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Reductive demetalation of copper corroles: first simple route to free-base β-octabromocorroles

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ABSTRACT: Although the chemistry of corroles has grown spectacularly in recent years, the field has been marred by the lack of convenient protocols for demetalation of metallocorroles. Reported herein is a superior procedure for demetalating copper corroles with concentrated H_2SO_4 and 5-200 equiv $FeCl_2$ or $SnCl_2$. The yields obtained with this reductive procedure are generally substantially better than with $CHCl_3/H_2SO_4$, CH_2Cl_2/H_2SO_4, or H_2SO_4 alone. With an oxidation-prone metallocorrole such as Cu[T(*p*-OMeP)C], the reductive protocol was essential for obtaining any measurable yield of the free base at all. Free-base β-octabromo-*meso*-triarylcorroles were also obtained in pure form, in good yields, and with relative ease *via* this procedure. Copyright © 2008 Society of Porphyrins & Phthalocyanines.

KEYWORDS: demetalation, corrole, octabromocorrole.

INTRODUCTION

Ever since the development of convenient one-pot syntheses of corroles a few years ago [1, 2], their chemistry has blossomed in the most extraordinary manner [3, 4]. Indeed, both the coordination chemistry and range of applications of corroles promise to be just as diverse as those of porphyrins. Unfortunately, the field has been marred by a crucial irritant: unlike metalloporphyrins, for which a host of demetalation procedures are available [5], no such broadly applicable procedure has been available for corroles. Thus, until most recently, just two isolated instances of demetalation of a corrole were documented, one of Mn[OEC] [Mn(III) octaethylcorrole)] with HBr/HOAc [6] and the other of Ag(III) triarylcorroles with aqueous HCl in a biphasic medium [7]. Earlier this year, while this paper was in preparation, Paolesse and coworkers reported a considerably more general method for corrole demetalation, involving $CHCl_3/H_2SO_4$ [8]. In our own studies, we also found concentrated H_2SO_4 to be the acid of choice, with, however, a crucial twist: concentrated H_2SO_4 with several equivalents of $FeCl_2$ or $SnCl_2$ (relative to the metallocorrole) resulted in dramatically better yields of free-base corrole, fewer impurities and somewhat shorter reaction times, compared to H_2SO_4 alone.

RESULTS AND DISCUSSION

Just as Ni(II), Cu(II), and Zn(II) porphyrins are most often used for porphyrin functionalization, Cu(III) corroles play a similar role in corrole chemistry. As stable, diamagnetic species that are readily characterized (although a number of them exhibit thermally accessible, paramagnetic Cu(II) corrole$^{\bullet 2-}$ excited states) [9], Cu corroles are ideally suited for peripheral functionalization and subsequent elaboration of the corrole macrocycle [10]. We therefore chose to focus our efforts on copper corroles in this study.

Table 1 presents our experimental results for six copper corroles, including three Cu triarylcorroles as well as their β-octabromo derivatives [10]. As shown, neat concentrated H_2SO_4 gave useful,

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[◊] SPP full member in good standing

*Correspondence to: Abhik Ghosh, email: abhik@chem.uit.no if rather low, yields for only a couple of the most electron-deficient copper corroles. Adding a solvent such as $CHCl_3$ or CH_2Cl_2 (the best conditions being about 20:1 v/v solvent:H_2SO_4) improved matters in certain cases, resulting in useful yields for the corroles in question. With two exceptions, Cu[TPC] (copper triphenylcorrole) and Cu[Br_8TPC], the complexes studied by us and Paolesse and coworkers are not the same, so an exact comparison is not possible. However, for Cu[TPC], we failed to reproduce the high yield of free-base corrole (83%), reported by Paolesse and coworkers [8]. The H_2SO_4/solvent procedure also led to a rather intractable, impure product for Cu[Br_8TPC].

Addition of several equivalents of $FeCl_2$ or $SnCl_2$ resulted in dramatic improvement in the demetalation yield for all the complexes studied. Thus, a yield of about 70% could be reliably obtained in nearly all cases. The importance of this finding for the entire corrole field can hardly be exaggerated. A wide variety of functionalized corroles that until now could only be obtained in metal-complexed form should now be available as free bases for re-complexation and further synthetic elaboration. Indeed, the present H_2SO_4/$FeCl_2$ or H_2SO_4/$SnCl_2$ method already provides the first simple, reasonably general route to free-base β-octabromo-*meso*-triarylcorroles.

The exact conditions that proved most effective for the different copper corroles studied suggests that the $FeCl_2$ plays multiple roles in the demetalation process. Almost certainly, the first role of the $FeCl_2$ is as a reductant; it reduces the small Cu(III) ion to the larger, much more easily displaced Cu(II) ion. However, the fact that vastly different amounts of $FeCl_2$ or $SnCl_2$ – from 5 to 200 equiv – are needed for different copper corroles suggests that a second factor must be involved. As may be seen from a perusal of the Experimental section, relatively electron-rich copper corroles required large quantities (100-200 equiv) of $FeCl_2$ or $SnCl_2$, whereas the more electron-deficient copper corroles needed only a few equivalents of $FeCl_2$. A plausible explanation for this difference is that the excess $FeCl_2$ or $SnCl_2$ protects the more easily oxidized free-base corroles from oxidative breakdown under the demetalation procedure.

EXPERIMENTAL

Materials

All reagents and solvents were used as purchased, except pyrrole, which was predried and distilled from CaH_2 at low pressure. Silica gel 60 (0.040-0.063 mm particle size; 230-400 mesh; Merck) was used for flash chromatography.

Instrumentation

Ultraviolet-visible spectra were recorded on an HP 8453 spectrophotometer using dichloromethane as solvent. Proton NMR spectra were recorded on a Mercury Plus Varian spectrometer (400 MHz for ^1H) at room temperature in chloroform-*d*. Proton chemical shifts (δ) in ppm were referenced to residual chloroform (δ = 7.2 ppm). MALDI-TOF mass spectra were recorded on a Waters Micromass MALDI micro MX Mass Spectrometer using α-cyano-4-hydroxycinnamic acid (CHCA) as the matrix. Satisfactory elemental analyses were obtained in each case from Atlantic Microlabs, Inc.

Synthesis of corrole starting materials

Free-base corroles were synthesized according to Gryko and coworkers [1c]. Copper triarylcorroles and their β-octabromo derivatives were synthesized, as described by Ghosh and coworkers [10].

General procedure for the demetalation of copper corroles

Into a 25 mL or 50 mL round-bottomed flask equipped with a magnetic stirrer, copper corrole (10 mg) and anhydrous $FeCl_2$ (Sigma-Aldrich) or $SnCl_2$ (Alfa-Aesar) (5-200 equiv) were introduced. Con-

Table 1. Comparison of demetalation yields (%) under different reaction conditions

Complex	H_2SO_4, $CHCl_3$	H_2SO_4, CH_2Cl_2	H_2SO_4 only	H_2SO_4 + $FeCl_2$	H_2SO_4 + $SnCl_2$
Cu[TPC]	18	18	-	68	77
Cu[T(*p*-OMeP)C]	-	-	-	75	77
Cu[T(*p*-CF_3P)C]	not attempted	26	37	74	inseparable mixture
Cu[Br_8TPC]	inseparable impurities	inseparable impurities	inseparable impurities	79	inseparable mixture
Cu[Br_8T(*p*-OMeP)C]	35	79	-	81	85
Cu[Br_8T(*p*-CF_3P)C]	10	22	33	82	85

centrated H_2SO_4 (95-97%, Merck, 0.8-2.0 mL) was added dropwise and the reaction mixture was alternately stirred/swirled and sonicated for 2 min to 1 h, depending on the particular copper corrole. The progress of the reaction, as measured by the disappearance of the copper corrole, was monitored by UV-vis spectroscopy and by TLC. After apparent consumption of the copper corrole, the reaction mixture was quenched with distilled H_2O and then extracted with $CHCl_3$. The green organic phase was repeatedly washed with distilled water and then twice with saturated aqueous $NaHCO_3$. The organic phase was then dried with anhydrous Na_2SO_4, filtered, mixed with about 0.5 g silica and evaporated under vacuum. The residue thus obtained was chromatographed on a silica gel column with *n*-hexane/CH_2Cl_2 as eluent to give the free-base corrole as the second or third band (small quantities of unreacted copper corrole was usually the first band). Spectroscopic data for free-base and copper triphenylcorrole, *meso*-tris(4-methoxyphenyl)corrole, *meso*-tris(4-trifluoromethylphenyl)corrole, β-octabromo-*meso*-triphenylcorrole were in agreement with those reported previously [10]. Additional details for each demetalation experiment are provided below.

Demetalation of copper 5,10,15-triphenylcorrole. Into a 25 mL round-bottomed flask containing the corrole (10 mg) and $FeCl_2$ (200 equiv), concentrated H_2SO_4 (0.8 mL) was added dropwise, with stirring. The resulting suspension was stirred for 3 min. After work-up of the reaction mixture (as described above), the green residue obtained was chromatographed on a silica gel column, first with 7:3 *n*-hexane/CH_2Cl_2 to elute unreacted Cu[TPC] (1.4 mg) as the first band and then with 2:3 *n*-hexane/CH_2Cl_2 to elute free-base *meso*-triphenylcorrole (6.1 mg). Yield: 68%. UV-vis (CH_2Cl_2): λ_{max}, nm (log ε, $M^{-1}.cm^{-1}$) 417 (5.13), 578 (4.20), 620 (4.11), 651 (4.08). MS (MALDI-TOF, major isotopomer): *m/z* $[M]^+$ 526.13 (expt.), 526.21 (calcd.). For the $SnCl_2$/H_2SO_4 demetalation, the corrole (10 mg), $SnCl_2$ (100 equiv) and H_2SO_4 (1 mL) were stirred and sonicated, alternately, for 5 min. After work-up and purification, Cu[TPC] (1.2 mg) and H_3[TPC] (6.9 mg) were obtained. Yield of H_3[TPC]: 77%.

Demetalation of copper 5,10,15-tris(4-methoxyphenyl)corrole. The reaction conditions and reaction time were exactly as in the above case. The green residue obtained at the end of the work-up phase was chromatographed on silica gel with 2:3 *n*-hexane/CH_2Cl_2 to afford the free-base *meso*-tris(4-methoxyphenyl)corrole. Yield: 75%. UV-vis (CH_2Cl_2): λ_{max}, nm (log ε, $M^{-1}.cm^{-1}$) 419 (4.52), 577 (3.63), 624 (3.61), 655 (3.58). MS (MALDI-TOF, major isotopomer): *m/z* $[M]^+$ 616.33 (expt.), 616.24 (calcd.). The $SnCl_2$/H_2SO_4 demetalation was performed exactly as with $FeCl_2$/H_2SO_4. After work-up and purification, the yield of the free-base was 77%.

Demetalation of copper 5,10,15-tris(4-trifluoromethylphenyl)corrole. To the copper corrole (10 mg) and $FeCl_2$ (5 equiv) in a 50 mL round-bottomed flask, concentrated H_2SO_4 (2.0 mL) was added. The suspension was stirred for 1 h. After work-up of the reaction mixture, the green residue obtained was chromatographed on silica gel with 2:1 *n*-hexane/CH_2Cl_2 to afford free-base *meso*-tris(4-trifluoromethylphenyl)corrole. Yield: 69%. UV-vis (CH_2Cl_2): λ_{max}, nm (log ε, $M^{-1}.cm^{-1}$) 418 (4.63), 580 (3.84), 617 (3.71), 647 (3.61). MS (MALDI-TOF, major isotopomer): *m/z* $[M]^+$ 730.30 (expt.), 730.18 (calcd.). On a larger scale, the copper complex (60 mg), $FeCl_2$ (5 equiv) and concentrated H_2SO_4 (3 mL) were introduced in that order into a 50 mL round-bottomed flask. The mixture was stirred and sonicated alternately for 1 h. Work-up and purification as described above gave 41 mg (74%) of the free-base. The $SnCl_2$/H_2SO_4 demetalation was performed exactly as with $FeCl_2$/H_2SO_4. After work-up and purification, however, an inseparable mixture of compounds was obtained.

Demetalation of copper β-octabromo-*meso*-triphenylcorrole. To the copper corrole (10 mg) and $FeCl_2$ (5 equiv) in a 50 mL round-bottomed flask, concentrated H_2SO_4 (1.0 mL) was added in a dropwise manner. The suspension was sonicated and stirred alternately for 50 min. After work-up, the green residue obtained was chromatographed on silica gel with 1:1 *n*-hexane/CH_2Cl_2. Unreacted copper corrole was obtained as the first band. The eluent was then changed to neat CH_2Cl_2 or $CHCl_3$ to yield free-base β-octabromo-*meso*-triphenylcorrole as the last band. After solvent removal, the green product was crystallized from 1:1 $CHCl_3$/*n*-hexane to afford 5.3 mg of the pure free base. Yield: 55%. UV-vis (CH_2Cl_2): λ_{max}, nm (log ε, $M^{-1}.cm^{-1}$) 444 (4.84), 553 (3.80), 593 (3.85), 703 (3.88). MS (MALDI-TOF, major isotopomer): *m/z* $[M + H]^+$ 1158.76 (expt.), 1158.49 (calcd.). On a larger scale, the copper complex (64 mg), $FeCl_2$ (5 equiv) and concentrated H_2SO_4 (2 mL) were introduced in that order into a 50 mL round-bottomed flask. The mixture was stirred and sonicated alternately for 2 h. Work-up and purification as described above gave 48 mg (79%) of the free base. The $SnCl_2$/H_2SO_4 demetalation was performed exactly as with $FeCl_2$/H_2SO_4. However, work-up and attempted purification led only to an inseparable mixture of compounds.

Demetalation of copper β-octabromo-*meso*-tris-(4-methoxyphenyl)corrole. To the copper corrole (10 mg) and $FeCl_2$ (100 equiv) in a 50 mL round-bottomed flask, concentrated H_2SO_4 (1.0 mL) was added in a dropwise manner. The suspension was sonicated and stirred alternately for 20 min. After work-up of the reaction mixture, the green residue obtained was chromatographed on silica gel with 2:3 *n*-hexane/CH_2Cl_2, yielding the green free-base β-octabromo-*meso*-tris(4-methoxyphenyl)corrole (7.7 mg). Yield: 81%. UV-vis (CH_2Cl_2): λ_{max}, nm (log ε, $M^{-1}.cm^{-1}$) 450 (4.41), 601(3.55), 715 (3.72). ^1H NMR: δ, ppm 7.85-7.75 (4H, 5,15- *o* or *m* and 2H, 10-*o* or *m*, Ph; overlapping doublets); 7.25-7.10 (4H, 5,15- *m* or *o* and 2H, 10- *m* or *o*, Ph); 3.99 (s, 6H, 5,15-*p*-OCH_3, Ph); 3.98 (s, 3H, 10- *p*-OCH_3, Ph). MS (MALDI-TOF, major isotopomer): *m/z* $[M + H]^+$ 1248.76 (expt.), 1248.53 (calcd.). Elemental analysis: 38.50% C (38.30% calcd.), 1.94% H (calcd. 1.88%), 4.49% N (calcd. 4.43%). For the $SnCl_2/H_2SO_4$ demetalation, the corrole (10mg), $SnCl_2$ (100 equiv) and H_2SO_4 (1 mL) were stirred and sonicated alternately for 20 min. After work-up and purification, 8.2 mg of the free base was obtained. Yield: 85%.

Demetalation of copper β-octabromo-*meso*-tris-(4-trifluoromethylphenyl)corrole. To the copper corrole (10 mg) and $FeCl_2$ (5 equiv) in a 50 mL round-bottomed flask, concentrated H_2SO_4 (2.0 mL) was added dropwise. The mixture was stirred and sonicated alternately for 1 h. After work-up of the reaction mixture, the green residue obtained was chromatographed on silica gel with 3:2 *n*-hexane/CH_2Cl_2 to give green free-base β-octabromo-*meso*-tris(4-trifluoromethylphenyl)corrole. Yield: 82%. UV-vis (CH_2Cl_2): λ_{max}, nm (log ε, $M^{-1}.cm^{-1}$) 447 (4.86), 597(5.04), 697 (3.97). ^1H NMR: δ 8.08-8.00 (4H, 5,15- *o* or *m* and 2H, 10-*o* or *m*, Ph); 7.96-7.86 (4H, 5,15- *m* or *o* and 2H, 10- *m* or *o*, Ph). MS (MALDI-TOF, major isotopomer): *m/z* $[M]^+$ 1361.63 (expt.), 1361.45 (calcd.). Demetalation with $SnCl_2/H_2SO_4$ was performed exactly as with $FeCl_2/H_2SO_4$. After work-up and purification, the yield of the free base was 85%.

CONCLUSION

In summary, reducing conditions, as afforded by an excess of $FeCl_2$, in concert with concentrated H_2SO_4, provide a reasonably general and convenient method for the demetalation of copper corroles. The added $FeCl_2$ results in sharp increases in the yield of the free base corrole as well as in fewer impurities, relative to H_2SO_4 alone. Thanks to the new method, free-base β-octabromo-*meso*-triarylcorroles, otherwise rather inaccessible, are now obtainable with comparative ease.

Supporting information

Details of analytical data (7 pages) are given in the supplementary material. This material is available at http://www.u-bourgogne.fr/jpp/.

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Reductive demetalation of copper corroles: first simple route to free-base β-octabromocorroles

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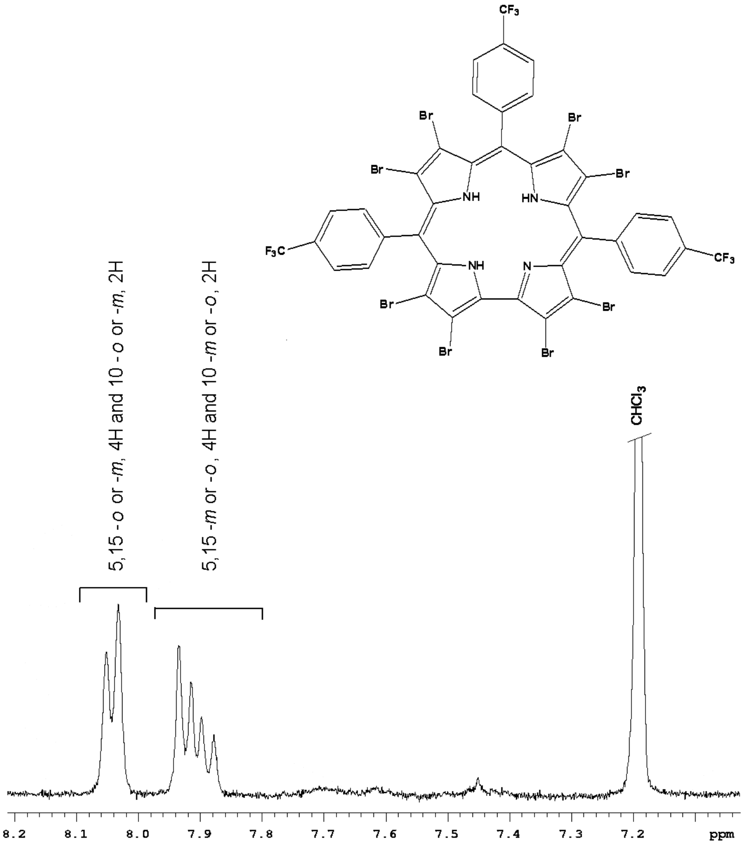
Proton NMR spectra

(a)



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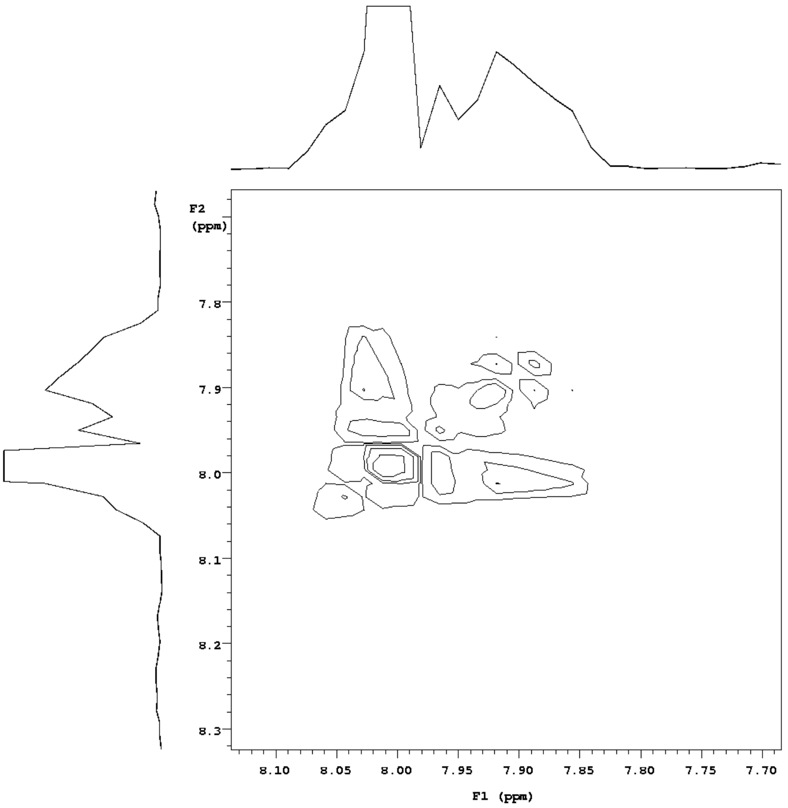


Figure S1. ^{1}H NMR spectra of Br$_8$T(p-CF$_3$P)C: (a) 1D ^{1}H NMR, and (b) the ^{1}H - ^{1}H COSY

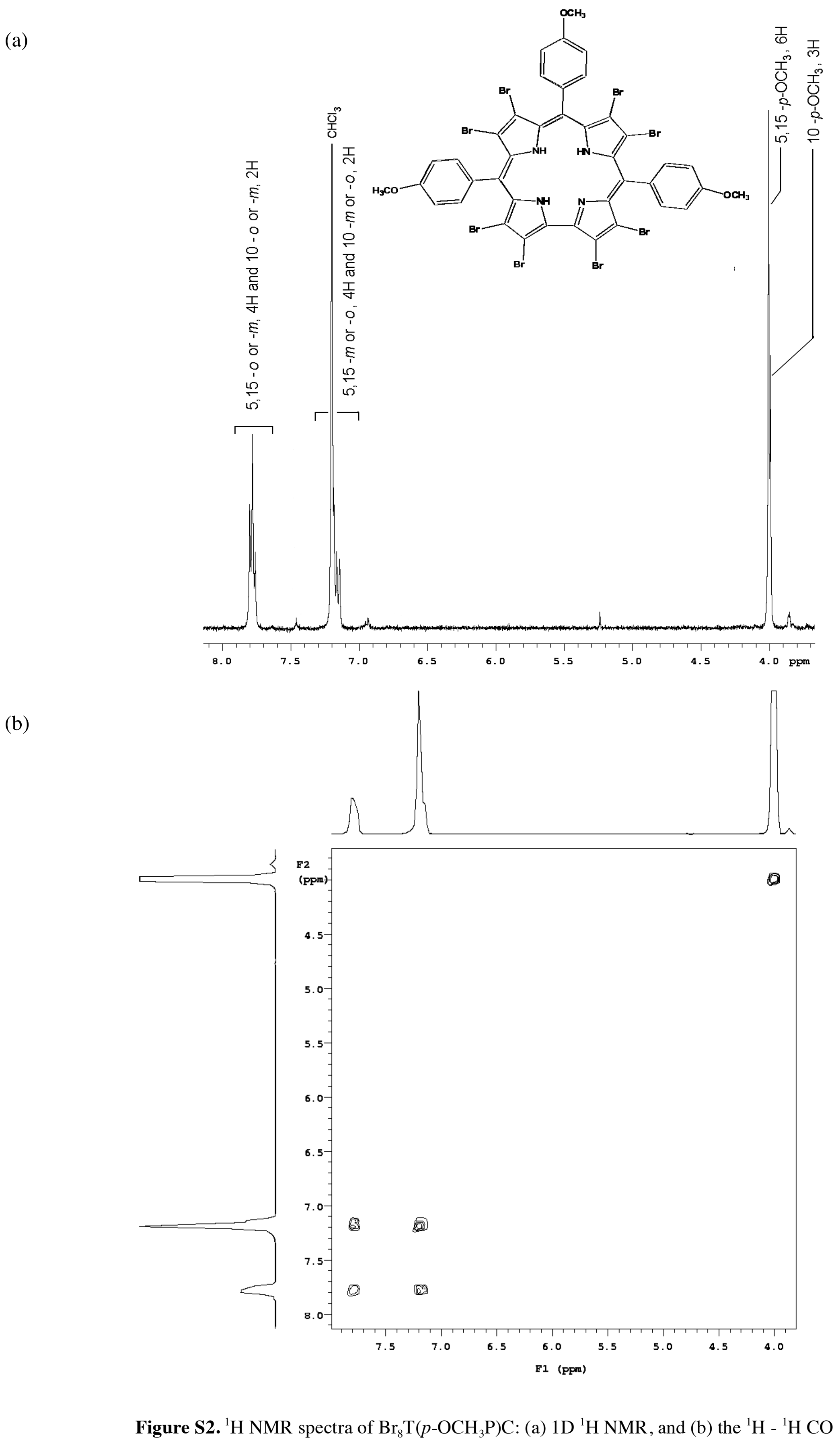


Figure S2. ^{1}H NMR spectra of Br$_8$T(p-OCH$_3$P)C: (a) 1D ^{1}H NMR, and (b) the ^{1}H - ^{1}H COSY

Ultraviolet-visible spectra

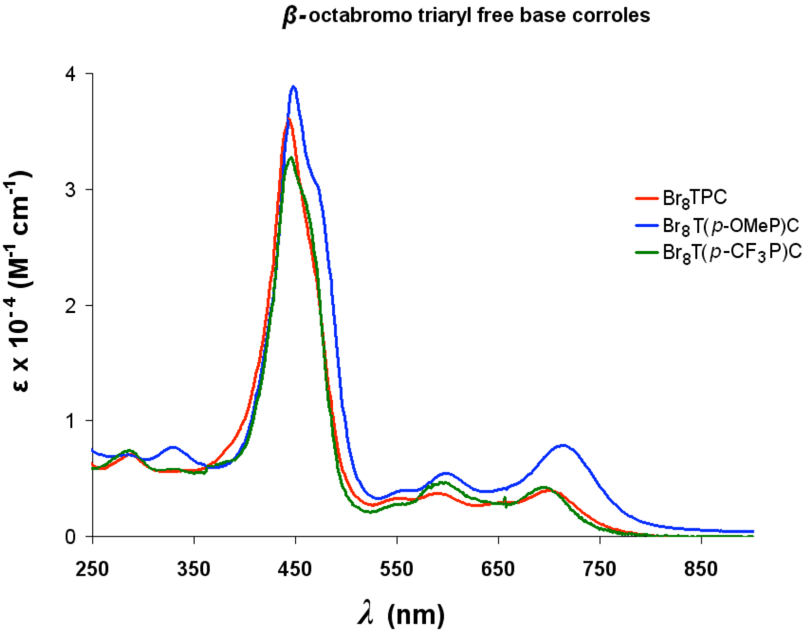


Figure S3. Ultraviolet-visible spectra of β-octabromo triaryl free base corroles

Mass spectra

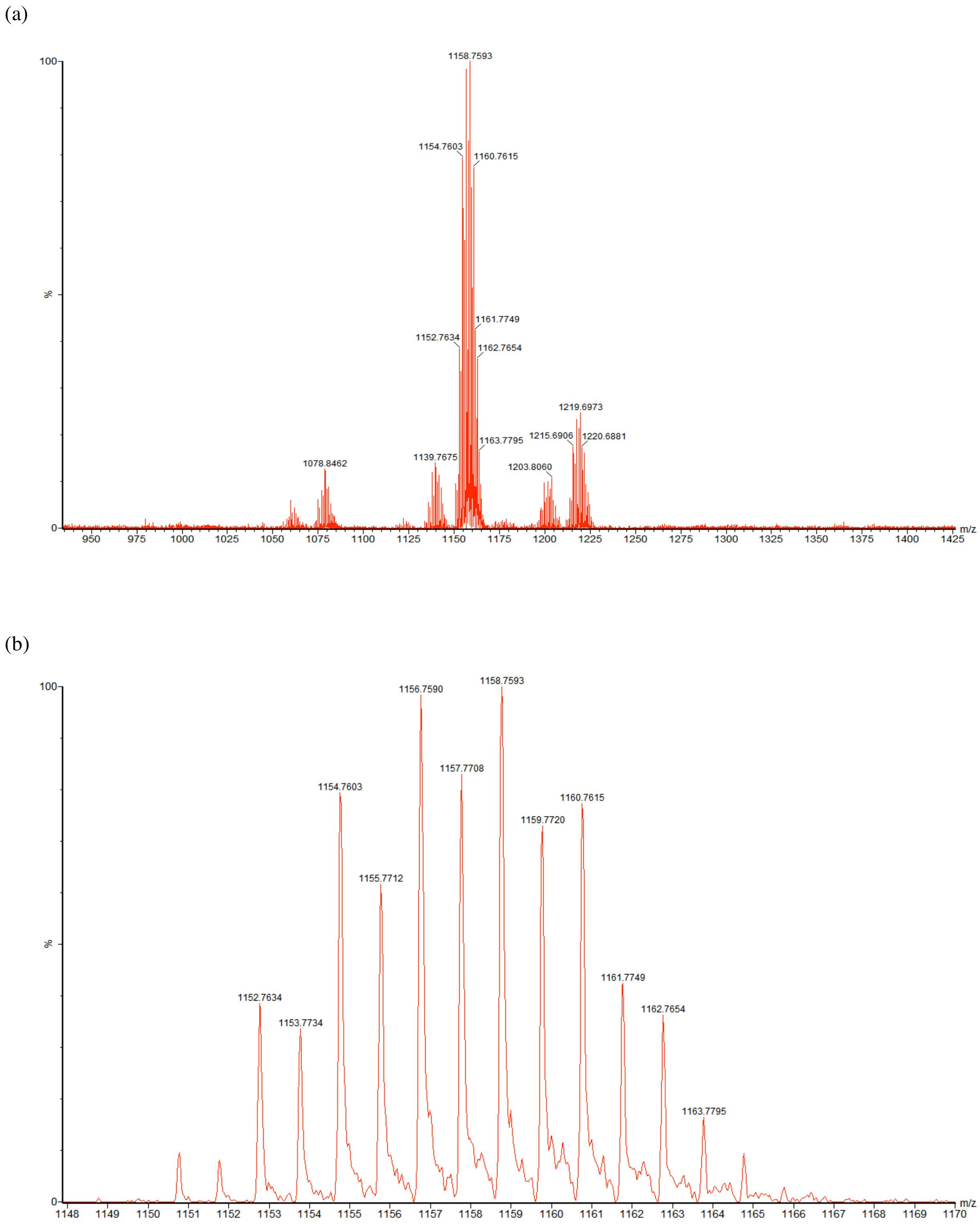


Figure S4. Mass spectra of Br_8TPC: (a) the full range, and (b) an expanded view of isotopomers

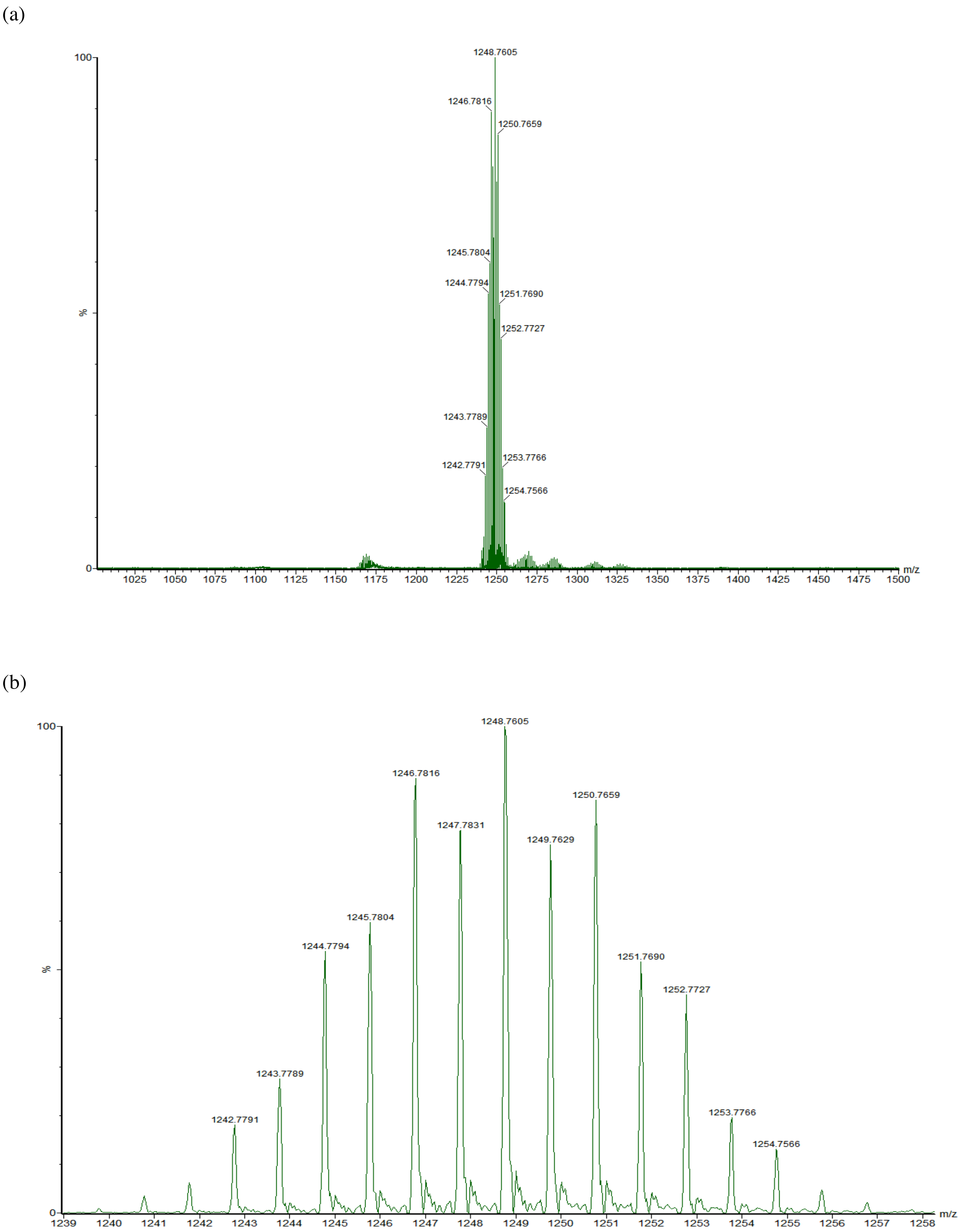


Figure S5. Mass spectra of Br_8T(*p*-OMeP)C]: (a) the full range, and (b) an expanded view of isotopomers

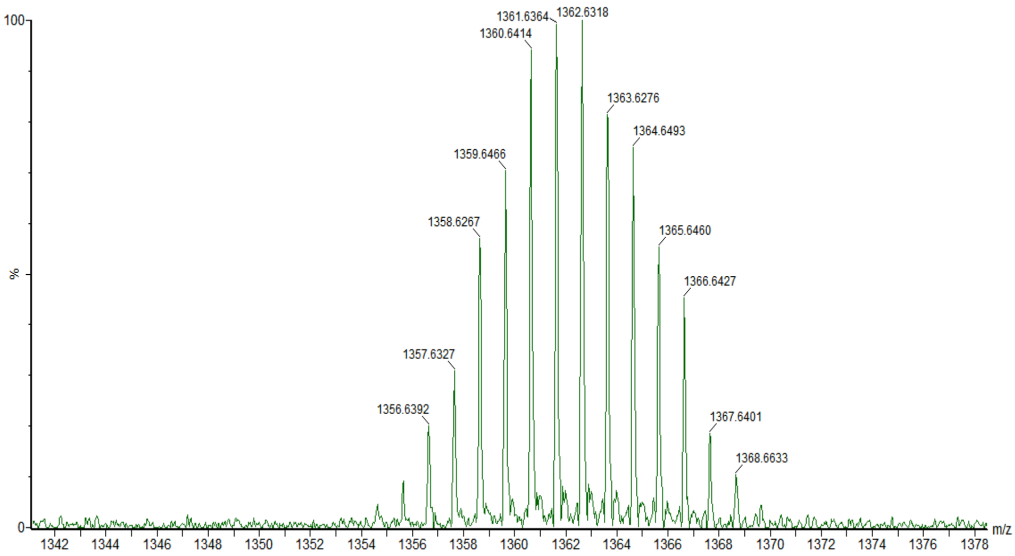
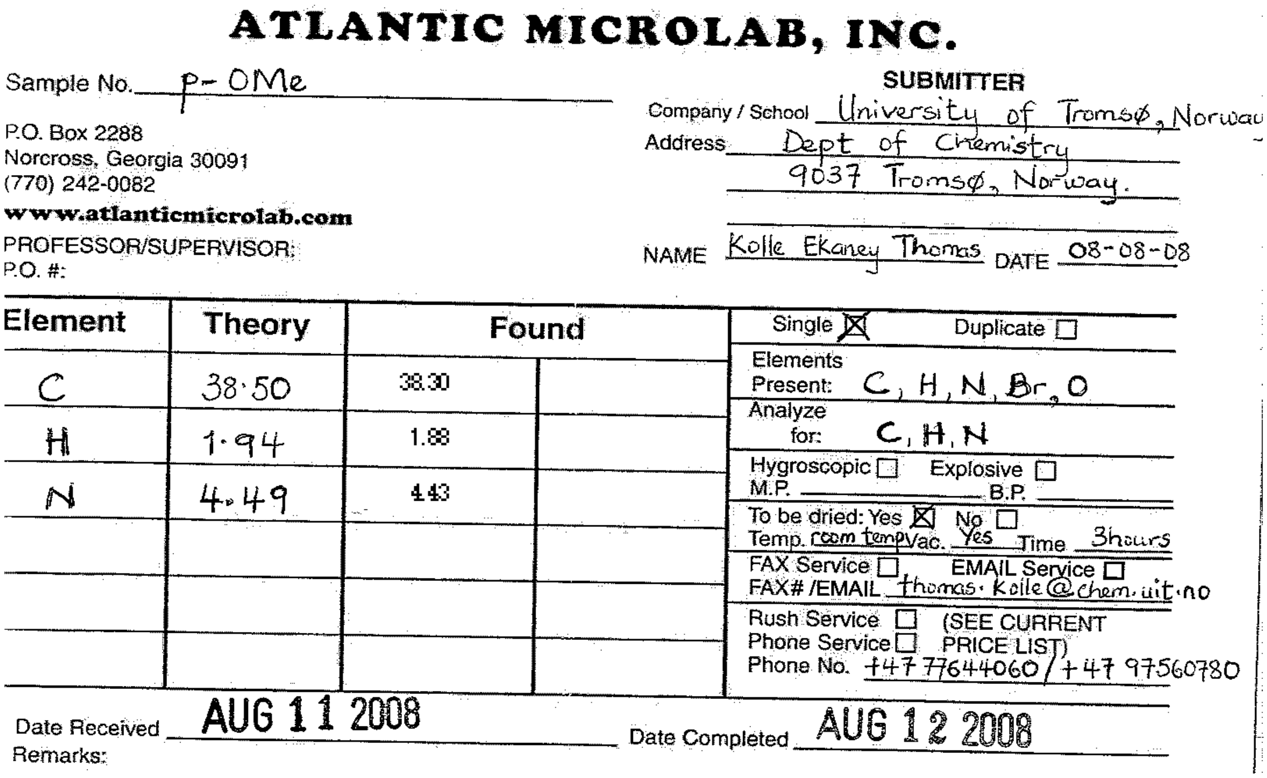


Figure S6. Expanded view of the mass spectrum of $Br_8T(p\text{-}CF_3P)C$ showing the various isotopomers

Elemental analysis



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9037 Tromsø, Norway.

NAME Kolle Ekaney Thomas DATE 08-08-08

Element	Theory	Found	
C	38·50	38.30	
H	1·94	1.88	
N	4.49	4.43	

Single ☒ Duplicate ☐
Elements Present: C, H, N, Br, O
Analyze for: C, H, N
Hygroscopic ☐ Explosive ☐
M.P. B.P.
To be dried: Yes ☒ No ☐
Temp. room temp Vac. Yes Time 3hours
FAX Service ☐ EMAIL Service ☐
FAX# /EMAIL thomas.kolle@chem.uit.no
Rush Service ☐ (SEE CURRENT
Phone Service ☐ PRICE LIST)
Phone No. +47 77644060 / +47 97560780

Date Received AUG 11 2008
Date Completed AUG 12 2008
Remarks:

Figure S7. Elemental composition of $Br_8T(p\text{-}OMeP)C$