

Supporting Information

Pentazadiene: a high nitrogen linkage in energetic materials

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Further optimization of reaction condition to synthesize **2a**

Besides EDCI and DCC, 1-[Bis(dimethylamino)methylene]-1*H*-1,2,3-triazolo[4,5-*b*]pyridinium 3-oxid hexafluorophosphate (HATU), another common condensation agent in the construction of amide bond, was utilized to activate **1a** (Table S1, entry 6). However, the product **2a** was not formed. Compared with DMAP, 1-hydroxybenzotriazole (HOBt) had no effect on this reaction (entries 3 and 5).

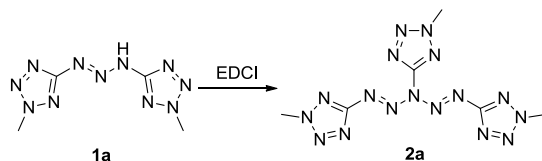
Table S1. Synthesis of **2a** in different activating conditions.^a

entry	activating reagent (equiv.)	yield(%) ^b
1 ^c	DCC (0.6)	trace
2 ^c	DCC (0.6), DMAP (0.2)	53
3	DCC (0.6), HOBt (0.6)	0
4	EDCI (0.6), DMAP (0.2)	56
5	EDCI (0.6), HOBt (0.6)	0
6	HATU (0.6), DIEA (1.0)	0

^a Reactions were carried out with tetrazolyl triazene (0.5 mmol), and activating reagent in CH₂Cl₂ (5 mL) at room temperature. ^b Isolated yield. ^c 72 h.

In EDCI/DMAP condition, low polar solvent provided higher yield (Table S2, entries 1-7). The yield in chloroform was slightly higher than dichloromethane (entry 2). Without DMAP, the yields in most solvents were increasing, whereas no solvent exceeded dichloromethane (entries 9-13). The solution concentration had no effect on this reaction (entries 16-18), neither did extension of time (entries 19 and 20). The reaction was smoothly scaled up to 5.0 mmol, giving **2a** in a 74% yield.

Table S2. Synthesis of **2a** in different reaction conditions.^a



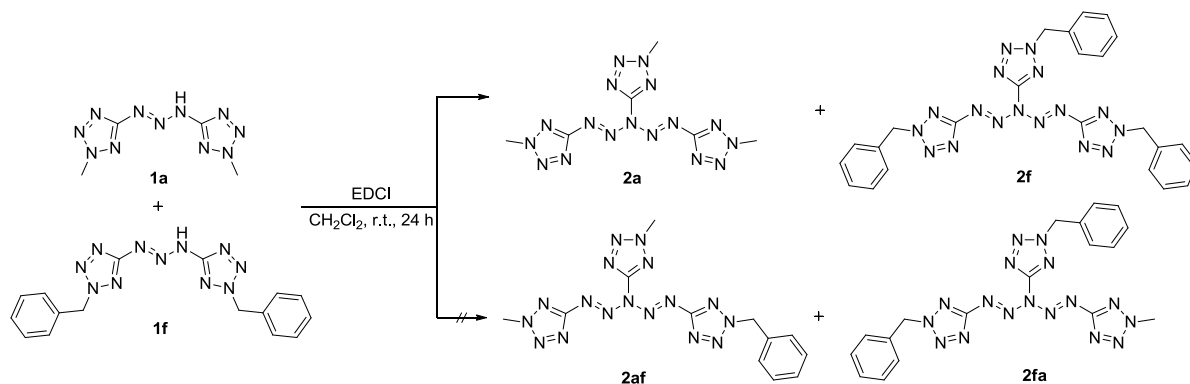
entry	EDCI (equiv.)	DMAP (equiv.)	solvent	conc. (M)	time (h)	yield (%) ^b
1	0.6	0.2	CH ₂ Cl ₂	0.1	24	56
2	0.6	0.2	CHCl ₃	0.1	24	60
3	0.6	0.2	DCE	0.1	24	48
4	0.6	0.2	CH ₃ CN	0.1	24	44
5	0.6	0.2	THF	0.1	24	38
6	0.6	0.2	acetone	0.1	24	35
7	0.6	0.2	DMF	0.1	24	n.r.
8	0.6	0.6	CH ₂ Cl ₂	0.1	24	21
9	0.6	0	CH ₂ Cl ₂	0.1	24	80
10	0.6	0	CHCl ₃	0.1	24	69
11	0.6	0	DCE	0.1	24	65
12	0.6	0	CH ₃ CN	0.1	24	50
13	0.6	0	THF	0.1	24	38
14 ^c	0.5	0	CH ₂ Cl ₂	0.1	24	65
15	1.2	0	CH ₂ Cl ₂	0.1	24	48
16	0.6	0	CH ₂ Cl ₂	0.05	24	78
17	0.6	0	CH ₂ Cl ₂	0.2	24	76
18	0.6	0	CH ₂ Cl ₂	0.5	24	78
19	0.6	0	CH ₂ Cl ₂	0.1	36	78
20	0.6	0	CH ₂ Cl ₂	0.1	48	78
21 ^d	0.6	0	CH ₂ Cl ₂	0.1	24	74

^a Reactions were carried out with tetrazolyltriazene (0.5 mmol), and EDCI at room temperature. ^b Isolated yield. ^c 72 h. ^d On 5.0 mmol scale.

Investigations of mechanism

When **1a** and **1f** were mixed of 1:1 ratio as starting material, cross-reacted product **2af** and **2fa** were not observed in mass spectrum (Scheme S1), which indicated that two molecules of triazenes forming pentaza-1,4-dienes connected with each other by intermolecular forces.

Scheme S1. Cross-reaction of two different substituted tetrazolyl triazenes



The dimer [**1a**] was observed in mass spectrum (Figure S1). In ¹H NMR spectra, the proton signal of amino in triazene employing CD₂Cl₂ as solvent (Figure S2 upper) shift up field, compared with the signal employing DMSO-D₆ (Figure S2 lower). One of the reason is the hydrogen bonds in dimers (-N-H ··· N-) are weaker than the ones between **1a** and DMSO (-N-H ··· O-). Another reason might be strong shielding effect on inner hydrogens surrounded by two molecules in a dimer [**1a**]. The solvents forming strong hydrogen bonds with **1a** (Table S2, entry 4-6) provide lower yield of **2a**, which also implies that the dimer [**1a**] is the active species in this reaction.

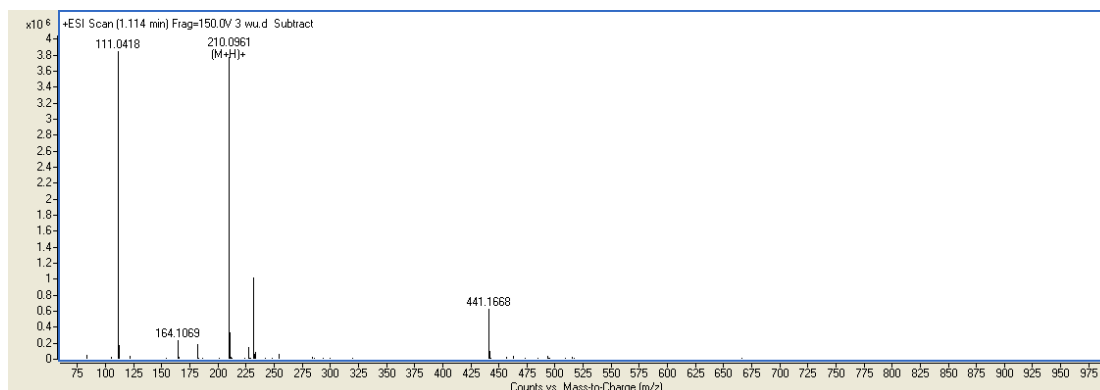


Figure S1. High resolution mass spectrum of **1a** and dimer [**1a**]

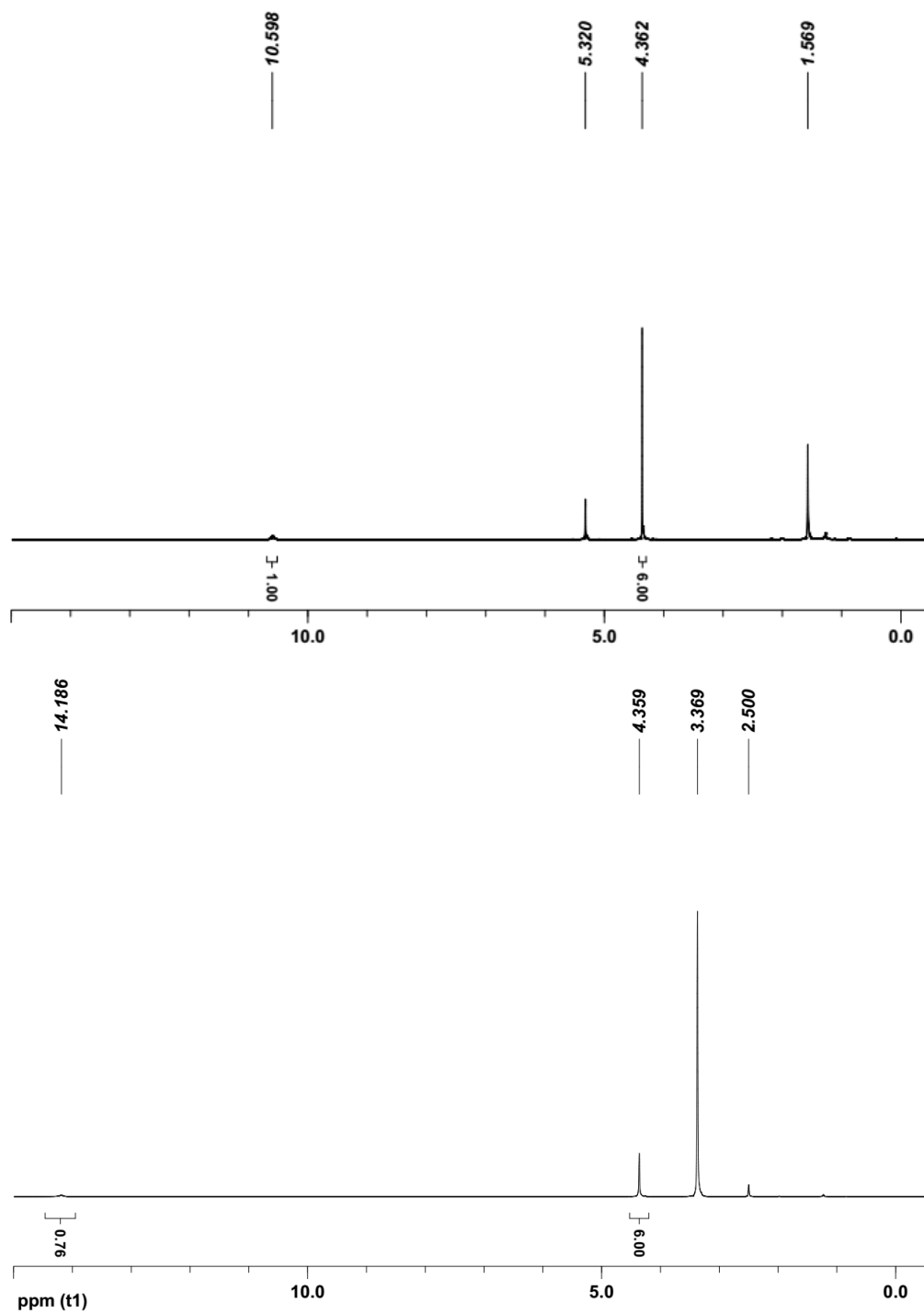


Figure S2. ¹H NMR spectra of **1a** in CD₂Cl₂ (upper) and DMSO-D₆ (lower). The x axis represents the chemical shift δ in ppm

Caution! Due to the fact that tetrazolyl pentazadienes are to some extent rather unstable toward external stimuli, proper safety precautions should be taken when handling the dry materials. Lab personnel and the equipment should be properly grounded and protective equipment such as leather coat, Kevlar gloves, ear protection and face shield are recommended.

General Methods: ^1H and ^{13}C NMR spectra were recorded on a 400 MHz (Bruker Avance 400) nuclear magnetic resonance spectrometers operating at 400 and 100 MHz, respectively, by using CDCl_3 , $[\text{D}_6]\text{DMSO}$ and CD_3CN as solvent and locking solvent. ^{15}N NMR spectra were recorded on a 700 MHz (Bruker Avance 700) nuclear magnetic resonance spectrometers operating at 70 MHz, respectively, by using CD_2Cl_2 and DMF-D7 as solvent and locking solvent. IR spectra were recorded using KBr pellets for solids on a Bruker ALPHA FT-IR-Spektrometer. The melting and decomposition points were obtained on a differential scanning calorimeter (METTLER TOLEDO) at a scan rate of $5\text{ }^\circ\text{C min}^{-1}$. Elemental analyses were carried out using an Elementar Vario EL element analyzer. High resolution mass spectrometry was recorded on Bruker Apex IV FTMS. Details of the X-ray diffraction analysis of **2a** are presented. Data were collected on a Rigaku Saturn 724 CCD diffractometer employing graphite-monochromated MoK α radiation ($\lambda=0.71073\text{ \AA}$) using omega scans.

X-ray diffraction: For compound **2a**, data were collected on a Rigaku Saturn 724 CCD diffractometer employing graphite-monochromated MoK α radiation ($\lambda=0.71073\text{ \AA}$) using omega scans. Data collection and reduction were performed and the unit cell was initially refined using Crystal Clear SM Expert 2.0 r2.¹ The reflection data were corrected for Lorentz-polarization factors. The structure was solved by direct methods and refined by the least-squares method on F^2 using the SHELXTL-97 suite of programs.² All non-hydrogen atoms were refined anisotropically. The structure of **2a** was solved in the space group $P2_1/c$ by analysis of systematic absences.

Compound **1a** and **1j** were synthesized according as literature.³

General procedure to synthesize substituted tetrazolyl triazene **1c-1h**

NaNO_2 (0.690 g, 10 mmol) in 40 mL water was added dropwise to a solution of 2-substituted-5-aminotetrazole (20 mmol) and concentrated HCl (4 mL, 48 mmol) in 100 mL water at $0\text{ }^\circ\text{C}$. After 2 h, the reaction stirred additional 2 h at room temperature. The precipitate was filtered, washed with water, and dried to provide high purity product.

In all the ^{13}C NMR spectra of the tetrazolyl triazene, the carbon atom of tetrazole rings (165.4-169.0 ppm) were hard to be found due to the weak resonance, even not in **1b** and **1f**.

1,3-bis(2-allyltetrazol-5-yl)triazene (1c). Yield 2.195 g (84%) of product **1c**.

White solid (**1c**): m.p. $50\text{-}52\text{ }^\circ\text{C}$. IR (KBr): $\tilde{\nu} = 3497, 3451, 2770, 1639, 1597, 1461, 1227, 1044, 930, 810, 557\text{ cm}^{-1}$. ^1H NMR (400 MHz, $[\text{D}_6]\text{DMSO}$): $\delta = 14.26$ (s, 1H), 6.07-6.14 (m, 2H), 5.31-5.36 (m, 8H) ppm. ^{13}C NMR (100 MHz, $[\text{D}_6]\text{DMSO}$): $\delta = 168.8, 130.6, 120.3, 55.3$ ppm. HRMS: calc. for $\text{C}_8\text{H}_{12}\text{N}_{11}$ $[\text{M}+\text{H}]^+$: 262.1272; found:

262.1270.

1,3-bis(2-tert-butyltetrazol-5-yl)triazene (1d). Yield 2.442 g (83%) of product **1d**.

White solid (**1d**): m.p. 169-170 °C. IR (KBr): $\tilde{\nu}$ = 3181, 3133, 2989, 2940, 1595, 1481, 1387, 1373, 1342, 1314, 1279, 1217, 1189, 1020, 941, 826, 760 cm^{-1} . ^1H NMR (400 MHz, [D6]DMSO): δ = 14.10 (s, 1H), 1.69 (s, 18H) ppm. ^{13}C NMR (100 MHz, [D6]DMSO): δ = 168.2, 64.2, 28.6 ppm. HRMS: calc. for $\text{C}_{10}\text{H}_{20}\text{N}_{11}$ $[\text{M}+\text{H}]^+$: 294.1898; found: 294.1901.

1,3-bis(2-bromoethyltetrazol-5-yl)triazene (1e). Yield 3.522 g (89%) of product **1e**.

White solid (**1e**): m.p. 131-133 °C. IR (KBr): $\tilde{\nu}$ = 3034, 2979, 2876, 1587, 1458, 1426, 1308, 1258, 1204, 1040, 959, 874, 744 cm^{-1} . ^1H NMR (400 MHz, [D6]DMSO): δ = 14.34 (s, 1H), 5.14 (t, $J=5.6$ Hz, 4H), 4.05 (t, $J=5.6$ Hz, 4H) ppm. ^{13}C NMR (100 MHz, [D6]DMSO): δ = 169.0, 54.6, 29.9 ppm. HRMS: calc. for $\text{C}_9\text{H}_{12}\text{Br}_3\text{N}_{17}$ $[\text{M}+\text{H}]^+$: 395.9467; found: 395.9463.

1,3-bis(2-methoxycarbonylmethyltetrazol-5-yl)triazene (1f). Yield 2.695 g (83%) of product **1f**.

White solid (**1f**): m.p. 84-86 °C. IR (KBr): $\tilde{\nu}$ = 3539, 3464, 3007, 2964, 1735, 1583, 1454, 1363, 1241, 1043, 986, 790, 738 cm^{-1} . ^1H NMR (400 MHz, [D6]DMSO): δ = 14.45 (s, 1H), 5.86 (s, 4H), 3.75 (s, 6H) ppm. ^{13}C NMR (100 MHz, [D6]DMSO): δ = 166.4, 53.6, 52.9 ppm. HRMS: calc. for $\text{C}_{12}\text{H}_{15}\text{N}_{17}\text{O}_6$ $[\text{M}+\text{H}]^+$: 326.1068; found: 326.1067.

1,3-bis(2-cyanomethyltetrazol-5-yl)triazene (1g). Yield 2.241 g (86%) of product **1g**.

White solid (**1g**): m.p. 79-81 °C. IR (KBr): $\tilde{\nu}$ = 3490, 3454, 2999, 1603, 1468, 1378, 1301, 1229, 1041, 936, 828, 776, 741 cm^{-1} . ^1H NMR (400 MHz, [D6]DMSO): δ = 14.61 (s, 1H), 6.24 (s, 4H) ppm. ^{13}C NMR (100 MHz, [D6]DMSO): δ = 166.2, 113.4, 41.1 ppm. HRMS: calc. for $\text{C}_9\text{H}_6\text{N}_{20}$ $[\text{M}+\text{H}]^+$: 260.0864; found: 260.0864.

1,3-bis(2-vinyltetrazol-5-yl)triazene (1h). Yield 1.990 g (85%) of product **1h**.

White solid (**1h**): m.p. 157-158 °C (dec.). IR (KBr): $\tilde{\nu}$ = 3180, 3135, 3018, 1600, 1488, 1386, 1328, 1228, 1196, 1010, 952, 936, 789, 722 cm^{-1} . ^1H NMR (400 MHz, [D6]DMSO): δ = 14.45 (s, 1H), 7.77 (dd, $J=15.4$, 8.6 Hz, 2H), 6.09 (d, $J=15.2$, 2H), 5.49 (d, $J=7.6$, 2H) ppm. ^{13}C NMR (100 MHz, [D6]DMSO): δ = 165.4, 130.1, 109.2 ppm. HRMS: calc. for $\text{C}_9\text{H}_9\text{N}_{17}$ $[\text{M}+\text{H}]^+$: 234.0959; found: 234.0962.

1,3-bis(2-benzyltetrazol-5-yl)triazene (1b). Yield 2.007 g (55%) of product **1b**.

NaNO_2 (0.690 g, 10 mmol) in 20 mL water was added dropwise to a solution of 2-benzyl-5-aminotetrazole (3.504 g, 20 mmol) and concentrated HCl (4 mL, 48 mmol) in 40 mL water and 40 mL THF at 0 °C. After 2 h, the reaction stirred additional 2 h at room temperature. The precipitate was filtered, washed with water, and dried to provide high purity product.

White solid (**1b**): m.p. 66-68 °C. IR (KBr): $\tilde{\nu}$ = 3535, 3474, 1602, 1466, 1225, 1034, 824, 744, 716 cm^{-1} . ^1H NMR (400 MHz, [D₆]DMSO): δ = 14.25 (s, 1H), 7.39 (s, 10H), 5.92 (s, 4H) ppm. ^{13}C NMR (100 MHz, [D₆]DMSO): δ = 133.7, 128.8, 128.6, 128.3, 56.4 ppm. HRMS: calc. for $\text{C}_{24}\text{H}_{21}\text{N}_{17}$ [M+H]⁺: 362.1585; found: 362.1589.

1,3-bis(2-hydroxyethyltetrazol-5-yl)triazene (1i). Yield 1.863 g (69%) of product **1i**.

NaNO_2 (0.690 g, 10 mmol) in 4 mL water was added dropwise to a solution of 2-hydroxyethyl-5-amino-tetrazole (2.582 g, 20 mmol) and concentrated HCl (2 mL, 24 mmol) in 10 mL water at 0 °C. After 2 h, the reaction stirred additional 2 h at room temperature. The precipitate was filtered, washed with filtrate, and dried to provide high purity product.

White solid (**1i**): m.p. 132-133 °C. IR (KBr): $\tilde{\nu}$ = 3412, 3309, 2931, 2816, 1603, 1472, 1316, 1220, 1068, 966, 862, 790, 744 cm^{-1} . ^1H NMR (400 MHz, [D₆]DMSO): δ = 14.19 (s, 1H), 5.09 (s, 2H), 4.70 (t, J =5.0 Hz, 4H), 3.93 (d, J =2.8 Hz, 4H) ppm. ^{13}C NMR (100 MHz, [D₆]DMSO): δ = 165.6, 59.0, 56.2 ppm. HRMS: calc. for $\text{C}_9\text{H}_{15}\text{N}_{17}\text{O}_3$ [M+H]⁺: 270.1170; found: 270.1172.

General procedure to synthesize substituted tetrazolyl pentazadiene **2a-2f**, **2h**, **2i**

1,3-Bis(2-substituted-tetrazol-5-yl)triazene (**1a-1f**, **1h**, **1i**, 0.5 mmol) and 1-(3-dimethylaminoprop-yl)-3-ethyl-carbodiimide hydrochloride (EDCI, 58 mg, 0.3 mmol) were dissolved in 5 mL CH_2Cl_2 at room temperature. After stirring for 24 h, the reaction mixture was concentrated under reduced pressure and the residue purified by column chromatography to provide 1,3,5-tri(2-substituted-tetrazol-5-yl)pentazadiene (**2a-2f**, **2h**, **2i**). After recrystallization from PE/ CH_2Cl_2 , high purity product was obtained.

1,3,5-tri(2-methyltetrazol-5-yl)pentazadiene (2a). Yield 64 mg (80%) of product **2a**.

White solid (**2a**): DSC (5 °C min⁻¹): 141 °C (dec.). IR (KBr): $\tilde{\nu}$ = 1495, 1466, 1397, 1202, 1154, 1077, 942, 761, 720, 576 cm^{-1} . ^1H NMR (400 MHz, CDCl_3): δ = 4.50 (s, 3H), 4.41 (s, 6H) ppm. ^{13}C NMR (100 MHz, CDCl_3): δ = 167.7, 153.8, 40.8, 40.2 ppm. ^{15}N NMR (70 MHz, CD_2Cl_2): δ = 85.3 (N6), 10.7 (N5), 9.5 (N3), 4.8 (N10), -44.0 (N4), -56.5 (N11), -69.3 (N1), -82.6 (N8), -97.1 (N2), -101.4 (N9), -138.4 (N7) ppm. Elemental analysis: ($\text{C}_6\text{H}_9\text{N}_{17}$, 319.12) calc.: C 22.57, H 2.84, N 74.59; found: C 22.83, H 2.87, N 74.30. HRMS: calc. for $\text{C}_6\text{H}_9\text{N}_{17}$ [M+H]⁺: 320.1300; found: 320.1295.

Another procedure to synthesize **2a**.

When the reaction completed, 20 mL CH_2Cl_2 and 10 mL concentrated HCl were added to the reaction mixture. After rapid extraction, the organic layer was washed with saturated NaHCO_3 (30 mL \times 2) and brine (30 mL), dry over Na_2SO_4 , evaporated under reduced pressure. The crude product was purified by recrystallization from PE/ CH_2Cl_2 (60 mg, 75%).

1,3,5-tri(2-benzyltetrazol-5-yl)pentazadiene (2b). Yield 94 mg (70%) of product **2b**.

White solid (**2b**): DSC (5 °C min⁻¹): 132 °C (dec.), 236 °C (dec.). IR (KBr): $\tilde{\nu}$ = 3065, 3032, 3017, 1487, 1472, 1334, 1246, 1204, 1159, 1117, 1071, 1037, 955, 723, 595 cm⁻¹. ¹H NMR (400 MHz, CDCl₃): δ = 7.38 (s, 15H), 5.85 (s, 2H), 5.78 (s, 4H) ppm. ¹³C NMR (100 MHz, CDCl₃): δ = 167.7, 153.8, 132.3, 131.9, 129.3, 129.2, 129.1, 128.6, 128.5, 58.1, 57.7 ppm. Elemental analysis: (C₂₄H₂₁N₁₇, 547.22) calc.: C 52.65, H 3.87, N 43.49; found: C 53.19, H 3.87, N 42.95. HRMS: calc. for C₂₄H₂₁N₁₇ [M+H]⁺: 548.2239; found: 548.2239.

1,3,5-tri(2-allyltetrazol-5-yl)pentazadiene (2c). Yield 72 mg (72%) of product **2c**.

White solid (**2c**): DSC (5 °C min⁻¹): 99 °C (m.p.); 100 °C (dec.). IR (KBr): $\tilde{\nu}$ = 3098, 2988, 1487, 1472, 1460, 1424, 1173, 1156, 1074, 1036, 957, 788, 720, 576 cm⁻¹. ¹H NMR (400 MHz, CDCl₃): δ = 6.03-6.20 (m, 3H), 5.40-5.49 (m, 6H), 5.33 (dt, ³J=6.4 Hz, 2H), 5.25 (dt, ³J=6.4 Hz, 4H) ppm. ¹³C NMR (100 MHz, CDCl₃): δ = 167.7, 153.8, 128.9, 128.6, 122.1, 121.8, 56.7, 56.2 ppm. Elemental analysis: (C₁₂H₁₅N₁₇, 397.17) calc.: C 36.27, H 3.80, N 59.92; found: C 37.11, H 3.41, N 59.47. HRMS: calc. for C₁₂H₁₅N₁₇ [M+H]⁺: 398.1769; found: 398.1772.

1,3,5-tri(2-tert-butyltetrazol-5-yl)pentazadiene (2d). Yield 83 mg (75%) of product **2d**.

White solid (**2d**): DSC (5 °C min⁻¹): 135 °C (dec.). IR (KBr): $\tilde{\nu}$ = 2989, 2940, 1486, 1455, 1373, 1313, 1240, 1190, 1172, 1144, 1067, 945, 758, 638 cm⁻¹. ¹H NMR (400 MHz, CDCl₃): δ = 1.80 (s, 9H), 1.75 (s, 18H) ppm. ¹³C NMR (100 MHz, CDCl₃): δ = 167.3, 153.2, 66.0, 65.2, 29.2 ppm. Elemental analysis: (C₁₅H₂₇N₁₇, 445.26) calc.: C 40.44, H 6.11, N 53.45; found: C 41.43, H 6.04, N 52.53. HRMS: calc. for C₁₅H₂₇N₁₇ [M+H]⁺: 446.2708; found: 446.2713.

1,3,5-tri(2-bromoethyltetrazol-5-yl)pentazadiene (2e). Yield 109 mg (73%) of product **2e**.

White solid (**2e**): DSC (5 °C min⁻¹): 123 °C (m.p.); 124 °C (dec.). IR (KBr): $\tilde{\nu}$ = 3013, 2968, 1492, 1459, 1430, 1401, 1364, 1309, 1257, 1165, 1077, 942, 881, 760, 587, 570 cm⁻¹. ¹H NMR (400 MHz, CDCl₃): δ = 5.16 (t, *J*=6.8 Hz, 2H), 5.07 (t, *J*=6.4 Hz, 4H), 3.94 (t, *J*=6.8 Hz, 2H), 3.90 (t, *J*=6.4 Hz, 4H) ppm. ¹³C NMR (100 MHz, CDCl₃): δ = 167.7, 153.9, 55.2, 54.8, 26.7, 26.1 ppm. HRMS: calc. for C₉H₁₂Br₃N₁₇ [M+H]⁺: 597.9069; found: 597.9055.

1,3,5-tri(2-methoxycarbonylmethyltetrazol-5-yl)pentazadiene (2f). Yield 92 mg (75%) of product **2f**.

White solid (**2f**): DSC (5 °C min⁻¹): 120 °C (m.p.); 121 °C (dec.), 221 °C (dec.). IR (KBr): $\tilde{\nu}$ = 3015, 2962, 1758, 1497, 1471, 1440, 1358, 1227, 1163, 1076, 992, 942, 804, 756, 595, 580 cm⁻¹. ¹H NMR (400 MHz, CDCl₃): δ = 5.57 (s, 2H), 5.47 (s, 4H), 3.85 (s, 3H), 3.81 (s, 6H) ppm. ¹³C NMR (100 MHz, CDCl₃): δ = 167.8, 164.8, 164.4, 154.0, 54.3, 53.8, 53.6, 53.5 ppm. Elemental analysis: (C₁₂H₁₅N₁₇O₆, 493.14) calc.: C 29.21, H 3.06, N 48.26; found: C 29.80, H 2.56, N 48.18. HRMS: calc. for C₁₂H₁₅N₁₇O₆ [M+H]⁺: 494.1464; found: 494.1465.

1,3,5-tri(2-vinyltetrazol-5-yl)pentazadiene (2h). Yield 72 mg (81%) of product **2h**.

White solid (**2h**): DSC (5 °C min⁻¹): 122 °C (dec.). IR (KBr): $\tilde{\nu}$ = 3129, 3104, 1644, 1493, 1468, 1410, 1385, 1175, 1153, 1074, 1032, 1007, 944, 914, 744 cm⁻¹. ¹H NMR (400 MHz, CDCl₃): δ = 7.58 (dd, *J*=15.8, 8.6 Hz, 1H), 7.54 (dd, *J*=15.6, 8.4 Hz, 2H), 6.33 (dd, *J*=15.6, 1.6 Hz, 1H), 6.32 (dd, *J*=15.8, 1.8 Hz, 2H), 5.58 (dd, *J*=8.8, 1.6 Hz, 1H), 5.50 (dd, *J*=8.4, 1.6 Hz, 2H) ppm. ¹³C NMR (100 MHz, CDCl₃): δ = 167.1, 153.6, 129.8, 129.7, 111.2, 110.4 ppm. HRMS: calc. for C₉H₉N₁₇ [M+H]⁺: 356.1300; found: 356.1305.

1,3,5-tri(2-hydroxyethyltetrazol-5-yl)pentazadiene (2i). Yield 38 mg (37%) of product **2i**.

White solid (**2i**): DSC (5 °C min⁻¹): 118 °C (m.p.); 119 °C (dec.). IR (KBr): $\tilde{\nu}$ = 3390, 2939, 1591, 1492, 1401, 1212, 1165, 1077, 944, 870, 760 cm⁻¹. ¹H NMR (400 MHz, CD₃CN): δ = 4.88 (t, *J*=5.2 Hz, 2H), 4.75 (t, *J*=5.0 Hz, 4H), 4.10 (dd, *J*=10.4, 5.2 Hz, 2H), 4.05 (dd, *J*=10.6, 5.8 Hz, 4H), 3.28 (t, *J*=5.8 Hz, 1H), 3.13 (t, *J*=6.0 Hz, 2H) ppm. ¹³C NMR (100 MHz, CD₃CN): δ = 168.5, 154.6, 60.4, 60.2, 58.4, 57.6 ppm. Elemental analysis: (C₉H₁₅N₁₇O₃, 409.15) calc.: C 26.41, H 3.69, N 58.17; found: C 27.02, H 3.66, N 57.59. HRMS: calc. for C₉H₁₅N₁₇O₃ [M+H]⁺: 410.1617; found: 410.1615.

1,3,5-tri(2-cyanomethyltetrazol-5-yl)pentazadiene (2g). Yield 79 mg (80%) of product **2g**.

1,3-Bis(2-cyanomethyltetrazol-5-yl)triazene (130 mg, 0.5 mmol) and 1-(3-dimethylaminoprop-yl)-3-ethyl-carbodiimide hydrochloride (EDCI, 58 mg, 0.3 mmol) were dissolved in 4 mL CH₂Cl₂ and 1 mL acetonitrile at room temperature. After stirring for 24 h, the solvent was evaporated in vacuum and the residue purified by column chromatography to provide **2g**. After recrystallization from PE/EtOAc, high purity product was obtained.

White solid (**2g**): DSC (5 °C min⁻¹): 128 °C (dec.). IR (KBr): $\tilde{\nu}$ = 3000, 2956, 1497, 1470, 1404, 1368, 1166, 1039, 1075, 941, 793, 756, 595 cm⁻¹. ¹H NMR (400 MHz, CD₃CN): δ = 5.94 (s, 2H), 5.83 (s, 4H) ppm. ¹³C NMR (100 MHz, CD₃CN): δ = 168.5, 154.9, 112.9, 112.8, 43.5, 42.6 ppm. HRMS: calc. for C₉H₆N₂₀ [M+H]⁺: 395.1157; found: 395.1162.

1,3,5-tri(1-methyltetrazol-5-yl)pentazadiene (2j). Yield 51 mg (64%) of product **2j**.

1,3-Bis(1-methyltetrazol-5-yl)triazene (105 mg, 0.5 mmol) and 1-(3-dimethylaminoprop-yl)-3-ethyl-carbodiimide hydrochloride (EDCI, 58 mg, 0.3 mmol) were dissolved in 5 mL acetonitrile at room temperature. After stirring for 24 h, the solvent was evaporated in vacuum and the residue purified by column chromatography to provide **2j**. After recrystallization from PE/EtOAc, high purity product was obtained.

White solid (**2j**): DSC (5 °C min⁻¹): 141 °C (dec.). IR (KBr): $\tilde{\nu}$ = 1518, 1467, 1140, 1089, 1039, 948, 744, 583 cm⁻¹. ¹H NMR (400 MHz, [D₆]DMSO): δ = 4.15 (s, 3H), 4.02 (s, 6H) ppm. ¹³C NMR (100 MHz, [D₆]DMSO): δ = 155.6, 144.6, 34.4, 34.4 ppm. ¹⁵N NMR (70 MHz, [D₇]DMF): δ = 82.6 (N6), 16.6 (N3), 10.6 (N10), 2.8 (N5), -0.6 (N2), -5.7 (N9), -47.6 (N4), -64.9 (N11), -145.1 (N7), -150.5 (N1), -156.7 (N8) ppm. Elemental analysis: (C₆H₉N₁₇, 319.12) calc.: C 22.57, H 2.84, N 74.59; found: C 23.41, H 2.80, N 73.79. The chemical stability of **2j** is very poor, so it will decomposed to **1j** in ESI-MS.

Reaction of tetrazolyl triazene with *N*-methyl-*p*-toluidine

1,3-Bis(2-methyltetrazol-5-yl)triazene (**1a**, 209 mg, 1.0 mmol), 1-(3-dimethylaminoprop-yl)-3-ethyl-carbodiimide hydrochloride (EDCI, 230 mg, 1.2 mmol) and *N*-methyl-*p*-toluidine (150 μ L, 1.2 mmol) were dissolved in 10 mL CH_2Cl_2 at room temperature. After stirring for 6 h, the reaction mixture was concentrated under reduced pressure and the residue purified by column chromatography to provide product **5** and **6**.

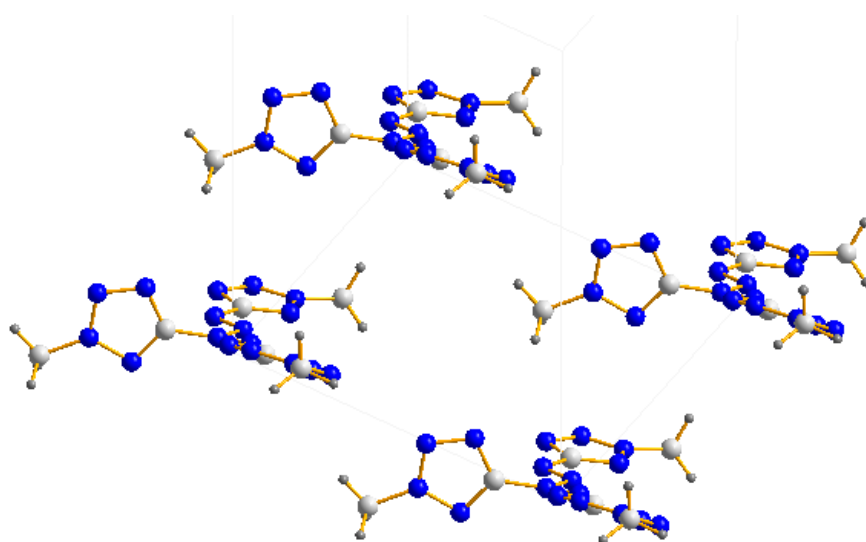
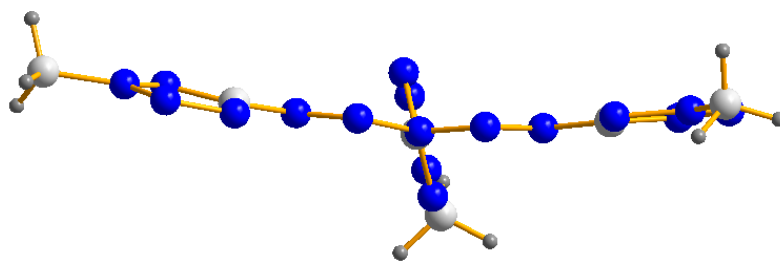
White solid (**5**): m.p. 99-100 $^\circ\text{C}$. IR (KBr): $\tilde{\nu}$ = 2959, 2926, 1726, 1600, 1514, 1458, 1378, 1286, 1119, 1072, 1039, 981, 822, 739 cm^{-1} . ^1H NMR (400 MHz, [D6]DMSO): δ = 7.45 (d, J =6.4 Hz, 2H), 7.28 (d, J =6.8 Hz, 2H), 4.35 (s, 3H), 3.68 (s, 3H), 2.32 (s, 3H) ppm. ^{13}C NMR (100 MHz, [D6]DMSO): δ = 170.1, 141.4, 134.8, 129.7, 118.4, 39.8, 34.1, 20.3 ppm. HRMS: calc. for $\text{C}_6\text{H}_9\text{N}_{17}$ $[\text{M}+\text{H}]^+$: 232.1305; found: 232.1308.

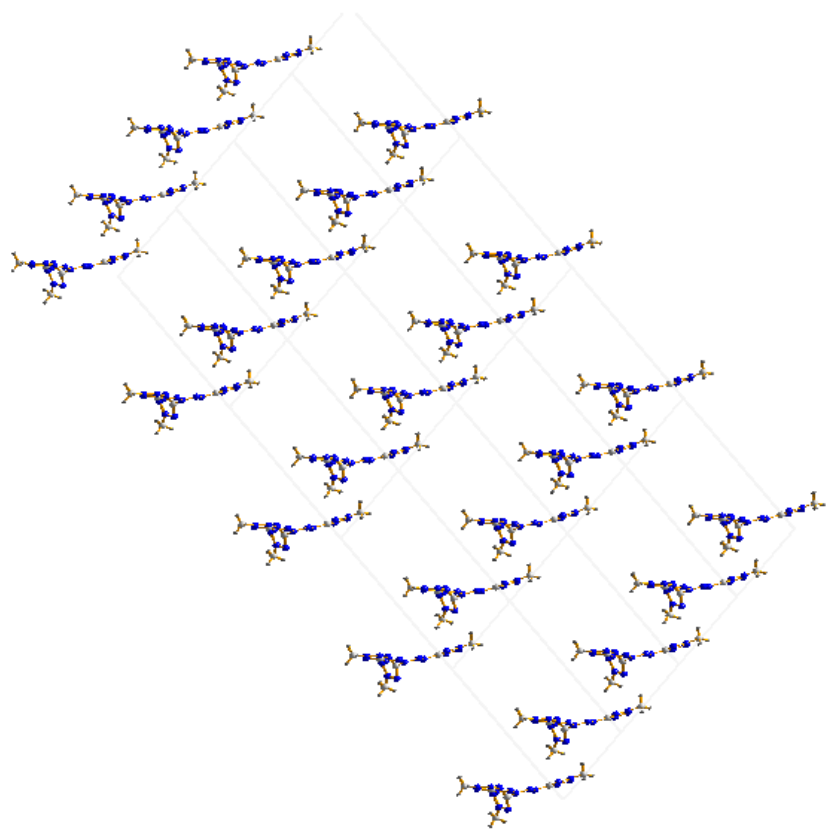
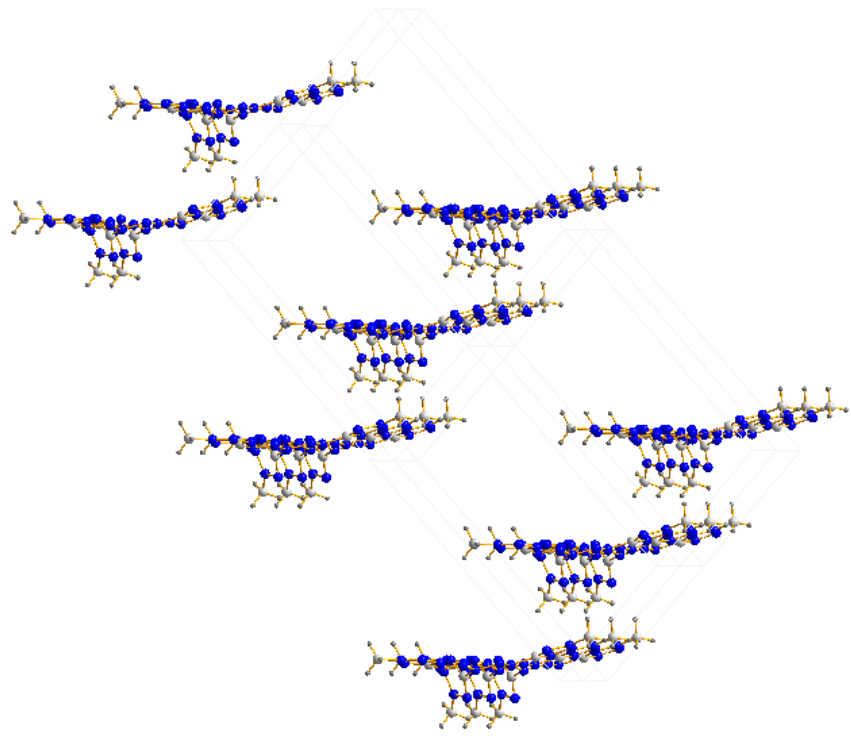
Scarlet solid (**6**): m.p. 88-90 $^\circ\text{C}$. IR (KBr): $\tilde{\nu}$ = 2959, 2924, 1726, 1571, 1527, 1469, 1392, 1286, 1174, 1137, 1073, 1038, 743 cm^{-1} . ^1H NMR (400 MHz, [D6]DMSO): δ = 8.53 (d, J =4.8 Hz, 1H), 7.57 (s, 1H), 7.30 (d, J =8.8 Hz, 1H), 6.86 (d, J =8.8 Hz, 1H), 4.43 (s, 3H), 2.97 (d, J =5.2 Hz, 3H), 2.26 (s, 3H) ppm. ^{13}C NMR (100 MHz, [D6]DMSO): δ = 171.6, 143.6, 137.1, 135.9, 128.5, 124.5, 112.6, 40.0, 29.1, 19.4 ppm. HRMS: calc. for $\text{C}_6\text{H}_9\text{N}_{17}$ $[\text{M}+\text{H}]^+$: 232.1305; found: 232.1309.

References

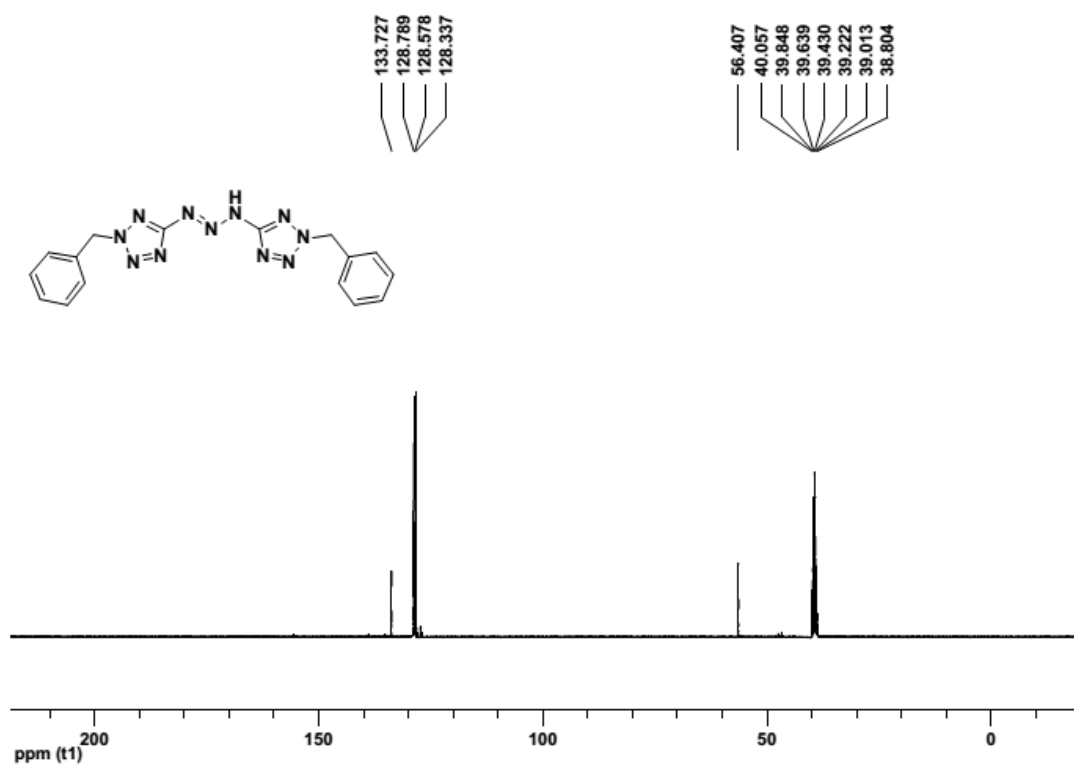
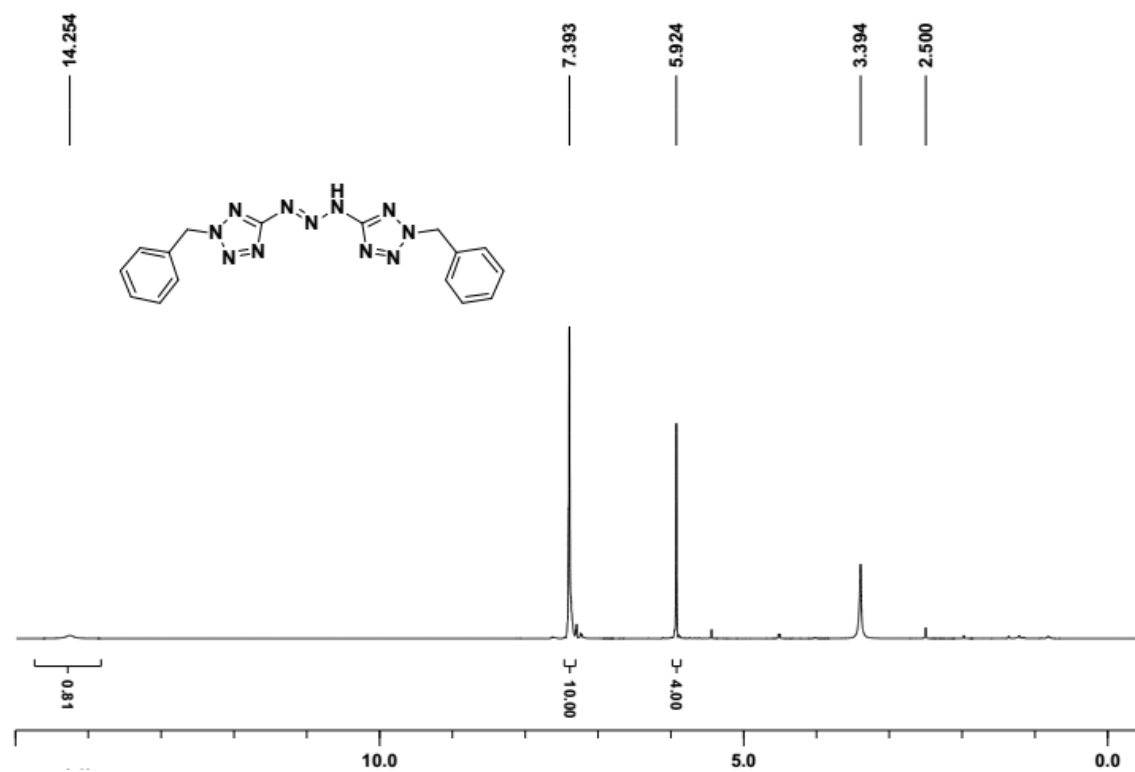
- 1 *CrystalClear: SM Expert 2.0 r2, An Integrated Program for the Collection and Processing of Area Detector Data*, Rigaku Corporation, England, **2009**.
- 2 G. M. Sheldrick, *SHELXTL-97, Structure Determination Software Suite*, Bruker AXS, Madison, **2008**.
- 3 T. M. Klapötke, N. K. Minar, J. Stierstorfer, *Polyhedron* **2009**, 28, 13–26.

X-ray crystallography of 2a

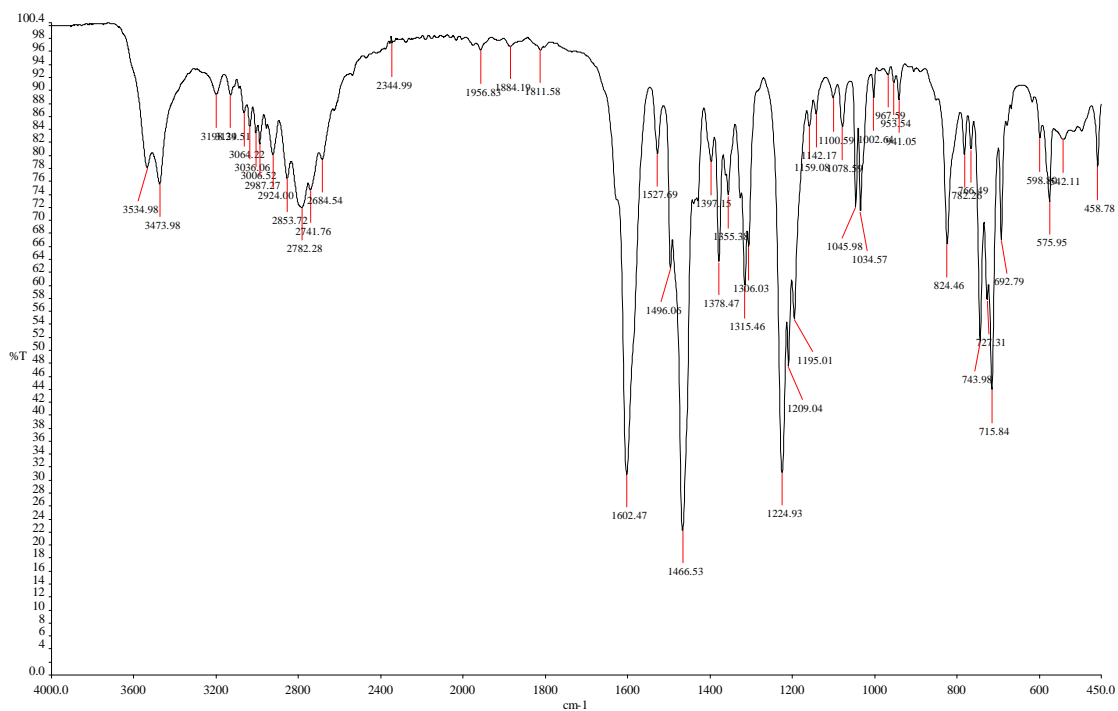




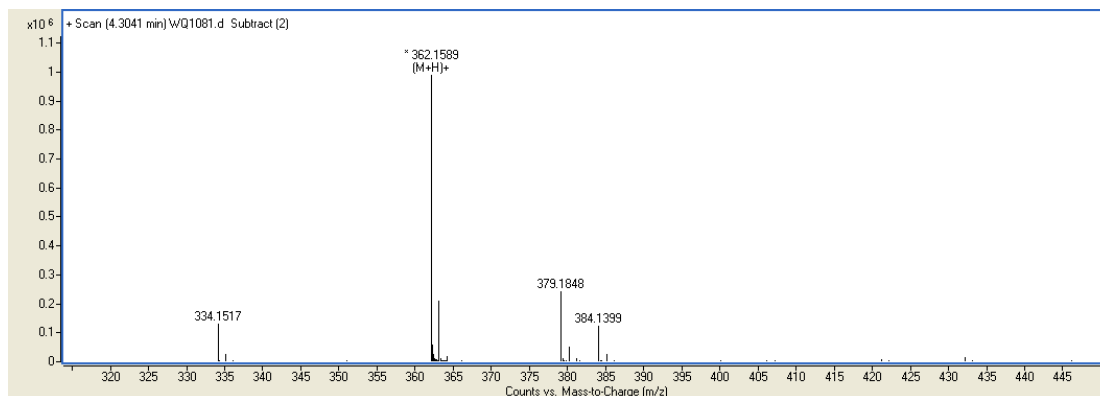
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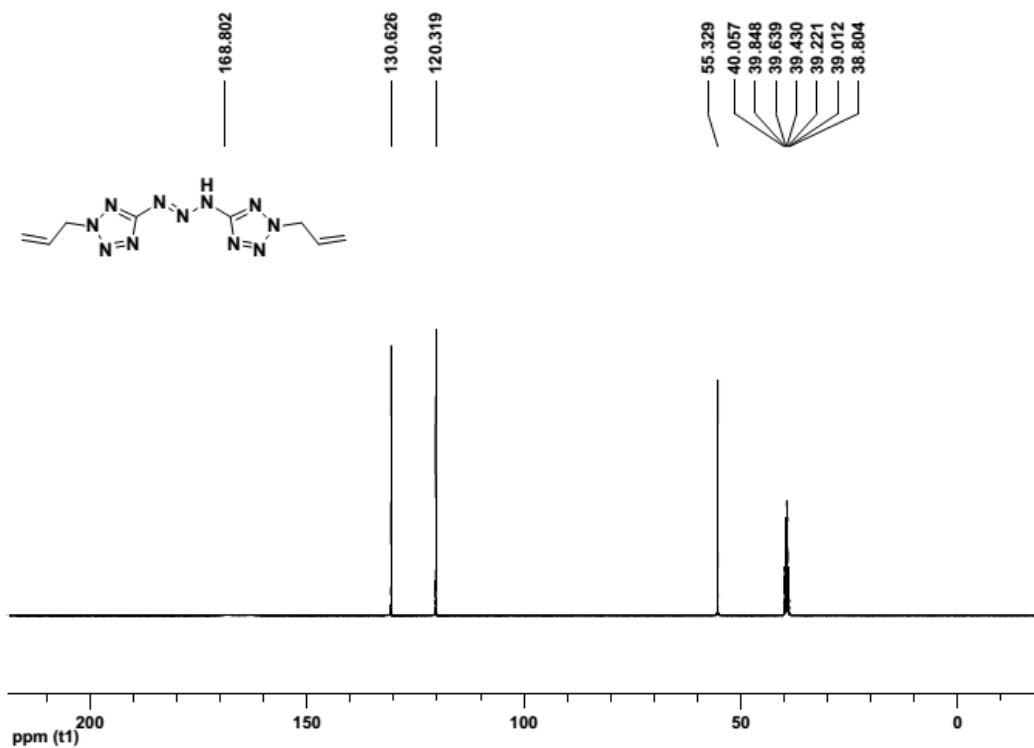
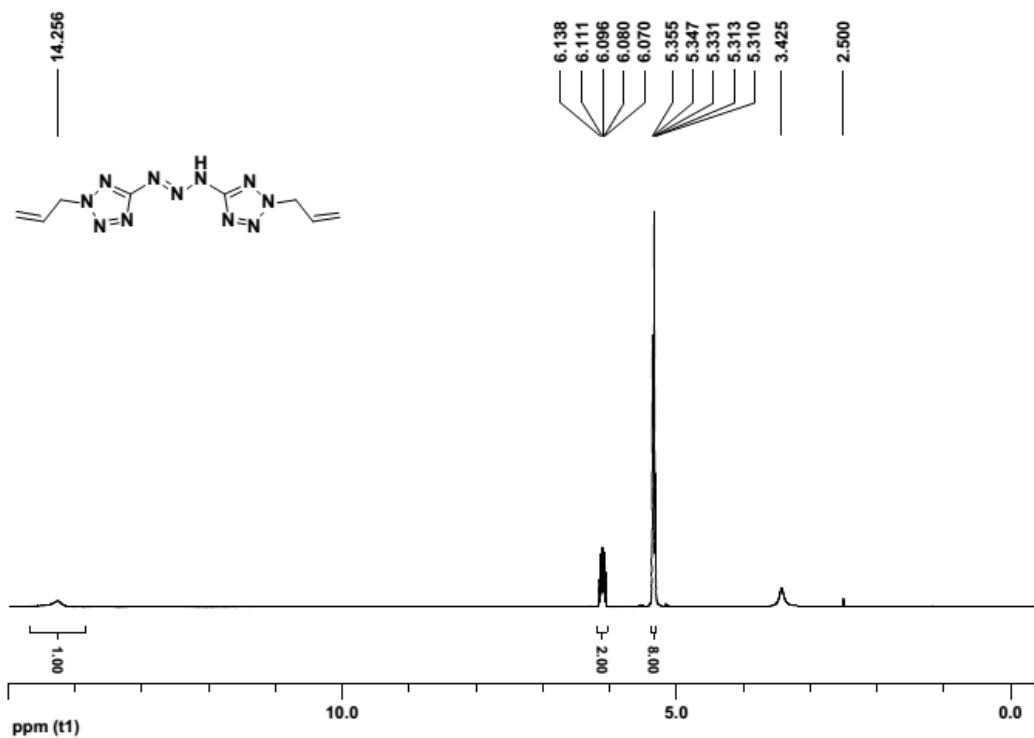
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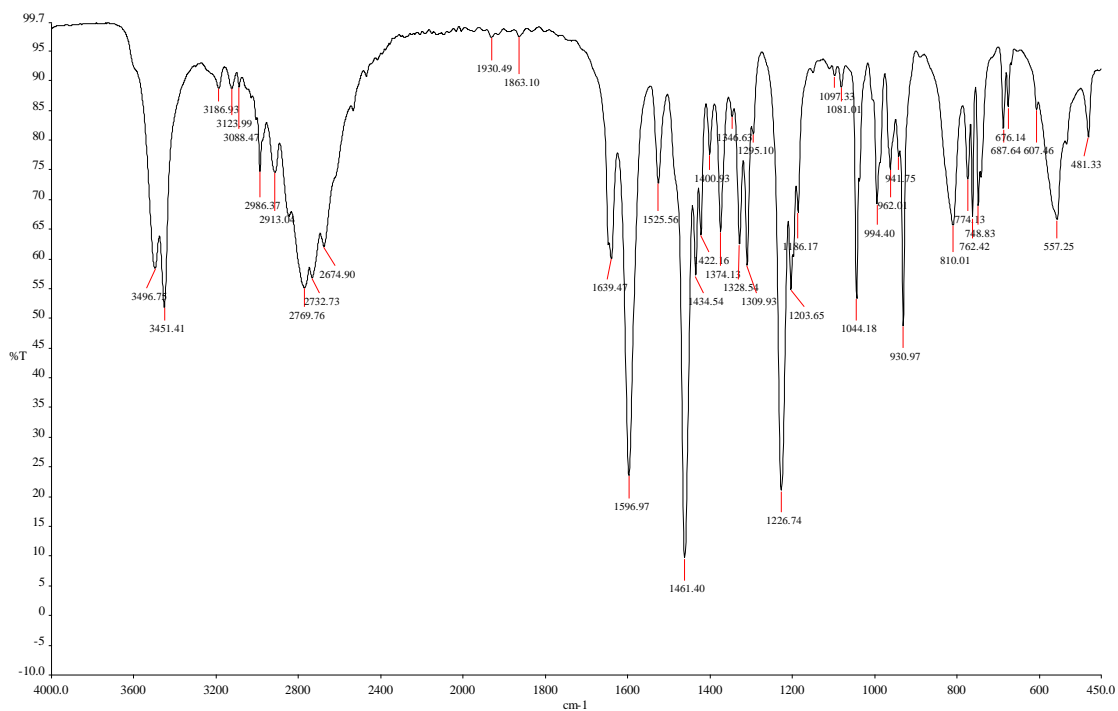
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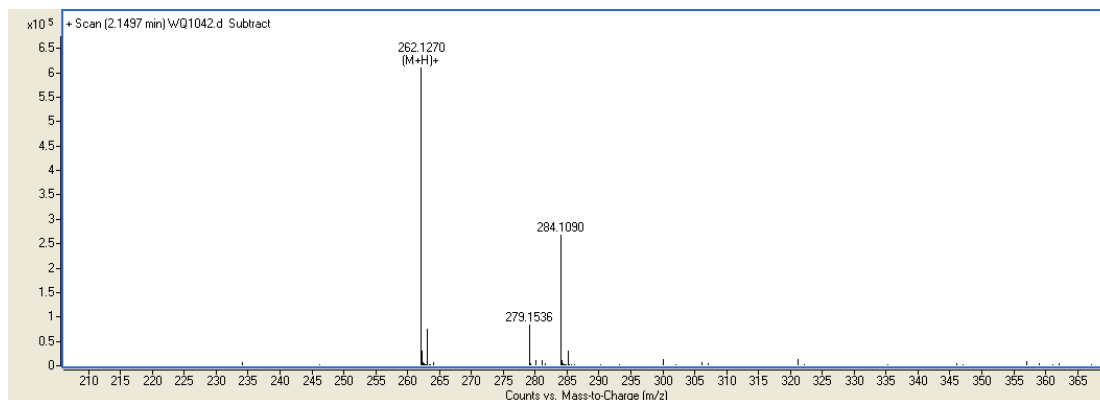
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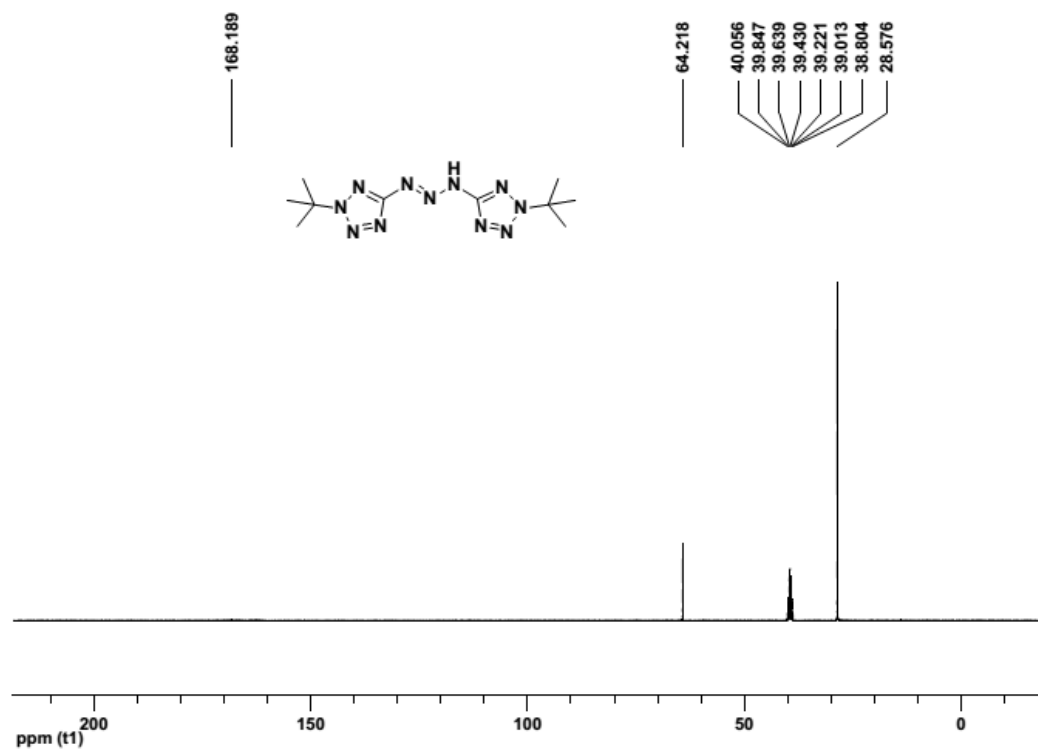
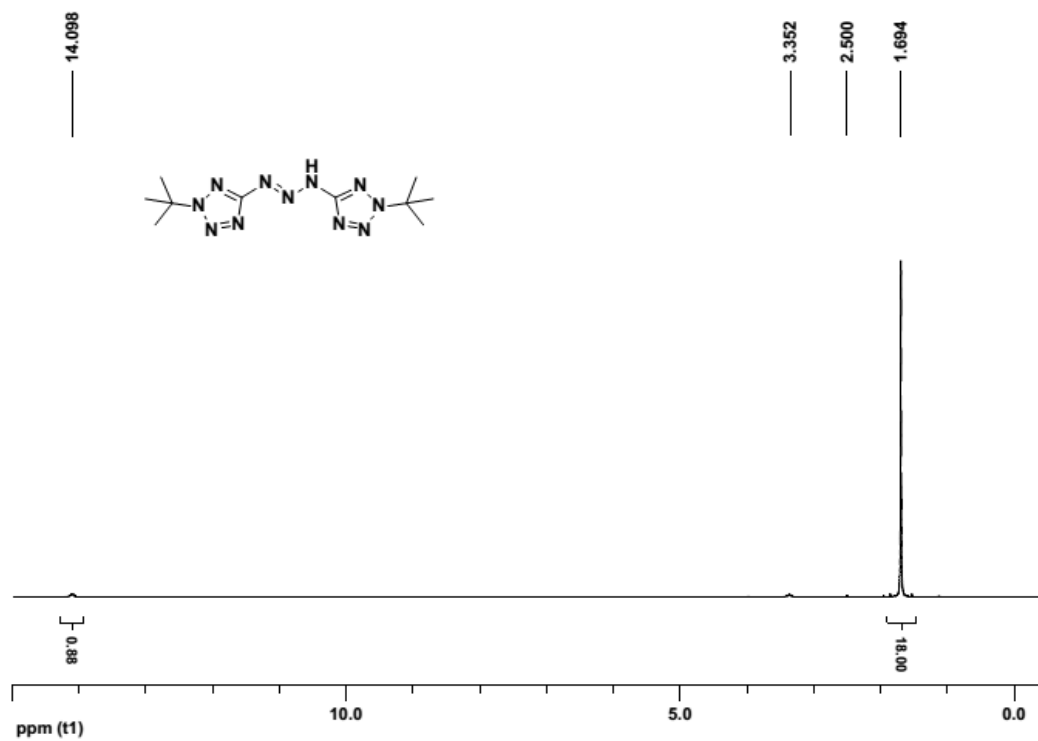
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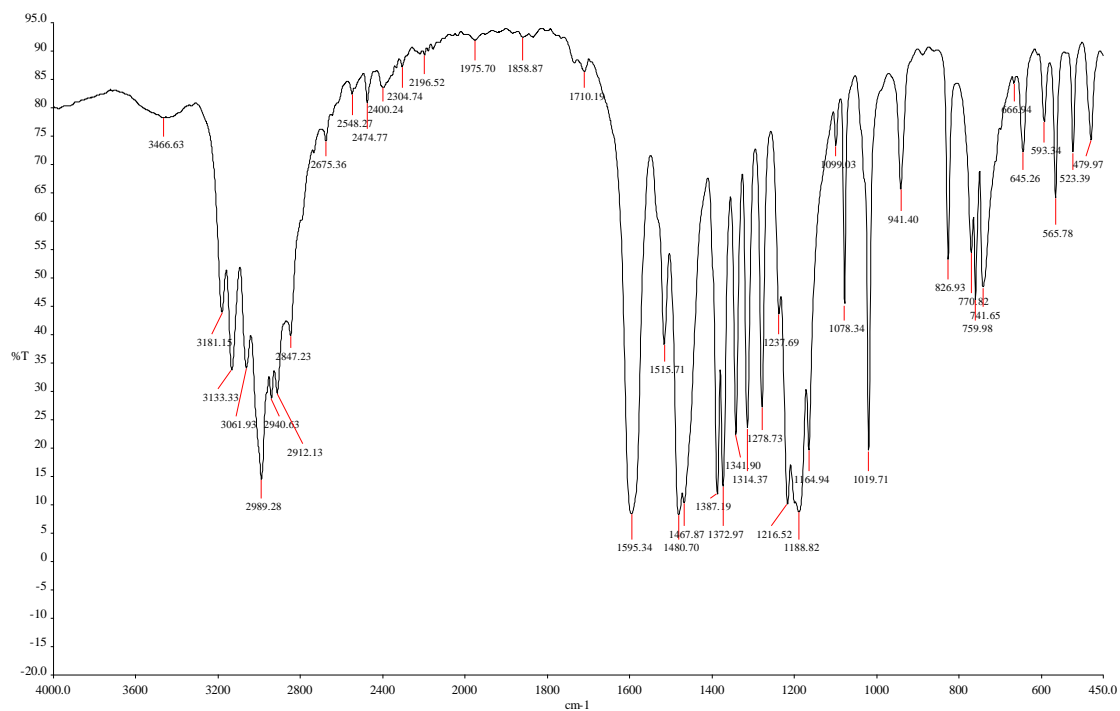
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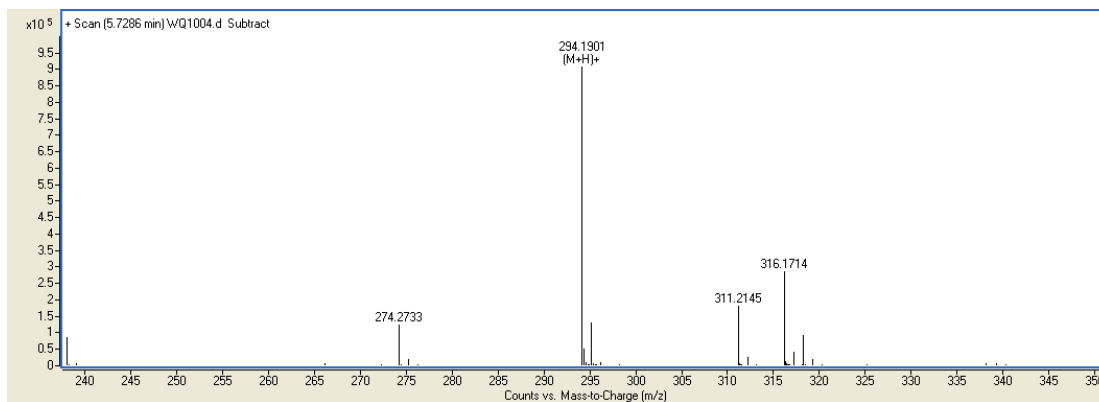
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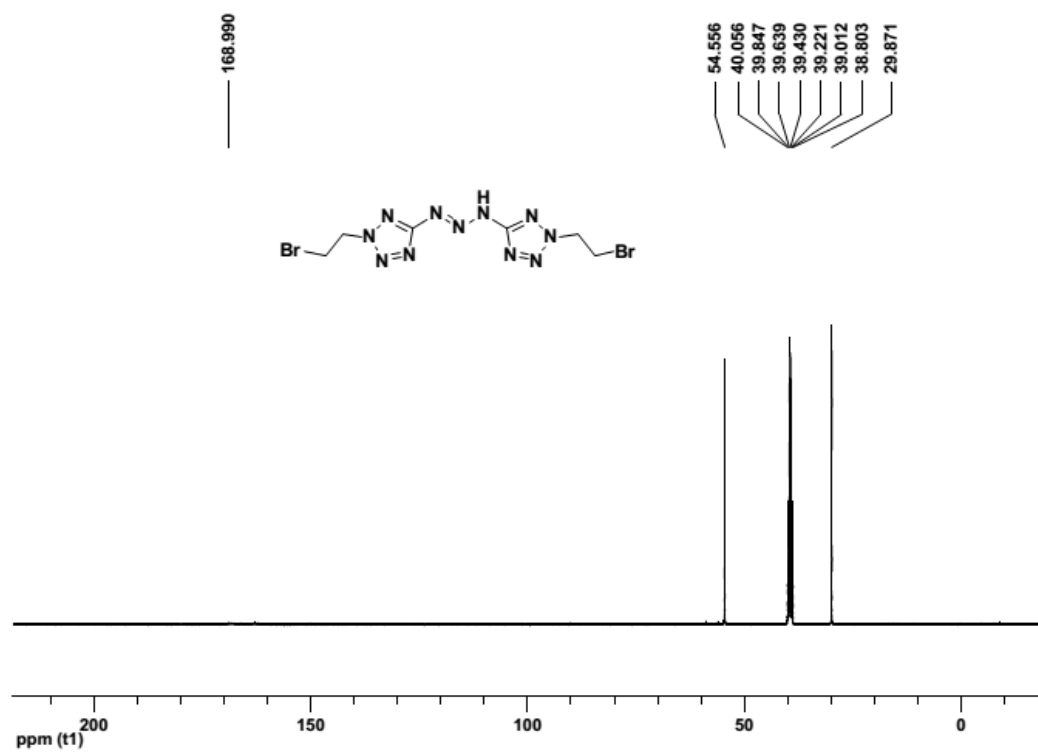
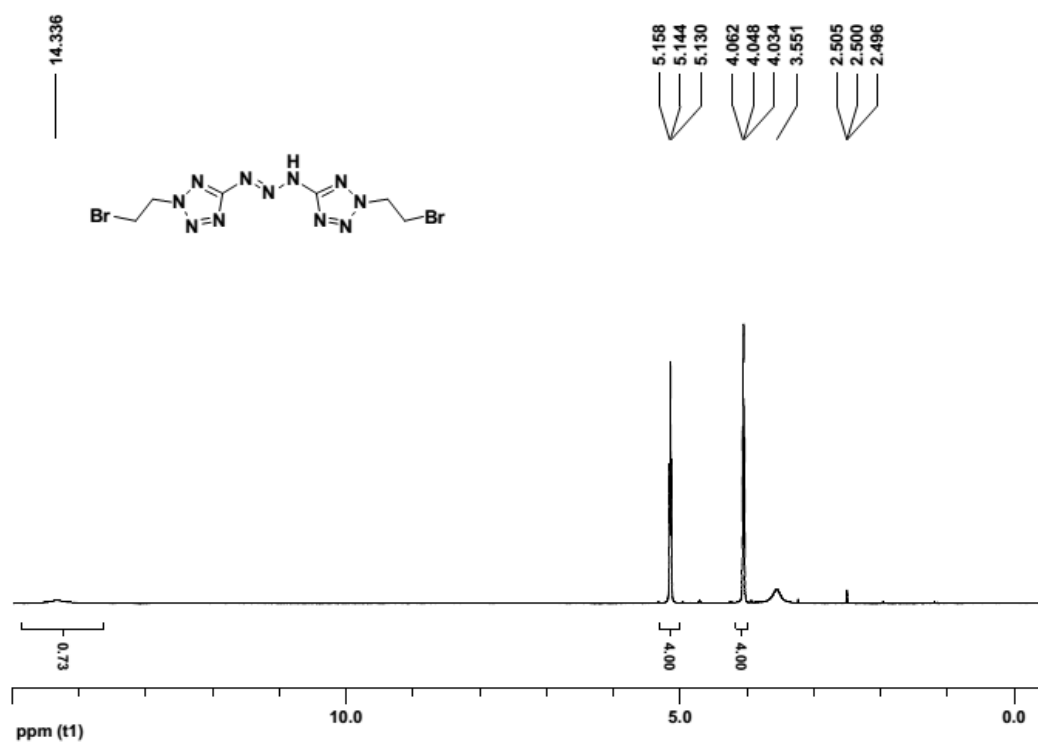
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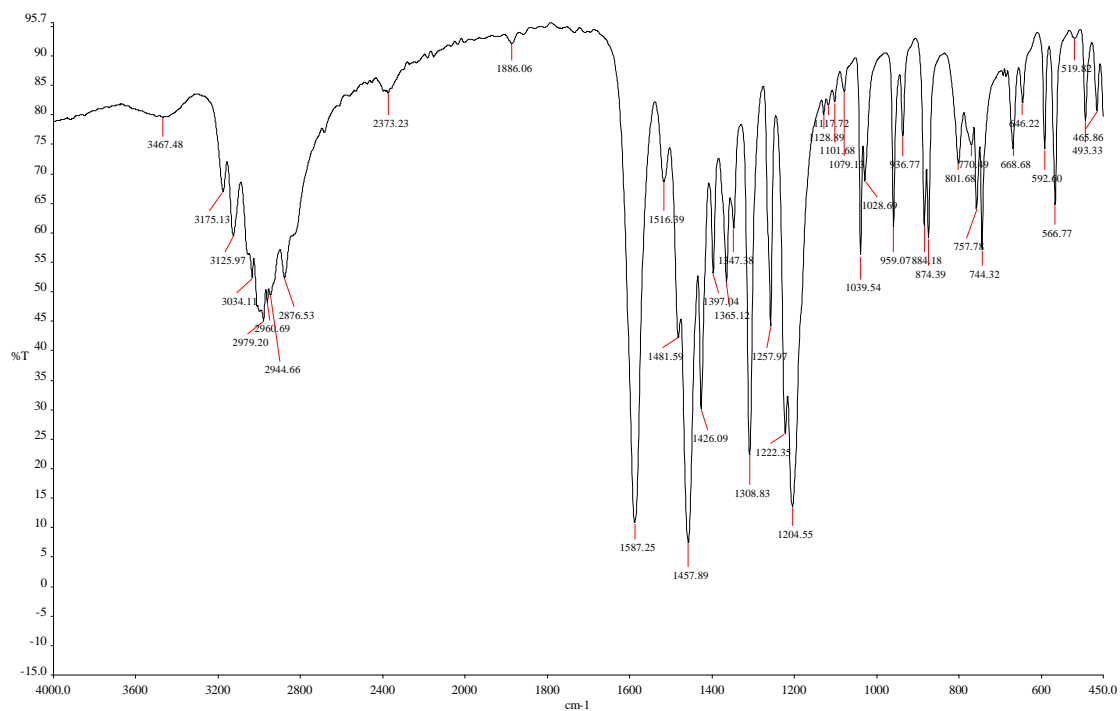
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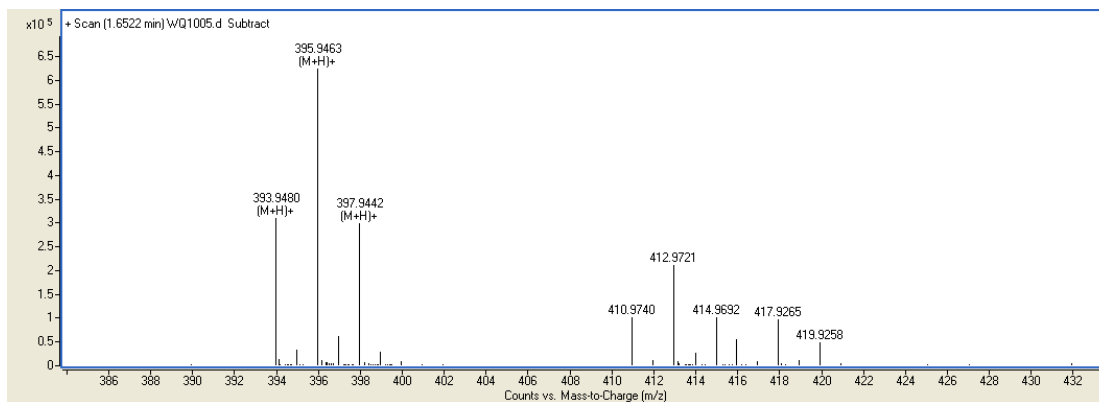
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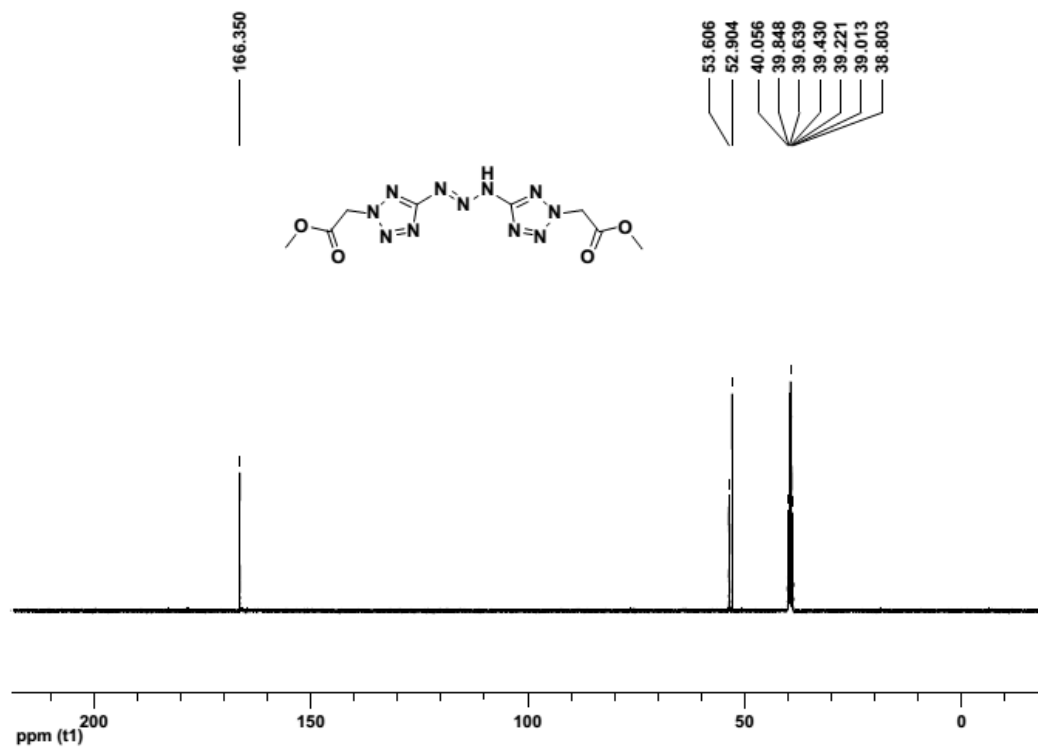
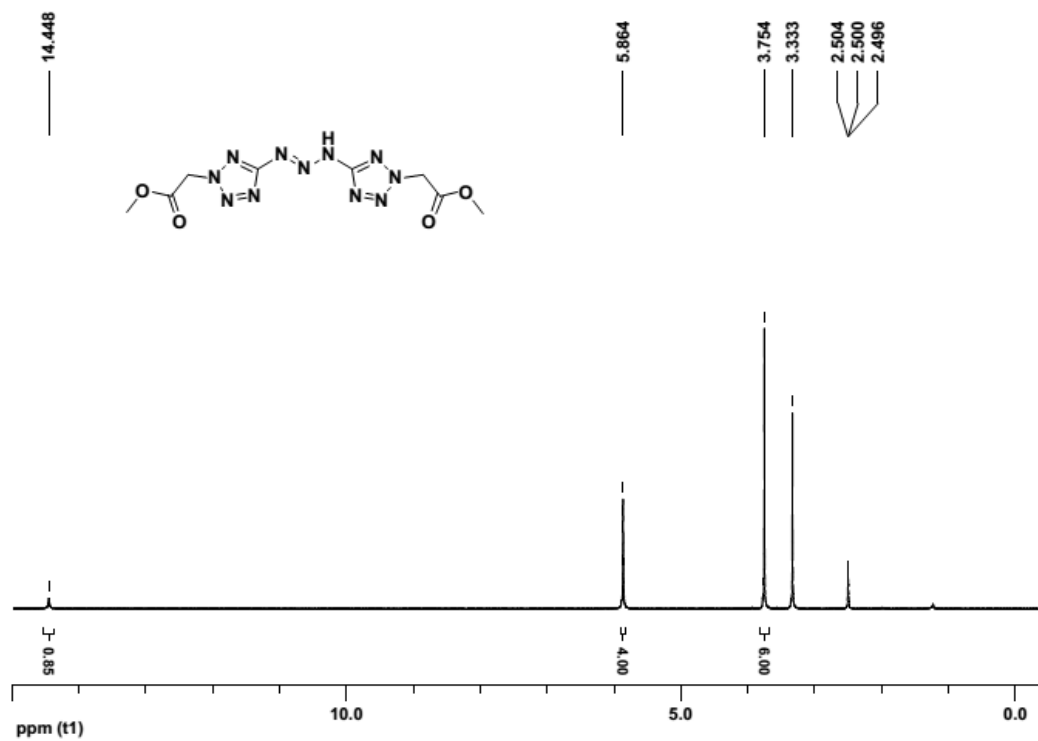
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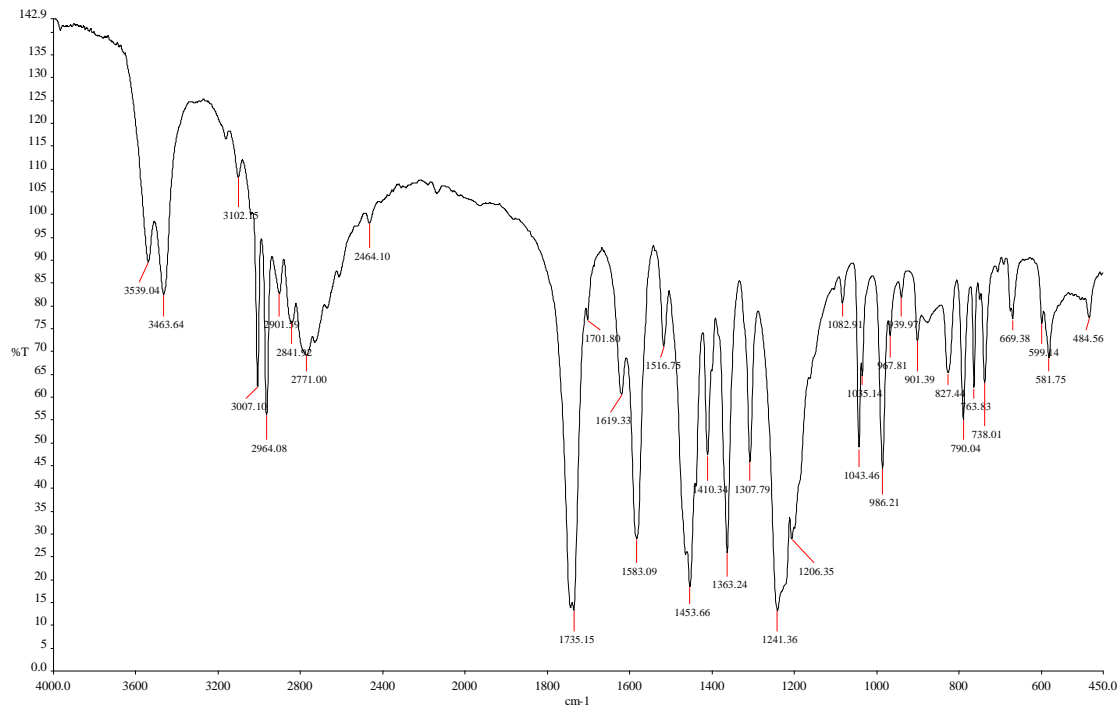
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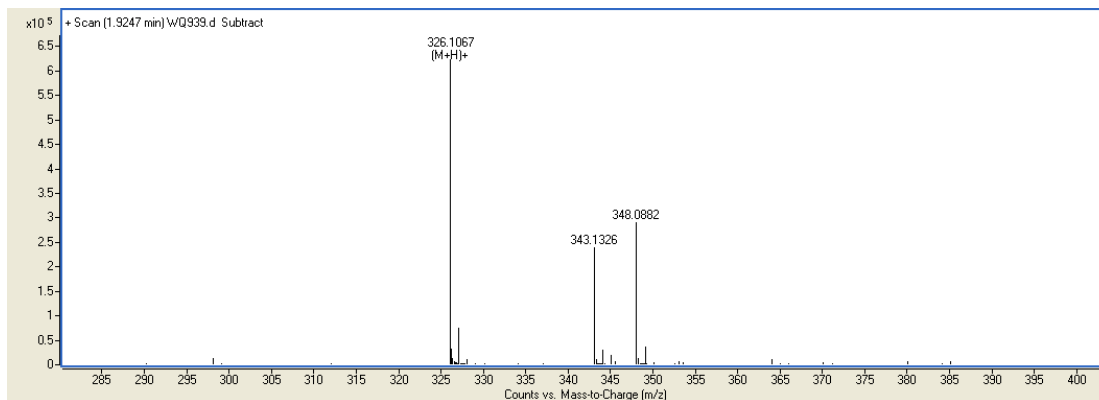
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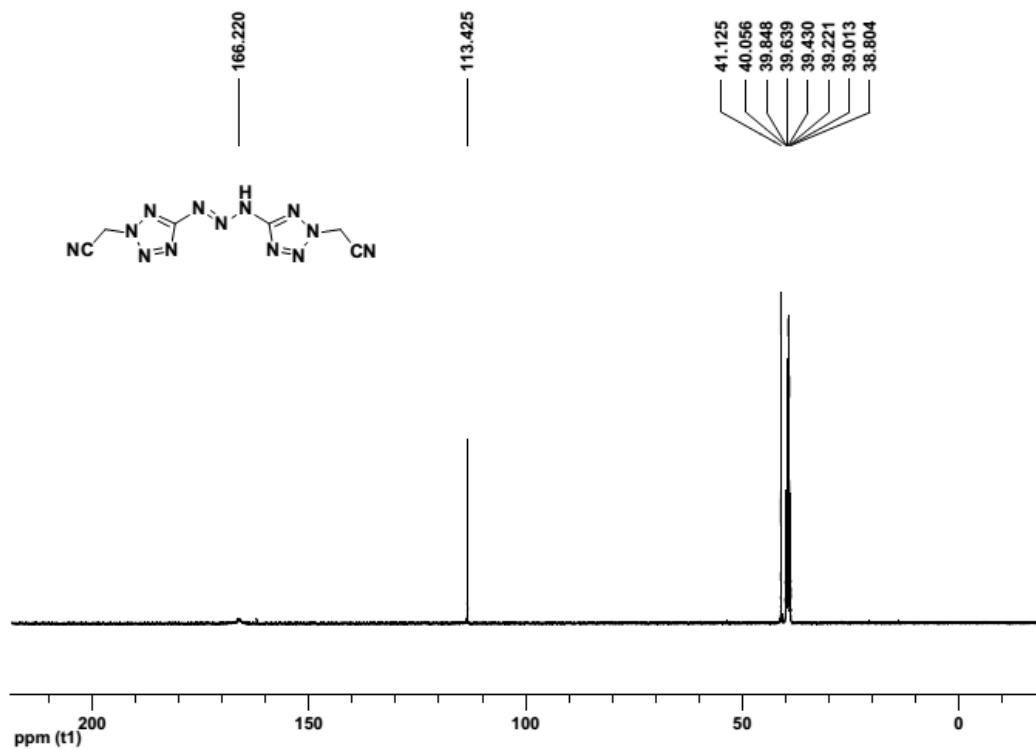
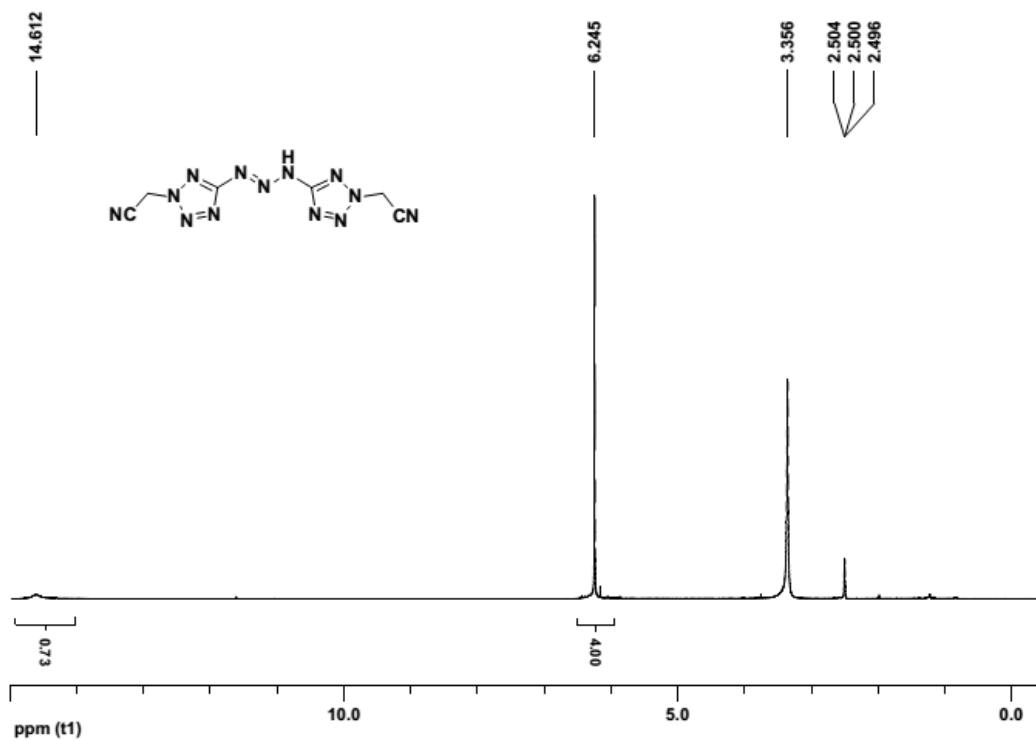
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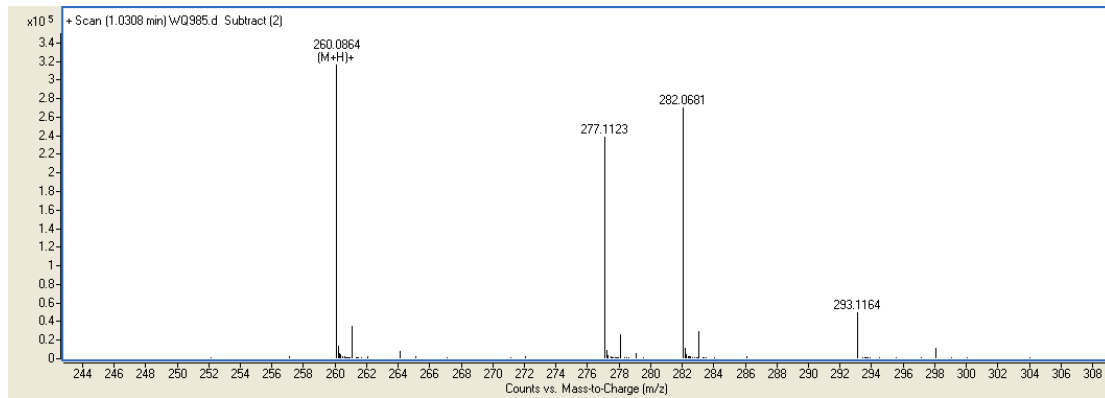
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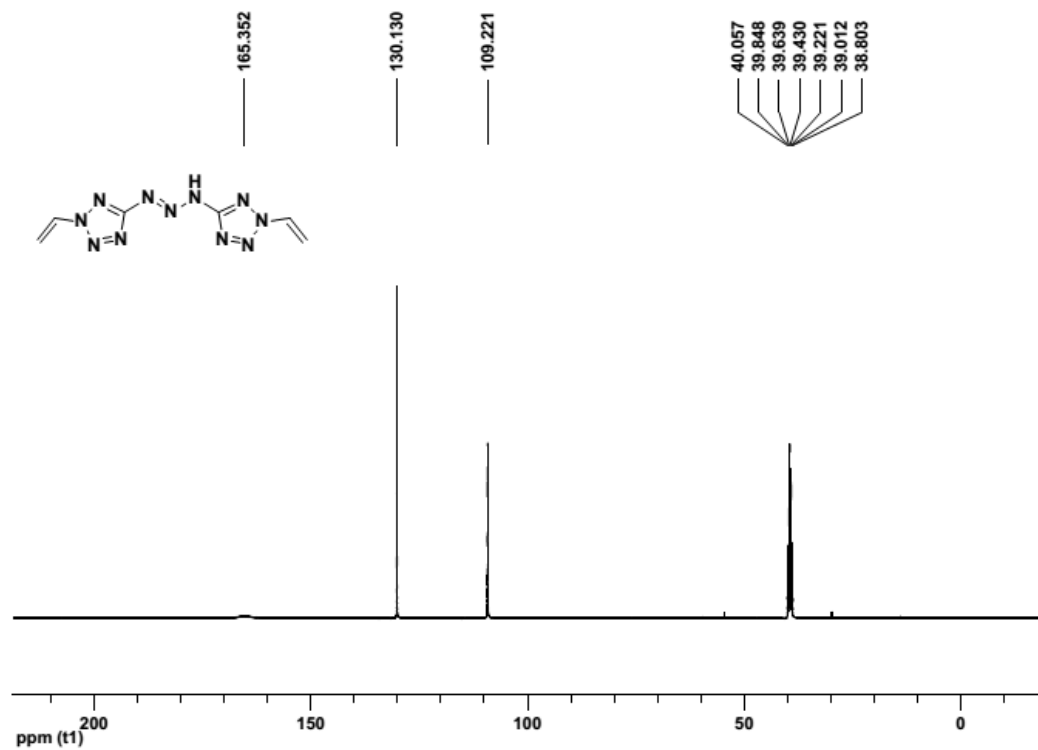
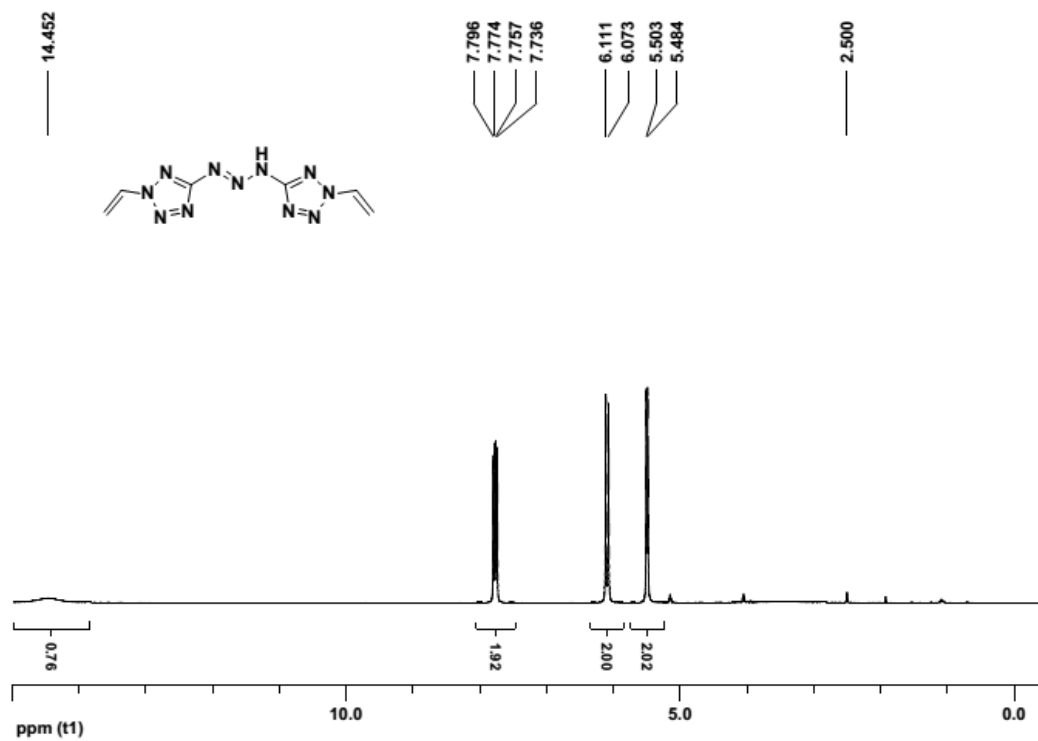
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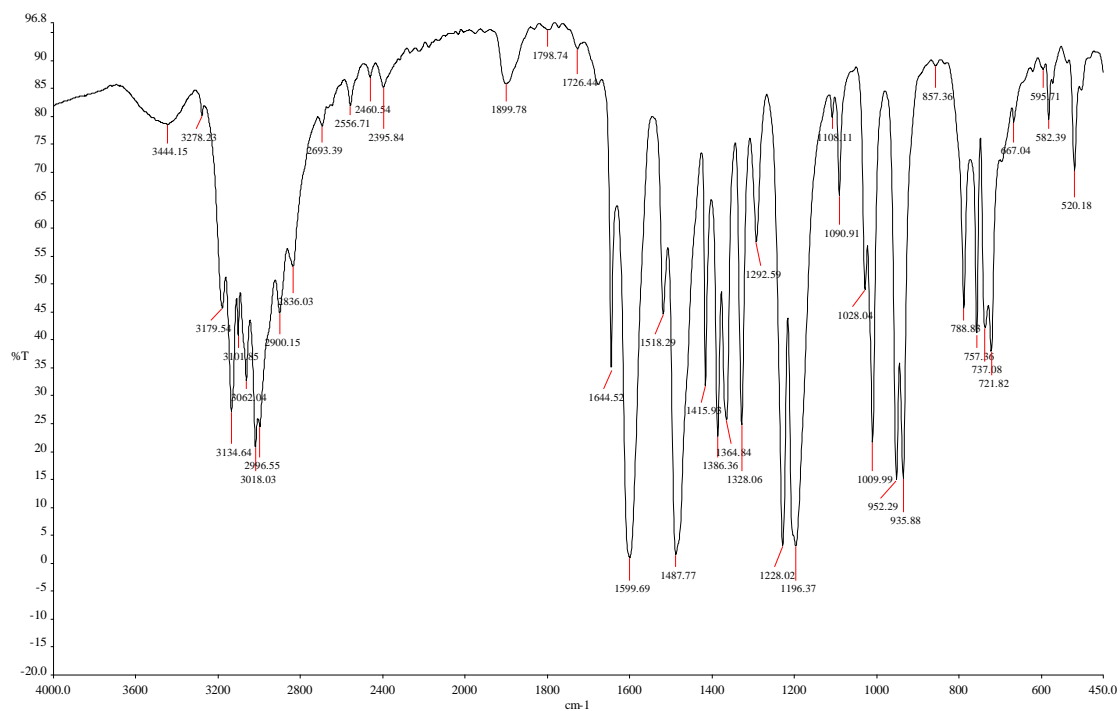
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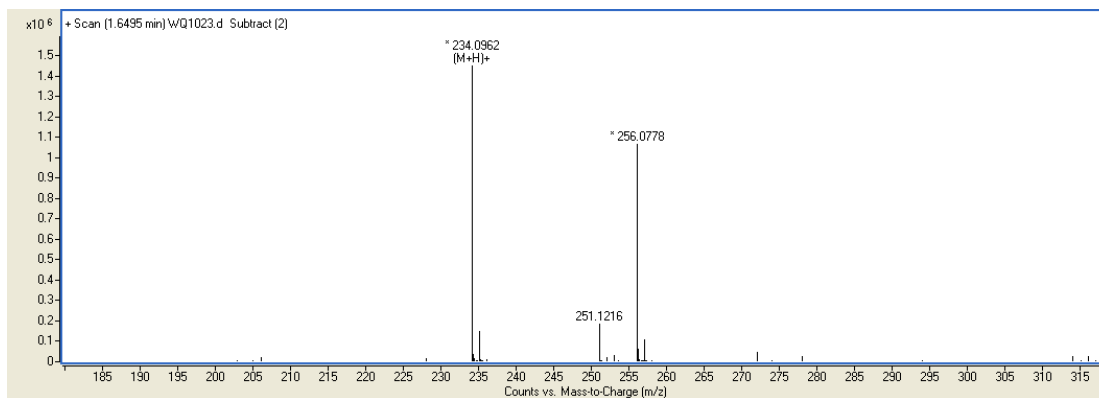
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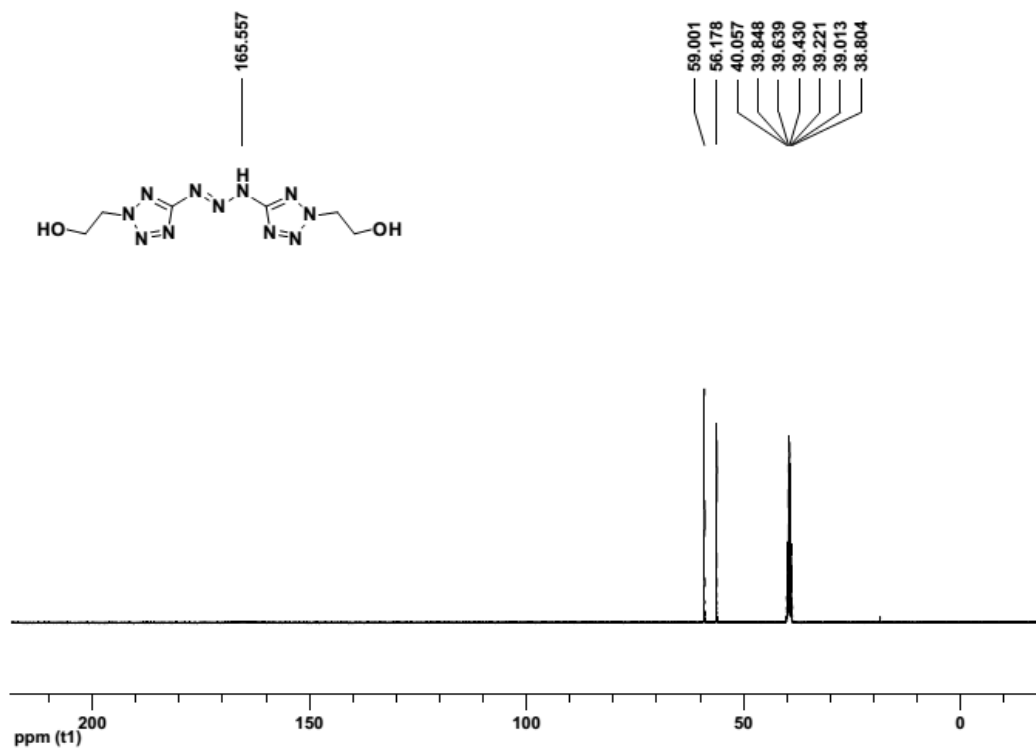
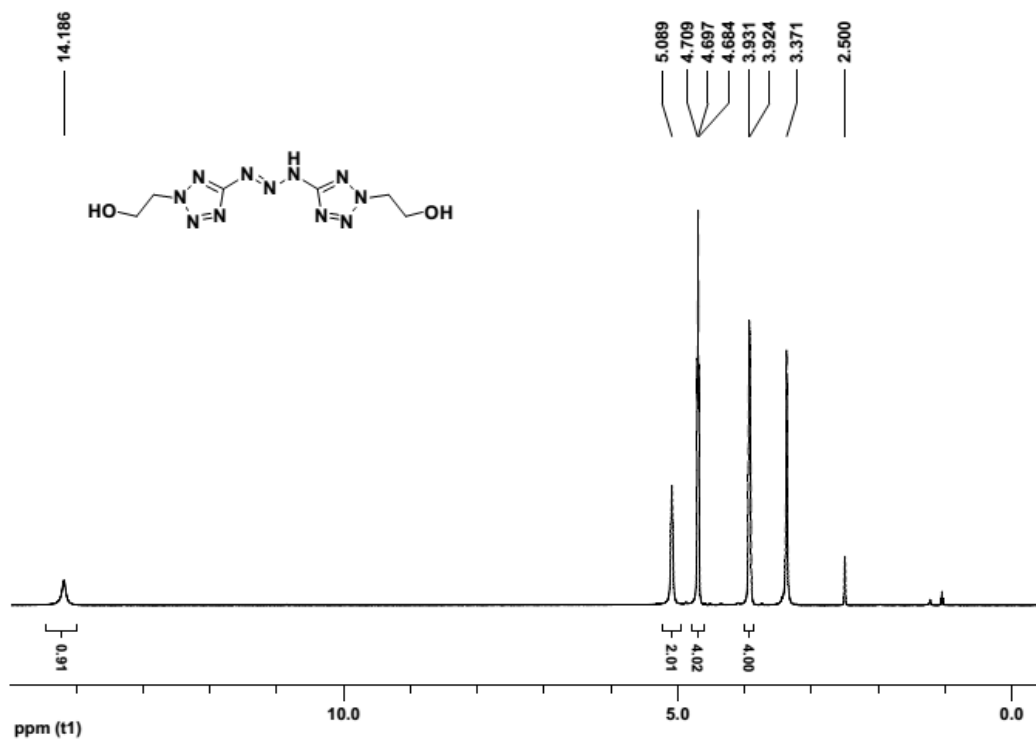
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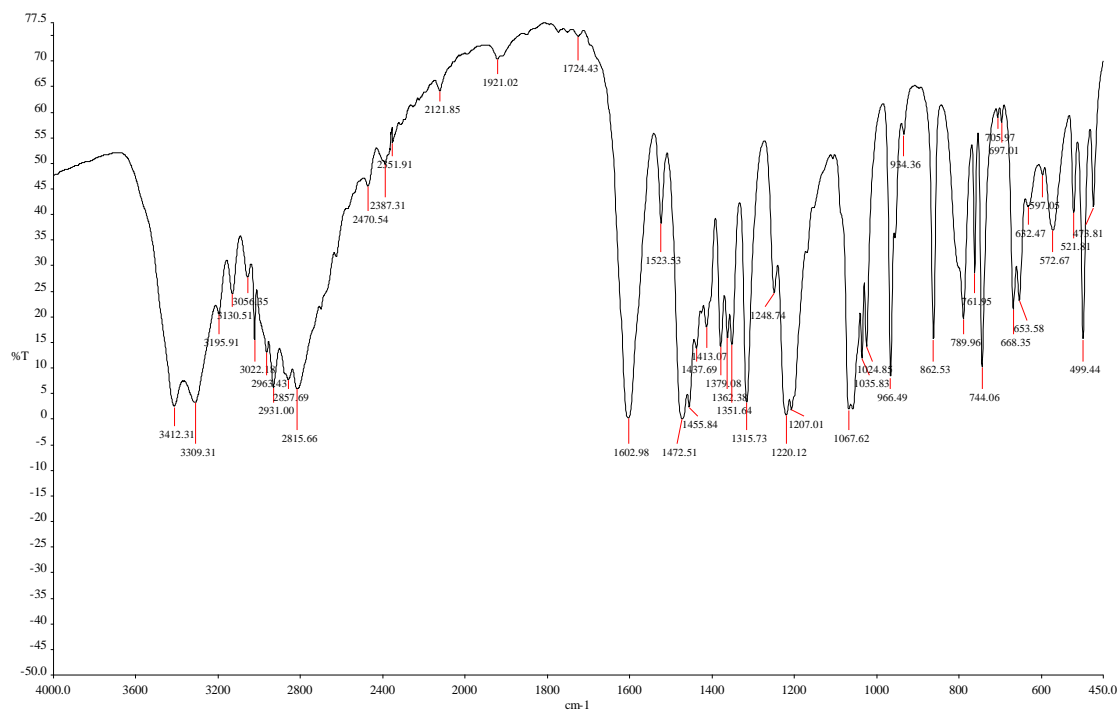
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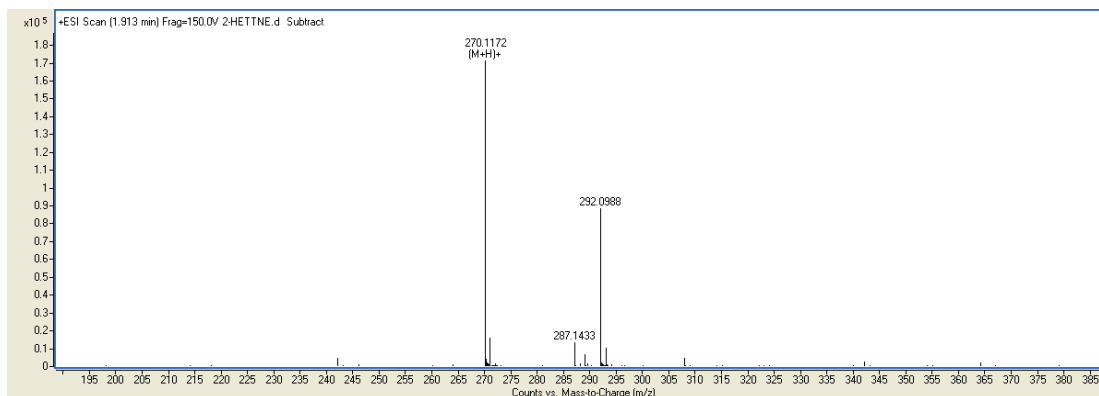
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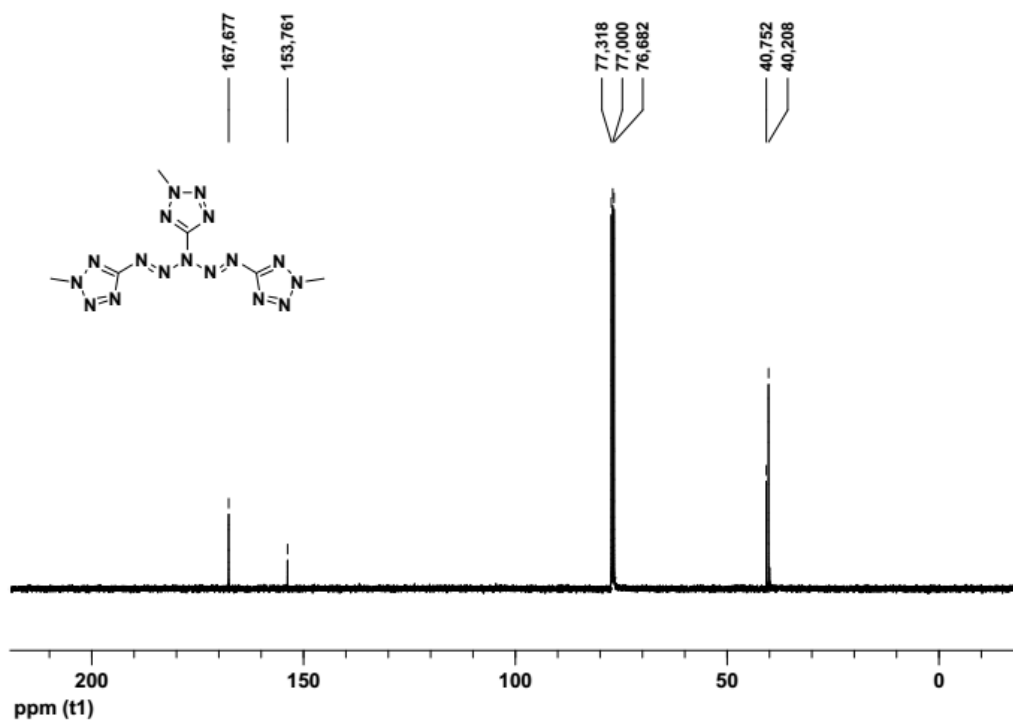
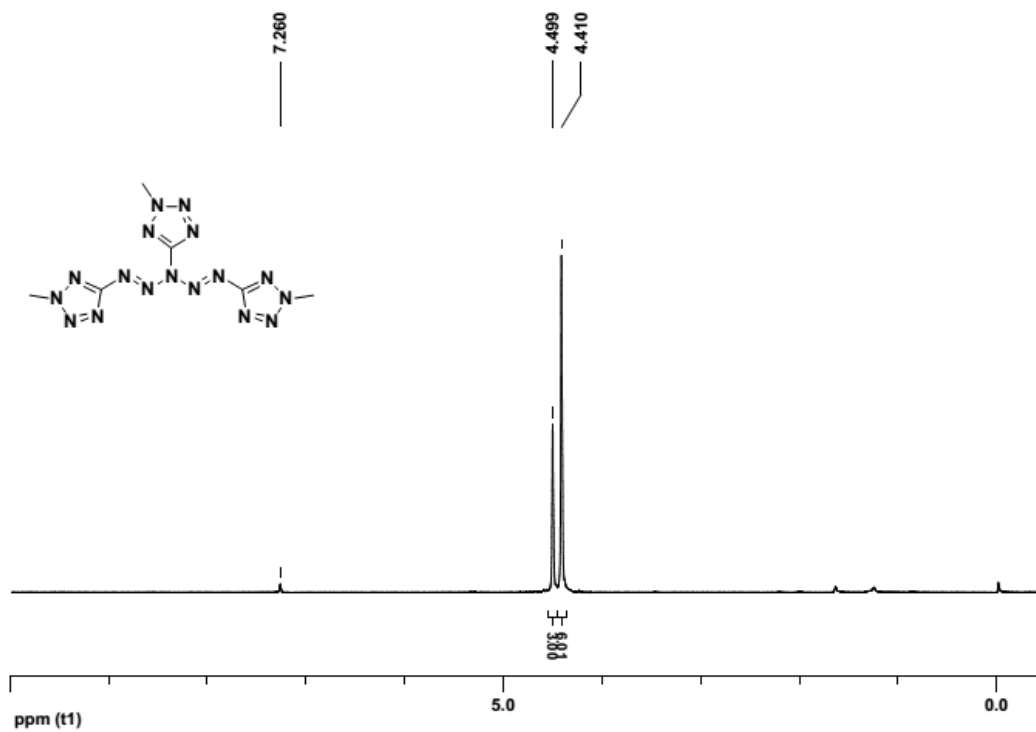
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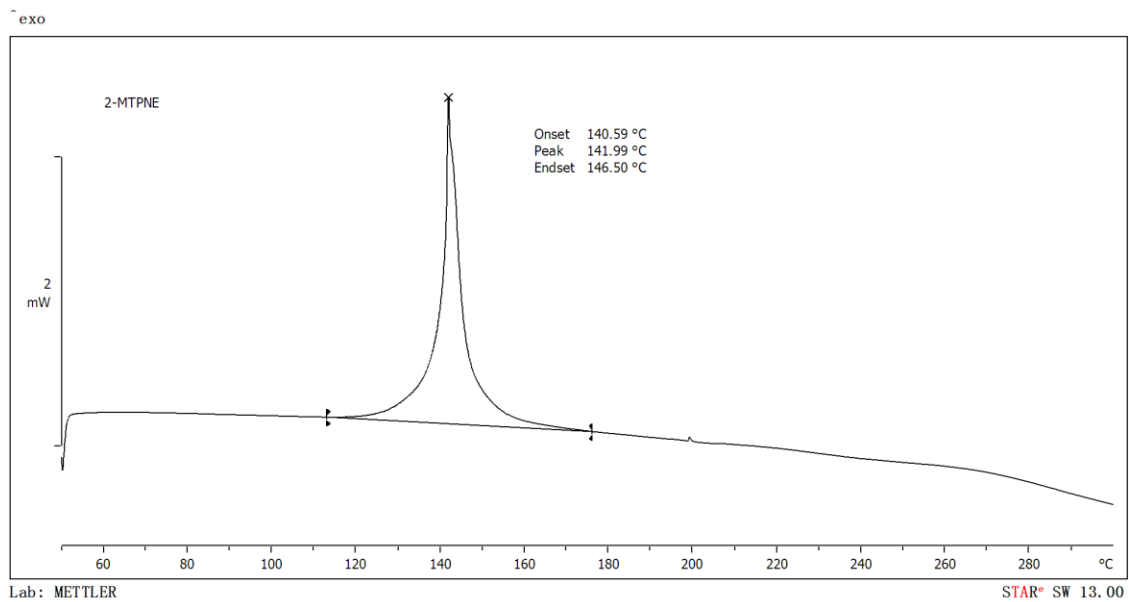
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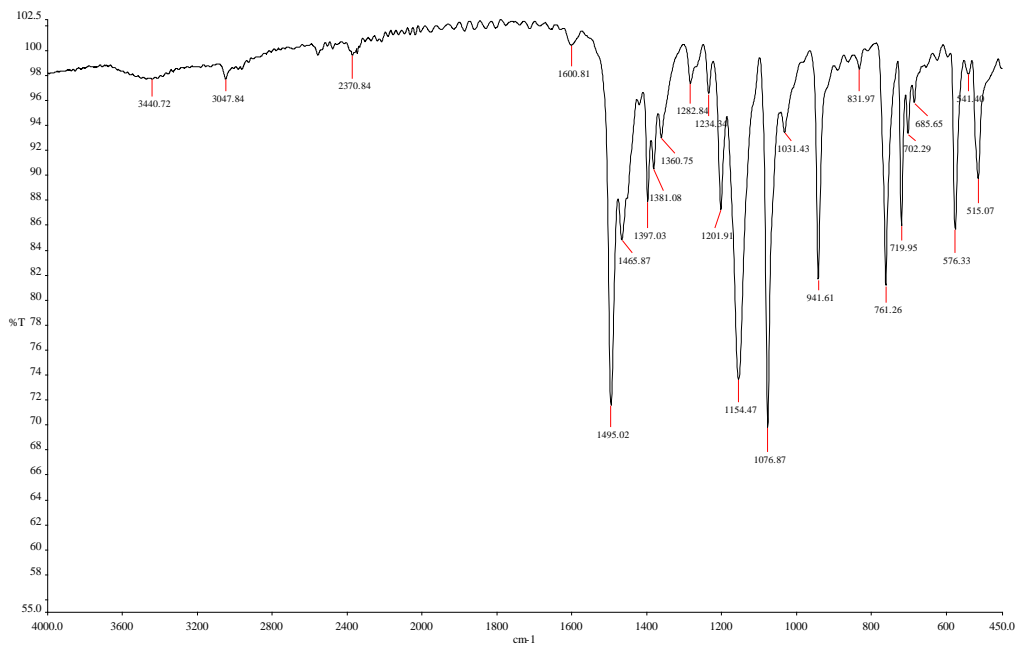
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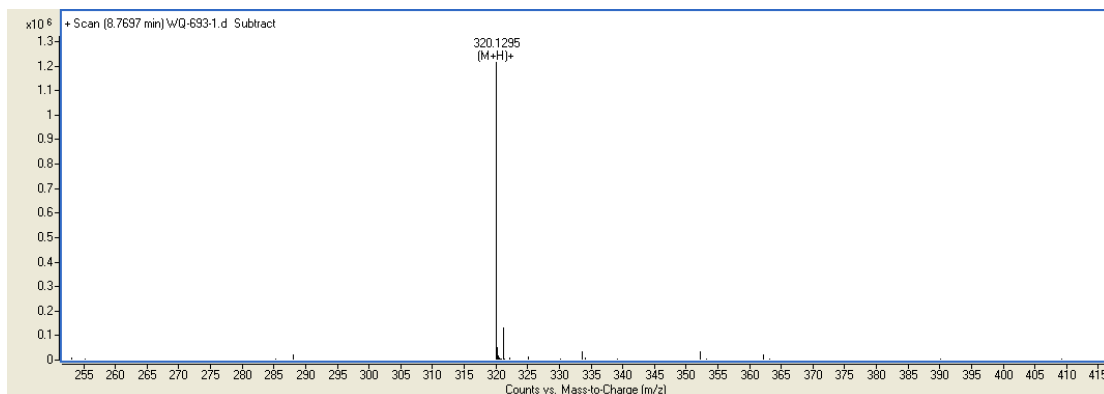
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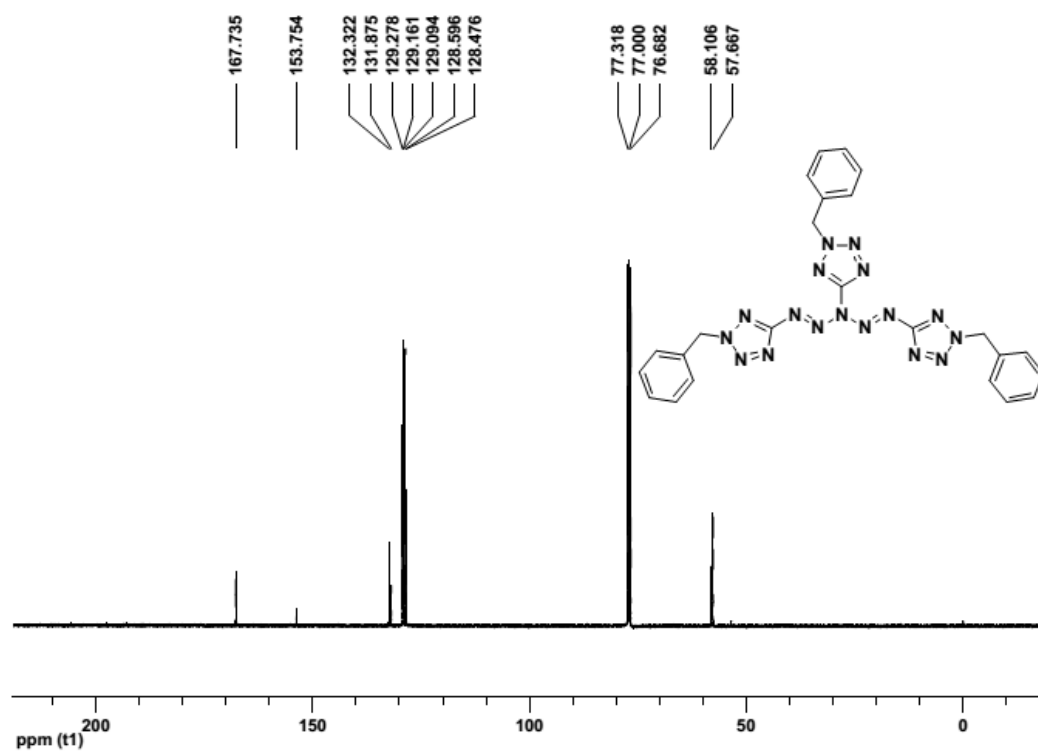
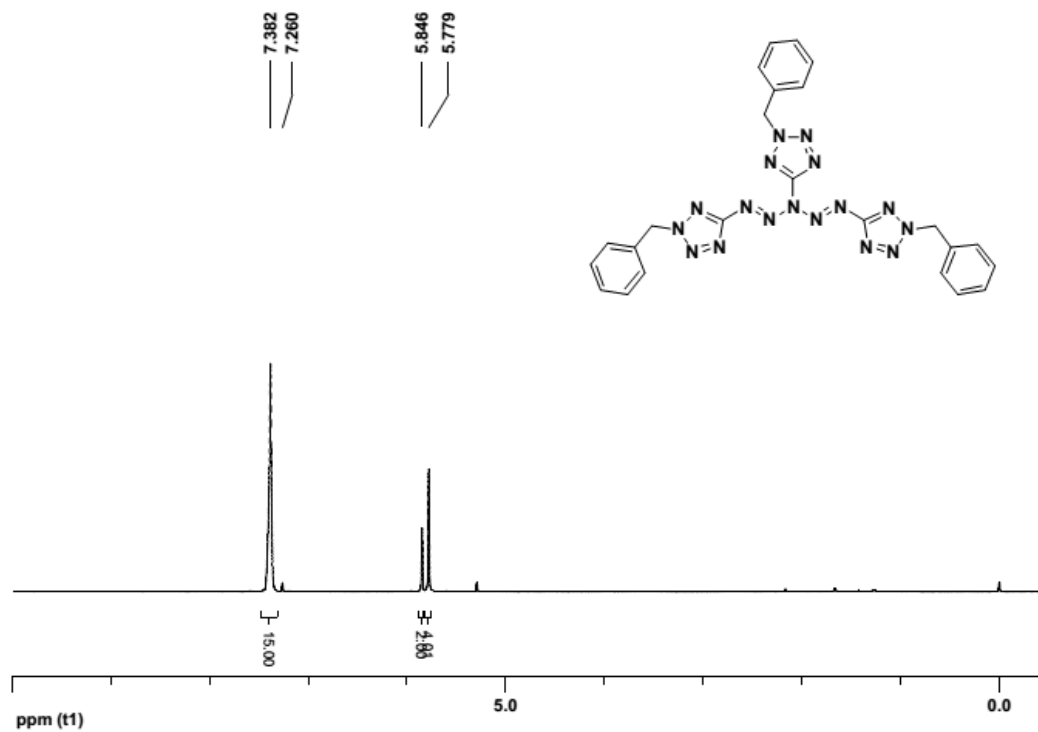
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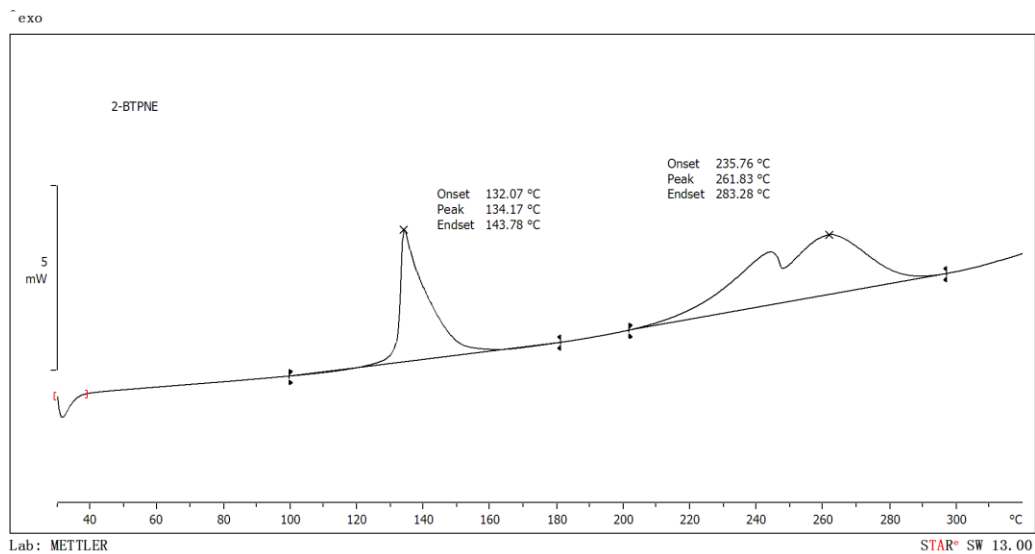
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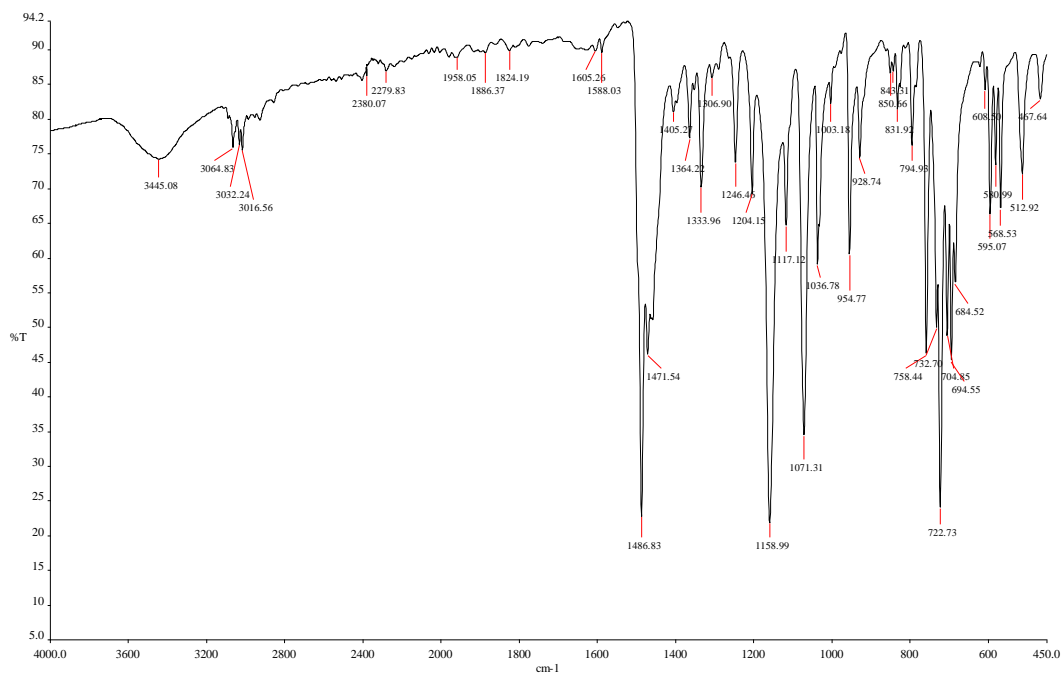
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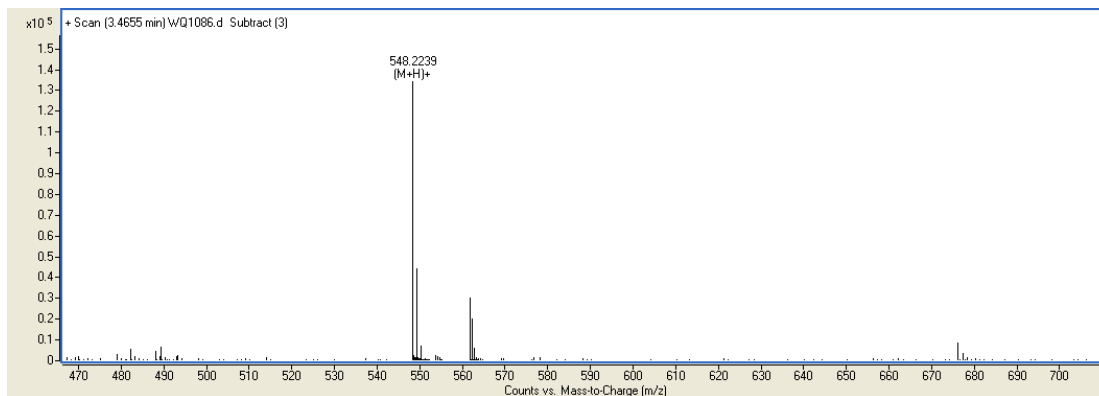
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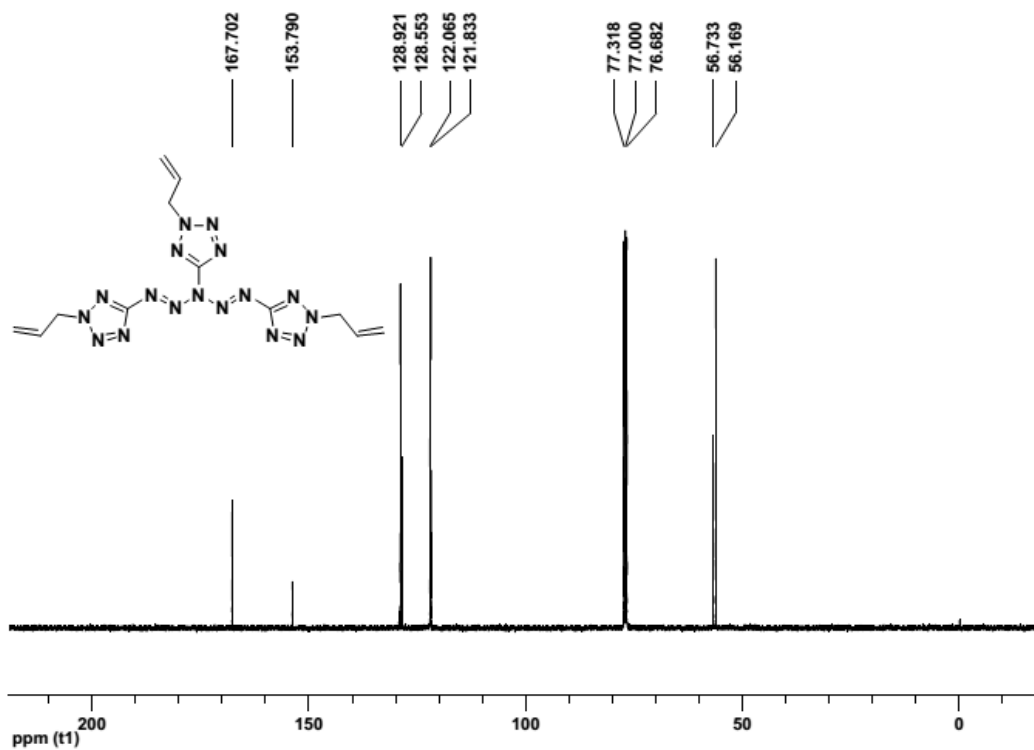
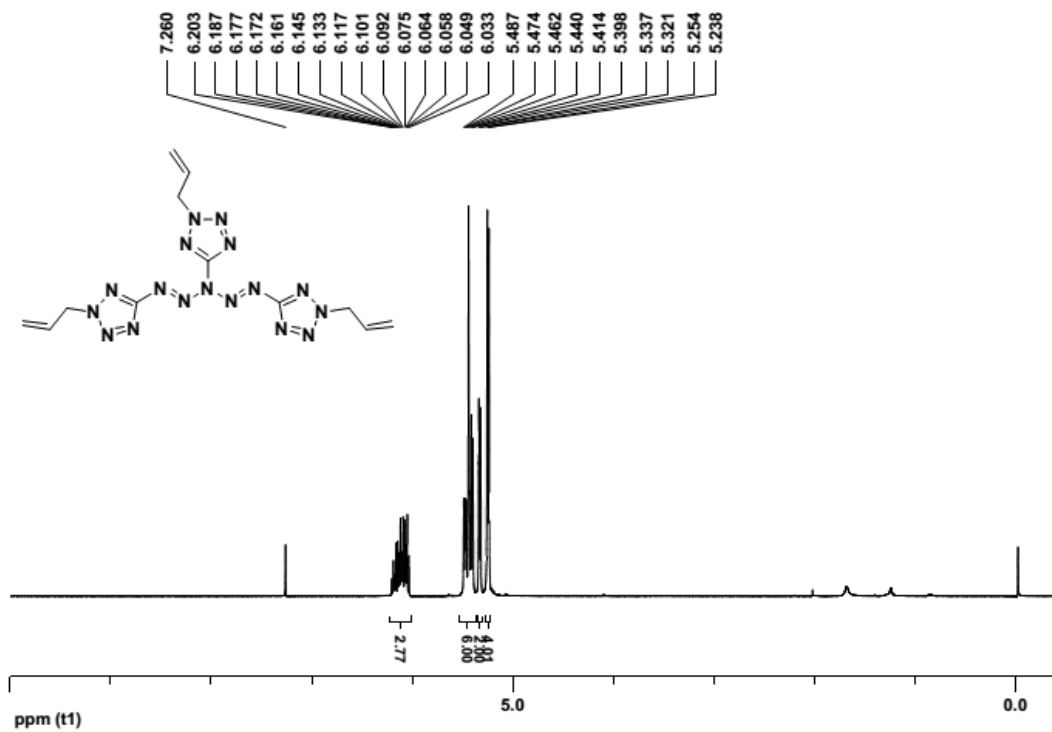
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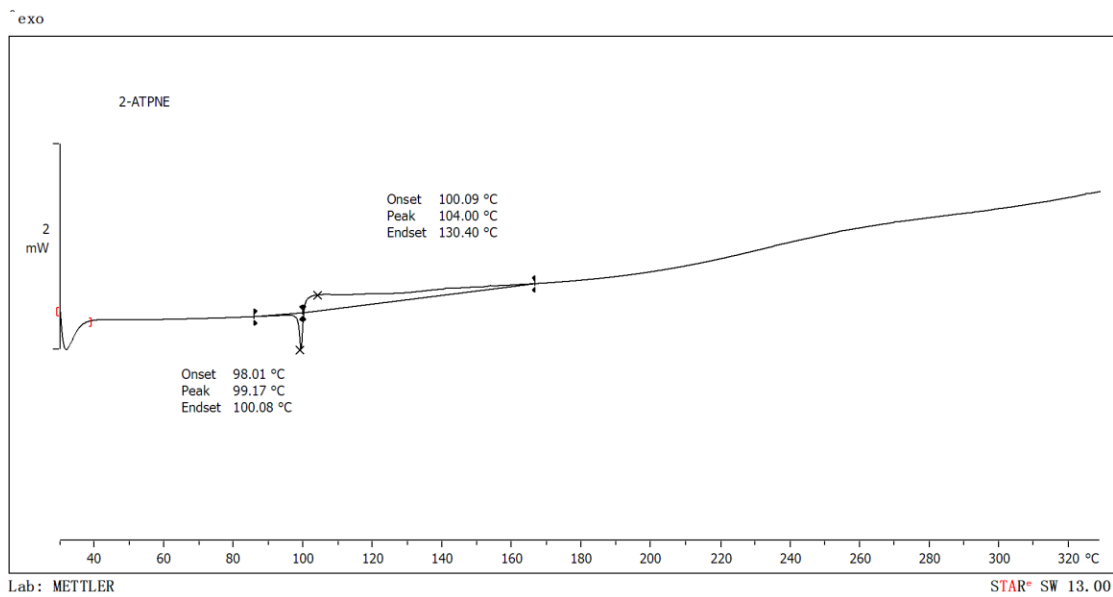
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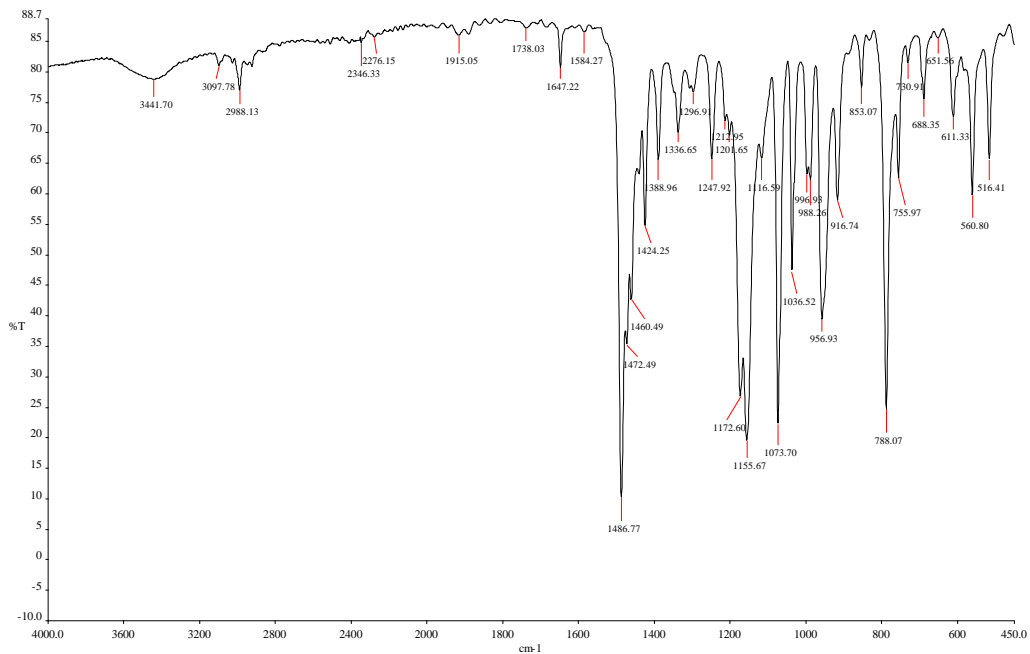
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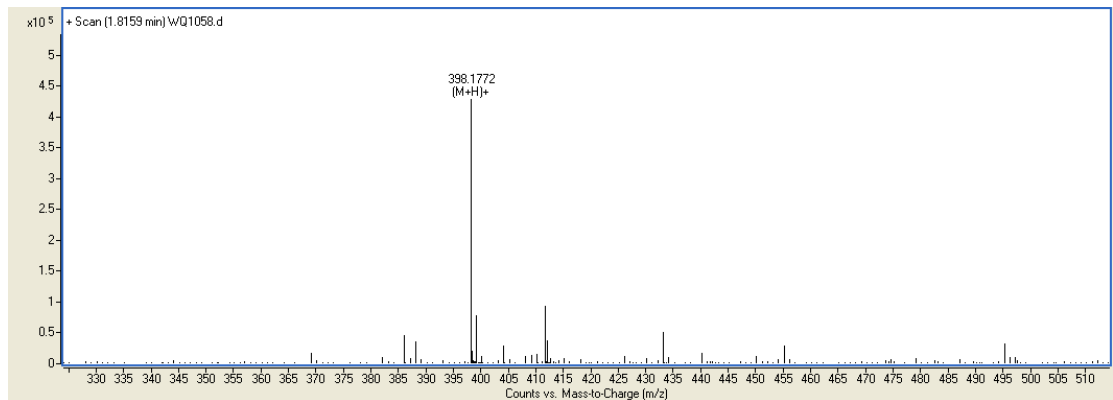
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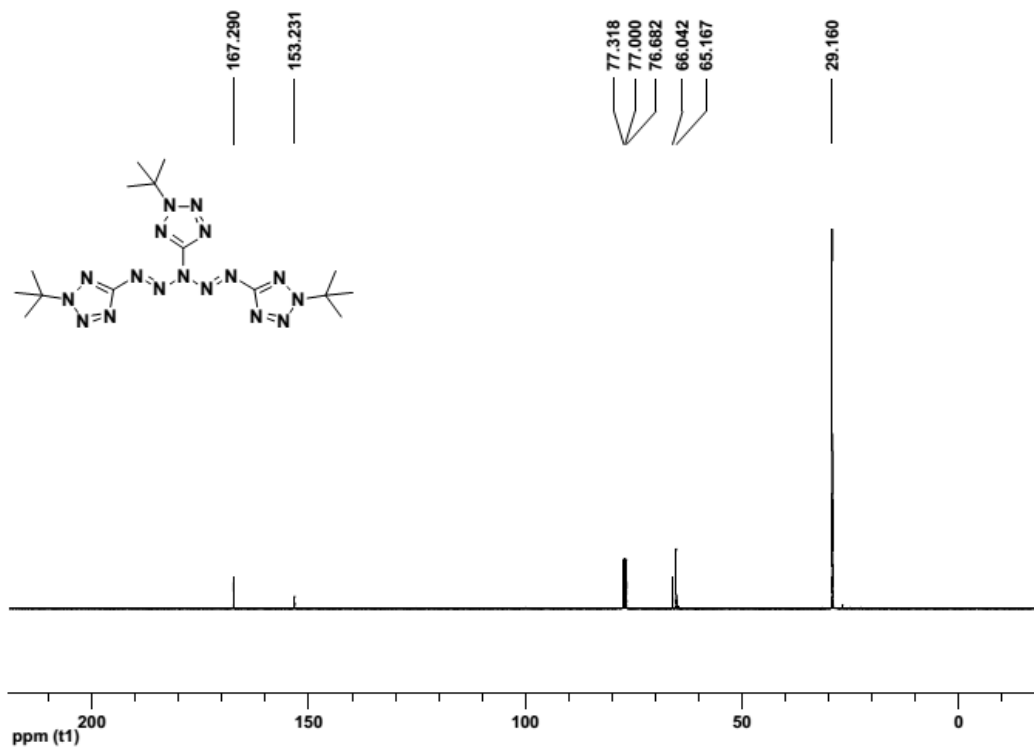
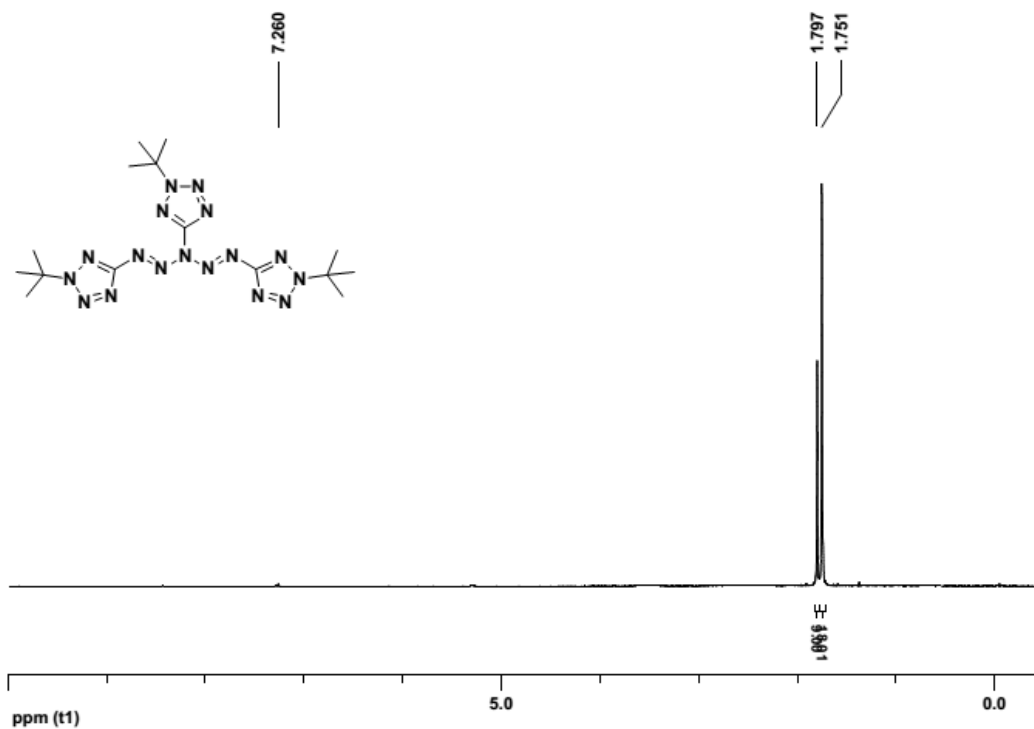
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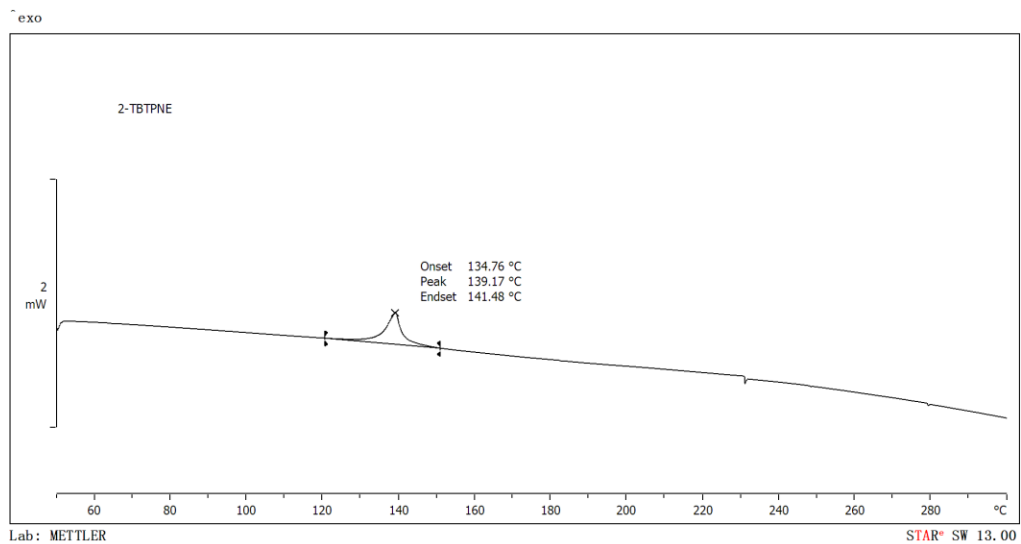
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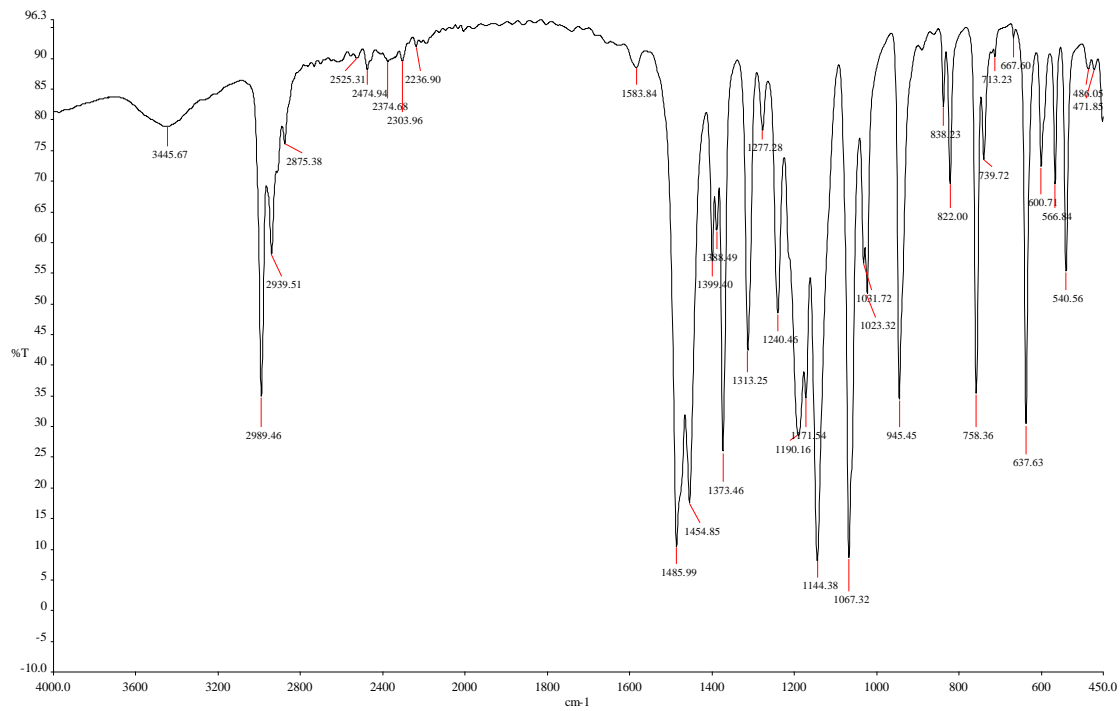
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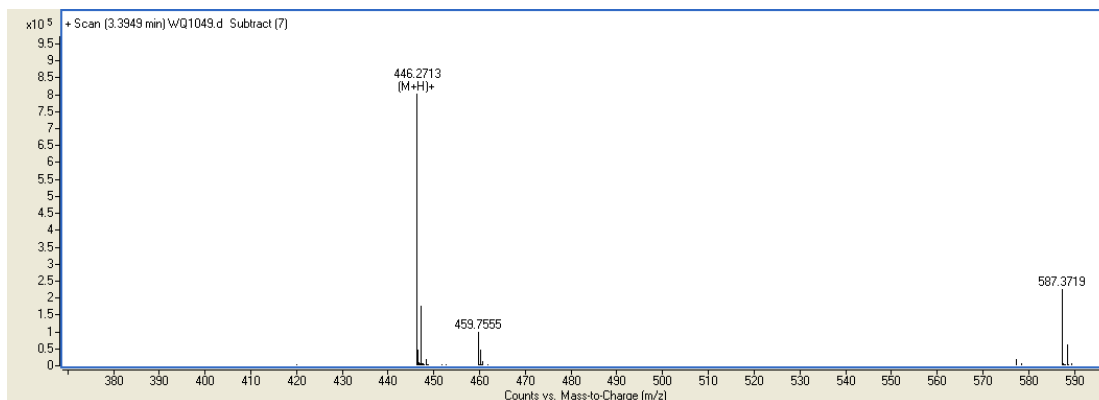
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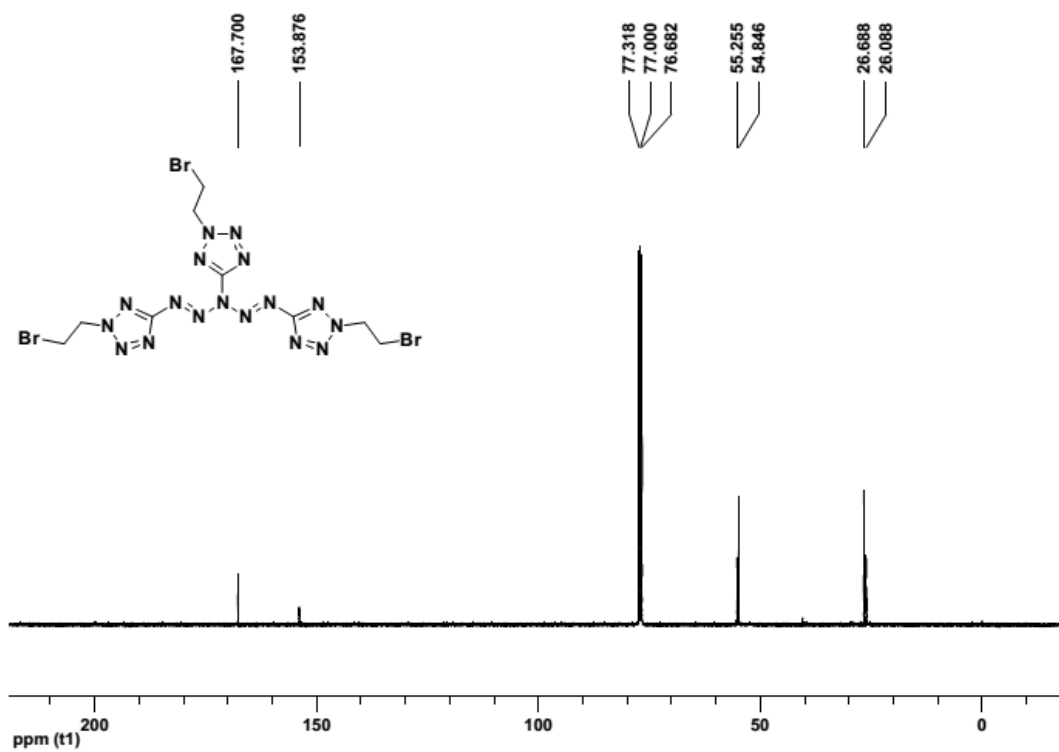
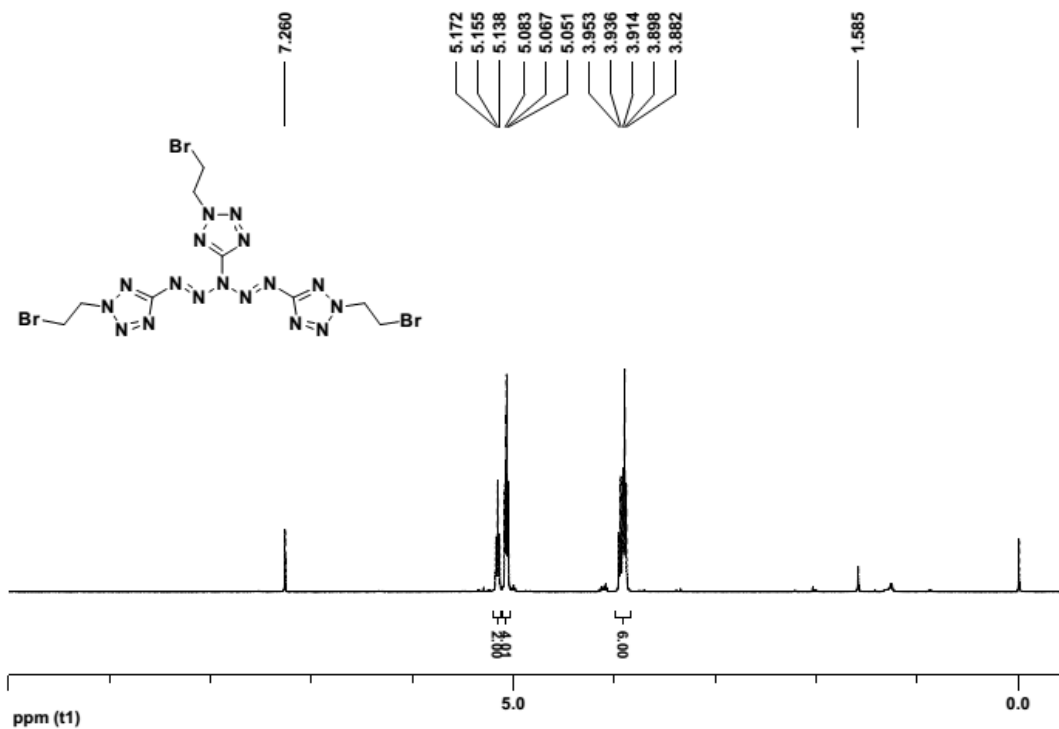
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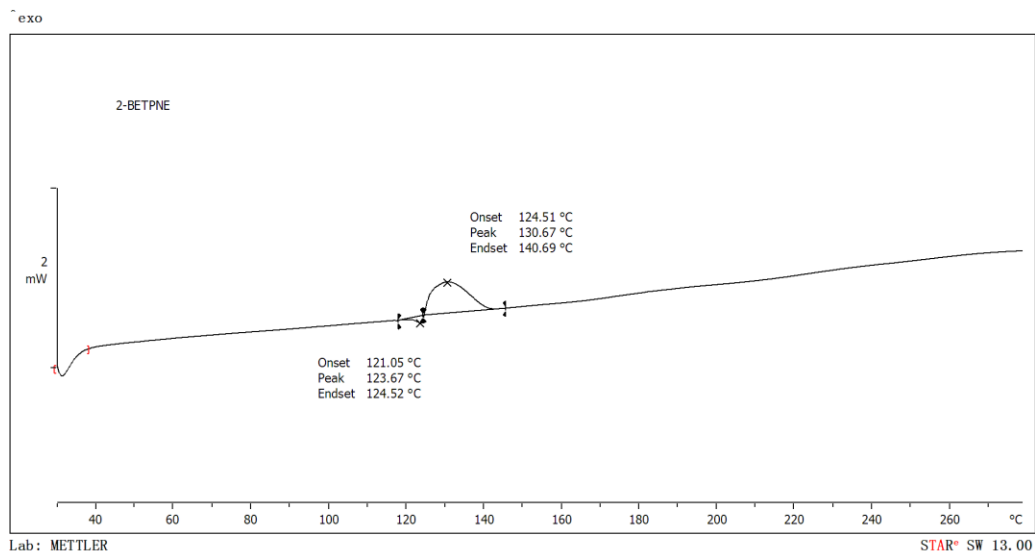
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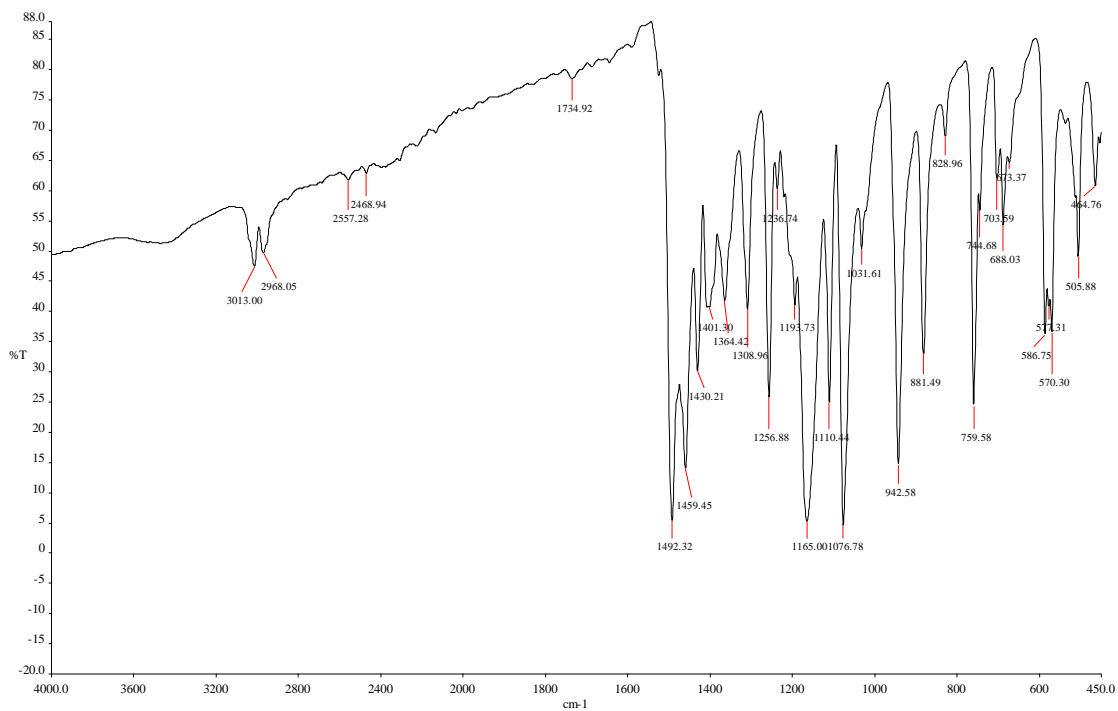
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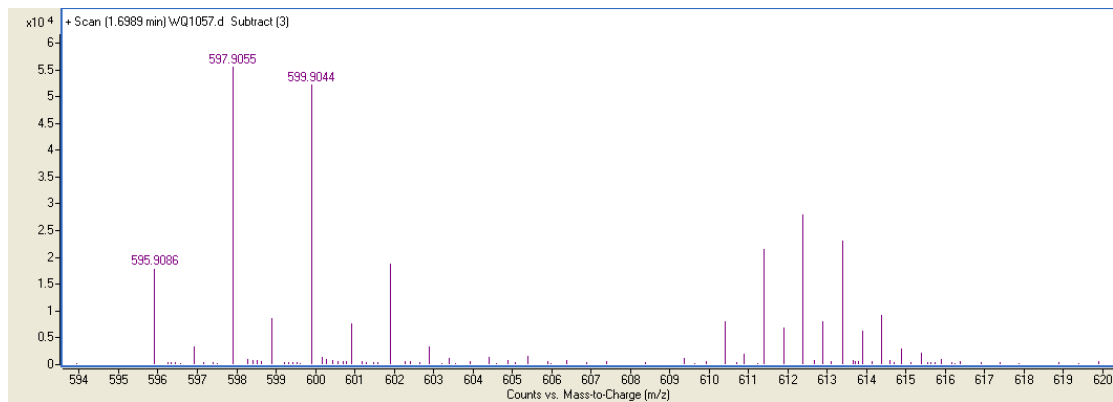
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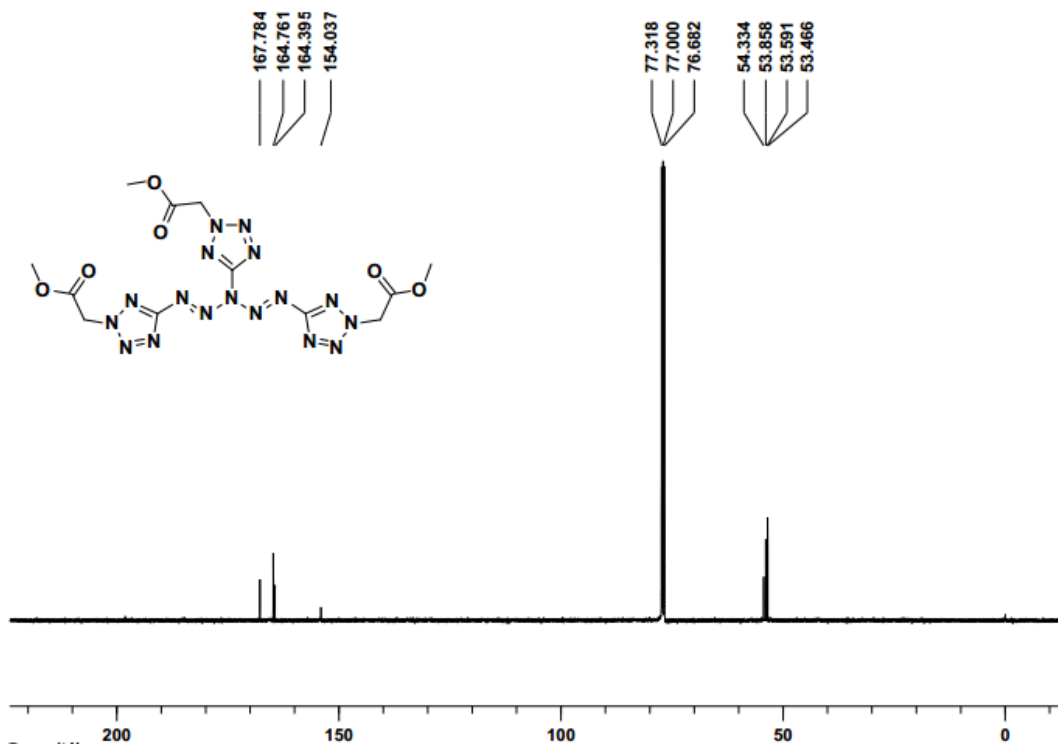
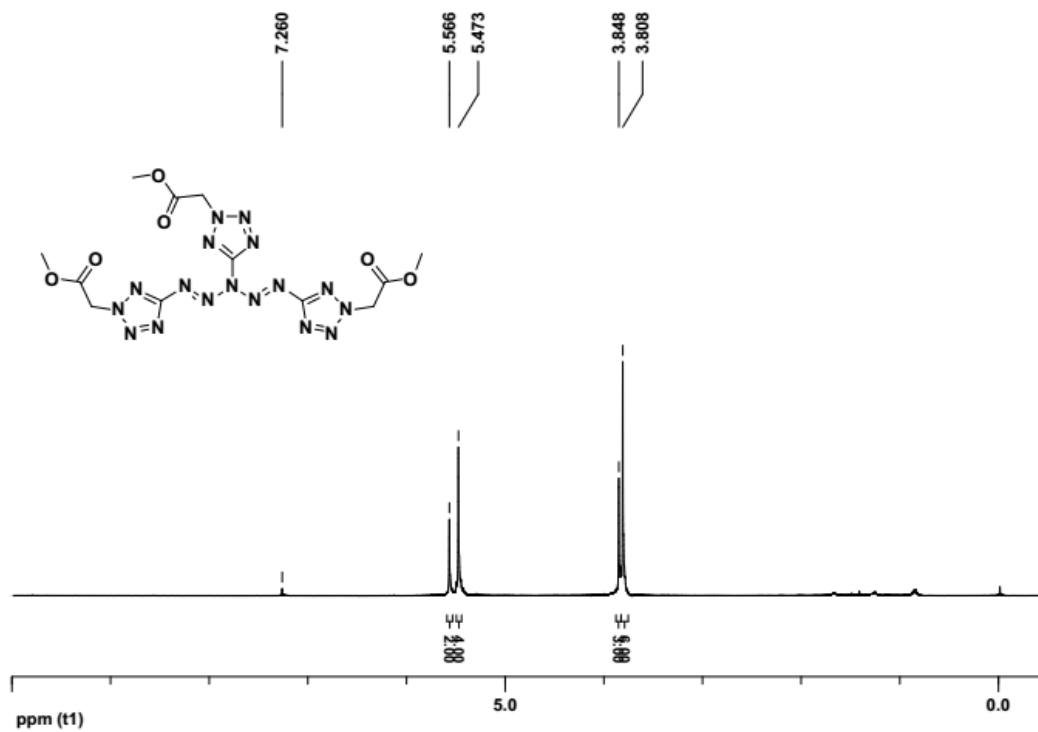
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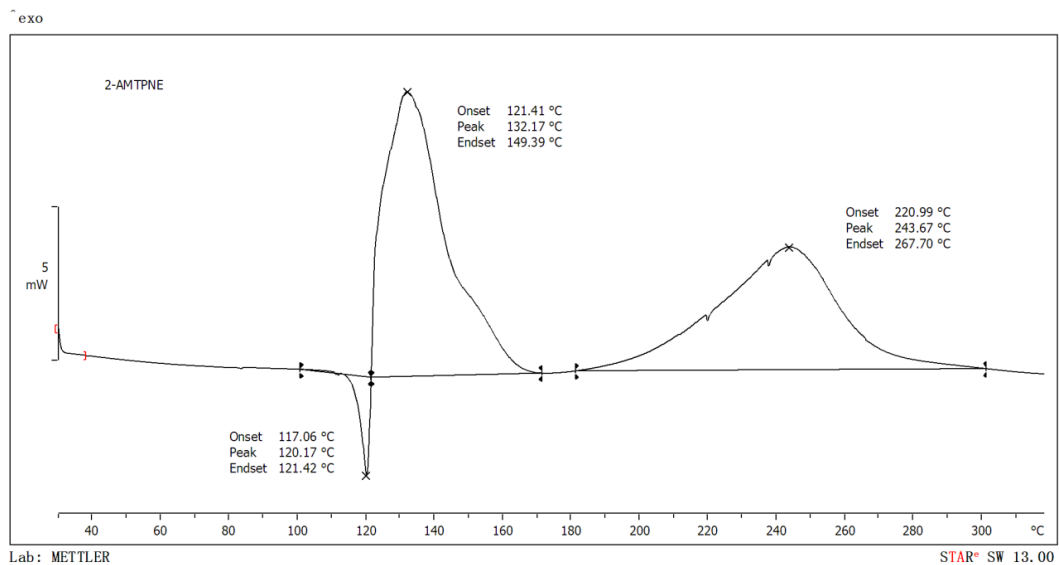
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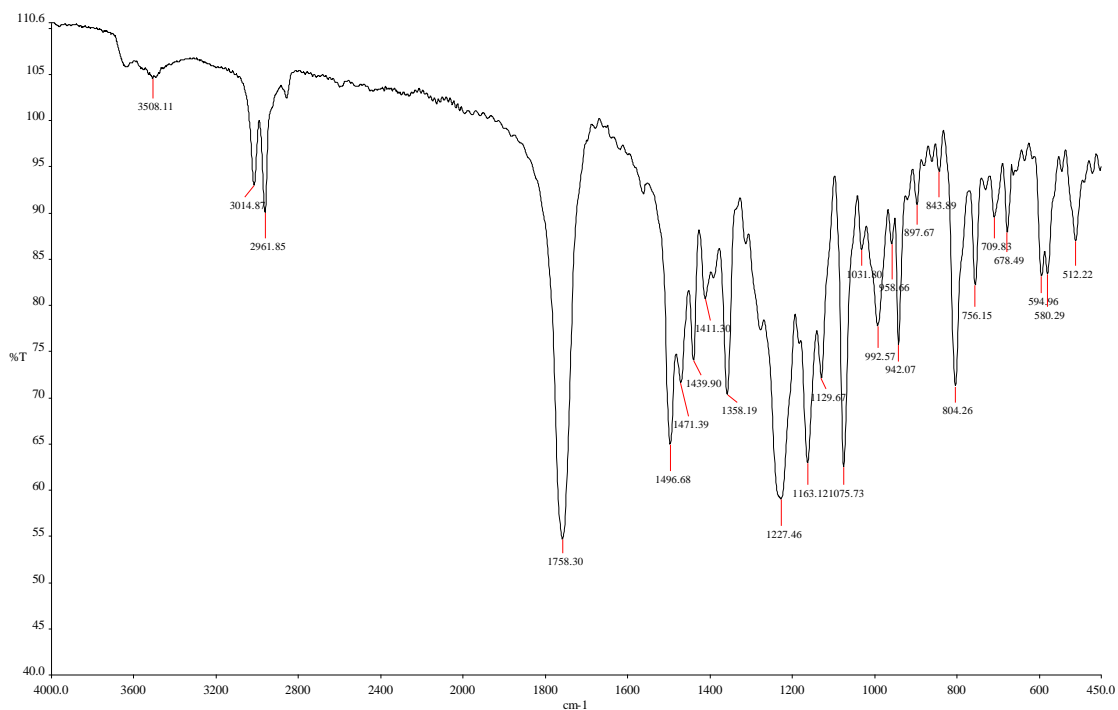
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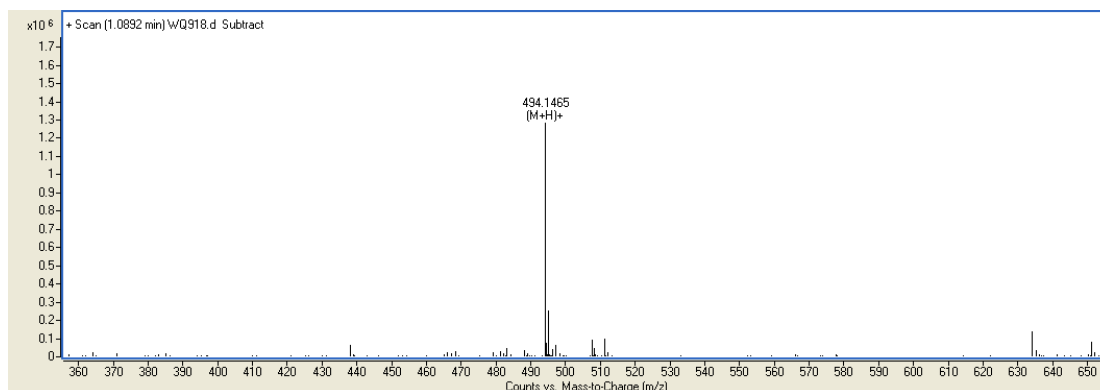
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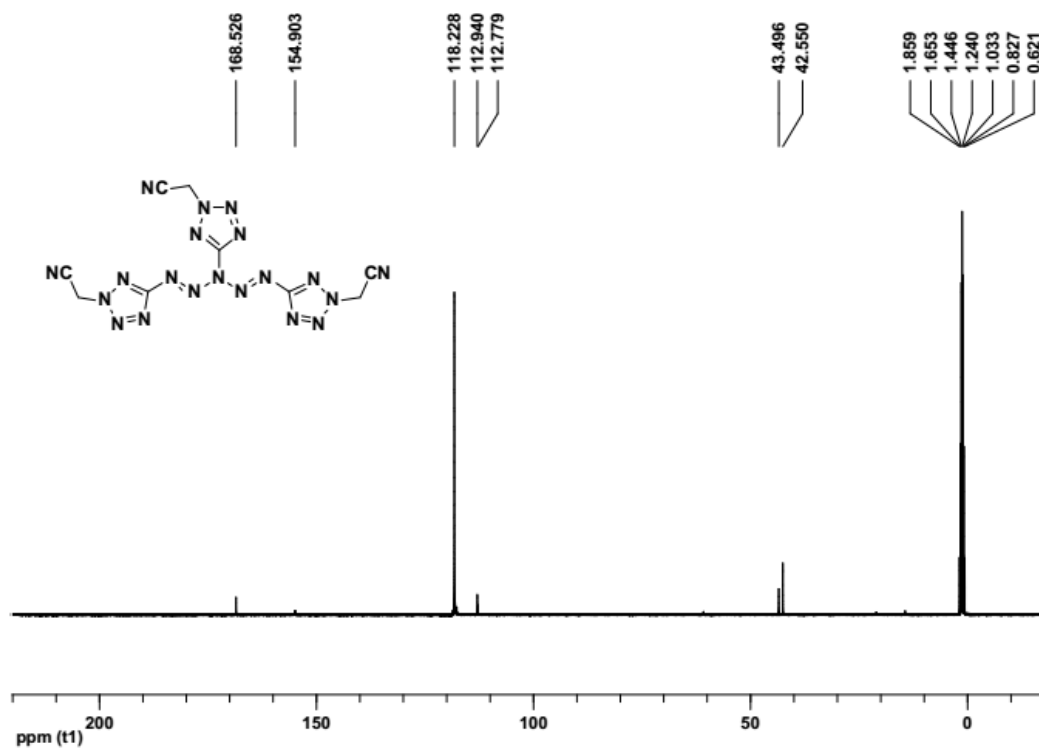
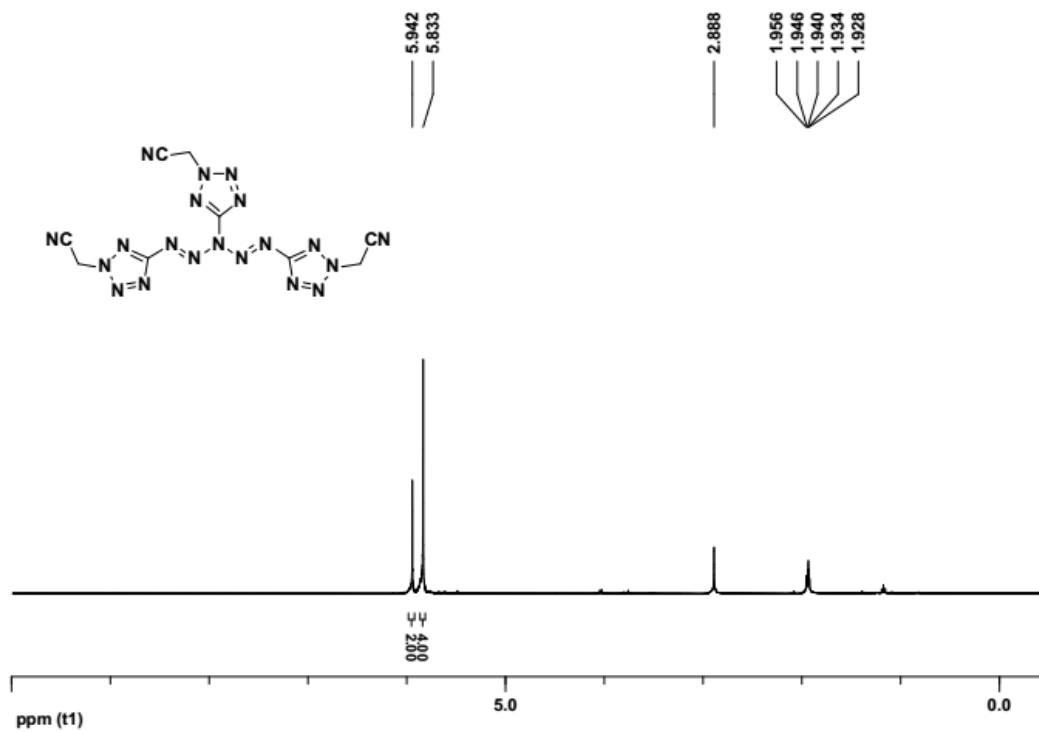
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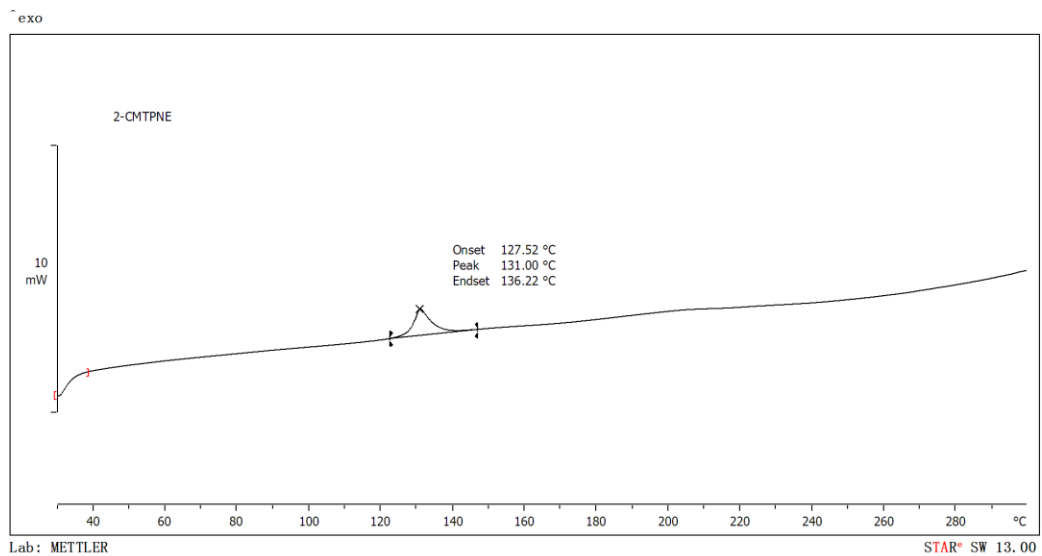
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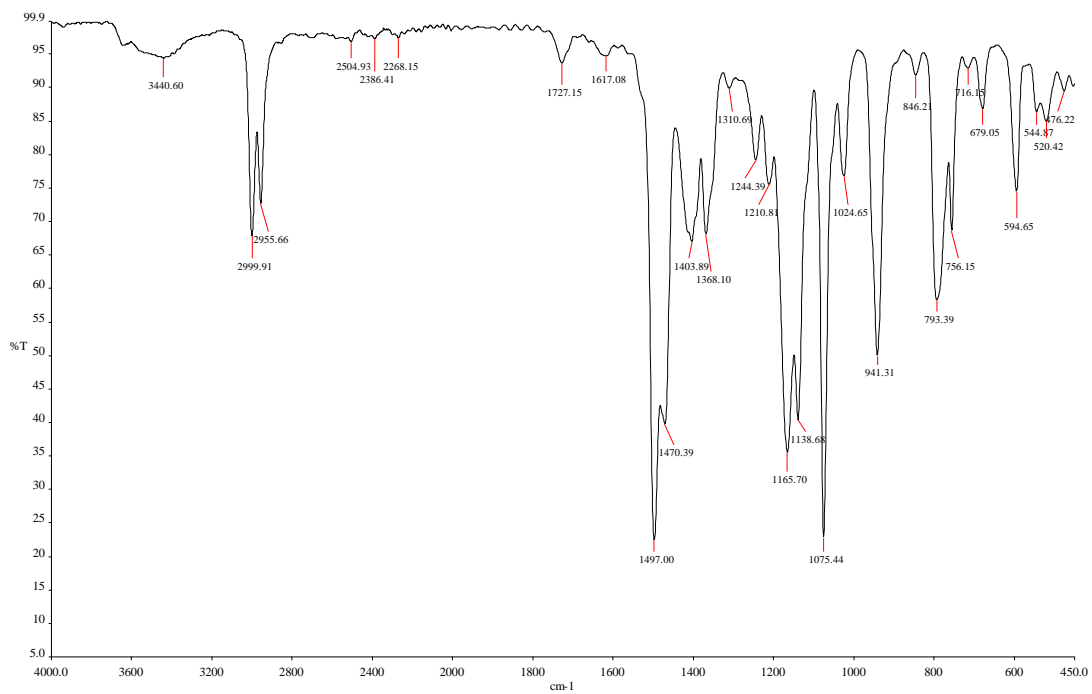
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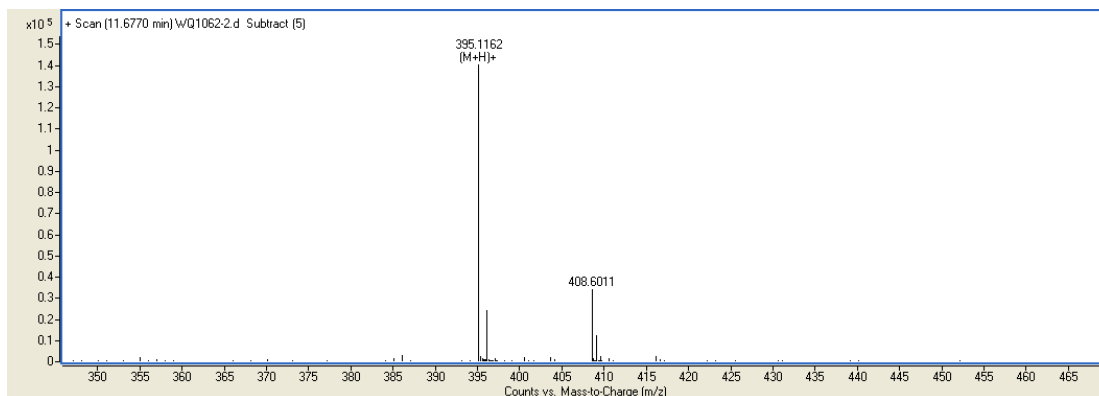
DSC



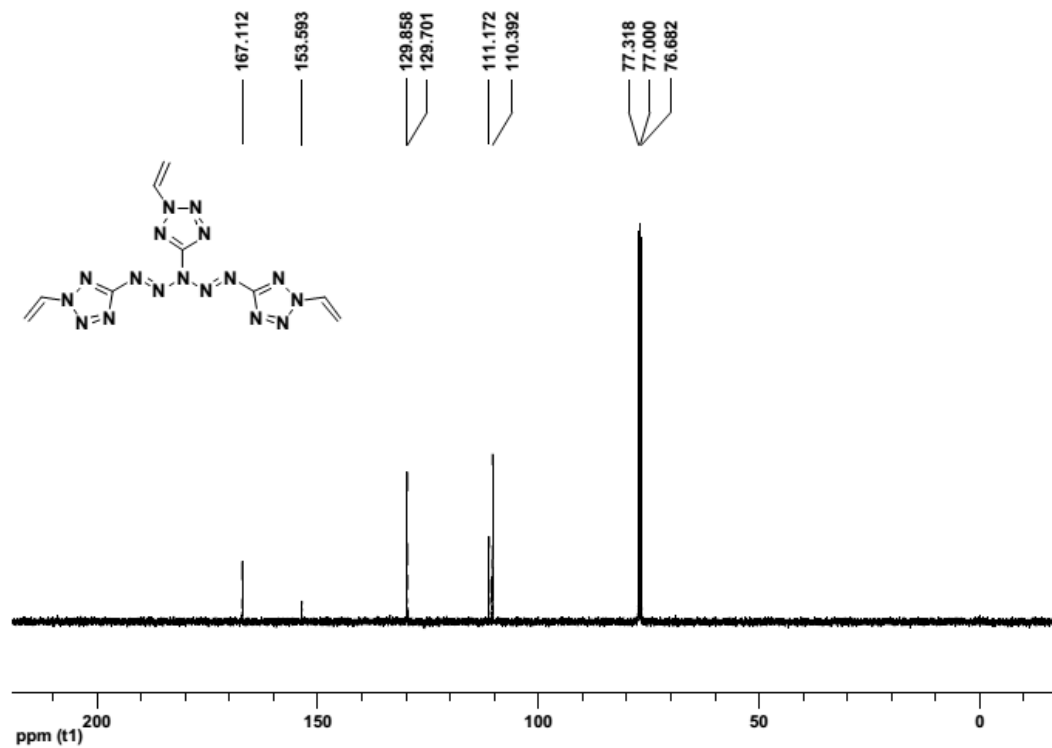
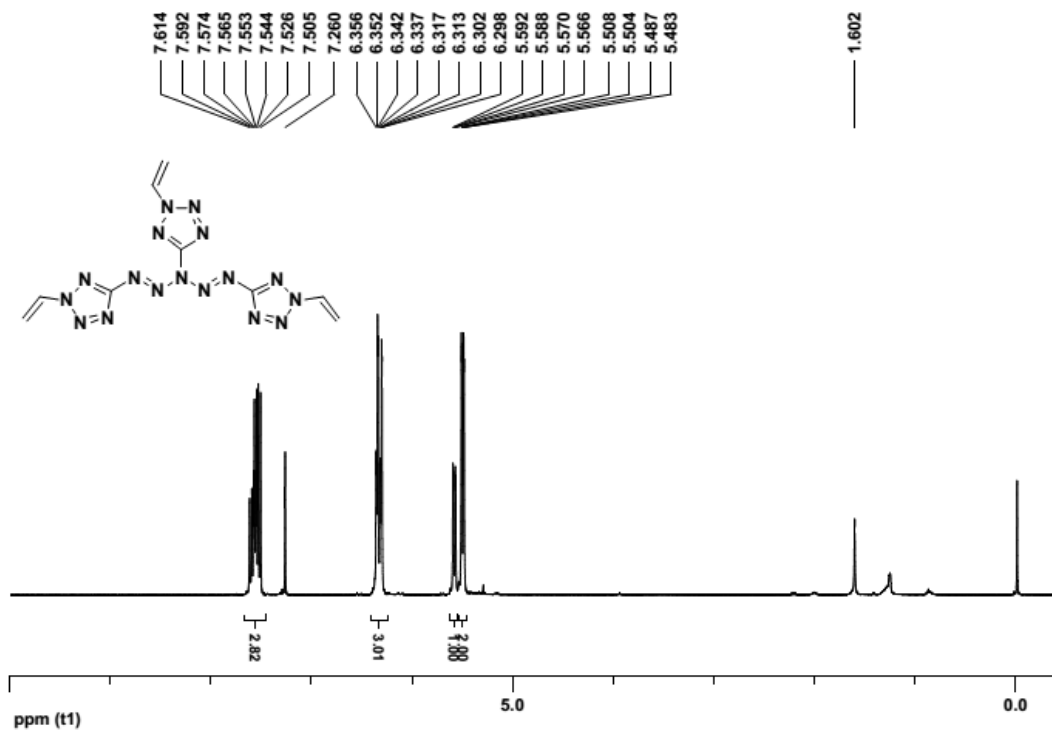
Infrared



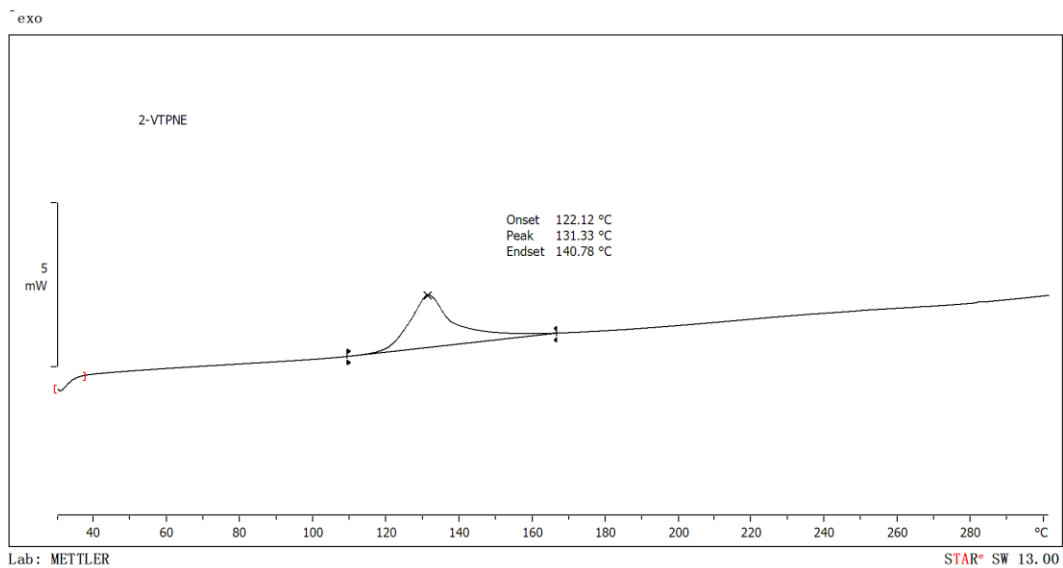
HRMS



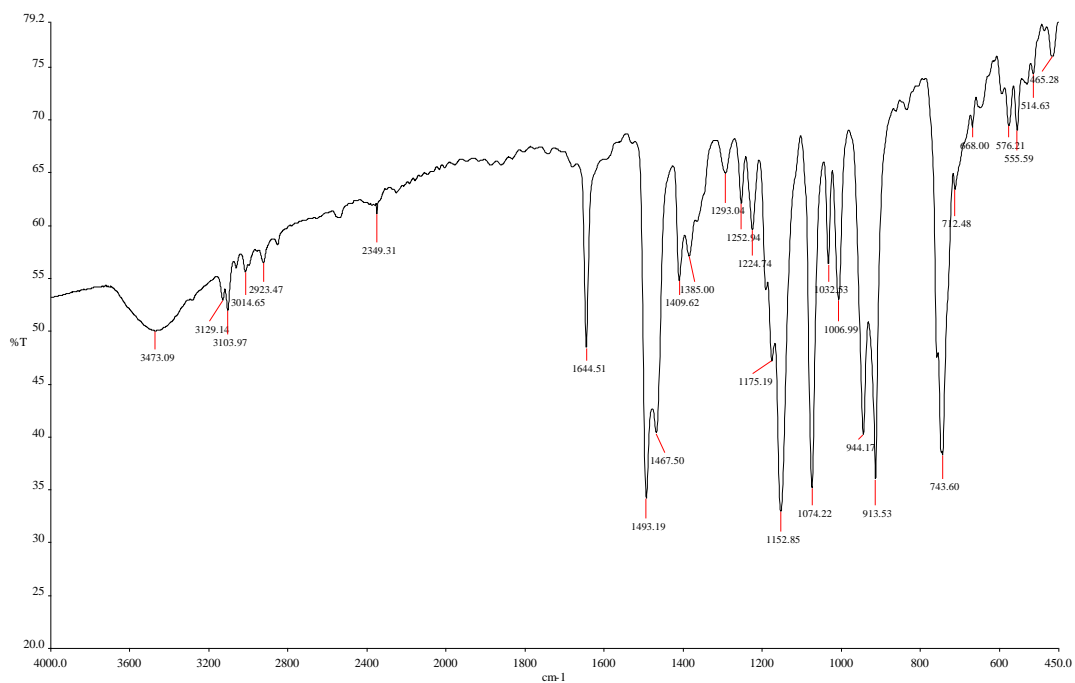
Spectral data of 2h



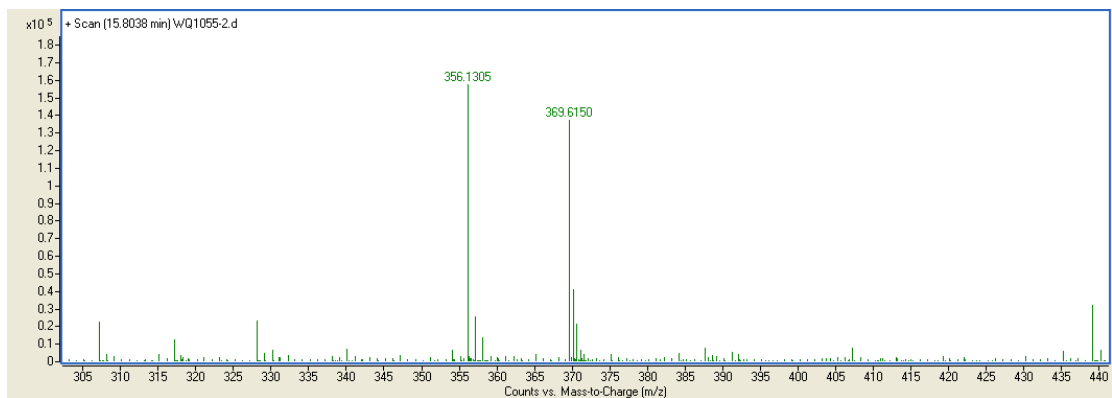
DSC



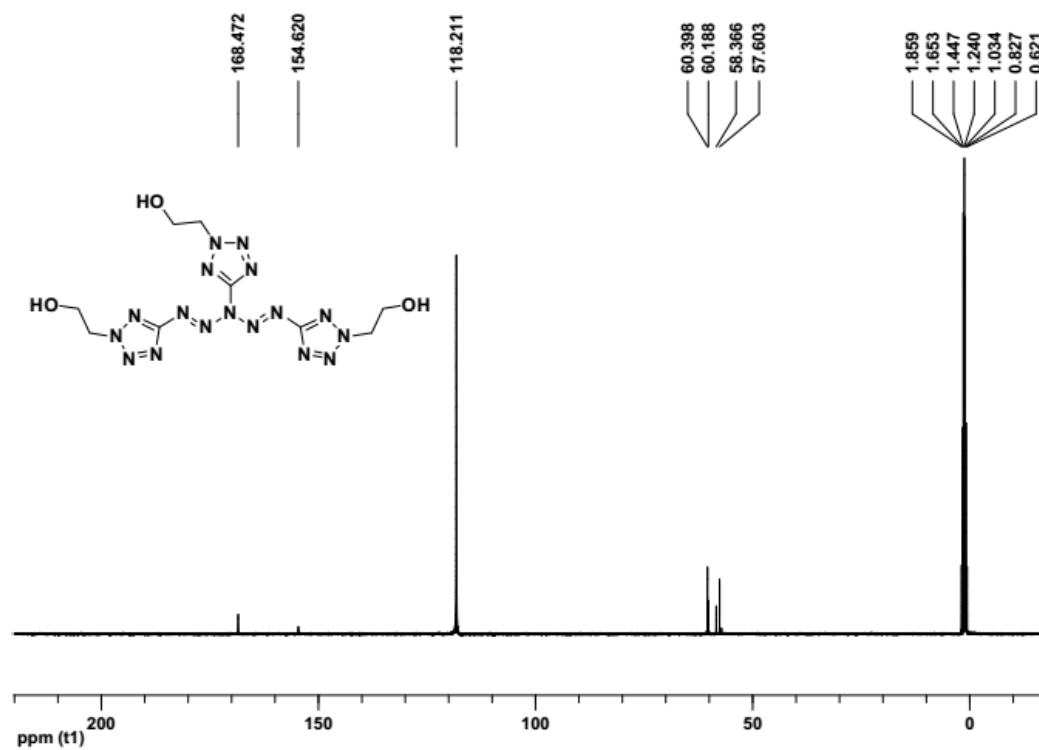
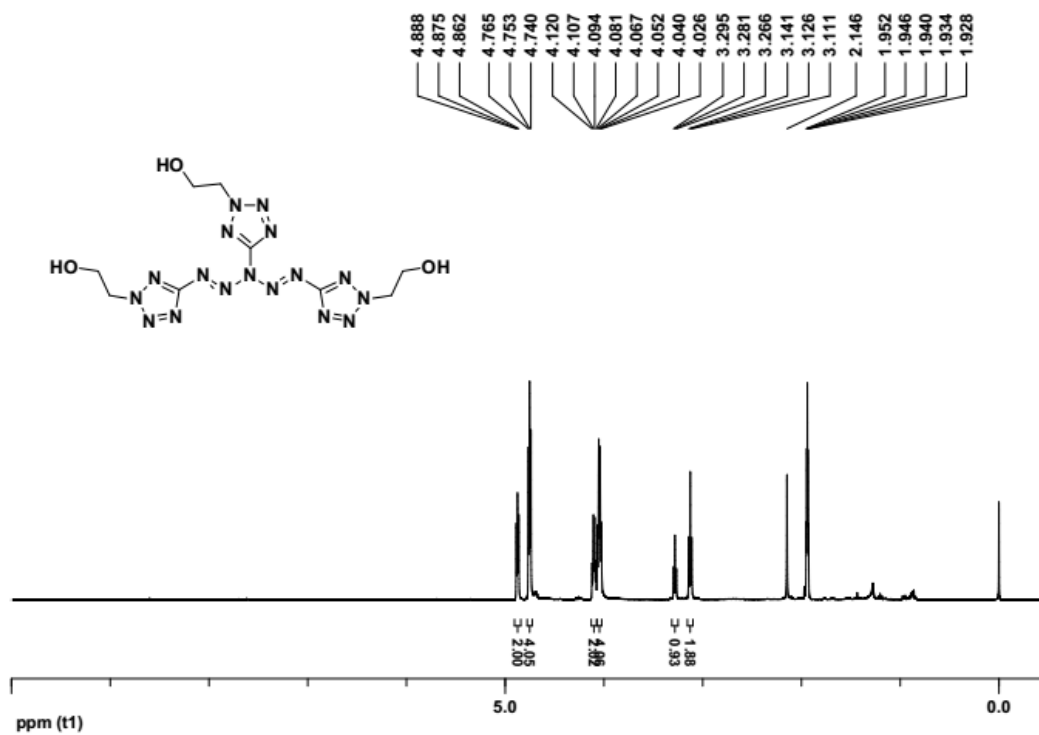
Infrared



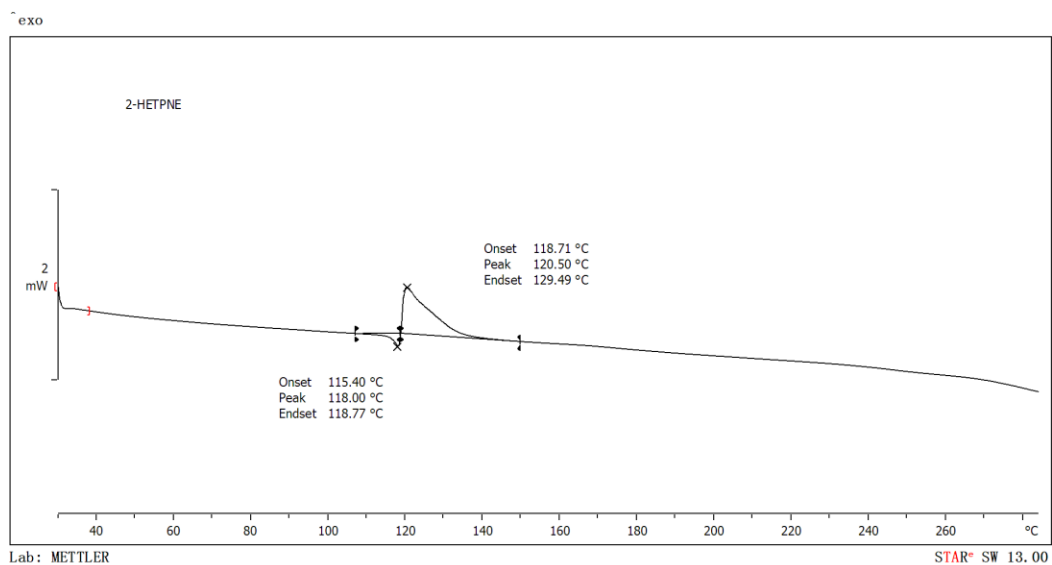
HRMS



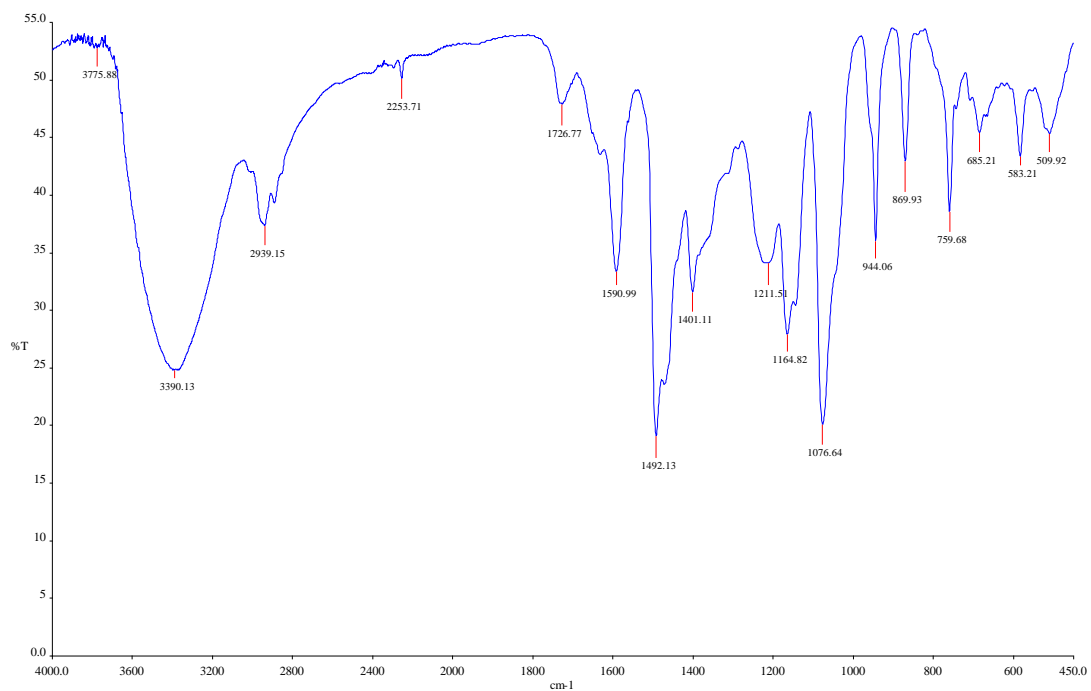
Spectral data of 2i



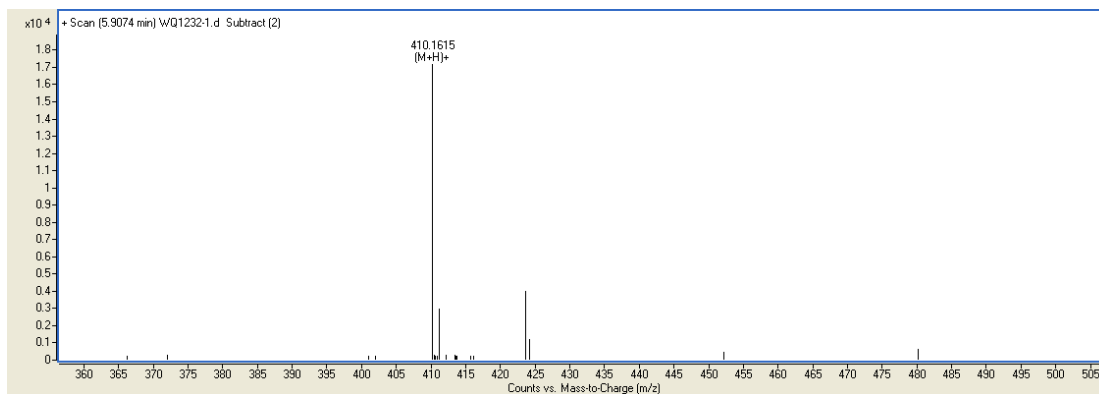
DSC



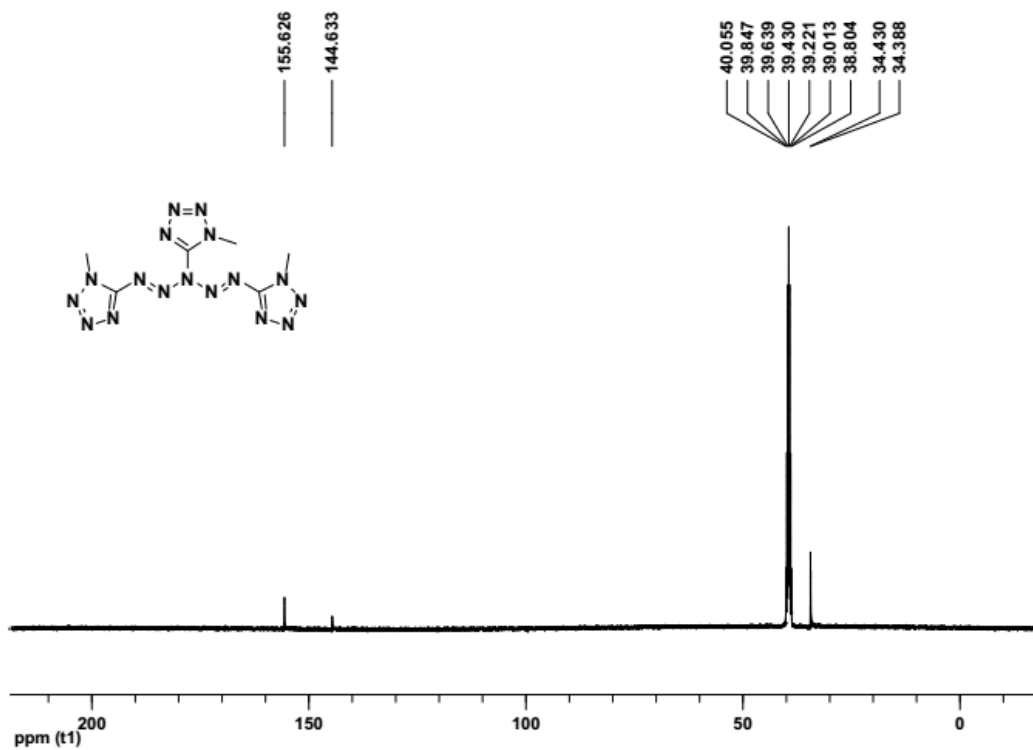
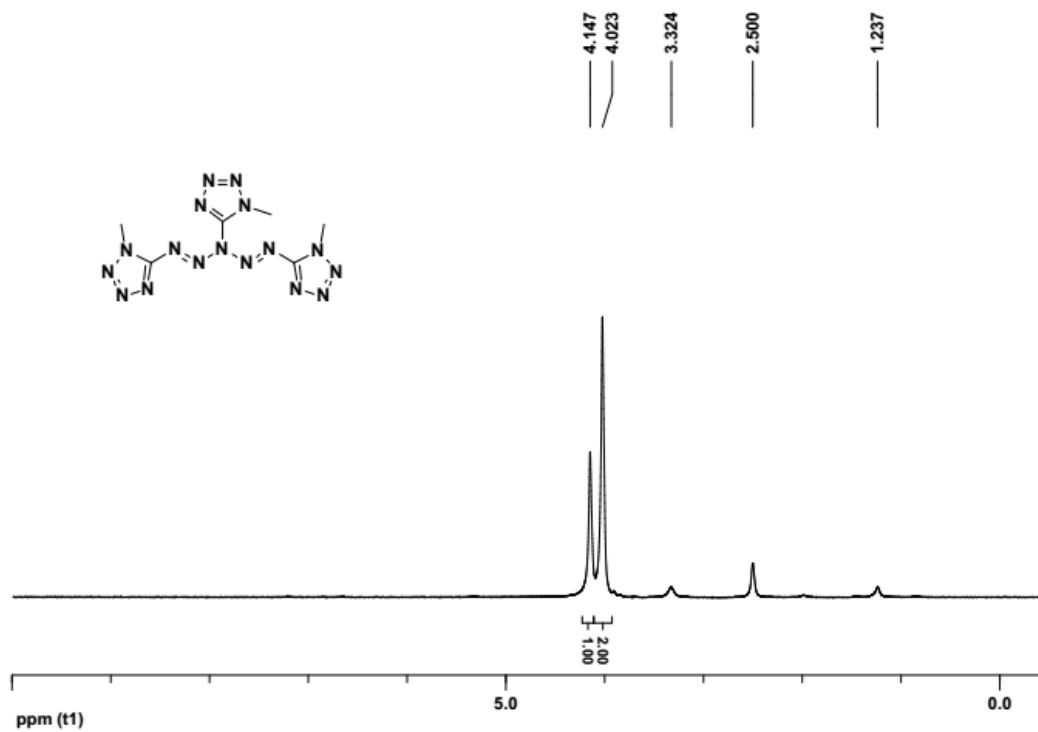
Infrared



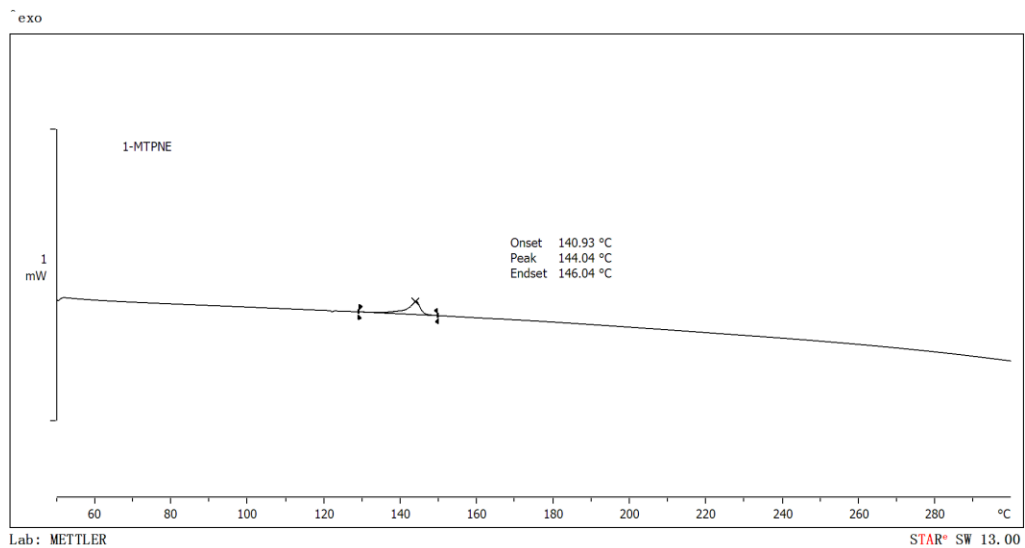
HRMS



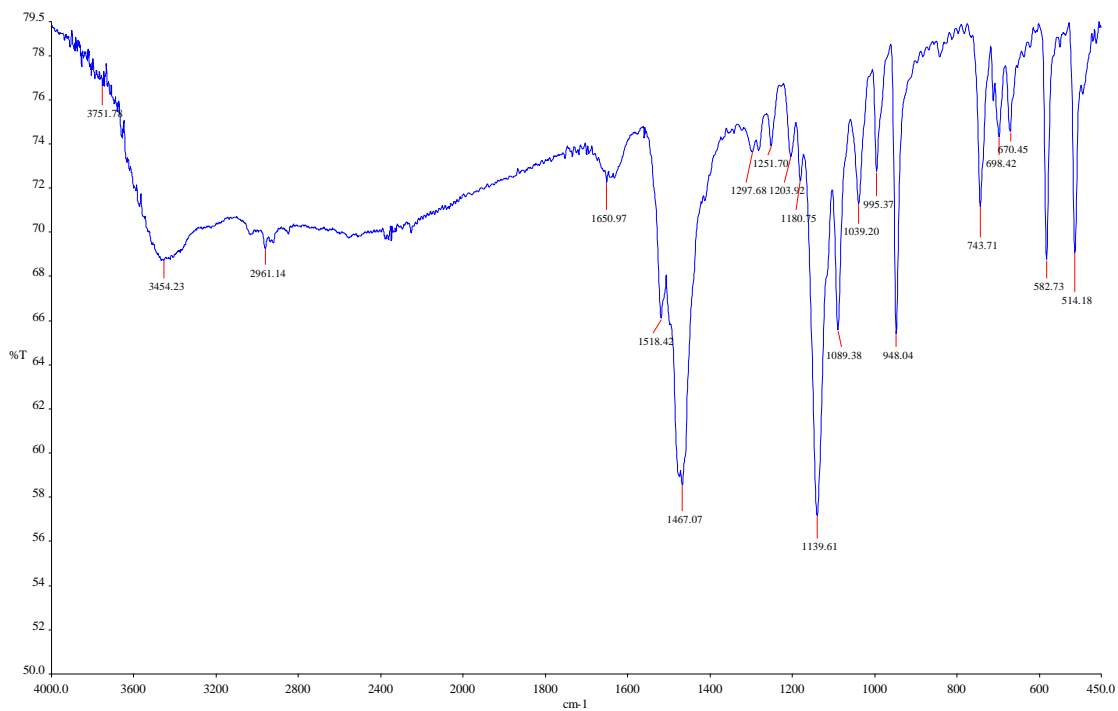
Spectral data of 2j



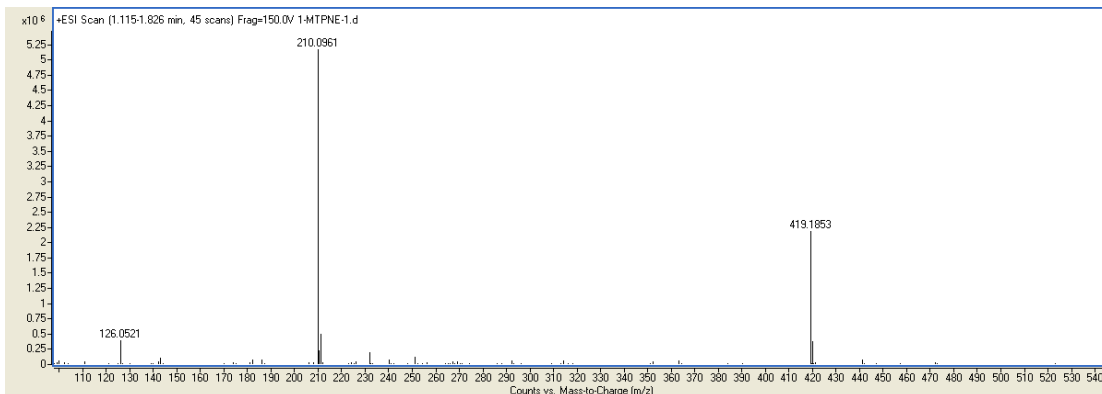
DSC



Infrared

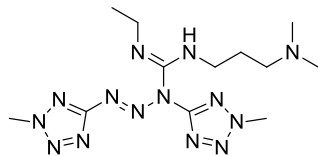


HRMS



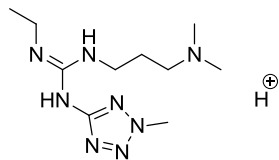
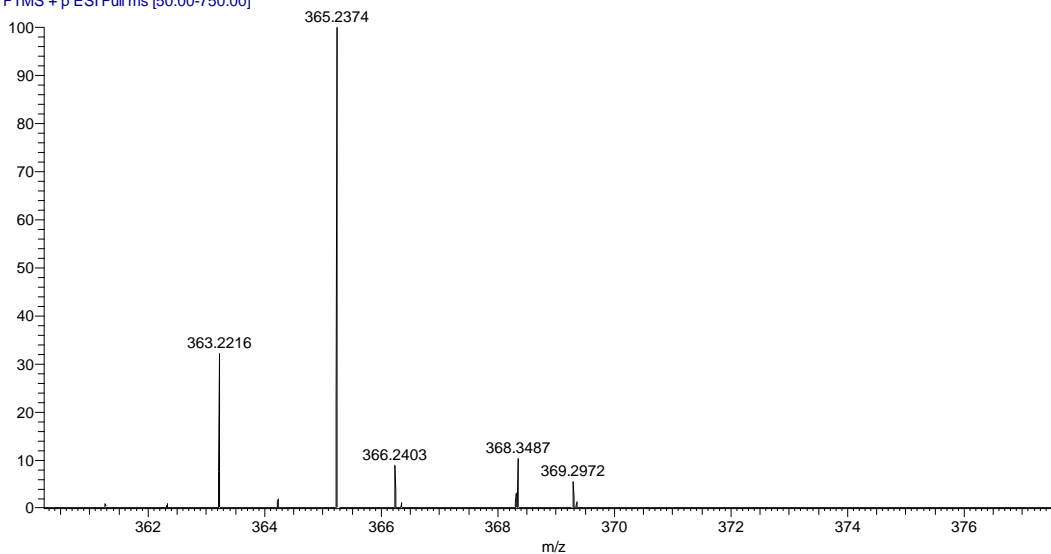
When R'-N=C=N-R'' was EDCI, the molecular weight of **3a** and **4a** was observed in HRMS.

HRMS of **3a**



calc.: 365.2381; found: 365.2374

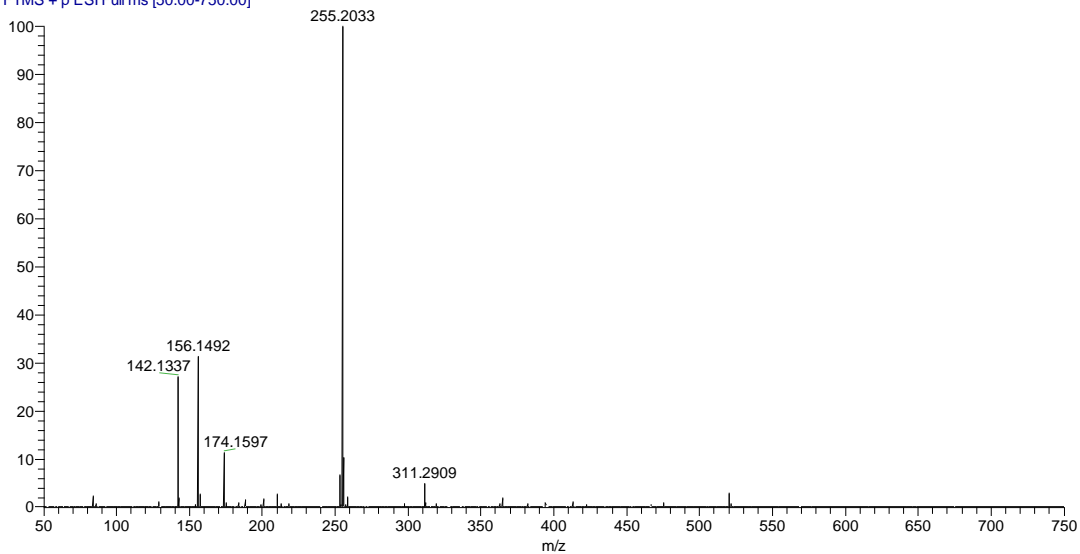
WQ#174 RT: 0.78 AV: 1 NL: 1.65E8
T: FTMS + p ESI Full ms [50.00-750.00]



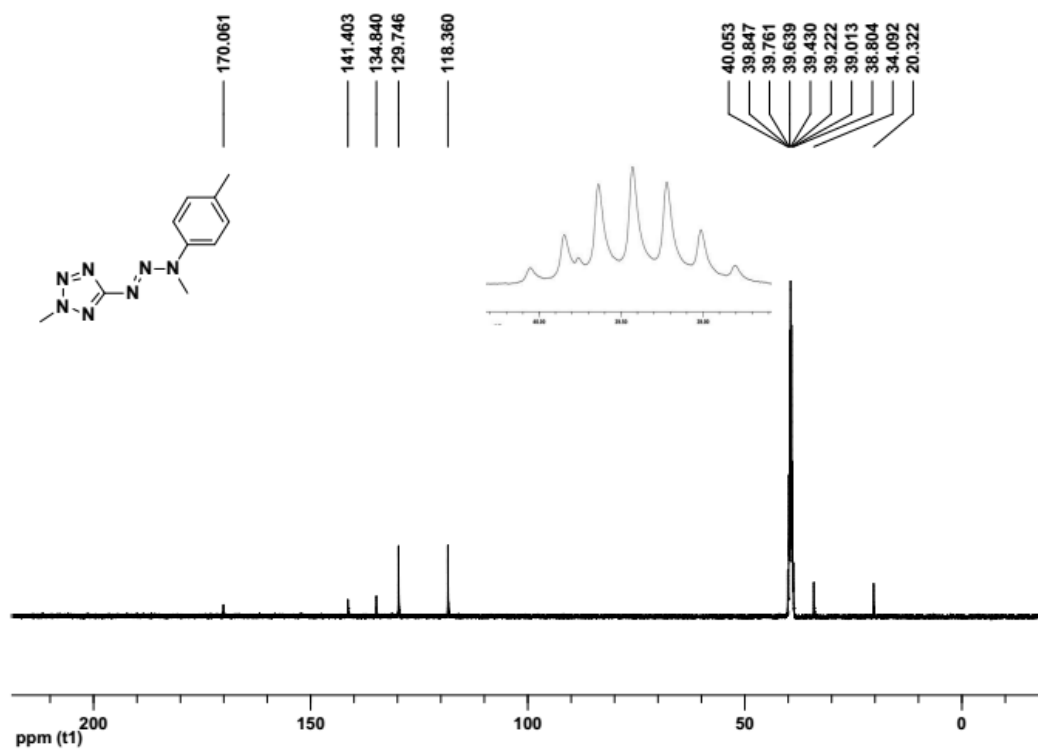
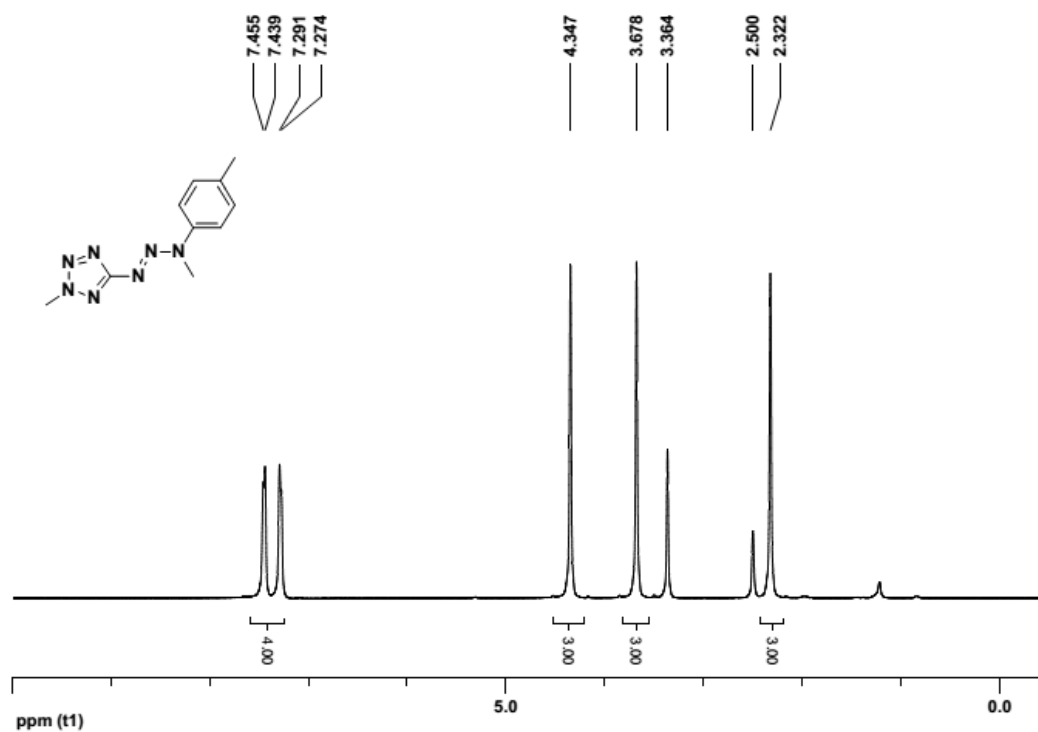
calc.: 255.2040; found: 255.2033

HRMS of **4a**

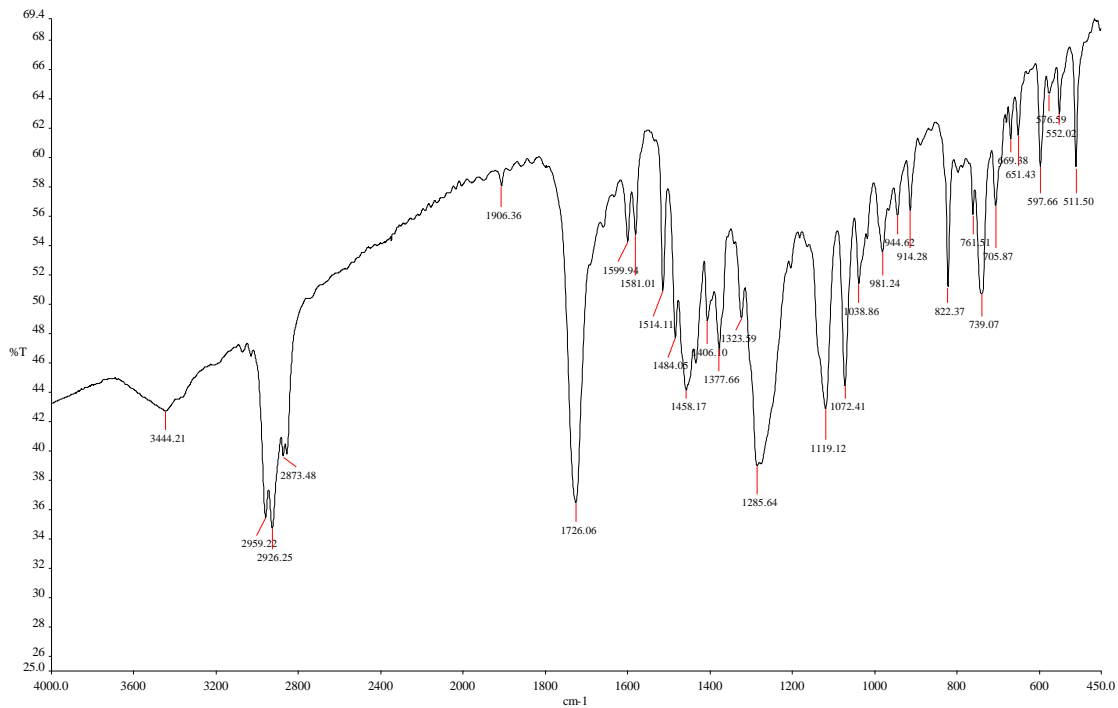
WQ#170 RT: 0.76 AV: 1 NL: 8.48E9
T: FTMS + p ESI Full ms [50.00-750.00]



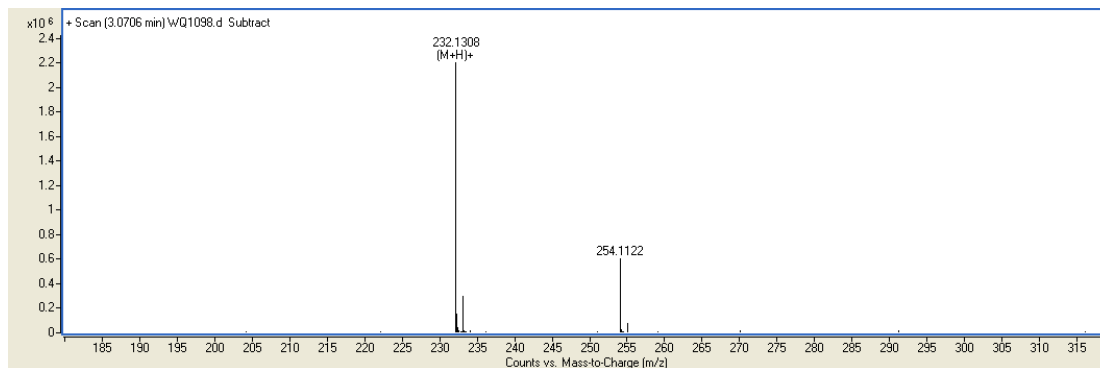
Spectral data of 5



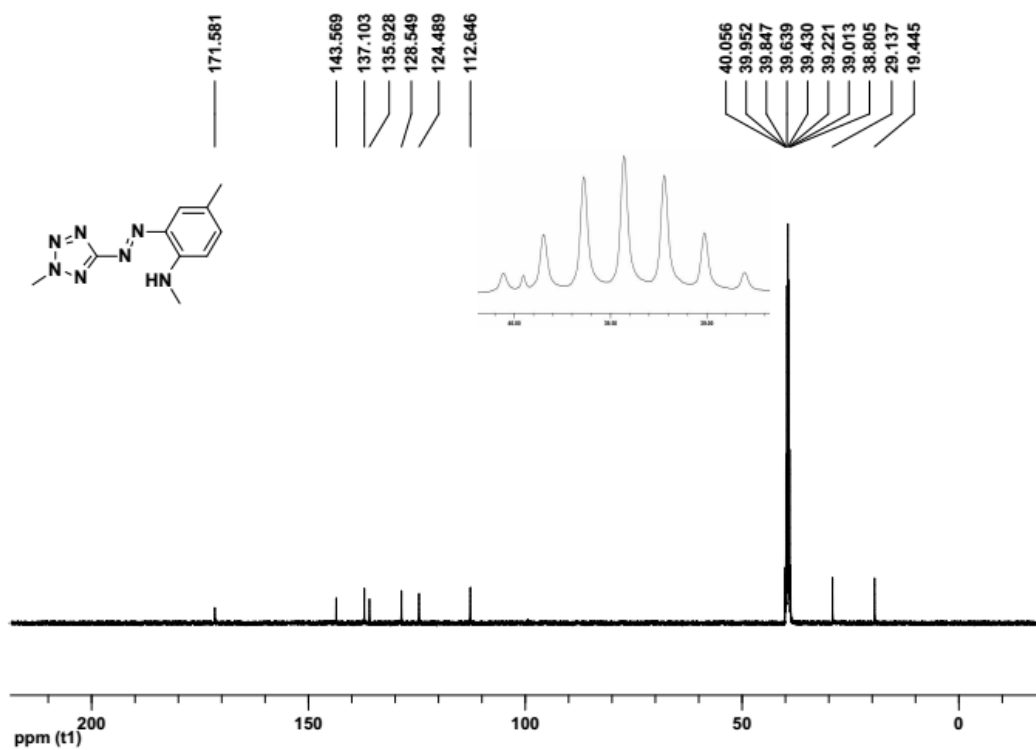
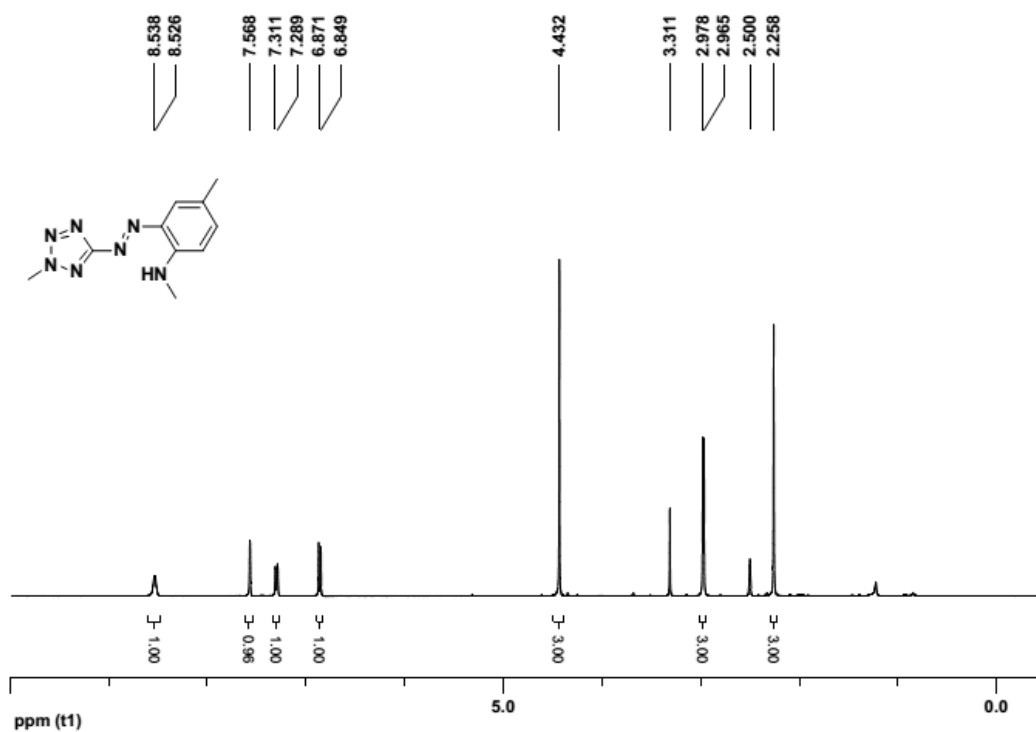
Infrared



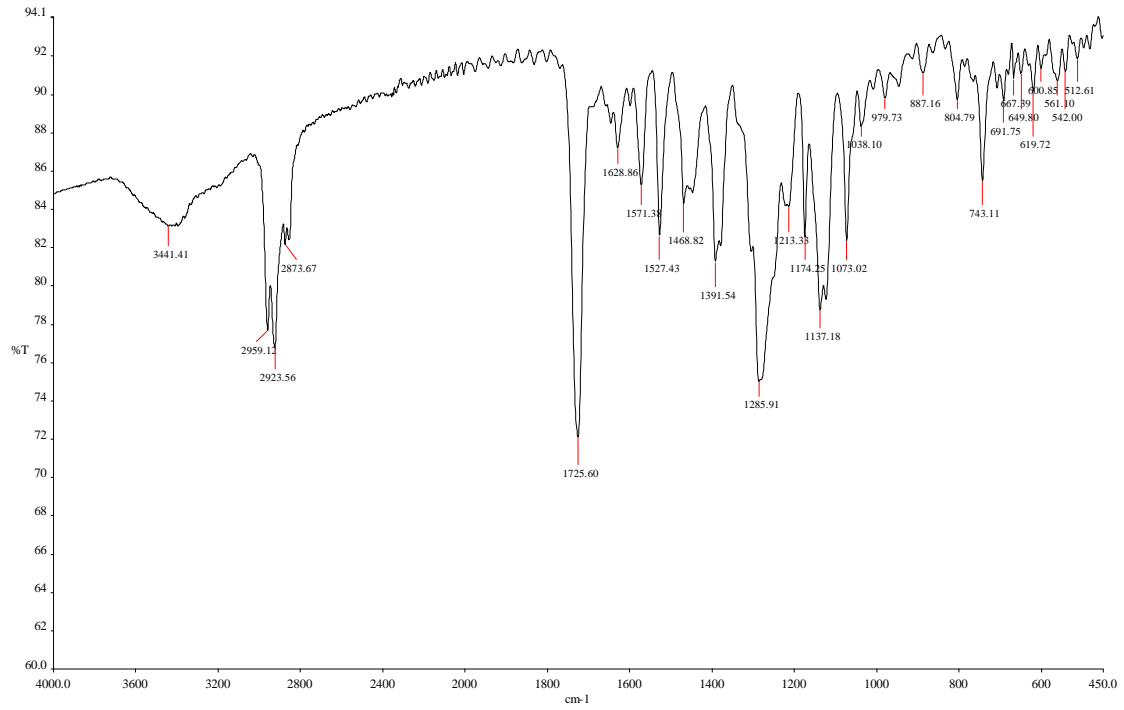
HRMS



Spectral data of 6



Infrared



HRMS

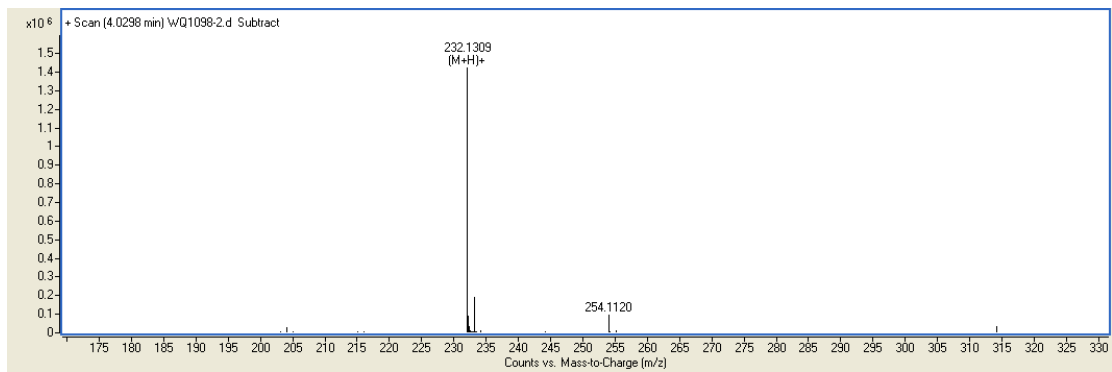


Table S3. Crystal data and structure refinement for **2a**.

Identification code	2a
CCDC deposition number	1499749
Empirical formula	C ₆ H ₉ N ₁₇
Formula weight	319.30
Temperature	153.15 K
Wavelength	0.71073 Å
Crystal system, space group	monoclinic, P2 ₁ /c
Unit cell dimensions	a = 15.804(3) Å α = 90.00 ° b = 10.785(2) Å β = 99.10(3) ° c = 8.1924(16) Å γ = 90.00 °
Volume	1378.8(5) Å ³
Z	4
Calculated density	1.538 g/cm ³
Absorption coefficient	0.118 mm ⁻¹
F(000)	656
Crystal size	0.16 x 0.05 x 0.04 mm
Theta range for data collection	2.6 to 50 °
Limiting indices	-17<=h<=18, -12<=k<=12, -9<=l<=8
Reflections collected / unique	8237 / 2410 [R _{int} = 0.0675]
Absorption correction	Multi-scan
Refinement method	Full-matrix least-squares on F ²
Data / restraints / parameters	2410 / 0 / 211
Goodness-of-fit on F ²	1.205
Final R indices [I>2σ(I)]	R ₁ = 0.1663, wR ₂ = 0.4342
R indices (all data)	R ₁ = 0.1853, wR ₂ = 0.4465
Largest diff. peak and hole	0.812 and -0.543 e.Å ⁻³

Table S4. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for **2a**. $U(\text{eq})$ is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	$U(\text{eq})$
N(1)	940(5)	8692(7)	-850(10)	26(19)
N(2)	489(5)	9252(7)	-2176(11)	27 (19)
N(3)	441(6)	10464(8)	-2029(10)	30(2)
N(4)	868(5)	10752(7)	-559(10)	27(19)
N(5)	1651(6)	9633(8)	1715(10)	28(2)
N(6)	1896(5)	8557(8)	2110(10)	27(2)
N(7)	2394(5)	8522(8)	3633(10)	27(2)
N(8)	2754(5)	7364(7)	3907(10)	27(2)
N(9)	3304(5)	7329(7)	5223(11)	27(2)
N(10)	3294(7)	5075(8)	4718(14)	46(3)
N(11)	3770(6)	4161(8)	5375(13)	40(2)
N(12)	4359(5)	4661(8)	6540(10)	26 (19)
N(13)	4289(6)	5887(8)	6658(11)	32(2)
N(14)	3399(6)	10154(8)	4674(13)	35(2)
N(15)	3371(6)	11121(8)	5630(12)	32(2)
N(16)	2606(6)	11108(7)	6110(10)	27(19)
N(17)	2109(6)	10152(8)	5475(11)	33(2)
C(1)	101(8)	8575(10)	-3626(15)	41(3)
C(2)	1154(6)	9650(9)	111(12)	24(2)
C(3)	3619(6)	6105(10)	5481(13)	28(2)
C(4)	4964(8)	3886(11)	7590(17)	44(3)
C(5)	2643(6)	9586(9)	4621(13)	28(2)
C(6)	2325(7)	12080(10)	7139(12)	30(2)

Table S5. Bond lengths [\AA] and angles [$^\circ$] for **2a**.

N(1)-N(2)	1.345(11)	N(1)-C(2)	1.311(13)
N(2)-N(3)	1.317(11)	N(2)-C(1)	1.445(14)
N(3)-N(4)	1.321(12)	N(4)-C(2)	1.356(13)
N(5)-N(6)	1.250(12)	N(5)-C(2)	1.420(13)
N(6)-N(7)	1.366(11)	N(7)-N(8)	1.376(11)
N(7)-C(5)	1.424(13)	N(8)-N(9)	1.273(12)
N(9)-C(3)	1.415(13)	N(10)-N(11)	1.303(13)
N(10)-C(3)	1.337(14)	N(11)-N(12)	1.337(13)
N(12)-N(13)	1.332(12)	N(12)-C(4)	1.446(14)
N(13)-C(3)	1.336(13)	N(14)-N(15)	1.309(13)
N(14)-C(5)	1.337(14)	N(15)-N(16)	1.329(12)
N(16)-N(17)	1.350(12)	N(16)-C(6)	1.458(12)
N(17)-C(5)	1.327(14)	C(1)-H(1A)	0.9800
C(1)-H(1B)	0.9800	C(1)-H(1C)	0.9800
C(4)-H(4A)	0.9800	C(4)-H(4B)	0.9800
C(4)-H(4C)	0.9800	C(6)-H(6A)	0.9800
C(6)-H(6B)	0.9800	C(6)-H(6C)	0.9800
<hr/>			
C(2)-N(1)-N(2)	100.7(8)	N(1)-N(2)-C(1)	122.6(8)
N(3)-N(2)-N(1)	113.8(8)	N(3)-N(2)-C(1)	123.6(9)
N(2)-N(3)-N(4)	106.7(8)	N(3)-N(4)-C(2)	104.7(8)
N(6)-N(5)-C(2)	110.8(8)	N(5)-N(6)-N(7)	111.9(8)
N(6)-N(7)-N(8)	109.7(8)	N(6)-N(7)-C(5)	124.3(8)
N(8)-N(7)-C(5)	124.7(8)	N(9)-N(8)-N(7)	112.0(8)
N(8)-N(9)-C(3)	109.3(8)	N(11)-N(10)-C(3)	106.4(9)
N(10)-N(11)-N(12)	106.3(9)	N(11)-N(12)-C(4)	120.8(9)
N(13)-N(12)-N(11)	113.3(8)	N(13)-N(12)-C(4)	125.8(9)
N(12)-N(13)-C(3)	100.8(8)	N(15)-N(14)-C(5)	105.7(9)
N(14)-N(15)-N(16)	106.7(8)	N(15)-N(16)-N(17)	113.3(8)
N(15)-N(16)-C(6)	122.6(8)	N(17)-N(16)-C(6)	124.0(9)
C(5)-N(17)-N(16)	100.1(8)	N(2)-C(1)-H(1A)	109.5
N(2)-C(1)-H(1B)	109.5	N(2)-C(1)-H(1C)	109.5
H(1A)-C(1)-H(1B)	109.5	H(1A)-C(1)-H(1C)	109.5

H(1B)-C(1)-H(1C)	109.5	N(1)-C(2)-N(4)	114.2(9)
N(1)-C(2)-N(5)	126.7(9)	N(4)-C(2)-N(5)	119.1(9)
N(10)-C(3)-N(9)	127.3(9)	N(13)-C(3)-N(9)	119.5(9)
N(13)-C(3)-N(10)	113.1(9)	N(12)-C(4)-H(4A)	109.5
N(12)-C(4)-H(4B)	109.5	N(12)-C(4)-H(4C)	109.5
H(4A)-C(4)-H(4B)	109.5	H(4A)-C(4)-H(4C)	109.5
H(4B)-C(4)-H(4C)	109.5	N(14)-C(5)-N(7)	123.6(9)
N(17)-C(5)-N(7)	121.9(9)	N(17)-C(5)-N(14)	114.3(9)
N(16)-C(6)-H(6A)	109.5	N(16)-C(6)-H(6B)	109.5
N(16)-C(6)-H(6C)	109.5	H(6A)-C(6)-H(6B)	109.5
H(6A)-C(6)-H(6C)	109.5	H(6B)-C(6)-H(6C)	109.5

Table S6. Anisotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for **2a**. The anisotropic displacement factor exponent takes the form: $-2\pi^2 [h^2 a^{*2} U^{11} + \dots + 2 h k a^* b^* U^{12}]$.

	U11	U22	U33	U23	U13	U12
N(1)	33(5)	18(4)	25(4)	-2(3)	5(4)	0(3)
N(2)	32(5)	16(4)	32(5)	4(4)	1(4)	0(4)
N(3)	36(5)	24(5)	28(4)	2(4)	1(4)	1(4)
N(4)	32(5)	19(4)	31(5)	-1(4)	5(4)	-1(4)
N(5)	35(5)	22(4)	26(4)	-5(4)	4(4)	-1(4)
N(6)	30(5)	23(4)	27(4)	0(4)	3(4)	3(4)
N(7)	30(5)	23(4)	24(4)	-5(3)	-1(4)	3(4)
N(8)	32(5)	14(4)	34(5)	9(4)	3(4)	7(3)
N(9)	28(4)	17(4)	36(5)	1(4)	8(4)	-2(3)
N(10)	51(6)	13(4)	68(7)	-6(4)	-10(6)	2(4)
N(11)	45(6)	21(5)	55(6)	9(4)	6(5)	7(4)
N(12)	20(4)	29(5)	31(5)	3(4)	7(3)	-2(4)
N(13)	34(5)	28(5)	35(5)	-3(4)	5(4)	5(4)
N(14)	34(5)	23(5)	51(6)	2(4)	10(4)	1(4)
N(15)	33(5)	20(4)	45(5)	-3(4)	11(4)	-8(4)
N(16)	42(5)	14(4)	24(4)	-1(3)	4(4)	-1(4)
N(17)	39(5)	21(4)	37(5)	-1(4)	-1(4)	-1(4)
C(1)	56(7)	19(5)	43(7)	-9(5)	-5(6)	0(5)
C(2)	22(5)	25(5)	27(5)	-1(4)	10(4)	3(4)
C(3)	24(5)	25(5)	35(6)	2(4)	6(4)	3(4)
C(4)	40(6)	34(6)	55(7)	-4(6)	0(6)	20(5)
C(5)	31(5)	12(5)	41(6)	0(4)	3(5)	5(4)
C(6)	36(6)	26(5)	26(5)	-8(4)	5(5)	10(4)

Table S7. Hydrogen coordinates ($\times 10^4$) and isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for **2a**.

	x	y	z	U(eq)
H(1A)	534	8405	-4330	61
H(1B)	-362	9072	-4242	61
H(1C)	-132	7791	-3288	61
H(4A)	4937	4074	8752	66
H(4B)	5544	4048	7362	66
H(4C)	4819	3012	7369	66
H(6A)	2265	11736	8223	44
H(6B)	1771	12407	6605	44
H(6C)	2748	12751	7281	44

Table S8. Torsion angles [°] for **2a**.

N(1)-N(2)-N(3)-N(4)	-0.3(12)	N(2)-N(1)-C(2)-N(4)	-0.7(11)
N(2)-N(1)-C(2)-N(5)	-179.5(9)	N(2)-N(3)-N(4)-C(2)	-0.2(10)
N(3)-N(4)-C(2)-N(1)	0.6(11)	N(3)-N(4)-C(2)-N(5)	179.5(8)
N(5)-N(6)-N(7)-N(8)	-170.8(8)	N(5)-N(6)-N(7)-C(5)	-3.1(13)
N(6)-N(5)-C(2)-N(1)	2.0(14)	N(6)-N(5)-C(2)-N(4)	-176.8(9)
N(6)-N(7)-N(8)-N(9)	172.1(8)	N(6)-N(7)-C(5)-N(14)	-97.3(12)
N(6)-N(7)-C(5)-N(17)	77.6(13)	N(7)-N(8)-N(9)-C(3)	177.1(8)
N(8)-N(7)-C(5)-N(14)	68.7(14)	N(8)-N(7)-C(5)-N(17)	-116.5(11)
N(8)-N(9)-C(3)-N(10)	-13.0(15)	N(8)-N(9)-C(3)-N(13)	170.6(9)
N(10)-N(11)-N(12)-N(13)	-0.6(12)	N(10)-N(11)-N(12)-C(4)	176.1(10)
N(11)-N(10)-C(3)-N(9)	-178.0(10)	N(11)-N(10)-C(3)-N(13)	-1.5(14)
N(11)-N(12)-N(13)-C(3)	-0.3(11)	N(12)-N(13)-C(3)-N(9)	177.9(9)
N(12)-N(13)-C(3)-N(10)	1.1(12)	N(14)-N(15)-N(16)-N(17)	-0.8(12)
N(14)-N(15)-N(16)-C(6)	-177.3(9)	N(15)-N(14)-C(5)-N(7)	176.5(9)
N(15)-N(14)-C(5)-N(17)	1.3(13)	N(15)-N(16)-N(17)-C(5)	1.5(11)
N(16)-N(17)-C(5)-N(7)	-176.9(9)	N(16)-N(17)-C(5)-N(14)	-1.7(12)
C(1)-N(2)-N(3)-N(4)	-179.8(10)	C(2)-N(1)-N(2)-N(3)	0.6(11)
C(2)-N(1)-N(2)-C(1)	-179.9(10)	C(2)-N(5)-N(6)-N(7)	178.5(8)
C(3)-N(10)-N(11)-N(12)	1.2(13)	C(4)-N(12)-N(13)-C(3)	-176.7(10)
C(5)-N(7)-N(8)-N(9)	4.4(13)	C(5)-N(14)-N(15)-N(16)	-0.3(11)
C(6)-N(16)-N(17)-C(5)	177.9(9)		

Computation details

The heats of formation of **2a-2j** were carried out by using the Gaussian09 (Revision B.01) suite of programs based on isodesmic reactions (Scheme S2).⁴ The elementary geometric optimization and the frequency analysis were performed at the level of B3LYP/6-311+G**. The total energy was performed at the level of MP2/6-311++G**.

Scheme S2. Isodesmic reactions for the calculation of heats of formation.

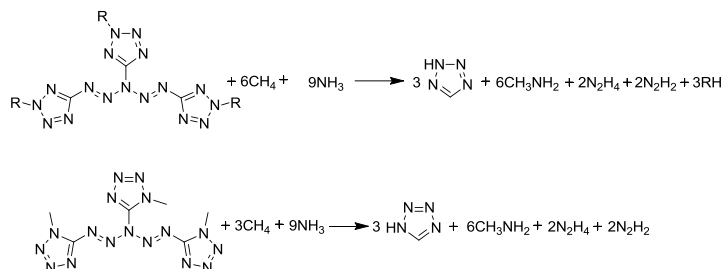


Table S9. Calculated (B3LYP/6-31+G**//MP2/6-311++G**) total energy (E_0), Zero-Point Energy (ZPE), values of thermal correction (H_T), and heats of formation (HOF) of **2a** and **2j**.

Name	E_0 (a.u.)	ZPE (a.u.)	H_T (a.u.)	HOF (kJ mol ⁻¹)
2a	-1161.953770	0.221028	0.021410	1699.2
2b	-1853.849328	0.465224	0.034320	1189.8
2c	-1393.897319	0.320857	0.027725	1059.3
2d	-1515.253398	0.473213	0.033226	550.6
2e	-8996.818310	0.279371	0.028024	871.5
2f	-1844.588827	0.349851	0.034265	-77.7
2g	-1438.437752	0.217076	0.025914	1387.1
2h	-1276.245240	0.234925	0.023308	1174.5
2i	-1505.196037	0.320841	0.028920	311.2
2j	-1162.180333	0.219624	0.021818	1179.8
2 <i>H</i> -tetrazole	-257.706842	0.047597	0.004364	318.2 ^a
1 <i>H</i> -tetrazole	-257.712578	0.046863	0.004429	327.4 ^a
CH ₄	-40.396999	0.044793	0.003812	-74.4 ^a
NH ₃	-56.427034	0.034372	0.003818	-46.0 ^a
CH ₃ NH ₂	-95.622396	0.064026	0.004375	-22.5 ^b
N ₂ H ₄	-111.609981	0.052611	0.003904	95.4 ^b
N ₂ H ₂	-110.391652	0.028442	0.003802	211.9 ^c

^aChen, Z.; Xiao, H.; Song, W. *J. Mol. Struct. (Theochem)* **1999**, *460*, 167–173. ^bZhang, X.; Zhu, W.; Wei, T.; Zhang, C.; Xiao, H. *J. Phys. Chem. C* **2010**, *114*, 13142–13152. ^cGurvich, L. V.; Veyts, I. V.; Alcock, C. B. *Thermodynamic properties of individual substances*,

Hemisphere Pub. Co., New York, **1989**.

References

- M. J. Frisch, et al., G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J. M. Millam, M. Klene, J. E. Knox, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, Ö. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski, D. J. Fox, *Gaussian 09, Revision B.01*, Gaussian, Inc., Wallingford CT, **2009**.