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Supporting Information

Reaction between Azidyl Radicals and Alkynes: A Straightforward Approach to *NH*-1,2,3-Triazoles

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Supporting Information

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General Remarks

$^{1}H/^{13}C$ NMR spectra were recorded on Bruker avance 400 MHz and Bruker AMX 400 MHz spectrometer at 400/100 MHz, respectively, in $CDCl_3$ unless otherwise stated, using either TMS or the undeuterated solvent residual signal as the reference. Chemical shifts are given in ppm and are measured relative to $CDCl_3$ (δ = 7.26 ppm), CD_3CN (δ = 1.94 ppm) or DMSO-d_6 (δ = 2.5 ppm) as an internal standard. ^{13}C-NMR spectra were obtained by using the same NMR spectrometers and calibrated with $CDCl_3$ (δ = 77.00 ppm), CD_3CN (δ = 118.70, 1.40 ppm) or DMSO-d_6 (δ = 39.60 ppm), Mass spectra were obtained by the electrospray ionization time-of-flight (ESI-TOF) mass spectrometry. GC yields were obtained using biphenyl as an internal standard. Flash column chromatography purification of compounds was carried out by gradient elution using ethyl acetate (EA) in light petroleum ether (PE).Unless otherwise noted, materials obtained from commercial suppliers were used without further purification.

The statement concerning safety issues

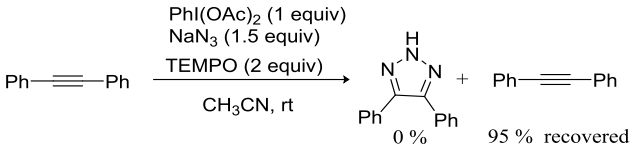
Sodium azide (NaN_3)

Sodium azide is toxic (LD_{50} oral = 27 mg/kg for rats) and can be absorbed through skin. Appropriate gloves are necessary when use it. It decomposes explosively upon heating to above 275 ℃. Sodium azide is relatively safe especially in aqueous solution, unless acidified to from HN_3, which is volatile and highly toxic.

General Experimental Procedure:

In a 10 mL round bottom flask, alkynes (0.2 mmol) was dissolved in MeCN (3 mL), NaN_3 (19.5 mg, 0.3 mmol), $PhI(OAc)_2$ (64.4 mg, 0.2 mmol) was added and the reaction mixture was stirred at room temperature under nitrogen atmosphere. The reaction is monitored by thin layer chromatography (TLC). After the alkyne was completely consumed, the reaction mixture was concentrated and purified by silica gel chromatography to give the *NH*-1,2,3-triazoles.

Control experiment:



In a 10 mL round bottom flask, 1,2-diphenylethyne (35.6 mg, 0.2 mmol) was dissolved in MeCN (3 mL), NaN_3 (19.5 mg, 0.3 mmol), TEMPO (62.4 mg, 0.4 mmol) and $PhI(OAc)_2$ (64.4 mg, 0.2 mmol) was added and the reaction mixture was stirred at room temperature under nitrogen atmosphere. Almost no reaction was observed based on TLC monitor. 95% (33.8 mg) of 1,2-diphenylethyne was recovered.

Isotopic experiment:

To confirm the origin of hydrogen atom, isotopic experiment was performed. Due to the extremely fast H/D exchange of *ND*-1,2,3-triazole, it is hard to identify *ND*-1,2,3-triazole by either LC-MS or GC-MS. Then we resorted to ^{1}H-NMR experiment and the results were shown in Figure 1. It is clearly demonstrated that 4,5-diphenyl-2D-1,2,3-triazole was obtained when the reaction was performed in CD_3CN. These ^{1}H-NMR experiment results together with computational calculation results unambiguously confirmed that the hydrogen atom of *NH*-1,2,3-triazole is come from acetonitrile.

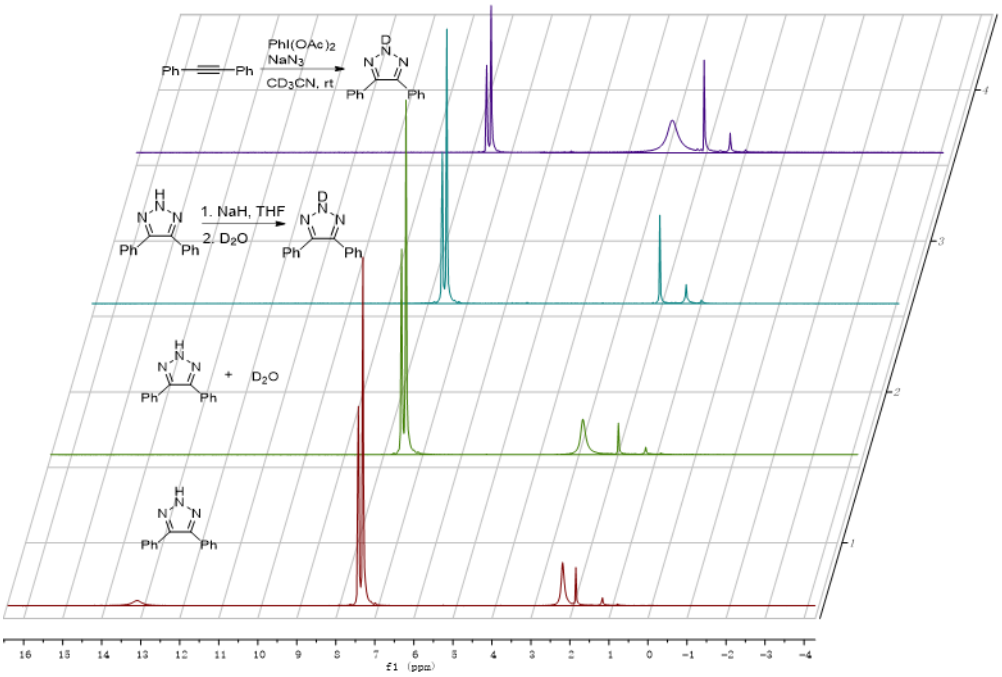
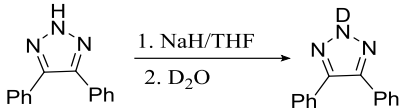


Figure **1.** ^{1}H-NMR spectra. CD_3CN was used as ^{1}H-NMR solvent. Red: 4,5-diphenyl-2H-1,2,3-triazole; Green: 4,5-diphenyl-2H-1,2,3-triazole treated with two drops of D_2O; Cyan: 4,5-diphenyl-2D-1,2,3-triazole prepared via procedure A; Purple: 4,5-diphenyl-2D-1,2,3-triazole prepared via procedure B.

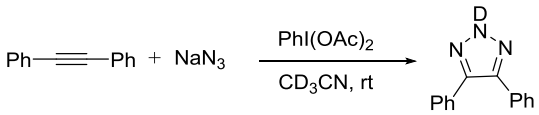
Procedures for preparation of 4,5-diphenyl-2D-1,2,3-triazole:

Procedure A:



0.5 mmol of 4,5-diphenyl-2H-1,2,3-triazole was dissolved in anhydrous THF and treated with 0.6 mmol (1.2 equiv.) of NaH at -5 ℃. The reaction mixture was stirred for 30 min. at -5 ℃ and quenched by addition of 2 mL of D_2O. The mixture was extracted by diethylether (2 × 3 mL) and the combined organic phase was discarded. The aqueous phase was treated with 2 drops of diethylether and kept at room temperature for several hours after which 65 mg of 4,5-diphenyl-2D-1,2,3-triazole was recrystallized from the mixture.

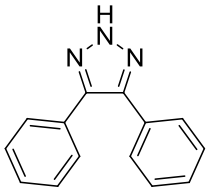
Procedure B:



In a 10 mL round bottom flask, alkynes (0.5 mmol) was dissolved in CD_3CN (5 mL), NaN_3 (48.8 mg, 0.75 mmol), $PhI(OAc)_2$ (161.0 mg, 0.5 mmol) was added and the reaction mixture was stirred at room temperature under nitrogen atmosphere. The reaction is monitored by thin layer chromatography (TLC). After the alkyne was completely consumed, the reaction mixture was concentrated. The residue was further purified by recrystallization with dichloromethane/hexane to give 4,5-diphenyl-2D-1,2,3-triazole in 70% yield (77.7 mg).

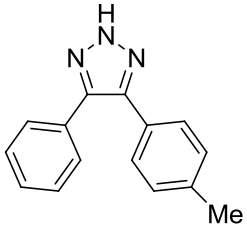
Characterization data

4,5-diphenyl-2H-1,2,3-triazole (2a)



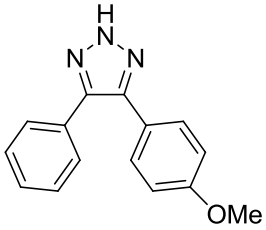
The mixture of 1,2-diphenylethyne **1a** (35.6 mg, 0.2 mmol), NaN_3 (19.5, 0.3 mmol), and $PhI(OAc)_2$ (64.4 mg, 0.2 mmol) in MeCN (3 mL) was stirred at room temperature under ambient nitrogen for 8 h, and afforded 42.0 mg (95 %) of **2a** as a light yellow solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.64 – 7.48 (m, 4H), 7.40 – 7.27 (m, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 142.1, 129.9, 128.6, 128.5, 128.2 ppm; IR(KBr): ν_{max} = 3443, 2952, 1608, 1450, 1538, 1237, 1009, 686 cm^{-1}; HRMS m/z (ESI) calcd for $C_{14}H_{12}N_3$ $(M+H)^+$: 222.1031, found 222.1028.

4-phenyl-5-(p-tolyl)-2H-1,2,3-triazole (2b)



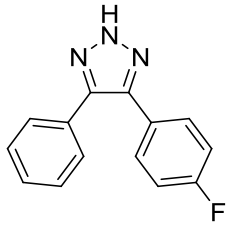
The mixture of 1-methyl-4-(phenylethynyl)benzene **1b** (38.4 mg, 0.2 mmol), NaN_3 (19.5, 0.3 mmol), and $PhI(OAc)_2$ (64.4 mg, 0.2 mmol) in MeCN (3 mL) was stirred at room temperature under ambient nitrogen for 8 h, and afforded 43.5 mg (92 %) of **2b** as a light yellow solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 12.62 (s, 1H), 7.71 – 7.52 (m, 2H), 7.44 (d, *J* = 8.0 Hz, 2H), 7.41 – 7.31 (m, 3H), 7.18 (d, *J* = 7.8 Hz, 2H), 2.38 (s, 3H) ; ^{13}C NMR (100 MHz, $CDCl_3$) δ 142.1, 141.9, 138.5, 130.2, 129.3, 128.6, 128.4, 128.2, 128.1, 126.9, 21.3 ppm; IR(KBr): ν_{max} = 3431, 3097, 2919, 1525, 1447, 1195, 1005, 823, 697 cm^{-1}; HRMS m/z (ESI) calcd for $C_{15}H_{14}N_3$ $(M+H)^+$: 236.1188, found 236.1182.

4-(4-methoxyphenyl)-5-phenyl-2H-1,2,3-triazole (2c)



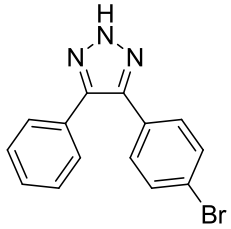
The mixture of 1-methoxy-4-(phenylethynyl)benzene **1c** (41.6 mg, 0.2 mmol), NaN_3 (19.5, 0.3 mmol), and $PhI(OAc)_2$ (64.4 mg, 0.2 mmol) in MeCN (3 mL) was stirred at room temperature under ambient nitrogen for 10 h, and afforded 39.7 mg (79 %) of **2c** as a light yellow solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.60 – 7.53 (m, 2H), 7.47 (d, *J* = 8.6 Hz, 2H), 7.40 – 7.31 (m, 3H), 6.89 (d, *J* = 8.7 Hz, 2H), 3.83 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.8, 142.1, 141.8, 130.3, 129.5, 128.6, 128.4, 128.1, 122.2, 114.1, 55.2 ppm; IR(KBr): ν_{max} = 3387, 3140, 2925, 1615, 1463, 1252, 1177, 835, 698 cm^{-1}; HRMS m/z (ESI) calcd for $C_{15}H_{14}N_3O$ $(M+H)^+$: 252.1137, found 252.1130.

4-(4-fluorophenyl)-5-phenyl-2H-1,2,3-triazole (2d)



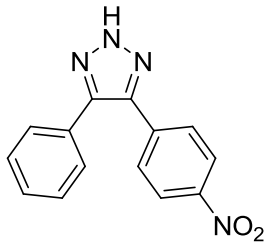
The mixture of 1-fluoro-4-(phenylethynyl)benzene **1d** (39.2.0 mg, 0.2 mmol), NaN_3 (19.5, 0.3 mmol), and $PhI(OAc)_2$ (64.4 mg, 0.2 mmol) in MeCN (3 mL) was stirred at room temperature under ambient nitrogen for 8 h, and afforded 39.2 mg (82 %) of **2d** as a white yellow solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.48 (s, 4H), 7.33 (d, *J* = 5.8 Hz, 3H), 7.00 (t, *J* = 7.7 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 162.8 (d, *J* = 248.4 Hz), 141.7, 141.4, 130.1, 123.0, 129.5, 128.7, 128.1, 126.0, 115.7 (d, *J* = 21.7 Hz) ppm; IR (KBr): ν_{max} = 3449, 3059, 2924, 1616, 1506, 1230, 1001, 836, 697 cm^{-1}; HRMS m/z (ESI) calcd for $C_{14}H_{11}N_3F$ $(M+H)^+$: 240.0937, found 240.0935.

4-(4-bromophenyl)-5-phenyl-2H-1,2,3-triazole (2e)



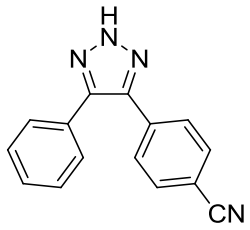
The mixture of 1-bromo-4-(phenylethynyl)benzene **1e** (51.4 mg, 0.2 mmol), NaN_3 (19.5, 0.3 mmol), and $PhI(OAc)_2$ (64.4 mg, 0.2 mmol) in MeCN (3 mL) was stirred at room temperature under ambient nitrogen for 12 h, and afforded 48.0 mg (80 %) of **2e** as a yellow solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.57 – 7.42 (m, 4H), 7.42 – 7.30 (m, 5H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 142.7, 142.3, 131.9, 129.7, 129.7, 129.3, 128.9, 128.8, 128.3, 122.8 ppm; IR (KBr): ν_{max} = 3462, 3147, 2922, 1600, 1500, 1069, 984, 830, 697 cm^{-1}; HRMS m/z (ESI) calcd for $C_{14}H_{11}N_3Br$ $(M+H)^+$: 300.0136, found 300.0135.

4-(4-nitrophenyl)-5-phenyl-2H-1,2,3-triazole (2f)



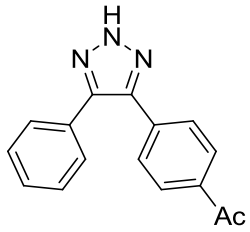
The mixture of 1-nitro-4-(phenylethynyl)benzene **2f** (44.6 mg, 0.2 mmol), NaN_3 (19.5, 0.3 mmol), and $PhI(OAc)_2$ (64.4 mg, 0.2 mmol) in MeCN (3 mL) was stirred at room temperature under ambient nitrogen for 12 h, and afforded 33.0 mg (62 %) of **2f** as a yellow solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.72 (d, *J* = 8.5 Hz, 2H), 7.65 (d, *J* = 8.6 Hz, 2H), 7.54 – 7.48 (m, 2H), 7.48 – 7.40 (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 147.6, 143.0, 141.7, 137.0, 129.5, 129.1, 128.9, 128.6, 128.4, 124.0 ppm; IR (KBr): ν_{max} = 3349, 3093, 2925, 1600, 1515, 1348, 1000, 866, 735 cm^{-1}; HRMS m/z (ESI) calcd for $C_{14}H_{11}N_4O_2$ $(M+H)^+$: 267.0882, found 267.0886

4-(5-phenyl-2H-1,2,3-triazol-4-yl)benzonitrile (2g)



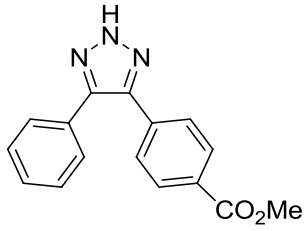
The mixture of 4-(phenylethynyl)benzonitrile **2g** (40.6 mg, 0.2 mmol), NaN_3 (19.5, 0.3 mmol), and $PhI(OAc)_2$ (64.4 mg, 0.2 mmol) in MeCN (3 mL) was stirred at room temperature under ambient nitrogen for 14 h, and afforded 31.0 mg (63 %) of **2g** as a yellow solid. ^1H NMR (400 MHz, $CDCl_3$) δ 7.72 (d, *J* = 8.5 Hz, 2H), 7.65 (d, *J* = 8.6 Hz, 2H), 7.54 – 7.48 (m, 2H), 7.48 – 7.40 (m, 3H); ^{13}C NMR (100 MHz, DMSO) δ 141.2, 140.2, 135.8, 132.8, 129.8, 129.1, 129.0, 128.4, 128.3, 118.8, 110.7 ppm; IR (KBr): ν_{max} =3441, 2921, 2253, 2167, 1655, 1078, 824, 763 cm^{-1}; HRMS m/z (ESI) calcd for $C_{15}H_{11}N_4$ $(M+H)^+$: 247.0984, found 247.0976.

1-(4-(5-phenyl-2H-1,2,3-triazol-4-yl)phenyl)ethanone (2h)



The mixture of 1-(4-(phenylethynyl)phenyl)ethanone **1h** (44.0 mg, 0.2 mmol), NaN_3 (19.5, 0.3 mmol), and $PhI(OAc)_2$ (64.4 mg, 0.2 mmol) in MeCN (3 mL) was stirred at room temperature under ambient nitrogen for 12 h, and afforded 38.9 mg (74 %) of **2h** as a yellow solid. ^1H NMR (400 MHz, $CDCl_3$) δ 7.91 (d, *J* = 8.5 Hz, 2H), 7.66 (d, *J* = 8.4 Hz, 2H), 7.52 – 7.47 (m, 2H), 7.39 – 7.32 (m, 3H), 2.60 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 198.3, 142.1, 141.4, 136.4, 135.1, 129.3, 128.9, 128.8, 128.7, 128.3, 128.0, 26.5 ppm; IR (KBr): ν_{max} = 3266, 2982, 1714, 1611, 1496, 1180, 984, 855, 786, 706 cm^{-1}; HRMS m/z (ESI) calcd for $C_{16}H_{14}N_3O$ $(M+H)^+$: 264.1137, found 264.1139.

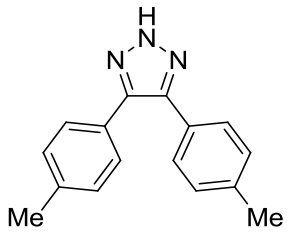
Methyl 4-(5-phenyl-2H-1,2,3-triazol-4-yl)benzoate (2i)



The mixture of methyl 4-(phenylethynyl)benzoate **1i** (47.2 mg, 0.2 mmol), NaN_3 (19.5, 0.3 mmol), and $PhI(OAc)_2$ (64.4 mg, 0.2 mmol) in MeCN (3 mL) was stirred at room temperature under ambient nitrogen for 12 h, and afforded 46.3 mg (83 %) of **2i** as a yellow solid. ^1H NMR (400 MHz, $CDCl_3$) δ 12.32 (s, 1H), 8.04 (d, *J* = 8.5 Hz, 2H), 7.67 (d, *J* = 8.5 Hz, 2H), 7.55 – 7.50 (m, 2H), 7.43 – 7.37 (m, 3H), 3.94 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.9, 142.5, 141.9, 134.8, 129.9, 129.8, 129.4, 129.0, 128.8, 128.3, 128.0, 52.3 ppm; IR (KBr): ν_{max} = 3423, 3140, 2924, 1722, 1614, 1437, 1280, 1113, 769, 699 cm^{-1};

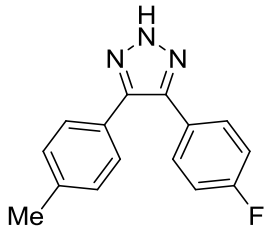
HRMS m/z (ESI) calcd for $C_{16}H_{14}N_3O_2$ $(M+H)^+$: 280.1086, found 280.1079.

4,5-di-p-tolyl-2H-1,2,3-triazole (2j)



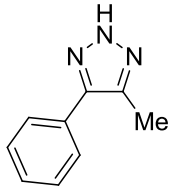
The mixture of 1,2-di-p-tolylethyne **1j** (41.2 mg, 0.2 mmol), NaN_3 (19.5, 0.3 mmol), and $PhI(OAc)_2$ (64.4 mg, 0.2 mmol) in MeCN (3 mL) was stirred at room temperature under ambient nitrogen for 10 h, and afforded 46.3 mg (93 %) of **2j** as a light yellow solid. ^1H NMR (400 MHz, $CDCl_3$) δ 7.44 (d, J = 8.2 Hz, 4H), 7.14 (d, J = 8.0 Hz, 4H), 2.37 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 141.8, 138.3, 129.3, 128.1, 127.1, 21.3 ppm; IR(KBr): ν_{max} = 3398, 3105, 2919, 1620, 1526, 1185, 1006, 819 cm^{-1}; HRMS m/z (ESI) calcd for $C_{16}H_{16}N_3$ $(M+H)^+$:250.1344, found 250.1346.

4-(4-fluorophenyl)-5-(p-tolyl)-2H-1,2,3-triazole (2k)



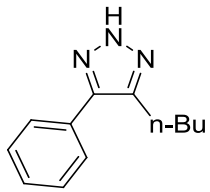
The mixture of 1-fluoro-4-(p-tolylethynyl)benzene **1k** (42.0 mg, 0.2 mmol), NaN_3 (19.5, 0.3 mmol), and $PhI(OAc)_2$ (64.4 mg, 0.2 mmol) in MeCN (3 mL) was stirred at room temperature under ambient nitrogen for 8 h, and afforded 44.5 mg (88 %) of **2k** as a white solid. ^1H NMR (400 MHz, $CDCl_3$) δ 7.53–7.49 (m, 2H), 7.37 (d, J = 7.8 Hz, 2H), 7.14 (d, J = 7.7 Hz, 2H), 7.02 (t, J = 8.5 Hz, 2H), 2.37 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.0, 161.6, 141.6, 138.7, 123.0 (d, J = 8.2 Hz), 129.4, 128.1, 126.5, 126.3, 115.6 (d, J = 21.7 Hz), 21.3 ppm; IR (KBr): ν_{max} = 3448, 3109, 2954, 1575, 1463, 1255, 1016, 845, 799 cm^{-1}; HRMS m/z (ESI) calcd for $C_{15}H_{13}N_3F$ $(M+H)^+$: 252.1094, found 252.1089.

4-methyl-5-phenyl-2H-1,2,3-triazole (2l)



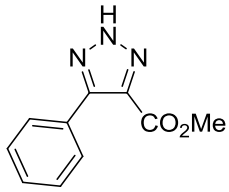
The mixture of prop-1-yn-1-ylbenzene **1l** (23.2 mg, 0.2 mmol), NaN_3 (19.5, 0.3 mmol), and $PhI(OAc)_2$ (64.4 mg, 0.2 mmol) in MeCN (3 mL) was stirred at room temperature under ambient nitrogen for 10 h, and afforded 28.2 mg (88 %) of **2l** as a light yellow solid. ^1H NMR (400 MHz, $CDCl_3$) δ 7.75 – 7.69 (m, 2H), 7.50 – 7.44 (m, 2H), 7.42 – 7.36 (m, 1H), 2.55 (s, 3H); ^{13}C NMR (100 MHz, DMSO) δ 142.8, 139.0, 130.9, 128.2, 127.1, 126.3, 10.95 ppm; IR (KBr): ν_{max} =3441, 3070, 1607, 1478, 1233, 1023, 773, 694 cm^{-1}; HRMS m/z (ESI) calcd for $C_9H_{10}N_3$ $(M+H)^+$: 160.0875, found 160.0877.

4-butyl-5-phenyl-2H-1,2,3-triazole (2m)



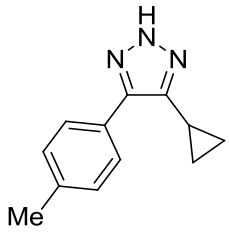
The mixture of hex-1-yn-1-ylbenzene **1m** (31.6 mg, 0.2 mmol), NaN_3 (19.5, 0.3 mmol), and $PhI(OAc)_2$ (64.4 mg, 0.2 mmol) in MeCN (3 mL) was stirred at room temperature under ambient nitrogen for 10 h, and afforded 31.0 mg (80 %) of **2m** as a light yellow solid. ^1H NMR (400 MHz, $CDCl_3$) δ 7.68 (d, *J* = 7.1 Hz, 2H), 7.50 – 7.31 (m, 3H), 2.96 – 2.74 (m, 2H), 1.71 (dt, *J* = 15.3, 7.7 Hz, 2H), 1.38 (td, *J* = 14.7, 7.4 Hz, 2H), 0.89 (t, *J* = 7.3 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 142.9, 142.0, 130.7, 128.7, 128.0, 127.4, 31.0, 24.6, 22.4, 13.7 ppm; IR (KBr): ν_{max} = 3451, 3086, 2989, 1584, 1491, 1004, 760, 697, 689 cm^{-1}; HRMS m/z (ESI) calcd for $C_{12}H_{16}N_3$ $(M+H)^+$: 202.1344, found 202.1341.

Methyl 5-phenyl-2H-1,2,3-triazole-4-carboxylate (2n)



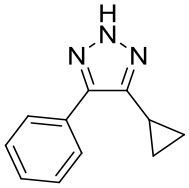
The mixture of methyl 3-phenylpropiolate **1n** (40.6 mg, 0.2 mmol), NaN_3 (19.5, 0.3 mmol), and $PhI(OAc)_2$ (64.4 mg, 0.2 mmol) in MeCN (3 mL) was stirred at room temperature under ambient nitrogen for 10 h, and afforded 31.0 mg (73 %) of **2n** as a light yellow solid. ^1H NMR (400 MHz, $CDCl_3$) δ 7.91 – 7.77 (m, 2H), 7.49 – 7.41 (m, 3H), 3.92 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 161.5, 146.7, 134.0, 130.0, 129.7, 129.2, 128.4, 52.4 ppm; IR (KBr): ν_{max} = 3434, 3001, 2936, 1687, 1579, 1418, 1013, 924, 649 cm^{-1}; HRMS m/z (ESI) calcd for $C_{10}H_{10}N_3O_2$ $(M+H)^+$: 204.0773, found 204.0771.

4-cyclopropyl-5-(p-tolyl)-2H-1,2,3-triazole (2o)



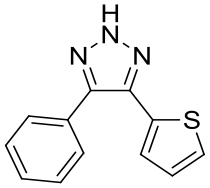
The mixture of 1-(cyclopropylethynyl)-4-methylbenzene **1o** (31.2 mg, 0.2 mmol), NaN_3 (19.5, 0.3 mmol),and $PhI(OAc)_2$ (64.4 mg, 0.2 mmol) in MeCN (3 mL) was stirred at room temperature under ambient nitrogen for 10 h, and afforded 31.0 mg (89 %) of **2o** as a light yellow solid. ^1H NMR (400 MHz, $CDCl_3$) δ 7.72 (d, *J* = 8.1 Hz, 2H), 7.21 (d, *J* = 7.9 Hz, 2H), 2.36 (s, 3H), 1.99 (tt, *J* = 8.1, 5.4 Hz, 1H), 1.04 – 0.88 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 142.9, 142.8, 137.6, 129.1, 127.3, 127. 1, 21.0, 7.5, 6.2 ppm; IR (KBr): ν_{max} = 3406, 3015, 2922, 1591, 1527, 1202, 1031, 823 cm^{-1}; HRMS m/z (ESI) calcd for $C_{12}H_{14}N_3$ $(M+H)^+$: 200.1188, found 200.186.

4-cyclopropyl-5-phenyl-2H-1,2,3-triazole (2p)



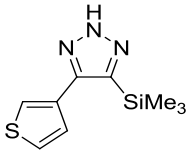
The mixture of (cyclopropylethynyl)benzene **1p** (28.4 mg, 0.2 mmol), NaN_3 (19.5, 0.3 mmol), and $PhI(OAc)_2$ (64.4 mg, 0.2 mmol) in MeCN (3 mL) was stirred at room temperature under ambient nitrogen for 10 h, and afforded 31.0 mg (90 %) of **2p** as a light yellow solid. ^1H NMR (400 MHz, $CDCl_3$) δ 7.97 – 7.78 (m, 2H), 7.54 – 7.33 (m, 3H), 2.07 – 2.00 (m,), 1.13 – 0.92 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 143.5, 143.3, 130.4, 128.5, 127.9, 127.3, 7.7, 6.3 ppm; IR (KBr): ν_{max} = 3365, 3144, 2950, 1068, 1588, 1014, 774, 696 cm^{-1}; HRMS m/z (ESI) calcd for $C_{11}H_{12}N_3$ $(M+H)^+$: 186.1031, found 186.1030.

4-phenyl-5-(thiophen-2-yl)-2H-1,2,3-triazole (2q)



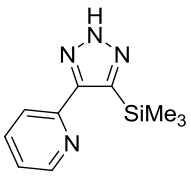
The mixture of 2-(phenylethynyl)thiophene **1q** (36.8 mg, 0.2 mmol), NaN_3 (19.5, 0.3 mmol), and $PhI(OAc)_2$ (64.4 mg, 0.2 mmol) in MeCN (3 mL) was stirred at room temperature under ambient nitrogen for 10 h, and afforded 34.5 mg (76 %) of **2q** as a yellow solid. ^1H NMR (400 MHz, $CDCl_3$) δ 7.65 – 7.52 (m, 2H), 7.40 – 7.38 (m, 3H), 7.32 – 7.27 (m, 1H), 7.23 – 7.16 (m, 1H), 6.99 (dd, *J* = 4.9, 3.7 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 141.6, 137.9, 131.5, 129.3, 128.9, 128.6, 128.5, 127.4, 126.5, 126.2 ppm; IR (KBr): ν_{max} =3424, 3107, 2924, 1610, 1491, 1470, 942, 697 cm^{-1}; HRMS m/z (ESI) calcd for $C_{12}H_{10}N_3S(M+H)^+$: 228.0595, found 228.0595.

4-(thiophen-3-yl)-5-(trimethylsilyl)-2H-1,2,3-triazole (2r)



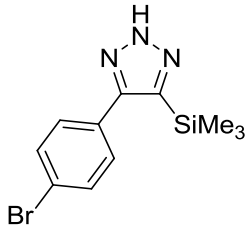
The mixture of trimethyl(thiophen-3-ylethynyl)silane **1r** (36 mg, 0.2 mmol), NaN_3 (19.5, 0.3 mmol), and $PhI(OAc)_2$ (64.4 mg, 0.2 mmol) in MeCN (3 mL) was stirred at room temperature under ambient nitrogen for 10 h, and afforded 26.7 mg (60 %) of **2r** as a yellow solid. ^1H NMR (400 MHz, $CDCl_3$) δ 7.52 (dd, *J* = 2.6, 1.5 Hz, 1H), 7.41 – 7.35 (m, 2H), 0.34 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 148.2, 133.1, 132.6, 128.0, 125.7, 123.5, -1.1 ppm; IR (KBr): ν_{max} = 3420, 3103, 2921, 1610, 1525, 1223, 990, 841, 823 cm^{-1}; HRMS m/z (ESI) calcd for $C_9H_{14}N_3SiS$ $(M+H)^+$: 224.0678, found 224.0673.

2-(5-(trimethylsilyl)-2H-1,2,3-triazol-4-yl)pyridine (2s)



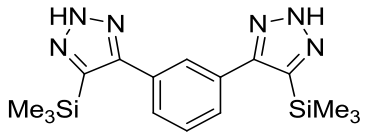
The mixture of 2-((trimethylsilyl)ethynyl)pyridine **1s** (35.0 mg, 0.2 mmol), NaN_3 (19.5, 0.3 mmol), and $PhI(OAc)_2$ (64.4 mg, 0.2 mmol) in MeCN (3 mL) was stirred at room temperature under ambient nitrogen for 10 h, and afforded 27.5 mg (63 %) of **2s** as a yellow solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 12.39 (s, 1H), 8.57 (d, *J* = 3.5 Hz, 1H), 8.23 (d, *J* = 7.9 Hz, 1H), 7.76 (dd, *J* = 11.0, 4.5 Hz, 1H), 7.20 (dd, *J* = 6.8, 5.1 Hz, 1H), 0.43 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 153.1, 151.1, 148.5, 136.4, 134.9, 122.3, 120.6, -1.2 ppm; IR (KBr): ν_{max} = 3394, 3128, 2965, 1595, 1497, 1245, 1016, 846, 744 cm^{-1}; HRMS m/z (ESI) calcd for $C_{10}H_{15}N_4Si$ $(M+H)^+$: 219.1066, found 219.1065.

4-(4-bromophenyl)-5-(trimethylsilyl)-2H-1,2,3-triazole(2t)



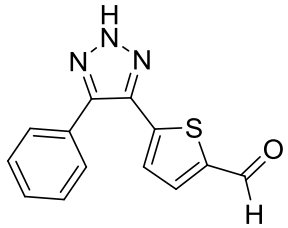
The mixture of ((4-bromophenyl)ethynyl)trimethylsilane **1t** (50.6 mg, 0.2 mmol), NaN_3 (19.5, 0.3 mmol), and $PhI(OAc)_2$ (64.4 mg, 0.2 mmol) in MeCN (3 mL) was stirred at room temperature under ambient nitrogen for 10 h, and afforded 54.9 mg (93 %) of **2t** as a white solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.55 (d, *J* = 8.2 Hz, 2H), 7.48 (d, *J* = 7.9 Hz, 2H), 0.29 (s, 9H) ; ^{13}C NMR (100 MHz, $CDCl_3$) δ 151.9, 133.3, 131.5, 131.1, 130.2, 122.4, -0.90 ppm; IR (KBr): ν_{max} = 3439, 3111, 2960, 2910, 1657, 1454, 1257, 1000, 844, 826 cm^{-1}; HRMS m/z (ESI) calcd for $C_{11}H_{15}BrN_3Si$ $(M+H)^+$: 296.0219, found 296.0217.

1,3-bis(5-(trimethylsilyl)-2H-1,2,3-triazol-4-yl)benzene(2u)



The mixture of 1,3-bis((trimethylsilyl)ethynyl)benzene **1u** (54.0 mg, 0.2 mmol), NaN_3 (39.0 mg, 0.6 mmol), and $PhI(OAc)_2$ (128.8 mg, 0.4 mmol) in MeCN (3 mL) was stirred at room temperature under ambient nitrogen for 10 h, and afforded 57.7 mg (81 %) of **2u** as a white solid. ^{1}H NMR (400 MHz, DMSO) δ 15.10 (s, 2H), 7.85 (s, 1H), 7.56 (m, 3H), 0.28 (s, 18H) ; ^{13}C NMR (100 MHz, DMSO) δ 152.3, 132.9, 130.3, 128.5, 128.4, 127.8, -0.8 ppm; IR (KBr): ν_{max} =3442, 3125, 2957, 2917, 1728, 1255, 1006, 845 cm^{-1}; HRMS m/z (ESI) calcd for $C_{16}H_{25}N_6Si_2$ $(M+H)^+$: 357.1679, found 357.1676.

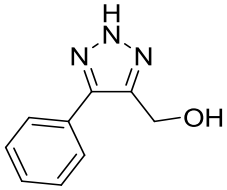
5-(5-phenyl-2H-1,2,3-triazol-4-yl)thiophene-2-carbaldehyde(2v)



The mixture of 5-(phenylethynyl)thiophene-2-carbaldehyde **1v** (42.4 mg, 0.2 mmol), NaN_3 (19.5, 0.3 mmol), and $PhI(OAc)_2$ (64.4 mg, 0.2 mmol) in MeCN (3 mL) was stirred at room temperature under ambient nitrogen for 10 h, and afforded 26.6 mg (52 %) of 2**v** as a yellow solid. ^{1}H NMR (400 MHz,

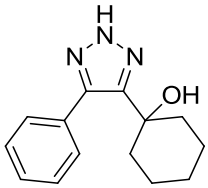
CD_3CN) δ 13.34 (s, 1H), 9.81 (s, 1H), 7.70 (d, *J* = 3.9 Hz, 1H), 7.62 – 7.50 (m, 2H), 7.50 – 7.40 (m, 3H), 7.23 (d, *J* = 3.9 Hz, 1H) ; ^{13}C NMR (100 MHz, CD_3CN) δ 185.0, 144.4, 143.3, 138.9, 130.9, 130.3, 130.2, 128.0 ppm; IR (KBr): ν_{max} =3442, 3156, 2925, 1644, 1635, 1491, 1239, 985 cm^{-1}; HRMS m/z (ESI) calcd for $C_{13}H_{10}N_3OS$ $(M+H)^+$: 256.0545, found 256.0543.

(5-phenyl-2H-1,2,3-triazol-4-yl)methanol(2w)



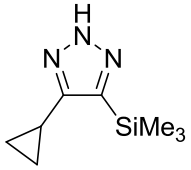
The mixture of 3-phenylprop-2-yn-1-ol **1w** (26.4 mg, 0.2 mmol), NaN_3 (19.5, 0.3 mmol), and $PhI(OAc)_2$ (64.4 mg, 0.2 mmol) in MeCN (3 mL) was stirred at room temperature under ambient nitrogen for 10 h, and afforded 22.4 mg (64 %) of **2w** as a yellow solid. ^{1}H NMR (400 MHz, DMSO) δ 14.80 (s, 1H), 7.82 (d, *J* = 37.8 Hz, 2H), 7.45 (m, 3H), 5.36 (s, 1H), 4.68 (d, *J* = 31.8 Hz, 2H) ; ^{13}C NMR (100 MHz, DMSO) δ 144.5, 143.768, 131.1, 128.8, 128.0, 127.2, 54.4 ppm; IR (KBr): ν_{max} =3394, 3156, 2922, 1646, 1313, 1059, 767, 687 cm^{-1}; HRMS m/z (ESI) calcd for $C_9H_{10}N_3O$ $(M+H)^+$: 176.0824, found 176.0827.

1-(5-phenyl-2H-1,2,3-triazol-4-yl)cyclohexanol(2x)



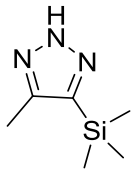
The mixture of 1-(phenylethynyl)cyclohexanol **1x** (40.0 mg, 0.2 mmol), NaN_3 (19.5, 0.3 mmol), and $PhI(OAc)_2$ (64.4 mg, 0.2 mmol) in MeCN (3 mL) was trirred at room temperature under ambient nitrogen for 10 h, and afforded 35.0 mg (72 %) of **2x** as a yellow solid. ^{1}H NMR (400 MHz, DMSO) δ 7.86 (m, 2H), 7.38 (m, 3H), 5.15 (s, 1H), 1.94 – 1.21 (m, 10H) ; ^{13}C NMR (100 MHz, DMSO) δ 149.9, 144.2, 133.0, 129.5, 127.9, 127.7, 68.1, 37.1, 25.4, 22.1 ppm; IR (KBr): ν_{max} =3296, 3090, 2930, 1448, 1261, 1150, 964, 773, 706 cm^{-1}; HRMS m/z (ESI) calcd for $C_{14}H_{17}N_3ONa$ $(M+Na)^+$: 266.1269, found 266.1268.

4-cyclopropyl-5-(trimethylsilyl)-2H-1,2,3-triazole(2z)



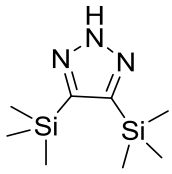
The mixture of (cyclopropylethynyl)trimethylsilane **1z** (27.6 mg, 0.2 mmol), NaN_3 (19.5, 0.3 mmol), and $PhI(OAc)_2$ (64.4 mg, 0.2 mmol) in MeCN (3 mL) was stirred at room temperature under ambient nitrogen for 10 h, and afforded 26.5 mg (73 %) of **2z** as a white solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.67 (m, 1H), 0.85 – 0.60 (m, 4H), 0.15 (s, 9H) ; ^{13}C NMR (100 MHz, $CDCl_3$) δ 153.6, 134.1, 7.6, 7.0, -1.2 ppm; IR (KBr): ν_{max} =3431, 3103, 2959, 2789, 1906, 1544, 1259, 1014, 842 cm^{-1}; HRMS m/z (ESI) calcd for $C_8H_{16}N_3Si$ $(M+H)^+$: 182.1113, found 182.1113.

4-methyl-5-(trimethylsilyl)-2H-1,2,3-triazole(2aa)



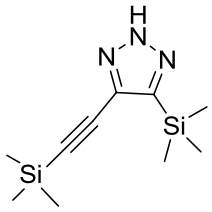
The mixture of trimethyl(prop-1-yn-1-yl)silane **1aa** (22.4 mg, 0.2 mmol), NaN_3 (19.5, 0.3 mmol), and $PhI(OAc)_2$ (64.4 mg, 0.2 mmol) in MeCN (3 mL) was stirred at room temperature under ambient nitrogen for 10 h, and afforded 21.7 mg (70 %) of **2aa** as a white solid. ^1H NMR (400 MHz, $CDCl_3$) δ 2.42 (s, 3H), 0.34 (s, 9H) ; ^{13}C NMR (100 MHz, $CDCl_3$) δ 147.7, 134.1, 11.4, -1.3 ppm; IR (KBr): ν_{max} =3431, 3117, 2957, 1535, 1255, 1037, 842, 763 cm^{-1}; HRMS m/z (ESI) calcd for $C_8H_{16}N_3Si$ $(M+H)^+$: 156.0957, found 156.0959.

4,5-bis(trimethylsilyl)-2H-1,2,3-triazole(2ab)



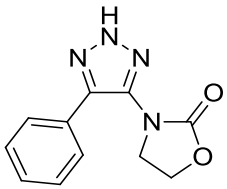
The mixture of 1,2-bis(trimethylsilyl)ethyne **1ab** (34.0 mg, 0.2 mmol), NaN_3 (19.5, 0.3 mmol), and $PhI(OAc)_2$ (64.4 mg, 0.2 mmol) in MeCN (3 mL) was stirred at room temperature under ambient nitrogen for 10 h, and afforded 29.8 mg (70 %) of **2ab** as a white solid. ^1H NMR (400 MHz, $CDCl_3$) δ 0.38 (s, 18H) ; ^{13}C NMR (100 MHz, $CDCl_3$) δ145.9, -0.2 ppm; IR (KBr): ν_{max} =3438, 3117, 2955, 1253, 1144, 856, 758, cm^{-1}; HRMS m/z (ESI) calcd for $C_8H_{20}N_3Si_2$ $(M+H)^+$: 214.1196, found 214.1198.

4-(trimethylsilyl)-5-((trimethylsilyl)ethynyl)-2H-1,2,3-triazole(2ac)



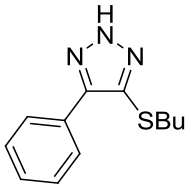
The mixture of 1,4-bis(trimethylsilyl)buta-1,3-diyne **1ac** (38.8 mg, 0.2 mmol), NaN_3 (39.0 mg, 0.6 mmol), and $PhI(OAc)_2$ (128.8 mg, 0.4 mmol) in MeCN (3 mL) was stirred at room temperature under ambient nitrogen for 10 h, and afforded 33.2 mg (70 %) of **2ac** as a white yellow solid. ^1H NMR (400 MHz, $CDCl_3$) δ 0.43 – 0.37 (m, 9H), 0.26 – 0.19 (m, 9H) ; ^{13}C NMR (100 MHz, $CDCl_3$) δ 139.3, 135.5, 99.5, 95.5, -0.4, -1.7 ppm; IR (KBr): ν_{max} =3421, 3090, 2961, 2166, 1316, 1253, 1007, 864, 846 cm^{-1}; HRMS m/z (ESI) calcd for $C_{10}H_{20}N_3Si_2$ $(M+H)^+$: 238.1196, found 238.1200.

3-(5-phenyl-2H-1,2,3-triazol-4-yl)oxazolidin-2-one(2ad)



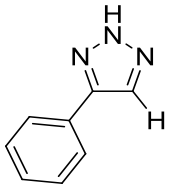
The mixture of 3-(phenylethynyl)oxazolidin-2-one **1ad** (37.4 mg, 0.2 mmol), NaN_3 (19.5, 0.3 mmol), and $PhI(OAc)_2$ (64.4 mg, 0.2 mmol) in MeCN (3 mL) was stirred at room temperature under ambient nitrogen for 10 h, and afforded 33.1 mg (72 %) of **2ad** as a white solid. ^{1}H NMR (400 MHz, DMSO) δ 7.69 (d, *J* = 7.5 Hz, 2H), 7.48 (t, *J* = 7.3 Hz, 2H), 7.45 – 7.38 (m, 1H), 4.56 (t, *J* = 7.8 Hz, 2H), 4.02 (t, *J* = 7.8 Hz, 2H) ; ^{13}C NMR (100 MHz, DMSO) δ 156.0, 134.0, 139.1, 129.7, 128.9, 128.7, 126.5, 63.1, 46.9 ppm ; IR (KBr): ν_{max} =3438, 2924, 2853, 1756, 1645, 1224, 1027, 763 cm^{-1}; HRMS m/z (ESI) calcd for $C_{11}H_{10}N_4O_2Na$ $(M+Na)^+$: 253.0701, found 231.253.0699.

4-(butylthio)-5-phenyl-2H-1,2,3-triazole(2ae)



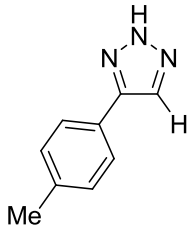
The mixture of butyl(phenylethynyl)sulfane **1ae** (38.0 mg, 0.2 mmol), NaN_3 (19.5, 0.3 mmol), and $PhI(OAc)_2$ (64.4 mg, 0.2 mmol) in MeCN (3 mL) was stirred at room temperature under ambient nitrogen for 10 h, and afforded 31.7 mg (68 %) of **2ae** as a white solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.94 (d, *J* = 7.4 Hz, 2H), 7.46 (t, *J* = 7.5 Hz, 2H), 7.39 (t, *J* = 7.3 Hz, 1H), 3.05 (t, *J* = 7.3 Hz, 2H), 1.65 (dt, *J* = 14.9, 7.4 Hz, 2H), 1.42 (dq, *J* = 14.5, 7.3 Hz, 2H), 0.88 (t, *J* = 7.3 Hz, 3H) ; ^{13}C NMR (100 MHz, $CDCl_3$) δ 144.7, 138.4, 129.6, 128.7, 128.7, 127.3, 33.8, 31.4, 21.8, 13.5 ppm; IR (KBr): ν_{max} =3439, 3161, 2958, 2927, 2855, 1658, 1456, 1009, 772, 694 cm^{-1}; HRMS m/z (ESI) calcd for $C_{12}H_{16}N_3S$ $(M+H)^+$: 234.1065, found 234.1063.

4-phenyl-2H-1,2,3-triazole (2af)



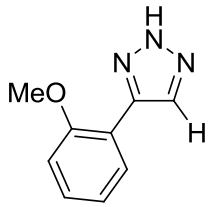
The mixture of ethynylbenzene **1af** (20.4 mg, 0.2 mmol), NaN_3 (19.5, 0.3 mmol), and $PhI(OAc)_2$ (64.4 mg, 0.2 mmol) in MeCN (3 mL) was stirred at room temperature under ambient nitrogen for 14 h, and afforded 9.3 mg (32 %) of **2af** as a white solid. ^{1}H NMR (400 MHz, DMSO) δ 8.27 (s, 1H), 7.87 (d, *J* = 7.2 Hz, 2H), 7.43 (t, *J* = 7.5 Hz, 2H), 7.33 (t, *J* = 7.1 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ146.4, 130.7, 129.0, 128.5, 128.2, 125.7 ppm; IR (KBr): ν_{max} = 3440, 3113, 2928, 2252, 1654, 1056, 1008, 822, 761 cm^{-1}; HRMS m/z (ESI) calcd for $C_8H_8N_3$ $(M+H)^+$: 146.0718, found 146.0717.

4-(p-tolyl)-2H-1,2,3-triazole (2ag)



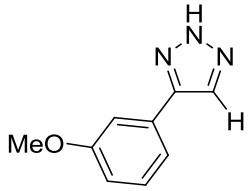
The mixture of 1-ethynyl-4-methylbenzene **1ag** (23.2 mg, 0.2 mmol), NaN_3 (19.5, 0.3 mmol), and $PhI(OAc)_2$ (64.4 mg, 0.2 mmol) in MeCN (3 mL) was stirred at room temperature under ambient nitrogen for 14 h, and afforded 16.5 mg (52 %) of **2ag** as a white solid. ^1H NMR (400 MHz, $CDCl_3$) δ 12.08 (s, 1H), 7.72 (d, *J* = 7.3 Hz, 2H), 7.49 – 7.37 (m, 3H), 2.55 (s, 3H); ^{13}C NMR (100 MHz, DMSO) δ 159.4, 146.3, 130.3, 127.1, 123.3, 114.5, 55.3 ppm; IR (KBr): ν_{max} =3432, 2924, 2253, 1655, 1027, 824, 762 cm^{-1}; HRMS m/z (ESI) calcd for $C_9H_{10}N_3$ $(M+H)^+$: 160.0875, found 160.0874.

4-(2-methoxyphenyl)-2H-1,2,3-triazole(2ah)



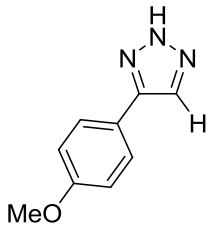
The mixture of 1-ethynyl-2-methoxybenzene **1ah** (26.4 mg, 0.2 mmol), NaN_3 (19.5, 0.3 mmol), and $PhI(OAc)_2$ (64.4 mg, 0.2 mmol) in MeCN (3 mL) was stirred at room temperature under ambient nitrogen for 12 h, and afforded 21.7 mg (62 %) of **2ah** as a light yellow solid. ^1H NMR (400 MHz, $CDCl_3$) δ 8.16 (s, 1H), 7.92 (d, *J* = 6.9 Hz, 1H), 7.36 (t, *J* = 7.8 Hz, 1H), 7.10 – 7.00 (m, 2H), 3.97 (s, 3H) ; ^{13}C NMR (100 MHz, $CDCl_3$) δ 156.0, 139.5, 130.3, 129.9, 128.1, 121.2, 117.0, 111.4, 55.6 ppm; IR (KBr): ν_{max} =3423, 2933, 1606, 1487, 1248, 1025, 754 cm^{-1}; HRMS m/z (ESI) calcd for $C_9H_{10}N_3O$ $(M+H)^+$: 176.0824, found 176.0825.

4-(3-methoxyphenyl)-2H-1,2,3-triazole(2ai)



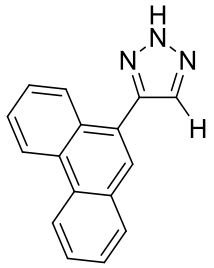
The mixture of 1-ethynyl-3-methoxybenzene **1ai** (26.4 mg, 0.2 mmol), NaN_3 (19.5, 0.3 mmol), and $PhI(OAc)_2$ (64.4 mg, 0.2 mmol) in MeCN (3 mL) was stirred at room temperature under ambient nitrogen for 12 h, and afforded 11.9 mg (34 %) of **2ai** as a light yellow solid. ^1H NMR (400 MHz, $CDCl_3$) δ 8.16 (s, 1H), 7.92 (d, *J* = 6.9 Hz, 1H), 7.36 (t, *J* = 7.8 Hz, 1H), 7.10 – 6.99 (m, 2H), 3.97 (s, 3H) ; ^{13}C NMR (100 MHz, $CDCl_3$) δ 160.1, 147.2, 131.2, 130.0, 129.9, 118.6, 114.6, 111.4, 55.4 ppm; IR (KBr): ν_{max} =3396, 3183, 2922, 2850, 1647, 1585, 1468, 1240, 1045, 784, 691 cm^{-1}; HRMS m/z (ESI) calcd for $C_9H_{10}N_3O$ $(M+H)^+$: 176.0824, found 176.0820.

4-(4-methoxyphenyl)-2H-1,2,3-triazole (2aj)



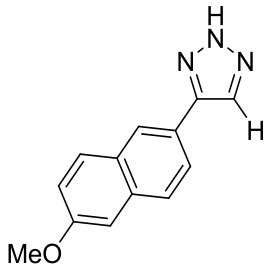
The mixture of 1-ethynyl-4-methoxybenzene **1aj** (26.4 mg, 0.2 mmol), NaN_3 (19.5, 0.3 mmol), and $PhI(OAc)_2$ (64.4 mg, 0.2 mmol) in MeCN (3 mL) was stirred at room temperature under ambient nitrogen for 14 h, and afforded 22.1 mg (63 %) of **2aj** as a light yellow solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.90 (s, 1H), 7.75 (d, *J* = 8.8 Hz, 2H), 6.99 (d, *J* = 8.8 Hz, 2H), 3.86 (s, 3H); ^{13}C NMR (100 MHz, DMSO) δ 159.4, 146.3, 130.3, 127.1, 123.3, 114.5, 55.3 ppm; IR (KBr): ν_{max} =3440, 3007, 2923, 2125, 1656, 1618, 1027, 823, 697 cm^{-1}; HRMS m/z (ESI) calcd for $C_9H_{10}N_3O$ $(M+H)^+$: 176.0824, found 176.0824.

4-(phenanthren-9-yl)-2H-1,2,3-triazole(2ak)



The mixture of 9-ethynylphenanthrene **1ak** (40.4 mg, 0.2 mmol), NaN_3 (19.5, 0.3 mmol), and $PhI(OAc)_2$ (64.4 mg, 0.2 mmol) in MeCN (3 mL) was stirred at room temperature under ambient nitrogen for 12 h, and afforded 25.0 mg (51 %) of **2ak** as a yellow solid. ^{1}H NMR (400 MHz, DMSO) δ 8.91 (dd, *J* = 26.4, 8.1 Hz, 2H), 8.52 (d, *J* = 8.3 Hz, 1H), 8.09 (m, 2H), 7.83 – 7.65 (m, 4H). IR (KBr): ν_{max} =3424, 2923, 1648, 1048, 1028, 1000, 827, 766, 633 cm^{-1}; HRMS m/z (ESI) calcd for $C_{16}H_{12}N_3$ $(M+H)^+$: 246.1031, found 246.1027.

4-(6-methoxynaphthalen-2-yl)-2H-1,2,3-triazole(2al)



The mixture of 2-ethynyl-6-methoxynaphthalene **1al** (36.4 mg, 0.2 mmol), NaN_3 (19.5, 0.3 mmol), and $PhI(OAc)_2$ (64.4 mg, 0.2 mmol) in MeCN (3 mL) was stirred at room temperature under ambient nitrogen for 12 h, and afforded 31.5 mg (70 %) of **2al** as a light yellow solid. ^{1}H NMR (400 MHz, DMSO) δ 14.98 (s, 1H), 8.33 (d, *J* = 8.6 Hz, 2H), 7.93 (dd, *J* = 36.0, 8.6 Hz, 3H), 7.34 (s, 1H), 7.20 (d, *J* = 8.6 Hz, 1H), 3.89 (s, 3H), ^{13}C NMR (100 MHz, DMSO) δ 157.6, 146.6, 134.1, 130.8, 129.6, 128.6, 127.4, 125.8, 124.4, 124.3, 119.2, 106.1, 55.3 ppm, IR (KBr): ν_{max} =3438, 3153, 2932, 1610, 1500, 1260, 1217, 1030, 858 cm^{-1}; HRMS m/z (ESI) calcd for $C_{13}H_{12}N_3O$ $(M+H)^+$: 226.0980, found 226.0975.

Supporting information: DFT calculations

All intermediates and transition structures were optimized using the B3LYP[1] hybrid functional. A triple zeta basis set with polarization functions (def2-TZVP)[2] was used in all geometry optimizations and energy calculations. After a determination of the harmonic vibrational frequencies, using analytical second energy derivatives, all stationary points were characterized as either minima (no negative eigenvalue of the hessian matrix **H**) or transition structures (one negative eigenvalue of **H**). The harmonic vibrational frequencies were used to calculate thermodynamic corrections to the enthalpy and Gibbs free energy under standard conditions (298 K, p = 1 atm). For vibrational modes with low frequencies (<100cm^{-1}), a rotor approximation[3] was used. Electronic energies were also evaluated with the double hybrid functional B2PLYP[4], which obtains part of the correlation energy in a perturbative approach including virtual Kohn-Sham orbitals.

All DFT calculations were conducted with functional-specific semiempirical corrections (D3) to correct the failure of most functionals to account for long-range London dispersion forces.[5]

The B3LYP calculations were performed with TURBOMOLE (Version 6.6)[6], the B2PLYP-D3 energies were obtained with ORCA (3.0.3)[7].

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[1] a) A. D. Becke, *J. Chem. Phys.* **1993**, *98*, 5648-5652. b) P. J. Stephens, F. J. Devlin, C. F. Chabalowski, M. J. Frisch, *J. Phys. Chem.* **1994**, *98*, 11623-11627.

[2] F. Weigend, R. Ahlrichs, *Phys. Chem. Chem. Phys.* **2005**, *7*, 3297–3305.

[3] S. Grimme, *Chem. Eur. J.* **2012**, *18*, 9955-9964.

[4] S. Grimme, *J. Chem. Phys.* **2006**, *124*, 034108.

[5] a) S. Grimme, J. Antony, S. Ehrlich, H. Krieg, *J. Chem. Phys.* **2010**, *132*, 154104. b) S. Grimme, S. Ehrlich, L. Goerigk, *J. Comput. Chem.* **2011**, *32*, 1456–1465.

[6] TURBOMOLE V6.6 2014, a development of University of Karlsruhe and Forschungszentrum Karlsruhe GmbH, 1989-2007, TURBOMOLE GmbH, since 2007; available from http://www.turbomole.com.

[7] F. Neese, The ORCA program system, *Wiley Interdisciplinary Reviews: Computational Molecular Science,* **2012**, *2*, 73-78.

Table 1: Electronic Energies (B3LYP-D3 and B2PLYP-D3) obtained with optimized geometries obtained with the B3LYP-D3 functional (def2-TZVP basis set). Thermodynamic corrections as evaluated from harmonic vibrational frequencies (B3LYP-D3/def2-TZVP).

Structure	E (B3LYP-D3) [E_h]	E (B2PLYP-D3) [E_h]	ZPE [kcal mol^{-1}]	H (298 K) [kcal mol^{-1}]	G (298 K) [kcal mol^{-1}]
1a	-539.3620599	-539.2653181	119.810	127.356	96.531
1a-TSA	-703.4915554	-703.3683919	126.608	136.229	100.747
1a-A	-703.5190669	-703.3972650	127.818	137.335	101.828
1a-TSB	-703.4965631	-703.3757769	127.616	136.545	102.405
1a-B	-703.5711229	-703.4479388	129.149	137.815	104.667
1a-TSHAT	-836.2874487	-836.1433070	155.741	166.968	128.215
2a	-704.2395283	-704.1231531	138.841	147.368	114.531
1z	-155.9431983	-155.9083401	52.63	56.83	35.13
1z-TSA	-320.0701469	-320.0103004	59.653	65.631	38.894
1z-A	-320.0926297	-320.0356724	61.421	67.089	41.127
1z-TSB	-320.0696196	-320.0119973	60.537	65.350	41.442
1z-B	-320.14779420	-320.0888513	61.202	66.549	41.527
1z-TSHAT	-452.8703055	-452.7883483	88.733	96.338	65.702
2z	-320.8248730	-320.7692797	71.848	76.830	52.496
TSD	-296.8394112	-296.7916125	31.644	36.450	12.358
1a-TSC	-836.2370812	-836.0943861	154.252	166.270	126.056
1z-TSC	-452.8157097	-452.7346733	87.461	95.829	63.540
1a-C	-704.1871885	-704.0700959	136.644	145.826	111.671
1z-C	-320.7698395	-320.7137904	69.837	75.365	49.846
N_3 (Rad.)	-164.1310324	-164.1074740	5.147	7.362	-8.142
HN_3	-164.7781460	-164.7573818	13.448	16.049	-0.956
CH_3CN	-132.7340274	-132.7123082	28.352	31.209	13.289
CH_2CN (Rad.)	-132.0759754	-132.0518895	19.450	22.314	4.649

Energy-optimized cartesian coordinates (B3LYP-D3/def2-TZVP) of all intermediates and transition structures discussed in this work in Å.

N3 radical

```
3
./N3-Rad/c1/b3lyp-d3.def2-TZVP
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N         0.00000        0.00000        0.00020
N         1.17320        0.00000       -0.00020
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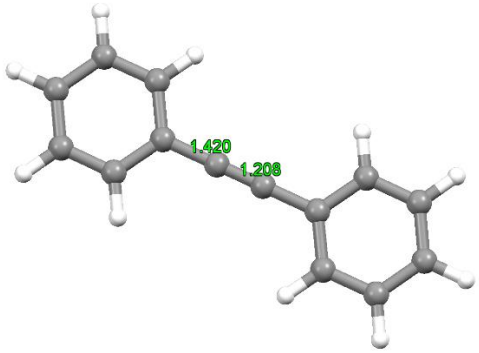
1a

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24

C        -0.00110       -0.00010        0.60410
C        -0.00090       -0.00010       -0.60400
C        -0.00080       -0.00010        2.02390
C         0.01460       -1.20780        2.73790
C        -0.01550        1.20780        2.73790
C        -0.01480        1.20320        4.12410
C         0.01540       -1.20320        4.12410
C         0.00070        0.00000        4.82260
H        -0.02740        2.14150        2.19160
H         0.02610       -2.14160        2.19180
H        -0.02650        2.14240        4.66250
H         0.02740       -2.14230        4.66270
H         0.00150        0.00010        5.90500
C        -0.00050       -0.00000       -2.02390
C         0.01480        1.20780       -2.73790
C        -0.01530       -1.20780       -2.73790
C        -0.01480       -1.20320       -4.12410
C         0.01540        1.20320       -4.12410
C         0.00060        0.00000       -4.82260
H        -0.02730       -2.14150       -2.19180
H         0.02640        2.14150       -2.19160
H        -0.02630       -2.14230       -4.66270
H         0.02760        2.14240       -4.66260
H         0.00090        0.00010       -5.90500
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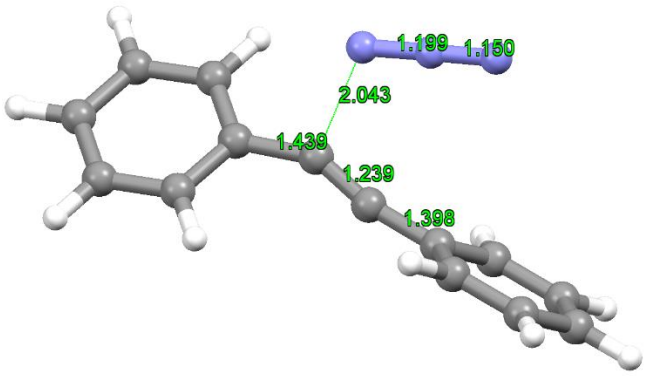
1a-TSA



27

N	0.43820	1.21040	3.25950
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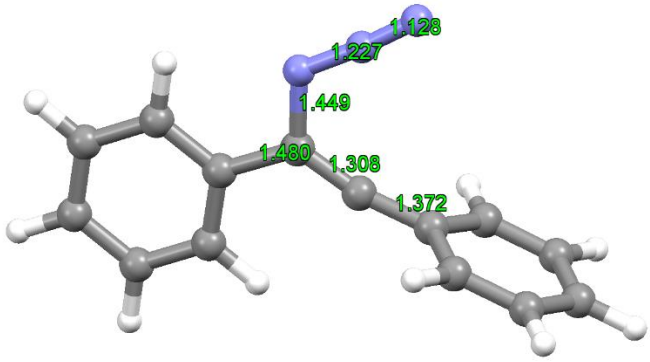
C	0.12710	0.50110	-0.00290
C	-0.16790	-0.67020	0.27120
C	0.46580	1.85660	-0.03350
C	-0.52510	2.84660	0.14640
C	1.80160	2.25950	-0.24930
C	2.12780	3.60170	-0.27170
C	-0.18320	4.18490	0.12270
C	1.14040	4.56810	-0.08570
H	2.56160	1.50210	-0.38480
H	-1.54750	2.53790	0.31510
H	3.15560	3.90210	-0.42910
H	-0.94710	4.93670	0.27200
H	1.40290	5.61790	-0.10050
C	-0.51210	-1.99840	-0.16340
C	-1.41960	-2.79780	0.53670
C	0.05900	-2.48380	-1.34720
C	-0.28220	-3.74020	-1.82360
C	-1.75760	-4.05230	0.05170
C	-1.19250	-4.52760	-1.12680
H	0.76760	-1.86640	-1.88290
H	-1.84110	-2.42920	1.45970
H	0.16610	-4.10660	-2.73830
H	-2.46300	-4.66410	0.59930
H	-1.45640	-5.50950	-1.49830

1a-A



27

N	3.54140	1.68510	0.07130
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C	0.27080	1.15750	0.01020
C	1.21390	-1.33670	0.00690
C	1.54380	-1.99930	-1.21270
C	1.50780	-2.01140	1.22900
C	2.10020	-3.25580	1.21880
C	2.13570	-3.24380	-1.19740
C	2.41940	-3.88300	0.01200
H	1.25950	-1.52420	2.16230
H	1.32300	-1.50280	-2.14790
H	2.32060	-3.74960	2.15690
H	2.38380	-3.72830	-2.13340
H	2.88440	-4.85990	0.01400
C	-1.11840	1.66640	-0.00730
C	-1.38930	3.03520	0.01870
C	-2.18850	0.76670	-0.04960
C	-3.49500	1.22490	-0.06490
C	-2.70230	3.49190	0.00310
C	-3.75880	2.59240	-0.03850
H	-1.98440	-0.29660	-0.07090
H	-0.57000	3.73870	0.05120
H	-4.31190	0.51510	-0.09800
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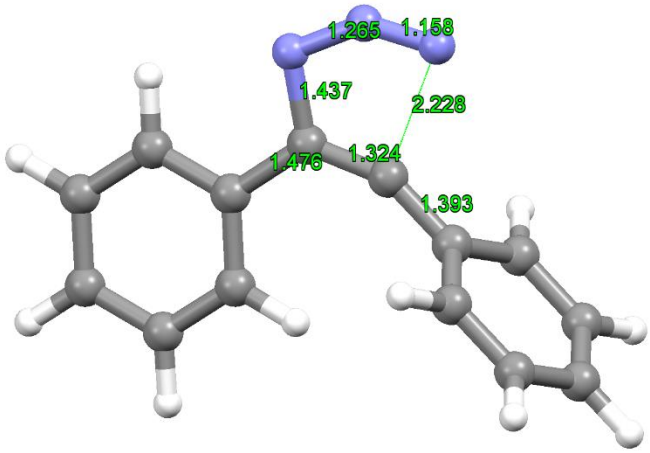
1a-TSB



27

N	0.19100	1.19240	3.36190
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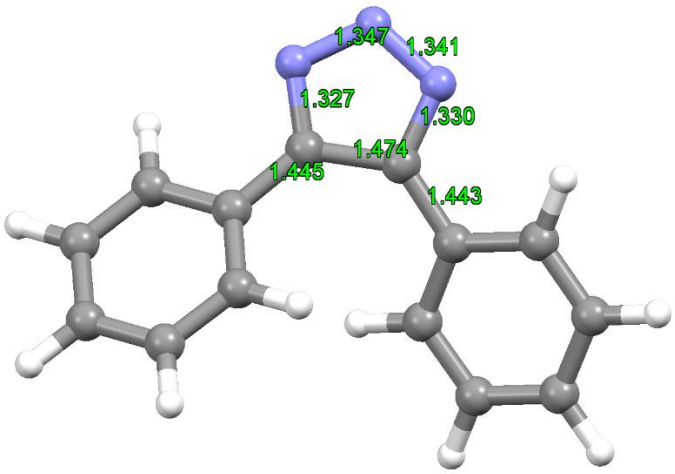
C	0.07600	-0.66920	1.52000
C	0.02230	1.71680	0.36010
C	1.22280	2.13710	-0.26540
C	-1.16280	2.44880	0.10380
C	-1.14510	3.53340	-0.75030
C	1.22510	3.22250	-1.11870
C	0.04480	3.92460	-1.36500
H	-2.07700	2.13930	0.59140
H	2.13220	1.58770	-0.06290
H	-2.05770	4.08310	-0.94170
H	2.14670	3.53110	-1.59510
H	0.05310	4.77720	-2.03180
C	-0.00910	-1.78410	0.55650
C	-0.11490	-3.09910	1.01780
C	0.01510	-1.55090	-0.82260
C	-0.06650	-2.60670	-1.71690
C	-0.19410	-4.15340	0.11740
C	-0.17110	-3.91360	-1.25090
H	0.09820	-0.53910	-1.19540
H	-0.12980	-3.28220	2.08210
H	-0.04590	-2.40920	-2.78120
H	-0.27410	-5.16710	0.48920
H	-0.23290	-4.73760	-1.95030

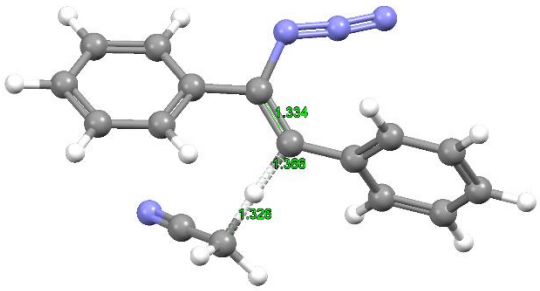
1a-B



27

N	-1.06250	2.94980	-0.07740
N	0.05300	3.68610	0.03080
N	1.15160	2.91270	0.12480
C	0.76070	1.64640	0.06360
C	-0.70930	1.66840	-0.03850
C	-1.68990	0.60980	-0.01940
C	-2.94840	0.83030	-0.60980
C	-1.44990	-0.61570	0.62630
C	-2.42920	-1.59410	0.65980
C	-3.91530	-0.15700	-0.58400
C	-3.65920	-1.37340	0.04770
H	-0.50730	-0.78190	1.12680
H	-3.13500	1.78220	-1.08660
H	-2.23720	-2.52820	1.17170
H	-4.87470	0.01740	-1.05360
H	-4.42050	-2.14270	0.06990
C	1.70890	0.55680	0.02840
C	2.96440	0.72010	0.64150
C	1.43920	-0.64090	-0.65540
C	2.38770	-1.64880	-0.70510
C	3.90050	-0.29630	0.59920
C	3.61550	-1.48500	-0.07120
H	0.49830	-0.76270	-1.17190
H	3.17420	1.65120	1.14870
H	2.17330	-2.56130	-1.24620
H	4.85810	-0.16600	1.08640
H	4.35270	-2.27700	-0.10650

1a-TSC

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33
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C     0.4107489   -0.3064659    0.0906415
C     0.1462560    0.9170072    0.5519260
C     1.5246885   -1.2082574    0.2027882
C     2.1331574   -1.7571893   -0.9386868
C     2.0028094   -1.5938428    1.4679656
C     3.0686486   -2.4718298    1.5815206
C     3.1931409   -2.6398040   -0.8177923
C     3.6665333   -2.9996092    0.4414788
H     1.5282636   -1.1908094    2.3535262
H     1.7784121   -1.4644119   -1.9186191
H     3.4328850   -2.7493670    2.5625101
H     3.6585124   -3.0453502   -1.7070873
H     4.4966905   -3.6878978    0.5328057
C    -1.1868362    1.5442740    0.4897388
C    -1.3250063    2.8915196    0.1496689
C    -2.3323610    0.7891995    0.7483859
C    -3.5925402    1.3584248    0.6326955
C    -2.5847729    3.4585258    0.0330851
C    -3.7219174    2.6928340    0.2672479
H    -2.2257403   -0.2408044    1.0617686
H    -0.4402511    3.4836867   -0.0399887
H    -4.4732864    0.7630552    0.8372028
H    -2.6808672    4.4988258   -0.2498465
H    -4.7043227    3.1371842    0.1724779
H    -0.5482245   -0.7706493   -0.7644604
C    -1.3902644   -1.2317933   -1.6784942
H    -0.8117069   -2.0121040   -2.1658988
H    -2.2276901   -1.6194446   -1.1067035
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N    -1.9548859    0.7763275   -3.1922446
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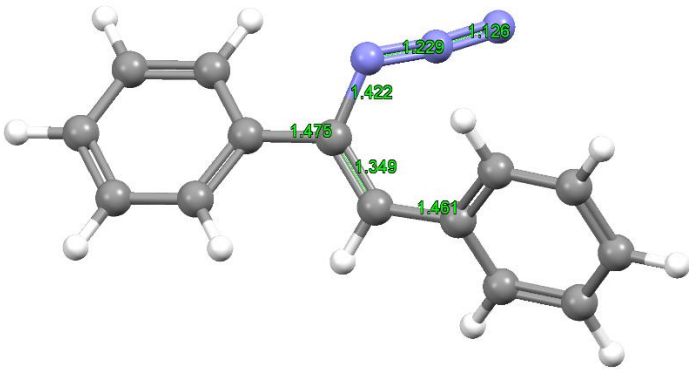
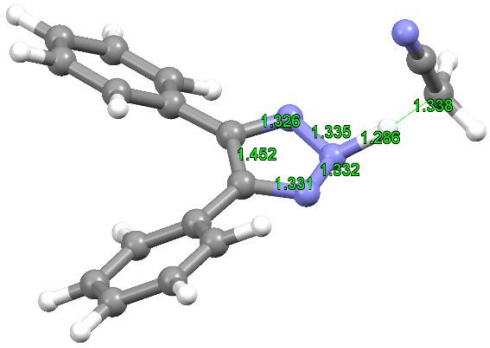
1a-C



28

N	3.0439849	1.5369072	0.4130454
N	1.9368854	1.4555268	0.6039605
N	0.7518372	1.4713580	0.9309030
C	0.0736086	-0.5220998	-0.3335826
C	-0.1875997	0.6868428	0.2060682
C	1.2463643	-1.3796109	-0.1789410
C	1.6100477	-2.2276028	-1.2350717
C	1.9890407	-1.4519187	1.0080394
C	3.0654587	-2.3189883	1.1211287
C	2.6911651	-3.0876386	-1.1238261
C	3.4275317	-3.1347293	0.0553465
H	1.7017054	-0.8459531	1.8570688
H	1.0359617	-2.1990743	-2.1535384
H	3.6215271	-2.3611658	2.0491110
H	2.9587474	-3.7255528	-1.9568052
H	4.2706858	-3.8073824	0.1456328
C	-1.5042693	1.3433187	0.0980482
C	-1.6087945	2.7377162	0.1292059
C	-2.6763766	0.5903248	-0.0397345
C	-3.9075389	1.2135140	-0.1756833
C	-2.8422981	3.3598089	-0.0021238
C	-3.9962844	2.6016520	-0.1605990
H	-2.6249500	-0.4898199	-0.0122430
H	-0.7136724	3.3308843	0.2534126
H	-4.8030194	0.6134475	-0.2766914
H	-2.9017358	4.4406747	0.0187201
H	-4.9587571	3.0870782	-0.2595856
H	-0.6992552	-0.9175174	-0.9812655

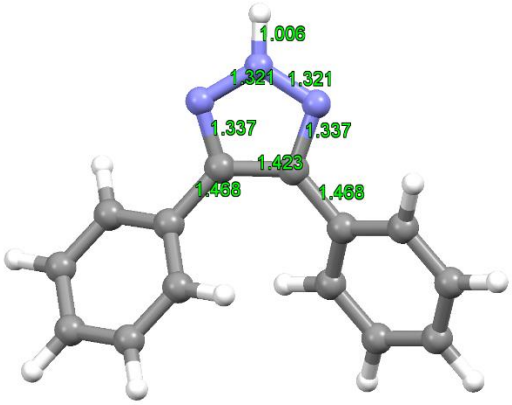
1a-TSHAT



33

N	-1.26580	1.76730	-0.59580
N	-0.22670	2.43380	-1.10420
N	0.92770	1.77310	-1.02700
C	0.60710	0.54810	-0.61770
C	-0.81510	0.55000	-0.32610
H	-0.16930	3.67250	-0.76530
C	-0.10060	4.89010	-0.21460
H	0.50770	5.42230	-0.94300
H	-1.14560	5.19150	-0.20830
C	0.48640	4.79060	1.07330
N	0.96830	4.66830	2.11750
C	-1.70700	-0.48150	0.20310
C	-3.06270	-0.47220	-0.15470
C	-1.25570	-1.44950	1.11050
C	-2.13580	-2.38290	1.63920
C	-3.93560	-1.41310	0.36930
C	-3.47590	-2.37270	1.26690
H	-0.22070	-1.45400	1.42350
H	-3.41570	0.27840	-0.84880
H	-1.77470	-3.11580	2.34980
H	-4.97840	-1.39860	0.07740
H	-4.15940	-3.10560	1.67710
C	1.60850	-0.51280	-0.58700
C	2.93830	-0.19670	-0.26710
C	1.28920	-1.83720	-0.91870
C	2.26930	-2.81880	-0.91600
C	3.91130	-1.18260	-0.25760
C	3.58070	-2.49680	-0.58070
H	0.27540	-2.09220	-1.19620
H	3.18940	0.82660	-0.02270
H	2.01050	-3.83590	-1.18230
H	4.93130	-0.92810	0.00190
H	4.34360	-3.26530	-0.57560

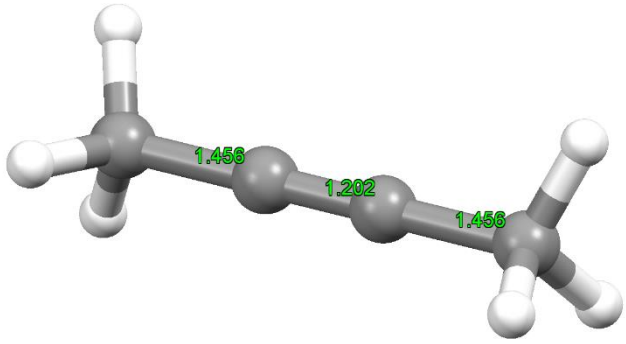
2a



28

N	-1.07520	3.01090	0.01840
N	0.05820	3.68930	0.03700
N	1.17000	2.97560	0.04000
C	0.73880	1.71030	0.01800
C	-0.68380	1.73260	0.01230
C	-1.66450	0.64100	0.03480
C	-2.86350	0.76120	-0.67270
C	-1.43220	-0.51880	0.77860
C	-2.37210	-1.53930	0.80300
C	-3.80290	-0.26020	-0.64510
C	-3.55920	-1.41540	0.08950
H	-0.51490	-0.61810	1.34260
H	-3.04880	1.66120	-1.24340
H	-2.17910	-2.43080	1.38610
H	-4.72610	-0.15510	-1.20100
H	-4.29100	-2.21280	0.10850
C	1.68490	0.58920	-0.02520
C	2.88430	0.65610	0.68870
C	1.41910	-0.54620	-0.79500
C	2.32670	-1.59500	-0.83880
C	3.79130	-0.39340	0.64160
C	3.51420	-1.52400	-0.11900
H	0.50130	-0.60420	-1.36390
H	3.09540	1.53710	1.27980
H	2.10810	-2.46700	-1.44210
H	4.71510	-0.32970	1.20260
H	4.22070	-2.34350	-0.15310
H	0.07390	4.69550	0.04850

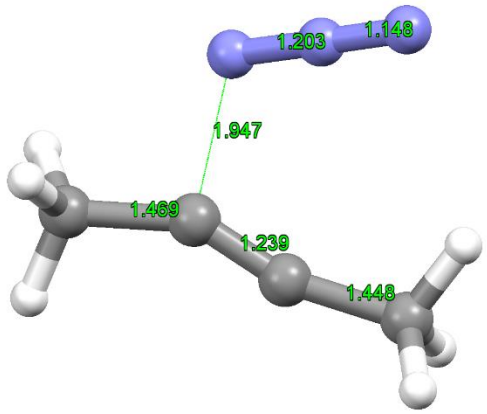
1z



10

C	0.00000	0.00000	0.60080
C	0.00000	-0.00000	-0.60080
C	-0.00000	0.00000	2.05710
H	-0.64100	0.79240	2.45120
H	1.00670	0.15890	2.45120
H	-0.36570	-0.95130	2.45120
C	-0.00000	-0.00000	-2.05710
H	-0.64100	-0.79240	-2.45120
H	1.00670	-0.15890	-2.45120
H	-0.36570	0.95130	-2.45120

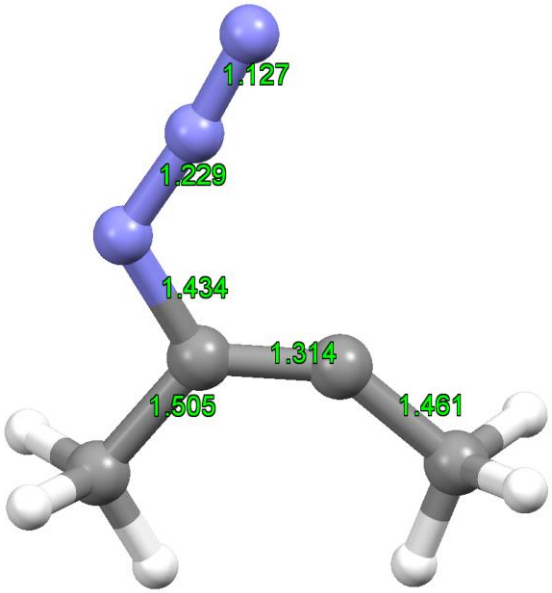
1z-TSA



13

N	1.61400	0.58030	2.46410
N	0.86370	-0.16560	2.01730
N	0.07530	-0.94920	1.55810
C	-0.13610	0.61850	-0.56590
C	-0.29290	-0.58590	-0.31900
C	0.14580	2.03540	-0.46610
H	-0.76240	2.63160	-0.57860
H	0.86540	2.35220	-1.22500
H	0.58010	2.26360	0.51520
C	-0.66850	-1.93340	-0.76640
H	0.17710	-2.61620	-0.67420
H	-0.99390	-1.90310	-1.80650
H	-1.47790	-2.32190	-0.14720

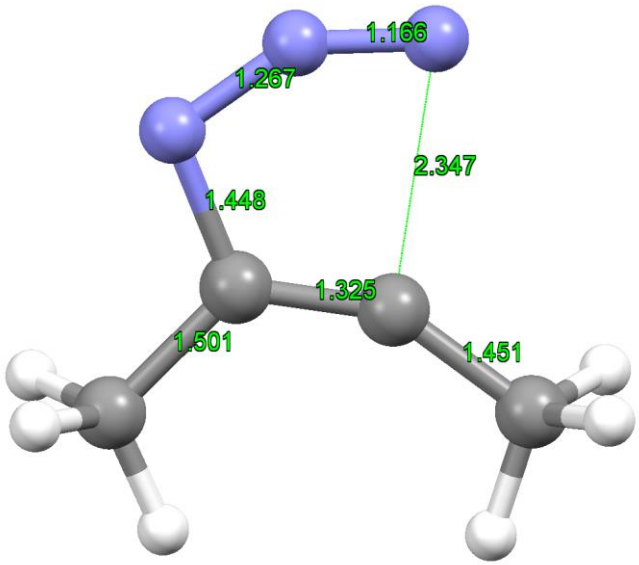
1z-A



13

N	-4.24600	-0.24990	-0.07770
N	-3.23600	0.24840	-0.02920
N	-2.19420	0.89860	0.02790
C	-0.88330	-1.14090	-0.04680
C	-0.95980	0.16910	0.01800
C	0.07940	-2.23910	-0.08210
H	-0.05720	-2.92200	0.76110
H	1.11020	-1.85980	-0.03470
H	-0.01170	-2.82590	-1.00040
C	0.21840	1.10210	0.09190
H	1.15610	0.54960	0.08870
H	0.16590	1.70260	1.00290
H	0.20970	1.78710	-0.75890

1z-TSB



13

N	2.67427	-0.20464	0.00000
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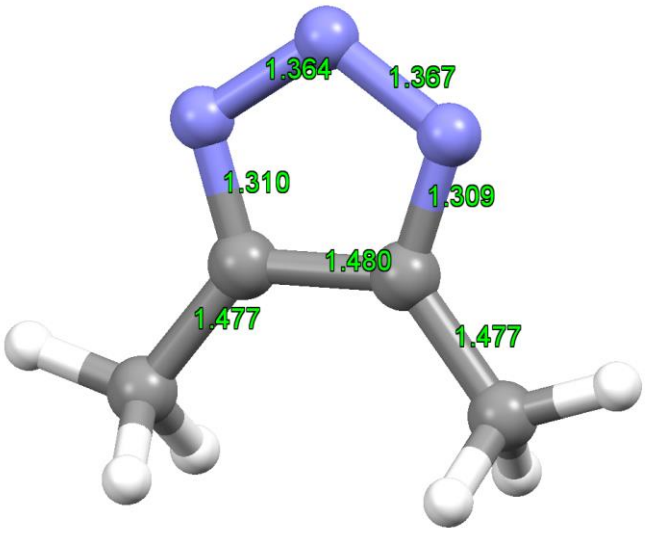
N	1.27949	1.65627	0.00000
C	0.35482	-0.56205	0.00000
C	0.15289	0.74721	0.00000
C	-0.13795	-1.92673	0.00000
H	0.18270	-2.48497	-0.89425
H	-1.24617	-1.91889	0.00000
H	0.18270	-2.48497	0.89425
C	-1.18301	1.43140	0.00000
H	-1.27332	2.06942	0.89494
H	-2.00521	0.70591	0.00000
H	-1.27332	2.06942	-0.89494

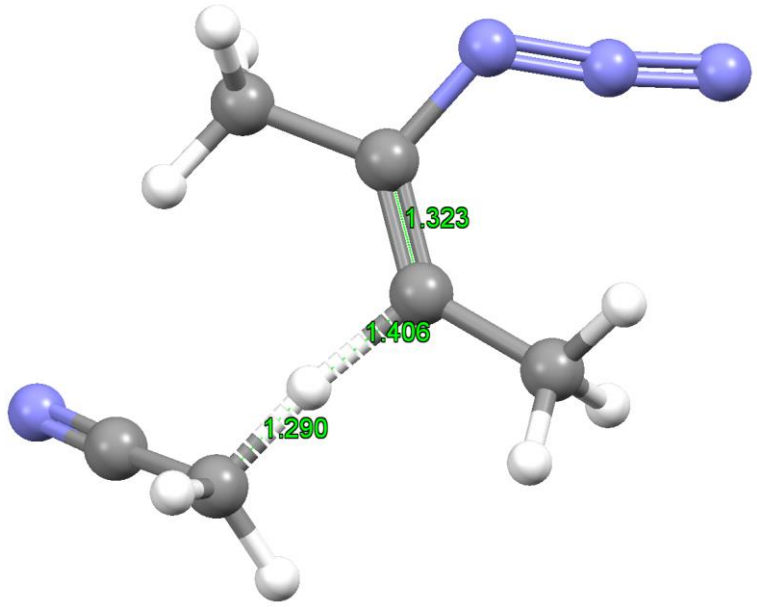
1z-B



13

N	-1.07990	1.78340	-0.17040
N	0.06790	2.51730	-0.27780
N	1.17250	1.71910	-0.21840
C	0.75260	0.48710	-0.07200
C	-0.72610	0.53000	-0.04060
C	-1.66490	-0.60080	0.10690
H	-1.52300	-1.32800	-0.69860
H	-2.69310	-0.24600	0.09150
H	-1.48240	-1.13430	1.04500
C	1.63040	-0.69560	0.03670
H	2.67570	-0.40010	-0.02080
H	1.41430	-1.41140	-0.76270
H	1.45590	-1.22070	0.98110

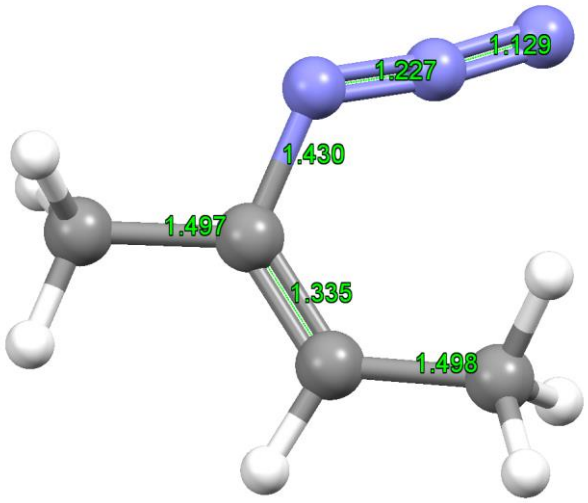
1z-TSC



19

N	3.4291545	1.7897919	0.9596837
N	2.3075928	1.7669365	1.0862359
N	1.1030684	1.8702658	1.2979087
C	0.4860256	-0.2445631	0.2695039
C	0.1829367	0.9964925	0.6140747
H	-0.5346270	-0.9214776	-0.4221133
C	-1.3806259	-1.6805372	-1.0318632
H	-0.7552378	-2.4116339	-1.5390892
H	-1.9716172	-2.1253290	-0.2346336
C	-2.1483132	-0.8746757	-1.9251873
N	-2.7452769	-0.1749791	-2.6226363
C	1.6611744	-1.1250328	0.4607374
H	2.3458916	-1.0943475	-0.3919501
H	1.3472393	-2.1643366	0.5873506
H	2.2246332	-0.8515455	1.3569942
C	-1.1379996	1.6718752	0.4162898
H	-1.8705005	1.0027514	-0.0259581
H	-1.0282667	2.5428333	-0.2332624
H	-1.5152517	2.0275113	1.3779146

1z-C



14

N	2.7625475	1.2727332	0.3430937
N	1.6499844	1.2027469	0.5205083
N	0.4558397	1.2543397	0.7987677
C	-0.2301922	-0.8156712	-0.3125359
C	-0.4724654	0.4375012	0.0799014
H	-1.0292962	-1.3038546	-0.8586722
C	1.0007792	-1.6280387	-0.0492249
H	1.7201683	-1.5728958	-0.8726674
H	0.7360210	-2.6797863	0.0715256
H	1.5160661	-1.3129196	0.8584243
C	-1.7774202	1.1449905	-0.1134374
H	-2.5051144	0.4902658	-0.5903337
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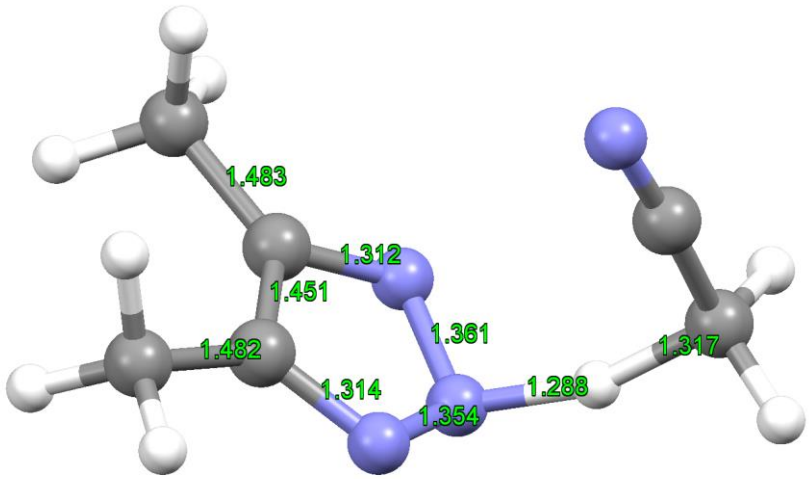
H	-2.1765570	1.4696632	0.8508683

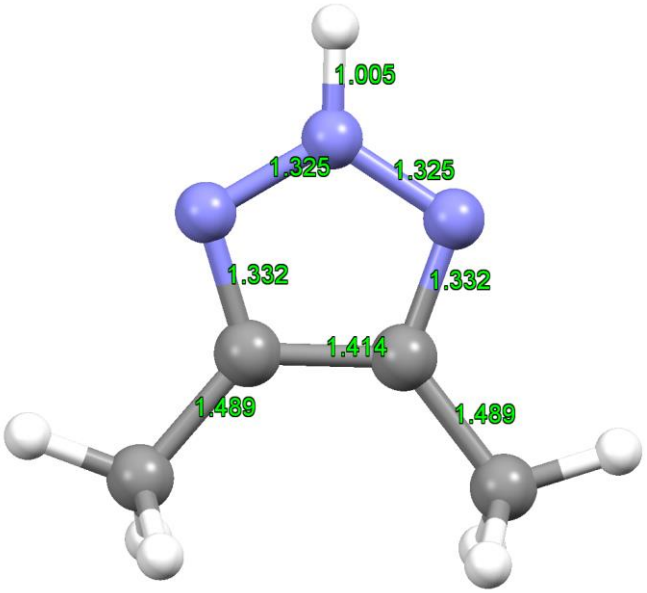
1z-TSHAT



19

N	-1.28876	0.37177	-0.59594
N	-0.25563	1.02885	-1.19015
N	0.91269	0.35060	-1.09722
C	0.60002	-0.82445	-0.59975
C	-0.81475	-0.80944	-0.27797
H	-0.12976	2.19128	-0.65105
C	0.01955	3.12513	0.26540
H	0.73760	3.80575	-0.18486
H	-0.98507	3.52973	0.35761
C	0.48213	2.44081	1.42098
N	0.84397	1.81343	2.32132
C	-1.62947	-1.89506	0.31976
H	-1.42996	-2.85382	-0.16331
H	-2.68970	-1.66452	0.23640
H	-1.38408	-2.00950	1.38028
C	1.56825	-1.93210	-0.42373
H	2.56725	-1.60967	-0.70964
H	1.28946	-2.80006	-1.02779
H	1.58626	-2.25874	0.61967

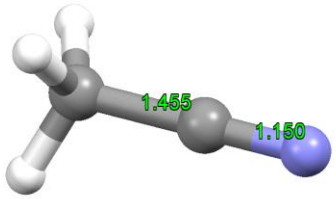
2z



14

N	-1.11530	0.89540	-0.13120
N	0.01820	1.57640	-0.21710
N	1.13310	0.86130	-0.17670
C	0.69890	-0.39180	-0.05330
C	-0.71460	-0.37040	-0.02470
C	-1.66950	-1.50630	0.10010
H	-1.53700	-2.22590	-0.71170
H	-2.69420	-1.13910	0.07110
H	-1.52260	-2.04600	1.03910
C	1.62330	-1.55610	0.03360
H	2.65650	-1.22070	-0.04110
H	1.43350	-2.27300	-0.76920
H	1.50110	-2.08920	0.97990
H	0.03150	2.57750	-0.31010

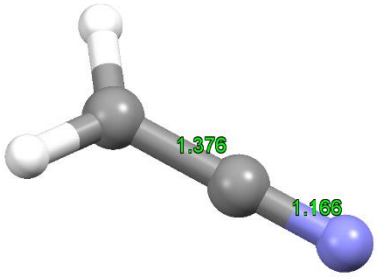
CH_3CN



6

C	-1.54100	0.44760	-0.00000
C	-0.09500	0.60750	-0.00000
N	1.04760	0.73380	0.00000
H	-1.80180	-0.61130	0.00000
H	-1.97070	0.91510	0.88660
H	-1.97070	0.91510	-0.88660

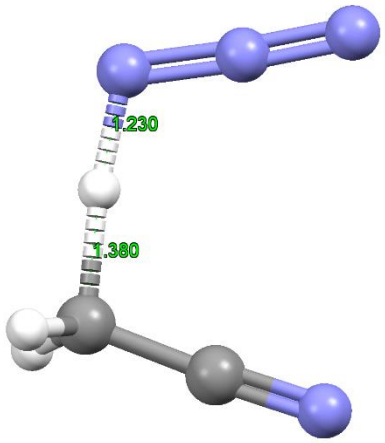
CH_2CN Radical



5

C	0.09210	0.01560	-0.29100
H	-0.42270	-0.92320	-0.43530
H	-0.45790	0.94340	-0.35350
C	1.44320	0.02920	-0.02820
N	2.58780	0.04020	0.19470

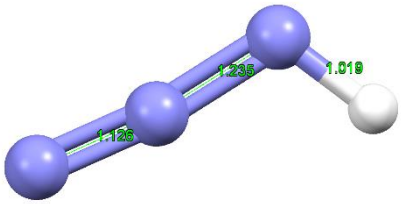
TSD



9

C	-0.0802115	-0.5339040	1.0771270
C	1.2300434	-0.0707925	0.8200246
N	2.2829334	0.3283062	0.5543120
N	-1.3539019	0.0718953	-1.1143191
N	-0.5643680	0.7174327	-1.7800915
N	0.1220739	1.3263325	-2.4529261
H	-0.8099100	-0.2473168	-0.0585284
H	-0.6324992	0.0211542	1.8298491
H	-0.1941602	-1.6131076	1.1245525

HN_3

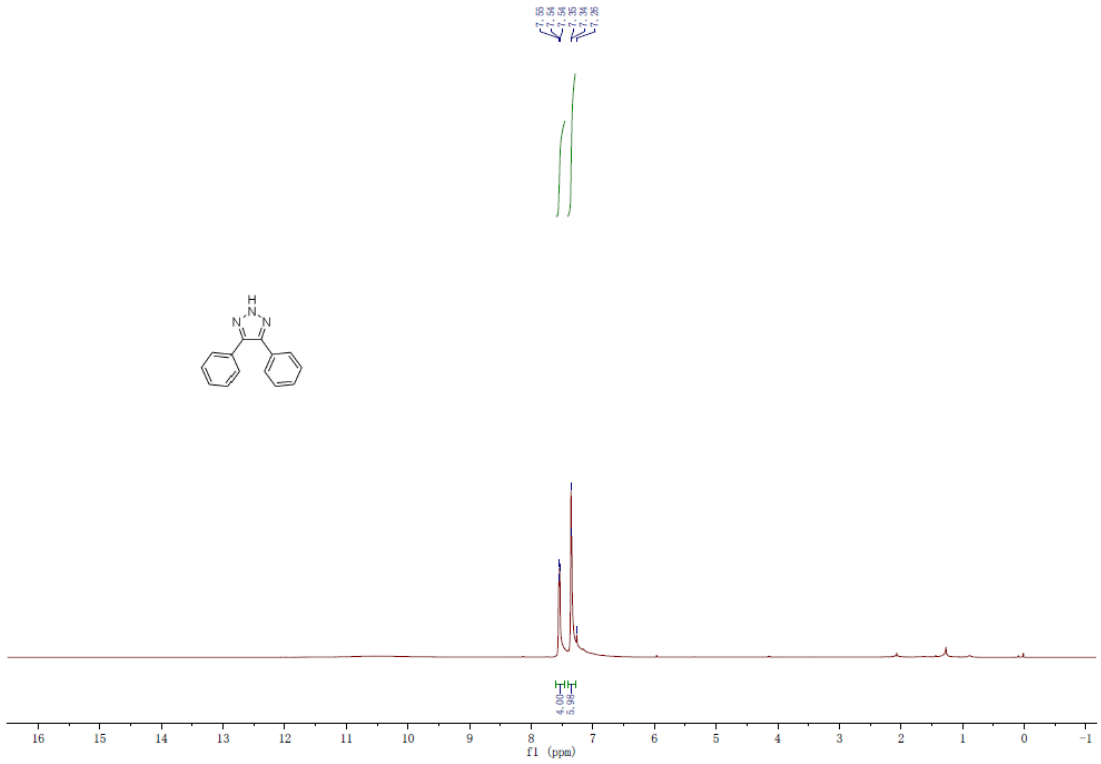


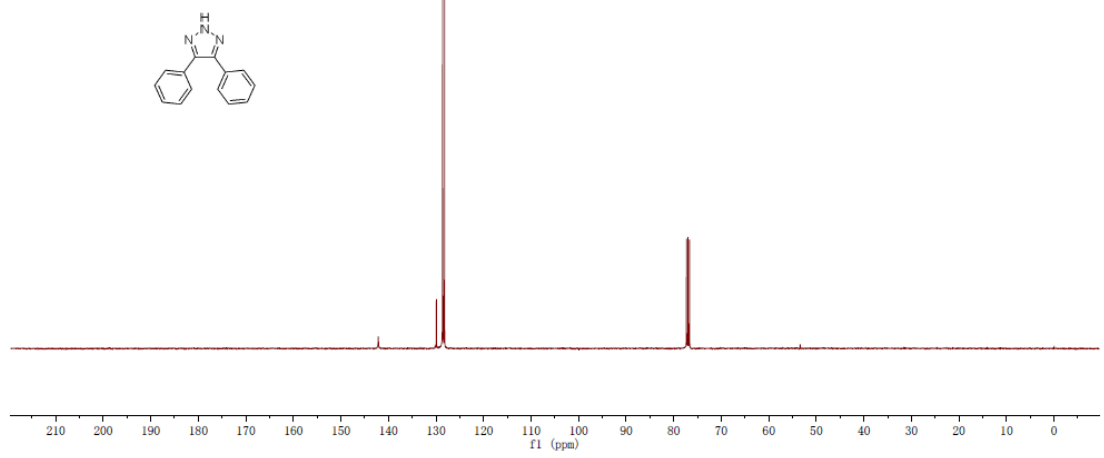
4

N	-0.7383958	-0.3802622	0.0000000
N	0.4626629	-0.0942257	0.0000000
N	1.5835083	0.0101334	0.0000000
H	-1.3077755	0.4643545	0.0000000

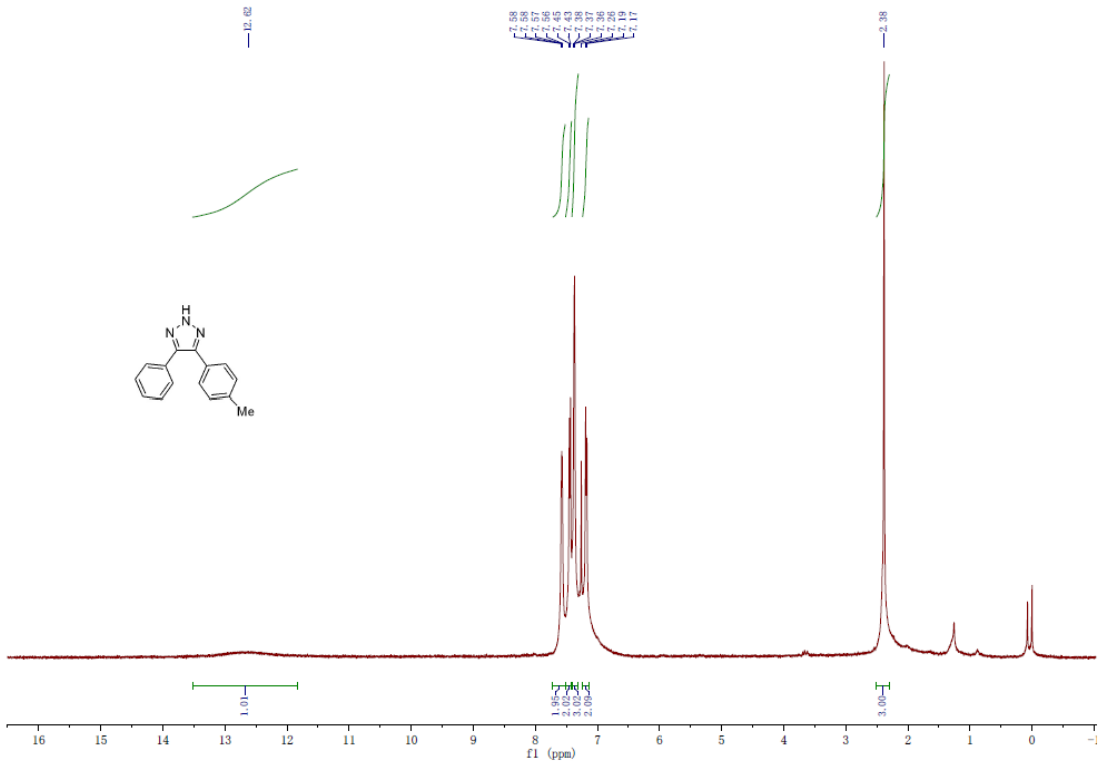
NMR spectra

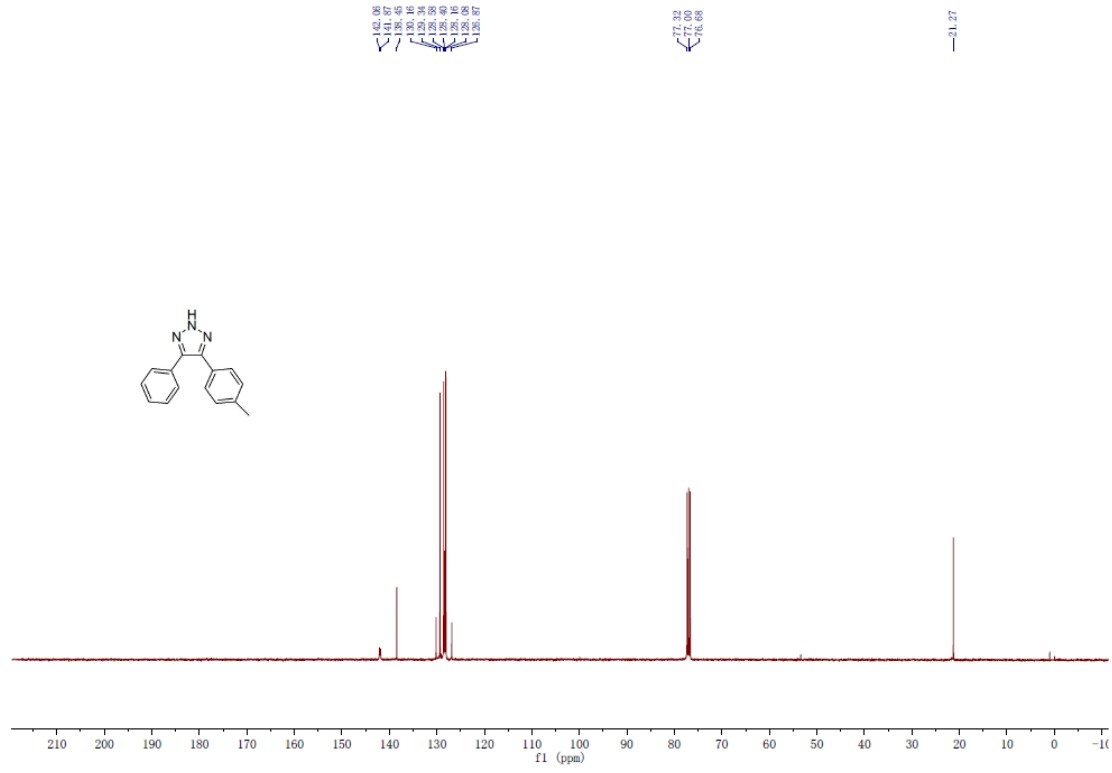
2a



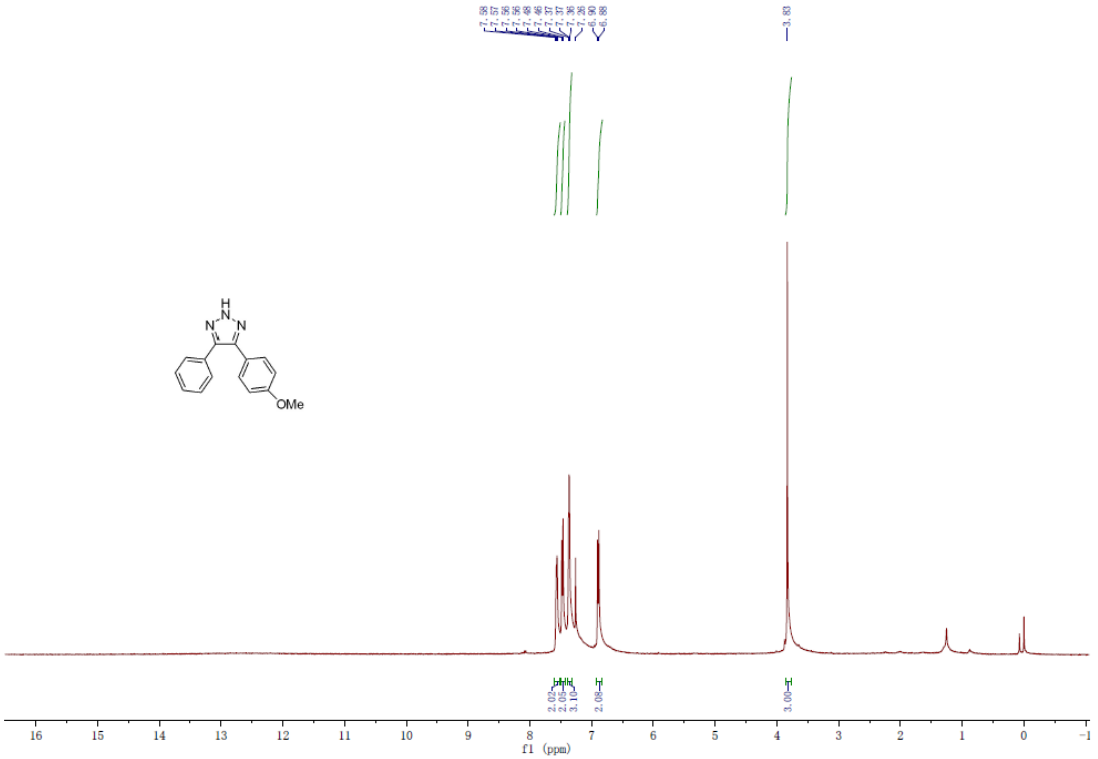


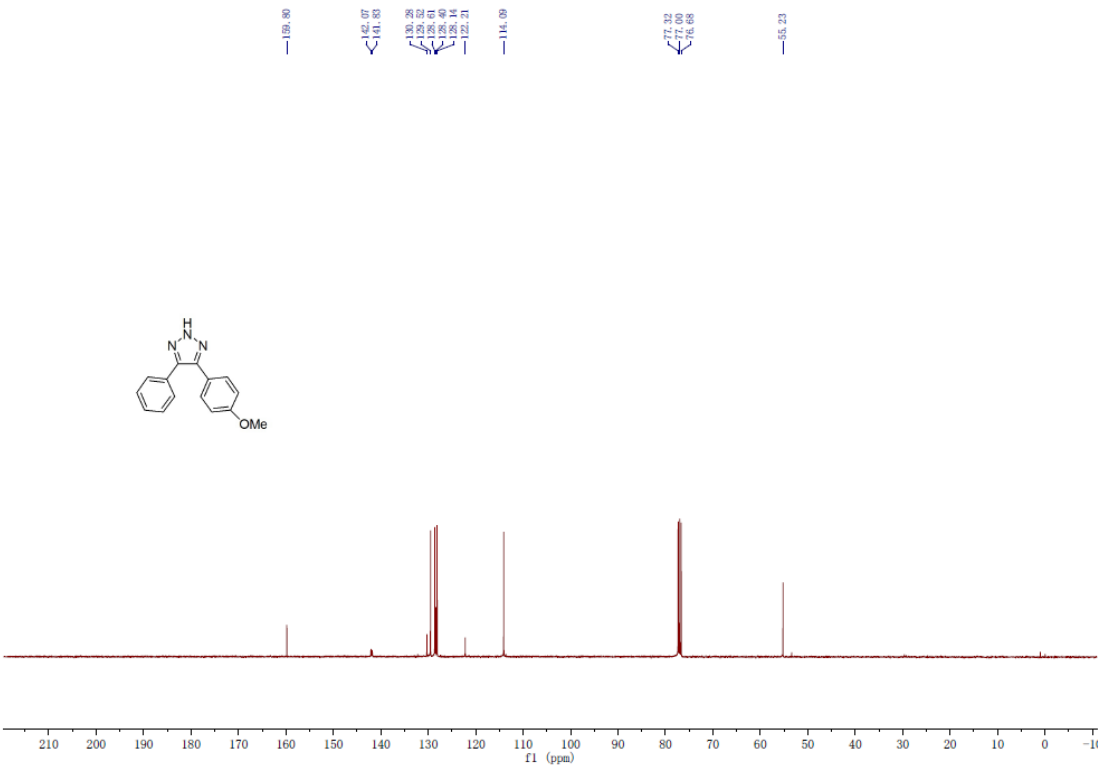
2b


12.62
7.58
7.58
7.57
7.57
7.56
7.45
7.43
7.39
7.37
7.36
7.26
7.19
7.17
2.38
Me
1.01
1.95
2.02
3.02
2.09
3.00
f1 (ppm)

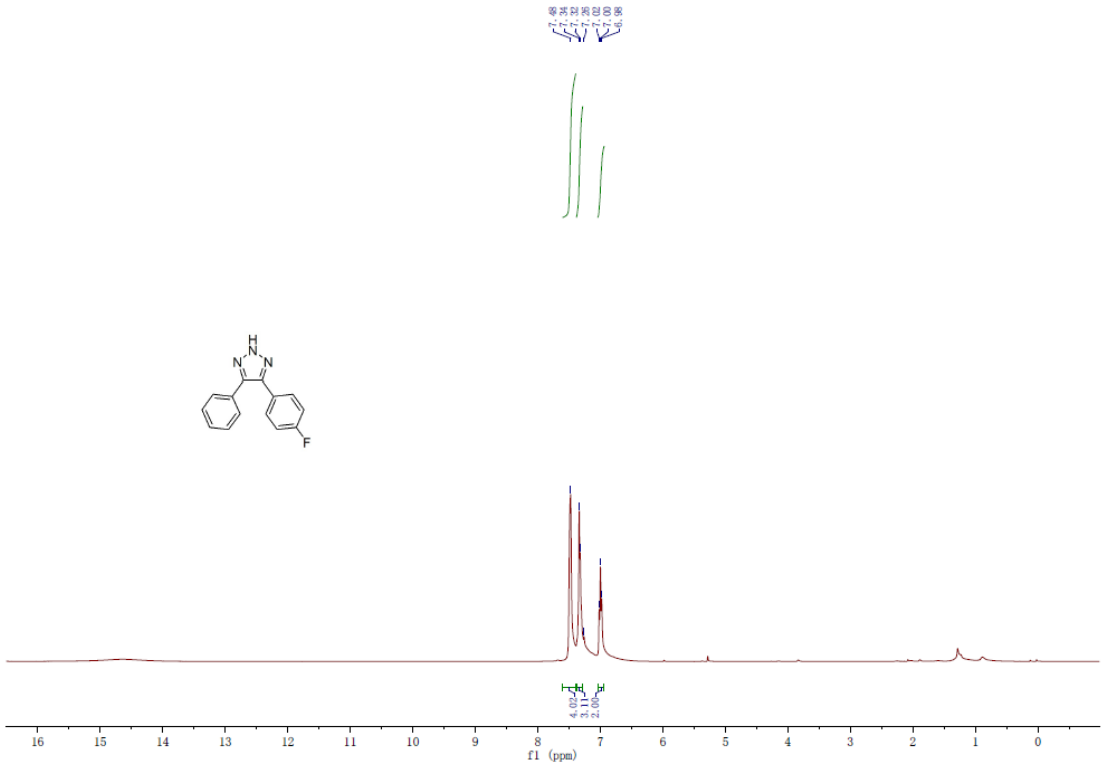

62.06
61.97
38.45
30.16
29.34
28.38
28.40
28.16
26.08
26.07
77.32
77.00
76.68
21.27
f1 (ppm)

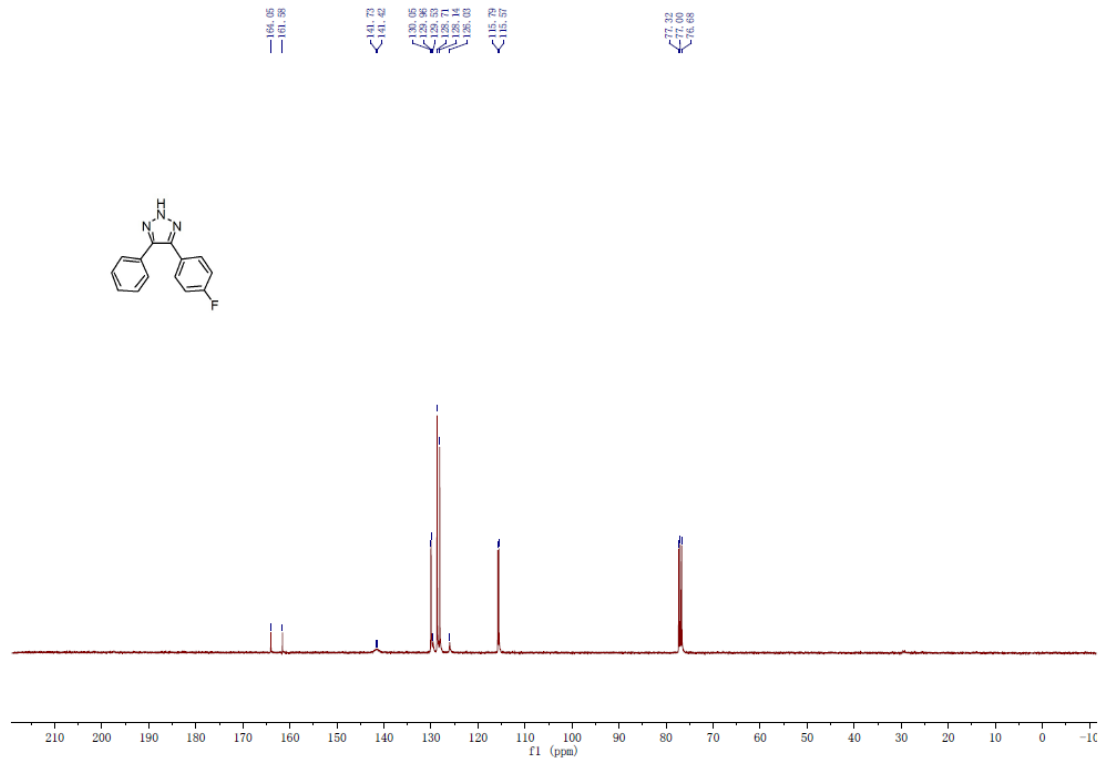
2c


7.58
7.57
7.56
7.56
7.48
7.46
7.37
7.36
7.35
6.89
6.88
3.83
OMe
2.07
2.03
3.10
2.08
3.00
16
15
14
13
12
11
10
9
8
7
6
5
4
3
2
1
0
f1 (ppm)

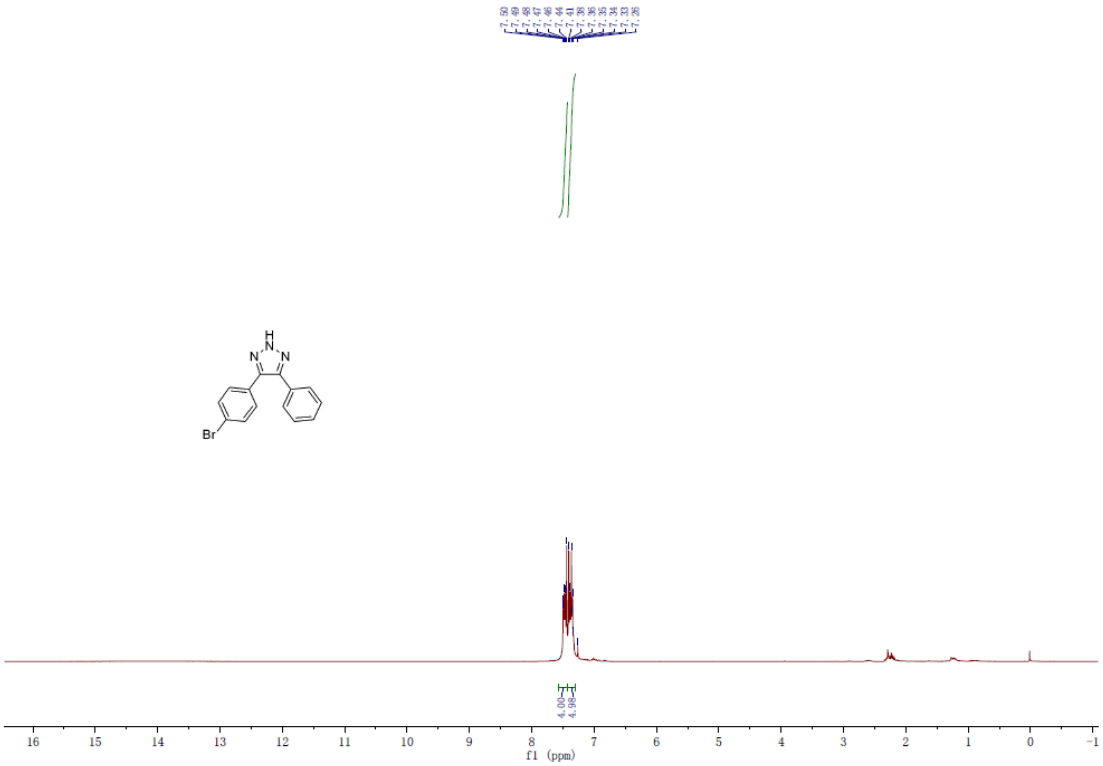

159.80
142.07
141.83
130.28
129.52
128.61
128.40
125.14
122.21
114.09
77.32
77.00
76.68
55.23
OMe
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

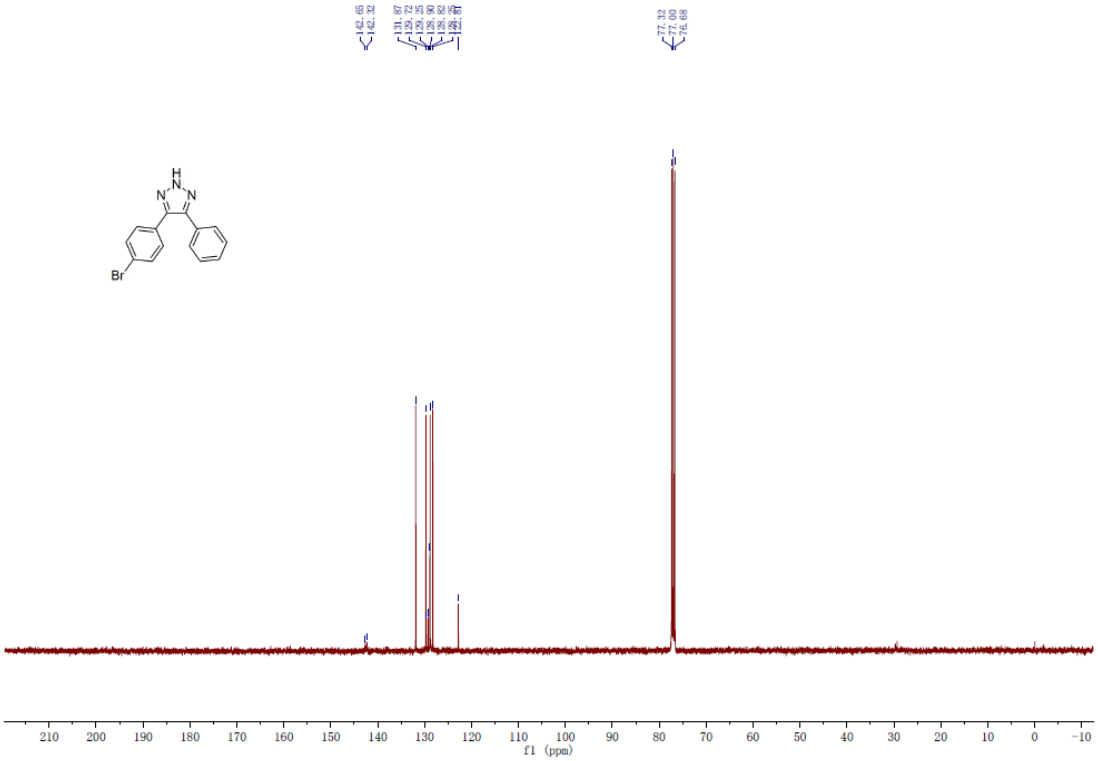
2d


7.49
7.34
7.32
7.35
7.02
7.00
6.98
4.07
3.11
2.00
f1 (ppm)

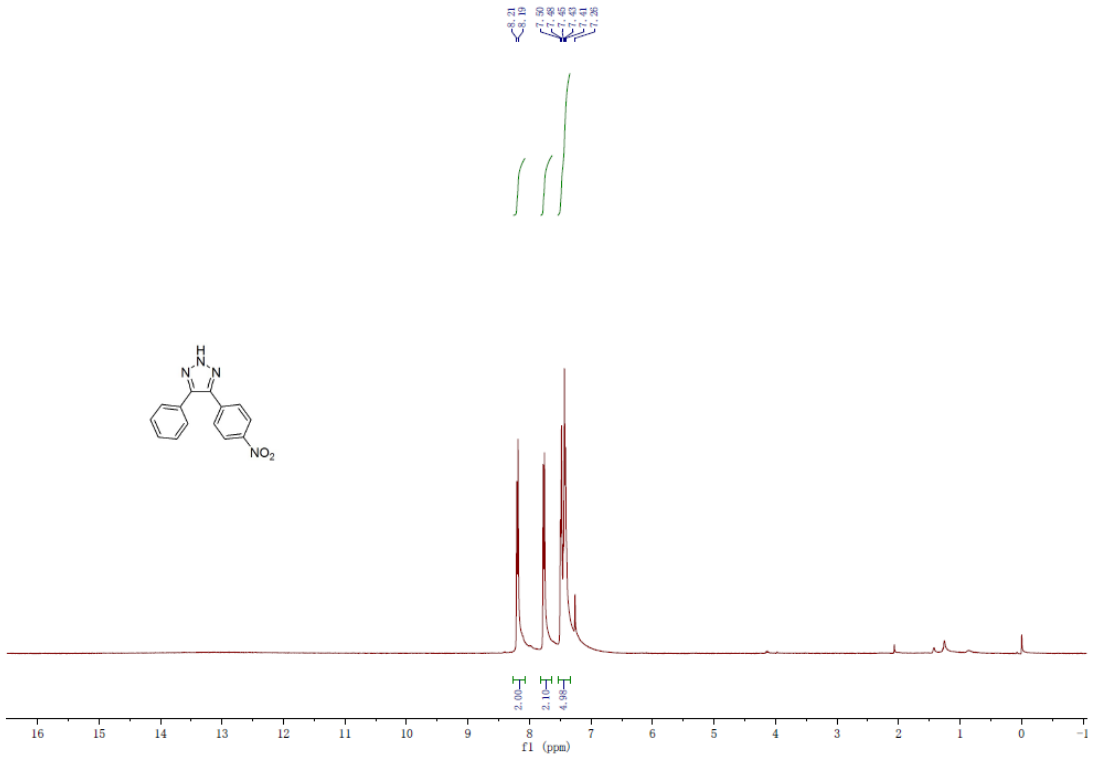

164.05
161.98
141.73
141.42
130.05
129.96
129.53
128.71
126.14
126.03
115.79
115.57
77.32
77.00
76.68
f1 (ppm)

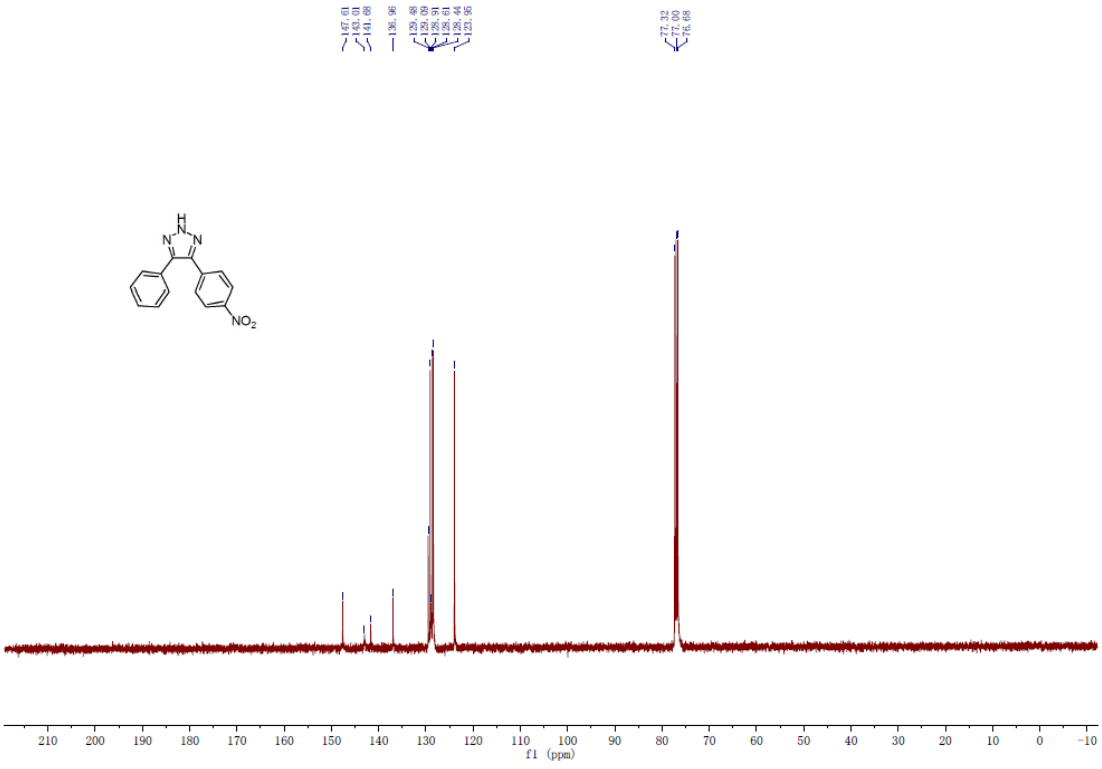
2e



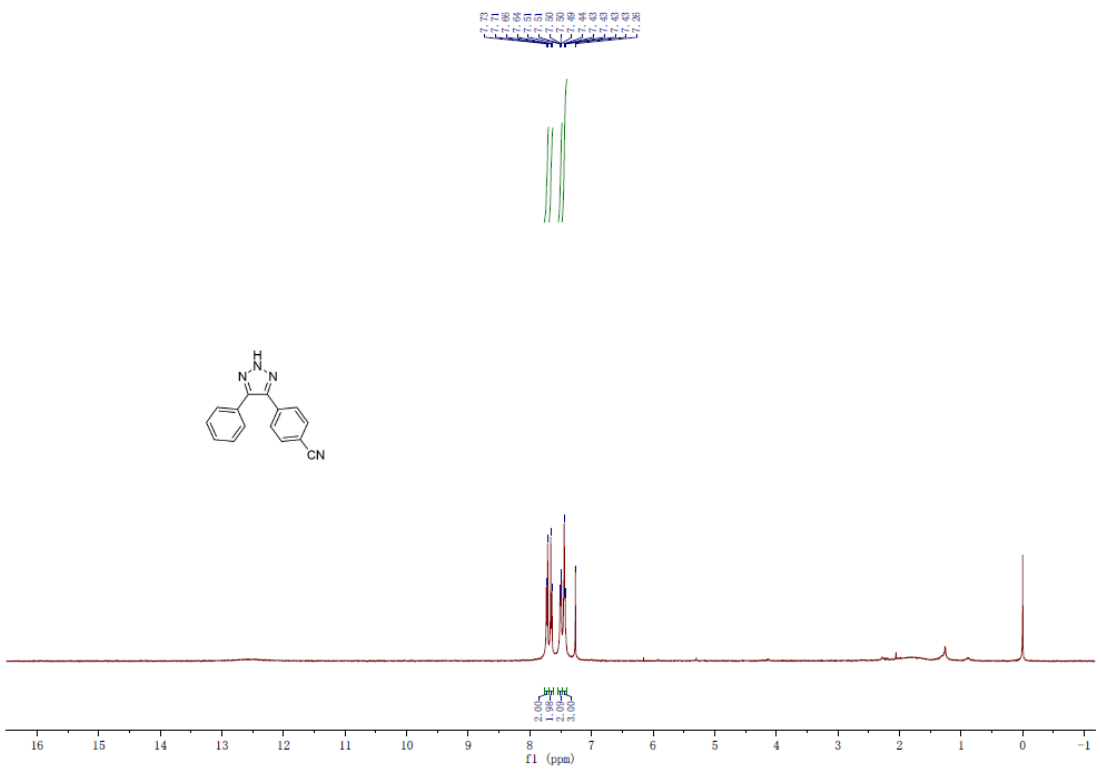


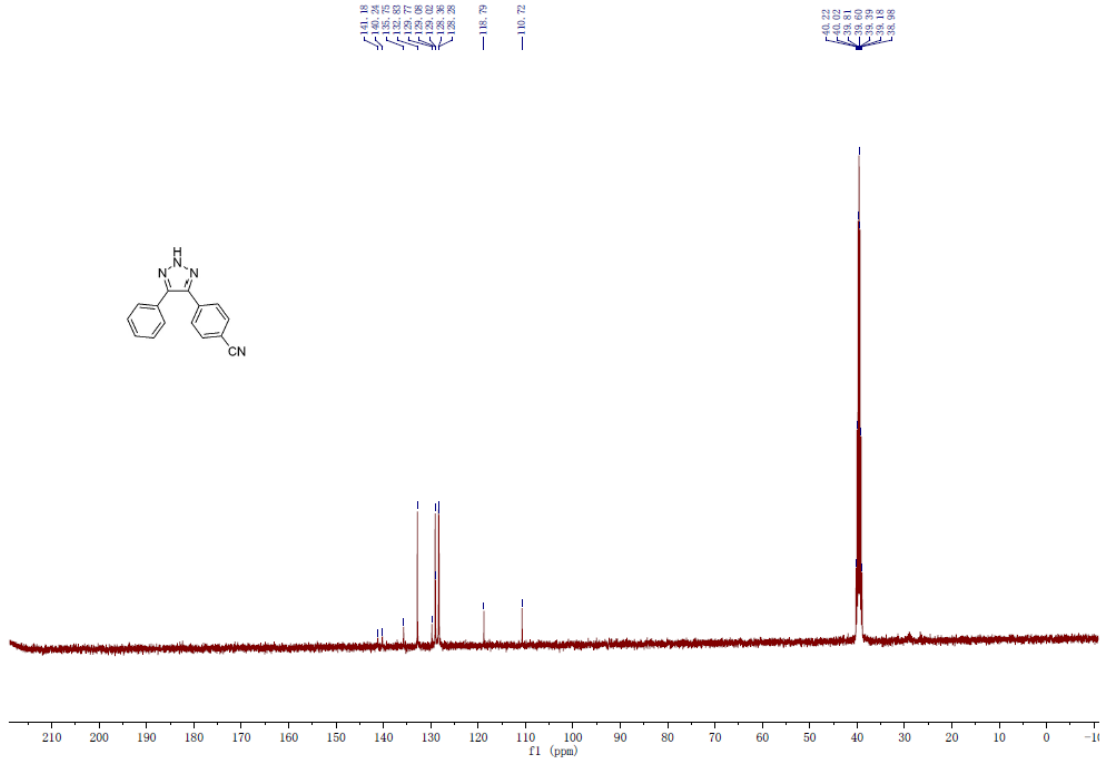
2f


8.21
8.19
7.50
7.48
7.45
7.43
7.41
7.26
2.00
2.10
4.08
f1 (ppm)

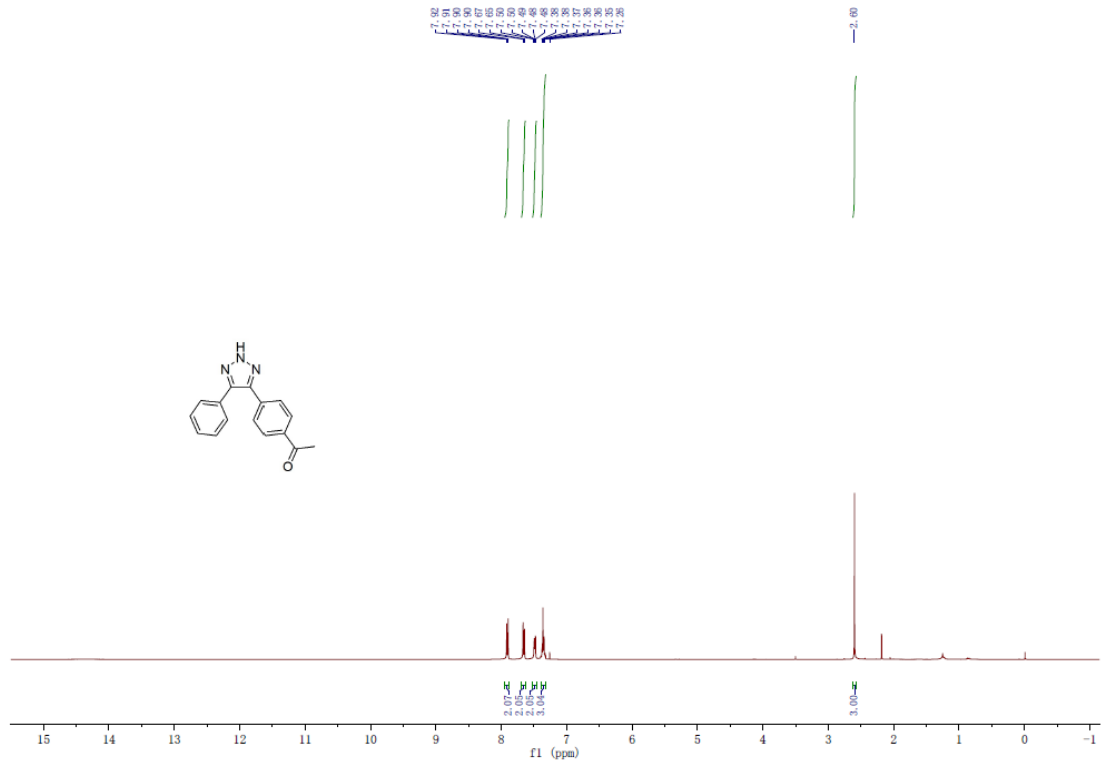

147.61
143.01
141.68
136.96
129.49
129.09
128.91
128.61
126.44
125.95
77.32
77.00
76.69
f1 (ppm)

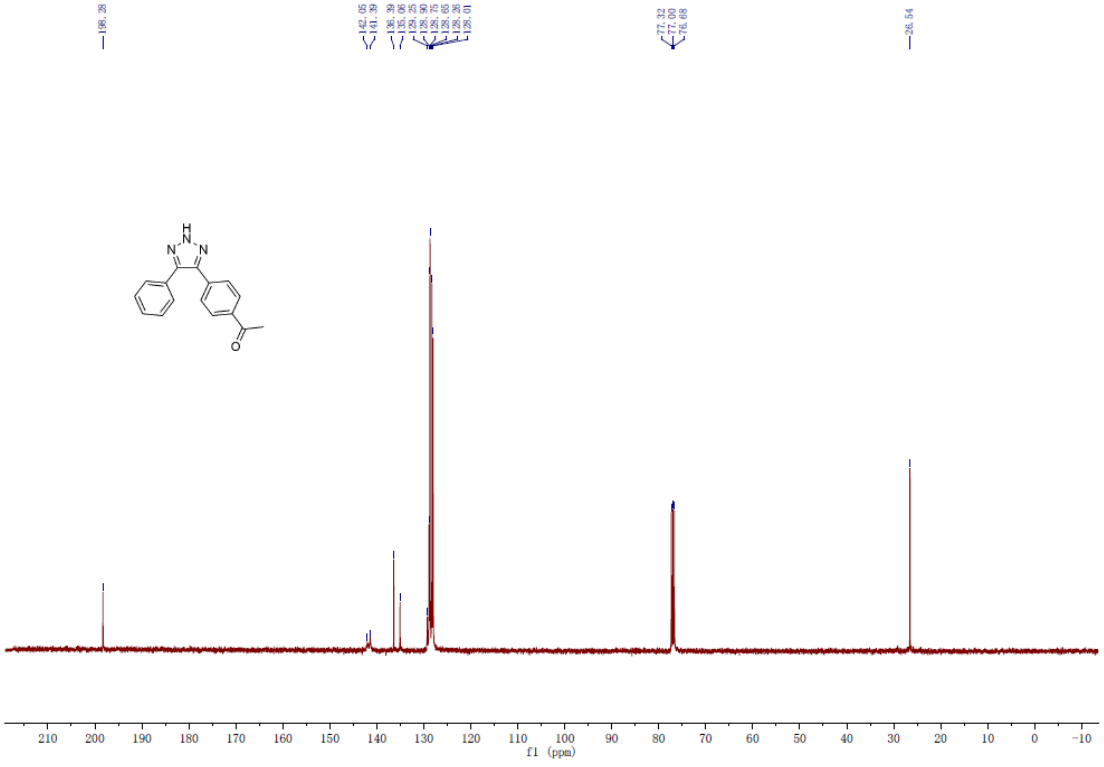
2g


7.73
7.71
7.65
7.64
7.51
7.50
7.49
7.48
7.44
7.43
7.43
7.43
7.26
CN
2.00
1.98
2.05
2.03
16 15 14 13 12 11 10 9 8 7 6 5 4 3 2 1 0 −1
f1 (ppm)

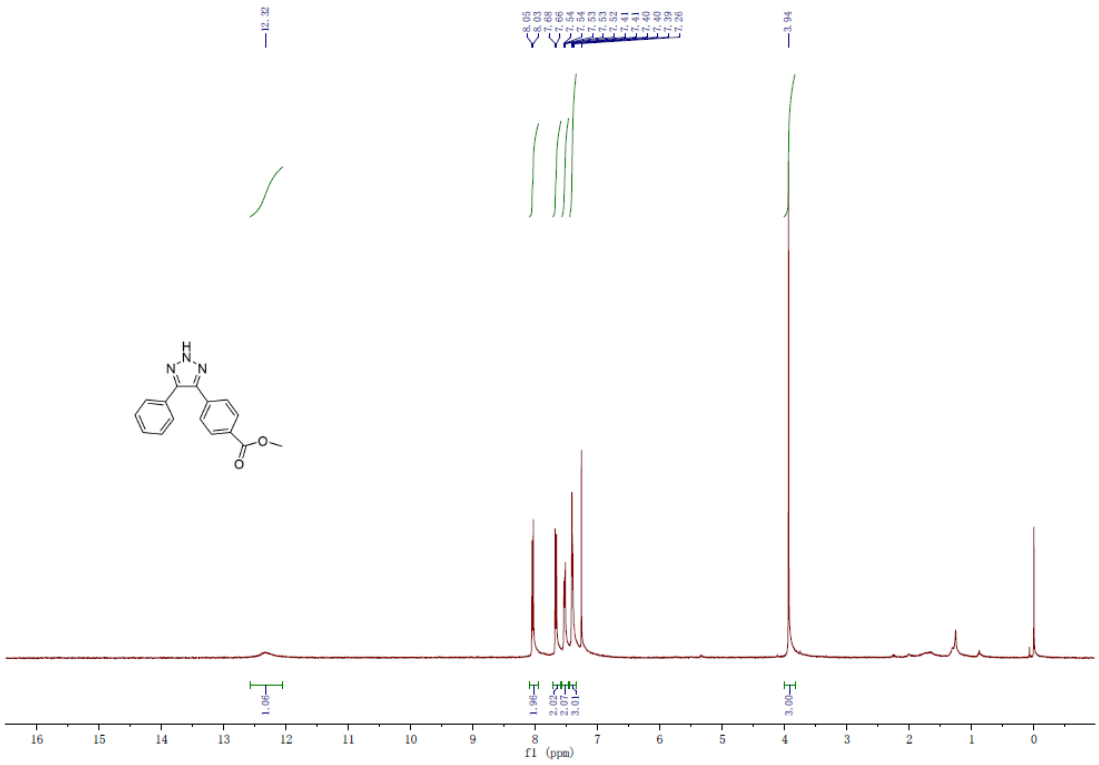

141.18
140.34
135.75
132.83
129.77
129.69
129.02
128.36
128.28
108.79
110.72
40.22
40.02
39.81
39.60
39.39
39.18
38.98
CN
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 −10
f1 (ppm)

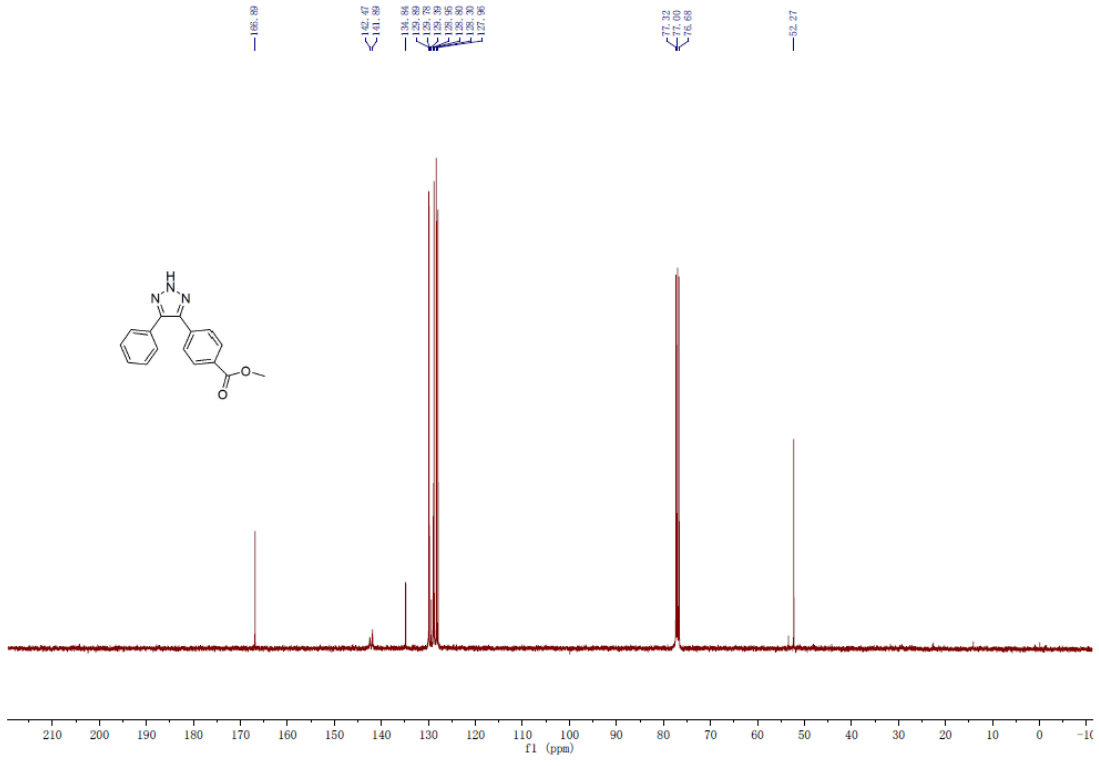
2h


7.92
7.91
7.90
7.67
7.65
7.50
7.49
7.48
7.38
7.38
7.37
7.36
7.36
7.35
7.25
2.60
2.07
2.05
2.03
3.04
3.00
15
14
13
12
11
10
9
8
7
6
5
4
3
2
1
0
−1
f1 (ppm)

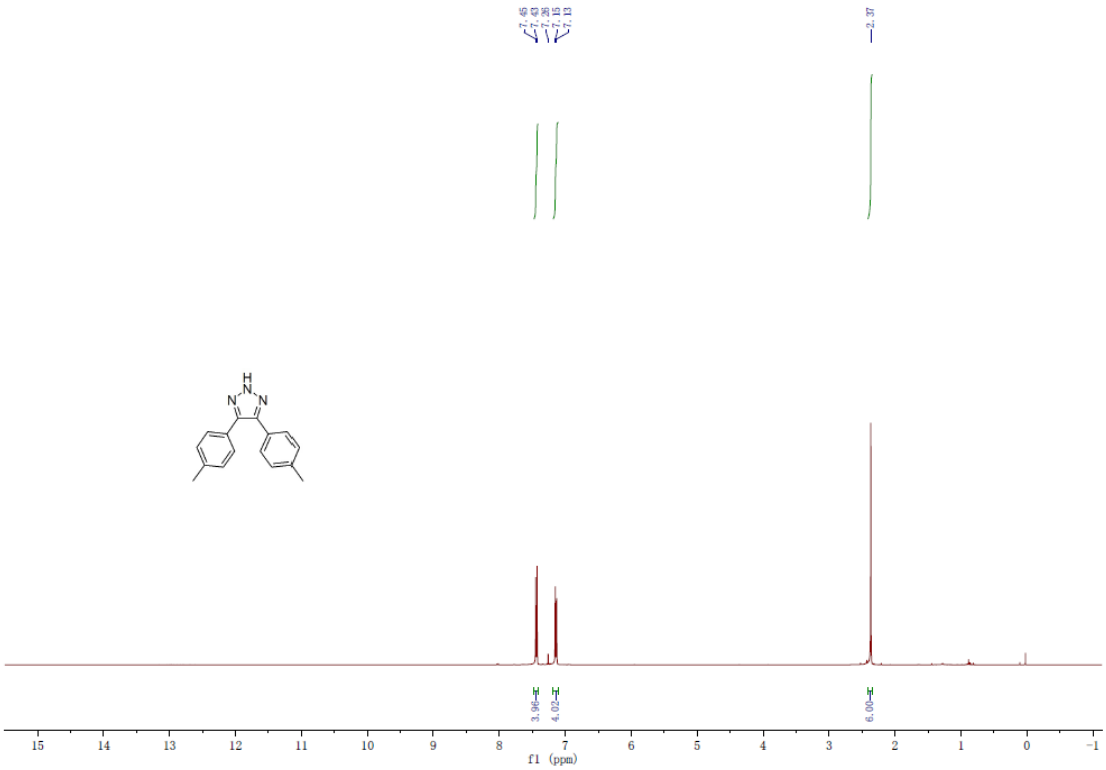

198.28
142.05
141.39
136.39
135.06
129.25
128.90
128.75
128.65
128.26
128.01
77.32
77.00
76.68
26.54
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
−10
f1 (ppm)

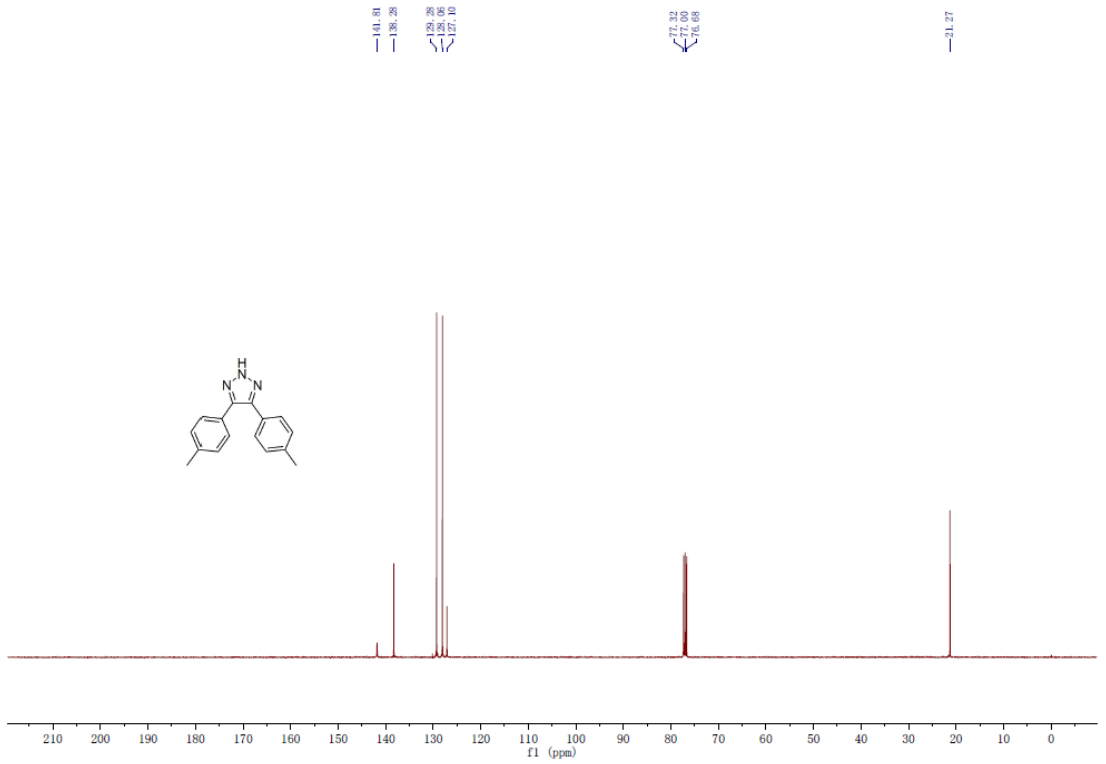
2i


12.32
8.05
8.03
7.68
7.66
7.54
7.53
7.52
7.41
7.40
7.39
7.26
3.94
1.00
1.98
2.02
2.07
3.01
3.00
f1 (ppm)

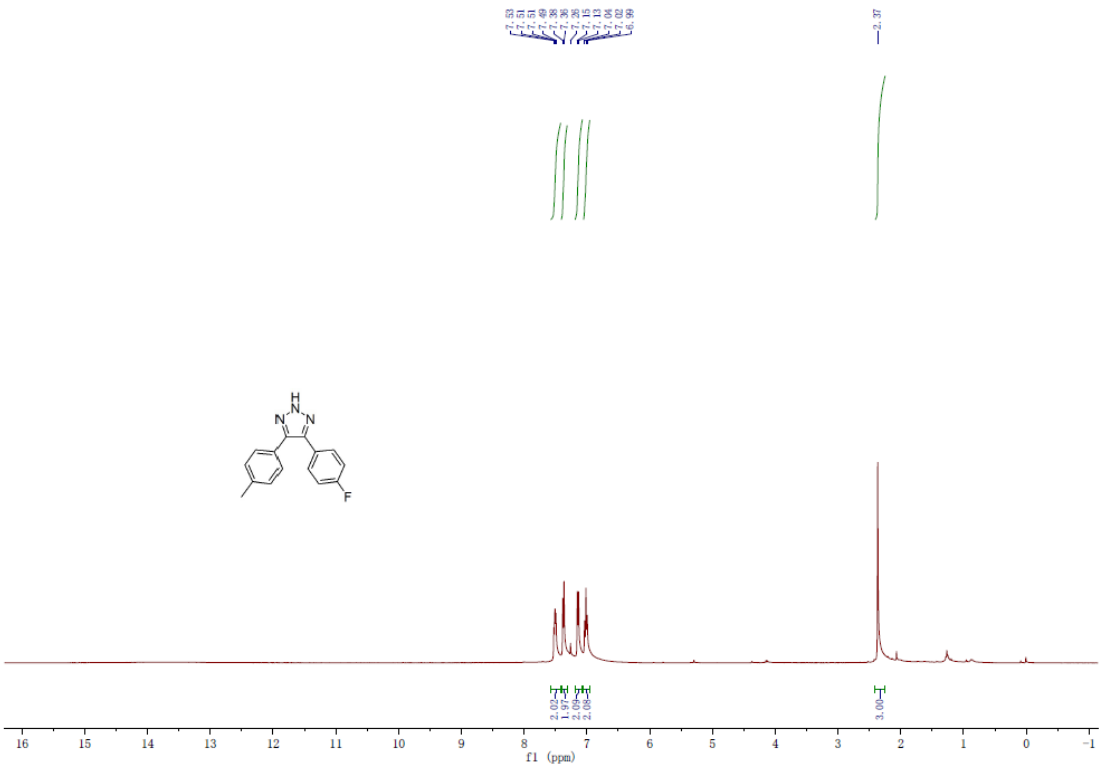

165.89
142.47
141.89
134.84
129.89
129.76
129.39
128.95
128.80
128.30
127.96
77.32
77.00
76.68
52.27
f1 (ppm)

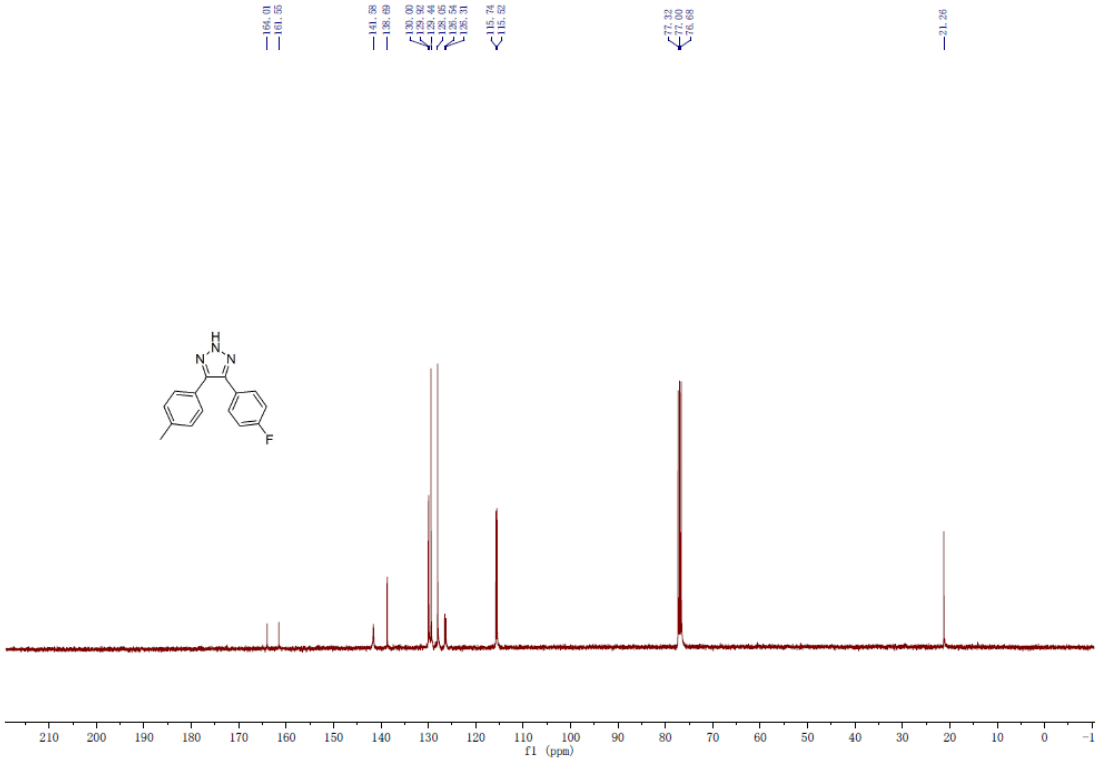
2j


7.65
7.63
7.26
7.15
7.13
2.37
3.96
4.02
6.00
f1 (ppm)

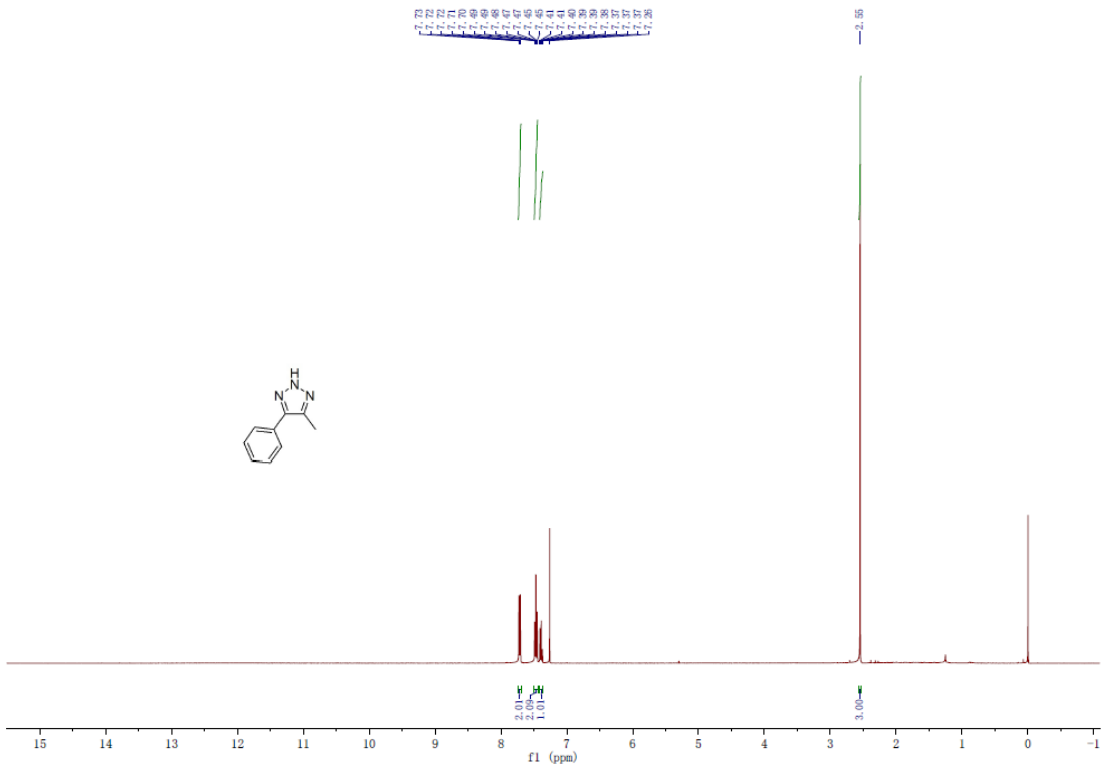

141.81
138.28
129.28
128.95
127.10
77.32
77.00
76.68
21.27
f1 (ppm)

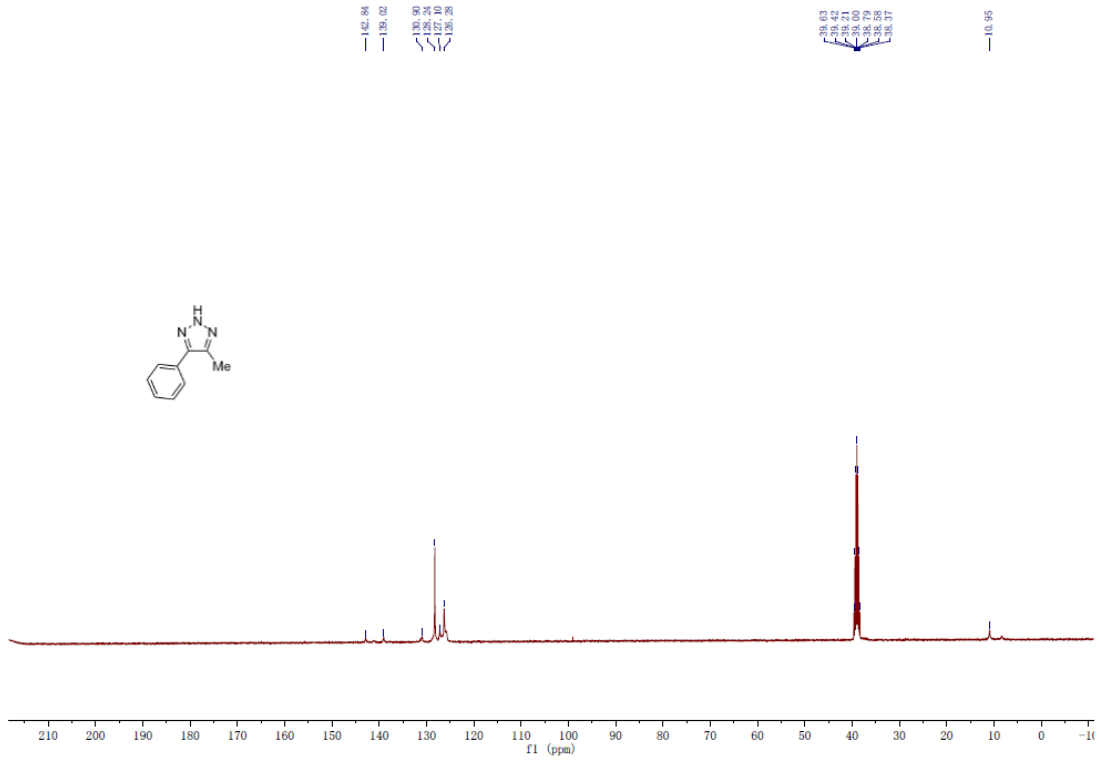
2k


7.53
7.51
7.51
7.49
7.38
7.36
7.26
7.15
7.13
7.04
7.02
6.99
2.37
3.02
1.97
2.08
2.08
3.00
f1 (ppm)

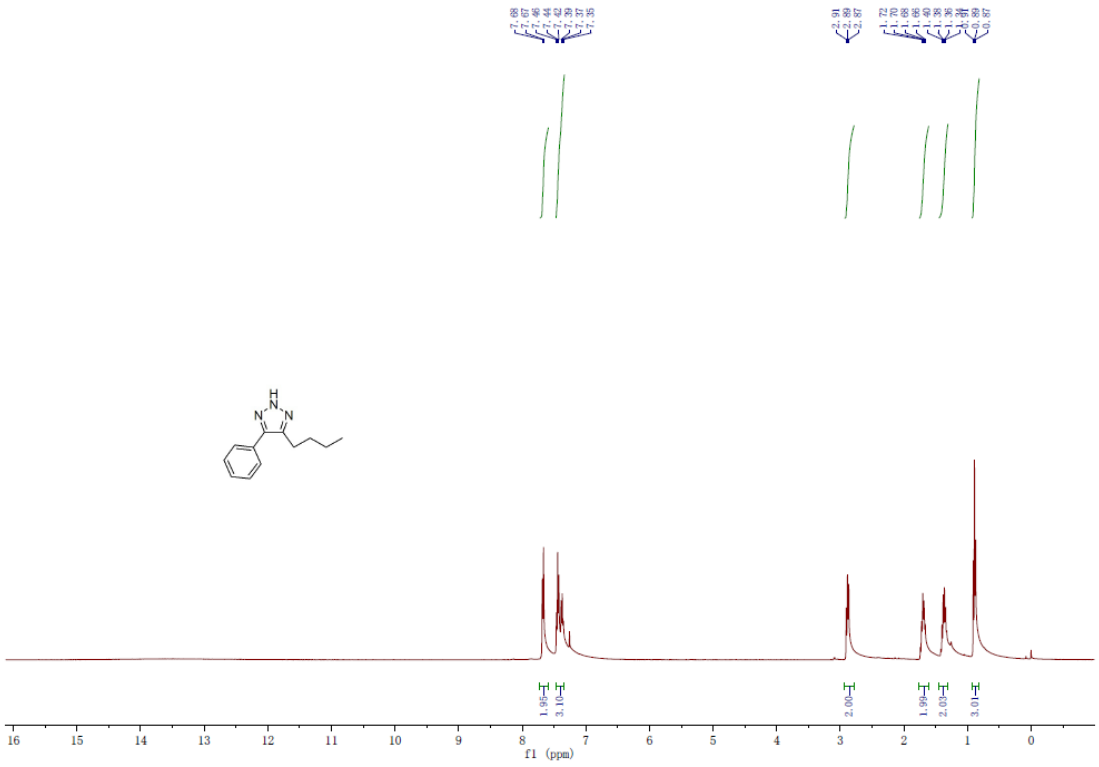

164.01
161.55
141.58
136.69
130.00
129.92
129.44
128.95
126.56
126.31
115.74
115.52
77.32
77.00
76.68
21.26
f1 (ppm)

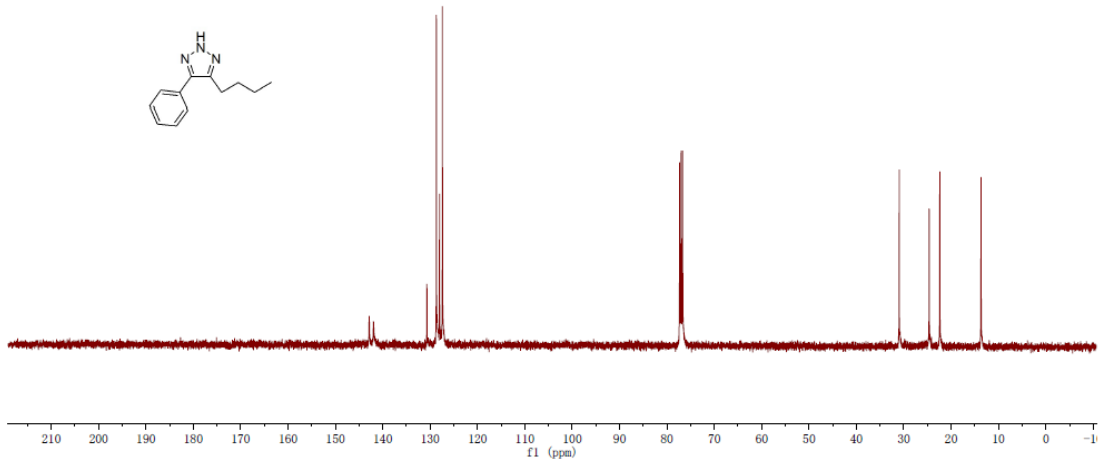
2l



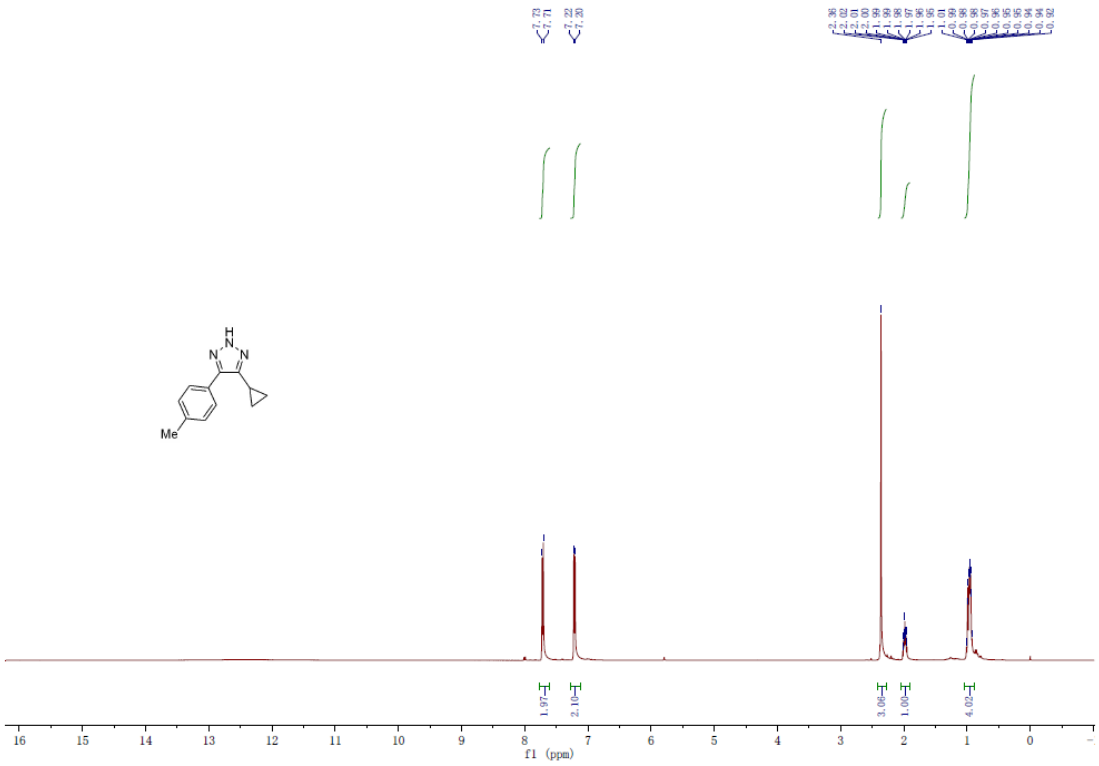


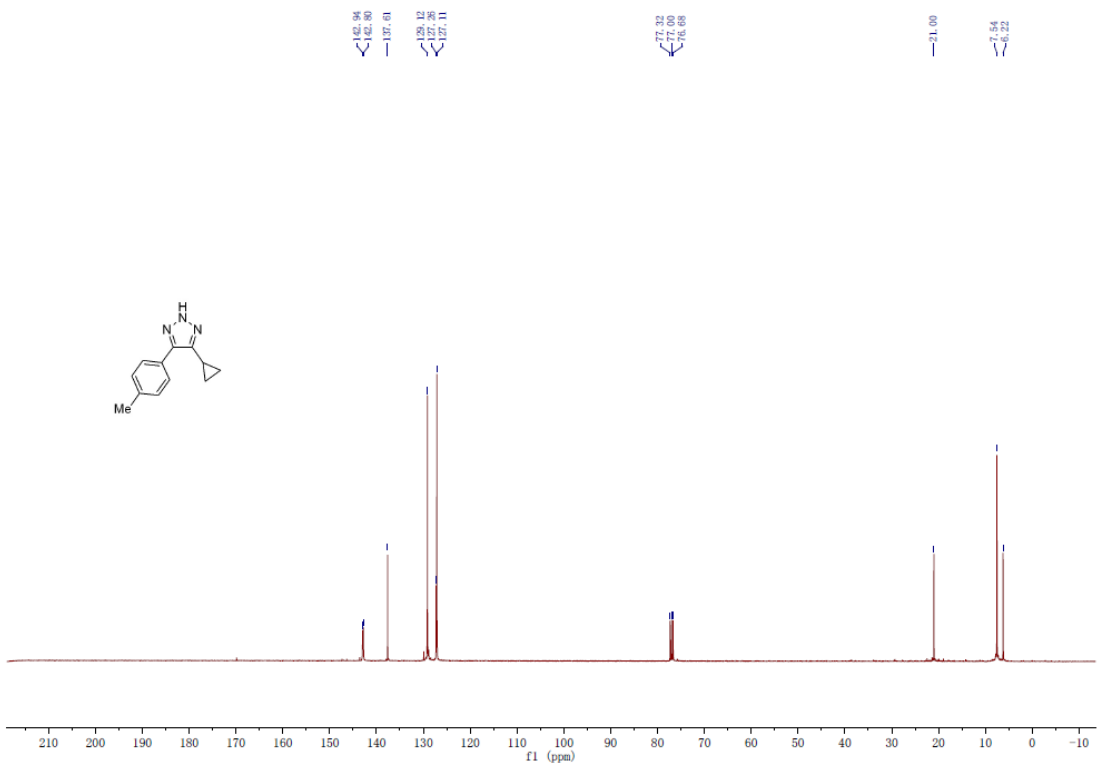
2m



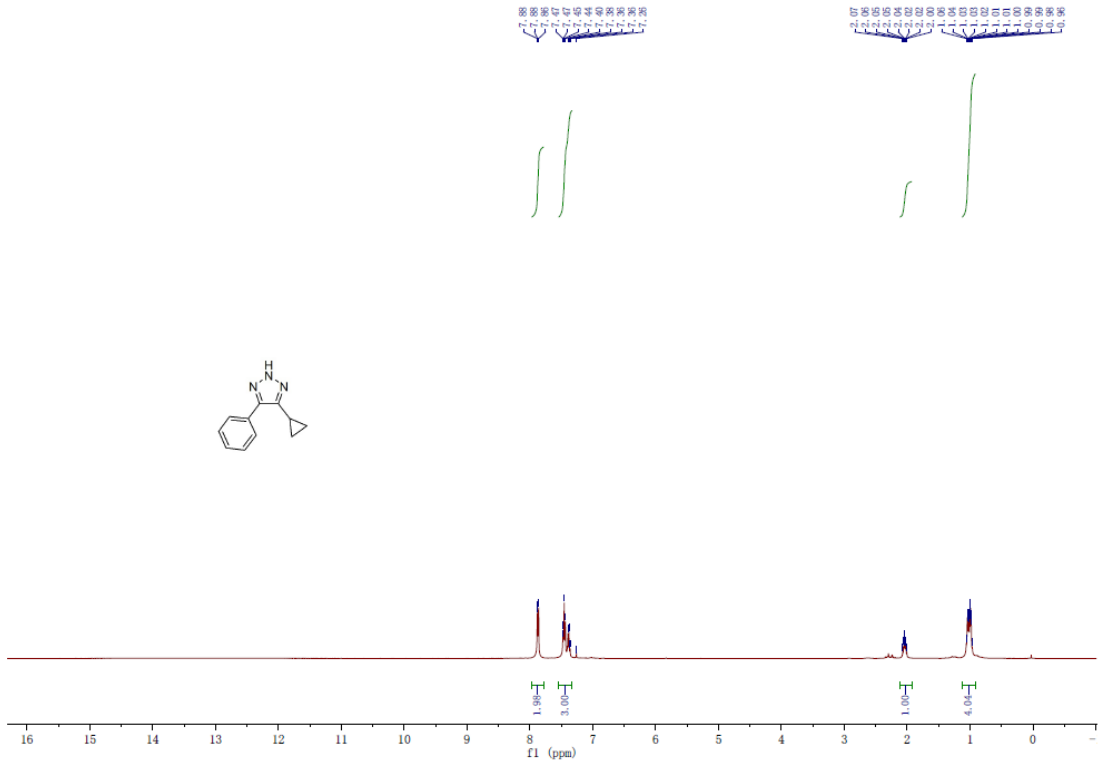


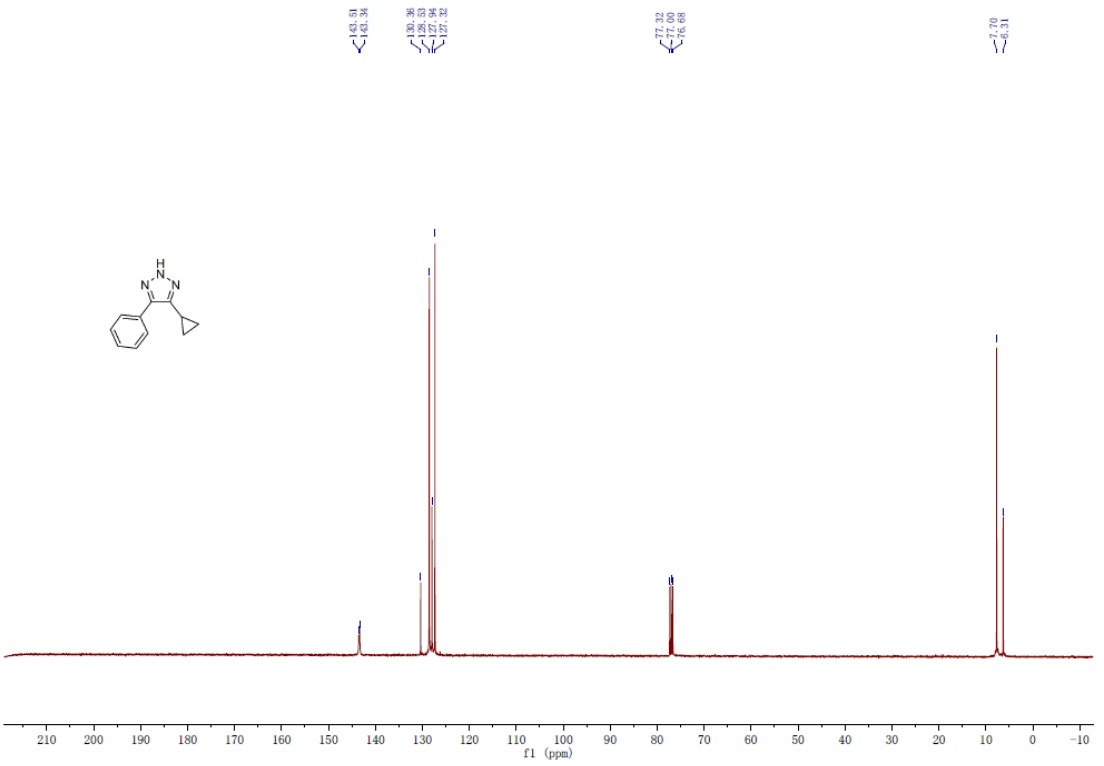
2o


7.73
7.71
7.22
7.20
2.36
2.02
2.01
2.00
1.99
1.98
1.97
1.96
1.95
1.01
1.00
0.99
0.98
0.97
0.96
0.95
0.95
0.94
0.94
0.92
Me
1.97
2.10
3.06
1.00
4.02
f1 (ppm)

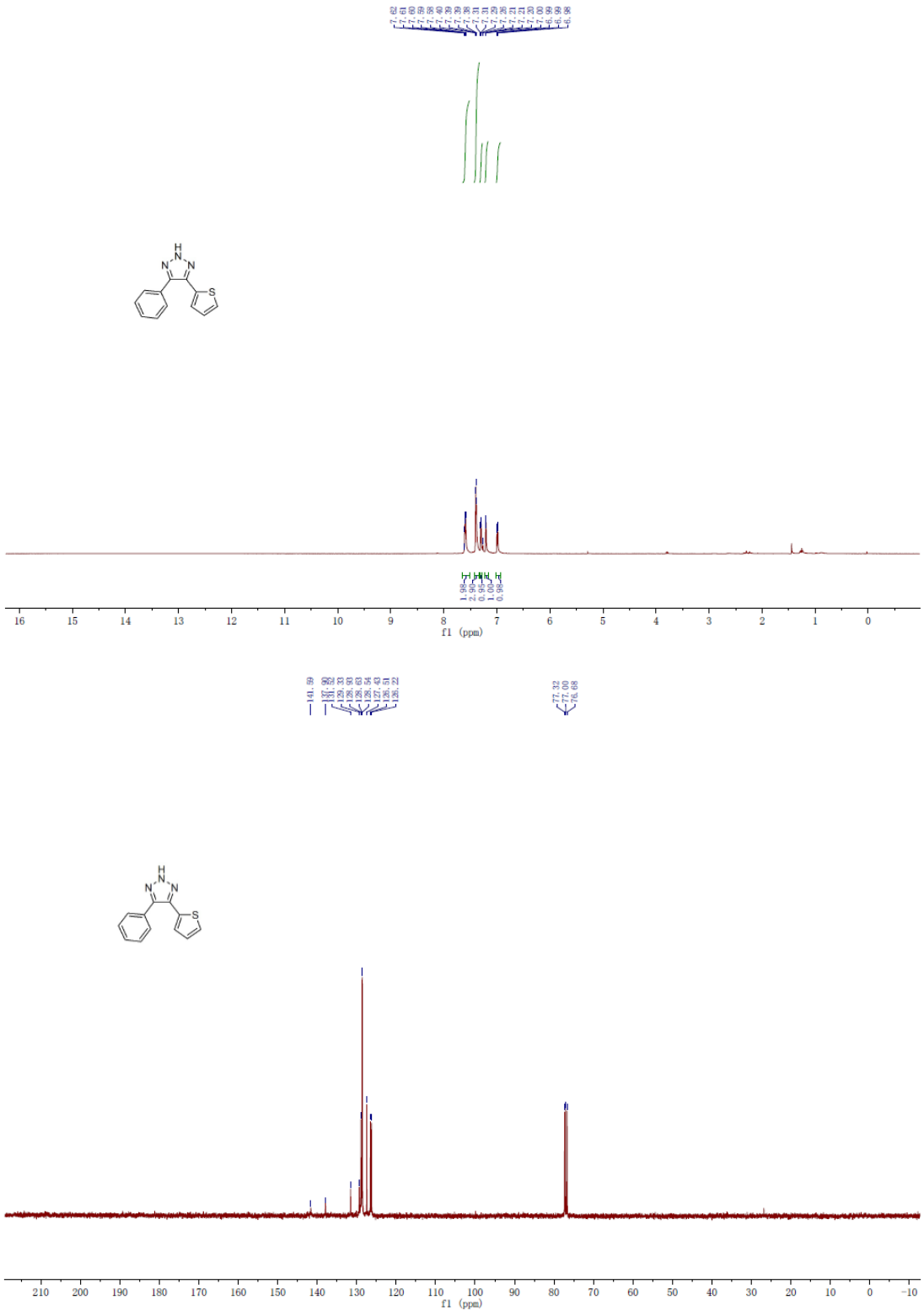

142.94
142.80
137.61
129.12
127.26
127.11
77.32
77.00
76.68
21.00
17.54
16.22
Me
f1 (ppm)

2p

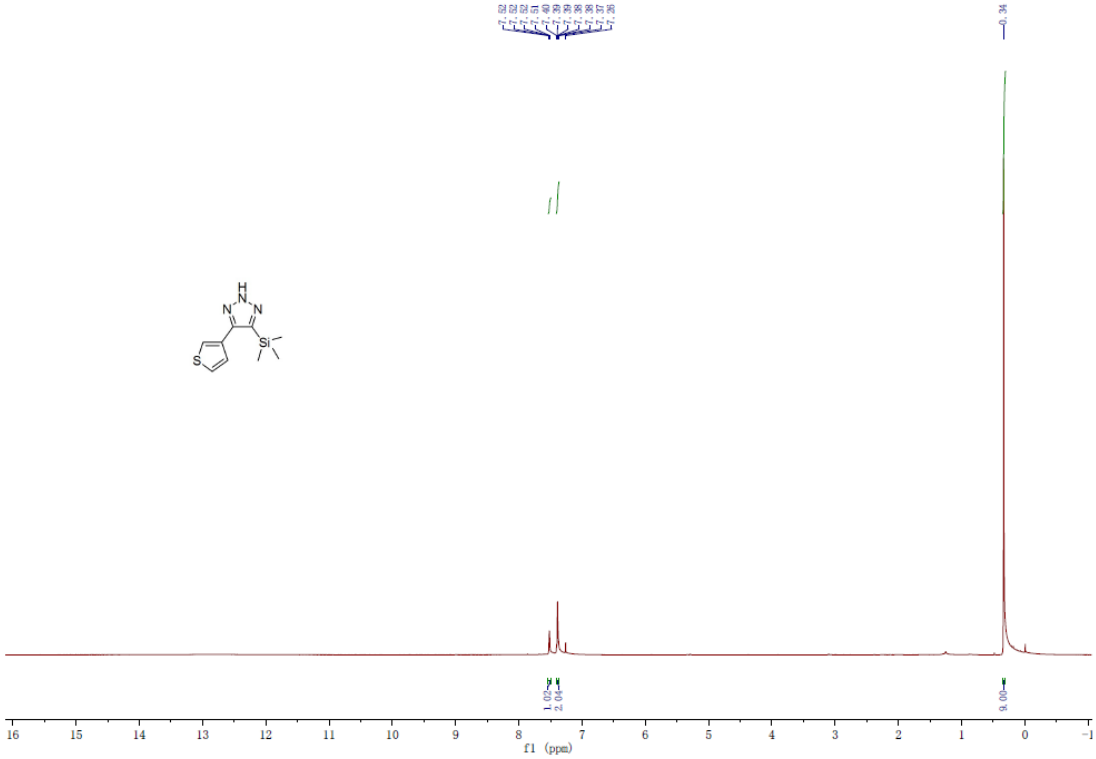


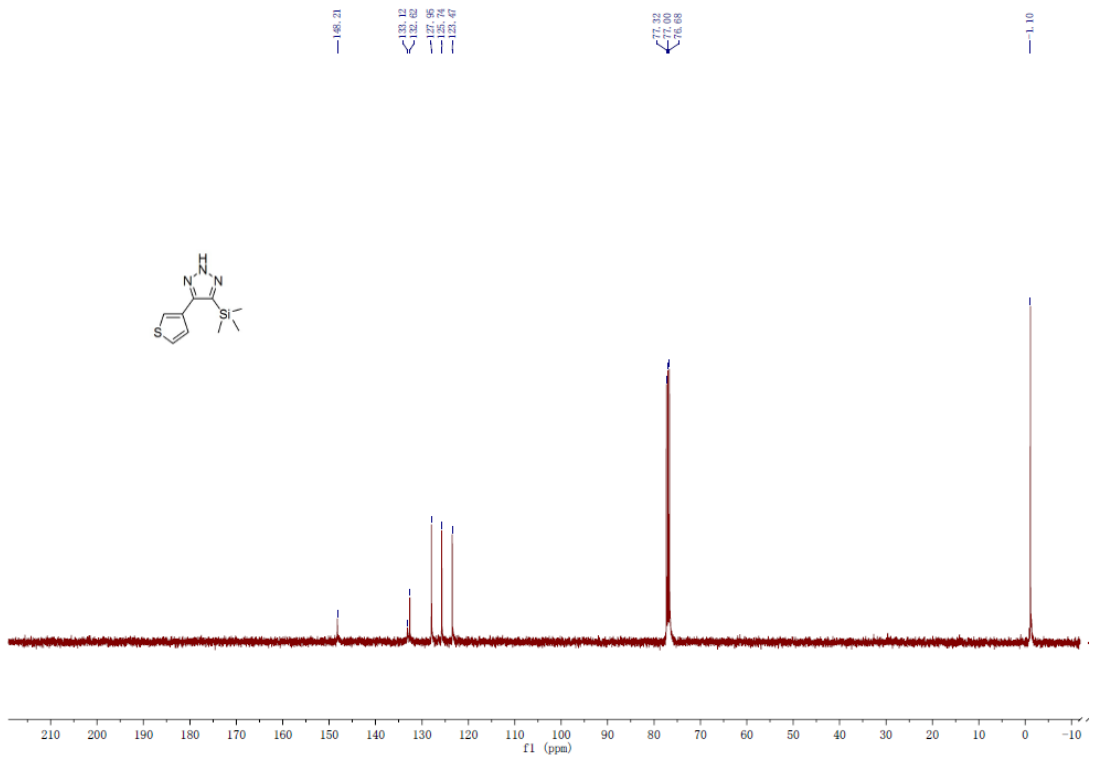


2q

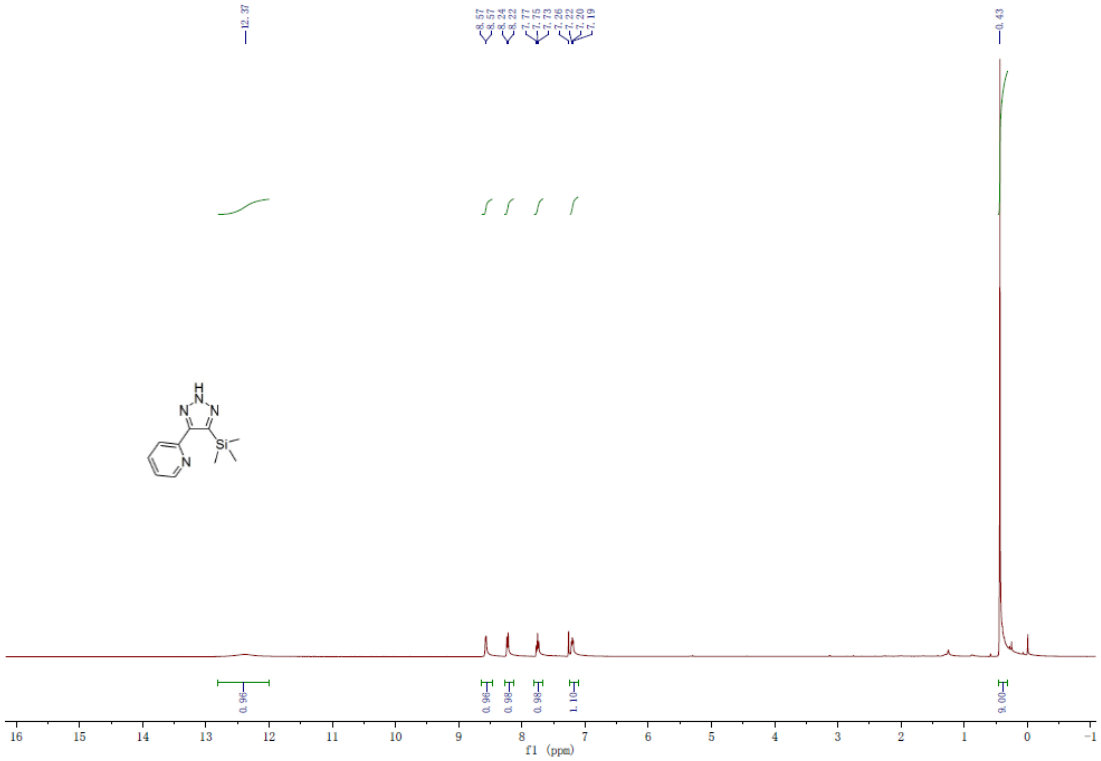


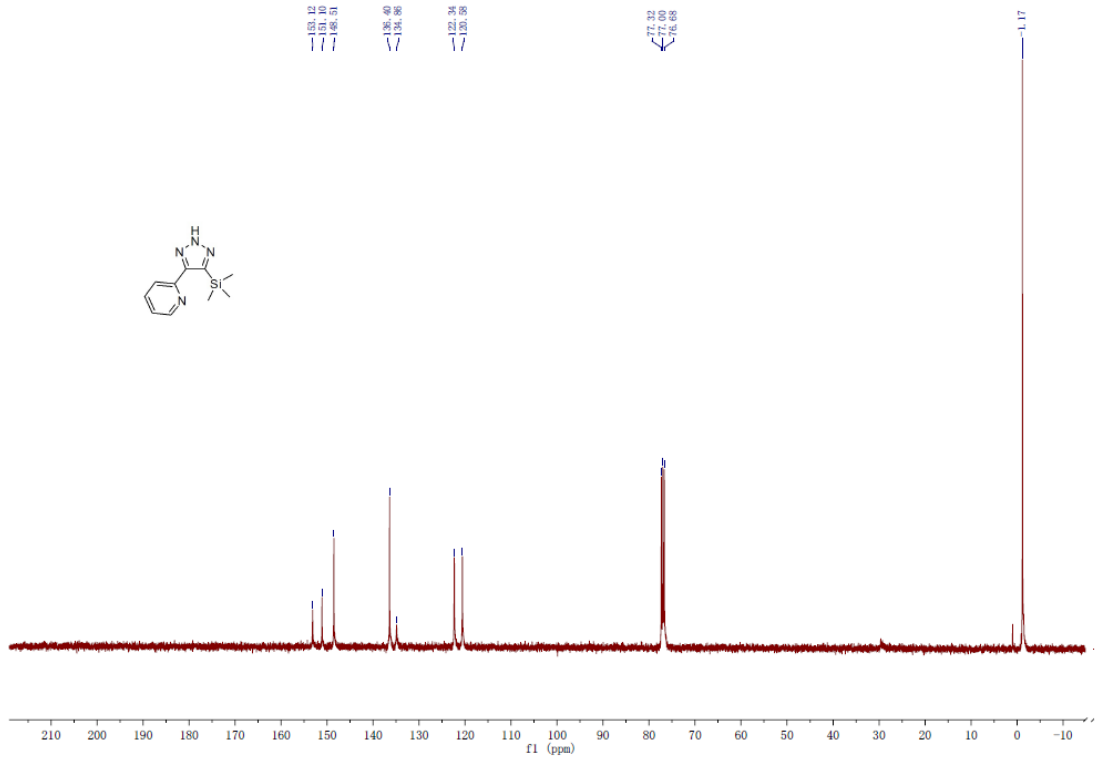
2r


7.52
7.52
7.51
7.40
7.39
7.39
7.38
7.38
7.37
7.26
0.34
1.02
2.04
9.00
f1 (ppm)

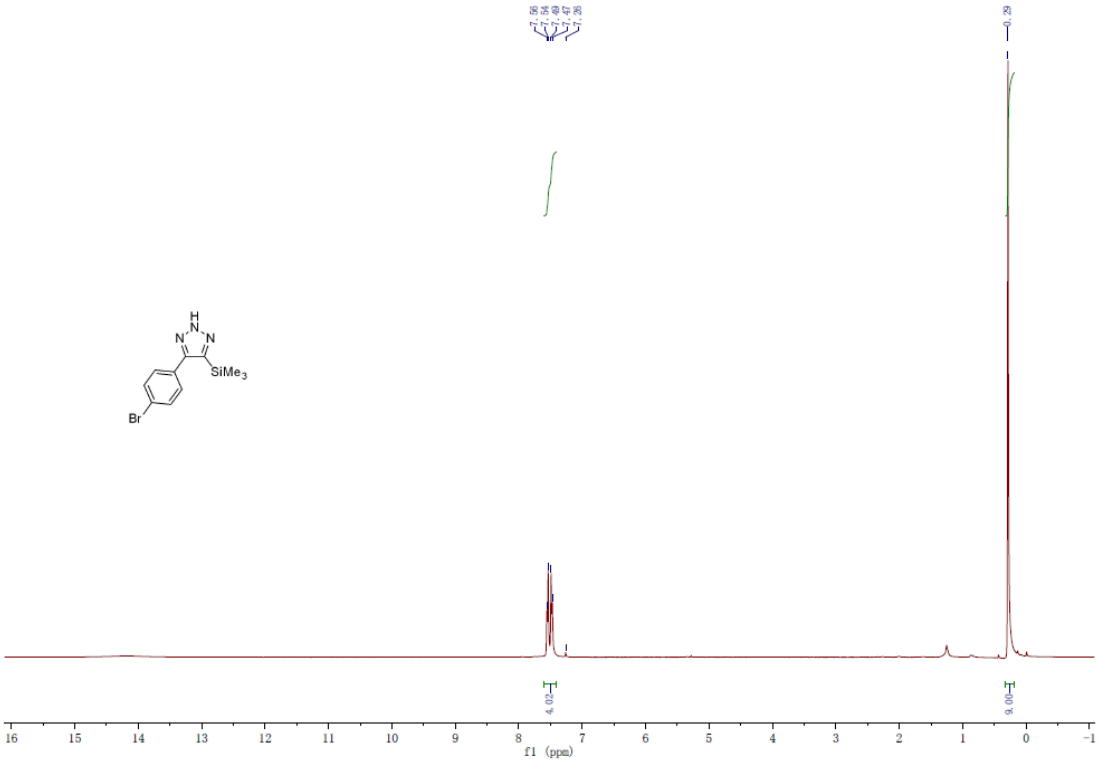

148.21
133.12
132.62
127.95
125.74
123.47
77.32
77.00
76.68
-1.10
f1 (ppm)

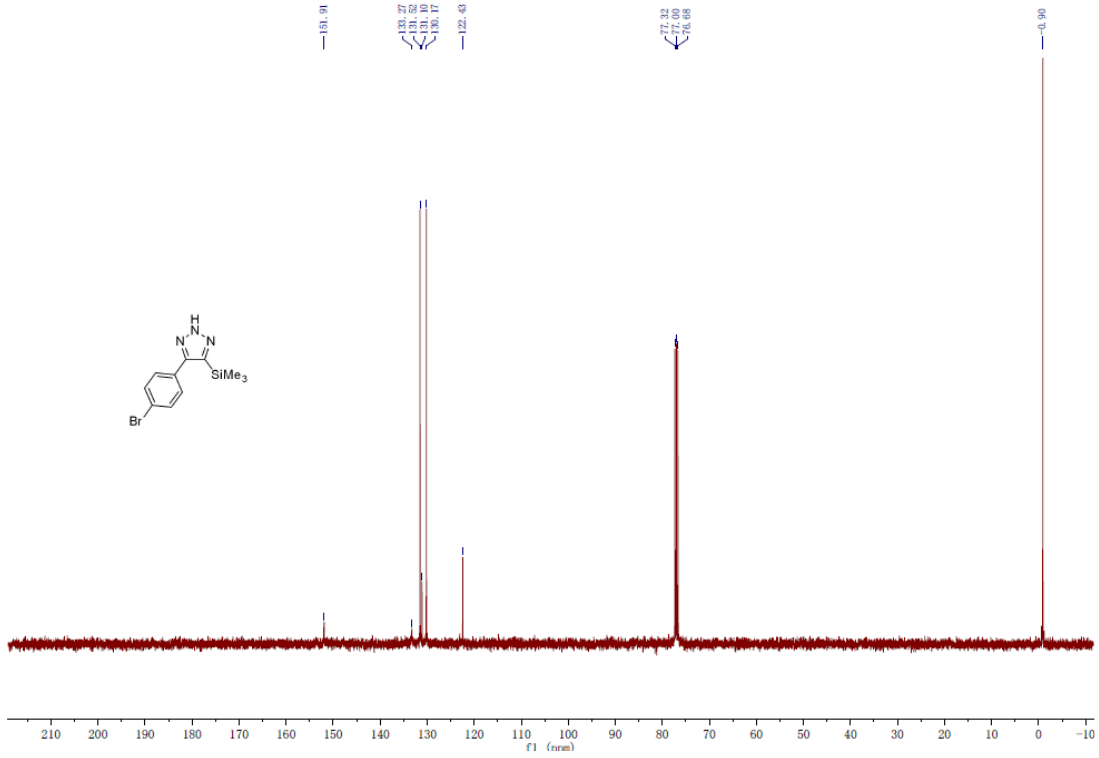
2s


12.37
8.57
8.57
8.24
8.22
7.77
7.75
7.73
7.26
7.22
7.20
7.19
0.43
0.98
0.98
0.98
1.10
9.00
f1 (ppm)

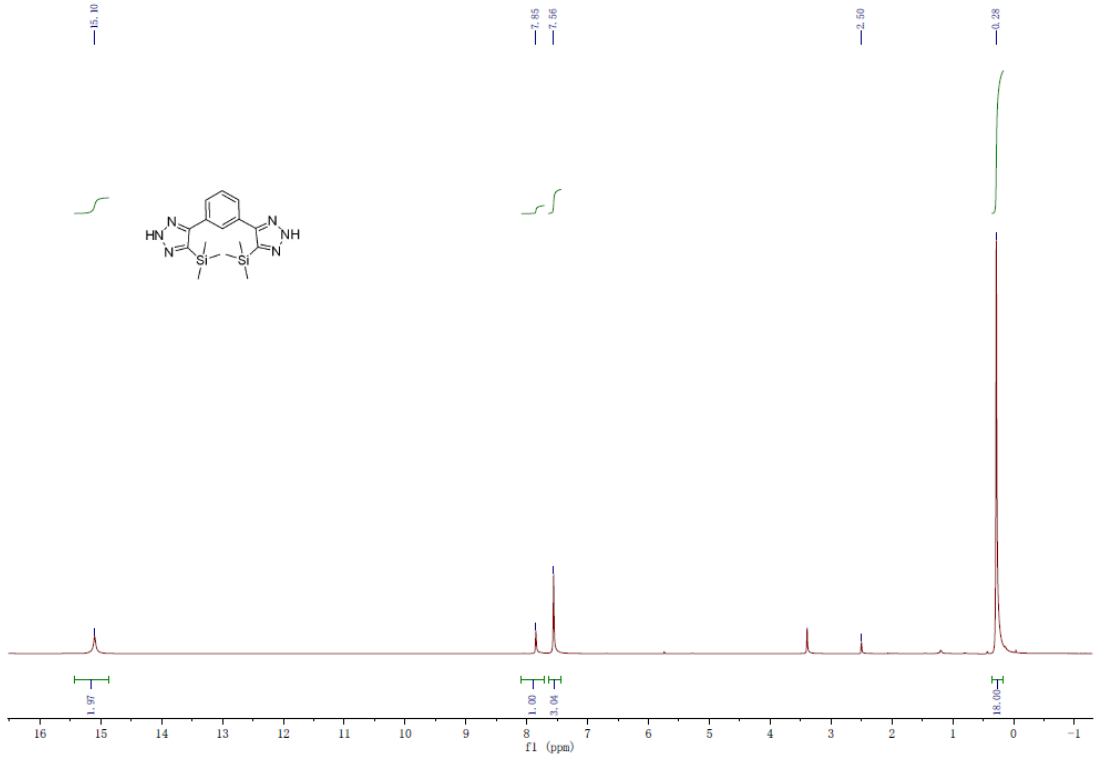

153.12
151.10
148.51
136.40
136.06
122.34
120.08
77.32
77.00
76.68
1.17
f1 (ppm)

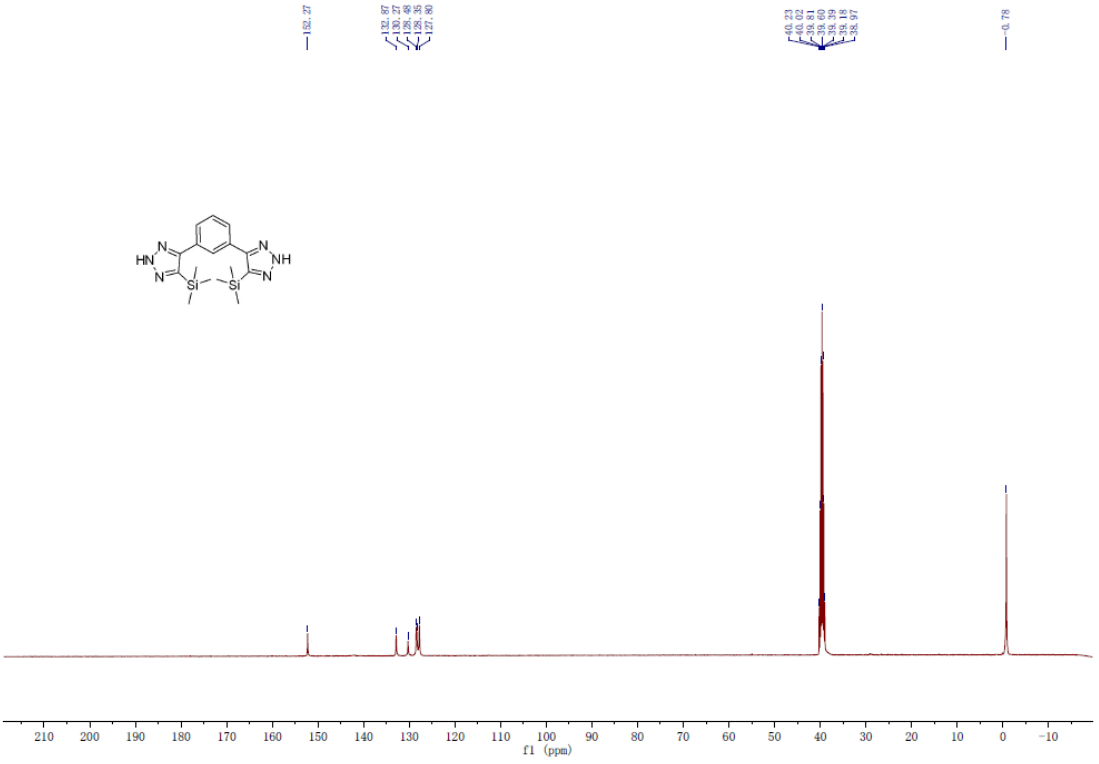
2t


7.56
7.54
7.49
7.47
7.26
0.29
SiMe3
Br
4.02
9.00
f1 (ppm)

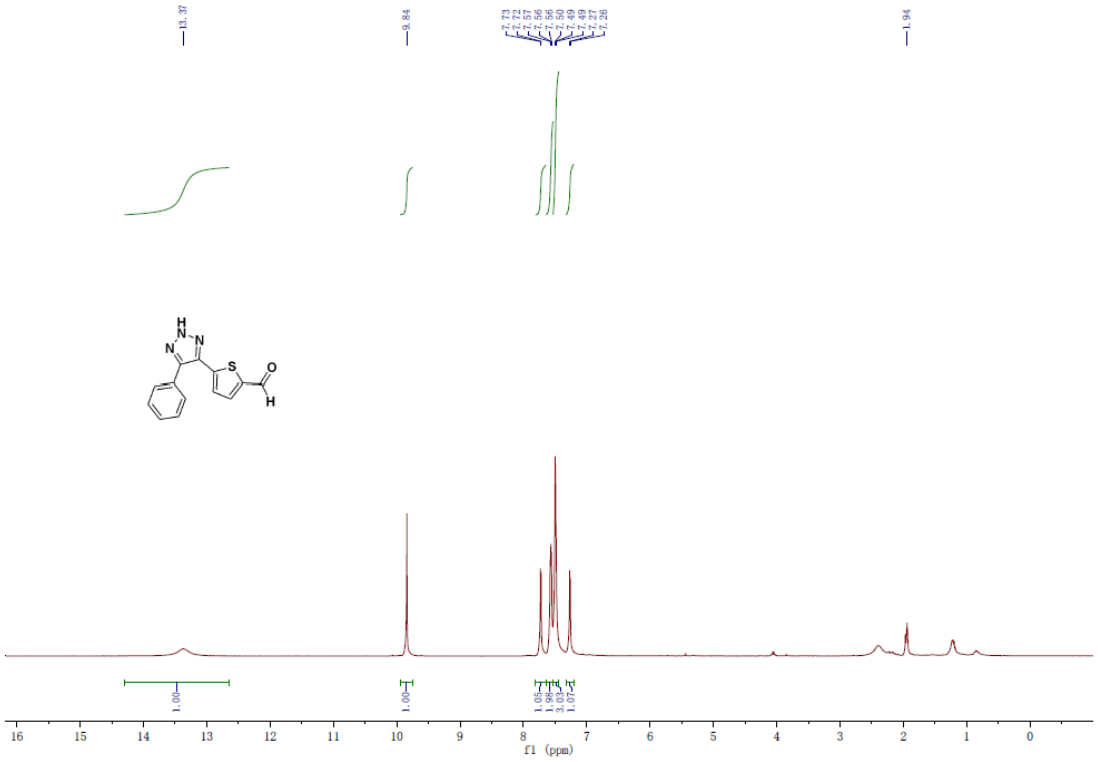

151.91
133.27
131.52
131.10
130.17
122.43
77.32
77.00
76.68
-0.90
SiMe3
Br
f1 (ppm)

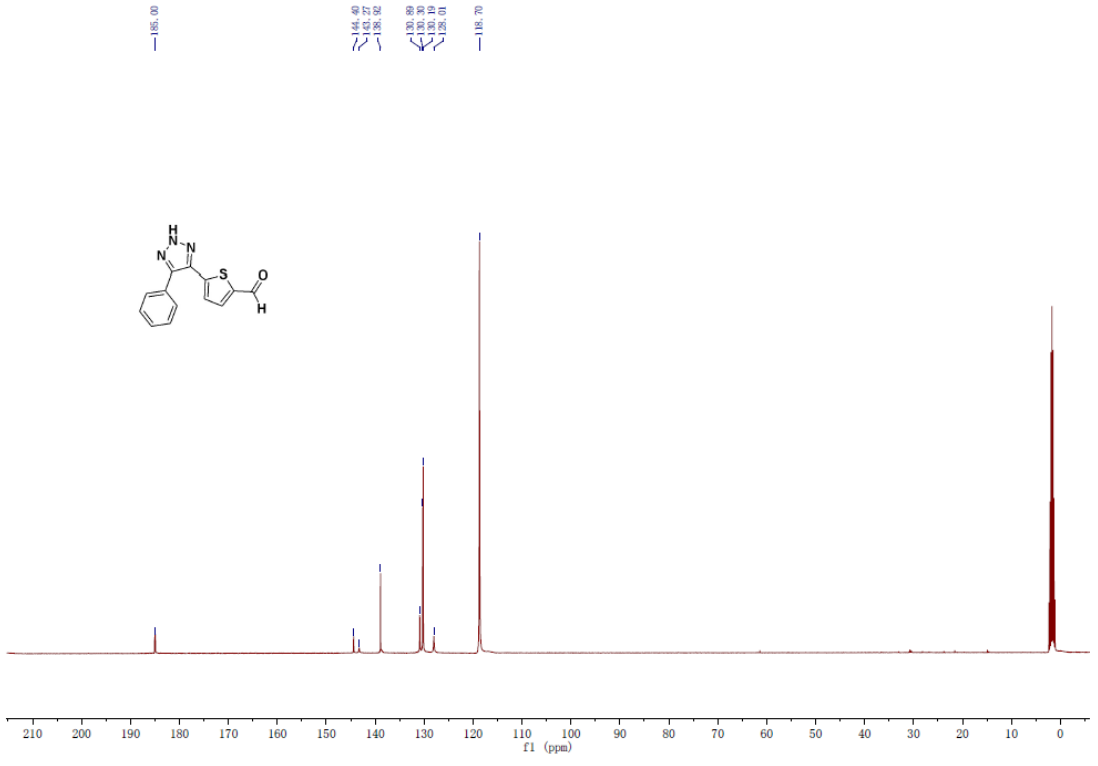
2u


15.10
7.85
7.56
2.50
0.28
HN
NH
Si
Si
1.97
1.00
3.04
18.00
f1 (ppm)

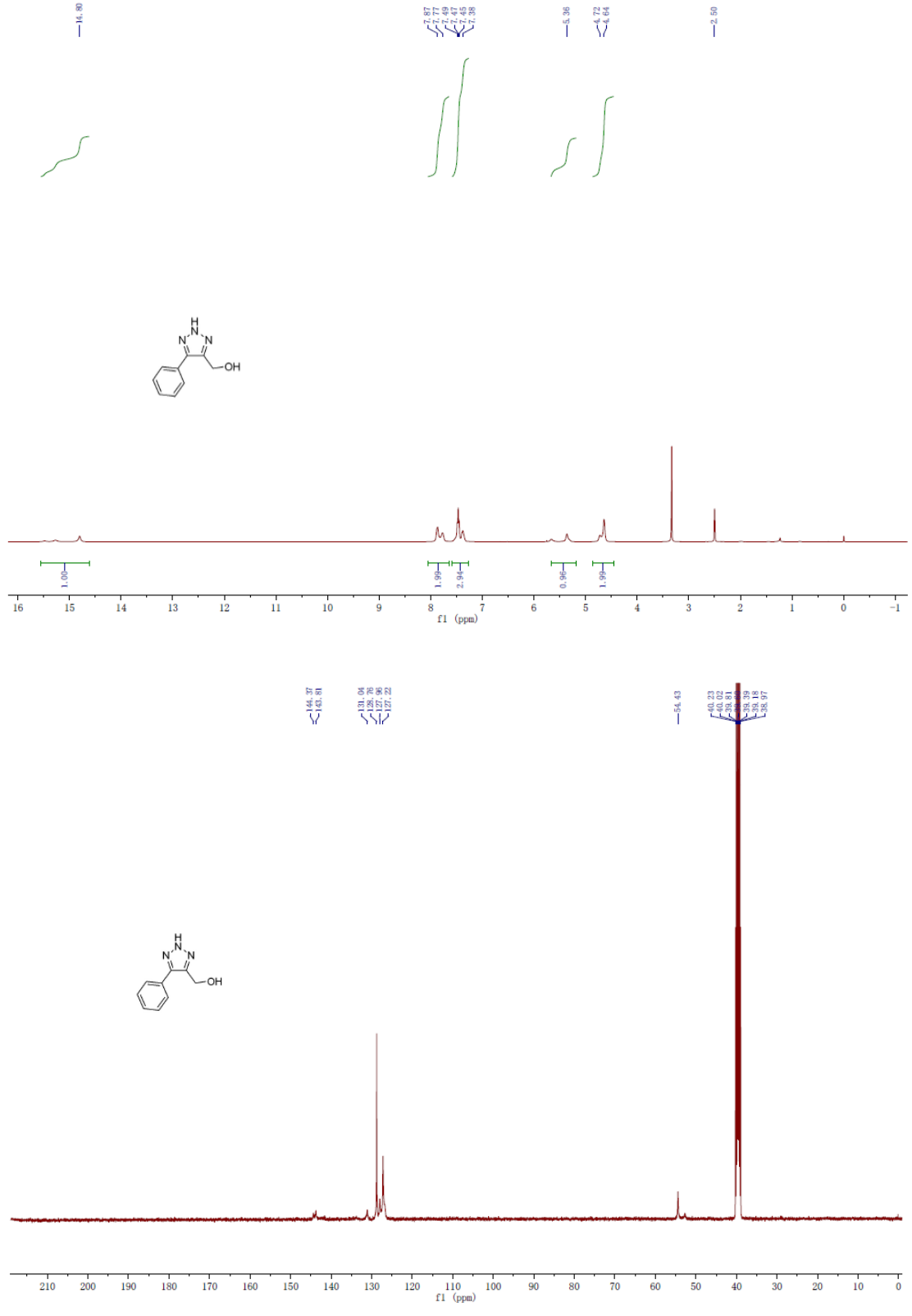

132.27
132.97
130.27
128.49
128.35
127.80
40.23
40.02
39.81
39.60
39.39
39.18
38.97
0.78
HN
NH
Si
Si
f1 (ppm)

2v

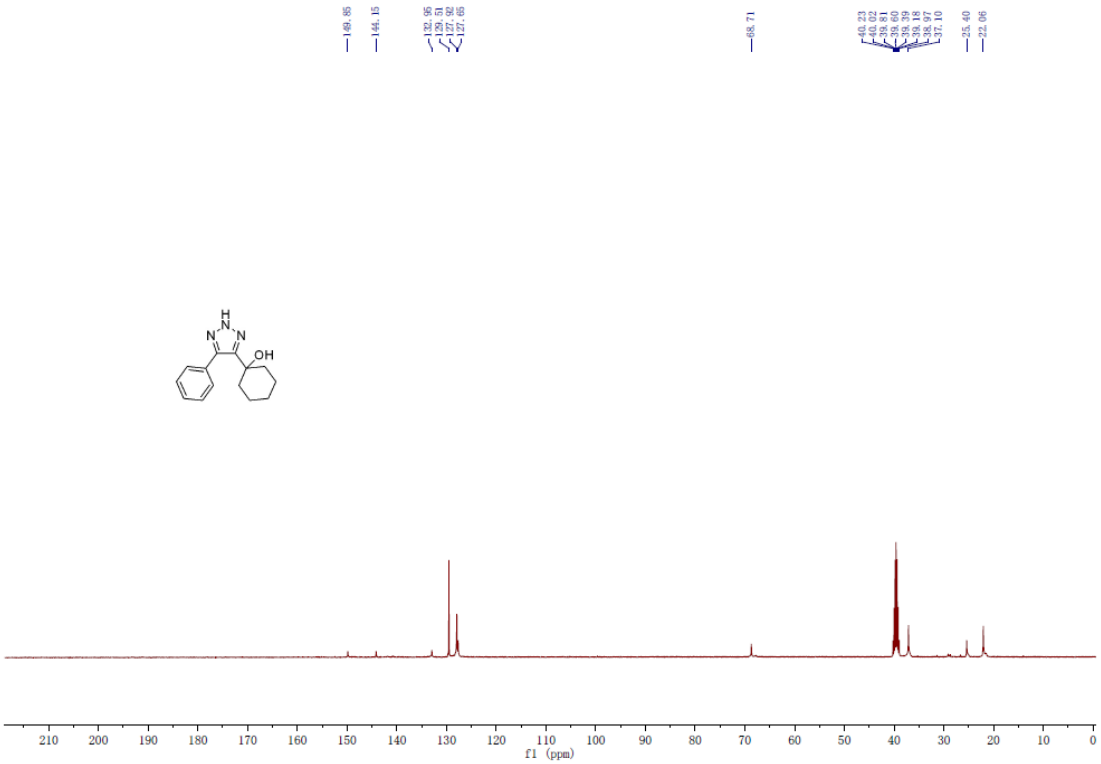

13.37
9.84
7.73
7.72
7.57
7.56
7.56
7.50
7.49
7.49
7.27
7.26
1.94
1.00
1.00
1.05
1.98
3.03
1.07
f1 (ppm)

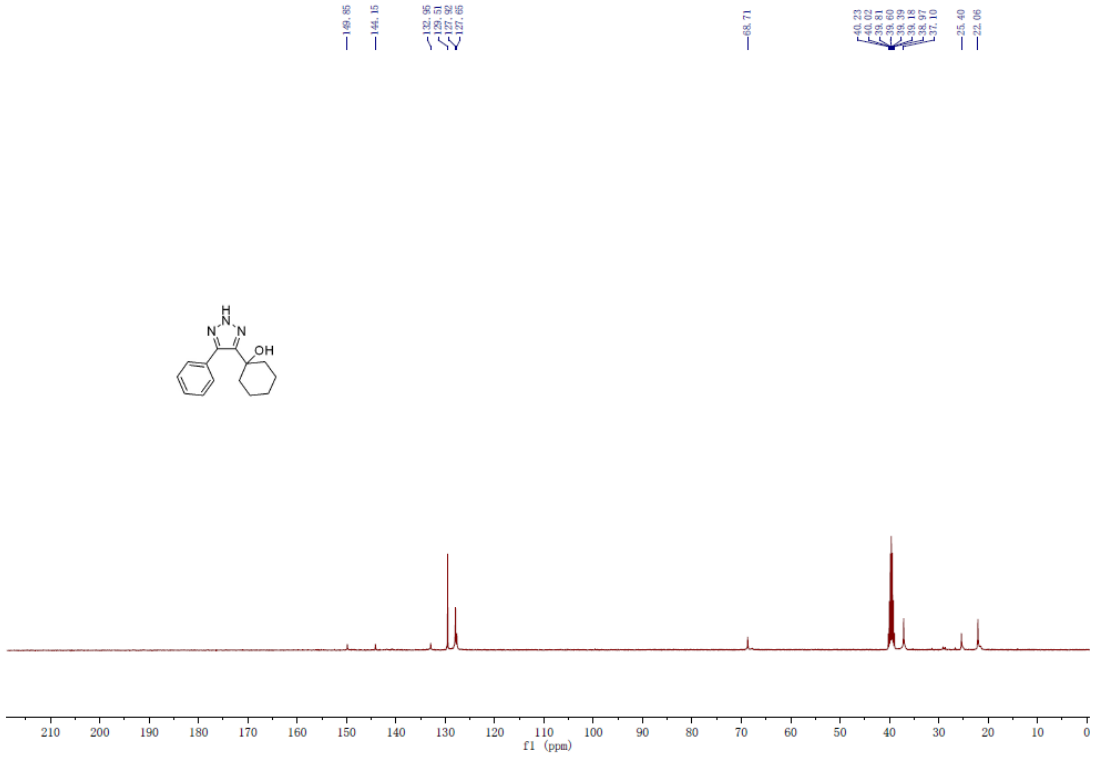

185.00
144.40
143.27
136.92
130.89
130.30
130.19
128.01
118.70
f1 (ppm)

2w

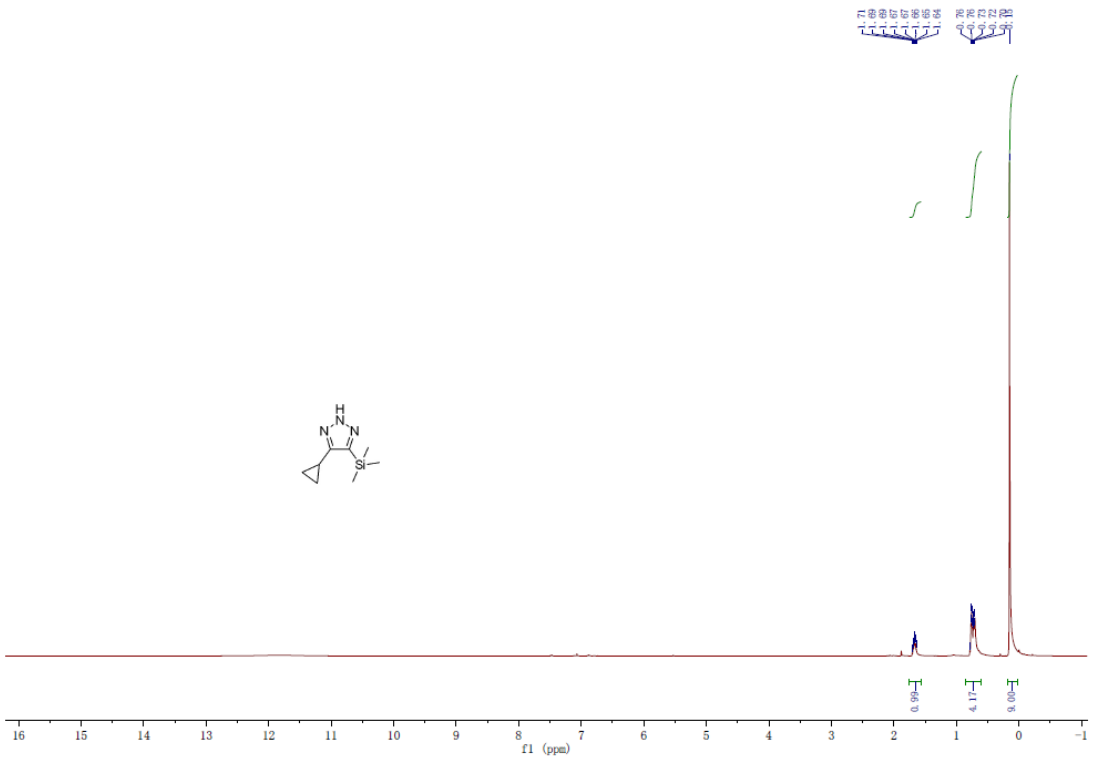

14.80
7.87
7.77
7.49
7.47
7.45
7.38
5.36
4.72
4.64
2.50
OH
1.00
1.99
2.94
0.96
1.99
f1 (ppm)
146.37
143.81
131.04
128.76
127.86
127.22
54.43
40.23
40.02
39.81
39.60
39.39
39.18
38.97
OH
f1 (ppm)

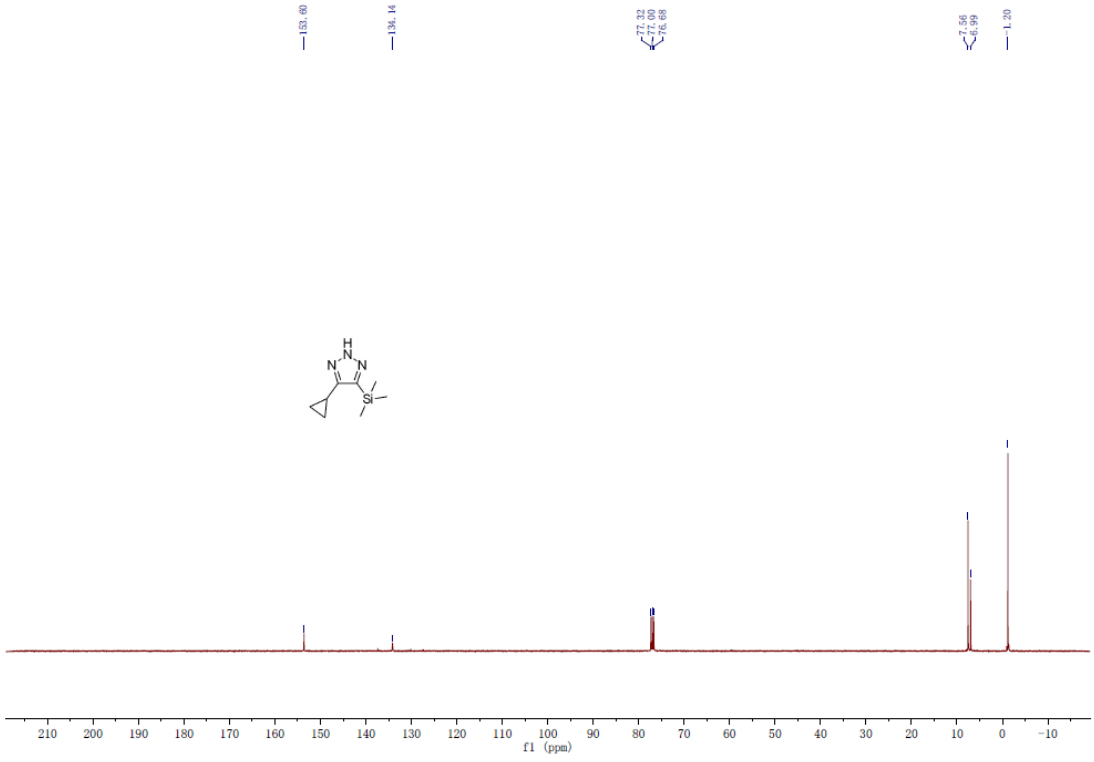
2x


149.85
144.15
132.96
129.51
127.92
127.65
68.71
40.23
40.02
39.81
39.60
39.39
39.18
38.97
37.10
25.40
22.06
OH
f1 (ppm)

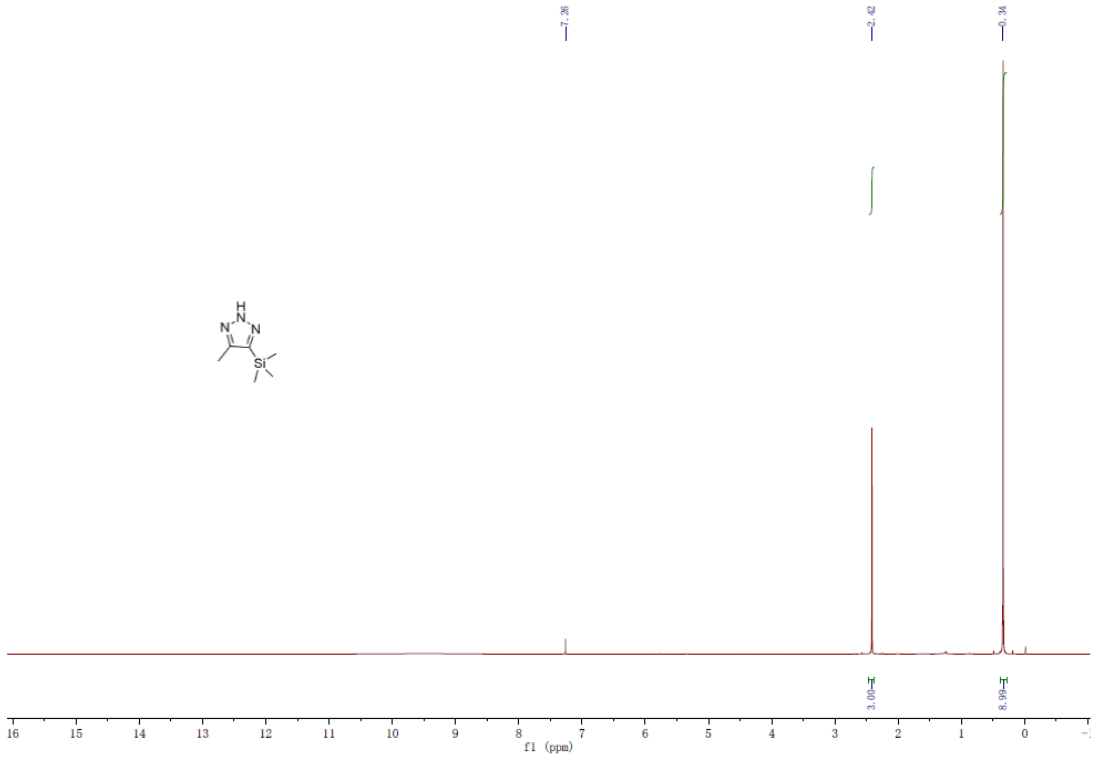

149.85
144.15
132.96
129.51
127.92
127.65
68.71
40.23
40.02
39.81
39.60
39.39
39.18
38.97
37.10
25.40
22.06
OH
f1 (ppm)

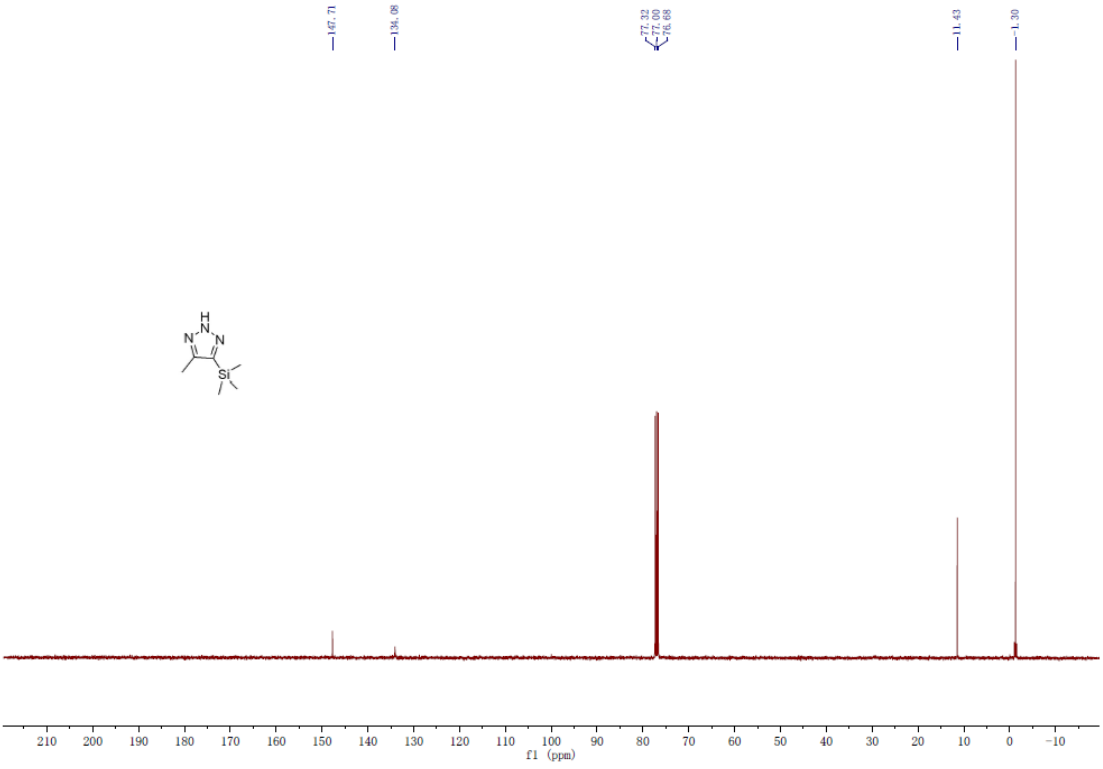
2z


1.71
1.69
1.68
1.67
1.67
1.66
1.65
1.64
0.76
0.75
0.73
0.72
0.72
0.70
0.69
0.99
4.17
9.00
f1 (ppm)

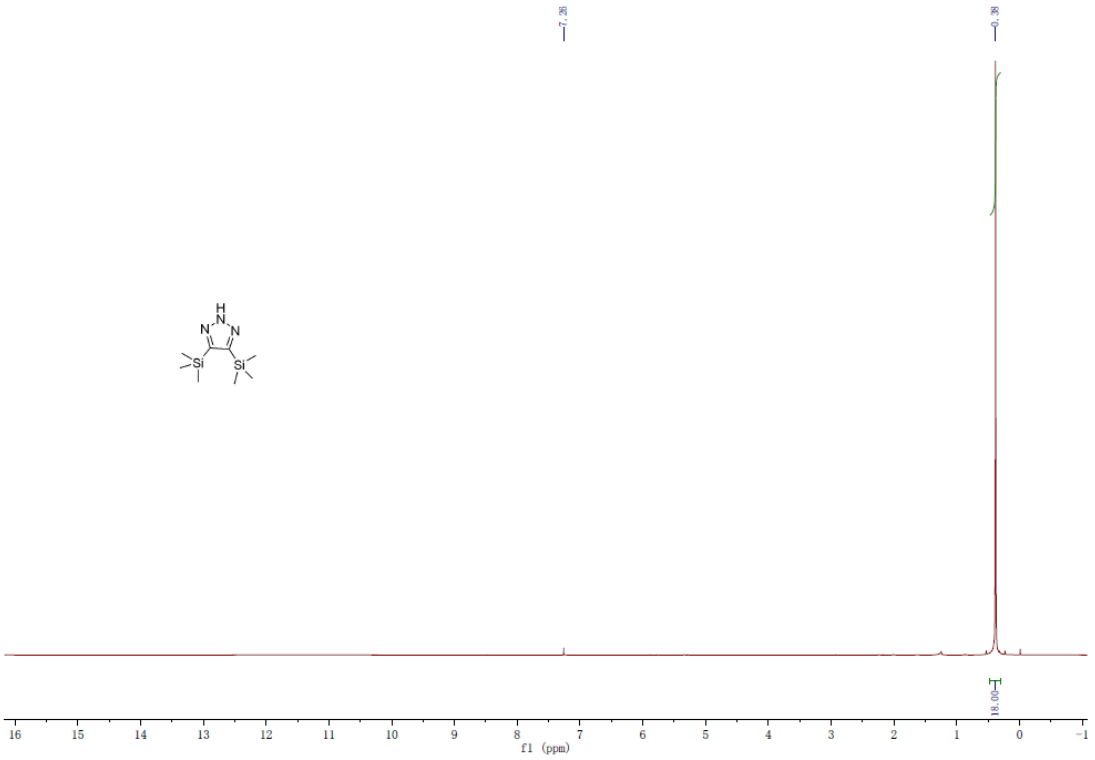

133.60
134.14
77.32
77.00
76.68
7.56
6.99
1.20
f1 (ppm)

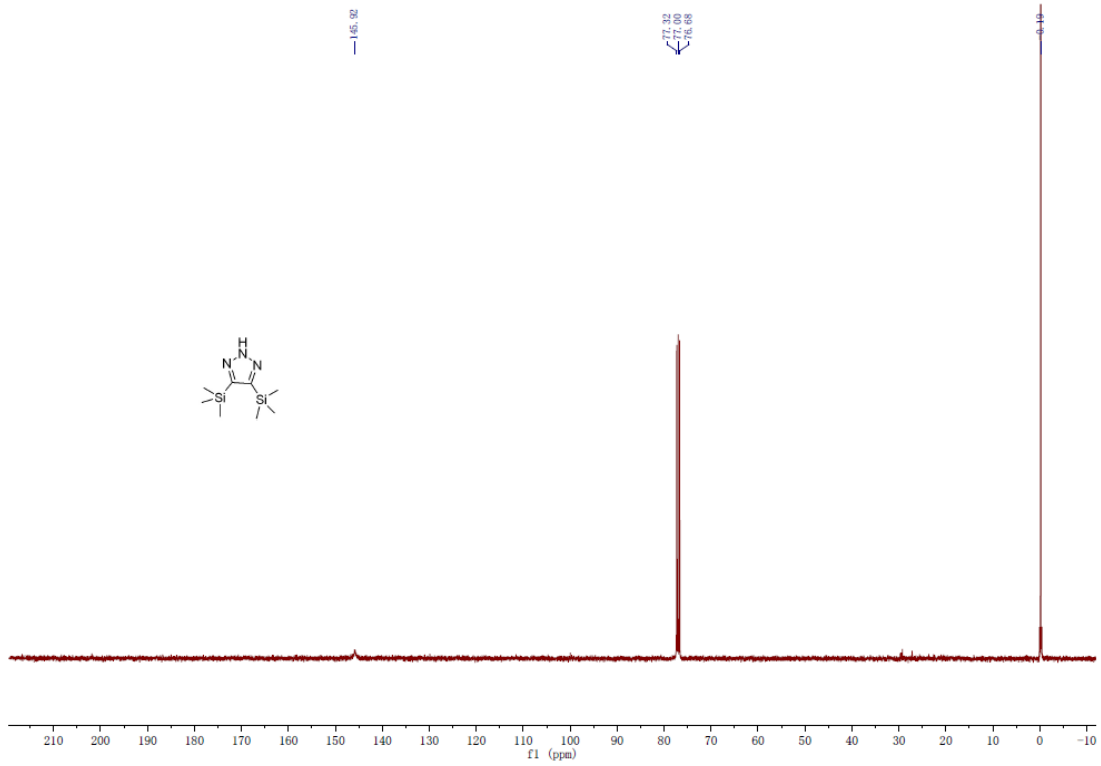
2aa


7.26
2.42
0.34
3.00
8.99
f1 (ppm)

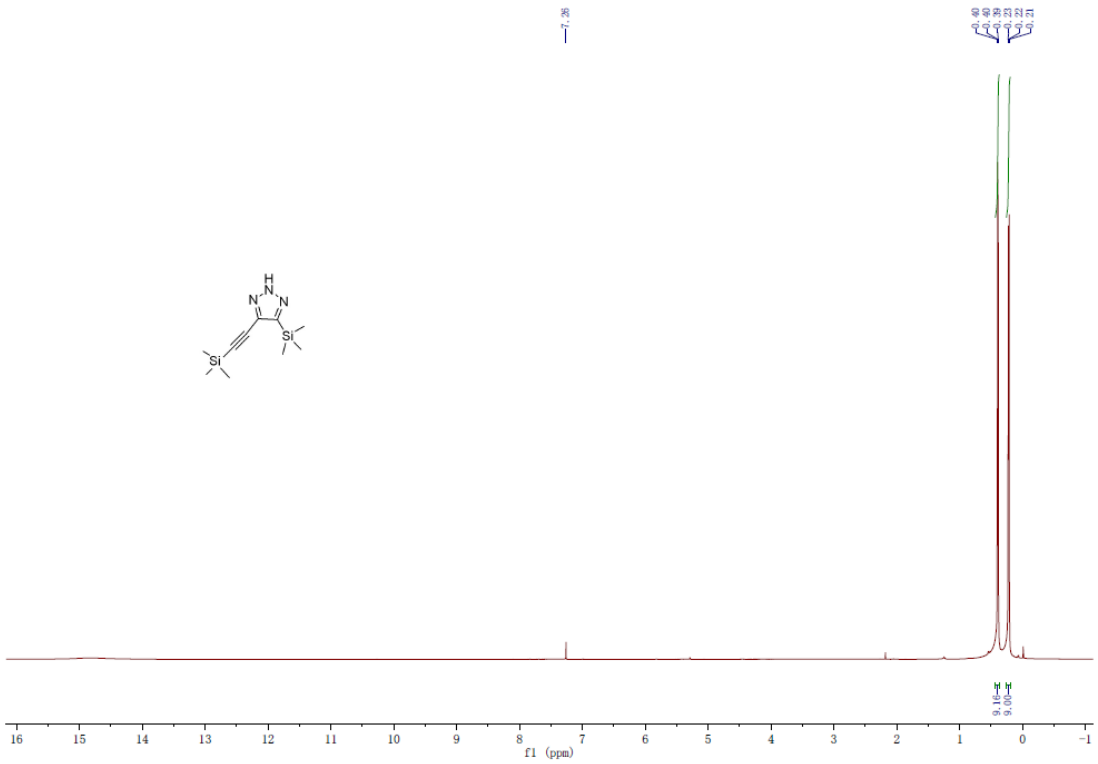

147.71
134.08
77.32
77.00
76.68
11.43
1.30
f1 (ppm)

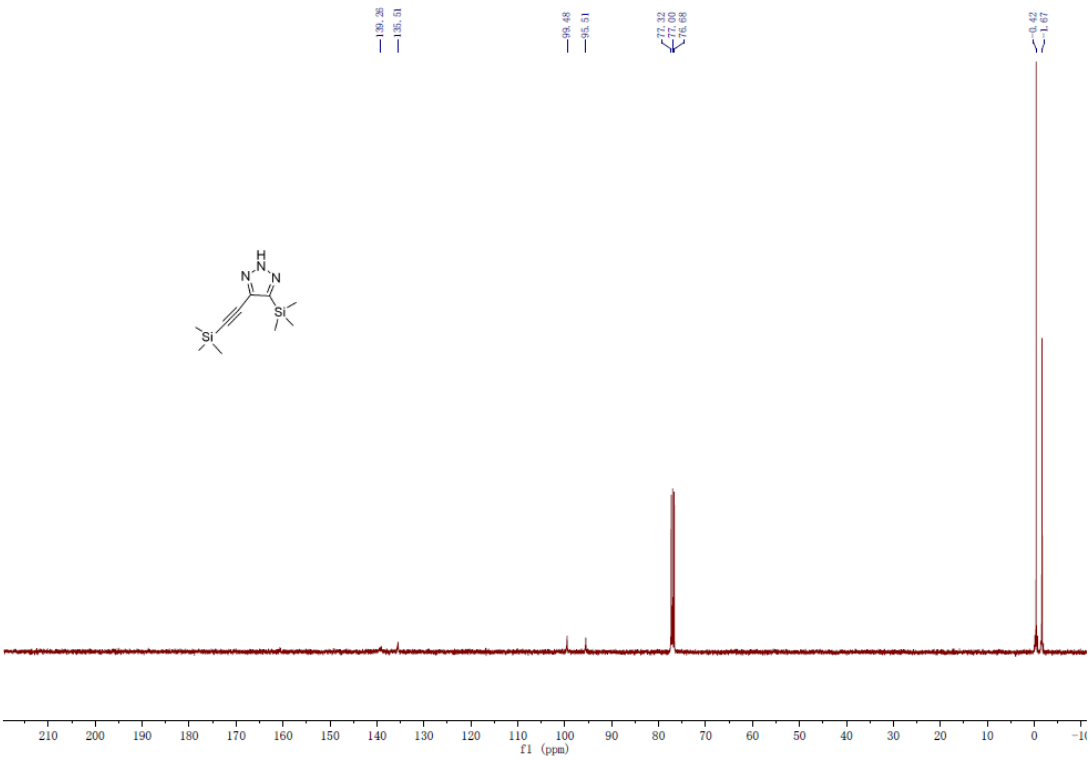
2ab



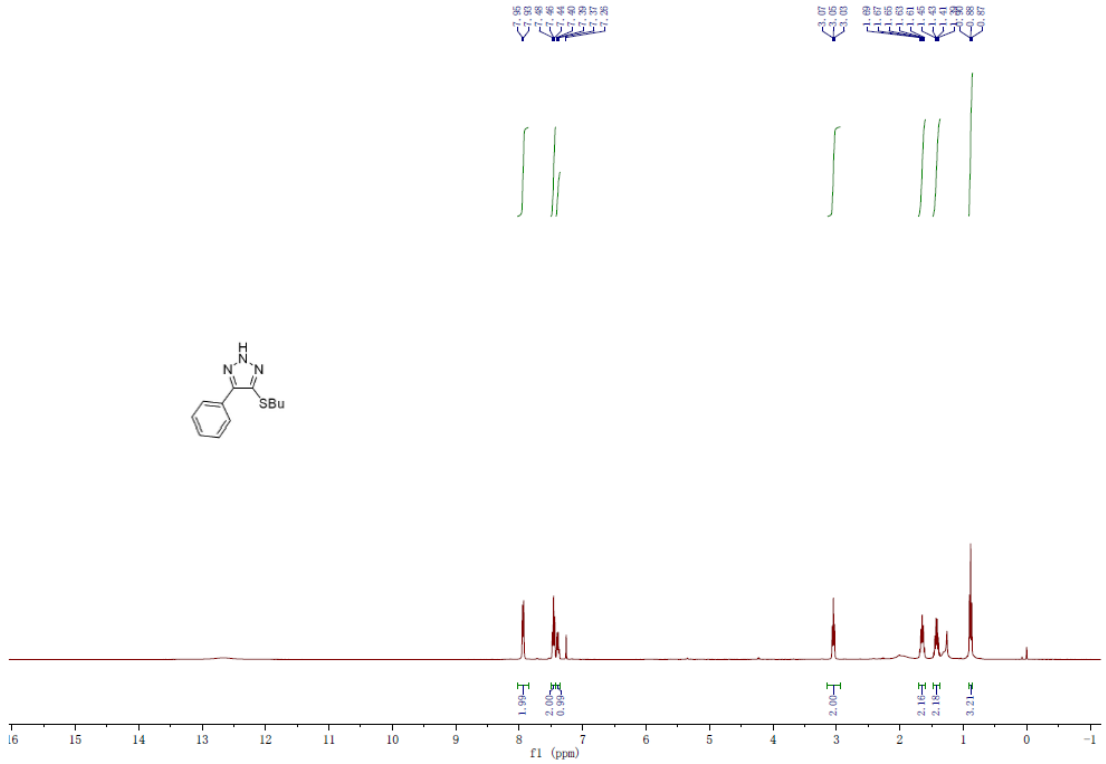


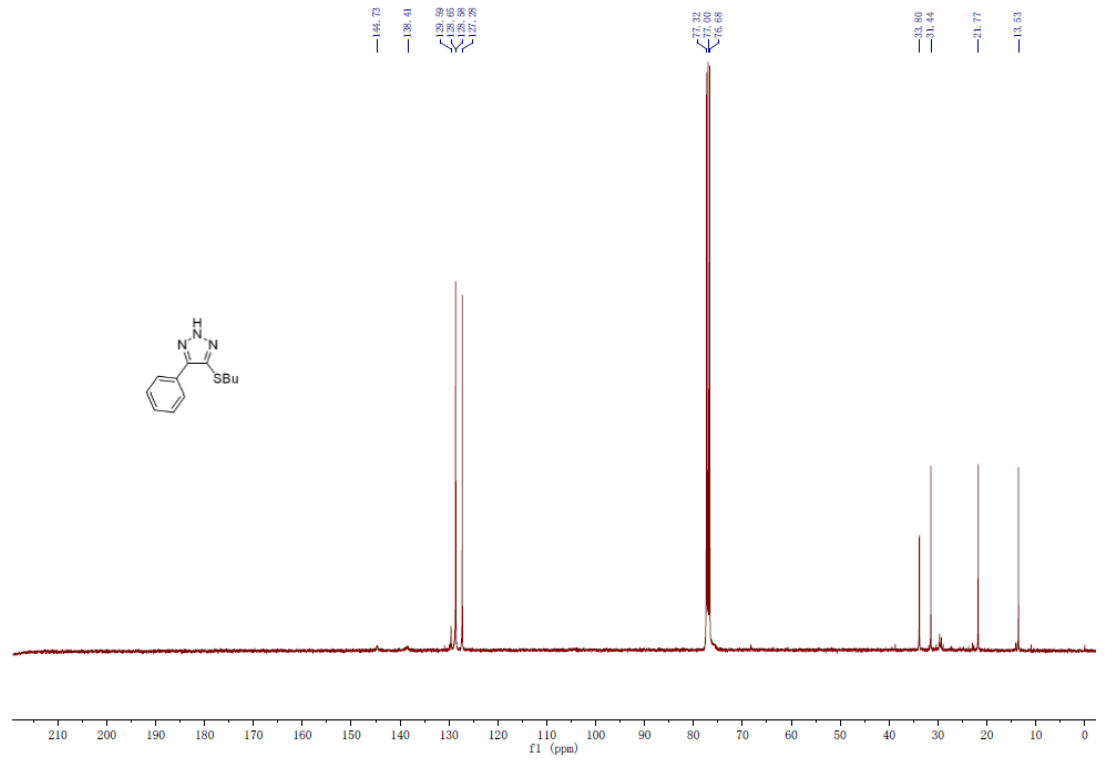
2ac


7.26
0.40
0.39
0.23
0.22
0.21
9.16
9.00
f1 (ppm)

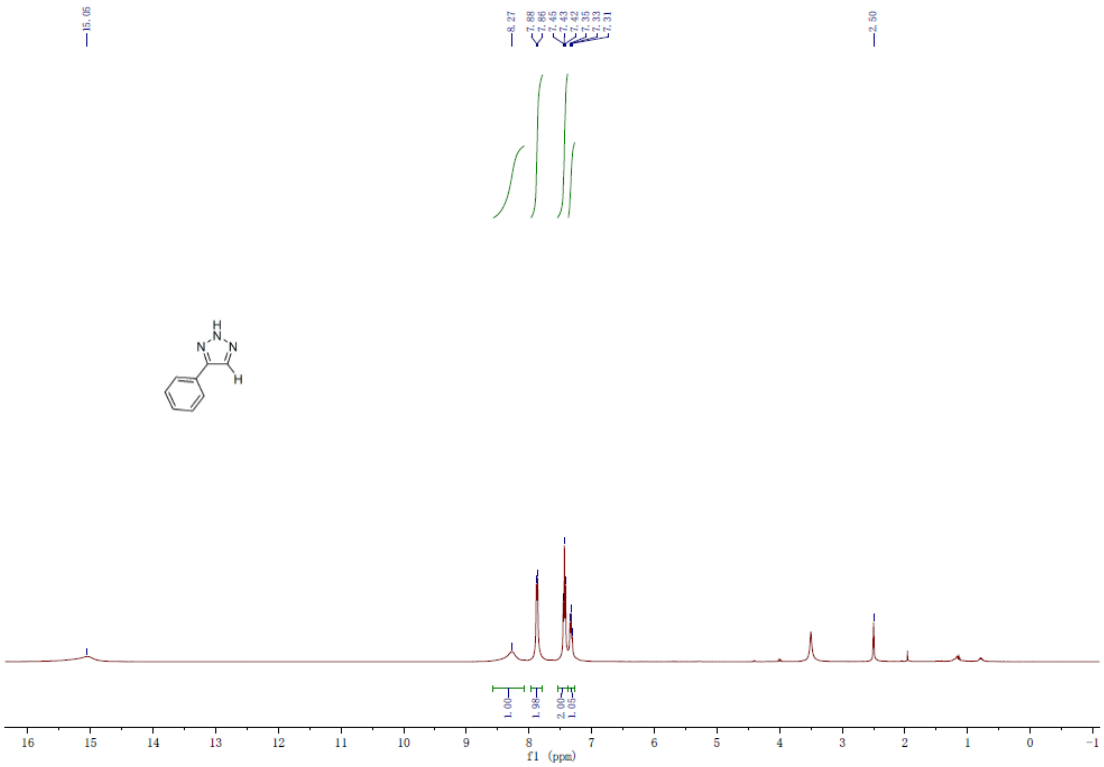

139.26
135.51
99.48
95.51
77.32
77.00
76.68
0.42
-1.67
f1 (ppm)

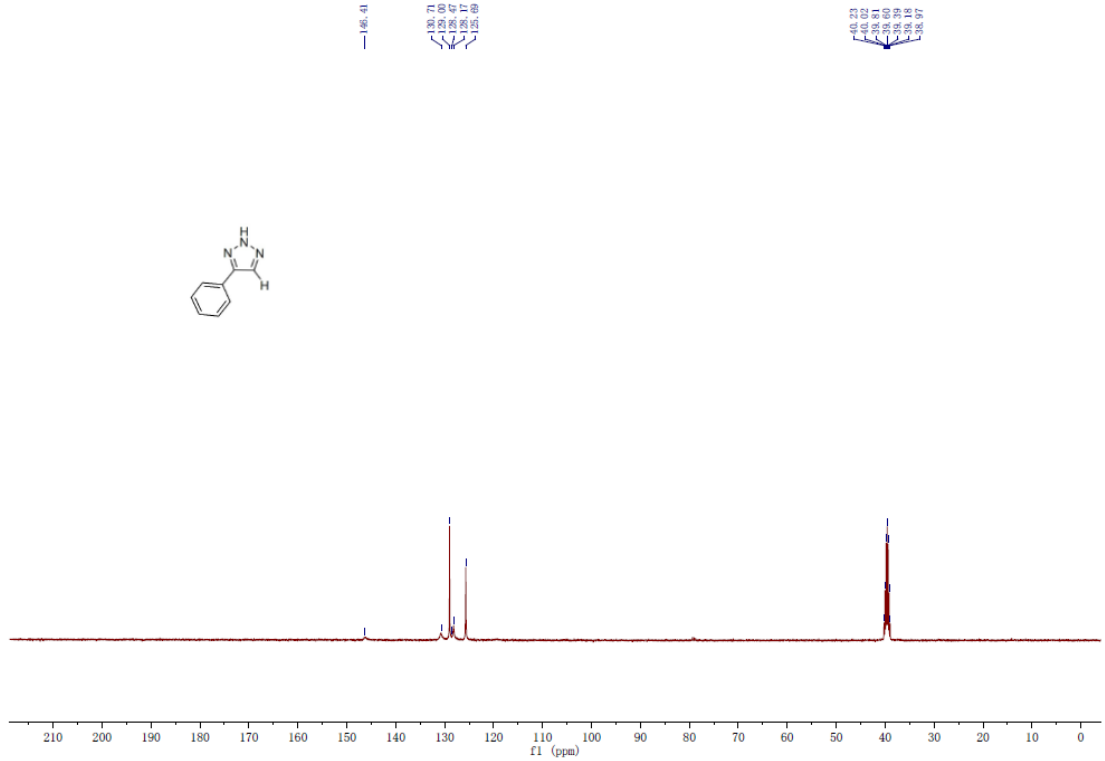
2ae



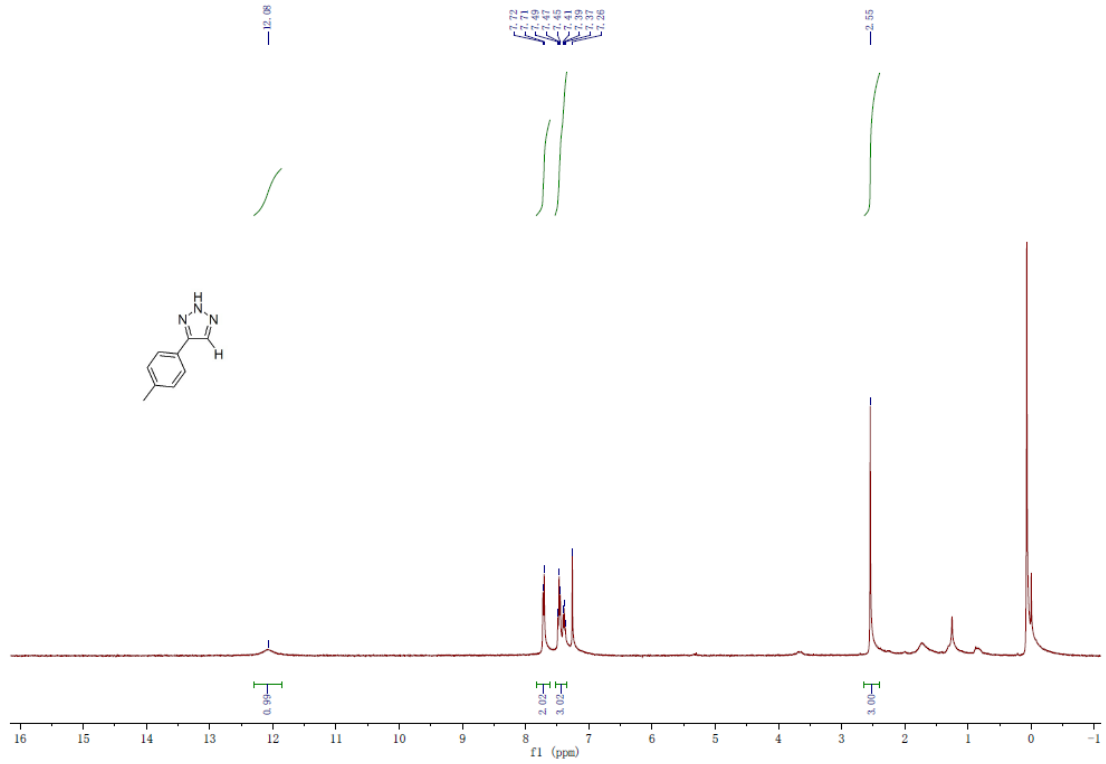


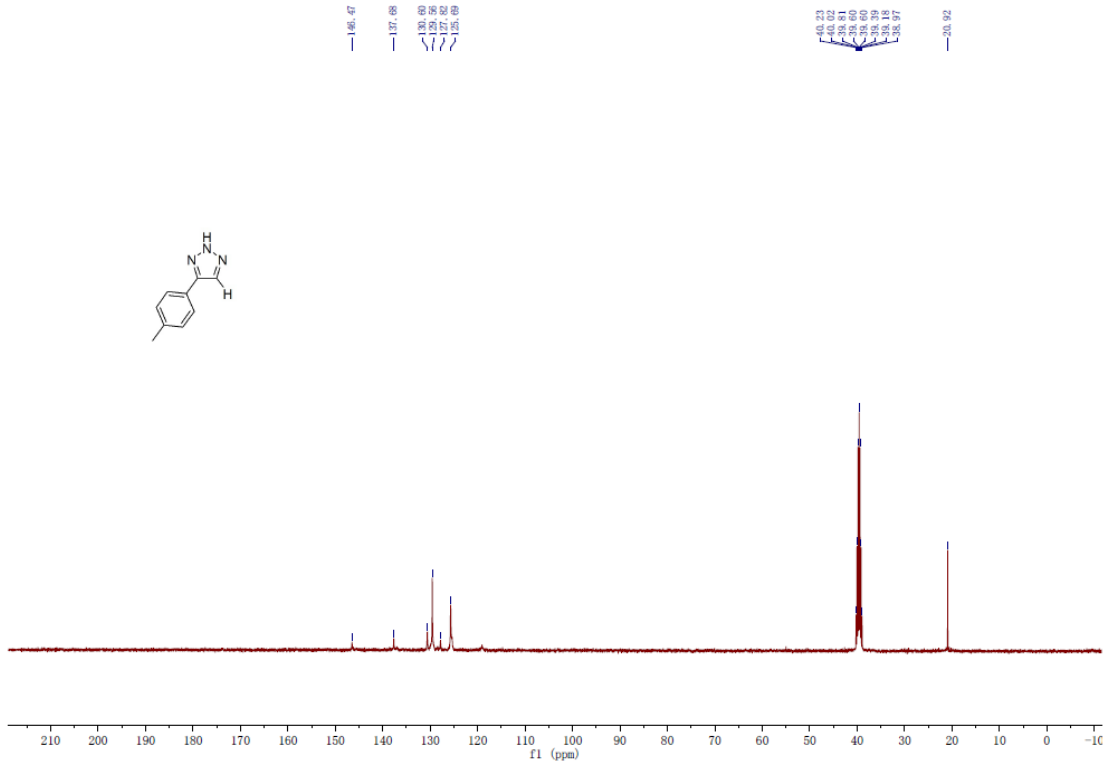
2af


15.05
8.27
7.88
7.86
7.45
7.43
7.42
7.35
7.33
7.31
2.50
1.00
1.98
2.00
1.05
f1 (ppm)

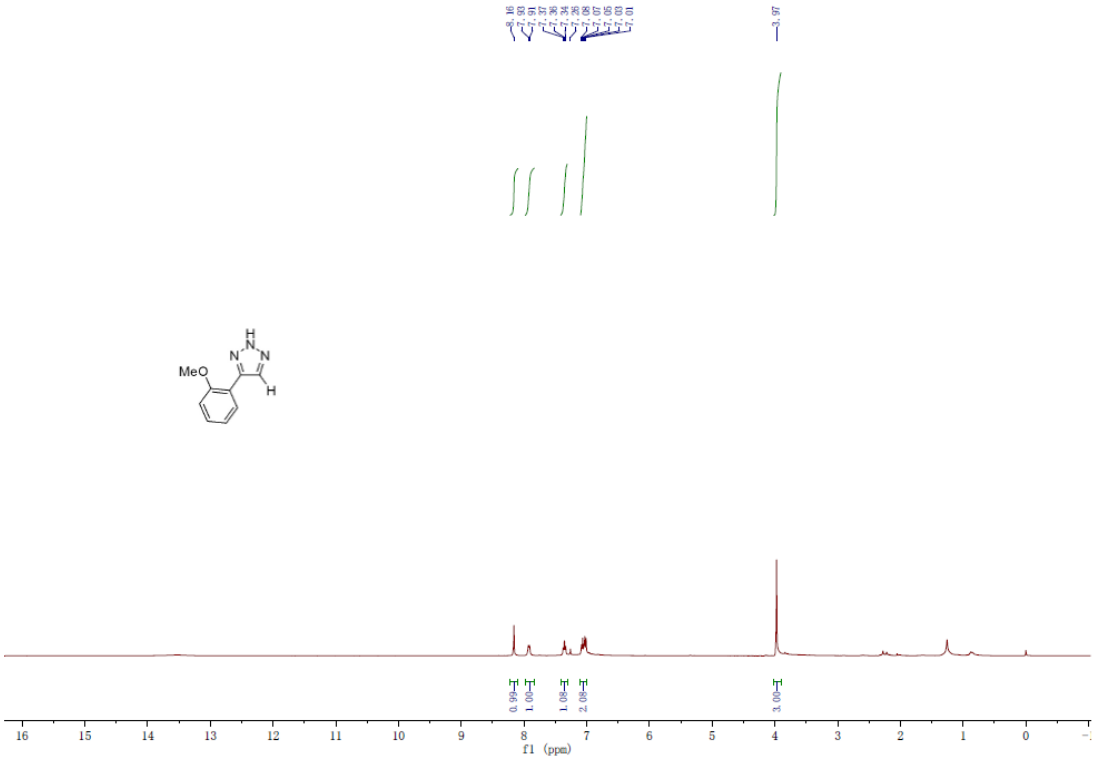

146.41
130.71
129.00
128.47
128.17
125.69
40.23
40.02
39.81
39.60
39.39
39.18
38.97
f1 (ppm)

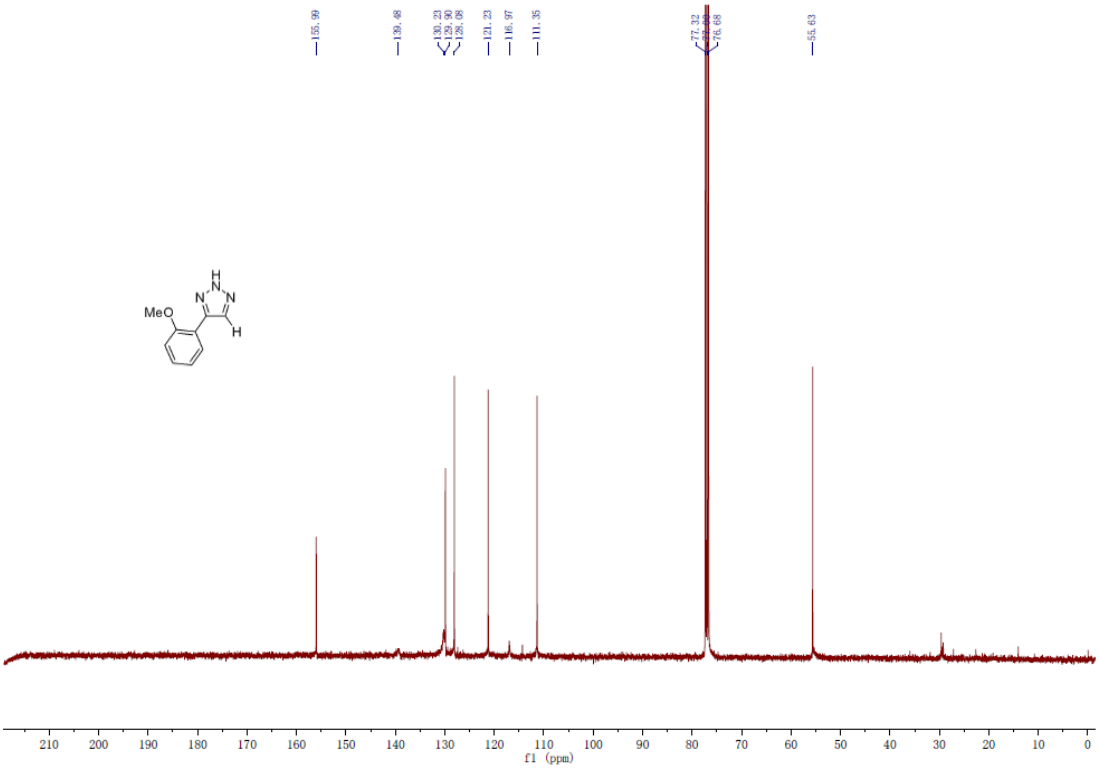
2ag


12.08
7.72
7.71
7.49
7.47
7.46
7.41
7.39
7.37
7.26
2.55
0.99
2.02
3.02
3.00
f1 (ppm)

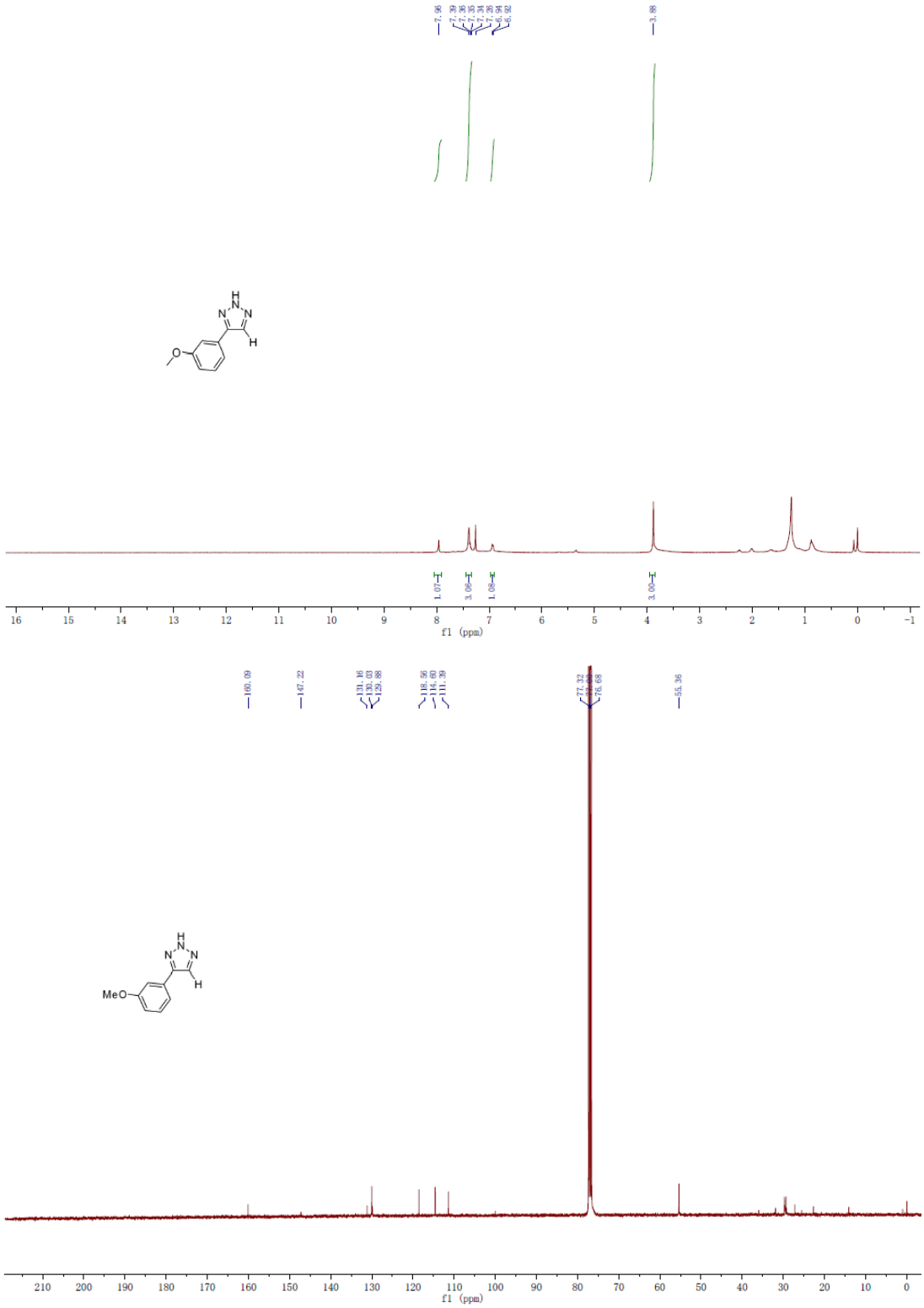

146.47
137.68
130.60
129.55
127.82
125.69
40.23
40.02
39.81
39.60
39.39
39.18
38.97
20.92
f1 (ppm)

2ah

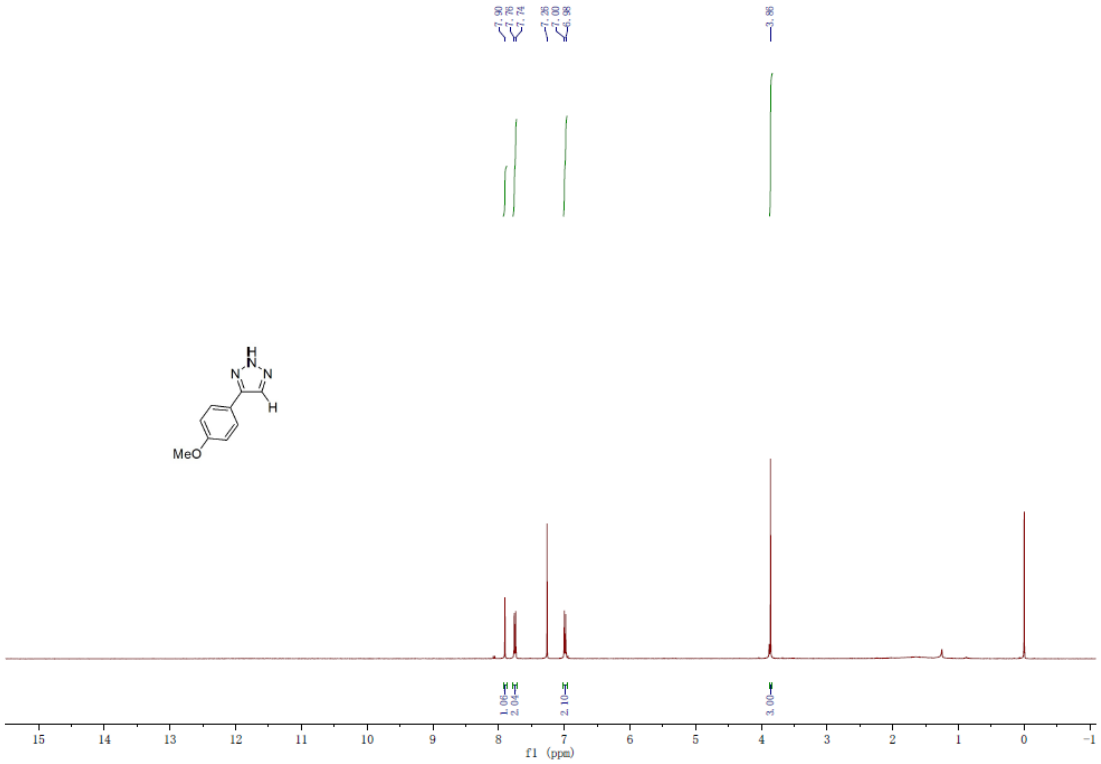

8.16
8.03
7.91
7.37
7.36
7.34
7.25
7.08
7.07
7.05
7.03
7.01
3.97
MeO
H
0.99
1.00
1.08
2.08
3.00
f1 (ppm)

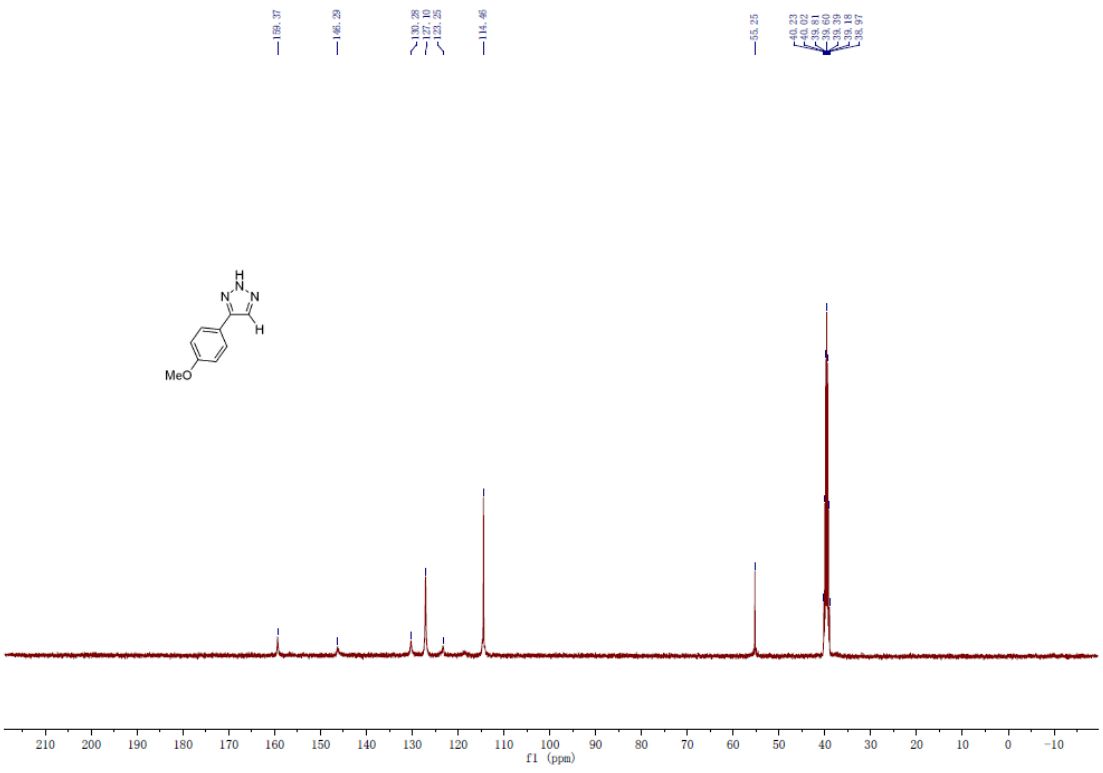

155.99
138.48
130.23
129.90
128.08
121.23
116.97
111.35
77.32
77.00
76.68
55.63
MeO
H
f1 (ppm)

2ai

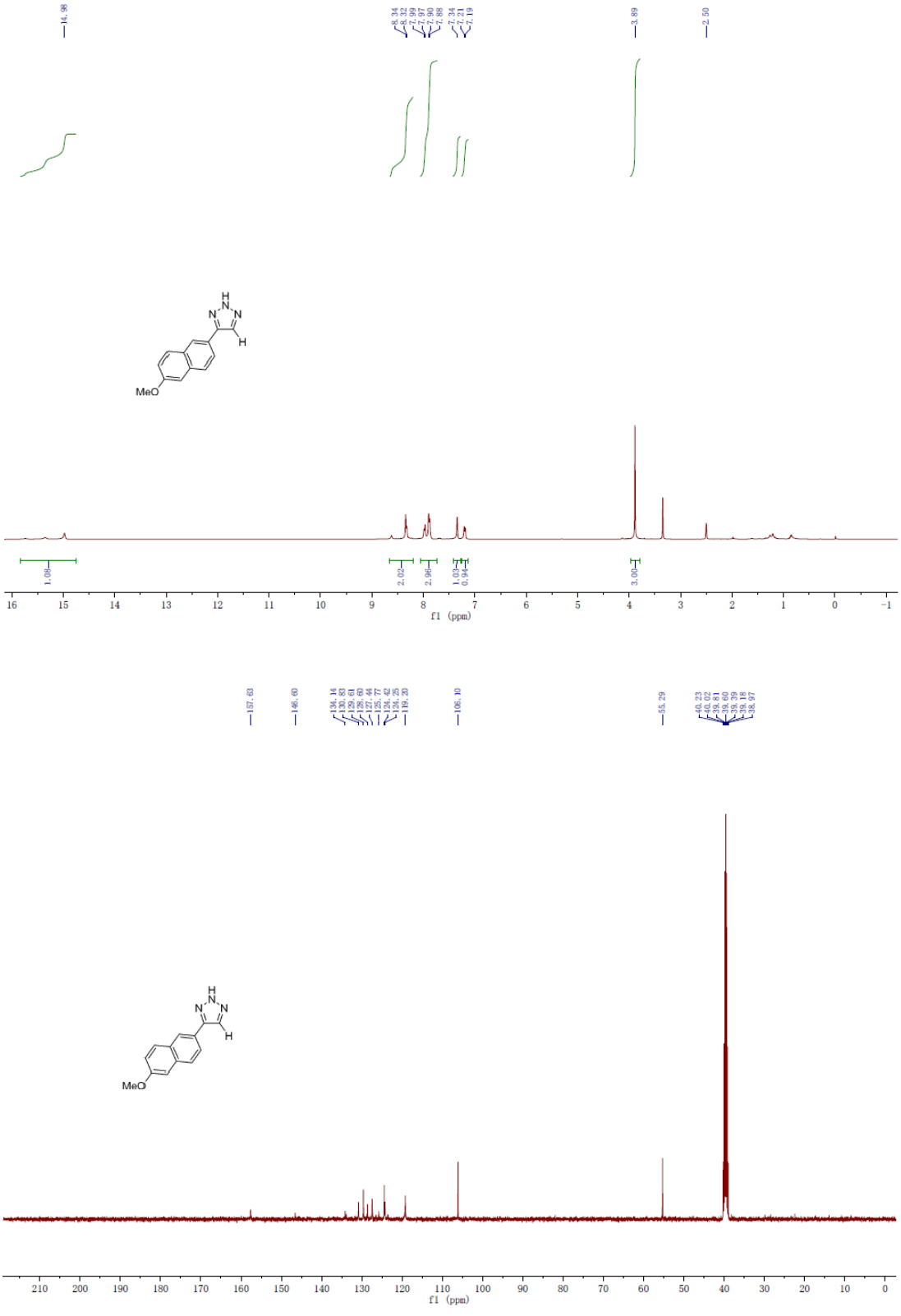

7.96
7.39
7.36
7.35
7.34
7.33
7.32
6.94
6.92
3.88
1.07
3.06
1.08
3.00
f1 (ppm)
160.09
147.22
131.16
130.03
129.88
116.56
114.60
111.39
77.32
76.68
55.36
MeO
f1 (ppm)

2aj


7.90
7.89
7.74
7.26
7.00
6.98
3.86
MeO
1.06
2.04
2.10
3.00
f1 (ppm)


189.37
146.29
130.28
127.40
123.25
114.46
55.25
40.23
40.02
39.81
39.60
39.39
39.18
38.97
MeO
f1 (ppm)

2al


14.98
8.34
8.32
7.99
7.97
7.90
7.88
7.34
7.21
7.19
3.89
2.50
MeO
1.00
2.02
2.98
1.03
0.94
3.00
f1 (ppm)
157.63
146.60
134.14
130.83
129.61
129.08
127.64
125.77
124.42
106.25
105.20
106.10
55.29
40.23
40.02
39.81
39.60
39.39
39.18
38.97
MeO
f1 (ppm)