Electronic Supplementary Material (ESI) for Journal of Materials Chemistry A.

Supporting Information

Single step synthesis of hierarchical B_xCN: A metal free catalyst for Low Temperature Oxidative dehydrogenation of Propane

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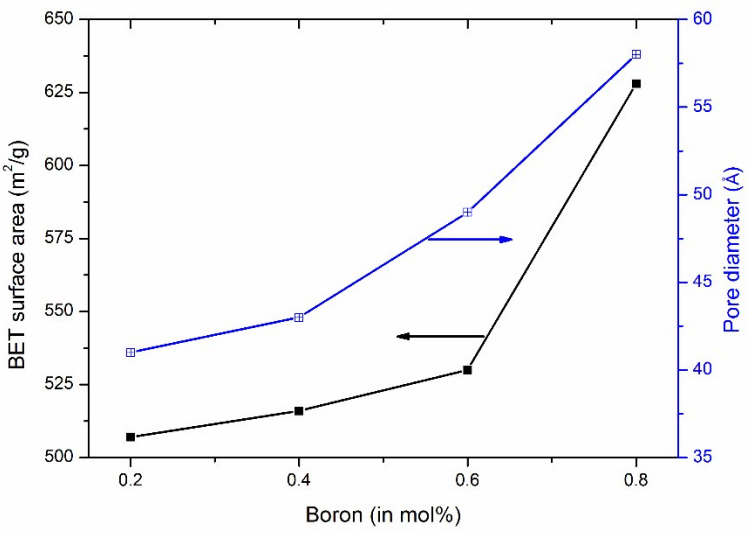


Figure S1. Boron content with BET surface area (m^2/g) and average pore diameter (nm).

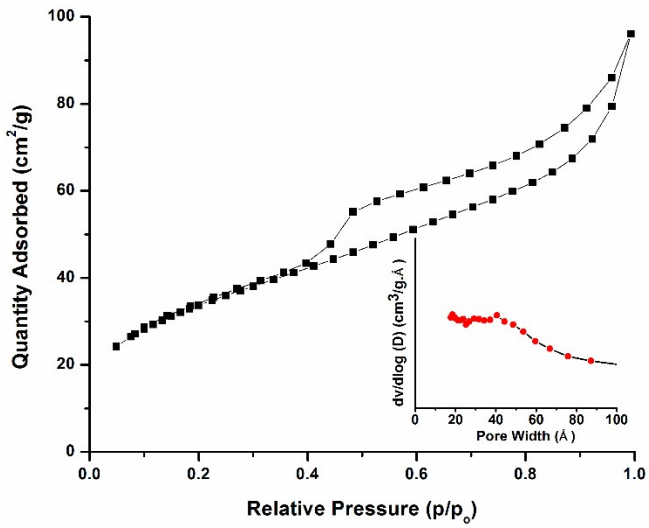


Figure S2. N_2 adsorption desorption isotherm and BJH plot of pore size distribution (inset).

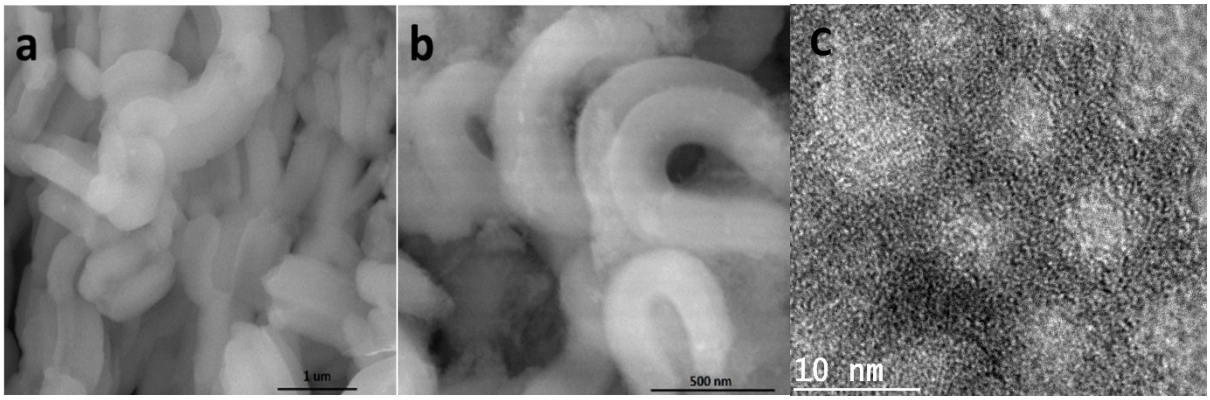


Figure S3. SEM and HRTEM images of SBA-15.

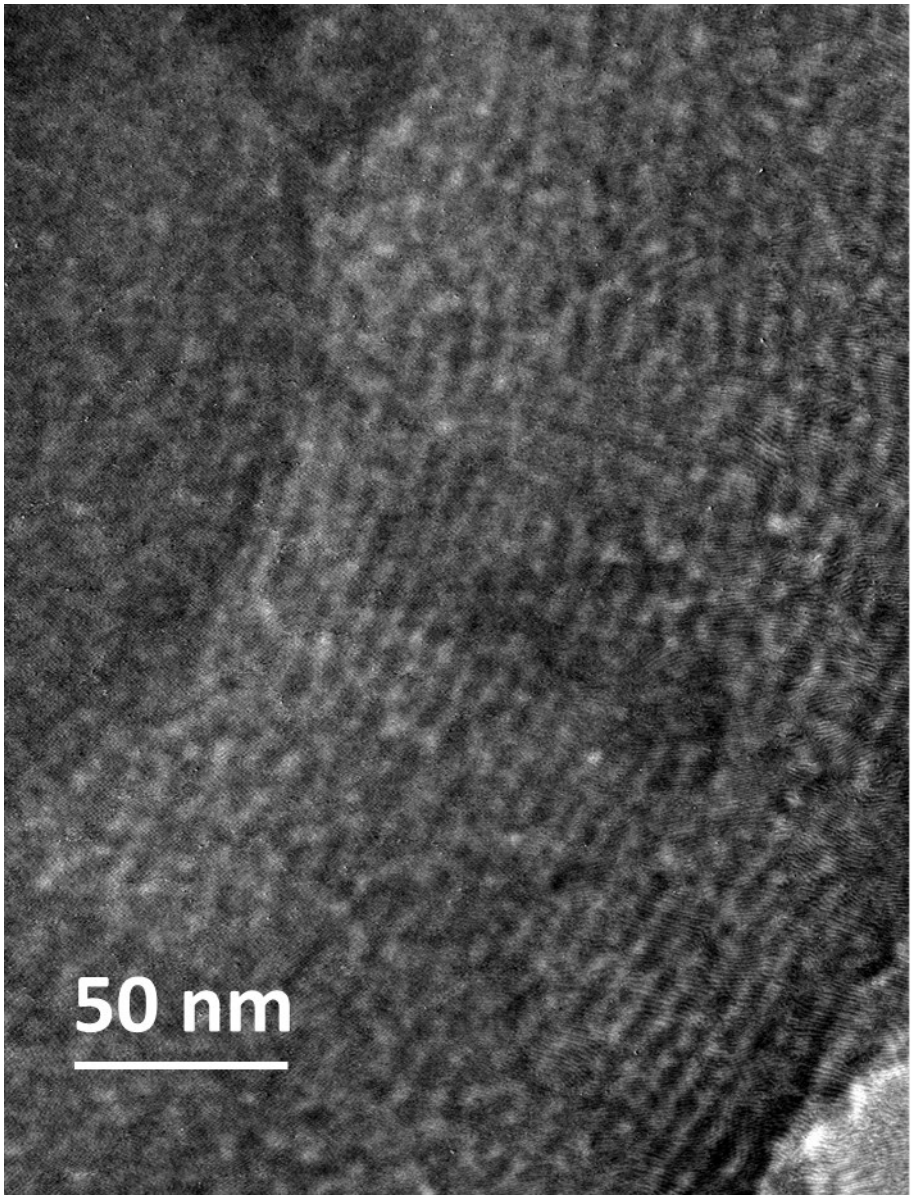


Figure S4. High resolution TEM image of BxCN material showing graphitic tubular network.

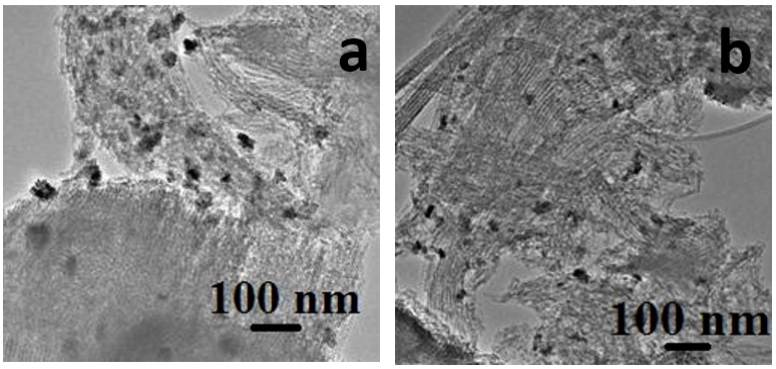


Figure S5. HRTEM images of TBCN papered using tri-ethyl borane.

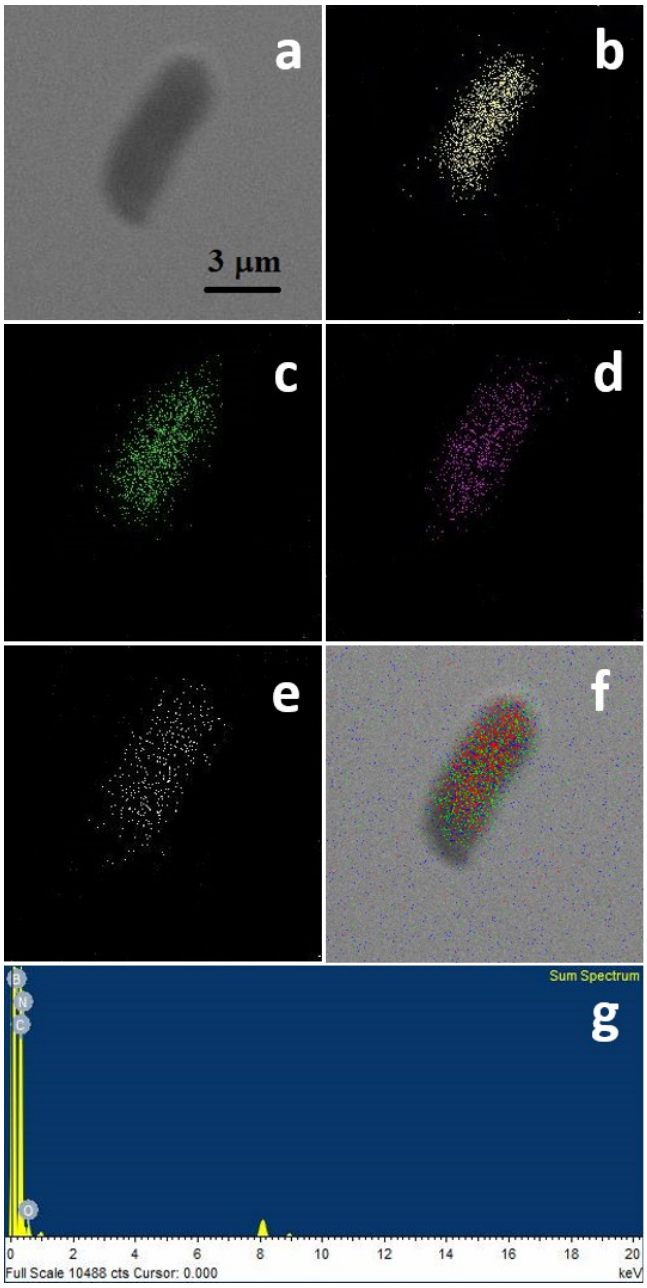


Figure S6. E-mapping (a-f) and EDAX (g) pattern of BxCN; (b) Carbon, (c) Nitrogen, (d) Oxygen, (e) Boron and (f) combined.

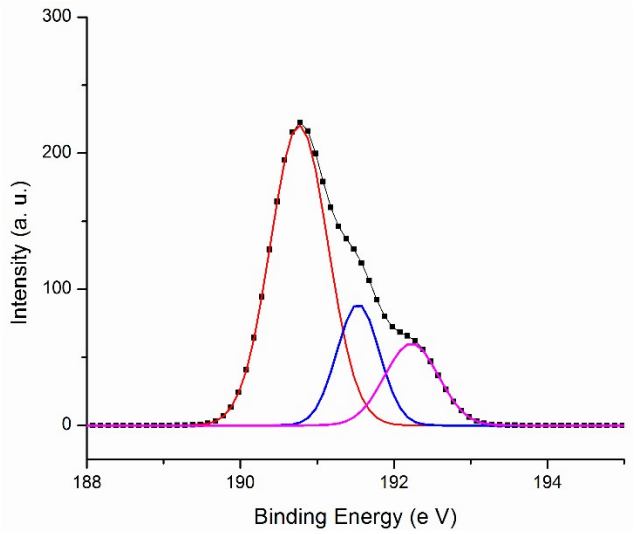


Figure S7. X-ray photoelectron spectroscopy of BxCN papered using tri-ethylborane.

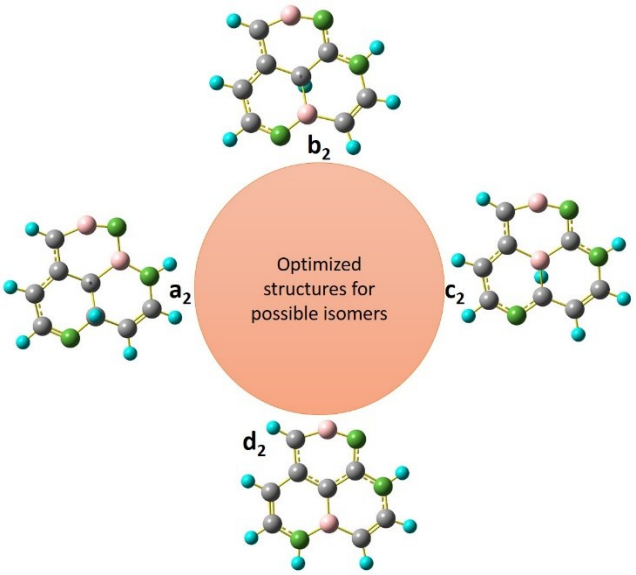


Figure S8. DFT-optimized di- substituted BxNyCz structures four possible isomers.

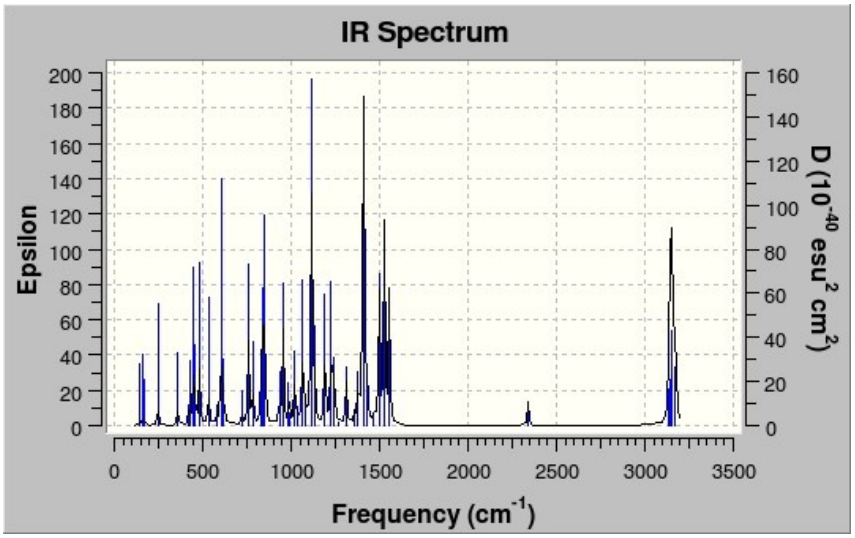
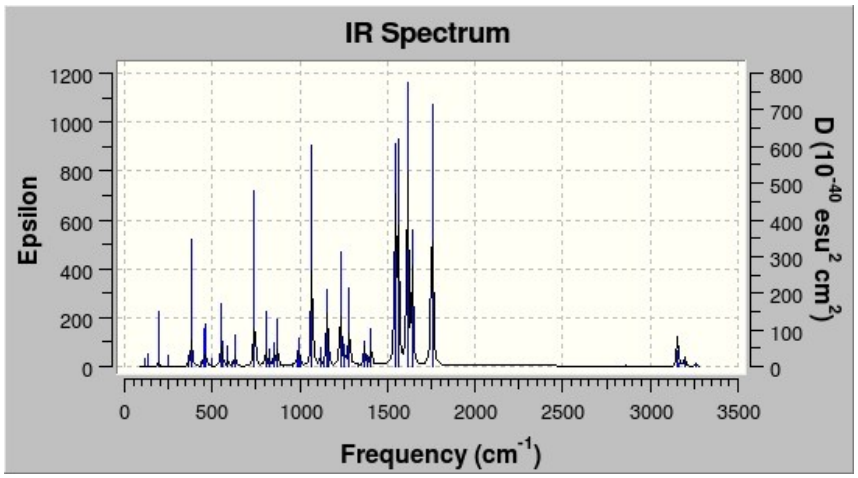
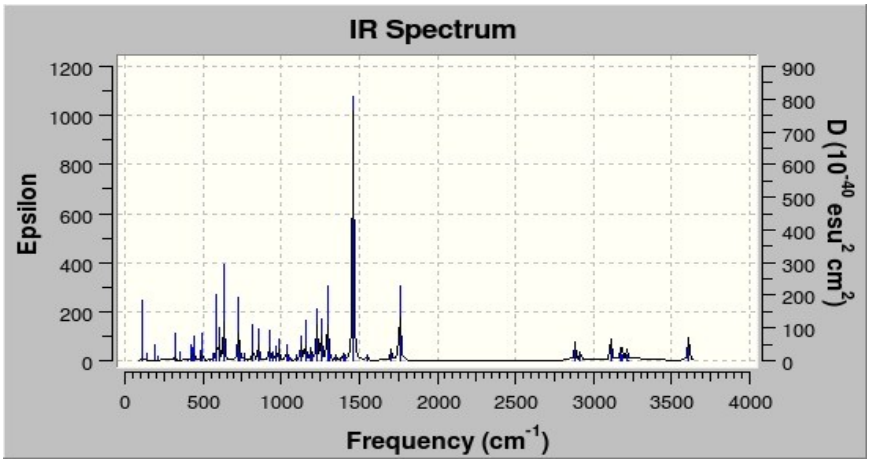


Figure S9. Computed IR spectra for the e_1 isomer.

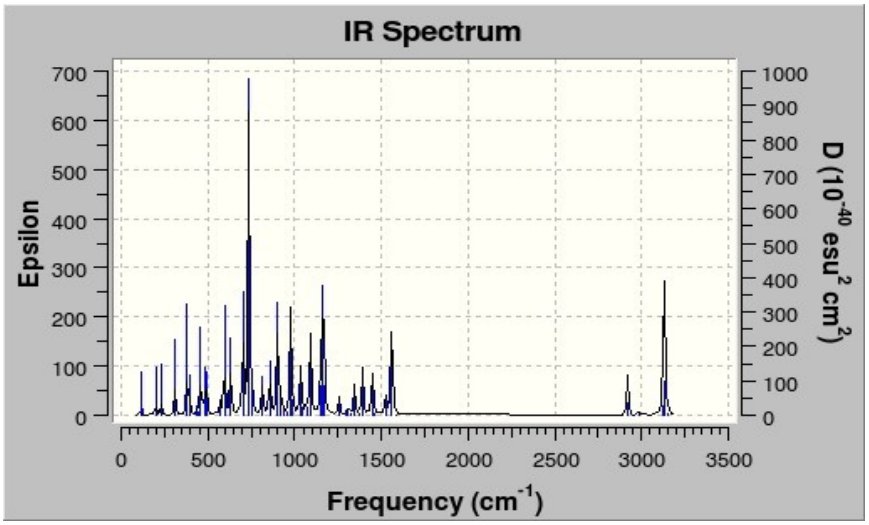
a_1



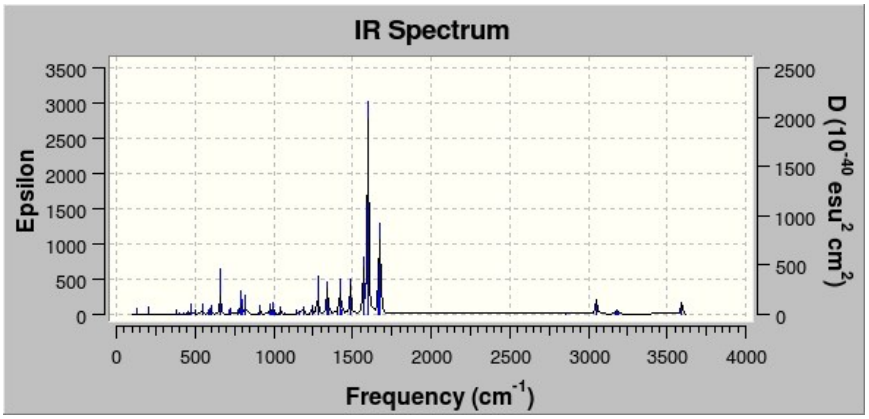
a_2



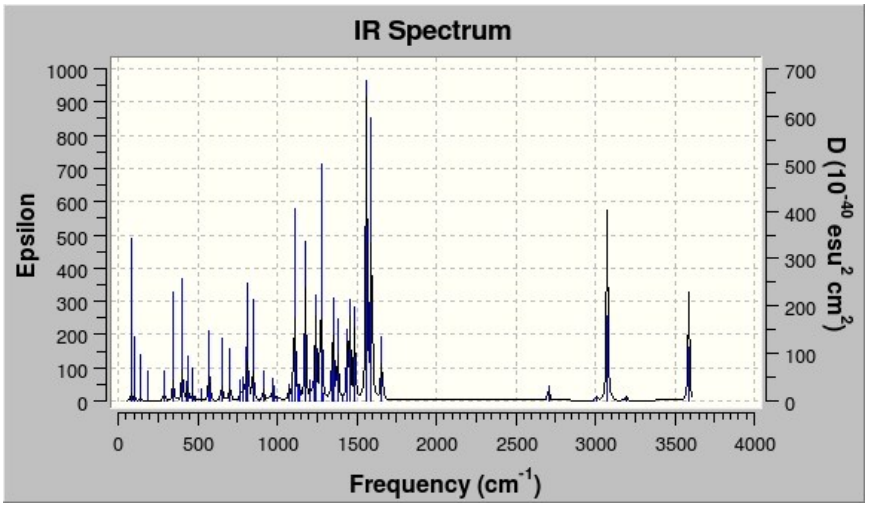
b_1


IR Spectrum
Epsilon
D (10^{-40} esu^2 cm^2)
Frequency (cm^{-1})
0
100
200
300
400
500
600
700
800
900
1000
0
500
1000
1500
2000
2500
3000
3500

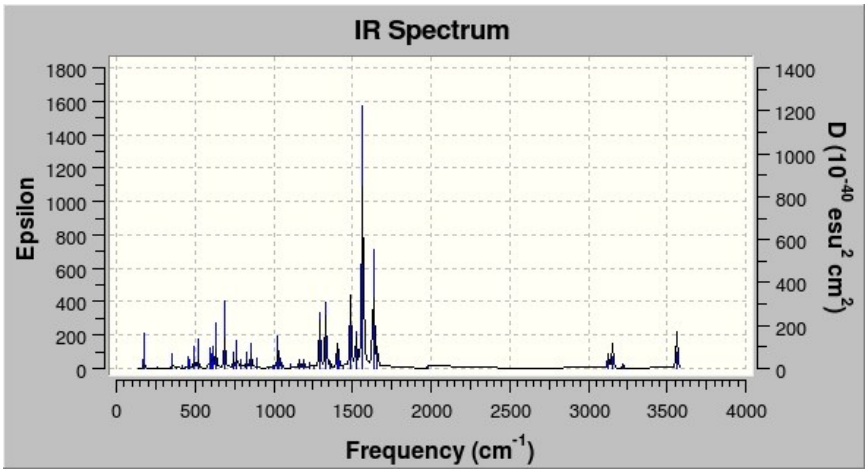
b_2


IR Spectrum
Epsilon
D (10^{-40} esu^2 cm^2)
Frequency (cm^{-1})
0
500
1000
1500
2000
2500
3000
3500
4000

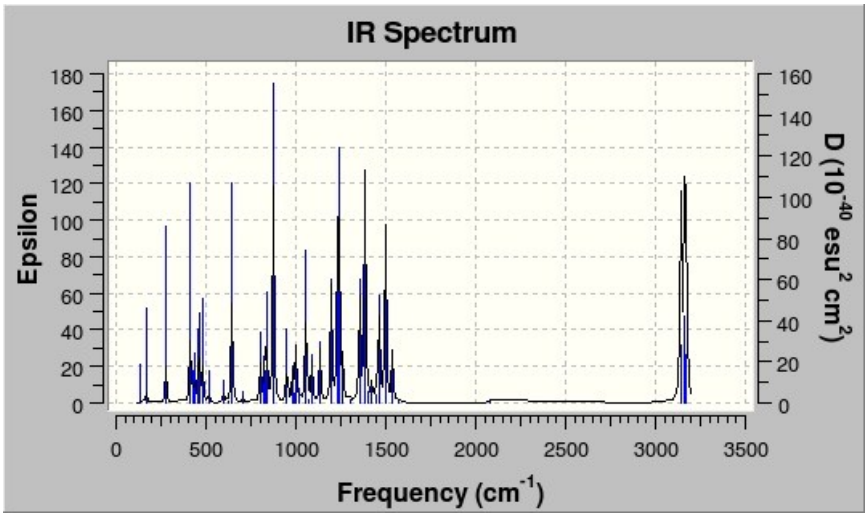
c_1


IR Spectrum
Epsilon
D (10^{-40} esu^2 cm^2)
Frequency (cm^{-1})
0
100
200
300
400
500
600
700
800
900
1000
0
500
1000
1500
2000
2500
3000
3500
4000

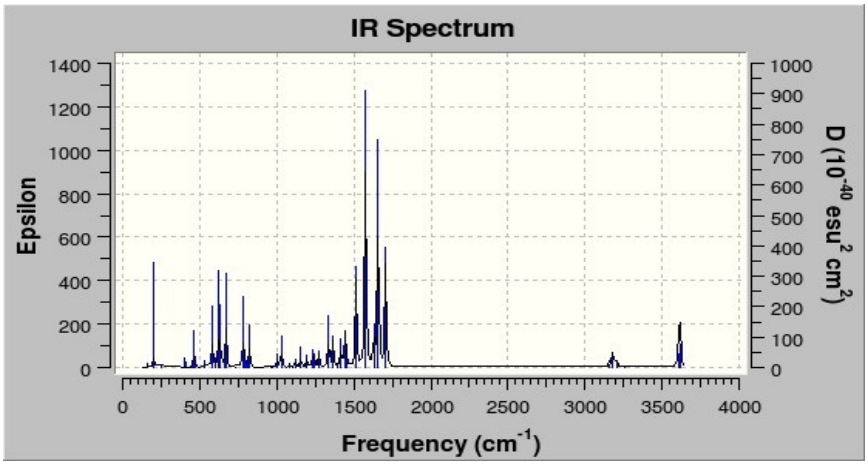
c_2


IR Spectrum
Epsilon
D (10^{-40} esu^2 cm^2)
Frequency (cm^{-1})

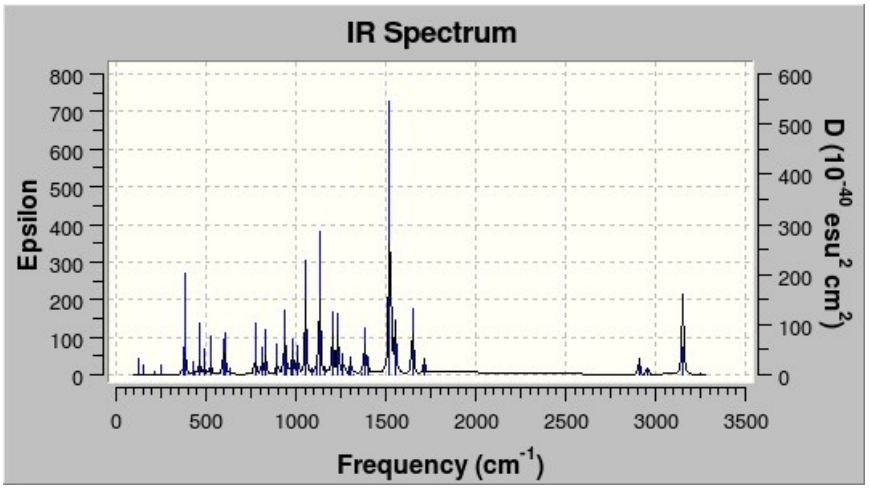
d_1


IR Spectrum
Epsilon
D (10^{-40} esu^2 cm^2)
Frequency (cm^{-1})

d_2


IR Spectrum
Epsilon
D (10^{-40} esu^2 cm^2)
Frequency (cm^{-1})

f_1



g_1

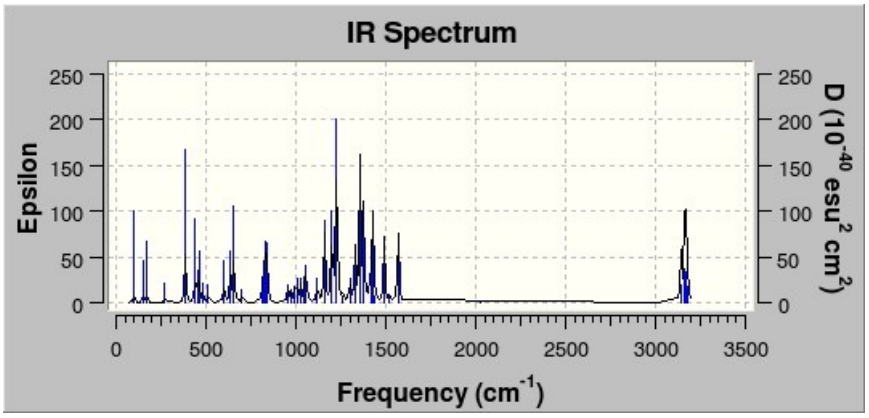
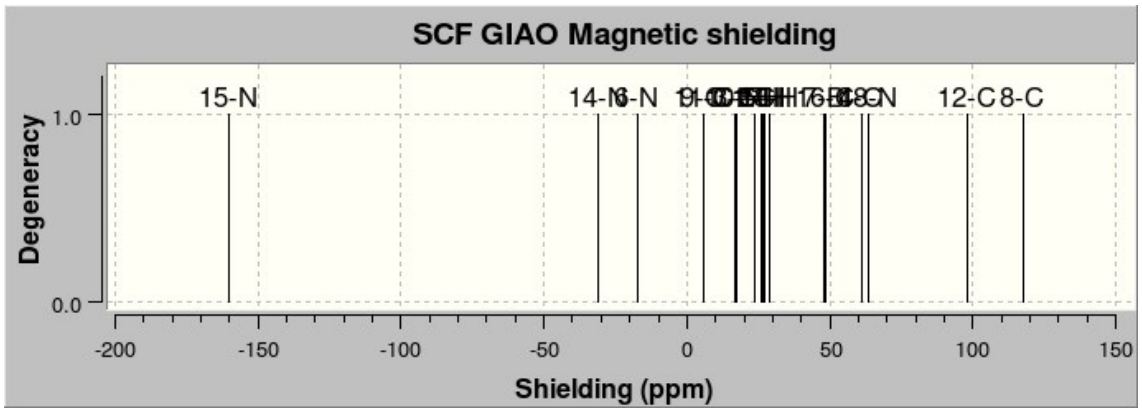
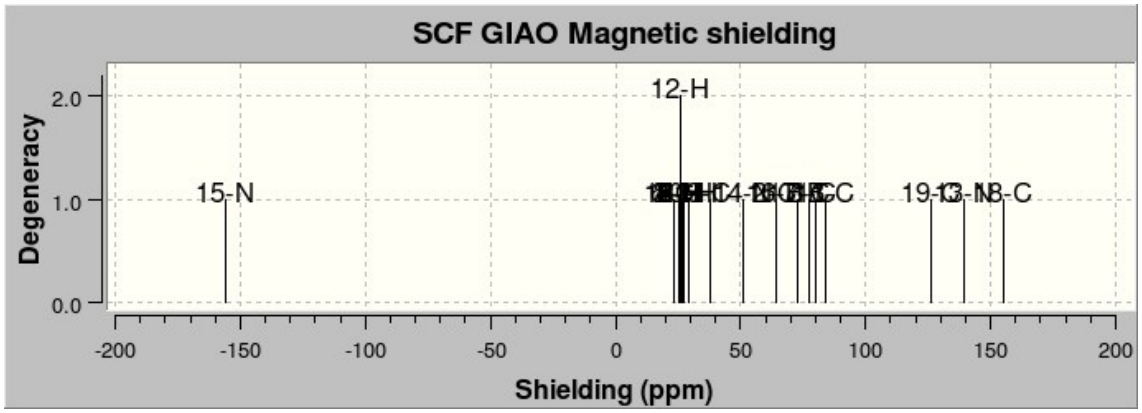


Figure 10. Computed spectra of IR of different possible structures (excluding e_1, which is listed in Figure xx).

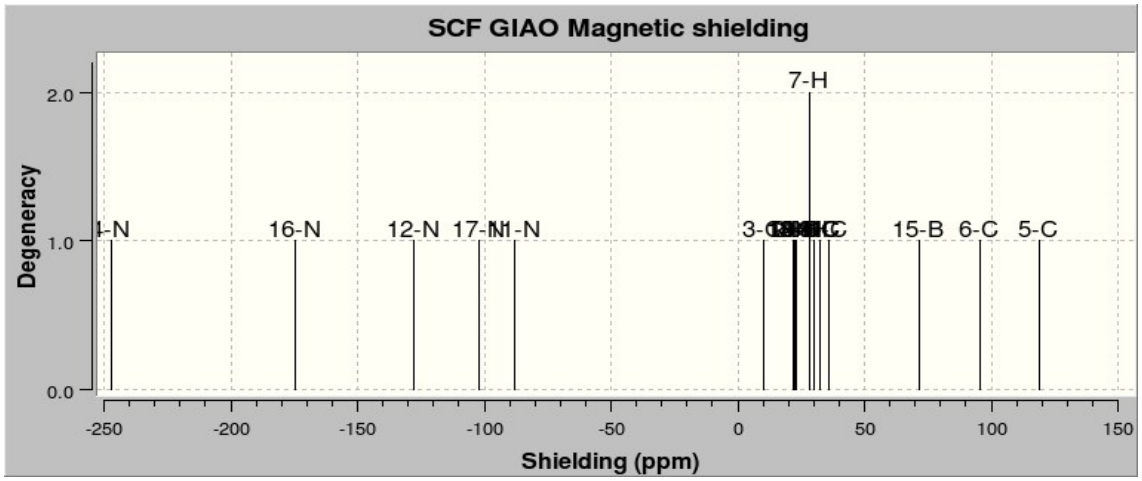
a_1



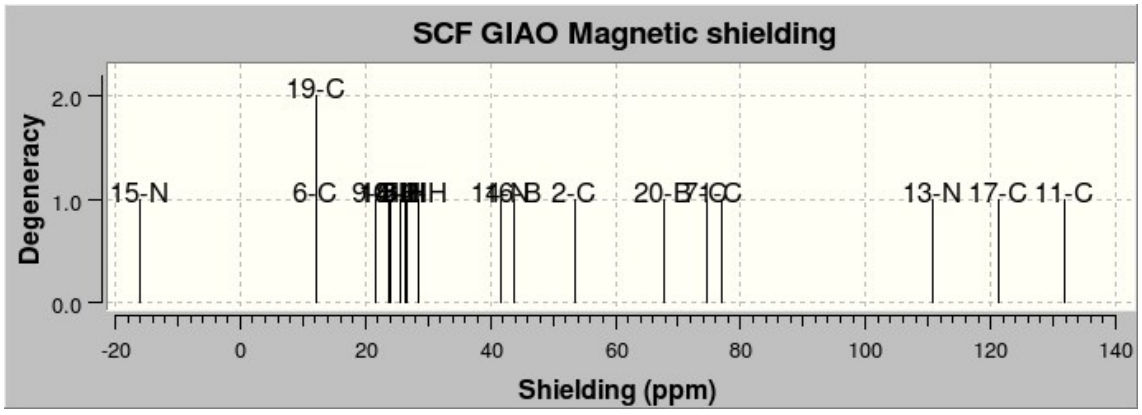
a_2


SCF GIAO Magnetic shielding
Degeneracy
2.0
1.0
0.0
12-H
15-N
-200
-150
-100
-50
0
50
100
150
200
Shielding (ppm)

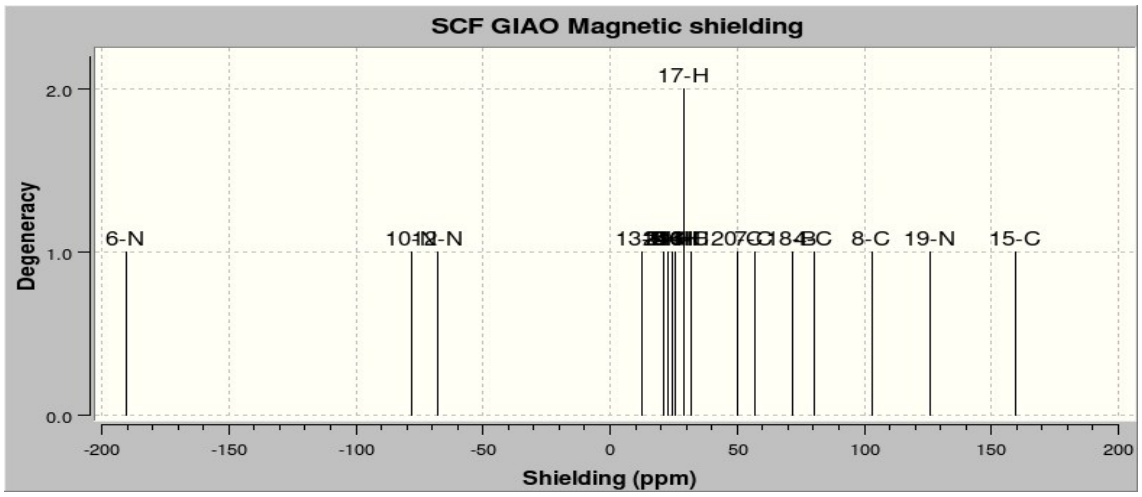
b_1


SCF GIAO Magnetic shielding
Degeneracy
2.0
1.0
0.0
7-H
16-N
12-N
15-B
6-C
5-C
-250
-200
-150
-100
-50
0
50
100
150
Shielding (ppm)

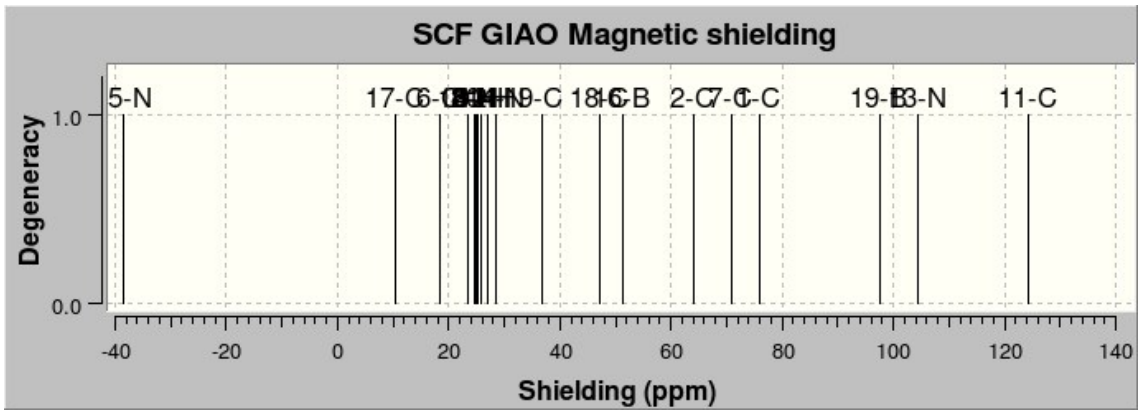
b_2


SCF GIAO Magnetic shielding
Degeneracy
2.0
1.0
0.0
19-C
15-N
6-C
13-N
17-C
11-C
-20
0
20
40
60
80
100
120
140
Shielding (ppm)

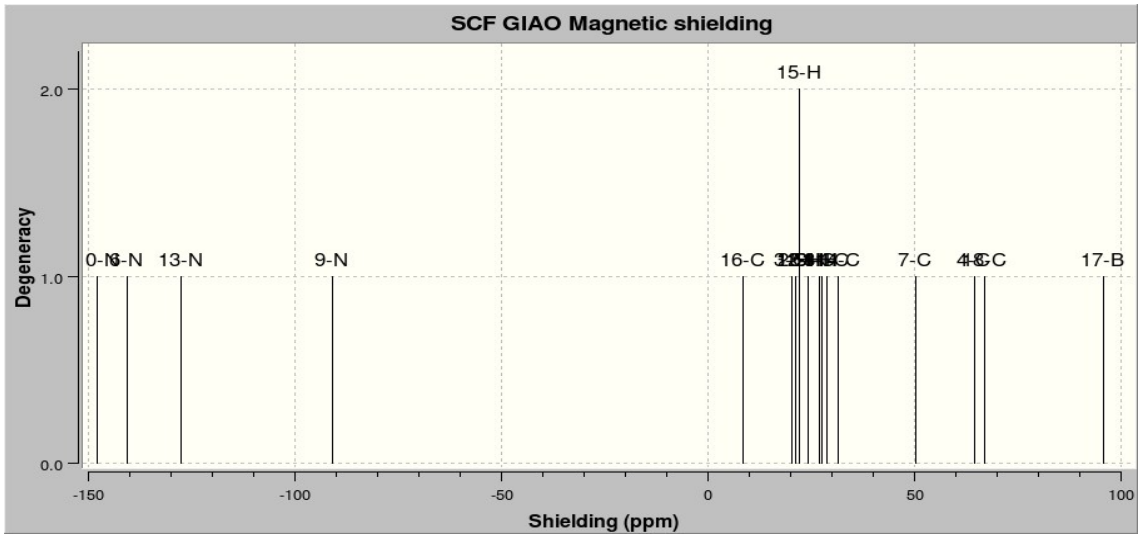
c_1


SCF GIAO Magnetic shielding
17-H
6-N
8-C
19-N
15-C
Degeneracy
2.0
1.0
0.0
-200
-150
-100
-50
0
50
100
150
200
Shielding (ppm)

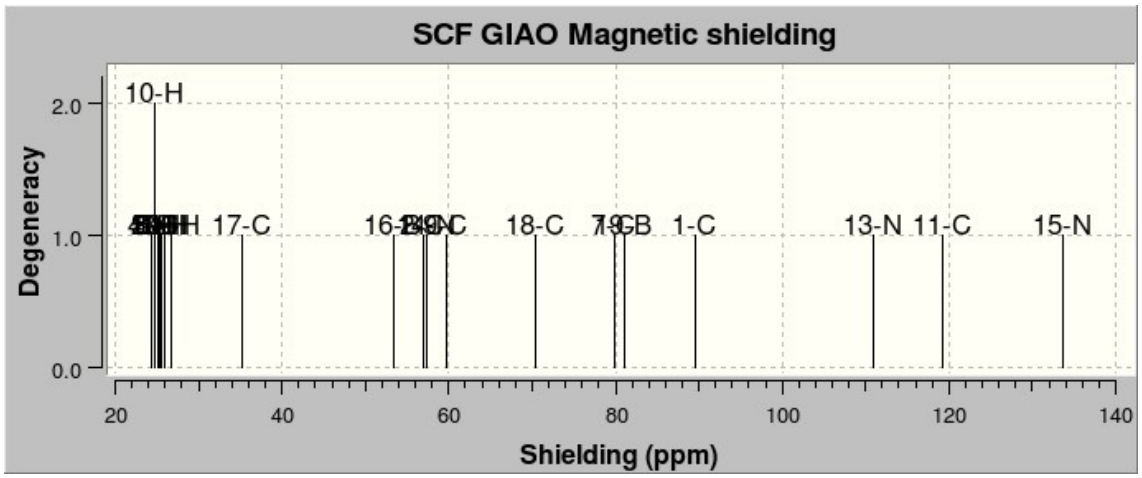
c_2

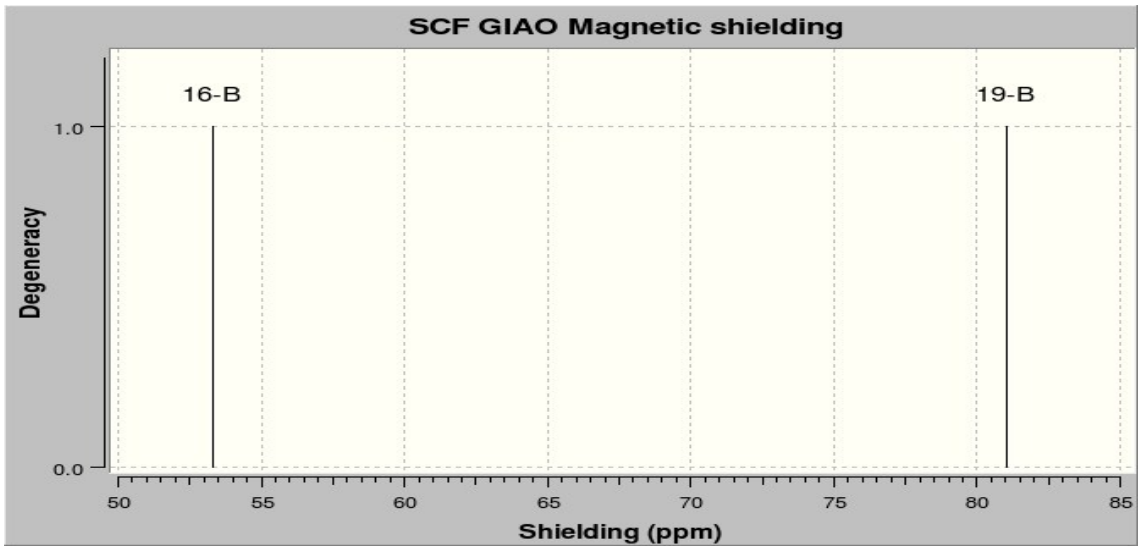

SCF GIAO Magnetic shielding
5-N
11-C
Degeneracy
1.0
0.0
-40
-20
0
20
40
60
80
100
120
140
Shielding (ppm)

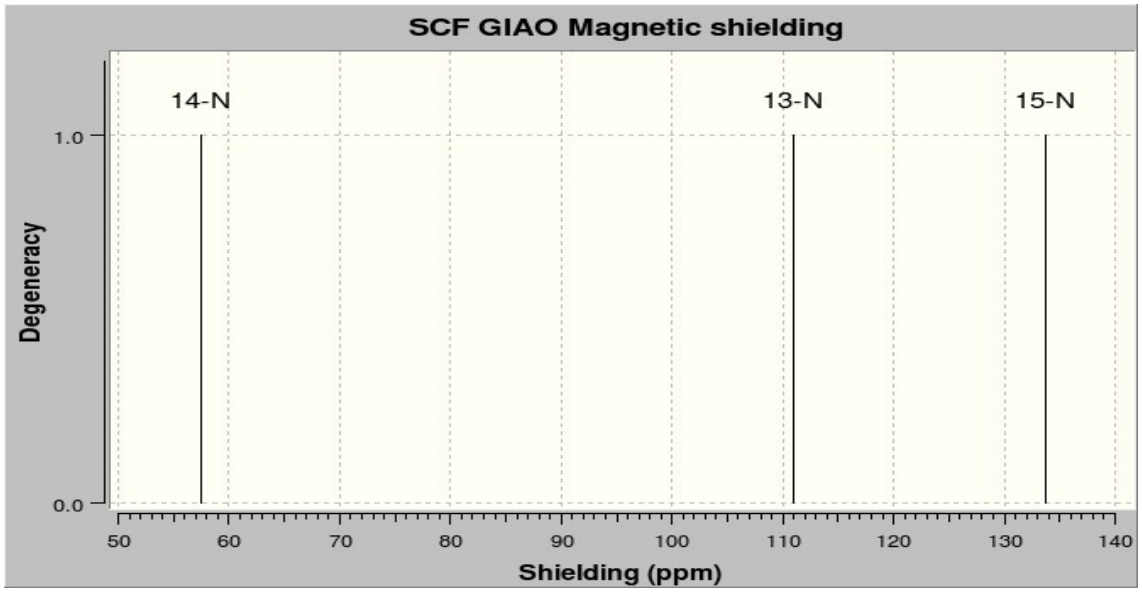
d_1


SCF GIAO Magnetic shielding
15-H
Degeneracy
2.0
1.0
0.0
13-N
9-N
7-C
17-B
-150
-100
-50
0
50
100
Shielding (ppm)

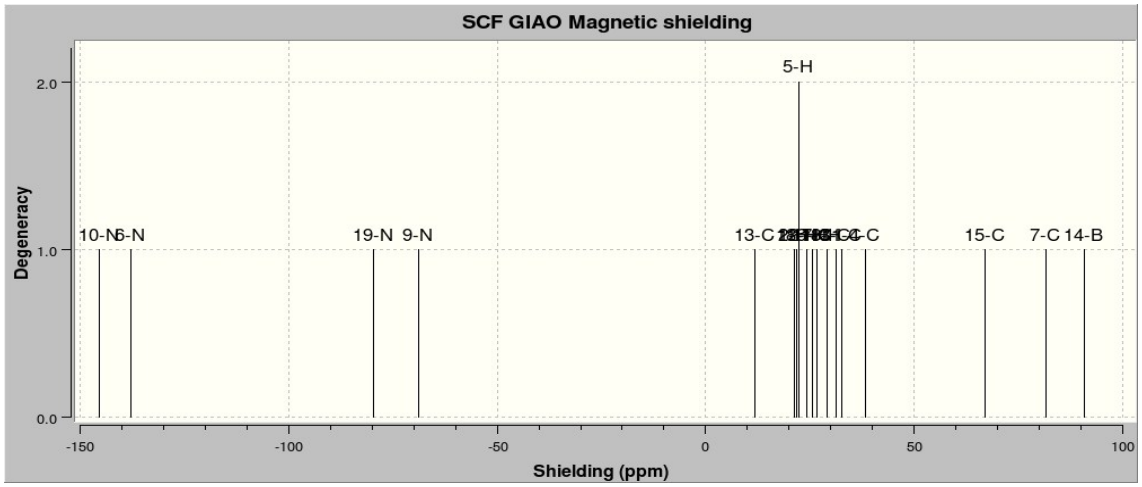
d_2


SCF GIAO Magnetic shielding
10-H
Degeneracy
2.0
1.0
0.0
17-C
18-C
1-C
13-N
11-C
15-N
20
40
60
80
100
120
140
Shielding (ppm)

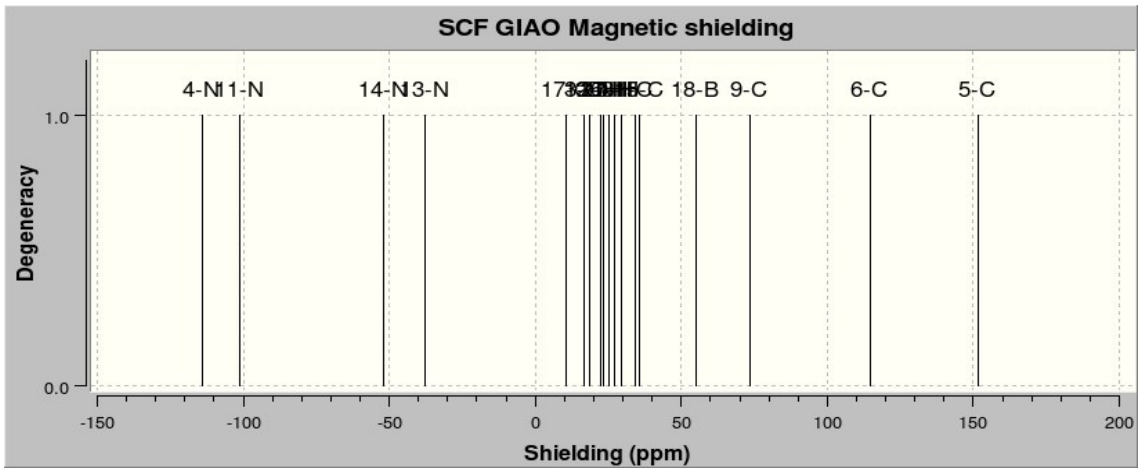

SCF GIAO Magnetic shielding
16-B
19-B
Degeneracy
1.0
0.0
50
55
60
65
70
75
80
85
Shielding (ppm)


SCF GIAO Magnetic shielding
14-N
13-N
15-N
1.0
0.0
Degeneracy
50
60
70
80
90
100
110
120
130
140
Shielding (ppm)

e_1


SCF GIAO Magnetic shielding
5-H
2.0
1.0
0.0
Degeneracy
10-N
6-N
19-N
9-N
15-C
7-C
14-B
-150
-100
-50
0
50
100
Shielding (ppm)

f_1


SCF GIAO Magnetic shielding
4-N
1-N
14-N
3-N
18-B
9-C
6-C
5-C
1.0
0.0
Degeneracy
-150
-100
-50
0
50
100
150
200
Shielding (ppm)

g_1

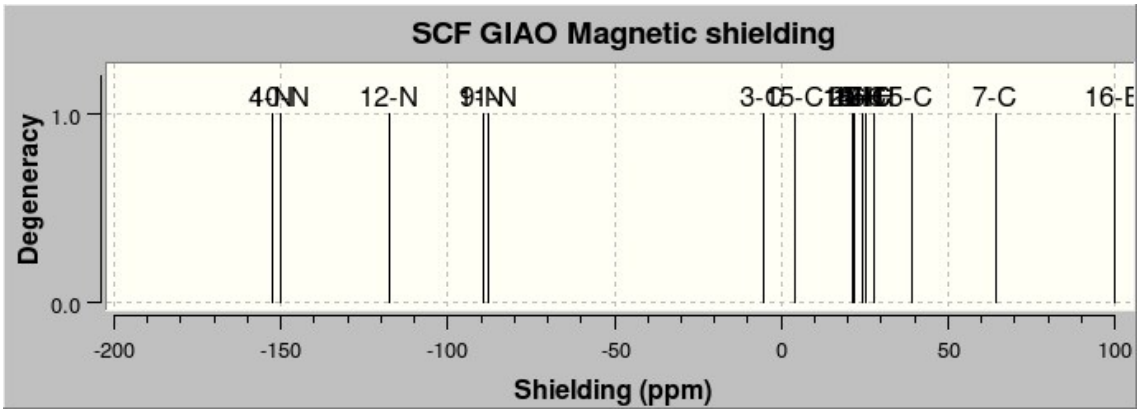
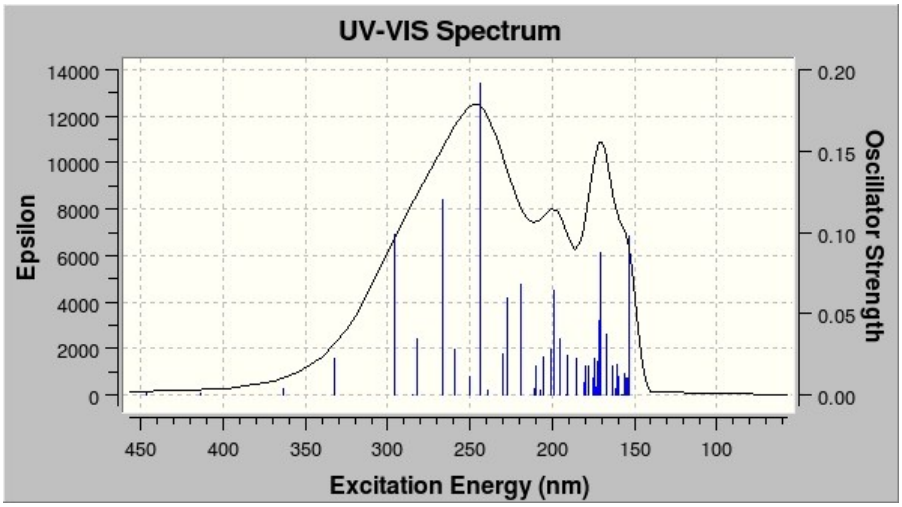
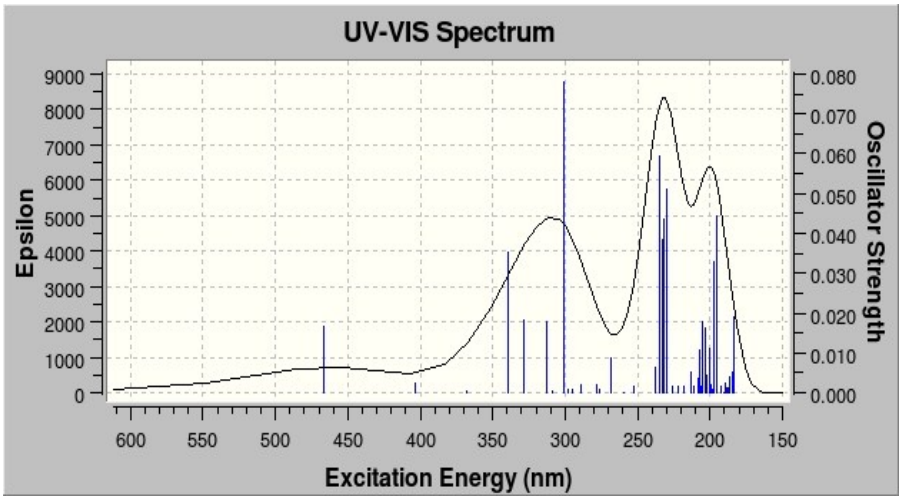


Figure S11. Computed spectra of NMR of different possible structures.

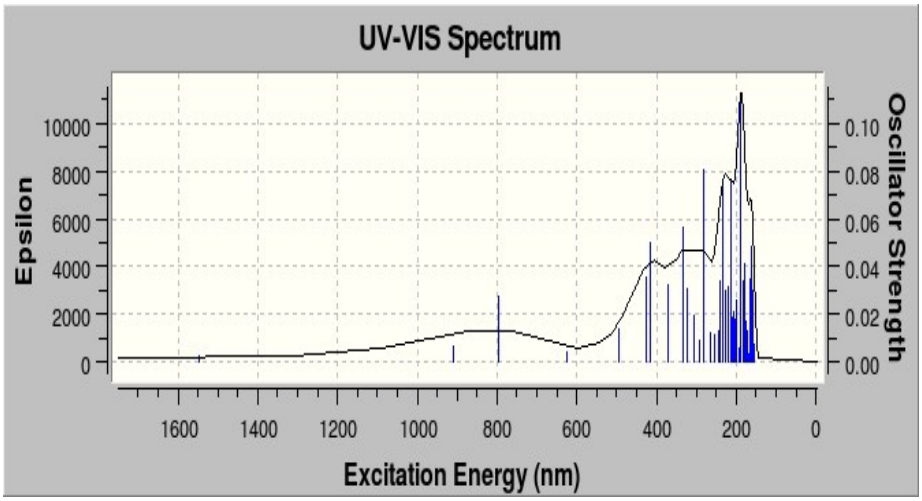
a_1



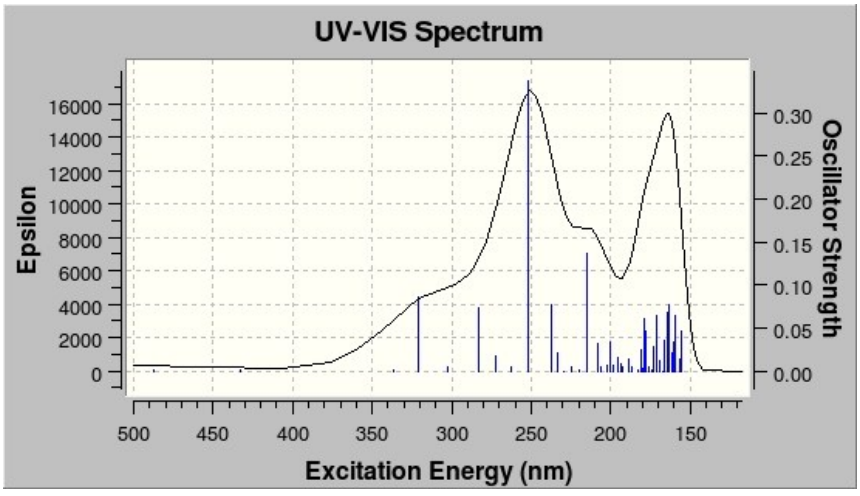
a_2


UV-VIS Spectrum
Epsilon
Oscillator Strength
Excitation Energy (nm)

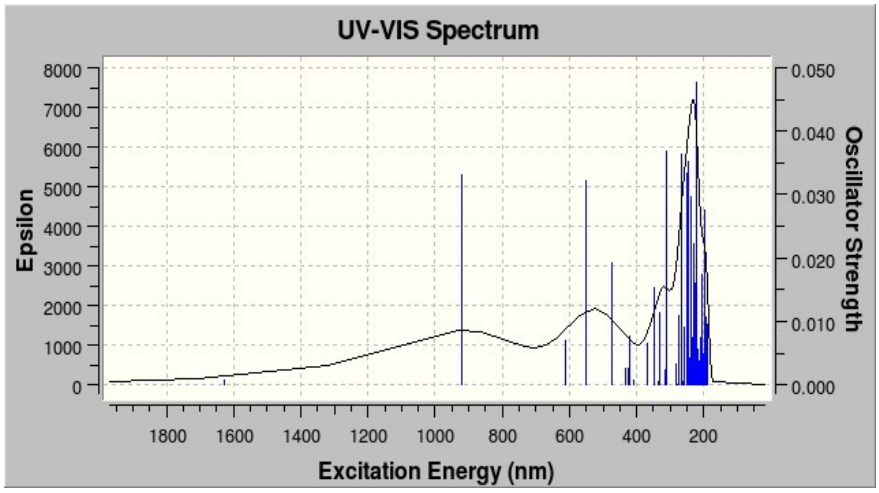
b_1


UV-VIS Spectrum
Epsilon
Oscillator Strength
Excitation Energy (nm)

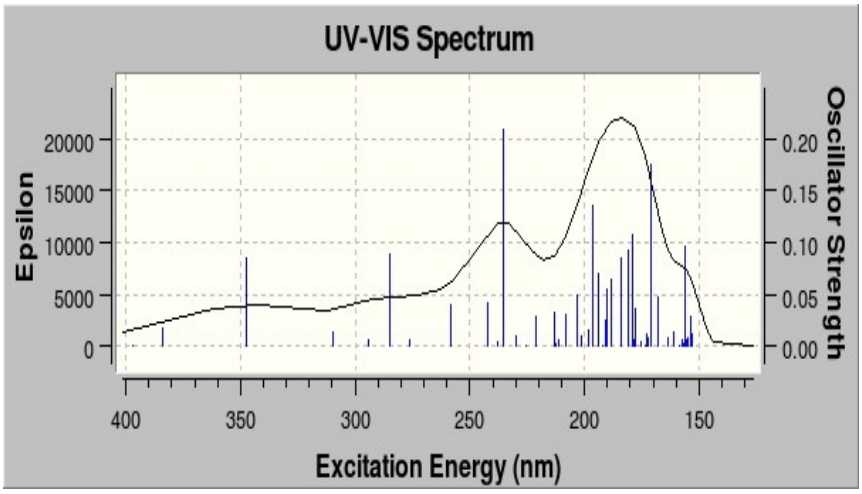
b_2


UV-VIS Spectrum
Epsilon
Oscillator Strength
Excitation Energy (nm)

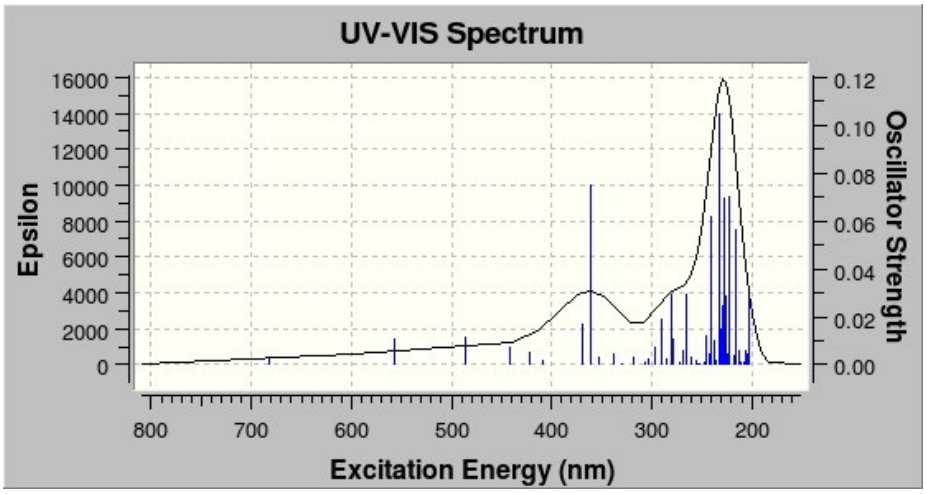
c_1


UV-VIS Spectrum
Epsilon
Oscillator Strength
Excitation Energy (nm)
8000
7000
6000
5000
4000
3000
2000
1000
0
0.050
0.040
0.030
0.020
0.010
0.000
1800
1600
1400
1200
1000
800
600
400
200

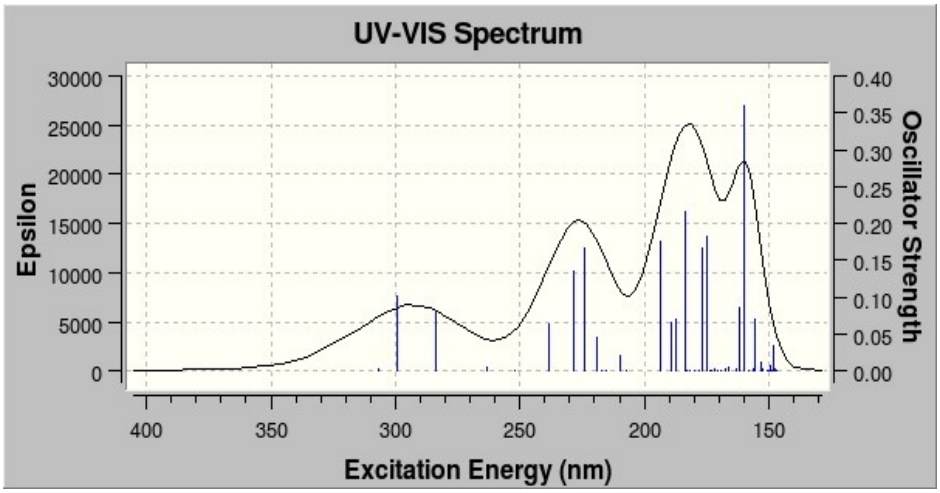
c_2


UV-VIS Spectrum
Epsilon
Oscillator Strength
Excitation Energy (nm)
20000
15000
10000
5000
0
0.20
0.15
0.10
0.05
0.00
400
350
300
250
200
150

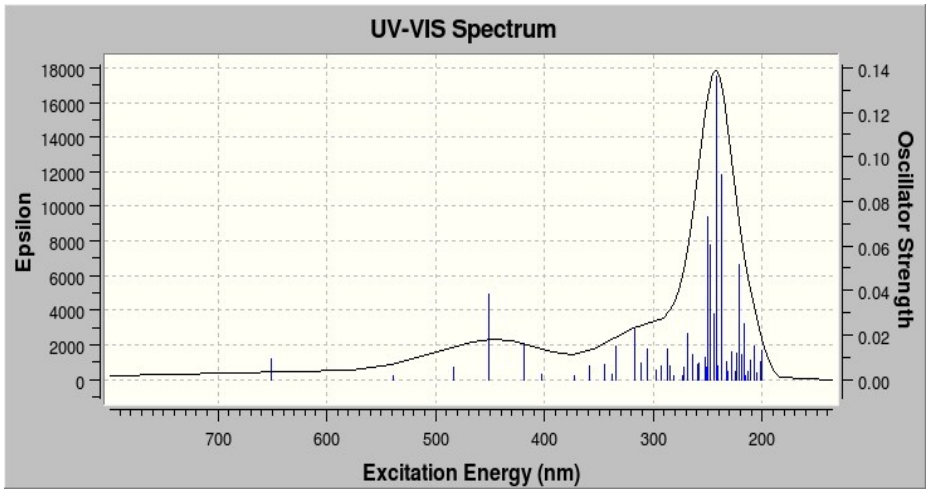
d_1


UV-VIS Spectrum
Epsilon
Oscillator Strength
Excitation Energy (nm)
16000
14000
12000
10000
8000
6000
4000
2000
0
0.12
0.10
0.08
0.06
0.04
0.02
0.00
800
700
600
500
400
300
200

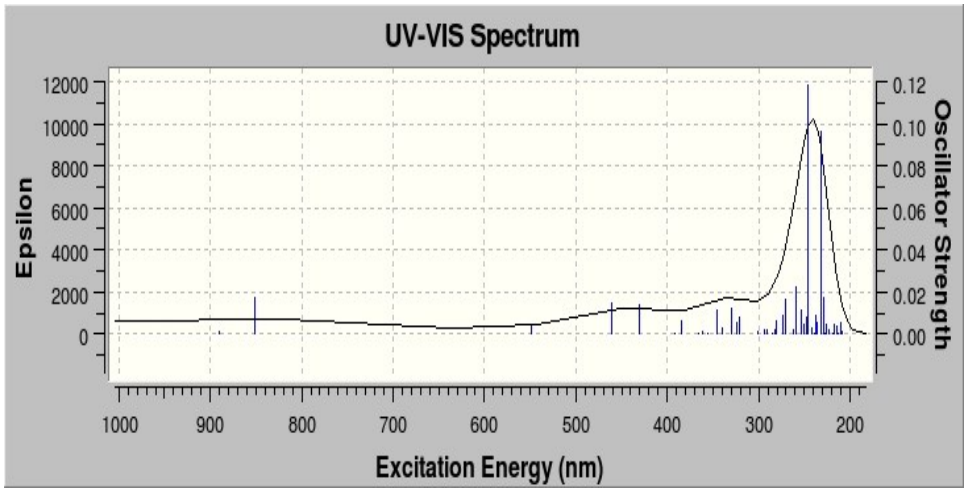
d_2


UV-VIS Spectrum
Epsilon
Oscillator Strength
Excitation Energy (nm)
30000
25000
20000
15000
10000
5000
0
0.40
0.35
0.30
0.25
0.20
0.15
0.10
0.05
0.00
400
350
300
250
200
150

e_1


UV-VIS Spectrum
Epsilon
Oscillator Strength
Excitation Energy (nm)
18000
16000
14000
12000
10000
8000
6000
4000
2000
0
0.14
0.12
0.10
0.08
0.06
0.04
0.02
0.00
700
600
500
400
300
200

f_1



g_1

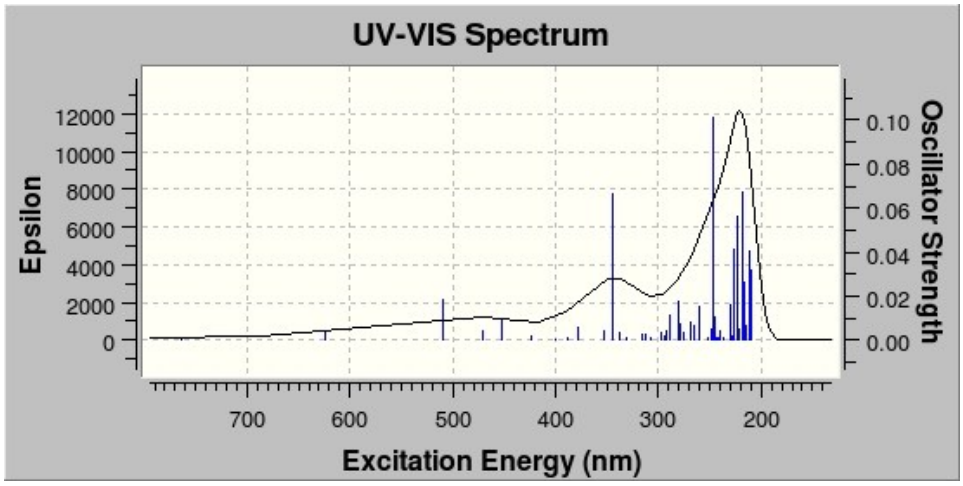


Figure S12. Computed spectra of UV of different possible structures.

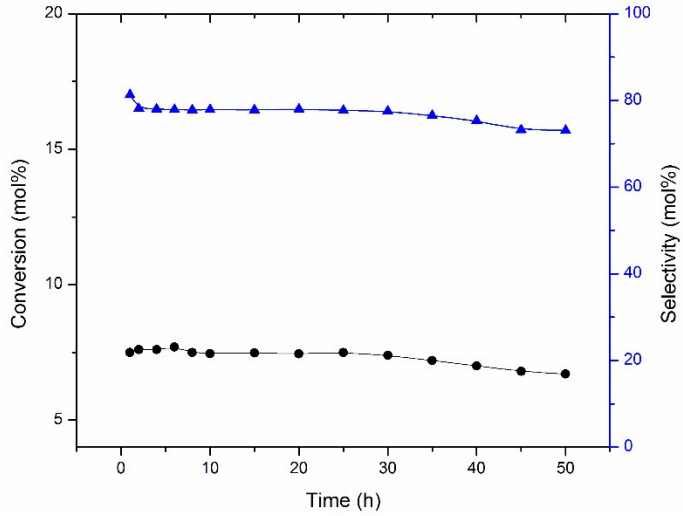


Figure S13. Catalytic activity during time on steam over 0.4BxCN catalyst. [Reaction condition: 0.1 g catalyst, C_3H_8:O_2: He of 2:2:9, temp. =350°C, GHSV=2000 ml g^{-1} h^{-1}]

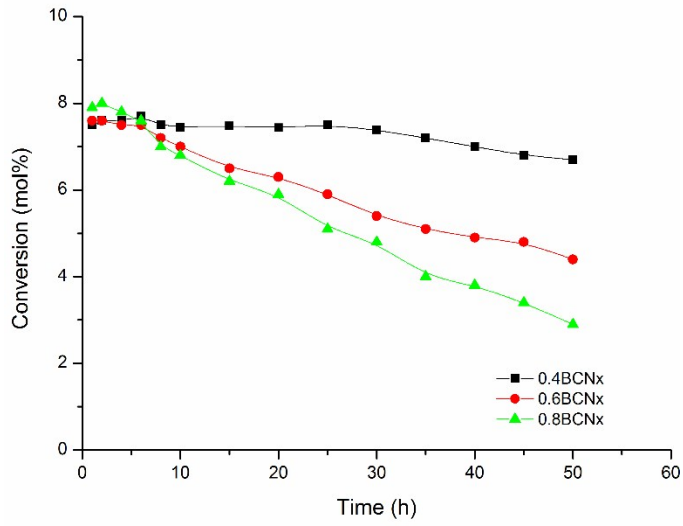


Figure S14. Catalytic activity during time on steam with different boron content. [Reaction condition: 0.1 g catalyst, C_3H_8:O_2: He of 2:2:9, temp. =350°C, GHSV=2000 ml g^{-1} h^{-1}]

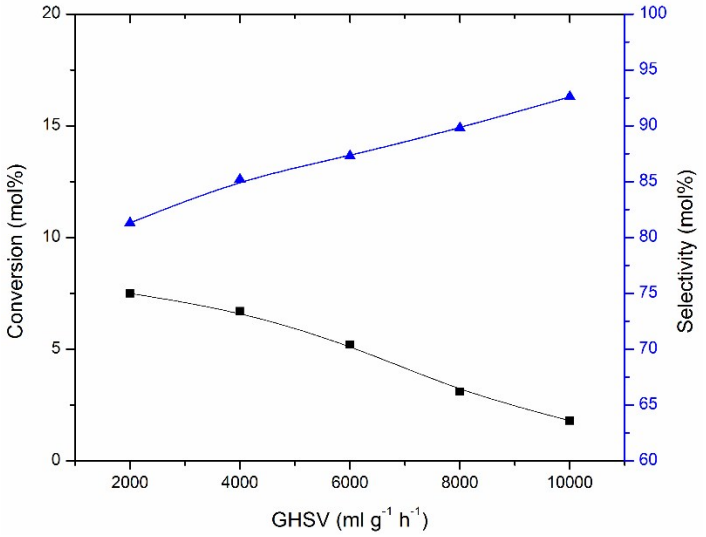


Figure S15. Catalytic activity during oxidative dehydrogenation of propane as a function of GHSV. [Reaction condition: 0.1 g catalyst, C_3H_8:O_2: He of 2:2:9, TOS=1h, temp. =350°C]

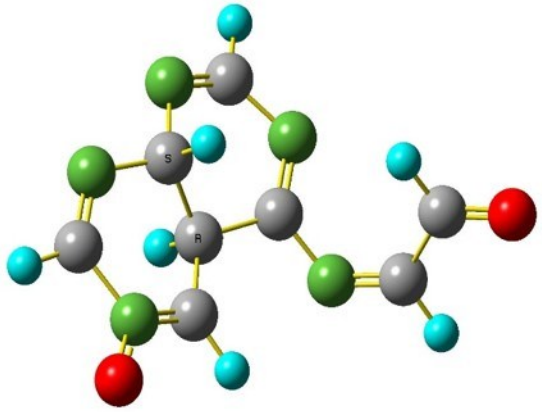


Figure S16. Oxidized product of boron free catalyst