Regioective Halogenation of 2-Substituted-1,2,3-Triazole via sp^2 C-H Activation

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Supporting Information

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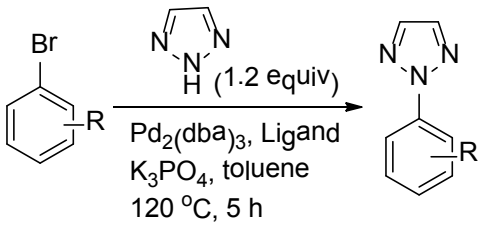
General Experimental Details:

All manipulations were carried out under argon using standard Schlenk techniques. All glassware was oven or flame dried immediately prior to use. Al solvents were purified and dried according to standard methods prior to use, unless stated otherwise.

All reagents were obtained from commercial sources and used without further purification. ^{1}H NMR spectra were obtained at 400 MHz and recorded relative to the tetramethylsilane signal (0 ppm) or residual protio-solvent. ^{13}C NMR spectra were obtained at 100 MHz, and chemical shifts were recorded relative to the solvent resonance (CDCl3, 77.0 ppm). Data for ^{1}H NMR are recorded as follows: chemical shift (δ, ppm), multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m =

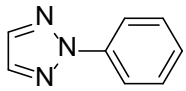
multiplet or unresolved, br = broad singlet, coupling constant(s) in Hz, integration). Data for ^{13}C NMR are reported in terms of chemical shift (δ, ppm).

2-Substituted-1,2,3-Triazoles were prepared according to known procedures（Scheme 1）.[1]

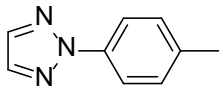


Reference:
1. S. Ueda, M. J. Su, S. L. Buchwald, *Angew. Chem.Int. Ed.,* 2011**, 50**, 8944-8947.

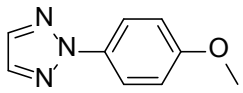
Spectral Data of Starting Materials (1a–k)



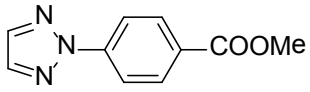
2-phenyl-2H-1,2,3-triazole (1a): Yield: 89%, colourless oil.[1] ^1H NMR (400 MHz, $CDCl_3$) δ 8.11 (d, *J* = 7.8 Hz, 2H), 7.84 (s, 2H), 7.51 (t, *J* = 7.9 Hz, 2H), 7.38 (t, *J* = 7.4 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 140.0, 135.86, 129.44, 128.50, 123.08, 120.00. HR-MS: m/z calcd for $C_8H_7N_3$:145.0640; found: 145.0641. IR:$_{max}$(thin film) (cm $^{-1}$)=3125, 3058, 2362, 1747, 1599, 1550, 1410, 1372, 1258, 1150, 1070, 953, 820, 759, 690, 667, 500, 455.



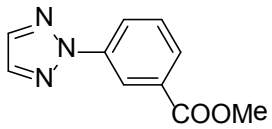
2-(p-tolyl)-2H-1,2,3-triazole (1b): Yield: 85%, brown solide , mp. 55.2–55.4°C. [1] ^1H NMR (400 MHz, $CDCl_3$) δ 7.98 (d, *J* = 8.5 Hz, 2H), 7.82 (s, 2H), 7.36 – 7.23 (m, 2H), 2.43 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 140.2, 137.86, 135.5, 129.44, 123.00, 21.54. HR-MS: m/z calcd for $C_9H_9N_3$:159.0796; found: 159.0797. IR:$_{max}$(thin film) (cm $^{-1}$)=3135, 3048, 2969, 1747, 1599, 1514, 1461, 1381, 1259, 1151, 1070, 951, 817, 759, 690, 667, 500, 455.



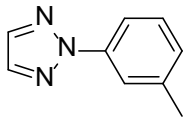
2-(4-methoxyphenyl)-2H-1,2,3-triazole (1c): Yield: 89%, colorless oil. [1] ^1H NMR (400 MHz, $CDCl_3$) δ 8.01 (d, *J* = 9.1 Hz, 2H), 7.80 (s, 2H), 7.02 (d, *J* = 9.1 Hz, 2H), 3.88 (s, 4H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.0, 135.26, 133.44, 120.10, 114.48, 55.59. HR-MS: m/z calcd for $C_9H_9N_3O$:175.0746; found: 175.0745. IR:$_{max}$(thin film) (cm $^{-1}$)=3740, 3010, 2362, 1513, 1450, 1412, 1308, 1170, 1060, 953, 820, 677, 500.



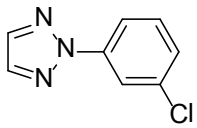
Mthyl 4-(2H-1,2,3-triazol-2-yl)benzoate (1d): Yield: 80%, white solid, mp. 100-102 °C. [2] ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.43 (d, *J* = 8.3 Hz, 2H), 8.13 (d, *J* = 8.3 Hz, 2H), 7.95 (s, 2H), 3.99 (s, 3H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 168.40, 140.1, 135.86, 129.44, 128.50, 123.08, 52.55. HR-MS: m/z calcd for $C_{10}H_9N_3O_2$:203.0695; found: 203.0695. IR:$_{max}$(thin film) (cm $^{-1}$)=3120, 3021, 2359, 1851, 1740, 1599, 1550, 1460, 1379, 1301, 1250, 1070, 820, 759, 667.



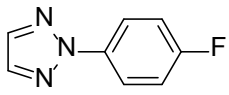
Methyl 3-(2*H*-1,2,3-triazole-2-yl)benzoate (1e): Yield: 80%, white solid, mp. 89.5 °C. [2] ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.78 (s, 1H), 8.31 dd, *J* = 8.1, 1.1 Hz, 1H), 8.06 (d, *J* = 7.8 Hz, 1H), 7.87 (s, 2H), 7.60 (t, *J* = 8.0 Hz, 1H), 3.99 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 135.86, 129.44, 128.50, 123.08, 120.00, 52.35. HR-MS: m/z calcd for $C_{10}H_9N_3O_2$:203.0695; found: 203.0695. IR:$_{max}$(thin film) (cm $^{-1}$)=3120, 3021, 2359, 1851, 1740, 1599, 1550, 1460, 1379, 1301, 1250, 1070, 820, 759, 667.



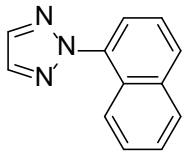
2-(m-tolyl)-2H-1,2,3-triazole (1f): Yield: 86%, colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.94 (s, 1H), 7.90 (d, *J* = 8.2 Hz, 1H), 7.83 (s, 2H), 7.39 (t, *J* = 7.8 Hz, 1H), 7.19 (d, *J* = 7.5 Hz, 1H), 2.47 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 139.34, 135.59, 135.34, 129.10, 128.31, 119.54, 116.14, 21.44.
HR-MS: m/z calcd for $C_9H_9N_3$: 159.0796; found: 159.0797. IR:$_{max}$(thin film) (cm $^{-1}$)=3131, 2970, 1748, 1605, 1524, 1463, 1380, 1261, 1150, 1070, 951, 817, 759, 690, 667, 500.



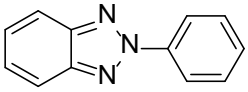
2-(3-chlorophenyl)-2H-1,2,3-triazole (1g): Yield: 88%, white solid, mp. 45-46 °C. [2] ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.15 (t, *J* = 1.8 Hz, 1H), 8.01 (dd, *J* = 8.1, 0.9 Hz, 1H), 7.85 (s, 2H), 7.44 (t, *J* = 8.1 Hz, 1H), 7.35 (dd, *J* = 8.0, 0.8 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 140.66, 135.93, 135.17, 130.37, 127.55, 119.30, 116.98. HR-MS: m/z calcd for $C_8H_6{}^{35}ClFN_3O$:179.0250; found: 179.0248. IR:$_{max}$(thin film) (cm $^{-1}$)=3747, 3080, 2366, 1590, 1488, 1440, 1376, 1260, 1153, 1105, 1074, 950, 869, 826, 778, 666, 488.



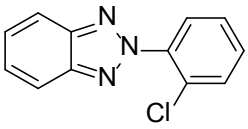
2-(4-fluorophenyl)-2H-1,2,3-triazole (1h): Yield: 82%, white solid , mp. 57 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.14-8.03 (m, 2H), 7.83 (s, 2H), 7.20 (t, *J* = 8.6 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 163.08, 160.63, 135.57, 120.77, 120.73, 116.25, 116.01. HR-MS: m/z calcd for $C_8H_6FN_3$: 163.0546; found: 163.0547. IR:$_{max}$(thin film) (cm $^{-1}$)=3547, 3097, 2356, 1590, 1488, 1440, 1376, 1260, 1153, 1105, 1074, 950, 869, 826, 778, 666, 488.



2-(1-naphthaleneyl)-2H-1,2,3-triazole (1i): Yield: 78%, white solid, mp. 110 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.15 (dd, *J* = 6.2, 3.4 Hz, 1H), 8.05-7.93 (m, 4H), 7.82 (d, *J* = 7.4 Hz, 1H), 7.64 – 7.52 (m, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 140.65, 136.17, 135.93, 135.17, 131.00, 130.38, 127.55, 120.81, 119.29, 118.02, 116.97. HR-MS: m/z calcd for $C_{12}H_9N_3$:195.0796; found: 195.0795. IR:$_{max}$(thin film) (cm $^{-1}$)= 3424, 3230, 2350, 1615, 1488, 1440, 1376, 1260, 1153, 1105, 1074, 950, 869, 826, 778, 615.



2-phenyl-2H-benzo[d]-1,2,3-triazole (1j): Yield: 70%, yellow solid, mp. 109-110 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.39 (d, *J* = 7.6 Hz, 2H), 7.97 (dd, *J* = 6.6, 3.1 Hz, 2H), 7.59 (t, *J* = 7.8 Hz, 2H), 7.52 – 7.41 (m, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 145.05, 140.39, 129.43, 128.98, 127.18, 120.66, 118.41. HR-MS: m/z calcd for $C_{12}H_9N_3$:195.0796; found: 195.0795. IR:$_{max}$(thin film) (cm $^{-1}$)= 3421, 3233, 1615, 1488, 1440, 1376, 1260, 1153, 1105, 1074, 950, 869, 826, 778, 615.



2-(2-chlorophenyl)-2H-benzo[d]-1,2,3-triazole (1k): Yield: 71%, yellow solid, mp. 51-52 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.99 (dd, *J* = 6.6, 3.1 Hz, 2H), 7.76 – 7.69 (m, 1H), 7.65-7.60 (m, 1H), 7.47 (qd, *J* = 7.3, 3.0 Hz, 4H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 144.92, 138.76, 131.02, 130.81, 129.75, 128.22, 127.43, 127.35, 118.52. HR-MS: m/z calcd for $C_{12}H_8ClN_3$:229.0407; found: 229.0408.
IR:$_{max}$(thin film) (cm $^{-1}$)= 3421, 3233, 1615, 1488, 1440, 1376, 1260, 1153, 1105, 1074, 950, 869, 826, 778, 615.

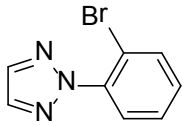
Reference:

1. F. Chevallier, T. Blin, E. Nagaradja, F. Lassagne, T. Roisnel, Y. S. Halauko, V. E. Matulis, O. A. Ivashkevich, F. Mongin, *Org. Biomol. Chem.,* 2012**, 10**, 4878.
2. S. Ueda, M. J. Su, S. L. Buchwald, *Angew. Chem.Int. Ed.*2011**, 50,** 8944.

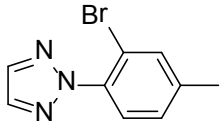
General Procedure for Palladium-catalyzed Halogenation of 2-Substituted -1,2,3-Triazoles:

A mixture of 2-Substituted-1,2,3-Triazole (**1**) (0.5 mmol)，NXS (0.55mmol)，$Pd(AcO)_2$（0.025 mmol）and PivOH (0.25 mmol) in toluene (2 ml) was stirred at 100 °C for 18 h in sealed tube. The mixture was diluted with EtOAc (10 ml) and washed with 15% aqueous NaOH solution (10 ml*3). The organic phase was dried over anhydrous Na_2SO_4, filtered and concentrated under reduced pressure. The resulting residue was purified on silica gel chromatography (EtOAc/ hexane=1/25) to give the products.

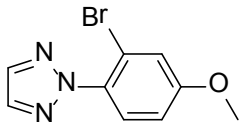
Spectral Data of Products (2a–l)



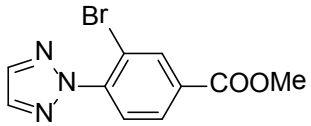
2-(2-bromophenyl)-2H-1,2,3-triazole (2a): colourless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.89 (s, 2H), 7.74 (dd, *J* = 8.0, 1.1 Hz, 1H), 7.55 (dd, *J* = 7.9, 1.5 Hz, 1H), 7.44 (td, *J* = 7.8, 1.2 Hz, 1H), 7.33 (td, *J* = 7.9, 1.6 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ139.76, 135.59, 134.10, 132.45, 130.64, 128.09, 128.11, 118.85. HR-MS: m/z calcd for $C_8H_6BrN_3$: 222.9745; found: 222.9746. IR:$_{max}$(thin film) (cm $^{-1}$)=3130, 3046, 2361, 1753, 1601, 1551, 1410, 1289, 1070, 953, 820, 690, 667, 510.



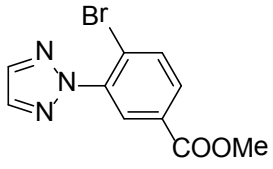
2-(2-bromo-4-methylphenyl)-2H-1,2,3-triazole (2b): White solid, mp. 93℃ ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.89 (s, 2H), 7.59 (s, 1H), 7.44 (d, *J* = 8.1 Hz, 1H), 7.26 (d, *J* = 8.1 Hz, 1H), 2.44 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 141.25, 135,62, 135.38, 134.32, 132.89, 128.73, 127.72, 20.93. HR-MS: m/z calcd for $C_9H_8BrN_3$: 236.9902; found: 236.9903. IR:$_{max}$(thin film) (cm $^{-1}$) =3230, 3003, 1751, 1600, 1540, 1454, 1386, 1300, 1154, 1066, 817, 688.



2-(2-bromo-4-methoxyphenyl)-2H-1,2,3-triazole (2c): white solid, mp. 105.5℃. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.88 (s, 2H), 7.46 (d, *J* = 8.8 Hz, 1H), 7.27 (d, *J* = 2.7 Hz, 1H), 6.98 (dd, *J* = 8.8, 2.7 Hz, 1H), 3.88 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 160.54, 135.27, 133.20, 128.80, 119.96, 118.74, 113.73, 55.89. HR-MS: m/z calcd for $C_9H_8BrN_3O$: 252.9851; found:252.9853. IR:$_{max}$(thin film) (cm $^{-1}$)=3747, 3016, 2352, 1543, 1459, 1422, 1318, 1169, 1068, 955, 825, 540.

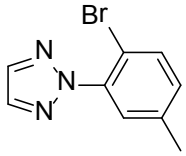


Methyl 4-bromo-3-(2*H*-1,2,3-triazol-2-yl)benzoate (2d): white solid, mp. 112.5℃. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.46 (d, *J* = 1.3 Hz, 1H), 8.13 (dd, *J* = 8.3, 1.4 Hz, 1H), 7.95 (s, 2H), 7.71 (d, *J* = 8.3 Hz, 1H), 4.00 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.04, 136.19, 132.59, 131.57, 128.94, 128.59, 127.26, 52.72. HR-MS: m/z calcd for $C_{10}H_8BrN_3O_2$: 280.9800; found: 280.9800. IR:$_{max}$(thin film) (cm $^{-1}$)=3130, 3121, 2360, 1851, 1733, 1599, 1550, 1460, 1379, 1301, 1250, 1070, 820, 759, 667.

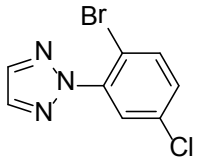


Methyl 4-bromo-3-(2*H*-1,2,3-triazol-2-yl)benzoate (2e): white solid, mp. 98.5℃. ^{1}H NMR (400

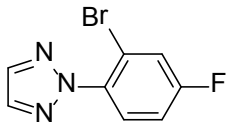
MHz, $CDCl_3$) δ 8.14 (d, *J* = 8.3 Hz, 2H), 7.94 (s, 2H), 7.86 (d, *J* = 8.3 Hz, 1H), 3.96 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.04, 136.19, 132.59, 131.57, 128.94, 128.59, 127.26, 52.72. HR-MS: m/z calcd for $C_{10}H_8BrN_3O_2$: 280.9800; found: 280.9800. IR:$_{max}$(thin film) (cm $^{-1}$)=3130, 3121, 2360, 1851, 1733, 1599, 1550, 1460, 1379, 1301, 1250, 1070, 820, 759, 667.



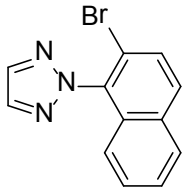
2-(2-bromo-5-methxylphenyl)-2H-1,2,3-triazole (2f): colorless oil. ^1H NMR (400 MHz, $CDCl_3$) δ 7.90 (s, 2H), 7.63 (d, *J* = 8.2 Hz, 1H), 7.38 (d, *J* = 12.2 Hz, 1H), 7.18 (dd, *J* = 8.2, 1.3 Hz, 1H), 2.39 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 139.41, 138.54, 135.46, 133.70, 131.47, 128.68, 115.25, 20.76. HR-MS: m/z calcd for $C_9H_8BrN_3$: 236.9902; found: 236.9904. IR:$_{max}$(thin film) (cm $^{-1}$)=3100, 2989, 1755, 1613, 1539, 1454, 1378, 1255, 1154, 1066, 817, 691.



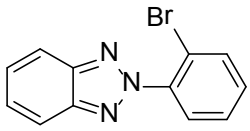
2-(2-bromo-5-chlorophenyl)-2H-1,2,3-triazole (2g): white solid, mp. 108℃. ^1H NMR (400 MHz, $CDCl_3$) δ 7.92 (s, 2H), 7.70 (d, *J* = 8.6 Hz, 1H), 7.62 (d, *J* = 2.3 Hz, 1H), 7.35 (dd, *J* = 8.6, 2.3 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 140.30, 135.95, 135.03, 133.88, 130.53, 128.14, 116.40. HR-MS: m/z calcd for C8H5ClN3: 256.9355; found: 256.9354. IR:$_{max}$(thin film) (cm $^{-1}$)=3730, 3100, 2356, 1590, 1490, 1434, 1377, 1260, 1153, 1108, 1074, 869, 780, 660.



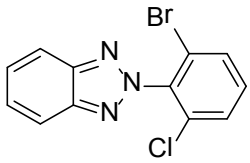
2-(2-bromo-4-fluorophenyl)-2H-1,2,3-triazole (2h): white solid, mp. 81℃. ^1H NMR (400 MHz, $CDCl_3$) δ 7.91 (s, 2H), 7.54 (m, 2H), 7.20 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 163.55, 161.02, 135.65, 129.31, 121.32, 121.06, 115.32, 115.09. HR-MS: m/z calcd for $C_8H_5BrFN_3$: 240.9651; found: 240.9651. IR:$_{max}$(thin film) (cm $^{-1}$)=3490, 3100, 2356, 1590, 1488, 1440, 1376, 1260, 1153, 1105, 950, 826, 778.



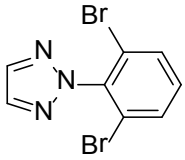
1-(2-bromo-naphthanenyl)-2H-1,2,3-triazole (2i): white solid, mp. 79℃. ^1H NMR (400 MHz, $CDCl_3$) δ 8.06 (s, 2H), 7.94 (dd, *J* = 8.5, 3.1 Hz, 2H), 7.78 (d, *J* = 8.8 Hz, 1H), 7.59 (t, *J* = 7.0 Hz, 1H), 7.51 (t, *J* = 7.2 Hz, 1H), 7.03 (d, *J* = 8.4 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 140.65, 136.17, 135.93, 135.17, 131.00, 130.38, 127.55, 120.81, 119.29, 118.02, 116.97. HR-MS: m/z calcd for $C_{12}H_8BrN_3$: 272.9902; found: 272.9903. IR:$_{max}$(thin film) (cm $^{-1}$)= 3420, 3229, 2366, 1610, 1490, 1445, 1380, 1260, 1150, 1105, 950, 826, 778, 615.



2-(2-bromophenyl)-2H-benzo[d]-1,2,3-triazole (2j): yellow solid, mp 74-75℃. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.02 – 7.94 (m, 2H), 7.79 (dd, *J* = 8.0, 1.1 Hz, 1H), 7.68 (dd, *J* = 7.9, 1.5 Hz, 1H), 7.53 – 7.36 (m, 4H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 144.81, 140.38, 134.05, 131.07, 128.40, 128.00, 127.22, 118.80, 118.49. HR-MS: m/z calcd for $C_{12}H_8BrN_3$: 272.9902; found: 272.9903. IR:$_{max}$(thin film) (cm $^{-1}$)= 3408, 3233, 1615, 1488, 1440, 1376, 1260, 1153, 1105, 1074, 950, 869, 826, 778, 615.

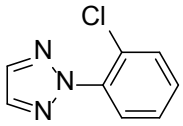


2-(2-bromo-6-chlorophenyl)-2H-benzo[d]-1,2,3-triazole (2k): white solid, mp 113-114℃. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.11 – 7.90 (m, 3H), 7.77 (dd, *J* = 7.2, 6.2 Hz, 1H), 7.53 (dd, *J* = 6.6, 3.0 Hz, 2H), 7.18 (t, *J* = 8.0 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 144.87, 143.27, 139.51, 138.65, 133.29, 132.78, 132.47, 127.51, 122.79, 121.79, 118.84, 96.35. HR-MS: m/z calcd for $C_{12}H_7BrClN_3O$: 306.9512; found: 306.9514. IR:$_{max}$(thin film) (cm $^{-1}$)= 3414, 3236, 1615, 1488, 1440, 1376, 1260, 1153, 1105, 1074, 950, 869, 826, 778, 618.

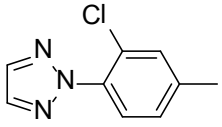


2-(2-bromo-6-bromophenyl)-2H-benzo[d]-1,2,3-triazole (2l): white solid, mp 100℃. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.96 (s, 2H), 7.71 (d, *J* = 8.1 Hz, 2H), 7.32 – 7.28 (t, *J* = 8.1 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 139.36, 135.75, 132.45, 132.29, 123.63. HR-MS: m/z calcd for $C_8H_5Br_2N_3$: 300.8850; found: 300.8853. IR:$_{max}$(thin film) (cm $^{-1}$)= 3414, 3236, 1615, 1488, 1440, 1376, 1260, 1153, 1105, 1074, 950, 869, 826, 778, 618.

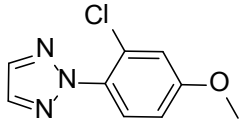
Spectral Data of Products (3a–i)



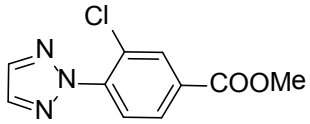
2-(2-chlorophenyl)-2H-1,2,3-triazole (3a): colourless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.90 (s, 2H), 7.63 – 7.54 (m, 2H), 7.45–7.37 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 135.64, 131.01, 130.24, 129.56, 127.75, 127.45. HR-MS: m/z calcd for $C_8H_6ClN_3$: 179.0250; found: 179.0251. IR:$_{max}$(thin film) (cm $^{-1}$)=3144, 3037, 2360, 1751, 1601, 1551, 1402, 1308, 1070, 953, 820, 690, 522.



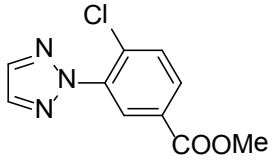
2-(2-chloro-4-methylphenyl)-2H-1,2,3-triazole (3b): colourless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.89 (s, 2H), 7.49 (d, *J* = 8.1 Hz, 1H), 7.40 (s, 1H), 7.22 (d, *J* = 8.1 Hz, 1H), 2.44 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 140.88, 135.44, 131.23, 129.16, 128.11, 127.40, 21.01. HR-MS: m/z calcd for $C_9H_8ClN_3$: 193.0407; found: 193.0408. IR:$_{max}$(thin film) (cm $^{-1}$) =3230, 3003, 1751, 1600, 1540, 1454, 1386, 1300, 1154, 1066, 817, 688.



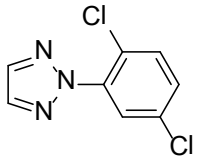
2-(2-chloro-methoxyphenyl)-2H-1,2,3-triazole (3c): colourless oil. ^{1}H NMR (400 MHz, $CDCl_3$) ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.16 (d, *J* = 2.5 Hz, 1H), 7.96 (dd, *J* = 8.9, 2.6 Hz, 1H), 7.81 (s, 2H), 7.04 (d, *J* = 9.0 Hz, 1H), 3.98 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 154.46, 135.68, 135.43, 121.30, 118.20, 112.11, 56.47. HR-MS: m/z calcd for $C_9H_8ClN_3O$: 209.0356; found: 209.0357. IR:$_{max}$(thin film) (cm $^{-1}$)=3440, 3016, 2344, 1540, 1460, 1432, 1323, 1170, 1086, 955, 825, 550.



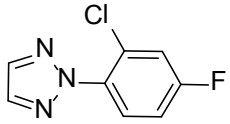
Methyl 3-chloro-4-(2H-1,2,3-triazol-2-yl)benzoate (3d): white solid, mp. 97℃. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.26 (d, *J* = 1.6 Hz, 1H), 8.07 (dd, *J* = 8.3, 1.7 Hz, 1H), 7.93 (s, 2H), 7.75 (d, *J* = 8.3 Hz, 1H), 3.97 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.04, 136.19, 132.59, 131.57, 128.94, 128.59, 127.26, 52.72. HR-MS: m/z calcd for $C_{10}H_8BrN_3O_2$:280.9800; found: 280.9801. IR:$_{max}$(thin film) (cm $^{-1}$)=3133, 2356, 1850, 1732, 1599, 1550, 1460, 1379, 1301, 1250, 1070, 820, 759, 668.



Methyl 4-chloro-3-(2H-1,2,3-triazol-2-yl)benzoate (3e): white solid, mp. 84℃. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.31 (d, *J* = 1.8 Hz, 1H), 8.10 (dd, *J* = 8.4, 1.8 Hz, 1H), 7.94 (s, 2H), 7.68 (d, *J* = 8.4 Hz, 1H), 3.96 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.04, 136.19, 132.59, 131.57, 128.94, 128.59, 127.26, 52.72. HR-MS: m/z calcd for $C_{10}H_8BrN_3O_2$:280.9800; found: 280.9801. IR:$_{max}$(thin film) (cm $^{-1}$)=3135, 2381, 1851, 1733, 1599, 1460, 1379, 1301, 1250, 1070, 820, 760.

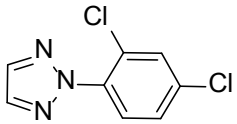


2-(2,5-dichlorophenyl)-2H-1,2,3-triazole (3f): white solid, mp. 71℃. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.92 (s, 2H), 7.68 (d, *J* = 2.2 Hz, 1H), 7.53 (d, *J* = 8.6 Hz, 1H), 7.41 (dd, *J* = 8.6, 2.3 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 138.55, 136.05, 133.12, 131.97, 130.12, 127.60. HR-MS: m/z calcd for $C_8H_5Cl_2N_3$: 212.9861; found: 212.9862. IR:$_{max}$(thin film) (cm $^{-1}$)=3650, 3210, 2210, 1590, 1490, 1434, 1377, 1260, 1153, 1108, 1074, 869, 7790, 664.

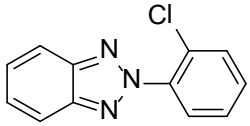


2-(2-chloro-4-fluorophenyl)-2H-1,2,3-triazole (3g): white solid, mp. 73℃. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.91 (s, 2H), 7.60 (dd, *J* = 8.9, 5.4 Hz, 1H), 7.34 (dd, *J* = 8.1, 2.7 Hz, 1H), 7.21 – 7.09 (m,

1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 140.88, 135.44, 131.23, 129.16, 128.11, 127.40. HR-MS: m/z calcd for $C_8H_5ClFN_3$: 197.0156; found: 197.0157. IR:$_{max}$(thin film) (cm $^{-1}$)=3450, 3130, 2278, 1590, 1490, 1440, 1376, 1260, 1153, 1105, 950, 828, 787.

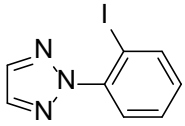


2-(2,4-dichlorophenyl)-2H-1,2,3-triazole (3h): white solid, mp. 61℃. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.92 (s, 2H), 7.60 (dd, *J* = 12.3, 5.3 Hz, 2H), 7.42 (dd, *J* = 8.6, 2.2 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 135.90, 135.52, 130.85, 130.24, 128.36, 127.76. HR-MS: m/z calcd for $C_8H_5Cl_2N_3$: 212.9861; found: 212.9862. IR:$_{max}$(thin film) (cm $^{-1}$)=3350, 3120, 2278, 1590, 1490, 1440, 1376, 1260, 1153, 1105, 949, 829, 779.

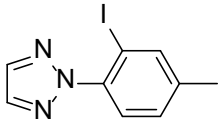


2-(2-chlorophenyl)-2H-benzo[d]-1,2,3-triazole (3i): yellow solide, mp 51-52 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.99 (dd, *J* = 6.6, 3.1 Hz, 2H), 7.76 – 7.69 (m, 1H), 7.65 – 7.60 (m, 1H), 7.47 (qd, *J* = 7.3, 3.0 Hz, 4H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 144.92, 138.76, 131.02, 130.81, 129.75, 128.22, 127.43, 127.35, 118.52. HR-MS: m/z calcd for $C_{12}H_8ClN_3$:229.0407; found: 229.0408. IR:$_{max}$(thin film) (cm $^{-1}$)= 3421, 3233, 1615, 1488, 1376, 1260, 115, 1074, 950, 869, 778, 615.

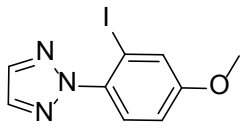
Spectral Data of Products (4a–i)



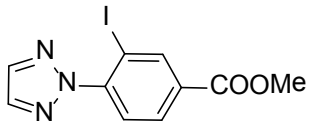
2-(2-iodophenyl)-2H-1,2,3-triazole (4a): Brown solid, mp. 63 ℃. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.89 (s, 2H), 7.85 (s, 1H), 7.38 (d, *J* = 8.0 Hz, 1H), 7.30 (s, 1H), 2.42 (s, 3H). ^{13}C NMR (100 MHz , CDCl3) 141.3, 141.0, 139.8, 135.4, 129.5, 127.1, 93.8. HR-MS: m/z calcd for $C_8H_6IN_3$: 270.9606; found: 270.9606. IR:$_{max}$(thin film) (cm $^{-1}$)=3044, 3037, 2360, 1751, 1601, 1551, 1402, 1308, 1070, 953, 820, 690, 522.



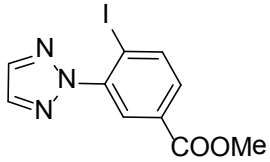
2-(2-iodo-4-methylphenyl)-2H-1,2,3-triazole (4b): Yellow solid, mp. 124℃. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.89 (s, 2H), 7.85 (s, 1H), 7.38 (d, *J* = 8.0 Hz, 1H), 7.30 (s, 1H), 2.42 (s, 3H). ^{13}C NMR (100 MHz , CDCl3) 141.5, 141.0, 140.8, 135.5, 129.7, 127.4, 92.8, 20.8. HR-MS: m/z calcd for $C_9H_8iN_3$:284.9763 ; found: 284.9764. IR:$_{max}$(thin film) (cm $^{-1}$) = 3139, 2956, 2922, 1600, 1514, 1498, 1411, 1251, 1150, 1024, 962, 951, 819, 757, 510.



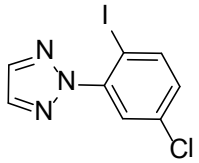
2-(4-Methoxy-2-iodophenyl)-2H-1,2,3-triazole (4c): Orange solid, mp. 92℃. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.87 (s, 2H), 7.49 (d, *J* = 2.7 Hz, 1H), 7.38 (d, *J* = 8.8 Hz, 1H), 7.00 (dd, *J* = 8.8, 2.7 Hz, 1H), 3.87 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 160.33, 135.28, 128.25, 124.96, 114.46, 93.72, 55.87.
HR-MS: m/z calcd for $C_9H_8IN_3O$: 300.9712; found: 300.9713. IR:$_{max}$(thin film) (cm $^{-1}$)=3445, 3023, 2345, 1599, 1540, 1460, 1432, 1323, 1170, 1086, 955, 838, 556.



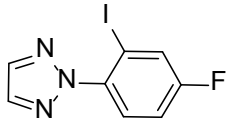
Methyl 3-iodo-4-(2H-1,2,3-triazol-2-yl)benzoate (4d): Yellow solid, mp. 89℃. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.25 (d, *J* = 1.9 Hz, 1H), 8.02 (dd, *J* = 8.4, 1.9 Hz, 1H), 7.94 (s, 2H), 7.87 (d, *J* = 8.4 Hz, 1H), 3.96 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.72, 146.10, 142.06, 140.54, 136.03, 131.88, 130.06, 127.19, 90.94, 52.69. HR-MS: m/z calcd for $C_{10}H_8IN_3O_2$: 328.9661; found: 328.9662.
IR:$_{max}$(thin film) (cm $^{-1}$)=3100, 2361, 1850, 1732, 1599, 1550, 1460, 1379, 1301, 1250, 1070, 820, 759, 668, 550.



Methyl 4-iodo-3-(2H-1,2,3-triazol-2-yl)benzoate (4e): Yellow solid, mp. 81℃. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.25 (d, *J* = 1.9 Hz, 1H), 8.02 (dd, *J* = 8.4, 1.9 Hz, 1H), 7.94 (s, 2H), 7.87 (d, *J* = 8.4 Hz, 1H), 3.96 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.21, 135.91, 134.44, 131.10, 130.45, 129.05, 124.04, 52.61. HR-MS: m/z calcd for $C_{10}H_8IN_3O_2$: 328.9661; found: 328.9662. IR:$_{max}$(thin film) (cm $^{-1}$)=3100, 2326, 1850, 1732, 1599, 1550, 1460, 1379, 1301, 1250, 1070, 820, 759, 668, 551.

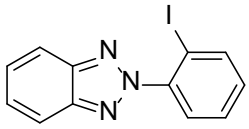


2-(5-chloro-2-iodophenyl)-2H-1,2,3-triazole (4f): Yellow solid, mp. 74℃. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.97 – 7.85 (m, 3H), 7.54 (d, *J* = 2.4 Hz, 1H), 7.20 (dd, *J* = 8.5, 2.4 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 162.33, 161.80, 139.76, 135.64, 134.68, 127.79, 127.46, 127.22, 116.18, 114.87, 93.19.
HR-MS: m/z calcd for $C_8H_5ClIN_3$: 304.9217; found: 304.9218. IR:$_{max}$(thin film) (cm $^{-1}$)=3559, 3210, 2210, 1590, 1490, 1434, 1377, 1260, 1153, 1108, 1074, 869, 7790, 664.

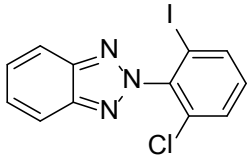


2-(2-iodo-4-fluorophenyl)-2H-1,2,3-triazole (4g): Yellow solid, mp. 65℃. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.91 (s, 2H), 7.74 (dd, *J* = 7.7, 2.7 Hz, 1H), 7.48 (dd, *J* = 8.8, 5.2 Hz, 1H), 7.26 – 7.16 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 163.33, 160.80, 139.86, 135.94, 135.68, 128.79, 127.36, 127.12,

116.10, 115.87, 93.09. HR-MS: m/z calcd for $C_8H_5FIN_3$: 288.9512; found: 288.9513. IR:$_{max}$(thin film) (cm $^{-1}$)=3350, 3110, 2283, 1590, 1490, 1376, 1260, 1153, 1105, 950, 828, 787.



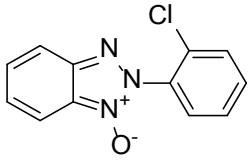
2-(2-iodophenyl)-2H-benzo[d][1,2,3]triazole (4h): Yellow solid, mp. 110℃. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.06 (d, *J* = 8.0 Hz, 1H), 8.00 (dt, *J* = 5.6, 1.5 Hz, 2H), 7.62 (dd, *J* = 7.9, 1.2 Hz, 1H), 7.54 (t, *J* = 7.7 Hz, 1H), 7.48 (dt, *J* = 5.6, 1.5 Hz, 2H), 7.27 (ddd, *J* = 8.3, 6.5, 1.0 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 144.90, 140.49, 131.25, 128.86, 128.00, 127.27, 118.59, 92.51. HR-MS: m/z calcd for $C_{12}H_8IN_3$: 320.9763; found: 320.9765. IR:$_{max}$(thin film) (cm $^{-1}$)= 3402, 3236, 1615, 1488, 1376, 1260, 1105, 1074, 950, 869, 778, 615.



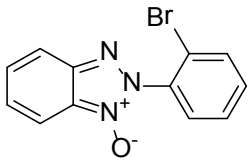
2-(2-chloro-6-iodophenyl)-2H-benzo[d][1,2,3]triazole (4i): Yellow solid, mp. 120℃. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.11 – 7.86 (m, 3H), 7.65 – 7.44 (m, 3H), 7.32 – 7.17 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 144.92, 138.01, 132.53, 130.19, 127.52, 118.82, 96.5. HR-MS: m/z calcd for $C_{12}H_7ClIN_3$: 354.9373; found: 354.9375. IR:$_{max}$(thin film) (cm $^{-1}$)= 3410, 3223, 1610, 1488, 1376, 1260, 1105, 1074, 950, 869, 778, 615.

General Procedure for Palladium-catalyzed Halogeantion 2-substituted-1,2,3 -triazole *N*-Oxides

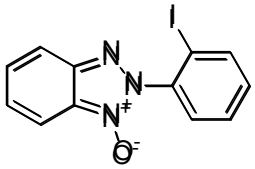
A mixture of N^2-Substituted-1,2,3-Triazole N-oxides (**1**) (0.5 mmol), NXS (0.55mmol), $Pd(AcO)_2$ （0.025 mmol）and PivOH (0.25 mmol) in toluene (2 ml) was stirred at 120 °C for 18 h in sealed tube. The mixture was diluted with EtOAc (10 ml) and washed with 15% aqueous NaOH solution (10 ml*3). The organic phase was dried over anhydrous Na_2SO_4, filtered and concentrated under reduced pressure. The resulting residue was purified on silica gel chromatography (EtOAc/ hexane=1/10) to give the products (**6**).



2-(2-chlorophenyl)-2H-benzo[d][1,2,3]triazole 1-oxide (6a): Brown solid, mp. 93℃. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.84 (dd, *J* = 15.8, 8.8 Hz, 2H), 7.72 – 7.58 (m, 3H), 7.58 – 7.47 (m, 2H), 7.41 (dd, *J* = 7.9, 6.9 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 142.14, 133.14, 132.82, 132.43, 130.81, 129.91, 129.36, 127.79, 126.56, 125.22, 119.44, 114.21. HR-MS: m/z calcd for $C_{12}H_8ClN_3O$: 245.0356; found: 245.0357. IR:$_{max}$(thin film) (cm $^{-1}$)= 3410, 3240, 3064, 1634, 1615,1507, 1479, 1460, 1394, 1318, 1163, 1105, 1074, 918, 869, 743, 615.



2-(2-bromophenyl)-2H-benzo[d][1,2,3]triazole 1-oxide (6b): Brown solid, mp. 91℃. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.84 (m, 3H), 7.57 (m, 4H), 7.46 – 7.36 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 142.03, 134.20, 133.90, 132.94, 130.12, 129.33, 128.40, 126.51, 125.21, 122.39, 119.45, 114.22. HR-MS: m/z calcd for $C_{12}H_8BrN_3O$: 288.9851; found: 288.9852. IR:$_{max}$(thin film) (cm $^{-1}$)= 3408, 3233, 2916, 1640, 1615,1507, 1479, 1460, 1394, 1318, 1163, 1105, 1074, 913, 743.



2-(2-iodophenyl)-2H-benzo[d][1,2,3]triazole 1-oxide (6c): Red brown solid, mp. 121℃. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.09 (d, *J* = 8.0 Hz, 1H), 7.85 (dd, *J* = 15.2, 8.8 Hz, 2H), 7.67 – 7.47 (m, 3H), 7.47 – 7.33 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 144.90, 143.94, 140.50, 131.31, 130.02, 128.91, 128.49, 127.87, 127.37, 126.79, 118.61, 118.41. HR-MS: m/z calcd for $C_{12}H_8IN_3O$: 336.9712; found: 336.9713. IR:$_{max}$(thin film) (cm $^{-1}$)= 3410, 3233, 3016, 1640, 1560, 1507, 1479, 1460, 1394, 1318, 1163, 1105, 1074, 963, 778.

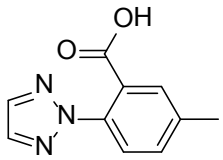
General Procedure for deoxygenation of 1,2,3-triazole *N*-oxides :

2-substituted-1,2,3-triazole *N*-oxides（**6**）(0.3 mmol) was dissolved in dry CH_2Cl_2 (10 ml) in and PBr_3 (50 mg, 0.36 mmol, 1.2 equiv.) added. The reaction mixture was heated at 60 °C for 1h. Under cooling in an ice bath the reaction mixture was basified with Na_2CO_3(aq) and the pH adjusted to 10-12 with 2M NaOH(aq). The mixture was extracted with CH_2Cl_2 until the extract showed no product as judged by TLC. The combined organic layers were dried over Na_2SO_4, filtered and concentrated to give **3i, 2j and 4h** in high yield.

General Procedure for the synthesis of compound 7 :

The mixture of **2b** (0.22 mmol) and CuCN (0.44 mmol) in DMF (2 ml) was heated at 120 ℃ for 12 h. The reaction was cooled to room temperature, water (10 ml) was added, the solution was extracted with CH_2Cl_2 (5 ml*3). The combined organic phases were washed with brine, dried over anhydrous Na_2SO_4 and concentrated. The residue was used in next step without purification.

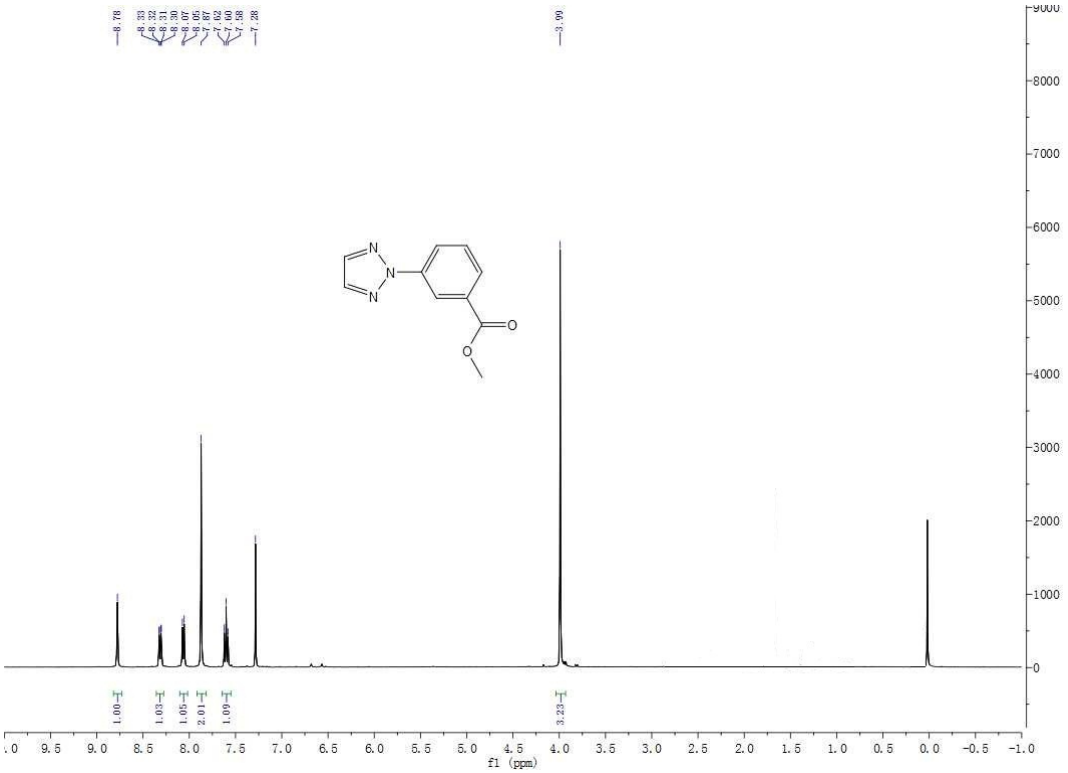
The product was heated in aq. NaOH solution (6 M, 3 ml) and EtOH (3 ml) for 6 h. The reaction mixture was cooled to room temperature, and acidified to PH 4-5 with diluted hydrochloride acid (6M aq.). The mixture was extracted with CH_2Cl_2 (5 ml*3). The combined organic phases were washed with brine, dried over anhydrous Na_2SO_4 and concentrated. The residue was purified on silica gel (CH_2Cl_2/MeOH=20/1) to give a white solid (yield: 80%).



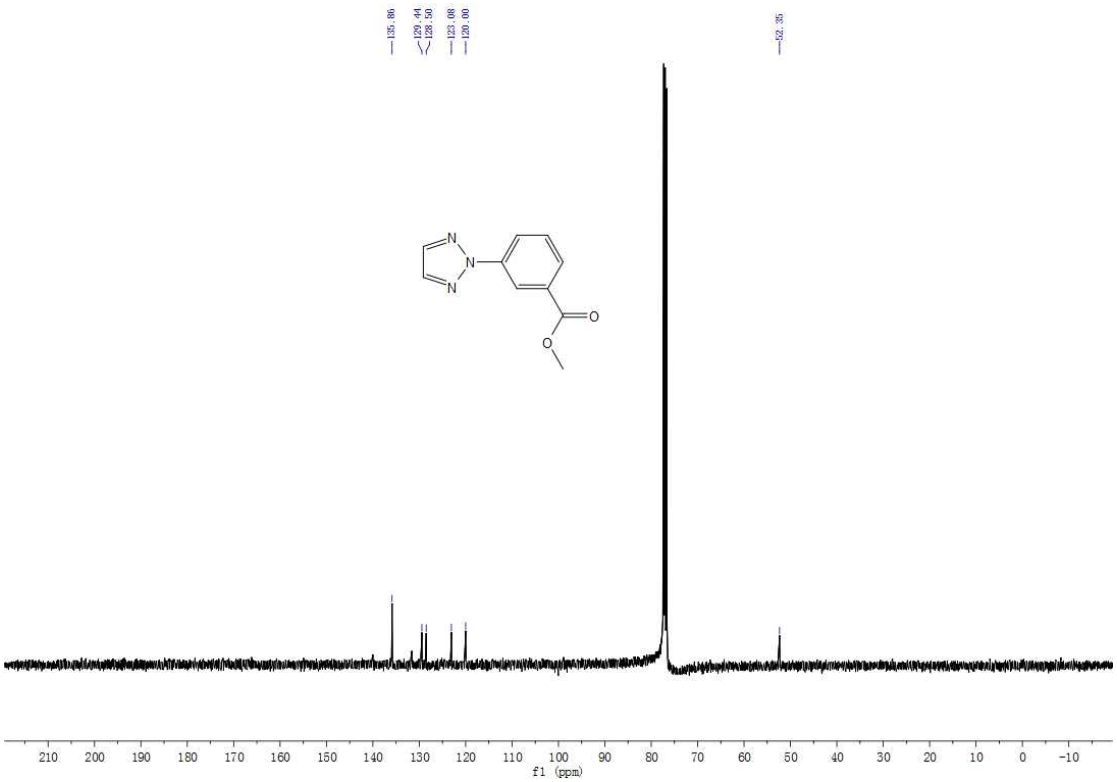
5-methyl-2-(2H-1,2,3-triazol-2-yl)benzoic acid (7): White solid, mp. 121℃. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.84 (s, 2H), 7.76 (s, 1H), 7.66 (d, J = 8.1 Hz, 1H), 7.48 (d, J = 8.1 Hz, 1H), 2.48 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 170.61, 139.19, 136.59, 135.59, 133.24, 131.30, 125.94, 125.24, 21.02. HR-MS: m/z calcd for $C_{10}H_9N_3O_2$: 203.0695; found: 203.0696.

SPECTRA

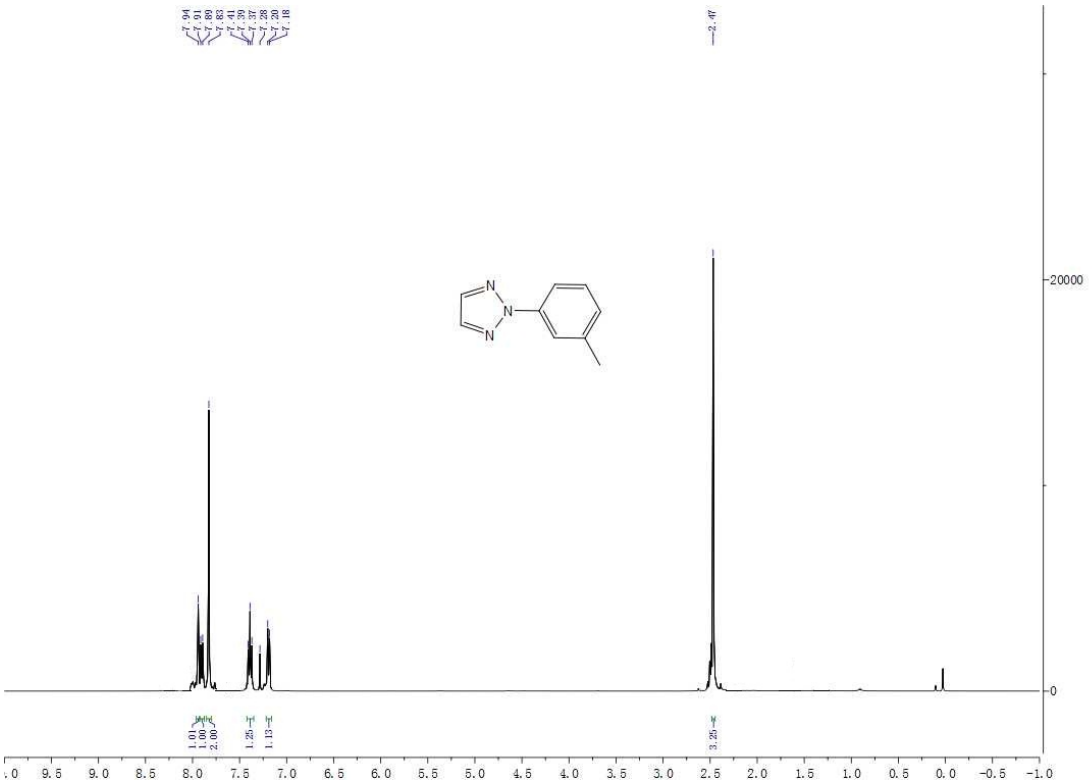
1e-^{1}H



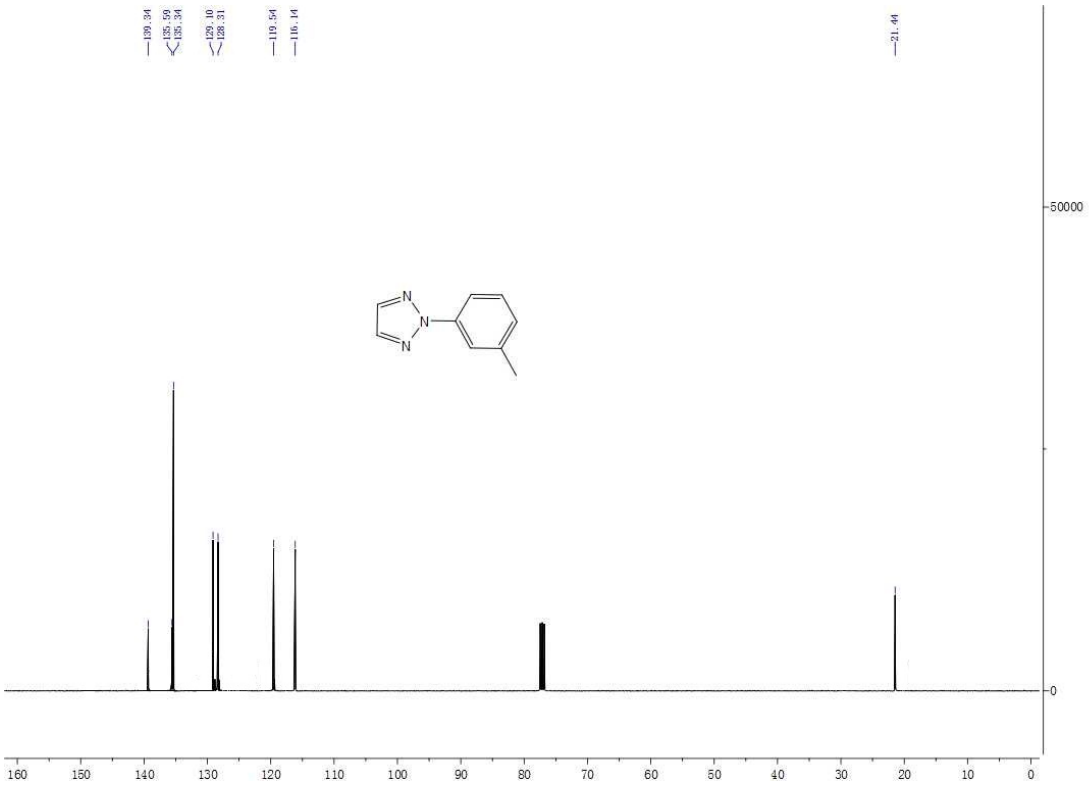
1e-^{13}C


135.86
129.44
128.50
123.08
120.00
52.35
f1 (ppm)

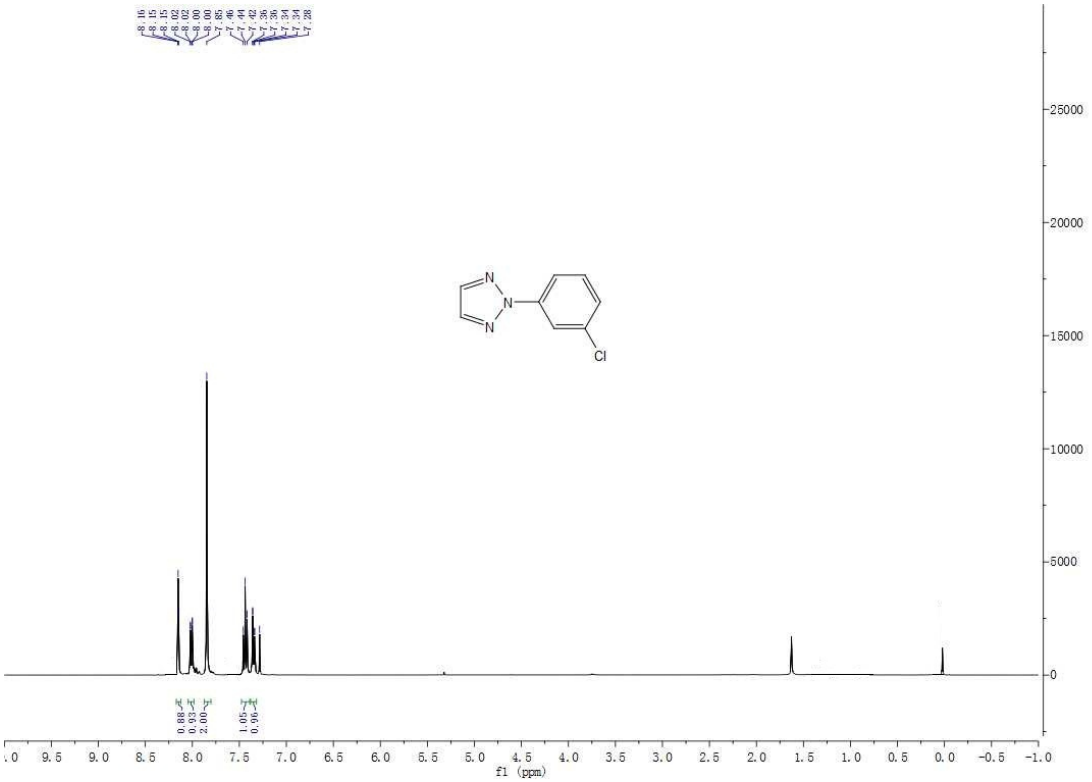
1f-^{1}H


7.94
7.91
7.89
7.83
7.41
7.39
7.37
7.28
7.20
7.18
2.47
20000
0
f1 (ppm)

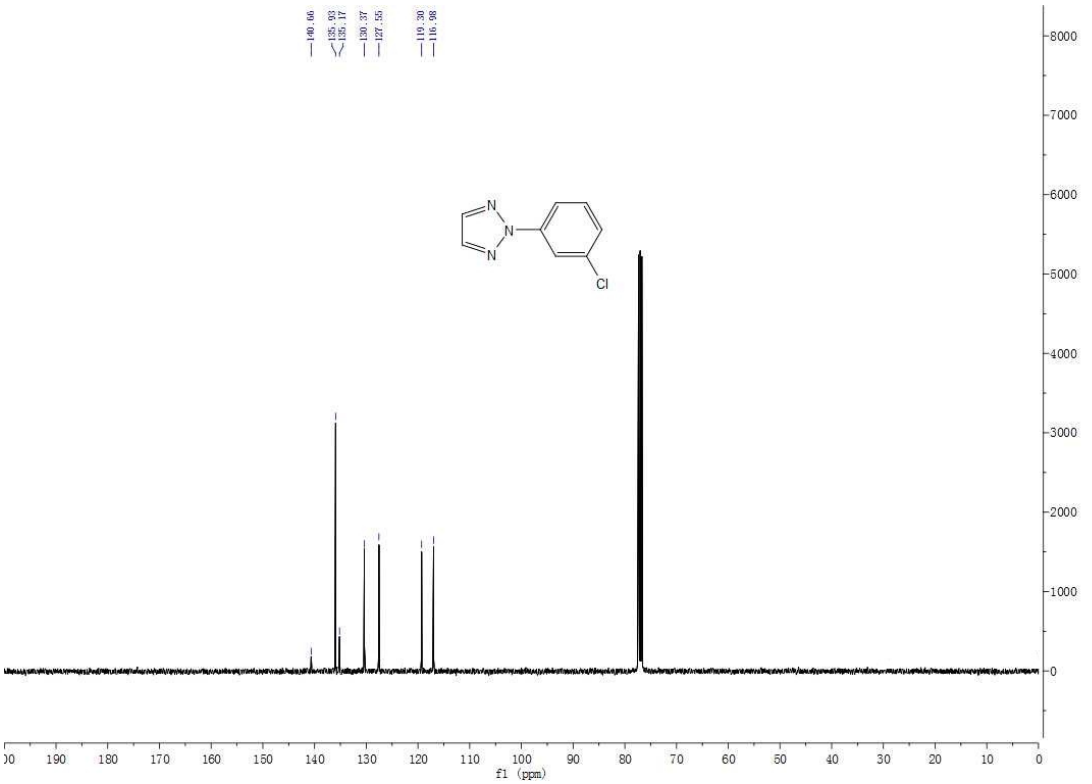
1f- ^{13}C



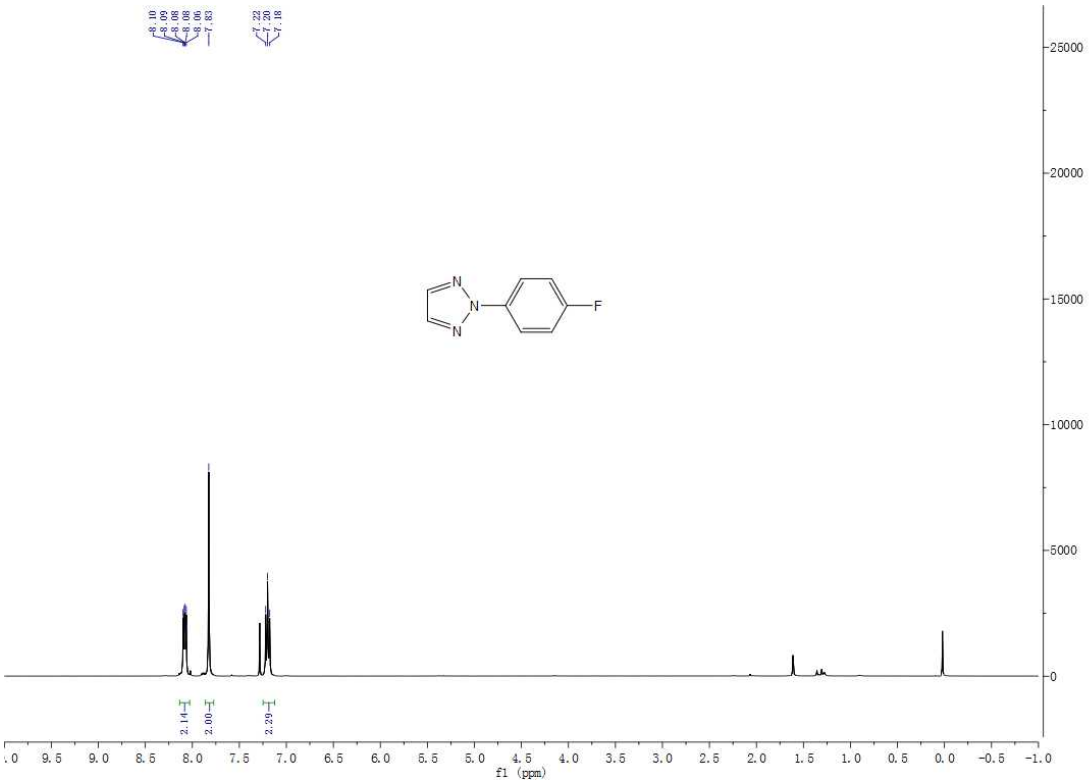
1g-^{1}H



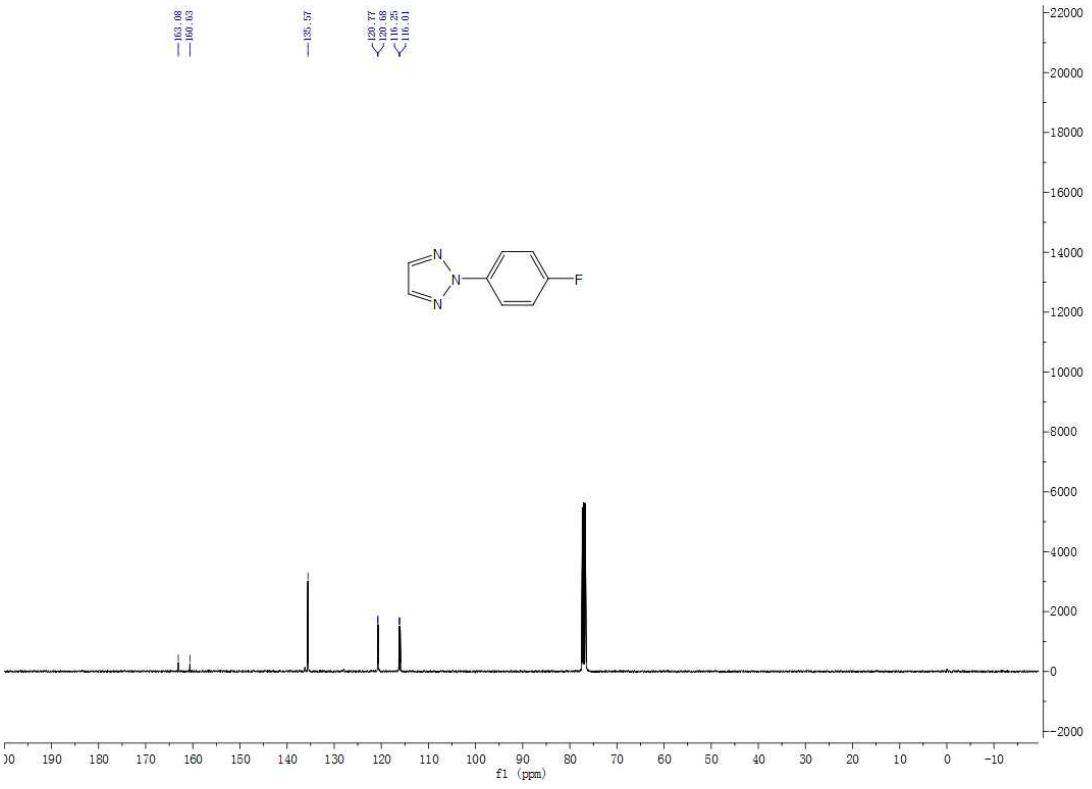
1g- ^{13}C


140.66
135.93
135.17
130.37
127.55
119.30
116.98
N
N
N
Cl
f1 (ppm)

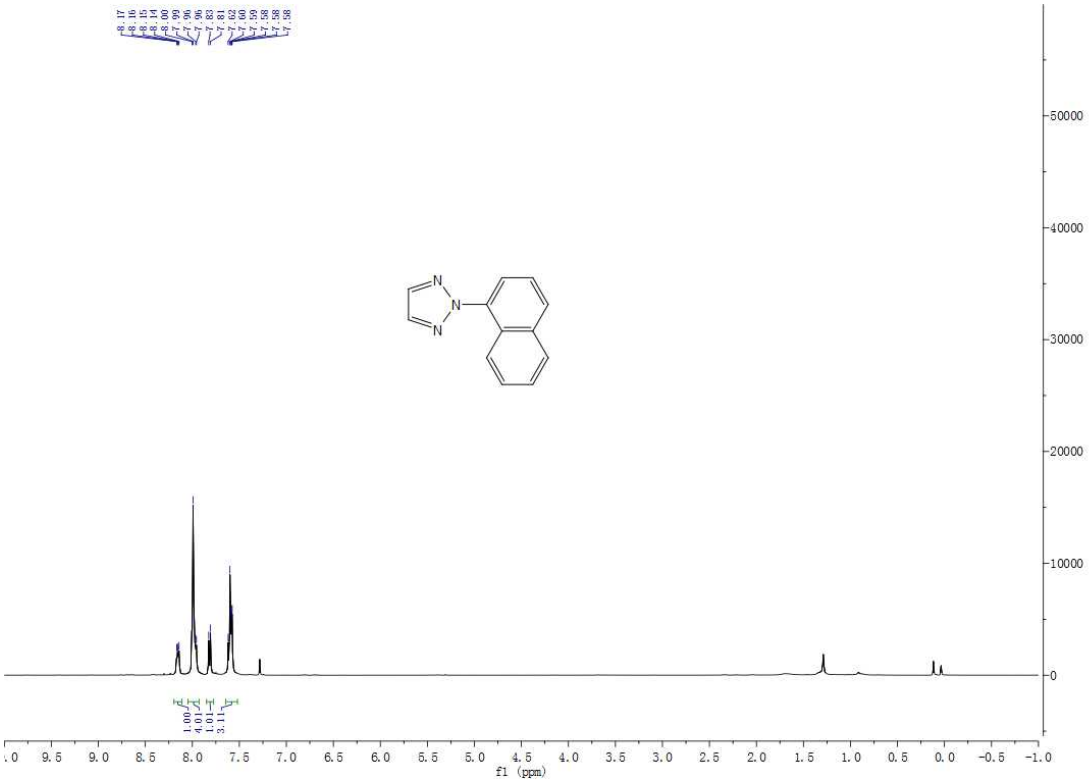
1h-^{1}H


8.10
8.09
8.08
8.08
8.06
7.83
7.22
7.20
7.18
N
N
N
F
2.14
2.00
2.29
f1 (ppm)

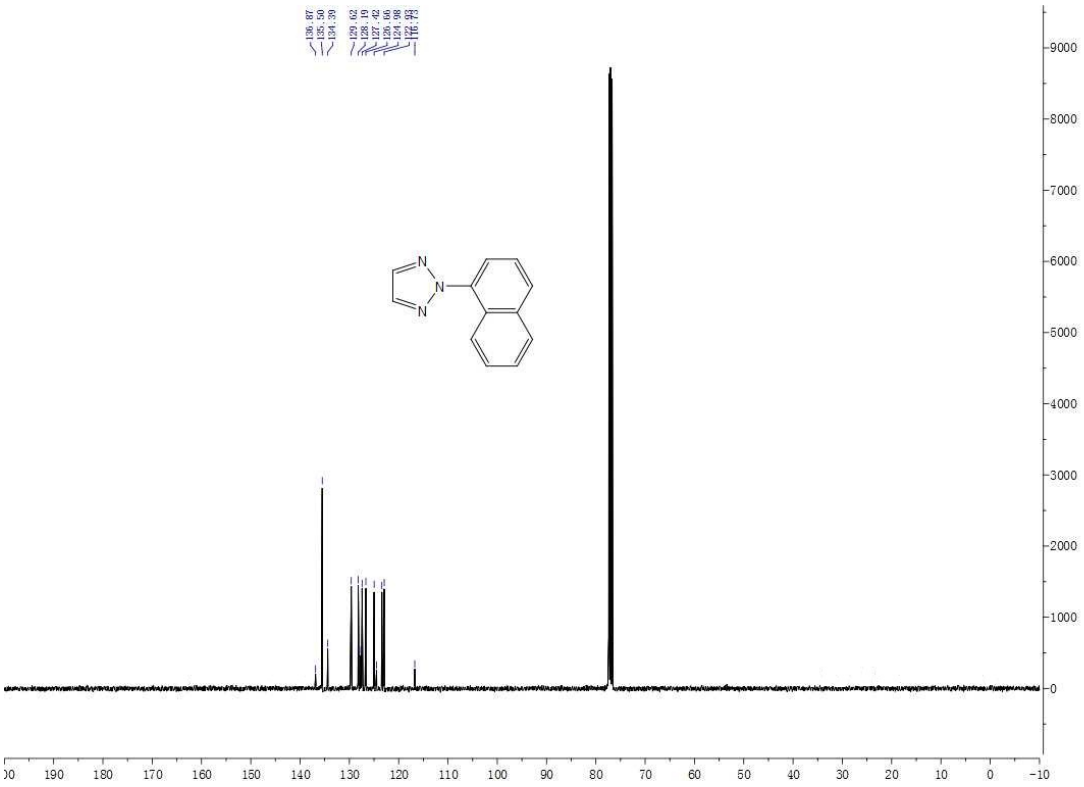
1h- ^{13}C



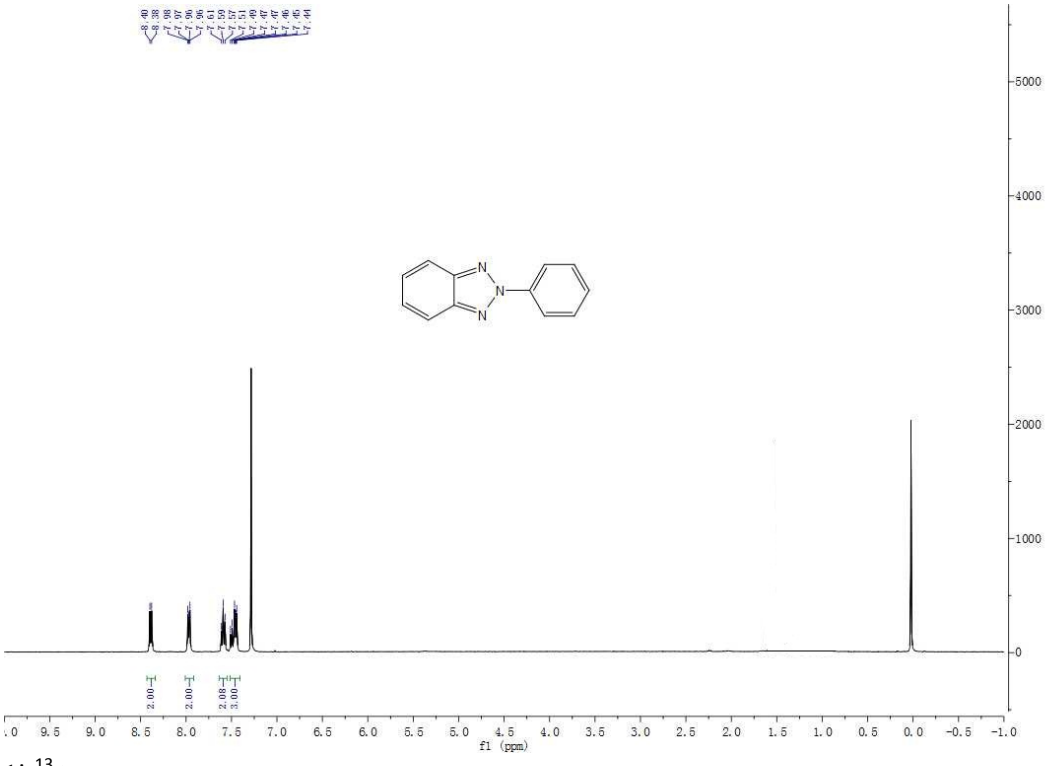
1i-^{1}H



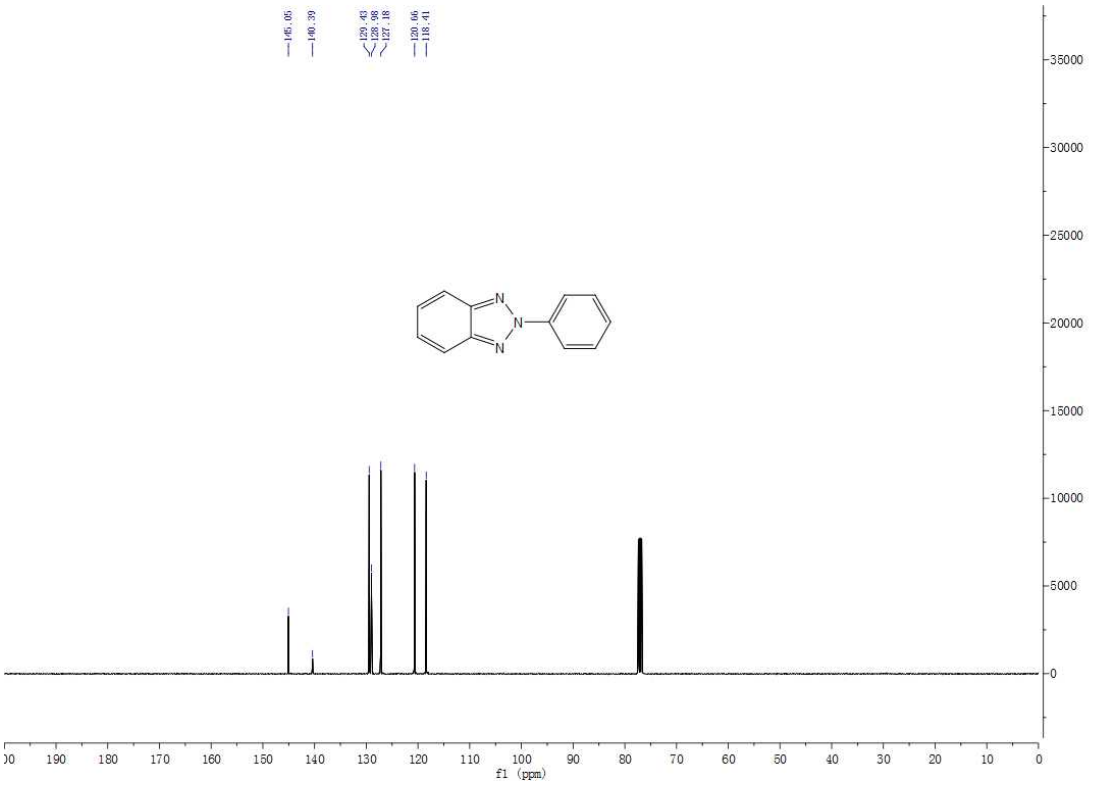
1i- ^{13}C



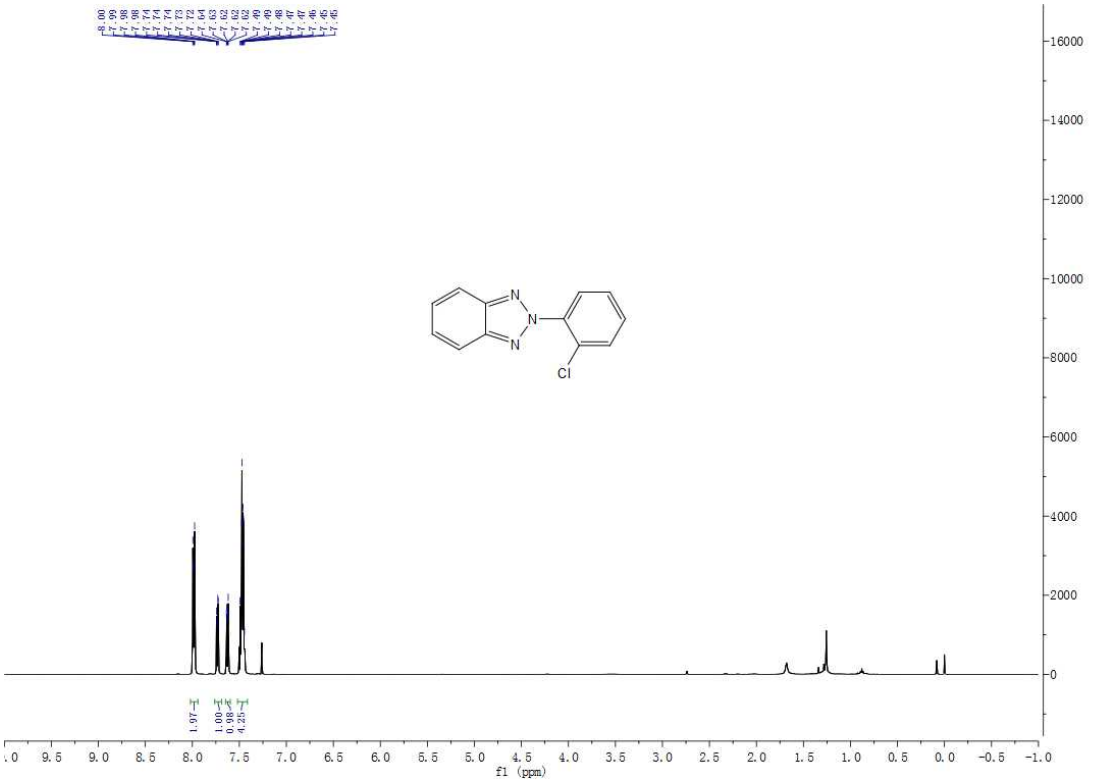
1j-^{1}H



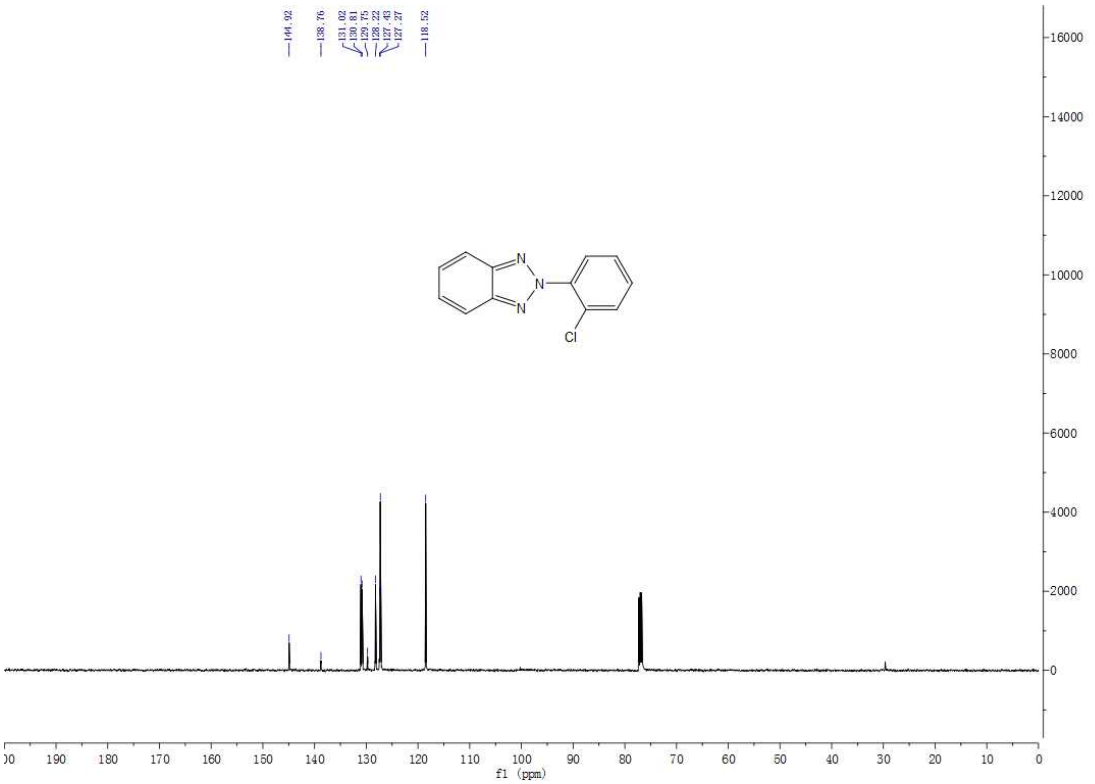
1j-^{13}C


145.05
140.39
129.43
128.98
127.18
120.66
118.41
f1 (ppm)

1k-^{1}H

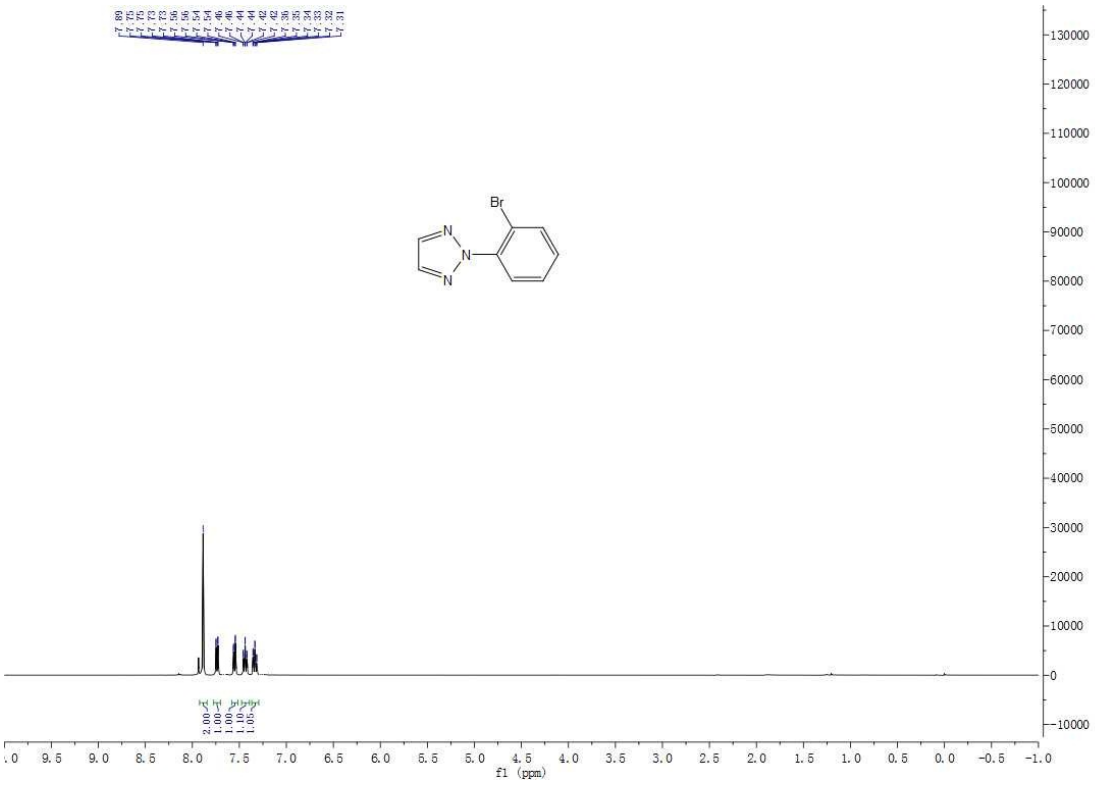

Cl
1.97
1.00
0.98
4.25
f1 (ppm)

1k- ^{13}C

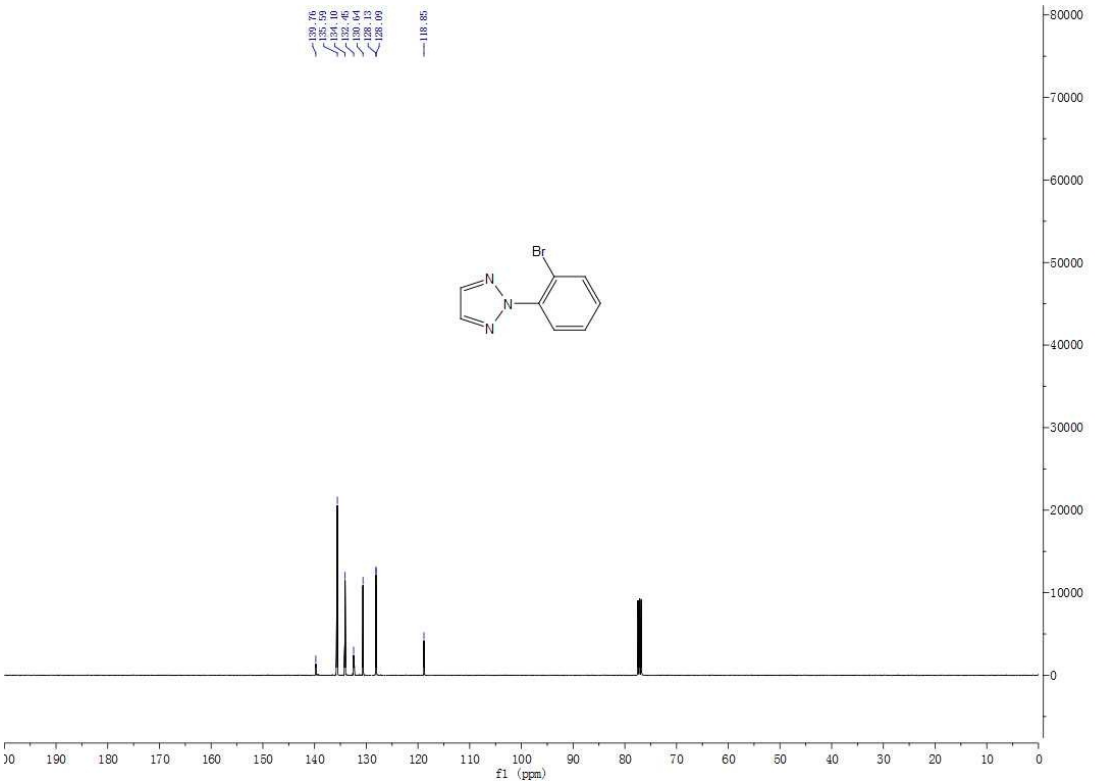


Compounds spectra(2, 3, 4, 6, 8)

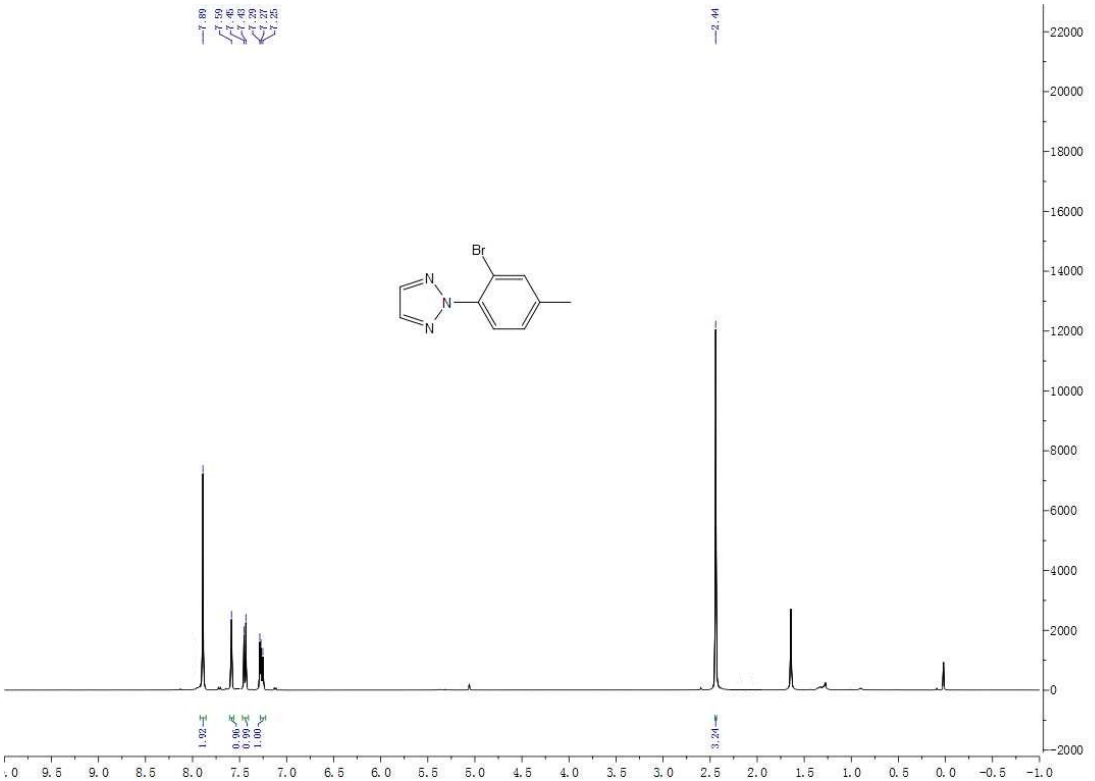
2a-^{1}H



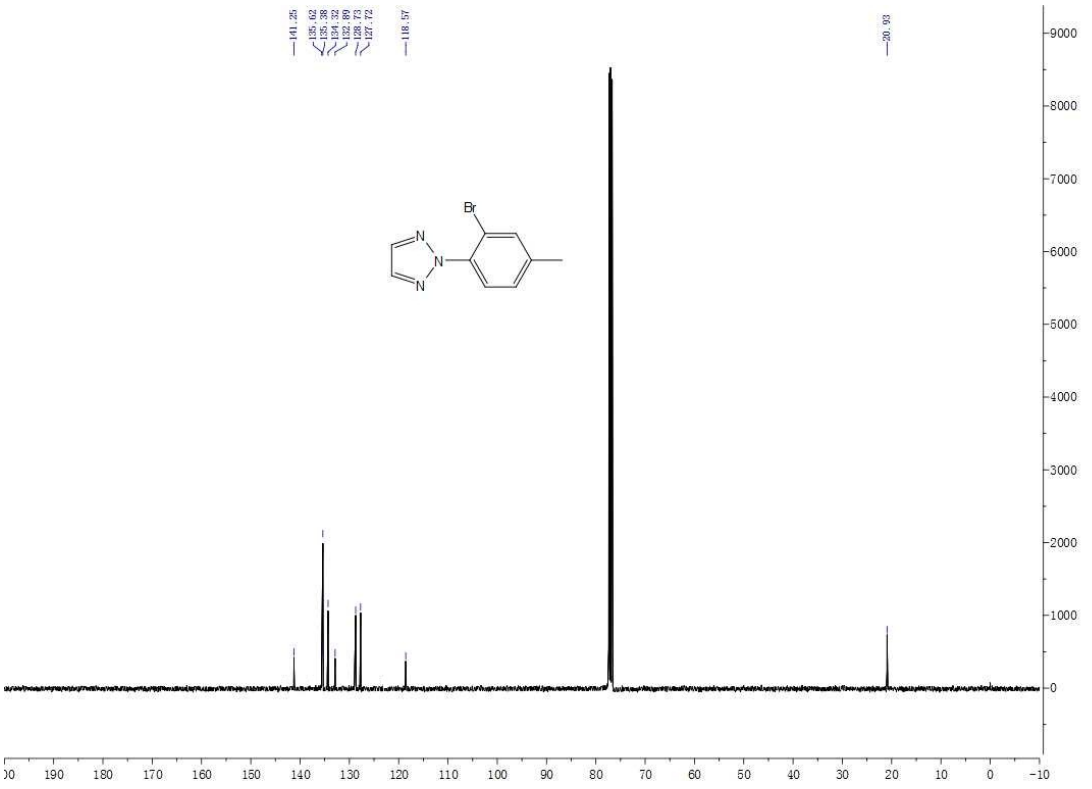
2a-^{13}C


139.75
135.50
134.10
132.45
130.64
128.13
126.09
118.85
Br
N
N
N
f1 (ppm)

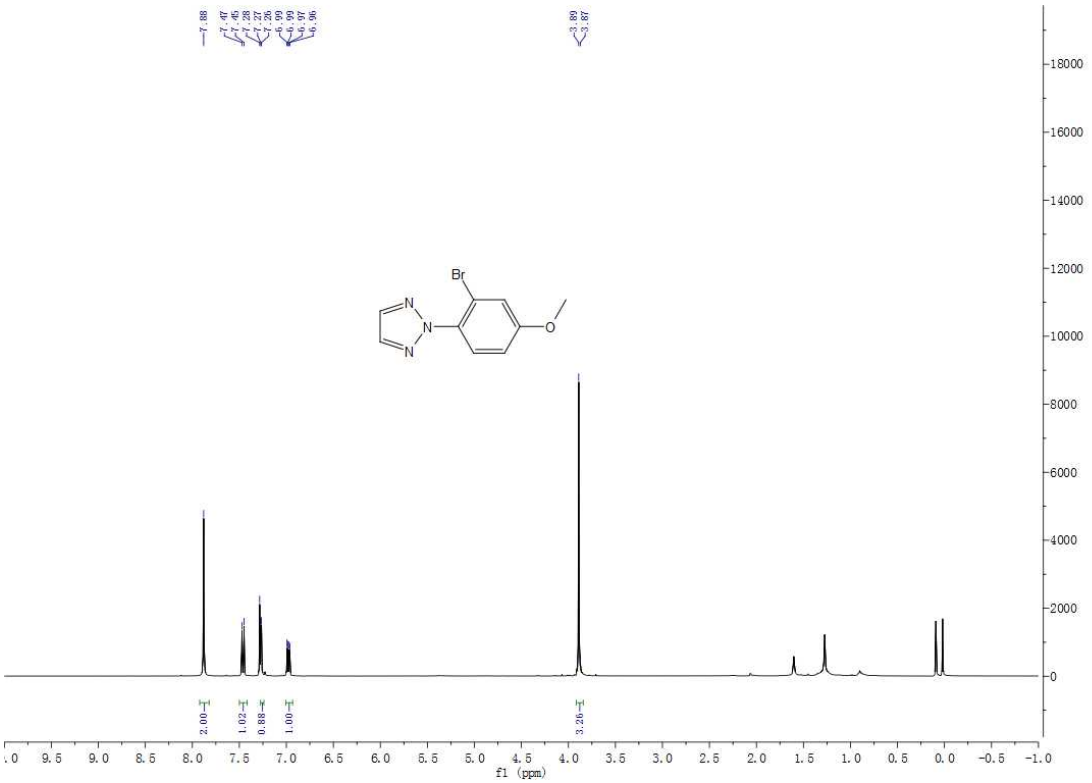
2b-^{1}H


7.89
7.59
7.45
7.43
7.29
7.27
7.25
2.44
Br
N
N
N
1.92
0.96
0.99
1.00
3.24

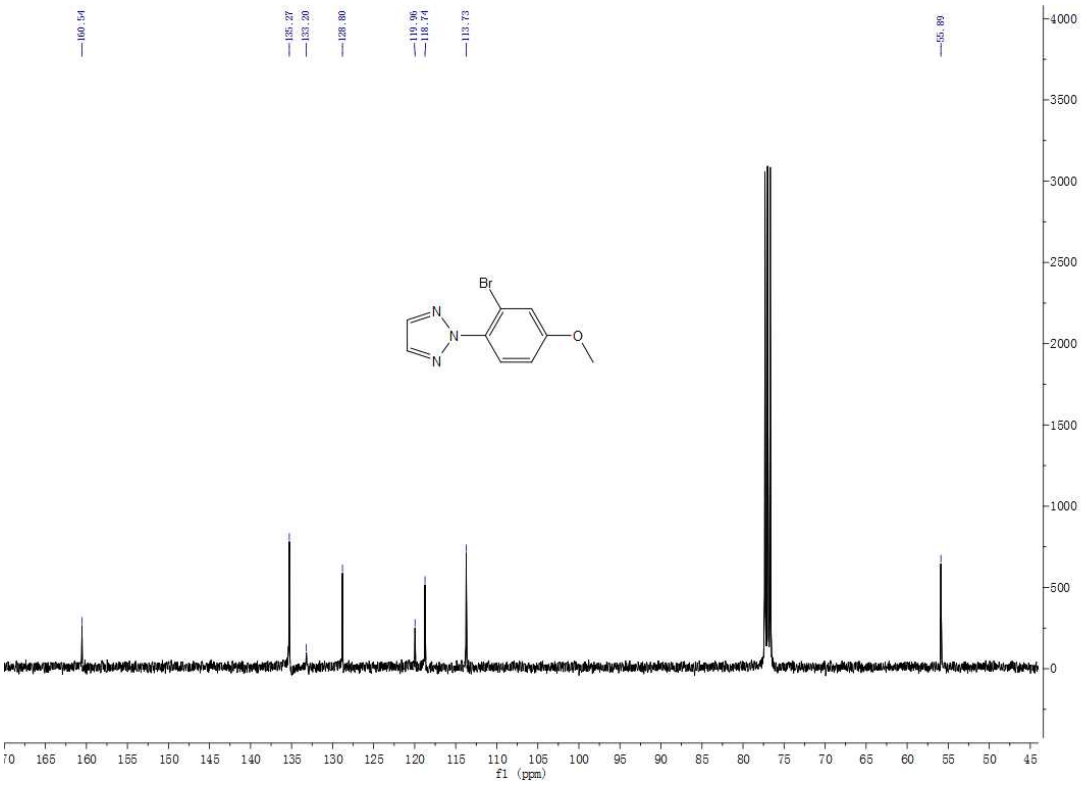
2b-^{13}C


141.25
135.62
135.38
134.32
132.89
128.73
127.72
118.57
20.93
Br
N
N
N

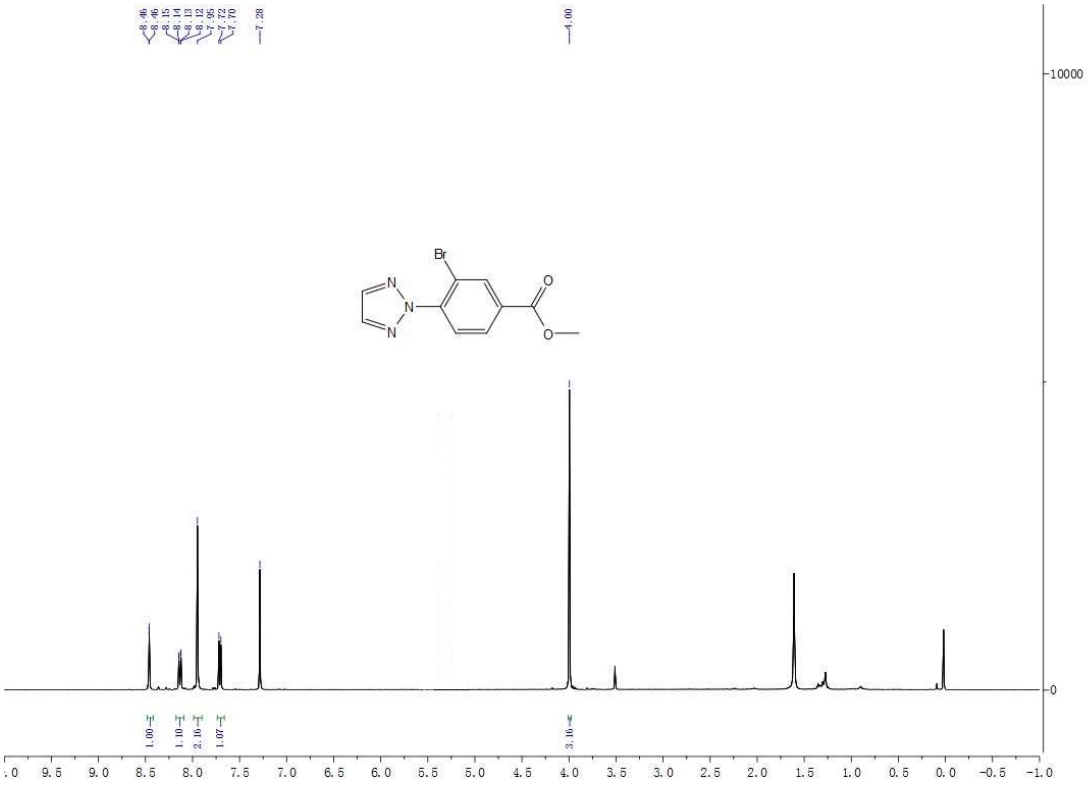
2c-^{1}H


7.88
7.47
7.45
7.28
7.27
7.26
6.99
6.97
6.96
3.89
3.87
Br
N
N
N
O
2.00
1.02
0.88
1.00
3.26
f1 (ppm)

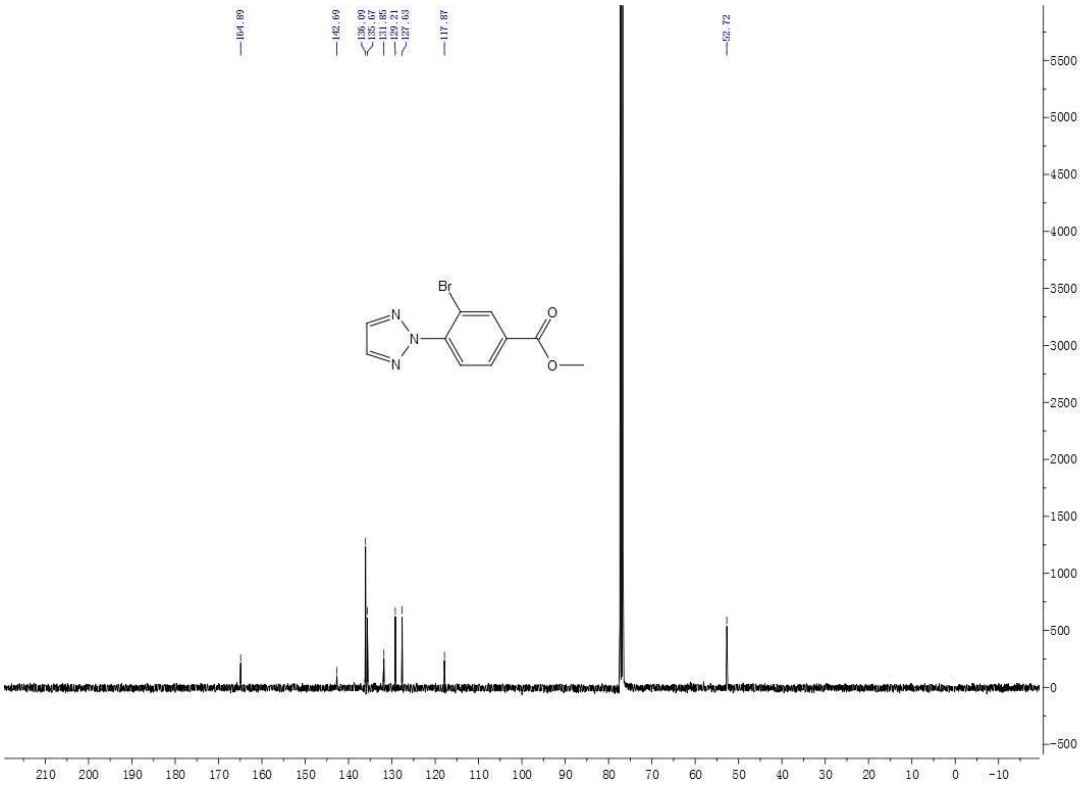
2c- ^{13}C


160.54
135.27
133.20
128.80
119.96
118.74
113.73
55.89
Br
N
N
N
O
f1 (ppm)

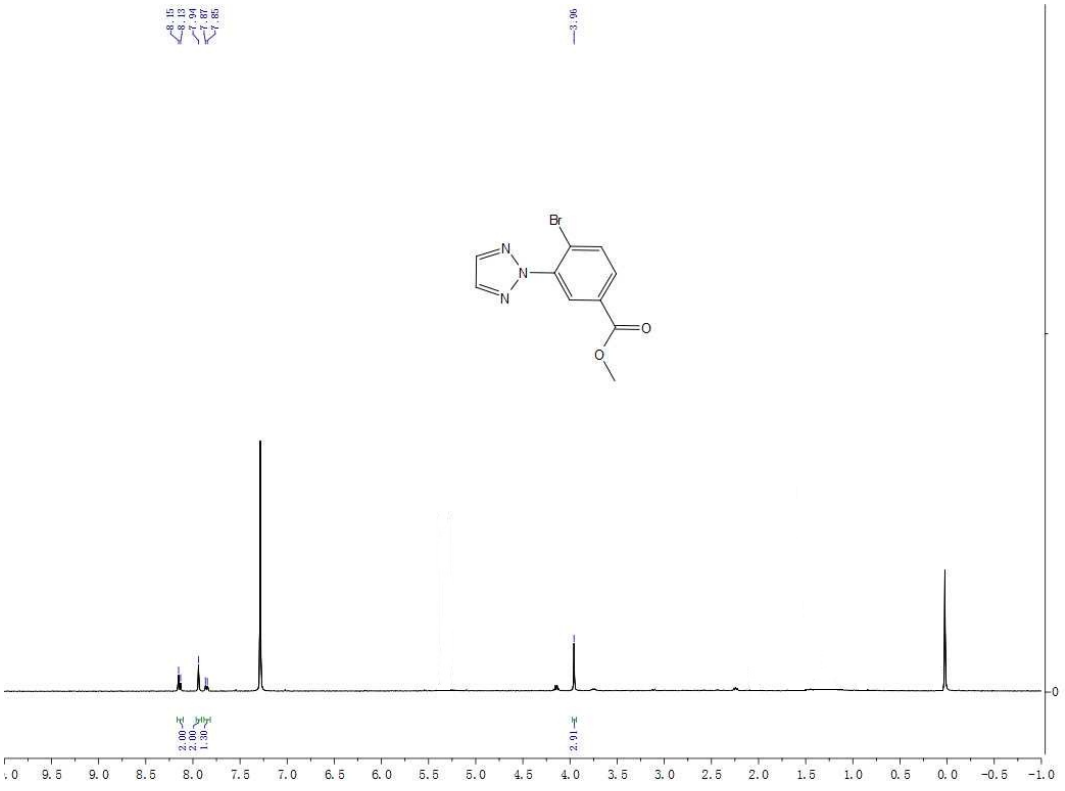
2d-^{1}H


8.46
8.46
8.15
8.14
8.13
8.12
7.72
7.70
7.28
4.00
Br
N
N
N
O
O
1.00
1.10
2.16
1.07
3.16

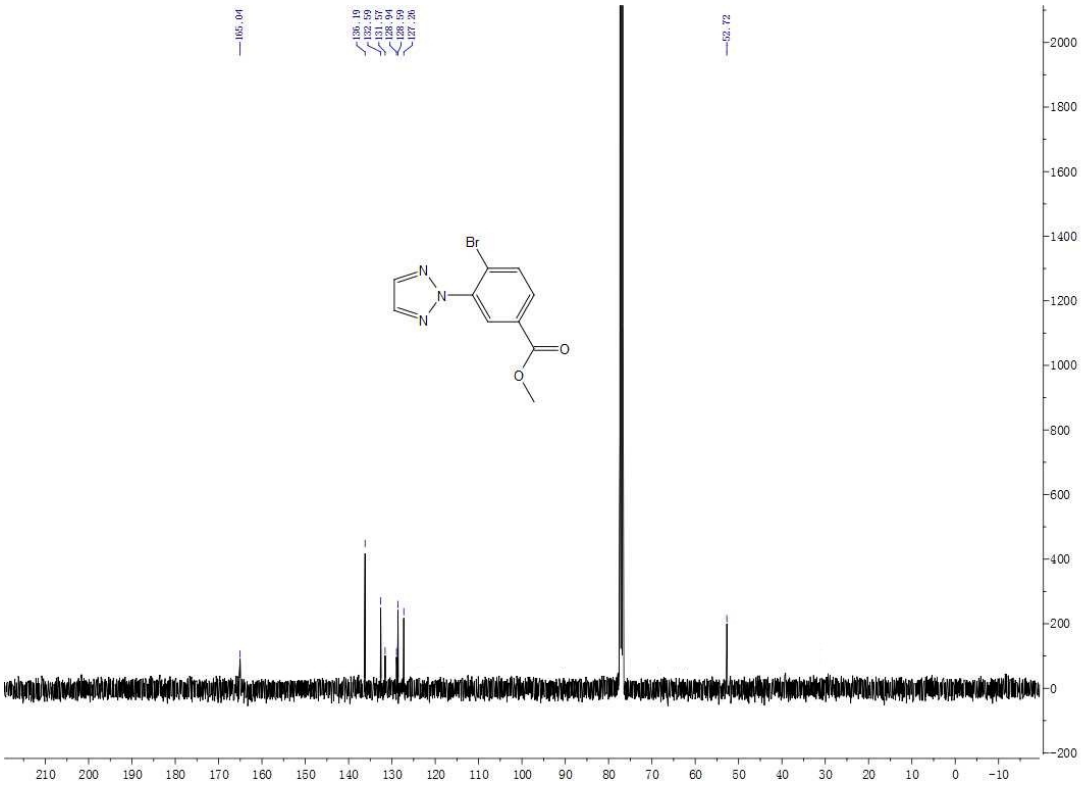
2d-^{13}C


164.89
142.69
136.09
135.67
133.85
129.21
127.63
117.87
52.72
Br
N
N
N
O
O

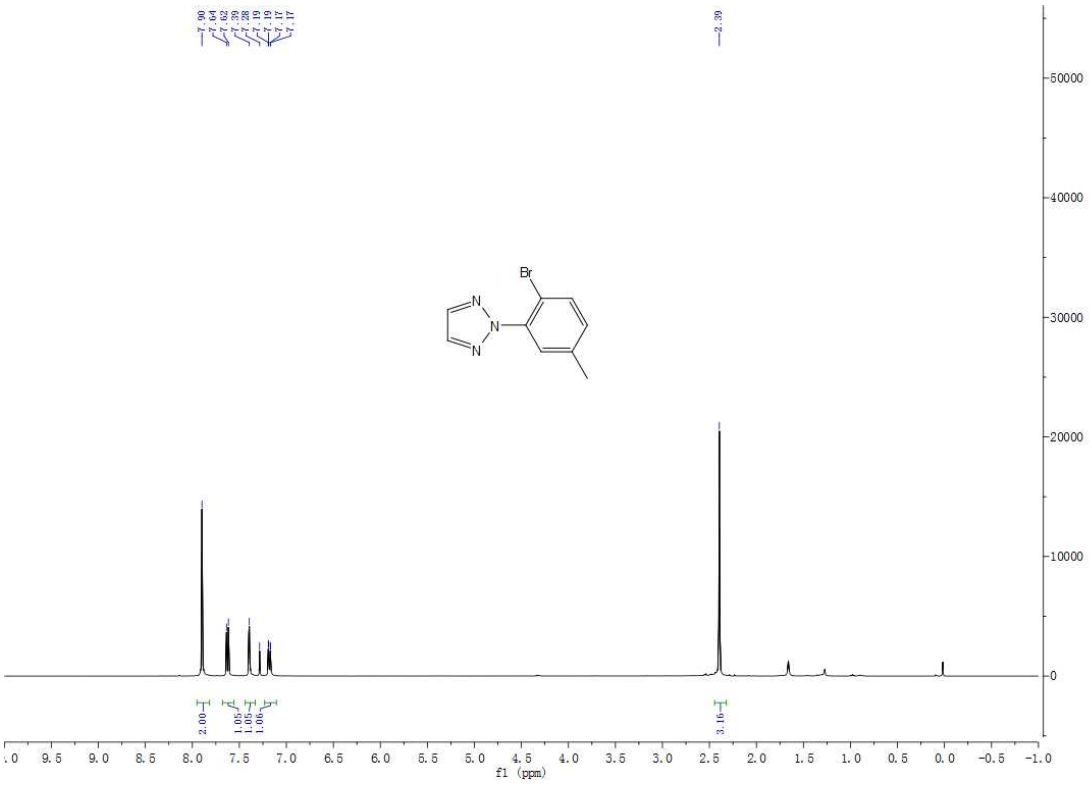
2e-^{1}H


8.15
8.13
7.94
7.87
7.85
3.96
Br
N
N
N
O
O

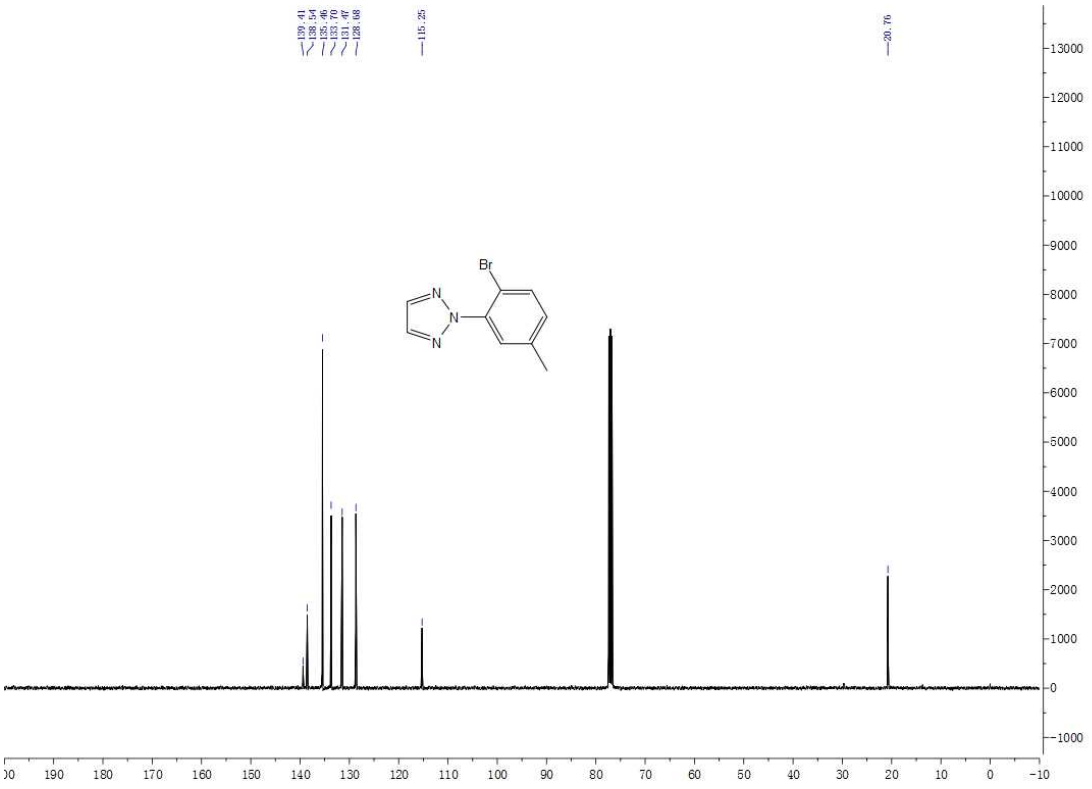
2e-^{13}C


165.04
136.19
132.59
131.57
128.94
128.59
127.26
52.72
Br
N
N
N
O
O

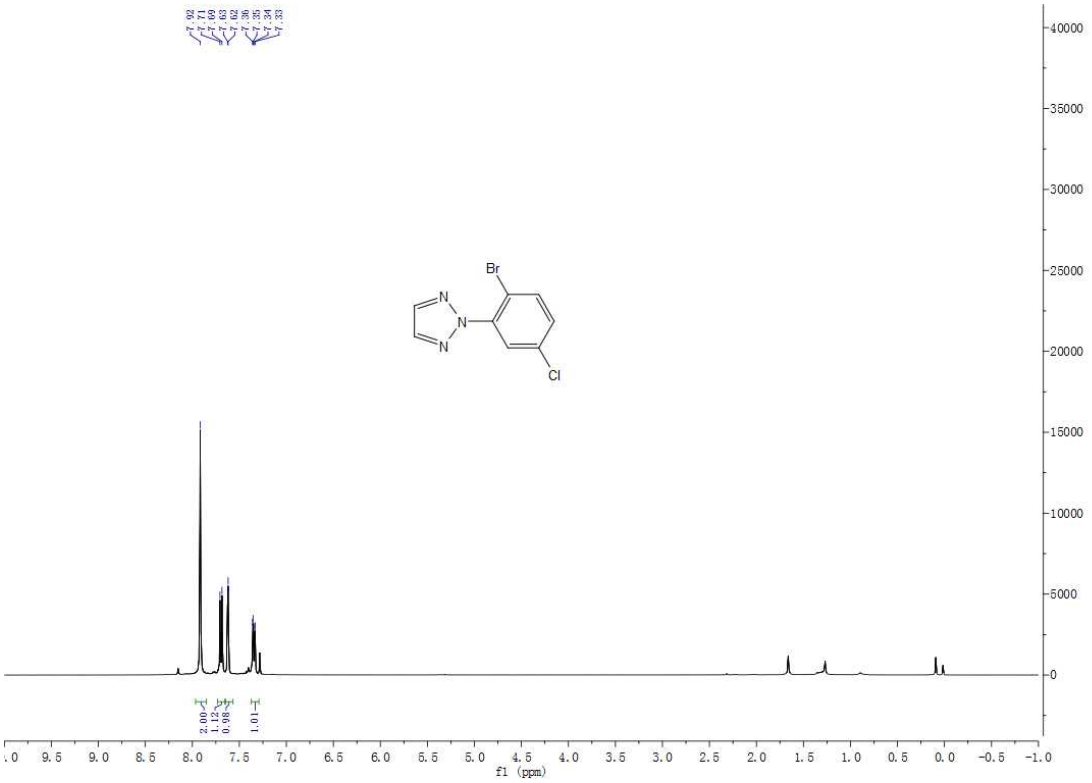
2f-^{1}H


7.90
7.64
7.62
7.39
7.28
7.19
7.19
7.17
7.17
2.39
Br
N
N
N
2.00
1.05
1.05
1.06
3.16
f1 (ppm)

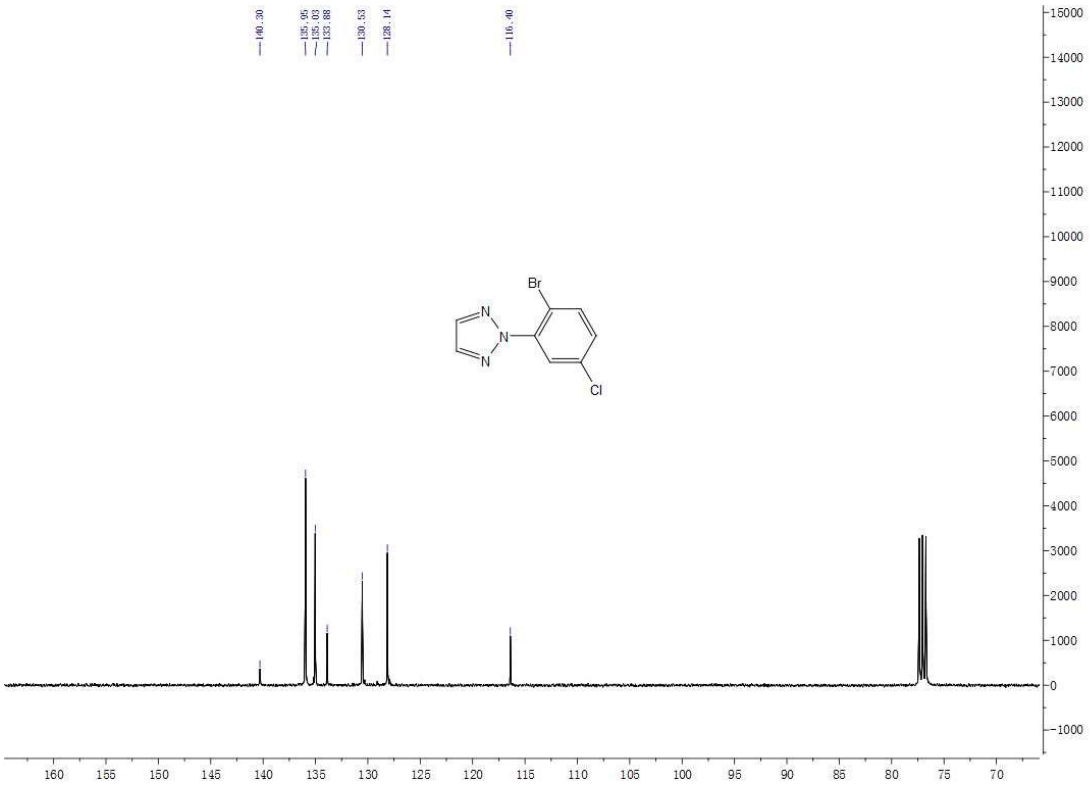
2f-^{13}C


139.41
138.54
135.46
133.76
131.47
128.68
115.25
20.76
Br
N
N
N

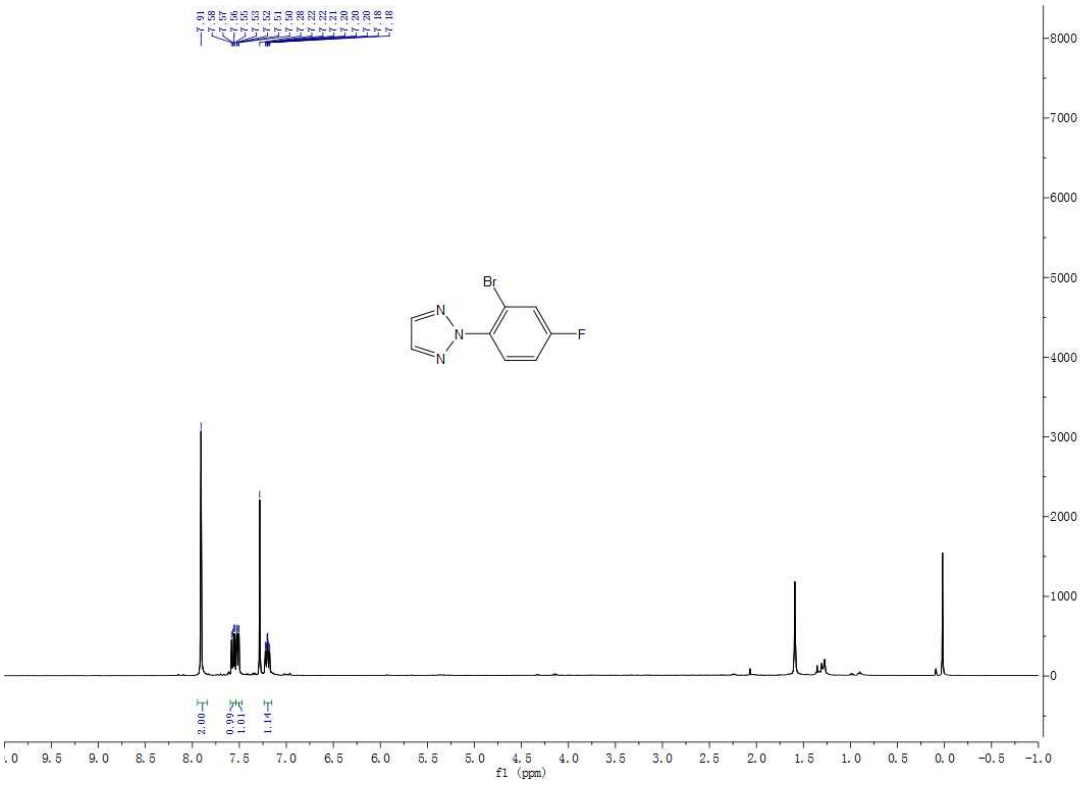
2g-^{1}H


7.92
7.71
7.69
7.63
7.62
7.36
7.35
7.34
7.33
Br
N
N
N
Cl
2.00
1.12
0.98
1.01
f1 (ppm)

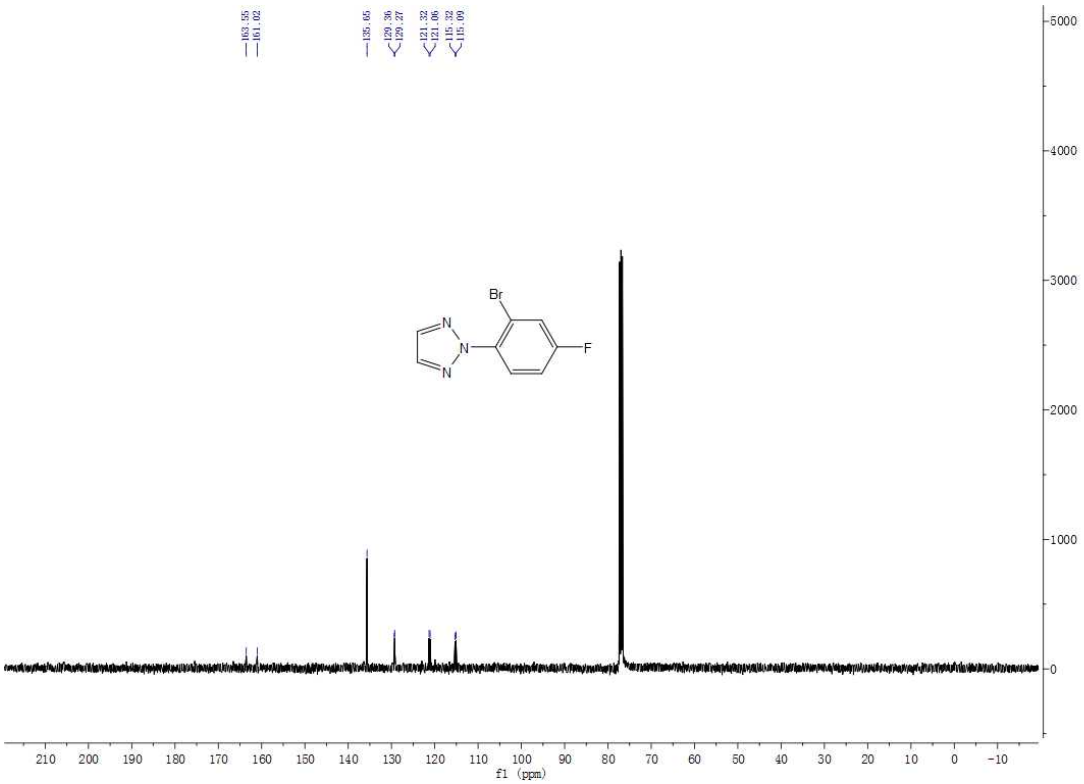
2g- ^{13}C


140.30
135.95
135.03
133.88
130.53
128.14
116.40
Br
N
N
N
Cl

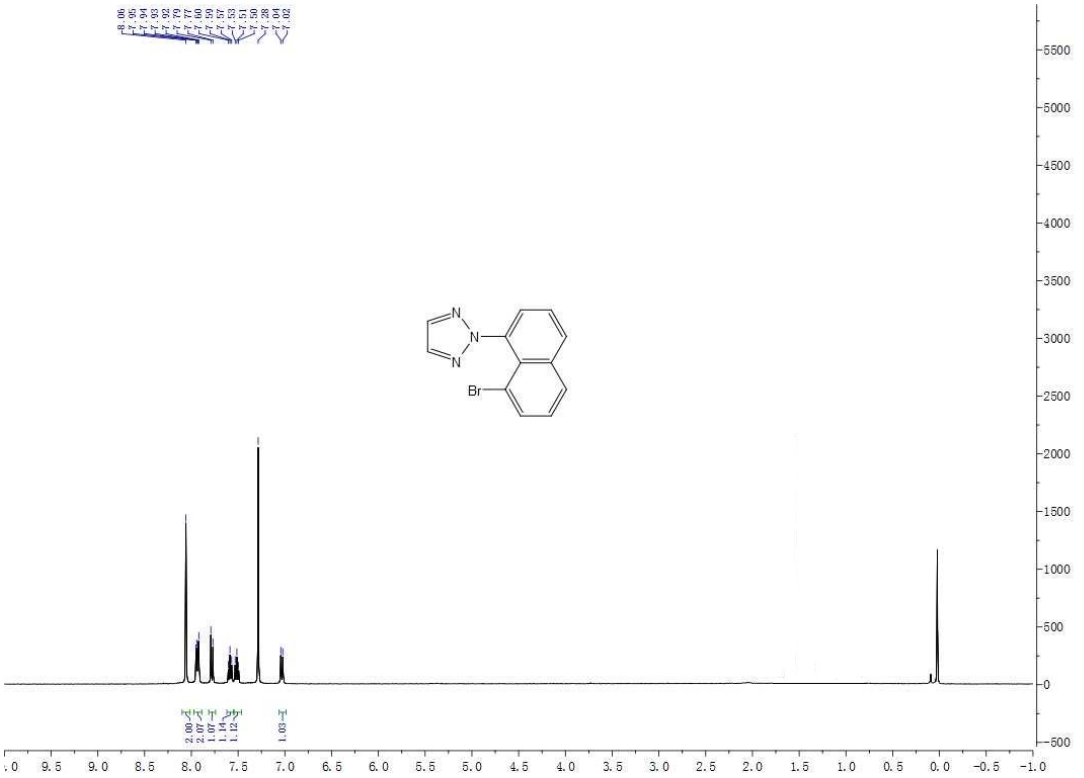
2h-^{1}H


7.91
7.58
7.57
7.56
7.55
7.53
7.52
7.51
7.50
7.28
7.22
7.22
7.21
7.20
7.20
7.19
7.18
7.18
Br
N
N
N
F
2.00
0.99
1.01
1.14
f1 (ppm)

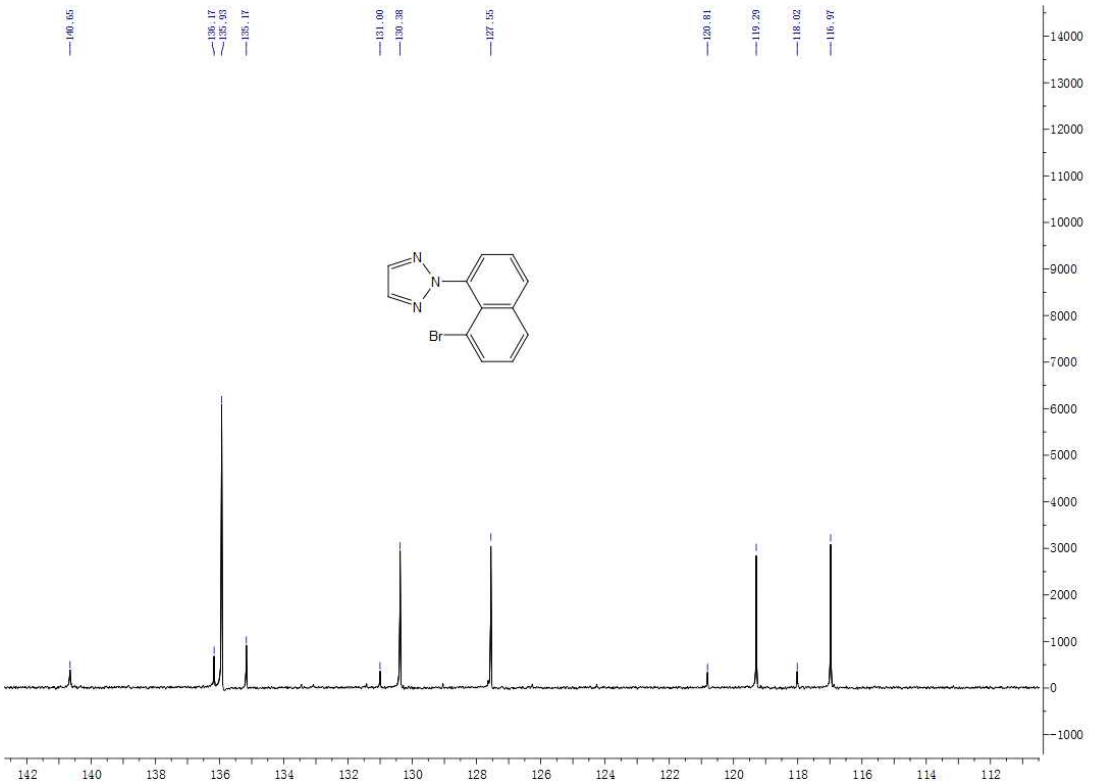
2h-^{13}C



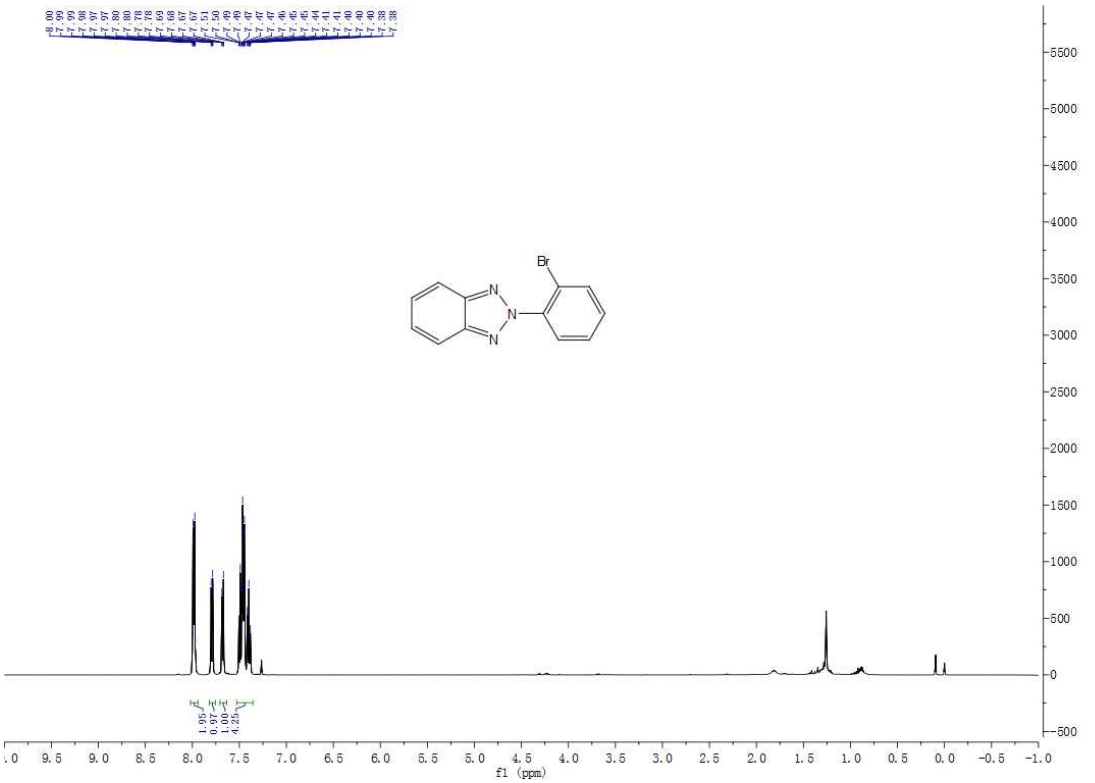
2i-^{1}H



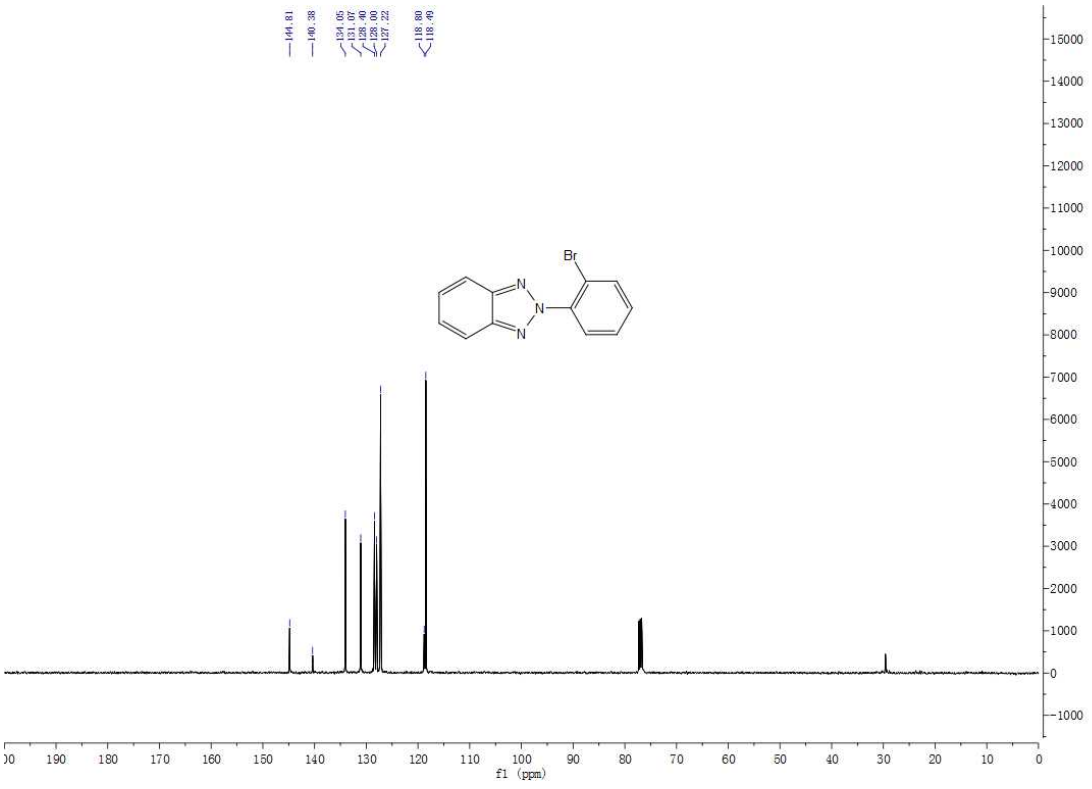
2i-^{13}C



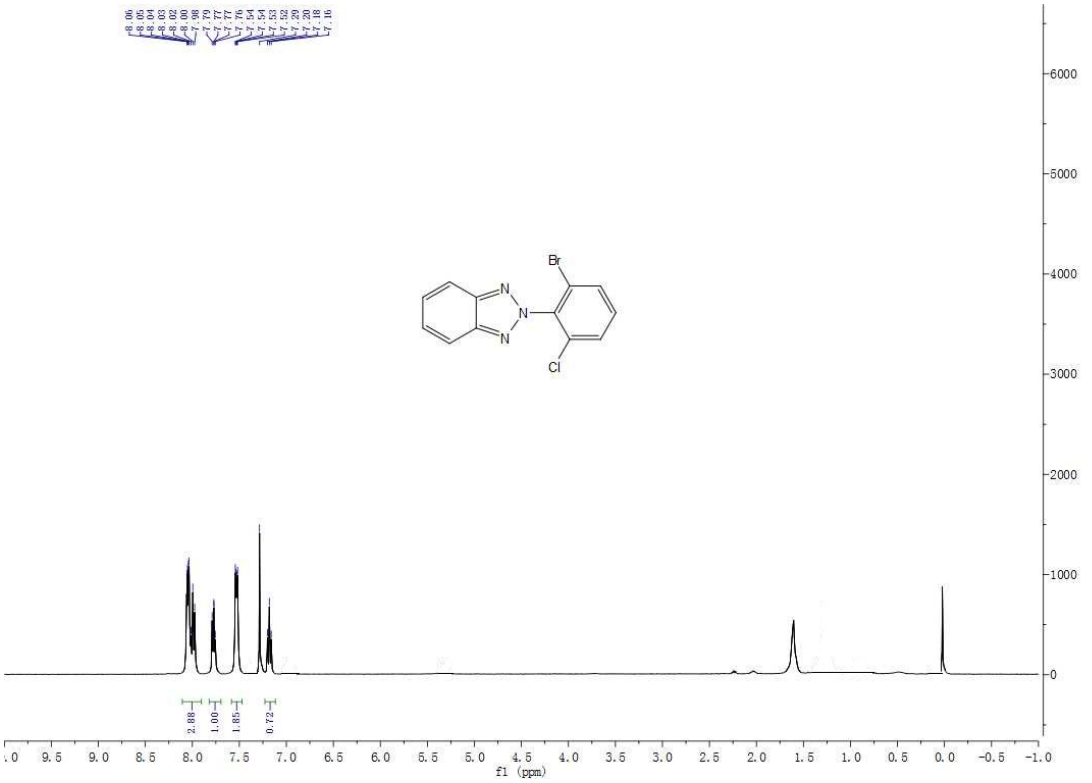
2j-^{1}H



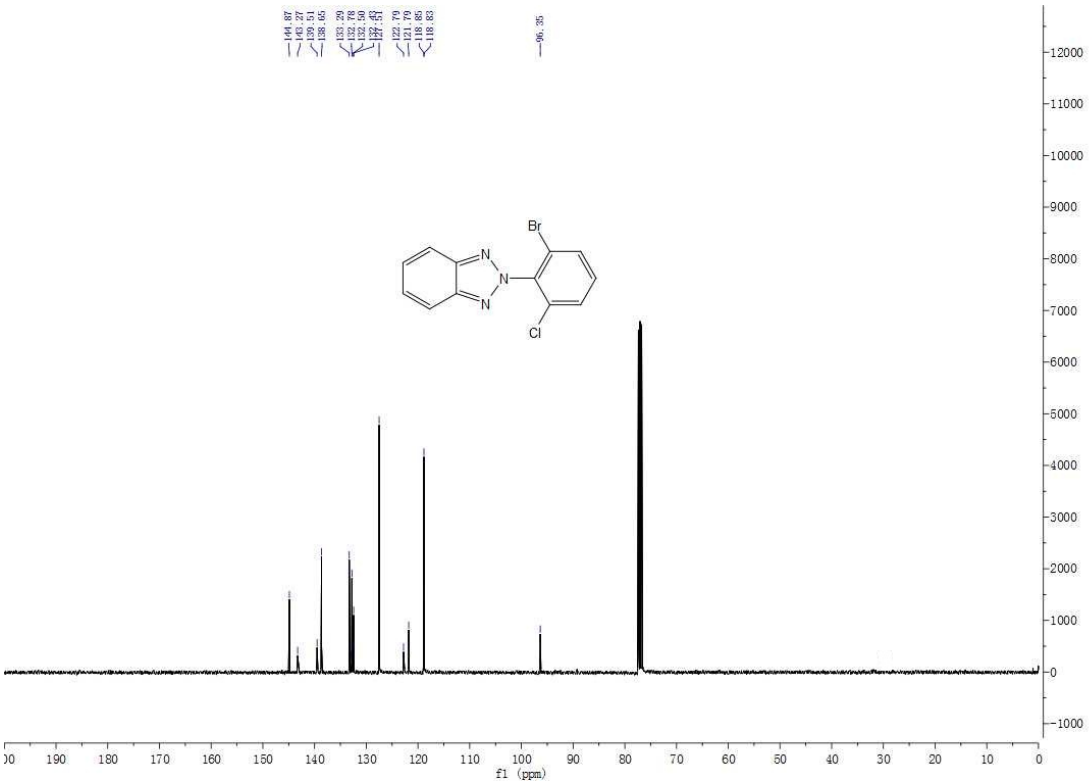
2j-^{13}C


144.81
140.38
134.05
131.07
128.40
128.00
127.22
118.80
118.49
Br
N
N
N
f1 (ppm)

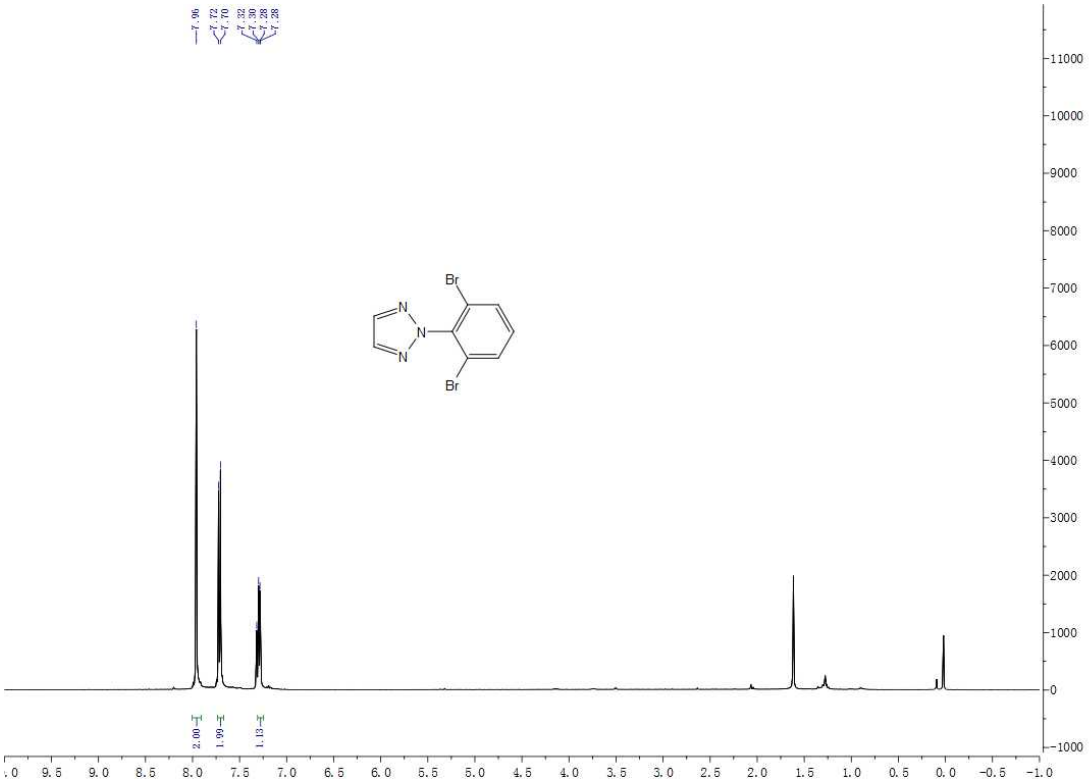
2k-^{1}H


Br
Cl
N
N
N
2.88
1.00
1.85
0.72
f1 (ppm)

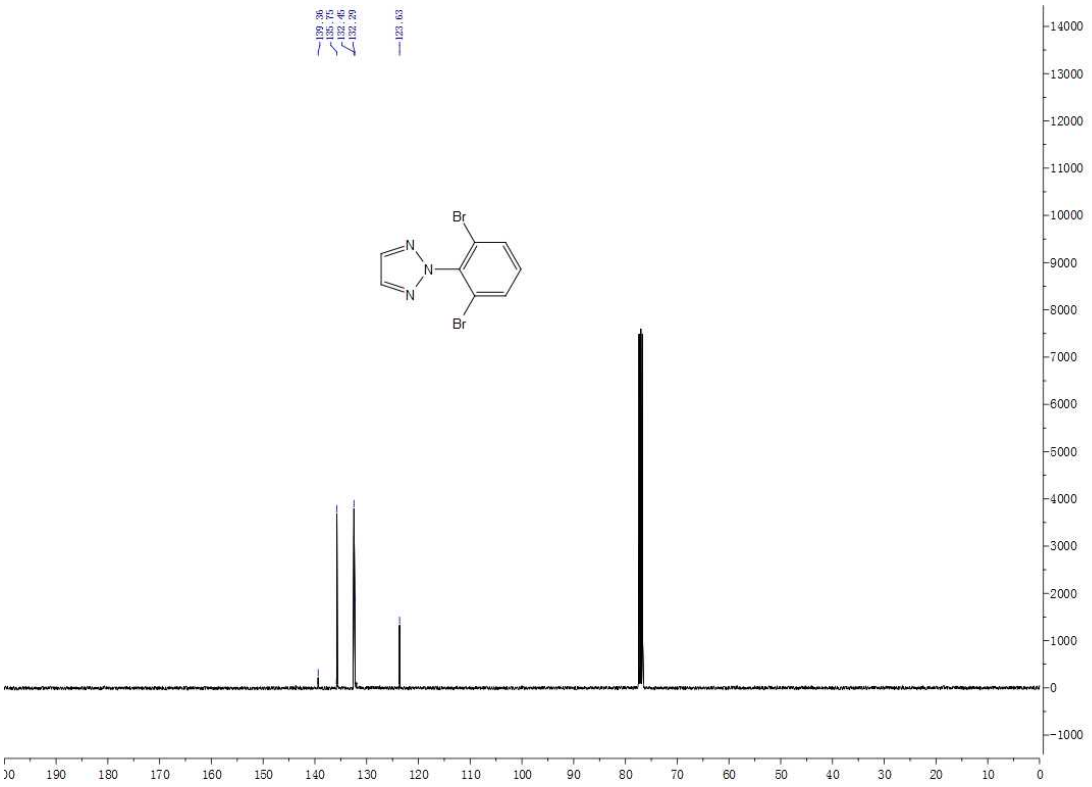
2k-^{13}C


144.87
143.27
139.51
138.65
133.29
132.79
132.50
127.51
122.79
121.79
118.86
118.83
96.35
Br
Cl
f1 (ppm)

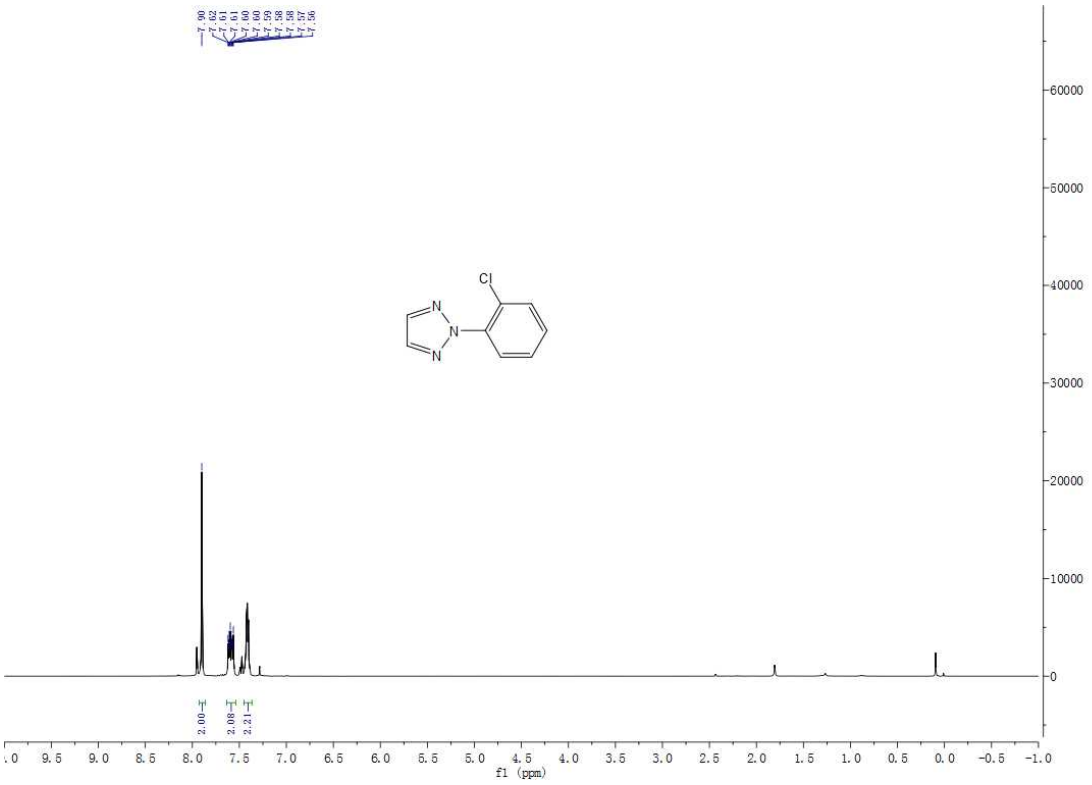
2l-^{1}H


7.96
7.72
7.70
7.32
7.30
7.28
Br
Br
2.00
1.99
1.13

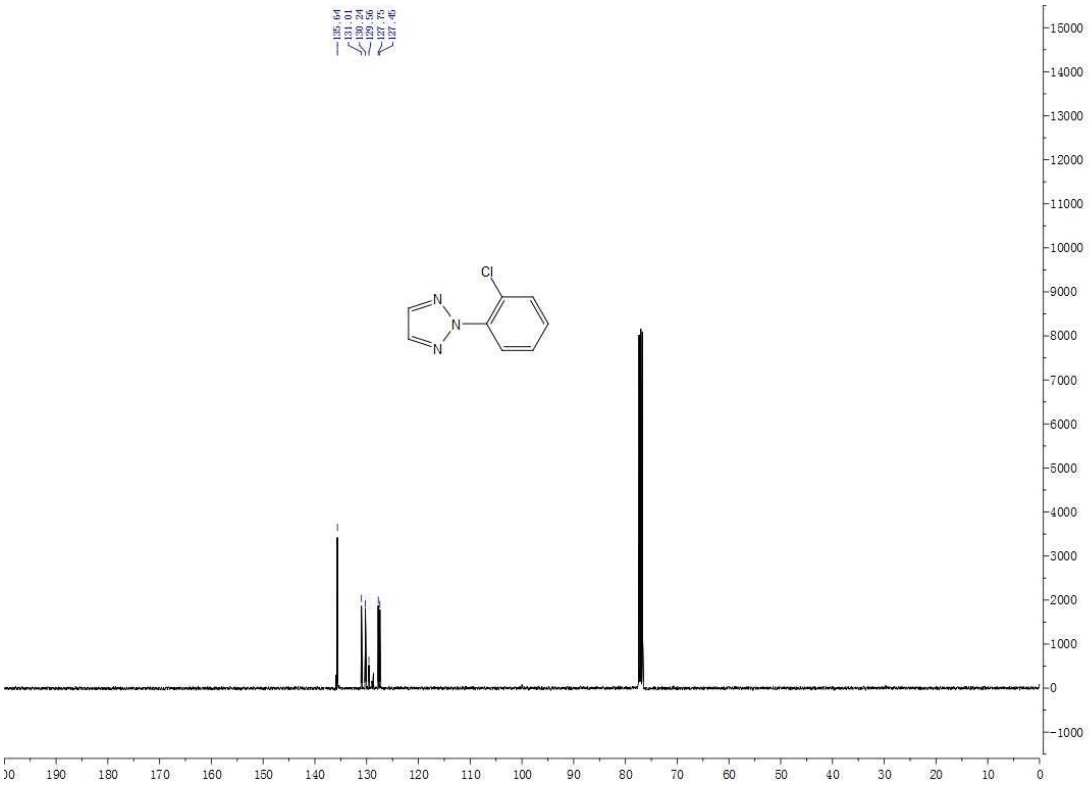
2l-^{13}C


139.36
135.75
132.46
132.29
123.63
Br
Br
N
N
N

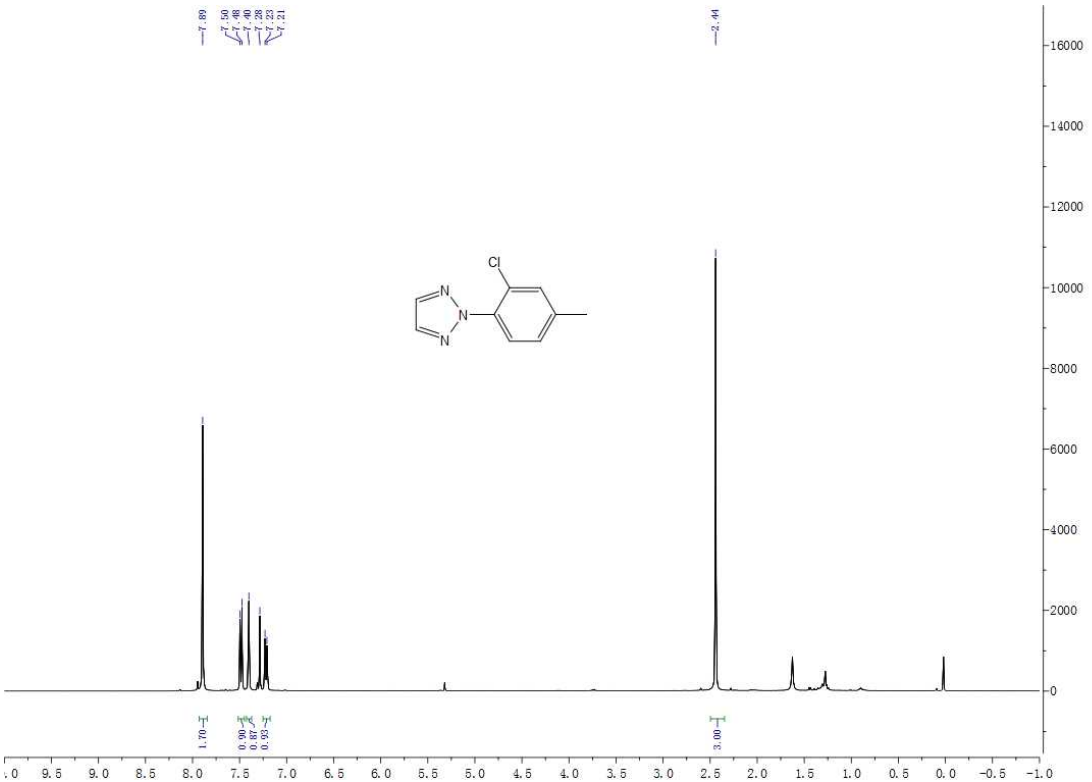
3a-^{1}H


7.90
7.62
7.61
7.61
7.60
7.59
7.59
7.58
7.58
7.57
7.56
Cl
N
N
N
2.00
2.08
2.21
f1 (ppm)

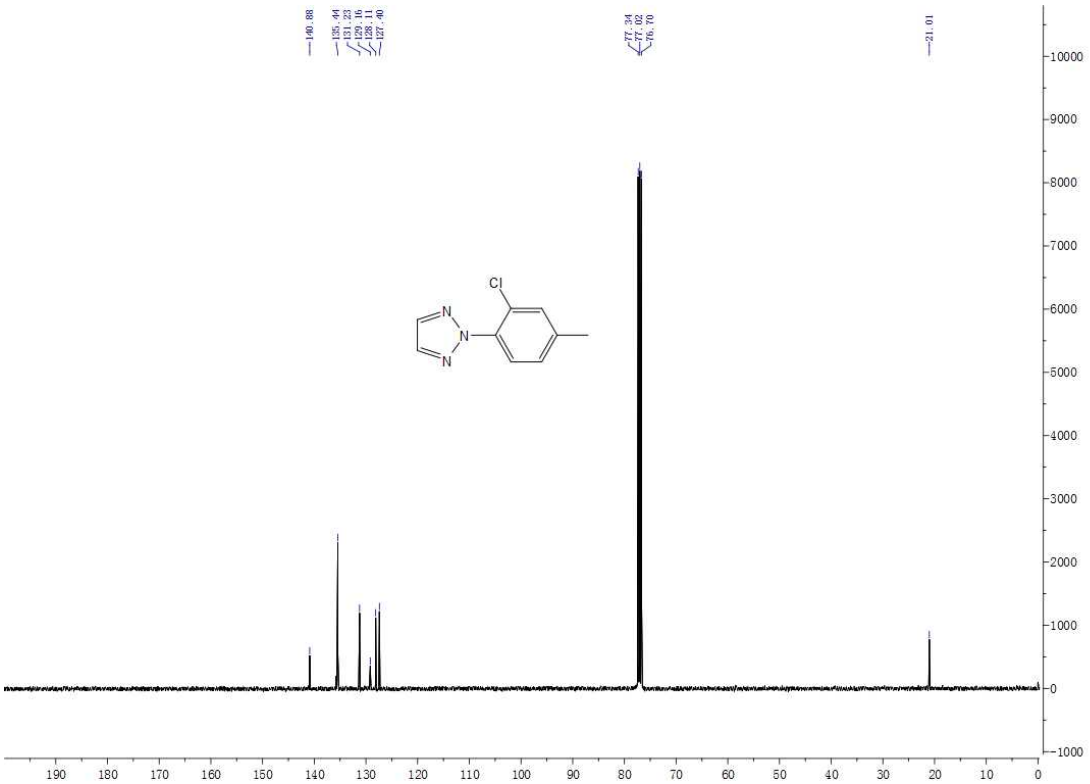
3a-^{13}C


125.64
131.01
130.24
129.56
127.75
121.46
Cl
N
N
N

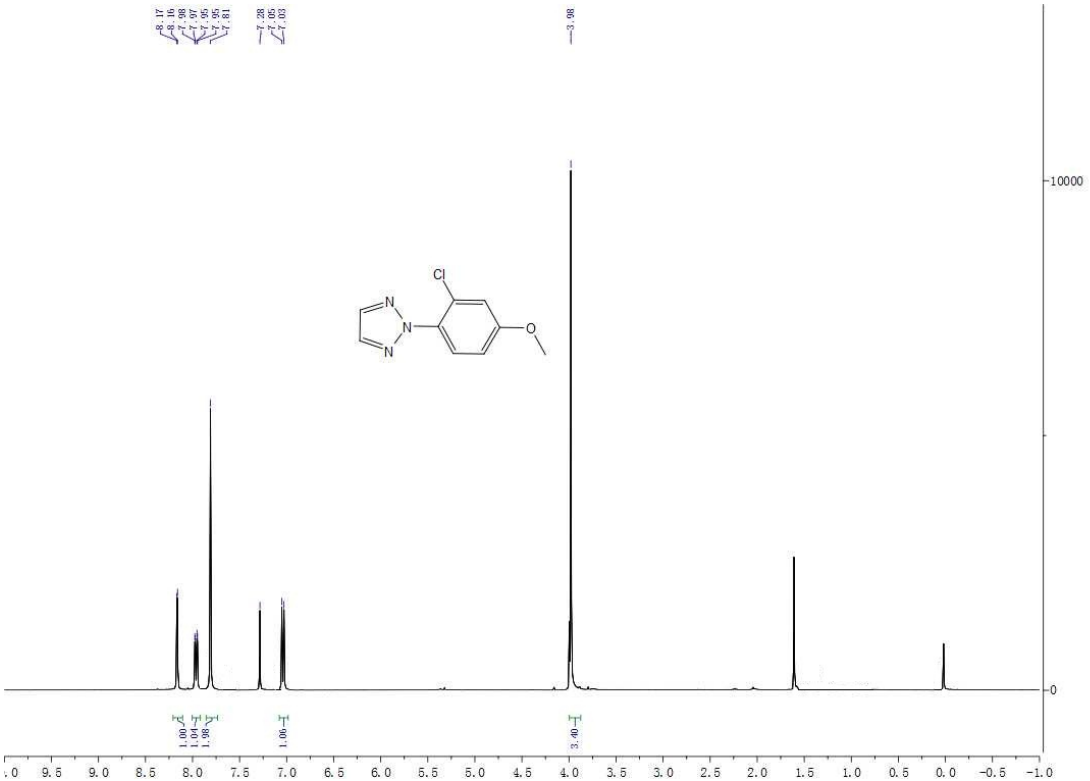
3b-^{1}H


7.89
7.50
7.48
7.40
7.28
7.23
7.21
2.44
Cl
N
N
N
1.70
0.99
0.97
0.93
3.00

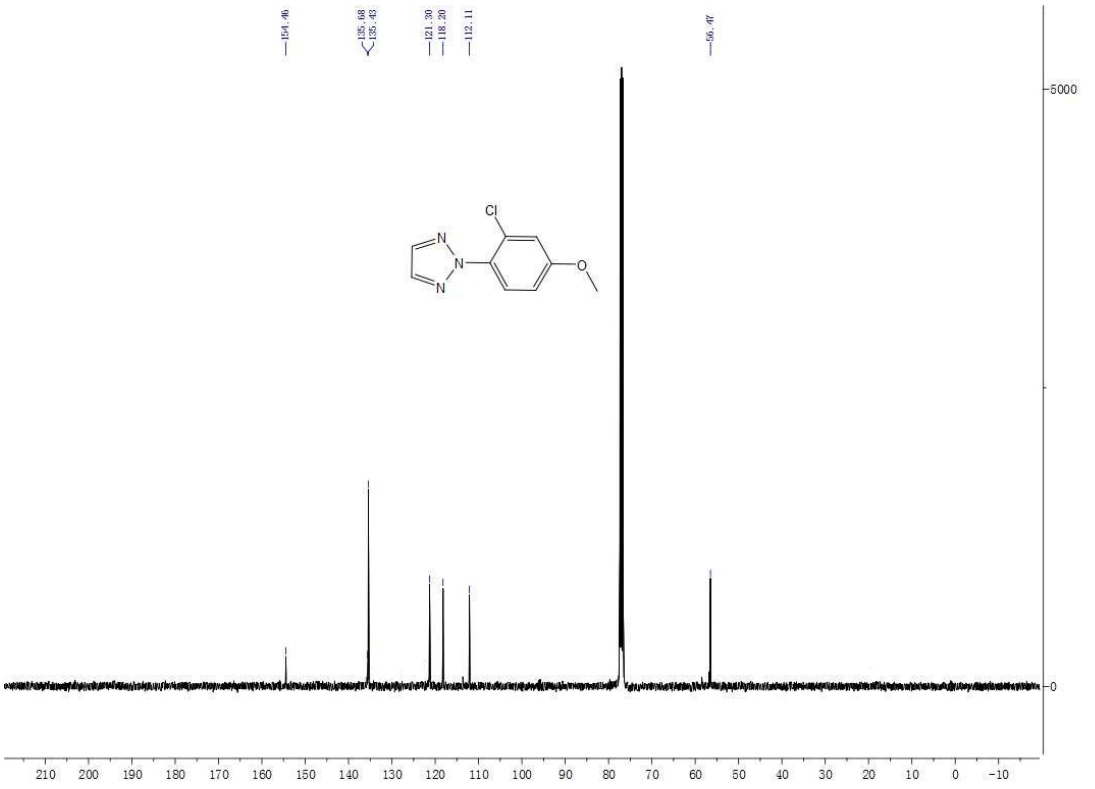
3b-^{1}H


140.88
135.44
131.23
129.16
128.11
127.40
77.34
77.02
76.70
21.01
Cl
N
N
N

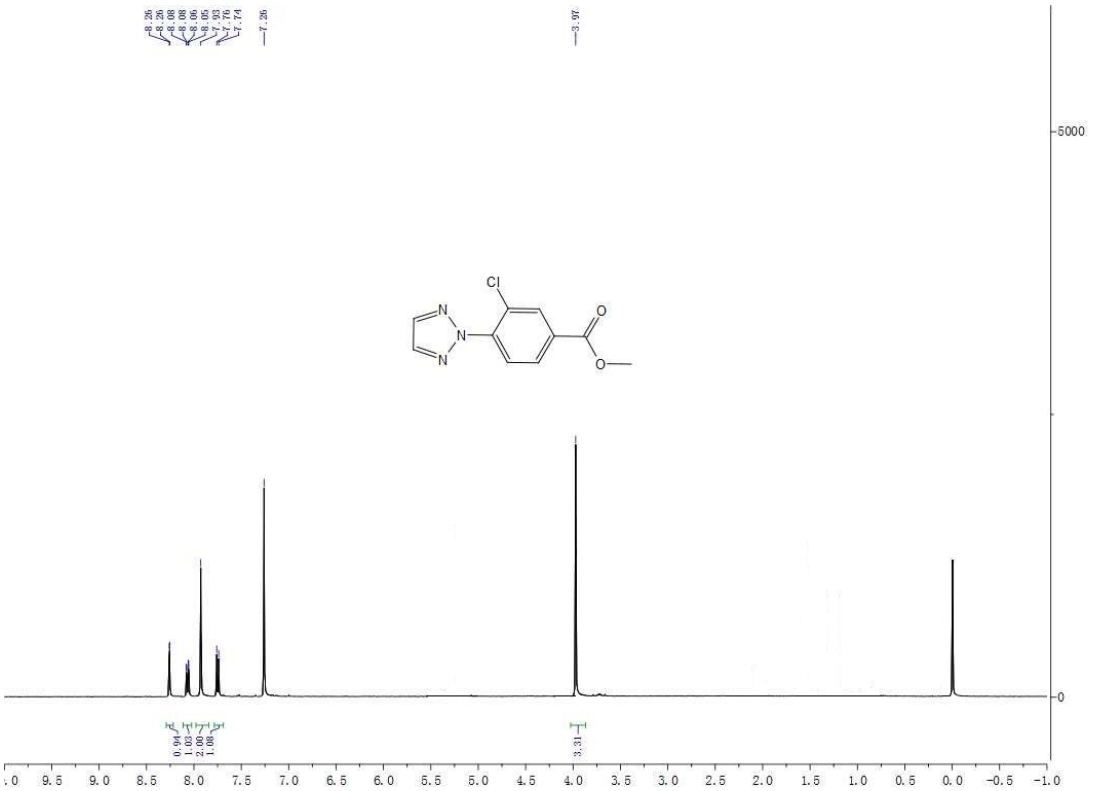
3C-^{1}H


8.17
8.16
7.98
7.97
7.95
7.95
7.81
7.28
7.05
7.03
3.98
Cl
N
N
N
O
1.00
1.04
1.98
1.06
3.40

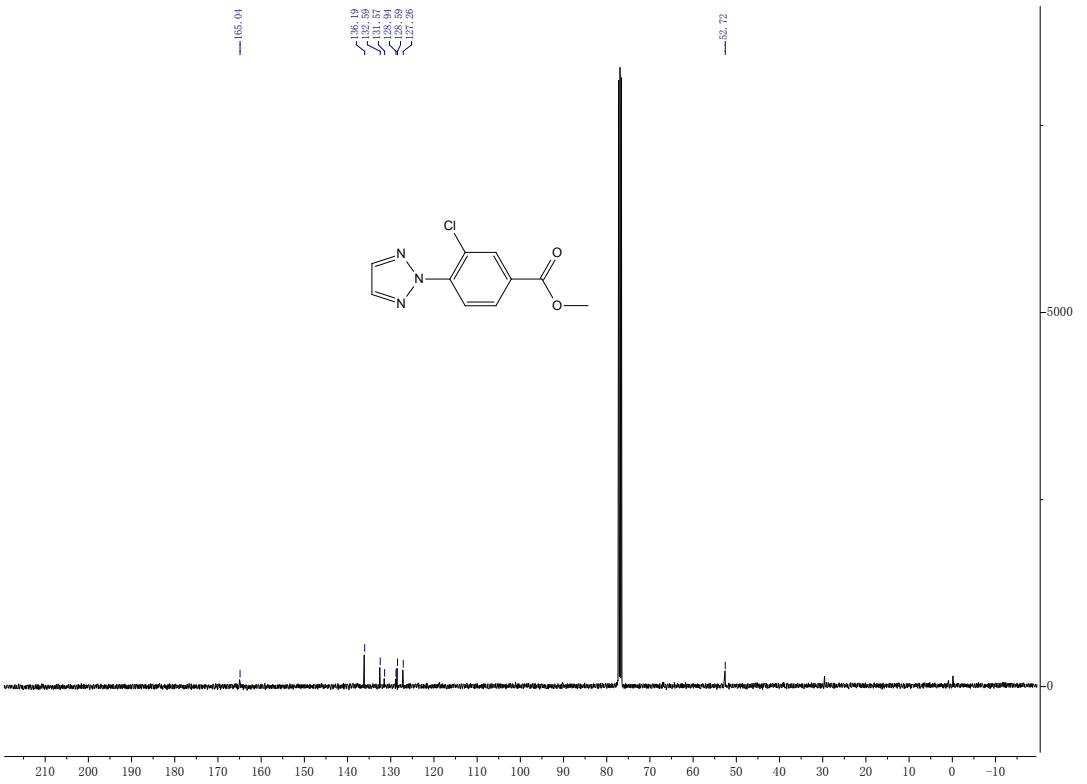
3c-^{13}C



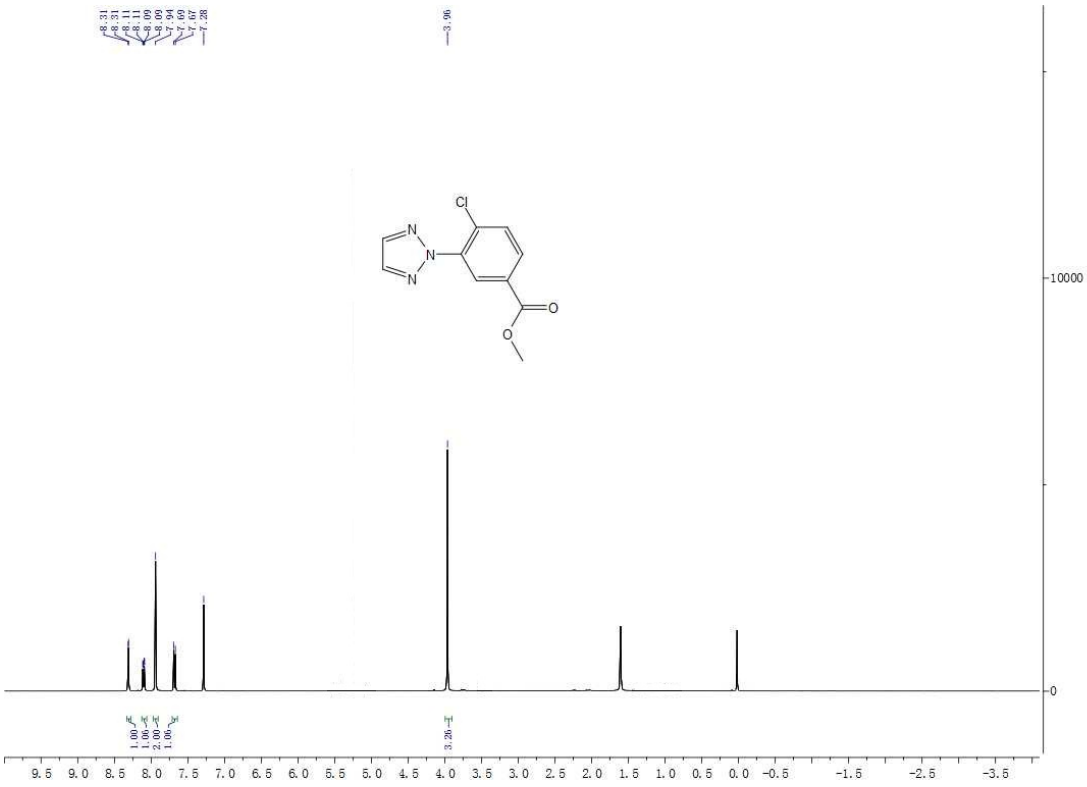
3d-^{1}H



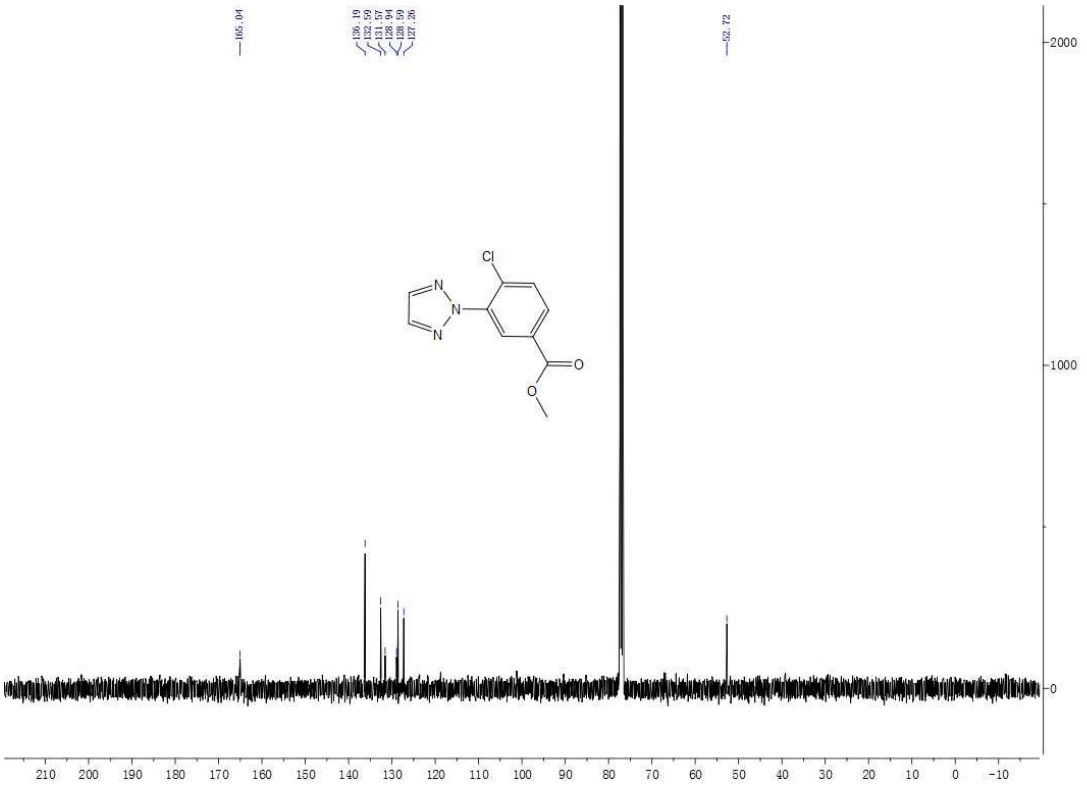
3d-^{13}C


165.04
136.19
132.89
131.57
128.94
128.59
127.26
52.72
Cl
N
N
N
O
O
5000
0
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10

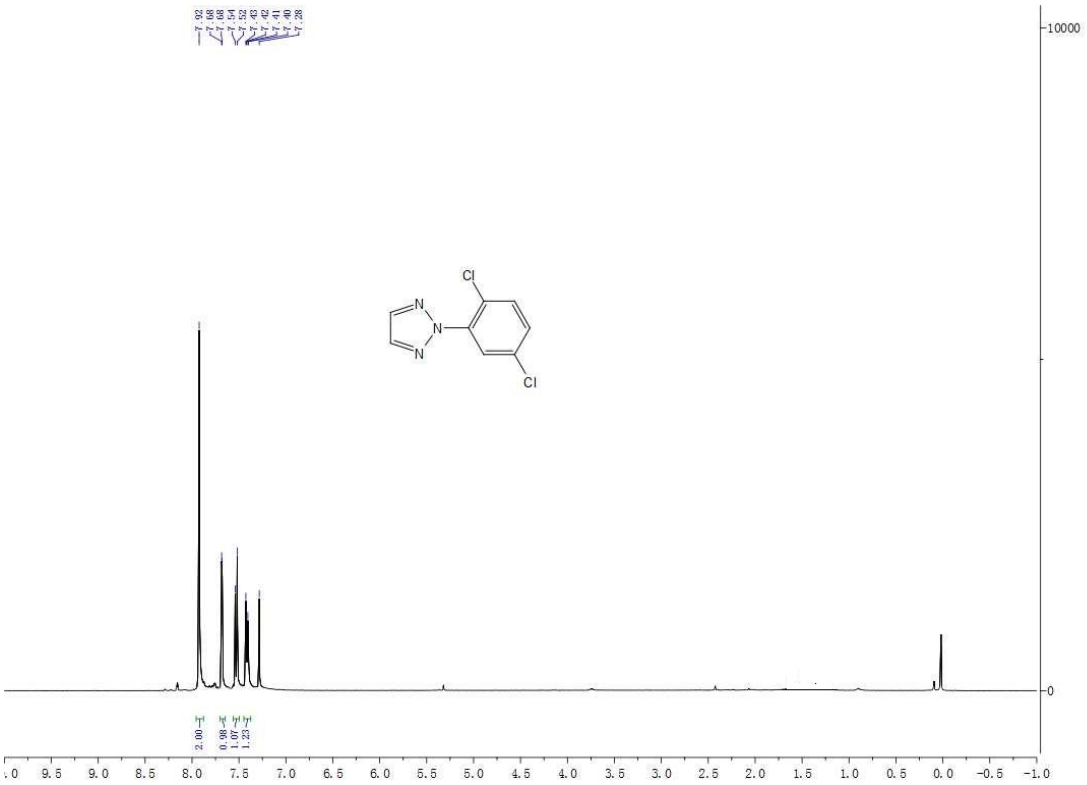
3e-^{1}H


8.31
8.31
8.11
8.11
8.09
8.09
7.94
7.94
7.69
7.67
7.28
3.96
Cl
N
N
N
O
O
10000
0
1.00
1.00
2.00
1.00
3.26
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.5 -2.5 -3.5

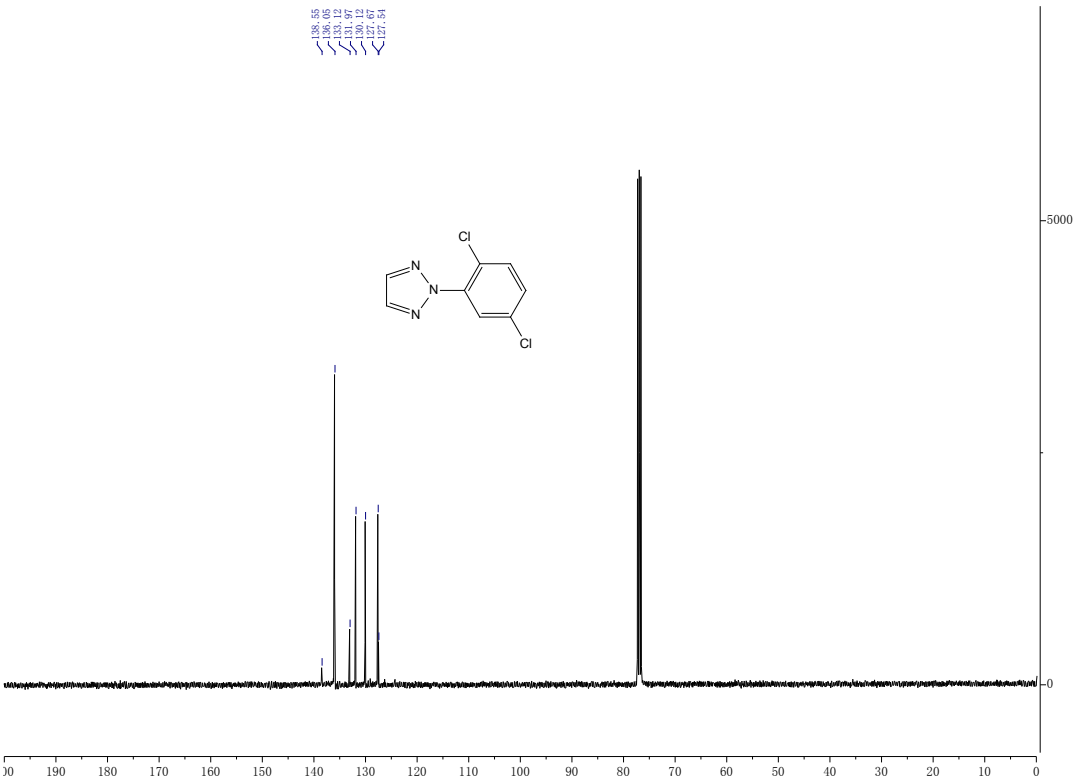
3e-^{13}C


165.04
136.19
132.59
131.57
128.94
128.59
127.26
52.72
Cl
N
N
N
O
O
2000
1000
0
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10

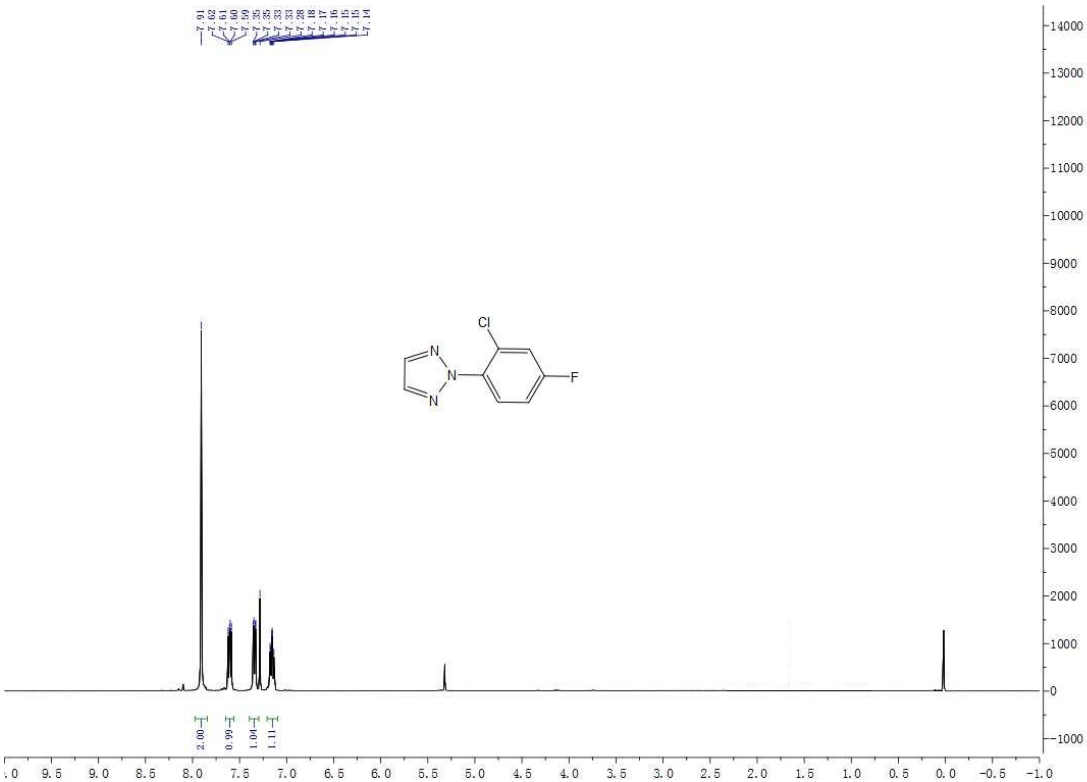
3f-^{1}H


7.92
7.68
7.54
7.52
7.42
7.41
7.40
7.28
Cl
N
N
N
Cl
10000
0
2.00
0.98
1.07
1.23
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0

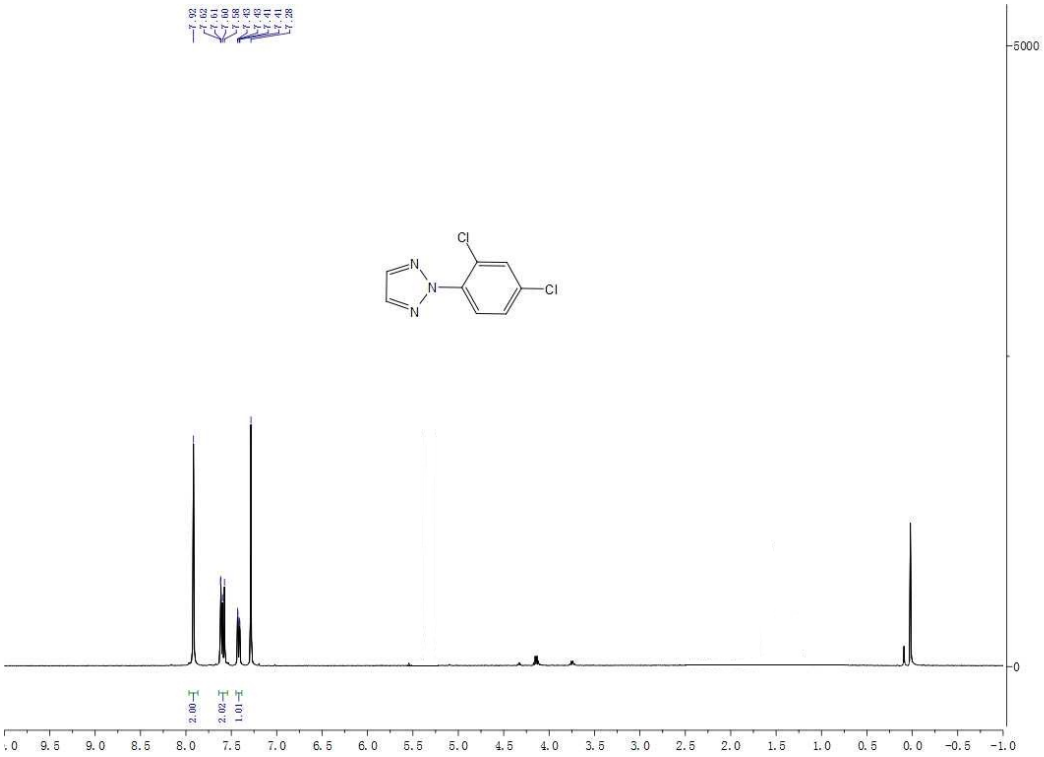
3f-^{13}C


138.55
136.05
133.23
131.97
130.12
127.67
127.54
Cl
N
N
N
Cl
5000
0
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0

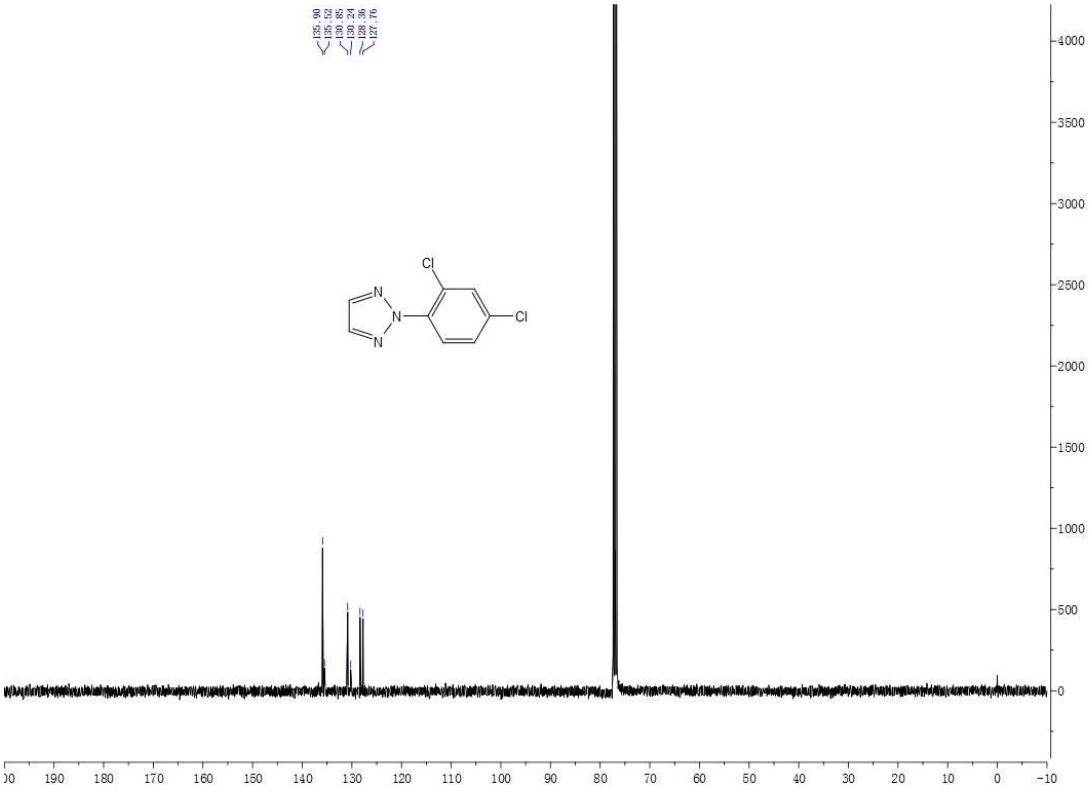
3g-^{1}H


7.91
7.62
7.61
7.60
7.59
7.35
7.34
7.33
7.28
7.18
7.17
7.16
7.15
7.14
Cl
N
N
N
F
14000
13000
12000
11000
10000
9000
8000
7000
6000
5000
4000
3000
2000
1000
0
-1000
2.00
0.99
1.04
1.11
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1.0

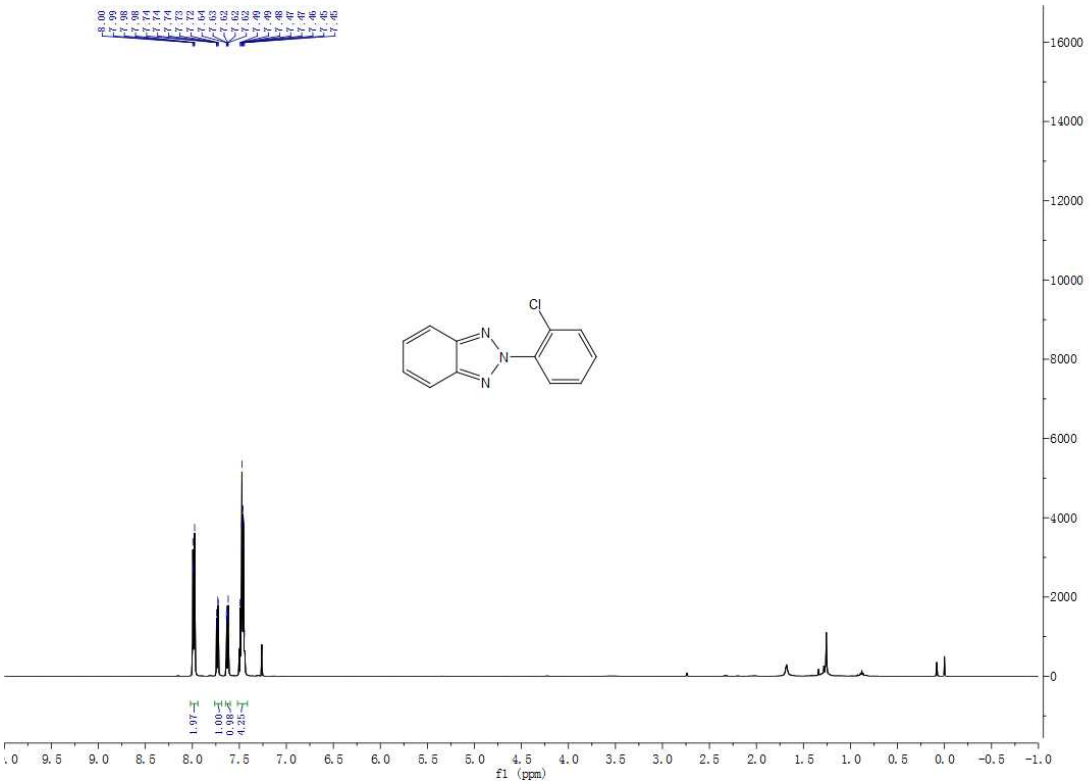
3h-^{1}H


Cl
N
N
N
Cl
5000
0
2.00
2.02
1.01
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1.0

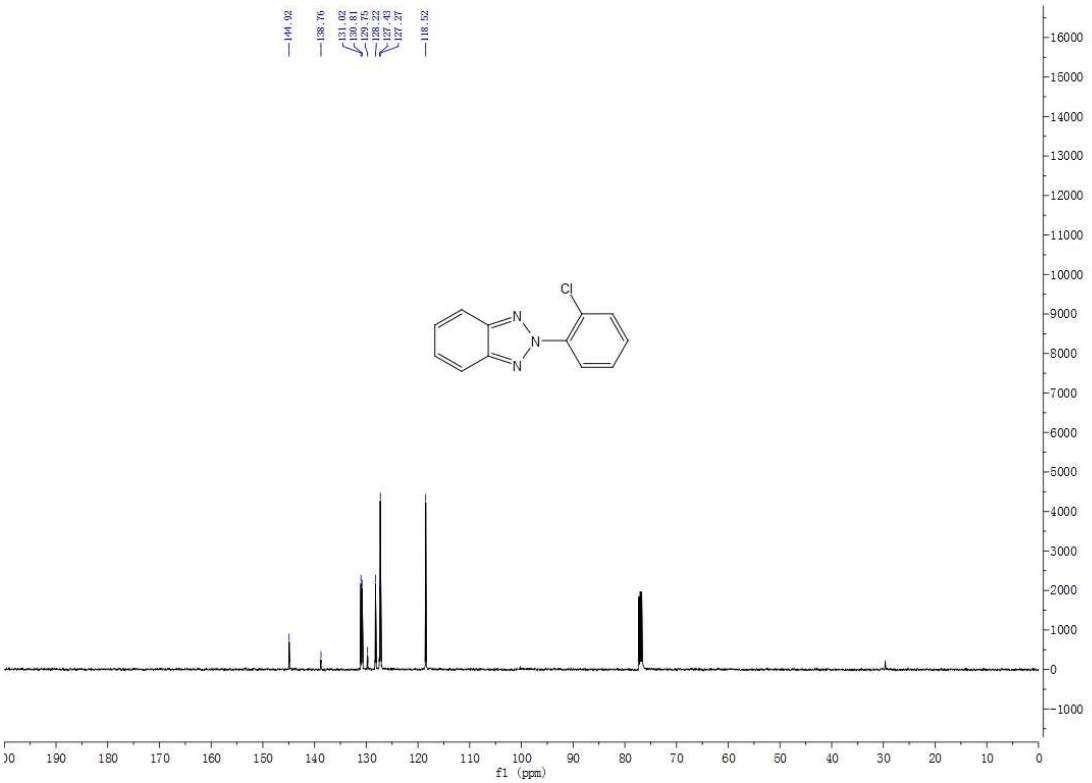
3h-^{13}C


135.90
135.52
130.85
129.24
128.36
127.70
Cl
N
N
N
Cl
4000
3500
3000
2500
2000
1500
1000
500
0
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10

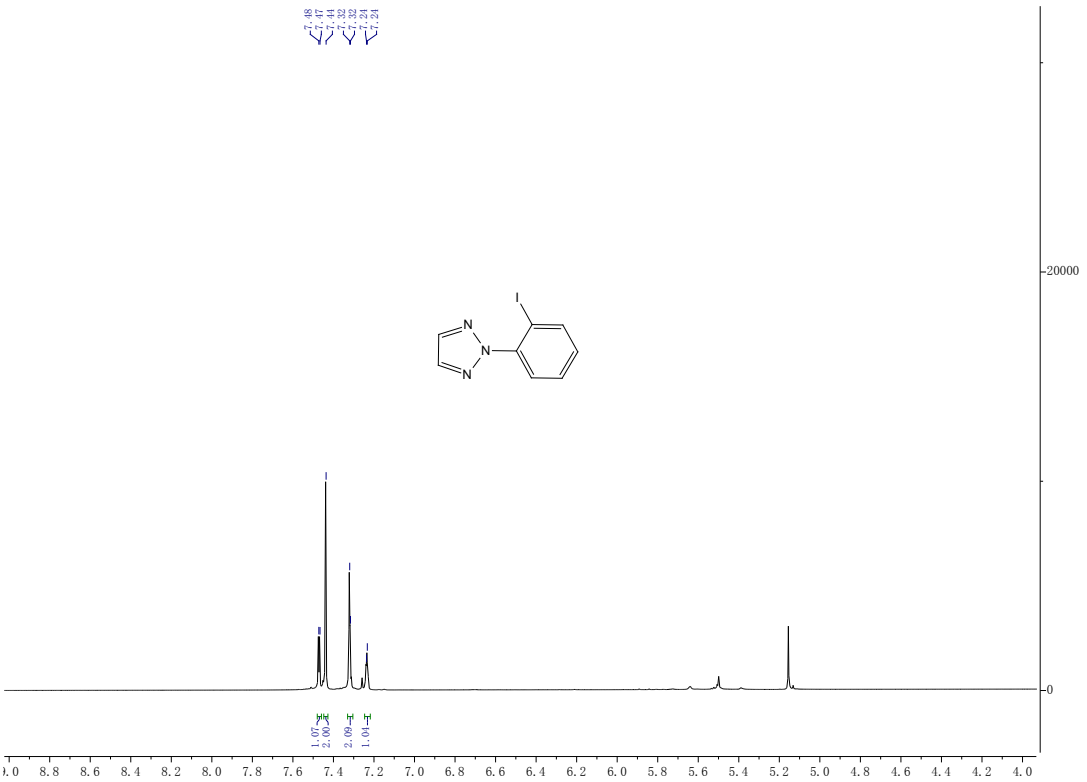
3i-^{1}H


Cl
N
N
N
f1 (ppm)

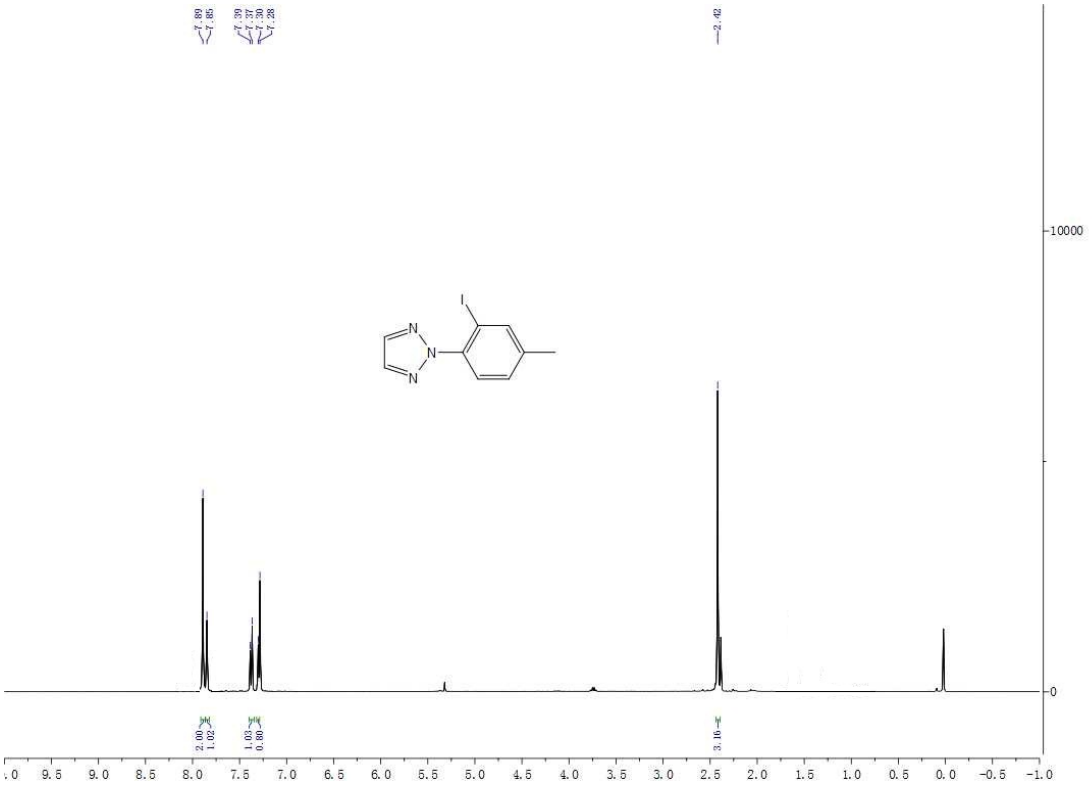
3i-^{13}C


144.92
138.76
131.02
130.81
129.75
128.22
127.43
127.27
118.52
Cl
N
N
N
f1 (ppm)

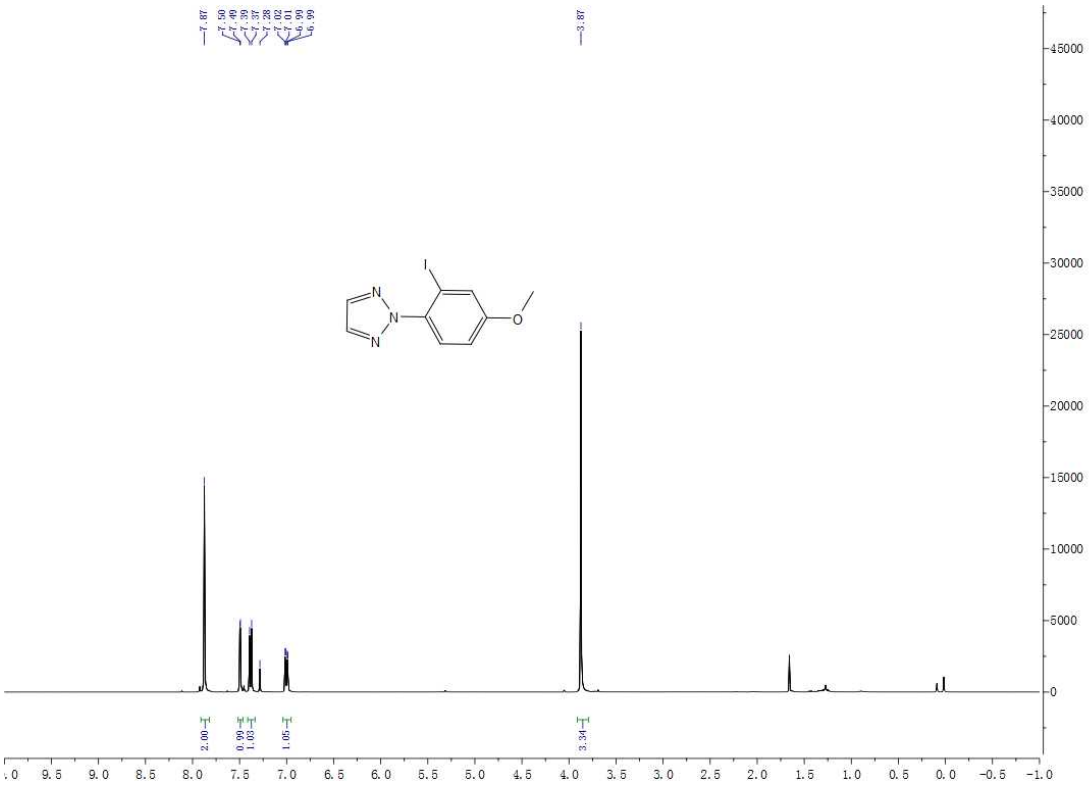
4a-^{1}H



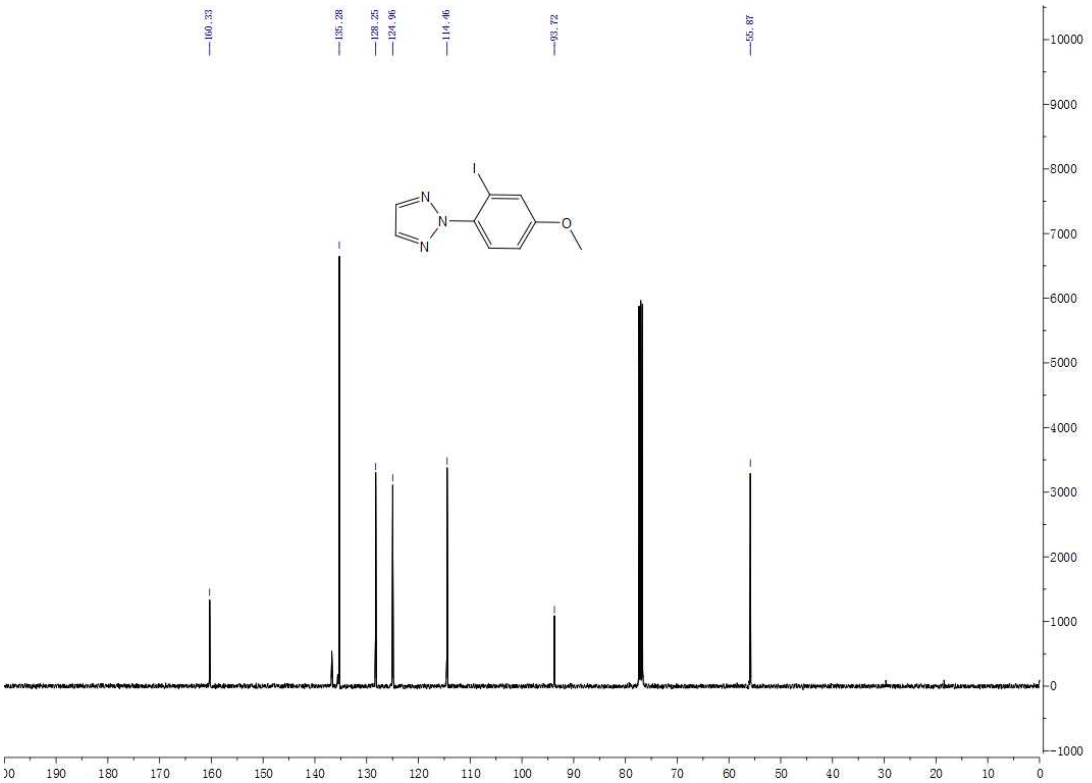
4b-^{1}H



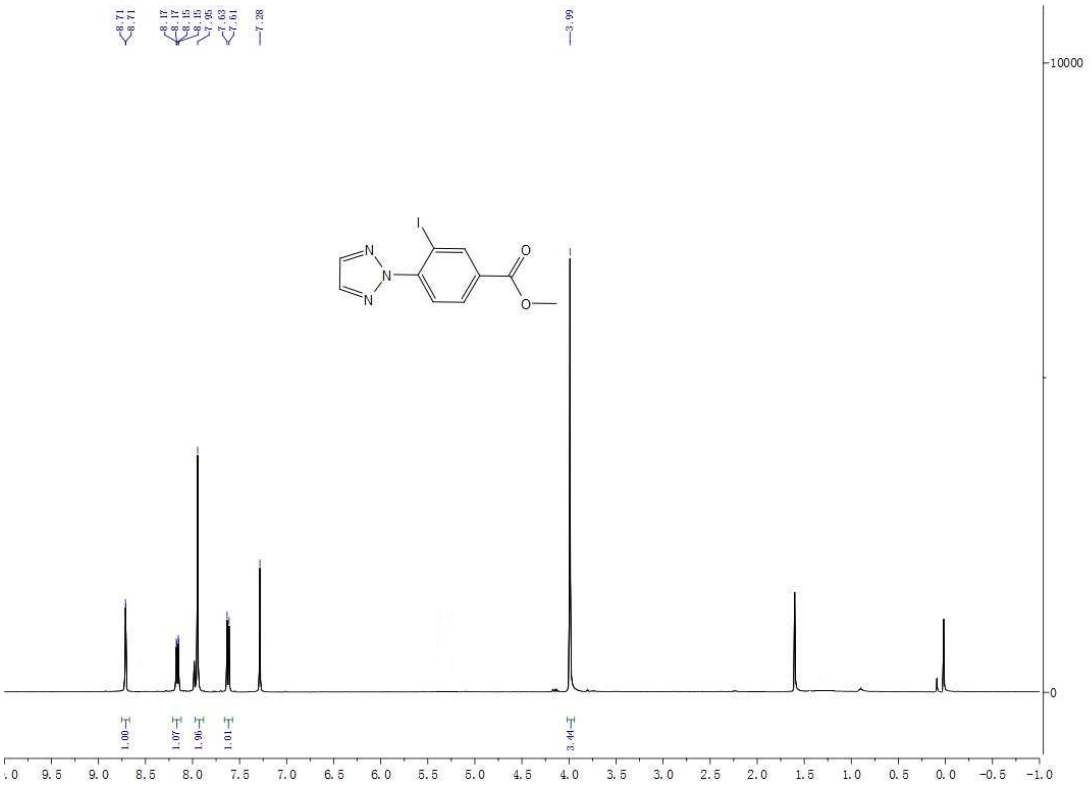
4c-^{1}H



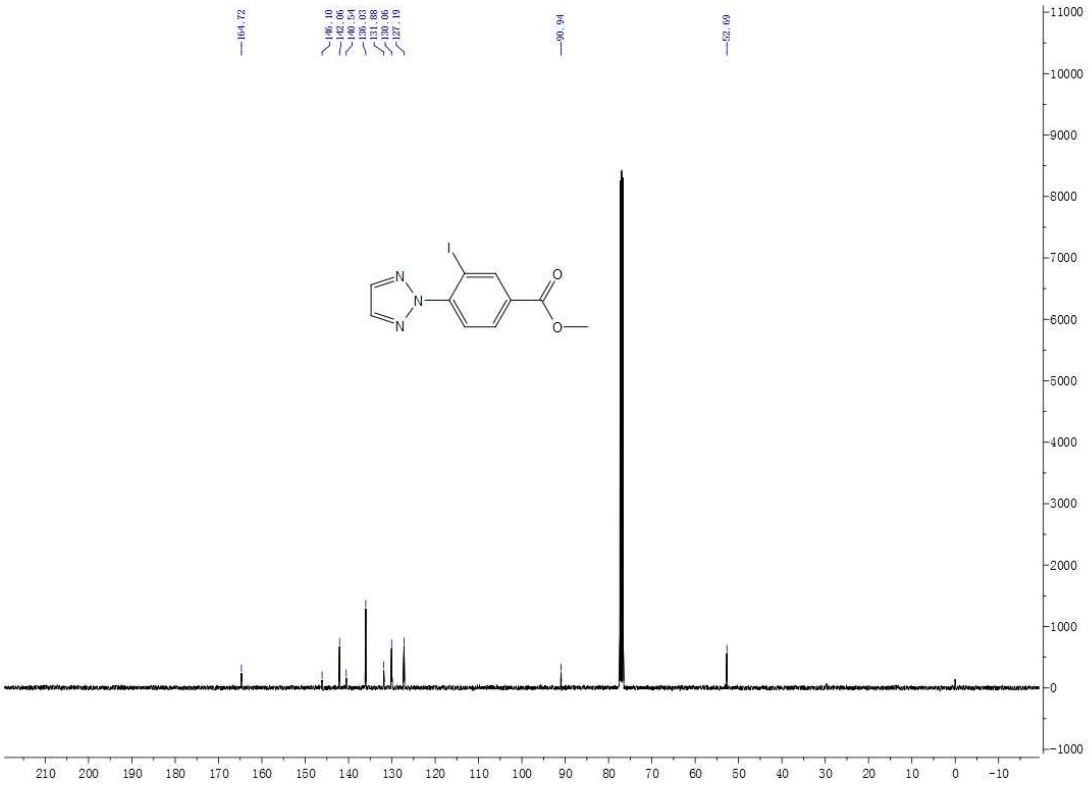
4c-^{13}C



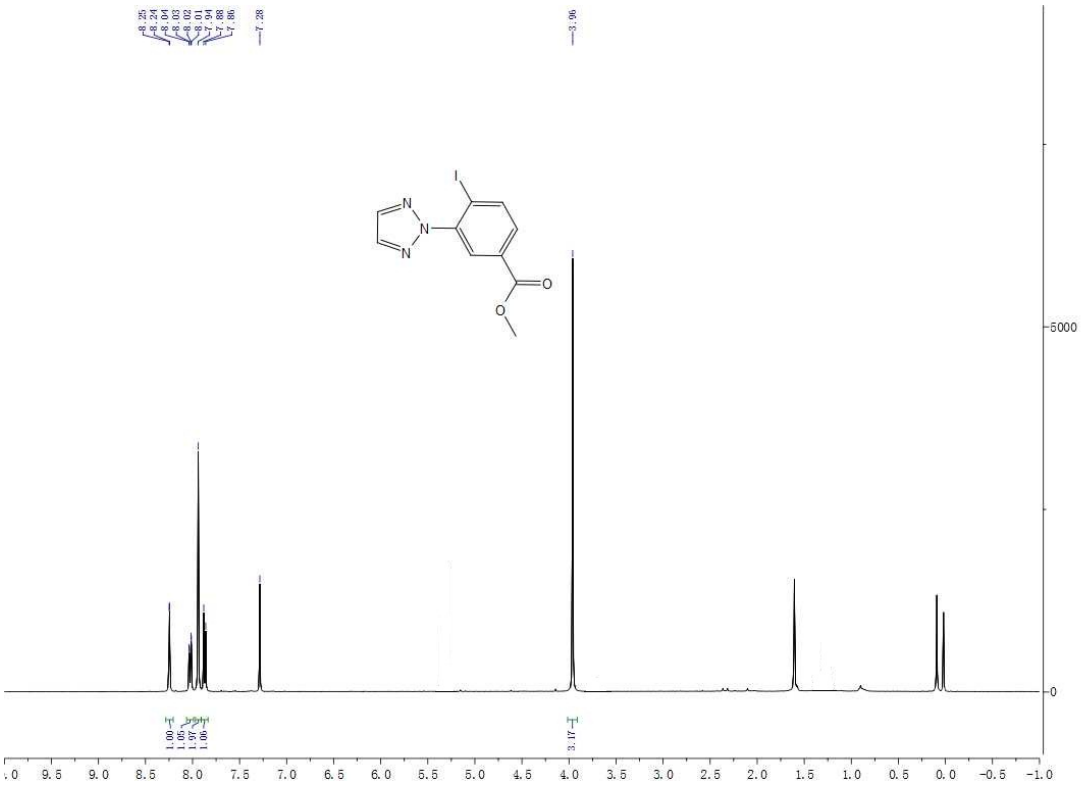
4d-^{1}H


8.71
8.71
8.17
8.17
8.15
8.15
7.95
7.63
7.61
7.28
3.99
1.00
1.07
1.96
1.01
3.44

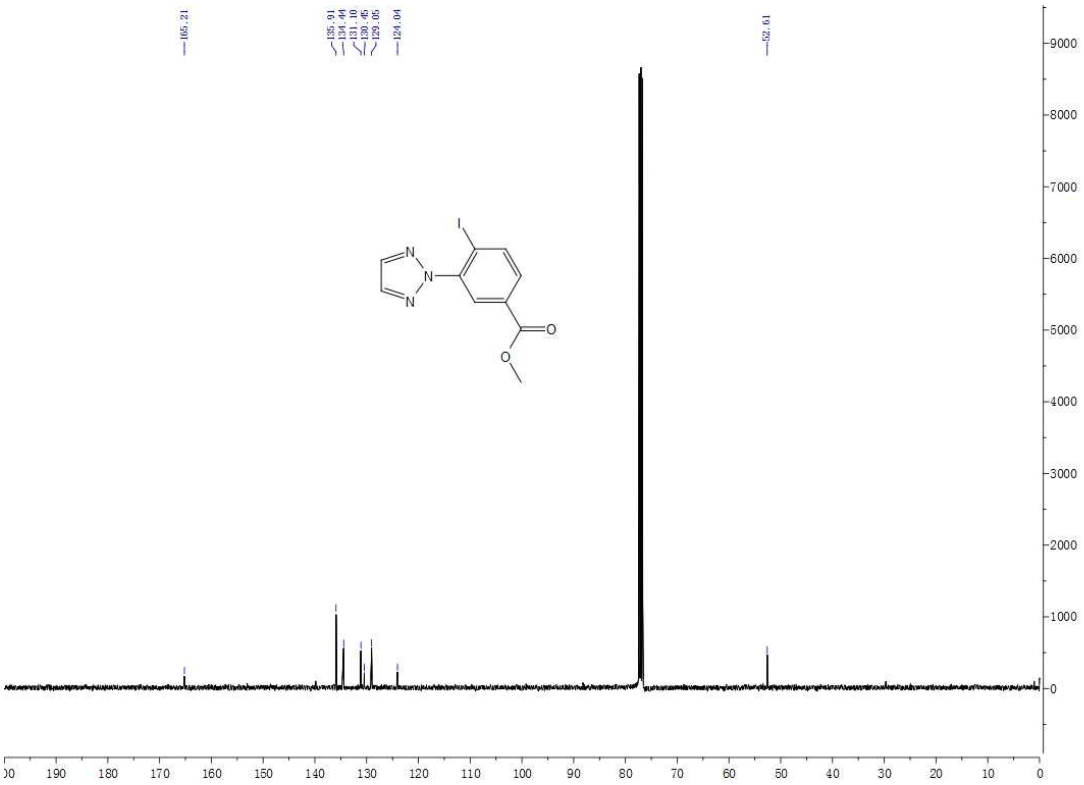
4d-^{13}C


164.72
146.10
142.06
140.54
136.03
131.88
130.06
127.19
90.94
52.69

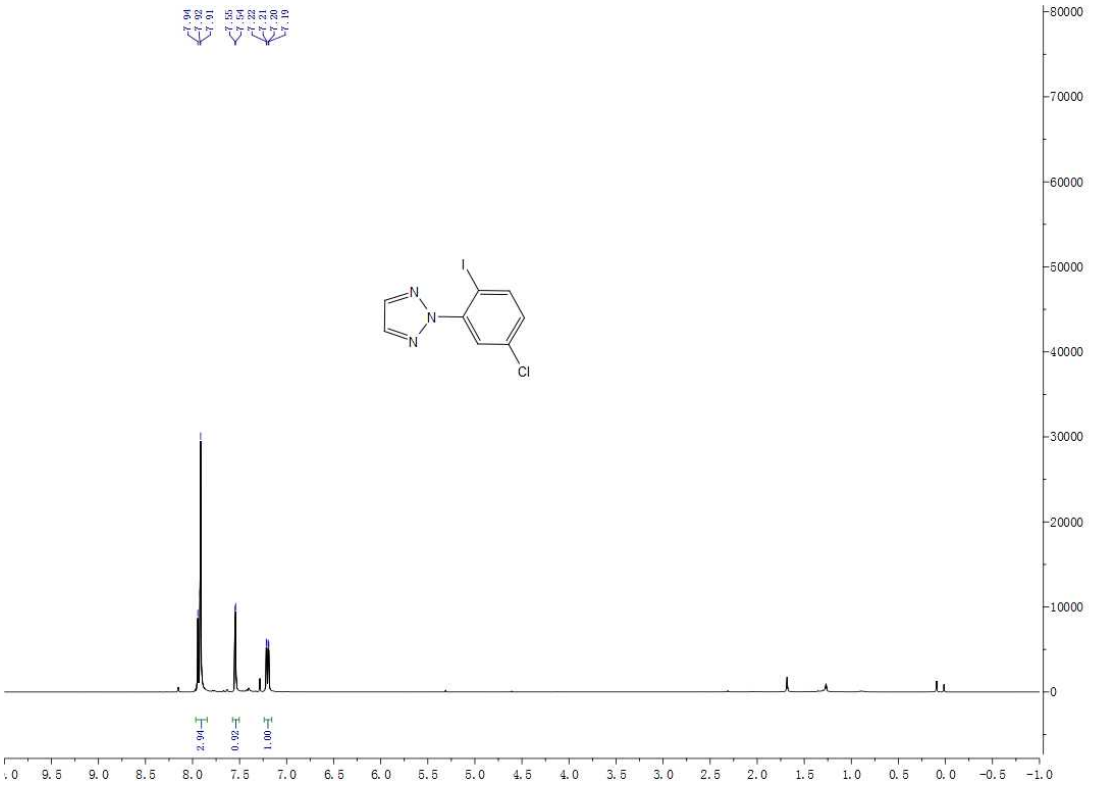
4e-^{1}H


8.25
8.24
8.04
8.03
8.02
7.94
7.88
7.86
7.28
3.96
1.00
1.05
1.97
1.06
3.17
5000
0

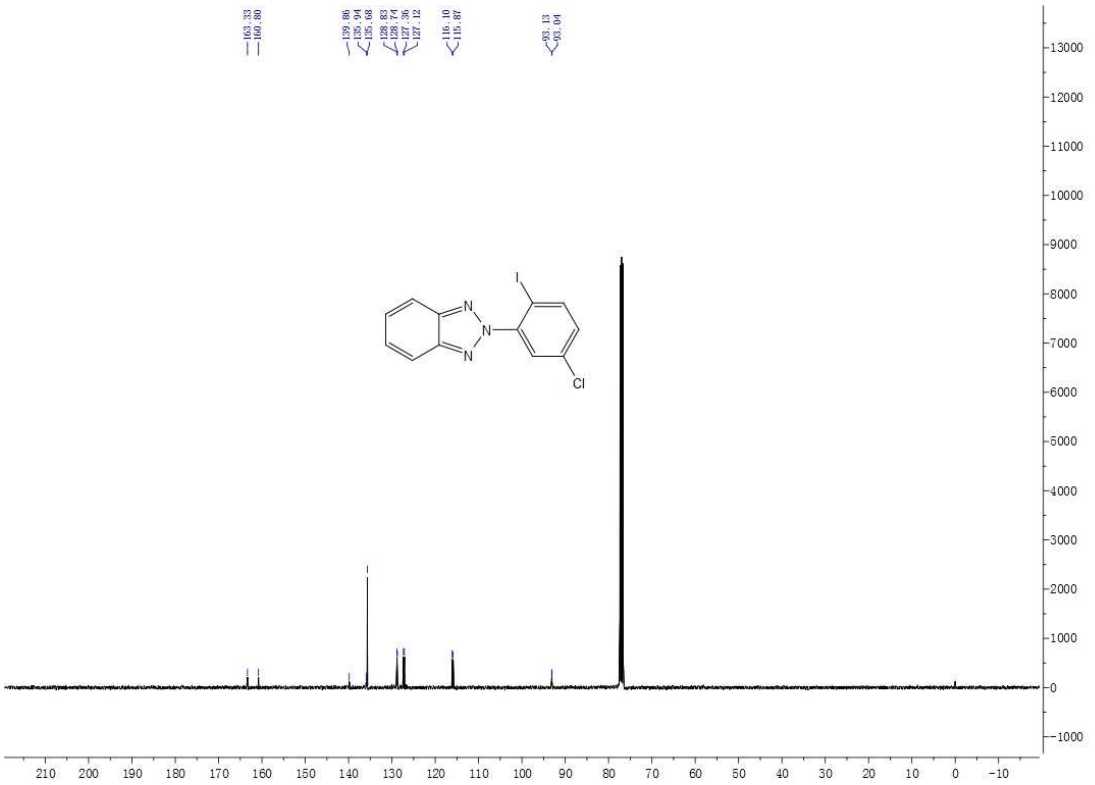
4e-^{13}C


165.21
135.91
134.44
131.10
130.46
129.05
124.04
52.61
9000
8000
7000
6000
5000
4000
3000
2000
1000
0

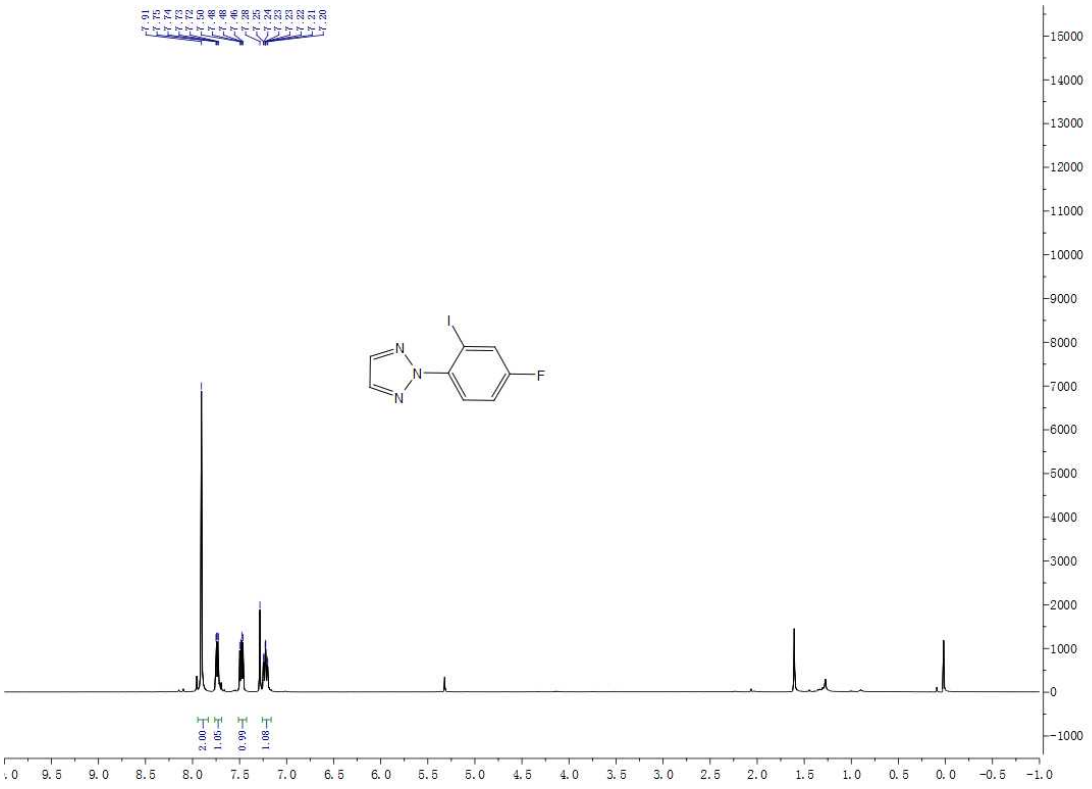
4f-^{1}H


7.94
7.92
7.91
7.55
7.54
7.22
7.21
7.20
7.19
I
N
N
N
Cl
2.94
0.92
1.00

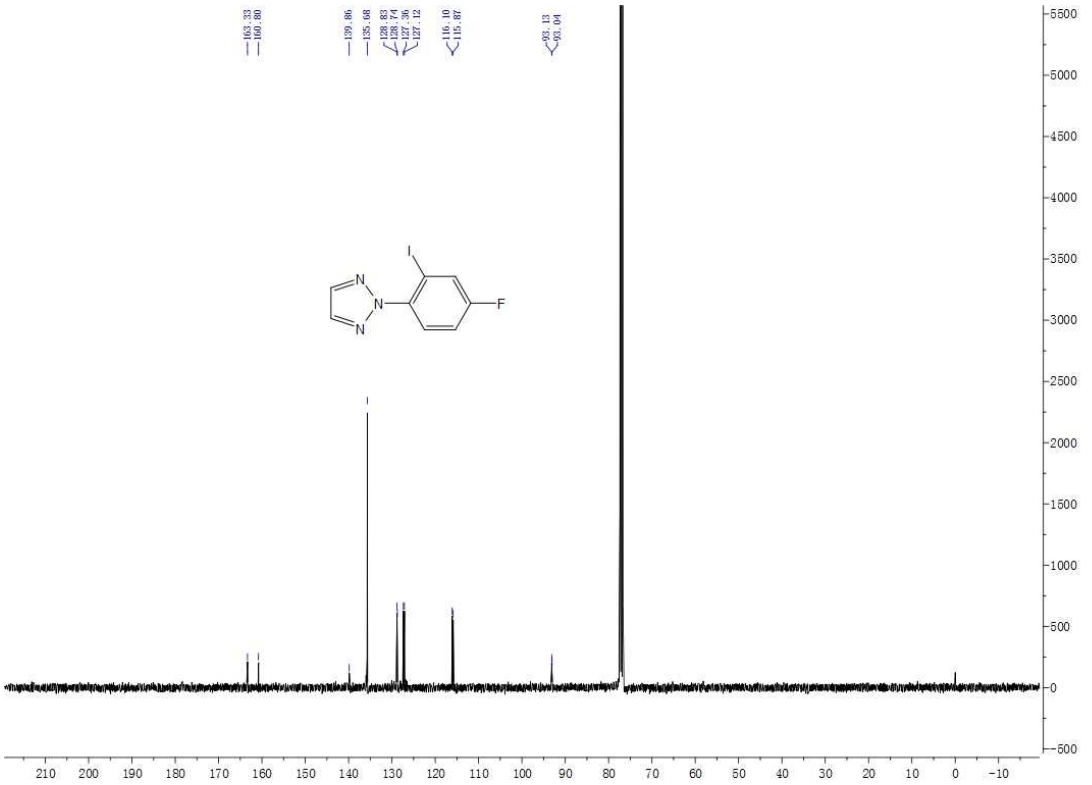
4f-^{13}C


163.33
160.80
139.86
135.94
135.68
128.83
128.74
127.36
127.12
116.10
115.87
93.13
93.04
I
N
N
N
Cl

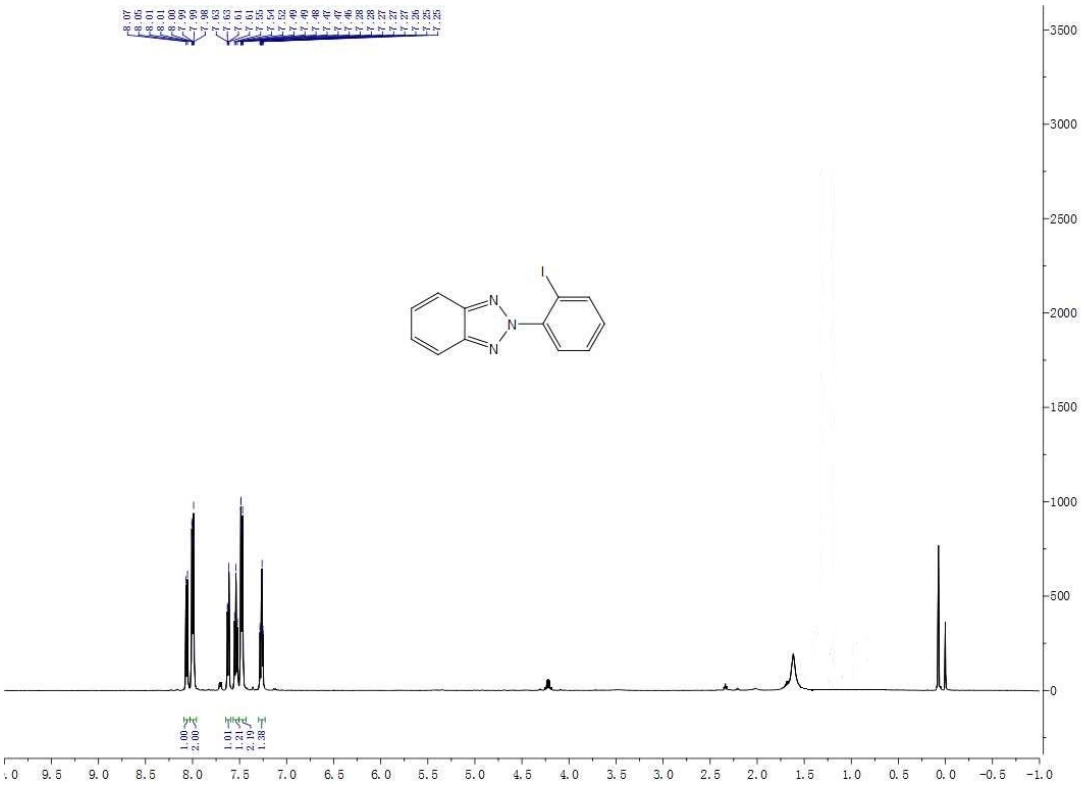
4g-^{1}H



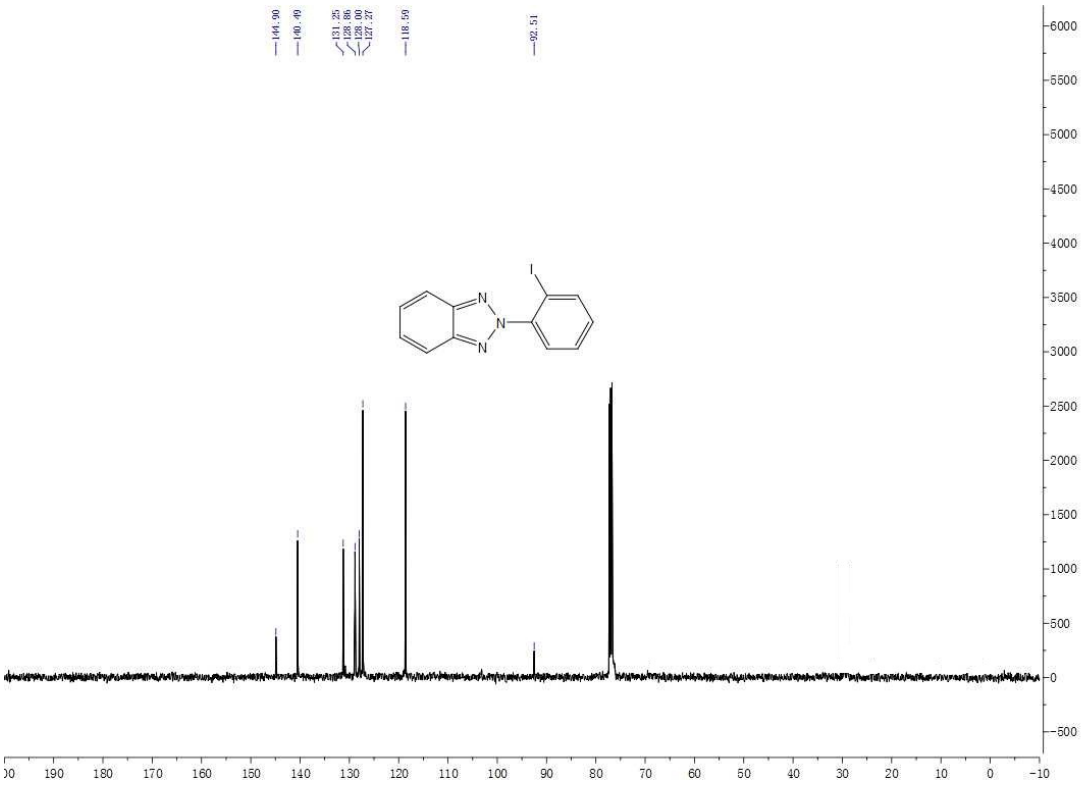
4g-^{1}H



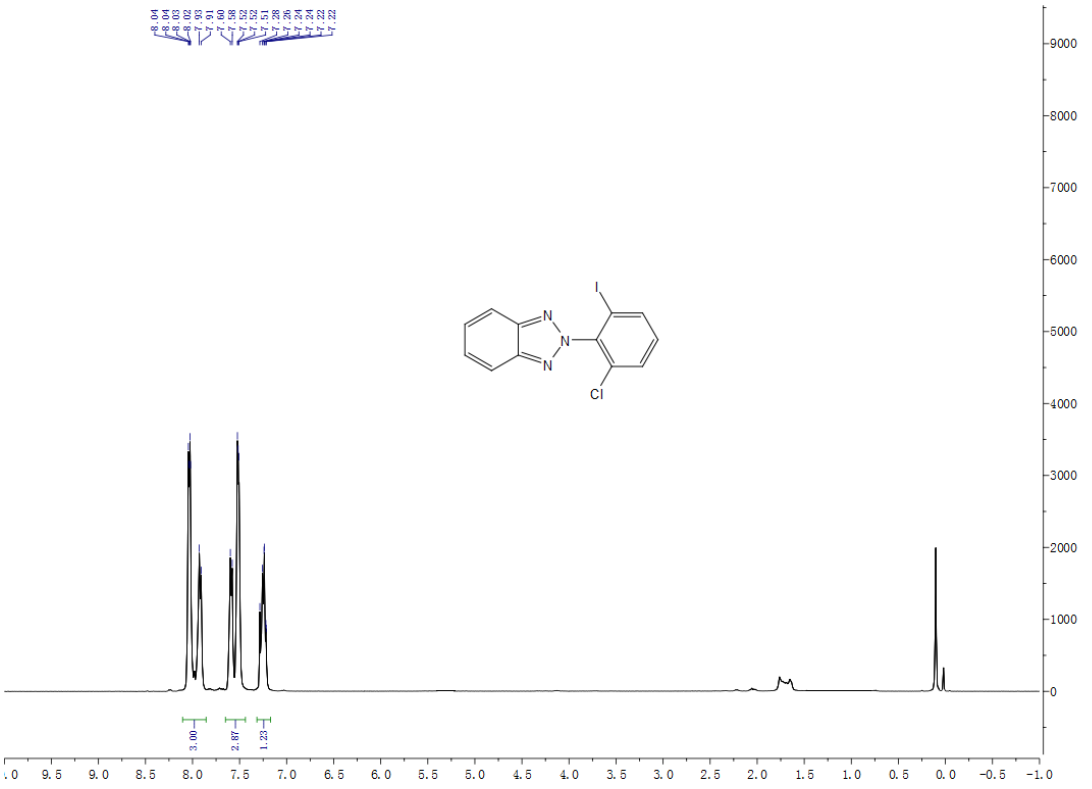
4h-^{1}H



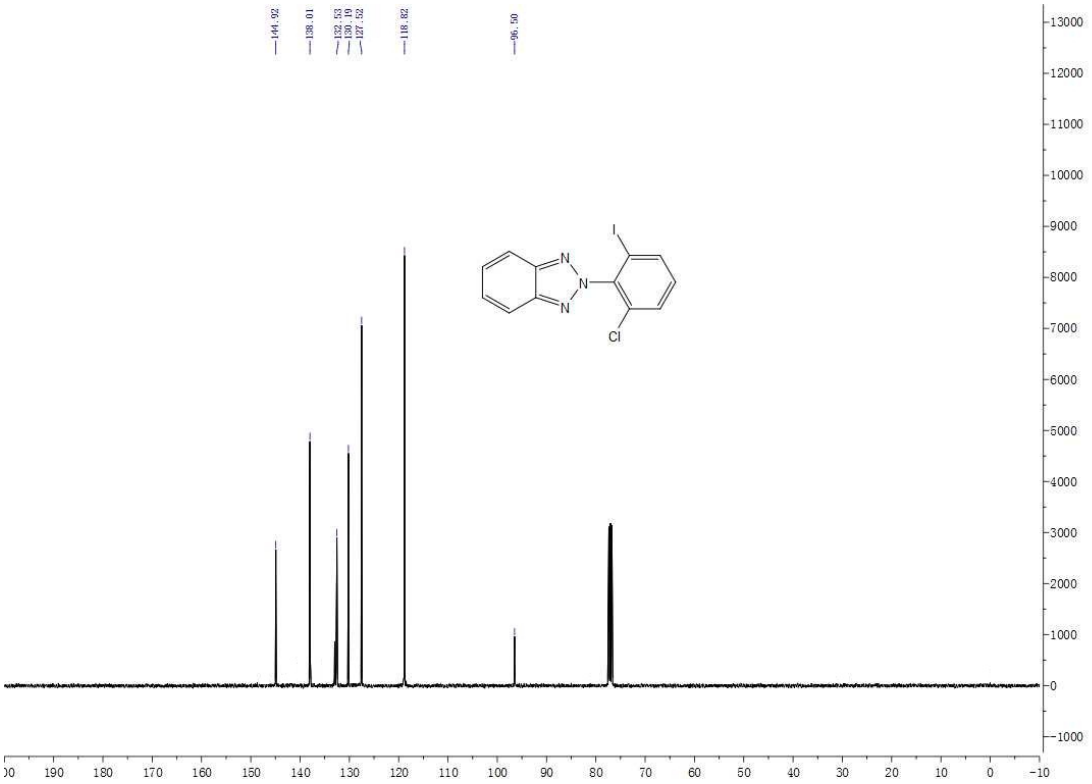
4h-^{13}C



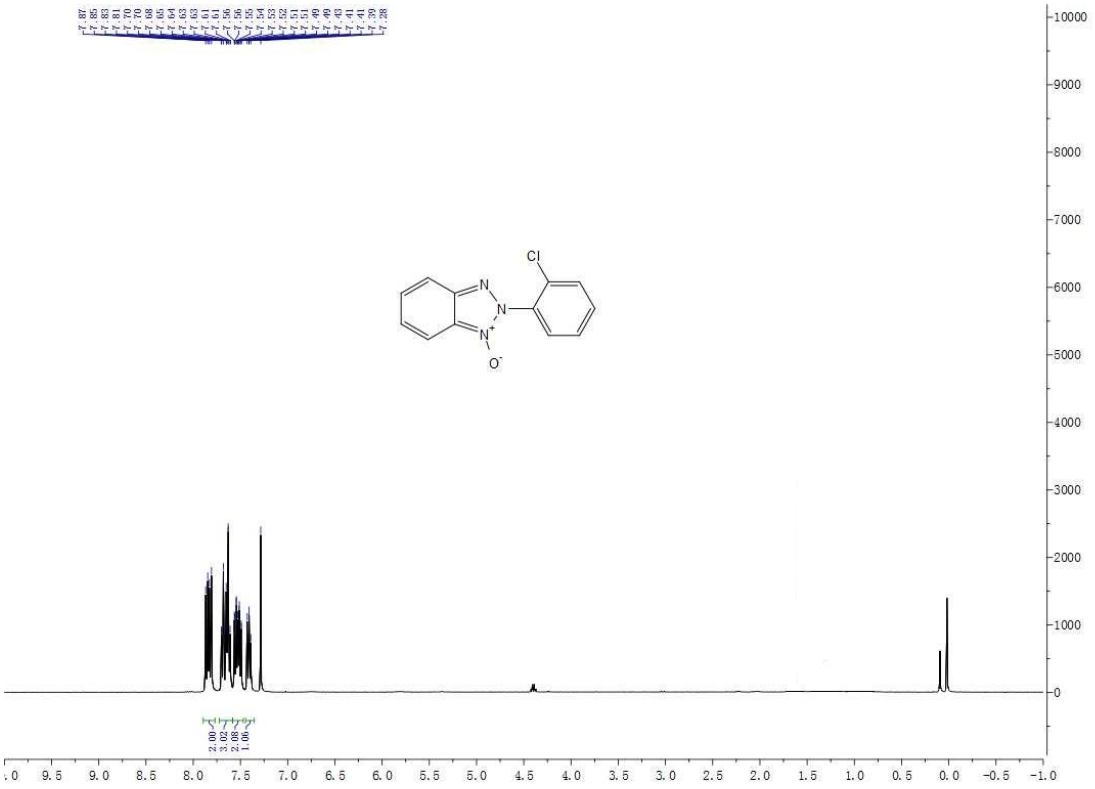
4i-^{1}H


I
N
N
N
Cl
3.00
2.87
1.23

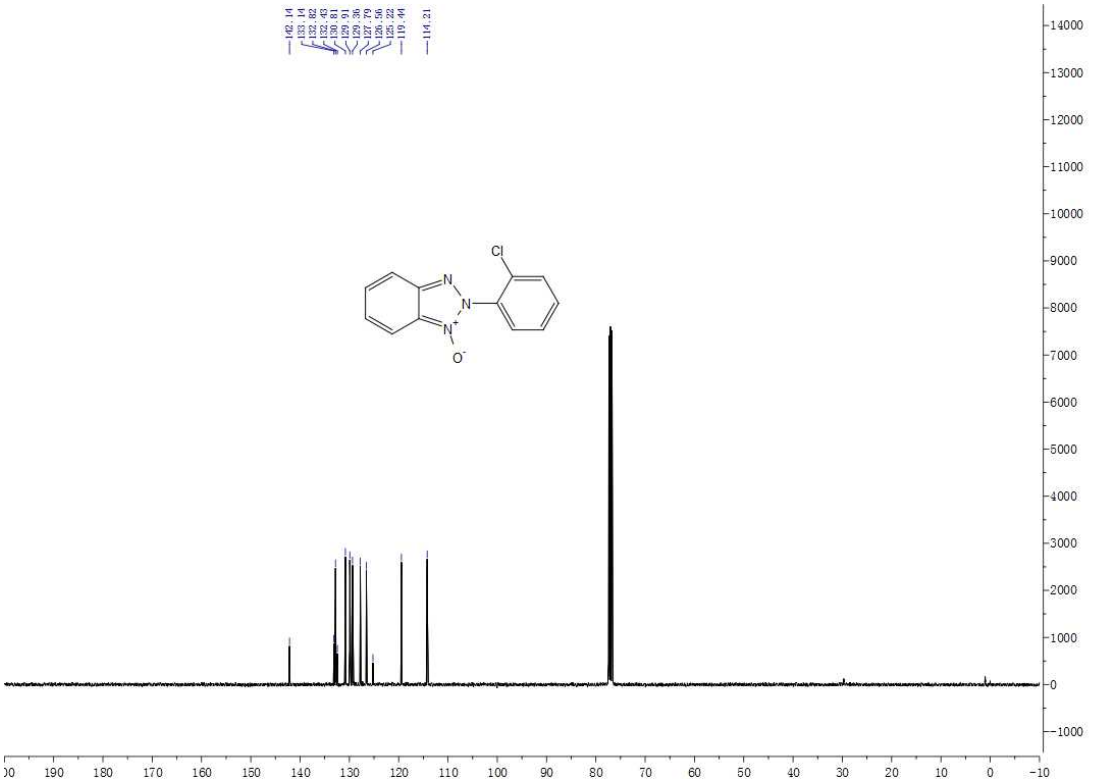
4i-^{13}C


144.92
138.01
132.53
130.19
127.52
118.82
96.50
I
N
N
N
Cl

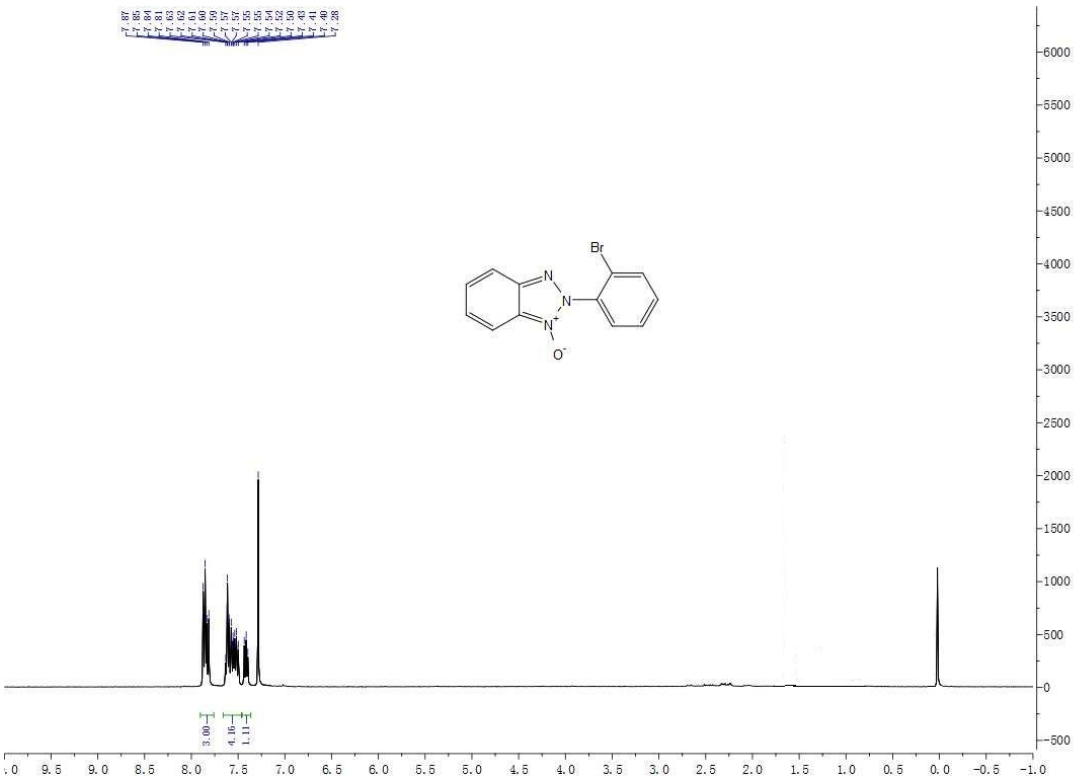
6a-^{1}H



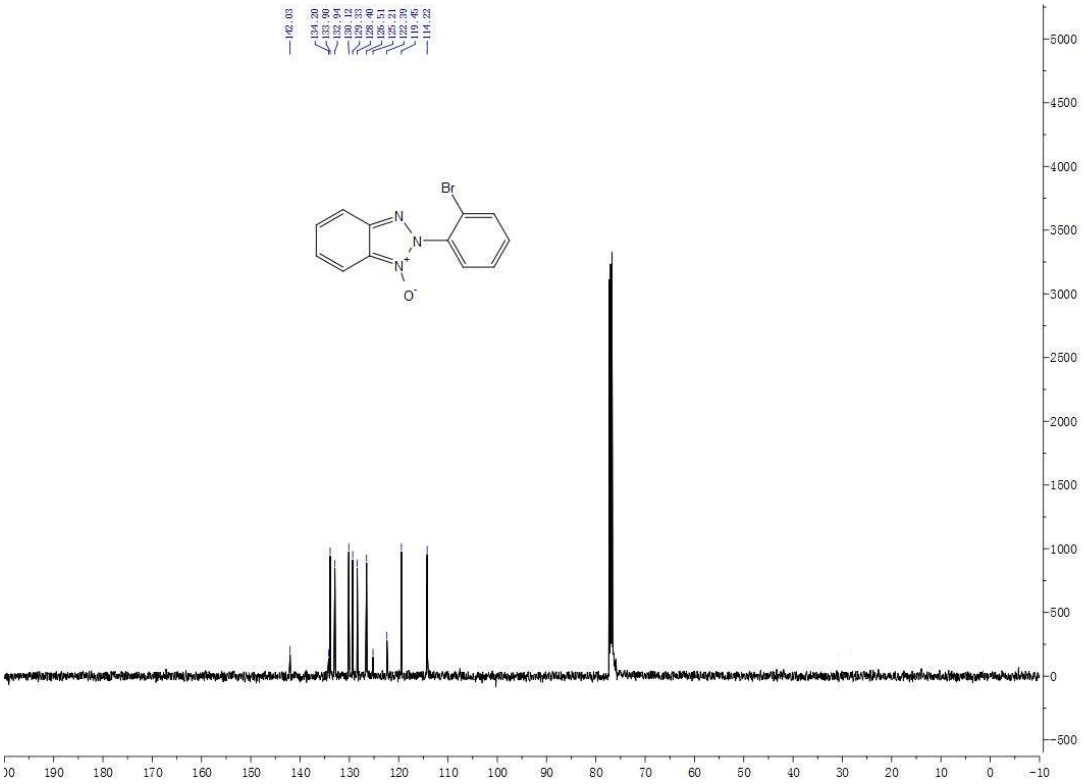
6a-^{13}C



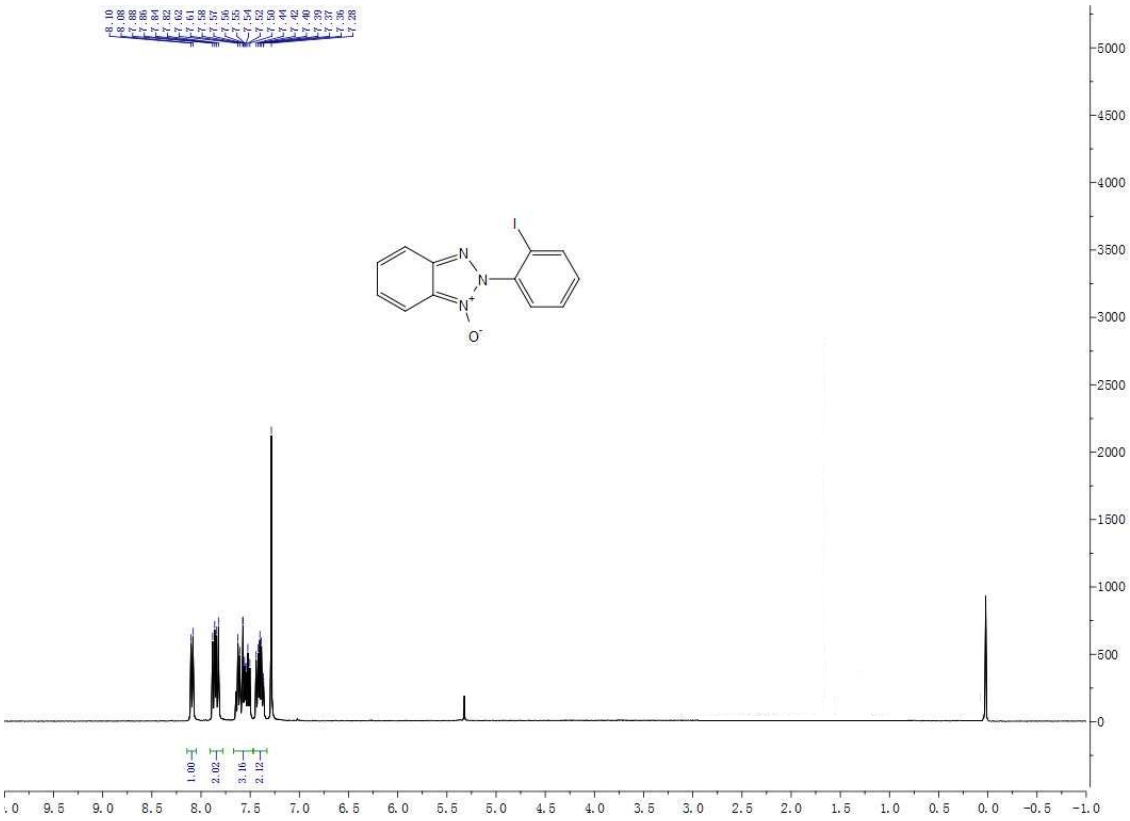
6b-^{1}H



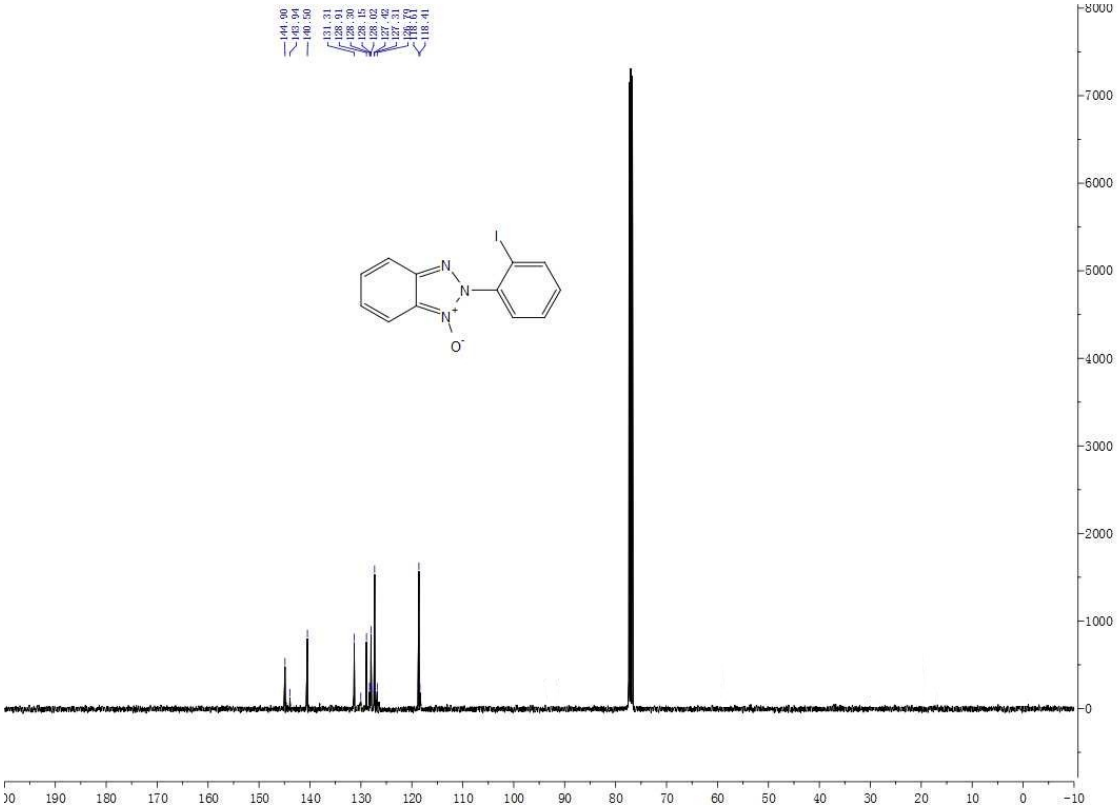
6b-^{13}C



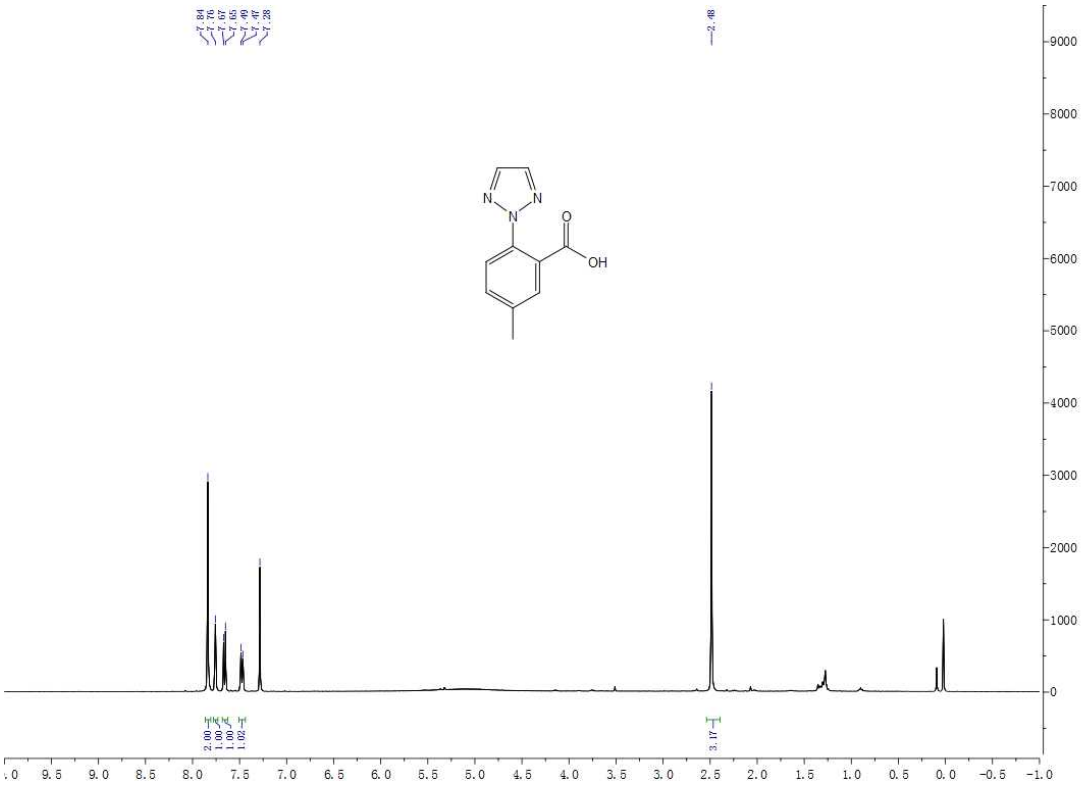
6c-^{1}H



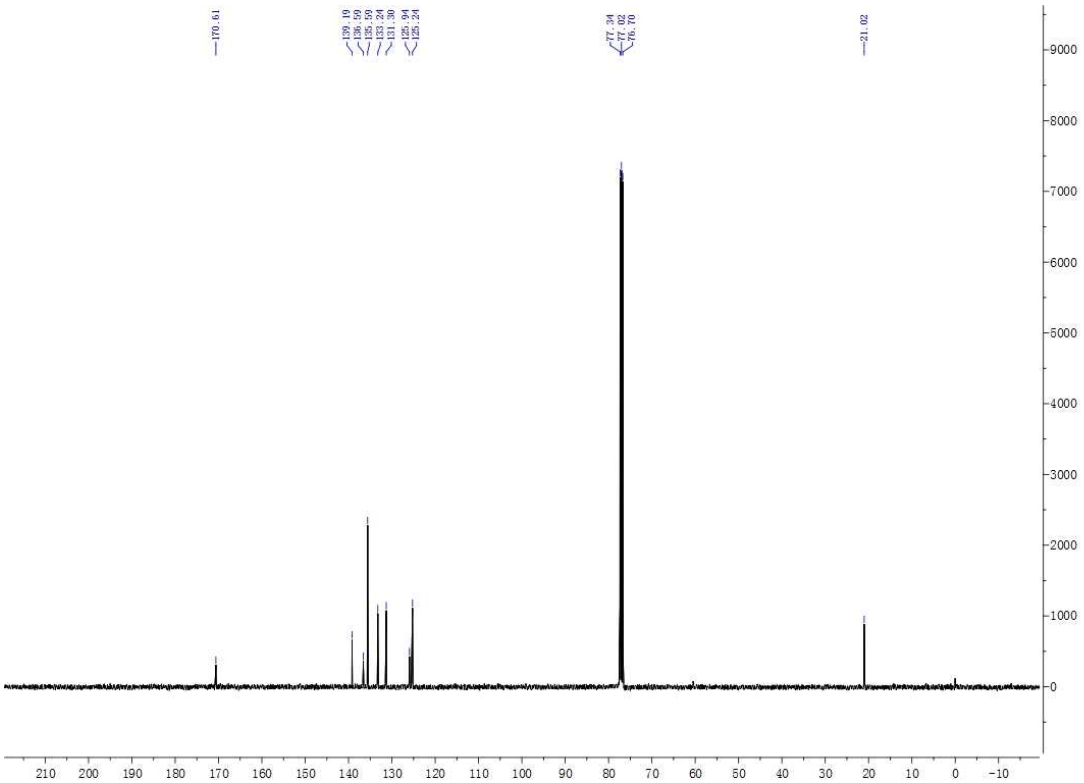
6c-^{13}C



7-^{1}H


7.84
7.76
7.67
7.65
7.49
7.47
7.28
2.48
N
N
N
O
OH
2.00
1.00
1.00
1.02
3.17

7-^{13}C


170.61
139.19
136.59
135.59
133.24
131.30
125.94
125.24
77.34
77.02
76.70
21.02