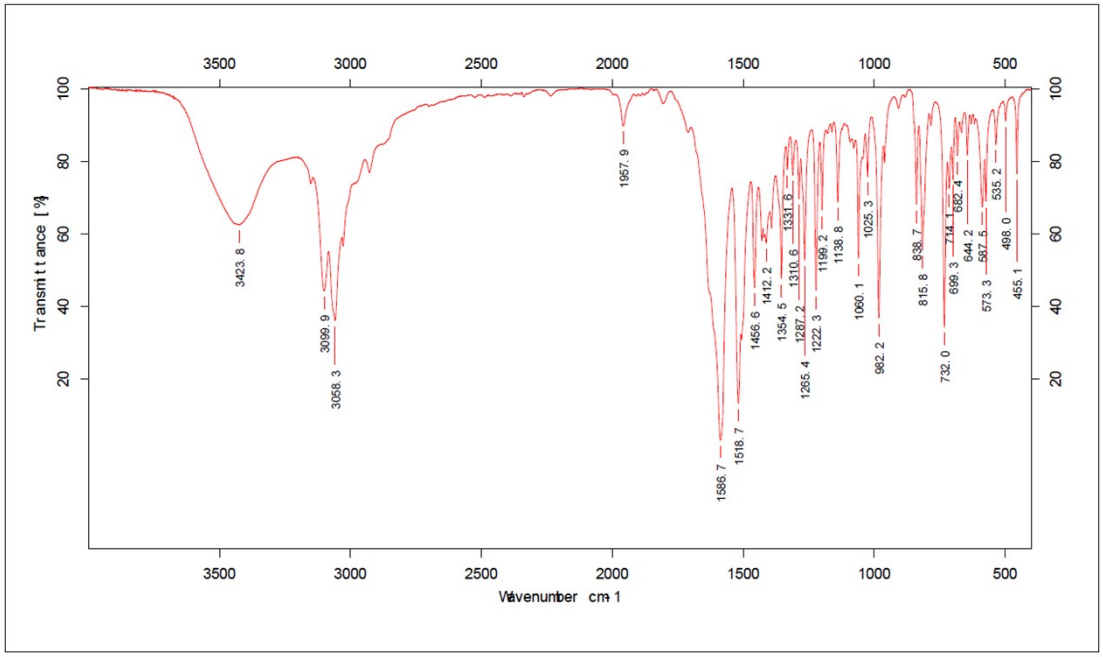


Figure S78. IR spectra of 3w

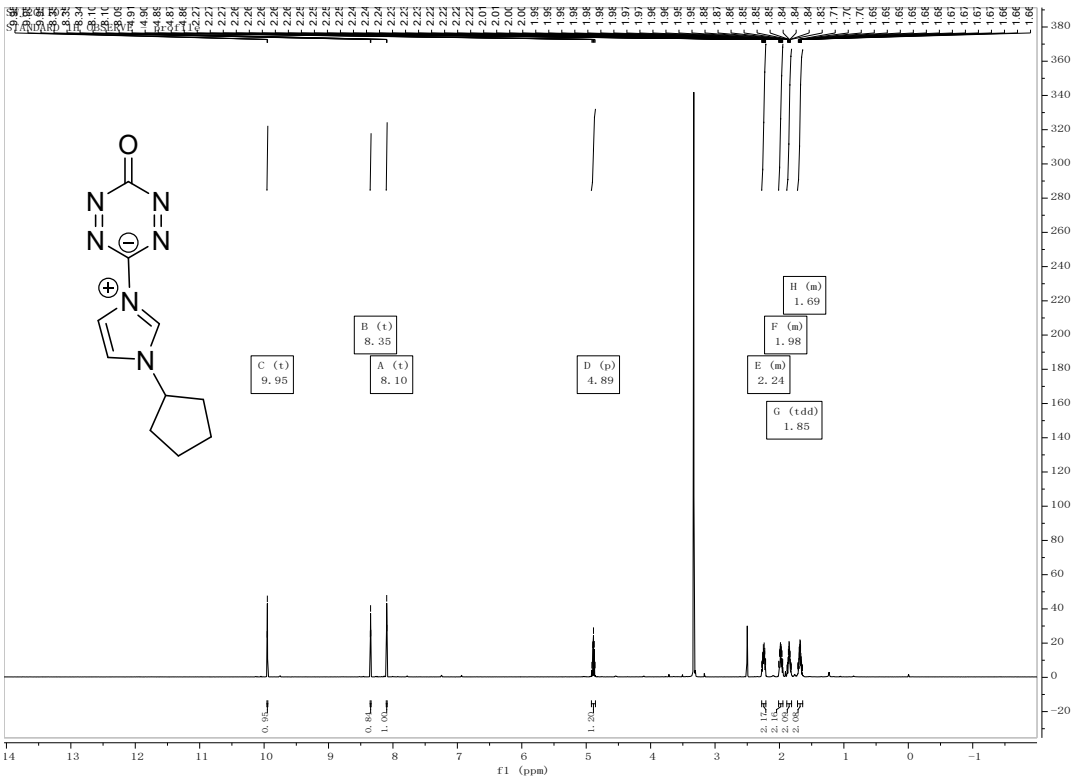


Figure S79. ^{1}H-NMR spectra of 3x in DMSO-d_6

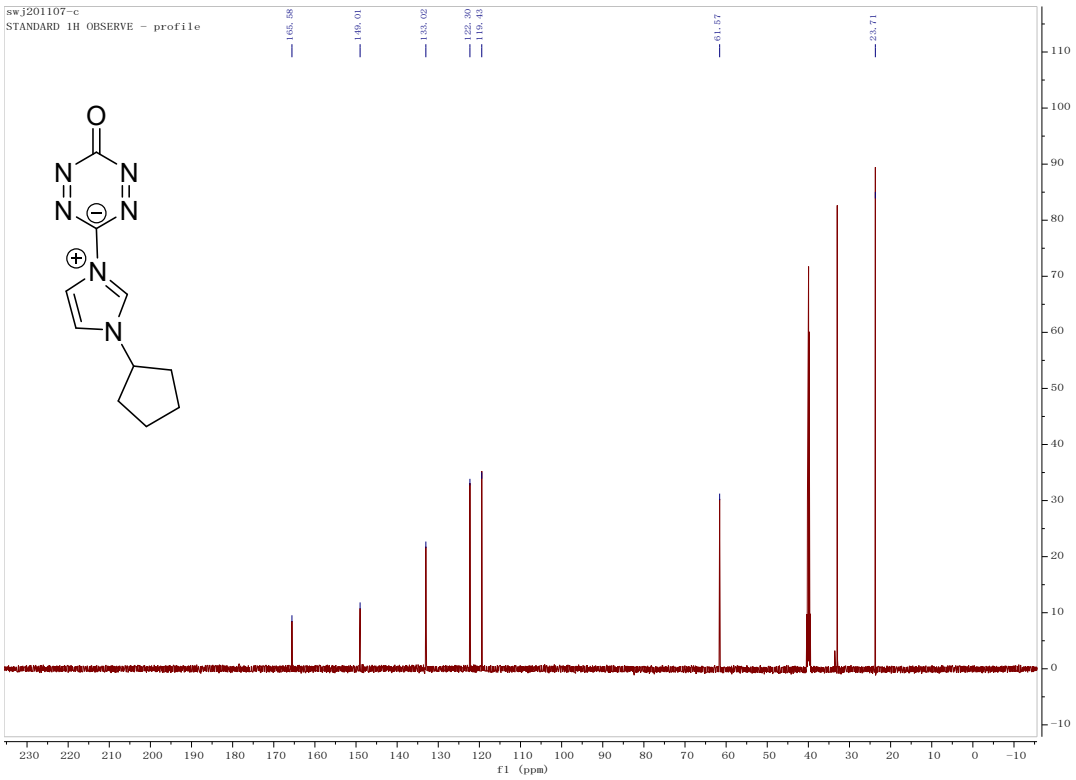


Figure S80. ^{13}C-NMR spectra of 3x in DMSO-d_6

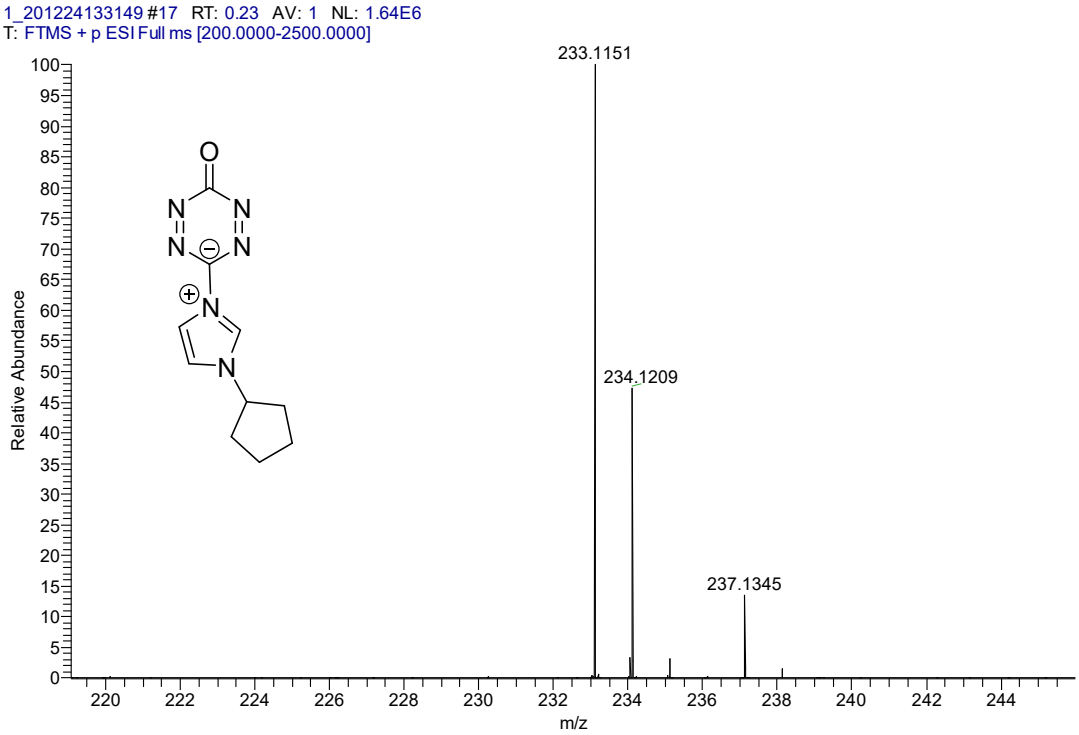


Figure S81. HRMS spectra of 3x in DMSO-d_6

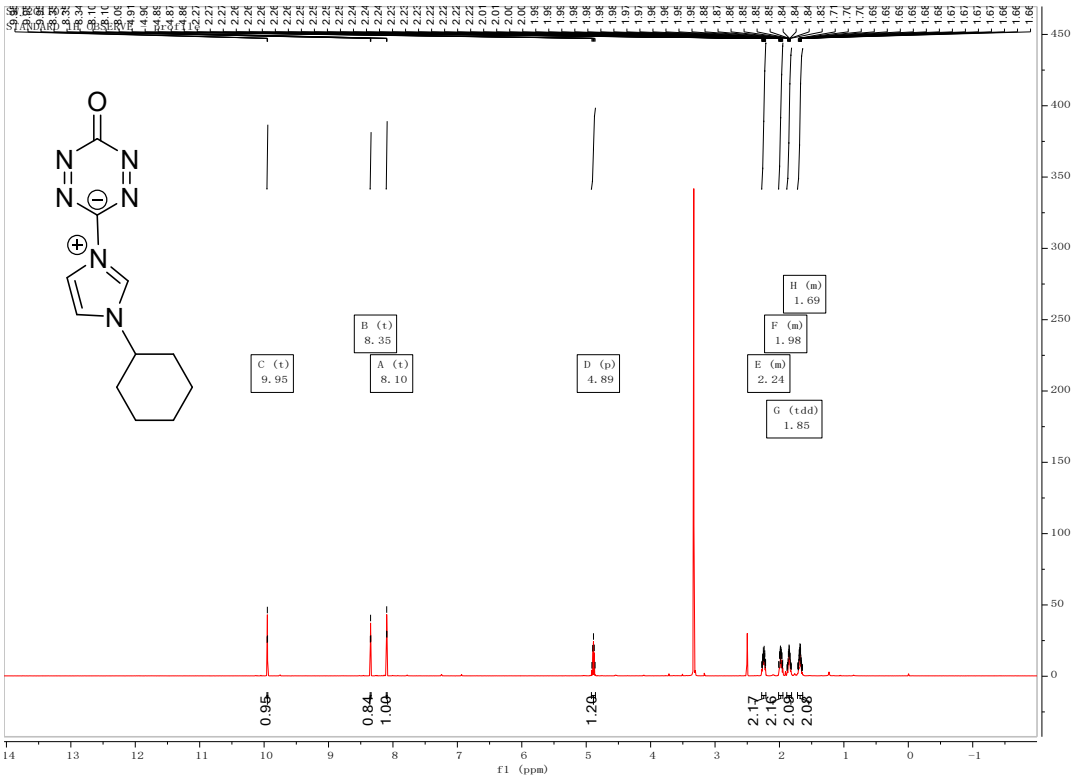


Figure S82. ^{1}H-NMR spectra of 3y in DMSO-d_6

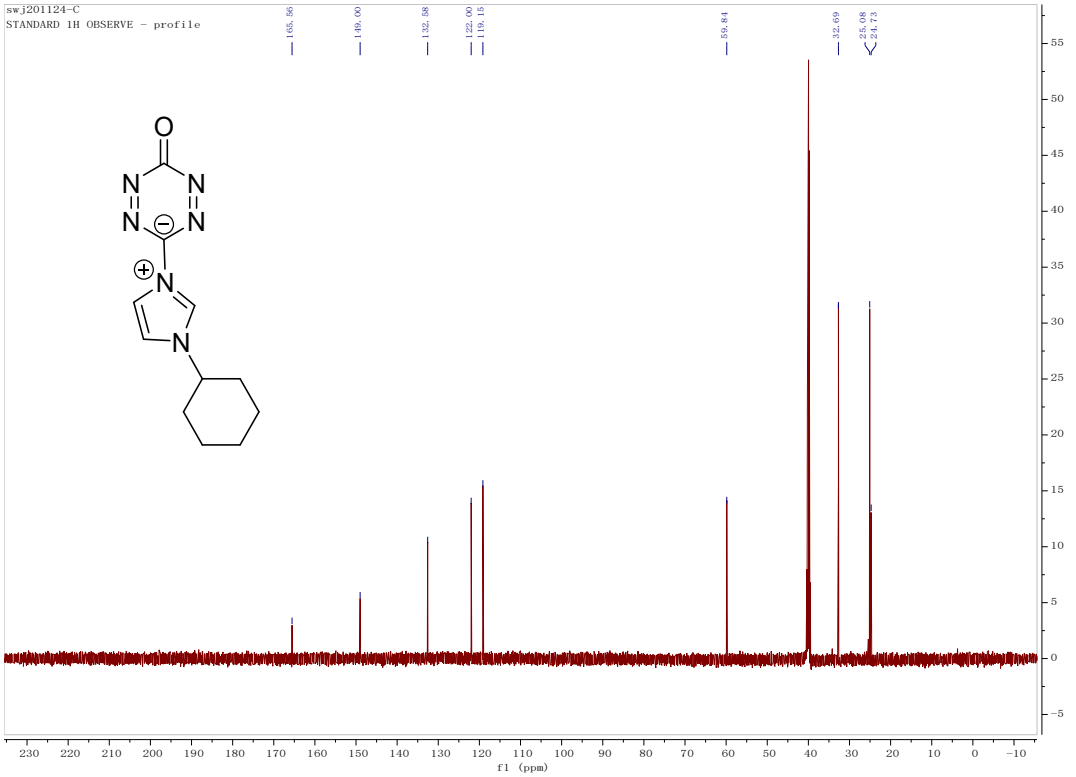


Figure S83. ^{13}C-NMR spectra of 3y in DMSO-d_6

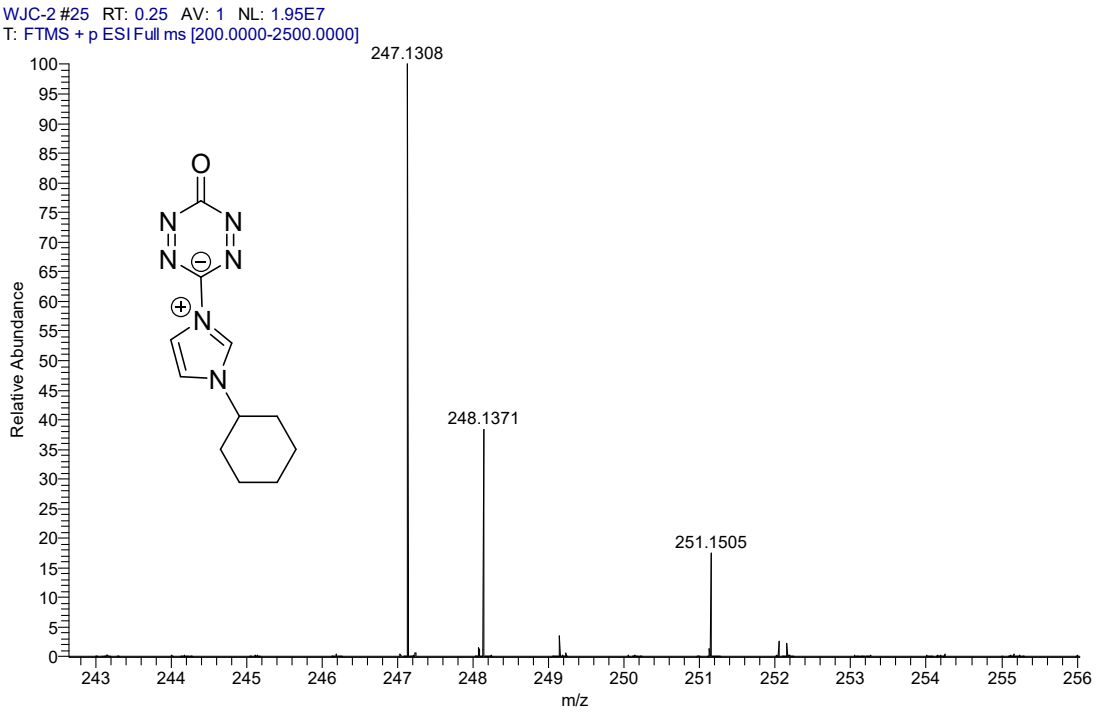


Figure S84. HRMS spectra of 3y in DMSO-d_6

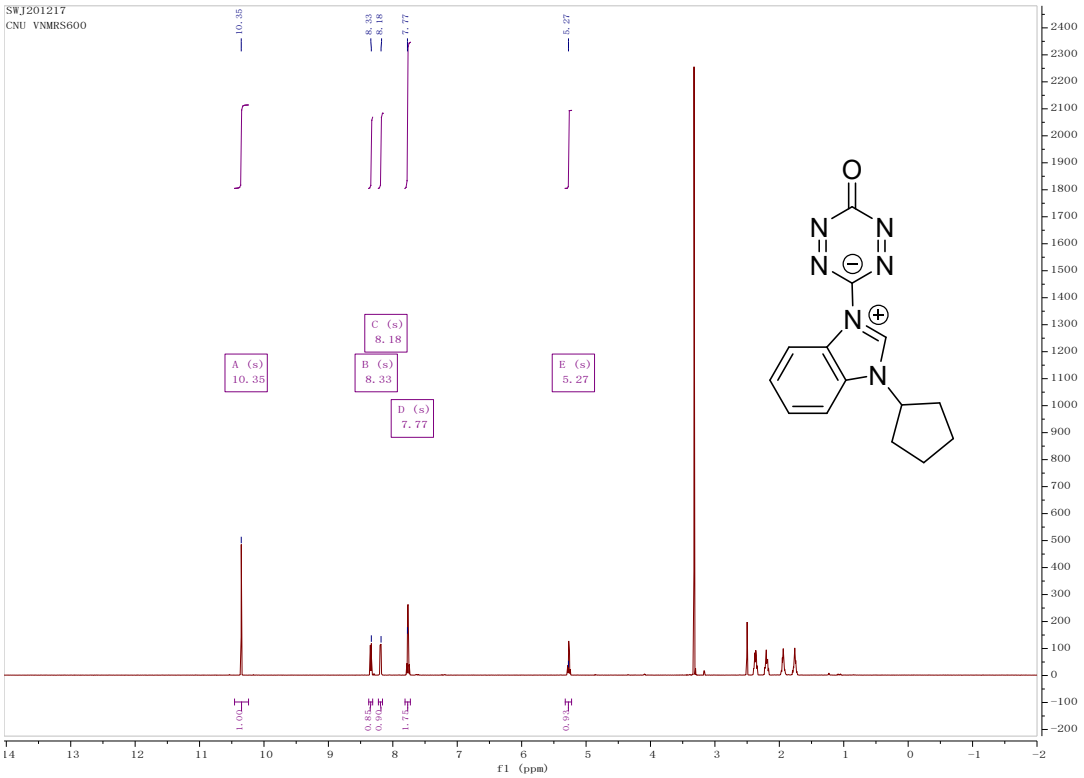


Figure S85. ^{1}H-NMR spectra of 3z in DMSO-d_6

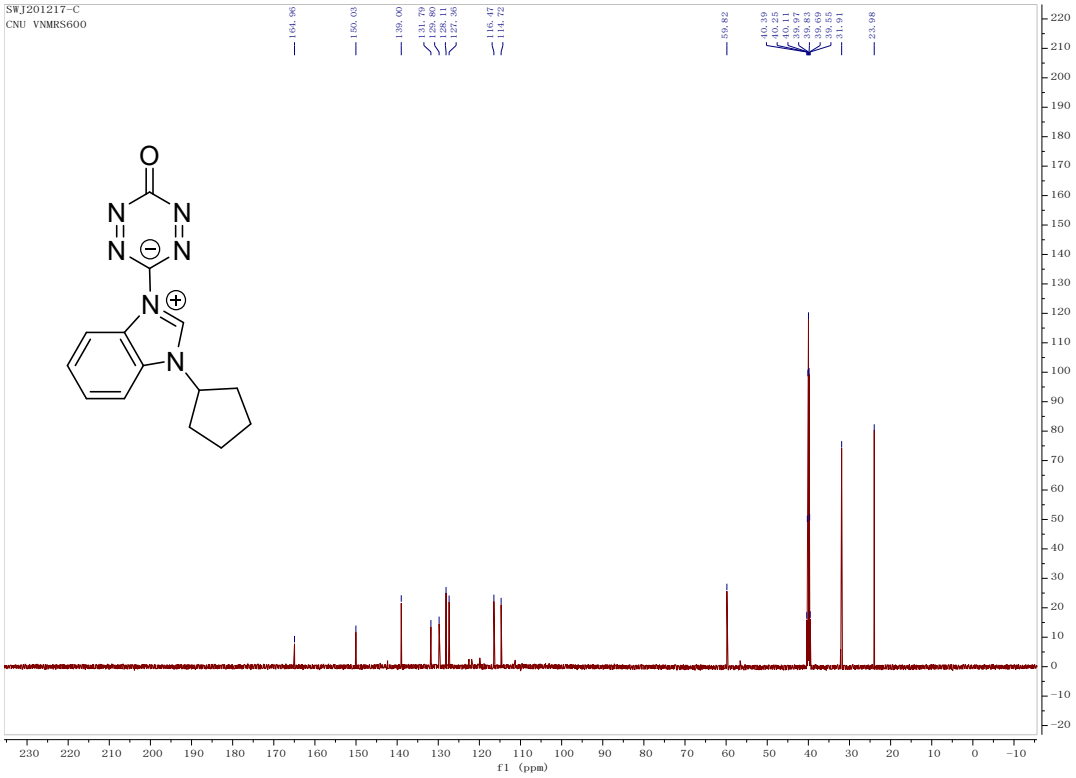


Figure S86. ^{13}C-NMR spectra of 3z in DMSO-d_6

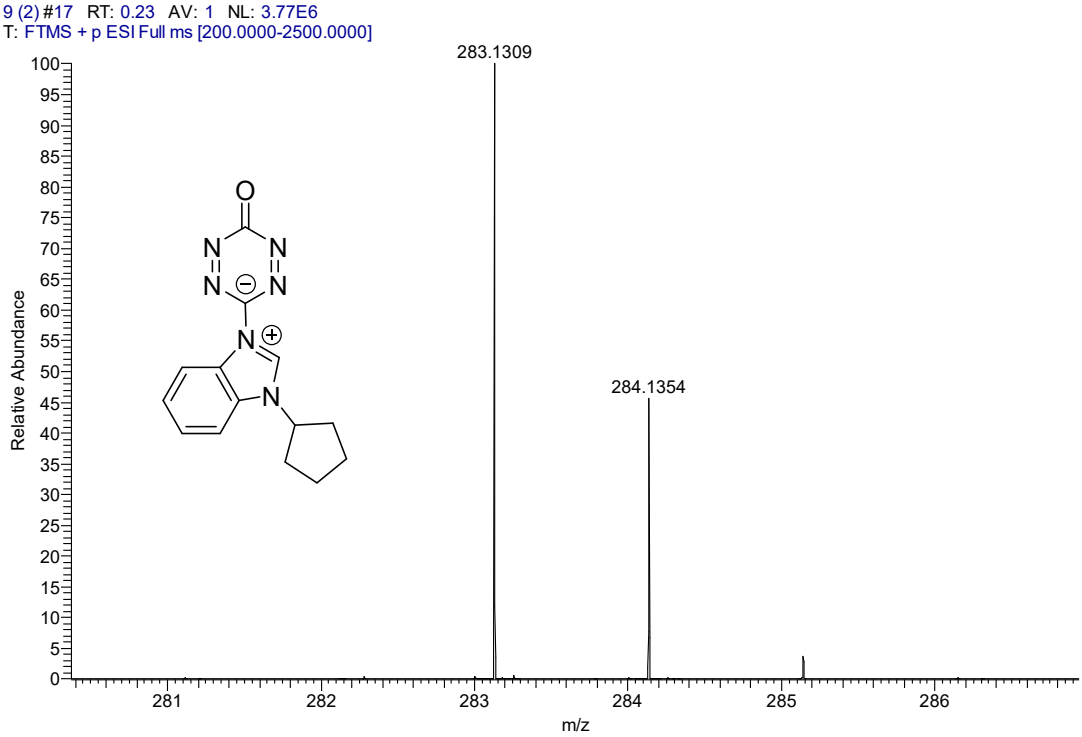


Figure S87. HRMS spectra of 3z in DMSO-d_6

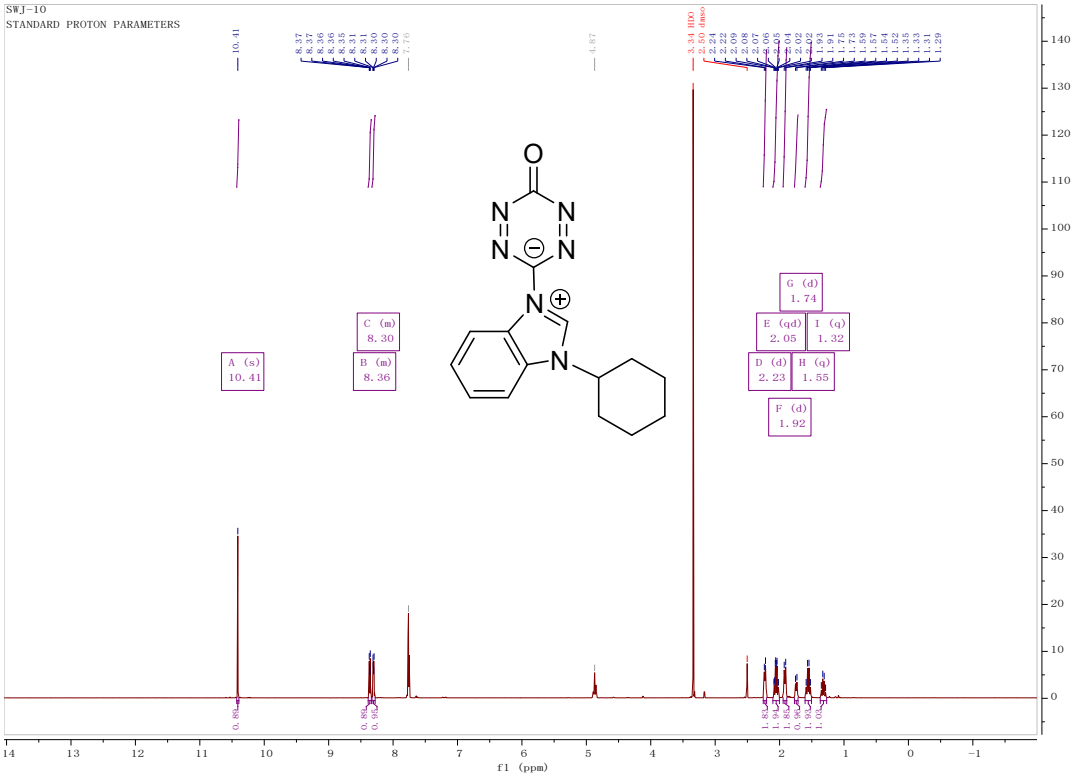


Figure S88. ^{1}H-NMR spectra of 3aa in DMSO-d_6

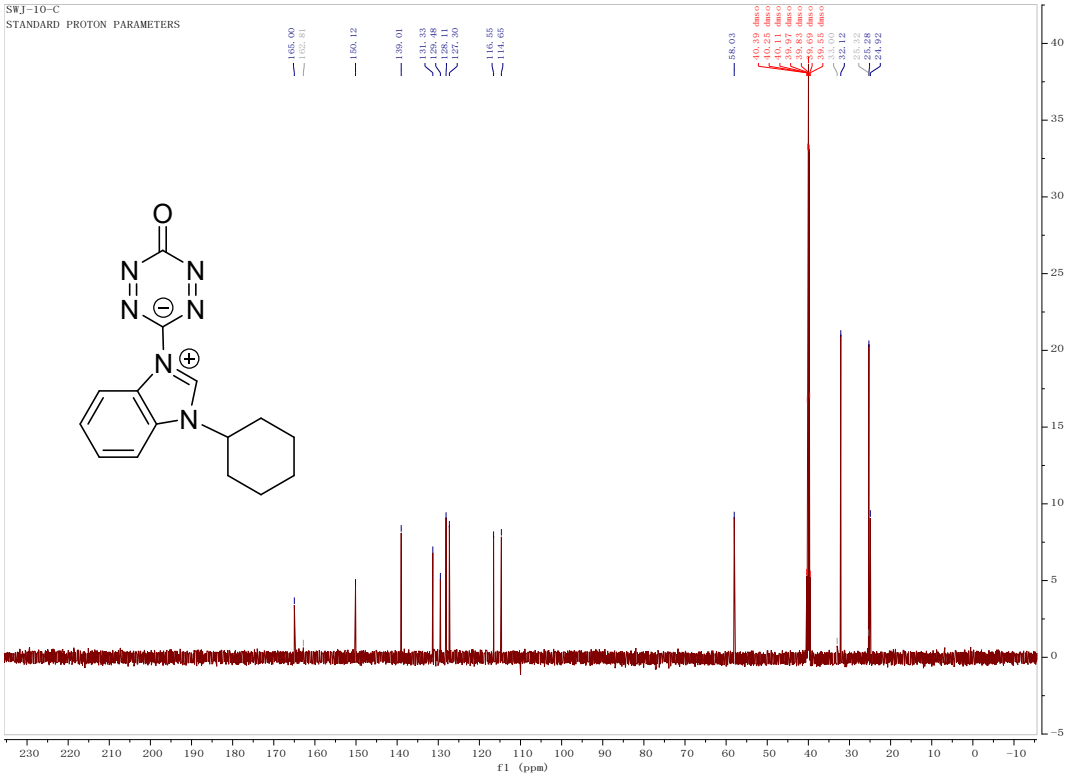


Figure S89. ^{13}C-NMR spectra of 3aa in DMSO-d_6

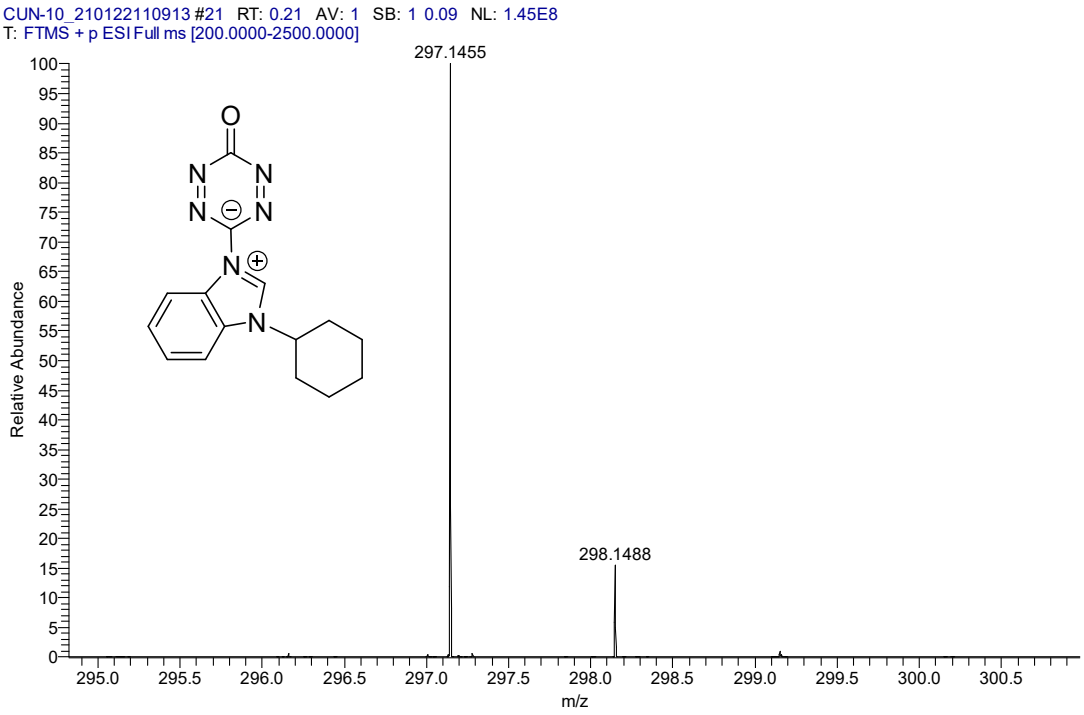


Figure S90. HRMS spectra of 3aa in DMSO-d_6

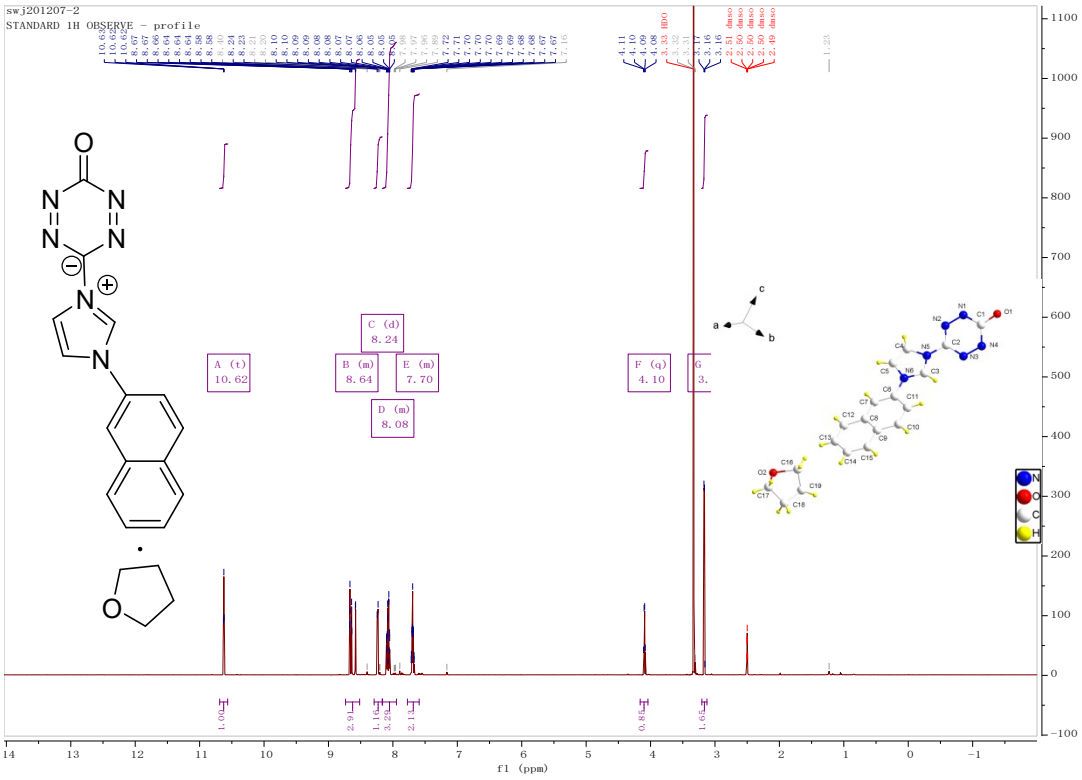


Figure S91. ^{1}H-NMR spectra of 3ab in DMSO-d_6

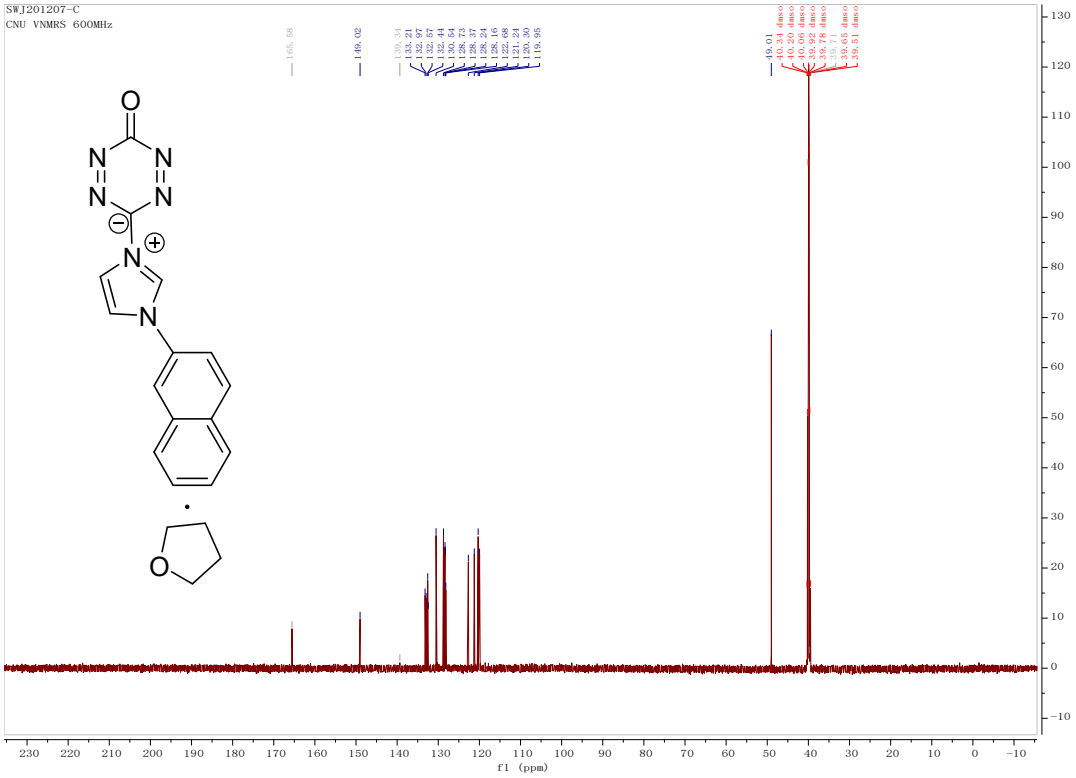


Figure S92. ^{13}C-NMR spectra of 3ab in DMSO-d_6

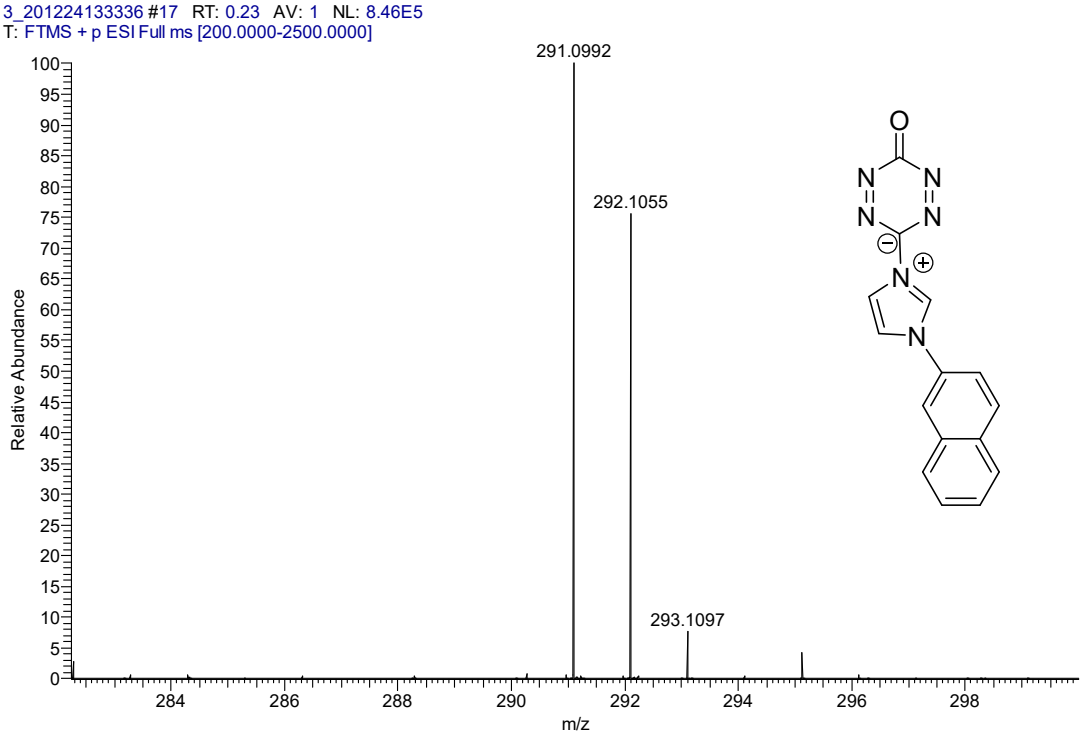


Figure S93. HRMS spectra of 3ab in DMSO-d_6

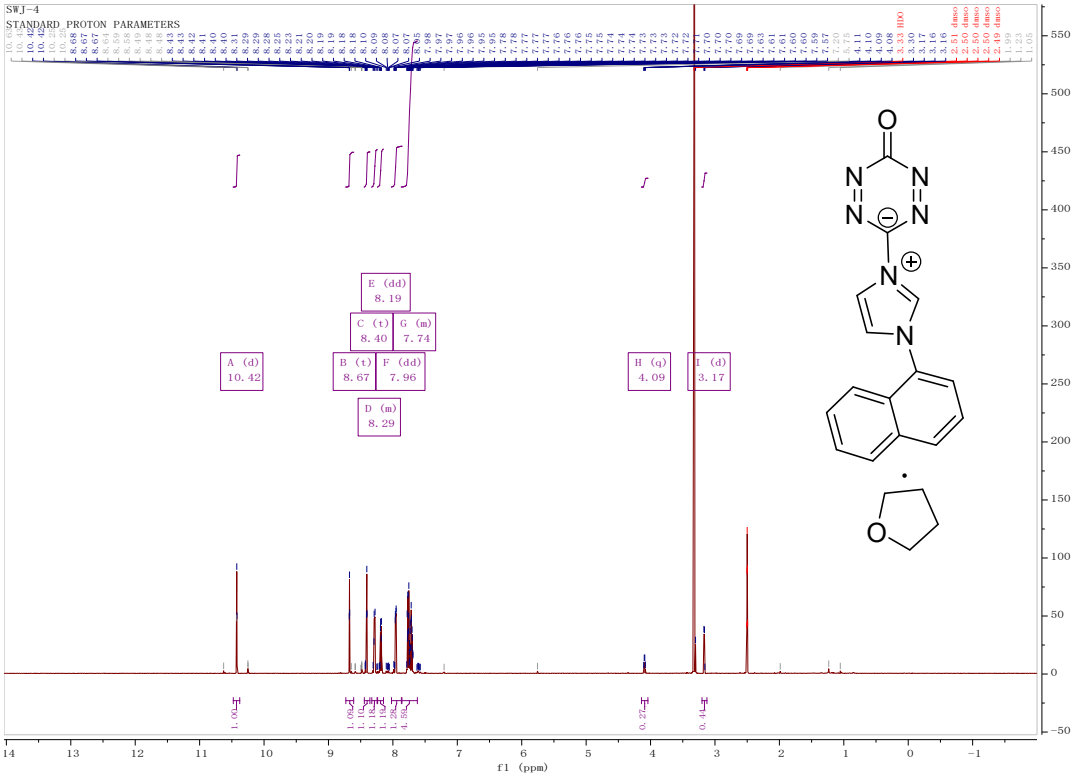


Figure S94. ^{1}H-NMR spectra of 3ac in DMSO-d_6

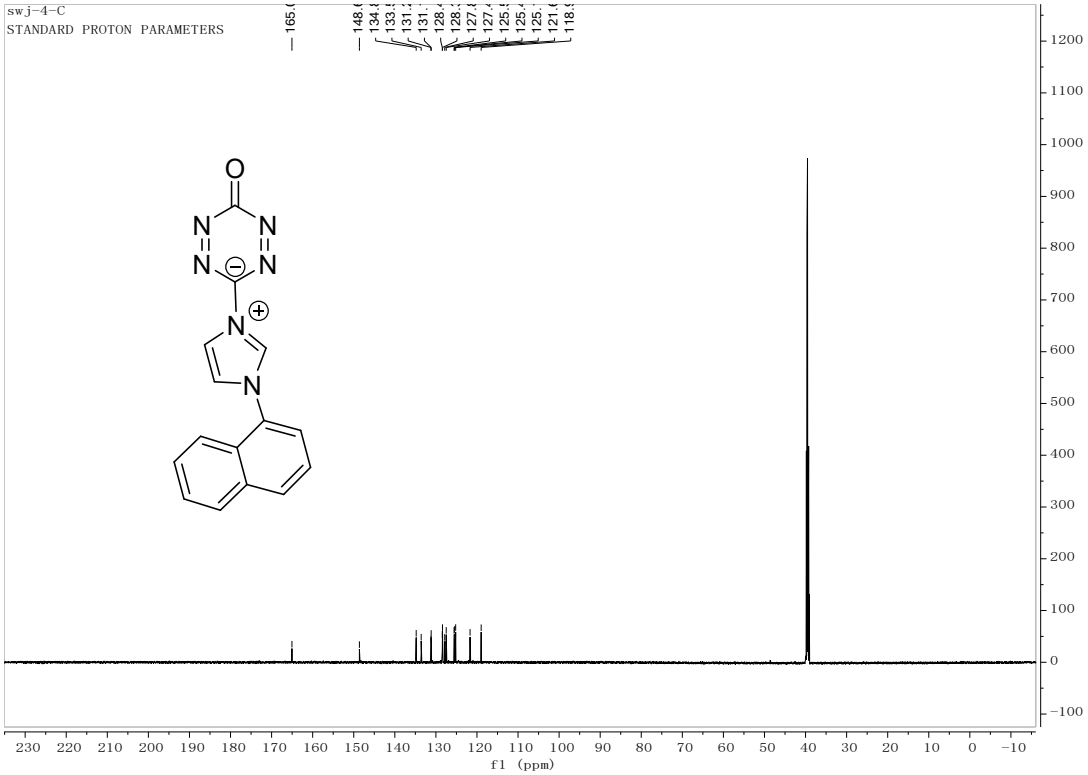


Figure S95. ^{13}C-NMR spectra of 3ac in DMSO-d_6

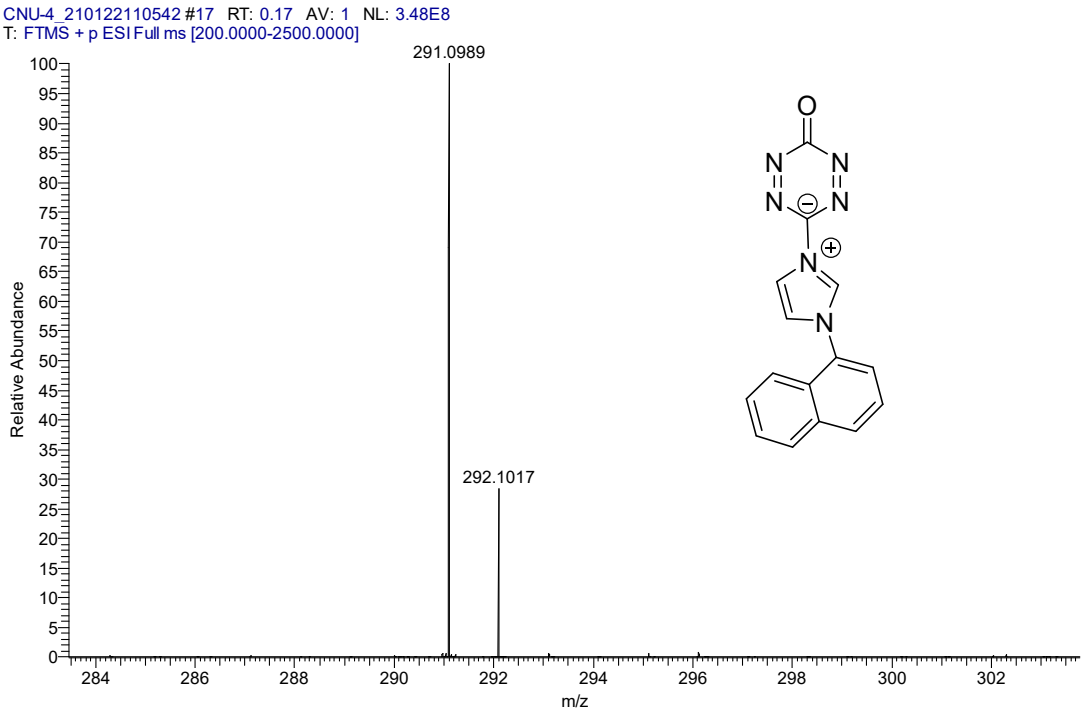


Figure S96. HRMS spectra of 3ac in DMSO-d_6

Figure S97. ^{1}H-NMR spectra of 3ad in DMSO-d_6

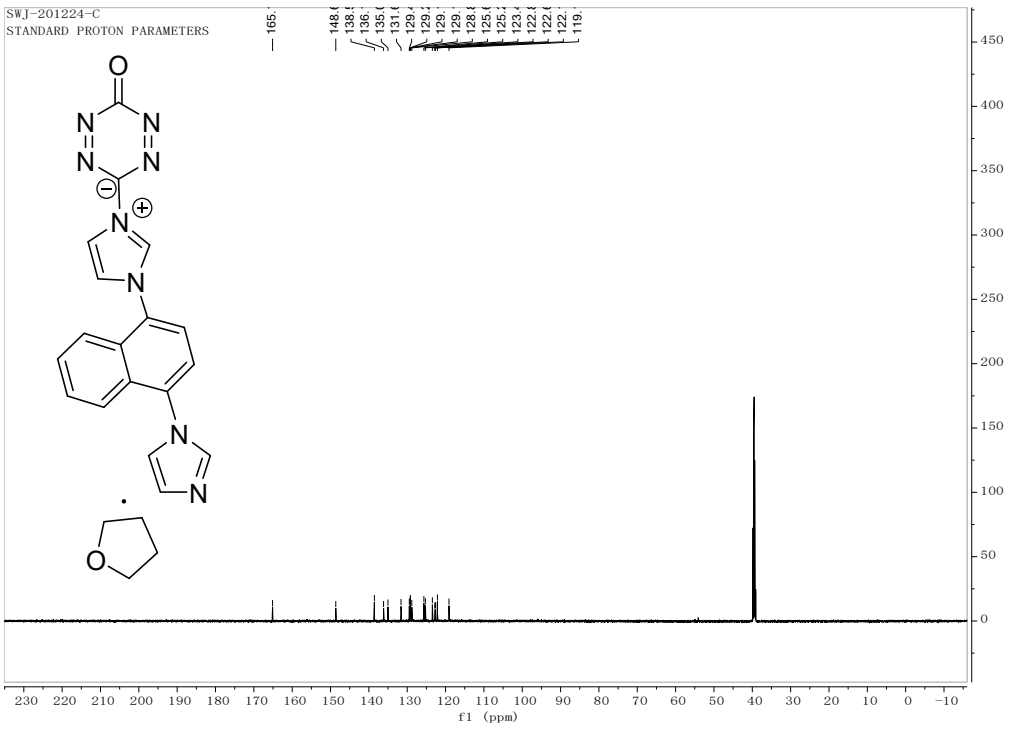


Figure S98. ^{13}C-NMR spectra of 3ad in DMSO-d_6

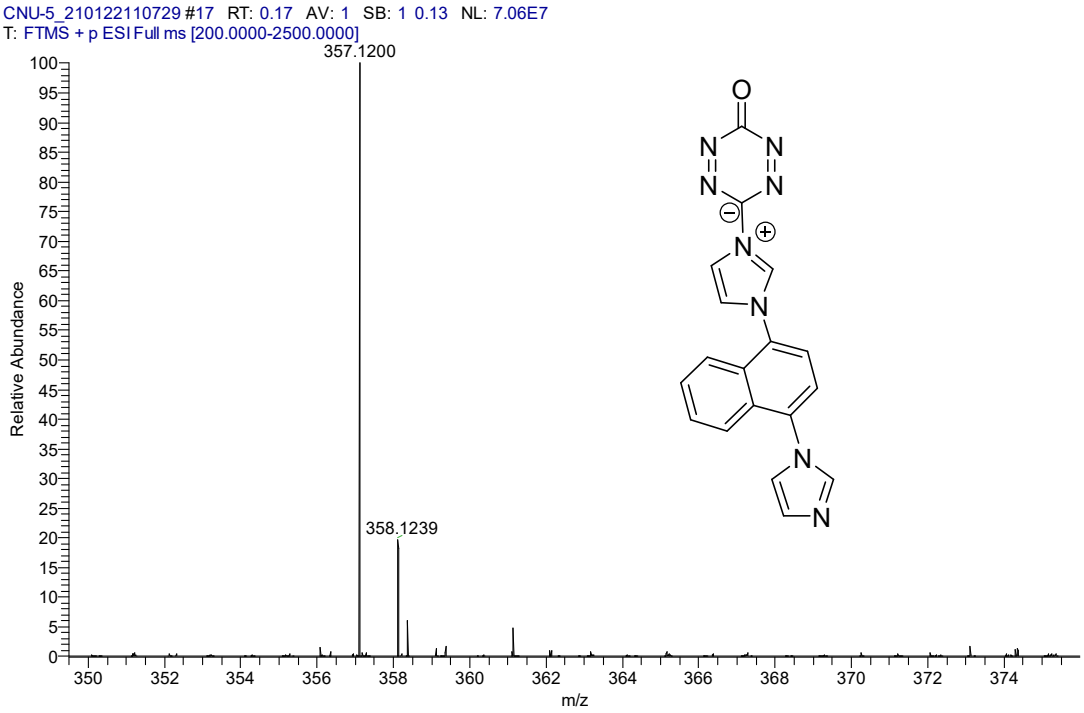


Figure S99. HRMS spectra of 3ad in DMSO-d_6

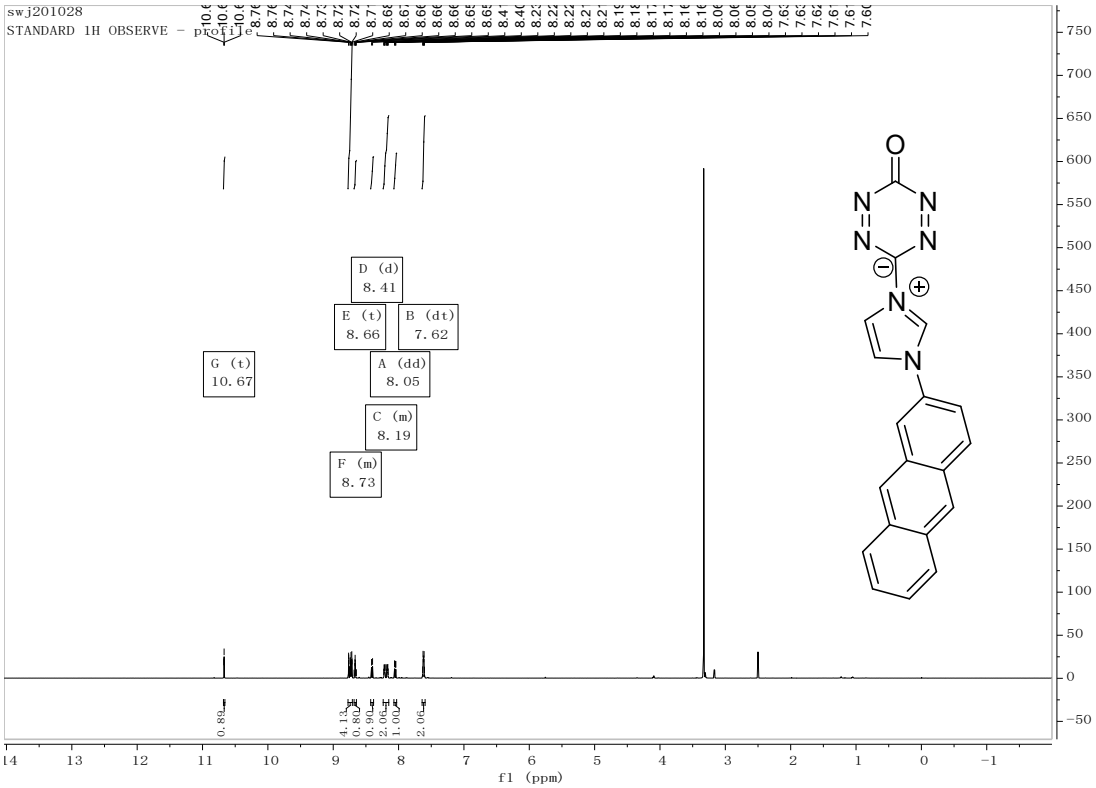


Figure S100. ^{1}H-NMR spectra of 3ae in DMSO-d_6

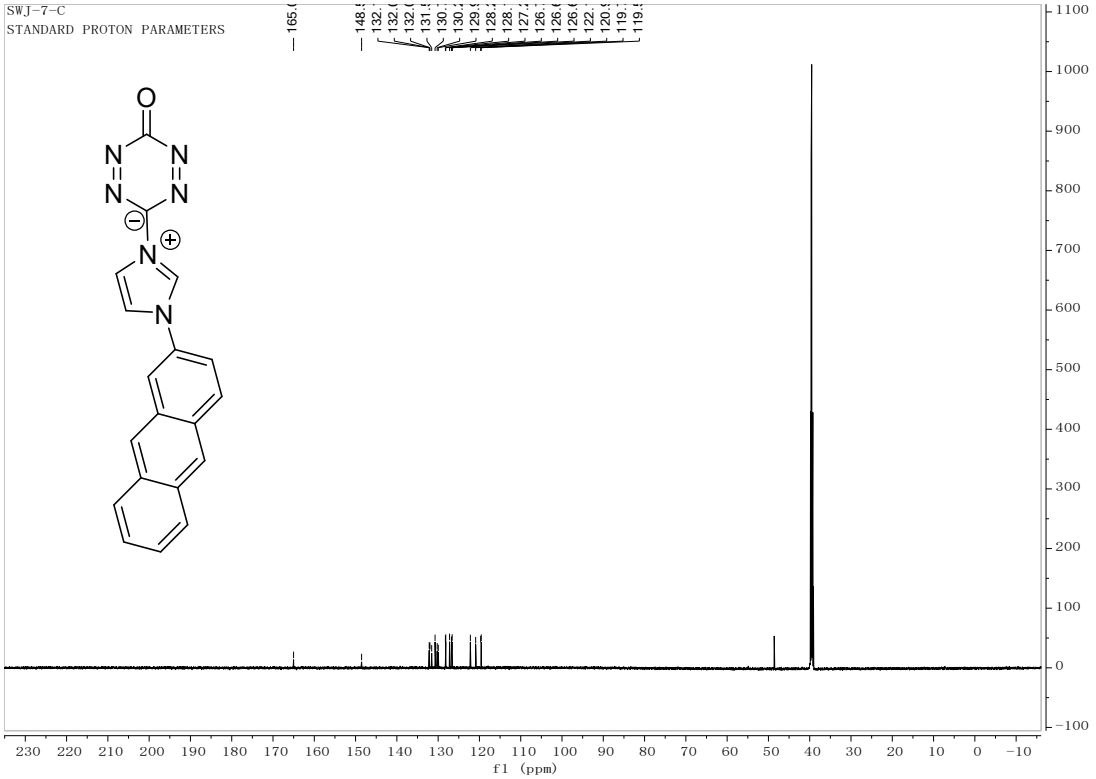


Figure S101. ^{13}C-NMR spectra of 3ae in DMSO-d_6

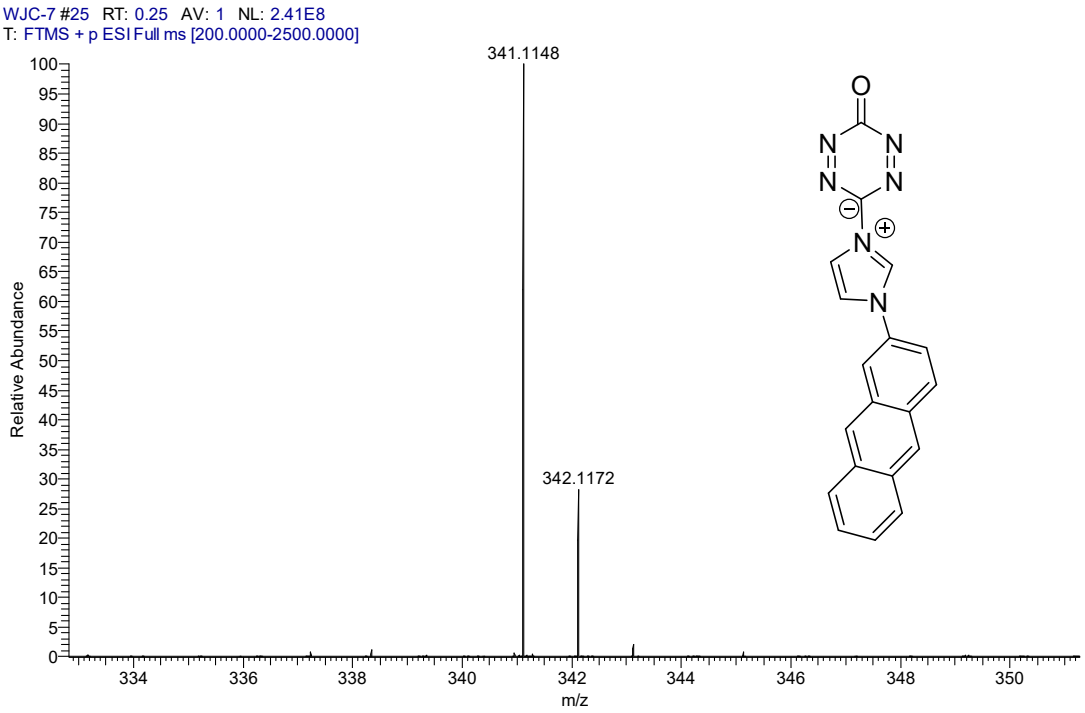


Figure S102. HRMS spectra of 3ae in DMSO-d_6

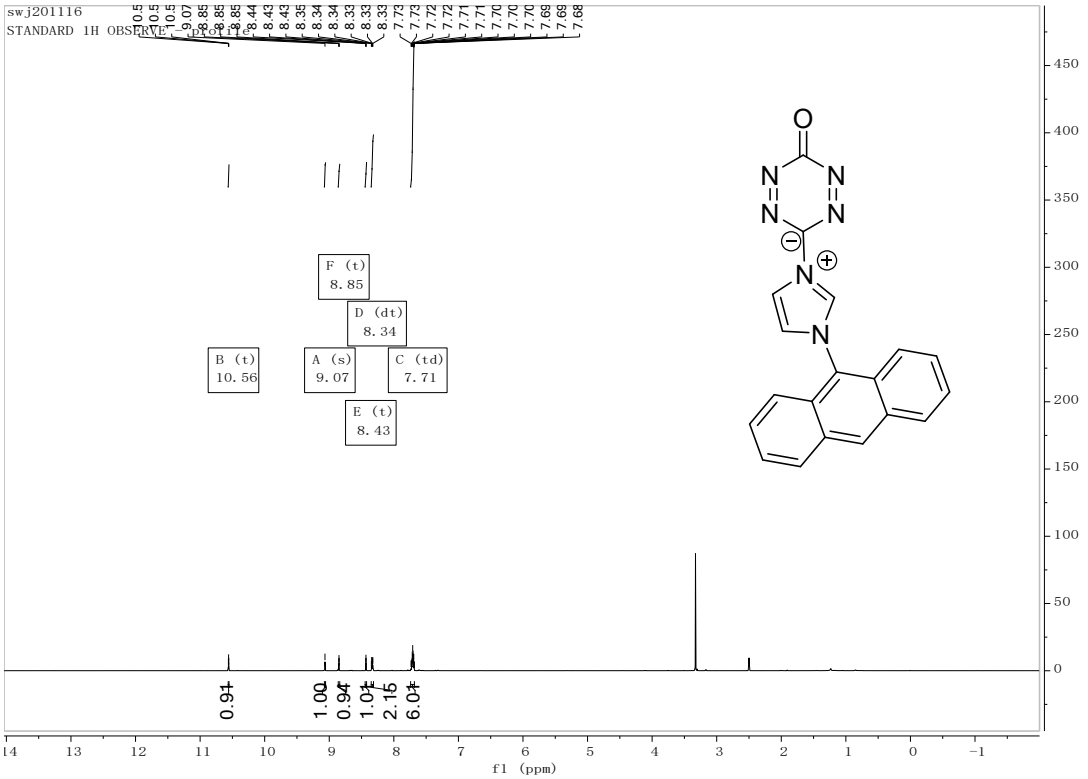


Figure S103. ^{1}H-NMR spectra of 3af in DMSO-d_6

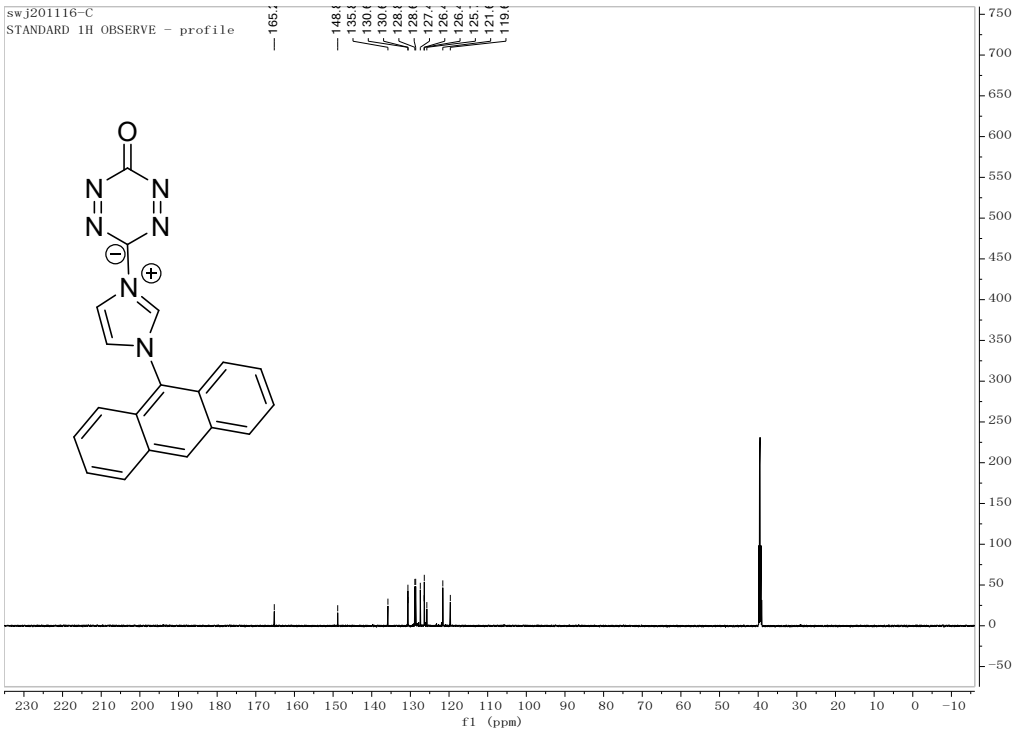


Figure S104. ^{13}C-NMR spectra of 3af in DMSO-d_6

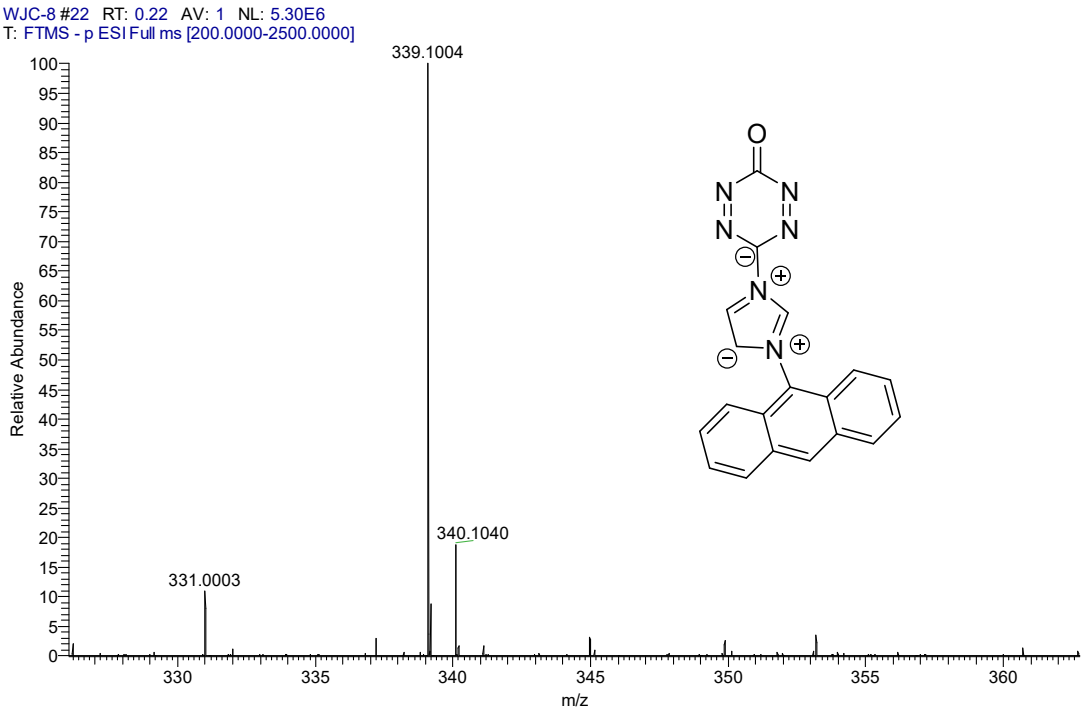


Figure S105. HRMS spectra of 3af in DMSO-d_6

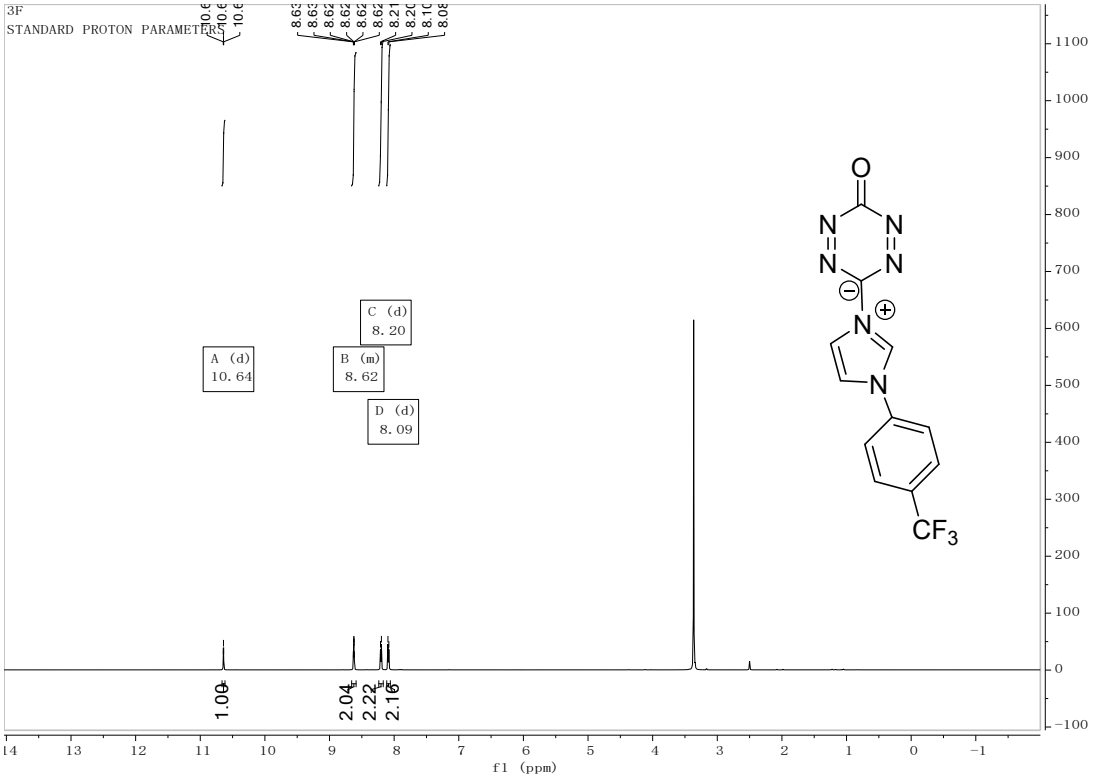


Figure S106. ^{1}H-NMR spectra of 3ag in DMSO-d_6

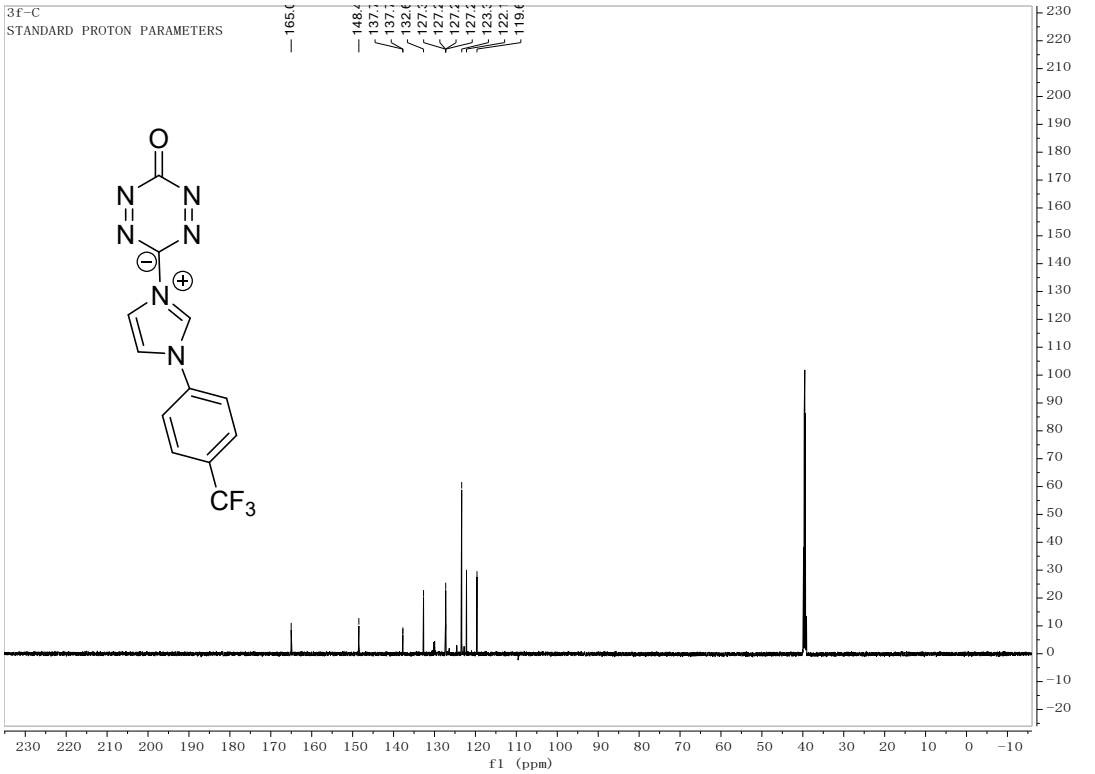


Figure S107. ^{13}C-NMR spectra of 3ag in DMSO-d_6

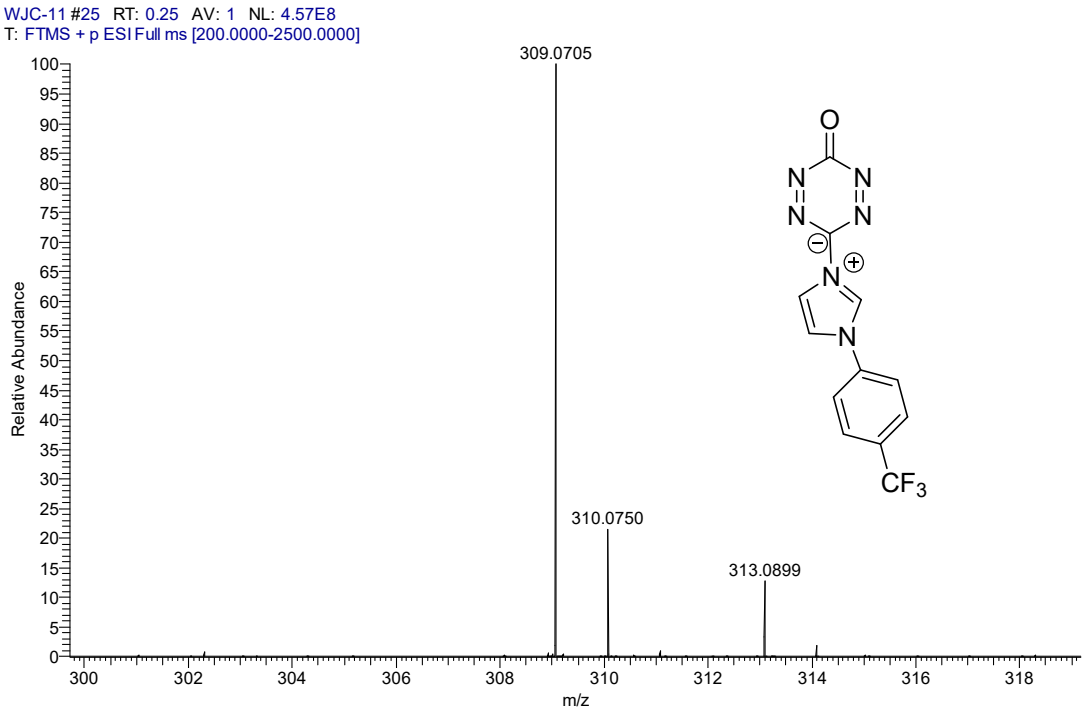


Figure S108. HRMS spectra of 3ag in DMSO-d_6

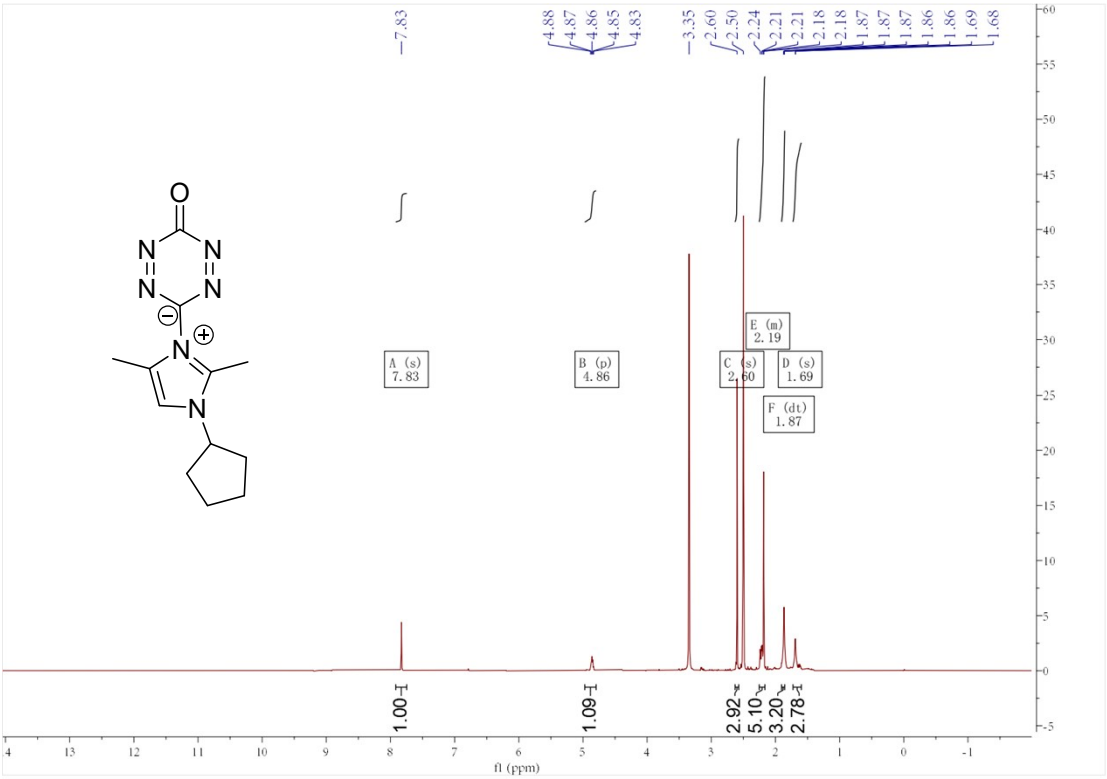


Figure S109. ^{1}H-NMR spectra of 3ah in DMSO-d_6

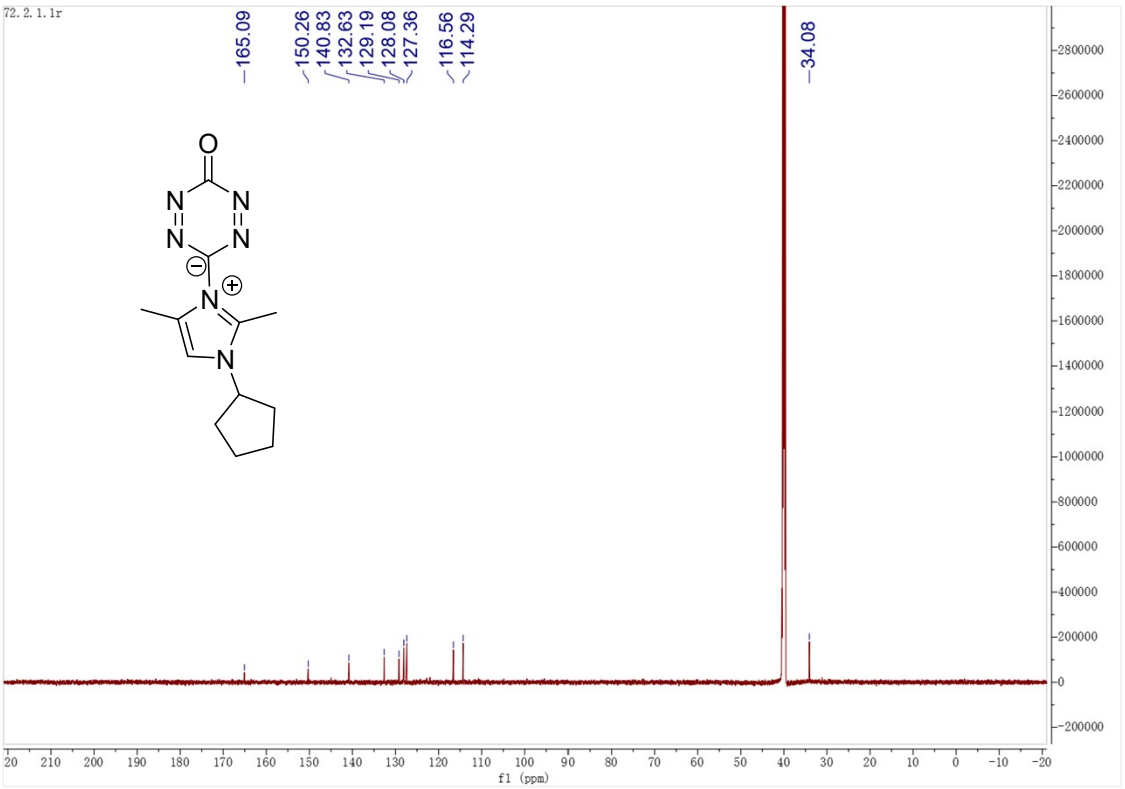


Figure S110. ^{13}C-NMR spectra of 3ah in DMSO-d_6

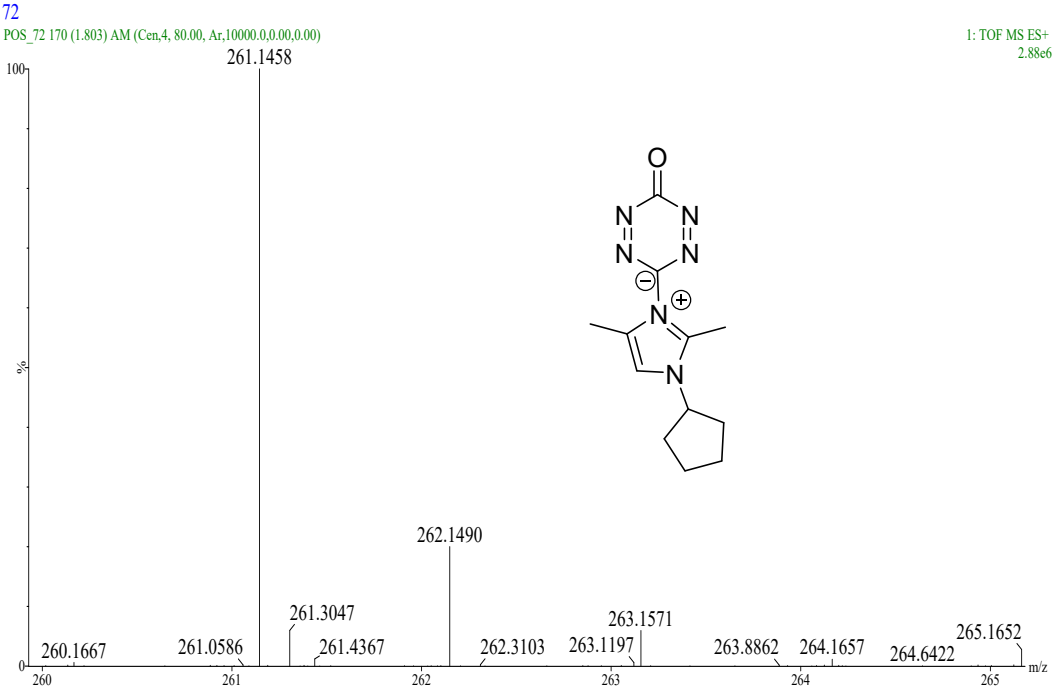


Figure S111. HRMS spectra of 3ah in DMSO-d_6

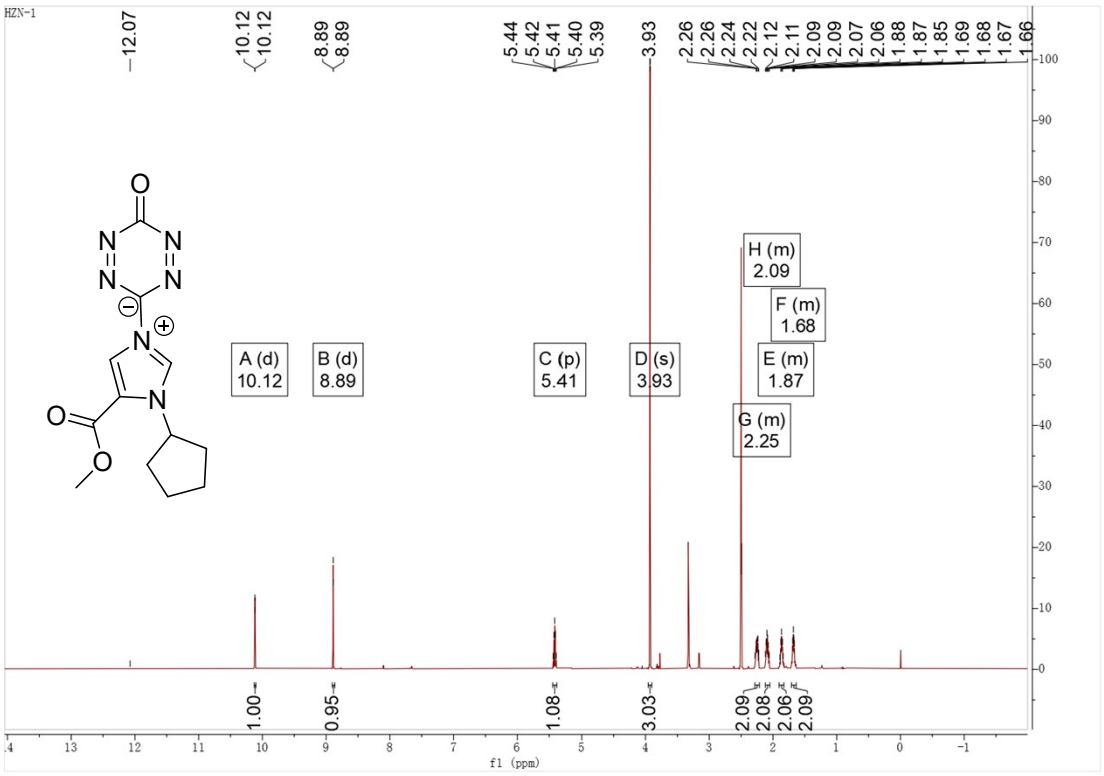


Figure S112. ^{1}H-NMR spectra of 3ai in DMSO-d_6

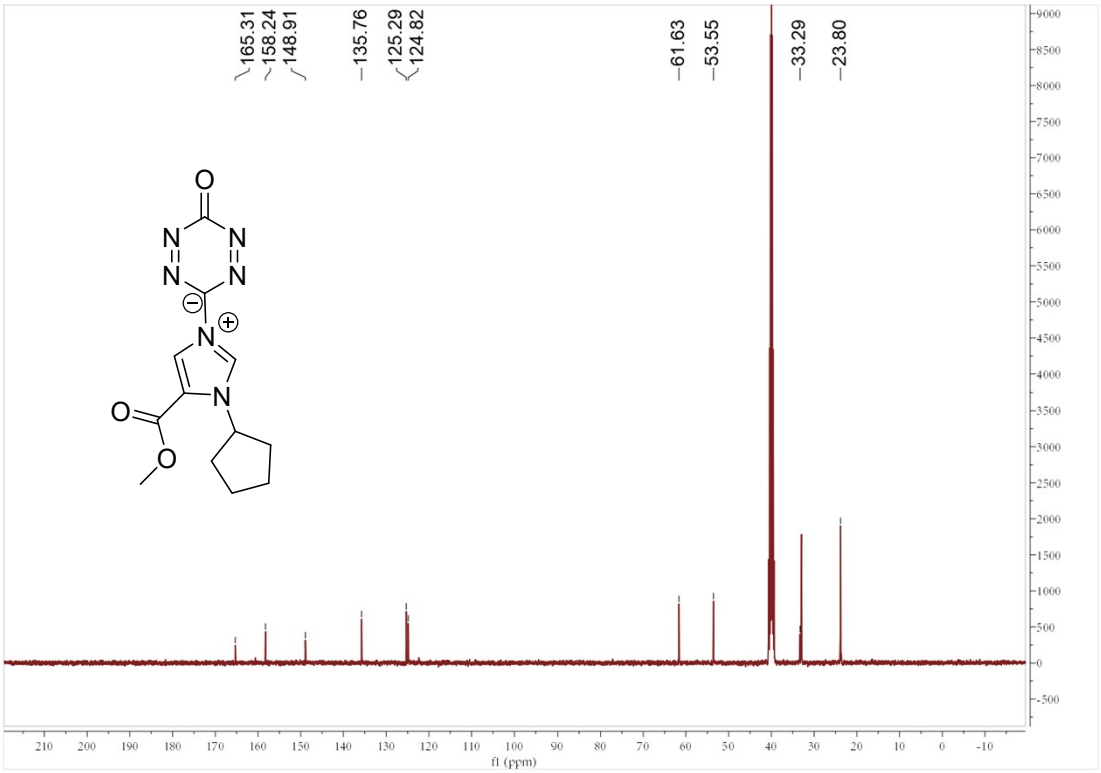


Figure S113. ^{13}C-NMR spectra of 3ai in DMSO-d_6

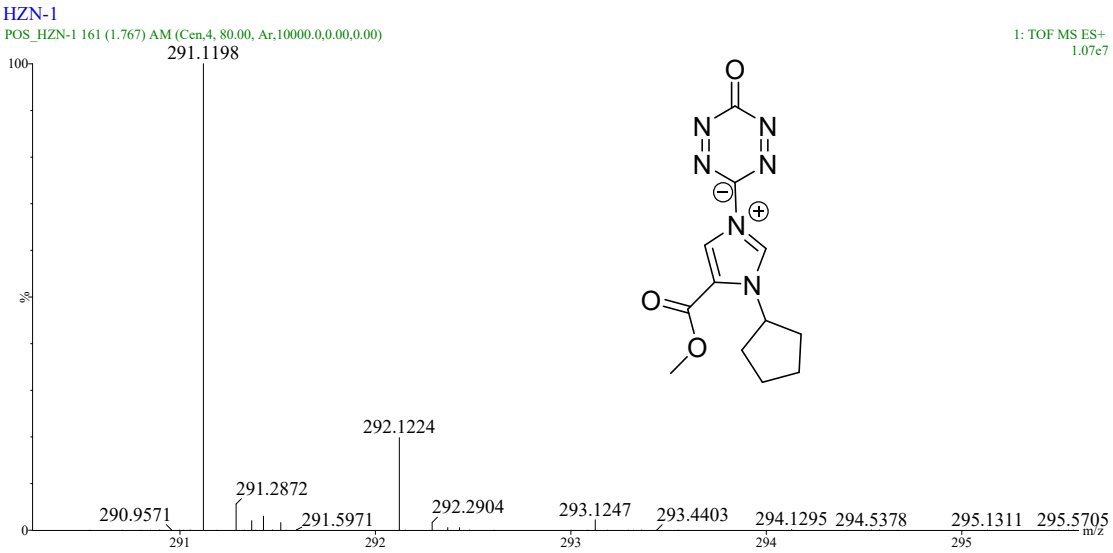


Figure S114. HRMS spectra of 3ai in DMSO-d_6

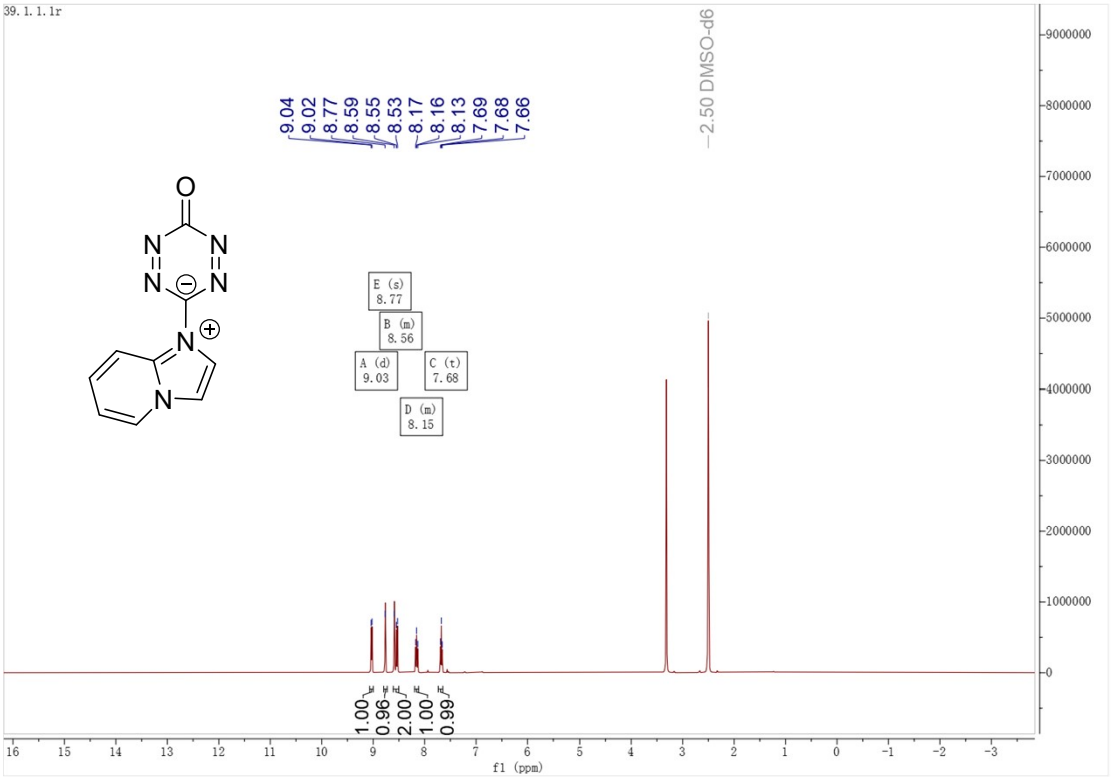


Figure S115. ^{1}H-NMR spectra of 3aj in DMSO-d_6

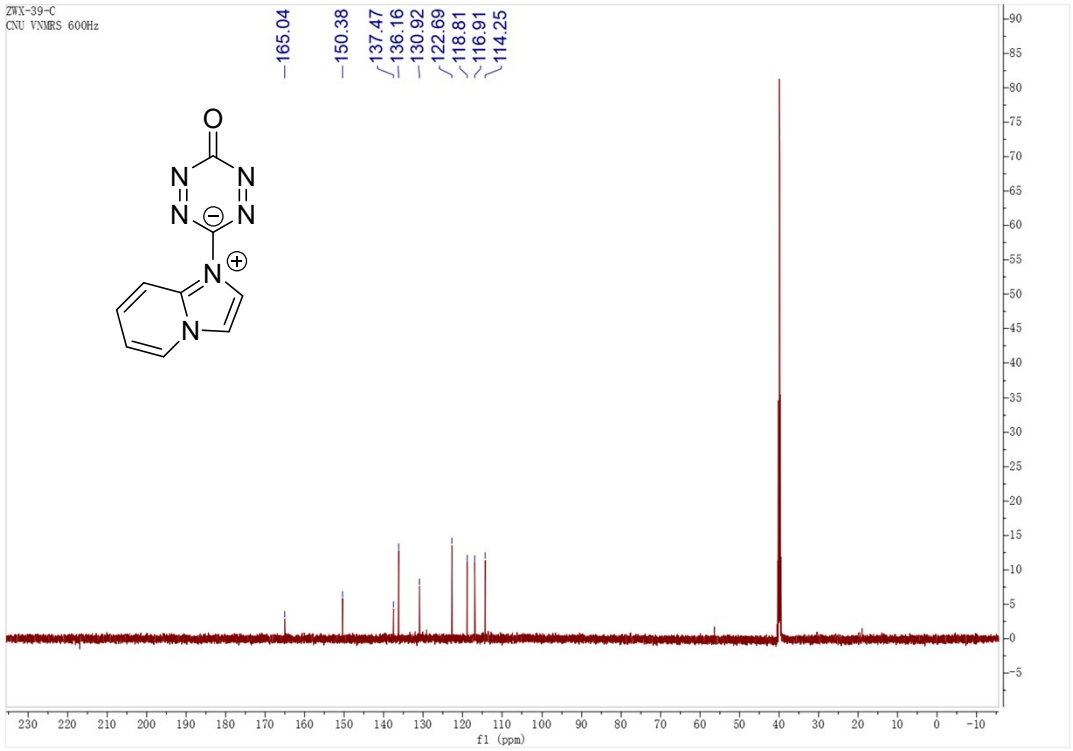


Figure S116. ^{13}C-NMR spectra of 3aj in DMSO-d_6

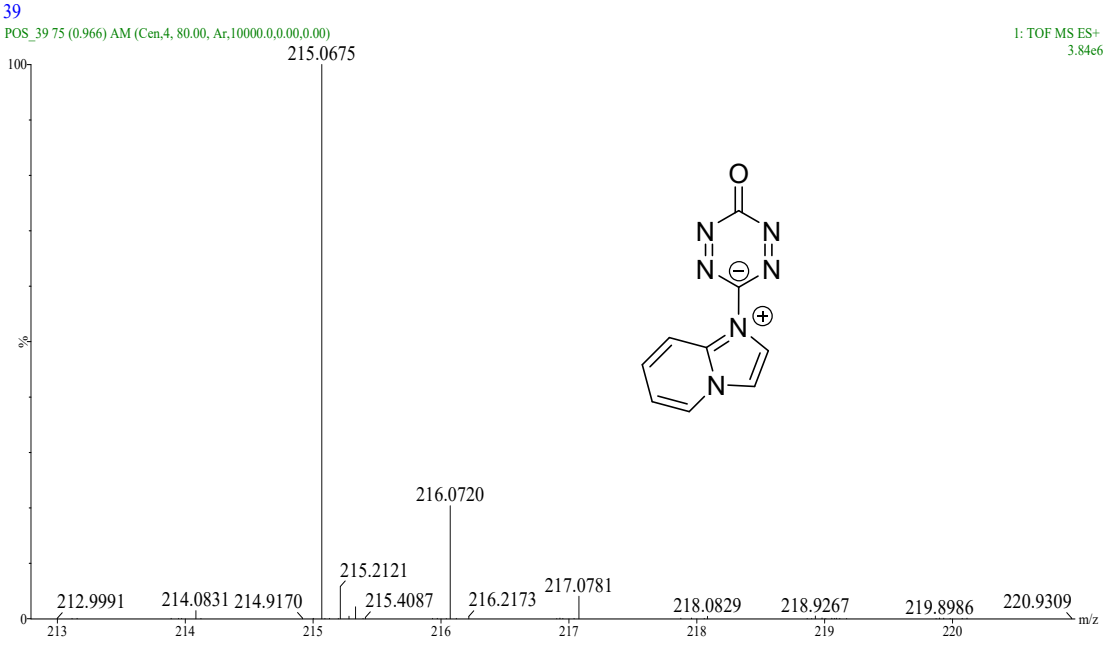


Figure S117. HRMS spectra of 3aj in DMSO-d_6

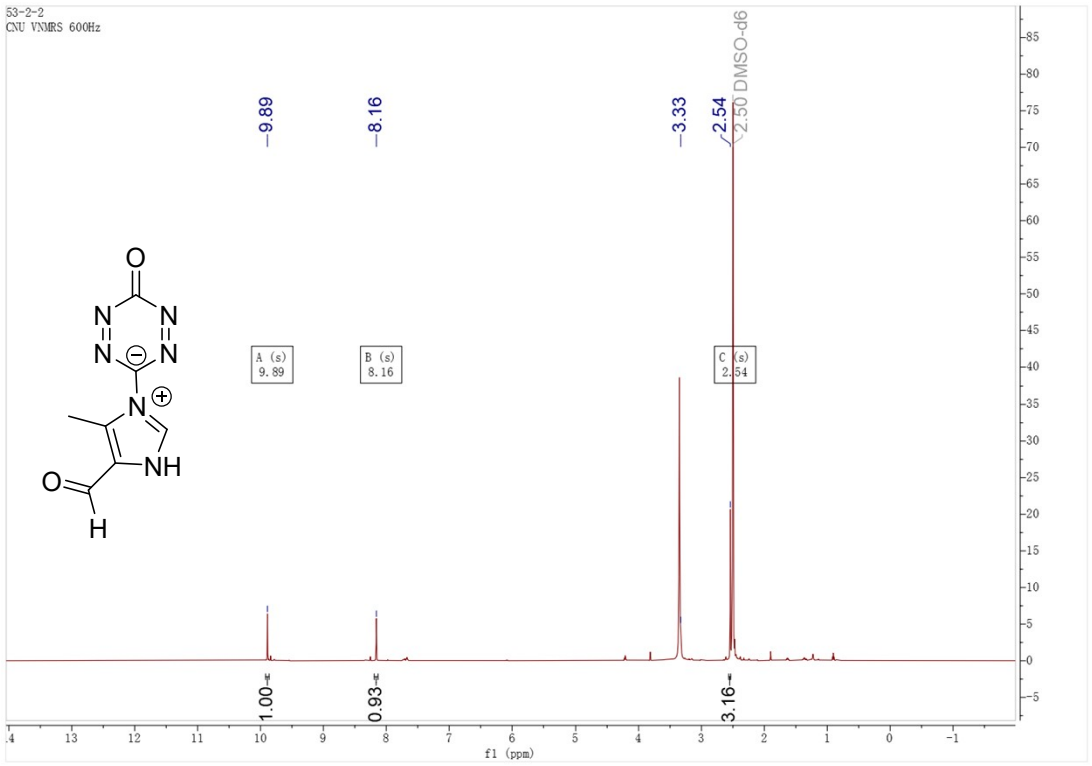


Figure S118. ^{1}H-NMR spectra of 3ak in DMSO-d_6

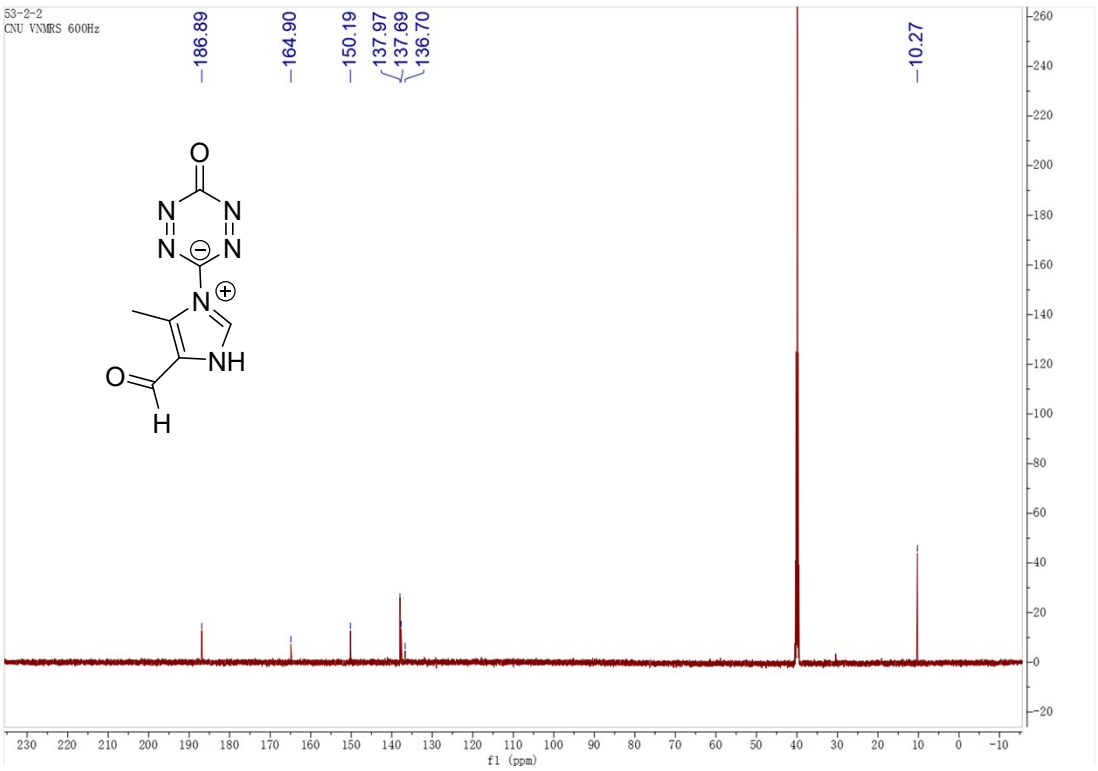


Figure S119. ^{13}C-NMR spectra of 3ak in DMSO-d_6

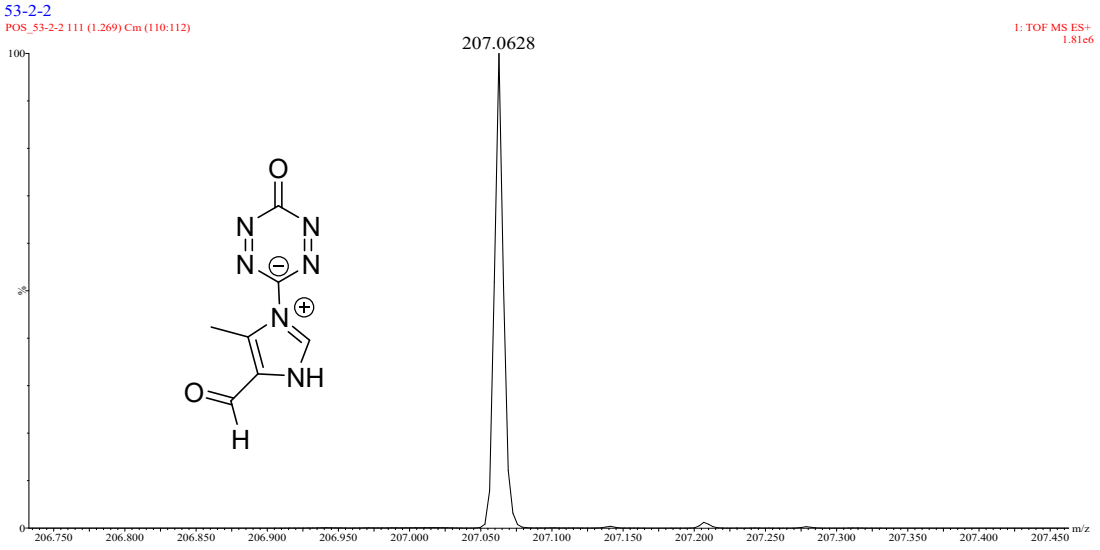


Figure S120. HRMS spectra of 3ak in DMSO-d_6

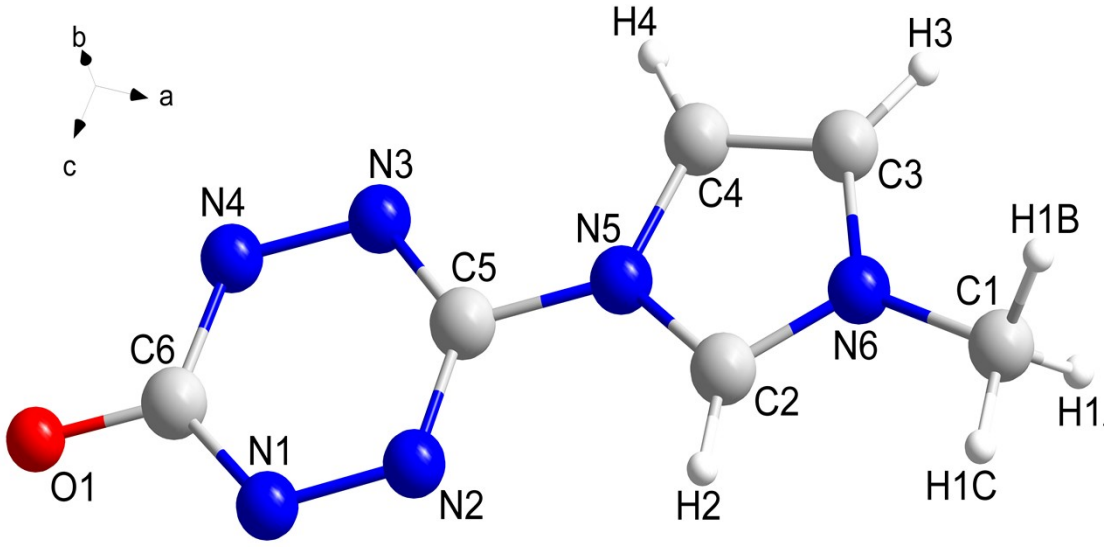


Figure S121. X-ray structure of 3a

Table S1. Crystallographic data and structural corrections of **3a**

Complex	**3a**
Formula	$C_6H_6N_6O,H_2O$
Formula weight	197.19
T/K	298.68(10)
Crystal system	orthorhombic
Space group	*Pca* Z_1
a(Å)	14.1035(3)
b(Å)	6.3113(2)
c(Å)	9.5102(2)
α(°)	90
β(°)	90

γ(°)	90
V(Å3)	846.52(4)
Z	4
Dcalc/g·cm^{-3}	1.547
F(000)	412
Goodness-of-fit on F2	1.071
Rint	0.1243
R_1[I⟩2σ(I)][a]	0.1170
wR_2[I⟩2σ(I)][b]	0.2392
R_1(all data)[a]	0.1227
wR_2(all data)[b]	0.2478

Table S2. Selected bond length (Å) of **3a**

atom	atom	bond length (Å)	atom	atom	bond length (Å)
O1	C6	1.234(4)	N1	N2	1.314(4)
N1	C6	1.375(5)	N2	C5	1.325(4)
N3	N4	1.317(3)	N3	C5	1.327(3)
N4	C6	1.381(5)	N5	C2	1.337(3)
N5	C4	1.391(3)	N5	C5	1.415(3)
N6	C1	1.456(4)	N6	C2	1.322(3)
N6	C3	1.378(4)	C1	H1A	0.9600
C1	H1C	0.9600	C1	H1B	0.9600
C2	H2	0.9300	C3	H3	0.9300
C3	C4	1.338(4)	C4	H4	0.9300

Table S3.Selected bond angel (°) of **3a**

atom	atom	atom	bond angel (°)	atom	atom	atom	bond angel (°)
N2	N1	C6	118.7(2)	N1	N2	C5	117.0(2)
N4	N3	C5	116.7(2)	N3	N4	C6	118.7(3)
C2	N5	C4	108.6(2)	C2	N5	C5	125.1(2)
C4	N5	C5	126.3(2)	C2	N6	C1	125.1(2)
C2	N6	C3	109.6(2)	C3	N6	C1	125.3(2)
N6	C1	H1A	109.5	N6	C1	H1C	109.5
N6	C1	H1B	109.5	H1A	C1	H1C	109.5
H1A	C1	H1B	109.5	H1C	C1	H1B	109.5
N5	C2	H2	126.1	N6	C2	N5	107.7(2)

N6	C2	H2	126.1	N6	C3	H3	126.4
C4	C3	N6	107.2(2)	C4	C3	H3	126.4
N5	C4	H4	126.6	C3	C4	N5	106.8(2)
C3	C4	H4	126.6	N2	C5	N3	127.4(2)
N2	C5	N5	116.3(2)	N3	C5	N5	116.3(2)
O1	C6	N1	120.1(3)	O1	C6	N4	118.4(3)
N1	C6	N4	121.5(3)				

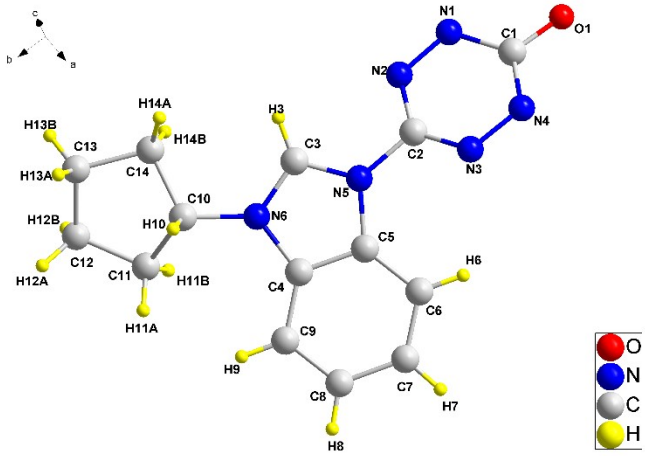


Figure S122. X-ray structure of 3z

Table S4. Crystallographic data and structural corrections of **3z**

Complex	**3z**
Formula	$C_{14}H_{14}N_6O$
Formulaweight	282.31
Temperature/K	100.00(10)
Crystalsystem	*Monoclinic*
Spacegroup	*Ia*
a(Å)	8.18400(10)
b(Å)	17.2477(2)
c(Å)	9.19330(10)

α(°)	90
β(°)	101.3680(10)
γ(°)	90
V(Å^3)	1272.22(3)
Z	4
ρ_{calc}g/cm^3	1.474
F(000)	592.0
Reflectionscollected	7256
Independentreflections	1883[R_{int}=0.0295，R_{sigma}=0.0203]
Goodness-of-fitonF^2	1.054
FinalRindexes[I>=2σ(I)]	R_1=0.0274，wR_2=0.0733
FinalRindexes[alldata]	R_1=0.0275，wR_2=0.0734

Table S5. Selected bond length (Å) of **3z**

atom	atom	bond length (Å)	atom	atom	bond length (Å)
O1	C1	1.243(2)	N4	C1	1.389(3)
N6	C4	1.397(2)	C4	C5	1.395(3)
N6	C10	1.490(2)	C4	C9	1.396(3)
N6	C3	1.334(2)	C5	C6	1.389(3)
N2	N1	1.317(2)	C6	C7	1.383(3)
N2	C2	1.325(3)	C10	C11	1.540(3)
N1	C1	1.389(3)	C10	C14	1.517(3)
N5	C5	1.408(3)	C9	C8	1.379(3)
N5	C2	1.425(2)	C11	C12	1.544(3)
N5	C3	1.343(3)	C8	C7	1.405(3)
N3	N4	1.322(2)	C14	C13	1.531(3)
N3	C2	1.328(3)	C13	C12	1.533(3)

Table S6. Selected bond angel (°) of **3z**

atom	atom	atom	bond angel (°)	atom	atom	atom	bond angel (°)
C4	N6	C10	126.18(16)	C6	C5	N5	132.32(19)
C3	N6	C4	108.40(16)	C6	C5	C4	122.23(18)
C3	N6	C10	124.63(16)	C7	C6	C5	116.29(18)
N1	N2	C2	117.41(17)	N2	C2	N5	116.12(17)
N2	N1	C1	117.78(17)	N2	C2	N3	127.27(18)
C5	N5	C2	126.30(17)	N3	C2	N5	116.46(18)
C3	N5	C5	108.87(16)	N6	C10	C11	114.06(16)
C3	N5	C2	124.58(17)	N6	C10	C14	113.40(16)
N4	N3	C2	116.78(18)	C14	C10	C11	104.28(17)
N3	N4	C1	118.11(17)	N6	C3	N5	109.82(17)
C5	C4	N6	107.45(16)	C8	C9	C4	116.80(18)
C5	C4	C9	121.16(18)	C10	C11	C12	104.15(16)
C9	C4	N6	131.39(18)	C9	C8	C7	121.70(19)
O1	C1	N1	119.57(18)	C10	C14	C13	101.47(16)
O1	C1	N4	119.22(17)	C14	C13	C12	103.56(17)
N1	C1	N4	121.14(17)	C6	C7	C8	121.82(19)
C4	C5	N5	105.45(17)	C13	C12	C11	106.62(17)

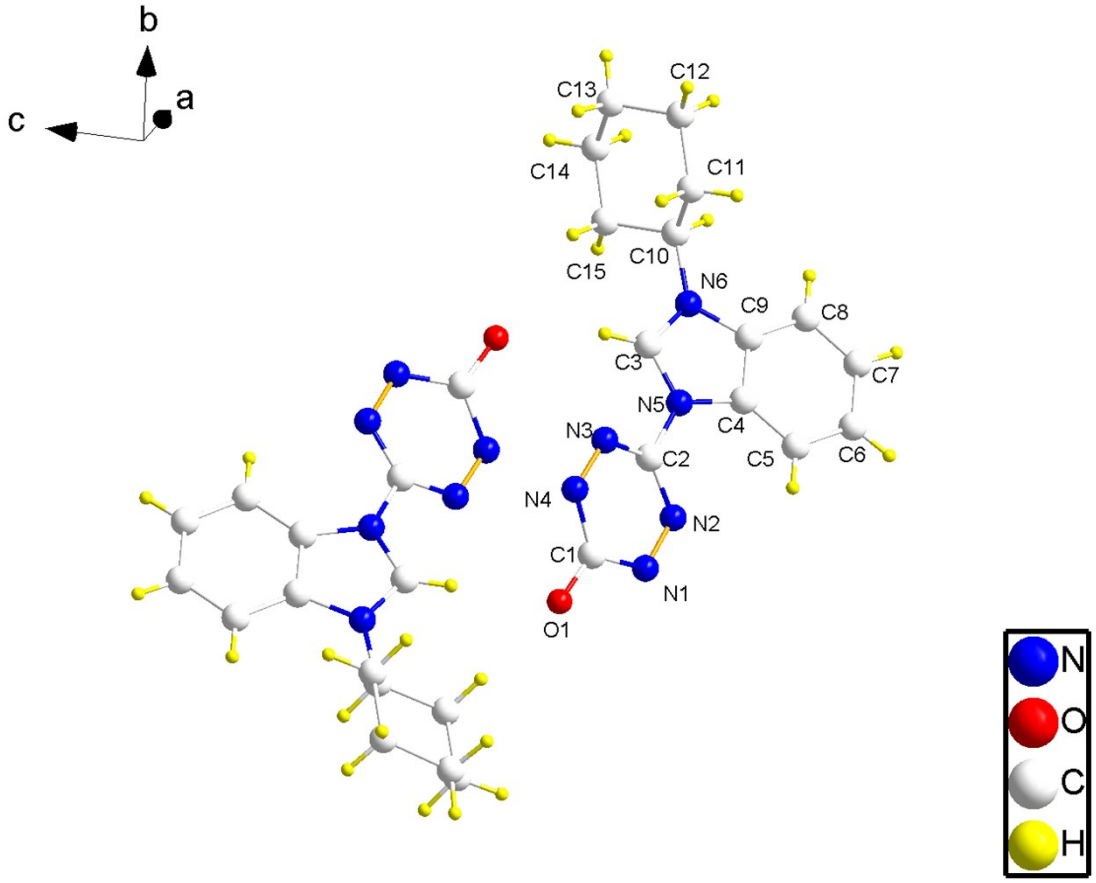


Figure S123. X-ray structure of 3aa

Table S7. Crystallographic data and structural corrections of **3aa**

Complex	**3aa**
Formula	$C_{30}H_{32}N_{12}O_2$
Formulaweight	592.67
Temperature/K	294.44(13)
Crystalsystem	orthorhombic
Spacegroup	Pbca
a(Å)	17.2325(2)
b(Å)	18.0052(2)
c(Å)	18.4076(2)
α(°)	90
β(°)	90

γ(°)	90
V(Å^3)	5711.41(11)
Z	8
ρ_{calc}g/cm^3	1.379
F(000)	2496.0
Reflectionscollected	22144
Independentreflections	5712[R_{int}=0.0240，R_{sigma}=0.0209]
Goodness-of-fitonF^2	1.061
FinalRindexes[I>=2σ(I)]	R_1=0.0446，wR_2=0.1121
FinalRindexes[alldata]	R_1=0.0488，wR_2=0.1151

Table S8. Selected bond length (Å) of **3aa**

atom	atom	bond length (Å)	atom	atom	bond length (Å)
O1	C1	1.2288(17)	N1	C1	1.3836(19)
N2	N1	1.3185(15)	N2	C2	1.3148(16)
N3	N4	1.3115(15)	N3	C2	1.3236(16)
N4	C1	1.385(2)	N5	C2	1.4265(14)
N5	C3	1.3371(15)	N5	C4	1.4001(14)
N6	C3	1.3270(15)	N6	C9	1.3924(15)
N6	C10	1.4802(15)	C4	C5	1.3845(17)
C4	C9	1.3903(17)	C5	C6	1.3786(19)
C6	C7	1.398(2)	C8	C7	1.370(2)
C9	C8	1.3929(17)	C10	C11	1.518(2)
C10	C15	1.5078(18)	C11	C12	1.526(2)
C13	C12	1.507(3)	C14	C15	1.5219(19)
C14	C13	1.510(2)			

Table S9. Selected bond angel (°) of **3aa**

atom	atom	atom	bond angel (°)	atom	atom	atom	bond angel (°)
C4	N5	C2	127.50(10)	N6	C3	N5	110.31(10)

C3	N5	C4	108.22(10)	N6	C10	C15	112.46(11)
C3	N5	C2	124.28(10)	N6	C10	C11	109.24(11)
C9	N6	C10	124.31(10)	C15	C10	C11	111.49(12)
C3	N6	C9	108.34(10)	C6	C5	C4	116.63(13)
C3	N6	C10	127.07(10)	C7	C8	C9	116.37(13)
N4	N3	C2	116.97(11)	O1	C1	N4	119.65(14)
N3	N4	C1	118.33(11)	O1	C1	N1	119.37(15)
C2	N2	N1	117.05(11)	N1	C1	N4	120.98(12)
N2	N1	C1	118.10(12)	C13	C14	C15	111.55(13)
C9	C4	N5	106.11(10)	C10	C15	C14	109.80(11)
C5	C4	N5	132.41(12)	C5	C6	C7	121.74(13)
C5	C4	C9	121.47(11)	C10	C11	C12	110.59(13)
N3	C2	N5	115.44(10)	C8	C7	C6	121.91(12)
N2	C2	N5	116.86(10)	C12	C13	C14	111.46(14)
N2	C2	N3	127.56(11)	C13	C12	C11	111.02(14)
N6	C9	C8	131.13(12)	C4	C9	N6	107.01(10)
C4	C9	C8	121.84(11)				

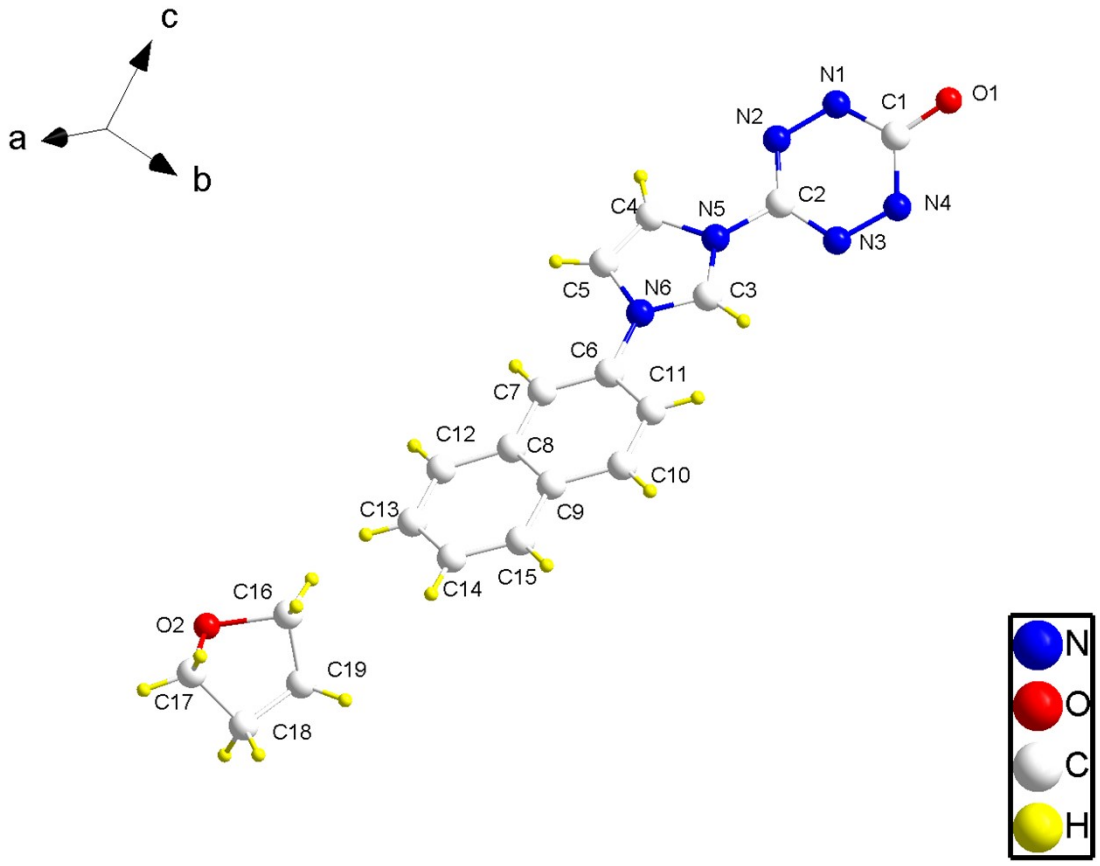


Figure S124. X-ray structure of 3ab

Table S10. Crystallographic data and structural corrections of **3ab**

Complex	**3ab**
Formula	$C_{19}H_{18}N_6O_2$
Formulaweight	362.39
Temperature/K	294.61(10)
Crystalsystem	monoclinic
Spacegroup	$P2_1/c$
a(Å)	14.0018(9)
b(Å)	10.3586(5)
c(Å)	12.8117(8)
α(°)	90
β(°)	105.501(7)
γ(°)	90

V(Å^3)	1790.61(19)
Z	4
ρ_{calc}g/cm^3	1.344
F(000)	760.0
Reflectionscollected	9859
Independentreflections	3158[R_{int}=0.0464，R_{sigma}=0.0338]
Goodness-of-fitonF^2	1.056
FinalRindexes[I>=2σ(I)]	R_1=0.0954，wR_2=0.2801
FinalRindexes[alldata]	R_1=0.1201，wR_2=0.2988

Table S11. Selected bond length (Å) of **3ab**

atom	atom	bond length (Å)	atom	atom	bond length (Å)
N5	C2	1.419(4)	C5	C4	1.322(6)
N5	C3	1.316(4)	C8	C7	1.412(6)
N5	C4	1.386(4)	C8	C9	1.385(7)
N6	C3	1.327(4)	C8	C12	1.421(6)
N6	C6	1.440(5)	C9	C10	1.410(6)
N6	C5	1.387(5)	C9	C15	1.417(6)
N2	N1	1.322(4)	C10	C11	1.356(6)
N2	C2	1.306(5)	C12	C13	1.347(7)
O1	C1	1.230(4)	C13	C14	1.384(8)
N1	C1	1.366(5)	C15	C14	1.367(8)
N3	C2	1.305(5)	O2	C16	1.612(17)
N3	N4	1.319(5)	O2	C17	1.301(16)
C1	N4	1.366(5)	C19	C18	1.441(12)
C6	C7	1.349(5)	C19	C16	1.399(2)
C6	C11	1.407(6)	C18	C17	1.472(13)

Table 12. Selected bond angel (°) of **3ab**

atom	atom	atom	bond angel (°)	atom	atom	atom	bond angel (°)
C3	N5	C2	125.9(3)	C4	C5	N6	107.9(3)
C3	N5	C4	108.6(3)	C5	C4	N5	106.9(3)
C4	N5	C2	125.5(3)	C7	C8	C12	122.0(4)
C3	N6	C6	126.5(3)	C9	C8	C7	119.7(4)
C3	N6	C5	107.6(3)	C9	C8	C12	118.4(4)
C5	N6	C6	126.0(3)	C6	C7	C8	120.2(4)
C2	N2	N1	117.6(3)	C8	C9	C10	118.5(4)
N2	N1	C1	117.2(3)	C8	C9	C15	119.6(5)
C2	N3	N4	116.8(3)	C10	C9	C15	121.9(5)
N2	C2	N5	117.4(3)	C11	C10	C9	121.7(4)
N2	C2	N3	126.0(4)	C10	C11	C6	118.9(4)
N3	C2	N5	116.3(3)	C13	C12	C8	121.2(5)
N5	C3	N6	109.1(3)	C12	C13	C14	120.3(5)
O1	C1	N1	120.0(4)	C14	C15	C9	119.9(5)
O1	C1	N4	120.2(4)	C15	C14	C13	120.6(5)
N4	C1	N1	119.7(4)	C17	O2	C16	98.3(13)
N3	N4	C1	118.2(3)	C16	C19	C18	106.8(8)
C7	C6	N6	120.8(3)	C19	C18	C17	103.6(9)
C7	C6	C11	121.0(4)	C19	C16	O2	88.1(7)
C11	C6	N6	118.2(3)	O2	C17	C18	96.3(10)

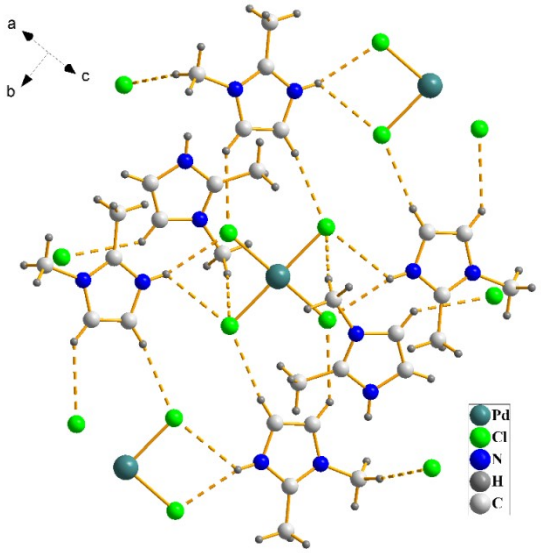


Figure S125. X-ray single crystal structure of Pd(II)Cl_4 • 1,2-dimethylimidazole complex(4k)

Table S13. Crystallographic data and structural corrections of **4k**

Complex	4k
Formula	$C_{10}H_{18}Cl_4N_4Pd$
Formula weight	442.48
T/K	163(2)
Crystal system	monoclinic
Space group	$P2_1/n$
a(Å)	8.6646(17)
b(Å)	8.0989(16)
c(Å)	12.187(2)
α(°)	90
β(°)	103.52(3)
γ(°)	90
V(Å3)	831.5(3)
Z	2
Dcalc/g·cm^{-3}	1.767
F(000)	440
Goodness-of-fit on F2	1.107
*R*int	0.0308
R_1[I⟩2σ(I)][a]	0.0390
wR_2[I⟩2σ(I)][b]	0.1043
R_1(all data)[a]	0.0411
wR_2(all data)[b]	0.1064

Table S14. Selected bond length (Å) of **4k**

atom	atom	bond length (Å)	atom	atom	bond length (Å)

Pd1	Cl1	2.3041(10)	Pd1	Cl2	2.3090(11)
N2	C1	1.297(5)	N2	C2	1.365(6)
N2	C5	1.478(5)	N1	C1	1.334(5)
N1	C3	1.369(5)	C1	C4	1.337(3)
C2	C3	1.328(7)			

Table 15. Selected bond angel (°) of **4k**

atom	atom	atom	bond angel (°)	atom	atom	atom	bond angel (°)
Cl1	Pd1	Cl1	180.0	Cl1	Pd1	Cl2	91.06(3)
Cl2	Pd1	Cl2	180.0	C1	N2	C2	109.4(3)
C1	N2	C5	124.9(4)	C2	N2	C5	125.6(4)
C1	N1	C3	109.1(3)	N2	C1	N1	107.6(3)
N2	C1	C4	127.6(3)	N1	C1	C4	124.8(4)
C3	C2	N2	107.7(4)	C2	C3	N1	106.2(3)

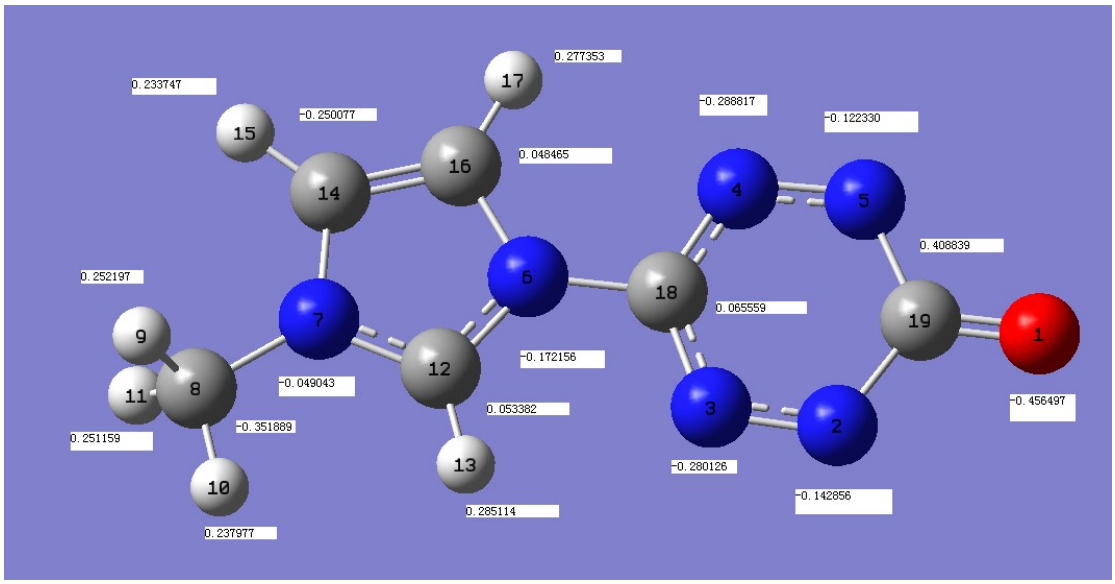


Figure S126. Charge density maps of each atom in 3a calculated from the B3LYP functional and the 6-31+G* basis set in Gaussian03 program