Electronic Supplementary Information

Rose Bengal Photocatalyzed Knoevenagel Condensation of Aldehydes and Ketones in Aqueous Medium

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1. General Information:

The analytical grade solvents and commercially available reagents were purchased from SDFCL, AVARICE, Fisher Scientific, MERCK, THOMAS BAKER, Spectrochem, AVRA, and LOBA Chemie. All the purchased reagents were used without further purification. Non-commercially available starting materials were synthesized by known literature procedures and their physical and spectroscopic data were compared with the reported values. Progress of the reactions was measured by thin-layer chromatography (TLC) on pre-coated aluminium backed plates. Purification of the derivatives was done by column chromatography on Silica gel (100-200 mess sizes well as 200-400 mess size). NMR spectra were acquired on a BRUKER 500 MHZ spectrometer for ^{1}H and ^{13}C respectively. Chemical shifts (δ) are reported in ppm relative to residual solvent signals ($CDCl_3$: 7.26 ppm for ^{1}H NMR and 77.16 ppm for ^{13}C NMR/ DMSO-d_6: 2.50 ppm for ^{1}H NMR and 39.52 ppm for ^{13}C NMR). ^{13}C NMR spectra were acquired on a broadband decoupled mode. The following abbreviations are used to describe peak patterns: s (singlet), d (doublet), t (triplet), q (quartet), quint (quintet), sept (septuplet), m (multiplet), dd (doublet of doublet) br s (broad singlet). High-Resolution Mass Spectra (HRMS) were acquired on a spectrometer Bruker micrOTOF-Q II using electrospray (TOF-ESI+) technique and making use of the mass-works software compass data-analysis 4.0 for the formula identification. Obtained data are expressed in mass/charge (m/z) units.

Theoretical computations

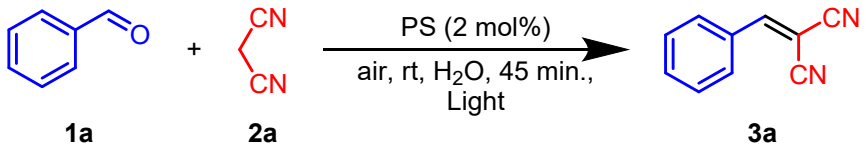
All the computational calculations were executed with the help of the Orca 4.2.1 program package. Stability of the intermediates, possible interaction in the transition states, ground state geometries and electronic properties were optimized under vacuum condition by using WB97X functional and 6-31G(d) basis set.

2. Experiments

Table S1. Literature photosensitizer properties.

Entry	Photosensitizer	Solvent	[a]First triplet state energy (E_T) ($KCalmol^{-1}$)	[b]Life time (μSec)	[c]Quantum Yield of ISC (Φ_{ISC})	[d]Singlet oxygen quantum yield (Φ_Δ)
1	Rose bengal	[a]DMF [b]CH_3CN [c]MeOH [d1]H_2O [d2]EtOH	42[1a]	30[1b]	0.77[1b]	d1: 0.75[1a] d2: 0.68[1a]
2	Eosin Y	[a] EtOH/ MeOH (9:1) [c]MeOH [d]H_2O	45.5[1b]	24[2a]	0.32[1b]	0.52[2b]
3	Eosin B	[a] EtOH/ MeOH (9:1) [d]H_2O	45.5[1b]	-	-	0.52[2b]
4	Rhodamine B	[a,c]MeOH	41.51[1C]	-	0.12[1b]	-

Table S2. Screening of different photocatalysts and light sources under the best conditions.[a]

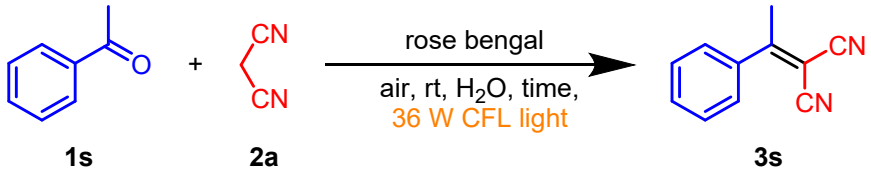


1a **2a** **3a**

Entry	**1a** (equiv.)	**2a** (equiv.)	Time (min.)	Light	Solvent	Photosensitizer	Yield (%)[b] **3a**
1	1	2	60	36 W CFL	EtOH	Rose bengal (1 mol%)	79
2	1	1.5	60	36 W CFL	EtOH	Rose bengal (1 mol%)	53
3	1	3	60	36 W CFL	EtOH	Rose bengal (1 mol%)	79
4	1	2	60	36 W CFL	EtOH	Rose bengal (2 mol%)	85
5	1	2	60	36 W CFL	EtOH	Rose bengal (0.5 mol%)	62
6	1	2	60	36 W CFL	EtOH	Rose bengal (3 mol%)	85
7	**1**	**2**	**45**	**36 W CFL**	**H_2O**	**Rose bengal (2 mol%)**	**90**
8	1	2	45	36 W CFL	H_2O	Eosin Y (2 mol%)	69
9	1	2	45	36 W CFL	H_2O	Eosin B (2 mol%)	38
10	1	2	45	36 W CFL	H_2O	Rhodamine B (2 mol%)	22
11	1	2	45	30 W white LED	H_2O	Rose bengal (2 mol%)	91
12	1	2	45	10 W blue LED	H_2O	Rose bengal (2 mol%)	79
13	1	2	45	18 W green LED	H_2O	Rose bengal (2 mol%)	68

Reaction conditions: [a] **1a** (0.94 mmol), **2a** (1.88 mmol), PS (0.018 mmol), H_2O (4 mL), 45 min., light. [b] Isolated yield.

Table S3. Optimization of Knoevenagel condensation for ketones.[a]

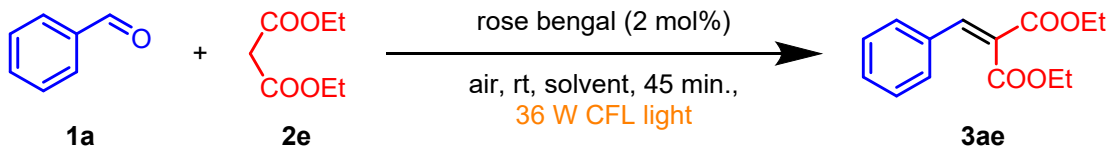


1s **2a** **3s**

Entry	**1s** (equiv.)	**2a** (equiv.)	Catalyst loading (mol%)	Time (h)	Solvent	Yield (%)[b] **3s**
1	1	2	2	36	H_2O	52
2	1	2	2	40	H_2O	64
3	**1**	**2**	**2**	**46**	**H_2O**	**71**
4	1	2	2	48	H_2O	71
5	1	2	4	46	H_2O	72
6	1	2	6	46	H_2O	71
7	1	2	2	46	EtOH	62
8[c]	1	2	2	46	H_2O	ND
9[d]	1	2	-	46	H_2O	ND

Reaction conditions: [a] **1s** (0.83 mmol), **2a** (1.66 mmol), rose bengal (0.016 mmol), H_2O (4 mL), 46 h., 36 W CFL light. [b] Isolated yield. [c] Reaction under dark. [d] Reaction without catalyst but in presence of light. (ND: Not Detected)

Table S4. Optimization of Knoevenagel condensation for different active methylene compounds.[a]



1a **2e** **3ae**

Entry	Time (min.)	Solvent	Yield (%)[b] **3s**
1	45	H_2O	Trace
2	**45**	**EtOH:H_2O (1:1)**	**93**
3	45	EtOH	87
4	120	EtOH:H_2O (1:1)	93

Reaction conditions: [a] **1a** (0.94 mmol), **2e** (1.88 mmol), rose bengal (0.018 mmol), EtOH:H_2O (1:1) (4 mL), 45 min., 36 W CFL light. [b] Isolated yield.

2.1. Confirmation for the formation of H_2O_2[3a]

An oven-dried glass vial was charged with benzaldehyde **1a** (100 mg, 0.94 mmol), malononitrile **2a** (124 mg, 1.88 mmol), rose bengal (18 mg, 0.018 mmol), and 4 mL distilled water. The reaction mixture in the glass vial was irradiated with 36 W CFL light for 45 min. The progress of the reaction was monitored by TLC. After completion of the reaction, 10 mL distilled water was added to the reaction mixture. The precipitation was filtered to get solid. It was washed with 90 mL of distilled water and all the aqueous part was collected in a 250 mL conical flask. In the aqueous part activated charcoal (with a surface area of 950 m^2/g) was added and shake the conical flask for several minutes until the colour of rose bengal became disappear. The aqueous part was passed through activated charcoal again and collected in a 250 mL conical flask. 6 mL 1(N) H_2SO_4 was added to this aqueous solution. 3 mL (3wt.%) starch solution and 1 mmol KI were added to 20 mL water in another conical flask. The liquids of the two flasks were mixed and stirred well. Within 15-20 seconds, the pale blue colour started appearing which became dark in the next 5-10 min (Figure S1).

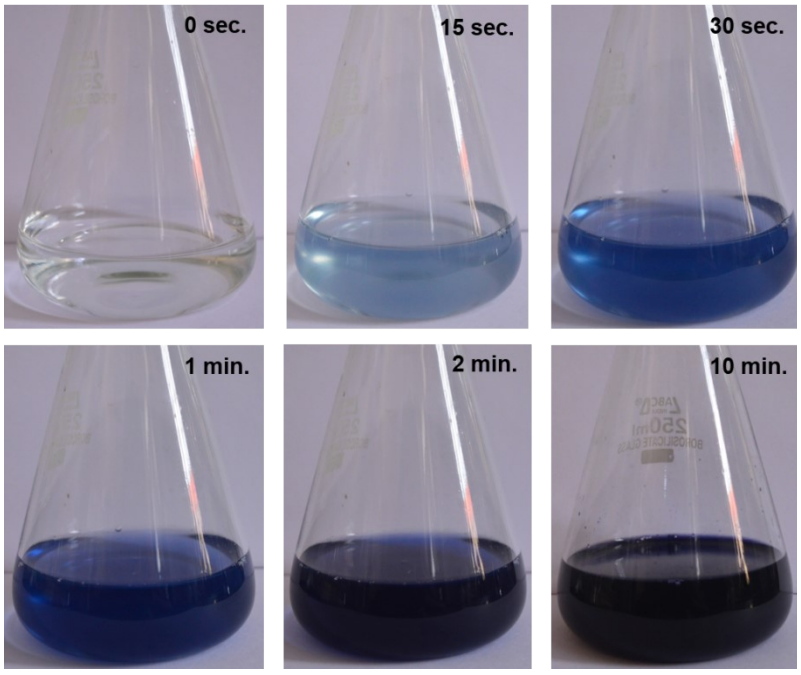
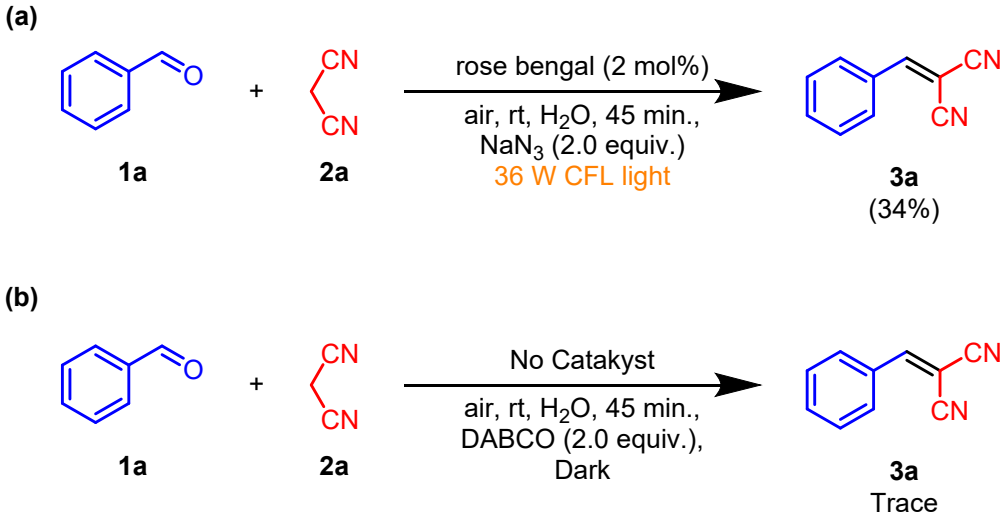


Figure S1. Aqueous part of the reaction mixture with KI- starch solution.

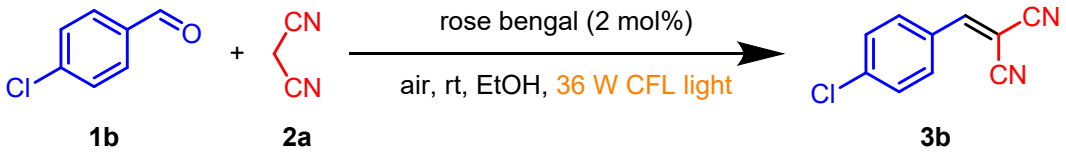
2.2. Control experiments for Knoevenagel condensation.

When the Knoevenagel condensation reaction was carried out by method-I procedure in presence of NaN_3 as a singlet oxygen quencher then only 34% of **3a** was observed (Scheme S1a).[3b] Further to nullify the viewer's question that for singlet oxygen quenching if we used DABCO then why does it reduce the yield of the reaction (Scheme 4e), though DABCO itself is a base and can help for Knoevenagel condensation reaction without any photocatalyst. Since here when the reaction was carried out in presence of DABCO but without the use of rose bengal (Scheme S1b) then only a trace amount of product was observed under dark condition. This indicates that under our standard condition DABCO will not going to help as a base for Knoevenagel condensation reaction.



Scheme S1. Control experiments for Knoevenagel condensation reaction.

2.3. Light on-off experiment



1b **2a** **3b**

An oven-dried glass vial was charged with 4-chloro benzaldehyde **1b** (100 mg, 0.71 mmol), malononitrile **2** (94 mg, 1.42 mmol), rose bengal (14 mg, 0.014 mmol). 4 mL EtOH was added to the reaction mixture and the glass vial was irradiated with 36 W CFL light for 235 min. as per the details given in table S5.

Table S5. Light on-off experiment details.

Entry	Time	Experiment	^{1}H-NMR Conversion (%)
1	30 min.	Dark	0
2	35 min.	Light	30
3	65 min.	Dark	31
4	75 min.	Light	49
5	105 min.	Dark	50
6	115 min.	Light	68
7	145 min.	Dark	70
8	155 min.	Light	85
9	185 min.	Dark	87
10	195 min.	Light	94
11	225 min.	Dark	96
12	235 min.	Light	100

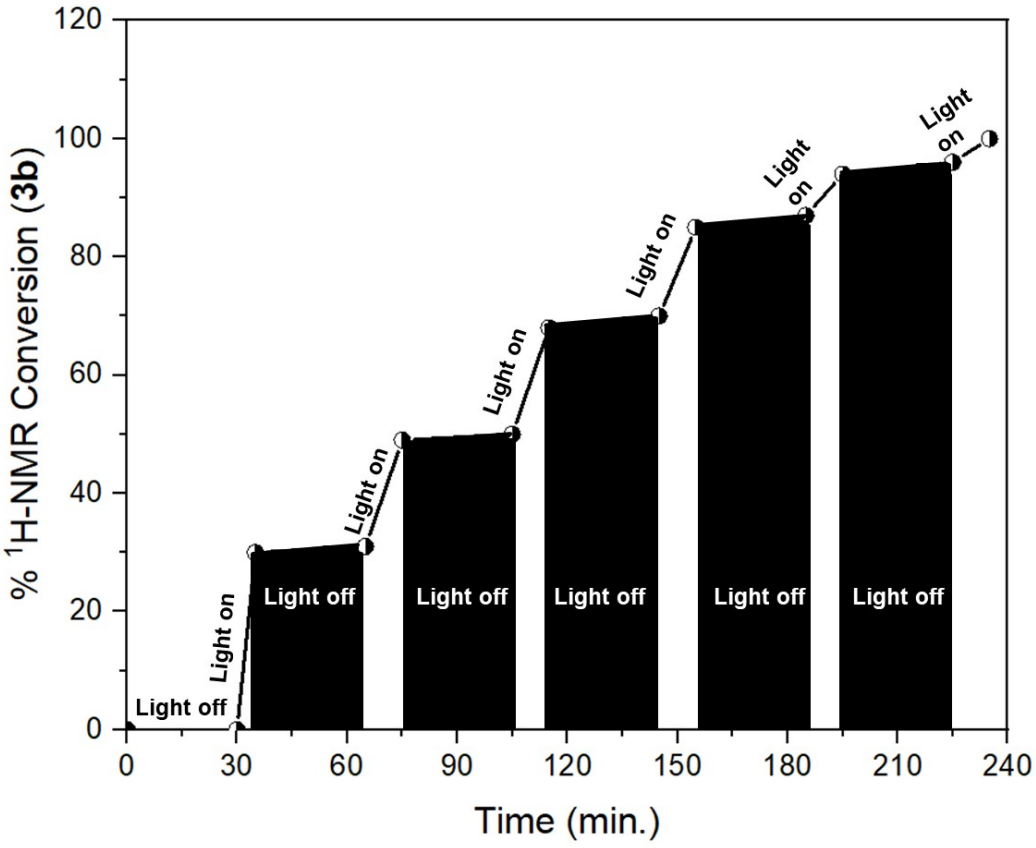


Figure S2. Light on-off experiment.

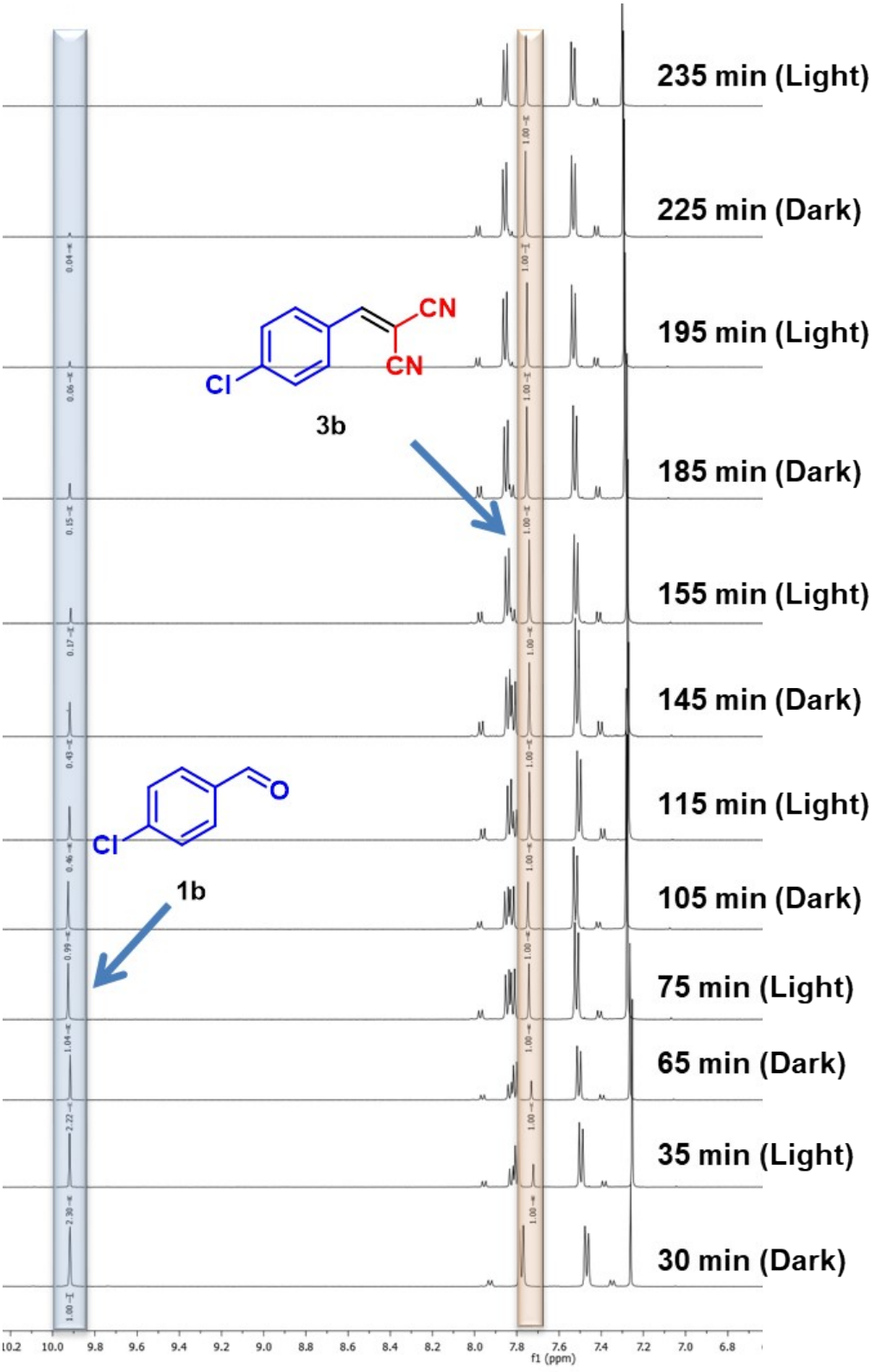


Figure S3. Crude ^{1}H-NMR for Light on-off experiment.

2.4. Experimental setup

2 × 18 W CFL light bulbs were attached at both sides of a magnetic stir. The distance between the two light bulbs was 14 cm. The reaction was carried out in a 30 mL borosilicate glass vial with a magnetic bar. During the reaction, the distance of CFL lights from the borosilicate glass vials was kept at 6 cm and the temperature was maintained at room temperature (20-25 ^{0}C) with air cooling.

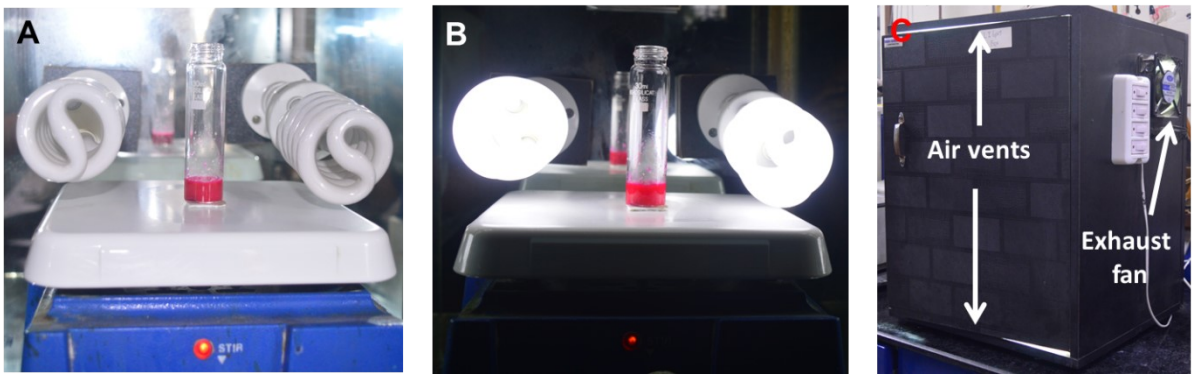
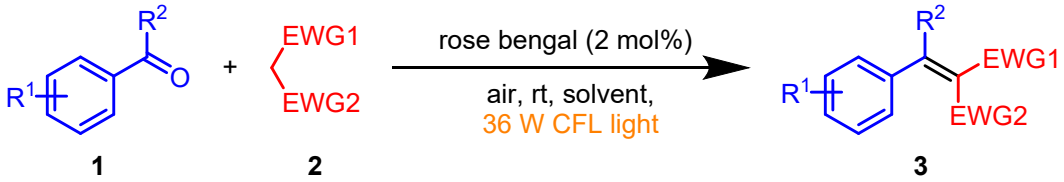


Figure S4. A typical photochemical reaction set up for Knoevenagel condensation reaction; [A] Light off, [B] Light on, [C] Photoreactor.

2.5. General Procedure

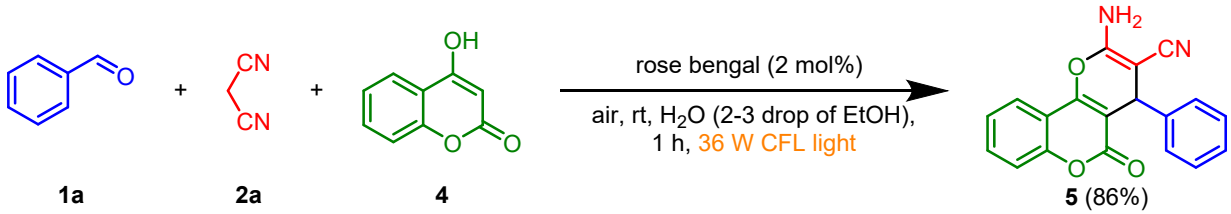
2.5.1. Photocatalytic Knoevenagel condensation:



An oven-dried glass vial was charged with aldehyde/ketone **1** (0.94 mmol), active methylene compound **2** (1.88 mmol), rose bengal (0.018 mmol). 4 mL distilled water/ EtOH:H_2O (1:1) was added to the reaction mixture and the glass vial was irradiated with 36 W CFL light for 45 min. (in case of aldehydes) or 46 h (in the case of ketones). The progress of the reaction

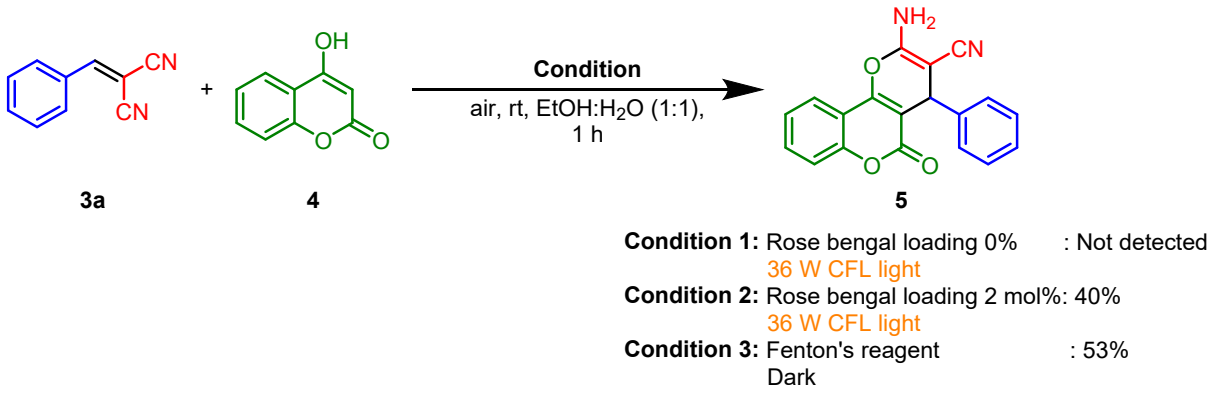
was monitored by TLC. After completion of the reaction, 10 mL of distilled water was added to the reaction mixture. In the case of aldehydes, precipitation appeared. The precipitation was filtered to get solid. It was washed several times with water and one to two times with 4:1 Water:EtOH to get pure product **3a-r, 3ab, 3ac**. In the case of **3ad**, **3ae**, **3af** and ketones, 6 mL water was added to the reaction mixture and extracted three times in ethyl acetate. The combined organic layer was washed with brine (10 mL), dried over anhydrous sodium sulfate, and the solvent was evaporated under reduced pressure. The product was purified by column chromatography on silica gel using hexane/ethyl acetate 6:1 as the eluent to give the product **3s-z**, **3ad**, **3ae, 3af**, **3sd**.

2.5.2. Synthesis of 2-amino-5-oxo-4-phenyl-4H,5H-pyrano[3,2-c]chromene-3-carbonitrile (5):



1a **2a** **4** **5** (86%)

An oven-dried glass vial was charged with benzaldehyde **1a** (100 mg, 0.94 mmol), malononitrile **2a** (124 mg, 1.88 mmol), 4-hydroxycoumarin **4** (153 mg, 0.94 mmol), and rose bengal (18 mg, 0.018 mmol). 4 mL distilled water with 2-3 drop of EtOH was added to the reaction mixture and the glass vial was irradiated with 36 W CFL light for 1 h. The progress of the reaction was monitored by TLC. After completion of the reaction, 20 mL of distilled water was added to the reaction mixture to get precipitation. The precipitation was filtered to get solid. It was washed several times with water and one to two times with 4:1 Water:EtOH to get pure product **5**.

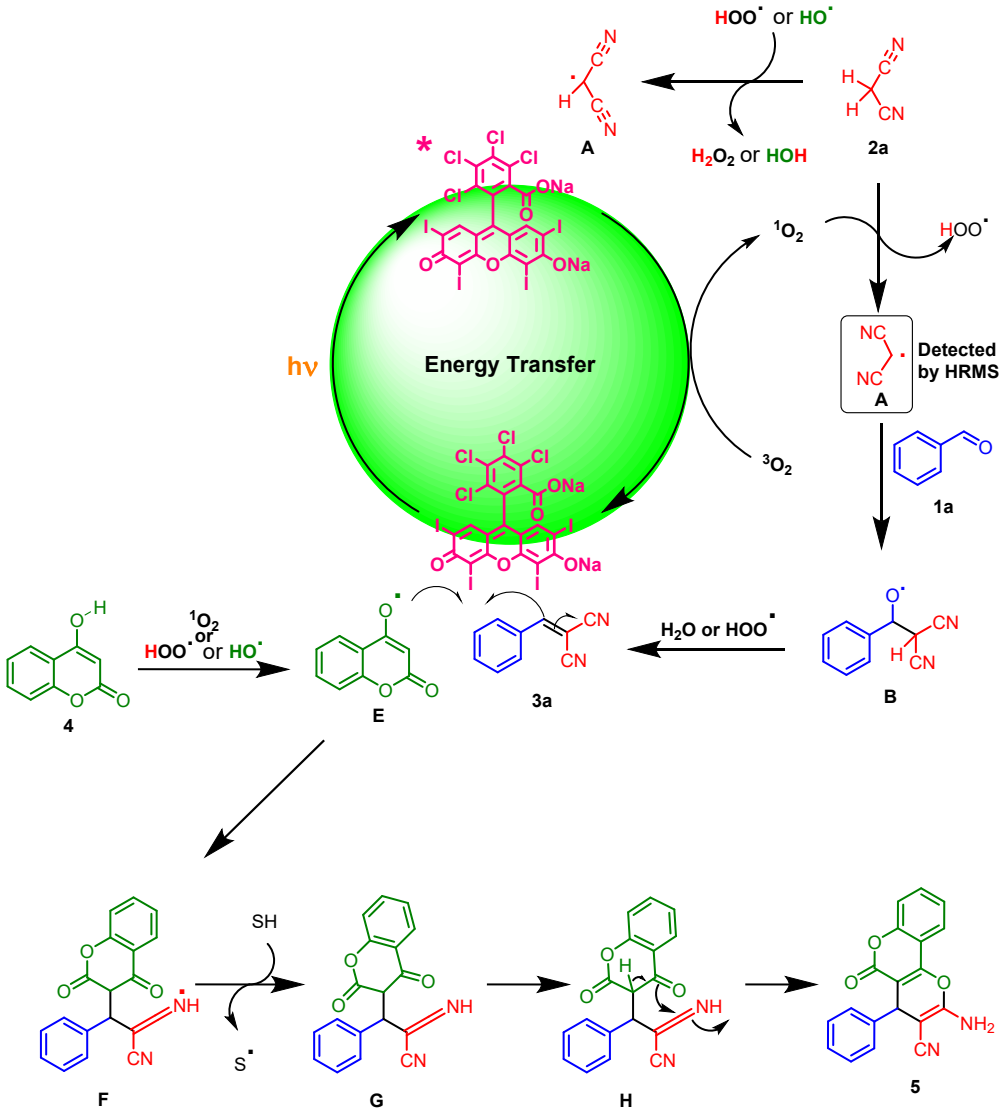


Scheme S2. Control experiments.

An oven-dried glass vial was charged with benzylidenemalononitrile **3a** (100 mg, 0.64 mmol) and 4-hydroxycoumarin **4** (115 mg, 0.71 mmol). 4 mL EtOH:H_2O (1:1) was added to the reaction mixture, and the glass vial was irradiated with 36 W CFL light for 1 h. The progress of the reaction was monitored by TLC. In absence of rose bengal no product (**5**) formation was detected but in presence of rose bengal (12 mg, 0.012 mmol) 40% of desired product **5** was observed. Even in presence of Fenton's reagent ($FeSO_4$, 0.64 mmol and H_2O_2, 1.29 mmol) 53% chromene **5** was detected after purification by column chromatography on silica gel using hexane/ethyl acetate = 1:19 as the eluent.

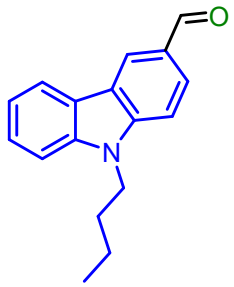
2.6. Mechanism for the synthesis of 2-amino-5-oxo-4-phenyl-4H,5H-pyrano[3,2-c]chromene-3-carbonitrile (5):

Based on control experiments and literature evidences[4c] a possible mechanism was established where 4-hydroxy-2H-chromen-2-one (**4**) can deprotonate in presence of either singlet oxygen or hydroxyl radical or hydroperoxyl radical species to produce radical intermediate **E.** Further, **E** can react with benzylidenemalononitrile **3a** to produce radical intermediate **F**. Finally in presence of proton source (**2** or H_2O or **4**) cyclization gave the desired product **5**.



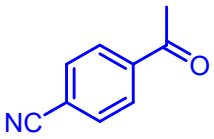
Scheme S3. Mechanism of photosensitized synthesis of dihydropyrano[2,3-c] chromene.

2.7. Synthesis of starting materials



9-Butyl-9*H*-carbazole-3-carbaldehyde (**1q**)

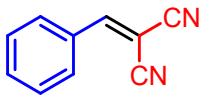
9-Butyl-9H-carbazole-3-carbaldehyde was prepared according to a published procedure; spectral data are in agreement with literature values.[4a]



4-Acetylbenzonitrile (**1x**)

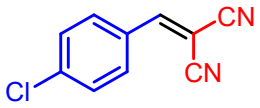
4-Acetylbenzonitrile was prepared according to a published procedure; spectral data are in agreement with literature values.[4b]

3. Spectroscopic characterization



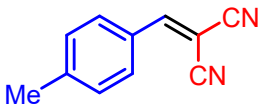
3a

2-Benzylidenemalononitrile (3a): White solid; yield: 90%; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.91 (d, *J* = 7.7 Hz, 2H), δ 7.78 (s, 1H), δ 7.64 (t, *J* = 7.5 Hz, 1H), δ 7.55 (t, *J* = 7.7 Hz, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 160.03, 134.73, 131.08, 130.84, 129.75, 113.81, 112.65, 83.06. Spectral data are in agreement with literature values.[5]



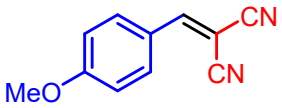
3b

2-(4-Chlorobenzylidene)malononitrile (3b): White solid; yield: 93%; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.86 (d, *J* = 8.7 Hz, 2H), δ 7.73 (s, 1H), δ 7.52 (d, *J* = 8.6 Hz, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 158.41, 141.28, 131.96, 130.20, 129.41, 113.56, 112.46, 83.50. Spectral data are in agreement with literature values.[5]



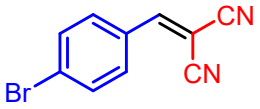
3c

2-(4-Methylbenzylidene)malononitrile (3c): White solid; yield: 85%; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.81 (d, *J* = 8.2 Hz, 2H), δ 7.72 (s, 1H), δ 7.34 (d, *J* = 8.1 Hz, 2H), δ 2.46 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 159.86, 146.49, 131.03, 130.50, 128.61, 114.12, 112.97, 81.37, 22.11. Spectral data are in agreement with literature values.[5]



3d

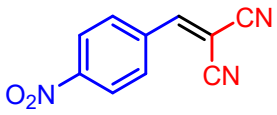
2-(4-Methoxybenzylidene)malononitrile (3d): White solid; yield: 82%; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.91 (d, *J* = 8.9 Hz, 2H), δ 7.65 (s, 1H), δ 7.01 (d, *J* = 8.9 Hz, 2H), δ 3.92 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 164.96, 158.98, 133.56, 124.14, 115.26, 114.56, 113.46, 78.59, 55.92. Spectral data are in agreement with literature values.[5]



3e

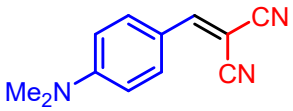
2-(4-Bromobenzylidene)malononitrile (3e): White solid; yield: 89%; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.77 (d, *J* = 8.5 Hz, 2H), 7.71-7.68 (m, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 158.53,

133.21, 131.92, 130.03, 129.81, 113.57, 112.45, 83.69. Spectral data are in agreement with literature values.[5a]



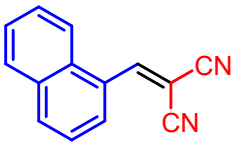
3f

2-(4-Nitrobenzylidene)malononitrile (3f): Off white solid; yield: 95%; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.39 (d, *J* = 8.8 Hz, 2H), δ 8.07 (d, *J* = 8.7 Hz, 2H), δ 7.88 (s, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 156.98, 150.54, 135.96, 131.44, 124.77, 112.76, 111.73, 87.73. Spectral data are in agreement with literature values.[5]



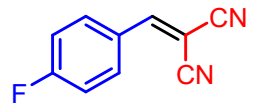
3g

2-(4-(Dimethylamino)benzylidene)malononitrile (3g): Orange solid; yield: 96%; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.81 (d, *J* = 9.0 Hz, 2H), δ 7.46 (s, 1H), δ 6.69 (d, *J* = 9.1 Hz, 2H), δ 3.14 (s, 6H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 158.19, 154.41, 133.91, 119.46, 116.08, 115.02, 111.75, 72.14, 40.19. Spectral data are in agreement with literature values.[6]



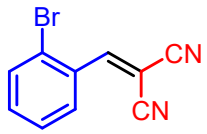
3h

2-(Naphthalen-1-ylmethylene)malononitrile (3h): Yellow solid; yield: 84%; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.67 (s, 1H), δ 8.28 (d, *J* = 7.4 Hz, 1H), δ 8.12 (d, *J* = 8.2 Hz, 1H), δ 7.97 (d, *J* = 8.4 Hz, 2H), δ 7.69 (t, *J* = 7.7 Hz, 1H), δ 7.66-7.61 (m, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 157.78, 135.02, 133.64, 131.18, 129.53, 128.67, 128.60, 127.62, 127.40, 125.48, 122.41, 113.83, 112.62, 85.26. Spectral data are in agreement with literature values.[5]



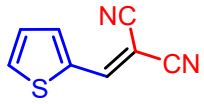
3i

2-(4-Fluorobenzylidene)malononitrile (3I): White solid; yield: 95%; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.97-7.95 (m, 2H), δ 7.74 (s, 1H), δ 7.26-7.22 (m, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 167.23, 165.17, 158.46, 133.57, 133.49, 127.49, 127.46, 117.38, 117.20, 113.68, 112.61, 82.50, 82.48. Spectral data are in agreement with literature values.[5]



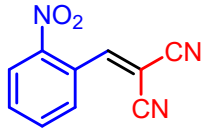
3j

2-(2-Bromobenzylidene)malononitrile (3j): White solid; yield: 92%; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.22 (s, 1H), δ 8.12 (d, J = 7.7 Hz, 1H), δ 7.75 (d, J = 7.8 Hz, 1H), δ 7.51-7.44 (m, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 158.85, 135.08, 134.14, 130.94, 129.95, 128.49, 126.58, 113.24, 111.92, 86.20. Spectral data are in agreement with literature values.[7]



3k

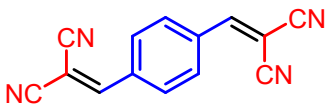
2-(Thiophen-2-ylmethylene)malononitrile (3k): Brown solid; yield: 87%; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.89-7.87 (m, 2H), δ 7.81 (d, J = 3.8 Hz, 1H), 7.27 (t, J = 4.8 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 151.23, 138.31, 137.03, 135.51, 129.15, 113.90, 113.07, 78.42. Spectral data are in agreement with literature values.[5b,8]



3l

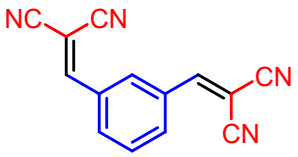
2-(2-Nitrobenzylidene)malononitrile (3l): Off-white solid; yield: 97%; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.45 (s, 1H), δ 8.36 (d, J = 8.0 Hz, 1H), δ 7.88 (t, J = 7.5 Hz, 1H), 7.83-7.79 (m,

2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 158.91, 146.90, 135.04, 133.51, 130.56, 126.80, 125.93, 112.33, 111.07, 88.60. Spectral data are in agreement with literature values.[9]



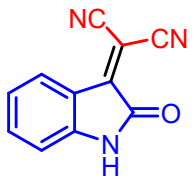
3m

2,2'-(1,4-Phenylenebis(methaneylylidene))dimalononitrile (3m): Light brown solid; yield: 88%; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.05 (s, 4H), δ 7.82 (s, 2H); ^{13}C NMR (125 MHz, DMSO-d_6) δ 159.75, 135.28, 130.80, 113.77, 112.73, 84.75. Spectral data are in agreement with literature values.[10]



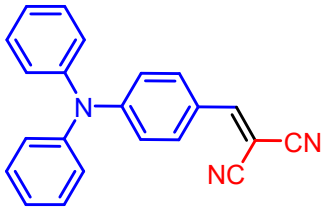
3n

2,2'-(1,3-Phenylenebis(methaneylylidene))dimalononitrile (3n): Off-white solid; yield: 86%; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.21-8.19 (m, 3H), δ 7.84 (s, 2H), δ 7.77 (t, J = 7.9 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 157.65, 134.71, 132.50, 132.27, 131.24, 112.90, 111.97, 86.33. Spectral data are in agreement with literature values.[11]



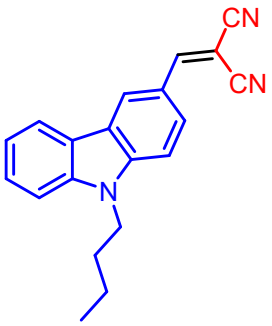
3o

2-(2-Oxoindolin-3-ylidene)malononitrile (3o): Red solid; yield: 91%; ^{1}H NMR (500 MHz, DMSO-d_6) δ 11.19 (s, 1H), δ 7.83 (d, J = 7.7 Hz, 1H), δ 7.54 (t, J = 7.6 Hz, 1H), δ 7.10 (t, J = 7.6 Hz, 1H), δ 6.91 (d, J = 7.9 Hz, 1H); ^{13}C NMR (125 MHz, DMSO-d_6) δ 163.69, 150.49, 146.38, 137.86, 125.79, 122.93, 118.50, 114.53, 112.94, 111.65, 80.55. Spectral data are in agreement with literature values.[12a]



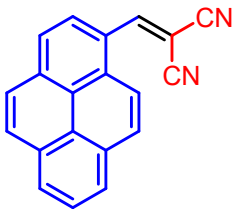
3p

2-(4-(Diphenylamino)benzylidene)malononitrile (3p): Orenge solid; yield: 74%; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.73 (d, *J* = 8.9 Hz, 2H), δ 7.51 (s, 1H), δ 7.38 (t, *J* = 7.7 Hz, 4H), δ 7.26-7.18 (m, 6H), δ 6.94 (d, *J* = 8.9 Hz, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 158.05, 153.58, 145.23, 133.12, 130.08, 126.83, 126.25, 122.87, 118.57, 115.35, 114.22, 75.55. Spectral data are in agreement with literature values.[12b]



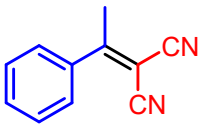
3q

2-((9-Butyl-9H-carbazol-3-yl)methylene)malononitrile (3q): Yellow solid; yield: 70%; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.63 (s, 1H), δ 8.15-8.09 (m, 2H), δ 7.86 (s, 1H), δ 7.56 (t, *J* = 7.7 Hz, 1H), δ 7.48 (d, *J* = 8.5 Hz, 2H), δ 7.36 (t, *J* = 7.5 Hz, 1 H), δ 4.35 (t, *J* = 7.2 Hz, 2H), δ 1.91-1.85 (m, 2H), δ 1.45-1.37 (m, 2H), δ 0.97 (t, *J* = 7.4 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 160.09, 143.91, 141.25, 128.60, 127.47, 125.07, 123.67, 122.60, 122.34, 121.09, 120.97, 115.04, 114.27, 109.84, 109.69, 76.26, 43.37, 31.09, 20.55, 13.87. Spectral data are in agreement with literature values.[12c]



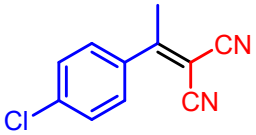
3r

2-(pyren-1-ylmethylene)malononitrile (3r): Orenge solid; yield: 82%; ^{1}H NMR (500 MHz, DMSO-d_6) δ 9.60 (s, 1H), δ 8.72-8.66 (m, 2H), δ 8.50-8.42 (m, 5H), δ 8.29 (d, J = 8.9 Hz, 1H), δ 8.21 (t, J = 7.6 Hz, 1H). Spectral data are in agreement with literature values.[12d]



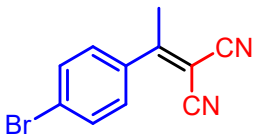
3s

2-(1-Phenylethylidene)malononitrile (3s): White solid; yield: 71%; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.57-7.49 (m, 5H), 2.65 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 175.61, 136.01, 132.36, 129.21, 127.44, 112.90, 112.82, 84.80, 24.36. Spectral data are in agreement with literature values.[13]



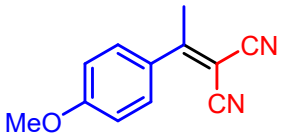
3t

2-(1-(4-Chlorophenyl)ethylidene)malononitrile (3t): White solid; yield: 76%; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.52-7.48 (m, 4H), δ 2.63 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 173.95, 138.79, 134.26, 129.60, 128.88, 112.68, 112.57, 85.27, 24.25. Spectral data are in agreement with literature values.[14]



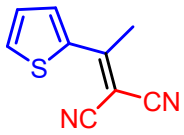
3u

2-(1-(4-Bromophenyl)ethylidene)malononitrile (3u): White solid; yield: 75%; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.65 (d, *J* = 8.6 Hz, 2H), δ 7.42 (d, *J* = 8.6 Hz, 2H), δ 2.62 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 174.00, 134.76, 132.63, 128.98, 127.24, 112.66, 112.56, 85.36, 24.23. Spectral data are in agreement with literature values.[14,15,16a]



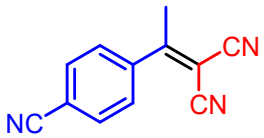
3v

2-(1-(4-Methoxyphenyl)ethylidene)malononitrile (3v): White solid; yield: 62%; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.62 (d, *J* = 9.0 Hz, 2H), δ 6.99 (d, *J* = 8.9 Hz, 2H), δ 3.88 (s, 3H), δ 2.62 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 174.05, 163.20, 129.89, 127.98, 114.54, 113.73, 113.46, 81.99, 55.66, 23.85. Spectral data are in agreement with literature values.[14,15,16a]



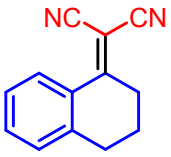
3w

2-(1-(Thiophen-2-yl)ethylidene)malononitrile (3w): Brown solid; yield: 64%; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.05 (d, *J* = 4.0 Hz, 1H), δ 7.78 (d, *J* = 5.1 Hz, 1H), δ 7.26-7.24 (m, 1H), δ 2.71 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 162.55, 138.32, 134.35, 133.56, 129.16, 114.01, 113.52, 78.87, 23.62. Spectral data are in agreement with literature values.[16]



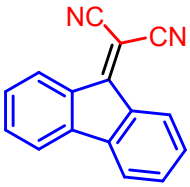
3x

2-(1-(4-Cyanophenyl)ethylidene)malononitrile (3x): White solid; yield: 79%; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.81 (d, *J* = 8.5 Hz, 2H), δ 7.63 (d, *J* = 8.5 Hz, 2H), δ 2.66 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 173.16, 140.06, 133.02, 128.09, 117.54, 115.81, 111.97, 111.94, 87.43, 24.38.



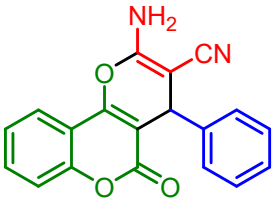
3y

2-(3,4-Dihydronaphthalen-1(2H)-ylidene)malononitrile (3y): White solid; yield: 67%; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.21 (d, *J* = 8.0 Hz, 1H), δ 7.50 (t, *J* = 7.5 Hz, 1H), δ 7.35 (t, *J* = 7.7 Hz, 1H), δ 7.29 (d, *J* = 7.6 Hz, 1H), δ 3.03 (t, *J* = 6.4 Hz, 2H), δ 2.89 (t, *J* = 6.3 Hz, 2H), δ 2.03-1.98 (m, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 172.65, 142.13, 133.81, 130.09, 129.56, 128.01, 126.91, 114.09, 113.48, 79.80, 33.11, 29.77, 22.20. Spectral data are in agreement with literature values.[13a,14,17]



3z

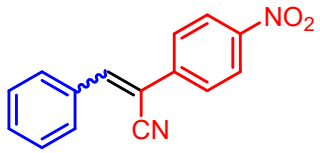
2-(9H-fluoren-9-ylidene)malononitrile (3z): Orange solid; yield: 73%; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.35 (d, *J* = 7.9 Hz, 2H), δ 7.55 (d, *J* = 7.4 Hz, 2H), δ 7.49 (t, *J* = 7.4 Hz, 2H), δ 7.31 (t, *J* = 7.5 Hz, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 161.61, 142.40, 134.83, 134.22, 129.33, 127.00, 120.81, 113.42, 75.97. Spectral data are in agreement with literature values.[18]



5

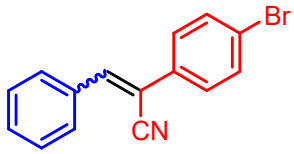
2-Amino-5-oxo-4-phenyl-4H,5H-pyrano[3,2-c]chromene-3-carbonitrile (5): White solid; yield: 86%; ^{1}H NMR (500 MHz, DMSO-d_6) δ 7.90 (d, *J* = 9.1 Hz, 1H), δ 7.72 (t, *J* = 8.6 Hz, 1H), δ 7.51-7.45 (m, 2H), δ 7.41 (s, 2H), δ 7.33-7.30 (m, 2H), δ 7.26-7.22 (m, 3H); ^{13}C NMR

(125 MHz, DMSO-d_6) δ 160.00, 158.45, 153.89, 152.61, 143.81, 133.39, 128.99, 128.10, 127.59, 125.13, 122.93, 119.70, 117.03, 113.43, 104.47, 58.46, 37.44. Spectral data are in agreement with literature values.[19]



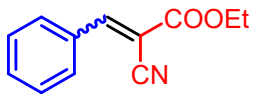
3ab

2-(4-Nitrophenyl)-3-phenylacrylonitrile (3ab): Light brown solid; yield: 92%; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.32 (d, *J* = 8.8 Hz, 2H), 7.96-7.94 (m, 2H), 7.86 (d, *J* = 8.8 Hz, 2H), 7.69 (s, 1H), 7.52-7.51 (m, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 148.08, 145.66, 140.72, 133.05, 131.83, 129.87, 129.34, 126.89, 124.48, 117.27, 109.70. Spectral data are in agreement with literature values.[20]



3ac

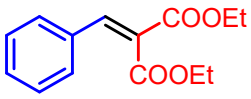
2-(4-Bromophenyl)-3-phenylacrylonitrile (3ac): White solid; yield: 89%; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.90-7.88 (m, 2H), 7.59-7.53 (m, 5H), 7.50-7.44 (m, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 142.68, 133.55, 132.33, 130.93, 129.43, 129.13, 127.58, 123.53, 117.69, 110.70. Spectral data are in agreement with literature values.[21]



3ad

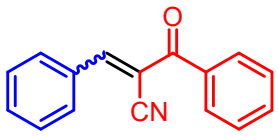
Ethyl 2-cyano-3-phenylacrylate (3ad): White solid; yield: 87%; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.26 (s, 1H), 7.99 (d, *J* = 7.5 Hz, 2H), 7.58-7.49 (m, 3H), 4.39 (q, *J* = 7.1 Hz, 2H),

1.40 (t, J = 7.1 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 162.56, 155.10, 133.38, 131.59, 131.16, 129.37, 115.56, 103.16, 62.82, 14.25. Spectral data are in agreement with literature values.[20]



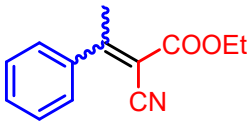
3ae

Diethyl 2-benzylidenemalonate (3ae): Pale yellow liquid; yield: 93%; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.74 (s, 1H), 7.46-7.44 (m, 2H), 7.40-7.36 (m, 3H), 4.36-4.29 (m, 4H), 1.35-1.27 (m, 6H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 166.79, 164.24, 142.24, 133.03, 130.63, 129.55, 128.89, 126.46, 61.80, 61.75, 14.25, 13.99. Spectral data are in agreement with literature values.[22]



3af

2-Benzoyl-3-phenylacrylonitrile (3af): Pale yellow solid; yield: 83%; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.07-8.03 (m, 3H), 7.90 (d, J = 7.6 Hz, 2H), 7.64 (t, J = 7.4 Hz, 1H), 7.59 (t, J = 7.3 Hz, 1H), 7.53 (t, J = 7.4 Hz, 4H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 188.91, 155.48, 135.84, 133.42, 133.37, 131.86, 131.10, 129.35, 129.33, 128.69, 116.84, 110.27. Spectral data are in agreement with literature values.[23]



3sd

Ethyl 2-cyano-3-phenylbut-2-enoate (3sd): Pale yellow liquid; yield: 69%; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.47-7.43 (m, 2H), 7.40-7.37 (m, 3H), 7.18-7.16 (m, 2H), 4.34 (q, J = 7.1 Hz,

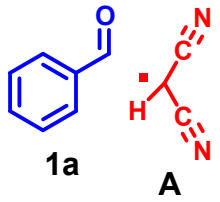
0.66H), 4.10 (q, J = 7.1 Hz, 2H), 2.69 (s, 1H), 2.55 (s, 3H), 1.39 (t, J = 7.1 Hz, 1H), 1.12 (t, J = 7.1 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 172.40, 169.71, 162.43, 161.50, 140.40, 139.09, 130.48, 129.55, 128.81, 128.40, 127.21, 126.30, 116.25, 115.66, 106.29, 105.31, 62.12, 61.98, 26.94, 23.39, 14.20, 13.80. Spectral data are in agreement with literature values.[24]

4. DFT calculations: optimized geometries

4.1. General methods for DFT calculations

Density functional theory (DFT) calculations were performed by using WB97X functional and 6-31G(d) basis set. All the calculations were carried out with the Orca 4.2.1 program package. All optimizations were performed without any geometrical constraint and harmonic vibrational frequencies have been also evaluated at the same level of theory to characterize minima and transition states in the potential energy surface. Transition states have been connected to products by optimization of geometries.

4.2. Cartesian Coordinate of optimized geometries:

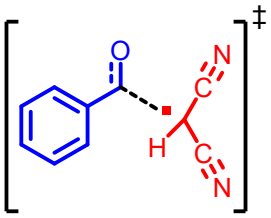


1a A

No. of imaginary frequency: 0

C	2.56078001927676	1.52446430752332	-0.05333479162762
C	1.49406464086115	0.63768413069473	-0.02627605349914
C	1.74071524428723	-0.73856305948092	-0.04826138316041
C	3.05030350176441	-1.21945351185055	-0.09759293177169
C	4.11693196927897	-0.32897295256224	-0.12487943911627
C	3.86882572250937	1.04131336279394	-0.10246428248763
H	2.37478834165042	2.59459323351617	-0.03600304338740
H	0.46915671096720	0.99696370034007	0.01135911600083
H	3.23047459324318	-2.29308375983324	-0.11462703681825
H	5.13735506513160	-0.69905387096144	-0.16291035554865
H	4.70175383807829	1.73962300789646	-0.12331262709474
C	0.62109213250709	-1.69961964182603	-0.01888052704509

O	-0.55363316766812	-1.39410610071318	0.02341100683628
H	0.91852079334698	-2.76882993397408	-0.03758512225014
C	-4.63176248413989	-0.12288850691747	0.16472433330601
H	-2.69180607326282	-1.09494430909015	0.09718550376953
C	-3.23069660330305	-0.15220198939189	0.11932667297655
N	-5.79674987380035	-0.12113178079581	0.20315668971981
C	-2.47740956111097	1.03218527796734	0.10172984986956
N	-1.83428080961749	2.00392639666497	0.08684742132847

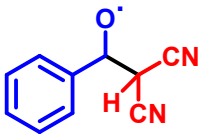


TS-1

No. of imaginary frequency: 1 (750.3 cm^{-1})

C	2.19469927484104	1.43217699316038	-0.14652910956771
C	1.04718623287145	1.15701383932501	0.58529335090758
C	0.43123214110520	-0.08988325352896	0.46807867724859
C	0.96919961533431	-1.06050833665439	-0.37623230093534
C	2.11923169950727	-0.78294018665721	-1.10773020693326
C	2.72951727883272	0.46278153305970	-0.99400736274227
H	2.67751944727056	2.40110341584024	-0.05442740630022
H	0.62542441213441	1.89139789752743	1.26656550905357
H	0.48782895958077	-2.03242317261242	-0.46537551871340
H	2.53712537369604	-1.53867430905086	-1.76651083487889
H	3.62776238503342	0.67951041319309	-1.56577128966303
C	-0.79515356446971	-0.38329616244008	1.27363826821251
O	-1.11999480279438	0.35516049351286	2.25498956725280
H	-1.09184912128405	-1.44872258822877	1.30473985708488

C	-2.14320699044547	-0.63279210737657	-1.08675110150389
H	-2.05430212257220	1.19676643449184	0.00315784620936
C	-2.29078181018099	0.14044179032484	0.11830789875752
N	-1.99022151809956	-1.28373919233466	-2.03301662484716
C	-3.49796067134680	-0.12215264307875	0.86072753685367
N	-4.46325621901400	-0.34122085847273	1.46085324450467

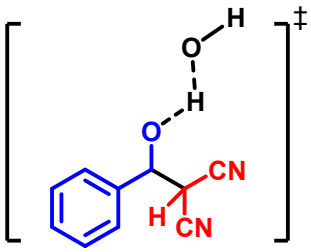


B

No. of imaginary frequency: 1 (750.3 cm^{-1})

C	-2.59126632215739	1.40638685925003	0.35837517405796
C	-1.55879497980242	0.52044309161944	0.07265939883655
C	-1.84601244460564	-0.80894548681121	-0.23815574457469
C	-3.16926381488168	-1.24742503664683	-0.26207867936780
C	-4.19965217827127	-0.35950710151899	0.02966572693917
C	-3.91207732483689	0.96635568557410	0.33934000461921
H	-2.36392047786444	2.44205499231834	0.59546460981292
H	-0.52676596332632	0.86337007286818	0.07558263591320
H	-3.39827777257324	-2.28320017896287	-0.50200037689740
H	-5.22890370046010	-0.70574774177586	0.01225443417538
H	-4.71879640380629	1.65840664422693	0.56546948320420
C	-0.69898806410064	-1.76449952129676	-0.52180585433656
O	0.36417209598600	-1.15221892585709	-1.11058220083518
H	-1.03044169980746	-2.51733440430117	-1.26344927831120
C	-0.23997687452933	-2.53321987269325	0.77016704736901
H	0.04895165767286	-1.78062022206395	1.51416051761498
C	-1.32522032677083	-3.34885888840132	1.33401344125342

N	-2.20291457832612	-3.97842701568719	1.74464978258901
C	0.93233245140436	-3.37096344903751	0.47565104155112
N	1.85056772105695	-4.02599950080297	0.22649983638669

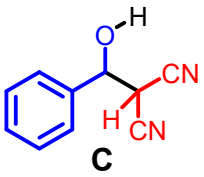


TS-2

No. of imaginary frequency: 1 (1900.9 cm^{-1})

C	-1.60124658102946	1.69138445240931	1.30912494153310
C	-0.46539573322993	1.18041907588668	0.69255681197267
C	-0.58541984106054	0.19142326971869	-0.28695771124357
C	-1.84958163700059	-0.28169456801048	-0.63193058429933
C	-2.98616377574685	0.22672637381745	-0.00993859364487
C	-2.86303321094010	1.21605552055286	0.95921919384495
H	-1.50044725466097	2.46366342591417	2.06703956578150
H	0.51448117884592	1.55762686763037	0.97851661400673
H	-1.94845556002702	-1.05559916582867	-1.39054558358890
H	-3.96668958483484	-0.14974473105327	-0.28713416987487
H	-3.74897632759769	1.61787284570438	1.44294506519749
C	0.63951395813801	-0.38614508134199	-0.96362344086106
O	1.49693814625187	0.55802251985778	-1.54383731302754
H	0.33302210719987	-1.01923278544003	-1.80634721080385
C	1.44136568608086	-1.29685039729542	0.02561708864452
H	1.63807615546504	-0.70897198741747	0.93019975469658
C	0.65438059571196	-2.48396974509457	0.38776208228159
N	0.00822306180118	-3.40388399464892	0.65432714968491

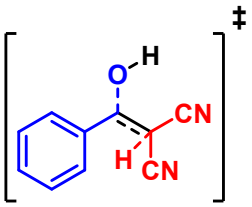
C	2.74690848591104	-1.67568988167817	-0.53670794352608
N	3.79057669404824	-1.92981334785339	-0.96255708713264
O	2.74550283803830	1.35419180370520	0.09845016012822
H	3.57761249651394	1.05321119944331	-0.31200656809934
H	1.92880810212177	1.28099833102218	-0.81417222167020



No. of imaginary frequency: 0

C	-1.78782344366582	-0.32587725025997	4.21989523122356
C	-1.04244378136289	-0.08101813761580	3.07145940503788
C	-1.67425063943998	0.31013307172228	1.89213831668605
C	-3.06086239723294	0.46425623010676	1.87764479504364
C	-3.80696782836301	0.21700470807176	3.02566709372597
C	-3.17201150931373	-0.18036784776340	4.19844579874358
H	-1.28453826331005	-0.62383040013148	5.13580994886847
H	0.04061539148510	-0.16974734565740	3.09951261787311
H	-3.56344575298620	0.78058518754534	0.96593797858380
H	-4.88620688520340	0.34223845529354	3.00338570949347
H	-3.75381391843043	-0.36901077806867	5.09652621757786
C	-0.86257195221568	0.53945823941465	0.62804968971655
O	0.45843522409793	0.92985560781904	0.85961418287257
H	-1.32208550797885	1.34130499508311	0.03981698406596
C	-0.89752312352126	-0.76609909790620	-0.24955281672598
H	-0.67013442670287	-1.62055023364273	0.40165049424340
C	-2.21986322016635	-0.98782768536434	-0.84973263758844

N	-3.27039987765873	-1.13420031094784	-1.30806703400128
C	0.14594712479939	-0.73527004403015	-1.28838473036916
N	1.01200250545220	-0.73479056867113	-2.05531248300357
O	2.04001598261985	-1.39420640340695	0.47979807584549
H	2.66697139592990	-1.06677025564741	-0.19890502430520
H	1.02155966316702	0.15139213405648	1.01812184639181

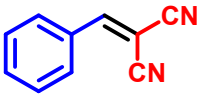


TS-3

No. of imaginary frequency: 1 (1459.7 cm^{-1})

C	-1.28700817266016	1.48974382412183	1.63626524369328
C	-0.17556233447559	0.95799233953887	0.99626174960884
C	-0.33357716860562	0.24655771218817	-0.19601648268420
C	-1.60810326454929	0.07781618845562	-0.73706102829350
C	-2.72089598166511	0.60233675682888	-0.08765376716662
C	-2.55978184224810	1.31024277364982	1.09823725879895
H	-1.15976770459490	2.03978908082484	2.56403798420494
H	0.81191989077357	1.09461507283140	1.42735116212765
H	-1.73377490617708	-0.47372288712156	-1.66643734082849
H	-3.71058937238496	0.46072728595488	-0.51208559527036
H	-3.42649540466535	1.72473698983172	1.60567746569639
C	0.82489722382427	-0.36714880913679	-0.90591459143603
O	1.92272381681096	0.78870796467604	-1.14732205431510
H	0.56196676135366	-0.69847723194156	-1.91171537684275
C	1.76733897876257	-1.30704921889644	-0.22055030361887

H	2.54898500262424	-0.00786327716796	-0.63012414562438
C	1.65939112100175	-1.52471749253436	1.19097437113950
N	1.58635228231222	-1.66162878030489	2.34095672001416
C	2.23917978359852	-2.39744408471113	-1.02413413828808
N	2.63590947994447	-3.22967428842007	-1.72994606295297
H	2.15689181101995	0.87446008133267	-2.09080106796235

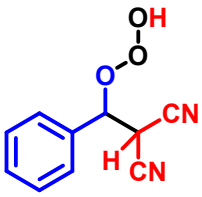


3a

No. of imaginary frequency: 0

C	-3.82686563941392	-0.53421253272489	2.99451779227941
C	-2.57551676821891	-0.77877356145369	2.44728258940103
C	-2.15074747226730	-0.06581348606806	1.31463650607242
C	-3.01236320393999	0.89029539666730	0.75390986636605
C	-4.26287861694051	1.13216035249209	1.30503587838145
C	-4.67163544479730	0.41810308943898	2.42758373195530
H	-4.14546450994083	-1.09184843695018	3.87043920186351
H	-1.93687239962321	-1.52578831877694	2.90493384777503
H	-2.68717346105521	1.44637444983551	-0.12261098882369
H	-4.91763119249930	1.87592123338328	0.86008808744736
H	-5.65039106297670	0.60214127356648	2.86253806138802
C	-0.86113527740670	-0.23852489679391	0.65219391547754
O	0.34938213907929	1.11451140922032	-1.99499448177394
H	-0.70732005522906	0.38133959228591	-0.23422243993059
C	0.18590750434405	-1.04535498986271	0.95215958227494
H	1.24455902262582	0.89358140158604	-1.69899053727328
C	0.25796349966685	-1.96331152177442	2.05467706634223

N	0.32465205896857	-2.70986135245130	2.93790852171212
C	1.34694628911335	-0.99280890746843	0.10215943095786
N	2.25925790861363	-0.91658079629639	-0.60820895133484
H	0.19486877189761	0.49879421214504	-2.72241764055806

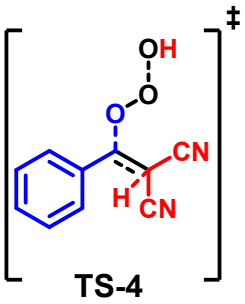


D

No. of imaginary frequency: 0

C	-0.17234136503981	-0.70732757577105	3.76487523684834
C	0.56654813346464	-0.71859422475365	2.58770535843555
C	0.36294762391964	-1.72508402848978	1.63966680193004
C	-0.58184856668550	-2.71885675235981	1.89454277935557
C	-1.31905324602710	-2.70944006565879	3.07390077676186
C	-1.11538319314976	-1.70192896045198	4.01035709606206
H	-0.00966740535567	0.08143900905536	4.49432250829815
H	1.28938986870145	0.07182719725525	2.40533381960377
H	-0.74104509182510	-3.51058611052578	1.16541809064705
H	-2.04955252338497	-3.49154343413016	3.26098402260339
H	-1.68802154552714	-1.69234551019315	4.93378621735233
C	1.13827366833818	-1.77726364172288	0.34367503618591
O	0.74199215874255	-0.81036069519093	-0.62777262429583
H	0.90528467865099	-2.70872434937140	-0.18335988432084
C	2.68087733369568	-1.73922527994338	0.56337016210336
H	2.95365306535153	-0.82301607853513	1.09698867990403
C	3.09359879210832	-2.89477005546805	1.37632007491183

N	3.39466251758757	-3.80902754642499	2.01519550832331
C	3.39648685384339	-1.73530539459242	-0.72296842530517
N	3.94689417146470	-1.73268507655565	-1.73860771598843
O	0.86507921040866	0.49465331000378	-0.11167110396852
O	2.18440811051868	0.92193058356295	-0.35838838155062
H	2.15998675019908	1.13700468026164	-1.30781403389714



TS-4

No. of imaginary frequency: 1 (616.6 cm^{-1})

C	-1.02923280606104	0.41597770258128	2.46546475466396
C	-0.26862790703142	0.44468741753358	1.30295627935824
C	-0.62656184016367	-0.35898413964388	0.21521920670992
C	-1.75238268645475	-1.18129095172274	0.31015992364640
C	-2.50500725583726	-1.21537778239907	1.47805637215566
C	-2.14374740907257	-0.41399102784017	2.55631657756490
H	-0.74323590713891	1.03869393445451	3.30807440490322
H	0.60688283318718	1.08385931121587	1.25345324376168
H	-2.03718694462221	-1.80469624776317	-0.53464827728024
H	-3.37317020976615	-1.86495390111140	1.54356005523338
H	-2.72972102797668	-0.43691374828338	3.47121997213060
C	0.12602785931234	-0.34982552363238	-1.07192862866600
O	-0.36682854377886	0.99405564620396	-1.87804697907381
H	-0.30060040786785	-1.04624131956372	-1.79716821538074

C	1.60254415729575	-0.31148491425011	-1.10936407046338
H	1.90674490753232	1.28948622877121	-1.45284588419711
C	2.36246330587961	-0.41859435314513	0.09902922747853
N	2.99892212652835	-0.46913700550677	1.06894062895211
C	2.19148113327466	-0.87586467313863	-2.28939205886079
N	2.62180078160126	-1.26599497346184	-3.29535225036618
O	0.00681088336447	2.05177572710834	-1.31189542497174
O	1.75034464173413	2.31321850234935	-1.68008637250149
H	1.70228031606129	2.38159609124430	-2.65172248479711

5. References

1 (a) M. C. DeRosa and R. J. Crutchley, *Coord. Chem. Rev.*, 2002, **233-234**, 351-371; (b) S. Yakubov and J. P. Barham, *Beilstein J. Org. Chem.***,** 2020**, 16***,* 2151-2192; (c) N. A. Romero and D. A. Nicewicz, *Chem. Rev*., 2016, **116**, 10075-10166.

2 (a) D. P. Hari and B. Konig, *Chem. Commun*., 2014, **50**, 6688-6699; (b) L. V. Lutkus, S. S. Rickenbach and T. M. McCormick, *J. Photochem. Photobiol. A: Chem.*, 2019, **378***,* 131-135.

3 (a) A. Monga, A. P. Pandey and A. Sharma, *Adv. Synth. Catal.*, 2019, **361**, 3554-3559; (b) S. Dadwal, H. Deol, M. Kumar and V. Bhalla, *Sci. Rep*., 2019, **9**, 11142.

4 (a) K. Aich, S. Das, S. Goswami, C. K. Quah, D. Sarkar, T. K. Mondal and H.-K. Fun, *New J. Chem*., 2016, **40**, 6907-6915; (b) M. Mahama and S. Bahari, *J. Chem. Res*., 2014, **38**, 291-294; (c) L. Chen, C. Lin, Y. Lan, Z. Li, D. Huang, W. Yang, Y. Li, *Environ. Chem. Lett*., 2020, **18**, 2157-2163.

5 (a) W. Wang, M. Luo, W. Yao, M. Ma, S. A. Pullarkat, L. Xu and P.-H. Leung, *ACS Sustainable Chem. Eng*., 2019, **7**, 1718−1722; (b) C. L. Yadav, Anamika, G. Rajput, K. Kumar, M. G. B. Drew and N. Singh, *Inorg. Chem*., 2020, **59**, 11417-11431.

6 (a) B. Chowhan, M. Gupta and N. Sharma, *ChemistrySelect*, 2019, **4**, 12689-12700; (b) I. Azada, T. Khana, R. Ahmadb, A. Kamal, A. R. Khana and M. Nasibullah, *J. Mol. Struct*., 2021, **1228**, 129451.

7 C. Li, D. Zhong, X. Huang, G. Shen, Q. Li, J. Du, Q. Li, S. Wang, J. Li and J. Dou, *New J. Chem*., 2019, **43**, 5813-5819.

8 J. S. Yadav, B. V. S. Reddy, A. K. Basak, B. Visali, A. V. Narsaiah and K. Nagaiah, *Eur. J. Org. Chem.*, 2004, 546-551.

9 (a) H. Goksu and E. Gultekin, *ChemistrySelect*, 2017, **2**, 458-463; (b) R. Takakura, K. Koyama, M. Kuwata, T. Yamada, H. Sajiki and Y. Sawama, *Org. Biomol. Chem*., 2020, **18**, 6594-6597.

10 (a) S. K. Panja, N. Dwivedi and S. Saha, *RSC Adv*., 2015, **5**, 65526-65531; (b) M. Gilanizadeh and B. Zeynizadeh, *Res. Chem. Intermed*., 2018, **44**, 6053-6070; c) S. Yuana, L. Fengc, A. Hed, L. Liud, B. Liuc, Y. Chenc and X. Li, *Colloids Surf. A*, 2020, **607**, 125475; d) R. Jangir, A. C. Kalita, D. Kaleeswaran, S. K. Gupta and R. Murugavel, *Chem. Eur. J*., 2018, **24**, 6178-6190.

11 (a) Y. Wang, L. Wang, C. Liu and R. Wang, *ChemCatChem,* 2015, **7**, 1559-1565; (b) S. N. Jadhav, S. P. Patil, D. P. Sahoo, D. Rath, K. Parida and C. V. Rode, *Catal. Lett*., 2020, **150**, 2331-2351.

12 (a) N. Gupta, T. Roy, D. Ghosh, S. H. R. Abdi, R. I. Kureshy, N.-u. H. Khanab and H. C. Bajaj, *RSC Adv*., 2015, **5**, 17843-17850; (b) F. Zhou, J. Shao, Y. Yang, J. Zhao, H. Guo, X. Li, S. Ji and Z. Zhang, *Eur. J. Org. Chem*., 2011, 4773–4787; (c) L. Kong, L. Yang, G.-b. Zhang, Q.-y. Chen, H. Wang, X.-p. Gan, H. Li, H.-p. Zhou, J.-x. Yang and Y.-p. Tian, *J. Mater. Sci*., 2018, **53**, 921–936; (d) A. Kathiravan, M. Panneerselvam, K. Sundaravel, N. Pavithra, V. Srinivasan, S. Anandand and M. Jaccob, *Phys. Chem. Chem. Phys.*, 2016, **18**, 13332-13345.

13 (a) D. Xue, Y.-C. Chen, X. Cui, Q.-W. Wang, J. Zhu and J.-G. Deng, *J. Org. Chem*., 2005, **70**, 3584-3591; (b) G. R. Krishnan and K. Sreekumar, *Eur. J. Org. Chem*., 2008, 4763-4768; (c) B. A. Robichaud and K. G. Liu, *Tetrahedron Lett*., 2011, **52**, 6935-6938.

14 (a) C. Mukhopadhyay, P. Das and R. J. Butcher, *Org. Lett*., 2011, **13**, 4664-4667; (b) H. Pan, M.-Y. Han, P. Li and L. Wang, *J. Org. Chem*., 2019, **84**, 14281-14290.

15 S. L. Broman, M. Jevric, A. D. Bond and M. B. Nielsen, *J. Org. Chem*., 2014, **79**, 41-64.

16 (a) D. M. Barnes, A. R. Haight, T. Hameury, M. A. McLaughlin, J. Mei, J. S. Tedrowy and J. D. R. Toma, *Tetrahedron,* 2006, **62**, 11311-11319; (b) S. Kotowicz, S. Kula, M. Filapek, A. Szłapa-Kula, M. Siwy, H. Janeczek, J. G. Małecki, K. Smolarek, S. Mackowski and E. Schab-Balcerzak, *Mater. Chem. Phys*., 2018, **209**, 249-261.

17 S. L. Broman, O. Kushnir, M. Rosenberg, A. Kadziola, J. Daub and M. B. Nielsen, *Eur. J. Org. Chem*., 2015, 4119-4130.

18 L. A. Estrada, A. Frances-Monerris, I. Schapiro, M. Olivucciac and D. Roca-Sanjuan, *Phys. Chem. Chem. Phys*., 2016, **18**, 32786-32795.

19 G. Zhang, Y. Zhang, J. Yan, R. Chen, S. Wang, Y. Ma and R. Wang, *J. Org. Chem*., 2012, **77**, 878-888.

20 G. Li, J. Xiao and W. Zhang, *Green Chem.*, 2012, **14**, 2234-2242.

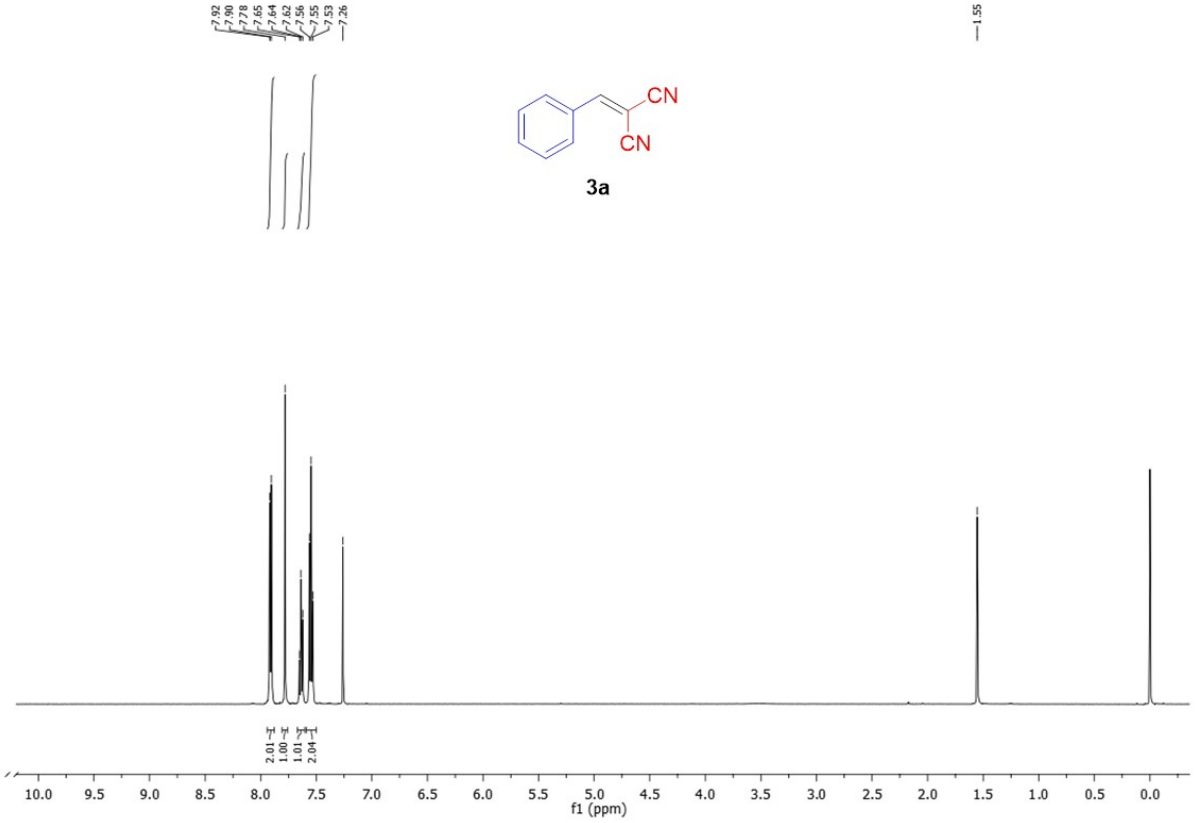
21 A. Gheath, A. Alawami, N. Alarafi, M. Aabdelrhman and A. Boulifa, *Res. J. Appl. Sci. Eng. Technol*., 2019, **16**, 204-211.

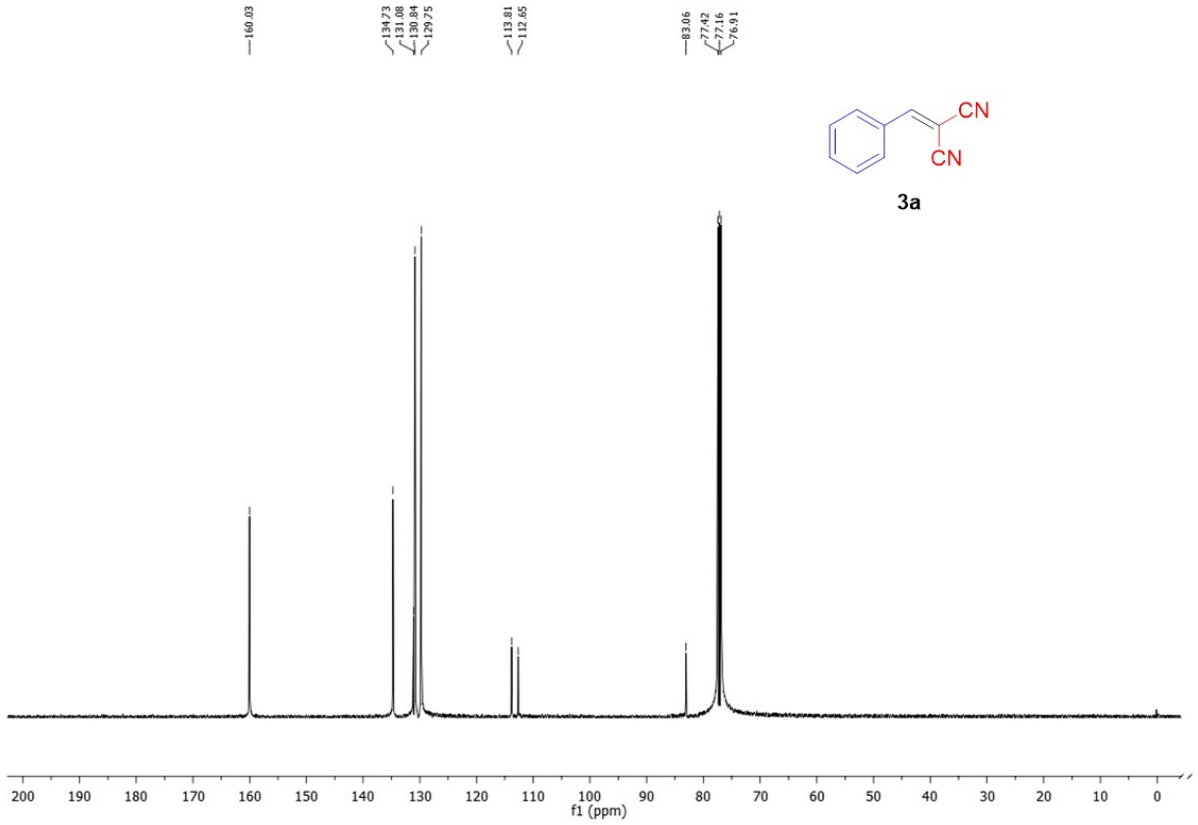
22 R. Qiu, Y. Qiu, S. Yin, X. Song, Z. Meng, X. Xu, X. Zhang, S. Luo, C.-T. Au and W.-Y. Wong, *Green Chem*., 2010, **12**, 1767-1771.

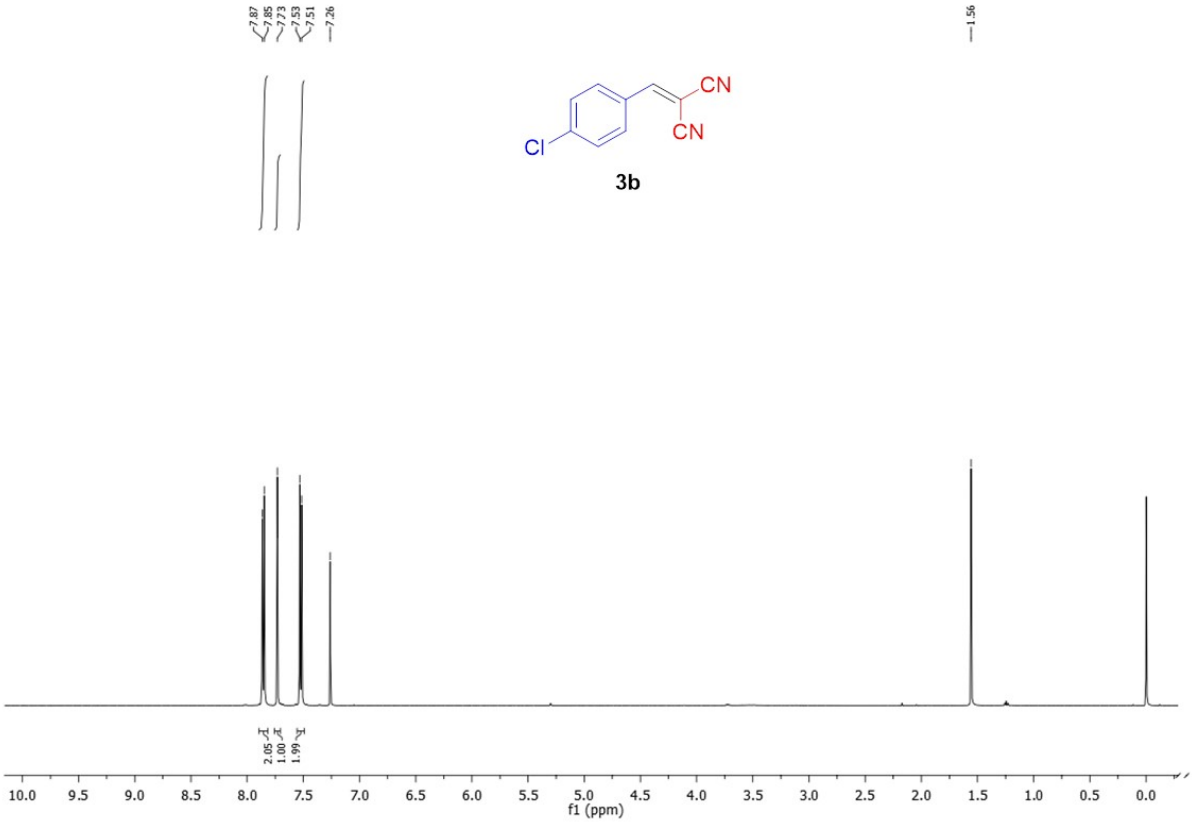
23 W. Zhou, S. Zhai, J. Pan, A. Cui, J. Qian, M. He, Z. Xu, and Q. Chen, *Asian J. Org. Chem*., 2017, **6**, 1536-1541.

24 (a) Z. Kibou, N. Cheikh, D. Villemin, N. Choukchou-Braham, B. Mostefa-Kara, M. Benabdallah, *Int. J. of Org. Chem*., 2011, **1**, 242-249; (b) H. Pan, M.-Y. Han, P. Li, and L. Wang, *J. Org. Chem*., 2019, **84**, 14281-14290.

6. ^{1}H and ^{13}C NMR Spectra



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CN
CN
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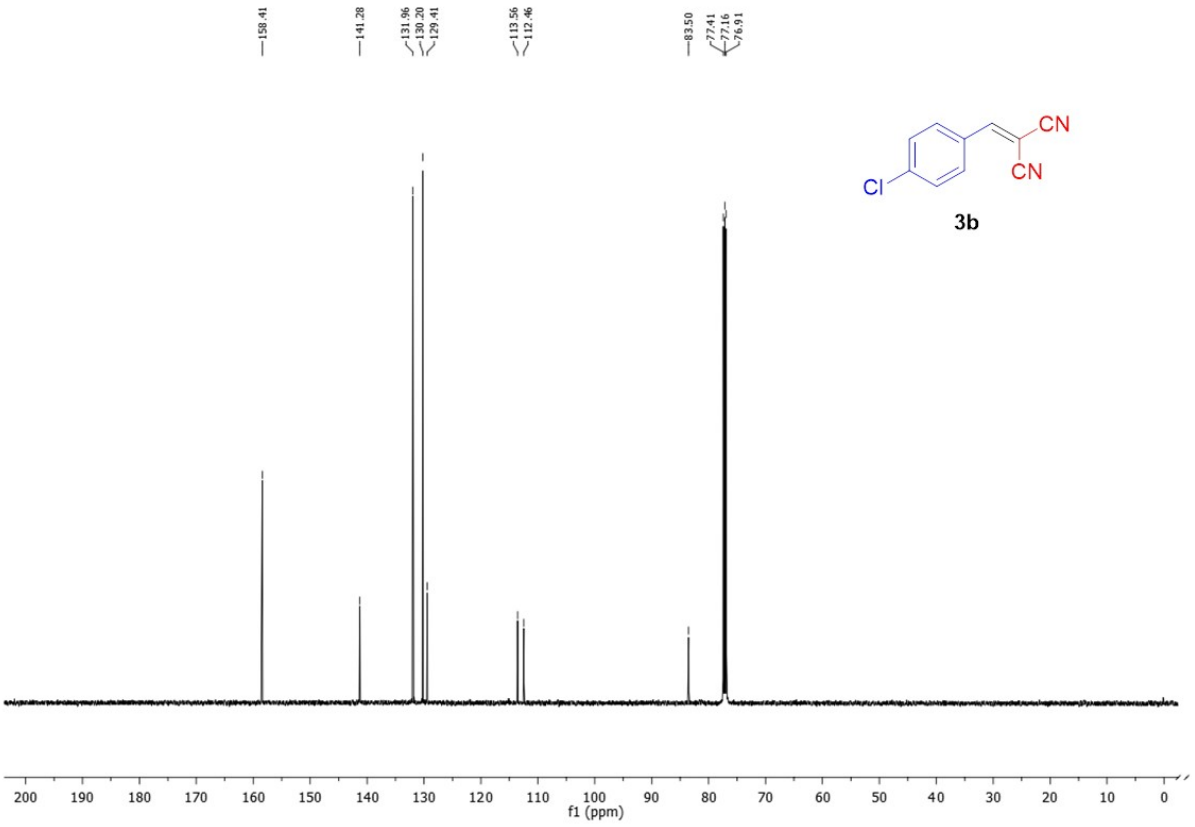
3b
2.05
1.00
1.99
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)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130.20
129.41
113.56
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83.50
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CN
Cl
3b
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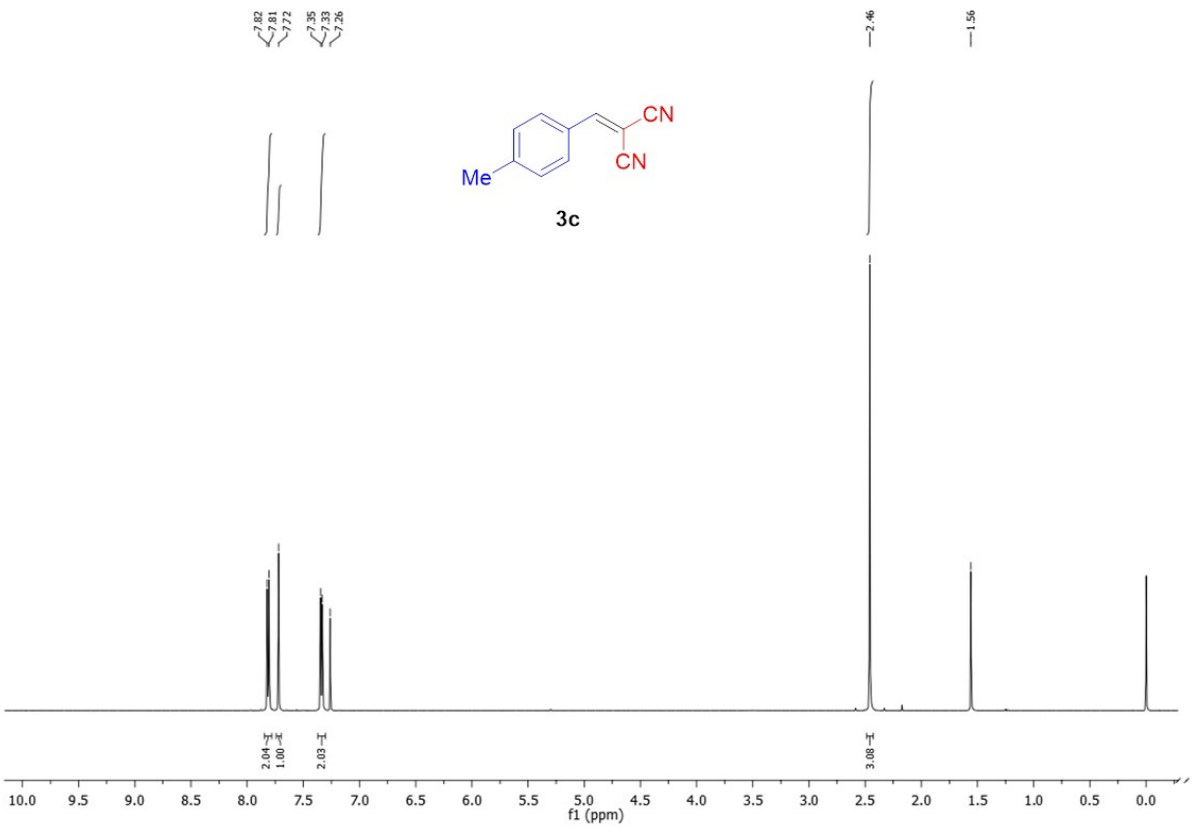
f1 (ppm)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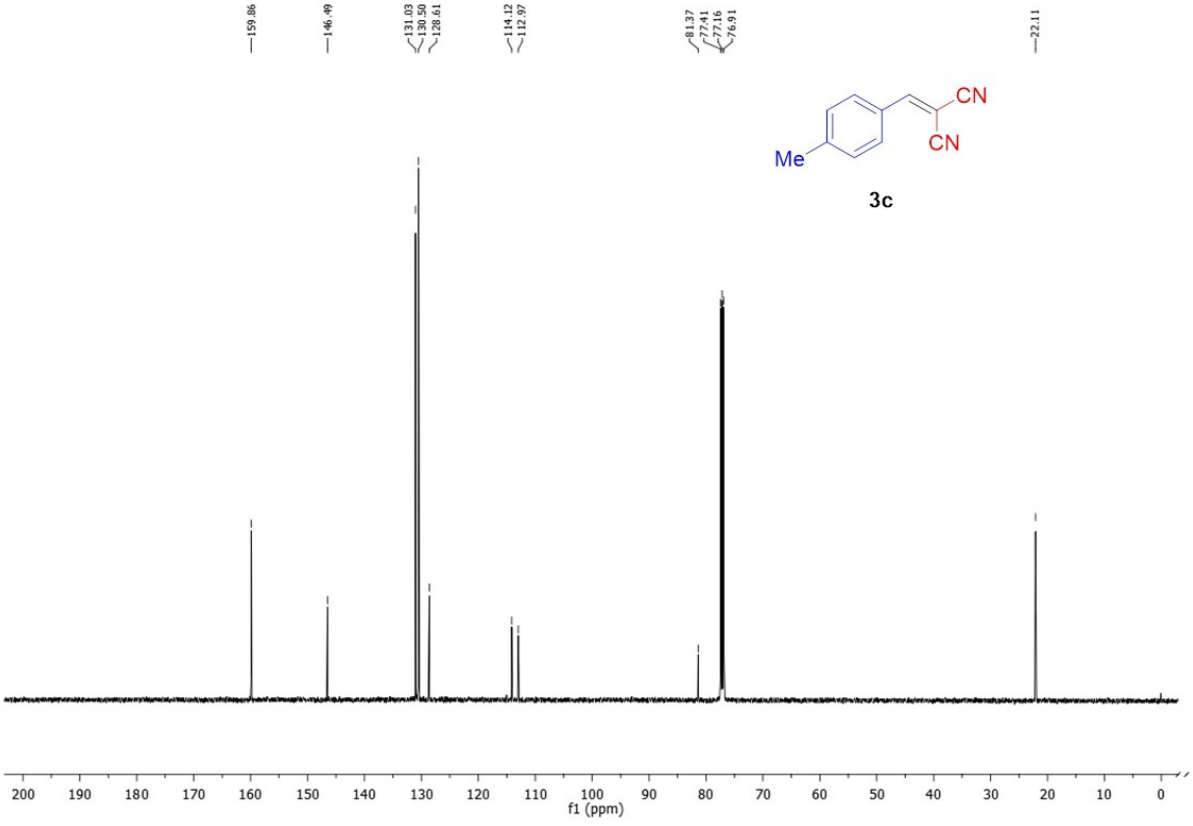
2.03
3.08
f1 (ppm)

3c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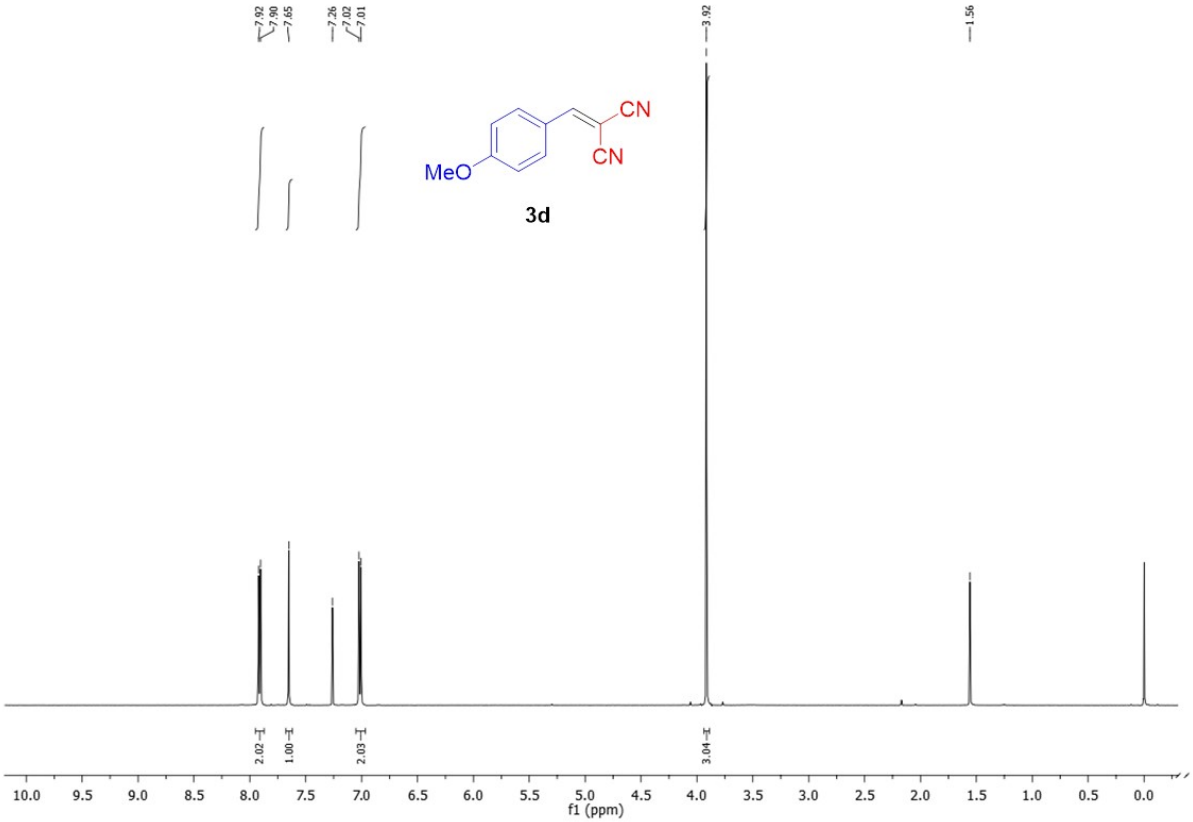
CN
CN
Me
f1 (ppm)

3c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CN
MeO
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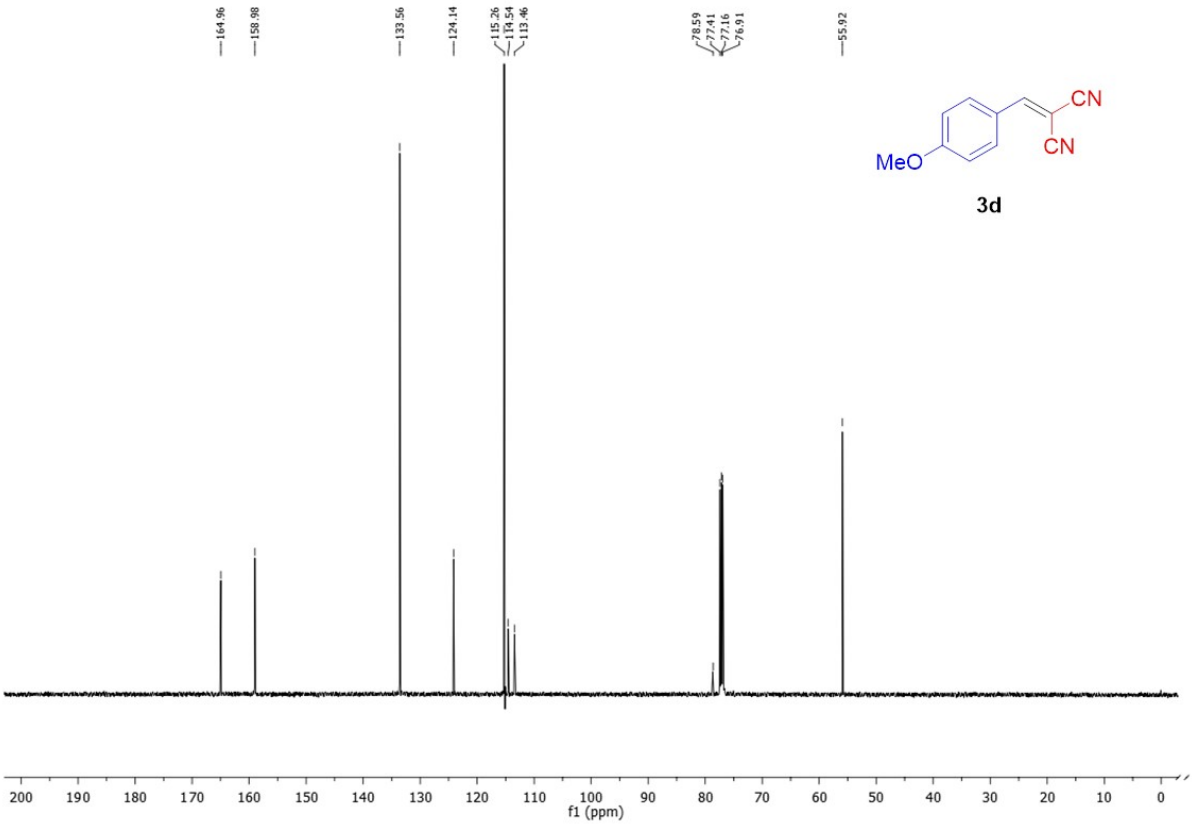
1.00
2.03
3.04
f1 (ppm)

3d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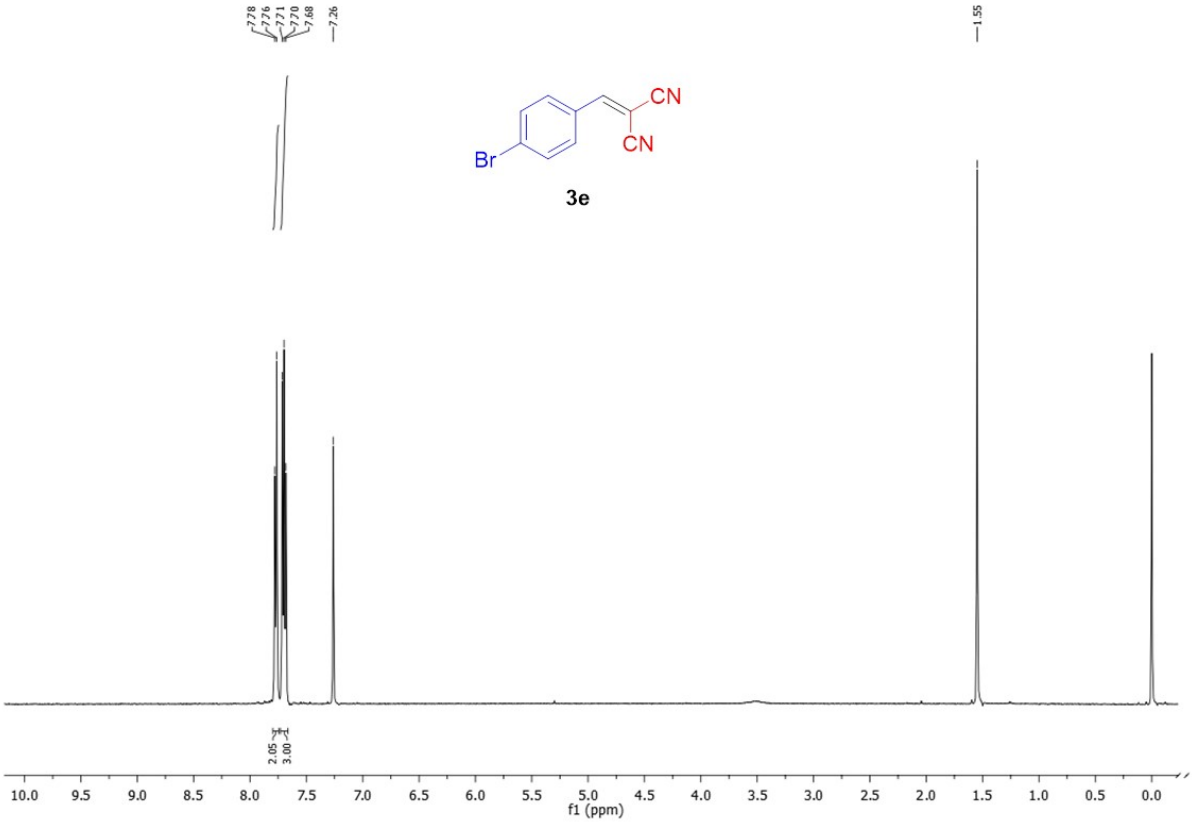
76.91
55.92
CN
CN
MeO
f1 (ppm)

3d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CN
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Br
3e
2.05
3.00
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
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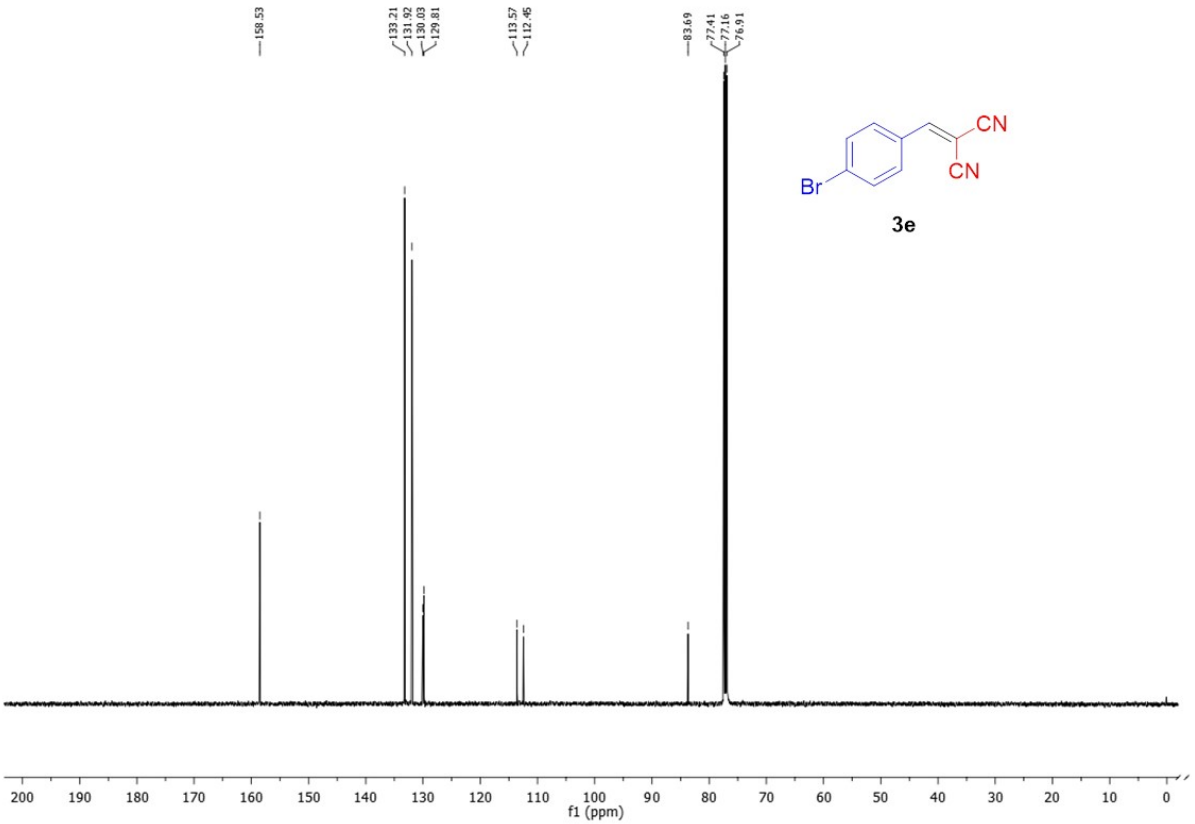
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CN
Br
3e
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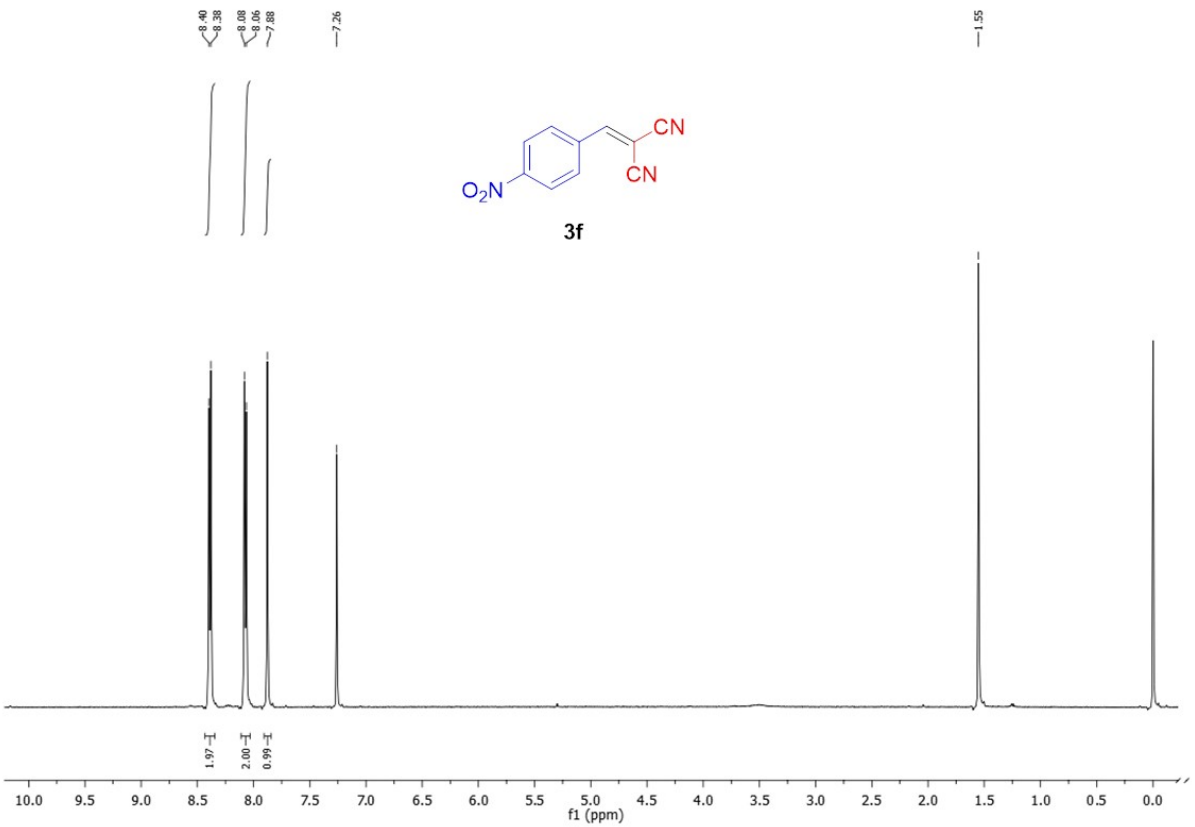
f1 (ppm)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1.55
CN
CN
O2N
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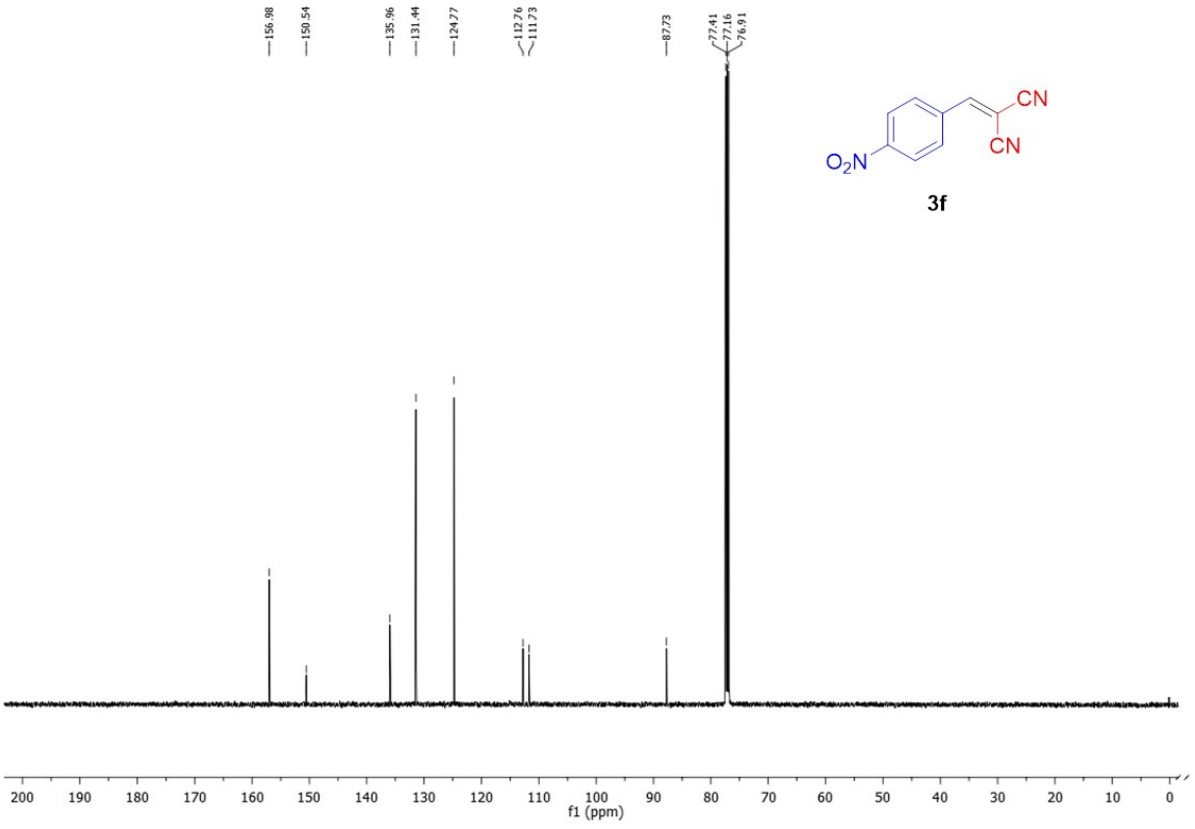
2.00
0.99
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

3f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CN
CN
O2N
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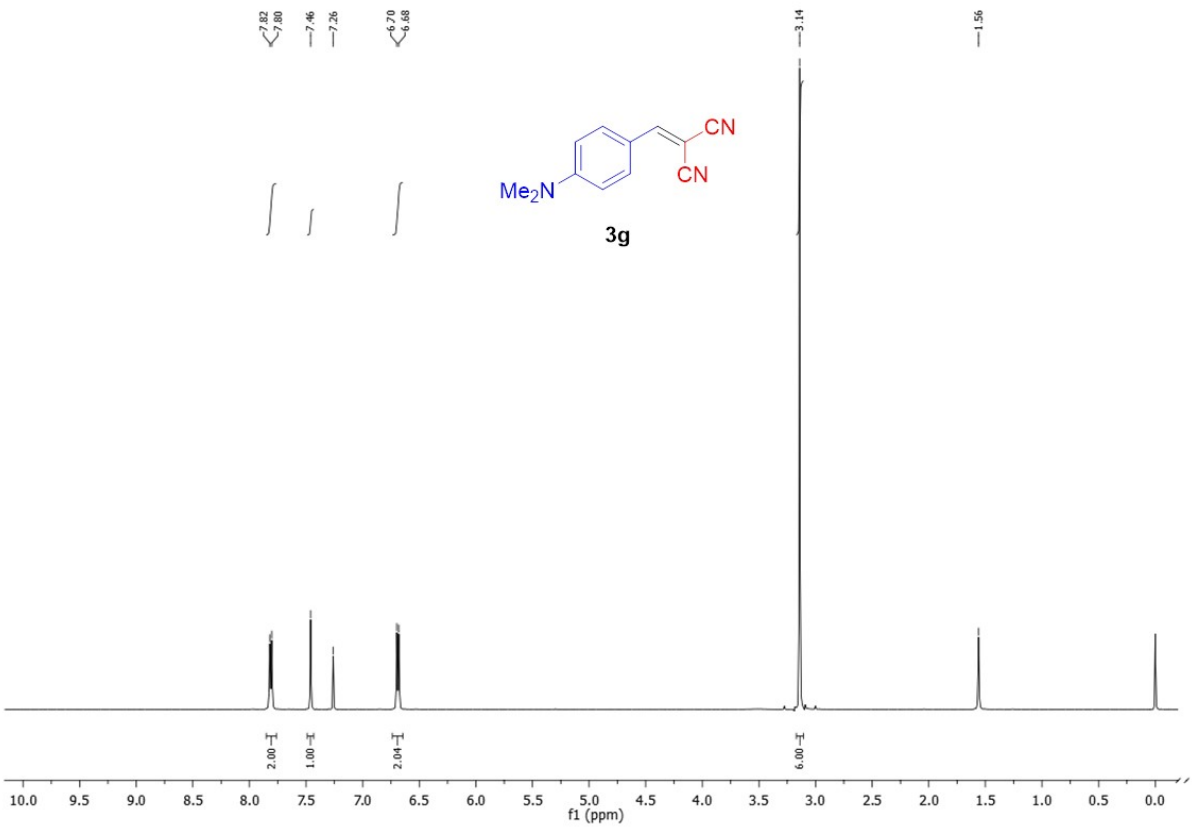
f1 (ppm)

3f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CN
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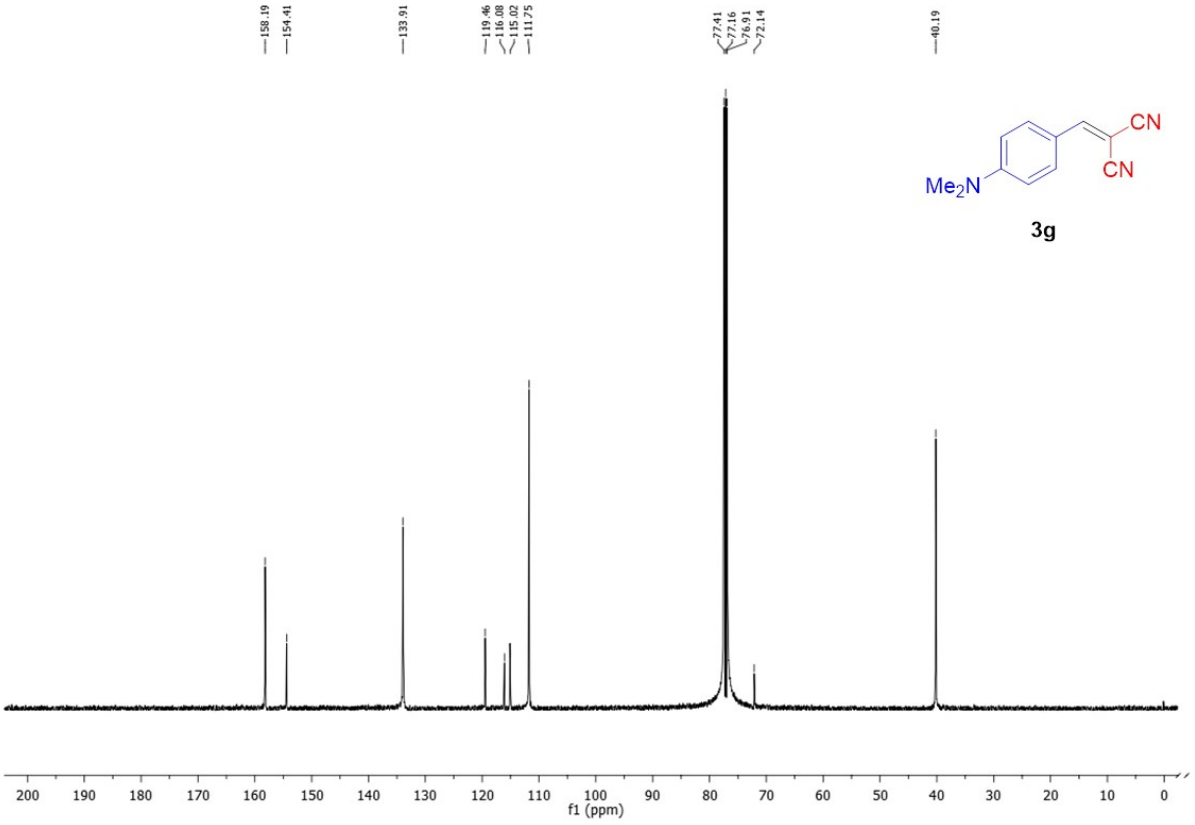
1.00
2.04
6.00
f1 (ppm)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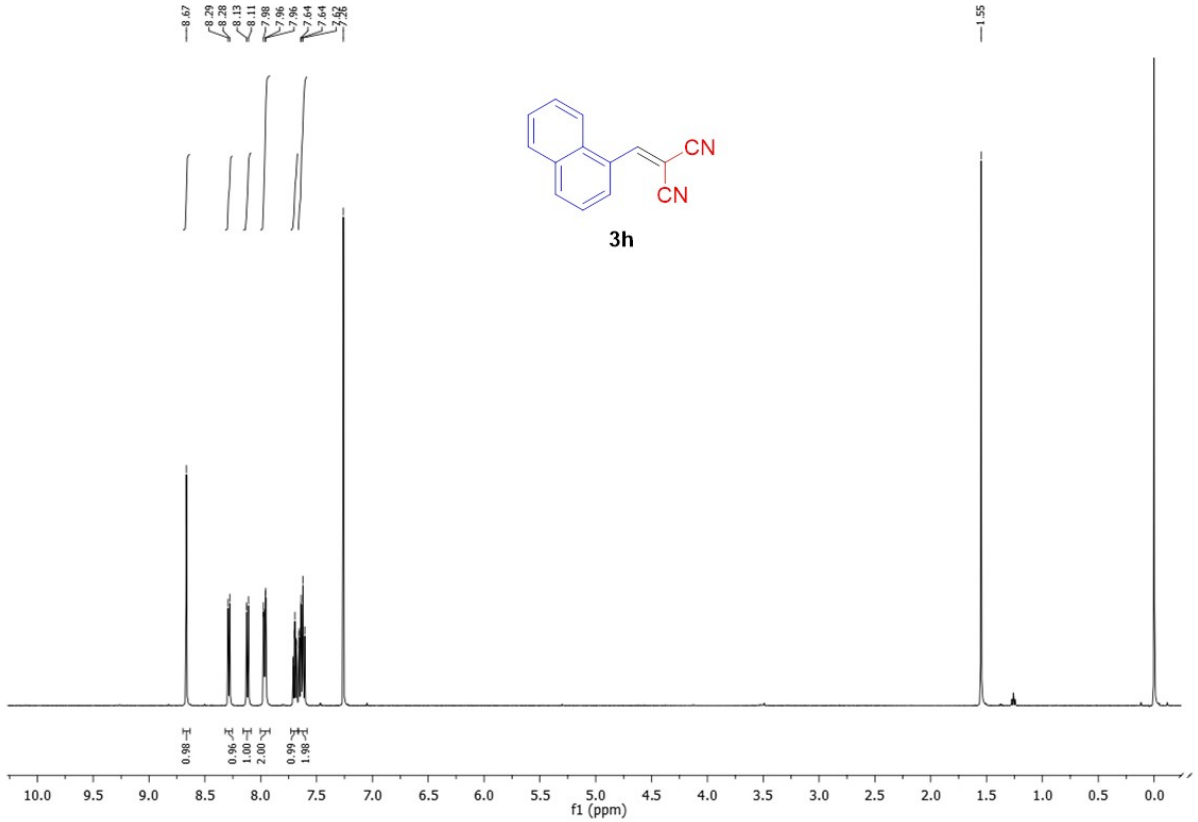
CN
CN
Me2N
3g
f1 (ppm)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7.62
1.55
CN
CN
3h
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0.96
1.00
2.00
0.99
1.98
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
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2.5
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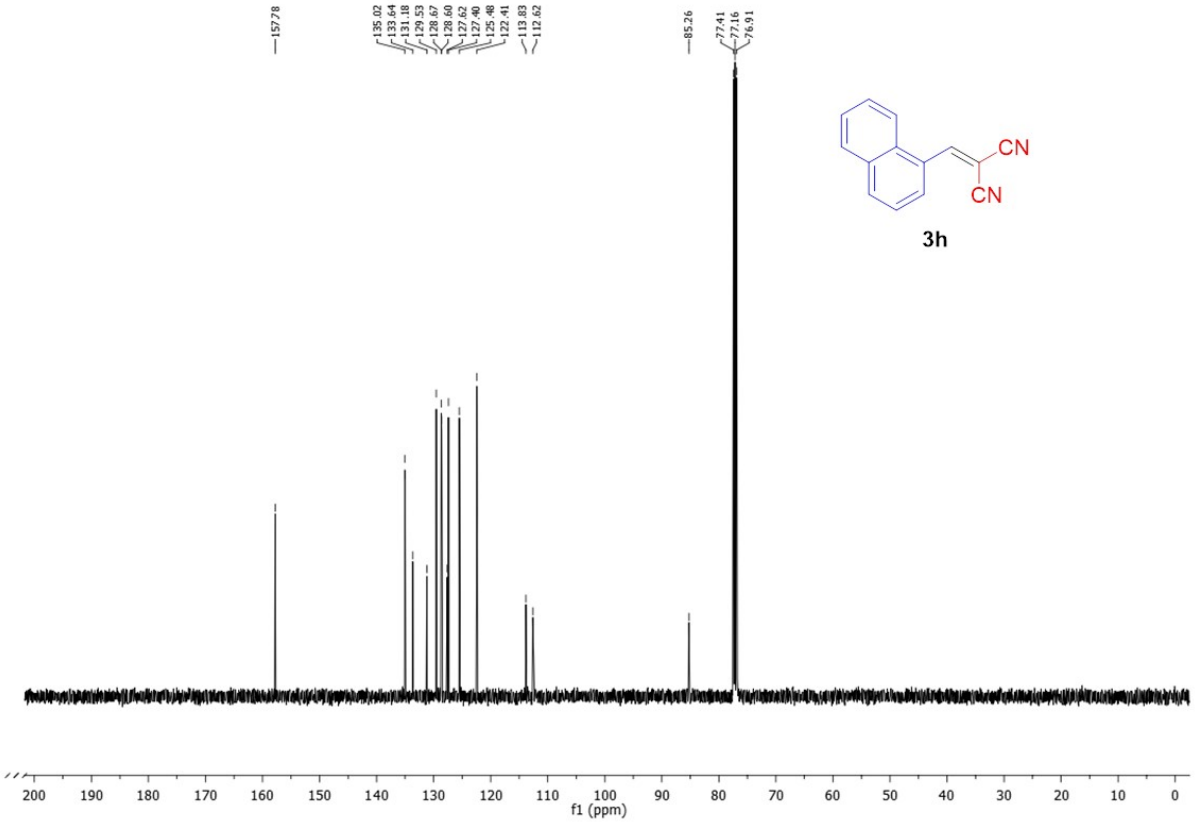
0.0
f1 (ppm)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85.26
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77.16
76.91
CN
CN
3h
200
190
180
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110
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90
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70
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50
40
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10
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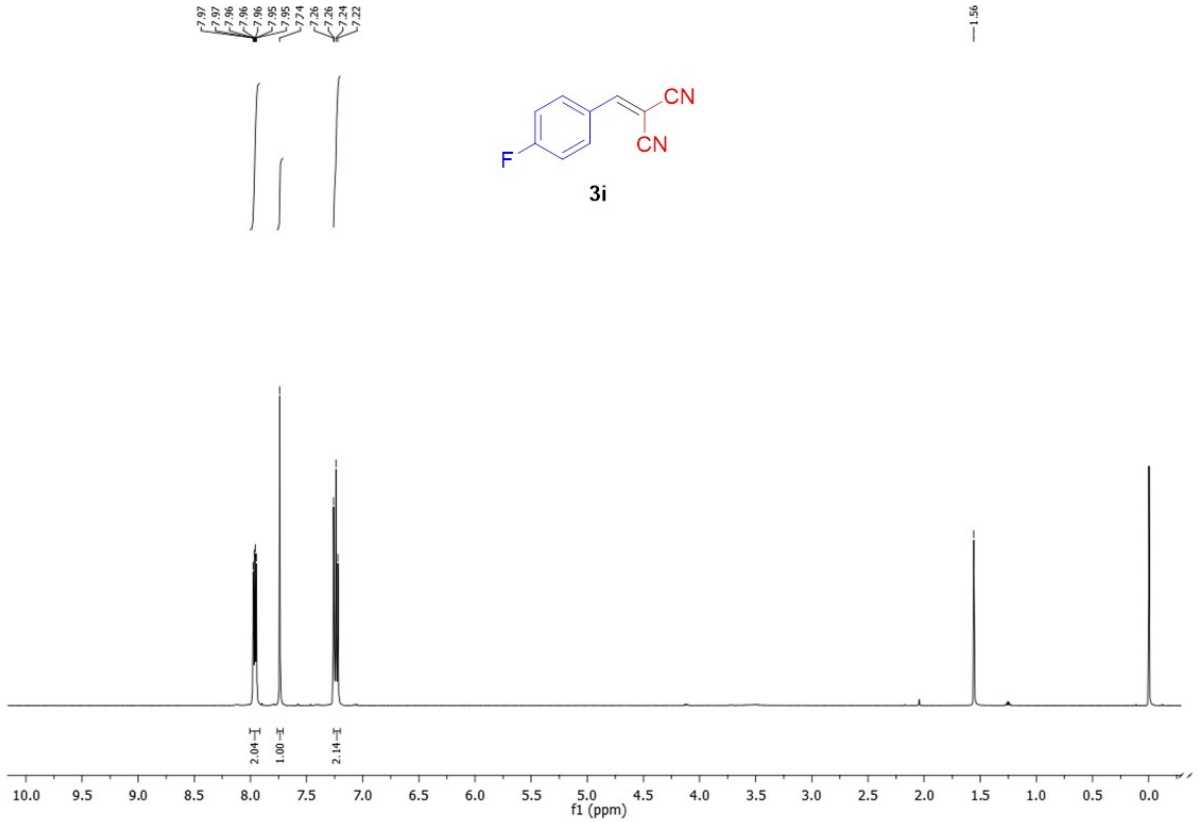
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CN
CN
F
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1.00
2.14
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
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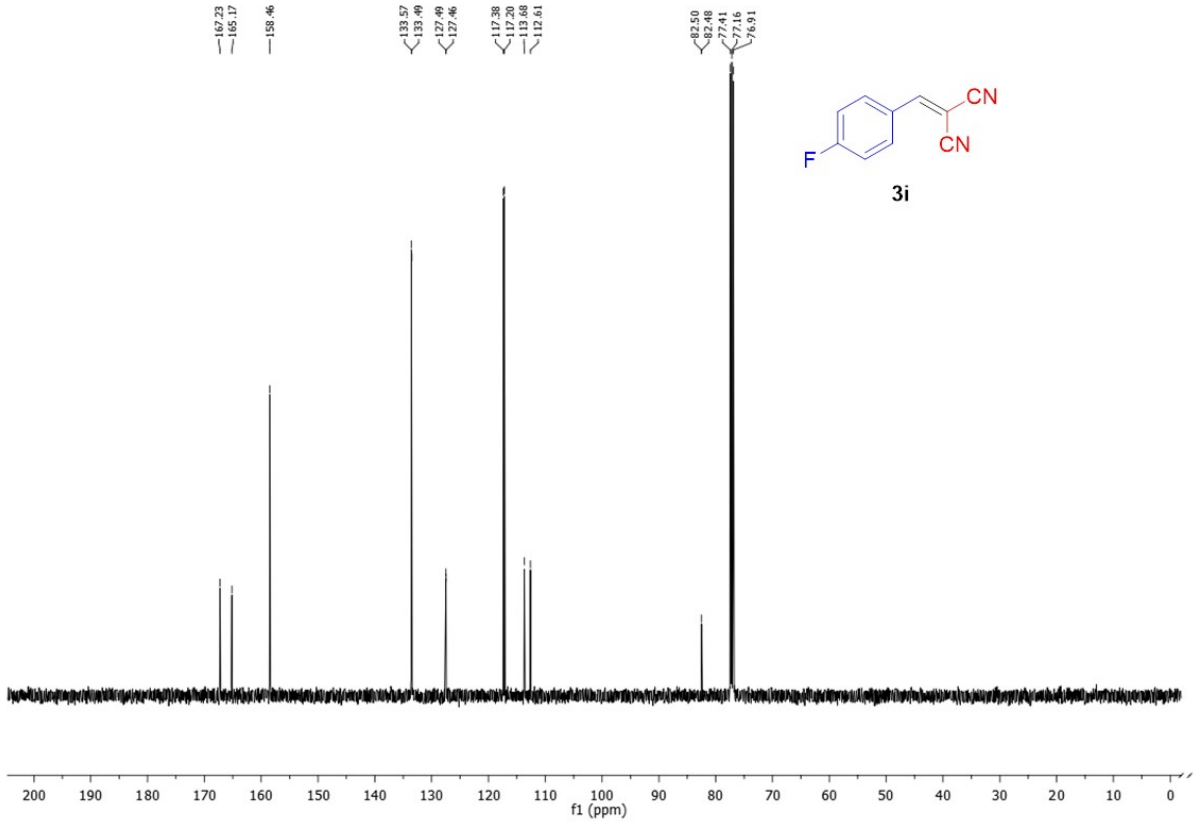
f1 (ppm)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CN
F
3i
200
190
180
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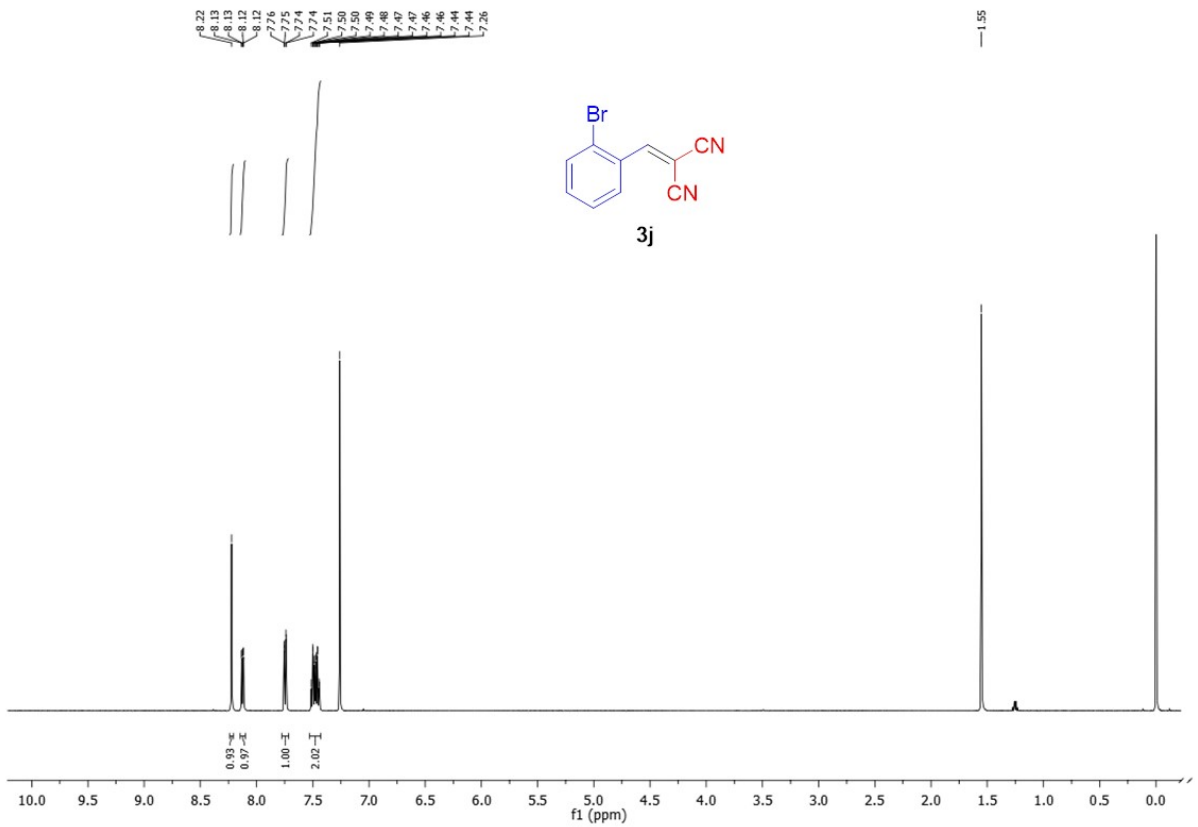
f1 (ppm)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7.49
7.48
7.47
7.47
7.46
7.46
7.44
7.44
7.26
1.55
Br
CN
CN
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0.97
1.00
2.02
10.0
9.5
9.0
8.5
8.0
7.5
7.0
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6.0
5.5
5.0
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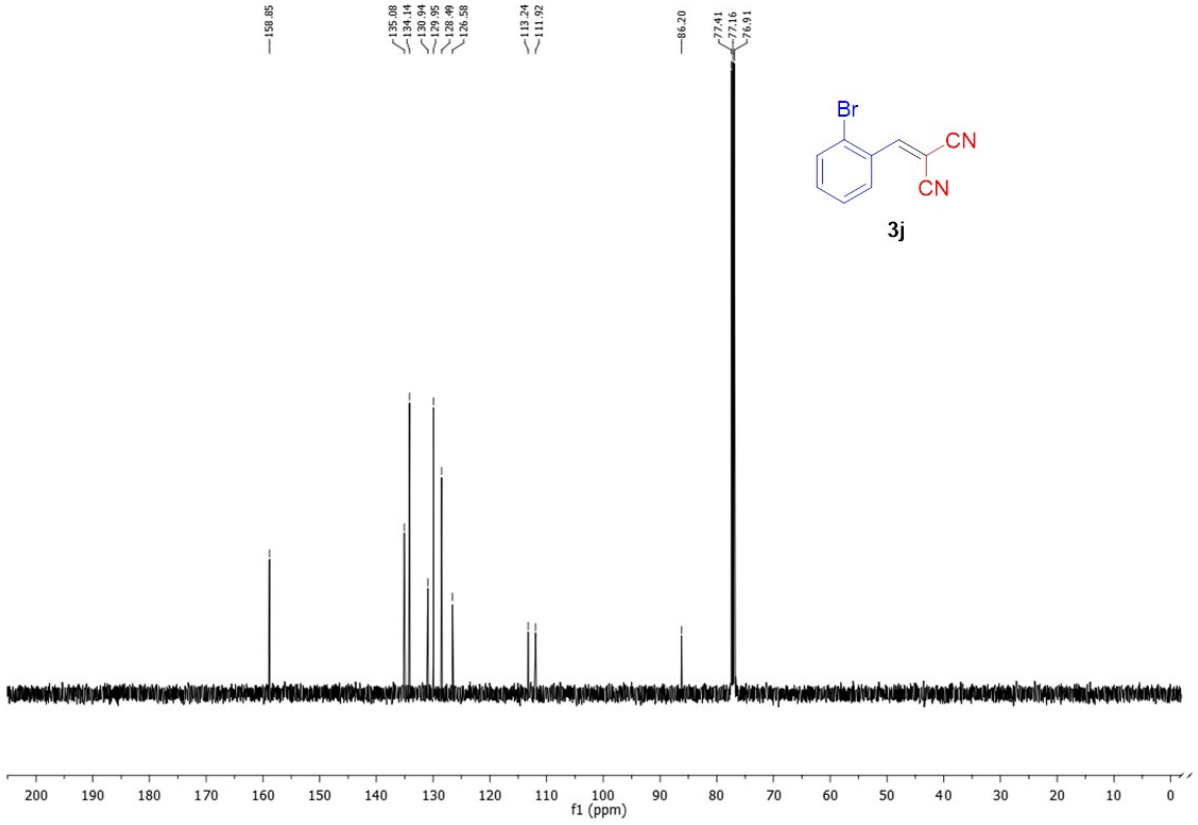
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

3j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76.91
Br
CN
CN
200
190
180
170
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150
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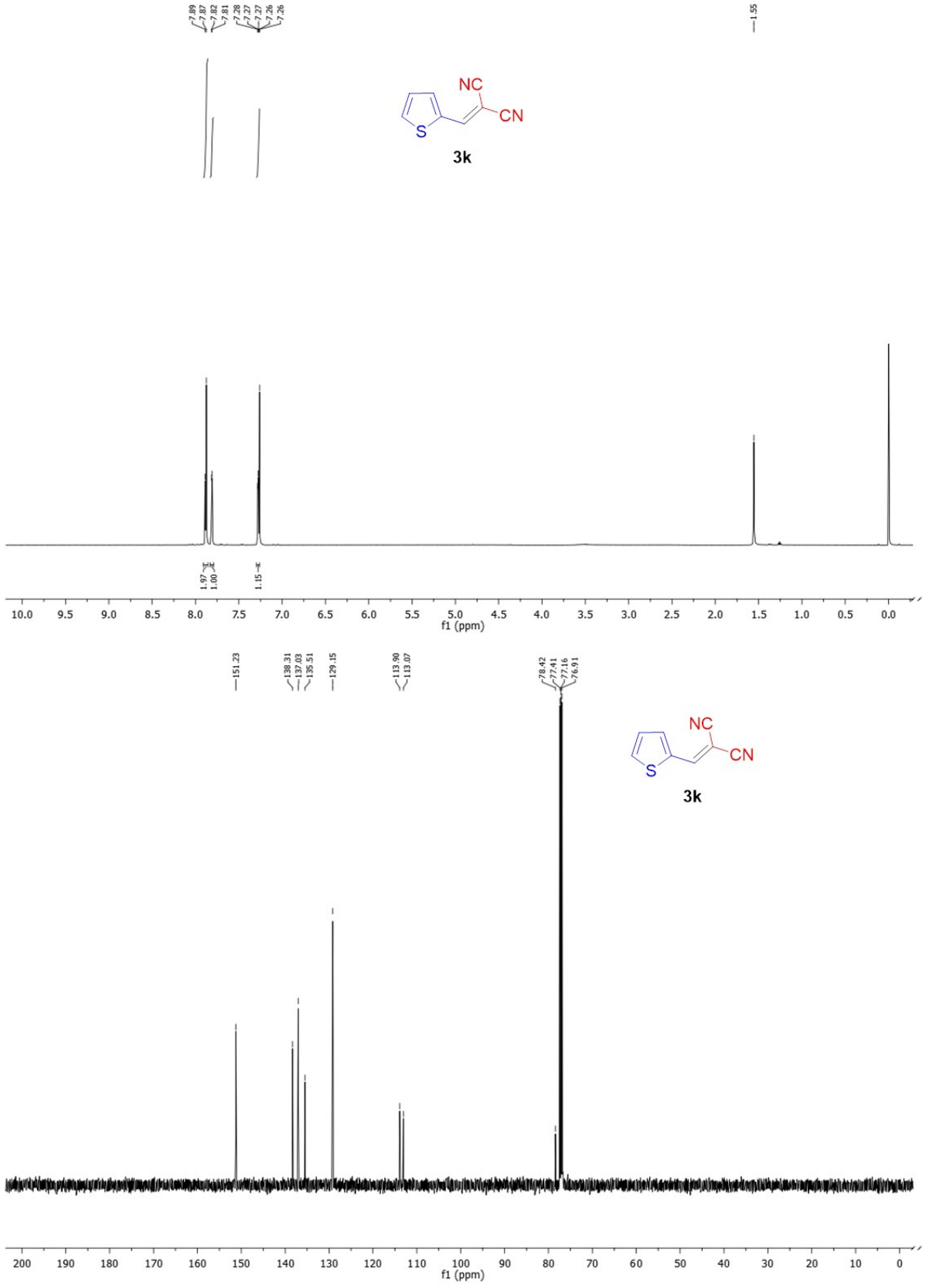
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

3j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CN
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1.00
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10.0
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9.0
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7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
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f1 (ppm)
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138.31
137.03
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77.16
76.91
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200
190
180
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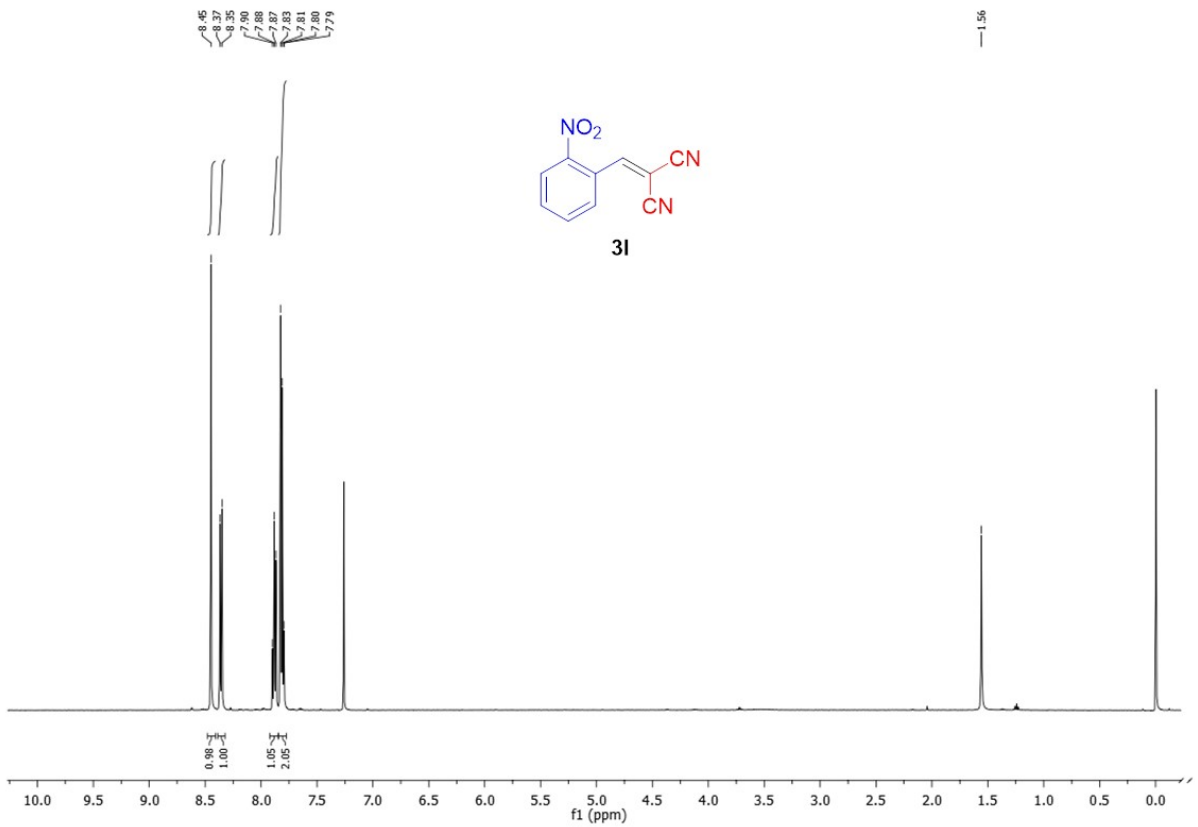
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7.79
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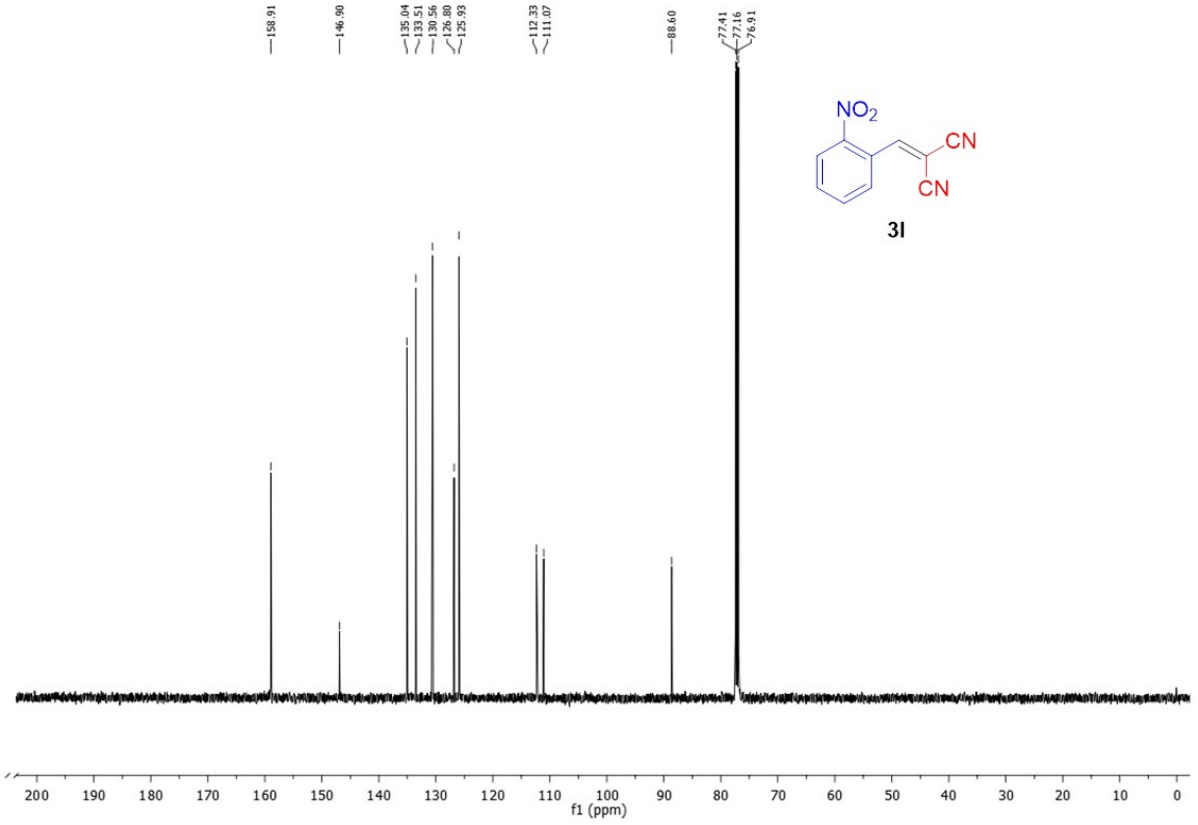
NO2
CN
CN
3l
0.98
1.00
1.05
2.05
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)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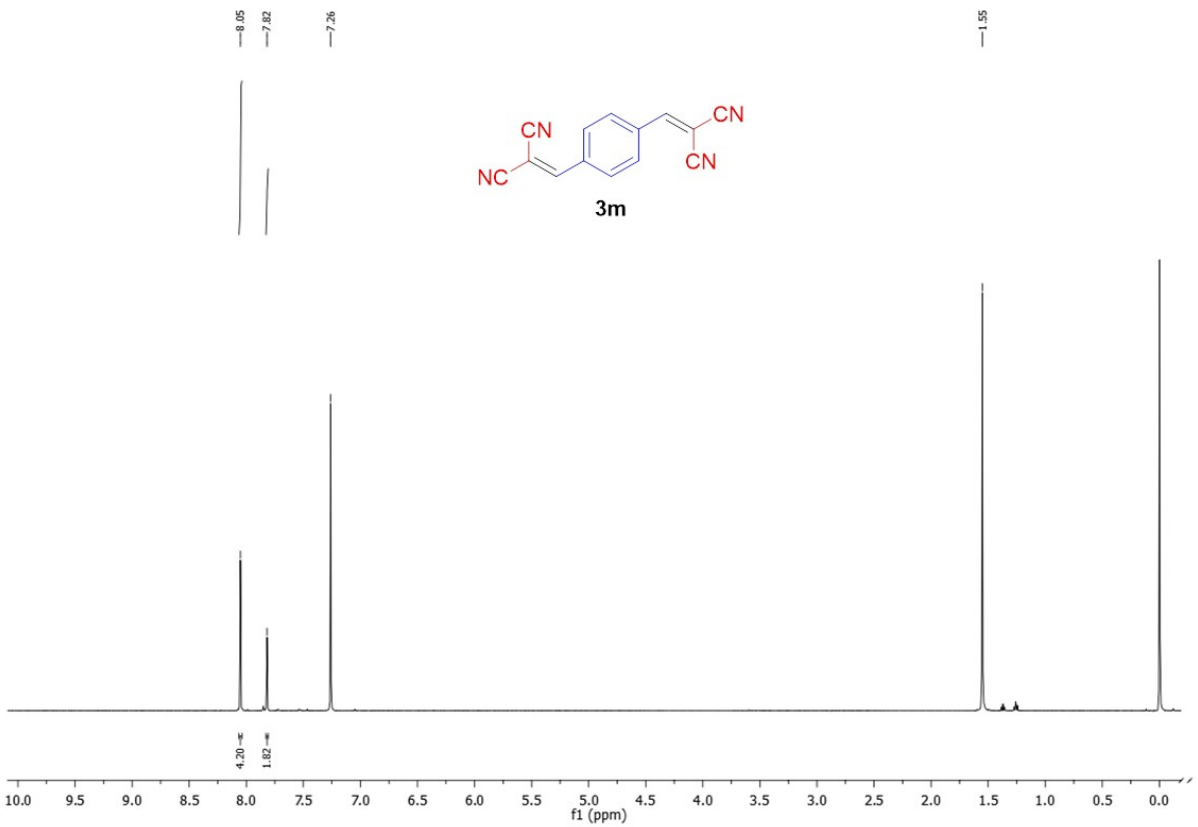
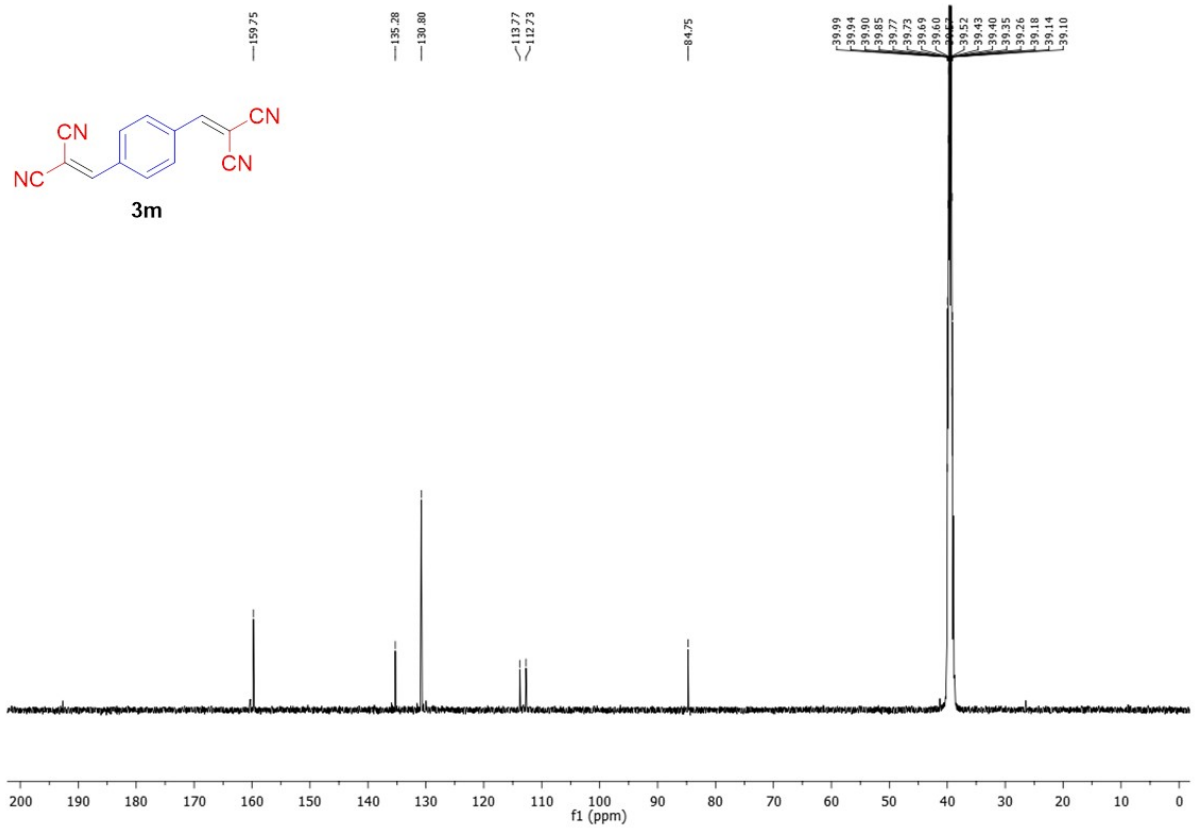
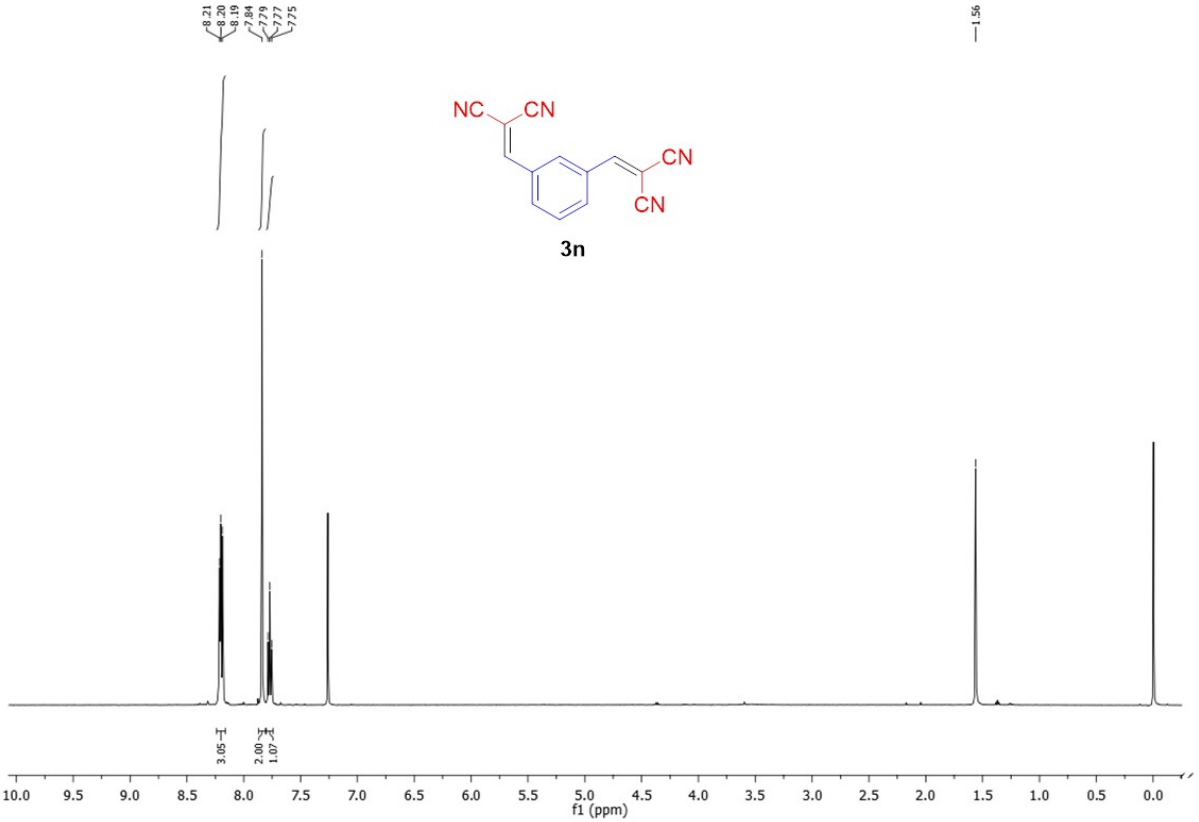
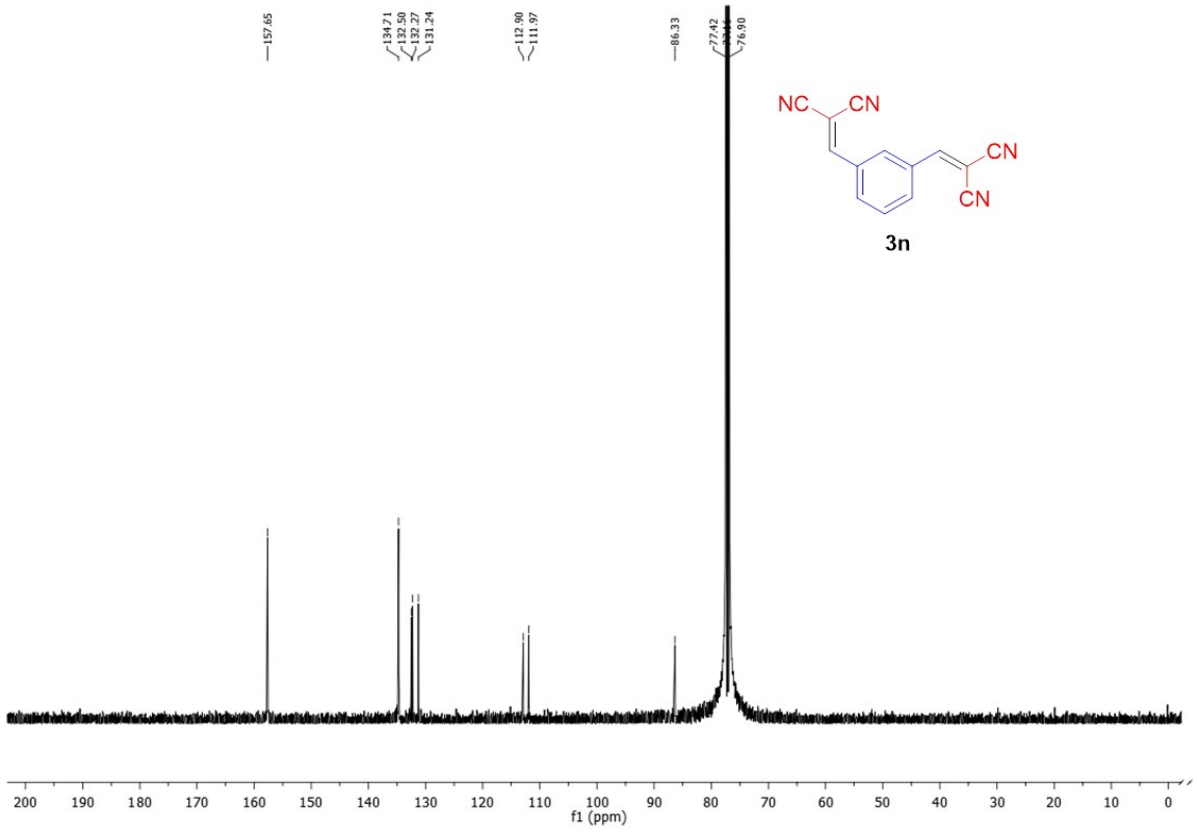
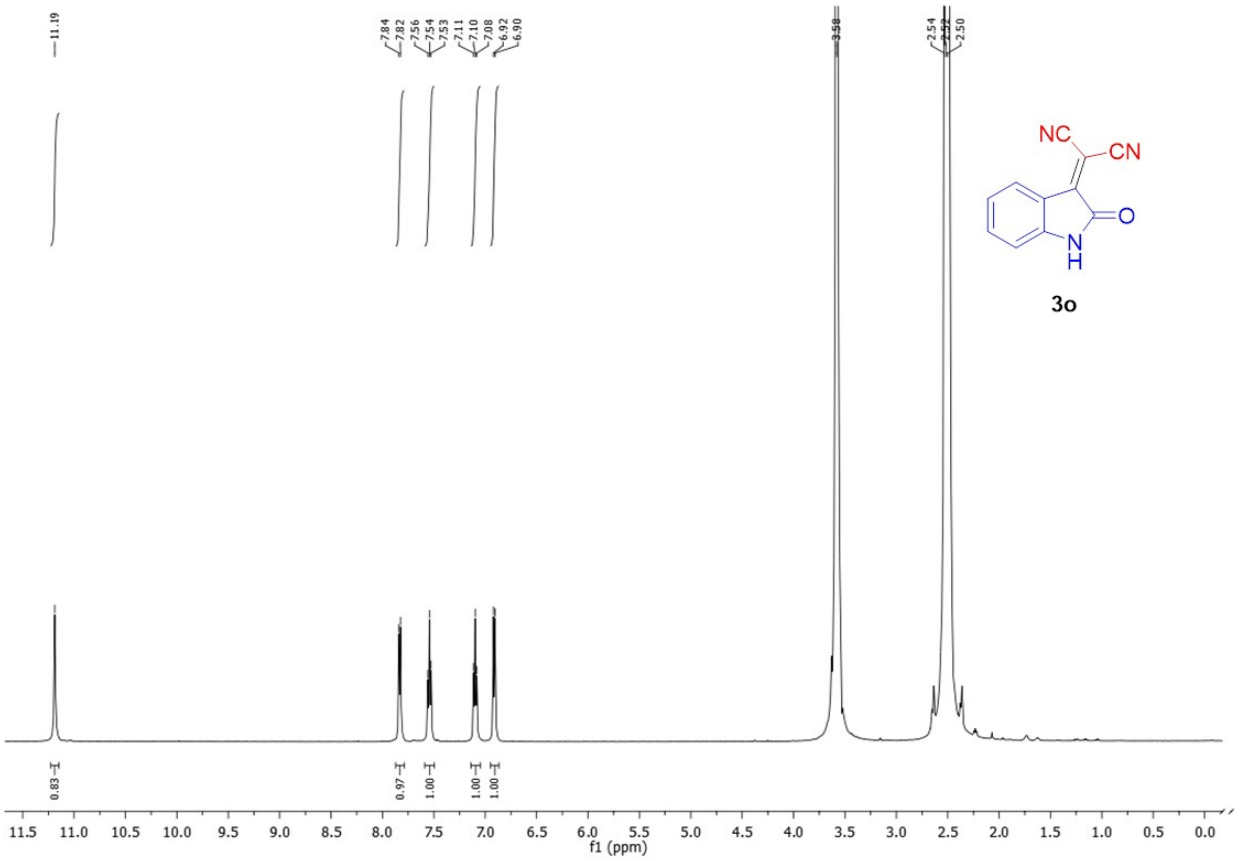
146.90
135.04
133.51
130.56
126.80
125.93
112.33
111.07
88.60
77.41
77.16
76.91
NO2
CN
CN
3l
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

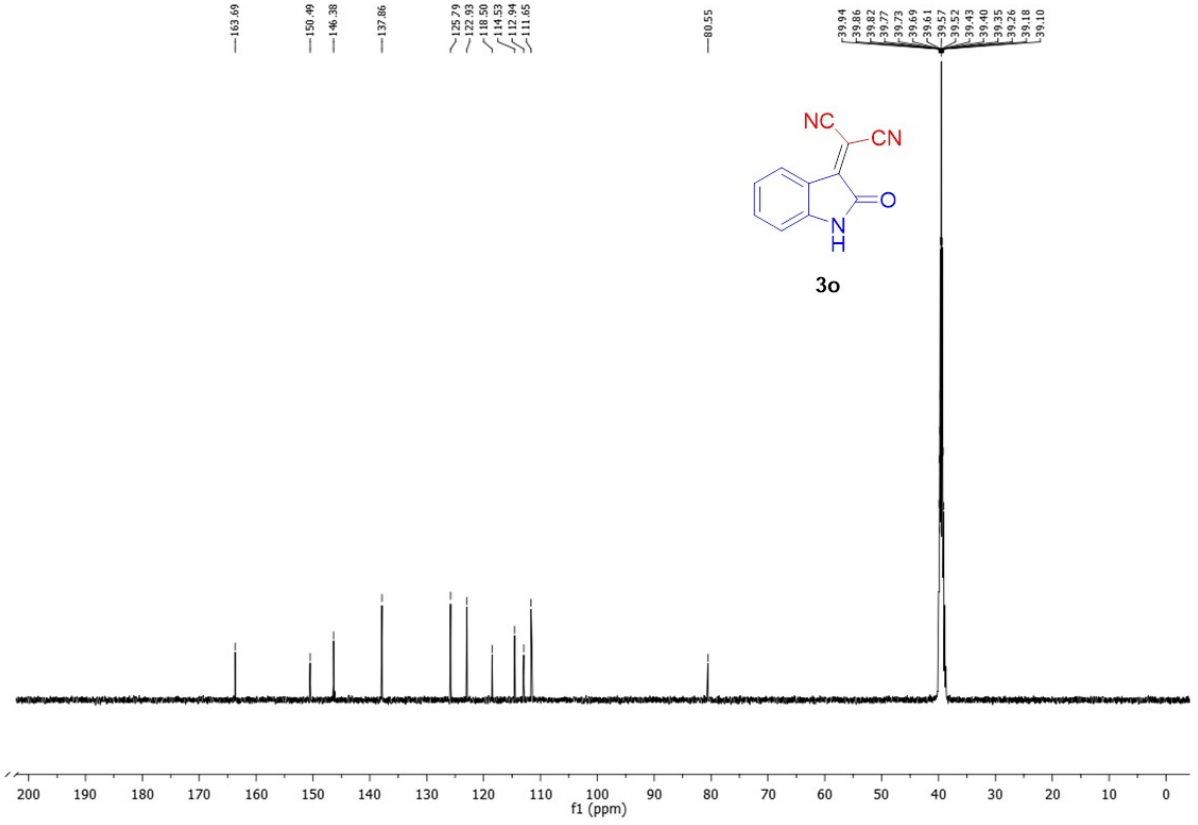

8.05
7.82
7.26
1.55
CN
CN
NC
CN
3m
4.20
1.82
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


159.75
135.28
130.80
113.77
112.73
84.75
39.99
39.94
39.90
39.85
39.77
39.73
39.69
39.60
39.52
39.43
39.40
39.35
39.26
39.18
39.14
39.10
CN
CN
NC
CN
3m
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


8.21
8.20
8.19
7.84
7.79
7.77
7.75
1.56
NC
CN
CN
CN
3n
3.05
2.00
1.07
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


157.65
134.71
132.50
132.27
131.24
112.90
111.97
86.33
77.42
76.90
NC
CN
CN
CN
3n
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


11.19
7.84
7.82
7.56
7.54
7.53
7.11
7.10
7.08
6.92
6.90
3.58
2.54
2.52
2.50
NC
CN
O
N
H
3o
0.83
0.97
1.00
1.00
1.00
f1 (ppm)


163.69
150.49
146.38
137.86
125.79
122.93
118.50
114.53
112.94
111.65
80.55
39.94
39.86
39.82
39.77
39.73
39.69
39.61
39.57
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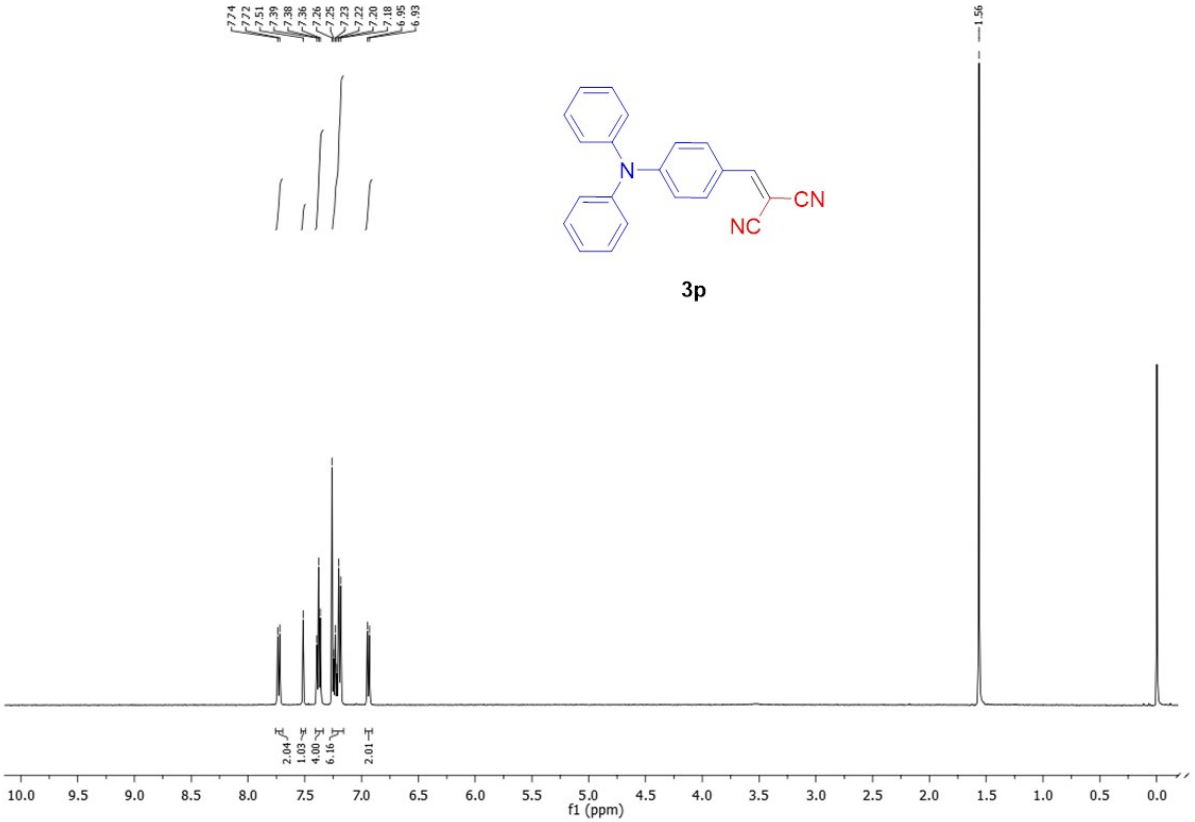
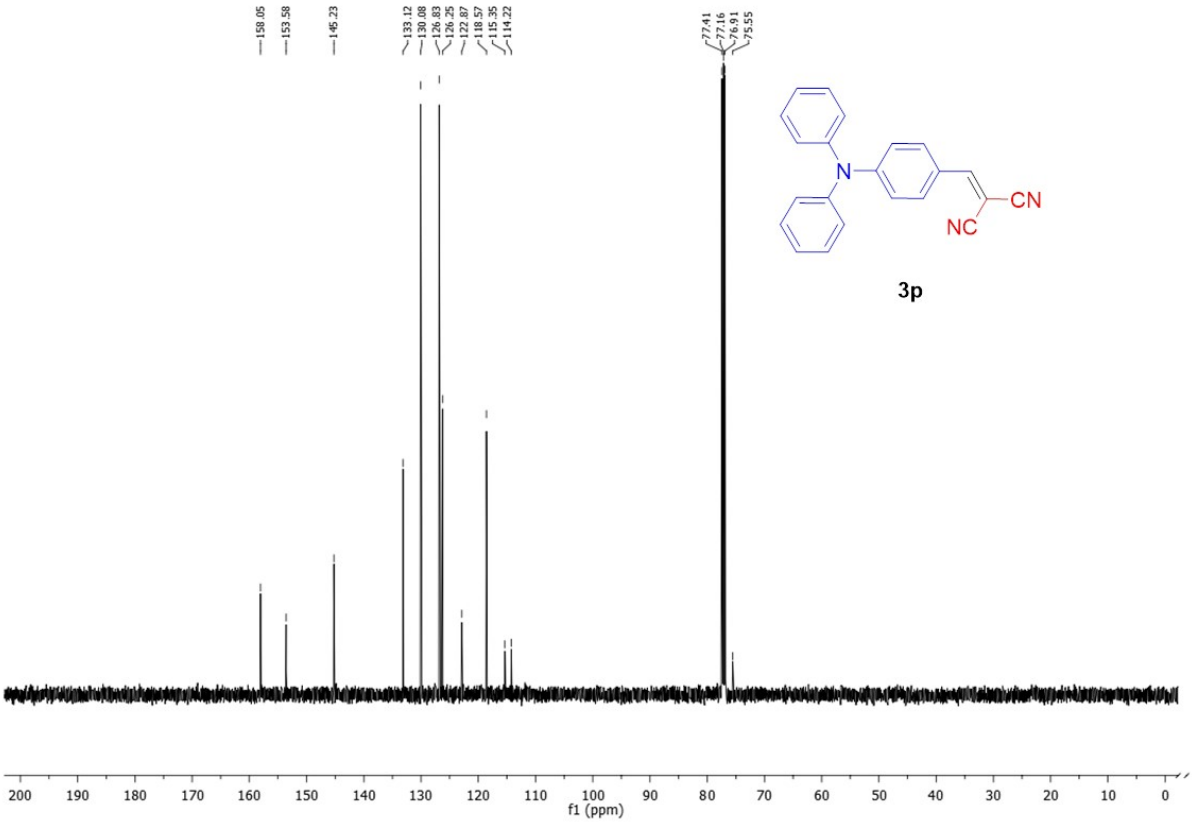
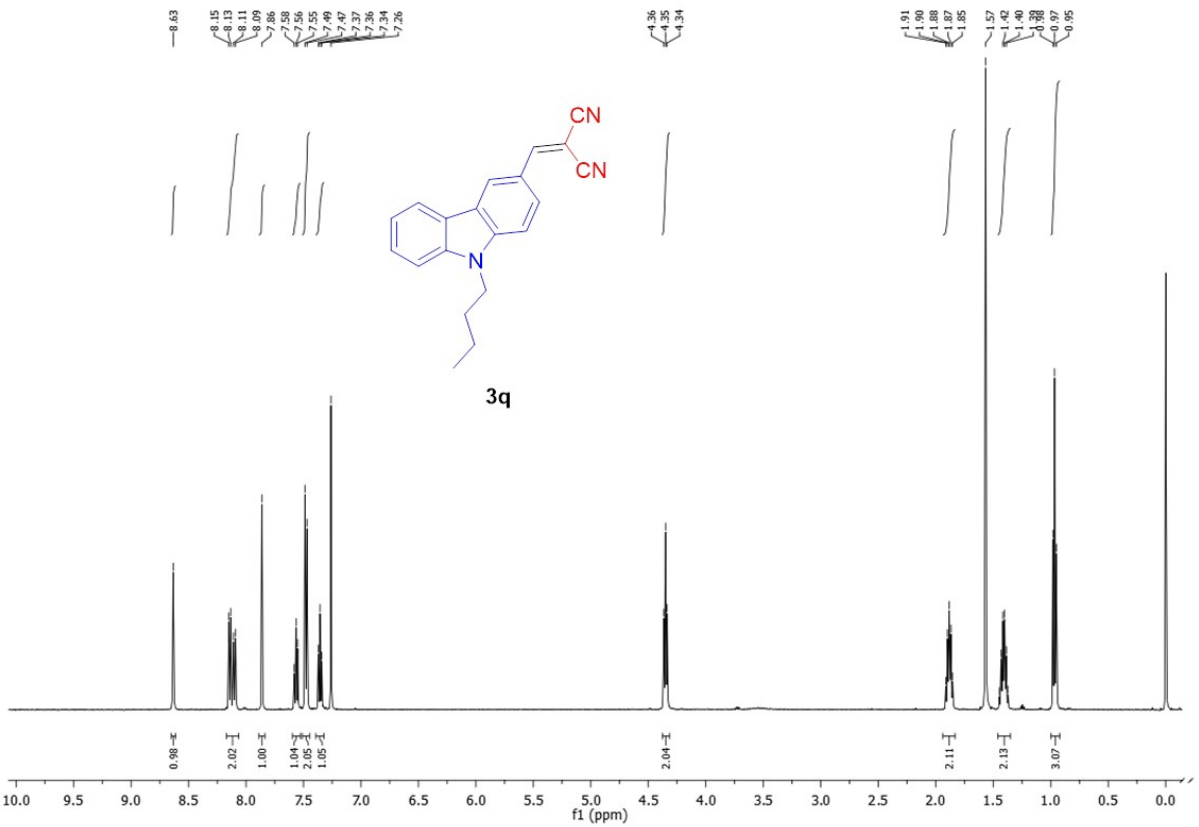
39.10
NC
CN
O
N
H
3o
f1 (ppm)

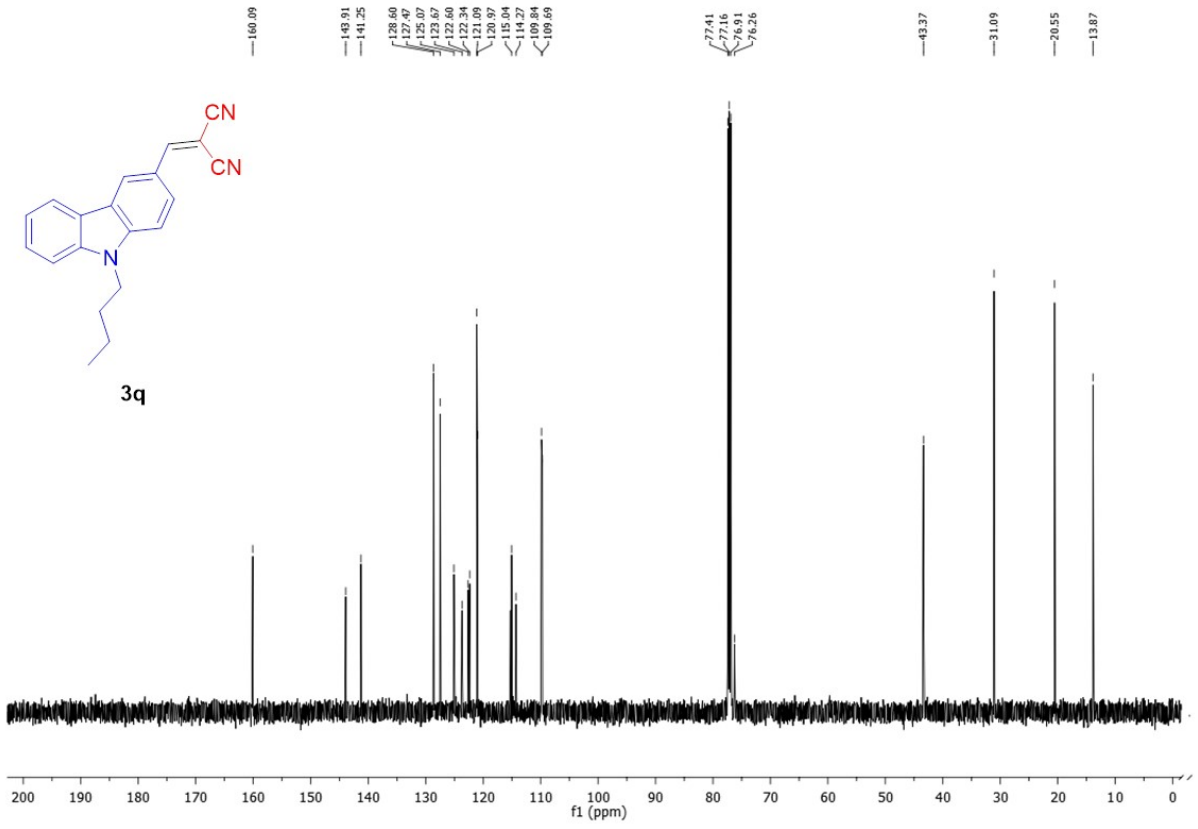

7.74
7.72
7.51
7.39
7.38
7.36
7.26
7.25
7.23
7.22
7.20
7.18
6.95
6.93
1.56
N
CN
NC
2.04
1.03
4.00
6.16
2.01
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

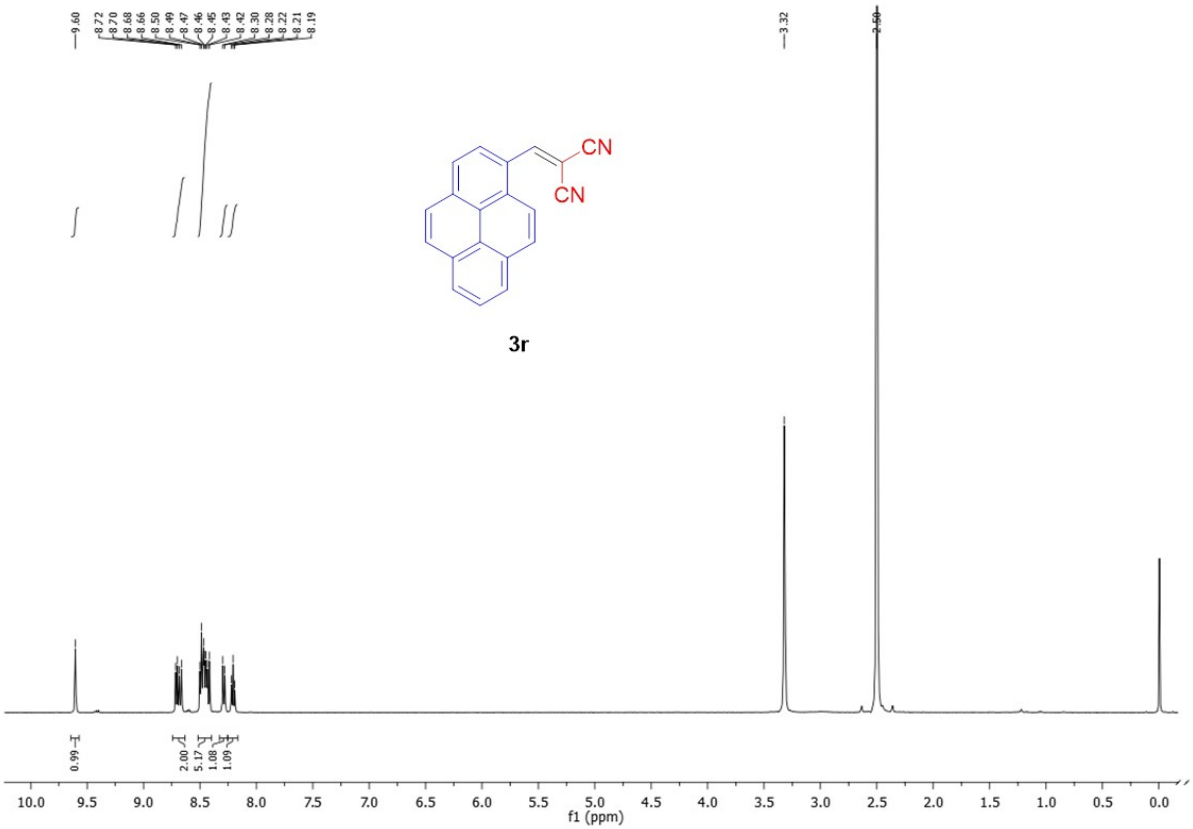
3p


158.05
153.58
145.23
133.12
130.08
126.83
126.25
122.87
118.57
115.35
114.22
77.41
77.16
76.91
75.55
N
CN
NC
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

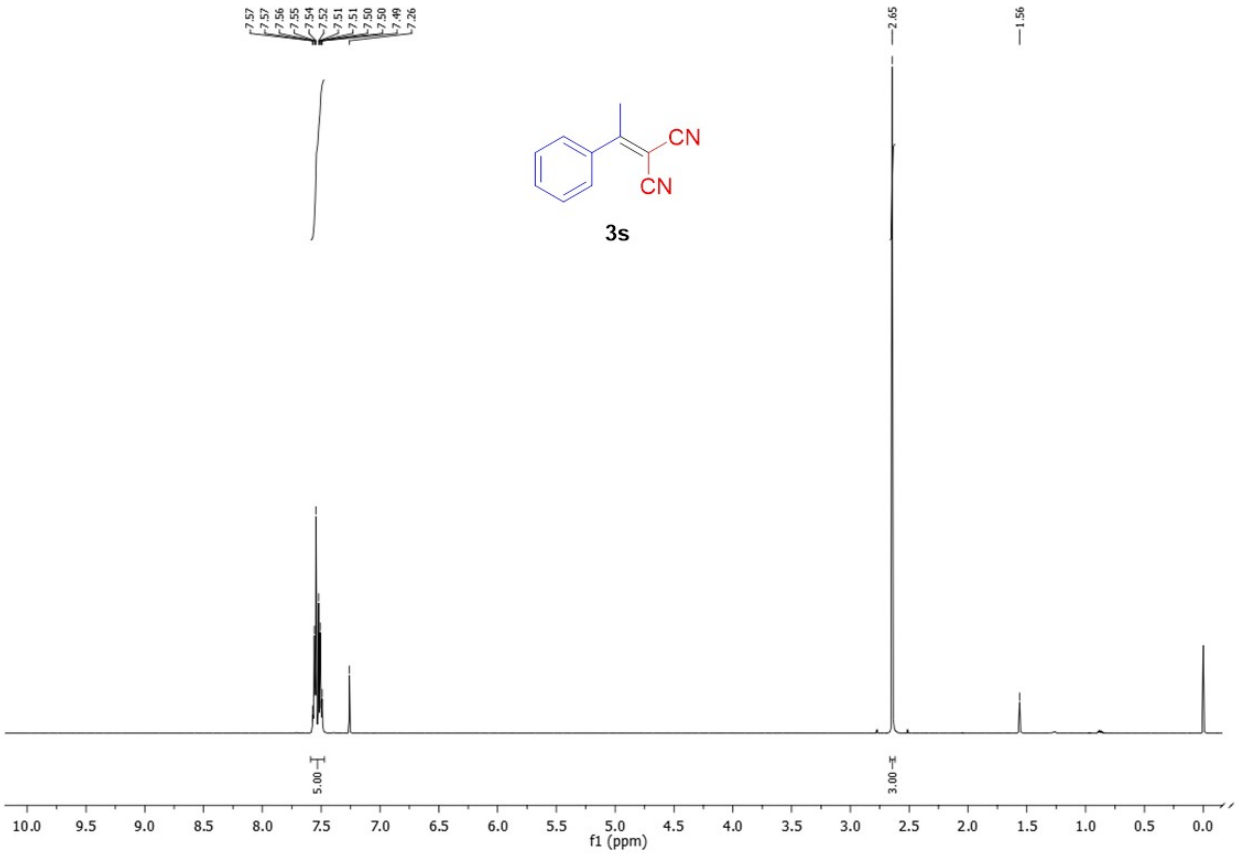
3p


8.63
8.15
8.13
8.11
8.09
7.86
7.58
7.56
7.55
7.49
7.47
7.37
7.36
7.34
7.26
4.36
4.35
4.34
1.91
1.90
1.88
1.87
1.85
1.57
1.42
1.40
0.98
0.97
0.95
CN
CN
N
3q
0.98
2.02
1.00
1.04
2.05
1.05
2.04
2.11
2.13
3.07
f1 (ppm)

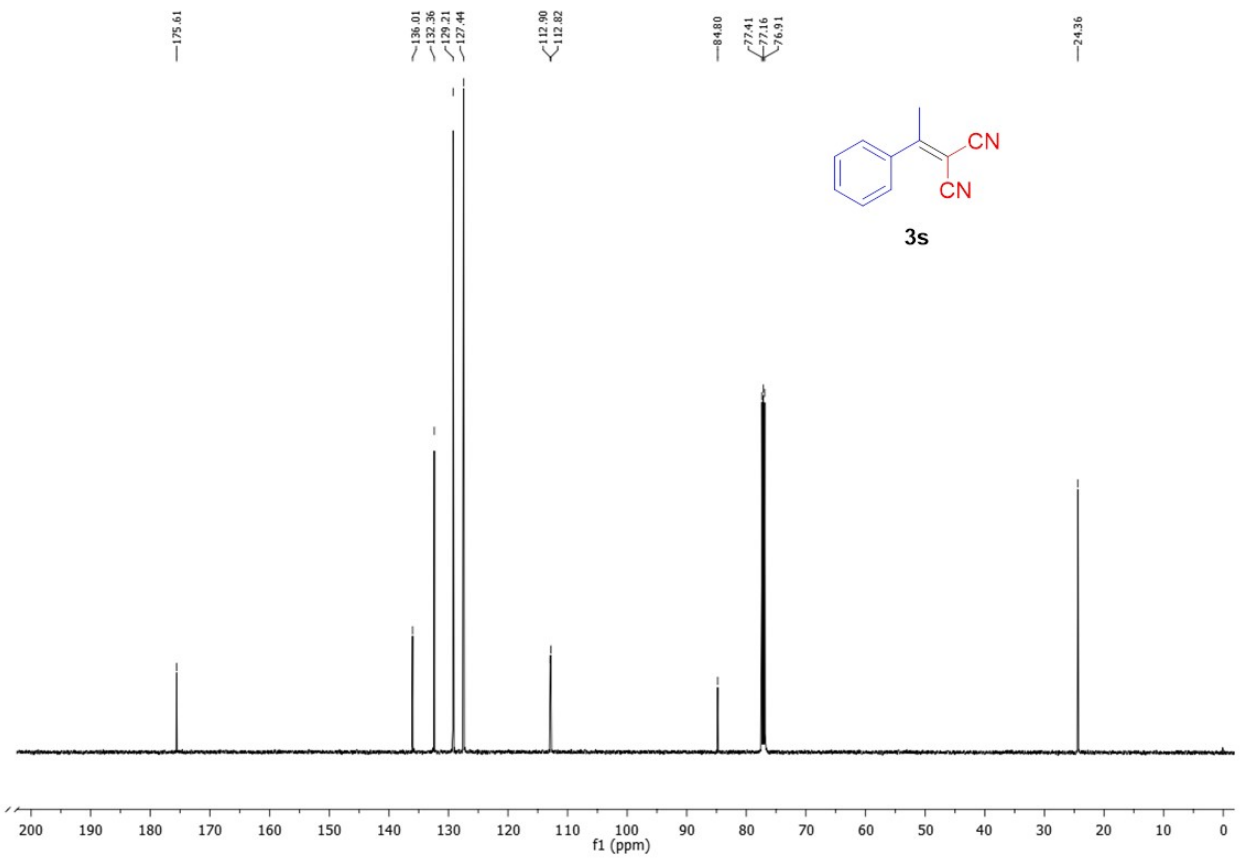

160.09
143.91
141.25
128.60
127.47
125.07
123.67
122.60
122.34
121.09
120.97
115.04
114.27
109.84
109.69
77.41
77.16
76.91
76.26
43.37
31.09
20.55
13.87
CN
CN
N
3q
f1 (ppm)


9.60
8.72
8.70
8.68
8.66
8.50
8.49
8.47
8.46
8.45
8.43
8.42
8.30
8.28
8.22
8.21
8.19
3.32
2.50
CN
CN
0.99
2.00
5.17
1.08
1.09
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

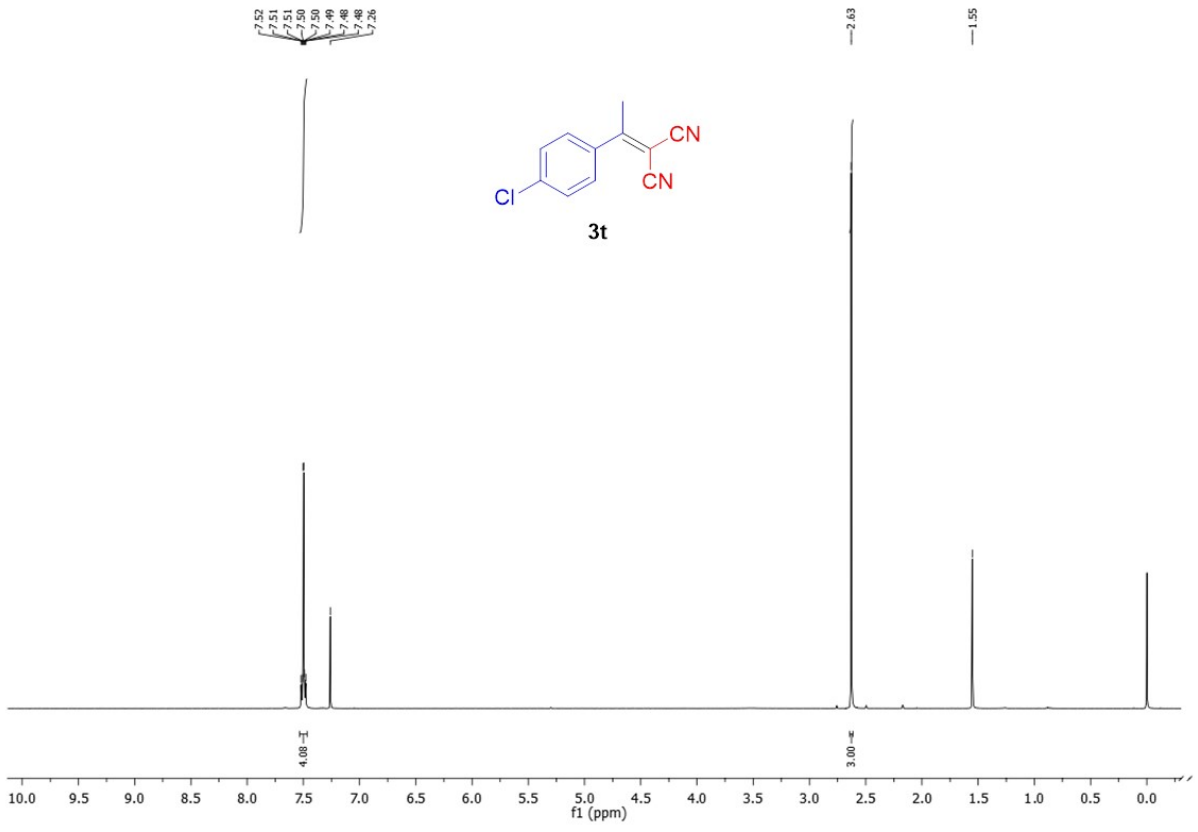
3r


7.57
7.57
7.56
7.55
7.54
7.52
7.51
7.51
7.50
7.50
7.49
7.26
2.65
1.56
CN
CN
5.00
3.00
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

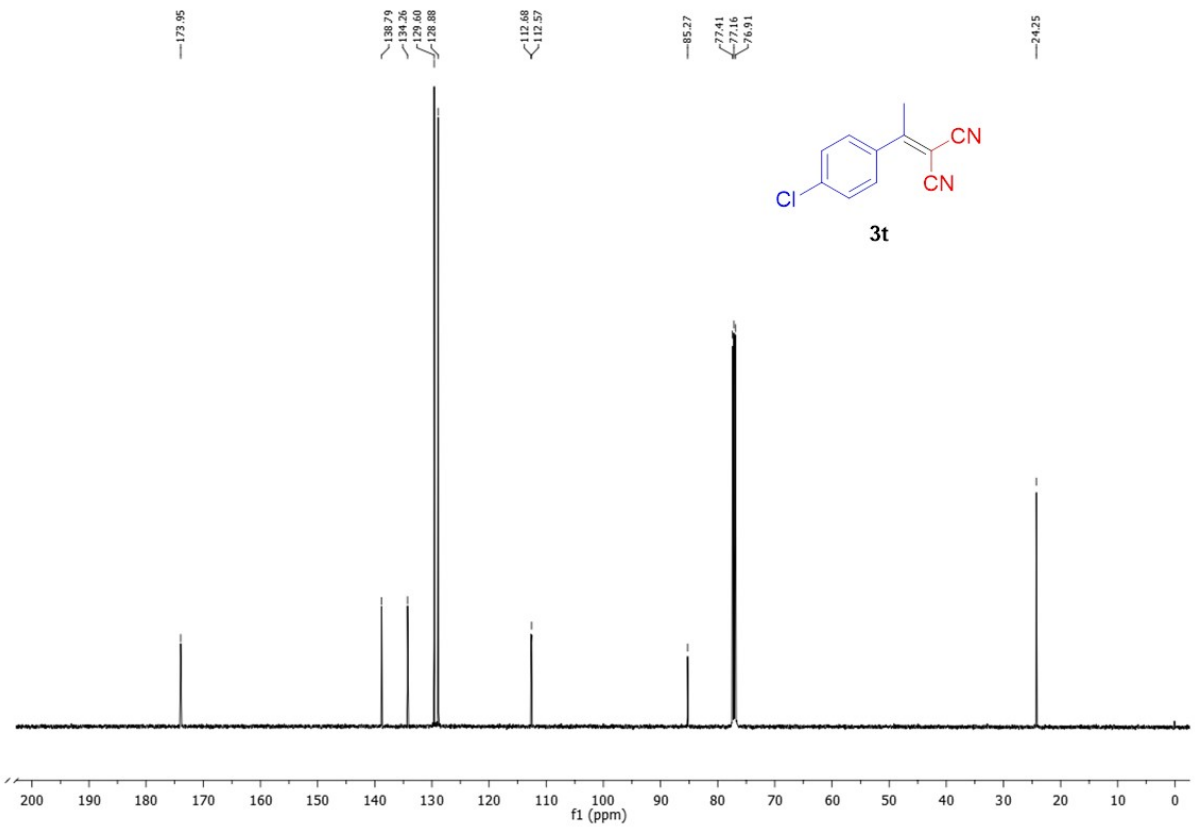
3s

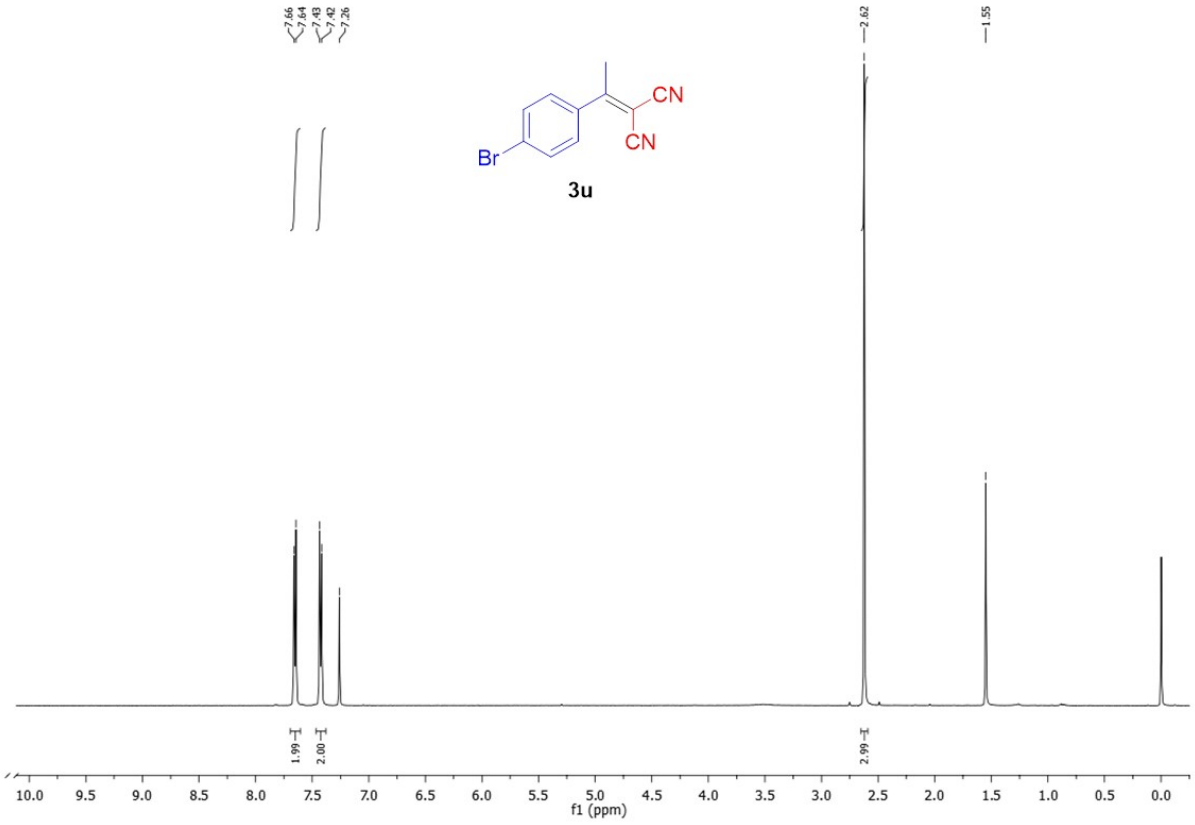

175.61
136.01
132.36
129.21
127.44
112.90
112.82
84.80
77.41
77.16
76.91
24.36
CN
CN
f1 (ppm)

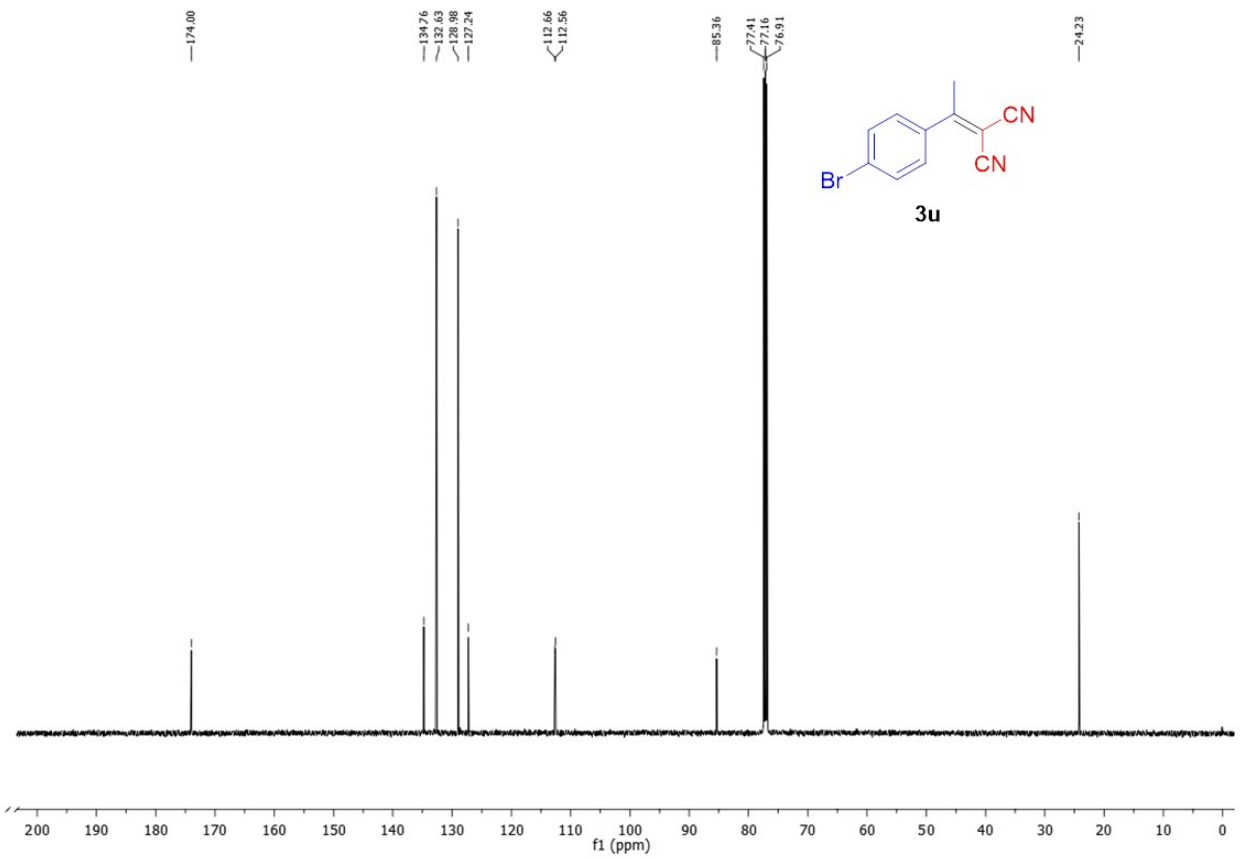
3s

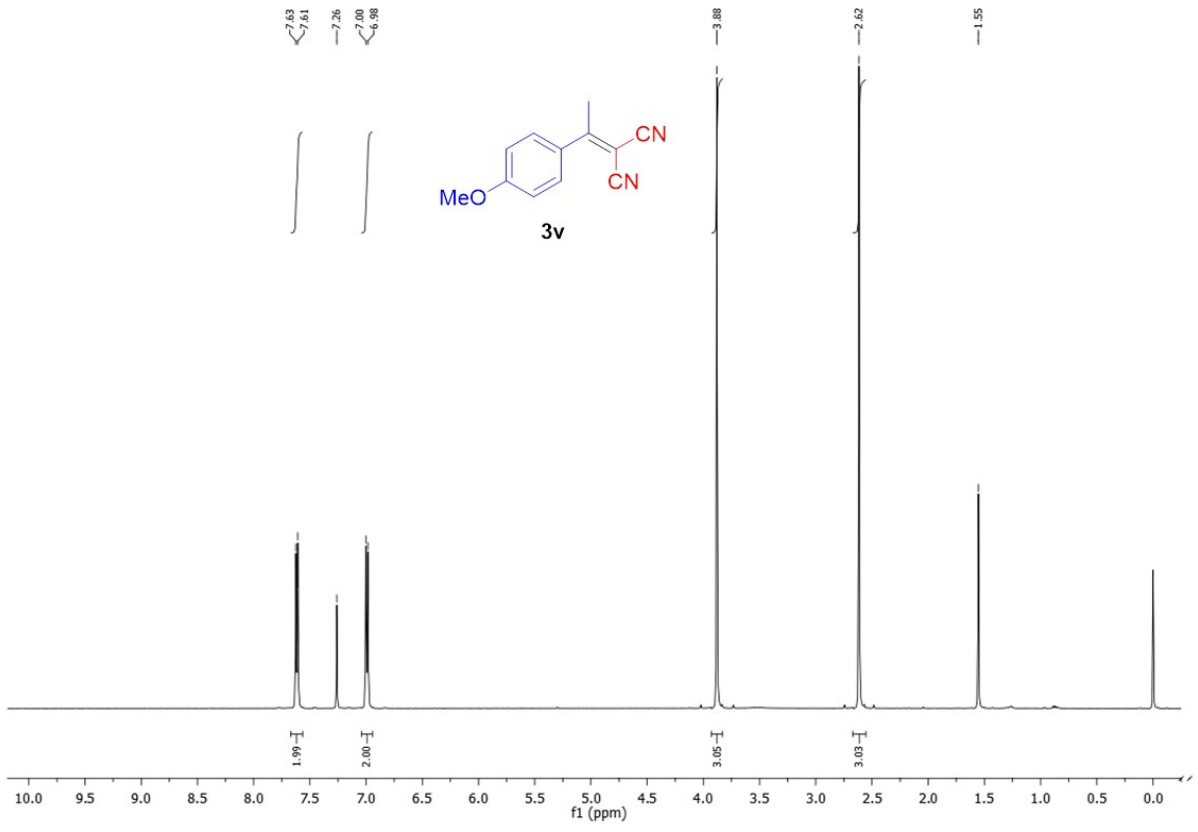

7.52
7.51
7.51
7.50
7.50
7.49
7.48
7.48
7.26
2.63
1.55
CN
CN
Cl
4.08
3.00
f1 (ppm)

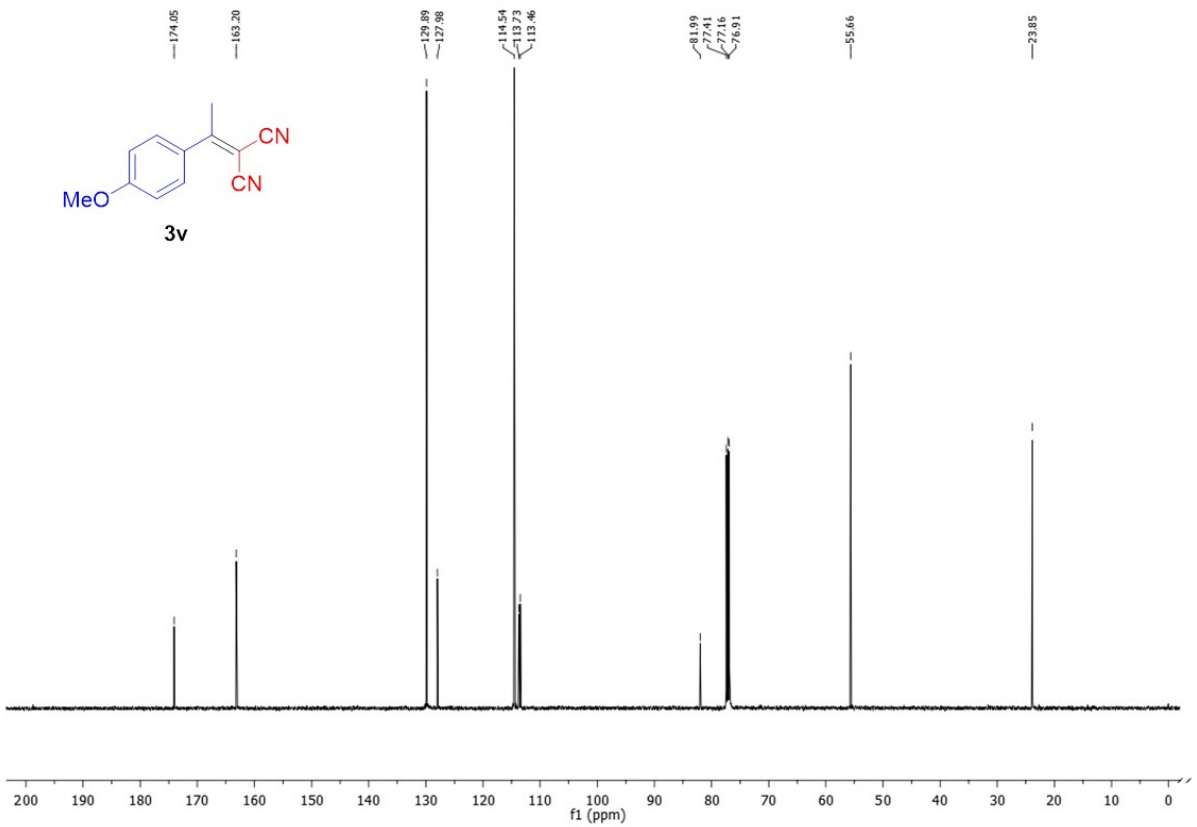
3t


173.95
138.79
134.26
129.60
128.88
112.68
112.57
85.27
77.41
77.16
76.91
24.25
CN
CN
Cl
3t
f1 (ppm)


7.66
7.64
7.43
7.42
7.26
2.62
1.55
CN
CN
Br
3u
1.99
2.00
2.99
f1 (ppm)


174.00
134.76
132.63
128.98
127.24
112.66
112.56
85.36
77.41
77.16
76.91
24.23
CN
CN
Br
3u
f1 (ppm)


7.63
7.61
7.26
7.00
6.98
3.88
2.62
1.55
CN
CN
MeO
3v
1.99
2.00
3.05
3.03
f1 (ppm)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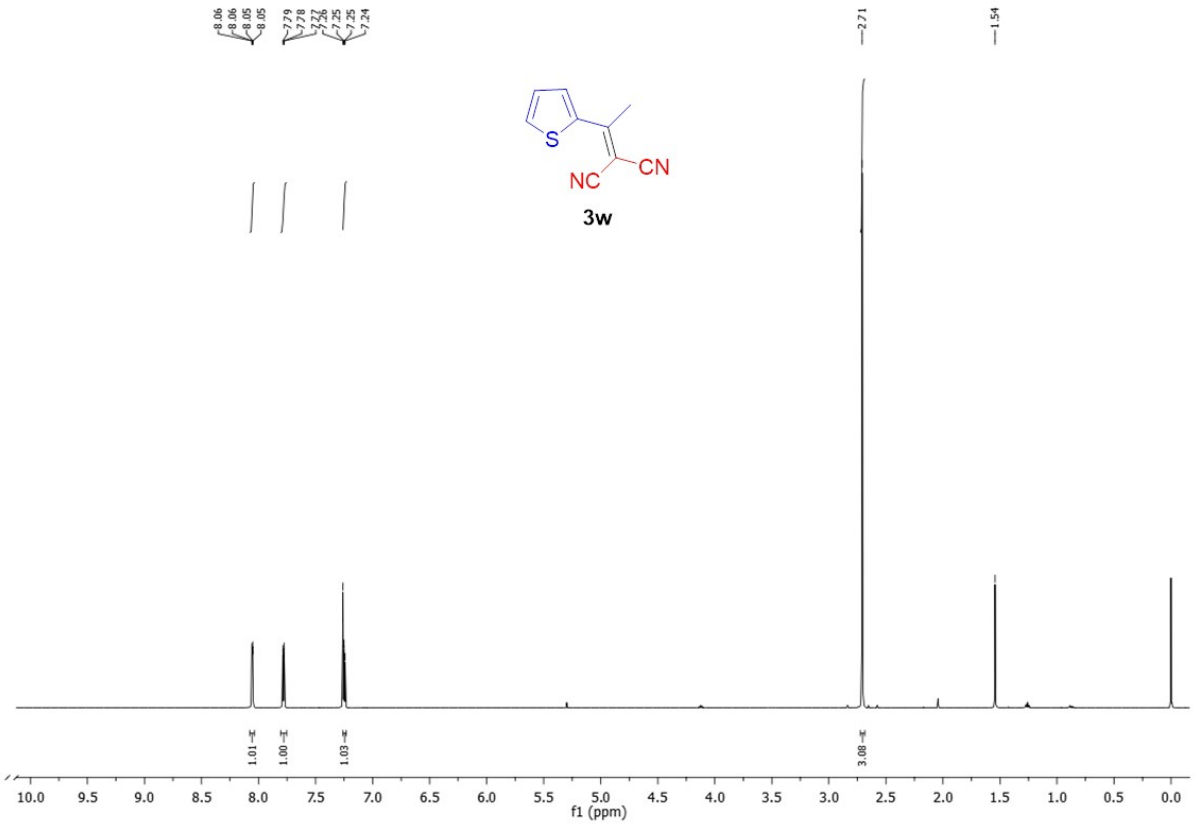
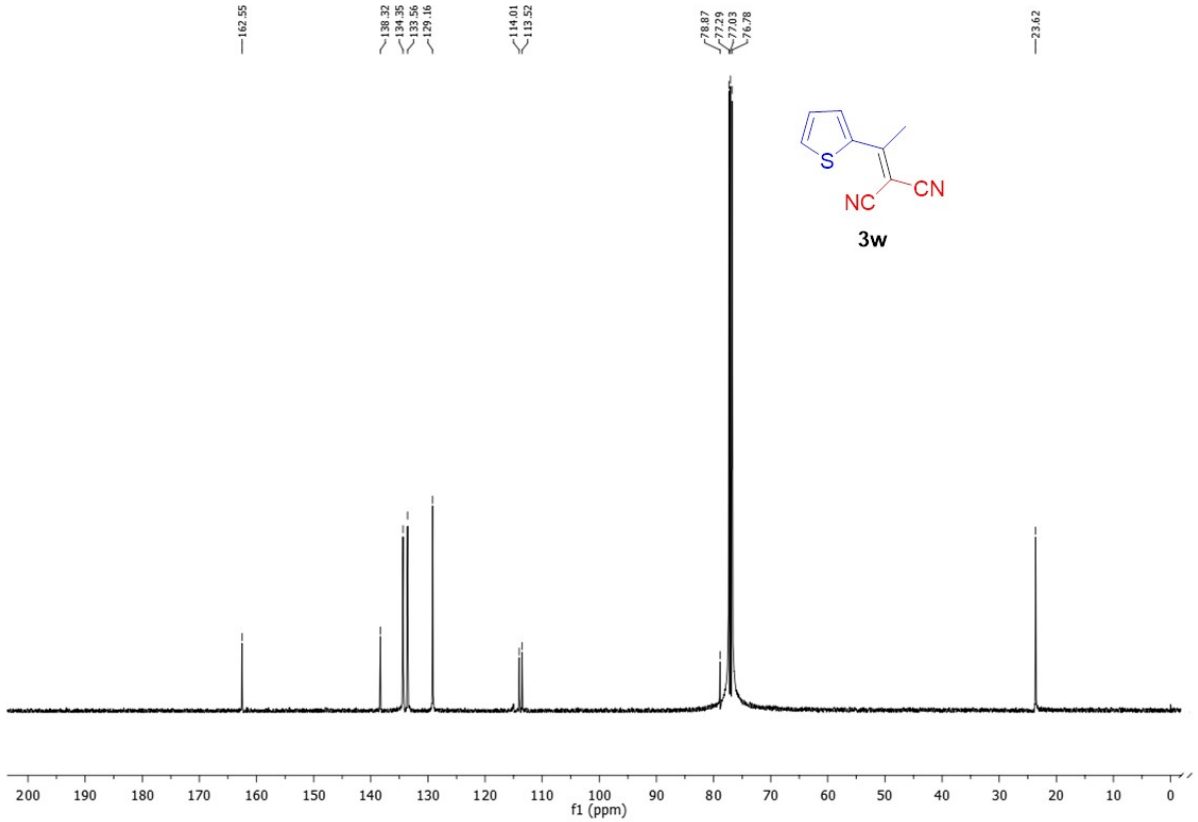
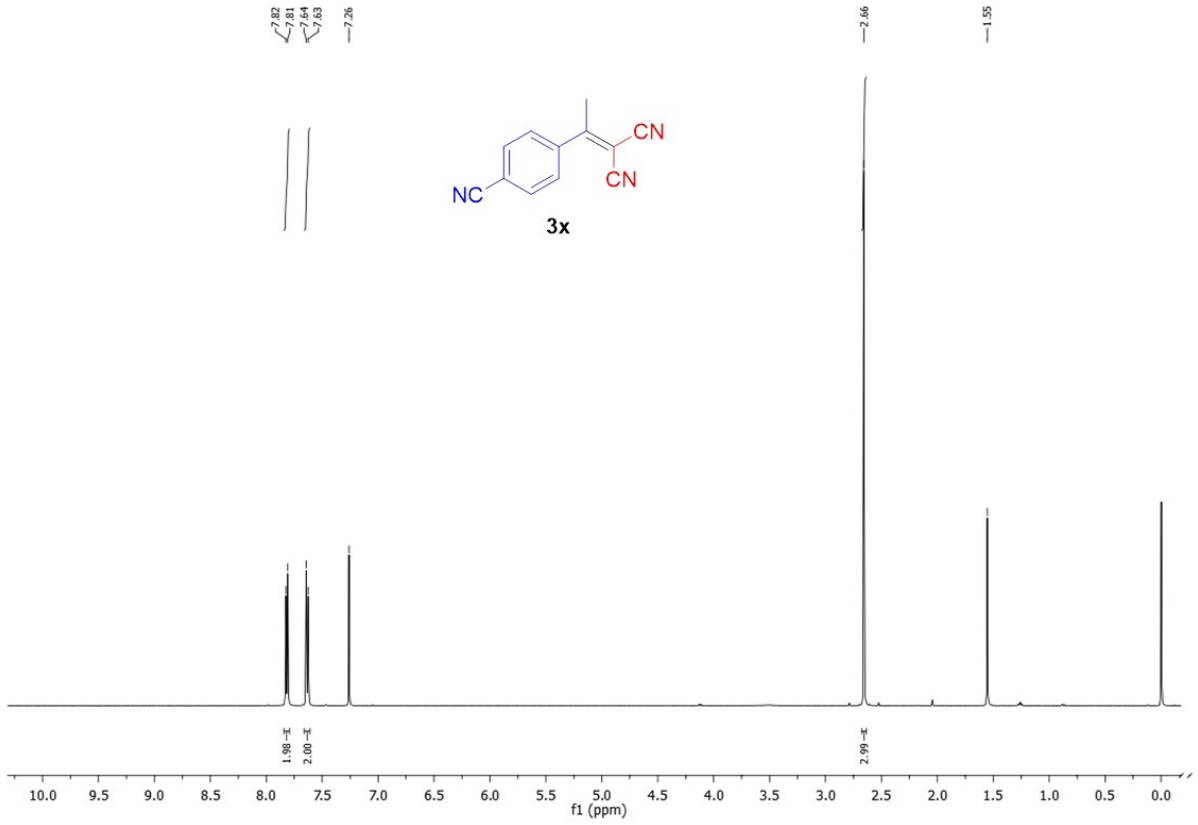
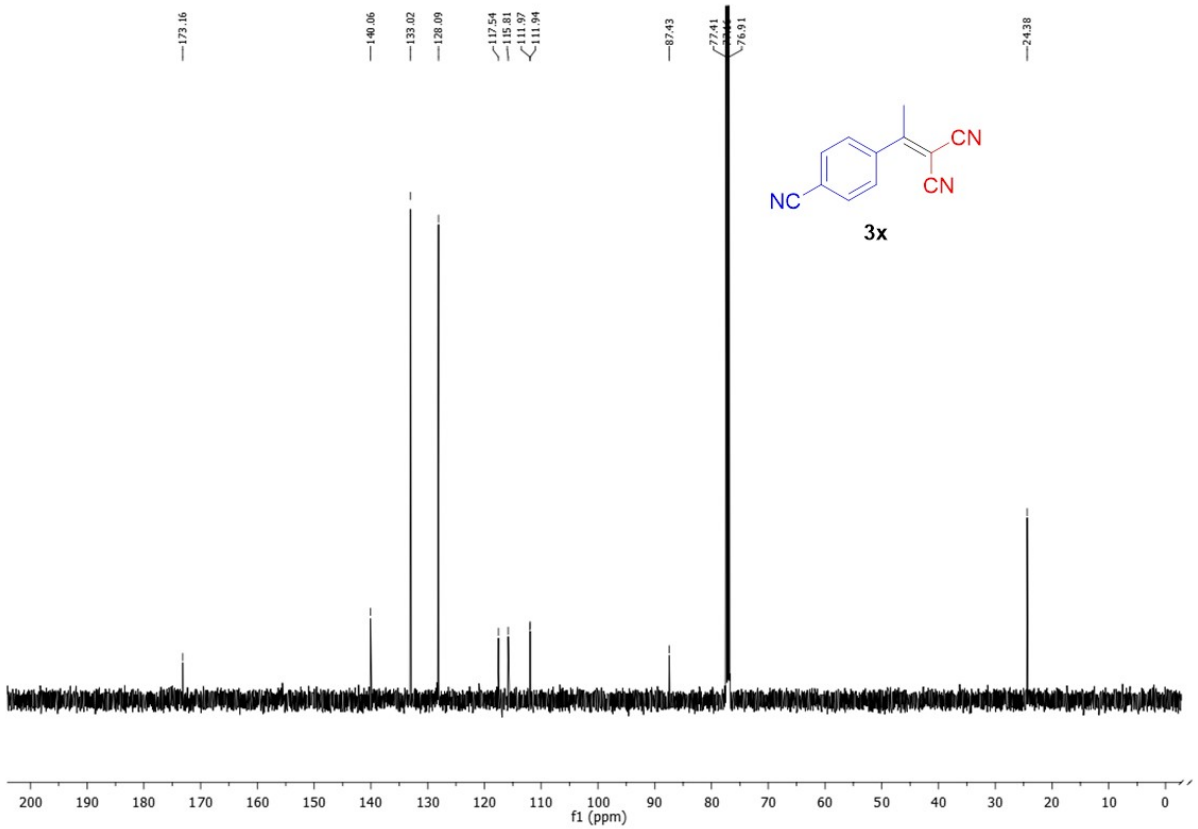
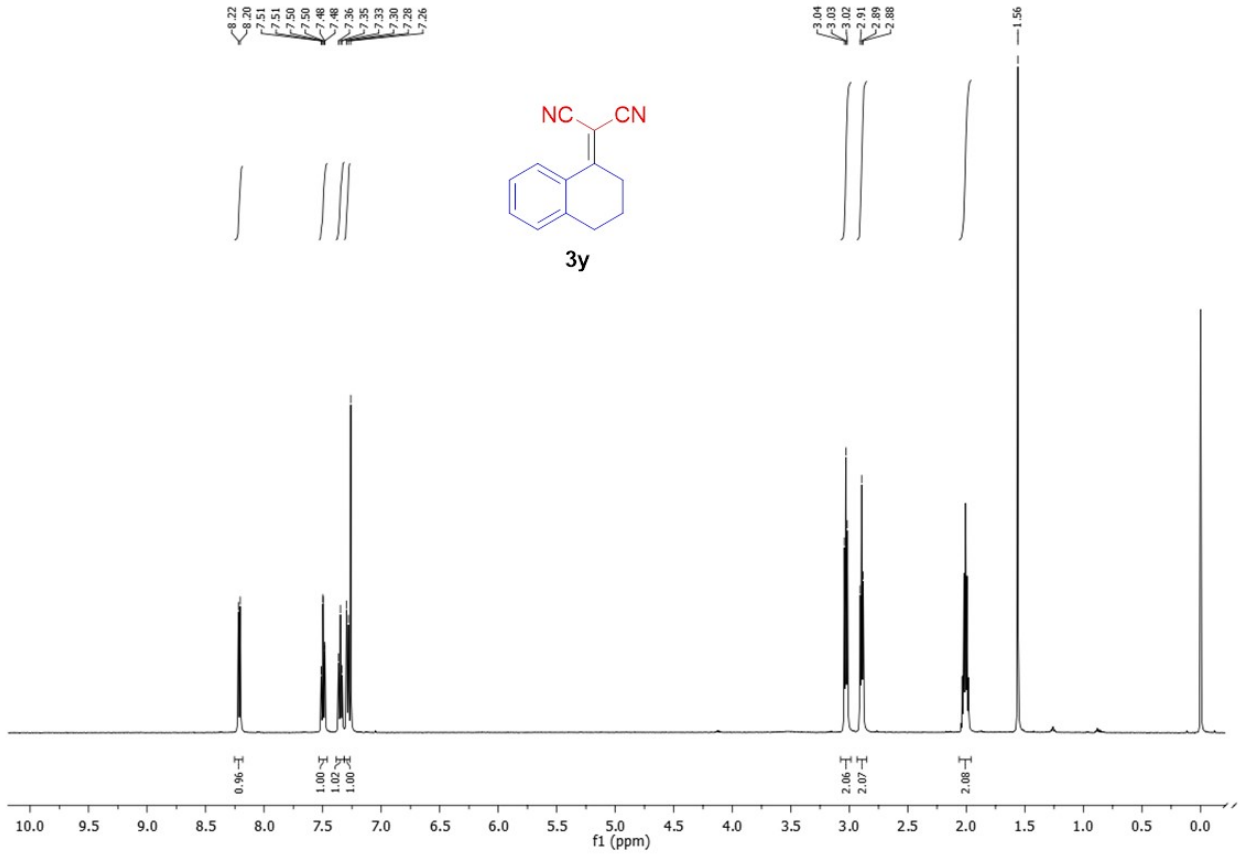
163.20
129.89
127.98
114.54
113.73
113.46
81.99
77.41
77.16
76.91
55.66
23.85
CN
CN
MeO
3v
f1 (ppm)


8.06
8.06
8.05
8.05
7.79
7.78
7.27
7.26
7.25
7.25
7.24
2.71
1.54
S
NC
CN
3w
1.01
1.00
1.03
3.08
f1 (ppm)


162.55
138.32
134.35
133.56
129.16
114.01
113.52
78.87
77.29
77.03
76.78
23.62
S
NC
CN
3w
f1 (ppm)


7.82
7.81
7.64
7.63
7.26
2.66
1.55
CN
CN
NC
3x
1.98
2.00
2.99
f1 (ppm)


173.16
140.06
133.02
128.09
117.54
115.81
111.97
111.94
87.43
77.41
76.91
24.38
CN
CN
NC
3x
f1 (ppm)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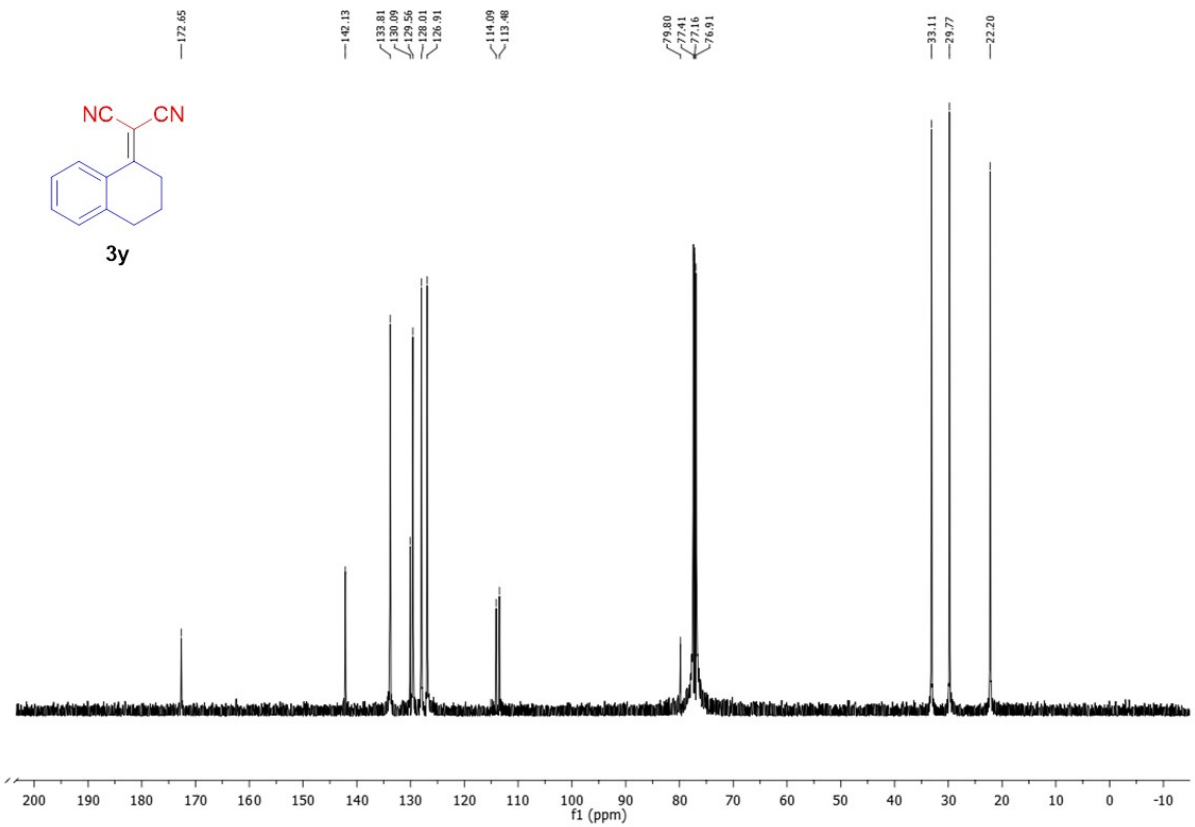
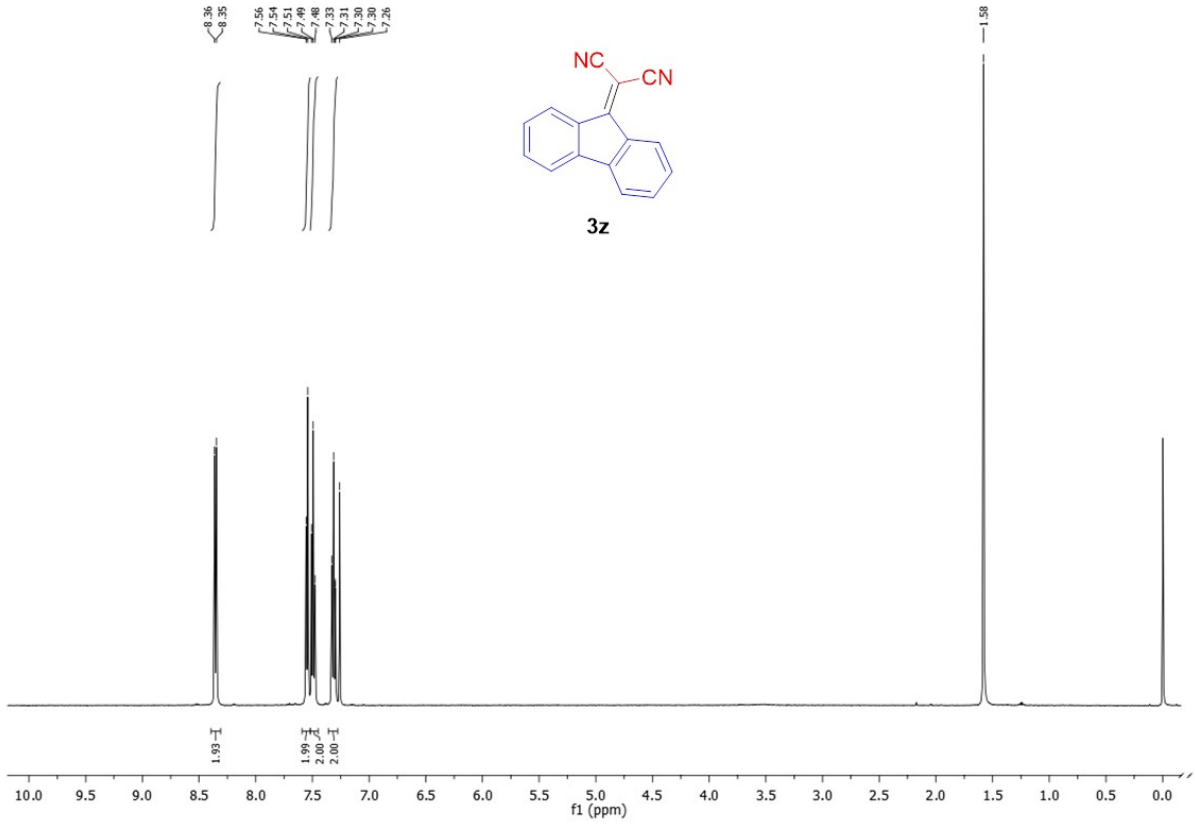
7.50
7.48
7.48
7.36
7.35
7.33
7.30
7.28
7.26
3.04
3.03
3.02
2.91
2.89
2.88
1.56
NC
CN
3y
0.96
1.00
1.02
1.00
2.06
2.07
2.08
f1 (ppm)


172.65
142.13
133.81
130.09
129.56
128.01
126.91
114.09
113.48
79.80
77.41
77.16
76.91
33.11
29.77
22.20
NC
CN
3y
f1 (ppm)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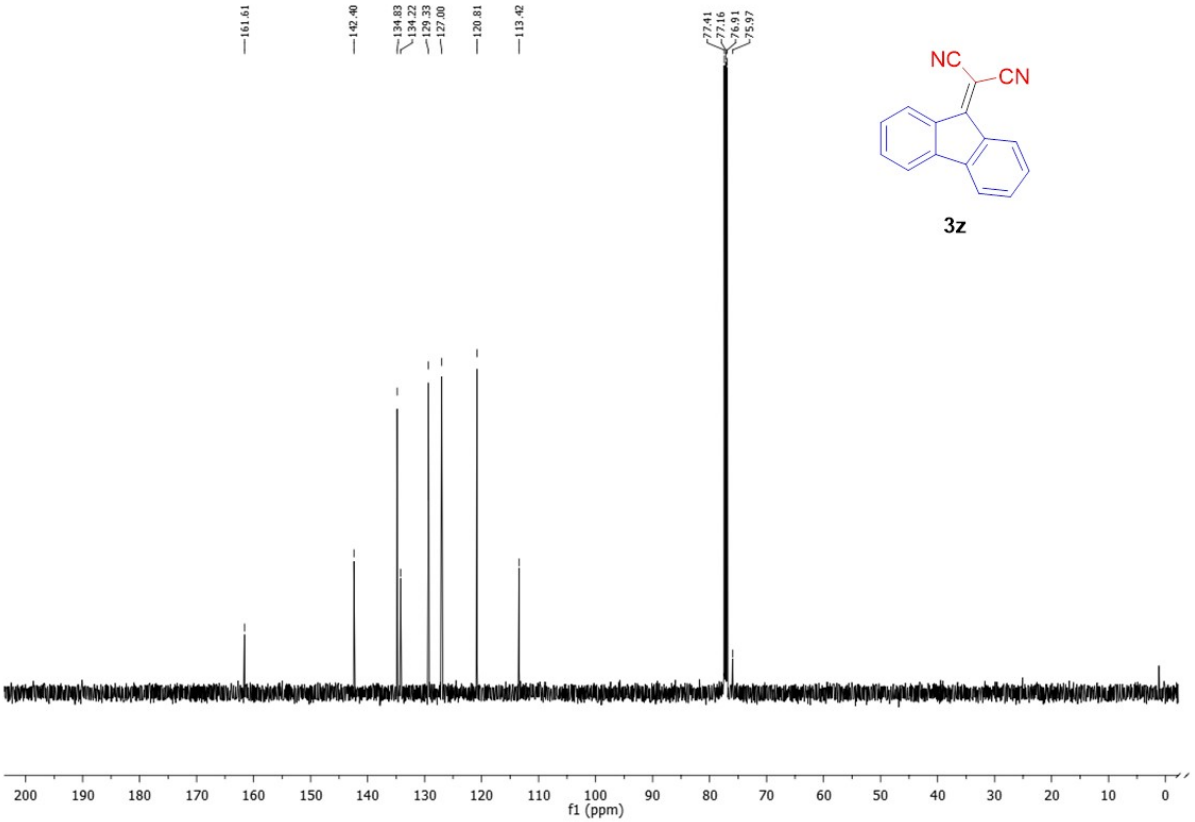
8.35
7.56
7.54
7.51
7.49
7.48
7.33
7.31
7.30
7.30
7.26
1.58
NC
CN
3z
1.93
1.99
2.00
2.00
f1 (ppm)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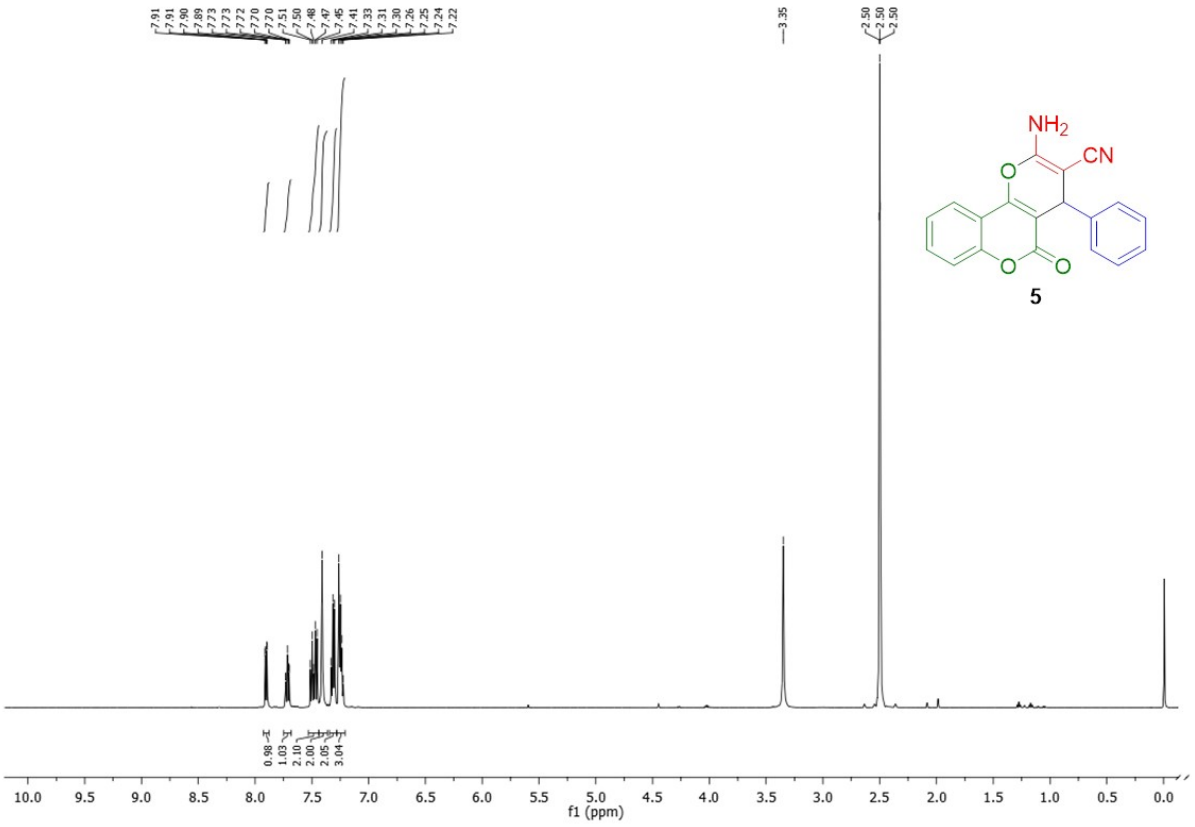
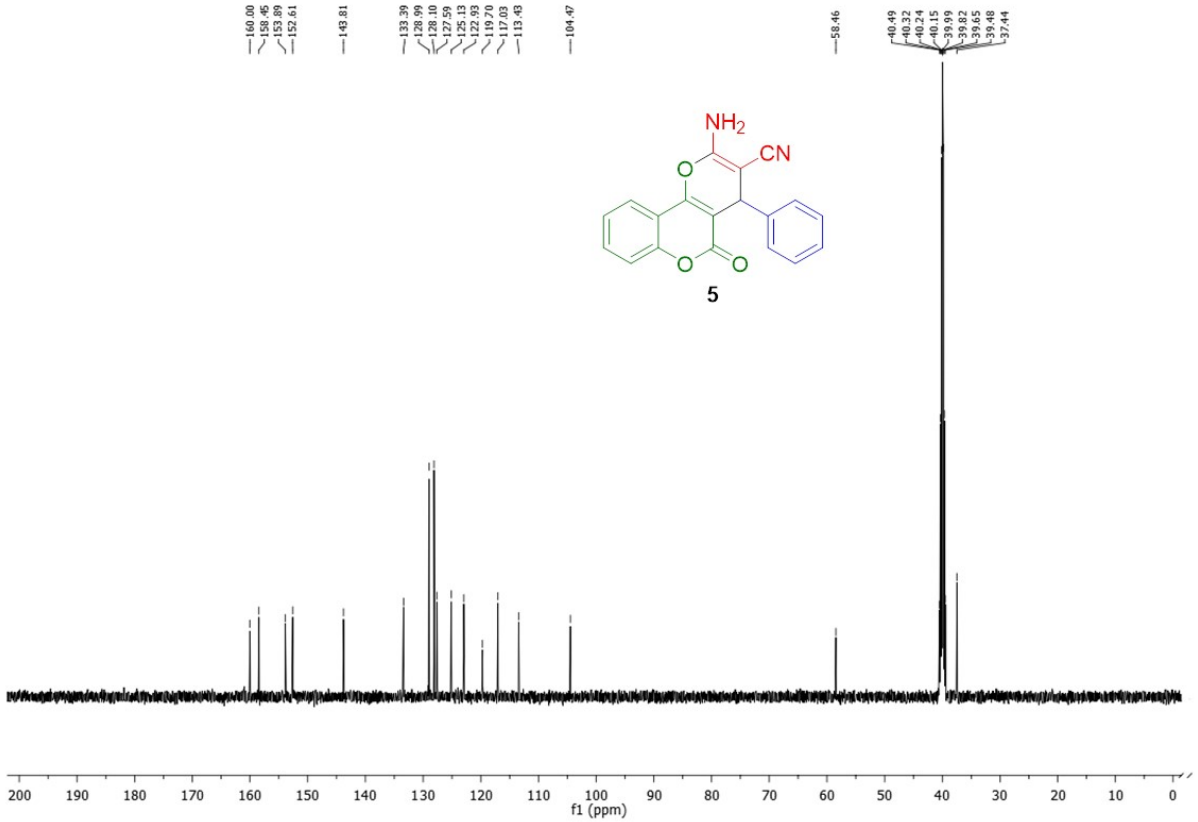
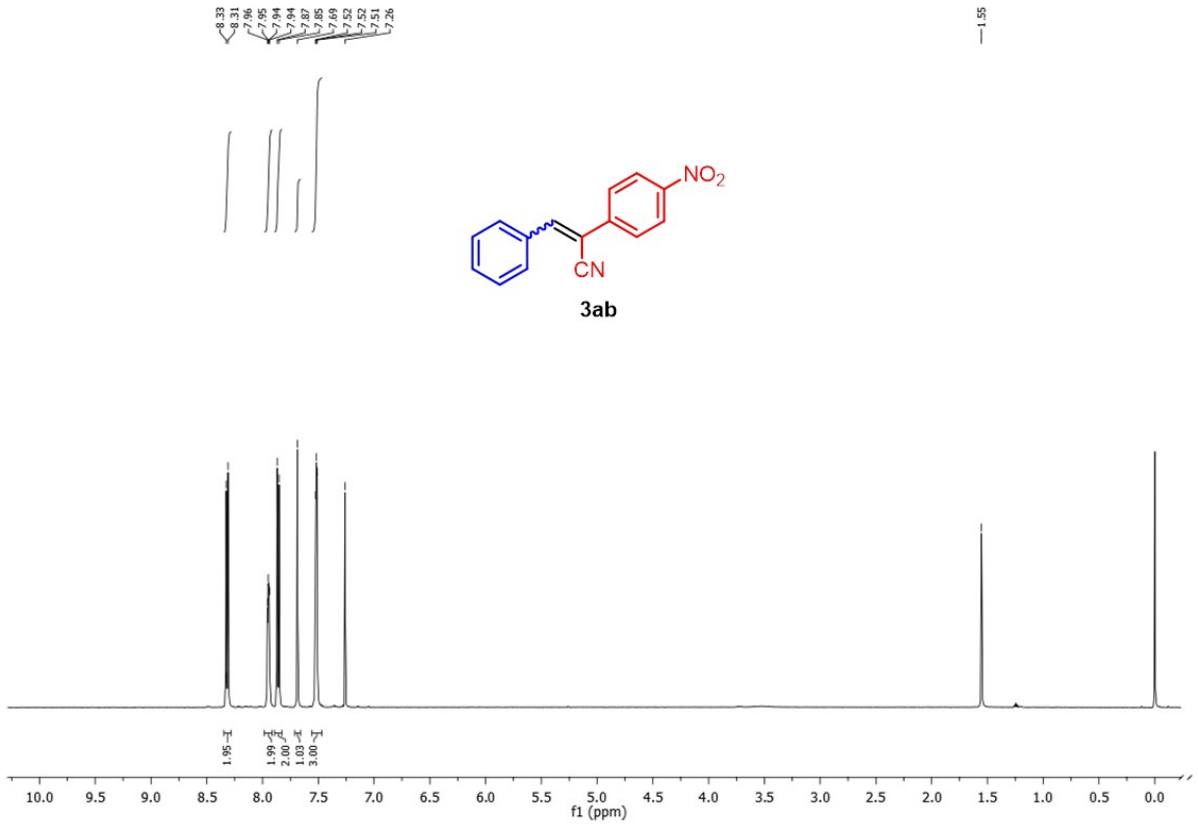
142.40
134.83
134.22
129.33
127.00
120.81
113.42
77.41
77.16
76.91
75.97
NC
CN
3z
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


7.91
7.91
7.90
7.89
7.73
7.73
7.72
7.70
7.70
7.51
7.50
7.48
7.47
7.45
7.41
7.33
7.31
7.30
7.26
7.25
7.24
7.22
3.35
2.50
2.50
2.50
NH2
CN
O
O
O
5
0.98
1.03
2.10
2.00
2.05
3.04
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


160.00
158.45
153.89
152.61
143.81
133.39
128.99
128.10
127.59
125.13
122.93
119.70
117.03
113.43
104.47
58.46
40.49
40.32
40.24
40.15
39.99
39.82
39.65
39.48
37.44
NH2
CN
O
O
O
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

5


8.33
8.31
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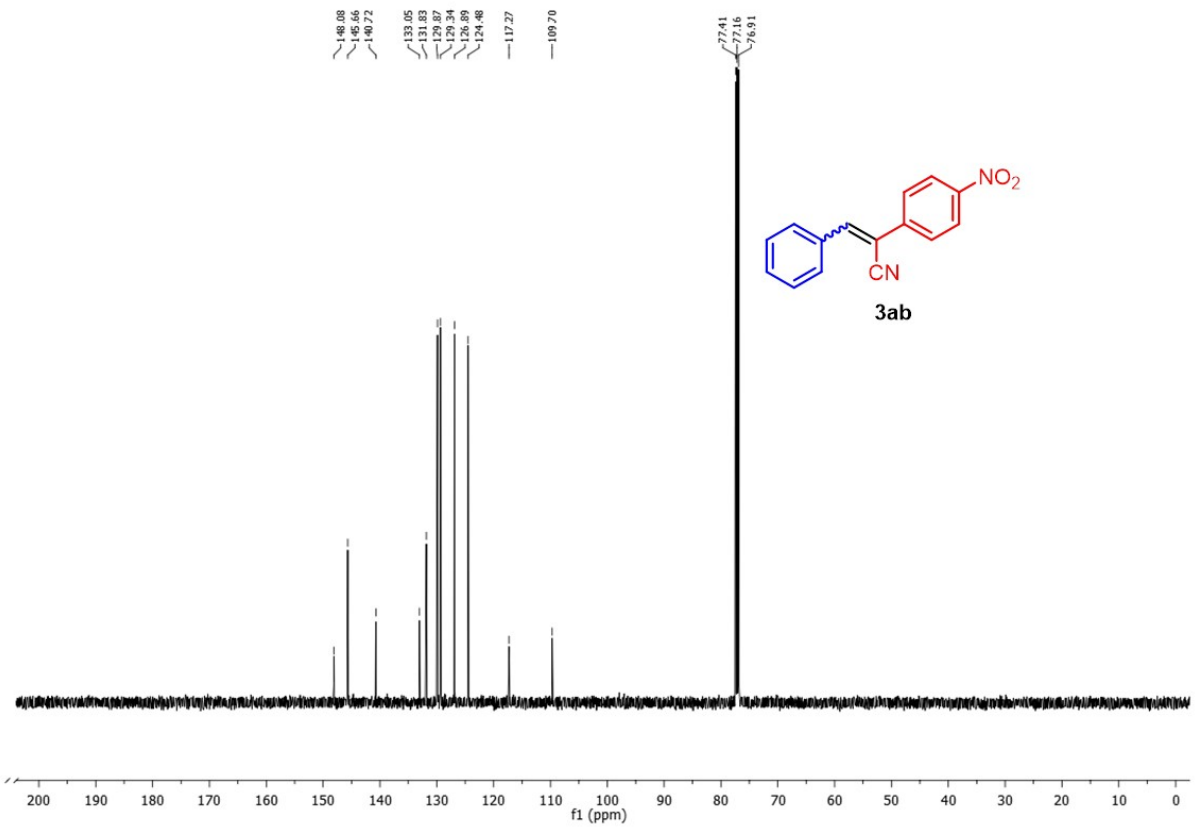
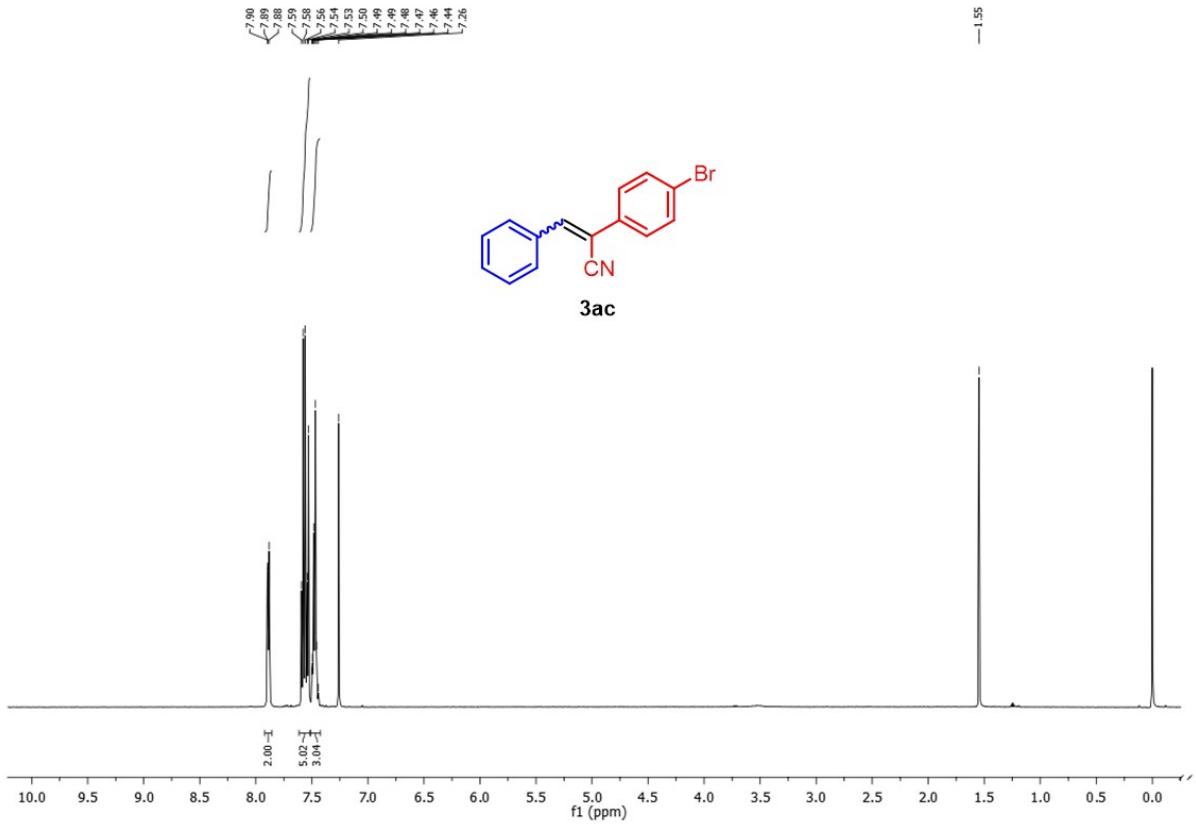
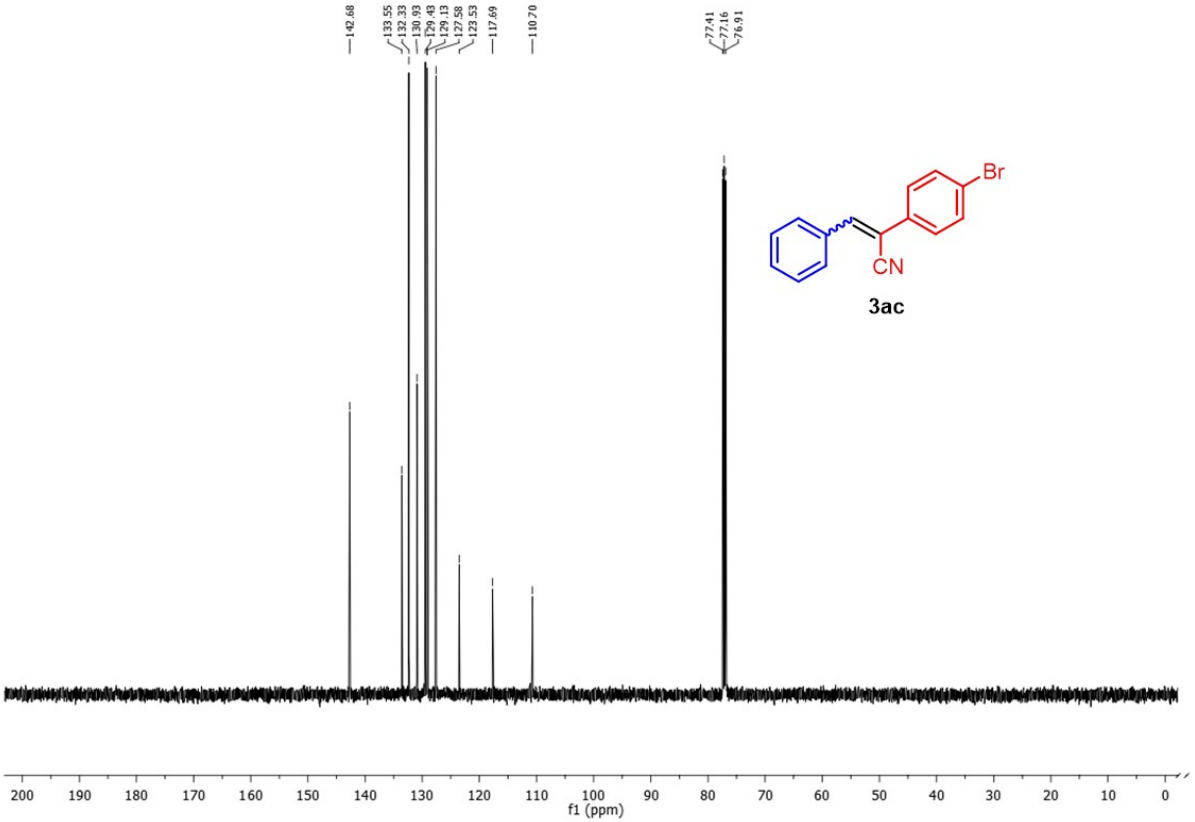
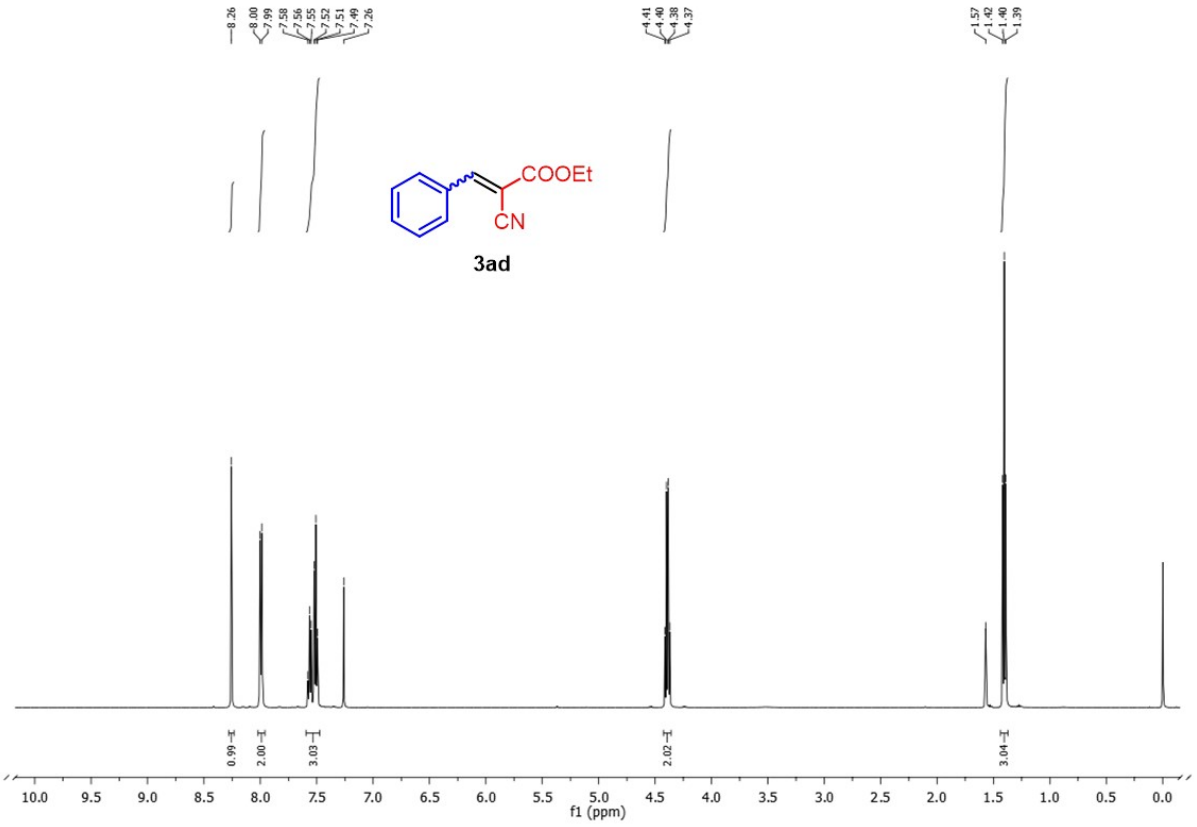
7.95
7.94
7.94
7.87
7.85
7.69
7.52
7.52
7.51
7.26
1.55
NO2
CN
1.95
1.99
2.00
1.03
3.00
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

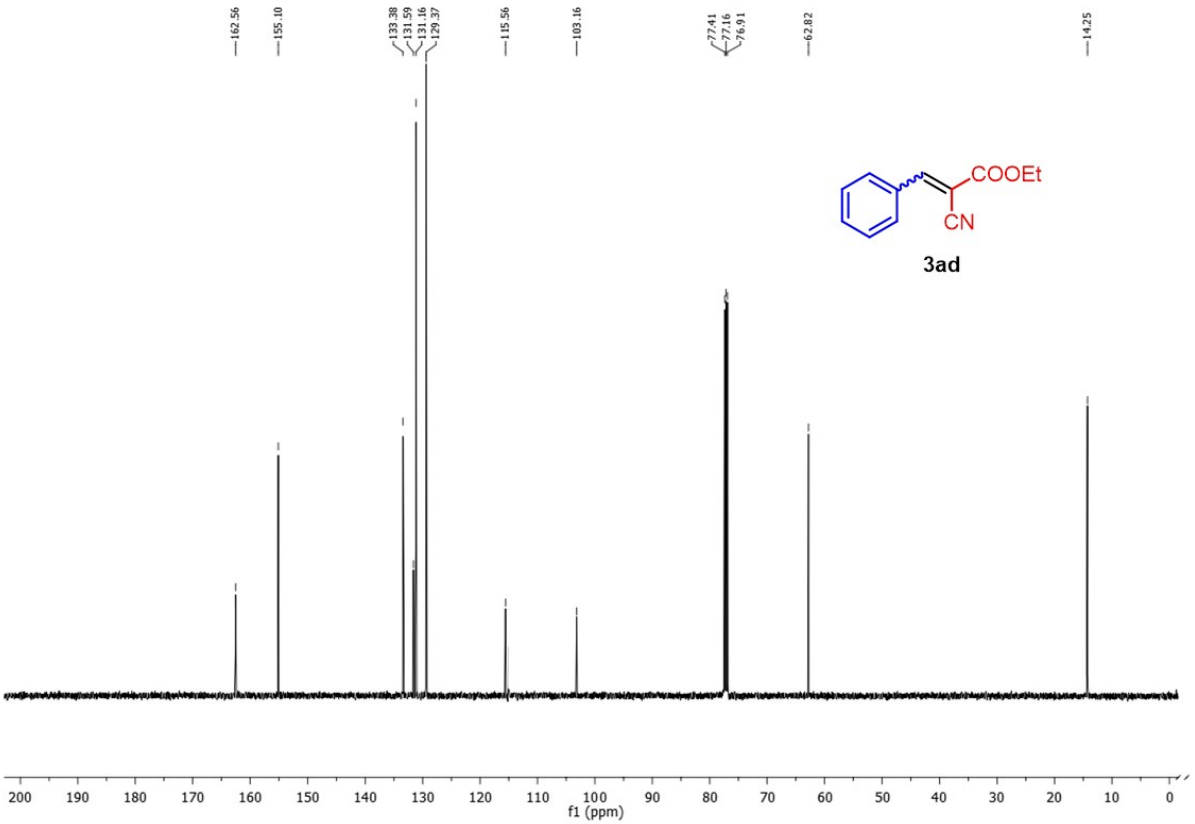
3ab

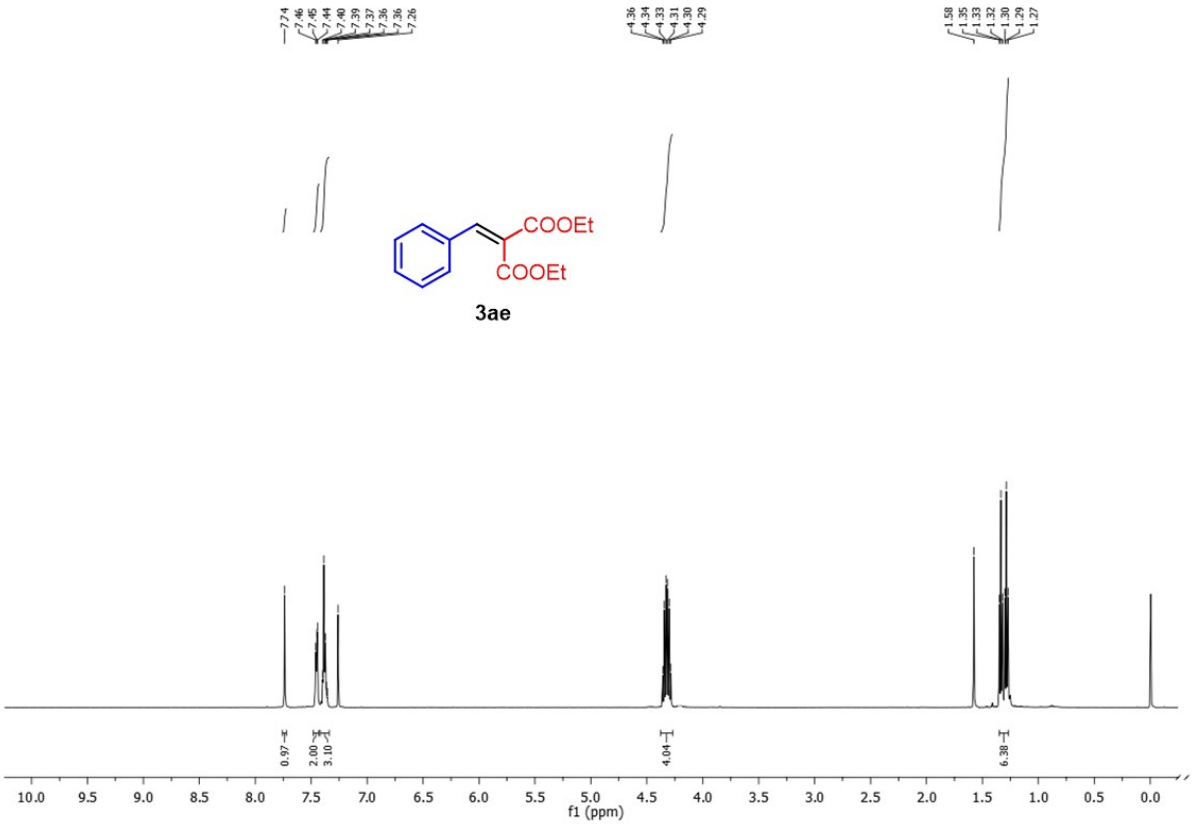

148.08
145.66
140.72
133.05
131.83
129.87
129.34
126.89
124.48
117.27
109.70
77.41
77.16
76.91
NO2
CN
3ab
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

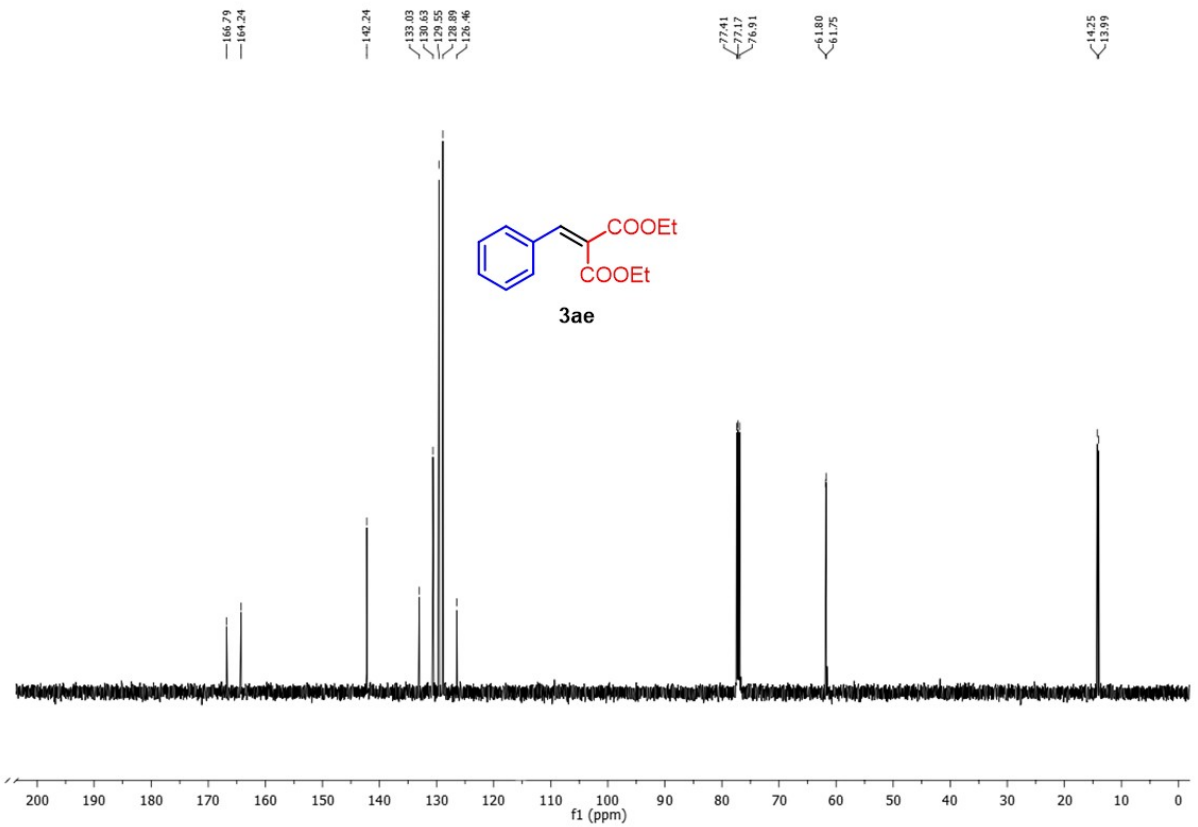

7.90
7.89
7.88
7.59
7.58
7.56
7.54
7.53
7.50
7.49
7.49
7.48
7.47
7.46
7.44
7.26
1.55
Br
CN
3ac
2.00
5.02
3.04
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

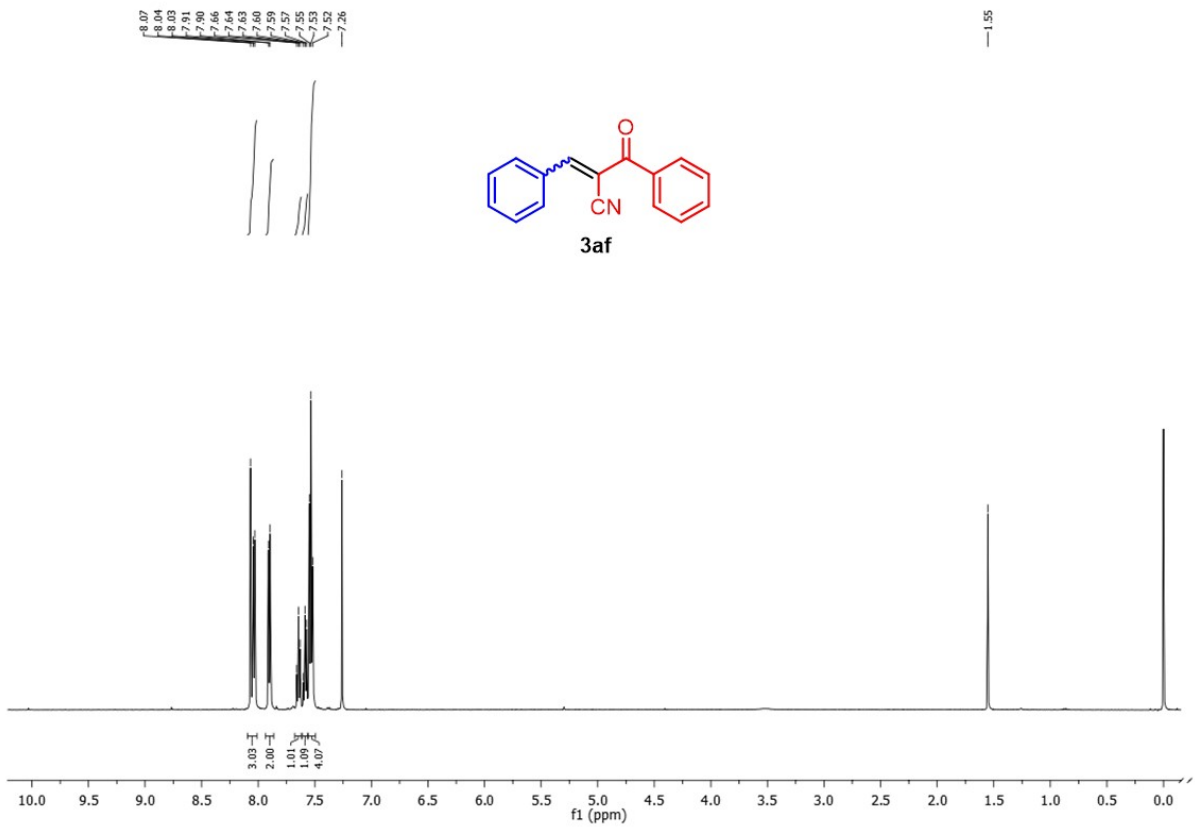

142.68
133.55
132.33
130.93
129.49
129.13
127.58
123.53
117.69
110.70
77.41
77.16
76.91
Br
CN
3ac
f1 (ppm)

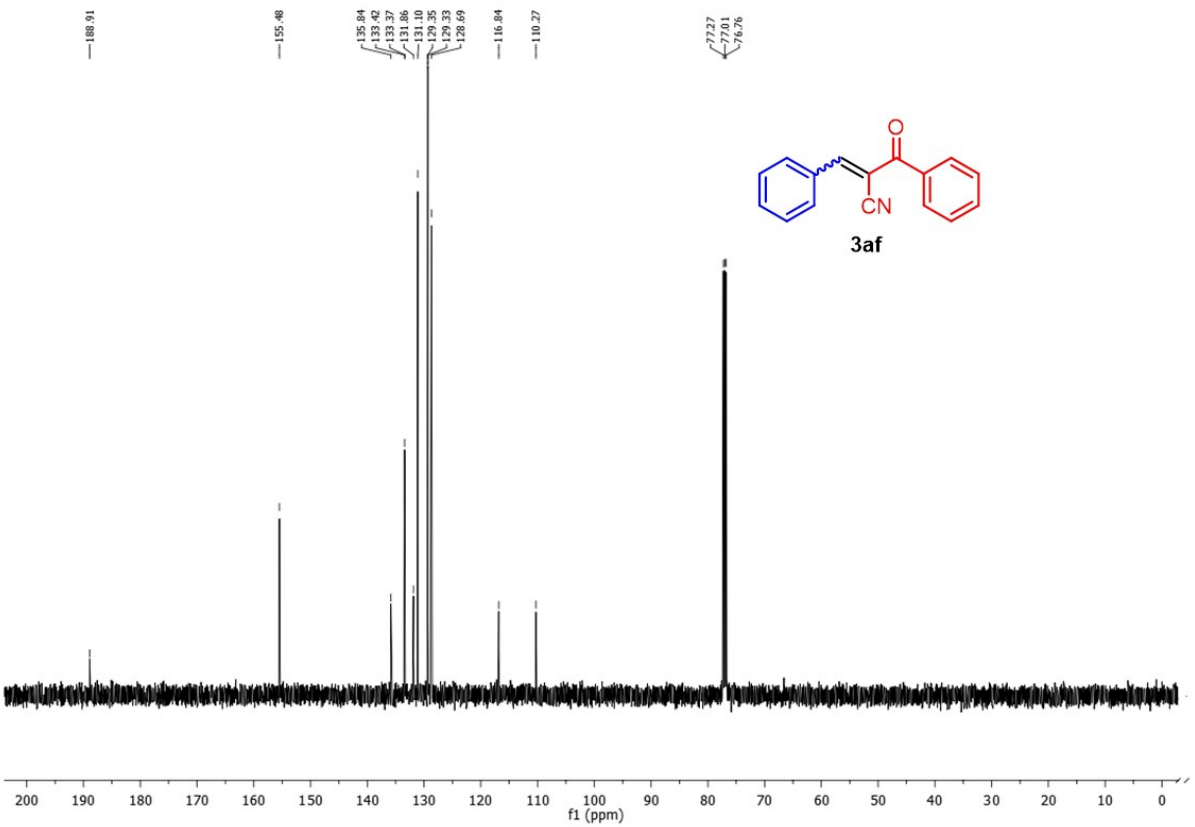

8.26
8.00
7.99
7.58
7.56
7.55
7.52
7.51
7.49
7.26
4.41
4.40
4.38
4.37
1.57
1.42
1.40
1.39
COOEt
CN
3ad
0.99
2.00
3.03
2.02
3.04
f1 (ppm)

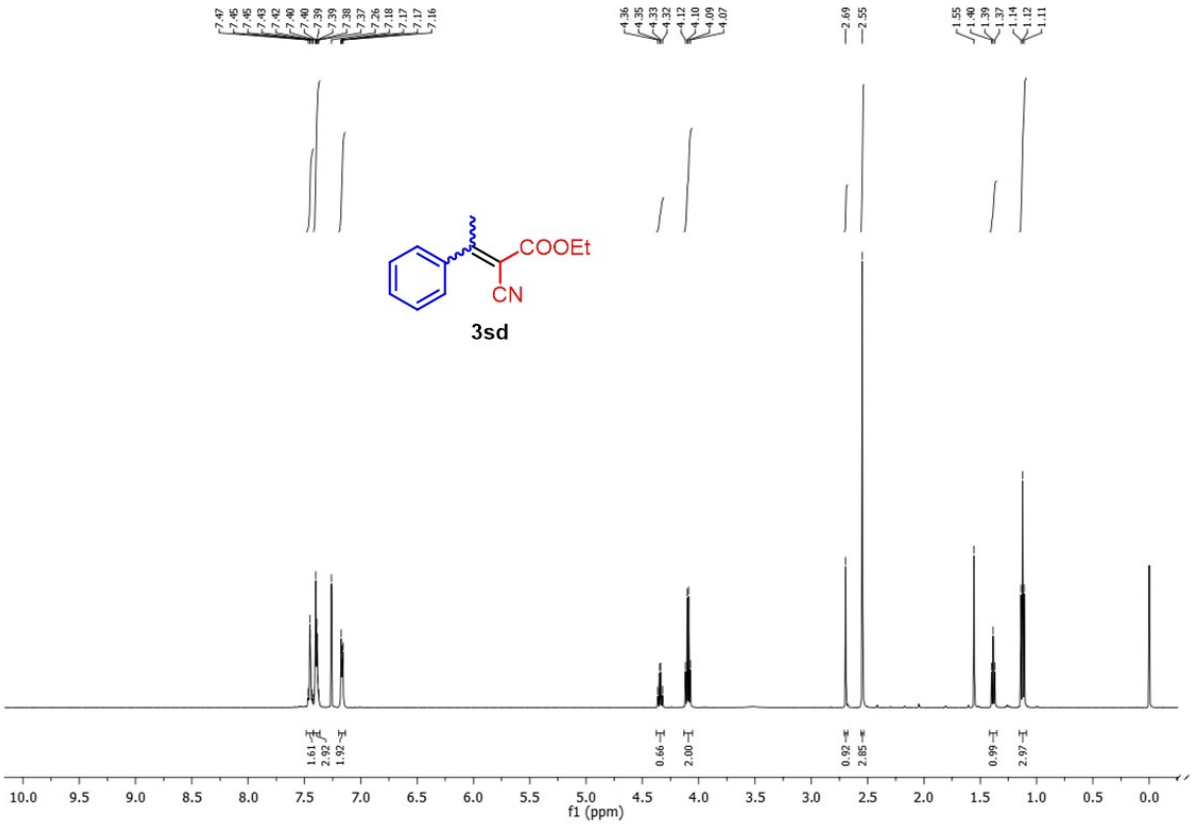

162.56
155.10
133.38
131.59
131.16
129.37
115.56
103.16
77.41
77.16
76.91
62.82
14.25
COOEt
CN
3ad
f1 (ppm)

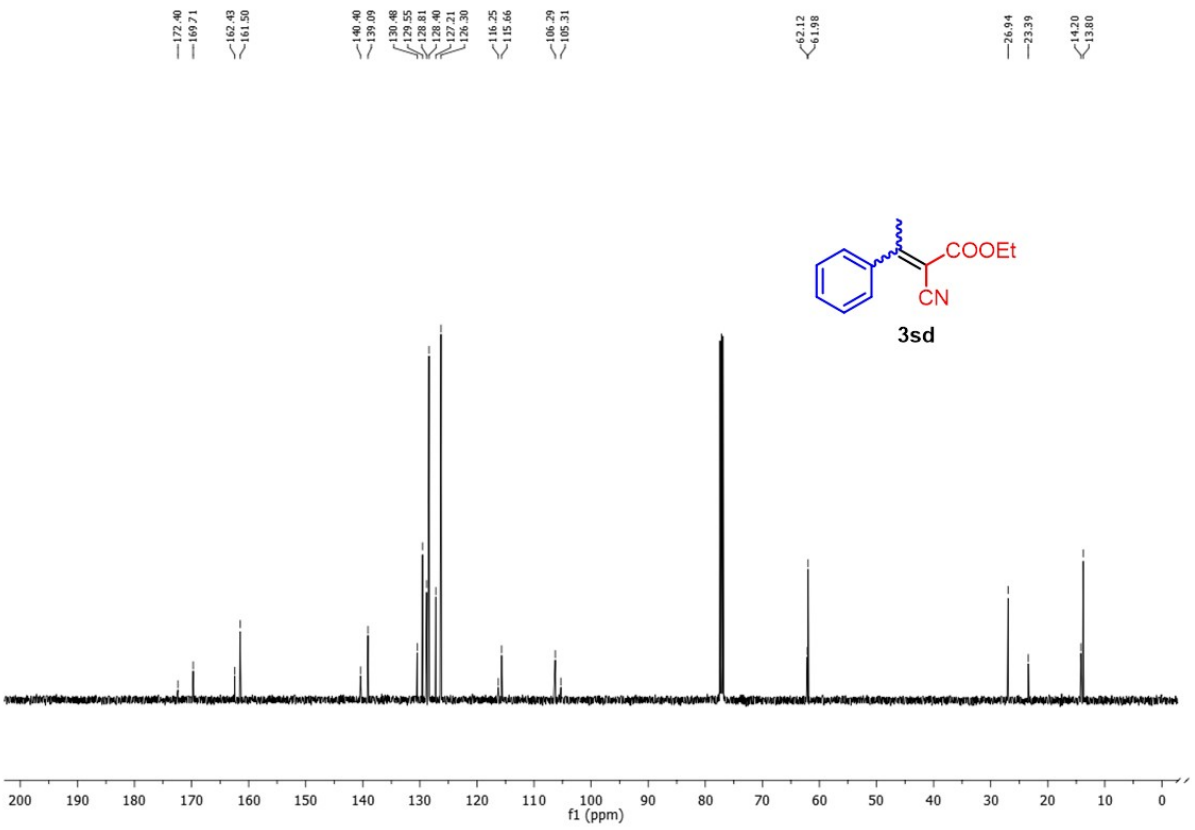

7.74
7.46
7.45
7.44
7.40
7.39
7.37
7.36
7.36
7.26
4.36
4.34
4.33
4.31
4.30
4.29
1.58
1.35
1.33
1.32
1.30
1.29
1.27
COOEt
COOEt
3ae
0.97
2.00
3.10
4.04
6.38
f1 (ppm)


166.79
164.24
142.24
133.03
130.63
129.55
128.89
126.46
77.41
77.17
76.91
61.80
61.75
14.25
13.99
COOEt
COOEt
3ae
f1 (ppm)


8.07
8.04
8.03
7.91
7.90
7.66
7.64
7.63
7.60
7.59
7.57
7.55
7.53
7.52
7.26
1.55
O
CN
3af
3.03
2.00
1.01
1.09
4.07
f1 (ppm)


188.91
155.48
135.84
133.42
133.37
131.86
131.10
129.35
129.33
128.69
116.84
110.27
77.27
77.01
76.76
O
CN
3af
f1 (ppm)


7.47
7.45
7.45
7.43
7.42
7.40
7.40
7.39
7.39
7.38
7.37
7.26
7.18
7.17
7.17
7.16
4.36
4.35
4.33
4.32
4.12
4.10
4.09
4.07
2.69
2.55
1.55
1.40
1.39
1.37
1.14
1.12
1.11
COOEt
CN
3sd
1.61
2.92
1.92
0.66
2.00
0.92
2.85
0.99
2.97
f1 (ppm)


172.40
169.71
162.43
161.50
140.40
139.09
130.48
129.55
128.81
128.40
127.21
126.30
116.25
115.66
106.29
105.31
62.12
61.98
26.94
23.39
14.20
13.80
COOEt
CN
3sd
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

7. HRMS spectra of TEMPO-adduct

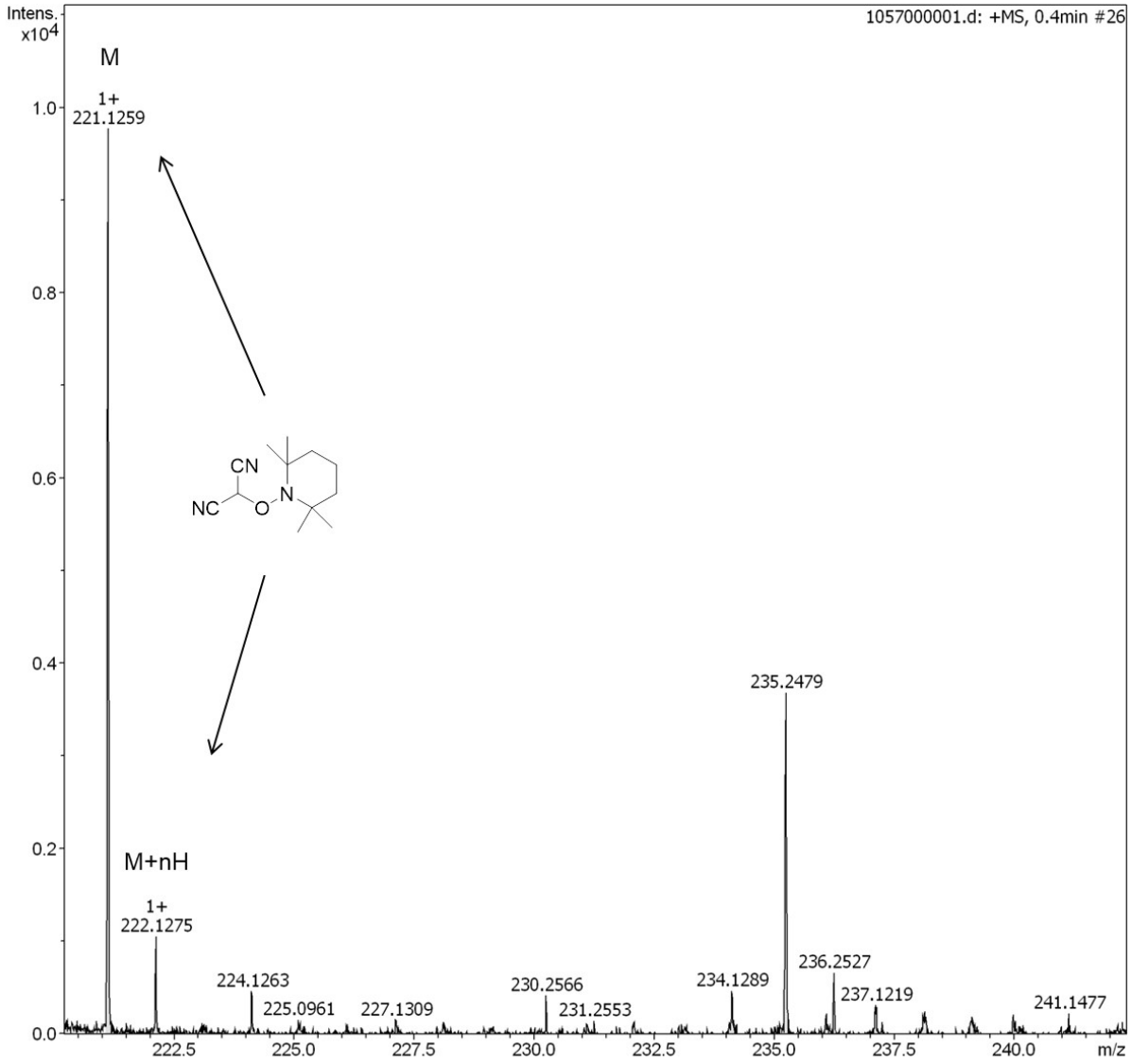


Figure S5. HRMS spectrum of TEMPO-adduct of rose bengal photocatalytic Knoevenagel condensation reaction mixture.