

Supporting Information

Towards the advanced N-rich energetic explosives: based on tetrazole and triazole groups with large conjugated systems & extensive hydrogen bonds

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1. Experimental Section

General methods

All the experimental reagents were purchased from energy chemical. ^1H and ^{13}C NMR spectras were obtained using a Bruker 500 MHz NMR at 500 and 126 MHz, respectively. The chemical shifts for ^1H and ^{13}C were reported relative to d6-DMSO. IR spectras were obtained on a Thermo Nicolet iS10 spectrometer. Densities of products were measured by using a gas pycnometer at room temperature. Elemental analysis datas were conducted using a Vario EL III CHNOS elemental analyzer. The decomposition (onset) temperature was measured by a differential scanning calorimeter (DSC, Mettler Toledo DSC823e) at a scan rate of $5\text{ K}\cdot\text{min}^{-1}$. The heats of formation were calculated by using Gaussian 16¹, detonation velocities (D_v) and pressures (P) were calculated by EXPLO5 v6.01², Impact and friction sensitivity measurements were obtained with a BAM Fallhammer and a BAM friction tester³.

Synthesis

Caution! All synthetic products discussed in this paper are high-energy compounds with significant sensitivity. While no explosions occurred during the experiments, it is strongly recommended to implement strict protective measures throughout all experimental procedures.

Potassium 5,5'-(3-nitro-1H-1,2,4-triazole-1,5-diyl)bis(tetrazol-1-ide) (N1-K): At $0\text{ }^\circ\text{C}$, sodium azide (3.412 g, 52.5 mmol) was dispersed in MeCN (100 mL), and followed by the addition of BrCN (1.59 g, 15 mmol). The reaction mixture was stirred at $0\text{ }^\circ\text{C}$ for 4 hours. After filtering off the inorganic salt, the resulting cyanogen azide solution was poured into a solution containing 5-(3-nitro-1H-1,2,4-triazol-5-yl)-1H-tetrazole (compound 1, 1.281 g, 10 mmol) and potassium hydroxide (0.561 g, 10 mmol) with 50 mL of H_2O at room temperature. The mixture was stirred for 4 hours at $25\text{ }^\circ\text{C}$, and then it was slowly evaporated, washed with acetonitrile, and dried to obtain compound N1-K as a pure yellow solid. Yield: 2.653 g, 81.30 %. ^{13}C NMR (126 MHz, DMSO- d_6) δ 166.03, 160.31, 157.84, 157.13. IR (KBr): $\tilde{\nu}$ = 1660.53, 1627.45, 1601.61, 1575.30, 1518.38, 1461.43, 1435.26, 1399.72, 1380.51, 1359.33, 1325.37, 1306.28, 1297.91, 1276.98, 1219.34, 1186.10, 1176.47, 1144.20, 1125.63, 1108.05, 1095.88, 1081.66, 1035.57, 1027.80, 1011.06, 994.05, 844.39, 740.32, 722.20, 703.27, 659.17, 616.14, 589.95, 577.52, 534.86, 520.44 cm^{-1} . Elemental analysis calcd for $\text{C}_4\text{K}_2\text{N}_{12}\text{O}_2$ (326.32): C 14.72, N 51.51, O 9.81 %; found: C 14.75, N 51.48, O 9.80 %.

5,5'-(3-nitro-1H-1,2,4-triazole-1,5-diyl)bis(1H-tetrazole) (N1): N1-K (3.263 g, 10mmol) was dissolved in 50mL H_2O at $0\text{ }^\circ\text{C}$, to which solution 36% HCl (5 mL) was supplemented dropwised solwly. The solution was stirred at $25\text{ }^\circ\text{C}$ for 2 h. Then the mixture was extracted with ethyl acetate and evaporated to obtain an oil product of N1. The product requires no further processing and can be used directly in the next step.

Ammonium 5,5'-(3-nitro-1H-1,2,4-triazole-1,5-diyl)bis(tetrazol-1-ide) (N1-1): At $25\text{ }^\circ\text{C}$, N1 (0.250 g, 1 mmol) was added in 20 mL MeCN, to which solution was added 0.5 mL $\text{NH}_3\cdot\text{H}_2\text{O}$ (26 %). The

reaction mixture was stirred at room temperature for 12 h. Then the precipitate was filtered off, washed with MeCN and dried out to obtain N1-1 as a pure, yellow solid. Yield: 0.225 g, 79.2 %. ¹H NMR (500 MHz, DMSO-d₆) δ 6.97. ¹³C NMR (126 MHz, DMSO-d₆) δ 165.32, 156.54, 156.03, 150.60. IR (KBr): $\tilde{\nu}$ = 3016.68, 2852.20, 1694.60, 1621.71, 1592.44, 1561.38, 1528.77, 1425.34, 1400.48, 1383.96, 1345.43, 1310.10, 1280.18, 1217.33, 1190.86, 1146.23, 1107.73, 1093.26, 1037.07, 1011.52, 994.84, 838.24, 722.58, 702.59, 654.73 cm⁻¹. Elemental analysis calcd for C₄H₈N₁₄O₂ (284.20): C 16.90, H 2.84, N 69.00, O 11.26 %; found: C 16.94, H 2.82, N 69.03, O 11.29 %.

Hydrazinium 5,5'-(3-nitro-1H-1,2,4-triazole-1,5-diyl)bis(tetrazol-1-ide) (N1-2): At 25 °C, N1 (0.250 g, 1 mmol) was added in 20 mL MeCN, to which solution was added 0.5 mL N₂H₄·H₂O (85 %). The reaction mixture was stirred at room temperature for 12 h. Then the precipitate was filtered off, washed with MeCN and dried out to obtain N1-2 as a pure, yellow solid. Yield: 0.231 g, 73.5 %. ¹H NMR (500 MHz, DMSO-d₆) δ 6.88. ¹³C NMR (126 MHz, DMSO-d₆) δ 165.57, 163.55, 156.39, 156.03. IR (KBr): $\tilde{\nu}$ = 3345.24, 3250.57, 1589.73, 1513.99, 1486.44, 1472.72, 1403.04, 1390.24, 1311.44, 1302.84, 1285.73, 1194.35, 1165.14, 1113.93, 1102.34, 1071.74, 1036.51, 1000.93, 967.63, 838.46, 718.03, 672.76, 658.31, 589.87, 563.21, 549.42, 504.31, 482.53 cm⁻¹. Elemental analysis calcd for C₄H₁₀N₁₆O₂ (314.23): C 15.29, H 3.21, N 71.32, O 10.18 %; found: C 15.32, H 3.23, N 71.30, O 10.15 %.

Hydroxylammonium 5,5'-(3-nitro-1H-1,2,4-triazole-1,5-diyl)bis(tetrazol-1-ide) (N1-3): At 25 °C, N1 (0.250 g, 1 mmol) was added in 20 mL MeCN, to which solution was added 0.5 mL NH₂OH·H₂O (50 %). The reaction mixture was stirred at room temperature for 12 h. Then the precipitate was filtered off, washed with MeCN and dried out to obtain N1-3 as a pure, yellow solid. Yield: 0.225 g, 71.2 %. ¹H NMR (500 MHz, DMSO-d₆) δ 8.26. ¹³C NMR (126 MHz, DMSO-d₆) δ 164.82, 155.24, 153.80, 153.61. IR (KBr): $\tilde{\nu}$ = 3625.52, 3564.05, 3006.86, 2700.90, 1616.13, 1528.08, 1467.72, 1431.78, 1407.01, 1387.95, 1345.45, 1308.41, 1283.95, 1234.48, 1191.03, 1145.40, 1113.50, 1102.75, 1047.12, 1010.71, 993.65, 837.71, 759.32, 729.51, 715.25, 701.78, 654.27, 613.28, 594.70, 572.84, 513.89, 503.86 cm⁻¹. Elemental analysis calcd for C₄H₈N₁₄O₄ (316.20): C 15.19, H 2.55, N 62.02, O, 20.24 %; found: C 15.21, H 2.57, N 62.01, O, 20.27 %.

3-(1H-tetrazol-1-yl)-1-(1H-tetrazol-5-yl)-1H-1,2,4-triazol-5-amine (N2): At 0 °C, sodium azide (3.412 g, 52.5 mmol) was dispersed in MeCN (100 mL), and followed by the addition of BrCN (1.59 g, 15 mmol). The reaction mixture was stirred at 0 °C for 4 hours. After filtering off the inorganic salt, the resulting cyanogen azide solution was poured into a solution containing 3-(1H-tetrazol-1-yl)-1H-1,2,4-triazol-5-amine (compound 2, 1.521 g, 10 mmol) and potassium hydroxide (0.561 g, 10 mmol) with 50 mL of H₂O at room temperature. The mixture was stirred for 4 hours at 25 °C, and then it was slowly evaporated, washed with acetonitrile, and dried out to obtain a white powder. The white powder was dissolved in 50 mL of water, and then 10 mL of hydrochloric acid (36%) was added slowly. The resulting precipitate was filtered off, washed with acetonitrile, and dried to obtain N2 as a pure white solid. Yield: 1.95 g, 88.6 %. ¹H NMR (500 MHz, DMSO-d₆) δ 10.04 (C-H), 7.92 (N-H for NH₂). ¹³C NMR (126 MHz, DMSO-d₆) δ 156.60, 154.07, 152.31, 143.37. ¹⁵N NMR (500 MHz, DMSO-d₆, Nitromethane was used as the external standard) δ 34.58, 1.32, -0.57, -30.48, -89.91, -112.17, -124.85, -164.22, -164.40, -192.13, -292.60. IR (KBr): $\tilde{\nu}$ = 3418.04, 3326.57, 3292.50, 3136.30, 1653.59, 1612.95, 1575.75, 1515.35, 1455.13, 1375.86, 1331.11, 1265.28, 1203.62, 1193.62, 1156.50, 1091.08, 1014.19, 994.95, 981.67, 970.85, 775.05, 738.95, 724.46, 689.13, 649.12, 471.32 cm⁻¹. Elemental analysis calcd for C₄H₄N₁₂ (220.16): C 21.82, H 1.83, N 76.35 %; found: C 21.80, H 1.85, N 76.38 %.

Ammonium 5-(5-amino-3-(1H-tetrazol-1-yl)-1H-1,2,4-triazol-1-yl)tetrazol-1-ide (N2-1): At 25 °C, N2 (0.220 g, 1 mmol) was added in 20 mL H₂O, to which solution was added 0.5 mL NH₃·H₂O (26 %). The reaction mixture was stirred at room temperature for 12 h. Then the solution was slowly evaporated, washed with acetonitrile, and dried out to obtain a white solid. Yield: 0.185 g, 78.0 %. ¹H NMR (500 MHz, DMSO-d₆) δ 10.08 (C-H), 7.67 (N-H for NH₂), 7.26 (N-H for NH₄⁺). ¹³C NMR (126 MHz, DMSO-d₆) δ 158.21, 155.71, 150.72, 143.19. IR (KBr): $\tilde{\nu}$ = 3604.69, 3388.77, 3256.40, 3188.39, 3086.86, 3029.71, 2840.37, 1649.99, 1618.97, 1572.07, 1517.73, 1456.51, 1430.52, 1416.67, 1328.37, 1262.94, 1194.63, 1153.14, 1128.02, 1094.52, 1066.70, 1023.24, 974.87, 919.29, 774.15, 735.34, 692.96, 657.97 cm⁻¹. Elemental analysis calcd for C₄H₇N₁₃ (237.19): C 20.26, H 2.97, N 76.77 %; found: C 20.25, H 2.99, N 76.73 %.

Hydrazinium 5-(5-amino-3-(1H-tetrazol-1-yl)-1H-1,2,4-triazol-1-yl)tetrazol-1-ide (N2-2): At 25 °C, N2 (0.220 g, 1 mmol) was added in 20 mL H₂O, to which solution was added 0.5 mL N₂H₄·H₂O (85 %). The reaction mixture was stirred at room temperature for 12 h. Then the solution was slowly evaporated, washed with acetonitrile, and dried out to obtain a white solid. Yield: 0.215 g, 85.2 %. ¹H NMR (500 MHz, DMSO-d₆) δ 10.08 (C-H), 7.67 (N-H for NH₂), 7.14 (N-H for N₂H₅⁺). ¹³C NMR (126 MHz, DMSO-d₆) δ 158.21, 155.70, 150.71, 143.19. IR (KBr): $\tilde{\nu}$ = 3431.19, 3066.42, 1640.33, 1567.17, 1508.05, 1448.37, 1391.17, 1328.28, 1262.64, 1217.96, 1191.83, 1162.04, 1087.35, 1027.70, 972.95, 878.68, 779.80, 736.15, 687.56, 651.14, 611.87, 514.67 cm⁻¹. Elemental analysis calcd for C₄H₈N₁₄ (252.20): C 19.05, H 3.20, N 77.75 %; found: C 19.01, H 3.23, N 77.77 %.

Hydroxylammonium 5-(5-amino-3-(1H-tetrazol-1-yl)-1H-1,2,4-triazol-1-yl)tetrazol-1-ide (N2-3) : At 25 °C, N2 (0.220 g, 1 mmol) was added in 20 mL H₂O, to which solution was added 0.5 mL NH₂OH·H₂O (50 %). The reaction mixture was stirred at room temperature for 12 h. Then the solution was slowly evaporated, washed with acetonitrile, and dried out to obtain a white solid. Yield: 0.205 g, 80.9 %. ¹H NMR (500 MHz, DMSO-d₆) δ 10.06 (C-H), 7.65 (N-H for NH₂), 6.41(N-H for NH₃OH). ¹³C NMR (126 MHz, DMSO-d₆) δ 158.19, 155.71, 150.70, 143.19. IR (KBr): $\tilde{\nu}$ = 3422.85, 3016.81, 1650.32, 1566.83, 1513.29, 1445.53, 1327.66, 1261.21, 1222.22, 1180.13, 1162.24, 1131.84, 1094.44, 1029.93, 975.49, 871.19, 780.54, 732.77, 684.35, 651.47, 611.85, 514.71 cm⁻¹. Elemental analysis calcd for C₄H₇N₁₃O (253.19): C 18.98, H 2.79, N 71.92, O 6.32 %; found: C 18.96, H 2.80, N 71.93, O 6.33 %.

(E)-3,3'-(diazene-1,2-diyl)bis(1-(1H-tetrazol-5-yl)-1H-1,2,4-triazol-5-amine) (N3): At 0 °C, sodium azide (6.824 g, 105 mmol) was dispersed in MeCN (200 mL), and followed by the addition of BrCN (3.18 g, 30 mmol). The reaction mixture was stirred at 0 °C for 4 hours. After filtering off the inorganic salt, the resulting cyanogen azide solution was poured into a solution containing (E)-3,3'-(diazene-1,2-diyl)bis(1H-1,2,4-triazol-5-amine) (compound 3, 1.941 g, 10 mmol) and potassium hydroxide (1.122 g, 20 mmol) with 50 mL of H₂O at room temperature. The mixture was stirred for 4 hours at 25 °C, and then it was slowly evaporated, washed with acetonitrile, and dried out to obtain a yellow powder. The yellow powder was dissolved in 50 mL of water, and then 10 mL of hydrochloric acid (36%) was added slowly. The resulting precipitate was filtered off, washed with acetonitrile, and dried to obtain N3 as a yellow solid. Yield: 2.76 g, 83.6 %. ¹H NMR (500 MHz, DMSO-d₆) δ 7.69. ¹³C NMR (126 MHz, DMSO-d₆) δ 168.41, 156.77, 153.82. IR (KBr): $\tilde{\nu}$ = 3412.14, 3315.15, 1644.04, 1604.96, 1563.41, 1498.74, 1415.99, 1353.23, 1252.72, 1222.33, 1191.24, 1149.50, 1076.86, 1038.57, 981.32, 823.48, 757.89, 725.18, 675.57, 641.14 cm⁻¹. Elemental analysis calcd for C₆H₆N₁₈ (330.24): C 21.82, H 1.83, N 76.35 %; found: C 21.85, H 1.81, N 76.37%.

Ammonium (E)-5,5'-(diazene-1,2-diyl)bis(5-amino-1H-1,2,4-triazole-3,1-diyl)bis(tetrazol-1-ide)

(N3-1): At 25 °C, N3 (0.330 g, 1 mmol) was added in 50 mL H₂O, to which solution was added 0.5 mL NH₃·H₂O (26 %). The reaction mixture was stirred at 60 °C for 12 h. Then the solution was slowly evaporated, washed with acetonitrile, and dried out to obtain a yellow solid. Yield: 0.305 g, 83.7 %. ¹H NMR (500 MHz, DMSO-d₆) δ 7.47, 7.28. ¹³C NMR (126 MHz, DMSO-d₆) δ 167.40, 158.56, 155.93. IR (KBr): $\tilde{\nu}$ = 3159.64, 1628.65, 1577.50, 1534.87, 1487.42, 1412.31, 1359.64, 1218.74, 1151.12, 1096.13, 1053.44, 1012.49, 830.27, 757.67, 736.82, 675.58 cm⁻¹. Elemental analysis calcd for C₆H₁₂N₂₀ (364.30): C 19.78, H 3.32, N 76.90 %; found: C 19.79, H 3.35, N 76.92 %.

Hydrazinium (E)-5,5'-(diazene-1,2-diylbis(5-amino-1H-1,2,4-triazole-3,1-diyl))bis(tetrazol-1-ide)

(N3-2): At 25 °C, N3 (0.330 g, 1 mmol) was added in 50 mL H₂O, to which solution was added 0.5 mL N₂H₄·H₂O (85 %). The reaction mixture was stirred at 60 °C for 12 h. Then the solution was slowly evaporated, washed with acetonitrile, and dried out to obtain a yellow solid. Yield: 0.316 g, 80.1 %. ¹H NMR (500 MHz, DMSO-d₆) δ 7.78, 7.10. ¹³C NMR (126 MHz, DMSO-d₆) δ 163.84, 158.73, 154.68. IR (KBr): $\tilde{\nu}$ = 3316.14, 3110.11, 1638.90, 1589.33, 1535.89, 1486.91, 1437.64, 1362.48, 1328.85, 1216.17, 1154.40, 1093.09, 1014.28, 950.47, 757.90, 736.91, 676.21 cm⁻¹. Elemental analysis calcd for C₆H₁₄N₂₂ (394.33): C 18.28, H 3.58, N 78.15 %; found: C 18.27, H 3.55, N 78.17 %.

Hydroxylammonium

(E)-5,5'-(diazene-1,2-diylbis(5-amino-1H-1,2,4-triazole-3,1-diyl))bis(tetrazol-1-ide) (N3-3): At 25 °C, N3 (0.330 g, 1 mmol) was added in 50 mL H₂O, to which solution was added 0.5 mL NH₂OH·H₂O (50 %). The reaction mixture was stirred at 60 °C for 12 h. Then the solution was slowly evaporated, washed with acetonitrile, and dried out to obtain a yellow solid. Yield: 0.311 g, 78.5 %. ¹H NMR (500 MHz, DMSO-d₆) δ 7.31. ¹³C NMR (126 MHz, DMSO-d₆) δ 167.42, 158.57, 155.91. IR (KBr): $\tilde{\nu}$ = 3143.05, 2359.84, 1631.51, 1537.71, 1486.23, 1437.43, 1409.76, 1358.93, 1153.22, 1092.88, 1012.45, 830.06, 756.66, 734.55, 674.96, 642.12 cm⁻¹. Elemental analysis calcd for C₆H₁₂N₂₀O₂ (396.30): C 18.18, H 3.05, N 70.69, O 8.07 %; found: C 18.20, H 3.07, N 70.70, O 8.05 %.

2. X-ray crystallographic data

Table S1. Crystallographic data for **N1-K**.

Empirical formula	C ₄ H ₂ K ₂ N ₁₂ O ₃
Formula weight	344.38
Temperature	296(2) K
Wavelength	0.71073 Å
Crystal system	Monoclinic
Space group	P2 ₁ /n
Unit cell dimensions	a = 6.6026(9) Å b = 13.5204(18) Å c = 13.4527(17) Å a = 90° b = 99.755(3)° g = 90°
Volume	1183.6(3) Å ³
Z	4
Density (calculated)	1.933 Mg/m ³
Absorption coefficient	0.838 mm ⁻¹
F(000)	688
Crystal size	0.120 x 0.020 x 0.020 mm ³
Theta range for data collection	3.013 to 27.570°.
Index ranges	-8<=h<=8, 0<=k<=17, 0<=l<=17
Reflections collected	2734
Independent reflections	2734 [R(int) = ?]
Completeness to theta = 25.242°	99.6 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.7456 and 0.6194
Refinement method	Full-matrix least-squares on F ²
Data / restraints / parameters	2734 / 3 / 197
Goodness-of-fit on F ²	1.049
Final R indices [I>2sigma(I)]	R1 = 0.0711, wR2 = 0.1396
R indices (all data)	R1 = 0.1305, wR2 = 0.1650
Extinction coefficient	n/a
Largest diff. peak and hole	0.525 and -0.589 e.Å ⁻³

CCDC : 2353053

Table S2. Crystallographic data for **N2-1**.

Empirical formula	C ₄ H ₉ N ₁₃ O
Formula weight	255.24
Temperature/K	223.00
Crystal system	triclinic
Space group	P-1
a/Å	6.8574(5)
b/Å	8.0972(6)
c/Å	9.8300(7)
α/°	84.665(5)
β/°	72.973(6)
γ/°	87.546(6)
Volume/Å ³	519.56(7)
Z	2
ρ _{calc} /cm ³	1.632
μ/mm ⁻¹	1.123
F(000)	264.0
Crystal size/mm ³	0.15 × 0.13 × 0.12
Radiation	CuKα (λ = 1.54178)
2θ range for data collection/°	9.442 to 145.43
Index ranges	-8 ≤ h ≤ 8, -10 ≤ k ≤ 9, -11 ≤ l ≤ 12

Reflections collected	6636
Independent reflections	2034 [$R_{\text{int}} = 0.0410$, $R_{\text{sigma}} = 0.0403$]
Data/restraints/parameters	2034/0/167
Goodness-of-fit on F^2	1.059
Final R indexes [$ I \geq 2\sigma(I)$]	$R_1 = 0.0589$, $wR_2 = 0.1700$
Final R indexes [all data]	$R_1 = 0.0688$, $wR_2 = 0.1793$
Largest diff. peak/hole / $e \text{ \AA}^{-3}$	0.58/-0.65

CCDC : 2371304

Table S3. Crystallographic data for **N3** (α -form).

Empirical formula	$\text{C}_{10}\text{H}_{18}\text{N}_{18}\text{O}_2\text{S}_2$
Formula weight	486.54
Temperature/K	223.15
Crystal system	monoclinic
Space group	$P2_1/c$
a/ \AA	19.516(6)
b/ \AA	6.990(2)
c/ \AA	15.323(5)
$\alpha/^\circ$	90
$\beta/^\circ$	96.90(2)
$\gamma/^\circ$	90
Volume/ \AA^3	2075.2(11)
Z	4
$\rho_{\text{calc}}/\text{cm}^3$	1.557
μ/mm^{-1}	2.809
F(000)	1008.0
Crystal size/ mm^3	$0.15 \times 0.13 \times 0.12$
Radiation	$\text{CuK}\alpha$ ($\lambda = 1.54184$)
2 θ range for data collection/ $^\circ$	4.56 to 145.244
Index ranges	$-24 \leq h \leq 23$, $-8 \leq k \leq 8$, $-18 \leq l \leq 18$
Reflections collected	14022
Independent reflections	4032 [$R_{\text{int}} = 0.0844$, $R_{\text{sigma}} = 0.0784$]
Data/restraints/parameters	4032/0/293
Goodness-of-fit on F^2	1.063
Final R indexes [$ I \geq 2\sigma(I)$]	$R_1 = 0.0842$, $wR_2 = 0.2493$
Final R indexes [all data]	$R_1 = 0.1124$, $wR_2 = 0.2716$
Largest diff. peak/hole / $e \text{ \AA}^{-3}$	0.95/-0.76

CCDC : 2376609

Table S4. Crystallographic data for **N3** (β -form).

Empirical formula	$\text{C}_{18}\text{H}_{30}\text{N}_{36}\text{O}_3\text{S}_3$
Formula weight	894.96
Temperature/K	223.00
Crystal system	monoclinic
Space group	$C2/c$
a/ \AA	36.782(2)
b/ \AA	6.9282(5)
c/ \AA	15.3841(11)
$\alpha/^\circ$	90
$\beta/^\circ$	105.657(5)
$\gamma/^\circ$	90
Volume/ \AA^3	3775.0(5)
Z	4
$\rho_{\text{calc}}/\text{cm}^3$	1.575
μ/mm^{-1}	2.510
F(000)	1848.0

Crystal size/mm ³	0.13 × 0.11 × 0.1
Radiation	CuKα (λ = 1.54178)
2θ range for data collection/°	4.99 to 136.846
Index ranges	-44 ≤ h ≤ 44, -8 ≤ k ≤ 8, -18 ≤ l ≤ 18
Reflections collected	19013
Independent reflections	3478 [R _{int} = 0.0777, R _{sigma} = 0.0436]
Data/restraints/parameters	3478/128/333
Goodness-of-fit on F ²	1.023
Final R indexes [I >= 2σ (I)]	R ₁ = 0.0530, wR ₂ = 0.1379
Final R indexes [all data]	R ₁ = 0.0830, wR ₂ = 0.1610
Largest diff. peak/hole / e Å ⁻³	0.28/-0.23

CCDC : 2378852 (The solvent DMSO in the crystal displays disordered characteristics)

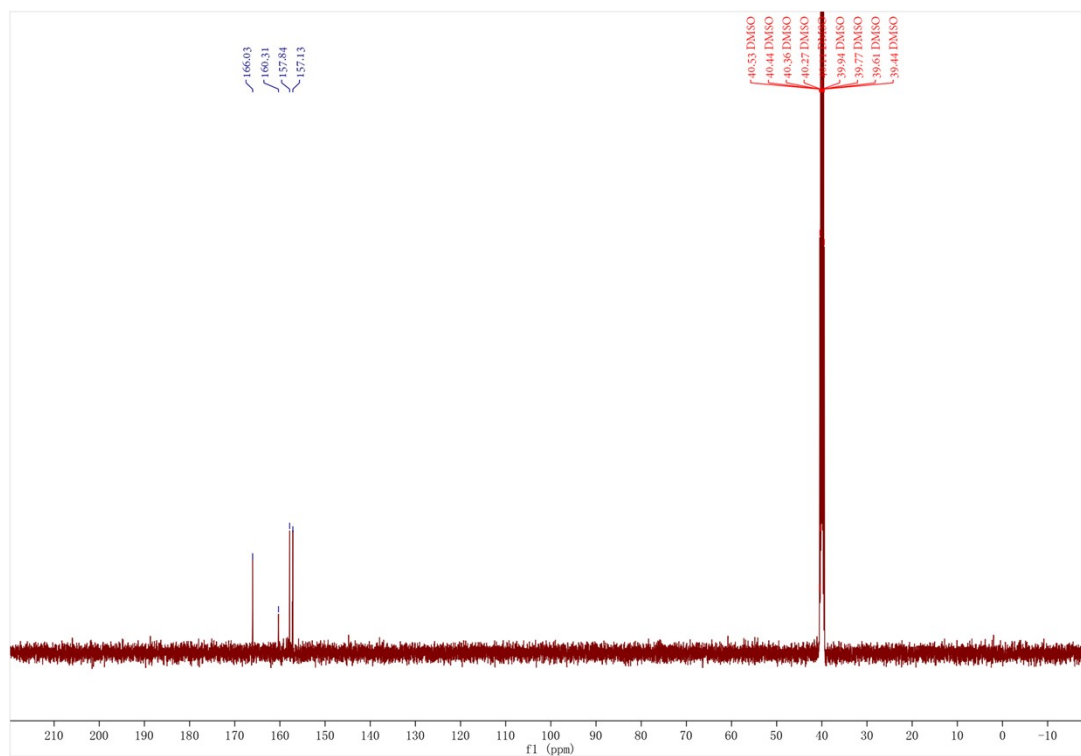


Figure S3. ^{13}C NMR spectra of N1-K.

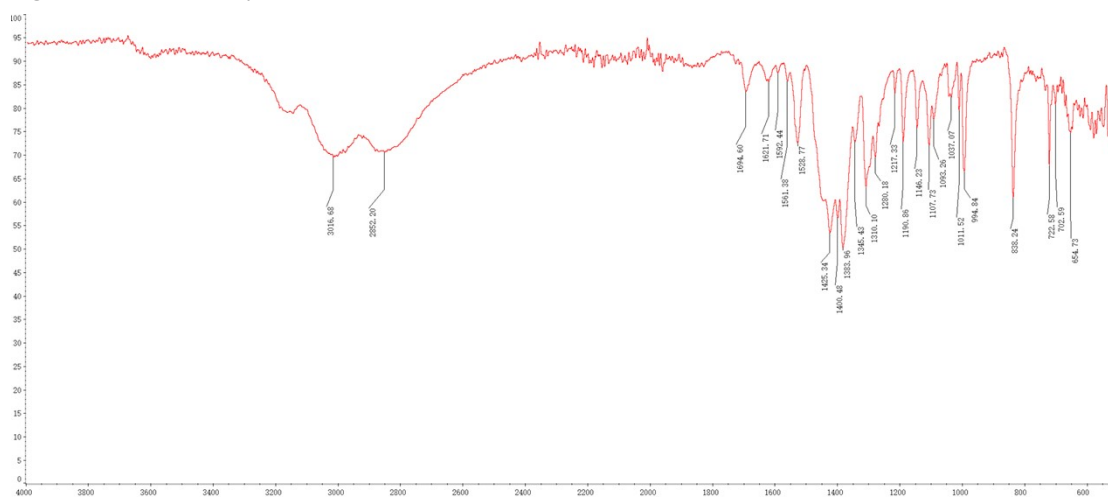


Figure S4. IR spectra of N1-1.

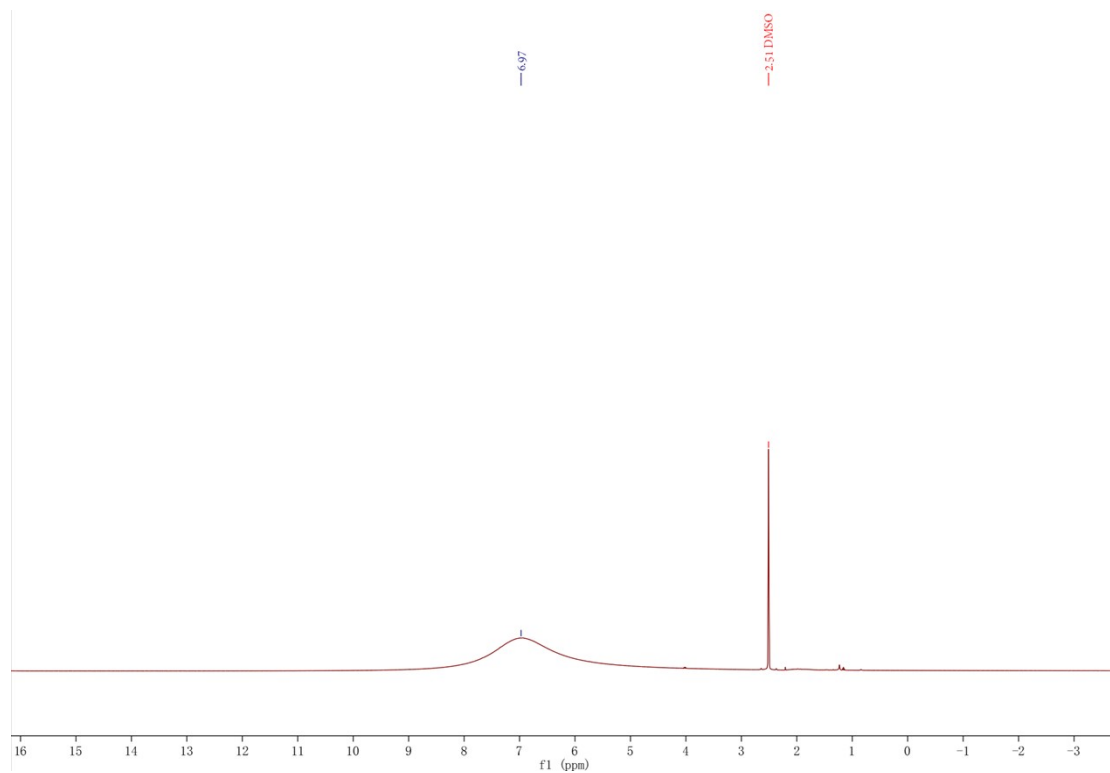


Figure S5. ¹H NMR spectra of N1-1.

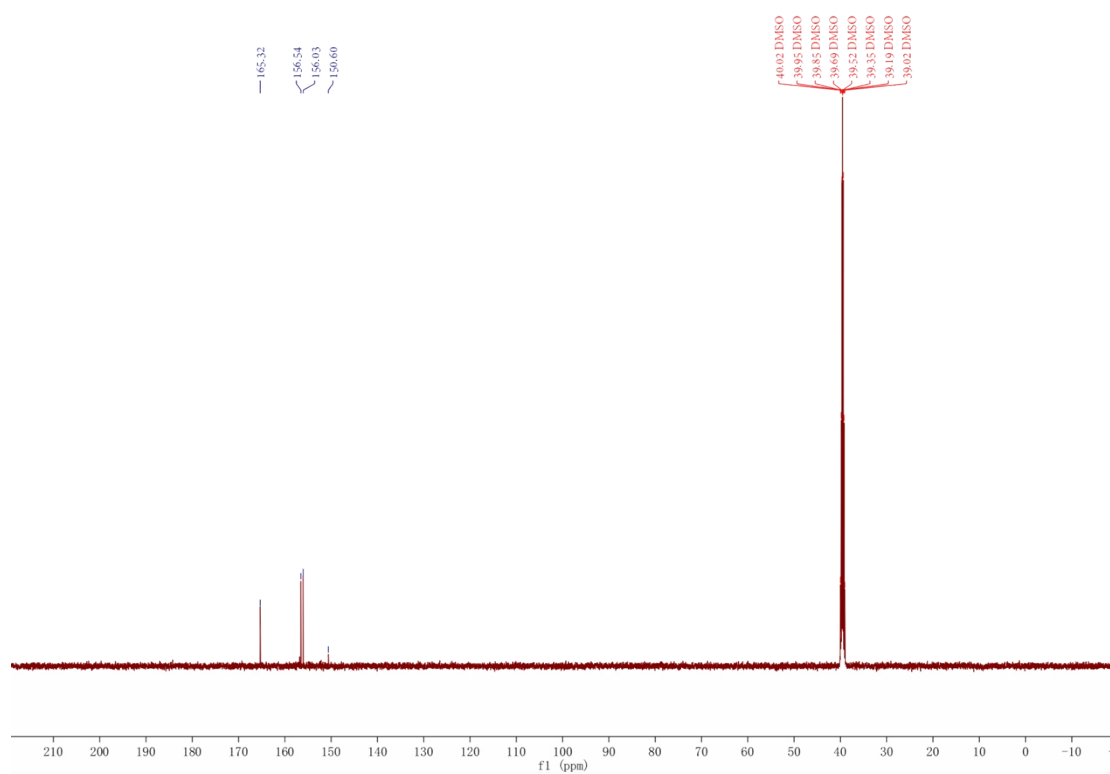


Figure S6. ¹³C NMR spectra of N1-1.

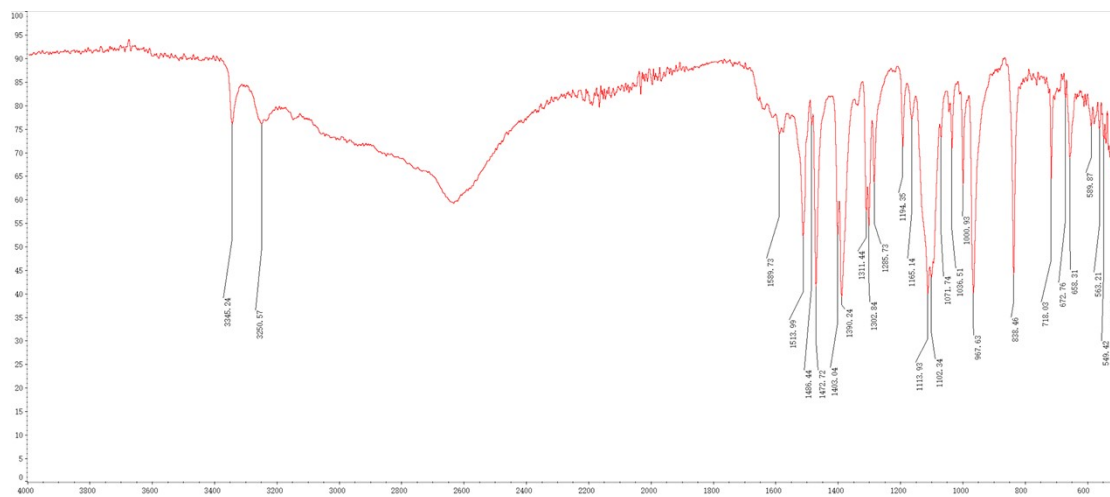


Figure S7. IR spectra of N1-2.

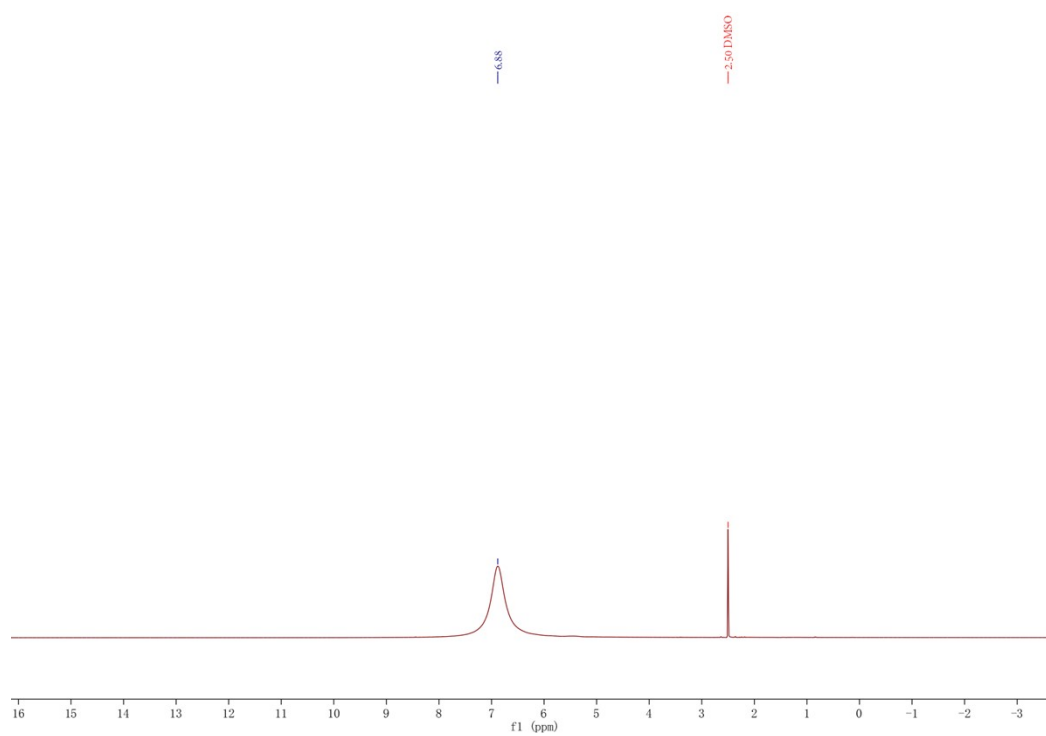


Figure S8. ¹H NMR spectra of N1-2.

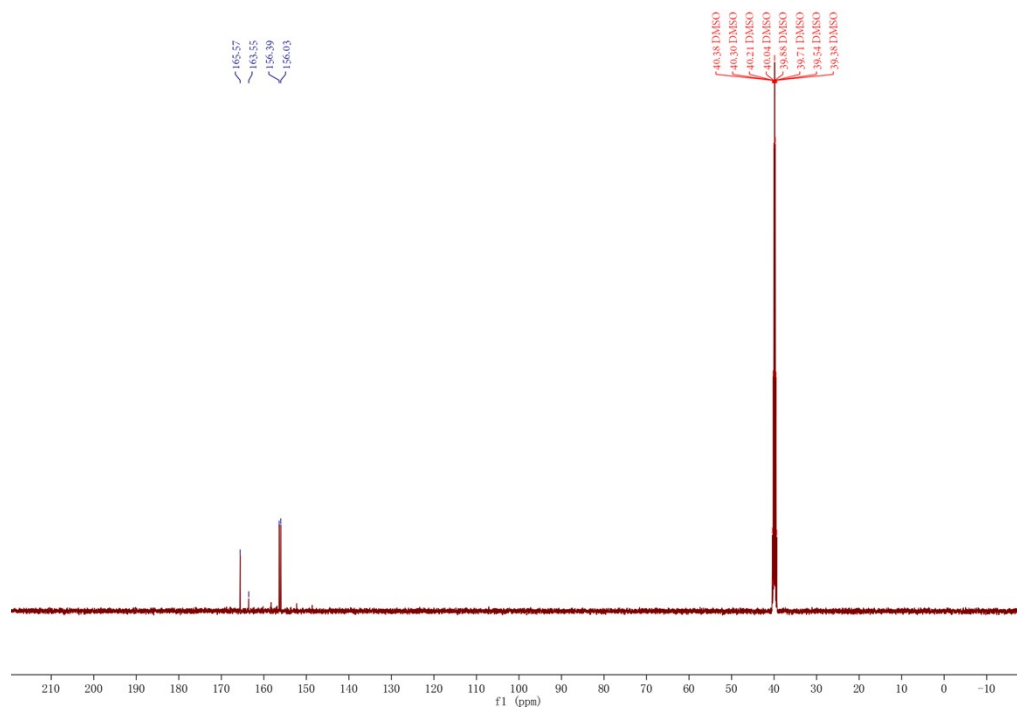


Figure S9. ^{13}C NMR spectra of N1-2.

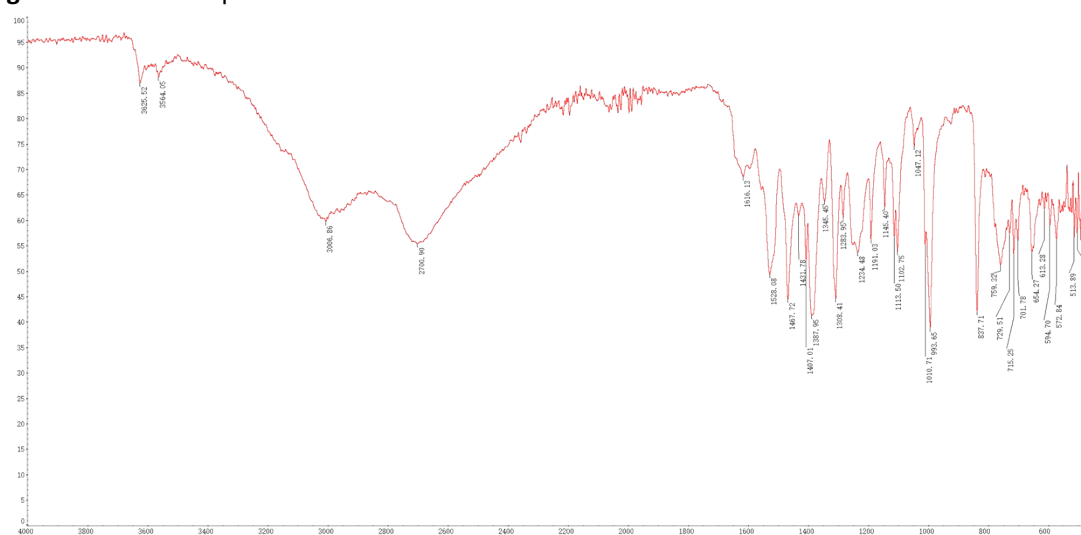


Figure S10. IR spectra of N1-3.

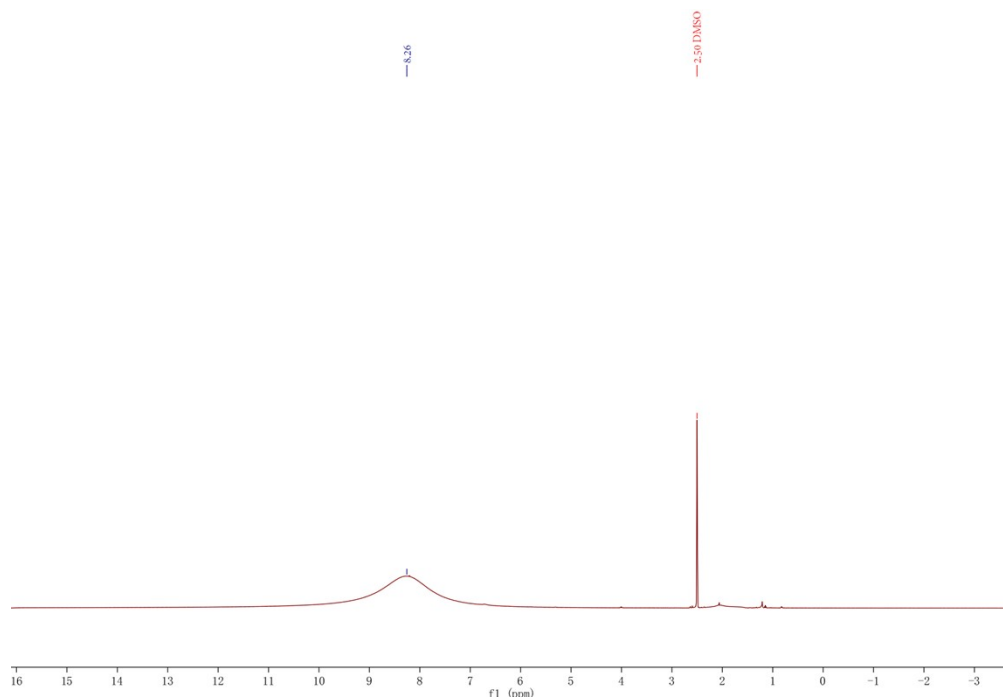


Figure S11. ^1H NMR spectra of N1-3.

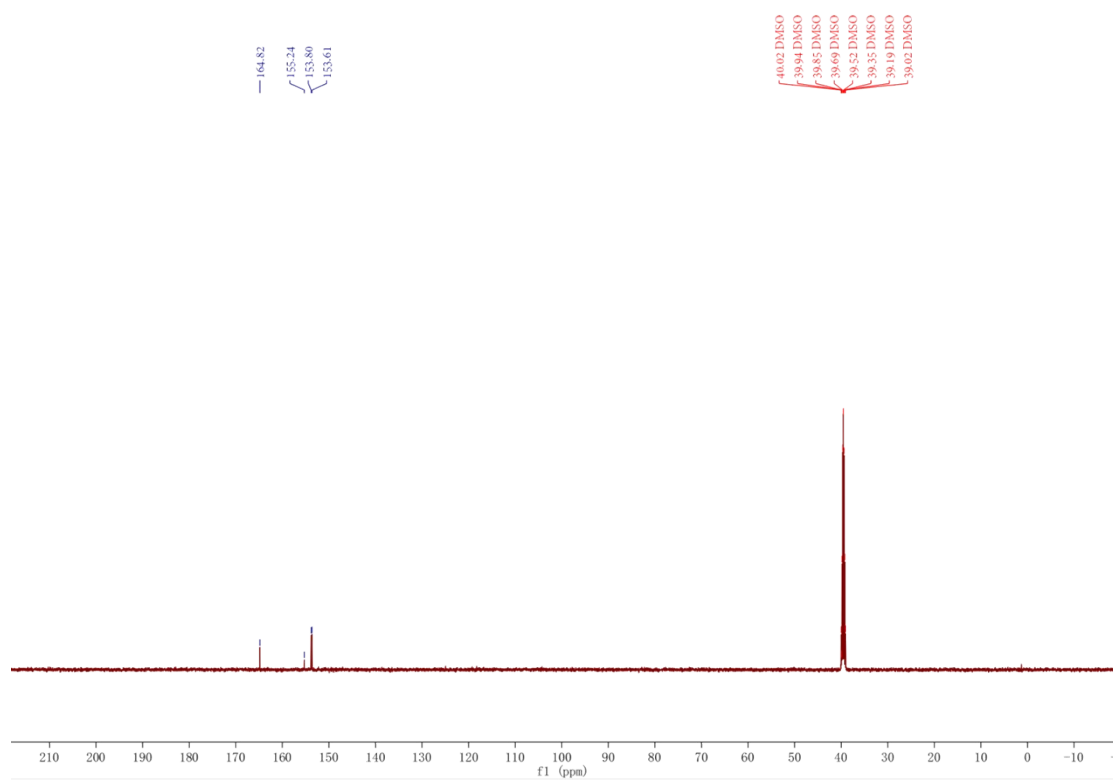


Figure S12. ^{13}C NMR spectra of N1-3.

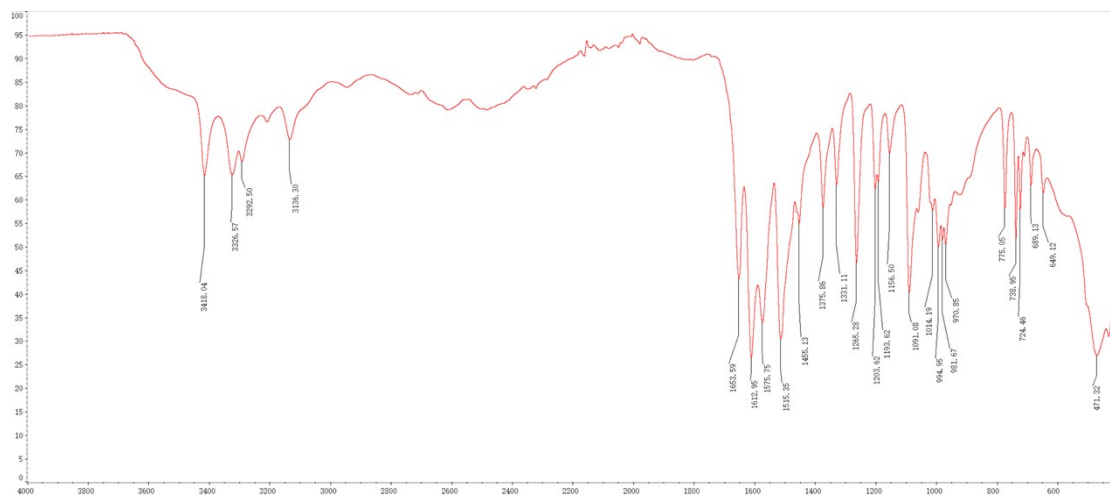


Figure S13. IR spectra of N2.

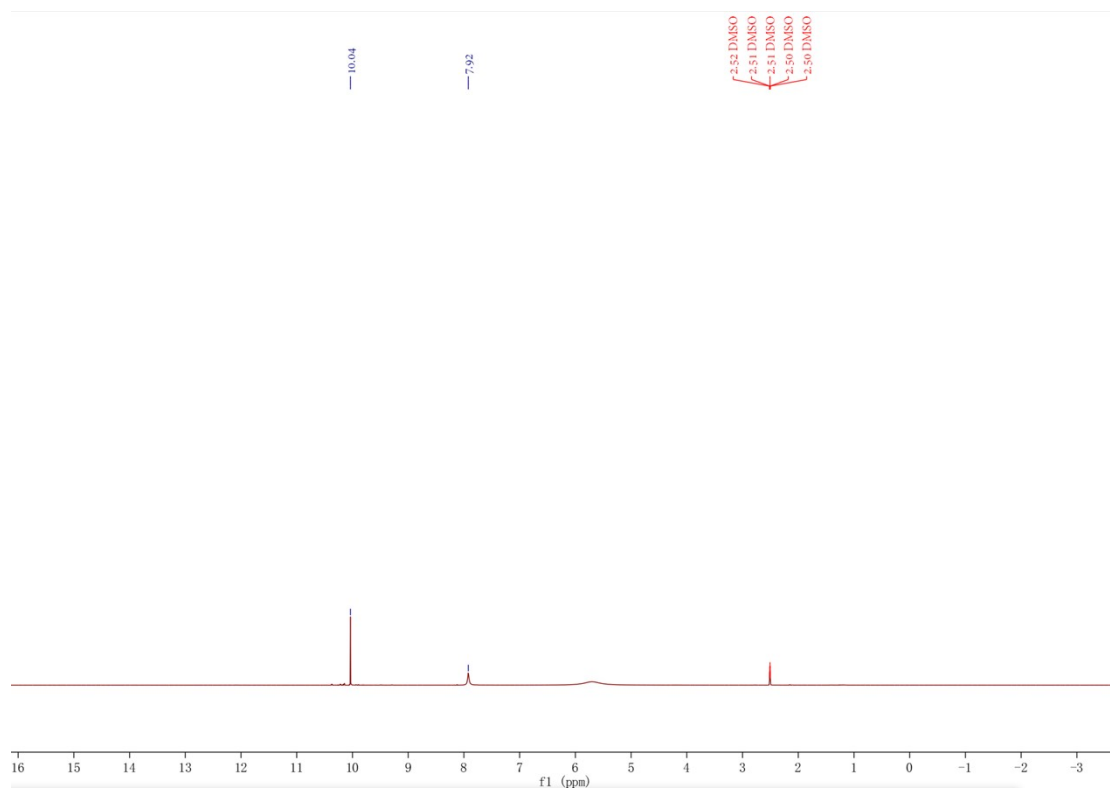


Figure S14. ¹H NMR spectra of N2.

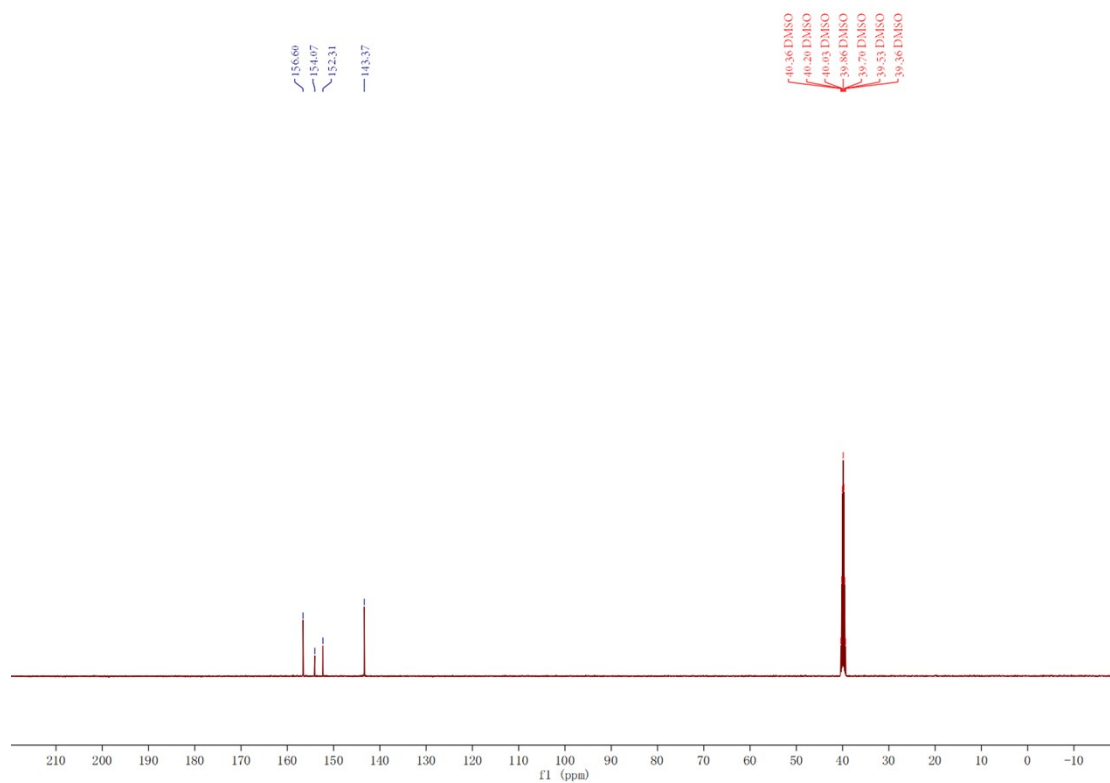


Figure S15. ^{13}C NMR spectra of N2.

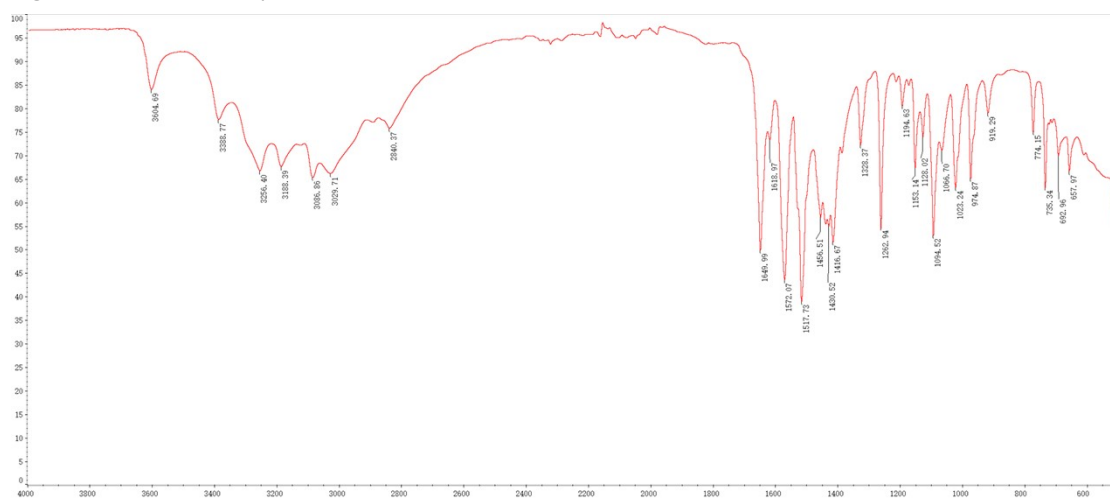


Figure S16. IR spectra of N2-1.

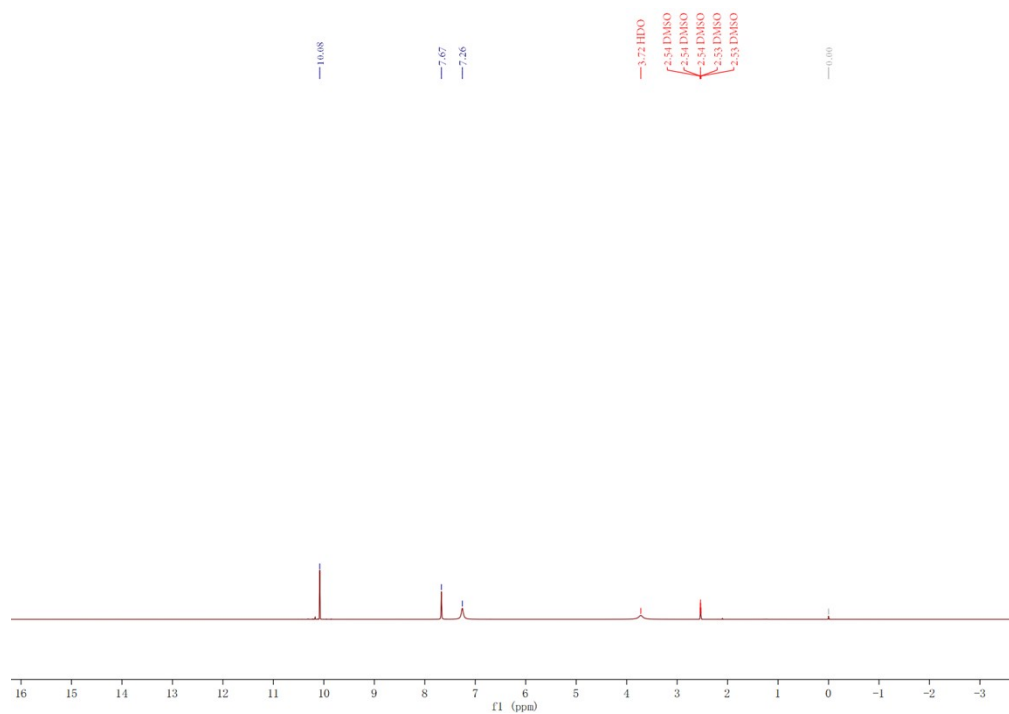


Figure S17. ¹H NMR spectra of N2-1.

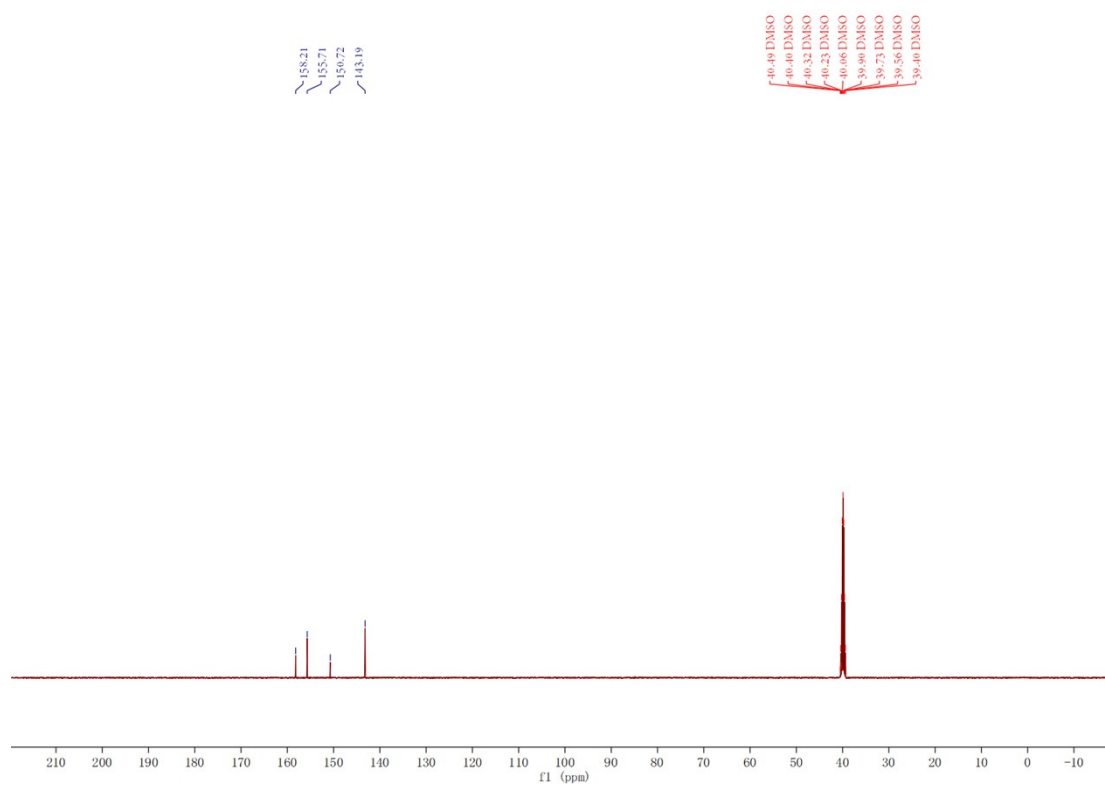


Figure S18. ¹³C NMR spectra of N2-1.

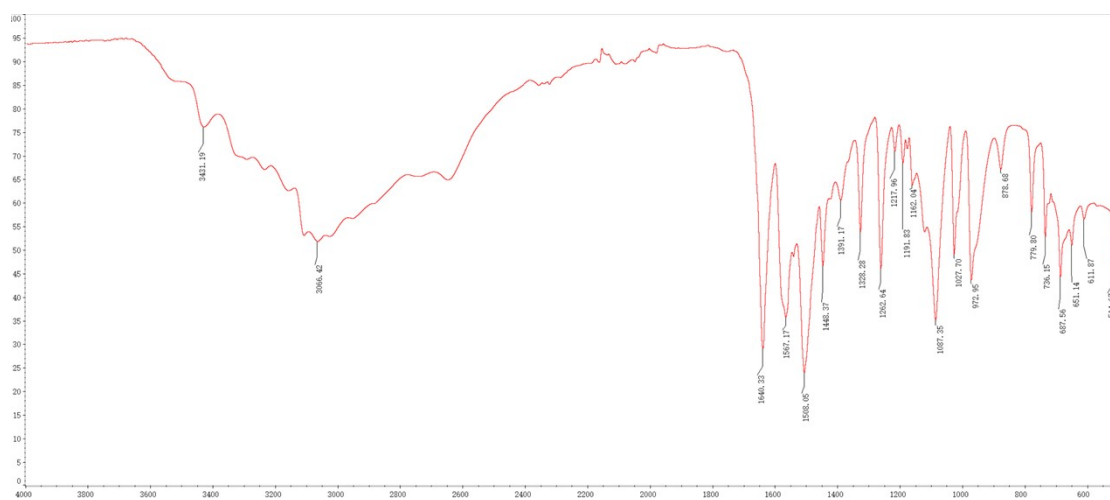


Figure S19. IR spectra of N2-2.

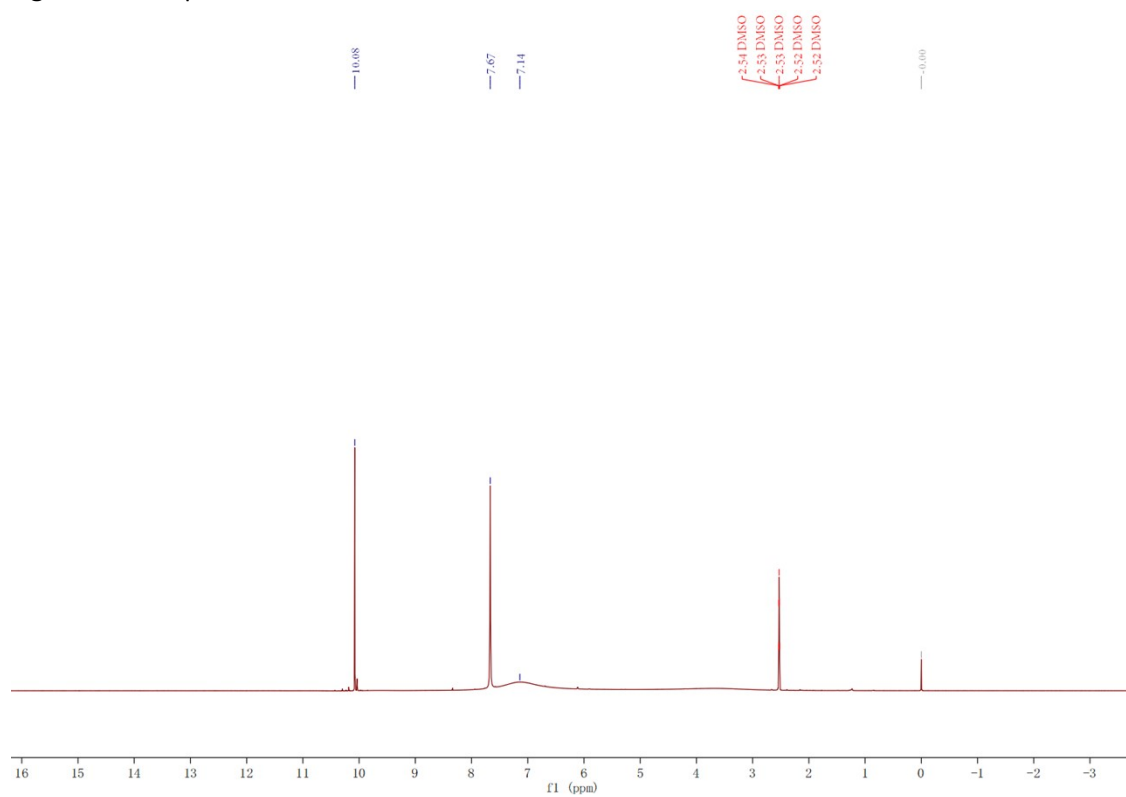


Figure S20. ¹H NMR spectra of N2-2.

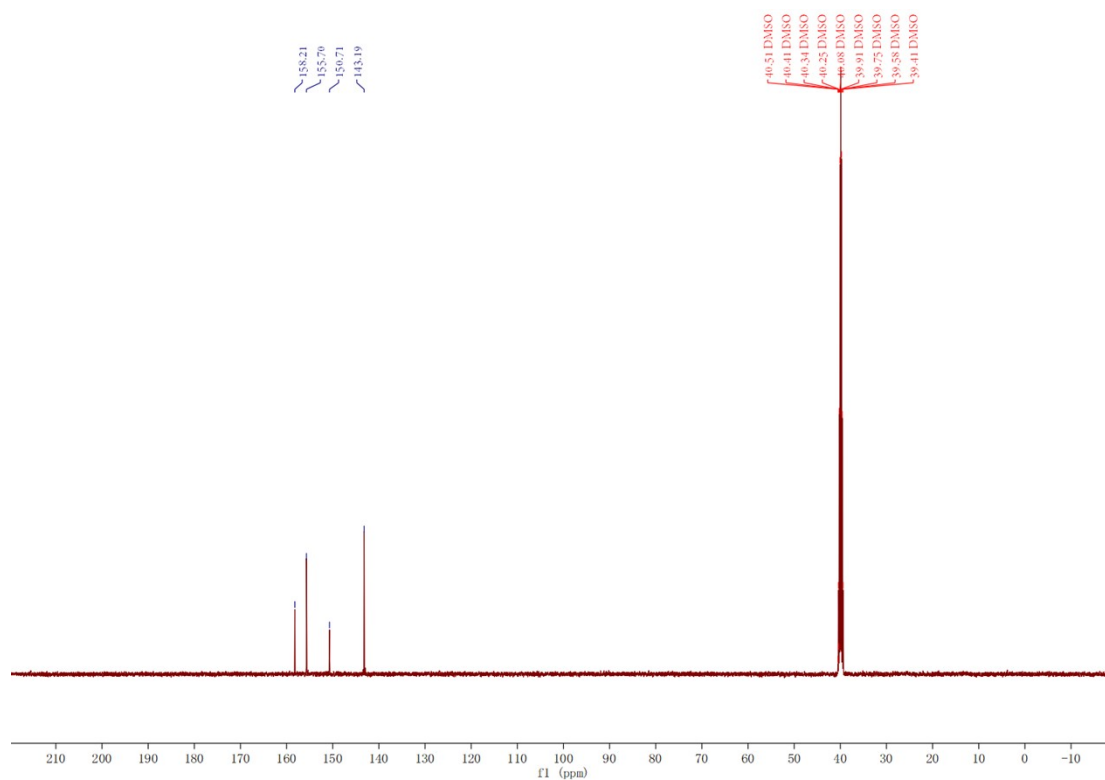


Figure S21. ^{13}C NMR spectra of N2-2.

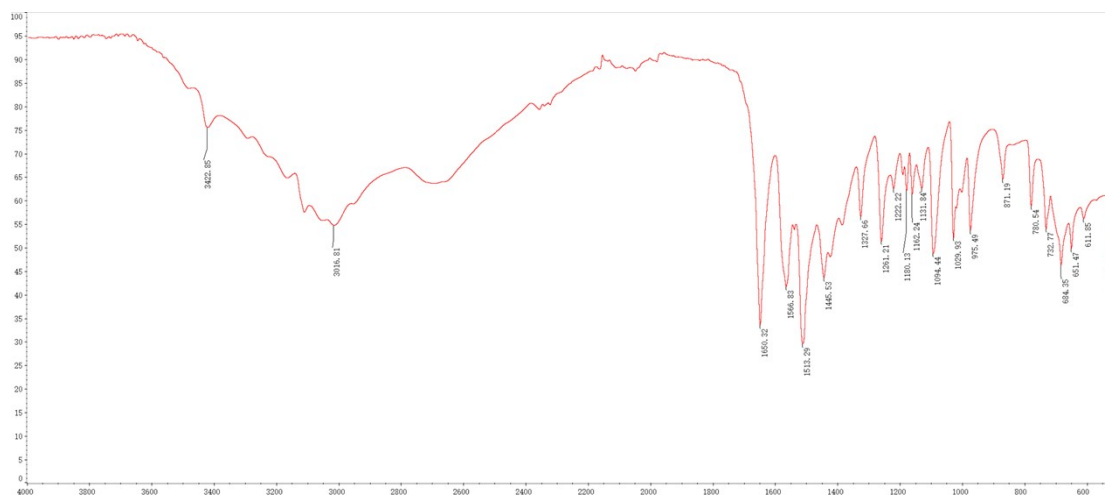


Figure S22. IR spectra of N2-3.

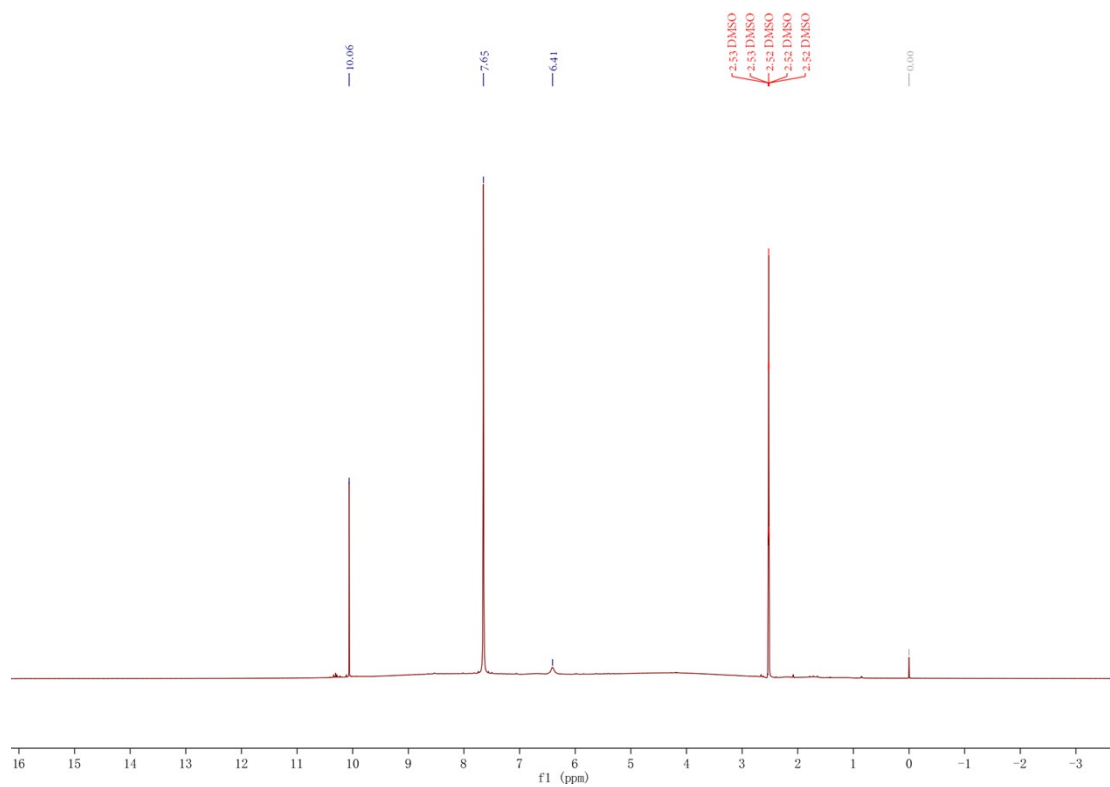


Figure S23. ^1H NMR spectra of N2-3.

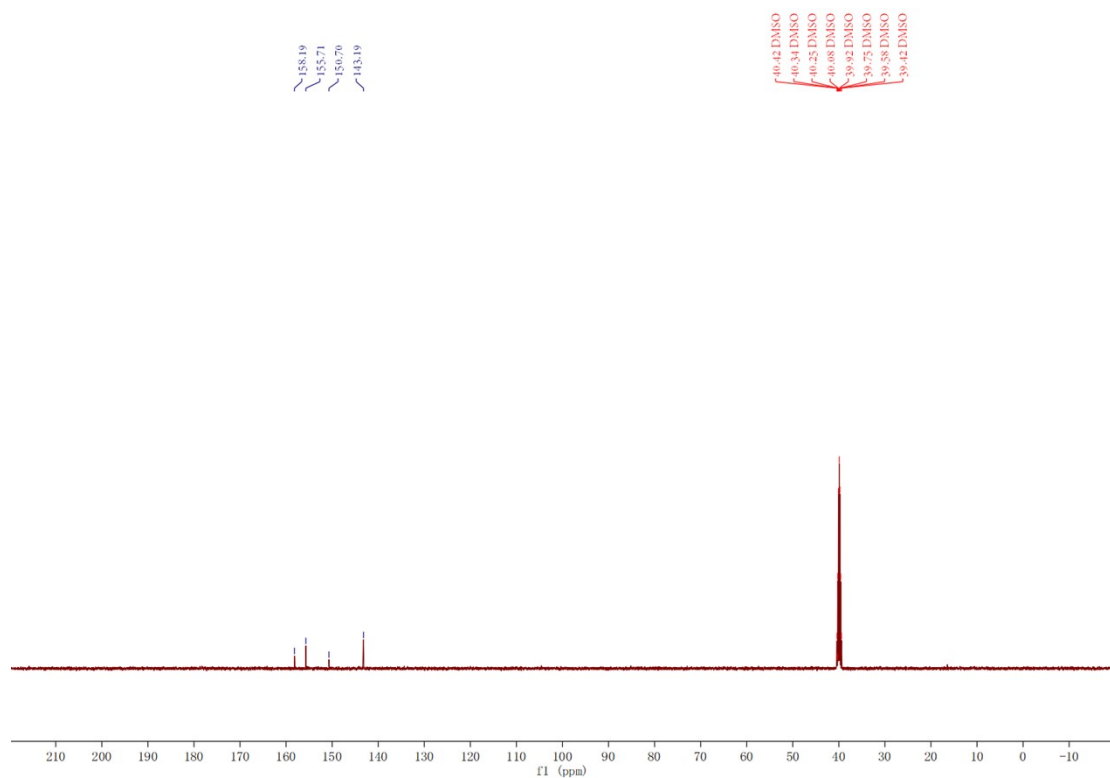


Figure S24. ^{13}C NMR spectra of N2-3.

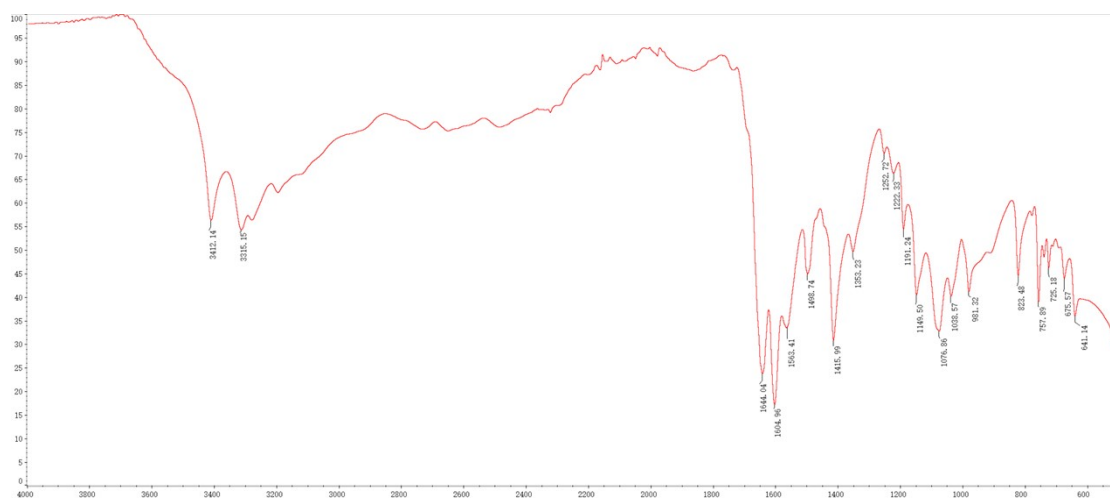


Figure S25. IR spectra of N3.

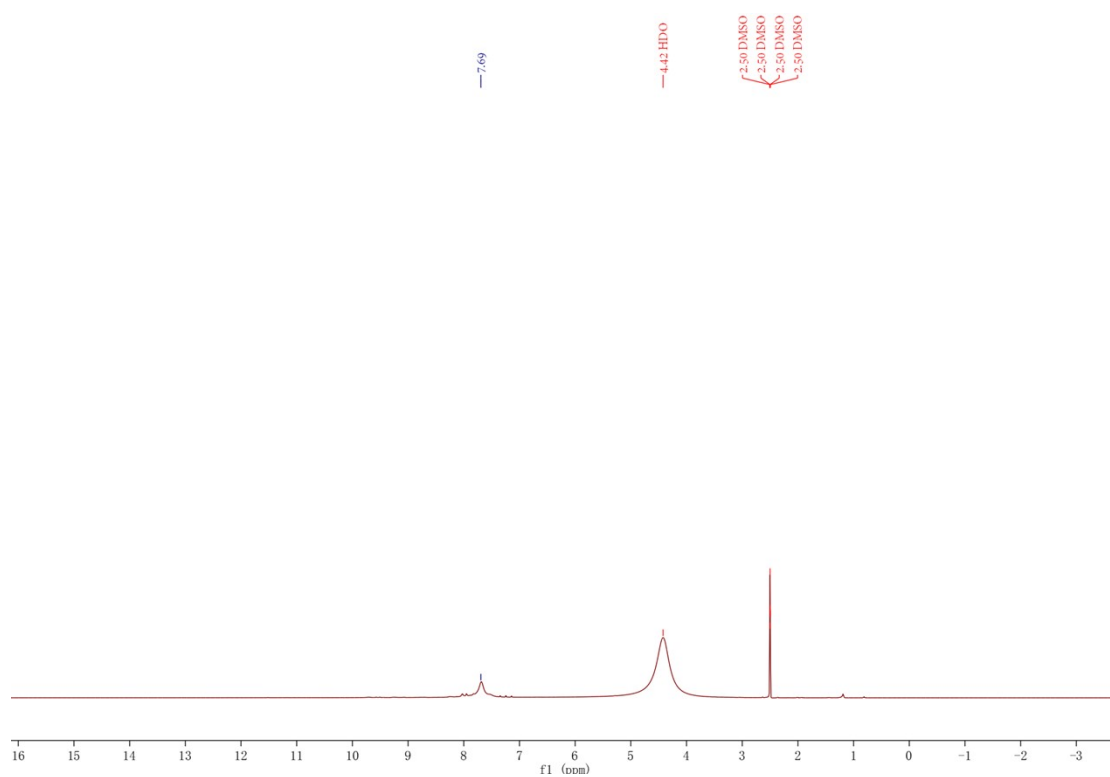


Figure S26. ¹H NMR spectra of N3.

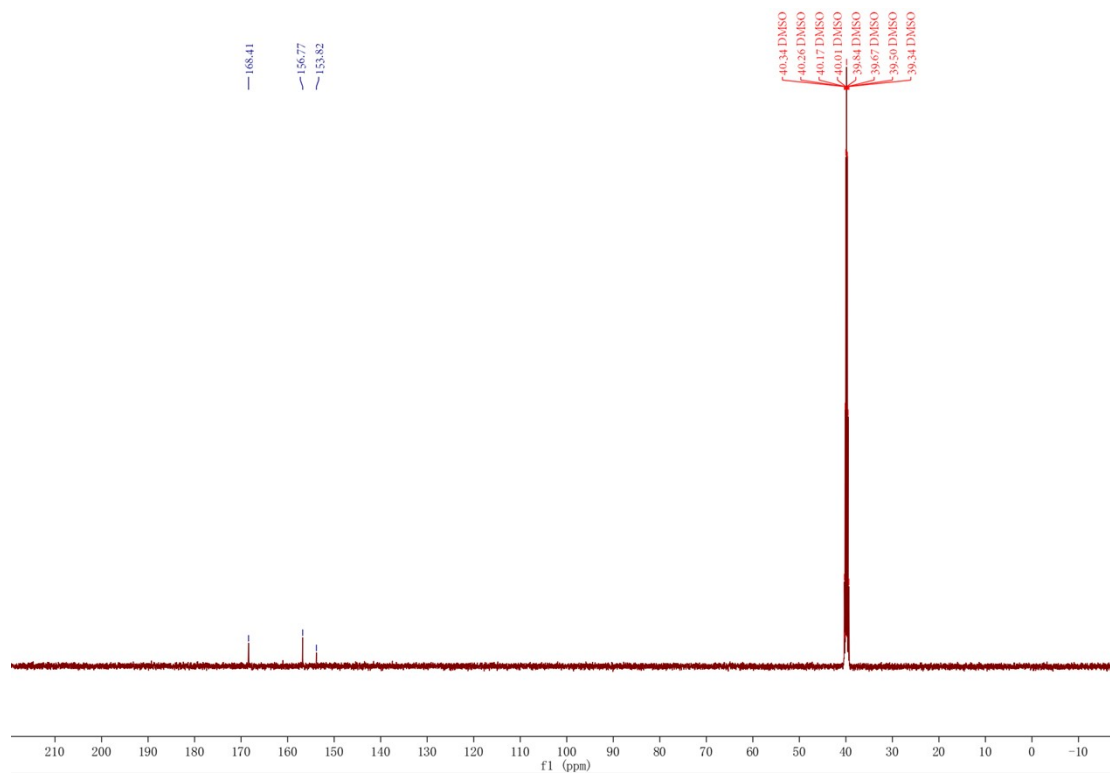


Figure S27. ^{13}C NMR spectra of N3.

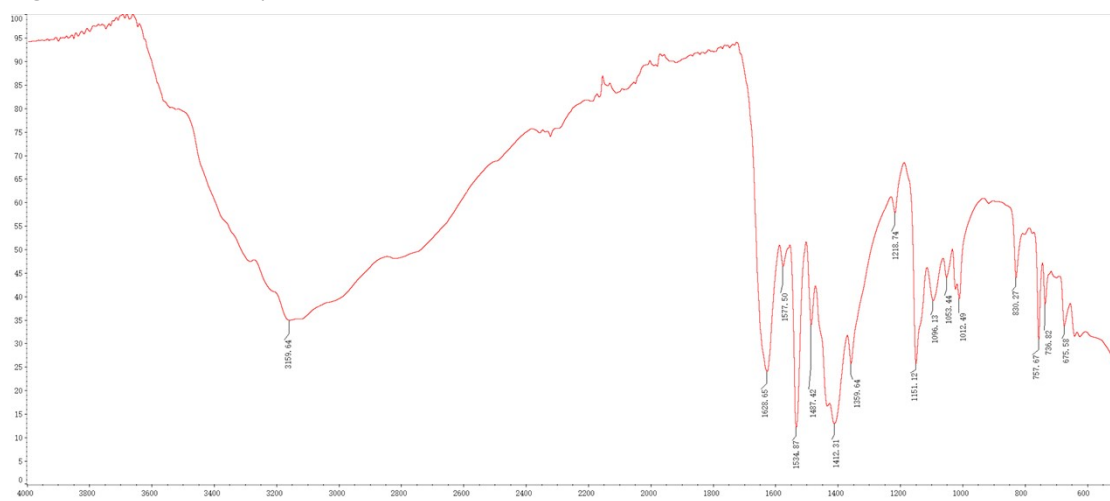


Figure S28. IR spectra of N3-1.

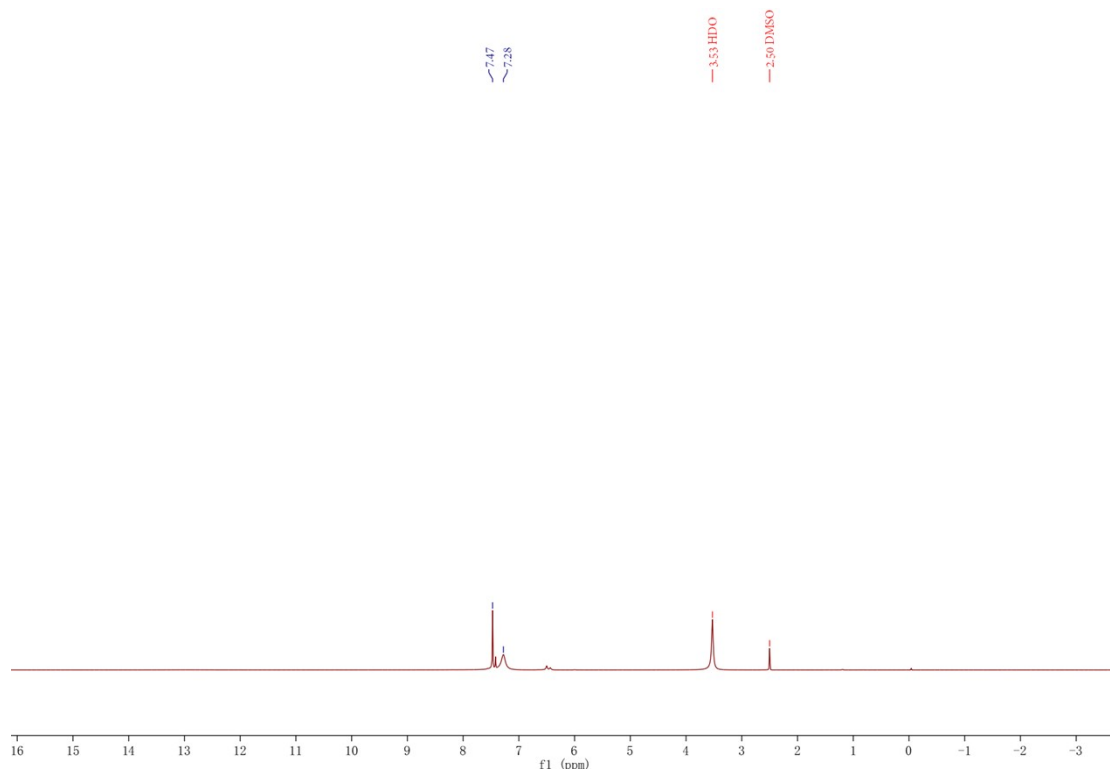


Figure S29. ¹H NMR spectra of N3-1.

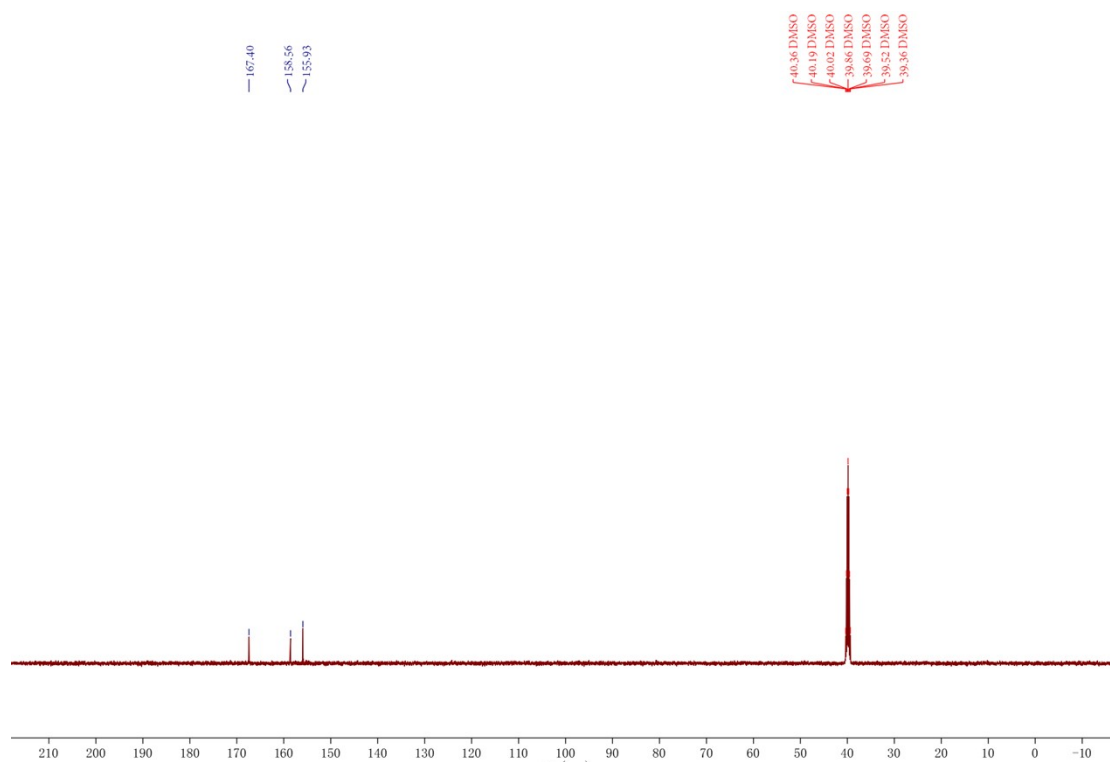


Figure S30. ¹³C NMR spectra of N3-1.

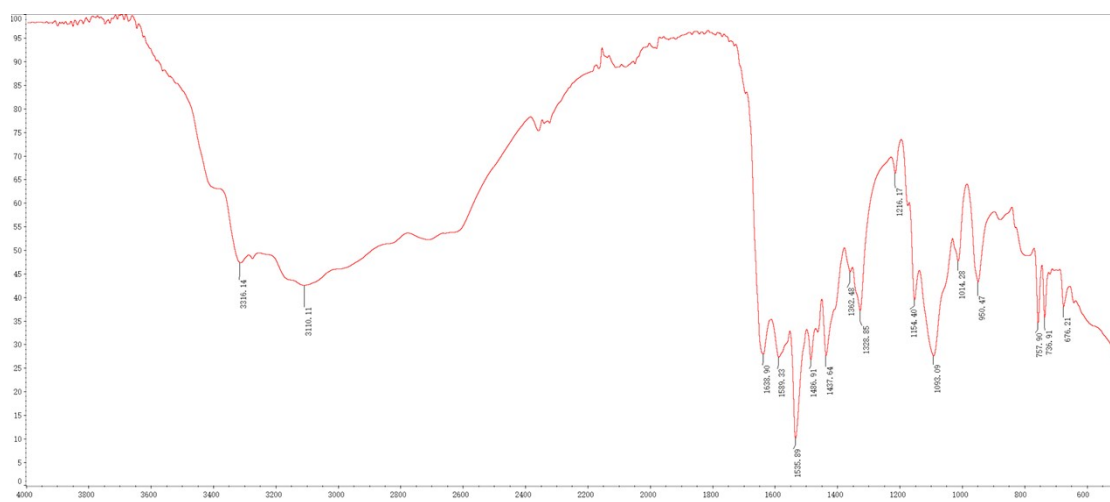


Figure S31. IR spectra of N3-2.

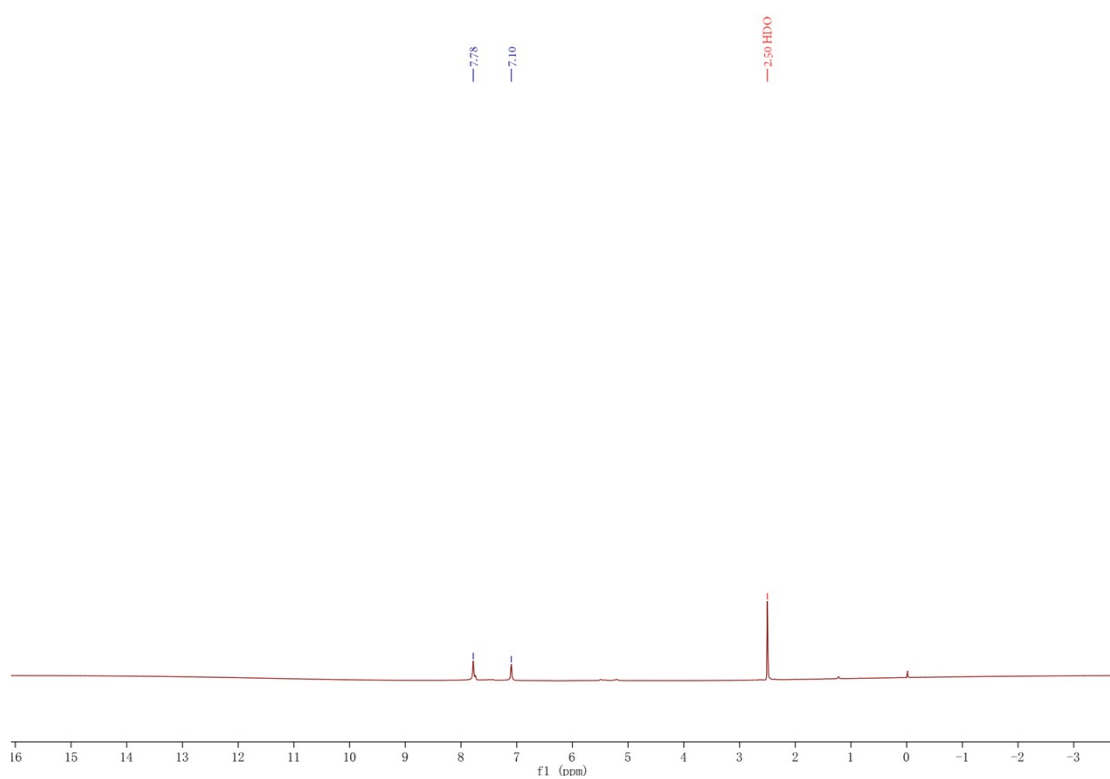


Figure S32. ¹H NMR spectra of N3-2.

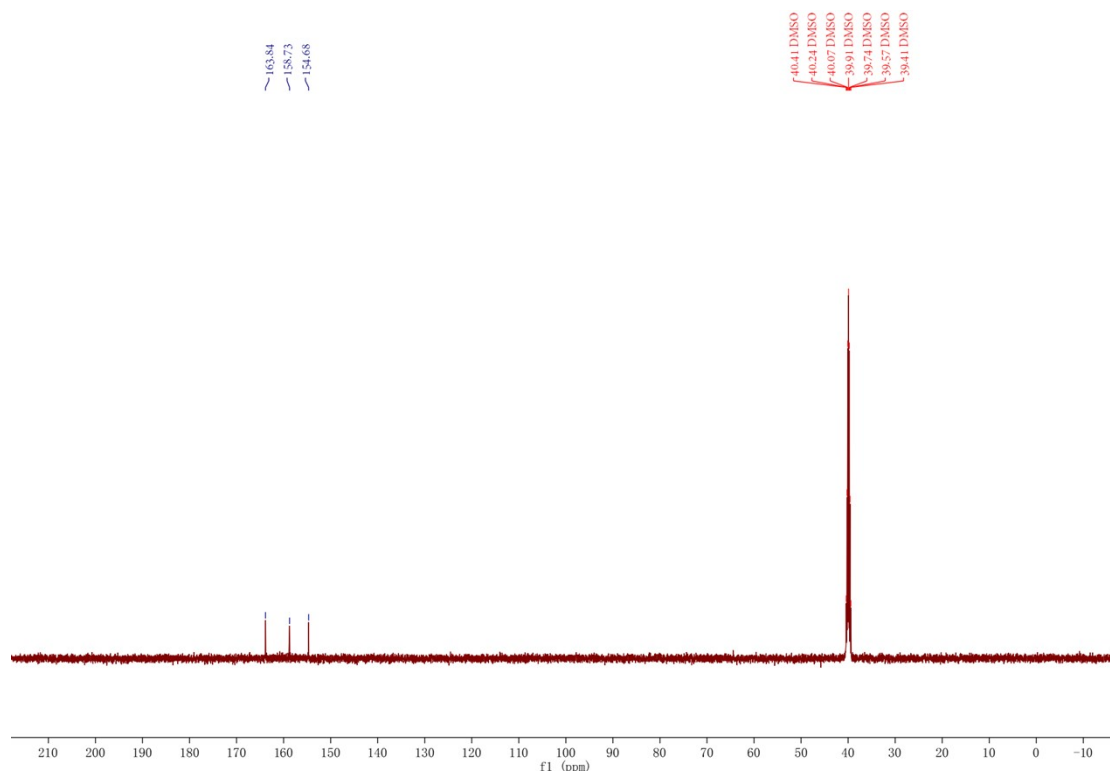


Figure S33. ^{13}C NMR spectra of N3-2.

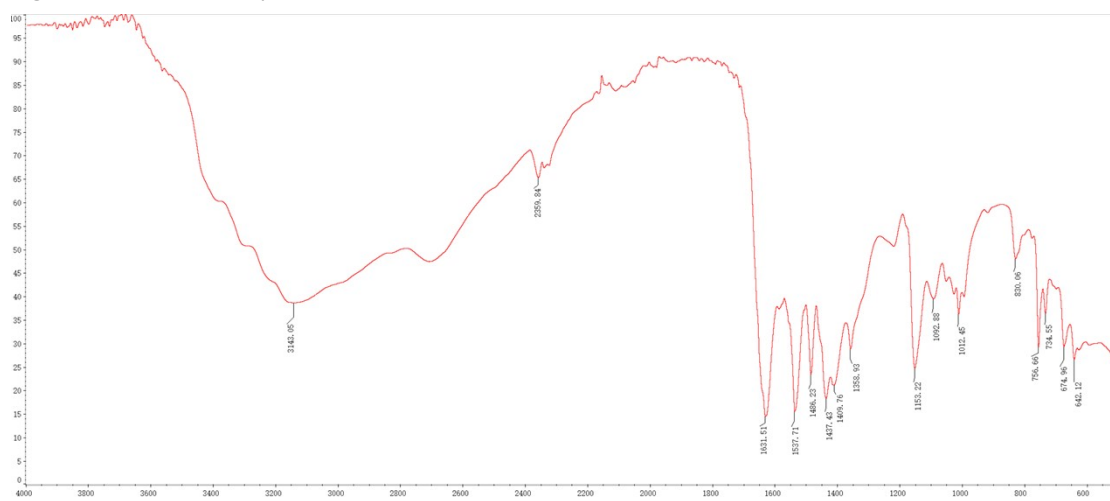


Figure S33. IR spectra of N3-3.

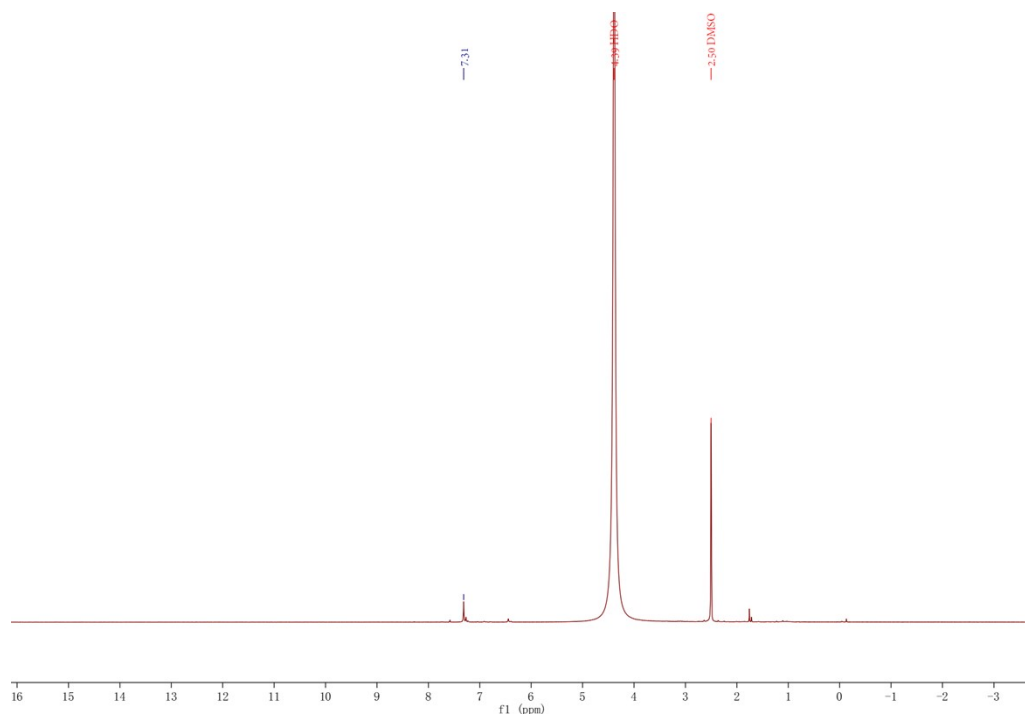


Figure S34. ¹H NMR spectra of N3-3.

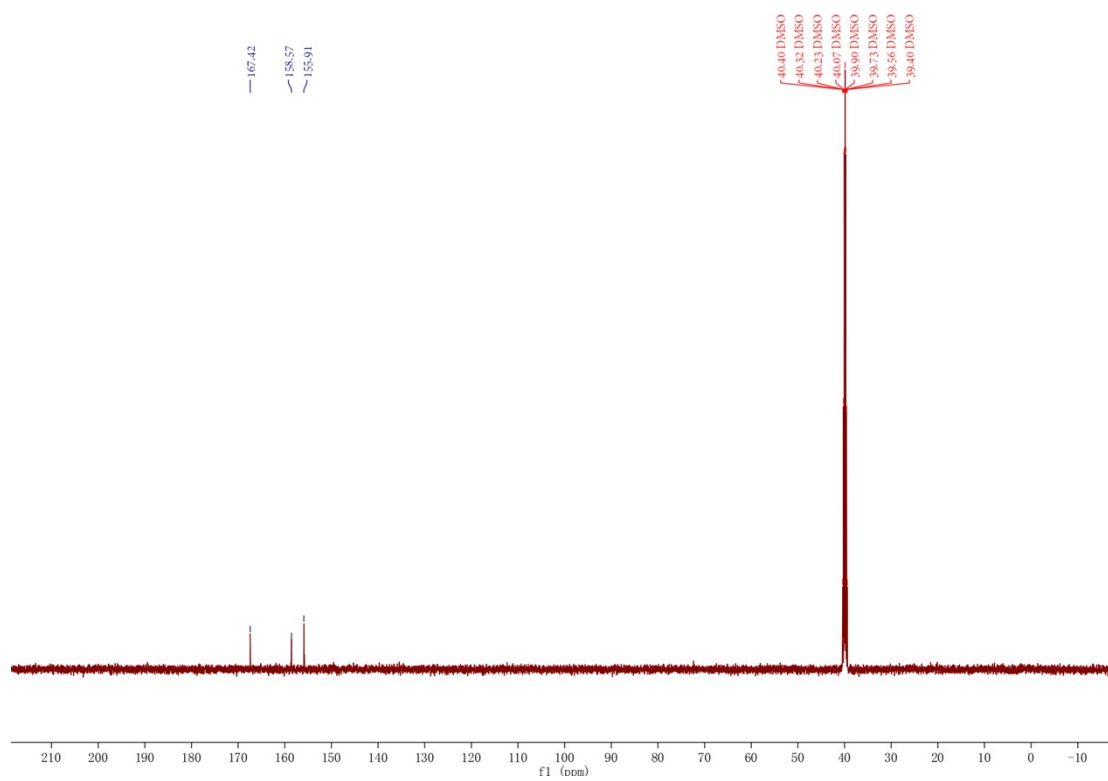


Figure S35. ¹³C NMR spectra of N3-3.

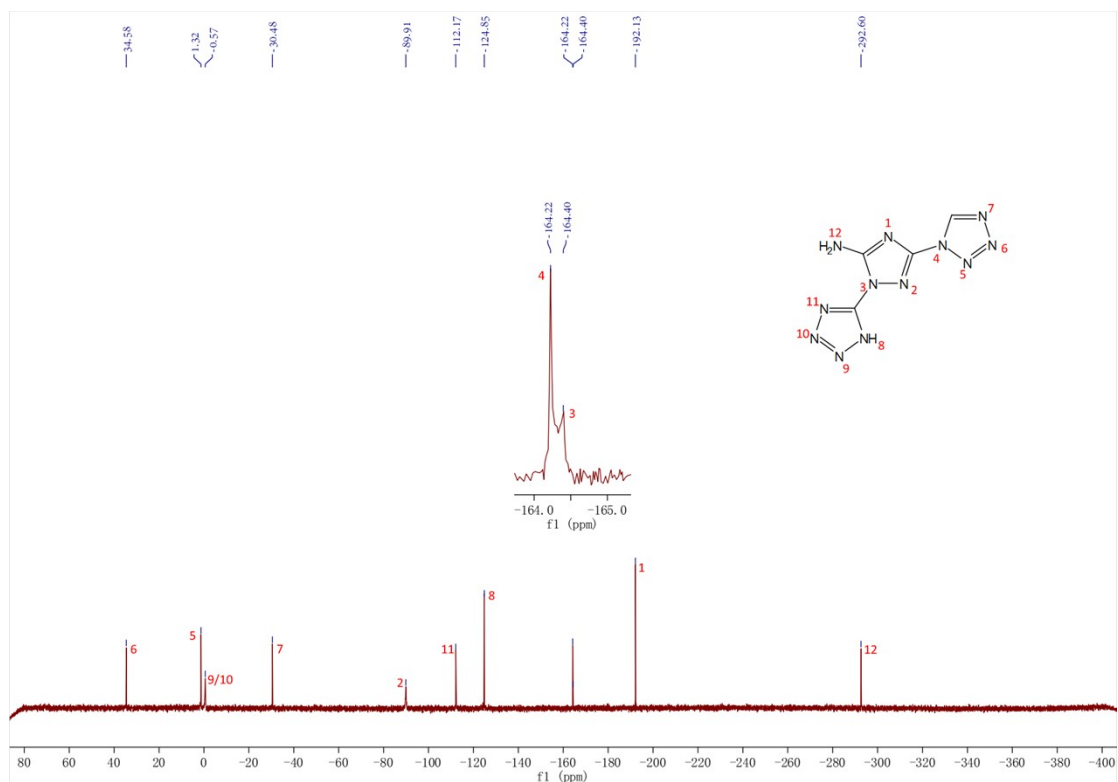


Figure S36. ^{15}N NMR spectra of N2 (Nitromethane was used as the external standard).

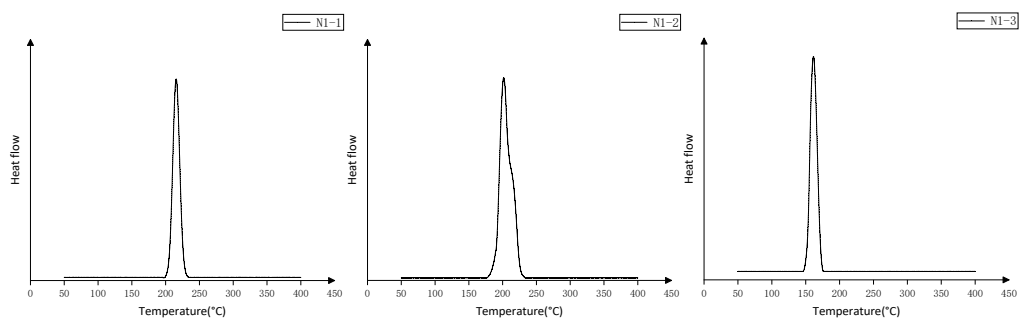


Figure S37. DSC curves of N1-1 to N1-3.

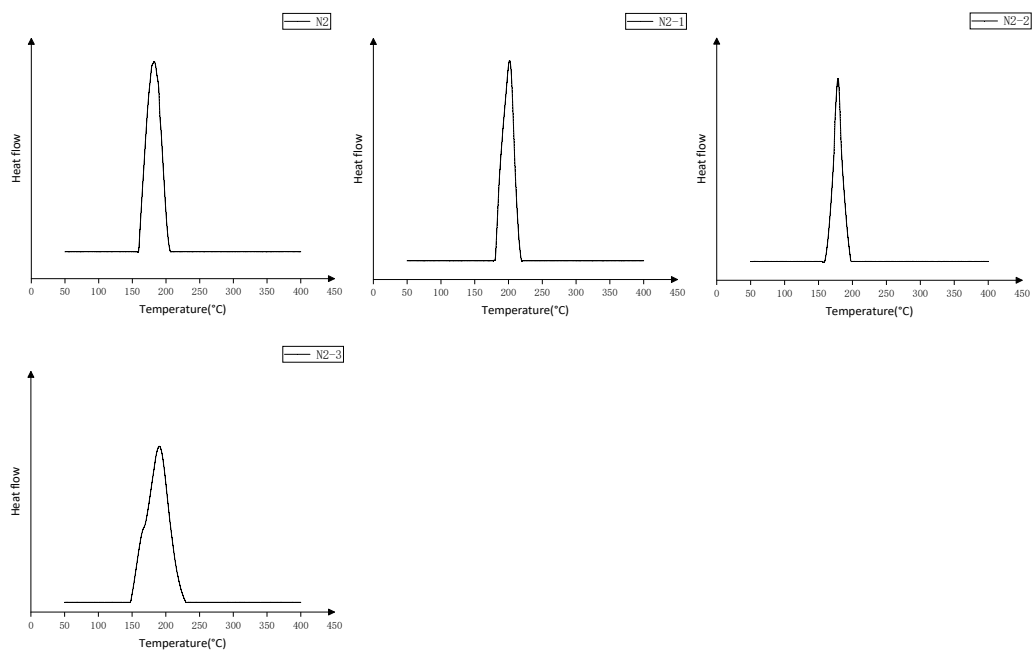


Figure S38. DSC curves of N2 and N2-1 to N2-3.

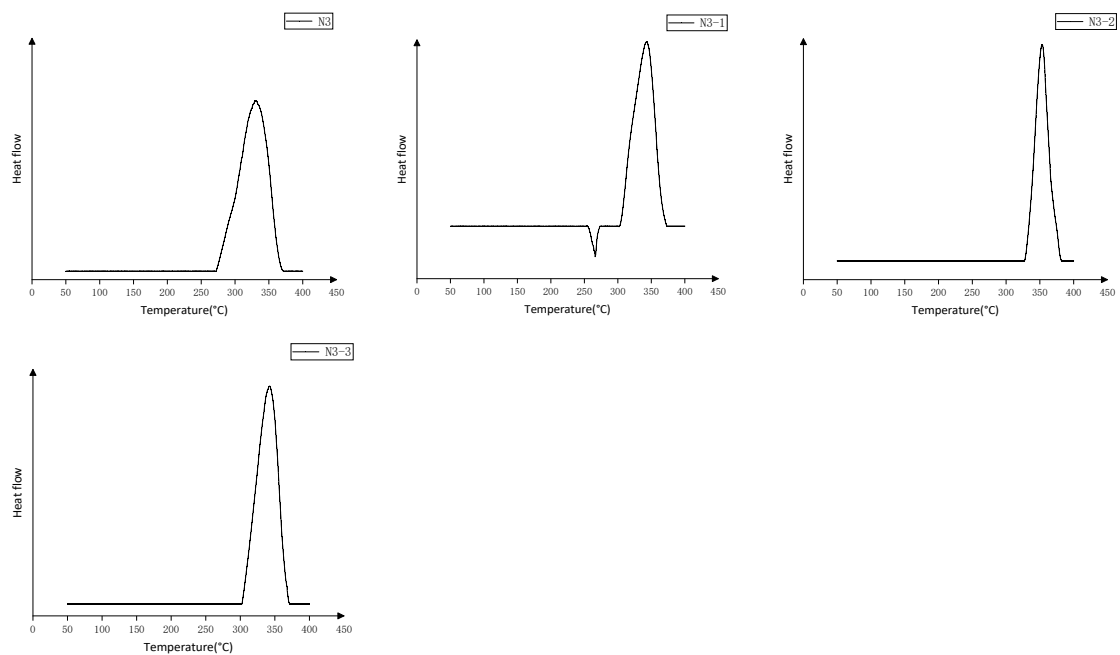
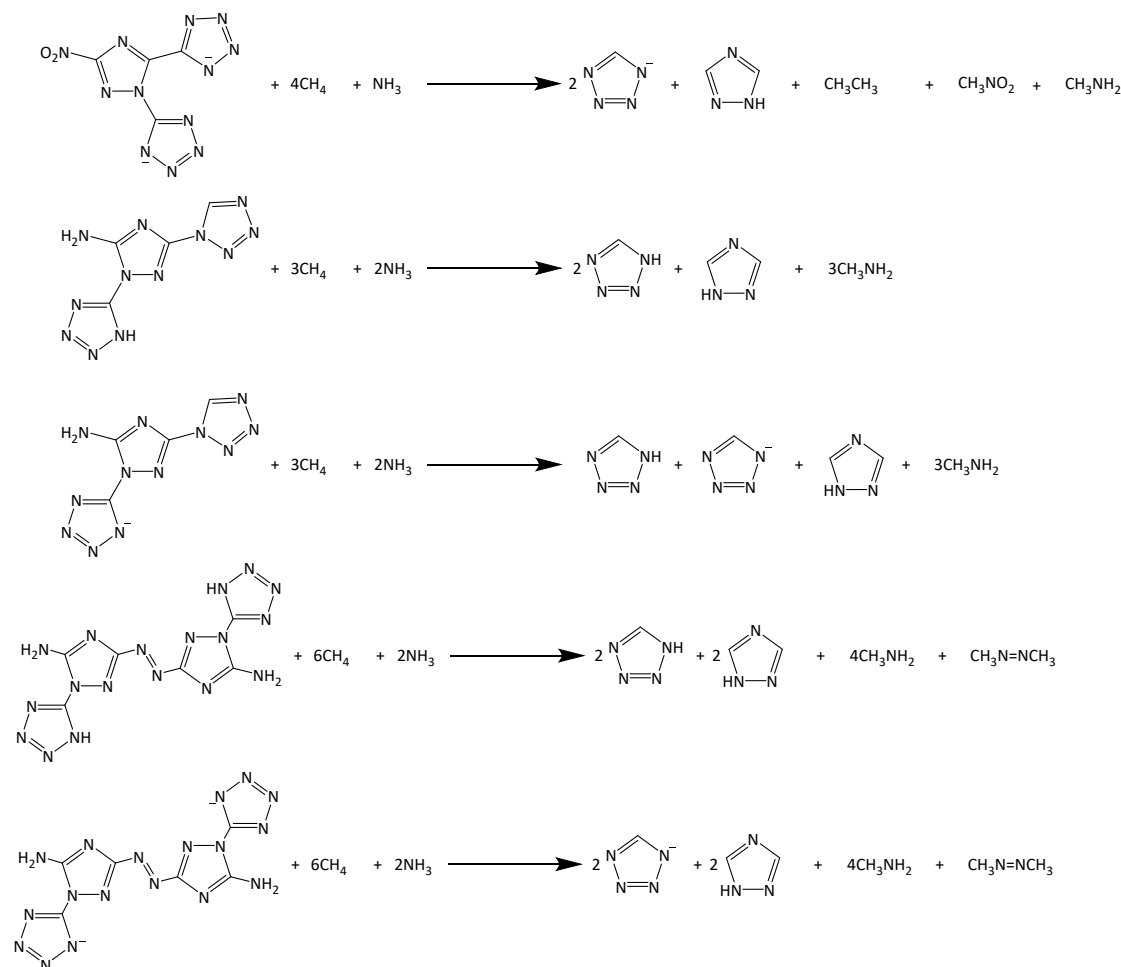


Figure S39. DSC curves of N3 and N3-1 to N3-3.

Computational Details

Computations were carried out by using the Gaussian 16 suite of programs.¹ The theoretical gas phase enthalpies of formation were calculated using the hybrid DFTB3LYP methods with 6-311++G** basis set based on isodesmic reactions (**Scheme S1**).



Scheme S1 Isodesmic reactions for calculating heats of formation.

Table S5 Calculated total energy (E_0), zero-point energy (ZPE), thermal correction to enthalpy (H_T) and gas phase heats of formation (HOF)

Compound	E_0 /a.u.	ZPE/kJ mol ⁻¹	ΔH_T /kJ mol ⁻¹	HOF/ kJ mol ⁻¹
CH ₄	-40.53	112.26	10.04	-74.6
NH ₃	-56.58	86.27	10.05	-45.9
CH ₃ NH ₂	-95.89	160.78	11.64	-22.5
CH ₃ N=NCH ₃	-189.33	211.85	16.32	147.85
CH ₃ CH ₃	-79.85	187.31	11.79	-84
CH ₃ NO ₂	-245.01	131.32	0.055294	-74.3
tetrazolium	-257.79	87.02	11.26	170
tetrazole	-258.25	123.13	11.83	333.2
1,2,4-triazole	-242.32	150.39	12.06	192.7
N ¹⁻	-959.69	218.47	40.56	694.8
N ₂	-811.92	334.18	35.19	1086.31
N ₂ ⁻	-811.25	297.76	34.09	1049.46
N ₃	-1217.16	511.35	54.17	1628.87
N ₃ ²⁻	-1215.82	440.17	50.84	1317.46

For energetic salts, the solid-phase heat of formation is calculated based on a Born-Haber energy cycle (Figure S40).⁴

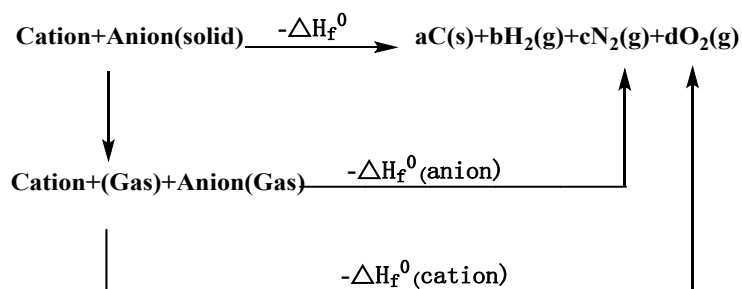


Figure S40. Born-Haber Cycle for the formation of energetic salts.

The number is simplified by equation 1:

$$H_f^0(\text{salt}, 298\text{ K}) = H_f^0(\text{cation}, 298\text{ K}) + H_f^0(\text{anion}, 298\text{ K}) - H_L \quad (1)$$

where H_L is the lattice energy of the salts, which could be predicted by using the formula suggested by Jenkins et al. [Eq. (2)]

$$H_L = U_{\text{POT}} + [p(n_M/2 - 2) + q(n_X/2 - 2)]RT \quad (2)$$

where n_M and n_X depend on the nature of the ions, M^{q+} and X^{p-} , and are equal to 3 for monatomic ions, 5 for linear polyatomic ions, and 6 for nonlinear polyatomic ions.

The equation for lattice potential energy U_{POT} [Eq. (3)] has the form:

$$U_{\text{POT}} [\text{kJ mol}^{-1}] = \gamma(\rho_m/M_m)^{1/3} + \delta \quad (3)$$

where ρ_m [g cm^{-3}] is the density of the salt, M_m is the chemical formula mass of the ionic material, and values for γ ($\text{kJ mol}^{-1} \text{cm}$) and δ (kJ mol^{-1}) are assigned literature values.³

The solid-state enthalpy of formation for neutral compound can be estimated by subtracting the heat of sublimation from gas-phase heat of formation. Based on the literature,⁴ the heat of sublimation can be estimated with Trouton's rule according to supplementary equation (4), where T represents either the melting point or the decomposition temperature when no melting occurs prior to decomposition:

$$\Delta H_{\text{sub}} = 188/\text{J mol}^{-1}\text{K}^{-1} \times T \quad (4)$$

4. References

- (1) Gaussian 16, Revision A.03, M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, G. A. Petersson, H. Nakatsuji, X. Li, M. Caricato, A. V. Marenich, J. Bloino, B. G. Janesko, R. Gomperts, B. Mennucci, H. P. Hratchian, J. V. Ortiz, A. F. Izmaylov, J. L. Sonnenberg, D. Williams-Young, F. Ding, F. Lipparini, F. Egidi, J. Goings, B. Peng, A. Petrone, T. Henderson, D. Ranasinghe, V. G. Zakrzewski, J. Gao, N. Rega, G. Zheng, W. Liang, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, K. Throssell, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. J. Bearpark, J. J. Heyd, E. N. Brothers, K. N. Kudin, V. N. Staroverov, T. A. Keith, R. Kobayashi, J. Normand, K. Raghavachari, A. P. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, J. M. Millam, M. Klene, C. Adamo, R. Cammi, J. W. Ochterski, R. L. Martin, K. Morokuma, O. Farkas, J. B. Foresman, and D. J. Fox, *Gaussian, Inc.*, Wallingford CT, 2016.
- (2) M. Suceska, *EXPLO5, Version 6.01*, Brodarski Institute, Zagreb, Croatia, 2013.
- (3) Z. Dong, and Z. Ye, *J. Mater. Chem. A*, 2020, **8**, 25035–25039.