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Supporting Information for:

Chemical sensing with shapeshifting organic molecules

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Materials and Methods. Unless otherwise noted, all reactions were carried out in oven-dried glassware sealed with rubber septa under an atmosphere of dry N_2 and were stirred with Teflon-coated magnetic stir bars. Dichloromethane (CH_2Cl_2), chlorobenzene (PhCl), and *N*,*N*-diisopropylethylamine (*i*Pr_2NEt) were distilled over CaH_2. Tetrahydrofuran (THF) was distilled over Na/benzophenone. Pyridine was distilled over KOH. Isobutyl chloroformate was distilled over $CaCl_2$. All other solvents were used as received unless otherwise noted. For NMR experiments, carbon disulfide purchased from Aldrich (Aldrich Reagent Plus, redistilled, ≥99.9%) and dichloromethane-d_2 (CD_2Cl_2) and THF-d_8 purchased from Cambridge Isotope (99.9%) were used. C_{70} (99.5%) and C_{60} (99.0%) were purchased from SES Fullerene. The pyrolidine-derivatived C_{60} was a gift from the research group of Dr. Yoko Yamakoshi (ETH Zürich). Thin layer chromatography (TLC) was performed on Merck TLC plates (0.25 mm) pre-coated with silica gel 60 F254 and visualized by UV irradiation and anisaldehyde or potassium permanganate stains. Silica gel preparative TLC was performed using plates prepared from Merck Kieselgel 60 PF254 (Art 7747). Flash column chromatography was performed on EMD silica gel 60 (230–400 Mesh). ^{1}H NMR were recorded on a Bruker AV-400 spectrometer (at 400 MHz) or a Bruker AV-III-500 spectrometer (at 500 MHz). ^{13}C NMR were recorded on a Bruker AV-400 spectrometer (at 100 MHz), a Bruker AV-III-500 spectrometer (at 125 MHz), or a Bruker AV-II-600 spectrometer with a cryoprobe (at 150 MHz). ^{1}H and ^{13}C Chemical shifts (δ) are reported relative to the residual solvent signal, DMSO (δ 2.50 for ^{1}H NMR and δ 39.52 for ^{13}C NMR), $CHCl_3$ (δ 7.26 for ^{1}H NMR and δ 77.16 for ^{13}C NMR), $CHDCl_2$ (δ 5.32 for ^{1}H), CD_2Cl_2 (δ 54.00 for ^{13}C). Data for ^{1}H NMR are reported as follows: chemical shift (multiplicity, coupling constants where applicable, number of hydrogens). Abbreviations are as follows: s (singlet), d (doublet), t (triplet), q (quartet), dd (doublet of doublet), dt (doublet of triplet), ddt (doublet of doublet of triplet), m (multiplet), br (broad). IR spectra were recorded on a Varian 800 FT-IR spectrometer or a Jasco FT/IR-4100 spectrometer and are reported in frequency of absorption (cm^{-1}). High resolution mass spectra were obtained from the mass spectrometry service of the ETH Zürich Laboratorium für Organische Chemie on a Varian

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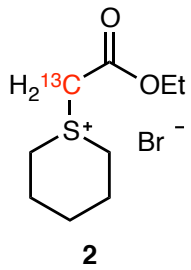
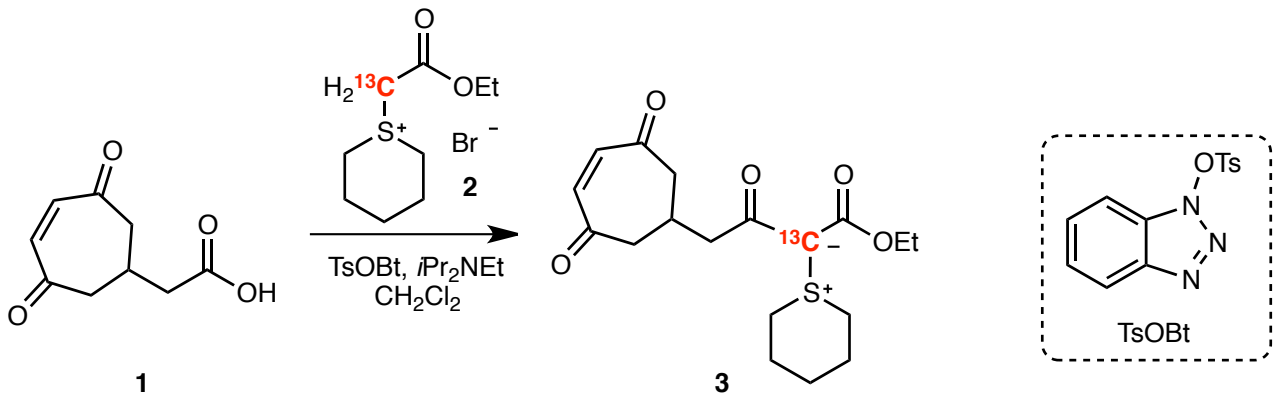
IonSpec FT-ICR (ESI), a Bruker Daltonics maXis ESI-QTOF spectrometer (ESI), or a Bruker Daltonics SOLARIX spectrometer (MALDI). Melting points were measured on an *Electrothermal Mel-Temp* melting point apparatus using open glass capillaries and are uncorrected.

Experimental Procedures and Spectral Data.



2

Sulfonium bromide 2. ^{13}C-Labeled sulfonium bromide **2** was prepared from [2-^{13}C]-ethylbromoacetate [1] according to the published procedure for the corresponding unlabeled sulfonium bromide.[2] Compound **2** was obtained as a white solid in 72% yield. **^{1}H NMR** (400 MHz, DMSO-*d6*) δ 4.74 (d, *J* = 146.7 Hz, 2H), 4.24 (q, *J* = 7.1 Hz, 2H), 3.68 – 3.50 (m, 2H), 3.50 – 3.30 (m, 2H), 2.20 – 1.98 (m, 2H), 1.95 – 1.74 (m, 2H), 1.68 – 1.47 (m, 2H), 1.25 (t, *J* = 7.1 Hz, 3H); **^{13}C NMR** (100 MHz, DMSO-*d6*) δ 164.7 (d, *J* = 61 Hz), 62.7, 40.2, 35.1, 22.0, 19.8, 13.8; **IR** (ATR) 2943, 2877, 1714, 1392, 1363, 1312, 1196, 1010, 966, 863 cm^{-1}; **mp** 137-139 °C; **HRMS** (ESI^{+}) calc'd for $[C_8{}^{13}CH_{17}O_2S]^+$ $(M-Br)^+$: *m/z* 190.0977, found 190.0973.



1 **3**

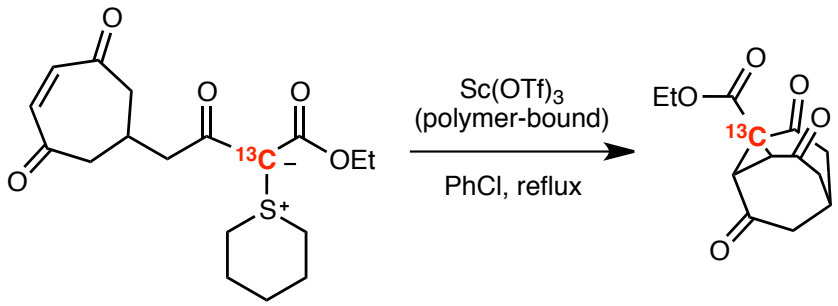
Ylide 3. Acid **1** (1.0 equiv, 13.2 mmol, 2.40 g) was suspended in 150 mL CH_2Cl_2 at RT. TsOBt[3] (1.0 equiv, 13.2 mmol, 3.82 g) and N, N-diisopropylethylamine (3.5 eq., 45.9 mmol, 7.94 mL) were added and the reaction mixture was stirred at RT until acid **1** was fully consumed as judged by TLC (4:1 EtOAc/acetone), approximately 5 min. ^{13}C-Labeled sulfonium bromide **2** (0.87 equiv, 11.5 mmol, 3.10 g) was added and the reaction mixture was stirred until TLC showed full conversion (~1 h). The reaction was quenched by addition of saturated aqueous NH_4Cl (100 mL) and extracted

(1) Prepared in two steps from [2-^{13}C] acetic acid: Ouwerkerk, N.; van Boom, J. H.; Lugtenburg, J.; Raap, J. *Eur. J. Org. Chem.* **2000**, 861-866 and Creemers, A. F. L.; Lugtenburg, J. *J. Am. Chem. Soc.* **2002**, *124*, 6324-6334.

(2) Aggarwal, V. K.; Smith, H. W.; Hynd, G.; Jones, R. V. H.; Fieldhouse, R.; Spey, S. E. *J. Chem. Soc., Perkin Trans. 1* **2000**, 3267-3276.

(3) Carpino, L. A.; Xia, J.; Zhang, C.; El-Faham, A. *J. Org. Chem*. **2004**, *69*, 62-71.

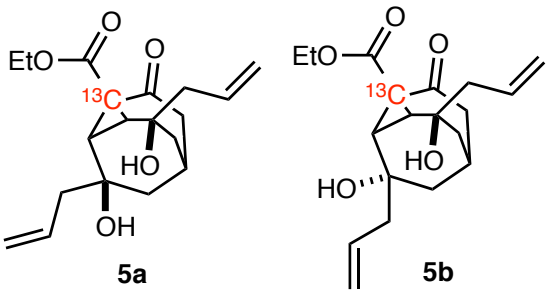
with CH_2Cl_2 (3 x 50 mL). The combined organic fractions were washed with brine (1 x 50 mL) and dried over Na_2SO_4. Concentration under reduced pressure yielded the crude product as a yellow oil, which was purified by flash chromatography (9:1 EtOAc/acetone) to give 3.57 g of ^{13}C-labeled ylide **3** (77% yield) as a colorless oil. **R_f** 0.37 (6:1 EtOAc/acetone); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 6.41 (s, 2H), 4.39 (dd, *J* = 20.2, 7.3 Hz, 2H), 4.11 (q, *J* = 7.1 Hz, 2H), 2.94 – 2.81 (m, 4H), 2.76 (d, *J* = 12.0 Hz, 2H), 2.70 – 2.55 (m, 2H), 2.24 – 2.10 (m, 2H), 1.85 – 1.68 (m, 4H), 1.55 – 1.35 (m, 1H), 1.32 – 1.22 (t, *J* = 7.2 Hz, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 200.8, 191.6 (d, *J* = 67 Hz), 166.6 (d, *J* = 92.0 Hz), 137.7, 75.0, 59.5, 49.9, 46.2 (d, *J* = 15.0 Hz), 36.8, 27.5, 25.1, 23.4, 14.8; **IR** (film) 3433, 2083, 1645, 1444, 1369, 1280, 1264, 1059, 964 cm^{-1}; **HRMS** (ESI^+) calc'd for $[C_{17}{}^{13}CH_{25}O_5S]$ $(M+H^+)$: *m/z* 354.1451, found 354.1454.



3 **4**

Triketone 4. ^{13}C-Labeled ylide **3** (1.0 equiv, 3.57 g, 10.1 mmol) was dissolved in chlorobenzene (450 mL) under a nitrogen atmosphere and 3.4 g polymer-bound $Sc(OTf)_3$ (0.5-1.5 mmol/g, Aldrich product #590312) were added. The mixture was heated to reflux in an oil bath until TLC showed full conversion (48 h). The reaction mixture was allowed to come to RT and filtered through fluted filter paper to remove the polymer beads. (Note: The polymer beads can be reused up to five times without significant loss of activity.) The resulting solution was loaded onto a dry-packed SiO_2 column, and the chlorobenzene was removed by eluting with hexane (500 mL). The desired ^{13}C-labeled triketone **4** was then eluted from the SiO_2 column with 1:1 hexane/EtOAc to give the pure product as an off-white solid (1.72 g, 68% yield). **R_f** 0.85 (9:1 EtOAc/acetone); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 4.15 (q, *J* = 7.1 Hz, 2H), 3.01 (d, *J* = 2.6 Hz, 2H), 2.89 – 2.81 (m, 2H), 2.75 (d, *J* =

4.3 Hz, 4H), 2.48 (dt, *J* = 8.6, 4.3 Hz, 1H), 1.21 (t, *J* = 7.1 Hz, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 201.8, 199.6 (d, *J* = 48.3 Hz), 166.3 (d, *J* = 75.4 Hz), 62.9, 49.7, 48.2 (d, *J* = 14 Hz), 47.1, 42.6 (d, *J* = 9.2 Hz), 22.1, 13.9; **IR** (film) 3434, 2090, 1644, 1240 cm^{-1}; **HRMS** (ESI^+) calc'd for $[C_{12}{}^{13}CH_{15}O_5]$ $(M+H^+)$: *m/z* 252.0948, found 252.0945.



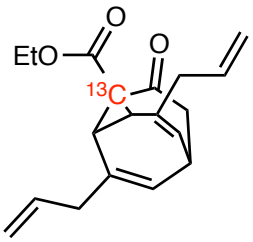
***meso*-Diol 5a and chiral diol 5b.** ^{13}C-Labeled diols **5a** and **5b** were prepared from ^{13}C-labeled triketone **4** according to the published procedure for the corresponding unlabeled *meso*- and chiral diols.[4] The diastereomeric diols were separated by flash chromatography (using a gradient of 2:1 to 1:1 hexane/EtOAc). The *meso*-Diol **5a** was obtained as a colorless oil in 35–40% yield. An analytically pure portion of the chiral diol **5b** was obtained in 15–20% yield, and an impure portion of the chiral diol was also collected and subjected to further purification under analogous conditions.

***meso*-Diol 5a.** **R_f** 0.33 (1:2 hexane/EtOAc); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 5.93 (ddt, *J* = 17.6, 10.2, 7.3 Hz, 2H), 5.28 – 5.16 (m, 4H), 4.21 (q, *J* = 7.1 Hz, 2H), 2.96 (d, *J* = 4.0 Hz, 2H), 2.47 (d, *J* = 7.4 Hz, 4H), 2.37 (s, 2H), 2.15 (d, *J* = 3.2 Hz, 2H), 2.04 (dd, *J* = 15.3, 3.0 Hz, 2H), 1.93 (dd, *J* = 15.2, 5.6 Hz, 2H), 1.82 (s, 1H), 1.29 (t, *J* = 7.1 Hz, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 204.7 (d, *J* = 50 Hz), 171.0 (d, *J* = 75 Hz), 132.8, 120.4, 74.3 (d, *J* = 1 Hz), 62.0, 51.14 (d, *J* = 2 Hz), 46.7, 46.4, 43.7, 42.8 (d, *J* = 10 Hz), 26.7, 14.2; **IR** (film) 3422 (br), 2979, 2931, 1708, 1674, 1261, 998, 917 cm^{-1}; **HRMS** (ESI^+) calc'd for $[C_{18}{}^{13}CH_{26}O_5Na]$ $(M+Na^+)$: *m/z* 358.1706, found 358.1707.

Chiral diol 5b. **R_f** 0.49 (1:2 hexane/EtOAc); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 6.04 – 5.79 (m, 2H), 5.27 – 5.10 (m, 4H), 4.30 – 4.09 (m, 2H), 3.36 (dt, *J* = 17.2, 1.6 Hz, 1H), 2.62 – 2.33 (m, 4H), 2.34 – 2.09 (m, 2H), 2.07 – 1.79 (m, 2H), 1.69 (d, *J* = 15.6 Hz, 1H), 1.30 – 1.24 (t, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 205.0 (d, *J* = 49 Hz), 170.9 (d, *J* = 74 Hz), 133.1, 132.5, 120.7, 120. 5, 75.1 (d, *J* =

(4) A. R. Lippert, J. Kaeobamrung, J. W. Bode, *J. Am. Chem. Soc.* **2006**, *128*, 14738-14739.

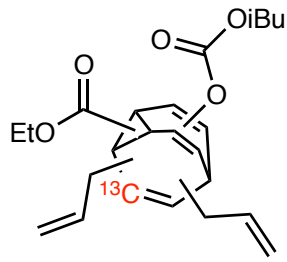
1 Hz), 74.6, 61.9, 51.4, 51.3, 48.2, 47.3, 39.8 (d, *J* = 10 Hz), 39.5, 26.5, 14.2; **IR** (film): 3431 (br), 2979, 2924, 1714, 1672, 1258, 916, 817 cm^{-1}; **HRMS** (ESI^+) calc'd for [$C_{18}{}^{13}CH_{26}O_5Na$] ($M+Na^+$): *m/z* 358.1706, found: 358.1701.



6

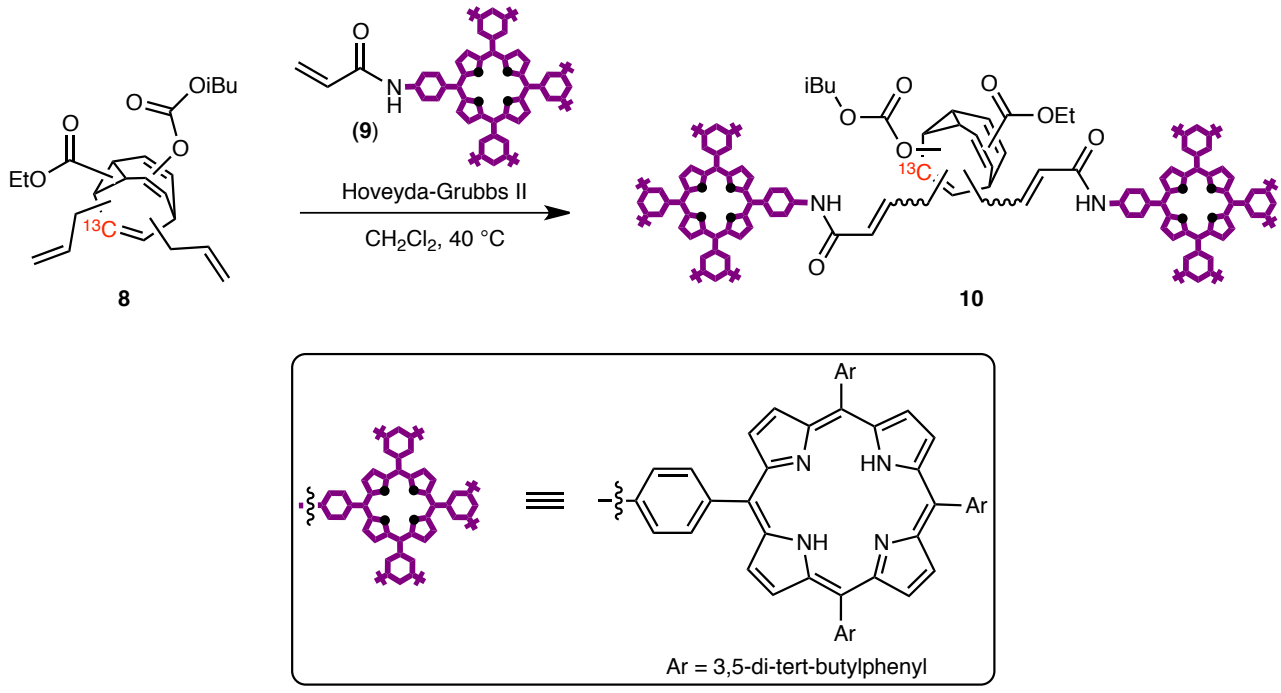
Bullvalone 6. ^{13}C-Labeled bullvalone **6** was prepared from ^{13}C-labeled *meso*-diol **5a** and ^{13}C-labeled chiral diol **5b** according to the published procedures[5] for the corresponding unlabeled bullvalone. Purification of the bullvalone derived from the *meso*-diol (**5a**) was conducted by initial flash chromatography using a gradient of 2:1 to 1:1 hexane/EtOAc to yield a pure and an impure portion of the bullvalone. Purification of the bullvalone derived from the chiral diol (**5b**) was conducted by flash chromatography using 19:1 hexane/EtOAc, followed by a second flash column using a gradient of 12:1 to 8:1 hexane/Et_2O, to yield a pure and an impure portion. The impure portions of bullvalone **6** were purified by normal-phase preparative HPLC on an Alltima column (22 x 250 mm, 3:7 hexane/CH_2Cl_2, flow rate 10 mL/min, 220 nm detection). CH_2Cl_2 (HiPerSolv CHROMANORM containing 0.1% ethanol as stabilizer) used for HPLC as purchased. In total, the pure bullvalone was obtained in 15–20% yield, over two steps starting from triketone **4**. **^{1}H NMR** (400 MHz, C_6D_6) δ 5.67 (ddt, *J* = 16.6, 10.2, 6.3 Hz, 2H), 5.45 (d, *J* = 8.5 Hz, 2H), 5.03 – 4.92 (m, 4H), 4.11 (q, *J* = 7.1 Hz, 2H), 2.70 – 2.62 (m, 4H), 2.62 – 2.57 (m, 2H), 2.34 (d, *J* = 3.1 Hz, 2H), 2.12 – 2.00 (m, 1H), 1.03 (dd, *J* = 9.7, 4.6 Hz, 3H); **^{13}C NMR** (100 MHz, C_6D_6) δ 200.5 (d, *J* = 52 Hz), 171.0 (d, *J* = 73 Hz), 135.9, 135.3, 126.0, 116.9, 61.7, 51.0, 48.86, 47.90 (d, *J* = 10 Hz), 44.1, 33.5 (d, *J* = 9 Hz), 29.5, 14.2; **IR** (film): 3078, 2979, 2933, 2900, 1732, 1683, 1636, 1245, 1034, 917 cm^{-1}; **HRMS** (ESI^+) calc'd for [$C_{18}{}^{13}CH_{22}O_3Na$] (M + Na^+): *m/z* 322.1495, found 322.1490.

(5) A. R. Lippert, J. Kaeobamrung, J. W. Bode, *J. Am. Chem. Soc.* **2006**, *128*, 14738-14739.



8

Bisallyl-bullvalene 8. ^{13}C-Labeled bullvalene **8** was prepared from ^{13}C-labeled bullvalone **6** according to the published procedure for the corresponding unlabeled bullvalene.[6] Compound **8** was obtained as a colorless oil in ~80% yield. **^{1}H NMR** (400 MHz, $CDCl_3$, major signals reported) δ 7.21 – 6.98 (m, 0.6H), 5.92 – 5.59 (m, 3.3H), 5.17 – 4.88 (m, 4.4H), 4.28 – 4.12 (m, 2.2H), 4.00 – 3.86 (m, 1.9H), 3.01 – 2.70 (m, 3.7H), 2.59 – 2.45 (m, 0.9H), 2.46 – 2.18 (m, 2.1H), 2.07 – 1.89 (m, 1.2H), 1.33 – 1.20 (m, 4H), 0.99 – 0.88 (m, 6.2H); **^{13}C NMR** (100 MHz, $CDCl_3$, major signals reported) δ 153.7, 135.9, 135.6, 135.0, 131.6, 131.3, 130.5, 130.5, 130.2, 130.0, 129.3, 129.2, 128.9, 128.7, 128.4, 128.4, 128.3, 128.1, 127.7, 124.2, 117.5, 117.0, 117.0, 116.9, 116.8, 75.3, 74.9, 74.9, 63.9, 60.9, 60.8, 53.6, 35.6, 27.9, 27.9, 19.0, 19.0, 14.4; **IR** (film): 3077, 2973, 1756, 1704, 1638, 1611, 1241, 917, 783 cm^{-1}; **HRMS** (ESI$^+$) calc'd for $[C_{23}{}^{13}CH_{30}O_5Na]$ (M+Na$^+$): *m/z* 422.2019, found 422.2019.



Bisporphyrin-bullvalene 10. A solution of bullvalene **8** (12.1 mg, 0.0303 mmol, 1.0 equiv) in CH_2Cl_2 (0.60 mL) was added to a vial under N_2 containing acrylamide porphyrin **9**[6] (77 mg, 0.075

(6) Lippert, A. R.; Keleshian, V. L.; Bode, J. W. *Org. Biomol. Chem.* **2009**, *7*, 1529-1532.

mmol, 2.5 equiv) and Hoveyda-Grubbs II (1.0 mg, 0.0016 mmol, 5.3 mol %). The vial was sealed and heated in an oil bath at 40 °C for 3 h. Additional portions of Hoveyda-Grubbs II (3.0 – 10 mol %) were added to the reaction mixture every 3-12 hours until no monoporphyrin bullvalene cross-metathesis product was observed by TLC (R_f 0.60 in 2:1 hexane/EtOAc) (10 portions/61 mol % total). The reaction mixture was concentrated under reduced pressure and purified by flash chromatography (using a gradient of 19:1 PhMe/EtOAc + 0.1% Et_3N to 11:1 PhMe/EtOAc + 0.1% Et_3N). Fractions containing the bisporphyrin-bullvalene product were combined, concentrated under reduced pressure, and further purified by preparative TLC (PhMe/EtOAc/Et_3N 98:1:1) to remove residual acrylamide porphyrin starting material. Final purification was achieved by preparative TLC (PhMe/EtOAc/Et_3N 93:6:1). The preparative TLC SiO_2 was extracted with CH_2Cl_2 + 0.3% Et_3N, which was then concentrated under reduced pressure to yield bisporphyrin-bullvalene **10** as a purple oil (19.6 mg, ~27% yield). (Note that the product is somewhat light-sensitive.) **R_f** 0.30-0.40 (2:1 hexane/EtOAc); **^{1}H NMR** (500 MHz, CD_2Cl_2, major peaks reported) δ 9.05 – 8.77 (m, 15.4 H), 8.29 – 8.16 (m, 4.5H), 8.14 – 7.98 (m, 15.2H), 7.90 – 7.75 (m, 6.0H), 7.34 – 6.82 (m, 3.3H), 6.55 – 6.04 (m, 2.8H), 6.01 – 5.73 (m, 1.5H), 4.40 – 3.90 (m, 5.2H), 3.40 – 3.00 (m, 3.9H), 2.71 – 2.43 (m, 2.1H), −2.66 – −2.89 (m, 4H); **^{13}C NMR** (150 MHz, CD_2Cl_2 + 3% CS_2, major peaks reported) δ 149.4, 141.7, 141.7, 135.6, 130.8, 130.3, 130.2, 129.9, 129.5, 129.2, 129.1, 128. 6, 128.3, 128.3, 121.9, 121.8, 121.8, 119.8, 118.4, 60.8, 35.5, 30.3, 28.4, 19.2, 14.7, 14.6; **IR** (film) 2962, 2904, 2870, 1694, 1592, 1519, 1475, 1363, 1245 cm^{-1}; **HRMS** (MALDI) calc'd for [$C_{161}{}^{13}CH_{184}N_{10}O_7$] ($M^+$): *m/z* 2382.4378, found 2382.4384.

Representative Procedure for ^{13}C NMR Analysis of ^{13}C-BPB Equilibrium Populations.

^{13}C-BPB (**10**) (3.9 mg, 1.6 μmol, 1 equiv)[7] and C_{70} (1.4 mg, 1.7 μmol, 1 equiv) were dissolved in 580 μL CS_2 and 20 μL CD_2Cl_2. The solution was transferred to a 5 mm NMR tube (Armar Chemicals 5 mm Ultra Precision), and ^{13}C NMR acquisition was commenced 25 min. after sample preparation.[8] (Note: Sample was kept protected from light.) A ^{1}H-decoupled ^{13}C NMR experiment was conducted at 295 K and 150 MHz (using a Bruker AV-II-600 spectrometer with a cryoprobe)[9] with 1500 scans (~1.2 h of acquisition time).[10]

Procedure for ^{13}C NMR Analysis of ^{13}C-Bisallyl-bullvalene Equilibrium Populations.

Without analyte. ^{13}C-Bisallyl-bullvalene **8** (2.5 mg, 6.3 μmol) was dissolved in 300 μL CS_2 and 300 μL THF-d_8, and the solution was transferred to a 5 mm NMR tube. A ^{1}H-decoupled ^{13}C NMR experiment was conducted at 298 K and 125 MHz (using a Bruker AV-III-500 spectrometer) with 5800 scans (~4 h of acquisition time).

With analyte. A solution of C_{70} (1.2 mg, 1.4 μmol, 1 equiv) in CS_2 (300 μL) was added to a solution of ^{13}C-bisallyl-bullvalene **8** (0.6 mg, 1.5 μmol, 1 equiv) in THF-d_8 (300 μL), and the resulting solution was transferred to a 5 mm NMR tube. A ^{1}H-decoupled ^{13}C NMR experiment was conducted at 298 K and 125 MHz (using a Bruker AV-III-500 spectrometer) with 44,000 scans (~34 h of acquisition time).

(7) The same concentration of ^{13}C-BPB (**10**) (3.9 mg ^{13}C-BPB/600 μL solvent) was used in each ^{13}C NMR experiment so as to avoid a concentration-dependent change in the NMR spectra.

(8) All solutions of ^{13}C-BPB (**10**) with analytes were allowed to equilibrate for at least 20 min. Allowing ^{13}C-BPB+analyte samples to stay in solution for more than 20 min. prior to commencing ^{13}C NMR experiments had no discernable effect on the spectra.

(9) All ^{13}C-BPB (**10**) ^{13}C NMR experiments were conducted on a Bruker AV-II-600 spectrometer with a cryoprobe.

(10) Between 1500 and 3700 acquisition scans (~1.2-2.8 h of acquisition time) were used in the ^{13}C NMR experiments. Varying the number of scans had no discernable effect on the spectra.

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General Procedure for Pattern Generation from ^{13}C NMR FID.

NMR Processing was carried out using MestReNova v. 6.1.1. Below are the sequential steps carried out for each NMR spectra.

1. Open the NMR's .fid file. Click [File], [Open…], select the file, [Open].

   When the file opens, MestReNova will automatically transform the FID into a NMR spectra via its default Cooley-Tukey fast-Fourier algorithm. Also, the spectra will be processed using a linear phase shift group delay, an exponential apodization line broadening factor of 2 Hz, and zero-filling to increase the original number of FID data points by a factor of two by default. These processing parameters can be checked or changed by clicking [Processing], [Processing Template…].

2. Apply a global automatic phase correction to the spectra. Click [Processing], [Phase Correction], [Options…], check Global, [OK], then click [Processing], [Phase Correction], [Automatic].

3. Reference chemical shifts to the CS_2 peak (192.950 ppm for samples in CS_2 with 3% CD_2Cl_2 and 193.370 ppm for samples in 1:1 CS_2/THF).

4. Pick the peaks in the region 127–131 ppm, which correspond to the ^{13}C-atom, using MestReNova's sensitivity algorithm with parabolic interpolation set to a value of 42 and a noise factor of 75.[11] These parameters can be checked or changed by clicking [Analysis], [Peak Picking], [Options…], [Advanced >>].

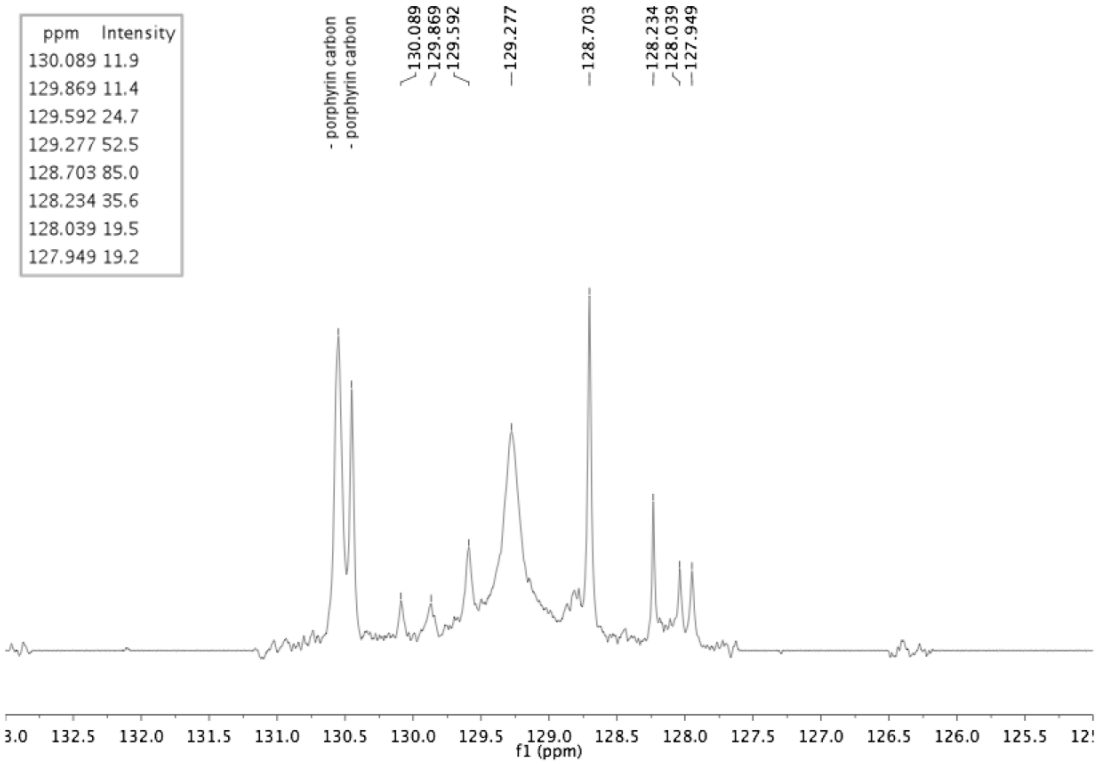
5. Correct the baseline of the region between 125–133 ppm using the Whittaker Smoother method along F1. The filter value was set to 100 and the smooth factor was set to 2. This baseline correction and its parameters can be checked or changed by clicking [Processing], [Baseline], [Baseline Correction…].

(11) The regions 129.55–129.48 ppm and 128.84–128.77 ppm of ^{13}C-BPB spectra were excluded due to overlapping residual toluene.

6. Normalize the most intense peak to a height of 85. Click [Processing], [Normalize…], Normalize by [Peak], set Value to [85], set Peak Position to the ppm value that corresponds to most intense peak.
7. Extract the chemical shifts and peak intensities in the region between 125–133 ppm. Click [View], [Tables], [Peaks]. Select and copy the desired peaks and their intensities.
8. For pattern generation, paste the chemical shifts and their intensities into the program Microsoft Excel 2011 (version 14.1.4) and graph the peak chemical shifts (on the x-axis) against their intensities (on the y-axis) as a Marked Scatter plot. Note that the x-axis was formatted with values in reverse order to match the appearance of peaks on the NMR spectra (from left to right, higher ppm to smaller ppm).

Figure S1. ^{13}C NMR of ^{13}C-BPB (10)
(2.8 mM in CS_2 with 3% CD_2Cl_2, 150 MHz, 295K, 133–125 ppm region)

A. Trial 1



B. Trial 2

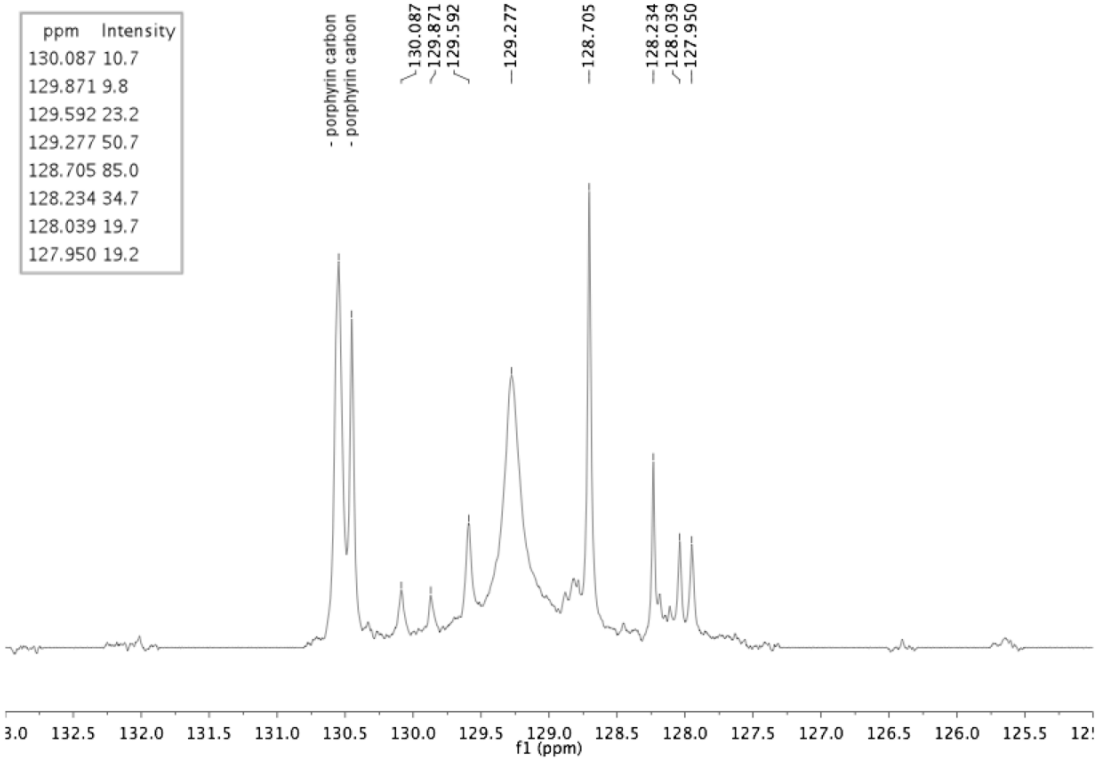
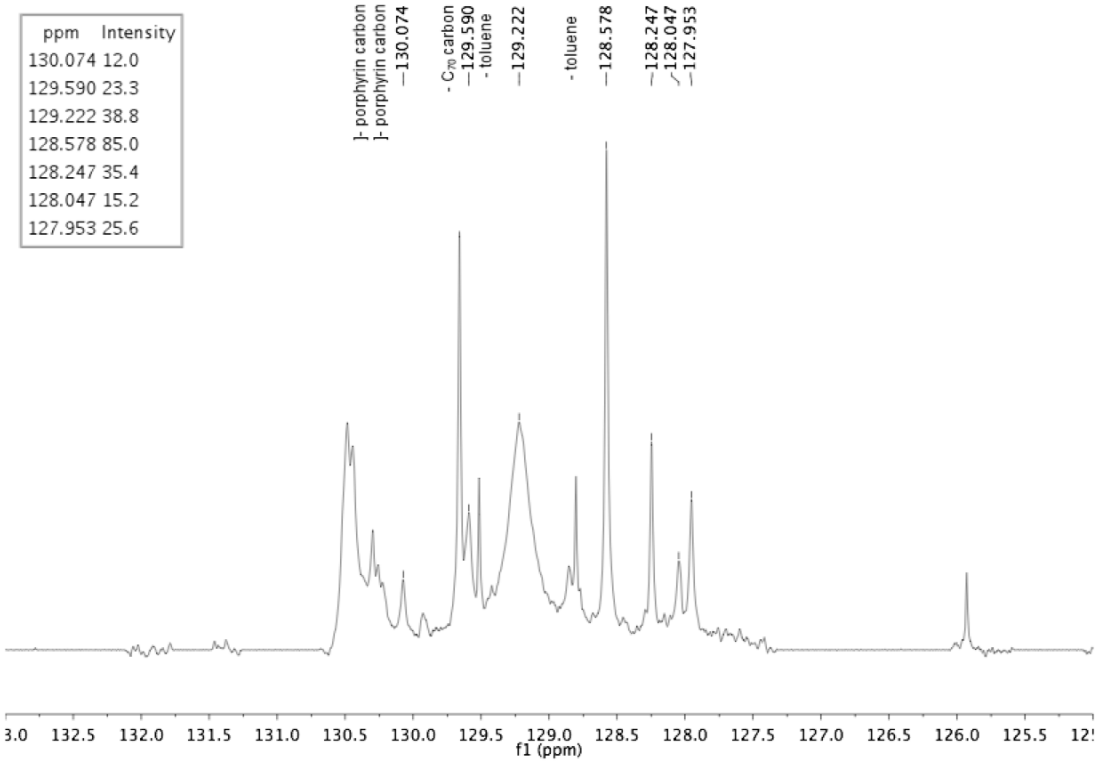


Figure S2. ^{13}C NMR of ^{13}C-BPB (10) + C_{70} (1 equiv)
(2.8 mM in CS_2 with 3% CD_2Cl_2, 150 MHz, 295K, 133–125 ppm region)

A. Trial 1



B. Trial 2

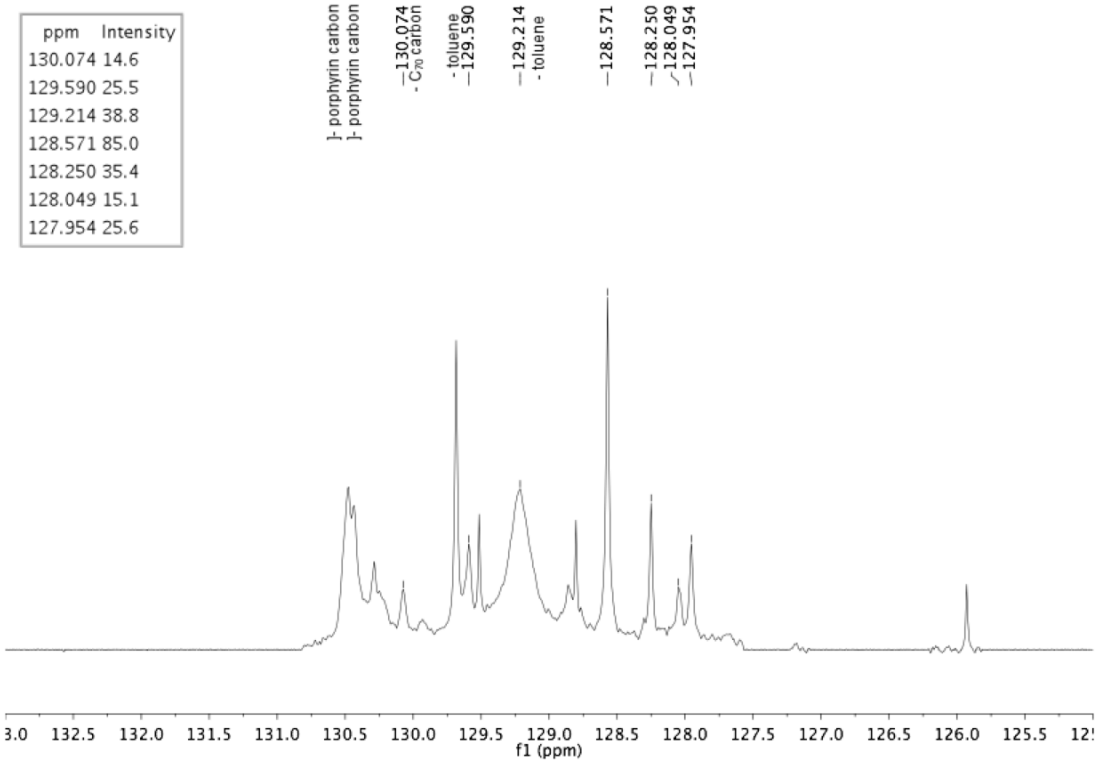
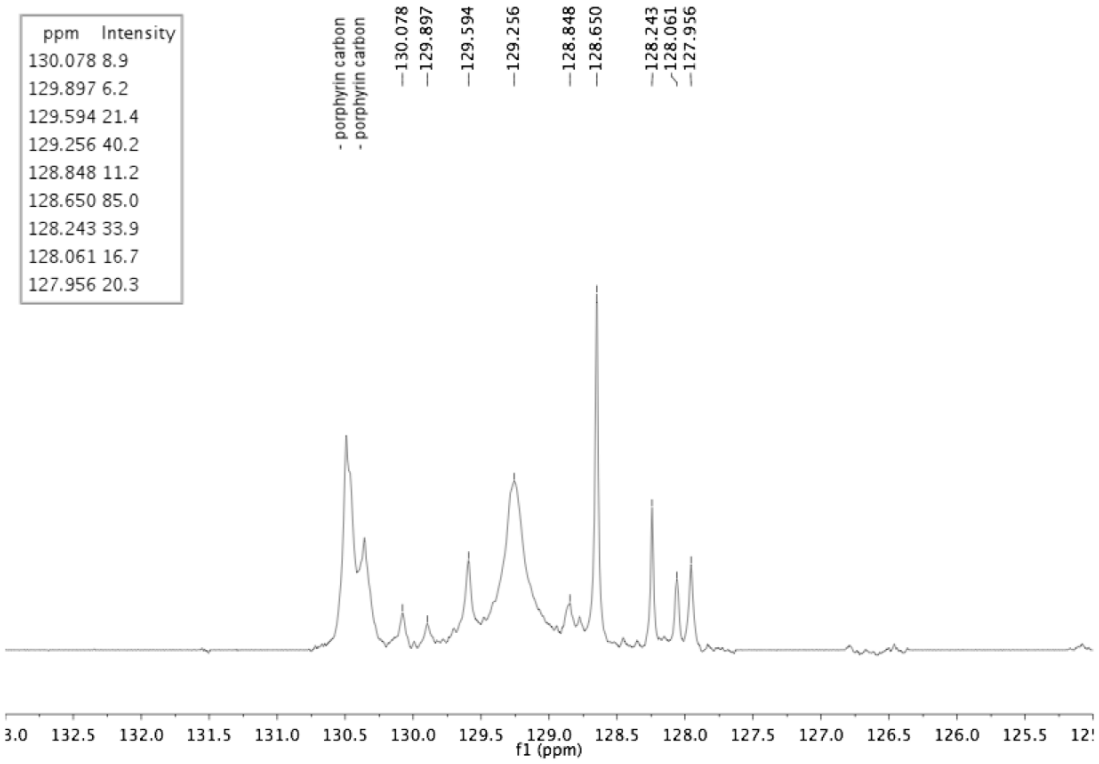


Figure S3. ^{13}C NMR of ^{13}C-BPB (10) + C_{60} (2 equiv)
(2.8 mM in CS_2 with 3% CD_2Cl_2, 150 MHz, 295K, 133–125 ppm region)

A. Trial 1



B. Trial 2

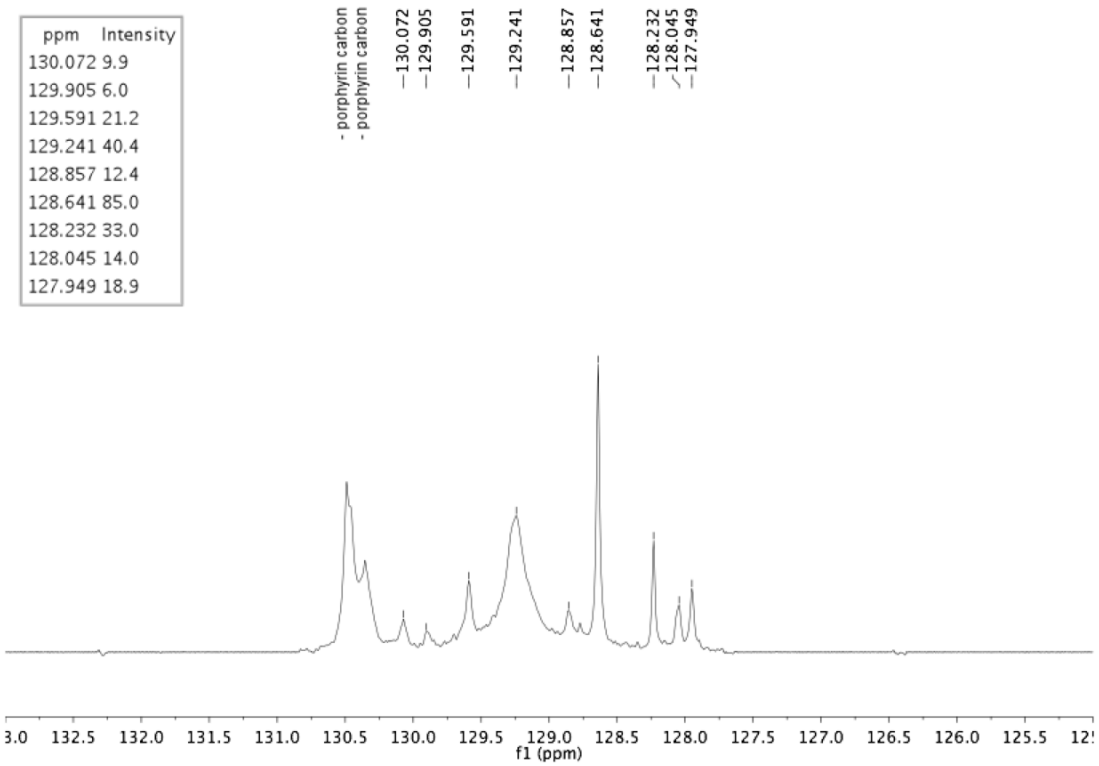


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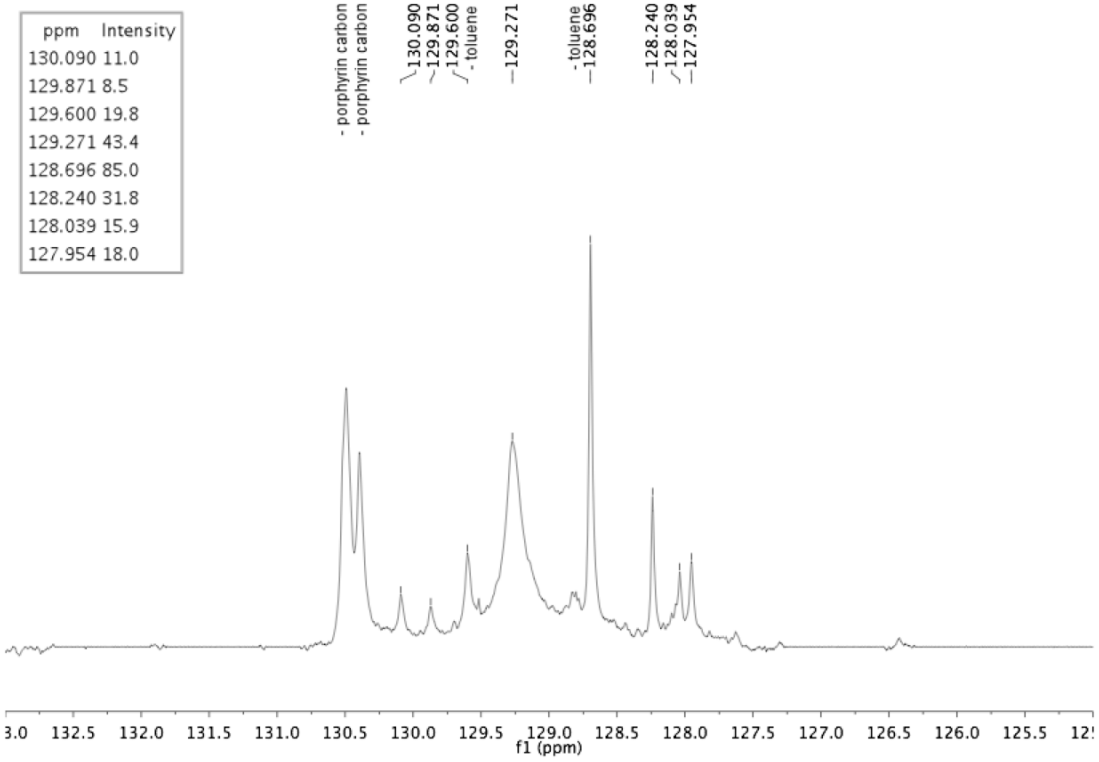
Figure S4. ^{13}C NMR of ^{13}C-BPB (10) + derC_{60} (4 equiv)
(2.8 mM in CS_2 with 3% CD_2Cl_2, 150 MHz, 295K, 133–125 ppm region)

A. Trial 1



B. Trial 2

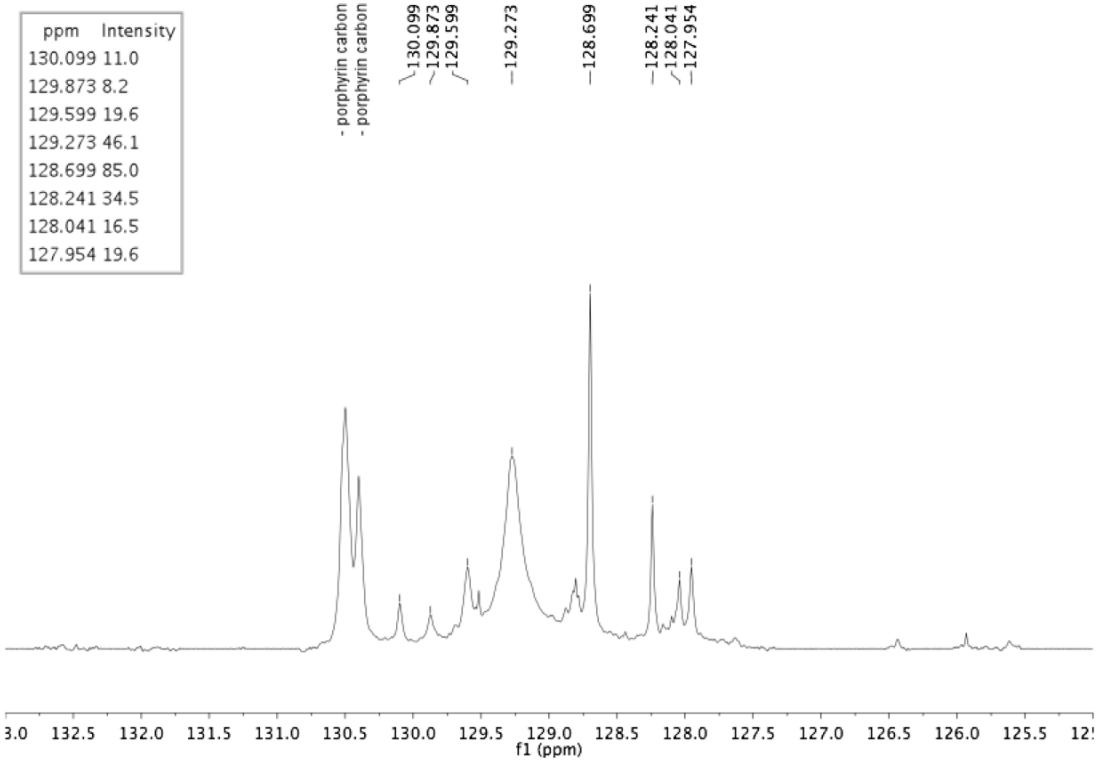


Figure S5. ^{13}C NMR of ^{13}C-bisallyl-bullvalene (8)
(10 mM in 1:1 CS_2/THF-d_8, 125 MHz, 298K, 133–125 ppm region)

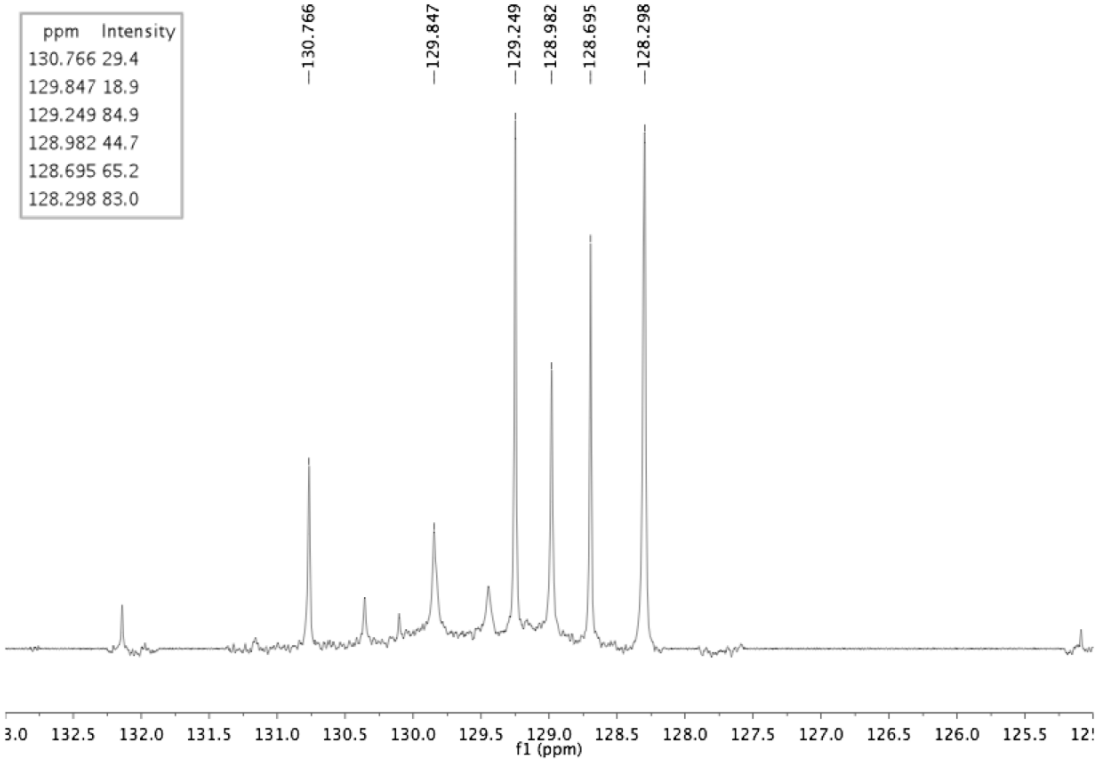
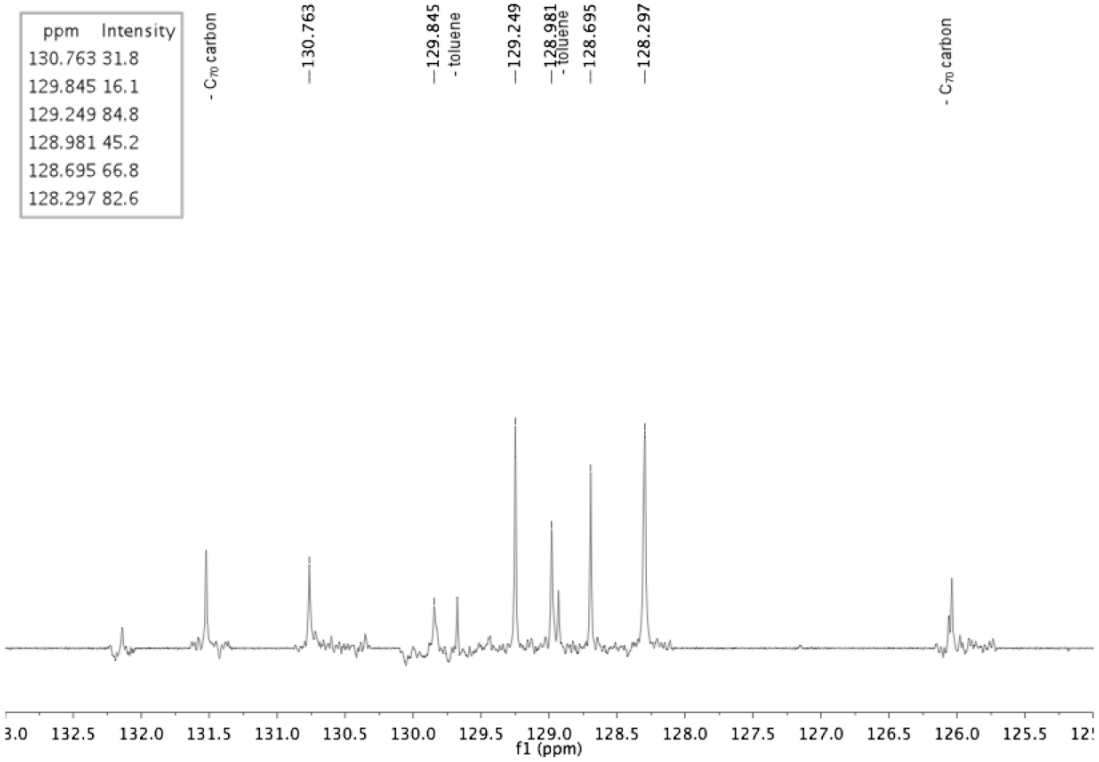
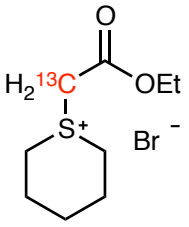


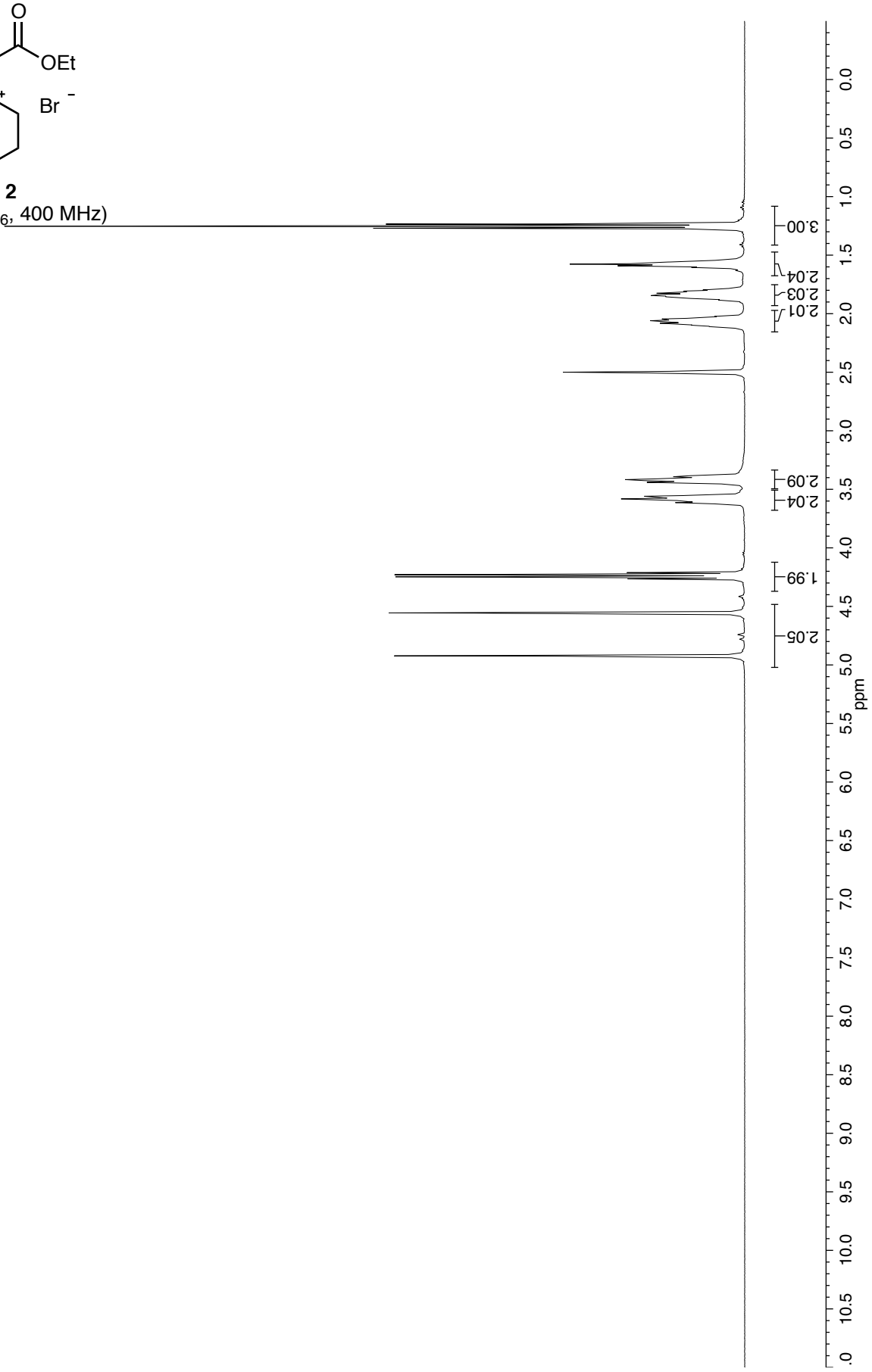
Figure S7. ^{13}C NMR of ^{13}C-bisallyl-bullvalene (8) + C_{70} (1 equiv)
(2.5 mM in 1:1 CS_2/THF-d_8, 125 MHz, 298K, 133–125 ppm region)

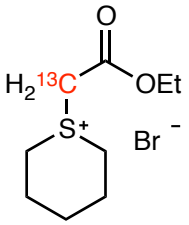




2

(DMSO-d_6, 400 MHz)





2
(DMSO-d_6, 100 MHz)

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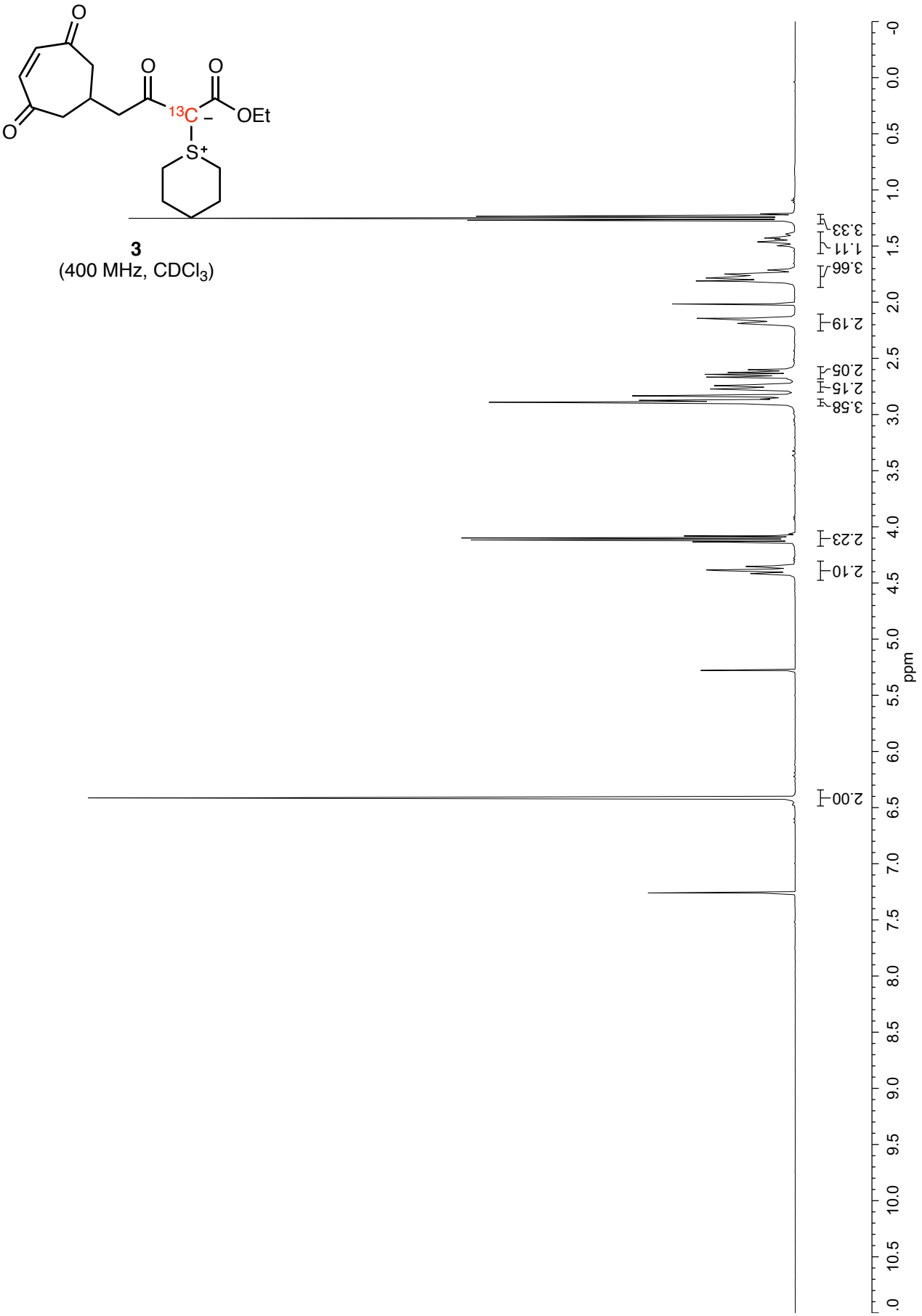
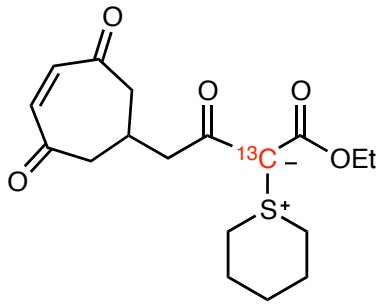
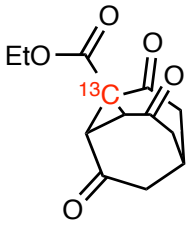


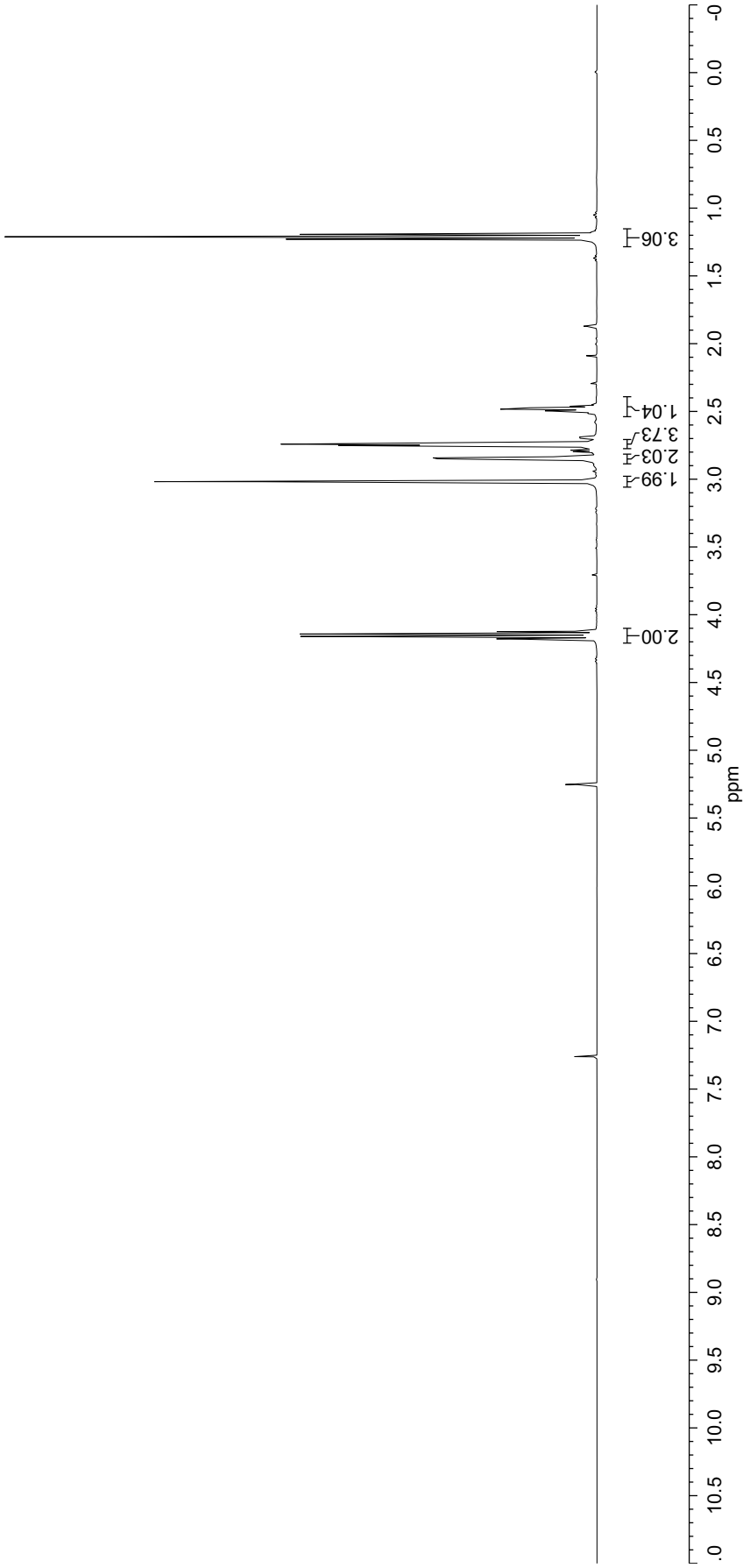
3
(400 MHz, $CDCl_3$)

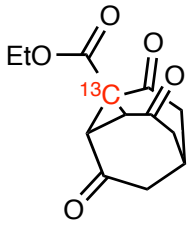


3
(100 MHz, $CDCl_3$)



4
(400 MHz, $CDCl_3$)





4
(100 MHz, $CDCl_3$)

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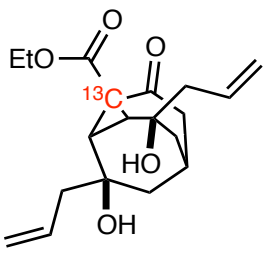
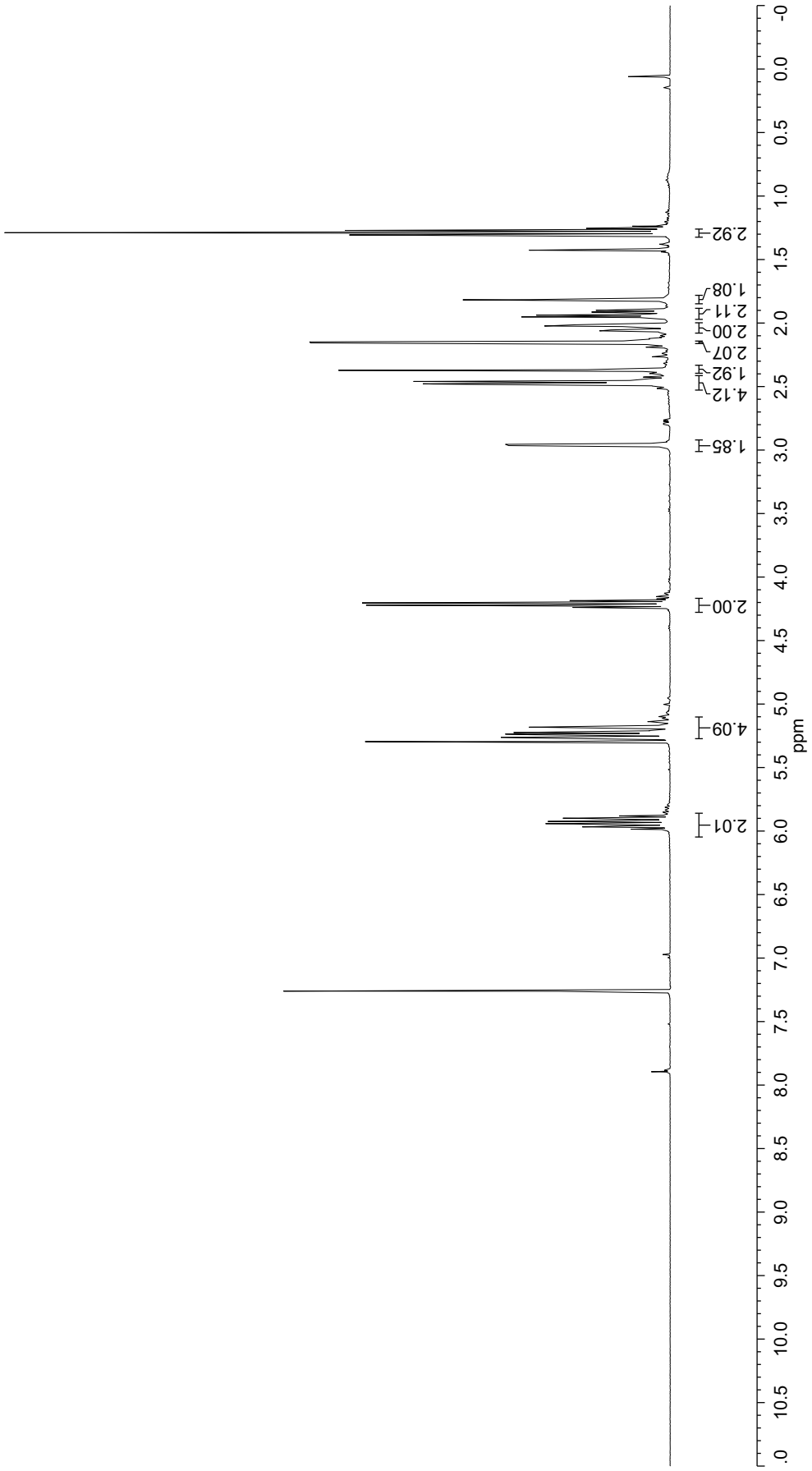


5a
(400 MHz, $CDCl_3$)



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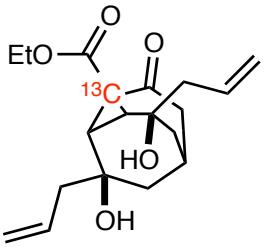
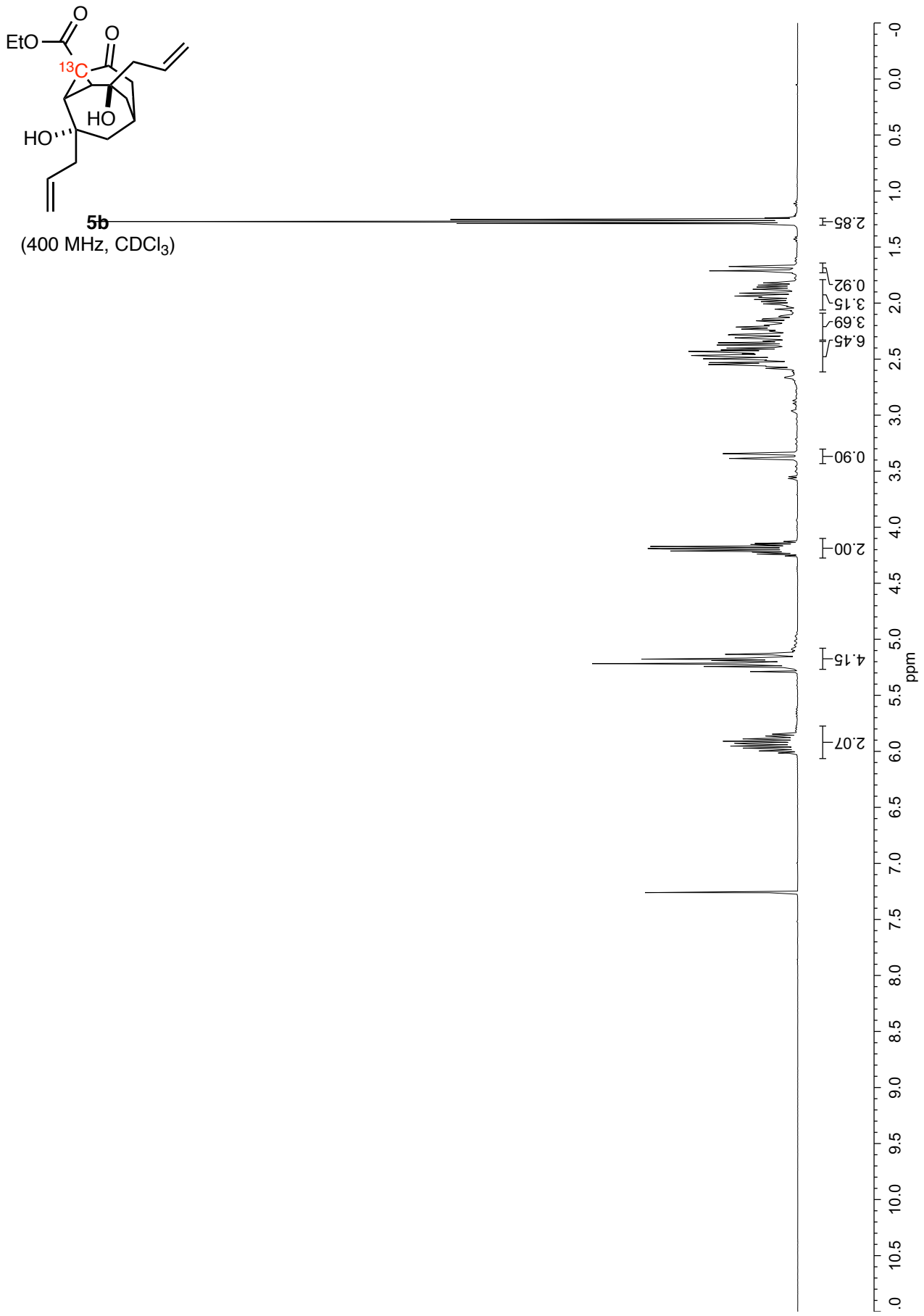


5a
(100 MHz, $CDCl_3$)



5b
(400 MHz, $CDCl_3$)

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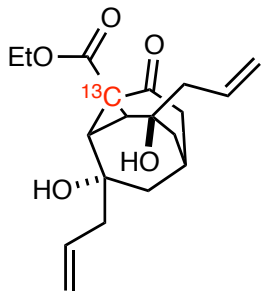

5b
(100 MHz, $CDCl_3$)

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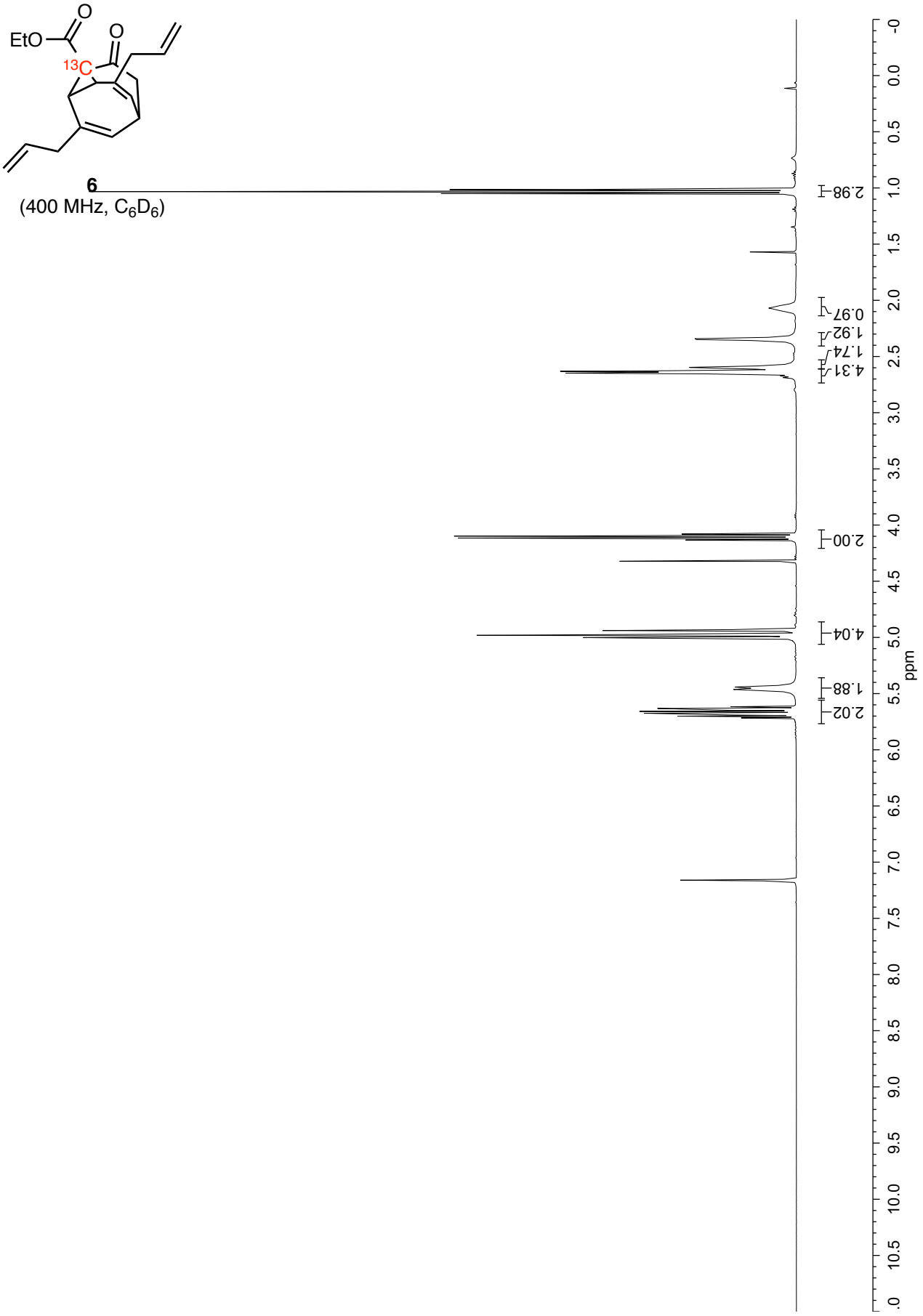
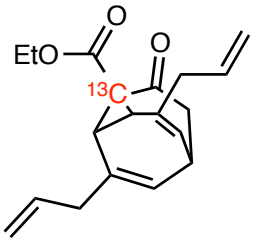
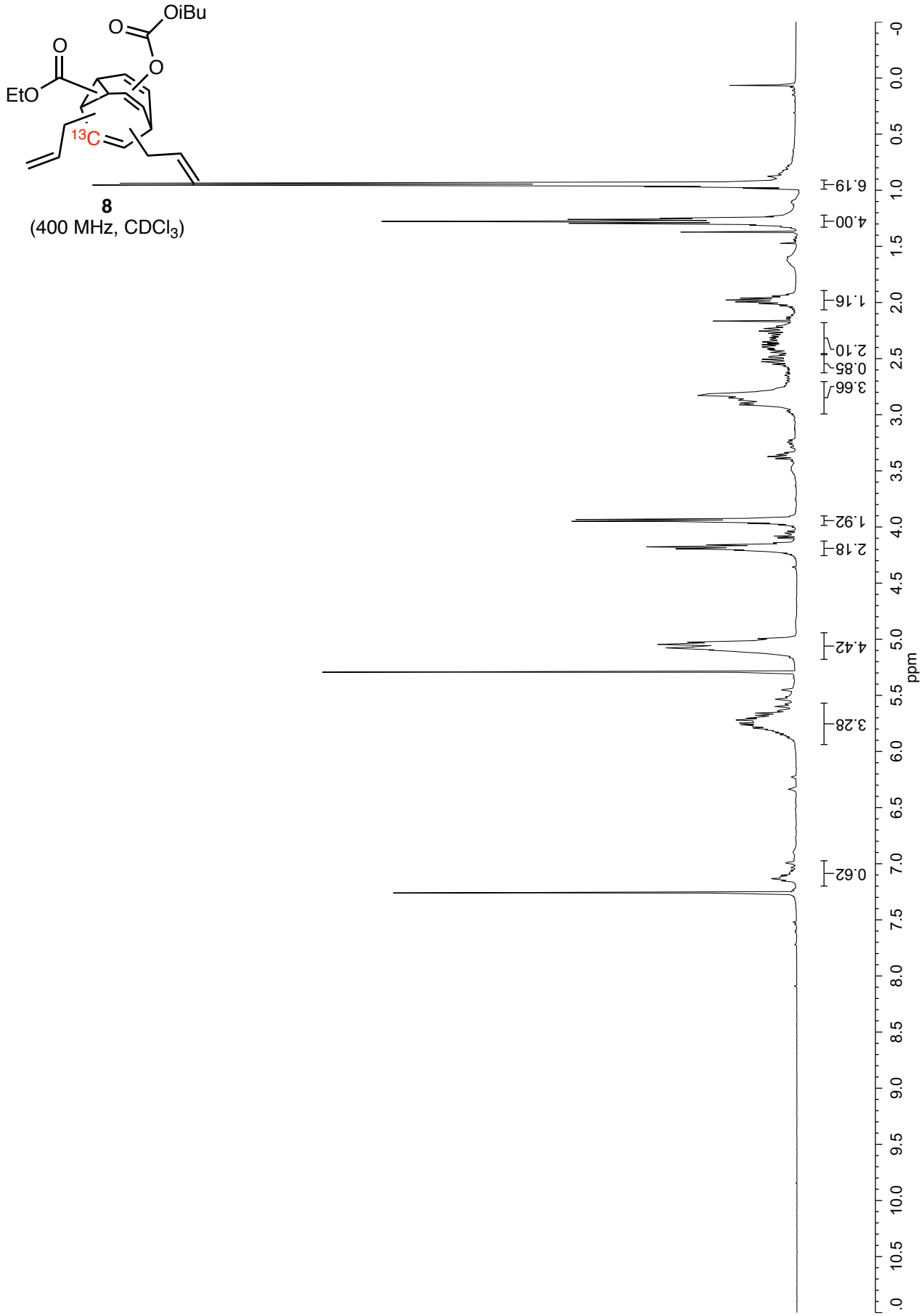
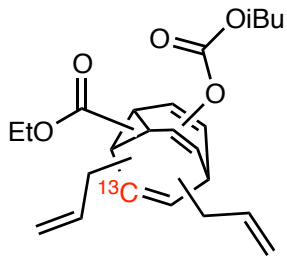




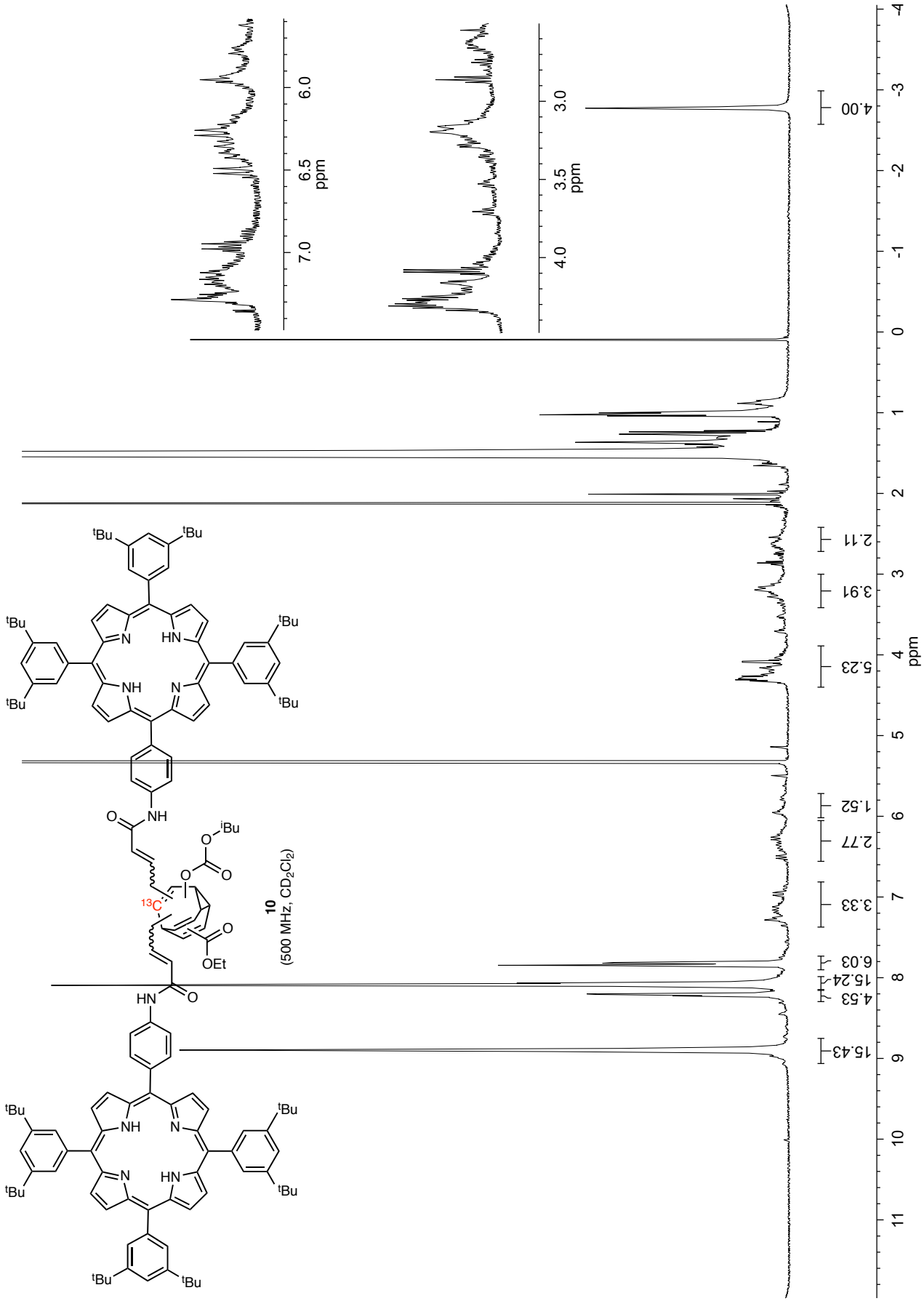
6
(100 MHz, C_6D_6)



8
(400 MHz, $CDCl_3$)



8
(100 MHz, $CDCl_3$)


4.00
2.11
3.91
5.23
1.52
2.77
3.33
6.03
15.24
4.53
15.43
ppm
10
(500 MHz, CD2Cl2)
tBu
iBu
OEt
NH
HN
N
O
13C

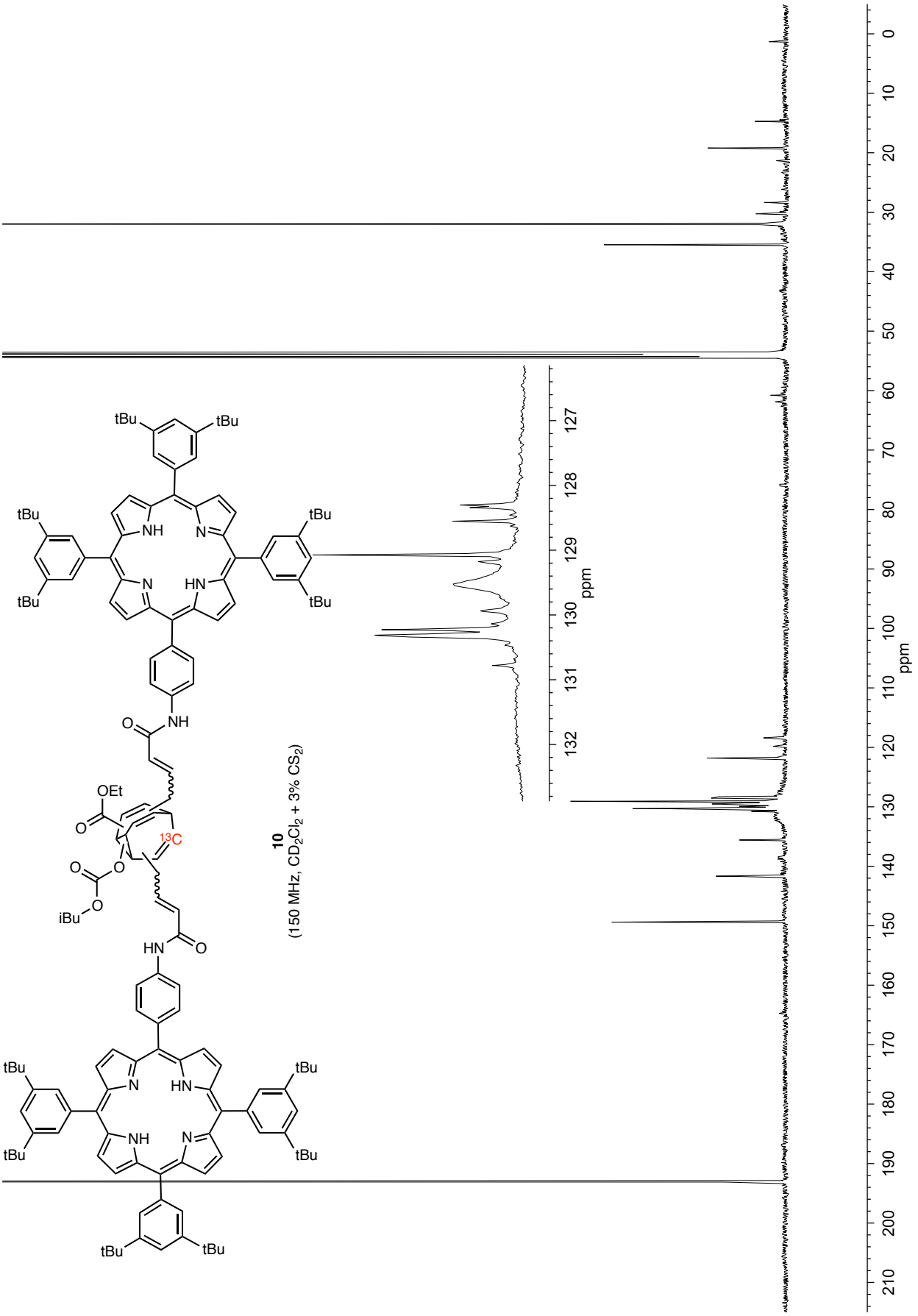

tBu
NH
N
HN
O
OEt
13C
iBu
10
(150 MHz, CD2Cl2 + 3% CS2)
ppm
ppm

Figure S6. 2D-EXSY of ^{13}C-BPB (**10**)
(CD_2Cl_2, 600 MHz, T_1=500 µs, positive and negative phases are differentiated by red and blue colors)

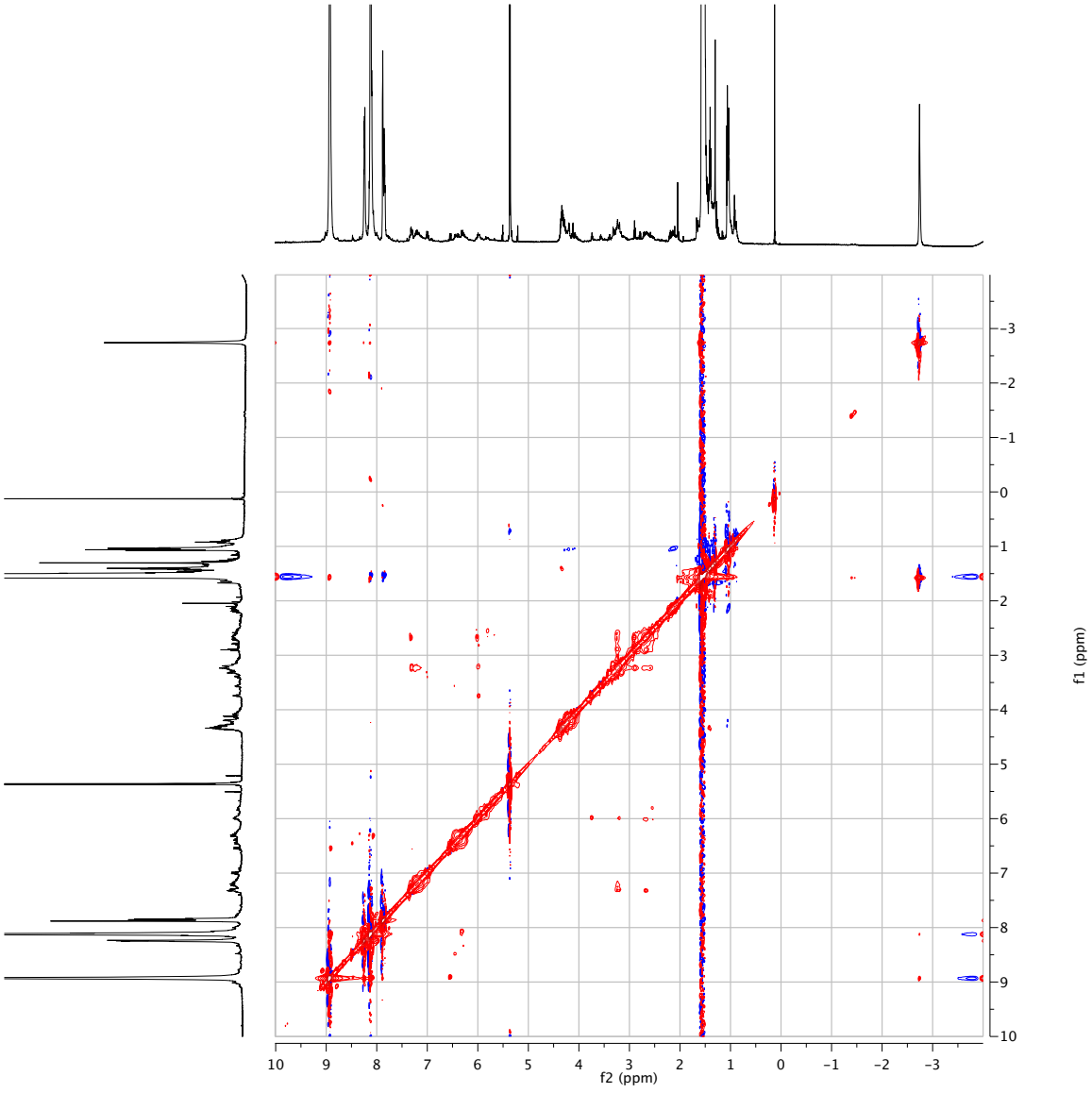


Figure S7. HR-MALDI spectrum of ^{13}C-BPB (**10**)