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for

Carborane isothiocyanates: synthesis, characterization and conjugation with *N*-nucleophiles

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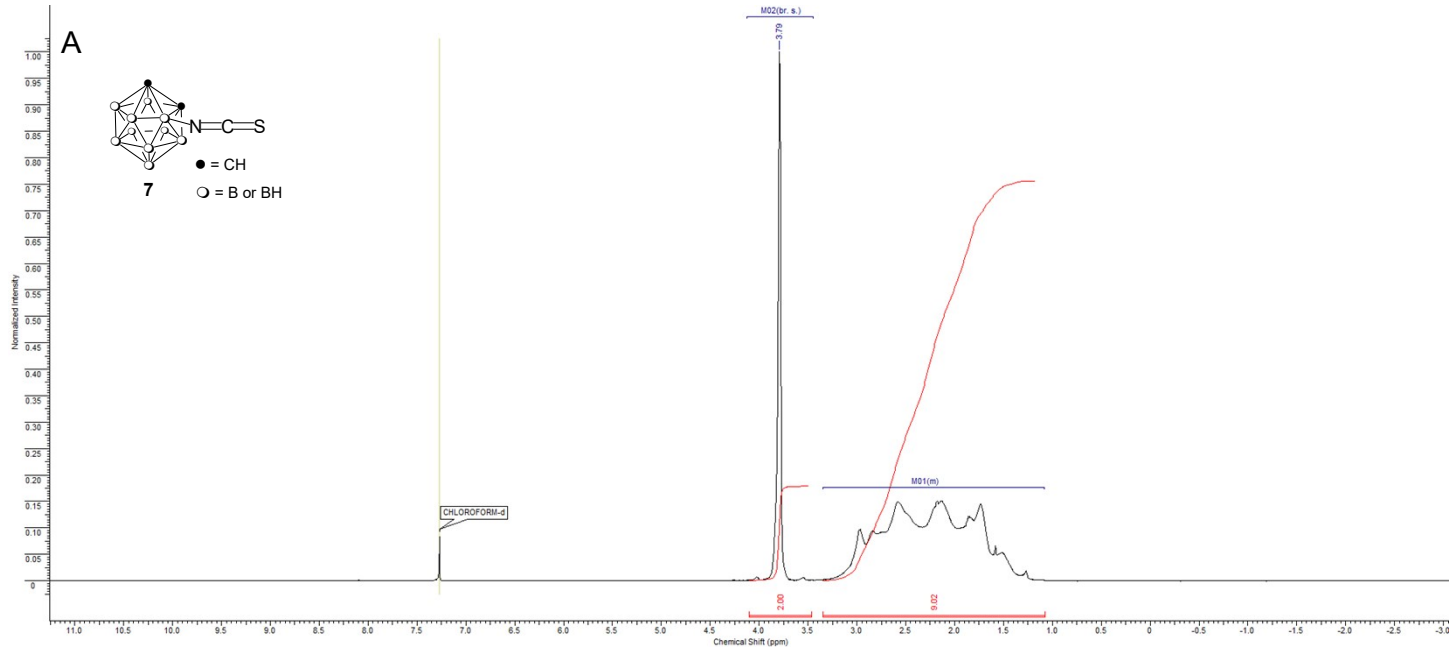
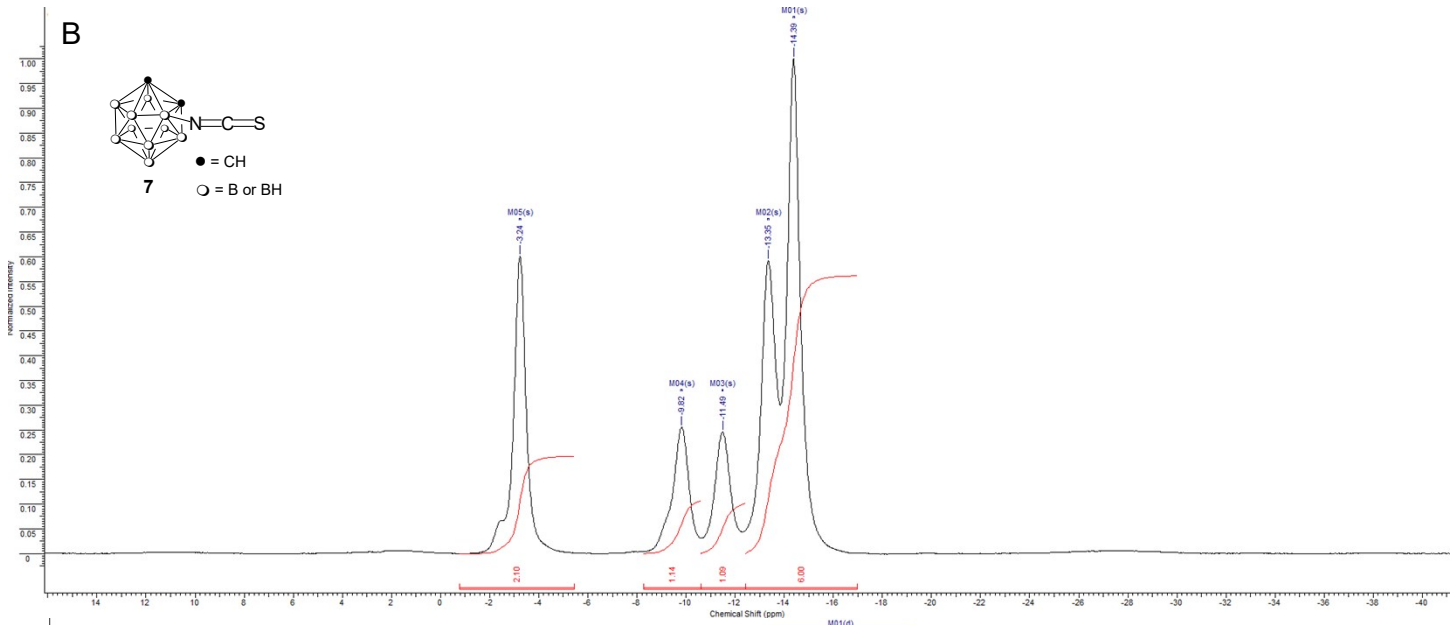
1. X-ray crystallography

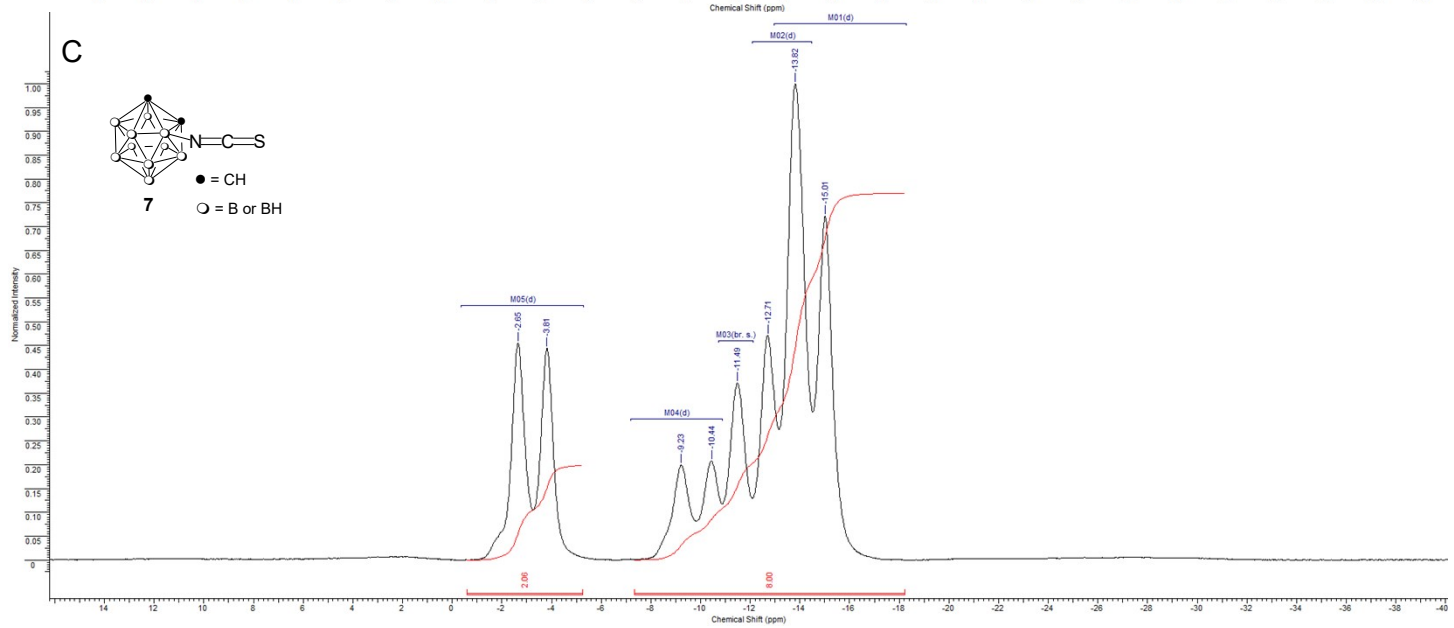
Table S1. Crystal data and structure refinement for carboranes **7**, **10** and **25**.

	7	**10**	**25**
Empirical formula	$C_3H_{11}B_{10}NS$	$C_5H_{15}B_{10}NS$	$C_9H_{24}B_{10}N_2O_3S$
Formula weight	201.29	229.34	348.46
Temperature/K	120	120	120
Crystal system	orthorhombic	monoclinic	monoclinic
Space group	$P2_12_12_1$	P2/n	$P2_1$
a/Å	6.9714(4)	15.4827(6)	7.6763(3)
b/Å	10.8737(7)	7.5722(3)	23.3782(9)
c/Å	14.1939(8)	21.8400(8)	10.1930(4)
α/°	90	90	90
β/°	90	94.311(2)	92.084(2)
γ/°	90	90	90
Volume/Å^3	1075.97(11)	2553.24(17)	1828.01(12)
Z	4	8	4
ρ_{calc}g/cm^3	1.243	1.193	1.266
μ/mm^{-1}	0.245	0.214	0.187
F(000)	408.0	944.0	728.0
Crystal size/mm^3	0.28 × 0.15 × 0.08	0.32 × 0.22 × 0.18	0.35 × 0.25 × 0.04
Radiation	MoKα (λ = 0.71073)	MoKα (λ = 0.71073)	MoKα (λ = 0.71073)
2Θ range for data collection/°	4.718 to 56.634	3.346 to 51.996	3.998 to 51.996
Index ranges	-9 ≤ h ≤ 9, -13 ≤ k ≤ 14, -17 ≤ l ≤ 18	-19 ≤ h ≤ 19, -9 ≤ k ≤ 9, -26 ≤ l ≤ 26	-9 ≤ h ≤ 9, -28 ≤ k ≤ 28, -12 ≤ l ≤ 12
Reflections collected	12057	34676	26505
Independent reflections	2679 [R_{int} = 0.0309, R_{sigma} = 0.0307]	5001 [R_{int} = 0.0354, R_{sigma} = 0.0295]	7158 [R_{int} = 0.0300, R_{sigma} = 0.0353]
Data/restraints/parameters	2679/0/136	5001/0/311	7158/1/459
Goodness-of-fit on F^2	1.080	1.123	1.067
Final R indexes [I>=2σ (I)]	R_1 = 0.0291, wR_2 = 0.0780	R_1 = 0.0380, wR_2 = 0.1175	R_1 = 0.0365, wR_2 = 0.0946
Final R indexes [all data]	R_1 = 0.0315, wR_2 = 0.0789	R_1 = 0.0561, wR_2 = 0.1248	R_1 = 0.0408, wR_2 = 0.0964
Largest diff. peak/hole / e Å^{-3}	0.19/-0.26	0.28/-0.27	0.67/-0.26
Flack parameter	0.02(2)		0.011(18)

2. NMR spectra of carboranes 7–11, 14, 15, 17, 19, 21, 24, 25







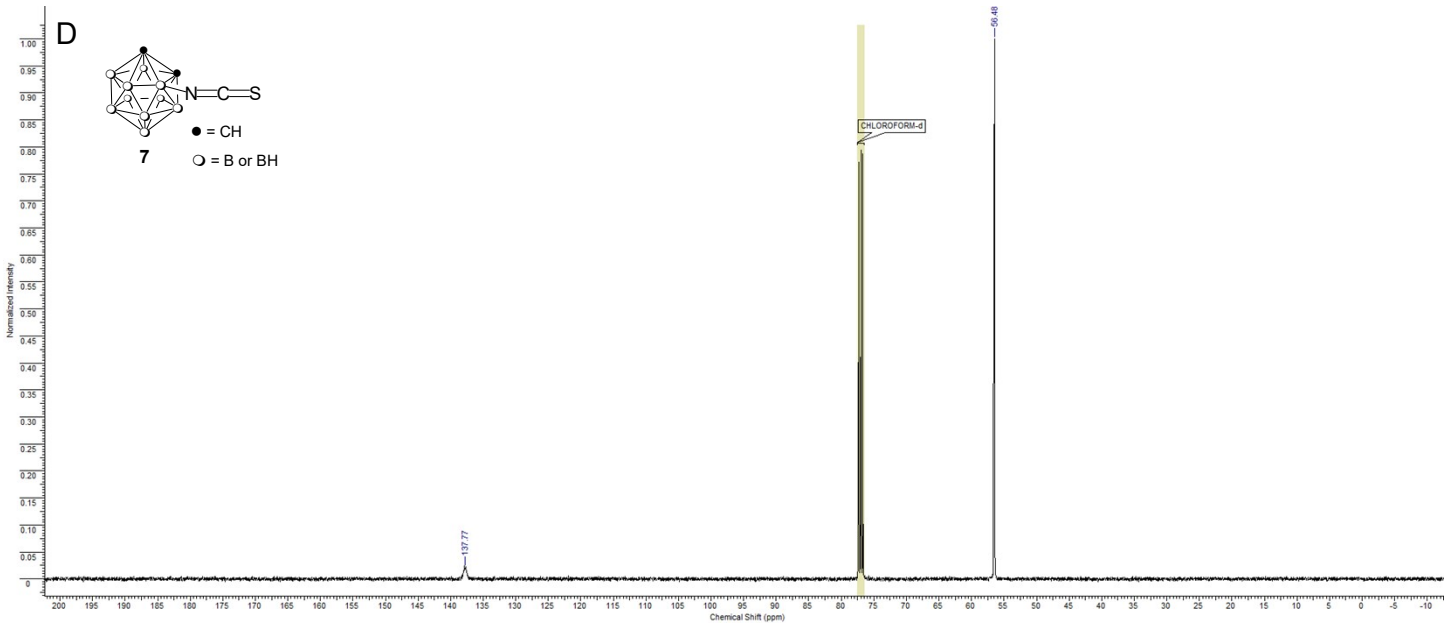
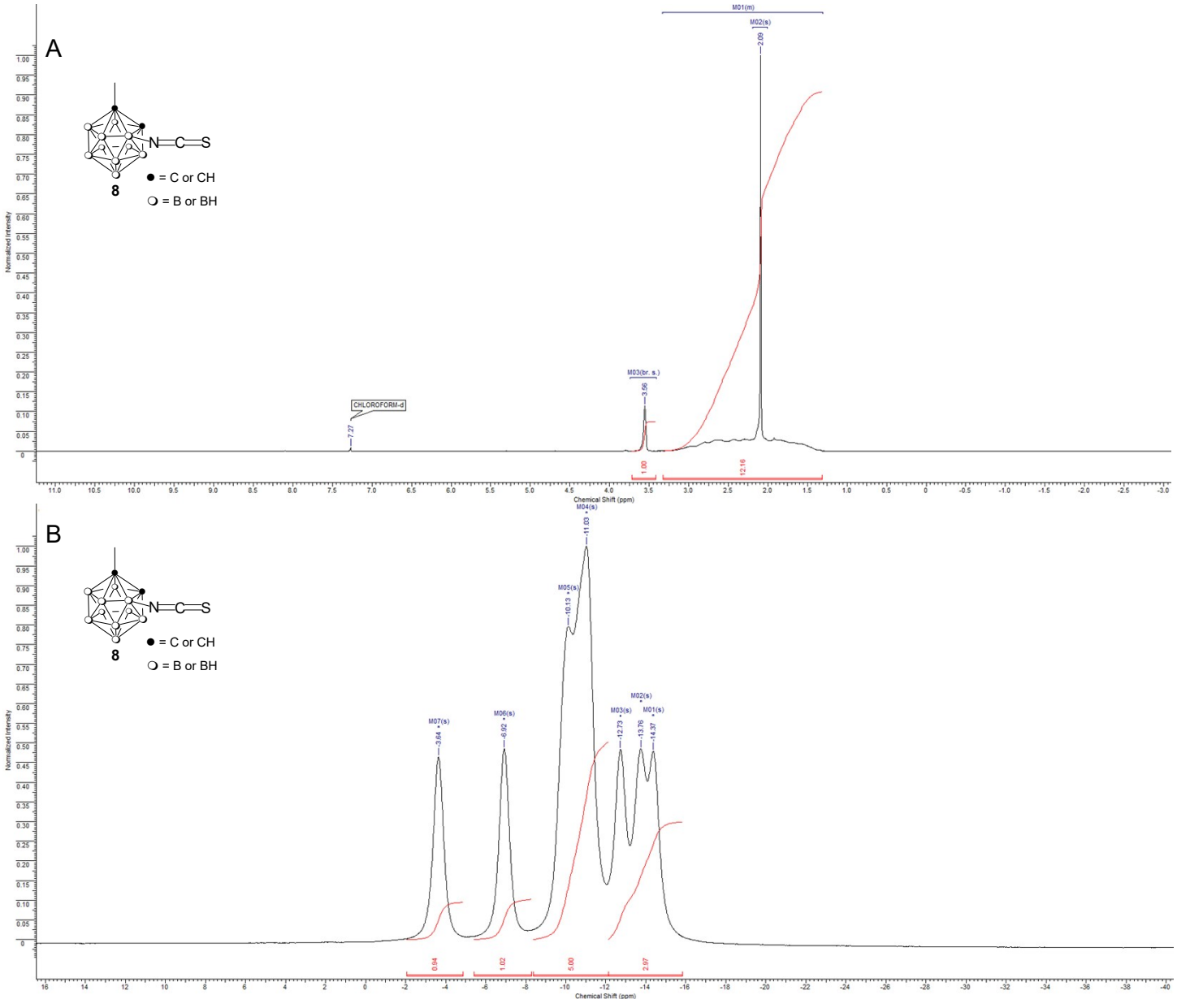


Figure S1. The ^{1}H (A), $^{11}B\{^{1}H\}$ (B), ^{11}B (C), and ^{13}C (D) spectra of 3-isothiocyanato-*o*-carborane (**7**) in $CDCl_3$.



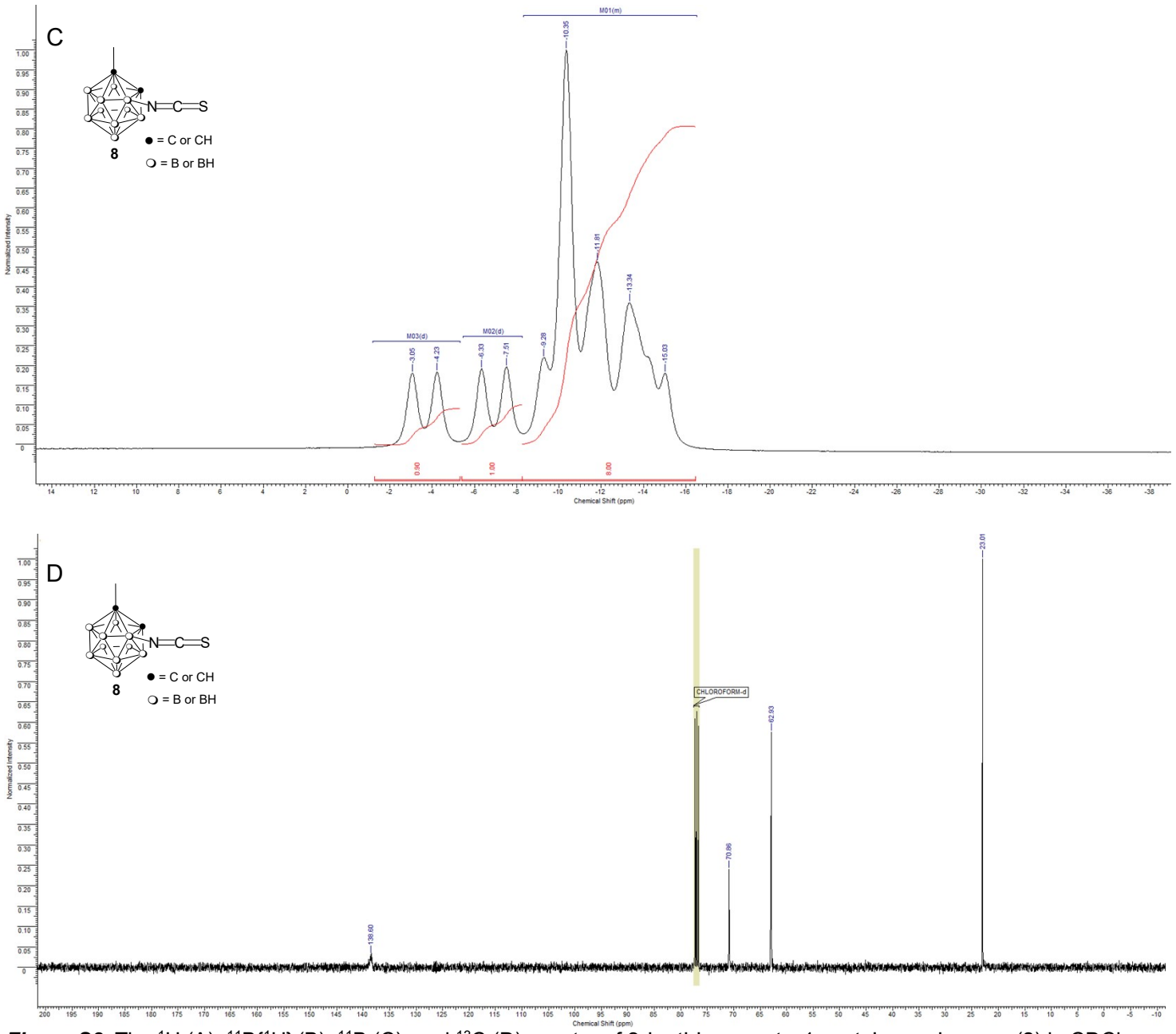
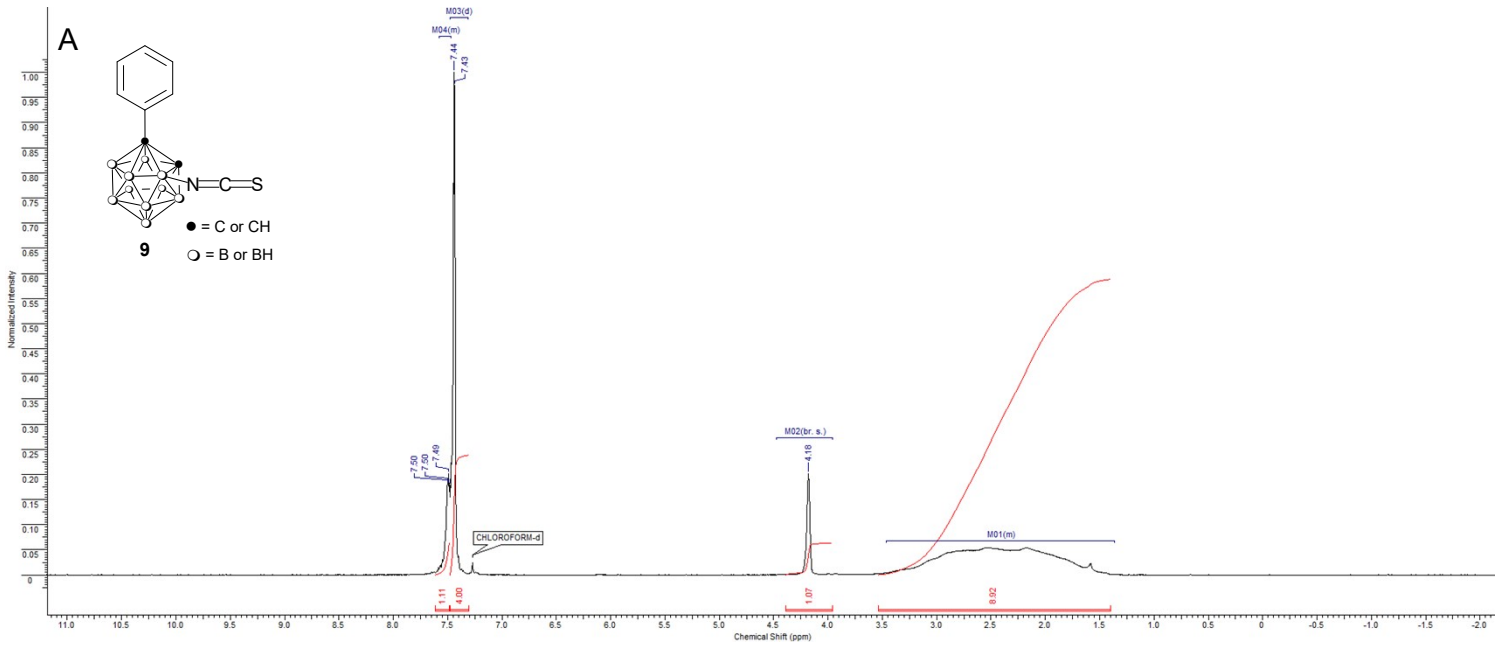


Figure S2. The ^{1}H (A), $^{11}B\{^{1}H\}$ (B), ^{11}B (C), and ^{13}C (D) spectra of 3-isothiocyanato-1-metyl-*o*-carborane (**8**) in $CDCl_3$.



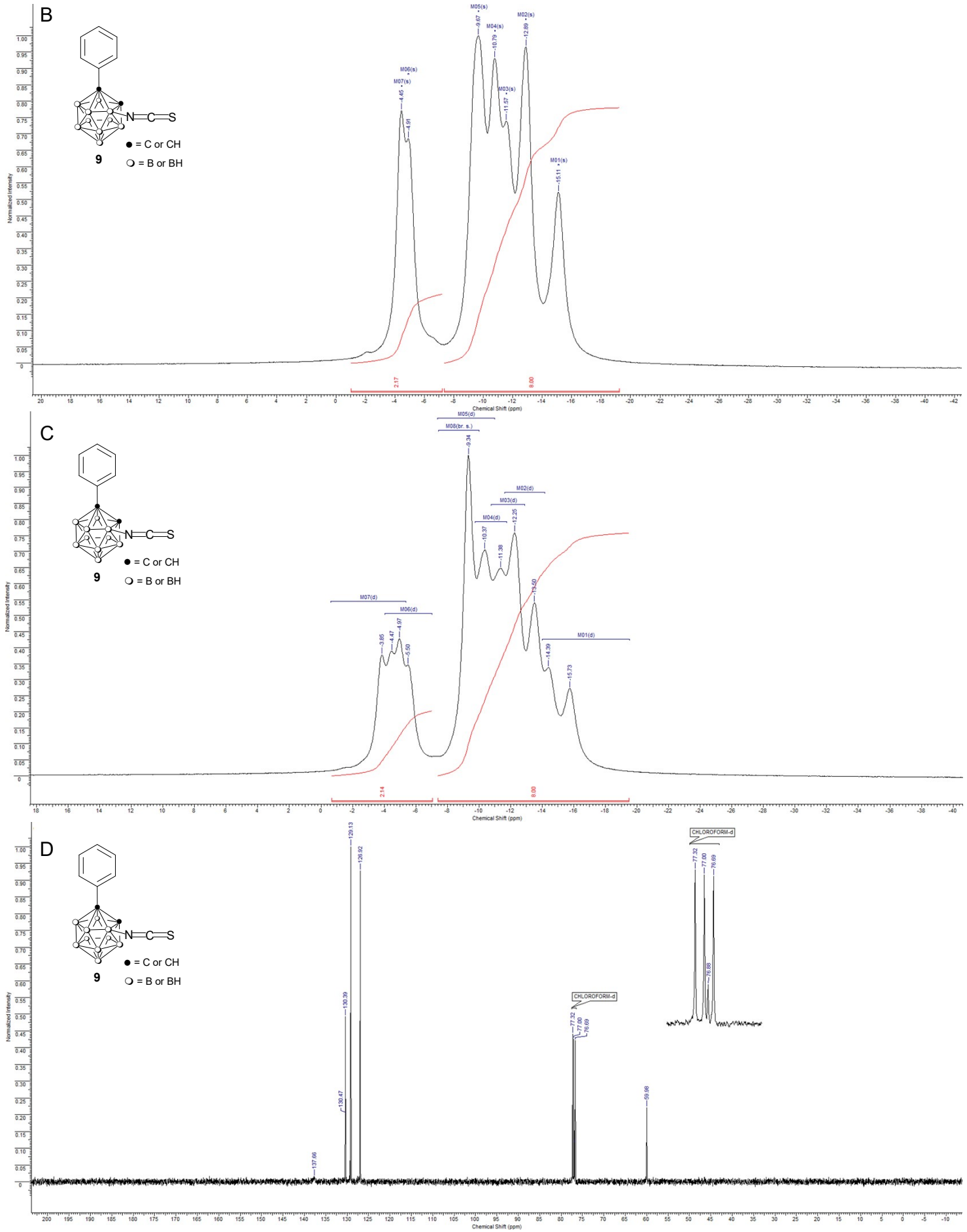
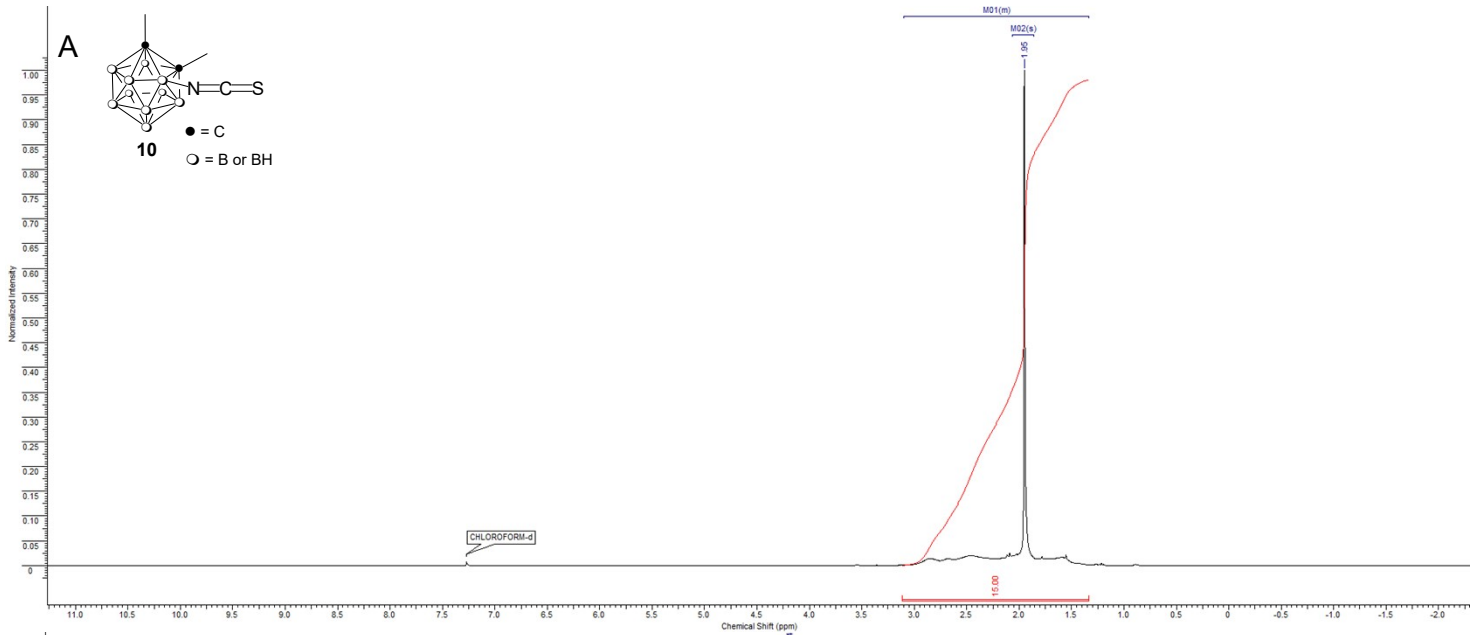


Figure S3. The ^{1}H (A), $^{11}B\{^{1}H\}$ (B), ^{11}B (C), and ^{13}C (D) spectra of 3-isothiocyanato-1-phenyl-*o*-carborane (**9**) in $CDCl_3$.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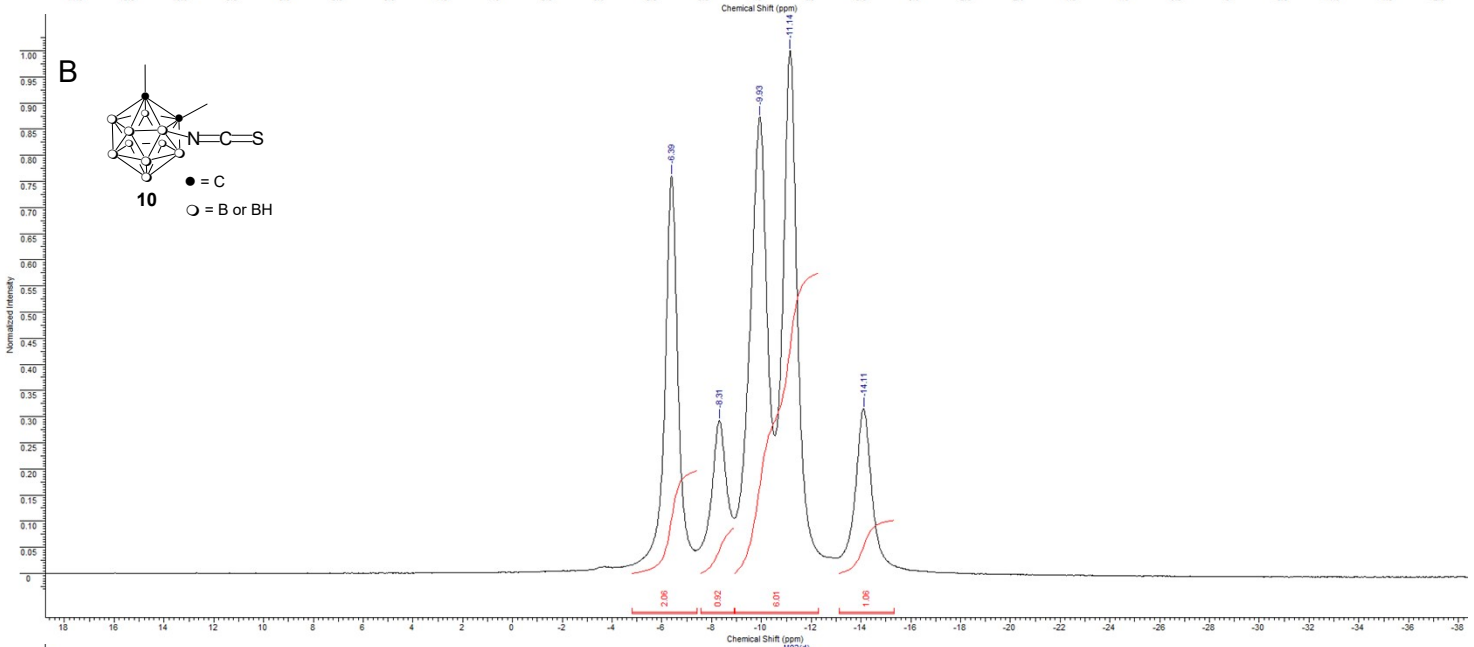
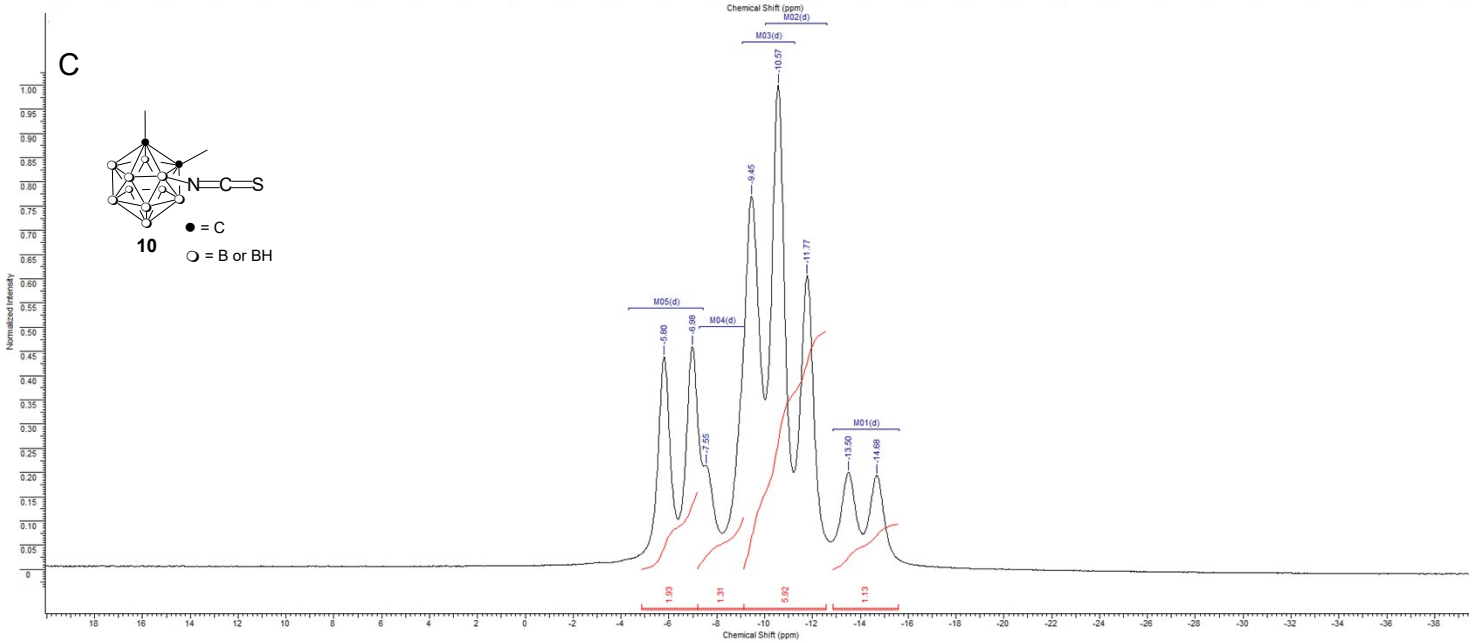
N=C=S
● = C
❍ = B or BH
10
M01(m)
M02(s)
1.95
CHLOROFORM-d
15.00
Normalized Intensity
Chemical Shift (ppm)


B
N=C=S
● = C
❍ = B or BH
10
-6.39
-8.31
-9.93
-11.14
-14.11
2.06
0.92
6.01
1.06
Normalized Intensity
Chemical Shift (ppm)


C
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● = C
❍ = B or BH
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M03(d)
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-9.45
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M05(d)
M04(d)
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-6.98
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1.93
1.31
5.92
1.13
Normalized Intensity
Chemical Shift (ppm)

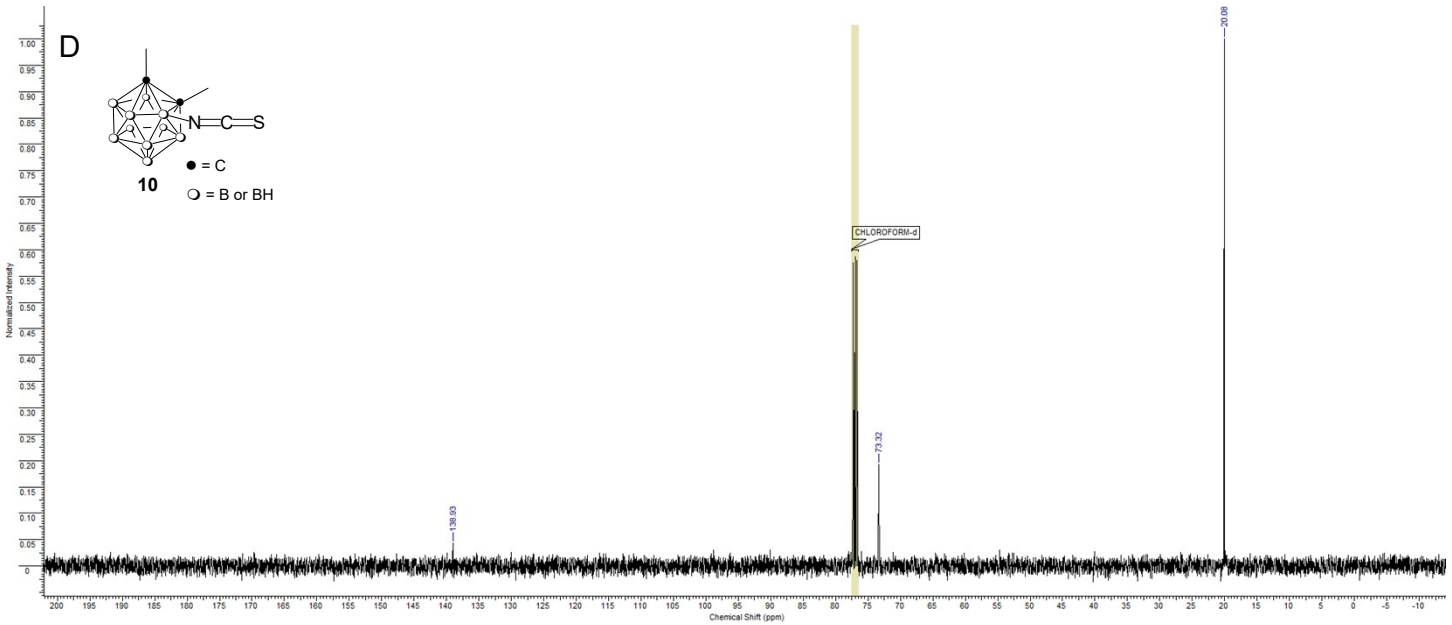
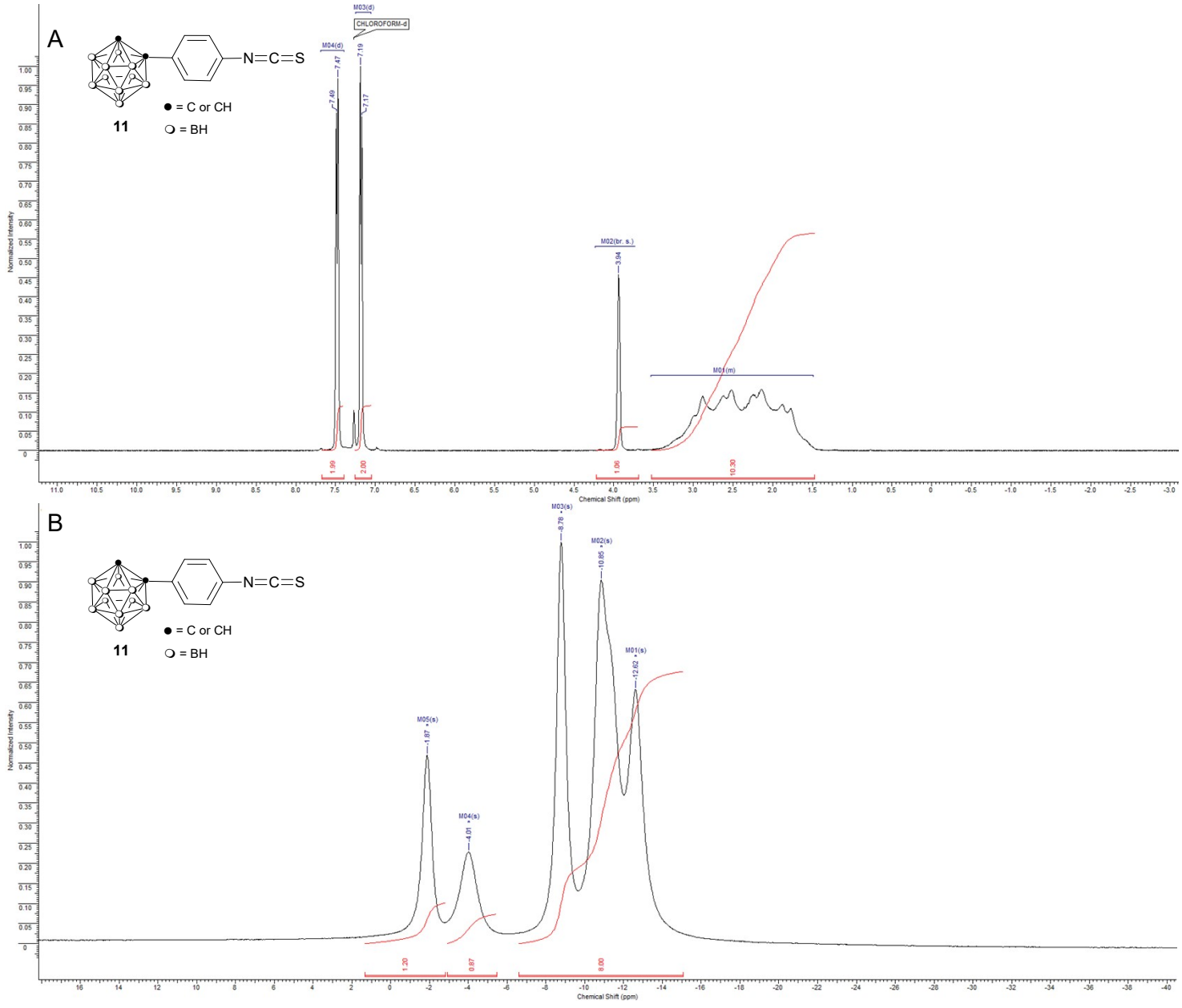
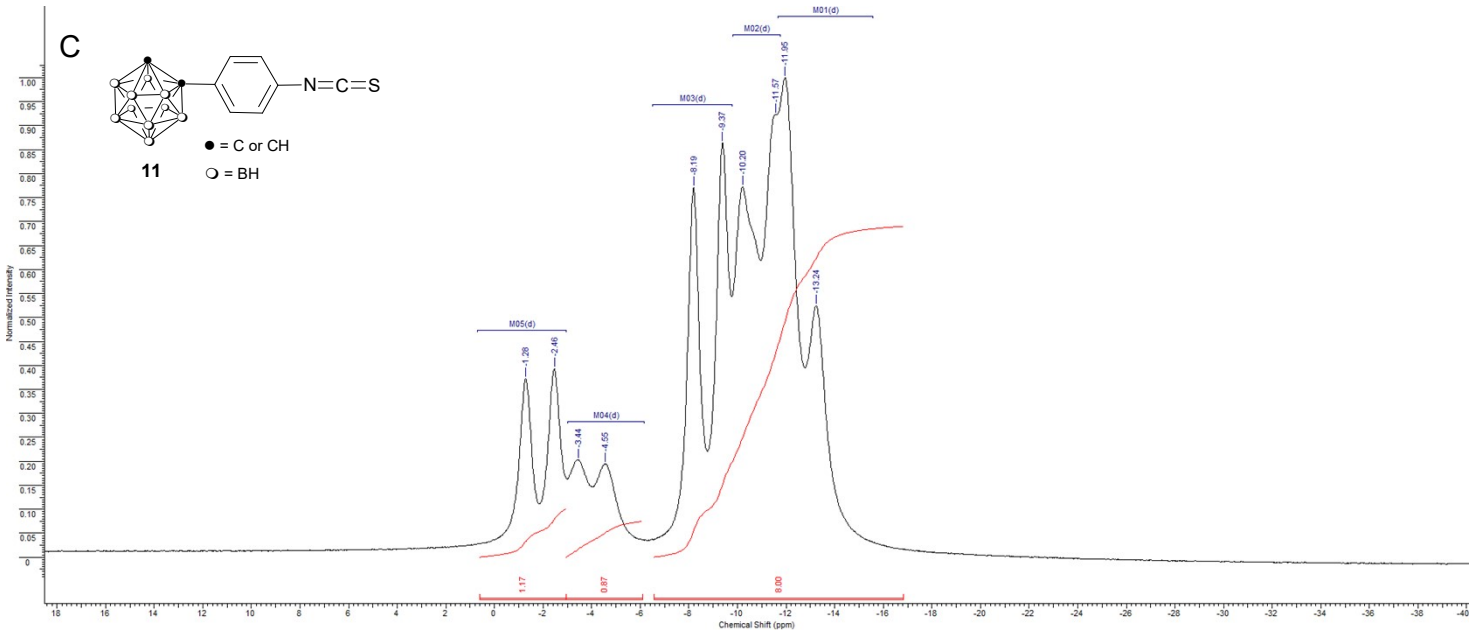


Figure S4. The ^{1}H (A), $^{11}B\{^{1}H\}$ (B), ^{11}B (C), and ^{13}C (D) spectra of 3-isothiocyanato-1,2-bis(dimethyl)-*o*-carborane (**10**) in $CDCl_3$.





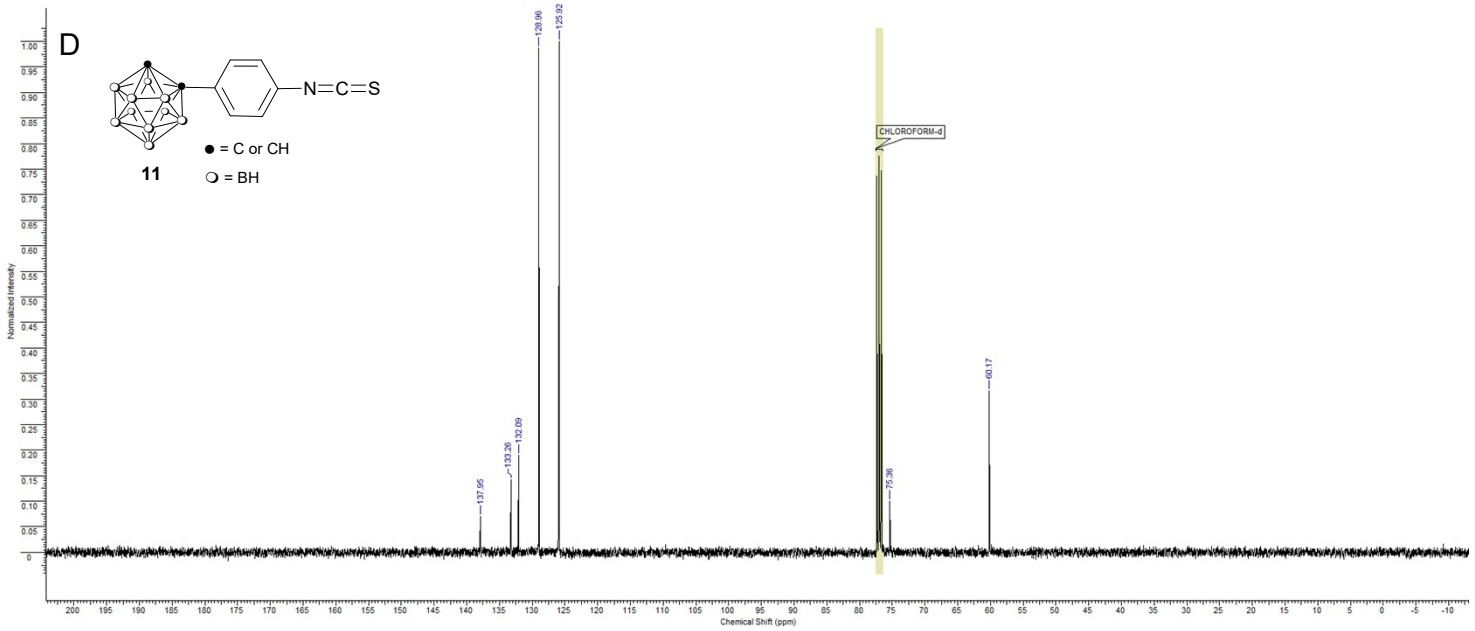
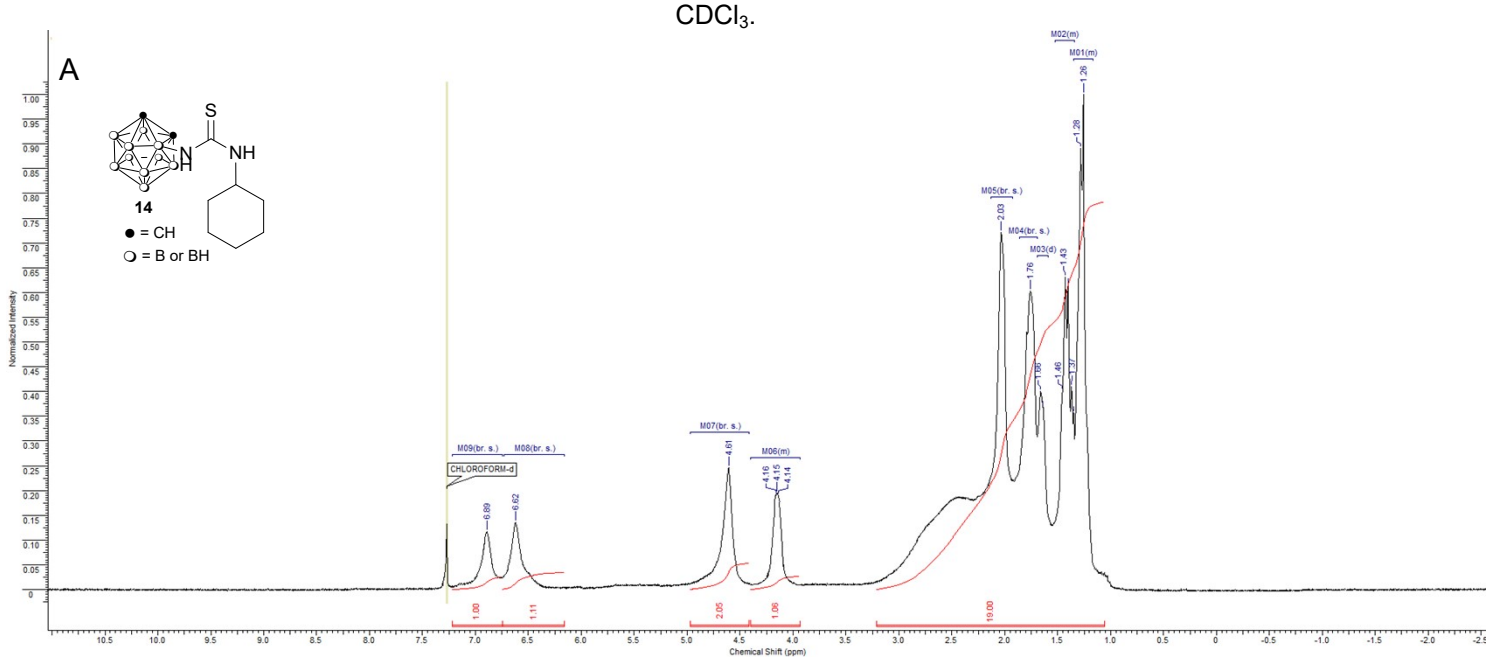


Figure S5. The ^{1}H (A), $^{11}B\{^{1}H\}$ (B), ^{11}B (C), and ^{13}C (D) spectra of 1-(4'-isothiocyanatophenyl)-*o*-carborane (**11**) in $CDCl_3$.



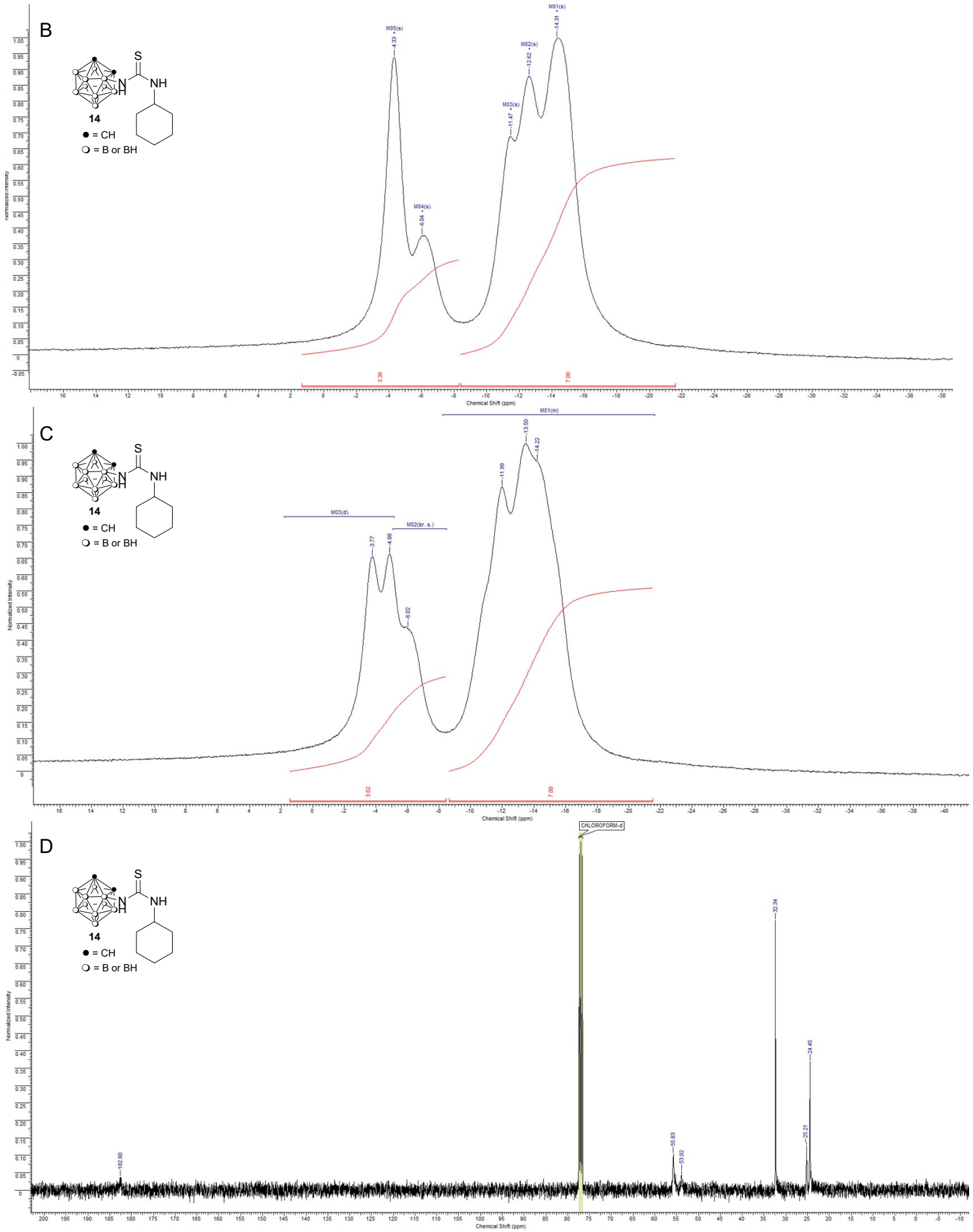
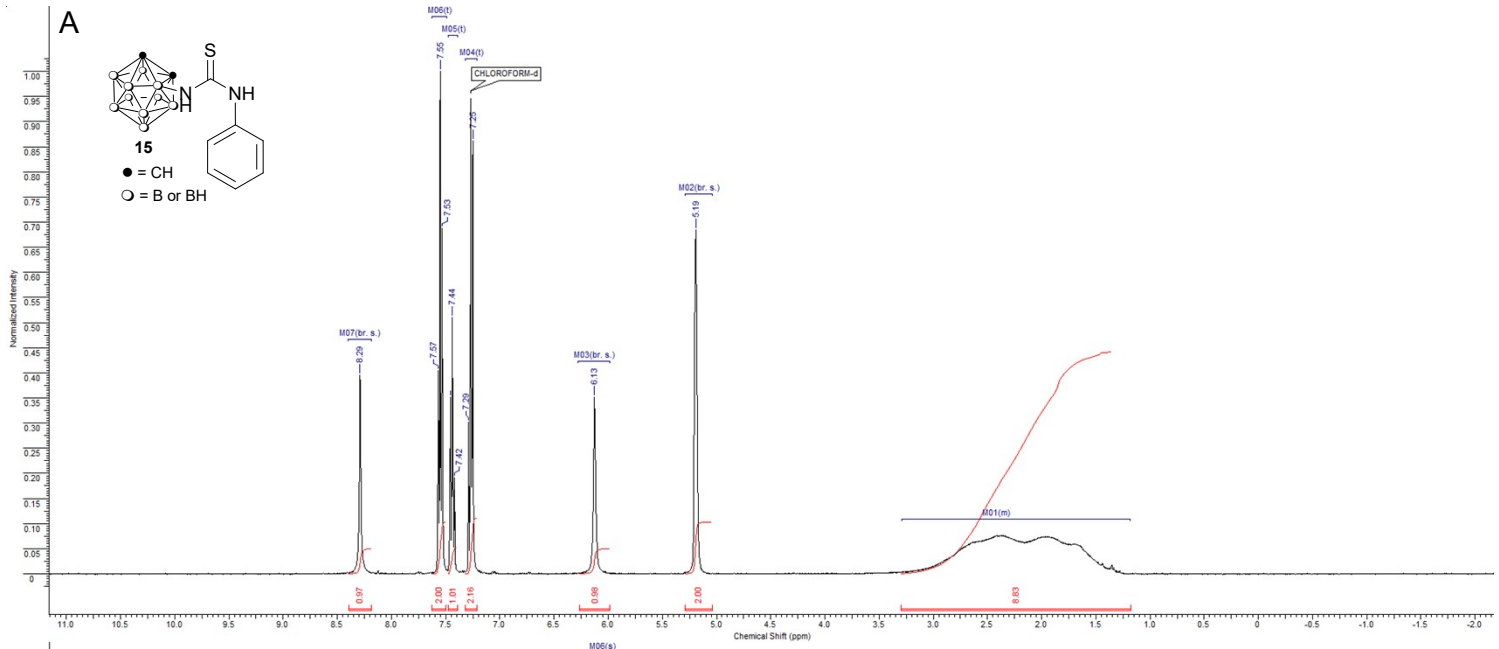
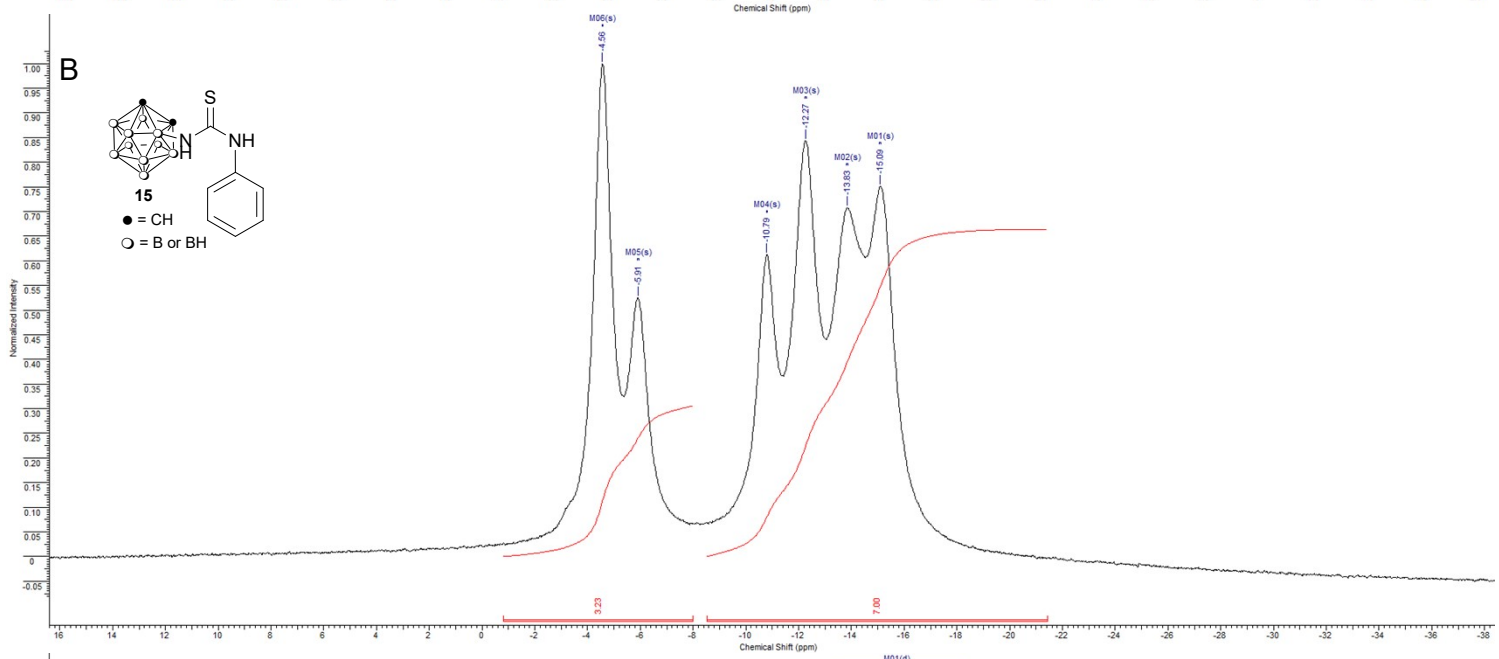
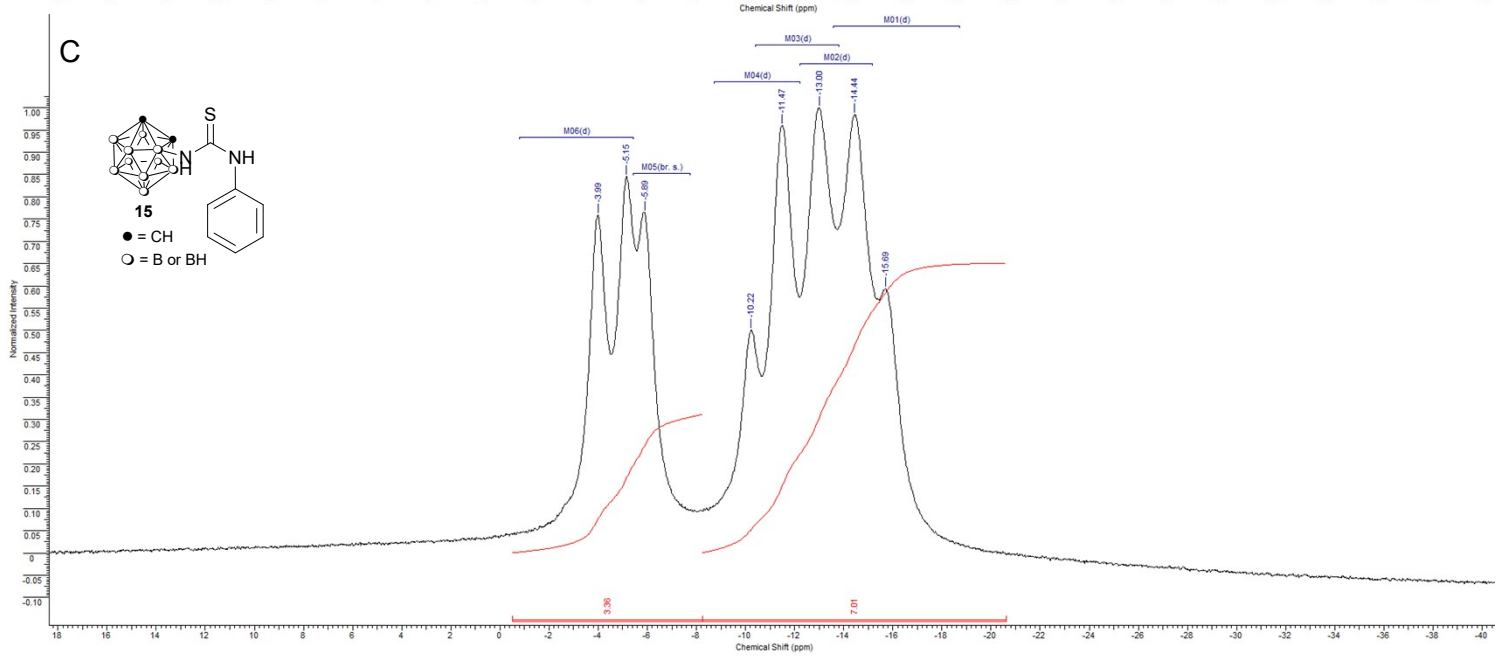


Figure S6. The ^{1}H (A), $^{11}B\{^{1}H\}$ (B), ^{11}B (C), and ^{13}C (D) spectra of *N*-(*o*-carboran-3-yl)-*N*'-(cyclohexyl)thiourea (**14**) in $CDCl_3$.


A
15
● = CH
❍ = B or BH
M06(t)
M05(t)
M04(t)
CHLOROFORM-d
M07(br. s.)
M03(br. s.)
M02(br. s.)
M01(m)
Normalized Intensity
Chemical Shift (ppm)


B
15
● = CH
❍ = B or BH
M06(s)
M05(s)
M04(s)
M03(s)
M02(s)
M01(s)
Normalized Intensity
Chemical Shift (ppm)


C
15
● = CH
❍ = B or BH
M06(d)
M05(br. s.)
M04(d)
M03(d)
M02(d)
M01(d)
Normalized Intensity
Chemical Shift (ppm)

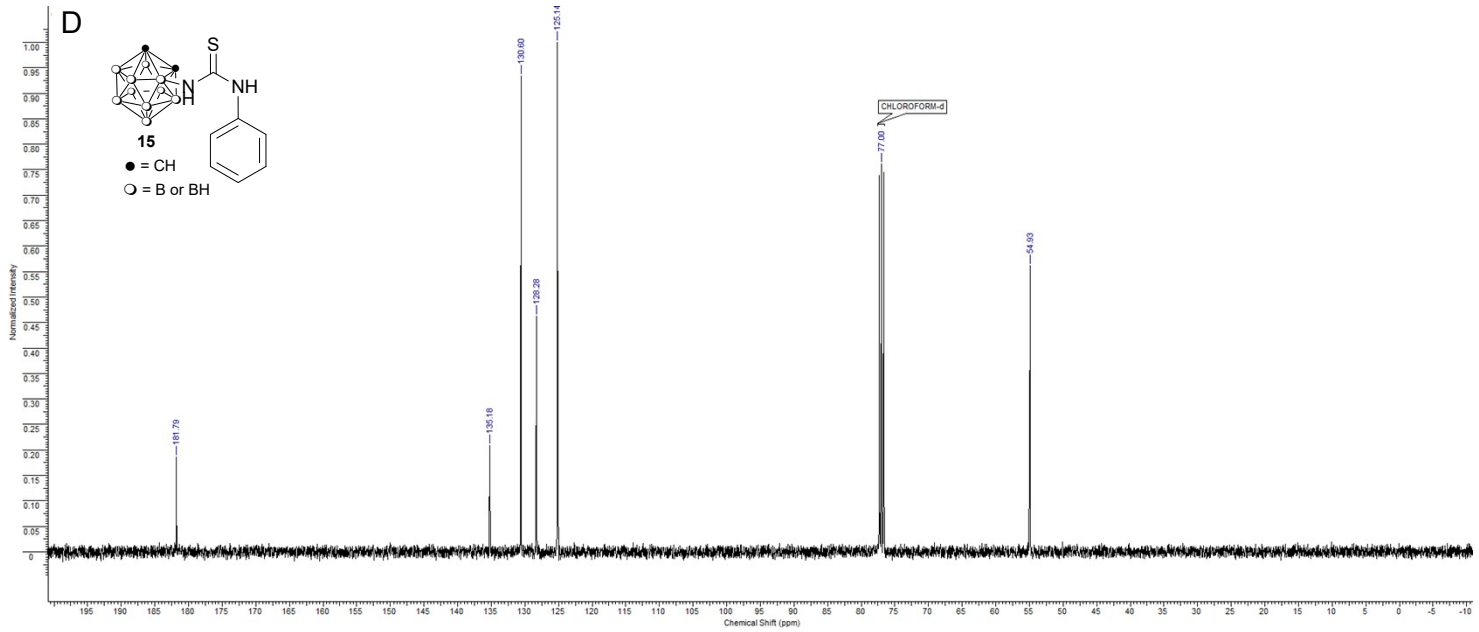
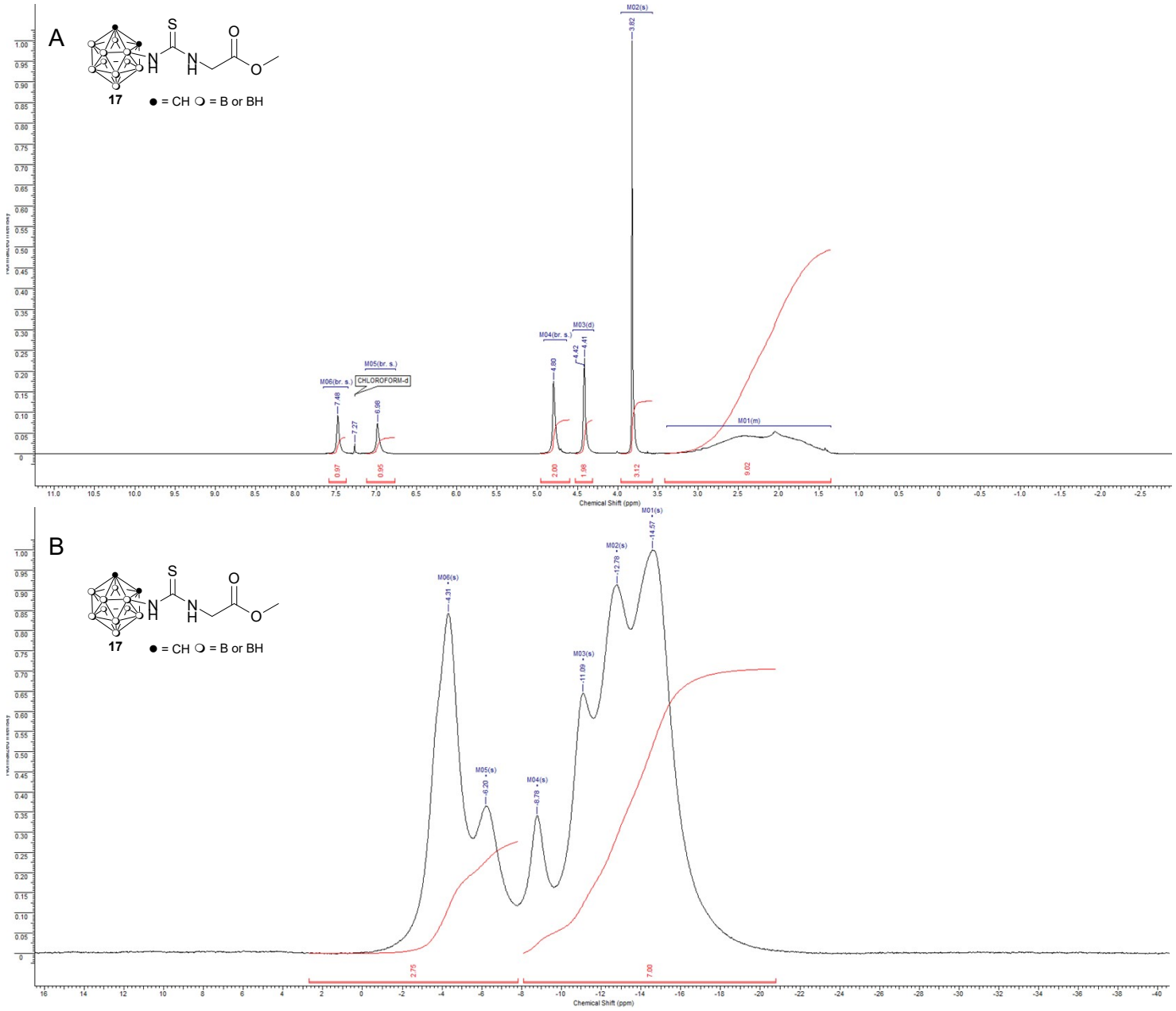


Figure S7. The ^{1}H (A), $^{11}B\{^{1}H\}$ (B), ^{11}B (C), and ^{13}C (D) spectra of *N*-(*o*-carboran-3-yl)-*N'*-(phenyl)thiourea (**15**) in $CDCl_3$.



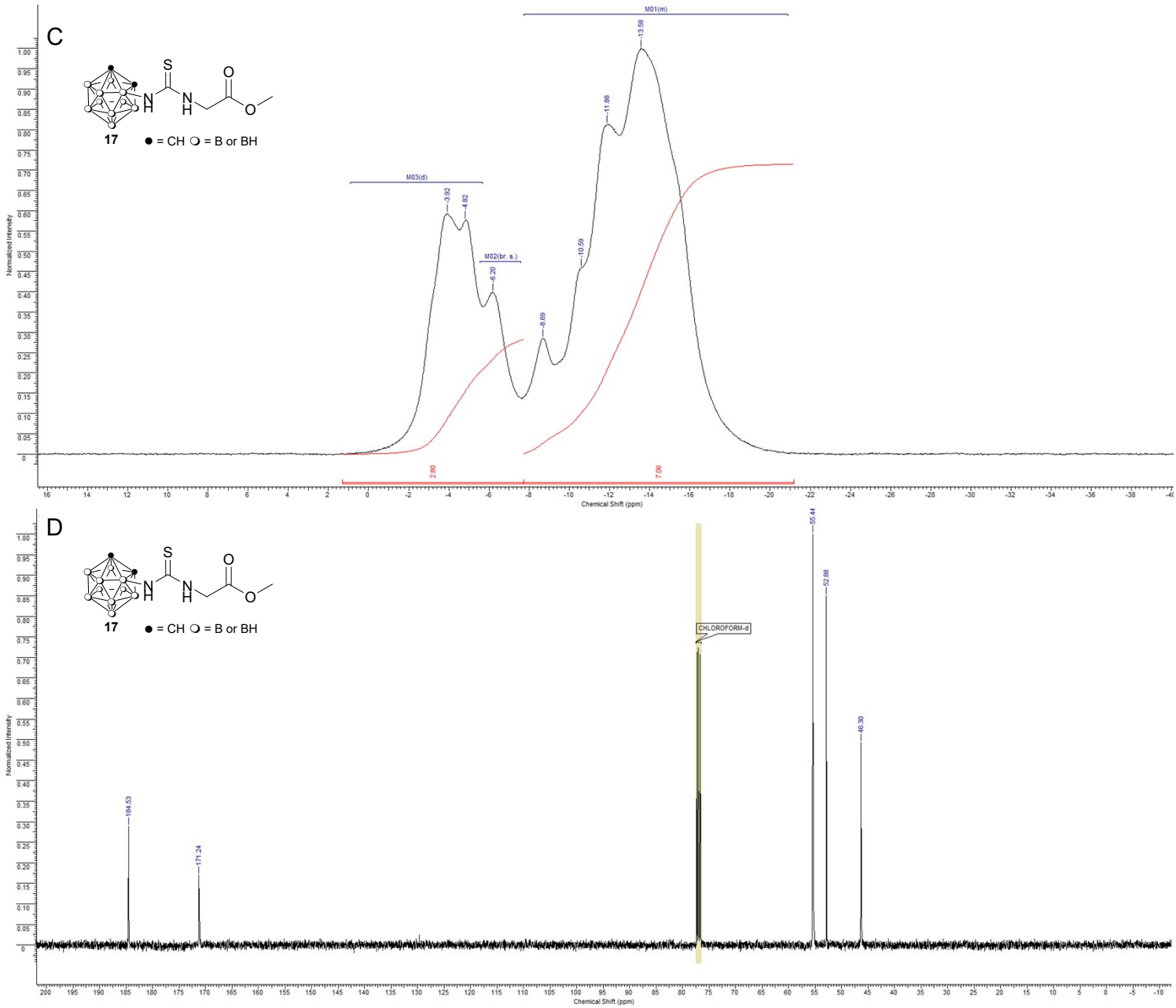
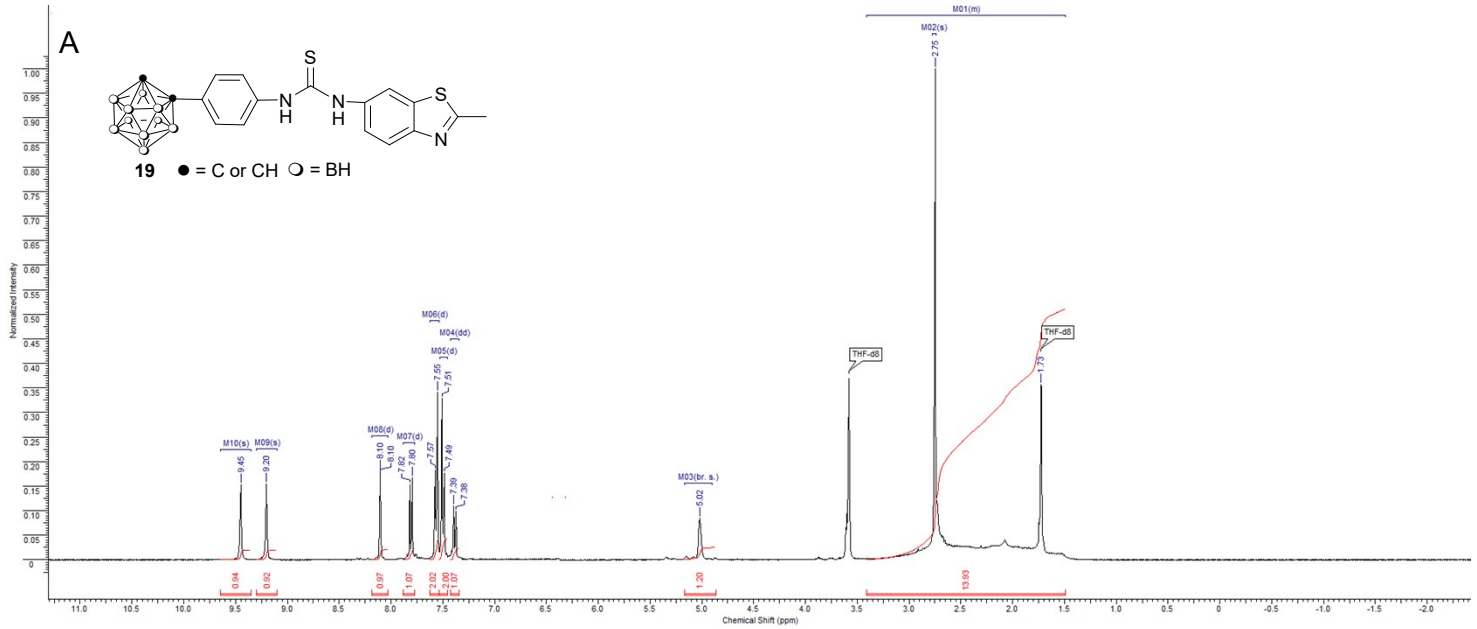


Figure S8. The ^{1}H (A), $^{11}B\{^{1}H\}$ (B), ^{11}B (C), and ^{13}C (D) spectra of methyl ester of 2-[*N*'-(*o*-carboran-3-yl)thioureido]acetic acid (**17**) in $CDCl_3$.



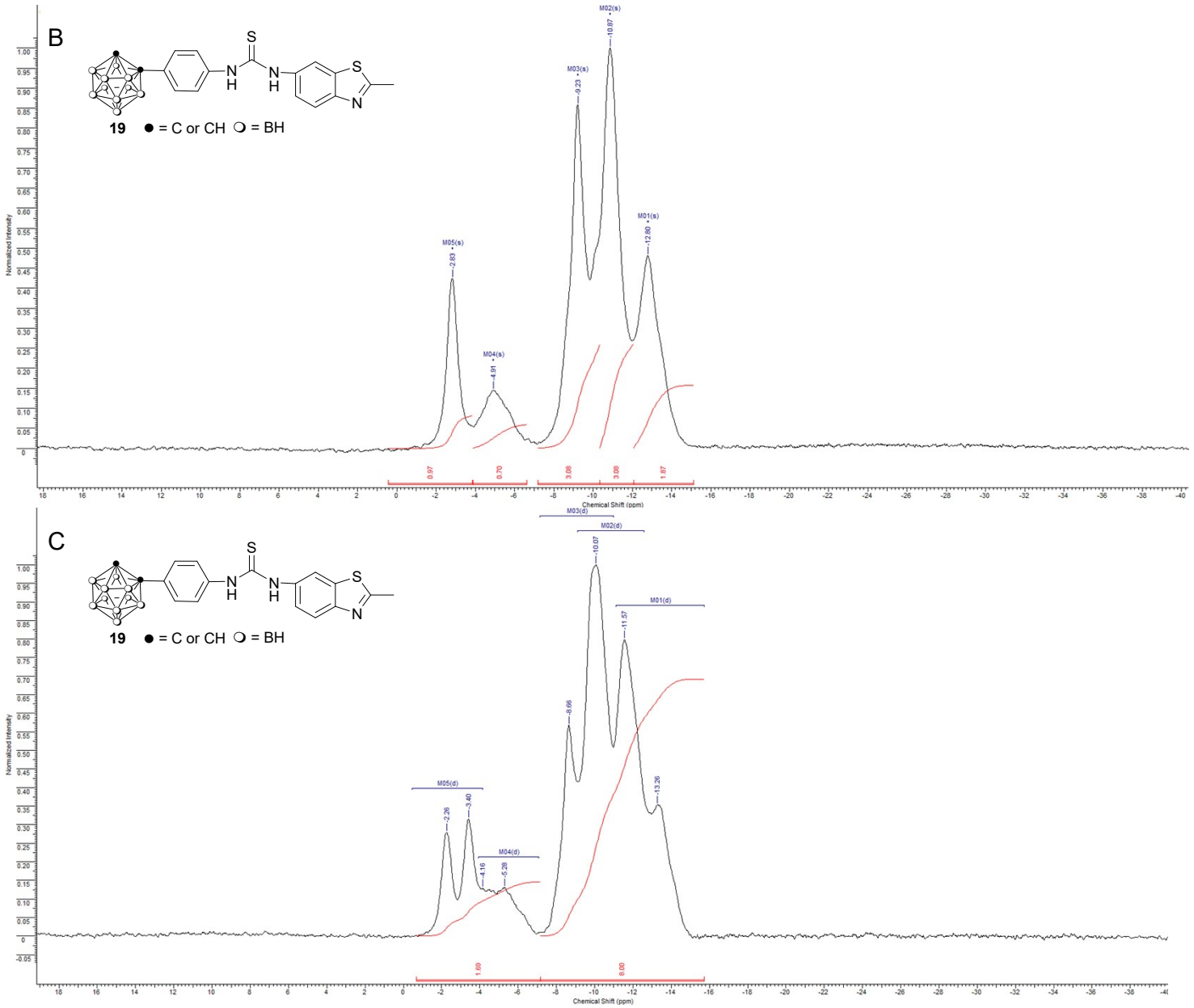
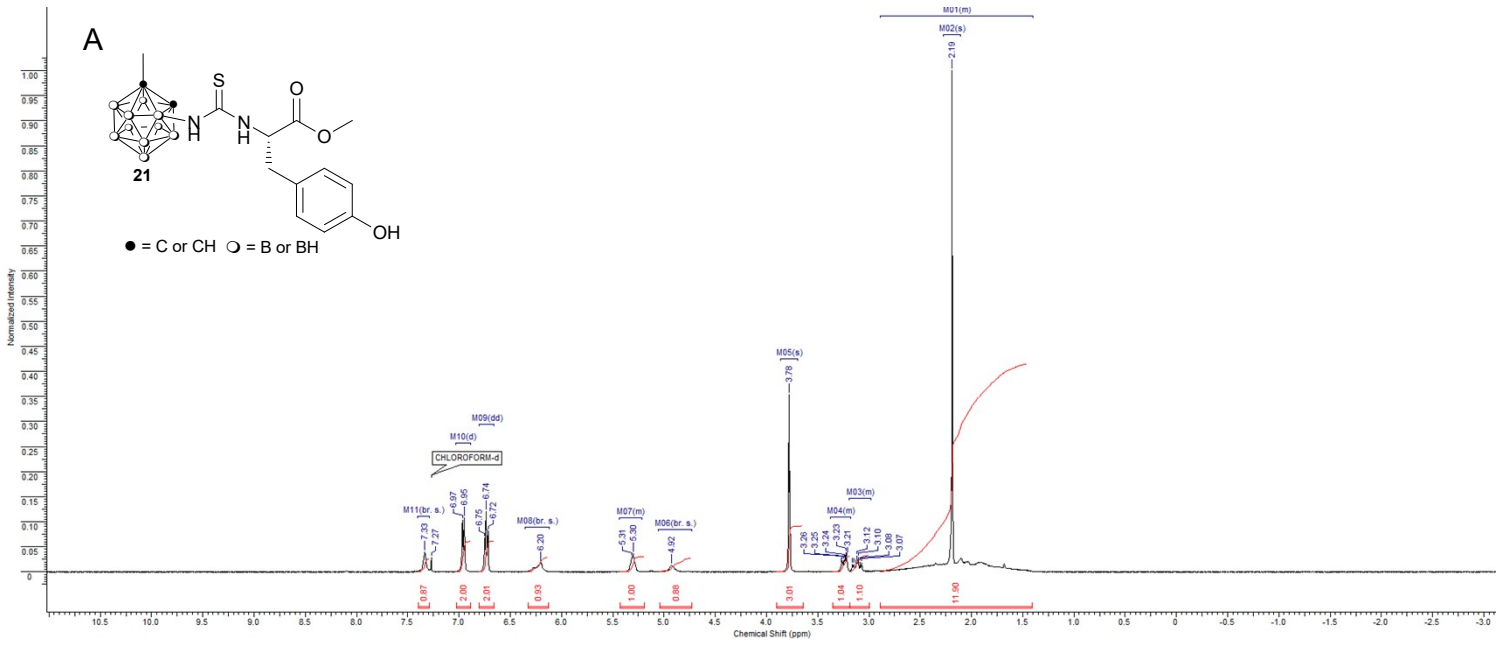


Figure S9. The ^{1}H (A), $^{11}B\{^{1}H\}$ (B) and ^{11}B (C) spectra of *N*-[4-(*o*-carboran-1-yl)phenyl]-*N*'-(2-methylbenzo[d]thiazol-6-yl)thiourea (**19**) in THF-d_8.



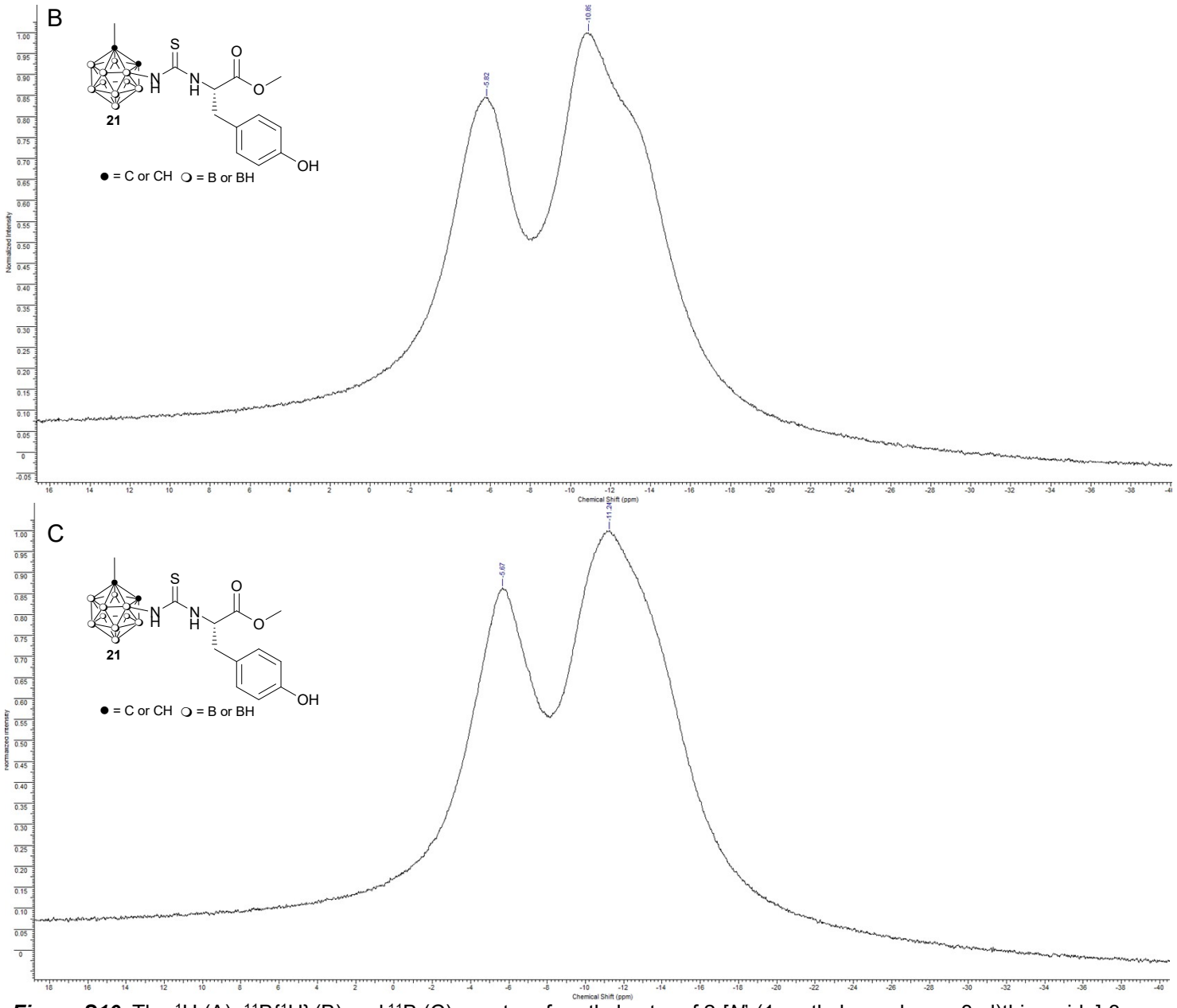
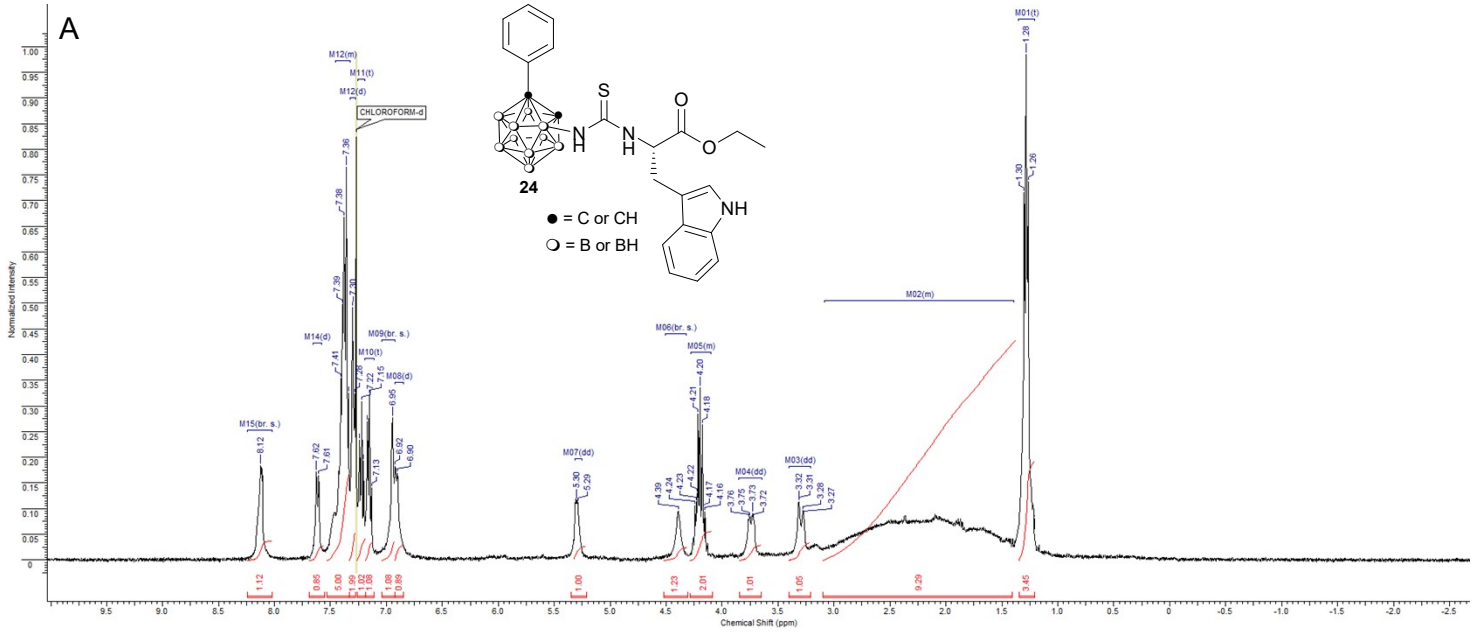


Figure S10. The ^{1}H (A), $^{11}B\{^{1}H\}$ (B) and ^{11}B (C) spectra of methyl ester of 2-[*N*'-(1-methyl-*o*-carboran-3-yl)thioureido]-3-(4-hydroxyphenyl)propanoic acid (**21**) in $CDCl_3$.



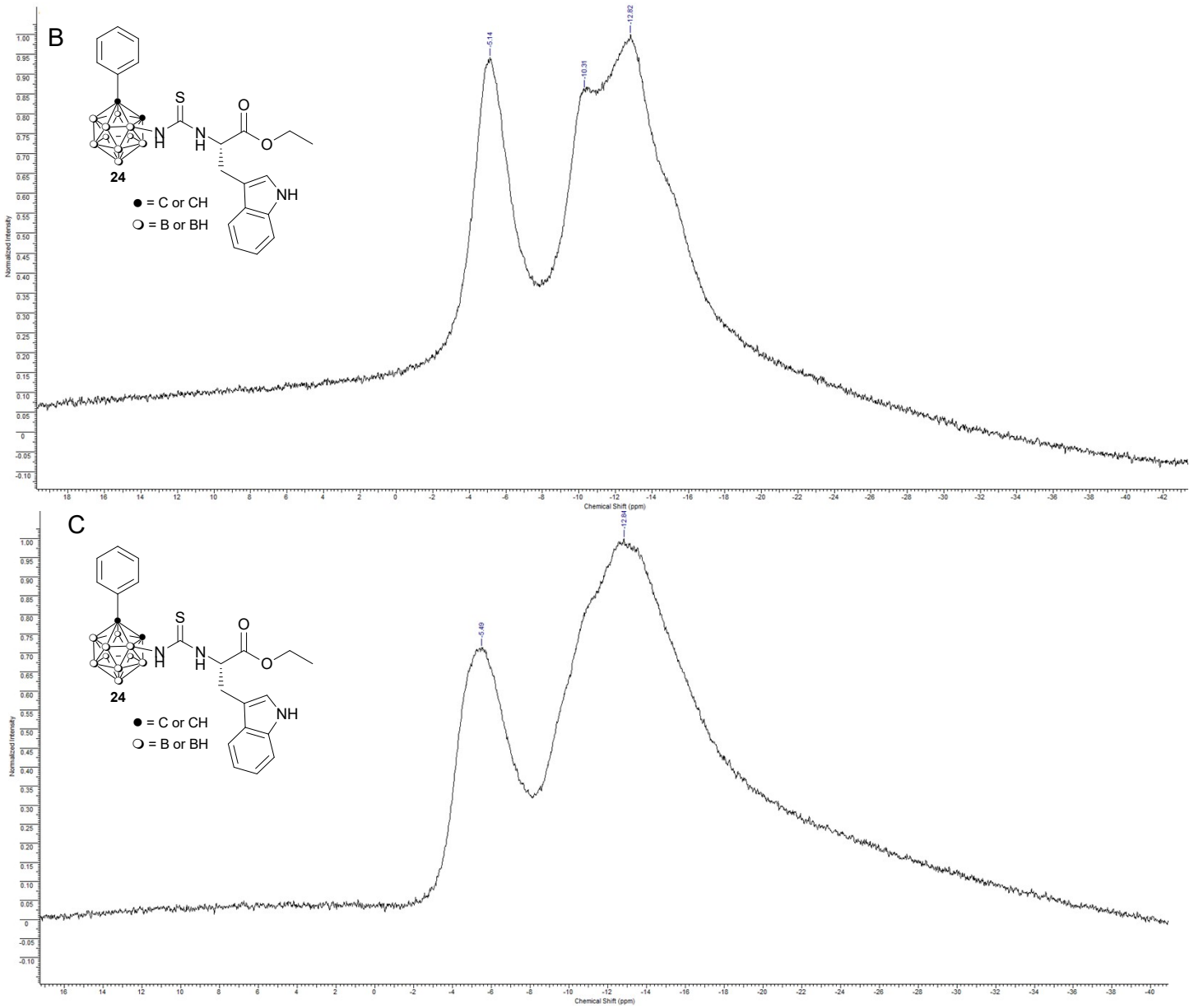
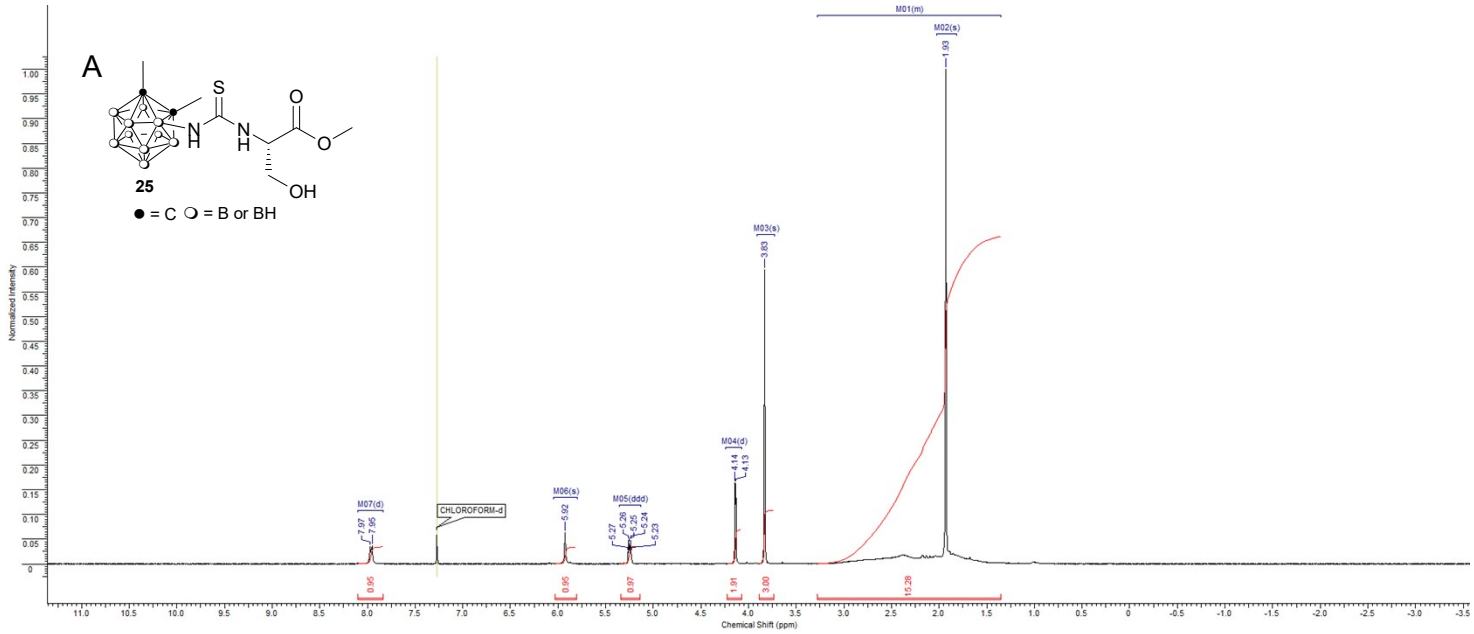


Figure S11. ^{1}H (A), $^{11}B\{^{1}H\}$ (B) and ^{11}B (C) spectra of ethyl ester of 2-[*N*'-(1-phenyl-*o*-carboran-3-yl)thioureido]-3-(1*H*-indol-3-yl)propanoic acid (**24**) in $CDCl_3$.



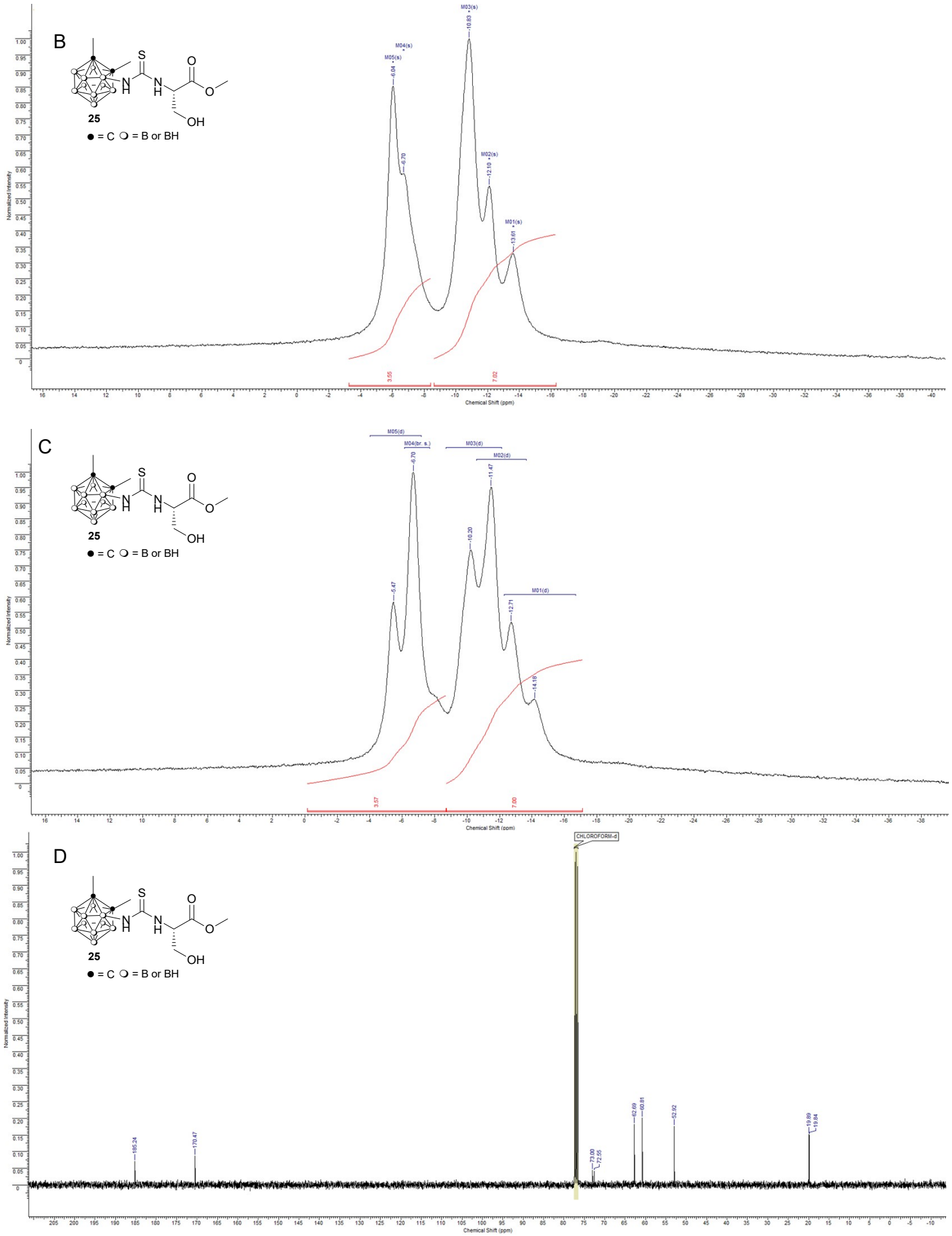


Figure S12. The ^{1}H (A), $^{11}B\{^{1}H\}$ (B) and ^{11}B (C) spectra of methyl ester of 2-{*N*'-[1,2-bis(dimethyl)-*o*-carboran-3-yl]thioureido}-3-hydroxypropanoic acid (**25**) in $CDCl_3$.