Supporting information

Design and Synthesis of Pyrene Containing Unusual α-Amino Acid Derivatives

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General information, characterization data, and copies of NMR spectra

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1. General information

All the commercially available chemicals were bought from TCI and Spectrochem Company and were used without further purification. Progress of all reactions was monitored by chromatographic technique (TLC analysis) with suitable solvent systems (EtOAc/Pet ether) and observation was done under UV light, and immersion in $KMnO_4$ solution. Moisture sensitive (dry/anhydrous) reactions were done with oven-dried glassware under nitrogen/argon atmosphere by using syringe-septum techniques. Column chromatography was done by 100-200 mesh silica gel in all cases with appropriate solvent systems. DCM was distilled with calcium hydride (CaH_2).

All IR samples were recorded with $CHCl_3$ as solvents on Nicolet Impact-400 FTIR spectrometer. Nuclear magnetic resonance (NMR) spectra (^{1}H and ^{13}CNMR) have been recorded on 400 and 500 MHz spectrometers (Bruker) with $CDCl_3$ and DMSO solvent and chemical shifts (δ ppm) are reported relative to internal standard such as TMS. The standard abbreviations s, d, t, q and m, refer to singlet, doublet, triplet, quartet, and multiplet, respectively.[1] Coupling constants (*J*) are reported in Hertz. Mass spectra (HRMS) have been recorded under positive ion electrospray ionization (ESI, Q-TOF) mode.

2.Procedure for the preparation of new compounds

Tetramethyl-1,4,5,8-naphthalenetetracarboxylate 16: To a solution of 3 g (11.1 mmol) of 1,4,5,8-naphthalic anhydride 1 in 35 mL of MeOH was added 9.7 g (70.49 mmol) of dimethyl sulfate under nitrogen atmosphere. The reaction mixture was stirred and added 4.7 g (83.85 mmol) of KOH in 120 ml of MeOH carefully. The reaction mixture was stirred for 2.5 hour and then cool down room temperature. The precipitated white solid (3.2 g, 81%) was filtered and dried. ^{1}H and ^{13}C NMR spectra matched with the literature reports.[2]

1,4,5,8-Tetrakis(hydroxymethyl)naphthalene 17: To a solution of 3 g (7.2 mmol) of tetramethyl-1,4,5,8-Naphthalenetetracarboxylate **2** in toluene 150 mL (86.5 mmol) diisobutylalumium hydride (1.0 M solution in hexane) was stirred for 36 hours under nitrogen atmosphere at reflux condition. The reaction mixture was poured into 60 mL of MeOH and 20 mL of HCl and filtrated. The white solid (1.6 g, 78%) was obtained. ^{1}H and ^{13}C NMR spectra matched with the literature reports.[2]

1,4,5,8-Tetrakis(bromomethyl)naphthalene 14: To a solution of 1 g (3.7 mmol) of 1,4,5,8-tetrakis (hydroxymethyl) naphthalene **3** in 65 mL of anhydrous dioxane was added 2.8 mL (29.6 mmol) of PBr_3 under nitrogen atmosphere. After 1 hour, additional 1.4 mL of PBr_3 was added, and stirred for 20 hours at room temperature. To 20 mL of H_2O, the reaction mixture was added. The white solid was formed. (1.77 g, 88%). ^1H and ^{13}C NMR spectra matched with the literature reports.[2]

Ethyl 6,7-bis(bromomethyl)-2isocyano-2,-dihydro-1H-phenalene-2-carboxylate 18: To a solution of Ethyl isocyanoacetate (EICA) 200 mg (1.7 mmol) in 20 ml dry acetonitrile was added K_2CO_3 (6.1 mmol, 3.5 equiv.), TBAB (1.7 mmol, 1 equiv.) was added stir reaction mixture 30 min and 1, 4, 5, 8 tetrakisbromomethyl naphthalene (1.7 mmol, 1 equiv.) was added reflux the reaction mixture for 12 h at same temperature. After completion of starting material (TLC monitoring), the reaction mixture was cooled and filtered through cintered funnel. The filtrate was evaporated at reduced pressure and purified by silica gel column chromatography. **Yield** (150 mg, 18%), colourless liquid. $\boldsymbol{R_f}$ = 0.38 (30% EtOAc-petroleum ether).

^{1}H NMR (500 MHz $CDCl_3$): δ 7.26 (d, *J* = 7.24 Hz, 2 H), 7.15 (d, *J* = 7.12 Hz, 2 H), 5.05 (s, 4H), 4.33 (q, *J* = 14.32 Hz, 2H), 3.66 (d, *J* = 15.66 Hz, 2H), 3.50 (d, *J* = 15.66 Hz, 2H), 1.35 (t, *J* = 7.14 Hz, 3H). **^{13}C NMR** (125 MHz $CDCl_3$): δ 168.3, 158.9, 132.0, 127.9, 127.3, 126.5, 125.2, 120.2, 69.2, 63.1, 61.7, 39.7, 14.0 ppm.

IR (neat): 501, 1222, 1350, 1696, 1735, 2150 cm^{-1}.

HRMS *m/z:* calculated $C_{19}H_{17}Br_2NO_2[M+H]^+$ 452.1580, found: 452.1580.

Diethyl 2,7-diisocyano-1,2,3,6,7,8-hexahydropyrene-2,7-dicarboxylate 13: Yield (449 mg, 68%), white solid. $\boldsymbol{R_f}$ = 0.38 (30% EtOAc-petroleum ether), **mp.** 144-146 ^oC

^{1}H NMR (500 MHz $CDCl_3$): δ 7.29 (s, 4H), 4.36 (q, *J* = 14.45 Hz, 4H), 3.66 (d, *J* = 15.38 Hz, 4H), 3.52 (d, *J* = 15.38 Hz, 4H), 1.35 (t, *J* = 7.10 Hz, 6 H). **^{13}C NMR** (125 MHz $CDCl_3$): δ 168.2, 158.8, 128.6, 127.7, 125.7, 63.2, 61.8. 39.7, 1 4.0 ppm.

IR (neat): 510, 1190, 1315, 1701, 1729, 2121 cm^{-1}.

HRMS *m/z*: calculated $C_{24}H_{22}N_2O_4[M+H]^+$ 403.1645, found: 403.1645.

Diethyl 2,7-diamino-1,2,3,6,7,8-hexahydropyrene-2,7-dicarboxylate 19: To a solution of isonitrile derivative 150 mg (0.3 mmol), in absolute ethanol (10 ml) were added 0.3 ml of conc. HCl. The reaction mixture was stirred at rt for 8 h. The solvent was evaporated at reduced pressure and the resulting product was dissolved in water and basified with aq. Ammonia solution (pH=10) and then extracted with

ethyl acetate (30 ml). The combined ethyl acetate extracts were washed with water and brine and then dried. Evaporation of ethyl acetate under reduced pressure on a rota evaporator gave amino ester. **Yield** (110 mg, 78%), brown solid. R_f = 0.38 (30% EtOAc-petroleum ether), **mp**. 158-160 ^{o}C

^{1}H NMR (500 MHz $CDCl_3$): δ 7.21 (s, 4H), 4.22 (q, *J* = 14.16 Hz, 4H), 3.54 (d, *J* = 15.47 Hz, 4H), 3.10 (d, *J* = 15.44 Hz, 4H), 1.90 (bs, 4H), 1.27 (t, *J* = 7.00 Hz, 6H). **^{13}C NMR** (125 MHz $CDCl_3$): δ 175.9, 130.7, 128.2, 125.6, 61.3, 56.5, 40.7, 14.1 ppm.

IR (neat): 495, 1202, 1350, 11350, 1741 cm^{-1}.

HRMS *m/z*: calculated $C_{22}H_{26}N_2O_4[M+H]^+$ 383.1960, found: 383.1960.

Diethyl 2,7-diacetamido-1,2,3,6,7,8-hexahydropyrene-2,7-dicarboxylate 12: To a solution of amino ester 100 mg (0.27 mmol) was added a solution of acetic anhydride (0.35 ml) in DCM at rt and the mixture was stirred for 8 h. After completion of the starting material (TLC monitoring), solvent was evaporated at reduced pressure and washed with diethyl ether. **Yield** (100 mg, 83%), white solid. R_f = 0.38 (30% EtOAc-petroleum ether), **mp**. 170-172 ^{o}C

^{1}H NMR (500 MHz DMSO): δ 8.02 (s, 2H), 7.19 (s, 4H), 4.06 (q, *J* = 14.16 Hz, 4 H), 3.32 (s, 8H), 1.63 (s, 6H), 1.11 (t, *J* = 7.07 6H). **^{13}C NMR** (125 MHz DMSO): δ 173.5, 170.2, 130.6, 128.2, 125.4, 60.8, 57.4, 37.3, 22.7, 14.5 ppm.

IR (neat): 760, 1069, 1242, 1650, 1737, 2140, 3867cm^{-1}.

HRMS *m/z*: calculated $C_{26}H_{30}N_2O_6[M+H]^+$ 467.2170, found: 467.2170.

6',7'-Bis(bromethyl)-1,3-dimethyl-1'H,3'H-spiro[imidazolidine-4,2'-phenalene]-2,5-dione 21: To a suspension of sodium hydride (15.6 mmol, 4 equiv.) in dry THF, the compound hydantoin (3.9 mmol, 1 equiv) was added and the reaction mixture was stirred at rt for 30 min. Later, tetrabromo compound (1.95 mmol, 1 equiv.), tetrabutyl ammonium bromide (3.9 mmol) was added and the reaction mixture reflux for 24 h. After completion of starting material (TLC monitoring), quenched with water and the aqueous layer was extracted with ethyl acetate (35 ml) and crude compounds were purified by column chromatography. **Yield** (500 mg, 28%), colourless liquid R_f = 0.38 (30% EtOAc-petroleum ether).

^{1}H NMR (500 MHz $CDCl_3$): δ 7.22 (d, *J* = 7.22 Hz, 2H), 7.14 (d, *J* = 7.09 Hz, 2H), 5.04 (s, 4H), 3.69 (d, *J* = 16.76 Hz, 2H), 3.14 (d, *J* = 16.42 Hz, 2H), 3.09 (s, 3H), 2.37 (s, 3H). **^{13}C NMR** (125 MHz $CDCl_3$): δ 175.2, 155.9, 131.5, 129.4, 128.0, 126.3, 124.2, 120.4, 69.2, 62.3, 36.9, 27.0, 25.2 ppm.

IR (neat): 713, 952, 1313, 1465, 1719, 1749, 2150, 1955 cm^{-1}.

HRMS *m/z:* $C_{19}H_{18}Br_2N_2O_2[M+H]^+$ 467.1730, found: 467.1730.

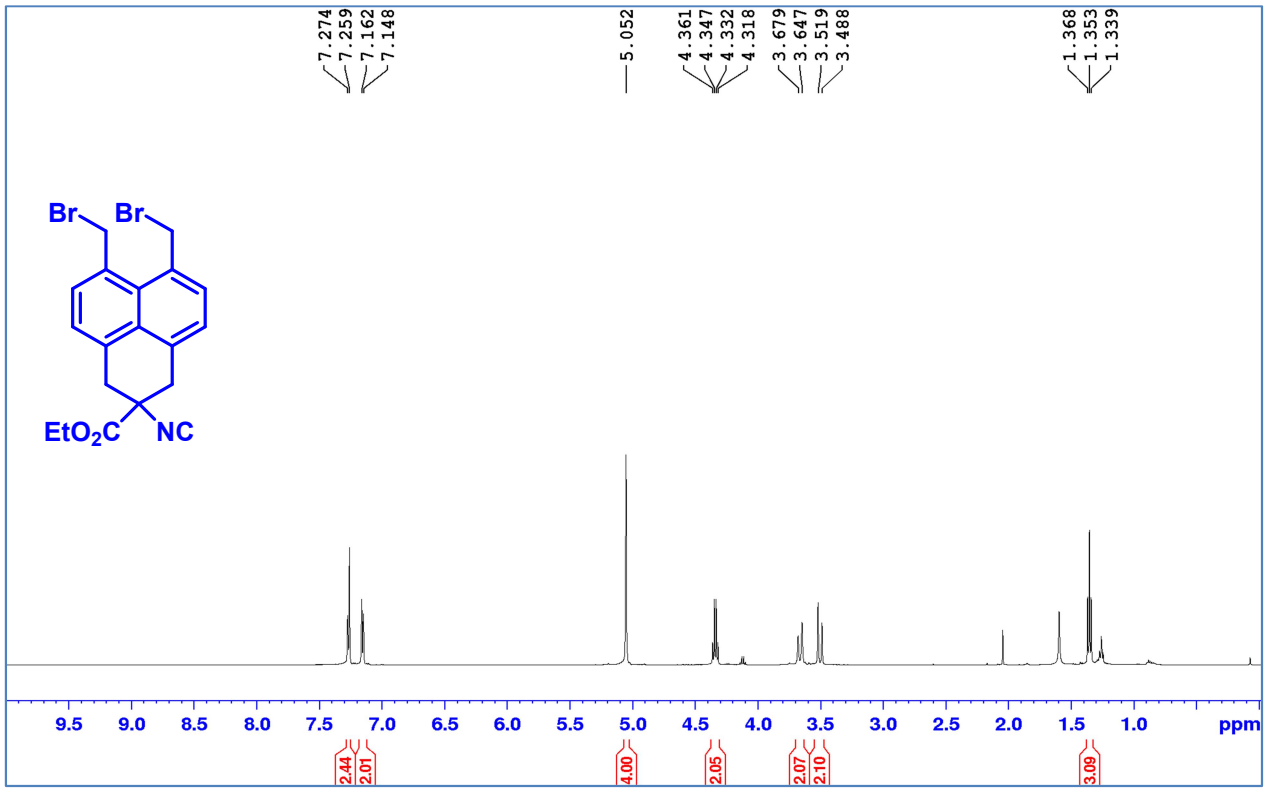
1,1”,3,3”-Tetramethyl-1’,3’,6,’8’-tetrahydrodispiro[imidazolidine-4,2’-pyrene-7’,4”-imidazolodine]-2,2”,5,5”-tetraone 22: **Yield** (860 mg, 54%), brown solid. R_f = 0.38 (30% EtOAc-petroleum ether). **mp.** 156-158 ^{o}C.

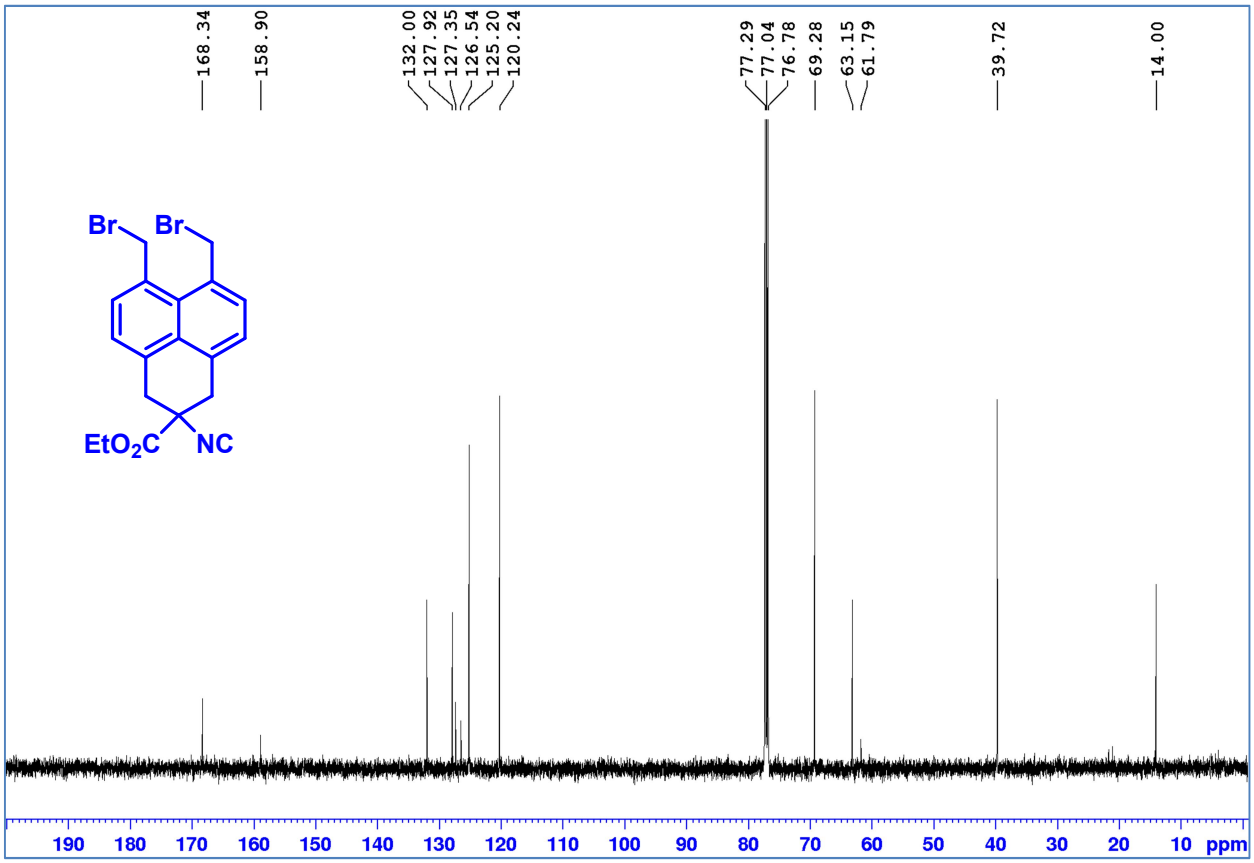
^{1}H NMR (500 MHz $CDCl_3$): δ 7.23 (s, 4H), 3.66 (dd, *J* = 15.99, 9.97 Hz, 4H), 3.17 (dd, *J* = 16.13, 11.86 Hz, 4H), 3.07 (s, 6H), 2.45 (s, 3H), 2.37 (s, 3H). **^{13}C NMR** (125 MHz $CDCl_3$): δ 175.1, 175.0, 155.9, 155.9, 129.9, 129.8, 128.3, 128.3, 125.0, 125.0, 62.2, 62.2, 37.1, 36.9, 26.9, 26.6, 25.1 ppm.

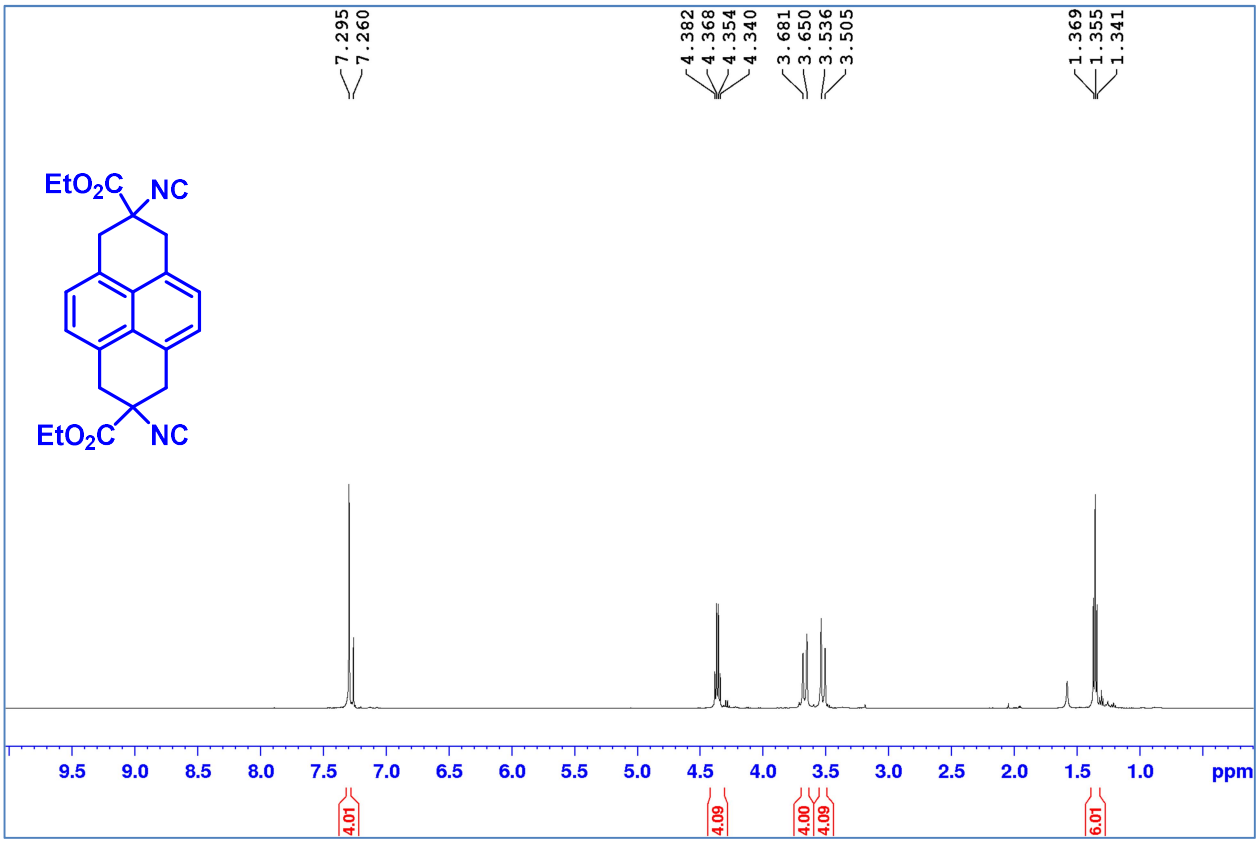
IR (neat): 760, 1064, 1330, 1400, 1460, 1711, 1755, 2150, 3000 cm^{-1}.

HRMS *m/z*: calculated $C_{24}H_{24}N_4O_4[M+H]^+$ 433.1870, found: 433.1870.

3.Plots of ^{1}H NMR & ^{13}C NMR spectral data all new compounds



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1.341
EtO2C
NC
EtO2C
NC
9.5
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8.0
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7.0
6.5
6.0
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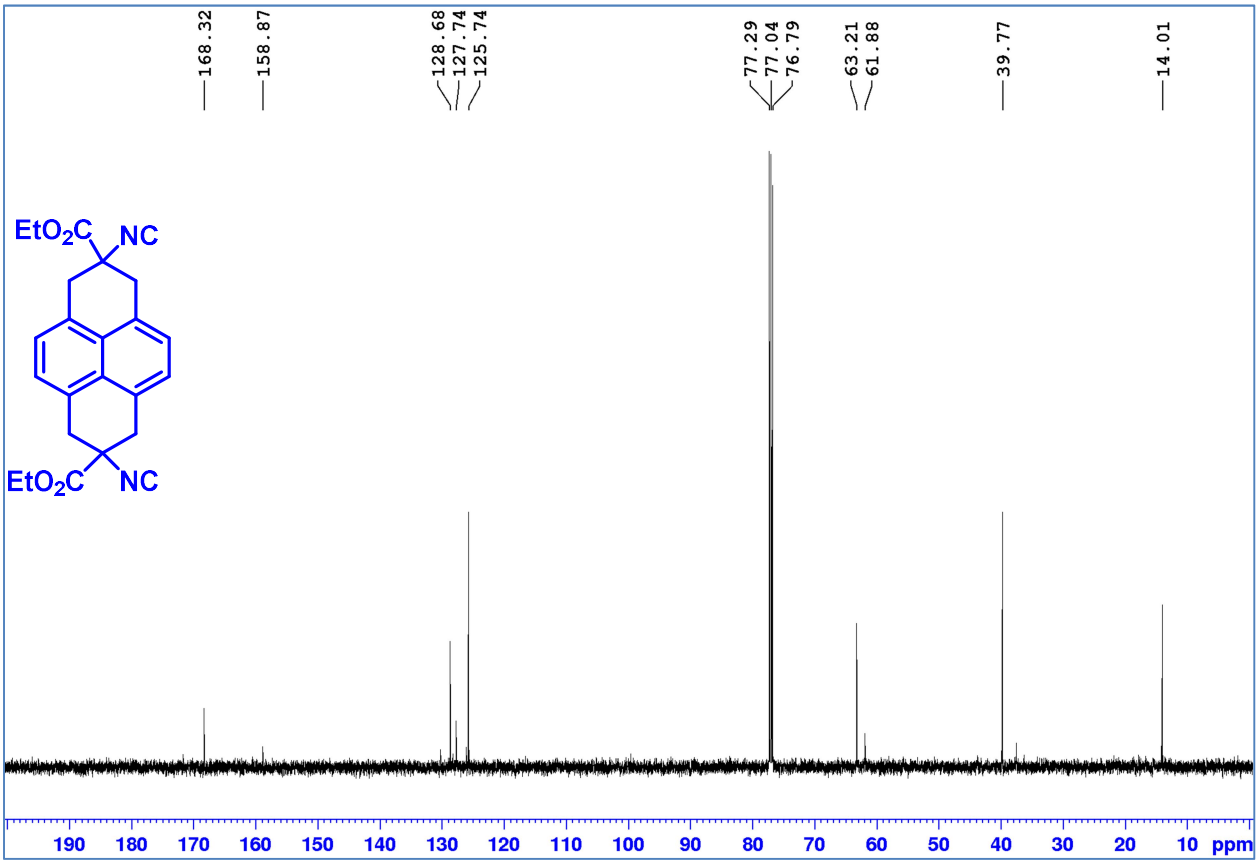
6.01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EtO2C
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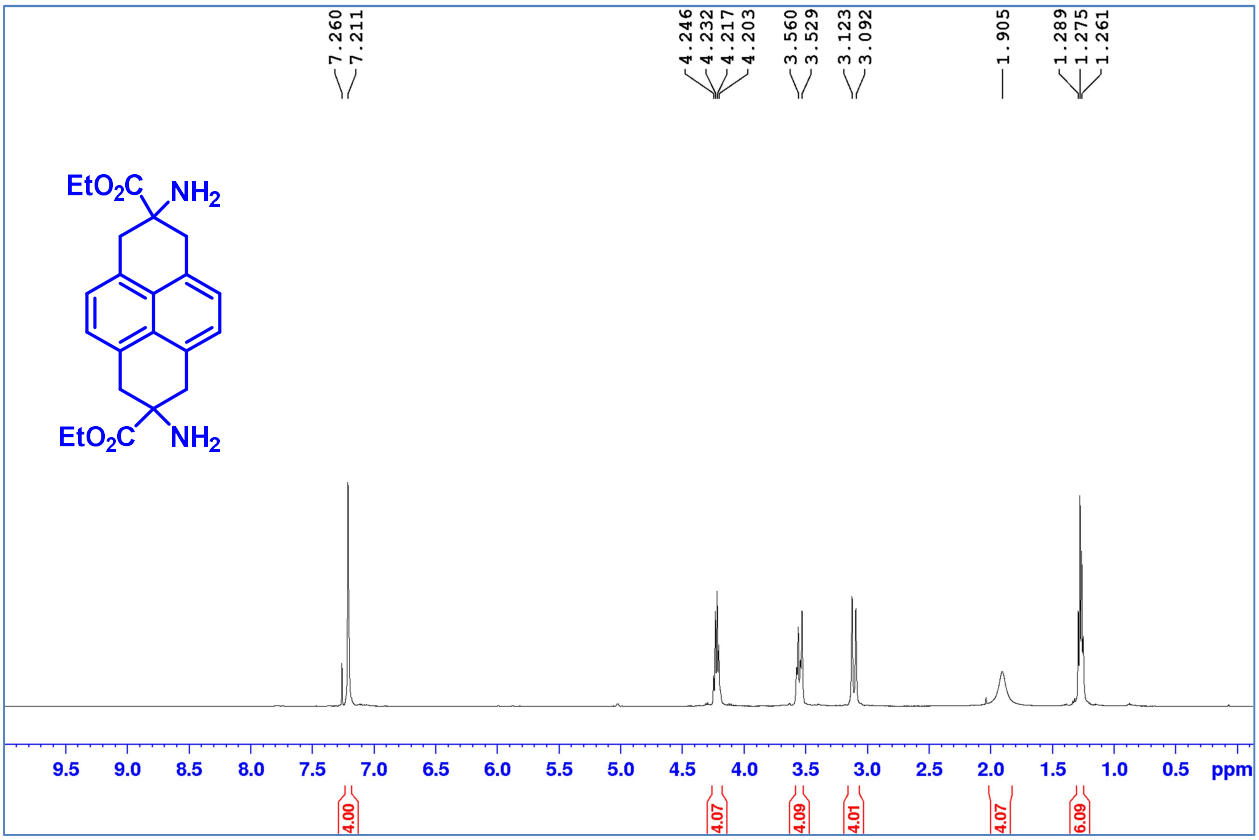
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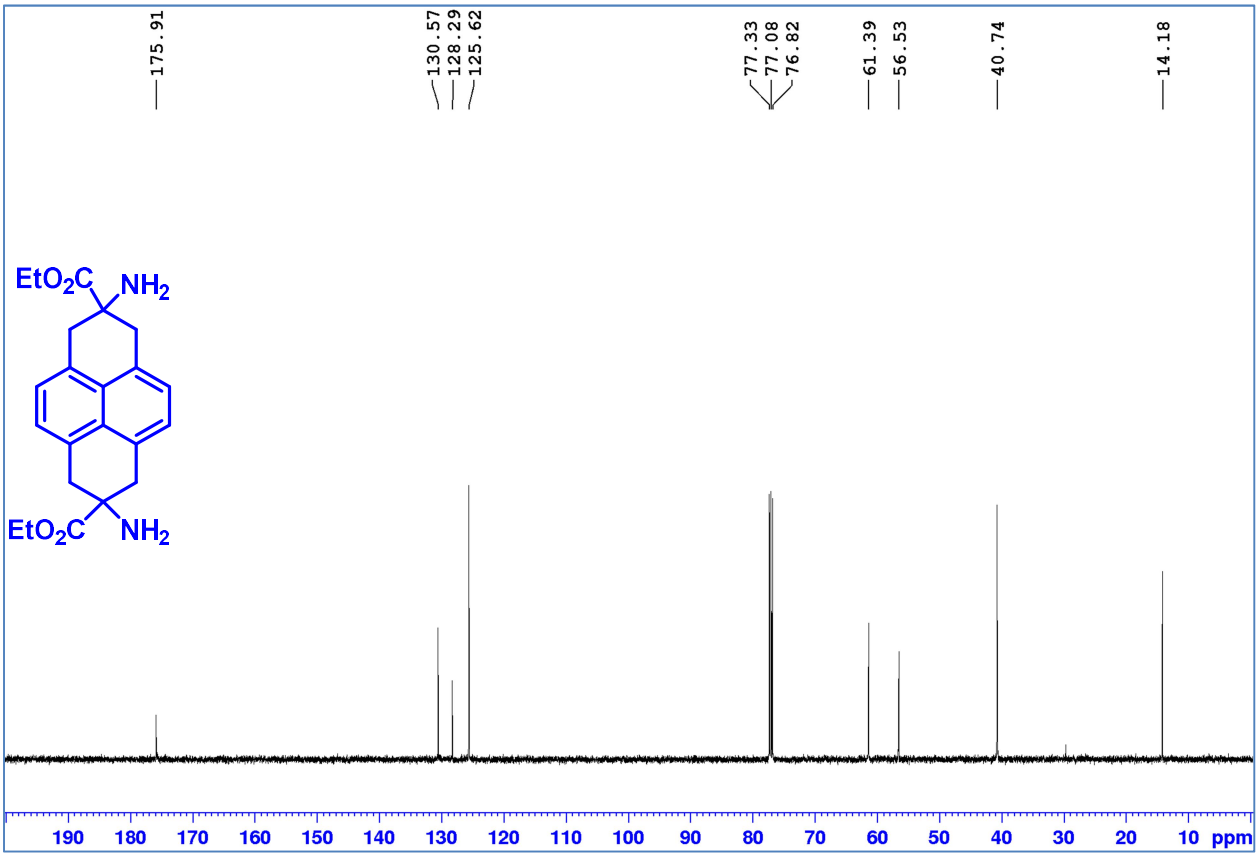
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EtO2C
NH2
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70
60
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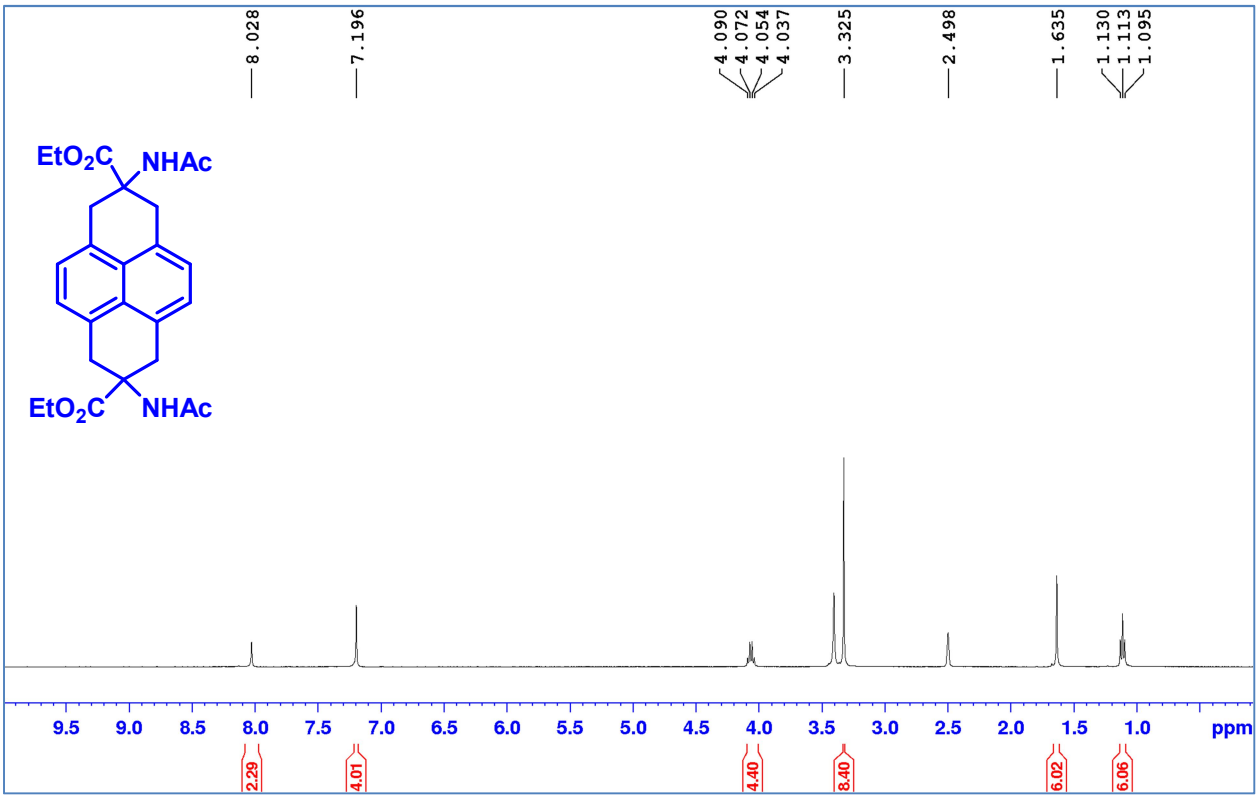
30
20
10
ppm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EtO2C
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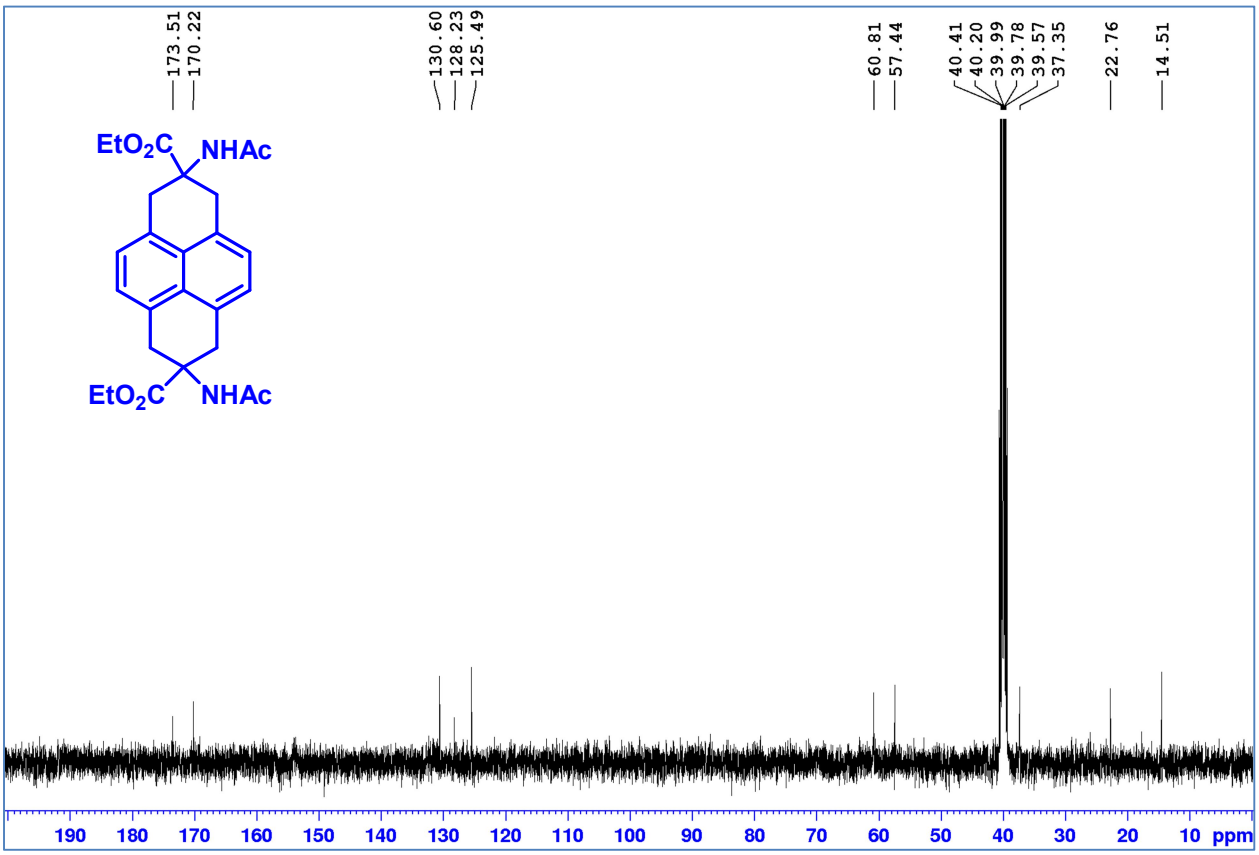
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EtO2C
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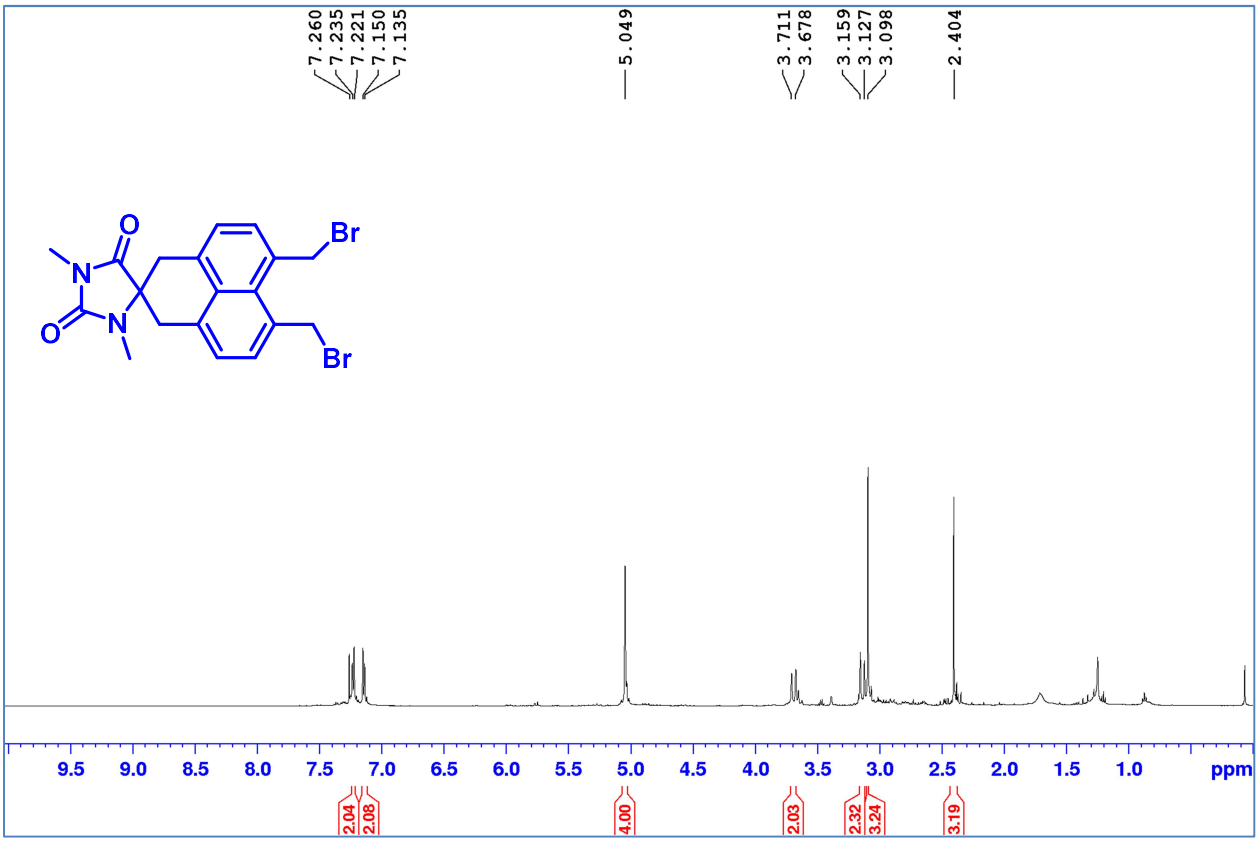
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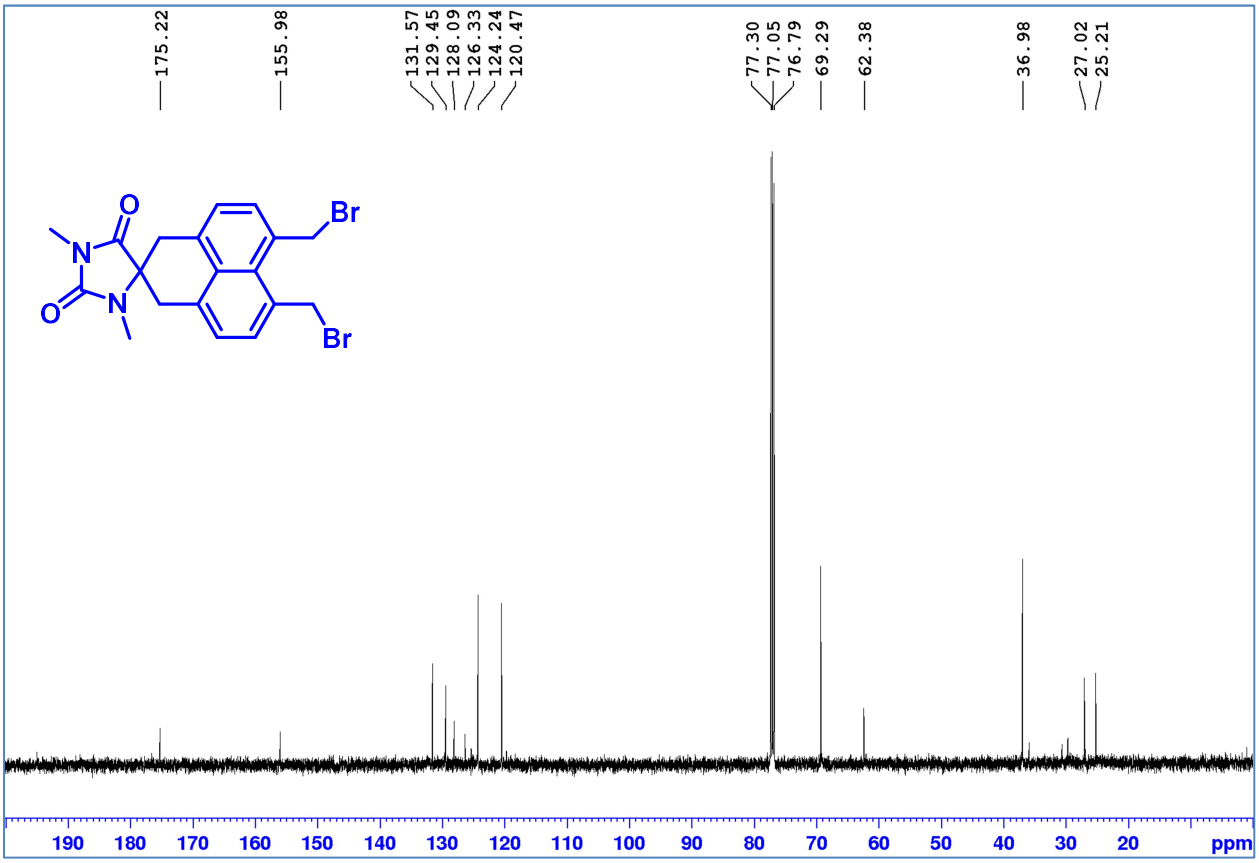
3.19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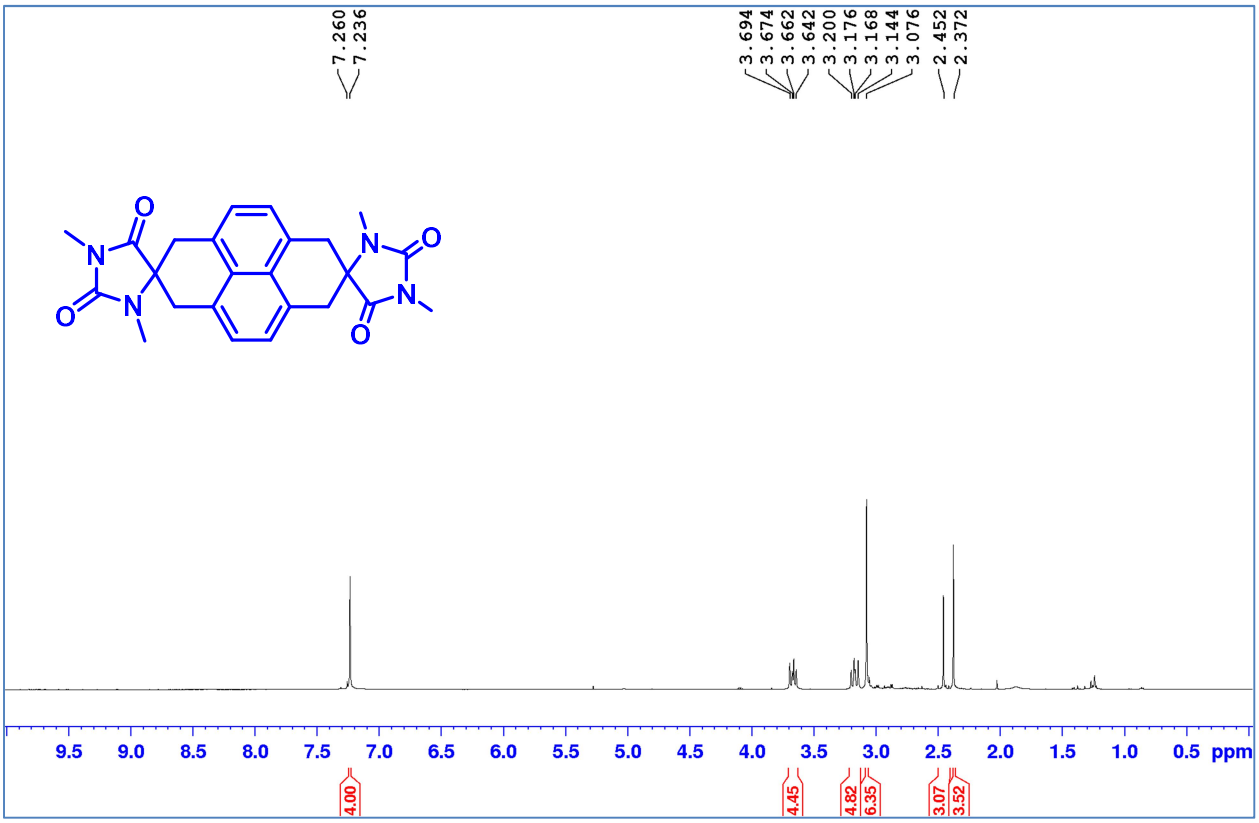
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9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 ppm
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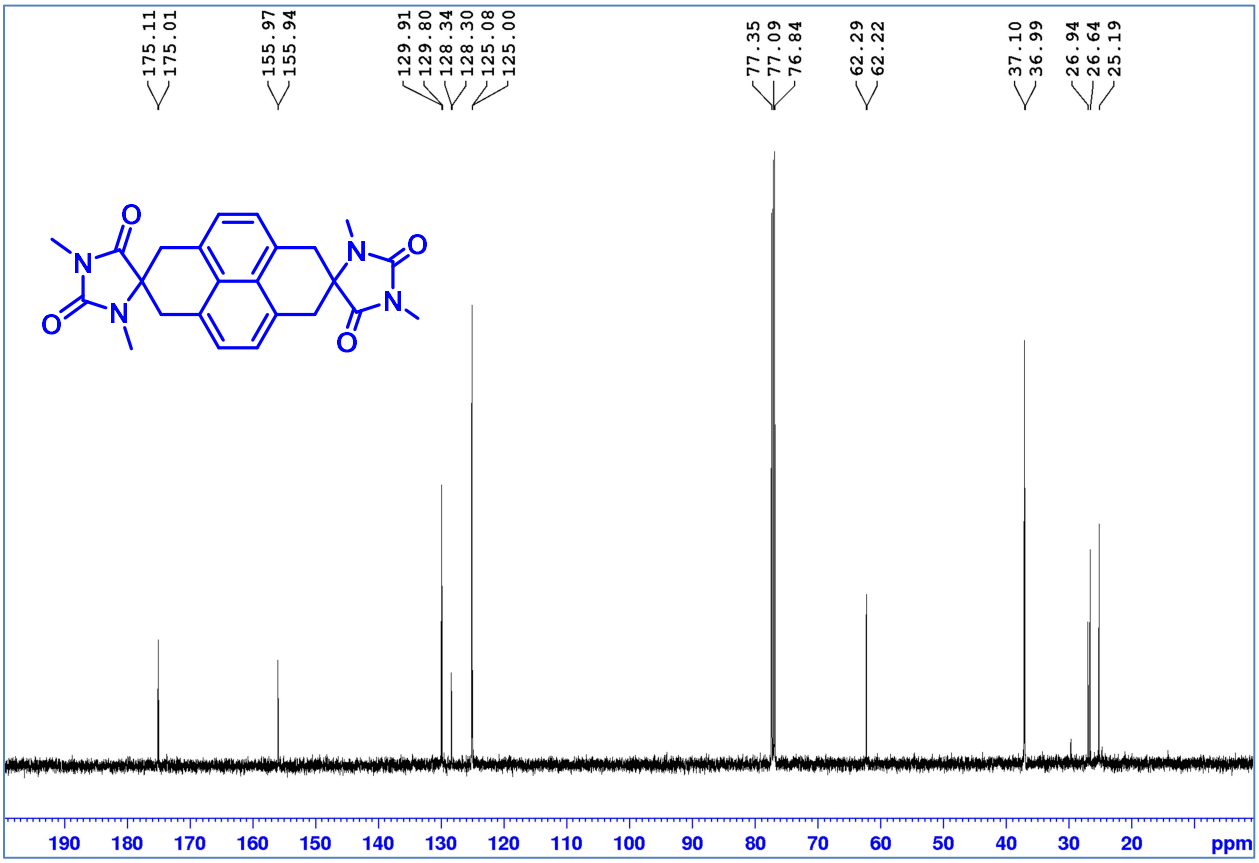
3.52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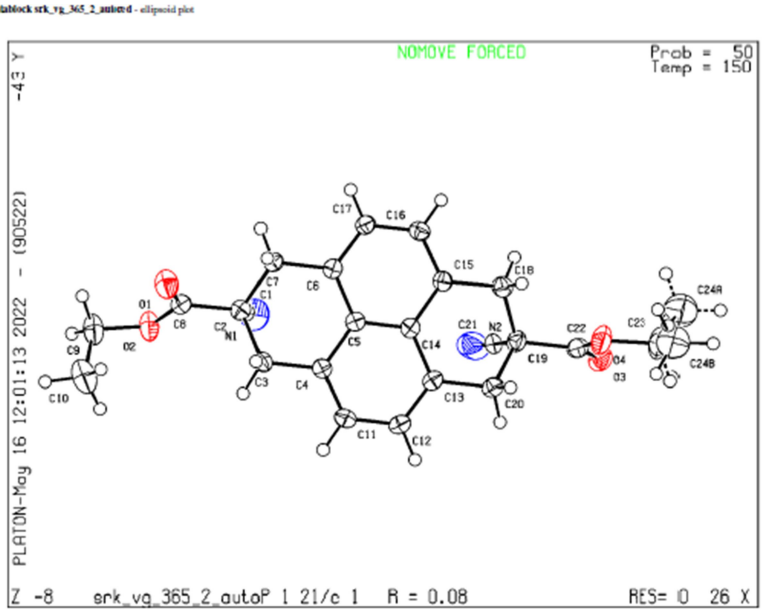
76.84
62.29
62.22
37.10
36.99
26.94
26.64
25.19
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 ppm

4. X-ray data and refinement parameter for compound

Diethyl 2,7-diisocyano-1,2,3,6,7,8-hexahydropyrene-2,7-dicarboxylate (13)

CCDC Number = 2172966



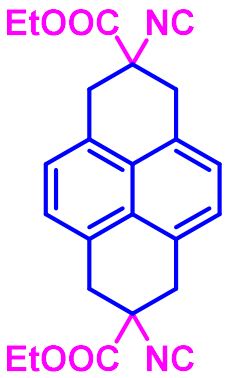


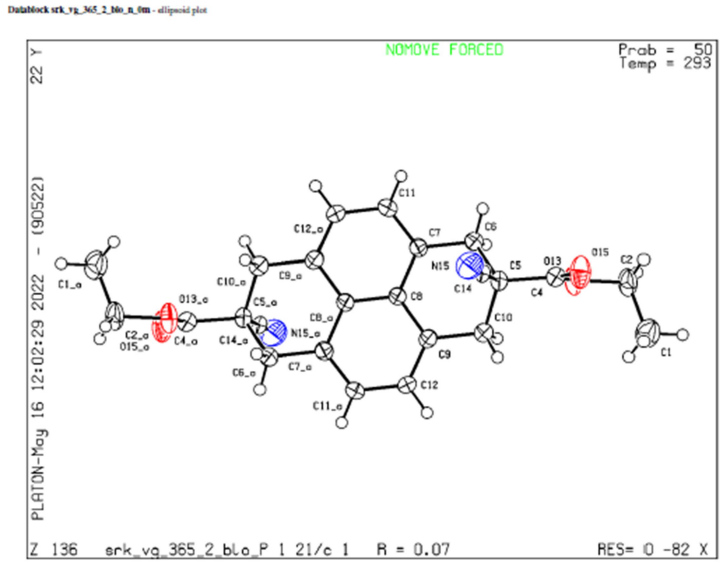
Table S1. X-ray crystallographic data and refinement parameters for **13 (CCDC 2172966)**

Identification code	SRK-VG-365-2	
Empirical formula	$C_{24}H_{22}N_2O_4$	
Formula weight	402.43	
Temperature	150.00 (10) K	
Crystal system	Monoclinic	
Space group	$P2_1/c$	
Unit cell dimensions	a = 14.5740(15) Å	α = 90
	b = 7.4889(6) Å	β = 94.479(9)
	c = 19.595(2) Å	γ = 90
Volume	2153.9 (4) $Å^3$	
Z	4	
Density	1.241 g/cm^3	
Absorption coefficient (μ)	0.085 mm^{-1}	
Absorption correction	Multi-scan	
F (000)	848.0	

Crystal size	0.244 x 0.143 x 0.024 mm^3
Index ranges	-17 ≤ h ≤ 17, -8 ≤ k ≤ 8, -23 ≤ l ≤ 23
Theta range for data collection	4.806 to 49.998°
Reflections collected	45097
Diffraction radiation wavelength	0.71073
Independent reflections	3788 [$R_{(int)}$ = 0.1200, $R_{(sigma)}$ = 0.0538]
Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameters	3788/18/284
Goodness-of-fit on F^2	1.033
Final *R* indices [I>=2σ (I)]	*R*1 = 0.0773, *wR*2 = 0.1906
R indices (all data)	*R*1 = 0.1064, *wR*2 = 0.2141
Largest diff. peak and hole	0.52/-0.58 e $Å^{-3}$

Diethyl 2,7-diisocyano-1,2,3,6,7,8-hexahydropyrene-2,7-dicarboxylate (13a)

CCDC Number = 2172972



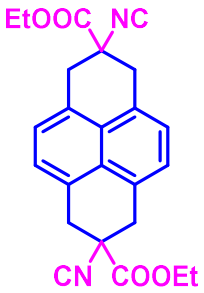


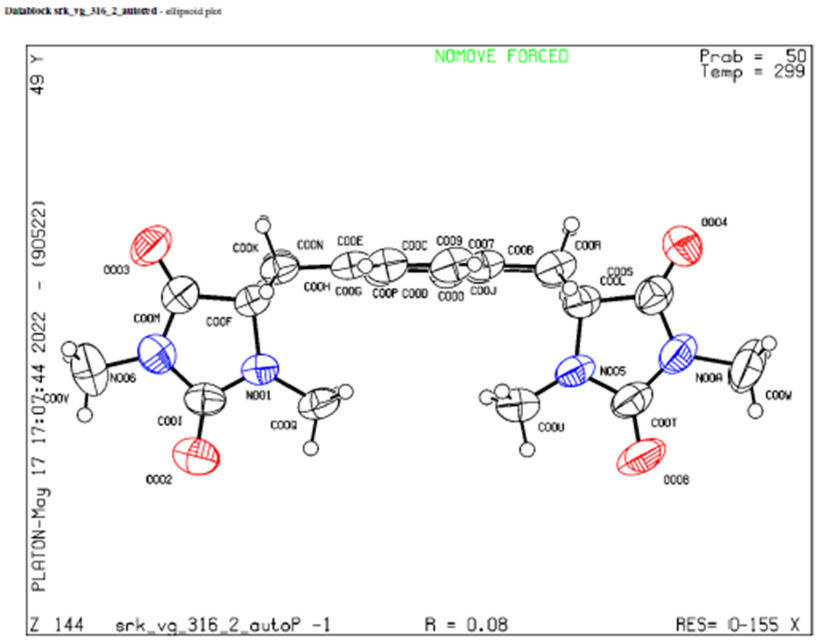
Table S2. X-ray crystallographic data and refinement parameters for **13a (CCDC 2172972)**

Identification code	SRK-VG-365-2-BLO-N
Empirical formula	$C_{12}H_{11}NO_2$
Formula weight	201.22

Temperature	293.15 K	
Crystal system	Monoclinic	
Space group	$P2_1/c$	
Unit cell dimensions	a = 8.829(4) Å	α = 90
	b = 11.070(4) Å	β = 109.863(15)
	c = 11.089(5) Å	γ = 90
Volume	1019.4 (8) $Å^3$	
Z	4	
Density (calculated)	1.311 g/cm^3	
Absorption coefficient (μ)	0.090 mm^{-1}	
Absorption correction	Multi-scan	
F (000)	424.1	
Crystal size	0.132 x 0.123 x 0.04 mm^3	
Index ranges	$-10 \le h \le 10, -13 \le k \le 13, -13 \le l \le 13$	
Theta range for data collection	4.906 to 50°	
Reflections collected	21092	
Diffraction radiation wavelength	0.71073	
Independent reflections	1801 [$R_{(int)}$ = 0.1288, $R_{(sigma)}$ = 0.0574]	
Refinement method	Full-matrix least-squares on F^2	
Data/restraints/parameters	1801/0/137	
Goodness-of-fit on F^2	1.064	
Final *R* indices [I>=2σ (I)]	*R*1 = 0.0707, *wR*2 = 0.1580	
R indices (all data)	*R*1 = 0.1123, *wR*2 = 0.1883	
Largest diff. peak and hole	0.44/-0.68 e $Å^{-3}$	

1,1”,3,3”-Tetramethyl-1’,3’,6,’8’-tetrahydrodispiro[imidazolidine-4,2’-pyrene-7’,4”-imidazolodine]-2,2”,5,5”-tetraone (22)

CCDC Number = 2173399



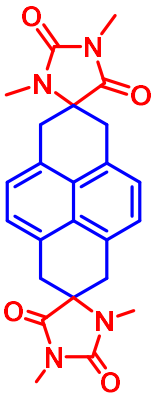


Table S3. X-ray crystallographic data and refinement parameters for **22 (CCDC 2173399)**

Identification code	SRK-VG-316-2	
Empirical formula	$C_{24}H_{24}N_4O4$	
Formula weight	432.47	
Temperature	298.5 (7) K	
Crystal system	Triclinic	
Space group	P -1	
Unit cell dimensions	a = 7.7538(3) Å	α = 67.978(5)
	b = 11.1660(6) Å	β = 76.718(4)
	c = 13.8612(8) Å	γ = 85.621(4)
Volume	1082.71 (10) $Å^3$	
Z	2	
Density (calculated)	1.327 g/cm^3	
Absorption coefficient (μ)	0.092 mm^{-1}	
Absorption correction	Multi-scan	

F (000)	456.0
Crystal size	0.352 x 0.255 x 0.122 mm^3
Index ranges	$-9 \leq h \leq 9, -13 \leq k \leq 13, -16 \leq l \leq 16$
Theta range for data collection	3.248 to 49.998°
Reflections collected	17291
Diffraction radiation wavelength	0.71073
Independent reflections	3806 [$R_{(int)}$ = 0.1427, $R_{(sigma)}$ = 0.0843]
Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameters	3806/0/293
Goodness-of-fit on F^2	1.016
Final *R* indices [I>=2σ (I)]	*R*1 = 0.0842, *wR*2 = 0.2303
R indices (all data)	*R*1 = 0.1204, *wR*2 = 0.2727
Largest diff. peak and hole	0.24/-0.30 e $Å^{-3}$

References

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(2) Yeo, Hyoung-Min; Jeon, N. J.; Nam, K. C. *Bull. Korean Chem. Soc.* **2011**, *32*, 3171.