Supporting Information

Practical Strategy for Construction and Regulation of Multi-Functional Triazepinium Salts via Highly-Efficient I_2-Catalyzed Cyclization

Lang Liu, [+a] Mengyao She, [+ab] Jun Zhang,[a] Zhaohui Wang,[a] Hua Liu,[a] Mi Tang,[a] Ping Liu,*[a] Shengyong Zhang [a] and Jianli Li*[a]

[a] Ministry of Education Key Laboratory of Synthetic and Natural Functional Molecule Chemistry, College of Chemistry & Materials Science, Northwest University, Xi'an. Shaanxi 710127, P. R. China, E-mail: lijianli@nwu.edu.cn.

[b] Ministry of Education Key Laboratory of Resource Biology and Modern Biotechnology in Western China, The College of Life Sciences, Faculty of Life and Health Science, Northwest University, Xi'an, Shaanxi Province, 710069, P. R. China.

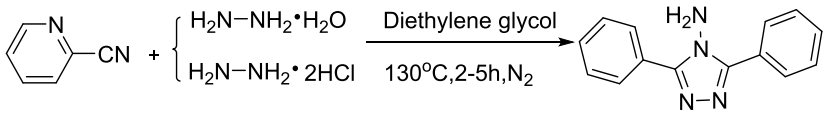
Table of Content

1. General information

^{1}H and ^{13}C NMR spectra were recorded on a 400 MHz (100 MHz for ^{13}C NMR) spectrometer. Chemical shift values are given in ppm (parts per million) with tetramethyl silane (TMS) as an internal standard. The peak patterns are reported as follows: s, singlet; d, doublet; t, triplet; q, quartet; quint, quintet; sext, sextet; hept, heptet; m, multiplet; dd, doublet of doublets; dt, doublet of triplets. The coupling constants (*J*) are reported in Hertz (Hz); Melting points were determined on a micro melting point apparatus and are uncorrected. High-resolution mass spectra (HRMS) were obtained on a Q-TOF Mass Spectrometer equipped with an electrospray ion source (ESI)and operated in the positive mode. Single crystal X-ray diffraction measurements were carried out on a Rigaku XtaLAB Synergy four-circle diffractometer under Mo-Kα radiation (λ = 0.71073 Å); Steady-state fluorescence spectroscopy were recorded by Edinburgh Steady-state fluorescence spectrometer FLS920; Luminescence decays were recorded by Edinburgh Full-featured steady-state/transient fluorescence spectrometer; Solid-state fluorescence were measured by Fluorescence Spectrophotometer F-4600. Cyclic voltammetry was measured by electrochemical workstation CHI 760D and Ag/AgCl electrode was reference electrode. Flash column chromatography was performed over silica gel 200-300 mesh. DMSO used for the synthesis of products Q**1** was analytical reagent grade and used without any pretreatment.

2. Typical procedure for preparation of 1a

A mixture of aromatic nitrile(5mmol), hydrazine dihydrochloride (5 mmol) and hydrazine hydrate (15 mmol) in ethylene or diethylene glycol (5 mL) was heated at 130°C with under nitrogen for 2-5 h (**Scheme S1**). After cooling, the reaction mixture was dilute with water (20 mL). The precipitate thus obtained was filtered, washed with water, dried and recrystallized from ethanol. [1]

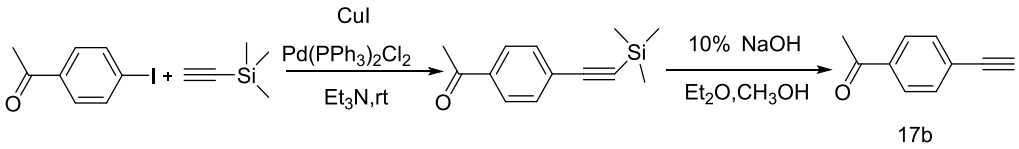


Scheme S1 Synthesis of 1a

3,5-di(pyridin-2-yl)-4*H*-1,2,4-triazol-4-amine(1a). ^{1}H NMR (400 MHz, DMSO-*d6*, TMS) δ 8.80 (d, 2H, *J* = 4 Hz), 8.25(d, 2H, *J*=8Hz), 8.08(t, 2H, *J*=8Hz), 7.84(s,2H),7.60 (t,2H, *J*=4Hz). δ ^{13}C NMR (101 MHz, DMSO-*d6*, TMS) δ 149.38, 149.25, 147.55, 138.23, 125.00, 123.27ppm.

3. Preparation of 4-acetylphenylacetylene (17b)

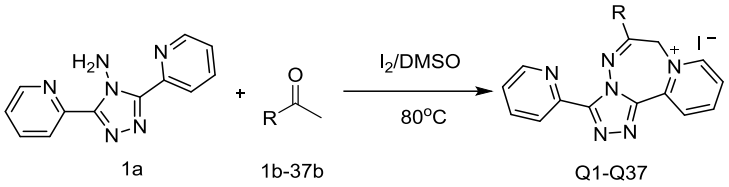
The mixture of 4'-iodoacetophenone (1.722 g, 7 mmol), $Pd(PPh_3)_2Cl_2$ (3 mol %, 147 mg) and CuI (5 mol%, 67 mg) in Et_3N (30 mL) was added dropwise via cannula a solution of (trimethylsilyl)acetylene (7.7 mmol, 0.571 g) in Et_3N (5 mL) at room temperature for 2 h (Monitored by TLC), and a purification by column chromatography on silica gel. [2]



Scheme S2 Synthesis of 17b

To a solution of 1-(4-((trimethylsilyl)ethynyl)phenyl)ethan-1-one (1.08 g ,5 mmol) in 50 mL of diethyl ether was added 50 mL of methanol and 20 mL of a 10% sodium hydroxide solution at rt for 15 min (Monitored by TLC). The reaction mixture was neutralized with a 1 mL HCl solution. Flash chromatography on silica gel (eluent: petroleum ether/ethyl acetate 20:1) afforded the product 17b as yellow solid. Yield: 0.52 g (72.2%).

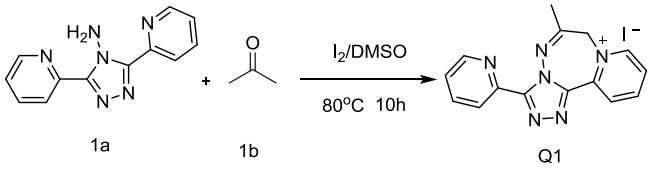
4. Typical procedure for the synthesis of Q1-Q37



Scheme S3 Typical procedure for the synthesis of Q1-Q37

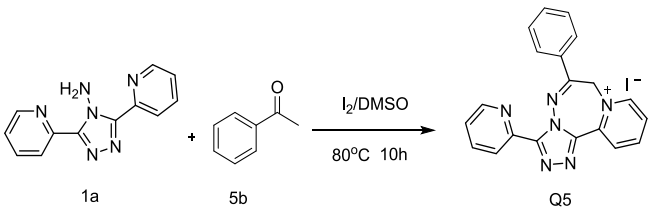
In a 25 mL round-bottomed flask, methyl ketones **(1b-37b)** (0.6 mmol, 1.2 equiv.), 3,5-di(pyridin-2-yl)-4H-1,2,4-triazol-4-amine **(1a)** (0.5 mmol,0.119 g, 1 equiv.), I_2 (0.3 mmol, 0.076 g) were stirred in Dimethyl sulfoxide (DMSO, 1 mL) at 80°C, under air, for 10 h. After completion (TLC), then cooling to room temperature, a small amount of ethyl acetate was added, followed by suction filtration, washed with a small portion of ethyl acetate, dried in vacuo and then recrystallized in methanol.

5. The gram-scale experiments of six products



Scheme S4 the gram-scale experiment of Q1

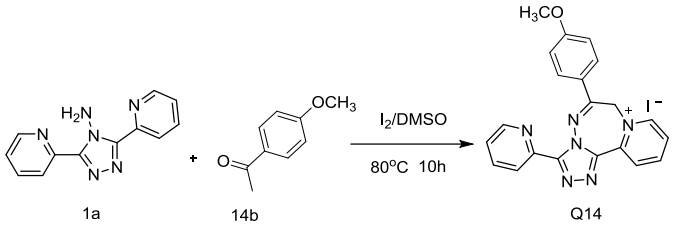
3,5-di(pyridin-2-yl)-4H-1,2,4-triazol-4-amine **(1a)** (5mmol,1.19 g), acetone**(1b)** (6mmol,0.348 g), I_2 (3 mmol, 0.76 g) and DMSO (7 mL) were added in a 50 mL round-bottomed flask. Then under condensing, stir it at 80°C for 10 h when it opened to air. After the reaction, cool to room temperature. Then ethyl acetate is added to the reaction mixture, followed by suction filtration, washed with a small portion of ethyl acetate, dried in vacuo and finally recrystallized in methanol. Yield:1.58g, 78.2%.



Scheme S5 the gram-scale experiment of Q5

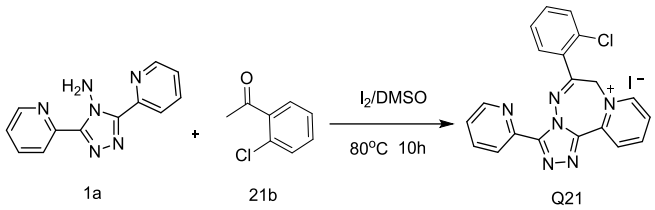
3,5-di(pyridin-2-yl)-4H-1,2,4-triazol-4-amine **(1a)** (5mmol,1.19 g), acetophenone **(5b)** (6mmol,0.72 g), I_2 (3 mmol, 0.76 g) and DMSO (7 mL) were added in a 50 mL round-bottomed flask. Then under condensing, stir it at 80°C for 10 h when it opened to air. After the reaction, cool to room temperature. Then ethyl acetate is added to the reaction mixture, followed by suction filtration, washed with a small portion of ethyl acetate, dried in vacuo and finally

recrystallized in methanol. Yield:1.87g, 80.3%.



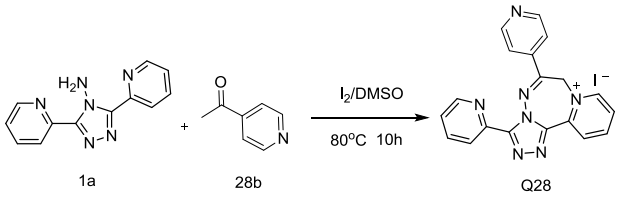
Scheme S6 the gram-scale experiment of Q14

3,5-di(pyridin-2-yl)-4H-1,2,4-triazol-4-amine **(1a)** (5mmol,1.19 g),4'-methoxyacetophenone **(14b)** (6mmol,0.90 g), I_2 (3 mmol, 0.76 g) and DMSO (7 mL) were added in a 50 mL round-bottomed flask. Then under condensing, stir it at 80°C for 10 h when it opened to air. Other subsequent operations are the same as the gram-scale synthesis of Q5. Yield:1.71g, 68.9%.



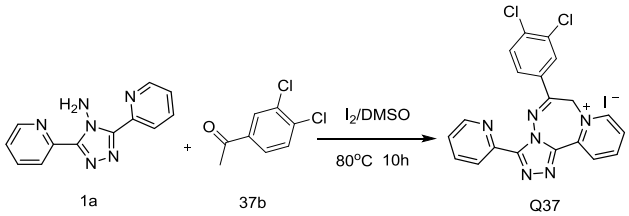
Scheme S7 the gram-scale experiment of Q21

3,5-di(pyridin-2-yl)-4H-1,2,4-triazol-4-amine **(1a)** (5mmol,1.19 g), 2'-chloroacetophenone **(21b)** (6mmol,0.93 g), I_2 (3 mmol, 0.76 g) and DMSO (7 mL) were added in a 50 mL round-bottomed flask. Then under condensing, stir it at 80°C for 10 h when it opened to air. Other subsequent operations are the same as the gram-scale synthesis of Q5. Yield:1.65g, 66%.



Scheme S8 the gram-scale experiment of Q28

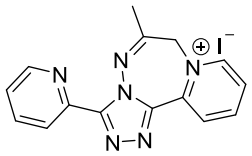
3,5-di(pyridin-2-yl)-4H-1,2,4-triazol-4-amine **(1a)** (5mmol,1.19 g), 4-acetylpyridine **(28b)** (6mmol,0.73 g), I_2 (3 mmol, 0.76 g) and DMSO (7 mL) were added in a 50 mL round-bottomed flask. Then under condensing, stir it at 80°C for 10 h when it opened to air. Other subsequent operations are the same as the gram-scale synthesis of Q5. Yield:1.91g, 81.6%.



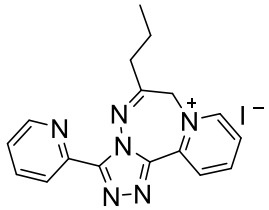
Scheme S9 the gram-scale experiment of Q37

3,5-di(pyridin-2-yl)-4H-1,2,4-triazol-4-amine **(1a)** (5mmol,1.19 g), 3',4'-dichloroacetophenone **(37b)** (6mmol,1.13 g), I_2 (3 mmol, 0.76 g) and DMSO (7 mL) were added in a 50 mL round-bottomed flask. Then under condensing, stir it at 80°C for 10 h when it opened to air. Other subsequent operations are the same as the gram-scale synthesis of Q5. Yield:2.14g, 80.1%.

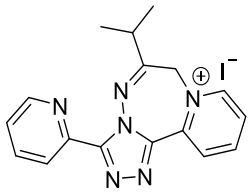
6. Spectral data of the synthesized compounds



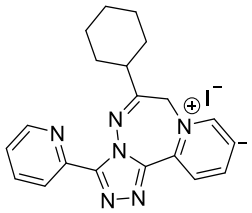
6-methyl-3-(pyridin-2-yl)-7H-pyrido[2,1-d][1,2,4]triazolo[4,3-b][1,2,5]triazepin-8-ium iodide(Q1)； Yield: 85%; pale-yellow solid; m.p:265-266°C; ^{1}H NMR (400 MHz, DMSO-*d*$_6$, TMS) δ9.16 (s,1H), 8.71 (s,2H),8.61(s,1H),8.27(d, *J*=4Hz,1H), 7.97(s,2H), 7.56(s,1H), 5.61(s,1H), 4.73(s, 3H); ^{13}C NMR (101 MHz, DMSO-*d*$_6$, TMS)δ165.73, 153.79, 150.58, 147.19, 146.65, 144.84, 144.57, 140.70, 137.81, 130.03, 128.61, 126.17, 126.05, 57.72,24.75; HRMS Calcd (ESI) m/z for $C_{15}H_{12}IN_6$: $[M-H]^-$403.0174, Found:403.0178



6-propyl-3-(pyridin-2-yl)-7H-pyrido[2,1-d][1,2,4]triazolo[4,3-b][1,2,5]triazepin-8-ium iodide(Q2)； Yield: 83%; yellow solid; m.p:244-245°C； ^{1}H NMR (400 MHz, DMSO-*d*$_6$, TMS) δ9.48(d, *J*=4HZ,1H), 8.88(d, *J*=4Hz,2H), 8.85(d, *J*=4Hz,1H), 8.46(dd, *J1*=12Hz, *J2*=4Hz,1H), 8.13(dd, *J1*=16H,*J2*=8Hz,2H), 7.68(m,1H), 5.77(s,2H), 2.88(t, *J*=8Hz,2H), 1.67(m,2H), 0.97(t, *J*=4Hz,3H); ^{13}C NMR (101 MHz, DMSO-*d*$_6$, TMS) δ167.14, 153.43, 150.06, 146.78, 145.92, 144.29, 144.00, 140.34, 137.24, 129.68, 128.30, 125.72, 125.60, 56.85, 39.10, 17.82, 13.29; HRMS Calcd (ESI) m/z for $C_{17}H_{16}IN_6$: $[M-H]^-$431.0487, Found:431.0497

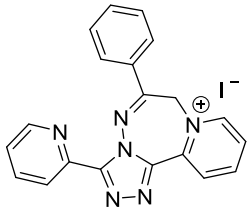


6-isopropyl-3-(pyridin-2-yl)-7H-pyrido[2,1-d][1,2,4]triazolo[4,3-b][1,2,5]triazepin-8-ium iodide(Q3)； Yield: 80%; yellow solid; m.p:258-259 °C;^{1}H NMR (400 MHz, DMSO-*d*$_6$, TMS) δ9.45 (d, *J*=8Hz,1H), 8.88-8.81(m,3H), 8.41(t, *J*=4H,1H), 8.11(d, *J*=4Hz,1H), 7.46(dd, *J*=8,4Hz,2H), 5.79(s,2H), 3.14(m,1H), 1.23(d, *J*=4Hz, 3H);^{13}C NMR (151 MHz, DMSO-*d*$_6$, TMS) δ169.92, 153.62, 150.13, 146.77, 145.46, 144.39, 144.02, 140.96, 137.18, 129.75, 128.42, 125.70, 125.57, 55.69, 36.39, 18.47; HRMS Calcd (ESI) m/z for $C_{17}H_{16}IN_6$: $[M-H]^-$431.0487, Found:431.0480

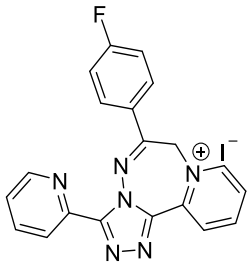


6-cyclohexyl-3-(pyridin-2-yl)-7H-pyrido[2,1-d][1,2,4]triazolo[4,3-b][1,2,5]triazepin-8-ium iodide(Q4) Yield: 66%; pale-yellow solid; m.p:249-250°C;^{1}H NMR (400 MHz, DMSO-*d*$_6$, TMS)δ 9.45 (d, *J*=8Hz,1H), 8.87-8.80(m,3H), 8.40(t, *J*=8Hz,1H), 8.10(s,2H), 7.65(t, *J*=8Hz,1H), 5.78(s,2H), 2.58(s,1H), 1.99(s,2H), 1.76(s,2H),1.67(d, *J*=12Hz,1H), 1.33(t, *J*=12Hz,4H), 1.17(d, *J*=8Hz,1H); ^{13}C NMR (101 MHz, DMSO-*d*$_6$, TMS) δ169.59, 154.05, 150.53, 147.16, 145.90, 144.73, 144.38, 141.24, 137.59, 130.17, 128.82, 126.11, 126.08, 56.29, 28.77, 25.74, 25.49; HRMS Calcd (ESI) m/z for

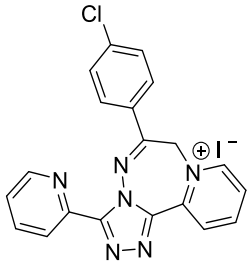
$C_{20}H_{20}IN_6$: $[M-H]^-$ 471.0800, Found:471.0811.



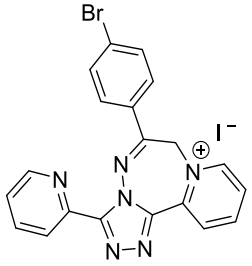
6-phenyl-3-(pyridin-2-yl)-7H-pyrido[2,1-d][1,2,4]triazolo[4,3-b][1,2,5]triazepin-8-ium iodide(Q5) Yield: 86%; yellow solid; m.p: 273-274°C; ^{1}H NMR (400 MHz, DMSO-*d*$_6$, TMS) δ 9.60 (d, *J* = 8 Hz, 1H), 8.91-8.81 (dt, *J* = 20, 12Hz,3H), 8.41 (t, *J* = 8Hz, 1H), 8.20 (d, *J* = 8 Hz,3H),8.14(t, *J*=8Hz,1H), 7.69(d, *J*=4Hz,2H), 7.62(t, *J*=8Hz,2H), 6.21(s,2H); ^{13}C NMR (101 MHz, DMSO-*d*$_6$, TMS)δ160.33, 154.31, 150.69, 147.30, 146.07, 144.92, 144.69, 141.40, 137.88, 133.47, 132.91, 130.36, 129.67, 129.23, 128.92, 126.24, 126.08, 54.86; HRMS Calcd (ESI) m/z for $C_{20}H_{14}IN_6$: $[M-H]^-$ 465.0330, Found: 465.0336.



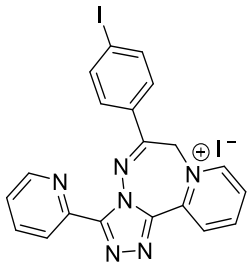
6-(4-fluorophenyl)-3-(pyridin-2-yl)-7H-pyrido[2,1-d][1,2,4]triazolo[4,3-b][1,2,5]triazepin-8-ium iodide(Q6) Yield: 79%; yellow solid; m.p:303-304 °C; ^{1}H NMR (400 MHz,DMSO-*d*$_6$, TMS) δ 9.59 (d, *J* = 4 Hz, 1H), 8.90-8.81 (m, 3H), 8.41 (t, *J*= 12Hz, 1H), 8.20 (dd, *J*= 5.2,8.8 Hz,3H), 8.21(d, *J*=8Hz,1H), 8.13(t, *J*=8Hz,1H), 7.48(t, *J*=8Hz,2H), 6.20(s,2H); ^{13}C NMR (101 MHz, DMSO-d6, TMS) δ164.90（d, *J*=251Hz）, 158.96, 153.82, 150.22, 146.84, 145.66, 144.47, 144.19, 140.90, 137.44, 131.66（d, *J*=9Hz）, 129.86, 129.11（d, *J*=2Hz）, 128.41, 125.77, 125.57, 116.34（d, *J*=22Hz）, 54.39; HRMS Calcd (ESI) m/z for $C_{20}H_{13}FIN_6$: $[M-H]^-$ 483.0236, Found: 483.0226.



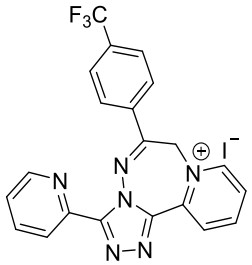
6-(4-chlorophenyl)-3-(pyridin-2-yl)-7H-pyrido[2,1-d][1,2,4]triazolo[4,3-b][1,2,5]triazepin-8-ium iodide(Q7);Yield: 90%; yellow solid; m.p:315-316°C; ^{1}H NMR (400 MHz, DMSO-*d*$_6$, TMS) δ 9.62 (d, *J* = 8 Hz, 1H), 8.91-8.82 (m, 3H), 8.42 (t, *J*= 8Hz, 1H), 8.20 (t, *J*= 8 Hz,3H), 8.13(t, *J*=8Hz,1H), 7.69(t, *J*=4Hz,3H), 6.22(s,2H); ^{13}C NMR (101 MHz, DMSO-*d*$_6$, TMS) δ159.45, 154.27, 150.67, 147.27, 146.14, 144.90, 144.65, 141.35, 138.34, 137.91, 131.88, 131.02, 130.27, 129.67, 128.83, 126.25, 125.98, 54.65; HRMS Calcd (ESI) m/z for $C_{20}H_{13}ClIN_6$: $[M-H]^-$ 498.9940, Found: 498.9942.



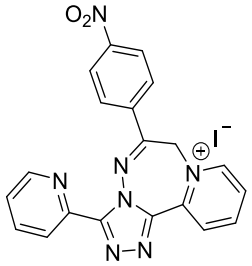
6-(4-bromophenyl)-3-(pyridin-2-yl)-7H-pyrido[2,1-d][1,2,4]triazolo[4,3-b][1,2,5]triazepin-8-ium iodide(Q8); Yield: 87%; pale-yellow solid; m.p:306-307°C; ^{1}H NMR (400MHz, DMSO-d_6, TMS) δ9.62(d, *J*=8Hz,1H), 8.91-8.82 (m,3H), 8.42(t, *J*=8Hz,1H), 8.20(d, *J*=8Hz,1H), 8.13(t, *J*=8Hz,3H), 7.84(d, *J*=8Hz,2H), 7.69(t, *J*=8Hz,2H), 6.22(s,2H); ^{13}C NMR (101 MHz, DMSO-d_6, TMS)δ159.62, 154.27, 150.67, 147.28, 146.17, 144.90, 144.63, 141.34, 137.90, 132.62, 132.23, 131.16, 130.29, 128.84, 127.43, 126.24, 126.00, 54.64; HRMS Calcd (ESI) m/z for $C_{20}H_{13}BrIN_6$: $[M-H]^-$ 542.9435, Found:542.9440



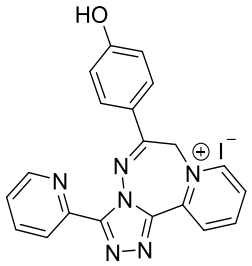
6-(4-iodophenyl)-3-(pyridin-2-yl)-7H-pyrido[2,1-d][1,2,4]triazolo[4,3-b][1,2,5]triazepin-8-ium iodide(Q9);Yield: 78%; yellow solid; m.p: 334-335°C;^{1}H NMR (400 MHz, DMSO-d_6, TMS) δ 9.57 (d, *J* = 4 Hz, 1H), 8.90-8.81 (m, 3H), 8.41 (t, *J* = 4Hz, 1H), 8.19 (d, *J* = 8 Hz,1H), 8.12(t, *J*=8Hz,1H), 8.01(d, *J*=8Hz,2H), 7.95(d, *J*=8Hz,2H), 7.69(t, *J*=4Hz,1H), 6.18(s,2H); ^{13}C NMR (101 MHz, DMSO-d_6, TMS) δ 159.89, 154.26, 150.67, 147.28, 146.12, 144.90, 144.64, 141.35, 138.47, 137.90, 132.45, 130.83, 130.28, 128.85, 126.24, 125.99, 101.99, 54.56,; HRMS Calcd (ESI) m/z for $C_{20}H_{13}I_2N_6$: $[M-H]^-$ 590.9297, Found: 590.9287.



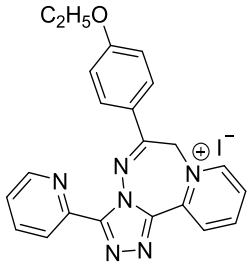
3-(pyridin-2-yl)-6-(4-(trifluoromethyl)phenyl)-7H-pyrido[2,1-d][1,2,4]triazolo[4,3-b][1,2,5]triazepin-8-ium iodide(Q10); Yield: 86%; yellow solid; m.p:331-332°C;^{1}H NMR (400 MHz,DMSO-d_6, TMS) δ9.62 (d, *J* = 8 Hz, 1H), 8.93-8.83 (m, 3H), 8.45-8.38(m,3H), 8.22(d, *J*=8Hz,1H), 8.14(t, *J*=8Hz,1H), 8.00(d, *J*=8Hz,2H), 7.70(s,1H), 6.27(s,2H); ^{13}C NMR (101 MHz, DMSO-d_6, TMS)δ159.04, 154.03, 150.36, 147.02, 145.94, 144.47, 144.23, 140.93, 137.65, 136.59, 132.30(q, *J*=33Hz), 129.96, 129.76, 129.76, 128.53, 126.03(q, *J*=2Hz), 125.66, 123.89(q, *J*=270Hz), 54.53; HRMS Calcd (ESI) m/z for $C_{21}H_{13}F_3IN_6$: $[M-H]^-$ 533.0204, Found: 533.0213.



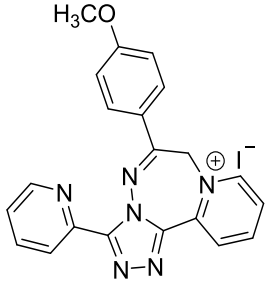
6-(4-nitrophenyl)-3-(pyridin-2-yl)-7H-pyrido[2,1-d][1,2,4]triazolo[4,3-b][1,2,5]triazepin-8-ium iodide(Q11);Yield: 85%; yellow solid; m.p: 327-328 °C;^{1}H NMR (400 MHz, DMSO-d_6, TMS) δ9.64 (d, *J* = 8 Hz, 1H), 8.95-8.85 (m, 3H), 8.44(s,5H), 8.25(d, *J*=8Hz,1H), 8.17(td, *J*=8,2Hz,1H), 7.73(t, *J*=4Hz,1H), 6.40(s,2H); ^{13}C NMR (101 MHz, DMSO-d_6, TMS) δ159.03, 154.39, 150.74, 150.08, 147.37, 146.38, 144.83, 144.55, 141.30, 138.94, 138.01, 130.70, 130.33, 128.84, 126.34, 126.00, 124.37, 54.87; HRMS Calcd (ESI) m/z for $C_{20}H_{13}IN_7O_2$: $[M-H]^-$ 510.0181, Found: 510.0191



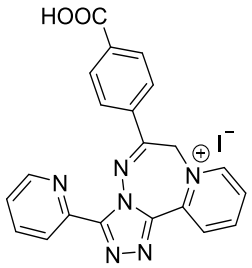
6-(4-hydroxyphenyl)-3-(pyridin-2-yl)-7H-pyrido[2,1-d][1,2,4]triazolo[4,3-b][1,2,5]triazepin-8-ium iodide(Q12) Yield: 70%; pale-yellow solid; m.p:300-301°C;^{1}H NMR (400 MHz, DMSO-d_6, TMS) δ10.61(s,1H), 9.61 (d, J = 8 Hz, 1H), 8.90-8.83 (m, 3H), 8.43(t, J=4Hz,1H), 8.21-8.12(m, 4H), 7.70(t, J=4Hz,1H), 6.98(d, J=8Hz,2H), 6.17(s,2H); ^{13}C NMR (101 MHz, DMSO-d_6, TMS) δ162.68, 159.82, 154.09, 150.59, 147.23, 145.82, 144.94, 144.78, 141.38, 137.81, 131.59, 130.24, 128.89, 126.11, 126.04, 123.28, 116.60, 54.63; HRMS Calcd (ESI) m/z for $C_{20}H_{14}IN_6O$: $[M-H]^-$ 481.0279, Found: 481.0273.



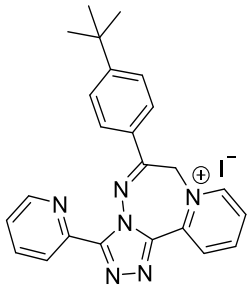
6-(4-ethoxyphenyl)-3-(pyridin-2-yl)-7H-pyrido[2,1-d][1,2,4]triazolo[4,3-b][1,2,5]triazepin-8-ium iodide(Q13); Yield: 72%; pale-yellow solid; m.p:287-288°C;^{1}H NMR (400 MHz, DMSO-d_6) δ9.60 (d, J = 4 Hz, 1H), 8.89-8.82 (m, 3H), 8.42(t, J=4Hz,1H), 8.18(d, J= 8Hz,3H), 8.13(t, J=8Hz,1H), 7.68(t, J=4Hz,1H), 7.14(d, J=8Hz,2H) 6.18(s,2H) 4.16(dd, J=16,8Hz,2H), 1.36(t, J=4Hz,3H); ^{13}C NMR (101 MHz, DMSO-d_6, TMS)δ162.97, 159.72, 154.19, 150.64, 147.24, 145.87, 145.00, 144.76, 141.42, 137.80, 131.38, 130.27, 128.89, 126.15, 126.04, 124.79, 115.56, 64.33, 54.63; HRMS Calcd (ESI) m/z for $C_{22}H_{18}IN_6O$: $[M-H]^-$ 509.0592, Found: 509.0598



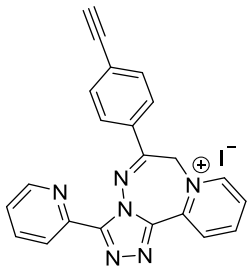
6-(4-methoxyphenyl)-3-(pyridin-2-yl)-7H-pyrido[2,1-d][1,2,4]triazolo[4,3-b][1,2,5]triazepin-8-ium iodide(Q14); Yield: 73%; Light yellow green solid; m.p:292-293°C;^{1}H NMR (400 MHz, DMSO-d_6, TMS) δ9.61 (d, J = 4 Hz, 1H), 8.89-8.82 (m, 3H), 8.42(t, J=4Hz,1H), 8.19(t, J= 8Hz,3H),8.13(t, J=8Hz,1H), 7.68(t, J=4Hz,1H), 7.16(d, J=12Hz,2H) 6.19(s,2H), 3.88(s,3H); ^{13}C NMR (101 MHz, DMSO-d_6, TMS)δ163.66, 159.71, 154.18, 150.62, 147.24, 145.87, 144.99, 144.73, 141.41, 137.78, 131.36, 130.26, 128.89, 126.13, 126.01, 124.95, 115.18, 56.34, 54.64; HRMS Calcd (ESI) m/z for $C_{21}H_{16}IN_6O$: $[M-H]^-$ 495.0436, Found:495.0441



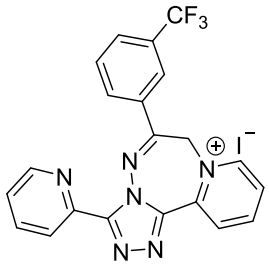
6-(4-carboxyphenyl)-3-(pyridin-2-yl)-7H-pyrido[2,1-d][1,2,4]triazolo[4,3-b][1,2,5]triazepin-8-ium iodide (Q15); Yield: 79%; yellow solid; m.p:317-318°C;^{1}H NMR (400 MHz, DMSO-d_6, TMS) δ13.43(s,1H), 9.63 (d, J = 8 Hz, 1H), 8.91-8.82 (m, 3H), 8.43(t, J=4Hz,1H), 8.31(d, J=8Hz,2H), 8.22(d, J=8Hz,1H), 8.16-8.11(m,3H), 7.70(t, J=8Hz,1H), 6.25(s,2H); ^{13}C NMR (101 MHz, DMSO-d_6, TMS)δ167.01, 159.69, 154.34, 150.71, 147.31, 146.22, 144.85, 144.62, 141.34, 137.93, 136.77, 134.62, 130.34, 130.17, 129.47, 128.87, 126.28, 126.04, 54.84; HRMS Calcd (ESI) m/z for $C_{21}H_{14}IN_6O_2$: $[M-H]^-$ 509.0228, Found: 509.0219.



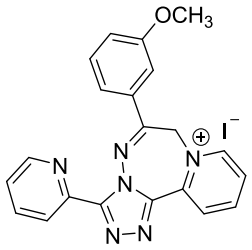
6-(4-(tert-butyl)phenyl)-3-(pyridin-2-yl)-7H-pyrido[2,1-d][1,2,4]triazolo[4,3-b][1,2,5]triazepin-8-ium iodide(Q16); Yield: 77%; yellow solid; m.p:306-307°C; ^{1}H NMR (400 MHz, DMSO-d_6, TMS) δ9.58 (d, J = 8 Hz, 1H), 8.90-8.86 (m, 3H), 8.41(t, J=8Hz,1H), 8.20-8.12(m, 4H), 7.69(t, J=4Hz,1H), 7.63(d, J=8Hz,2H), 6.22(s,2H), 1.33(s,9H); ^{13}C NMR (101 MHz, DMSO-d_6, TMS)δ160.09, 156.77, 154.26, 150.66, 147.28, 145.99, 144.91, 144.69, 141.33, 137.81, 130.31, 130.04, 129.18, 128.91, 126.52, 126.19, 126.08, 54.66,35.40, 31.26; HRMS Calcd (ESI) m/z for $C_{24}H_{22}IN_6$: $[M-H]^-$ 521. 0956, Found: 521.0964



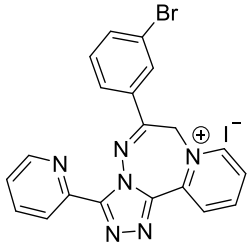
6-(4-ethynylphenyl)-3-(pyridin-2-yl)-7H-pyrido[2,1-d][1,2,4]triazolo[4,3-b][1,2,5]triazepin-8-ium iodide(Q17) Yield: 76%; yellow solid; m.p: 290-291°C; ^{1}H NMR (400 MHz, DMSO-d_6, TMS) δ9.63 (d, J=8 Hz, 1H), 8.90-8.82 (m, 3H), 8.42(t, J=4Hz,1H), 8.20 (t, J=8Hz, 3H), 8.13(t, J=8Hz,1H), 7.70(t, J=8Hz,3H), 6.22(s,2H),4.57(s,1H); ^{13}C NMR (101 MHz, DMSO-d_6, TMS)δ159.62, 154.30, 150.69, 147.30, 146.17, 144.86, 144.64, 141.33, 137.90, 133.15, 132.74, 130.33, 129.47, 128.86, 126.42, 126.25, 126.06, 85.06, 83.15, 54.66; HRMS Calcd (ESI) m/z for $C_{22}H_{14}IN_6$: $[M-H]^-$ 489.0330, Found: 489.0339



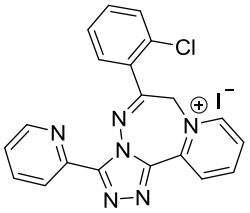
3-(pyridin-2-yl)-6-(3-(trifluoromethyl)phenyl)-7H-pyrido[2,1-d][1,2,4]triazolo[4,3-b][1,2,5]triazepin-8-ium iodide(Q18); Yield: 86%; yellow solid; m.p:317-318°C;^{1}H NMR (400 MHz, DMSO-*d*$_6$, TMS) δ9.61 (d, *J* = 4 Hz, 1H), 8.92 (d, *J*=8Hz, 1H),8.86-8.83(m,2H), 8.45(q, *J*=8Hz,3H), 8.23(d, *J*= 8Hz,1H), 8.15-8.12(m,1H), 8.07(d, *J*=8Hz,1H), 7.87(t, *J*=8Hz,1H), 7.70(t, *J*=8Hz,1H), 6.28(s,2H); ^{13}C NMR (151 MHz, DMSO-*d*$_6$, TMS)δ159.06, 153.85, 150.15, 149.63, 146.89, 145.97, 144.49, 144.14, 140.83, 137.51, 133.91, 132.88, 130.36, 129.81(q, *J*=32Hz),129.11(q, *J*=3Hz),128.38, 125.91, 125.55, 125.32(q, *J*=4.5Hz), 123.84(q, *J*=272Hz), 54.44; HRMS Calcd (ESI) m/z for $C_{21}H_{13}F_3IN_6$: $[M-H]^-$ 533.0204, Found: 533.0210



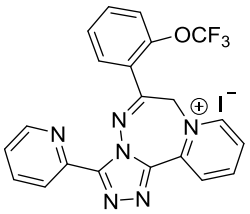
6-(3-methoxyphenyl)-3-(pyridin-2-yl)-7H-pyrido[2,1-d][1,2,4]triazolo[4,3-b][1,2,5]triazepin-8-ium iodide(Q19); Yield: 74%; yellow solid; m.p:282-283°C;^{1}H NMR (400 MHz, DMSO-*d*$_6$, TMS) δ9.62 (d, *J* = 4 Hz, 1H), 8.90-8.83 (m,3H), 8.44(t, *J*=8Hz,1H), 8.21(d, *J*= 8Hz,1H), 8.14(t, *J*=8Hz,1H), 7.80(d, *J*=8Hz,1H), 7.68(d, *J*=8Hz,2H), 7.55(t, *J*=8Hz,1H), 7.29(d, *J*=8Hz,1H) 6.23(s,2H), 3.85(s,3H); ^{13}C NMR (101 MHz, DMSO-*d*$_6$, TMS)δ160.12, 160.03, 154.23, 150.63, 147.33, 146.06, 144.89, 144.64, 141.35, 137.82, 134.22, 130.87, 130.43, 128.94, 126.25, 126.08, 121.76, 119.16, 114.24, 56.09, 54.95; HRMS Calcd (ESI) m/z for $C_{21}H_{16}IN_6O$: $[M-H]^-$ 495.0436, Found: 495.0435



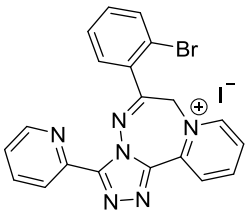
6-(3-bromophenyl)-3-(pyridin-2-yl)-7H-pyrido[2,1-d][1,2,4]triazolo[4,3-b][1,2,5]triazepin-8-ium iodide(Q20); Yield: 88%; yellow solid; m.p:293-294°C;^{1}H NMR (400 MHz, DMSO-*d*$_6$, TMS) δ9.60 (d, *J* = 8 Hz, 1H), 8.92-8.83 (m,3H), 8.44(t, *J*=8Hz,1H), 8.32(s, 1H), 8.22-8.12(m,3H), 7.90(d, *J*=8Hz,1H), 7.70(t, *J*=8Hz,1H), 7.58(t, *J*=8Hz,1H), 6.22(s,2H); ^{13}C NMR (101 MHz, DMSO-*d*$_6$, TMS)δ158.83, 153.82, 150.17, 146.84, 145.80, 144.39, 144.10, 140.78, 137.43, 135.40, 134.88, 131.20, 131.18, 129.92, 128.37, 127.87, 125.83, 125.57, 122.28, 54.38; HRMS Calcd (ESI) m/z for $C_{20}H_{13}BrIN_6$: $[M-H]^-$ 542.9435, Found: 542.9439



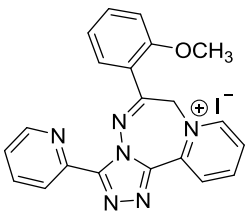
6-(2-chlorophenyl)-3-(pyridin-2-yl)-7H-pyrido[2,1-d][1,2,4]triazolo[4,3-b][1,2,5]triazepin-8-ium iodide(Q21); Yield: 69%; yellow solid; m.p:293-294°C;^{1}H NMR (400 MHz, DMSO-d_6, TMS) δ9.44 (d, J = 4 Hz, 1H), 8.98 (d, J=8Hz,1H), 8.93-8.88(m,2H), 8.44(t, J=8Hz 1H), 8.19(d, J=8Hz,1H), 8.14(t, J=8Hz,1H), 7.77(t, J=8Hz,2H), 7.68(t, J=4Hz,2H), 7.58(t, J=4Hz,1H), 6.22(s,2H); ^{13}C NMR (101 MHz, DMSO-d_6, TMS)δ161.10, 154.45, 150.71, 147.61, 146.68, 144.78, 144.37, 141.50, 137.87, 134.07, 133.56, 132.54, 132.27, 130.57, 130.25, 129.08, 128.24, 126.28, 126.10, 57.64; HRMS Calcd (ESI) m/z for $C_{20}H_{13}ClIN_6$: $[M-H]^-$ 498.9940, Found: 498.9936



3-(pyridin-2-yl)-6-(2-(trifluoromethoxy)phenyl)-7H-pyrido[2,1-d][1,2,4]triazolo[4,3-b][1,2,5]triazepin-8-ium iodide(Q22); Yield: 62%; pale-yellow solid; m.p: 252-253°C;1H NMR (400 MHz, DMSO-d_6, TMS) δ9.48(d, J=4Hz,1H), 9.01-8.93(m,2H), 8.90(d, J=8Hz,^{1}H), 8.51 (t, J=8Hz,1H), 8.21(d, J=8Hz,1H), 8.15(t,8Hz,1H), 7.91(d, J=4Hz,1H), 7.83(t, J=8Hz,1H), 7.72-7.63(m,3H), 6.24(s,2H); ^{13}C NMR (151 MHz, DMSO-d_6, TMS) δ 159.13, 154.06, 150.26, 147.30, 146.44, 146.44, 146.26, 144.23, 140.87, 137.40, 133.85, 132.24, 129.78, 128.65, 127.88, 127.53, 125.85, 125.70, 120.85,119.88(q, J=258Hz), 57.33; HRMS Calcd (ESI) m/z for $C_{21}H_{13}F_3IN_6O$: $[M-H]^-$549.0153, Found:549.0158

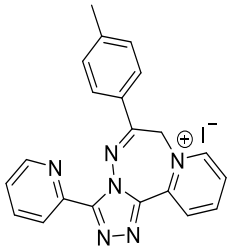


6-(2-bromophenyl)-3-(pyridin-2-yl)-7H-pyrido[2,1-d][1,2,4]triazolo[4,3-b][1,2,5]triazepin-8-ium iodide(Q23); Yield: 67%; pale-yellow solid; m.p:250-251°C;^{1}H NMR (400MHz, DMSO-d_6, TMS)δ9.37(d, J=8Hz,1H), 8.92(d, J=8Hz,1H), 8.87-8.82(m,2H), 8.37(t, J=8Hz,1H),8.13(d, J=8Hz,1H), 8.10-8.05(td, J=12,4Hz,1H), 7.70(t, J=8Hz,2H), 7.62 (t, J=8Hz 2H), 7.51(t, J=4Hz,1H), 6.15(s,2H); ^{13}C NMR (101 MHz, DMSO-d_6, TMS) δ 162.11, 154.43, 150.72, 147.66, 146.71, 144.73, 144.28, 141.28, 137.85, 136.23, 133.50, 133.43, 132.38, 130.40, 129.14, 128.60, 126.27, 126.09, 121.34, 57.70; HRMS Calcd (ESI) m/z for $C_{20}H_{13}BrIN_6$: [M-H]-542.9435, Found:542.9428

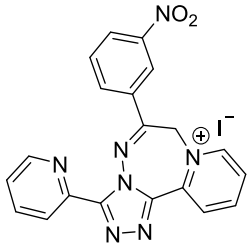


6-(2-methoxyphenyl)-3-(pyridin-2-yl)-7H-pyrido[2,1-d][1,2,4]triazolo[4,3-b][1,2,5]triazepin-8-ium iodide(Q24); Yield: 68%; pale-yellow solid; m.p:302-303°C;^{1}H NMR (400MHz, DMSO-d_6, TMS) δ9.29(d, J=8Hz,1H), 8.93(d,

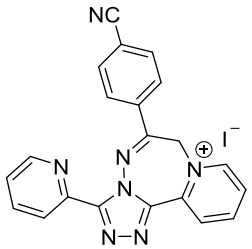
J=8Hz,1H), 8.90(d, *J*=4Hz, 2H), 8.52(dd, *J*=9.6,4.8Hz), 8.25(d, *J*=8Hz,1H), 8.17(t, *J*=8Hz,1H), 7.74-7.63(m,3H), 7.29(d, *J*=8Hz,1H), 7.16(t, *J*=8Hz,1H), 6.05(s,2H); ^{13}C NMR (101 MHz, DMSO-*d*$_6$, TMS) δ 161.75, 158.52, 154.25, 150.68, 147.44, 146.68, 144.94, 144.69, 141.45, 137.89, 134.45, 131.31, 129.73, 128.87, 126.20, 125.99, 123.14, 121.48, 112.59, 57.78, 56.45; HRMS Calcd (ESI) m/z for $C_{21}H_{16}IN_6O$: $[M-H]^-$496.0509, Found:496.0501



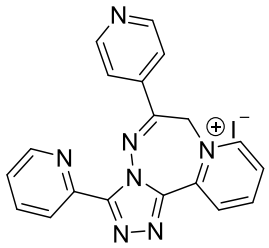
3-(pyridin-2-yl)-6-(p-tolyl)-7H-pyrido[2,1-d][1,2,4]triazolo[4,3-b][1,2,5]triazepin-8-ium iodide(Q25) Yield: 84%; yellow solid; m.p:296-297°C;^{1}H NMR (400 MHz, DMSO-*d*$_6$, TMS) δ 9.62(d, *J*=8Hz,1H), 8.90-8.82(m,3H), 8.42(t, *J*=8Hz,1H), 8.19(d, *J*=8Hz,1H), 8.13(t, *J*=8Hz,3H), 7.69(dd, *J*=7.6,4.8Hz,1H), 7.43(d, *J*=8Hz,1H), 6.20(s,2H), 2.42(s,3H); ^{13}C NMR (101 MHz, DMSO-*d*$_6$, TMS) δ159.73, 153.77, 150.18, 146.82, 145.52, 144.43, 144.24, 143.60, 140.90, 137.35, 129.86, 129.81, 129.58, 128.79, 128.45, 125.73, 125.61, 54.28, 21.23; HRMS Calcd (ESI) m/z for $C_{21}H_{16}IN_6$: $[M-H]^-$479.0487, Found:479.0498



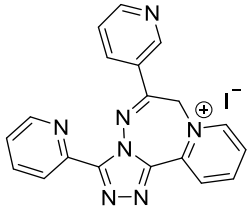
6-(3-(nitrooxy)phenyl)-3-(pyridin-2-yl)-7H-pyrido[2,1-d][1,2,4]triazolo[4,3-b][1,2,5]triazepin-8-ium iodide(Q26) Yield: 87%; yellow solid; m.p:315-316°C;^{1}H NMR (400 MHz, DMSO-*d*$_6$, TMS)δ9.66(s,1H), 8.96-8.88(m,4H), 8.62(t, *J*=8Hz,1H), 8.54-8.44(m,2H), 8.25(t, *J*=8Hz,1H), 8.18-8.13(m,1H), 7.97-7.90(m,1H), 7.72(t, *J*=8Hz,1H), 6.33(d, *J*=12Hz,2H); ^{13}C NMR (101 MHz, DMSO-*d*$_6$, TMS) δ 159.21, 154.28, 150.64, 148.56, 147.35, 146.49, 144.87, 144.55, 141.24, 137.97, 135.71, 134.96, 131.13, 130.32, 128.80, 127.33, 126.35, 126.01, 123.89, 54.99; HRMS Calcd (ESI) m/z for $C_{20}H_{13}IN_7O_2$: $[M-H]^-$510.0181, Found:510.0176



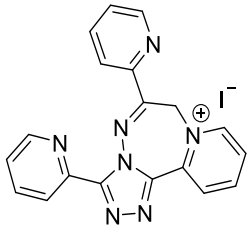
6-(4-cyanophenyl)-3-(pyridin-2-yl)-7H-pyrido[2,1-d][1,2,4]triazolo[4,3-b][1,2,5]triazepin-8-ium iodide(Q27); Yield: 76%; yellow solid; m.p:316-317°C;^{1}H NMR (400 MHz, DMSO-*d*$_6$, TMS) δ 10.61(s,1H), 9.61 (d, *J* = 4 Hz, 1H), 8.90-8.83 (m, 3H), 8.43 (t, *J* = 4Hz, 1H), 8.21-8.12 (m,4H), 7.70(t, *J*=8Hz,1H), 6.98(d, *J*=8Hz,2H), 6.17(s,2H); ^{13}C NMR (101 MHz, DMSO-*d*$_6$, TMS)δ159.21, 154.34, 150.69, 147.33, 146.34, 144.81, 144.54, 141.25, 137.96, 137.28, 133.30, 130.33, 129.88, 128.82, 126.30, 126.00, 118.60, 115.10, 54.70; HRMS Calcd (ESI) m/z for $C_{21}H_{13}IN_7$: $[M-H]^-$ 490.0283, Found: 490.0287.



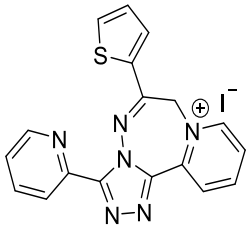
3-(pyridin-2-yl)-6-(pyridin-4-yl)-7H-pyrido[2,1-d][1,2,4]triazolo[4,3-b][1,2,5]triazepin-8-ium iodide(Q28); Yield: 85%; Brownish yellow solid; m.p:283-284°C;^{1}H NMR (400 MHz, DMSO-*d*$_6$, TMS) δ9.64 (d, *J* = 8 Hz, 1H), 8.92-8.85 (m, 5H), 8.43(t, *J*=8Hz,1H), 8.22 (d, *J*=8Hz, 1H), 8.15(t, *J*=8Hz,1H), 8.10(d, *J*=4Hz,2H), 7.71(t, *J*=4Hz,1H), 6.22(s,2H); ^{13}C NMR (101 MHz, DMSO-*d*$_6$, TMS)δ159.10, 154.34, 151.01, 150.73, 147.38, 146.44, 144.73, 144.57, 141.21, 140.52, 137.99, 130.40, 128.87, 126.35, 126.08, 122.55, 54.48; HRMS Calcd (ESI) m/z for $C_{19}H_{13}IN_7$: $[M-H]^-$ 466.0283, Found: 466.0280



3-(pyridin-2-yl)-6-(pyridin-3-yl)-7H-pyrido[2,1-d][1,2,4]triazolo[4,3-b][1,2,5]triazepin-8-ium iodide(Q29); Yield: 83%; yellow solid; m.p:292-293°C;^{1}H NMR (400 MHz, DMSO-*d*$_6$, TMS) δ9.62 (d, *J* = 8 Hz, 1H), 9.34(s,1H), 8.92-8.83 (m, 4H), 8.50(d, *J*=8Hz,1H), 8.43 (t, *J*=8Hz, 1H), 8.22(d, *J*=8Hz,1H), 8.14(t, *J*=8Hz,1H), 7.71-7.65(m, 2H), 6.25(s,2H); ^{13}C NMR (101 MHz, DMSO-*d*$_6$, TMS)δ159.13, 154.27, 153.38, 150.69, 149.93, 147.33, 146.44, 144.81, 144.59, 141.22, 137.94, 136.68, 130.35, 129.36, 128.82, 126.28, 126.04, 124.44, 54.79; HRMS Calcd (ESI) m/z for $C_{19}H_{13}IN_7$: $[M-H]^-$ 466.0283, Found:466.0274

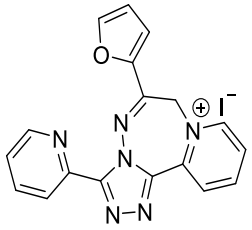


3-(pyridin-2-yl)-6-(pyridin-2-yl)-7H-pyrido[2,1-d][1,2,4]triazolo[4,3-b][1,2,5]triazepin-8-ium iodide(Q30); Yield: 77%; pale-yellow solid; m.p: 284-285°C;^{1}H NMR (400 MHz, DMSO-*d*$_6$, TMS) δ9.43 (d, *J* = 8 Hz, 1H), 8.89-8.83 (m, 4H), 8.40(s,1H), 8.24-8.06 (m, 4H), 7.72(s, 2H), 6.38(s,2H); ^{13}C NMR (151 MHz, DMSO-*d*$_6$, TMS) δ159.58, 153.73, 150.30, 150.16, 149.65, 146.87, 146.28, 144.39, 144.33, 140.96, 138.17, 137.51, 129.80, 128.52, 127.15, 125.86, 125.62, 122.88, 53.21;HRMS Calcd (ESI) m/z for $C_{19}H_{13}IN_7$: $[M-H]^-$ 466.0283, Found:466.0278.

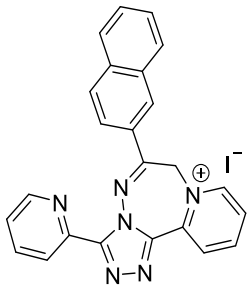


3-(pyridin-2-yl)-6-(thiophen-2-yl)-7H-pyrido[2,1-d][1,2,4]triazolo[4,3-b][1,2,5]triazepin-8-ium iodide(Q31); Yield: 78%; yellow solid; m.p:310-311 °C;^{1}H NMR (400 MHz, DMSO-*d*$_6$, TMS)δ9.55(d, *J*=8Hz,1H), 8.89-8.82(m,3H),

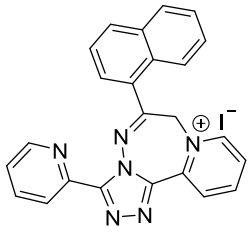
8.55(s,1H), 8.42(*t*, J=8Hz,1H), 8.16-8.10(m,2H), 8.05(d, *J*=4Hz,1H), 7.68(t, *J*=4Hz,1H), 7.39(s,1H), 6.23(s,2H); ^{13}C NMR (151 MHz, DMSO-d_6, TMS)δ155.29, 153.43, 150.18, 146.89, 145.50, 144.41, 144.37, 141.00, 137.25, 137.18, 135.75, 135.56, 129.84, 128.90, 128.62, 125.76, 125.62, 54.68; HRMS Calcd (ESI) m/z for $C_{18}H_{12}IN_6S$: $[M-H]^-$ 470.9894, Found:470.9890.



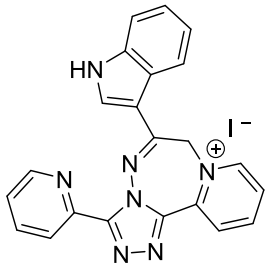
6-(furan-2-yl)-3-(pyridin-2-yl)-7H-pyrido[2,1-d][1,2,4]triazolo[4,3-b][1,2,5]triazepin-8-ium iodide(Q32); Yield: 75%;yellow solid; m.p:284-285°C;^{1}H NMR (400 MHz, DMSO-d6, TMS) δ9.50(s,1H), 8.85(dd, *J*=16,8Hz,3H), 8.42(t, *J*=8Hz,1H), 8.13(dd, *J*=16,8Hz,4H), 7.67(t, *J*=8Hz,1H), 6.93(s, 1H), 6.12(s,2H);^{13}C NMR (101 MHz, DMSO-d_6, TMS)δ154.20, 150.63, 150.08, 150.06, 147.48, 147.36, 145.78, 144.83, 144.71, 141.32, 137.77, 130.32, 129.02, 126.20, 126.17, 122.33, 114.08, 54.98; HRMS Calcd (ESI) m/z for $C_{18}H_{12}IN_6O$: $[M-H]^-$ 455.0123, Found:455. 0130.



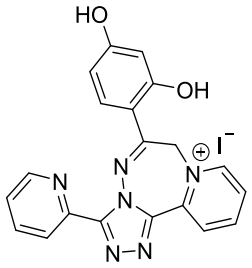
6-(naphthalen-2-yl)-3-(pyridin-2-yl)-7H-pyrido[2,1-d][1,2,4]triazolo[4,3-b][1,2,5]triazepin-8-ium iodide(Q33); Yield: 76%; pale-yellow solid; m.p:306-307°C; ^{1}H NMR (400MHz, DMSO-d_6, TMS) δ9.78(d, *J*=8Hz,1H), 9.07(s,1H), 8.94-8.87(m,3H), 8.47(t, *J*=8Hz,1H), 8.26-8.20(m,2H), 8.18-8.07(m,3H), 8.05(t, *J*=8Hz,1H), 7.73(dd, *J*=8.8,3.6Hz,3H), 6.37(s,2H); ^{13}C NMR (101 MHz, DMSO-d_6, TMS) δ 159.65, 153.85, 150.24, 146.83, 145.69, 145.64, 144.51, 144.28, 140.94, 137.41, 134.62, 132.40, 131.03, 129.90, 129.75, 129.37, 129.01, 128.45, 127.81, 127.40, 125.79, 125.63, 123.65, 54.15; HRMS Calcd (ESI) m/z for $C_{24}H_{16}IN_6$: $[M-H]^-$515.0487, Found:515.0483.



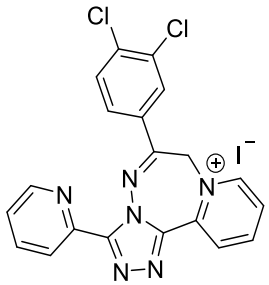
6-(naphthalen-1-yl)-3-(pyridin-2-yl)-7H-pyrido[2,1-d][1,2,4]triazolo[4,3-b][1,2,5]triazepin-8-ium iodide(Q34); Yield: 73%; pale-yellow solid; m.p:290-291°C;^{1}H NMR (400 MHz, DMSO-d_6, TMS)δ9.67(s,1H), 9.03-8.97(m,3H), 8.90(d, *J*=2Hz,1H), 8.48(d, *J*=8Hz,1H), 8.28(s,1H), 8.21(s,1H), 8.14(d, *J*=8Hz,1H), 8.08(s,1H), 7.98(s,1H), 7.71(s,4H), 6.31(s,2H); ^{13}C NMR (151 MHz, DMSO-d_6, TMS) δ 161.01, 154.02, 150.17, 146.92, 145.62, 144.68, 144.40, 141.23, 137.70, 133.44, 132.42, 131.03, 130.12, 129.83, 129.33, 128.70, 128.66, 127.83, 126.88, 126.46, 125.94, 125.45, 125.06, 58.14; HRMS Calcd (ESI) m/z for $C_{24}H_{16}IN_6$: $[M-H]^-$515.0487, Found:515.0493



6-(1H-indol-3-yl)-3-(pyridin-2-yl)-7H-pyrido[2,1-d][1,2,4]triazolo[4,3-b][1,2,5]triazepin-8-ium iodide(Q35); Yield: 60%; pale-yellow solid; m.p:294-295°C;^{1}H NMR (400 MHz, DMSO-*d*$_6$, TMS)δ12.46(s,1H), 9.60(d, *J*=4Hz,1H), 8.96(d, *J*=4Hz,1H), 8.87-8.81(m,3H), 8.41(t, *J*=8Hz,1H), 8.24(d, *J*=8Hz,1H), 8.10(t, *J*=8Hz,2H), 7.69(t, *J*=8Hz,1H), 7.54(d, *J*=8Hz,1H), 7.26(t, *J*=8Hz,1H), 7.11(t, *J*=8Hz,1H), 6.12(s,2H); ^{13}C NMR (101 MHz, DMSO-*d*$_6$, TMS) δ 157.35, 153.72, 150.43, 147.11, 145.53, 145.45, 145.07, 141.44, 138.08, 137.58, 135.73, 130.13, 128.93, 126.05, 125.99, 124.78, 124.40, 122.91, 122.61, 113.00, 111.22, 56.16; HRMS Calcd (ESI) m/z for $C_{22}H_{15}IN_7$: $[M-H]^-$504.0439, Found:504.0435



6-(2,4-dihydroxyphenyl)-3-(pyridin-2-yl)-7H-pyrido[2,1-d][1,2,4]triazolo[4,3-b][1,2,5]triazepin-8-ium iodide(Q36); Yield: 69%; pale-yellow solid; m.p:298-299°C;^{1}H NMR (400 MHz, DMSO-*d*$_6$, TMS) δ11.45(s,1H), 10.49(s,1H), 9.65 (d, *J* = 8 Hz, 1H), 8.88-8.85 (m, 3H), 8.43(dt, *J*=9.6,2.8Hz,1H), 8.35(d, *J*=8Hz,2H), 8.18(dt, *J*=14,1.6Hz,1H), 7.85(d, *J*=8Hz,1H), 7.71(t, *J*=8Hz,1H), 6.50(t, *J*=2.4Hz,2H), 6.07(s,2H); ^{13}C NMR (101 MHz, DMSO-*d*$_6$, TMS)δ163.89, 161.44, 160.87, 152.63, 150.20, 147.33, 146.52, 145.36, 145.15, 141.51, 138.33, 132.90, 129.77, 128.84, 126.24, 125.27, 110.86, 109.09, 103.75, 56.03; HRMS Calcd (ESI) m/z for $C_{20}H_{14}IN_6O_2$: $[M-H]^-$ 497.0228, Found: 497.0240



6-(3,4-dichlorophenyl)-3-(pyridin-2-yl)-7H-pyrido[2,1-d][1,2,4]triazolo[4,3-b][1,2,5]triazepin-8-ium iodide(Q37); Yield: 84%; yellow solid; m.p: 319-320°C;^{1}H NMR (400 MHz, DMSO-*d*$_6$, TMS) δ9.60 (d, *J* = 8 Hz, 1H), 8.91-8.84 (m, 3H), 8.43(d, *J*=8Hz,2H), 8.21(d, *J*=8Hz,1H), 8.13(t, *J*=8Hz,2H), 7.90(d, *J*=8Hz,1H), 7.69(t, *J*=8Hz,1H), 6.22(s,2H); ^{13}C NMR (101 MHz, DMSO-*d*$_6$, TMS)δ158.70, 154.27, 150.65, 147.31, 146.40, 144.87, 144.56, 141.19, 137.96, 136.06, 133.71, 132.44, 131.75, 131.11, 130.34, 129.21, 128.79, 126.32, 125.98, 54.65; HRMS Calcd (ESI) m/z for $C_{20}H_{12}Cl_2IN_6$: $[M-H]^-$ 532.9551, Found: 532.9560

7. X-ray Crystallographic Data of Q5, Q21, Q12, Q35

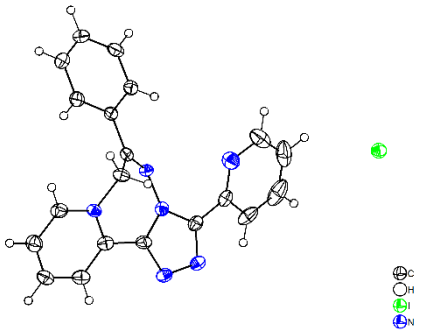


Fig.S1 X-ray crystal structure of Q5 (CCDC number: 1944954)

Table S1 Summary of X-ray crystallographic data for compound Q5

formula	$C_{20}H_{15}IN_6$
Fw.	466.04
crystal system	triclinic
space group	P-1
a/Å	9.7382(14)
b/Å	10.0324(13)
c/Å	11.2964(15)
α/°	73.551(7)
β/°	87.711(7)
γ/°	74.719(7)
V/Å^3	1020.3(2)
Z	2
D/g cm^{-3}	1.632
cryst size/mm	0.150 × 0.140 × 0.130
reflns collected	9970
ind reflns, *Rint*	5013，0.0616
goodness-of-fit on F^2	1.065
R1, wR2 [I > 2σ(I)]	0.0466，0.1191
R1, wR2 (all data)	0.0532，0.1240

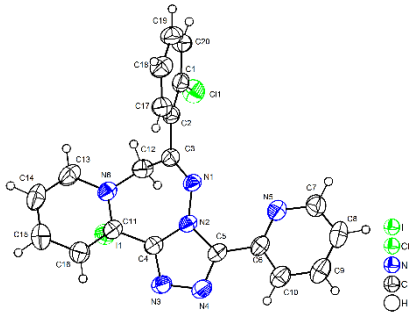


Fig.S2 X-ray crystal structure of compound Q21(CCDC number: 1944955)

Table S2 Summary of X-ray crystallographic data for compound Q21

formula	$C_{20}H_{14}ClIN_6$
Fw.	500.00
crystal system	triclinic
space group	P-1
a/Å	7.6849(4)
b/Å	11.3310(5)
c/Å	14.1776(7)
α/°	94.684(2)
β/°	94.245(2)
γ/°	106.982(2)
V/Å^3	1170.56(10)
Z	2
D/g cm^{-3}	1.642
cryst size/mm	0.160×0.0.150×0.130
reflns collected	33753
ind reflns, *Rint*	4290, 0.0316
goodness-of-fit on F^2	1.095
R1, wR2 [I > 2σ(I)]	0.0193, 0.0469
R1, wR2 (all data)	0.0220, 0.0481

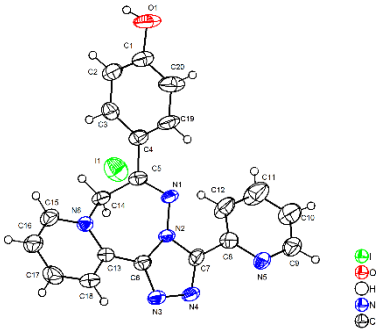


Fig.S3 X-ray crystal structure of compound Q12(CCDC number: 1944956)

Table S3 Summary of X-ray crystallographic data for compound Q12

formula	$C_{20}H_{15}IN_6O$
Fw.	482.28
crystal system	monoclinic
space group	$P2_1/c$
a/Å	8.0435(6)
b/Å	11.5711(10)
c/Å	27.338(2)
α/°	90
β/°	95.054(5)
γ/°	90

V/Å^3	2534.5(3)
Z	4
D/g cm^{-3}	1.264
cryst size/mm	0.210×0.180×0.140
reflns collected	26413
ind reflns, *Rint*	6311, 0.1080
goodness-of-fit on F^2	1.041
R1, wR2 [I > 2σ(I)]	0.0722, 0.1699
R1, wR2 (all data)	0.1421, 0.1942

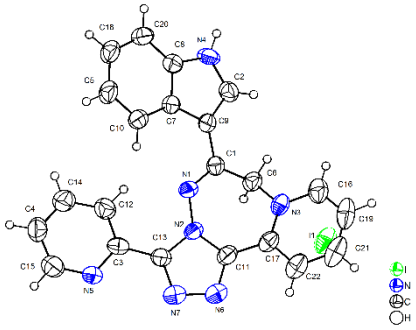


Fig.S4 X-ray crystal structure of compound Q35(CCDC number: 1944957)

Table S4 Summary of X-ray crystallographic data for compoundQ35

formula	$C_{22}H_{16}IN_7$
Fw.	505.32
crystal system	orthorhombic
space group	Pbca
a/Å	21.618(3)
b/Å	7.8792(10)
c/Å	23.619(3)
α/°	90
β/°	90
γ/°	90
V/Å^3	4023.2(9)
Z	8
D/g cm^{-3}	1.669
cryst size/mm	0.250×0.220×0.210
reflns collected	20750
ind reflns, *Rint*	4042 ,0.0780
goodness-of-fit on F^2	1.021
R1, wR2 [I > 2σ(I)]	0.0487, 0.1005
R1, wR2 (all data)	0.1005, 0.1206

8. PL decay lifetime of fluorescence

The luminescent decays and double-exponential fits of substances, respectively, in the solid-state. And the lifetime measurements were determined by monitoring the λ_{max} of emission in all cases (Ex = 390 nm).

Table S4 Different lifetime of Q3, Q5, Q6, Q8, Q9, Q10, Q11, Q15, Q16, Q18, Q19, Q26, Q28

Compound [a]	λabs[nm]	χ2 > 1	τ1(ns)	Rel%	τ2(ns)	Rel%
Q3	390	1.052	47.07	33.72	149.05	66.28
Q5	390	1.237	272.69	21.26	1093.01	78.74
Q6	390	1.013	98.47	35.47	338.48	64.53
Q8	390	1.005	210.46	23.22	520.46	76.78
Q9	390	1.107	76.27	36.19	213.09	63.81
Q10	390	1.144	84.50	27.90	209.69	72.10
Q11	390	1.012	29.20	34.09	90.17	65.91
Q15	390	1.000	200.18	46.99	925.68	53.01
Q16	390	1.000	52.39	24.29	129.85	75.71
Q18	390	1.117	391.18	18.70	1060.60	81.30
Q19	390	1.110	197.07	14.45	626.32	85.55
Q26	390	1.015	164.12	22.52	458.57	77.48
Q28	390	1.098	56.32	44.50	258.02	55.50

[a] The luminescence decay curves were all obtained at room temperature

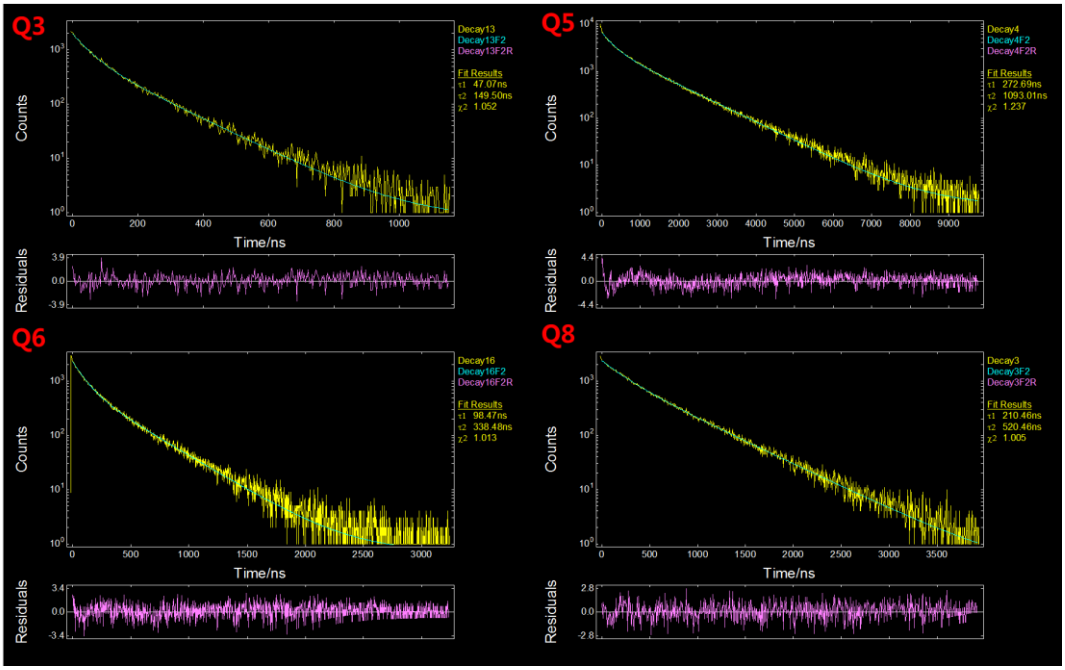


Fig.S5 PL decay lifetime of Q3, Q5, Q6, Q8

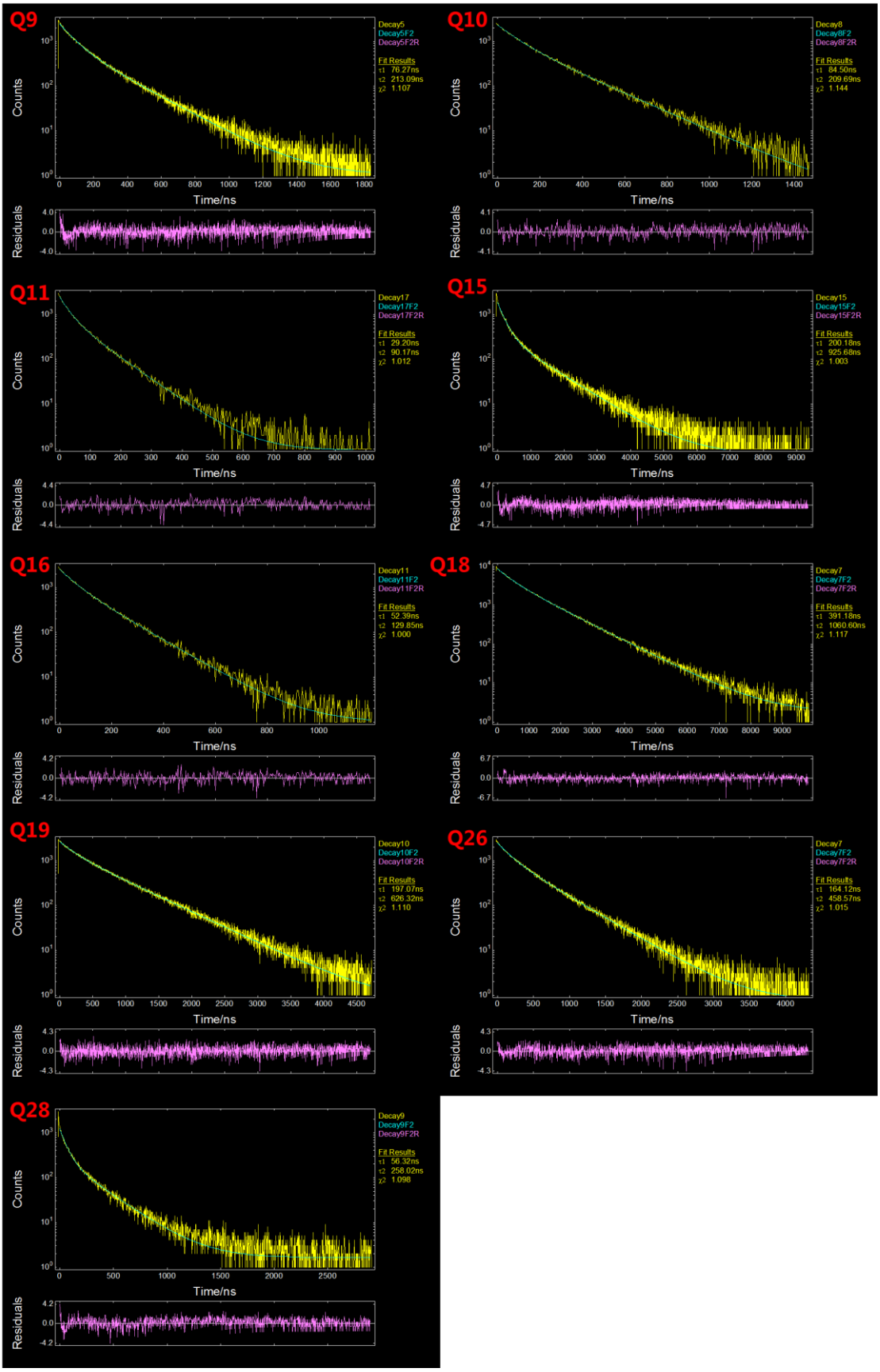


Fig.S6 PL decay lifetime of Q9, Q10, Q11, Q15, Q18, Q19, Q26, Q28

8. Computational results from density functional theory analysis

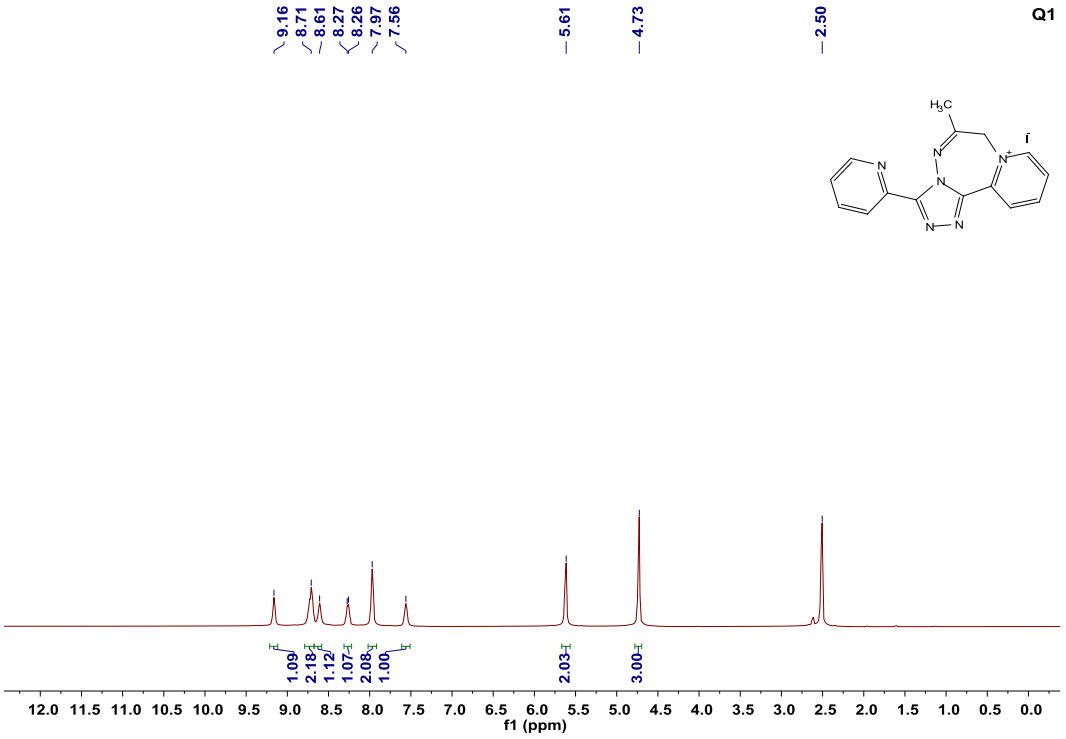
Table S5 Computational results of Q5, Q12, Q21, Q35

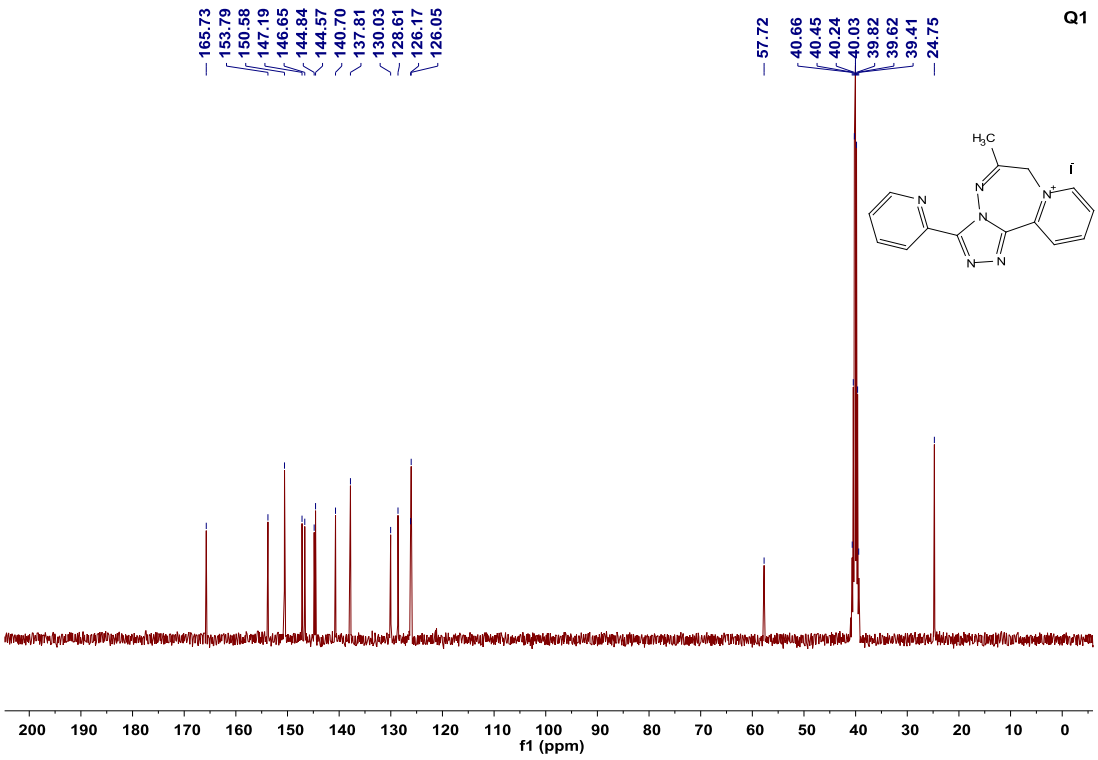
Compounds	Excitation energies	oscillator strengths(*f*)
Q5	3.2051 eV	0.1233
Q12	3.0471eV	0.0009
Q21	3.1555eV	0.0029
Q35	2.8901eV	0.0294

DFT[3]calculations have been applied to clarify the structure-functional relationship of these triazepinium salts via Gaussian 09 program[4]. The structures were optimized under a combination of basis of 6-31G basis set for H, C elements and 6-31+G**for N, O, Cl elements with B3LYP functional[5]. The optimized structures were confirmed to be local minimums due to the non-existence of imaginary frequency.

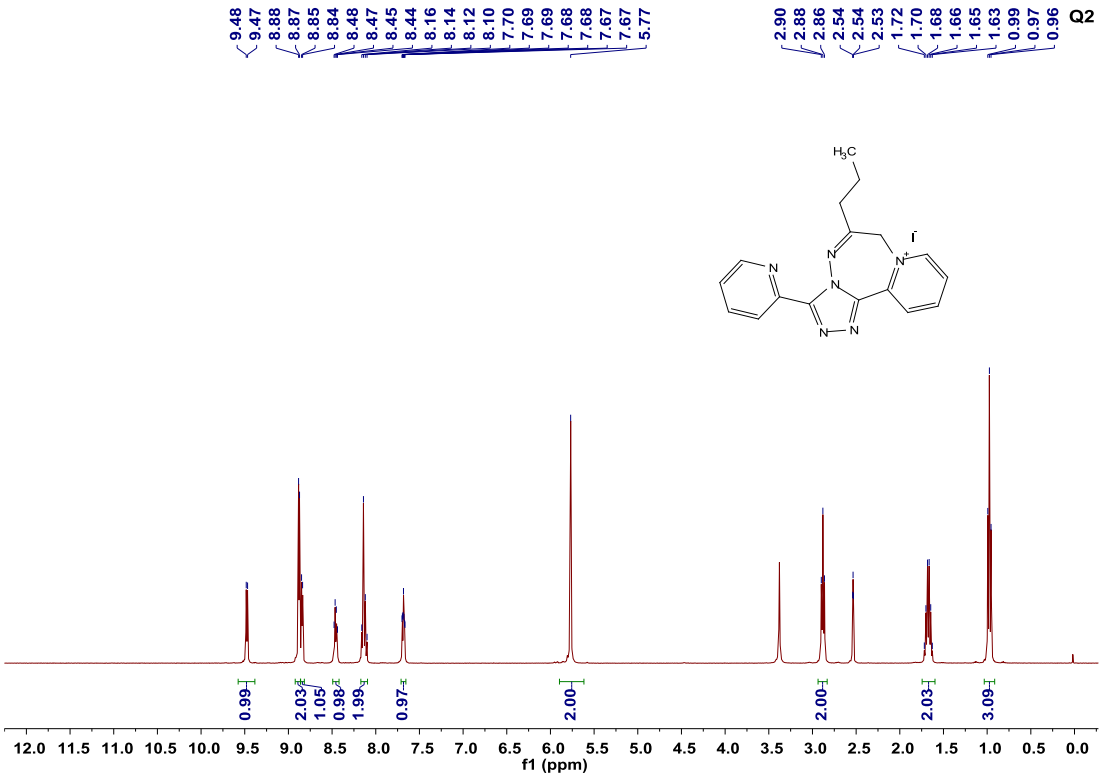
9. Appendix (copies of ^{1}H and ^{13}C NMR spectra)

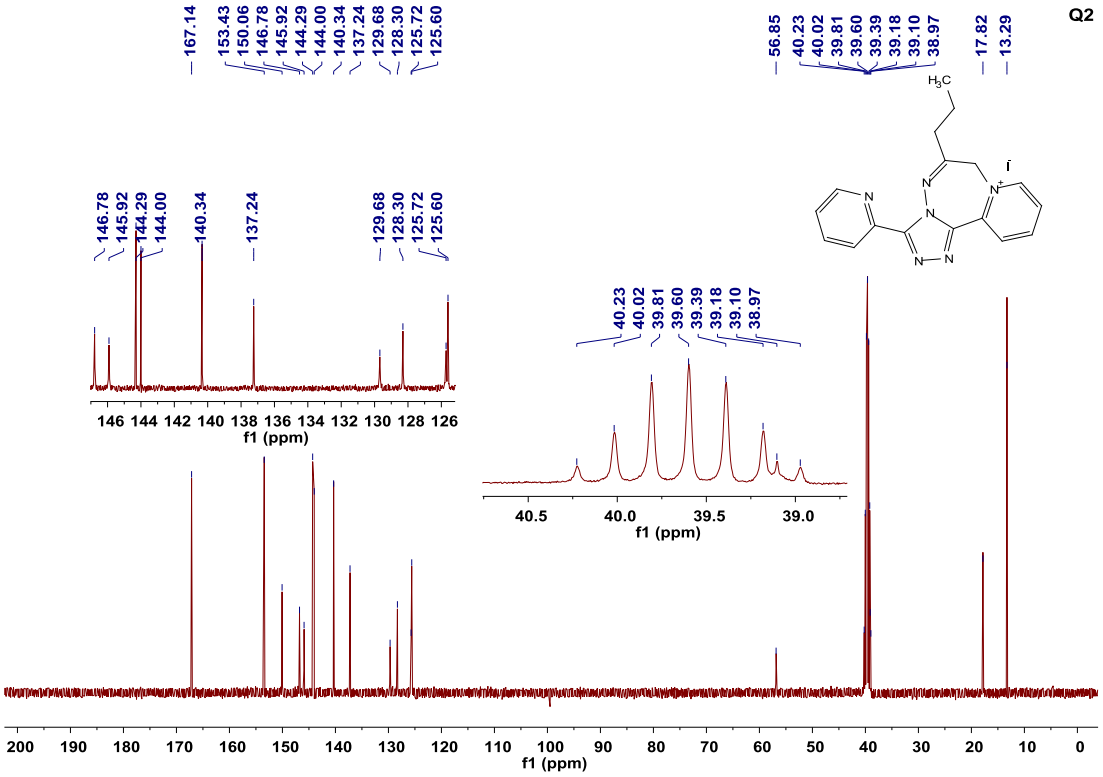
6-methyl-3-(pyridin-2-yl)-7H-pyrido[2,1-d][1,2,4]triazolo[4,3-b][1,2,5]triazepin-8-ium iodide(Q1)



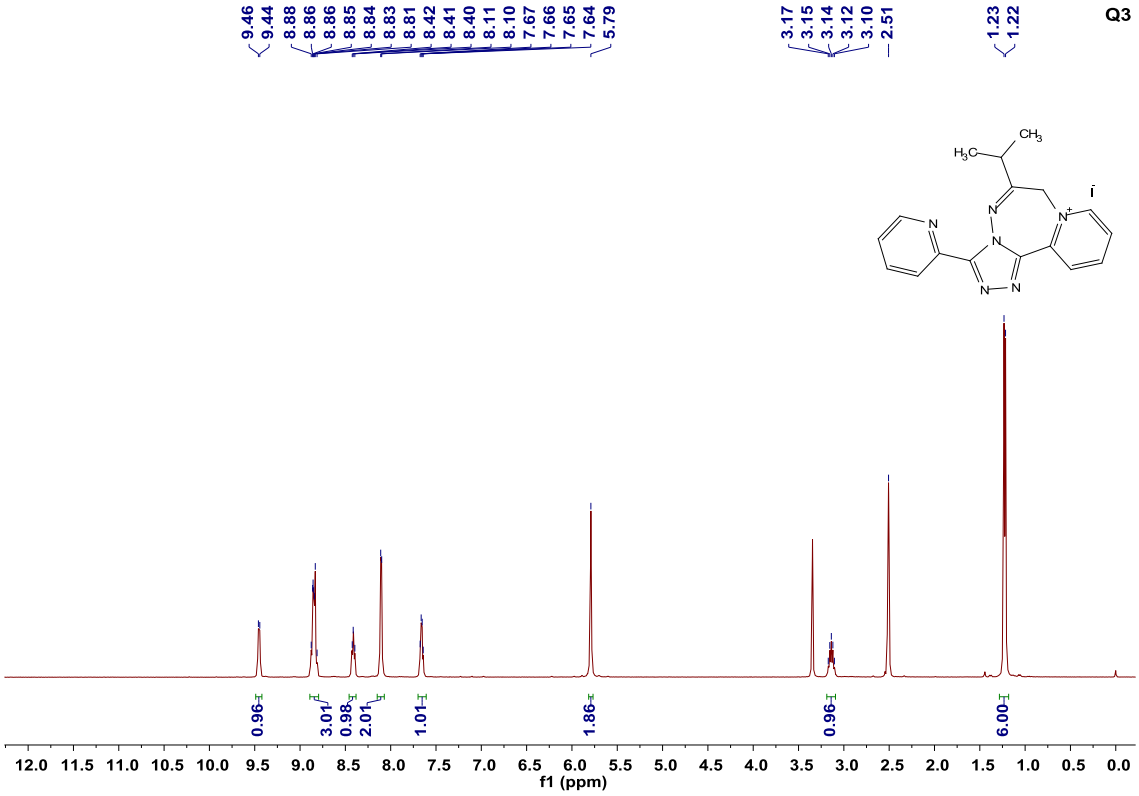


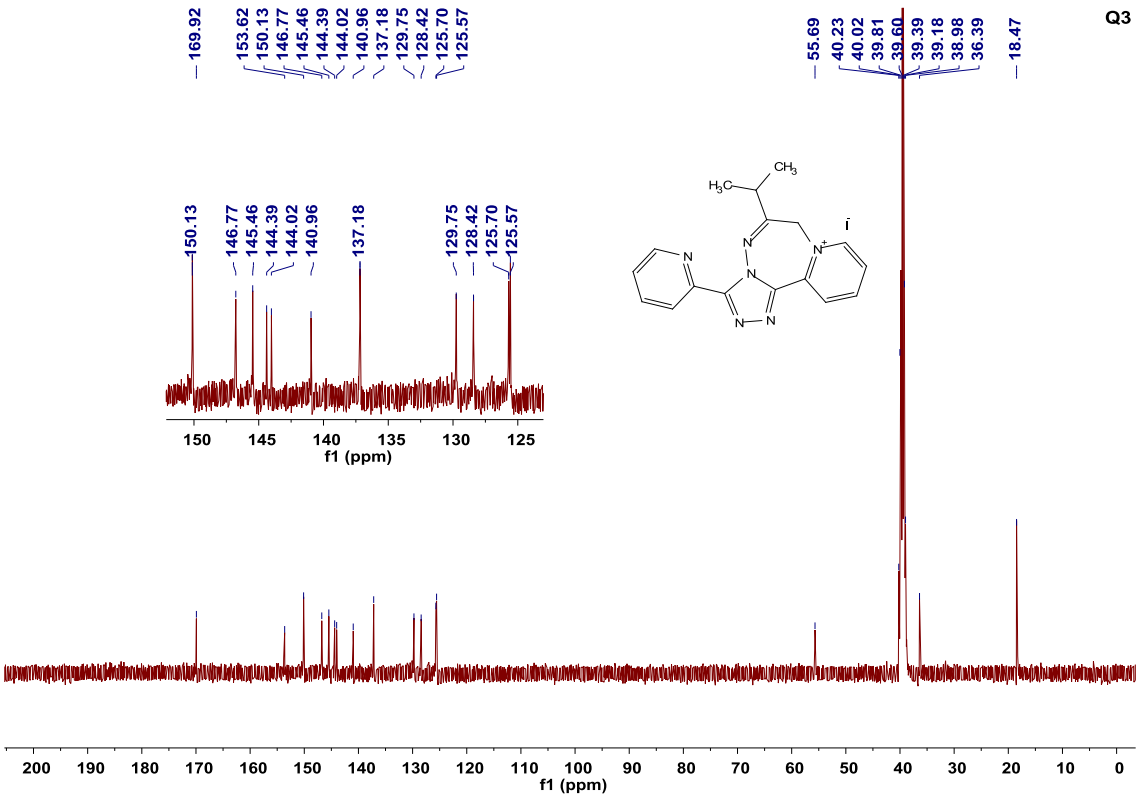
6-propyl-3-(pyridin-2-yl)-7H-pyrido[2,1-d][1,2,4]triazolo[4,3-b][1,2,5]triazepin-8-ium iodide(Q2)



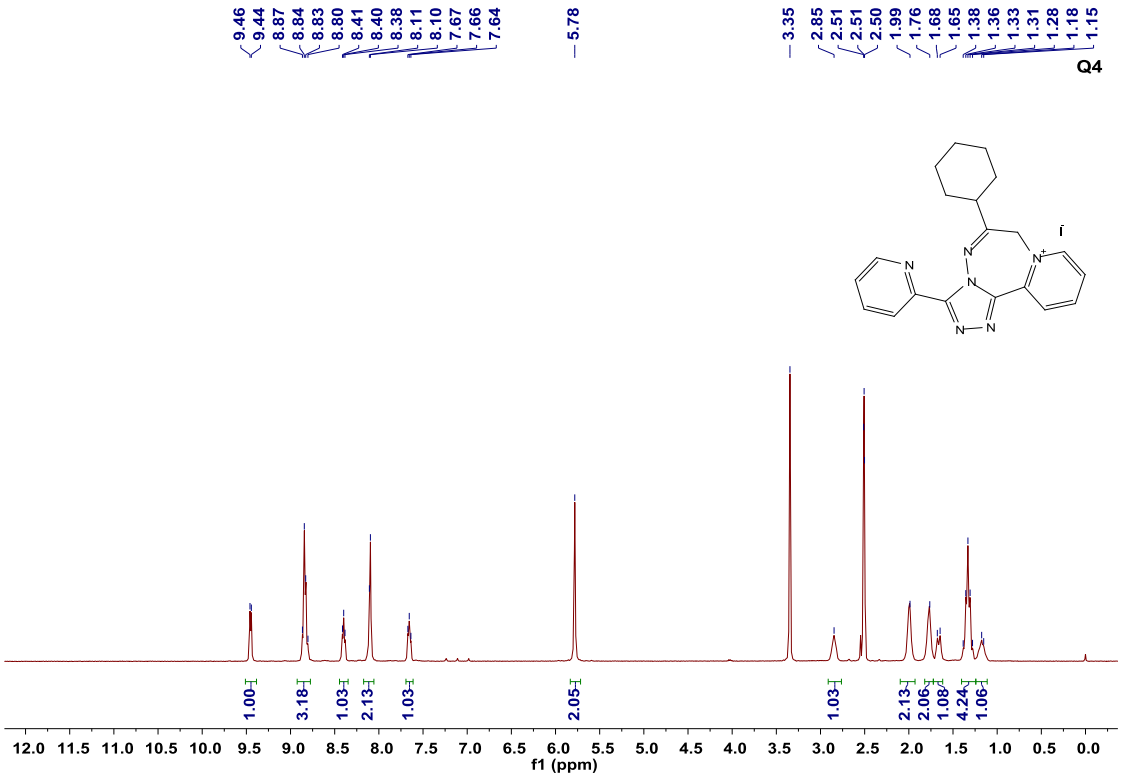


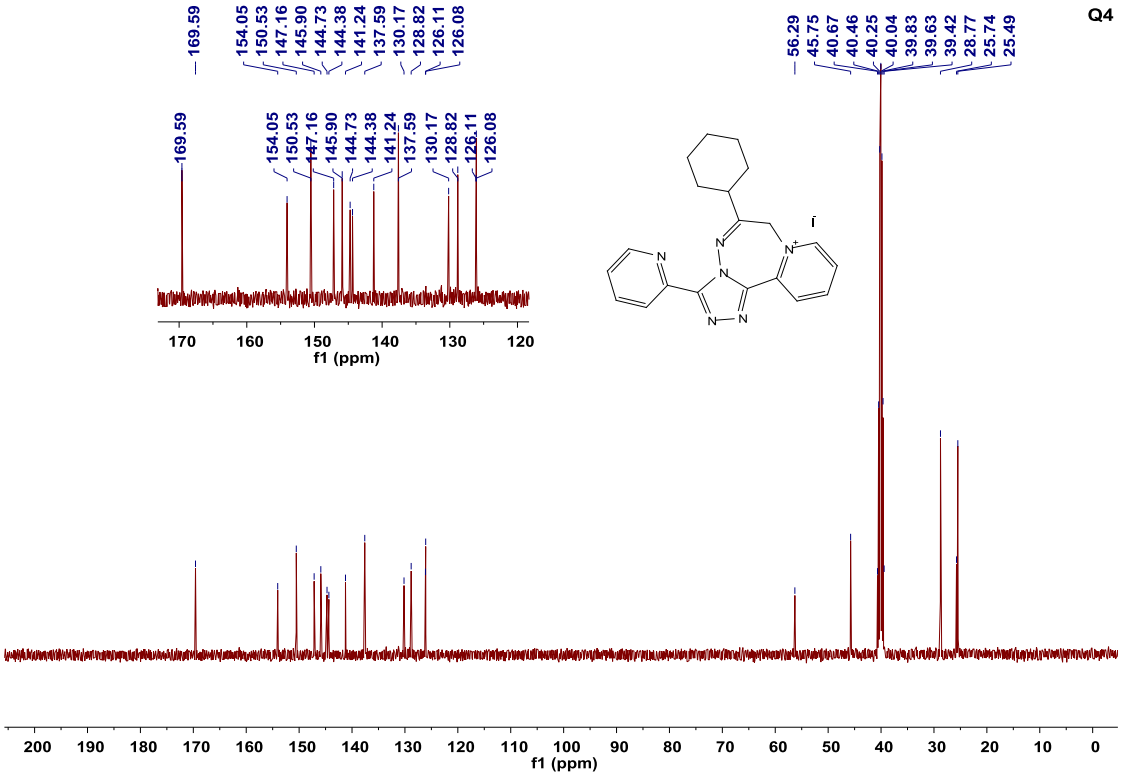
6-isopropyl-3-(pyridin-2-yl)-7H-pyrido[2,1-d][1,2,4]triazolo[4,3-b][1,2,5]triazepin-8-ium iodide(Q3)



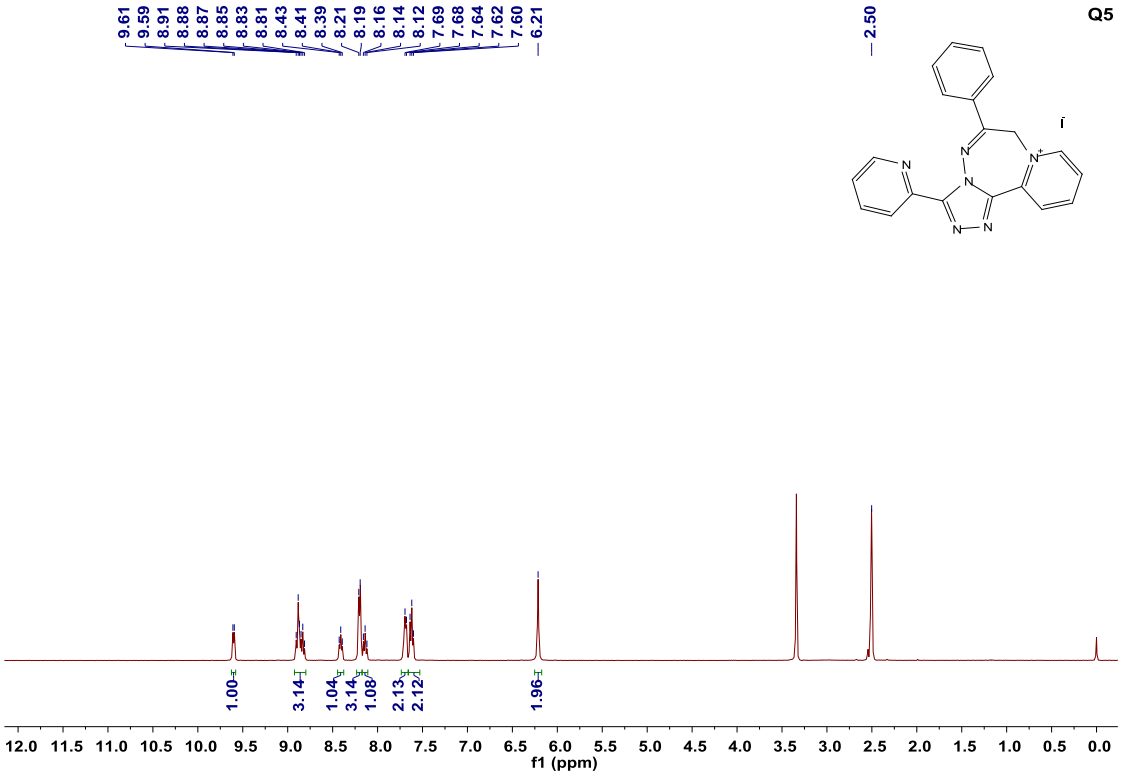


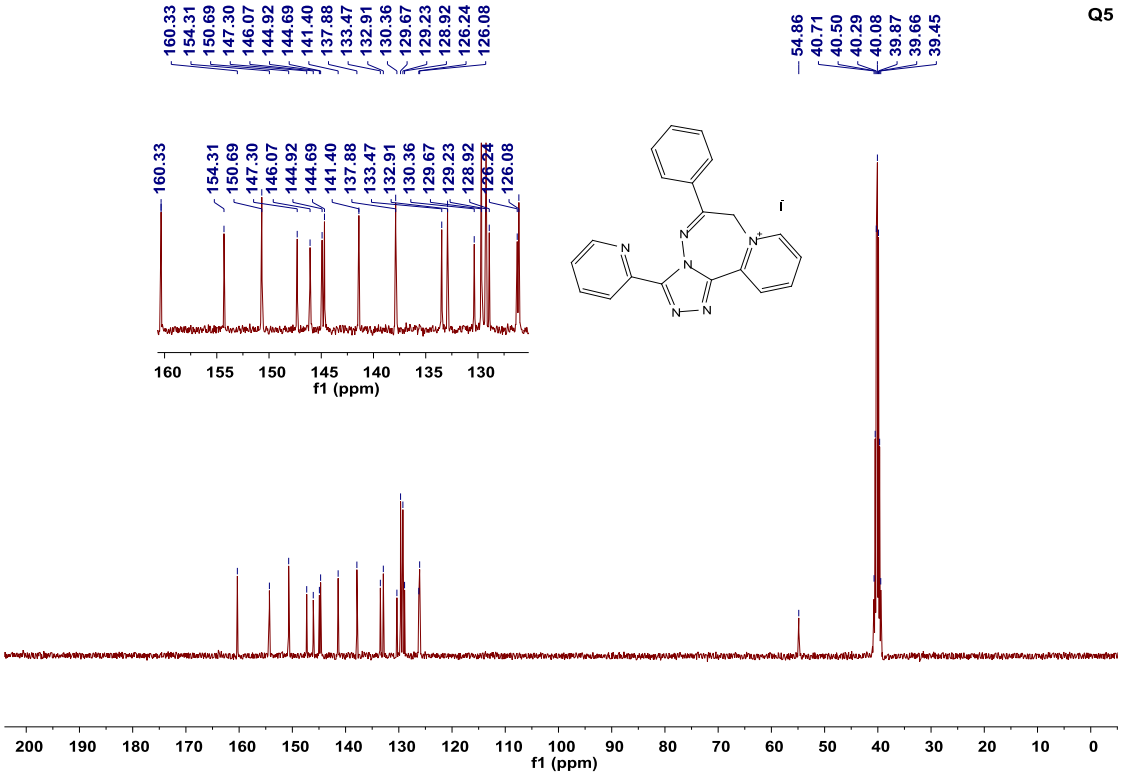
6-cyclohexyl-3-(pyridin-2-yl)-7H-pyrido[2,1-d][1,2,4]triazolo[4,3-b][1,2,5]triazepin-8-ium iodide(Q4)



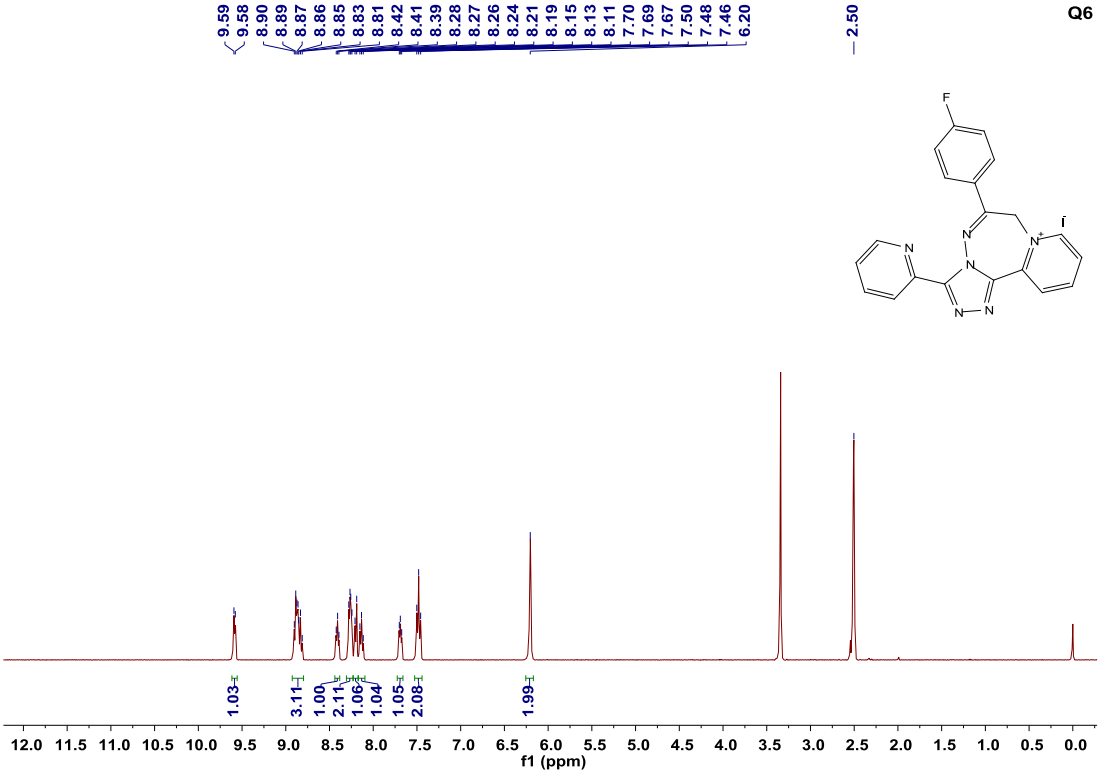


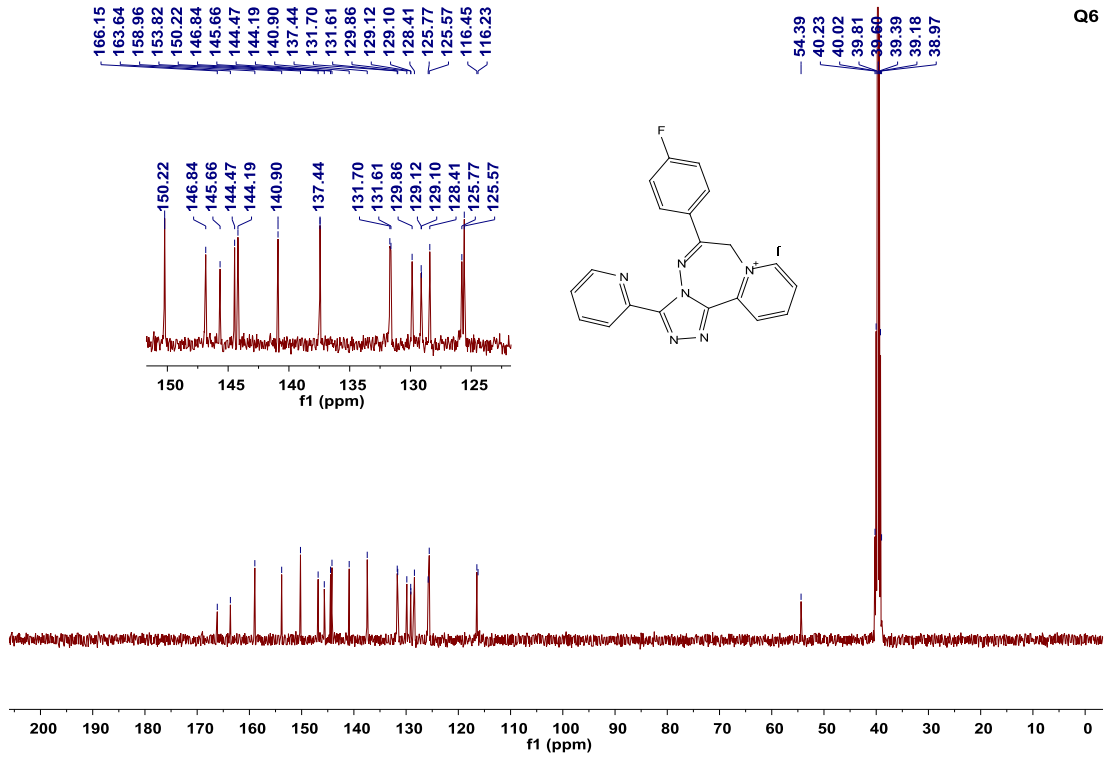
6-phenyl-3-(pyridin-2-yl)-7H-pyrido[2,1-d][1,2,4]triazolo[4,3-b][1,2,5]triazepin-8-ium iodide(Q5)



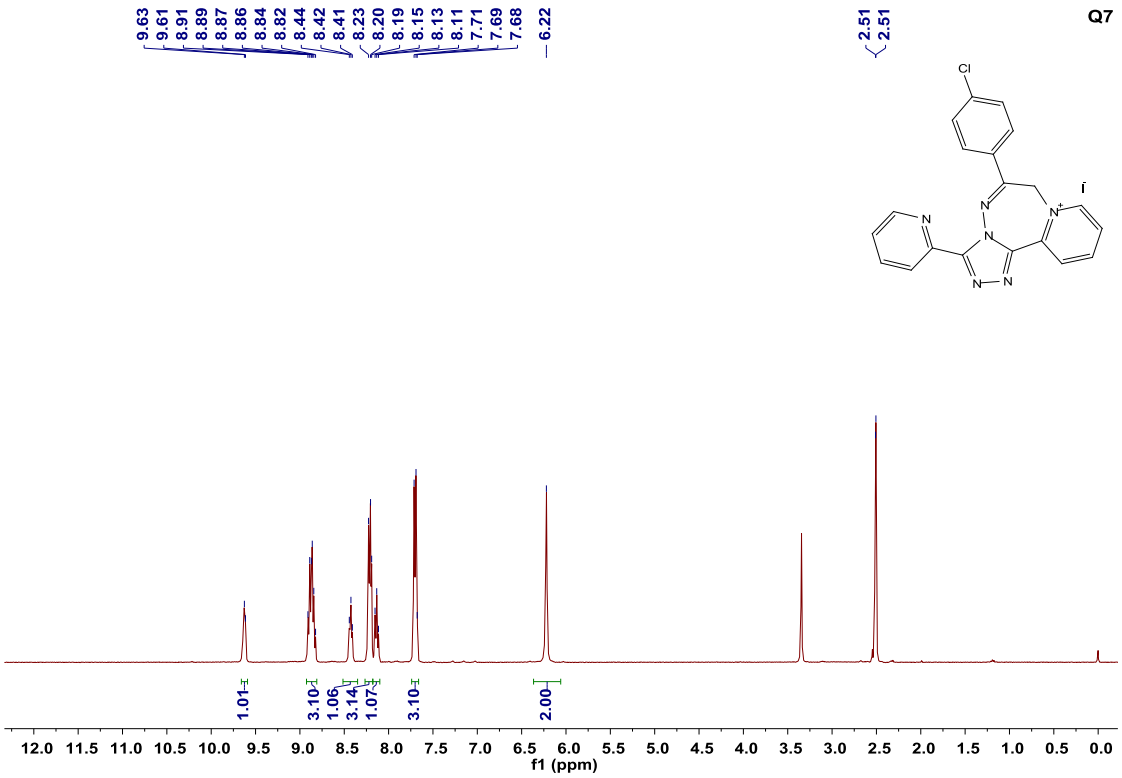


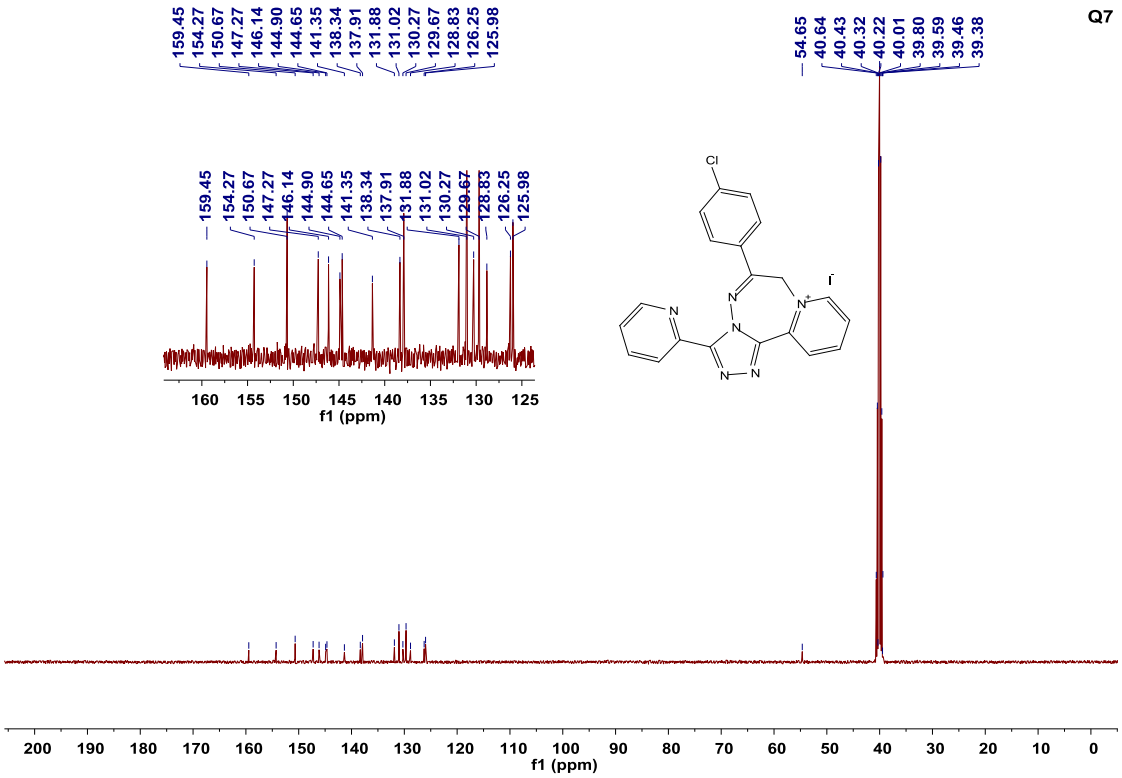
6-(4-fluorophenyl)-3-(pyridin-2-yl)-7H-pyrido[2,1-d][1,2,4]triazolo[4,3-b][1,2,5]triazepin-8-ium iodide(Q6)



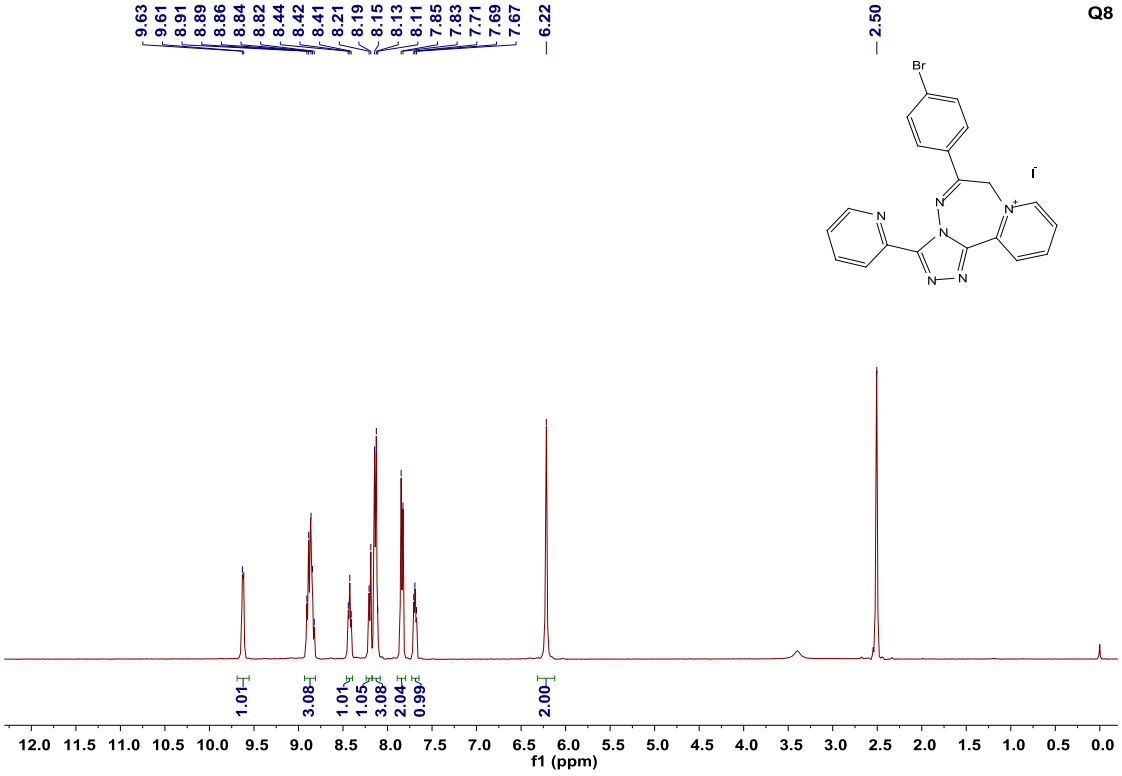


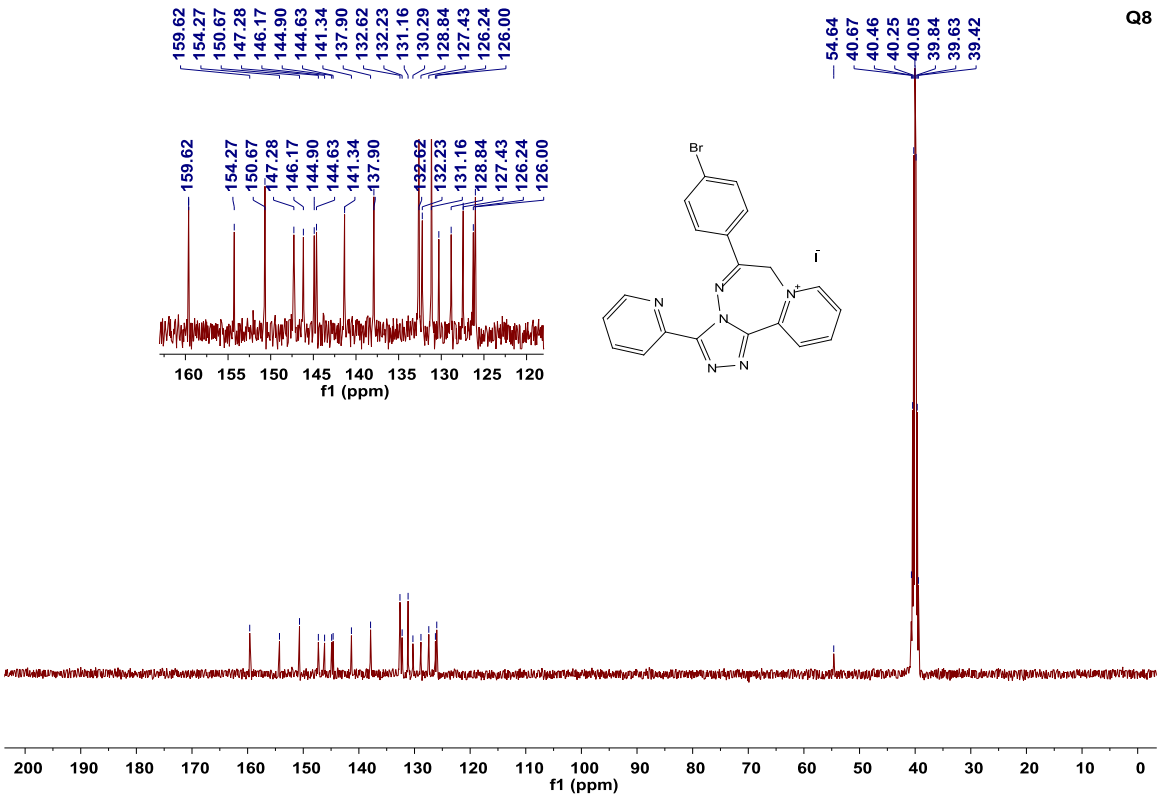
6-(4-chlorophenyl)-3-(pyridin-2-yl)-7H-pyrido[2,1-d][1,2,4]triazolo[4,3-b][1,2,5]triazepin-8-ium iodide(Q7)



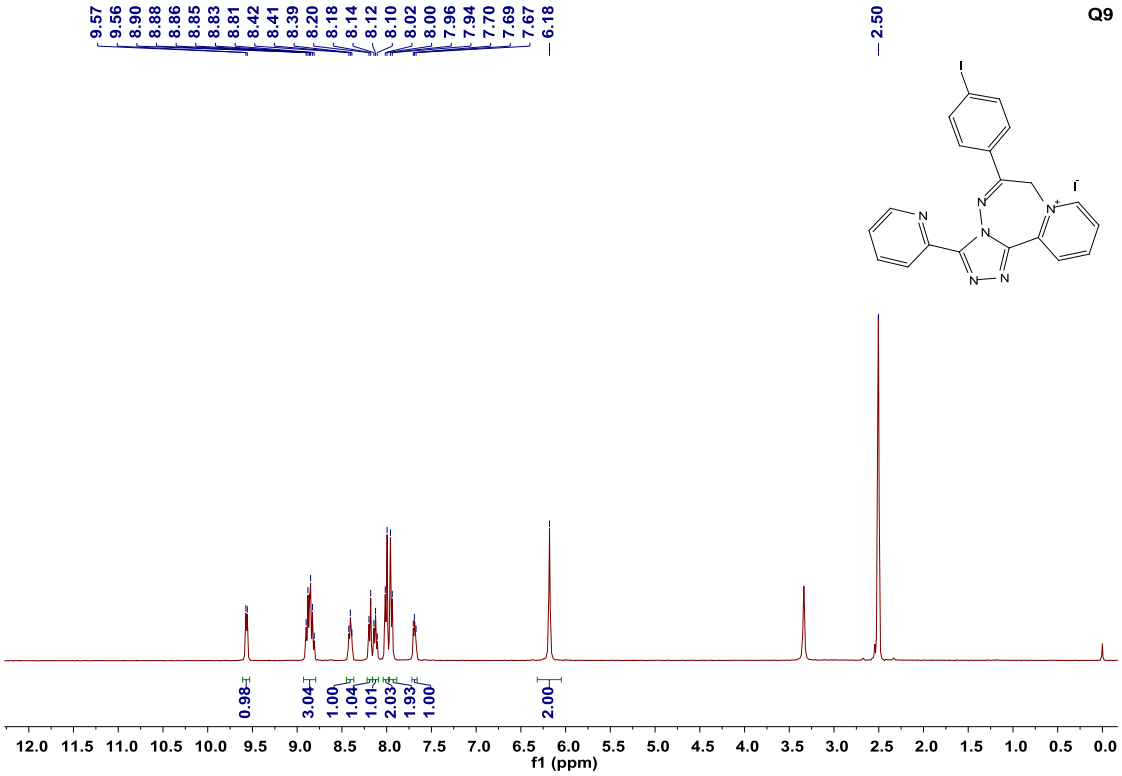


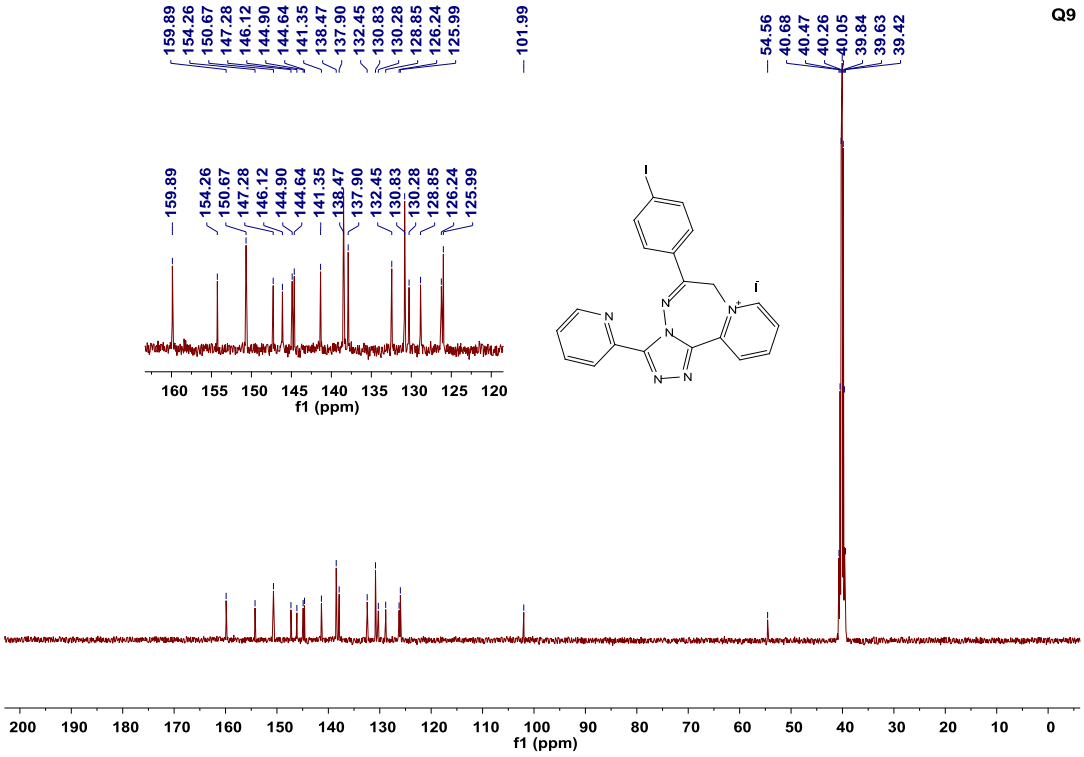
6-(4-bromophenyl)-3-(pyridin-2-yl)-7H-pyrido[2,1-d][1,2,4]triazolo[4,3-b][1,2,5]triazepin-8-ium iodide(Q8)



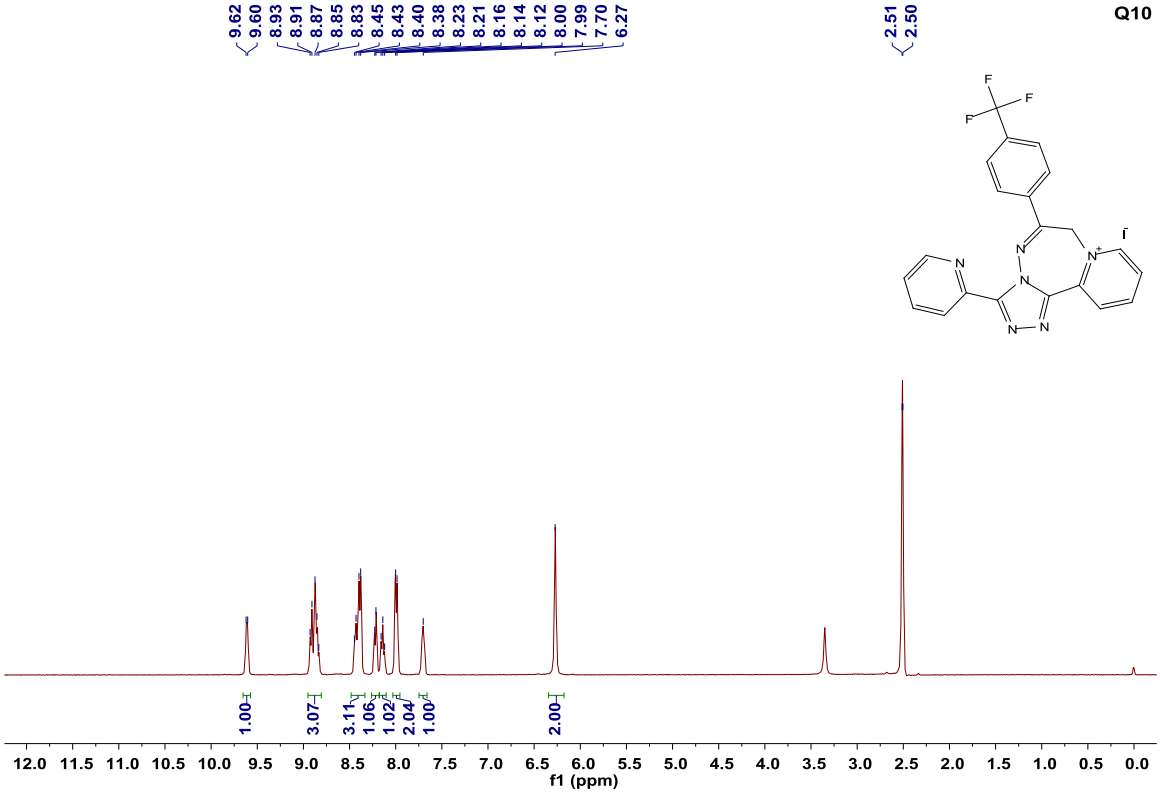


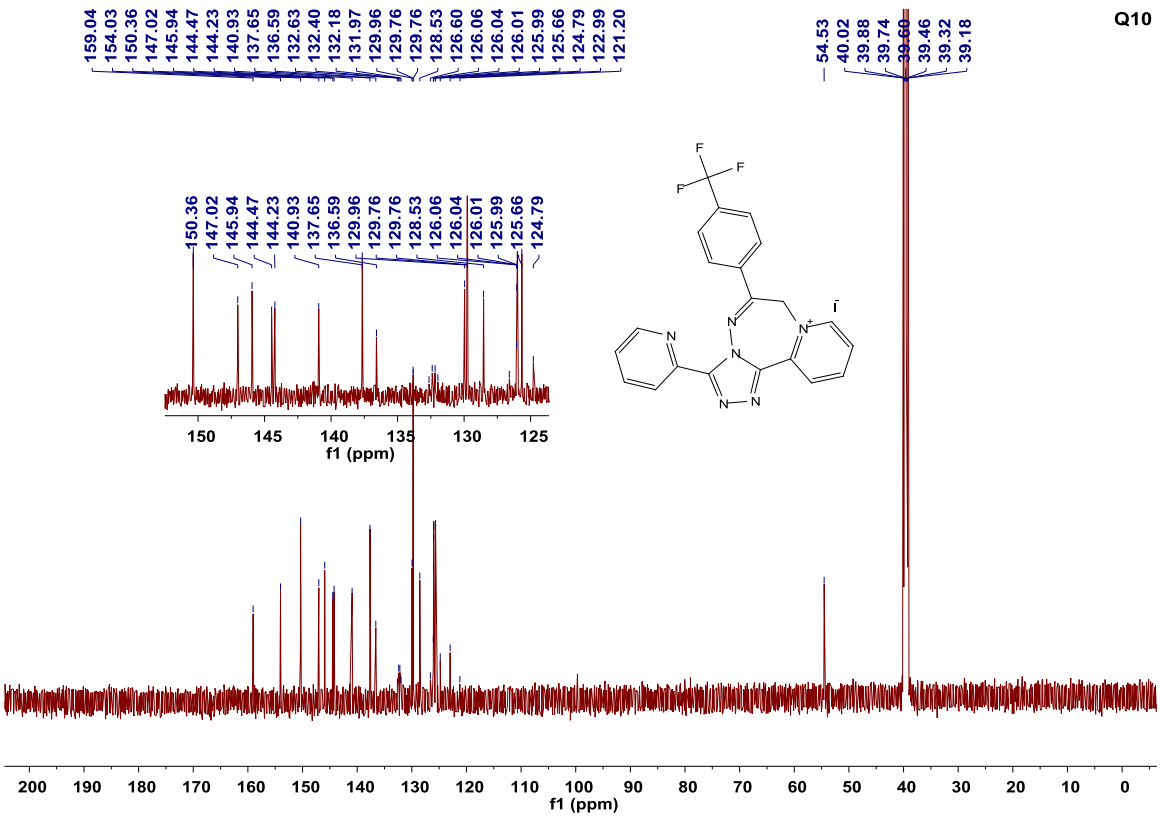
6-(4-iodophenyl)-3-(pyridin-2-yl)-7H-pyrido[2,1-d][1,2,4]triazolo[4,3-b][1,2,5]triazepin-8-ium iodide(Q9)



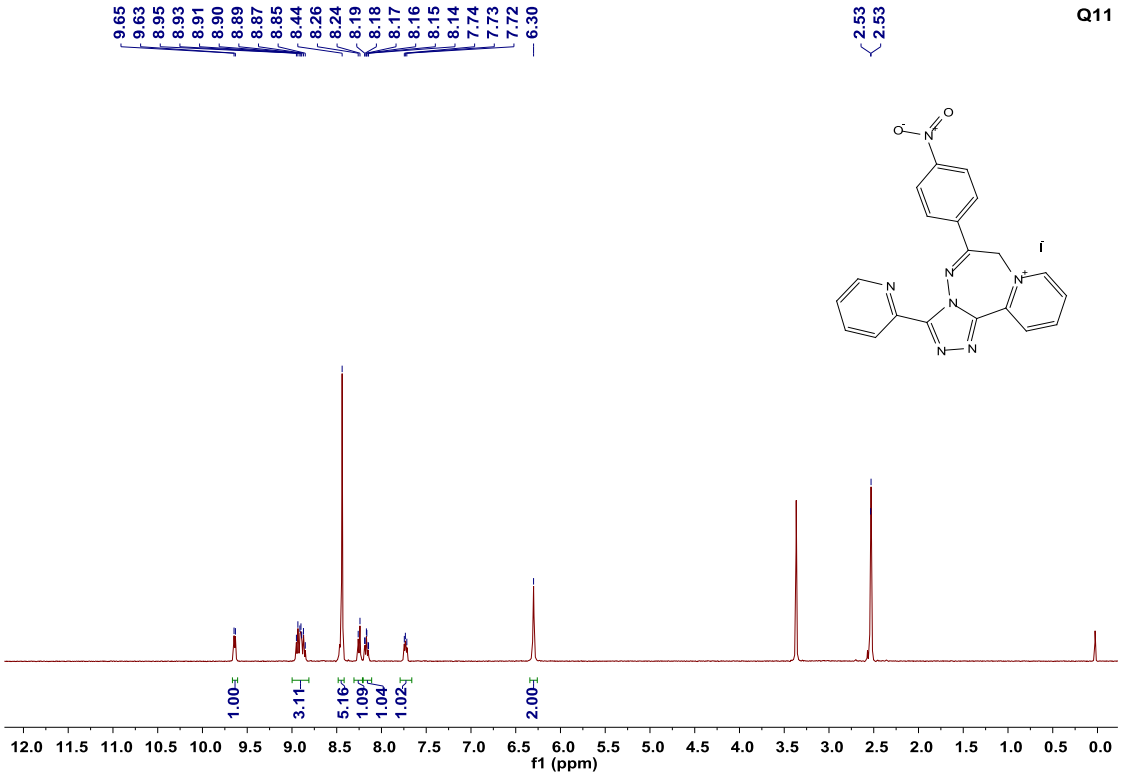


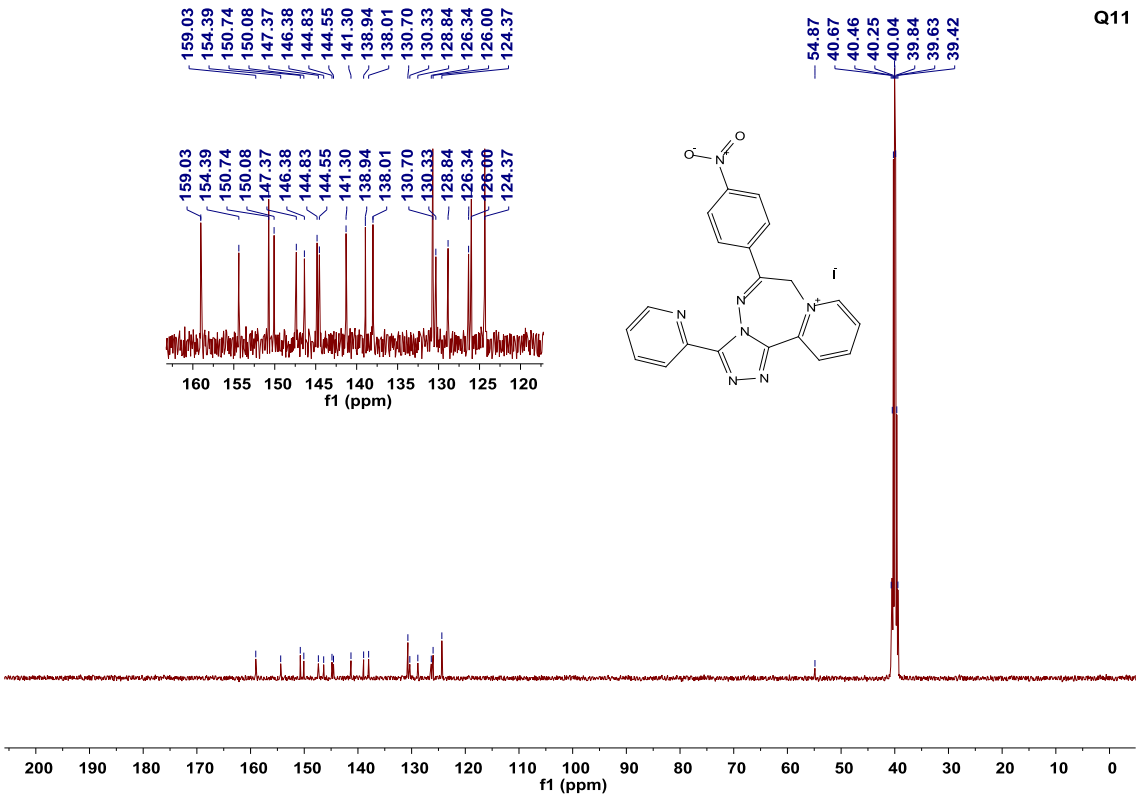
3-(pyridin-2-yl)-6-(4-(trifluoromethyl)phenyl)-7H-pyrido[2,1-d][1,2,4]triazolo[4,3-b][1,2,5]triazepin-8-ium iodide(Q10)



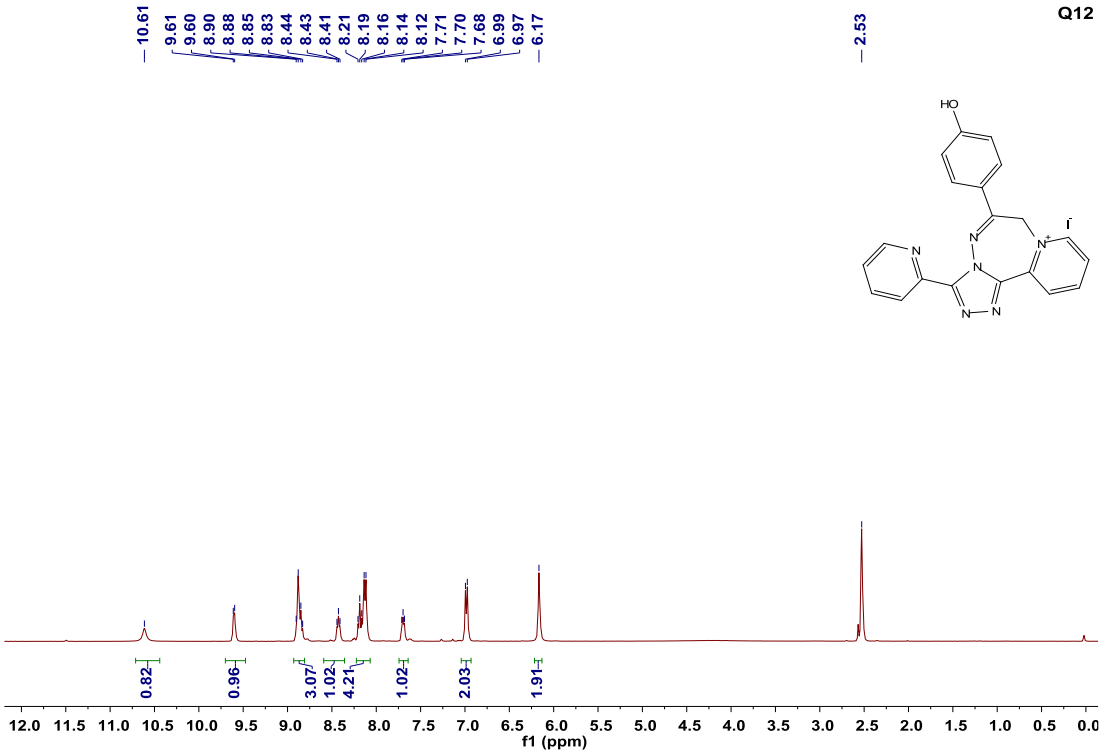


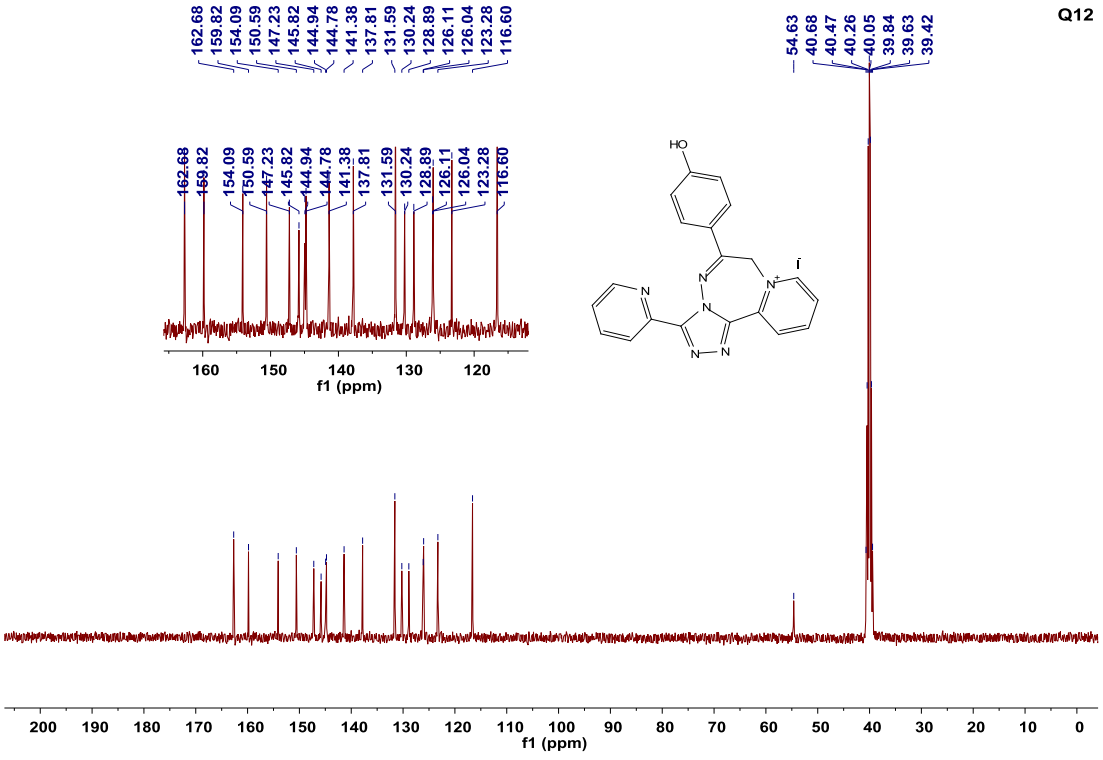
6-(4-nitrophenyl)-3-(pyridin-2-yl)-7H-pyrido[2,1-d][1,2,4]triazolo[4,3-b][1,2,5]triazepin-8-ium iodide(Q11)



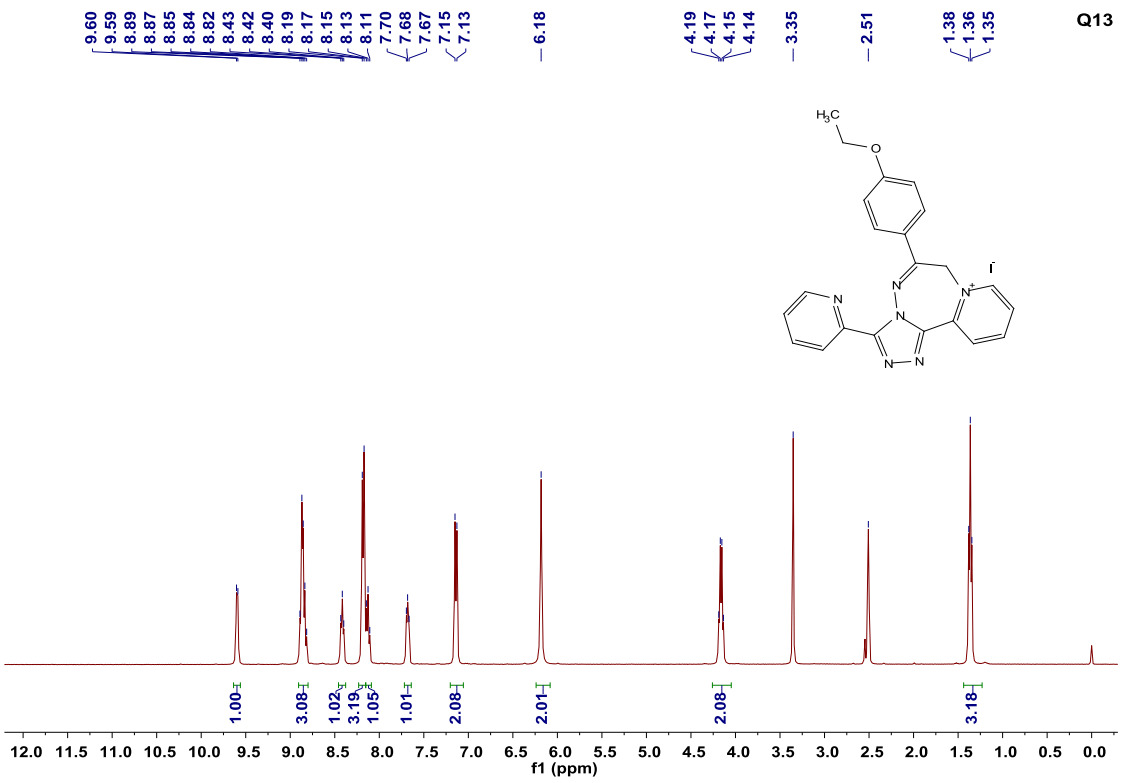


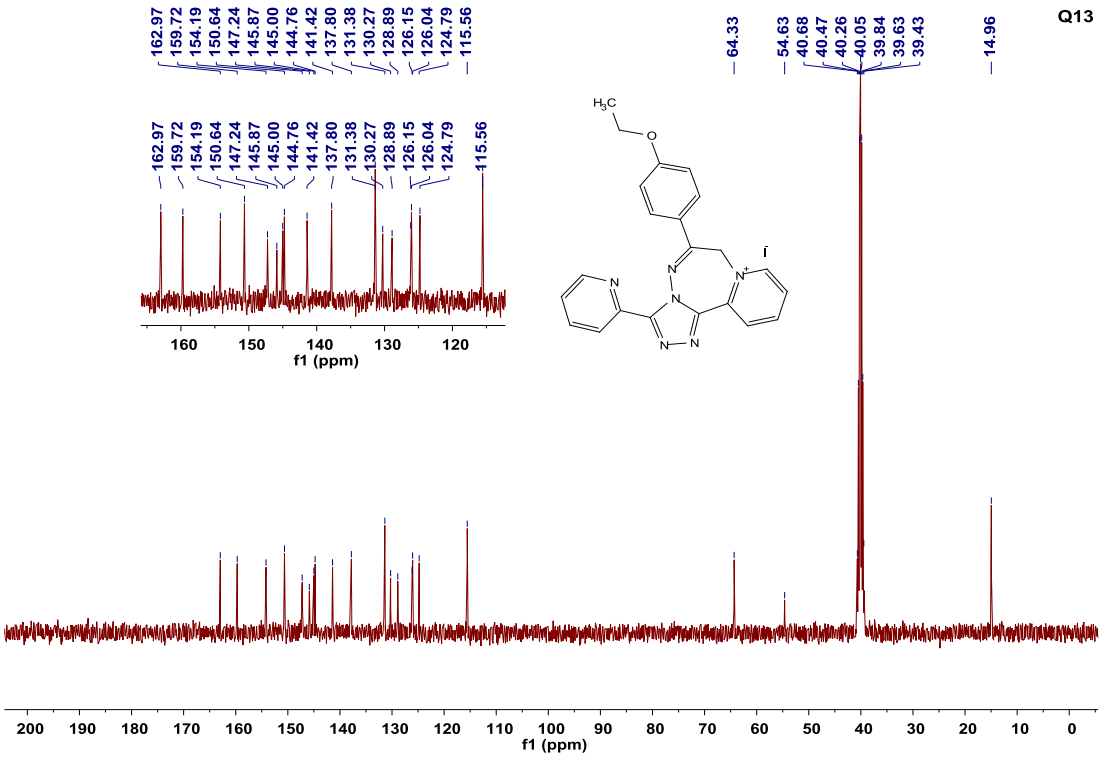
6-(4-hydroxyphenyl)-3-(pyridin-2-yl)-7H-pyrido[2,1-d][1,2,4]triazolo[4,3-b][1,2,5]triazepin-8-ium iodide(Q12)



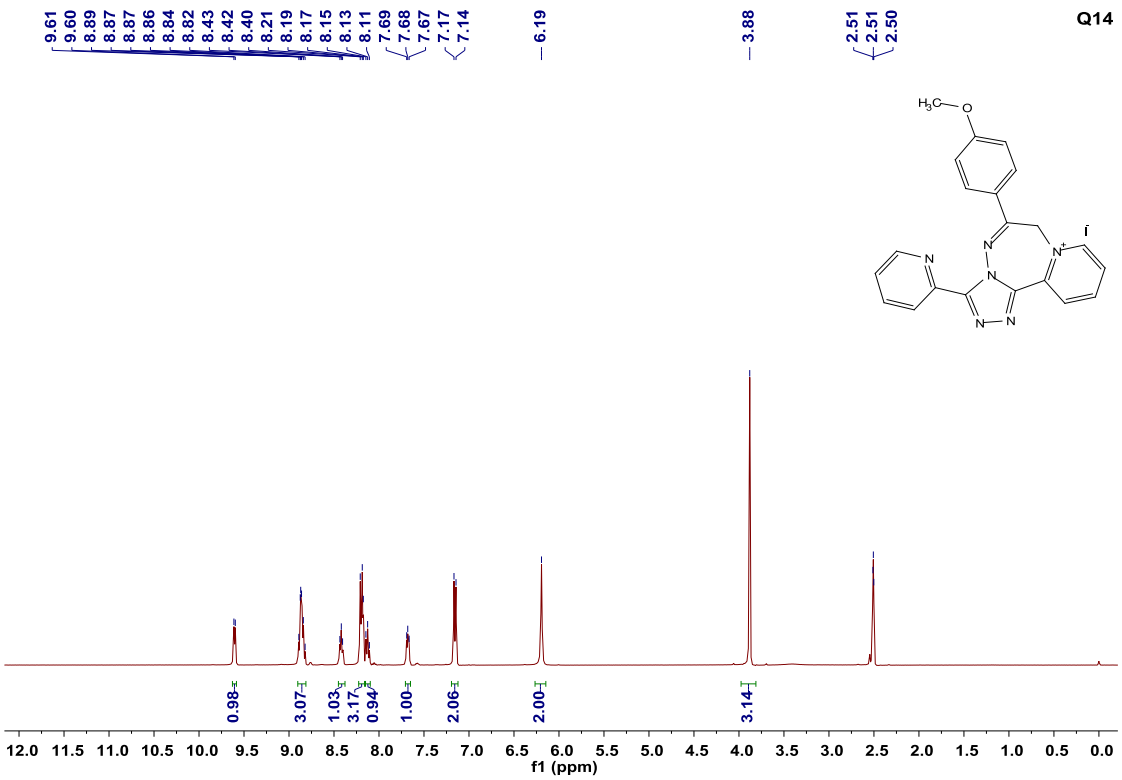


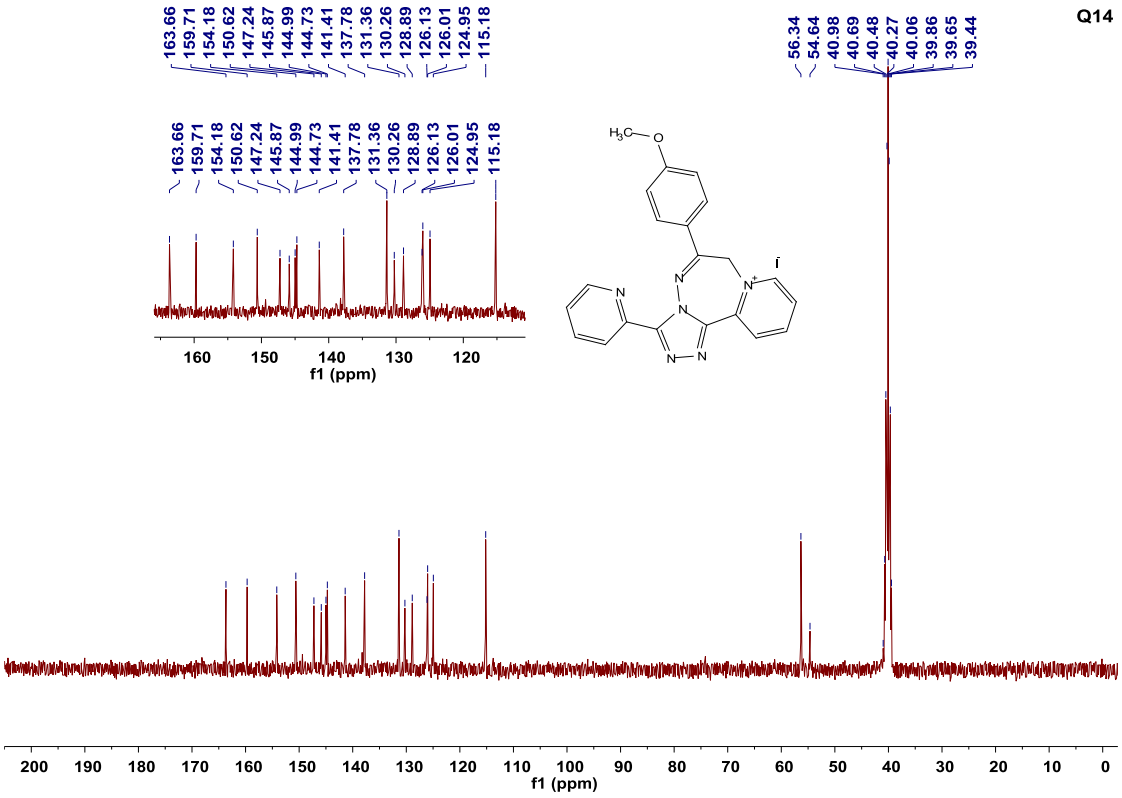
6-(4-ethoxyphenyl)-3-(pyridin-2-yl)-7H-pyrido[2,1-d][1,2,4]triazolo[4,3-b][1,2,5]triazepin-8-ium iodide(Q13)



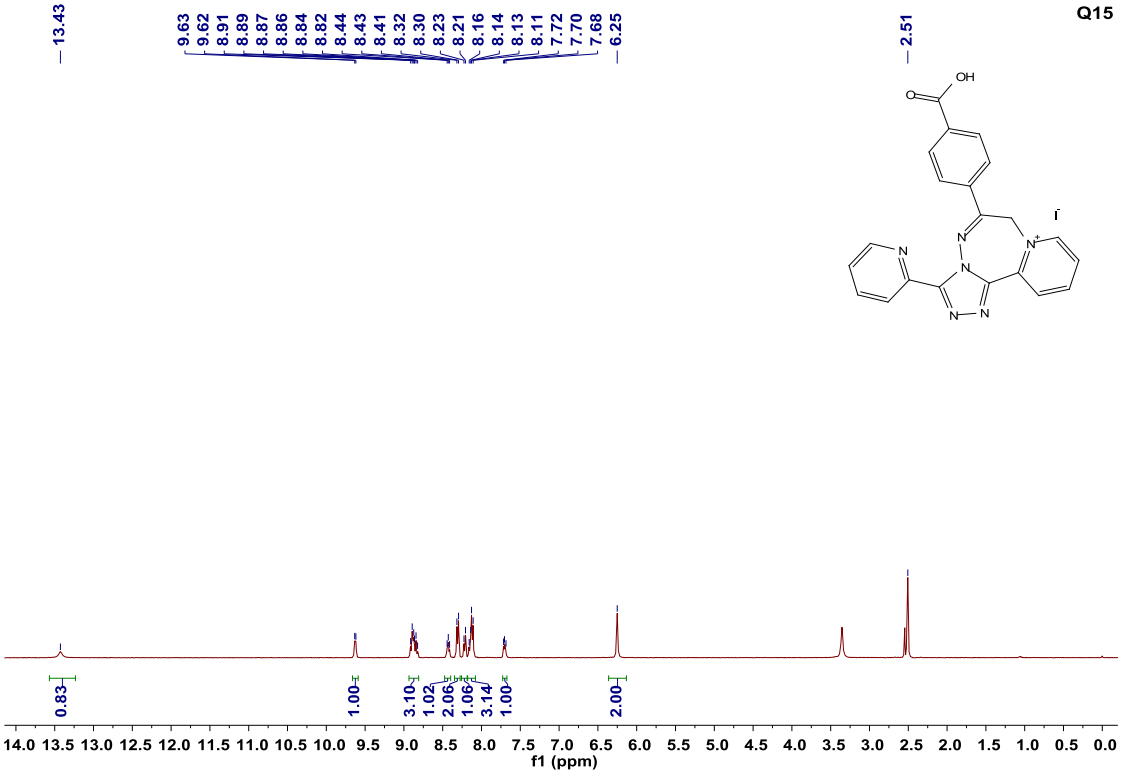


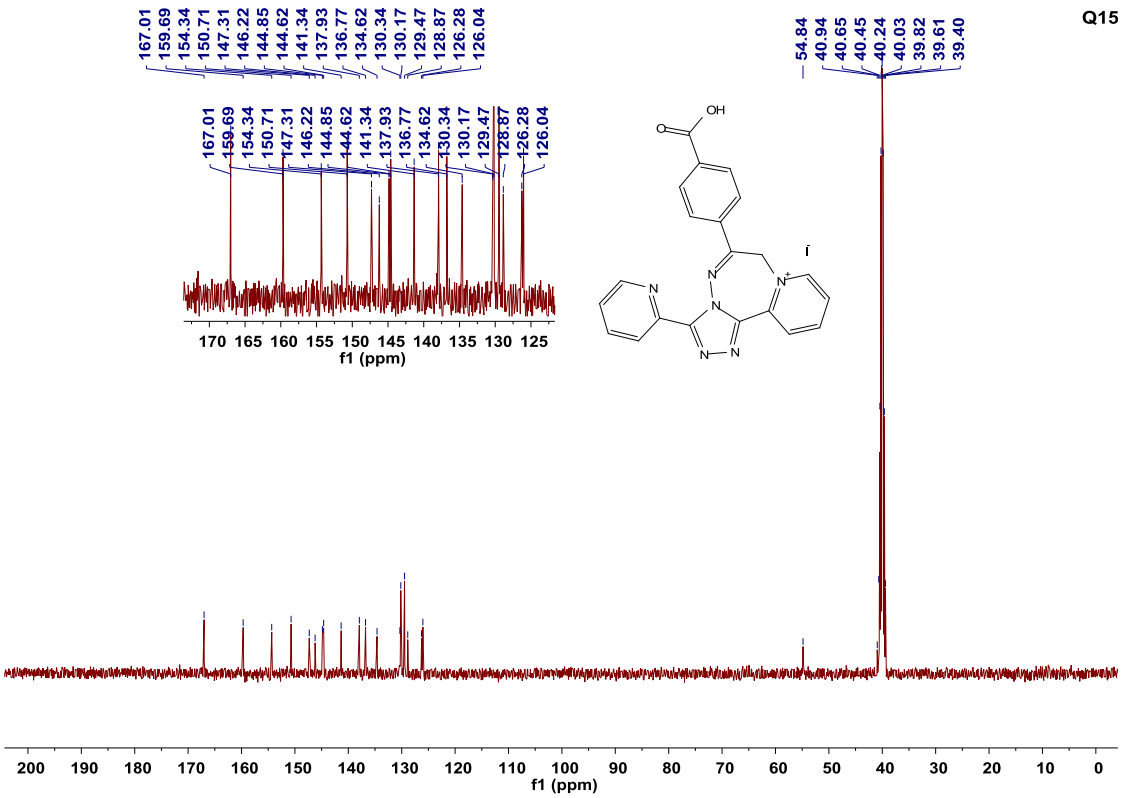
6-(4-methoxyphenyl)-3-(pyridin-2-yl)-7H-pyrido[2,1-d][1,2,4]triazolo[4,3-b][1,2,5]triazepin-8-ium iodide(Q14)



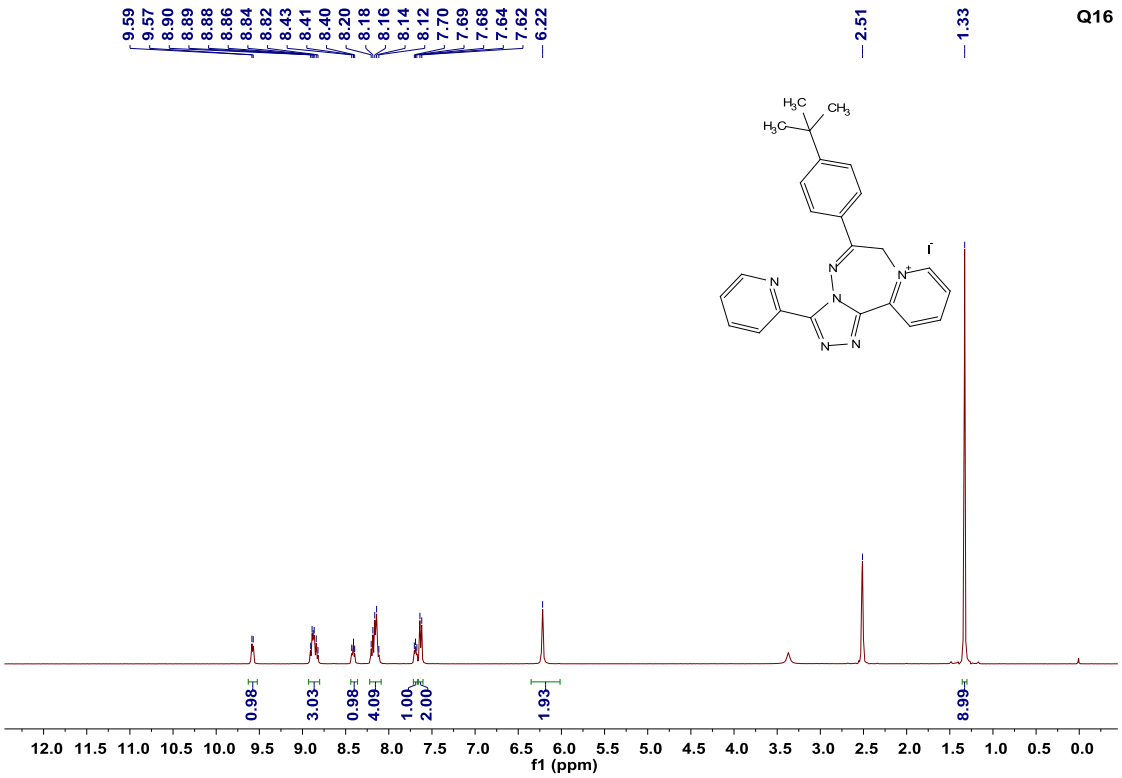


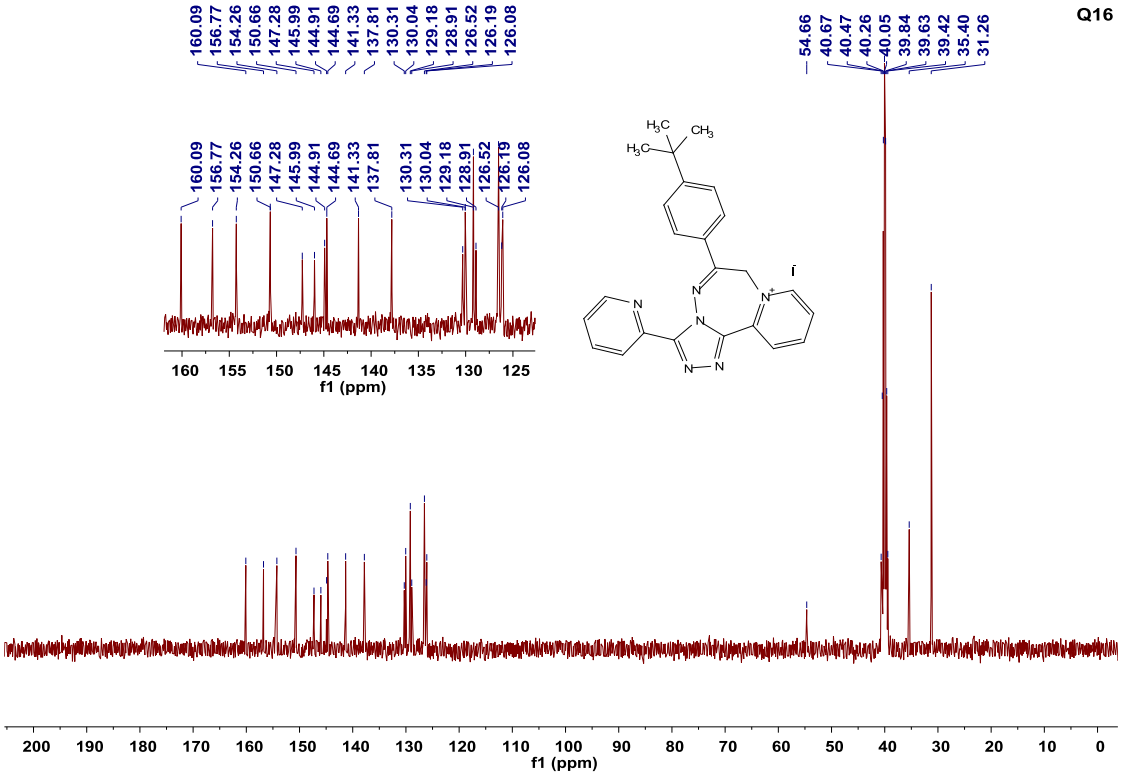
6-(4-carboxyphenyl)-3-(pyridin-2-yl)-7H-pyrido[2,1-d][1,2,4]triazolo[4,3-b][1,2,5]triazepin-8-ium iodide (Q15)



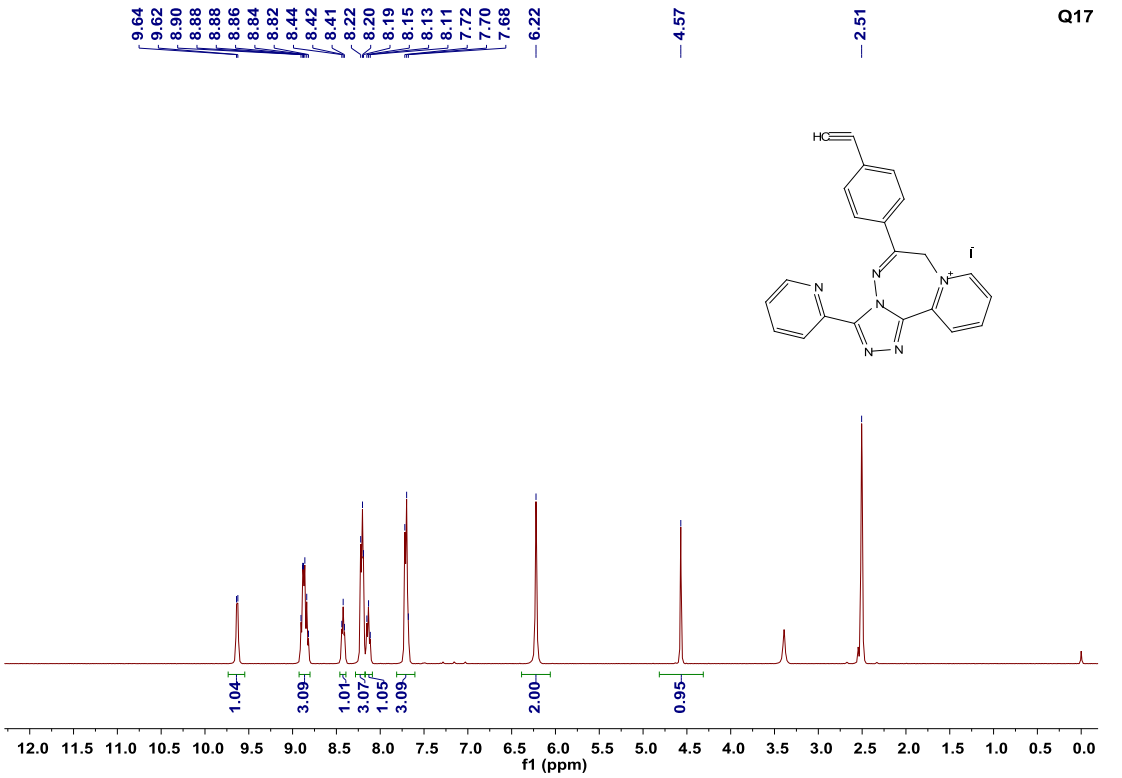


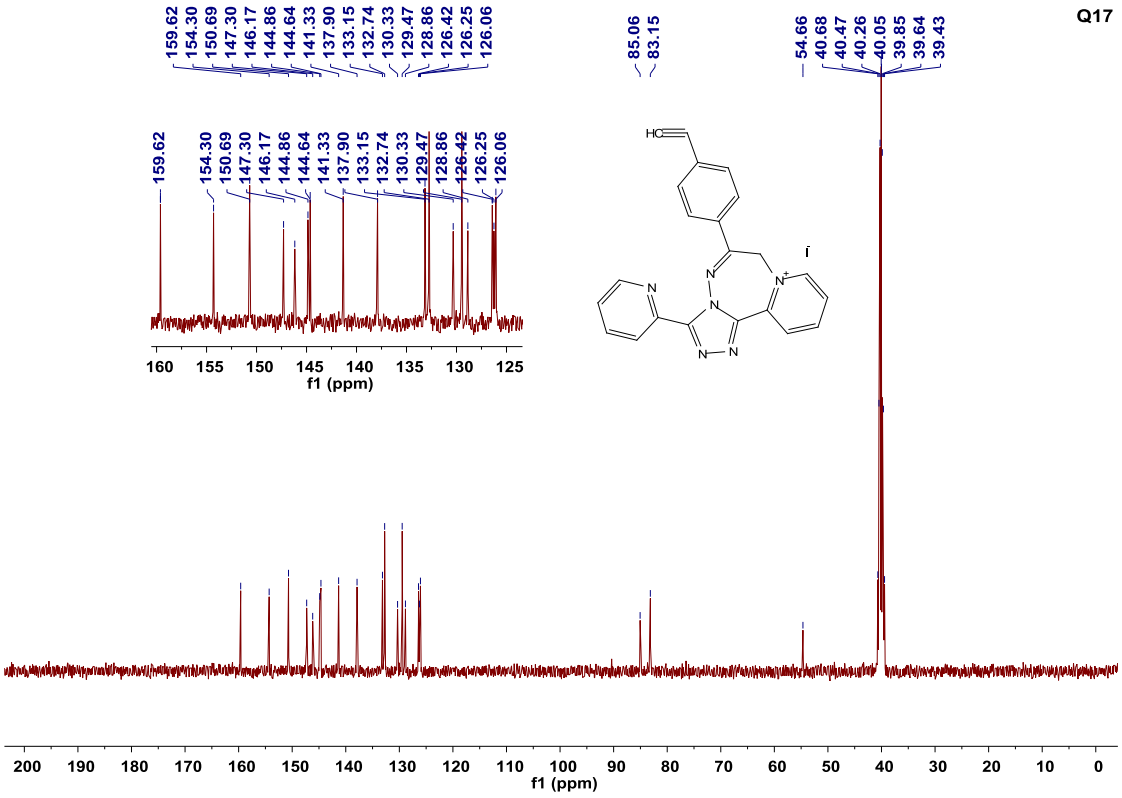
6-(4-(tert-butyl)phenyl)-3-(pyridin-2-yl)-7H-pyrido[2,1-d][1,2,4]triazolo[4,3-b][1,2,5]triazepin-8-ium iodide(Q16)



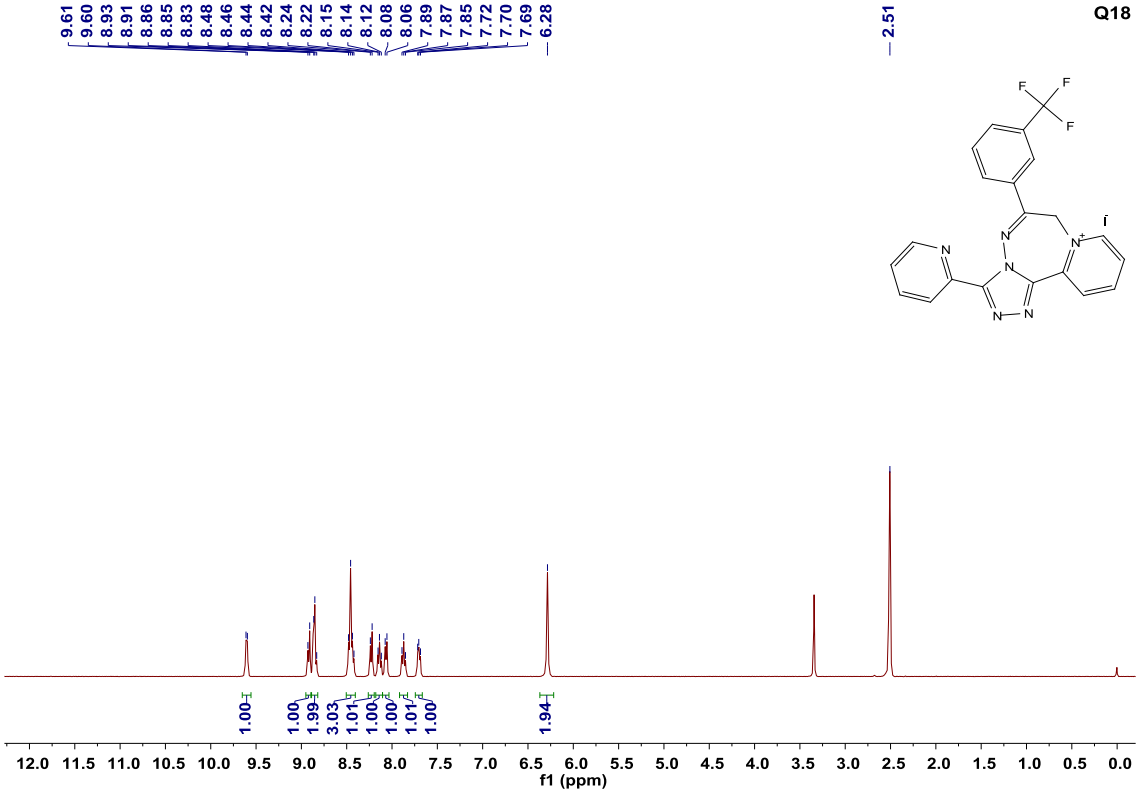


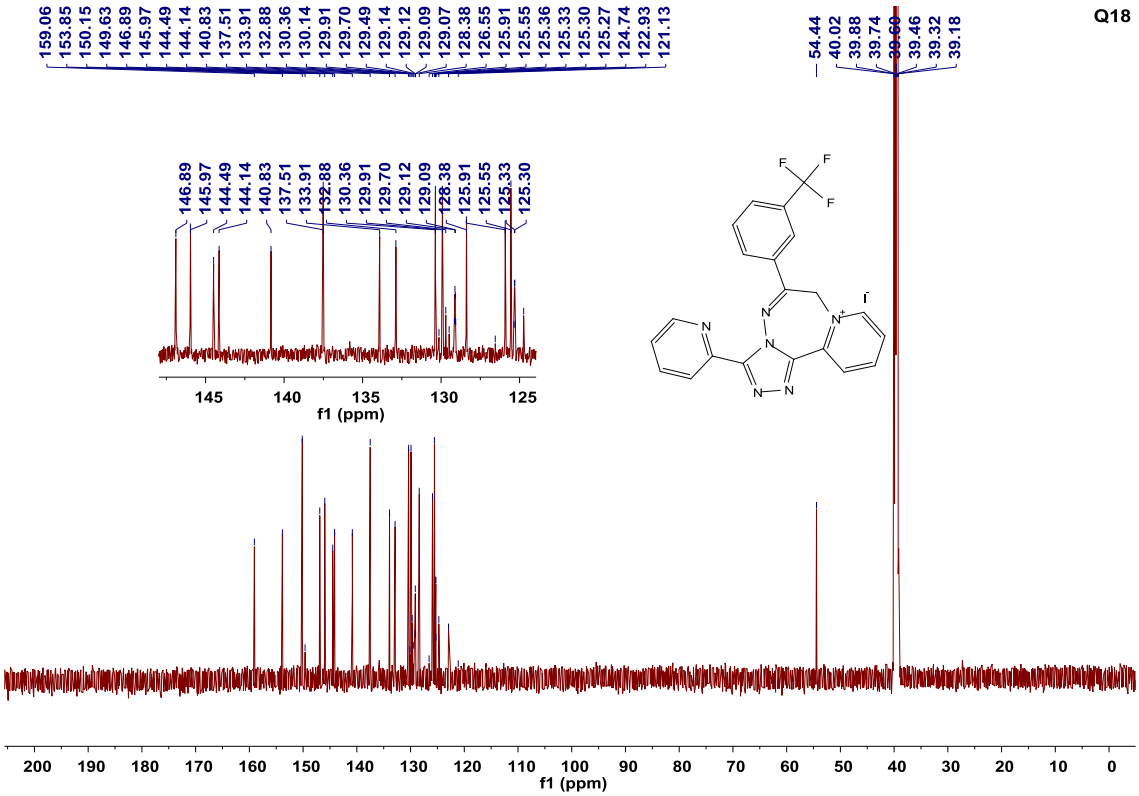
6-(4-ethynylphenyl)-3-(pyridin-2-yl)-7H-pyrido[2,1-d][1,2,4]triazolo[4,3-b][1,2,5]triazepin-8-ium iodide(Q17)



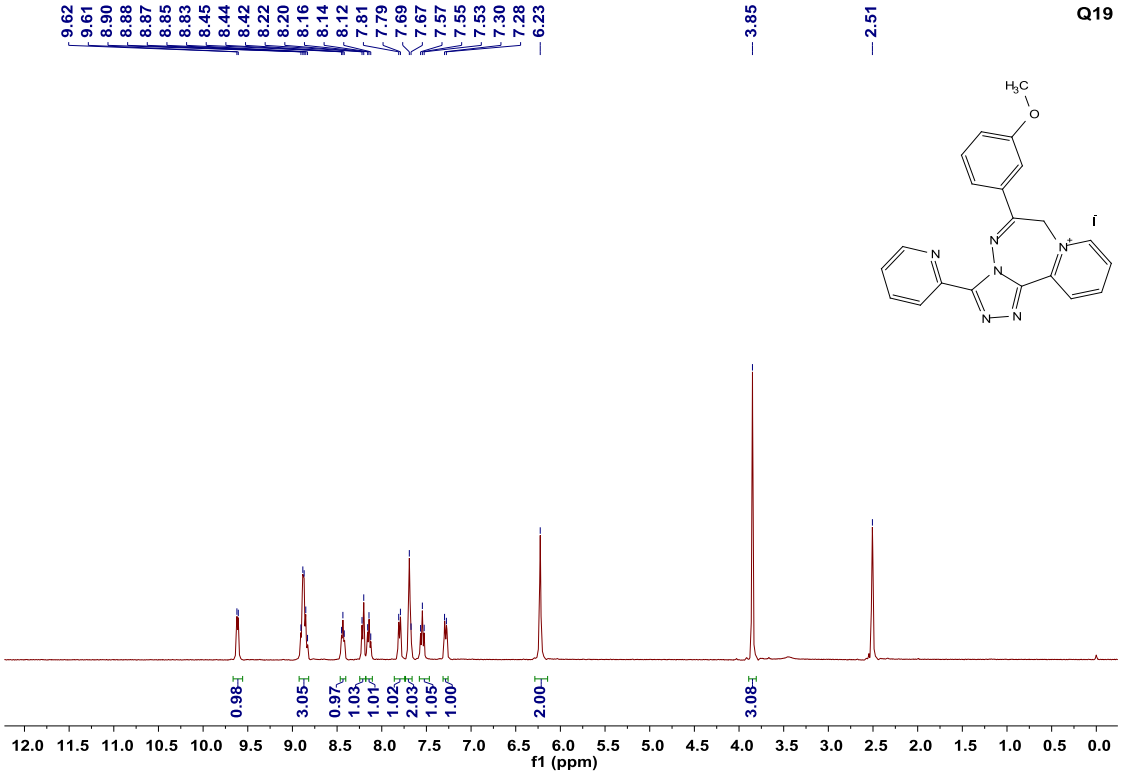


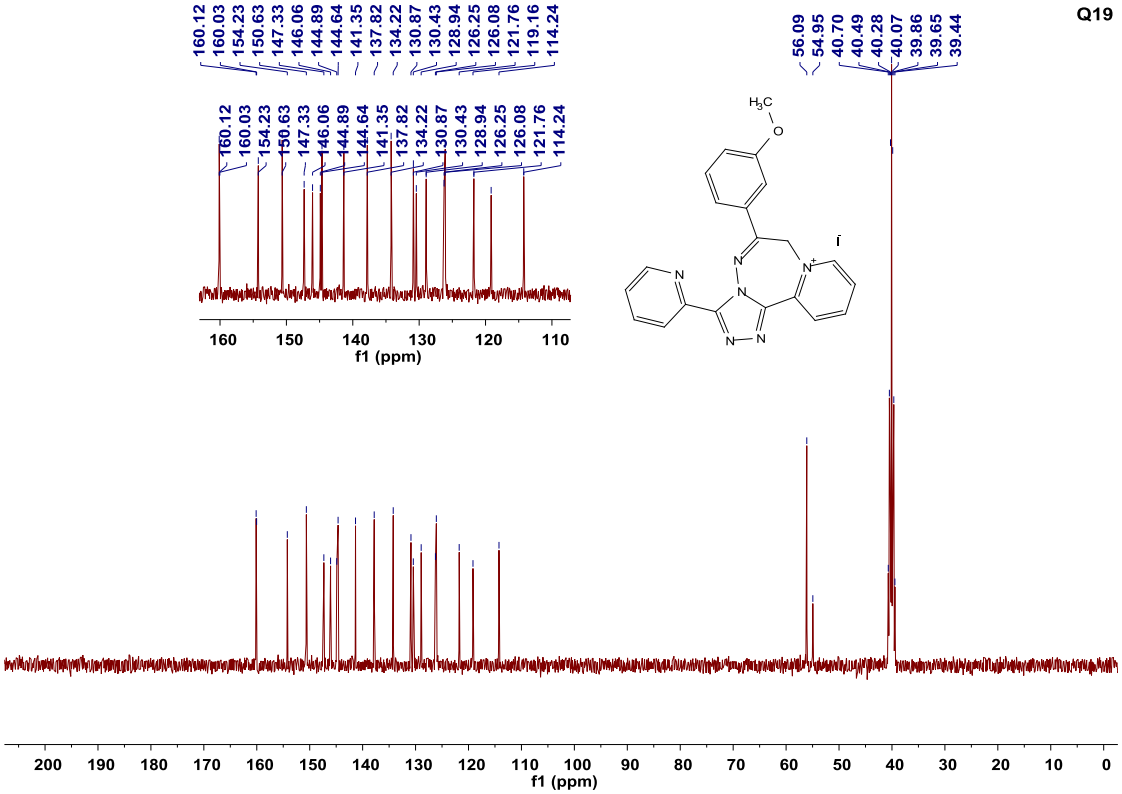
3-(pyridin-2-yl)-6-(3-(trifluoromethyl)phenyl)-7H-pyrido[2,1-d][1,2,4]triazolo[4,3-b][1,2,5]triazepin-8-ium iodide(Q18)



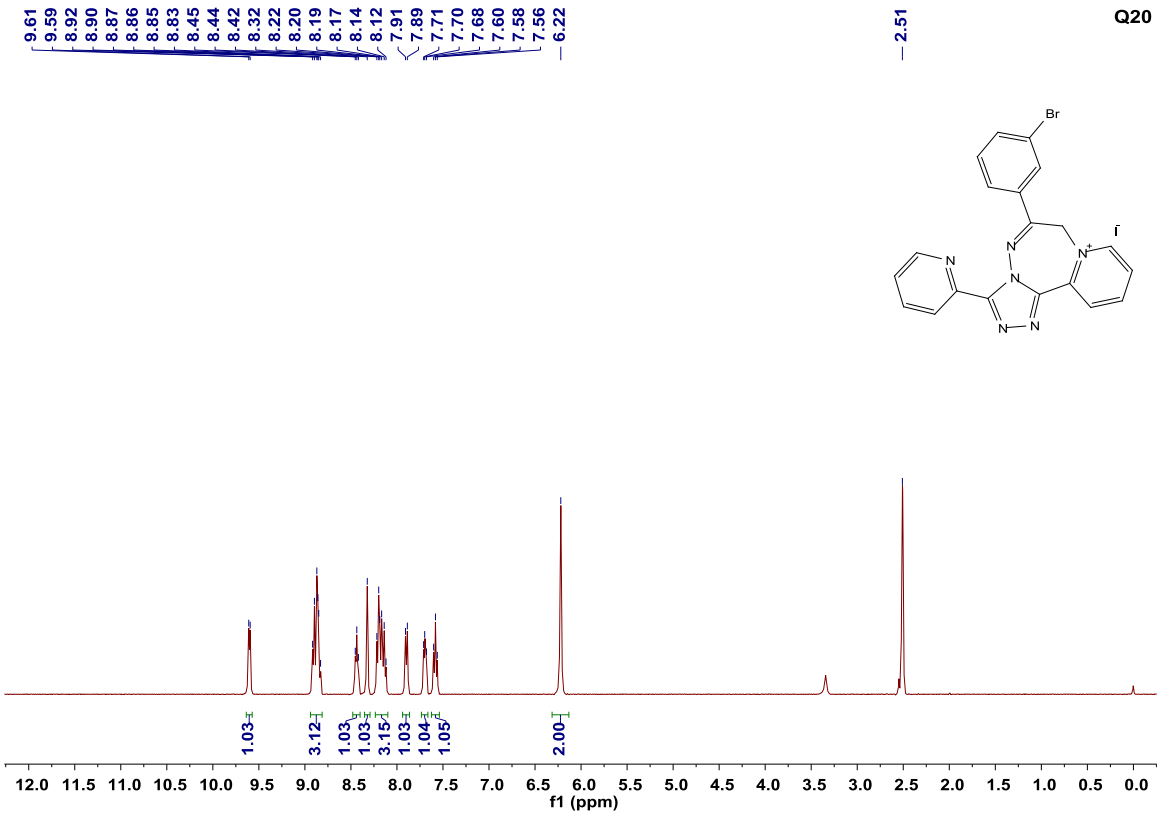


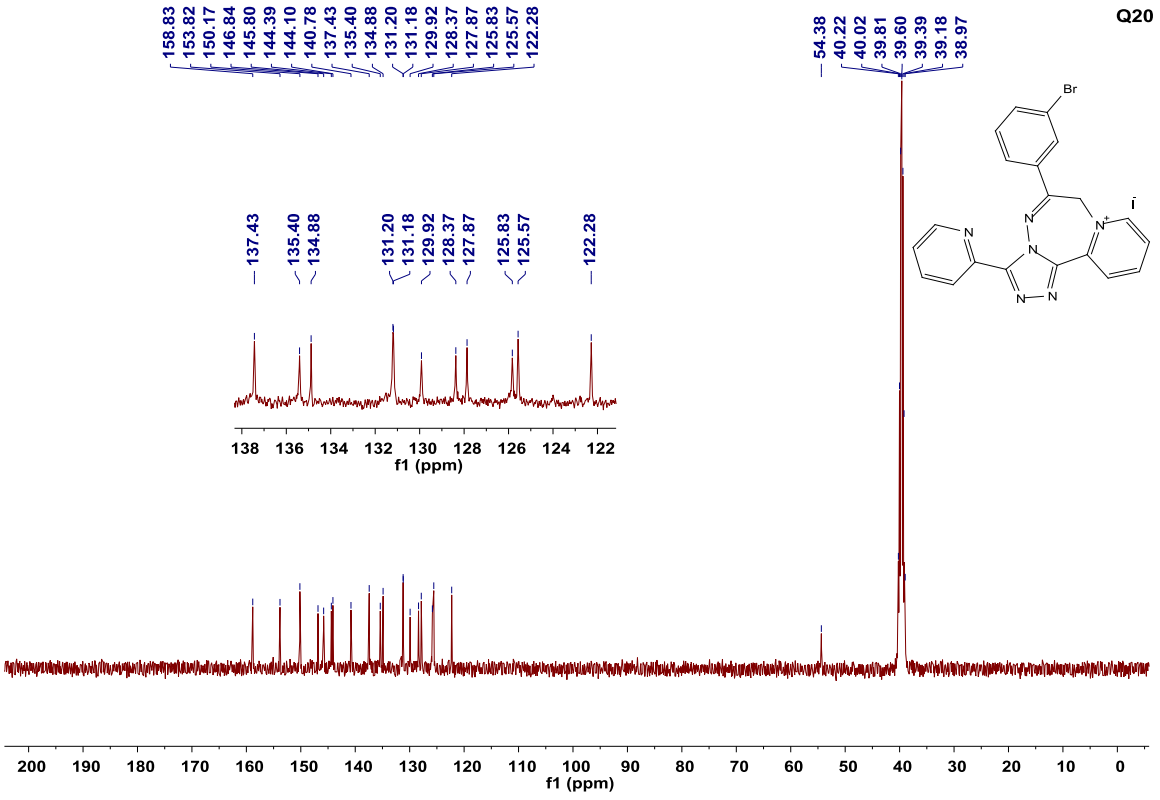
6-(3-methoxyphenyl)-3-(pyridin-2-yl)-7H-pyrido[2,1-d][1,2,4]triazolo[4,3-b][1,2,5]triazepin-8-ium iodide(Q19)



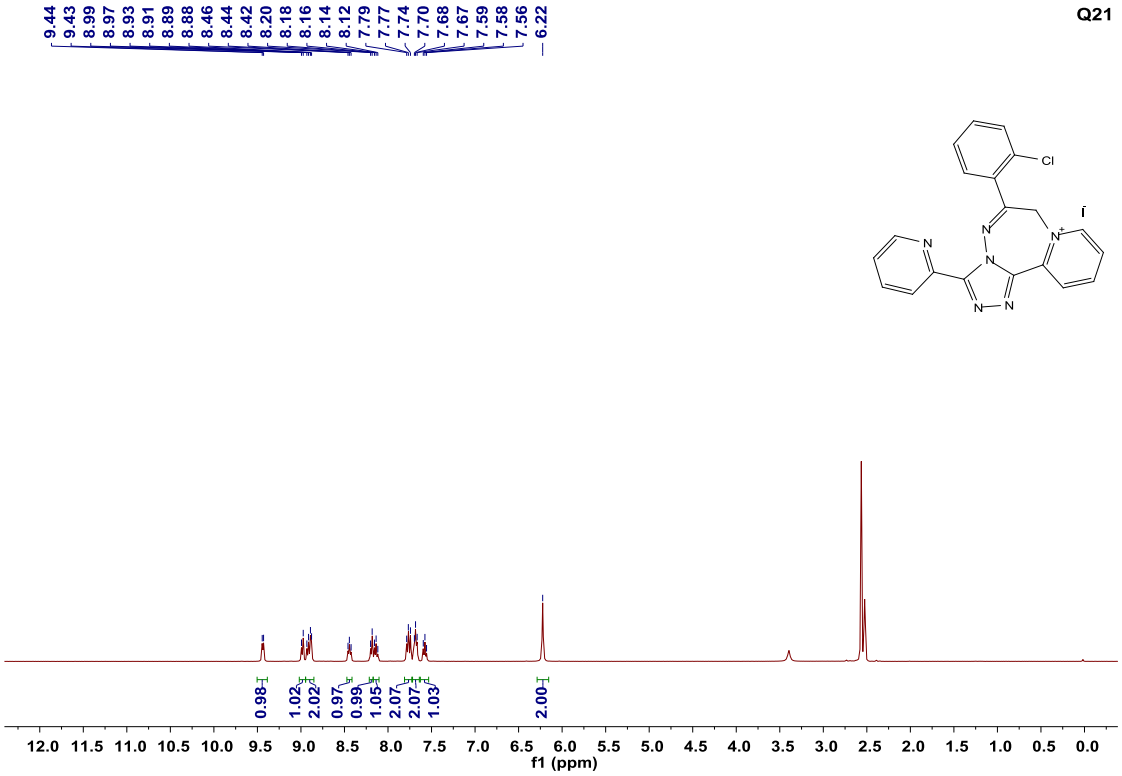


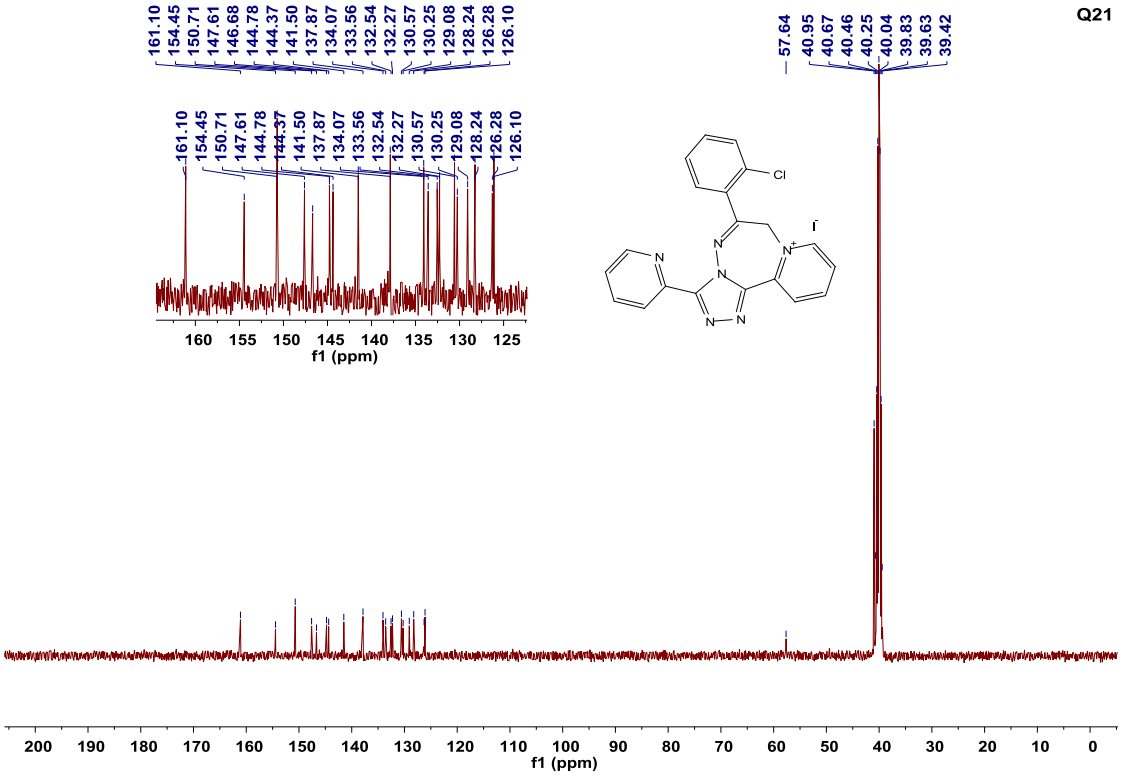
6-(3-bromophenyl)-3-(pyridin-2-yl)-7H-pyrido[2,1-d][1,2,4]triazolo[4,3-b][1,2,5]triazepin-8-ium iodide(Q20)



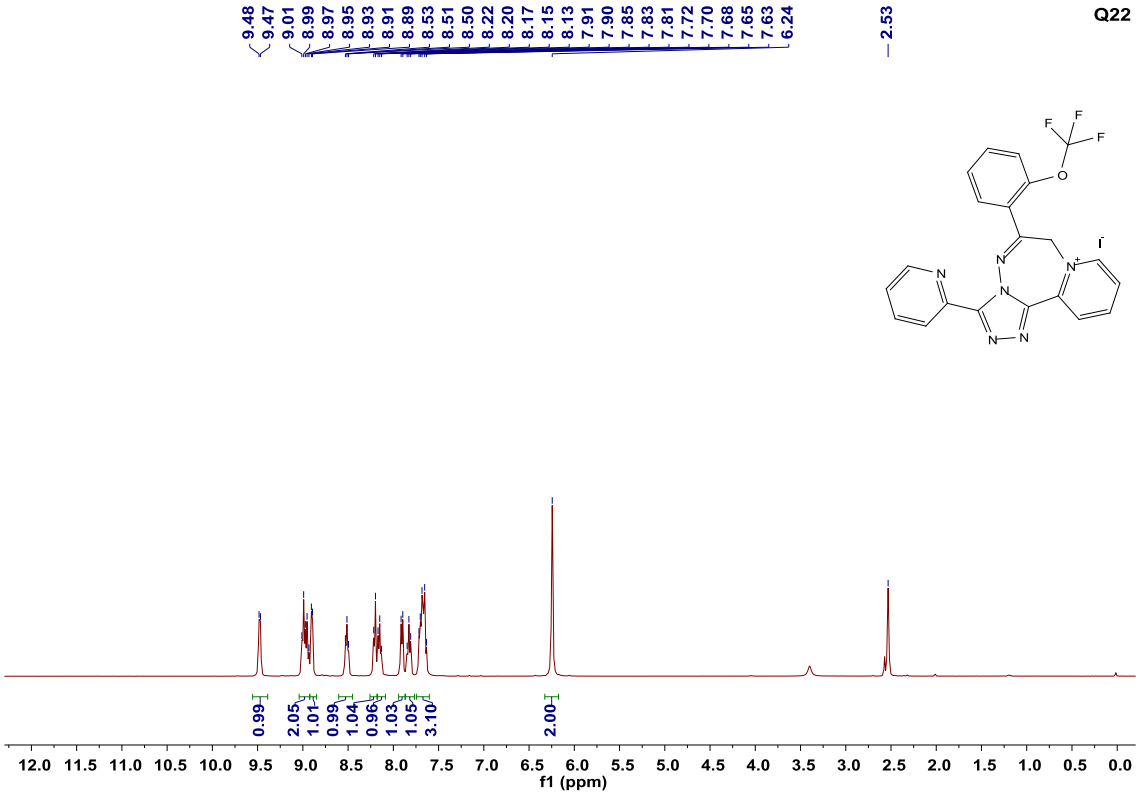


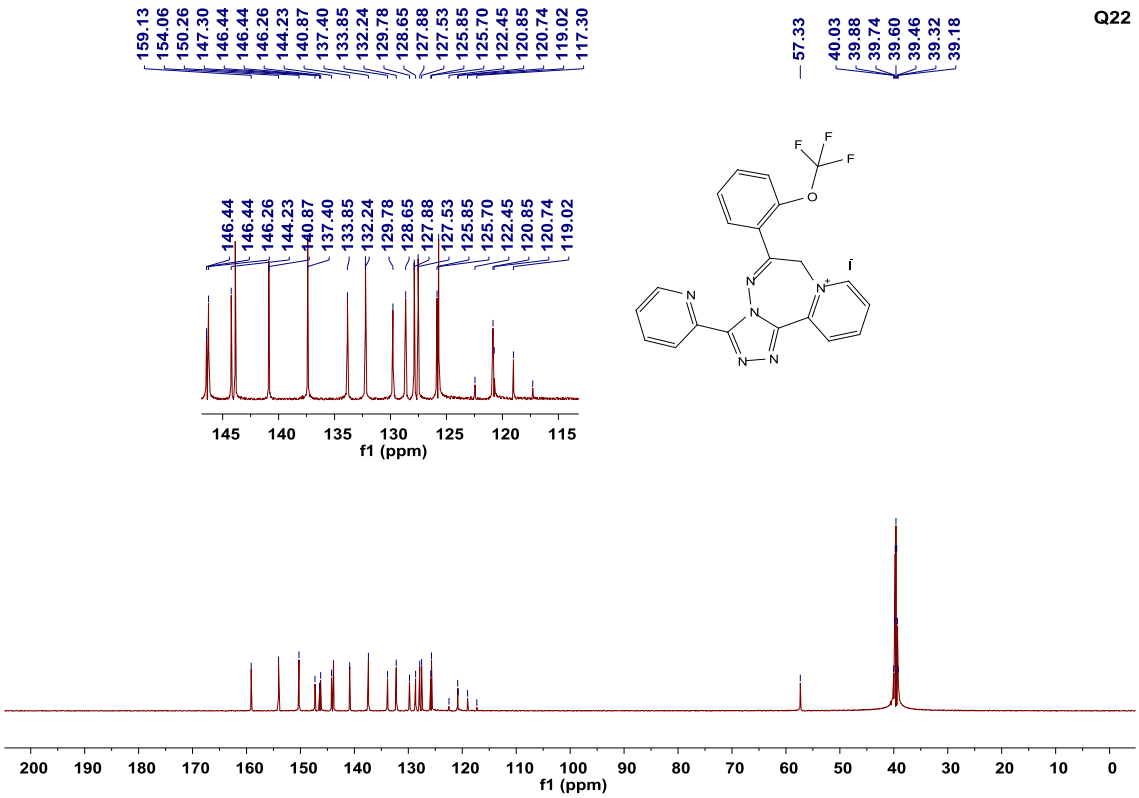
6-(2-chlorophenyl)-3-(pyridin-2-yl)-7H-pyrido[2,1-d][1,2,4]triazolo[4,3-b][1,2,5]triazepin-8-ium iodide(Q21)



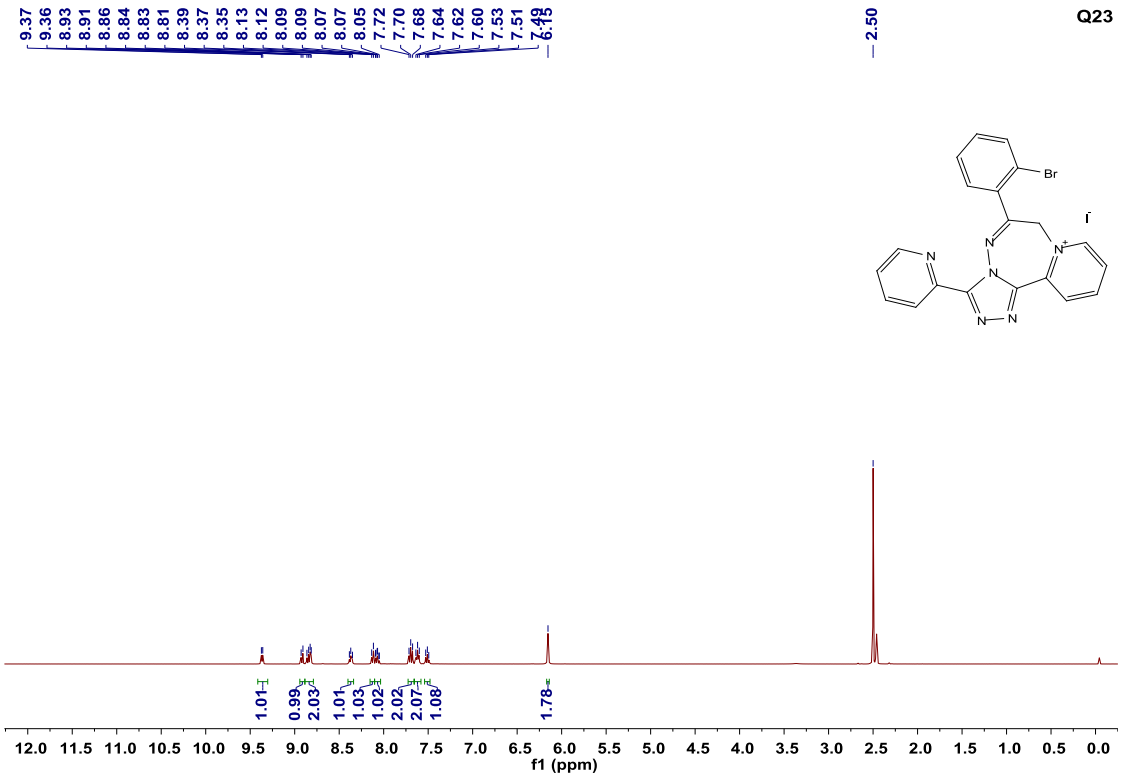


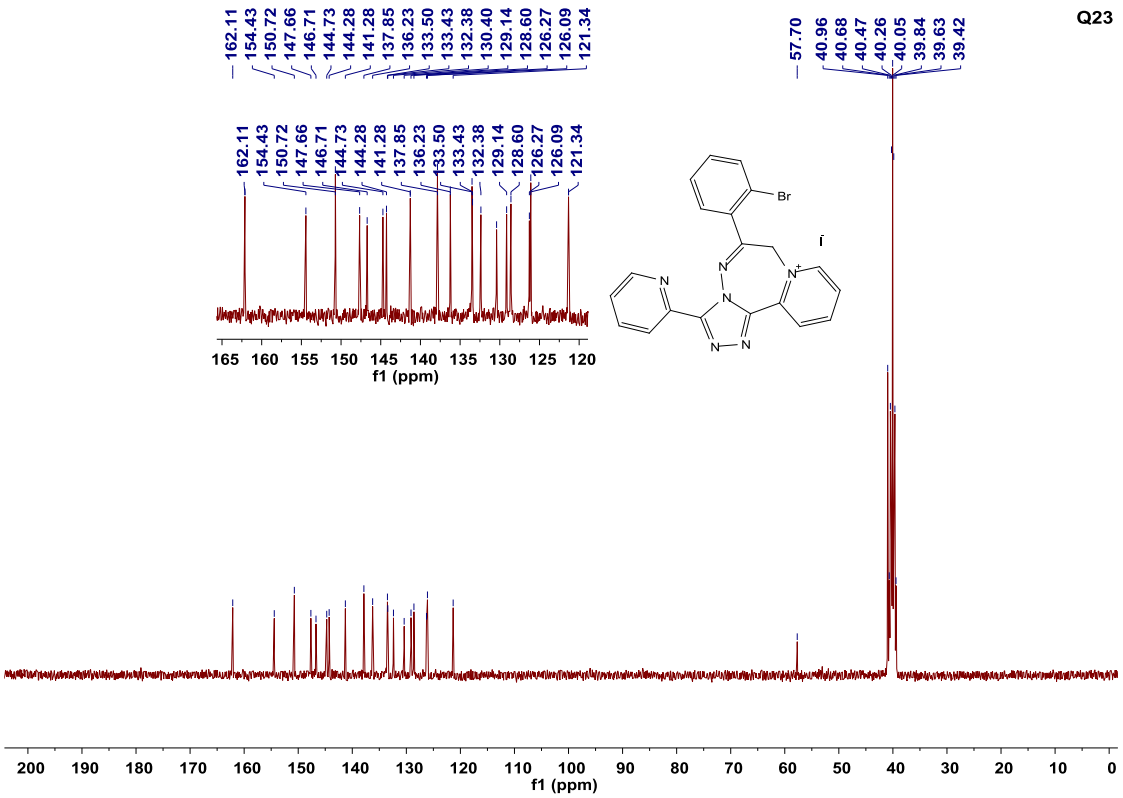
3-(pyridin-2-yl)-6-(2-(trifluoromethoxy)phenyl)-7H-pyrido[2,1-d][1,2,4]triazolo[4,3-b][1,2,5]triazepin-8-ium iodide(Q22)



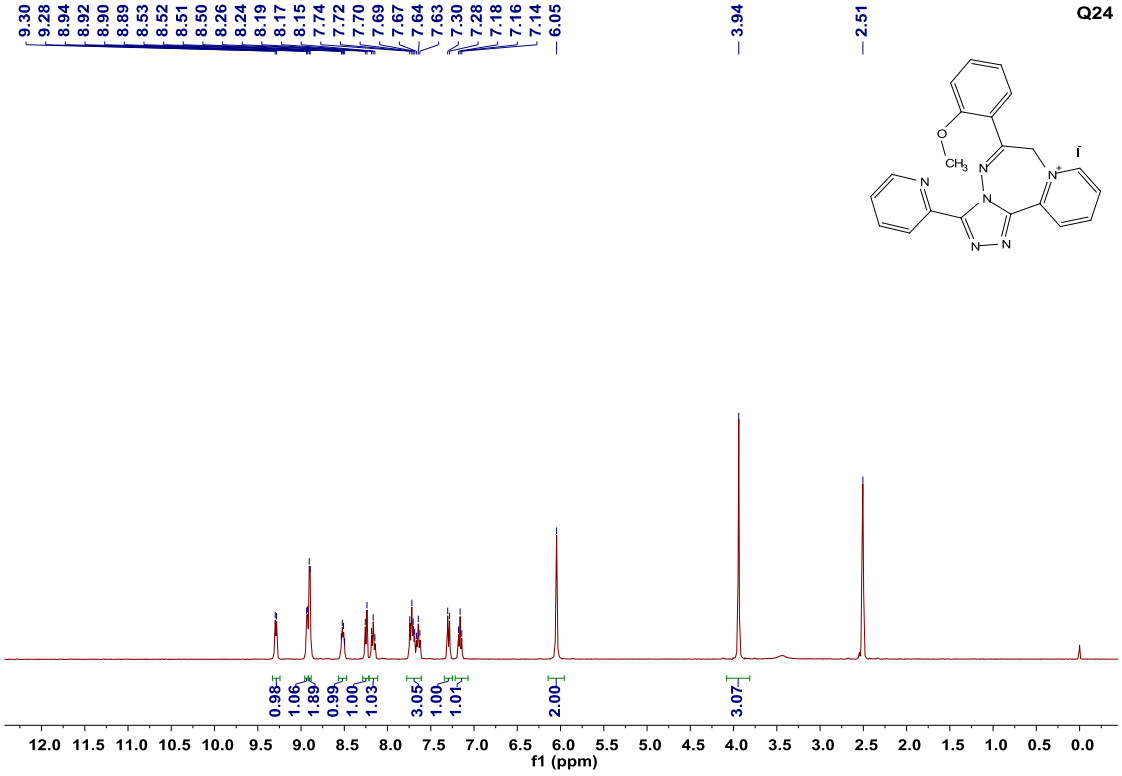


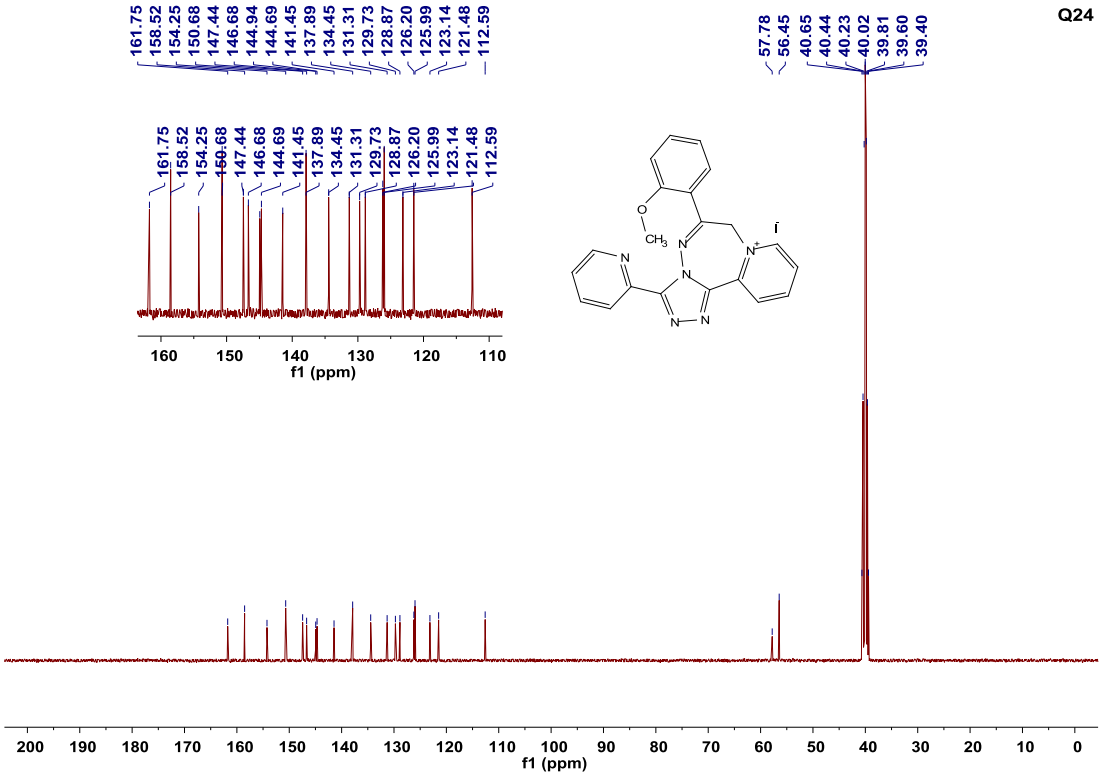
6-(2-bromophenyl)-3-(pyridin-2-yl)-7H-pyrido[2,1-d][1,2,4]triazolo[4,3-b][1,2,5]triazepin-8-ium iodide(Q23)



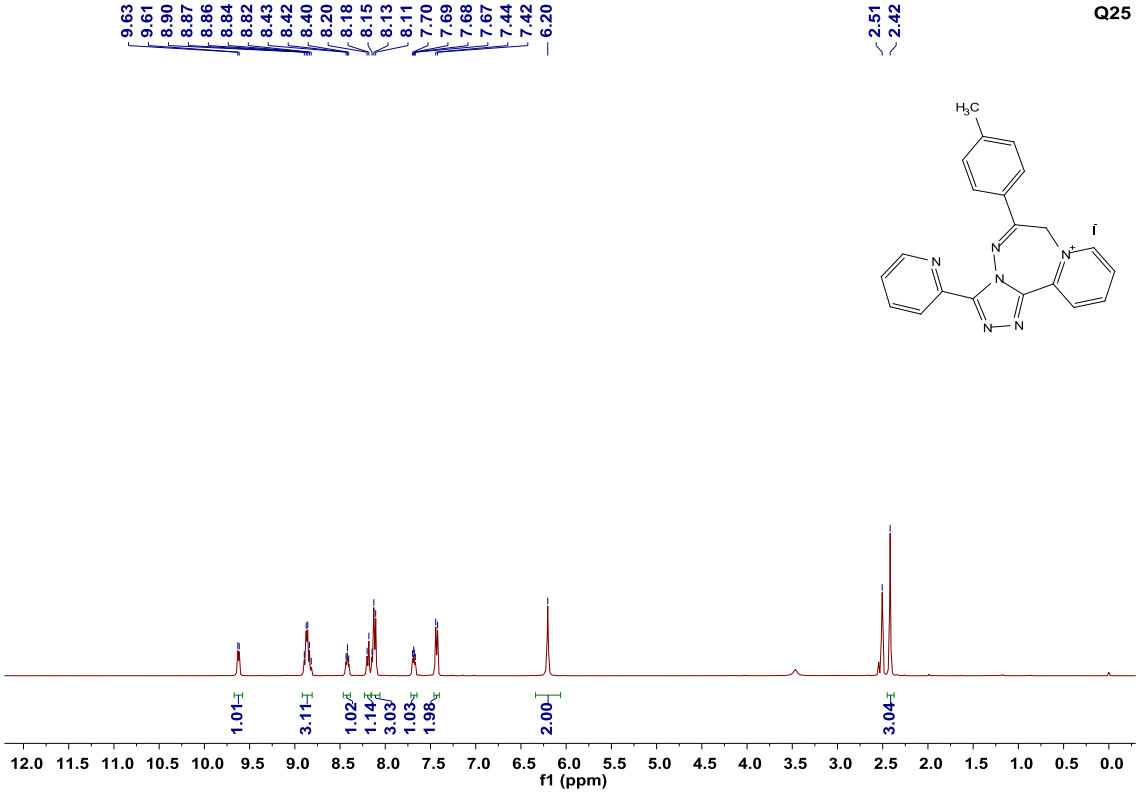


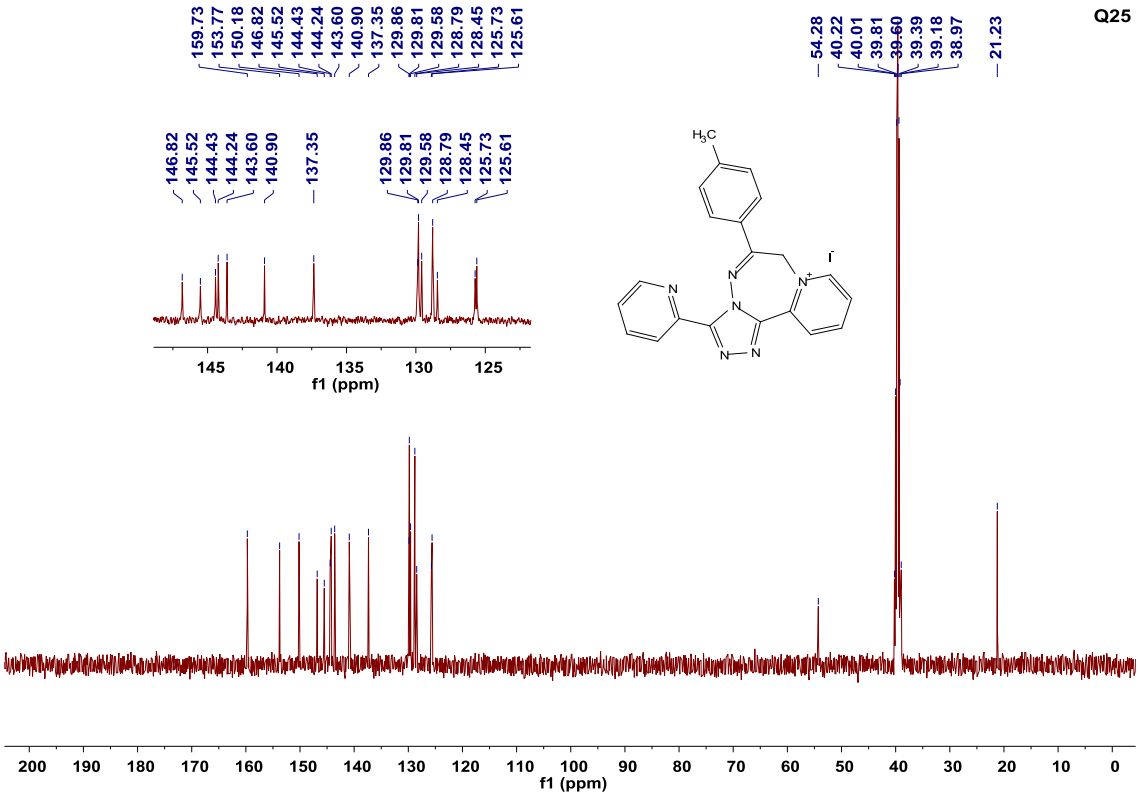
6-(2-methoxyphenyl)-3-(pyridin-2-yl)-7H-pyrido[2,1-d][1,2,4]triazolo[4,3-b][1,2,5]triazepin-8-ium iodide(Q24)



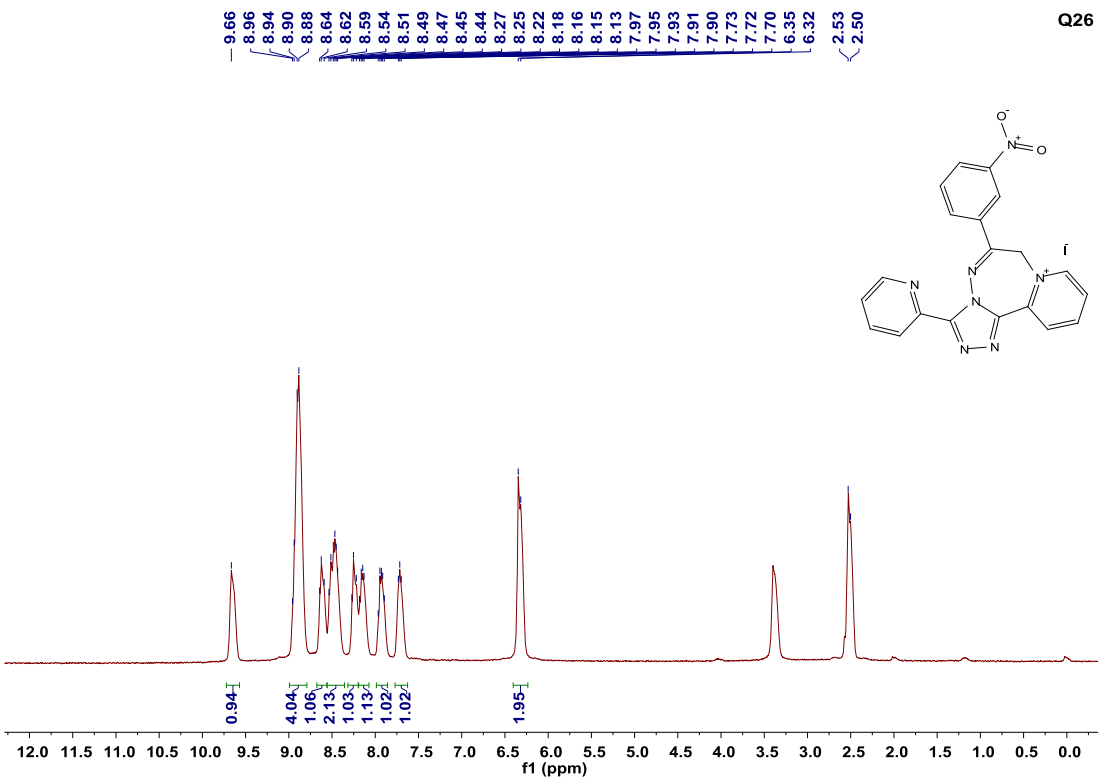


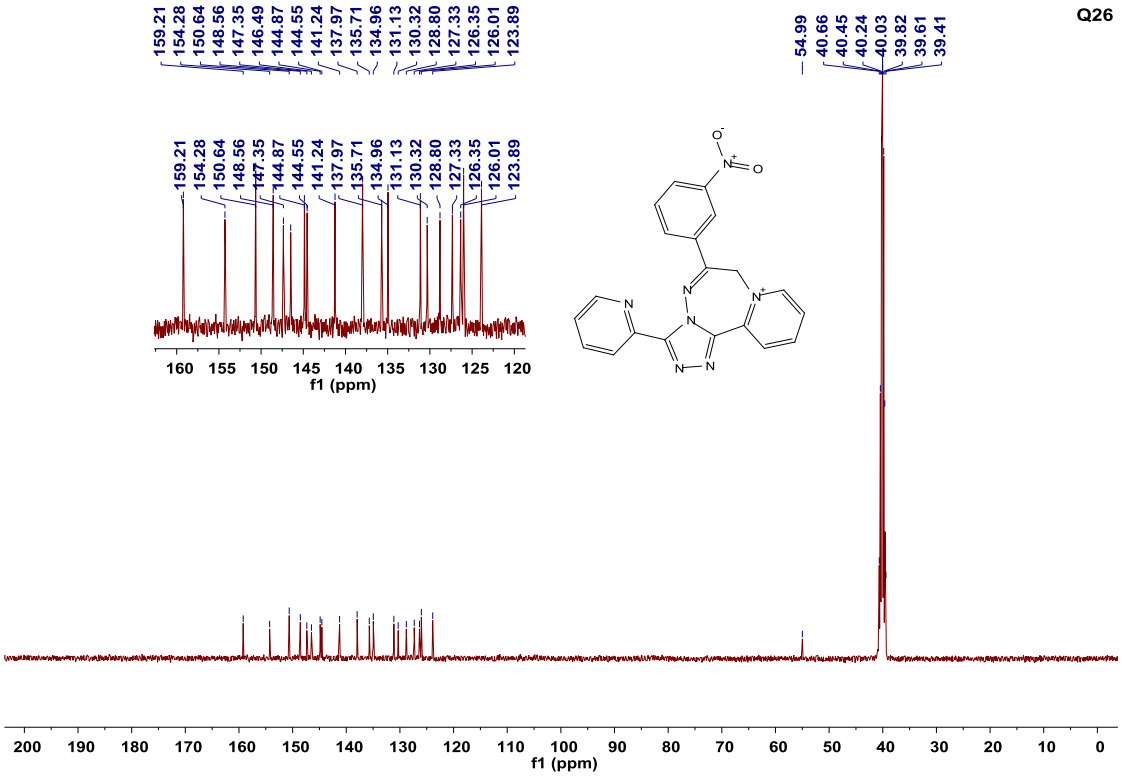
3-(pyridin-2-yl)-6-(p-tolyl)-7H-pyrido[2,1-d][1,2,4]triazolo[4,3-b][1,2,5]triazepin-8-ium iodide(Q25)



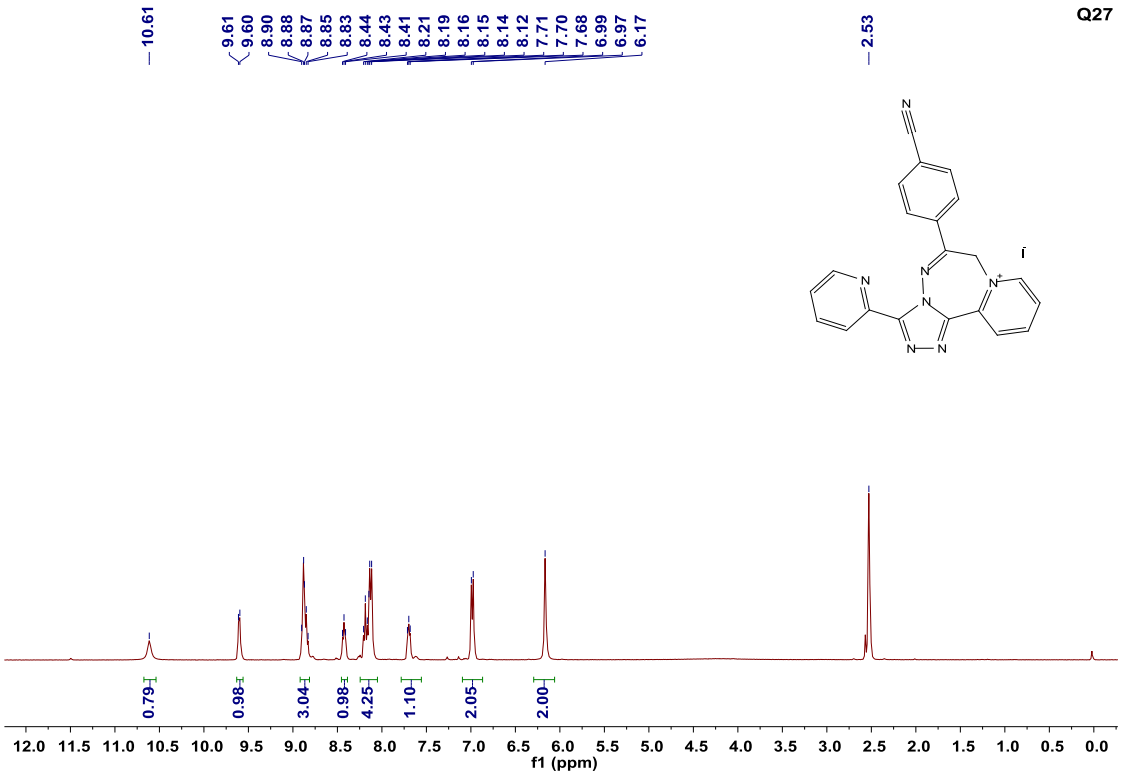


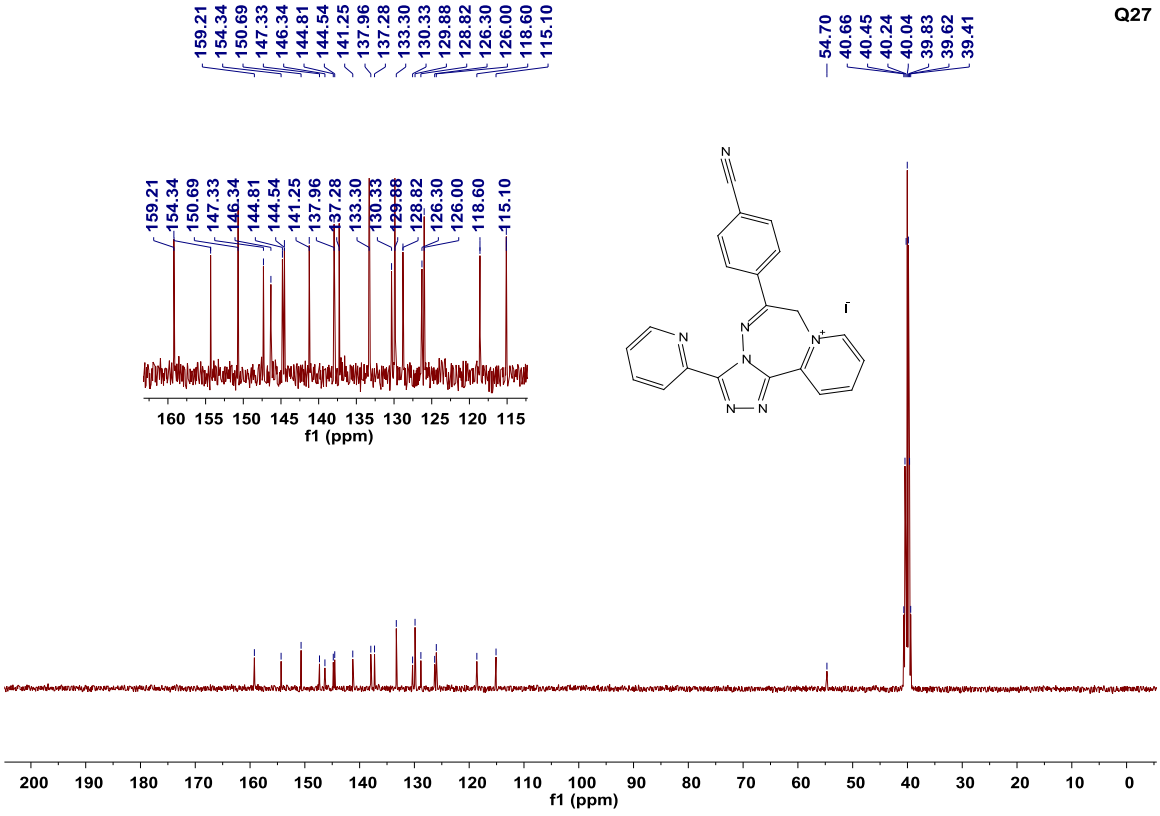
6-(3-(nitrooxy)phenyl)-3-(pyridin-2-yl)-7H-pyrido[2,1-d][1,2,4]triazolo[4,3-b][1,2,5]triazepin-8-ium iodide(Q26)



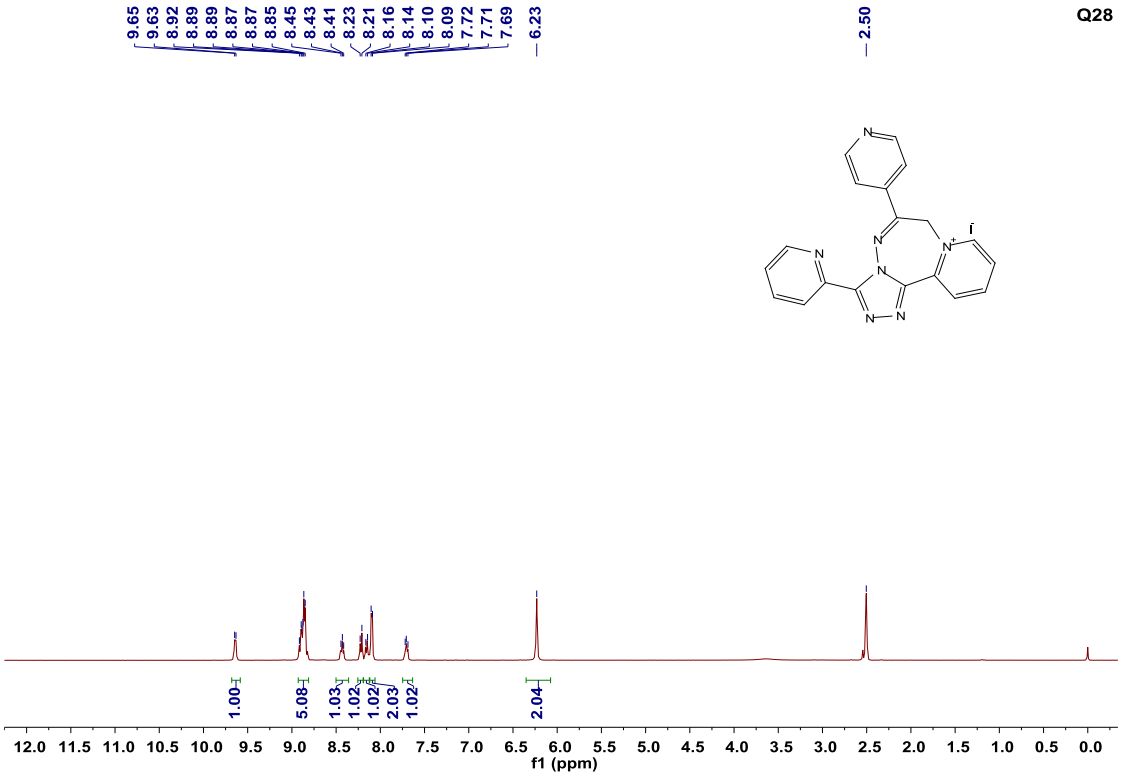


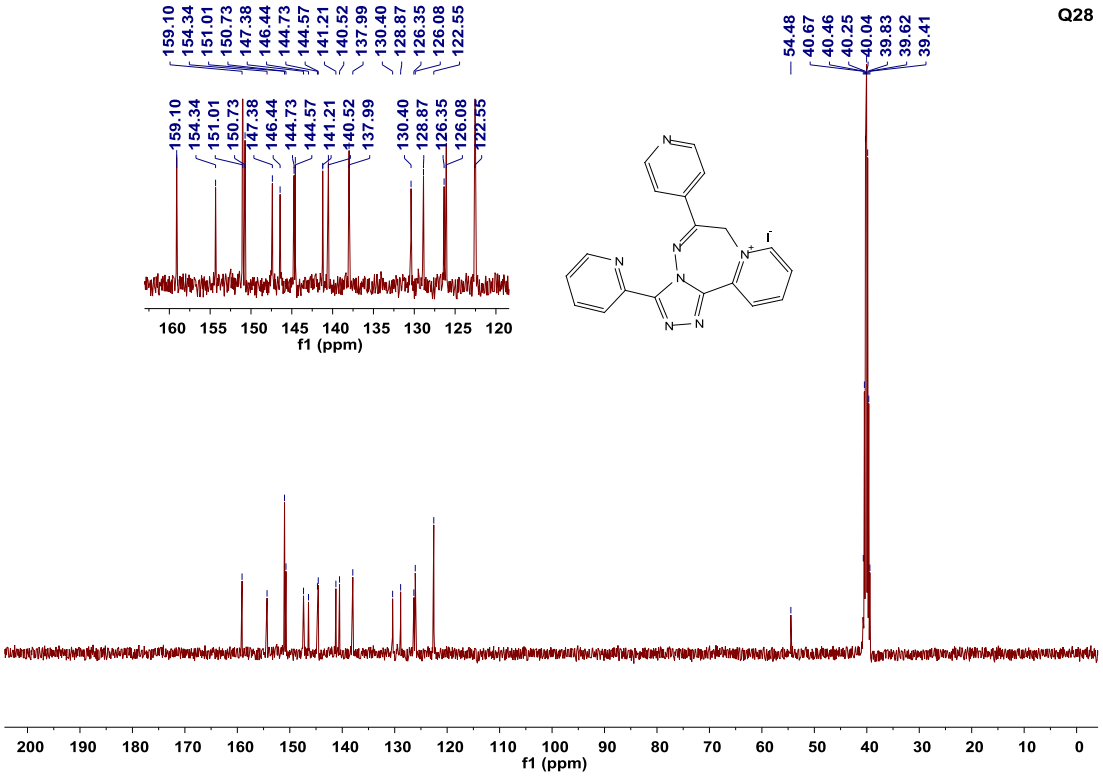
6-(4-cyanophenyl)-3-(pyridin-2-yl)-7H-pyrido[2,1-d][1,2,4]triazolo[4,3-b][1,2,5]triazepin-8-ium iodide(Q27)



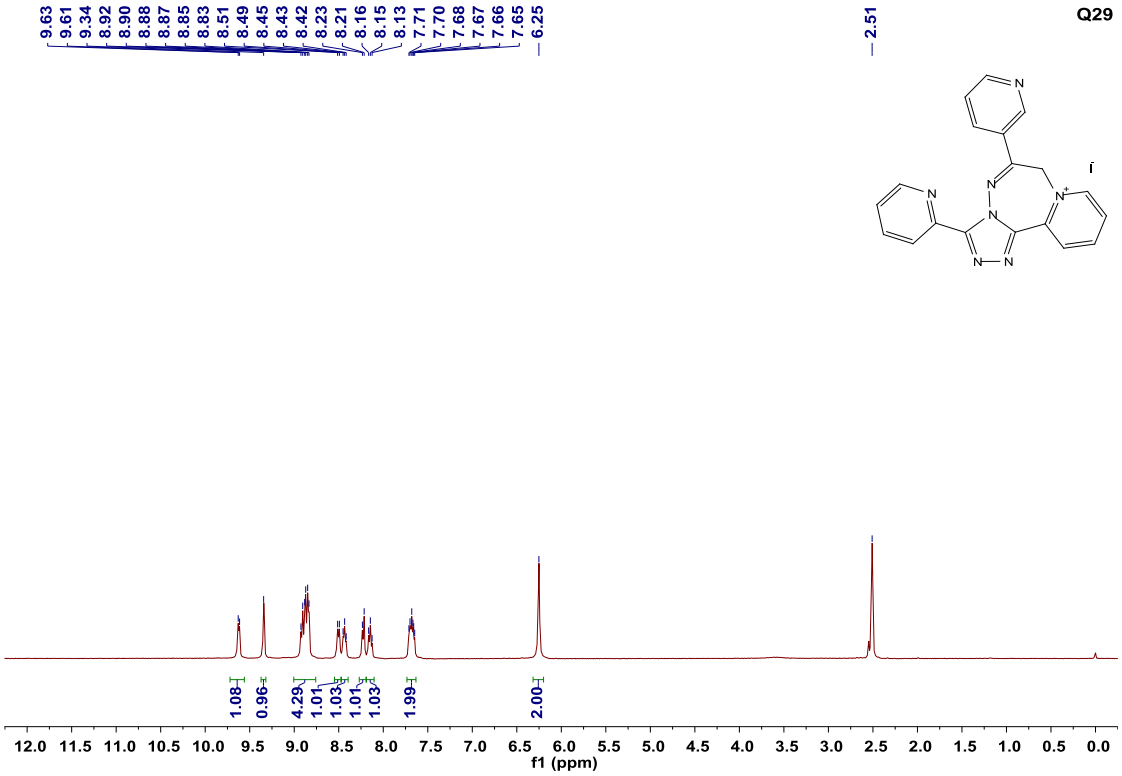


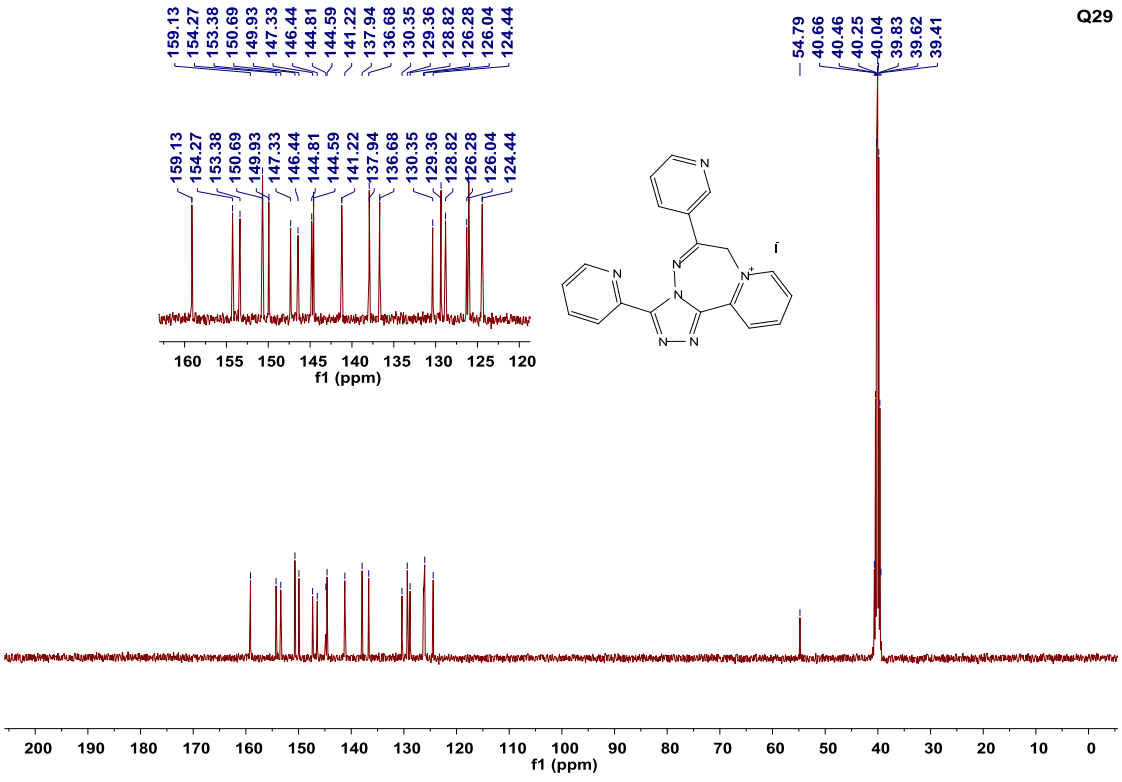
3-(pyridin-2-yl)-6-(pyridin-4-yl)-7H-pyrido[2,1-d][1,2,4]triazolo[4,3-b][1,2,5]triazepin-8-ium iodide(Q28)



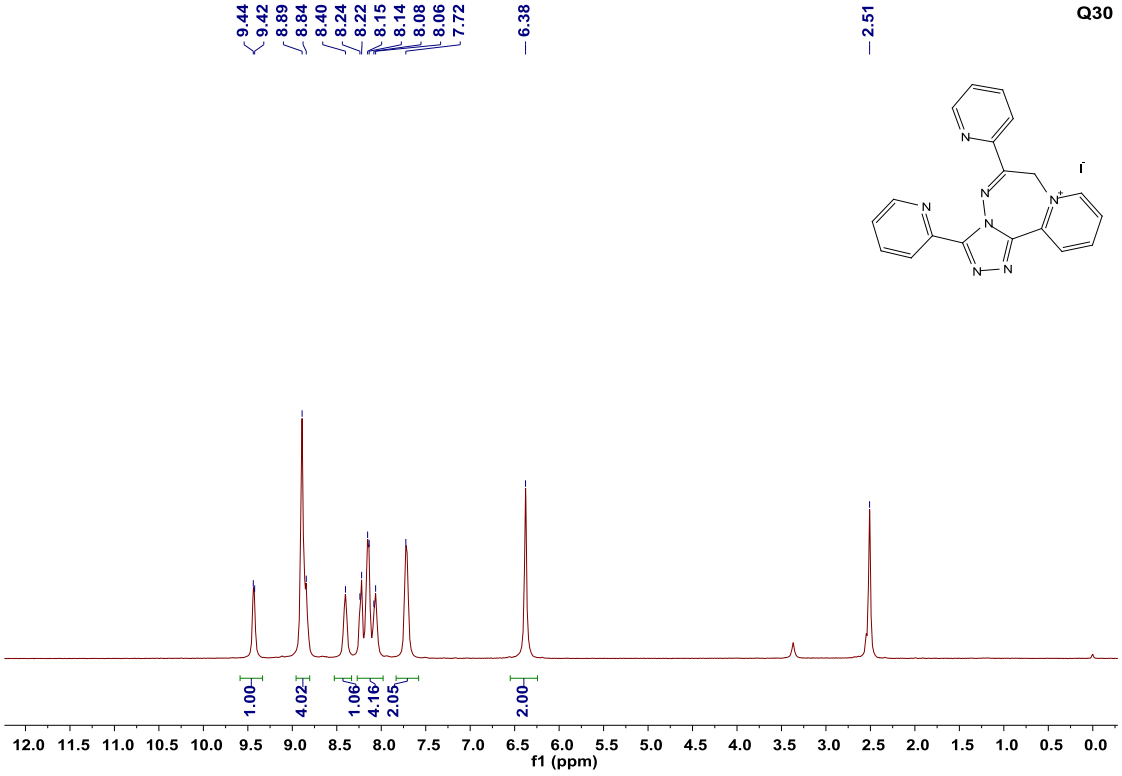


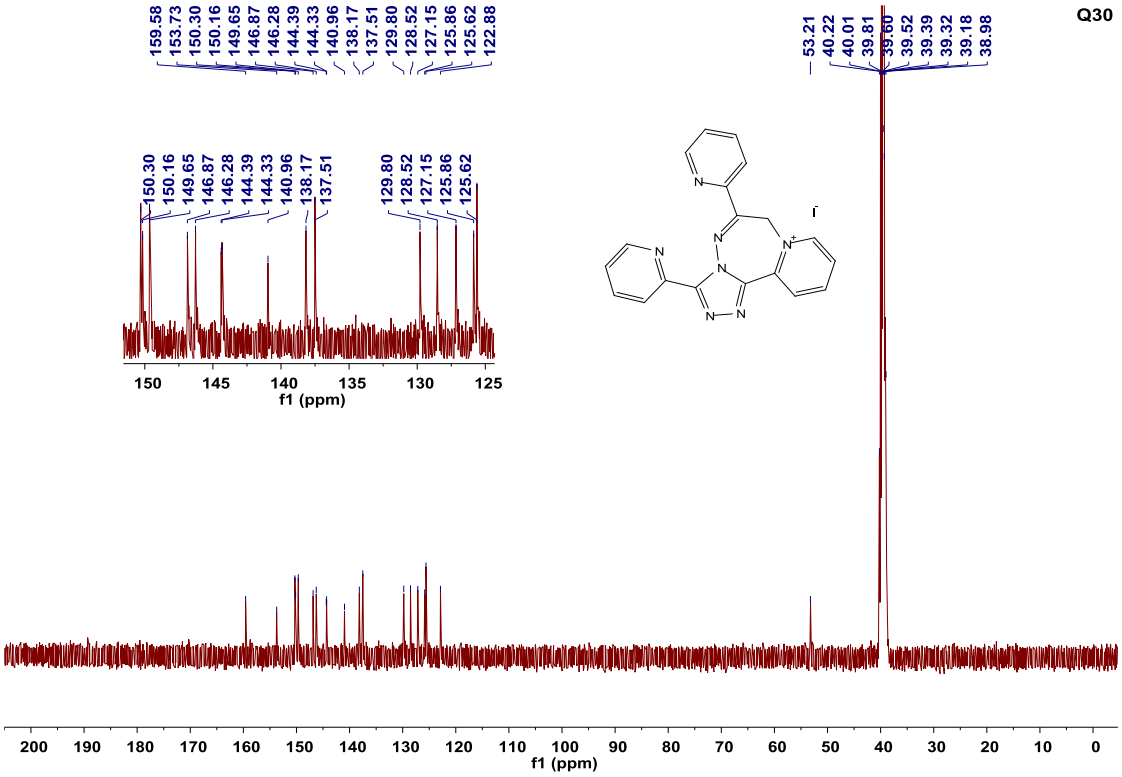
3-(pyridin-2-yl)-6-(pyridin-3-yl)-7H-pyrido[2,1-d][1,2,4]triazolo[4,3-b][1,2,5]triazepin-8-ium iodide(Q29)



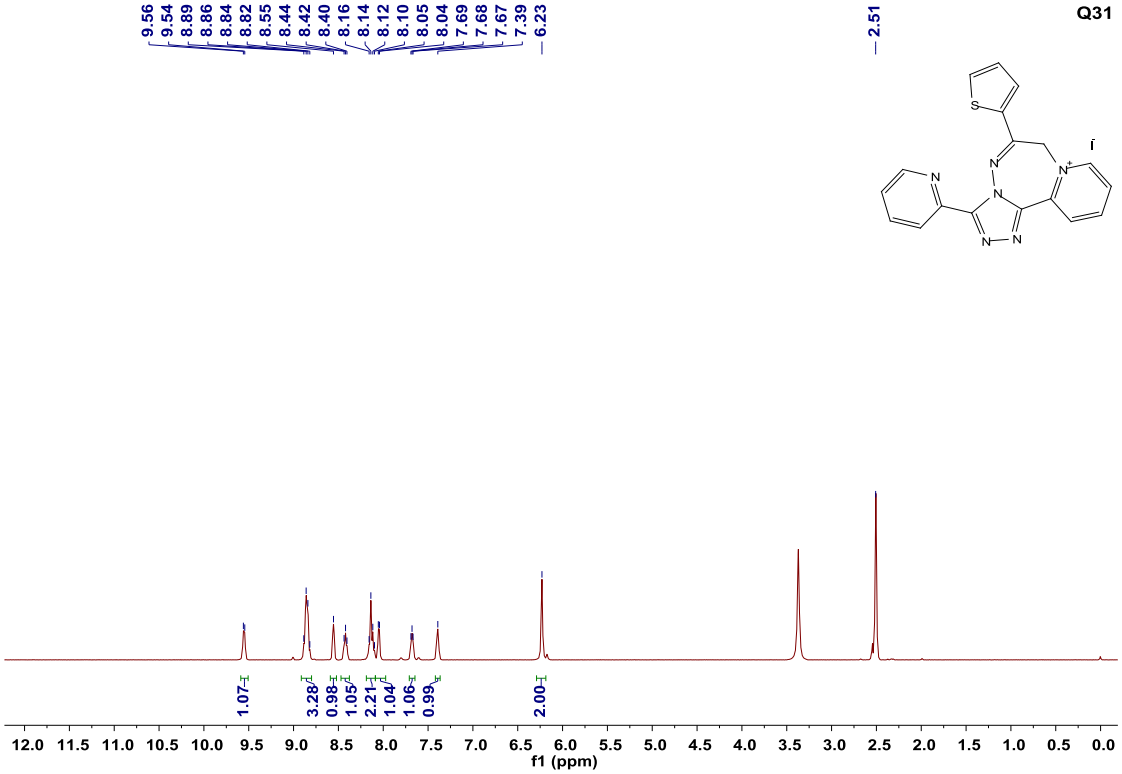


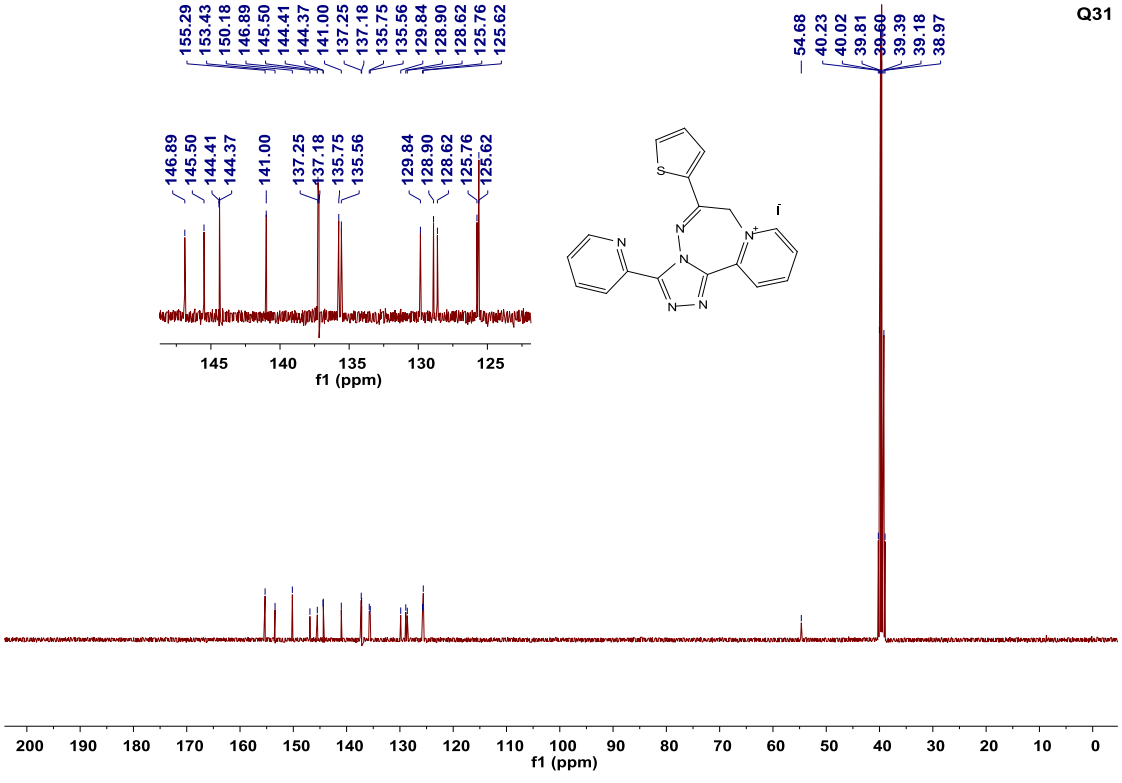
3-(pyridin-2-yl)-6-(pyridin-2-yl)-7H-pyrido[2,1-d][1,2,4]triazolo[4,3-b][1,2,5]triazepin-8-ium iodide(Q30)



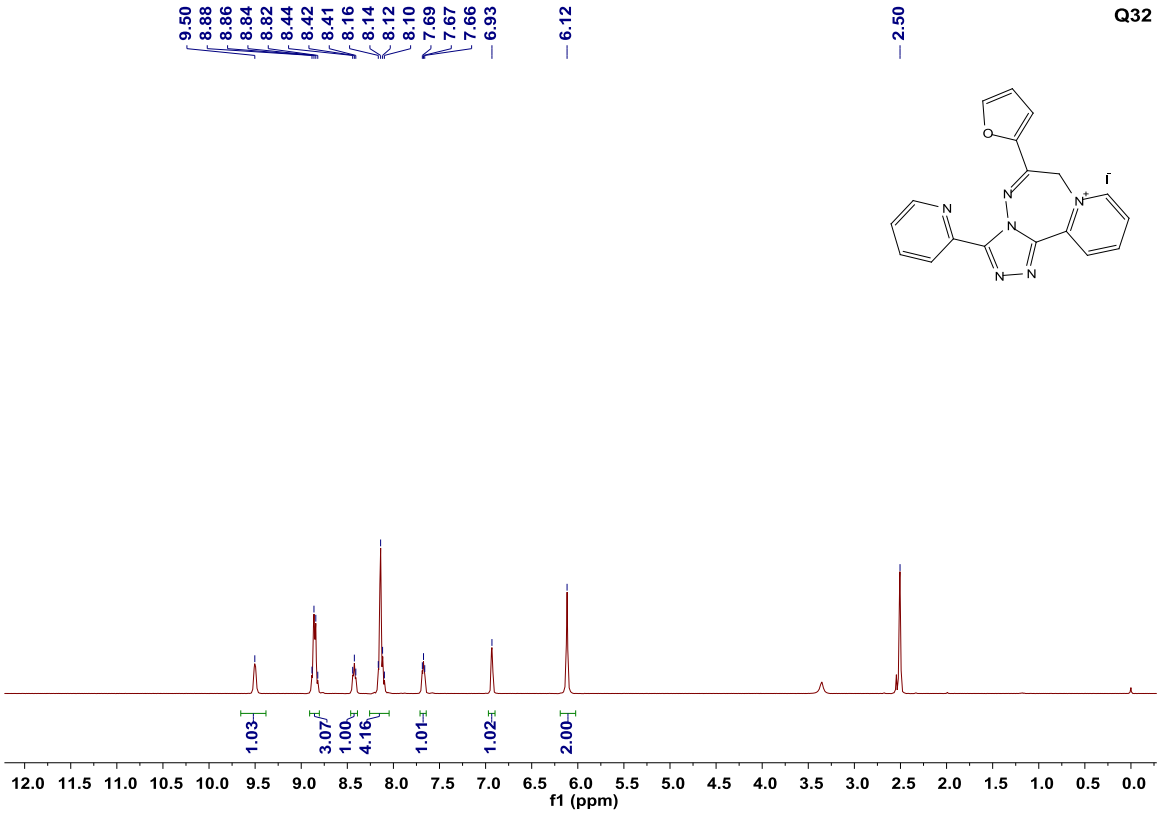


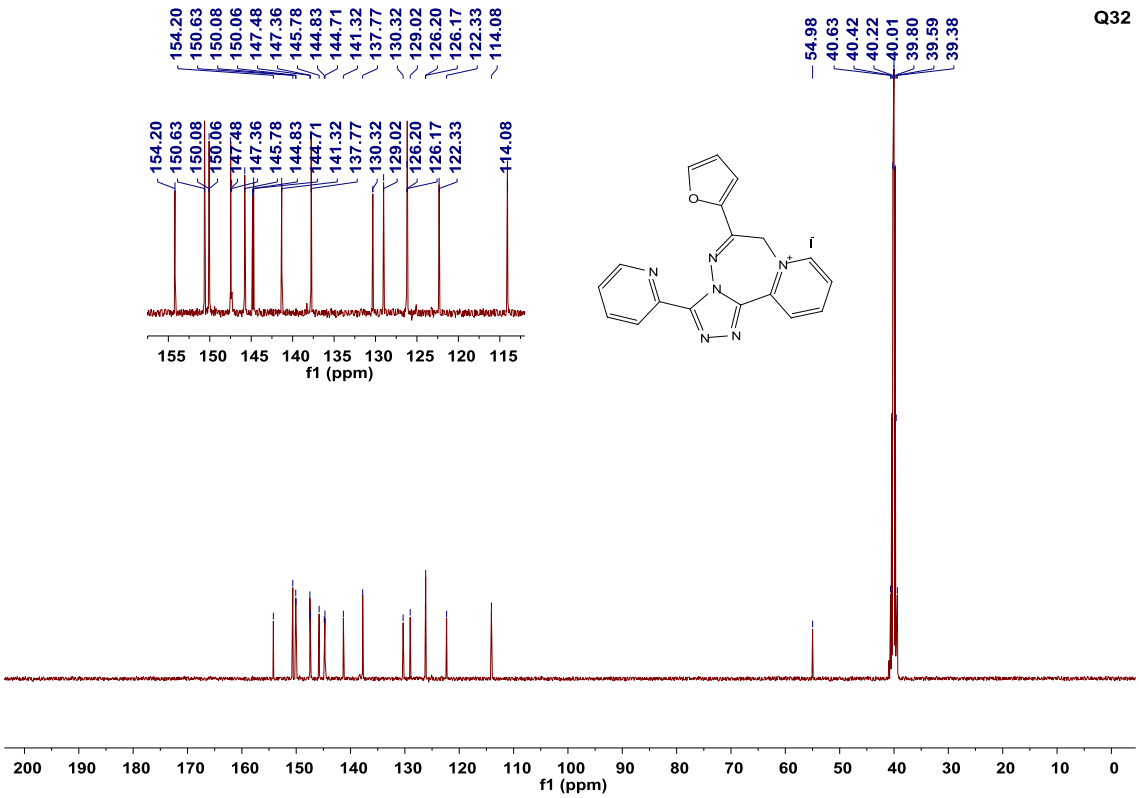
3-(pyridin-2-yl)-6-(thiophen-2-yl)-7H-pyrido[2,1-d][1,2,4]triazolo[4,3-b][1,2,5]triazepin-8-ium iodide(Q31)



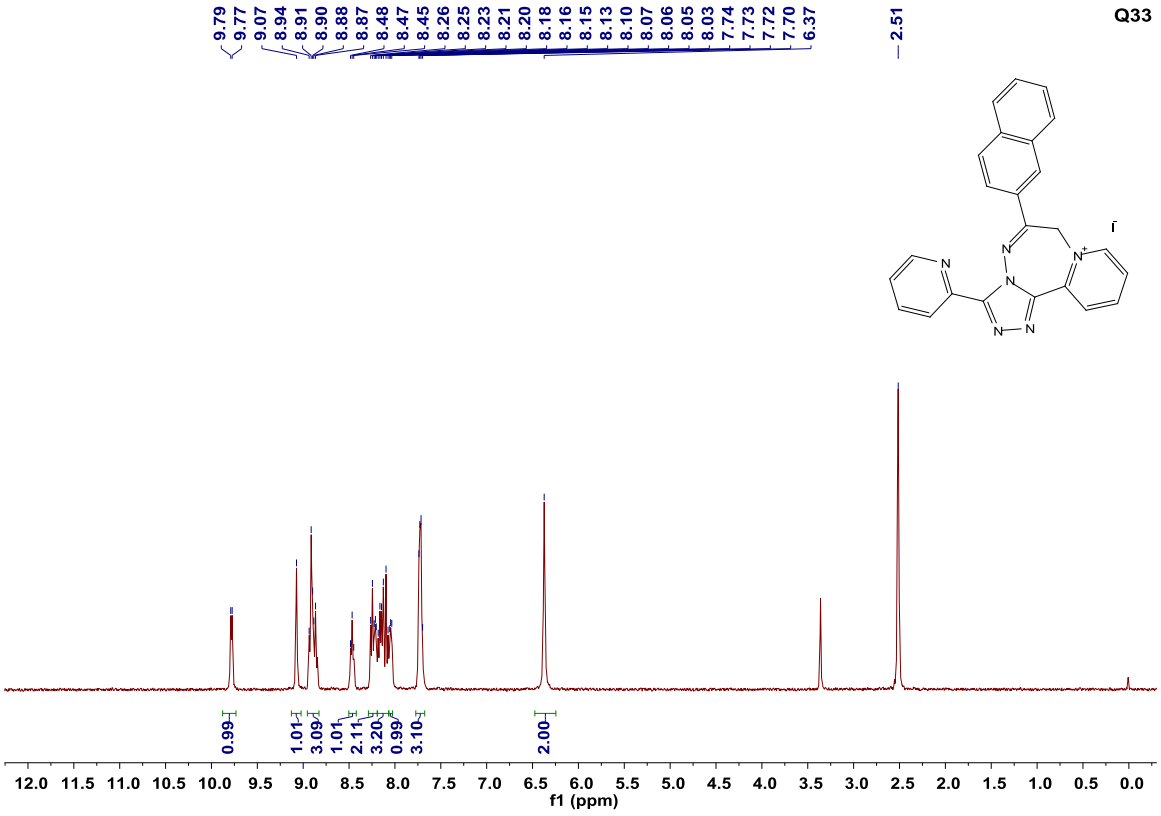


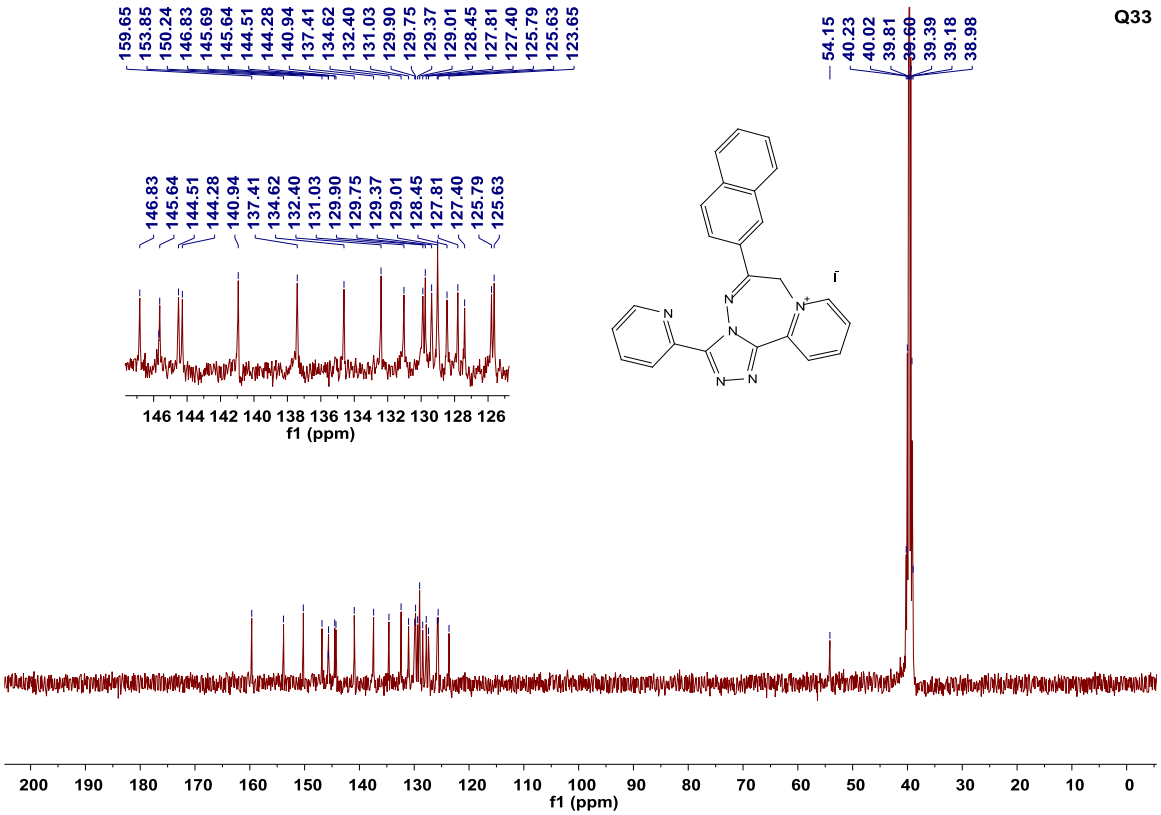
6-(furan-2-yl)-3-(pyridin-2-yl)-7H-pyrido[2,1-d][1,2,4]triazolo[4,3-b][1,2,5]triazepin-8-ium iodide(Q32)



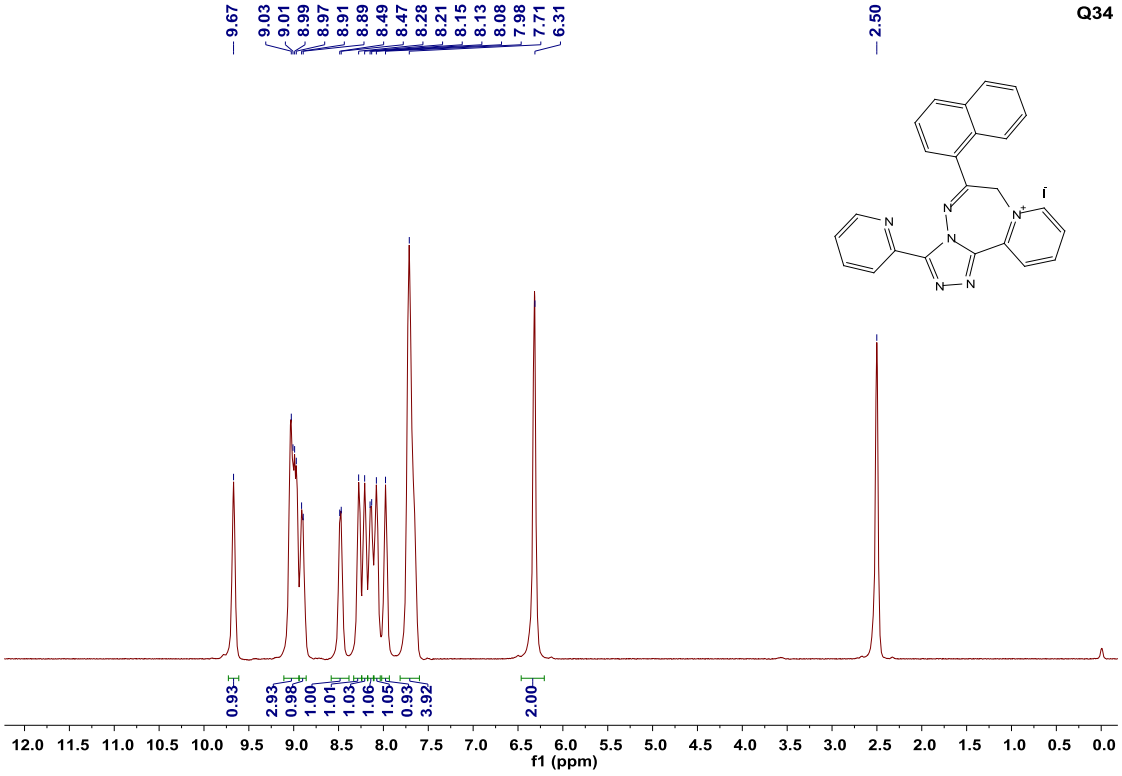


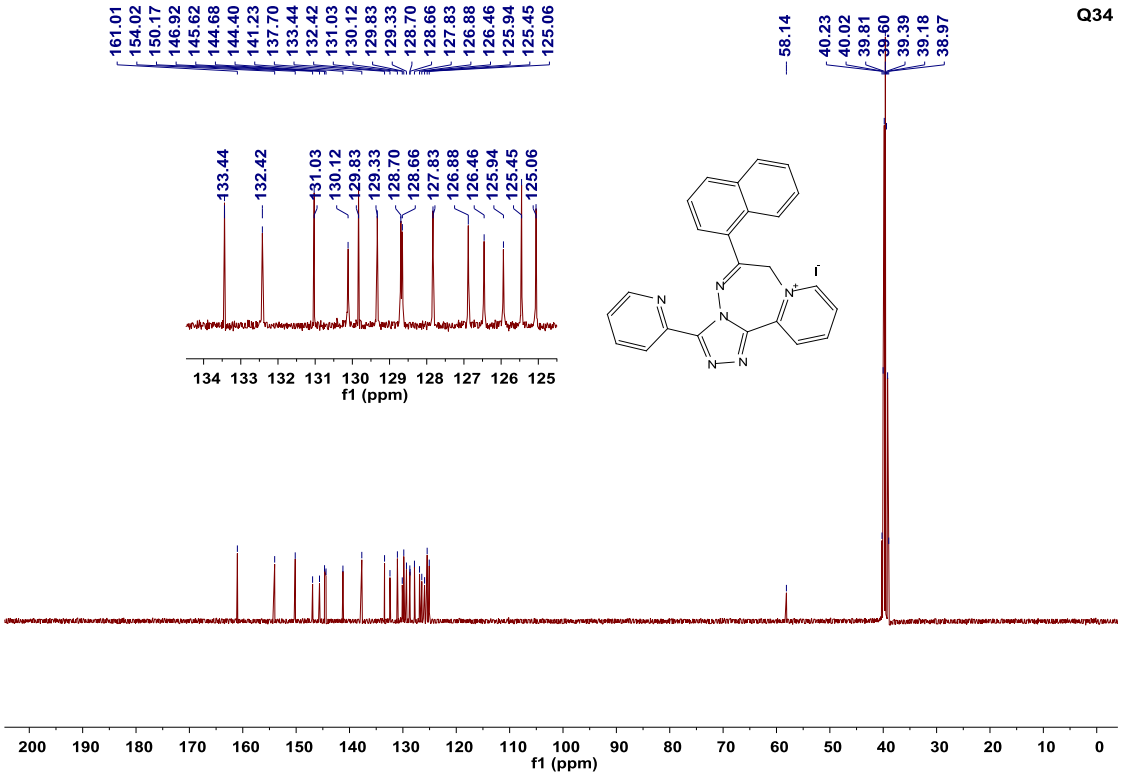
6-(naphthalen-2-yl)-3-(pyridin-2-yl)-7H-pyrido[2,1-d][1,2,4]triazolo[4,3-b][1,2,5]triazepin-8-ium iodide(Q33)



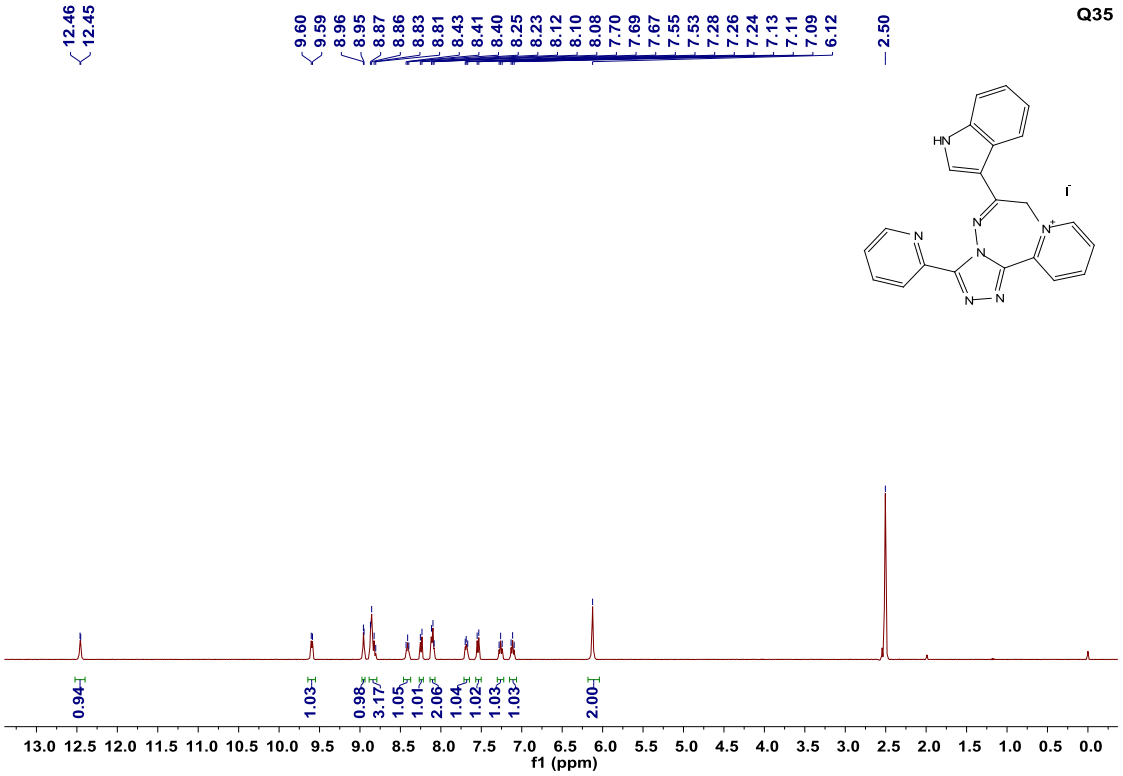


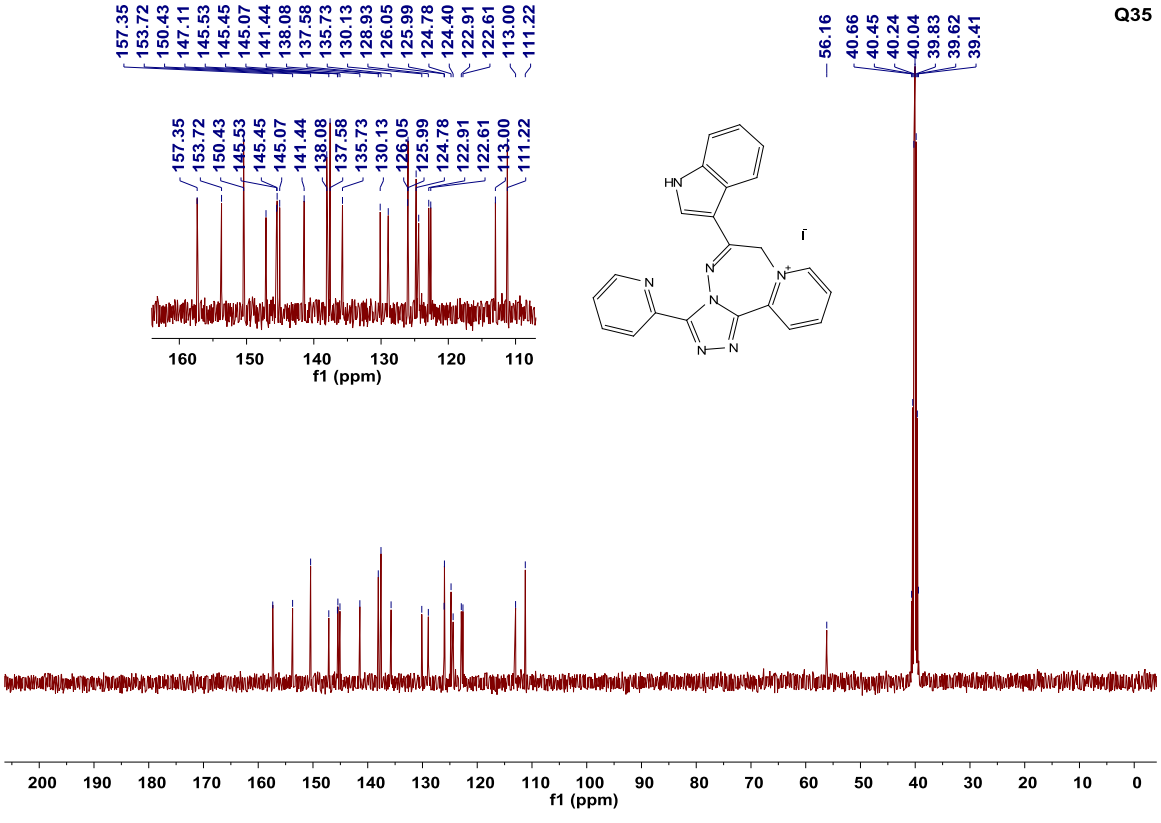
6-(naphthalen-1-yl)-3-(pyridin-2-yl)-7H-pyrido[2,1-d][1,2,4]triazolo[4,3-b][1,2,5]triazepin-8-ium iodide(Q34)



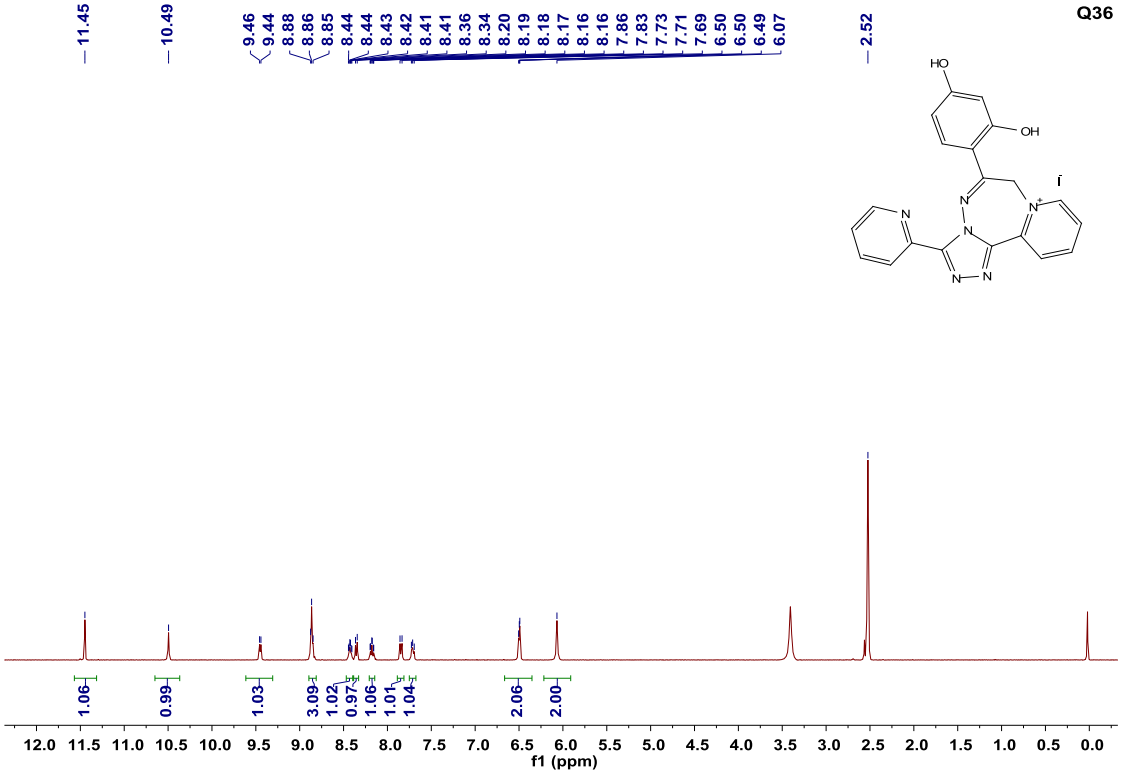


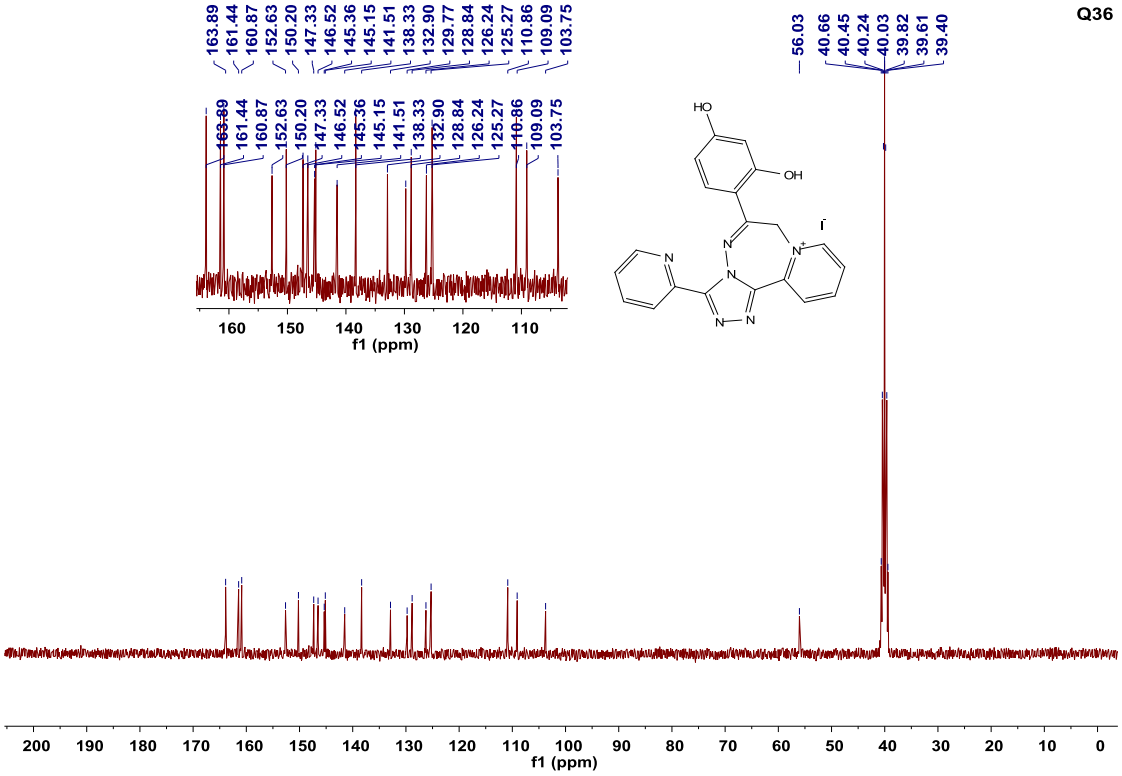
6-(1H-indol-3-yl)-3-(pyridin-2-yl)-7H-pyrido[2,1-d][1,2,4]triazolo[4,3-b][1,2,5]triazepin-8-ium iodide(Q35)



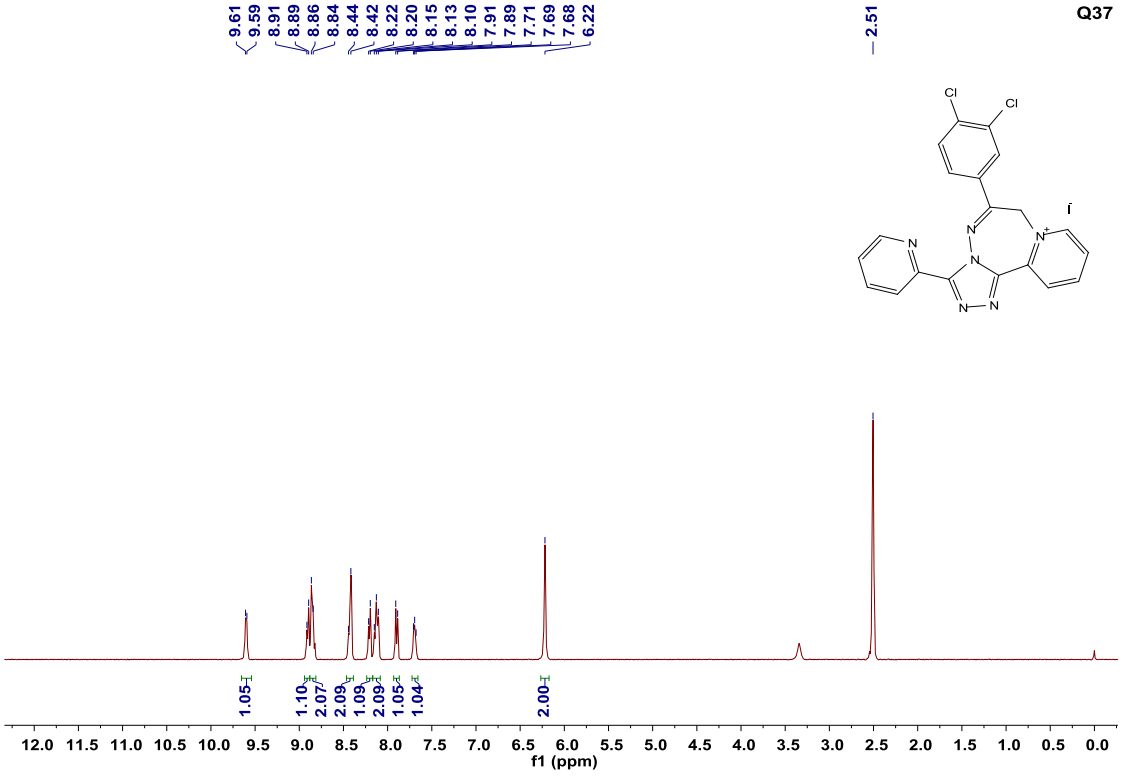


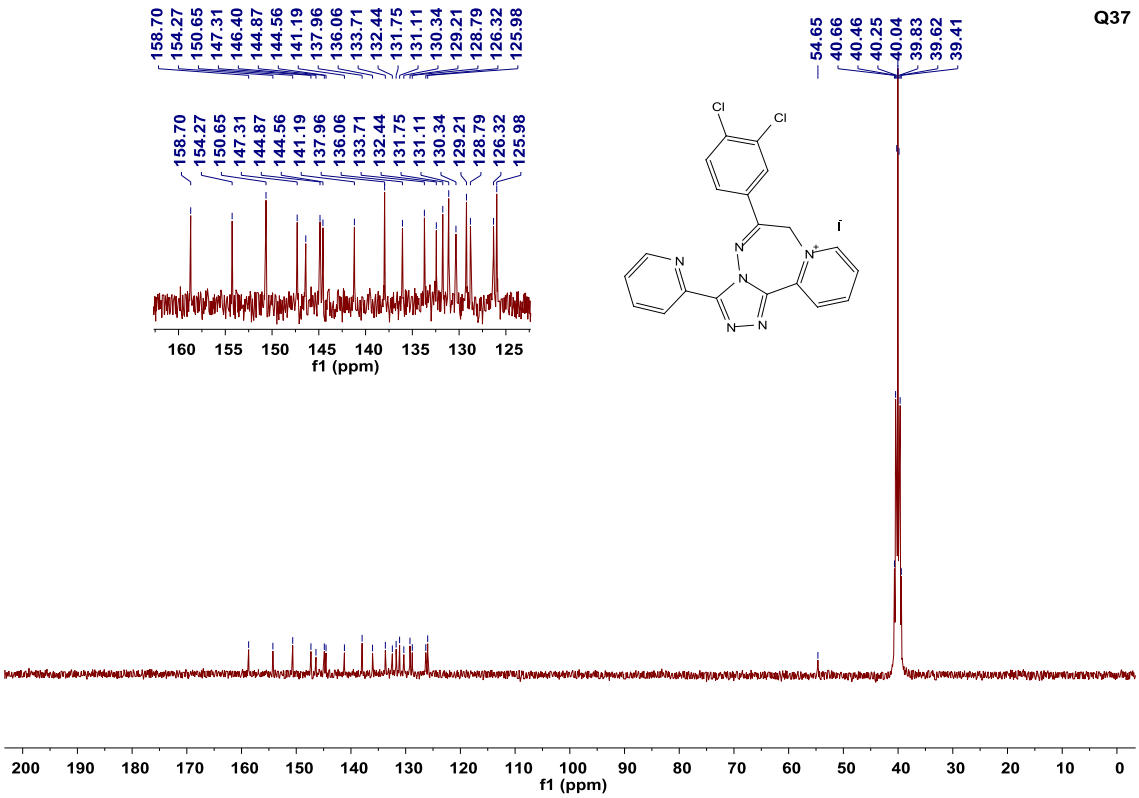
6-(2,4-dihydroxyphenyl)-3-(pyridin-2-yl)-7H-pyrido[2,1-d][1,2,4]triazolo[4,3-b][1,2,5]triazepin-8-ium iodide(Q36)





6-(3,4-dichlorophenyl)-3-(pyridin-2-yl)-7H-pyrido[2,1-d][1,2,4]triazolo[4,3-b][1,2,5]triazepin-8-ium iodide(Q37)





10. References

[1] F. Bentiss, M. Lagrenee, M. Traisnel, B. Mernari and H. Elattari, *J. Heterocyclic chem.*, 1999, **36**, 149-152.

[2] Y.S. Feng, C.Q. Xie, W. L. Qiao, and H.J. Xu., *Org. Lett.*,2013, **15**(4),936-939

[3] A. D. Becke, *J. Chem. Phys.,* 1993, **98**, 5648-5652.

[4] M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. A. Montgomery Jr., J. E. Peralta, F. Ogliaro, M. J. Bearpark, J. Heyd, E. N. Brothers, K. N. Kudin, V. N. Staroverov, R. Kobayashi, J. Normand, K. Raghavachari, A. P. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, N. J. Millam, M. Klene, J. E. Knox, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, Ö. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski and D. J. Fox, Gaussian 09, Wallingford, CT, USA, 2009.

[5] D. M. Ceperley and B. J. Alder, *Phys. Rev. Lett.*, 1980, **45**, 566-569.