Electronic Supplementary Material (ESI) for Organic Chemistry Frontiers.

Supporting Information

Metal-Free Aerobic Oxidative Direct C-H Amination of Electron-Deficient Alkenes via Photoredox Catalysis

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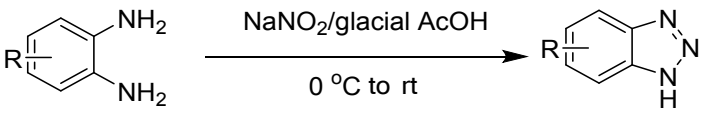
1. General experimental details

Rose Bengal was purchased from aladdin industrial corporation Shanghai, China. R104993-1g. Unless otherwise noted, all reagents were purchased from commercial suppliers and used without further purification. Reactions were monitored by thin-layer chromatography (TLC) with Haiyang GF 254 silica gel plates (Qingdao Haiyang chemical industry Co Ltd, Qingdao, China) using UV light and vanillic aldehyde as visualizing agents. Flash column chromatography was performed using 200–300 mesh silica gel at increased pressure. ^{1}H NMR spectra and ^{13}C NMR spectra were respectively recorded on 600 MHz and 150 MHz NMR spectrometers. Chemical shifts (δ) were expressed in ppm with TMS as the internal standard, and coupling constants (*J*) were reported in Hz. High-resolution mass spectra were obtained by using ESI ionization sources (Varian 7.0 T FTICR-MS) and ESI-TOF. Melting points were taken on a WPX-4 apparatus (Yice instrument equipment Co Ltd, Shanghai) and were uncorrected.

2. Experimental Procedures

2.1. General procedure for the preparation of substituted benzotriazoles 1 [1]



1,2-phenylenediamine derivative (3.26 mmol) was dissolved in a mixture of 0.45 mL of glacial acetic acid and 1.2 mL of water and cooled to 4 °C. A solution of sodium nitrite (0.26 g, 3.76 mmol) in 1 mL of water was added. The reaction temperature rose to 50 °C for 30 min, and then was allowed to reach r.t. and stirred at this temperature for 12 h. The mixture was cooled to 0 °C for 1 h. Produced precipitate was collected by suction filtration, and washed with water, and dried to provide substituted benzotriazoles **1**.

2.2. General procedure for the preparation of benzylidenemalononitriles 2 [2]

Malononitrile (10.0 mmol) was added to a stirred solution of aromatic aldehyde (10.0 mmol) and piperidine (1.0 mmol) in ethanol (10 mL). The reaction mixture was stirred at r.t. for 1 h. A precipitate was formed and collected by suction filtration, and then purified by recrystallization from CH_2Cl_2 and petroleum ether to afford the products **2**.

2.3. General procedure for the synthesis of product 3

A round-bottom flask was charged with Rose Bengal (3 mol%, 6.1 mg), substituted azole **1** (0.2 mmol) and 2-benzylidenemalononitrile **2** (0.4 mmol) in acetone (1.0 ml), The resultant mixture was stirred at r.t. under irradiation of 12 W CFL (Philips) in air and monitored by TLC. After completion of the reaction, the solvent was removed in vacuo and purified by flash column chromatography (petroleum ether/ethyl acetate 10/1-4/1, v/v) to afford the products **3**.

3. Extra information for the optimization of reaction conditions

Table S1. Optimization of molar ratio of substrates [a]

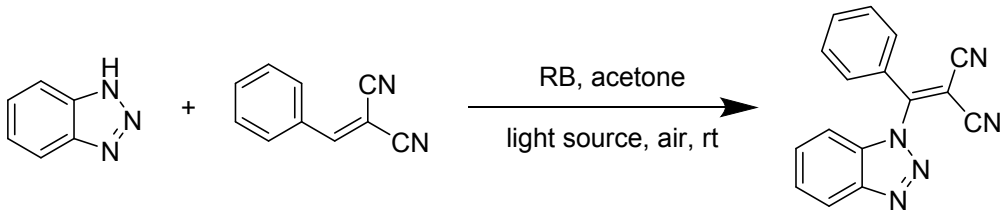
1a **2a** **3aa**

Entry	Molar ratio (1a:2a)	Yield (%)[b]
1	0.2:0.2	45
2	0.2:0.3	56
3	**0.2:0.4**	**57**
4	0.2:0.5	41
5	0.2:0.6	35
6	0.3:0.2	37
7	0.4:0.2	30

[a] Reaction conditions: a mixture of **1a**, **2a**, and Rose Bengal (2 mol%) in acetone (1.0 mL) was irradiated using a 3 W green LED in air at rt for 24 h.

[b] Yield of the isolated product.

Table S2. Optimization of light source [a]



1a **2a** **3aa**

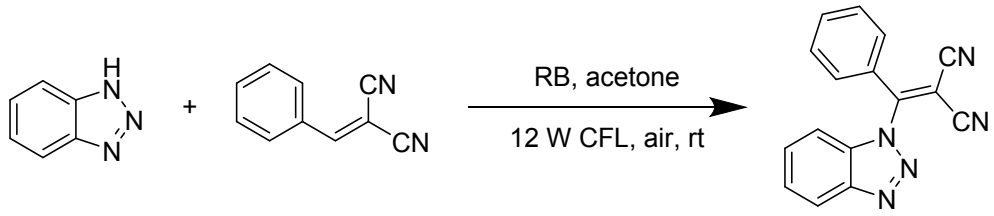
Entry	Light source	Yield (%) [b]

1	3 W green LED	57
2	8 W CFL	55
3	**12 W CFL**	**64**
4	23 W CFL	57

[a] Reaction conditions: a mixture of **1a** (0.2 mol), **2a** (0.4 mol), and Rose Bengal (2 mol%) in acetone (1.0 mL) was irradiated using a light source in air at rt for 24 h.

[b] Yield of the isolated product.

Table S3. Optimization of Rose Bengal dosage [a]



1a **2a** **3aa**

Entry	RB (mol%)	Yield (%)[b]
1	0.5	45
2	1	56
3	2	64
4	**3**	**79**
5	4	63
6	5	57

[a] Reaction conditions: a mixture of **1a** (0.2 mol), **2a** (0.4 mol), and Rose Bengal in acetone (1.0 mL) was irradiated using a 12 W CFL in air at rt for 24 h.

[b] Yield of the isolated product.

Table S4. Optimization of solvent volume [a]

1a **2a** **3aa**

Entry	Acetone (ml)	Yield (%) [b]
1	0.5	55
2	**1**	**79**
3	2	76

4	3	68

[a] Reaction conditions: a mixture of **1a** (0.2 mol), **2a** (0.4 mol), and Rose Bengal (3 mol%) in acetone was irradiated using a 12 W CFL in air at rt for 24 h.

[b] Yield of the isolated product.

4. Crystallographic data

X-ray crystal structure analysis of 3aa

Crystal	**3aa**
Empirical formula	$C_{16}H_9N_5$
Formula weight	271.28
Temperature/K	291.74(10)
Crystal system	monoclinic
Space group	$P2_1/c$
a/Å	17.5111(7)
b/Å	18.0998(6)
c/Å	8.8623(3)
α/°	90
β/°	98.023(4)
γ/°	90
Volume/Å^3	2781.41(16)
Z	8
ρ_{calc}g/cm^3	1.296
μ/mm^{-1}	0.664
F(000)	1120.0
Crystal size/mm^3	0.23 × 0.2 × 0.18
Radiation	CuKα (λ = 1.54184)
2Θ range for data collection/°	7.06 to 134.158
Index ranges	-20 ≤ h ≤ 20, -21 ≤ k ≤ 16, -10 ≤ l ≤ 8

Reflections collected	12400
Independent reflections	4794 [R_{int} = 0.0328, R_{sigma} = 0.0321]
Data/restraints/parameters	4794/19/379
Goodness-of-fit on F^2	1.092
Final R indexes [I>=2σ (I)]	R_1 = 0.0585, wR_2 = 0.2017
Final R indexes [all data]	R_1 = 0.0739, wR_2 = 0.2344
Largest diff. peak/hole / e $Å^{-3}$	0.24/-0.24
Empirical formula	$C_{16}H_9N_5$
Formula weight	271.28

Crystallographic data (excluding structure factors) for the structures reported in this work have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC 1553472. Copy of the data can be obtained free of charge on application to The Director, CCDC, 12 Union Road, Cambridge DB21EZ, UK (fax:+ 44 (1223) 336033; e-mail: deposit@ccdc.cam.ac.uk).

5. The UV-visible absorption spectra

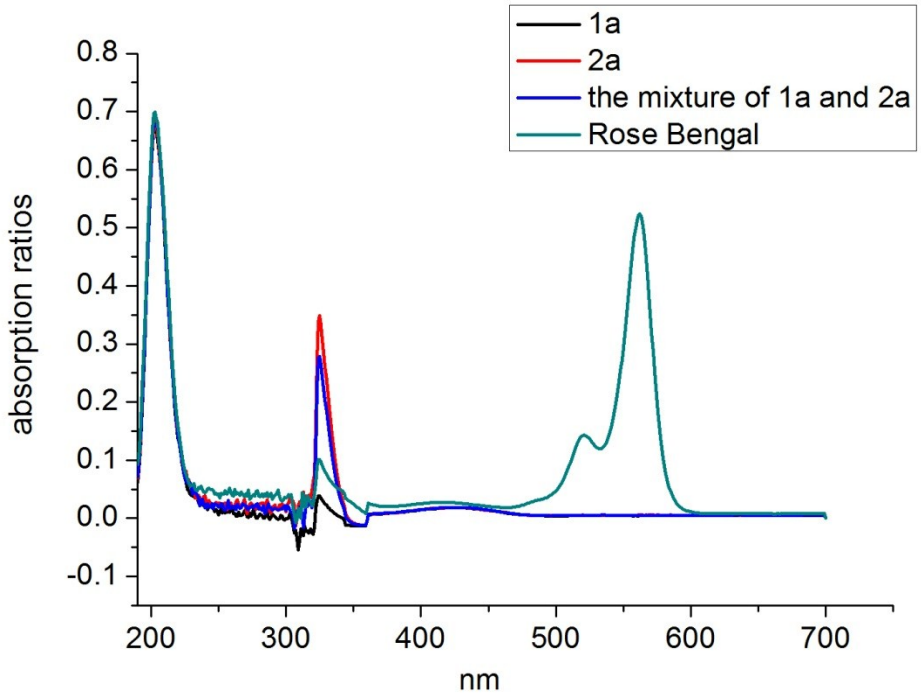


Figure S1. The UV-visible absorption spectra of Rose Bengal (c=6×10^{-6} mol/L), **1a** (c=2*10^{-5} mol/L), **2a** (c=4*10^{-5} mol/L), the mixture of **1a**(c=2*10^{-5} mol/L) and **2a**(c=4*10^{-5} mol/L) recorded in MeCN.

6. Emission Quenching of Rose Bengal

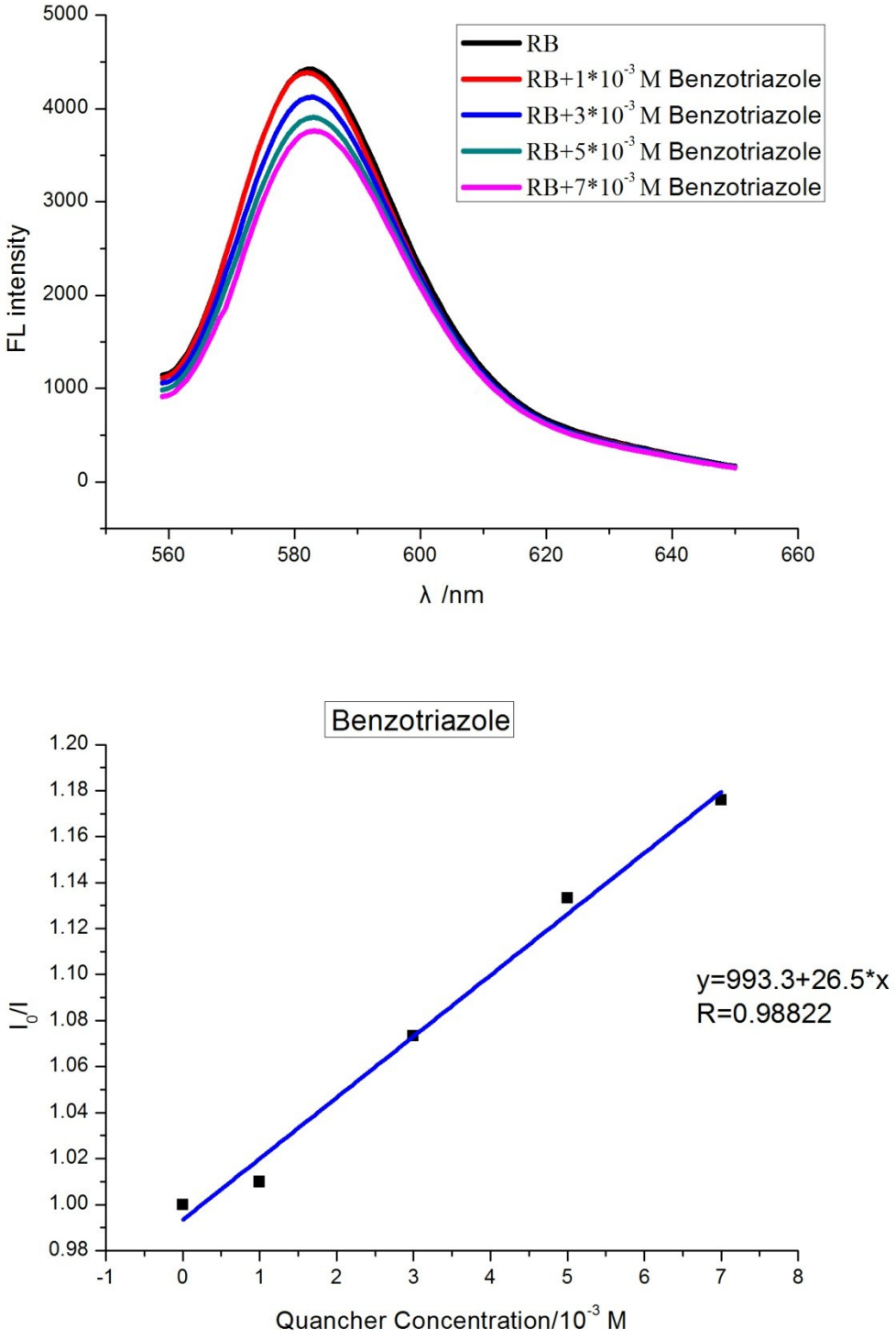


Figure S2. Fluorescence titration of $6*10^{-3}$ mM Rose Bengal (MeCN) with increasing concentration of Benzotriazole **1a**.

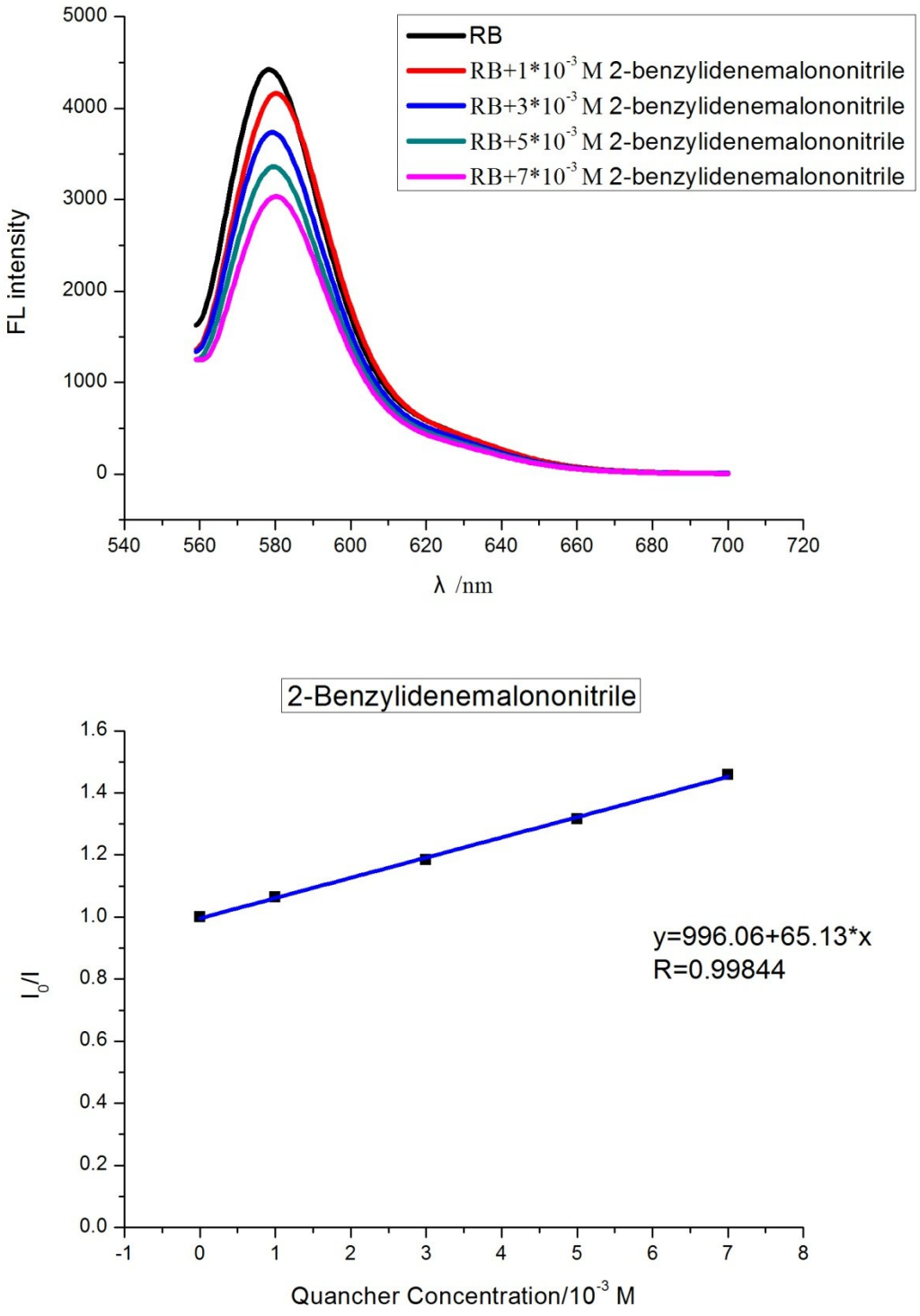


Figure S3. Fluorescence titration of $6*10^{-3}$ mM Rose Bengal (acetone) with increasing concentration of **2a**.

7. Cyclic voltammetry[3]

The electrochemical measurements were carried out by a computer-controlled electrochemical analyzer. Electrochemical measurements (cyclic voltammetry) were performed in a three-electrode cell (volume 10 mL; acetonitrile as solvent, nBu$_4$N$^+$ClO$_4^-$ 0.1 M as the supporting electrolyte, 2 mM concentration of the tested compound) with glassy carbon (diameter 3 mm) as the working electrode, Pt wire as the auxiliary electrode, and Ag/AgCl (3 M KCl) as the reference electrode. The scan speed was 100 mV·s^{-1}. The potential ranges investigated for oxidations were 0 to +2.0 V vs Ag/AgCl (3 M KCl) for **1a** and **2a**.

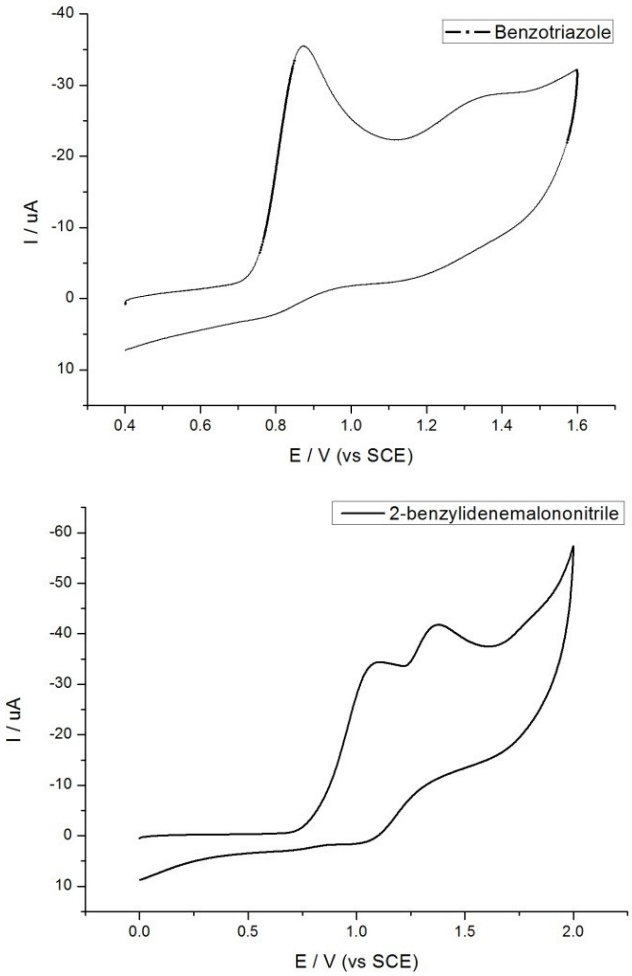
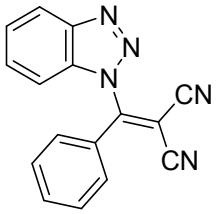


Figure S4. Cyclic voltammetry (CV) of benzotriazole and 2-benzylidenemalononitrile.

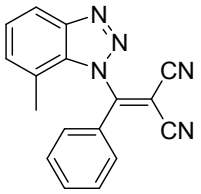
8. Characterization data of the products



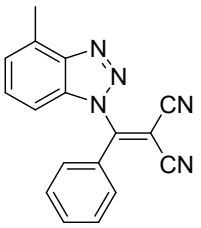
3aa

2-((1H-benzo[d][1,2,3]triazol-1-yl)(phenyl)methylene)malononitrile (**3aa**)

White solid, m.p. 149-151 ^{o}C, ^{1}H NMR (600 MHz, d-DMSO) δ 8.32-8.29 (m, 1H), 7.86-7.86 (m, 1H), 7.81-7.75 (m, 2H), 7.66-7.73 (m, 2H), 7.58-7.52 (m, 2H), 6.47-6.56 (m, 1H). ^{13}C NMR (151 MHz, d-DMSO) δ 160.1, 146.6, 135.0, 132.5, 131.1, 130.7, 130.1, 129.2, 126.8, 121.2, 113.8, 113.1, 76.9. HRMS(ESI) m/z: calcd for $C_{16}H_9N_5$ $[M+Na]^+$ 294.0750, found 294.0752.



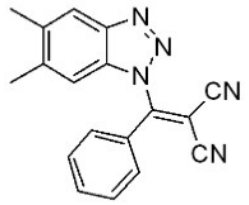
3ba



3ba'

2-((7-methyl-1H-benzo[d][1,2,3]triazol-1-yl)(phenyl)methylene)malononitrile (**3ba**) and *2-((4-methyl-1H-benzo[d][1,2,3]triazol-1-yl)(phenyl)methylene)malononitrile* (**3ba'**)

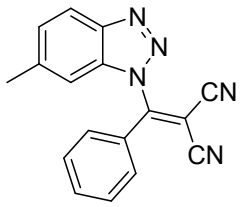
Isomer (1.5:1 based on NMR), white solid, m.p. 187-189 ^{o}C, ^{1}H NMR (600 MHz, d-DMSO) δ 8.17 (m, 1H), 8.07 (m, 0.68H), 7.87-7.81 (m, 2.08H), 7.79-7.75 (m, 3.82H), 7.71-7.66 (m, 4.04H), 7.47-7.32 (m, 3.28H), 6.40-6.37 (m, 1H), 6.36-6.34 (m, 1H), 2.46 (s, 2.07H), 2.78 (s, 3.04H). ^{13}C NMR (151 MHz, d-DMSO) δ = 160.1, 160.1, 147.2, 146.4, 145.2, 141.3, 135.0, 132.9, 132.5, 132.4, 131.9, 131.1, 130.6, 130.1, 129.3, 129.1, 128.7, 126.7, 120.7, 120.1, 113.9, 113.2, 113.1, 113.1, 112.6, 112.3, 110.3, 76.8, 22.0, 16.7. HRMS(ESI) m/z: calcd for $C_{17}H_{11}N_5$ $[M+Na]^+$ 286.1087, found 286.1088.



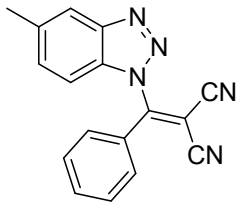
3ca

2-((5,6-dimethyl-1H-benzo[d][1,2,3]triazol-1-yl)(phenyl)methylene)malononitrile (**3ca**)

White solid, m.p. 115-117 °C, ^{1}H NMR (600 MHz, d-DMSO) δ 8.05 (s, 1H), 7.87-7.81 (m, 1H), 7.77-7.73 (m, 2H), 7.72-7.66 (d, *J* = 7.6 Hz, 2H), 6.31 (s, 1H), 2.36 (s, 3H), 2.18 (s, 3H). ^{13}C NMR (151 MHz, d-DMSO) δ 160.1, 145.6, 141.0, 136.7, 134.9, 131.4, 131.0, 130.1, 129.3, 120.1, 113.9, 113.1, 112.5, 76.3, 21.0, 20.1. HRMS(ESI) m/z: calcd for $C_{18}H_{13}N_5$ $[M+Na]^+$ 322.1063, found 322.1065.



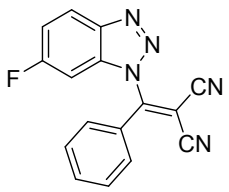
3da



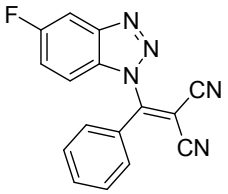
3da'

2-((6-methyl-1H-benzo[d][1,2,3]triazol-1-yl)(phenyl)methylene)malononitrile (**3da**) and *2-((5-methyl-1H-benzo[d][1,2,3]triazol-1-yl)(phenyl)methylene)malononitrile* (**3da'**)

Isomer (1.5:1 based on NMR), white solid, m.p. 154-156 °C, ^{1}H NMR (600 MHz, d-DMSO) δ 8.19-8.15 (m, 1H), 8.09-8.06 (s, 0.64H), 7.87-7.82 (m, 1.67H), 7.79-7.74 (m, 3.22H), 7.72-7.66 (m, 3.42H), 7.43-7.36 (m, 2.09H), 6.40-6.37 (m, 0.68H), 6.36-6.34 (m, 0.99H), 2.46 (s, 1.82H), 2.31 (s, 3H). ^{13}C NMR (151 MHz, d-DMSO) δ = 160.1, 160.0, 147.2, 145.2, 141.3, 136.9, 135.0, 135.0, 132.9, 132.4, 131.1, 130.9, 130.1, 129.3, 129.2, 128.7, 128.2, 127.7, 120.7, 120.1, 113.9, 113.9, 113.2, 113.1, 112.6, 112.3, 76.8, 76.4, 22.0, 21.2. HRMS(ESI) m/z: calcd for $C_{17}H_{11}N_5$ $[M+Na]^+$ 286.1087, found 286.1088.



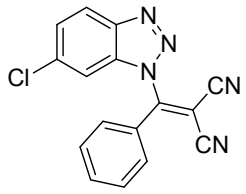
3ea



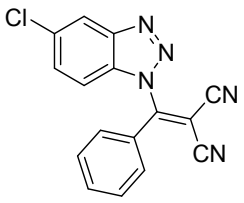
3ea'

2-((6-fluoro-1H-benzo[d][1,2,3]triazol-1-yl)(phenyl)methylene)malononitrile (**3ea**) and *2-((5-fluoro-1H-benzo[d][1,2,3]triazol-1-yl)(phenyl)methylene)malononitrile* (**3ea'**)

Isomer (1.5:1 based on NMR), pale yellow solid, m.p. >200 °C, ^{1}H NMR (600 MHz, d-DMSO) δ 8.44-8.35 (m, 1H), 8.26-8.19 (m, 0.63H), 7.88-7.82 (m, 1.62H), 7.81-7.75 (m, 3.17H), 7.74-7.66 (m, 4H), 7.55-7.46 (m, 1.68H), 6.63-6.57 (m, 0.66H), 6.48-6.41 (m, 1H). ^{13}C NMR (151 MHz, d-DMSO) δ = 163.8, 162.1, 159.8, 159.8, 143.4, 135.2, 131.2, 130.1, 129.1, 129.0, 128.2, 127.7, 123.4, 123.3, 120.1, 119.9, 116.4, 116.2, 114.6, 114.5, 113.7, 113.6, 112.9, 112.9, 106.4, 106.3, 99.8, 99.6, 77.7, 77.5. HRMS(ESI) m/z: calcd for $C_{16}H_8FN_5$ $[M+Na]^+$ 312.0656, found 312.0655.



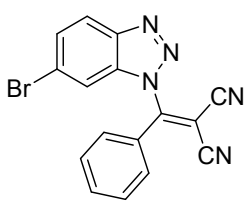
3fa



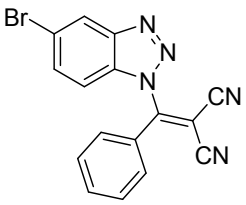
3fa'

2-((6-chloro-1H-benzo[d][1,2,3]triazol-1-yl)(phenyl)methylene)malononitrile (**3fa**) and *2-((5-chloro-1H-benzo[d][1,2,3]triazol-1-yl)(phenyl)methylene)malononitrile* (**3fa'**)

Isomer (1:1 based on NMR), pale yellow solid, m.p. 145-146 °C, ^{1}H NMR (600 MHz, d-DMSO) δ 8.52-8.48 (m, 0.93H), 8.38-8.34 (d, *J* = 8.8 Hz, 1.14H), 7.88-7.82 (m, 2H), 7.80-7.75 (m, 4H), 7.72-7.68 (m, 4H), 7.66-7.62 (m, 2H), 6.74-6.72 (m, 1H), 6.61-6.57(m, 1H). ^{13}C NMR (151 MHz, d-DMSO) δ = 159.8, 159.7, 147.3, 145.3, 135.5, 135.2, 133.3, 131.3, 131.2, 131.2, 131.0, 130.1, 130.1, 129.2, 129.0, 128.2, 127.7, 127.5, 122.7, 120.6, 114.5, 113.7, 113.6, 113.0, 112.9, 112.8, 77.9, 77.7. HRMS(ESI) m/z: calcd for $C_{16}H_8ClN_5$ $[M+Na]^+$ 328.0360, found 328.0355.



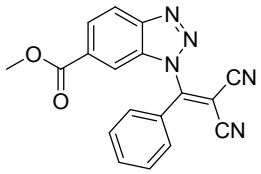
3ga



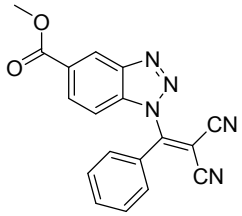
3ga'

2-((6-bromo-1H-benzo[d][1,2,3]triazol-1-yl)(phenyl)methylene)malononitrile (**3ga**) and *2-((5-bromo-1H-benzo[d][1,2,3]triazol-1-yl)(phenyl)methylene)malononitrile* (**3ga'**)

Isomer (1:1 based on NMR), white solid, m.p. 129-132 °C, ^{1}H NMR (600 MHz, d-DMSO) δ 8.67-8.61 (m, 1H), 8.31-8.27 (m, 1H), 7.88-7.82 (m, 2H), 7.74-7.65 (m, 4H), 7.60-7.55 (m, 1H), 7.41-7.36 (m, 1H), 6.90-6.86 (m, 1H), 6.57-6.50 (m, 1H). ^{13}C NMR (151 MHz, d-DMSO) δ = 159.8, 159.7, 147.8, 145.5, 135.2, 135.2, 133.6, 133.6, 131.8, 131. 2, 131.2, 130.1, 130.1, 130.1, 129.2, 129.0, 124.1, 123.7, 122.8, 119.1, 116.0, 114.8, 113.7, 113.6, 112.9, 112.9, 77.9, 77.6. HRMS(ESI) m/z: calcd for $C_{16}H_8BrN_5$ $[M+Na]^+$ 371.9855, found 371.9852.



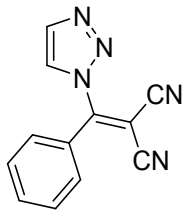
3ha



3ha'

methyl 1-(2,2-dicyano-1-phenylvinyl)-1H-benzo[d][1,2,3]triazole-6-carboxylate (**3ha**) and *methyl 1-(2,2-dicyano-1-phenylvinyl)-1H-benzo[d][1,2,3]triazole-5-carboxylate* (**3ha'**)

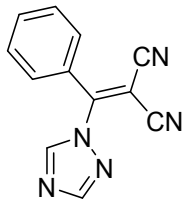
Isomer (2:1 based on NMR), pale yellow solid, m.p. 170-172 °C, ^{1}H NMR (600 MHz, d-DMSO) δ 8.85-8.81 (m, 1H), 8.45-8.40 (m, 0.46H), 8.12-8.08 (m, 1.45H), 7.89-7.78 (m, 5H), 7.73-7.65 (m, 3.50H), 7.16-7.14 (m, 0.52H), 6.74-6.70 (m, 1H), 3.91 (s, 3H), 3.82 (s, 1.50H). ^{13}C NMR (151 MHz, d-DMSO) δ = 166.5, 165.6, 165.5, 159.8, 159.7, 148.6, 146.5, 135.3, 135.1, 135.0, 132.5, 131.2, 130.7, 130.2, 129.1, 129.0, 128.4, 128.2, 127.7, 126.8, 126.6, 122.9, 121.6, 114.9, 113.6, 113.6, 112.9, 78.1, 77.8, 53.3, 53.1, 52.8. HRMS(ESI) m/z: calcd for $C_{18}H_{11}N_5O_2$ $[M+Na]^+$ 352.0805, found 352.0809.



3ia

2-((4,5-dihydro-1H-1,2,3-triazol-1-yl)(phenyl)methylene)malononitrile (**3ia**)

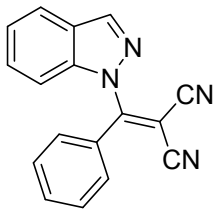
White solid, m.p. 176-178 °C, ^{1}H NMR (600 MHz, d-DMSO) δ 8.50 (s, 2H), 7.76-7.68 (m, 3H), 7.65-7.58 (m, 2H). ^{13}C NMR (151 MHz, d-DMSO) δ 161.0, 141.5, 133.4, 131.3, 129.9, 129.1, 114.1, 113.1, 74.1. HRMS(ESI) m/z: calcd for $C_{12}H_7N_5$ $[M+H]^+$ 222.0774, found 222.0775.



3ja

2-(phenyl(1H-1,2,4-triazol-1-yl)methylene)malononitrile (**3ja**)

White solid, m.p. >200 °C, ^{1}H NMR (600 MHz, d-DMSO) δ 8.73 (s, 1H), 8.60 (s, 1H), 7.79-7.75 (m, 3H), 7.69-7.64 (m, 2H). ^{13}C NMR (151 MHz, d-DMSO) δ 159.9, 154.9, 148.9, 134.4, 131.2, 129.8, 129.0, 113.8, 112.7, 75.6. HRMS(ESI) m/z: calcd for $C_{12}H_7N_5$ $[M+Na]^+$ 244.0594, found 244.0591.

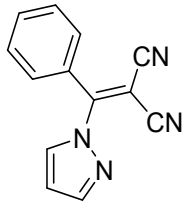


3ka

2-((1H-indazol-1-yl)(phenyl)methylene)malononitrile (**3ka**)

Pale yellow solid, m.p. 150-152 °C, ^{1}H NMR (600 MHz, DMSO) δ 8.86 (s, 1H), 7.98-7.92 (m, 1H), 7.86-7.81 (m, 1H), 7.79-7.75 (m, 2H), 7.72-7.67 (m, 2H), 7.39-7.34 (m, 1H), 7.33-7.28 (m, 1H), 6.02-5.95 (m, 1H). ^{13}C NMR (151 MHz, DMSO) δ 162.6, 143.3, 140.1, 134.2, 130.8, 130.1,

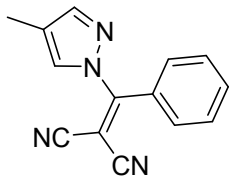
129.5, 127.6, 125.3, 123.1, 115.1, 114.2, 113.7, 70.9. HRMS(ESI) m/z: calcd for $C_{17}H_{10}N_4$ $[M+Na]^+$ 293.0798, found 293.0802.



3la

2-(phenyl(1H-pyrazol-1-yl)methylene)malononitrile (**3la**)

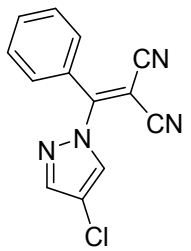
White solid, m.p. 163-165 °C, ^{1}H NMR (600 MHz, d-DMSO) δ 8.22-8.18 (d, *J* = 1.5 Hz, 1H), 7.78-7.73 (m, 1H), 7.72-7.69 (m, 2H), 7.67-7.62 (m, 3H), 6.76-6.71 (m, 1H). ^{13}C NMR (151 MHz, d-DMSO) δ 162.1, 146.9, 134.8, 133.7, 130.9, 130.3, 129.6, 114.7, 113.7, 112.2, 71.7. HRMS(ESI) m/z: calcd for $C_{13}H_{10}N_4$ $[M+Na]^+$ 245.0798, found 245.0796.



3ma

2-((4-methyl-1H-pyrazol-1-yl)(phenyl)methylene)malononitrile (**3ma**)

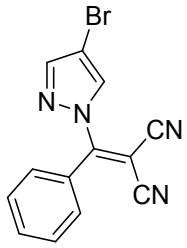
White solid, m.p. 138-140 °C, ^{1}H NMR (600 MHz, d-DMSO) δ 8.06 (s, 1H), 7.77-7.72 (m, 1H), 7.72-7.67 (m, 2H), 7.66-7.62 (m, 2H), 7.38 (s, 1H), 2.03 (s, 3H). ^{13}C NMR (151 MHz, d-DMSO) δ 161.8, 148.5, 133.5, 132.0, 130.7, 130.4, 129.6, 122.7, 114.9, 113.9, 70.0, 8.9. HRMS(ESI) m/z: calcd for $C_{14}H_{10}N_4$ $[M+Na]^+$ 235.0978, found 235.0980.



3na

2-((4-chloro-1H-pyrazol-1-yl)(phenyl)methylene)malononitrile (**3na**)

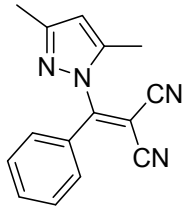
White solid, m.p. >200 °C, ^{1}H NMR (600 MHz, d-DMSO) δ 8.34 (s, 1H), 8.02 (s, 1H), 7.78-7.74 (m, 1H), 7.73-7.70 (m, 2H), 7.67-7.62 (m, 2H). ^{13}C NMR (151 MHz, d-DMSO) δ 161.8, 144.9, 134.0, 132.1, 131.1, 129.75, 129.70, 115.7, 114.4, 113.3, 72.9. HRMS(ESI) m/z: calcd for $C_{13}H_7ClN_4$ $[M+H]^+$ 255.0432, found 255.0435.



3oa

2-((4-bromo-1H-pyrazol-1-yl)(phenyl)methylene)malononitrile (**3oa**)

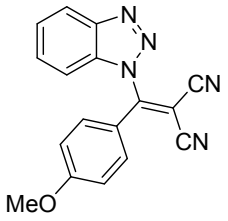
White solid, m.p. >200 °C, ^{1}H NMR (600 MHz, d-DMSO) δ 8.35 (s, 1H), 8.01 (s, 1H), 7.78-7.70 (m, 3H), 7.67-7.62 (m, 2H). ^{13}C NMR (151 MHz, d-DMSO) δ 161.6, 146.8, 134.2, 134.0, 131.1, 129.8, 129.7, 114.4, 113.3, 100.2, 72.8. HRMS(ESI) m/z: calcd for $C_{13}H_7BrN_5$ $[M+H]^+$ 298.9927, found 298.9932.



3pa

2-((3,4-dimethyl-1H-pyrazol-1-yl)(phenyl)methylene)malononitrile (**3pa**)

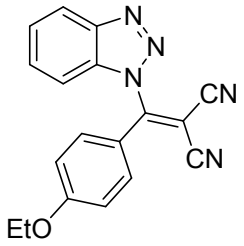
White solid, m.p. 155-157 °C, ^{1}H NMR (600 MHz, d-DMSO) δ 7.75 (dt, J = 5.2, 4.2 Hz, 1H), 7.67-7.57 (m, 4H), 6.37 (s, 1H), 2.25 (s, 3H), 1.59 (s, 3H). ^{13}C NMR (151 MHz, d-DMSO) δ 163.4, 153.9, 144.4, 134.3, 131.0, 130.7, 129.9, 114.7, 113.8, 113.8, 74.8, 13.8, 13.0. HRMS(ESI) m/z: calcd for $C_{15}H_{12}N_4$ $[M+Na]^+$ 271.0954, found 271.0956.



3ab

2-((1H-benzo[d][1,2,3]triazol-1-yl)(4-methoxyphenyl)methylene)malononitrile (**3ab**)

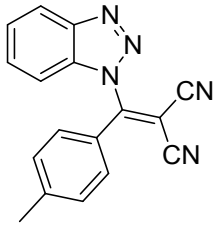
White solid, m.p. 120-122 °C, ^{1}H NMR (600 MHz, d-DMSO) δ 8.33-8.27 (m, 1H), 7.77-7.67 (m, 2H), 7.62-7.55 (m, 2H), 7.26-7.18 (m, 2H), 6.80-6.74 (m, 1H), 3.92 (s, 3H). ^{13}C NMR (151 MHz, d-DMSO) δ 165.1, 159.8, 146.6, 133.7, 132.8, 130.6, 126.7, 121.1, 120.9, 115.7, 114.3, 113.4, 113.1, 74.9, 56.5. HRMS(ESI) m/z: calcd for $C_{17}H_{11}N_5O$ $[M+Na]^+$ 324.0856, found 324.0857.



3ac

2-((1H-benzo[d][1,2,3]triazol-1-yl)(4-ethoxyphenyl)methylene)malononitrile (**3ac**)

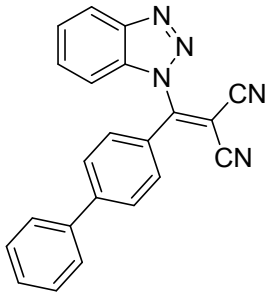
White solid, m.p. 147-149 °C, ^{1}H NMR (600 MHz, d-DMSO) δ 8.33-8.27 (m, 1H), 7.75-7.67 (m, 2H), 7.62-7.55 (m, 2H), 7.23-7.16 (m, 2H), 6.79-6.75 (m, 1H), 4.20 (q, *J* = 7.0 Hz, 2H), 1.38 (t, *J* = 7.0 Hz, 3H). ^{13}C NMR (151 MHz, d-DMSO) δ 164.5, 159.8, 146.6, 133.8, 132.7, 130.6, 126.7, 121.1, 120.7, 116.1, 114.3, 113.4, 113.1, 74.8, 64.7, 14.9. HRMS(ESI) m/z: calcd for $C_{18}H_{13}N_5O$ $[M+Na]^+$ 338.1012, found 338.1014.



3ad

2-((1H-benzo[d][1,2,3]triazol-1-yl)(p-tolyl)methylene)malononitrile (**3ad**)

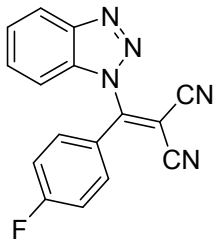
White solid, m.p. >200 °C, ^{1}H NMR (600 MHz, d-DMSO) δ 8.35-8.26 (m, 1H), 7.68-7.62 (m, 2H), 7.60-7.54 (m, 2H), 7.50-7.47 (m, 2H), 6.67-6.58 (m, 1H), 2.47 (s, 3H). ^{13}C NMR (151 MHz, d-DMSO) δ 160.2, 146.6, 146.3, 132.6, 131.2, 130.7, 130.6, 126.8, 126.3, 121.2, 114.0, 113.2, 113.1, 76.3, 21.9. HRMS(ESI) m/z: calcd for $C_{17}H_{11}N_5$ $[M+Na]^+$ 308.0907, found 308.0904.



3ae

2-([1,1'-biphenyl]-4-yl(1H-benzo[d][1,2,3]triazol-1-yl)methylene)malononitrile (**3ae**)

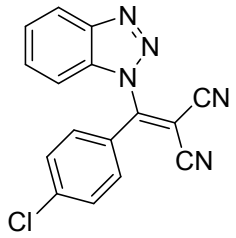
Pale yellow solid, m.p. >200 °C, ^{1}H NMR (600 MHz, d-DMSO) δ 8.35-8.29 (m, 1H), 8.05-7.99 (m, 2H), 7.89-7.82 (m, 4H), 7.61-7.52 (m, 4H), 7.50-7.46 (m, 1H), 6.78-6.73 (m, 1H). ^{13}C NMR (151 MHz, d-DMSO) δ 159.8, 146.6, 146.4, 138.5, 132.6, 132.0, 130.7, 129.7, 129.5, 128.0, 128.0, 127.7, 127.6, 126.8, 121.2, 114.0, 113.2, 76.8. HRMS(ESI) m/z: calcd for $C_{22}H_{13}N_5$ $[M+Na]^+$ 370.1063, found 370.1065.



3af

2-((1H-benzo[d][1,2,3]triazol-1-yl)(4-fluorophenyl)methylene)malononitrile (**3af**)

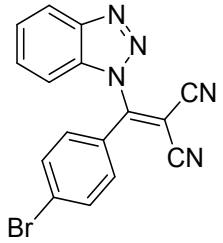
White solid, m.p. 137-139 °C, ^{1}H NMR (600 MHz, d-DMSO) δ 8.33-8.28(m, 1H), 7.95-7.86 (m, 2H), 7.61-7.52 (m, 4H), 6.69-6.56 (m, 1H). ^{13}C NMR (151 MHz, d-DMSO) δ 166.9, 165.2, 159.0, 146.6, 134.4, 134.3, 132.4, 130.8, 126.9, 121.2, 117.7, 117.5, 113.8, 113.2, 113.0, 76.9. HRMS(ESI) m/z: calcd for $C_{16}H_8FN_5$ $[M+Na]^+$ 312.0656, found 312.0659.



3ag

2-((1H-benzo[d][1,2,3]triazol-1-yl)(4-chlorophenyl)methylene)malononitrile (**3ag**)

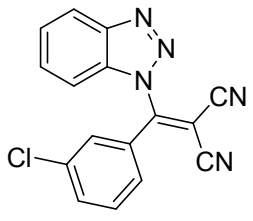
White solid, m.p. >200 °C, ^{1}H NMR (600 MHz, d-DMSO) δ 8.34-8.29 (d, *J* = 7.4 Hz, 1H), 7.87-7.76 (m, 4H), 7.63-7.56 (m, 2H), 6.68-6.64 (m, 1H). ^{13}C NMR (151 MHz, d-DMSO) δ 158.9, 146.6, 140.1, 133.0, 130.8, 130.4, 129.5, 128.2, 126.9, 121.2, 113.7, 113.2, 113.0, 77.3. HRMS(ESI) m/z: calcd for $C_{16}H_8ClN_5$ $[M+Na]^+$ 328.0360, found 328.0362.



3ah

2-((1H-benzo[d][1,2,3]triazol-1-yl)(4-bromophenyl)methylene)malononitrile (**3ah**)

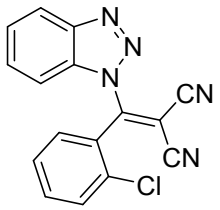
White solid, m.p. >200 °C, ^{1}H NMR (600 MHz, d-DMSO) δ 8.34-8.27 (m, 1H), 7.95-7.91 (m, 2H), 7.77-7.71 (m, 2H), 7.63-7.56 (m, 2H), 6.70-6.65 (m, 1H). ^{13}C NMR (151 MHz, d-DMSO) δ 159.0, 146.6, 133.3, 133.0, 132.4 130.8, 129.3, 8.3, 126.9, 121.2, 113.7, 113.2 113.0, 77.3. HRMS(ESI) m/z: calcd for $C_{16}H_8BrN_5$ $[M+H]^+$ 350.0036, found 350.0034.



3ai

2-((1H-benzo[d][1,2,3]triazol-1-yl)(3-chlorophenyl)methylene)malononitrile (**3ai**)

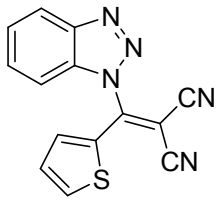
White solid, m.p. 154-156 °C, ^{1}H NMR (600 MHz, d-DMSO) δ 8.34-8.28 (m, 1H), 8.02-7.98 (m, 1H), 7.93-7.88 (m, 1H), 7.79-7.75 (m, 1H), 7.75-7.70 (m, 1H), 7.62-7.57 (m, 2H), 6.64-6.57 (m, 1H). ^{13}C NMR (151 MHz, d-DMSO) δ 158.4, 146.6, 134.7, 134.6, 132.3, 132.1, 131.1, 130.9, 130.6, 129.9, 127.0, 121.3, 113.6, 113.1, 112.9, 77.6. HRMS(ESI) m/z: calcd for $C_{16}H_8ClN_5$ $[M+Na]^+$ 328.0360, found 328.0357.



3aj

2-((1H-benzo[d][1,2,3]triazol-1-yl)(2-chlorophenyl)methylene)malononitrile (**3aj**)

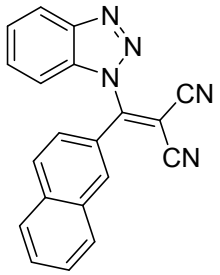
White solid, m.p. 125-127 °C, ^{1}H NMR (600 MHz, d-DMSO) δ 8.36-8.30 (m, 1H), 8.24-8.18 (m, 1H), 7.92-7.85 (m, 1H), 7.84-7.79 (m, 1H), 7.79-7.74 (m, 1H), 7.64-7.57 (m, 2H), 6.46-6.41 (m, 1H). ^{13}C NMR (151 MHz, d-DMSO) δ 156.9, 146.6, 136.1, 133.7, 133.0, 131.8, 131.6, 131.4, 129.3, 128.0, 127.3, 121.6, 113.0, 112.6, 112.2, 78.5. HRMS(ESI) m/z: calcd for $C_{16}H_8ClN_5$ $[M+Na]^+$ 328.0360, found 328.0365.



3ak

2-((1H-benzo[d][1,2,3]triazol-1-yl)(thiophen-2-yl)methylene)malononitrile (**3ak**)

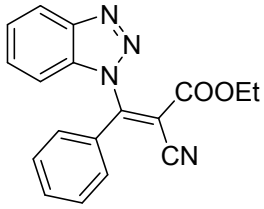
White solid, m.p. >200 °C, ^{1}H NMR (600 MHz, d-DMSO) δ 8.49-8.40 (m, 1H), 8.31 (d, J = 8.3 Hz, 1H), 7.91-7.86 (m, 1H), 7.74-7.69 (m, 1H), 7.64-7.59 (m, 1H), 7.44 (dd, J = 4.8, 4.1 Hz, 1H), 7.38 (d, J = 8.4 Hz, 1H). ^{13}C NMR (151 MHz, d-DMSO) δ 153.2, 146.0, 140.4, 139.1, 133.0, 131.6, 130.6, 130.4, 126.7, 121.0, 113.9, 112.70, 112.67, 76.2. HRMS(ESI) m/z: calcd for $C_{14}H_7N_5S$ $[M+Na]^+$ 300.0314, found 300.0323.



3al

2-((1H-benzo[d][1,2,3]triazol-1-yl)(naphthalen-2-yl)methylene)malononitrile (**3al**)

White solid, m.p. >200 °C, ^{1}H NMR (600 MHz, d-DMSO) δ 8.61-8.54 (m, 1H), 8.37-8.29 (m, 1H), 8.21-8.16 (m, 1H), 8.14-8.09 (m, 2H), 7.83-7.77 (m, 1H), 7.74-7.66 (m, 2H), 7.59-7.54 (m, 1H), 7.53-7.48 (m, 1H), 6.62-6.57(m, 1H). ^{13}C NMR (151 MHz, d-DMSO) δ 160.1, 146.7, 135.7, 133.3, 132.6, 132.5, 130.7, 130.4, 129.94, 129.92, 128.6, 128.3, 126.8, 126.4, 125.9, 121.2, 114.0, 113.18, 113.15, 77.0. HRMS(ESI) m/z: calcd for $C_{20}H_{11}N_5$ $[M+Na]^+$ 344.0907, found 344.0905.



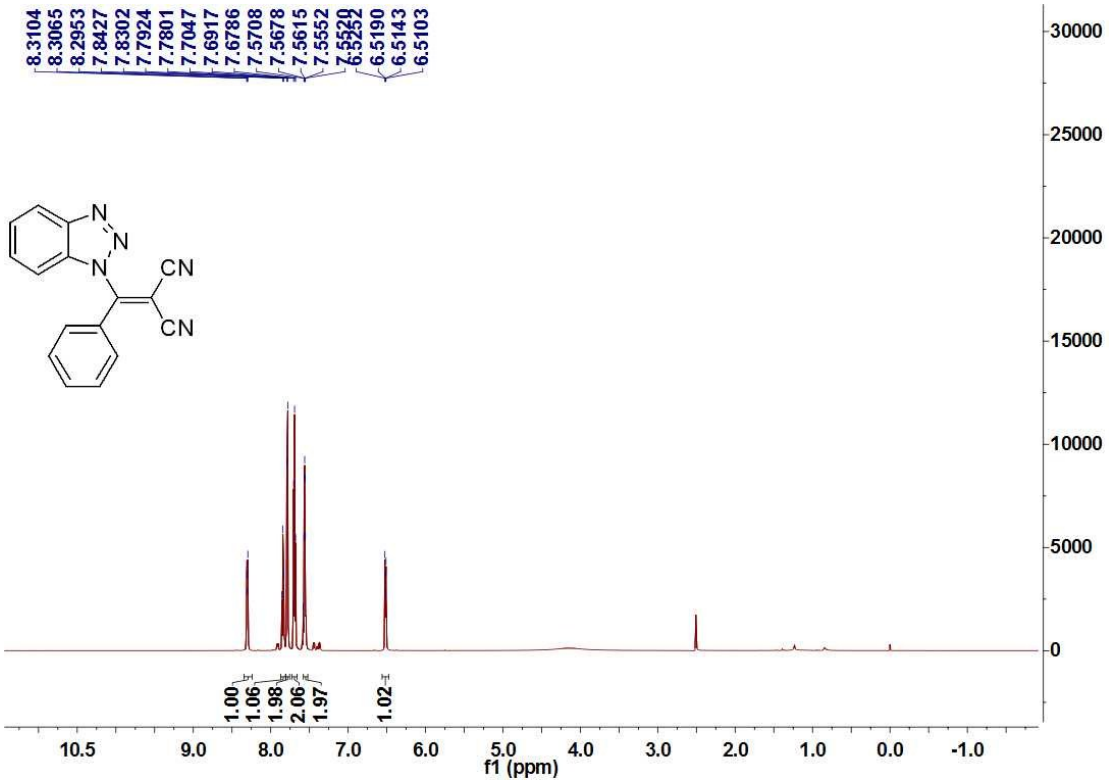
3am

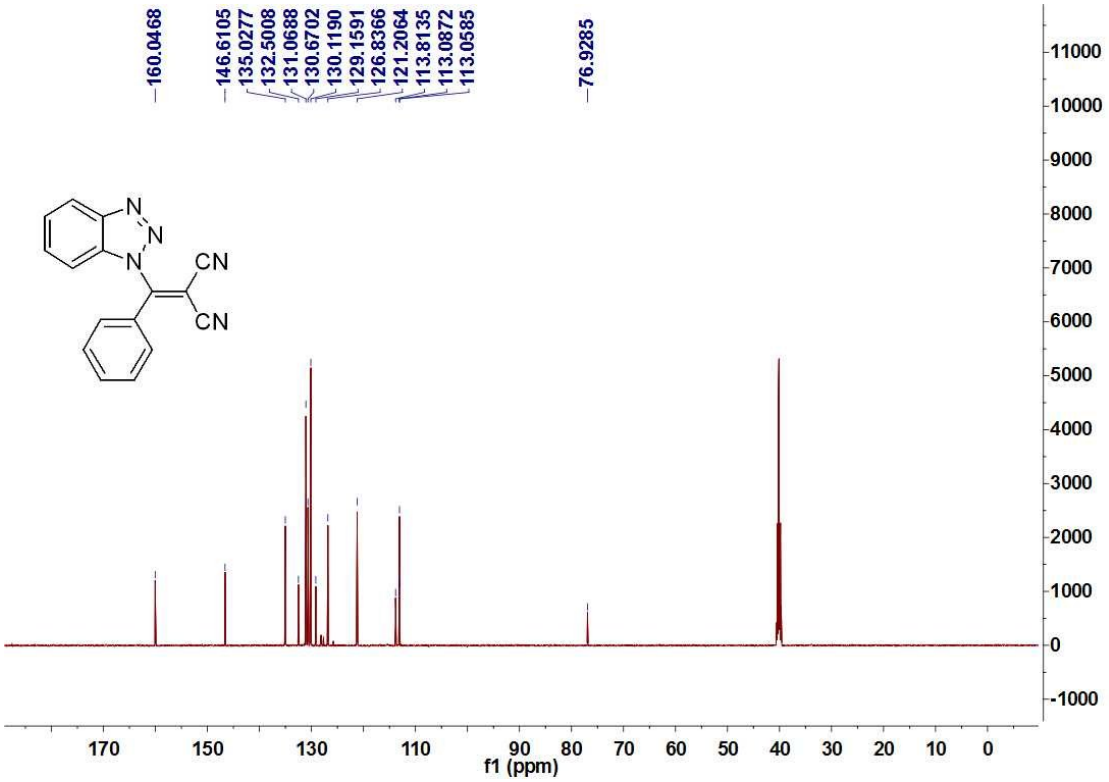
ethyl (Z)-3-(1H-benzo[d][1,2,3]triazol-1-yl)-2-cyano-3-phenylacrylate (**3am**)

White solid, m.p. >200 °C, ^{1}H NMR (600 MHz, d-DMSO) δ 8.29-8.21 (m, 1H), 7.79-7.74 (m, 1H), 7.73-7.66 (m, 2H), 7.66-7.60 (m, 2H), 7.57-7.50 (m, 2H), 6.85-6.81 (m, 1H), 4.06 (q, J = 7.1 Hz, 2H), 0.94 (t, J = 7.1 Hz, 3H). ^{13}C NMR (151 MHz, d-DMSO) δ 161.1, 154.3, 146.3, 134.5, 133.1, 131.0 , 130.9, 130.2, 130.0, 126.1, 120.8, 116.1, 111.7, 100.6, 62.9, 13.9. HRMS(ESI) m/z: calcd for $C_{18}H_{14}N_5O_2$ $[M+H]^+$ 319.1190, found 319.1198.

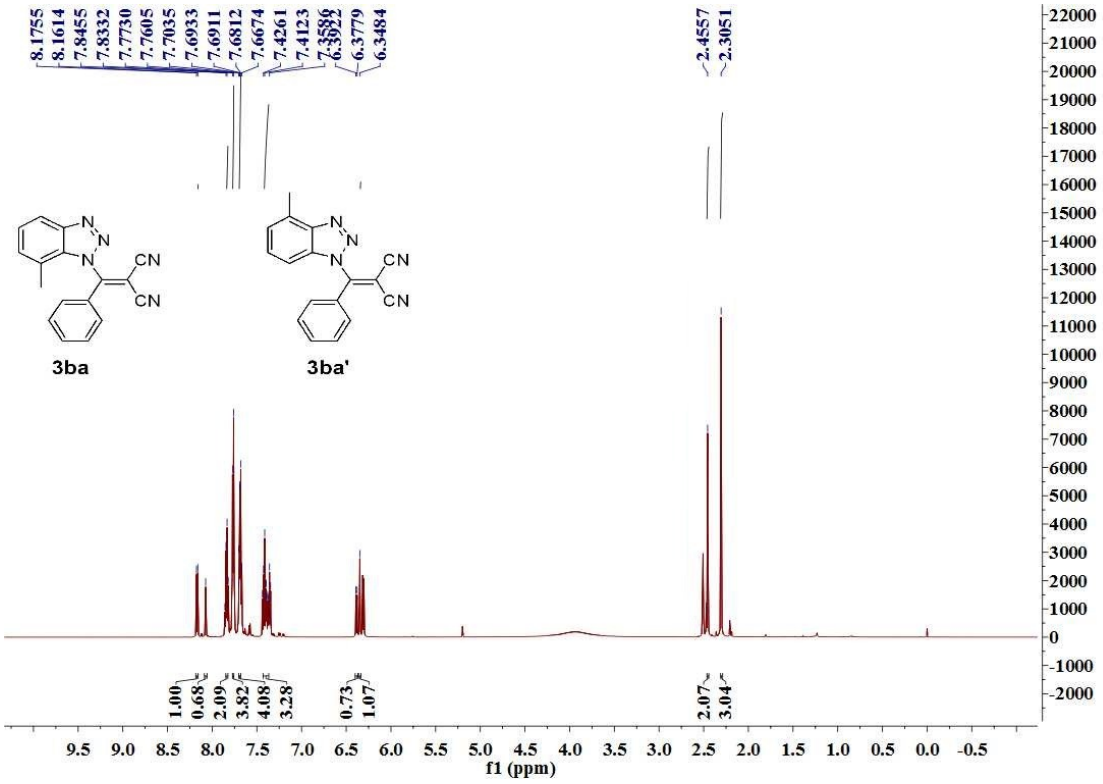
9. ^{1}H NMR and ^{13}C NMR spectra of products

3aa





3ba 3ba'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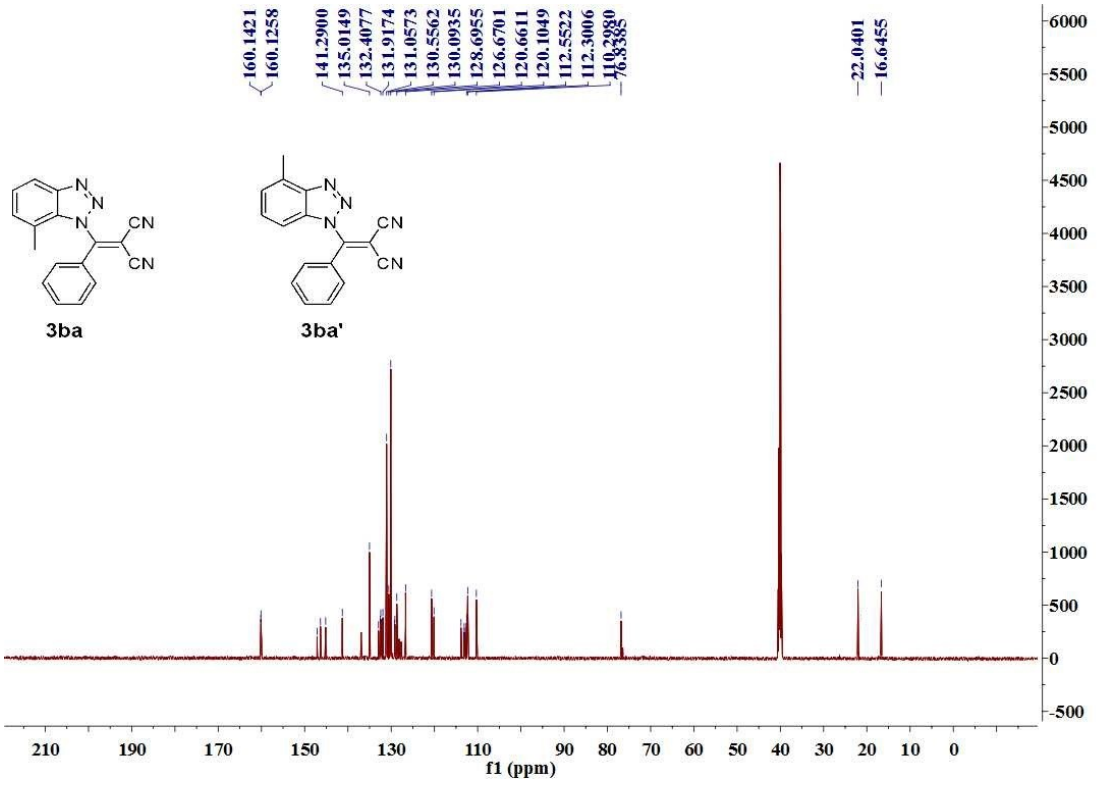
7.7035
7.6933
7.6911
7.6812
7.6674
7.4261
7.4123
6.3779
6.3484
2.4557
2.3051
3ba
3ba'
1.00
0.68
2.09
3.82
4.08
3.28
0.73
1.07
2.07
3.04
f1 (ppm)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141.2900
135.0149
132.4077
131.9174
131.0573
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128.6955
126.6701
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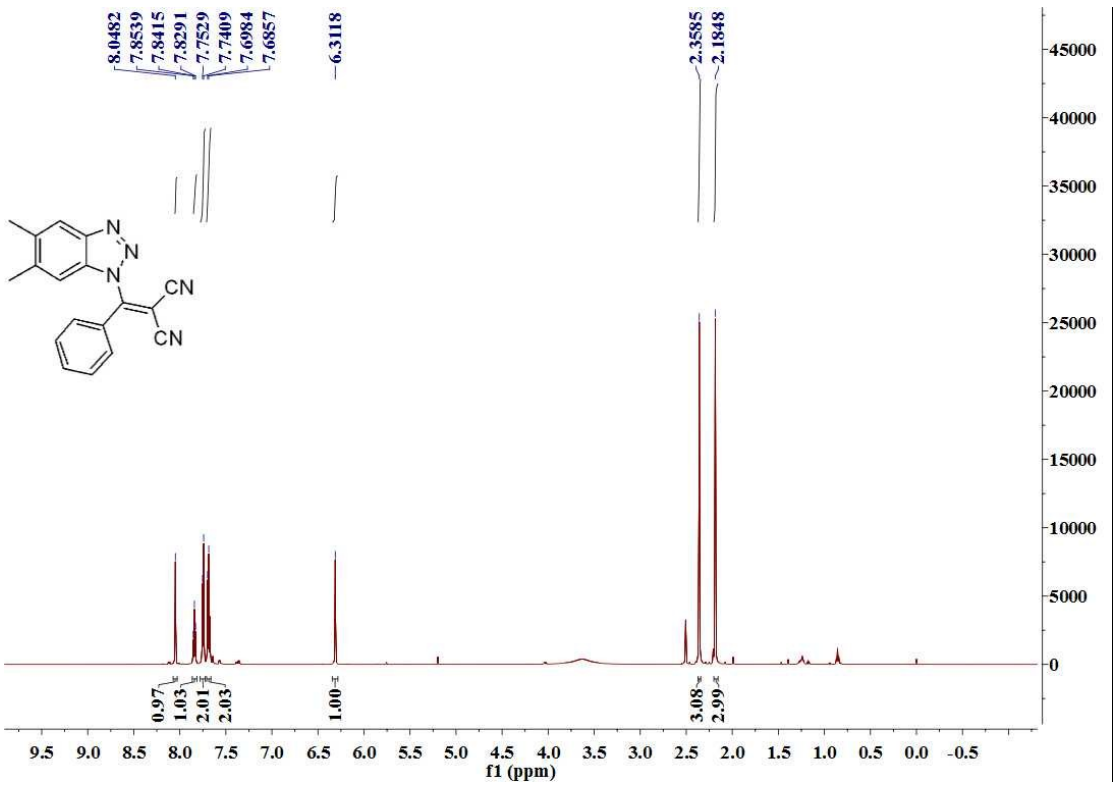
112.5522
112.3006
22.0401
16.6455
3ba
3ba'
f1 (ppm)

3ca

.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7.8415
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7.7529
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7.6984
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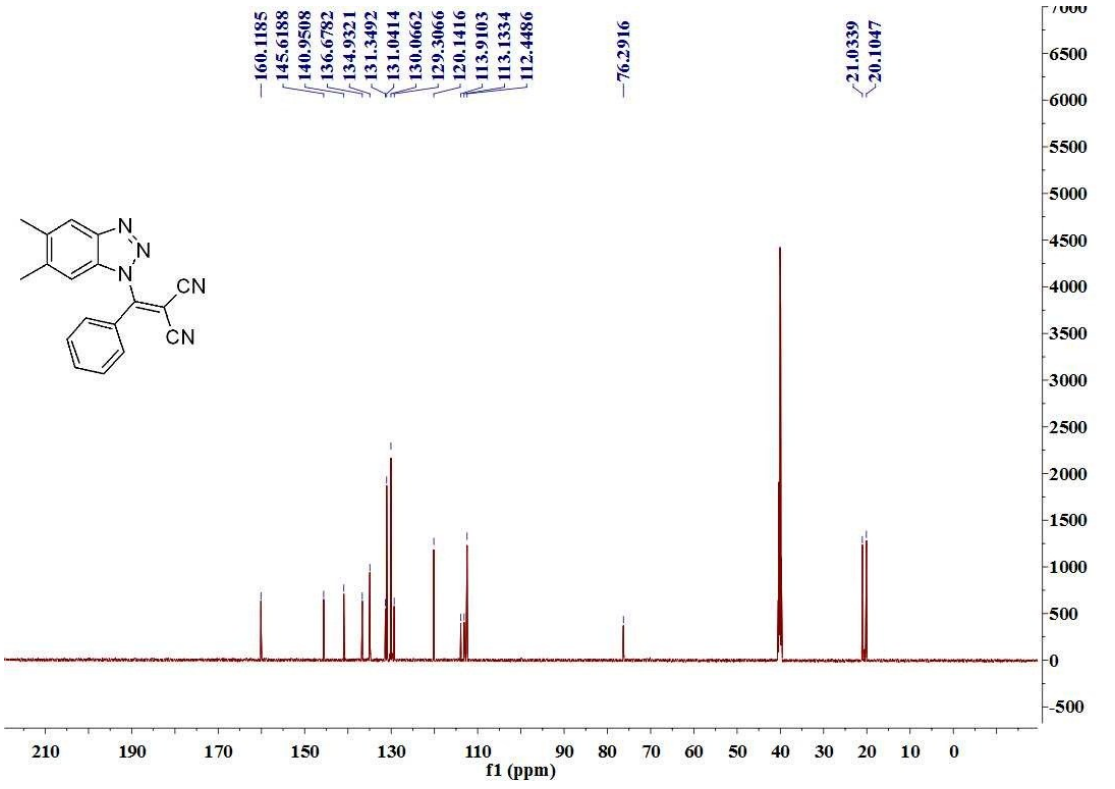
2.1848
0.97
1.03
2.01
2.03
1.00
3.08
2.99
f1 (ppm)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145.6188
140.9508
136.6782
134.9321
131.3492
131.0414
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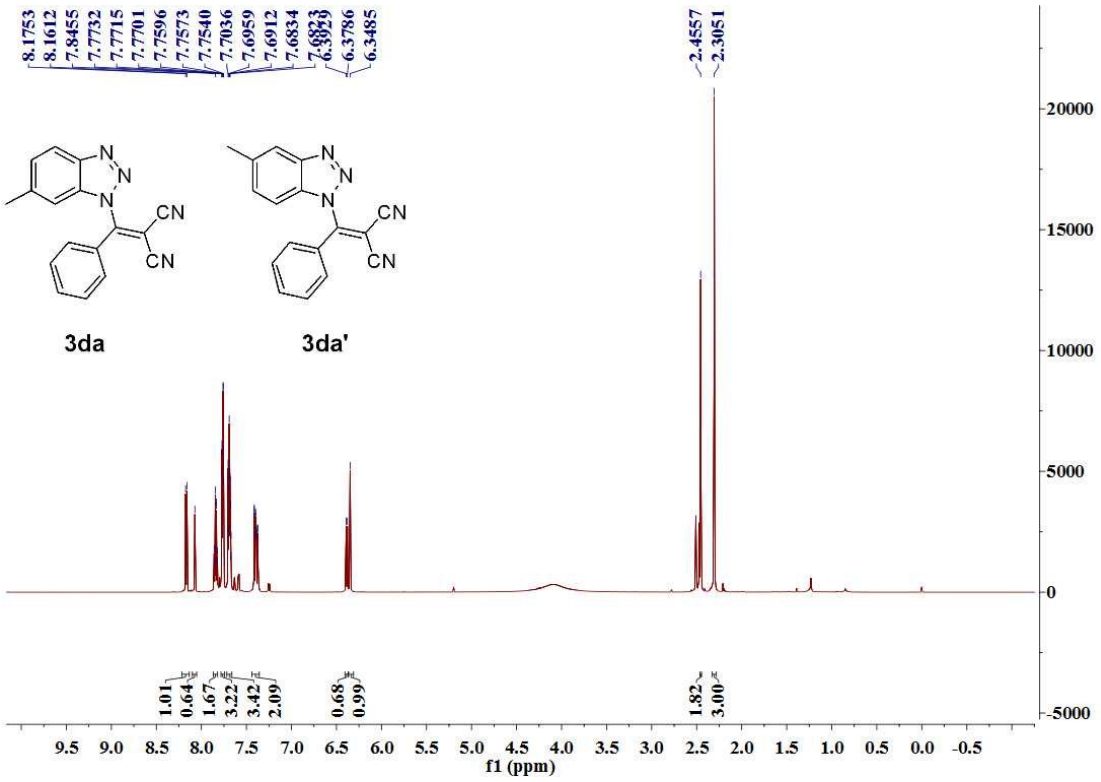
113.1334
112.4486
76.2916
21.0339
20.1047
f1 (ppm)

3da 3da'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7.8455
7.7732
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7.7596
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7.7540
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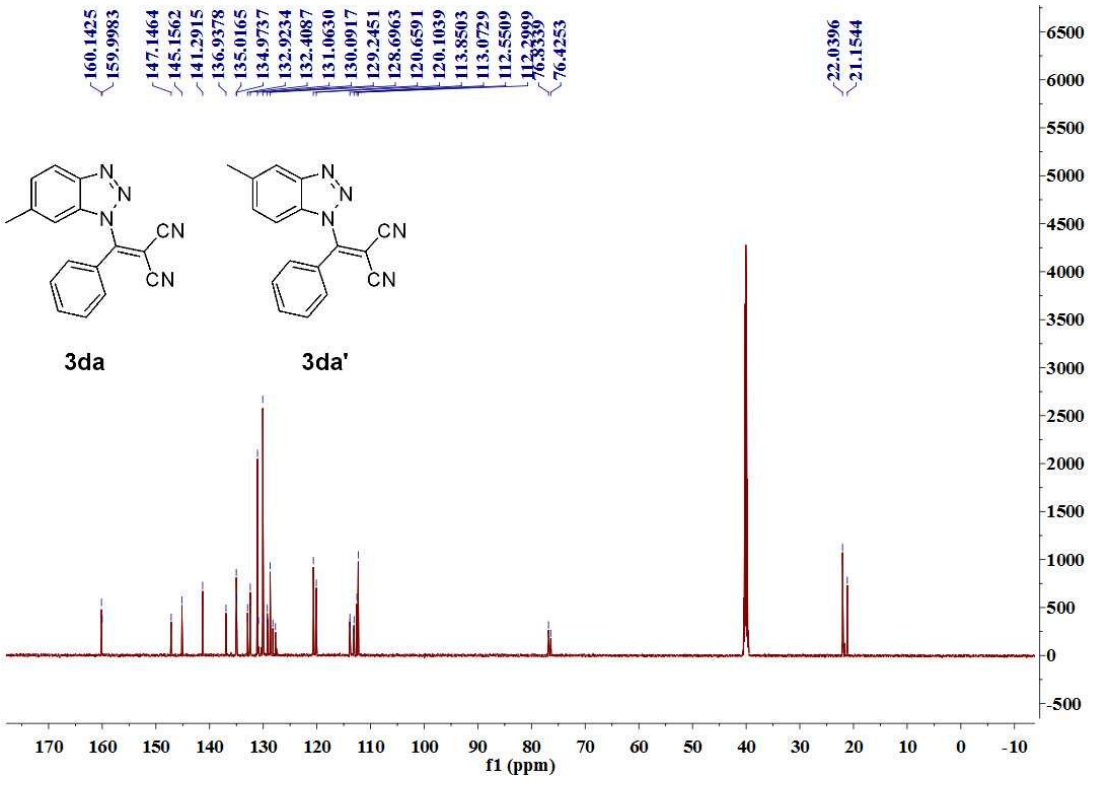
7.6959
7.6912
7.6834
6.3786
6.3485
2.4557
2.3051
3da
3da'
1.01
0.64
1.67
3.22
3.42
2.09
0.68
0.99
1.82
3.00
f1 (ppm)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130.0917
129.2451
128.6963
120.6591
120.1039
113.8503
113.0729
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76.3330
76.4253
22.0396
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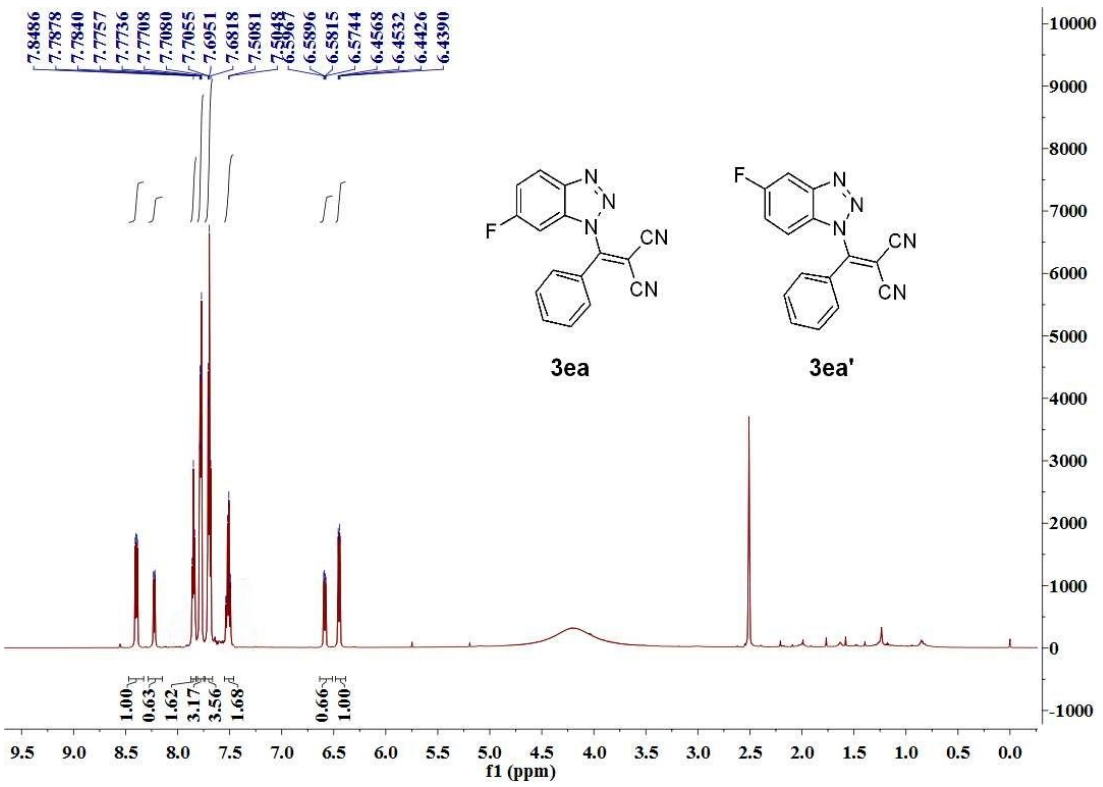
3da'
f1 (ppm)

3ea 3ea'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7.6818
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7.5048
6.5967
6.5896
6.5815
6.5744
6.4568
6.4532
6.4426
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1.62
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3.56
1.68
0.66
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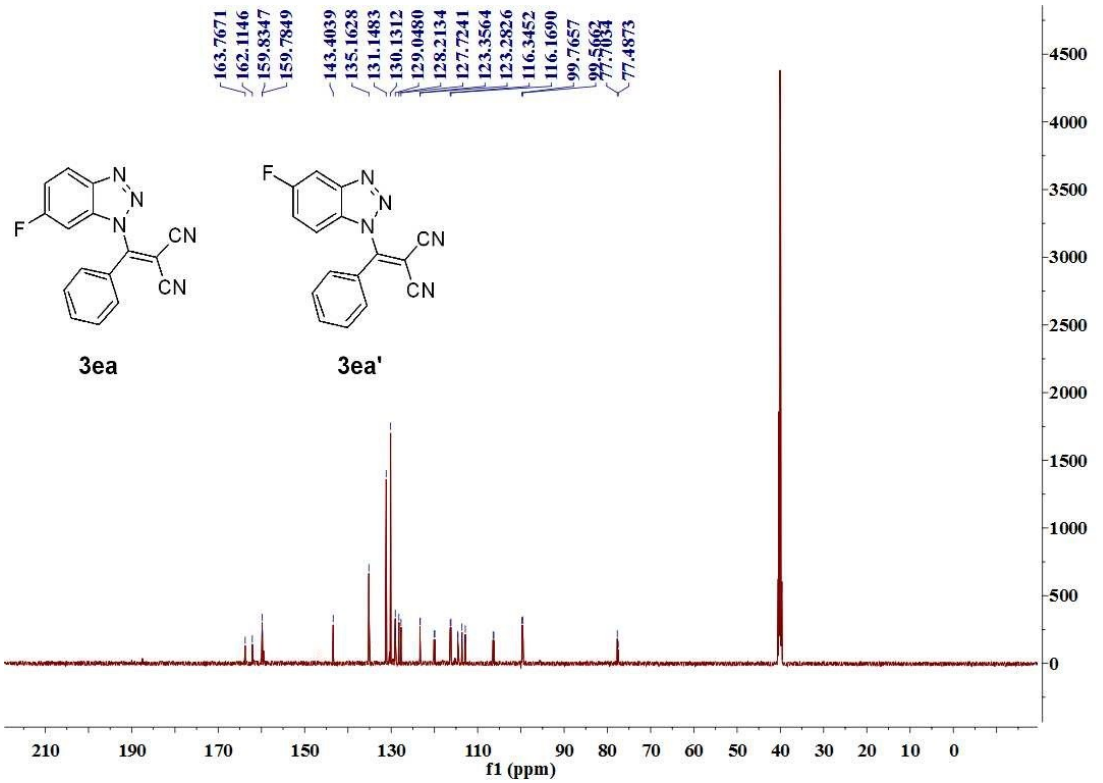
3ea'
f1 (ppm)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159.7849
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135.1628
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127.7241
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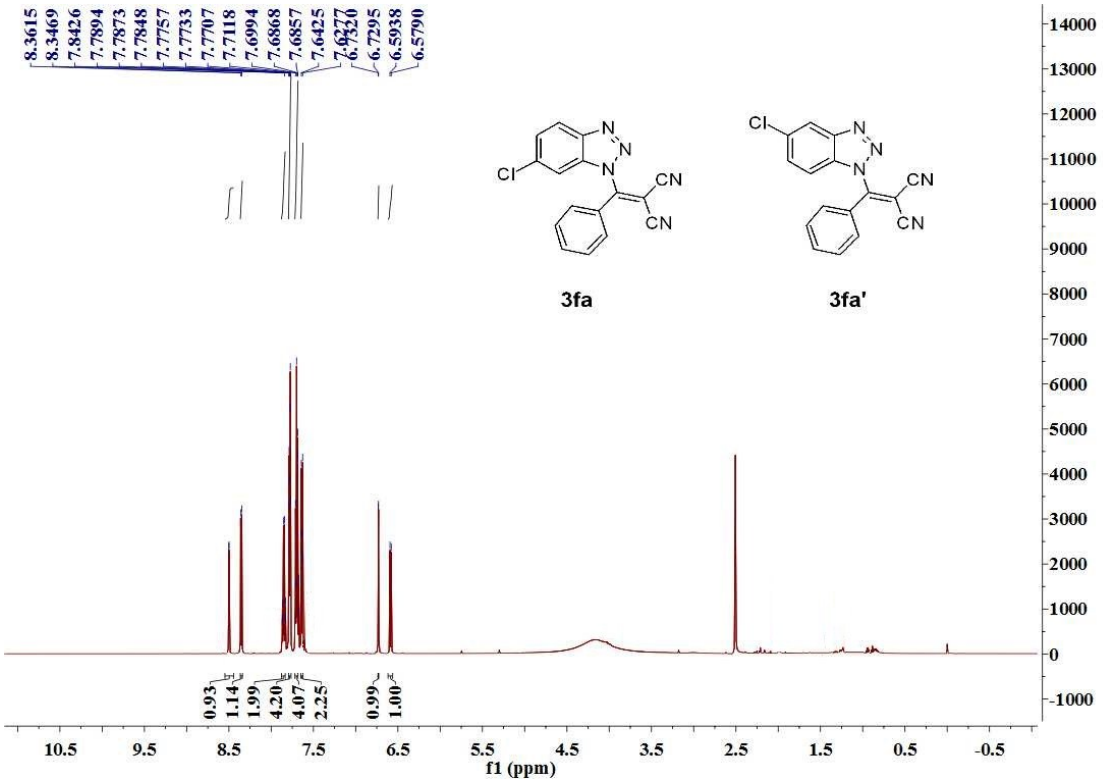
116.1690
99.7657
77.4873
3ea
3ea'
f1 (ppm)

3fa 3fa'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7.6868
7.6857
7.6425
7.6277
7.6220
6.7295
6.5938
6.5790
3fa
3fa'
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1.99
4.20
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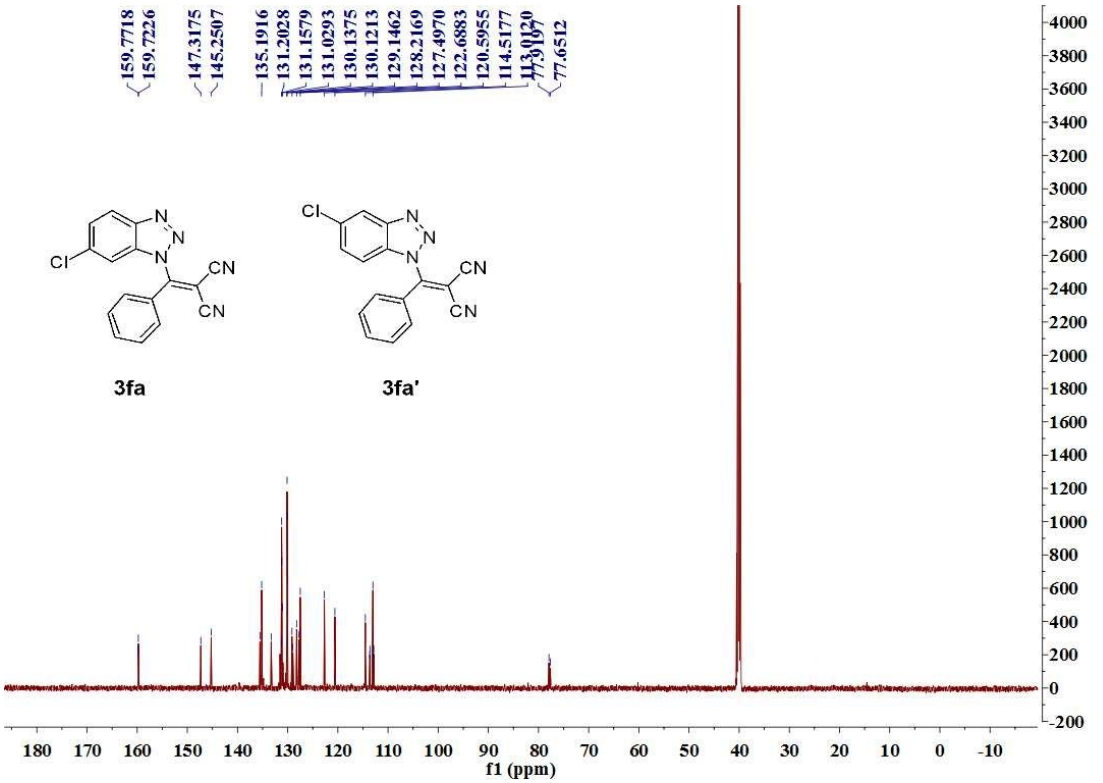
2.25
0.99
1.00
f1 (ppm)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128.2169
127.4970
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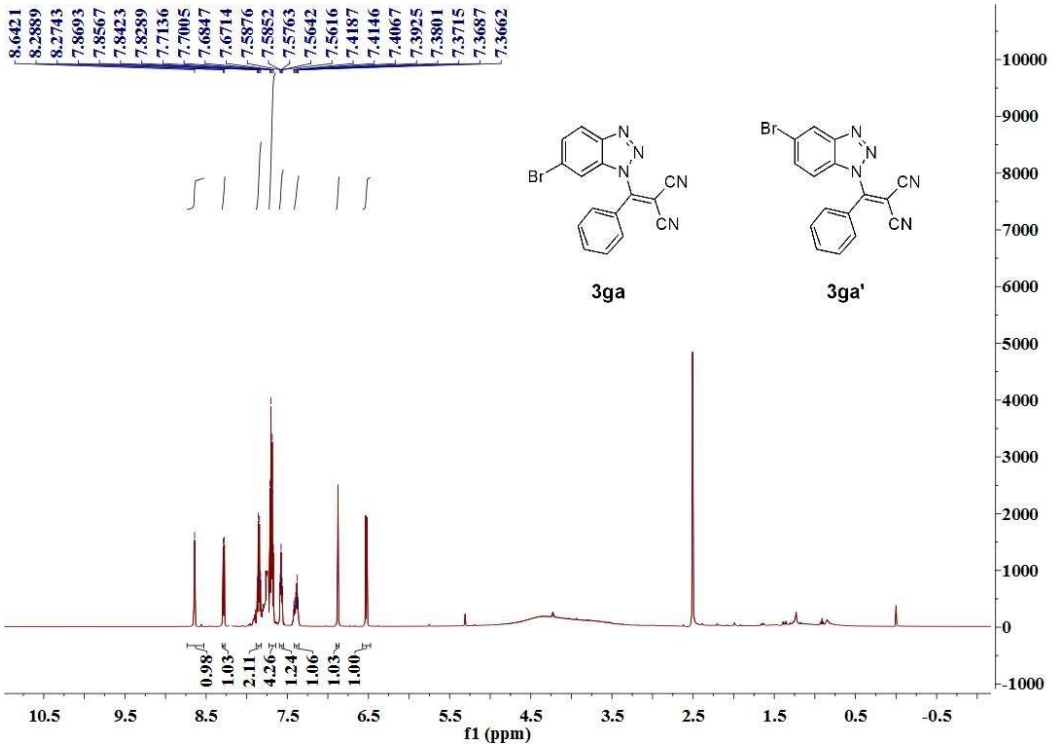
f1 (ppm)

3ga 3ga'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7.8289
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7.5876
7.5852
7.5763
7.5642
7.5616
7.4187
7.4146
7.4067
7.3925
7.3801
7.3715
7.3687
7.3662
Br
N
N
N
CN
CN
3ga
3ga'
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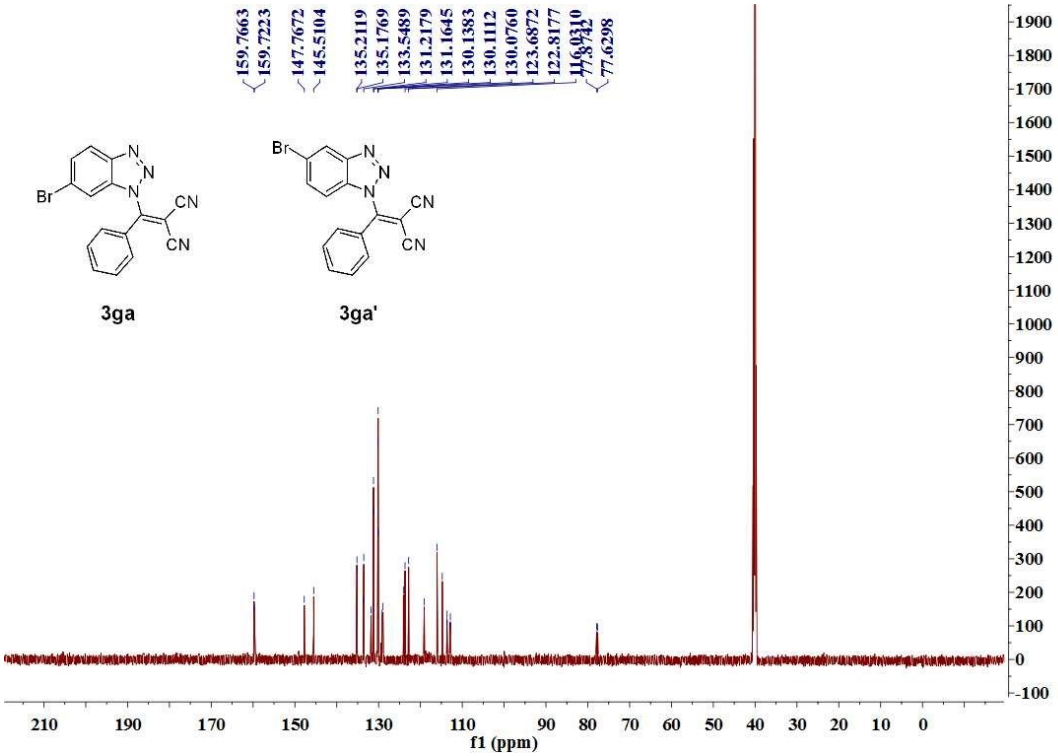
2.11
4.26
1.24
1.06
1.03
1.00
f1 (ppm)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130.1112
130.0760
123.6872
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Br
N
N
N
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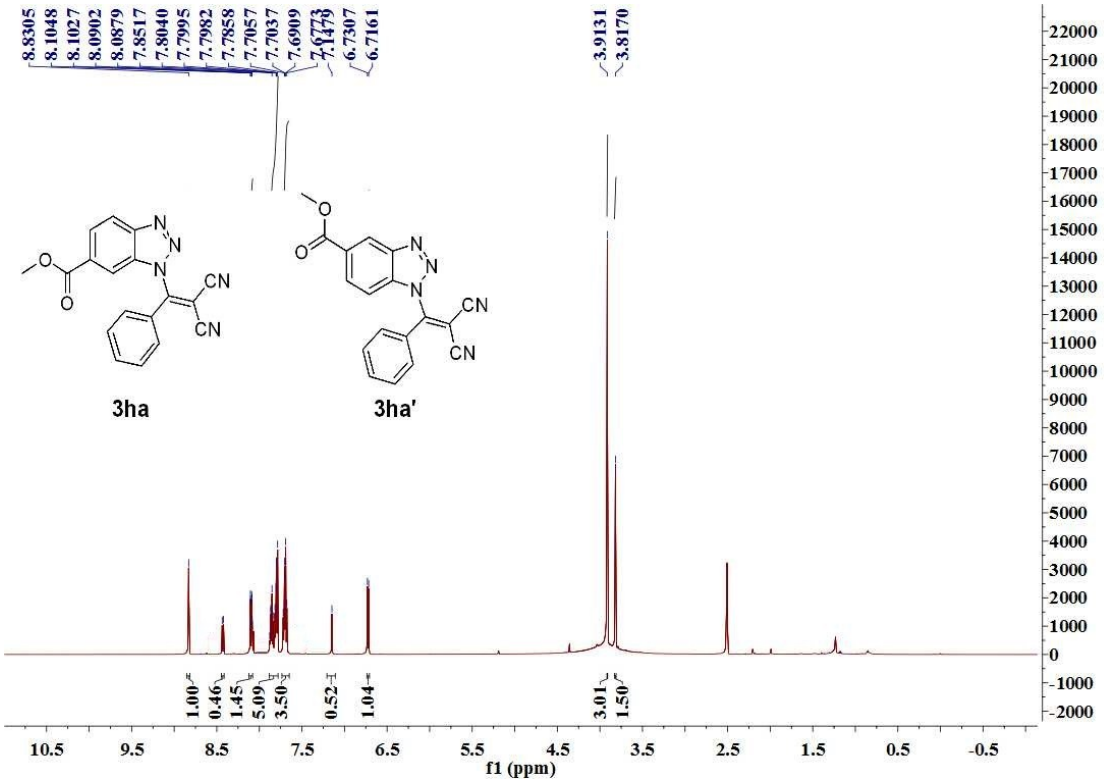
CN
3ga
3ga'
f1 (ppm)

3ha 3ha'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7.8040
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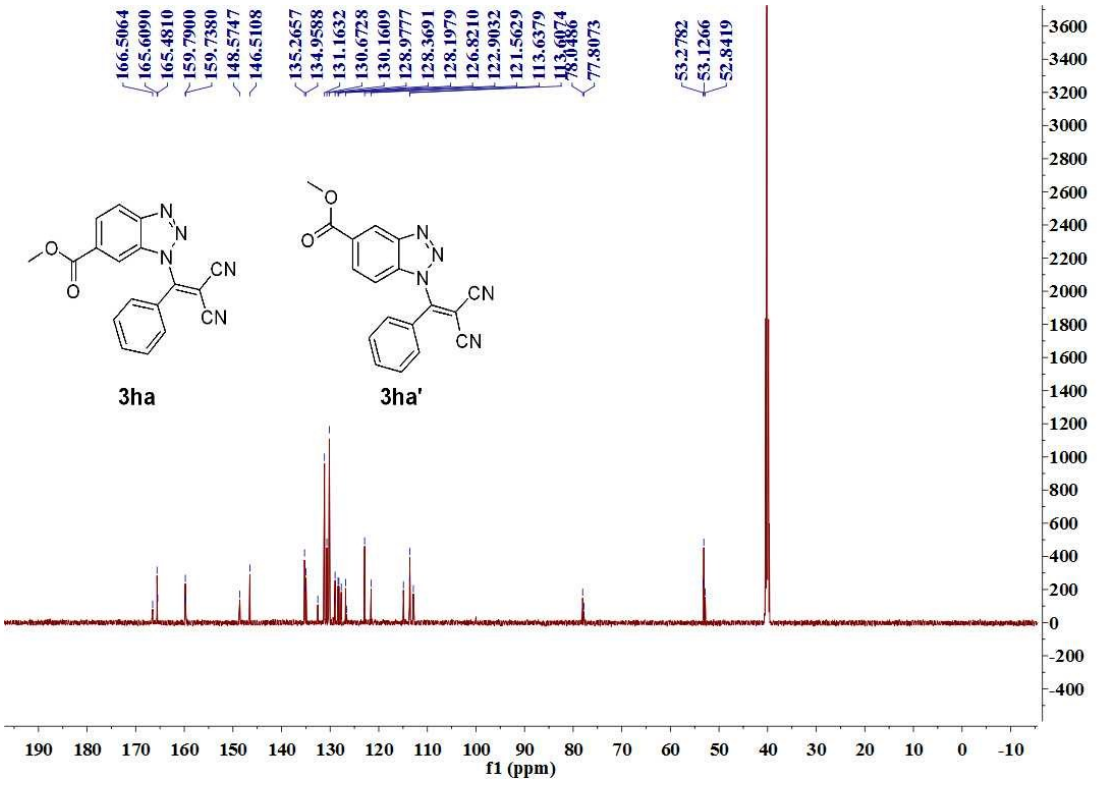
7.7982
7.7858
7.7057
7.7037
7.6909
7.6773
7.6753
7.6307
7.6161
3.9131
3.8170
1.00
0.46
1.45
5.09
3.50
0.52
1.04
3.01
1.50
f1 (ppm)
3ha
3ha'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148.5747
146.5108
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134.9588
131.1632
130.6728
130.1609
128.9777
128.3691
128.1979
126.8210
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77.8073
53.2782
53.1266
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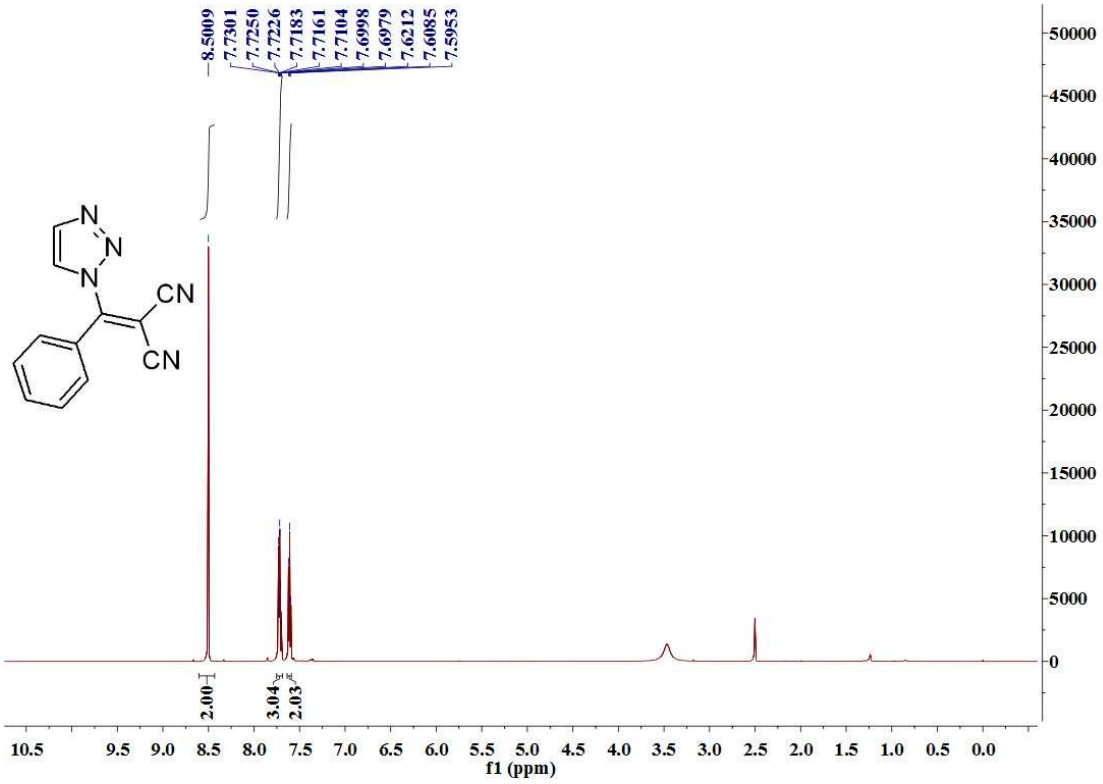
f1 (ppm)
3ha
3ha'

3ia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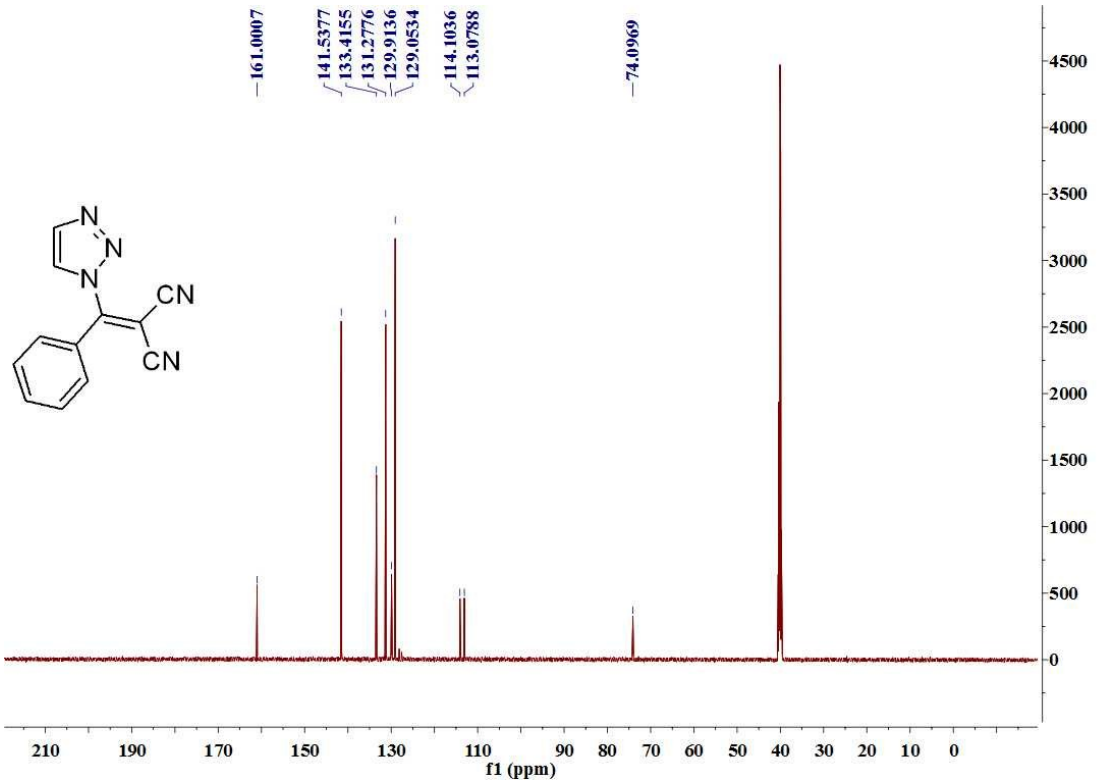
2.03
f1 (ppm)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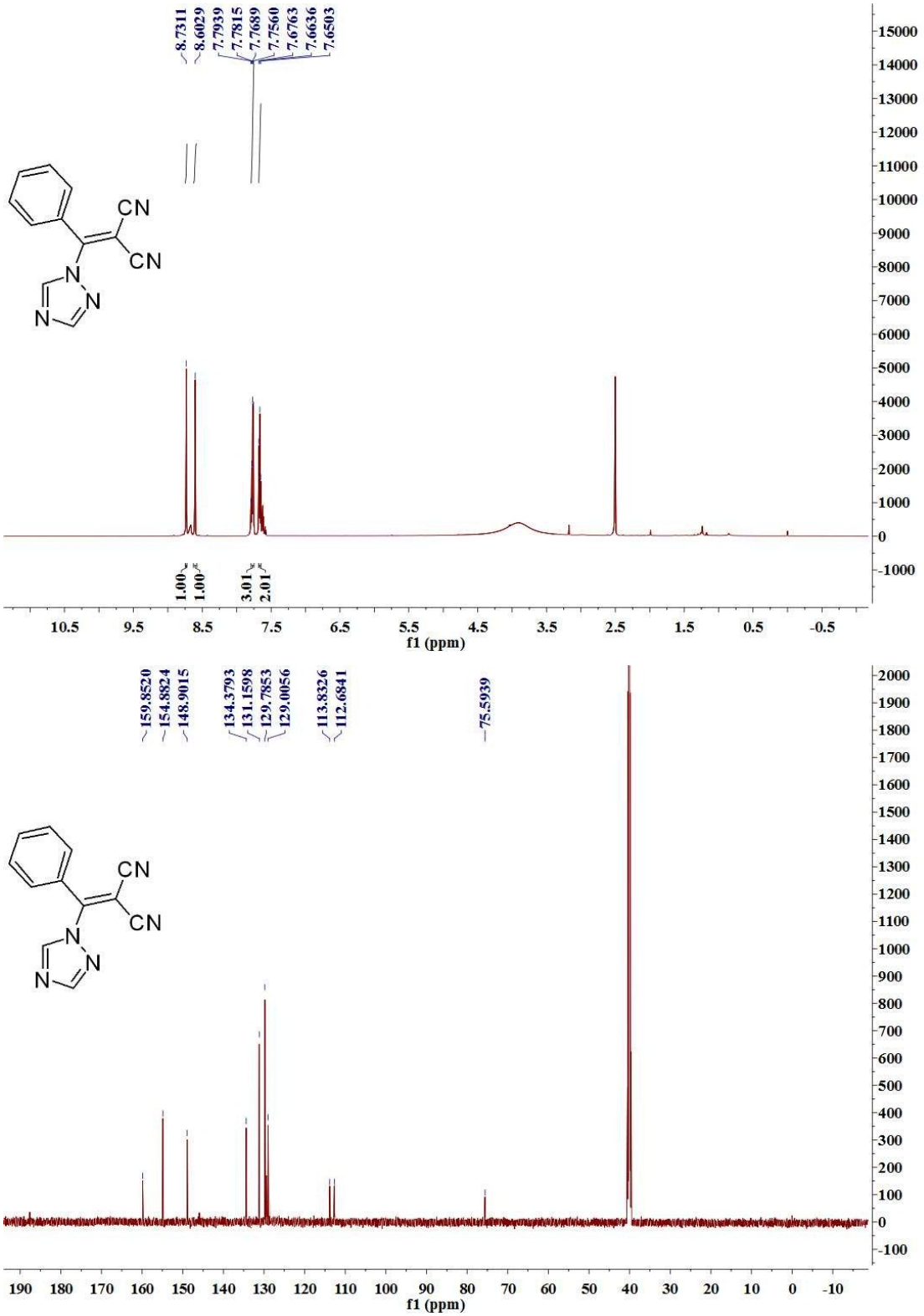
3ja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7.7939
7.7815
7.7689
7.7560
7.6763
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7.6503
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CN
N
N
N
1.00
1.00
3.01
2.01
f1 (ppm)
159.8520
154.8824
148.9015
134.3793
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129.0056
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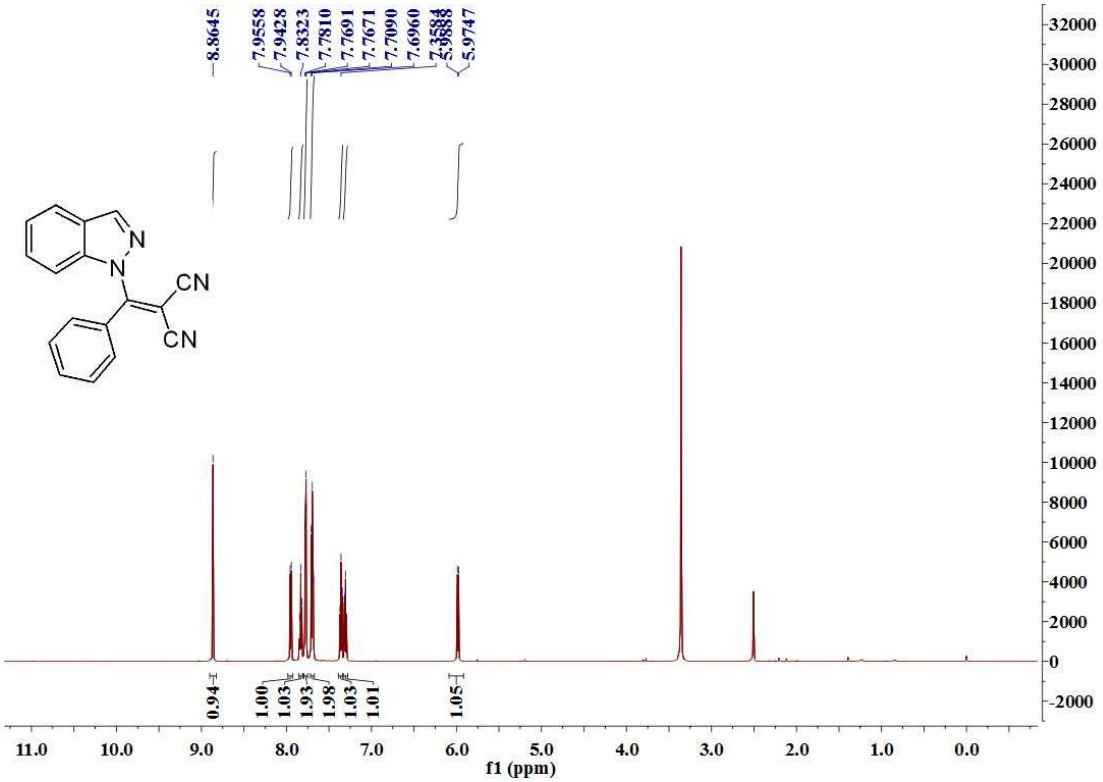
N
N
f1 (ppm)

3ka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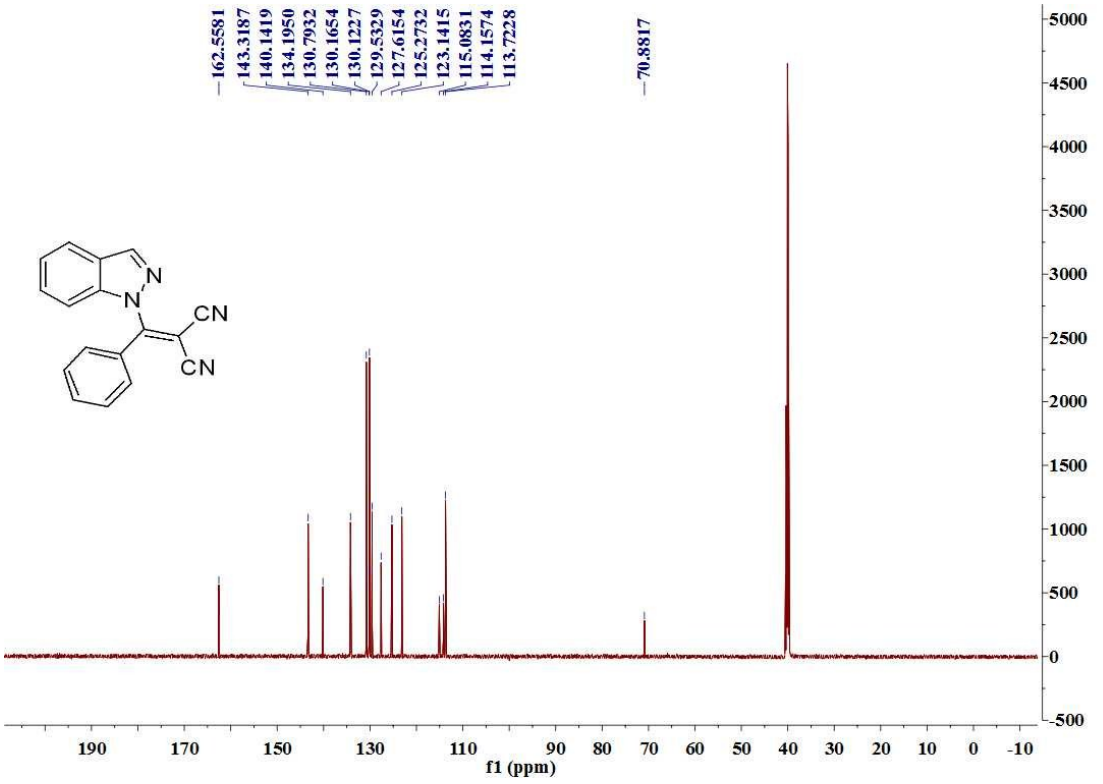
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113.7228
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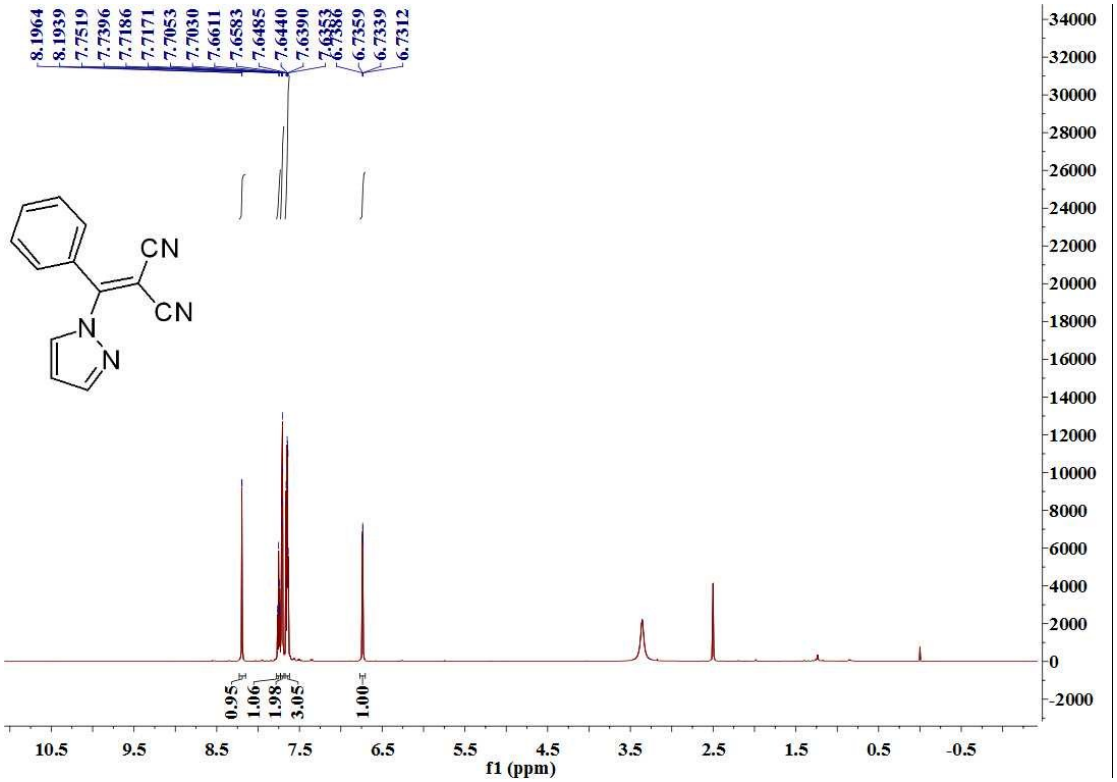
3la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7.6485
7.6440
7.6390
7.6353
7.6336
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CN
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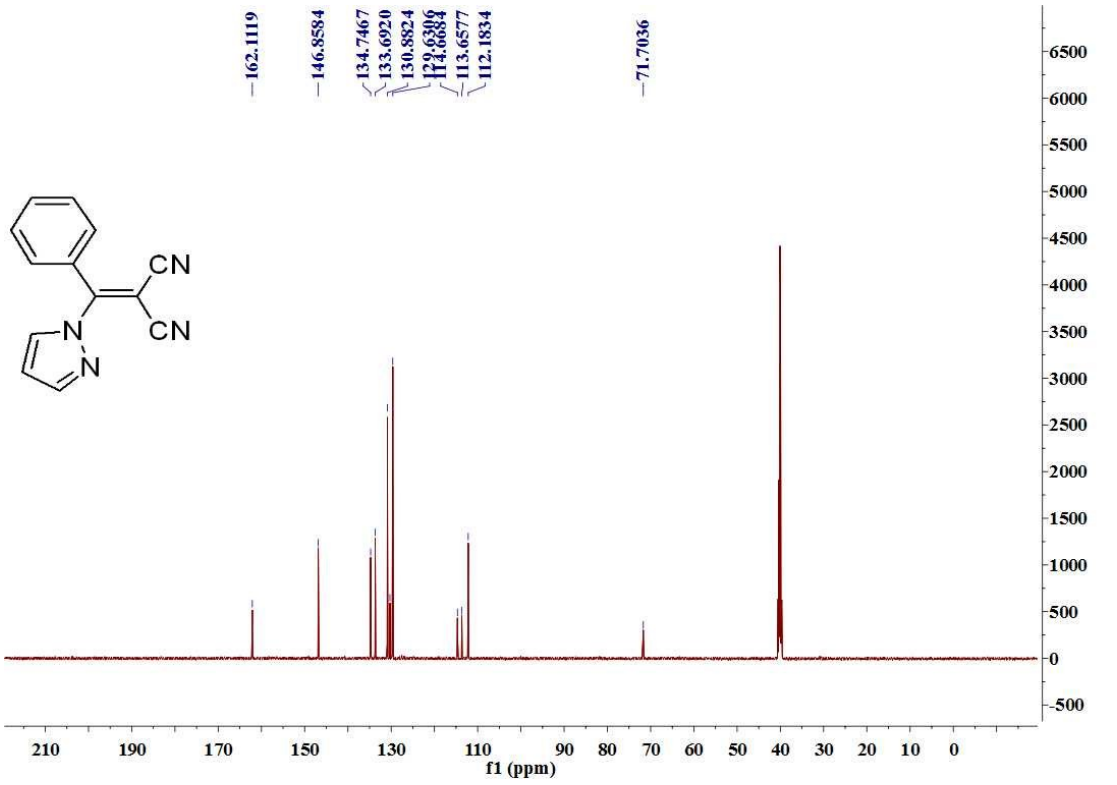
3.05
1.00
f1 (ppm)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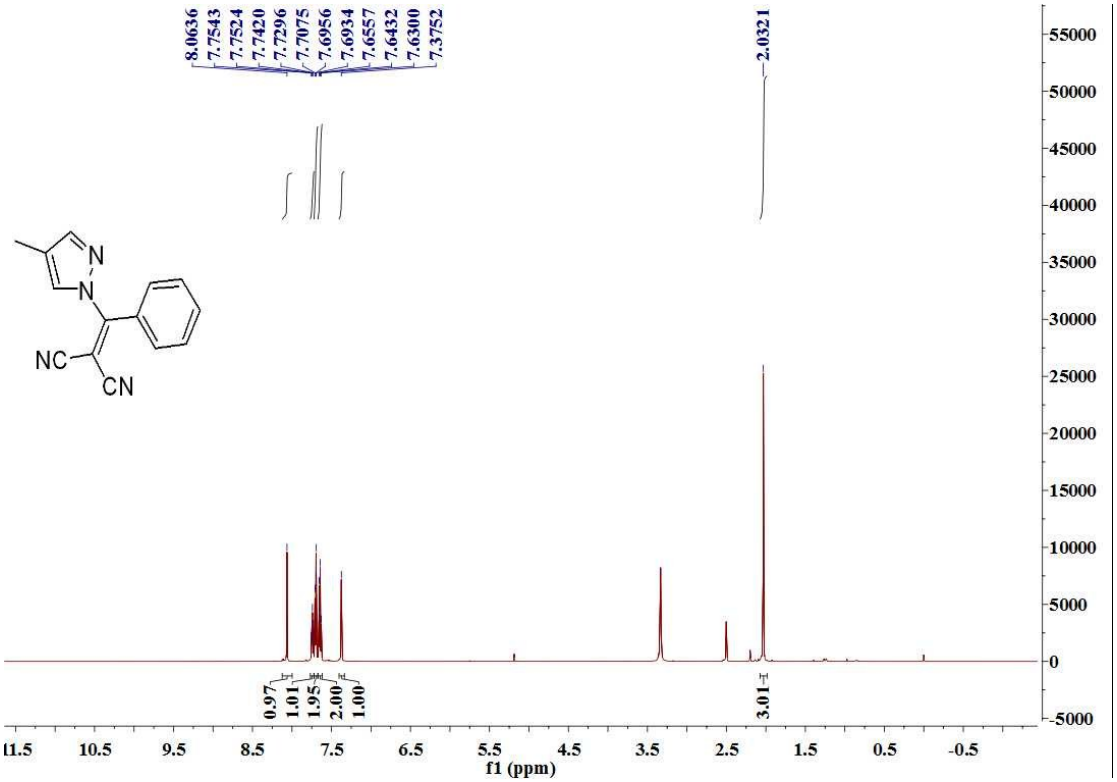
N
f1 (ppm)

3ma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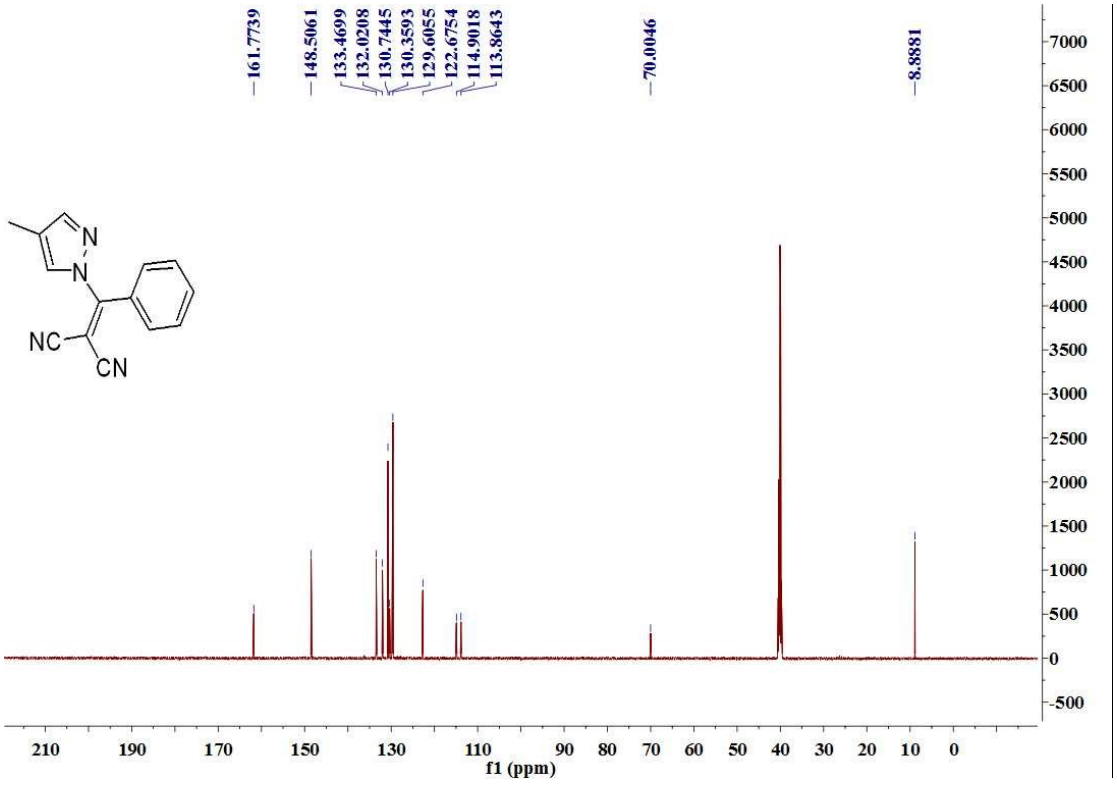
f1 (ppm)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N
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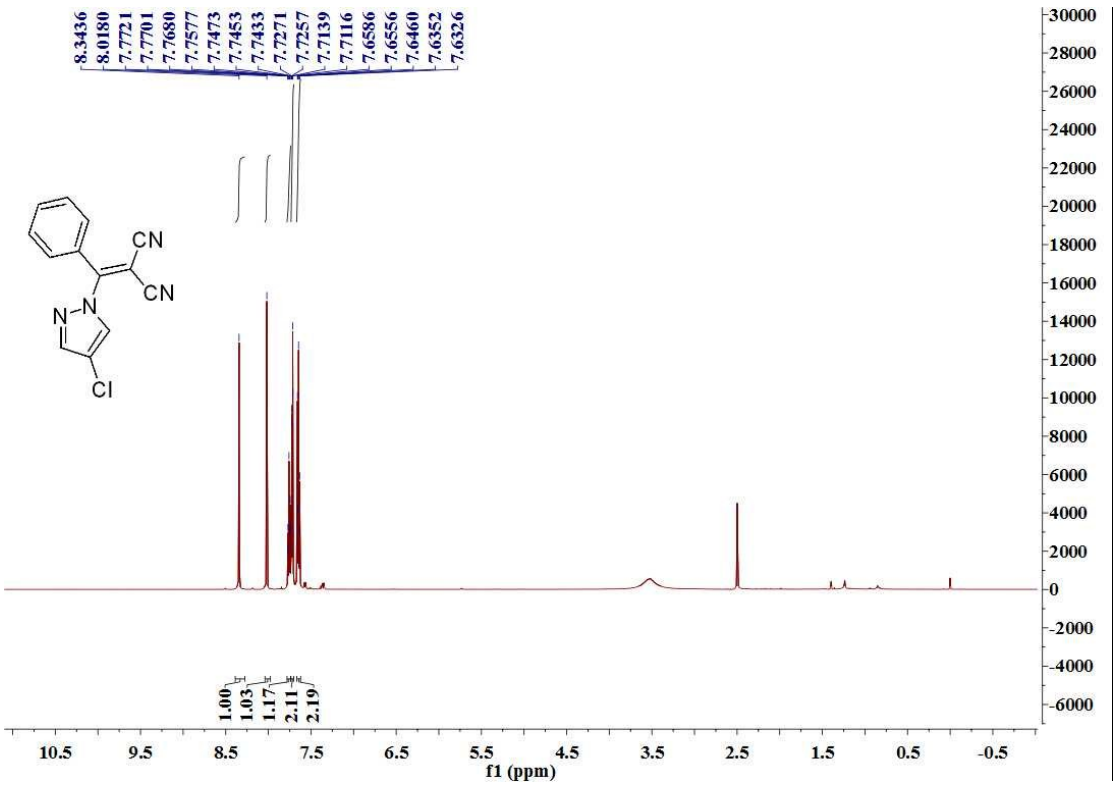
CN
f1 (ppm)

3na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7.7257
7.7139
7.7116
7.6586
7.6556
7.6460
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CN
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N
Cl
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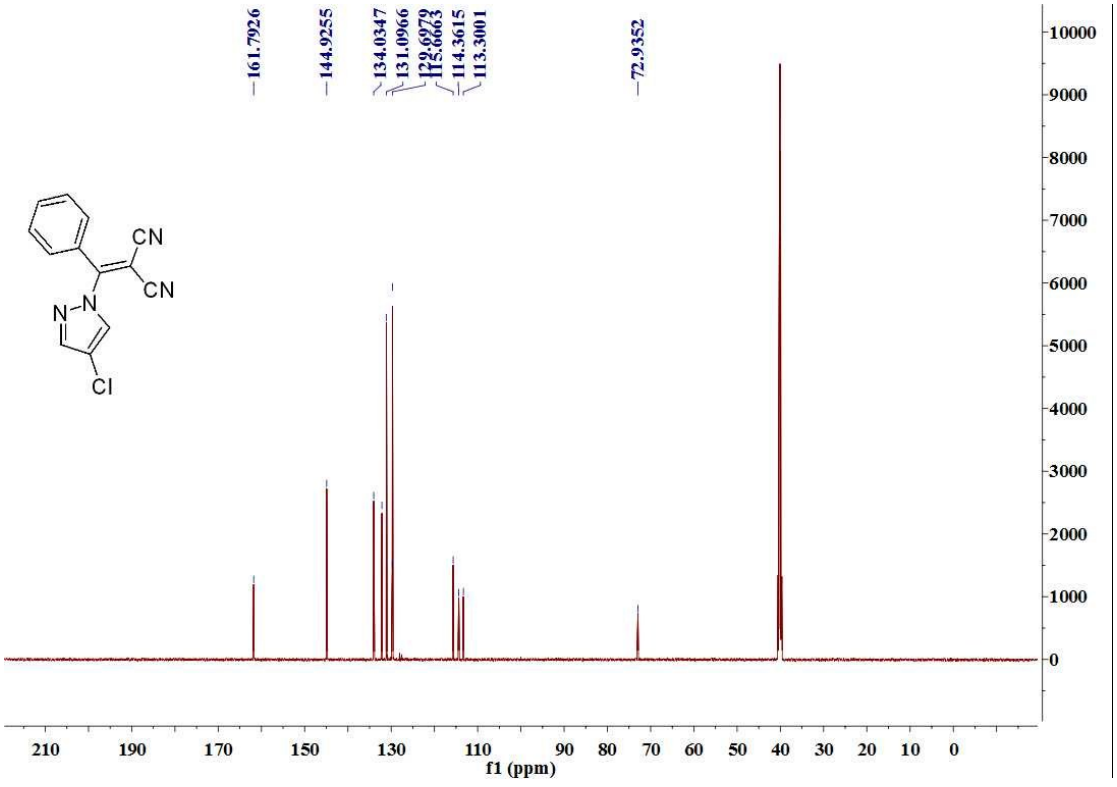
1.17
2.11
2.19
f1 (ppm)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72.9352
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113.3001
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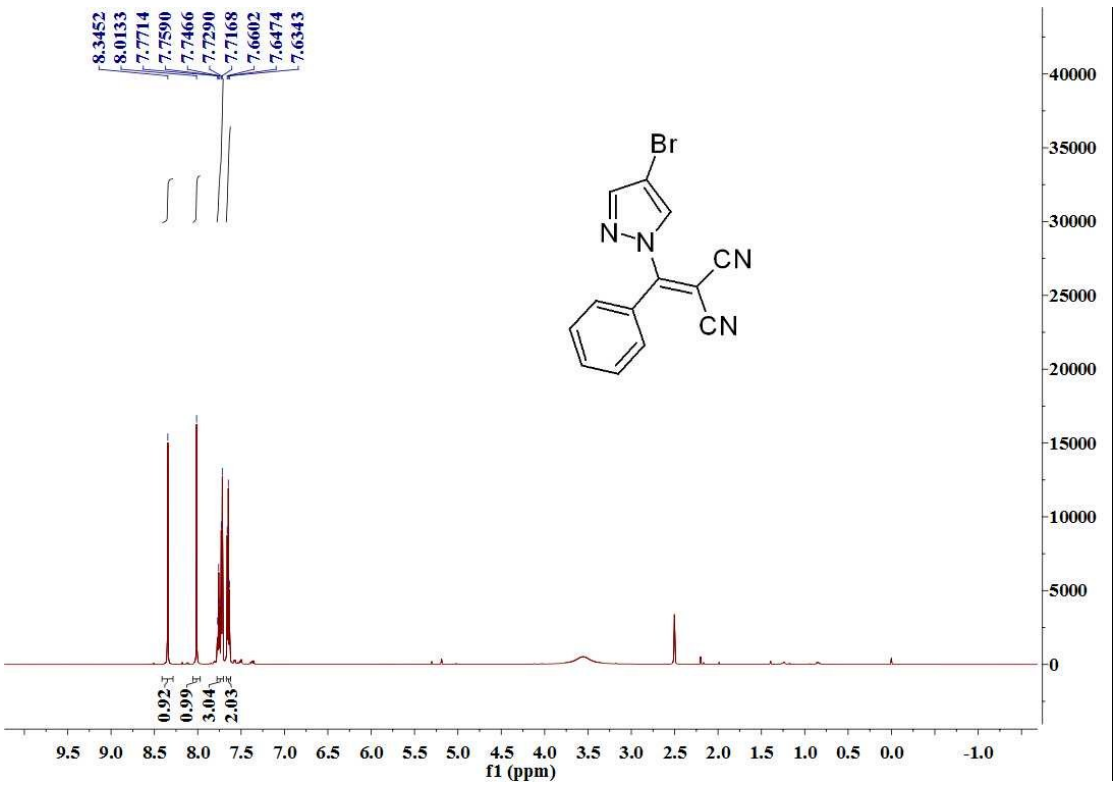
CN
N
N
Cl
f1 (ppm)

3oa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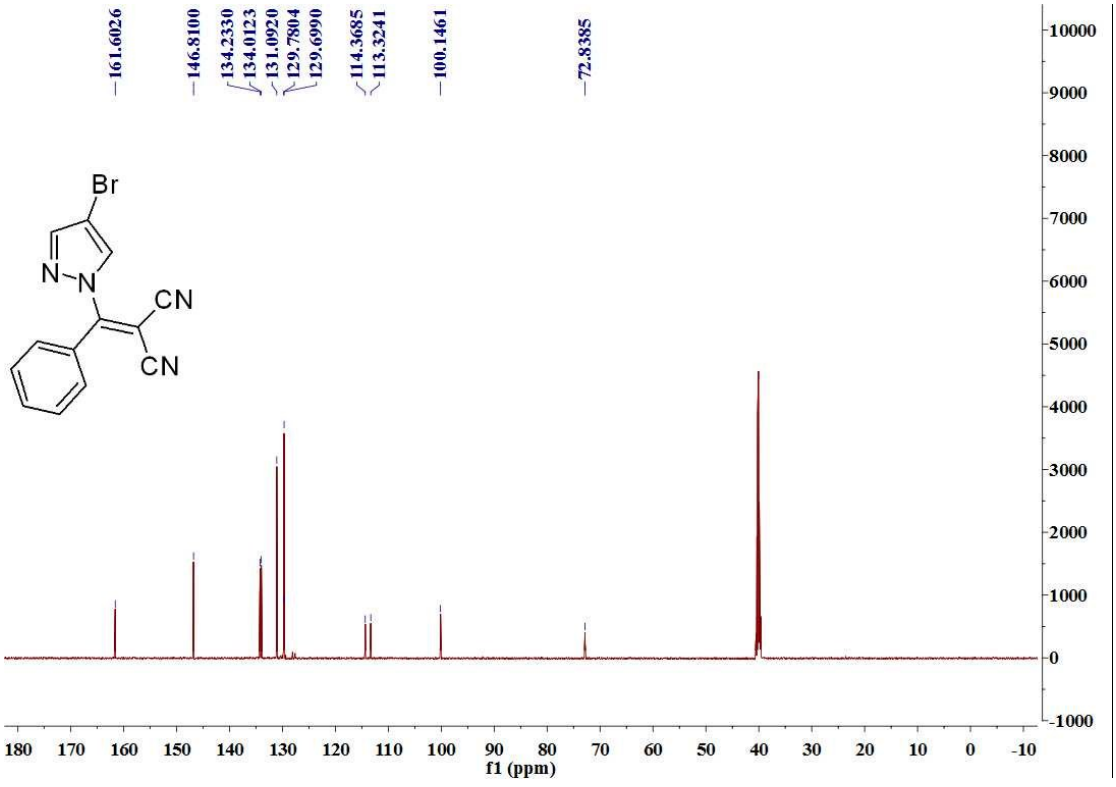
2.03
f1 (ppm)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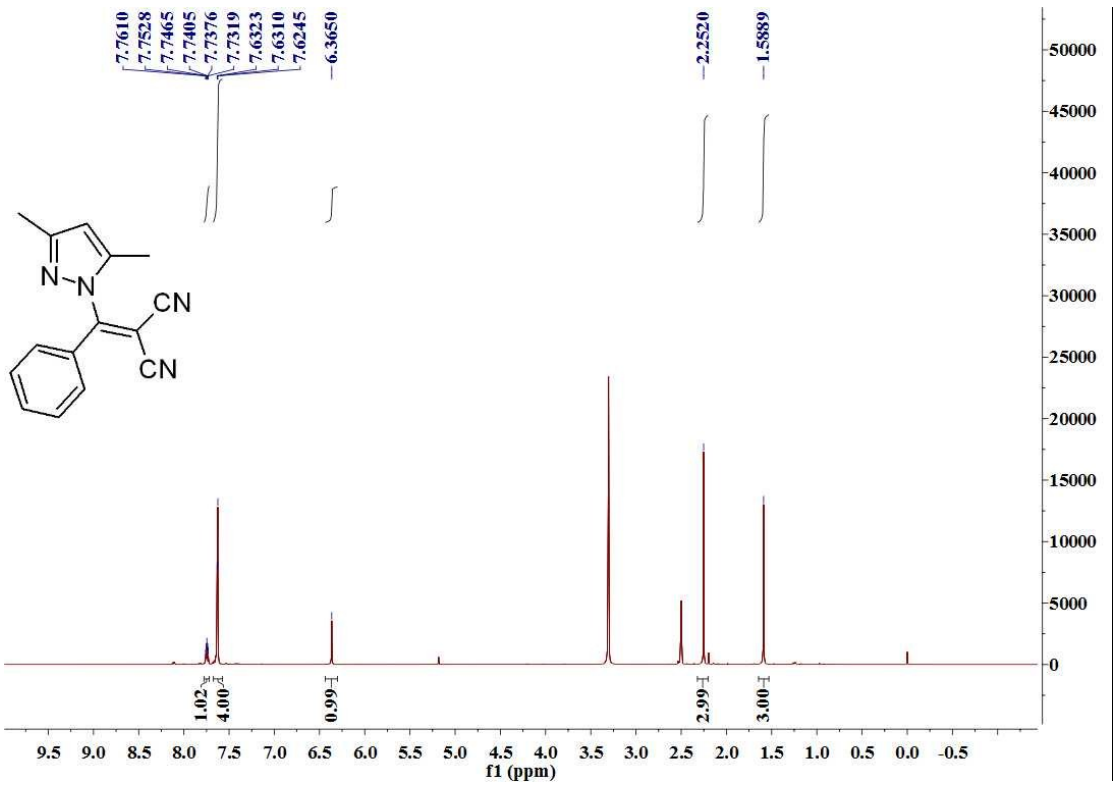
CN
CN
f1 (ppm)

3pa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CN
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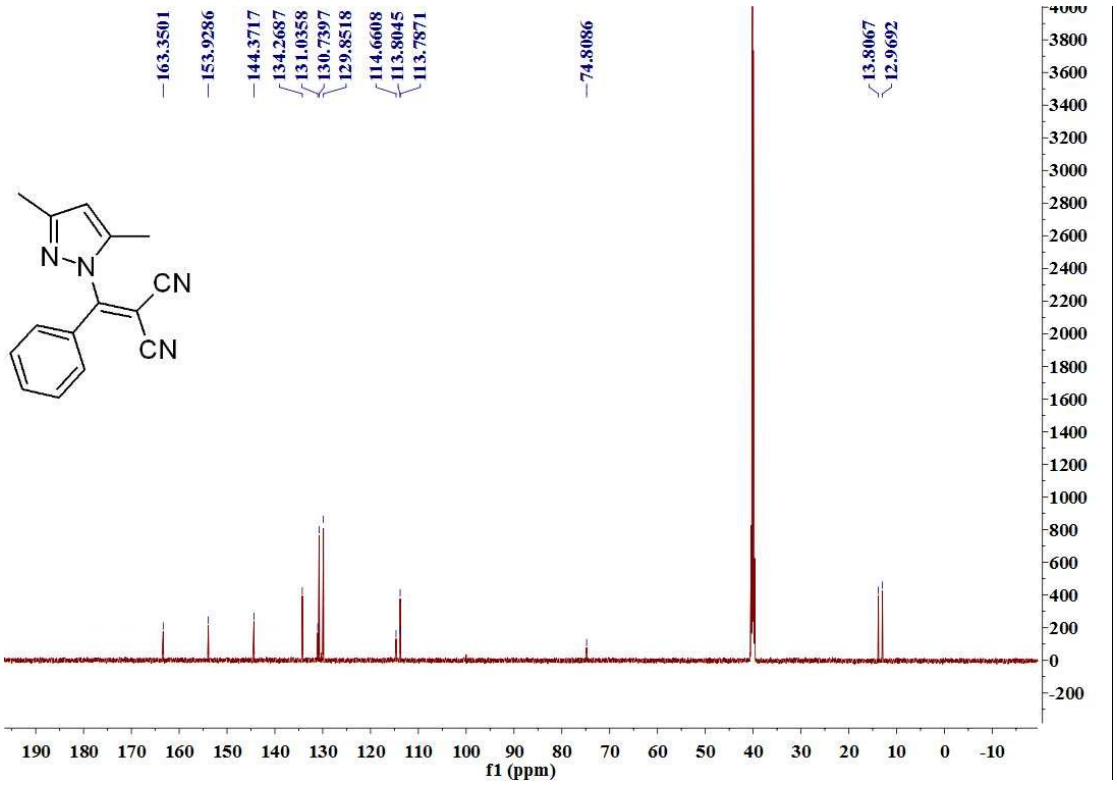
f1 (ppm)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113.8045
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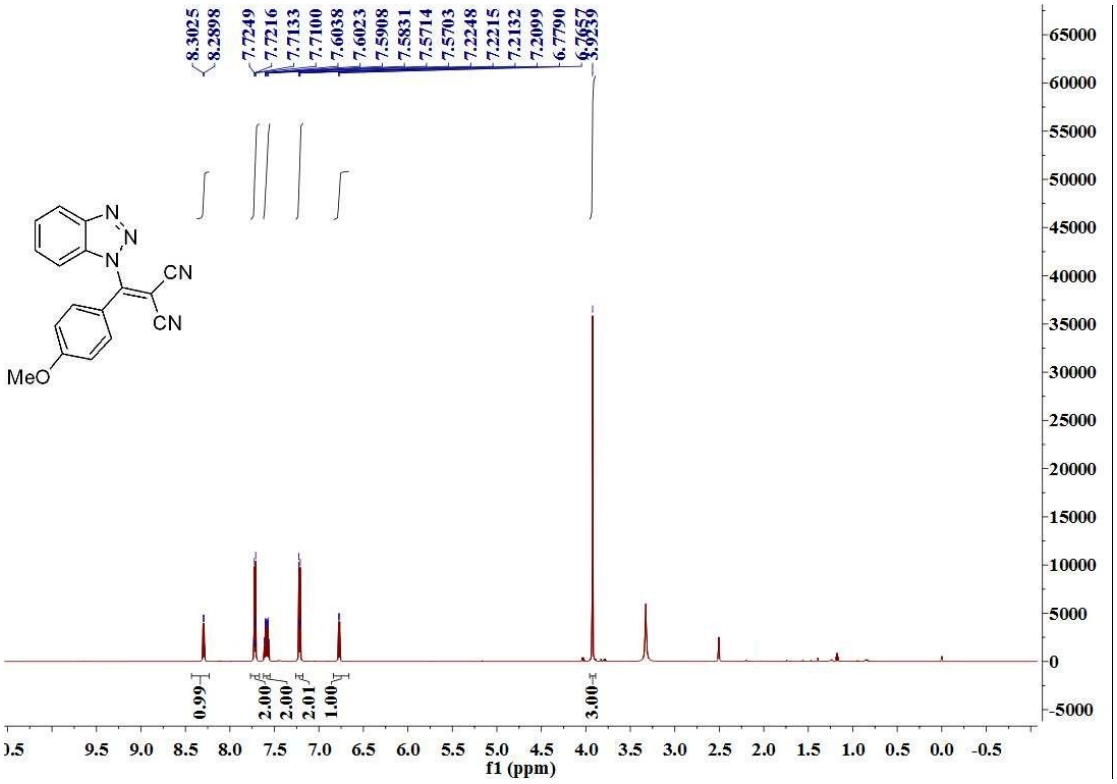
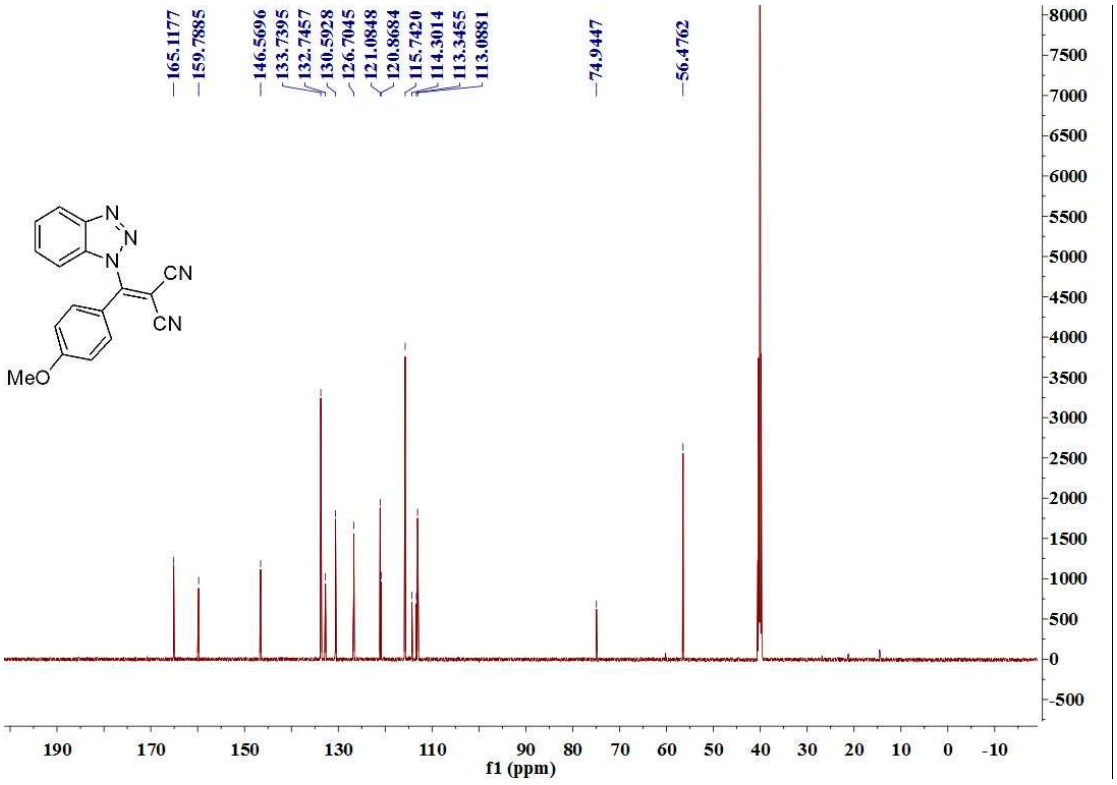
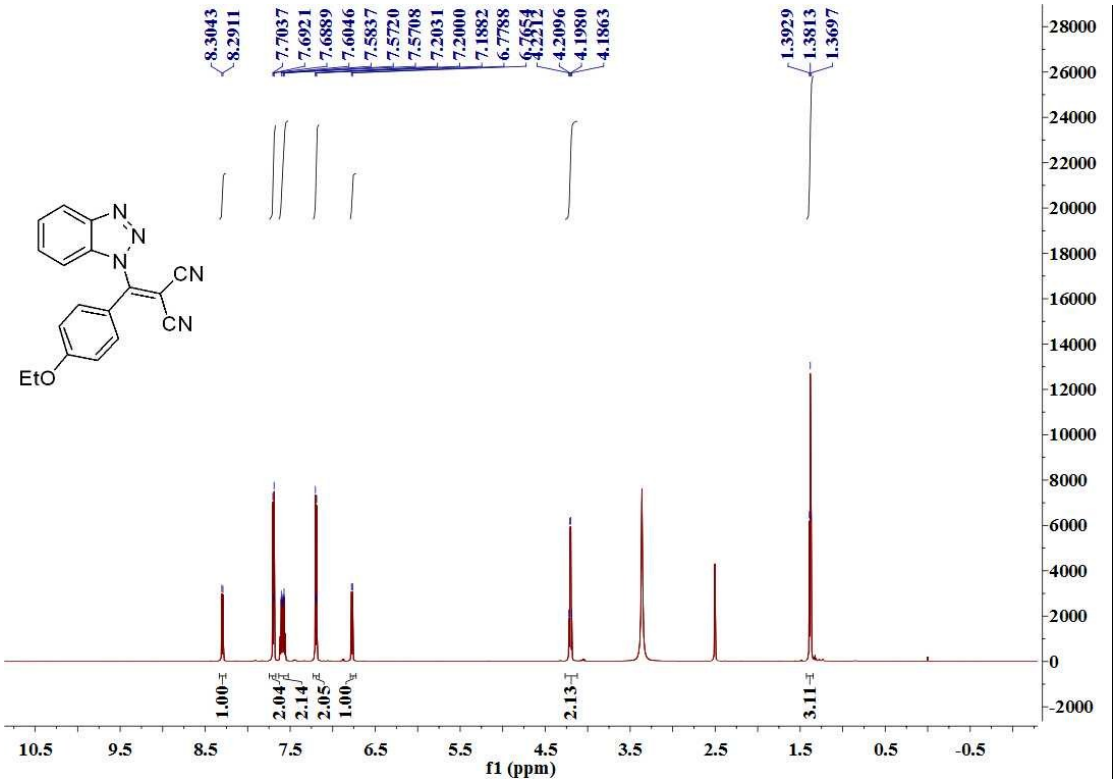
74.8086
13.8067
12.9692
N
N
CN
CN
f1 (ppm)

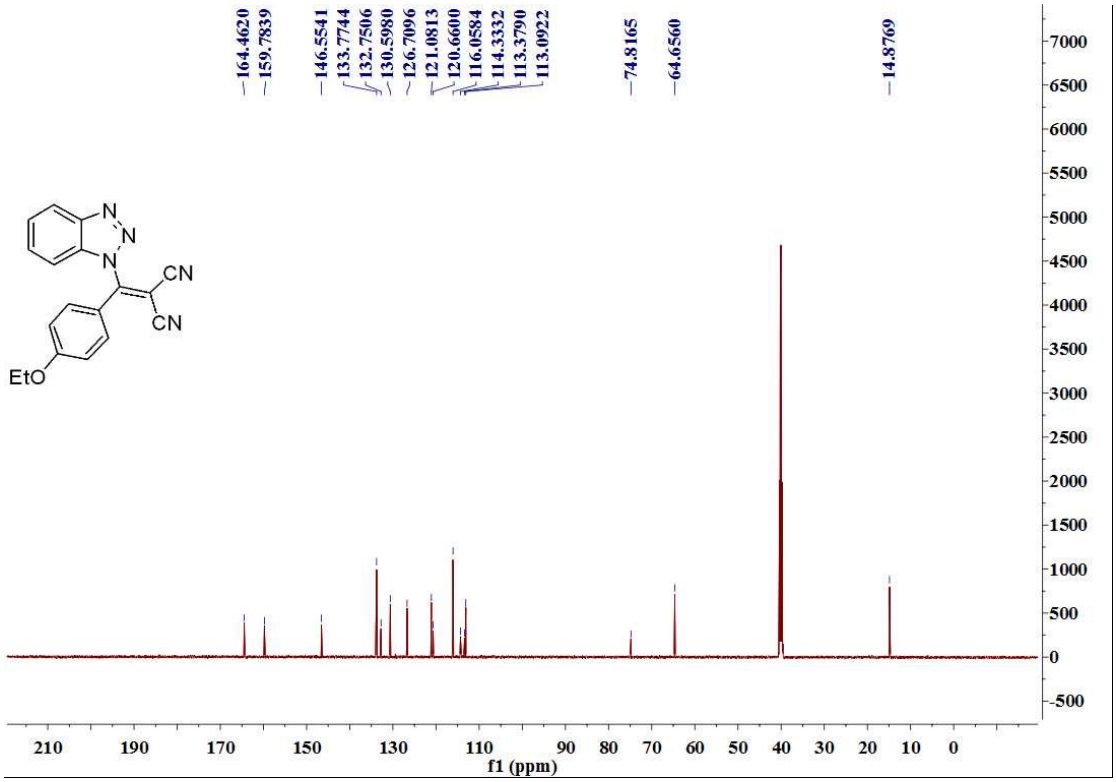
3ab


8.3025
8.2898
7.7249
7.7216
7.7133
7.7100
7.6038
7.6023
7.5908
7.5831
7.5714
7.5703
7.2248
7.2215
7.2132
7.2099
6.7790
6.7657
3.9239
N
N
N
CN
CN
MeO
0.99
2.00
2.00
2.01
1.00
3.00
f1 (ppm)

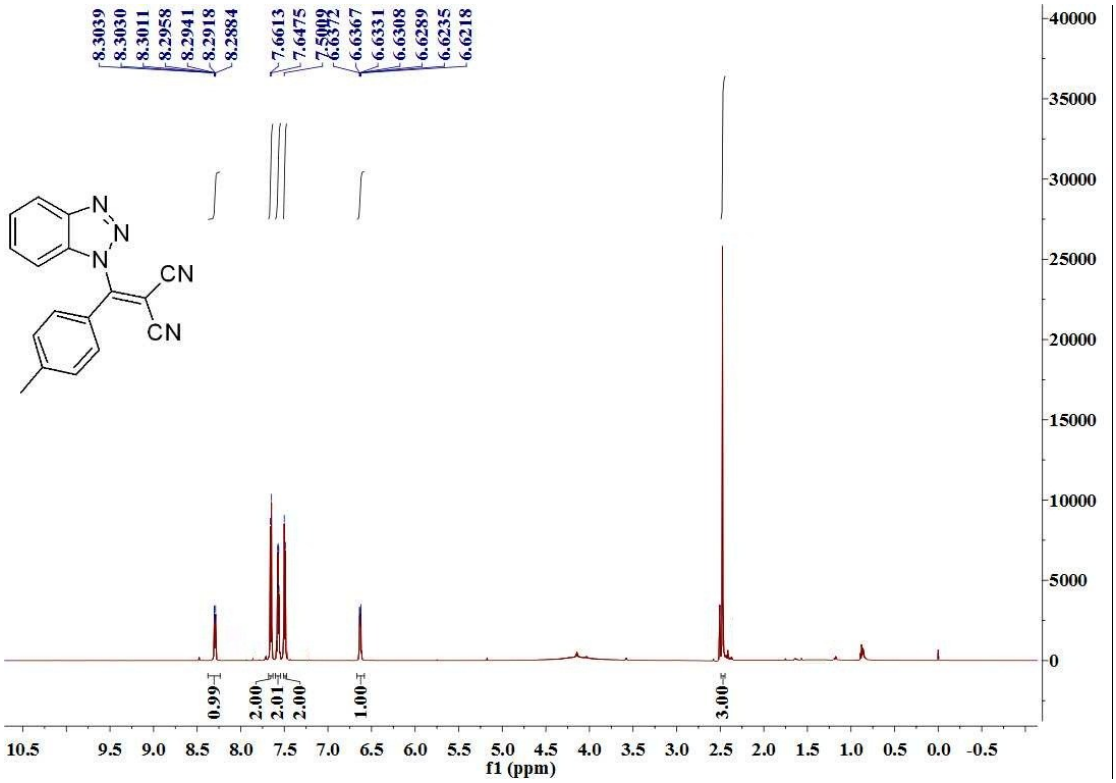

165.1177
159.7885
146.5696
133.7395
132.7457
130.5928
126.7045
121.0848
120.8684
115.7420
114.3014
113.3455
113.0881
74.9447
56.4762
N
N
N
CN
CN
MeO
f1 (ppm)

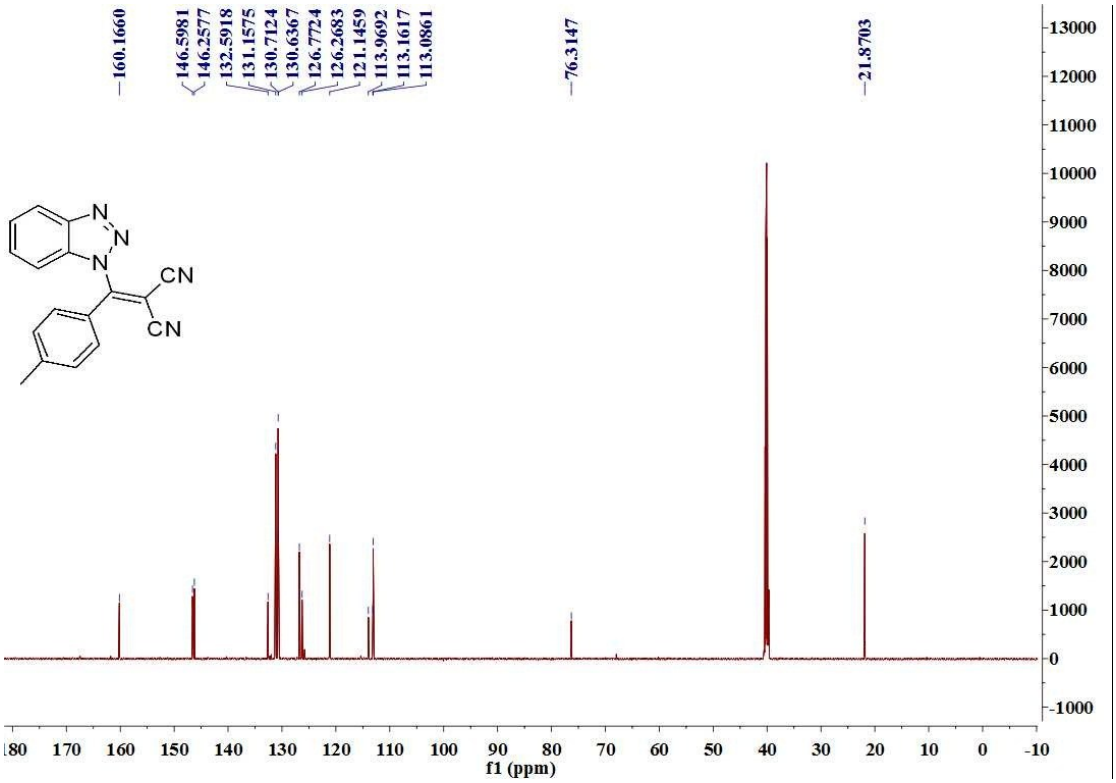
3ac


8.3043
8.2911
7.7037
7.6921
7.6889
7.6046
7.5837
7.5720
7.5708
7.2031
7.2000
7.1882
6.7788
4.2212
4.2096
4.1980
4.1863
1.3929
1.3813
1.3697
1.00
2.04
2.14
2.05
1.00
2.13
3.11
f1 (ppm)

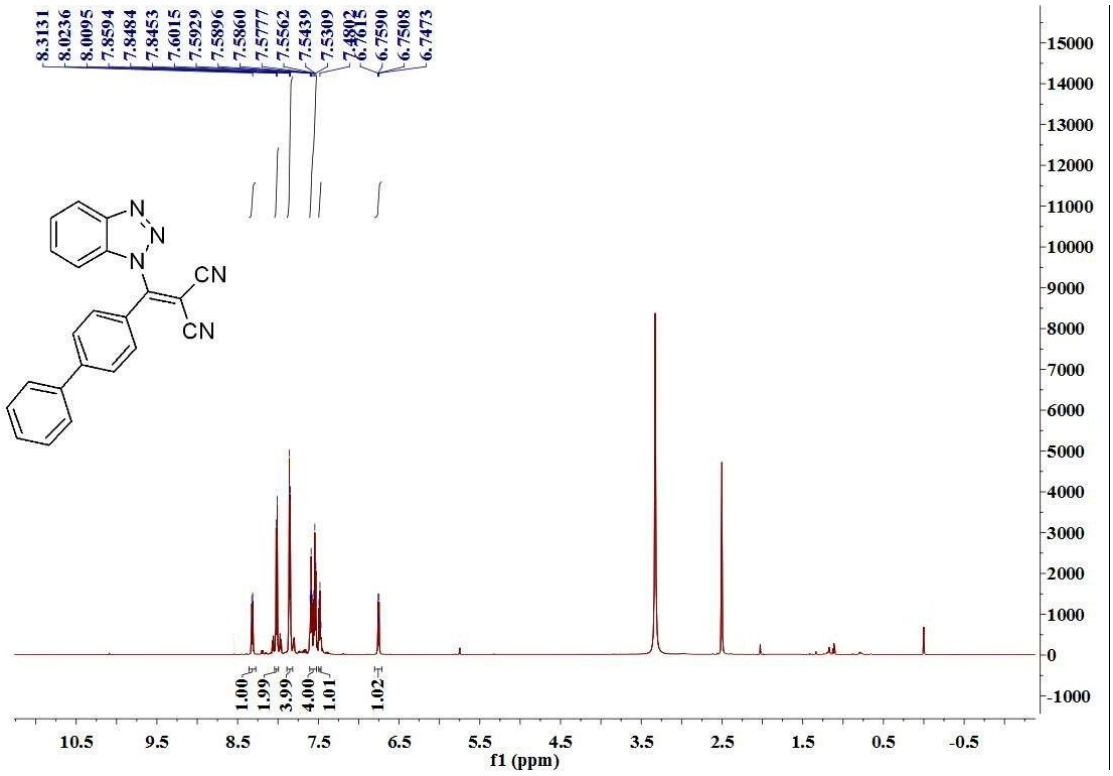

164.4620
159.7839
146.5541
133.7744
132.7506
130.5980
126.7096
121.0813
120.6600
116.0584
114.3332
113.3790
113.0922
74.8165
64.6560
14.8769
f1 (ppm)

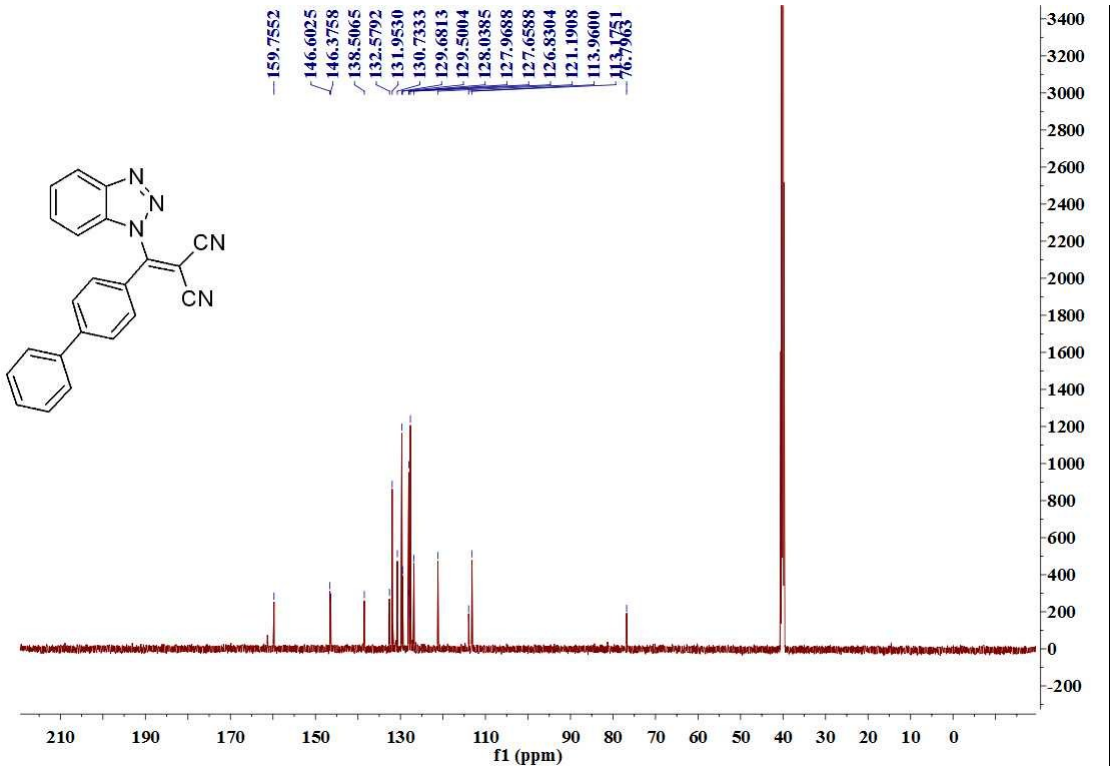
3ad


8.3039
8.3030
8.3011
8.2958
8.2941
8.2918
8.2884
7.6613
7.6475
7.5009
6.6367
6.6331
6.6308
6.6289
6.6235
6.6218
CN
CN
0.99
2.00
2.01
2.00
1.00
3.00
f1 (ppm)

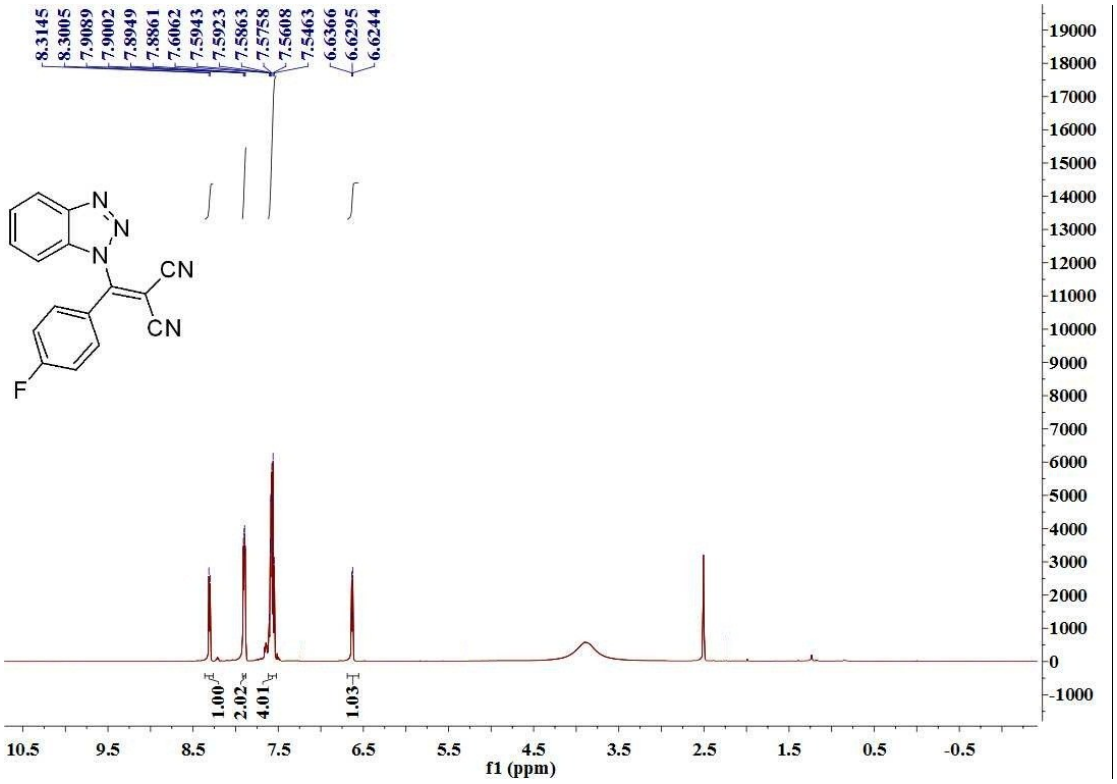

160.1660
146.5981
146.2577
132.5918
131.1575
130.7124
130.6367
126.7724
126.2683
121.1459
113.9692
113.1617
113.0861
76.3147
21.8703
CN
CN
f1 (ppm)

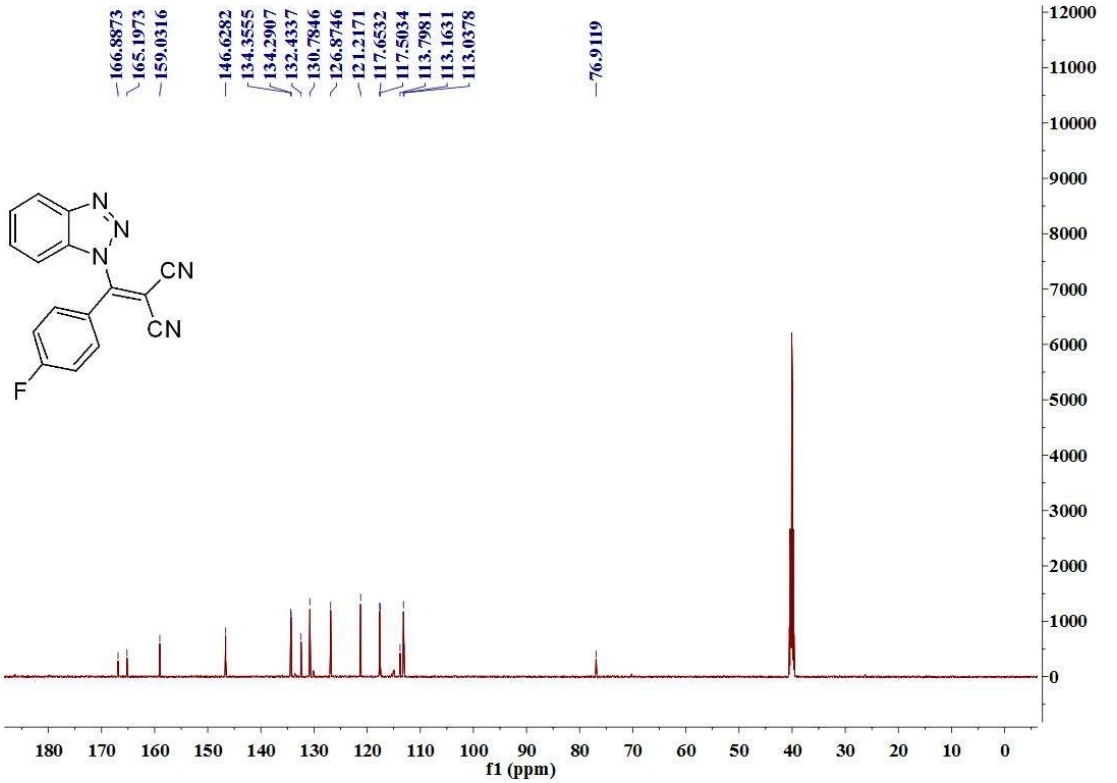
3ae


8.3131
8.0236
8.0095
7.8594
7.8484
7.8453
7.6015
7.5929
7.5896
7.5860
7.5777
7.5562
7.5439
7.5309
7.4802
6.7590
6.7508
6.7473
N
N
N
CN
CN
1.00
1.99
3.99
4.00
1.01
1.02
f1 (ppm)

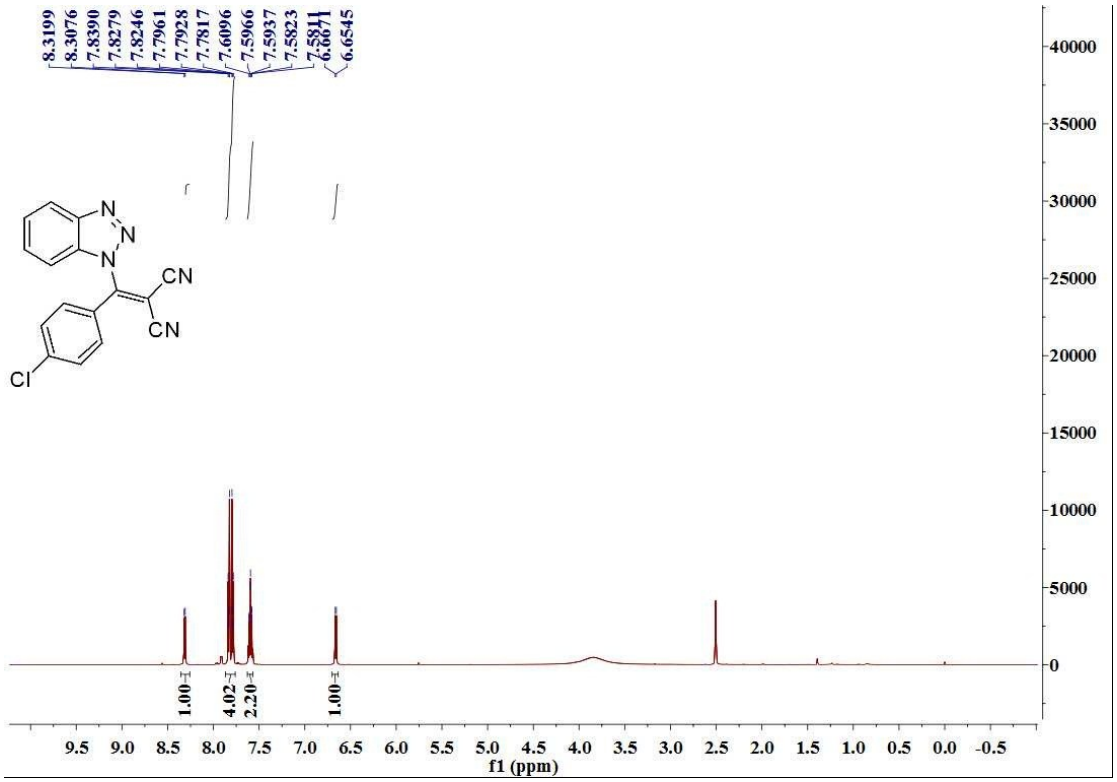

159.7552
146.6025
146.3758
138.5065
132.5792
131.9530
130.7333
129.6813
129.5004
128.0385
127.9688
127.6588
126.8304
121.1908
113.9600
N
N
N
CN
CN
f1 (ppm)

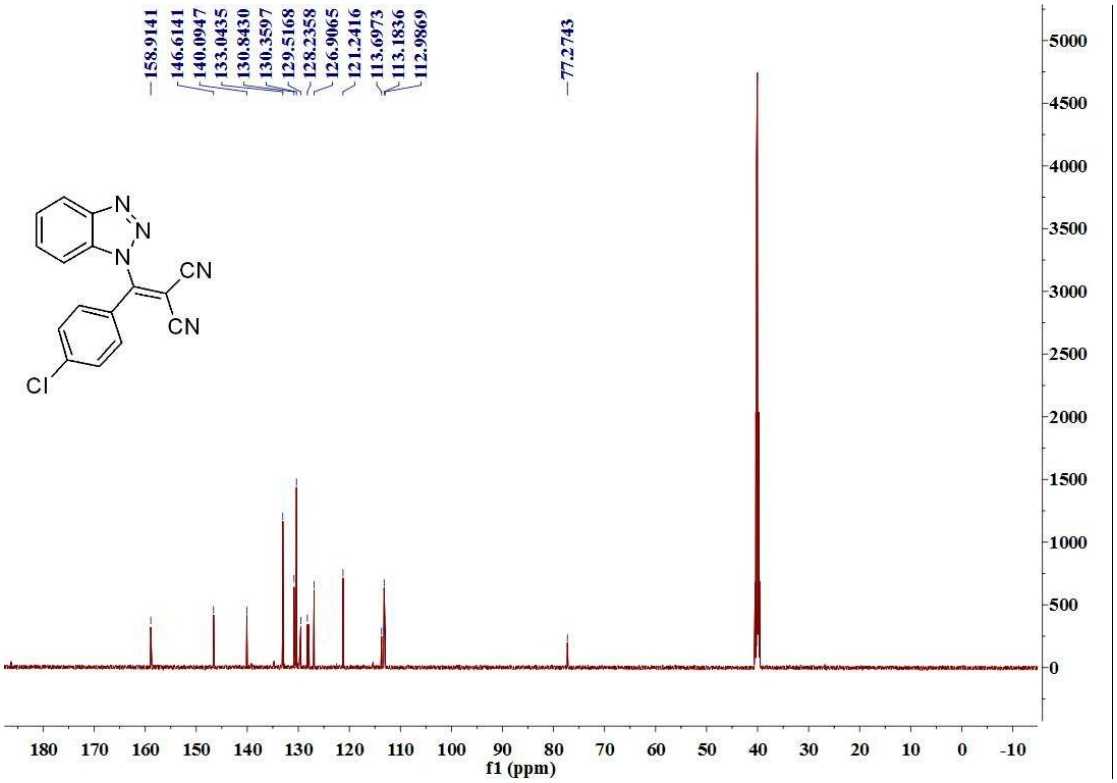
3af


8.3145
8.3005
7.9089
7.9002
7.8949
7.8861
7.6062
7.5943
7.5923
7.5863
7.5758
7.5608
7.5463
6.6366
6.6295
6.6244
N
N
N
CN
CN
F
1.00
2.02
4.01
1.03
f1 (ppm)

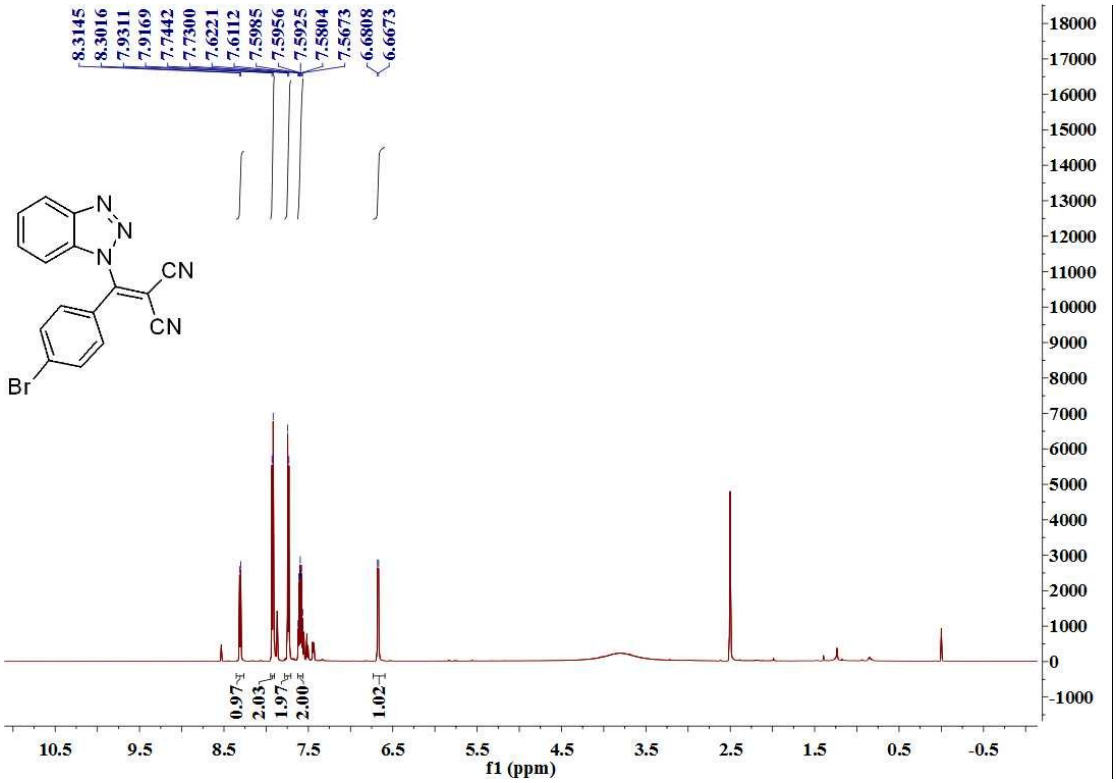

166.8873
165.1973
159.0316
146.6282
134.3555
134.2907
132.4337
130.7846
126.8746
121.2171
117.6532
117.5034
113.7981
113.1631
113.0378
76.9119
N
N
N
CN
CN
F
f1 (ppm)

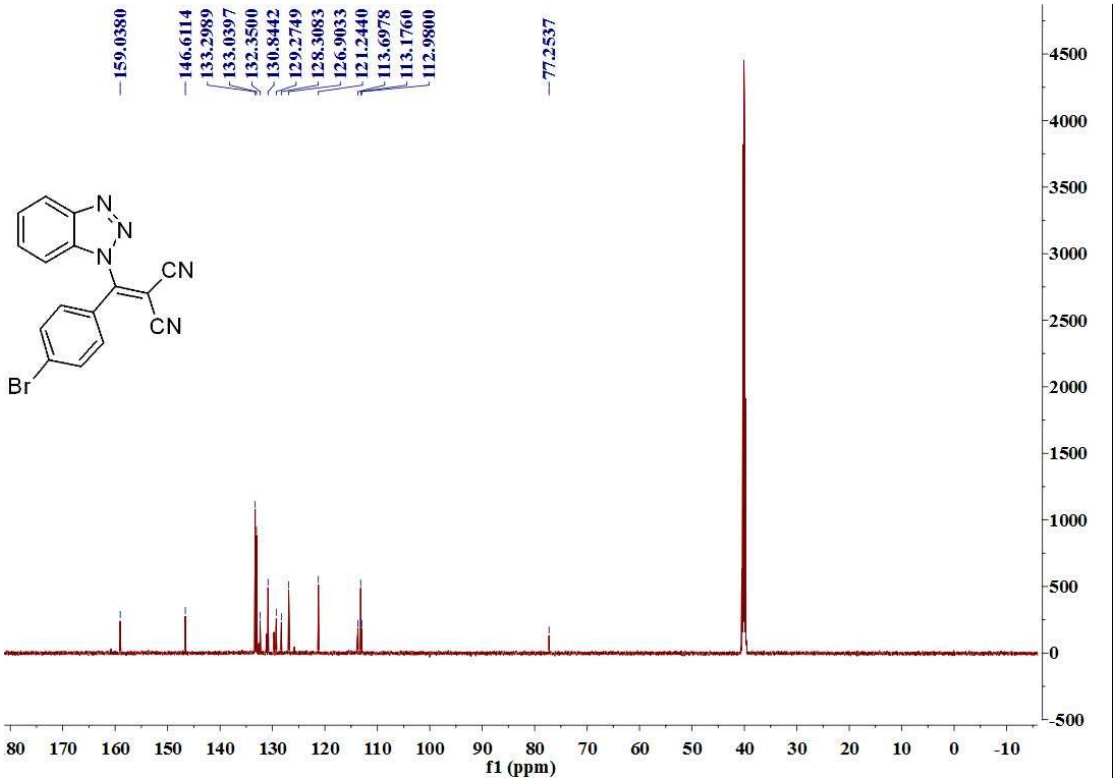
3ag


8.3199
8.3076
7.8390
7.8279
7.8246
7.7961
7.7928
7.7817
7.6096
7.5966
7.5937
7.5823
6.6871
6.6545
N
N
N
CN
CN
Cl
1.00
4.02
2.20
1.00
f1 (ppm)

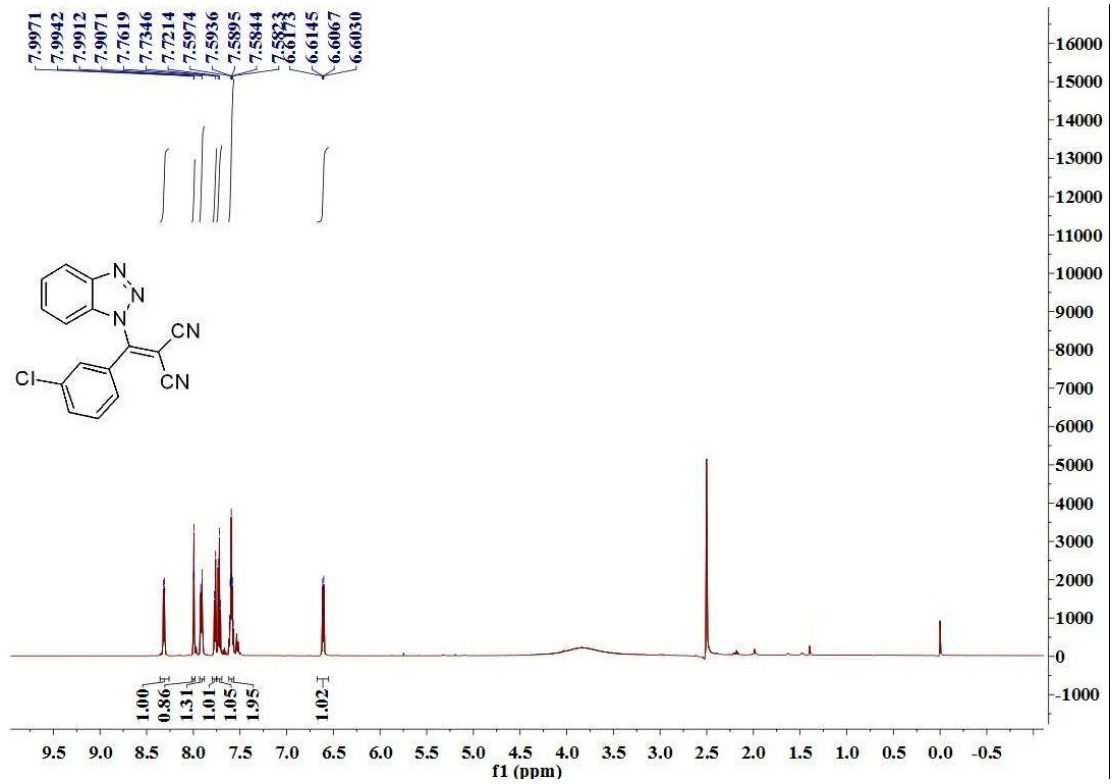

158.9141
146.6141
140.0947
133.0435
130.8430
130.3597
129.5168
128.2358
126.9065
121.2416
113.6973
113.1836
112.9869
77.2743
N
N
N
CN
CN
Cl
f1 (ppm)

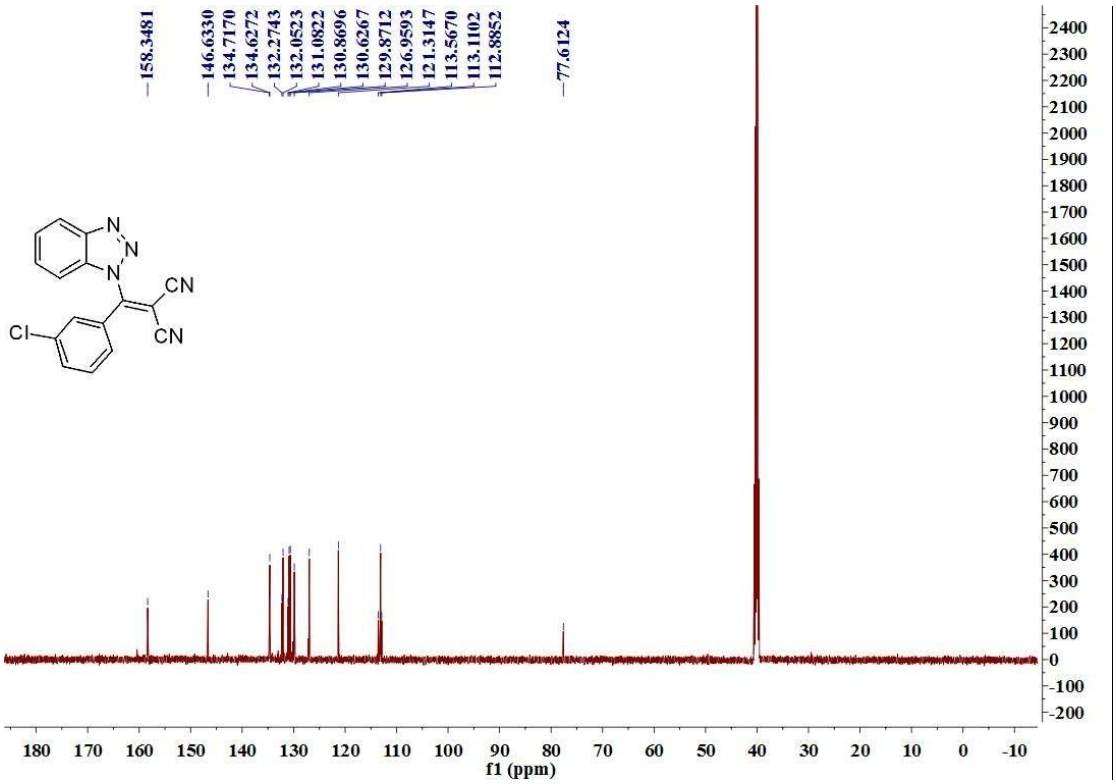
3ah


8.3145
8.3016
7.9311
7.9169
7.7442
7.7300
7.6221
7.6112
7.5985
7.5956
7.5925
7.5804
7.5673
6.6808
6.6673
N
N
N
CN
CN
Br
0.97
2.03
1.97
2.00
1.02
f1 (ppm)

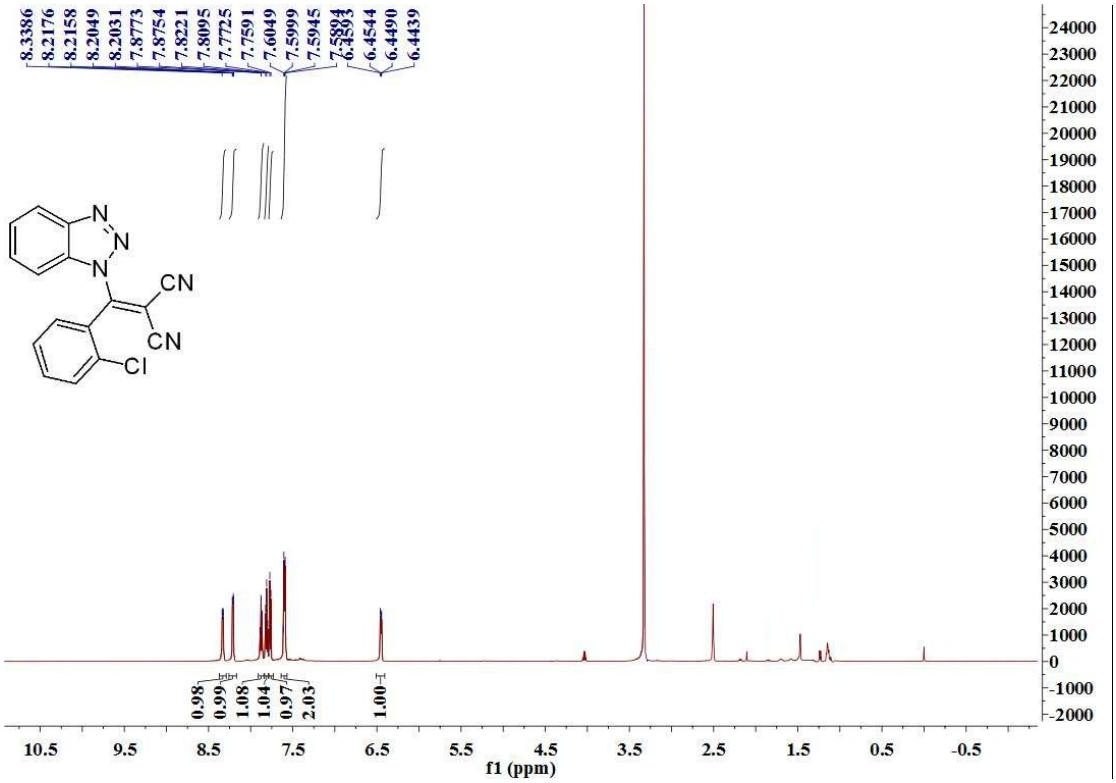

159.0380
146.6114
133.2989
133.0397
132.3500
130.8442
129.2749
128.3083
126.9033
121.2440
113.6978
113.1760
112.9800
77.2537
N
N
N
CN
CN
Br
f1 (ppm)

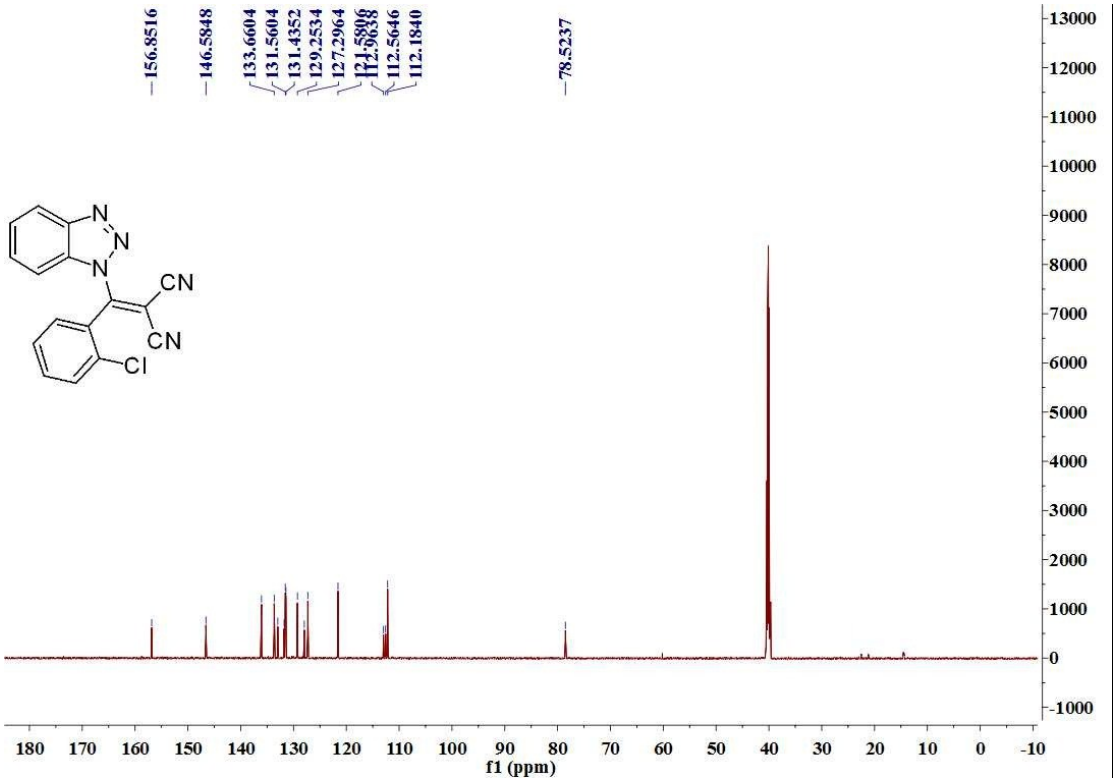
3ai


7.9971
7.9942
7.9912
7.9071
7.7619
7.7346
7.7214
7.5974
7.5936
7.5895
7.5844
7.5823
6.6173
6.6145
6.6067
6.6030
N
N
N
CN
CN
Cl
1.00
0.86
1.31
1.01
1.05
1.95
1.02
f1 (ppm)

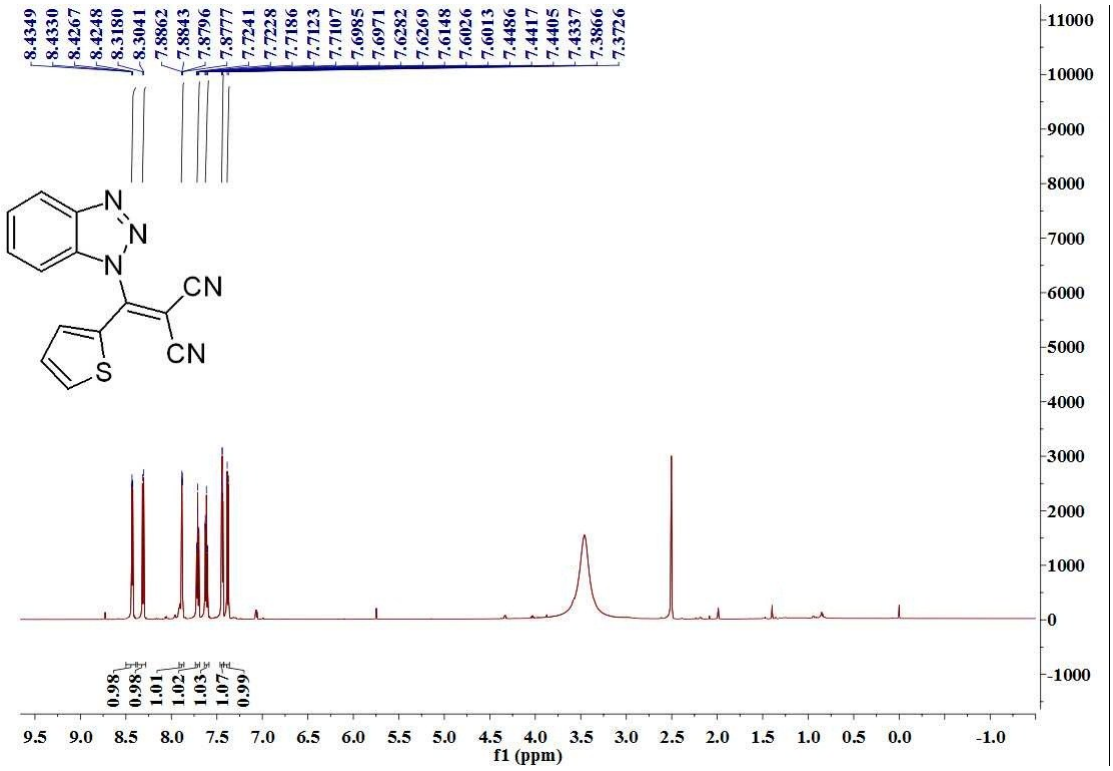

158.3481
146.6330
134.7170
134.6272
132.2743
132.0523
131.0822
130.8696
130.6267
129.8712
126.9593
121.3147
113.5670
113.1102
112.8852
77.6124
N
N
N
CN
CN
Cl
f1 (ppm)

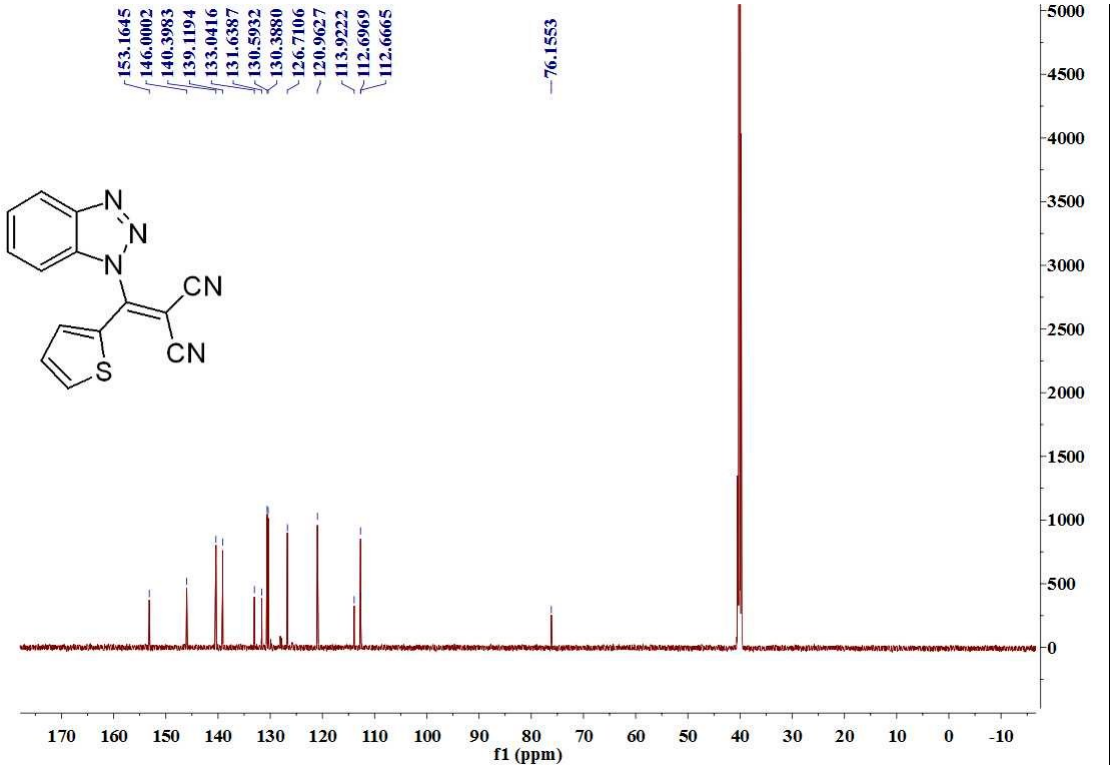
3aj


8.3386
8.2176
8.2158
8.2049
8.2031
7.8773
7.8754
7.8221
7.8095
7.7725
7.7591
7.6049
7.5999
7.5945
6.4544
6.4490
6.4439
0.98
0.99
1.08
1.04
0.97
2.03
1.00
f1 (ppm)

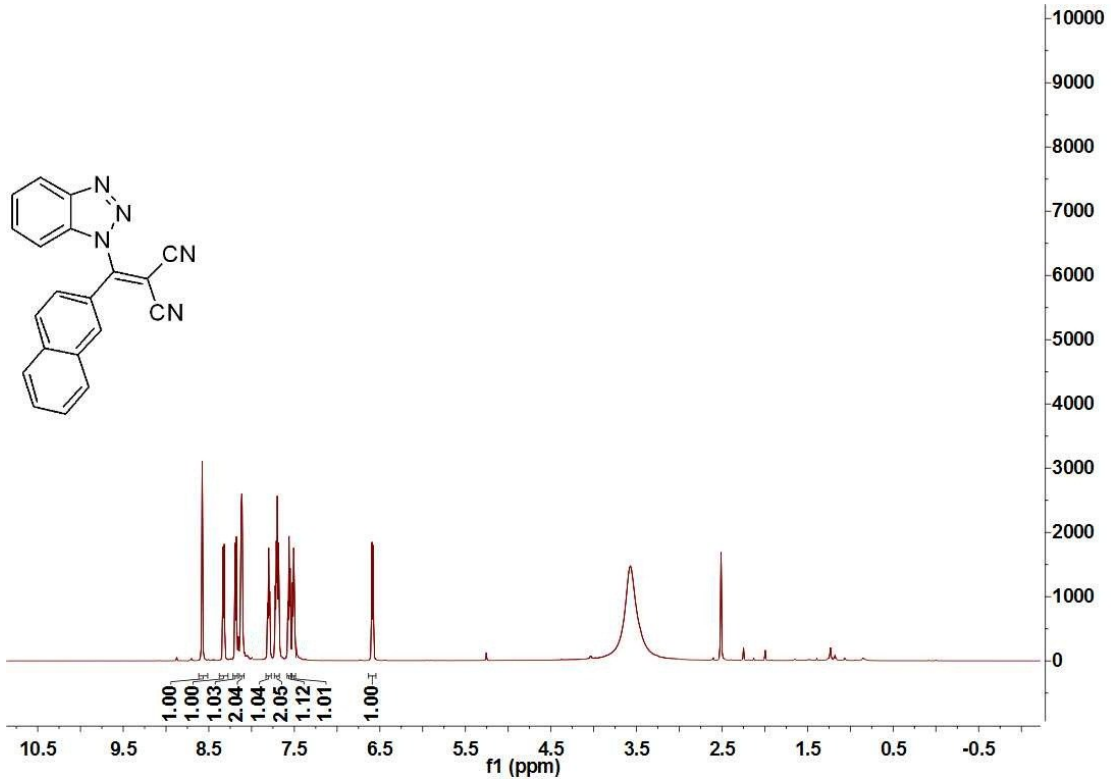

156.8516
146.5848
133.6604
131.5604
131.4352
129.2534
127.2964
112.5646
112.1840
78.5237
f1 (ppm)

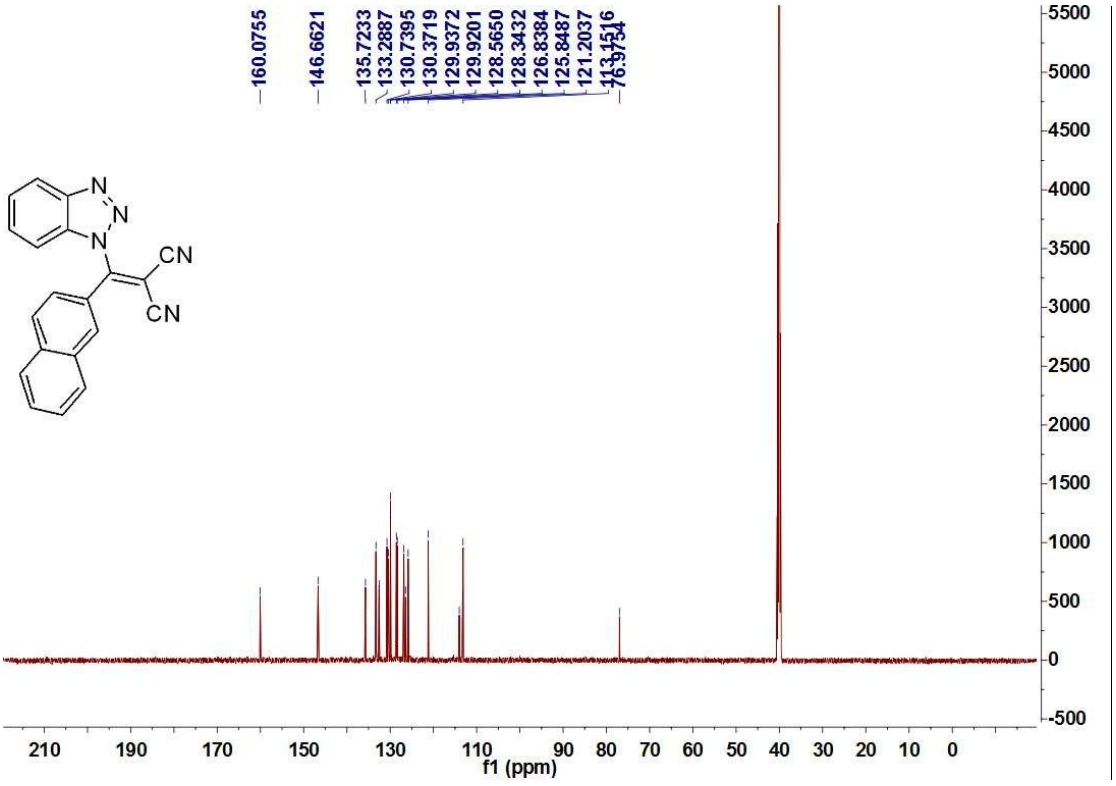
3ak


8.4349
8.4330
8.4267
8.4248
8.3180
8.3041
7.8862
7.8843
7.8796
7.8777
7.7241
7.7228
7.7186
7.7123
7.7107
7.6985
7.6971
7.6282
7.6269
7.6148
7.6026
7.6013
7.4486
7.4417
7.4405
7.4337
7.3866
7.3726
N
N
N
CN
CN
S
0.98
0.98
1.01
1.02
1.03
1.07
0.99
f1 (ppm)

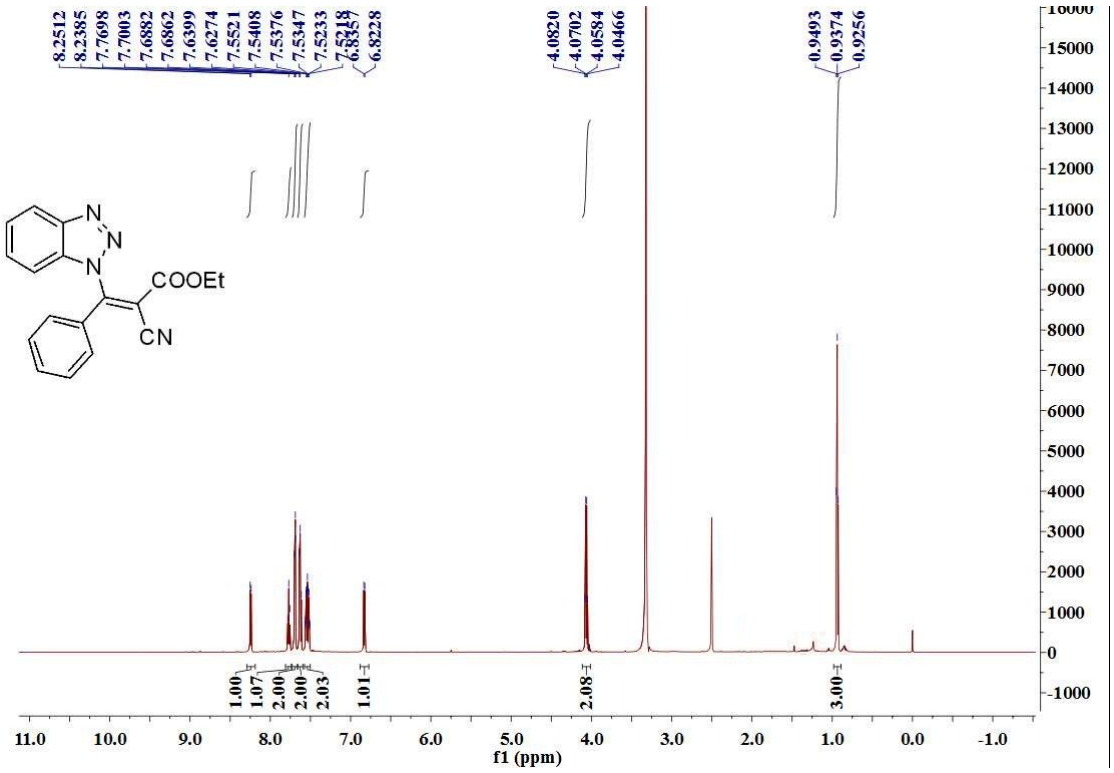

153.1645
146.0002
140.3983
139.1194
133.0416
131.6387
130.5932
130.3880
126.7106
120.9627
113.9222
112.6969
112.6665
76.1553
N
N
N
CN
CN
S
f1 (ppm)

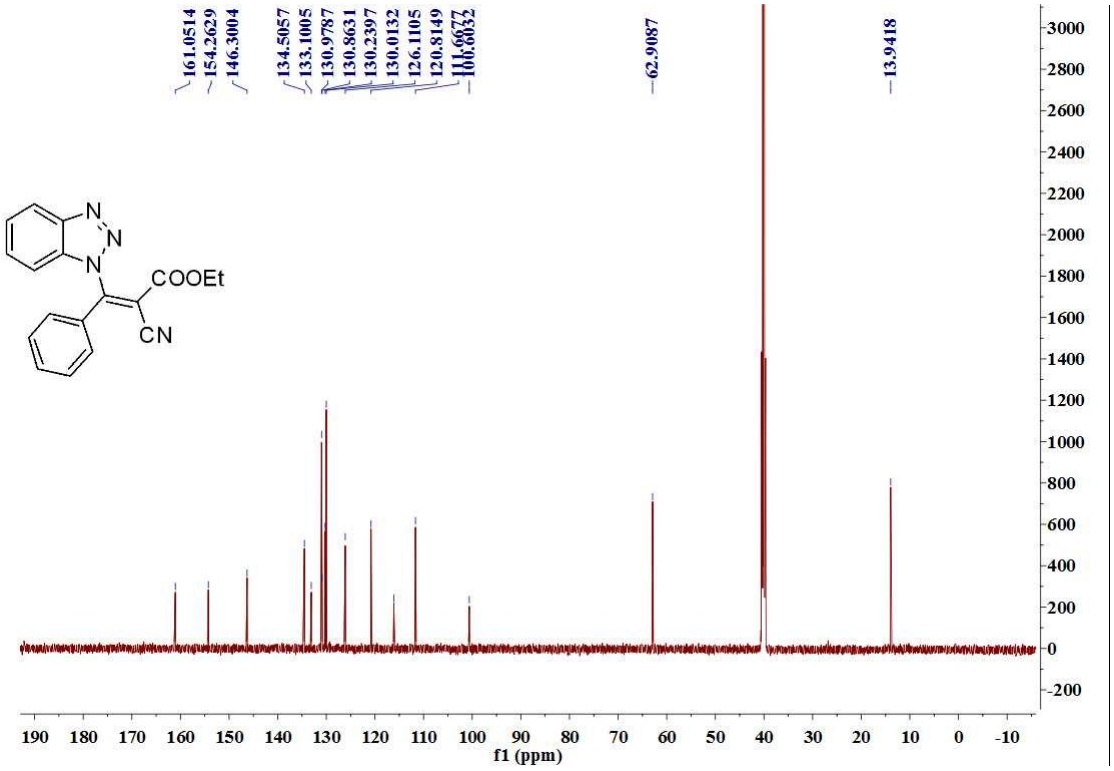
3al


N
N
N
CN
CN
1.00
1.00
1.03
2.04
1.04
2.05
1.12
1.01
1.00
10.5
9.5
8.5
7.5
6.5
5.5
4.5
3.5
2.5
1.5
0.5
-0.5
f1 (ppm)
10000
9000
8000
7000
6000
5000
4000
3000
2000
1000
0


160.0755
146.6621
135.7233
133.2887
130.7395
130.3719
129.9372
129.9201
128.5650
128.3432
126.8384
125.8487
121.2037
113.1516
76.9734
N
N
N
CN
CN
210
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
f1 (ppm)
5500
5000
4500
4000
3500
3000
2500
2000
1500
1000
500
0
-500

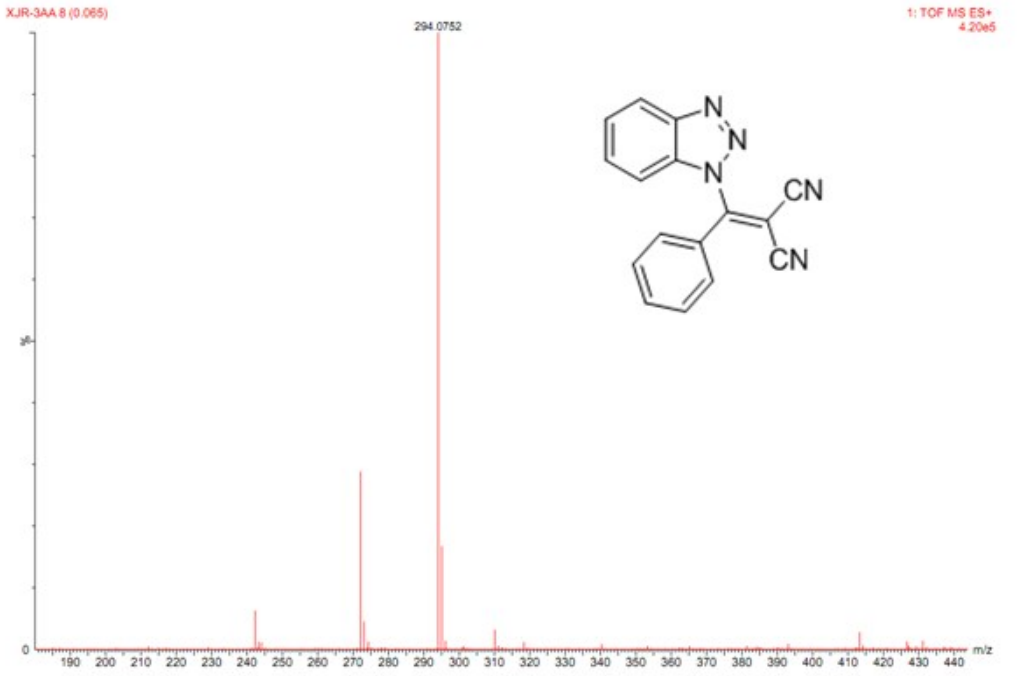
3am


8.2512
8.2385
7.7698
7.7003
7.6882
7.6862
7.6399
7.6274
7.5521
7.5408
7.5376
7.5347
7.5233
7.5218
6.8357
6.8228
4.0820
4.0702
4.0584
4.0466
0.9493
0.9374
0.9256
COOEt
CN
1.00
1.07
2.00
2.00
2.03
1.01
2.08
3.00
f1 (ppm)

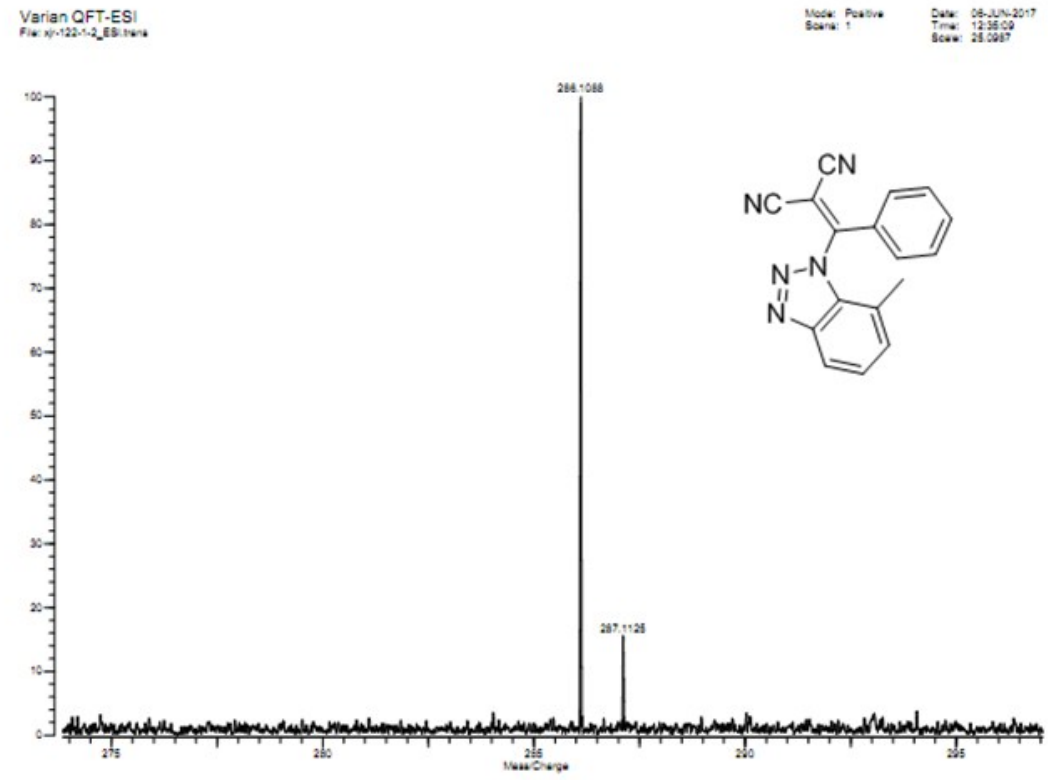

161.0514
154.2629
146.3004
134.5057
133.1005
130.9787
130.8631
130.2397
130.0132
126.1105
120.8149
111.6677
100.6032
62.9087
13.9418
COOEt
CN
f1 (ppm)

10. HRMS of products

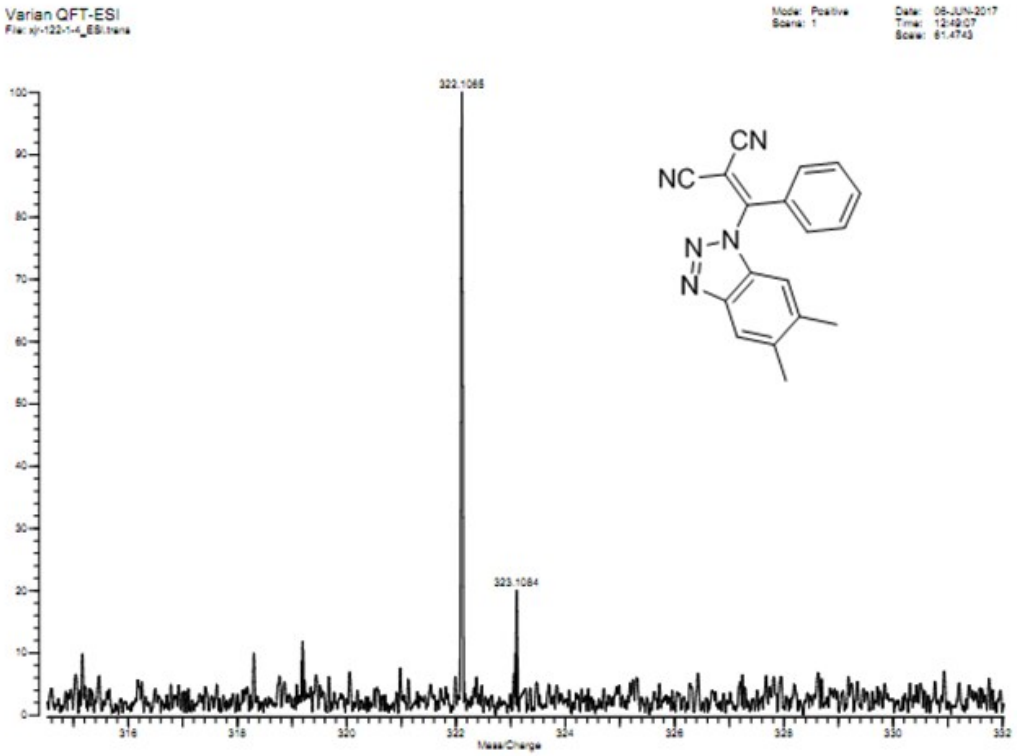
3aa



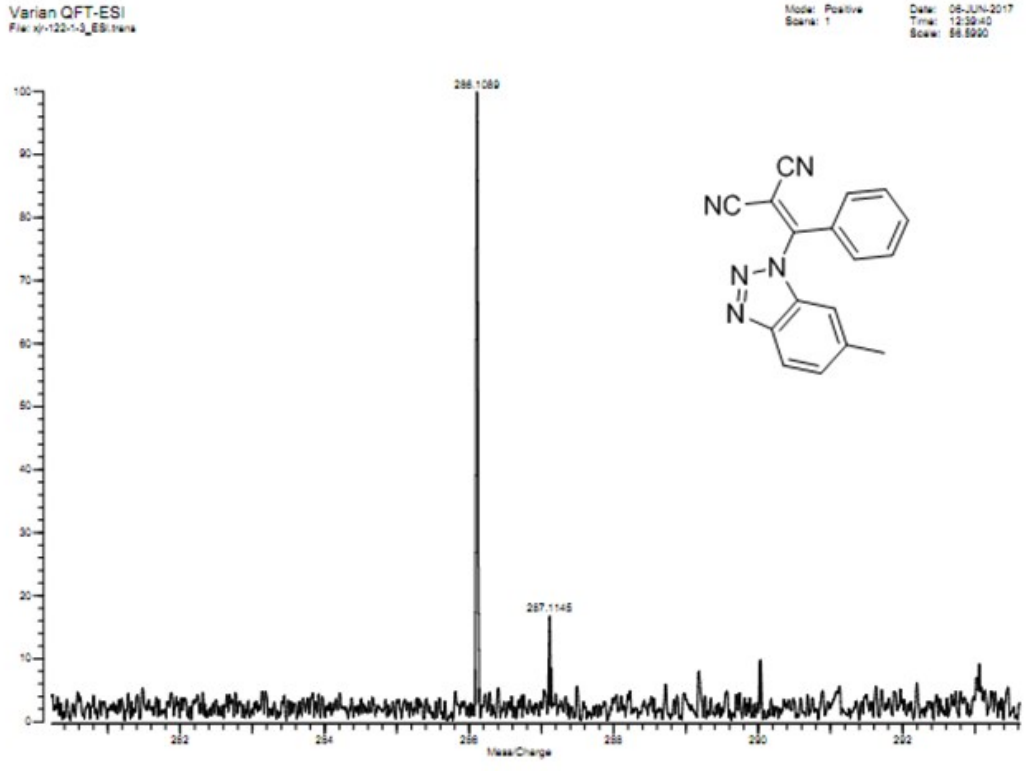
3ba



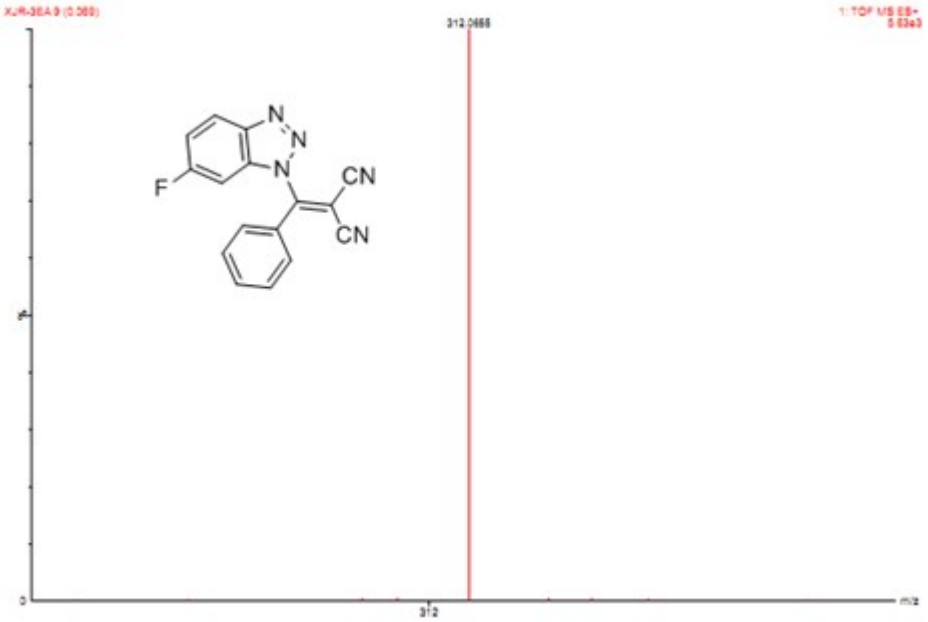
3ca


Varian QFT-ESI
322.1066
323.1084
CN
NC
N
N
N
Mass/Charge

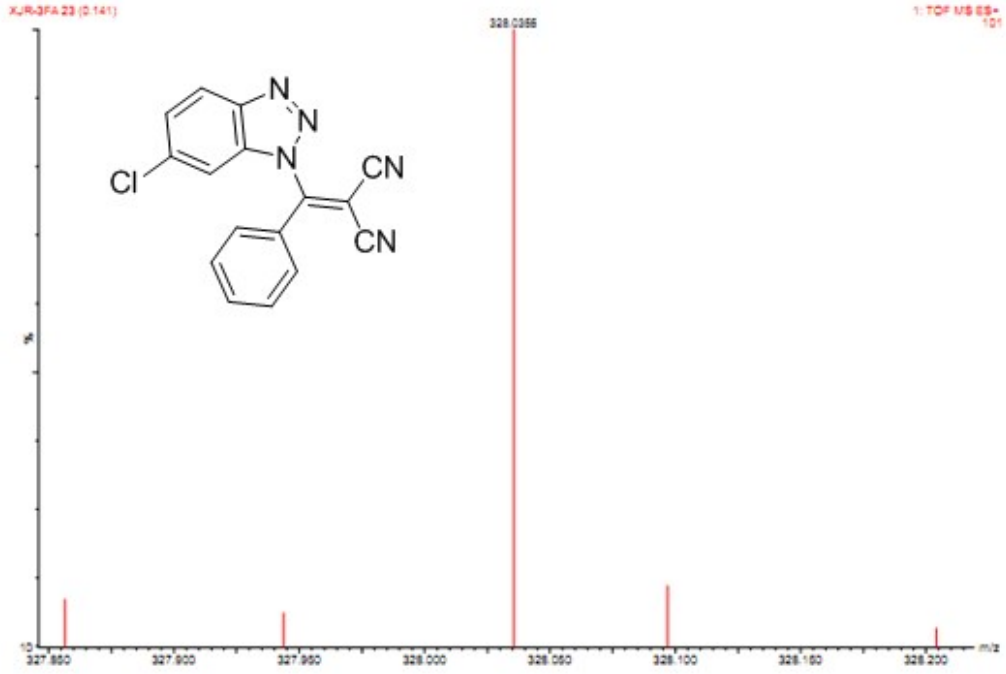
3da


Varian QFT-ESI
286.1089
287.1145
CN
NC
N
N
N
Mass/Charge

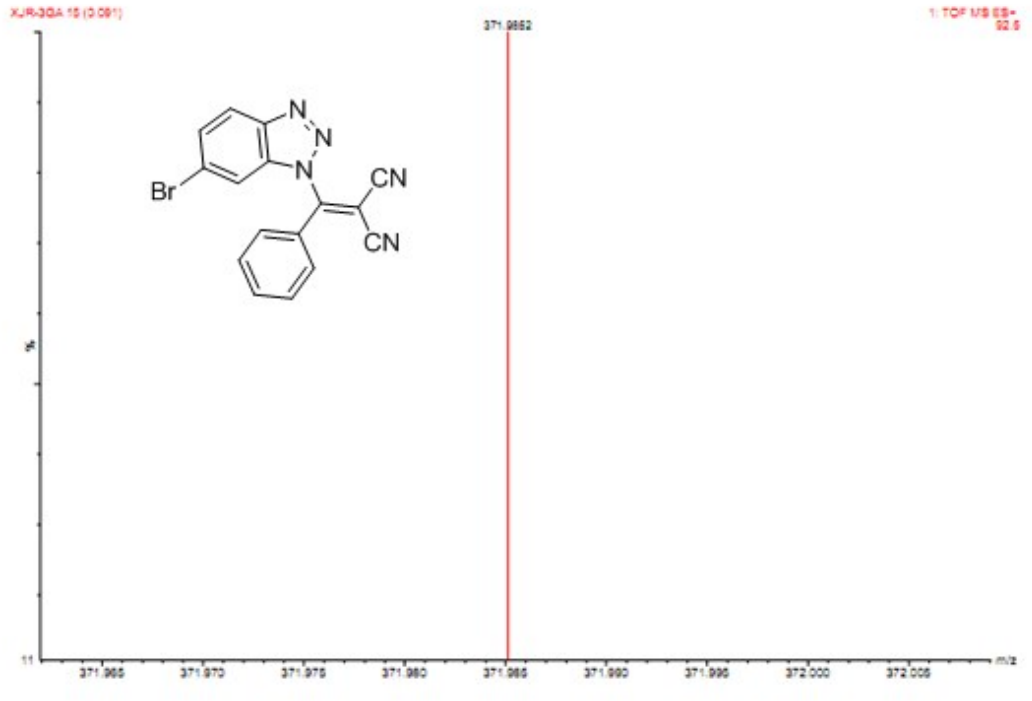
3ea


312.0466
N
N
N
F
CN
CN
%
0
312
m/z

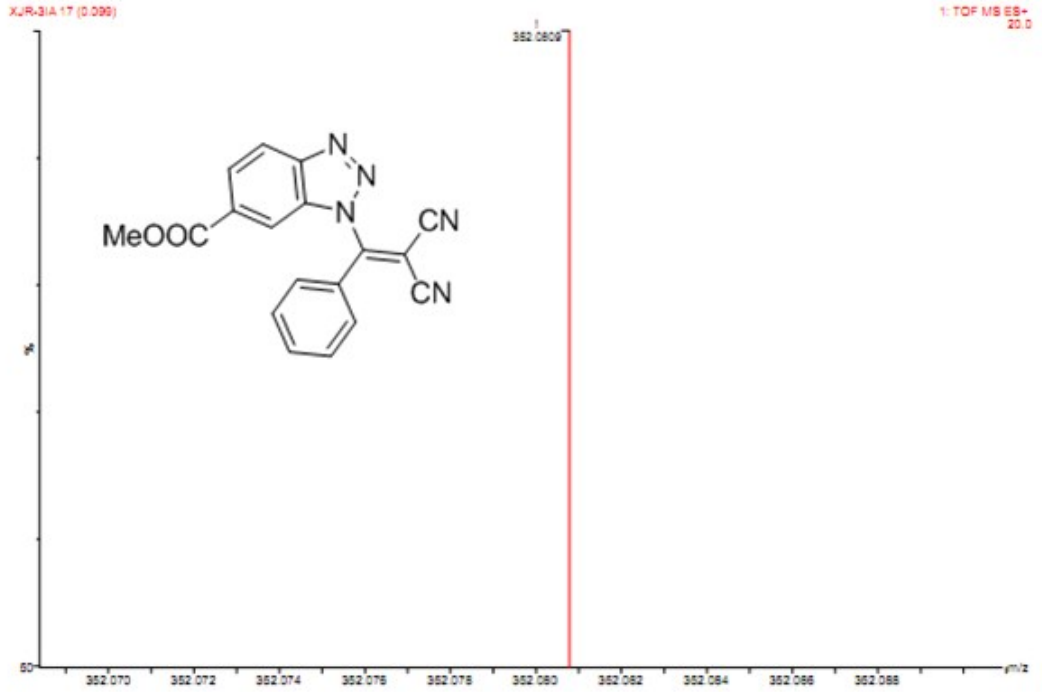
3fa


328.0366
N
N
N
Cl
CN
CN
%
327.850
327.900
327.950
328.000
328.050
328.100
328.150
328.200
m/z

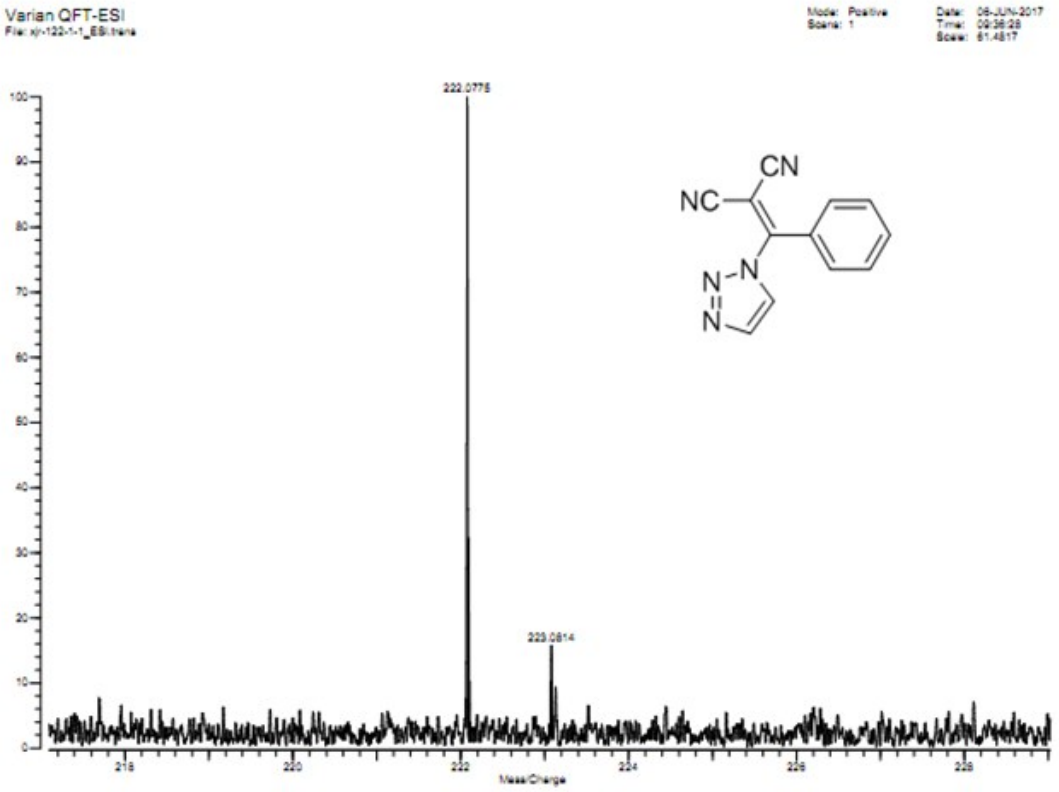
3ga


XJR-3GA 15 (0.091)
1: TOF MS ES+
92.6
371.9852
Br
N
N
N
CN
CN
%
11
371.965
371.970
371.975
371.980
371.985
371.990
371.995
372.000
372.005
m/z

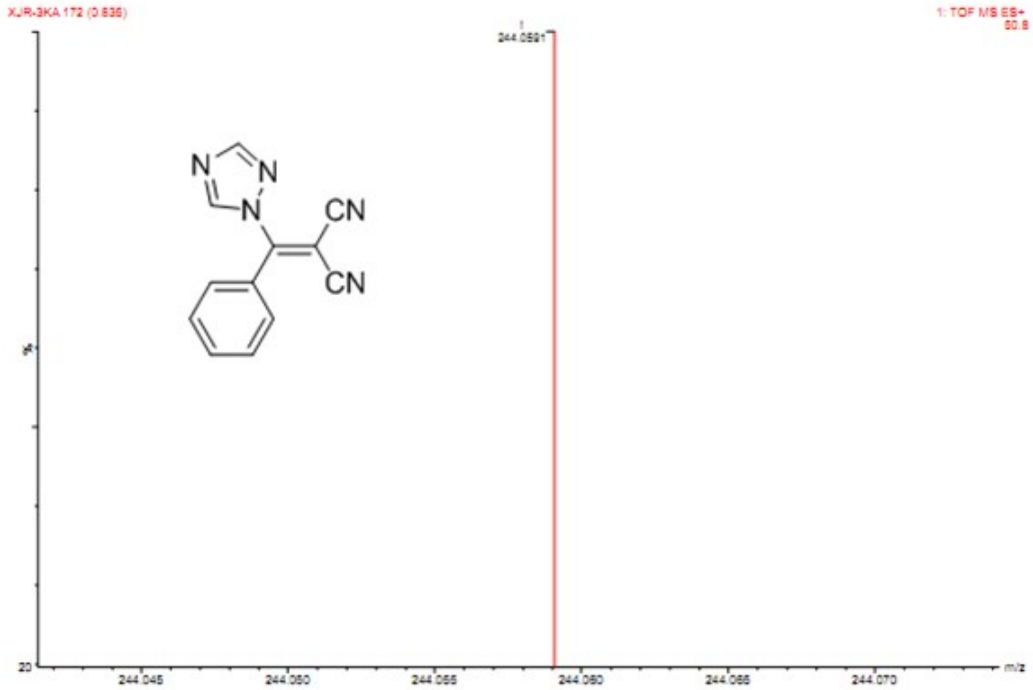
3ha


XJR-3IA 17 (0.099)
1: TOF MS ES+
20.0
352.0809
MeOOC
N
N
N
CN
CN
%
60
352.070
352.072
352.074
352.076
352.078
352.080
352.082
352.084
352.086
352.088
m/z

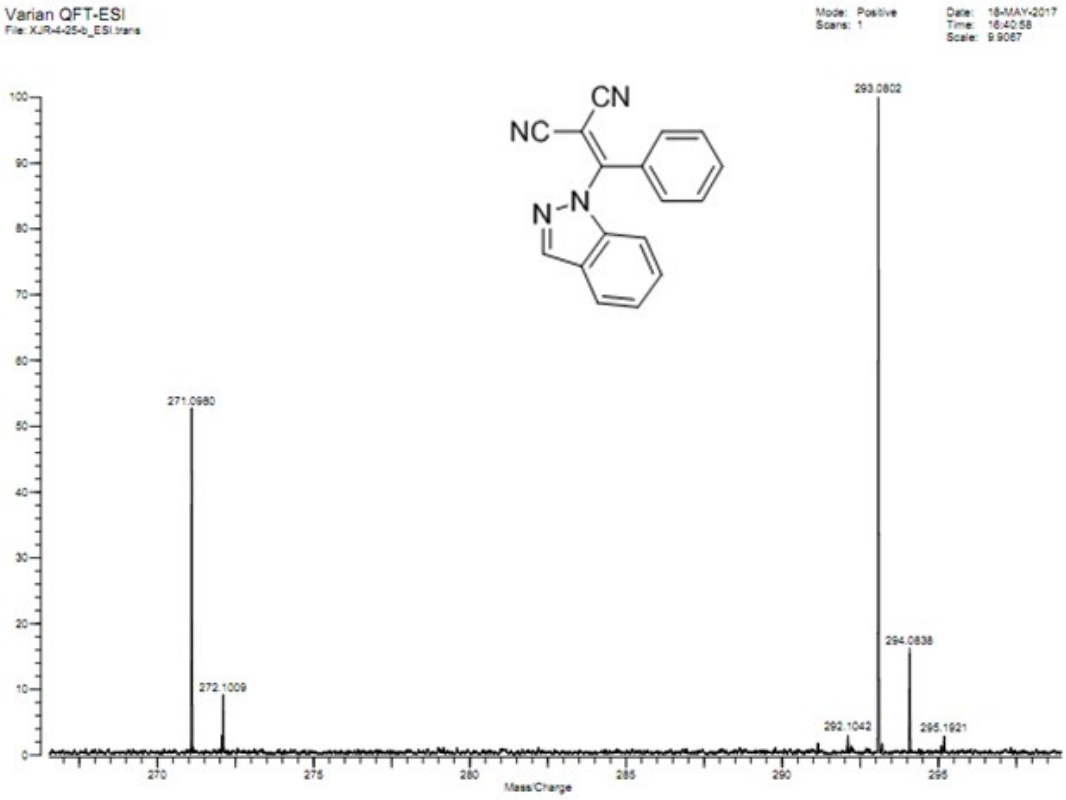
3ia


Varian QFT-ESI
222.0775
223.0814
CN
NC
N
N
N
Mass/Charge

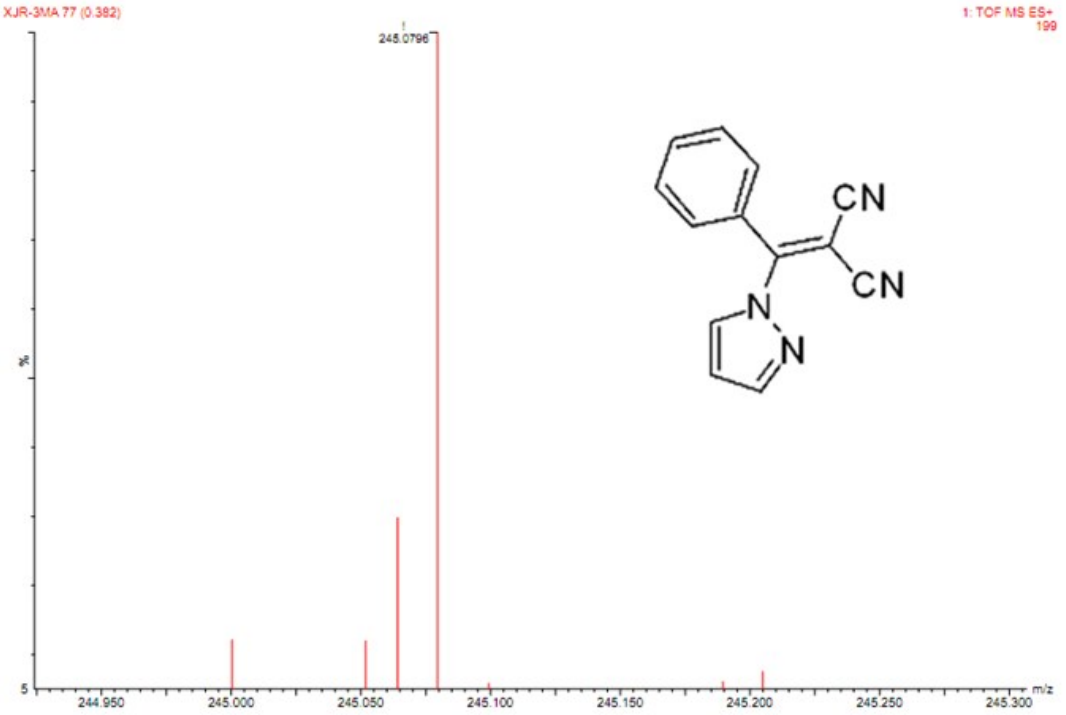
3ja


XJR-3KA 172 (0.836)
1: TOF MS ES+
244.0591
N
N
N
CN
CN
%
m/z

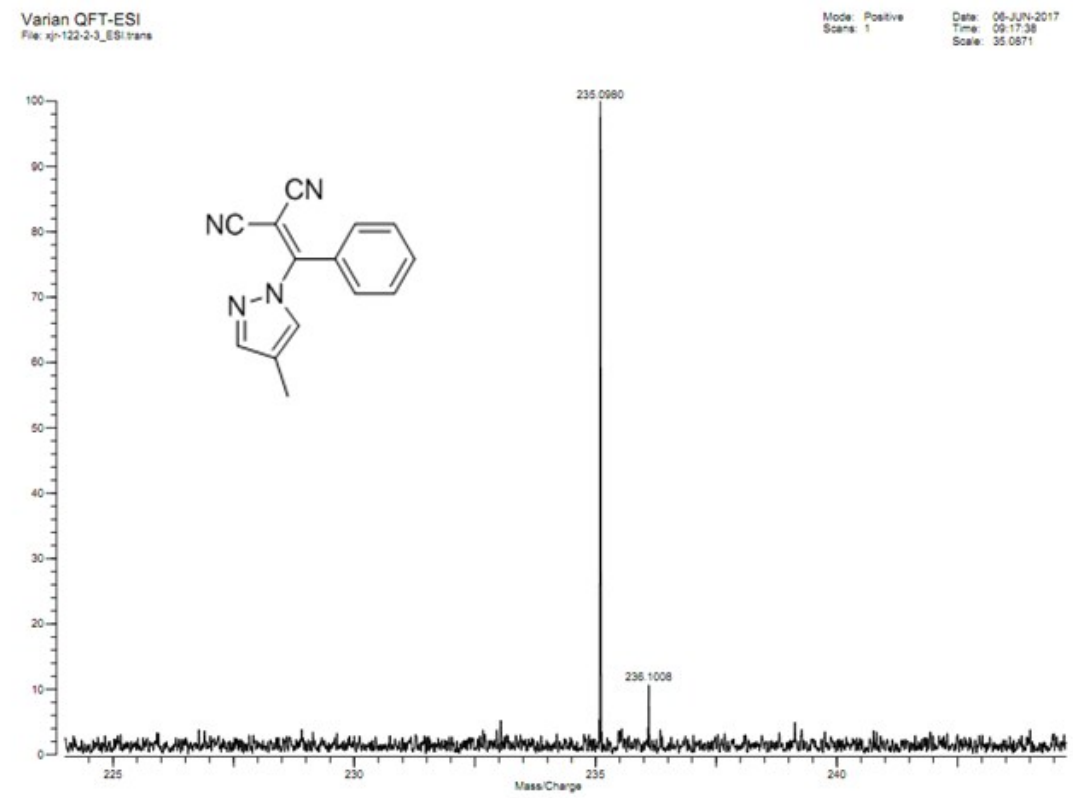
3ka


Varian QFT-ESI
File: XJR-4-254b_ESI.trans
Mode: Positive
Scans: 1
Date: 18-MAY-2017
Time: 16:40:58
Scale: 9.9067
CN
NC
N
N
293.0802
271.0980
294.0838
272.1009
292.1042
295.1921
Mass/Charge

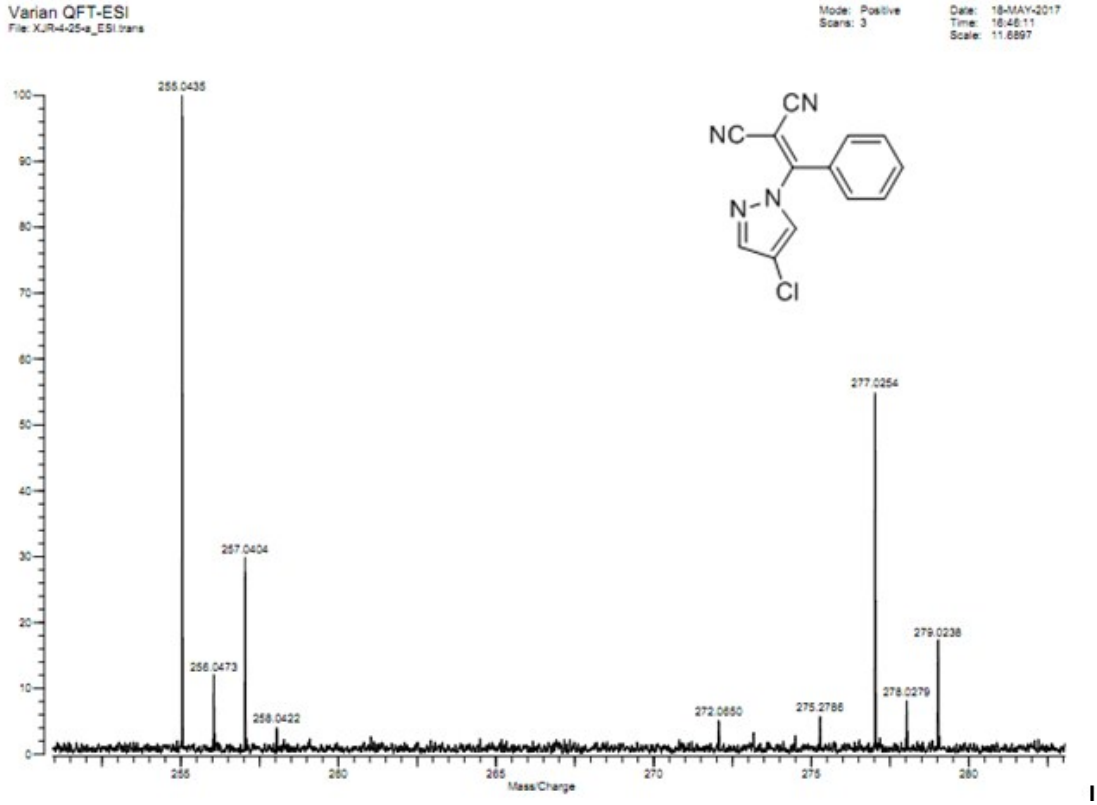
3la


XJR-3MA 77 (0.382)
1: TOF MS ES+
199
245.0796
CN
CN
N
N
%
m/z

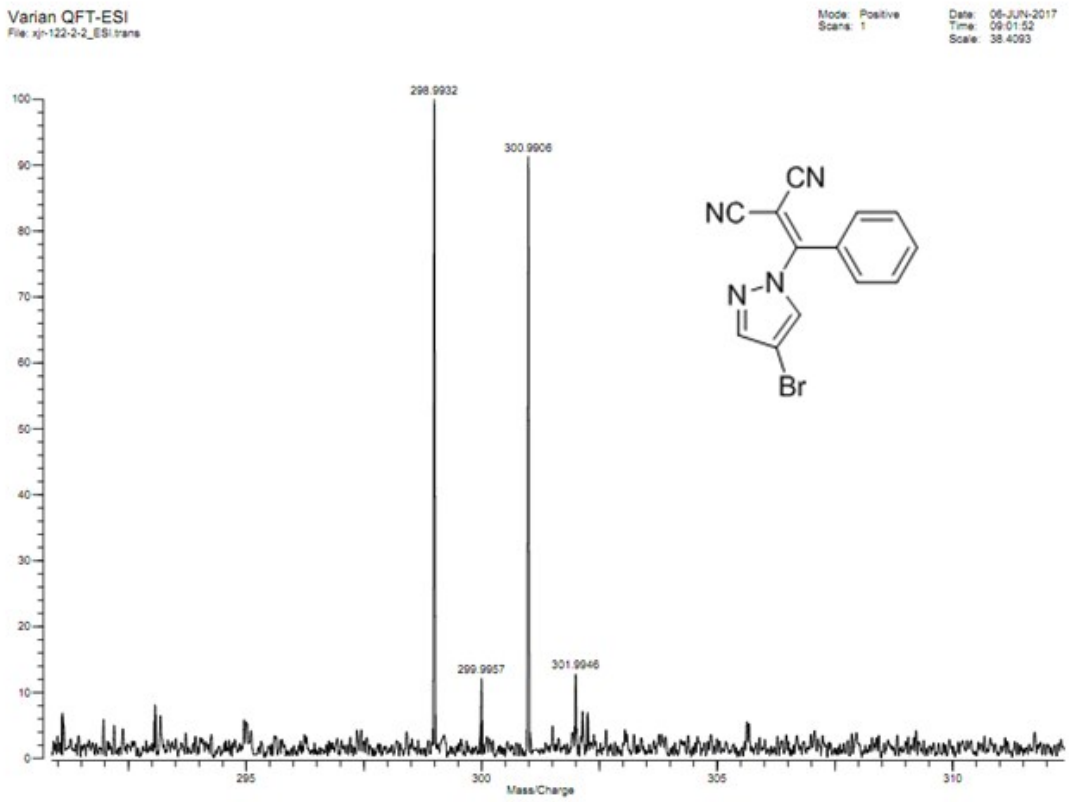
3ma


Varian QFT-ESI
File: xjn-122-2-3_ESI.trans
Mode: Positive
Scans: 1
Date: 06-JUN-2017
Time: 09:17:38
Scale: 35.0871
235.0980
236.1008
CN
NC
N-N
Mass/Charge

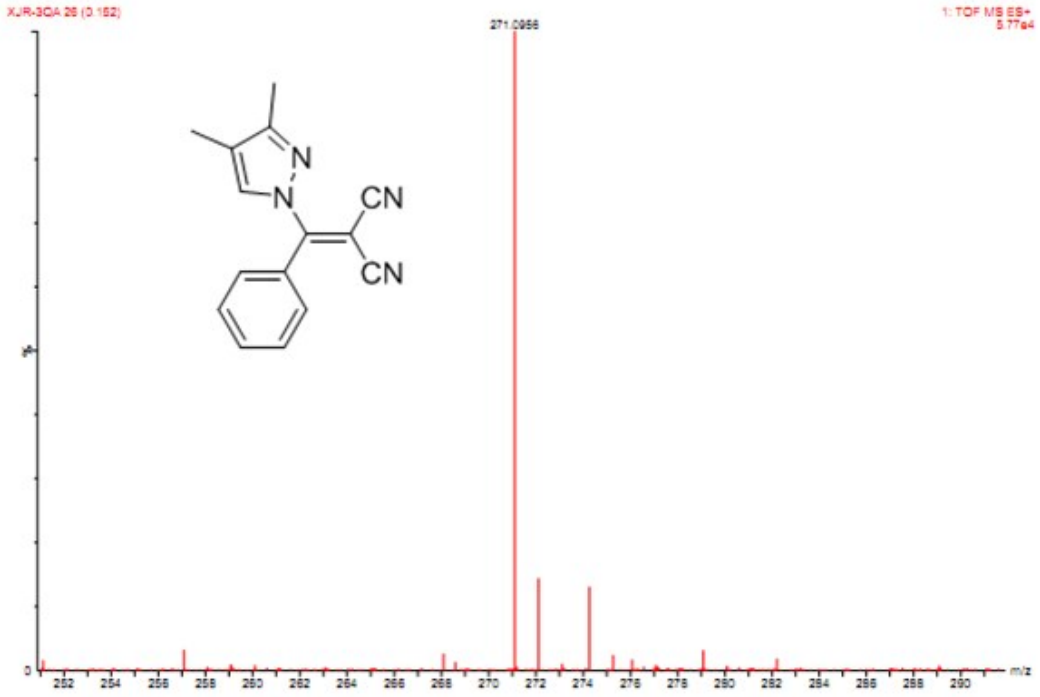
3na


Varian QFT-ESI
File: XJR4-25-e_ESI.trans
Mode: Positive
Scans: 3
Date: 18-MAY-2017
Time: 16:46:11
Scale: 11.6897
255.0435
257.0404
256.0473
258.0422
272.0650
275.2786
277.0254
278.0279
279.0238
CN
NC
N-N
Cl
Mass/Charge

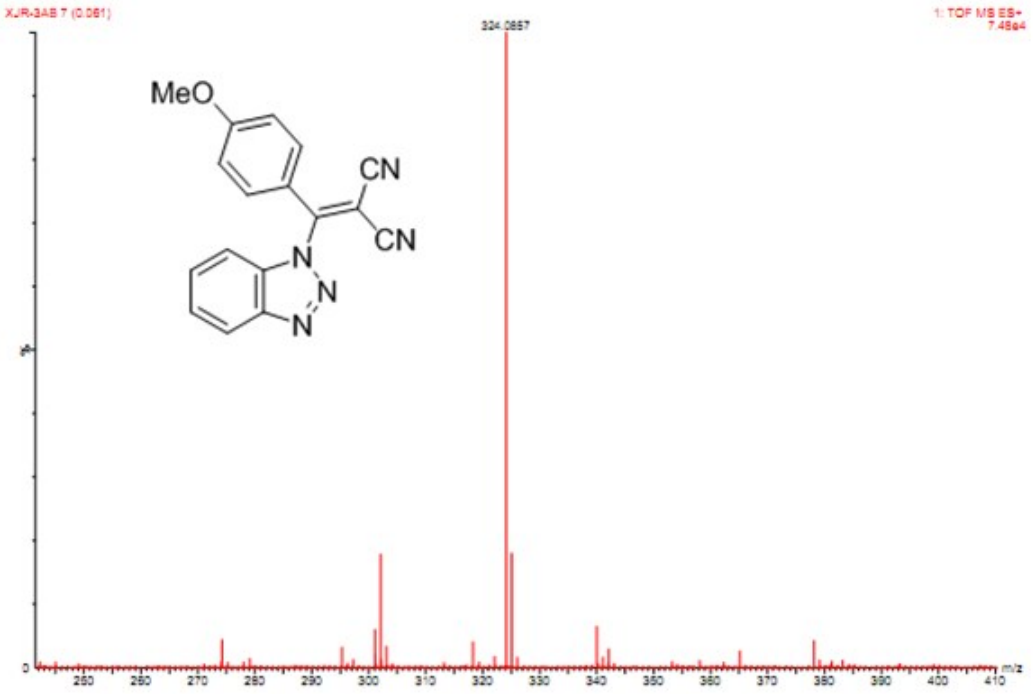
3oa


Varian QFT-ESI
Mode: Positive
Scans: 1
Date: 06-JUN-2017
Time: 09:01:52
Scale: 38.4093
298.9932
300.9906
299.9957
301.9946
CN
NC
N
N
Br
Mass/Charge

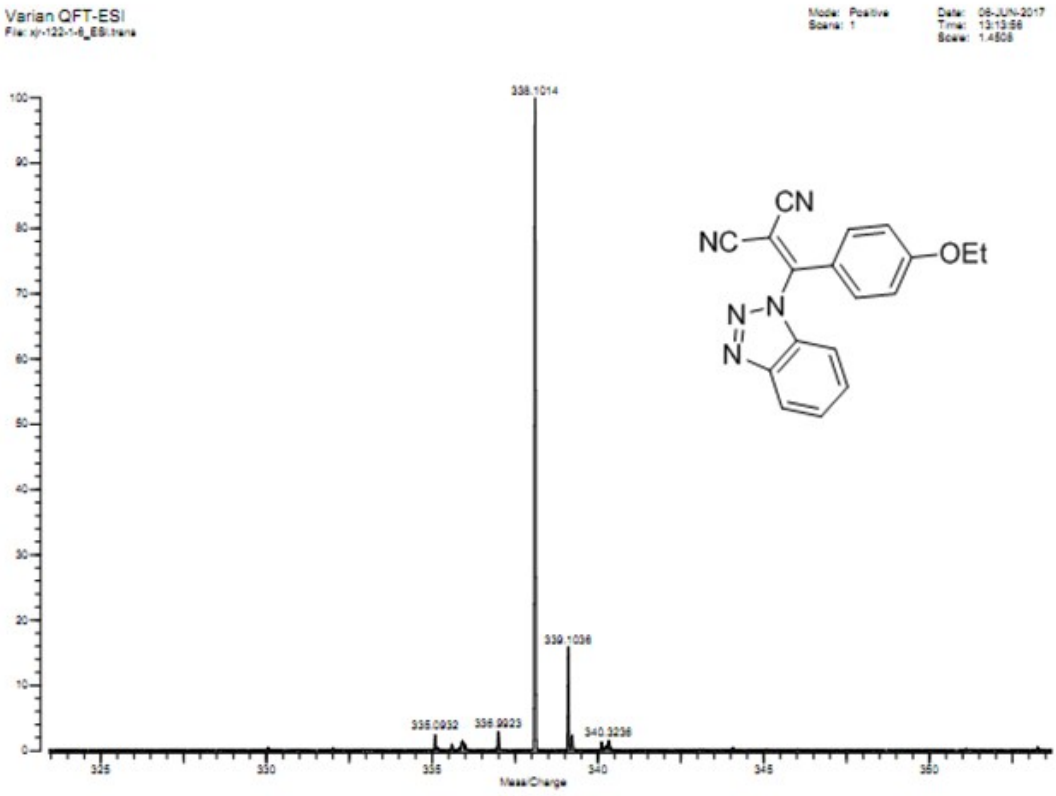
3pa


271.0956
N
N
CN
CN
m/z

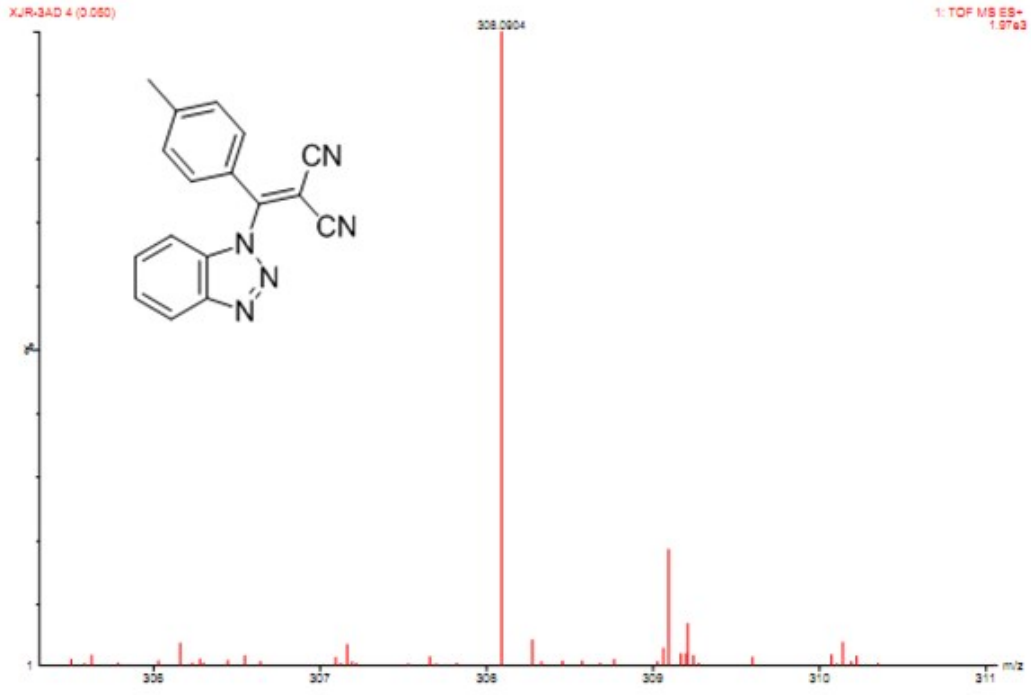
3ab


XJR-3AB 7 (0.061)
1: TOF MS ES+
7.48e4
324.0857
MeO
CN
CN
N
N
N
%
0
260
270
280
290
300
310
320
330
340
350
360
370
380
390
400
410
m/z

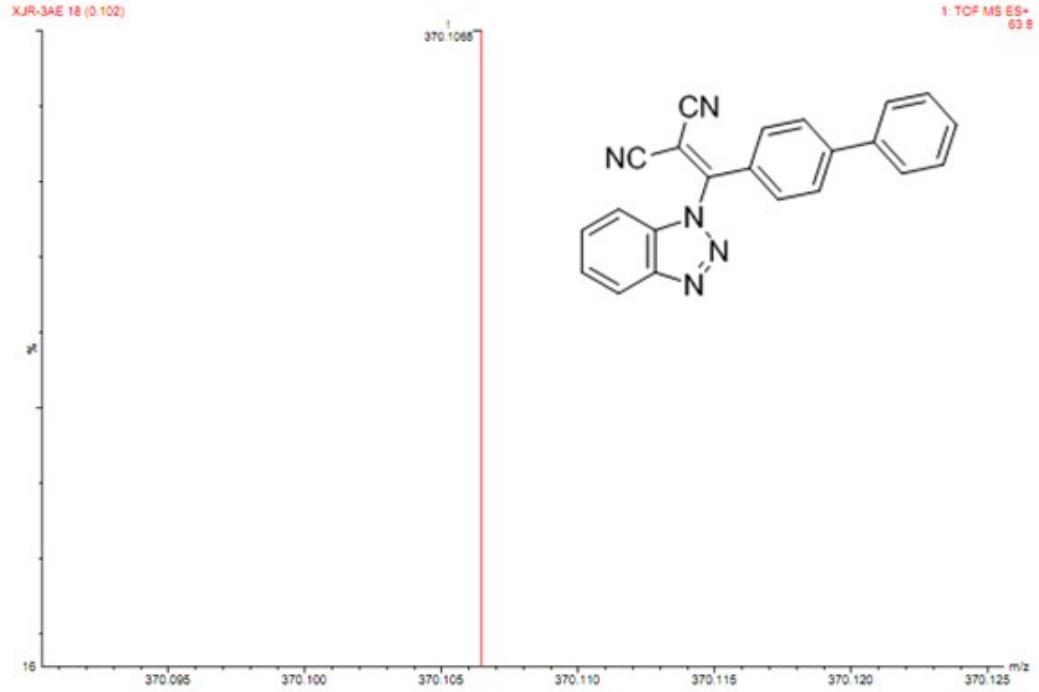
3ac


Varian QFT-ESI
Mode: Positive
Scans: 1
Date: 06-JUN-2017
Time: 13:13:56
Scan: 1.4808
338.1014
339.1036
336.0932
336.9923
340.3236
CN
NC
OEt
N
N
N
100
90
80
70
60
50
40
30
20
10
0
325
330
335
340
345
350
Mass/Charge

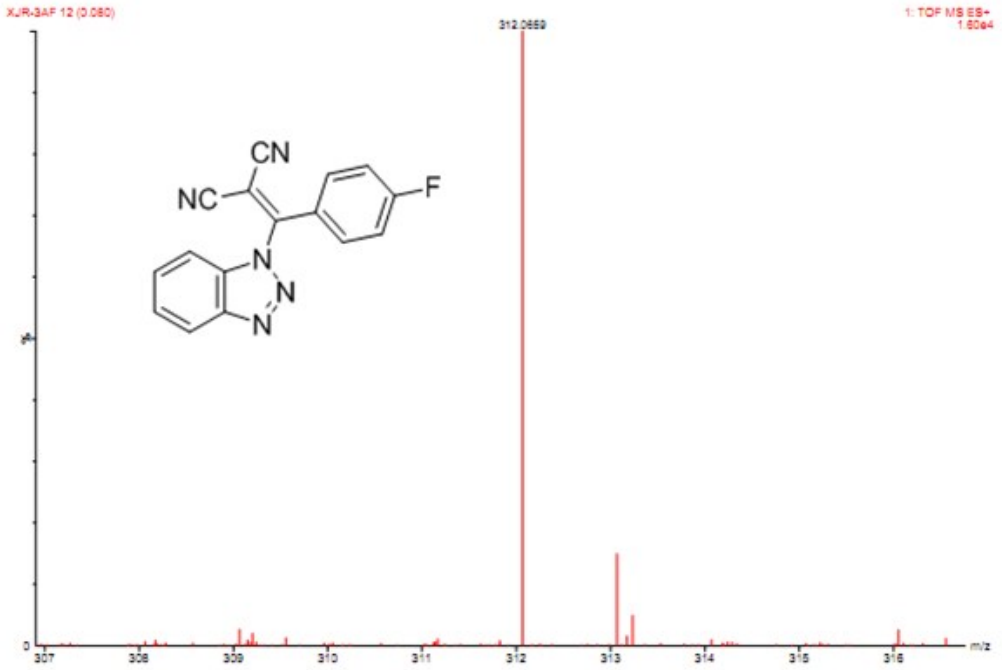
3ad


XJR-3AD 4 (0.060)
1: TOF MS ES+
1.97e3
308.0904
CN
CN
N
N
N
%
1
308
307
308
309
310
311
m/z

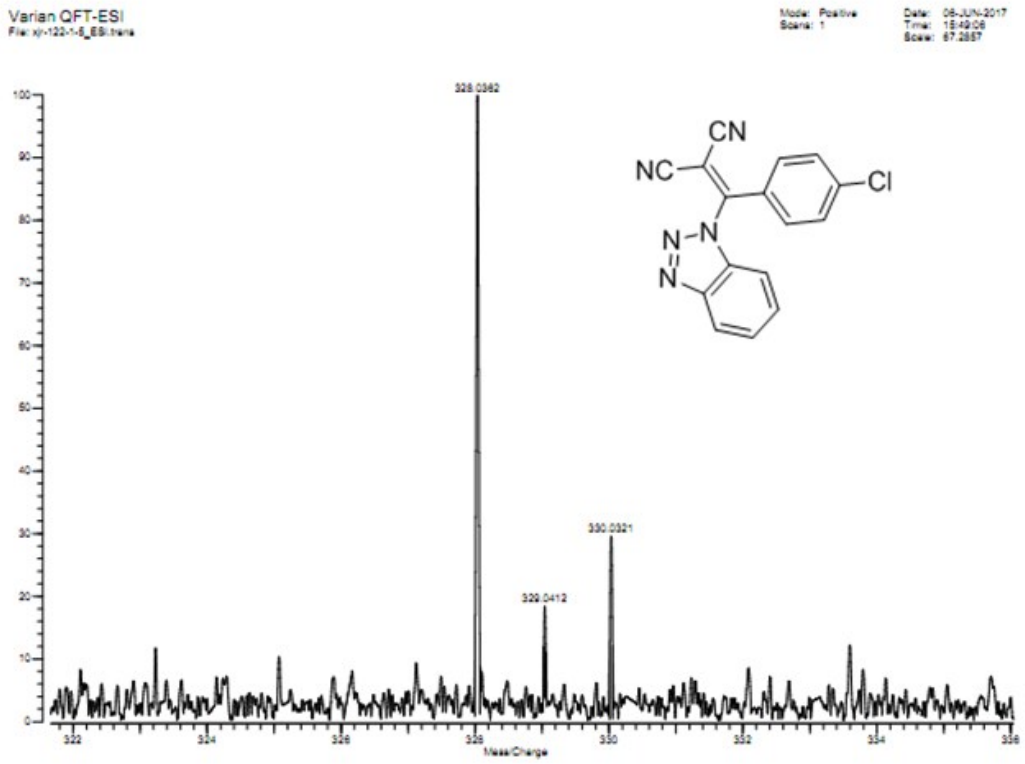
3ae


XJR-3AE 18 (0.102)
1: TOF MS ES+
63.8
370.1068
CN
NC
N
N
N
%
16
370.095
370.100
370.105
370.110
370.115
370.120
370.125
m/z

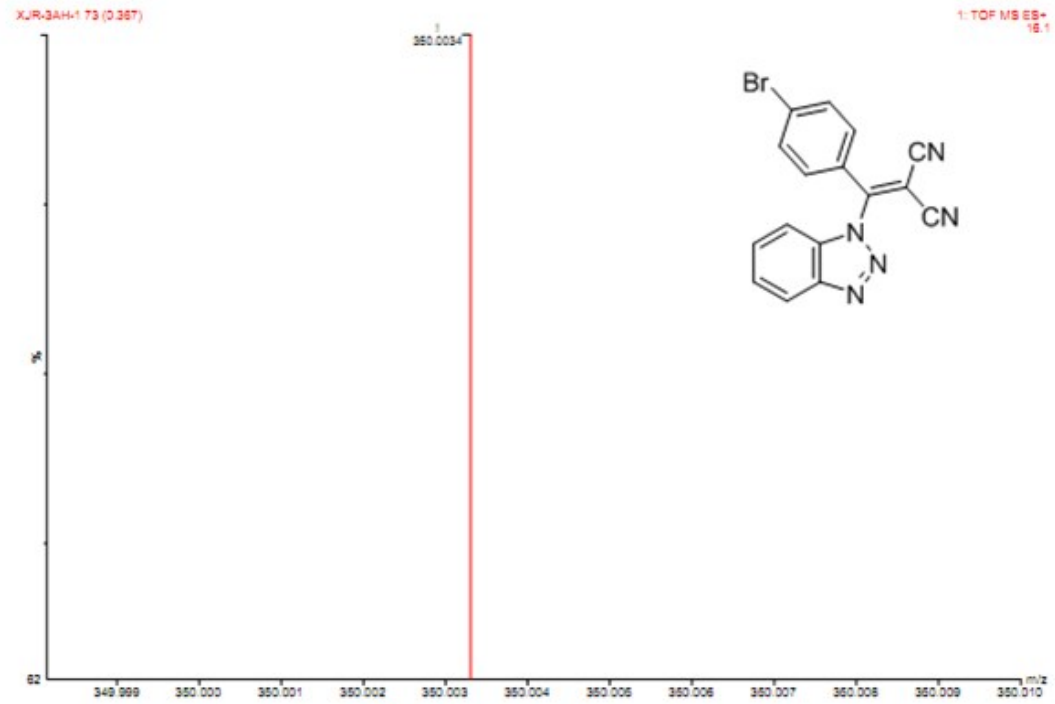
3af


XJR-3AF 12 (0.080)
1: TOF MS ES+
1.60e4
312.0659
CN
NC
F
N
N
N
%
0
307
308
309
310
311
312
313
314
315
316
m/z

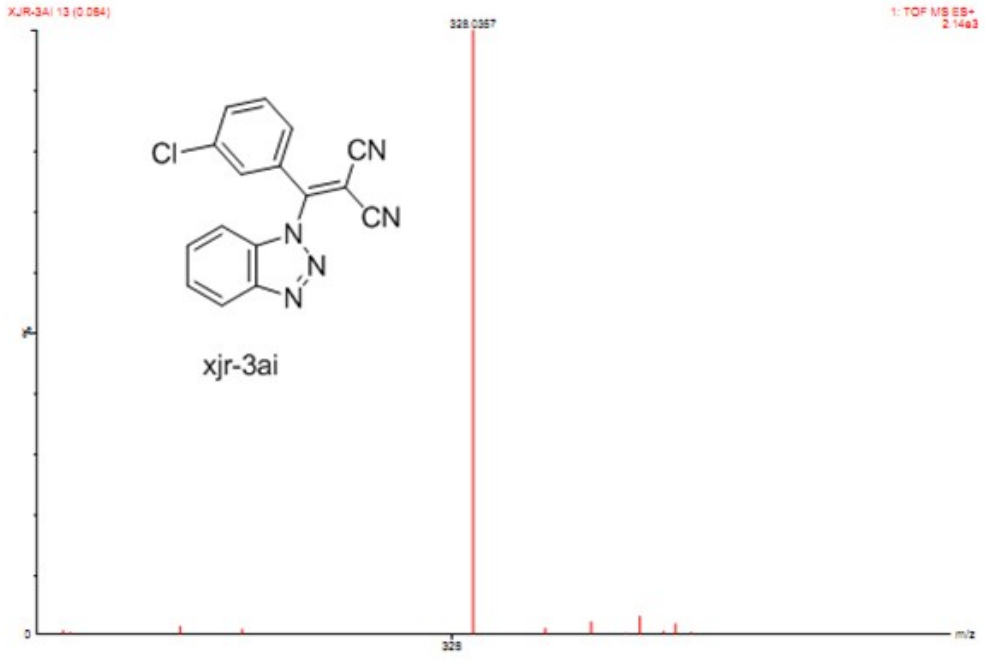
3ag


Varian QFT-ESI
Mode: Positive
Scans: 1
Date: 06-JUN-2017
Time: 15:49:06
Scan: 67.2857
328.0362
330.0321
329.0412
CN
NC
Cl
N
N
N
100
90
80
70
60
50
40
30
20
10
0
322
324
326
328
330
332
334
336
Mass/Charge

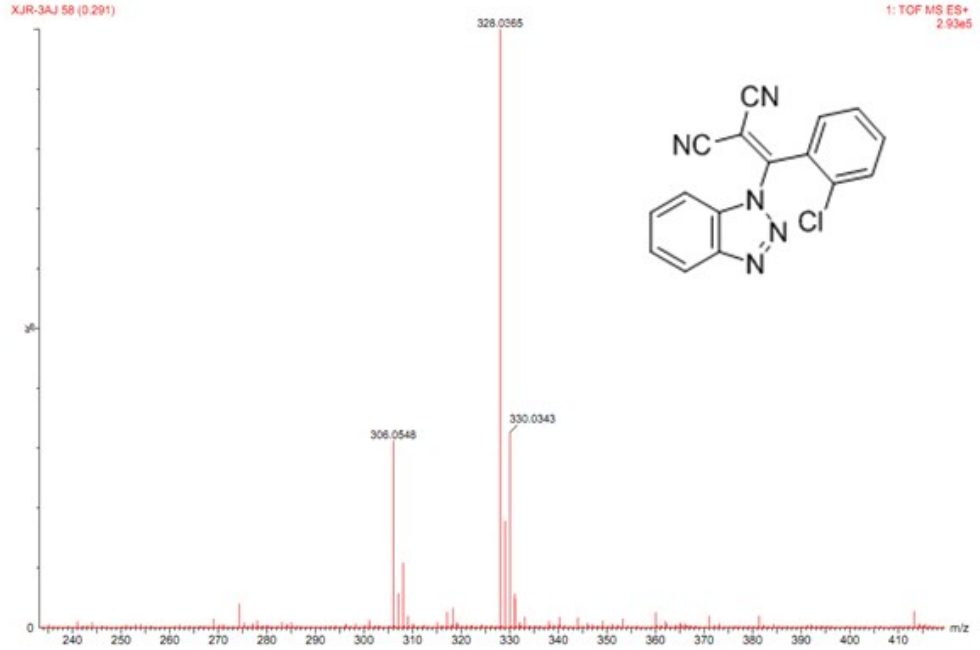
3ah


XJR-3AH-1 T3 (0.367)
1: TOF MS ES+
16.1
360.0034
Br
CN
CN
N
N
N
%
62
349.999
360.000
360.001
360.002
360.003
360.004
360.005
360.006
360.007
360.008
360.009
360.010
m/z

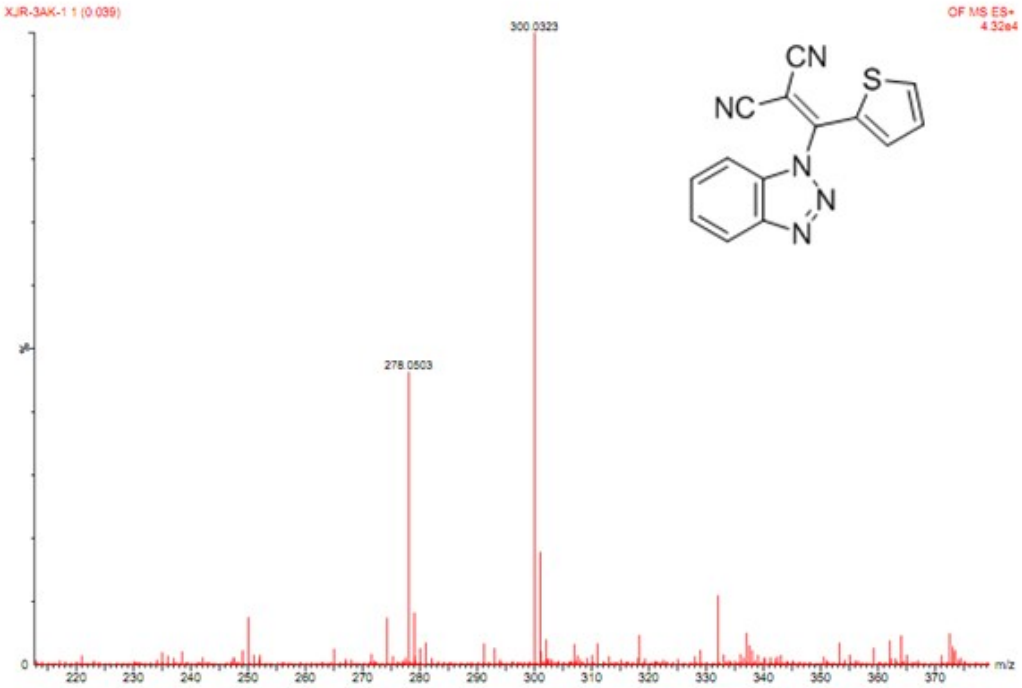
3ai


XJR-3AI 13 (0.084)
1: TOF MS ES+
2.14e3
328.0367
Cl
CN
CN
N
N
N
xjr-3ai
%
0
328
m/z

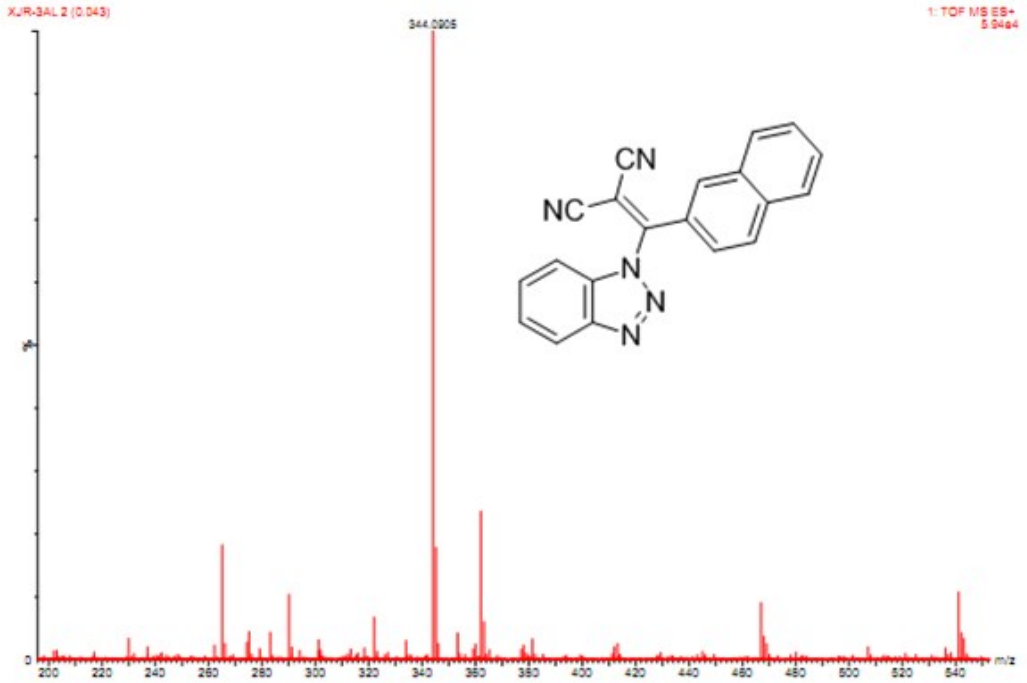
3aj


XJR-3AJ 58 (0.291)
1: TOF MS ES+
2.93e5
328.0365
330.0343
306.0548
CN
NC
N
N
N
Cl
%
0
240 250 260 270 280 290 300 310 320 330 340 350 360 370 380 390 400 410
m/z

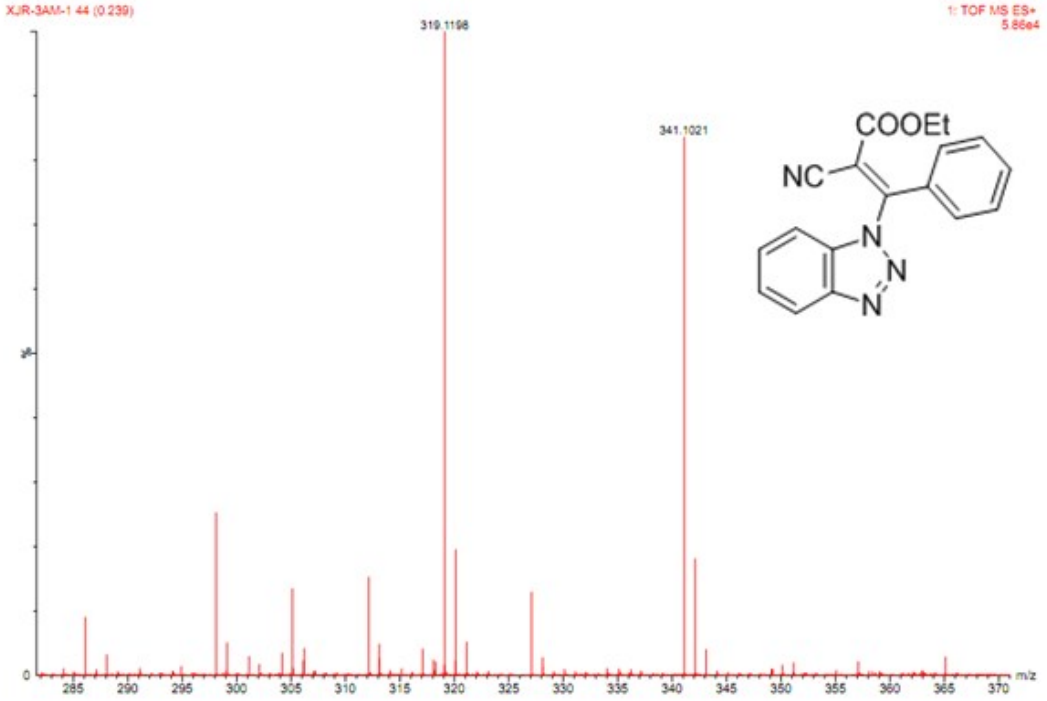
3ak


XJR-3AK-1 1 (0.039)
OF MS ES+
4.32e4
300.0323
278.0503
CN
NC
S
N
N
N
%
0
220 230 240 250 260 270 280 290 300 310 320 330 340 350 360 370
m/z

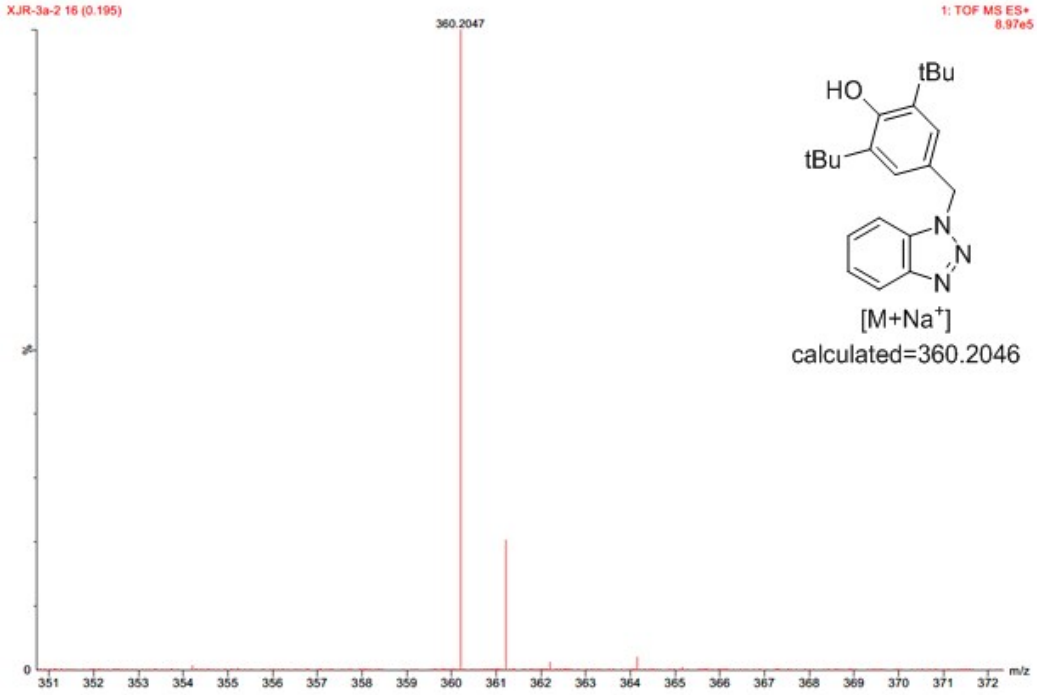
3al


XJR-3AL 2 (0.043)
344.0905
1: TOF MS ES+
5.94e4
CN
NC
N
N
N
%
0
200 220 240 260 280 300 320 340 360 380 400 420 440 460 480 500 520 540
m/z

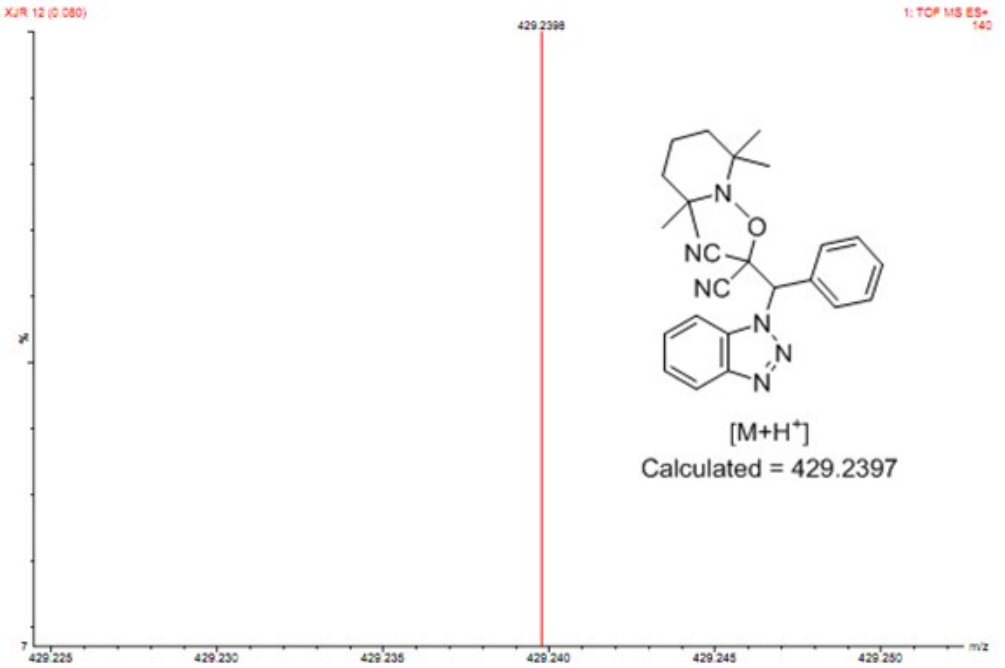
3am


XJR-3AM-1 44 (0.239)
319.1198
341.1021
1: TOF MS ES+
5.86e4
COOEt
NC
N
N
N
%
0
285 290 295 300 305 310 315 320 325 330 335 340 345 350 355 360 365 370
m/z

Intermediate 7



Intermediate 8



11. References

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2. J. G. McCoy, J. J. Marugan, K. Liu, W. Zheng, N. Southall, W. Huang, M. Heilig and C. P. Austin, *ACS Chem. Neurosci*, 2010, **1**, 559-574.
3. L. Capaldo, L. Buzzetti, D. Merli, M. Fagnoni and D. Ravelli, *J. Org. Chem*, 2016, **81**, 7102-7109.