The Functionalization of Organic Semiconductor Crystals via the Diels-Alder Reaction

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Electronic Supplementary Information

General Methods of Characterization

X-ray photoelectron spectroscopy (XPS) measurements. A Thermo Scientific ESCALAB 250Xi XPS system at 3×10^{-7} mBar was used to acquire photoelectron spectra. A monochromatic Al X-ray source at 140 W was used with an analytical spot size of 200 μm and a 90º takeoff angle, with a pass energy of 50 eV. Surface samples were referenced against internal C 1s line at 284.5 eV.

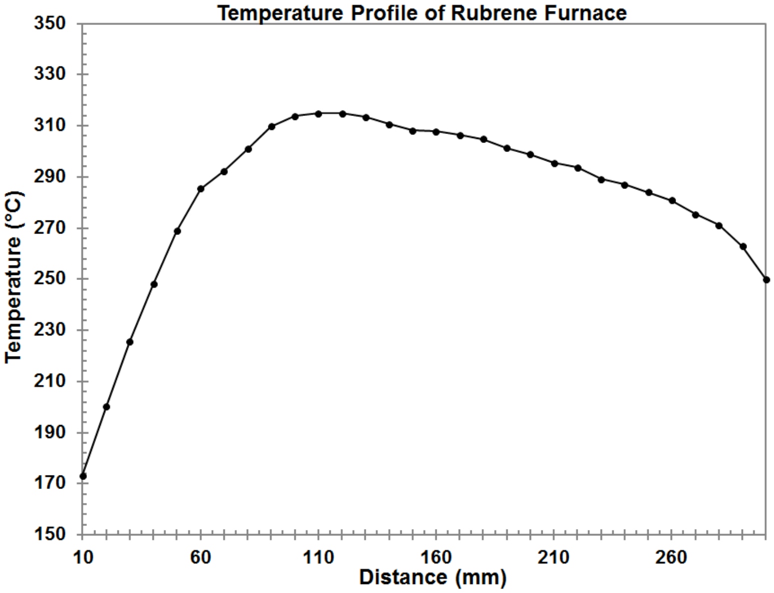
Mass spectrometry measurements. Full scan mass spectra and accurate mass measurements were acquired with a JEOL GCmate II BE sector mass spectrometer (Tokyo, Japan) at the University of Illinois-Chicago's Research Resource Center using electron impact ionization (EI) in the positive ion mode. Standard adduct samples, synthesized in solution, were dissolved in a minimum of methanol and applied to a direct insertion solids probe for analysis (about 0.5 μg). Crystal samples prepared by solid-vapor phase reactions were applied to solids probe directly without any prior solvation (neat). The temperature of the solids was ramped at a rate of 64 ^{0}C per minute to a final temperature of 350 ^{0}C. The mass spectrometer was scanned from m/z 10 to m/z 800 at a rate of 530 ms per scan. Accurate mass measurements of molecular ions were carried out after the acquisition of full scans in unit mass resolution mode.

Substrate Preparation and Reaction

Gold substrate preparation. Chromium (5 nm, 1 Å/s) and gold (30-40 nm, 1 Å/s) were thermally deposited onto pre-cut and cleaned glass slides (1 cm × 1 cm) in a Kurt J. Lesker NANO38 evaporator (base pressure $\leq 1.00 \times 10^{-6}$ Torr).

Organic crystal preparation. Tetracene and rubrene crystals were grown using physical vapor transport in a horizontal quartz tube under a stream of argon (a modified version of Laudise et al. 1998).[1]

Quartz tubes were purchased from National Scientific Co. or MTI Corp. For producing a thermal gradient, resistive type K thermocouple wire was wrapped between tubes of 27×30 mm and 37×40 mm diameters, both 20" in length. This constituted our furnace and the thermal gradient for rubrene can be seen below (the same gradient was used with tetracene but at a lower temperature setting). Five 17×19 mm diameter, 3" length tubes were used as the source/collection tubes and placed within a long reactor tube having 25 mm OD × 21 mm ID and a length of 24".



Prior to use, the reactor tube and the inner growth tubes were cleaned with acetone wetted Kimwipes. Upon air drying, the reactor tube was placed into the furnace tubes followed by the five inner source/collection tubes (the first of which contained amorphous sublimed grade source material, 99.99% Sigma). Both ends of the long tube were sealed using vacuum accessories (o-ring, flange). Prior to use, the system was flushed with argon at 80 mL/min for at least 1 h. Growth occurred over 16-24 h in the dark at atmospheric pressure with an argon flow rate of 40-45 mL/min. Single crystals for use in XPS and MS were taken from collection zone and if not used immediately, were placed in a vacuum chamber in the dark.

Microscale crystal substrates for XPS analysis consisted of small single crystals of the organic semiconductor grown on gold coated glass slides which were located in the growth zone. All other conditions were identical. In our hands, we found that runs containing the substrates for microcrystal growth also yielded larger single crystals in the collection tubes.

General procedure for all vapor dosed reactions. A reaction chamber comprised of a Schlenk round bottomed flask fitted with a hollow ended stopper was used to dose the sample with dienophiles **3-7**. Organic semiconductor samples were placed in the bottom of a flame dried round bottomed flask approximately 8 cm away from powder resting in the tip of the hollow stopper. When evacuated, the setup readily reaches 10^{-1} Torr, although the ultimate pressure is limited by the vapor pressure of the dienophile. The flask was then placed in an oven at ~ 85 °C, for three days. Upon removal from the oven, the tip of the stopper was cooled with liquid nitrogen or a dry ice/IPA bath to condense excess dienophile away from the sample. Vacuum on the system was released using an N_2 filled schlenk line.

Reaction for XPS. Tetracene and rubrene microscale crystal substrates, as well as tetracene single crystals, were reacted with 2,3-dichloromaleic anhydride (**3**) according to the general vapor dosed reaction procedure at 85 °C.

Reaction for mass spectrometry. Tetracene single crystals were reacted with maleic anhydride (**4**), *N*-methylmaleimide (**5**), fumarodinitrile (**6**) or tetracyanoethylene (**7**) according to the general vapor dosed reaction procedure at 85 ºC.

X-ray Photoelectron Spectroscopy and Analysis

Figure S1. The solution generated standard Diels-Alder adduct between tetracene and 2,3-dichloromaleic anhydride was dispersed onto a carbon tab for XPS analysis. The binding energy of the Cl 2p electrons were 200.5 eV and 202.1 eV.

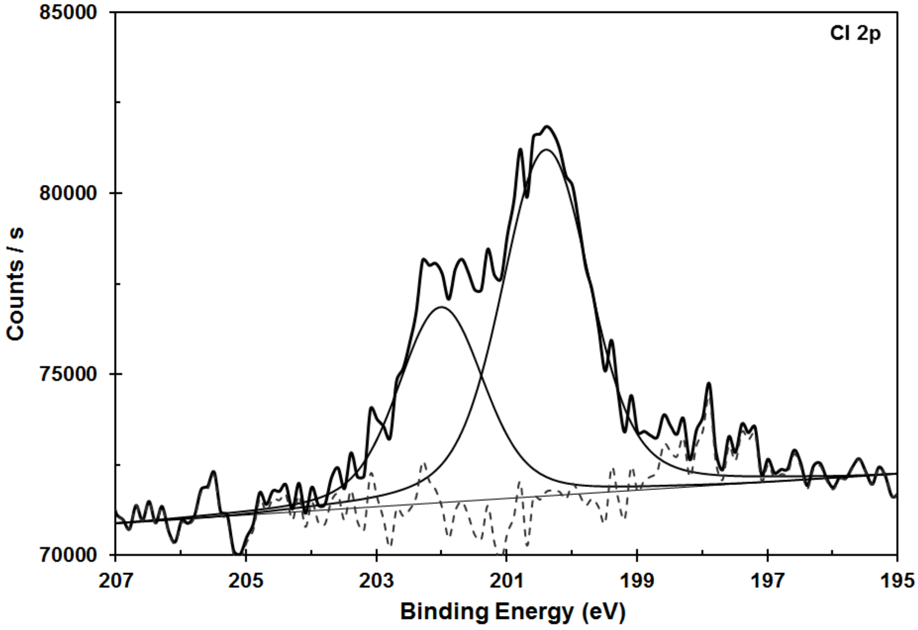
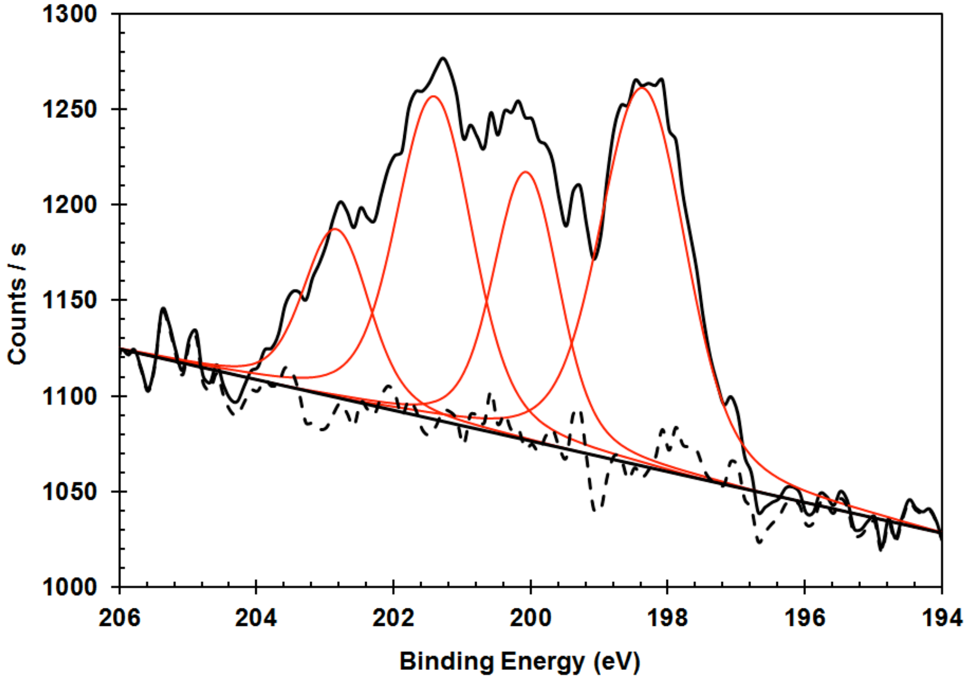


Figure S2. A rubrene sample grown on a gold coated glass substrate was reacted with 2,3-dichloromaleic anhydride and analyzed using XPS to detect chlorine. The binding energies of the two Cl 2p signals occurred at 198.4, 200.1 eV and 201.4, 202.8 eV.



Mass Spectrometry and Analysis

Figure S3. Electron impact ionization mass spectra of the tetracene-maleic anhydride reaction product A) formed in solution and B) formed by gas phase reaction on tetracene crystal.

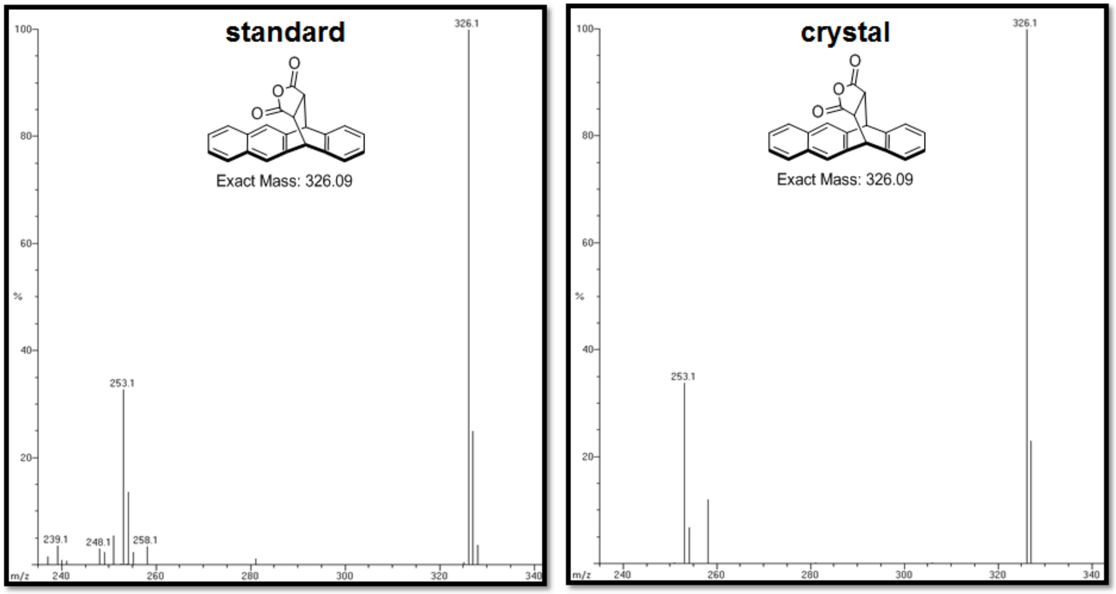


Figure S4. Plots of ion current versus time for the analysis of the fumarodinitrile adduct formed on the surface of the tetracene crystal. **(top)** m/z 306.1 (adduct). **(middle)** m/z 78 (fumarodinitrile; first represents physisorbed material, the second is a fragment from adduct). **(bottom)** Probe temperature as a function of time.

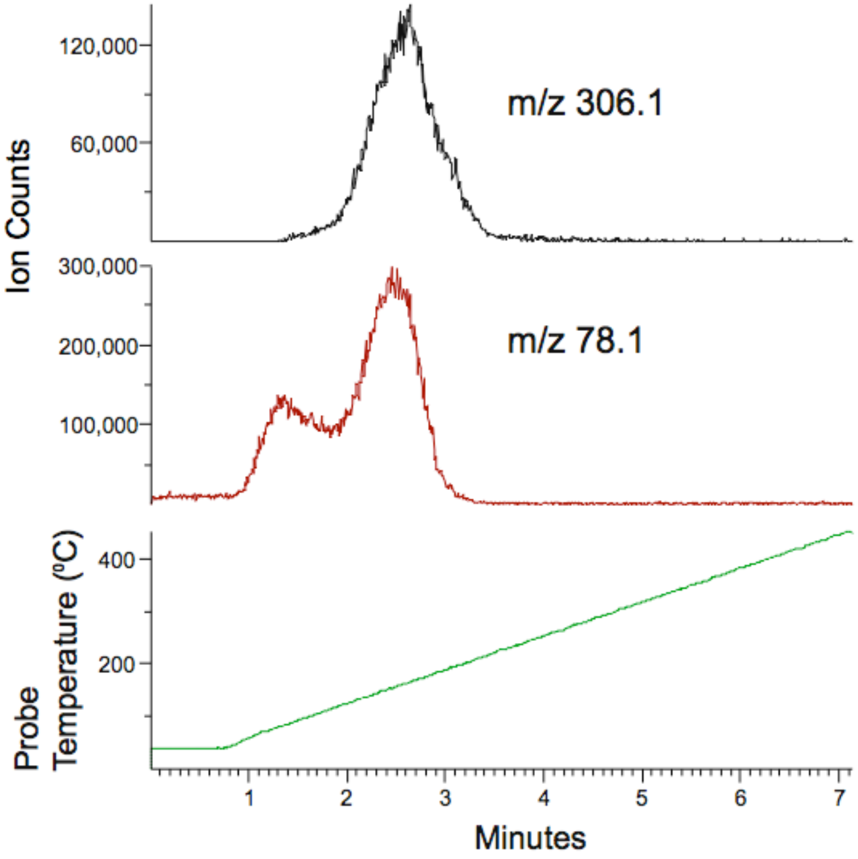


Figure S5. Electron impact ionization mass spectra of the tetracene-fumarodinitrile reaction product formed by gas phase reaction on a tetracene crystal (HRMS: theoretical m/z 306.11570, measured m/z 306.11573, 1.2 ppm error).

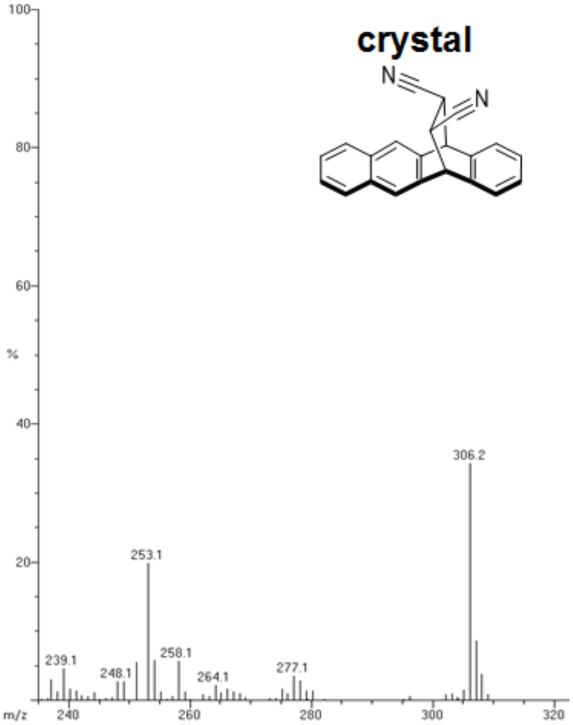


Figure S6. Electron impact ionization mass spectra of the tetracene-tetracyanoethylene reaction product formed by gas phase reaction on a tetracene crystal (HRMS: theoretical m/z 356.10620, measured m/z 356.10519, 2.8 ppm error).

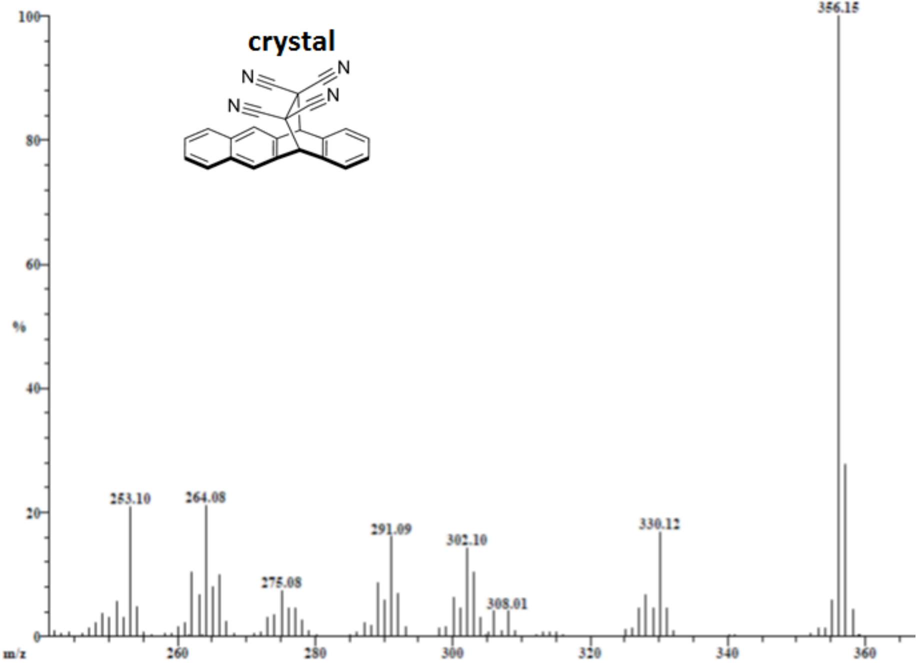
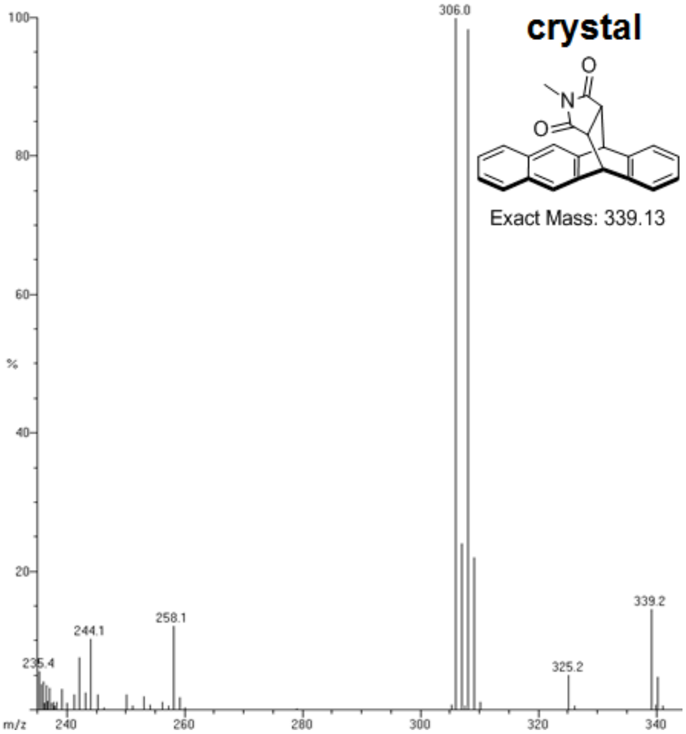


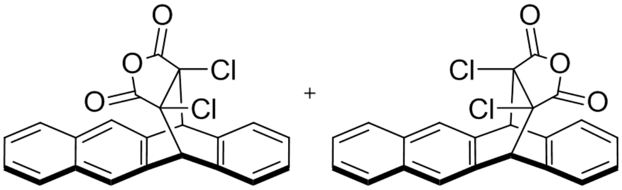
Figure S7. Electron impact ionization mass spectra of the tetracene-N-methylmaleimide reaction formed by gas phase reaction on a tetracene crystal (HRMS theoretical m/z 339.12593, measured m/z 339.12737, 4.2 ppm error).



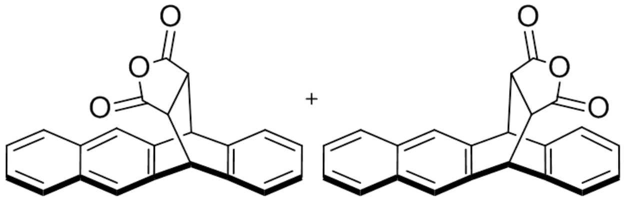
Synthetic Methods

Reagent grade toluene was degassed prior to use. All other reagents were used as shipped (Sigma-Aldrich). Tetracene used in solution reactions was 98% pure. ^{1}H and ^{13}C NMR spectra were taken in $CDCl_3$ and recorded on a Varian 500 MHz spectrometer. All proton chemical shifts (δ) are downfield from tetramethylsilane reported in ppm. All ^{13}C NMR spectra were referenced to $CDCl_3$ at 77.23 ppm. All IR spectra were obtained on a Bruker Tensor 37 equipped with a liquid nitrogen cooled MCT detector and were completed as KBr pellets.

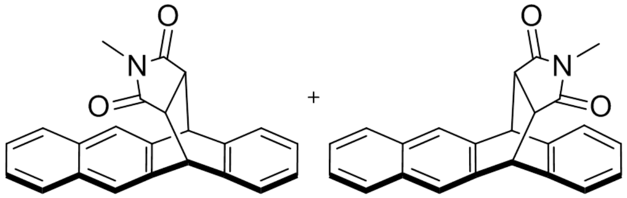
General Procedure for all Diels-Alder Reactions. Sealed tubes containing tetracene and dienophile were evacuated and filled with nitrogen three times prior to addition of solvent. Toluene was added via syringe while stirring. The tube was sealed and the reaction was stirred in the dark. After the reaction was complete, it was cooled to 4 °C and the precipitate was collected by simple filtration. The remaining residue collected by rotary evaporation of the filtrant, although not spectroscopically pure in every case, was useful in characterizing stereoisomers of adducts formed with 2,3-dichloromaleic anhydride (**3**), maleic anhydride (**4**), and *N*-methyl maleimide (**5**). There was no attempt, however, at further purification of this material to improve yield. All attached spectra are representative of the collected precipitate except in the case of *N*-methyl maleimide where the solid residue contained a spectroscopically single isomer; here the spectra are of the filtrate containing both.



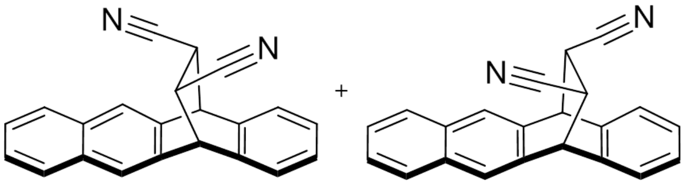
5,12-Dihydro-5,12-ethano-napthacene-13,14-dichlorodicarboxylic acid anhydride: Tetracene (**1**) (0.151 g, 0.661 mmol), 2,3-dichloromaleic anhydride (**3**) (0.122 g, 0.731 mmol) and toluene (4.0 mL) were placed in a sealed tube according to the general Diels-Alder procedure. The reaction mixture was stirred for 72 h at 120 °C. The Diels-Alder adduct (0.129 g, 0.326 mmol) was collected by simple filtration as a tan crystal in a 1:1.5 mixture of stereoisomers inseparable by silica gel chromatography, in a 50% yield. mp = 319-321 °C. Selected definitive ^{1}H NMR peaks were used for determination of stereoisomers. Major stereoisomer: ^{1}H NMR (500 MHz) δ 7.94 (s, 2H), 7.87 (dd, *J* = 6.2, 3.3 Hz, 2H), 7.55-7.51 (m, 2H), 7.39 (dd, J = 5.5, 3.2 Hz, 2H), 7.30 (dd, *J* = 5.5, 3.2 Hz, 2H), 4.98 (s, 2H). ^{13}C NMR (125 MHz) δ 165.9, 136.1, 132.7, 132.4, 129.4, 128.0, 126.9, 126.24, 126.19, 71.4, 54.46. Minor stereoisomer: ^{1}H NMR (500 MHz) δ 7.81 (s, 2H), 7.79 (dd, *J* = 6.4, 3.4 Hz, 2H), 7.55-7.51 (m, 4H), 7.35 (dd, *J* = 5.6, 3.2 Hz, 2H), 4.99 (s, 2H). ^{13}C NMR (125 MHz) δ 165.8, 135.8, 133.0, 132.5, 128.3, 128.1, 127.4, 127.1, 125.5, 71.9, 54.52. IR (cm^{-1}) 3053, 1868, 1798, 1608, 1504, 1480, 1462, 1403, 1350, 1262, 1216, 1139.



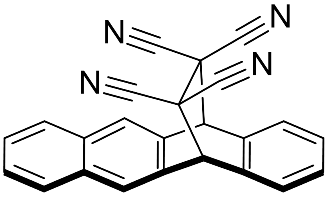
5,12-Dihydro-5,12-ethano-napthacene-13,14-dicarboxylic acid anhydride: Tetracene (**1**) (0.073 g, 0.32 mmol), maleic anhydride (**4**) (0.036 g, 0.36 mmol) and toluene (2.0 mL) were placed in a sealed tube according to the general Diels-Alder procedure. The reaction mixture was stirred for 8 h at 120 °C. The Diels-Alder adduct (0.061 g, 0.15 mmol) was collected by simple filtration as a tan crystal in a 1:2.5 mixture of stereoisomers inseparable by silica gel chromatography, in a 60% yield. mp = 276-280 °C. Selected definitive ^{1}H NMR peaks were used for determination of stereoisomers. Major stereoisomer: ^{1}H NMR (500 MHz) δ 7.83 (s, 2H), 7.81-7.77 (m, 2H), 7.49-7.45 (m, 2H), 7.37 (dd, *J* = 5.4, 3.4 Hz, 2H), 7.23 (dd, *J* = 5.4, 3.2 Hz, 2H), 4.95-4.94 (m, 2H), 3.61 (dd, *J* = 2.2, 1.5 Hz, 2H). ^{13}C NMR (125 MHz) δ 170.70, 138.0, 137.8, 132.6, 128.3, 128.0, 126.7, 125.6, 123.2, 48.0, 45.6. Minor stereoisomer: ^{1}H NMR (500 MHz) δ 7.79-7.77 (m, 4H), 7.49-7.45 (m, 2H), 7.42 (dd, *J* = 5.5, 3.3 Hz, 2H), 7.22 (dd, *J* = 5.6, 3.2 Hz, 2H), 4.94-4.93 (m, 2H), 3.62 (dd, *J* = 2.1, 1.3 Hz, 2H). ^{13}C NMR (125 MHz) δ 170.69, 140.6, 135.3, 132.8, 129.3, 128.5, 128.1, 124.8, 124.3, 48.3, 45.5. IR (cm^{-1}) 3055, 3020, 2957, 1860, 1778, 1402, 1228, 1071, 923.



5,12-Dihydro-5,12-ethano-napthacene-15-*N*-methylpyrrolidine-14,16-dione:
Tetracene (0.080 g, 0.35 mmol), *N*-methylmaleimide (**5**) (0.043 g, 0.39 mmol) and toluene (2.0 mL) were placed in a sealed tube according to the general Diels-Alder procedure. The reaction mixture was stirred for 24 h at 120 °C. The Diels-Alder adduct (0.074 g, 0.22 mmol) was collected by filtration as a white and tan crystal in a 1:1.6 mixture of stereoisomers inseparable by silica gel chromatography, in a combined 62% yield. mp = 319-321 °C. Selected definitive ^{1}H NMR peaks were used for determination of stereoisomers. Major stereoisomer: ^{1}H NMR (500 MHz) δ 7.80-7.78 (m, 4H), 7.45 (dd, *J* = 6.2, 3.3 Hz, 2H), 7.29 (dd, J = 5.5, 3.3 Hz, 2H), 7.14 (dd, *J* = 5.4, 3.2 Hz, 2H), 4.91-4.90 (m, 2H), 3.30-3.28 (m, 2H), 2.54 (s, 3H). ^{13}C NMR (125 MHz) δ 176.93, 138.7, 138.2, 132.40, 127.7, 127.3, 126.1, 125.0, 122.7, 46.9, 45.45, 24.36. Minor stereoisomer: ^{1}H NMR (500 MHz) δ 7.74 (dd, *J* = 6.1, 3.4 Hz, 2H), 7.70 (s, 2H), 7.43-7.39(m, 4H), 7.19 (dd, *J* = 5.6, 3.2 Hz, 2H), 4.90-4.88 (m, 2H), 3.31-3.30 (m, 2H), 2.43 (s, 3H). ^{13}C NMR (125 MHz) δ 176.97, 141.2, 135.9, 132.39, 127.8, 127.0, 126.0, 124.4, 123.5, 47.1, 45.36, 24.38. IR (cm^{-1}) 3044, 2943, 1780, 1702, 1434, 1379, 1299, 1281, 1142.



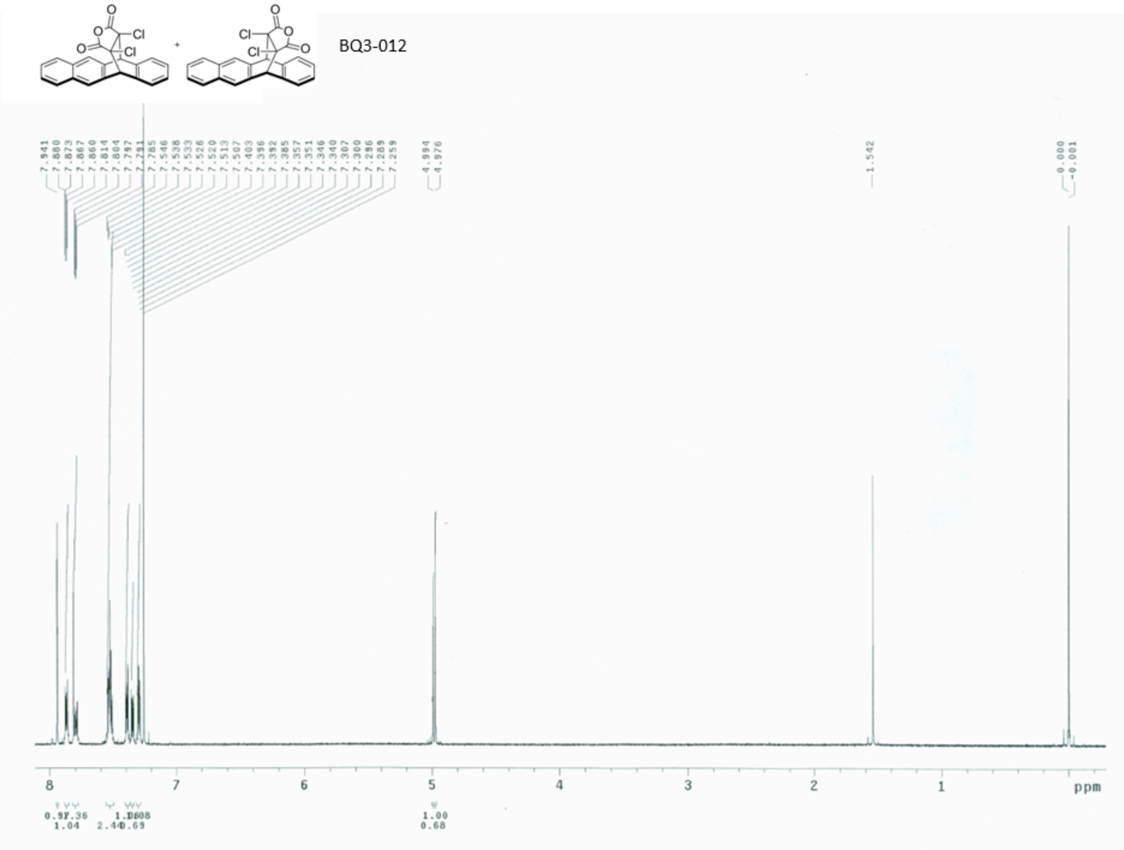
13, 14-Dicyano-5,12-dihydro-5,12-ethano-napthacene: Tetracene (**1**) (0.076 g, 0.33 mmol), fumarodinitrile (**6**) (0.027 g, 0.33 mmol) and toluene (1.5 mL) were placed in a sealed tube according to the general Diels-Alder procedure. The reaction mixture was stirred for 42 h at 150 °C. The Diels-Alder adduct (0.056 g, 0.18 mmol) was collected by simple filtration as a tan crystal in a 55% yield. mp = 240-244 °C. Stereoisomers are not distinguishable by NMR. ^{1}H NMR (500 MHz) δ 7.91 (s, 1H), 7.85-7.79 (m, 3H), 7.52-7.48 (m, 3H), 7.41-7.39 (m, 1H), 7.32-7.26 (m, 2H), 4.75 (d, J = 2.4 Hz, 1H), 4.74 (d, J = 2.4 Hz, 1H), 3.25 (dd, J = 5.1, 2.4 Hz, 1H), 3.24 (dd, J = 5.1, 2.4 Hz, 1H). ^{13}C NMR (125 MHz) δ 139.1, 137.1, 136.3, 134.1, 132.7, 132.6, 128.2, 128.14, 128.06, 127.8, 126.75, 126.68, 125.9, 124.8, 124.3, 123.0, 118.49, 118.47, 46.4, 46.3, 35.7, 35.6. IR (cm^{-1}) 3057, 2941, 2245, 1501, 1477, 1461, 1400, 894.



13, 13, 14, 14-Tetracyano-5,12-dihydro-5,12-ethano-napthacene: Tetracene (**1**) (0.083 g, 0.36 mmol), tetracyanoethylene (**7**) (0.054 g, 0.40 mmol) and toluene (2.0 mL) were placed in a sealed tube according to the general Diels-Alder procedure. The reaction mixture was stirred for 20 h at 120 °C. The Diels-Alder adduct (0.109 g, 0.31 mmol) was collected by simple filtration as a tan crystal in an 84% yield. mp > 282 °C (dec.) ^{1}H NMR (500 MHz) δ 8.04 (s, 2H), 7.91 (dd, J = 6.2, 3.3 Hz, 2H), 7.64-7.58 (m, 4H), 7.48 (dd, J = 5.4, 3.2 Hz, 2H), 5.16 (s, 2H). ^{13}C NMR (125 MHz) δ 134.1, 133.1, 130.2, 129.9, 128.4, 128.0, 126.8, 126.5, 110.76, 110.75, 53.1, 46.5. IR (cm^{-1}) 3062, 3017, 2991, 2250, 1608, 1503, 1480, 1464, 1270, 881.

References

1 R. A. Laudise, C. Kloc, P. G. Simpkins, T. Siegrist, *J. Cryst. Growth* 1998, **187**, 449.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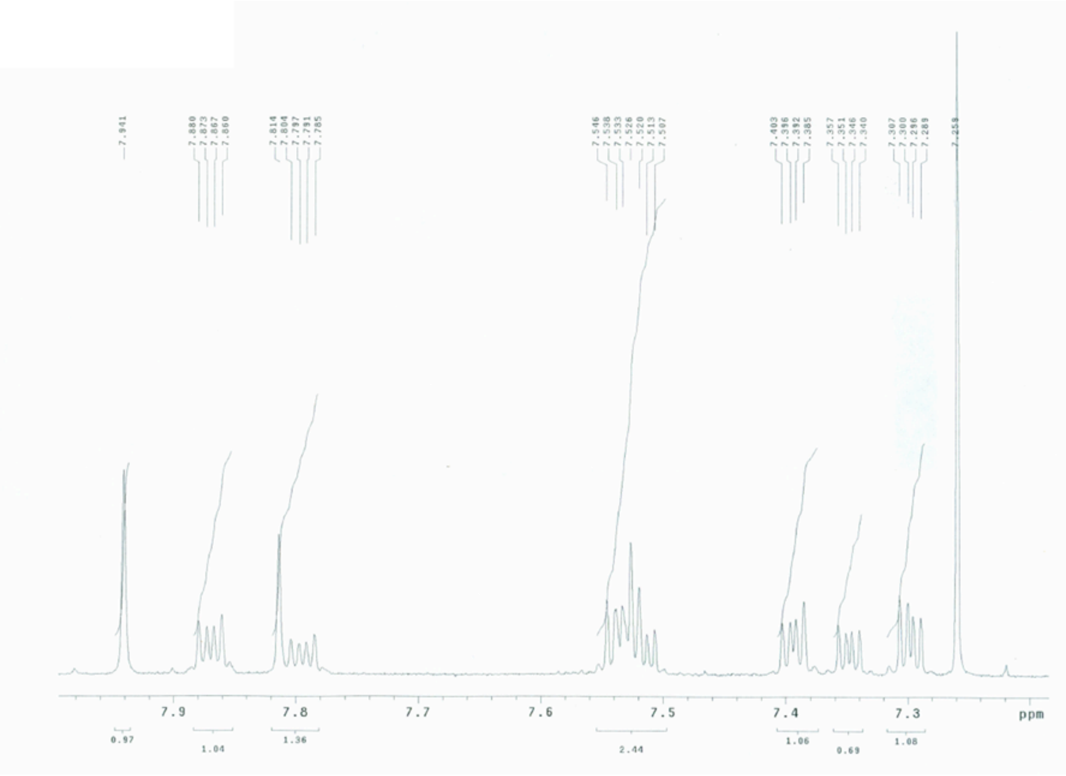
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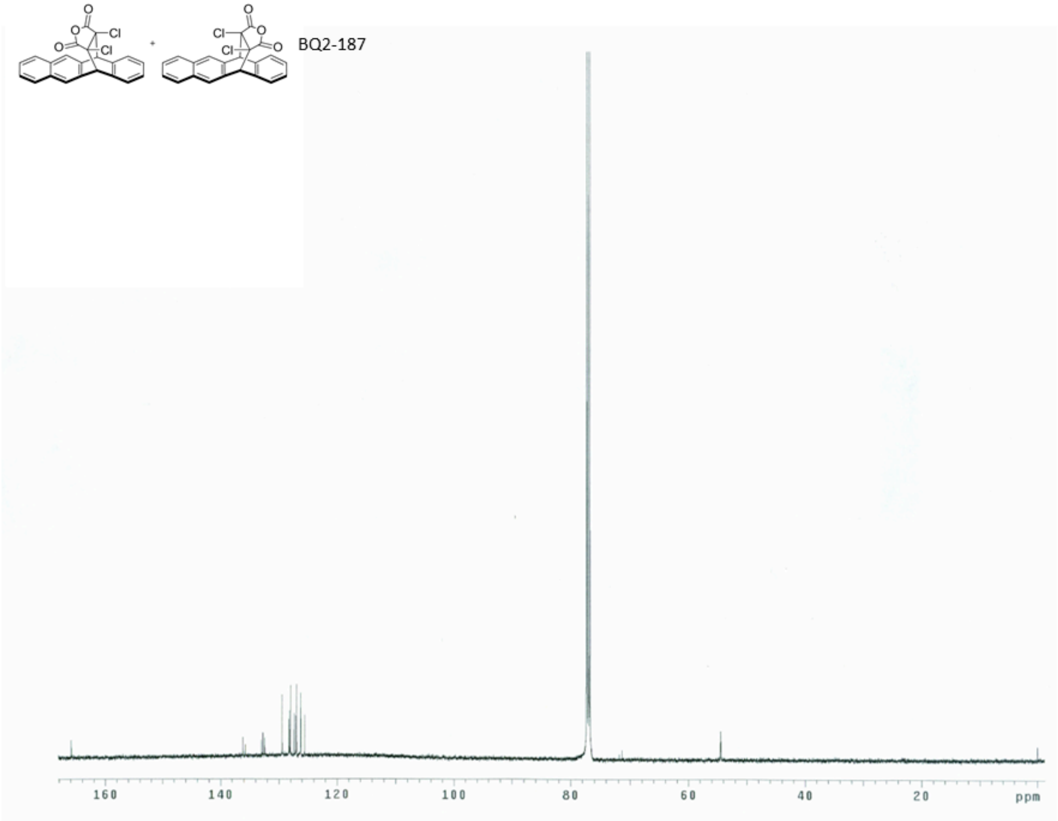
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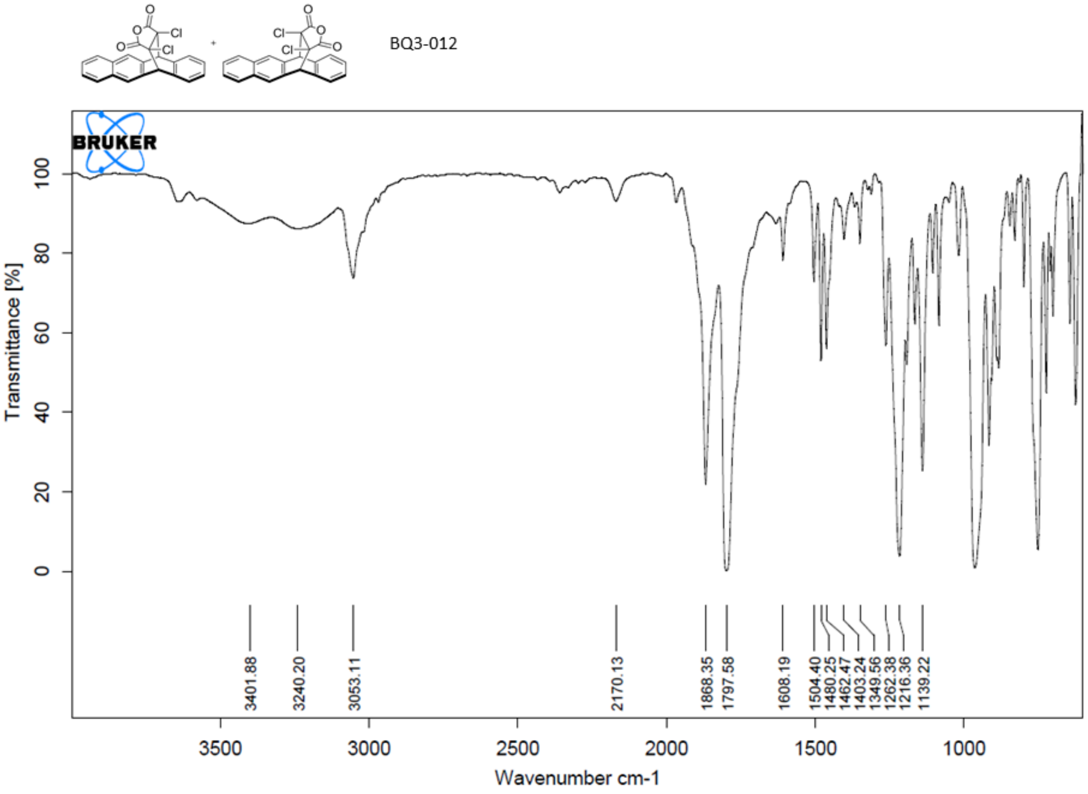
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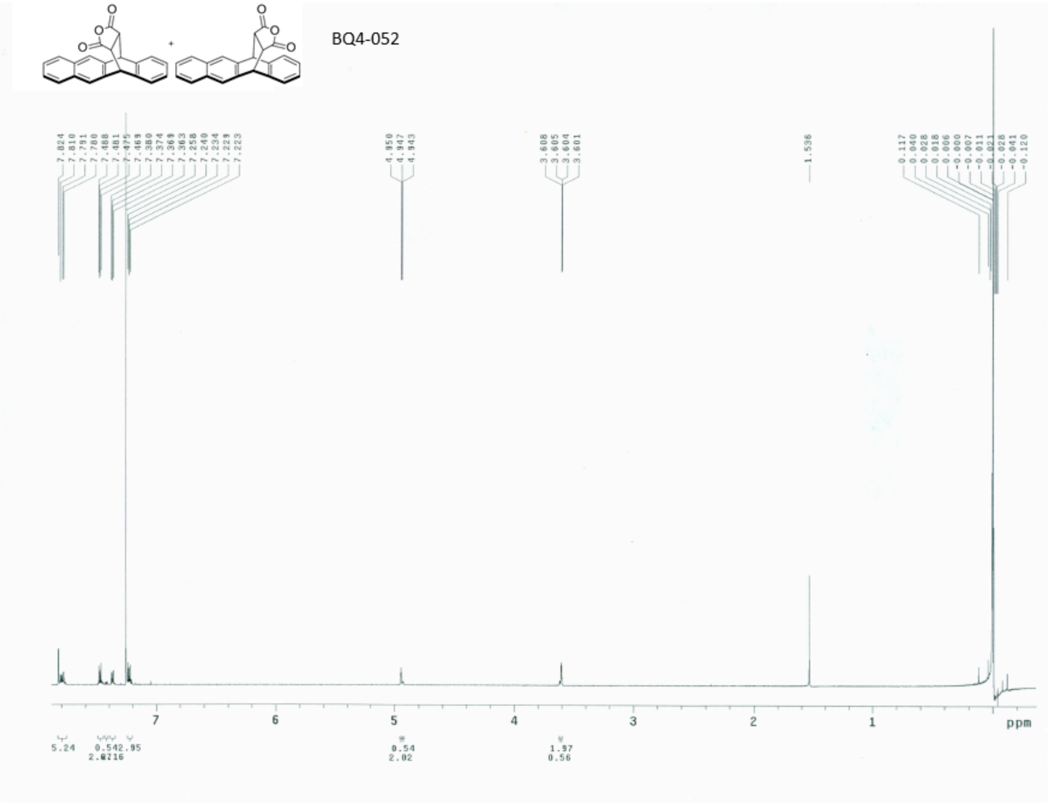
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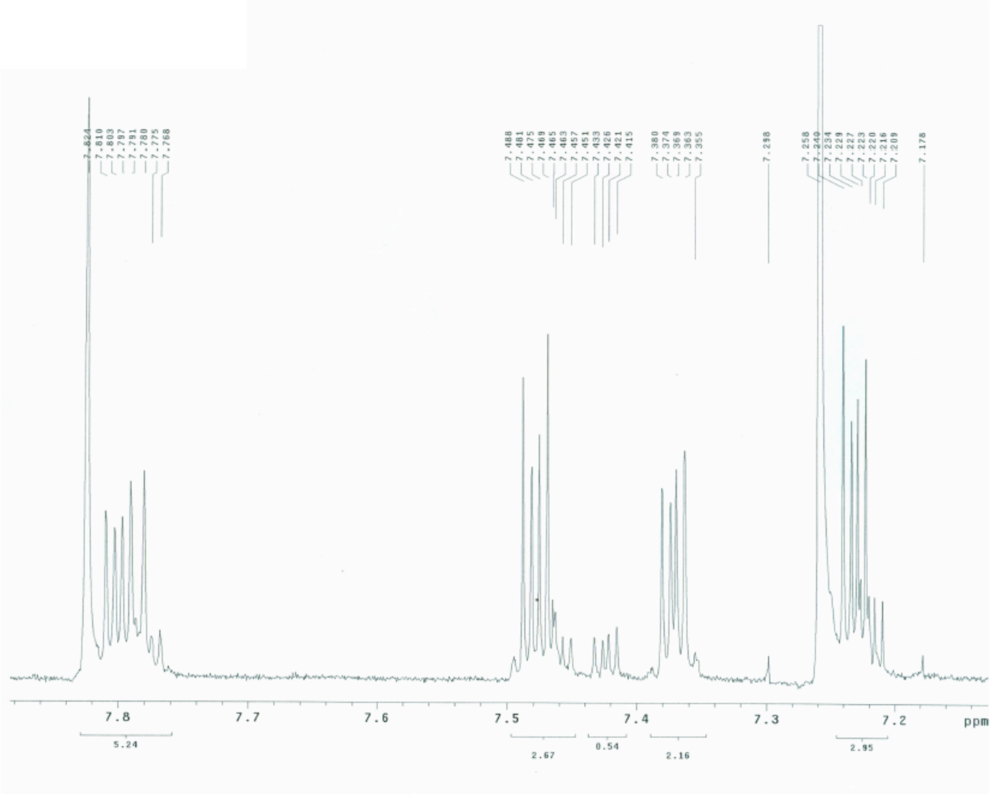
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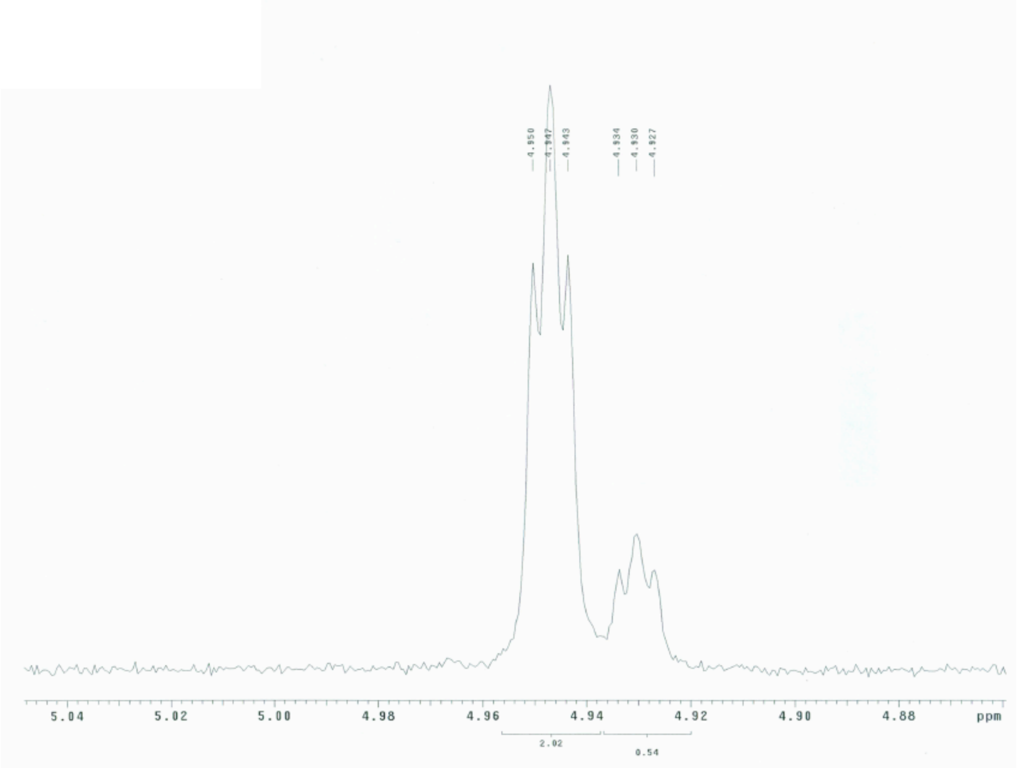
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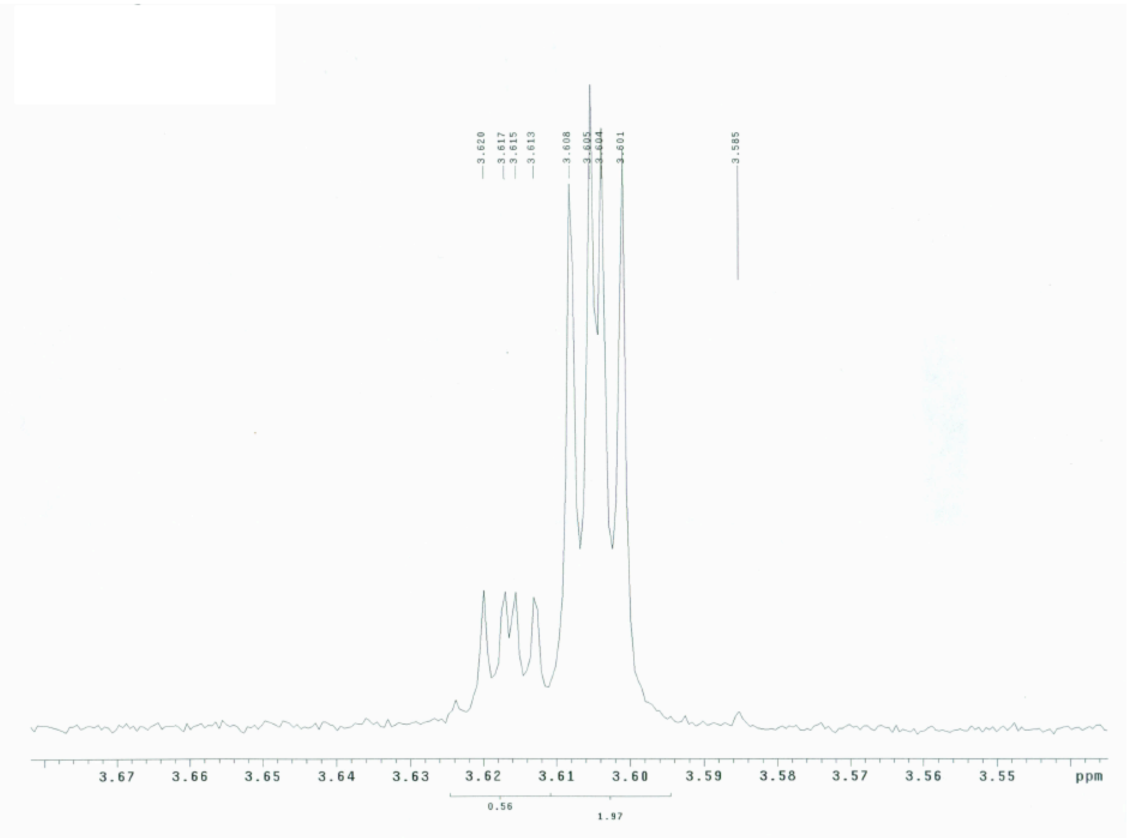
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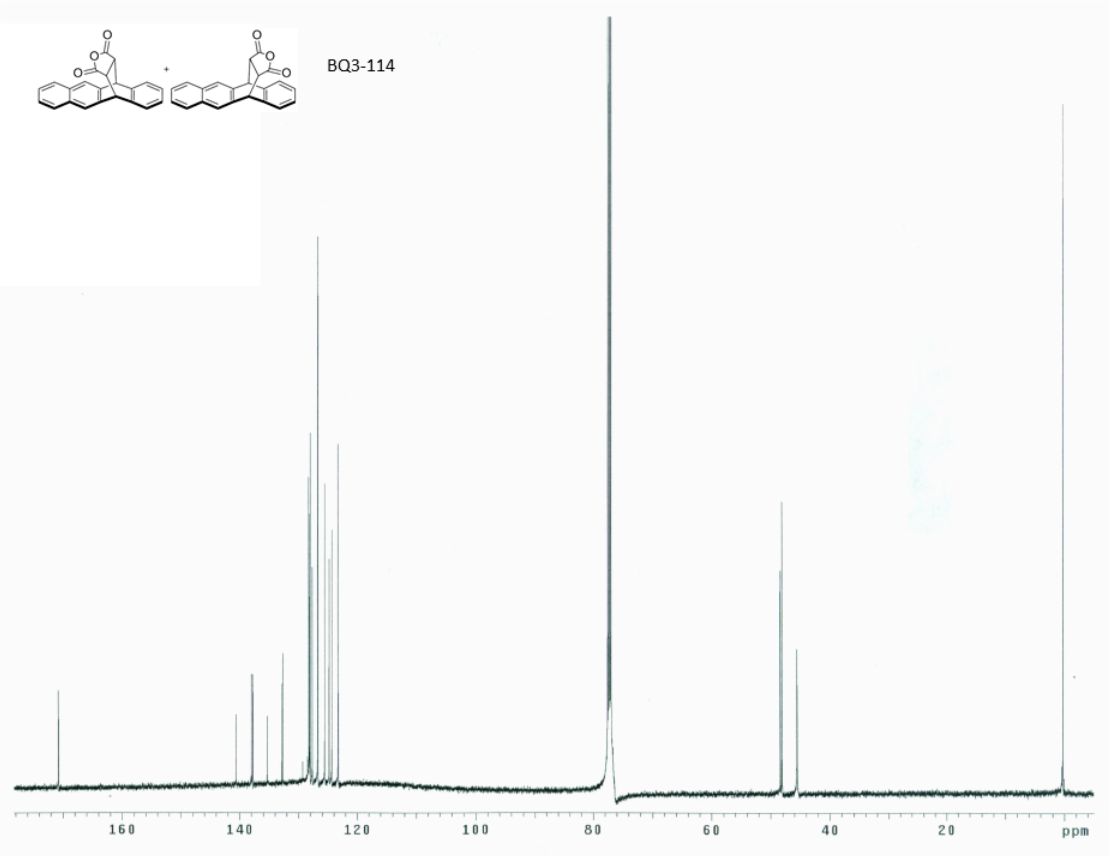
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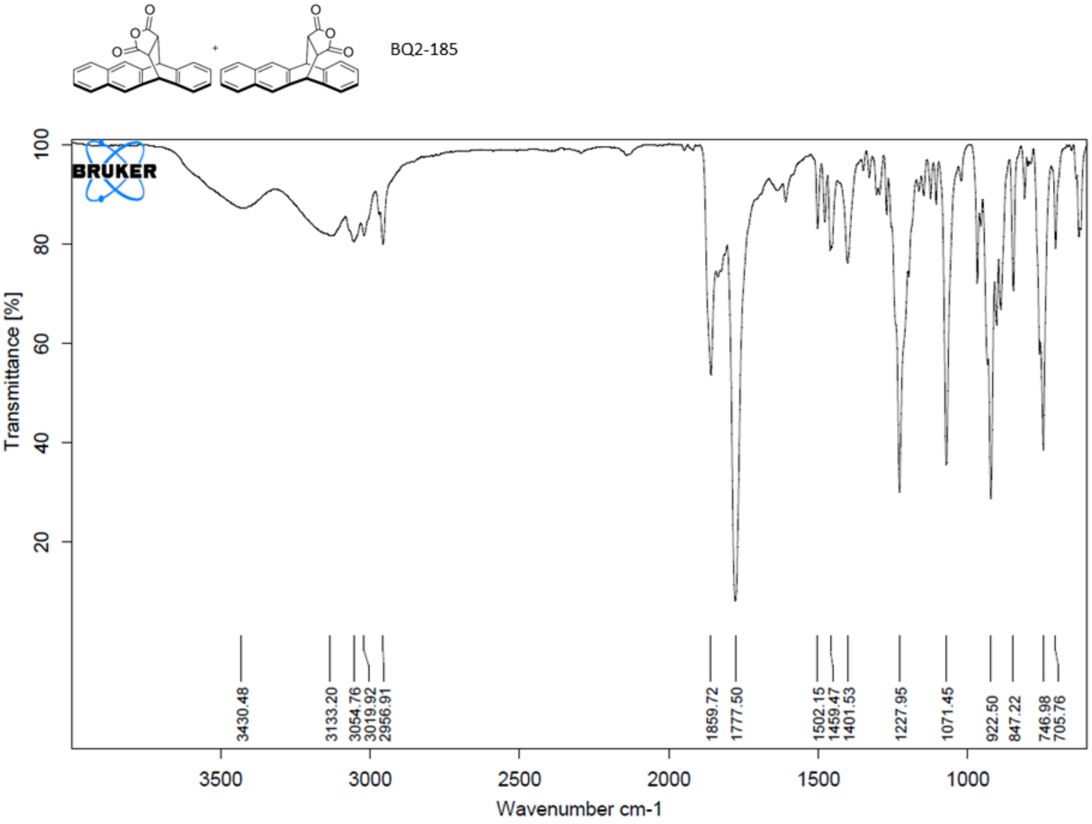
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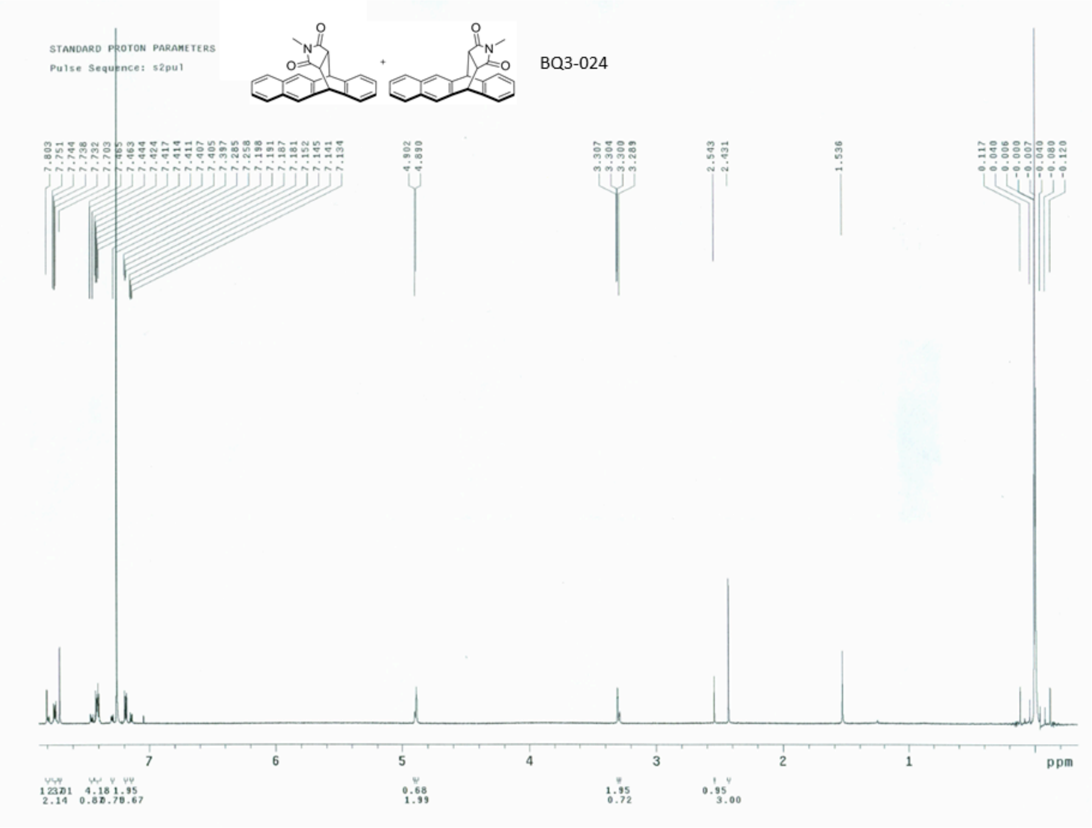
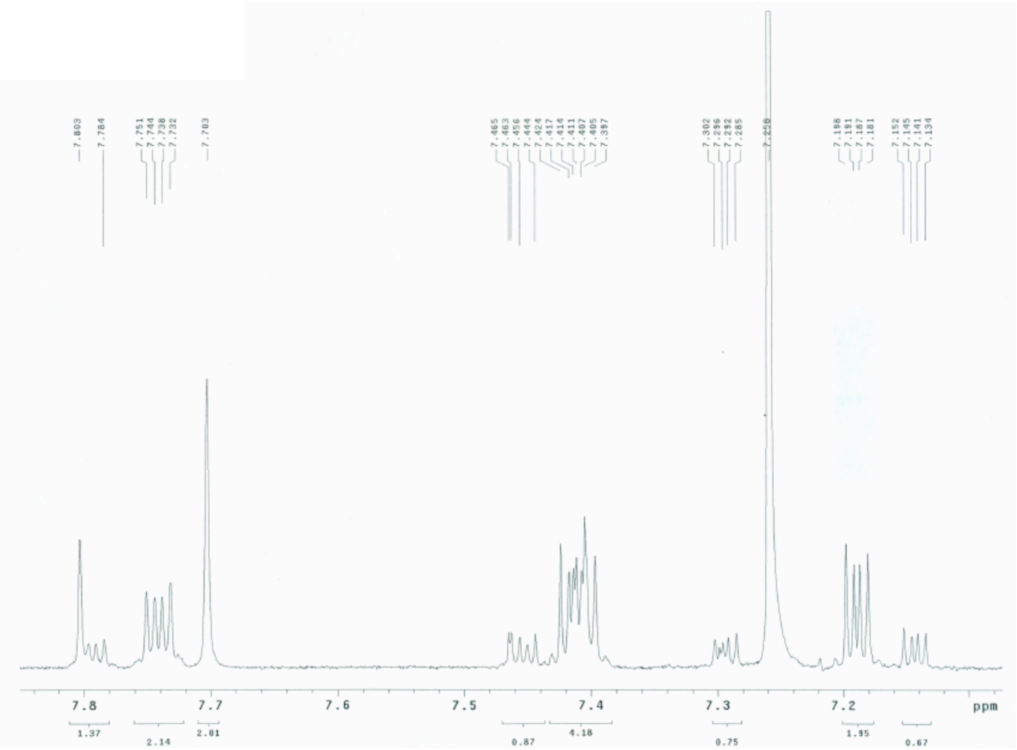
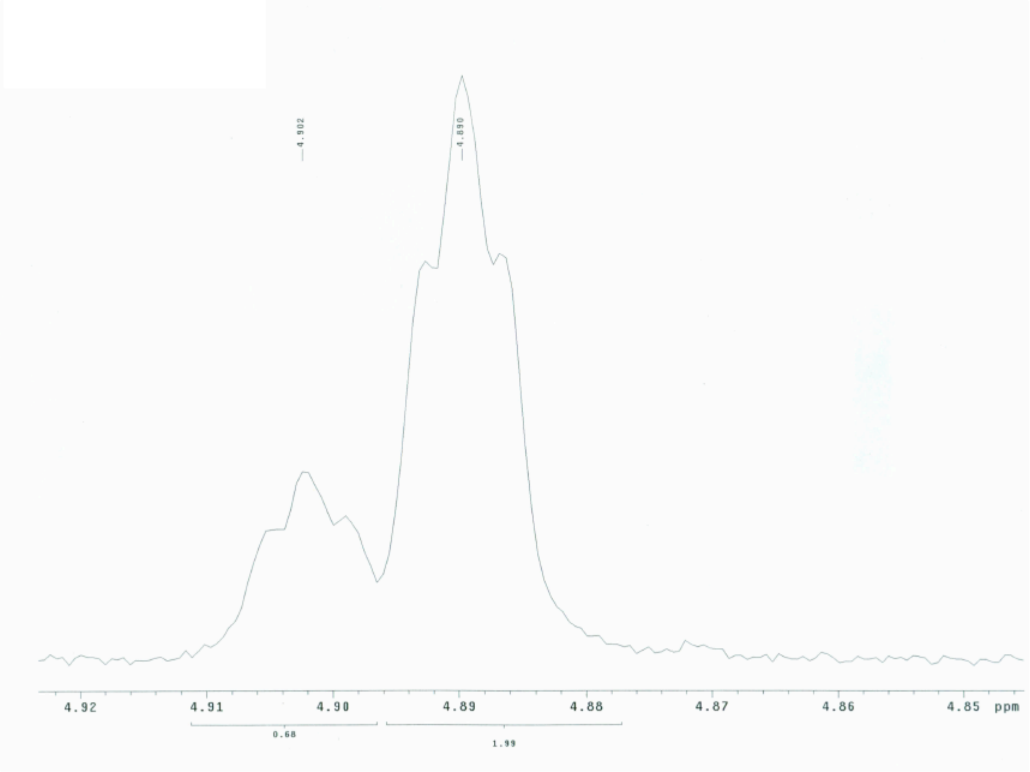
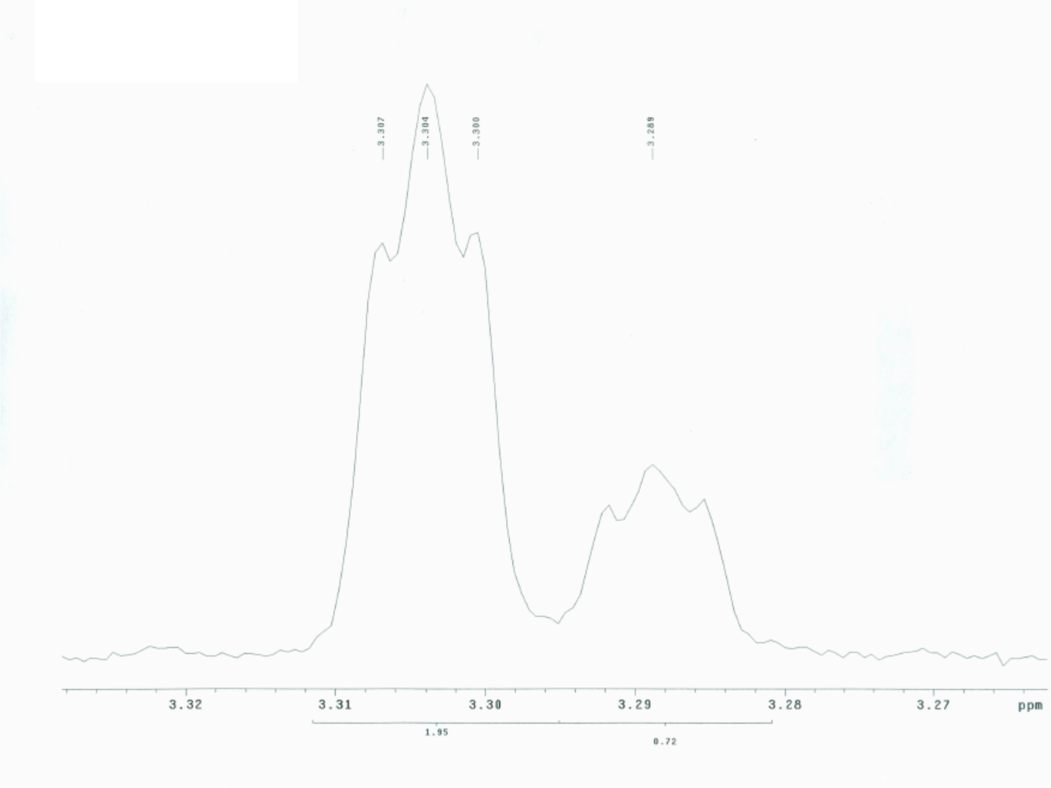
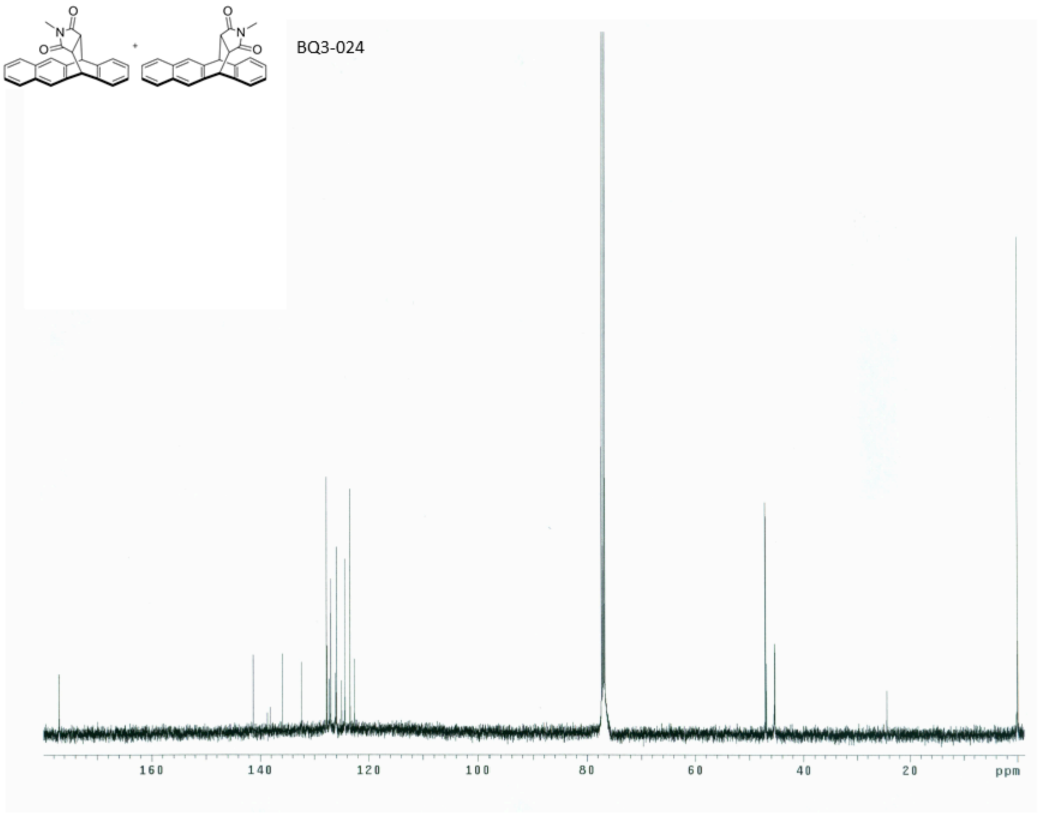
1000
Wavenumber cm-1

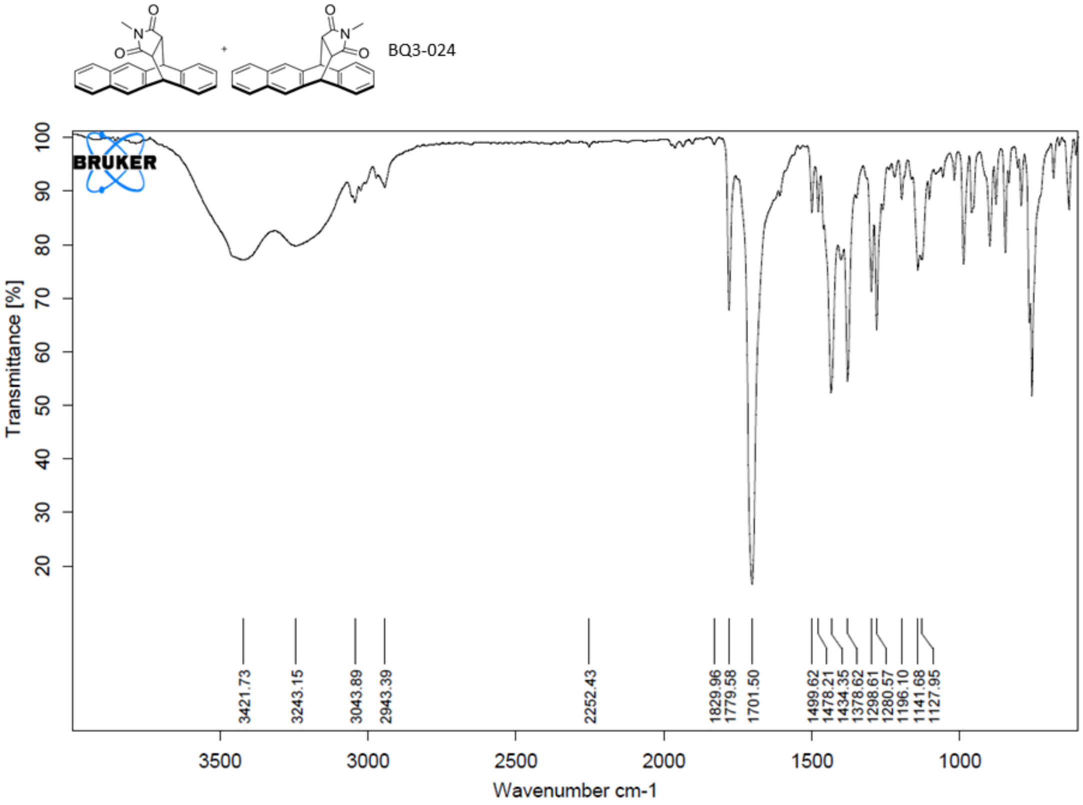

STANDARD PROTON PARAMETERS
Pulse Sequence: s2pul
BQ3-024
+
7.803 7.751 7.744 7.738 7.732 7.703 7.465 7.463 7.444 7.424 7.417 7.414 7.411 7.407 7.405 7.397 7.285 7.258 7.198 7.191 7.187 7.181 7.152 7.145 7.141 7.134
4.902 4.890
3.307 3.304 3.300 3.289
2.543 2.431
1.536
0.117 0.049 0.006 0.000 -0.007 -0.049 -0.080 -0.120
7 6 5 4 3 2 1 ppm
1.37 2.01 2.14 4.18 0.87 0.75 1.95 0.67 0.68 1.99 1.95 0.72 0.95 3.00

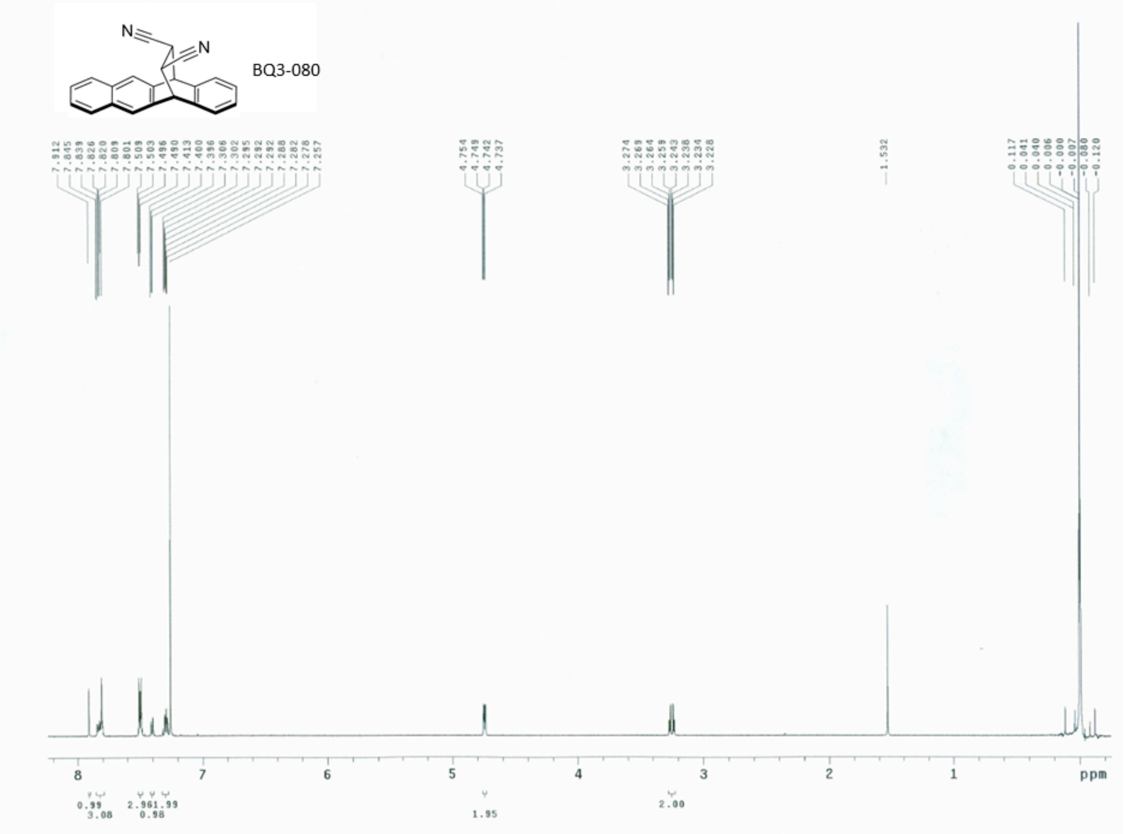

7.803 7.784 7.751 7.744 7.738 7.732 7.703
7.465 7.463 7.456 7.444 7.424 7.417 7.414 7.411 7.407 7.405 7.397
7.302 7.296 7.292 7.285 7.258
7.198 7.191 7.187 7.181 7.152 7.145 7.141 7.134
7.8 7.7 7.6 7.5 7.4 7.3 7.2 ppm
1.37 2.14 2.01 0.87 4.18 0.75 1.95 0.67

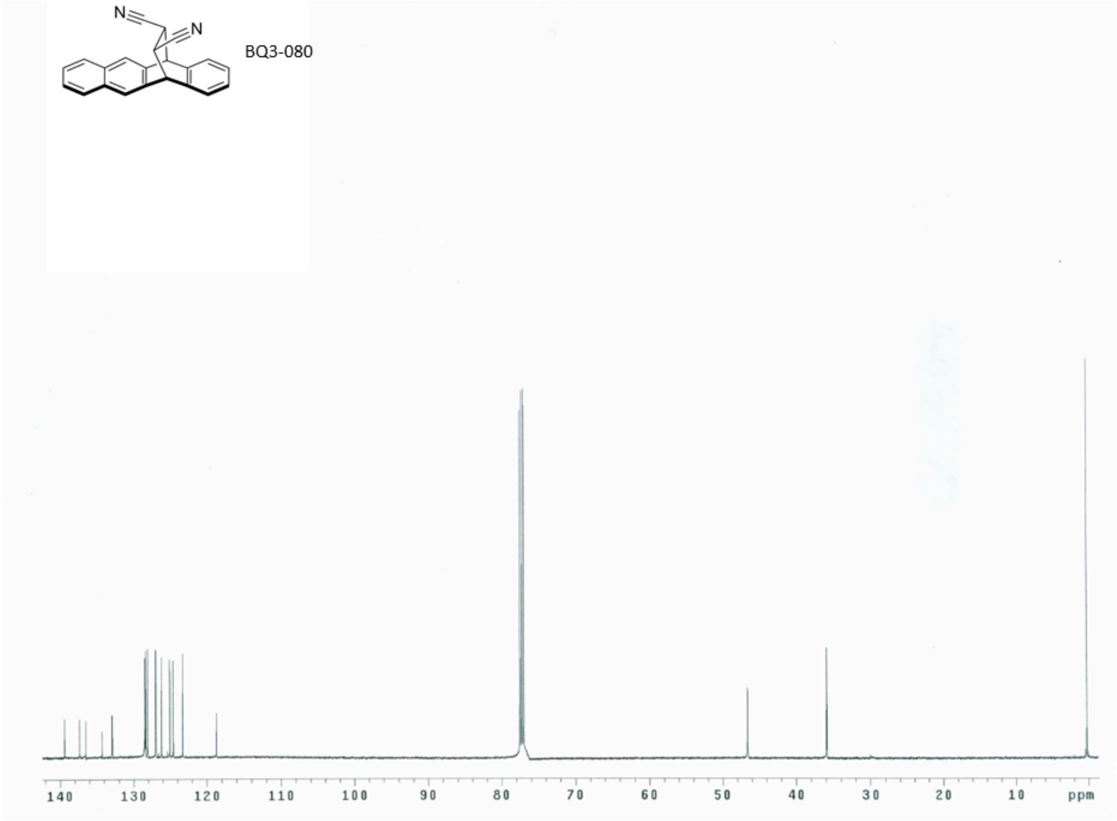

4.902
4.890
4.92
4.91
4.90
4.89
4.88
4.87
4.86
4.85 ppm
0.68
1.99

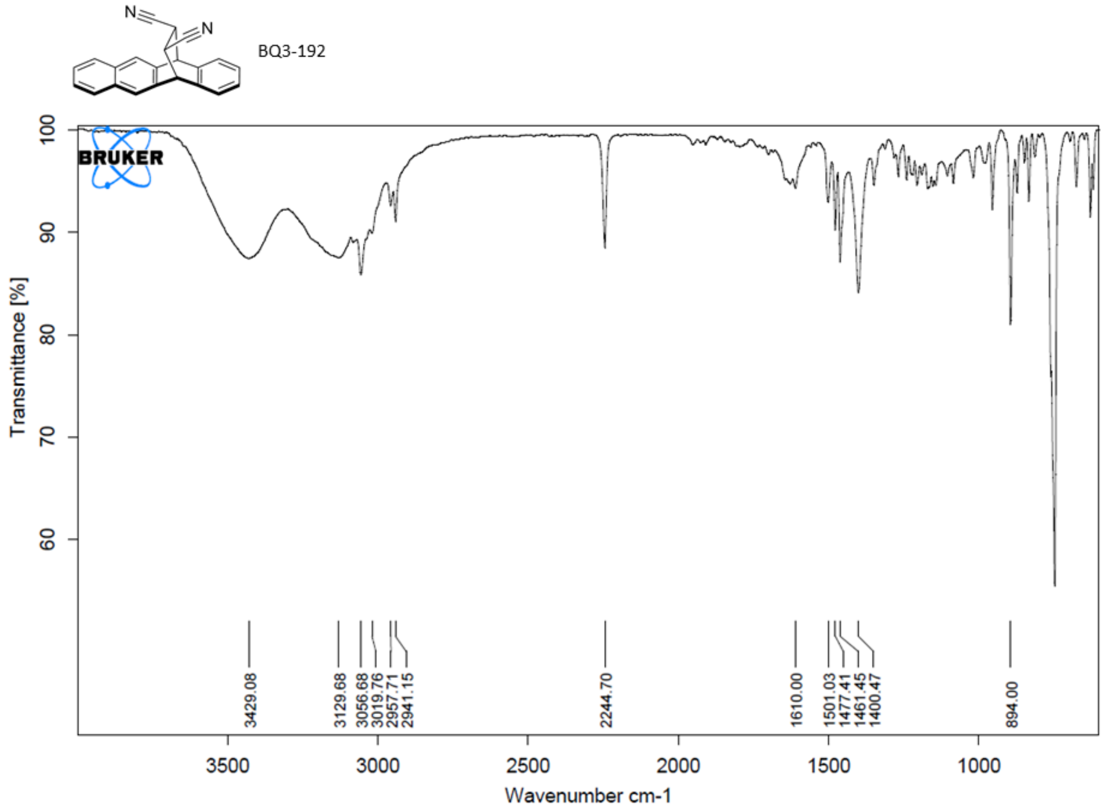

3.307
3.304
3.300
3.289
3.32
3.31
3.30
3.29
3.28
3.27
ppm
1.95
0.72

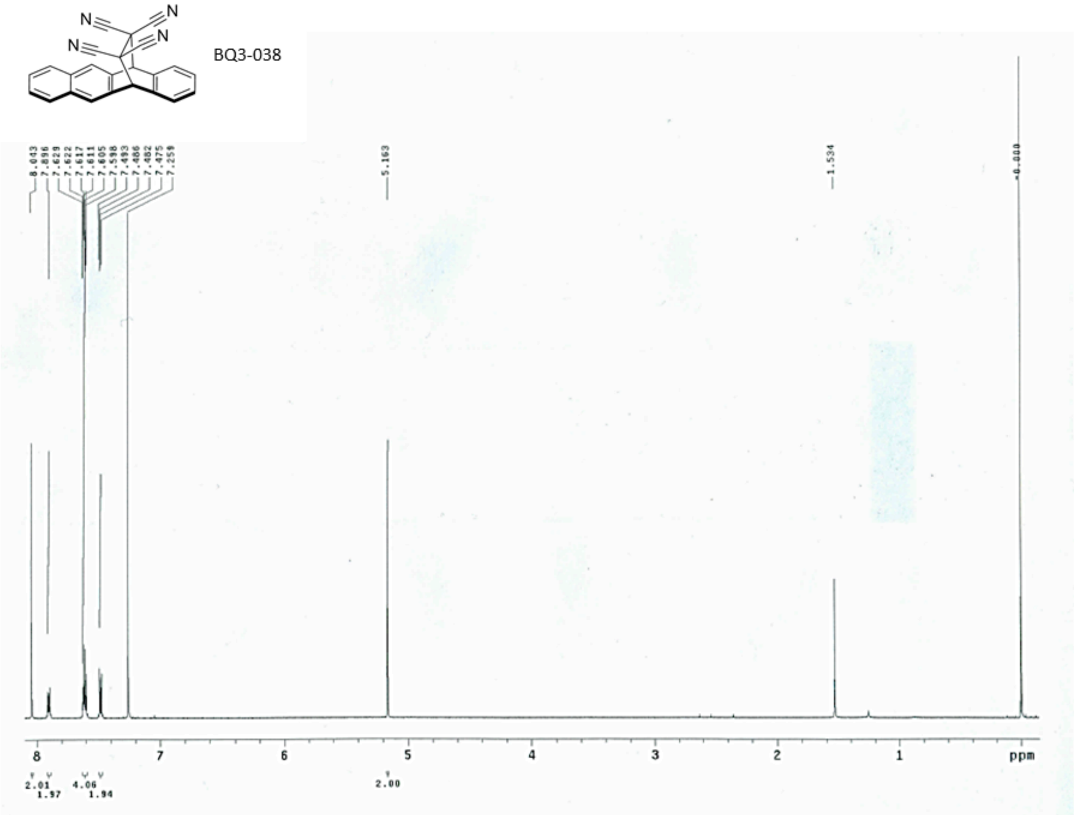

O
N
O
+
O
N
O
BQ3-024
160
140
120
100
80
60
40
20
ppm

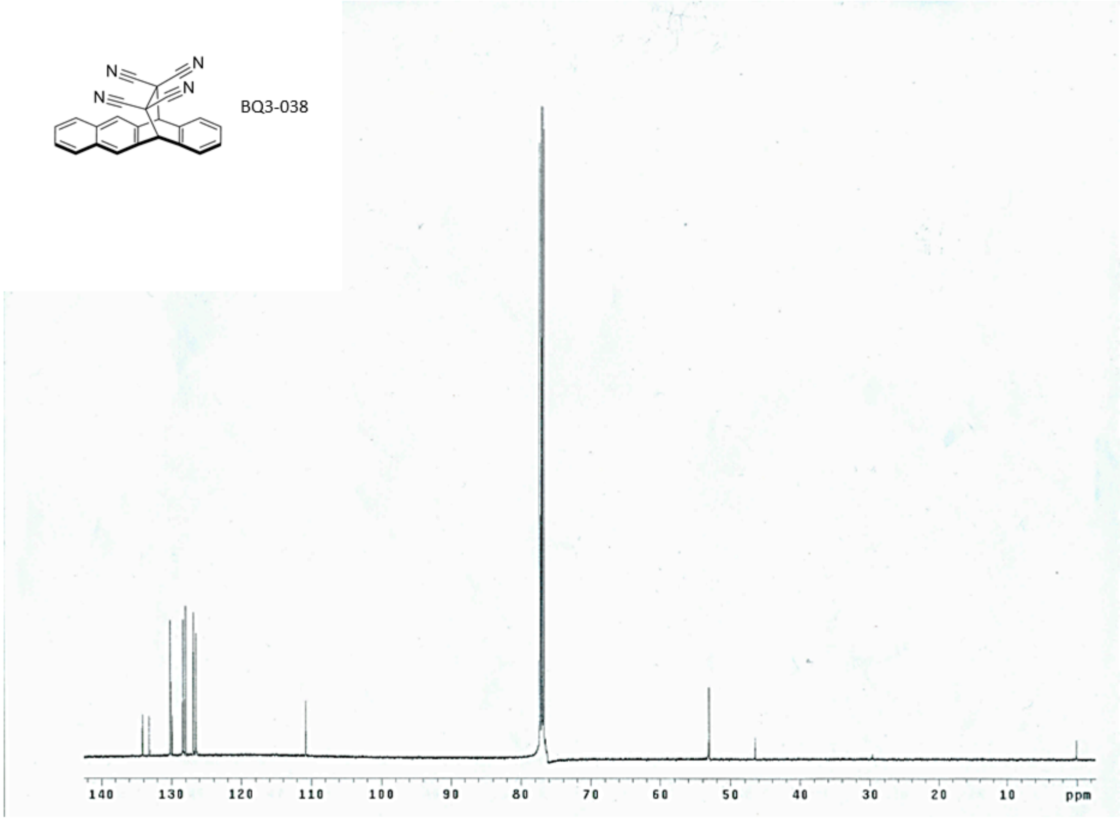

O
N
O
+
O
N
O
BQ3-024
BRUKER
Transmittance [%]
100
90
80
70
60
50
40
30
20
3421.73
3243.15
3043.89
2943.39
2252.43
1829.96
1779.58
1701.50
1499.62
1478.21
1434.35
1378.62
1298.61
1280.57
1196.10
1141.68
1127.95
3500
3000
2500
2000
1500
1000
Wavenumber cm-1

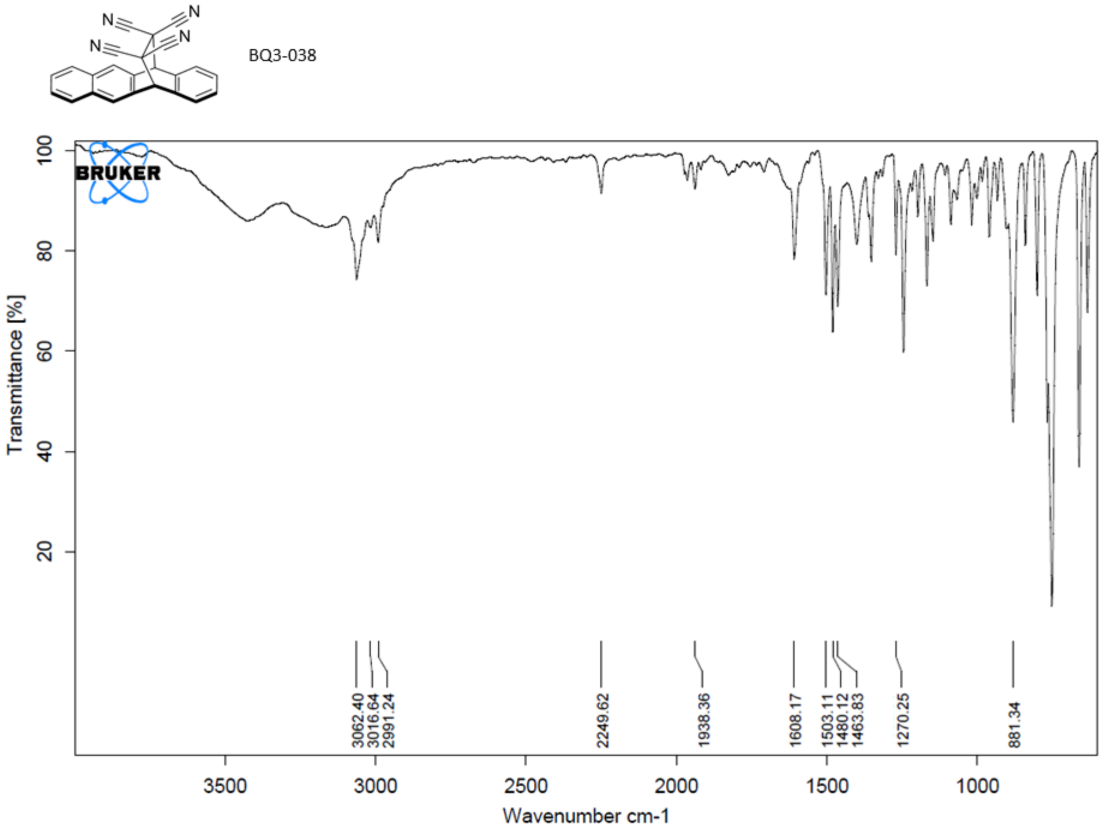

BQ3-080
7.912 7.845 7.839 7.826 7.820 7.809 7.801 7.509 7.503 7.496 7.490 7.413 7.400 7.396 7.306 7.302 7.295 7.292 7.292 7.288 7.282 7.278 7.257
4.754 4.749 4.742 4.737
3.274 3.269 3.264 3.259 3.243 3.238 3.234 3.228
1.532
0.117 0.041 0.040 0.006 -0.000 -0.007 -0.080 -0.120
8
7
6
5
4
3
2
1
ppm
0.99
3.08
2.96
1.99
0.98
1.95
2.00


BQ3-080
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm


N
N
BQ3-192
BRUKER
Transmittance [%]
100
90
80
70
60
3429.08
3129.68
3056.68
3019.76
2957.71
2941.15
2244.70
1610.00
1501.03
1477.41
1461.45
1400.47
894.00
3500
3000
2500
2000
1500
1000
Wavenumber cm-1


BQ3-038
8.043
7.896
7.629
7.622
7.617
7.611
7.605
7.598
7.493
7.486
7.482
7.475
7.259
5.163
1.534
0.000
8
7
6
5
4
3
2
1
ppm
2.01
1.97
4.06
1.94
2.00


BQ3-038
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm


N
N
N
N
BQ3-038
BRUKER
100
80
60
40
20
Transmittance [%]
3062.40
3016.64
2991.24
2249.62
1938.36
1608.17
1503.11
1480.12
1463.83
1270.25
881.34
3500
3000
2500
2000
1500
1000
Wavenumber cm-1