Electronic Supplementary Material (ESI) for Organic Chemistry Frontiers.

Supporting Information

Visible-light-induced cyclization of 2-alkenyl-1,1'-biphenyls

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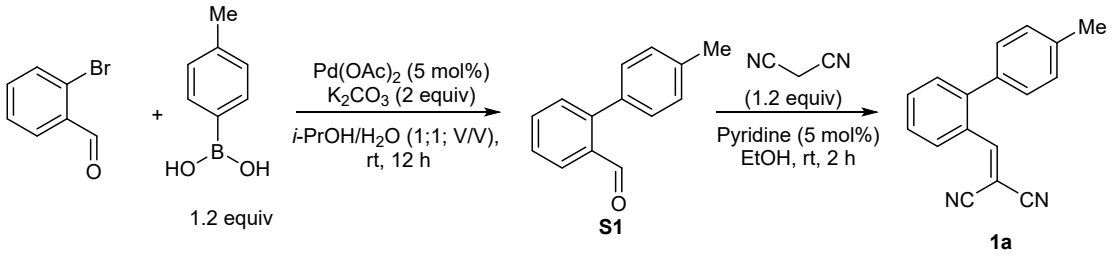
1. General considerations

All materials were purchased from commercial sources, which were used without purification or prepared according to standard procedure unless otherwise indicated. The products were purified by column chromatography over silical gel (300- 400 size). All ^{1}H NMR, ^{13}C NMR and ^{19}F NMR spectra were recorded in $CDCl_3$ with a 600 MHz Bruker FT-NMR spectrometer. All chemical shifts of ^{1}H NMR are given as δ value (ppm) with reference to tetramethylsilane (TMS) as an internal standard. The peak patterns are indicated as follows: s (singlet), d (doublet), t (triplet), q (quartet), m (multiplet), dd (doublet of doublet) and td (triplet of doublet). The coupling constants, *J*, are reported in Hertz (Hz). High resolution mass spectroscopy data of the products were measured on a Thermo Scientific Q Exactive and Agilent Technologies 6540 UHD Accurate-Mass Q-TOF LC/MS (ESI).

2. Experimental section

2.1 Typical procedure for the preparation of starting materials

2.1.1 Procedure for the preparation of 1a



Synthesis of 4'-methyl-[1,1'-biphenyl]-2-carbaldehyde (S1):

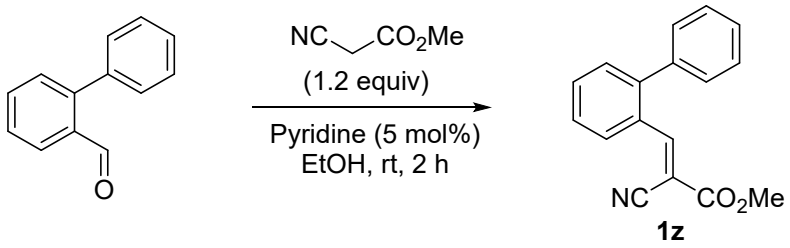
A solution of 2-bromobenzaldehyde (1.85 g, 10 mmol), 4-methylphenylboronic acid (1.63 g, 12 mmol, 1.2 equiv), $Pd(OAc)_2$ (112 mg, 0.5 mmol, 5 mol%), and K_2CO_3 (2.76 g, 20 mmol, 2 equiv) in 2-propanol/water (12 mL, 1:1, V/V) was stirred at room temperature for 12 h. After completion, the mixture was diluted with water (10 mL), and then extracted with ethyl acetate (3*15 mL), and the combined organic layers were dried over Na_2SO_4, filtered and evaporated under reduced pressure. The residue was purified by flash chromatography on silica gel using petroleum

ether/ethyl acetate (20:1, V/V) as the eluent to yield the desired product **S1** as a yellow oil in 90% yield.

Synthesis of 2-([1,1'-biphenyl]-2-ylmethylene)malononitrile (1a):

To a solution of **S1** (980 mg, 5 mmol) in ethanol (5 mL), malononitrile (396 mg, 6 mmol, 1.2 equiv) and a catalytic amount of pyridine (20 mg, 0.25 mmol, 5 mol%) were added. Then the resulting mixture was stirred at room temperature for 2 h. After completion, the crude product was suction filtered and washed with cold ethanol (3*5 mL) to yield the desired product 2-([1,1'-biphenyl]-2-ylmethylene)malononitrile in 80% yield (**1a**, white solid, 976 mg).

2.1.2 T Procedure for the preparation of 1z

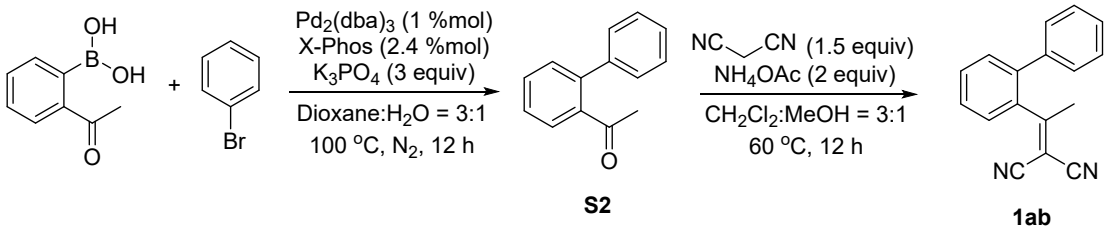


1z

Synthesis of methyl-3-([1,1'-biphenyl]-2-yl)-2-cyanoacrylate (1z) :

To a solution of [1,1'-biphenyl]-2-carbaldehyde (910 mg, 5 mmol) and methyl 2-cyanoacetate (594 mg, 6 mmol, 1.2 equiv) in ethanol (5 mL), a catalytic amount of pyridine (20 mg, 0.25 mmol, 5 mol%) was added. Then the resulting mixture was stirred at room temperature for 2 h. After completion, the crude product was suction filtered and washed with cold ethanol (3*5 mL) to yield the desired product methyl-3-([1,1'-biphenyl]-2-yl)-2-cyanoacrylate in 75% yield (**1z**, white solid, 986 mg).

2.1.3 Procedure for the preparation of 1ab



S2 **1ab**

Synthesis of 1-([1,1'-biphenyl]-2-yl)ethan-1-one (S2) :

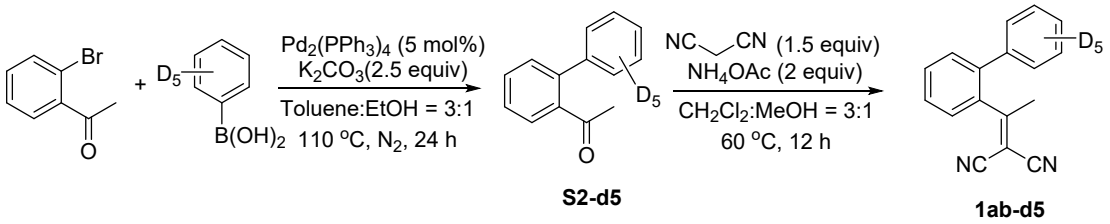
A solution of bromobenzene (471 mg, 3 mmol), (2-acetylphenyl)boronic acid (738 mg, 4.5 mmol, 1.5 equiv), $Pd(dba)_2$ (17.3 mg, 0.03 mmol, 1 mol%), X-Phos (42

mg, 0.072 mmol, 2.4 mol%) and K_3PO_4 (1.9 g, 9 mmol, 3 equiv) in dioxane/water (12 mL, 3:1, V/V) was stirred in nitrogen atmosphere at 100 °C for 12 h. After completion, the mixture was diluted with water (25 mL), extracted with ethyl acetate (3*10 mL), and the combined organic layers were dried over Na_2SO_4, filtered and evaporated under reduced pressure. The residue was purified by flash chromatography on silica gel using petroleum ether/ethyl acetate (20:1, V/V) as the eluent to yield the desired product 1-([1,1'-biphenyl]-2-yl)ethan-1-one in 70% yield (**S2**, yellow oil, 412 mg).

Synthesis of 2-(1-([1,1'-biphenyl]-2-yl)ethylidene)malononitrile (1ab) :

A solution of **S2** (392 mg, 2 mmol), malononitrile (198 mg, 3 mmol, 1.5 equiv), NH_4OAc (308 mg, 4 mmol, 2 equiv) in dichloromethane/methanol (8 mL, 3:1, V/V) was stirred in air at 60 °C for 12 h. After completion, the mixture was rotary evaporated, then the crude product was purified by flash chromatography on silica gel using petroleum ether/ethyl acetate (9:1, V/V) as the eluent to yield the desired product 2-(1-([1,1'-biphenyl]-2-yl)ethylidene)malononitrile in 50% yield (**1ab**, white solid, 244 mg).

2.1.4 Procedure for the preparation of D5-1ab



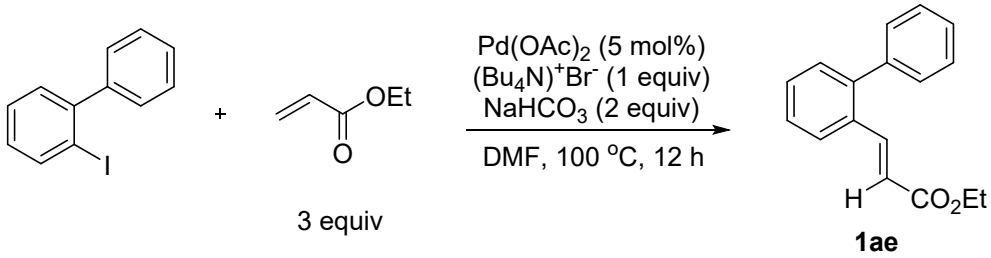
Synthesis of 1-([1,1'-biphenyl]-2-yl)ethan-1-one (S2-d5) :

A solution of 1-(2-bromophenyl)ethan-1-one (1.0 g, 5 mmol), (phenyl-d5)boronic acid (762 mg, 6 mmol, 1.2 equiv), $Pd_2(PPh_3)_4$ (289 mg, 0.25 mmol, 5 mol%), K_2CO_3 (1.04 g, 7.5 mmol, 2.5 equiv) in toluene/ethanol (20 mL, 3:1, V/V) was stirred in nitrogen atmosphere at 110 °C for 24 h. After completion, the mixture was diluted with water (30 mL), extracted with ethyl acetate (3*15 mL), and the combined organic layers were dried over Na_2SO_4, filtered and evaporated under reduced pressure. The residue was purified by flash chromatography on silica gel using petroleum ether/ethyl acetate (20:1, V/V) as the eluent to yield the desired product **S2-d5** in 95% yield (light yellow oil, 955 mg).

Synthesis of 2-(1-([1,1'-biphenyl]-2-yl)ethylidene)malononitrile (1ab-d5) :

A solution of **S2-d5** (402 mg, 2 mmol), malononitrile (198 mg, 3 mmol, 1.5 equiv), NH_4OAc (308 mg, 4 mmol, 2 equiv) in dichloromethane/methanol (8 mL, 3:1, V/V) was stirred in air at 60 °C for 12 h. After completion, the mixture was rotary evaporated, then the crude product was purified by flash chromatography on silica gel using petroleum ether/ethyl acetate (9:1, V/V) as the eluent to yield the desired product 2-(1-([1,1'-biphenyl]-2-yl)ethylidene)malononitrile in 50% yield (**1ab-d5**, white solid, 249 mg).

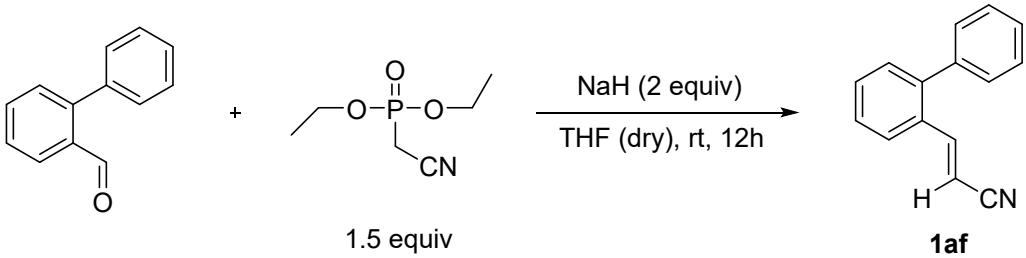
2.1.5 Procedure for the preparation of 1ae



1ae

A solution of 2-iodo-1,1'-biphenyl (280 g, 1 mmol), ethyl acrylate (300 mg, 3 mmol, 3 equiv), tetrabutylammonium tribromide (322 mg, 1 mmol, 1 equiv), $Pd(OAc)_2$ (11.2 mg, 0.05 mmol, 5 mol%) and $NaHCO_3$ (168 mg, 2 mmol, 2 equiv) in *N*,*N*-dimethylformamide (4 mL) was stirred at 100 °C for 12 h. After completion, the mixture was diluted with water (15 mL), extracted with ethyl acetate (3*10 mL), and the combined organic layer was washed with water (2*5 mL) and dried over Na_2SO_4. Then the mixture was rotary evaporated, and the crude product was purified by flash chromatography on silica gel using petroleum ether/ethyl acetate (20:1, V/V) as eluent to yield the desired product ethyl 3-([1,1'-biphenyl]-2-yl)acrylate in 80% yield (**1ae**, yellow soil, 202 mg).

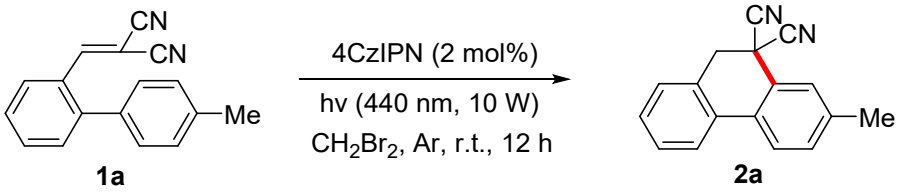
2.1.6 Procedure for the preparation of 1af

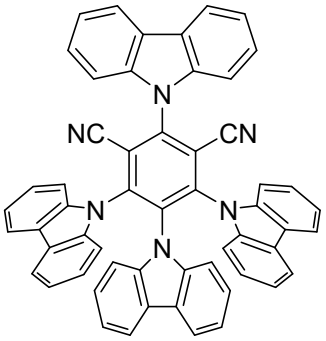


1af

A solution of [1,1'-biphenyl]-2-carbaldehyde (910 mg, 5 mmol), diethyl (cyanomethyl)phosphonate (1.33 g, 7.5 mmol, 1.5 equiv), sodium hydride (240 mg, 10 mmol, 2 equiv) in anhydrous tetrahydrofuran (10 mL) was stirred in air at room temperature for 12 h. After completion, the mixture was diluted with water (25 mL), extracted with ethyl acetate (3*15 mL), and the combined organic layer was washed with water (2*5 mL) and dried over Na_2SO_4. Then the mixture was rotary evaporated, the crude product was purified by flash chromatography on silica gel using petroleum ether/ethyl acetate (20:1, V/V) as eluent to yield the desired product 3-([1,1'-biphenyl]-2-yl)acrylonitrile in 50% yield (**1af**, white solid, 513 mg).

2.2 Typical procedure for the cyclization reaction

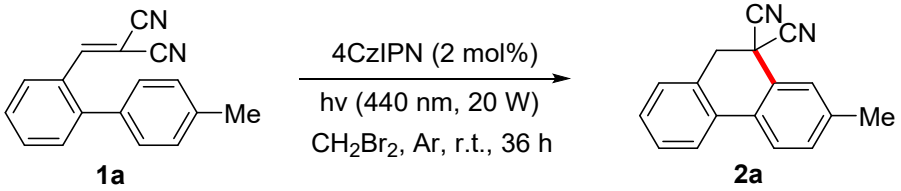




Synthesis of 7-methylphenanthrene-9,9(10*H*)-dicarbonitrile (**2a**) :

A solution of **1a** (48.8 mg, 0.2 mmol), 4CzIPN (3.2 mg, 0.004 mmol, 2 mol%) in dibromomethane (2 mL) was stirred and exposed to blue LED (440 nm, 10 W) irradiation in argon atmosphere at room temperature for 12 h. After completion, the mixture was rotary evaporated, the crude product was purified by flash chromatography on silica gel using petroleum ether/ethyl acetate (9:1, V/V) as eluent to yield the desired product 7-methylphenanthrene-9,9(10*H*)-dicarbonitrile in 97% yield (**2a**, white solid, 47.3 mg).

2.3 Typical procedure for gram-scale synthesis

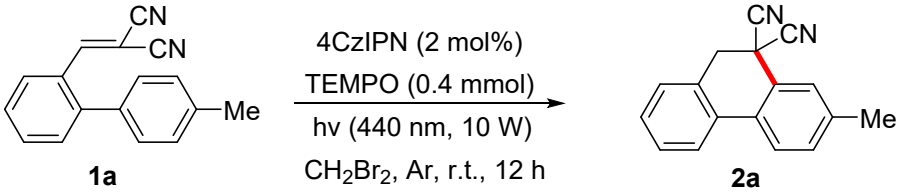


Synthesis of 7-methylphenanthrene-9,9(10*H*)-dicarbonitrile (**2a**) :

A solution of **1a** (1.22 g, 5 mmol), 4CzIPN (80 mg, 0.1 mmol, 2 mol%) in dibromomethane (20 mL) was stirred and exposed to blue LED (440 nm, 20 W) irradiation in argon atmosphere at room temperature for 36 h. After completion, the mixture was rotary evaporated, the crude product was purified by flash chromatography on silica gel using petroleum ether/ethyl acetate (9:1, V/V) as eluent to yield the desired product 7-methylphenanthrene-9,9(10*H*)-dicarbonitrile in 86% yield (**2a**, white solid, 1.05 g).

2.4 Preliminary mechanistic study

2.4.1 Radical inhibition experiment



A solution of **1a** (48.8 mg, 0.2 mmol), 4CzIPN (3.2 mg, 0.004 mmol, 2 mol%) and TEMPO (62.4 mg, 0.4 mmol, 2 equiv) in dibromomethane (2 mL) was stirred and exposed to blue LED (440 nm, 10 W) irradiation in argon atmosphere at room temperature for 12 h. In the reaction mixture, only trace amount of desired product **2a** was detected.

2.4.2 UV-visible absorption spectra of 4CzIPN, 1a and 2a in dibromomethane

The ultraviolet/visible absorption spectra of 4CzIPN, **1a** and **2a** in dibromomethane with standard concentration (0.4 mM) was recorded on a UV-Visible U-4100 spectrophotometer, as shown in Figure S1-S2. The absorption

spectrum of **1a** and **2a** contains a maximum at 320 nm and 305 nm. The absorption spectrum of 4CzIPN contains a maximum at 385 nm with a wide absorption range from 270 nm to 500 nm, which is consistent with the wavelength of the LED used in the experiment (440 nm).

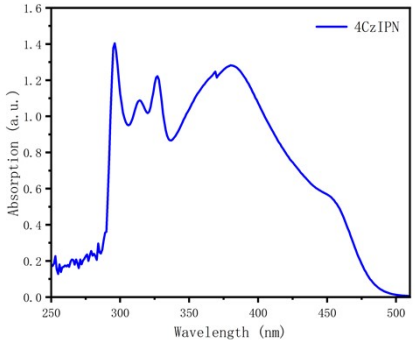


Figure S1. Absorption spectra of 4CzIPN in dibromomethane

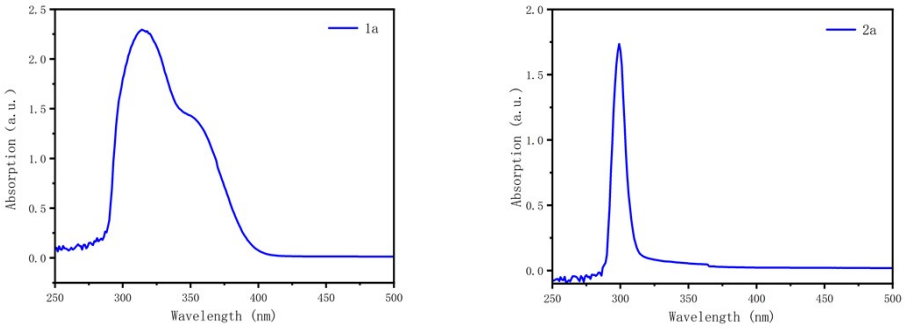


Figure S2. Absorption spectra of **1a** and **2a** in dibromomethane

2.4.3 Fluorescence quenching experiment

To further elucidate the possible reaction pathway, the related fluorescence quenching experiments were performed and the results were shown in Figure S3. In the experiment, measurement was carried out mixing a $1.25*10^{-5}$ mol/L solution of 4CzIPN in dibromomethane with appropriate amount of quencher (**1a**) in quartz cuvette. Increasing amounts of **1a** were added to the solution of 4CzIPN in dibromomethane. Emission spectrum were recorded after each addition. The results in Figure S3 (left) shows an obvious change in the emission intensity of 4CzIPN with a calculated Ksv of 0.12 mM^{-1} [Figure S3 (right)].

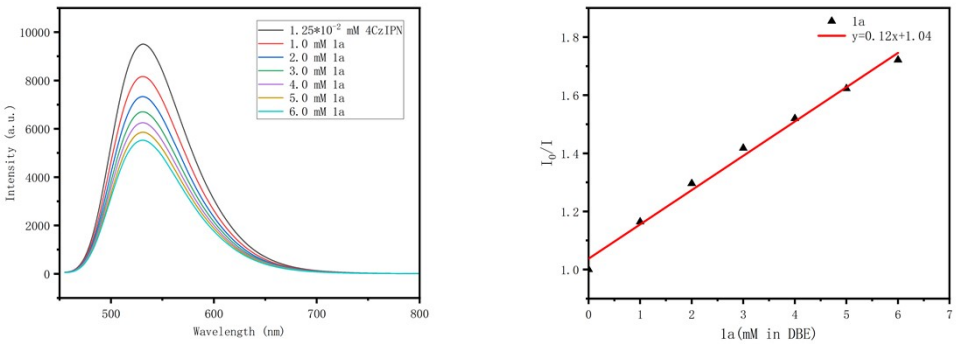


Figure S3. Fluorescence quenching of 4CzIPN by **1a** in dibromomethane (left); Stern-Volmer plots of 4CzIPN quenching with **1a** (right).

2.4.4 On/Off experiments

A solution of **1a** (48.8 mg, 0.2 mmol), 4CzIPN (3.2 mg, 0.004 mmol, 2 mol%) in dibromomethane (2 mL) was stirred and exposed to blue LED (440 nm, 10 W) irradiation in argon atmosphere at room temperature for 2 h. The first sample was collected under argon atmosphere and made preparation for the GC analysis. The reaction was continued stirred in the dark for another 2 h and collected the second sample. In the following step, the intermittent irradiation (2 hours interval) was carried out to demonstrate the importance of visible-light irradiation, and the results demonstrate that uninterrupted irradiation is necessary for this transformation.

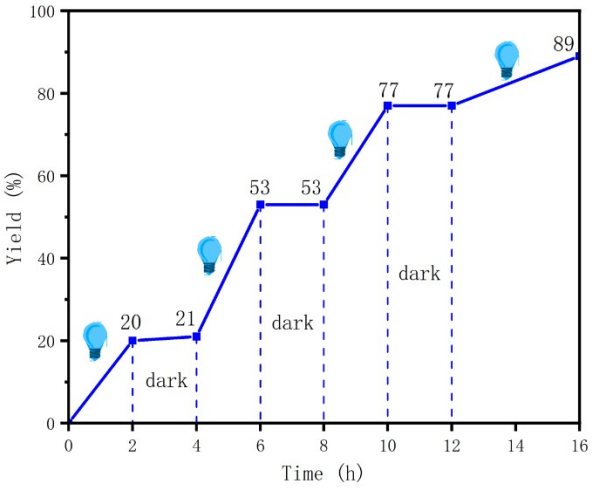
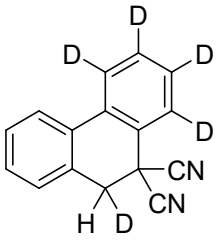
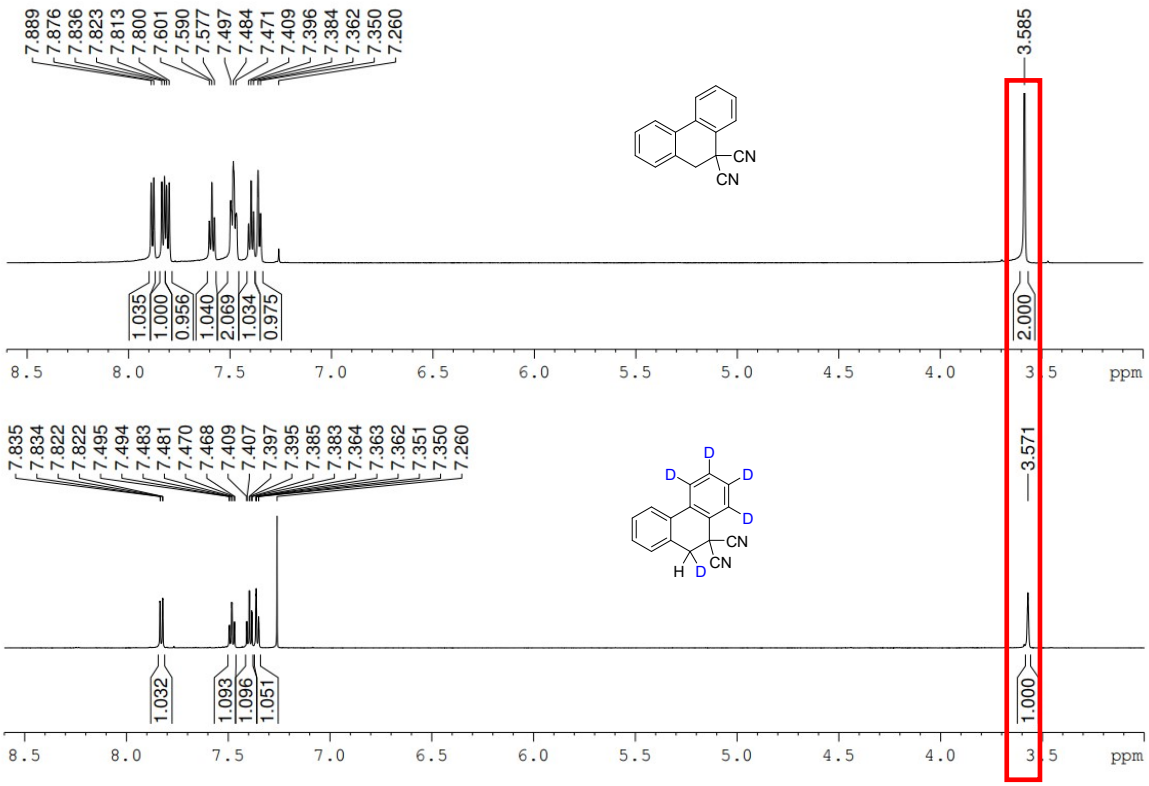


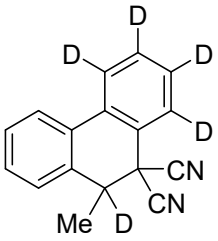
Figure S4. On/Off experiments

2.4.5 Deuterium labeling experiment



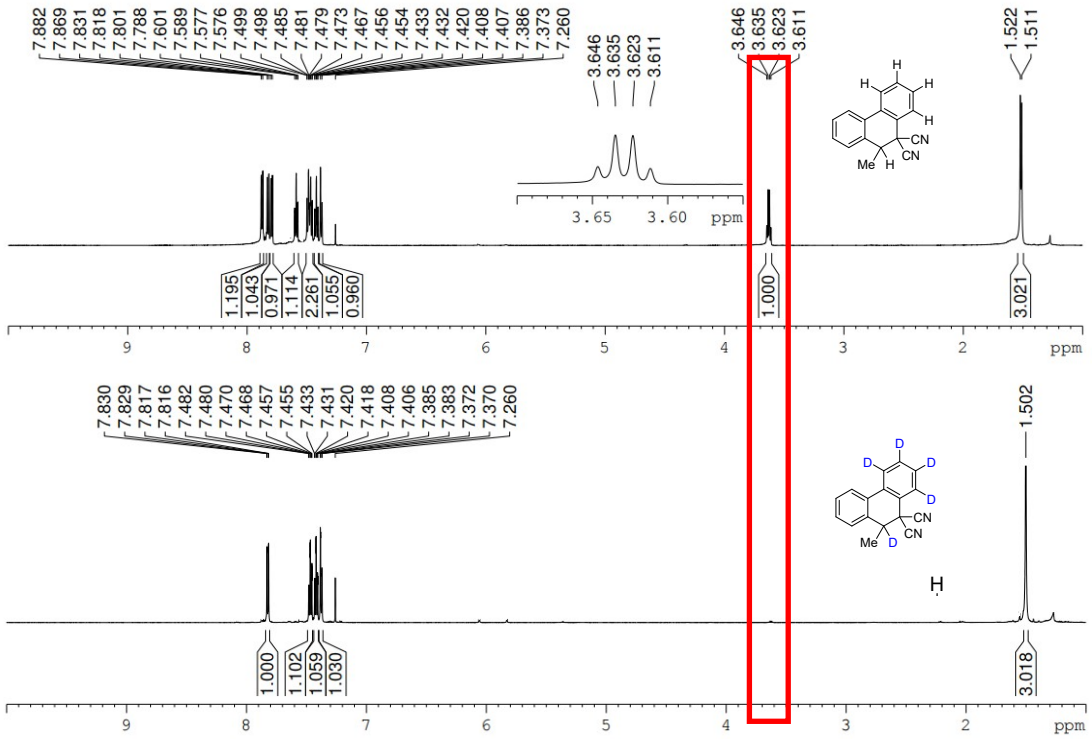
Phenanthrene-9,9(10H)-dicarbonitrile-5,6,7,8,10-d5 (2b-d5). White solid, 42.3 mg, 90% yield. ^{1}H NMR (600 MHz, $CDCl_3$) δ: 7.83 (d, J = 7.8 Hz, 1H), 7.49-7.46 (m, 1H), 7.41-7.38 (m, 1H), 7.36-7.35 (m, 1H), 3.56 (s, 1H).

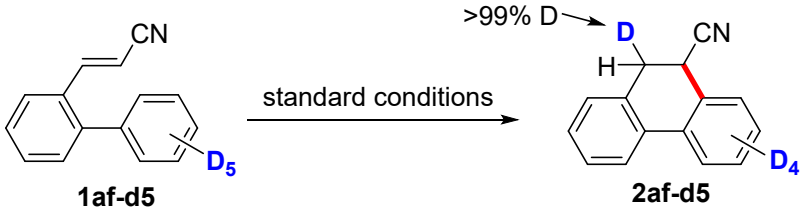


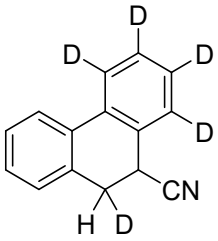


10-methylphenanthrene-9,9(10H)-dicarbonitrile-5,6,7,8,10-d5 (2ab-d5).

White solid, 39.8 mg, 80% yield. ^{1}H NMR (600 MHz, $CDCl_3$) δ: 7.82 (dd, J = 7.7, 0.9 Hz, 1H), 7.47 (td, J = 7.4, 1.4 Hz, 1H), 7.42 (td, J = 7.4, 1.2 Hz, 1H), 7.38 (dd, J = 7.6, 1.2 Hz, 1H), 1.50 (s, 3H).

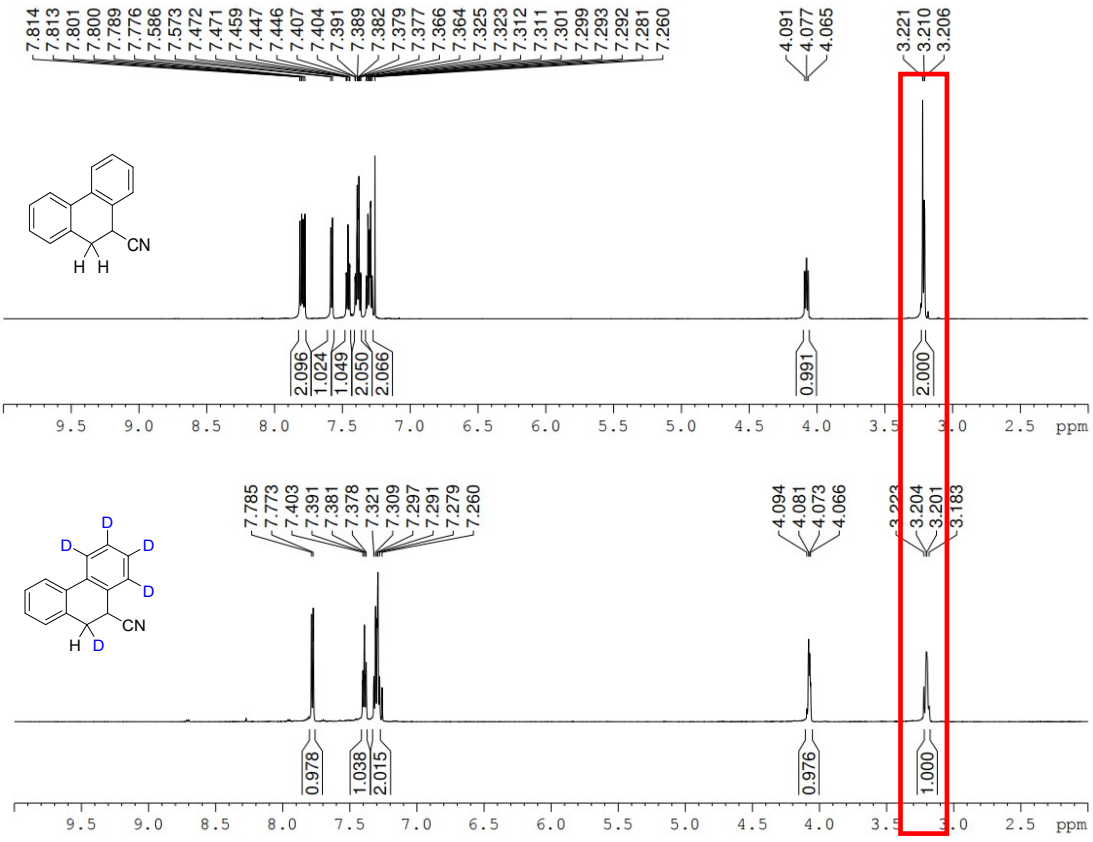






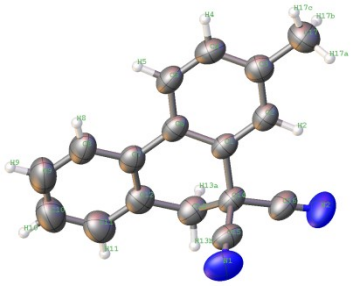
9,10-Dihydrophenanthrene-9-carbonitrile-5,6,7,8,10-d5 (2af-d5).

White solid, 27.3 mg, 65% yield. ^{1}H NMR (600 MHz, $CDCl_3$) δ: 7.78 (d, J = 7.9 Hz, 1H), 7.40-7.38 (m, 1H), 7.32-7.28 (m, 2H), 4.09-4.07 (m, 1H), 3.22-3.18 (s, 1H).



3. X-Ray crystallographic data of products

3.1 X-Ray crystallographic data of product 2a (CCDC: 2222087)



checkCIF/PLATON report

Structure factors have been supplied for datablock(s) 1_a

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No syntax errors found. CIF dictionary Interpreting this report

Datablock: 1_a

```
Bond precision:   C-C = 0.0021 A          Wavelength=0.71073

Cell:          a=8.7405(15)       b=8.9958(14)      c=9.1291(18)
               alpha=107.326(7)   beta=99.505(7)    gamma=97.845(7)
Temperature:   273 K

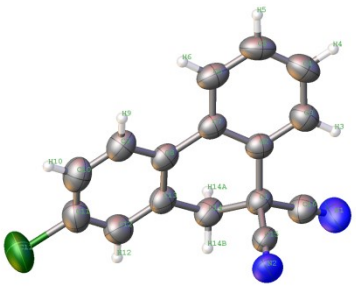
                Calculated                Reported
Volume          662.6(2)                  662.6(2)
Space group     P -1                      P -1
Hall group      -P 1                      -P 1
Moiety formula  C17 H12 N2                C17 H12 N2
Sum formula     C17 H12 N2                C17 H12 N2
Mr              244.29                    244.29
Dx,g cm-3       1.224                     1.224
Z               2                         2
Mu (mm-1)       0.073                     0.073
F000            256.0                     256.0
F000'           256.09
h,k,lmax        11,11,11                  11,11,11
Nref            3037                      2946
Tmin,Tmax       0.984,0.986
Tmin'           0.984

Correction method= Not given

Data completeness= 0.970          Theta(max)= 27.479

R(reflections)= 0.0540( 2188)                wR2(reflections)=
                                             0.1712( 2946)
S = 1.073                 Npar= 174
```

3.2 X-Ray crystallographic data of product 2v (CCDC: 2222108)



checkCIF/PLATON report

Structure factors have been supplied for datablock(s) 1_a

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No syntax errors found. CIF dictionary Interpreting this report

Datablock: 1_a

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Bond precision:   C-C = 0.0023 A          Wavelength=0.71073

Cell:          a=8.437(3)          b=9.166(3)          c=9.274(3)
               alpha=108.582(10)   beta=99.894(11)    gamma=94.050(11)
Temperature:   297 K
```

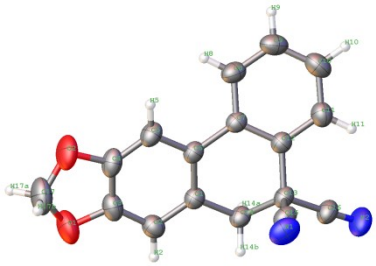
	Calculated	Reported
Volume	663.6(4)	663.6(3)
Space group	P -1	P -1
Hall group	-P 1	-P 1
Moiety formula	C16 H9 Cl N2	C16 H9 Cl N2
Sum formula	C16 H9 Cl N2	C16 H9 Cl N2
Mr	264.70	264.70
Dx,g cm-3	1.325	1.325
Z	2	2
Mu (mm-1)	0.273	0.273
F000	272.0	272.0
F000'	272.38	
h,k,lmax	10,11,12	10,11,12
Nref	3025	2997
Tmin,Tmax	0.942,0.947	
Tmin'	0.942	

```
Correction method= Not given

Data completeness= 0.991          Theta(max)= 27.475

R(reflections)= 0.0484( 2246)                wR2(reflections)=
                                             0.1470( 2997)
S = 1.041                 Npar= 182
```

3.3 X-Ray crystallographic data of product 2w (CCDC: 2222106)



checkCIF/PLATON report

Structure factors have been supplied for datablock(s) 1_a

THIS REPORT IS FOR GUIDANCE ONLY. IF USED AS PART OF A REVIEW PROCEDURE FOR PUBLICATION, IT SHOULD NOT REPLACE THE EXPERTISE OF AN EXPERIENCED CRYSTALLOGRAPHIC REFEREE.

No syntax errors found. CIF dictionary Interpreting this report

Datablock: 1_a

Bond precision: C-C = 0.0016 A Wavelength=0.71073

Cell: a=8.4260(7) b=8.8146(8) c=8.9781(6)
alpha=83.027(3) beta=83.022(3) gamma=86.110(4)
Temperature: 297 K

	Calculated	Reported
Volume	656.03(9)	656.03(9)
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Hall group	-P 1	-P 1
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Sum formula	C17 H10 N2 O2	C17 H10 N2 O2
Mr	274.27	274.27
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F000'	284.13	
h,k,lmax	10,11,11	10,11,11
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Tmin,Tmax	0.980,0.982	
Tmin'	0.980	

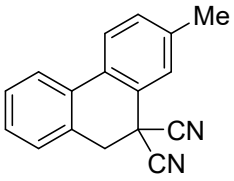
Correction method= Not given

Data completeness= 0.996 Theta(max)= 27.479

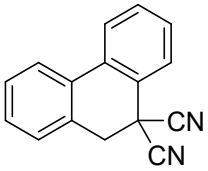
R(reflections)= 0.0415(2627) wR2(reflections)= 0.1248(2994)

S = 1.057 Npar= 190

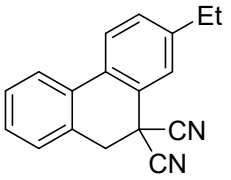
4. Characterization data for the products



7-Methylphenanthrene-9,9(10*H*)-dicarbonitrile (2a). White solid, 47.3 mg, 97% yield. ^{1}H NMR (600 MHz, $CDCl_3$) δ: 7.79 (d, *J* = 7.8 Hz, 1H), 7.77 (d, *J* = 8.0 Hz, 1H), 7.60 (s, 1H), 7.47-7.44 (m, 1H), 7.39-7.35 (m, 2H), 7.34-7.33 (m, 1H), 3.57 (s, 2H), 2.47 (s, 3H). ^{13}C NMR (150 MHz, $CDCl_3$) δ: 139.8, 132.4, 132.2, 130.4, 129.5, 129.0 (2C), 128.4, 127.4, 126.4, 125.5, 124.4, 114.9 (2C), 39.3, 36.3, 21.4. HRMS (ESI) m/z: $[M+H]^+$ Calcd For $C_{17}H_{13}N_2^+$ 245.1073; Found 245.1073.

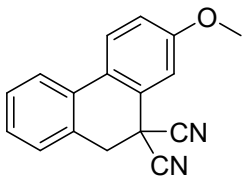


Phenanthrene-9,9(10*H*)-dicarbonitrile (2b). White solid, 42.3 mg, 92% yield. ^{1}H NMR (600 MHz, $CDCl_3$) δ: 7.88 (d, *J* = 7.8 Hz, 1H), 7.83 (d, *J* = 7.8 Hz, 1H), 7.81 (d, *J* = 7.7 Hz, 1H), 7.60-7.58 (m, 1H), 7.50-7.47 (m, 2H), 7.41-7.38 (m, 1H), 7.36-7.35 (m, 1H), 3.59 (s, 2H). ^{13}C NMR (150 MHz, $CDCl_3$) δ: 133.1, 132.2, 129.6, 129.4, 129.3, 129.0, 128.7, 126.9, 126.5, 125.6, 124.7, 114.8 (2C), 39.2, 36.3. HRMS (ESI) m/z: $[M+H]^+$ Calcd For $C_{16}H_{11}N_2^+$ 231.0917; Found 231.0916.

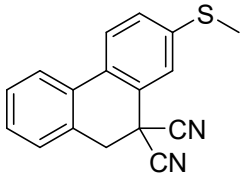


7-Ethylphenanthrene-9,9(10*H*)-dicarbonitrile (2c). White solid, 48.0 mg, 93% yield. ^{1}H NMR (600 MHz, $CDCl_3$) δ: 7.80-7.78 (m, 2H), 7.60 (s, 1H), 7.46 (td, *J* = 7.6, 1.3 Hz, 1H), 7.41 (dd, *J* = 8.1, 1.5 Hz, 1H), 7.38-7.33 (m, 2H), 3.58 (s, 2H), 2.77 (q, *J* = 7.6 Hz, 2H), 1.32 (t, *J* = 7.7Hz, 3H). ^{13}C NMR (150 MHz, $CDCl_3$) δ: 146.1, 132.5, 131.1, 130.6, 129.6, 129.0(2C), 128.5, 126.5, 126.4, 125.7, 124.5, 115.0 (2C), 39.4, 36.4, 28.8, 15.5. HRMS (ESI) m/z: $[M+H]^+$ Calcd For $C_{18}H_{15}N_2^+$ 259.1230;

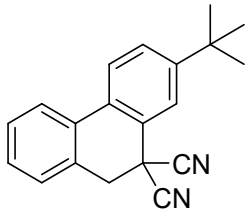
Found 259.1230.



7-Methoxyphenanthrene-9,9(10*H*)-dicarbonitrile (2d). Yellow solid, 46.8 mg, 90% yield. ^{1}H NMR (600 MHz, $CDCl_3$) δ: 7.80 (d, *J* = 8.7 Hz, 1H), 7.73 (d, *J* = 7.8 Hz, 1H), 7.45-7.43 (m, 1H), 7.33-7.32 (m, 2H), 7.30 (d, *J* = 2.5 Hz, 1H), 7.10 (dd, *J* = 8.6, 2.5 Hz, 1H), 3.92 (s, 3H), 3.56 (s, 2H). ^{13}C NMR (150 MHz, $CDCl_3$) δ: 160.3, 132.3, 129.6, 128.9, 128.5, 127.8, 127.7, 127.1, 125.7, 124.0, 117.1, 114.8 (2C), 112.3, 55.9, 39.3, 36.5. HRMS (ESI) m/z: $[M+H]^+$ Calcd For $C_{17}H_{13}N_2O^+$ 261.1022; Found 261.1021.

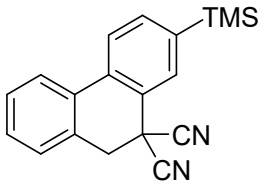


7-Methylphenanthrene-9,9(10*H*)-dicarbonitrile (2e). Yellow solid, 48.6 mg, 88% yield. ^{1}H NMR (600 MHz, $CDCl_3$) δ: 7.77 (d, *J* = 8.2 Hz, 1H), 7.61 (d, *J* = 1.8 Hz, 1H), 7.47-7.44 (m, 1H), 7.42 (dd, *J* = 8.3, 1.9 Hz 1H), 7.38-7.35 (m, 1H), 7.34-7.33 (m, 1H), 3.57 (s, 2H), 2.58 (s, 3H). ^{13}C NMR (150 MHz, $CDCl_3$) δ: 141.1, 132.0, 129.6 (2C), 129.1, 129.0, 128.8, 128.2, 127.0. 125.9, 124.3, 123.9, 114.6 (2C), 39.2, 36.3, 15.6. HRMS (ESI) m/z: $[M+H]^+$ Calcd For $C_{17}H_{13}N_2S^+$ 277.0794; Found 277.0797.

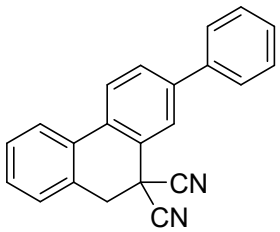


7-(*tert*-butyl)phenanthrene-9,9(10*H*)-dicarbonitrile (2f). White solid, 53.8 mg, 94% yield. ^{1}H NMR (600 MHz, $CDCl_3$) δ: 7.81-7.80 (m, 1H), 7.80-7.79 (m, 1H), 7.77 (d, *J* = 2.0 Hz, 1H), 7.60 (dd, *J* = 8.2, 2.0 Hz, 1H), 7.46 (td, *J* = 7.6, 1.5 Hz, 1H), 7.38-7.33

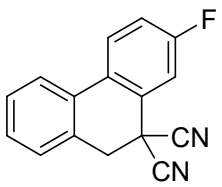
(m, 2H), 3.59 (s, 2H), 1.40 (s, 9H).^{13}C NMR (150 MHz, $CDCl_3$) δ: 153.1, 132.4, 130.4, 129.6, 129.1, 129.0, 128.6 (2C), 126.2, 125.4, 124.5, 123.9, 115.0 (2C), 39.5, 36.6, 35.3, 31.4. HRMS (ESI) m/z: $[M+H]^+$ Calcd For $C_{20}H_{19}N_2^+$ 287.1543; Found 287.1543.



8-(Trimethylsilyl)phenanthrene-9,9(10*H*)-dicarbonitrile (2g). White solid, 50.7 mg, 84% yield. ^{1}H NMR (600 MHz, $CDCl_3$) δ: 7.87 (d, *J* = 0.7 Hz, 1H), 7.84 (t, *J* = 7.7 Hz, 2H), 7.72 (dd, *J* = 7.6, 1.0 Hz, 1H), 7.49-7.46 (m, 1H), 7.39 (td, *J* = 7.5, 0.9 Hz, 1H), 7.35 (d, *J* = 7.3 Hz, 1H), 3.59 (s, 2H), 0.35 (s, 9H). ^{13}C NMR (150 MHz, $CDCl_3$) δ: 143.1, 136.5, 132.4, 131.5, 129.6, 129.5, 129.1, 128.9, 125.8, 124.8 (2C), 114.9 (2C), 39.5, 36.4, 1.0. HRMS (ESI) m/z: $[M+H]^+$ Calcd For $C_{19}H_{19}N_2Si^+$ 303.1312; Found 303.1313.

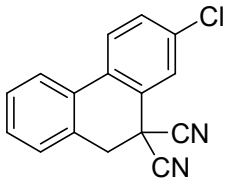


8-Phenylphenanthrene-9,9(10*H*)-dicarbonitrile (2h). Yellow solid, 53.9 mg, 88% yield. ^{1}H NMR (600 MHz, $CDCl_3$) δ: 8.02 (d, *J* = 1.5 Hz, 1H), 7.95 (d, *J* = 8.1 Hz, 1H), 7.86 (d, *J* = 7.7 Hz, 1H), 7.81 (dd, *J* = 8.1, 1.7 Hz 1H), 7.69 (d, *J* = 7.3 Hz, 2H), 7.53-7.48 (m, 3H), 7.46-7.37 (m, 3H), 3.63 (s, 2H). ^{13}C NMR (150 MHz, $CDCl_3$) δ: 142.4, 139.2, 132.0, 131.9, 130.0, 129.7, 129.4, 129.3 (2C), 129.1, 128.7, 128.5, 127.2 (2C), 127.0, 126.1, 125.5, 124.7, 114.8 (2C), 39.3 36.4. HRMS (ESI) m/z: $[M+H]^+$ Calcd For $C_{22}H_{15}N_2^+$ 307.1230; Found 307.1230.

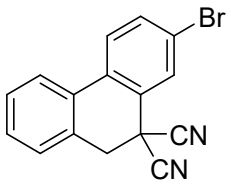


8-Fluorophenanthrene-9,9(10*H*)-dicarbonitrile (2i). White solid, 41.2 mg, 83%

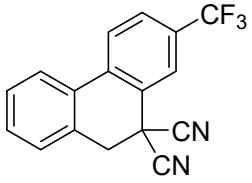
yield. ^{1}H NMR (600 MHz, $CDCl_3$) δ: 7.87 (dd, *J* = 8.7, 5.3Hz, 1H), 7.77 (d, *J* = 7.8 Hz, 1H), 7.54 (dd, *J* = 8.3, 2.5 Hz 1H), 7.48 (t, *J* = 7.4 Hz, 1H), 7.41-7.35 (m, 2H), 7.30 (td, 1H), 3.59 (s, 2H). ^{13}C NMR (150 MHz, $CDCl_3$) δ: 162.6 (d, *J* = 251.7 Hz), 131.5, 129.8, 129.5 (d, *J* = 3.9 Hz), 129.4, 129.1, 128.4 (d, *J* = 7.2 Hz), 128.2, 127.7 (d, *J* = 8.3 Hz), 124.6, 118.7 (d, *J* = 21.5 Hz), 114.5 (d, *J* = 24.3 Hz), 114.3 (2C), 39.1, 36.2. HRMS (ESI) m/z: $[M+H]^+$ Calcd For $C_{16}H_{10}FN_2^+$ 249.0823; Found 249.0823.



7-Chlorophenanthrene-9,9(10*H*)-dicarbonitrile (2j). White solid, 45.4 mg, 86% yield. ^{1}H NMR (600 MHz, $CDCl_3$) δ: 7.82-7.80 (m, 1H), 7.80-7.78 (m, 2H), 7.56 (dd, *J* = 8.4, 2.2 Hz, 1H), 7.48 (td, *J* = 7.6, 1.1 Hz, 1H), 7.41 (td, *J* = 7.5, 1.1 Hz, 1H), 7.37-7.35 (m, 1H), 3.58 (s, 2H). ^{13}C NMR (150 MHz, $CDCl_3$) δ: 135.1, 131.8, 131.7, 131.4, 129.8 (2C), 129.1, 128.5, 128.0, 127.1, 127.0, 124.7, 114.3 (2C), 39.1, 36.0. HRMS (ESI) m/z: $[M+H]^+$ Calcd For $C_{16}H_{10}ClN_2^+$ 265.0527; Found 265.0526.

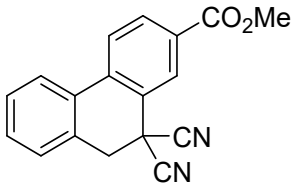


7-Bromophenanthrene-9,9(10*H*)-dicarbonitrile (2k). White solid, 53.8 mg, 87% yield. ^{1}HNMR (600 MHz, $CDCl_3$) δ: 7.93-7.92 (m, 1H), 7.79 (d, *J* = 7.7 Hz, 1H), 7.75-7.73 (m, 1H), 7.72-7.70 (m, 1H),7.48 (t, *J* = 7.6 Hz 1H), 7.41 (t, *J* = 7.4 Hz 1H), 7.36-7.35 (m, 1H), 3.58 (s, 2H). ^{13}C NMR (150 MHz, $CDCl_3$) δ: 134.8, 132.2, 131.4, 130.0 129.9 (2C), 129.2, 128.5, 128.2, 127.2, 124.7, 123.0, 114.3 (2C), 39.1, 25.9. HRMS (ESI) m/z: $[M+H]^+$ Calcd For $C_{16}H_{10}BrN_2^+$ 309.0022; Found 309.0023.

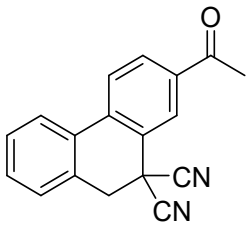


9-(Trifluoromethyl)phenanthrene-9,9(10*H*)-dicarbonitrile (2l). White solid, 47.7 mg, 80% yield. ^{1}H NMR (600 MHz, $CDCl_3$) δ: 8.04 (s, 1H), 8.01 (d, *J* = 8.2 Hz, 1H),

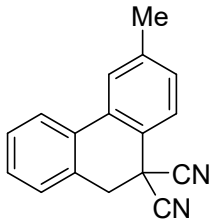
7.88-7.85 (m, 2H), 7.53 (td, *J* = 7.6, 1.0 Hz, 1H), 7.48 (td, *J* = 7.4, 1.1 Hz, 1H), 7.41 (d, *J* = 7.5 Hz, 1H), 3.64 (s, 2H). ^{13}C NMR (150 MHz, $CDCl_3$) δ: 136.7, 131.3 (q, *J* = 34.3 Hz), 131.2, 130.7, 130.6 (q, *J* = 15.4 Hz), 130.0, 129.3, 129.2, 128.5 (q, *J* = 3.6 Hz), 127.3, 126.3, 125.4, 124.1 (q, *J* = 4.1 Hz), 114.1 (2C), 39.1, 36.1. HRMS (ESI) m/z: $[M+H]^+$ Calcd For $C_{17}H_{10}F_3N_2^+$ 299.0791; Found 299.0792.



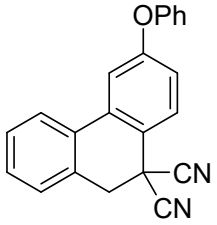
Methyl 10,10-dicyano-9,10-dihydrophenanthrene-2-carboxylate (2m). White solid, 47.2 mg, 82% yield. ^{1}H NMR (600 MHz, $CDCl_3$) δ: 845 (d, *J* = 8.0 Hz, 1H), 8.25 (dd, *J* = 8.5, 1.6 Hz, 1H), 7.96 (d, *J* = 8.1 Hz, 1H), 7.88 (d, *J* = 7.7 Hz, 1H), 7.52 (td, *J* = 7.7, 1.0 Hz, 1H), 7.46 (td, *J* = 7.4, 1.2 Hz, 1H), 7.39 (d, *J* = 7.7 Hz, 1H), 3.99 (s, 3H), 3.63 (s, 2H). ^{13}C NMR (150 MHz, $CDCl_3$) δ: 165.7, 137.3, 132.7, 131.5, 130.9, 130.6, 129.9, 129.3 (2C), 128.2, 126.9, 125.8, 125.5, 114.4 (2C), 52.8, 39.2, 36.2. HRMS (ESI) m/z: $[M+H]^+$ Calcd For $C_{18}H_{13}N_2O_2^+$ 289.0972; Found 289.0974.



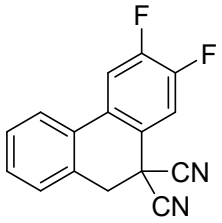
8-Acetylphenanthrene-9,9(10*H*)-dicarbonitrile (2n). White solid, 44.1 mg, 81% yield. ^{1}H NMR (600 MHz, $CDCl_3$) δ: 835 (d, *J* = 1.6 Hz, 1H), 8.16 (dd, *J* = 8.2, 1.8 Hz, 1H), 7.98 (d, *J* = 8.0 Hz, 1H), 7.88 (d, *J* = 7.8 Hz, 1H), 7.52 (td, *J* = 7.5, 0.9 Hz, 1H), 7.46 (td, *J* = 7.5, 1.1 Hz, 1H), 7.39 (d, *J* = 7.2 Hz, 1H), 3.63 (s, 3H), 2.69 (s, 2H). ^{13}C NMR (150 MHz, $CDCl_3$) δ: 196.2, 137.4, 137.3, 131.3 (2C), 130.6, 129.9, 129.3 (2C), 127.0, 126.0, 125.5, 114.4 (2C), 39.1, 36.2, 26.8. HRMS (ESI) m/z: $[M+H]^+$ Calcd For $C_{18}H_{13}N_2O^+$ 273.1022; Found 273.1023.



6-Methylphenanthrene-9,9(10*H*)-dicarbonitrile (2o). White solid, 45.4 mg, 93% yield. ^{1}H NMR (600 MHz, $CDCl_3$) δ: 7.82 (d, *J* = 7.8 Hz, 1H), 7.68-7.66 (m, 2H), 7.47 (t, *J* = 7.3 Hz, 1H), 7.38 (td, *J* = 7.5, 0.8 Hz, 1H), 7.35-7.34 (m, 1H), 7.29 (d, *J* = 7.8 Hz, 1H), 3.56 (s, 2H), 2.47 (s, 3H). ^{13}C NMR (150 MHz, $CDCl_3$) δ: 141.8, 132.9, 132.4, 130.0, 129.6, 129.3, 129.1, 128.9, 126.9, 126.3, 124.7, 123.8, 115.0 (2C), 39.5, 36.1, 21.7. HRMS (ESI) m/z: $[M+H]^+$ Calcd For $C_{17}H_{13}N_2^+$ 245.1073; Found 245.1075.

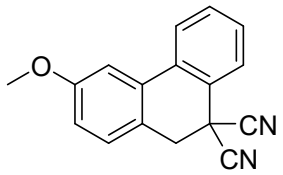


Phenoxyphenanthrene-9,9(10*H*)-dicarbonitrile (2p). Yellow solid, 58.0 mg, 90% yield. ^{1}H NMR (600 MHz, $CDCl_3$) δ: 7.82 (d, *J* = 8.7 Hz, 1H), 7.76 (d, *J* = 7.7 Hz, 1H), 7.48-7.43 (m, 4H), 7.38-7.34 (m, 2H), 7.25-7.22 (m, 1H), 7.16 (dd, *J* = 8.6, 2.4 Hz, 1H), 7.13-7.12 (m, 2H), 3.58 (s, 2H). ^{13}C NMR (150 MHz, $CDCl_3$) δ: 158.5, 155.8, 131.9, 130.3 (2C), 129.6, 129.0, 128.9, 128.1, 127.7, 127.2, 124.7, 124.3, 120.6, 119.8 (2C), 116.7, 114.5 (2C), 39.2, 36.3. HRMS (ESI) m/z: $[M+H]^+$ Calcd For $C_{22}H_{15}N_2O^+$ 323.1179; Found 323.1179.

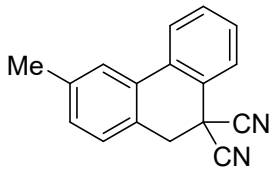


6,7-Difluorophenanthrene-9,9(10*H*)-dicarbonitrile (2q). White solid, 42.6 mg, 80% yield. ^{1}H NMR (600 MHz, $CDCl_3$) δ: 7.71-7.64 (m, 3H), 7.50 (t, *J* = 7.4 Hz, 1H), 7.43 (t, *J* = 7.4 Hz, 1H), 7.37 (d, *J* = 7.5 Hz, 1H), 3.60 (s, 2H). ^{13}C NMR (150 MHz, $CDCl_3$) δ: 152.4 (d, *J* = 253.3 Hz), 152.3 (d, *J* = 252.7 Hz), 150.2 (d, *J* = 254.0 Hz), 150.1 (d,

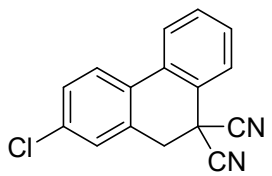
J = 254.0 Hz), 130.8 (d, *J* = 4.4 Hz), 130.7, 130.1, 130.0, 129.2, 128.4, 116.7 (d, *J* = 19.4 Hz), 115.0 (d, *J* = 19.4 Hz), 114.1 (2C), 39.0, 35.6. HRMS (ESI) m/z: $[M+H]^+$ Calcd For $C_{16}H_9F_2N_2^+$ 267.0728; Found 267.0726.



3-Methoxyphenanthrene-9,9(10*H*)-dicarbonitrile (2t). Yellow solid, 46.3 mg, 89% yield. ^{1}H NMR (600 MHz, $CDCl_3$) δ: 7.84 (d, *J* = 7.8 Hz, 1H), 7.80 (dd, *J* = 7.7, 1.0 Hz, 1H), 7.58 (t, *J* = 7.6 Hz, 1H), 7.48 (td, *J* = 7.6, 1.0 Hz, 1H), 7.33 (d, *J* = 2.5 Hz, 1H), 7.27 (d, *J* = 8.3 Hz, 1H), 6.93 (dd, *J* = 8.3, 2.5 Hz 1H), 3.88 (s, 3H), 3.52 (s, 2H). ^{13}C NMR (150 MHz, $CDCl_3$) δ: 160.6, 133.4, 133.2, 131.5, 130.1, 129.4, 126.9, 126.8, 125.7, 120.9, 114.9, 114.6, 110.6, 55.6, 38.7, 36.5. HRMS (ESI) m/z: $[M+H]^+$ Calcd For $C_{17}H_{13}N_2O^+$ 261.1022; Found 261.1023.

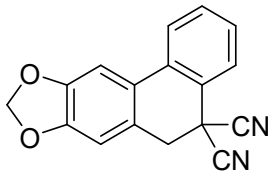


3-Methylphenanthrene-9,9(10*H*)-dicarbonitrile (2u). White solid, 45.4 mg, 93% yield. ^{1}H NMR (600 MHz, $CDCl_3$) δ: 7.84 (d, *J* = 7.7 Hz, 1H), 7.79 (d, *J* = 7.7 Hz, 1H), 7.71 (d, *J* = 8.0 Hz, 1H), 7.58-7.55 (m, 1H), 7.46-7.44 (m, 1H), 7.28 (d, *J* = 7.8 Hz, 1H), 7.36-7.35 (m, 1H), 7.16 (s, 1H), 3.54 (s, 2H), 2.41 (s, 3H). ^{13}C NMR (150 MHz, $CDCl_3$) δ: 139.7, 133.3, 131.4, 130.4, 129.7, 129.5, 128.8, 128.6, 126.9, 126.2, 125.3, 124.7, 114.9 (2C), 39.3, 36.3, 21.4. HRMS (ESI) m/z: $[M+H]^+$ Calcd For $C_{17}H_{13}N_2^+$ 245.1073; Found 245.1073.

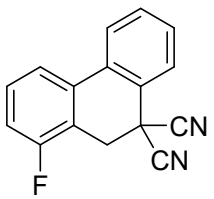


2-Chlorophenanthrene-9,9(10*H*)-dicarbonitrile (2v). White solid, 45.4 mg, 86% yield. ^{1}H NMR (600 MHz, $CDCl_3$) δ: 7.84 (d, *J* = 7.7 Hz, 1H), 7.80 (dd, *J* = 7.7, 0.9

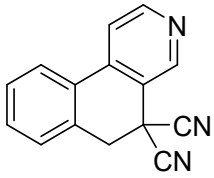
Hz, 1H), 7.75 (d, *J* = 8.4 Hz, 1H), 7.59 (td, *J* = 7.7, 1.1 Hz, 1H), 7.50 (td, *J* = 7.7, 1.1 Hz, 1H), 7.45 (dd, *J* = 8.3, 1.9 Hz, 1H), 7.36 (d, *J* = 2.0 Hz, 1H), 3.56 (s, 2H). ^{13}C NMR (150 MHz, $CDCl_3$) δ: 135.2, 132.2, 131.7, 130.8, 130.4, 129.9, 129.7, 129.1, 127.1, 126.3, 126.1, 125.6, 114.5 (2C), 38.9, 36.1. HRMS (ESI) m/z: $[M+H]^+$ Calcd For $C_{16}H_{10}ClN_2^+$ 265.0527; Found 265.0525.



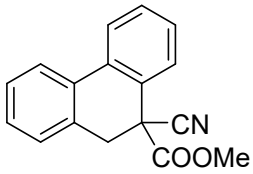
Phenanthro[2,3-d][1,3]dioxole-5,5(6*H*)-dicarbonitrile (2w). White solid, 45.5 mg, 83% yield. ^{1}H NMR (600 MHz, $CDCl_3$) δ: 7.76 (d, *J* = 7.7 Hz, 1H), 7.70 (d, *J* = 7.9 Hz, 1H), 7.56-7.54 (m, 1H), 7.44-7.41 (m, 1H), 7.26 (s, 1H), 6.81 (s, 1H), 6.05 (s, 2H), 3.47 (s, 2H). ^{13}C NMR (150 MHz, $CDCl_3$) δ: 149.2, 148.6, 133.3, 131.5, 128.6, 126.8, 126.6, 125.9, 125.1, 123.0, 114.9, 109.2, 105.2, 102.0, 39.3, 36.5. HRMS (ESI) m/z: $[M+H]^+$ Calcd For $C_{17}H_{11}N_2O_2^+$ 275.0815; Found 275.0817.



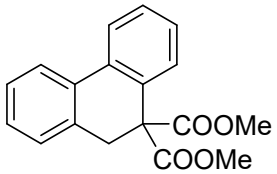
1-Fluorophenanthrene-9,9(10*H*)-dicarbonitrile (2x). White solid, 46.1 mg, 93% yield. ^{1}H NMR (600 MHz, $CDCl_3$) δ: 7.88 (d, *J* = 7.6 Hz, 1H), 7.83 (dd, *J* = 7.7, 0.7 Hz, 1H), 7.64 (d, *J* = 7.9 Hz 1H), 7.60 (td, *J* = 7.7, 1.1 Hz 1H), 7.52 (td, *J* = 7.6, 1.1 Hz 1H), 7.47-7.43 (m, 1H), 7.17-7.14 (m, 1H), 3.65 (s, 2H). ^{13}C NMR (150 MHz, $CDCl_3$) δ: 160.3 (d, *J* = 247.5 Hz), 134.3 (d, *J* = 3.6 Hz), 132.3 (d, *J* = 3.0 Hz), 131.6, 130.5 (d, *J* = 8.3 Hz), 129.9, 127.1, 126.4, 126.0, 120.4 (d, *J* = 3.2 Hz), 116.1 (d, *J* = 21.5 Hz), 116.0 (d, *J* = 17.1 Hz), 114.5 (2C), 35.7, 31.4 (d, *J* = 4.3 Hz). HRMS (ESI) m/z: $[M+H]^+$ Calcd For $C_{16}H_{10}FN_2^+$ 249.0823; Found 249.0824.



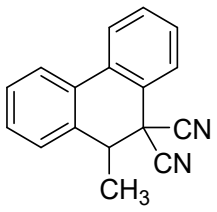
Benzo[f]isoquinoline-5,5(6*H*)-dicarbonitrile (2y). White solid, 36.5 mg, 79% yield. ^{1}H NMR (600 MHz, $CDCl_3$) δ: 9.02 (s, 1H), 8.82 (d, *J* = 5.1 Hz, 1H), 7.89-7.88 (m, 1H), 7.74 (d, *J* = 5.3 Hz, 1H), 7.55-7.50 (m, 2H), 7.42-7.41 (m, 1H), 3.65 (s, 2H). ^{13}C NMR (150 MHz, $CDCl_3$) δ: 153.0, 147.9, 140.5, 131.7, 130.0, 129.8, 129.7, 129.5, 125.4, 122.1, 118.9, 113.9 (2C), 39.0, 33.6 HRMS (ESI) m/z: $[M+H]^+$ Calcd For $C_{15}H_{10}N_3^+$ 232.0869; Found 232.0869.



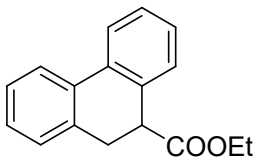
Methyl 9-cyano-9,10-dihydrophenanthrene-9-carboxylate (2z). White solid, 48.4 mg, 92% yield. ^{1}H NMR (600 MHz, $CDCl_3$) δ: 7.84 (d, *J* = 7.8 Hz, 1H), 7.77 (d, *J* = 7.7 Hz, 1H), 7.62 (d, *J* = 7.7 Hz, 1H), 7.50 (t, *J* = 7.6 Hz, 1H), 7.42-7.37 (m, 2H), 7.33-7.28 (m, 2H), 3.73 (s, 3H), 3.70 (d, *J* = 15.1 Hz, 1H), 3.48 (d, *J* = 15.1 Hz, 1H). ^{13}C NMR (150 MHz, $CDCl_3$) δ: 167.4, 133.6, 132.7, 130.8, 130.2, 129.8, 128.8, 128.7, 128.6 (2C), 127.7, 124.9, 124.2 118.7, 54.2, 48.1, 37.9. HRMS (ESI) m/z: $[M+H]^+$ Calcd For $C_{17}H_{14}NO_2^+$ 264.1019; Found 264.1019.



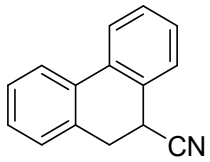
Dimethyl phenanthrene-9,9(10*H*)-dicarboxylate (2aa). White solid, 52.1 mg, 88% yield. ^{1}H NMR (600 MHz, $CDCl_3$) δ: 7.79 (d, *J* = 7.8 Hz, 1H), 7.70 (d, *J* = 7.7 Hz, 1H), 7.40 (td, *J* = 7.6, 1.2 Hz, 1H), 7.32-7.28 (m, 2H), 7.26-7.20 (m, 3H), 3.69 (s, 6H), 3.54 (s, 2H). ^{13}C NMR (150 MHz, $CDCl_3$) δ: 171.3 (2C), 134.0 133.5, 133.4, 132.9, 128.9, 128.6, 128.3, 128.0, 127.9, 127.6, 124.5, 124.0, 60.0, 53.2 (2C), 36.6. HRMS (ESI) m/z: $[M+H]^+$ Calcd For $C_{18}H_{17}O_4^+$ 297.1121; Found 297.1122.



9-Methylphenanthrene-9,9(10*H*)-dicarbonitrile (2ab). White solid, 40.5 mg, 83% yield. ^{1}H NMR (600 MHz, $CDCl_3$) δ: 7.88 (d, *J* = 7.7 Hz, 1H), 7.82 (d, *J* = 7.7 Hz, 1H), 7.79 (d, *J* = 7.7 Hz, 1H), 7.60-7.58 (m, 1H), 7.50-7.45 (m, 1H), 7.43-7.41 (m, 1H), 7.38 (d, *J* = 7.4 Hz, 1H), 3.63 (q, *J* = 6.9 Hz, 1H), 1.52 (d, *J* = 6.9 Hz, 3H). ^{13}C NMR (150 MHz, $CDCl_3$) δ: 134.3, 132.8, 131.5, 131.3, 129.7, 129.4, 129.3, 127.7, 127.6, 125.5, 125.0, 115.1, 114.1 (2C), 42.5, 42.4, 16.3. HRMS (ESI) m/z: $[M+H]^+$ Calcd For $C_{17}H_{13}N_2^+$ 245.1073; Found 245.1075.

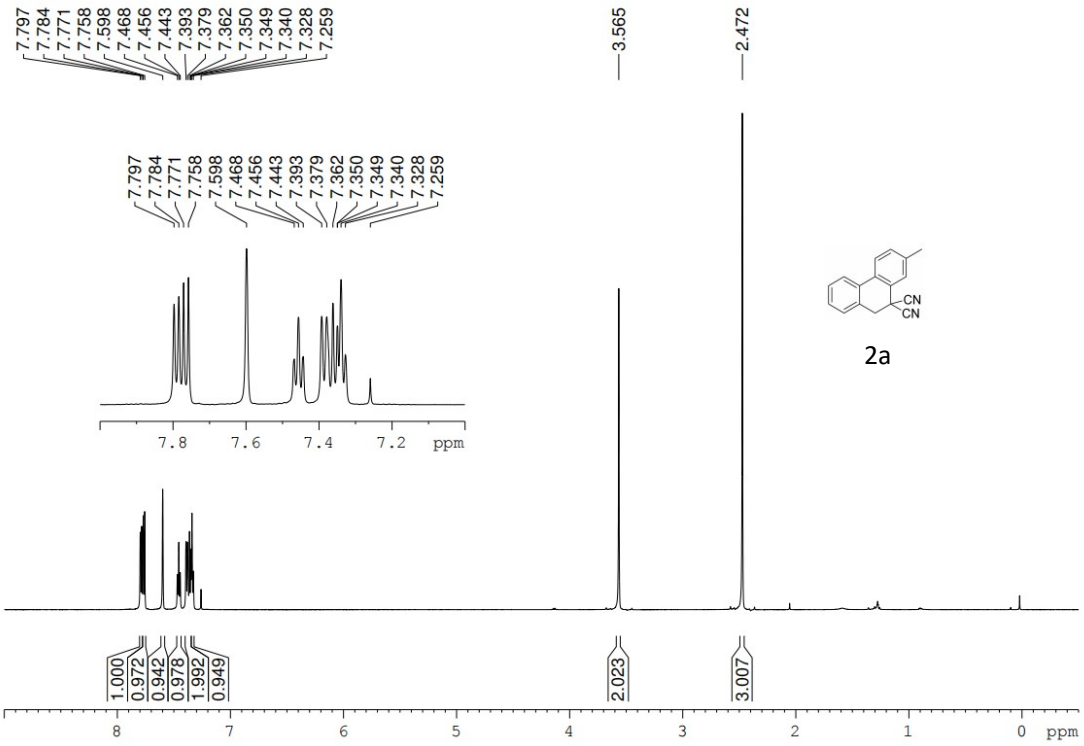


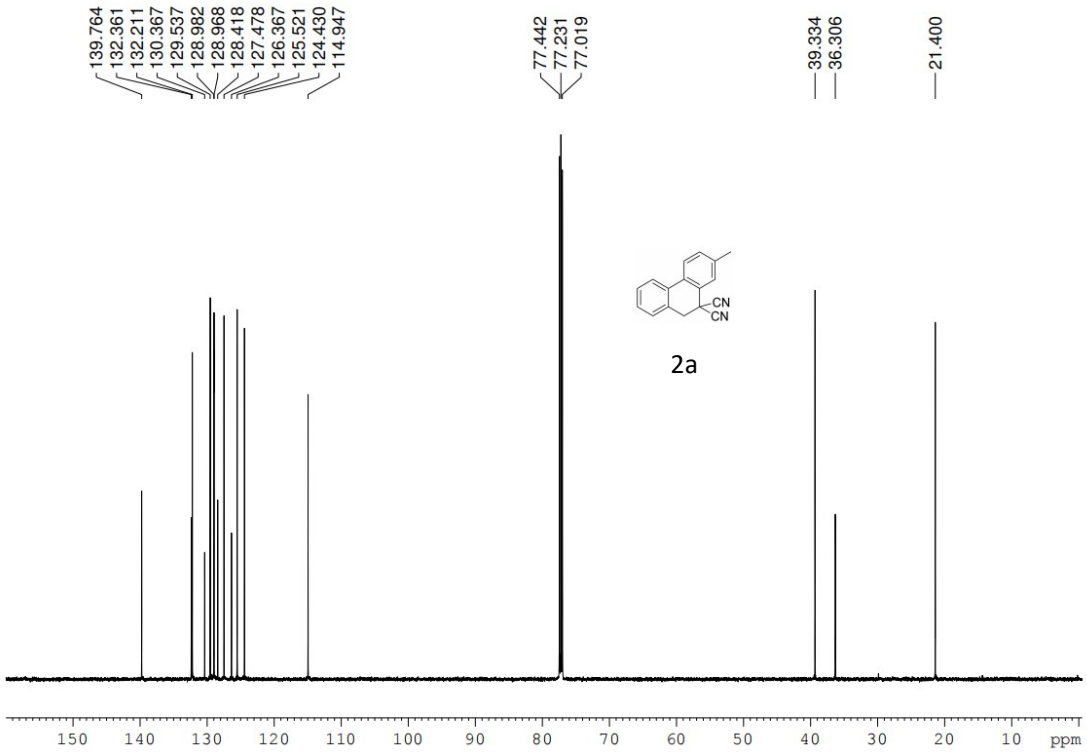
Ethyl 9,10-dihydrophenanthrene-9-carboxylate (2ae). White solid, 41.8 mg, 83% yield. ^{1}H NMR (600 MHz, $CDCl_3$) δ: 7.82 (d, *J* = 7.7 Hz, 1H), 7.78 (d, *J* = 7.7 Hz, 1H), 7.42-7.39 (m, 1H), 7.36-7.31 (m, 3H), 7.30-7.26 (m, 2H), 4.12 (q, *J* = 7.1 Hz, 1H), 3.91 (t, *J* = 5.9 Hz, 1H), 3.34 (dd, *J* = 15.2, 6.1 Hz, 1H), 3.15 (dd, *J* = 15.2, 6.1 Hz, 1H), 1.17 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (150 MHz, $CDCl_3$) δ: 173.3, 134.8, 134.4, 134.2, 133.9, 128.6 (2C), 127.9, 127.8, 127.5, 124.2, 123.9, 61.0, 45.0, 32.1, 14.3. HRMS (ESI) m/z: $[M+H]^+$ Calcd For $C_{17}H_{17}O_2^+$ 253.1123; Found 253.1125.

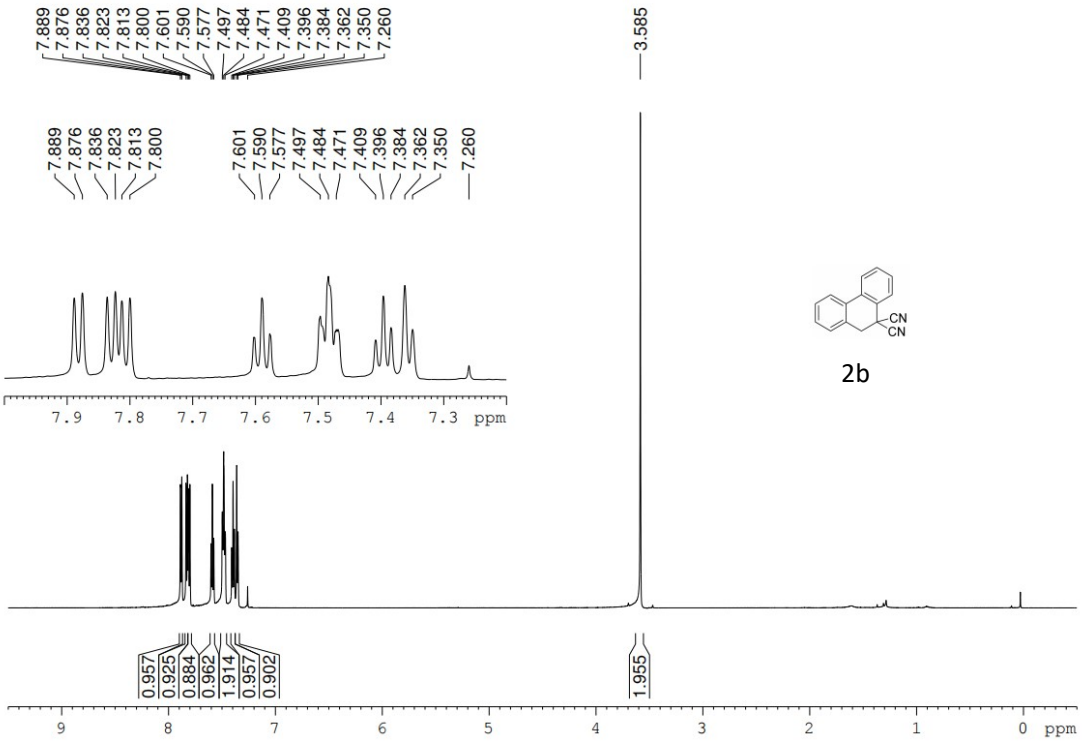


9,10-Dihydrophenanthrene-9-carbonitrile (2af). White solid, 26.7 mg, 65% yield. ^{1}H NMR (600 MHz, $CDCl_3$) δ: 7.81-7.78 (m, *2*H), 7.58 (d, *J* = 7.6 Hz, 1H), 7.47-7.45 (m, 1H), 7.41-7.36 (m, 2H), 7.32-7.28 (m, 2H), 4.08(t, *J* = 8.1 Hz, 1H), 3.22-3.21 (m, 2H). ^{13}C NMR (150 MHz, $CDCl_3$) δ: 133.8, 133.4, 132.9, 130.0, 129.4, 128.6, 128.5 (2C), 128.4, 127.2, 124.7, 124.3, 120.2, 33.1, 31.4. HRMS (ESI) m/z: $[M+H]^+$ Calcd For $C_{15}H_{12}N^+$ 206.0964; Found 206.0965.

5. ^{1}H NMR, ^{13}C NMR, ^{19}F NMR and HRMS spectra of the products



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7.350
7.260
3.585
7.9 7.8 7.7 7.6 7.5 7.4 7.3 ppm
CN
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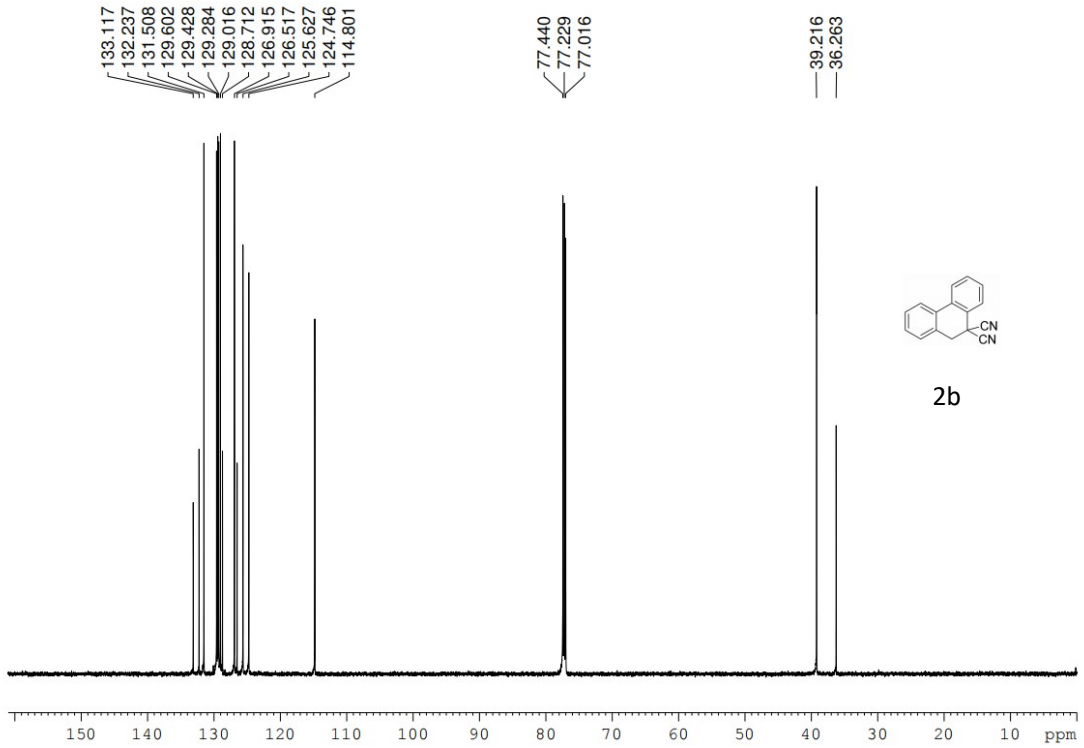
2b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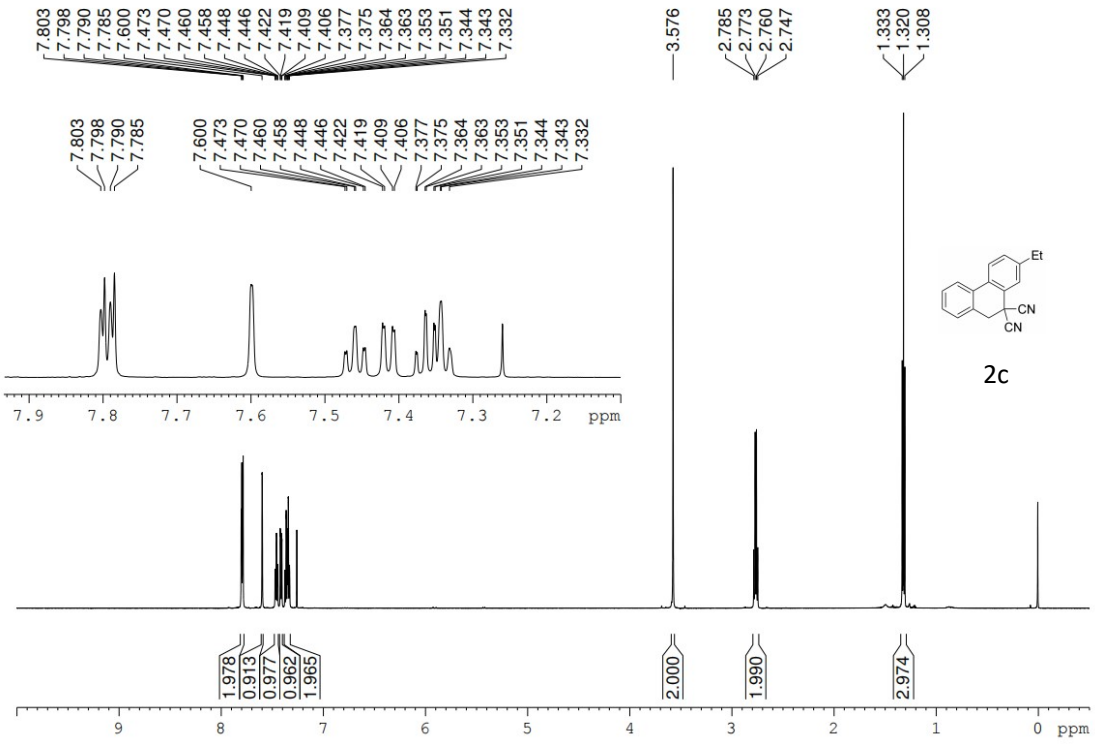
2b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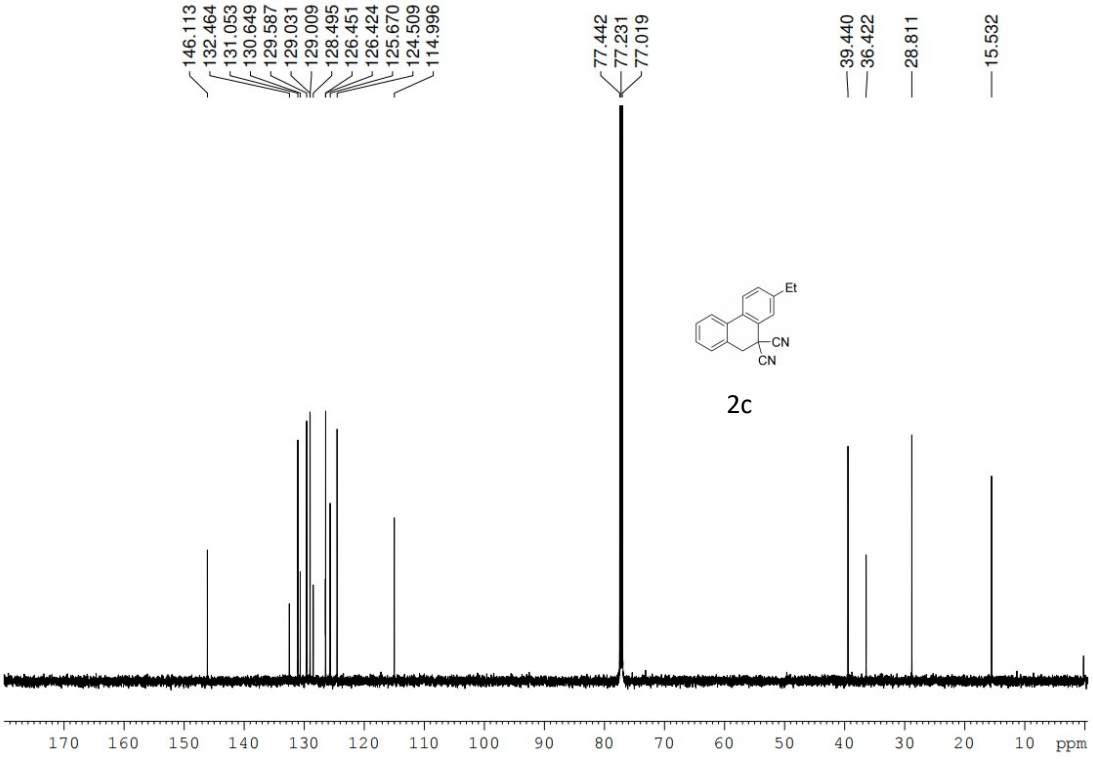
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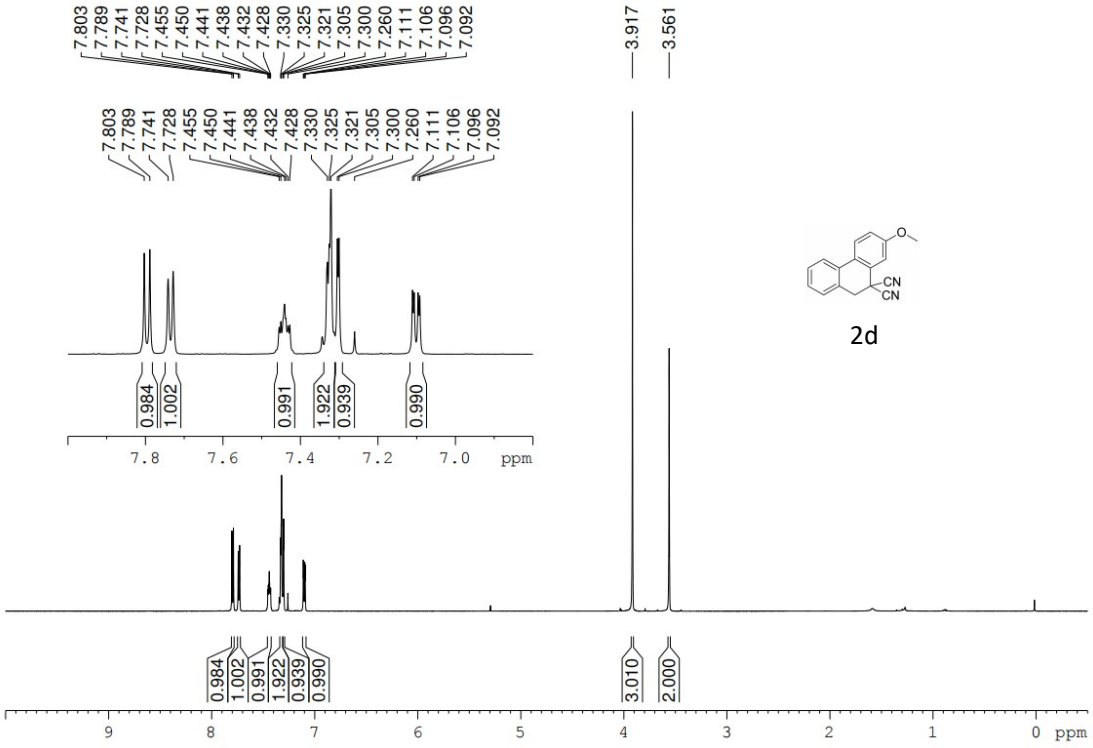
ppm

2c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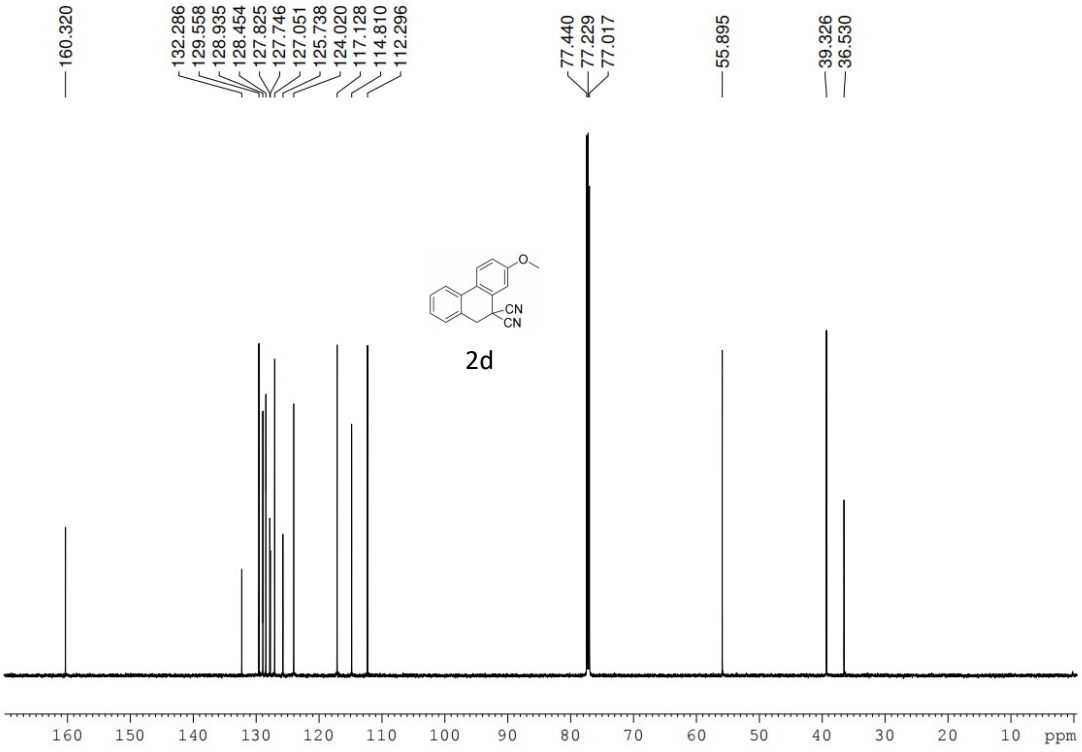
O

2d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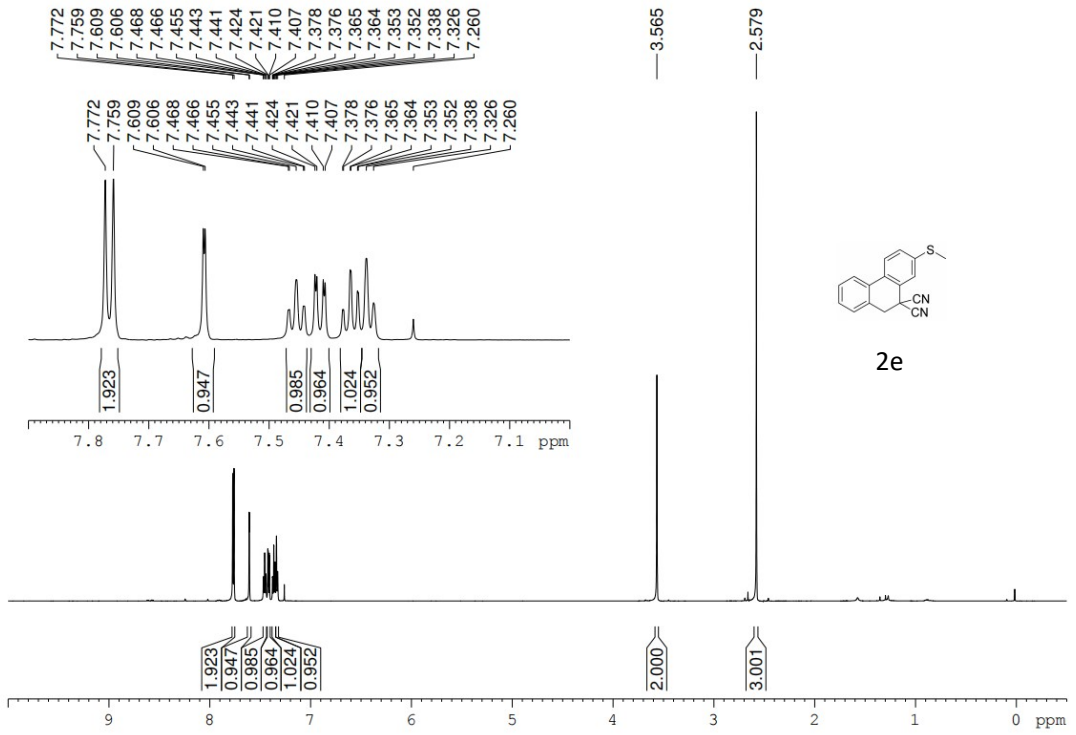
O

2d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7.365
7.364
7.353
7.352
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7.260
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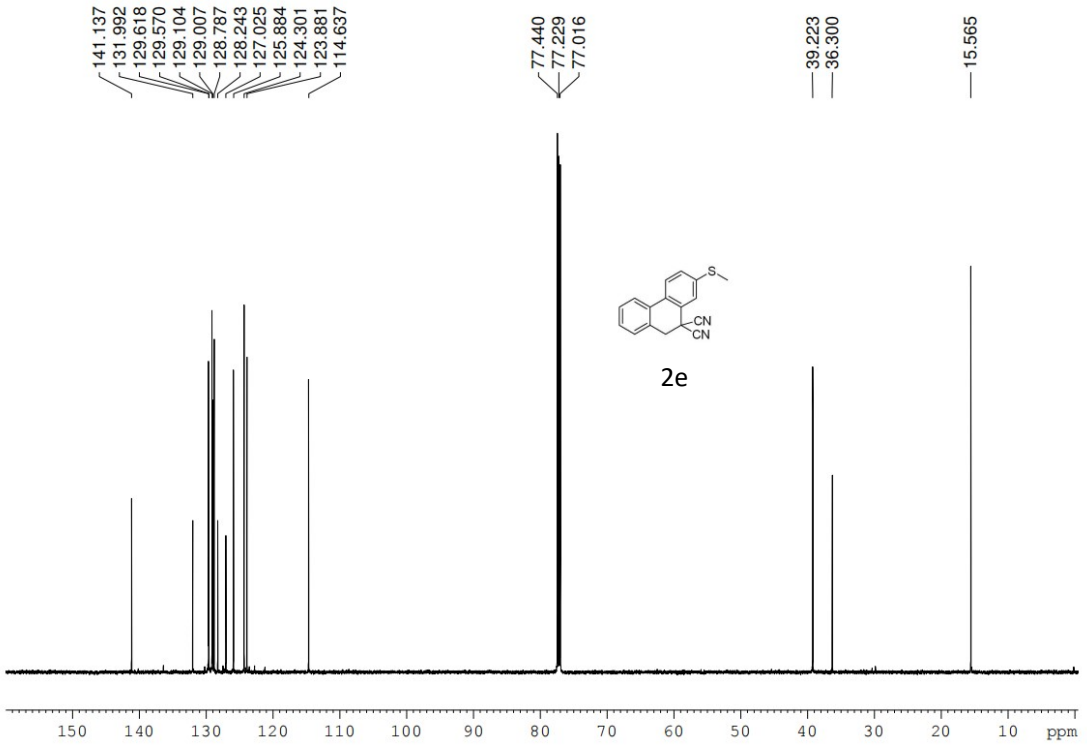
CN
CN
S

2e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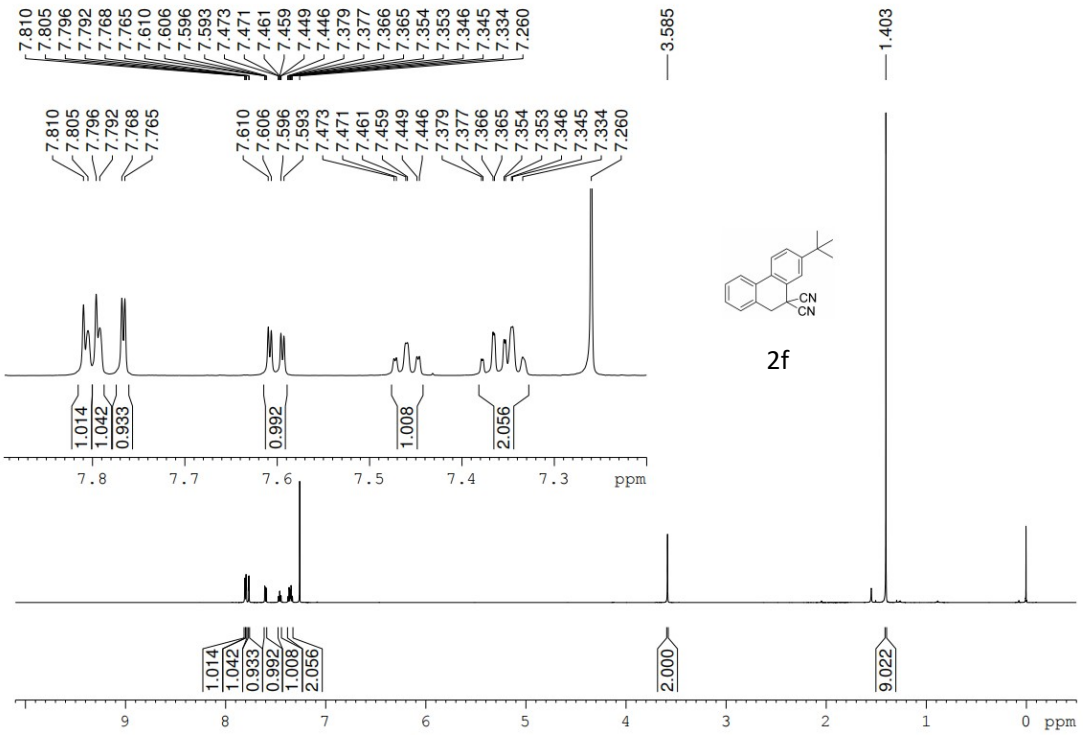
S

2e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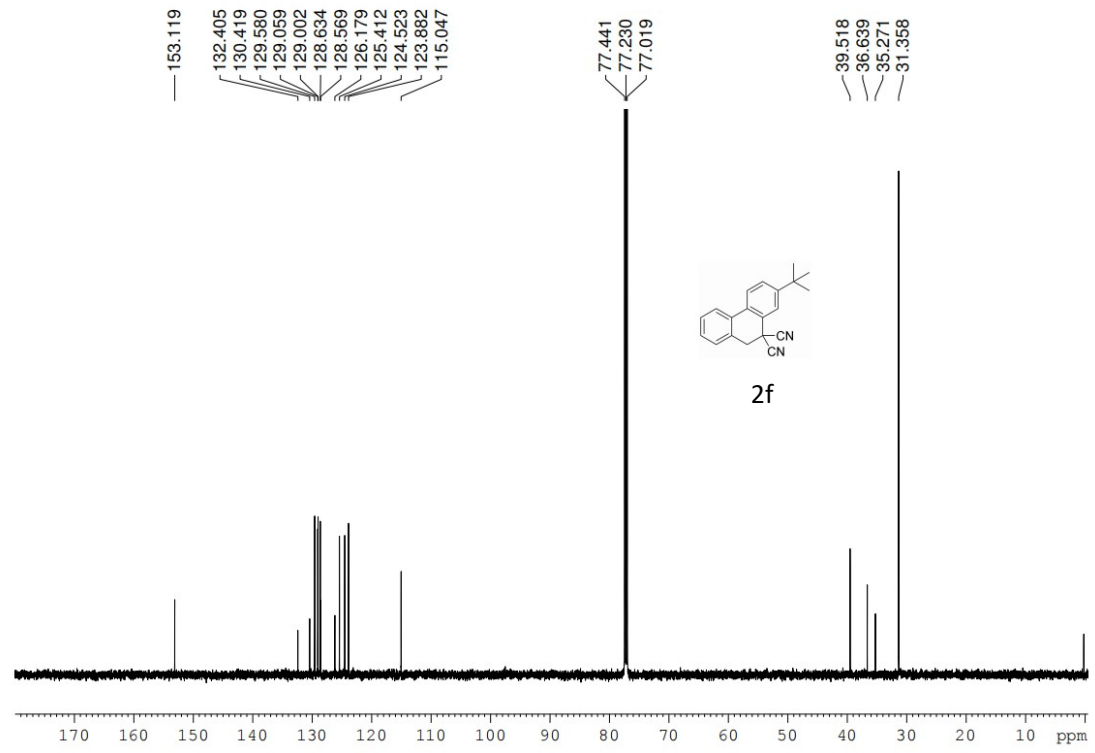
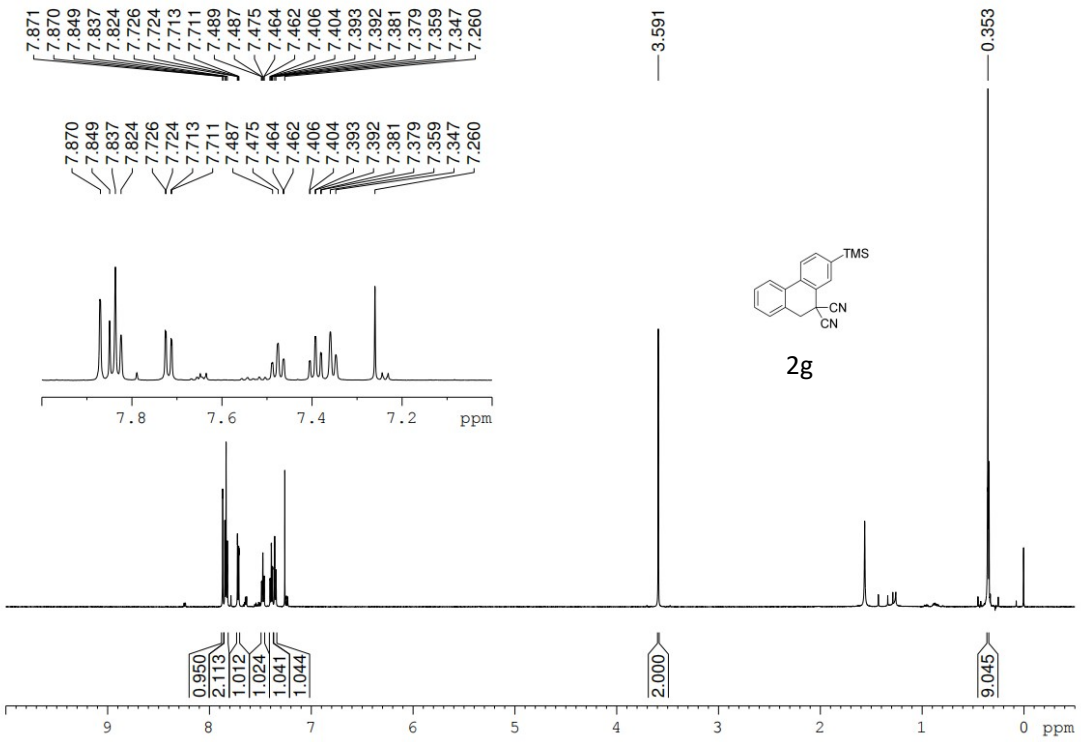
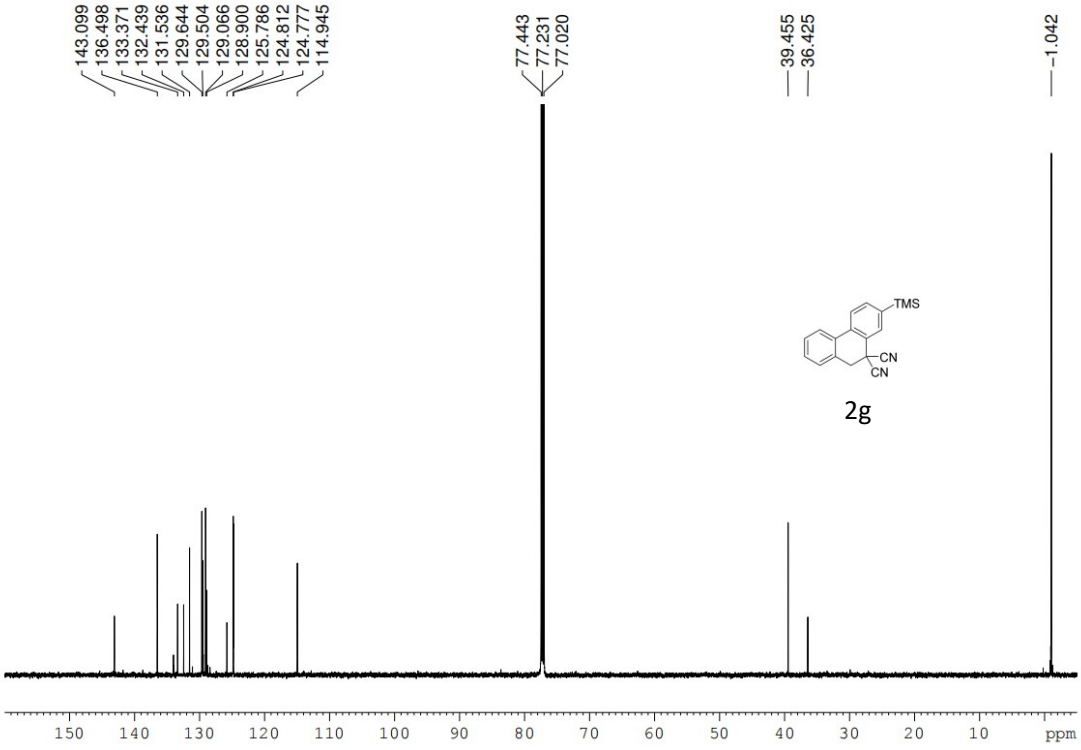
7.461
7.459
7.449
7.446
7.379
7.377
7.366
7.365
7.354
7.353
7.346
7.345
7.334
7.260
3.585
1.403
1.014
1.042
0.933
0.992
1.008
2.056
2.000
9.022
ppm
CN
CN

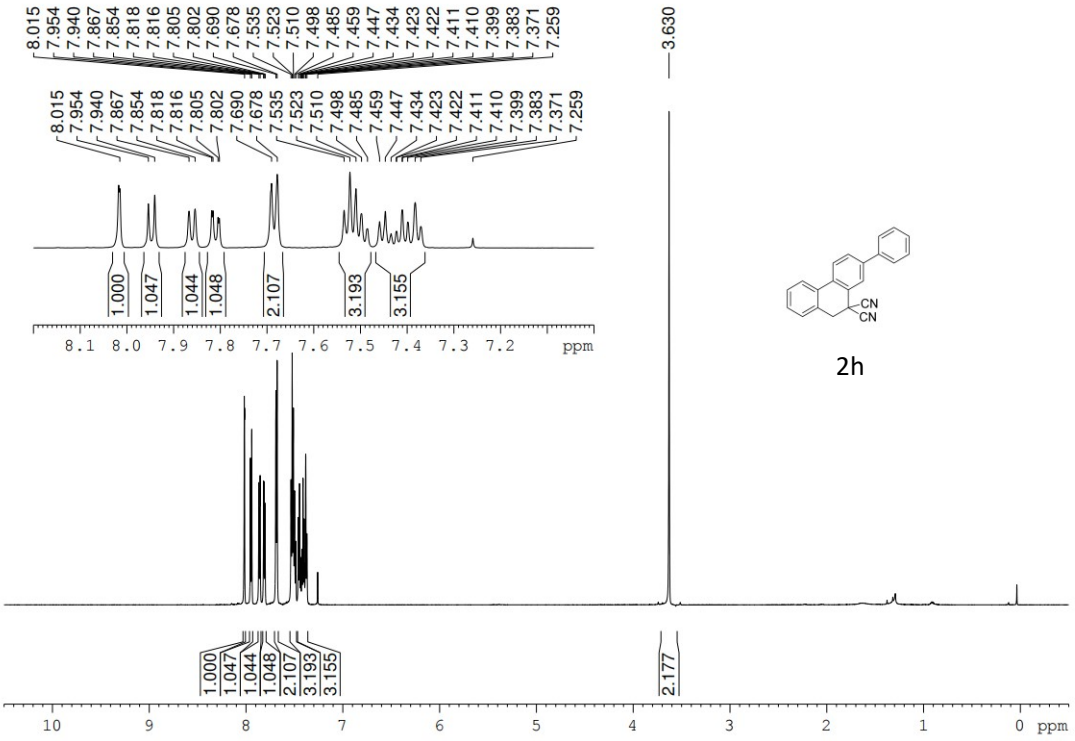
2f

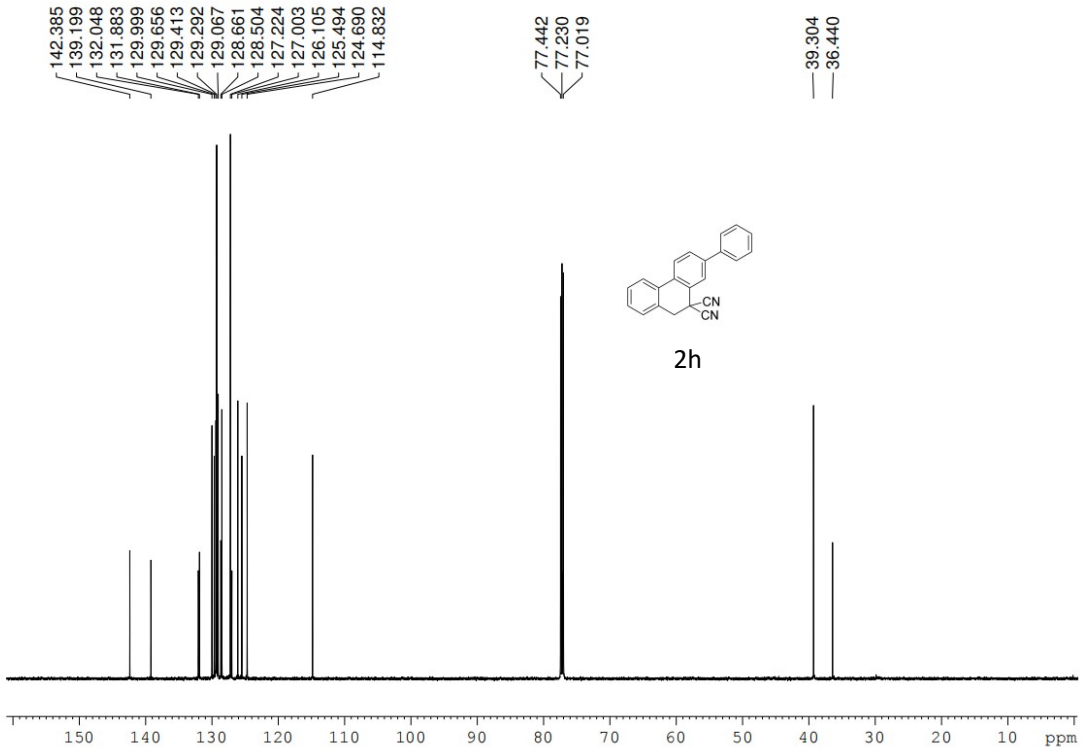

153.119
132.405
130.419
129.580
129.059
129.002
128.634
128.569
126.179
125.412
124.523
123.882
115.047
77.441
77.230
77.019
39.518
36.639
35.271
31.358
ppm
CN
CN

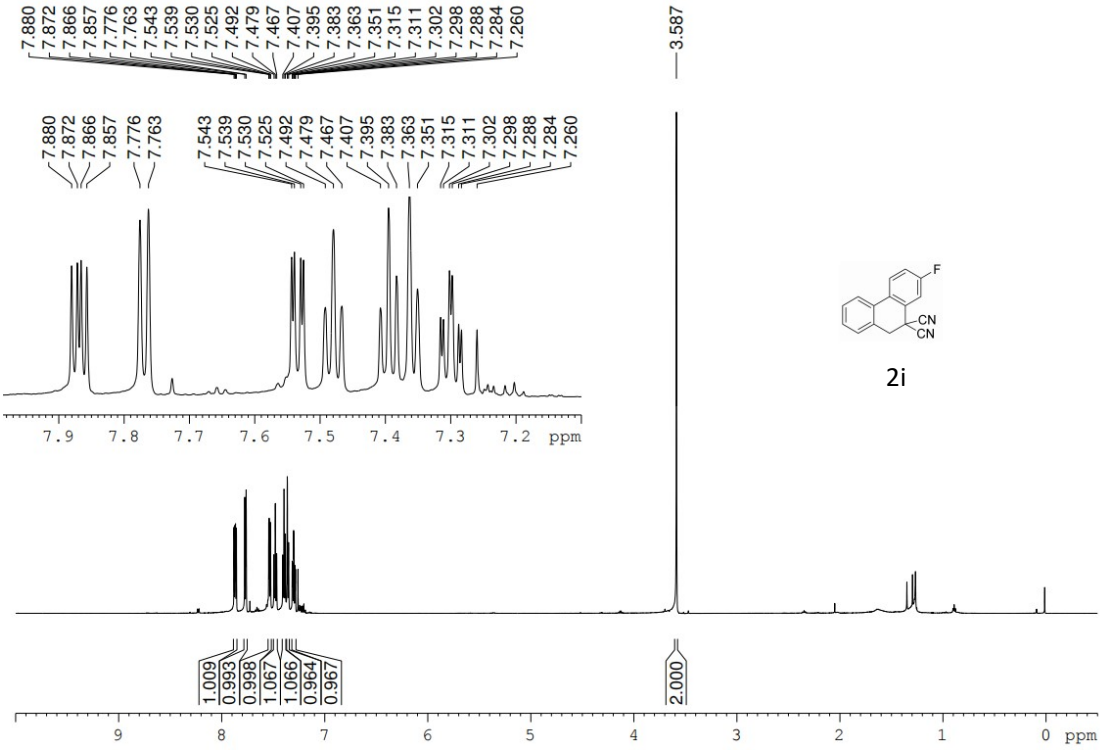
2f

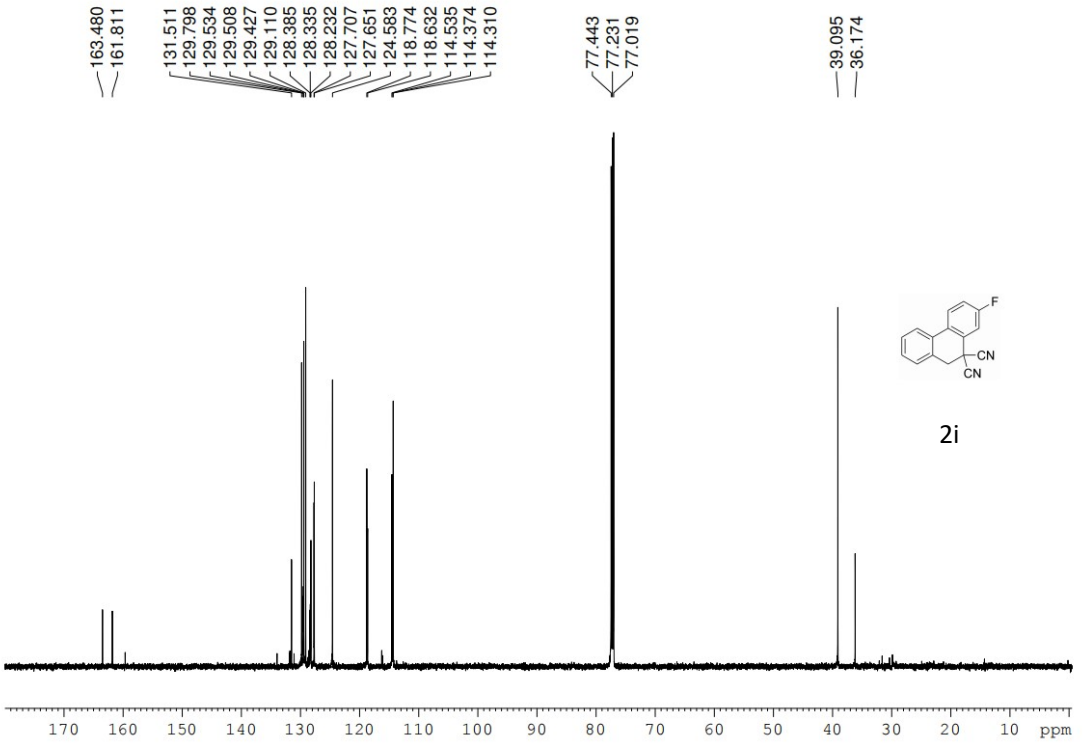

7.871
7.870
7.849
7.837
7.824
7.726
7.724
7.713
7.711
7.489
7.487
7.475
7.464
7.462
7.406
7.404
7.393
7.392
7.381
7.379
7.359
7.347
7.260
3.591
0.353
TMS
CN
CN
2g
7.8
7.6
7.4
7.2
ppm
0.950
2.113
1.012
1.024
1.041
1.044
2.000
9.045
9
8
7
6
5
4
3
2
1
0
ppm

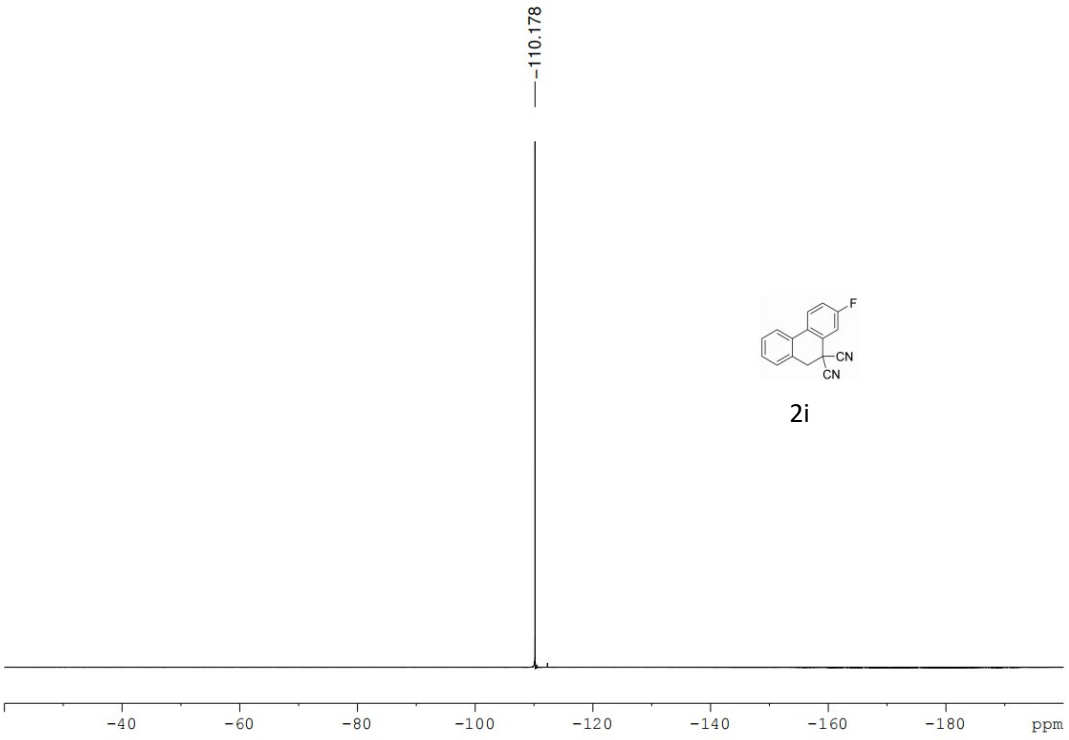

143.099
136.498
133.371
132.439
131.536
129.644
129.504
129.066
128.900
125.786
124.812
124.777
114.945
77.443
77.231
77.020
39.455
36.425
1.042
TMS
CN
CN
2g
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm


8.015
7.954
7.940
7.867
7.854
7.818
7.816
7.805
7.802
7.690
7.678
7.535
7.523
7.510
7.498
7.485
7.459
7.447
7.434
7.423
7.422
7.411
7.410
7.399
7.383
7.371
7.259
3.630
1.000
1.047
1.044
1.048
2.107
3.193
3.155
2.177
CN
CN
2h
ppm

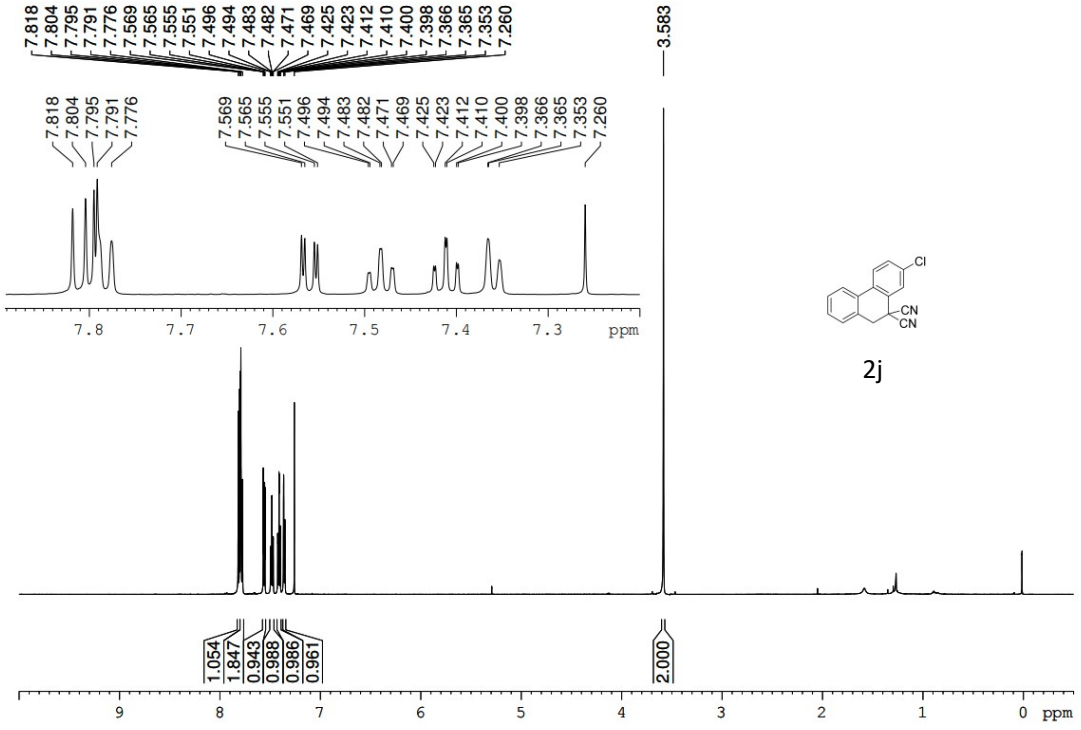

142.385
139.199
132.048
131.883
129.999
129.656
129.413
129.292
129.067
128.661
128.504
127.224
127.003
126.105
125.494
124.690
114.832
77.442
77.230
77.019
39.304
36.440
CN
CN
2h
ppm


7.880
7.872
7.866
7.857
7.776
7.763
7.543
7.539
7.530
7.525
7.492
7.479
7.467
7.407
7.395
7.383
7.363
7.351
7.315
7.311
7.302
7.298
7.288
7.284
7.260
3.587
F
CN
CN
2i
7.9 7.8 7.7 7.6 7.5 7.4 7.3 7.2 ppm
1.009
0.993
0.998
1.067
1.066
0.964
0.967
2.000
9 8 7 6 5 4 3 2 1 0 ppm

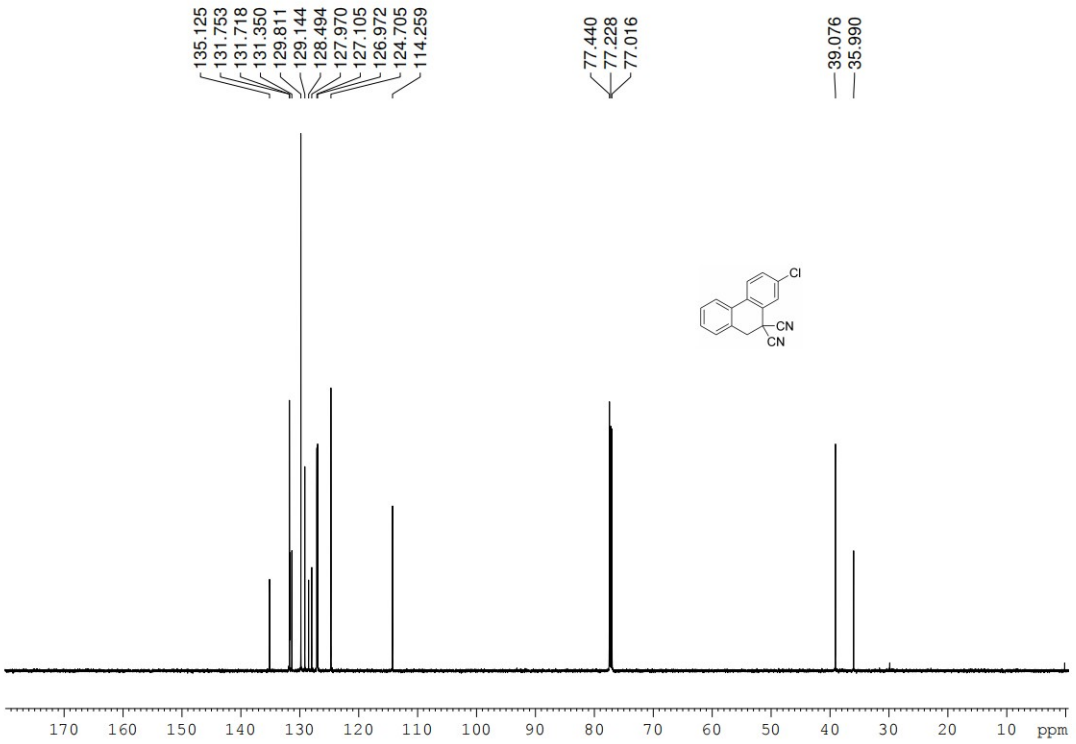

163.480
161.811
131.511
129.798
129.534
129.508
129.427
129.110
128.385
128.335
128.232
127.707
127.651
124.583
118.774
118.632
114.535
114.374
114.310
77.443
77.231
77.019
39.095
36.174
F
CN
CN
2i
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm

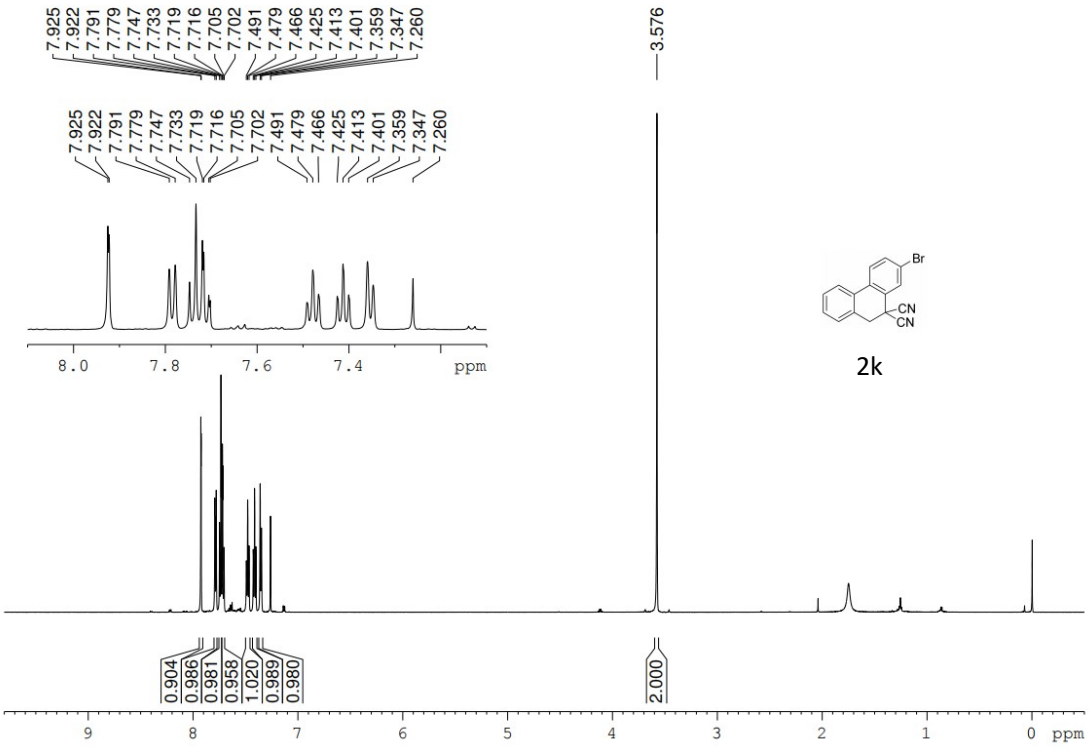

-110.178
F
CN
CN
-40
-60
-80
-100
-120
-140
-160
-180
ppm

2i

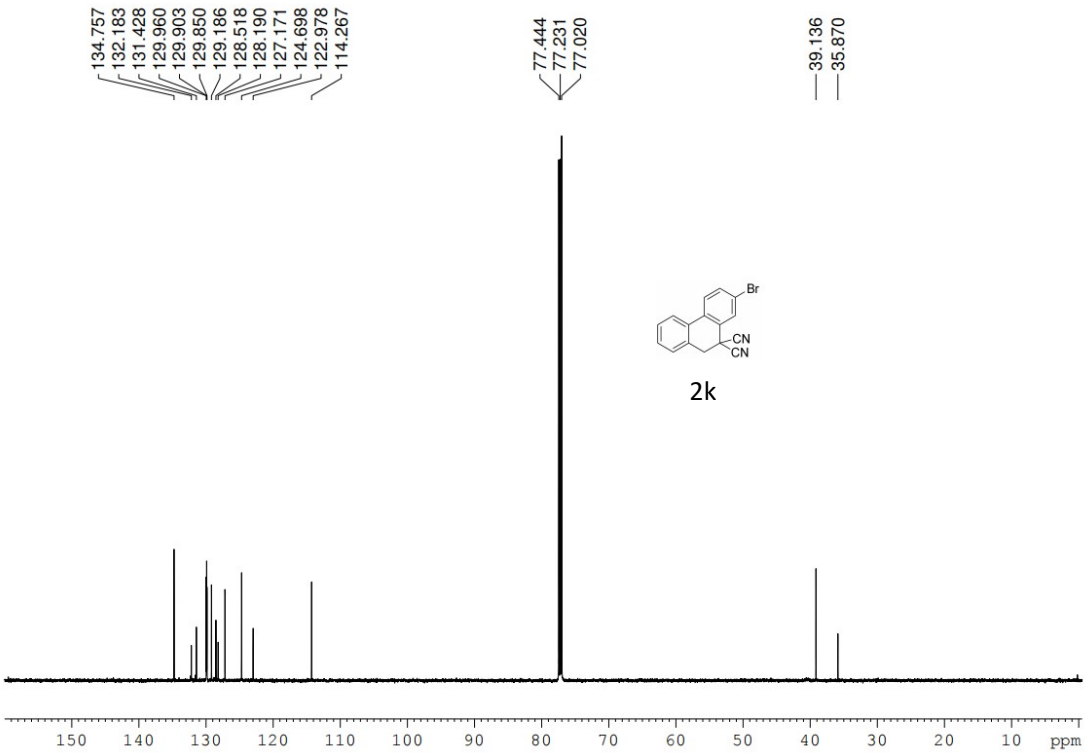

7.818
7.804
7.795
7.791
7.776
7.569
7.565
7.555
7.551
7.496
7.494
7.483
7.482
7.471
7.469
7.425
7.423
7.412
7.410
7.400
7.398
7.366
7.365
7.353
7.260
3.583
7.8
7.7
7.6
7.5
7.4
7.3
ppm
Cl
CN
CN
1.054
1.847
0.943
0.988
0.986
0.961
2.000
9
8
7
6
5
4
3
2
1
0
ppm

2j

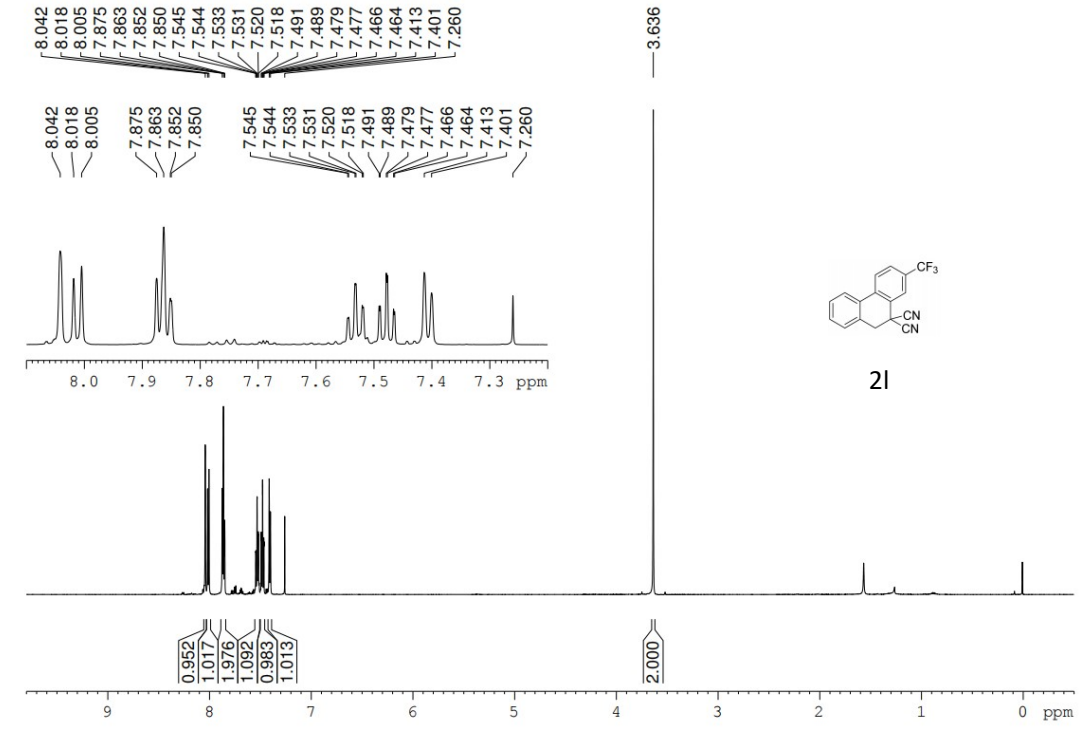

135.125
131.753
131.718
131.350
129.811
129.144
128.494
127.970
127.105
126.972
124.705
114.259
77.440
77.228
77.016
39.076
35.990
Cl
CN
CN
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm


7.925
7.922
7.791
7.779
7.747
7.733
7.719
7.716
7.705
7.702
7.491
7.479
7.466
7.425
7.413
7.401
7.359
7.347
7.260
3.576
8.0 7.8 7.6 7.4 ppm
Br
CN
CN
0.904
0.986
0.981
0.958
1.020
0.989
0.980
2.000
9 8 7 6 5 4 3 2 1 0 ppm

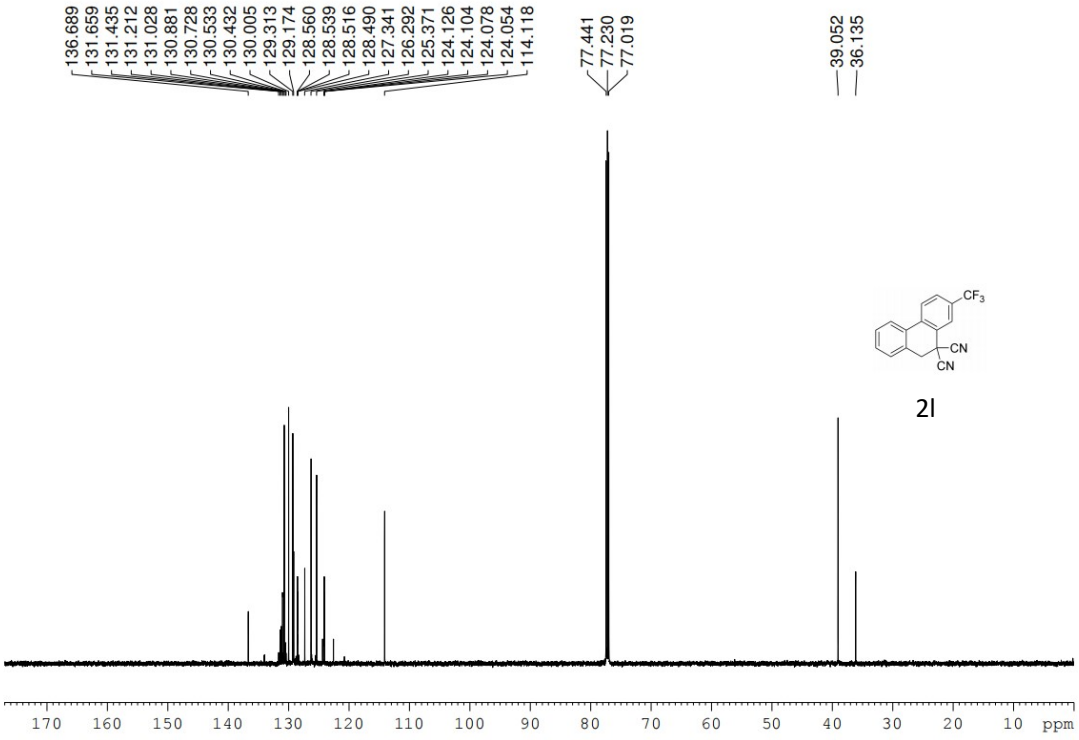
2k


134.757
132.183
131.428
129.960
129.903
129.850
129.186
128.518
128.190
127.171
124.698
122.978
114.267
77.444
77.231
77.020
39.136
35.870
Br
CN
CN
150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm

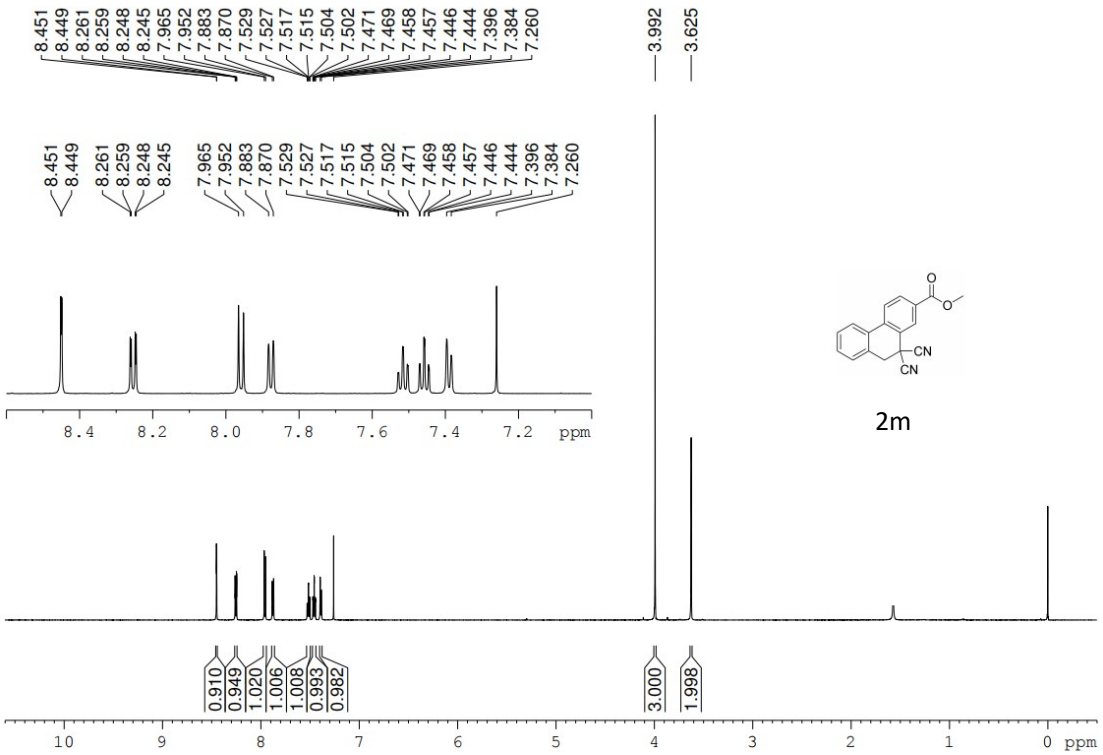
2k


8.042
8.018
8.005
7.875
7.863
7.852
7.850
7.545
7.544
7.533
7.531
7.520
7.518
7.491
7.489
7.479
7.477
7.466
7.464
7.413
7.401
7.260
3.636
CF3
CN
CN
8.0 7.9 7.8 7.7 7.6 7.5 7.4 7.3 ppm
0.952
1.017
1.976
1.092
0.983
1.013
2.000
9 8 7 6 5 4 3 2 1 0 ppm

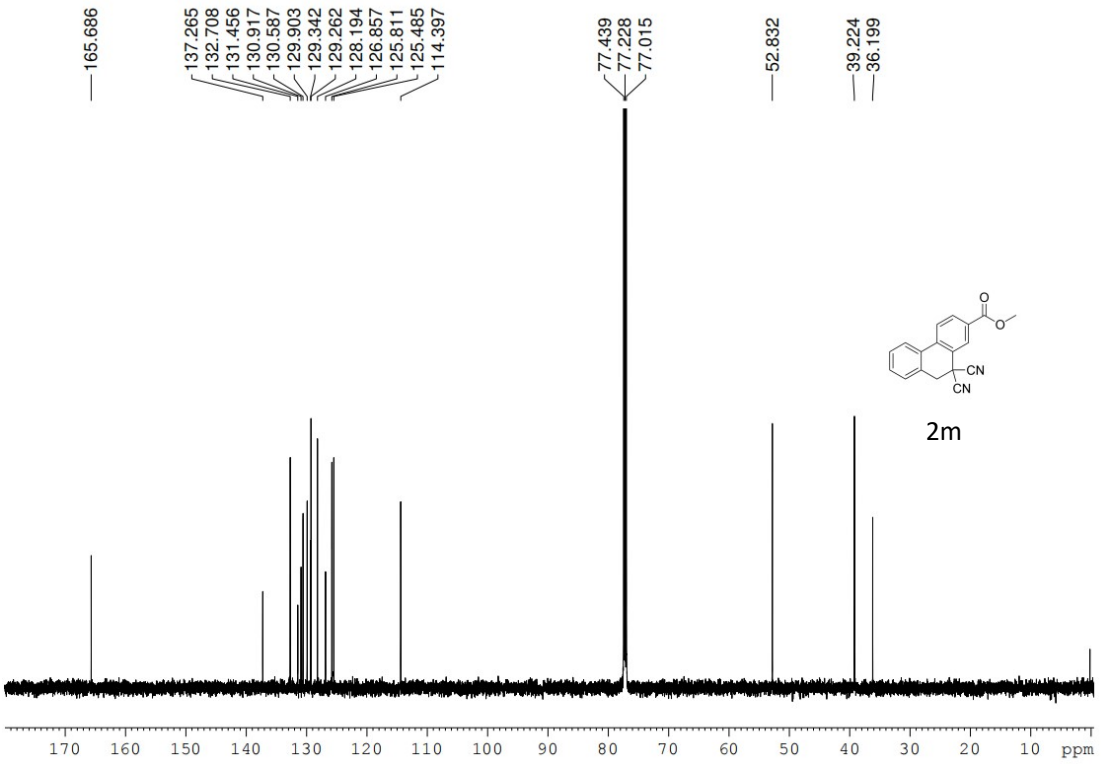
2l


136.689
131.659
131.435
131.212
131.028
130.881
130.728
130.533
130.432
130.005
129.313
129.174
128.560
128.539
128.516
128.490
127.341
126.292
125.371
124.126
124.104
124.078
124.054
114.118
77.441
77.230
77.019
39.052
36.135
CF3
CN
CN
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm

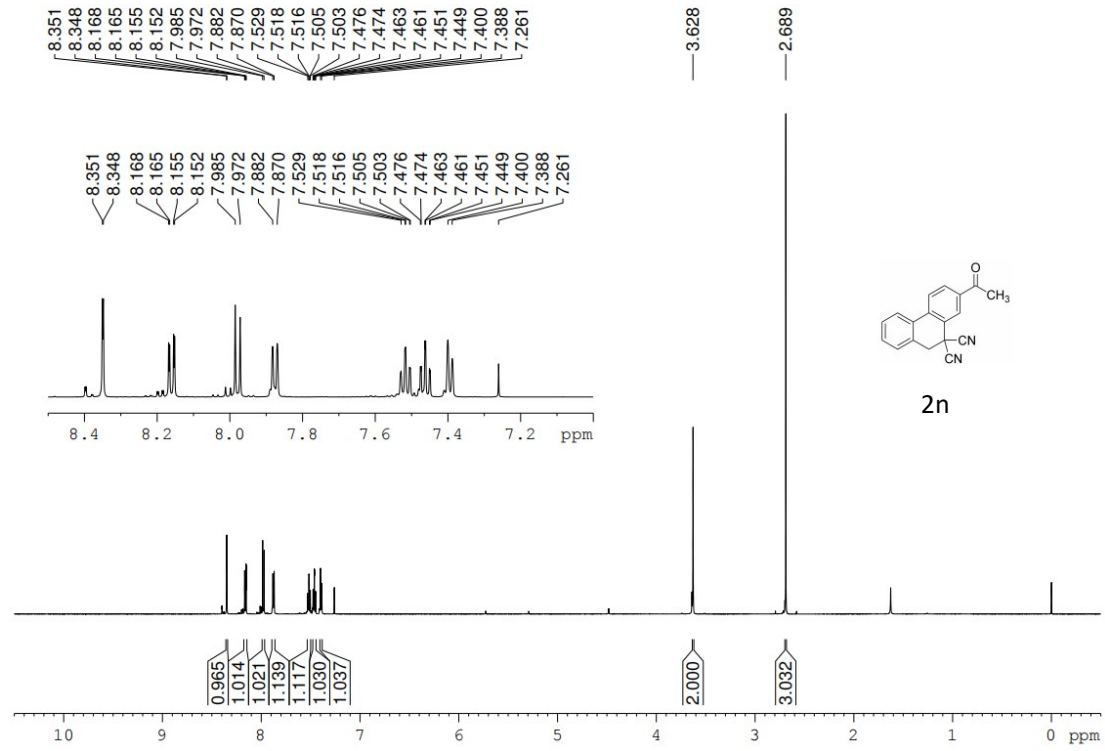
2l


8.451
8.449
8.261
8.259
8.248
8.245
7.965
7.952
7.883
7.870
7.529
7.527
7.517
7.515
7.504
7.502
7.471
7.469
7.458
7.457
7.446
7.444
7.396
7.384
7.260
3.992
3.625
8.4 8.2 8.0 7.8 7.6 7.4 7.2 ppm
CN
CN
0.910
0.949
1.020
1.006
1.008
0.993
0.982
3.000
1.998
10 9 8 7 6 5 4 3 2 1 0 ppm

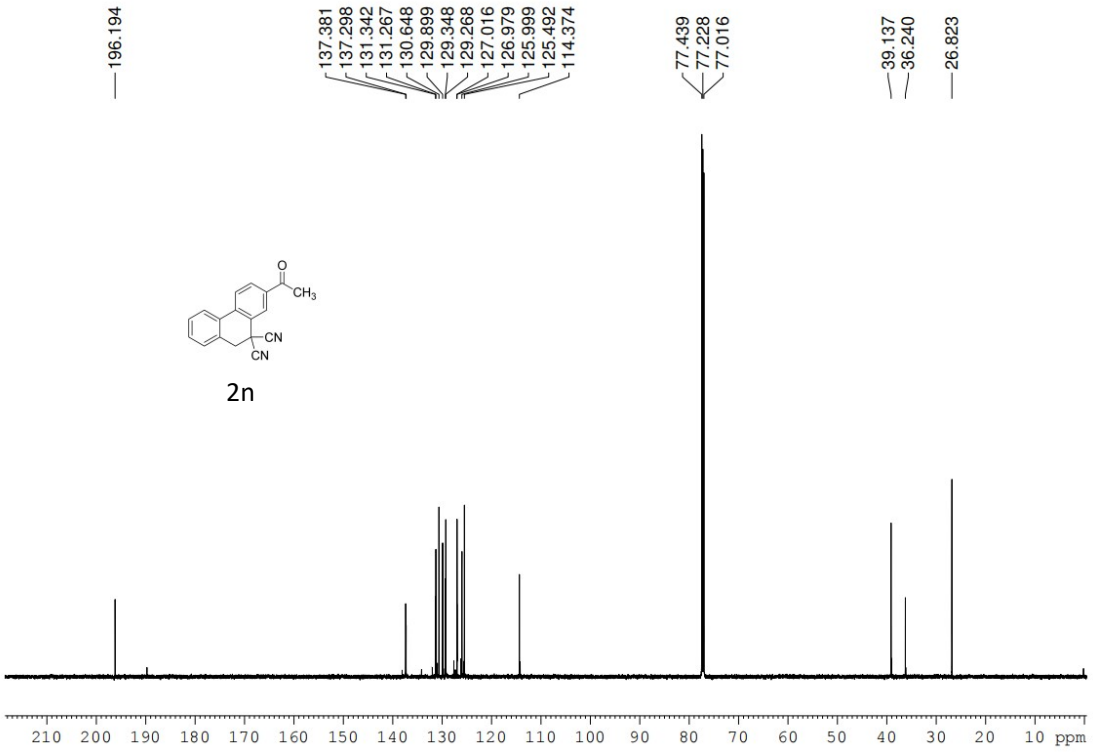
2m


165.686
137.265
132.708
131.456
130.917
130.587
129.903
129.342
129.262
128.194
126.857
125.811
125.485
114.397
77.439
77.228
77.015
52.832
39.224
36.199
O
O
CN
CN
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm

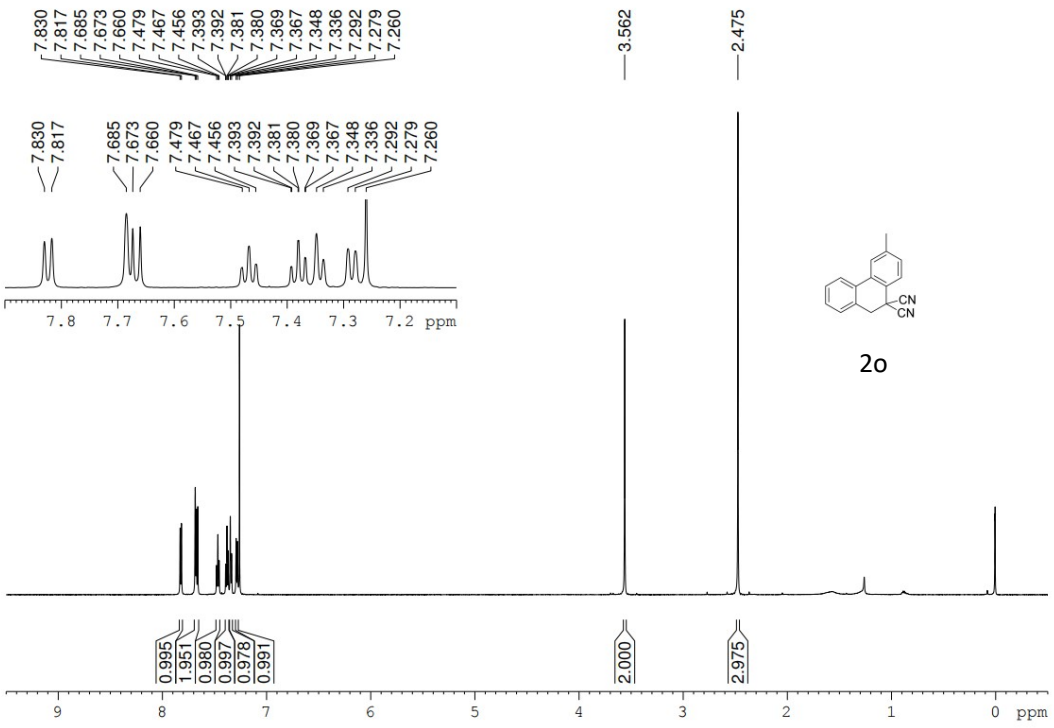
2m


8.351
8.348
8.168
8.165
8.155
8.152
7.985
7.972
7.882
7.870
7.529
7.518
7.516
7.505
7.503
7.476
7.474
7.463
7.461
7.451
7.449
7.400
7.388
7.261
3.628
2.689
8.4 8.2 8.0 7.8 7.6 7.4 7.2 ppm
O
CH3
CN
CN
0.965
1.014
1.021
1.139
1.117
1.030
1.037
2.000
3.032
10 9 8 7 6 5 4 3 2 1 0 ppm

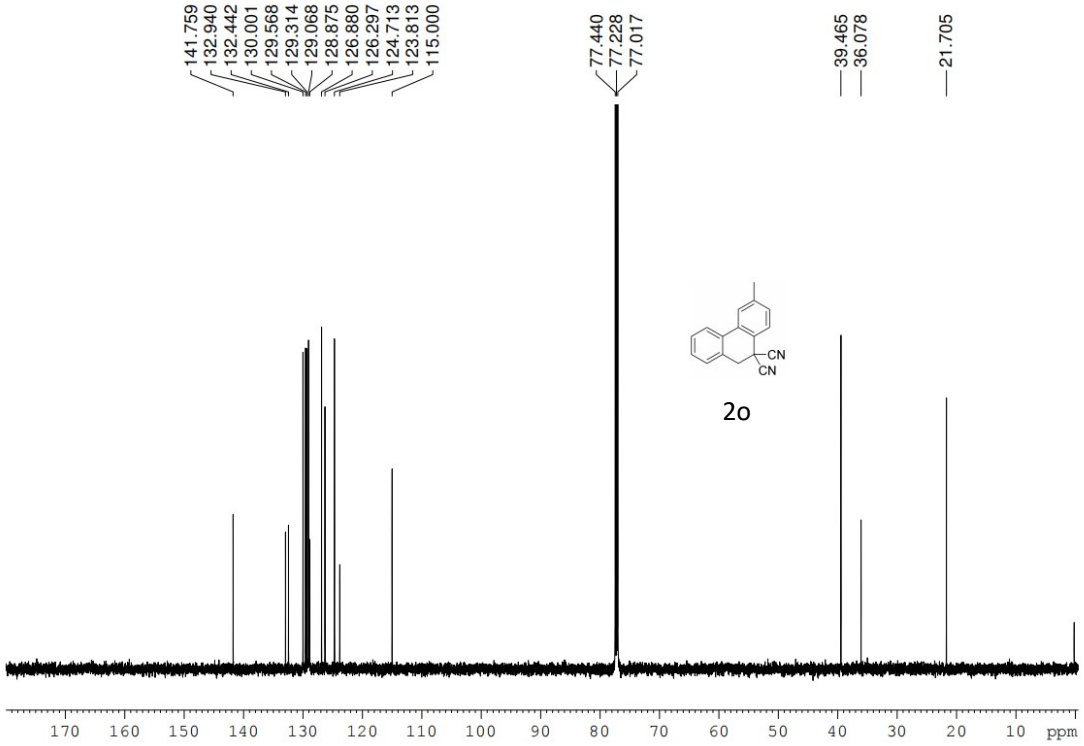
2n


196.194
137.381
137.298
131.342
131.267
130.648
129.899
129.348
129.268
127.016
126.979
125.999
125.492
114.374
77.439
77.228
77.016
39.137
36.240
26.823
O
CH3
CN
CN
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm

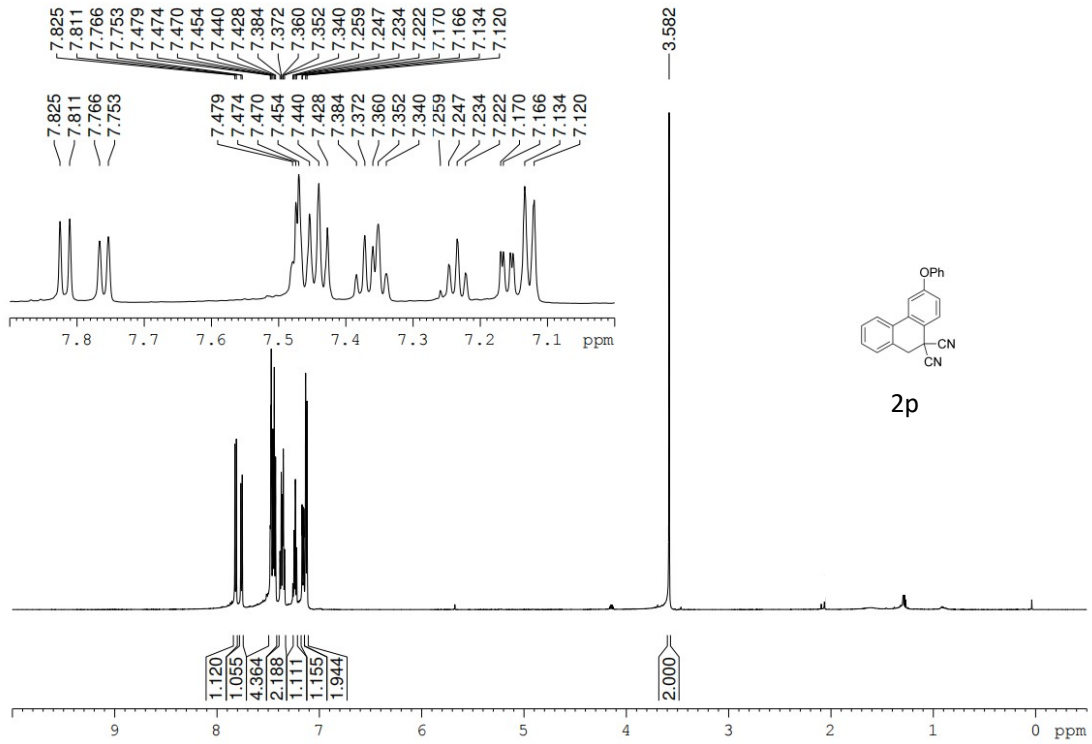
2n


7.830
7.817
7.685
7.673
7.660
7.479
7.467
7.456
7.393
7.392
7.381
7.380
7.369
7.367
7.348
7.336
7.292
7.279
7.260
3.562
2.475
7.8 7.7 7.6 7.5 7.4 7.3 7.2 ppm
CN
CN
0.995
1.951
0.980
0.997
0.978
0.991
2.000
2.975
9 8 7 6 5 4 3 2 1 0 ppm

2o

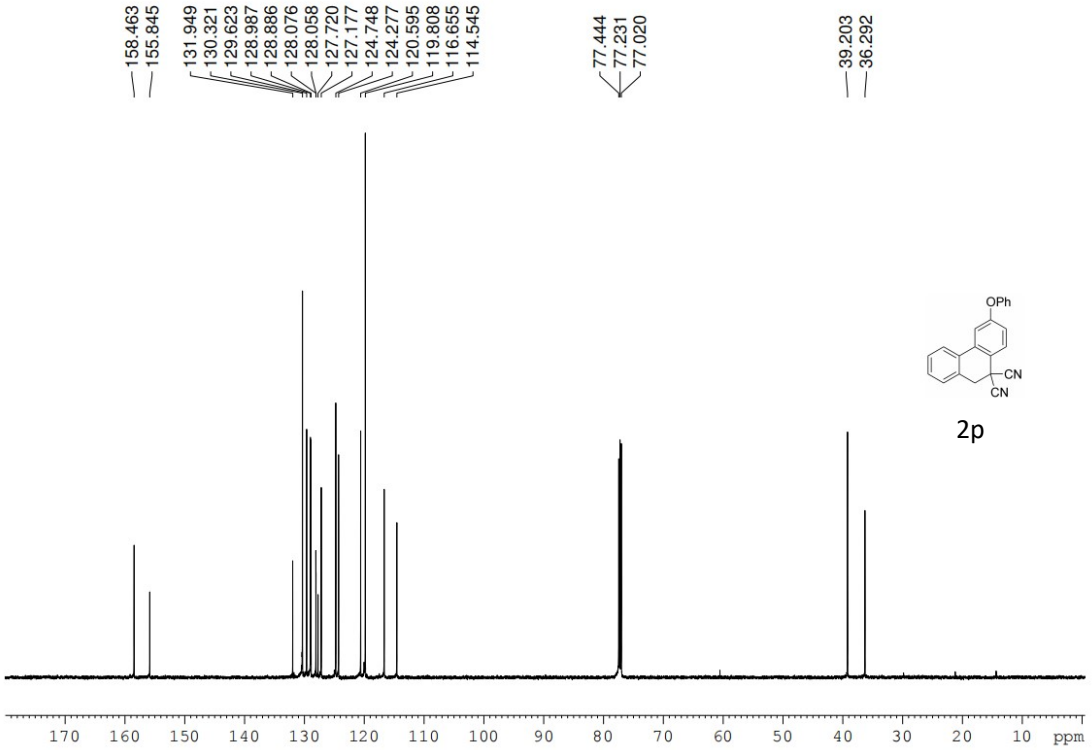

141.759
132.940
132.442
130.001
129.568
129.314
129.068
128.875
126.880
126.297
124.713
123.813
115.000
77.440
77.228
77.017
39.465
36.078
21.705
CN
CN
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm

2o

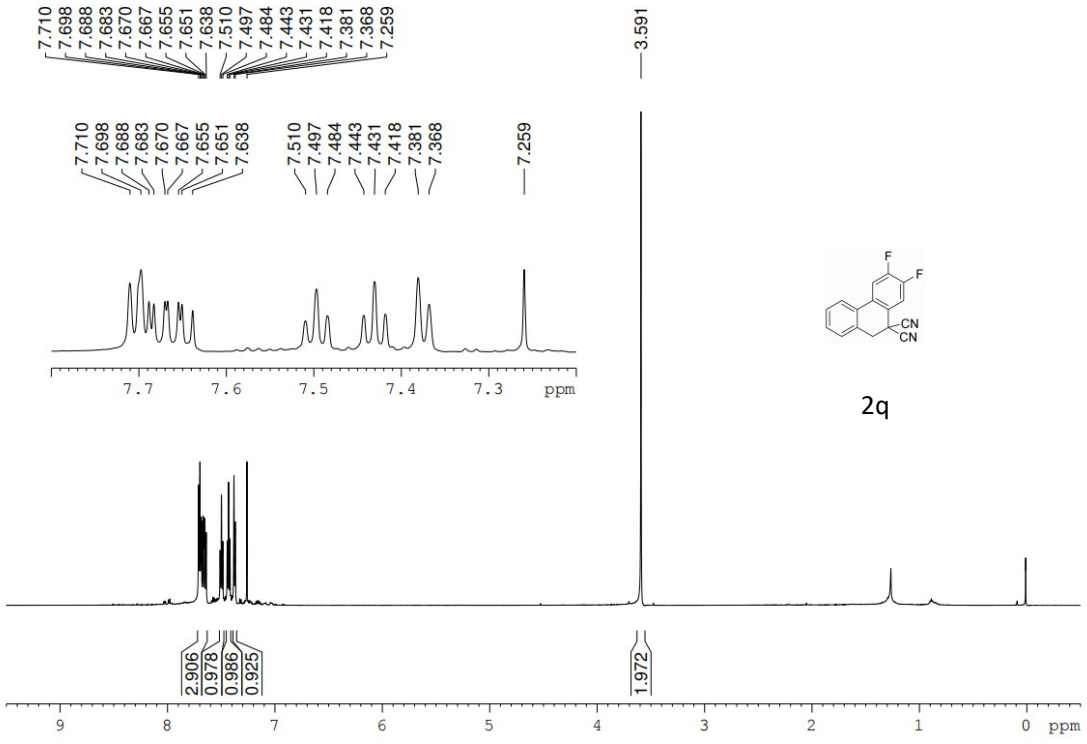

7.825
7.811
7.766
7.753
7.479
7.474
7.470
7.454
7.440
7.428
7.384
7.372
7.360
7.352
7.340
7.259
7.247
7.234
7.222
7.170
7.166
7.134
7.120
3.582
7.8 7.7 7.6 7.5 7.4 7.3 7.2 7.1 ppm
1.120
1.055
4.364
2.188
1.111
1.155
1.944
2.000
9 8 7 6 5 4 3 2 1 0 ppm

OPh
CN
CN

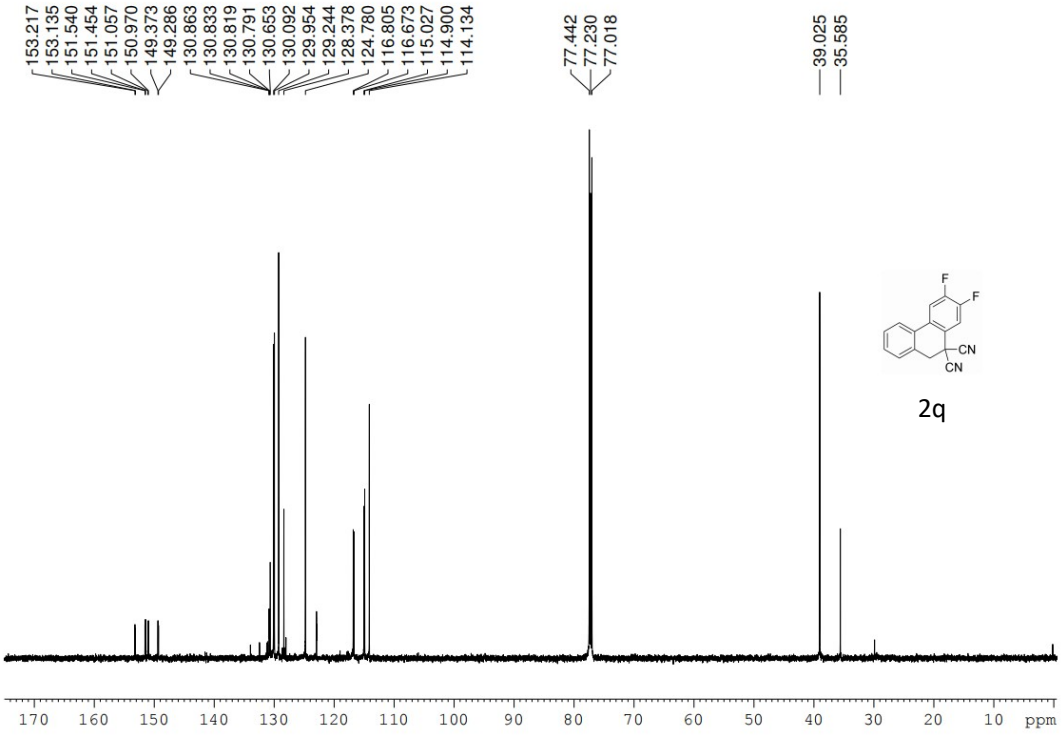
2p


158.463
155.845
131.949
130.321
129.623
128.987
128.886
128.076
128.058
127.720
127.177
124.748
124.277
120.595
119.808
116.655
114.545
77.444
77.231
77.020
39.203
36.292
OPh
CN
CN
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm

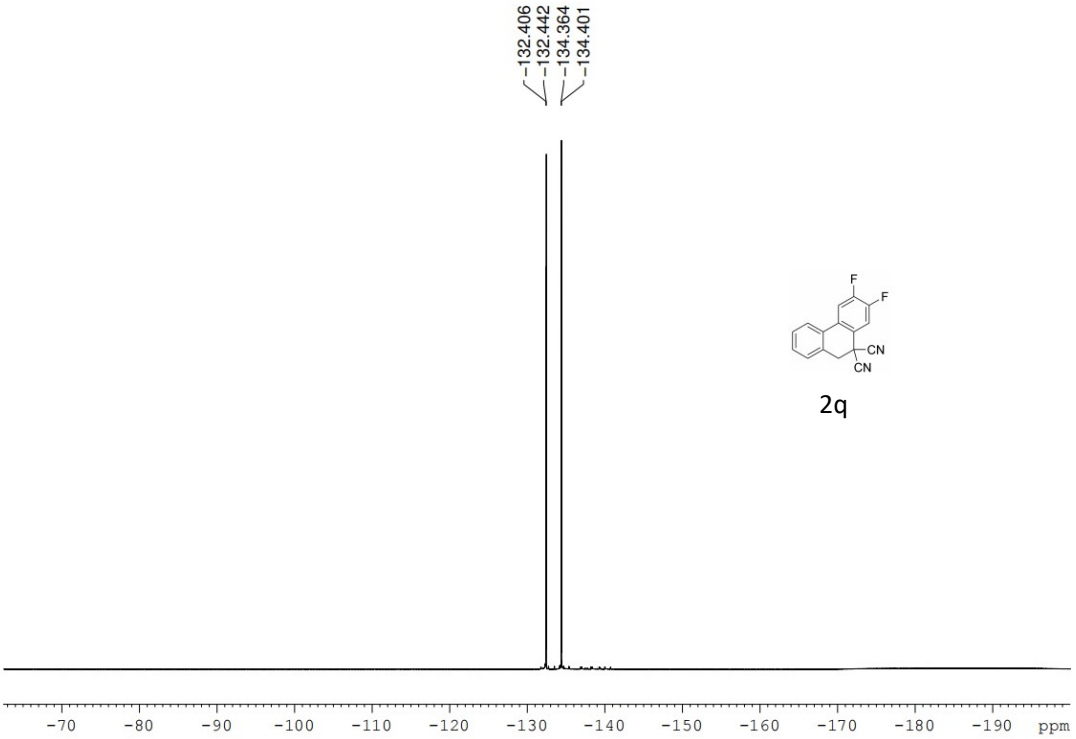
2p


7.710
7.698
7.688
7.683
7.670
7.667
7.655
7.651
7.638
7.510
7.497
7.484
7.443
7.431
7.418
7.381
7.368
7.259
3.591
7.7 7.6 7.5 7.4 7.3 ppm
F
F
CN
CN
2.906
0.978
0.986
0.925
1.972
9 8 7 6 5 4 3 2 1 0 ppm

2q

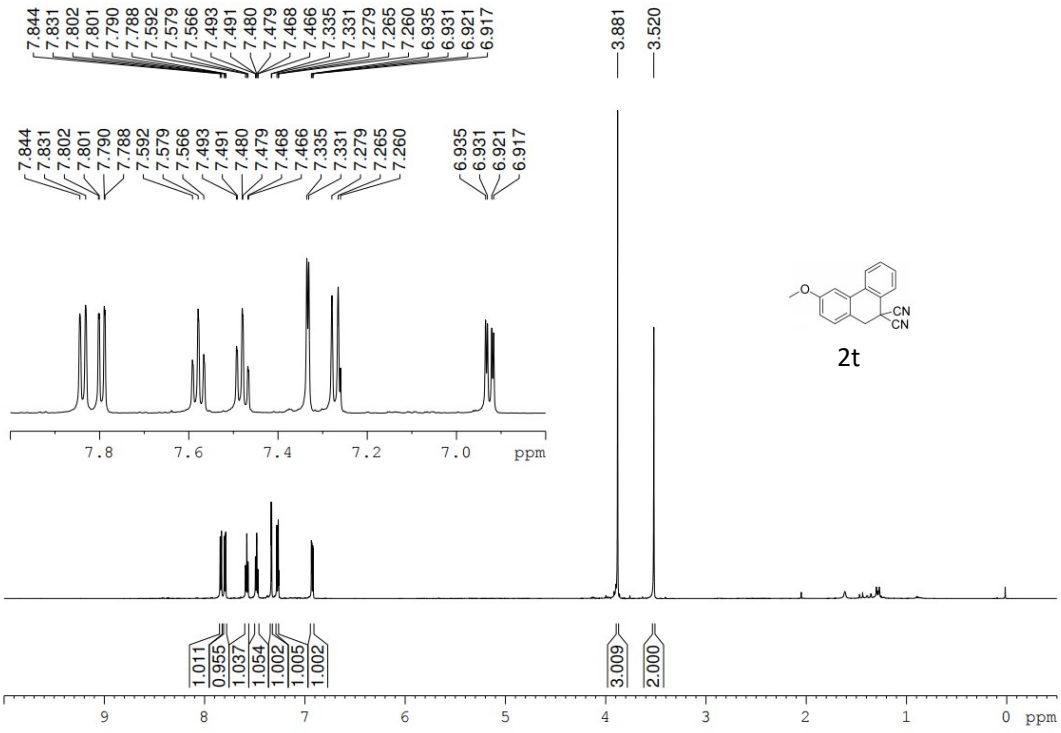

153.217
153.135
151.540
151.454
151.057
150.970
149.373
149.286
130.863
130.833
130.819
130.791
130.653
130.092
129.954
129.244
128.378
124.780
116.805
116.673
115.027
114.900
114.134
77.442
77.230
77.018
39.025
35.585
F
F
CN
CN
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm

2q

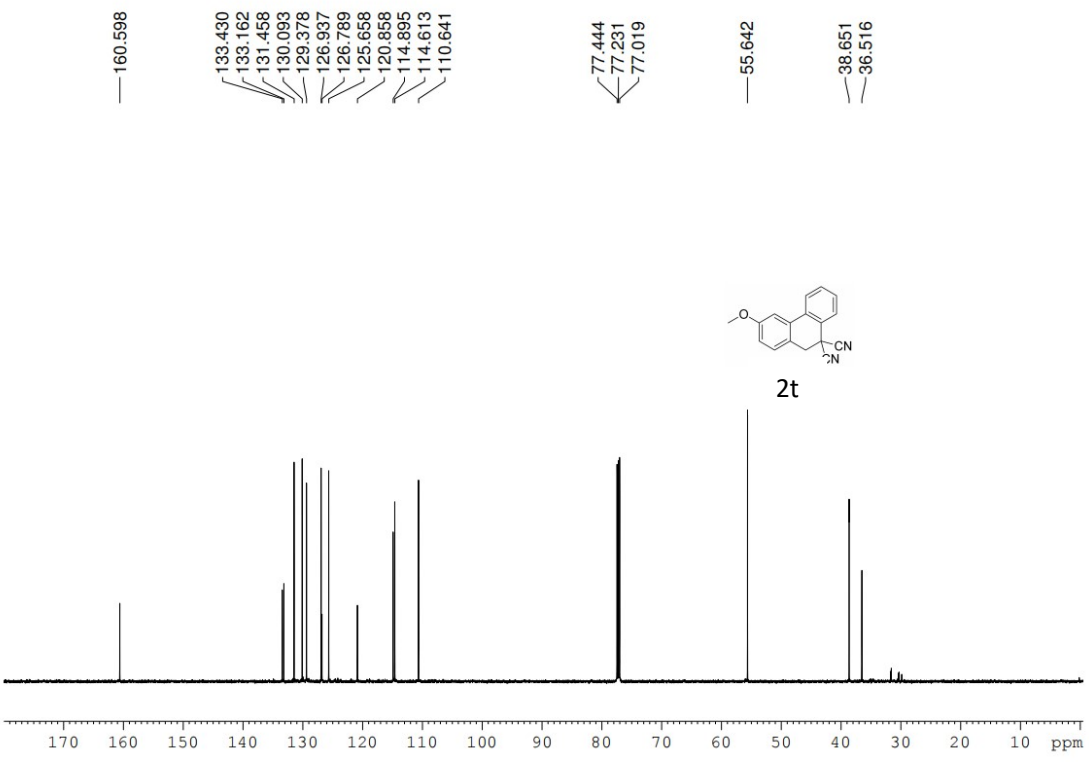

-132.406
-132.442
-134.364
-134.401
-70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 ppm

F
F
CN
CN

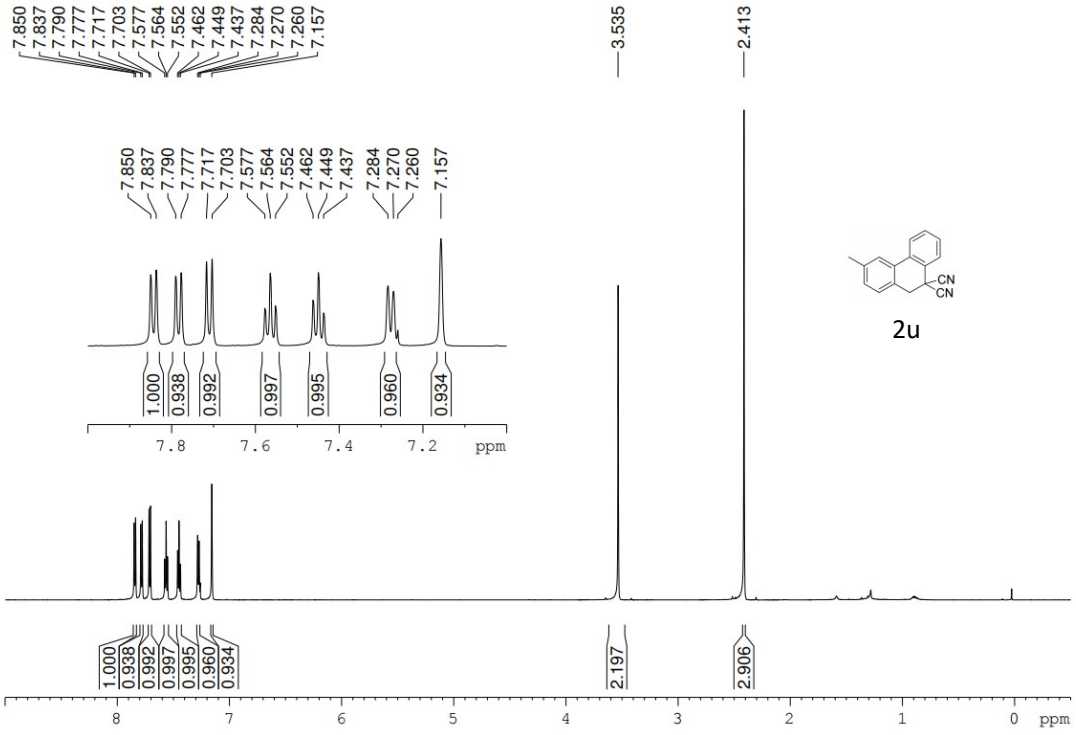
2q

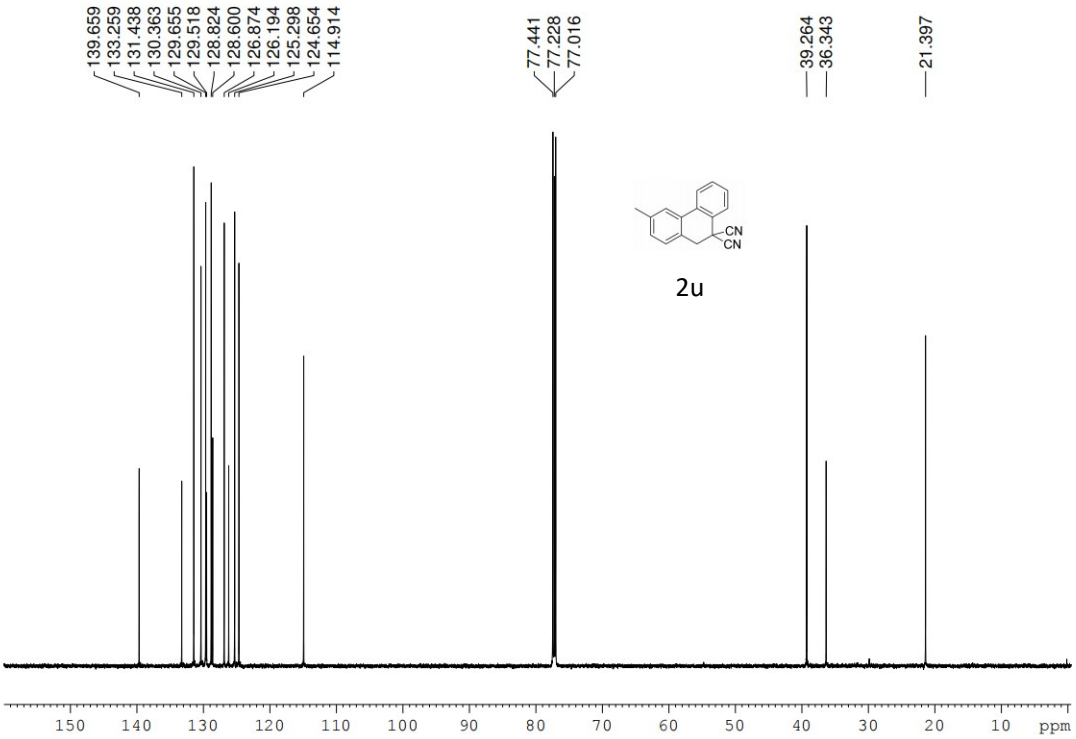

7.844
7.831
7.802
7.801
7.790
7.788
7.592
7.579
7.566
7.493
7.491
7.480
7.479
7.468
7.466
7.335
7.331
7.279
7.265
7.260
6.935
6.931
6.921
6.917
3.881
3.520
7.8
7.6
7.4
7.2
7.0
ppm
1.011
0.955
1.037
1.054
1.002
1.005
1.002
3.009
2.000
9
8
7
6
5
4
3
2
1
0 ppm
CN
CN

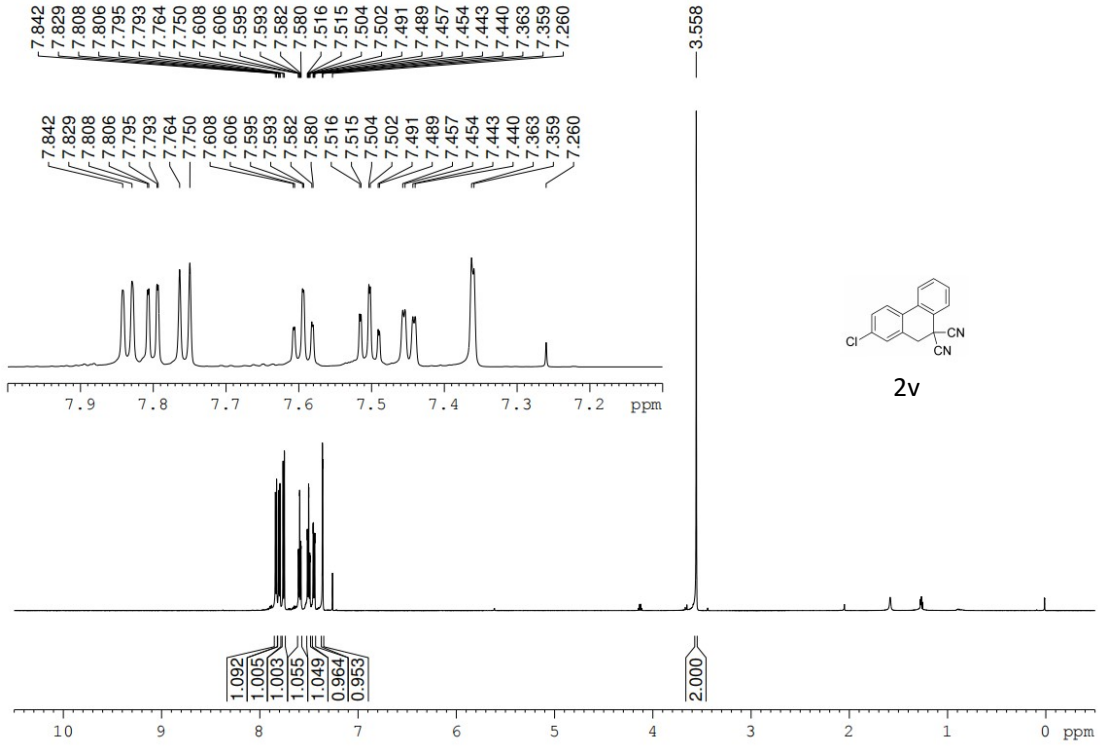
2t


160.598
133.430
133.162
131.458
130.093
129.378
126.937
126.789
125.658
120.858
114.895
114.613
110.641
77.444
77.231
77.019
55.642
38.651
36.516
CN
CN
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

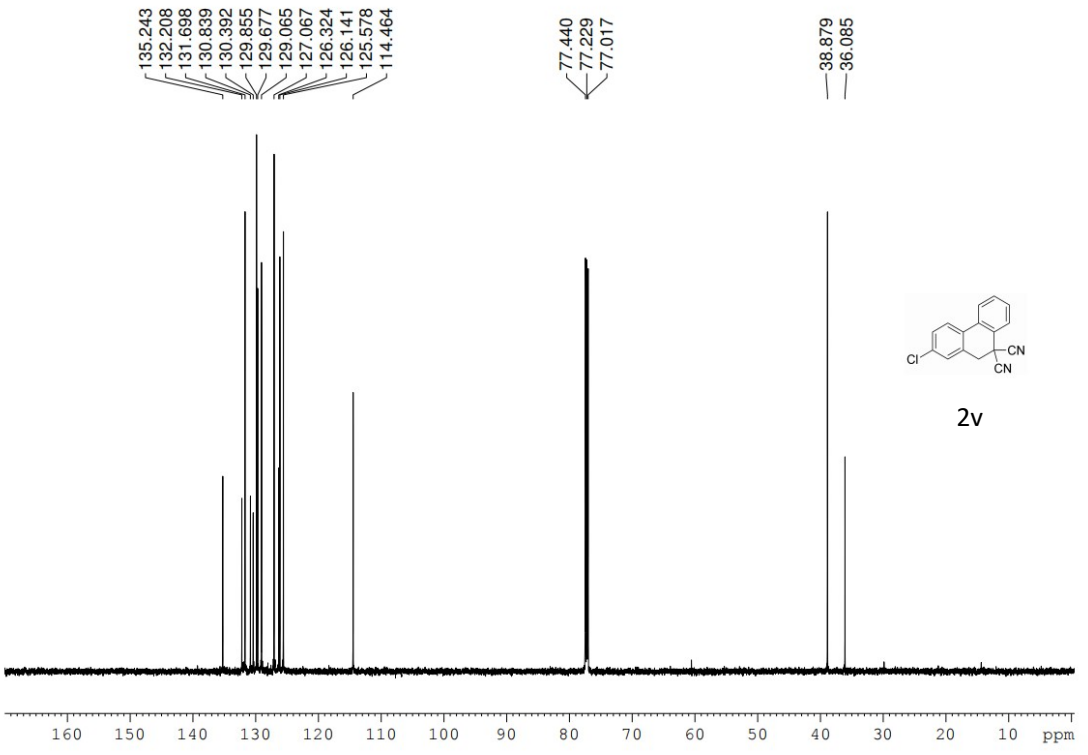
2t


7.850
7.837
7.790
7.777
7.717
7.703
7.577
7.564
7.552
7.462
7.449
7.437
7.284
7.270
7.260
7.157
3.535
2.413
1.000
0.938
0.992
0.997
0.995
0.960
0.934
2.197
2.906
CN
CN
2u
ppm

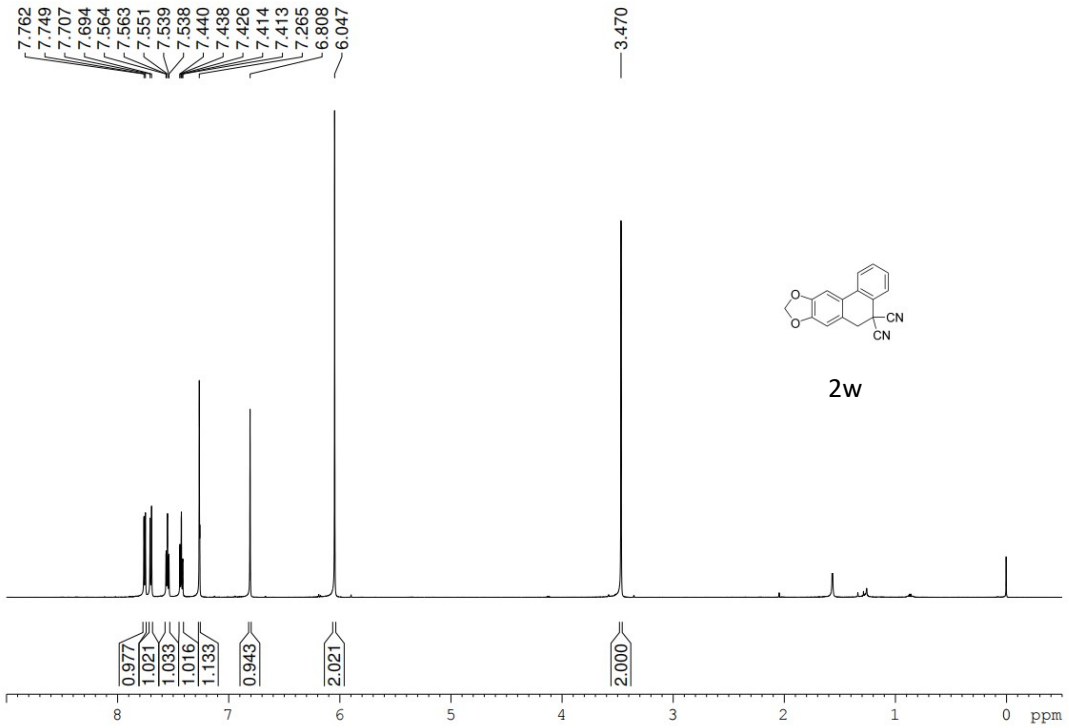

139.659
133.259
131.438
130.363
129.655
129.518
128.824
128.600
126.874
126.194
125.298
124.654
114.914
77.441
77.228
77.016
39.264
36.343
21.397
CN
CN
2u
ppm


7.842
7.829
7.808
7.806
7.795
7.793
7.764
7.750
7.608
7.606
7.595
7.593
7.582
7.580
7.516
7.515
7.504
7.502
7.491
7.489
7.457
7.454
7.443
7.440
7.363
7.359
7.260
3.558
7.9
7.8
7.7
7.6
7.5
7.4
7.3
7.2
ppm
1.092
1.005
1.003
1.055
1.049
0.964
0.953
2.000
10
9
8
7
6
5
4
3
2
1
0 ppm
Cl
CN
CN

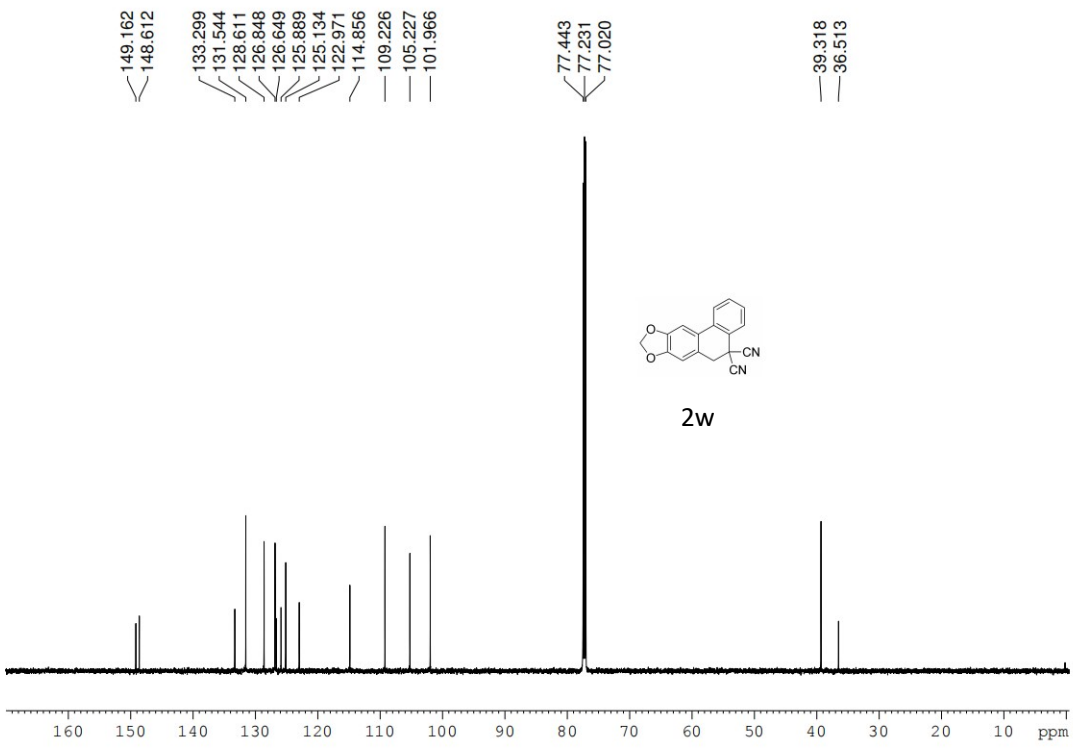
2v


135.243
132.208
131.698
130.839
130.392
129.855
129.677
129.065
127.067
126.324
126.141
125.578
114.464
77.440
77.229
77.017
38.879
36.085
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm
Cl
CN
CN

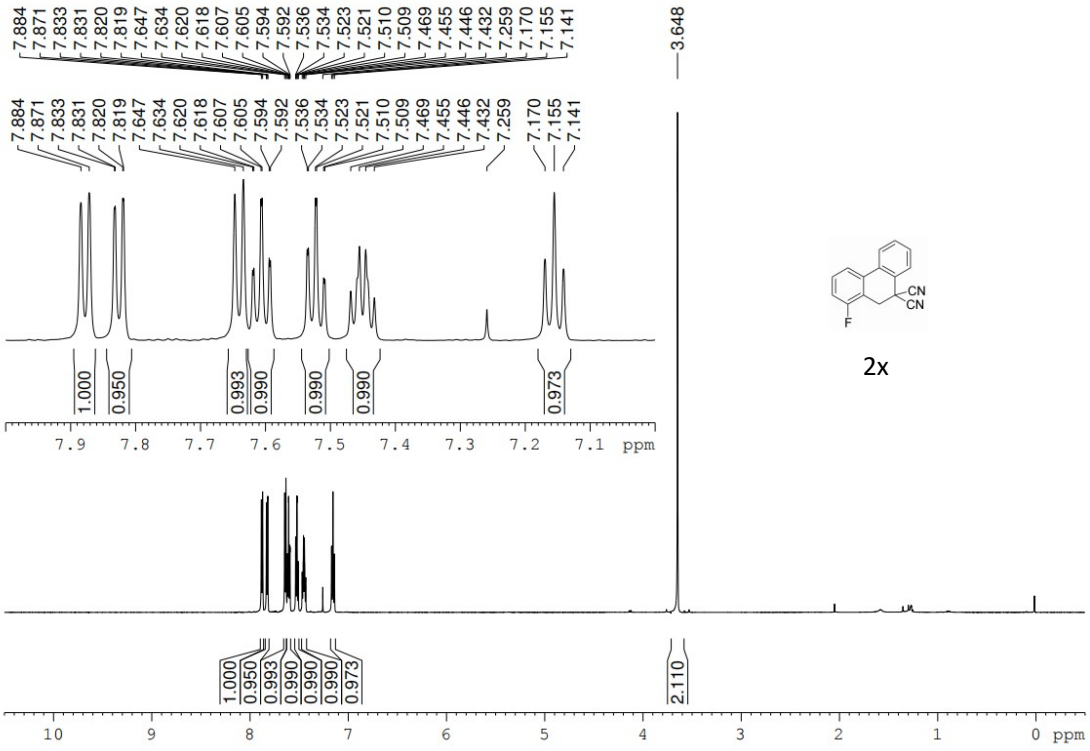
2v

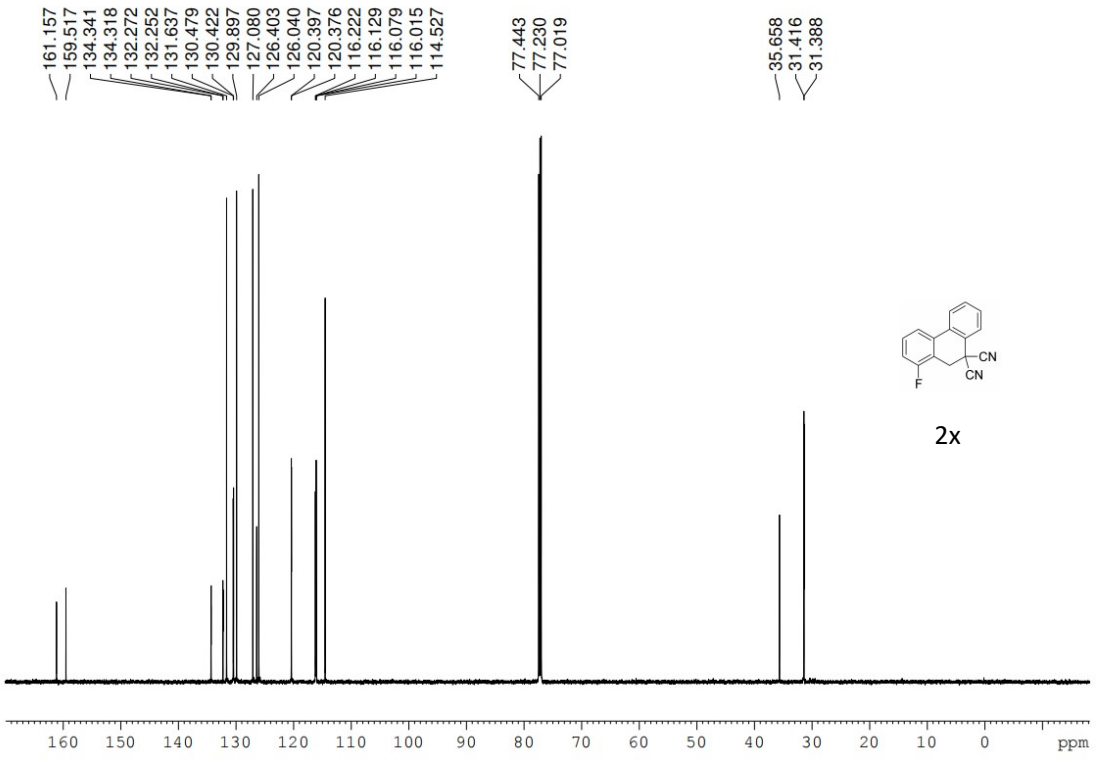

7.762
7.749
7.707
7.694
7.564
7.563
7.551
7.539
7.538
7.440
7.438
7.426
7.414
7.413
7.265
6.808
6.047
3.470
CN
CN
0.977
1.021
1.033
1.016
1.133
0.943
2.021
2.000
8
7
6
5
4
3
2
1
0
ppm

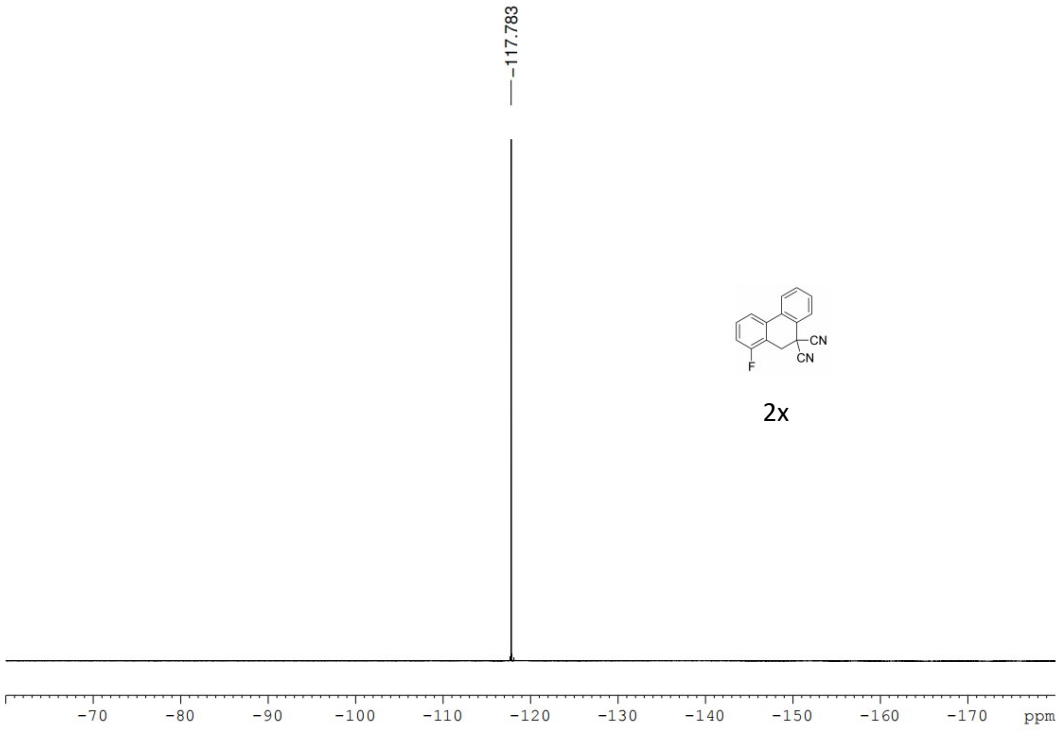
2w


149.162
148.612
133.299
131.544
128.611
126.848
126.649
125.889
125.134
122.971
114.856
109.226
105.227
101.966
77.443
77.231
77.020
39.318
36.513
CN
CN
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

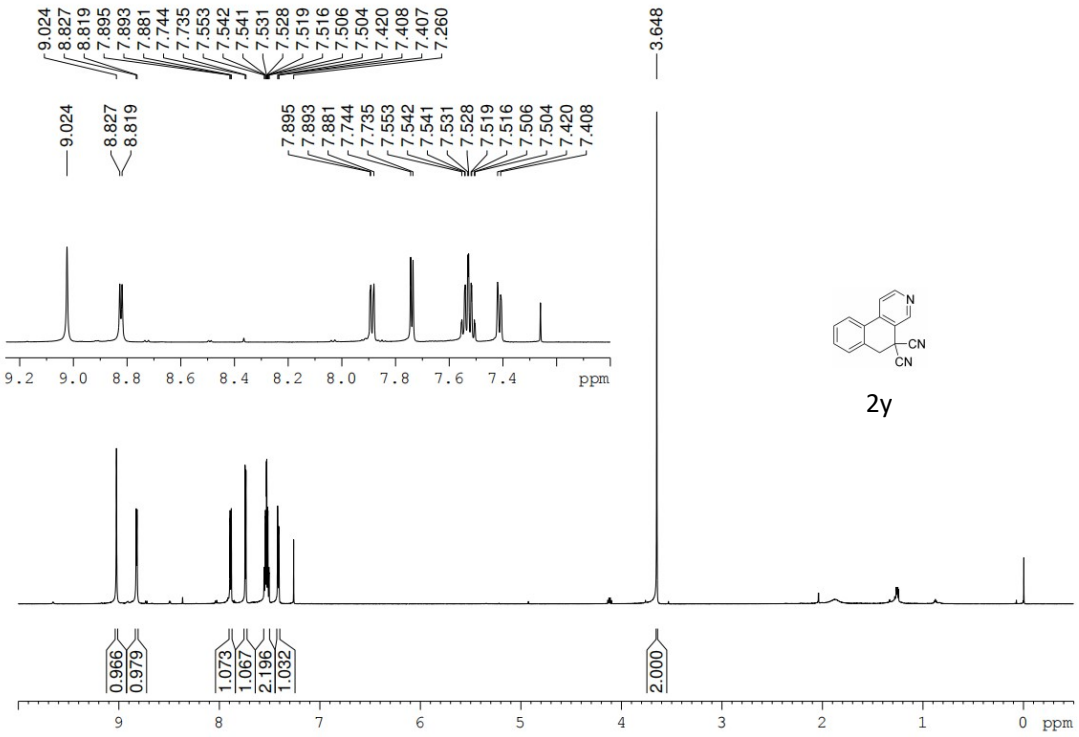
2w


7.884
7.871
7.833
7.831
7.820
7.819
7.647
7.634
7.620
7.618
7.607
7.605
7.594
7.592
7.536
7.534
7.523
7.521
7.510
7.509
7.469
7.455
7.446
7.432
7.259
7.170
7.155
7.141
3.648
1.000
0.950
0.993
0.990
0.990
0.990
0.973
2.110
CN
CN
F
2x
ppm

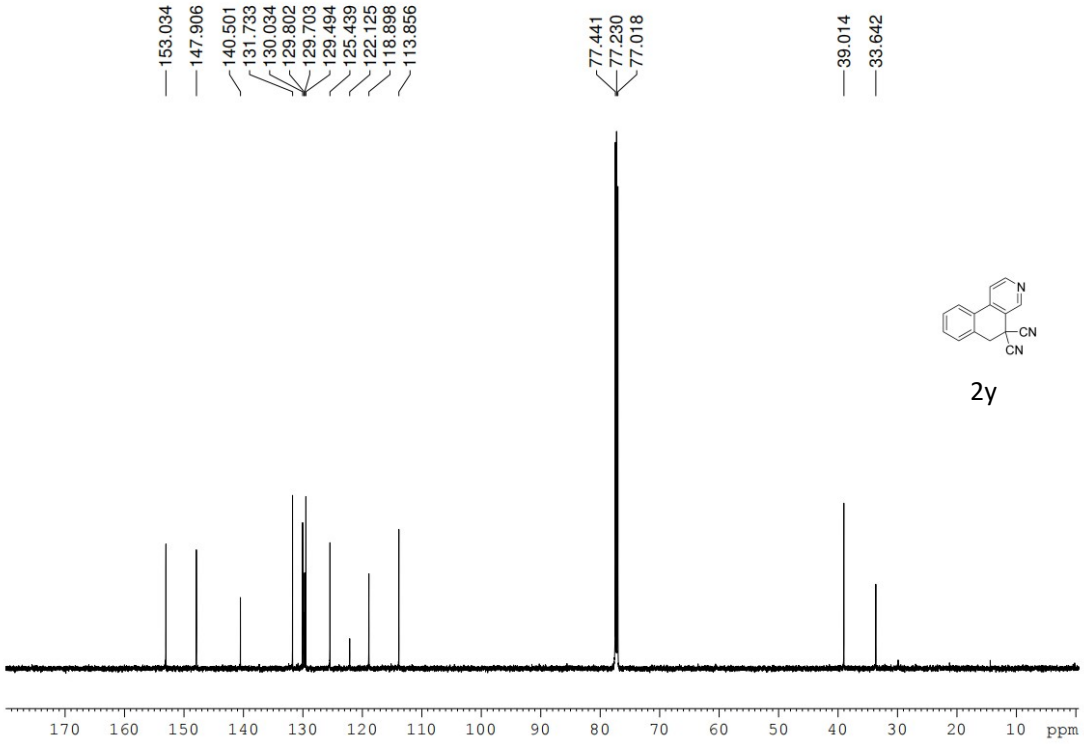

161.157
159.517
134.341
134.318
132.272
132.252
131.637
130.479
130.422
129.897
127.080
126.403
126.040
120.397
120.376
116.222
116.129
116.079
116.015
114.527
77.443
77.230
77.019
35.658
31.416
31.388
CN
CN
F
2x
ppm


-117.783
CN
CN
F
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
ppm

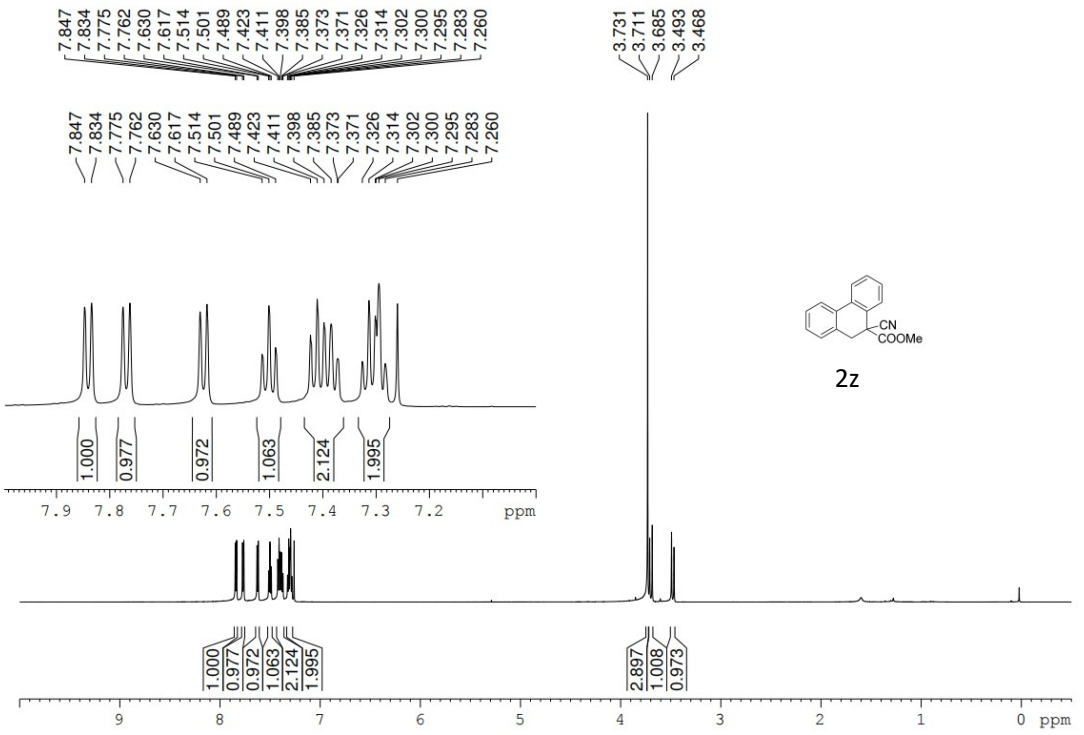
2x


9.024
8.827
8.819
7.895
7.893
7.881
7.744
7.735
7.553
7.542
7.541
7.531
7.528
7.519
7.516
7.506
7.504
7.420
7.408
7.407
7.260
3.648
9.2
9.0
8.8
8.6
8.4
8.2
8.0
7.8
7.6
7.4
ppm
N
CN
CN
0.966
0.979
1.073
1.067
2.196
1.032
2.000
9
8
7
6
5
4
3
2
1
0
ppm

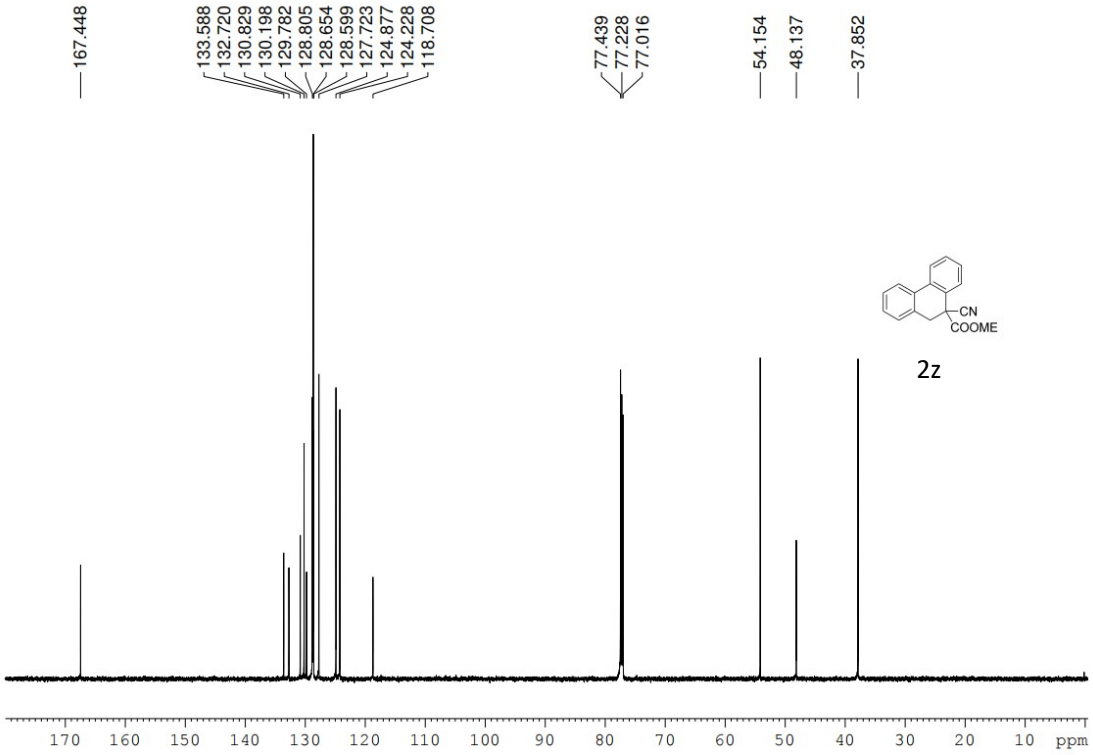
2y


153.034
147.906
140.501
131.733
130.034
129.802
129.703
129.494
125.439
122.125
118.898
113.856
77.441
77.230
77.018
39.014
33.642
N
CN
CN
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm

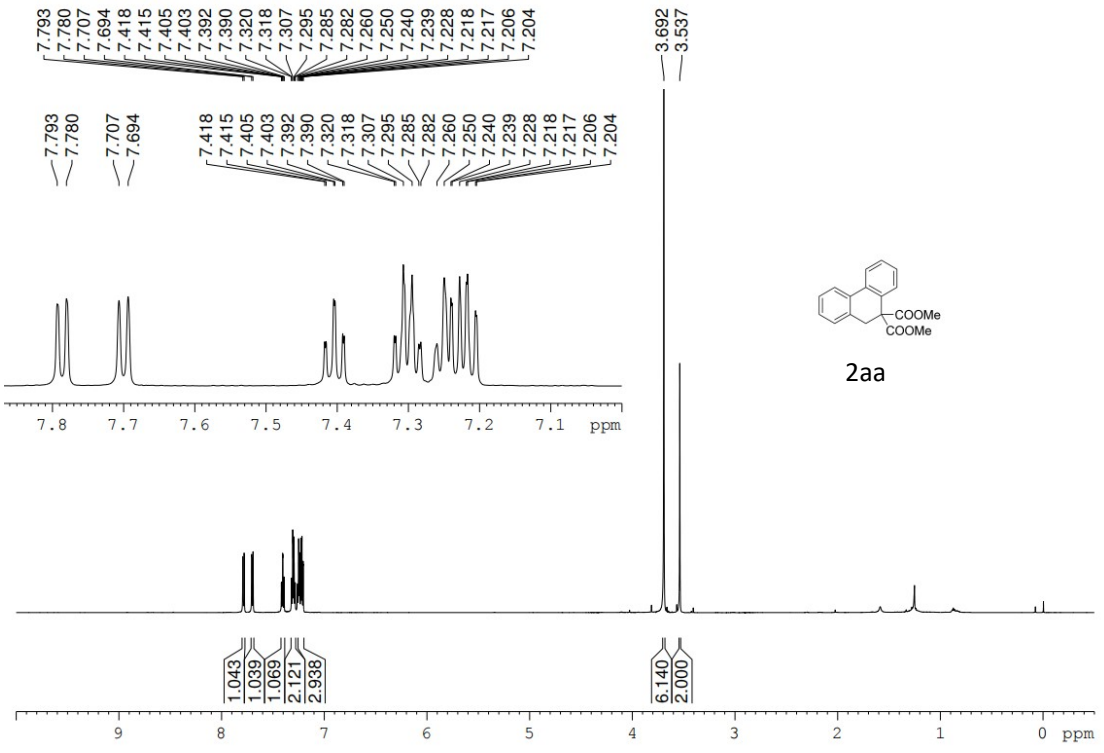
2y


7.847
7.834
7.775
7.762
7.630
7.617
7.514
7.501
7.489
7.423
7.411
7.398
7.385
7.373
7.371
7.326
7.314
7.302
7.300
7.295
7.283
7.260
3.731
3.711
3.685
3.493
3.468
1.000
0.977
0.972
1.063
2.124
1.995
2.897
1.008
0.973
CN
COOMe
7.9 7.8 7.7 7.6 7.5 7.4 7.3 7.2 ppm
9 8 7 6 5 4 3 2 1 0 ppm

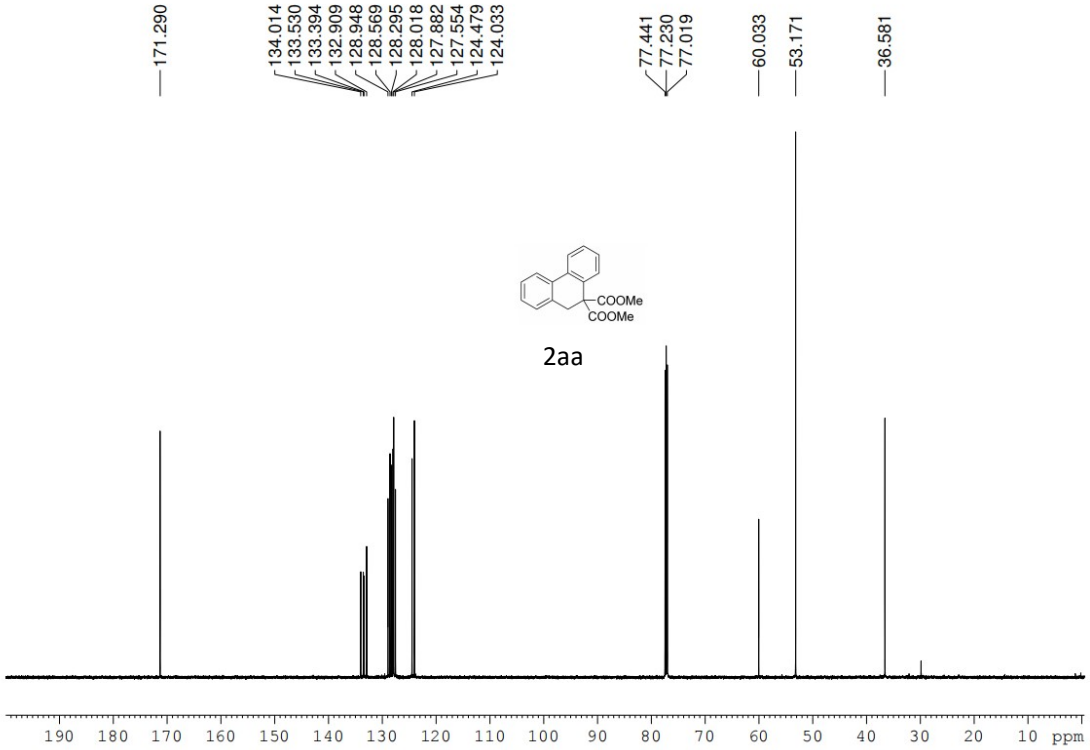
2z


167.448
133.588
132.720
130.829
130.198
129.782
128.805
128.654
128.599
127.723
124.877
124.228
118.708
77.439
77.228
77.016
54.154
48.137
37.852
CN
COOME
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm

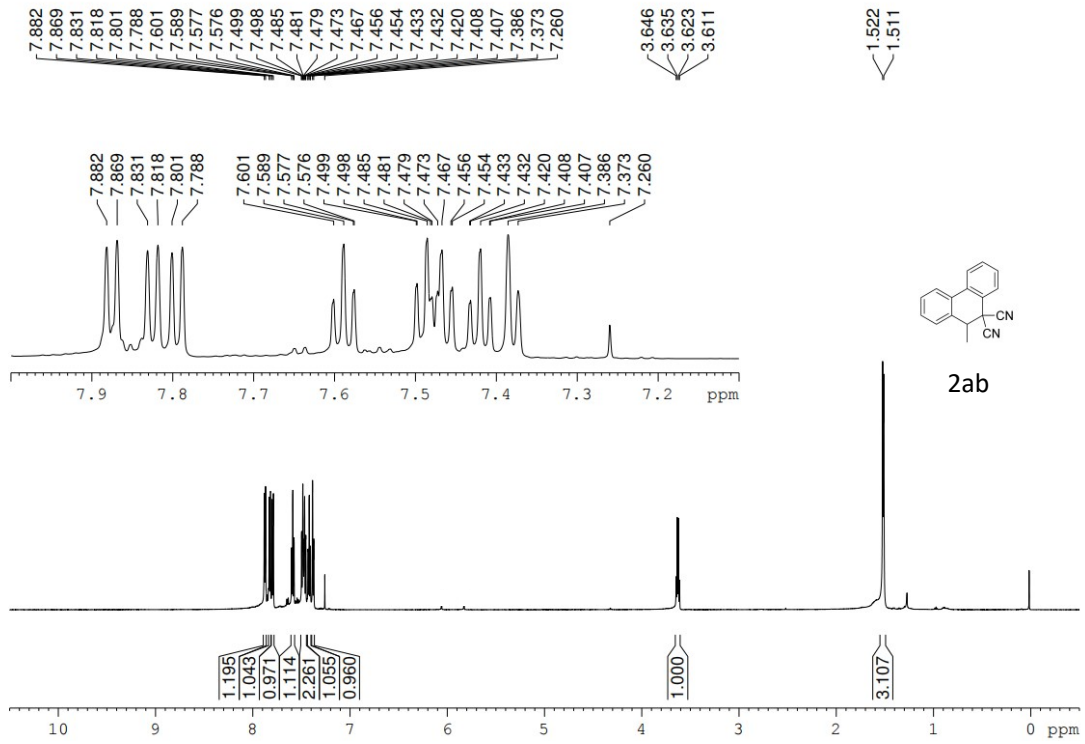
2z


7.793
7.780
7.707
7.694
7.418
7.415
7.405
7.403
7.392
7.390
7.320
7.318
7.307
7.295
7.285
7.282
7.260
7.250
7.240
7.239
7.228
7.218
7.217
7.206
7.204
3.692
3.537
COOMe
COOMe
7.8 7.7 7.6 7.5 7.4 7.3 7.2 7.1 ppm
1.043
1.039
1.069
2.121
2.938
6.140
2.000
9 8 7 6 5 4 3 2 1 0 ppm

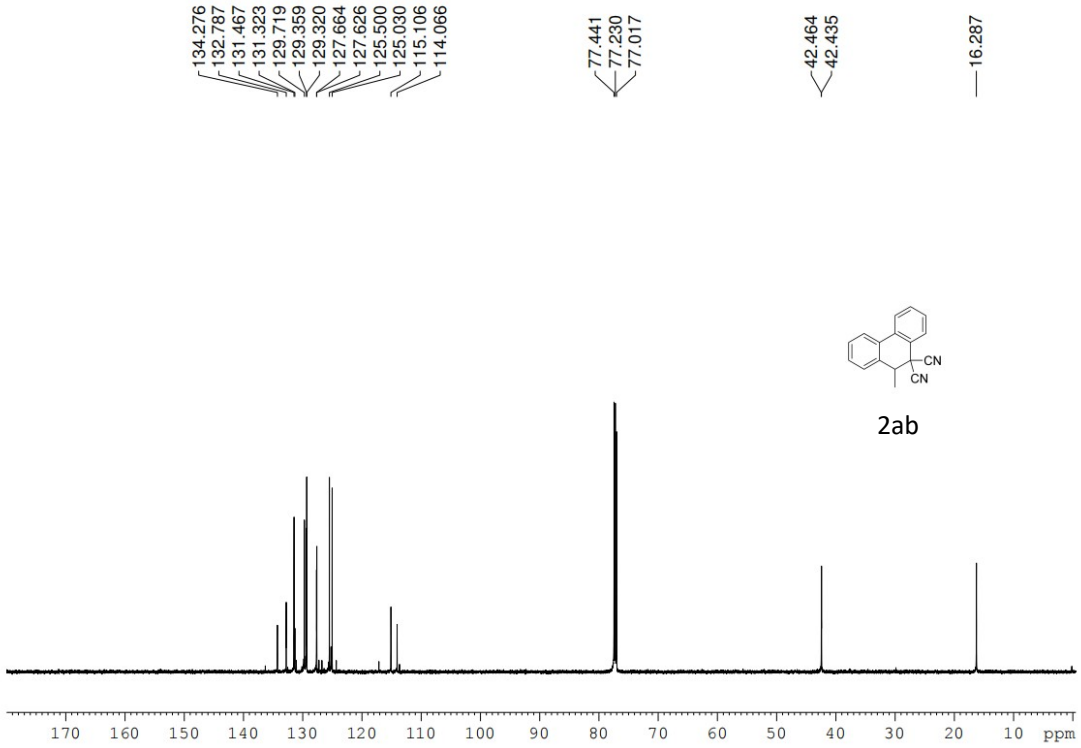
2aa

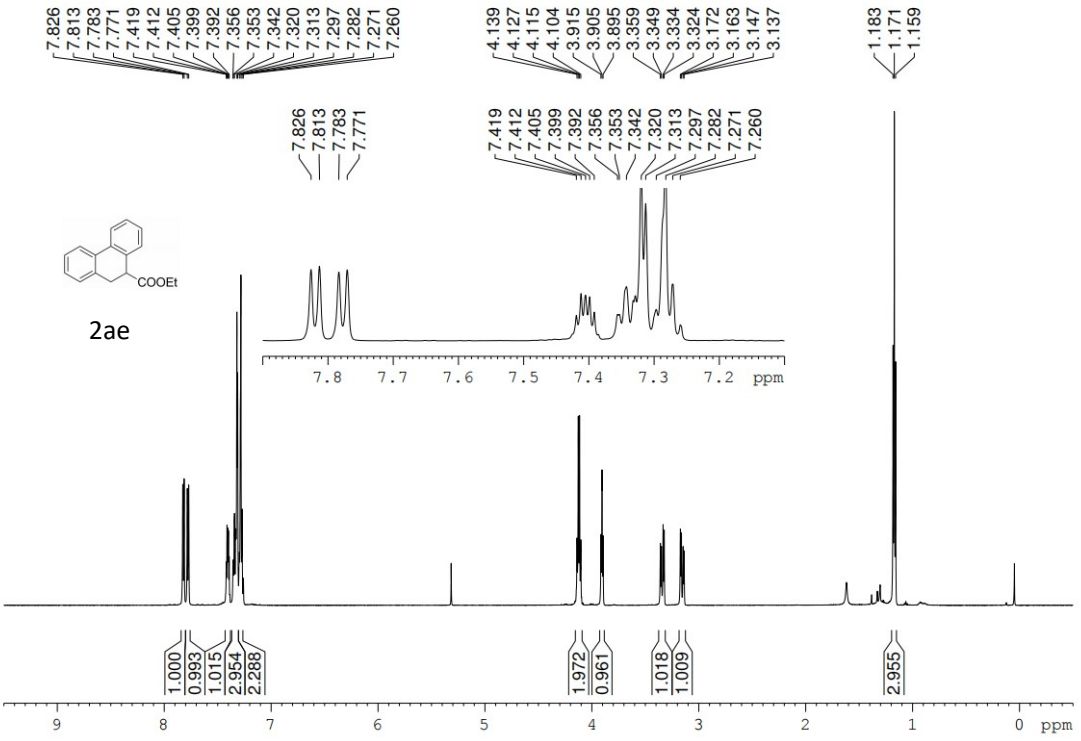

171.290
134.014
133.530
133.394
132.909
128.948
128.569
128.295
128.018
127.882
127.554
124.479
124.033
77.441
77.230
77.019
60.033
53.171
36.581
COOMe
COOMe
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm

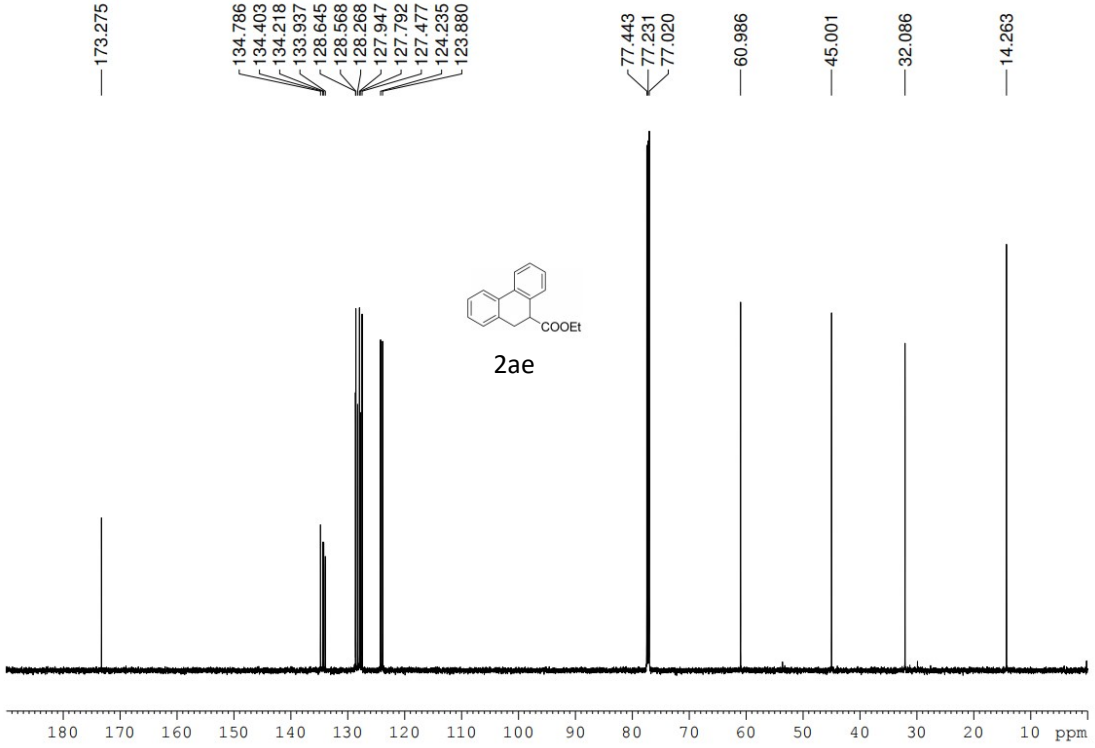
2aa


7.882
7.869
7.831
7.818
7.801
7.788
7.601
7.589
7.577
7.576
7.499
7.498
7.485
7.481
7.479
7.473
7.467
7.456
7.454
7.433
7.432
7.420
7.408
7.407
7.386
7.373
7.260
3.646
3.635
3.623
3.611
1.522
1.511
CN
CN
7.9 7.8 7.7 7.6 7.5 7.4 7.3 7.2 ppm
1.195
1.043
0.971
1.114
2.261
1.055
0.960
1.000
3.107
10 9 8 7 6 5 4 3 2 1 0 ppm

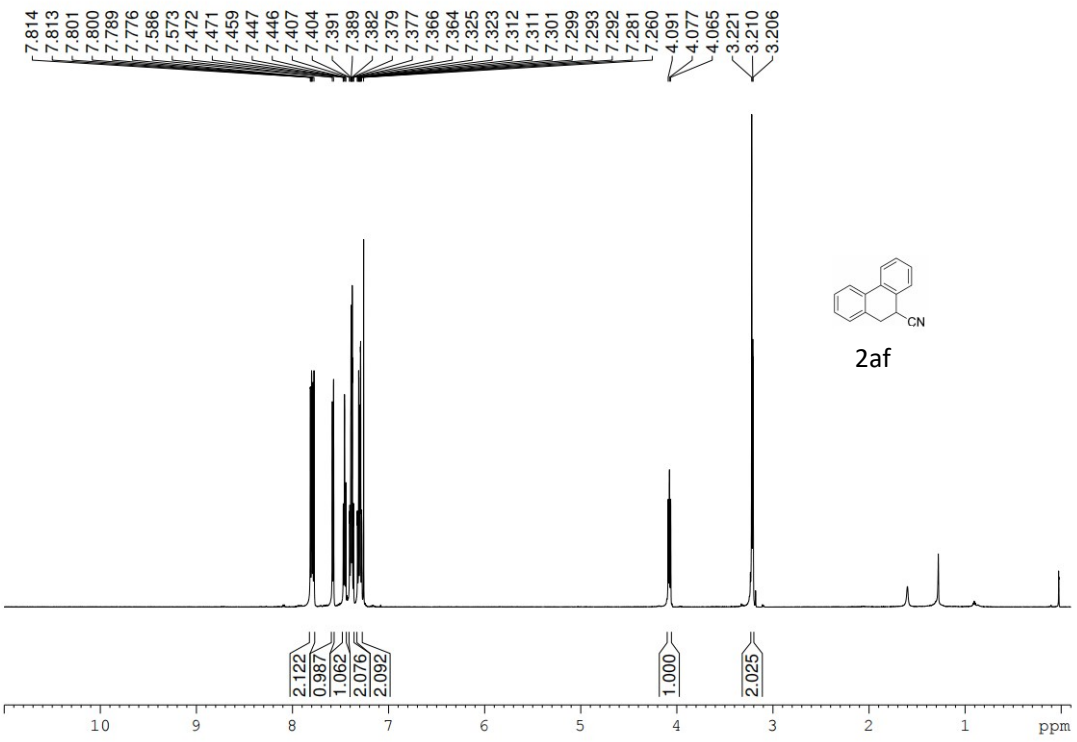
2ab


134.276
132.787
131.467
131.323
129.719
129.359
129.320
127.664
127.626
125.500
125.030
115.106
114.066
77.441
77.230
77.017
42.464
42.435
16.287
CN
CN
2ab
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm

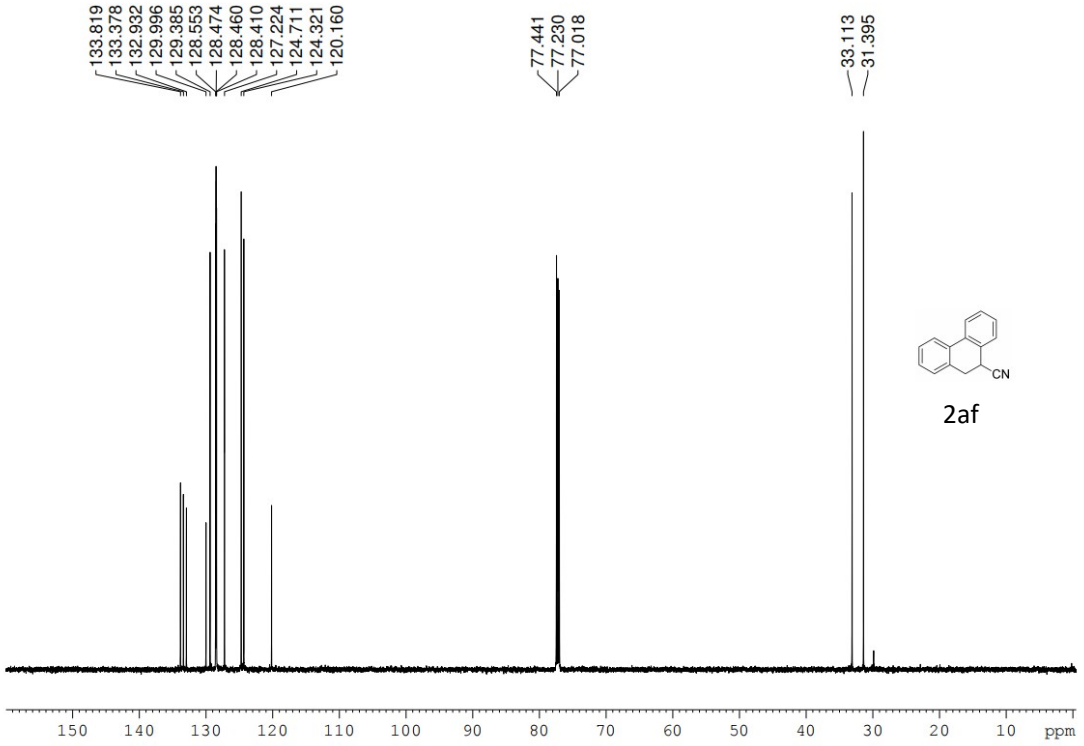

7.826
7.813
7.783
7.771
7.419
7.412
7.405
7.399
7.392
7.356
7.353
7.342
7.320
7.313
7.297
7.282
7.271
7.260
4.139
4.127
4.115
4.104
3.915
3.905
3.895
3.359
3.349
3.334
3.324
3.172
3.163
3.147
3.137
1.183
1.171
1.159
COOEt
2ae
7.8 7.7 7.6 7.5 7.4 7.3 7.2 ppm
1.000
0.993
1.015
2.954
2.288
1.972
0.961
1.018
1.009
2.955
9 8 7 6 5 4 3 2 1 0 ppm


173.275
134.786
134.403
134.218
133.937
128.645
128.568
128.268
127.947
127.792
127.477
124.235
123.880
77.443
77.231
77.020
60.986
45.001
32.086
14.263
COOEt
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm

2ae


7.814
7.813
7.801
7.800
7.789
7.776
7.586
7.573
7.472
7.471
7.459
7.447
7.446
7.407
7.404
7.391
7.389
7.382
7.379
7.377
7.366
7.364
7.325
7.323
7.312
7.311
7.301
7.299
7.293
7.292
7.281
7.260
4.091
4.077
4.065
3.221
3.210
3.206
CN
2.122
0.987
1.062
2.076
2.092
1.000
2.025
10 9 8 7 6 5 4 3 2 1 ppm

2af


133.819
133.378
132.932
129.996
129.385
128.553
128.474
128.460
128.410
127.224
124.711
124.321
120.160
77.441
77.230
77.018
33.113
31.395
CN
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

2af