

Supporting information

Fluorescence and visual sensing of nitroaromatic explosives using electron rich discrete fluorophores

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Materials and methods. All the fluorophores (**1-5**) were synthesized under dry nitrogen atmosphere using standard Schlenk technique. Triethylamine was dried over sodium/KOH and distilled freshly under nitrogen atmosphere. All the solvents used for photophysical studies were of spectroscopy grade. 1,4-diiodobenzene, 4,4'-biphenyldibromide, 3,6-dibromocarbazole, 9,10-dibromoanthracene, trimethylsilylacetylene (TMS) were purchased from commercial sources and used without further purification. 1,3,6,8-tetrabromopyrene,¹ 1,4-bis[trimethylsilylethynyl]benzene² (**1**), 3,6-bis[trimethylsilylethynyl]carbazole³ (**3**), 1,3,6,8-tetrakis[trimethylsilylethynyl]pyrene¹ (**5**) were synthesized following the reported procedures. All the nitroaromatic compounds (NAC) and other quenchers including benzoic acid (BA), benzoquinone (BQ), 4-methoxybenzoic acid (4-MeOBA) were of analytical grade and used directly without further purification [For the above references see in main text].

Caution!: TNT and other nitroaromatic compounds used in the present study are highly explosive and should be handled only in small quantity.

NMR spectra were recorded on a Bruker 400 MHz spectrometer. The chemical shifts (δ) in ^1H NMR spectra are reported in ppm relative to tetramethylsilane (Me_4Si) as internal standard (0.0 ppm) or proton resonance resulting from incomplete deuteration of the NMR solvents: CDCl_3 (7.26). ^{13}C NMR were recorded at 75 MHz, and the chemical shifts (δ) are reported in ppm relative to external CDCl_3 at 77.8-77.2 ppm. IR spectra were recorded on a Bruker ALPHA FT-IR spectrometer. Electronic absorption spectra were recorded on a Perkin Elmer LAMBDA 750 UV/visible spectrophotometer. Fluorescence emission studies were carried out on HORIBA JOBIN YVON Fluoromax-4 spectrometer. Thin-film for solid state fluorescence quenching study was made in PRS 400 spin-coater.

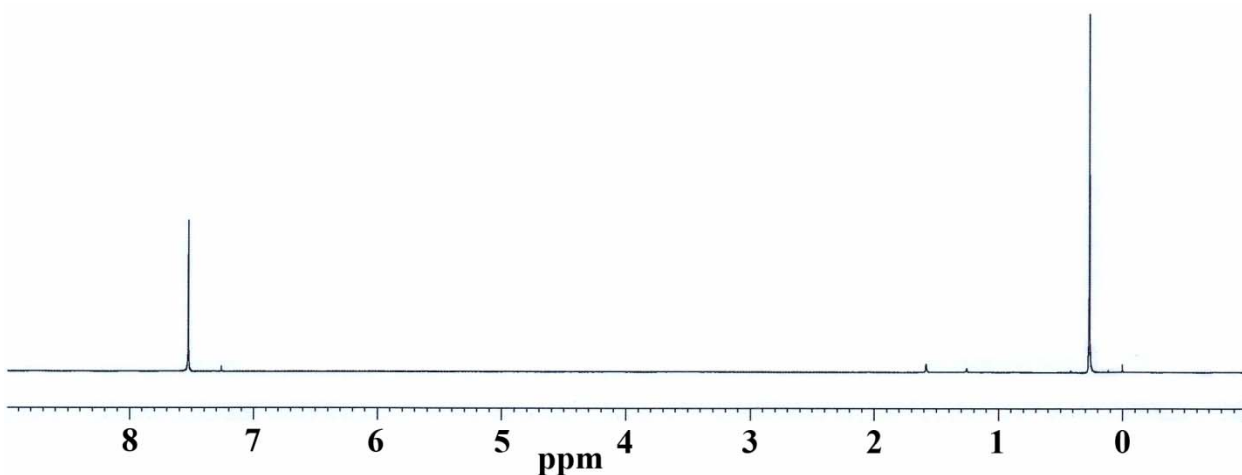


Fig.S1. ^1H NMR spectrum of **2** in CDCl_3 .

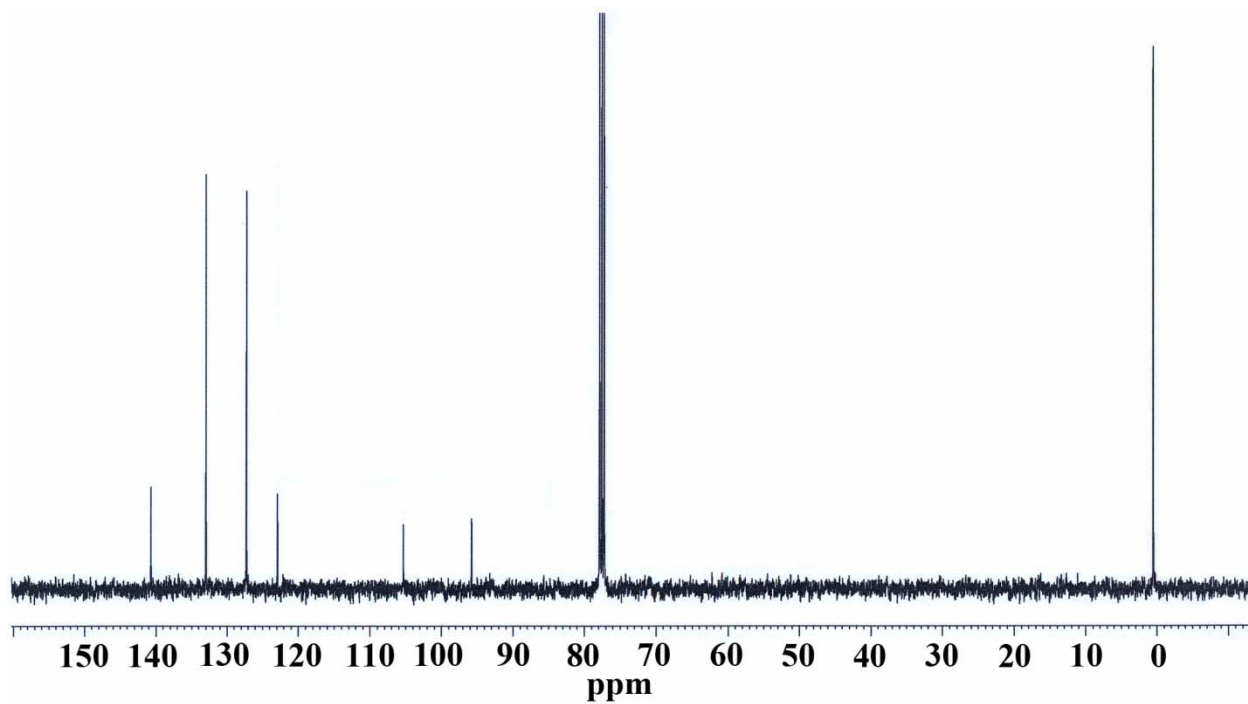


Fig. S2. ^{13}C NMR spectrum of **2** in CDCl_3 .

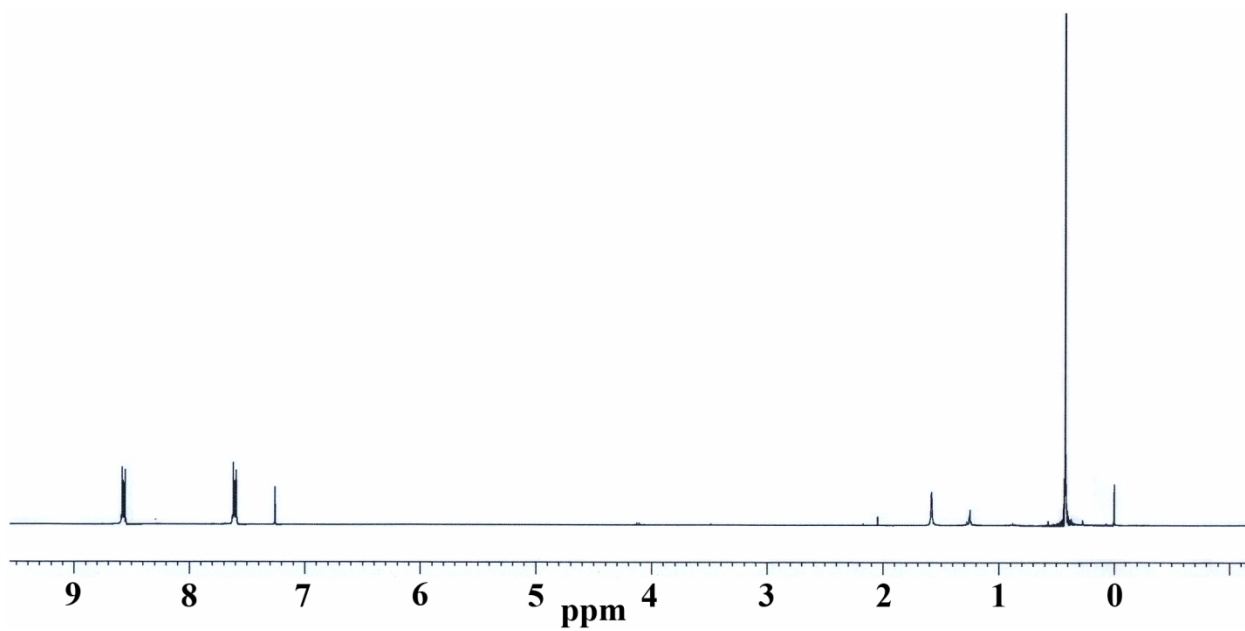


Fig. S3. ^1H NMR spectrum of **4** in CDCl_3 .

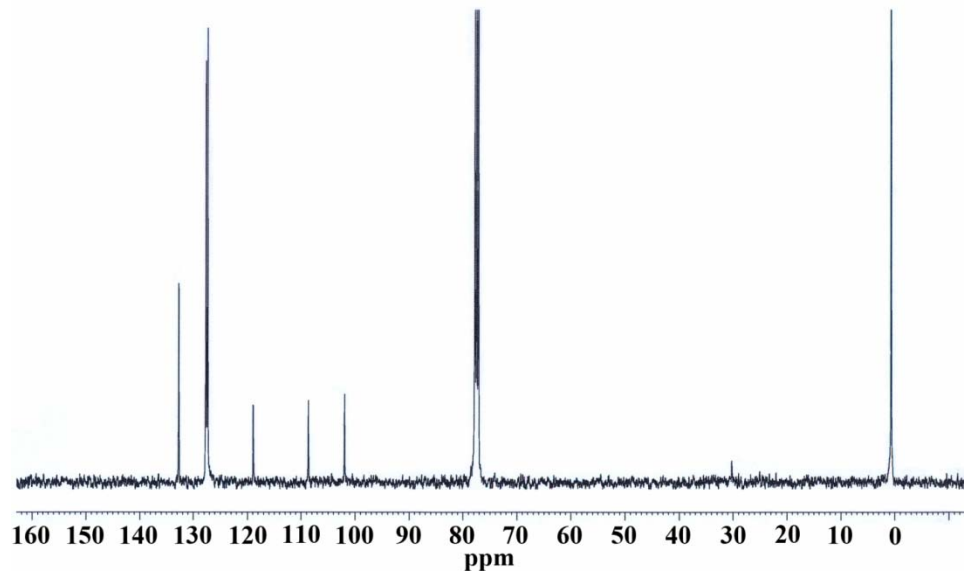


Fig. S4. ^{13}C NMR spectrum of **4** in CDCl_3 .

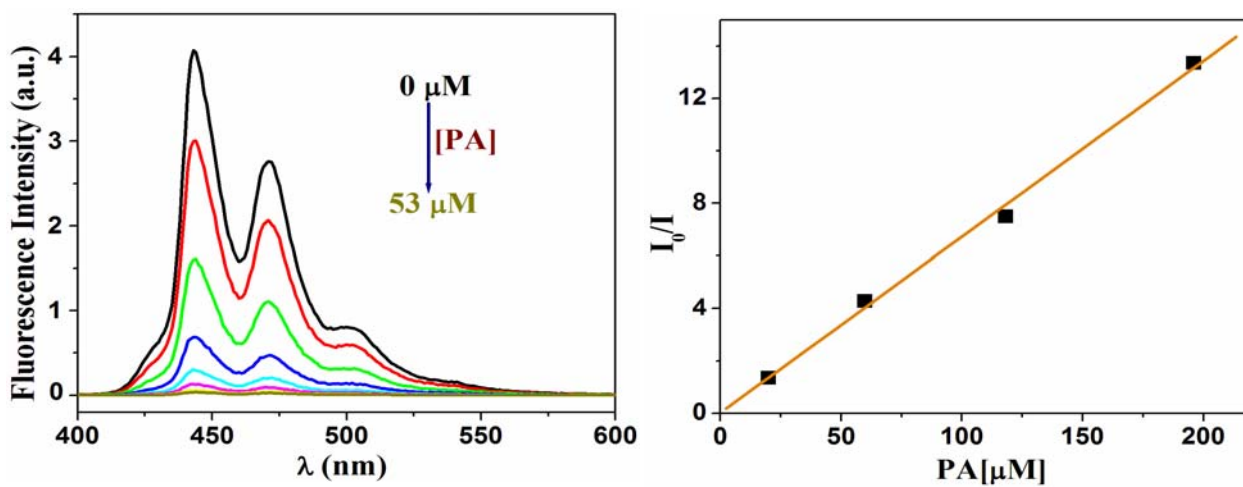


Fig. S5. Fluorescence quenching (left) of fluorophore **4** ($10\ \mu\text{M}$) with picric acid in chloroform solution ($\lambda_{\text{ex}} = 270\ \text{nm}$, excitation and emission slit width is $1\ \text{nm}$) and obtained Stern-Volmer plot (right).

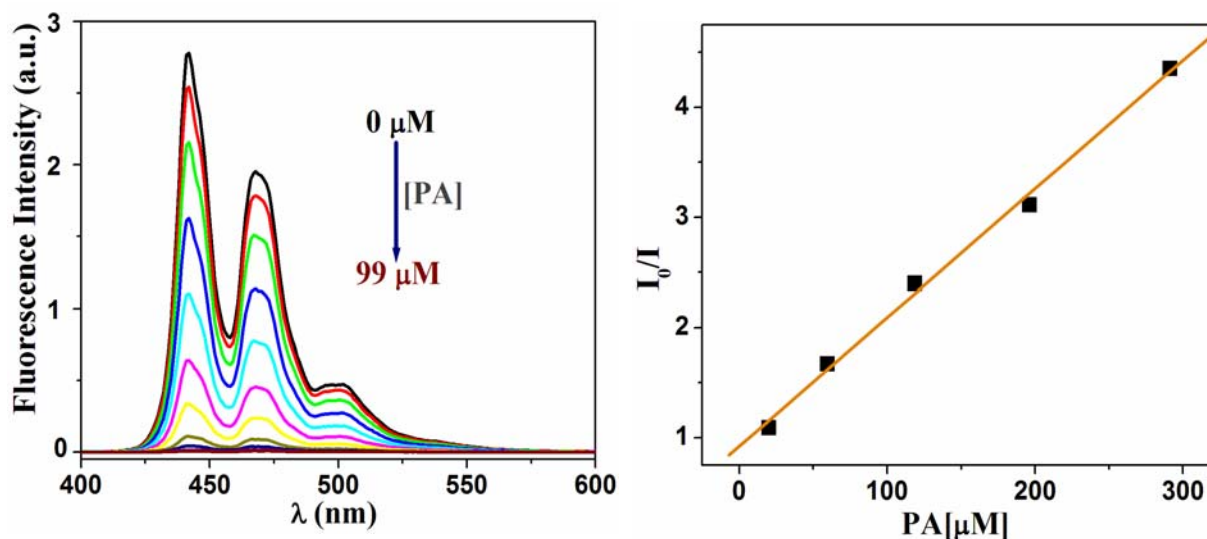


Fig. S6. Fluorescence quenching (left) of fluorophore **5** (10 μM) with picric acid in chloroform solution ($\lambda_{\text{ex}} = 316$ nm, excitation and emission slit width is 1 nm) and obtained Stern-Volmer plot (right).

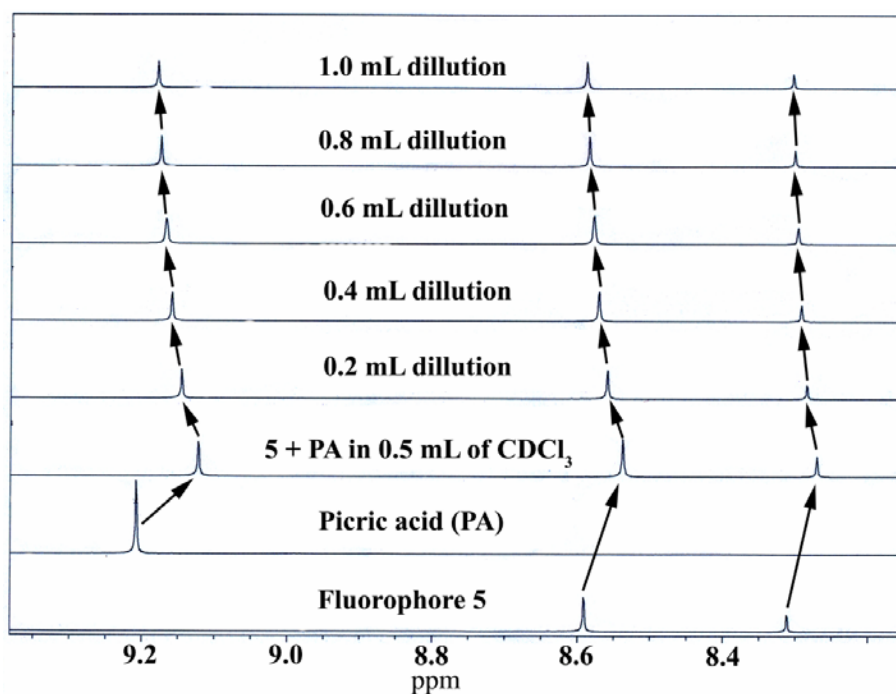


Fig.S7. Partial ^1H NMR spectra for the charge transfer complex formation of fluorophore **5** and picric acid (PA) taken CDCl_3 . Upon further dilution of charge-transfer complex exhibited a

significant downfield shifting of resonance corresponding to **5** and PA (arrow indicates the shifting of peak position).

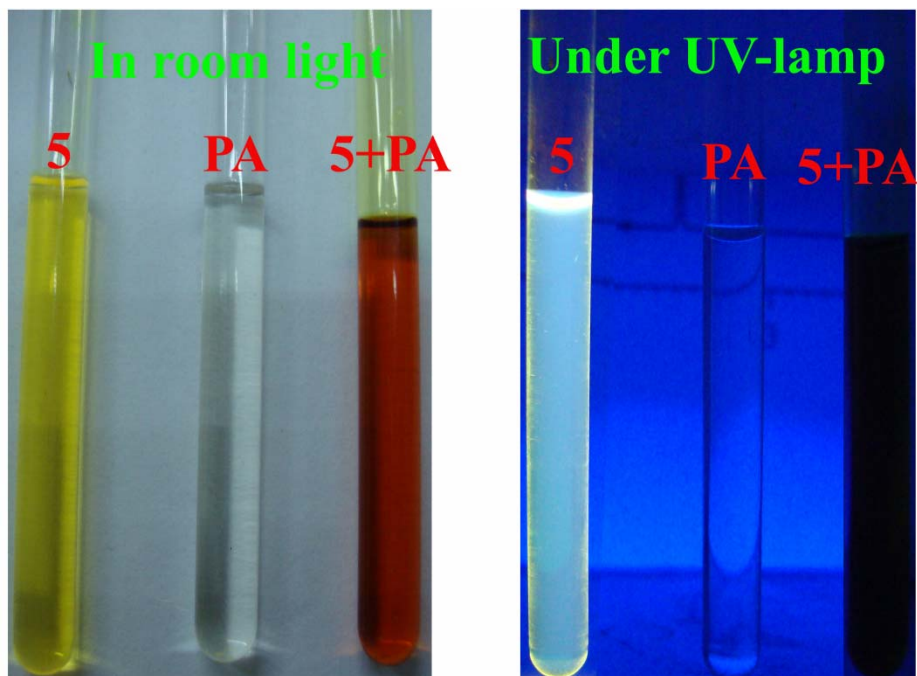


Fig.S8. Visual color changes observed upon mixing of fluorophore **5** in CDCl_3 with increasing quantity of picric acid (PA) in CDCl_3 (left; in room light and right; under hand hold UV light).

Cartesian coordinates for the DFT calculation of complex **4.PA**

C	-0.72953800	2.46861400	-2.29372300
C	-1.37257500	1.35158200	-1.86567700
C	-0.64618100	0.19590100	-1.48117000
C	0.77258900	0.22332100	-1.55335000
C	1.40830900	1.40877300	-2.00053700
C	0.68000600	2.49473300	-2.36749000
C	-1.30009100	-0.95826300	-1.01509700
C	1.51174300	-0.89405100	-1.12712900
C	0.85786400	-2.05410600	-0.67512400
C	-0.56264200	-2.08491400	-0.61547000
C	-1.20046800	-3.24867000	-0.11836500
H	-2.27865600	-3.26295800	-0.08242200
C	-0.47247400	-4.31203500	0.30447400
C	0.93856100	-4.27686500	0.25518300
C	1.58388000	-3.18251400	-0.21991400

H	-1.29297300	3.34553400	-2.57170600
H	-2.44925500	1.32458100	-1.79957700
H	2.48596200	1.42782500	-2.03830000
H	1.17987000	3.39318900	-2.69534400
H	-0.97070800	-5.19029100	0.68495200
H	1.50477200	-5.12683200	0.60328800
H	2.66115300	-3.14552500	-0.25485700
C	2.92486900	-0.81628400	-1.07194800
C	4.12686600	-0.71157300	-0.94834800
C	-2.71375400	-0.94867700	-0.91270800
C	-3.92179300	-0.88005000	-0.82893400
Si	5.90757200	-0.45930400	-0.57809700
Si	-5.75231000	-0.66761000	-0.79673800
C	5.97459100	0.41856600	1.07250200
H	5.50325100	-0.18267600	1.84881100
H	7.00258500	0.60947900	1.37774300
H	5.45833100	1.37652600	1.02638300
C	6.74483600	-2.12602800	-0.48379400
H	6.29675300	-2.74831700	0.28830100
H	6.67078300	-2.65943000	-1.42939100
H	7.80191500	-2.01126900	-0.24764800
C	6.66206600	0.58917700	-1.92695500
H	6.59033400	0.09791500	-2.89524600
H	6.16280500	1.55312100	-2.00247400
H	7.71597200	0.77530900	-1.72426700
C	-6.38249100	-0.81470300	0.95168800
H	-5.94453200	-0.05446600	1.59294700
H	-7.46555800	-0.69606900	0.96531800
H	-6.14624900	-1.78662800	1.38011600
C	-6.49249600	-2.00115900	-1.87971400
H	-6.11603300	-1.93770000	-2.89864100
H	-6.26125000	-2.99408400	-1.49908200
H	-7.57686400	-1.90332100	-1.91691400
C	-6.11184100	1.02701900	-1.49654500
H	-5.63840200	1.79850300	-0.89287600
H	-5.74552000	1.12018300	-2.51720800
H	-7.18370900	1.22086800	-1.50737400
C	0.50288900	0.19890900	1.83795200
C	-0.85900200	0.07037100	1.98735600
C	1.10974600	1.37686500	1.34243200
C	-1.66456900	1.12432300	1.63541600
H	-1.27609000	-0.84865800	2.36291200
C	0.22685600	2.42682600	1.01982500
C	-1.13656700	2.29766500	1.14536600
H	-1.77521000	3.11575100	0.86003900
O	2.39219700	1.50371500	1.16530100
H	2.82035000	0.65053000	1.38136100
N	0.70614600	3.70435000	0.52268200
N	1.30078300	-0.93652700	2.22961500
N	-3.09429000	0.98629700	1.77791100
O	-0.13592000	4.48175600	0.13232400
O	1.88982000	3.91877100	0.53235200
O	-3.78933600	1.83399500	1.26847800
O	-3.49503500	0.03183000	2.39787600
O	0.74200600	-1.90175700	2.67126300
O	2.51488100	-0.86076800	2.09692900

Cartesian coordinates for the DFT calculation of complex **5.PA**

C	3.11616600	0.11287900	-1.37391000
C	2.45560200	-1.10397500	-1.30184100
C	1.05001400	-1.13901300	-1.22165400
C	0.33557000	0.07641400	-1.16121900
C	1.01905200	1.31010700	-1.21960900
C	2.42204700	1.31339700	-1.35008500
C	0.33683800	-2.36518000	-1.13432000
C	-1.07748500	0.05532900	-1.00268000
C	-1.75732700	-1.17921400	-0.92676700
C	-1.00610700	-2.38415800	-0.99647300
C	-3.15420600	-1.18280300	-0.76592800
C	-3.83931500	0.01834800	-0.65687000
C	-3.17845700	1.23616000	-0.69428400
C	-1.78311900	1.27071300	-0.87535600
C	-1.05936700	2.49353600	-0.89534500
C	0.28022500	2.51506700	-1.06987400
H	0.82142300	3.44818300	-1.08618100
H	-1.61295700	3.41073700	-0.76907300
H	0.89770100	-3.28600000	-1.18108200
H	4.19242900	0.12895300	-1.42110900
H	-1.53906000	-3.31991600	-0.93136300
H	-4.90756700	0.00388000	-0.51889300
C	-4.50344400	-3.43634600	-0.62636800
C	-3.87561500	-2.40231900	-0.69276800
C	-3.91933700	2.43635300	-0.54110300
C	-4.55854300	3.45653000	-0.40770400
C	3.14241200	2.53399600	-1.36224900
C	3.75510700	3.57597200	-1.29198800
C	3.19820300	-2.30891700	-1.20748800
C	3.80216100	-3.34948900	-1.06075500
Si	-5.54301000	4.98446200	-0.15767300
Si	4.62120500	-4.96773200	-0.76592700
Si	-5.48299800	-4.98304700	-0.50546200
Si	4.63718300	5.14439200	-0.92632300
C	-4.54977100	6.15528400	0.90794500
H	-3.61193000	6.42848700	0.42819800
H	-5.10740100	7.07206100	1.09561800
H	-4.31287200	5.70415500	1.86931400
C	-5.89020900	5.75185100	-1.82675300
H	-6.45312200	5.07238600	-2.46353000
H	-6.47305200	6.66536600	-1.71476600
H	-4.96767000	6.00637500	-2.34467400
C	-7.14004200	4.51658200	0.69258200
H	-7.71845200	3.81965900	0.08937200
H	-6.94842900	4.04574800	1.65461800
H	-7.75575600	5.39800700	0.86752400
C	5.52030600	5.73380400	-2.46528000
H	4.82111000	5.91646400	-3.27889400
H	6.05319300	6.66319900	-2.26797900
H	6.24715300	4.99985100	-2.80773000
C	3.34692000	6.38097400	-0.38026500

H	2.80557500	5.99929700	0.48347200
H	3.80553300	7.32844400	-0.10025500
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H	6.62736600	4.11591000	0.13358200
H	6.30947600	5.71205000	0.80994400
H	5.32235100	4.32661900	1.29017200
C	5.40151300	-5.53965300	-2.36507400
H	5.88188300	-6.50836700	-2.23266600
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H	6.15734000	-4.83659600	-2.70938400
C	5.92580700	-4.74774100	0.55331000
H	6.65679600	-3.99348900	0.26886500
H	5.48302700	-4.45038200	1.50152600
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C	3.29560200	-6.15469900	-0.19810400
H	2.78020300	-5.76064200	0.67560700
H	2.55550100	-6.32066900	-0.97885100
H	3.72260000	-7.12097700	0.06709000
C	-4.89641400	-5.93922200	0.98970300
H	-5.46101200	-6.86440500	1.09898200
H	-3.84310200	-6.19930000	0.90576200
H	-5.02477600	-5.35957200	1.90154900
C	-5.21789300	-5.97956400	-2.06476400
H	-5.78713800	-6.90763000	-2.02815100
H	-5.53778200	-5.42603000	-2.94526900
H	-4.16885300	-6.23727800	-2.19622900
C	-7.28436000	-4.52028000	-0.32219500
H	-7.44783100	-3.92175600	0.57171100
H	-7.63237000	-3.94467800	-1.17755900
H	-7.90450900	-5.41250700	-0.24525700
H	0.32218600	2.26392700	2.13346800
C	0.61035000	1.22671300	2.12403800
C	-0.33915400	0.23378000	2.20146500
C	1.93596600	0.88869500	1.99099500
C	0.00402900	-1.09309900	2.13373700
C	2.36453400	-0.45323200	1.96090500
C	1.33803200	-1.42357100	2.04550400
H	-0.74867100	-1.86359900	2.15106700
O	3.62536800	-0.75094900	1.82941700
H	3.70947600	-1.72395500	1.80559500
N	2.86284900	1.99827900	1.82362700
N	-1.73592600	0.59966500	2.30580600
N	1.64935100	-2.82981400	1.98759700
O	2.36909500	3.09858200	1.72242800
O	4.04117400	1.76134000	1.78478400
O	2.82542200	-3.16050800	2.04752100
O	0.74495400	-3.61349500	1.89608400
O	-1.99340700	1.77471000	2.40400500
O	-2.54243100	-0.29793700	2.28747700

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