Electronic Supplementary Material (ESI) for Dalton Transactions.

Supporting information

A fast and simple B-C bond forming in metallacarboranes avoiding halometallacarboranes and transition metal catalysts.

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1. Experimental section.

1.1. Instrumentation.

NMR measurements: The ^{1}H NMR (600 MHz) spectra were recorded with a Bruker Advance II+ (400MHz) instrument. The ^{1}H NMR (400 MHz), ^{11}B NMR and $^{11}B\{^{1}H\}$ NMR (128.38 MHz), and $^{13}C\{^{1}H\}$ NMR (100 MHz) spectra were recorded with a Bruker Advance III (400MHz) instrument equipped with the appropriate decoupling accessories. All NMR spectra were performed in deuterated acetone (purchased from Sigma-Aldrich) at 22 ºC. ^{11}B NMR and $^{11}B\{^{1}H\}$ NMR resonances were referenced to external $BF_3{\cdot}OEt_2$, while $^{13}C\{^{1}H\}$ NMR shifts were referenced to $SiMe_4$. Chemical shifts are reported in units of parts per million downfield from reference, and all coupling constants in Hz.

MALDI-TOF Mass Spectra were collected in the negative mode using a Brucker Biflex instrument (N_2 laser; λ_{exc} 337 nm, pulses of 0.5 ns), with an ion source of 20000 kV (Uis1) and 17500 kV (Uis2). Due to the nature of the compounds, a matrix was not necessary.

Elemental Analyses were performed using a Carlo Erbo EA 1108 microanalyser.

1.2. Materials and methods.

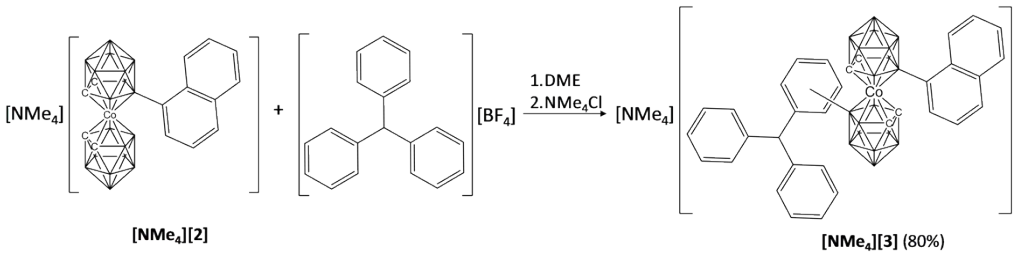
The reactions reported in the sections 2.2. and 2.3.1. were carried out under dinitrogen atmosphere using classic standard Schlenck techniques. All other reactions were carried out in open conditions, in presence of air and using solvents without previous drying. Cesium salt of cobaltabisdicarbollide was purchased from Katchem. Cesium salt of 8-Iodo-cobaltabisdicarbollide and the $[NMe_4][2]$ were synthesized following the literature method.[1] Magnesium, 1-bromonaphthalene, triphenylcarbenium tetrafluoroborate and $MgSO_4$ were purchased from Sigma-Aldrich and used as received. Bromotriphenylmethane, benhydryl bromide and benzylbromide were purchased from Alfa Aesar and used as received too. DME were purchased from Carlo Erba reagents. THF and DME were dried over Na/Benzophenone as described in the literature.

2. Synthesis and characterization.

2.1. Synthesis of Ag[1][2].

100 mg (0.21 mmol) of Cesium Cobaltabisdicarbollide was dissolved in 10mL Et_2O and extracted with HCl 0.1 M 3x20 mL. The solvent was evaporated under vacuum, the compound was dissolved in water and a saturated solution of $AgNO_3$ was added since no more precipitate appear, promoting the precipitation of the desired compound Ag[1] in a quantitative yield (94 mg, 99%). **MALDI-TOF:** Calculated 323.92 m/z Found: 324.25.

2.2. Synthesis and characterization of $[NMe_4][3]$.



$[NMe_4][2]$ **$[NMe_4][3]$** (80%)

Scheme S1. Reaction conditions for the synthesis of **NMe_4[3]**.

99.2 mg (0.3 mmol) of triphenylcarbenium tetrafluoroborate were added into a 10 mL round bottom flask (previously filled with nitrogen using the pump and fill method) inside a glove bag. 157.5 mg (0.3 mmol) of NMe_4**[2]** were then added under nitrogen and 5 mL of DME were added to dissolve the mixture. The reaction was left stirring overnight. After evaporation of the solvent using the rotary evaporator, the residue was dissolved in 20 mL Et_2O and extracted with HCl 0.1 M 3x20 mL; the combined organic fractions were then washed with water, dried over $MgSO_4$ and the solvent was removed under reduced pressure. Further purification was performed by silica column chromatography using a mixture of CH_2Cl_2-MeCN 7:3 as eluent. The first orange fraction was the desired compound with triphenylmethyl as impurity. The compound was then washed several times with n-hexane until no signal for the triphenylmethyl appears in the ^{1}H-NMR. The final step was the precipitation as NMe_4 salt by dissolving the compound in the minimal amount of EtOH and adding dropwise a saturated solution of $[NMe_4]Cl$ in water until full precipitation. The compound was then dried under vacuum obtaining 184 mg (80% yield) of an orange powder. **^{1}H NMR (400 MHz, CD_3COCD_3), δ:** 7.84 (m, 2H, H_{Naph}), 7.77 (m, 2H, H_{Naph}), 7.72-7.69 (m, 2H, H_{Napht}), 7.52 (t, $^3J_{H-H}$ 8.8, 1H, H_{Naph}), 7.40-7.12 (m, 12H, H_{Tr})), 6.99 (d, $^3J_{H-H}$ 8.0, 1H, H_{Tr}), 6.88 (d, $^3J_{H-H}$ 7.6, 1H, H_{Tr}), 5.59 and 5.57 (s, 1H, C**H**-Ph_3 (isomers)), 3.97, 3.93, 3.89 and 3.86 (s, 4H, $C_{Cluster}$-H), 3.45 (s, 12H, NMe_4). **^{11}B NMR (128.38 MHz, CD_3COCD_3), δ:** 11.1 (s, 2B, B-C_{Ar}), 2.0 (d, $^1J_{B-H}$ 133.12, 2B, B-H), -5.2 (m, 8B, B-H), -19.1 (d, $^1J_{B-H}$ 116.5, 4B, B-H), -22.48 (d, 2B, B-H). **^{13}C{^{1}H} NMR (100 MHz, CD_3COCD_3), δ:** 145.46 and 145.37(C**P**h_3), 143.35 and

141.96 (C-B), 134.16, 134.0, 132.91, 132.65, 131.48, 131.3, 130.85, 130.18, 130.10, 129.01, 128.96, 128.41, 128.26, 127.89, 127.40, 126.86, 126.19 and 125.54 ($C_{Aromatic}$), 57.54 and 57.22 (**C**-Ph_3), 55.9 (NMe_4) 54.9 and 54.4 ($C_{Cluster}$). **MALDI-TOF:** Theor. 691.444 m/z Found, 692.68.

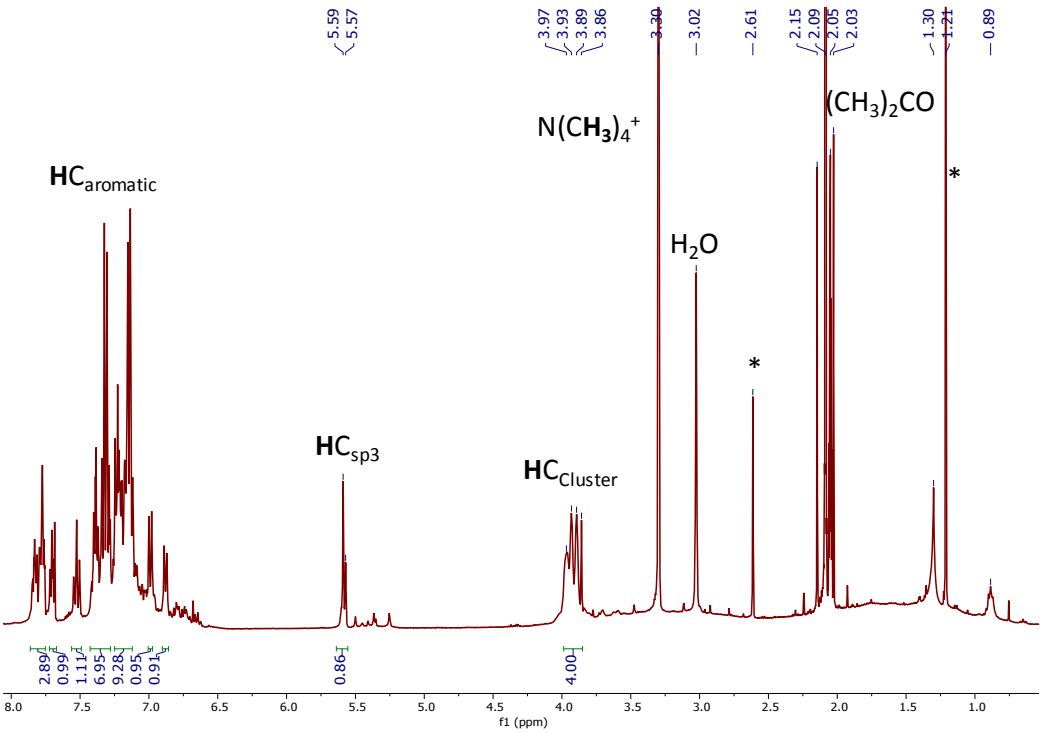


Figure S1. ^{1}H-NMR of [NMe_4][**3**]. *Unidentified solvents.

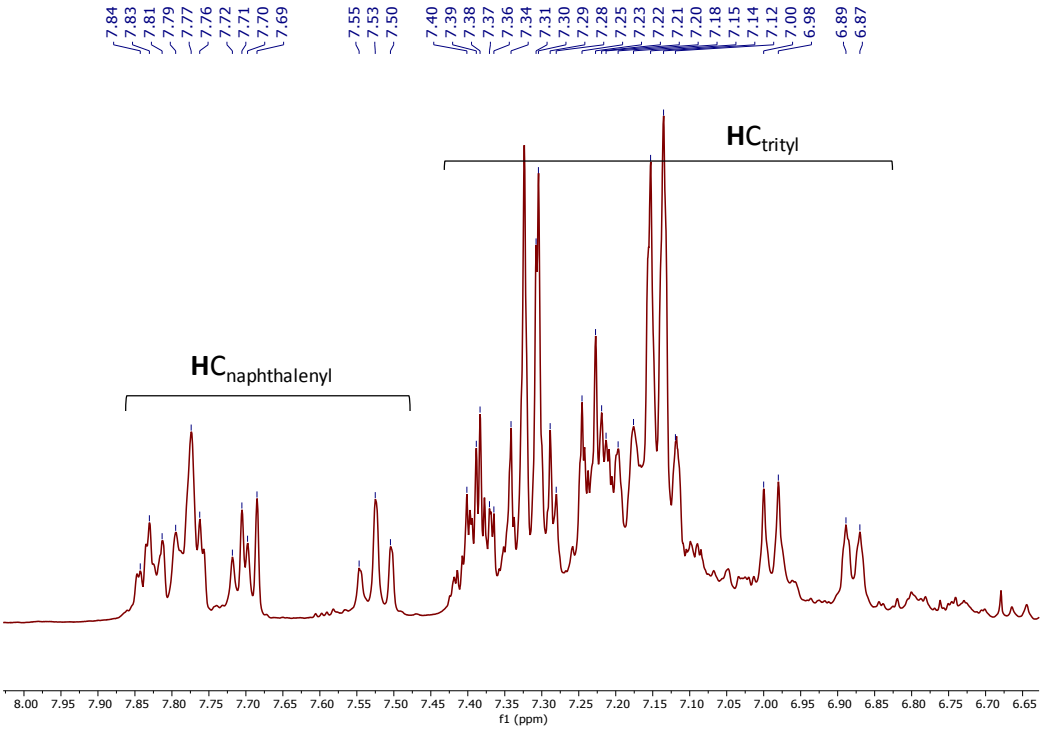


Figure S2. ^{1}H-NMR amplified spectrum of [NMe_4][**3**]$^-$.

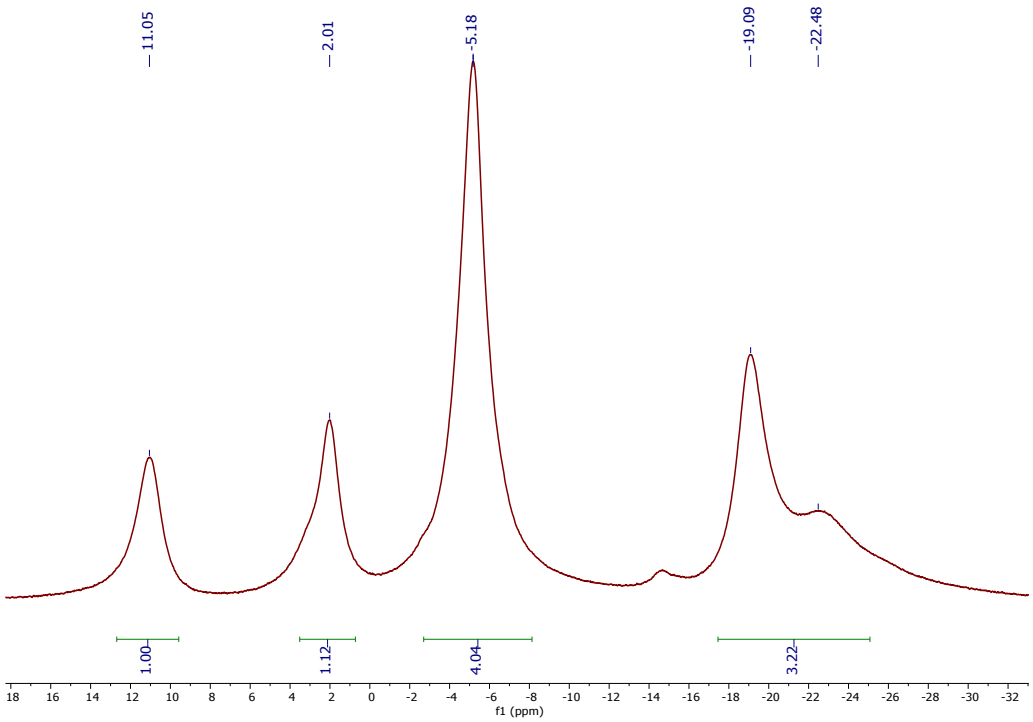


Figure S3. $^{11}B\{^{1}H\}$-NMR of $[NMe_4][\mathbf{3}]$.

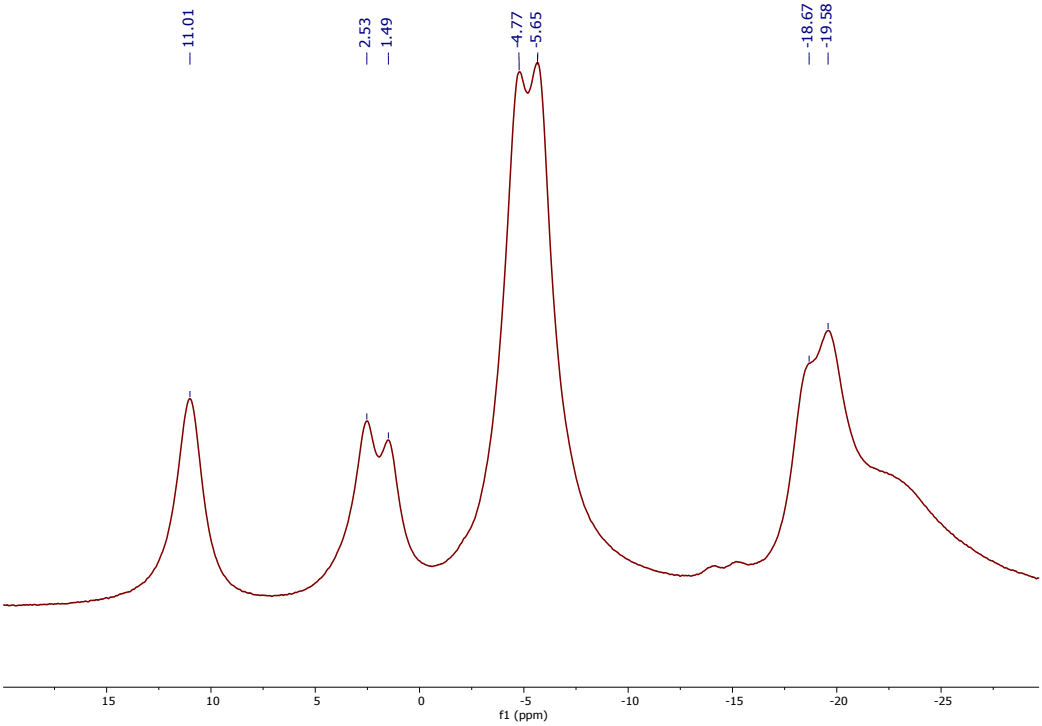


Figure S4. ^{11}B-NMR of $[NMe_4][\mathbf{3}]$.

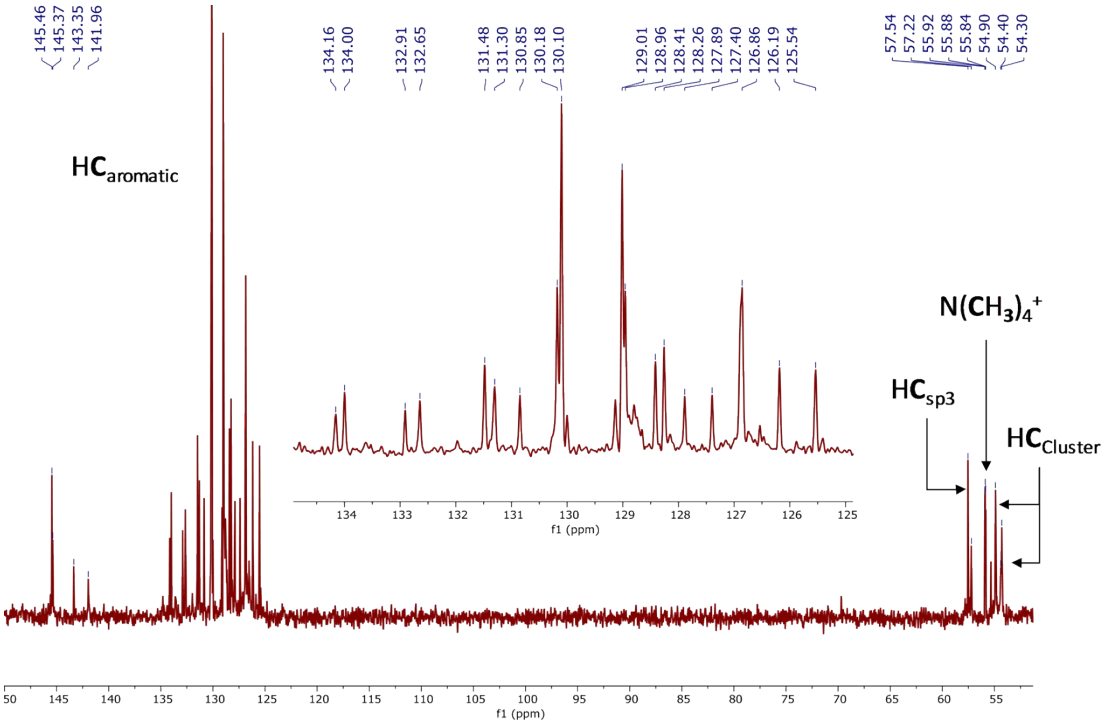


Figure S5. $^{13}C\{^{1}H\}$-NMR of [NMe_4][**3**].

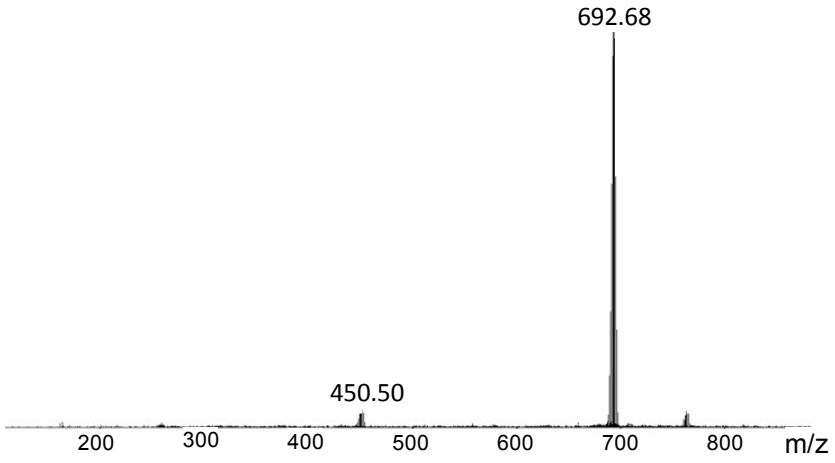
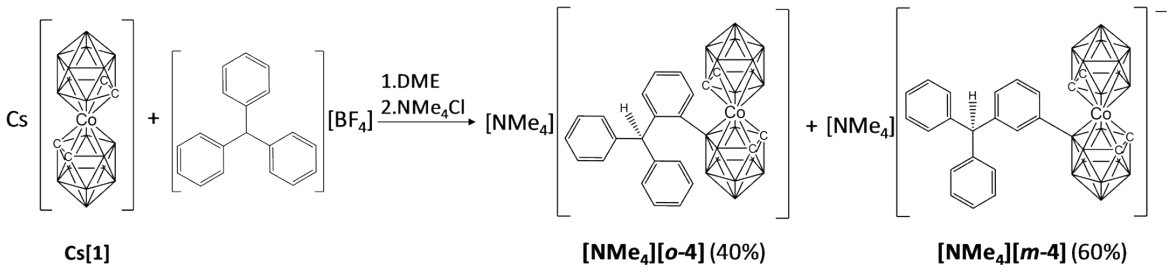


Figure S6. MALDI-TOF spectrum of [NMe_4][**3**].

2.3. Reactions of Cobaltabisdicarbollide with triphenylmethane derivatives

2.3.1. Via triphenylcarbenium salts.

2.3.1.1. Synthesis and characterization of [NMe_4][4].



Scheme S2. Reaction conditions for the synthesis of [NMe_4][**4**].

69.5 mg (0.21 mmol) of triphenylcarbenium tetrafluoroborate were added into a 10 mL round bottom flask (previously filled with nitrogen using the pump and fill method) inside a glove bag. 95.6 mg (0.21 mmol) of Cs**[1]** were then added under nitrogen and 5 mL of DME were added to dissolve the mixture. The reaction was left stirring overnight. After evaporation of the solvent using the rotary evaporator, the residue was dissolved in 20 mL Et_2O and extracted with HCl 0.1 M 3x20 mL; the combined organic fractions were then washed with water, dried over $MgSO_4$ and the solvent was removed under reduced pressure. Further purification was performed by silica column chromatography using a mixture of CH_2Cl_2-MeCN 7:3 as eluent. The fraction with a Rf=0.3 was the desired compound with triphenylmethyl as impurity. The compound was then washed several times with n-hexane until no signal for the triphenylmethyl appears in the ^{1}H-NMR. The final step was the precipitation as NMe_4 salt by dissolving the compound in the minimal amount of EtOH and adding dropwise a saturated solution of [NMe_4]Cl in water until full precipitation. The compound is then dried under vacuum obtaining 100 mg (60% yield) of the mixture NMe_4[*o*-4] (40%) and NMe_4[*m*-4] (60%) in an orange powder. The integration of 6.90 (d, $^3J_{H\text{-}H}$ 7.8, 1H, H_{Ar}) and 6.79 (d, $^3J_{H\text{-}H}$ 7.2, 1H, H_{Ar}) signals provide us an approximated isomeric ratio . **^{1}H NMR (600 MHz, CD_3COCD_3), δ:** 7.29-7.26 (m, 9H, H_{Ar} (*o*- and *m*-isomers)), 7.25 (dd, $^3J_{H\text{-}H}$ 8.4, 1H, H_{Ar} (*m*-isomer)), 7.20-7.17(m, 4H, H_{Ar} (*o*- and *m*-isomers)), 7.17 (t, $^3J_{H\text{-}H}$ 7.2, 1H, H_{Ar} (*o*-isomer)), 7.13(s, 1H, H_{Ar} (*m*-isomer)), 7.11-7.08 (m, 9H, H_{Ar} (*o*- and *m*-isomers)), 7.05 (t, $^3J_{H\text{-}H}$ 7.2, 1H, H_{Ar} (*o*-isomer)), 6.90 (d, $^3J_{H\text{-}H}$ 7.8, 1H, H_{Ar} (*m*-isomer)), 6.79 (d, $^3J_{H\text{-}H}$ 7.2, 1H, H_{Ar} (*o*-isomer)), 5.53 (s, 1H, C_{sp3}-H (*m*-isomer)v), 5.52 (s, 1H, C_{sp3}-H (*o*-isomer)), 4.60 (s, 2H, C_C-H (*o*-isomer)), 4.57 (s, 2H, C_C-H (*m*-isomer)), 3.74 (s, 2H, C_C-H (*o*-isomer)) and 3.67 (s, 2H, C_C-H (*m*-isomer)). **^{11}B NMR (128.38 MHz, CD_3COCD_3), δ**: 12.2 (s, 1B, B-C_{Ar}), 4.5 (d, $^1J_{B\text{-}H}$ 140.8, 1B, B-H), 1.7 (d, $^1J_{B\text{-}H}$ 119.0, 2B, B-H), -3.4 (d, $^1J_{B\text{-}H}$ 152.3, 2B, B-H), -5.6 (d, $^1J_{B\text{-}H}$ 162.6, 4B, B-H), -6.9 (d, $^1J_{B\text{-}H}$ 152.3, 2B, B-H), -17.4 (d, $^1J_{B\text{-}H}$ 162.6, 2B, B-H), -18.7 (d, $^1J_{B\text{-}H}$ 152.3, 2B, B-H), -21.8 (d, $^1J_{B\text{-}H}$ 140.8, 1B, B-H), -23.0 (d, $^1J_{B\text{-}H}$ 157.4, 1B, B-H). **^{13}C{^{1}H} NMR (100 MHz, CD_3COCD_3), δ:** 145.59, 145.54(**C_{Ar}**-C_{sp3}), 142.83, 141.40 (**C_{Ar}**-B), 133.98, 132.76, 131.10, 130.21, 130.15,

128.95, 128.70, 127.50, 126.99, 126.79 ($\mathbf{C}_{Ar}$-H), 57.60 and 57,25 (H$\mathbf{C}_{sp3}$-Ph_3(*o*- and *m*-isomers)), 55.50 and 5.73 ($C_{carborane}$). **MALDI-TOF:** Theor. 565.397 m/z Found, 566.36. **Elemental analysis.** Found: C, 42.62; H, 6.44. Calc. for Cs[3,3'-Co-8-CH(C_6H_5)$_3$-1,2-$C_2B_9H_{10}$-1',2'-$C_2B_9H_{11}$]·2CH_3COCH_3: C, 42.76; H, 5.94%.

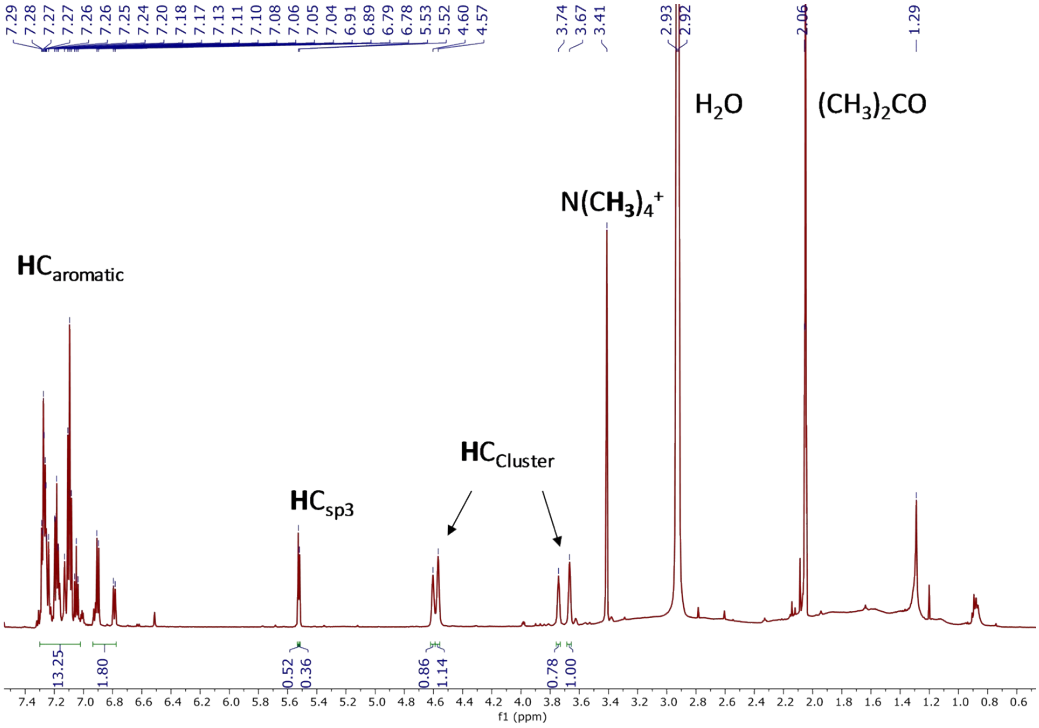


Figure S7. ^{1}H-NMR of [NMe_4][**4**]$^-$.

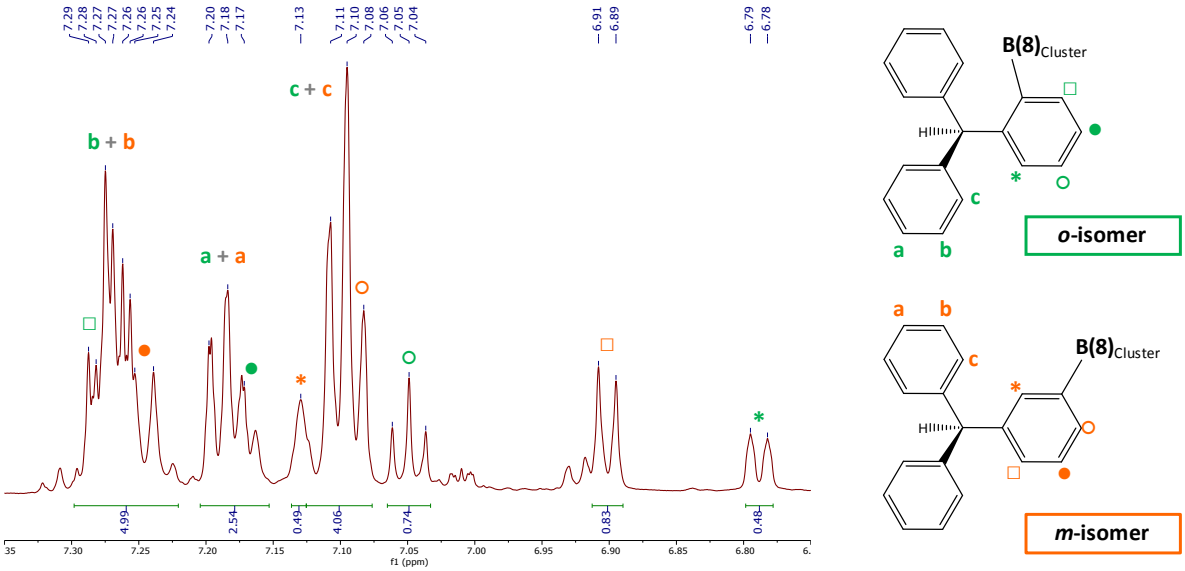


Figure S8. ^{1}H-NMR amplified spectrum of [NMe_4][**4**]$^-$ with the complete characterization of the isomers *ortho* and *meta*. It is possible to obtain an approximated isomeric ratio from the integration of the doublets at 6.9 and 6.79 ppm.

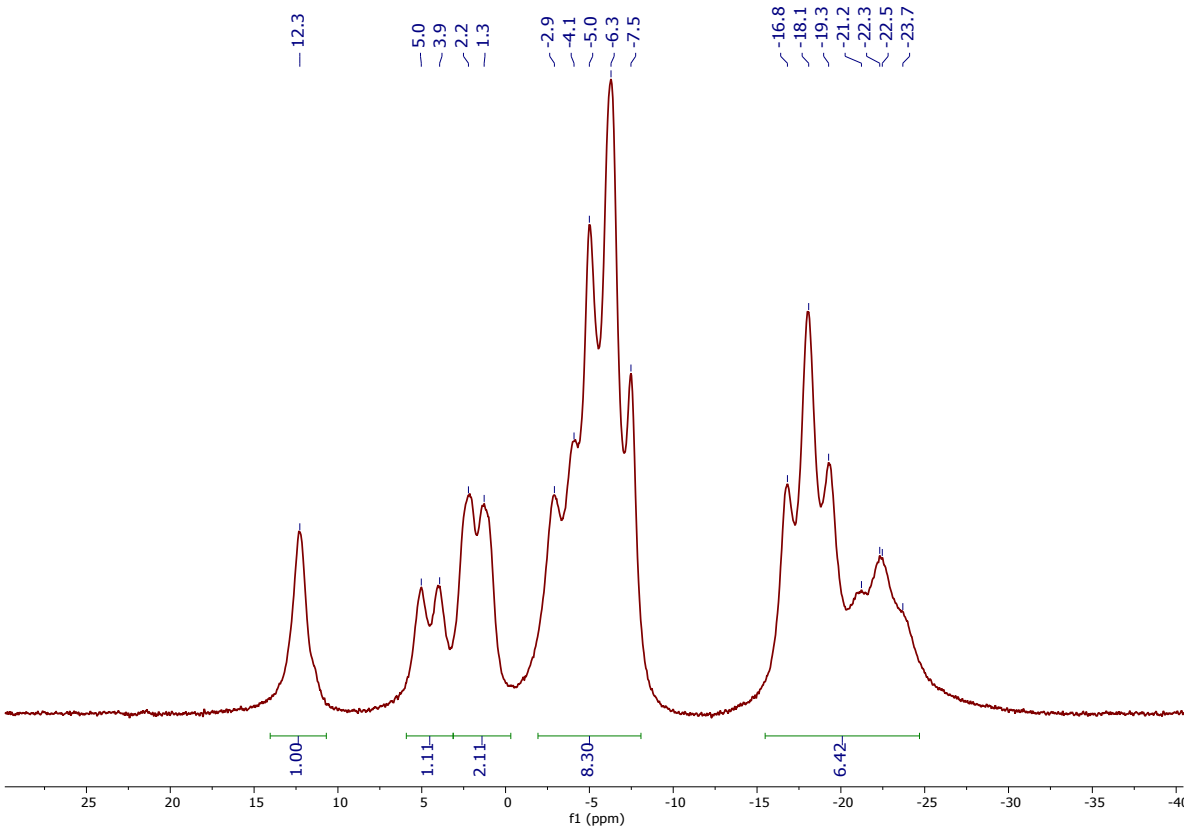


Figure S9. ^{11}B-NMR of [NMe_4][**4**]$^-$.

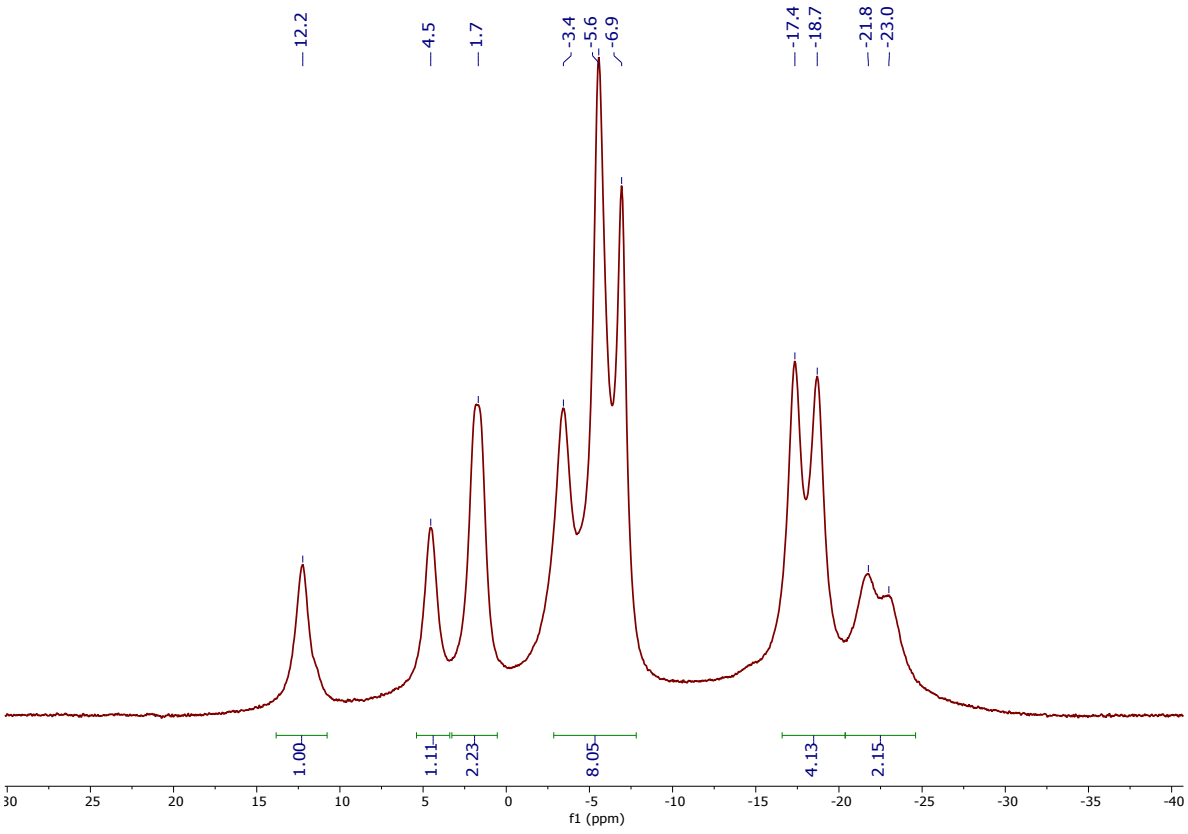


Figure S10. ^{11}B{^{1}H}-NMR of [NMe_4][**4**]$^-$.

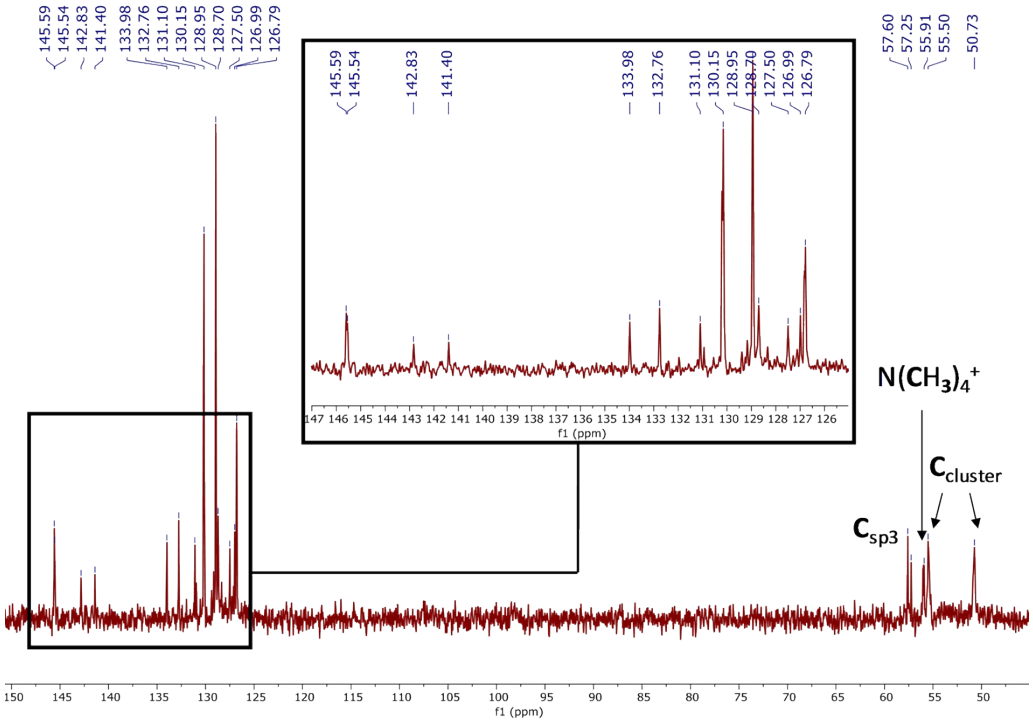


Figure S11. $^{13}C\{^{1}H\}$-NMR of $[NMe_4][\mathbf{4}]^-$.

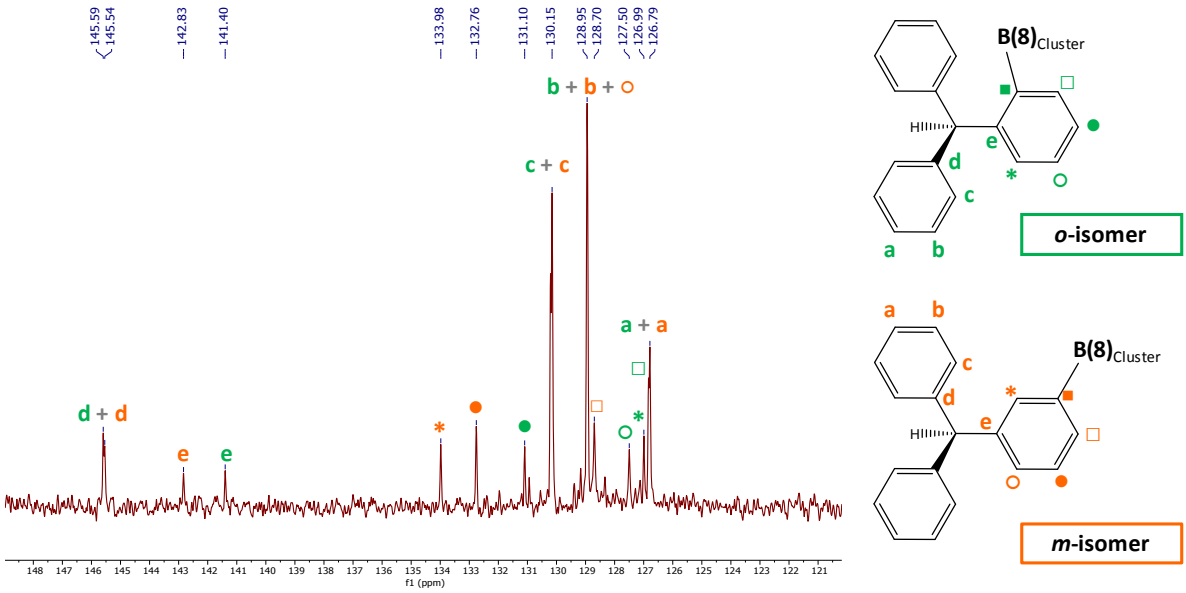


Figure S12. $^{13}C\{^{1}H\}$-NMR amplified spectrum of $[NMe_4][\mathbf{4}]^-$ with the complete characterization of the isomers ortho and meta.

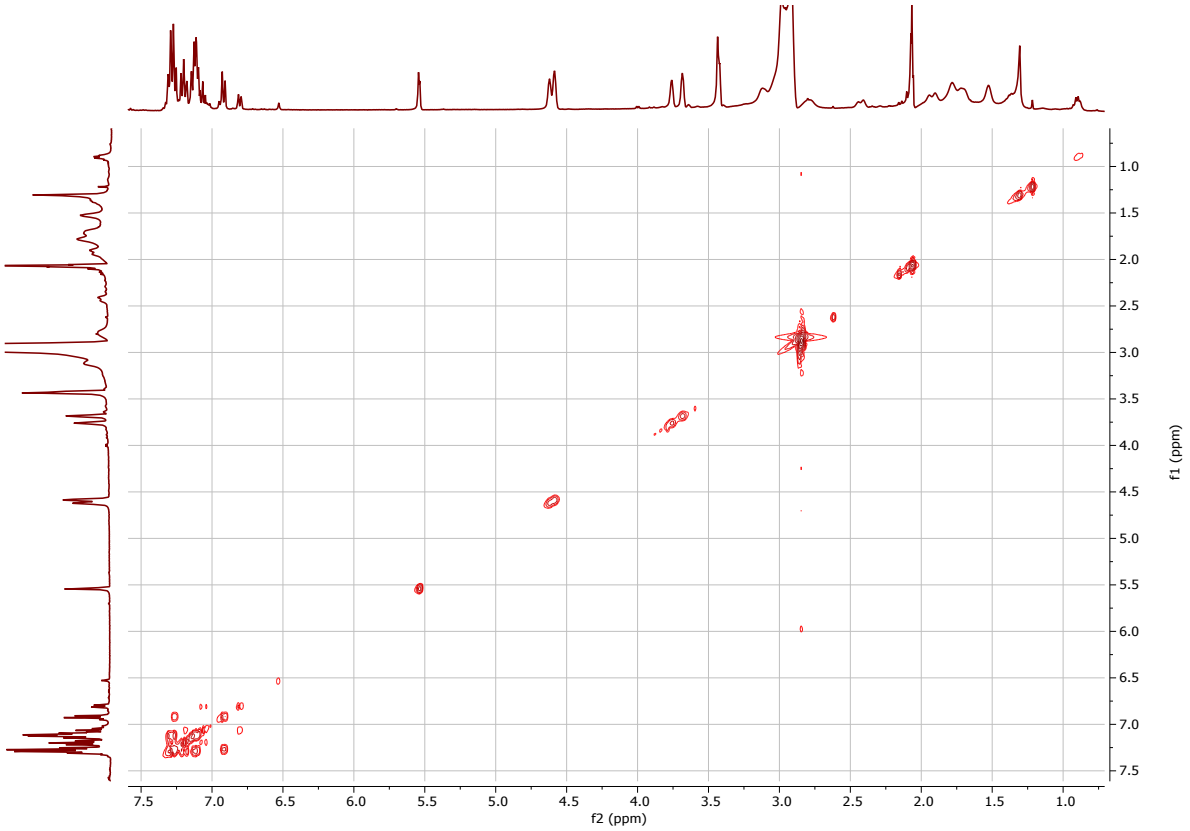


Figure S13. ^{1}H COSY spectrum of [NMe_4][**4**]$^{-}$.

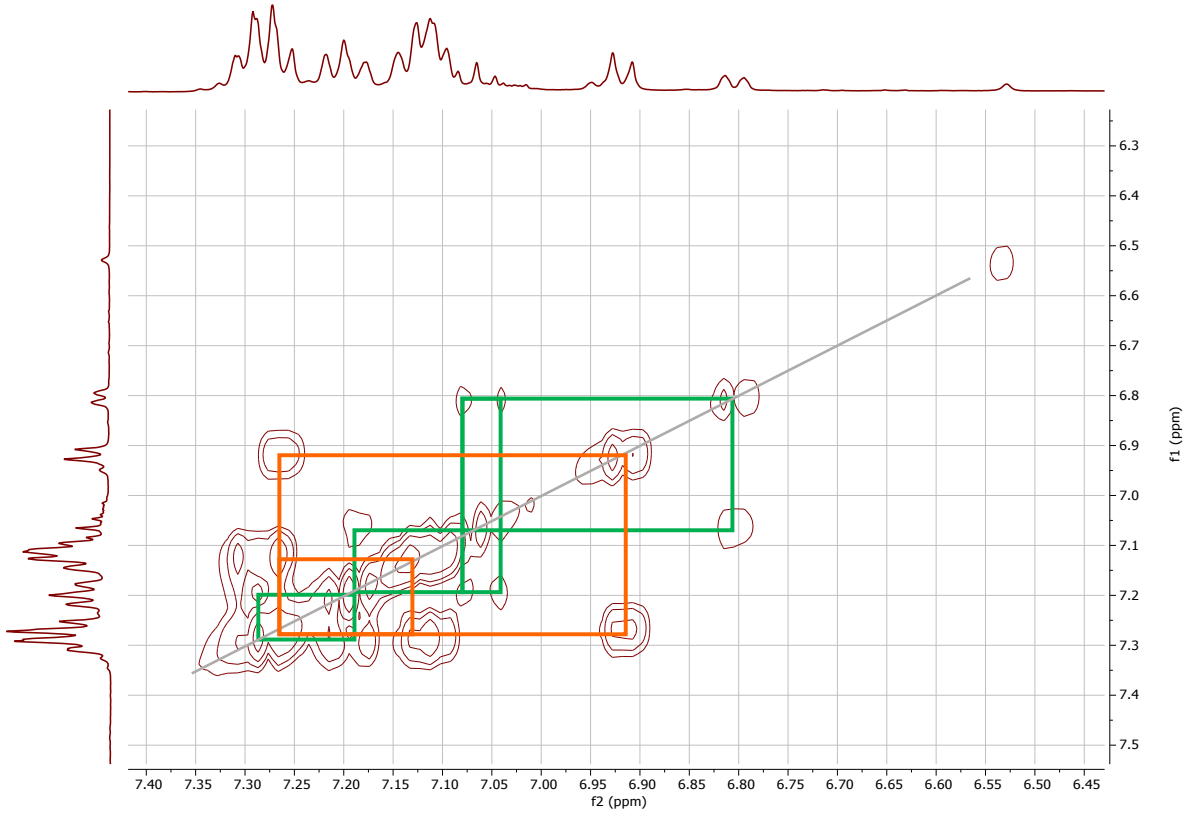


Figure S14. ^{1}H COSY amplified spectrum of [NMe_4][**4**]$^{-}$.

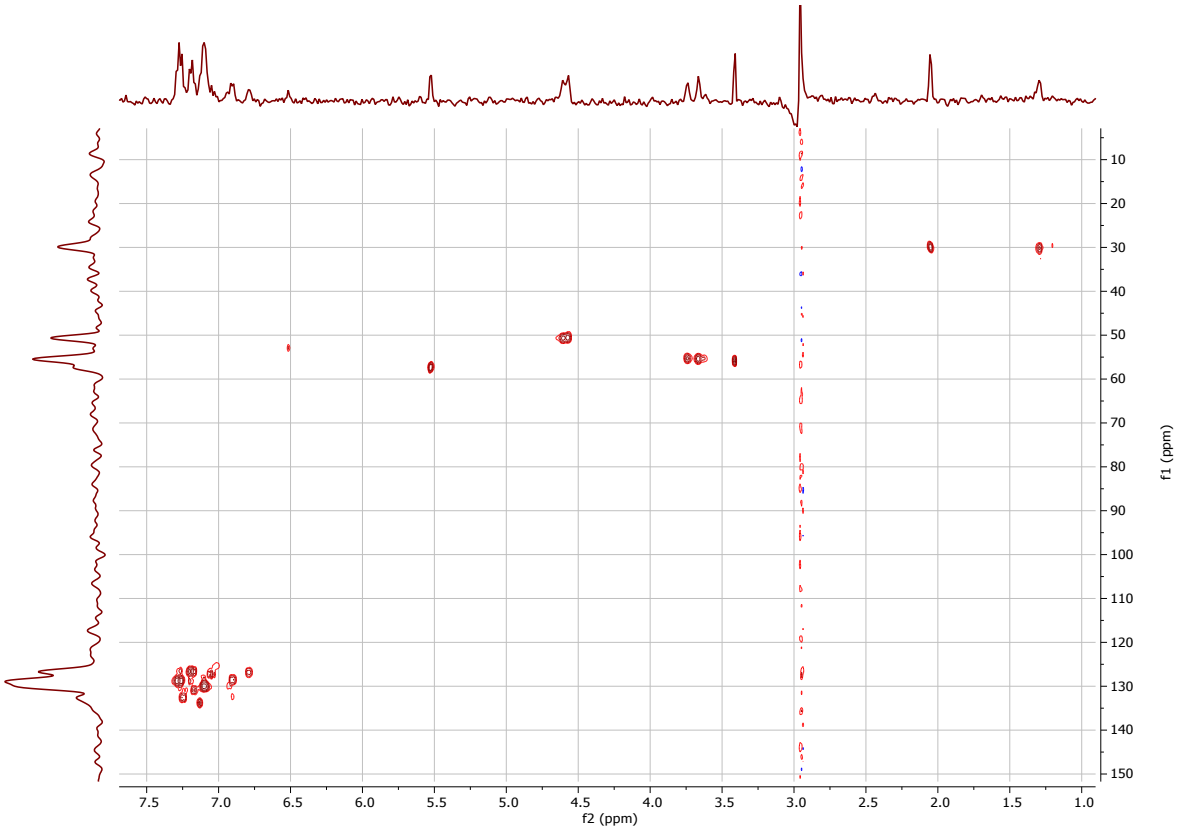


Figure S15. ^{1}H-^{13}C HSQC spectrum of $[NMe_4][\mathbf{4}]^-$.

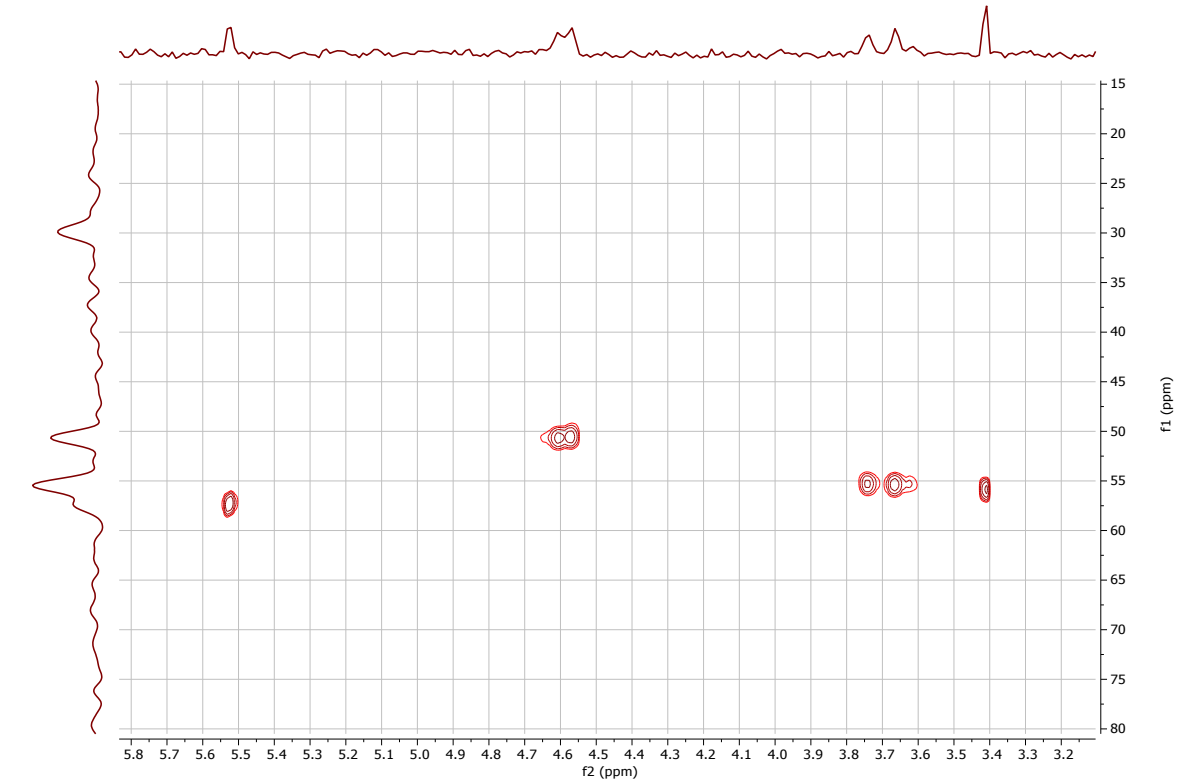


Figure S16. ^{1}H-^{13}C HSQC amplified spectrum of $[NMe_4][\mathbf{4}]^-$.

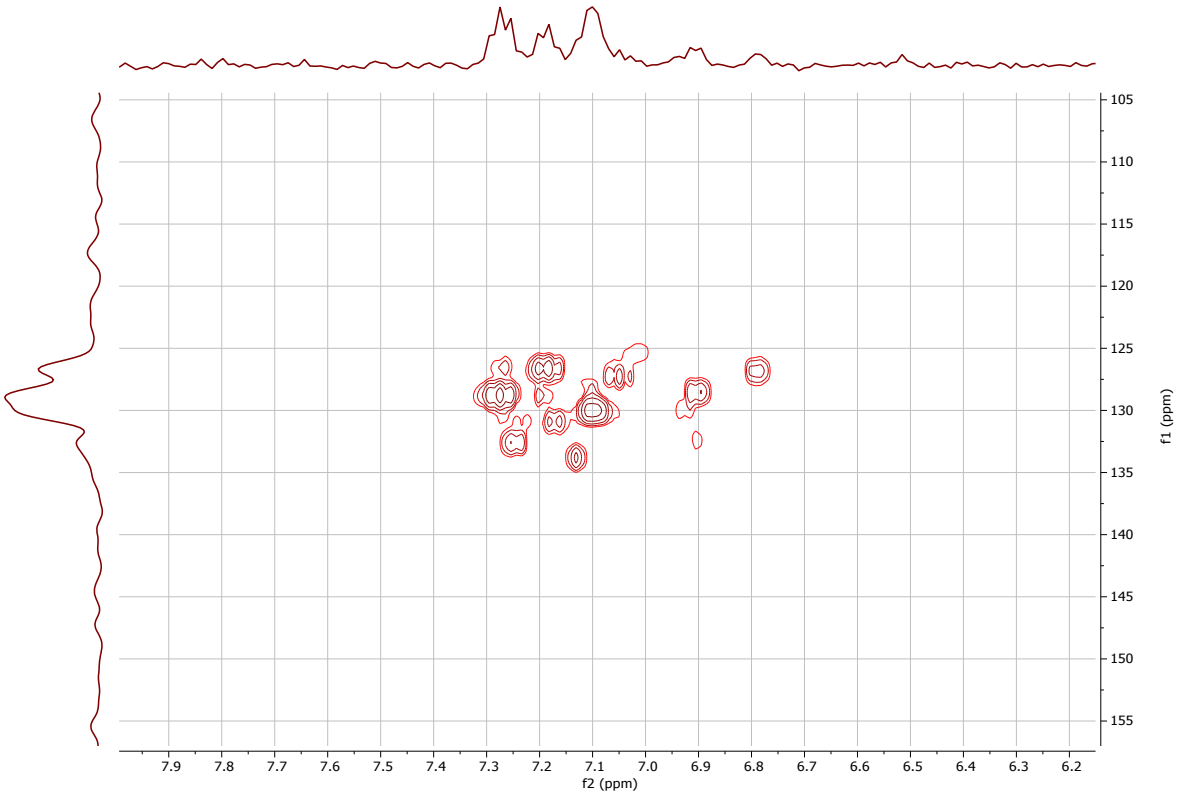


Figure S17. ^{1}H-^{13}C HSQC amplified spectrum of $[NMe_4][\mathbf{4}]^-$.

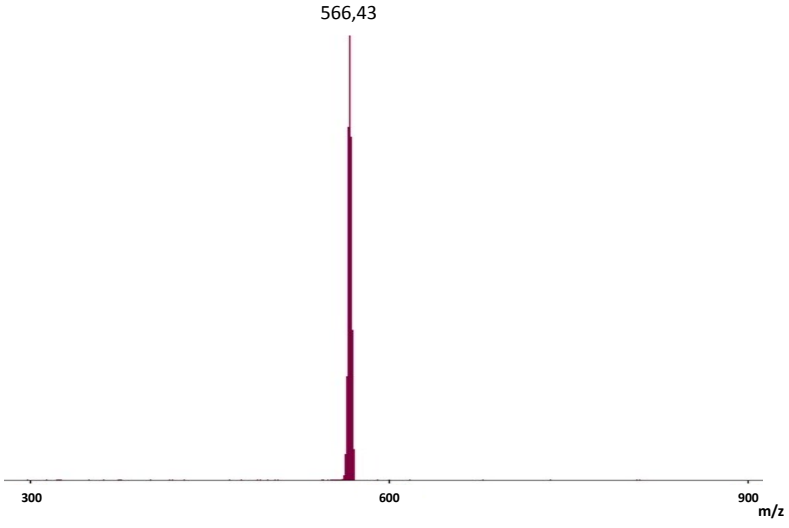
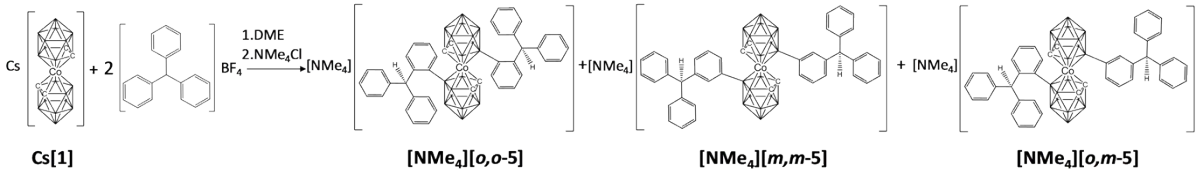


Figure S18. MALDI-TOF spectrum of $[NMe_4][\mathbf{4}]^-$.

2.3.1.2. Synthesis and characterization of [NMe_4][5]



Scheme S3. Reaction conditions for the synthesis of [NMe_4][**5**].

117.4 mg (0.35 mmol) of triphenylcarbenium tetrafluoroborate were added into a 10 mL round bottom flask (previously filled with nitrogen using the pump and fill method) inside a glove bag. 83.7 mg (0.18 mmol) of Cs[**1**] were then added under nitrogen and 5 mL of DME were added to dissolve the mixture. The reaction was left stirring overnight. After evaporation of the solvent using the rotary evaporator, the residue was dissolved in 20 mL Et_2O and extracted with HCl 0.1 M 3x20 mL; the combined organic fractions were then washed with water, dried over $MgSO_4$ and the solvent was removed under reduced pressure. Further purification was performed by silica column chromatography using a mixture of CH_2Cl_2-MeCN 7:3 as eluent. The fraction with a Rf=0.5 was the desired compound with triphenylmethyl as impurity. The compound was then washed several times with n-hexane until no signal for the triphenylmethyl appear in the ^{1}H-NMR. The final step was the precipitation as NMe_4 salt by dissolving the compound in the minimal amount of EtOH and adding dropwise a saturated solution of [NMe_4]Cl in water until full precipitation. The compound is then dried under vacuum obtaining 130 mg (83% yield) of the isomeric mixture [NMe_4][*o,o*-**5**], [NMe_4][*m,m*-**5**] and [NMe_4][*o,m*-**5**] as an orange powder. **^{1}H NMR (600 MHz, CD_3COCD_3), δ:** 7.31-6.84 (m, 28H, H_{Ar} (*o,o*-,*m,m*- and *o,m*-isomers)), 5.56, 5.55, 5.54(s, 1H, C_{sp3}-H (*o,o*-,*m,m*- and *o,m*-isomers)), 3.89 (s, 4H, $C_{Cluster}$-H), 3.85 and 3.83 (s, 4H, $C_{Cluster}$-H), 3.78 (s, 4H, $C_{Cluster}$-H), 3.41 (s, 12H, NMe_4). **^{11}B NMR (128.38 MHz, CD_3COCD_3), δ:** 10.9 (s, 2B, B-C_{Ar}), 2.0 (d, $^1J_{B-H}$ 122.9, 2B, B-H), -5.3 (d, 8B, $^1J_{B-H}$ 105.0, B-H), -19.2 (d, $^1J_{B-H}$ 81.92, 4B, B-H),-22.6 (br s, 2B, B-H). **^{13}C NMR (100 MHz, CD_3COCD_3), δ:** 145.42, 145.35 (**C**$_{Ar}$-C_{sp3}), 143.32 and 141.89 (C-B), 133.95, 132.60, 130.81, 130.15, 130.06, 129.22, 129.09, 128.98, 128.93, 128.31, 127.84, 127.33 and 126.83 (H**C**$_{Ar}$), 57.55 and 57.21 (H**C**$_{sp3}$), 55.9 (NMe_4), 54.64 ($C_{Cluster}$). **MALDI-TOF:** Theor. 808.503 m/z Found, 808.42. **Elemental analysis.** Found: C, 53.51; H, 5.56. Calc. for Cs[3,3'-Co-8,8'-($CH(C_6H_5)_3$-1,1',2,2'-$C_2B_9H_{10})_2$]: C, 53.59; H, 5.35 %.

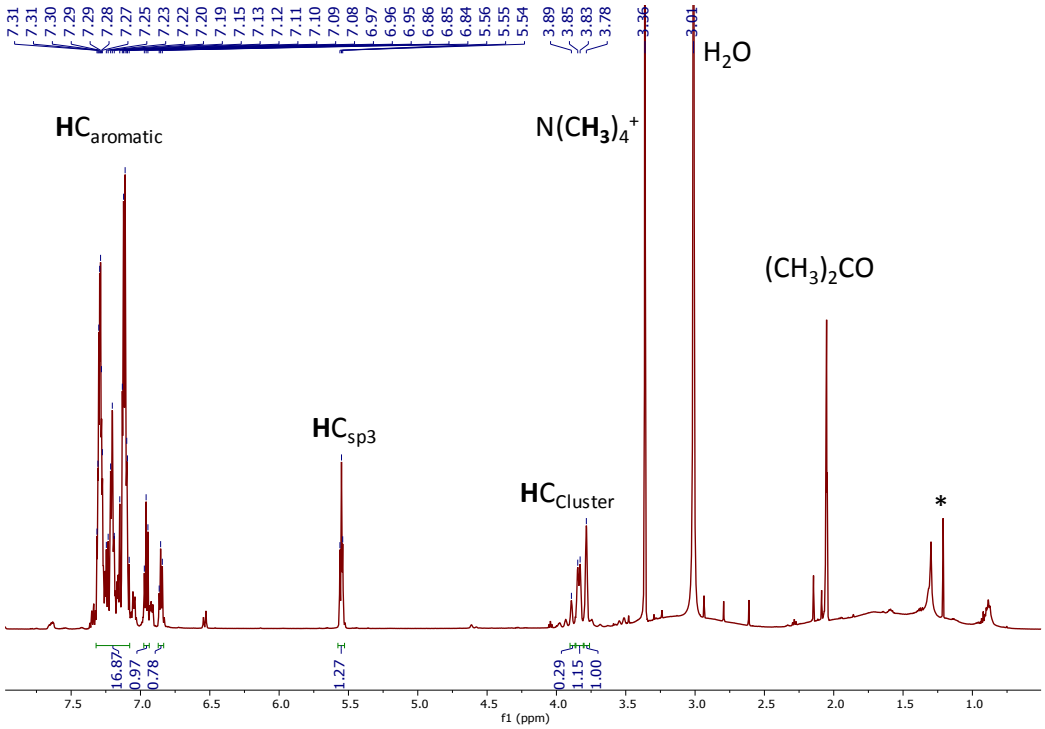


Figure S19. ^{1}H-NMR of [NMe$_4$][**5**]$^-$. *Unidentified solvents.

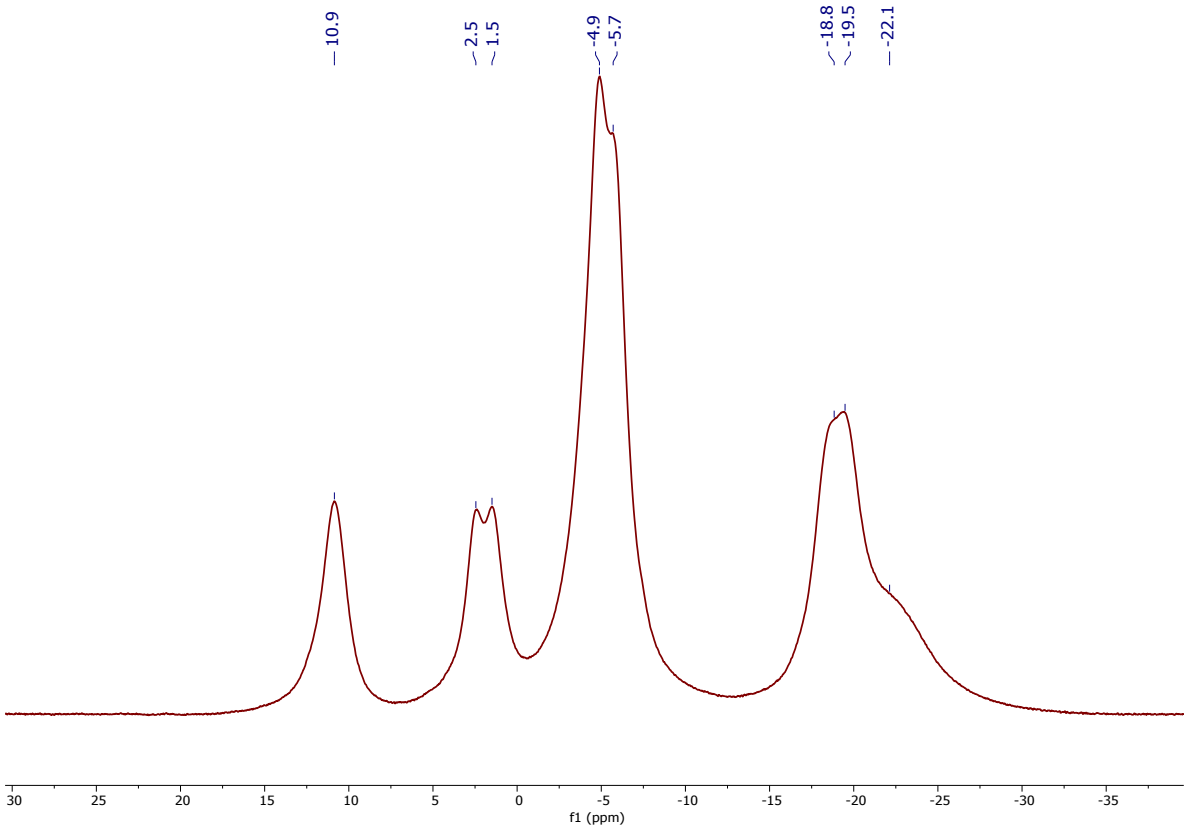


Figure S20. ^{11}B-NMR of [NMe$_4$][**5**]$^-$.

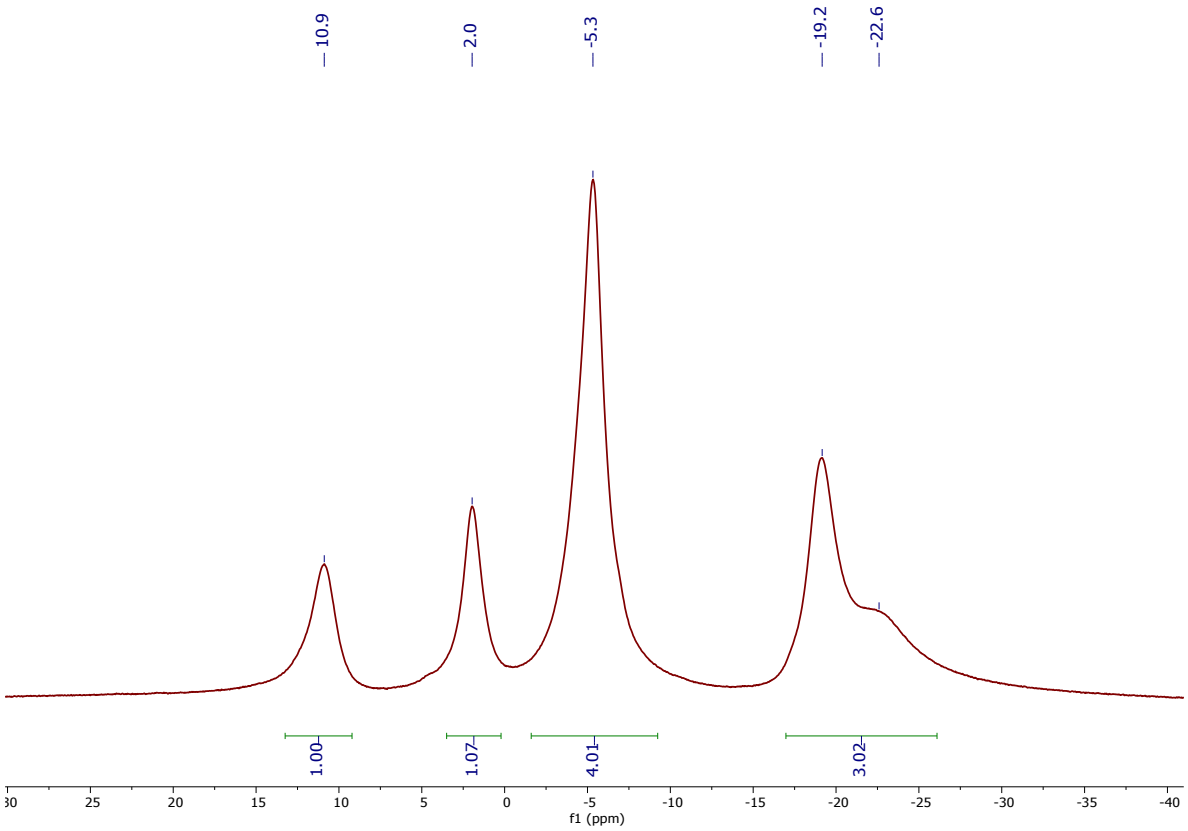


Figure S21. $^{11}B\{^{1}H\}$-NMR of $[NMe_4][\mathbf{5}]^-$.

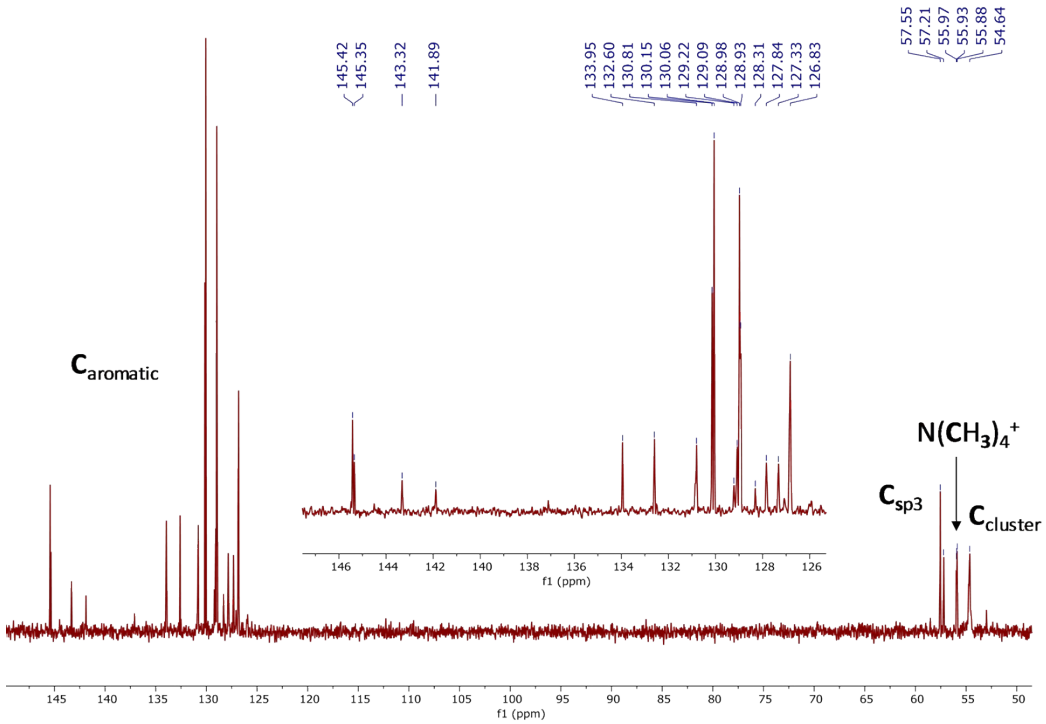


Figure S22. $^{13}C\{^{1}H\}$-NMR of $[NMe_4][\mathbf{5}]^-$.

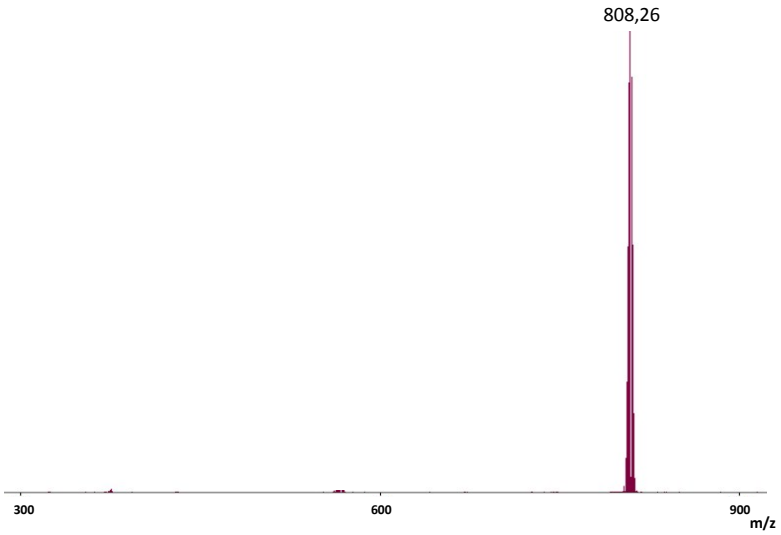
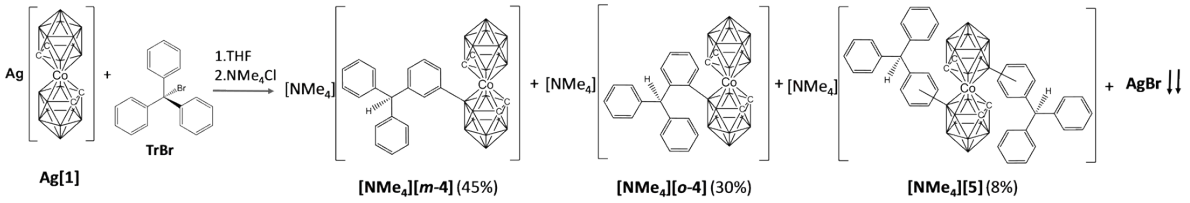


Figure S23. MALDI-TOF spectrum of $[NMe_4][\mathbf{5}]^-$.

2.3.2. Via carbocation generation in situ.

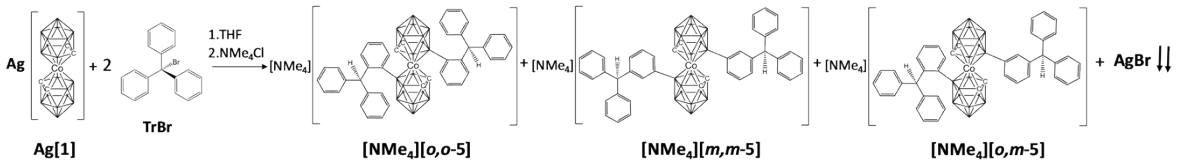
2.3.2.1. Synthesis of NMe_4[4].



Scheme S4. Reaction conditions for obtain NMe_4[***o*-4**] and NMe_4[***m*-4**] instantaneously.

A solution of 150mg (0.46 mmol) of bromotriphenylmethane in 2 mL of THF was added drop by drop in a solution of 200 mg (0.46 mmol) of Ag[**1**] in 3 mL of THF. The precipitation of AgBr is instantaneous. The solution was filtered, and extracted with a saturated solution of NaCl in HCl 0.1 M 3x10 mL. The organic fraction was dried over $MgSO_4$ and the solvent was removed under reduced pressure. Further purification was performed by silica column chromatography using a mixture of CH_2Cl_2-MeCN 7:3 as eluent. The yellow fraction with Rf=0.3 was the desired compound $[4]^-$, and the fraction with Rf=0.5 was the disubstituted product $[5]^-$. Finally, every product was precipitated like cesium salt by dissolving the compounds in the minimal amount of water and adding a saturated solution of CsCl in water until full precipitation. The compounds were filtered and dried obtaining 196.2mg (75% yield) of the *ortho*- and *meta*-isomers in the same isomeric ratio as the reaction via triphenylmethylcarbenium salts. Finally, 36 mg (8% yield) for the product Cs[**5**] was obtained too.

2.3.2.2. Synthesis of [NMe_4][5].



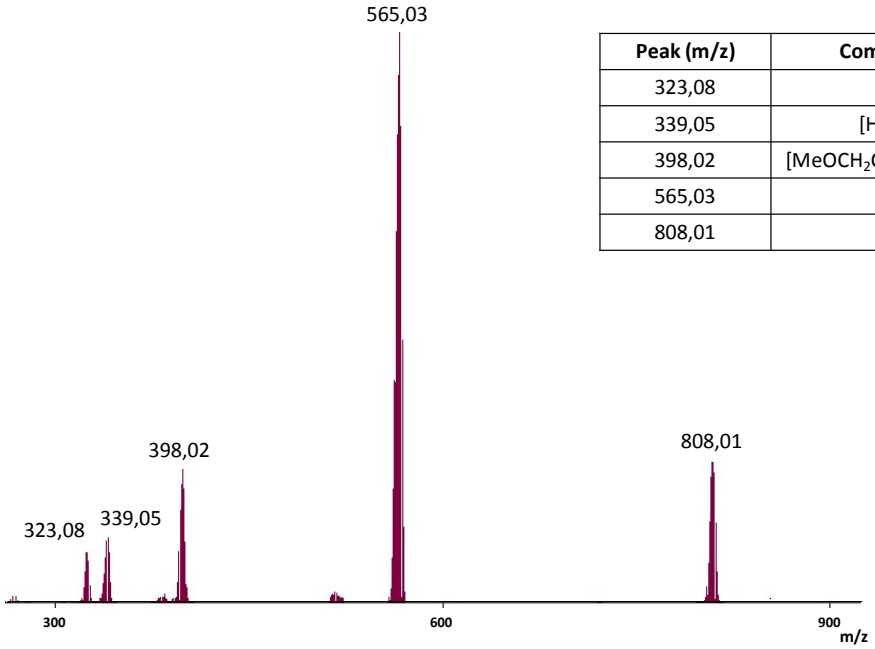
Scheme S5. Reaction conditions for obtain NMe_4[***o,o*-5**], NMe_4[***m,m*-5**] and NMe_4[***o,m*-5**] instantaneously.

A solution of 300mg (0.92 mmol) of bromotriphenylmethane in 4 mL of THF was added drop by drop in a solution of 200 mg (0.46 mmol) of Ag[**1**] in 3 mL of THF. The precipitation of AgBr is instantaneous. The solution was filtered, and extracted with a saturated solution of NaCl in HCl 0.1 M 3x10 mL. The organic fraction was dried over $MgSO_4$ and the solvent was removed under reduced pressure. Further purification was performed by silica column chromatography using a mixture of CH_2Cl_2-MeCN 7:3 as eluent. The yellow fraction with Rf= =0.5 was the disubstituted product [**5**]$^-$. Finally, the product was precipitated like cesium salt by dissolving the compound in the minimal amount of water and adding a saturated solution of CsCl in water until full precipitation. The compound were filtered and dried obtaining 393 mg (90% yield) for the product Cs[**5**] of the *ortho,ortho-*, *meta,meta-* and *ortho,meta-*isomers.

2.3.2.3. Synthesis of [**4**]$^-$ in presence of 10 equivalents of benzene.

A solution of 38 mg (0.12 mmol) of bromotriphenylmethane in 2 mL of DME was added drop by drop in a solution of 50 mg (0.12 mmol) of Ag[**1**] and 0.11 mL (1.2mmol) of benzene in 3 mL of DME. The precipitation of AgBr is instantaneous. The solution was filtered, and extracted with a saturated solution of NaCl in HCl 0.1 M 3x10 mL. The organic fraction was dried over $MgSO_4$ and the solvent was removed under reduced pressure. Finally, the organic fraction was precipitated like cesium salt by dissolving the compounds in the minimal amount of water and adding a saturated solution of CsCl in water until full precipitation.

The MALDI-TOF spectrum shows the formation of different products. Among them one at 398 m/z that corresponds to cobaltabisdicarbollide with the benzene ([Ph-**1**]$^-$, 399 m/z).



Peak (m/z)	Compound
323,08	[**1**]$^-$
339,05	[HO-1]$^-$
398,02	[$MeOCH_2CH_2O$-1]$^-$or Ph
565,03	[**4**]$^-$
808,01	[**5**]$^-$

Figure S24. MALDI-TOF spectrum of the resulting crude of the reaction of the formation of [4]$^-$ in presence of 10 equivalents of benzene and table with the assigned products.

2.3.2.4. Synthesis of the compound [4]$^-$ by the same methodology in different solvents.

A first round of the same reaction previously commented in the section 3.3.2.1 was developed in different solvents to obtain products isomerically pure. However, in all the cases the reaction gave the same isomers, demonstrating the similar stability of both isomers. The isomeric yields have been obtained from the integration of the doublets at 6.9 and 6.79 of ^{1}H NMR spectrum of the reactions.

Table S1. Product yields of the synthesis of [**4**]$^-$ in different solvents.

Solvents	Yield of product (%)		
	Total yield	*Meta*-isomer	*Ortho*- isomer
THF	75	50	50
DME	80	65	35
Diethylether	50	60	40
DMF	75	55	45
DMF -40°C	75	55	45

The synthesis of [**4**]$^-$ was carried on in different solvents and at different temperatures to improve the unsatisfactory results previously presented. In a second round the selected solvents were toluene, benzene and dichloromethane (DCM).

Synthesis at room temperature. A solution of 22.3 mg (0.07mmol) of TrBr in 1mL of solvent (toluene, benzene or DCM) was added drop by drop to a solution of 30 mg (0.07 mmol) of Ag[**1**] in 2 mL of the same solvent. The reaction is left with vigorous stirring at room temperature during 5 minutes. The

precipitation of AgBr is instantaneous. The solution was filtered and the solvent was removed under reduced pressure. Finally, the products were analyzed by MALDI-TOF-MS

Synthesis at reflux temperature. A solution of 22.3 mg (0.07mmol) of TrBr in 1mL of solvent (toluene, benzene or DCM) was added drop by drop to a boiling solution of 30 mg (0.07 mmol) of Ag[**1**] in 2 mL of the same solvent. The reaction is left with vigorous stirring at reflux during 5 minutes. The precipitation of AgBr is instantaneous. The solution was filtered and the solvent was removed under reduced pressure. Finally, the products were analyzed by MALDI-TOF-MS

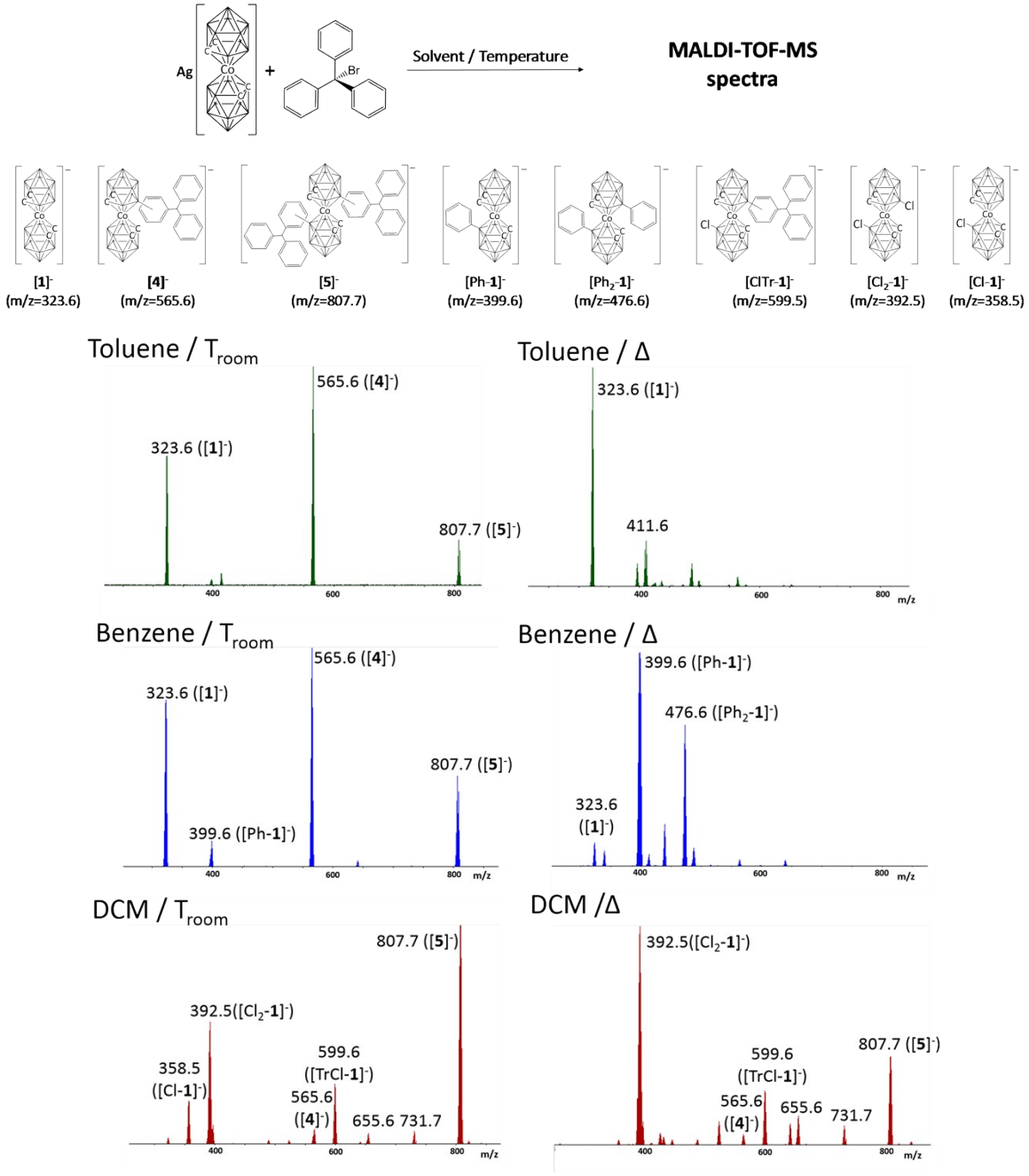


Figure S25. From top to bottom: The general reaction scheme, the proposed structures for de different MALDI-TOF peaks and the MALDI-TOF-MS of the reactions with the peaks and the structure name in parenthesis (the peaks without descriptive structure are the ones we were not able to assign).

2.3.2.5. Synthesis of $[4]^-$ in absence of bromotriphenylmethane.

The MALDI-TOF-MS peaks of the previous reaction present some unexplained signals corresponding to the reaction of $[\mathbf{1}]^-$ with the solvent. In consequence, the same reactions in absence of trityl carbocation were run in toluene, benzene and DCM and at room temperature and relux.

Synthesis at room temperature. A solution of 30 mg (0.07 mmol) of Ag[**1**] in 2 mL of solvent (toluene, benzene or DCM) was left with vigorous stirring at room temperature during 5 minutes. The solvent was removed under reduced pressure and the products were analyzed by MALDI-TOF-MS.

Synthesis at reflux temperature. A solution of 30 mg (0.07 mmol) of Ag[**1**] in 2 mL of solvent (toluene, benzene or DCM) was left with vigorous stirring at reflux during 5 minutes. The solvent was removed under reduced pressure and the products were analyzed by MALDI-TOF-MS.

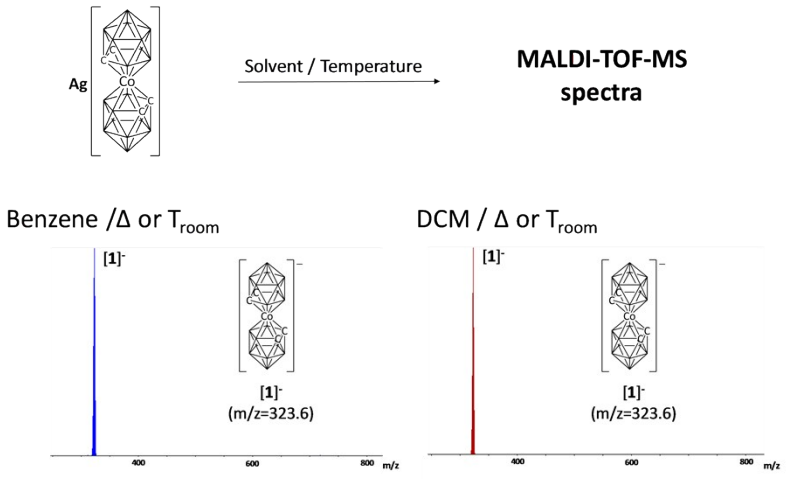
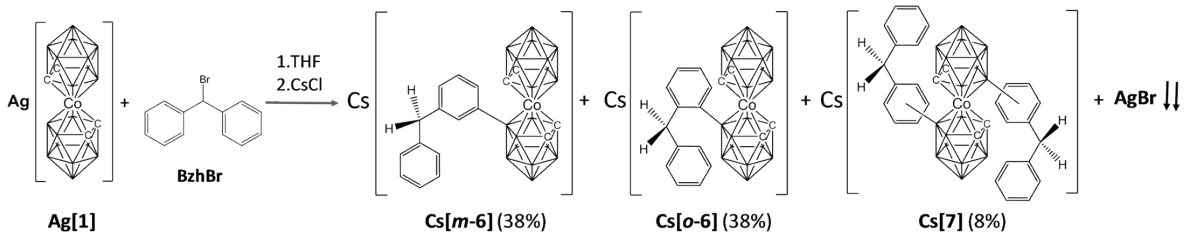


Figure S26. From top to bottom: The general reaction scheme and the MALDI-TOF-MS spectra of the reactions with the corresponding structure.

The result of the experiment was the experimental demonstration of the hydride scavenger behavior of the trityl carbocation in presence of cobaltabisdicarbollide.

2.4. Synthesis and characterization of Cs[6] via carbocation generation in situ.



Scheme S6. Reaction conditions by the synthesis of s Cs[***o*-6**], Cs[***m*-6**]and Cs[**7**].

A solution of 57.3mg (0.23 mmol) of benzhydryl bromide in 1 mL of THF was added drop by drop in a solution of 100 mg (0.23 mmol) of Ag[**1**] in 2 mL of THF. The precipitation of AgBr is instantaneous, but the reaction remained with constant agitation for 10 minutes. The solution was filtered and extracted with a saturated solution of 10mL of NaCl in HCl 0.1 M 3 times. The organic fraction was dried over $MgSO_4$ and the solvent was removed under reduced pressure. Further purification was performed by silica column chromatography using a mixture of CH_2Cl_2-MeCN 7:3 as eluent. The third yellow fraction with Rf=0.3 was the desired compound [**6**]$^-$, and the fourth fraction with Rf=0.15 was the disubstituted product [**7**]$^-$. Finally, both products were precipitated like cesium salt by dissolving the compounds in the minimal amount of water and adding a saturated solution of CsCl in water until full precipitation. The compounds were filtered and dried obtaining 85mg (76 % yield) for the isomeric mixture Cs[***o*-** and ***m*-6**] with and approximate ratio of 1:1 and 12mg (8% yield) for the product Cs[**7**]. It is possible to obtain an approximate isomeric ratio from the integration of doublet signals at 6.98 and 6.89 ppm (Figure S28). **^{1}H NMR (600 MHz, CD_3COCD_3), δ:** 7.25-7.22 (m, 6H, H_{Ar}), 7.20 (s, 1H, H_{Ar} (m-isomer)), 7.16-7.13 (m, 8H, H_{Ar} (o- and m-isomers)), 7.05 (t, 1H, $^3J_{H-H}$ 7.6, H_{Ar} (o-isomer)), 6.98 (d, 1H, $^3J_{H-H}$ 8, H_{Ar} (m-isomer)), 6.89 (d, 1H, $^3J_{H-H}$ 7.6, H_{Ar} (o-isomer)), 4.59 (s, 2H, C_C-H), 3.90 and 3.87 (s, 2H, H_2-C_{sp3} (o- and m-isomers)), 3.75 and 3.72 (s, 2H, C_C-H (o- and m-isomers)). **^{11}B NMR (128.38MHz, CD_3COCD_3), δ:** 12.5 (s, 1B, B-C_{Ar}), 4.7 (d, 1B, $^1J_{B-H}$ 139.5, B-H), 1.9 (d, 2B, $^1J_{B-H}$ 145.2, B-H), 1.4 (d, 2B, $^1J_{B-H}$ 145.2, B-H), -3.4 (d, 2B, $^1J_{B-H}$ 142.1, B-H), -5.5 (d, 4B, $^1J_{B-H}$ 140.8, B-H), -7.0 (d, 2B, $^1J_{B-H}$ 138.2, B-H), -17.4 (d, 2B, $^1J_{B-H}$ 163.8, B-H), -18.8 (t, 2B, $^1J_{B-H}$ 163.8, B-H), -21.8 (d, 1B, $^1J_{B-H}$ 177.9, B-H), -23.2 (d, 1B, $^1J_{B-H}$ 177.9, B-H). **^{13}C NMR (100 MHz, CD_3COCD_3), δ:** 143.15, 142.93 (**C_{AR}**- C_{sp3} (o- and m-isomers)), 139.80, 138.45 (**C_{Ar}**-$B_{Cluster}$ (o- and m-isomers)), 133.67, 133.0, 130.83 129.53, 129.36, 129.05, 129.02, 128.29, 127.67, 126.67, 126.48, 126.41 (**C_{Ar}**–H) 55.38, 50.75 ($C_{Cluster}$), 42.58, 42.19 (HC_{sp3} (o- and m-isomers)). **MALDI-TOF:** Theor. 490.362 and Found, 490.34 m/z. **Elemental analysis:** Found: C, 41.67; H, 6.58. Calc. for Cs[3,3'-Co-8-(C_6H_9)CH_2(C_6H_5) -1,2-$C_2B_9H_{10}$-1',2'- $C_2B_9H_{11}$]: C, 41.59; H, 6.78 %.

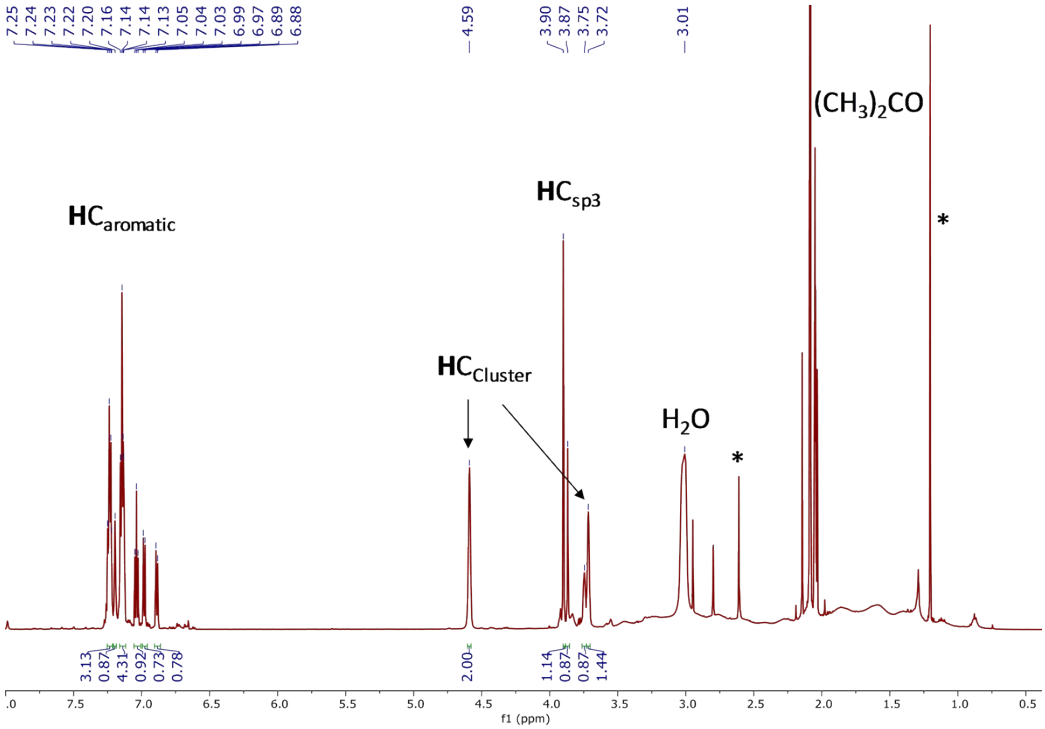


Figure S27. ^{1}H-NMR of Cs[**6**]. *Unidentified solvents.

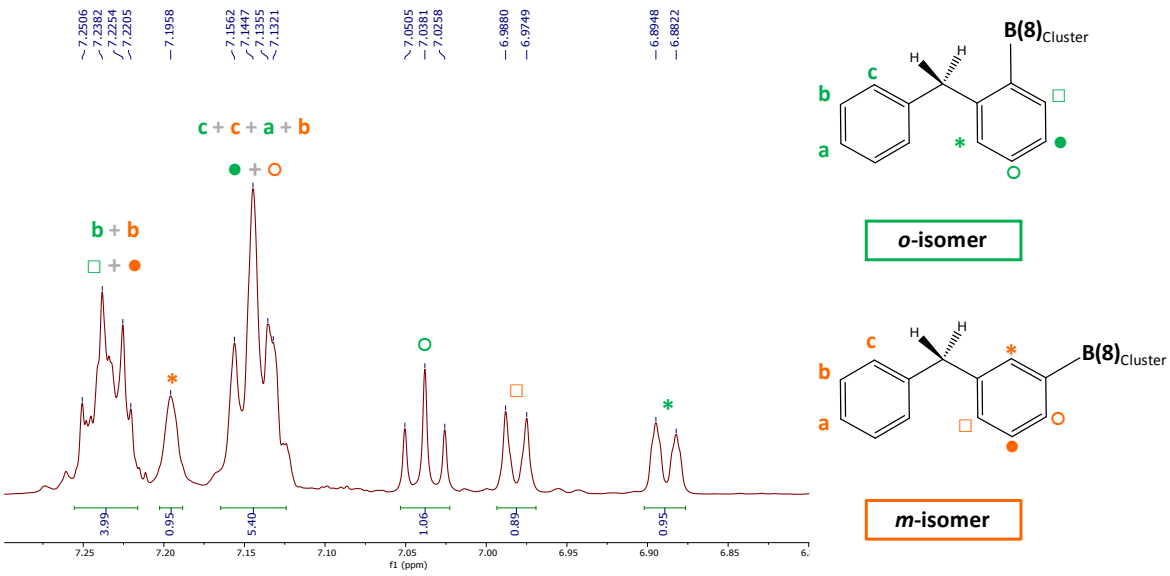


Figure S28. ^{1}H NMR amplified spectrum of Cs[**6**] with the complete characterization of the isomers *ortho*- and *meta*-. It is possible to obtain an approximate isomeric ratio from the integration of doublet signals at 6.98 and 6.89 ppm

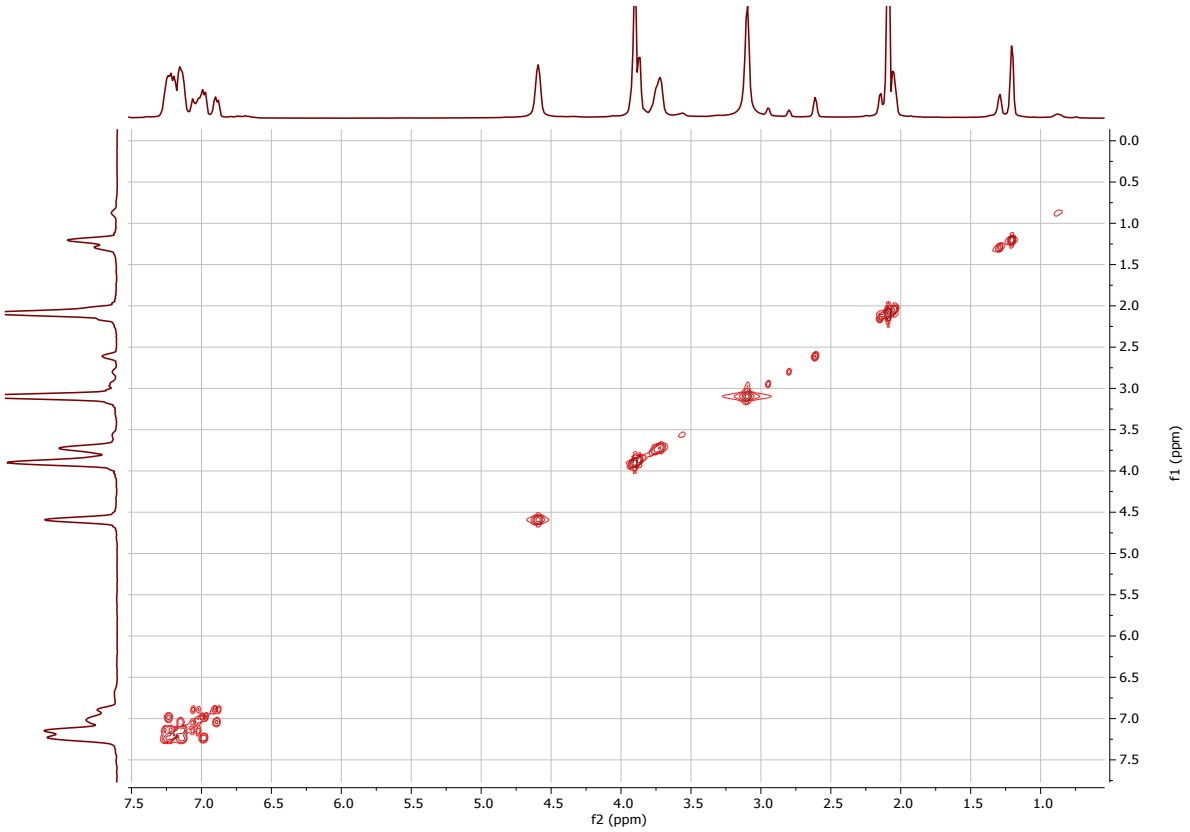


Figure S29. ^{1}H-COSY spectrum of Cs[**6**].

Figure S30. ^{1}H-COSY amplified spectrum of Cs[**6**].

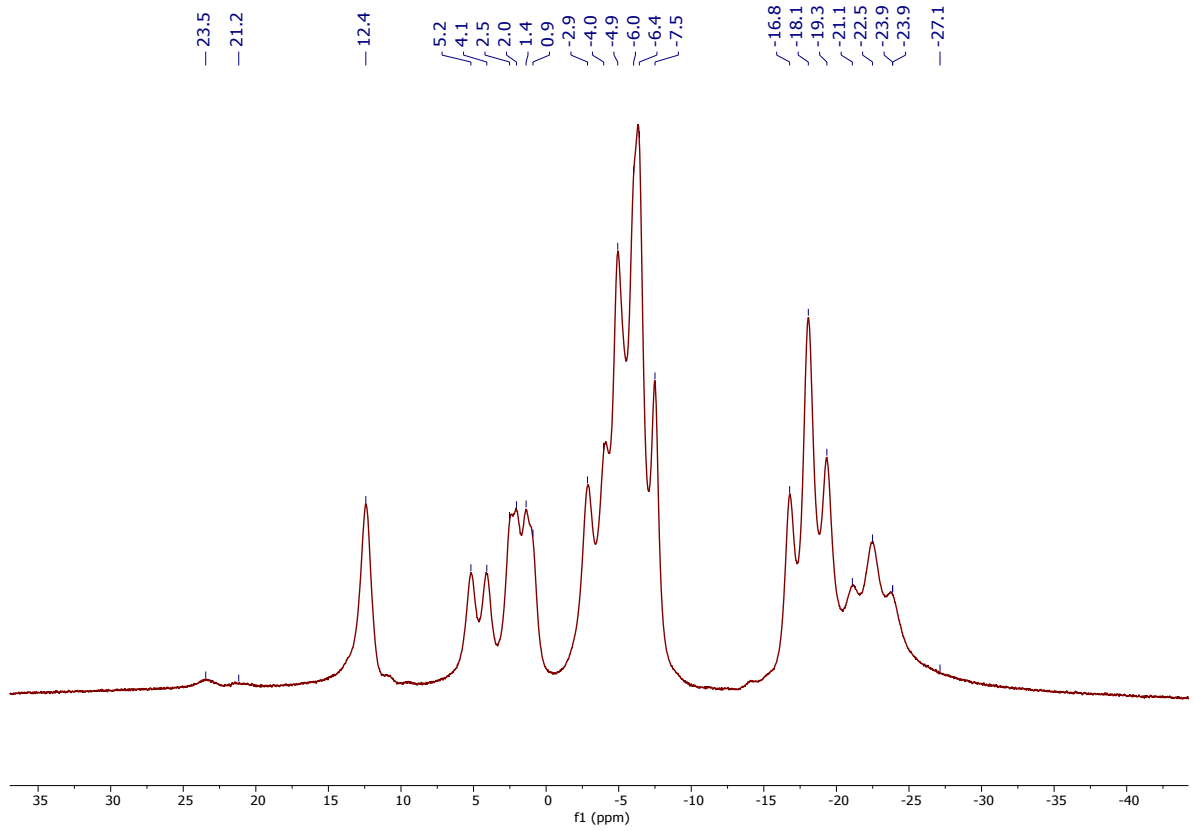


Figure S31. ^{11}B-NMR of Cs[**6**].

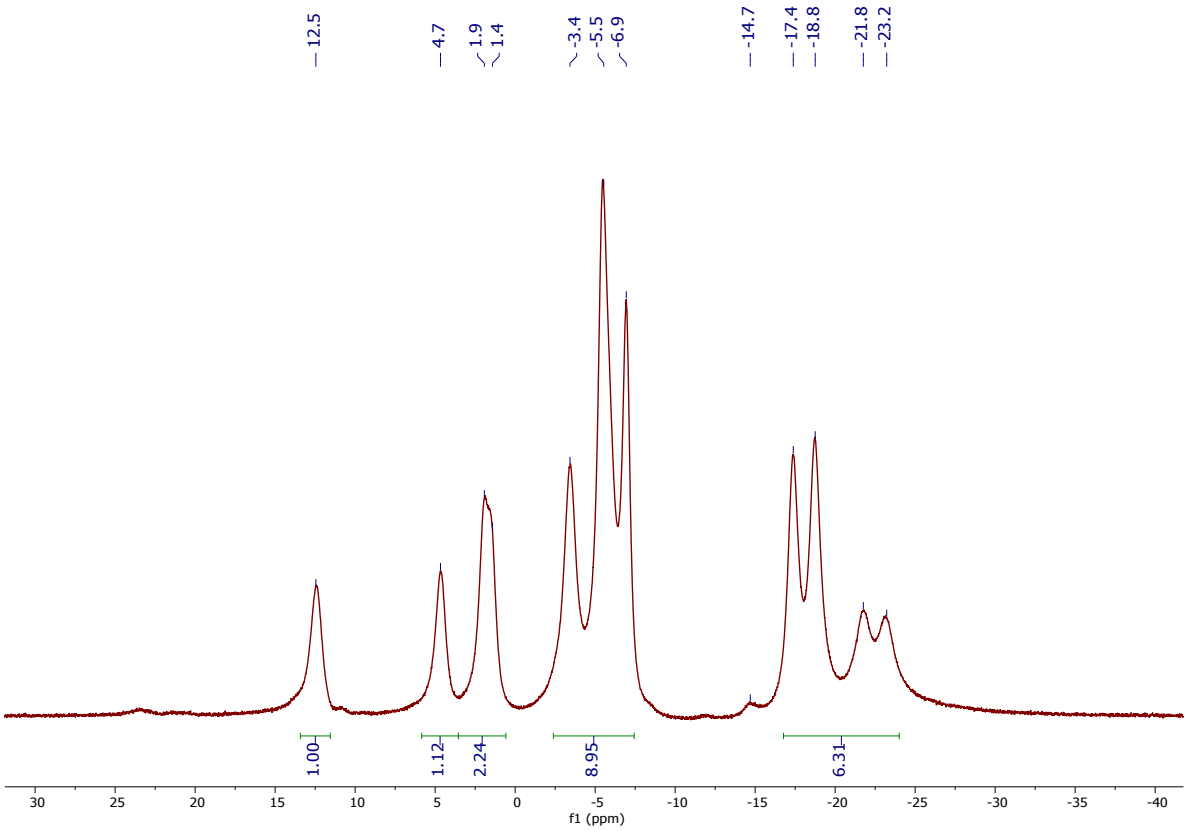


Figure S32. $^{11}B\{^{1}H\}$-NMR of Cs[**6**].

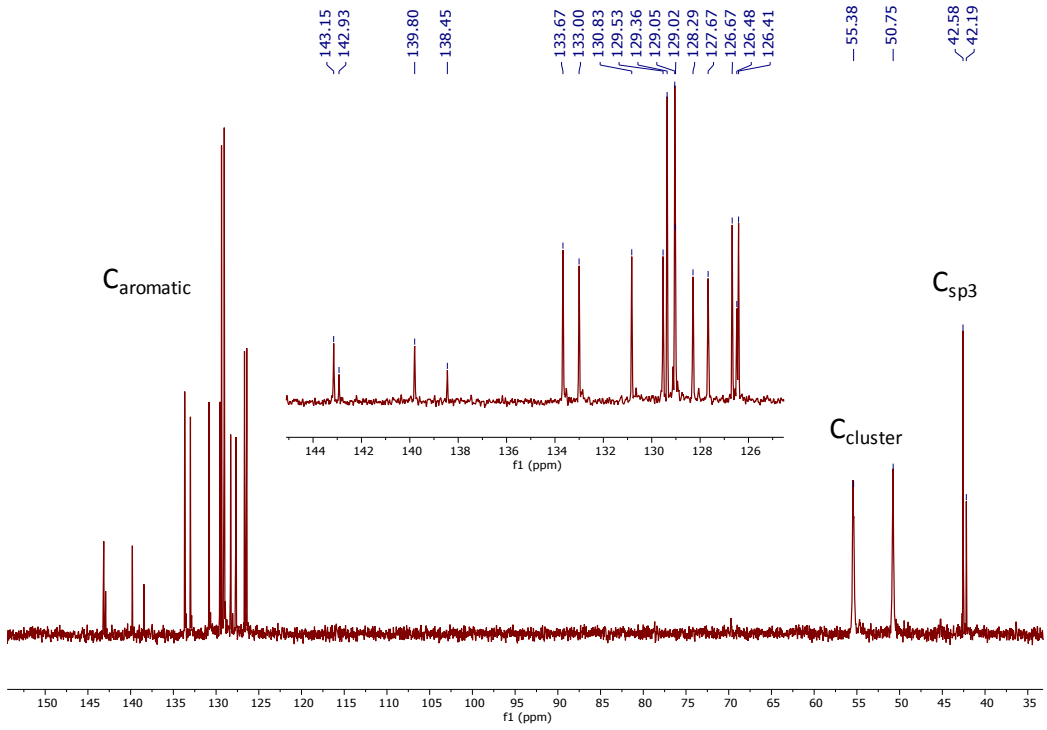


Figure S33. $^{13}C\{^{1}H\}$-NMR of Cs[**6**].

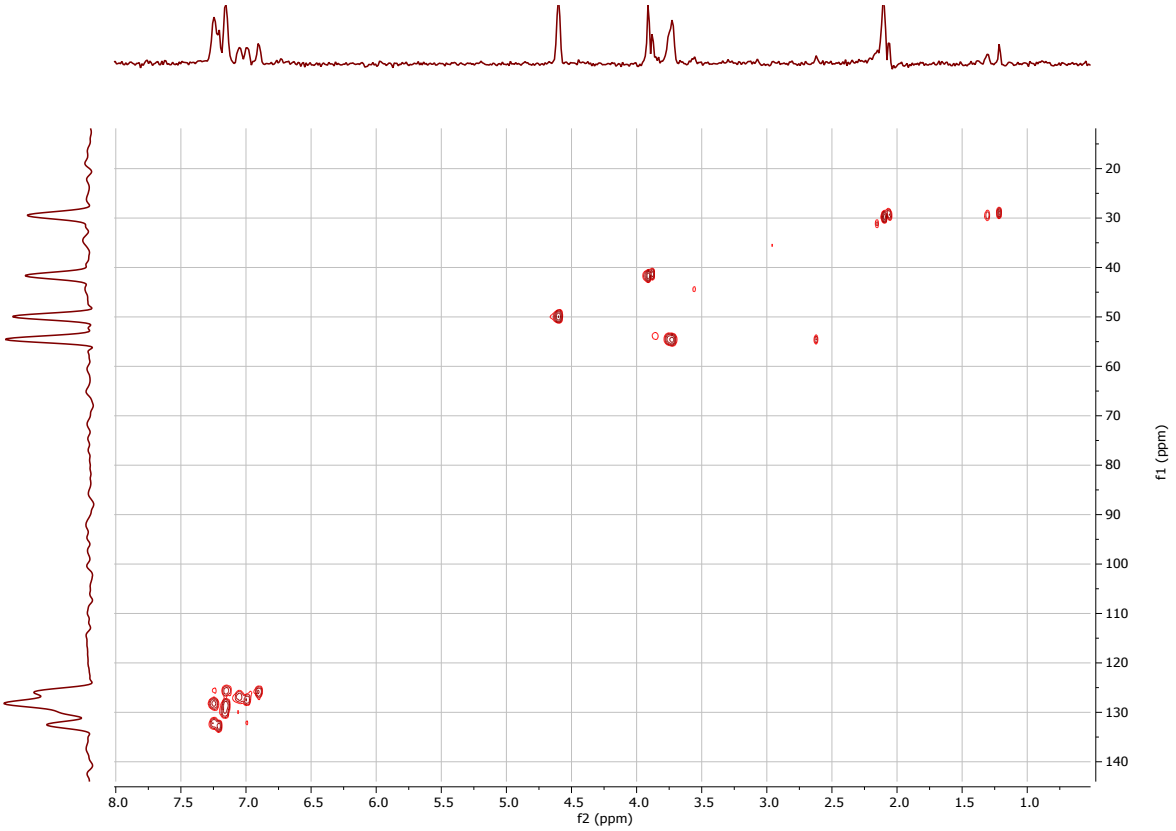


Figure S34. ^{1}H-^{13}HSQC spectrum of Cs[**6**].

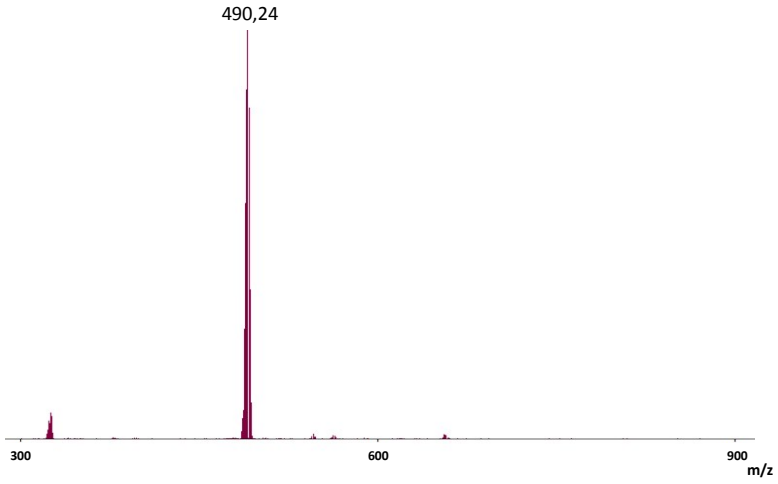
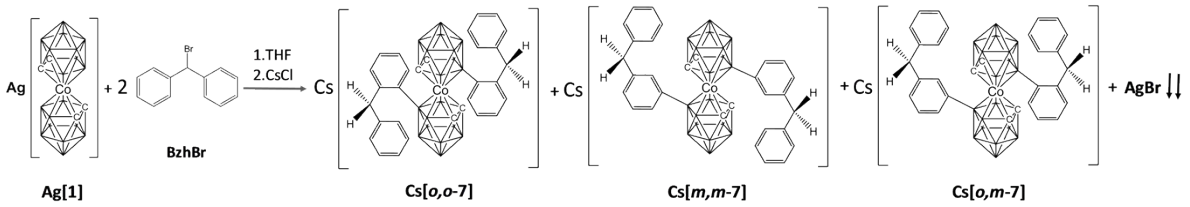


Figure S35. MALDI-TOF spectrum of Cs[**6**].

2.5. Synthesis and characterization of Cs[7] via carbocation generation in situ.



Scheme S7. Reaction conditions for the synthesis of Cs[***o,o*-7**], Cs[***m,m*-7**] and Cs[***o,m*-7**].

A solution of 114.6 mg (0.46 mmol) of benzhydryl bromide in 2 mL of THF was added drop by drop in a solution of 100 mg (0.23 mmol) of Ag[**1**] in 2 mL of THF. The precipitation of AgBr is instantaneous, but the reaction remained with constant agitation for 10 minutes. The solution was filtered and extracted with a saturated solution of 10mL of NaCl in HCl 0.1 M 3 times. The organic fraction was dried over $MgSO_4$ and the solvent was removed under reduced pressure. Further purification was performed by silica column chromatography using a mixture of CH_2Cl_2-MeCN 7:3 as eluent. The third yellow fraction with Rf=0.5 was the desired compound [**7**]$^-$. Finally, the product was precipitated like cesium salt by dissolving the compound in the minimal amount of water and adding a saturated solution of CsCl in water until full precipitation. The compounds were filtered and dried obtaining 160mg (87 % yield) for the isomeric mixture Cs[***o,o-, m,m-*** and ***o,m*-7**]. **^{1}H NMR (600 MHz, CD_3COCD_3), δ:** 7.28-7.22 (m, 8H, H_{Ar} (isomers)), 7.19-7.15 (m, 12H, H_{Ar} (isomers)), 7.09 (t, 2H, $^3J_{H-H}$ 7.6, H_{Ar} (o,o-isomer)), 7.04 (d, 1H, $^3J_{H-H}$ 8, H_{Ar} (m,m-isomer)), 6.95 (d, 1H, $^3J_{H-H}$ 7.6, H_{Ar} (o,o-isomer)), 3.92 and 3.89 (s, 4H, H_2-C_{sp3} (isomers)), 3.85 and 3.83 (s, 4H, C_C-H (isomers)). **^{11}B NMR (128.38 MHz, CD_3COCD_3), δ:** 10.9 (s, 2B, B-C_{Ar}), 1.9 (d, 2B, $^1J_{B-H}$ 146.4, B-H), -5.3 (d, 8B, $^1J_{B-H}$ 137.0, B-H), -19.1 (d, 4B, $^1J_{B-H}$ 151.04, B-H), -22.8 (br, 2B, B-H). **^{13}C NMR (100 MHz, CD_3COCD_3), δ:** 143.10, 142.88 (**C_{AR}**- C_{sp3} (o- and m-isomers)), 140.39, 139.02 (**C_{Ar}**-$B_{Cluster}$ (o- and m-isomers)), 133.57, 132.89, 130.68, 129.57, 129.38, 129.15, 129.08, 128.78, 128.10, 127.09, 126.57, 126.51 (**C_{Ar}**–H (o- and m-isomers)) 54.72, 54.64 ($C_{Cluster}$), 42.55 and 42.18 (HC_{sp3} (o- and m-isomers)). **MALDI-TOF:** Theor. 655.44 m/z Found, 656.26. **Elemental analysis:** Found: C, 54.83; H, 6.6. Calc. for Cs[3,3'-Co-8-$CH_2(C_6H_5)_2$-1,2-$C_2B_9H_{10}$-1',2'- $C_2B_9H_{11}$]: C, 54.91; H, 6.45 %.

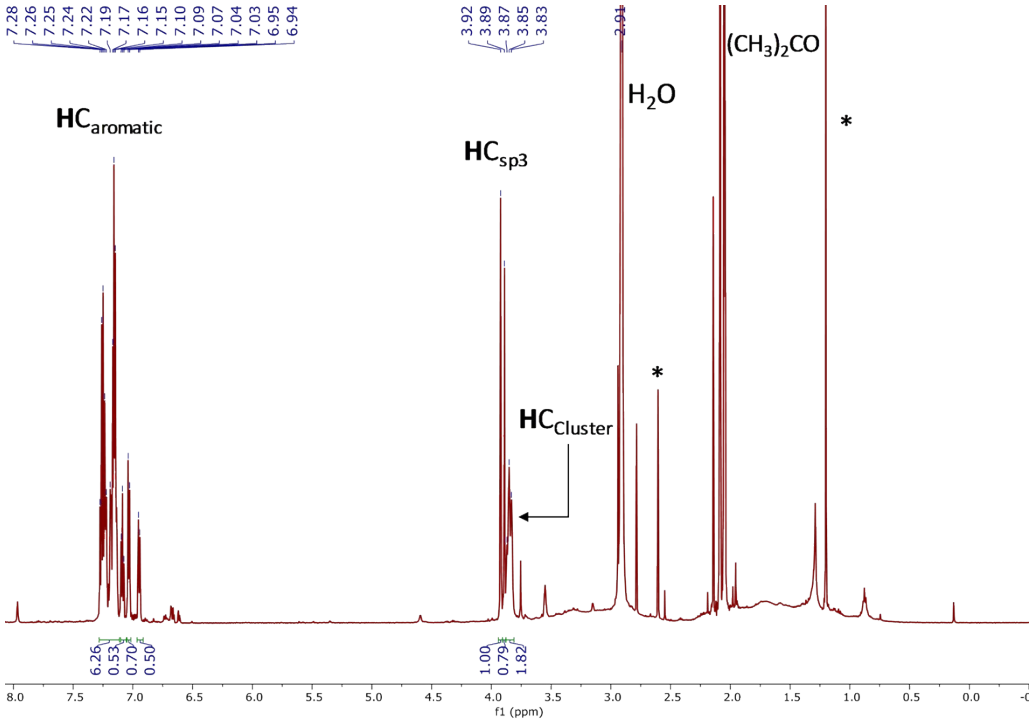


Figure S36. ^{1}H-NMR spectrum of Cs[**7**]. *Unidentified solvents.

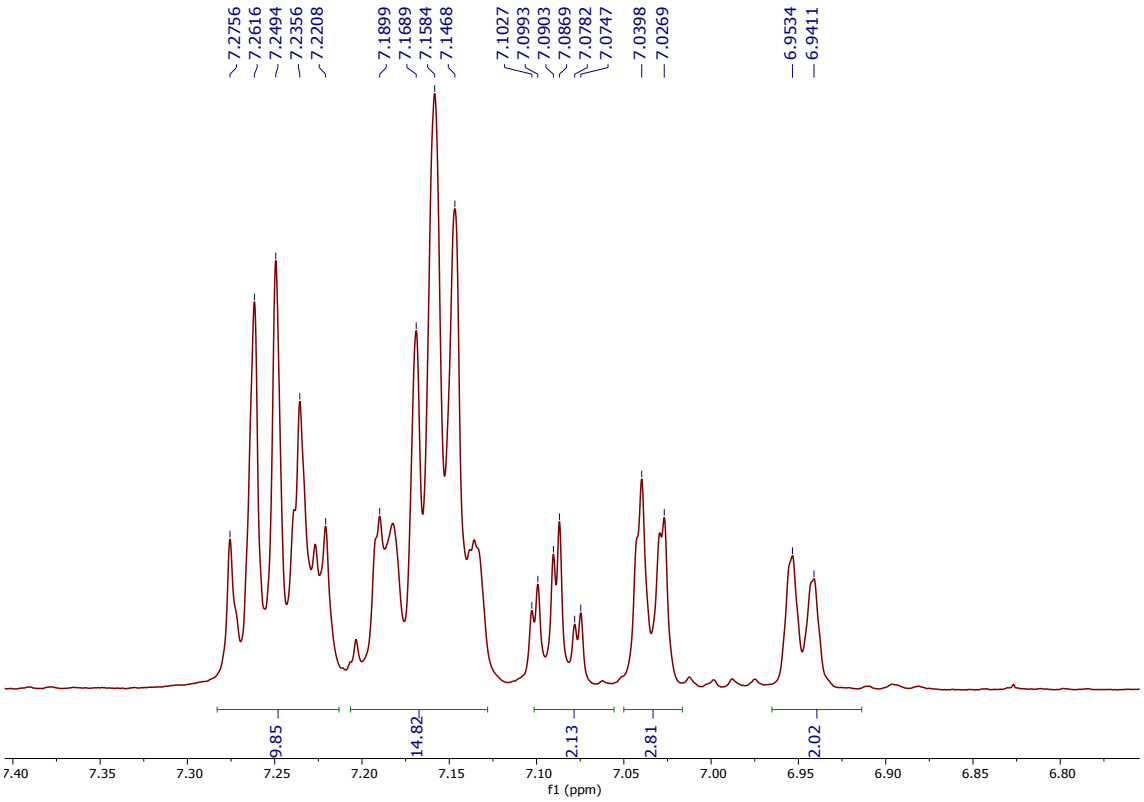


Figure S37. ^{1}H-NMR amplified spectrum of Cs[**7**].

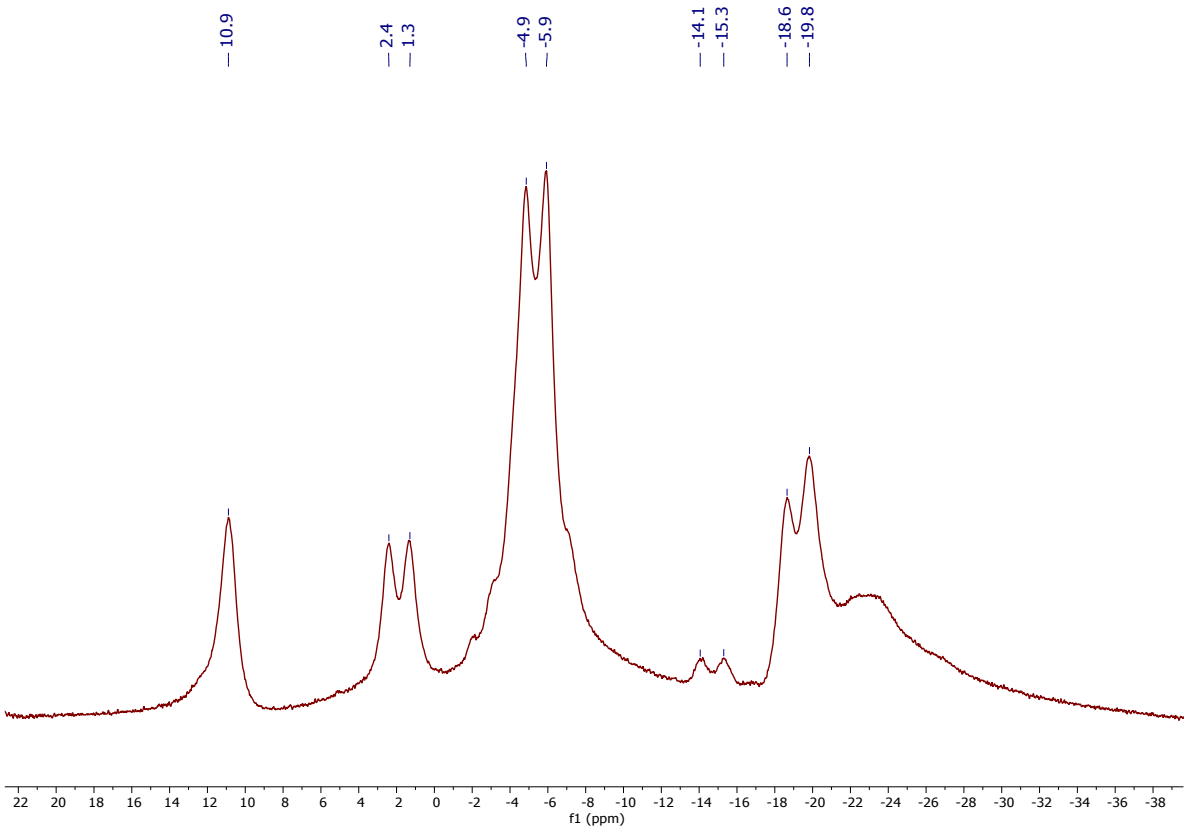


Figure S38. ^{11}B-NMR of Cs[**7**].

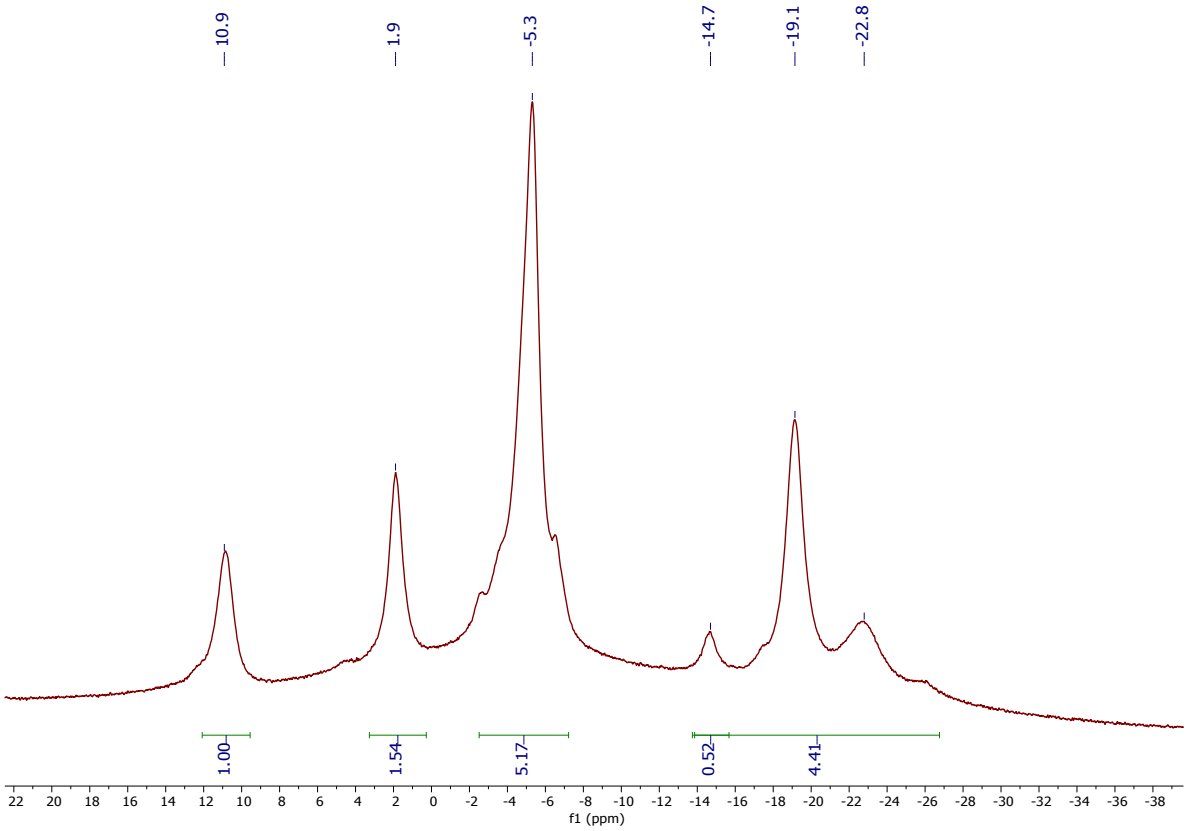


Figure S39. ^{11}B{^{1}H}-NMR of Cs[**7**].

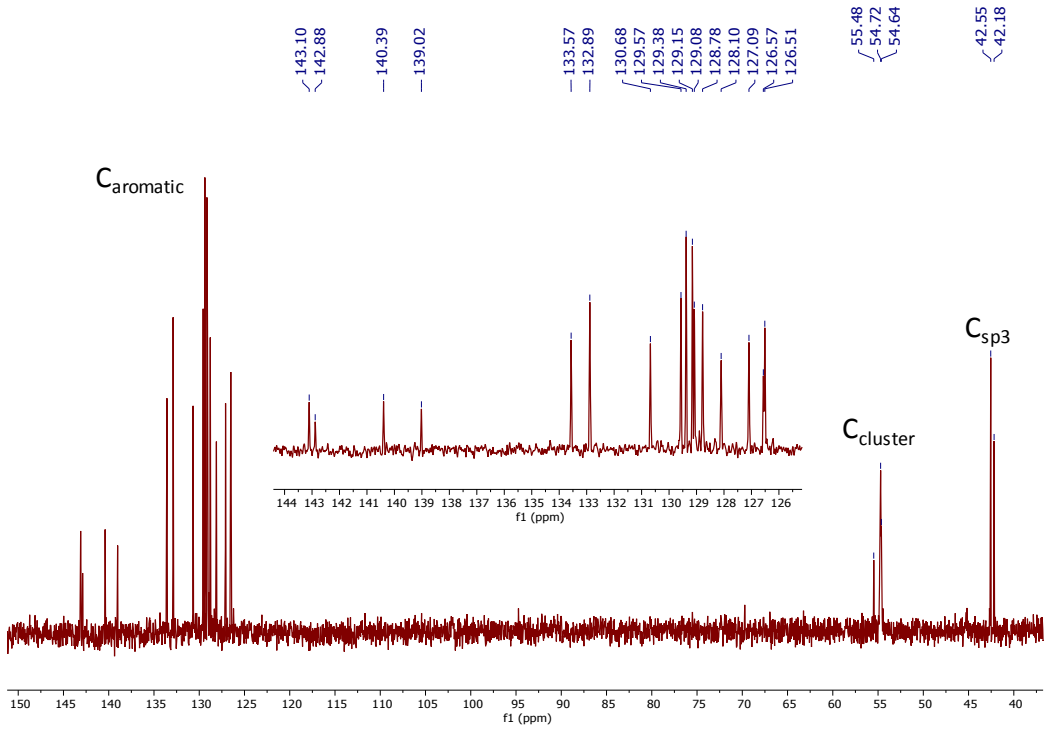


Figure S40. $^{13}C\{^{1}H\}$ NMR of Cs[**7**].

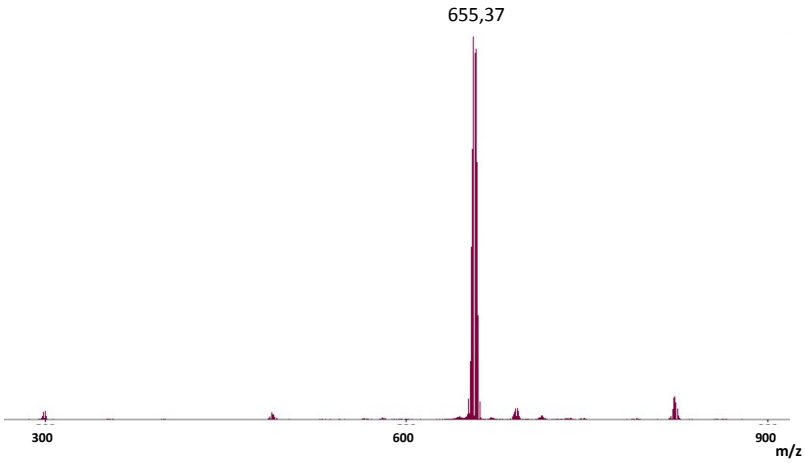
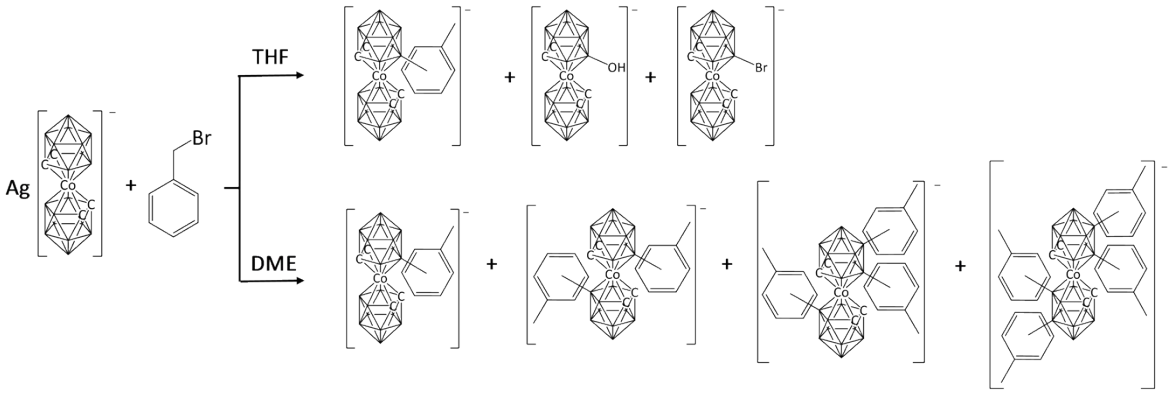


Figure S41. MALDI-TOF spectrum of Cs[**7**].

2.6. Analysis of the crude of reaction with the benzyl cation.

A solution of 0.0275mL (0.23 mmol) of benzylbromide in 1 mL of THF or DME was added drop by drop in a solution of 100mg (0.23 mmol) of Ag[**1**] in 2 mL of THF or DME. The precipitation of AgBr is instantaneous, but the reaction remained with constant agitation for 10 minutes. The solution was filtered and the reaction crude analysed.

The outcome of the reaction is compromise by the polymerization of the THF.



Scheme S8. Drawing of the possible products and subproducts for the reaction of silver salt of cobaltabisdicarbollide and bromobenzyl in THF or DME.

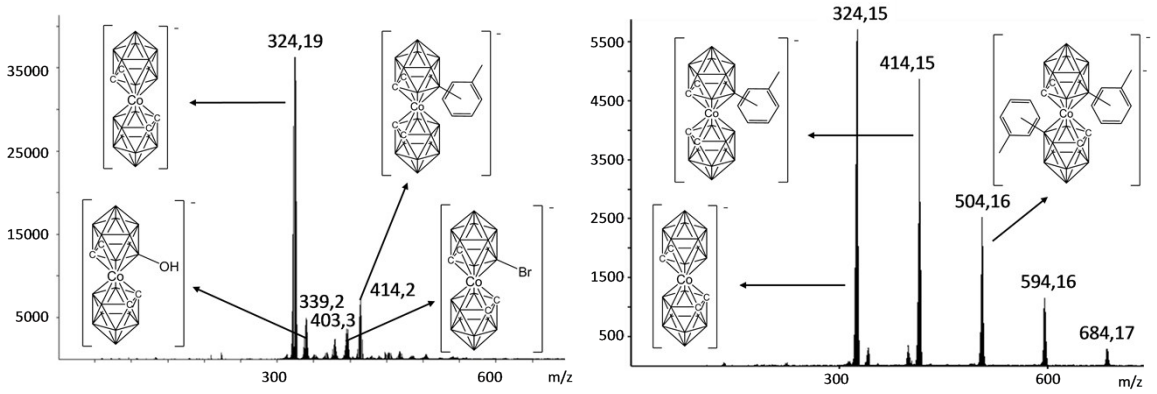


Figure S42. MALDI-TOF spectra of the crude of the reaction between bromobenzyl and the silver salt of cobaltabisdicarbollide in THF at left and in DME at right.

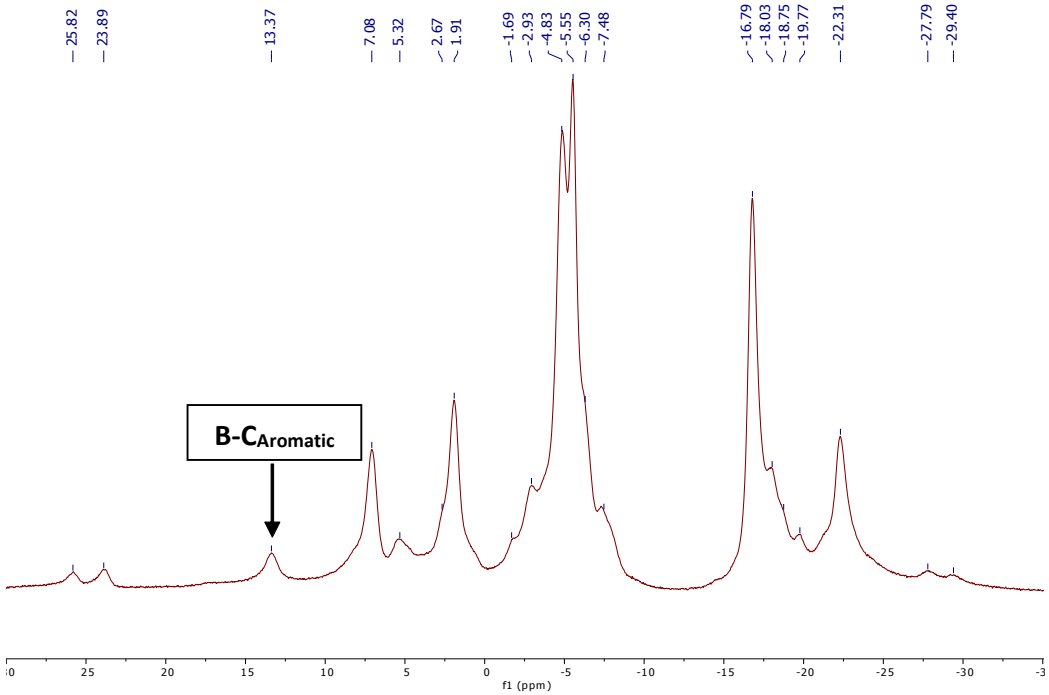


Figure S43. $^{11}B\{^{1}H\}$-NMR of the crude of the reaction between bromobenzyl and the silver salt of cobaltabisdicarbollide in DME.

There are four different possible compounds for the reaction depending on which carbocation has reacted with the cobaltabisdicarbollide; those four compounds are shown in Figure S44, being the base on the bibliography.[1a, 3] The ^{11}BNMR shows a peak at 13.59 ppm corresponding to B-$C_{Aromatic}$ as consequence, the product should be one or mixture of compound b), c) and d) (See Figure S44). Unfortunately, the big number of reaction products makes not possible to isolate a pure compound to obtain a ^{1}H NMR and get more information about the isomeric ratios.

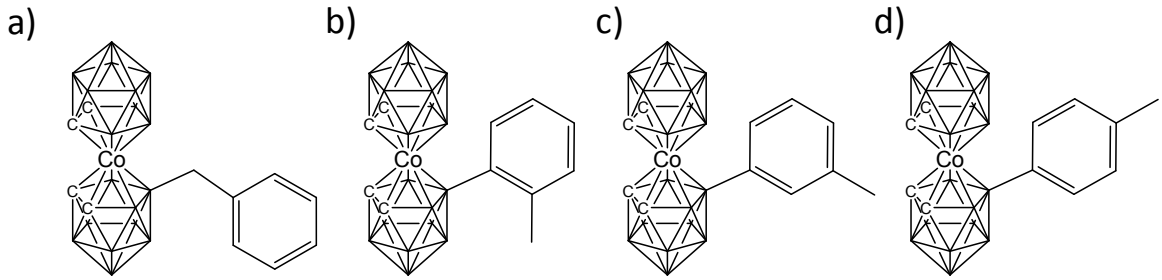


Figure S44. Drawing of the three possible isomers for the reaction of the silver salt of cobaltabisdicarbollide and bromobenzyl.

2.7. Relation between the peak intensity on MALDI nd the quantity of samples

Heights of MALDI peaks for the different species:

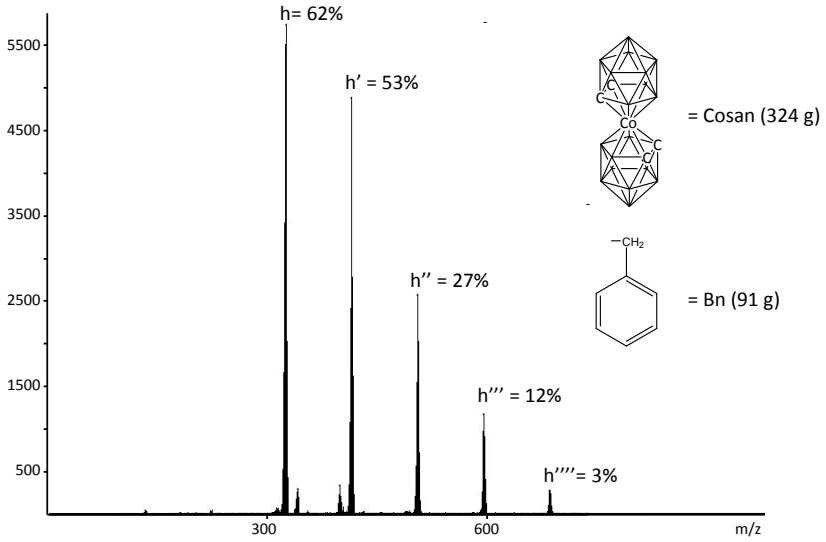


Figure S45. Heights of MALDI-TOF peaks for the different products of the reaction between silver cobaltabisdicarbollide and benzyl bromide in DME.

To demonstrate the relation between the peak height and the amount of every cobaltabisdicarbollide derivative we start from the next premise:

$$h + h^{'} + h^{''} + h^{'''} + h^{''''} = X$$

$$X \rightarrow 100$$

[h] = mol of $[Co(C_2B_9H_{11})_2]^-$

The result of the addition of different peaks heights is:

$$62+53+27+12+3=157$$

Then: $157 \rightarrow 100\%$

Relation Cosan:Bn(1:1) $\rightarrow$ [Cosan] = [Bn]

$[Cosan]^- + [Bn] = 0.62[Cosan]+0.53[CosanBn]+0.27[CosanBn_2]+0.12[CosanBn_3]+0.03[CosanBn_4]$

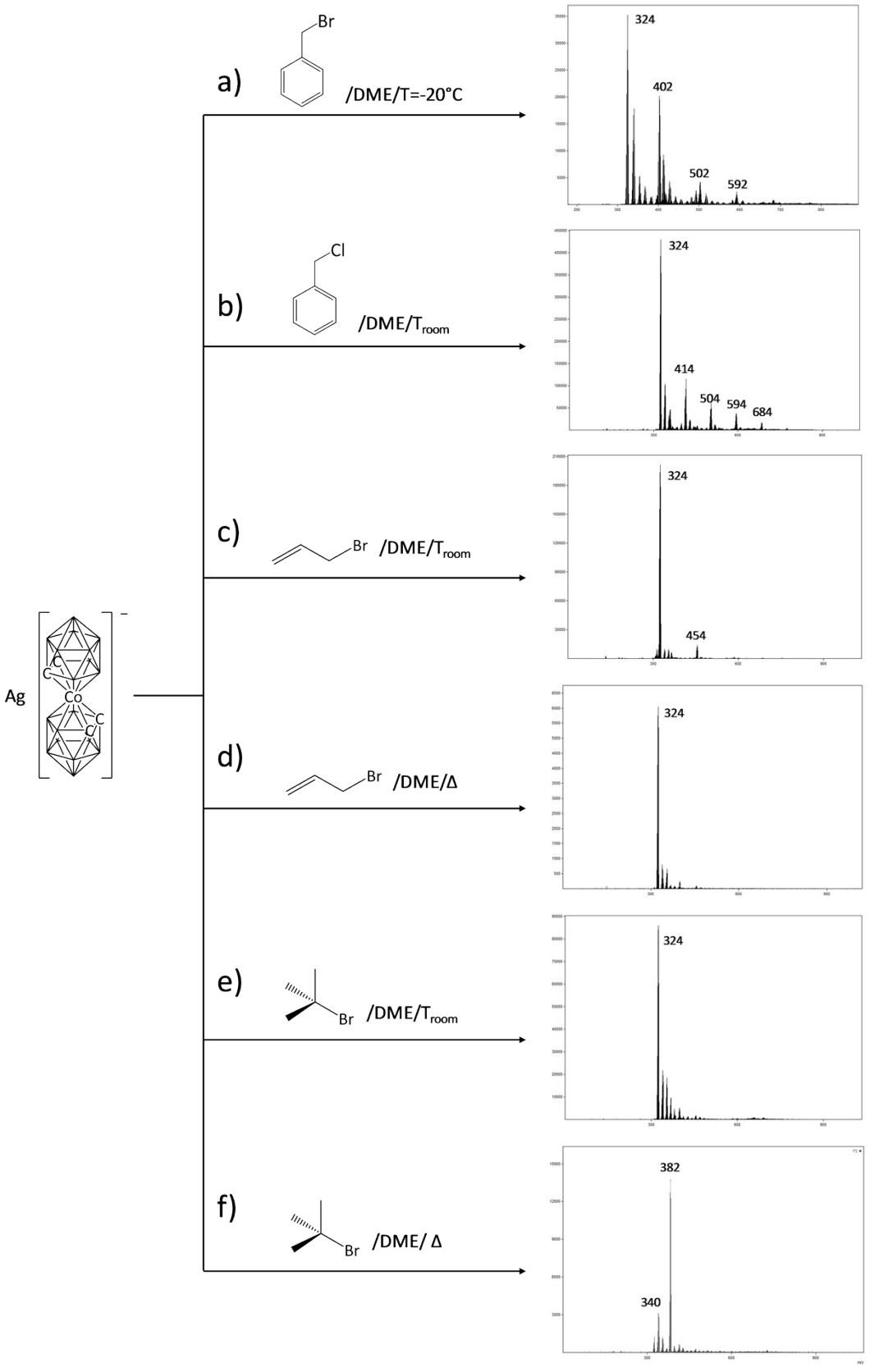
$[Cosan]^- + [Bn] = [Cosan]\cdot(0.62+0.53+0.27+0.12+0.03)+[Bn]\cdot(0.53+0.54+0.36+0.12)$

$[Cosan]^- + [Bn] = = 1.57[Cosan] + 1.55[B]$

$[Cosan]-1.57[Cosan] = 1.55[Bn]-[Bn]$

$[Bn] = - 0.57[Cosan]/0.55 \rightarrow [Bn]=-1.03[Cosan]$

2.8. Tests with different type of electrophiles



Scheme S9. Very preliminary studies with different carbocations.

In the Scheme S9 it is possible to observed the preliminary studies taken a place with different electrolytes to demonstrated the importance of use electrolytes able to generate stable carbocations with high number of resonance positions or delocalised resonance

In the reactions a) and b) the goal was to try increase the reaction time to avoid the subproducts formation and increase the yield of the reaction. However, as the MALDI-TOF spectra shows the reactions are so fast that it was not possible due to the low number of resonance positions. The reaction c) and d) was taking a place with a known stable carbocation but as only have two resonance position the reaction did not work, it is possible see the only major peak at 324m/z corresponding to cobaltabisdicarbollide anion. For the reactions with 2-bromo-2-methylpropane the result is different depending the reaction temperature. If the reaction is taking a place at room temperature (reaction e)) the reaction did not work but if the reaction is at refluxing temperature (reaction f)) the carbocation was stabilized by hyperconjugation but the reaction is so fast that the carbocation react with the solvent because it is the “major” compound.

3. Computational details.

All calculations were carried out with the Gaussian 09 program package[4] at ωB97XD/6-31+G* level of theory as it was implemented in G09. Full geometry optimization calculations were performed and harmonic vibrational frequencies were calculated to establish the nature of the stationary points obtained, as characterized by none negative eigenvalue of the Hessian for minima structures. For the visualization of the molecules and orbitals the MOLDEN[5] and VMD program[6] were used.

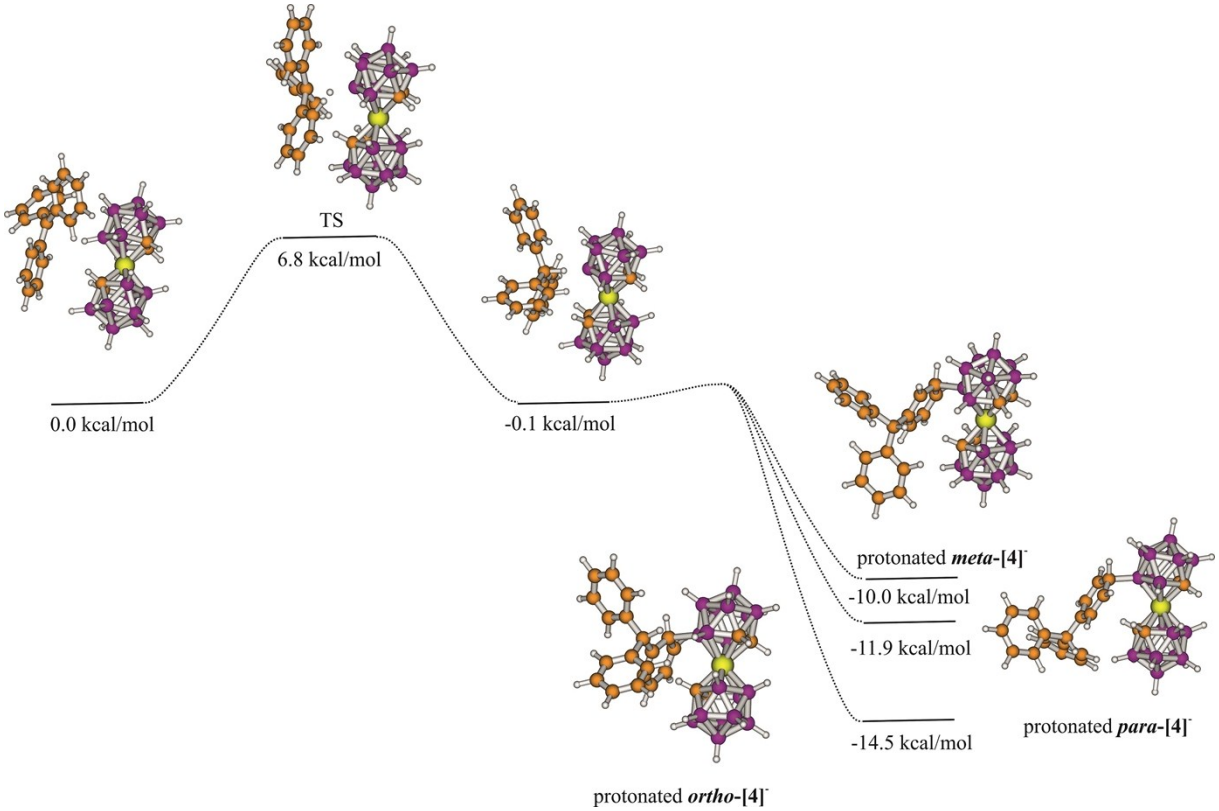


Figure S46. Calculated mechanism of the hydride transfer and the electrophilic attack.

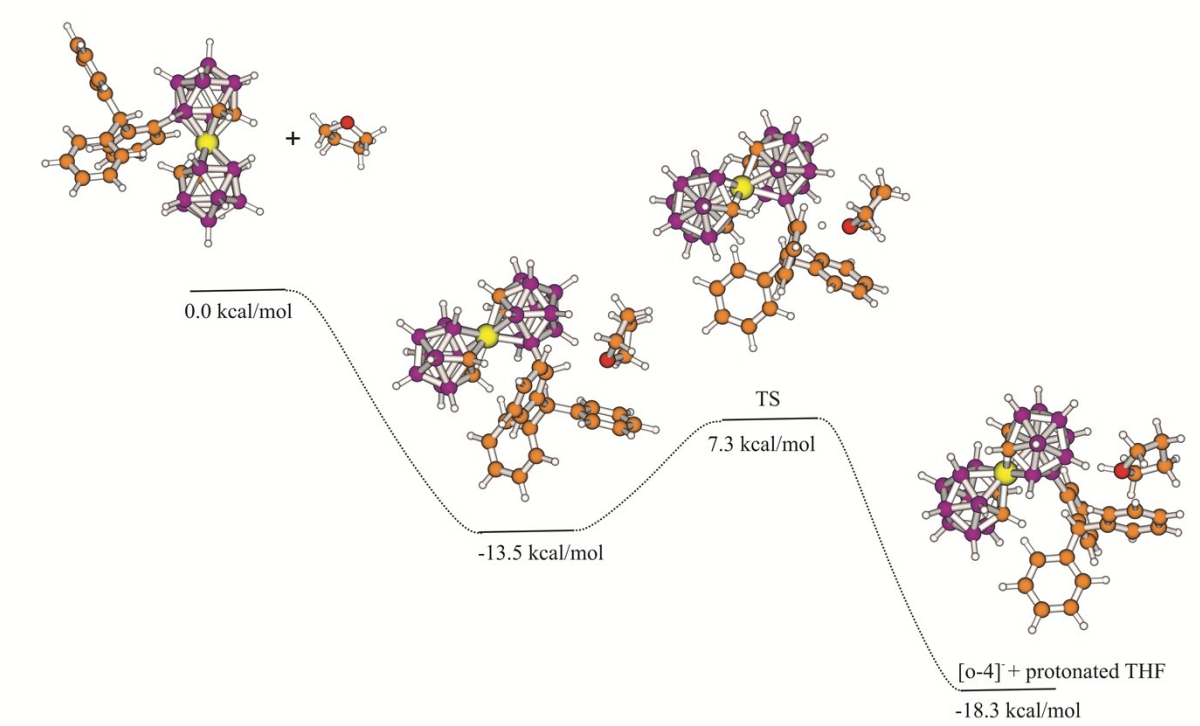


Figure S47. Deprotonation step in the presence of one THF molecule and the formation of $[o\text{-}4]^-$.

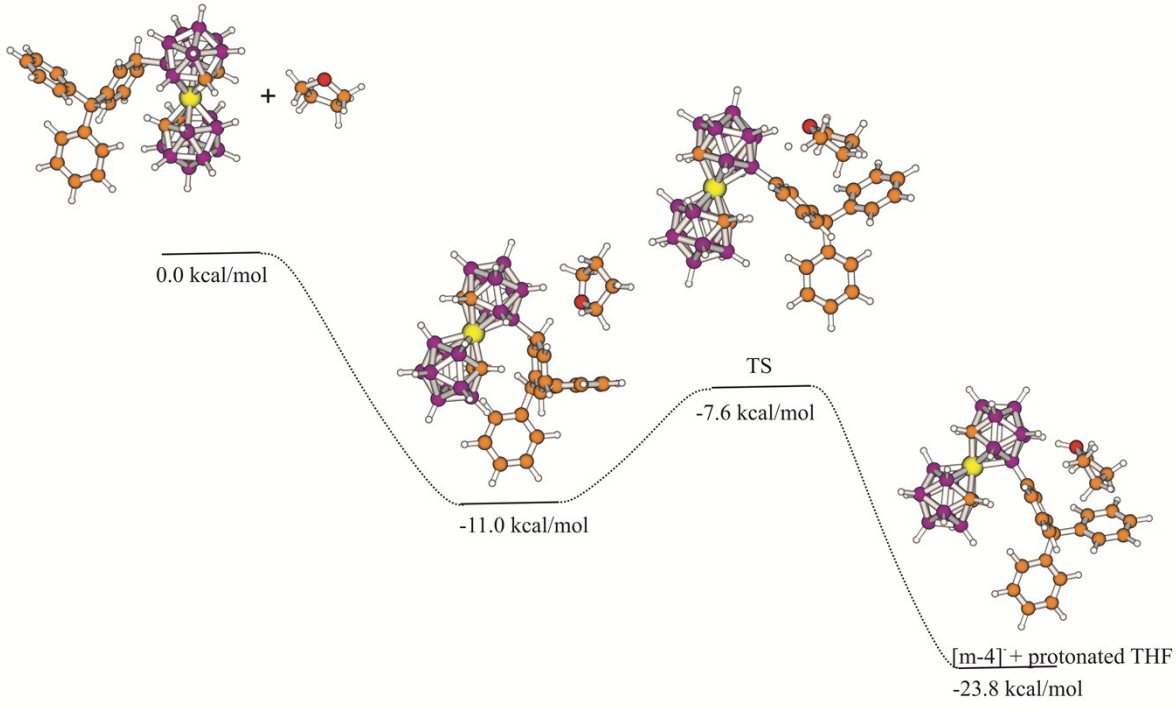


Figure S48. Deprotonation step in the presence of one THF molecule and the formation of $[m\text{-}4]^-$.

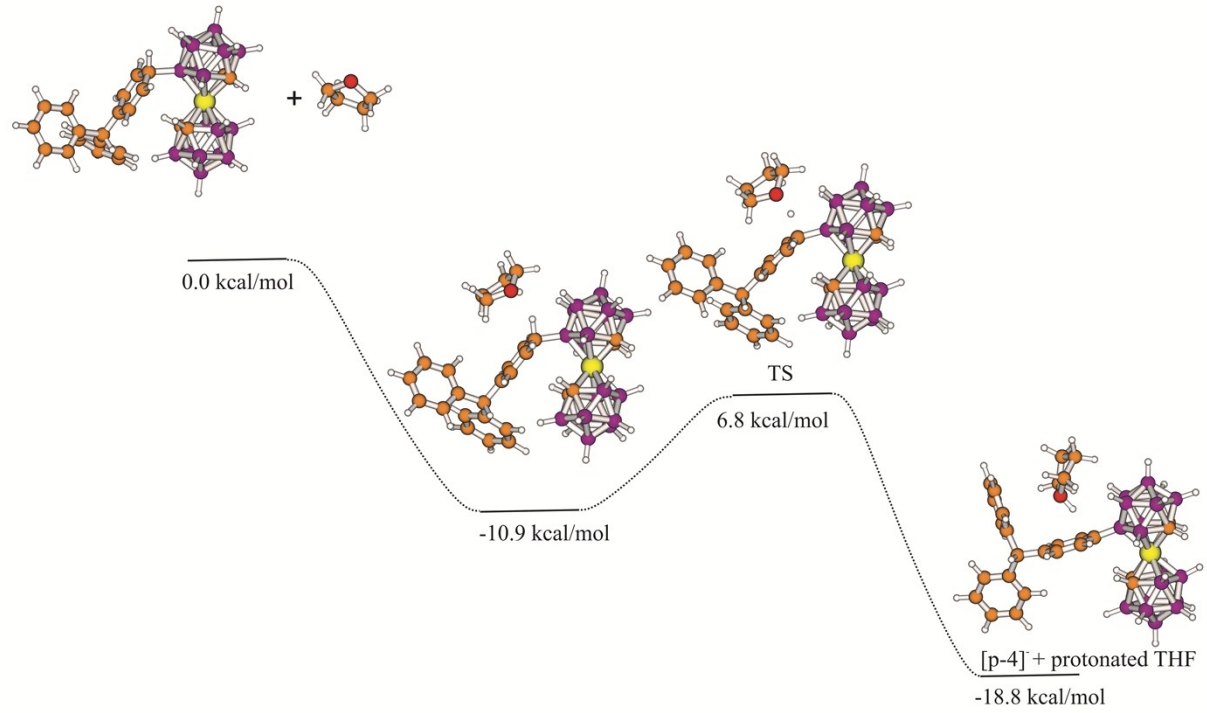


Figure S49. Deprotonation step in the presence of one THF molecule and the formation of $[p\text{-}4]^-$.

3.1. XYZ coordinates and total energies of the investigated systems

Starting complex of trityl cation and $[COSAN]^-$

E(ωB97XD/6-31+G*)= -2728.639943

C	1.496828	2.547968	-0.948244
C	2.164878	2.145951	0.229743
C	2.119106	2.983191	1.363729
C	1.434571	4.188662	1.314062
C	0.768121	4.562966	0.147645
C	0.797278	3.741310	-0.981189
C	2.857578	0.875576	0.270264
C	2.883195	0.097114	1.480160
C	3.978305	-0.749670	1.772010
C	3.973384	-1.526663	2.916144
C	2.869311	-1.497281	3.772786
C	1.778268	-0.675079	3.497698
C	1.786943	0.126875	2.369690
C	3.513361	0.383398	-0.921169
C	4.136366	1.274542	-1.823986
C	4.748512	0.789781	-2.967260
C	4.713089	-0.579318	-3.249867
C	4.082735	-1.466658	-2.379748
C	3.501413	-0.996779	-1.211465
B	-0.850926	-1.603238	1.099152
Co	-2.216593	-0.661121	-0.190822

C	-2.048524	1.203665	0.541925
C	-2.269720	1.153813	-1.056089
B	-2.630210	2.621690	-0.237717
B	-3.667813	2.004185	-1.517694
B	-4.370743	2.587067	0.004918
B	-4.752915	1.163159	1.000871
B	-3.240287	0.314593	1.368426
B	-3.274854	2.092573	1.311833
B	-0.115913	-1.069127	-0.426823
B	-1.169882	-1.635013	-1.739021
B	0.314466	-2.524737	-1.350436
B	-0.120407	-3.958015	-0.390681
B	-1.870456	-3.962900	-0.192829
B	-1.170023	-3.415534	-1.716076
C	-2.397218	-2.517024	-0.961224
C	-2.215922	-2.498132	0.639964
B	-0.846995	-3.381915	1.122712
B	0.514157	-2.503249	0.411462
B	-4.316824	-0.303002	0.088619
B	-4.997726	1.107316	-0.760161
B	-3.632516	0.226296	-1.471611
H	5.172818	-0.952381	-4.160385
H	-1.034233	1.341722	0.897484
H	-4.961356	-1.306306	0.208792
H	-1.393681	1.249107	-1.686800
H	-3.007904	-0.164884	2.433643
H	-3.686307	-0.322416	-2.526772
H	-6.076540	1.074881	-1.269251
H	-5.650213	1.173050	1.787829
H	-3.658697	2.569116	-2.566132
H	-2.986411	2.720677	2.282735
H	-1.883541	3.534851	-0.367293
H	-4.973442	3.615136	0.058454
H	-1.357004	-1.130579	-2.801831
H	-3.107194	-2.588882	1.248688
H	0.562159	-0.083949	-0.522040
H	-0.808961	-1.083390	2.170007
H	1.583706	-2.513573	0.954997
H	-0.878574	-3.959026	2.163567
H	1.231757	-2.544876	-2.118758
H	-2.642600	-4.858387	-0.093761
H	-1.431241	-4.018882	-2.707517
H	0.474363	-4.990972	-0.444674
H	-3.402402	-2.620286	-1.351508
H	2.653371	2.697327	2.264279

H	1.413142	4.835183	2.185354
H	0.207442	5.492329	0.121127
H	0.246473	4.021951	-1.872731
H	1.477187	1.879127	-1.802616
H	4.840197	-0.758055	1.112744
H	4.822101	-2.163694	3.142748
H	2.856110	-2.131508	4.654273
H	0.904008	-0.688293	4.139596
H	0.907548	0.708373	2.119640
H	2.964925	-1.678054	-0.560224
H	4.021063	-2.523379	-2.617667
H	5.249342	1.473559	-3.645104
H	4.168799	2.335655	-1.596889

TS of the hydride abstraction

E(ωB97XD/6-31+G*)= -2728.6290935

C	1.023676	-1.011735	-2.353328
C	1.503981	-1.582787	-1.158876
C	1.198480	-2.923516	-0.873305
C	0.448227	-3.676748	-1.768576
C	-0.023351	-3.099196	-2.944871
C	0.264326	-1.763880	-3.234980
C	2.261830	-0.770670	-0.195890
C	2.482676	-1.319521	1.173098
C	3.762587	-1.806851	1.474248
C	4.002412	-2.435101	2.692457
C	2.981985	-2.553634	3.632988
C	1.716055	-2.043009	3.350404
C	1.468004	-1.438576	2.124906
C	3.251342	0.205108	-0.651218
C	3.767217	0.201280	-1.960244
C	4.731701	1.126496	-2.334190
C	5.185346	2.074295	-1.417564
C	4.693493	2.081113	-0.112610
C	3.747609	1.145755	0.271812
B	0.150437	1.168884	0.254033
B	0.767175	2.616163	-0.527114
B	-0.621921	3.566886	-1.061069
B	-0.674749	1.788559	-1.170770
C	-1.971396	2.677639	-0.535376
B	-1.521256	4.067870	0.370615
B	-0.721332	3.395585	1.792922
B	0.237544	4.017689	0.429377
B	0.707340	2.510634	1.246617

B	-0.768854	1.615383	1.690352
C	-2.028096	2.583372	1.071592
Co	-1.979465	0.778002	0.170107
C	-2.184621	-1.046358	1.010680
B	-3.635459	-1.798502	1.471876
B	-4.389462	-2.296784	-0.054504
B	-3.266468	-1.867272	-1.359901
B	-2.651203	-2.473425	0.175120
C	-1.975124	-1.084948	-0.584621
B	-3.092098	-0.097452	-1.393006
B	-4.107216	0.582107	-0.089659
B	-4.889975	-0.783869	0.741608
B	-3.456005	-0.027569	1.455863
B	-4.663184	-0.828497	-1.022226
H	-2.995458	2.687044	1.547015
H	0.941784	0.193459	0.191233
H	-0.711879	1.355308	-2.276810
H	-0.882693	1.038407	2.727082
H	-2.903915	2.835154	-1.062272
H	-2.274784	4.983053	0.399726
H	-0.889103	3.925454	2.843769
H	-0.719021	4.215886	-2.052362
H	1.676627	2.443698	1.941888
H	1.784452	2.615714	-1.155292
H	0.858055	5.031736	0.511295
H	-2.832687	0.376152	-2.452969
H	-3.447644	0.505970	2.520619
H	-0.982901	-1.294144	-0.951367
H	-1.330463	-1.237361	1.643541
H	-1.955222	-3.429855	0.288264
H	-3.660888	-2.371937	2.514231
H	-3.034579	-2.493591	-2.346159
H	-5.959601	-0.666896	1.256414
H	-5.564732	-0.748203	-1.799219
H	-5.077062	-3.268207	-0.120629
H	-4.673986	1.632671	-0.182062
H	3.448894	-0.552081	-2.671407
H	5.134995	1.105288	-3.341663
H	5.928468	2.806070	-1.720223
H	5.038809	2.821865	0.601039
H	3.346298	1.164082	1.278363
H	4.561350	-1.715245	0.744300
H	4.992857	-2.824347	2.907452
H	3.174968	-3.029964	4.589393
H	0.921877	-2.103242	4.087929

H	0.500181	-1.000035	1.920097
H	1.553001	-3.376572	0.046371
H	0.212348	-4.709987	-1.536116
H	-0.639412	-3.680262	-3.623793
H	-0.140344	-1.298984	-4.128014
H	1.180260	0.044742	-2.542432

Van der Waals complex of triphenylmethane and netural **[COSAN]**

E(ωB97XD/6-31+G*)= -2728.640086

C	-3.248764	-2.194656	1.289278
C	-2.212752	-1.255871	1.217626
C	-1.416135	-1.043984	2.338415
C	-1.623981	-1.775465	3.507476
C	-2.638172	-2.724495	3.564768
C	-3.453935	-2.928268	2.450988
C	-2.018983	-0.493978	-0.082876
C	-1.442313	-1.307517	-1.226118
C	-1.108153	-2.655693	-1.081510
C	-0.531605	-3.359338	-2.137980
C	-0.269290	-2.723001	-3.346482
C	-0.594230	-1.374742	-3.499284
C	-1.178765	-0.677355	-2.450153
C	-3.259830	0.321292	-0.410358
C	-3.745239	1.217349	0.548541
C	-4.895122	1.959001	0.312974
C	-5.600505	1.794181	-0.878728
C	-5.148972	0.877306	-1.821340
C	-3.984550	0.146084	-1.591360
B	-0.049863	1.335785	0.184287
B	-0.599121	2.696797	1.107903
B	0.880868	3.503164	1.640463
B	0.819659	1.722636	1.638771
C	2.140080	2.563015	0.987281
B	1.746986	4.046864	0.207956
B	0.843329	3.547635	-1.222120
B	0.786313	1.768973	-1.273561
B	-0.626881	2.721045	-0.680071
B	-0.014167	4.123870	0.228056
Co	1.965600	0.707152	0.146669
C	1.893189	-1.192648	0.810396
B	3.196636	-2.081605	1.442057
B	4.189855	-2.495674	0.030793
B	4.715540	-0.975554	-0.727499
B	3.348324	-1.880397	-1.405232

B	2.430849	-2.567901	-0.068521
C	1.985079	-1.075328	-0.796295
B	3.280255	-0.108095	-1.290807
B	4.080132	0.383059	0.229899
B	4.620421	-1.100652	1.047333
B	3.126682	-0.311072	1.578458
C	2.120938	2.590527	-0.621160
H	3.074561	2.660436	-1.129065
H	-1.167913	0.288917	0.171508
H	0.853327	1.205274	2.705110
H	0.819226	1.277940	-2.350876
H	3.104752	2.615434	1.475611
H	2.557563	4.910713	0.211984
H	1.001254	4.141607	-2.238056
H	1.054900	4.063228	2.672500
H	-1.640091	2.725216	-1.307894
H	-1.576718	2.705755	1.783574
H	-0.566301	5.177664	0.255722
H	2.973035	0.131762	2.670659
H	3.222340	0.488894	-2.319002
H	0.917882	-1.379061	1.242866
H	1.069469	-1.166242	-1.361766
H	1.680712	-3.479611	-0.166700
H	3.259233	-2.395543	-2.473130
H	3.003309	-2.744543	2.410603
H	5.749204	-0.883367	-1.314463
H	5.582756	-1.104025	1.750416
H	4.823188	-3.503516	-0.006235
H	4.701495	1.400552	0.329864
H	-3.658358	-0.571391	-2.335724
H	-5.699941	0.725294	-2.745035
H	-6.502743	2.369628	-1.063754
H	-5.243859	2.661462	1.063650
H	-3.219488	1.329706	1.491143
H	-1.276133	-3.161206	-0.136835
H	-0.266384	-4.403053	-2.001332
H	0.198423	-3.267318	-4.160965
H	-0.379879	-0.861806	-4.432068
H	-1.411957	0.375836	-2.573895
H	-3.893772	-2.349180	0.427896
H	-4.255821	-3.659641	2.488774
H	-2.801478	-3.295330	4.474107
H	-0.991379	-1.593271	4.370894
H	-0.639946	-0.287410	2.321297

Protonated [p-4]$^-$

E(ωB97XD/6-31+G*)= -2728.658880

C	-0.260945	-2.057354	-1.111105
C	0.279188	-2.341481	0.184935
C	-0.431444	-1.829505	1.315248
C	-1.522951	-1.001893	1.161113
C	-2.009786	-0.715014	-0.125057
C	-1.360319	-1.247997	-1.258073
C	-3.250817	0.133625	-0.342702
C	-3.584865	1.014556	0.855307
C	-2.835966	2.178487	1.052747
C	-3.054454	2.985358	2.164596
C	-4.034796	2.640078	3.093827
C	-4.793121	1.488641	2.898143
C	-4.570676	0.679592	1.784186
B	1.966168	-1.744449	0.328872
B	2.559618	-0.765392	1.671344
B	2.755513	-2.540279	1.695144
B	3.106603	-3.071051	0.038809
B	4.646394	-2.370763	-0.442715
C	4.397624	-0.696831	-0.360684
B	5.265738	-1.435278	0.923415
B	4.418230	-2.944507	1.225540
B	4.081770	-1.515661	2.232166
C	4.078068	-0.213391	1.145673
Co	2.639082	0.266232	-0.184856
C	1.334292	0.852781	-1.593928
B	1.482383	2.186051	-2.635469
B	0.213253	2.136817	-1.414609
C	0.930720	1.314135	-0.090140
B	0.780823	3.002268	0.012594
B	2.411179	3.604399	-0.322259
B	1.179003	3.599807	-1.608321
B	2.848594	3.096288	-1.970298
B	2.902161	1.325953	-1.997672
B	3.489398	2.210655	-0.565646
B	2.195826	2.146722	0.664289
C	-4.409897	-0.742280	-0.808189
C	-5.311145	-0.238334	-1.748617
C	-6.409000	-0.992897	-2.153686
C	-6.618085	-2.264401	-1.622955
C	-5.722316	-2.776145	-0.687334
C	-4.624245	-2.019624	-0.284490
B	3.118892	-1.628501	-1.005101

H	-3.934573	-2.431044	0.448775
H	4.527686	0.711531	1.483971
H	5.000820	-3.890094	1.654052
H	1.928419	-0.185361	2.496978
H	4.650558	2.284236	-0.285175
H	0.861205	-0.027223	-2.004302
H	0.200426	0.729832	0.451905
H	3.532064	0.693315	-2.784419
H	2.304448	2.134102	1.848730
H	2.801881	4.616478	0.172195
H	3.560369	3.738195	-2.679267
H	-0.025345	3.449080	0.765610
H	1.170301	2.039593	-3.773981
H	-0.929666	1.906416	-1.653144
H	0.675015	4.586875	-2.045808
H	5.047611	-0.074536	-0.962825
H	2.915283	-1.683630	-2.177211
H	2.721307	-4.117922	-0.392860
H	5.419862	-2.791336	-1.240528
H	2.119766	-3.207862	2.458050
H	6.404651	-1.141298	1.068654
H	4.450468	-1.328529	3.345931
H	0.231954	-2.485565	-1.980023
H	-1.753314	-1.022578	-2.245543
H	-2.020037	-0.580681	2.028477
H	-0.072220	-2.083818	2.307896
H	-5.157381	0.756557	-2.160173
H	-7.101337	-0.587141	-2.885563
H	-7.473840	-2.853694	-1.938816
H	-5.876427	-3.766058	-0.267730
H	-5.175291	-0.211057	1.639464
H	-5.564795	1.216671	3.612577
H	-4.209820	3.268301	3.962243
H	-2.459270	3.883657	2.300247
H	-2.071350	2.457134	0.332617
H	0.652056	-3.361586	0.302595
H	-3.004809	0.804742	-1.175798

Protonated [p-4]+THF

E(ωB97XD/6-31+G*)= -2961.062588

C	5.314837	-0.880082	-1.897174
C	4.430273	-0.322255	-0.972026
C	4.678652	0.968996	-0.497281
C	5.789498	1.685312	-0.934657

C	6.667458	1.119962	-1.856891
C	6.427182	-0.165669	-2.336627
C	3.240195	-1.140553	-0.479552
C	3.492365	-1.914496	0.810390
C	2.565531	-2.895340	1.182195
C	2.710014	-3.594354	2.374894
C	3.793689	-3.327444	3.212147
C	4.726898	-2.363551	2.842916
C	4.577355	-1.658657	1.647633
C	2.020334	-0.242020	-0.387796
C	1.586939	0.280758	0.843680
C	0.512356	1.139856	0.882882
C	-0.227122	1.472999	-0.295614
C	0.271271	0.958240	-1.534707
C	1.355044	0.113451	-1.576025
B	-1.930307	1.293616	-0.036095
B	-3.145216	1.089847	-1.303097
Co	-2.867453	-0.671689	-0.159634
B	-2.568231	-2.400473	1.010439
B	-3.918064	-2.553920	-0.147746
B	-3.319094	-2.010280	-1.735750
B	-3.431903	-3.743352	-1.381143
B	-1.800991	-4.338945	-0.981215
B	-2.964677	-3.983208	0.318852
B	-1.268750	-3.497153	0.486477
C	-1.265271	-1.852408	0.074701
B	-0.692654	-2.972980	-1.094632
B	-2.019795	-3.113463	-2.244576
C	-1.695488	-1.635561	-1.473676
B	-2.570011	2.408455	1.175703
B	-2.600810	0.652441	1.472178
C	-4.192009	0.211968	1.080264
B	-3.993511	1.678125	1.910821
B	-4.185067	2.935506	0.666677
B	-5.225134	1.518062	0.655852
C	-4.500762	0.455822	-0.483383
B	-4.544915	2.107926	-0.865296
B	-2.911419	2.682102	-0.543355
O	0.346723	4.343607	-0.581454
C	-0.103255	5.256638	0.414737
C	0.693196	4.882767	1.665018
C	2.041961	4.396730	1.090588
C	1.751327	4.192714	-0.412812
H	4.005357	1.422530	0.226148
H	-4.737987	-0.574487	1.586057

H	-4.634863	4.008027	0.924900
H	-2.013021	0.156644	2.381111
H	-5.066022	-2.453090	0.176215
H	-1.161217	-0.898756	-2.055763
H	-0.454385	-1.258079	0.472378
H	-3.920083	-1.470634	-2.610181
H	-2.617315	-2.166981	2.175565
H	-3.422204	-4.845103	1.004208
H	-4.233586	-4.428989	-1.936761
H	-0.467810	-3.877316	1.281813
H	-1.750477	-3.211680	-3.399331
H	0.454551	-2.901459	-1.405310
H	-1.414398	-5.436327	-1.238930
H	-5.243773	-0.176025	-0.953852
H	-2.980291	0.901179	-2.467880
H	-2.420642	3.578719	-1.161097
H	-5.292996	2.475168	-1.712351
H	-1.833612	3.106865	1.808885
H	-6.385992	1.401364	0.865557
H	-4.338972	1.744472	3.046001
H	-0.233150	1.257278	-2.450347
H	1.714669	-0.281825	-2.521984
H	2.106764	0.003461	1.755061
H	0.188587	1.567897	1.827521
H	5.136558	-1.885348	-2.271840
H	7.105323	-0.614393	-3.056577
H	7.533149	1.678075	-2.200839
H	5.968164	2.686448	-0.552741
H	5.315564	-0.912025	1.370945
H	5.578274	-2.154826	3.484528
H	3.910002	-3.870929	4.145163
H	1.974813	-4.345719	2.647558
H	1.717158	-3.111223	0.536995
H	-0.385345	2.576165	-0.377439
H	3.014867	-1.878824	-1.260096
H	2.020673	3.196876	-0.781867
H	2.272289	4.937534	-1.029135
H	2.832498	5.138778	1.235753
H	2.371556	3.469323	1.568976
H	0.803672	5.721853	2.356945
H	0.181415	4.075120	2.197459
H	0.109973	6.286610	0.092135
H	-1.182362	5.125937	0.514781

TS of proton abstraction with THF

E(ωB97XD/6-31+G*)= -2961.055979

C	1.843316	3.717144	-0.430589
O	0.401943	3.787428	-0.520555
C	-0.006098	4.847021	0.379100
C	0.885072	4.661818	1.601351
C	2.193434	4.070297	1.023741
C	-0.281831	1.248482	-0.199180
C	0.507568	0.914281	0.938992
C	1.682881	0.195713	0.835779
C	2.137764	-0.234141	-0.419313
C	1.424746	0.134051	-1.567553
C	0.246384	0.850018	-1.459331
C	3.403594	-1.061370	-0.563632
C	3.612521	-1.989053	0.630874
C	2.639143	-2.965634	0.877827
C	2.751737	-3.824469	1.963783
C	3.848714	-3.723914	2.820725
C	4.823826	-2.761764	2.578751
C	4.706906	-1.896230	1.488764
B	-1.904739	1.356278	0.018061
B	-2.809942	2.794425	-0.484267
B	-4.473689	2.328877	-0.828573
C	-4.538956	0.672857	-0.462065
B	-5.209377	1.770849	0.676998
B	-4.080215	3.119066	0.714713
B	-3.987430	1.841336	1.948111
C	-4.263588	0.397328	1.101178
B	-2.656360	0.738859	1.511589
B	-2.508944	2.484256	1.239146
C	4.591039	-0.167010	-0.897658
C	5.509708	-0.581575	-1.863999
C	6.614125	0.204899	-2.183418
C	6.814089	1.423175	-1.538402
C	5.905618	1.845004	-0.569547
C	4.802908	1.055312	-0.252794
B	-3.136301	1.229392	-1.255364
Co	-2.980691	-0.556420	-0.130708
C	-1.865054	-1.571808	-1.459537
B	-2.273651	-3.024773	-2.239846
B	-0.930403	-2.965293	-1.102381
C	-1.434605	-1.822195	0.079264
B	-1.517187	-3.468236	0.480710
B	-3.238955	-3.863643	0.325956
B	-2.109067	-4.270117	-0.987656

B	-3.708701	-3.586413	-1.367853
B	-3.508992	-1.859377	-1.711479
B	-4.121687	-2.382769	-0.121126
B	-2.754891	-2.308541	1.024985
H	4.106302	1.393199	0.510704
H	-4.862776	-0.357740	1.594290
H	-4.465506	4.216519	0.976518
H	-2.112480	0.198476	2.422636
H	-5.261143	-2.228360	0.213252
H	-1.294909	-0.861330	-2.040532
H	-0.586970	-1.274355	0.469459
H	-4.088722	-1.283018	-2.577547
H	-2.781467	-2.084145	2.192702
H	-3.735602	-4.706478	1.008404
H	-4.550747	-4.225376	-1.920258
H	-0.724716	-3.891416	1.263427
H	-2.020717	-3.127938	-3.398138
H	0.214282	-2.952378	-1.426838
H	-1.786025	-5.385486	-1.257187
H	-5.314517	0.093834	-0.947981
H	-2.972800	1.040857	-2.421330
H	-2.282758	3.670542	-1.103484
H	-5.186554	2.752163	-1.680319
H	-1.747634	3.120483	1.910008
H	-6.377994	1.728086	0.872639
H	-4.343044	1.921144	3.079606
H	-0.304570	1.128167	-2.355435
H	1.791347	-0.172223	-2.544112
H	2.234512	-0.082108	1.729383
H	0.146594	1.217115	1.919018
H	5.362445	-1.533931	-2.368010
H	7.317536	-0.134448	-2.938150
H	7.672582	2.039673	-1.788284
H	6.056283	2.791200	-0.056908
H	5.478457	-1.152866	1.309803
H	5.683920	-2.680250	3.237482
H	3.941215	-4.395567	3.669215
H	1.982474	-4.570967	2.138587
H	1.778002	-3.051762	0.218373
H	-0.089479	2.560259	-0.297862
H	3.243869	-1.706826	-1.436921
H	2.138056	2.713350	-0.740878
H	2.242043	4.440704	-1.147692
H	3.017127	4.788098	1.057069
H	2.501159	3.181096	1.580158

H	1.045222	5.604811	2.129430
H	0.413616	3.961587	2.296806
H	0.182322	5.792372	-0.141497
H	-1.072230	4.728852	0.556657

[p-4]$^-$ + protonated THF

E(ωB97XD/6-31+G*)= -2961.075238

C	4.883273	-1.201724	1.166288
C	4.649478	-0.101296	0.337186
C	5.078700	-0.168033	-0.991554
C	5.718097	-1.306724	-1.478615
C	5.940880	-2.400867	-0.643272
C	5.522558	-2.342637	0.685538
C	3.845865	1.084358	0.876505
C	4.265722	2.440058	0.314572
C	3.333145	3.420703	-0.028666
C	3.749211	4.673543	-0.479866
C	5.104707	4.965941	-0.589299
C	6.044909	3.998937	-0.235007
C	5.627373	2.750579	0.214287
C	2.376804	0.732674	0.695128
C	1.820118	0.611772	-0.583445
C	0.547151	0.086505	-0.758446
C	-0.235016	-0.353668	0.330278
C	0.312657	-0.157120	1.610743
C	1.589621	0.381208	1.789909
B	-1.635849	-1.068757	0.104331
B	-2.882113	-1.267977	1.360506
Co	-3.386515	0.194196	-0.075533
B	-3.925839	1.623950	-1.523332
B	-5.167372	1.376538	-0.265950
B	-4.339806	1.454788	1.312822
B	-5.232242	2.862368	0.712679
B	-4.063692	4.030872	0.052406
B	-4.977195	2.967877	-1.044639
B	-3.249506	3.256854	-1.321137
C	-2.487100	1.892158	-0.661950
B	-2.449278	3.349363	0.248088
B	-3.661283	3.089665	1.502081
C	-2.718295	1.797096	0.935179
B	-1.641948	-2.554559	-0.874445
B	-2.478295	-1.110871	-1.464015
C	-4.104313	-1.399052	-1.084831
B	-3.210688	-2.723896	-1.659973

B	-2.839136	-3.684834	-0.212805
B	-4.426260	-2.944211	-0.399850
C	-4.333586	-1.488076	0.510922
B	-3.616317	-2.879735	1.167239
B	-1.892412	-2.651672	0.875659
O	1.872907	-2.466551	0.391774
C	1.686555	-3.675298	1.224151
C	1.311695	-4.736992	0.214136
C	2.173552	-4.366604	-1.004226
C	2.193236	-2.842743	-1.014357
H	4.925553	0.683271	-1.649342
H	-4.932672	-1.058555	-1.694061
H	-2.713508	-4.871190	-0.263164
H	-2.163694	-0.563274	-2.474548
H	-6.154957	0.722837	-0.448884
H	-1.878362	1.490741	1.547182
H	-1.503481	1.649405	-1.043310
H	-4.615905	0.881021	2.318593
H	-3.892246	1.172064	-2.624523
H	-5.796762	3.397199	-1.798146
H	-6.239131	3.216069	1.246333
H	-2.730506	3.794672	-2.247653
H	-3.439288	3.510366	2.592993
H	-1.391211	3.858409	0.431369
H	-4.215520	5.212297	0.102937
H	-5.304493	-1.203598	0.897658
H	-2.867912	-0.835324	2.470600
H	-1.083746	-3.108084	1.633936
H	-4.133834	-3.411769	2.096295
H	-0.646736	-2.947203	-1.417559
H	-5.492159	-3.432189	-0.579455
H	-3.437927	-3.146179	-2.748203
H	-0.266946	-0.456627	2.481845
H	1.988886	0.490455	2.796133
H	2.403288	0.903186	-1.453571
H	0.149295	-0.022787	-1.765586
H	4.555307	-1.164801	2.203264
H	5.711050	-3.178904	1.354116
H	6.450062	-3.283140	-1.020708
H	6.051371	-1.334504	-2.512388
H	6.370623	2.005443	0.487325
H	7.106737	4.216355	-0.309203
H	5.428473	5.940200	-0.943904
H	3.005640	5.419995	-0.743542
H	2.269815	3.218665	0.059224

H	4.031214	1.124522	1.958148
H	1.409880	-2.395611	-1.624237
H	3.162010	-2.386745	-1.214188
H	3.189476	-4.758666	-0.894166
H	1.751263	-4.753509	-1.934193
H	1.529791	-5.739744	0.588787
H	0.244969	-4.669825	-0.017838
H	2.658026	-3.835743	1.694977
H	0.925437	-3.425875	1.961291
H	1.099626	-1.831233	0.448508

protonated [o-4]$^{-}$

E(ωB97XD/6-31+G*)=-2728.223763

C	-2.142397	1.068564	2.269692
C	-1.588441	0.277994	1.254437
C	-0.489037	-0.565759	1.533948
C	-0.060114	-0.611640	2.875325
C	-0.627471	0.157802	3.883643
C	-1.670942	1.025362	3.574848
C	-2.261280	0.301494	-0.117256
C	-2.504891	1.719362	-0.623925
C	-1.492288	2.376309	-1.329662
C	-1.652125	3.691360	-1.758410
C	-2.840911	4.370768	-1.501022
C	-3.868117	3.718649	-0.820840
C	-3.700768	2.404592	-0.389512
B	0.357136	-1.430474	0.477418
B	0.490518	-3.192203	0.757426
B	-0.410306	-2.587660	-0.647750
B	0.616119	-2.796403	-2.073947
C	1.986716	-1.844608	-1.753600
B	2.125141	-3.549115	-1.565494
B	0.612679	-4.033322	-0.803847
B	2.062181	-3.773020	0.181818
C	2.801688	-2.398161	-0.485575
B	1.929488	-2.175983	0.949322
Co	2.191475	-0.484576	-0.273425
C	1.645859	1.419831	0.081008
B	2.336185	2.811571	-0.605241
B	2.463317	2.513101	1.127758
C	2.586236	0.802231	1.231571
B	4.004833	1.715088	1.436364
B	4.857603	1.542685	-0.106872
B	3.893529	3.003013	0.222218

B	3.819981	2.227183	-1.377324
B	2.341957	1.251443	-1.458689
B	3.911717	0.461492	-1.160265
B	4.010737	0.150035	0.592176
C	-3.517231	-0.566201	-0.182373
C	-4.040335	-1.246477	0.916237
C	-5.172018	-2.053445	0.784188
C	-5.795517	-2.196266	-0.450542
C	-5.274515	-1.527290	-1.559388
C	-4.149365	-0.723650	-1.422589
B	0.491965	-1.201993	-1.299212
H	-2.118338	1.655347	4.339573
H	3.883121	-2.390117	-0.539933
H	0.174195	-5.126538	-0.999880
H	2.516616	-2.065775	1.981313
H	4.472378	-0.218714	-1.974933
H	0.582457	1.443744	0.283926
H	2.097431	0.436469	2.125740
H	1.661847	1.198874	-2.435874
H	4.568220	-0.742196	1.154108
H	6.051853	1.578035	-0.153631
H	4.253268	2.764588	-2.353622
H	4.472796	1.798109	2.529107
H	1.606633	3.679394	-0.972301
H	1.819757	3.075921	1.951925

protonated [o-4]$^-$ + THF

E(ωB97XD/6-31+G*)= -2961.070888

C	-1.379560	4.259694	-0.131596
C	-0.762593	3.104211	-0.618354
C	0.428314	3.228516	-1.338768
C	1.007787	4.478144	-1.545364
C	0.395712	5.622890	-1.041490
C	-0.803503	5.510587	-0.339670
C	-1.326078	1.716476	-0.335435
C	-2.851409	1.686870	-0.372619
C	-3.640682	1.686221	0.776416
C	-5.031345	1.718968	0.680091
C	-5.646355	1.753694	-0.566886
C	-4.863529	1.747180	-1.721960
C	-3.477288	1.711245	-1.622848
C	-0.782431	1.109020	0.945556
C	-0.901474	-0.313855	1.147574
C	-0.579363	-0.839421	2.441729
C	-0.036739	-0.049792	3.431152

C	0.153740	1.310843	3.164266
C	-0.208482	1.884043	1.943660
B	0.092133	-1.294841	0.022244
B	1.130802	-2.634513	0.542775
B	0.775994	-4.026337	-0.516579
B	-0.461423	-3.538610	-1.697253
B	0.242275	-2.239526	-2.682816
B	1.230124	-3.610387	-2.170233
C	2.088969	-2.995697	-0.813114
C	1.788186	-1.990508	-2.029667
B	0.598325	-0.851827	-1.620755
B	-0.861088	-1.839139	-1.370534
B	-0.527237	-2.950038	-0.028166
Co	2.244436	-1.045258	-0.304704
C	2.530070	0.877863	0.191552
B	3.876571	1.840589	-0.180698
B	3.505011	1.426005	1.492923
C	2.852115	-0.157470	1.390818
B	4.451953	0.007004	1.937192
B	5.430988	-0.460358	0.535483
B	5.158044	1.261409	0.900246
B	5.074042	0.681658	-0.782044
B	3.368803	0.491886	-1.221862
B	4.339990	-0.940741	-0.786144
B	3.946591	-1.351766	0.907322
O	-3.695969	-1.597049	1.074446
C	-4.495300	-1.683093	-0.099333
C	-4.339015	-3.128233	-0.566736
C	-4.196564	-3.905209	0.758856
C	-3.902964	-2.803317	1.799889
H	0.587505	1.948237	3.930370
H	3.079484	-3.428025	-0.747871
H	-1.245940	-4.317815	-2.142282
H	1.485576	-2.904635	1.646883
H	4.682321	-1.761934	-1.587100
H	1.576375	1.382414	0.202497
H	2.094722	-0.320323	2.143360
H	2.922268	0.786454	-2.286206
H	3.928507	-2.425336	1.420358

TS of H+ abstraction with THF

E(ωB97XD/6-31+G*)= -2961.061005

C	0.138989	3.216354	-1.145378
C	-1.092955	2.941235	-0.547134
C	-1.900126	4.013806	-0.156335

C	-1.470017	5.327049	-0.330693
C	-0.229082	5.588929	-0.908189
C	0.572099	4.527943	-1.320706
C	-1.505606	1.482439	-0.340060
C	-2.997166	1.282769	-0.586362
C	-3.965189	1.390259	0.412803
C	-5.319285	1.258974	0.107226
C	-5.721676	1.006246	-1.201402
C	-4.760480	0.890623	-2.205409
C	-3.411121	1.032163	-1.898462
C	-1.045724	0.926075	1.000751
C	-0.583295	-0.444448	1.117827
C	-0.242219	-0.878828	2.448586
C	-0.377312	-0.087902	3.564926
C	-0.811682	1.229810	3.398561
C	-1.134006	1.721552	2.137631
B	0.203797	-1.289719	-0.075233
B	0.672754	-0.730991	-1.704215
B	0.459126	-2.083332	-2.842637
B	-0.093319	-3.501890	-1.931272
B	1.197921	-3.919023	-0.786865
B	1.594132	-3.361840	-2.412478
C	2.387929	-2.734928	-1.022770
C	1.973238	-1.699041	-2.173111
Co	2.323853	-0.820340	-0.379468
B	1.400252	-2.560750	0.343805
B	-0.208508	-3.014685	-0.230475
B	-0.672549	-1.876428	-1.506304
B	4.082526	-1.037566	0.769775
C	2.847148	-0.081568	1.419887
C	2.347428	1.040817	0.375986
B	3.539768	2.222824	0.118186
B	3.281070	1.551818	1.727678
B	4.424539	0.231948	1.967838
B	5.420171	0.092551	0.507803
B	4.920983	1.696366	1.098407
B	4.870593	1.334139	-0.642737
B	3.197249	0.962736	-1.089295
B	4.369668	-0.361708	-0.857083
O	-2.994893	-1.633352	1.260512
C	-2.982582	-2.740300	2.176362
C	-3.588376	-3.940800	1.426010
C	-3.823617	-3.420808	-0.003869
C	-3.918837	-1.919739	0.194635
H	-0.899329	1.883763	4.262735

H	3.420474	-3.058058	-0.980703
H	-0.793105	-4.333225	-2.422785
H	1.805886	-2.865096	1.422617
H	4.803453	-1.017320	-1.760494
H	1.331641	1.399988	0.474807
H	2.140237	-0.437357	2.157497
H	2.697317	1.332522	-2.105273
H	4.227699	-2.160182	1.139363
H	6.551801	-0.278444	0.572824
H	5.601020	1.871529	-1.417723
H	4.698871	-0.074931	3.084320
H	3.185280	3.340159	-0.083869
H	2.709079	2.114786	2.604088
H	5.672907	2.483014	1.584532
H	2.743398	-1.365816	-2.857283
H	0.534512	0.330418	-2.219296
H	-1.796020	-1.535897	-1.716916
H	0.266719	-1.854505	-3.993244
H	-0.976256	-3.528533	0.521225
H	2.238623	-3.979030	-3.193038
H	1.530687	-5.011827	-0.458062
H	-1.450214	2.755423	2.040821
H	-0.120742	-0.467487	4.549479
H	0.125372	-1.893997	2.557561
H	-1.601953	-0.997693	1.015065
H	0.769490	2.402902	-1.490334
H	1.538425	4.711864	-1.780669
H	0.106158	6.613059	-1.043946
H	-2.111957	6.147197	-0.021157
H	-2.881507	3.828941	0.272750
H	-2.663715	0.940245	-2.682761
H	-5.060899	0.690775	-3.229915
H	-6.776249	0.897905	-1.437984
H	-6.059854	1.346586	0.897434
H	-3.671449	1.564081	1.443440
H	-0.995387	0.905577	-1.107743
H	-1.944583	-2.907197	2.477310
H	-3.563132	-2.457247	3.060017

[o-4]$^{-}$

E(ωB97XD/6-31+G*)= -2961.078573

C	-3.264883	-1.786060	2.019431
O	-2.966913	-1.662417	0.582225
C	-3.797703	-2.576439	-0.242115
C	-4.665743	-3.279832	0.791008

C	-4.685260	-2.310330	1.982770
C	-0.351444	-0.284725	1.176793
C	-1.055283	0.933298	0.999773
C	-1.412951	1.696241	2.120253
C	-1.163185	1.266417	3.417681
C	-0.537112	0.038973	3.613286
C	-0.140869	-0.703296	2.507405
C	-1.475679	1.437630	-0.382940
C	-2.938534	1.143486	-0.714529
C	-3.976578	1.205348	0.218541
C	-5.295034	0.943631	-0.152453
C	-5.602409	0.615248	-1.471521
C	-4.576878	0.554584	-2.414271
C	-3.262465	0.816589	-2.035444
B	0.321481	-1.205240	0.031796
Co	2.457385	-0.866966	-0.322109
B	4.232093	-1.105350	0.791668
B	4.498203	-0.478977	-0.858970
B	3.354064	0.872508	-1.094624
B	5.048132	1.206938	-0.699866
B	5.155821	1.610464	1.028855
B	5.594294	-0.020875	0.467535
B	4.641292	0.182510	1.948195
C	3.041904	-0.097192	1.449790
B	3.530814	1.529981	1.706864
B	3.760815	2.149741	0.073187
C	2.545401	1.010223	0.395282
C	-1.120697	2.906976	-0.607336
C	-2.013439	3.949004	-0.346240
C	-1.627710	5.277163	-0.519228
C	-0.343300	5.583038	-0.962455
C	0.548528	4.550511	-1.244991
C	0.158515	3.225584	-1.074005
B	1.453288	-2.534374	0.479610
B	-0.181212	-2.925113	-0.065498
B	-0.584828	-1.815521	-1.387244
B	0.807921	-0.751502	-1.636723
C	2.049378	-1.806153	-2.073539
C	2.414697	-2.814408	-0.881348
B	1.581591	-3.457878	-2.242153
B	0.516375	-2.138346	-2.720171
B	-0.105682	-3.487131	-1.747393
B	1.167984	-3.928676	-0.593731
H	-1.446441	1.888309	4.262331
H	3.428887	-3.190228	-0.828192

H	-0.861105	-4.294438	-2.198491
H	1.856345	-2.825564	1.561646
H	4.891060	-1.170836	-1.754425
H	1.537185	1.385298	0.518563
H	2.335790	-0.412098	2.207006
H	2.838906	1.236789	-2.104458
H	4.352653	-2.223297	1.185358

protonated [m-4]$^-$ + THF

E(ωB97XD/6-31+G*)= -2961.059825

C	-4.275810	1.990479	-0.083179
C	-4.107207	0.978650	0.862794
C	-4.911413	0.989729	2.006921
C	-5.863784	1.984418	2.199636
C	-6.028399	2.989101	1.246076
C	-5.231831	2.988777	0.105674
C	-3.118364	-0.167405	0.680087
C	-3.779154	-1.466026	0.230214
C	-3.127546	-2.672399	0.496550
C	-3.636043	-3.878508	0.027301
C	-4.819531	-3.893115	-0.709604
C	-5.485472	-2.697044	-0.966660
C	-4.968173	-1.488573	-0.500393
C	-1.960745	0.210616	-0.236045
C	-1.931735	-0.143029	-1.593007
C	-0.899086	0.251638	-2.453854
C	0.151831	0.989787	-1.954043
C	0.206953	1.326597	-0.567605
C	-0.902268	0.959845	0.249347
B	1.730776	0.855729	0.174216
Co	2.393361	-1.228401	0.261666
B	3.015402	-2.600212	-1.221230
B	3.217945	-3.210498	0.442528
B	1.682917	-2.919258	1.305997
B	2.049295	-4.532160	0.670281
B	1.143601	-4.757406	-0.846631
B	2.873463	-4.335650	-0.893845
B	1.736214	-3.555992	-2.007662
C	1.416418	-2.056522	-1.281895
B	0.221442	-3.282155	-1.144227
B	0.415595	-3.873635	0.505202
C	0.661570	-2.234209	0.141955
B	1.869182	0.143272	1.787583
C	3.439738	-0.513033	1.828525

C	4.190520	-0.331315	0.413270
B	3.204024	0.467778	-0.722941
B	2.990844	2.084795	-0.011295
B	4.555964	1.293818	0.103725
B	4.712558	0.635280	1.735375
B	3.906434	2.180188	1.503226
B	2.157076	1.883688	1.545668
B	3.217551	0.973407	2.614103
H	-0.930734	-0.039535	-3.498890
H	4.941892	-1.062922	0.144093
H	4.407846	3.186246	1.899254
H	3.338174	0.298532	-1.894148
H	4.277883	-3.233769	0.998640
H	-0.142689	-1.550700	0.378961
H	1.085859	-1.264916	-1.937298
H	1.517341	-2.688768	2.461963
H	3.838469	-2.127394	-1.938870
H	3.697446	-5.100035	-1.292136
H	2.269596	-5.438261	1.413553
H	1.697305	-3.621968	-3.195062
H	-0.557415	-4.182990	1.116456
H	-0.828914	-3.090644	-1.667800
H	0.707717	-5.807031	-1.205329
H	3.719753	-1.359227	2.443363
H	0.998763	-0.264352	2.490934
H	1.369083	2.676314	1.969143
H	3.250765	1.001646	3.801524
H	2.822632	3.027309	-0.724058
H	5.745870	0.367652	2.250756
H	5.546153	1.550906	-0.501151
H	-2.744440	-0.745154	-1.991773
H	0.971233	1.301116	-2.596320
H	0.508732	2.385759	-0.391767
H	-0.891582	1.279770	1.289180
H	-2.203607	-2.671154	1.069615
H	-3.103058	-4.801957	0.234668
H	-5.221963	-4.832005	-1.078561
H	-6.413767	-2.700874	-1.531147
H	-5.497597	-0.561333	-0.702955
H	-4.794486	0.202744	2.748863
H	-6.477284	1.977026	3.096031
H	-6.771102	3.767494	1.394616
H	-5.348043	3.768196	-0.642097
H	-3.660004	2.013172	-0.978243
H	-2.674116	-0.362410	1.664920

O	0.400428	4.319720	-0.543001
C	0.555193	4.591528	-1.936197
C	1.160346	5.988877	-2.026218
C	2.038155	6.018038	-0.771071
C	1.189347	5.238488	0.231376
H	1.236260	3.846289	-2.374812
H	-0.425311	4.499851	-2.413191
H	0.375019	6.750851	-1.966562
H	1.720272	6.142270	-2.952684
H	2.263968	7.030233	-0.425133
H	2.984022	5.496881	-0.953795
H	0.502091	5.893080	0.781423
H	1.785308	4.665829	0.944752

[m-4]$^-$ + protonated THF

E(ωB97XD/6-31+G*)= -2961.080216

C	-4.608259	1.669400	0.402353
C	-4.468770	0.403515	0.979325
C	-5.438971	-0.020102	1.901397
C	-6.523870	0.789851	2.227328
C	-6.659041	2.049116	1.636501
C	-5.696181	2.485173	0.728164
C	-3.312246	-0.542935	0.659296
C	-3.770471	-1.859798	0.023381
C	-2.917898	-2.970543	0.105152
C	-3.255944	-4.177640	-0.500332
C	-4.459249	-4.294753	-1.201752
C	-5.313422	-3.196387	-1.289339
C	-4.971853	-1.985884	-0.680285
C	-2.189543	0.065575	-0.175043
C	-2.363967	0.336752	-1.538954
C	-1.305029	0.850382	-2.285848
C	-0.056422	1.051103	-1.693389
C	0.161864	0.757944	-0.336568
C	-0.942211	0.299810	0.405966
B	1.599718	0.842373	0.312344
Co	2.728143	-1.052550	0.310293
B	3.501768	-2.241039	-1.264174
B	3.849611	-2.905885	0.358147
B	2.308300	-2.901521	1.263068
B	2.900641	-4.415892	0.531215
B	1.992563	-4.696808	-0.988061
B	3.644233	-4.003420	-1.043588
B	2.362517	-3.345567	-2.094556
C	1.824700	-1.942169	-1.272582

B	0.835817	-3.370635	-1.186786
B	1.168951	-4.007662	0.436853
C	1.150446	-2.320067	0.160691
B	2.002528	0.138444	1.910387
C	3.674930	-0.181311	1.869986
C	4.312098	0.204635	0.417850
B	3.120013	0.812633	-0.634712
B	2.583435	2.329180	0.133635
B	4.305046	1.894376	0.162653
B	4.679167	1.233323	1.770050
B	3.538361	2.577573	1.625480
B	1.881888	1.905888	1.725826
B	3.179759	1.215421	2.725899
H	-1.445658	1.074417	-3.338652
H	5.179677	-0.346134	0.085228
H	3.832871	3.651286	2.040982
H	3.230983	0.681077	-1.809351
H	4.914458	-2.797248	0.889862
H	0.263082	-1.780039	0.453256
H	1.355992	-1.168734	-1.864095
H	2.157238	-2.760494	2.431093
H	4.229860	-1.612022	-1.958381
H	4.557141	-4.610695	-1.505744
H	3.275694	-5.321215	1.206078
H	2.308588	-3.368626	-3.278555
H	0.270132	-4.496618	1.038669
H	-0.236315	-3.339379	-1.683374
H	1.723056	-5.779736	-1.397804
H	4.147799	-0.971997	2.433868
H	1.285491	-0.484653	2.621961
H	0.985378	2.513913	2.217756
H	3.277578	1.221691	3.907302

protonated [m-4]$^{-}$

E(ωB97XD/6-31+G*)= -2728.655982

C	-4.502816	-1.753299	0.777023
C	-4.049527	-1.170089	-0.407884
C	-4.701248	-1.484241	-1.603615
C	-5.781779	-2.360427	-1.617062
C	-6.228775	-2.937048	-0.428865
C	-5.587001	-2.630210	0.767625
C	-2.902077	-0.168676	-0.439846
C	-3.364505	1.282834	-0.426590
C	-2.542677	2.248337	-1.012734
C	-2.858801	3.600437	-0.931811

C	-4.018464	4.003449	-0.271517
C	-4.856177	3.046311	0.296566
C	-4.531135	1.692076	0.221309
C	-1.871778	-0.442023	0.652544
C	-1.675430	0.404548	1.749198
C	-0.725568	0.138206	2.746681
C	0.058381	-0.990642	2.657863
C	-0.079379	-1.867024	1.540615
C	-1.096110	-1.591434	0.585672
B	1.460581	-1.776422	0.527903
Co	2.495834	0.028583	-0.151753
B	3.587803	1.545263	0.844196
B	3.691663	1.642561	-0.934506
B	2.025263	1.521447	-1.569875
B	2.814497	3.103375	-1.439335
B	2.190629	3.922893	0.015314
B	3.779140	3.118618	0.055339
B	2.662392	2.950674	1.420300
C	1.937110	1.438439	1.167075
B	1.022486	2.840664	0.778287
B	1.115578	2.928370	-0.979836
C	1.051912	1.424122	-0.190898
B	1.523657	-1.532692	-1.216750
C	3.175261	-1.270427	-1.535373
C	4.045986	-1.257551	-0.176554
B	3.069080	-1.511537	1.200458
B	2.462519	-3.172179	0.958671
B	4.125023	-2.793278	0.530892
B	4.204759	-2.609946	-1.224356
B	3.151116	-3.834205	-0.535066
B	1.500373	-3.185225	-0.534908
B	2.576354	-2.818260	-1.878310
H	-0.611245	0.832764	3.572824
H	4.953378	-0.667119	-0.165108
H	3.391082	-4.990817	-0.681850
H	3.373374	-1.091187	2.271407
H	4.647498	1.266263	-1.548116
H	0.096252	0.919936	-0.170659
H	1.540250	0.943973	2.040710
H	1.657837	1.049463	-2.599085
H	4.379786	1.086915	1.604792
H	4.796466	3.730253	0.165070
H	3.122622	3.706357	-2.420647
H	2.801904	3.322136	2.541661
H	0.159891	3.301537	-1.580040

H	0.034087	3.051099	1.404903
H	2.042847	5.102246	0.097796
H	3.538106	-0.688531	-2.373138
H	0.669424	-1.134109	-1.944814
H	0.536251	-3.879561	-0.668711
H	2.454001	-3.143180	-3.014366
H	2.189902	-3.853210	1.902574
H	5.200585	-2.707357	-1.859303
H	5.112364	-3.100120	1.115824
H	-2.269514	1.311331	1.825200
H	0.803613	-1.220951	3.413799
H	0.126630	-2.919098	1.731104
H	-1.244009	-2.298747	-0.226292
H	-1.637638	1.941889	-1.531831
H	-2.195537	4.334330	-1.380208
H	-4.268982	5.058037	-0.203890
H	-5.768009	3.351815	0.801921
H	-5.193306	0.953875	0.665620
H	-4.360251	-1.031556	-2.532043
H	-6.273427	-2.595110	-2.556654
H	-7.069034	-3.625003	-0.437321
H	-5.927107	-3.075365	1.698302
H	-4.010661	-1.526992	1.719684
H	-2.373919	-0.322555	-1.390404

[m-4]$^{-}$

E(ωB97XD/6-31+G*)= -2728.225799

C	-4.722115	-2.248401	0.187151
C	-4.588600	-1.020434	-0.464506
C	-5.693461	-0.522533	-1.167213
C	-6.897054	-1.219208	-1.202771
C	-7.021532	-2.438570	-0.537236
C	-5.927344	-2.950303	0.153606
C	-3.262127	-0.265037	-0.507265
C	-3.395156	1.249403	-0.363419
C	-2.497596	2.078408	-1.040962
C	-2.514843	3.458129	-0.856384
C	-3.442667	4.033202	0.008552
C	-4.346648	3.217167	0.686354
C	-4.321173	1.836776	0.502640
C	-2.209772	-0.746216	0.483857
C	-2.419729	-0.680541	1.864311
C	-1.398049	-1.037096	2.737667
C	-0.150250	-1.419923	2.244800
C	0.101922	-1.475346	0.868710

C	-0.966721	-1.163769	0.014706
B	1.550242	-1.759186	0.288177
Co	2.740174	0.029705	-0.139129
B	3.510350	1.526929	1.130153
B	3.957255	1.753720	-0.580147
B	2.462629	1.588215	-1.533928
B	3.099966	3.201414	-1.164515
B	2.151080	3.883038	0.179471
B	3.750367	3.163375	0.488136
B	2.402774	2.840370	1.592402
C	1.828242	1.314046	1.116893
B	0.928697	2.697027	0.635516
B	1.357228	2.900094	-1.063238
C	1.239224	1.350195	-0.384068
B	2.006793	-1.482386	-1.417331
C	3.682186	-1.215541	-1.404474
C	4.271665	-1.250701	0.099511
B	3.046451	-1.545514	1.237539
B	2.470610	-3.176071	0.847260
B	4.199533	-2.814823	0.758415
B	4.622381	-2.575195	-0.937135
B	3.440198	-3.806447	-0.502659
B	1.820789	-3.136676	-0.807431
B	3.155960	-2.751177	-1.901555
H	-1.566129	-0.990713	3.811236
H	5.159164	-0.665043	0.305329
H	3.709283	-4.962218	-0.638112
H	3.148338	-1.146532	2.356401
H	5.042511	1.481869	-1.015273
H	0.326959	0.797376	-0.567331
H	1.279405	0.736497	1.851249
H	2.336077	1.176766	-2.645498
H	4.171850	1.071166	2.010306
H	4.679132	3.830659	0.837779
H	3.549876	3.896459	-2.027430
H	2.298916	3.151685	2.737760
H	0.507860	3.251092	-1.823387
H	-0.168577	2.825632	1.070039
H	1.919330	5.049100	0.298667
H	4.203708	-0.608602	-2.134211
H	1.329987	-1.038573	-2.293004
H	0.909988	-3.823784	-1.165224
H	3.273676	-3.043184	-3.050635
H	2.033870	-3.892032	1.699712
H	5.723797	-2.670610	-1.373724

H	5.059769	-3.152745	1.510490
H	-3.376665	-0.341886	2.254758
H	0.648673	-1.665215	2.941586
H	-0.804185	-1.219304	-1.061486
H	-1.755739	1.639983	-1.705895
H	-1.787207	4.076192	-1.374221
H	-3.453914	5.108972	0.161297
H	-5.071564	3.654639	1.368345
H	-5.029765	1.210150	1.038443
H	-5.609120	0.429371	-1.685566
H	-7.740893	-0.807798	-1.750857
H	-7.961782	-2.983277	-0.560649
H	-6.005200	-3.903492	0.670095
H	-3.875727	-2.664045	0.725139
H	-2.847319	-0.446366	-1.508062

TS of the H^+ abstraction with THF

E(ωB97XD/6-31+G*)= -2961.054504

C	0.390795	4.778798	-0.160035
O	0.675262	3.653028	0.722963
C	0.516607	4.043677	2.106882
C	0.554867	5.564264	2.085448
C	-0.130439	5.880523	0.752598
C	-0.114322	1.098718	0.500197
C	0.006272	0.872472	1.902612
C	1.121480	0.258494	2.444882
C	2.124535	-0.212465	1.597127
C	2.059477	-0.039539	0.207078
C	0.961560	0.626453	-0.310266
C	3.114759	-0.630147	-0.716194
C	3.404882	-2.067489	-0.285416
C	2.442057	-3.047020	-0.545937
C	2.602598	-4.347648	-0.081932
C	3.742056	-4.690598	0.645075
C	4.713299	-3.725386	0.898375
C	4.545180	-2.419443	0.437953
B	-1.593451	1.216614	-0.186850
B	-1.799962	2.302460	-1.570306
B	-3.072147	1.678280	-2.615142
B	-3.423245	3.019575	-1.502401
B	-4.585313	1.714045	-1.707333
B	-4.244804	2.322770	-0.086110
B	-2.527804	2.709057	-0.001629
B	-3.119652	1.196232	0.717625

C	-4.286839	0.651324	-0.388536
C	-3.627607	0.290563	-1.815182
B	-1.951629	0.555726	-1.803479
Co	-2.748528	-0.645676	-0.264518
C	-1.257220	-1.981275	-0.122324
B	-1.343283	-3.635917	-0.485639
B	-1.051282	-3.100226	1.167203
C	-1.973066	-1.654251	1.291306
B	-2.599268	-3.056265	2.013610
B	-3.860029	-3.589086	0.888135
B	-2.251841	-4.354717	0.856737
B	-3.077248	-3.950644	-0.668324
B	-2.385097	-2.446849	-1.298278
B	-3.956822	-2.417500	-0.450881
B	-3.647842	-1.860036	1.214144
C	4.362356	0.231754	-0.869583
C	4.620101	1.359623	-0.091463
C	5.789355	2.100804	-0.277427
C	6.712063	1.724659	-1.246817
C	6.458590	0.601861	-2.036476
C	5.295399	-0.133390	-1.847862
H	1.201452	0.101175	3.516137
H	-5.186426	0.121875	-0.099480
H	-3.673450	4.115622	-1.899438
H	-3.273277	1.060031	1.892469
H	-4.995377	-2.224687	-1.015136
H	-0.325035	-1.477568	-0.344060
H	-1.489758	-0.948873	1.952606
H	-2.168517	-2.262688	-2.453797
H	-4.361994	-1.225286	1.924972

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