Electronic Supplementary Information for:

Annulated Bacteriochlorins for Near-Infrared Photophysical Studies

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1. Synthetic studies toward β,β-annulated bacteriochlorins

Several general approaches to β,β-annulated bacteriochlorins are outlined in Chart S1 and developed further in the following text and diagrams.

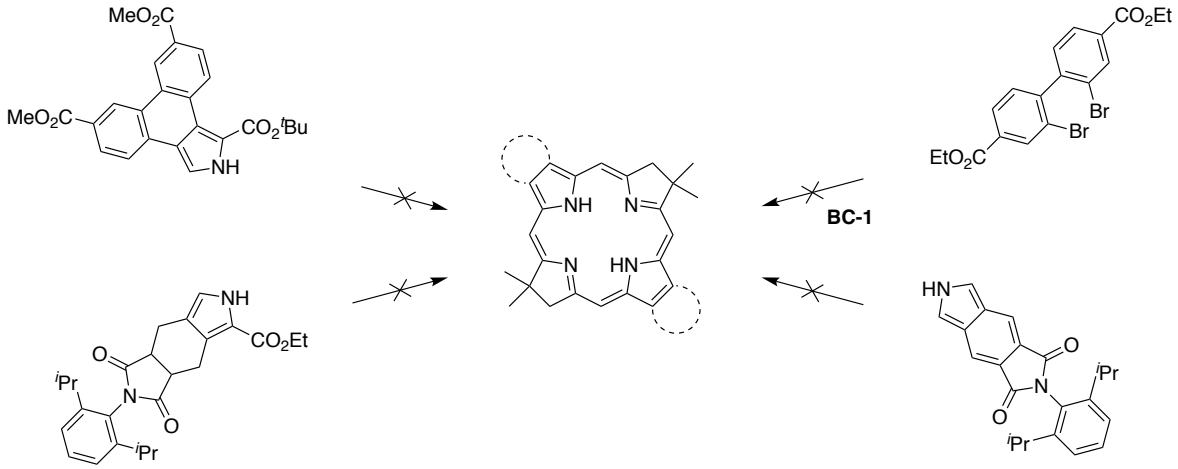
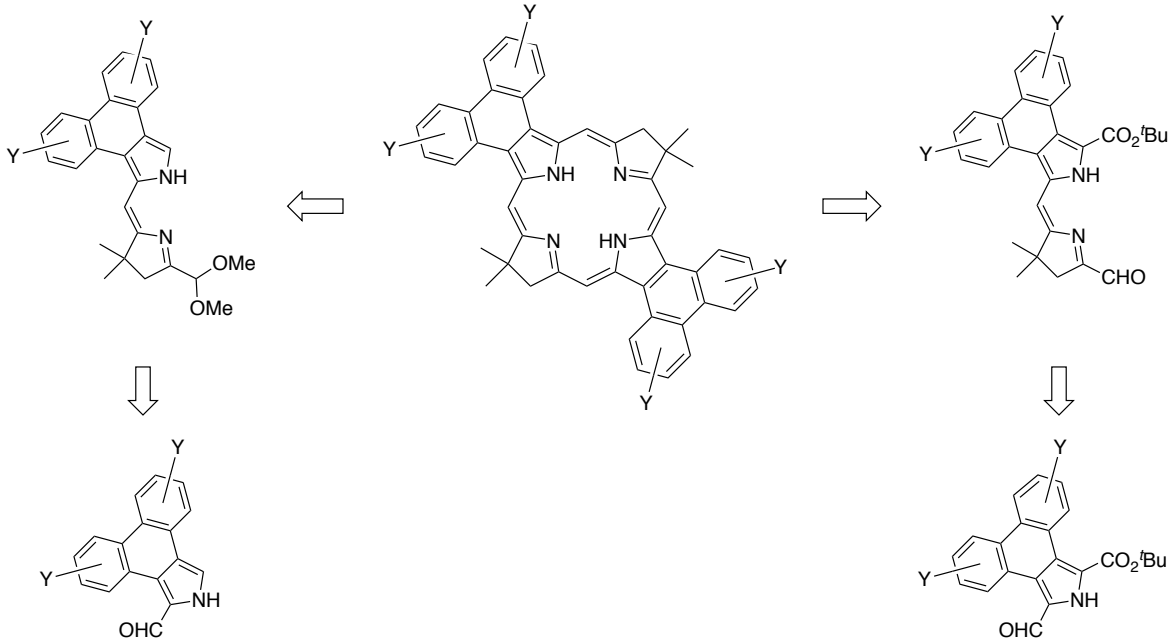


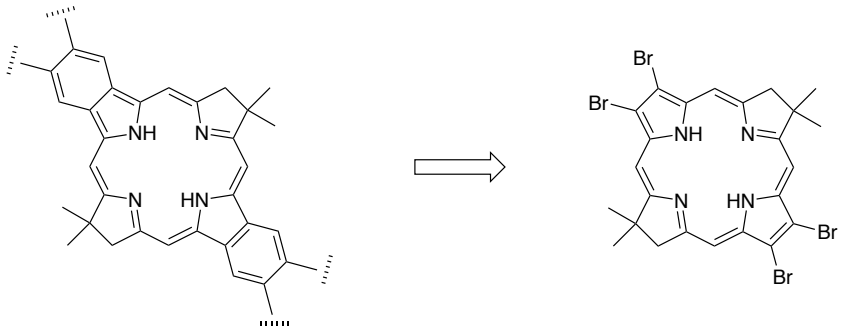
Chart S1. Summary of attempted syntheses toward β,β-annulated bacteriochlorins bearing electron-withdrawing groups.

Inspired by the success of the synthesis of phenanthrene-annulated porphyrins,[68] we first pursued the synthesis of phenanthrene-annulated bacteriochlorins as outlined in Scheme S1.



Scheme S1. Retrosynthetic analysis of a phenanthrene-annulated bacteriochlorin starting from a phenanthrene-annulated pyrrole (Y = H, COR).

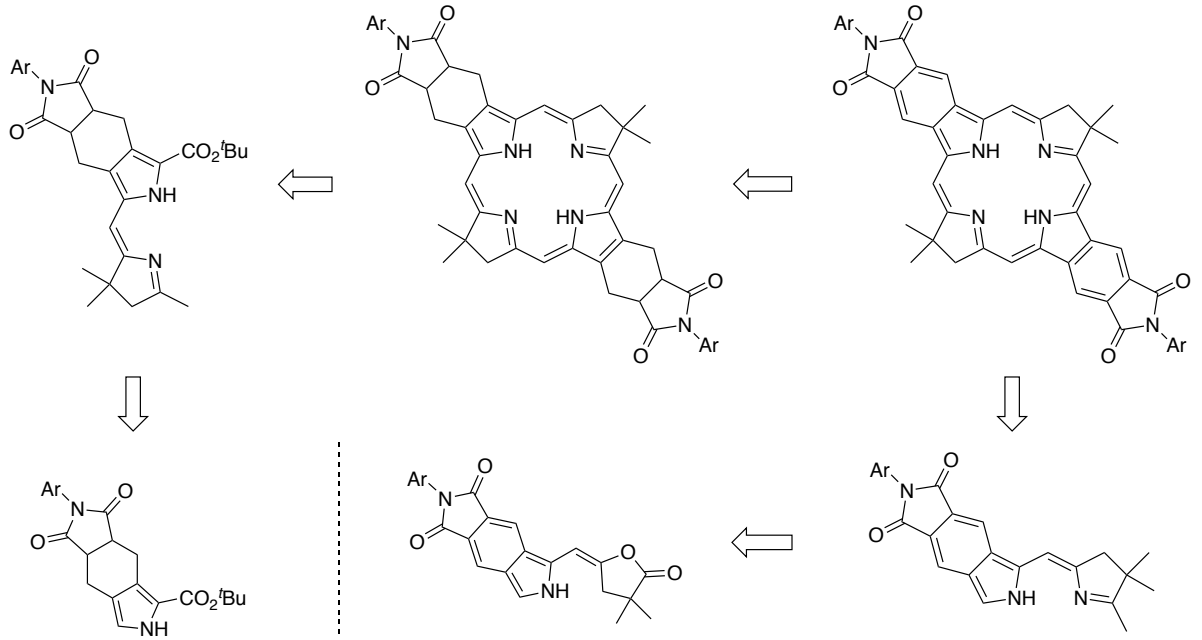
During our trials concerning the synthesis of β,β-phenanthrene-annulated bacteriochlorins, we found that electron-withdrawing groups, such as ester groups, were crucial to stabilize the target bacteriochlorin; the presence of ester groups was also considered a potential means to improve the solubility. Various attempts were explored towards the synthesis of tetraester-substituted dibenzannulated bacteriochlorins from a tetrabromo-bacteriochlorin (Scheme S2), but these turned out to be unsuccessful. Generally speaking, several different types of coupling reaction are known to work well on the tetrabromo-bacteriochlorin, but the stability of bacteriochlorins and/or products derived therefrom became a critical limitation for ring-closure processes.



Scheme S2. Retrosynthetic analysis of a benzannulated bacteriochlorin starting from a tetrabromobacteriochlorin.

We tried to simplify the annulated aromatic structure from phenanthrene to a single benzene ring. Two possible routes were taken into consideration (Scheme S3). An imide was introduced to improve the stability and solubility. The first route started from an imide-substituted isoindole, which was not sufficiently stable for further coupling reactions. The

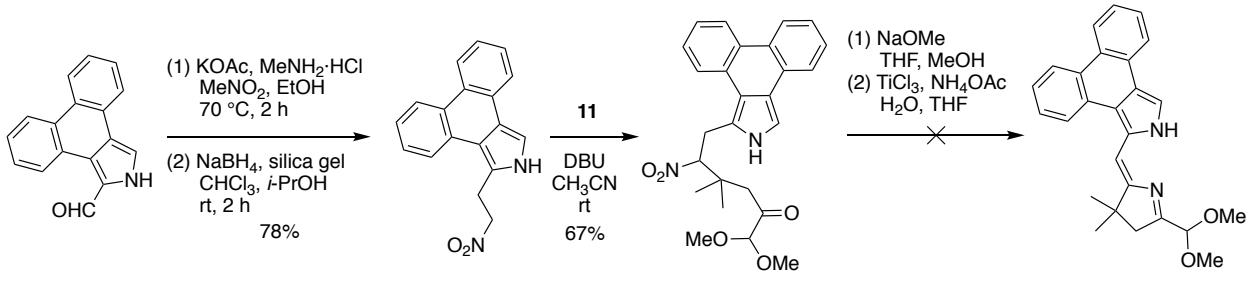
second route started from a pyrrole annulated with a cyclohexane ring following the synthesis of tetraalkylbacteriochlorins[44] with the aim to finish the aromatization at the last stage. This route failed at the beginning, however, owing to incompatible reaction conditions leading to the precursor dihydrodipyrrin.



Scheme S3. Retrosynthetic analysis of a dibenzo-annulated bacteriochlorin, starting from an isoindole or tetrahydroisoindole.

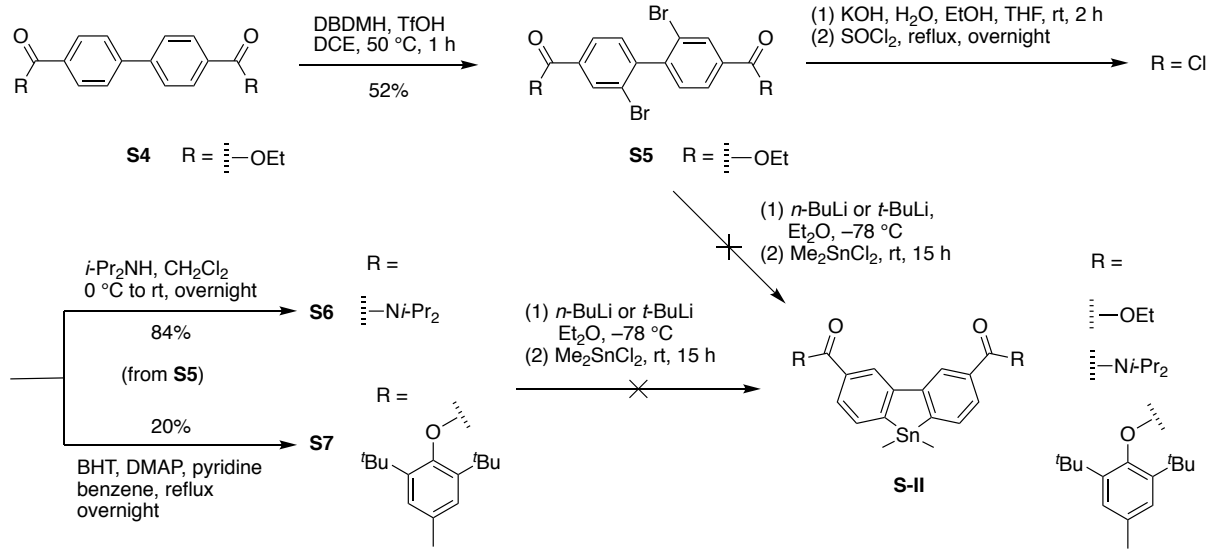
Altogether, we attempted to gain access to compounds **S-I – S-VII**. These various routes are outlined below and are accompanied by synthetic procedures and characterization data in the Experimental Section.

The phenthanthrene-annulated dihydrodipyrrin **S-I** was perhaps the simplest target. Reaction of **S1**[S1] via the Henry reaction and reduction afforded **S2**, which upon Michael addition with Michael acceptor **11** gave **S3**, but the McMurry-like reaction leading to the dihydrodipyrrin was not successful because the target compound decomposed (Scheme S4). To our knowledge, compounds **S2** and **S3** are new.



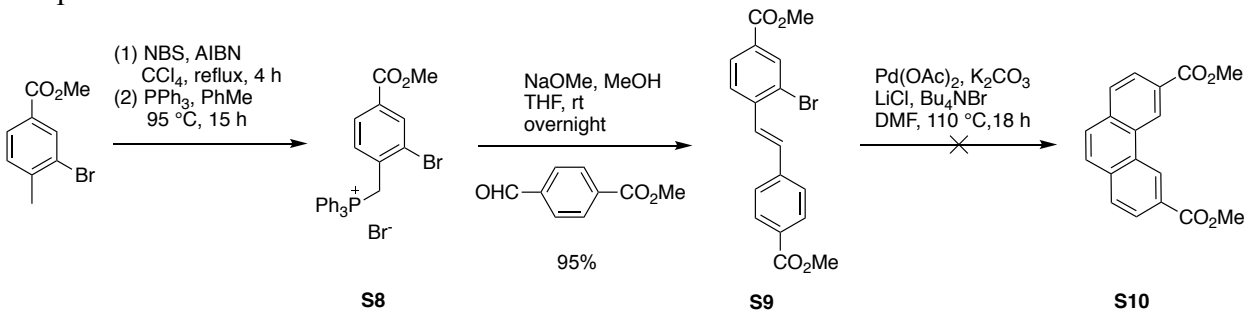
Scheme S4. Attempted synthesis of a phenanthrene-annulated dihydrodipyrrin–acetal (**S-I**).

A set of stannafluorenes (**S-II**) was prepared with expectations that one or more of such compounds might be used in annulation of the tetrabromobacteriochlorin. But the requirement for the solubilizing motifs appeared to thwart the synthesis, which began with commercially available biphenyldiester **S4** (Scheme S5). To our knowledge, compounds **S5–S7** are new.



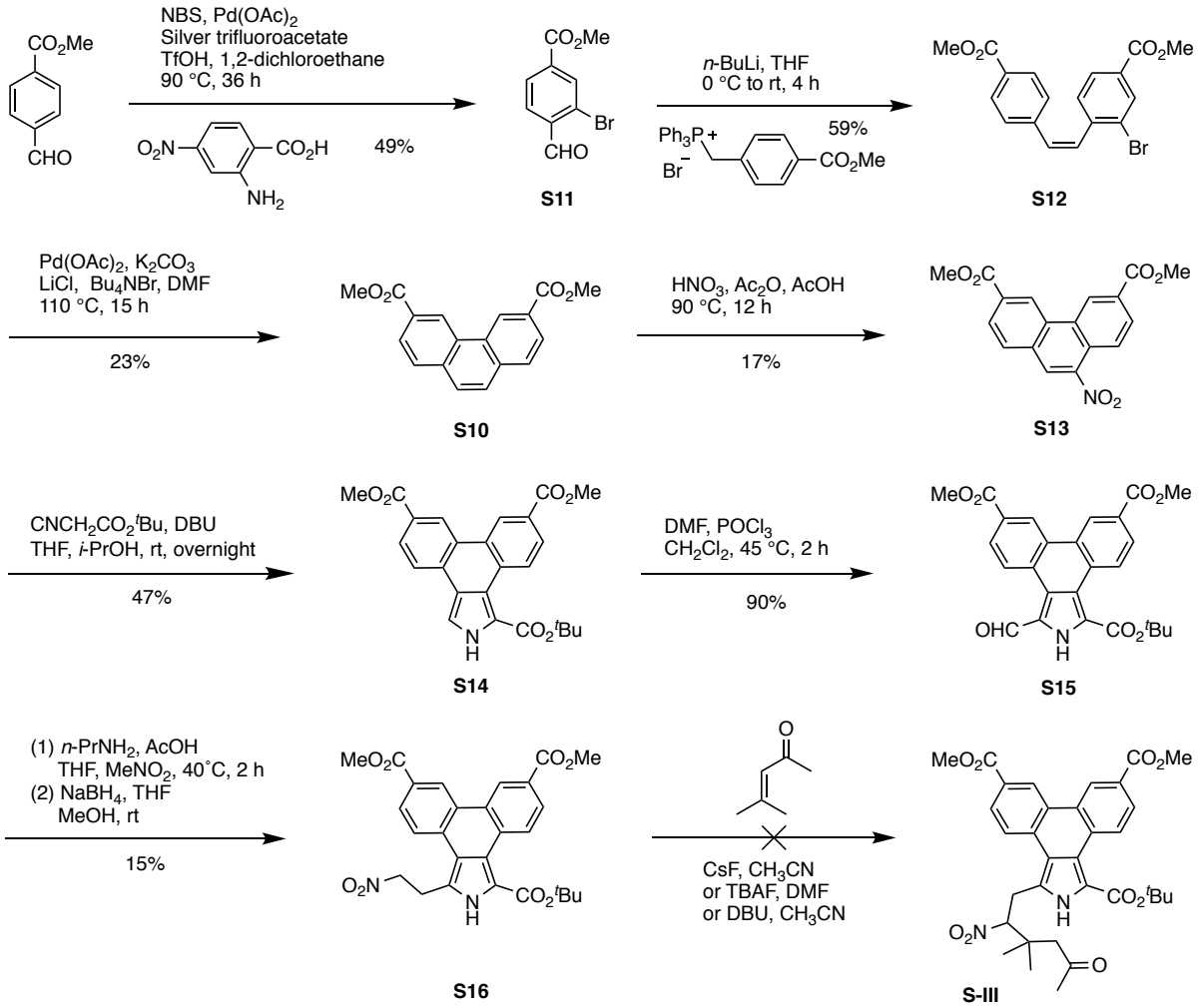
Scheme S5. Attempted synthesis of carbonyl-substituted stannafluorenes (**S-II**).

We next turned to the synthesis of a phenanthrene-annulated pyrrole bearing two esters on the phenanthrene unit for solubility, and one ester on the pyrrole for electronic stabilization. Such a pyrrole could then be subjected to the standard pathway for dihydrodipyrrin synthesis. An early method via the intermediates **S8** and **S9** was pursued to prepare the requisite phenanthrene-diester **S10**, but the route was not successful (Scheme S6). To our knowledge, compounds **S8** and **S9** are new.



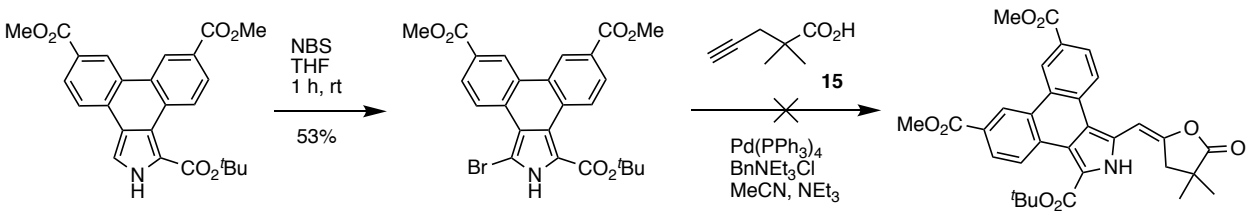
Scheme S6. Attempted synthesis of diester-substituted phenanthrenes.

A longer route to the phenanthrene-annulated pyrrole bearing two esters on the phenanthrene unit and one ester on the pyrrole was then pursued (Scheme S7). Known benzaldehyde **S11**[S2] was converted successfully, via crude **S12**, to the desired phenanthrene-diester **S10**. Subsequent elaboration successfully afforded the phenanthrene-annulated pyrrole bearing two esters on the phenanthrene unit and one ester on the pyrrole (**S14**), which was subjected to Vilsmeier formylation to give **S15**. Henry reaction and reduction were successful, yielding the 2-(2-nitroethyl)pyrrole **S16**, but Michael addition with **S16** and mesityl oxide failed, thwarting access to the target compound **S-III**, which would ultimately lead to a diester analogue of **S-I**. To our knowledge, compounds **S10** and **S12–S16** are new.



Scheme S7. Attempted synthesis of a diester-substituted phenanthrene-annulated pyrrole (**S-III**).

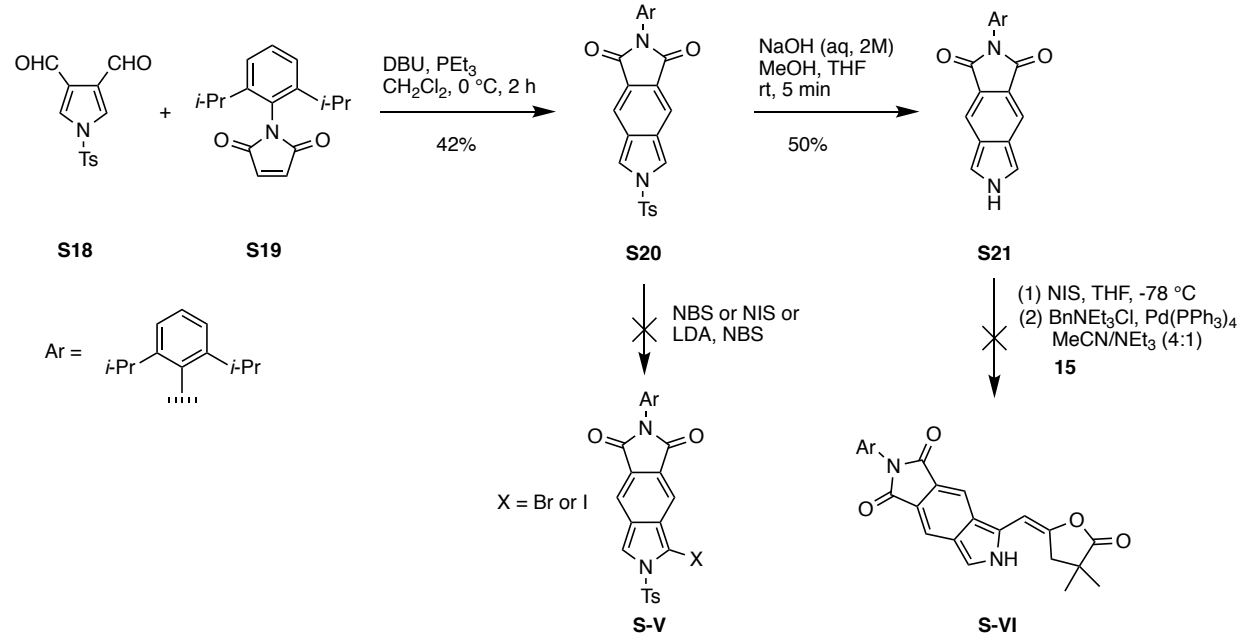
We then pursued the "Northern-Southern" route[45] to access a dihydrodipyrrin rather than the "Eastern-Western" route[42] explored in Scheme S4 and Scheme S7. The Northern-Southern route requires an α-halopyrrole. The phenanthrene-annulated pyrrole **S14** was brominated smoothly to give **S17** (Scheme S8). Here, attempts to couple **S17** with an alkynoic acid only gave the debrominated pyrrole **S14**, without the formation of the target pyrrole–lactone **S-IV**. Compound **S-IV**, like **S-III**, was to be an intermediate on the path to a diester analogue of **S-I**. Explanations of this failure might stem from steric hindrance of the phenanthrene ring, and/or the change in reactivity of the aromatic system due to the presence of the two ester groups. Still, this outcome is surprising, as previously we converted a *tert*-butyl 3,4-dialkylpyrrole-2-carboxylate via the Northern-Southern route to form the corresponding dihydrodipyrrin.[44] Regardless of precedent, in both cases the routes to the diester-substituted β,β-phenanthrene-annulated dihydrodipyrrin were unsuccessful. To our knowledge, compound **S17** is new.



S14 **S17** **S-IV**

Scheme S8. Attempted coupling of a diester-substituted phenanthrene-annulated pyrrole and an alkynoic acid to form an annulated pyrrole–ene–lactone (**S-IV**).

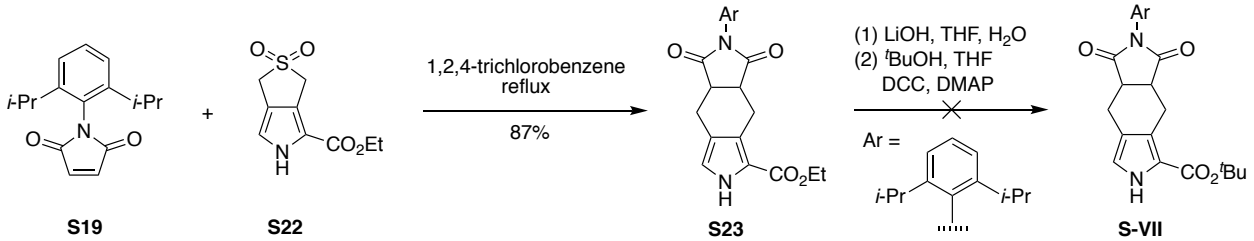
At this point we reconnoitered and targeted imide-substituted benzannulated pyrroles in the dihydrodipyrrin precursors to bacteriochlorins. The specific initial targets were **S-V** and **S-VI** (Scheme S9), which were to be elaborated via chemistry established as part of the Northern-Southern route into the corresponding dihydrodipyrrins. Thus, reaction of *N*-tosylpyrrole-3,4-dicarboxaldehyde (**S18**)[S3] with *N*-(2,6-diisopropylphenyl)maleimide (**S19**)[S4] gave the isoindole **S20**, which was detosylated to give **S21**. Neither **S20** nor **S21** could be converted (the latter upon iodination and Pd-mediated alkynylation with alkynoic acid **15**) to the target **S-V** or **S-VI**, respectively. To our knowledge, compounds **S20** and **S21** are new.



S18 **S19** **S20** **S21** **S-V** **S-VI**

Scheme S9. Attempted synthesis of an isoindole–lactone (**S-V**) and an annulated pyrrole–ene–lactone (**S-VI**).

Finally, maleimide **S19** and sulfono-pyrrole **S22**[S5,S6] were reacted to give the cyclohexane-annulated pyrrole **S23** in good yield (Scheme S10). Note that **S23** is expected as a racemic mixture. Saponification followed by esterification with *tert*-butyl alcohol on the target pyrrole failed, however. The imide was hydrolyzed prior to the ester group, which can be attributed to the extra strain from the diisopropyl-substituted phenyl group. Thus, the target pyrrole **S-VII**, again an intermediate on the path to a dihydrodipyrrin, was not obtained. To our knowledge, compound **S23** is new.



Scheme S10. Attempted synthesis of a cyclohexane-annulated pyrrole (**S-VII**).

Experimental Section

Non-commercial compounds **S1**,[S1] **S11**,[S2] **S18**,[S3] **S19**,[S4] and **S22**[S5,S6] were prepared via literature procedures.

1-(2-Nitroethyl)-2*H*-dibenzo[*e,g*]isoindole (S2). Following a general procedure,[43] a mixture of **S1** (0.490 g, 2.00 mmol), potassium acetate (0.157 g, 1.60 mmol), and methylamine hydrochloride (0.108 g, 1.60 mmol) in absolute ethanol (4 mL) was treated with nitromethane (0.54 mL, 10 mmol). The reaction mixture was heated at 70 °C for 2 h, and then CH_2Cl_2 and water were added. The organic layer was dried (Na_2SO_4) and concentrated. The resulting yellow solid was dried under high vacuum, and then used directly in the next step. The crude solid material was dissolved in $CHCl_3$/2-propanol (3:1, 60 mL), treated with silica (4 g) and $NaBH_4$ (0.151 g, 4 mmol), and stirred at room temperature under argon for 2 h. The reaction mixture was filtered. The filtrate was concentrated. The resulting crude material was dissolved in CH_2Cl_2. The organic solution was washed (water, brine), dried (Na_2SO_4), and concentrated to afford a pale brown solid (0.45 g, 78%): mp 260–262 °C; ^{1}H NMR (400 MHz) δ 3.78 (t, J = 6.8 Hz, 2H), 4.68 (t, J = 6.8 Hz, 2H), 7.37–7.53 (m, 5H), 7.89 (d, J = 3.2 Hz, 1H), 7.96 (d, J = 8.4 Hz, 1H), 8.42 (d, J = 7.6 Hz, 1H), 8.50 (d, J = 8.0 Hz, 1H), 8.83 (br s, 1H); ^{13}C NMR (100 MHz) δ 26.9, 73.9, 109.2, 115.2, 118.9, 121.1, 122.8, 123.0, 123.5, 124.2, 125.0, 125.4, 127.25, 127.28, 128.50, 128.52, 129.0, 129.6; ESI-MS obsd 291.1121, calcd 291.1128 [$(M + H)^+$, M = $C_{18}H_{14}N_2O_2$].

6-(2*H*-Dibenzo[*e,g*]isoindol-1-yl)-1,1-dimethoxy-4,4-dimethyl-5-nitrohexan-2-one (S3). Following a general procedure,[43] a mixture of **S2** (58 mg, 0.20 mmol) and **11** (38 mg, 0.24 mmol) in CH_3CN (0.2 mL) was treated with DBU (89 µL, 0.60 mmol). The reaction mixture was stirred at room temperature under argon for 16 h, diluted with ethyl acetate (30 mL), and washed with water and brine. The organic layer was dried (Na_2SO_4) and concentrated. The resulting crude solid was triturated with diethyl ether. Filtration afforded a pale brown solid (60 mg, 67%); ^{1}H NMR (400 MHz) δ 1.26 (s, 3H), 1.45 (s, 3H), 2.75 (ABq, $\Delta\delta_{AB}$ = 0.10, J = 18.8 Hz, 2H), 3.41 (s, 3H), 3.43 (s, 3H), 3.76 (d, J = 6.8 Hz, 1H), 3.78 (s, 1H), 4.36 (s, 1H), 5.40–5.44 (m, 1H), 7.40–7.56 (m, 5H), 7.95–8.00 (m, 2H), 8.42–8.44 (m, 1H), 8.51 (dd, J = 8.0 Hz and 1.2 Hz, 1H), 8.75 (br s, 1H); ^{13}C NMR (100 MHz) δ 24.0, 24.3, 27.8, 36.7, 44.7, 55.18, 55.24, 93.7, 104.7, 109.4, 115.4, 118.9, 120.9, 123.0, 123.3, 123.4, 124.0, 124.8, 125.2, 127.0, 127.1, 128.5, 128.7, 129.2, 129.5, 203.4; ESI-MS obsd 449.2070, calcd 449.2071 [$(M + H)^+$, M = $C_{26}H_{28}N_2O_5$].

(*Z*)-1-((5-(Dimethoxymethyl)-3,3-dimethyl-3,4-dihydro-*2H*-pyrrol-2-ylidene)methyl)-2H-dibenzo[*e,g*]isoindole (S-I). Following a general procedure,[43] in a first flask a solution of **S3** (30 mg, 0.067 mmol) in freshly distilled THF (3.0 mL) and anhydrous MeOH (30 µL) at 0 °C was treated with NaOMe (11 mg, 0.21 mmol). The mixture was stirred and degassed by bubbling argon through the solution for 45 min. In a second flask purged with argon, $TiCl_3$ (0.41 mL, 20% w/v in 2N HCl solution, 0.54 mmol), 5 mL of THF, and NH_4OAc

(284 mg, 3.69 mmol) were combined under argon, and the mixture was degassed by bubbling with argon for 45 min. Then the first flask mixture was transferred via cannula to the buffered $TiCl_3$ mixture. The resulting mixture was stirred at room temperature for 16 h under argon. Saturated aqueous $NaHCO_3$ was added, and the resulting mixture was then extracted with ethyl acetate. The organic phase was washed with brine, dried (Na_2SO_4), and concentrated. The crude product decomposed immediately.

2,2′-Dibromo-4,4′-diethoxycarbonylbiphenyl (S5). A solution of 4,4′-diethoxycarbonylbiphenyl (**S4**, 2.983 g, 9.999 mmol) and 1,3-dibromo-5,5-dimethylhydantoin (3.002 g, 10.50 mmol) in 1,2-dichloroethane (20.0 mL) was treated with TfOH (1.8 mL, 20 mmol) at room temperature. The reaction mixture was heated at 50 °C for 1 h and then allowed to cool to room temperature. The mixture was washed with saturated aqueous $NaHCO_3$ (60 mL) and brine (20 mL). The organic layer was dried (Na_2SO_4), filtered, and concentrated under reduced pressure. Column chromatography [silica, hexanes/ethyl acetate (40:1)] afforded a white solid (2.39 g, 52%): ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.36 (d, J = 1.4 Hz, 2H), 8.01 (dd, J = 1.4, 8.2 Hz, 2H), 7.31 (d, J = 8.2 Hz, 2H), 4.42 (q, J = 7.0 Hz, 4H), 1.43 (t, J = 7.0 Hz, 6H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 165.1, 145.6, 133.9, 132.1, 130.7, 128.4, 123.2,61.7, 14.4; ESI-MS obsd 456.9483, calcd 456.9488 [$(M + H)^+$, M = $C_{18}H_{16}Br_2O_4$].

2,2′-Dibromo-*N*,*N*,*N*′,*N*′-tetraisopropyl-[1,1′-biphenyl]-4,4′-dicarboxamide (S6). A mixture containing **S5** (0.228 g, 0.500 mmol) in EtOH/H_2O/THF (1/1/1, 1.5 mL) was treated with KOH (0.084 g, 1.50 mmol), and the resulting mixture was stirred at room temperature for 2 h. Then the mixture was carefully quenched with 2 M HCl, extracted with ethyl acetate (2 x 5 mL) and dried over Na_2SO_4. The combined organic extract was concentrated under reduced pressure to afford the corresponding dicarboxylic acid as a white solid (0.200 g, quantitative), which was used directly for further transformations. The dicarboxylic acid was refluxed with $SOCl_2$ (1.5 mL) under argon for 18 h. Then, excess $SOCl_2$ was removed under vacuum, and the resulting residue was used as such for further transformations. Thus, the residue was treated with diisopropylamine (0.42 mL, 3.0 mmol) at 0 °C in CH_2Cl_2 (2.0 mL). Then, the reaction mixture was allowed to warm to room temperature, and stirring was continued for 18 h. The reaction mixture was washed with 2 M HCl and saturated aqueous NH_4Cl solution, treated with ethyl acetate (2 x 5 mL), and washed with brine. The organic layer was dried (Na_2SO_4), concentrated and chromatographed [silica, hexanes/ethyl acetate (9:1)] to afford a colorless solid (0.239 g, 84%): ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.22 (br s, 12H), 1.54 (br s, 12H), 3.55 (br s, 2H), 3.91 (br s, 2H), 7.24 (s, 1H), 7.26 (s, 1H), 7.32 (dd, J = 7.6, 1.6 Hz, 2H), 7.63 (d, J = 1.6 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 20.8, 46.1, 51.1, 123.5, 124.5, 130.0, 131.1, 140.1, 141.8, 168.9; ESI-MS obsd 565.1057, calcd 565.1060 [$(M + H)^+$, M = $C_{26}H_{34}Br_2N_2O_2$].

Bis(2,6-di-*tert*-butyl-4-methylphenyl) 2,2′-dibromo-[1,1′-biphenyl]-4,4′-dicarboxylate (S7). A reaction mixture of **S5** (0.456 g, 1.00 mmol) in EtOH/H_2O/THF (1/1/1, 3.0 mL) was treated with KOH (0.168 g, 2.99 mmol), and the resulting mixture was stirred at room temperature for 2 h. Then the mixture was carefully quenched with 2 M HCl, extracted with ethyl acetate (2 x 10 mL), and dried over Na_2SO_4. The combined organic extract was concentrated under vacuum to afford the corresponding dicarboxylic acid as a white solid (0.400 g, quantitative), which was used directly for further transformations. The dicarboxylic acid was refluxed with $SOCl_2$ (3.0 mL) under argon atmosphere for 18 h. Then, the excess $SOCl_2$ was removed under vacuum, and the resulting residue was used as such for further transformations. Thus, the resulting residue was treated overnight with 2,6-di-*tert*-butyl-4-hydroxytoluene (0.441 g, 2.00 mmol) and DMAP (0.244 g, 2.00 mmol) in benzene/pyridine (1:1, 3.0 mL) under reflux. Then, the reaction mixture was allowed to cool to room temperature. The reaction mixture was

washed with saturated aqueous NH_4Cl solution, extracted with ethyl acetate (2 x 10 mL) and washed with brine. The organic layer was dried (Na_2SO_4) and concentrated. The resulting crude material was chromatographed [silica, hexanes/ethyl acetate (9:1)] to afford a pale yellow solid (0.162 g, 20%): ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.36 (s, 36H), 2.37 (s, 6H), 6.98 (s, 1H), 7.19 (s, 4H), 7.47 (d, J = 7.6 Hz, 2H), 8.26 (dd, J = 7.6, 1.2 Hz, 2H), 8.54 (d, J = 1.6 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 21.3, 21.7, 30.4, 31.8, 34.3, 35.4, 123.6, 125.6, 127.3, 128.3, 129.0, 131.2, 132.3, 134.6, 135.0, 135.8, 142.2, 145.8, 146.0, 151.6, 165.5; ESI-MS obsd 820.2571, calcd 820.2571 [$(M + NH_4)^+$, M = $C_{44}H_{52}Br_2O_4$]. Note: The presence of atropisomers may account for the observed number of protons and carbons.

(2-Bromo-4-(methoxycarbonyl)benzyl)triphenylphosphonium bromide (S8). Following a literature procedure[S7] with slight modification, a mixture of methyl 3-bromo-4-methylbenzoate (0.23 g, 1.0 mmol) and reagent-grade (not recrystallized) NBS (0.18 g, 1.0 mmol) in CCl_4 (26.0 mL) was treated with AIBN (3.0 mg, 16 μmol). The resulting mixture was heated overnight at reflux. After allowing to cool to room temperature, the mixture was filtered. The filtrate was concentrated under vacuum. The resulting residue was chromatographed (silica, gradient of 0–5% ethyl acetate in hexanes) to afford methyl 3-bromo-4-(bromomethyl)benzoate as a colorless solid (121 mg, 39%): ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.92 (s, 3H), 4.60 (s, 2H), 7.52 (d, J = 7.6 Hz, 1H), 7.95 (d, J = 6.4 Hz, 1H), 8.23 (s, 1H); ^{13}C NMR (400 MHz, $CDCl_3$) δ 32.3, 52.6, 124.4, 129.0, 131.2, 131.8, 134.5, 141.8, 165.3. ESI-MS obsd 306.8966, calcd 306.8964 [$(M + H)^+$, M = $C_9H_8Br_2O_2$]. The resulting methyl 3-bromo-4-(bromomethyl)benzoate (69.0 mg, 0.224 mmol) was treated with PPh_3 (58.8 mg, 0.224 mmol) in toluene and refluxed overnight. After allowing to cool to room temperature, the mixture was filtered. The solid phosphonium bromide was dried under high vacuum and utilized directly for the next reaction.

Methyl (*E*)-3-bromo-4-(4-(methoxycarbonyl)styryl)benzoate (S9). Following a reported procedure[S8] with slight modification, a mixture of **S8** (128 mg, 0.224 mmol) and methyl 4-formylbenzoate (36.8 mg, 0.224 mmol) in THF (1.0 mL) was treated with a solution of NaOMe in MeOH (97 μL of 25 wt% solution, 0.45 mmol). The reaction mixture was stirred overnight under nitrogen and was then neutralized by the addition of 1M HCl. The resulting mixture was extracted with CH_2Cl_2. The extract was washed with water (2x) and brine (2x), dried over Na_2SO_4, and filtered. The filtrate was concentrated and chromatographed [silica, hexanes/ethyl acetate (10:1)] to obtain a colorless solid (80 mg, 95%): ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.94 (s, 6H), 7.17 (d, J = 16.0 Hz, 1H), 7.58 (d, J = 16.4 Hz, 1H), 7.62 (d, J = 8.4 Hz, 2H), 7.74 (d, J = 8.4 Hz, 1H), 7.98 (dd, J = 8.0, 1.2 Hz, 1H), 8.06 (d, J = 8.0 Hz, 2H), 8.27 (d, J = 1.2 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 52.1, 52.4, 124.0, 126.4, 126.7, 126.9, 128.5, 128.7, 129.7, 130.0, 130.6, 132.3, 133.3, 134.3, 140.6, 140.7, 165.4, 166.6; ESI-MS obsd 375.0228, calcd 375.0227 [$(M + H)^+$, M = $C_{18}H_{15}BrO_4$].

Dimethyl phenanthrene-3,6-dicarboxylate (S10). Following a general procedure,[S9] a mixture of **S9** (2.01 g, 5.36 mmol), K_2CO_3 (3.71 g, 26.8 mmol), LiCl (0.34 g, 8.0 mmol), *n*-Bu_4NBr (10.7 mmol, 3.45 g), and $Pd(OAc)_2$ (0.24 g, 1.07 mmol) in DMF (60 mL) was added to a Schlenk flask and deaerated by three freeze-pump-thaw cycles, followed by heating at 110 °C for 15 h. After allowing to cool to room temperature, the mixture was poured into water (250 mL) and extracted with CH_2Cl_2 (2 x 200 mL). The combined organic extract was washed with brine (2 x 200 mL), dried over Na_2SO_4 and concentrated. The resulting residue was chromatographed [silica, hexanes/ethyl acetate/CH_2Cl_2 (15:1:0 to 20:2:5)] to give a colorless crystalline solid (696.4 mg, 23.4%): mp 207–208 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.06 (s, 6H), 7.86 (s, 2H), 7.95 (d, J = 11.2 Hz, 2H), 8.25 (dd, J = 10.8, 2.0 Hz, 2H), 9.48 (s, 2H); ^{13}C NMR

(100 MHz, $CDCl_3$) δ 52.5, 125.3, 127.2, 128.6, 128.8, 128.9, 130.1, 134.9, 167.3; ESI-MS obsd 295.0966, calcd 295.0965 [$(M + H)^+$, M = $C_{18}H_{14}O_4$].

Methyl (*Z*)-3-bromo-4-(4-(methoxycarbonyl)styryl)benzoate (S12). Following a general procedure,[S9] a reaction mixture of (4-(methoxycarbonyl)benzyl)triphenylphosphonium bromide (3.78 g, 7.69 mmol) in THF (30.0 ml) under argon at 0 °C was treated dropwise with a 1.6 M solution of *n*-BuLi in hexane (4.82 mL, 7.7 mmol). The resulting red solution was stirred for 30 min. A solution of **S11** (1.87 g, 7.69 mmol) in THF (20.0 mL) was added dropwise, discoloring the solution. The solution was then allowed to warm to room temperature, and then further stirred for 30 min. After addition of water (50 mL), the mixture was extracted with hexanes (3 x 50 mL). The combined organic extract was dried over Na_2SO_4 and concentrated. TLC analysis showed three components. The residue was chromatographed [silica, hexanes/ethyl acetate (10:1)] to give a viscous liquid (1.7 g, 59%) comprised of two components – the title compound and a closely chromatographing unknown – followed by **S9** (0.82 g, 28%). The mixture of the title compound and the unknown could be used directly in the next step. Note that **S9** and **S12** are *E* and *Z* isomers, respectively.

Dimethyl 9-nitrophenanthrene-3,6-dicarboxylate (S13). Following a general procedure with modification,[68] a slurry of **S12** (0.87 g, 3.0 mmol) in glacial acetic acid (3.2 mL) and acetic anhydride (2.0 mL) was heated to 45 °C, whereupon HNO_3 (2.0 mL, 70%) was slowly added dropwise to avoid an overly vigorous reaction. Then the mixture was heated at 90 °C for 12 h. After allowing to cool to room temperature, the resulting orange solution was poured into 20 mL of ice-water and extracted with CH_2Cl_2 (2 x 25 mL). The combined organic extract was washed with water (25.0 mL), saturated aqueous $NaHCO_3$ solution (25.0 mL), and brine (25.0 mL). The resulting crude material showed two spots on TLC [silica, hexanes/ethyl acetate (4:1)]: starting material (R_f = 0.40) and product (R_f = 0.27). The organic layer was dried over Na_2SO_4, concentrated and chromatographed [silica, hexanes/ethyl acetate/CH_2Cl_2 (15:1:0 to 20:2:5)] to give unreacted starting material (178 mg, 20%) and then a light-yellow solid (172 mg, 17%): mp 215–216 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 4.09 (s, 6H), 8.11 (d, *J* = 8.4 Hz, 1H), 8.25-8.40 (m, 2H), 8.50-8.60 (s, 2H), 9.49 (s, 1H), 9.54 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 52.6, 52.7, 124.3, 124.9, 125.1, 125.7, 126.3, 128.1, 128.4, 129.6, 130.6, 130.9, 131.4, 131.5, 131.7, 147.0, 166.4, 166.5; ESI-MS obsd 340.0811, calcd 340.0816 [$(M + H)^+$, M = $C_{18}H_{13}NO_6$].

1-*tert*-Butyl-6,9-dimethyl 2*H*-dibenzo[*e*,*g*]isoindole-1,6,9-tricarboxylate (S14). Following a general procedure,[68] a mixture of **S13** (398.3 mg, 1.174 mmol) and *tert*-butyl isocyanoacetate (331.4 mg, 2.348 mmol) in THF/2-propanol (1:1, 10.0 mL) was treated dropwise with DBU (354 µL, 2.36 mmol). The mixture was stirred overnight at room temperature. Then the reaction mixture was diluted with ethyl acetate (50 mL), washed with water (30 mL), dried over Na_2SO_4, and concentrated. The resulting residue was chromatographed [silica, hexanes/ethyl acetate (4:1 to 2:1)] to give a pale yellow solid (242 mg, 48%): mp 210–211 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.72 (s, 9H), 4.03 (s, 3H), 4.04 (s, 3H), 7.75 (d, *J* = 3.6 Hz, 1H), 8.01 (d, *J* = 8.4 Hz, 1H), 8.11 (dd, *J* = 8.8, 1.6 Hz, 1H), 8.20 (dd, *J* = 8.8,1.6 Hz, 1H), 9.20 (s, 1H), 9.22 (s, 1H), 9.74 (d, *J* = 8.8 Hz, 1H), 10.10 (br s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 28.6, 52.3, 82.5, 115.2, 118.7, 122.5, 122.9, 125.2, 125.8, 127.3, 127.6, 127.8, 127.9, 128.2, 128.6, 129.8, 131.3, 131.4, 159.9, 167.3, 167.4; ESI-MS obsd 434.1592, calcd 434.1598 [$(M + H)^+$, M = $C_{25}H_{23}NO_6$].

1-*tert*-Butyl-6,9-dimethyl 3-formyl-2*H*-dibenzo[*e*,*g*]isoindole-1,6,9-tricarboxylate (S15). Following a reported procedure[S1] with slight modification, a mixture of **S14** (175.0 mg, 0.4037 mmol) in CH_2Cl_2 (0.8 mL) was treated with DMF (93 µL, 1.2 mmol), cooled in an ice-

bath, and then $POCl_3$ (112 μL, 1.20 mmol) was added dropwise. Then the ice-bath was removed, and the mixture was stirred at 40 °C for 2 h. The mixture was then allowed to cool to 25–30 °C, whereupon a solution of sodium acetate (1.0 g) in water (4.0 mL) was added dropwise, and the reaction mixture was refluxed for an additional 15 min. The two layers were separated, and the aqueous portion of the mixture was extracted with ethyl acetate. The combined organic extract was washed with saturated Na_2CO_3 solution, dried over Na_2SO_4, and concentrated to afford a brown solid (116.0 mg, 90%): mp 178 °C (dec.); ^{1}H NMR (400 MHz, THF-d_8) δ 1.75 (s, 9H), 3.99 (s, 3H), 4.00 (s, 3H), 8.15-8.18 (m, 2H), 9.20 (s, 2H), 9.34 (dd, J = 8.5, 1.9 Hz, 2H), 9.55 (dd, J = 8.6, 2.0 Hz, 2H), 10.36 (s, 1H); ^{13}C NMR (100 MHz, THF-d_8) δ 27.44, 51.35, 51.38, 83.24, 123.0, 123.8, 124.3, 124.5, 124.6, 127.1, 127.5, 127.8, 127.9, 128.3, 128.8, 129.3, 129.6, 130.2, 130.3, 159.8, 165.9, 166.0, 179.8; ESI-MS obsd 462.1539, calcd 462.1547 [$(M + H)^+$, M = $C_{26}H_{23}NO_7$].

1-*tert*-Butyl-6,9-dimethyl 3-(2-nitroethyl)-2*H*-dibenzo[*e*,*g*]isoindole-1,6,9-tricarboxylate (S16). Following a reported procedure,[43] a mixture of **S15** (60.3 mg, 0.131 mmol), acetic acid (12 μL) and *n*-propylamine (24 μL) in nitromethane (2 mL) and THF (4 mL) was heated at 40 °C for 1.5 h. Then the resulting solution was concentrated and dried under high vacuum. The resulting oil was dissolved in $CHCl_3$/2-propanol (4 mL, 3:1) and treated with silica (100 mg). $NaBH_4$ (12.5 mg, 0.33 mmol) was added, and the mixture was stirred at room temperature under argon for 1 h. Then 5 drops of methanol were added, and stirring was continued for 30 min. The reaction mixture was filtered. The filtrate was concentrated and chromatographed (silica, hexanes/ethyl acetate, 1:1) to afford a viscous oil (26 mg), which comprised a mixture of pyrrole **S14** and desired compound **S16**. The formation of the desired 2-(2-nitroethyl)pyrrole **S16** was identified by mass spectrometry and by ^{1}H NMR spectroscopy: two triplet peaks at 4.86 (J = 6.9 Hz, 2H) and 3.97 (J = 7.0 Hz, 2H) ppm. However, this mixture could not be further separated and purified due to the essentially identical R_f values of **S14** and **S16** on TLC. The ratio of **S14** and **S16** (60:40) was evaluated by integration of the ^{1}H NMR spectrum. ESI-MS obsd 507.1742, calcd 507.1762 [$(M + H)^+$, M = $C_{27}H_{26}N_2O_8$].

1-*tert*-Butyl-6,9-dimethyl 3-bromo-2*H*-dibenzo[*e*,*g*]isoindole-1,6,9-tricarboxylate (S17). A mixture of **S14** (31.5 mg, 72.7 μmol) in THF (1.5 mL) was treated with NBS (15.6 mg, 87.6 μmol) at room temperature and stirred for 1 h. The mixture was concentrated and chromatographed [silica, hexanes/ethyl acetate (4:1)] to afford a light yellow solid (20.0 mg, 54%): ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.73 (s, 9H), 4.04 (s, 6H), 7.75 (m, 2H), 9.07 (d, J = 8.5 Hz, 1H), 9.32 (d, J = 8.6 Hz, 2H), 9.77 (d, J = 8.6 Hz, 1H), 9.88 (br s, 1H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 28.53, 29.71, 52.35, 83.24, 122.5, 125.3. 125.6, 127.8, 127.9, 128.6, 129,1. 130.0, 167.1; ESI-MS obsd 512.0680, calcd 512.0703 [$(M + H)^+$, M = $C_{25}H_{22}BrNO_6$].

2-(2,6-Diisopropylphenyl)-6-tosylpyrrolo[3,4-*f*]isoindole-1,3(2*H*,6*H*)-dione (S20). Following a reported procedure[S10] with slight modification, a solution of **S18** (0.335 g, 1.21 mmol) and **S19** (0.467 g, 1.81 mmol) in anhydrous CH_2Cl_2 (6 mL) in a 50 mL flask was chilled to 0 °C under argon. A second solution of triethylphosphine (265 μL, 1.80 mmol) and DBU (19 μL, 1.3 mmol) in anhydrous CH_2Cl_2 (6 mL) was added in one portion. The resulting solution became orange immediately and slowly turned to brown. After 2 h, the mixture was concentrated and chromatographed (silica, hexanes/ethyl acetate, 5:1) to afford a light yellow solid (253 mg, 42%): mp 124 °C (dec.); ^{1}H NMR (600 MHz, acetone-d_6) δ 1.13 (d, J = 6.8 Hz, 12H), 2.44 (s, 3H), 2.77 (septet, J = 6.9 Hz, 2H, overlapped by HDO peak in acetone-d_6), 7.33 (d, J = 7.8 Hz, 2H), 7.46 (t, J = 7.8 Hz, 1H), 7.53 (d, J = 7.7 Hz, 2H), 8.07 (d, J = 8.5 Hz, 2H), 8.23 (s, 2H), 8.25 (s, 2H); ^{13}C NMR (150 MHz, acetone-d_6) δ 22.49, 25.02, 25.05, 25.07, 26.71, 36.15, 118.0, 121.7, 125.4, 125.5, 127.3, 127.8, 129.5, 130.0, 131.3, 131.4, 131.6, 132.4, 136.5, 148.2,

148.8, 148.9, 168.9, 178.9; ESI-MS obsd 501.1835, calcd 501.1843 [$(M + H)^+$, M = $C_{29}H_{28}N_2O_4S$].

2-(2,6-Diisopropylphenyl)pyrrolo[3,4-*f*]isoindole-1,3(2*H*,6*H*)-dione (S21). A solution of **S20** (216 mg, 0.431 mmol) in methanol and THF (4 mL, 3:1) was treated with aqueous NaOH (1 mL of 2 M solution, 2 mmol). The mixture turned black in a few seconds and was further stirred for 5 min. Water (30 mL) and ethyl acetate (2 x 15 mL) were added. The organic phase was dried over Na_2SO_4 and concentrated. The resulting residue was chromatographed (silica, deactivated by 5% triethylamine in hexanes, hexanes/ethyl acetate, 2:1 to 1:1) to afford a brown solid (75 mg, 50%): mp 150 °C (dec.); ^{1}H NMR (600 MHz, CD_3OD) δ 1.72 (d, J = 6.8 Hz, 12H), 2.76 (septet, J = 6.9 Hz, 2H), 7.32 (d, J = 7.8 Hz, 2H), 7.46 (t, J = 7.9 Hz, 1H), 7.67 (s, 2H), 8.27 (s, 2H); ^{13}C NMR (150 MHz, CD_3OD) δ 22.80, 29.16, 114.5, 119.9, 121.8, 123.5, 124.3, 127.8, 129.6, 147.2, 169.2; ESI-MS obsd 347.1744, calcd 347.1754 [$(M + H)^+$, M = $C_{22}H_{22}N_2O_2$].

Iodination and coupling trial of S21. A solution of isoindole **S21** (32.3 mg, 93.2 μmol) in freshly distilled THF (6 mL) was chilled to –78 °C, stirred vigorously for a few minutes, and treated with NIS (21.0 mg, 93.3 μmol) in three portions. After 15 min, the mixture was concentrated in the dark and quickly chromatographed [deactivated silica, hexanes/ethyl acetate (2:1 to 1:1)]. The resulting crude product with impurities was concentrated, dried under high vacuum with avoidance of light, and used directly in the next step. The formation of the mono-iodinated isoindole was inferred by three peaks in the ^{1}H NMR spectrum: 7.84 (d, J = 1 Hz, 1H), 7.93 (s, 1H) and 8.24 (d, J = 1 Hz, 1H).

Ethyl 6-(2,6-diisopropylphenyl)-5,7-dioxo-2,4,4a,5,6,7,7a,8-octahydropyrrolo[3,4-*f*]isoindole-1-carboxylate (S23). Followed a reported procedure,[S6] a solution of **S22** (779.7 mg, 3.401 mmol) in 1,2,4-trichlorobenzene (67 mL) was treated with **S19** (1.77 g, 6.88 mmol), and the mixture was refluxed for 3.5 h. The solution was allowed to cool to room temperature, and then directly transferred to a column packed with silica. The solvent was eluted with hexanes and the residue was further eluted [silica, hexanes/ethyl acetate (5:1 to 2:1)] and concentrated to give a grey solid (1.25 g, 87%): mp 225–227 °C; ^{1}H NMR (600 MHz, $CDCl_3$) δ 0.78 (d, J = 6.8 Hz, 3H), 0.81 (d, J = 6.8 Hz, 3H), 1.14 (d, J = 2.3 Hz, 3H), 1.15 (d, J = 2.3 Hz, 3H), 1.26 (sextet, J = 6.2 Hz, 1H), 1.34 (t, J = 7.1 Hz, 3H), 2.58 (septet, J = 6.8 Hz, 1H), 2.76 (dd, J =14.9, 6.3 Hz, 1H), 2.83 (dd, J = 15.3, 7.0 Hz, 1H), 3.35 (d, J = 14.9 Hz, 1H), 3.51–3.57 (m, 2H), 3.98 (d, J = 14.6 Hz, 1H), 4.25–4.29 (m, 1H), 4.31–4.38 (m, 1H), 6.79 (d, J = 2.8 Hz, 1H), 7.09 (d, J = 7.7 Hz, 1H), 7.18 (d, J = 7.8 Hz, 1H), 7.32 (t, J = 7.7 Hz, 1H), 8.92 (br, 1H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 14.44, 21.89, 22.58, 23.83, 23.84, 23.90, 24.17, 28.43, 29.25, 40.47, 40.86, 60.36, 118.2, 118.7, 120.0, 123.7, 124.0, 127.5, 129.9, 145.5, 146.2, 179.5, 179.6; ESI-MS obsd 423.2278, calcd 423.2257 [$(M + H)^+$, M = $C_{25}H_{30}N_2O_4$].

2. X-Ray structure of 18

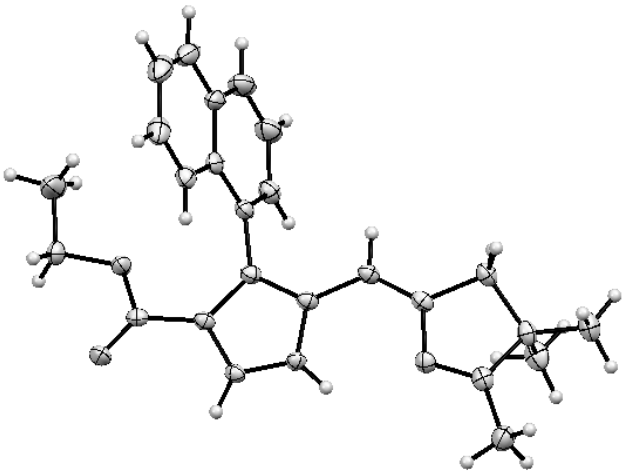


Figure S1. ORTEP drawing of the single-crystal X-ray structure of dihydrodipyrrin **18**. All ellipsoids are contoured at the 50% level.

Table S1. Summary of single-crystal X-ray data for dihydrodipyrrin **18.**

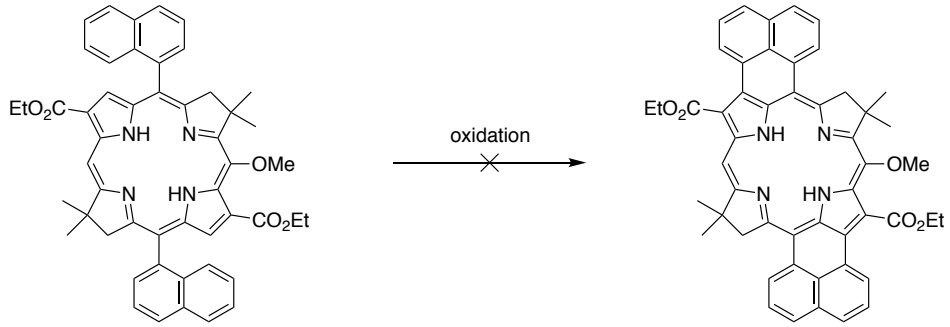
CCDC registry	1900118
Formula	$C_{25}H_{26}N_2O_2$
Formula Weight (g/mol)	386.48
Crystal Dimensions (mm)	0.088×0.144×0.199
Crystal System	monoclinic
Space Group	P 1 21/n 1
Temperature (K)	121(2)
a (Å)	15.7670(4)
b (Å)	7.3416(2)
c (Å)	18.1519(4)
α (°)	90
β (°)	94.7904(10)
γ (°)	90
V (Å^3)	2093.83(9)
Number of reflections to determine final unit cell	30616
Min and Max 2θ for cell determination (°)	4.503, 50.98
Z	4
F(000)	824
ρ (g/cm^3)	1.226
λ (Å, Mo Kα)	0.71073
μ (mm^{-1})	0.078
Max 2θ for data collection (°)	1.79, 27.11
Measured fraction of data	0.999
Number of reflections measured	30616
Unique reflections measured	4625
R_{merge}	0.0439
Number of parameters in least-squares	269
R_1	0.0476
wR_2	0.1138
R_1 (all data)	0.0724
wR_2 (all data)	0.1264

3. Attempted oxidative annulations

Table S2. Bacteriochlorins subjected to oxidative conditions for annulation.

Bacteriochlorin	Conditions	Results
BC-4	DDQ, CH_2Cl_2	Decomposition to oxidized products (oxobacteriochlorin, tentatively assigned by MALDI *m/z* = 780)
BC-4	$FeCl_3$, $CH_2Cl_2/MeNO_2$	No reaction
BC-5	DDQ, CH_2Cl_2	Decomposition to oxidized products
BC-5	DDQ, $Sc(OTf)_3$, CH_2Cl_2	Decomposition to oxidized products
BC-5	$FeCl_3$, DTBP, $CH_2Cl_2/MeNO_2$	No reaction
BC-6	$FeCl_3$, $CH_2Cl_2/MeNO_2$	Decomposition to a mixture of unidentified porphyrins, chlorins, and bacteriochlorins
BC-7	DDQ, $Sc(OTf)_3$, CH_2Cl_2	Decomposition
BC-7	$FeCl_3$, DTBP, $CH_2Cl_2/MeNO_2$	Decomposition
BC-8	DDQ, $Sc(OTf)_3$, CH_2Cl_2	Decomposition to oxidized products
BC-8	DDQ, DTBP, $Sc(OTf)_3$, CH_2Cl_2	Decomposition to oxidized products
BC-8	$FeCl_3$, DTBP, CH_2Cl_2	Decomposition

Table S3. Summary of reaction conditions from attempted oxidative annulation of **BC-9**.

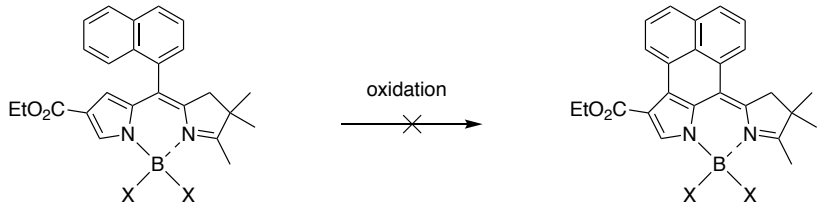


BC-9

Entry	Oxidizing reagent (equiv)	Solvent	Temperature (°C)/Time	Observation
1	DDQ (3)	CH_2Cl_2	rt/3 h	decomposed[b]
2	DDQ (5)/$Sc(OTf)_3$ (5)	CH_2Cl_2	rt/2 h	decomposed[b]
3	$FeCl_3$ (10)	CH_2Cl_2	rt/12 h	no reaction
4	$FeCl_3$ (10)	$CH_2Cl_2/MeNO_2$	40/20 h	no reaction
4	$PhI(OCOCH_3)_2$ (1)	CH_2Cl_2	40/12 h	no reaction
5	$PhI(OCOCF_3)_2$ (1)	CH_2Cl_2	40/12 h	no reaction
6	$PhI(OCOCF_3)_2$ (1) /$BF_3{\cdot}OEt_2$ (2)	CH_2Cl_2	rt/12 h	no reaction
7	$AlCl_3$ (26)/NaCl (11)	neat	140/5 h	no reaction

[a]Reactions were conducted using **BC-9** (4 mM) and monitored by absorption spectroscopy. [b]Bacteriochlorin **BC-9** was slowly oxidized into an oxobacteriochlorin and then decomposed.

Table S4. Summary of reaction conditions from attempted oxidative annulation of **S23** and **S24**.



S24, X = F
S25, X = Bu

Entry	Compound	Oxidizing reagent	Solvent	Temperature (°C)/Time	Observation
1[a]	**S24**	$FeCl_3$	$CH_2Cl_2/MeNO_2$	rt/30 min	decomposed
2[a]	**S24**	$FeCl_3$	$CH_2Cl_2/MeNO_2$	0 °C/30 min	decomposed
3[a]	**S24**	$FeCl_3$/DTBP	$CH_2Cl_2/MeNO_2$	rt/30 min	no reaction
4[b]	**S24**	$PhI(OCOCF_3)_2$/ $BF_3{\cdot}OEt_2$	CH_2Cl_2	rt/2 h	no reaction
5[c]	**S24**	$FeCl_3$/ cat. $BF_3{\cdot}OEt_2$	CH_2Cl_2	rt/30 min	decomposed
6[a]	**S24**	DDQ/$Sc(OTf)_3$	CH_2Cl_2	rt/1 h	decomposed
7[a]	**S24**	DDQ/ $BF_3{\cdot}OEt_2$	CH_2Cl_2	rt/1 h	decomposed
8[a]	**S24**	$FeBr_3$	$CH_2Cl_2/MeNO_2$	rt/30 min	decomposed
9[b]	**S24**	$PhI(OCOCF_3)_2$/ $BF_3{\cdot}OEt_2$	toluene	110 °C/5 h	no reaction
10[d]	**S24**	$AuCl_3$/AgOTf	DCE	rt/15 h	no reaction
11[d]	**S24**	$AuCl_3$/AgOTf	DCE	80 °C/6 h	decomposed
12[e]	**S24**	$AlCl_3$/NaCl	neat	150 °C/15 h	no reaction
13[a]	**S24**	$Fe(ClO_4)_3{\cdot}2H_2O$	$CH_2Cl_2/MeNO_2$	rt/30 min	decomposed
14[f]	**S25**	$FeCl_3$	$CH_2Cl_2/MeNO_2$	rt/6 h	multiple spots observed in TLC
15[f]	**S25**	DDQ/$Sc(OTf)_3$	CH_2Cl_2	rt/15 h	decomposed
16[f]	**S25**	$Fe(ClO_4)_3{\cdot}2H_2O$	$CH_2Cl_2/MeNO_2$	rt/30 min	multiple spots observed in TLC

[a]Reactions were conducted using **S24** (5 mM), oxidizing reagent (25 mM), DTBP (50 mM). [b]$PhI(OCOCF_3)_2$ (2.5 mM), $BF_3{\cdot}OEt_2$ (5 mM). [c]$FeCl_3$ (50 mM), $BF_3{\cdot}OEt_2$ (2.5 mM). [d]$AuCl_3$ (1.5 mM), AgOTf (9 mM); DCE refers to 1,2-dichloroethane. [e]$AlCl_3$ (26 equiv), NaCl (11 equiv). [f]**S25** (5 mM), oxidizing reagent (25 mM).

4. X-Ray structure of 21

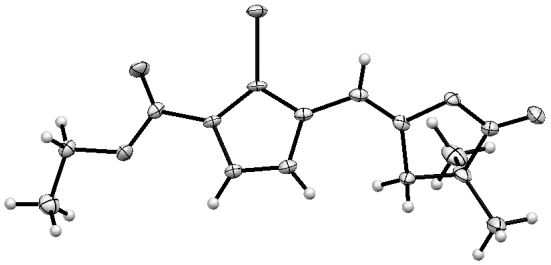


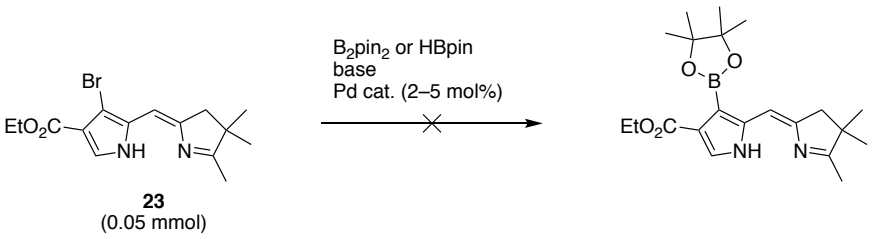
Figure S2. ORTEP drawing of the single-crystal X-ray structure of lactone–pyrrole **21**. All ellipsoids are contoured at the 50% level.

Table S5. Summary of single-crystal X-ray data for **21**.

CCDC registry	1900109
Formula	$C_{14}H_{16}BrNO_4$
Formula Weight (g/mol)	342.19
Crystal Dimensions (mm)	0.087×0.121×0.151
Crystal System	orthorhombic
Space Group	P 21 21 21
Temperature (K)	100(2)
a (Å)	9.6116 (5)
b (Å)	21.6883 (12)
c (Å)	7.1486 (4)
α (°)	90
β (°)	90
γ (°)	90
V (Å^3)	1490.19 (14)
Number of reflections to determine final unit cell	9959
Min and Max 2θ for cell determination (°)	4.635, 58.78
Z	4
F(000)	696
ρ (g/cm^3)	1.525
λ (Å, Mo Kα)	0.71073
μ (mm^{-1})	2.770
Max 2θ for data collection (°)	62.00
Measured fraction of data	0.998
Number of reflections measured	32573
Unique reflections measured	4721
R_{merge}	3.99%
Number of parameters in least-squares	184
R_1	0.0400
wR_2	0.0898
R_1 (all data)	0.0531
wR_2 (all data)	0.0938

5. Attempted Pd-coupling reactions

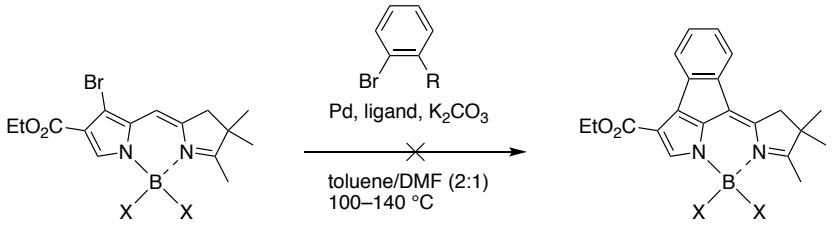
Table S6. Summary of reaction conditions from attempted borylation of **23**.



23
(0.05 mmol)

Entry	Reaction conditions
1	B_2pin_2, KOAc, $PdCl_2(dppf)$, 1,4-dioxane, 90 °C, 30 h
2	B_2pin_2, KOAc, $Pd_2(dba)_3{\cdot}CHCl_3$, SPhos, 1,4-dioxane, 90 °C, 30 h
3	HBpin, NEt_3, $PdCl_2(PhCN)_2$, SPhos, 1,4-dioxane, 80 °C, 33 h

Table S7. Summary of reaction conditions from attempted annulation of a dihydrodipyrrin.



23-BBu$_2$ (X = Bu)
23-BF$_2$ (X = F)

Entry	Compound	R	Pd/Ligand
1	**23-BBu$_2$**	$B(OH)_2$	$Pd(PPh_3)_4$
2	**23-BBu$_2$**	$B(OH)_2$	$Pd_2(dba)_3{\cdot}CHCl_3$/SPhos
3	**23-BBu$_2$**	$B(OH)_2$	$Pd_2(dba)_3{\cdot}CHCl_3$/P(o-tol)$_3$
4	**23-BBu$_2$**	$B(OH)_2$	$Pd_2(dba)_3{\cdot}CHCl_3$/P^{t}Bu$_3{\cdot}HBF_4$
5	**23-BBu$_2$**	$B(OH)_2$	$Pd_2(dba)_3{\cdot}CHCl_3$/PCy$_3{\cdot}HBF_4$
6	**23-BBu$_2$**	$Bpin_2$	$Pd_2(dba)_3{\cdot}CHCl_3$/SPhos
7	**23-BBu$_2$**	$Bpin_2$	$Pd_2(dba)_3{\cdot}CHCl_3$/P(o-tol)$_3$
8	**23-BBu$_2$**	$Bpin_2$	$Pd_2(dba)_3{\cdot}CHCl_3$/P^{t}Bu$_3{\cdot}HBF_4$
9	**23-BBu$_2$**	$Bpin_2$	$Pd_2(dba)_3{\cdot}CHCl_3$/PCy$_3{\cdot}HBF_4$
10[a]	**23-BF$_2$**	$B(OH)_2$	$Pd(PPh_3)_4$
11[b]	**23-BF$_2$**	$B(OH)_2$	$Pd_2(dba)_3{\cdot}CHCl_3$/SPhos
12[c]	**23-BF$_2$**	$B(OH)_2$	$Pd_2(dba)_3{\cdot}CHCl_3$/SPhos

[a]The reaction was carried out at 80 °C. [b]The solvent was *o*-xylene/DMF (2:1). [c]The reaction was carried out at 60 °C.

6. X-Ray structure of 24

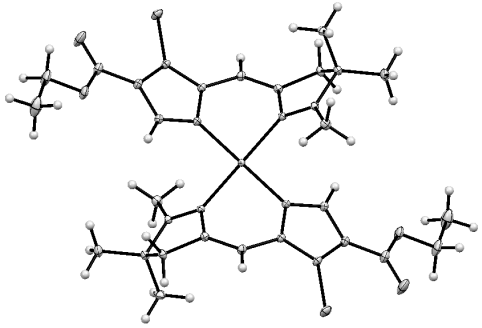


Figure S3. ORTEP drawing of the single-crystal X-ray structure of bis(dipyrrinato)Pd(II) complex **24**. All ellipsoids are contoured at the 50% level.

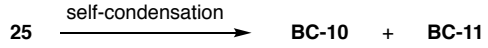
Table S8. Summary of single-crystal X-ray data for bis(dipyrrinato)Pd(II) complex **24**.

CCDC registry	1900117
Formula	$C_{30}H_{36}Br_2N_4O_4Pd$
Formula Weight (g/mol)	782.85
Crystal Dimensions (mm)	0.142×0.212×0.363
Crystal System	monoclinic
Space Group	P 1 21/c 1
Temperature (K)	100(2)
a (Å)	13.0158(3)
b (Å)	8.1799(2)
c (Å)	14.3232(3)
α (°)	90
β (°)	94.1060(9)
γ (°)	90
V (Å^3)	1521.05(6)
Number of reflections to determine final unit cell	505
Min and Max 2θ for cell determination (°)	5.729, 68.65
Z	2
F(000)	784
ρ (g/cm^3)	1.709
λ (Å, Mo Kα)	0.71073
μ (mm^{-1})	3.279
Max 2θ for data collection (°)	80.86
Measured fraction of data	0.998
Number of reflections measured	71519
Unique reflections measured	9654
R_{merge}	2.23%
Number of parameters in least-squares	191
R_1	0.0174
wR_2	0.0421
R_1 (all data)	0.0211
wR_2 (all data)	0.0431

The most pronounced changes in the ^{1}H NMR spectrum upon complexation of dihydrodipyrrin **23** to give Pd(II) complex **24** were as follows: (1) a upfield chemical shift of the resonance of the 1-methyl group from 2.14 ppm to 1.71 ppm; (2) a downfield chemical shift of H^5 from 5.98 ppm to 6.30 ppm; and (3) an upfield chemical shift of the pyrrole-H from 7.45 ppm to 6.80 ppm.

7. Screening of reaction conditions for self-condensation of dihydrodipyrrin 25

Table S9. Summary of reaction conditions from self-condensation of dihydrodipyrrin **25**.



Entry[a]	solvent	TMSOTf (equiv)	DTBP (equiv)	**BC-10** (%)[b]	**BC-11** (%)[b]
1	$CHCl_3$[c]	5	20	1.5	3.3
2	CH_2Cl_2	5	20	7.3	14
3	DCE[d]	5	20	8.5	17
4	DCE	7.5	30	20	22

[a]All reactions were carried out with 18 mM of **25** (0.002 mmol) at room temperature for 20 h. [b]Yields were determined by absorption spectroscopy of samples isolated by chromatography. The measured molar absorption coefficients were used. [c]The $CHCl_3$ (stabilized with amylenes) was dried over 4Å molecular sieves prior to use. [d]DCE refers to 1,2-dichloroethane.

8. Photophysical data for bacteriochlorin BC-2

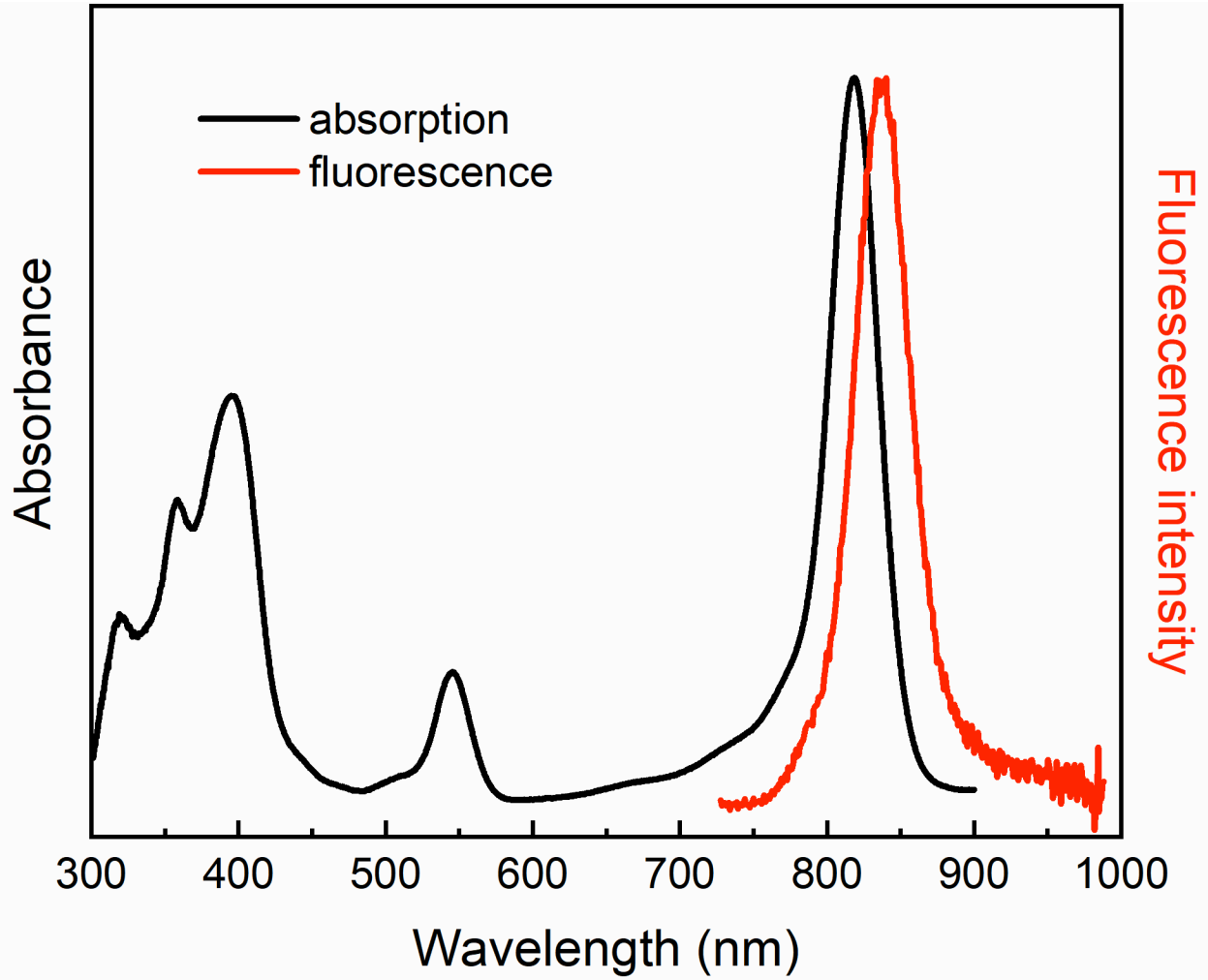


Figure S4. Steady-state absorption (black) and fluorescence emission (red) spectra of **BC-2** recorded in toluene at room temperature, normalized at the maximum. Fluorescence emission was taken after excitation at 357 nm. The same fluorescence spectra were obtained using excitation at 530, 548 and 555 nm.

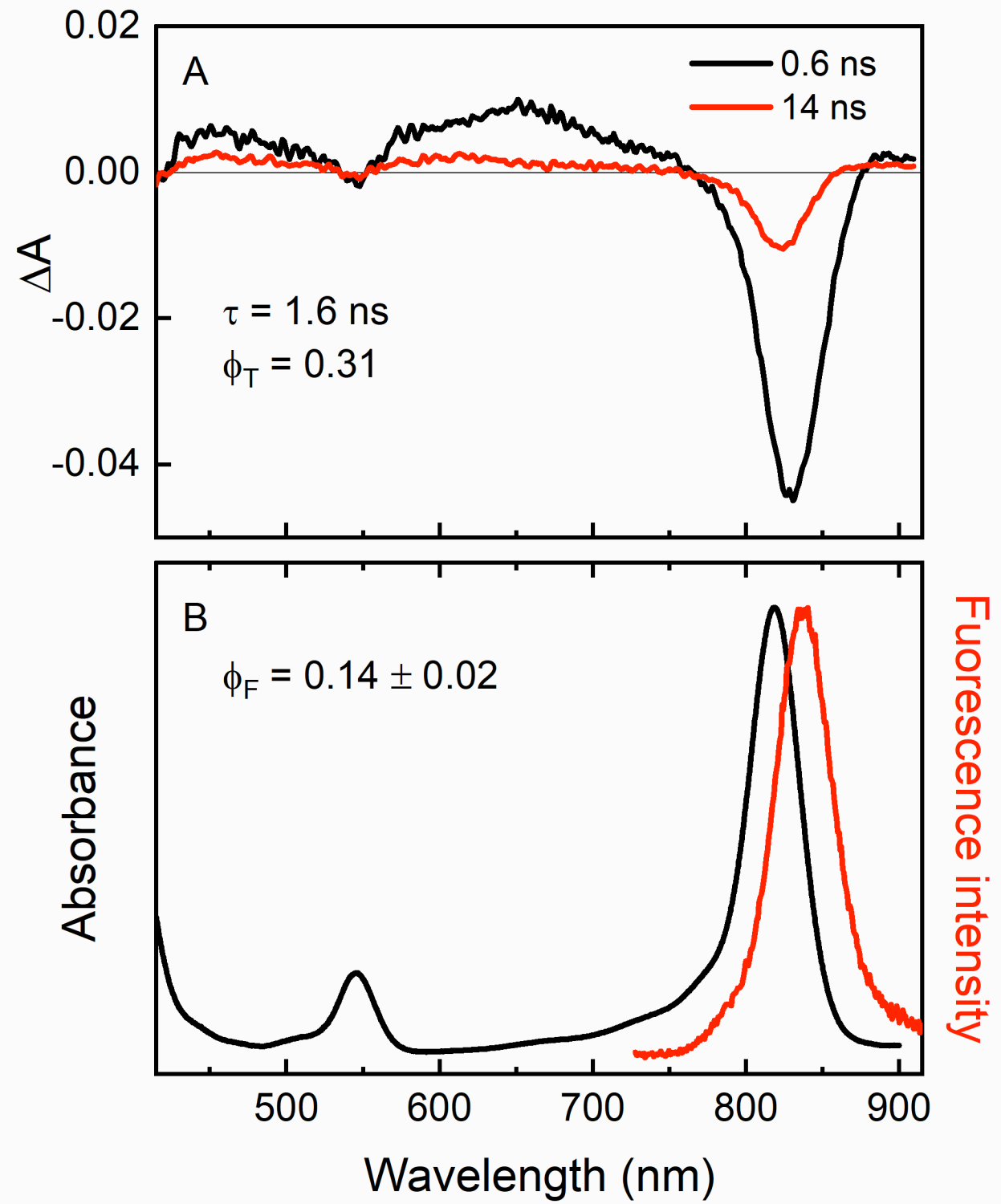


Figure S5. Transient absorption spectra recorded at the indicated time delays (A), and normalized static absorption and fluorescence spectra (B) of **BC-2** taken in toluene at room temperature. τ, singlet lifetime; Φ_T, triplet yield; Φ_F, fluorescence quantum yield. The Φ_F value shown is the average value calculated using fluorescence data obtained after excitation at 357, 530, 548 and 555 nm.

9. Results of TDDFT calculations

Table S10. TDDFT results for **Es-BC** in toluene.[a]

State	λ (nm)	f	filled MO	empty MO	Coefficient[b]	%
S_1	763	0.51	H	L	0.963	93
			H-1	L+1	-0.225	5
S_2	551	0.19	H-1	L	0.918	84
			H	L+1	0.393	15
S_3	351	1.13	H	L+1	0.920	85
			H-1	L	-0.368	14
S_4	321	1.56	H-1	L+1	0.946	90
			H-1	L	0.237	6

[a]H = HOMO and L = LUMO. [b]Coefficient for the configuration, obtained by multiplying the value given from Gaussian by the square root of two. The percent contribution to the state is obtained by squaring the coefficient; in some cases a small contribution from an 'emissive' contribution involving the same orbitals was subtracted to obtain the percentage shown.

Table S11. TDDFT results for **Phen-BC** in toluene.[a]

State	λ (nm)	f	filled MO	empty MO	Coefficient[b]	%
S_1	973	1.0	H	L	0.954	91
			H-1	L	0.208	4
			H-1	L+1	-0.160	3
S_2	682	0.32	H-1	L	0.909	83
			H	L+1	0.309	10
			H	L	-0.218	5
S_3	417	0.06	H-2	L	0.901	81
			H	L+2	0.342	12
S_4	406	0.53	H	L+1	0.899	81
			H-1	L	-0.330	11
			H	L+2	-0.145	2
S_6	376	0.88	H-3	L	0.723	52
			H-1	L+1	0.535	29
			H	L+3	0.226	5
			H-2	L+2	0.186	3
			H	L+1	0.156	2

[a]H = HOMO and L = LUMO. [b]Coefficient for the configuration, obtained by multiplying the value given from Gaussian by the square root of two. The percent contribution to the state is obtained by squaring the coefficient; in some cases a small contribution from an 'emissive' contribution involving the same orbitals was subtracted to obtain the percentage shown.

Table S12. TDDFT results for **Benz-BC** in toluene.[a]

State	λ (nm)	f	filled MO	empty MO	Coefficient[b]	%
S_1	1056	0.38	H	L	0.962	93
			H-1	L	0.147	2
			H-1	L+1	0.148	2
S_2	704	0.41	H-1	L	0.947	90
			H	L+1	-0.248	6
S_4	417	0.23	H	L+1	0.764	58
			H-3	L	0.582	34
			H-2	L+2	-0.155	2
S_5	371	1.4	H-3	L	0.656	43
			H	L+1	-0.526	28
			H-1	L+1	-0.435	19
			H-1	L	-0.234	5
S_7	339	1.4	H-1	L+1	0.842	71
			H-3	L	0.374	14
			H	L+1	-0.230	5
			H	L	-0.167	3

[a]H = HOMO and L = LUMO. [b]Coefficient for the configuration, obtained by multiplying the value given from Gaussian by the square root of two. The percent contribution to the state is obtained by squaring the coefficient; in some cases a small contribution from an 'emissive' contribution involving the same orbitals was subtracted to obtain the percentage shown.

10. References

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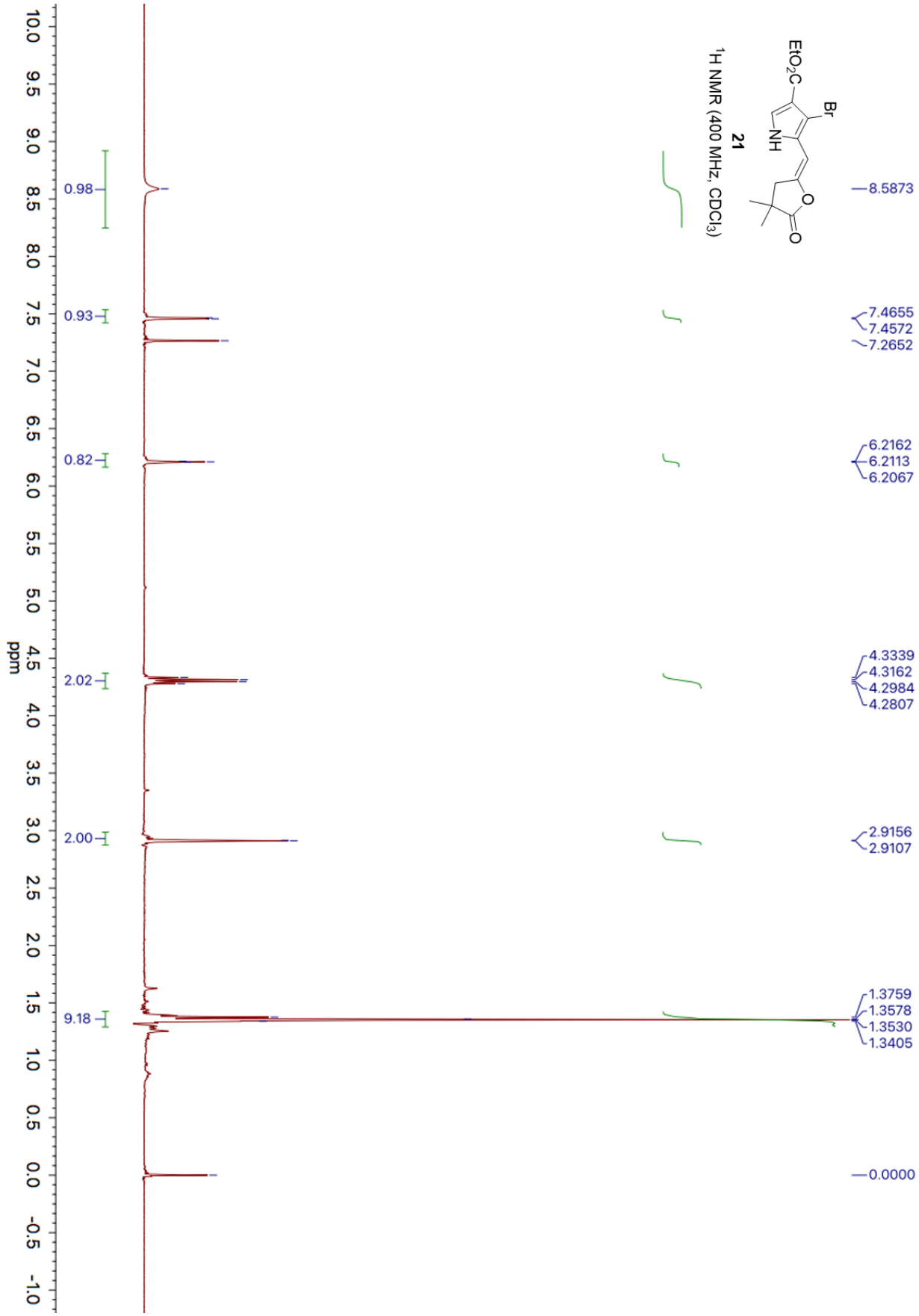
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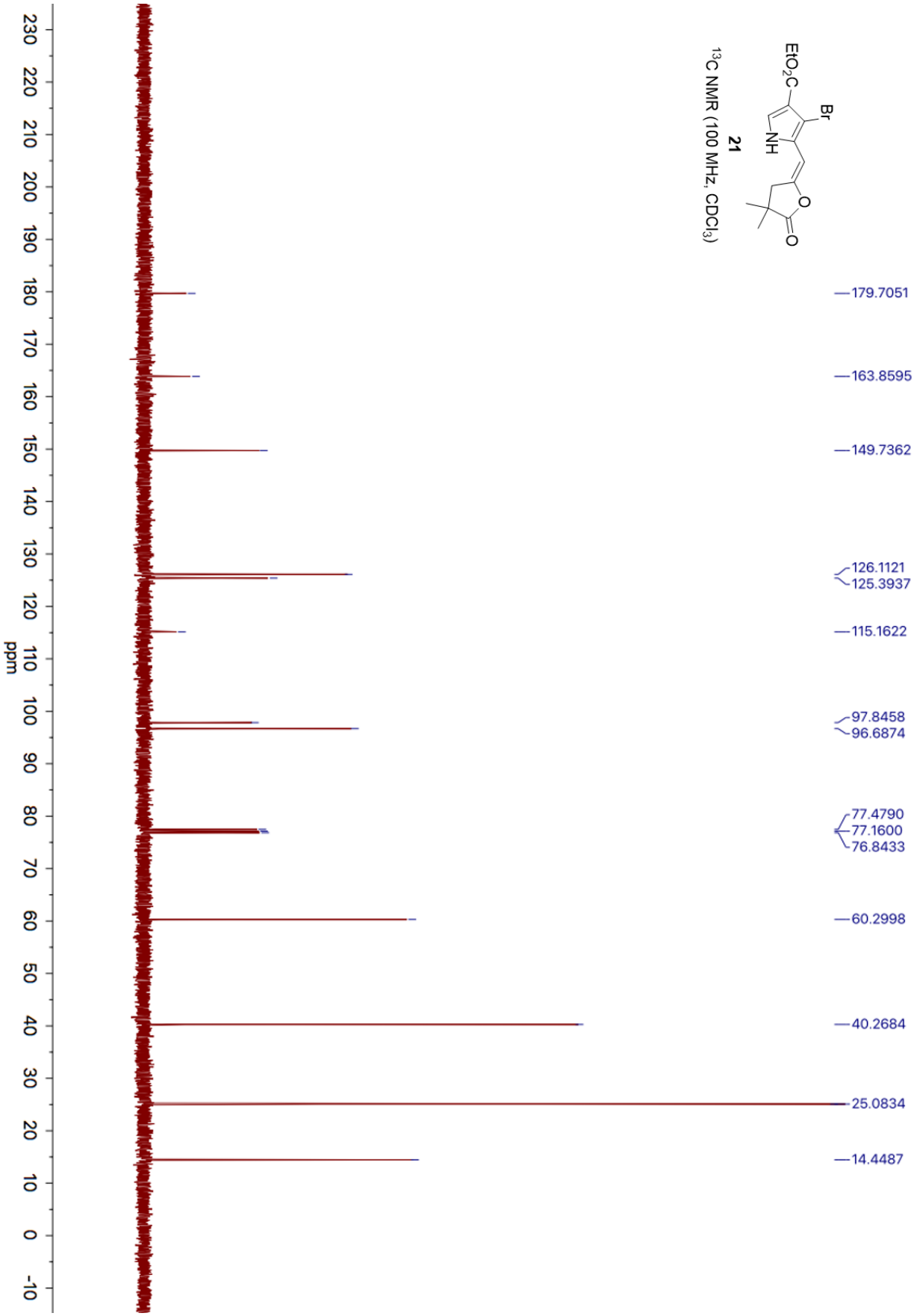
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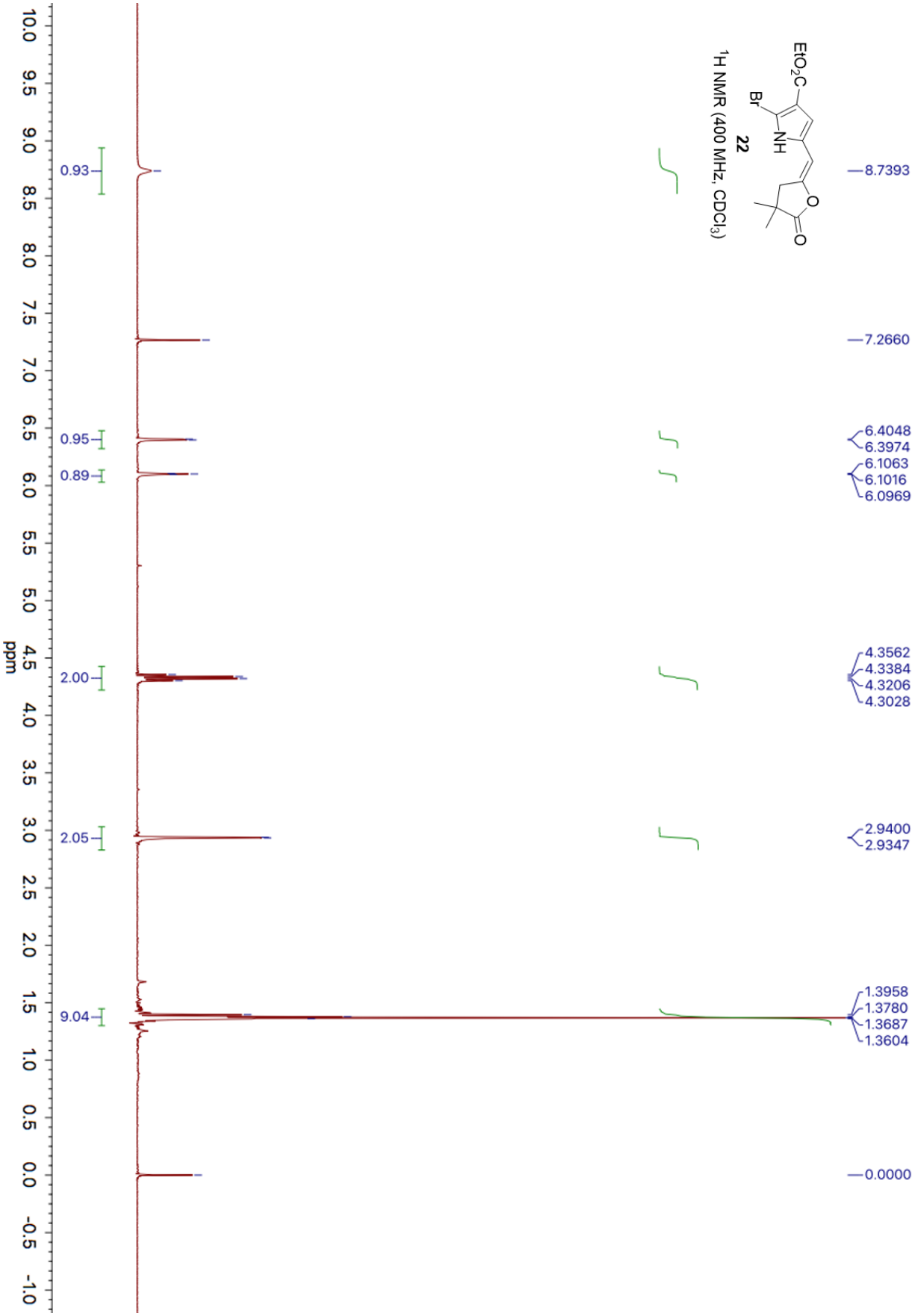
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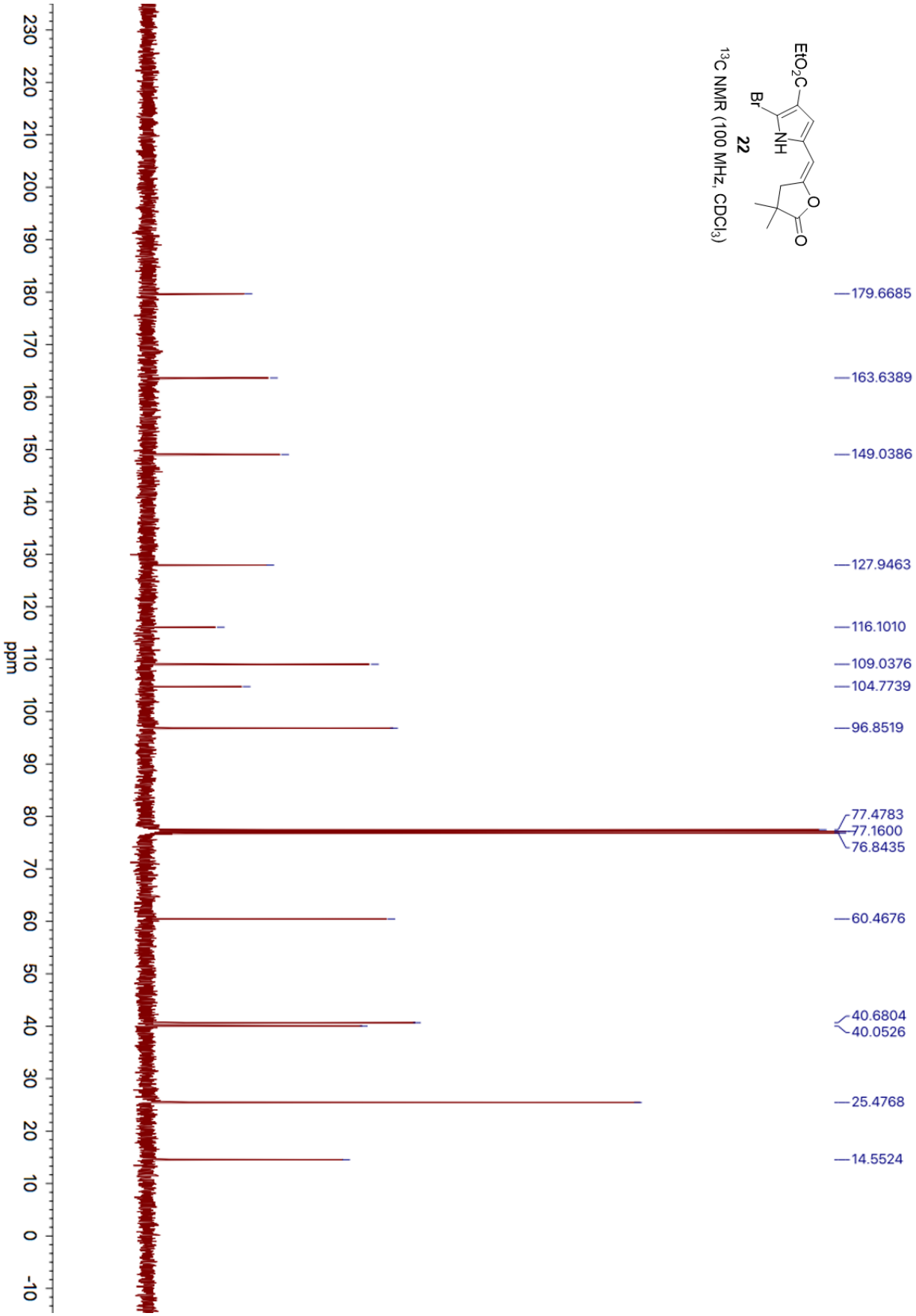
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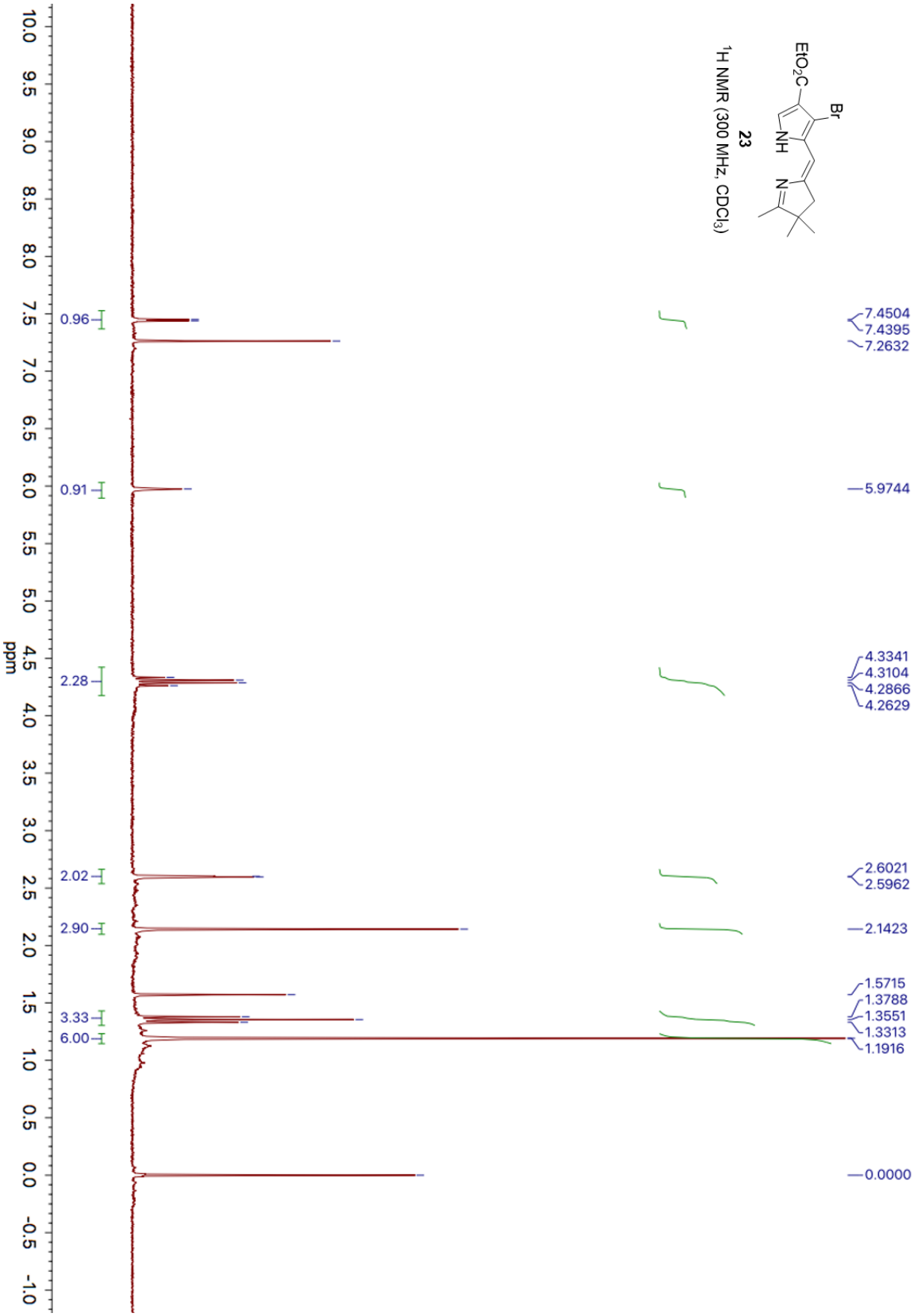
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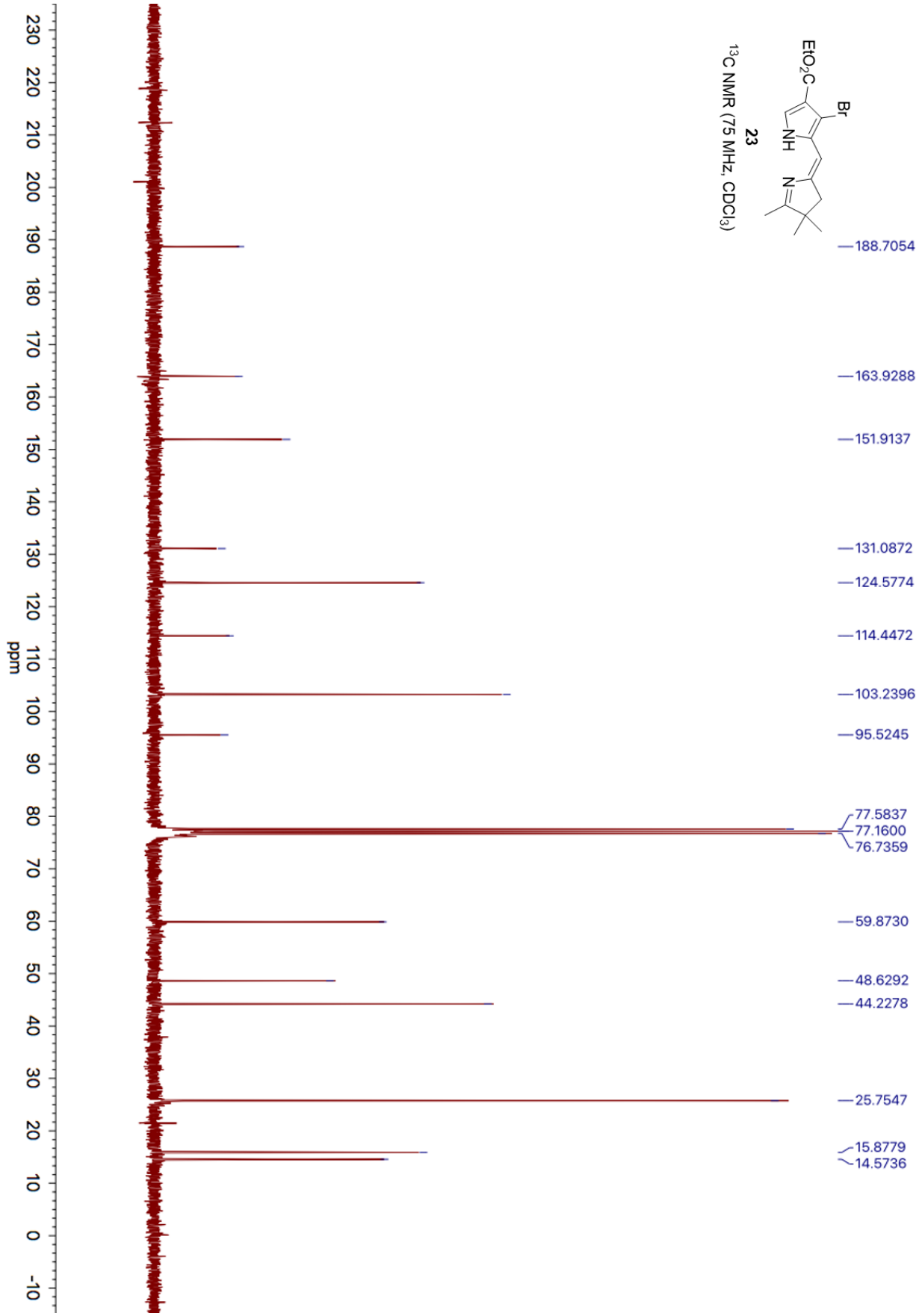
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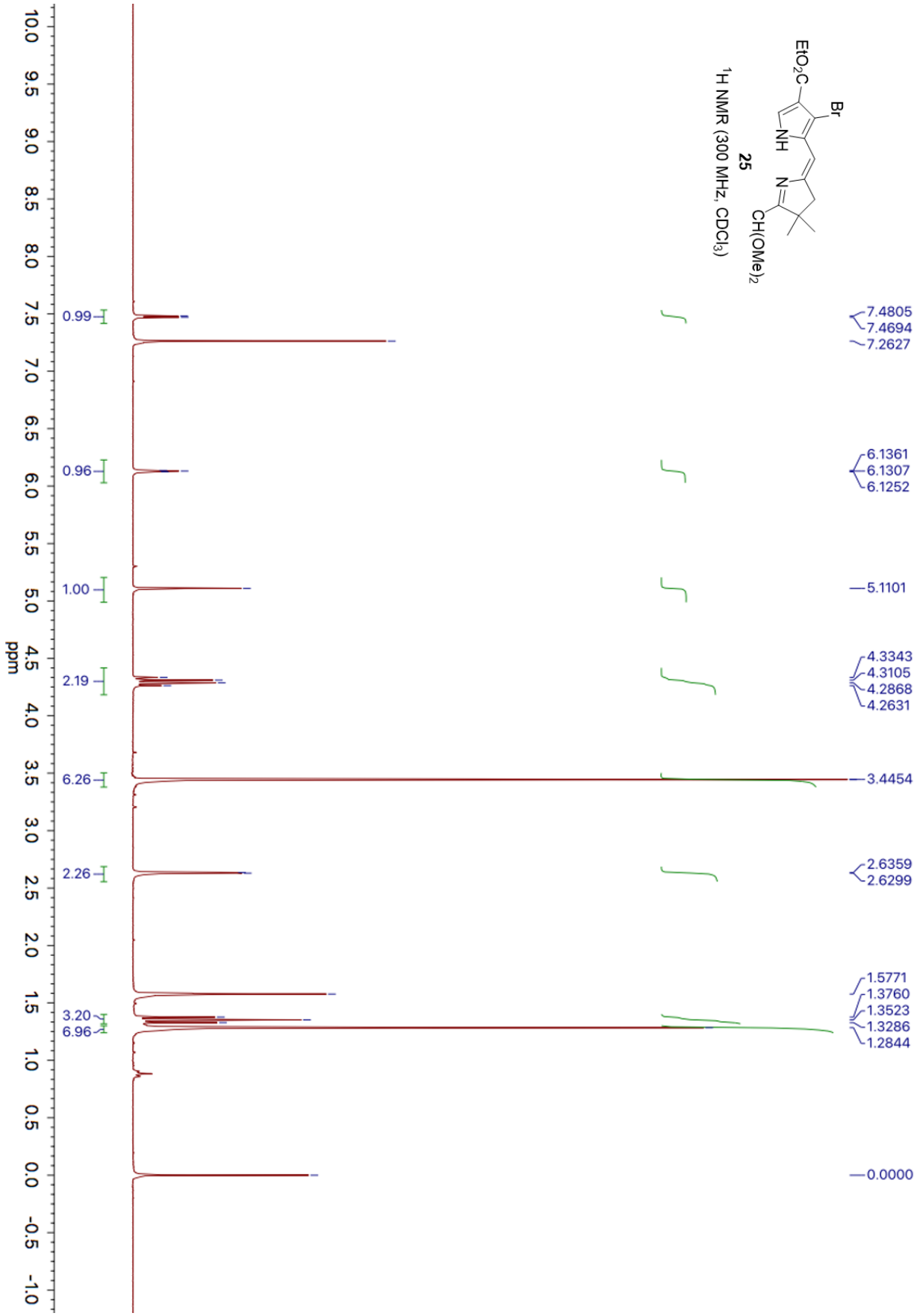
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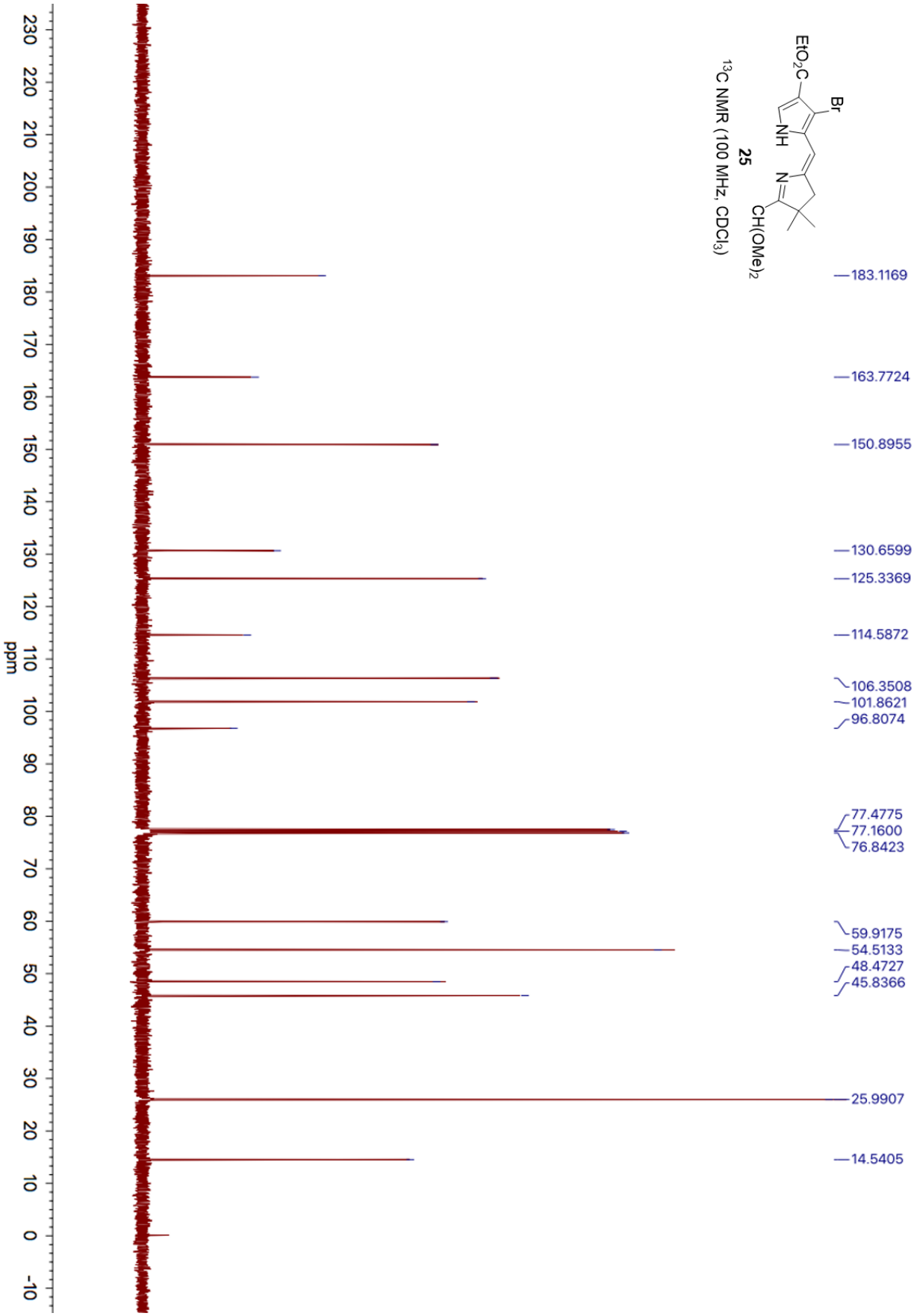
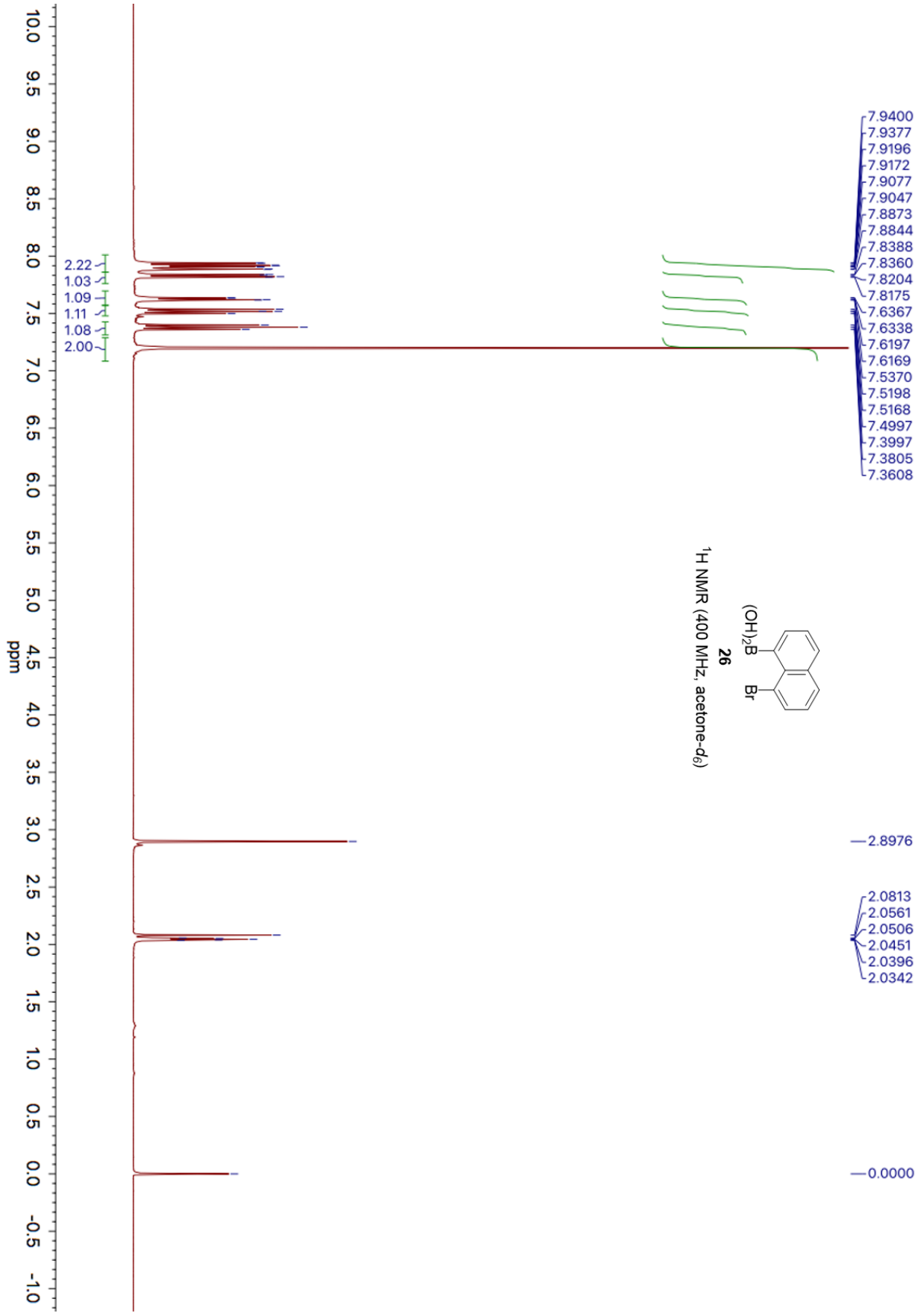
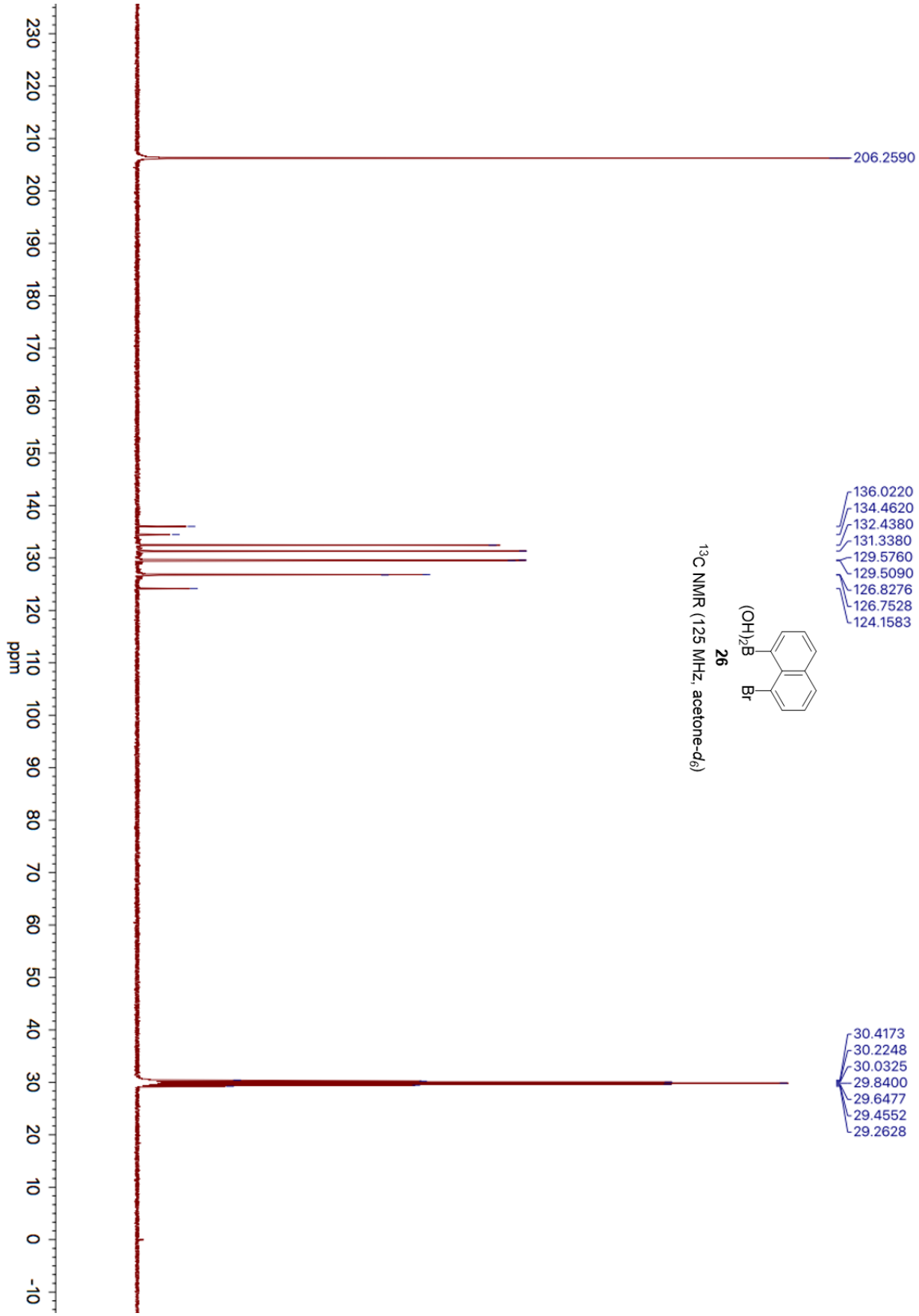
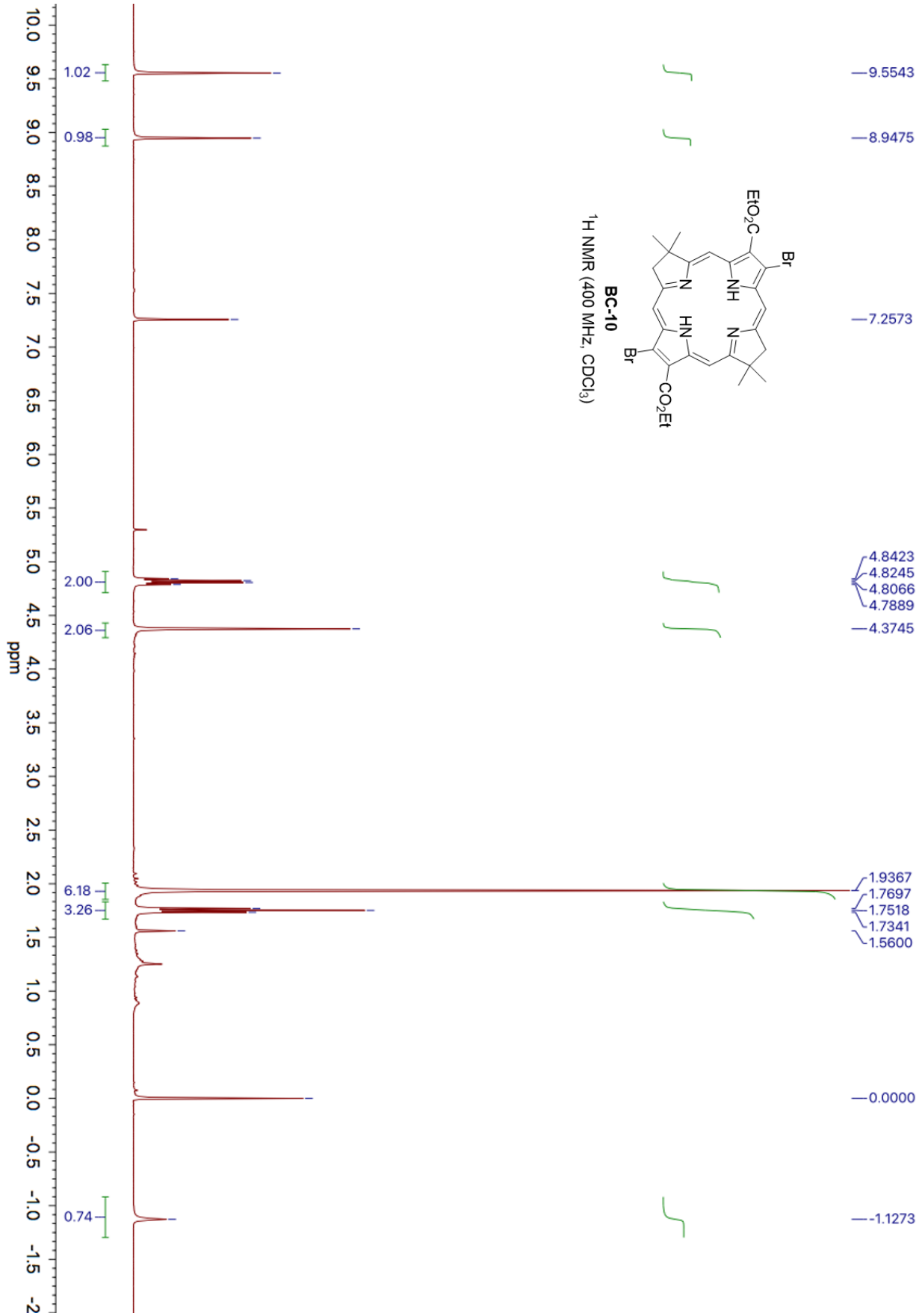
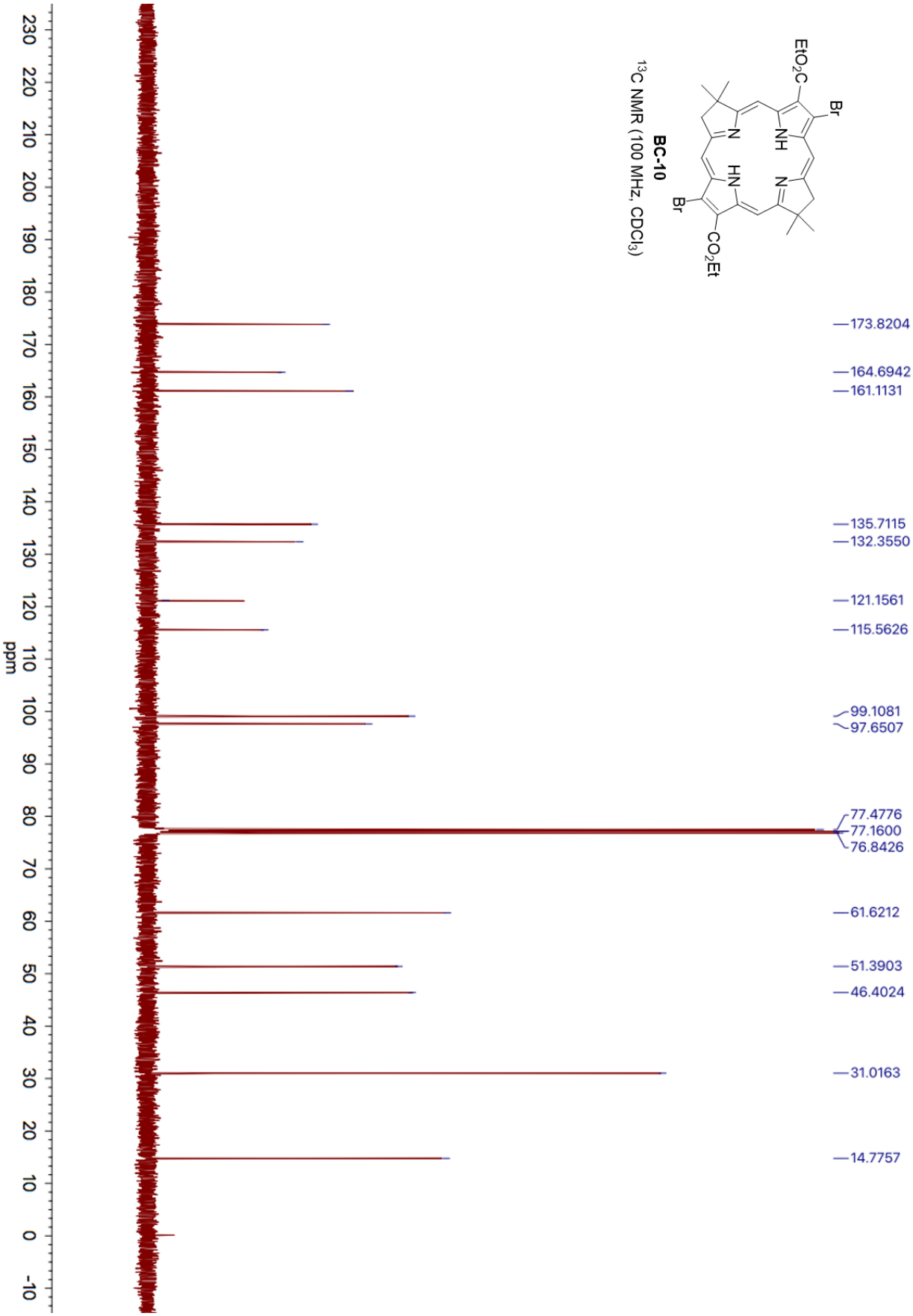
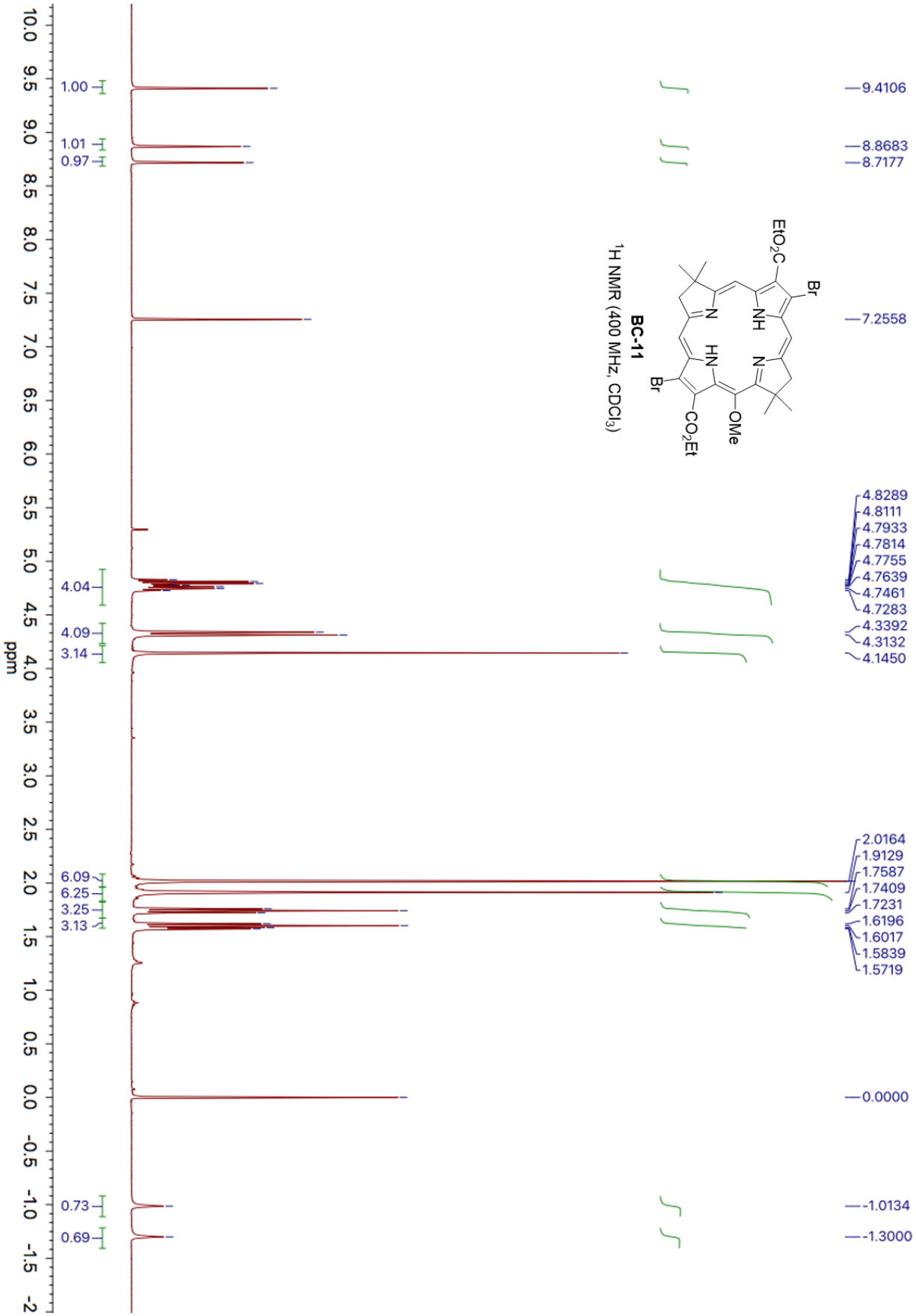

25
^{13}C NMR (100 MHz, CDCl$_3$)
EtO$_2$C
Br
NH
N
CH(OMe)$_2$
183.1169
163.7724
150.8955
130.6599
125.3369
114.5872
106.3508
101.8621
96.8074
77.4775
77.1600
76.8423
59.9175
54.5133
48.4727
45.8366
25.9907
14.5405
ppm
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10

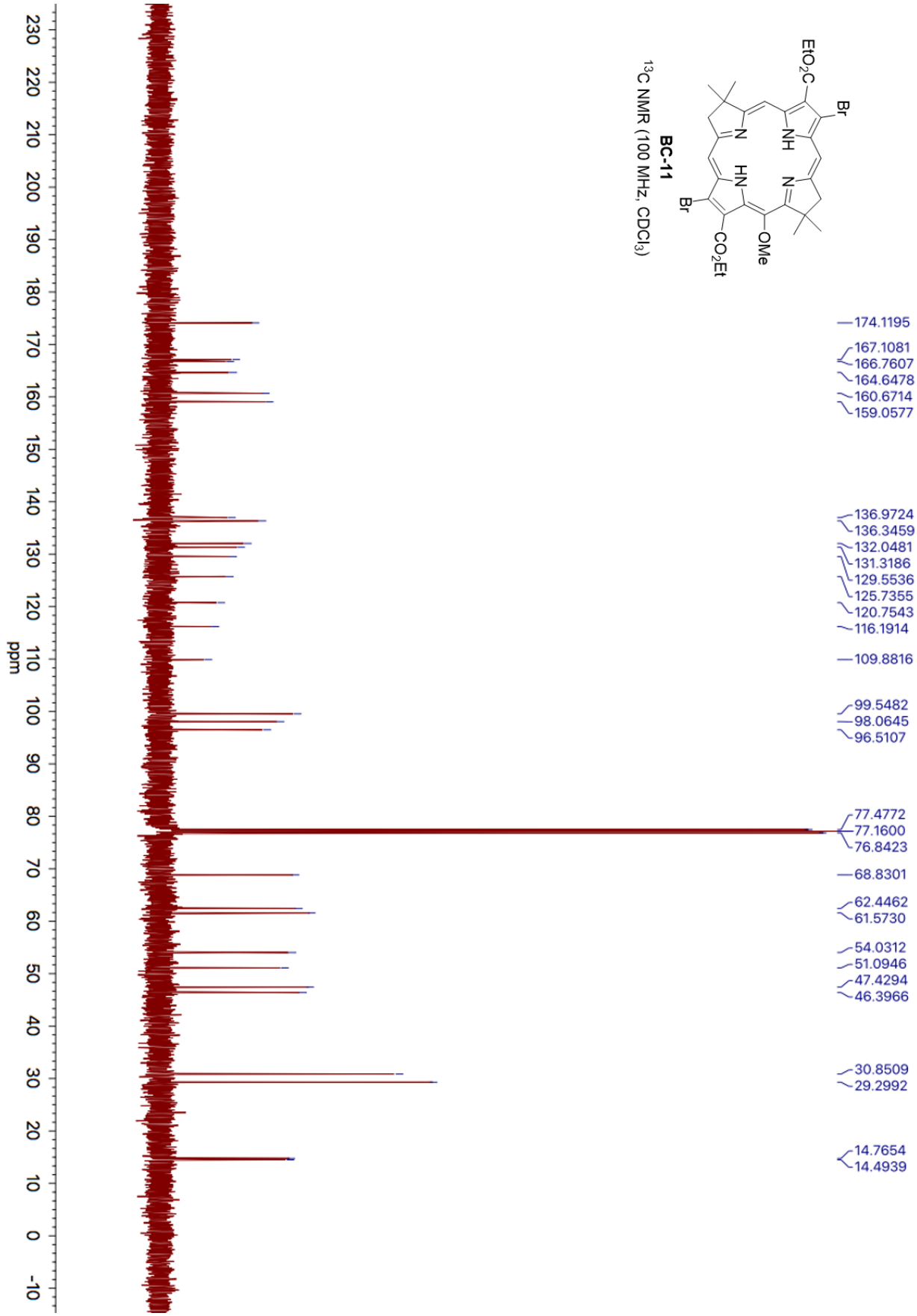

7.9400
7.9377
7.9196
7.9172
7.9077
7.9047
7.8873
7.8844
7.8388
7.8360
7.8204
7.8175
7.6367
7.6338
7.6197
7.6169
7.5370
7.5198
7.5168
7.4997
7.3997
7.3805
7.3608
2.22
1.03
1.09
1.11
1.08
2.00
(OH)2B
Br
26
1H NMR (400 MHz, acetone-d6)
2.8976
2.0813
2.0561
2.0506
2.0451
2.0396
2.0342
0.0000
ppm

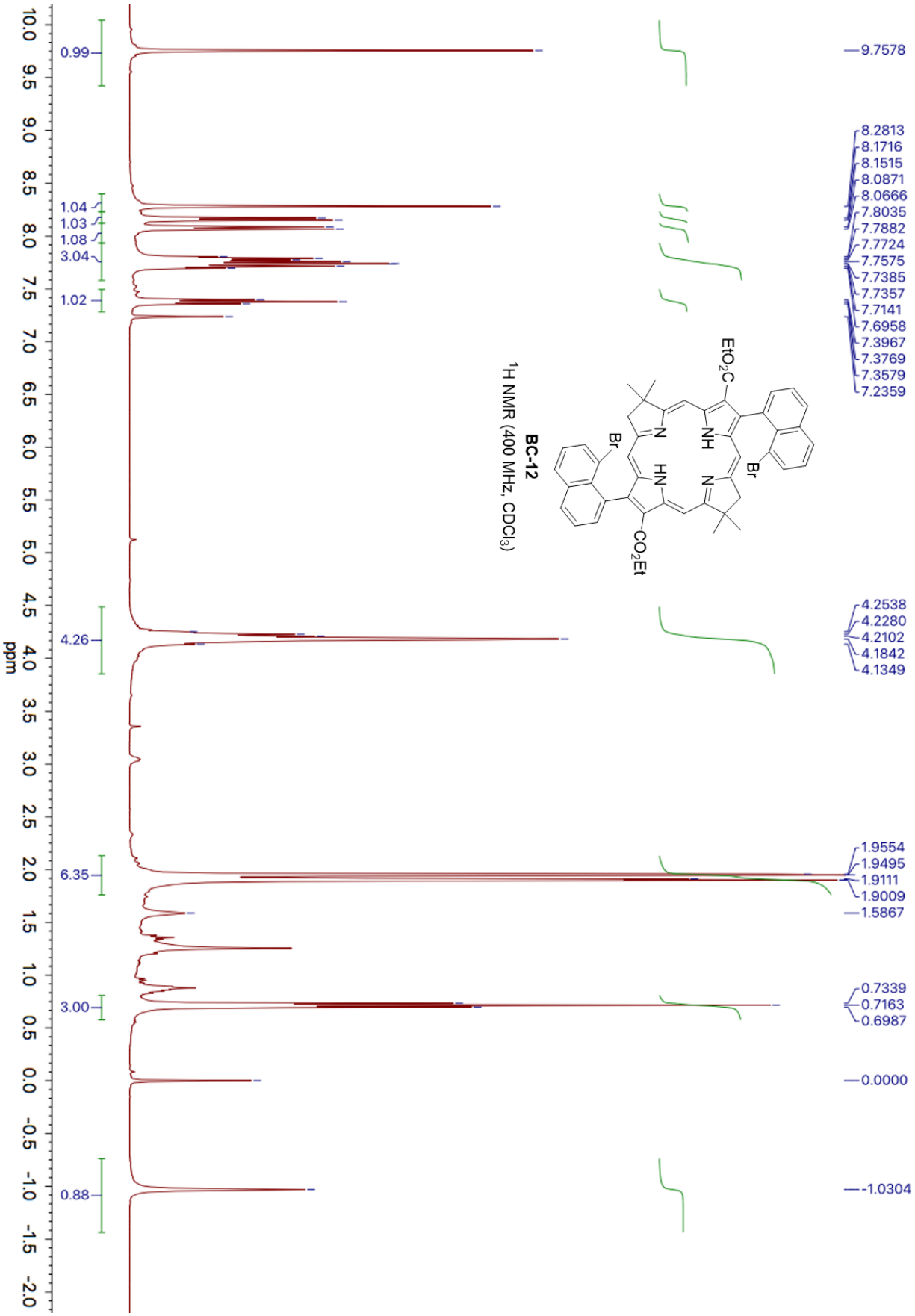

206.2590
136.0220
134.4620
132.4380
131.3380
129.5760
129.5090
126.8276
126.7528
124.1583
30.4173
30.2248
30.0325
29.8400
29.6477
29.4552
29.2628
(OH)2B
Br
26
13C NMR (125 MHz, acetone-d6)
ppm
230
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10

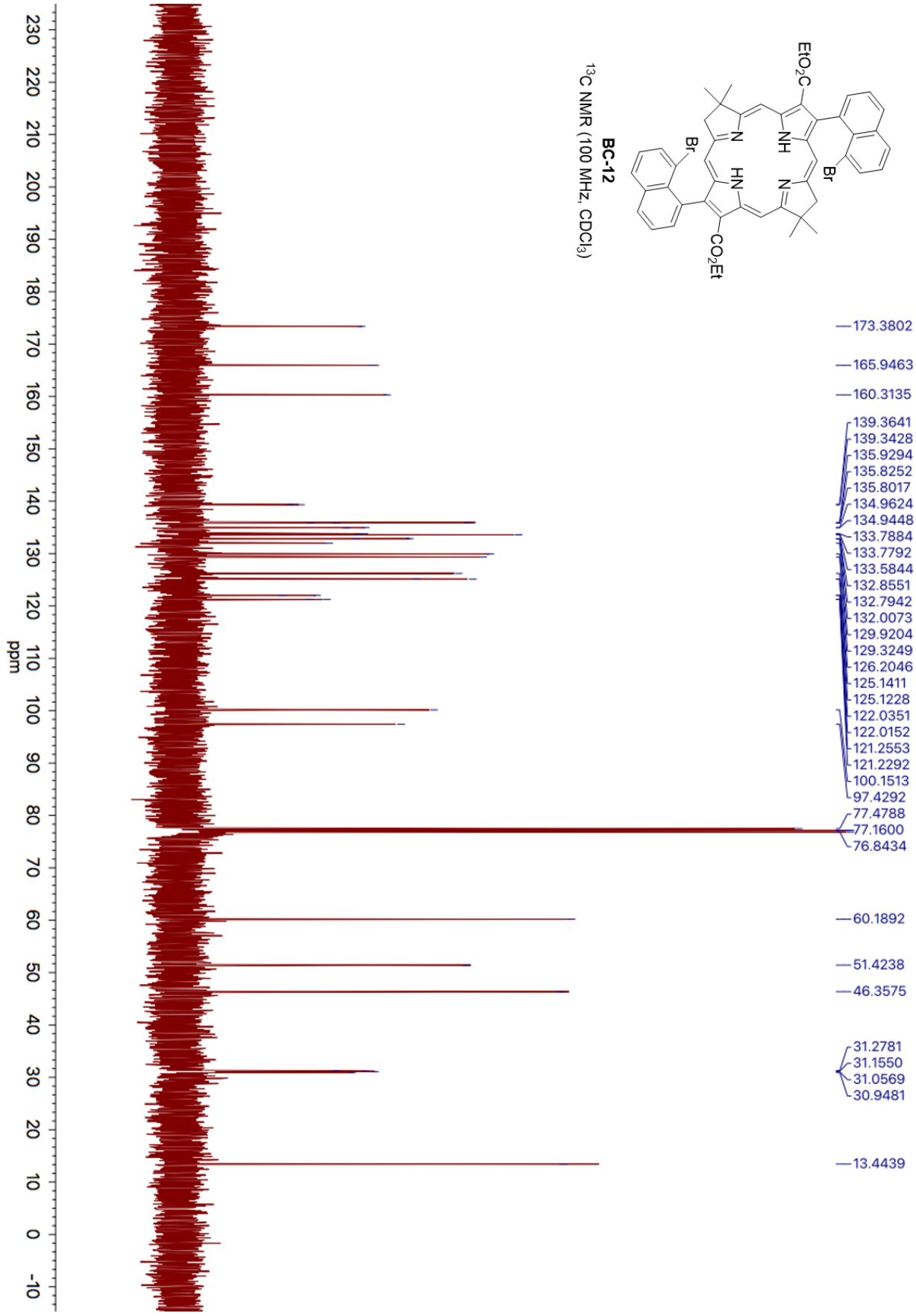

BC-10
^{1}H NMR (400 MHz, CDCl$_3$)
EtO$_2$C
Br
NH
N
HN
N
Br
CO$_2$Et
9.5543
8.9475
7.2573
4.8423
4.8245
4.8066
4.7889
4.3745
1.9367
1.7697
1.7518
1.7341
1.5600
0.0000
-1.1273
1.02
0.98
2.00
2.06
6.18
3.26
0.74
ppm

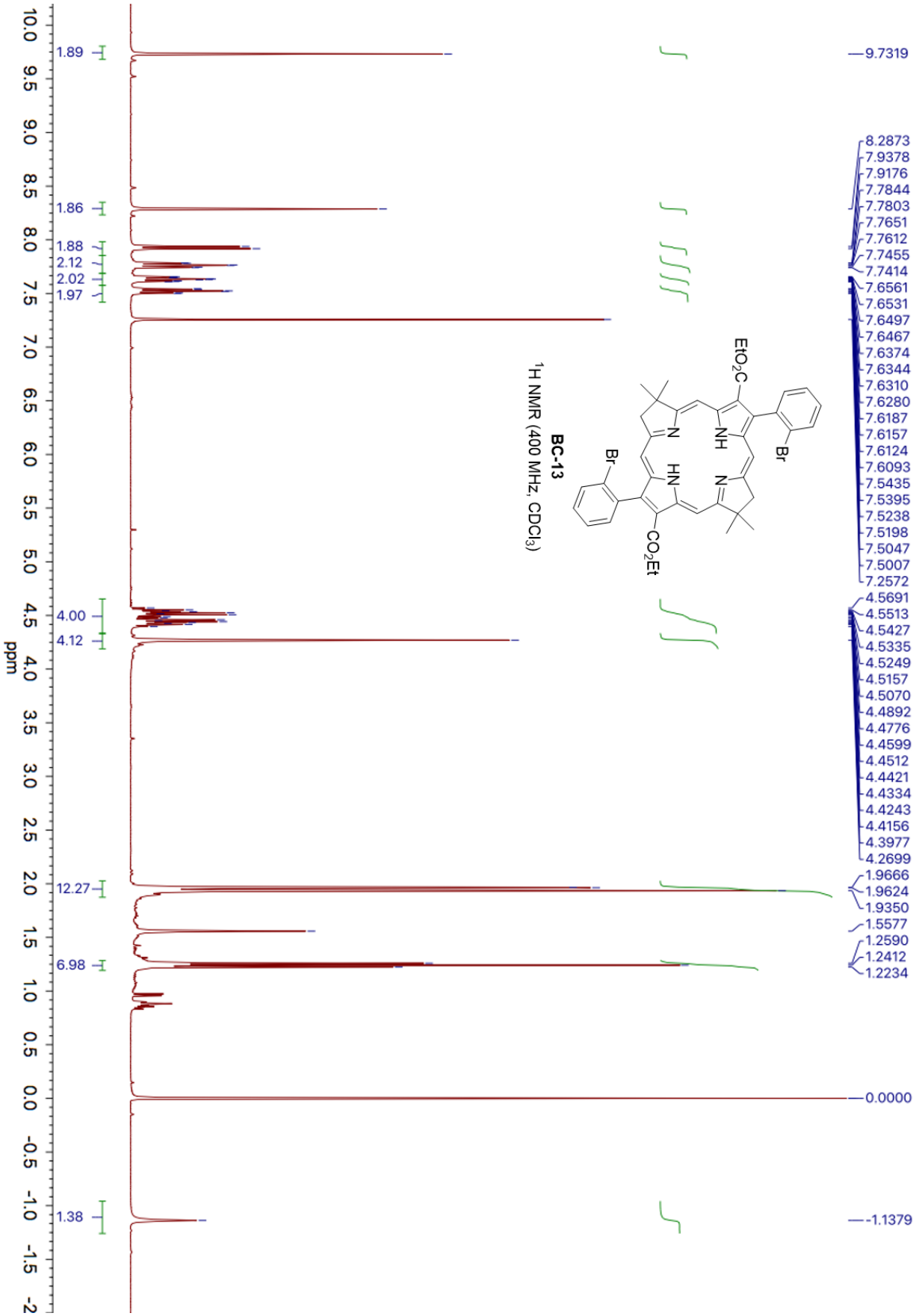

BC-10
^{13}C NMR (100 MHz, CDCl$_3$)
EtO$_2$C
Br
NH
N
HN
N
Br
CO$_2$Et
ppm
230
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
173.8204
164.6942
161.1131
135.7115
132.3550
121.1561
115.5626
99.1081
97.6507
77.4776
77.1600
76.8426
61.6212
51.3903
46.4024
31.0163
14.7757

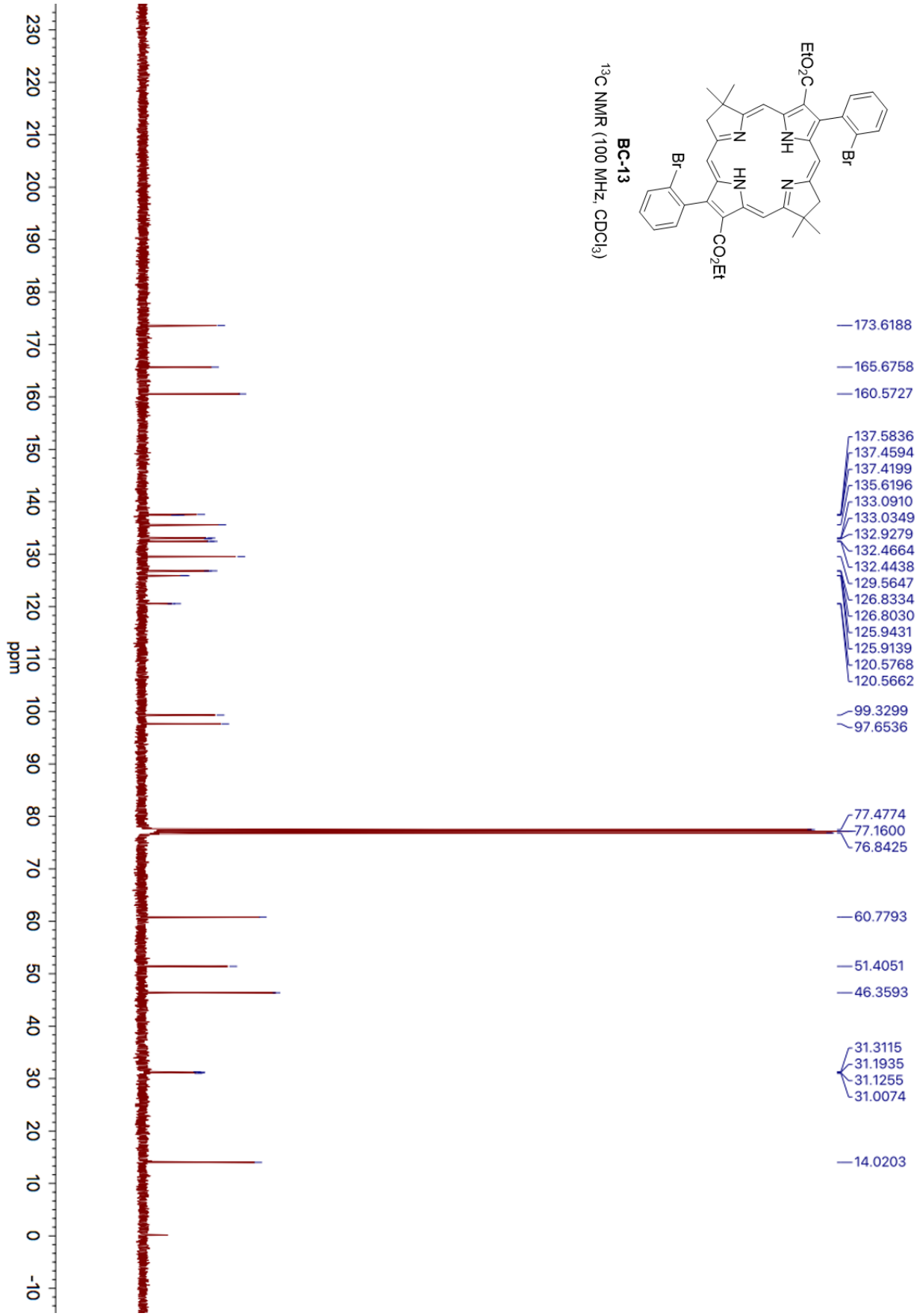

BC-11
^{1}H NMR (400 MHz, CDCl$_3$)
EtO$_2$C
Br
NH
N
HN
N
Br
CO$_2$Et
OMe
ppm
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0 -1.5 -2
1.00
1.01
0.97
4.04
4.09
3.14
6.09
6.25
3.25
3.13
0.73
0.69
9.4106
8.8683
8.7177
7.2558
4.8289
4.8111
4.7933
4.7814
4.7755
4.7639
4.7461
4.7283
4.3392
4.3132
4.1450
2.0164
1.9129
1.7587
1.7409
1.7231
1.6196
1.6017
1.5839
1.5719
0.0000
-1.0134
-1.3000

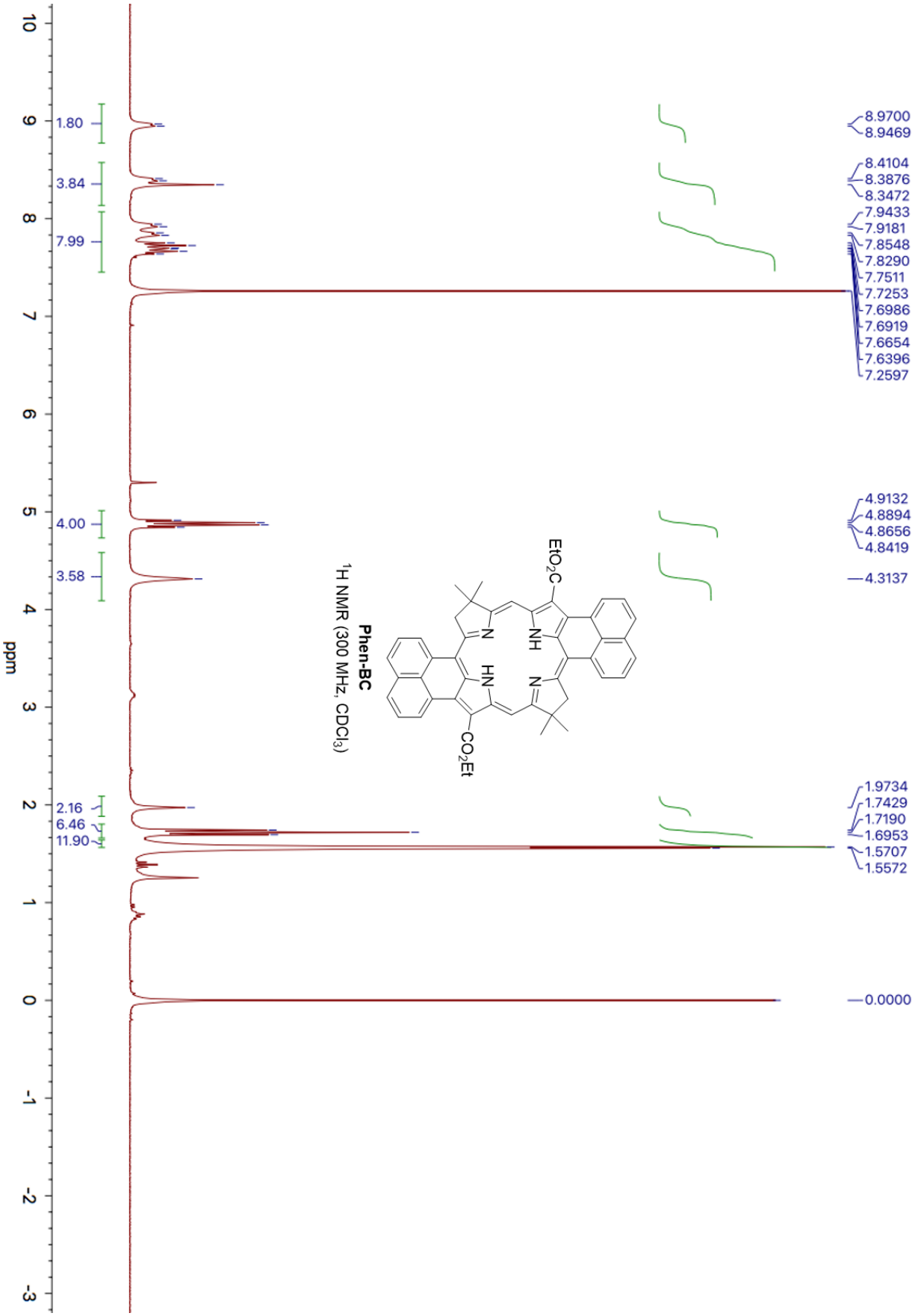

BC-11
^{13}C NMR (100 MHz, CDCl$_3$)
EtO$_2$C
Br
NH
N
HN
N
Br
CO$_2$Et
OMe
ppm
230
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
174.1195
167.1081
166.7607
164.6478
160.6714
159.0577
136.9724
136.3459
132.0481
131.3186
129.5536
125.7355
120.7543
116.1914
109.8816
99.5482
98.0645
96.5107
77.4772
77.1600
76.8423
68.8301
62.4462
61.5730
54.0312
51.0946
47.4294
46.3966
30.8509
29.2992
14.7654
14.4939

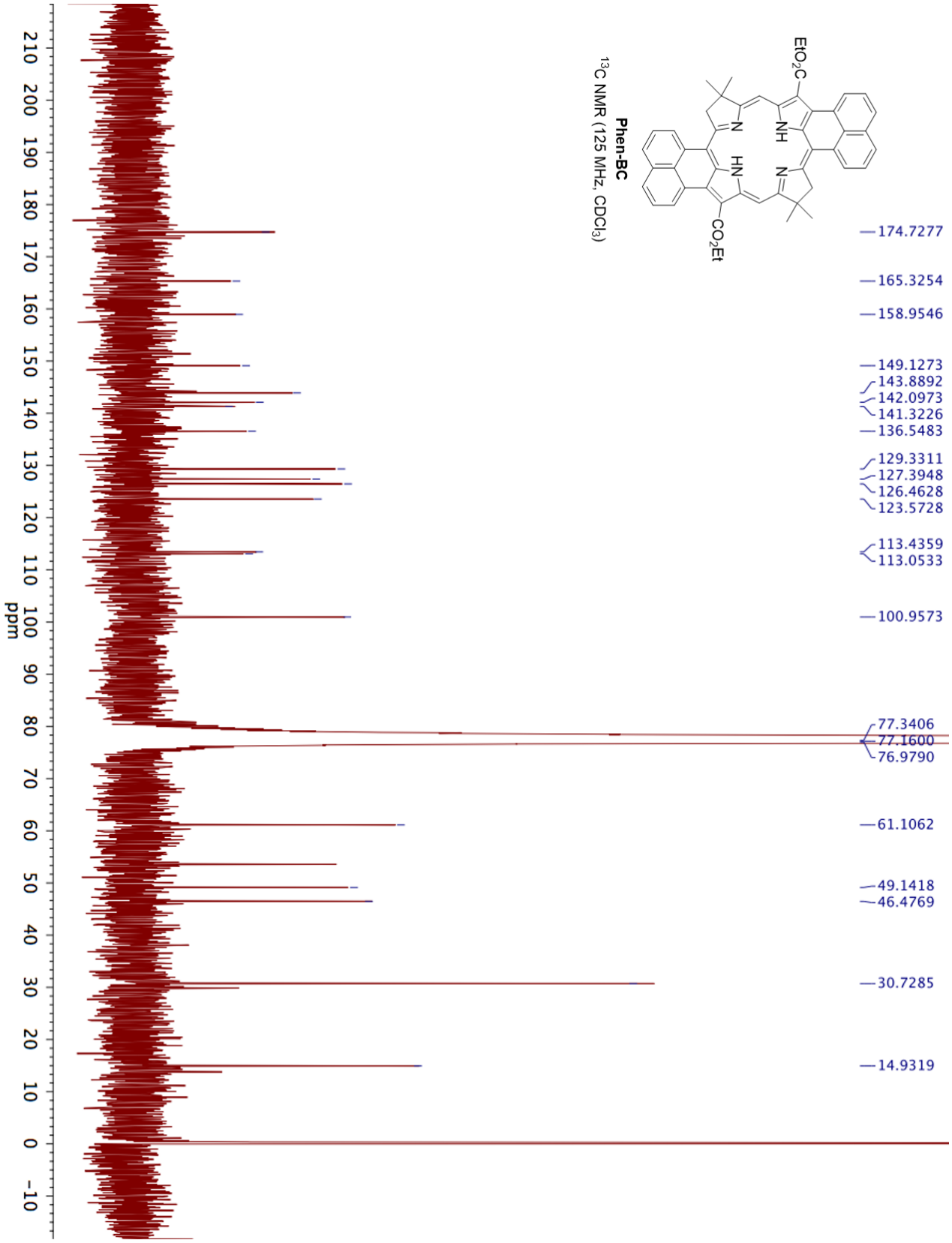

BC-12
^{1}H NMR (400 MHz, CDCl$_3$)
EtO$_2$C
CO$_2$Et
Br
Br
NH
HN
N
N
ppm
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0 -1.5 -2.0
0.99
1.04
1.03
1.08
3.04
1.02
4.26
6.35
3.00
0.88
9.7578
8.2813
8.1716
8.1515
8.0871
8.0666
7.8035
7.7882
7.7724
7.7575
7.7385
7.7357
7.7141
7.6958
7.3967
7.3769
7.3579
7.2359
4.2538
4.2280
4.2102
4.1842
4.1349
1.9554
1.9495
1.9111
1.9009
1.5867
0.7339
0.7163
0.6987
0.0000
-1.0304

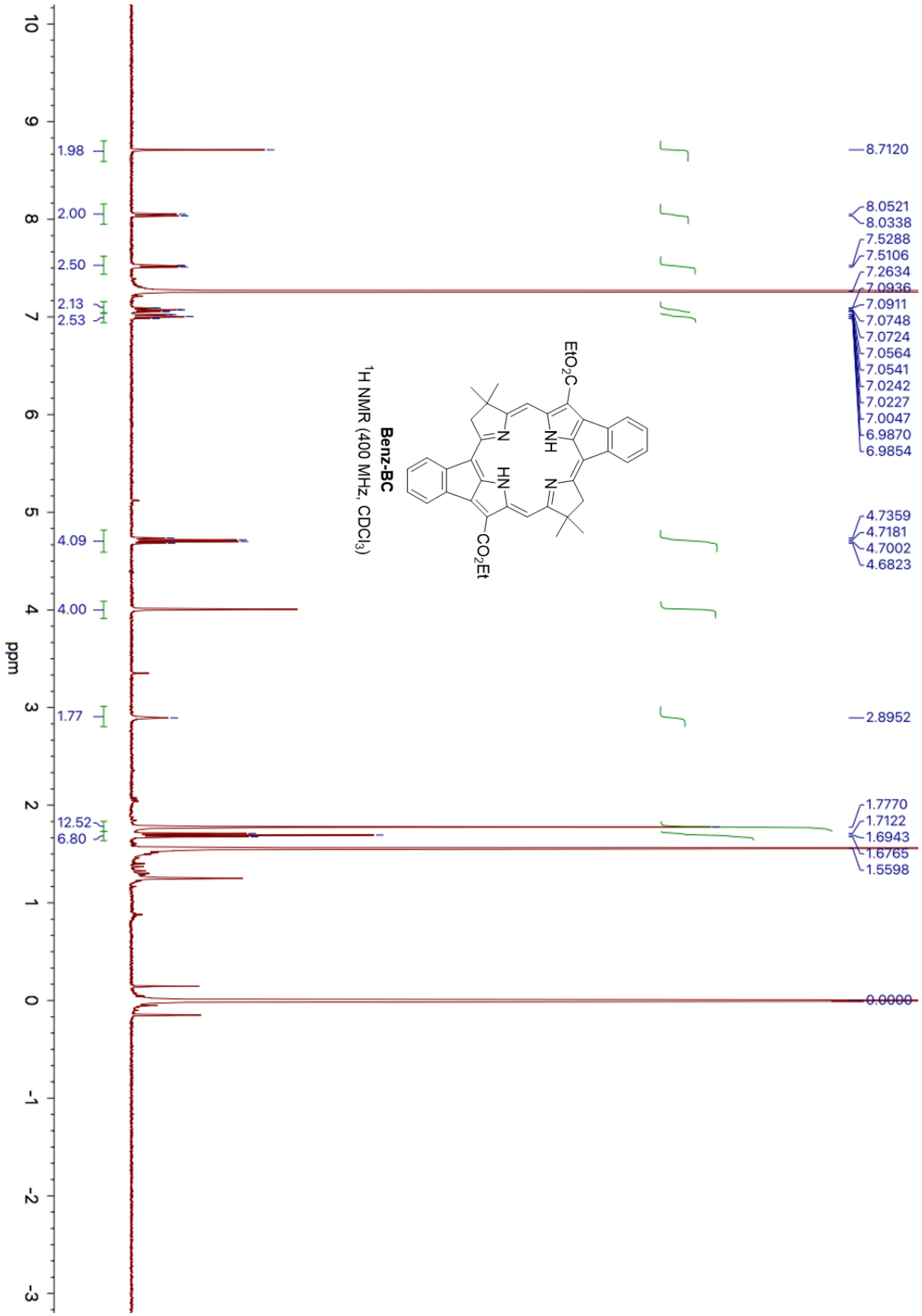

BC-12
^{13}C NMR (100 MHz, $CDCl_3$)
EtO_2C
CO_2Et
Br
Br
NH
HN
N
N
ppm
230
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
173.3802
165.9463
160.3135
139.3641
139.3428
135.9294
135.8252
135.8017
134.9624
134.9448
133.7884
133.7792
133.5844
132.8551
132.7942
132.0073
129.9204
129.3249
126.2046
125.1411
125.1228
122.0351
122.0152
121.2553
121.2292
100.1513
97.4292
77.4788
77.1600
76.8434
60.1892
51.4238
46.3575
31.2781
31.1550
31.0569
30.9481
13.4439

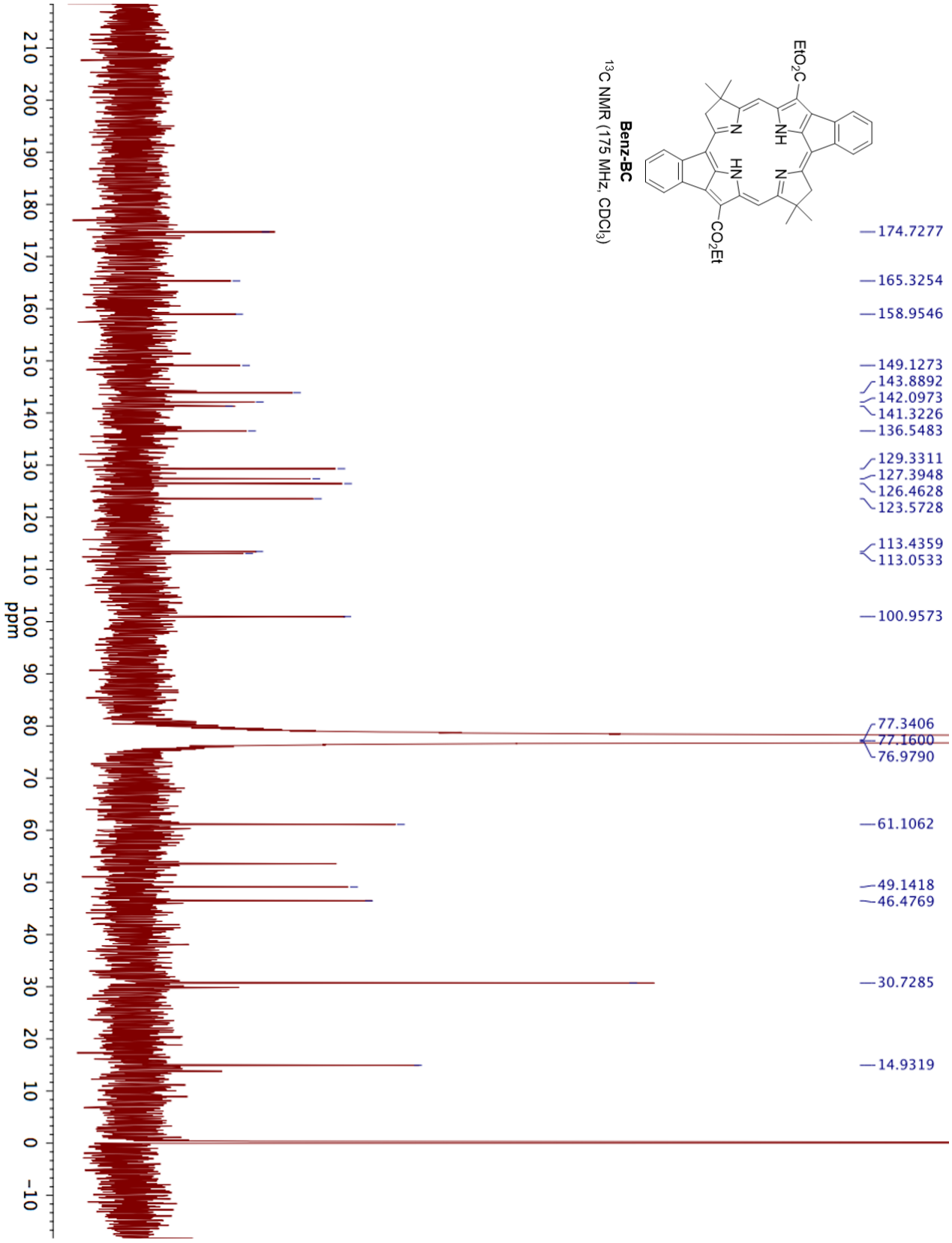

BC-13
^{1}H NMR (400 MHz, CDCl$_3$)
ppm
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0 -1.5 -2
1.89
1.86
1.88
2.12
2.02
1.97
4.00
4.12
12.27
6.98
1.38
9.7319
8.2873
7.9378
7.9176
7.7844
7.7803
7.7651
7.7612
7.7455
7.7414
7.6561
7.6531
7.6497
7.6467
7.6374
7.6344
7.6310
7.6280
7.6187
7.6157
7.6124
7.6093
7.5435
7.5395
7.5238
7.5198
7.5047
7.5007
7.2572
4.5691
4.5513
4.5427
4.5335
4.5249
4.5157
4.5070
4.4892
4.4776
4.4599
4.4512
4.4421
4.4334
4.4243
4.4156
4.3977
4.2699
1.9666
1.9624
1.9350
1.5577
1.2590
1.2412
1.2234
0.0000
-1.1379
EtO$_2$C
Br
N
NH
HN
N
Br
CO$_2$Et


BC-13
^{13}C NMR (100 MHz, $CDCl_3$)
EtO_2C
CO_2Et
Br
Br
N
NH
HN
N
ppm
230
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
173.6188
165.6758
160.5727
137.5836
137.4594
137.4199
135.6196
133.0910
133.0349
132.9279
132.4664
132.4438
129.5647
126.8334
126.8030
125.9431
125.9139
120.5768
120.5662
99.3299
97.6536
77.4774
77.1600
76.8425
60.7793
51.4051
46.3593
31.3115
31.1935
31.1255
31.0074
14.0203


Phen-BC
^{1}H NMR (300 MHz, $CDCl_3$)
EtO_2C
CO_2Et
NH
HN
N
N
ppm
10
9
8
7
6
5
4
3
2
1
0
-1
-2
-3
1.80
3.84
7.99
4.00
3.58
2.16
6.46
11.90
8.9700
8.9469
8.4104
8.3876
8.3472
7.9433
7.9181
7.8548
7.8290
7.7511
7.7253
7.6986
7.6919
7.6654
7.6396
7.2597
4.9132
4.8894
4.8656
4.8419
4.3137
1.9734
1.7429
1.7190
1.6953
1.5707
1.5572
0.0000


Phen-BC
^{13}C NMR (125 MHz, CDCl$_3$)
EtO$_2$C
CO$_2$Et
NH
HN
N
N
ppm
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
174.7277
165.3254
158.9546
149.1273
143.8892
142.0973
141.3226
136.5483
129.3311
127.3948
126.4628
123.5728
113.4359
113.0533
100.9573
77.3406
77.1600
76.9790
61.1062
49.1418
46.4769
30.7285
14.9319


Benz-BC
^{1}H NMR (400 MHz, $CDCl_3$)
EtO_2C
CO_2Et
NH
HN
N
N
ppm
10
9
8
7
6
5
4
3
2
1
0
-1
-2
-3
1.98
2.00
2.50
2.13
2.53
4.09
4.00
1.77
12.52
6.80
8.7120
8.0521
8.0338
7.5288
7.5106
7.2634
7.0936
7.0911
7.0748
7.0724
7.0564
7.0541
7.0242
7.0227
7.0047
6.9870
6.9854
4.7359
4.7181
4.7002
4.6823
2.8952
1.7770
1.7122
1.6943
1.6765
1.5598
0.0000


Benz-BC
^{13}C NMR (175 MHz, $CDCl_3$)
EtO_2C
CO_2Et
NH
HN
N
N
174.7277
165.3254
158.9546
149.1273
143.8892
142.0973
141.3226
136.5483
129.3311
127.3948
126.4628
123.5728
113.4359
113.0533
100.9573
77.3406
77.1600
76.9790
61.1062
49.1418
46.4769
30.7285
14.9319
ppm
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10