In-Depth Assessment of the Pd-Catalyzed Fluorination of 5-Membered Heteroaryl Bromides

General Supporting Information

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General Procedures.

Anhydrous, oxygen-free toluene, ether (Et_2O), tetrahydrofuran (THF), and dichloromethane (CH_2Cl_2) were purchased from J. T. Baker and passed through two activated alumina columns followed by sparging with argon before use. All other anhydrous solvents were purchased from Aldrich in Sure-Seal^{TM} bottles and sparged with argon before use. Potassium fluoride (99.0 %) was purchased from Aldrich and dried at 180 °C under vacuum for 24 h. The dried KF was then transferred to a nitrogen-filled glovebox where it was thoroughly ground using an oven-dried mortar and pestle. The finely ground KF was then filtered through a 45 μm stainless-steel sieve (purchased from Cole Parmer) to obtain KF with particle size of < 45 μm. **L1**,[1] **L2**,[2] **L3**,[3] **P1**,[4] **P2**,[2] and **P3**,[3] were prepared according to literature procedures. The **P3** used in this work was received as a gift from Dr. Aaron Sather (MIT), to whom we are grateful. Di(1-adamantyl)phosphine was received as a gift from Sigma-Aldrich, for which we are grateful, and was converted to di(1-adamantyl)chlorophosphine following the literature procedure. [5] [(1,5-COD)Pd($CH_2TMS)_2$] was prepared according to the literature procedure[6] and stored at –20 °C in a nitrogen-filled glovebox when not in use. XPhos-based precatalyst **S17** and XantPhos-based precatalyst **S18** were prepared according to the literature procedure (see Figure S1 for structures).[7] Degassed *aq.* K_3PO_4 solutions were obtained by dissolving K_3PO_4 in deionized water, and degassing the solution by performing several evacuation/argon refill cycles while sonicating the solution. N-bromosuccinimide was recrystallized from hot water and stored at 0 °C in the dark when not in use. All other reagents were purchased from commercial sources and used as received, or prepared as described below. All compounds were analyzed by ^{1}H, ^{13}C, ^{31}P,

^{19}F NMR, and IR, where appropriate. New compounds were also analyzed by elemental analysis or high resolution ESI-MS. All ^{19}F NMR yields stated for fluorination reactions are calculated from ^{19}F NMR spectra relative to an internal standard of 1-fluoronaphthalene. ^{1}H and ^{13}C NMR spectra were recorded on a Varian XL 300 MHz, Varian Inova 500 MHz, or Bruker AVANCE-600 MHz spectrometers and were calibrated using residual solvent ($CDCl_3$: ^{1}H NMR: δ 7.26 ppm; ^{13}C NMR: δ 77.24 ppm) as an internal reference. ^{19}F and $^{31}P\{^{1}H\}$ spectra were recorded on Varian XL 300 MHz or Varian Inova 500 MHz spectrometers. ^{19}F NMR spectra were calibrated to an external standard of neat $CFCl_3$ (δ 0 ppm). $^{31}P\{^{1}H\}$ NMR spectra were calibrated to an external standard of neat H_3PO_4 (δ 0.0 ppm). The following abbreviations were used to explain multiplicities: s = singlet, d = doublet, t = triplet, pt = pseudotriplet, q = quartet, p = pentet, m = multiplet. IR spectra were recorded on a Thermo Scientific Nicolet iS5 Fourier Transform IR Spectrometer. HRMS data were collected on a Bruker Daltonics APEXIV 4.7 Tesla Fourier Transform Ion Cyclotron Resonance Mass Spectrometer. Elemental analysis was performed by Atlantic Microlabs Inc., Norcross, GA, USA. Low-temperature X-ray diffraction data (ϕ-and ω-scans) were collected on a Siemens Platform three-circle diffractometer coupled to a Bruker-AXS Smart Apex CCD detector with graphite-monochromated Mo Kα radiation (λ = 0.71073 Å) or a Bruker-AXS X8 Kappa Duo diffractometer coupled to a Smart Apex2 CCD detector with Mo K_α radiation (λ = 0.71073 Å). Screw-cap reaction tube refers to Fisher 16 x 125 mm tubes (Cat. No. 1495925C) or Fisher 20 x 150 mm tubes (Cat. No. 1495937C) tubes equipped with SPTA PTFE/SIL F/15-425 10 (Cat. No. 03394A) septa or SPTA SPTA PTFE/SIL F/18-400 10

(Cat. No. 03394B), respectively. All reactions carried out at high temperatures should be performed behind a blast shield and/or closed hood sash.

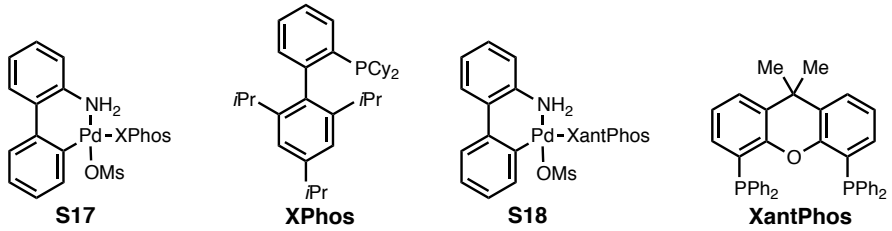
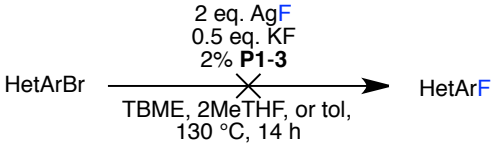
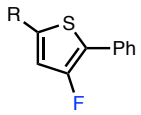


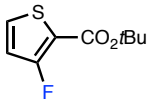
Figure S1. Structures of precatalysts used in this work.

Table S1. Additional examples of unsuccessful fluorinations of 5-membered heteroaryl bromides.

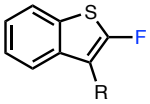




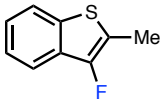
S1a (R = CHO)[b]
S1b (R = C(O)Me)[b]
S1c (R = CN)[b]
S1d (R = NO_2)[b]



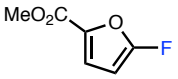
S2



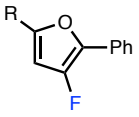
S3a (R = H)
S3b (R = Me)[b]



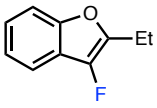
S4[b]



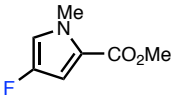
S5



S6a (R = CO_2Me)
S6b (R = Ph)



S7[b]



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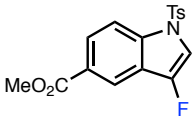
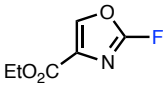
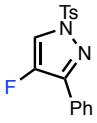


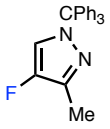
S9



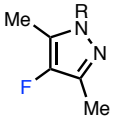
S10[b]



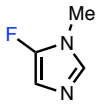
S11[c]



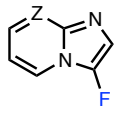
S12



S13a (R = Ts)[c]
S13b (R = Tris)[c]
S13c (R = CPh_3)
S13d (R = Me)



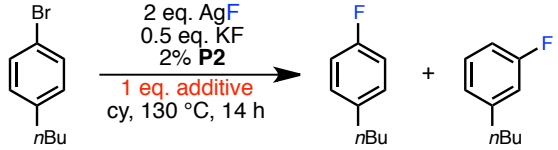
S14



S15a (Z = CH)
S15b (Z = N)

[a]Reaction conditions: ArBr (0.10 mmol), AgF (2.0 eq.), KF (0.05 eq.), **P1-3** (2 %), solvent (1.0 mL), 130 °C, 14 h. [b]Significant decomposition observed by ^{19}F NMR and GC/MS. [c]$ArSO_2F$ observed by ^{19}F NMR and GC/MS.

Table S2. Inhibition of the Pd-catalyzed fluorination of 4-(*n*Bu)PhBr by nitrogen-containing 5-membered heteroarenes.[a]



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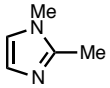
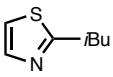
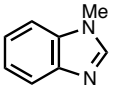
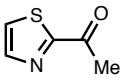
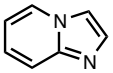
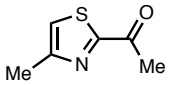
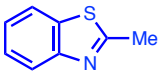
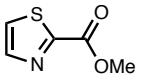
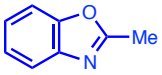
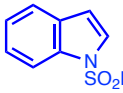
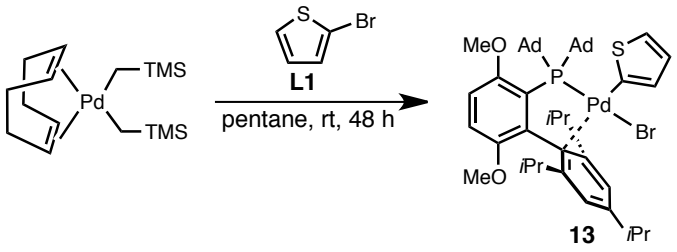
2		n/o	9		3%
3		18%	10		31%
4		n/o	11		52%
5		22%	12		86%
6		26%	13		85%
7		89%	14		83%

[a]Reaction conditions: 4-(*n*Bu)PhBr (0.10 mmol), additive (0.10 mmol), AgF (0.20 mmol), KF (0.05 mmol), **P2** (2%), cyclohexane (1.0 mL), 130 °C, 14 h. ^{19}F NMR yields.

Synthesis of new complexes.

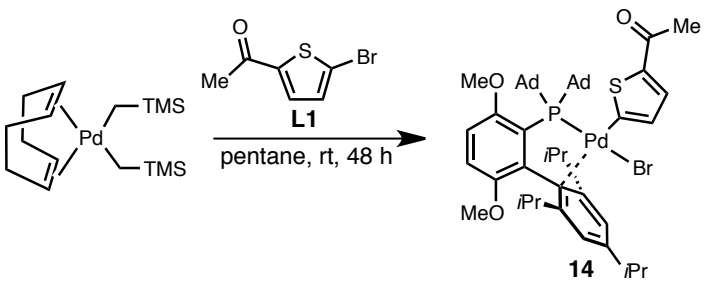


In a nitrogen-filled glovebox, an oven-dried 20 mL vial equipped with a stir bar was charged with **L1** (133 mg, 0.21 mmol, 1.00 eq.) and 2-bromothiophene (60.1 μl, 062 mmol, 3.00 eq.). Pentane (5 mL) was added, and the non-homogenous reaction mixture was vigorously stirred as [(1,5-)Pd($CH_2TMS)_2$[(80.0 mg, 0.21 mmol, 1.00 eq.) was added in one portion. The reaction mixture was allowed to vigorously stir for 48 h, at which time it was filtered through a sintered glass frit. The resulting yellow solid was thoroughly washed with pentane (3 × 5 mL), affording **13** (130 mg, 65%) as a dark yellow solid. Clean ^{1}H, ^{13}C, and ^{31}P NMR spectra of **13** could not be obtained due to its slow decomposition (CD_2Cl_2, $CDCl_3$, THF-d_8) or poor solubility (C_6D_6) in solution. It was detected by ^{1}H NMR (500 MHz, CD_2Cl_2) signals at δ 7.37 (d, J = 6 Hz, 1H), 6.88-7.15 (m, 5H), 6.60 (bs, 1H), 3.85 (s, 3H), 3.42 (bs, 3H), 2.91 (bs, 1H), 2.57 (bs, 2H), 2.33 (bs, 6H), 2.13 (bs, 6H), 1.94 (bs, 6H), 1.58-1.78 (bs, 17H), 1.25 (bs, 6H), 0.88 (bs, 6H) ppm. ^{31}P NMR (202 MHz, CD_2Cl_2): δ ~76 ppm (bs). Anal. Calcd. for $C_{47}H_{64}BrO_2PPdS$: C, 62.01; H, 7.09; found: C, 62.20; H, 7.04.

X-ray quality crystals of **13** were obtained by layering a CH_2Cl_2/Et_2O solution of **13** with pentane and cooling the mixture to –20 °C in a nitrogen-filled glovebox. The thiophene ring in **13** is disordered over two positions.

Identification code	14036
Empirical formula	C47 H64 Br O2 P Pd S
Formula weight	910.32

Temperature	100(2) K	
Wavelength	0.71073 Å	
Crystal system	Triclinic	
Space group	P -1	
Unit cell dimensions	a = 11.4610(3) Å	a= 66.5161(12)°.
	b = 13.5662(3) Å	b= 89.9625(13)°.
	c = 15.6083(4) Å	g = 74.4572(12)°.
Volume	2128.89(9) $Å^3$	
Z	2	
Density (calculated)	1.420 Mg/m^3	
Absorption coefficient	1.498 mm^{-1}	
F(000)	948	
Crystal size	0.600 x 0.090 x 0.050 mm^3	
Theta range for data collection	1.433 to 30.032°.	
Index ranges	-16<=h<=16, -19<=k<=19, -21<=l<=21	
Reflections collected	104796	
Independent reflections	12442 [R(int) = 0.0293]	
Completeness to theta = 25.242°	100.0 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.7461 and 0.6043	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	12442 / 198 / 499	
Goodness-of-fit on F^2	1.082	
Final R indices [I>2sigma(I)]	R1 = 0.0240, wR2 = 0.0586	
R indices (all data)	R1 = 0.0288, wR2 = 0.0608	
Extinction coefficient	n/a	
Largest diff. peak and hole	0.693 and -1.021 $e.Å^{-3}$	



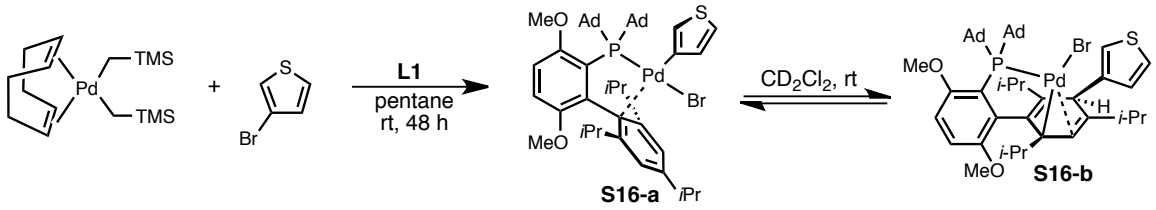
In a nitrogen-filled glovebox, an oven-dried 20 mL vial equipped with a stir bar was charged with **L1** (200 mg, 0.31 mmol, 1.00 eq.) and 2-bromo-5-acetylthiophene (69.7 mg, 0.31 mmol, 1.10 eq.). Pentane (10 mL) was added, and the non-homogenous reaction mixture was vigorously stirred as [(1,5-COD)Pd($CH_2TMS)_2$[(121 mg, 0.31 mmol, 1.00 eq.) was added in one portion. The reaction mixture was allowed to vigorously stir for 48 h, at which time it was filtered through a sintered glass frit. The resulting yellow solid was thoroughly washed with pentane (3 × 5 mL), affording **14** (206 mg, 70%) as a yellow solid. Clean ^{1}H, ^{13}C, and ^{31}P NMR spectra of **14** could not be obtained due to its slow decomposition (CD_2Cl_2, $CDCl_3$, THF-d_8) or poor solubility (C_6D_6) in solution. It was detected by ^{1}H NMR (500 MHz, CD_2Cl_2) signals at δ 7.46 (d, J = 4 Hz, 1H), 7.08 (s, 2H), 6.97 (dd, J = 9, 3 Hz, 1H), 6.89 (d, J = 9 Hz), 6.78 (d, J = 4 Hz), 3.84 (s, 3H), 3.34 (s, 3H), 3.01 (septet, J = 7 Hz), 2.34-2.39 (m, 9H), 2.08-2.17 (m, 6H), 1.95 (bs, 7H), 1.59-1.79 (m, 19H), 1.34 (d, J = 7 Hz, 6H), 0.83 (bs, 6H) ppm. ^{31}P NMR (202 MHz, CD_2Cl_2): δ ~73.8 ppm (bs) (free **L1** was also detected). Anal. Calcd. for $C_{49}H_{66}BrO_3PPdS$: C, 61.79; H, 6.98; found, C, 60.79; H, 7.13.

X-ray quality crystals of **14** were obtained by layering a CH_2Cl_2/Et_2O solution of **14** with pentane and cooling the mixture to –20 °C. The crystal of **14** was low quality and split into multiple domains, each rotated just a couple of degrees from the next or previous one(s), respectively. Integration as "not twinned" resulted in a very large

(refined) box size. This is clearly suboptimal; however, integration as a non-merohedral twin was not stable and resulted in unusable data. Three molecules of CH_2Cl_2 (one disordered) are present in the unit cell.

Identification code	X14114	
Empirical formula	C52 H72 Br Cl6 O3 P Pd S	
Formula weight	1207.13	
Temperature	100(2) K	
Wavelength	1.54178 Å	
Crystal system	Triclinic	
Space group	P -1	
Unit cell dimensions	a = 13.5389(7) Å	a= 70.077(4)°.
	b = 14.0092(8) Å	b= 77.005(4)°.
	c = 17.1535(11) Å	g = 62.377(3)°.
Volume	2701.4(3) $Å^3$	
Z	2	
Density (calculated)	1.484 Mg/m^3	
Absorption coefficient	7.324 mm^{-1}	
F(000)	1244	
Crystal size	0.330 x 0.300 x 0.005 mm^3	
Theta range for data collection	2.749 to 68.244°.	
Index ranges	-15<=h<=16, -16<=k<=16, -20<=l<=20	
Reflections collected	72957	
Independent reflections	9735 [R(int) = 0.0790]	

Completeness to theta = 67.679°	98.9 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.7531 and 0.5592
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	9735 / 1134 / 646
Goodness-of-fit on F^2	1.035
Final R indices [I>2sigma(I)]	R1 = 0.0618, wR2 = 0.1710
R indices (all data)	R1 = 0.0701, wR2 = 0.1784
Extinction coefficient	n/a
Largest diff. peak and hole	3.273 and -0.992 e.Å^{-3}



In a nitrogen-filled glovebox, an oven-dried 20 mL vial equipped with a stir bar was charged with **L1** (256 mg, 0.40 mmol, 1.00 eq.) and 3-bromothiophene (112 μl, 1.20 mmol, 3.00 eq.). Pentane (10 mL) was added, and the non-homogenous reaction mixture was vigorously stirred as [(1,5-COD)Pd(CH_2TMS)$_2$[(156 mg, 0.40 mmol, 1.00 eq.) was added in one portion. The reaction mixture was allowed to vigorously stir for 48 h, at which time it was filtered through a sintered glass frit. The resulting yellow solid was thoroughly washed with pentane (3 × 5 mL), affording **S16-a** (255 mg, 70%) as a dark yellow solid. Clean ^{1}H, ^{13}C, and ^{31}P NMR spectra of **S16-a** could not be obtained due to its rearrangement to **S16-b** in solution (~18 % rearranged after 15 min.). It was detected

by ^{1}H NMR (500 MHz, CD_2Cl_2) signals at δ 7.03-7.11 (m, 3H), 6.96 (bs, 1H), 6.91 (bs, 2H), 6.43 (bs, 1H), 3.84 (s, 3H), 3.36 (s, 3H), 2.98 (bs, 1H), 2.57 (bs, 2H), 2.28 (bs, 6H), 2.13 (bs, 6H), 1.93 (bs, 6H), 1.57-1.78 (m, 18H), 1.33 (bs, 6H), 0.85 (bs, 6H) ppm. ^{31}P NMR (122 MHz, CD_2Cl_2): δ ~74 ppm (bs). (The observed broadening of the ^{1}H and ^{31}P NMR signals is likely due to rapid exchange between **S16-a** and **S16-b**).

After 24 h in solution, a 1:1.1 mixture of **S16-a** and **S16-b** was obtained. **S16-b** was detected by ^{1}H NMR (500 MHz, CD_2Cl_2) signals at δ 7.34 (s, 2H), 5.78 (s, 1H), 3.84 (s, 3H), 3.71 (s, 3H), 1.23 (d, J = 7 Hz, 3H), 1.15 (bs, 3H), 1.09 (d, J = 7 Hz, 3h), 0.74 (d, J = 7 Hz, 3H), 0.07 (bs, 3H) ppm. ^{31}P NMR (122 MHz, CD_2Cl_2): δ 83.7 ppm. A ^{13}C NMR (150 MHz, CD_2Cl_2) spectrum of the 1:1.1 mixture of **S16-a** and **S16-b** is included for reference. HRMS (ESI) m/z for $C_{47}H_{64}O_2PPdS$ ($M–Br^–$): 829.3394; found: 829.3390.

Synthesis of heteroaryl bromides.

When available, heteroaryl bromides were purchased from commercial suppliers and used without further purification. In cases where the commercially available aryl bromide was an oil, it was filtered through a short plug of non-basic alumina in a nitrogen-filled glovebox prior to use. 5-bromo-2-phenylthiazole (**9b-Br**),[8] 4-bromo-1-trityl-1*H*-pyrazole (**12b-Br**),[9] 5-bromo-*N,N*-diethylthiophene-2-sulfonamide,[10] 2-bromo-3-phenylthiophene (**21c-Br**),[11] 2-*iso*-butyl-5-phenylthiazole,[12] 4-bromo-3-phenyl-1*H*-pyrazole,[13] *t*-butyl 4-methylthiazole-5-carboxylate (**27c-H**),[14] 2-methylbenzo[b]thiophene,[15] 3-bromo-2-methylbenzo[b]thiophene (**S4-Br**),[16] methyl 3-bromo-1-tosyl-1*H*-indole-5-carboxylate (**S9**),[17] 4-bromo-3-methyl-1-trityl-1*H*-pyrazole

(**S12-Br**), [18] 4-bromo-3,5-dimethyl-1-trityl-1*H*-pyrazole (**S13c-Br**),[18] and 2-bromo-1-methyl-1*H*-benzimidazole[19] were prepared according to literature procedures.

General Procedure A (Bromination with NBS). The heteroarene (1.00 eq.) was dissolved in DMF in a roundbottom flask equipped with a stir bar and open to air. The flask was cooled to 0 °C, and N-bromosuccinimide (1.10-2.00 eq.) was added portionwise. The reaction was allowed to stir for 12 h at the indicated temperature. At this time, the reaction mixture was brought to room temperature and diluted with water and either hexanes or ether. The phases were separated, and the aqueous phase was extracted with additional ether or hexanes. The combined organic phases were washed with H_2O (3×) and brine, dried over $MgSO_4$, filtered through a short silica gel plug, and concentrated with the aid of a rotary evaporator. The product was further purified as indicated.

General Procedure B (Suzuki-Miyaura Coupling). This procedure is adapted from the literature.[20] To a reaction tube equipped with a stir bar was added precatalyst **S17** or **S18** (2-10%, see Figure S1), additional ligand (if necessary), and boronic acid (1.10-3.50 eq.) (if the aryl halide was a solid, it was also added at this point). The tube was capped, placed under high vacuum, and backfilled with argon. This process was repeated a total of three times. THF and degassed *aq.* K_3PO_4 solution (2.0-4.0 eq.) were then added (if the aryl halide was a liquid, it was added at this point). The cap was replaced with one that had not been punctured, and the reaction tube was placed in an oil bath that had been pre-heated to the desired temperature and allowed to vigorously stir overnight. At this

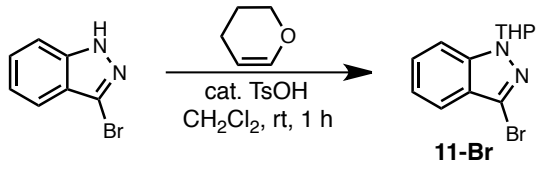
time, the reaction mixture was cooled to room temperature and diluted with ether and water. The phases were separated, and the aqueous phase was extracted with additional ether. The combined organic phases were dried over $MgSO_4$, filtered through a short celite plug, and concentrated with the aid of a rotary evaporator. The crude reaction mixture was purified as described.

General Procedure C (Bromination with Br_2). The heteroarene (1.00 eq.) was dissolved in DMF in a roundbottom flask equipped with a stir bar and open to air. The roundbottom flask was cooled to 0 °C. An equal volume of DMF was added to a separate roundbottom flask equipped with a stir bar and cooled to 0 °C. Br_2 (4.00 eq.) was added dropwise to the second flask, which was allowed to stir at 0 °C for 2 min. At this time, the Br_2/DMF solution was cannulated dropwise to the first flask, maintaining the temperature of the reaction mixture near 0 °C. The reaction mixture was allowed to stir for the indicated time, and then diluted with Et_2O and carefully quenched with saturated *aq*. Na_2SO_3. The phases were separated, and the aqueous phase was extracted with additional ether. The combined organic phases were washed with H_2O (2×) and brine, dried over $MgSO_4$, filtered through a short silica gel plug, and concentrated using a rotary evaporator. The product was further purified as indicated.

General Procedure D (Negishi Coupling). This procedure is adapted from the literature.[21] Under an atmosphere of argon, the heteroarene (1.30 eq.) and THF were added to an oven-dried roundbottom flask equipped with a stir bar. The flask was cooled to –78 °C, and *n*BuLi (2.5 M in hexanes, 1.43 eq.) was added dropwise. The reaction mixture was allowed to vigorously stir at –78 °C for 1 h, at which time $ZnCl_2$ (1.9 M in

2MeTHF, 1.56 eq.) was added dropwise. The reaction mixture was allowed to warm toroom temperatureand stir for 1 h, during which time it became homogenous. Next, bromobenzene (1.00 eq.) was added via syringe. The septum was removed, and under a positive pressure of argon **S17** (2%) and XPhos (2%) were quickly added. The reaction mixture was allowed to stir atroom temperaturefor 12 h. At this time, ether and water were added, and the phases were separated. The aqueous phase was further extracted with ether (2×). The combined organic phases were washed with brine (2×), dried over $MgSO_4$, filtered through a plug of celite, eluting with ether, and concentrated. The product was further purified as indicated.

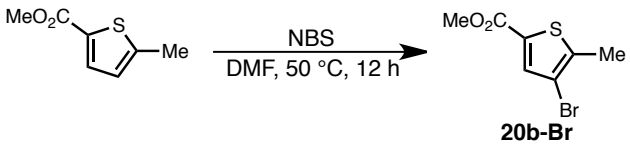
General Procedure E (N-Protection of Azoles). The azole (1.00 eq.) was dissolved in CH_2Cl_2 in a roundbottom flask equipped with a stir bar. Then, triethylamine (2.00 eq.) and the arylsulfonyl chloride (1.10 eq.) or trityl chloride (1.50 eq.) was added in one portion, and the reaction mixture was allowed to stir at room temperature for 12 h. At this time, water was added, and the phases were separated. The aqueous phase was further extracted with CH_2Cl_2, dried over $MgSO_4$, and filtered through a silica gel plug, eluting with CH_2Cl_2, and concentrated. The product was further purified as indicated.



11-Br

3-bromo-1*H*-indazole (500 mg, 2.54 mmol, 1.00 eq.) was suspended in CH_2Cl_2 (10 mL) in a 50 mL roundbottom flask equipped with a stir bar. 3,4-Dihydro-2*H*-pyran (694 μL, 7.61 mmol, 3.00 eq.) and *p*-TsOH (43.0 mg, 0.25 mmol, 0.10 eq.) were added, and the reaction mixture was allowed to stir at room

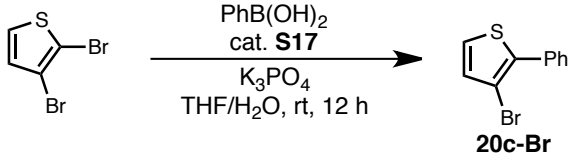
temperature for 1 h, during which time all of the starting material dissolved and the solution turned dark brown. The reaction mixture was diluted with CH_2Cl_2 (40 mL) and saturated *aq*. $NaHCO_3$ (50 mL) was added. The phases were separated, and the aqueous phase was further extracted with CH_2Cl_2 (2 × 30 mL). The combined organic phases were washed with saturated *aq*. $NaHCO_3$ (50 mL) and brine (50 mL), dried over $MgSO_4$, filtered, and concentrated. Purification of the crude reaction mixture by flash chromatography (0 → 2 → 4% EtOAc/hexanes) afforded 3-bromo-1-(tetrahydro-2*H*-pyran-2-yl)-1*H*-indazole (**11-Br**) (585 mg, 82%) as a white solid. Melting Point: 66 °C (Lit. 65 °C).[22] ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.51 (d, J = 10 Hz, 1H), 7.47 (7.47 (d, J = 9 Hz, 1H), 7.34 (pt, J = 9 Hz, 1H), 7.13 (pt, J = 8 Hz, 1H), 5.58 (dd, J = 10, 3 Hz, 1H), 3.90-3.94 (m, 1H), 3.63 (td, J = 12, 2 Hz, 1H), 2.42-2.49 (m, 1H), 2.00-2.09 (m, 1H), 1.93-2.00 (m, 1H), 1.60-1.70 (m, 2H), 1.51-1.59 (m, 1H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$): δ 140.7, 127.9, 124.5, 122.2, 122.1, 120.5, 110.4, 85.6, 67.6, 29.4, 25.1, 22.6 ppm. IR: 2952, 2850, 1617, 1496, 1462, 1444, 1411, 1318, 1211, 1181, 1123, 1077, 1052, 1038, 1005, 963, 909, 874, 754, 654, 627, 579 cm^{-1}. These spectra are consistent with those reported in the literature.[22]



20b-Br

20b-Br was prepared according to General Procedure A. Thus, methyl 5-methylthiophene-2-carboxylate (312 mg, 2.00 mmol, 1.00 eq.), N-bromosuccinimide (712 mg, 4.00 mmol, 2.00 eq.), and DMF (5 mL) were combined in a 25 mL

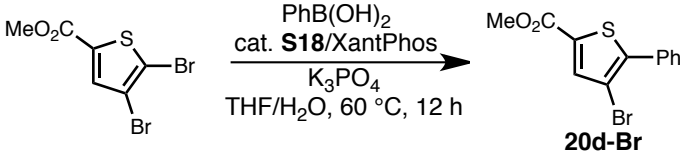
roundbottom flask and allowed to stir at 50 °C overnight. Purification of the crude product mixture by filtration through a silica gel plug, eluting with Et_2O, provided methyl 4-bromo-5-methylthiophene-2-carboxylate (395 mg, 84%) as a light brown solid. Melting Point: 42-44 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.58 (s, 1H), 3.86 (s, 3H), 2.42 (s, 3H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$): δ 161.8, 142.4, 135.9, 130.2, 110.4, 99.9, 52.4, 15.5 ppm. IR: 3091, 2950, 1706, 1452, 1334, 1244, 1151, 1081, 1002, 806, 750, 631 cm^{-1}. Anal. Calcd. for $C_7H_7BrO_2S$: C, 35.76; H, 3.00; found: C, 35.80; H, 2.98. It should be noted that the ^{1}H NMR shift of the proton located on the thiophene ring in the potentially formed regioisomeric compound methyl 3-bromo-5-methylthiophene-2-carboxylate is predicted to be more than 1 ppm (~6.5 ppm) upfield from where it is observed (~7.6 ppm), suggesting that the desired product formed exclusively.



20c-Br

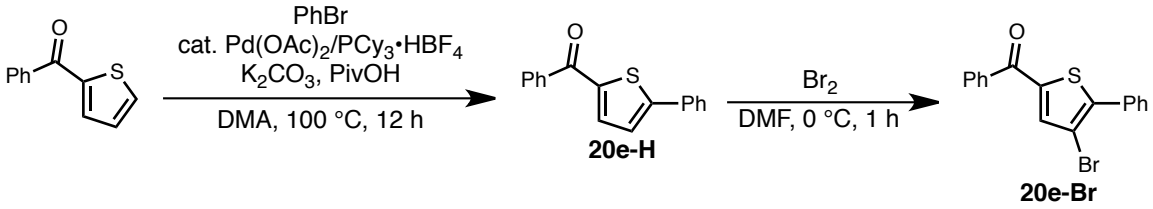
20c-Br was prepared according General Procedure B. Thus, 2,3-dibromothiophene (1.13 mL, 10.0 mmol, 1.00 eq.), phenylboronic acid (1.34 g, 11.0 mmol, 1.10 eq.), **S17** (169 mg, 0.20 mmol, 2%), THF (20 mL), and *aq*. K_3PO_4 (1.0 M, 20 mL, 20 mmol, 2.0 eq.) were combined in a 100 mL roundbottom flask and allowed to stir at room temperature for 12 h. Purification of the crude reaction mixture by flash chromatography (pentane) yielded 3-bromo-2-phenylthiophene (1.58 g, 66%) as a colorless oil. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.67 (d, J = 8 Hz, 2H), 7.45 (pt, J = 8 Hz, 2H), 7.39 (t, J = 8 Hz, 1H), 7.29 (dd, J = 5, 2 Hz, 1H), 7.07 (dd, J = 5, 3 Hz, 1H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$): δ 138.3, 133.0, 131.8, 129.2, 128.6, 128.4, 125.1, 107.6 ppm. IR: 3106, 3056, 1523, 1484, 1444, 1343, 1146,

1073, 863, 755, 690, 624, 608 cm^{-1}. These spectra are consistent with those reported in the literature.[23]



20d-Br

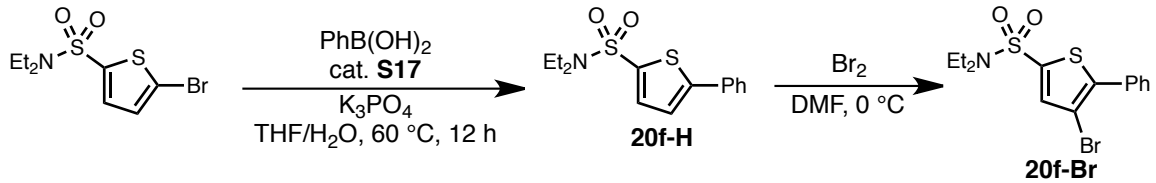
20d-Br was prepared according to General Procedure B.[24] Thus, methyl 4,5-dibromothiophene-2-carboxylate (1.20 g, 4.00 mmol, 1.00 eq.), phenylboronic acid (540 mg, 4.40 mmol, 4.40 eq.), **S18** (190 mg, 0.20 mmol, 5%), XantPhos (116 mg, 0.20 mmol, 5%), THF (4.0 mL), *aq*. K_3PO4 (1M, 8.0 mL, 8.0 mmol, 2.0 eq.) were combined in a 50 mL Schlenk flask and allowed to stir at 60 °C for 12 h. Purification of the crude reaction mixture by flash chromatography (5% EtOAc/hexanes) yielded methyl 4-bromo-5-phenylthiophene-2-carboxylate (1.04 g, 88%) as a white solid. The regioselectivity was confirmed by comparison of the ^1H NMR spectrum with that of the potentially formed regioisomeric compound methyl 5-bromo-4-phenylthiophene-2-carboxylate (**21a-Br**). Melting Point: 70 °C. ^1H NMR (500 MHz, $CDCl_3$): δ 7.73 (s, 1H), 7.64-7.68 (m, 2H), 7.41-7.48 (m, 3H), 3.90 (s, 3H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$): δ 162.4, 145.9, 137.9, 132.7, 132.6, 129.9, 129.7, 129.4, 108.7, 53.2 ppm. IR: 3100, 3025, 2960, 1728, 1714, 1528, 1450, 1438, 1291, 1182, 1080, 1069, 924, 862, 840, 755, 746, 714, 692, 669, 629, 611 cm^{-1}. HRMS (ESI) for $C_{12}H_{13}BrNO_2S$ ($M+NH_4^+$, $M+2+NH_4^+$): 313.9845, 315.9825; found: 313.9858, 315.9842.



This procedure was adapted from the literature.[12] 2-benzoylthiophene (1.00 g, 5.31 mmol, 1.00 eq.), $Pd(OAc)_2$ (119 mg, 0.53 mmol, 10%), tricyclohexylphosphine tetrafluoroborate (293 mg, 0.80 mmol, 15%), and K_2CO_3 (1.10 g, 7.97 mmol, 1.50 eq.) were combined in a 100 mL Schlenk tube equipped with a stir bar. The tube was placed under high vacuum and backfilled with argon. This process was repeated a total of three times. The screw-cap was replaced with a septum, and bromobenzene (558 μL, 5.31 mmol, 1.00 eq.), pivalic acid (183 μL, 1.59 mmol, 0.30 eq.), and N,N-dimethylacetamide (25 mL) were added. The septum was replaced with the screw-cap, and the tube was placed in an oil bath that had been pre-heated to 100 °C and allow to stir for 12 h. At this time, the tube was cooled to room temperature, and the reaction mixture was diluted with ether (50 mL) and water (50 mL). The phases were separated, and the aqueous phase was further extracted with ether (2 × 25 mL). The combined organic phases were washed with water (2 × 25 mL) and brine (25 mL), dried over $MgSO_4$, filtered through a silica gel plug, eluting with ether, and concentrated. The resulting brown solid was recrystallized from hot methanol to afford 2-benzoyl-5-phenylthiophene (**20e-H**) (889 mg, 63%) as a pale yellow solid. Melting Point: 130 °C (Lit. 132 °C).[25] ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.89 (d, J = 7 Hz, 2H), 7.70 (d, J = 9 Hz, 2H), 7.58-7.63 (m, 2H), 7.51 (pt, J = 8 Hz, 2H), 7.44 (pt, J = 8 Hz, 2H), 7.39 (d, J = 8 Hz, 1H), 7.36 (d, J = 4 Hz, 1H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$): δ 188.2, 153.4, 142.4, 138.2, 136.1, 133.4, 132.3, 129.3, 129.2, 128.6, 126.5, 124.0 ppm. IR: 2951, 2849, 1617, 1495, 1462, 1318, 1211, 1177, 1077, 1037,

1005, 909, 754, 703, 668 cm^{-1}. These spectra are consistent with those reported in the literature.[26]

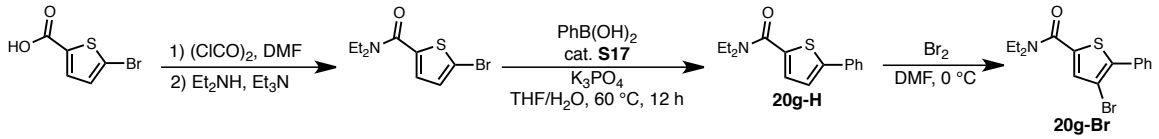
20e-Br was prepared according to General Procedure C. Thus, **20e-H** (211 mg, 0.80 mmol, 1.00 eq.), Br_2 (163 μL, 3.20 mmol, 4.00 eq.), and DMF (8 mL) were combined in a 25 mL roundbottom flask and allowed to stir at 0 °C for 1 h. Purification of the crude reaction mixture by filtration through a silica gel plug, eluting with ether, followed by recrystallization of the resulting solid from MeOH, afforded 5-benzoyl-3-bromo-2-phenylthiophene (163 mg, 59%) as a pale yellow solid. Melting Point: 84 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.89 (dd, J = 8, 2 Hz, 2H), 7.72 (dd, J = 8, 2 Hz, 2H), 7.63 (tt, J = 8, 2 Hz, 1H), 7.59 (s, 1H), 7.54 (pt, J = 8 Hz, 2H), 7.4-7.51 (m, 3H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$): δ 187.2, 147.3, 141.5, 138.5, 137.4, 132.8, 132.2, 126.9, 129.3, 129.2, 128.9, 128.8, 108.2 ppm. IR: 3057, 1630, 1596, 1575, 1520, 1447, 1426, 1426, 1324, 1286, 1223, 1152, 1115, 1075, 874, 764, 709, 694, 652, 631 cm^{-1}. Anal. Calcd. for $C_{17}H_{11}BrOS$: C, 59.49; H, 3.23; found: C, 59.45; H, 3.39.



This compound was prepared according to General Procedure B. Thus, 5-bromo-*N*,*N*-diethylthiophene-2-sulfonamide[10] (2.00 g, 6.71 mmol, 1.00 eq.), phenylboronic acid (1.23

g, 10.1 mmol, 1.50 eq.), **S17** (114 mg, 0.13 mmol, 2%), THF (7 mL), and *aq*. K_3PO_4 (1 M, 13.4 mL, 13.4 mmol, 2.0 eq.) were combined in a 100 mL Schlenk tube and allowed to stir at 60 °C overnight. Purification of the crude reaction mixture by flash chromatography (10 → 20% EtOAc/hexanes) afforded 5-phenyl-*N*,*N*-diethylthiophene-2-sulfonamide (**20f-H**) (1.41 g, 71%) as a light brown solid. Melting Point: 80-81 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.59 (d, J = 7 Hz, 2H), 7.50 (d, J = 4 Hz, 1H), 7.41 (pt, J = 7 Hz, 2H), 7.36 (t, J = 7 Hz, 1H), 7.24 (d, J = 4 Hz, 1H), 3.28 (q, J = 8 Hz, 4H), 1.20 (t, J = 7 Hz, 6H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$): δ 150.4, 139.0, 132.9, 132.3, 129.3, 129.1, 126.2, 122.9, 42.8, 14.4 ppm. IR: 2983, 2941, 2873, 1448, 1334, 1294, 1243, 1201, 1143, 1011, 940, 812, 791, 754, 704, 685, 647, 579 cm^{-1}. Anal. Calcd. for $C_{14}H_{17}NO_2S_2$: C, 56.92; H, 5.80; found: C, 57.15; H, 5.76.

20f-Br was prepared according to General Procedure C. Thus, **20f-H** (1.41 g, 4.77 mmol, 1.00 eq.), Br_2 (984 μL, 19.1 mmol, 4.00 eq.), and DMF (20 mL) were combined in a 100 mL roundbottom flask at 0 °C and allowed to stir at 0 °C overnight. The crude product mixture was purified by flash chromatography (5% EtOAc/hexanes) to afford 4-bromo-5-phenyl-*N,N*-diethylthiophene-2-sulfonamide (1.67 g, 93%) as a thick yellow oil. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.62-7.65 (m, 2H), 7.42-7.49 (m, 4H), 3.20 (q, J = 8 Hz, 4H), 1.23 (t, J = 7 Hz, 6H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$): δ 144.0, 139.6, 134.8, 131.5, 129.6, 129.2, 129.0, 107.5, 43.1, 14.6 ppm. IR: 2974, 2935, 2873, 1445, 1431, 1339, 1305, 1200, 1149, 1019, 934, 828, 784, 757, 718, 691, 580 cm^{-1}. Anal. Calcd. for $C_{14}H_{16}BrNO_2S_2$: C, 44.92; H, 4.31; found: C, 44.91; H, 4.21.



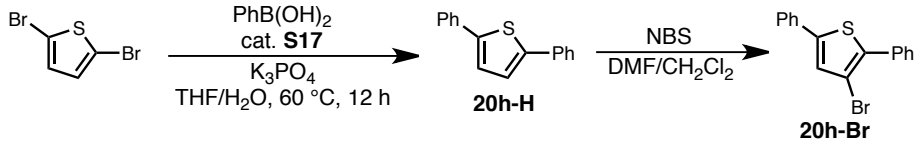
An oven-dried 100 mL roundbottom flask equipped with a stir bar was charged with 2-bromothiophene carboxylic acid (2.00 g, 9.66 mmol, 1.00 eq.). The roundbottom flask was placed under high vacuum and backfilled with nitrogen. Then, anhydrous CH_2Cl_2 (30 mL) and DMF (2.5 mL) were added (the solid should dissolve at this point). The septum was fitted with a vent needle, and oxalyl chloride (1.66 mL, 19.3 mmol, 2.00 eq.) was added dropwise (Caution: evolution of toxic gases!). The reaction mixture was allowed to stir at room temperature for 1 h, at which time it was concentrated with the aid of a rotary evaporator. The roundbottom flask was placed under high vacuum and backfilled with nitrogen. The resulting thick yellow oil was dissolved in anhydrous CH_2Cl_2 (30 mL) and the flask was cooled to 0 °C. Then, diethylamine (4.99 mL, 48.3 mmol, 5.00 eq.) was added dropwise (Caution: evolution of HCl!). The reaction mixture was allowed to stir at room temperature for 12 h. At this time, the reaction mixture was diluted with CH_2Cl_2 (40 mL), and saturated *aq*. $NaHCO_3$ (50 mL) was *carefully* added. The phases were separated, and the aqueous phase was further extracted with CH_2Cl_2 (2 × 40 mL). The combined organic phases were washed with water (2 × 50 mL) and brine (50 mL), dried over $MgSO_4$, filtered, and concentrated. The resulting material was purified by flash chromatography (10 → 20% → 30% EtOAc/hexanes) to afford 5-bromo-*N,N*-diethyl-thiophene-2-carboxamide (1.27 g, 52%) as a greasy pale yellow solid that melted close to room temperature. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.08 (d, J = 4 Hz, 1H), 6.99 (d, J = 4 Hz, 1H), 3.52 (q, J = 7 Hz, 4H), 1.24 (t, J = 7 Hz, 6H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$): δ 146.1, 132.4, 130.9, 130.4, 129.2, 107.4, ~43 (bs), ~15 (bs) ppm.

IR: 3068, 2982, 2964, 2934, 1600, 1528, 1433, 1383, 1313, 1281, 1223, 1050, 969, 940, 843, 824, 748, 726, 692, 633 cm^{-1}. Anal. Calcd. for $C_9H_{12}BrNOS$: C, 41.23; H, 4.61; found: C, 41.38; H, 4.52.

20g-H was prepared according to General Procedure B. Thus, 5-bromo-*N,N*-diethyl-thiophene-2-carboxamide (800 mg, 3.05 mmol, 1.00 eq.), phenylboronic acid (558 mg, 4.58 mmol, 1.50 eq.), **S17** (51.6 mg, 0.06 mmol, 2%), THF (3 mL), and *aq*. K_3PO_4 (1M, 6.0 mL, 6.0 mmol, 2.0 eq.) were combined in a 50 mL Schlenk tube and allowed to stir at 60 °C for 12 h. Purification of the crude reaction mixture by flash chromatography (10 → 20 → 30% EtOAc/hexanes) afforded 5-phenyl-*N,N*-diethyl-thiophene-2-carboxamide (587 mg, 74%) as a white solid. Melting Point: 45-47 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.60-7.63 (m, 2H), 7.39 (pt, J = 8 Hz, 2H), 7.29-7.34 (m, 2H), 7.22 (d, J = 4 Hz, 1H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$): δ 146.1, 132.4, 130.9, 130.4, 129.2, 129.2, 107.4 ~43 (bs), ~15 (bs) ppm. IR: 3061, 2986, 1601, 1538, 1459, 1385, 1367, 1307, 1285, 1180, 1103, 1054, 915, 845, 822, 750, 731, 703, 688, 675, 622 cm^{-1}. Anal. Calcd. for $C_{15}H_{17}NOS$: C, 69.46; H, 6.61; found: C, 69.69; H, 6.63.

20g-Br was prepared according to General Procedure C. Thus, **20g-H** (1.14 mg, 4.40 mmol, 1.00 eq.), Br_2 (906 μL, 17.6 mmol, 4.00 eq.), and DMF (20 mL) were combined at 0 °C and allowed to stir at 0 °C for 1 h. Purification of the crude reaction mixture by flash chromatography (20% EtOAc/hexanes) afforded 4-bromo-5-phenyl-*N,N*-diethyl-thiophene-2-carboxamide (1.29 mg, 87%) as a thick pale yellow oil. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.64-7.67 (m, 2H), 7.38-7.47 (m, 3H), 7.26 (s, 1H), 3.57 (q, J = 7 Hz, 4H),

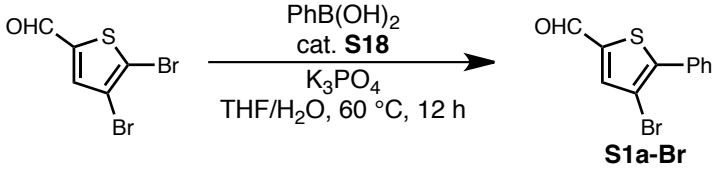
1.28 (t, J = 7 Hz, 6H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$): δ 162.4, 141.5, 137.5, 132.2, 131.9, 129.1, 128.9, 128.8, 106.7, ~43 (bs), ~15 (bs) ppm. IR: 2971, 2932, 1609, 1529, 1440, 1380, 1319, 1277, 1216, 1056, 844, 815, 758, 729, 693, 628 cm^{-1}. Anal. Calcd. for $C_{15}H_{16}BrNOS$: C, 53.26; H, 4.77; found: C, 53.53; H, 4.83.



20h-H was prepared according to General Procedure B. Thus, 2,5-dibromothiophene (1.13 mL, 10.0 mmol, 1.00 eq.), phenylboronic acid (3.05 g, 25.0 mmol, 2.50 eq.), **S17** (169 mg, 0.20 mmol, 2%), THF (10 mL), and *aq*. K_3PO_4 (1.5 M, 20 mL, 30 mmol, 3.0 eq.) were combined in a 100 Schlenk flask and allowed to stir at 60 °C for 12 h. Purification of the crude reaction mixture by flash chromatography (1% EtOAc/hexanes) yielded 2,5-diphenylthiophene (1.13 g, 48%) as a pale yellow crystalline solid. Melting Point: 153 °C (Lit. 152-153 °C).[27] ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.63-7.66 (m, 4H), 7.38-7.42 (m, 4H), 7.26-7.31 (m, 4H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$): δ 143.8, 134.4, 129.1, 127.7, 125.8, 124.1 ppm. IR: 3055, 3017, 1593, 1480, 1454, 1273, 1157, 1079, 1028, 940, 902, 804, 747, 683 cm^{-1}. These spectra are consistent with those reported in the literature.[28]

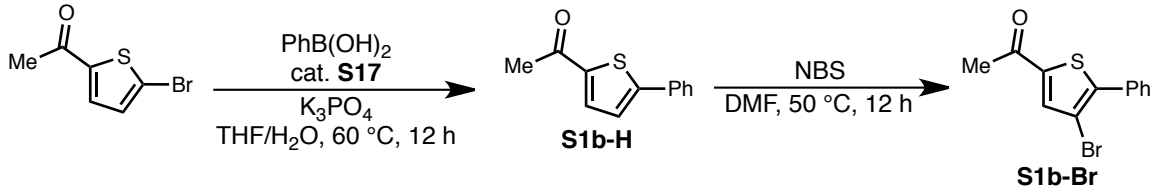
20h-Br was prepared according to a slightly modified General Procedure A. Thus, **20h-H** (1.12 g, 4.75 mmol, 1.00 eq.), N-bromosuccinimide (934 mg, 5.22 mmol, 1.10 eq.), DMF (10 mL), and CH_2Cl_2 (20 mL, added to solubilize the starting material) were combined and allowed to stir at room temperature for 12 h. Purification by flash

chromatography (hexanes), followed by recrystallization of the resulting solid from hot MeOH, yielded 3-bromo-2,5-diphenylthiophene (725 mg, 48%) as a pale yellow solid. Melting Point: 42-43 °C (Lit. 43-44 °C).[27] ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.73 (d, J = 9 Hz, 2H), 7.61 (d, J = 9 Hz, 2H), 7.40-7.49 (m, 5H), 7.31-7.37 (m, 1H), 7.29 (s, 1H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$): δ 143.3, 137.4, 133.2, 133.0, 129.2, 129.0, 128.7, 128.4, 128.3, 127.5, 125.6, 108.0 ppm. IR: 3055, 3026, 1598, 1533, 1496,1442, 1326, 1275, 1156, 1073, 1036, 969, 908, 824, 752, 715, 624, 608 cm^{-1}. These spectra are consistent with those reported in the literature.[29]



S1a was prepared according to General Procedure B. Thus, 4,5-dibromothiophene-2-carboxaldehyde (540 mg, 2.00 mmol, 1.00 eq.), phenylboronic acid (270 mg, 2.20 mmol, 1.10 eq.), **S18** (95 mg, 0.1 mmol, 5%), THF (2 mL), and *aq*. K_3PO_4 (1.0 M, 4.0 mL, 4.0 mmol, 2.0 eq.) were combined in a 25 mL roundbottom flask and allowed to stir at 60 °C for 12 h. Purification of the crude reaction mixture by flash chromatography (0 → 2 → 4 → 6% EtOAc/hexanes) yielded 4-bromo-5-phenylthiophene-2-carboxaldehyde (370 mg, 69%) as a pale yellow solid. The regioselectivity is assumed based on that observed for the preparation of methyl 3-bromo-2-phenylthiophene-5-carboxylate. Melting Point: 83 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ 9.86 (s, 1H), 7.73 (s, 1H), 7.68-7.70 (m, 2H), 7.46-7.50 (m, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 182.2, 148.5, 141.7, 140.3, 132.2, 130.1, 129.4, 129.2, 109.2 ppm. IR: 3309, 3082, 3054, 2847, 1678, 1663, 1450, 1432, 1306,

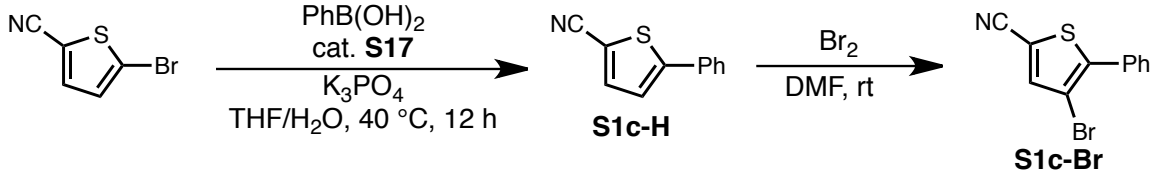
1219, 1125, 1076, 915, 848, 837, 754, 724, 690, 662, 633 cm $^{-1}$. HRMS (ESI) m/z calcd. for $C_{11}H_8BrOS$ ($M+H^+$, $M+2+H^+$): 266.9474, 268.9454; found: 266.9476, 268.9451.



S1b-H was prepared according to General Procedure B. Thus, 2-acetyl-5-bromothiophene (1.03 g, 5.00 mmol, 1.00 eq.), phenylboronic acid (914 mg, 7.50 mmol, 1.50 eq.), **S17** (85 mg, 0.10 mmol, 2%), THF (5 mL), and *aq*. K_3PO_4 (1.0 M, 10 mL, 10 mmol, 2.0 eq.) were combined in a 50 mL roundbottom flask and allowed to stir at 60 °C for 12 h. Purification of the crude reaction mixture by flash chromatography (0 → 2.5 → 5 → 7.5% EtOAc/hexanes) yielded 2-acetyl-5-phenylthiophene (840 mg, 83%) as a pale yellow solid. Melting Point: 114-116 °C (Lit. 115 °C).[30] ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.64-7.67 (m, 3H), 7.42 (pt, J = 7 Hz, 2H), 7.37 (tt, J = 8, 2 Hz, 1H), 7.32 (d, J = 4 Hz, 1H), 2.57 (s, 3H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$): δ 190.7, 152.9, 143.2, 133.6, 133.4, 129.2, 126.4, 124.0, 26.7 ppm. IR: 3081, 3001, 1645, 1530, 1441, 1362, 1275, 1087, 1036, 926, 908, 809, 756, 687, 661, 611, 586 cm^{-1}. These spectra are consistent with those reported in the literature.[30]

S1b-Br was prepared according to General Procedure A. Thus, **S1b-H** (700 mg, 3.46 mmol, 1.00 eq.), N-bromosuccinimide (862 mg, 4.84 mmol, 1.40 eq.), and DMF (10 mL) were combined in a 25 mL roundbottom flask and allowed to stir at 50 °C overnight. Purification of the crude reaction mixture by filtration through a silica gel plug, eluting

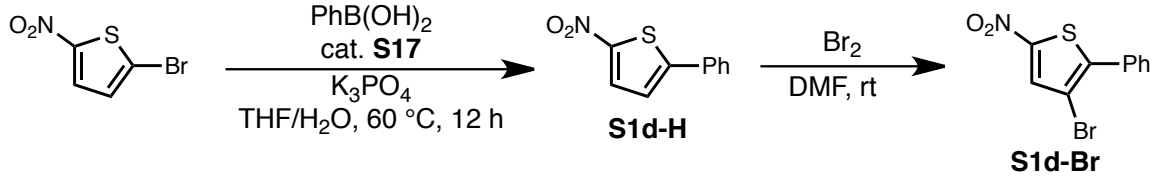
with ether, followed by trituration of the resulting solid with cold MeOH, yielded 2-acetyl-4-bromo-5-phenylthiophene (740 mg, 76%) as a pale yellow solid. Melting Point: 70 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.67 (dd, J = 8, 2 Hz, 2H), 7.63 (s, 1H), 7.43-7.48 (m, 3H), 2.56 (s, 3H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$): δ 189.8, 146.9, 142.3, 136.4, 132.1, 129.5, 129.1, 128.8, 108.1, 26.5 ppm. IR: 3077, 1652, 1446, 1431, 1359, 1312, 1270, 1223, 1155, 1078, 1046, 922, 882, 861, 831, 760, 697, 682, 632, 608, 595 cm^{-1}. Anal. Calcd. for $C_{12}H_9BrOS$: C, 51.26; H, 3.23; found: C, 51.08; H, 3.07.



S1c-H was prepared according to General Procedure B. Thus, 2-bromo-5-cyanothiophene (940 mg, 5.00 mmol, 1.00 eq.), phenylboronic acid (915 mg, 7.50 mmol, 1.50 eq.), **S17** (169 mg, 0.20 mmol, 4%), THF (5.0 mL), and *aq*. K_3PO_4 (1.0 M, 10 mL, 10 mmol, 2.0 eq.) were combined in a 50 mL Schlenk tube and allowed to stir at 40 °C for 12 h. The crude reaction mixture was purified by flash chromatography (0 → 4% EtOAc/hexanes); all of the fractions containing the desired product were collected and concentrated to afford a yellow solid, which was recrystallized from hot hexanes to afford 2-cyano-5-phenylthiophene (387 mg, 42%) as a yellow solid. Melting Point: 85-87 °C (Lit. 86-87 °C).[31] ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.59-7.62 (m, 3H), 7.38-7.46 (m, 3H), 7.28 (d, J = 4 Hz, 1H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$): δ 152.0, 138.5, 132.4, 129.6, 129.4, 126.5, 123.4, 114.5, 108.3 ppm. IR: 3097, 2219, 1493, 1455, 1254, 1239, 1157,

1058, 999, 954, 909, 816, 753, 684 cm^{-1}. These spectra are consistent with those reported in the literature.[31]

S1c-Br was prepared according to General Procedure C. Thus, **S1c-H** (463 mg, 2.50 mmol, 1.00 eq.), Br_2 (516 μL, 10.0 mmol, 4.00 eq.), and DMF (10 mL) were combined at 0 °C and allowed to stir at room temperature for 12 h. The crude reaction mixture was filtered through a silica gel plug, eluting with ether, and concentrated. The resulted yellow solid was recrystallized from hot hexanes to afford 4-bromo-2-cyano-5-phenylthiophene (355 mg, 54%) as a fluffy pale yellow solid. Melting Point: 76-78 °C. ^1H NMR (500 MHz, $CDCl_3$): δ 7.61-7.65 (m, 2H), 7.57 (s, 1H), 7.46-7.50 (m, 3H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$): δ 145.8, 141.0, 130.9, 130.0, 129.3, 129.1, 113.2, 108.2, 99.9 ppm IR: 3093, 2223, 1448, 1433, 1321, 1220, 1167, 1116, 1073, 868, 838, 753, 721, 688, 629 cm^{-1}. HRMS (ESI) m/z calcd. for $C_{11}H_{10}BrN_2S$ ($M+NH_4^+$, $M+2+NH_4^+$): 280.9743, 282.9723; found: 280.9745, 282.9721.

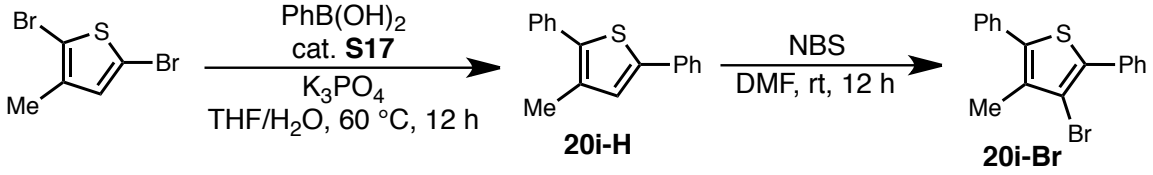


S1d-H was prepared according to General Procedure B. Thus, 2-bromo-5-nitrothiophene (1.64 g, 8.00 mmol, 1.00 eq.), phenylboronic acid (1.46 g, 12.0 mmol, 1.50 eq.), **S17** (272 mg, 0.32 mmol, 4%), THF (8.0 mL), and *aq*. K_3PO_4 (1.0 M, 16.0 mL, 16 mmol, 2.0 eq.) were combined in a 100 mL roundbottom flask and allowed to stir at 60 °C overnight. The crude reaction mixture was purified by flash chromatography (2 → 4 → 6%

EtOAc/hexanes); all of the fractions containing the desired product were collected and concentrated to provide a brown solid. This solid was recrystallized from hot MeOH to afford 5-phenyl-2-nitrothiophene (927 mg, 57 %) as an orange-brown solid. Melting Point: 126 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.91 (d, J = 4 Hz, 1H), 7.61-7.64 (m, 2H), 7.42-7.48 (m, 3H), 7.24 (d, J = 5 Hz, 1H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$): δ 152.2, 132.2, 130.2, 129.8, 129.5, 126.4, 122.5 ppm (the ^{13}C-NO_2 signal could not be readily observed). IR: 3110, 1536, 1496, 1449, 1425, 1353, 1326, 1248, 1043, 1028, 958, 812, 755, 731 cm^{-1}. Anal. Calcd. for $C_{10}H_7NO_2S$; C, 58.52; H, 3.44; found: C, 58.46; H, 3.54.

S1d-Br was prepared according to General Procedure C. Thus, **S1d-H** (920 mg, 4.52 mmol, 1.00 eq.), Br_2 (932 μL, 18.1 mmol, 4.00 eq.), and DMF (20 mL) were combined at 0 °C and allowed to stir at room temperature for 12 h. The crude reaction mixture was filtered through a silica gel plug, eluting with ether, and concentrated to afford an orange solid. This solid was triturated with cold methanol, filtered, and washed with additional cold methanol, to afford 4-bromo-5-phenyl-2-nitrothiophene (897 mg, 70%) as a bright yellow solid. Melting Point: 69 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.91 (s, 1H), 7.64-7.69 (m, 2H), 7.48-7.32 (m, 3H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$): δ 146.1, 132.4, 130.9, 130.4, 129.2, 129.2, 107.4 ppm (the ^{13}C-NO_2 signal could not be readily observed). IR: 3110, 1596, 1525, 1509, 1489, 1446, 1421, 1350, 1319, 1218, 1162, 1084, 1071, 1033, 1000, 960, 910, 855, 842, 804, 753, 779, 718, 689 cm^{-1}. Anal. Calcd. for $C_{10}H_6BrNO_2S$: C, 42.27; H, 2.13; found: C, 42.01; H, 2.12. It should be noted that the ^{1}H NMR shift of the proton located on the thiophene ring in the potentially formed regioisomeric compound 3-bromo-2-nitro-5-phenylthiophene is predicted to be more than

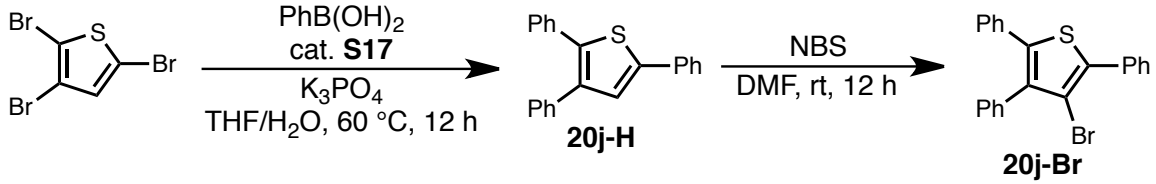
0.8 ppm (~7.1 ppm) upfield from where it is observed (~7.9 ppm), suggesting that the desired product formed exclusively.



20i-H was prepared according to General Procedure B. Thus, 2,5-dibromo-3-methylthiophene (1.50 g, 5.90 mmol, 1.00 eq.), phenylboronic acid (1.79 g, 14.7 mmol, 2.50 eq.), **S17** (250 mg, 0.30 mmol, 5%), THF (6 mL), and *aq*. K_3PO_4 (2M, 9 mL, 18.0 mmol, 3 eq.) were combined in a 50 mL Schlenk tube and allowed to stir at 60 °C for 12 h. Purification of the crude reaction mixture by flash chromatography (hexanes) provided 2,5-diphenyl-3-methylthiophene (780 mg, 53%) as an off-white solid. Melting Point: 85 °C (Lit. 86-87 °C).[32] ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.65 (dd, J = 9, 2 Hz, 2H), 7.56 (dd, J = 7, 1 Hz, 2H), 7.46 (pt, J = 8 Hz, 2H), 7.41 (pt, J = 7 Hz, 2H), 7.36 (tt, J = 8, 2 Hz, 1H), 7.31 (tt, J = 8, 1 Hz, 1H), 7.20 (s, 1H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$): δ 141.9, 137.5, 134.8, 134.4, 134.3, 129.0, 128.9, 128.7, 127.5, 127.4, 127.3, 125.6, 15.3 ppm. IR: 3049, 2926, 1596, 1486, 1448, 1182, 1075, 1012, 838, 755, 722, 695, 627 cm^{-1}. These spectra are consistent with those reported in the literature.[32]

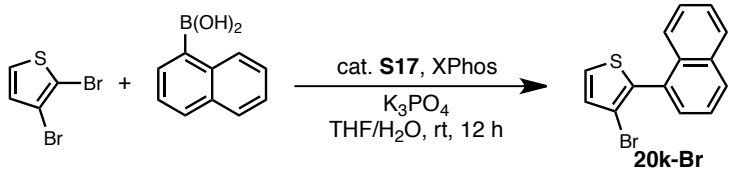
20i-Br was prepared according to a slightly modified General Procedure A. Thus, **20i-H** (200 mg, 0.80 mmol, 1.00 eq.), N-bromosuccinimide (214 mg, 1.20 mmol, 1.50 eq.), DMF (2 mL), and CH_2Cl_2 (1 mL, to solubilize the starting material) were combined and allowed to stir at room temperature overnight. Purification of the crude reaction mixture

by filtration through a silica gel plug, eluting with hexanes, afforded 3-bromo-2,5-diphenyl-4-methylthiophene (154 mg, 59%) as a white crystalline solid. Melting Point: 104 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.71 (d, J = 8 Hz, 2H), 7.44-7.50 (m, 6H), 7.40 (pt, J = 7 Hz, 2H), 2.37 (s, 3H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$): δ 137.4, 136.7, 134.3, 133.8, 133.5, 129.3, 129.2, 128.8, 128.6, 128.3, 128.0, 112.0, 15.9 ppm. IR: 3049, 2994, 2916, 1597, 1485, 1440, 1346, 1251, 1178, 1080, 1035, 1024, 1010, 919, 810, 753, 698, 586 cm^{-1}. HRMS (ESI) m/z calcd. for $C_{17}H_{14}BrS$ [$M+H^+$, $M+2+H^+$]: 328.9994, 330.9979; found: 328.9996, 330.9977.



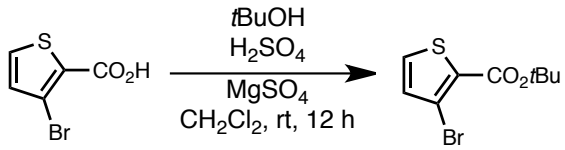
20j-H was prepared according to General Procedure B. Thus, 2,3,5-tribromothiophene (646 μL, 5.00 mmol, 1.00 eq.), phenylboronic acid (2.13 g, 17.5 mmol, 3.50 eq.), **S17** (212 mg, 0.25 mmol, 5%), THF (5 mL), and *aq*. K_3PO_4 (1M, 20 mL, 20 mmol, 4.0 eq.) were combined in a 100 mL Schlenk tube and allowed to stir at 60 °C for 12 h. Purification of the crude reaction mixture by flash chromatography (hexanes → 1% EtOAc/hexanes) yielded 2,3,5-triphenylthiophene (1.23 g, 79%) as a fluffy yellow solid. Melting Point: 139-141 °C (Lit. 144-145 °C).[33] ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.66 (d, J = 7 Hz, 2H), 7.37-7.43 (m, 3H), 7.25-7.36 (m, 11H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$): δ 142.7, 139.1, 138.1, 136.7, 134.3, 134.2, 129.3, 129.2, 129.1, 128.6, 128.6, 127.8, 127.6, 127.2, 126.7, 125.7 ppm. IR: 3058, 3021, 1597, 1484, 1446, 1070, 1029, 914, 846, 754, 695 cm^{-1}. These spectra are consistent with those reported in the literature.[33]

20j-Br was prepared according to a slightly modified General Procedure A. Thus, **20j-H** (625 mg, 2.00 mmol, 1.00 eq.), N-bromosuccinimide (392 mg, 2.20 mmol, 1.10 eq.), DMF (5 mL), and CH_2Cl_2 (2 mL, to solubilize the starting material) were combined and allowed to stir at room temperature overnight. The crude reaction mixture was filtered through a silica gel plug, eluting with CH_2Cl_2, and concentrated. The resulting solid was recrystallized from hot methanol to afford 4-bromo-2,3,5-triphenylthiophene (590 mg, 75%) as a pale yellow solid. Melting Point: 129 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.75 (dd, J = 7, 2 Hz, 2H), 7.49 (pt, J = 8 Hz, 2H), 7.36-7.44 (m, 5H), 7.32 (dd, J = 8, 2 Hz, 2H), 7.23 (bs, 5H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$): δ 139.4, 139.1, 137.2, 136.0, 133.7, 133.4, 130.9, 129.5, 128.9, 128.7, 128.6, 128.5, 128.4, 127.9, 127.8, 111.2 ppm. IR: 3058, 3021, 1598, 1484, 1446, 1070, 1029, 914, 846, 754, 695 cm $^{-1}$. Anal. Calcd. for $C_{22}H_{15}BrS$: C, 67.52; H, 3.86; found: C, 67.56; H, 3.94.



20k-Br was prepared according to General Procedure B. Thus, 2,3-dibromothiophene (566 μL, 5.00 mmol, 1.00 eq.), 1-naphthylboronic acid (946 mg, 5.50 mmol, 1.10 eq.), **S17** (85.0 mg, 0.10 mmol, 2%), XPhos (48.0 mg, 0.10 mmol, 2%), THF (10 mL), and *aq*. K_3PO_4 (0.5 M, 20 mL, 10 mmol, 2.0 eq.) were combined in a 100 mL roundbottom flask and allowed to stir at room temperature for 12 h. Purification of the crude reaction mixture by flash chromatography (hexanes) yielded 3-bromo-2-(1-naphthyl)thiophene (848 mg, 59%) as a white solid. The regioselectivity is assumed

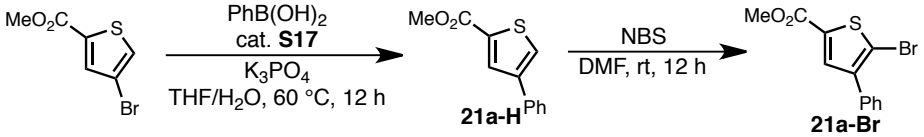
based on that observed for the preparation of 3-bromo-2-phenylthiophene. Melting Point: 80 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.93-7.98 (m, 2H), 7.79-7.82 (m, 1H), 7.43-7.58 (m, 4H), 7.44 (d, J = 5 Hz), 7.19 (d, J = 5 Hz) ppm; ^{13}C NMR (125 MHz, $CDCl_3$): δ 136.7, 133.7, 132.2, 130.6, 130.3, 129.6, 129.5, 128.5, 126.7, 126.3, 126.2, 126.2, 125.2, 111.1 ppm. IR: 3040, 1591, 1503, 1385, 1341, 1146, 1014, 858, 794, 777, 708, 683, 617 cm^{-1}. Anal. Calcd. for $C_{14}H_9BrS$: C, 58.25; H, 3.14; found: C, 58.69; H, 3.28.



S2-Br

A 50 mL roundbottom flask equipped with a stir bar was charged with $MgSO_4$ (1.44 g, 12.0 mmol, 4.00 eq.) and anhydrous CH_2Cl_2 (12 mL) under an atmosphere of N_2. Concentrated H_2SO_4 (~170 μL, ~3.00 mmol, ~1.00 eq.) was added dropwise, and the mixture was allowed to stir atroom temperaturefor 10 min. Next, 3-bromothiophene-2-carboxylic acid (621 mg, 3.00 mmol, 1.00 eq.) was added under a positive pressure of N_2, followed immediately by *t*BuOH (1.4 mL, 15 mmol, 5.0 eq.). The reaction mixture was allowed to stir at room temperature for 12 h. At this time, saturated *aq*. $NaHCO_3$ (10 mL) was *carefully* added, followed by additional CH_2Cl_2 (20 mL). The phases were separated, and the aqueous phase was extracted with additional CH_2Cl_2 (2 × 20 mL). The combined organic phases were washed with saturated *aq*. $NaHCO_3$ (20 mL), H_2O (20 mL), and brine (20 mL), dried over $MgSO_4$, filtered, and concentrated. The crude product mixture was purified by flash chromatography (0 → 5% EtOAc/hexanes) to yield *tert*-butyl 3-bromothiophene-2-carboxylate (**S2-Br**) (308 mg, 39%) as a pale yellow oil. ^{1}H NMR (500 MHz, $CDCl_3$): δ 2.67 (s, 3H), 1.54 (s, 9H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$): δ 160.2, 159.3, 139.1,

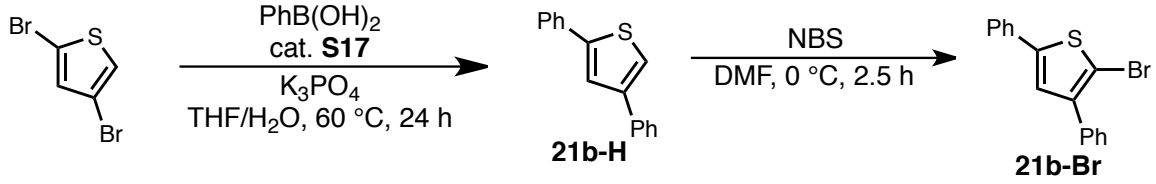
127.7, 83.2, 28.3, 17.3 ppm. IR: 2978, 2931, 1714, 1697, 1532, 1401, 1368, 1331, 1303, 1255, 1163, 1090, 1050, 1015, 841, 827, 762 cm^{-1}. Anal. Calcd. for $C_9H_{11}BrO_2S$: C, 41.08; H, 4.21; found: C, 41.33; H, 4.15.



21a-H was prepared according to General Procedure B. Thus, methyl 4-bromo-thiophene-2-carboxylate (1.00 g, 4.52 mmol, 1.00 eq.), phenylboronic acid (827 mg, 6.80 mmol, 1.50 eq.), **S17** (77.0 mg, 0.09 mmol, 2%), THF (4.5 mL), and *aq*. K_3PO_4 (1 M, 9.0 mL, 9.0 mmol, 2.0 eq.) were combined in a Schlenk tube and allowed to stir at 60 °C for 12 h. Purification of the crude reaction mixture by flash chromatography (0 → 2.5 → 5% EtOAc/hexanes) yielded methyl 4-phenylthiophene-2-carboxylate (689 mg, 70%) as an off-white solid. Melting Point: 95 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.09 (d, J = 2 Hz, 1H), 7.65 (d, J = 2 Hz, 1H), 7.59 (d, J = 7 Hz, 2H), 7.42 (pt, J = 8 Hz, 2H), 7.33 (t, J = 7 Hz, 1H), 3.92 (s, 3H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$): δ 162.7, 143.0, 134.9, 134.2, 132.3, 129.1, 127.9, 127.0, 126.4, 52.4 ppm. IR: 3099, 2950, 1705, 1547, 1440, 1259, 1205, 1084, 869, 853, 791, 748, 688, 628 cm^{-1}. Anal. Calcd. for $C_{12}H_{10}O_2S$: C, 66.03; H, 4.62; found: C, 65.93; H, 4.63.

21a-Br was prepared according to General Procedure A. Thus, **21a-H** (600 mg, 2.75 mmol, 1.00 eq.), N-bromosuccinimide (684 mg, 3.85 mmol, 1.40 eq.), and DMF (10 mL) were combined in a 25 mL roundbottom flask and allowed to stir at room temperature

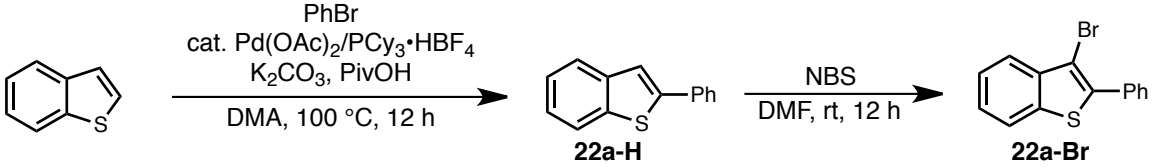
overnight. Filtration of the crude reaction mixture through a silica gel plug, eluting with ether, was sufficient to provide methyl 5-bromo-4-phenylthiophene-2-carboxylate (770 mg, 94%) as a pale yellow solid. Recrystallization from MeOH provided the desired material as an off-white solid. Melting Point: 80 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.72 (s, 1H), 7.54 (d, J = 9 Hz, 2H), 7.45 (pt, J = 9 Hz, 2H), 7.39 (t, J = 7 Hz, 1H), 3.90 (s, 3) ppm; ^{13}C NMR (125 MHz, $CDCl_3$): δ 161.8, 142.4, 134.7, 134.2, 133.1, 128.7, 128.6, 128.3, 116.5, 52.5 ppm. IR: 3099, 2950, 1705, 1547, 1440, 1259, 1205, 1084, 869, 853, 791, 748, 688 cm^{-1}. Anal. Calcd. for $C_{12}H_9BrO_2S$: C, 48.50; H, 3.05; found: C, 48.59; H, 3.03.



21b-H was prepared according to General Procedure B. Thus, 2,4-dibromothiophene (1.12 mL, 10.0 mmol, 1.00 eq.), phenylboronic acid (3.05 g, 25.0 mmol, 2.50 eq.), **S17** (169 mg, 0.20 mmol, 2%), THF (10 mL), and *aq*. K_3PO_4 (1 M, 20 mL, 10 mmol, 3.0 eq.) were combined in a 100 mL Schlenk tube and allowed to stir at 60 °C for 12 h. Purification of the crude reaction mixture by flash chromatography (0 → 1% EtOAc/hexanes) yielded a white solid that was ~95% **21b-H**, as judged by ^{1}H NMR. Recrystallization of this material from MeOH yielded 2,4-diphenylthiophene (1.88 g, 80%) as a white crystalline solid. Melting Point: 120 °C (Lit. 124-125 °C).[34] ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.63-7.70 (m, 4H), 7.62 (d, J = 2 Hz, 1H), 7.40-7.46 (m, 5H), 7.31-7.36 (m, 2H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$): δ 145.2, 143.3, 136.0, 134.4, 129.1,

129.0, 127.8, 127.4, 126.4, 126.0, 122.5, 119.8 ppm. IR: 3053, 3037, 1595, 1481, 1447, 1365, 1198, 1155, 1075, 1028, 965, 910, 885, 834, 751, 734, 691 cm^{-1}. These spectra are consistent with those reported in the literature.[35]

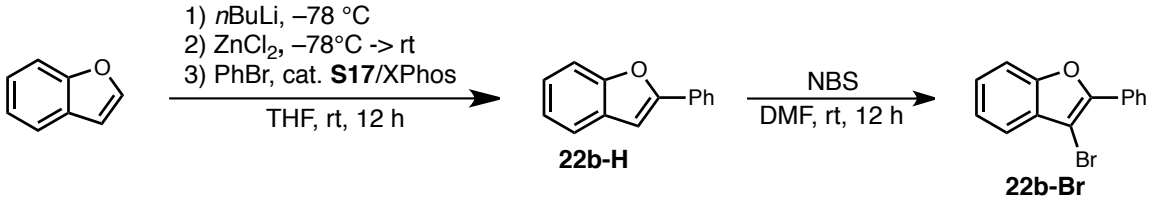
21b-Br was prepared according to a modification of General Procedure A to prevent formation of dibrominated and regioisomeric monobrominated side products. 2,4-diphenylthiophene (945 mg, 4.00 mmol, 1.00 eq.) was dissolved in CH_2Cl_2 (10 mL) and DMF (10 mL) in a 50 mL roundbottom flask wrapped in aluminum foil. The flask was cooled to 0 °C. N-bromosuccinimide (1.07 g, 6.00 mmol, 1.50 eq.) was added in one portion, and the reaction mixture was allowed to stir at 0 °C for 2.5 h. At this time, saturated *aq*. Na_2SO_3 (20 mL) and ether (20 mL) were added, and the organic phase was carefully removed with the aid of a rotary evaporator. The resulting suspension was diluted with ether (20 mL), and the phases were separated. The aqueous phase was further extracted with ether (2 × 20 mL), and the combined organic phases were washed with water (2 × 20 mL) and brine (20 mL), dried over $MgSO_4$, filtered, and concentrated, to afford 2-bromo-3,5-diphenylthiophene (1.18 g, 94%) as a thick yellow oil that solidified upon standing at 0 °C. Melting Point: 54-56 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.62 (dd, J = 9, 2 Hz, 2H), 7.57 (dd, J = 9, 1 Hz, 2H), 7.47 (t, J = 8 Hz, 2H), 7.38-7.43 (m, 3H), 7.34 (tt, J = 8, 2 Hz, 1H), 7.25 (s, 1H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$): δ 144.3, 142.3, 131.2, 133.6, 129.3, 128.7, 128.6, 128.2, 127.9, 125.7, 124.8, 107.9 ppm. IR: 3054, 3023, 1598, 1505, 1487, 1446, 1215, 1072, 1030, 992, 951, 837, 751, 687 cm^{-1}. Anal. Calcd. for $C_{16}H_{11}BrS$: C, 60.96; H, 3.52; found: C, 60.98; H, 3.59.



This procedure was adapted from the literature.[12] $Pd(OAc)_2$ (90.0 mg, 0.40 mmol, 5%), tricyclohexylphosphine tetrafluoroborate (220 mg, 0.60 mmol, 6%), and K_2CO_3 (2.08 g, 15.0 mmol, 1.50 eq.) were combined in a 100 mL Schlenk tube equipped with a stir bar. The tube was placed under high vacuum and backfilled with argon. This process was repeated a total of three times. The screw-cap was replaced with a septum, and benzo[b]thiophene (1.17 mL, 10.0 mmol, 1.00 eq., warmed gently prior to use), bromobenzene (1.05 mL, 10.0 mmol, 1.00 eq.), pivalic acid (345 μL, 3.00 mmol, 0.30 eq.), and DMA (25 mL) were added. The septum was replaced with the screw-cap, and the tube was placed in an oil bath pre-heated to 100 °C and allow to stir for 12 h. At this time, the tube was cooled to room temperature, and the reaction mixture was diluted with hexanes (50 mL) and water (50 mL). The phases were separated, and the aqueous phase was further extracted with hexanes (2 × 25 mL). The combined organic phases were washed with water (2 × 25 mL) and brine (25 mL), dried over $MgSO_4$, filtered through a silica gel plug, eluting with hexanes, and concentrated. The resulting solid was recrystallized from hot hexanes to afford 2-phenylbenzo[b]thiophene (**22a-H**) (1.15 g, 55%) as an off-white solid. Melting Point: 172 °C (Lit. 168-169 °C).[36] ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.84 (d, J = 8 Hz, 1H), 7.79 (d, J = 8 Hz, 1H), 7.74 (d, J = 8 Hz, 2H), 7.56 (s, 1H), 7.44 (t, J = 8 Hz, 2H), 7.30-7.38 (m, 3H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$): δ 144.4, 140.8, 139.6, 134.4, 129.1, 128.4, 126.6, 124.7, 124.5, 123.7, 122.4,

119.6 ppm. IR: 3052, 1486, 1446, 1427, 1335, 1194, 1071, 1028, 944, 825, 756, 724, 685 cm^{-1}. These spectra are consistent with those reported in the literature.[36]

22a-Br was prepared according to General Procedure A. Thus, **22a-H** (1.00 g, 4.76 mmol, 1.00 eq.), N-bromosuccinimide (933 mg, 5.24 mmol, 1.10 eq.), and DMF (10 mL) were combined in a 50 mL roundbottom flask and allowed to stir at room temperature for 12 h. Purification of the crude reaction mixture by filtration through a silica gel plug, eluting with ether, followed by recrystallization of the resulting solid from MeOH, provided 3-bromo-2-phenylbenzo[b]thiophene (1.27 g, 92%) as a pale yellow solid. Melting Point: 62 °C (Lit. 62-63 °C).[37] ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.91 (d, J = 8 Hz, 1H), 7.83 (d, J = 8 Hz, 1H), 7.79 (dd, J = 9, 2 Hz, 2H), 7.41-7.47 (m, 2H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$): δ 139.9, 138.9, 137.2, 134.0, 130.1, 128.7, 128.2, 124.9, 123.0, 121.8, 113.4 ppm. IR: 3055, 3021, 1600, 1481, 1443, 1431, 1299, 1249, 1015, 886, 794, 743, 723, 686 cm^{-1}. These spectra are consistent with those reported in the literature.[37]

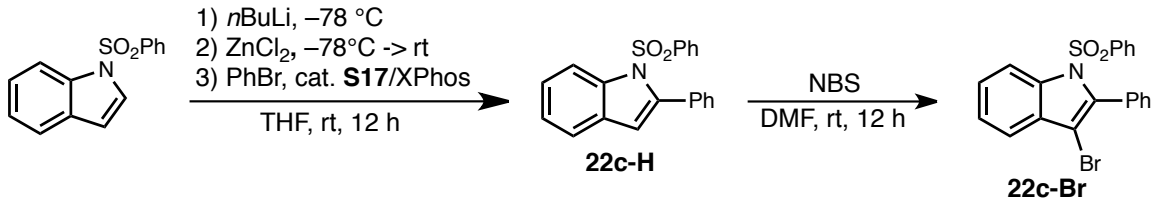


22b-H was prepared according to General Procedure D. Thus, benzo[b]furan (576 μL, 5.20 mmol, 1.30 eq.), THF (10 mL), *n*BuLi (2.5 M in hexanes, 2.28 mL, 5.72 mmol, 1.43 eq.), $ZnCl_2$ (1.9 M in 2MeTHF, 3.28 mL, 6.24 mmol, 1.56 eq.), bromobenzene (420 μL, 4.00 mmol, 1.00 eq.), **S17** (72.8 mg, 0.08 mmol, 2%), and XPhos (38.4 mg, 0.08 mmol, 2%) were combined and allowed to stir atroom temperaturefor 12 h. Purification of the

crude reaction mixture by flash chromatography (hexanes) afforded 2-phenylbenzo[b]furan (**22b-H**) (492 mg, 60%) as a fluffy white solid. Melting Point: 120 °C (Lit. 118-119).[38] ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.88 (dd, J = 8, 2 Hz, 2H), 7.60 (ddd, J = 8, 2, 1 Hz, 1H), 7.54 (d, J = 8 Hz, 1H), 7.46 (pt, J = 8 Hz, 2H), 7.36 (tt, J = 8, 1 Hz, 1H), 7.22-7.32 (m, 2H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$): δ 156.0, 155.0, 130.6, 129.3, 128.9, 128.7, 125.1, 124.4, 123.1, 121.0, 111.3, 101.4 ppm. IR: 3035, 1491, 1470, 1455, 1441, 1259, 1208, 1169, 1105, 1038, 1020, 919, 882, 806, 762, 739, 689, 646 cm^{-1}. These spectra are consistent with those reported in the literature.[38]

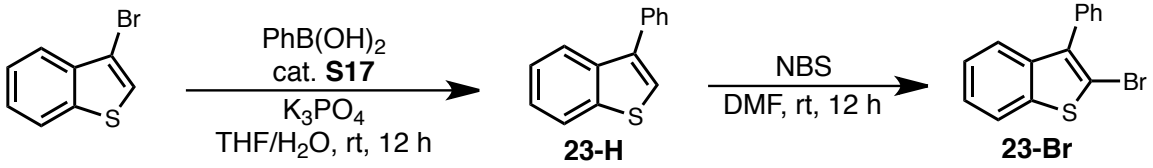
22b-Br was prepared according to a modified General Procedure A. Thus, **22b-H** (1.30 g, 6.69 mmol, 1.00 eq.), N-bromosuccinimide (1.52 g, 8.70 mmol, 1.30 eq.), DMF (15 mL) and CH_2Cl_2 (15 mL, to solubilize the starting material) were combined in a 100 mL roundbottom flask and allowed to stir at room temperature for 12 h. At this time, the CH_2Cl_2 was removed with the aid of a rotary evaporator. The resulting solution was diluted with water (30 mL) and ether (30 mL), and the phases were separated. The aqueous phase was further extracted with ether (2 × 30 mL). The combined organic phases were washed with water (2 × 30 mL) and brine (30 mL), dried over $MgSO_4$, filtered, and concentrated. The resulting yellow oil was purified by flash chromatography (hexanes) to afford 3-bromo-2-phenylbenzo[b]furan (1.33 g, 73%) as a colorless oil that solidified to a white solid upon standing at 0 °C. Melting Point: 63 °C (Lit. 62-63 °C).[39] ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.19 (dd, J = 8, 1 Hz, 2H), 7.58 (ddd, J = 8, 2, 1 Hz, 1H), 7.48-7.53 (m, 3H), 7.43 (tt, J = 8, 1 Hz, 1H), 7.31-7.39 (m, 2H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$): δ 153.3, 150.4, 129.7, 129.7, 1299.2, 128.7, 126.9, 125.7, 123.6, 120.0,

111.4, 94.0 ppm. IR: 3060, 1490, 1452, 1442, 1254, 1205, 1082, 1065, 1029, 986, 890, 820, 763, 738, 686, 581 cm^{-1}. These spectra are consistent with those reported in the literature.[39]



22c-H was prepared according to General Procedure D. Thus, 1-(phenylsulfonyl)-1*H*-indole (1.42 g, 5.50 mmol, 1.10 eq.), THF (10 mL), *n*BuLi (2.5 M in hexanes, 2.42 mL, 6.05 mmol, 1.21 eq.), $ZnCl_2$ (1.9 M in 2MeTHF, 3.47 mL, 6.60 mmol, 1.32 eq.), bromobenzene (527 μL, 5.00 mmol, 1.00 eq.), **S17** (84.6 mg, 0.10 mmol, 2%), XPhos (47.7 mg, 0.10 mmol, 2%) were combined and allowed to stir at room temperature for 12 h. The crude reaction mixture was purified by flash chromatography (2.5 → 5% EtOAc/hexanes); all of the fractions containing **22c-H** were collected and concentrated to afford a yellow solid, which was recrystallized from hot MeOH to afford 2-phenyl-1-(phenylsulfonyl)-1*H*-indole (936 mg, 56%) as an off-white solid. Melting Point: 95-97 °C (Lit. 103-104 °C).[40] ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.33 (d, J = 9 Hz, 1H), 7.35-7.52 (m, 10H), 7.24-7.30 (m, 3H), 6.56 (d, J = 1 Hz, 1H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$): δ 142.2, 138.4, 137.6, 133.7, 132.4, 130.7, 130.5, 128.8, 128.7, 127.7, 126.9, 125.0, 124.5, 120., 116.8, 113.9 ppm. IR: 3057, 1449, 1372, 11070, 1089, 1049, 979, 836, 761, 732, 698, 682, 635 cm^{-1}. These spectra are consistent with those reported in the literature.[40]

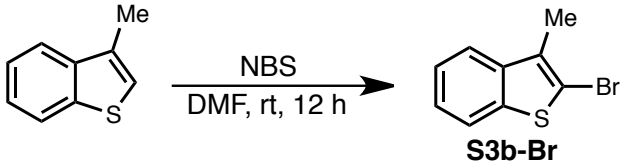
22c-Br was prepared according to General Procedure A. Thus, **22c-H** (400 mg, 1.20 mmol, 1.00 eq.), N-bromosuccinimide (235 mg, 1.32 mmol, 1.10 eq.), and DMF (5.0 mL) were combined at room temperature and allowed to stir overnight. The crude reaction mixture was filtered through a silica gel plug, eluting with ether, and concentrated to yield a red foam. Trituration of this foam with cold MeOH (4 mL) resulted in precipitation of a white solid from solution. The resulting non-homogenous mixture was filtered, and the filtrate was washed with cold MeOH (2 × 2 mL) to afford 3-bromo-2-phenyl-1-(phenylsulfonyl)-1*H*-indole (376 mg, 76%) as a white solid. Melting Point: 109-111 °C (Lit. 107-108 °C).[41] ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.36 (d, J = 8 Hz, 1H), 7.36-7.53 (m, 11H), 7.30 (pt, J = 7 Hz, 2H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$): δ 137.7, 137.7, 134.0, 131.7, 130.0, 129.9, 129.4, 129.0, 127.7, 127.0, 126.3, 124.9, 120.1, 116.3, 104.0 ppm. IR: 3066, 1446, 1373, 1183, 1121, 1086, 1009, 770, 751, 731, 684, 632, 589 cm^{-1}. These spectra are consistent with those reported in the literature.[41]



23-H was prepared according to General Procedure B. Thus, 3-bromobenzo[b]thiophene (1.31 mL, 10.0 mmol, 1.00 eq.), phenylboronic acid (1.46 g, 12.0 mmol, 1.20 eq.), **S17** (170 mg, 0.20 mmol, 2%), THF (10 mL), *aq*. K_3PO_4 (2M, 10 mL, 20 mmol, 2 eq.) were combined in a 100 mL roundbottom flask and allowed to stir at room temperature for 12 h. Purification of the crude reaction mixture by flash chromatography (hexanes) provided 3-phenylbenzo[b]thiophene (1.85 g, 88%). ^{1}H NMR (500 MHz, $CDCl_3$): δ

7.95-7.99 (m, 2H), 7.62-7.65 (m, 2H), 7.53 (pt, J = 10 Hz, 2H), 7.42-7.47 (m, 4H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$): δ 140.8, 138.2, 138.0, 136.1, 128.9, 128.8, 127.7, 124.5, 124.5, 123.5, 123.0 ppm. IR: 3055, 1600, 1524, 1483, 1441, 1425, 1347, 1259, 1073, 1061, 1027, 940, 914, 833, 760, 729, 696, 637, 573 cm^{-1}. These spectra are consistent with those reported in the literature.[42]

23-Br was prepared according to General Procedure B. Thus, **23-H** (1.05 g, 5.00 mmol, 1.00 eq.), N-bromosuccinimide (979 mg, 5.50 mmol, 1.10 eq.), and DMF (10 mL) were combined in a 50 mL roundbottom flask and allowed to stir at room temperature for 12 h. Purification of the crude reaction mixture by filtration through a silica gel plug, eluting with hexanes, provided 2-bromo-3-phenylbenzo[b]thiophene (511 mg, 35%) as a white solid. Melting Point: 72 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.79 (ddd, J = 8, 2, 1 Hz, 1H), 7.47-7.61 (m, 7H), 7.32-7.40 (m, 2H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$): δ 139.9, 138.9, 137.2, 134.0, 130.1, 1128.7, 128.2, 124.9, 123.0, 121.8, 113.4 ppm. IR: 3052, 1598, 1482, 1455, 1440, 1427, 1332, 1259, 1153, 1130, 1071, 1027, 990, 886, 858, 758, 729, 710, 696, 640, 609 cm^{-1}. Anal. Calcd. for $C_{14}H_9BrS$: C, 58.15; H, 3.14; found: C, 58.42; H, 3.25.



S3b-Br

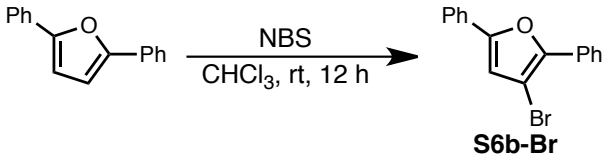
S3b-Br was prepared according to General Procedure A. Thus, 3-methylbenzo[b]thiophene (1.96 g, 11.0 mmol, 1.10 eq.), and DMF (10 mL) were combined in a 50 mL roundbottom flask and allowed to stir at room temperature for 12 h. Purification of the crude reaction mixture

by filtration through a silica gel plug, eluting with hexanes, provided 2-bromo-3-methylbenzo[b]thiophene (1.86 g, 82%) as a colorless oil. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.71-7.74 (m, 1H), 7.62-7.65 (m, 1H), 7.31-7.39 (m, 2H), 2.39 (d, J = 1 Hz, 3H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$): δ 139.7, 139.0, 131.9, 124.6, 124.6, 121.9, 121.8, 112.6, 13.2 ppm. IR: 3060, 2914, 2853, 1936, 1899, 1779, 1569, 1530, 1458, 1425, 1377, 1256, 1136, 1097, 1052, 1011, 944, 747, 724, 707, 604, 585 cm^{-1}. These spectra are consistent with those reported in the literature.[43]

S6a-H was prepared according to General Procedure B. Thus, methyl 5-bromofuran-2-carboxylate (820 mg, 4.00 mmol, 1.00 eq.), phenylboronic acid (731 mg, 6.00 mmol, 1.50 eq.), **S17** (67.7 mg, 0.08 mmol, 2%), THF (4 mL), and *aq*. K_3PO_4 (1M, 8.0 mL, 8.0 mmol, 2.0 eq.) were combined in a 50 mL Schlenk flask and allowed to stir at 60 °C overnight. Purification of the crude reaction mixture by flash chromatography (0 → 2.5 → 5% EtOAc/hexanes) yielded methyl 5-phenylfuran-2-carboxylate (666 mg, 82%) as a white solid. Melting Point: 66 °C (Lit. 58-60°C).[44] ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.78 (dd, J = 9, 1 Hz, 2H), 7.40-7.44 (m, 2H), 7.35 (tt, J = 8, 2 Hz, 1H), 7.25 (d, J = 4 Hz, 1H), 6.74 (d, J = 4 Hz, 1H), 3.92 (s, 3H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$): δ 159.3, 157.7, 143.7, 129.6, 129.1, 128.9, 124.9, 120.2, 107.0, 52.0 ppm. IR: 3124, 3030, 2954, 1713, 1525, 1475, 1452, 1434, 1374, 1308, 1276, 1224, 1196, 1145, 1035, 989, 917, 811, 797, 758, 764, 670 cm^{-1}. These spectra are consistent with those reported in the literature.[44]

S6a-Br was prepared according to General Procedure C. Thus, **S6a-H** (408 mg, 2.00 mmol, 1.00 eq.), Br_2 (412 μL, 8.00 mmol, 4.00 eq.), and DMF (10 mL) were combined

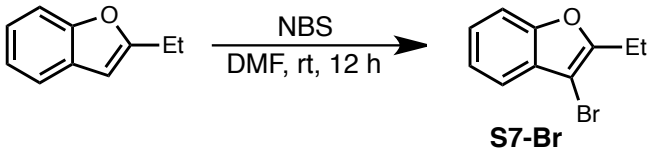
and allowed to stir at 0 °C for 30 min. Purification of the crude reaction mixture by filtration through a silica gel plug, eluting with ether, provided 4-bromo-5-phenylfuran-2-carboxylate (461 mg, 82%) as a white solid. Melting Point: 89 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.05 (dd, J = 7, 2 Hz, 2H), 7.46 (pt, J = 7 Hz, 2H), 7.41 (tt, J = 8, 2 Hz, 1H), 7.26 (s, 1H), 3.92 (s, 3H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$): δ 158.5, 152.5, 142.8, 129.5, 128.7, 128.7, 126.6, 123.4, 97.2, 52.3 ppm. IR: 3128, 2953, 2845, 1723, 1568, 1532, 1473, 1444, 1368, 1303, 1196, 1116, 990, 956, 881, 798, 772, 758, 688, 665 cm^{-1}. Anal. Calcd. for $C_{12}H_9BrO_3$: C, 51.27; H, 3.23; found: C, 51.00; H, 3.31.



S6b-Br

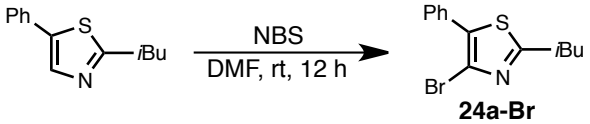
S6b-Br was prepared according to a modified General Procedure A. A 25 mL roundbottom flask equipped with a stir bar and wrapped in aluminum foil was charged with 2,5-diphenylfuran (220 mg, 1.00 mmol, 1.00 eq.). $CHCl_3$ (6 mL) was added, followed by N-bromosuccinimide (214 mg, 1.20 mmol, 1.20 eq.), and the reaction mixture was allowed to stir at room temperature for 12 h. The solvent was removed, and the resulting solid was partitioned between Et_2O (10 mL) and water (10 mL). The phases were separated, and the aqueous phase was further extracted with Et_2O (2 × 10 mL). The combined organic phases were washed with brine (10 mL), dried over $MgSO_4$, and filtered through a silica gel plug, eluting with Et_2O. The solvent was removed in *vacuo*, and the resulting yellow solid was recrystallized from hot MeOH, which yielded 3-bromo-2,5-diphenylfuran (127 mg, 43%) as a pale orange solid. Melting Point: 82 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.06 (d, J = 6 Hz, 2H), 7.71 (d, J = 7 Hz, 2H), 7.40-7.49 (m, 4H), 7.30-7.38 (m, 2H), 6.79 (s, 1H)

ppm; ^{13}C NMR (125 MHz, $CDCl_3$): δ 152.8, 148.2, 129.9, 129.8, 129.0, 128.7, 128.3, 128.1, 125.6, 124.0, 111.5, 98.1 ppm. IR: 3125, 3055, 2981, 1589, 1448, 1193, 1068, 1053, 1034, 953, 911, 802, 757, 685, 662 cm^{-1}. Anal. Calcd. for $C_{16}H_{11}BrO$: C, 64.24; H, 3.71; found: C, 64.21; H, 3.84.



S7-Br

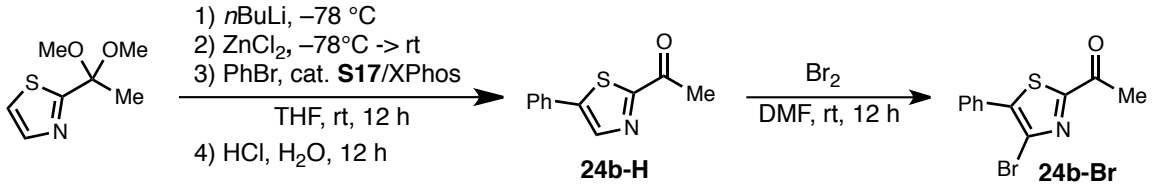
S7-Br was prepared according to General Procedure A. Thus, 2-ethylbenzo[b]furan (292 mg, 2.00 mmol, 1.00 eq.), N-bromosuccinimide (463 mg, 2.60 mmol, 1.30 eq.), and DMF (2.0 mL) were combined in a 10 mL roundbottom flask and allowed to stir at room temperature overnight.[45] Purification of the crude reaction mixture by flash chromatography (hexanes) afforded 3-bromo-2-ethylbenzo[b]furan (185 mg, 41%) as a colorless oil. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.40-7.47 (m, 2H), 7.27-7.31 (m, 2H), 2.87 (q, J = 8 Hz, 2H), 1.34 (t, J = 8 Hz, 3H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$): δ 156.8, 153,5, 128.5, 124.5, 123.2, 119.2, 111.2, 93.5 ppm. IR: 2975, 2939, 2877, 1599, 1450, 1261, 1173, 1106, 1010, 999, 838, 739 cm^{-1}. HRMS (ESI) m/z calcd. for $C_{10}H_8BrO$ [M-H$^+$, M+2-H$^+$]: 222.9753, 224.9738; found: 222.9779, 224.9759.



24a-Br

24-Br was prepared according to General Procedure A. Thus, 2-*iso*-butyl-5-phenylthiazole[12] (611 mg, 2.87 mmol, 1.00 eq.), N-bromosuccinimide (668 mg, 3.73 mmol, 1.30 eq.), and DMF (5 mL) were combined and allowed to stir at room temperature for 12 h. The crude reaction mixture was filtered through a silica gel plug,

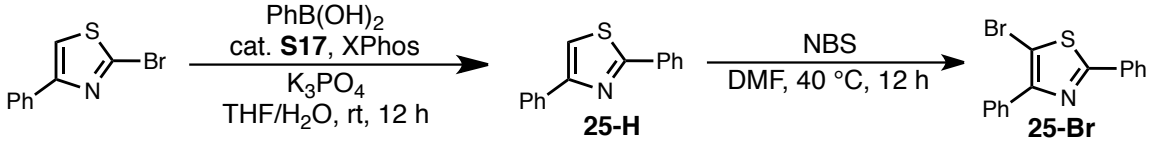
eluting with ether, and concentrated. The resulting oil was further purified by flash chromatography (2% EtOAc/hexanes) to afford 4-bromo-2-*iso*-butyl-5-phenylthiazole (714 mg, 84%) as a pale yellow oil. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.62 (dd, J = 9, 2 Hz, 2H), 7.36-7.45 (m, 3H), 2.86 (d, J = 8 Hz, 2H), 2.13 (nonet, J = 7 Hz, 1H), 1.03 (d, J = 7 Hz, 6H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$): δ 169.8, 132.4, 130.5, 129.2, 128.8, 128.7, 121.0, 42.7, 29.9, 22.4 ppm. IR: 2956, 2928, 2868, 1519, 1480, 1386, 1206, 1157, 1066, 965, 853, 755, 692 cm^{-1}. Anal. Calcd. for $C_{13}H_{14}BrNS$: C, 52.71; H, 4.76; found: C, 52.98; H, 4.78.



24b-H was prepared according to General Procedure D, followed by hydrolysis. Thus, 2-(1,1-dimethoxyethyl)thiazole[46] (1.13 g, 6.50 mmol, 1.30 eq.), THF (13 mL), *n*BuLi (2.5 M in hexanes, 2.86 mL, 7.15 mmol, 1.43 eq.), $ZnCl_2$ (1.9 M in 2MeTHF, 4.11 mL, 7.80 mmol, 1.56 eq.), bromobenzene (525 μL, 5.00 mmol, 1.00 eq.), **S17** (84.6 mg, 0.10 mmol, 2%) and XPhos (47.7 mg, 0.10 mmol, 2%) were combined and allowed to stir atroom temperaturefor 12 h. After workup and concentration, the crude product was dissolved in CH_2Cl_2 (30 mL) in a 100 mL roundbottom flask equipped with a stir bar. Then, 1 M HCl (30 mL) was added, and the reaction mixture was allowed to vigorously stir atroom temperaturefor 12 h. At this time, the reaction mixture was carefully neutralized with saturated *aq.* $NaHCO_3$ (~50 mL), and the phases were separated. The aqueous phase was further extracted with CH_2Cl_2 (2 × 30 mL). The combined organic phases were dried over $MgSO_4$, filtered, and concentrated. This material was further

purified by flash chromatography (5 → 10 → 15% EtOAc/hexanes); all of the fractions containing the desired product were collected and concentrated to yield a pale yellow solid. This solid was triturated with cold hexanes and filtered to afford 2-acetyl-5-phenylthiazole (735 mg, 72%) as a white solid. Melting Point: 124 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.14 (s, 1H), 7.61-7.65 (m, 2H), 7.40-7.49 (m, 3H), 2.72 (s, 3H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$): δ 191.8, 165.6, 147.2, 140.3, 130.6, 129.7, 129.5, 127.3, 25.8 ppm. IR: 3088, 3026, 1674, 1574, 1520, 1451, 1421, 1397, 1357, 1282, 1181, 1160, 1055, 1019, 933, 876, 758, 687, 662, 592 cm^{-1}. Anal. calcd. for $C_{11}H_9NOS$: C, 65.00; H, 4.46; found: C, 64.56, H, 4.52.

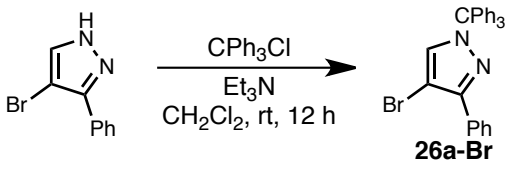
24b-Br was prepared according to General Procedure C. Thus, **24b-H** (406 mg, 2.00 mmol, 1.00 eq.), Br_2 (412 μL, 8.00 mmol, 4.00 eq.), and DMF (5.0 mL) were combined at 0 °C and allowed to stir atroom temperaturefor 12 h. The crude product mixture was filtered through a silica gel plug, eluting with ether, and concentrated. The resulting solid was recrystallized from hot methanol to afford 2-acetyl-4-bromo-5-phenylthiazole (222 mg, 39%) as a white solid. Melting Point: 99 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.63-7.70 (m, 2H), 7.42-7.51 (m, 3H), 2.71 (s, 3H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$): δ 190.8, 164.3, 142.2, 129.9, 129.5, 129.4, 129.0, 123.9, 25.7 ppm. IR: 3037, 1684, 1508, 1446, 1403, 1354, 1275, 1223, 1055, 1000, 935, 852, 751, 610, 596 cm^{-1}. HRMS (ESI) m/z calcd. for $C_{11}H_9BrNOS$ ($M+H^+$, $M+2+H^+$): 281.9583, 283.9563; found: 281.9583, 283.9549.



25-H was prepared according to General Procedure B. Thus, 2-bromo-4-phenylthiazole (720 mg, 3.00 mmol, 1.00 eq.), phenylboronic acid (549 mg, 4.50 mmol, 1.50 eq.), **S17** (102 mg, 0.12 mmol, 4%), THF (3.0 mL), and *aq*. K_3PO_4 (1M, 6.0 mL, 6.0 mmol, 2.0 eq.) were combined in a 50 mL Schlenk tube and allowed to stir at 60 °C overnight. Purification of the crude reaction mixture by flash chromatography (0 → 2% EtOAc/hexanes) afforded 2,4-diphenylthiazole (640 mg, 90%) as a white crystalline solid. Melting Point: 92 °C (Lit. 91-92 °C).[47] ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.06 (dd, J = 9, 2 Hz, 2H), 8.01 (dd, J = 9, 2 Hz, 2H), 7.43-7.49 (m, 6H), 7.37 (tt, J = 8, 1 Hz, 1H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$): δ 168.0, 156.4, 134.6, 133.8, 130.2, 129.0, 128.9, 128.3, 126.7, 126.6, 112.8 ppm. IR: 3116, 3047, 1479, 1443, 1070, 1056, 1027, 974, 921, 837, 757, 733, 714, 686, 671, 595 cm^{-1}. These spectra are consistent with those reported in the literature.[47]

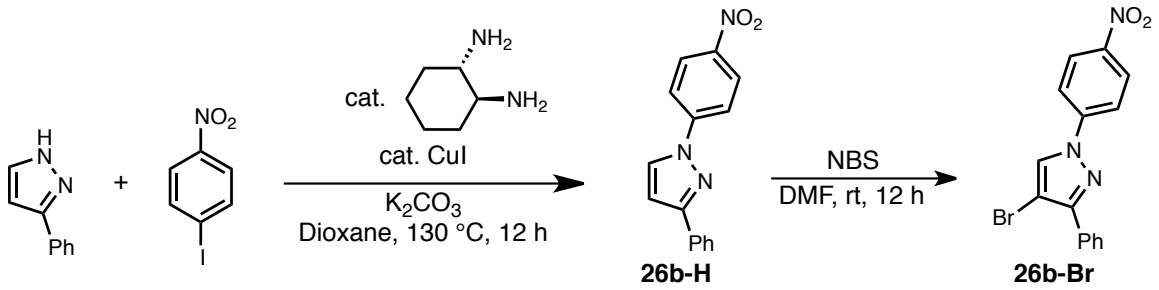
25-Br was prepared according to General Procedure A. Thus, **25-H** (500 mg, 2.11 mmol, 1.00 eq.), N-bromosuccinimide (450 mg, 2.53 mmol, 1.20 eq.), and DMF (5.0 mL) were combined and allowed to stir at 40 °C for 12 h. Purification of the crude reaction mixture by filtration through a silica gel plug, eluting with ether, followed by recrystallization of the resulting solid from MeOH, afforded 5-bromo-2,4-diphenylthiazole (540 mg, 81%) as a white solid. Melting Point: 88 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.04 (d, J = 8 Hz, 2H), 7.94 (dd, J = 7, 2 Hz, 2H), 7.40-7.51 (m, 6H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$): δ

167.3, 153.3, 133.6, 133.2, 130.7, 129.2, 128.8, 128.7, 128.5, 126.4, 103.5 ppm. IR: 3064, 1477, 1443, 1271, 1245, 1068, 997, 975, 907, 857, 757, 710, 676, 633, 598 cm^{-1}. Anal. Calcd. for $C_{15}H_{10}BrNS$: C, 56.97; H, 3.19; found: C, 56.88; H, 3.28.



26a-Br

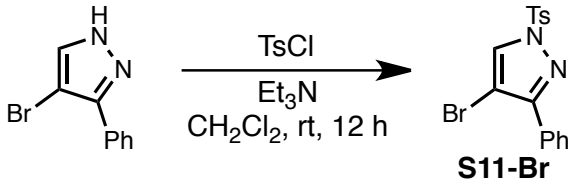
26a-Br was prepared according to General Procedure E. Thus, 4-bromo-3-phenyl-1*H*-pyrazole (223 mg, 1.00 mmol, 1.00 eq.), triethylamine (420 μL, 3.00 mmol, 3.00 eq.), trityl chloride (420 mg, 1.50 mmol, 1.50 eq.), and CH_2Cl_2 (2.0 mL) were combined in a 10 mL roundbottom flask and allowed to stir at room temperature overnight. The crude reaction mixture was purified by filtration through a silica gel plug, eluting with CH_2Cl_2, and concentrated to a minimal volume of CH_2Cl_2 (~5 mL). This solution was slowly triturated with methanol, which resulted in precipitation of a white crystalline solid from solution. Filtration of the non-homogenous mixture and washing the resulting solid with cold methanol (2 × 5 mL) afforded 4-bromo-3-phenyl-1-trityl-1*H*-pyrazole (398 mg, 69 %) as a white crystalline solid. Melting Point: 182-184 °C (Lit. 181-183 °C).[13] ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.94 (dd, J = 7, 2 Hz, 1H), 7.221-7.43 (m, 20H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$): δ 148.4, 142.9, 134.5, 132.4, 130.4, 128.3, 128.1, 128.0, 127.9, 127.8, 91.1, 79.6 ppm. IR: 3129, 3059, 1604, 1490, 1446, 1363, 1186, 1161, 1111, 1086, 1030, 1000, 903, 871, 813, 749, 693, 654, 642 cm^{-1}. These spectra are consistent with those reported in the literature.[13]



26b-H **26b-Br**

26b-H was prepared using a procedure was adapted from the literature.[48] Copper (I) iodide (38.0 mg, 0.20 mmol, 10%), K_2CO_3 (580 mg, 4.20 mmol, 2.10 eq.), 3-phenyl-1*H*-pyrazole (346 mg, 2.40 mmol, 1.20 eq.), and 1-iodo-4-nitrobenzene (498 mg, 2.00 mmol, 1.00 eq.) were combined in a reaction tube equipped with a stir bar. The tube was placed under high vacuum and backfilled with argon. This process was repeated a total of three times. Then, (±)-trans-1,2-diaminocyclohexane (96.0 μL, 0.40 mmol, 20%) and 1,4-dioxane (4.0 mL) were added to the tube. The cap was replaced with one that had not been punctured, and the tube was placed in an oil bath that had been pre-heated to 130 °C and allowed to stir for 12 h. At this time, the reaction mixture was cooled to room temperature and diluted with EtOAc (10 mL). The reaction mixture was filtered through a silica gel plug, eluting with EtOAc, and concentrated, to afford 1-(4-nitrophenyl)-3-phenyl-1*H*-pyrazole (300 mg, 57%) as a yellow solid. Melting Point: 169-171 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.35 (dt, J = 9, 3 Hz, 2H), 8.07 (d, J = 3 Hz, 1H), 7.91-7.97 (m, 4H), 7.47 (t, J = 8 Hz, 2H), 7.39 (tt, J = 8, 1 Hz, 1H), 6.88 (d, J = 3 Hz, 1H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$): δ 154.7, 145.4, 144.5, 132.3, 128.9, 128.4, 126.2, 125.6, 118.4, 107.1 ppm. IR: 3143, 3120, 1599, 1534, 1509, 1456, 1394, 1364, 1329, 1308, 1286, 1183, 1111, 1045, 951, 855, 840, 751, 746, 691, 683 cm^{-1}. Anal. Calcd. for $C_{15}H_{11}N_3O_2$: C, 67.92; H, 4.18; found: C, 67.63; H, 4.25.

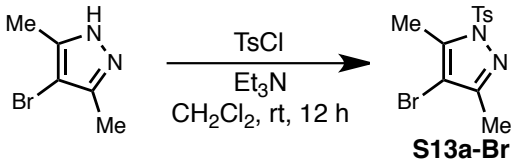
26b-Br was prepared according to General Procedure A. Thus, **26b-H** (265 mg, 1.00 mmol, 1.00 eq.), N-bromosuccinimide (196 mg, 1.10 mmol, 1.10 eq.), and DMF (4.0 mL) were combined in a 25 mL roundbottom flask and allowed to stir at room temperature for 12 h. Purification of the crude reaction mixture by filtration through a silica gel plug, eluting with ether, afforded 1-(4-nitrophenyl)-3-phenyl-1*H*-pyrazole (263 mg, 76%) as a golden yellow solid. Melting Point: 169 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.34 (d, J = 9, 2 Hz, 2H), 8.12 (s, 1H), 8.00 (dt, J = 7, 1 Hz, 2H), 7.89 (dt, J = 10, 3 Hz, 2H), 7.43-7.51 (m, 3H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$): δ 151.7, 145.8, 143.6, 131.0, 129.2, 129.1, 128.6, 127.9, 125.6, 118.3, 96.6 ppm. IR: 3151, 1598, 1509, 1448, 1394, 1332, 1310, 1227, 1183, 1111, 1058, 970, 950, 843, 796, 767, 474, 680 cm^{-1}. Anal. Calcd. for $C_{15}H_{10}BrN_3O_2$: C, 52.35; H, 2.93; found: C, 52.36; H, 2.99.



S11-Br

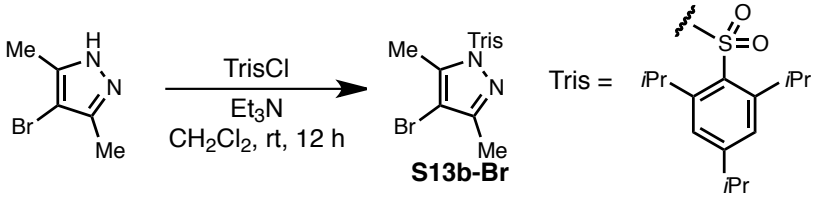
S11-Br was prepared according to General Procedure E. Thus, 4-bromo-3-phenyl-1*H*-pyrazole (669 mg, 3.00 mmol, 1.00 eq.), triethylamine (0.80 mL, 6.00 mmol, 2.00 eq.), 4-toluenesulfonyl chloride (630 mg, 3.30 mmol, 1.10 eq.), and CH_2Cl_2 (10 mL) were combined and allowed to stir at room temperature overnight. Purification of the crude reaction mixture by filtration through a silica gel plug, eluting with CH_2Cl_2, afforded 4-bromo-3-phenyl-1-(4-toluenesulfonyl)-1*H*-pyrazole (1.05 g, 93%) as a white solid. Melting Point: 111-113 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.19 (s, 1H), 7.94 (d, J = 9 Hz, 2H), 7.83-7.86 (m, 2H), 7.39-7.44 (m, 3H), 7.34 (d, J = 9 Hz, 2H), 2.42 (s, 3H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$): δ 154.2, 146.4 133.6, 132.4, 130.3, 130.3, 129.5, 128.5, 128.5, 128.3, 96.8, 21.9 ppm. IR: 3126,

3056, 1594, 1531, 1590, 1440, 1381, 1301, 1175, 1149, 1071, 981, 816, 764, 693, 671, 591, 567 cm^{-1}. Anal. Calcd. for $C_{16}H_{13}BrN_2O_2S$: C, 50.94; H, 3.47; found: C, 51.09; H, 3.52.



S13a-Br

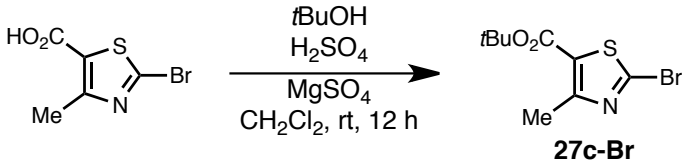
S13a-Br was prepared according to General Procedure E. Thus, 4-bromo-3,5-dimethyl-1*H*-pyrazole (875 mg, 5.00 mmol, 1.00 eq.), triethylamine (1.40 mL, 10.0 mmol, 2.00 eq.), 4-toluenesulfonyl chloride (1.05 g, 5.50 mmol, 1.10 eq.), and CH_2Cl_2 (30 mL) were combined and allowed to stir at room temperature overnight. Purification of the crude reaction mixture by filtration through a silica gel plug, eluting with CH_2Cl_2, afforded 4-bromo-3,5-dimethyl-1-(4-toluenesulfonyl)-1*H*-pyrazole (1.26 g, 76%) as a white solid. Melting Point: 130-133 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.82 (d, J = 9 Hz, 2H), 7.30 (d, J = 8 Hz, 2H), 2.49 (s, 3H), 2.40 (s, 3H), 2.20 (s, 3H), 1.16 (d, J = 7 Hz, 12H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$): δ 152.1, 145.8, 141.1, 134.7, 130.1, 127.8, 101.0, 21.8, 12.9, 12.3 ppm. IR: 2930, 1592, 1562, 1449, 1386, 1368, 1296, 1188, 1175, 1141, 1058, 1015, 975, 813, 779, 702, 668, 604, 585 cm^{-1}. Anal. Calcd. for $C_{12}H_{13}BrN_2O_2S$: C, 43.78; H, 3.98; found: C, 44.01; H, 4.00.



S13b-Br

S13b-Br was prepared according to General Procedure E. Thus, 4-bromo-3,5-dimethyl-1*H*-pyrazole (525 mg, 3.00 mmol, 1.00 eq.), triethylamine (0.80 mL,

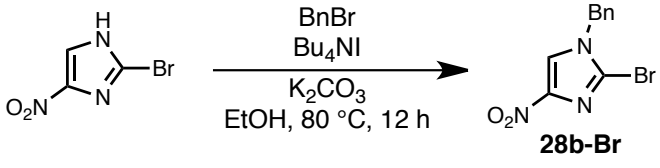
6.00 mmol, 2.00 eq.), 2,4,6-triisopropylphenyl-1-sulfonyl chloride (1.00 g, 3.30 mmol, 1.10 eq.), and CH_2Cl_2 (10 mL) were combined and allowed to stir at room temperature overnight. Purification of the crude reaction mixture by flash chromatography (0 → 20 → 40 → 60% CH_2Cl_2/hexanes) afforded 4-bromo-3,5-dimethyl-1-(2,4,6-triisopropylphenyl-1-sulfonyl)-1*H*-pyrazole (157 mg, 12%) as an oil that solidified to a white solid upon standing at 0 °C. Melting Point: 68-70 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.19 (s, 2H), 4.13 (septet, J = 7 Hz, 2H), 2.92 (septet, J = 7 Hz, 1H), 2.39 (s, 3H), 2.20 (2, 3H), 1.26 (d, J = 7 Hz, 6H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$): δ 155.0, 152.2, 150.1, 140.1, 124.3, 99.8, 34.3, 29.8, 24.6, 23.6, 12.8, 11.9 ppm. IR: 2958, 2929, 2866, 1595, 1558, 1425, 1373, 1343, 1299, 1176, 1141, 1115, 1062, 1034, 977, 879, 784, 672, 588 cm^{-1}. Anal. Calcd. for $C_{20}H_{29}BrN_2O_2S$: C, 54.42; H, 6.62; found: C, 54.62; H, 6.71.



27c-Br

A 50 mL roundbottom flask equipped with a stir bar was charged with $MgSO_4$ (1.08 g, 9.00 mmol, 4.00 eq.) and flame-dried under high vacuum. The flask was backfilled with nitrogen, and anhydrous CH_2Cl_2 (15 mL) was added. Concentrated H_2SO_4 (~128 μL, ~2.25 mmol, ~1.00 eq.) was added dropwise, and the mixture was allowed to stir at for 10 min. Next, 2-bromo-4-methylthiazole-5-carboxylic acid (500 mg, 2.25 mmol, 1.00 eq.) was added under a positive pressure of N_2, followed immediately by *t*BuOH (1.05 mL, 11.3 mmol, 5.00 eq.). The reaction mixture was allowed to stir at room temperature for 12 h. At this time, saturated *aq*. $NaHCO_3$ (10 mL) was *carefully* added, followed by

additional CH_2Cl_2 (20 mL). The phases were separated, and the aqueous phase was extracted with additional CH_2Cl_2 (2 × 20 mL). The combined organic extracts were washed with saturated *aq*. $NaHCO_3$ (20 mL), H_2O (20 mL), and brine (20 mL), dried over $MgSO_4$, filtered, and concentrated. The crude product mixture was purified by flash chromatography (5% EtOAc/hexanes) to yield *tert*-butyl 2-bromo-4-methylthiazole-5-carboxylate (**27c-Br**) (334 mg, 53%) as a pale yellow solid. Melting Point: 48 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ 2.67 (s, 3H), 1.54 (s, 9H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$): δ 160.2, 159.3, 139.1, 127.7, 83.2, 28.3, 17.3 ppm. IR: 2978, 2931, 1714, 1697, 1532, 1401, 1368, 1331, 1303, 1255, 1163, 1090, 1050, 1015, 841, 827, 762 cm^{-1}. HRMS (ESI) m/z calcd. for $C_9H_{13}BrNO_2S$ ($M+H^+$, $M+2+H^+$): 277.9845, 279.9825; found: 277.9833, 279.9817.



28b-Br

A reaction tube equipped with a stir bar was charged with 2-bromo-4-nitro-1*H*-pyrazole (384 mg, 2.00 mmol, 1.00 eq.), K_2CO_3 (415 mg, 3.00 mmol, 1.50 eq.), and tetrabutylammonium iodide (148 mg, 0.40 mmol, 0.20 eq.). The tube was placed under high vacuum and backfilled with nitrogen. Next, benzyl bromide (262 μL, 2.20 mmol, 1.10 eq.) and EtOH (5.0 mL) were added, and the reaction mixture was placed in an oil bath that had been preheated to 80 °C and allowed to vigorously stir for 12 h. The reaction mixture was allowed to cool to room temperature and diluted with water (10 mL) and EtOAc (10 mL). The phases were separated, and the aqueous phase was further extracted with EtOAc (2 × 10 mL). The combined organic phases were washed with water (10 mL) and brine (10 mL), dried

over $MgSO_4$, filtered, and concentrated. The resulting yellow oil was purified by flash chromatography (20 → 40% EtOAc/hexanes) to afford a colorless oil, which was triturated with a minimal amount of ether, resulting in precipitation of a white solid from solution. The non-homogenous mixture was filtered, and the filtrate was washed with cold ether (2 × 5 mL) to afford 1-benzyl-2-bromo-4-nitro-1*H*-pyrazole (**28b-Br**) (248 mg, 44%) as a white solid. Melting Point: 91-93 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.70 (s, 1H), 7.40-7.44 (m, 3H), 7.23-7.26 (m, 2H), 5.17 (s, 2H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$): δ 133.1, 129.6, 129.5, 128.1, 121.5, 120.7, 52.8 ppm. IR: 3152, 3112, 1535, 1504, 1443, 1393, 1370, 1337, 1279, 1179, 1160, 1136, 1090, 1079, 992, 824, 781, 753, 709 cm^{-1}. Anal. Calcd. for $C_{10}H_8BrN_3O_2$: C, 42.58; H, 2.86; found: C, 42.59; H, 2.91.

Synthesis of heteroaryl fluorides.

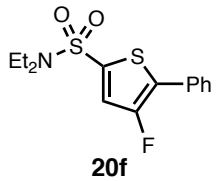
General Procedure for Pd-catalyzed fluorination reactions.

In a nitrogen-filled glovebox, an oven-dried screw-cap reaction tube equipped with a stir bar was charged (in this order) with silver fluoride (26 mg, 0.20 mmol, 2.00 eq.), additive (0.05 mmol, 0.50 eq.), **P1-3** (4.0 mg, 2%), aryl bromide (0.10 mmol, 1.00 eq.), and solvent (1.0 mL). The tube was capped, removed from the glovebox, and placed in an oil bath that had been pre-heated to 130 °C and allowed to vigorously stir for 14 h (Caution: perform behind a barrier such as a blast shield!). At this time, the tube was allowed to cool to room temperature, and 1-fluoronaphthalene (20 μL, 1.55 eq.) was added. The reaction mixture was analyzed directly by ^{19}F NMR. Afterwards, the reaction mixture was filtered through a silica gel plug, eluting with EtOAc, and analyzed by GC (or GC/MS).

General Procedure F. Large scale Pd-catalyzed fluorination reactions.

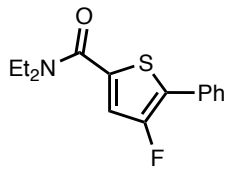
For cases in which the reaction proceeded to full conversion on 0.5 mmol scale, the heteroaryl fluoride was prepared and isolated on this scale. In a nitrogen-filled glovebox, an oven-dried screw-cap reaction tube equipped with a stir bar was charged with silver fluoride (127 mg, 1.00 mmol, 2.00 eq.), potassium fluoride (14.5 mg, 0.25 mmol, 0.50 eq.), **P3** (19.5 mg, 0.01 mmol, 2%), heteroaryl bromide (0.50 mmol, 1.00 eq.), and solvent (5.0 mL). The tube was capped, removed from the glovebox, and placed in an oil bath that had been pre-heated to 130 °C and allowed to vigorously stir for 14 h (Caution: perform behind a barrier such as a blast shield!). At this time, the tube was allowed to cool to room temperature, and the reaction mixture was diluted with EtOAc

(10 mL), and filtered through a pad of celite, eluting with EtOAc (20 mL). The resulting solution was concentrated, and the crude reaction mixture was purified by flash chromatography.



20f

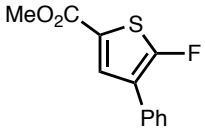
20f was prepared according to General Procedure F. Thus, **20f-Br** (187 mg, 0.50 mmol, 1.00 eq.), silver fluoride (127 mg, 1.00 mmol, 2.00 eq.), potassium fluoride (14.5 mg, 0.25 mmol, 0.50 eq.), **P3** (19.5 mg, 0.01 mmol, 2%), and toluene (5.0 mL) were combined and allowed to stir at 130 °C for 14 h. Purification of the crude reaction mixture by flash chromatography (5 → 10% Et_2O/hexanes) afforded 4-fluoro-5-phenyl-*N,N*-diethylthiophene-2-sulfonamide (146 mg, 93%) as a yellow oil contaminated with <5 % of a second fluorothiophene with the same mass as the desired product (likely 3-fluoro-5-phenyl-*N,N*-diethylthiophene-2-sulfonamide). ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.62 (d, J = 8 Hz, 2H), 7.41-7.49 (m, 2H), 7.37 (tt, J = 8 Hz, 2 Hz, 1H), 7.31 (s, 1H), 3.29 (bq, J = 8 Hz, 4H), 1.22 (bt, J = 7 Hz, 6H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$): δ 152.0 (d, J = 264 Hz), 136.1, 134.8, 128.9-129.9 (m), 127.3 (d, J = 5 Hz), 121.9 (d, J = 27 Hz), 43.0, 14.5 ppm; ^{19}F NMR (470 MHz, $CDCl_3$): δ –126.3 ppm (a minor contaminant was detected at –126.4 ppm). IR: 2975, 2937, 2873, 1724, 1557, 1443, 1386, 1340, 1201, 1145, 1024, 984, 934, 839, 758, 725, 697, 583 cm^{-1}. HRMS (ESI) m/z calcd. for $C_{14}H_{17}FNO_2S_2$ ($M+H^+$): 314.0679; found: 314.0661.



20g

20g was prepared according to General Procedure F. Thus, **20g-Br** (169 mg, 0.50 mmol, 1.00 eq.), silver fluoride (127 mg, 1.00 mmol,

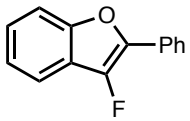
2.00 eq.), potassium fluoride (14.5 mg, 0.25 mmol, 0.50 eq.), **P3** (19.5 mg, 0.01 mmol, 2%), and TBME (5.0 mL) were combined and allowed to stir at 130 °C for 14 h. Purification of the crude reaction mixture by flash chromatography (10 → 20% EtOAc/hexanes) afforded 4-fluoro-5-phenyl-*N,N*-diethylthiophene-2-carboxamide (131 mg, 94%) as a yellow solid. Melting Point: 47 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.65 (dd, J = 9, 2 Hz, 2H), 7.41 (pt, J = 8 Hz), 7.33 (tt, J = 7 Hz, 1H), 7.11 (bs, 1H), 3.56 (bq, J = 7 Hz, 4H), 1.28 (bt, J = 7 Hz, 6H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$): δ 162.5, 152.0 (d, J = 261 Hz), 133.8 (d, J = 7 Hz,), 130.5 (d, J = 4 Hz), 129.1, 128.3 (d, J = 1 Hz), 127.2 (d, J = 5 Hz), 125.2 (d, J = 11 Hz), 119.3 (d, J = 27 Hz), ~42 (bs), ~13 (bs) ppm; ^{19}F NMR (470 MHz, $CDCl_3$): δ –127.4 ppm. IR: 2970, 2931, 2871, 1599, 1575, 1522, 1468, 1428, 1390, 1363, 1335, 1311, 1283, 1259, 1169, 1087, 1058, 1007, 981, 939, 905, 854, 829, 759, 728, 684, 641 cm^{-1}. Anal. Calcd. for $C_{15}H_{16}FNOS$: C, 64.96; H, 5.81; found: C, 64.90; H, 5.91.



21a

21a was prepared according to General Procedure F. Thus, **21a-Br** (149 mg, 0.50 mmol, 1.00 eq.), silver fluoride (127 mg, 1.00 mmol, 2.00 eq.), potassium fluoride (14.5 mg, 0.25 mmol, 0.50 eq.), **P3** (19.5 mg, 0.01 mmol, 2%), and TBME (5.0 mL) were combined and allowed to stir at 130 °C for 14 h. Purification of the crude reaction mixture by flash chromatography (2 → 4% Et_2O/hexanes) afforded methyl 5-fluoro-4-phenylthiophene-2-carboxylate (115 mg, 97%) as a pale yellow solid contaminated with 4% of the corresponding reduction product **21a-H** (confirmed by ^{1}H NMR and GC/MS analysis), which could not be readily separated from the desired product by flash chromatography. Melting Point: 57 °C. ^{1}H NMR (500

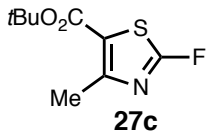
MHz, $CDCl_3$): δ 7.80 (d, J = 5 Hz), 7.59 (dd, J = 8, 1 Hz, 2H), 7.44 (pt, J = 8 Hz, 2H), 7.34 (tt, J = 8, 2 Hz, 1H), 3.90 (s, 3H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$): δ 164.4 (d, J = 298 Hz), 162.4, 131.7 (d, J = 2 Hz), 131.4 (d, J = 4 Hz), 129.0, 128.0 (d, J = 1 Hz), 127.4 (d, J = 4 Hz), 123.6 (d, J = 5 Hz), 120.2 (d, J = 4 Hz), 52.5 ppm; ^{19}F NMR (470 MHz, $CDCl_3$): δ –123.4 ppm. IR: 3063, 2954, 1711, 1603, 1585, 1569, 1469, 1443, 1374, 1257, 1127, 1073, 956, 892, 870, 764, 743, 725, 689, 613 cm^{-1}. HRMS (ESI) m/z calcd. for $C_{12}H_{10}FO_2S$ ($M+H^+$): 237.0380; found: 237.0389.



22b

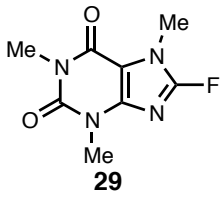
22b was prepared according to General Procedure F. Thus, **22b-Br** (137 mg, 0.50 mmol, 1.00 eq.), silver fluoride (127 mg, 1.00 mmol, 2.00 eq.), potassium fluoride (14.5 mg, 0.25 mmol, 0.50 eq.), **P3** (19.5 mg, 0.01 mmol, 2%), and TBME (5.0 mL) were combined and allowed to stir at 130 °C for 14 h. Purification of the crude reaction mixture by flash chromatography (hexanes) afforded 3-fluoro-2-phenylbenzo[b]furan (93 mg, 88%) as a white solid. Melting Point: 61 °C. ^1H NMR (500 MHz, $CDCl_3$): δ 7.93 (d, J = 9 Hz, 2H), 7.62 (d, J = 9 Hz, 1H), 7.46-7.52 (m, 3H), 7.25-7.38 (m, 3H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$): δ 151.3 (d, J = 9 Hz), 144.7 (d, J = 256 Hz), 138.2 (d, J = 20 Hz), 128.9, 128.8 (d, J = 5 Hz), 128.3 (d, J = 2 Hz), 125.5 (d, J = 1 Hz), 124.9 (d, J = 6 Hz), 123.123.4, 120.8 (d, J = 19 Hz), 117.8 (d, J = 3 HZ), 111.9 (d, J = 2 Hz) ppm; ^{19}F NMR (470 MHz, $CDCl_3$): δ –170.4 ppm. IR: 3063, 1631, 1497, 1454, 1443, 1390, 1258, 1210, 1136, 1112, 1073, 1028, 1007, 913, 895, 830,

768, 743, 688, 654, 615 cm^{-1}. Anal. Calcd. for $C_{14}H_9FO$: C, 79.23; H, 4.27; found: C, 79.17; H, 4.35.



27c

27c was prepared according to General Procedure F. Thus, **27c-Br** (139 mg, 0.50 mmol, 1.00 eq.), silver fluoride (127 mg, 1.00 mmol, 2.00 eq.), potassium fluoride (14.5 mg, 0.25 mmol, 0.50 eq.), **P3** (19.5 mg, 0.01 mmol, 2%), and toluene (5.0 mL) were combined and allowed to stir at 130 °C for 14 h. Purification of the crude reaction mixture by flash chromatography (5% Et_2O/hexanes) afforded *tert*-butyl 2-fluoro-4-methylthiazole-5-carboxylate (73 mg, 67%) as a yellow oil. ^1H NMR (500 MHz, $CDCl_3$): δ 2.58 (s, 3H), 1.55 (s, 9H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$): δ 170.2 (d, J = 286 Hz), 160.8, 154.1 (d, J = 14 Hz), 120.4 (d, J = 2 Hz), 83.1, 28.3, 17.4 ppm; ^{19}F NMR (470 MHz, $CDCl_3$): δ –74.4 ppm. IR (in $CDCl_3$): 2981, 1702, 1557, 1493, 1370, 1343, 1313, 1241, 1166, 905, 728, 650 cm^{-1}. Anal. Calcd. for $C_9H_{12}FNO_2S$: C, 49.75; H, 5.57; found: C, 49.63; H, 5.62.

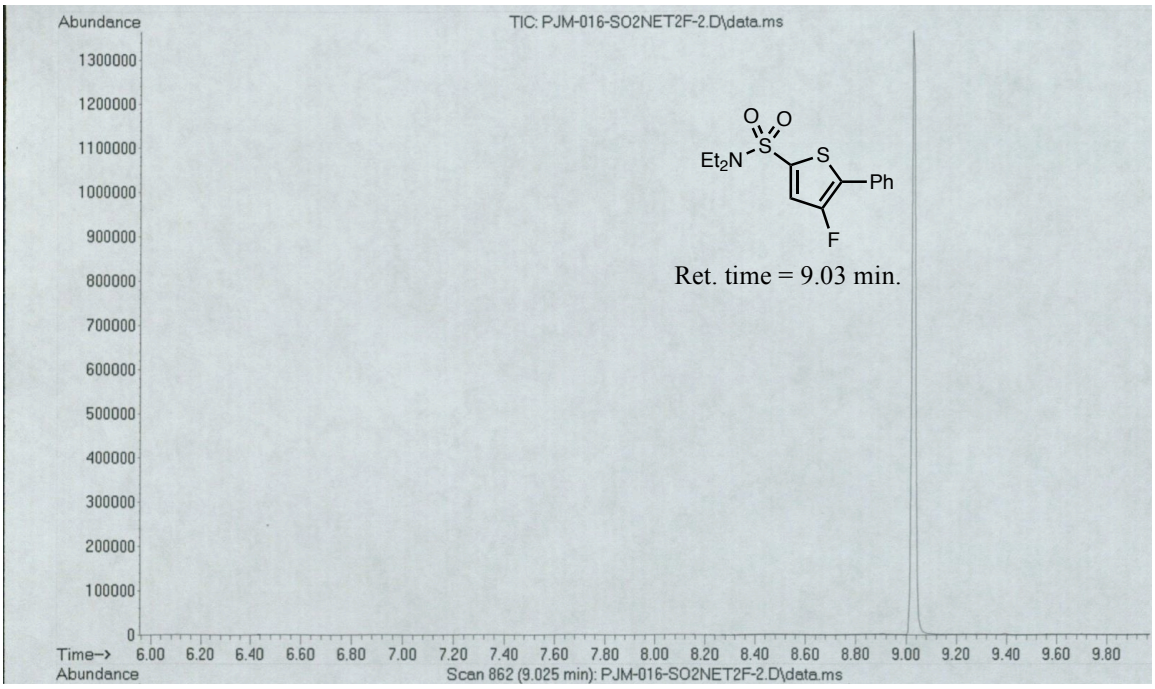


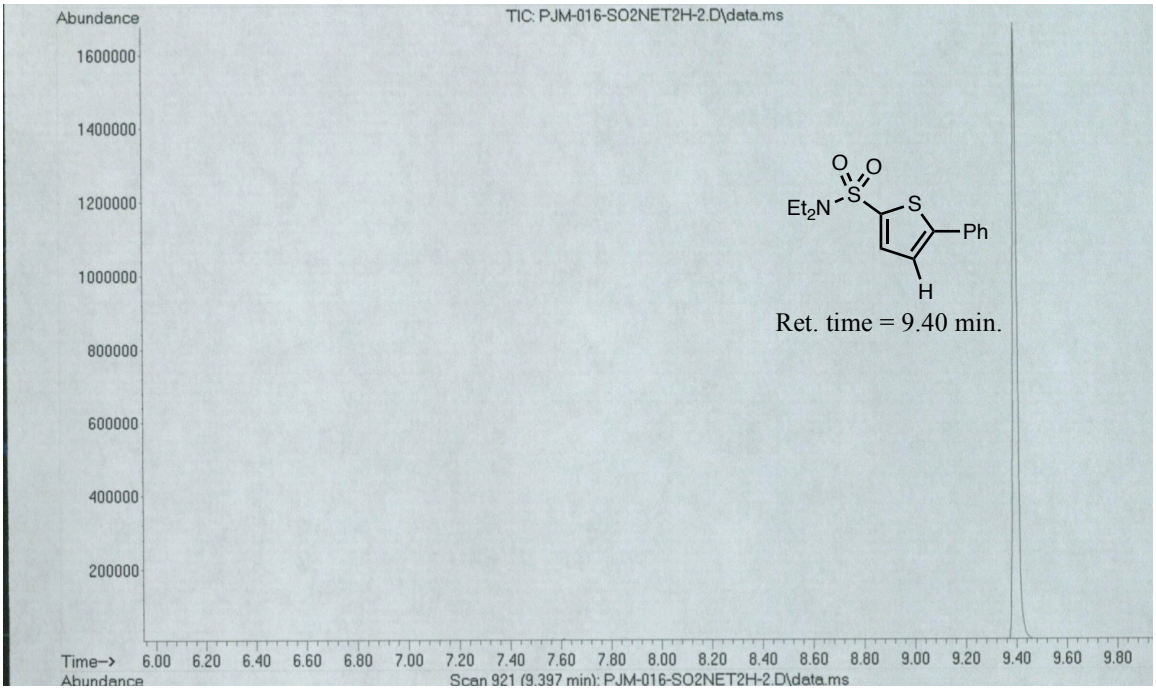
29

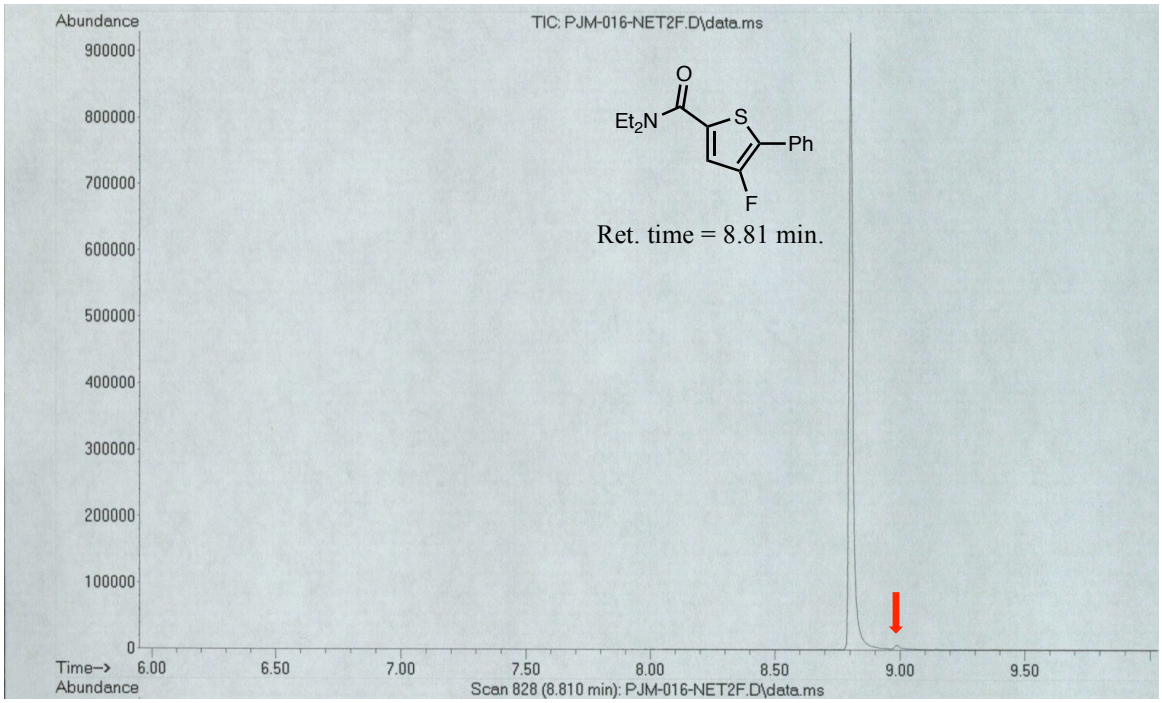
29 was prepared according to General Procedure F. Thus, 8-bromocaffeine (137 mg, 0.50 mmol, 1.00 eq.), silver fluoride (127 mg, 1.00 mmol, 2.00 eq.), potassium fluoride (14.5 mg, 0.25 mmol, 0.50 eq.), **P3** (19.5 mg, 0.01 mmol, 2%), and toluene (5.0 mL) were combined and allowed to stir at 130 °C for 14 h. Purification of the crude reaction mixture by flash chromatography (1:1 EtOAc/hexanes) afforded 8-fluorocaffeine (91 mg, 86%) as an off-white solid. Melting Point: 158-162 °C. ^1H NMR (500 MHz, $CDCl_3$): δ 3.83 (s, 3H), 3.49 (s, 3H), 3.37 (s, 3H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$): δ 154.2 (d, J = 230 Hz),

151.5, 151.3, 144.5 (d, J = 15 Hz), 103.8 (d, J = 3 Hz), 30.7, 30.0, 28.0 ppm; ^{19}F NMR (470 MHz, $CDCl_3$): δ –107.8 ppm. IR (in $CDCl_3$): 2959, 1704, 1654, 1614, 1539, 1456, 1329, 1288, 1212, 1041, 971, 821, 783, 742, 733, 666 cm^{-1}. Anal. Calcd. for $C_8H_9FN_4O_2$: C, 45.28; H, 4.28; found: C, 45.58; H, 4.18.

Determination of reduction product content in isolated products.



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Et2N
S
Ph
F
Ret. time = 8.81 min.
Time-->
6.00
6.50
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9.50
Abundance
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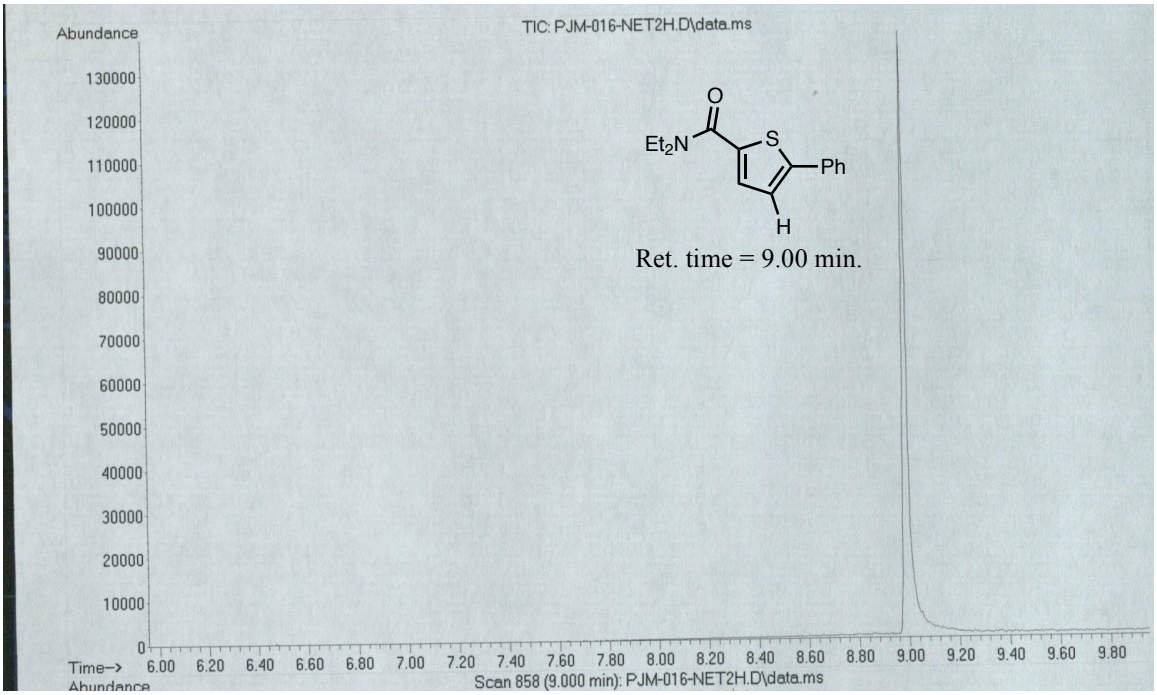
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S
Ph
H
Ret. time = 9.00 min.
Time-->
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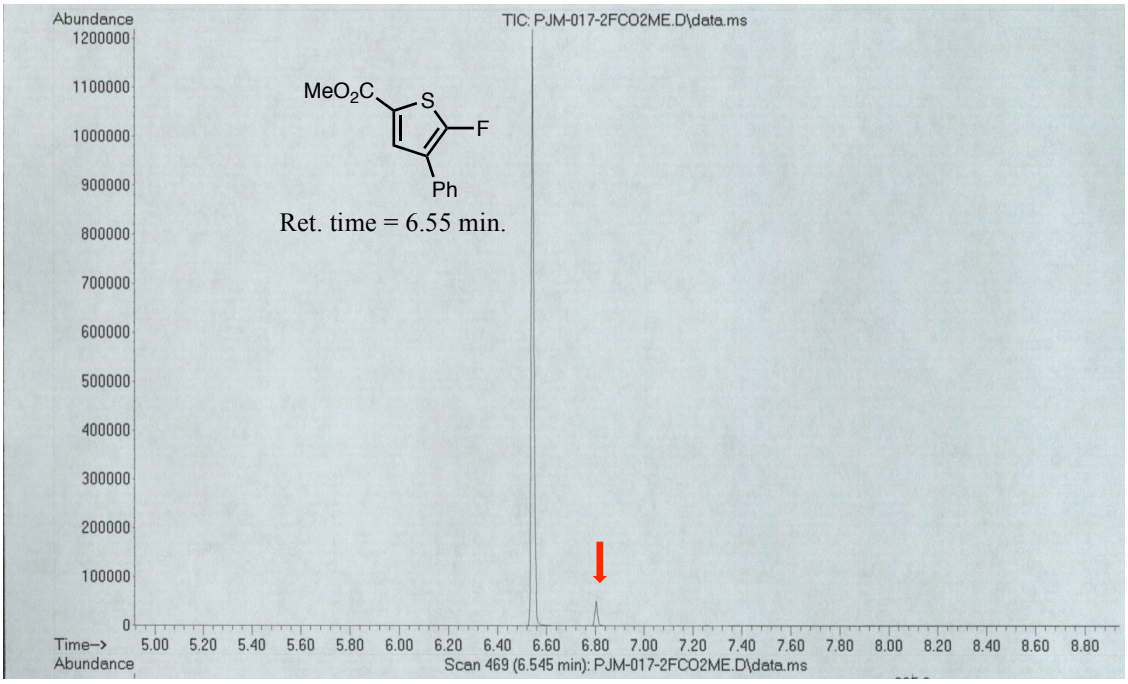
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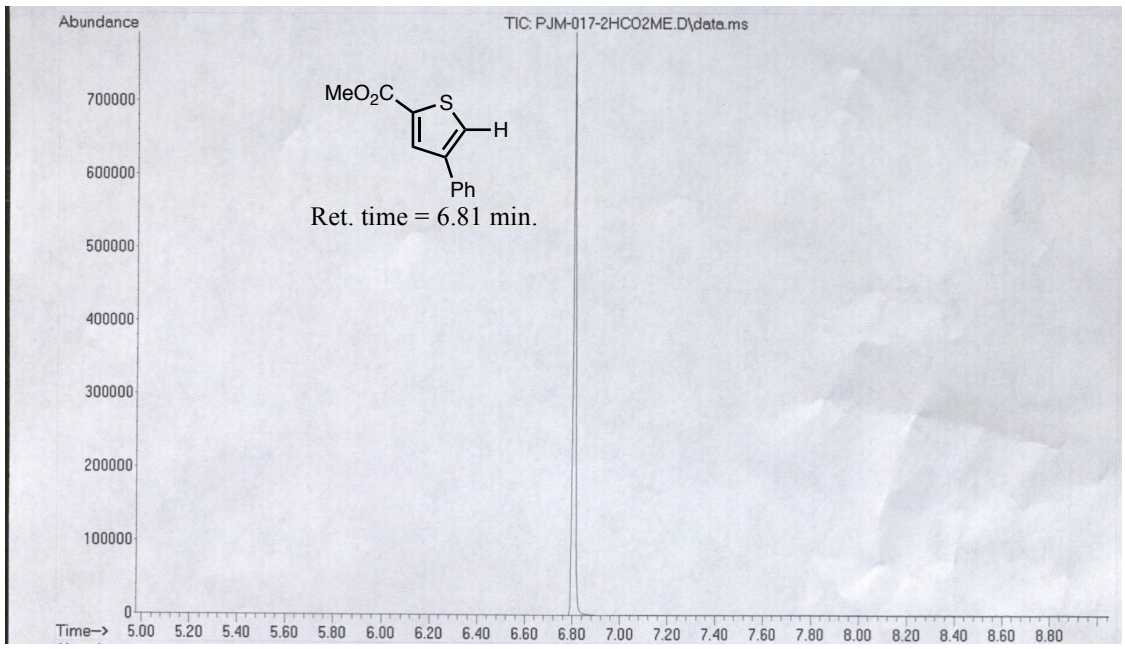
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100000
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Time-->
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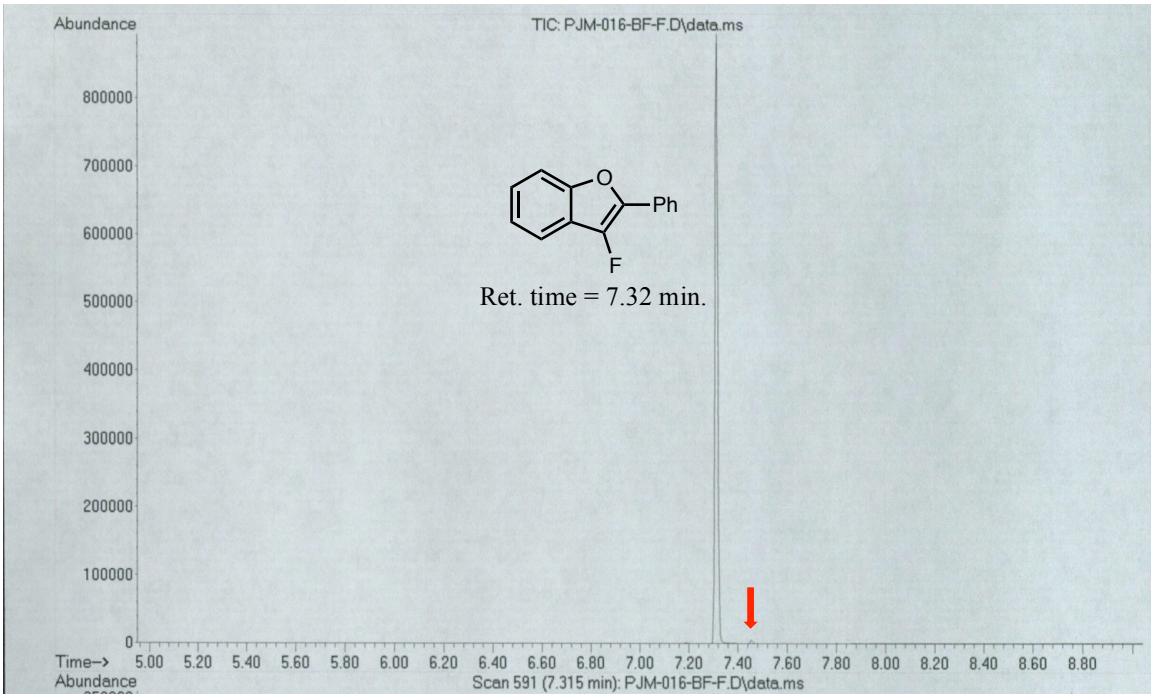
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F
Ret. time = 7.32 min.
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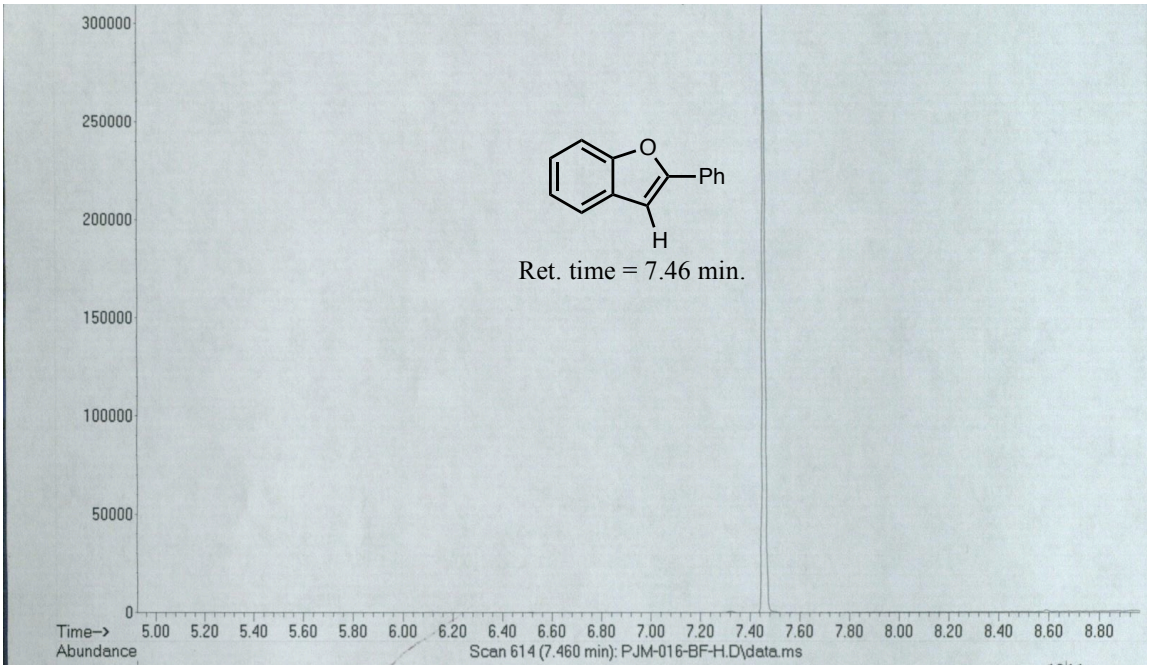
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O
Ph
H
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Time-->
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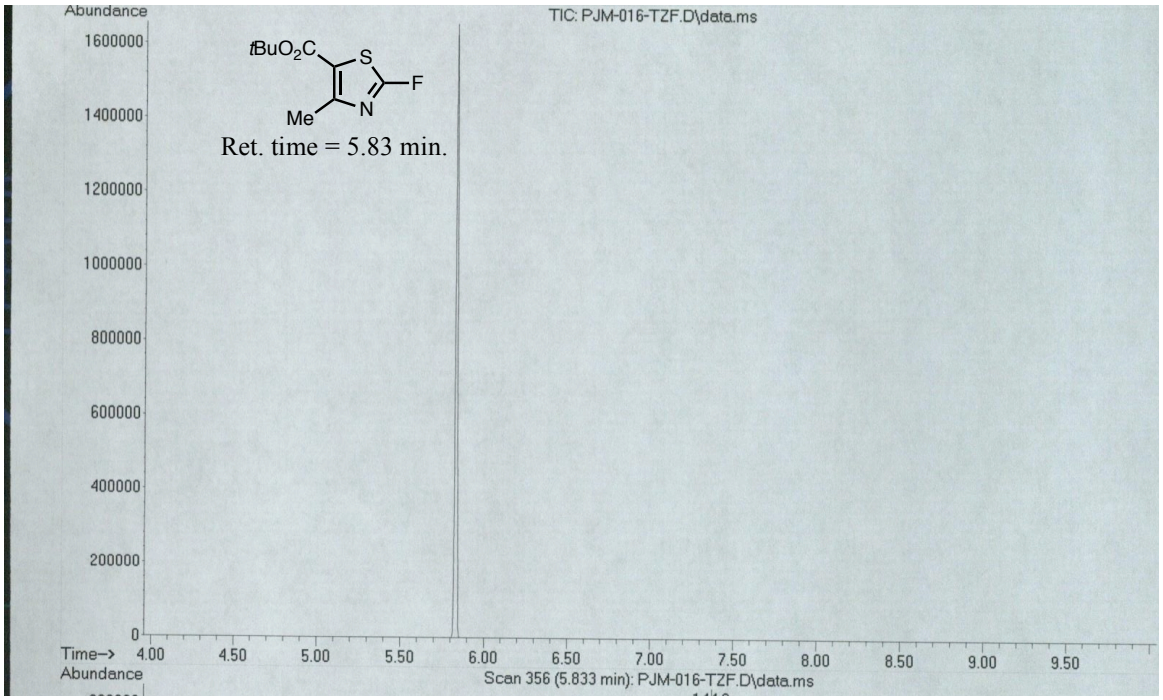
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F
N
Me
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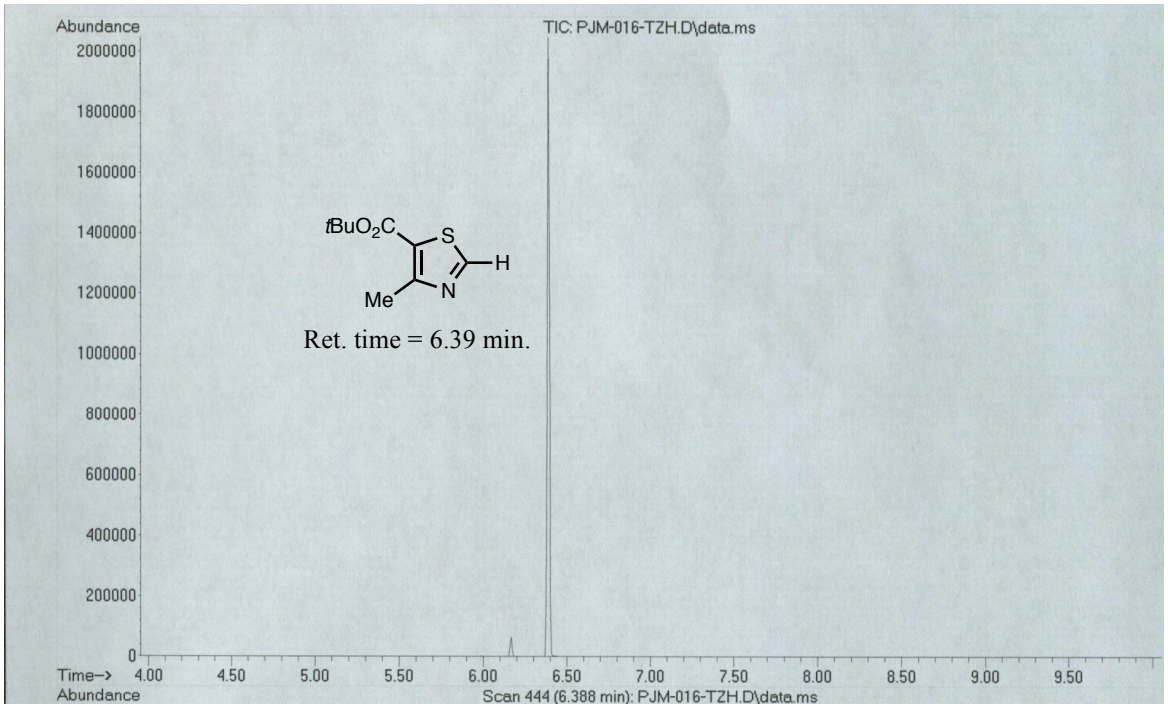
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S
H
N
Me
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Time-->
4.00
4.50
5.00
5.50
6.00
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8.00
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9.00
9.50
Abundance
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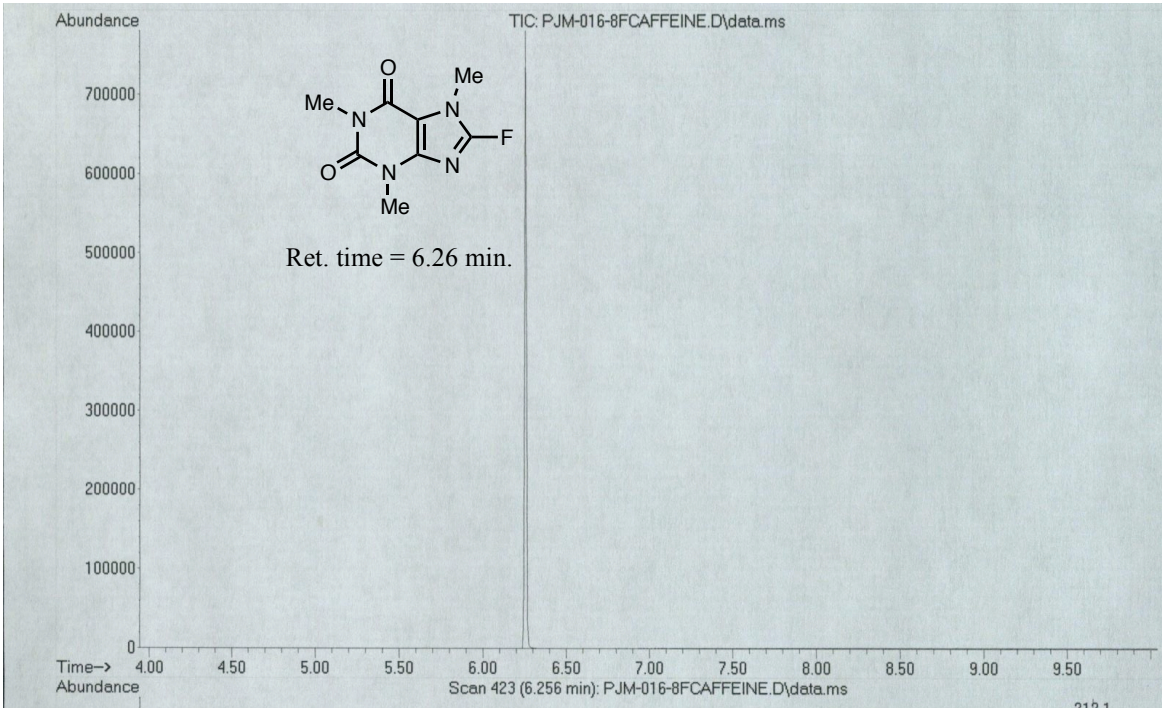

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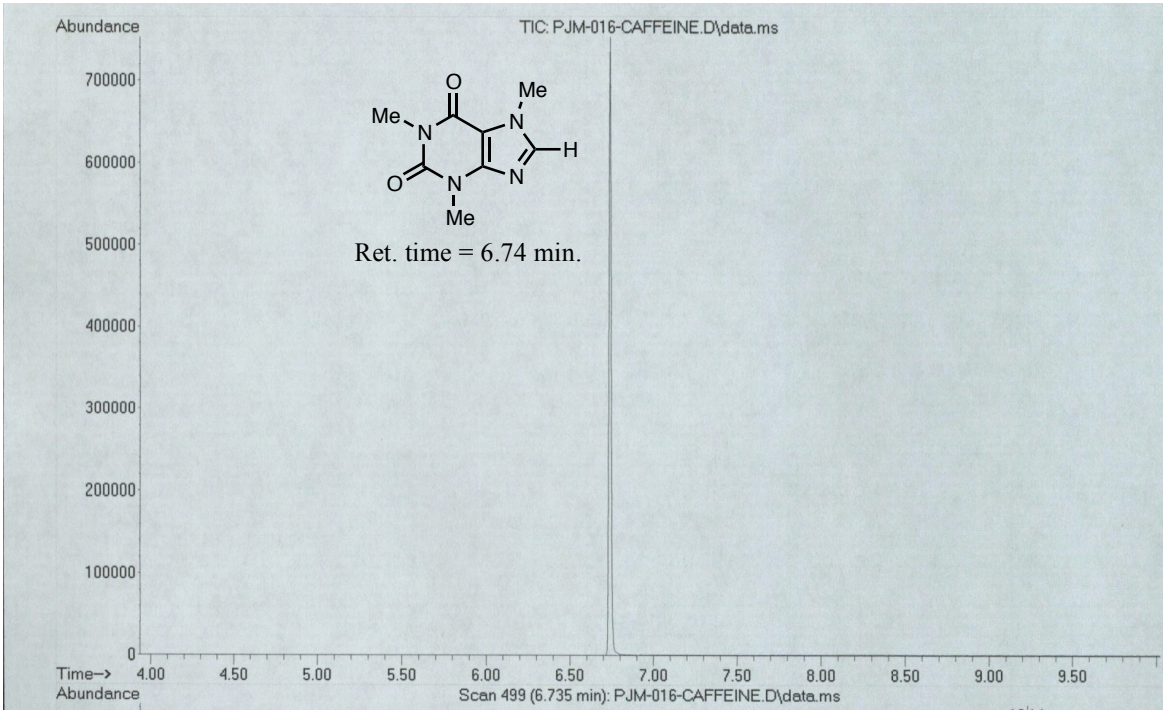
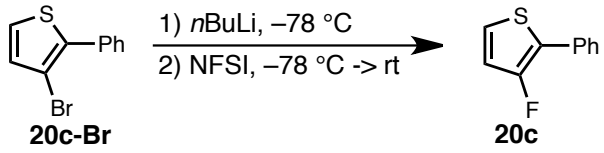


Ret. time = 6.74 min.

Preparation of authentic heteroaryl fluoride samples.

General Procedure G. Fluorination of lithiated heteroarenes.

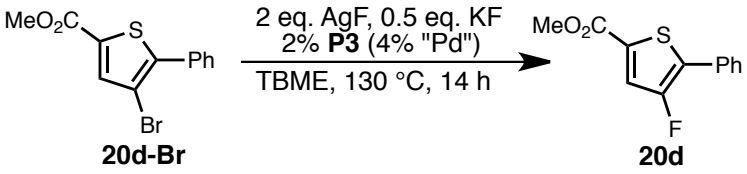
An oven-dried reaction tube equipped with a stir bar was charged with the heteroaryl bromide (0.20 mmol, 1.00 eq.) and evacuated. The tube was backfilled with argon, and anhydrous THF (1.0 mL) was added. The tube was cooled to –78 °C, and *n*BuLi (2.5 M in hexanes, 0.08 mL, 0.22 mmol, 1.10 eq.) was added dropwise. The reaction mixture was allowed to stir at –78 °C for 30 min. At this time, a separately prepared solution of N-fluorobenzenesulfonimide (NFSI) (75.8 mg, 0.24 mmol, 1.20 eq.) in anhydrous THF (0.5 mL) was added dropwise to the heteroaryllithium reagent, and the reaction mixture was allowed to warm to room temperature and stir for 1 h. The reaction mixture was quenched with saturated *aq*. $NaHCO_3$ (2 mL) and EtOAc (5 mL), and the phases were separated. The aqueous phase was further extracted with EtOAc (2 × 5 mL), and the combined organic extracts were dried over $MgSO_4$, filtered, and concentrated. Purification of the crude reaction mixtures by preparative thin layer chromatography afforded the desired heteroaryl fluoride



20c-Br **20c**

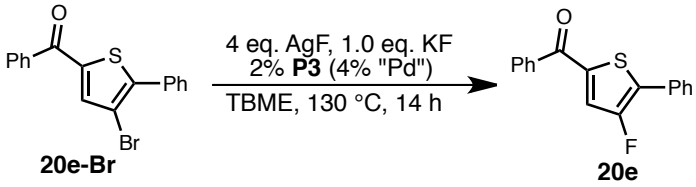
20c was prepared according to a slightly modified General Procedure G. An oven-dried reaction tube equipped with a stir bar was charged with **20c-Br** (47.8 mg, 0.20 mmol, 1.00 eq.) and evacuated. The tube was backfilled with argon, and anhydrous Et_2O (1.0 mL) was added. The tube was cooled to –78 °C, and *n*BuLi (2.5 M in hexanes, 0.08 mL, 0.22 mmol, 1.10 eq.) was added dropwise. The reaction mixture was allowed to stir at –78 °C for 30 min. At this

time, a separately prepared solution of N-fluorobenzenesulfonimide (NFSI) (75.8 mg, 0.24 mmol, 1.20 eq.) in anhydrous THF (0.5 mL) was added dropwise to the heteroaryllithium reagent, and the reaction mixture was allowed to stir for at –78 °C for 2 h (allowing the reaction to warm to room temperature led to a complex mixture of products). The reaction mixture was quenched with saturated *aq*. $NaHCO_3$ (2 mL) and EtOAc (5 mL), and the phases were separated. The aqueous phase was further extracted with EtOAc (2 × 5 mL), and the combined organic extracts were dried over $MgSO_4$, filtered, and concentrated. Purification of the crude reaction mixture by preparative thin layer chromatography (pentane) afforded **20c** (24.0 mg, 67%) as a pale yellow oil. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.66 (dd, J = 8, 2 Hz, 2H), 7.41 (pt, J = 8 Hz, 2H), 7.30 (tt, J = 8, 1 Hz, 1H), 7.13 (dd, J = 6, 3 Hz, 1H), 6.89 (d, J = 6 Hz, 1H) ppm; ^{13}C NMR (150 MHz, $CDCl_3$): δ 154.1 (d, J = 259 Hz), 131.4 (d, J = 4 Hz), 129.0, 127.6, 126.9 (d, J = 5 Hz), 122.1 (d, J = 10 Hz), 121.5 (d, J = 13 Hz), 118.9 (d, J = 28 Hz) ppm; ^{19}F NMR (282 MHz, $CDCl_3$): δ –130.5 ppm. IR (in $CDCl_3$): 3062, 1557, 1494, 1448, 1395, 983, 905, 760, 730, 690, 633 cm^{-1}. GC/MS m/z calcd. for $C_{10}H_7FS$: 178.0; found: 178.0. (Note: this compound should not be placed under high vacuum due to its volatility).



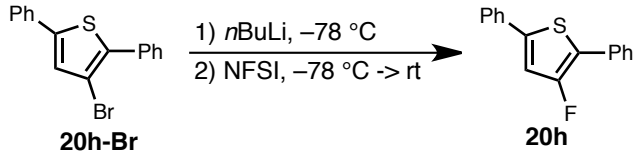
20d was prepared according to General Procedure F. Thus, silver fluoride (50.8 mg, 0.40 mmol, 2.00 eq.), potassium fluoride (5.80 mg, 0.10 mmol, 0.50 eq.), **P3** (8.00 mg, 0.004 mmol, 2%), **20d-Br** (59.4 mg, 0.20 mmol, 1.00 eq.), and TBME (1.0 mL) were combined and allowed to stir at 130 °C for 14 h. Purification of the crude reaction

mixture by preparative thin layer chromatography (5% Et_2O/pentane) afforded methyl 4-fluoro-5-phenylthiophene-2-carboxylate (16.0 mg, 34%) as a white sold. Contaminated with <5% of **20d-Br**, as judged by ^1H NMR and GC analysis. Melting Point: 45 °C. ^1H NMR (500 MHz, $CDCl_3$): δ 7.67 (dd, J = 8, 2 Hz, 2H), 7.53 (s, 1H), 7.43 (pt, J = 8 Hz, 2H), 7.36 (tt, J = 8, 2 Hz, 1H), 3.91 (s, 3H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$): δ 162.6, 153.6 (d, J = 261 Hz), 130.9 (d, J = 4 Hz), 129.8, 129.5 (d, J = 1 Hz), 128.5 (d, J = 9 Hz), 127.9 (d, J = 5 Hz), 125.5, 124.4 (d, J = 26 Hz), 53. 2 ppm; ^{19}F NMR (470 MHz, $CDCl_3$): δ –126.6 ppm. IR (in $CDCl_3$): 3097, 3000, 1713, 1576, 1561, 1461, 1434, 1400, 1287, 1246, 1166, 1069, 1006, 852, 758, 722, 687, 645 cm^{-1}. HRMS (ESI) m/z calcd. for $C_{12}H_{10}FO_2S$ ($M+H^+$): 237.0380; found: 237.0378.



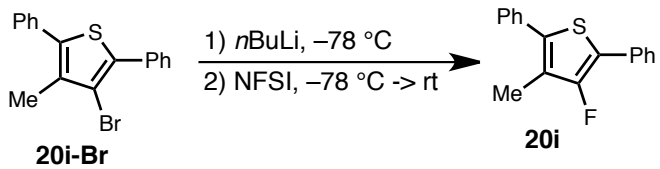
20e was prepared according to General Procedure F. Thus, silver fluoride (50.8 mg, 0.40 mmol, 2.00 eq.), potassium fluoride (5.80 mg, 0.10 mmol, 0.50 eq.), **P3** (8.00 mg, 0.004 mmol, 2%), **20e-Br** (68.6 mg, 0.20 mmol, 1.00 eq.), and TBME (1.0 mL) were combined and allowed to stir at 130 °C for 14 h. Purification of the crude reaction mixture by preparative thin layer chromatography (5% Et_2O/pentane) afforded 5-benzoyl-3-fluoro-2-phenylthiophene (41.0 mg, 73%) as a yellow sold. Melting Point: 83 °C. ^1H NMR (500 MHz, $CDCl_3$): δ 7.88 (d, J = 7 Hz, 2H), 7.73 (d, J = 8 Hz, 2H), 7.63 (pt, J = 8 Hz, 1H), 7.53 (pt, J = 8 Hz, 2H), 7.46 (pt, J = 8 Hz, 2H), 7.43 (s, 1H), 7.39 (pt, J = 7 Hz, 1H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$): δ 187.2 (d, J = 2 Hz), 153.1 (d, J = 263 Hz), 137.3, 137.1 (d, J = 6 Hz), 132.8, 130.3 (d, J = 4 Hz), 129.2, 129.2, 128.7, 127.5 (d, J = 5 Hz), 126.9

(d, J = 5 Hz), 125.1 (d, J = 26 Hz) ppm; ^{19}F NMR (470 MHz, $CDCl_3$): δ –125.8 ppm. IR (in $CDCl_3$): 3061, 1634, 1599, 1575, 1555, 1455, 1398, 1287, 1170, 1118, 1007, 906, 860, 730, 661, 647 cm^{-1}. Anal. Calcd. for $C_{17}H_{11}FOS$: C, 72.32; H, 3.93; found: C, 72.27; H, 4.01.



20h-Br **20h**

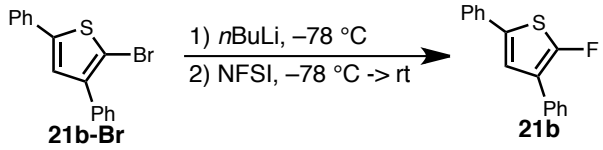
20h was prepared according to General Procedure G. Thus, **20h-Br** (63.0 mg, 0.20 mmol, 1.00 eq.), *n*BuLi (2.5 M in hexanes, 0.08 mL, 0.22 mmol, 1.10 eq.), NFSI (75.8 mg, 0.24 mmol, 1.20 eq.), and THF (1.5 mL) were combined and allowed to stir at room temperature for 1 h. Purification of the crude reaction mixture by preparative thin layer chromatography (pentane) afforded 3-fluoro-2,5-diphenylthiophene (33 mg, 65%) as a white solid. Melting Point: 96 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.68 (dd, J = 9, 2 Hz, 2H), 7.60 (dd, J = 9, 2 Hz, 2H), 7.39-7.45 (m, 4H), 7.28-7.36 (m, 2H), 7.12 (s, 1H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$): δ 153.9 (d, J = 260 Hz), 139.8 (d, J = 9 Hz), 133.6, 131.3 (d, J = 4 Hz), 129.1, 129.0, 128.4, 127.6 (d, J = 1 Hz), 126.8 (d, J = 5 Hz), 125.2, 120.8, 114.5 (d, J = 28 Hz), ppm; ^{19}F NMR (470 MHz, $CDCl_3$): δ –126.7 ppm. IR: 3053, 1596, 1573, 1562, 1487, 1466, 1449, 1395, 1331, 1307, 1184, 1074, 1011, 966, 910, 818, 754, 720, 690, 641 cm^{-1}. HRMS (ESI) m/z calcd. for $C_{16}H_{11}FS$ (M^+): 254.0560; found: 254.0579.



20i-Br **20i**

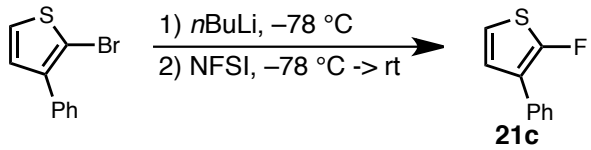
20i was prepared according to General Procedure G. Thus, **20i-Br** (50.0 mg, 0.15 mmol, 1.00 eq.),

*n*BuLi (2.5 M in hexanes, 0.06 mL, 0.17 mmol, 1.10 eq.), NFSI (58.3 mg, 0.18 mmol, 1.20 eq.), and THF (1.5 mL) were combined and allowed to stir at room temperature for 1 h. Purification of the crude reaction mixture by preparative thin layer chromatography (pentane) afforded 3-fluoro-4-methyl-2,5-diphenylthiophene (32 mg, 80%) as a white solid. Melting Point: 104-106 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.57 (dd, J = 9 Hz, 2H), 7.24-7.41 (m, 7H), 7.19 (tt, J = 8, 2 Hz, 1H), 2.17 (d, J = 1 Hz, 3H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$): δ 152.7 (d, J = 262 Hz), 134.5 (d, J = 7 Hz), 134.4 (d, J = 2 Hz), 131.6 (d, J = 4 Hz), 129.0, 128.9, 128.6, 1278.0, 127.4 (d, J = 1 Hz), 126.8 (d, J = 5 Hz), 124.2 (d, J = 24 Hz), 11.6 ppm; ^{19}F NMR (470 MHz, $CDCl_3$): δ –126.9 ppm. IR (in $CDCl_3$): 3050, 2926, 1598, 1487, 1434, 1405, 1295, 1113, 974, 902, 753, 731, 694 cm^{-1}. HRMS (ESI) m/z calcd. for $C_{17}H_{14}FS$ ($M+H^+$): 269.0795; found: 269.0803.



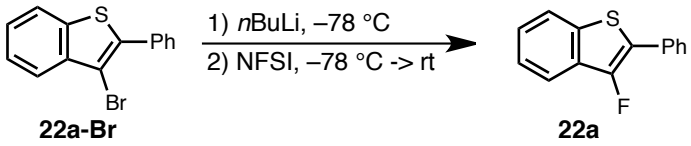
21b was prepared according to General Procedure G. Thus, **21b-Br** (63.0 mg, 0.20 mmol, 1.00 eq.), *n*BuLi (2.5 M in hexanes, 0.08 mL, 0.22 mmol, 1.10 eq.), NFSI (75.8 mg, 0.24 mmol, 1.20 eq.), and THF (1.5 mL) were combined and allowed to stir at room temperature for 1 h. Purification of the crude reaction mixture by preparative thin layer chromatography (pentane) afforded 2-fluoro-3,5-diphenylthiophene (44 mg, 86%) as a white solid. Melting Point: 94-96 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.64 (d, J = 9 Hz, 2H), 7.54 (dd, J = 7, 2 Hz, 2H), 7.44 (pt, J = 8 Hz, 2H), 7.40 (pt, J = 8 Hz, 2H), 7.29-7.35 (m, 2H), 7.21 (d, J = 4 Hz, 1H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$): δ 159.6 (d, J = 291 Hz), 133.9, 132.5 (d, J = 4 Hz), 131.0 (d, J = 3 Hz), 129.1, 128.9, 127.8 (d, J = 1 Hz), 127.5 (d, J = 1 Hz), 127.4 (d, J = 33 Hz),

125.4 (d, J = 2 Hz), 122.4 (d, J = 4 Hz), 120.1 (d, J = 1 Hz) ppm; ^{19}F NMR (470 MHz, $CDCl_3$): δ –133.1 ppm. IR (in $CDCl_3$): 3063, 1587, 1513, 1494, 1476, 1450, 1368, 1234, 1142, 905, 729, 691, 652 cm^{-1}. HRMS (ESI) m/z calcd. for $C_{16}H_{12}FS$ ($M+H^+$): 255.0638; found: 255.0631.



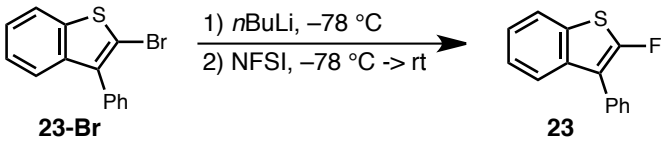
21c

21c was prepared according to a slightly modified General Procedure G. Thus, 2-bromo-3-phenylthiophene (47.8 mg, 0.20 mmol, 1.00 eq.), *n*BuLi (2.5 M in hexanes, 0.08 mL, 0.22 mmol, 1.10 eq.), NFSI (75.8 mg, 0.24 mmol, 1.20 eq.), and THF (1.5 mL) were combined and allowed to stir at –78 °C for 1 h (allowing the reaction to warm to room temperature led to a complex mixture of products). Purification of the crude reaction mixture by preparative thin layer chromatography (pentane) afforded 2-fluoro-3-phenylthiophene (19 mg, 53%) as a pale yellow oil contaminated with ~4% of a second fluorothiophene with the same mass as the desired product (likely 2-fluoro-4-phenylthiophene). ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.60 (d, J = 9 Hz, 2H), 7.43 (pt, J = 8 Hz, 2H), 7.31 (tt, J = 8, 2 Hz, 1H), 7.00 (dd, J = 7, 4 Hz, 1H), 6.70 (dd, J = 7, 4 Hz, 1H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$): δ 160.7 (d, J = 288 Hz), 132.6 (d, J = 4 Hz), 128.9, 127.4 (d, J = 4 Hz), 127.4, 124.8 (d, J = 3 Hz), 121.6 (d, J = 48 Hz), 112.6 (d, J = 3 Hz) ppm; ^{19}F NMR (470 MHz, $CDCl_3$): δ –136.2 ppm (a minor contaminant was detected at –130.4 ppm). IR (in $CDCl_3$): 3058, 1605, 1585, 1568, 1498, 1442, 1275, 1188, 1124, 907, 880, 732, 707 cm^{-1}. GC/MS M/z for $C_{10}H_7FS$: 178.0, found, 178.0. (Note: this compound should not be placed under high vacuum due to its volatility).



22a-Br **22a**

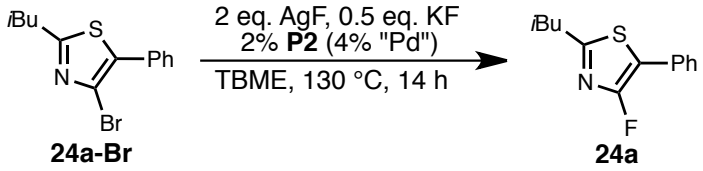
22a was prepared according to General Procedure G. Thus, **22a-Br** (57.8 mg, 0.20 mmol, 1.00 eq.), *n*BuLi (2.5 M in hexanes, 0.09 mL, 0.22 mmol, 1.10 eq.), NFSI (75.8 mg, 0.24 mmol, 1.20 eq.), and THF (1.5 mL) were combined and allowed to stir at room temperature for 1 h. Purification of the crude reaction mixture by preparative thin layer chromatography (pentane) afforded 3-fluoro-2-phenylbenzo[b]thiophene (34 mg, 75%) as a white solid. Melting Point: 94 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.74-7.80 (m, 4H), 7.34-7.49 (m, 5H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$): δ 147.6 (d, J = 264 Hz), 134.3 (d, J = 9 Hz), 131.3 (d, J = 4 Hz), 130.8 (d, J = 24 Hz), 129.1, 128.2, 127.6 (d, J = 3 Hz), 125.8, 124.9, 122.8, 120.9 (d, J = 14 Hz), 120.2 (d, J = 2 Hz) ppm; ^{19}F NMR (470 MHz, $CDCl_3$): δ –135.5 ppm. IR: 3062, 1586, 1491, 1445, 1370, 1277, 1088, 1018, 955, 850, 749, 726, 691, 595 cm^{-1}. Anal. Calcd. for $C_{14}H_9FS$: C, 73.66; H, 3.97; found: C, 73.40; H, 4.07.



23-Br **23**

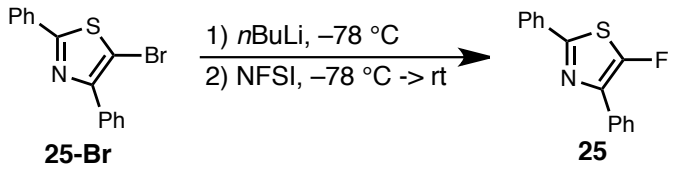
23 was prepared according to General Procedure G. Thus, **23-Br** (57.8 mg, 0.20 mmol, 1.00 eq.), *n*BuLi (2.5 M in hexanes, 0.09 mL, 0.22 mmol, 1.10 eq.), NFSI (75.8 mg, 0.24 mmol, 1.20 eq.), and THF (1.5 mL) were combined and allowed to stir at room temperature for 1 h. Purification of the crude reaction mixture by preparative thin layer chromatography (pentane) afforded 2-fluoro-3-phenylbenzo[b]thiophene (42 mg, 92%). ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.73-7.76 (m, 2H), 7.60 (d, J = 8 Hz, 2H), 7.54 (pt, J = 8 Hz, 2H), 7.35-7.47 (m, 3H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$): δ 159.8 (d, J =

290 Hz), 136. (d, J = 4 Hz), 131.2 (d, J = 42 Hz), 129.5 (d, J = 2 Hz), 128.9, 128.0, 125.8, 125.3, 124.7 (d, J = 5 Hz), 122.7, 122.7, 117.1 (d, J = 7 Hz) ppm; ^{19}F NMR (470 MHz, $CDCl_3$): δ –131.0 ppm. IR: 3058, 1605, 1586, 1492, 1460, 1443, 1435, 1351, 1207, 1149, 1020, 907, 859, 763, 748, 728, 696, 679, 640, 622 cm^{-1}. HRMS (ESI) m/z calcd. for $C_{14}H_9FS$ (M^+): 228.0404; found: 228.0403.



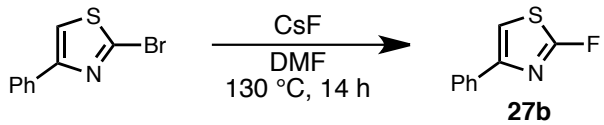
24a was prepared according to General Procedure F using **P2** in place of **P3**. Thus, silver fluoride (50.8 mg, 0.40 mmol, 2.00 eq.), potassium fluoride (5.80 mg, 0.10 mmol, 0.50 eq.), **P2** (7.40 mg, 0.004 mmol, 2%), **24a-Br** (59.2 mg, 0.20 mmol, 1.00 eq.), and TBME (1.0 mL). The tube was capped, removed from the glovebox, and placed in an oil bath that had been pre-heated to 130 °C and allowed to vigorously stir for 14 h. At this time, the tube was allowed to cool to room temperature, and the reaction mixture was diluted with EtOAc (10 mL), and filtered through a pad of celite, eluting with EtOAc (20 mL). The resulting solution was concentrated and purified by preparative thin layer chromatography (5% Et_2O/hexanes) to afford 2-*iso*-butyl-4-fluoro-5-phenylthiazole (13.0 mg, 28%) as a yellow oil. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.56 (dd, J = 9, 2 Hz, 2H), 7.40 (t, J = 8 Hz, 2H), 7.29 (tt, J = 7, 2 Hz, 1H), 2.77 (d, J = 7 Hz, 2H), 2.13 (septet, J = 7 Hz, 1H), 1.02 (d, J = 7 Hz, 6H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$): δ 164.8 (d, J = 19 Hz), 155.8 (d, J = 249 Hz), 129.5 (d, J = 6 Hz), 129.1, 127.8 (d, J = 1 Hz), 127.0 (d, J = 5 Hz), 112.2 (d, J = 26 Hz), 43.0, 29.7, 22.4 ppm; ^{19}F NMR (470 MHz, $CDCl_3$): δ –107.9 ppm.

IR (in $CDCl_3$): 2959, 1559, 1357, 1017, 907, 732, 692 cm^{-1}. HRMS (ESI) m/z calcd. for $C_{13}H_{15}FNS$ ($M+H^+$): 236.0904; found: 236.0877.



25-Br **25**

25 was prepared according to General Procedure G. Thus, **25-Br** (63.2 mg, 0.20 mmol, 1.00 eq.), *n*BuLi (2.5 M in hexanes, 0.09 mL, 0.22 mmol, 1.10 eq.), NFSI (75.8 mg, 0.24 mmol, 1.20 eq.), and THF (1.5 mL) were combined and allowed to stir at room temperature for 1 h. Purification of the crude reaction mixture by preparative thin layer chromatography (15% CH_2Cl_2/hexanes) afforded 5-fluoro-2,4-diphenylthiazole (29 mg, 57%) as a white solid. Melting Point: 78 °C (Lit. 84-85 °C).[49] ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.03 (d, J = 8 Hz, 2H), 7.89-7.93 (m, 2H), 7.44-7.51 (m, 5H), 7.37 (tt, J = 8, 1 Hz, 1H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$): δ 157.4 (d, J = 301 Hz), 154.9 (d, J = 10 Hz), 135.9 (d, J = 5 Hz), 133.7, 132.1 (d, J = 6 Hz), 130.3 (d, J = 1 Hz), 129.1, 128.8, 128.2 (d, J = 2 Hz), 127.1 (d, J = 6 Hz), 126.0 (d, J = 2 Hz) ppm; ^{19}F NMR (470 MHz, $CDCl_3$): δ –147.1 ppm. IR: 3053, 3029, 1581, 1490, 1475, 1447, 1349, 1301, 1195, 1183, 1072, 1029, 1002, 973, 911, 871, 756, 683, 658, 591 cm^{-1}. These spectra are consistent with those reported in the literature.[49]



27b

In a nitrogen-filled glovebox, an oven-dried screw-cap reaction tube equipped with a stir bar was charged with cesium fluoride (152 mg, 1.00 mmol, 5.00 eq.), 2-bromo-4-phenylthiazole (48.0 mg, 0.20 mmol, 1.00 eq.), and anhydrous DMF (2.0 mL).

The tube was capped, removed from the glovebox, and placed in an oil bath that had been pre-heated to 130 °C and allowed to stir for 14 h. The reaction tube was allowed to cool to room temperature and dilute with ether (5 mL) and water (5 mL). The phases were separated, and the aqueous phase was further extracted with ether (2 × 5 mL). The combined organic phases were washed with brine (5 mL), dried over $MgSO_4$, filtered, and concentrated. The resulting yellow solid was purified by preparative thin layer chromatography (2% Et_2O/hexanes) to afford 2-fluoro-4-phenylthiazole (**27b**, 23 mg, 64%) as a white solid. Melting Point: 65 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.80 (dd, J = 8, 2 Hz, 2H), 7.42 (t, J = 8 Hz, 2H), 7.35 (tt, J = 7, 2 Hz, 1H), 7.06 (d, J = 2 Hz) ppm; ^{13}C NMR (125 MHz, $CDCl_3$): δ 169.9 (d, J = 281 Hz), 148.4 (d, J = 15 Hz), 133.6, 128.9, 128.7, 126.0 (d, J = 1 Hz), 10.9 (d, J = 4 Hz) ppm; ^{19}F NMR (470 MHz, $CDCl_3$): δ –79.5 ppm. IR: 3096, 3063, 3034, 1540, 1525, 1480, 1445, 1323, 1301, 1235, 1197, 1064, 1025, 914, 843, 743, 688, 669, 656 cm^{-1}. HRMS (ESI) m/z calcd. for C_9H_7FNS ($M+H^+$): 180.0278; found: 180.0283.

Computational Details.

The geometries of all intermediates and transition states were optimized with B3LYP[50] in the gas phase. A basis set of 6-31G(d) for other atoms was used in geometry optimizations. Single point energy calculations were performed with the M06[51] functional and a basis set of 6-311+G(d,p). The SMD[52] solvation model was used in M06 single point energy calculations with toluene as the solvent. The reported free energies and enthalpies include zero-point energies and thermal corrections calculated at 298K by B3LYP. All calculations were performed with Gaussian 09.[53] In this study, the calculations were performed at the M06/SDD–6-311+G(d,p)/SMD(THF)//B3LYP/SDD–6-31G(d) level. A similar level of theory has been used for recent computational studies on transition metal-catalyzed reactions.[54]

The Cartesian coordinates (Å), SCF energies, and enthalpies at 298K for the optimized structures.

16-GS

B3LYP SCF energy:	-3297.2346885500 a.u.
B3LYP enthalpy:	-3295.981899 a.u.
B3LYP free energy:	-3296.146654 a.u.
M06 SCF energy in solution:	-3296.1192216900 a.u.

Cartesian coordinates

ATOM	X	Y	Z
Pd	-0.582335	-0.141863	-1.111913
P	-2.461439	0.203040	0.284015
C	-4.156259	-0.269337	-0.577820
C	-4.398517	-1.796257	-0.436779
H	-3.524473	-2.345004	-0.800204
H	-4.543094	-2.066701	0.613274
C	-5.642232	-2.234701	-1.245336
H	-5.775739	-3.317191	-1.114878
C	-5.439297	-1.910475	-2.737545
H	-6.313608	-2.236400	-3.317988
H	-4.571492	-2.457695	-3.129902
C	-5.226124	-0.393665	-2.895712

H	-5.055371	-0.149864	-3.952687
C	-3.980697	0.033964	-2.089011
H	-3.102978	-0.504227	-2.458833
H	-3.782383	1.098803	-2.249411
C	-5.427059	0.472623	-0.082989
H	-5.592184	0.271638	0.975384
H	-5.312916	1.554047	-0.197548
C	-6.669786	0.026030	-0.890453
H	-7.543410	0.569253	-0.504782
C	-6.884134	-1.489770	-0.720770
H	-7.780052	-1.810670	-1.270158
H	-7.053773	-1.733043	0.337787
C	-6.467601	0.357479	-2.380411
H	-6.338292	1.440601	-2.513212
H	-7.355815	0.067866	-2.958963
C	-2.544206	1.987445	1.041231
C	-2.880327	2.990088	-0.099708
H	-2.197518	2.849505	-0.940290
H	-3.893634	2.820258	-0.477292
C	-2.780096	4.446344	0.408927
H	-3.023610	5.119213	-0.423680
C	-1.346841	4.726526	0.899370
H	-0.637606	4.595524	0.072757
H	-1.259254	5.767716	1.240084
C	-1.010196	3.762721	2.053274
H	0.017465	3.939496	2.397792
C	-1.116296	2.302396	1.559709
H	-0.871851	1.624332	2.385842
H	-0.382752	2.124103	0.768940
C	-3.519555	2.230493	2.223638
H	-4.551099	2.015421	1.935192
H	-3.271448	1.562990	3.054124
C	-3.424946	3.696265	2.714142
H	-4.139350	3.828241	3.538575
C	-3.774537	4.660566	1.564897
H	-4.802923	4.483141	1.219304
H	-3.731247	5.700411	1.917741
C	-1.997346	3.984671	3.213968
H	-1.924716	5.016521	3.584703
H	-1.749594	3.322668	4.055824
C	-2.199289	-1.019146	1.699392
C	-3.167956	-1.241463	2.718455
C	-2.962693	-2.153178	3.757470
H	-3.712406	-2.293873	4.526033
C	-1.795349	-2.908276	3.785886
H	-1.636964	-3.631189	4.581431

C	-0.848151	-2.745191	2.787477
H	0.050688	-3.351929	2.791976
C	-1.019767	-1.806837	1.750297
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C	-5.310680	-0.653496	3.639925
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H	-4.908879	-0.342874	4.612229
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C	1.355548	-1.139781	1.065511
C	2.495443	-1.399703	0.278946
C	2.463717	-2.368509	-0.752383
C	1.291954	-3.088763	-0.949003
H	1.280531	-3.856550	-1.715059
C	0.118459	-2.837565	-0.242653
C	1.403681	-0.263671	2.329897
H	0.361662	-0.100404	2.612461
C	2.034927	1.140720	2.208630
H	3.120383	1.116925	2.329695
H	1.638473	1.776515	3.009214
H	1.807517	1.617967	1.253065
C	2.057283	-1.015660	3.512760
H	1.513499	-1.930112	3.763726
H	2.058331	-0.373654	4.402434
H	3.091387	-1.293489	3.295404
C	3.671310	-2.679095	-1.631357
H	4.409810	-1.885721	-1.484098
C	3.314736	-2.682021	-3.130366
H	2.698230	-3.548279	-3.399370
H	4.231642	-2.737367	-3.729757
H	2.758492	-1.778953	-3.395147
C	4.334294	-4.005829	-1.204821
H	4.641427	-3.979865	-0.154192
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H	3.644213	-4.848816	-1.333558
C	-1.082908	-3.743258	-0.509816
H	-1.936167	-3.352615	0.050092
C	-1.469735	-3.774035	-2.001534
H	-1.602594	-2.762412	-2.398964
H	-2.402174	-4.335218	-2.139549
H	-0.699768	-4.263189	-2.608510
C	-0.823301	-5.172706	0.009843
H	0.030716	-5.631937	-0.501173
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H	-0.613841	-5.176508	1.084650
C	3.785885	-0.661760	0.485101

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F	4.680087	-2.380254	1.860072
C	6.059475	-0.541314	1.366577
F	7.019528	-1.121352	2.114703
C	6.307826	0.684163	0.749665
C	7.635154	1.394797	0.866968
H	8.155418	1.029790	1.758135
H	7.451617	2.465888	1.013301
C	8.534730	1.203515	-0.371697
H	8.000881	1.566687	-1.259523
H	8.710000	0.130343	-0.527752
C	9.877842	1.932452	-0.243847
H	9.693692	3.003247	-0.076818
H	10.404341	1.569571	0.650335
C	10.773880	1.753548	-1.474060
H	11.006086	0.695250	-1.645205
H	11.723299	2.288233	-1.356736
H	10.285028	2.135595	-2.378562
C	5.262166	1.212687	-0.009097
F	5.437073	2.395814	-0.631221
C	4.039244	0.562944	-0.142591
F	3.083178	1.153900	-0.873814
C	-0.707579	1.431471	-2.367420
C	-1.341522	1.368487	-3.613026
H	-1.905864	0.488991	-3.902670
C	-1.230894	2.425629	-4.524483
H	-1.733333	2.353590	-5.486981
C	-0.469923	3.552935	-4.214427
C	0.201193	3.603530	-2.991599
H	0.826295	4.459176	-2.744729
C	0.091578	2.547410	-2.080106
H	0.656471	2.596750	-1.154358
H	-0.383536	4.371572	-4.924435
F	0.925164	-0.579927	-2.326222

16-TS

B3LYP SCF energy:	-3297.1982057900 a.u.
B3LYP enthalpy:	-3295.947596 a.u.
B3LYP free energy:	-3296.112061 a.u.
M06 SCF energy in solution:	-3296.0840389700 a.u.

Cartesian coordinates

ATOM	X	Y	Z
Pd	-0.768155	-0.443773	1.111742
P	-2.327250	0.342448	-0.413266

C	-1.971227	-0.584226	-2.028230
C	-2.802228	-0.460906	-3.176677
C	-2.575383	-1.184641	-4.351057
H	-3.224621	-1.064191	-5.209338
C	-1.519929	-2.087348	-4.404439
H	-1.348205	-2.668695	-5.306235
C	-0.695500	-2.244579	-3.300967
C	-0.884079	-1.500083	-2.119651
O	-3.864788	0.387844	-3.069779
C	-4.686254	0.628335	-4.202364
H	-4.106321	1.036167	-5.039563
H	-5.423742	1.366097	-3.881469
H	-5.204547	-0.282667	-4.527125
C	0.141504	-1.825296	-1.046570
C	-0.090803	-2.953291	-0.213347
C	0.932287	-3.385294	0.630921
C	2.171376	-2.755316	0.705694
C	2.426735	-1.678642	-0.174535
C	1.441684	-1.226493	-1.084052
C	-1.379763	-3.772636	-0.262200
H	-2.117507	-3.206327	-0.835993
C	-1.974810	-4.029380	1.135596
H	-1.346432	-4.703043	1.729443
H	-2.961647	-4.499767	1.046127
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H	-0.800537	-4.940786	-2.027871
H	-2.086627	-5.679128	-1.056156
H	-0.407754	-5.723213	-0.487743
C	3.215443	-3.289474	1.684460
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H	2.147620	-2.600945	3.464774
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H	1.928276	-4.326735	3.134202
C	1.742182	-0.195511	-2.188129
H	0.767561	0.121283	-2.566406
C	2.479038	1.102098	-1.788105
H	2.158785	1.481552	-0.815348
H	2.263583	1.873603	-2.537136
H	3.564041	0.974159	-1.767543
C	2.477371	-0.849680	-3.380825

H	3.445587	-1.260287	-3.083813
H	2.651647	-0.101214	-4.163882
H	1.893151	-1.662242	-3.820544
C	-0.609309	0.512116	3.023422
C	0.158934	1.690353	3.049965
H	1.008950	1.797196	2.385547
C	-0.187575	2.707037	3.940883
H	0.393227	3.626994	3.938334
C	-1.246067	2.548736	4.841794
C	-1.943938	1.335694	4.858806
H	-2.747030	1.179630	5.576090
C	-1.617097	0.303231	3.980184
H	-2.141169	-0.645635	4.020459
H	-1.501235	3.341569	5.538746
F	0.383219	-0.849468	2.848849
H	0.747507	-4.241096	1.271358
C	-4.171683	-0.048399	0.099559
C	-4.542644	-1.475302	-0.383709
C	-5.274128	0.932817	-0.381529
C	-4.189809	-0.060553	1.654774
H	-4.555314	-1.515631	-1.477528
H	-3.788337	-2.190886	-0.039920
C	-5.928706	-1.897464	0.156089
C	-6.660553	0.503853	0.155732
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H	-5.302383	0.963511	-1.470723
H	-3.427525	-0.757145	2.018068
H	-3.916064	0.922664	2.053272
C	-5.576506	-0.474634	2.193254
H	-6.152511	-2.908567	-0.210594
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C	-6.647740	0.513272	1.695505
H	-5.541062	-0.463404	3.290847
H	-7.032230	-0.922272	-1.449768
H	-7.993482	-1.215161	0.002529
H	-5.171682	-2.611541	2.070381
H	-6.892015	-2.211680	2.085391
H	-7.636165	0.234125	2.086784
H	-6.431360	1.525081	2.065788
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C	-2.832916	2.894115	-1.911250
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H	-2.545935	2.406486	-2.848013
H	-3.914764	2.777312	-1.807813
H	0.000614	1.961493	-0.160555
H	-0.277260	1.929231	-1.901718
C	-0.206609	3.931991	-1.070094
H	-2.382824	4.971338	1.421587
C	-2.880946	5.110627	-0.690873
C	-0.589122	4.640820	0.242867
H	-3.046730	4.835516	-2.839970
C	-0.975018	4.569942	-2.242530
H	0.874665	4.022146	-1.240185
H	-3.962978	5.018805	-0.520117
H	-2.659528	6.184879	-0.762206
H	-0.031982	4.208991	1.084111
H	-0.322724	5.705877	0.189468
H	-0.719907	5.635285	-2.330731
H	-0.688380	4.091803	-3.190017
C	3.779657	-1.034855	-0.090100
C	4.017306	0.049895	0.759329
C	4.890188	-1.526294	-0.776559
C	5.279482	0.617191	0.892005
C	6.153883	-0.954107	-0.648382
C	6.387684	0.130848	0.195936
C	7.751405	0.762728	0.341526
H	8.511967	0.036633	0.037450
H	7.924013	0.989382	1.400309
C	7.914009	2.056637	-0.482719
H	7.728798	1.835190	-1.542675
H	7.144653	2.776128	-0.173049
C	9.303075	2.686074	-0.321861
H	10.068517	1.958998	-0.628067
H	9.485374	2.891936	0.742380
C	9.471915	3.977649	-1.129076
H	10.472345	4.404029	-0.993743
H	9.328916	3.796862	-2.201541
H	8.741666	4.735810	-0.820722
F	3.001157	0.585643	1.459660
F	5.433644	1.668828	1.720856
F	7.172466	-1.484184	-1.353934
F	4.755584	-2.589003	-1.597595
H	0.120877	-2.957528	-3.337073

17-GS

B3LYP SCF energy:	-3617.9916779800 a.u.
B3LYP enthalpy:	-3616.772560 a.u.
B3LYP free energy:	-3616.937592 a.u.
M06 SCF energy in solution:	-3616.9200301900 a.u.

Cartesian coordinates

ATOM	X	Y	Z
Pd	-0.623171	-0.197469	-1.106670
P	-2.509858	0.189810	0.263052
C	-4.192407	-0.420072	-0.533228
C	-4.362873	-1.940497	-0.274647
H	-3.477152	-2.476061	-0.626638
H	-4.464116	-2.140292	0.796351
C	-5.605280	-2.490310	-1.014214
H	-5.687678	-3.564551	-0.800234
C	-5.448335	-2.270722	-2.530897
H	-6.319842	-2.675009	-3.064252
H	-4.566236	-2.809288	-2.902696
C	-5.304884	-0.762367	-2.807034
H	-5.168462	-0.592988	-3.883383
C	-4.062594	-0.218930	-2.066446
H	-3.165968	-0.736836	-2.423421
H	-3.924155	0.840416	-2.303342
C	-5.484078	0.302336	-0.062578
H	-5.617442	0.174076	1.011245
H	-5.421362	1.375974	-0.260072
C	-6.722906	-0.255361	-0.803933
H	-7.610634	0.278466	-0.437919
C	-6.867339	-1.761336	-0.516904
H	-7.759094	-2.160381	-1.019869
H	-7.004830	-1.931086	0.560468
C	-6.567227	-0.027880	-2.318884
H	-6.488965	1.046743	-2.534146
H	-7.453889	-0.398028	-2.852125
C	-2.643763	2.026313	0.870233
C	-3.057936	2.924625	-0.329983
H	-2.395787	2.747607	-1.180101
H	-4.073652	2.684572	-0.659351
C	-3.011181	4.417784	0.069089
H	-3.309598	5.014606	-0.802785
C	-1.580966	4.800223	0.494307
H	-0.886485	4.641662	-0.339037
H	-1.537813	5.866049	0.759266
C	-1.168636	3.938651	1.702600
H	-0.141035	4.184742	2.001240

C	-1.217006	2.442968	1.314959
H	-0.913318	1.837997	2.177439
H	-0.501336	2.247722	0.511103
C	-3.595341	2.311611	2.062866
H	-4.622614	2.026401	1.824186
H	-3.288818	1.722804	2.932670
C	-3.558129	3.812825	2.441237
H	-4.255640	3.972495	3.275238
C	-3.984798	4.670729	1.235070
H	-5.012042	4.419016	0.934933
H	-3.983407	5.734889	1.509193
C	-2.132518	4.200438	2.874349
H	-2.097667	5.258989	3.167183
H	-1.831926	3.614527	3.754746
C	-2.175010	-0.906570	1.758939
C	-3.110135	-1.090520	2.815793
C	-2.840328	-1.911595	3.913848
H	-3.564740	-2.024778	4.710716
C	-1.640465	-2.612974	3.966927
H	-1.432061	-3.266225	4.809751
C	-0.724724	-2.487350	2.933972
C	-0.962884	-1.638644	1.834918
O	-4.306625	-0.450727	2.689754
C	-5.250289	-0.514050	3.749532
H	-5.599824	-1.540304	3.917095
H	-6.091357	0.105527	3.433861
H	-4.833371	-0.112803	4.681390
C	0.152050	-1.674528	0.802804
C	1.377390	-0.953617	1.055754
C	2.520560	-1.262933	0.294781
C	2.496953	-2.306985	-0.662276
C	1.337437	-3.059531	-0.798787
H	1.337906	-3.883689	-1.503655
C	0.165040	-2.779615	-0.102960
C	1.405868	0.046793	2.223851
H	0.360496	0.209667	2.493955
C	1.993786	1.445829	1.935625
H	3.080542	1.465236	2.045524
H	1.586331	2.158388	2.662537
H	1.744746	1.802397	0.933625
C	2.082538	-0.549958	3.479406
H	1.565023	-1.445894	3.832246
H	2.063620	0.187932	4.290927
H	3.124601	-0.819466	3.293548
C	3.706110	-2.667286	-1.519367
H	4.438836	-1.860555	-1.428278

C	3.345437	-2.774658	-3.013677
H	2.728927	-3.657755	-3.220709
H	4.260533	-2.869235	-3.610711
H	2.787719	-1.892610	-3.339743
C	4.379001	-3.956965	-1.003932
H	4.681953	-3.858930	0.043782
H	5.270215	-4.187389	-1.600033
H	3.697047	-4.812903	-1.078694
C	-1.012844	-3.735490	-0.280043
H	-1.868867	-3.324167	0.259532
C	-1.414312	-3.896089	-1.759452
H	-1.572973	-2.923575	-2.237167
H	-2.335628	-4.485921	-1.840204
H	-0.640414	-4.417850	-2.333342
C	-0.707931	-5.110908	0.349638
H	0.154711	-5.585927	-0.131377
H	-1.568369	-5.780985	0.233022
H	-0.490972	-5.023073	1.419378
C	3.813871	-0.517586	0.455655
C	4.846287	-0.998962	1.263059
C	6.073657	-0.350743	1.360911
C	6.348506	0.815166	0.647149
C	7.688341	1.505502	0.734058
H	8.081466	1.392266	1.750491
H	7.547629	2.576870	0.556248
C	8.715901	0.950476	-0.273767
H	8.312797	1.054489	-1.290151
H	8.845301	-0.125717	-0.096171
C	10.074778	1.655554	-0.182658
H	9.936117	2.732649	-0.352789
H	10.467145	1.555352	0.839338
C	11.099963	1.107335	-1.180899
H	11.282298	0.038529	-1.014777
H	12.060554	1.627292	-1.091732
H	10.750428	1.227025	-2.213646
C	5.325630	1.287231	-0.176389
C	4.094865	0.642705	-0.273565
F	0.914894	-0.644574	-2.265795
C	-0.884812	1.253006	-2.469589
C	-1.558703	1.306376	-3.665308
S	0.223150	2.607431	-2.365622
C	-1.230855	2.447998	-4.469424
H	-2.258111	0.547328	-3.993629
C	-0.290757	3.255874	-3.895899
H	-1.683009	2.645938	-5.436787
H	0.130459	4.177791	-4.275624

F	7.019447	-0.873775	2.167867
F	4.665719	-2.128833	1.980570
F	5.524891	2.405427	-0.900758
F	3.162809	1.173737	-1.074896
H	0.199385	-3.054499	2.958898

17-TS

B3LYP SCF energy:	-3617.9450359000 a.u.
B3LYP enthalpy:	-3616.728479 a.u.
B3LYP free energy:	-3616.892622 a.u.
M06 SCF energy in solution:	-3616.8733755600 a.u.

Cartesian coordinates

ATOM	X	Y	Z
Pd	0.758086	-0.470790	-1.078329
P	2.353093	0.358529	0.390899
C	2.017675	-0.541448	2.021718
C	2.862563	-0.403485	3.157798
C	2.641226	-1.103586	4.347405
H	3.299516	-0.972858	5.197301
C	1.578747	-1.996398	4.427113
H	1.410699	-2.558751	5.341542
C	0.743298	-2.169934	3.334057
C	0.927339	-1.449802	2.137349
O	3.930703	0.433543	3.021579
C	4.766173	0.690816	4.140474
H	4.197919	1.119633	4.975130
H	5.505395	1.416467	3.796895
H	5.281111	-0.217418	4.477947
C	-0.102400	-1.792288	1.072854
C	0.121365	-2.944869	0.268613
C	-0.909109	-3.398568	-0.554973
C	-2.150340	-2.772704	-0.632702
C	-2.399280	-1.674300	0.222959
C	-1.405431	-1.195470	1.108429
C	1.410412	-3.763141	0.324944
H	2.154020	-3.183638	0.877571
C	1.989218	-4.052603	-1.073539
H	1.357906	-4.746278	-1.640625
H	2.980517	-4.513537	-0.985256
H	2.081235	-3.131982	-1.660136
C	1.191380	-5.078769	1.100667
H	0.849736	-4.889099	2.123581
H	2.126352	-5.649697	1.156503
H	0.441901	-5.708291	0.606515

C	-3.204981	-3.335261	-1.583695
H	-4.000621	-2.591178	-1.685720
C	-3.845039	-4.609890	-0.993083
H	-3.098910	-5.405621	-0.877023
H	-4.634756	-4.985192	-1.655153
H	-4.284178	-4.415708	-0.009368
C	-2.655989	-3.592896	-2.999564
H	-2.160448	-2.702759	-3.398773
H	-3.476841	-3.870257	-3.671651
H	-1.932448	-4.416641	-3.014722
C	-1.692951	-0.129303	2.181132
H	-0.713503	0.196178	2.538804
C	-2.429031	1.155953	1.741535
H	-2.121950	1.494234	0.749505
H	-2.198411	1.955087	2.456155
H	-3.514838	1.033310	1.742679
C	-2.417871	-0.739997	3.402685
H	-3.389231	-1.159746	3.129903
H	-2.584243	0.036336	4.159884
H	-1.830431	-1.536813	3.866439
F	-0.369064	-0.918277	-2.847308
H	-0.729692	-4.270409	-1.174833
C	4.181471	-0.056186	-0.156893
C	4.553334	-1.477051	0.342469
C	5.299097	0.924426	0.289078
C	4.168018	-0.092682	-1.711777
H	4.586854	-1.499097	1.436505
H	3.788818	-2.193288	0.024854
C	5.925975	-1.916544	-0.217728
C	6.671979	0.479194	-0.269427
H	5.090618	1.936324	-0.070643
H	5.349045	0.968755	1.377302
H	3.394581	-0.789544	-2.050453
H	3.891870	0.885091	-2.121254
C	5.541829	-0.523517	-2.269760
H	6.150328	-2.923278	0.160413
C	7.011777	-0.930025	0.252191
C	5.881314	-1.936254	-1.757889
H	7.432735	1.193936	0.073657
C	6.628378	0.465593	-1.808589
H	5.485245	-0.529436	-3.366508
H	7.068596	-0.924078	1.350048
H	7.997516	-1.245497	-0.117175
H	5.127400	-2.655705	-2.105631
H	6.849294	-2.266514	-2.160194
H	7.607175	0.174679	-2.215087

H	6.410378	1.473000	-2.189749
C	2.129074	2.257911	0.666845
C	2.481532	2.973336	-0.669464
C	2.909881	2.930453	1.825426
C	0.618446	2.480864	0.938754
H	3.546426	2.862828	-0.898918
H	1.924857	2.522393	-1.496699
C	2.150080	4.480701	-0.581211
C	2.585589	4.443109	1.891850
H	2.633207	2.464512	2.776246
H	3.987884	2.797185	1.704703
H	0.029134	2.008040	0.145590
H	0.341202	1.996897	1.882957
C	0.281486	3.986720	1.018581
H	2.417228	4.949388	-1.537573
C	2.962152	5.121097	0.560423
C	0.644422	4.666603	-0.315094
H	3.169455	4.885986	2.710791
C	1.081848	4.636476	2.162586
H	-0.794873	4.092973	1.208708
H	4.039128	5.010403	0.369388
H	2.757305	6.199567	0.614864
H	0.062120	4.227361	-1.134430
H	0.395851	5.736528	-0.273680
H	0.841874	5.706486	2.235162
H	0.809958	4.180464	3.125279
C	-3.756455	-1.040019	0.139412
C	-4.010608	0.015807	-0.741350
C	-4.853573	-1.515817	0.857388
C	-5.278113	0.572337	-0.872571
C	-6.121958	-0.954552	0.729619
C	-6.373189	0.102048	-0.145038
C	-7.742597	0.721483	-0.290628
H	-8.494771	-0.000608	0.042554
H	-7.929422	0.918446	-1.352877
C	-7.902896	2.036103	0.500547
H	-7.703385	1.844247	1.563694
H	-7.141726	2.751301	0.162100
C	-9.297652	2.653051	0.340305
H	-10.054933	1.929602	0.674224
H	-9.493786	2.830401	-0.726600
C	-9.464714	3.963897	1.116170
H	-10.469268	4.380879	0.982059
H	-9.307854	3.811470	2.191108
H	-8.742759	4.718032	0.779754
C	0.610252	0.401302	-3.004642

C	1.562220	0.360611	-4.013551
S	-0.393858	1.850310	-3.158299
C	1.570500	1.546355	-4.804740
H	2.225130	-0.482026	-4.165936
C	0.592984	2.447392	-4.478628
H	2.293486	1.720862	-5.596564
H	0.410811	3.431175	-4.889336
F	-3.007094	0.531510	-1.471437
F	-5.451377	1.596347	-1.730860
F	-7.127851	-1.467609	1.465654
F	-4.700929	-2.553212	1.707760
H	-0.077119	-2.876896	3.390709

18-GS

B3LYP SCF energy:	-3617.9912734100 a.u.
B3LYP enthalpy:	-3616.772282 a.u.
B3LYP free energy:	-3616.935958 a.u.
M06 SCF energy in solution:	-3616.9180288500 a.u.

Cartesian coordinates

ATOM	X	Y	Z
Pd	-0.593598	-0.113043	-1.090625
P	-2.465210	0.160943	0.310938
C	-4.155460	-0.288607	-0.564592
C	-4.372489	-1.823674	-0.500372
H	-3.493273	-2.339140	-0.898136
H	-4.501944	-2.149109	0.536225
C	-5.616067	-2.240121	-1.320050
H	-5.732064	-3.329742	-1.243793
C	-5.428858	-1.837287	-2.795181
H	-6.301456	-2.148199	-3.386184
H	-4.554438	-2.348665	-3.219859
C	-5.242615	-0.311085	-2.876997
H	-5.085525	-0.011491	-3.921853
C	-3.999085	0.100055	-2.058675
H	-3.109120	-0.390846	-2.466318
H	-3.833139	1.177266	-2.155444
C	-5.433076	0.407992	-0.022465
H	-5.585903	0.151190	1.025592
H	-5.334984	1.495469	-0.082225
C	-6.675538	-0.016302	-0.842671
H	-7.554198	0.492370	-0.422905
C	-6.864782	-1.541985	-0.749432
H	-7.760063	-1.848625	-1.307844
H	-7.022105	-1.841637	0.296465

C	-6.491750	0.392832	-2.315555
H	-6.381068	1.483142	-2.395401
H	-7.380105	0.117991	-2.901019
C	-2.547699	1.917379	1.130657
C	-2.914241	2.964990	0.040193
H	-2.246507	2.869320	-0.818672
H	-3.933029	2.801798	-0.326007
C	-2.819134	4.398176	0.611368
H	-3.084394	5.103868	-0.186591
C	-1.379988	4.671560	1.087804
H	-0.685057	4.580700	0.243732
H	-1.295771	5.698138	1.470996
C	-1.014791	3.662856	2.193687
H	0.016711	3.835273	2.528817
C	-1.113560	2.225196	1.636412
H	-0.845653	1.512856	2.425520
H	-0.393805	2.093427	0.823675
C	-3.505722	2.096784	2.338406
H	-4.539431	1.883536	2.055644
H	-3.237464	1.394864	3.133644
C	-3.417330	3.540236	2.891723
H	-4.118560	3.628147	3.733173
C	-3.795727	4.550428	1.792257
H	-4.828120	4.377738	1.456241
H	-3.756700	5.574023	2.190142
C	-1.984260	3.822270	3.379238
H	-1.916541	4.837833	3.793327
H	-1.714861	3.127613	4.187546
C	-2.182181	-1.115882	1.672462
C	-3.140050	-1.392341	2.688119
C	-2.918141	-2.349008	3.682268
H	-3.659743	-2.531560	4.450008
C	-1.744361	-3.094483	3.665740
H	-1.573168	-3.852173	4.425445
C	-0.806854	-2.877431	2.668246
C	-0.995252	-1.893892	1.676969
O	-4.311361	-0.698582	2.626264
C	-5.277063	-0.859722	3.655209
H	-5.661325	-1.886640	3.690321
H	-6.092390	-0.178909	3.404743
H	-4.866571	-0.589064	4.635726
C	0.139455	-1.840077	0.668516
C	1.372215	-1.177080	1.013504
C	2.509638	-1.392702	0.211851
C	2.476878	-2.304338	-0.871439
C	1.309745	-3.022371	-1.097814

H	1.298541	-3.750800	-1.901271
C	0.138306	-2.815895	-0.373199
C	1.420324	-0.360415	2.317354
H	0.378490	-0.215435	2.610680
C	2.043005	1.051558	2.256074
H	3.129342	1.029008	2.369514
H	1.647732	1.648311	3.086692
H	1.807278	1.570226	1.324471
C	2.082149	-1.160207	3.463569
H	1.544822	-2.088148	3.675640
H	2.081889	-0.557785	4.380450
H	3.117302	-1.421799	3.231878
C	3.680462	-2.556678	-1.774275
H	4.409401	-1.761108	-1.594886
C	3.311032	-2.491811	-3.268766
H	2.704529	-3.352571	-3.575389
H	4.223638	-2.504931	-3.876956
H	2.740995	-1.584408	-3.484925
C	4.364696	-3.893402	-1.418200
H	4.679344	-3.915168	-0.369806
H	5.249449	-4.048236	-2.047337
H	3.685260	-4.738558	-1.583866
C	-1.052741	-3.725738	-0.671700
H	-1.909329	-3.368008	-0.095336
C	-1.444342	-3.707575	-2.162321
H	-1.591200	-2.684561	-2.523872
H	-2.370396	-4.274769	-2.317209
H	-0.671206	-4.166004	-2.788894
C	-0.771063	-5.170237	-0.207373
H	0.087934	-5.596655	-0.738125
H	-1.639896	-5.809480	-0.406187
H	-0.558257	-5.212803	0.865889
C	3.802243	-0.670118	0.456546
C	4.850234	-1.247888	1.174611
C	6.077755	-0.611202	1.339889
C	6.333788	0.642958	0.787088
C	7.667126	1.336036	0.936622
H	8.187723	0.920435	1.805108
H	7.492967	2.399351	1.139823
C	8.559541	1.202333	-0.314679
H	8.025802	1.618203	-1.179109
H	8.722658	0.137309	-0.528871
C	9.911167	1.909153	-0.154836
H	9.739571	2.971169	0.071146
H	10.438157	1.492461	0.715249
C	10.798457	1.787647	-1.398287

H	11.018643	0.737804	-1.627478
H	11.754006	2.305605	-1.258119
H	10.308545	2.222745	-2.277891
C	5.290808	1.217298	0.058504
C	4.063288	0.583794	-0.106579
F	0.933041	-0.447491	-2.308111
F	7.034698	-1.236267	2.054711
F	4.687144	-2.465734	1.735454
F	5.473260	2.429222	-0.502999
F	3.111365	1.217474	-0.807630
H	0.096679	-3.476425	2.637478
C	-0.747035	1.545002	-2.218881
C	-1.450428	1.736898	-3.373867
C	0.169510	2.630256	-1.972129
S	-1.040335	3.248377	-4.156113
H	-2.161787	1.086719	-3.860040
C	0.113153	3.618928	-2.914605
H	0.864486	2.653283	-1.141208
H	0.693219	4.531485	-2.962122

18-TS

B3LYP SCF energy:	-3617.9456817400 a.u.
B3LYP enthalpy:	-3616.729167 a.u.
B3LYP free energy:	-3616.894207 a.u.
M06 SCF energy in solution:	-3616.8734820300 a.u.

Cartesian coordinates

ATOM	X	Y	Z
Pd	-0.665658	-0.031118	-1.077706
P	-2.438100	0.104377	0.387122
C	-4.159173	-0.247556	-0.469610
C	-4.429932	-1.774704	-0.467342
H	-3.570470	-2.303608	-0.891567
H	-4.561019	-2.136694	0.557112
C	-5.693642	-2.113624	-1.291065
H	-5.849017	-3.200761	-1.260593
C	-5.506525	-1.654488	-2.749691
H	-6.395321	-1.909693	-3.343638
H	-4.654860	-2.178099	-3.205004
C	-5.266829	-0.132771	-2.771019
H	-5.110924	0.203851	-3.804883
C	-4.000820	0.198905	-1.951041
H	-3.131462	-0.303690	-2.388763
H	-3.789269	1.272159	-2.008215
C	-5.405785	0.470430	0.112688

H	-5.558013	0.177354	1.152160
H	-5.267027	1.555977	0.096230
C	-6.670440	0.124921	-0.710622
H	-7.528177	0.644682	-0.261749
C	-6.911849	-1.396367	-0.679437
H	-7.822669	-1.648349	-1.240371
H	-7.069960	-1.733918	0.354816
C	-6.485372	0.589496	-2.166964
H	-6.336490	1.677653	-2.201406
H	-7.388483	0.371368	-2.754128
C	-2.449545	1.815434	1.288374
C	-2.717948	2.902721	0.207828
H	-2.027158	2.774190	-0.631436
H	-3.732580	2.807777	-0.193983
C	-2.552917	4.317461	0.806718
H	-2.755410	5.053694	0.017767
C	-1.113332	4.495068	1.325336
H	-0.401669	4.379962	0.497648
H	-0.977769	5.507287	1.731854
C	-0.836235	3.444081	2.417149
H	0.195343	3.547717	2.779704
C	-1.009740	2.027733	1.826160
H	-0.792785	1.280950	2.599770
H	-0.289397	1.871033	1.015665
C	-3.420552	2.031079	2.477954
H	-4.458595	1.882140	2.170451
H	-3.211783	1.299389	3.264082
C	-3.258942	3.457273	3.058543
H	-3.972976	3.577113	3.885234
C	-3.548672	4.505891	1.967468
H	-4.580155	4.399046	1.602745
H	-3.460535	5.519018	2.384190
C	-1.822857	3.642160	3.583255
H	-1.702159	4.644103	4.018430
H	-1.616101	2.917739	4.383804
C	-2.147246	-1.256982	1.673523
C	-3.096997	-1.555804	2.689111
C	-2.908346	-2.585019	3.615928
H	-3.647569	-2.784299	4.382006
C	-1.768407	-3.376544	3.533627
H	-1.621427	-4.190385	4.238448
C	-0.829112	-3.128239	2.544304
C	-0.982604	-2.075398	1.620269
O	-4.231803	-0.798067	2.698257
C	-5.191780	-0.988477	3.726569
H	-5.628451	-1.994473	3.690367

H	-5.973878	-0.250062	3.541817
H	-4.756953	-0.815132	4.718792
C	0.161910	-1.983981	0.624307
C	1.385880	-1.335697	0.986626
C	2.484582	-1.407460	0.097918
C	2.412892	-2.164303	-1.094109
C	1.244756	-2.877427	-1.350125
H	1.204528	-3.502474	-2.235811
C	0.119191	-2.814666	-0.528828
C	1.483232	-0.680454	2.376566
H	0.452760	-0.572689	2.721871
C	2.107420	0.729467	2.469636
H	3.197481	0.696637	2.541317
H	1.742566	1.216914	3.381634
H	1.837359	1.361035	1.620480
C	2.183572	-1.615543	3.389520
H	1.651707	-2.564268	3.500226
H	2.218589	-1.134912	4.375167
H	3.209224	-1.843457	3.088154
C	3.580846	-2.285058	-2.071638
H	4.308296	-1.504360	-1.829827
C	3.157190	-2.057739	-3.535167
H	2.514215	-2.865228	-3.904881
H	4.044163	-2.028512	-4.179499
H	2.610467	-1.116530	-3.645862
C	4.295762	-3.642515	-1.902457
H	4.645635	-3.782385	-0.874707
H	5.161151	-3.707725	-2.573197
H	3.621658	-4.473343	-2.144346
C	-1.066909	-3.719925	-0.861255
H	-1.910934	-3.418782	-0.235413
C	-1.514435	-3.610079	-2.331480
H	-1.694672	-2.567817	-2.615103
H	-2.438381	-4.180194	-2.487331
H	-0.763371	-4.016938	-3.018250
C	-0.743546	-5.187526	-0.509471
H	0.108782	-5.553830	-1.093891
H	-1.604046	-5.831820	-0.727908
H	-0.497067	-5.301124	0.551276
C	3.771573	-0.685626	0.370904
C	4.863160	-1.305905	0.981204
C	6.071819	-0.644714	1.179527
C	6.267798	0.674096	0.769838
C	7.588162	1.378973	0.969178
H	8.018207	1.061804	1.925836
H	7.408479	2.457110	1.034490

C	8.599459	1.094319	-0.160301
H	8.166129	1.410276	-1.118852
H	8.760775	0.010257	-0.230833
C	9.942629	1.802022	0.057805
H	9.772460	2.884933	0.139549
H	10.365701	1.485199	1.021636
C	10.952428	1.525172	-1.060916
H	11.169762	0.453139	-1.142525
H	11.900198	2.044452	-0.879214
H	10.569206	1.860388	-2.032399
C	5.185040	1.289151	0.139777
C	3.976422	0.628623	-0.056311
F	0.676418	0.257559	-2.715478
F	7.080209	-1.306851	1.781209
F	4.761900	-2.585568	1.397410
F	5.301258	2.561493	-0.288167
F	2.975250	1.298858	-0.656950
H	0.051644	-3.756673	2.469839
C	-0.387918	1.513376	-2.572222
C	-1.284963	1.722945	-3.594059
C	0.290353	2.718817	-2.161525
S	-1.399925	3.424883	-3.982493
H	-1.880695	1.000248	-4.129952
C	-0.176838	3.822610	-2.811742
H	1.082453	2.731960	-1.423607
H	0.135196	4.850614	-2.681416

19-GS

B3LYP SCF energy:	-3849.0435984200 a.u.
B3LYP enthalpy:	-3847.738272 a.u.
B3LYP free energy:	-3847.911568 a.u.
M06 SCF energy in solution:	-3847.8566966800 a.u.

Cartesian coordinates

ATOM	X	Y	Z
Pd	-0.455192	0.651811	0.073448
P	-2.284702	-0.860939	0.034073
C	-3.997732	0.034813	-0.243485
C	-4.146747	0.341708	-1.756352
H	-3.264772	0.885317	-2.107492
H	-4.210619	-0.588973	-2.329703
C	-5.406753	1.197014	-2.023364
H	-5.474535	1.386955	-3.103335
C	-5.302771	2.531416	-1.260975
H	-6.188526	3.150090	-1.462516

H	-4.429050	3.102587	-1.600805
C	-5.185942	2.241346	0.246797
H	-5.081065	3.183922	0.795752
C	-3.921699	1.392120	0.506608
H	-3.041556	1.946980	0.176218
H	-3.798016	1.232891	1.583561
C	-5.276596	-0.702752	0.239353
H	-5.374513	-1.663320	-0.263579
H	-5.225263	-0.898839	1.314267
C	-6.536471	0.153180	-0.039351
H	-7.415284	-0.410314	0.303792
C	-6.655763	0.429684	-1.550316
H	-7.561729	1.015985	-1.757000
H	-6.752754	-0.515765	-2.103026
C	-6.437307	1.485046	0.725507
H	-6.379040	1.297004	1.806833
H	-7.338768	2.089948	0.554178
C	-2.375820	-2.056232	1.559927
C	-2.816550	-1.240218	2.808380
H	-2.181635	-0.360060	2.933533
H	-3.843123	-0.881258	2.688179
C	-2.745122	-2.113568	4.082034
H	-3.061332	-1.501993	4.937172
C	-1.299248	-2.598813	4.297592
H	-0.632343	-1.737952	4.429543
H	-1.233102	-3.201673	5.214027
C	-0.860240	-3.437849	3.082160
H	0.177185	-3.772396	3.216117
C	-0.937614	-2.583558	1.796932
H	-0.628926	-3.195497	0.941016
H	-0.237237	-1.747597	1.859816
C	-3.295097	-3.301405	1.430531
H	-4.330733	-3.007753	1.245951
H	-2.975098	-3.914446	0.582343
C	-3.230093	-4.161076	2.716750
H	-3.901977	-5.020856	2.587743
C	-3.681776	-3.327193	3.929861
H	-4.719541	-2.991179	3.794506
H	-3.661421	-3.942135	4.840383
C	-1.789611	-4.657664	2.938768
H	-1.737645	-5.285171	3.839295
H	-1.469559	-5.283059	2.093319
C	-1.925672	-1.930882	-1.480355
C	-2.835734	-2.905826	-1.981583
C	-2.522796	-3.732490	-3.064348
H	-3.227496	-4.477990	-3.410337

C	-1.306979	-3.575507	-3.719740
H	-1.063865	-4.205894	-4.570632
C	-0.424138	-2.594734	-3.297250
C	-0.705708	-1.772632	-2.188268
O	-4.053250	-2.978395	-1.375143
C	-4.977335	-3.981052	-1.773103
H	-5.282777	-3.854532	-2.818958
H	-5.847454	-3.854064	-1.126741
H	-4.563371	-4.986996	-1.631518
C	0.362628	-0.719408	-1.949462
C	1.609362	-1.083517	-1.324465
C	2.697387	-0.191316	-1.399023
C	2.603216	1.007738	-2.144958
C	1.427866	1.268485	-2.840557
H	1.377488	2.165110	-3.448534
C	0.302979	0.453103	-2.764300
C	1.734062	-2.487821	-0.708662
H	0.713109	-2.869129	-0.643529
C	2.320036	-2.590228	0.716912
H	3.411973	-2.630624	0.711149
H	1.967966	-3.520043	1.178997
H	2.013991	-1.756530	1.352384
C	2.495431	-3.455590	-1.644258
H	1.994518	-3.568286	-2.609311
H	2.550241	-4.447742	-1.179417
H	3.516364	-3.117355	-1.837099
C	3.750141	2.008440	-2.252449
H	4.504720	1.742621	-1.506937
C	3.296518	3.445507	-1.931544
H	2.639280	3.847865	-2.711908
H	4.169759	4.105972	-1.868606
H	2.751873	3.473322	-0.984146
C	4.425732	1.924433	-3.637381
H	4.799847	0.915330	-3.838144
H	5.270335	2.621810	-3.692497
H	3.722169	2.189307	-4.436241
C	-0.891158	0.799165	-3.653867
H	-1.726909	0.153265	-3.375131
C	-1.352172	2.260309	-3.489272
H	-1.529931	2.514784	-2.439894
H	-2.279879	2.426344	-4.050161
H	-0.608332	2.965290	-3.877780
C	-0.568994	0.506880	-5.135108
H	0.272978	1.116349	-5.483322
H	-1.436237	0.739287	-5.765091
H	-0.310656	-0.545336	-5.291133

C	3.995508	-0.453868	-0.692726
C	5.101006	-0.987907	-1.356881
C	6.334441	-1.152883	-0.732878
C	6.538391	-0.786027	0.596759
C	7.878542	-0.932778	1.276467
H	8.439769	-1.735384	0.787030
H	7.716993	-1.235127	2.317388
C	8.709034	0.367175	1.250274
H	8.133564	1.167698	1.733715
H	8.860307	0.675594	0.206828
C	10.067375	0.216492	1.945909
H	9.907907	-0.099103	2.986739
H	10.634055	-0.592907	1.464044
C	10.895264	1.505822	1.923057
H	11.101289	1.826452	0.894500
H	11.857853	1.370306	2.429074
H	10.366361	2.324871	2.425487
C	5.437702	-0.241026	1.259566
C	4.203063	-0.075388	0.638489
F	1.024565	1.975373	-0.054813
F	7.351624	-1.679369	-1.444333
F	4.988690	-1.358152	-2.650745
F	5.568228	0.136848	2.546566
F	3.196670	0.439482	1.357905
H	0.505915	-2.438796	-3.832288
C	-0.671231	1.508814	1.894842
C	-1.160074	2.757354	2.213315
C	-0.019998	0.881028	3.011806
S	-0.874213	3.117237	3.925470
C	-0.063147	1.611412	4.167138
H	0.478850	-0.078389	2.952487
H	0.343338	1.353336	5.136679
C	-1.731109	3.840967	1.391898
C	-2.792003	4.633994	1.867976
C	-1.179932	4.144005	0.131431
C	-3.299801	5.685985	1.104998
H	-3.227542	4.414455	2.839651
C	-1.701997	5.189437	-0.632189
H	-0.320320	3.571270	-0.205371
C	-2.762390	5.963994	-0.153981
H	-4.119555	6.285325	1.493674
H	-1.260143	5.414592	-1.600179
H	-3.157756	6.782760	-0.749813

19-TS

B3LYP SCF energy:	-3849.0021233000 a.u.
B3LYP enthalpy:	-3847.699366 a.u.
B3LYP free energy:	-3847.874358 a.u.
M06 SCF energy in solution:	-3847.8177627700 a.u.

Cartesian coordinates

ATOM	X	Y	Z
Pd	-0.563493	0.677717	-0.044164
P	-2.213798	-0.947827	0.103011
C	-4.011496	-0.249464	-0.195658
C	-4.287480	-0.206968	-1.722226
H	-3.480965	0.332309	-2.230141
H	-4.313933	-1.221019	-2.134584
C	-5.631836	0.496085	-2.019359
H	-5.789684	0.499911	-3.106712
C	-5.592923	1.942313	-1.490339
H	-6.540293	2.452543	-1.714870
H	-4.796956	2.511670	-1.988075
C	-5.348336	1.916627	0.030324
H	-5.289426	2.942641	0.411765
C	-4.002526	1.216707	0.323089
H	-3.188295	1.771883	-0.151153
H	-3.801336	1.241840	1.400250
C	-5.187689	-0.988469	0.497031
H	-5.237728	-2.023354	0.159402
H	-5.044213	-1.003652	1.581898
C	-6.532124	-0.285713	0.190595
H	-7.335533	-0.846300	0.688608
C	-6.775601	-0.272769	-1.330795
H	-7.741242	0.200692	-1.556907
H	-6.826756	-1.301603	-1.715333
C	-6.495703	1.158572	0.722345
H	-6.347815	1.156395	1.811452
H	-7.455121	1.659685	0.531092
C	-2.107479	-1.887303	1.790177
C	-2.487050	-0.883447	2.915609
H	-1.893209	0.030474	2.817947
H	-3.540145	-0.594712	2.836303
C	-2.247824	-1.511318	4.307374
H	-2.531906	-0.776706	5.072426
C	-0.758422	-1.873122	4.462133
H	-0.143769	-0.968459	4.372420
H	-0.570896	-2.296614	5.458869
C	-0.370271	-2.890385	3.371936
H	0.695614	-3.140371	3.459702

C	-0.617113	-2.272427	1.978284
H	-0.324140	-2.991380	1.203828
H	0.010613	-1.384446	1.846606
C	-2.940521	-3.183966	1.964789
H	-4.006842	-2.987887	1.830146
H	-2.650533	-3.915960	1.204729
C	-2.706677	-3.795159	3.367868
H	-3.325044	-4.698941	3.458706
C	-3.107689	-2.780953	4.456254
H	-4.173841	-2.529196	4.365018
H	-2.968365	-3.221379	5.453537
C	-1.220540	-4.164409	3.530524
H	-1.046079	-4.619061	4.515742
H	-0.931370	-4.910761	2.777052
C	-1.817541	-2.190760	-1.272219
C	-2.678223	-3.280104	-1.587306
C	-2.403092	-4.183299	-2.618425
H	-3.076499	-5.005223	-2.826587
C	-1.265370	-4.007148	-3.396753
H	-1.052378	-4.694610	-4.210787
C	-0.413990	-2.945325	-3.134183
C	-0.655782	-2.039722	-2.082168
O	-3.815810	-3.393161	-0.843691
C	-4.680483	-4.500417	-1.049175
H	-5.110014	-4.495575	-2.058729
H	-5.482112	-4.389102	-0.317048
H	-4.161861	-5.451801	-0.877444
C	0.395758	-0.947299	-1.989891
C	1.658221	-1.205438	-1.363823
C	2.674468	-0.224777	-1.449478
C	2.487888	0.960011	-2.198345
C	1.289184	1.118887	-2.889431
H	1.163614	1.997796	-3.512879
C	0.240231	0.201604	-2.814753
C	1.887745	-2.584846	-0.718183
H	0.893377	-3.022395	-0.606402
C	2.529092	-2.627418	0.686679
H	3.620833	-2.607525	0.644167
H	2.246818	-3.567376	1.175641
H	2.195533	-1.804795	1.322697
C	2.669635	-3.529576	-1.660399
H	2.150508	-3.678350	-2.610694
H	2.784244	-4.511869	-1.185405
H	3.667819	-3.145526	-1.884741
C	3.569090	2.030310	-2.335950
H	4.330225	1.844848	-1.572073

C	3.033272	3.453232	-2.089674
H	2.338751	3.771010	-2.876368
H	3.864584	4.168333	-2.082985
H	2.509013	3.516174	-1.131441
C	4.267343	1.927435	-3.708833
H	4.697750	0.932791	-3.862958
H	5.073260	2.667333	-3.785760
H	3.559266	2.118046	-4.524579
C	-0.976710	0.416069	-3.715908
H	-1.764783	-0.266688	-3.388756
C	-1.542188	1.845968	-3.644386
H	-1.746527	2.145408	-2.612026
H	-2.476931	1.907704	-4.214561
H	-0.851744	2.579856	-4.076828
C	-0.634983	0.052168	-5.176715
H	0.162340	0.696822	-5.565437
H	-1.515536	0.181746	-5.817705
H	-0.301541	-0.986625	-5.265893
C	3.994446	-0.394556	-0.755692
C	5.117195	-0.912978	-1.402079
C	6.350885	-1.028808	-0.765987
C	6.539066	-0.620811	0.554178
C	7.874536	-0.733097	1.249760
H	8.452371	-1.535026	0.779048
H	7.705838	-1.022754	2.293285
C	8.688492	0.576800	1.214831
H	8.097935	1.377008	1.680316
H	8.849537	0.872680	0.169259
C	10.039157	0.449584	1.929911
H	9.869008	0.144507	2.972196
H	10.620368	-0.359615	1.465382
C	10.854496	1.746694	1.902844
H	11.070925	2.057653	0.873488
H	11.811620	1.626075	2.422739
H	10.311470	2.566161	2.389265
C	5.423633	-0.078006	1.194217
C	4.191878	0.036008	0.559364
F	0.729490	2.349736	0.290243
F	7.383670	-1.551309	-1.456191
F	5.022371	-1.323825	-2.683924
F	5.536411	0.342900	2.469510
F	3.163293	0.554813	1.255047
H	0.463955	-2.794644	-3.752379
C	-0.353898	2.120402	1.543773
C	-1.228784	3.167149	1.824487
C	0.338204	1.613716	2.701585

S	-1.307219	3.393134	3.584643
C	-0.099259	2.177323	3.860093
H	1.112844	0.860524	2.639719
H	0.218165	1.948689	4.869388
C	-1.970021	4.061073	0.944049
C	-3.064220	4.820159	1.414805
C	-1.603009	4.220539	-0.411233
C	-3.759290	5.687048	0.575034
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H	-4.595713	6.257489	0.971740
H	-2.002195	5.183136	-2.286929
H	-3.937257	6.495407	-1.422482

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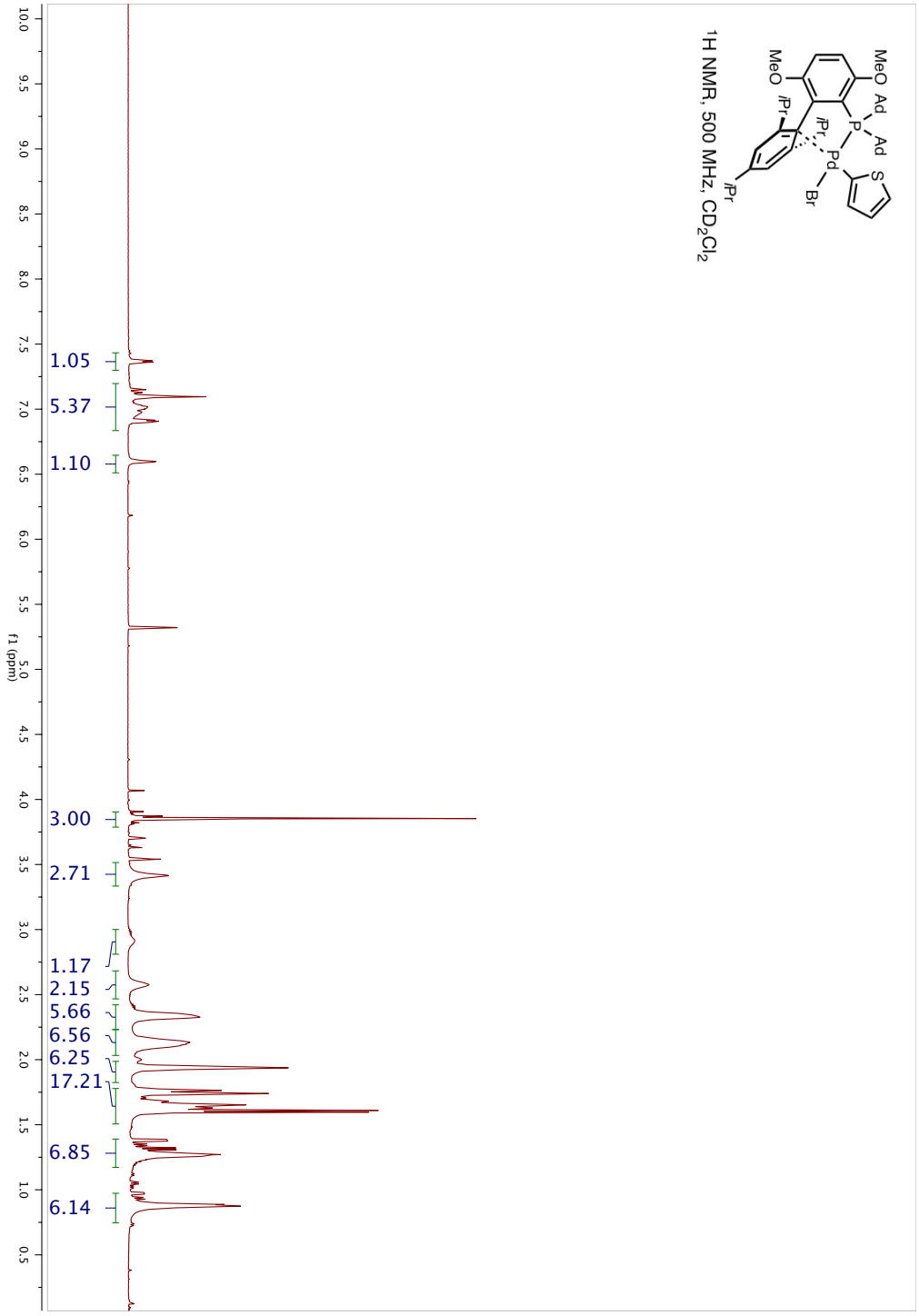
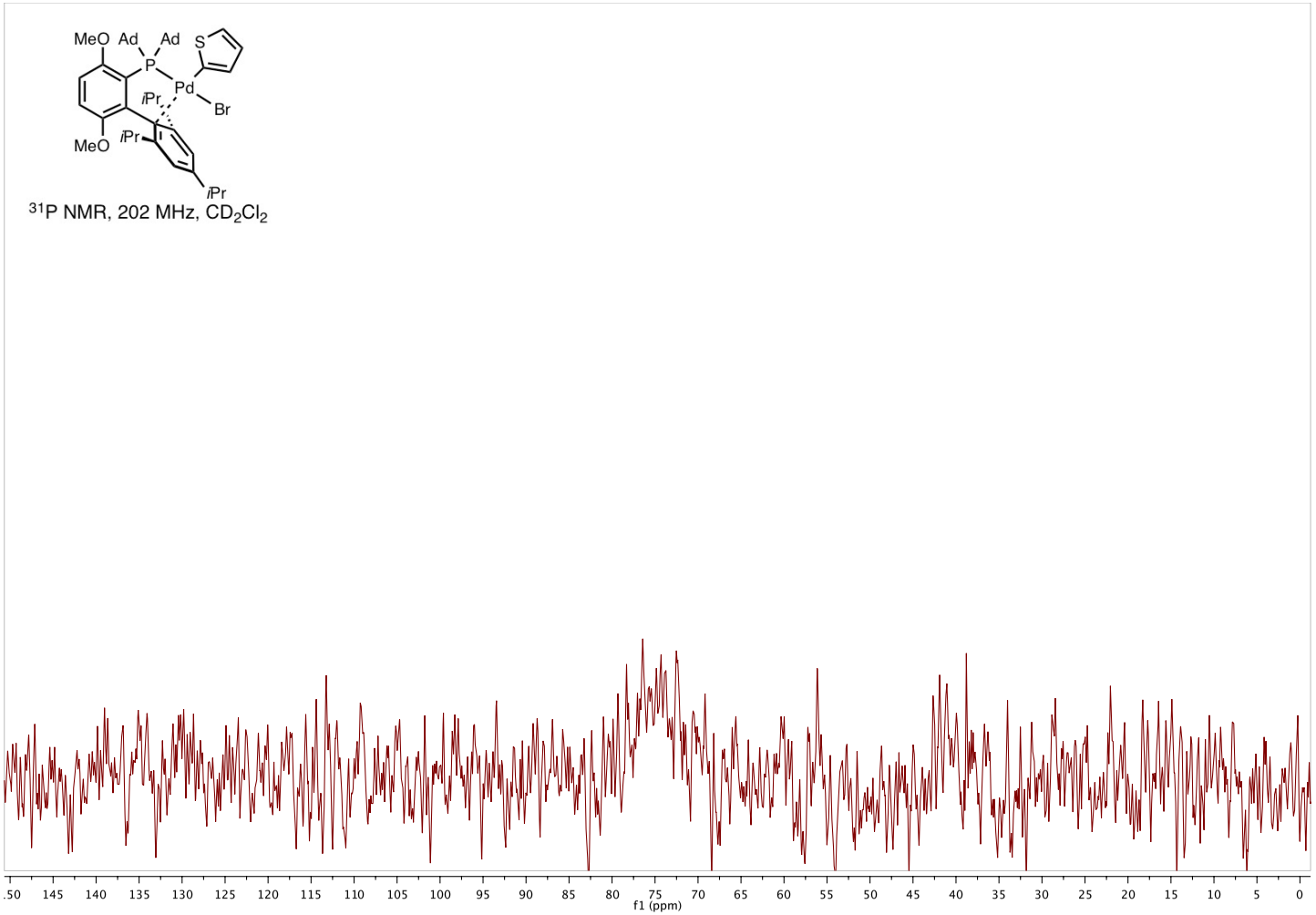
NMR spectra of complexes, new heteroaryl bromides, and heteroaryl fluorides.

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P
Pd
Br
iPr
MeO
iPr
iPr
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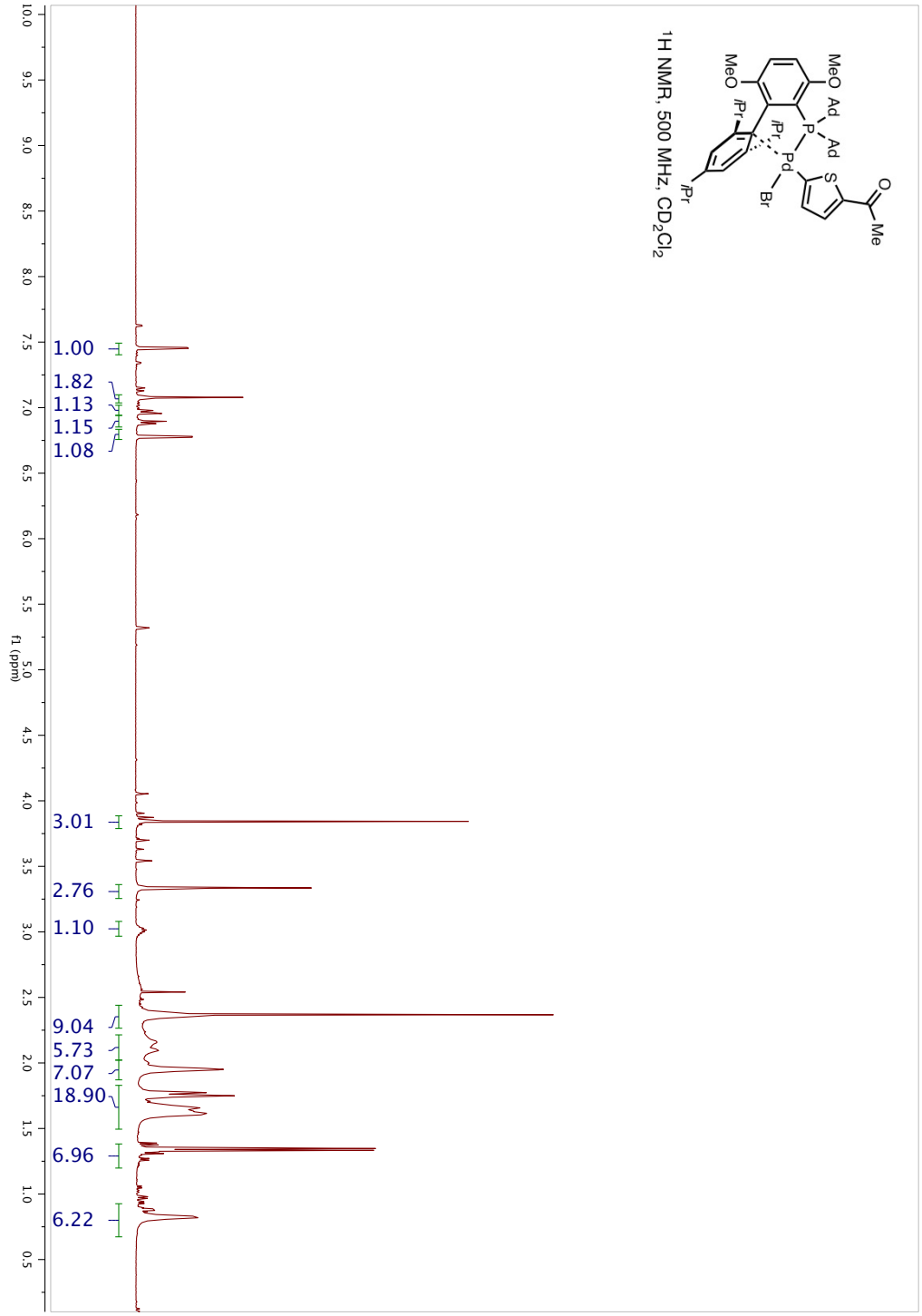
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P
Pd
Br
S
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1.13
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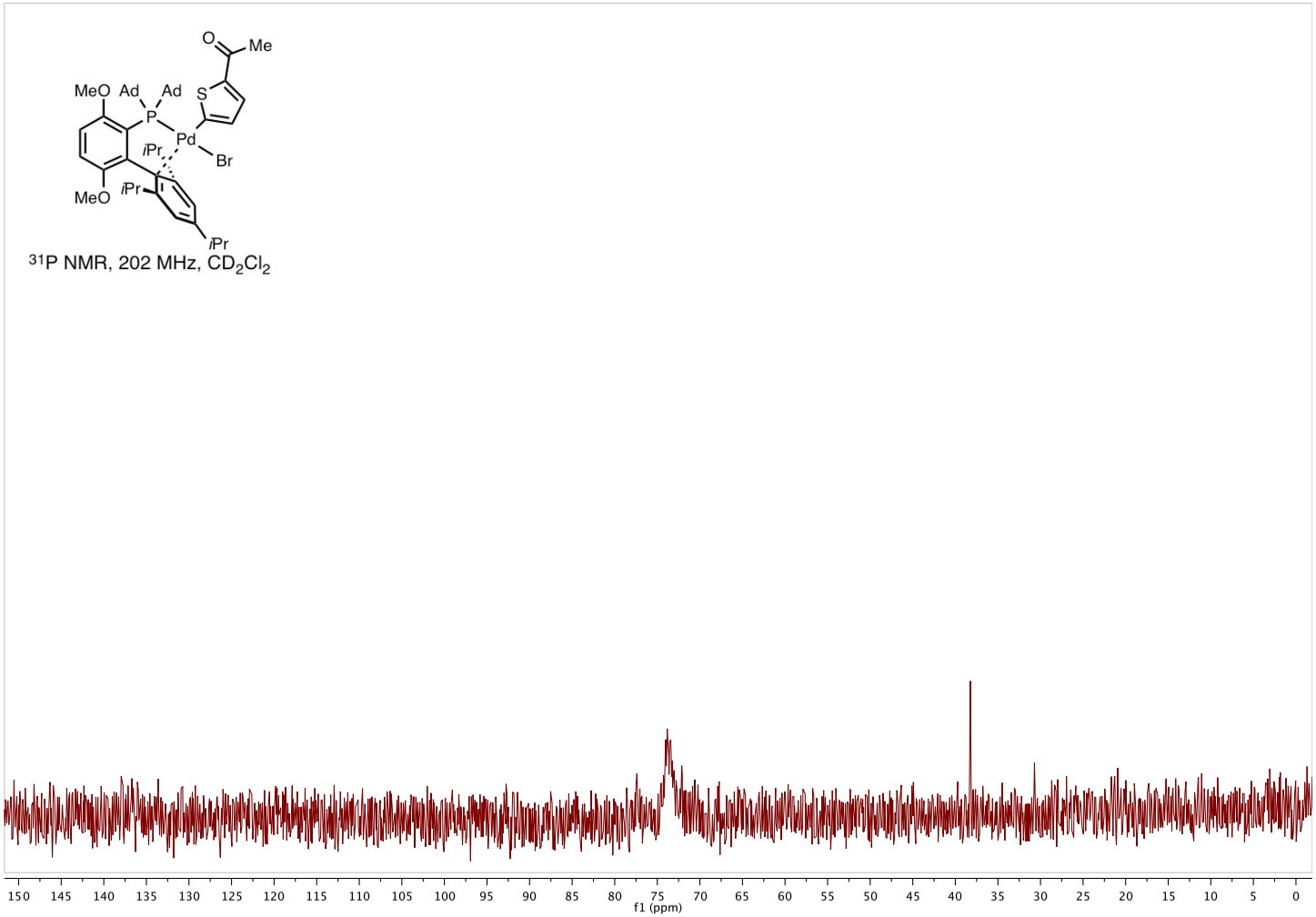
18.90
6.96
6.22
f1 (ppm)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Br
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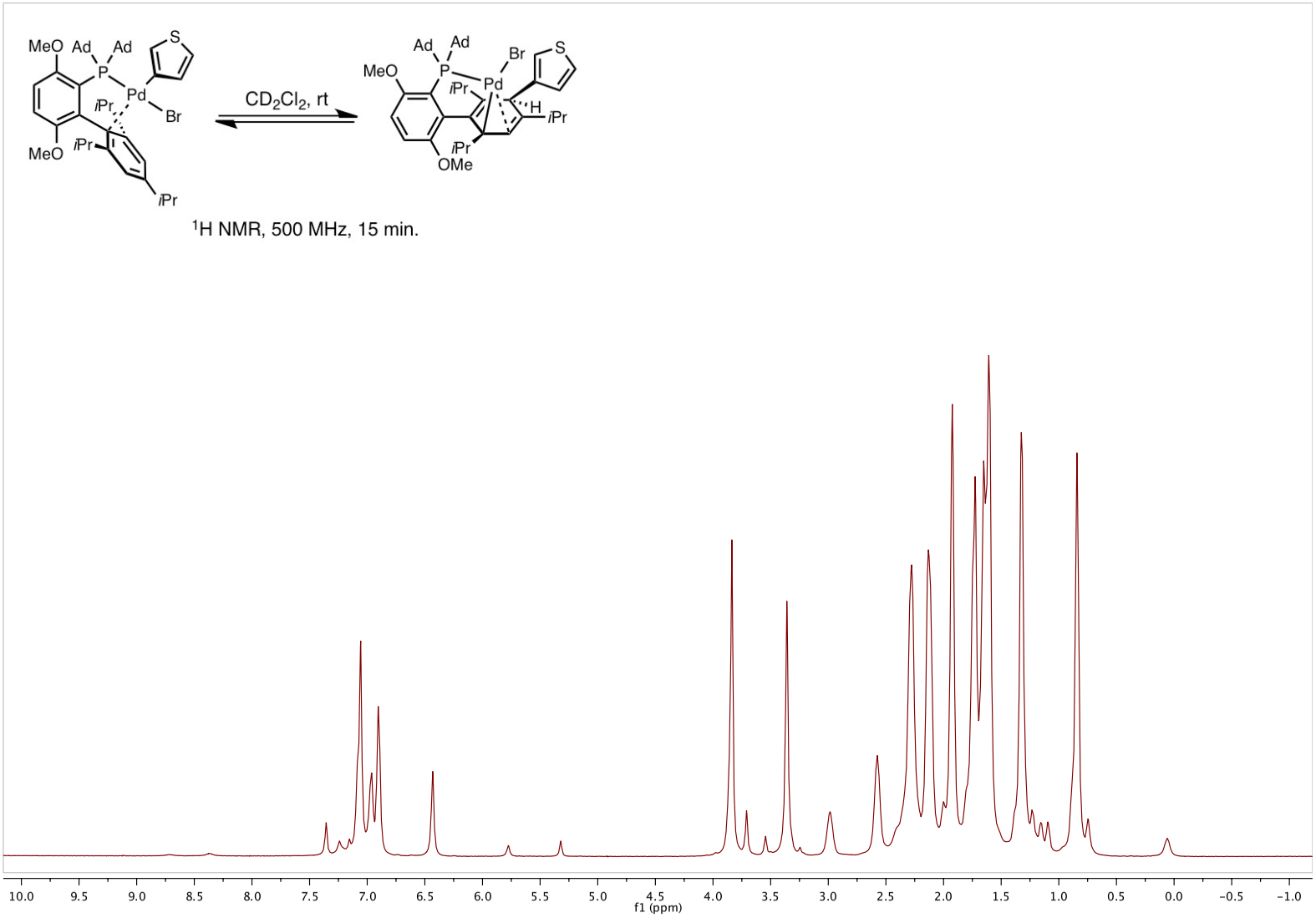
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Pd
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Ad
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Br
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MeO
P
Pd
iPr
H
iPr
iPr
OMe
1H NMR, 500 MHz, 15 min.
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9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
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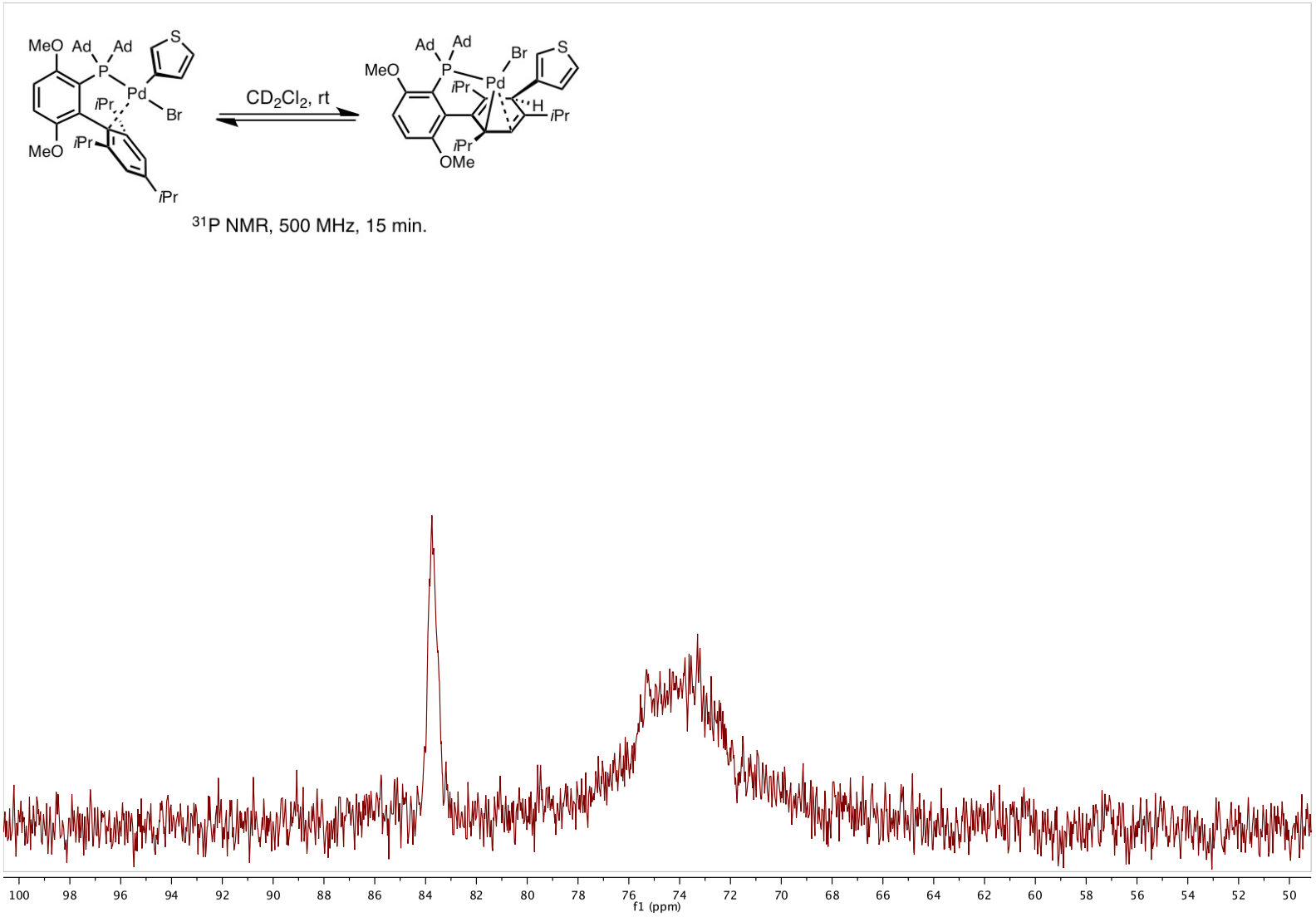
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Pd
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iPr
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iPr
CD2Cl2, rt
Ad
Ad
P
Br
S
MeO
Pd
iPr
H
iPr
iPr
OMe
31P NMR, 500 MHz, 15 min.
100
98
96
94
92
90
88
86
84
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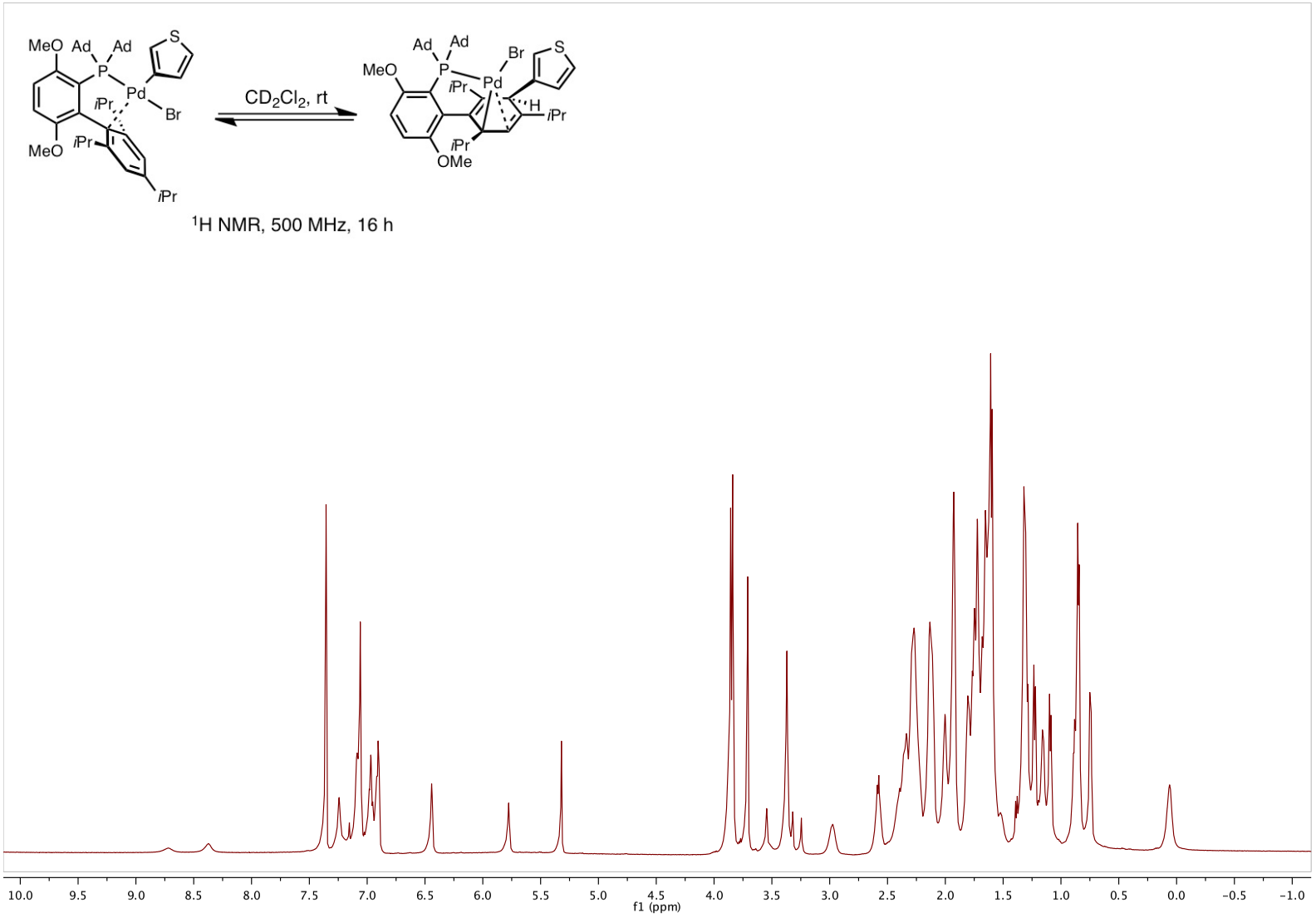
76
74
72
70
68
66
64
62
60
58
56
54
52
50
f1 (ppm)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Ad
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MeO
P
Pd
iPr
H
iPr
iPr
OMe
1H NMR, 500 MHz, 16 h
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9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
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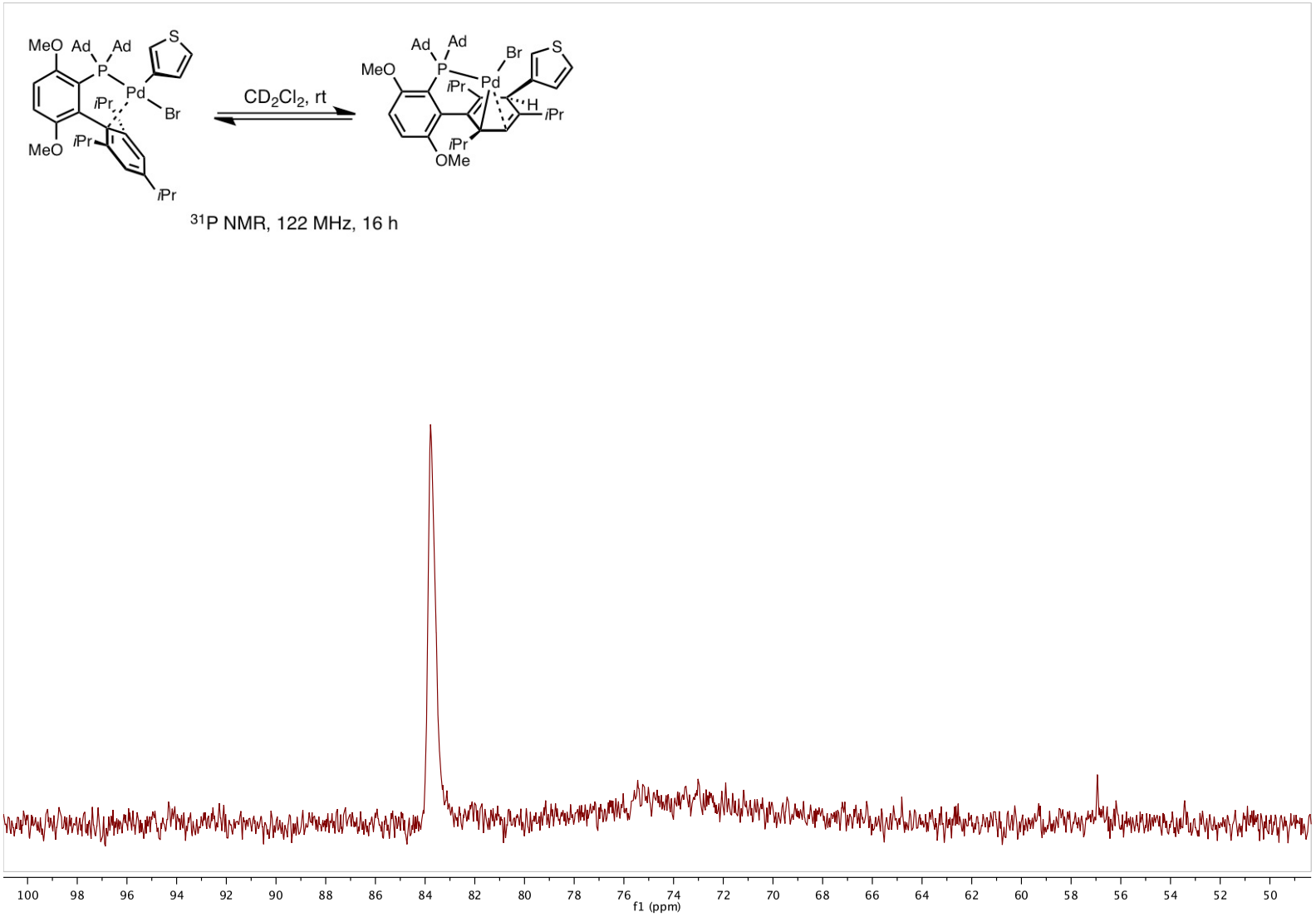
f1 (ppm)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H
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iPr
OMe
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96
94
92
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58
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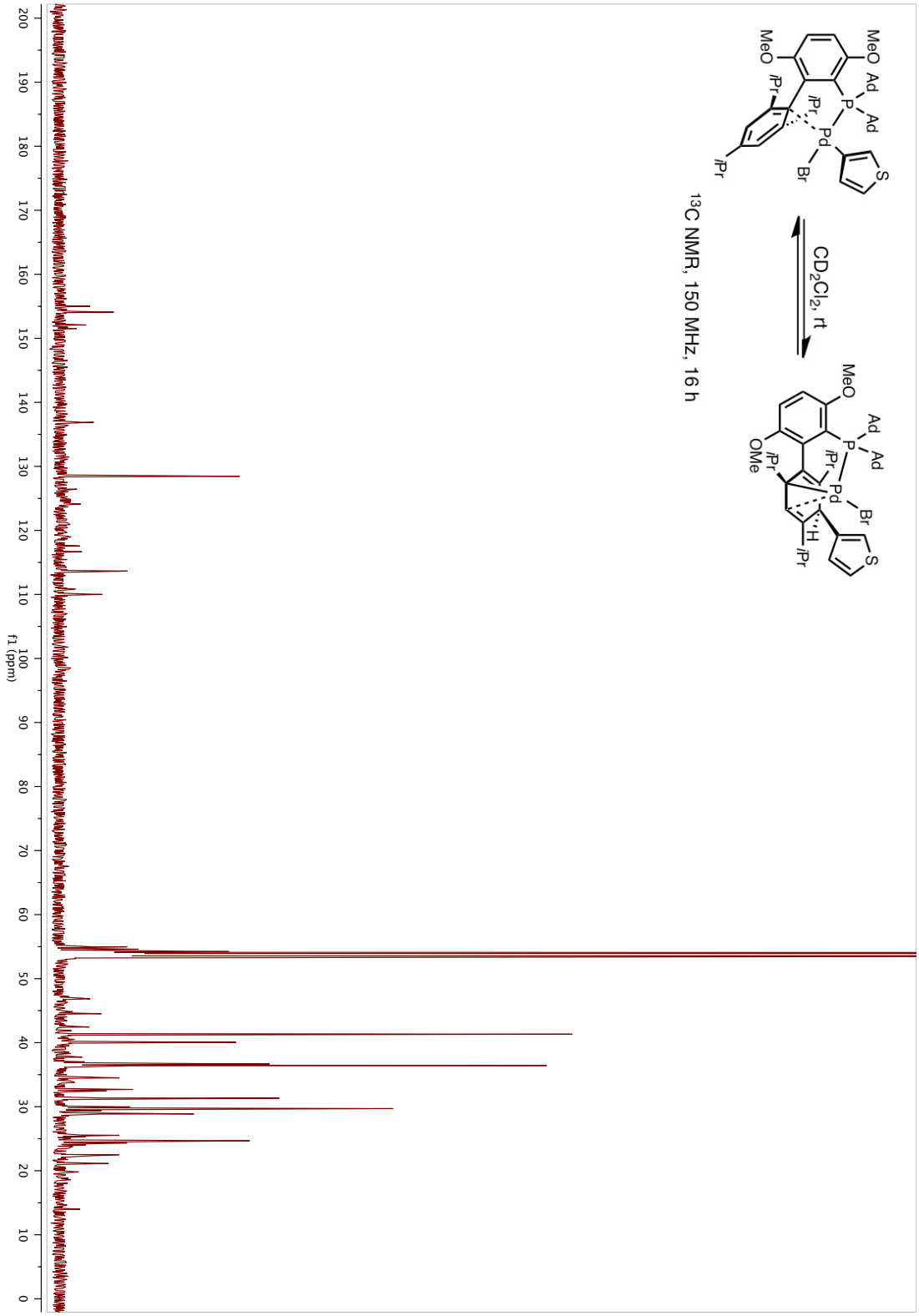
54
52
50
f1 (ppm)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Pd
Br
S
iPr
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OMe
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Pd
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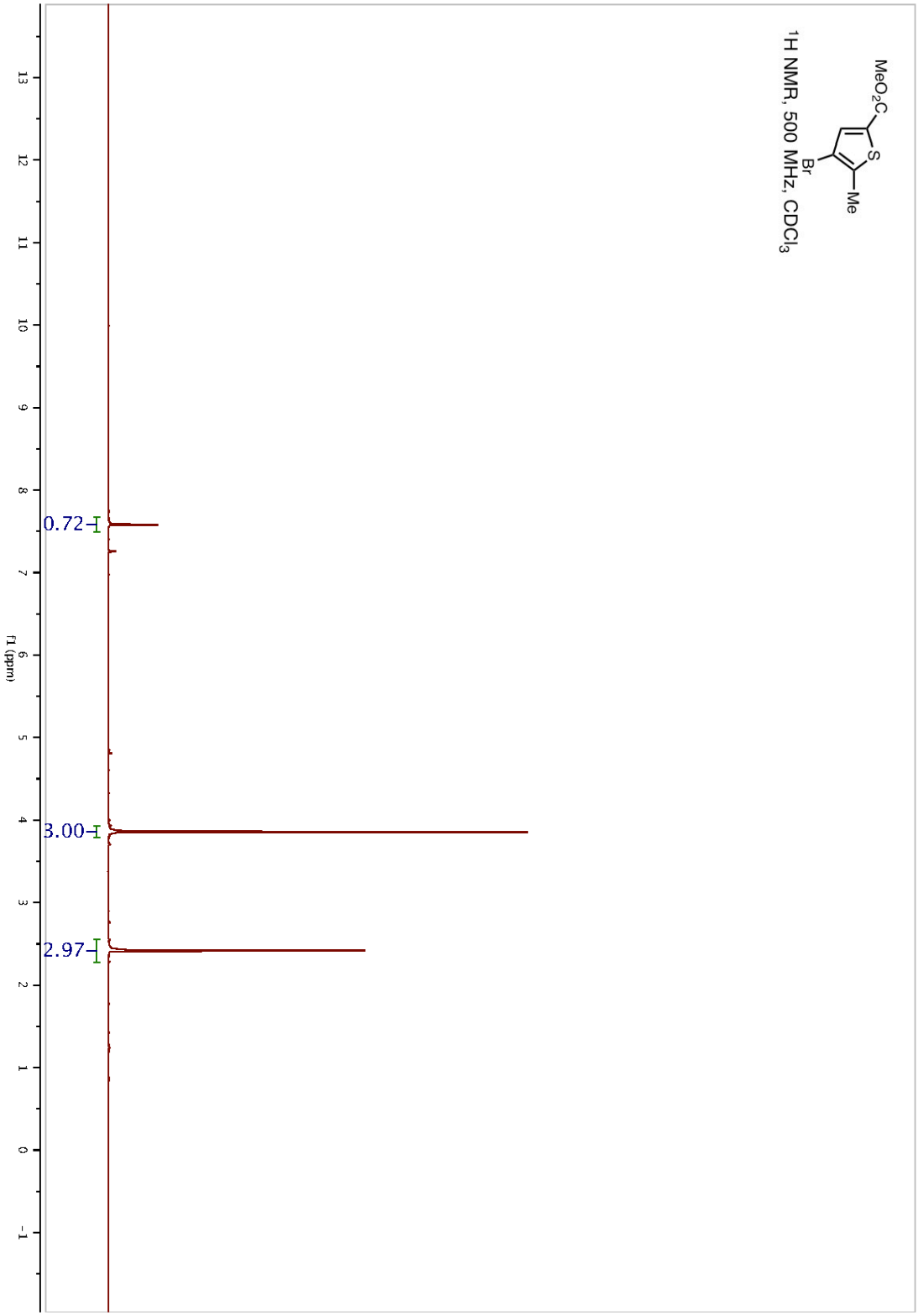
S
iPr
13C NMR, 150 MHz, 16 h
f1 (ppm)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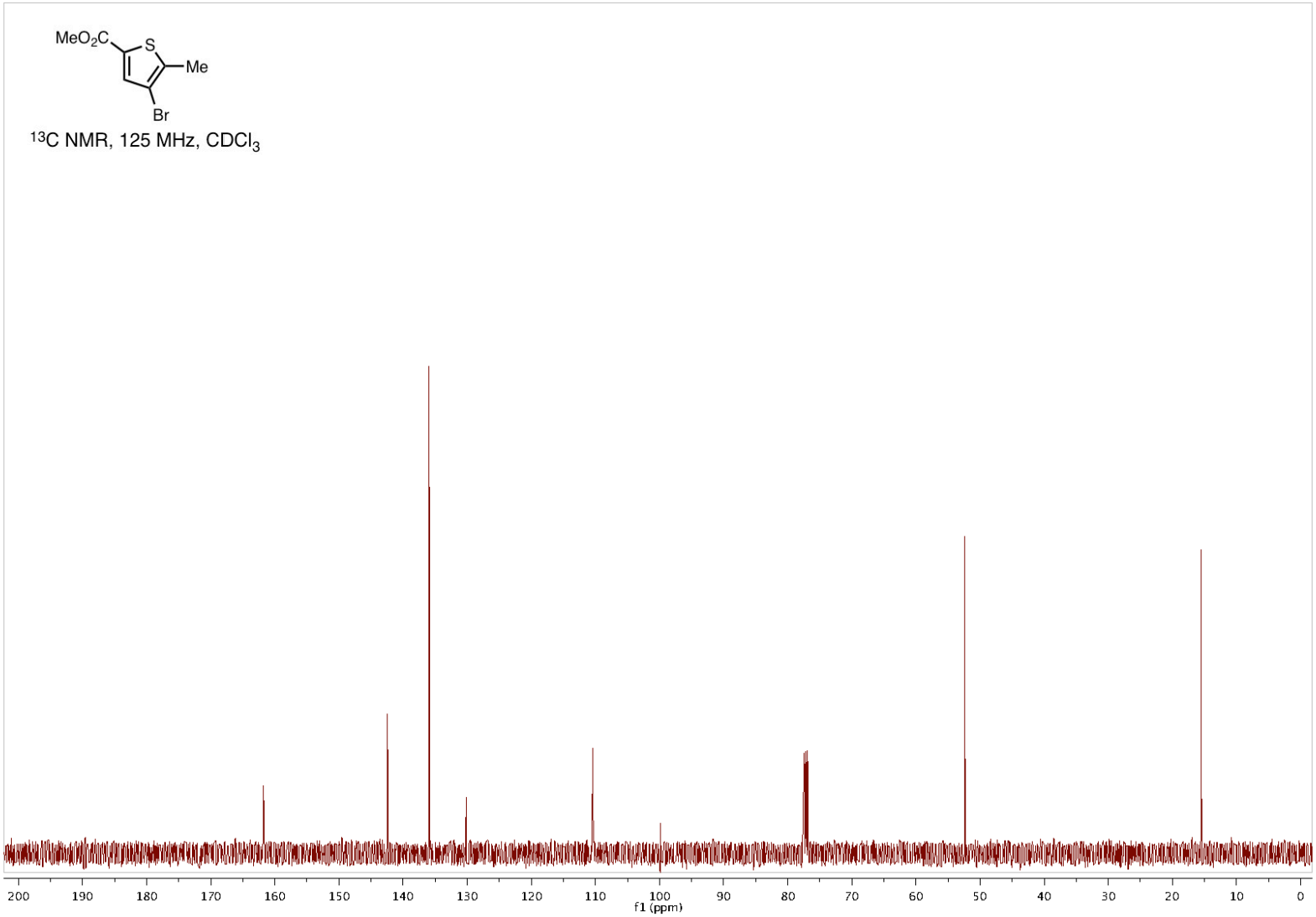
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10
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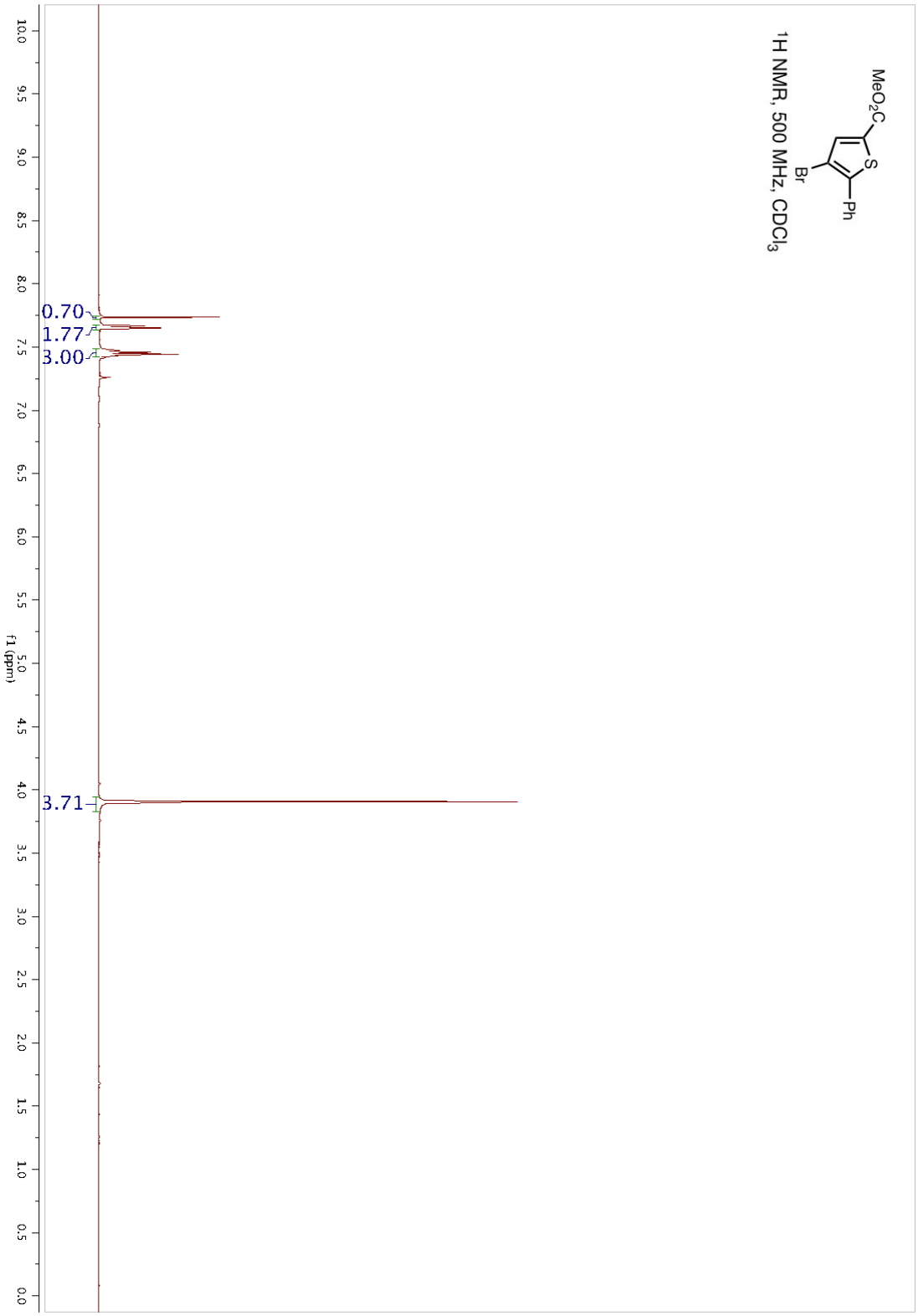
f1 (ppm)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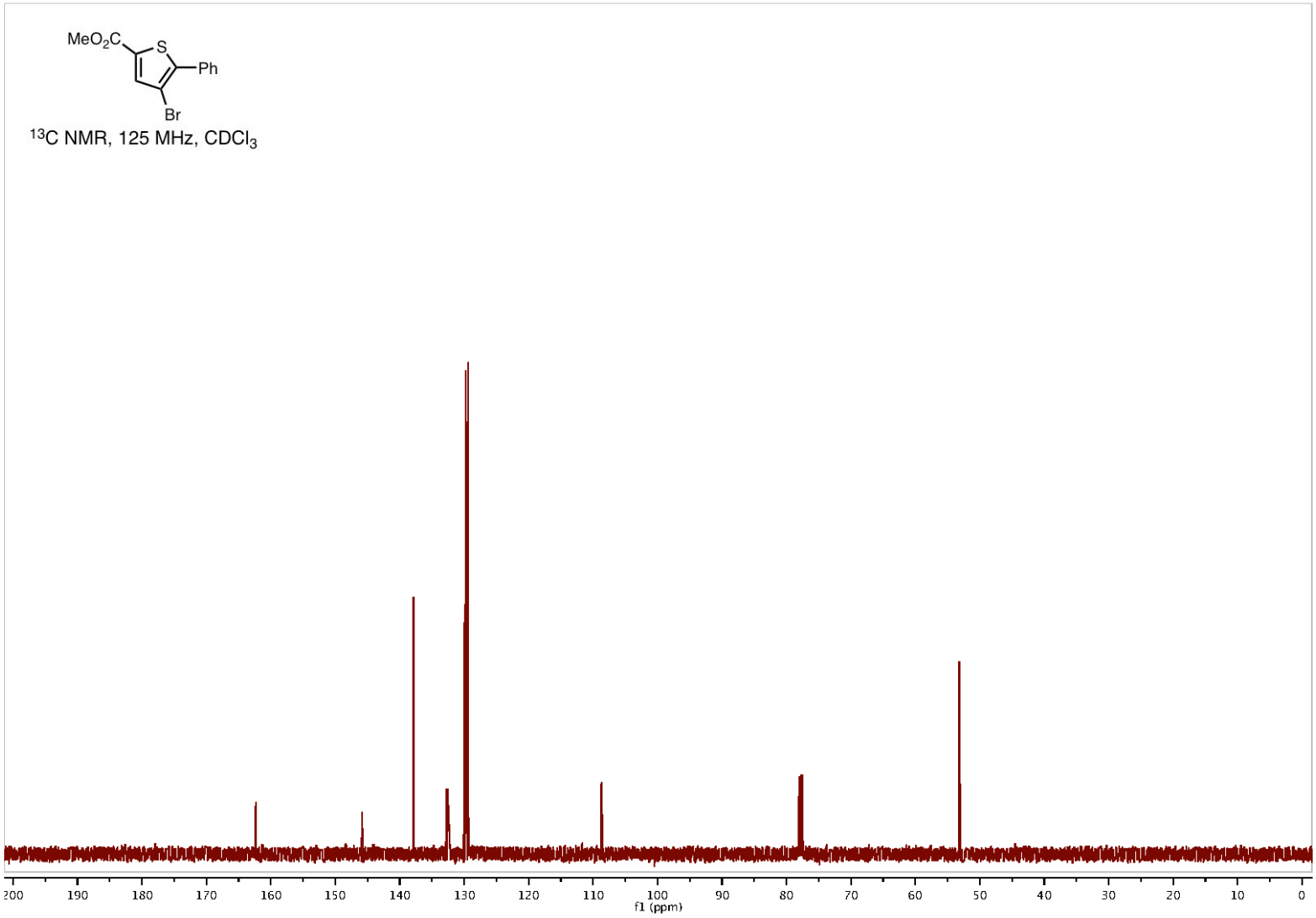
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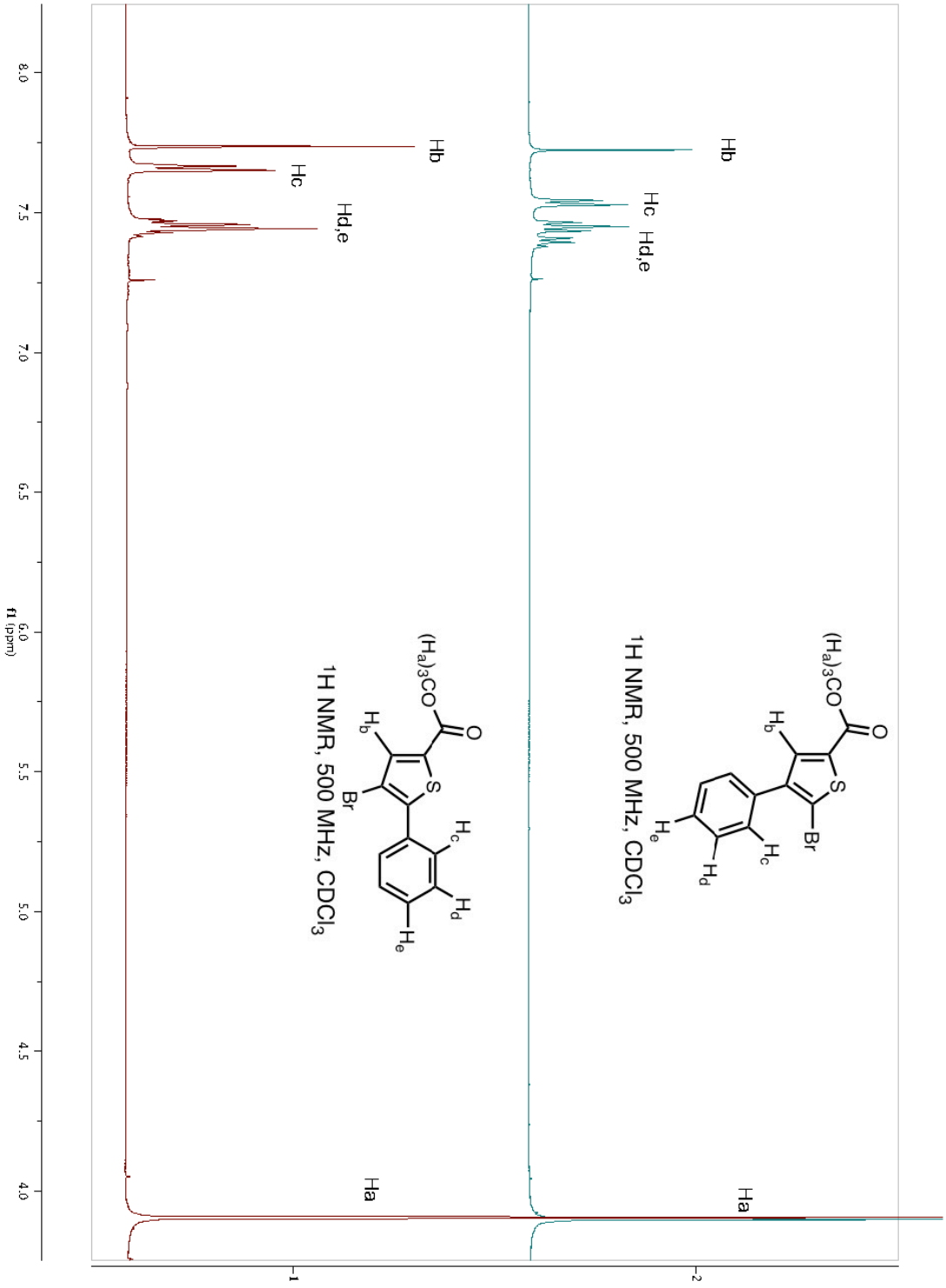
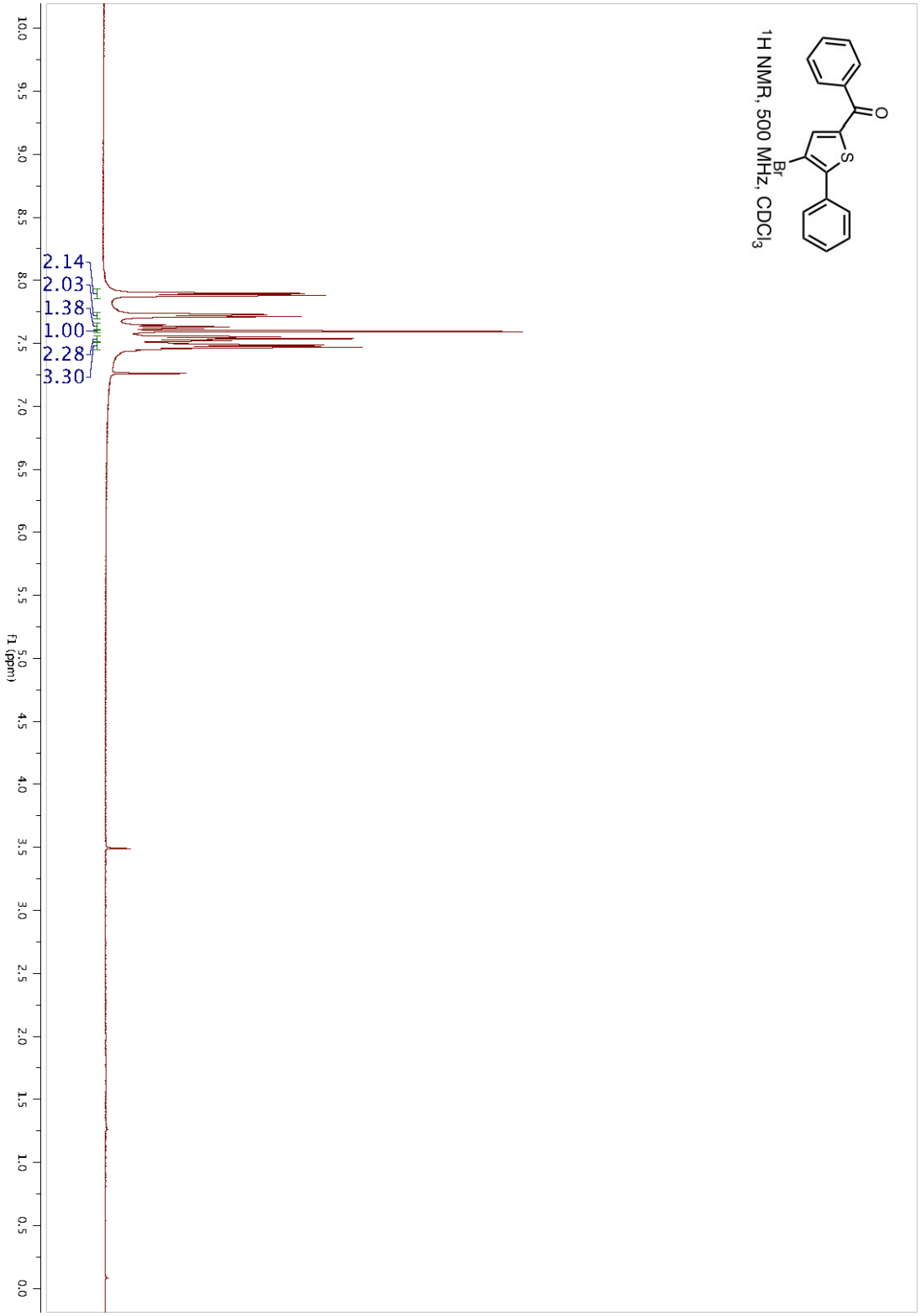
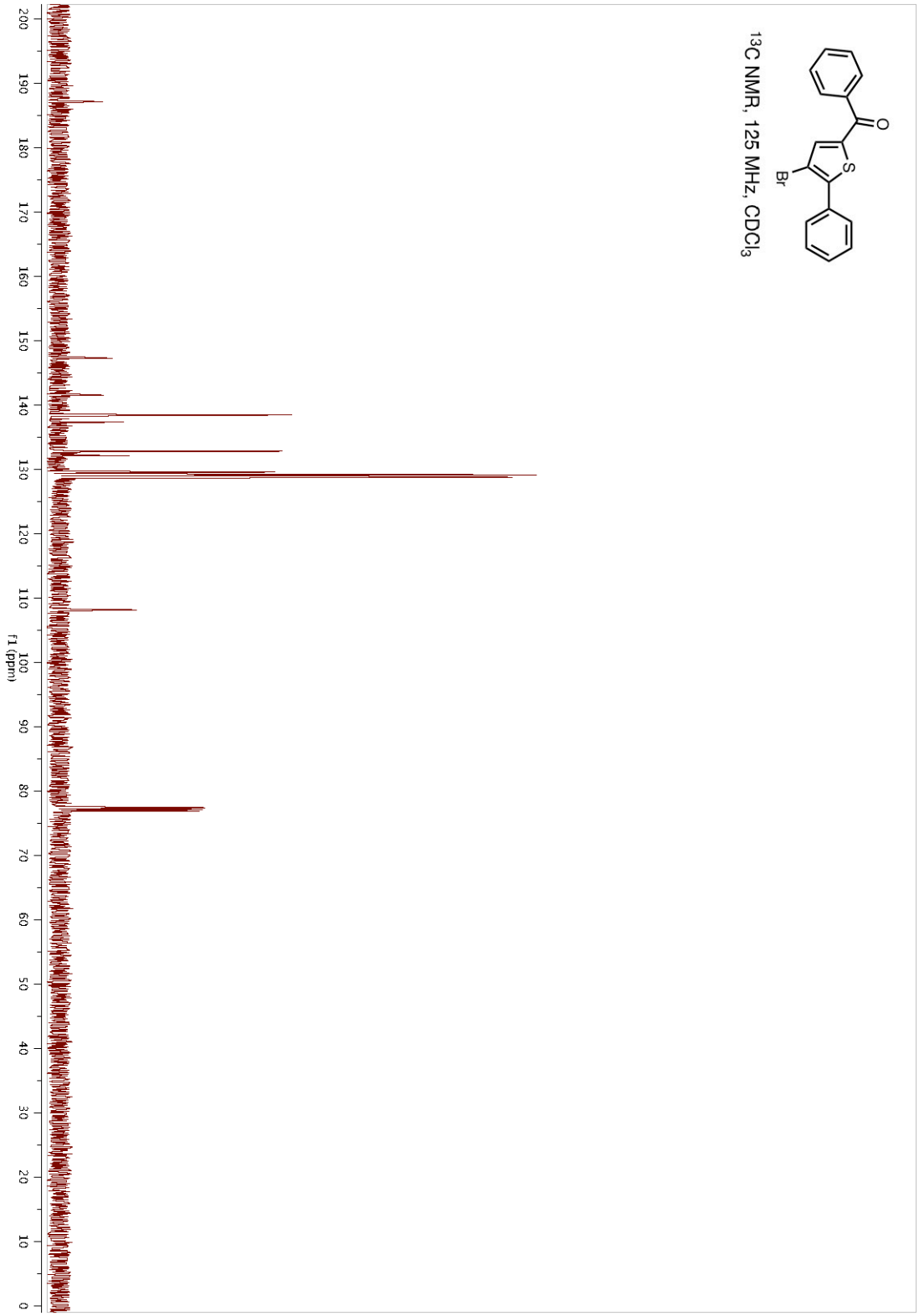
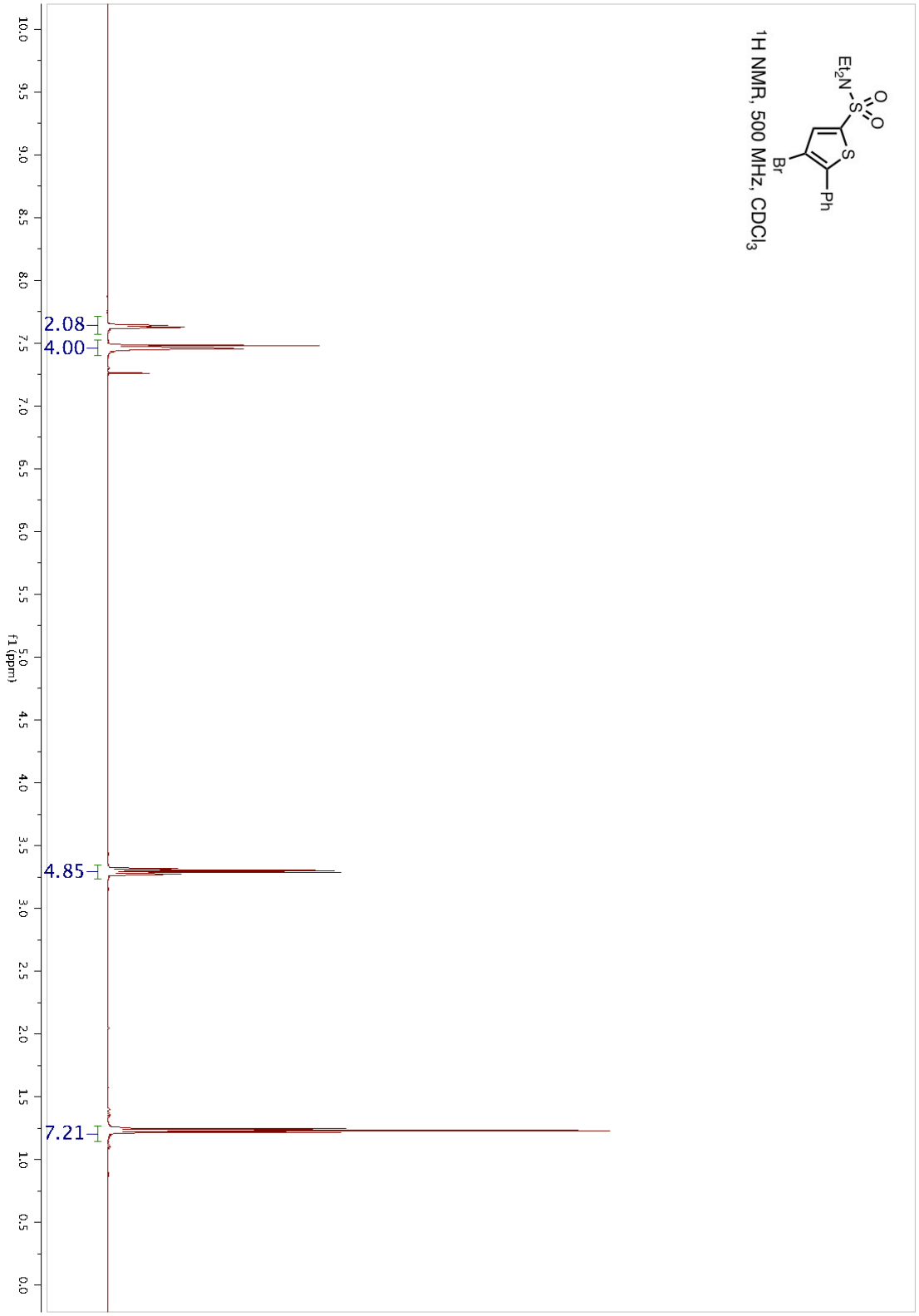
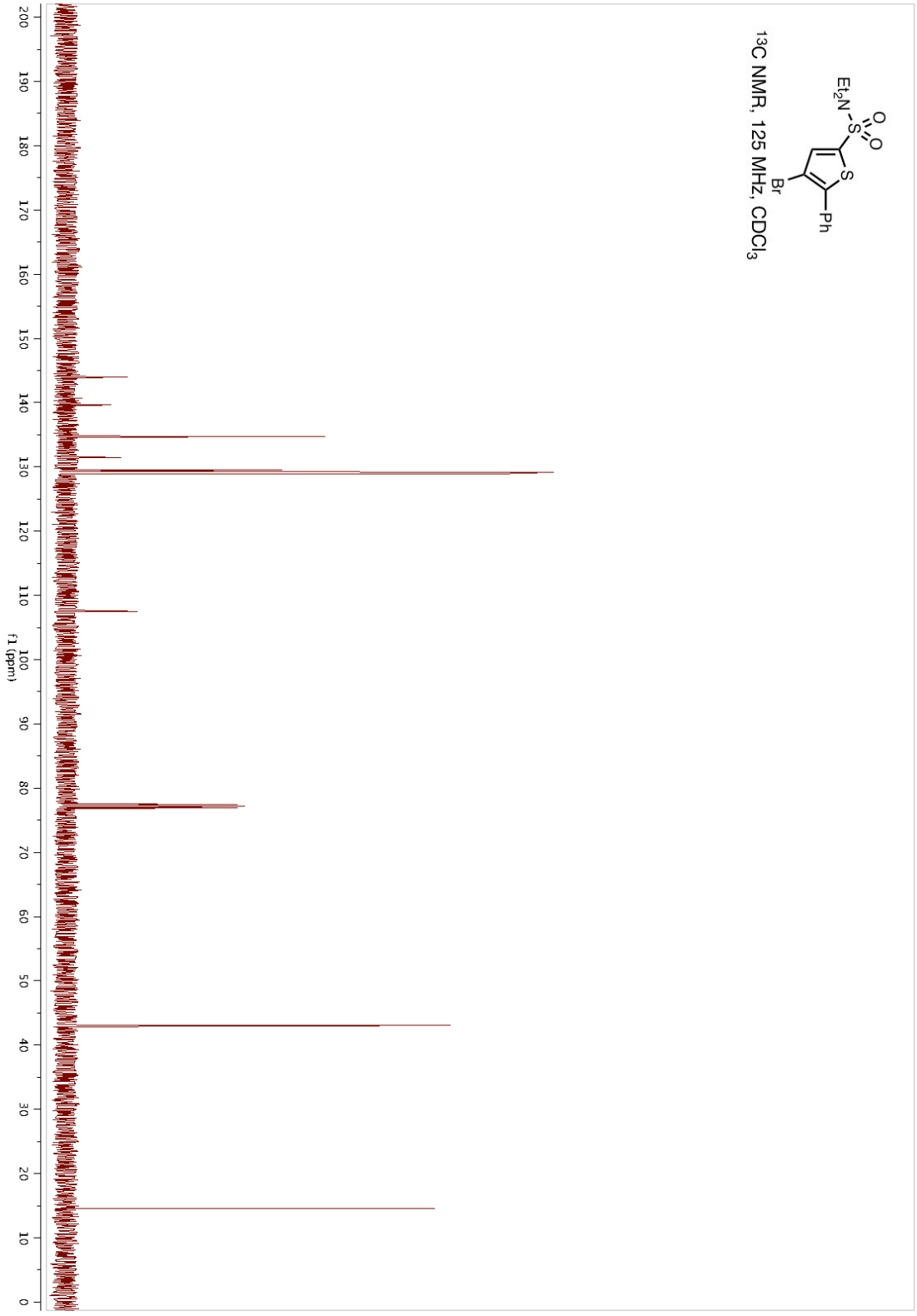
80
70
60
50
40
30
20
10
0
f1 (ppm)

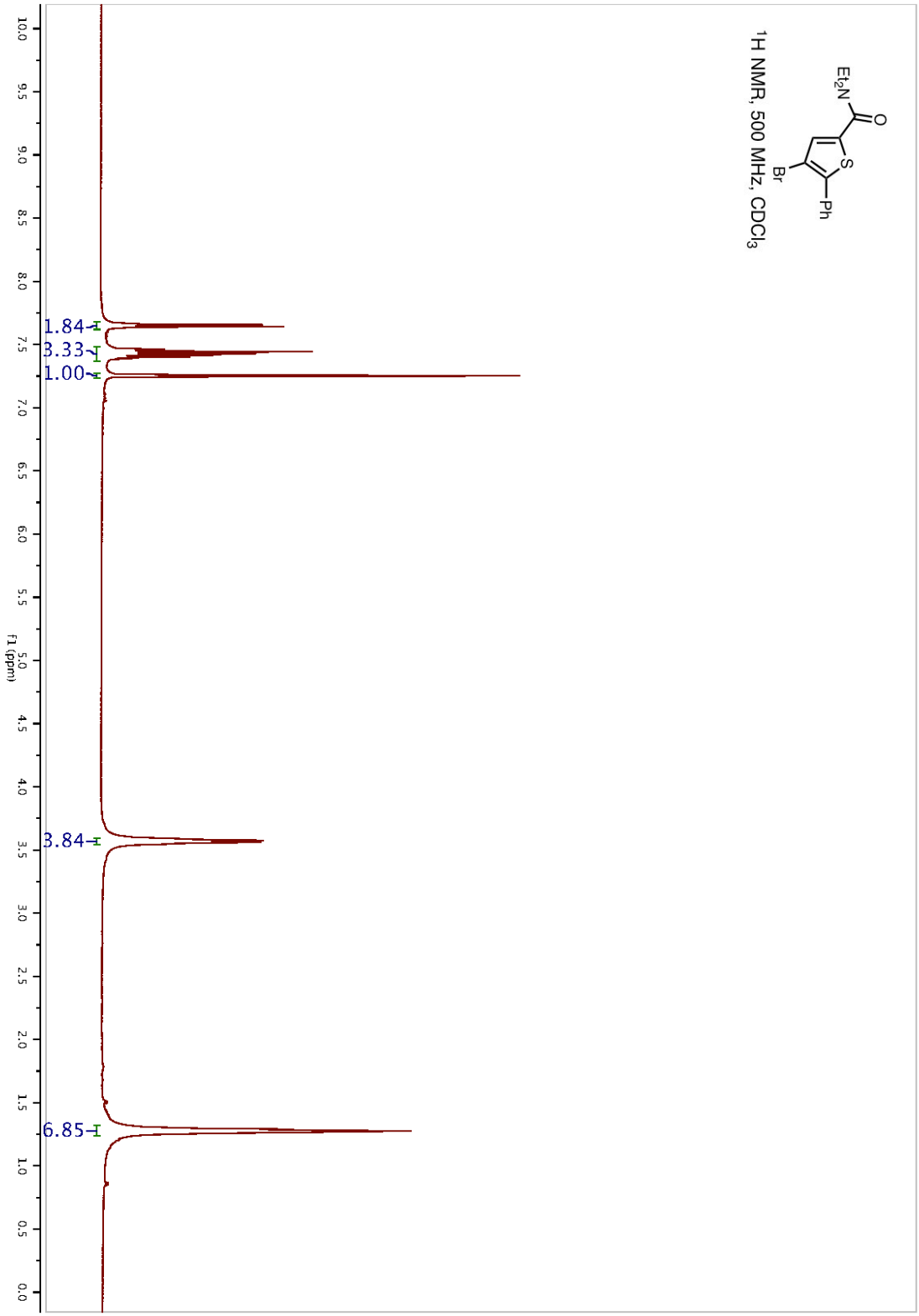

Hb
Hc
Hd,e
Ha
^{1}H NMR, 500 MHz, CDCl$_3$
$(H_a)_3CO$
O
H_b
S
Br
H_c
H_d
H_e
Hb
Hc
Hd,e
Ha
^{1}H NMR, 500 MHz, CDCl$_3$
$(H_a)_3CO$
O
H_b
S
Br
H_c
H_d
H_e
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
f1 (ppm)
2
1

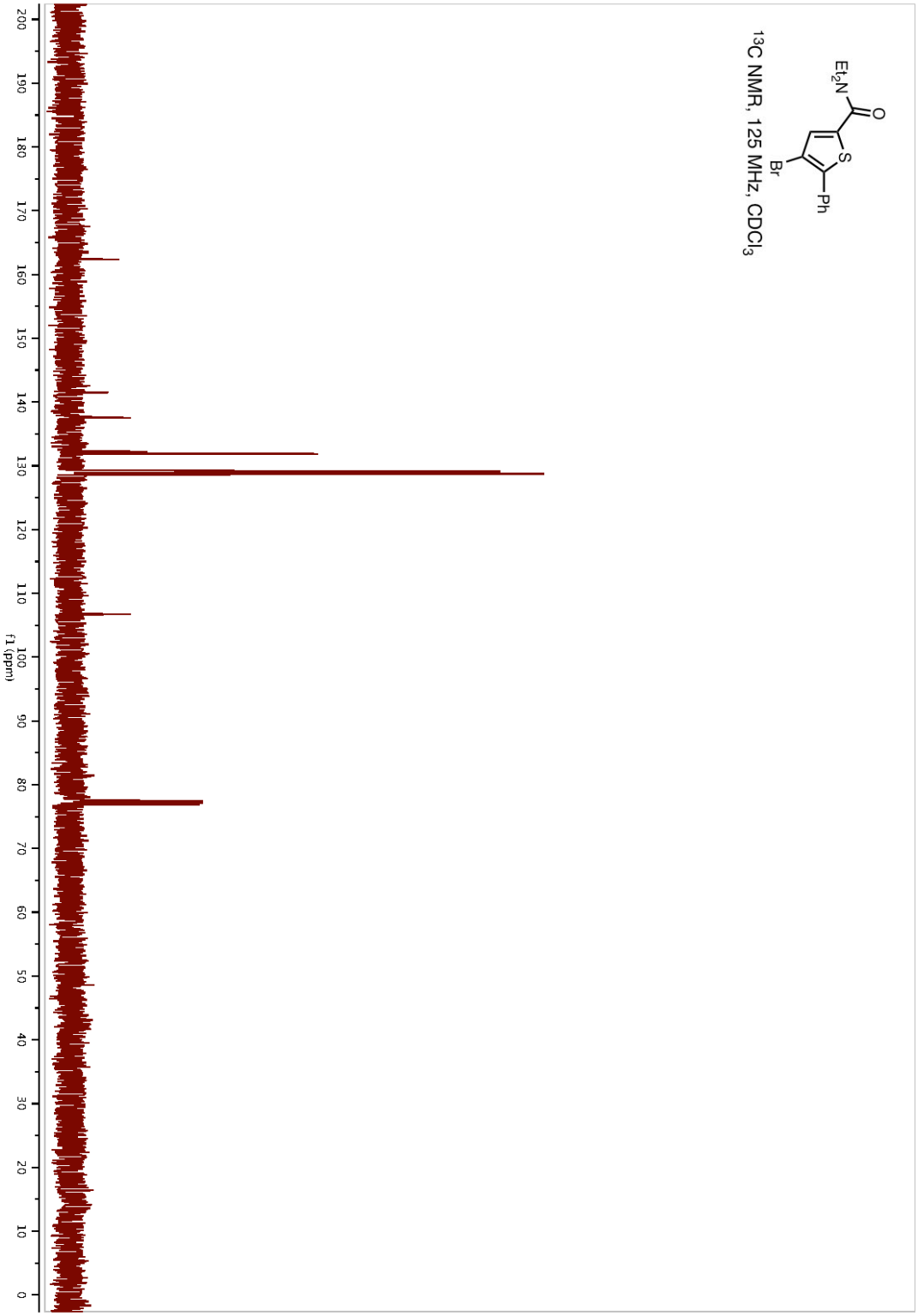

^{1}H NMR, 500 MHz, $CDCl_3$
O
S
Br
2.14
2.03
1.38
1.00
2.28
3.30
f1 (ppm)

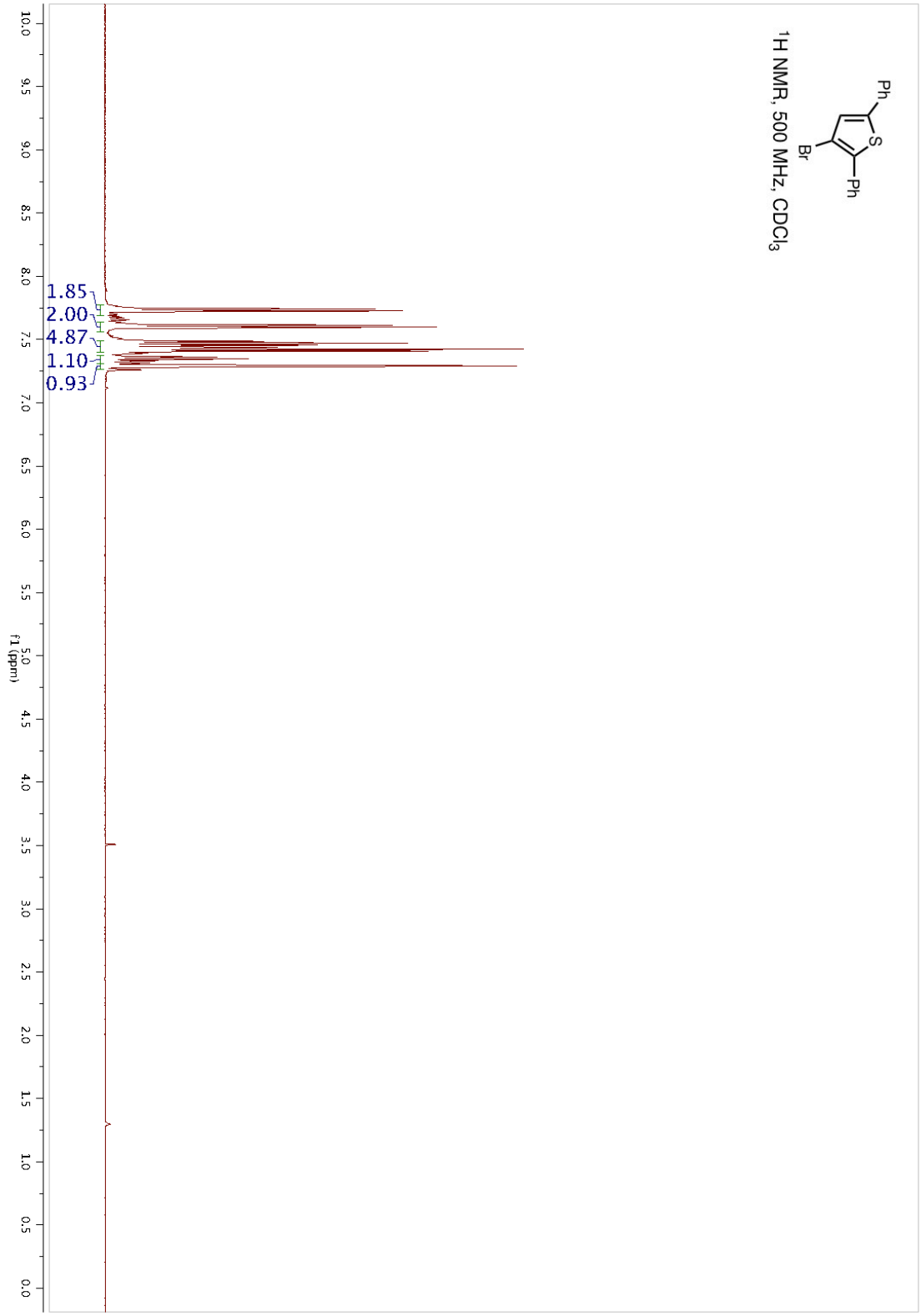

^{13}C NMR, 125 MHz, $CDCl_3$
O
S
Br
f1 (ppm)
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0

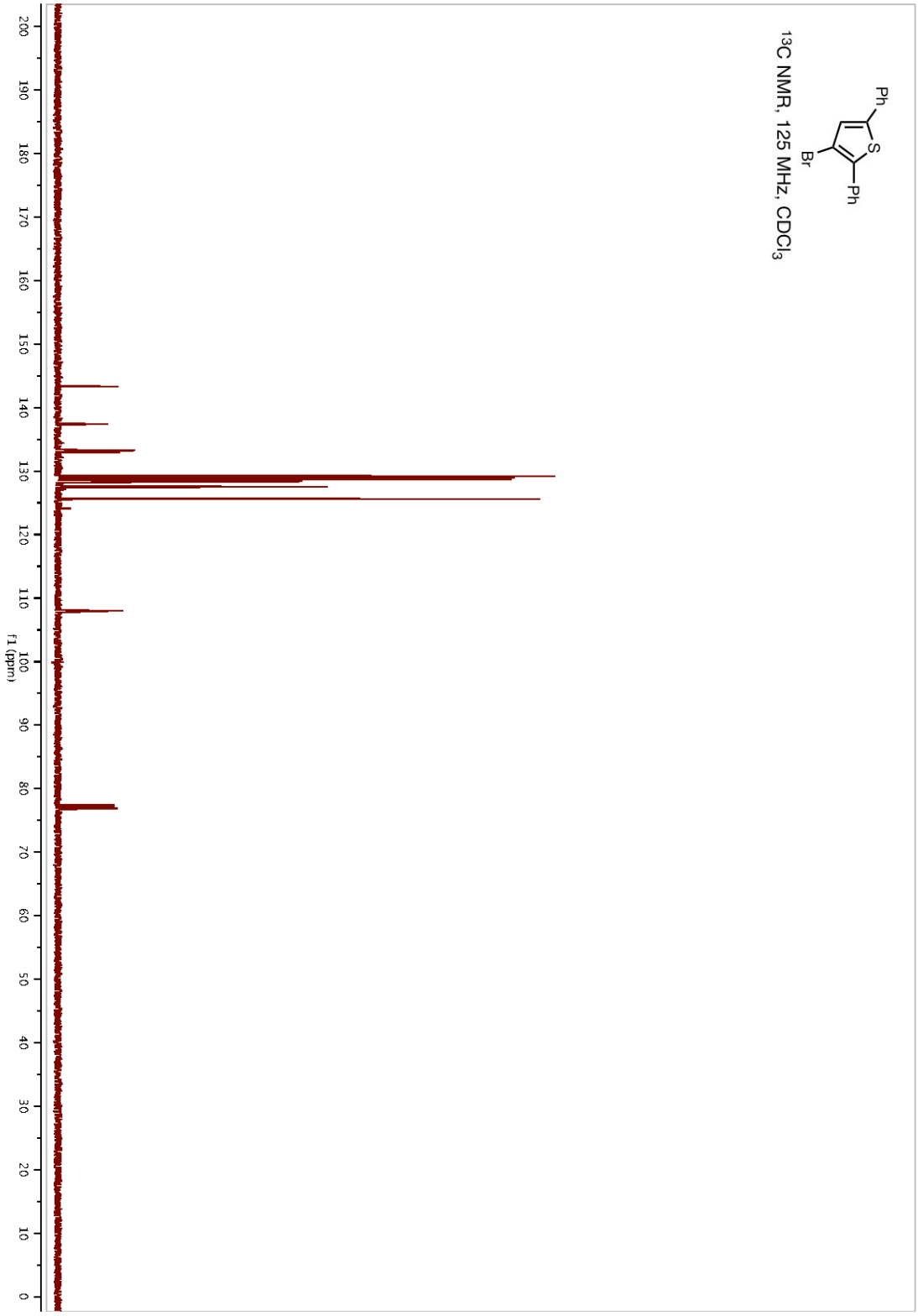

^{1}H NMR, 500 MHz, CDCl$_3$
Et$_2$N
S
O
O
S
Br
Ph
2.08
4.00
4.85
7.21
f1 (ppm)

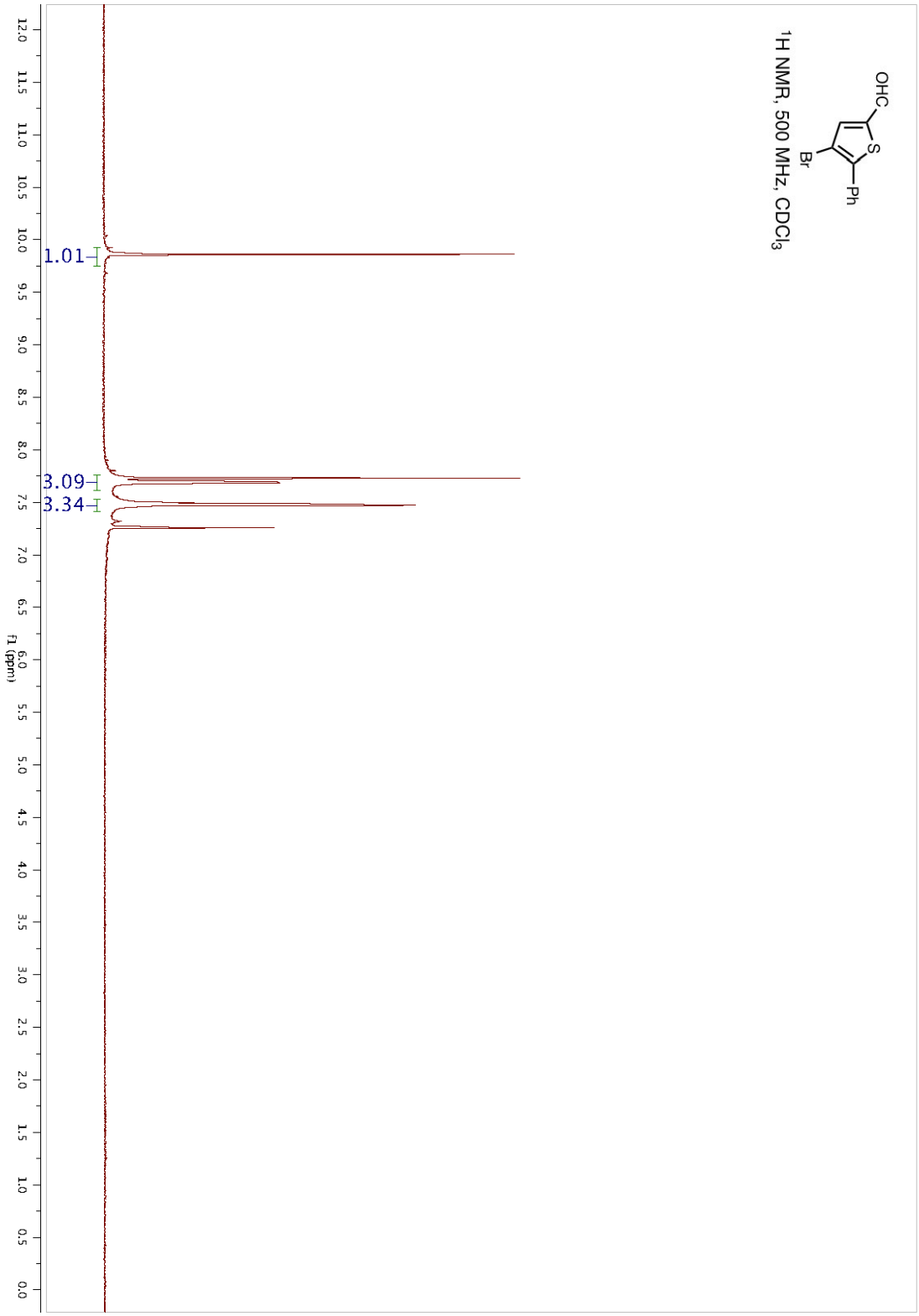

^{13}C NMR, 125 MHz, CDCl$_3$
f1 (ppm)

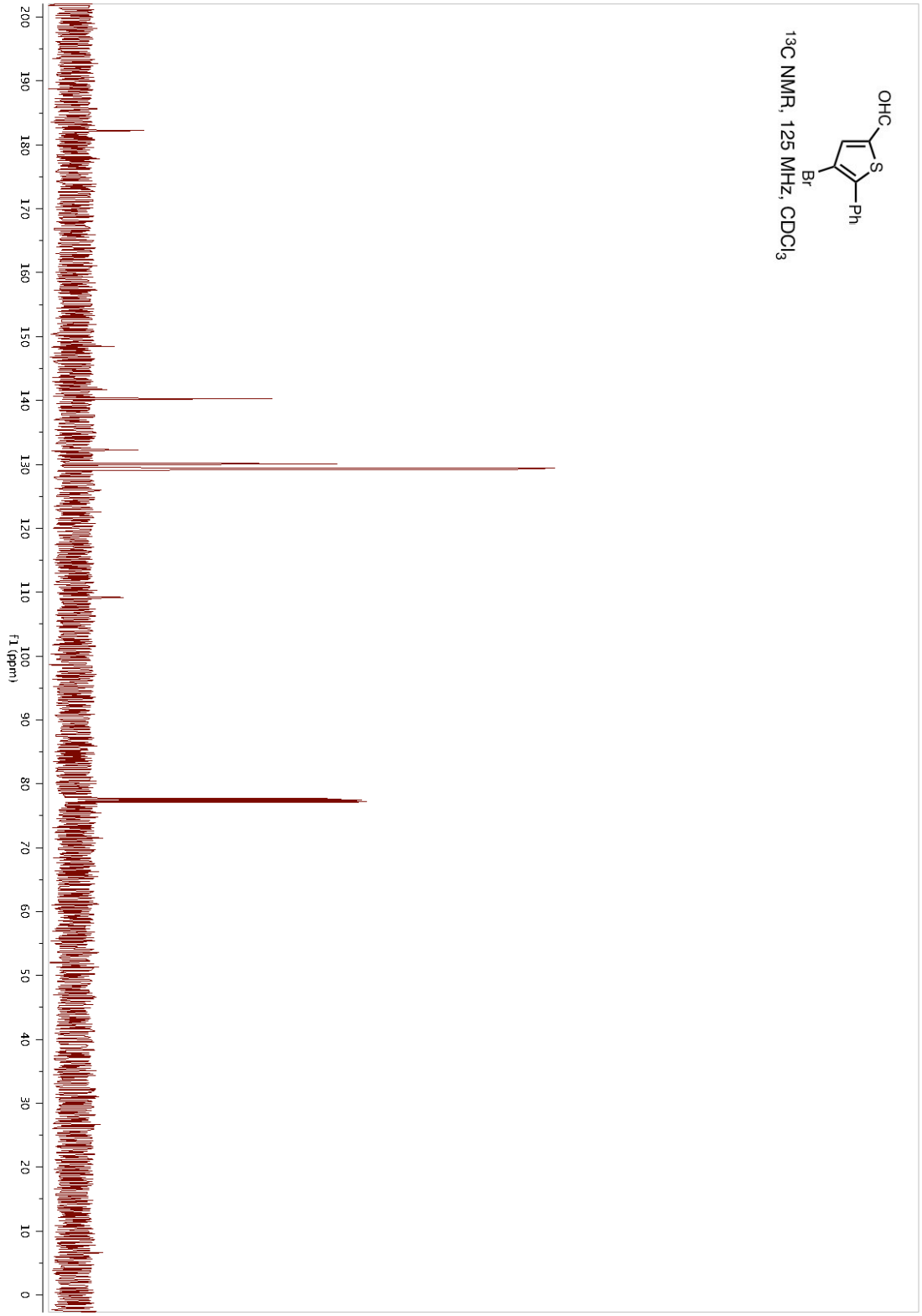

^{1}H NMR, 500 MHz, CDCl$_3$
Et$_2$N
O
S
Br
Ph
1.84
3.33
1.00
3.84
6.85
f1 (ppm)

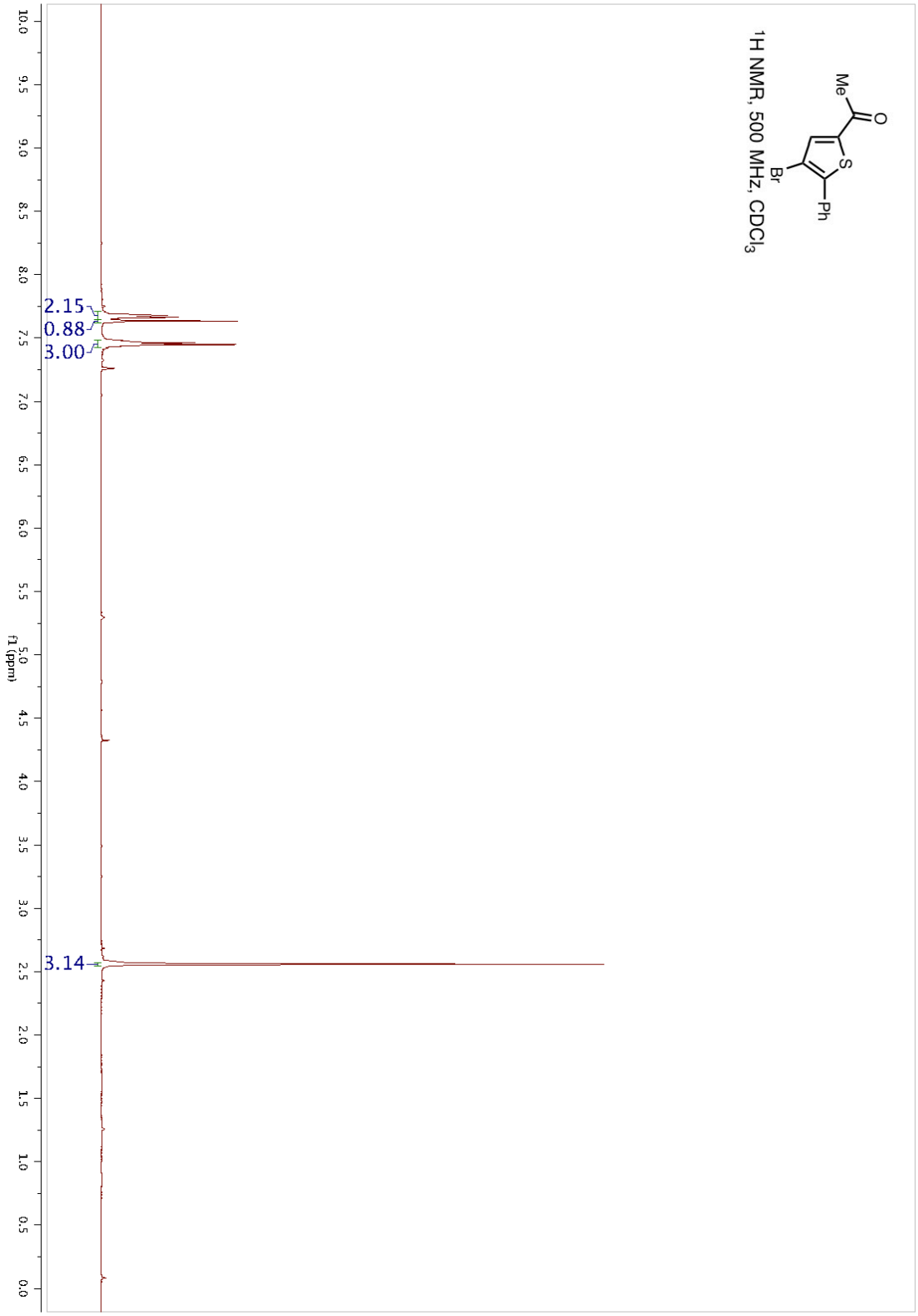

Et2N
O
S
Br
Ph
13C NMR, 125 MHz, CDCl3
f1 (ppm)
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0

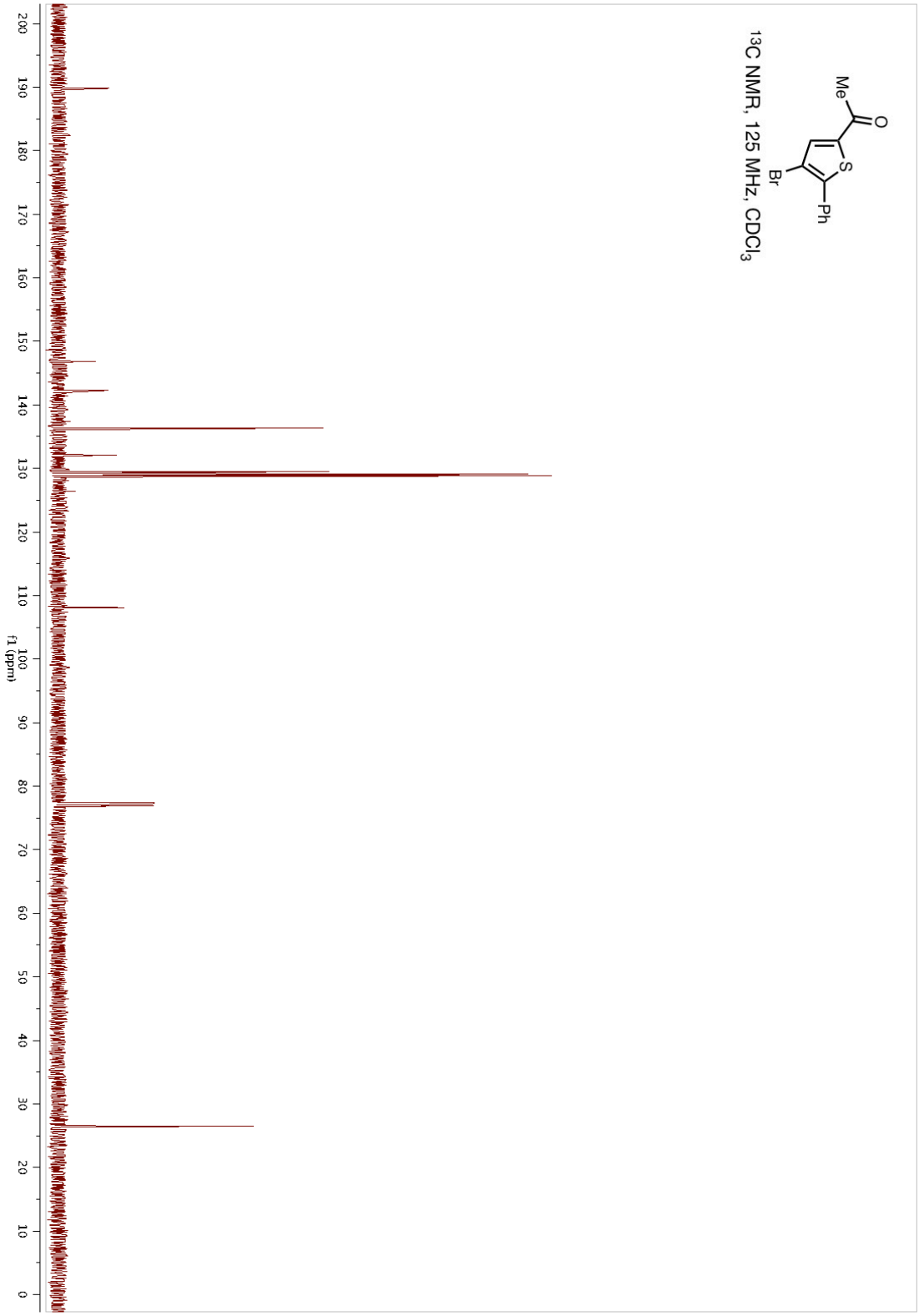

^{1}H NMR, 500 MHz, $CDCl_3$
Ph
S
Br
Ph
1.85
2.00
4.87
1.10
0.93
f1 (ppm)
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0

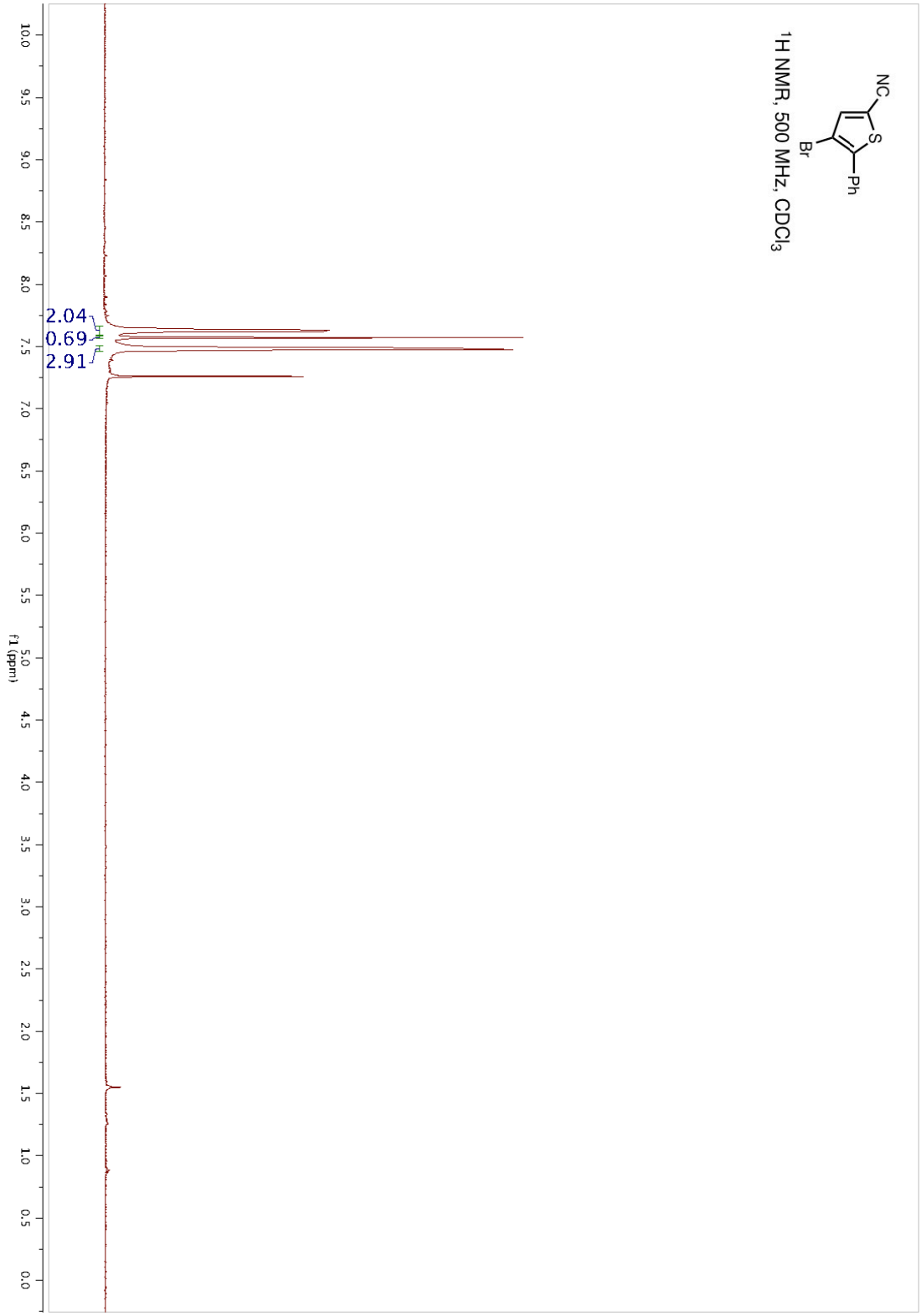

Ph
S
Br
Ph
^{13}C NMR, 125 MHz, $CDCl_3$
f1 (ppm)
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0

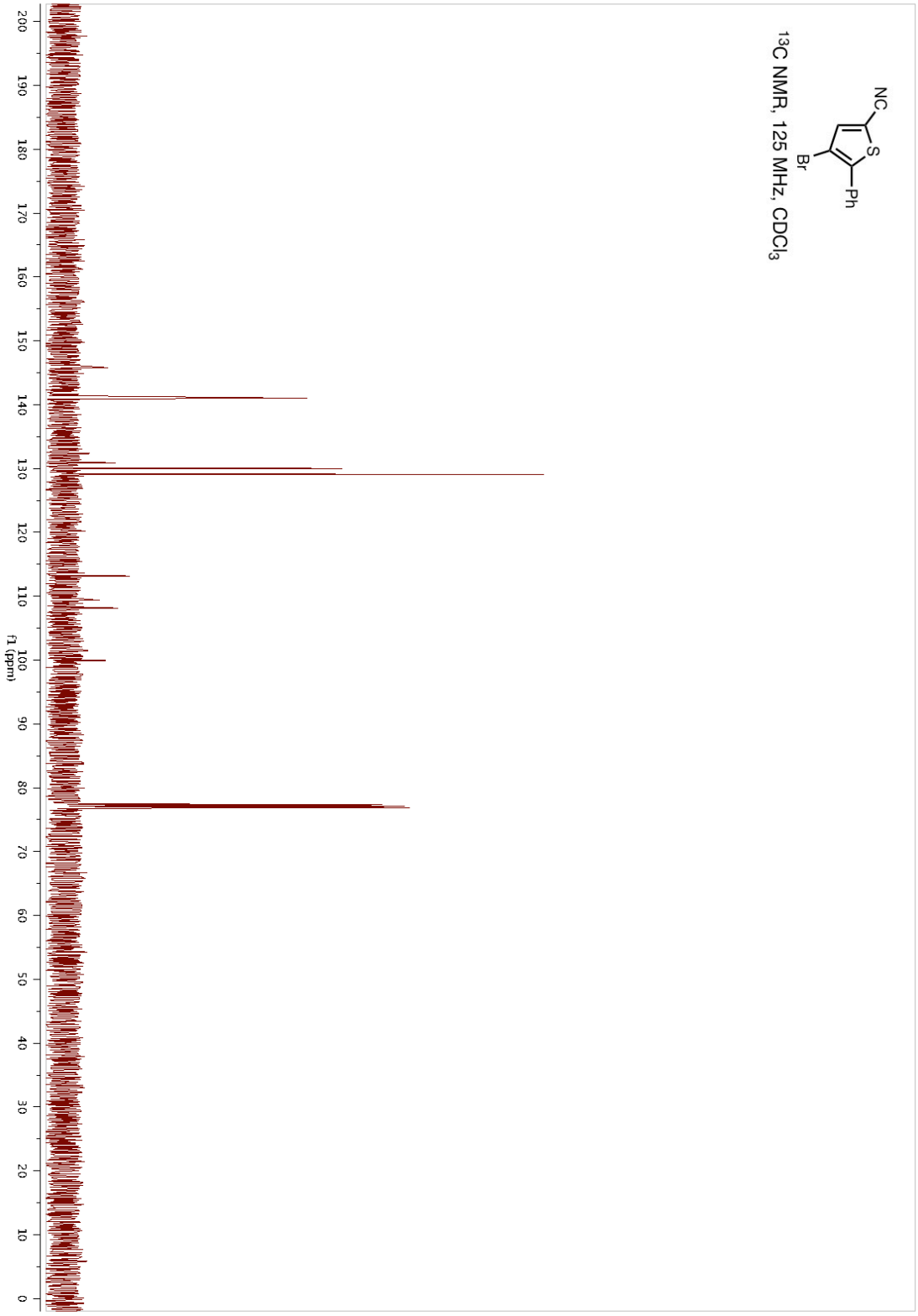

^{1}H NMR, 500 MHz, CDCl$_3$
OHC
S
Br
Ph
1.01
3.09
3.34
f1 (ppm)

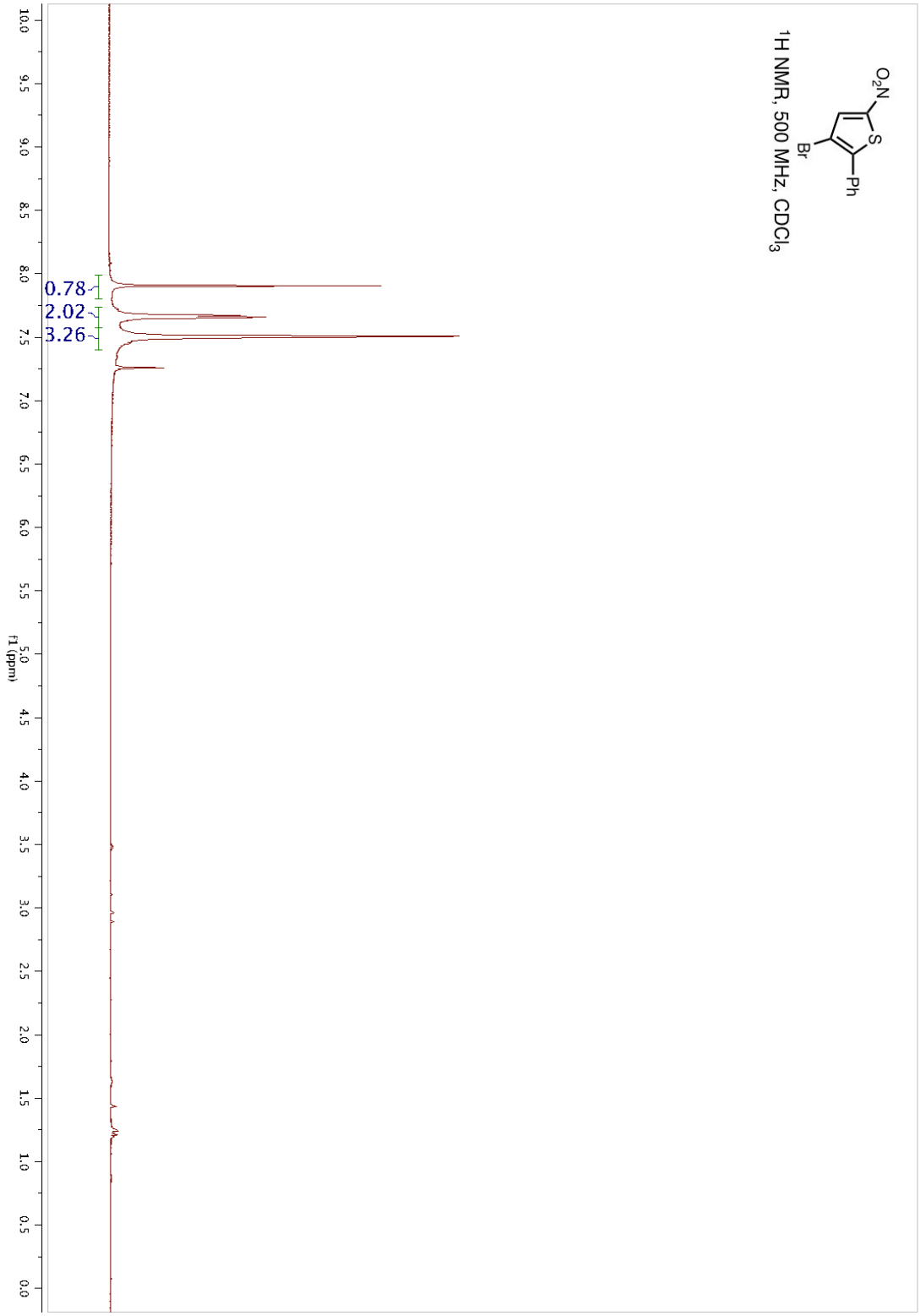

OHC
S
Br
Ph
^{13}C NMR, 125 MHz, $CDCl_3$
f1 (ppm)
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0

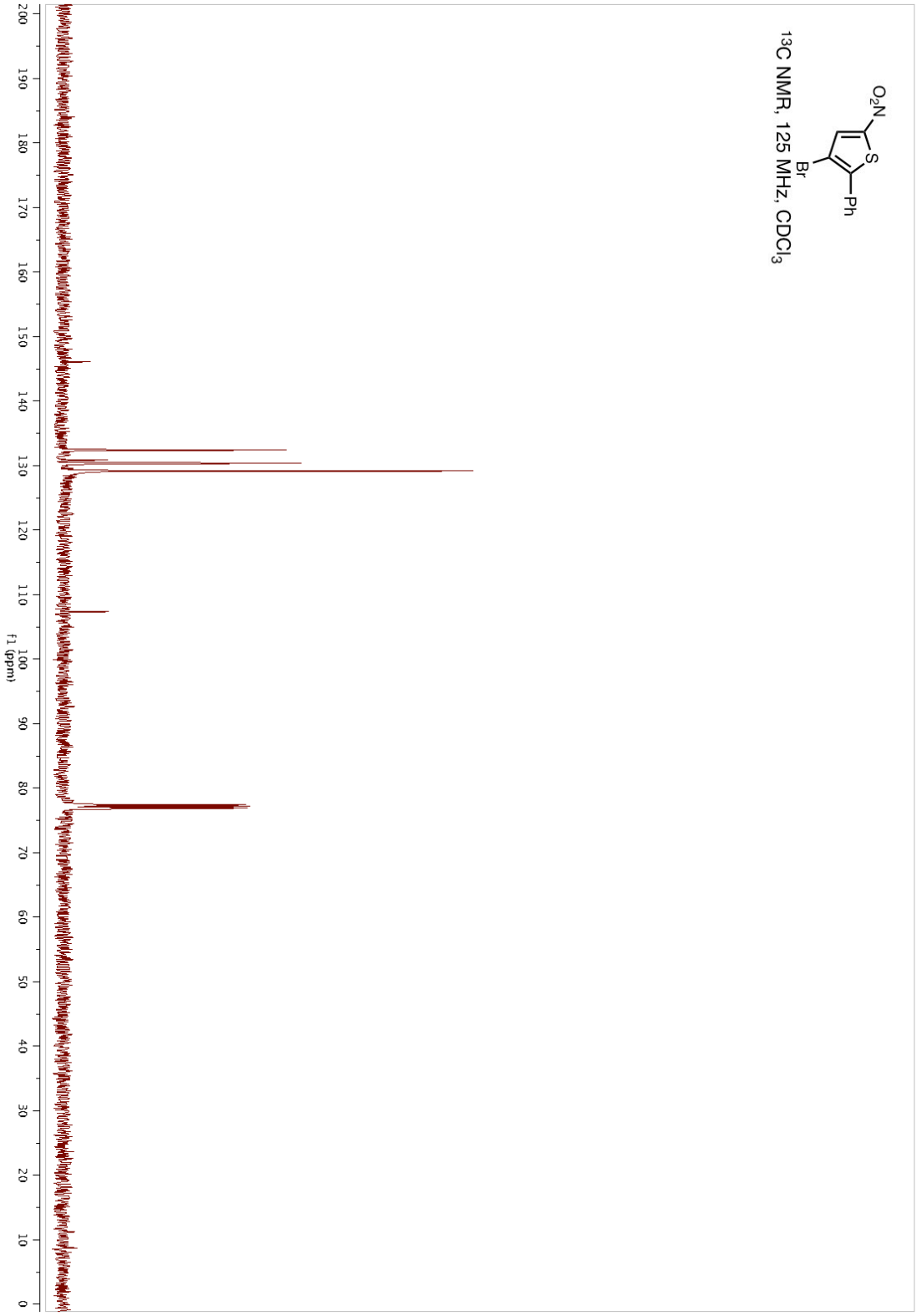

^{1}H NMR, 500 MHz, $CDCl_3$
Me
O
S
Br
Ph
2.15
0.88
3.00
3.14
f1 (ppm)

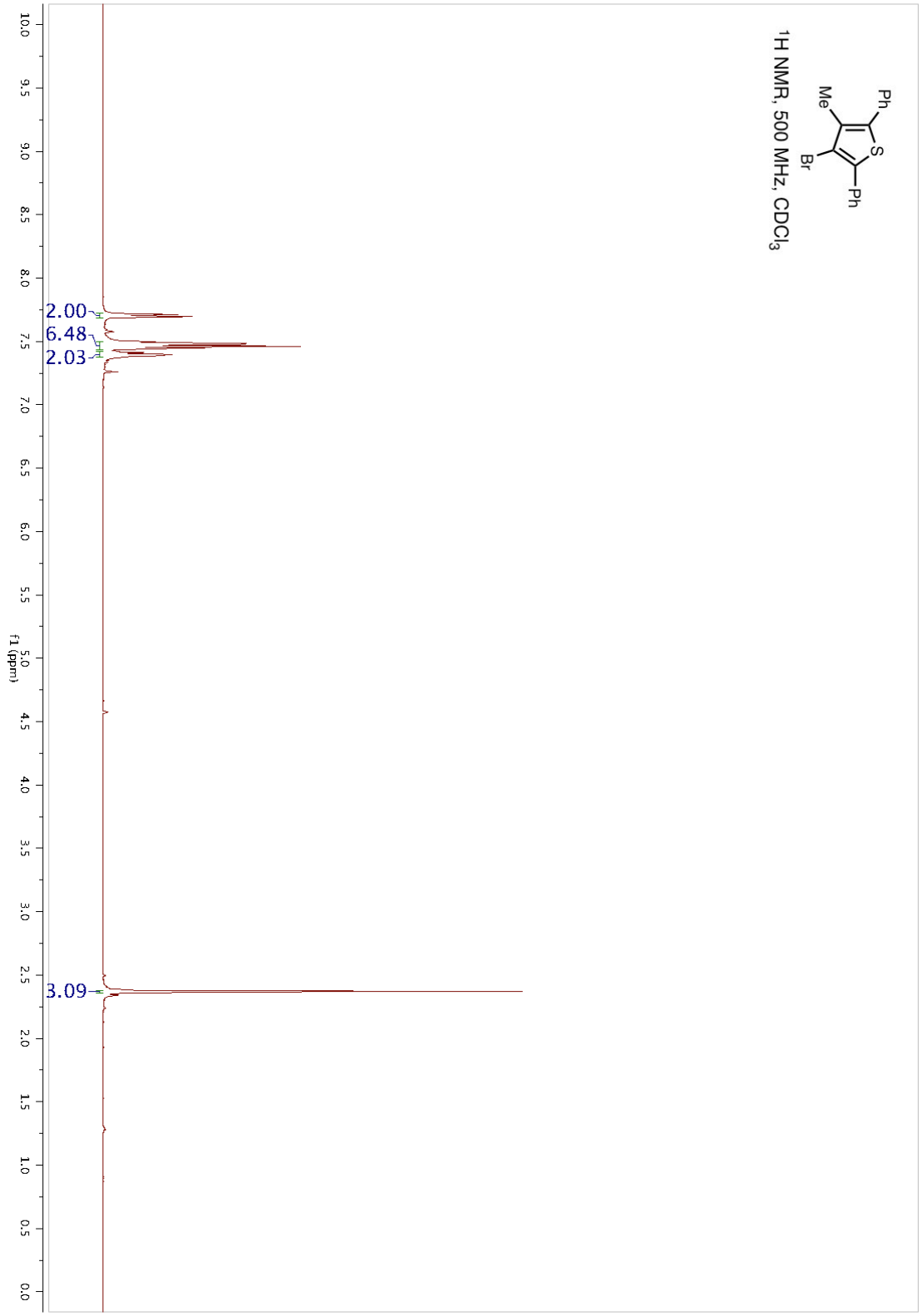

Me
O
S
Br
Ph
^{13}C NMR, 125 MHz, $CDCl_3$
f1 (ppm)
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0

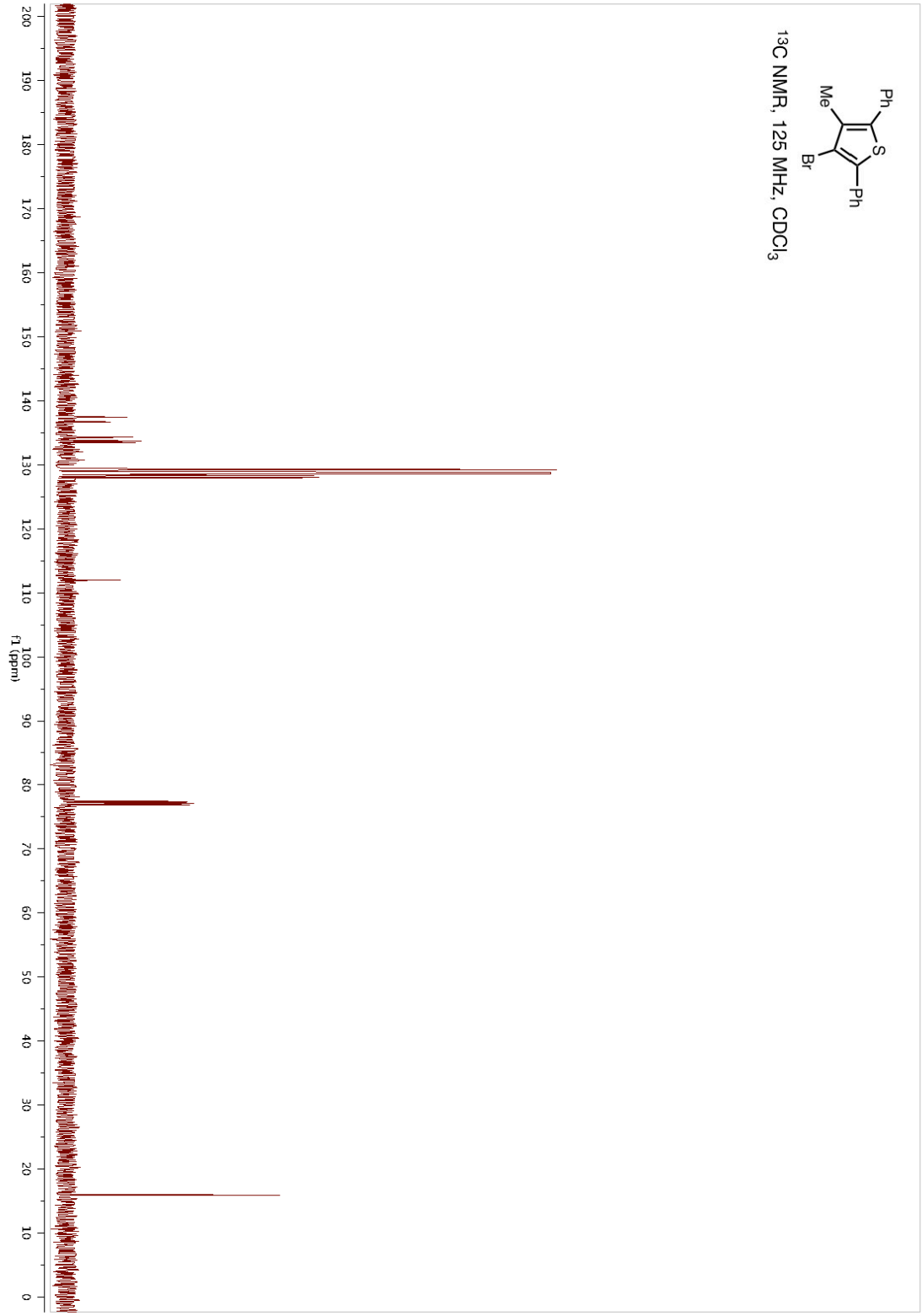

^{1}H NMR, 500 MHz, $CDCl_3$
NC
S
Ph
Br
2.04
0.69
2.91
f1 (ppm)

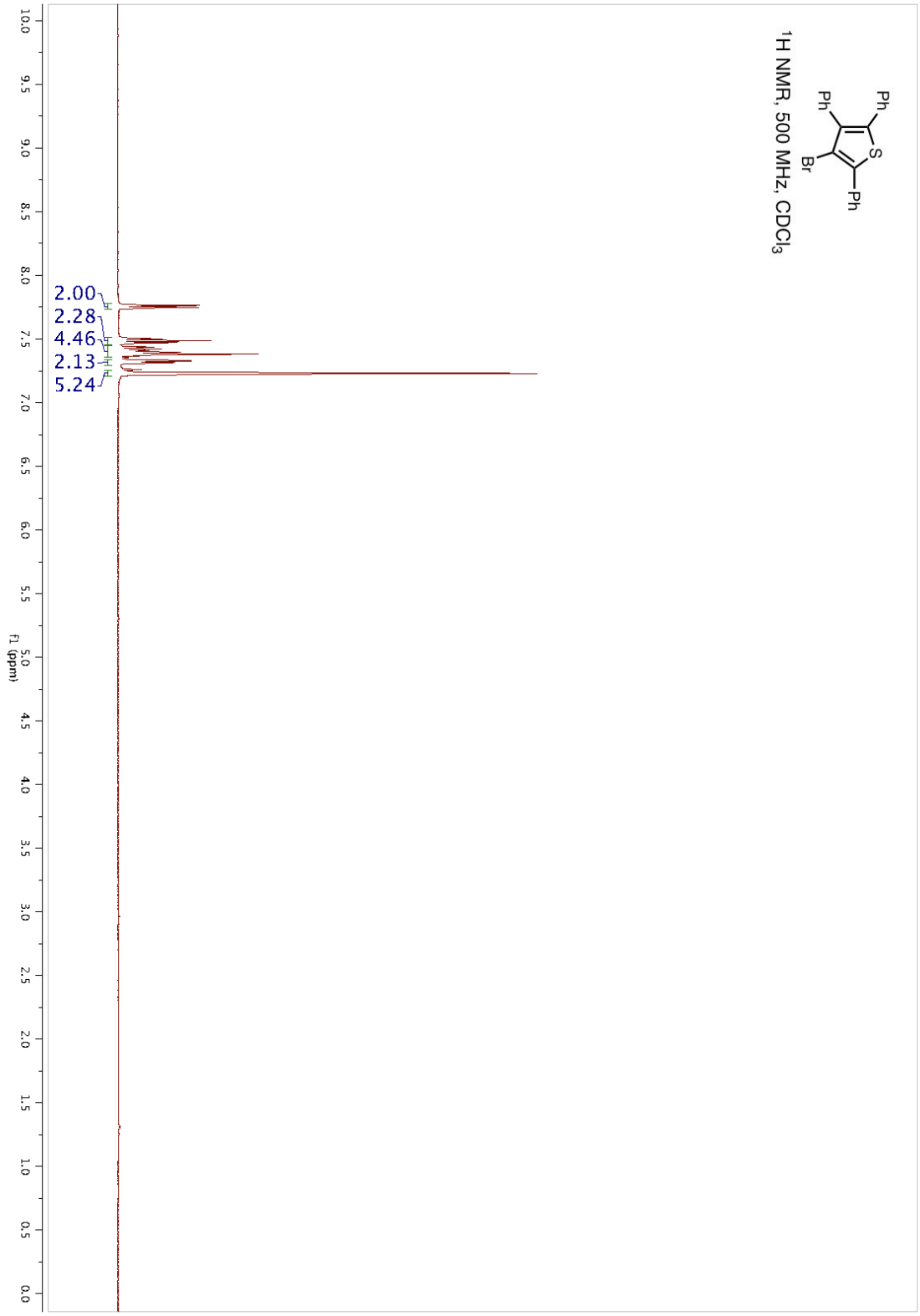

NC
S
Ph
Br
^{13}C NMR, 125 MHz, $CDCl_3$
f1 (ppm)
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0

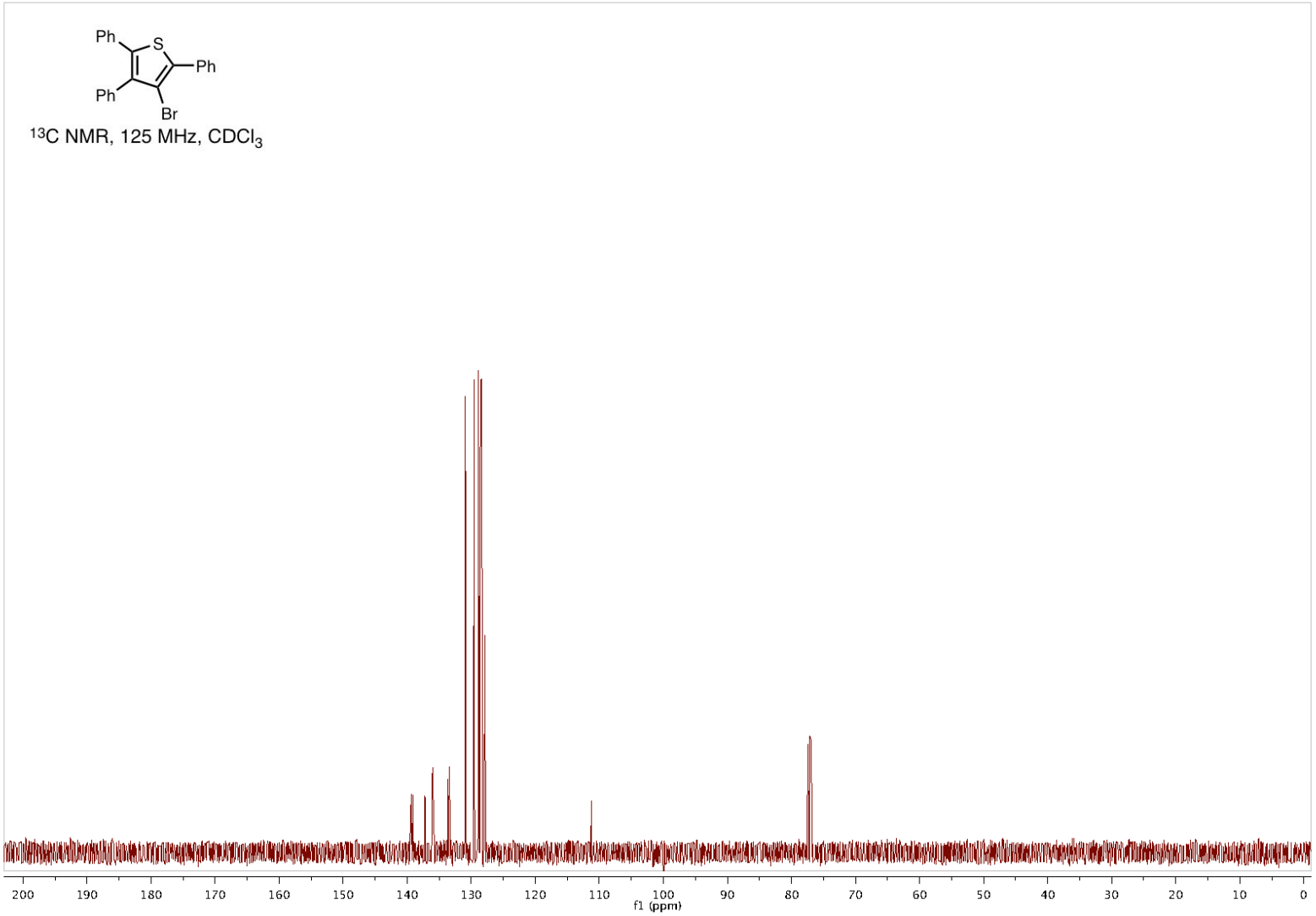

^{1}H NMR, 500 MHz, $CDCl_3$
O_2N
S
Br
Ph
0.78
2.02
3.26
f1 (ppm)
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0

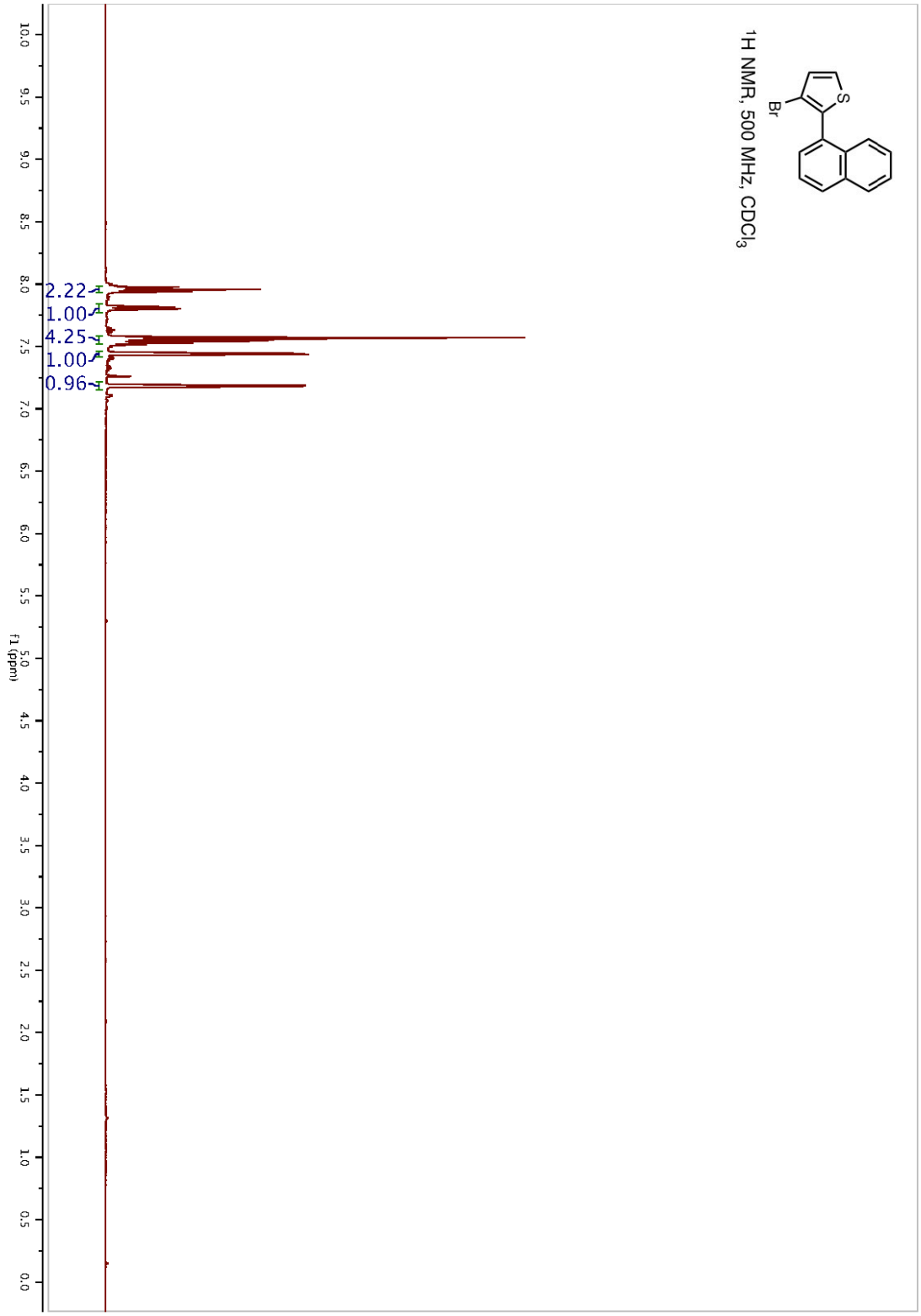

^{13}C NMR, 125 MHz, CDCl$_3$
O$_2$N
S
Ph
Br
f1 (ppm)
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0

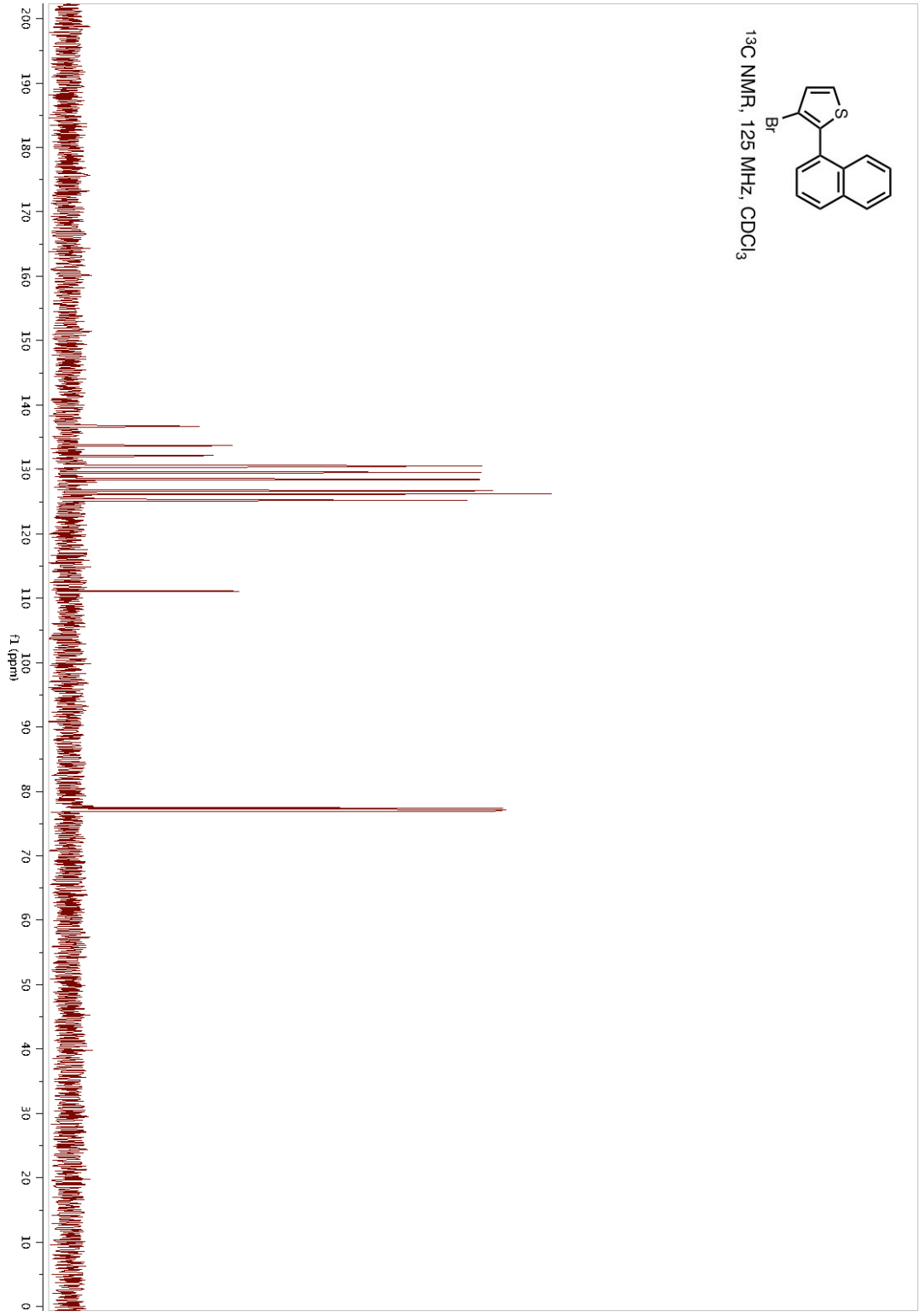

^{1}H NMR, 500 MHz, CDCl$_3$
Ph
Me
S
Br
Ph
2.00
6.48
2.03
3.09
f1 (ppm)

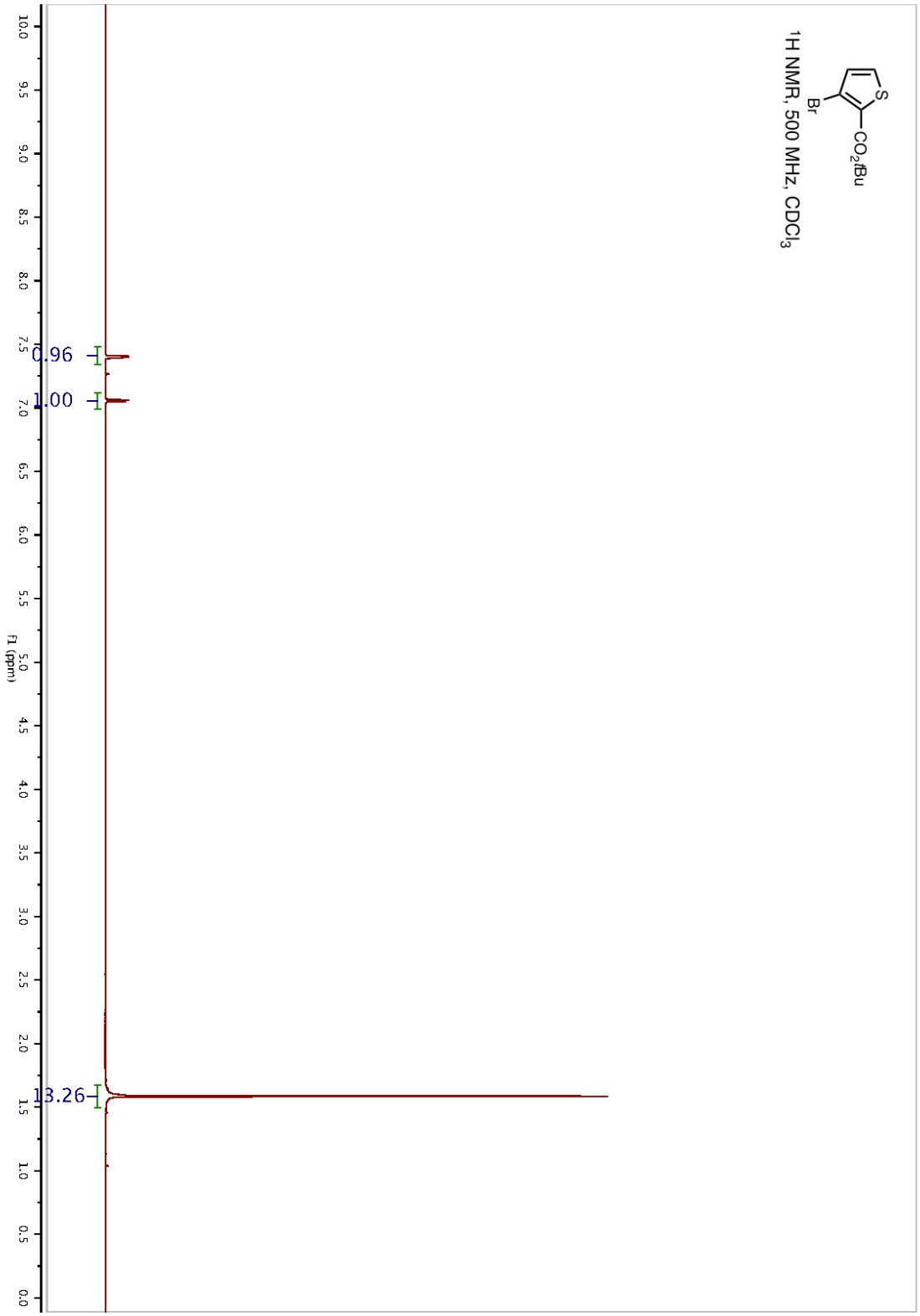

Ph
Me
S
Br
Ph
^{13}C NMR, 125 MHz, $CDCl_3$
f1 (ppm)
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0

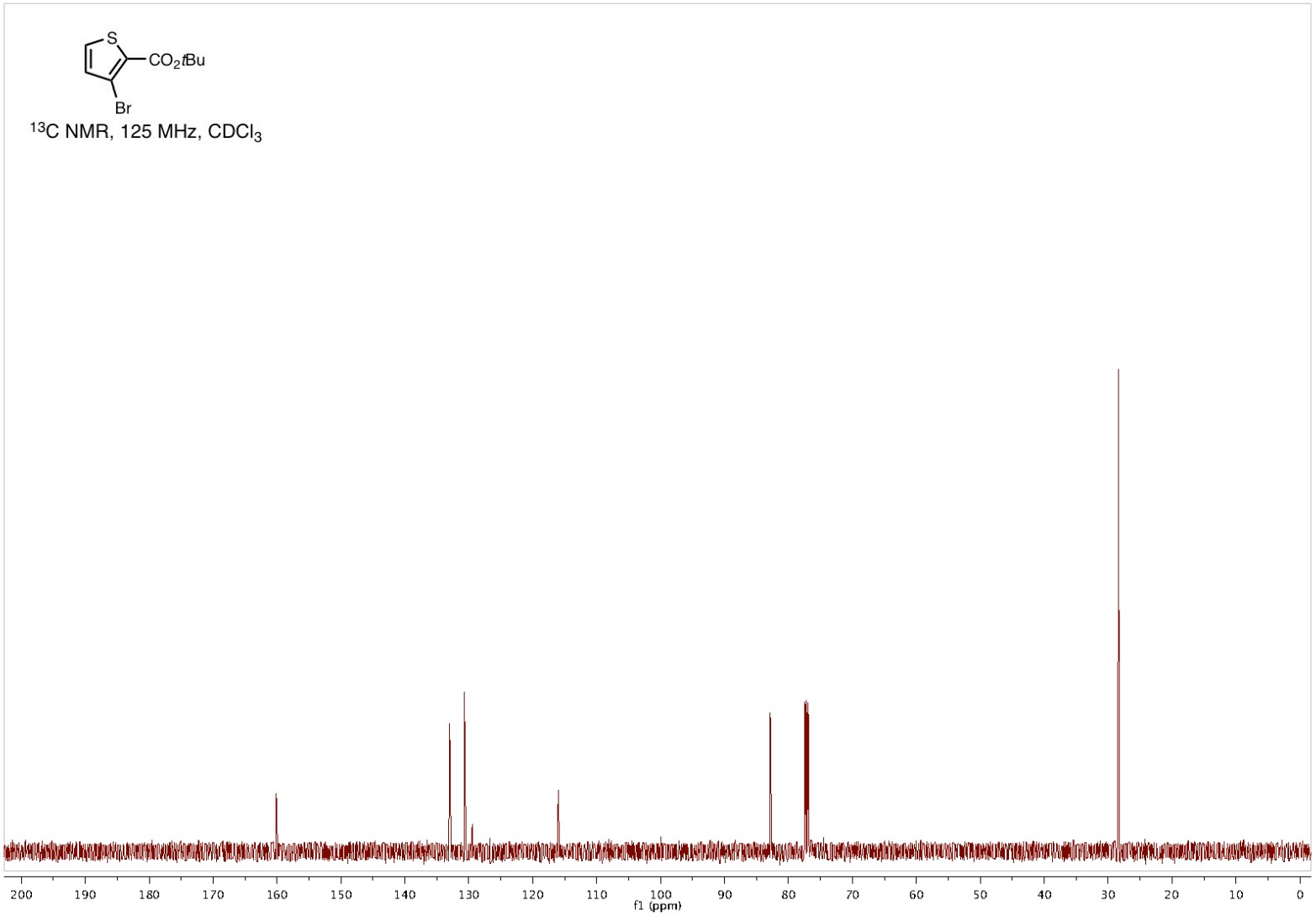

^{1}H NMR, 500 MHz, $CDCl_3$
Ph
Ph
S
Br
Ph
2.00
2.28
4.46
2.13
5.24
f1 (ppm)
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0

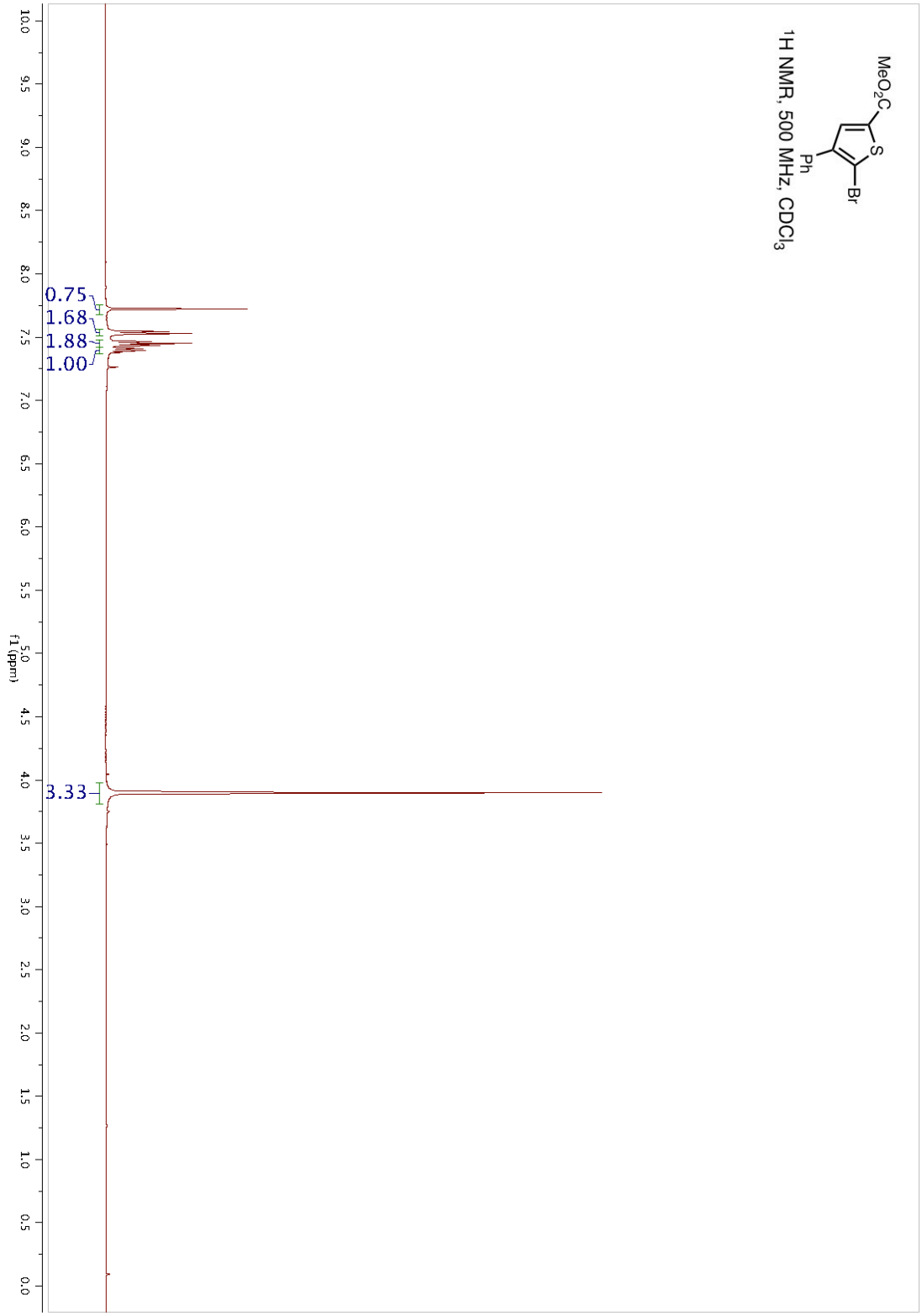

Ph
S
Ph
Ph
Br
^{13}C NMR, 125 MHz, $CDCl_3$
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

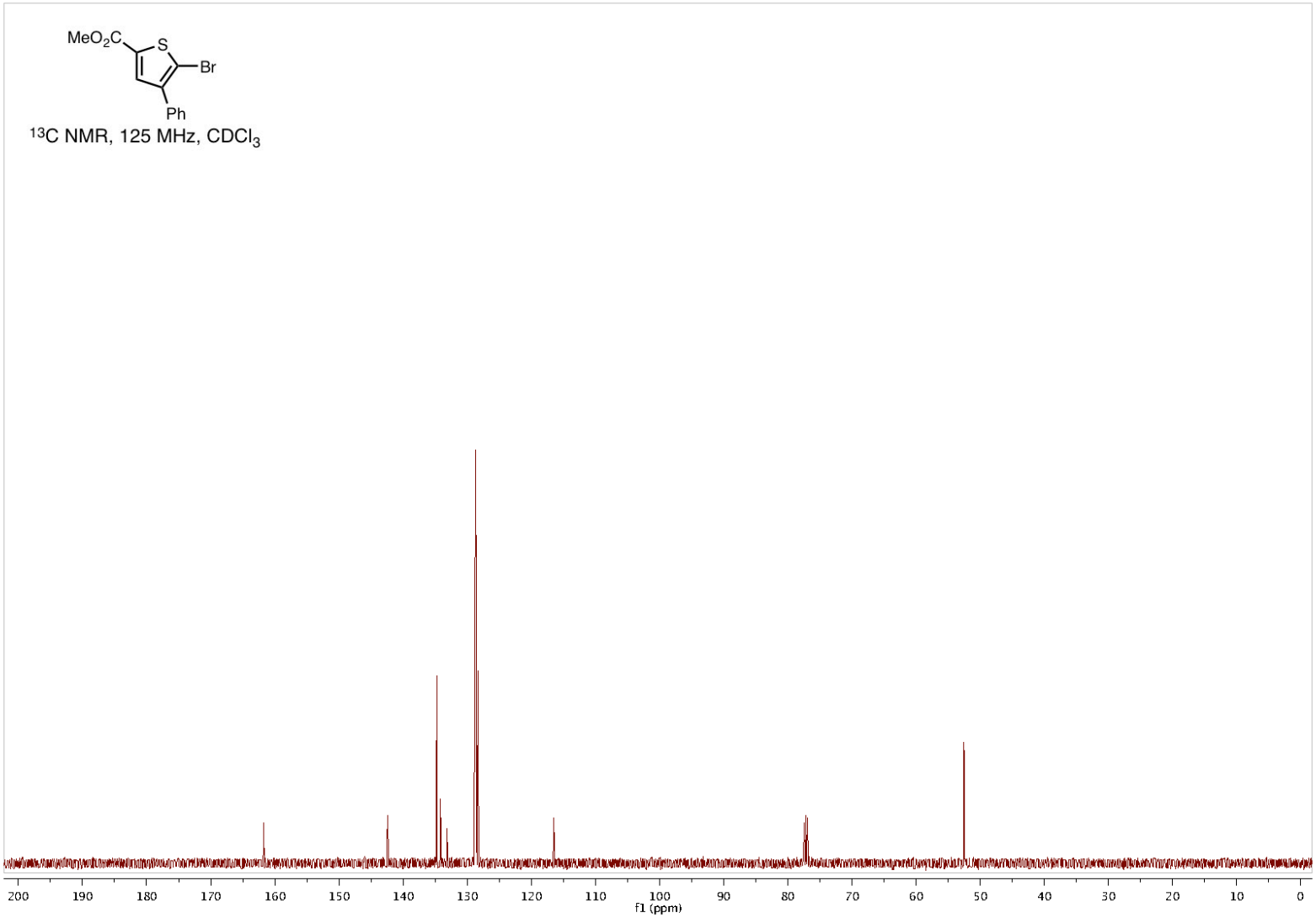

^{1}H NMR, 500 MHz, $CDCl_3$
Br
S
2.22
1.00
4.25
1.00
0.96
F1 (ppm)

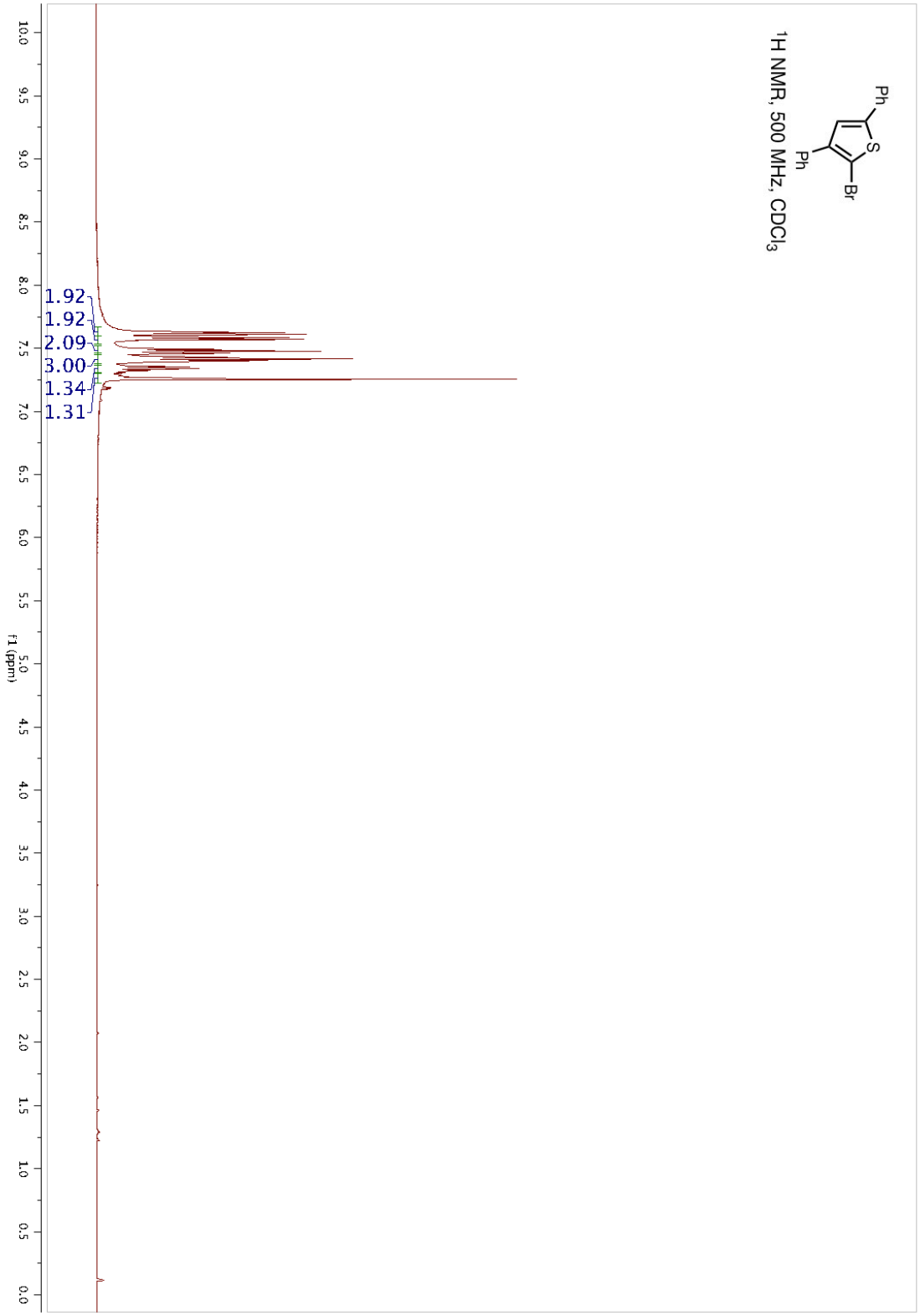

^{13}C NMR, 125 MHz, $CDCl_3$
Br
S
f1 (ppm)
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0

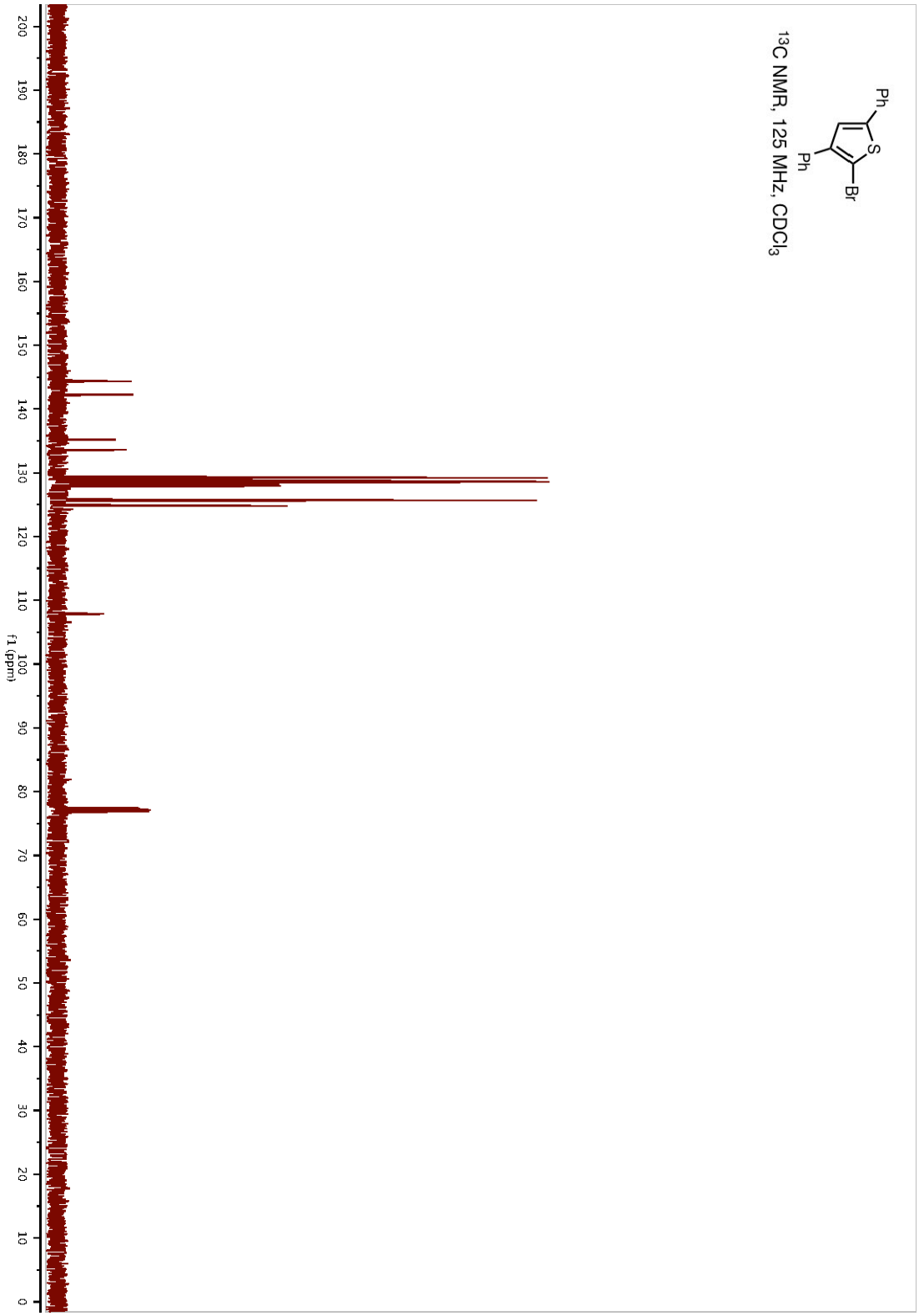

^{1}H NMR, 500 MHz, CDCl$_3$
Br
S
CO$_2$tBu
0.96
1.00
13.26
f1 (ppm)

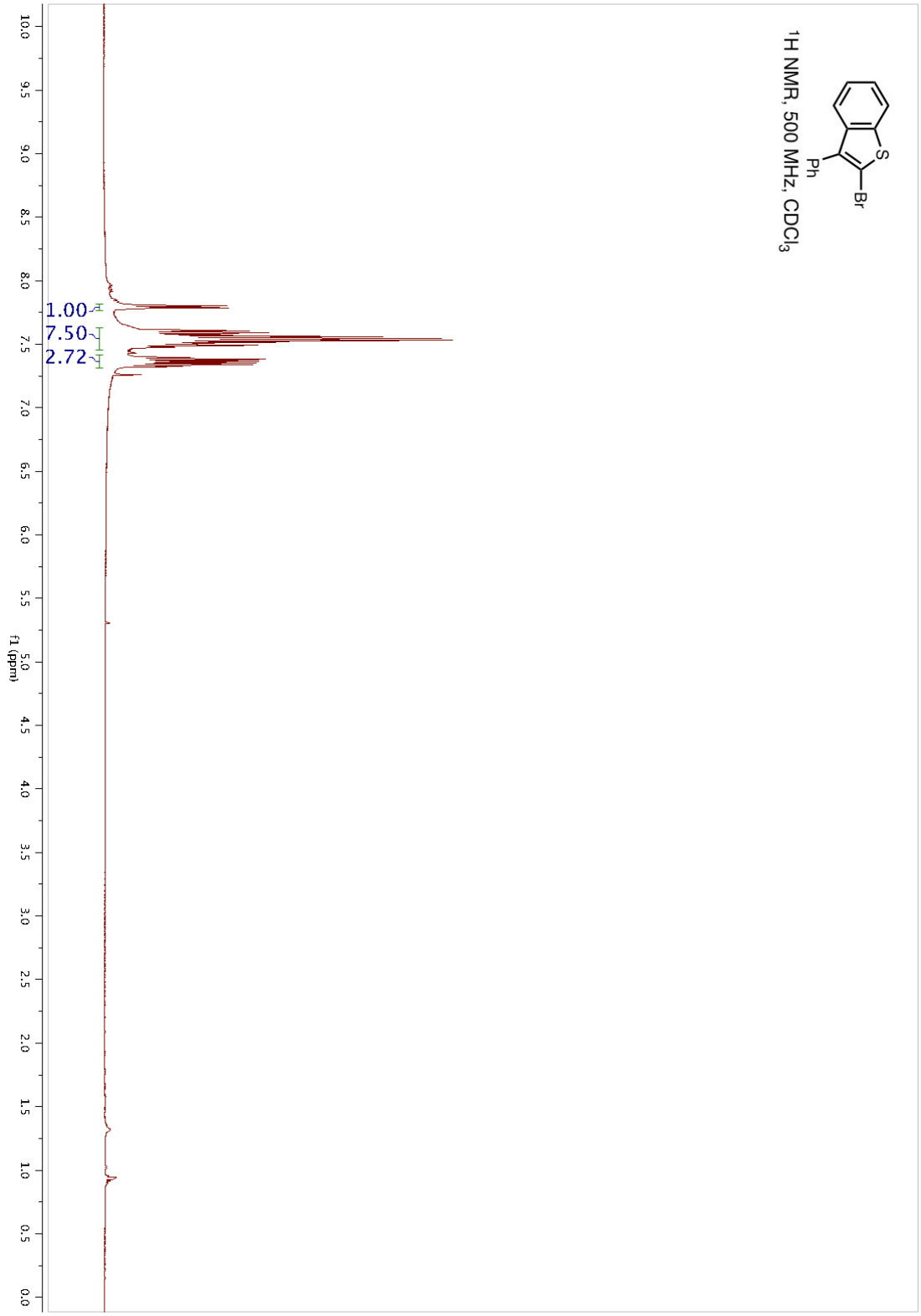

S
CO2tBu
Br
13C NMR, 125 MHz, CDCl3
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

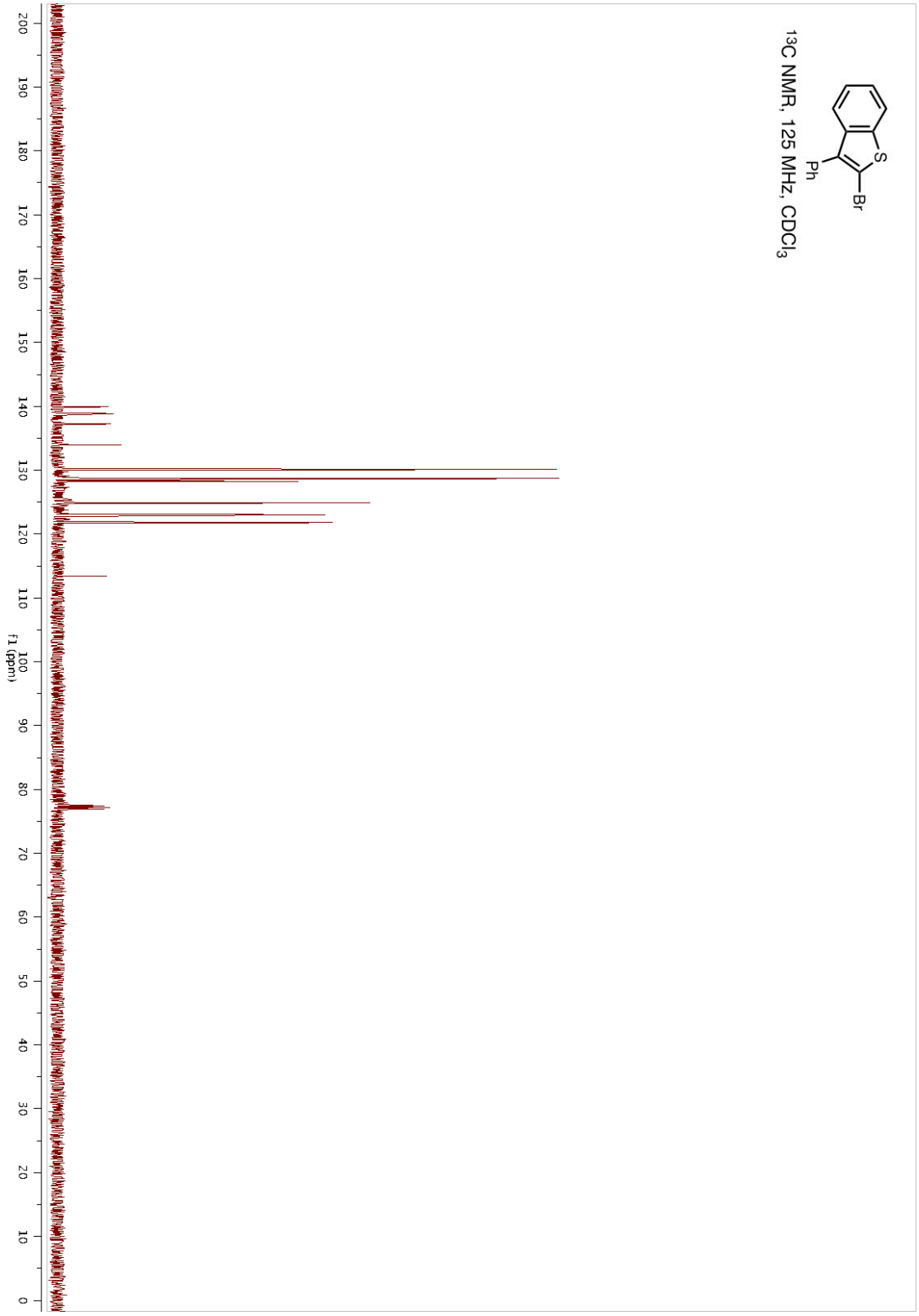

MeO2C
S
Br
Ph
1H NMR, 500 MHz, CDCl3
0.75
1.68
1.88
1.00
3.33
f1 (ppm)

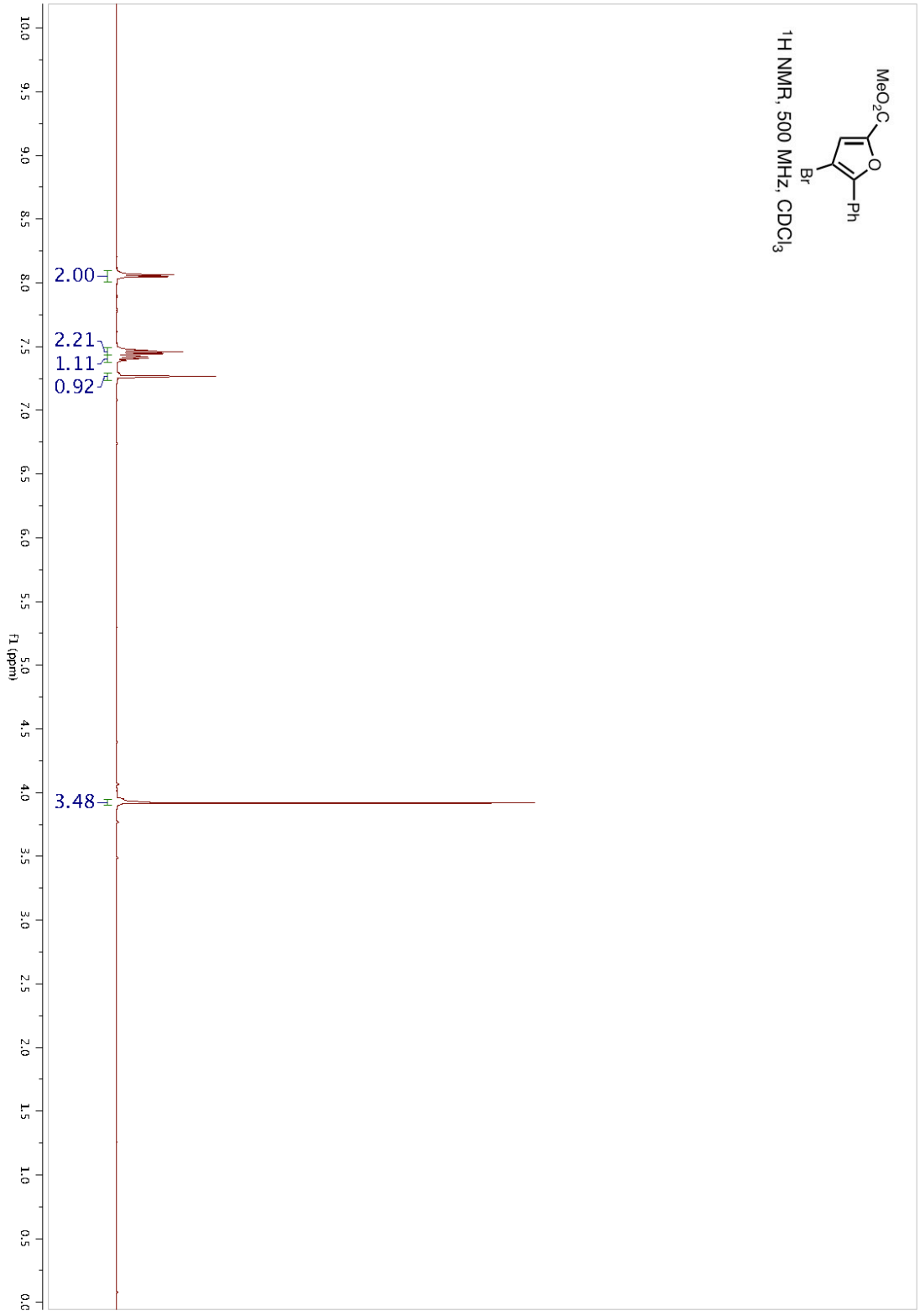

MeO2C
S
Br
Ph
13C NMR, 125 MHz, CDCl3
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

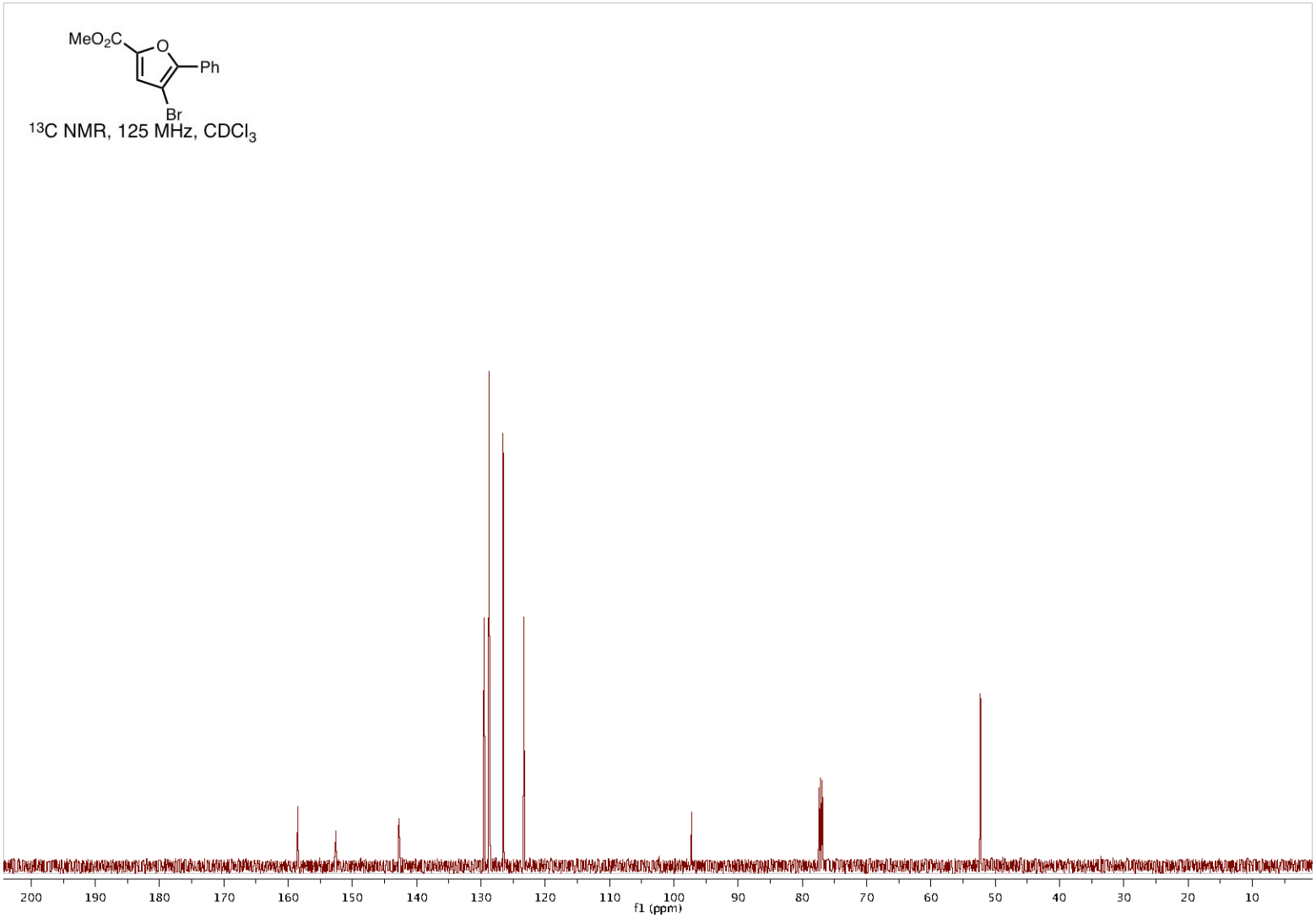

^{1}H NMR, 500 MHz, $CDCl_3$
Ph
S
Br
Ph
1.92
1.92
2.09
3.00
1.34
1.31
f1 (ppm)

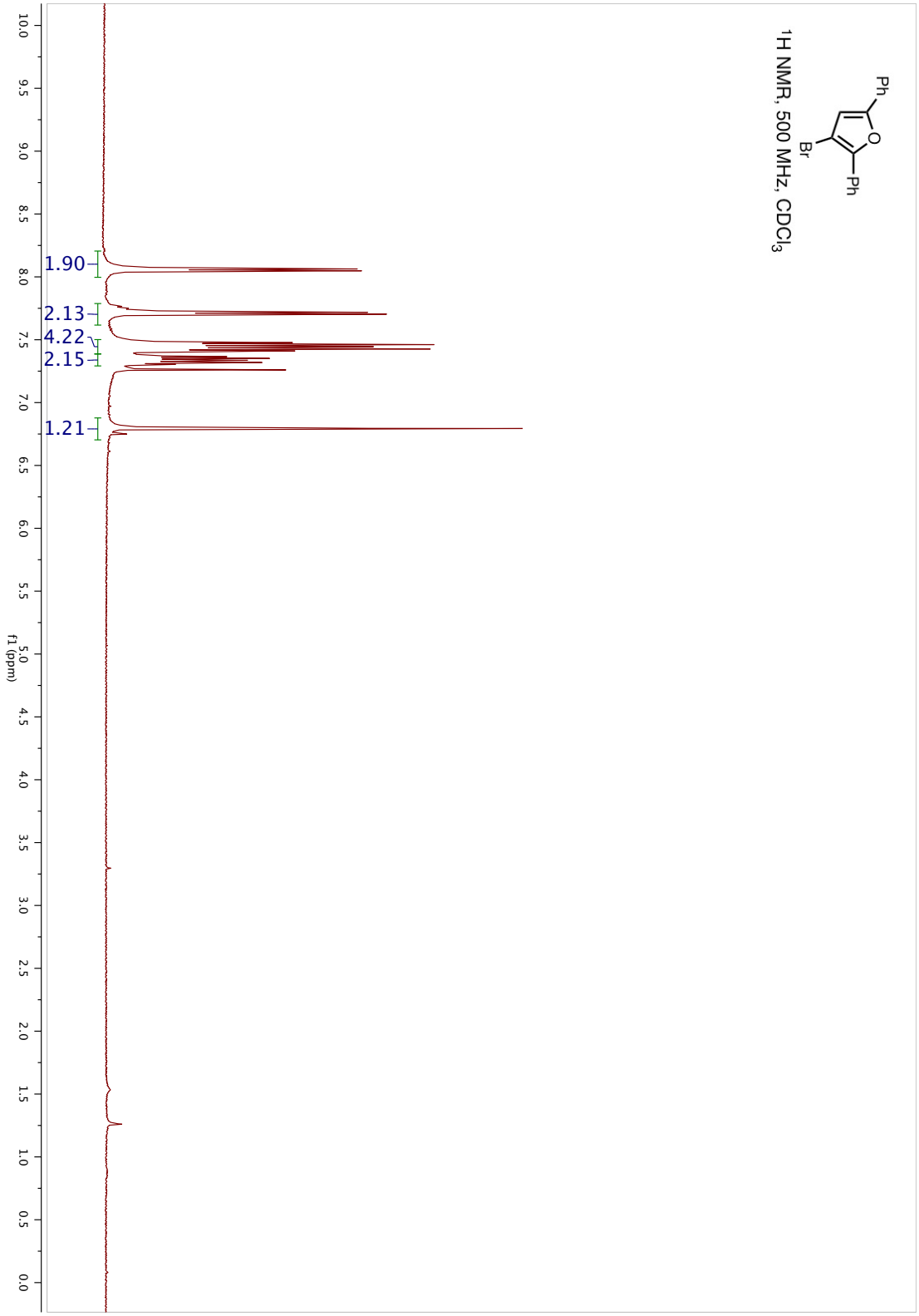

Ph
S
Br
Ph
^{13}C NMR, 125 MHz, $CDCl_3$
f1 (ppm)
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0

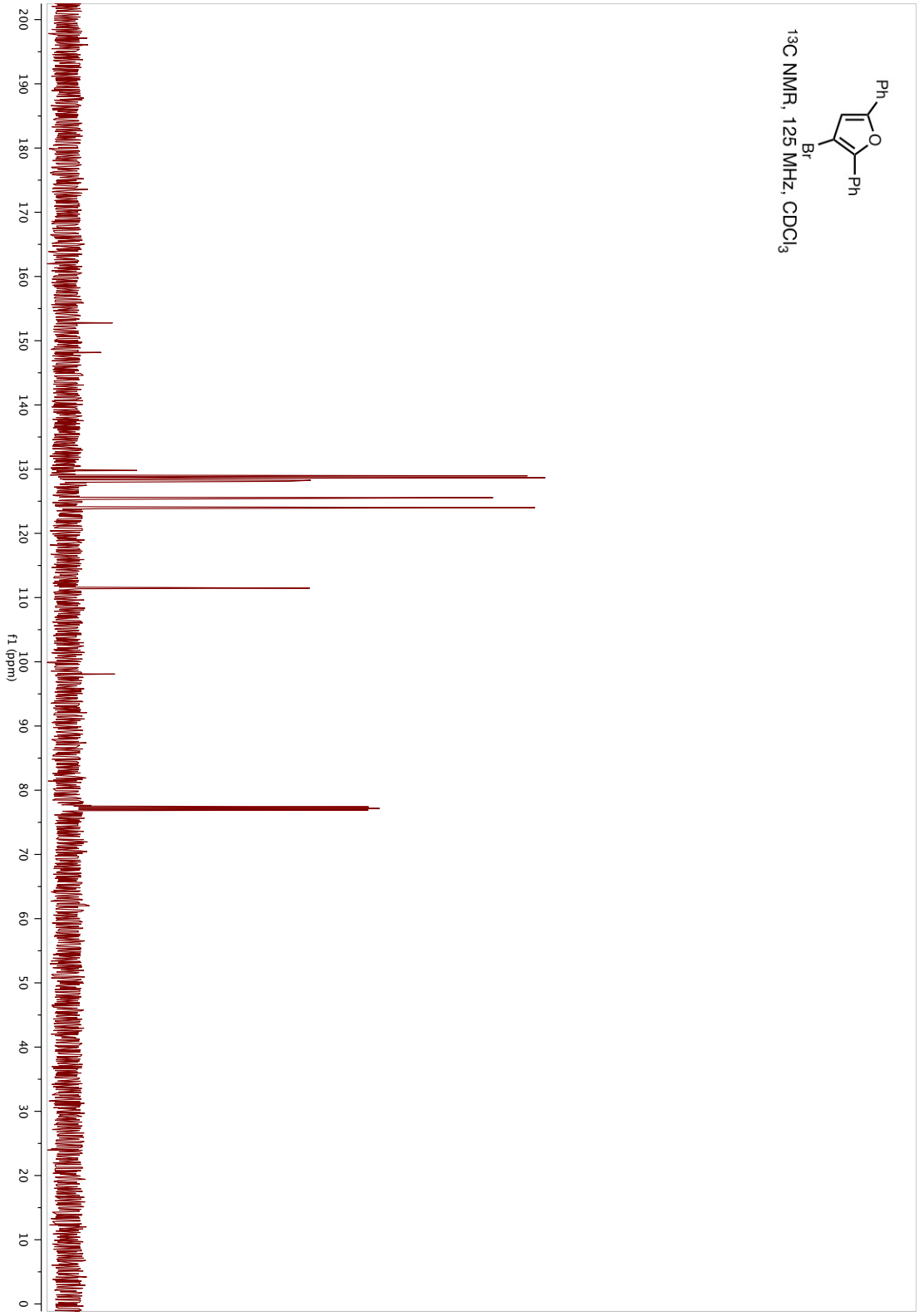

1H NMR, 500 MHz, CDCl3
Ph
S
Br
1.00
7.50
2.72
f1 (ppm)

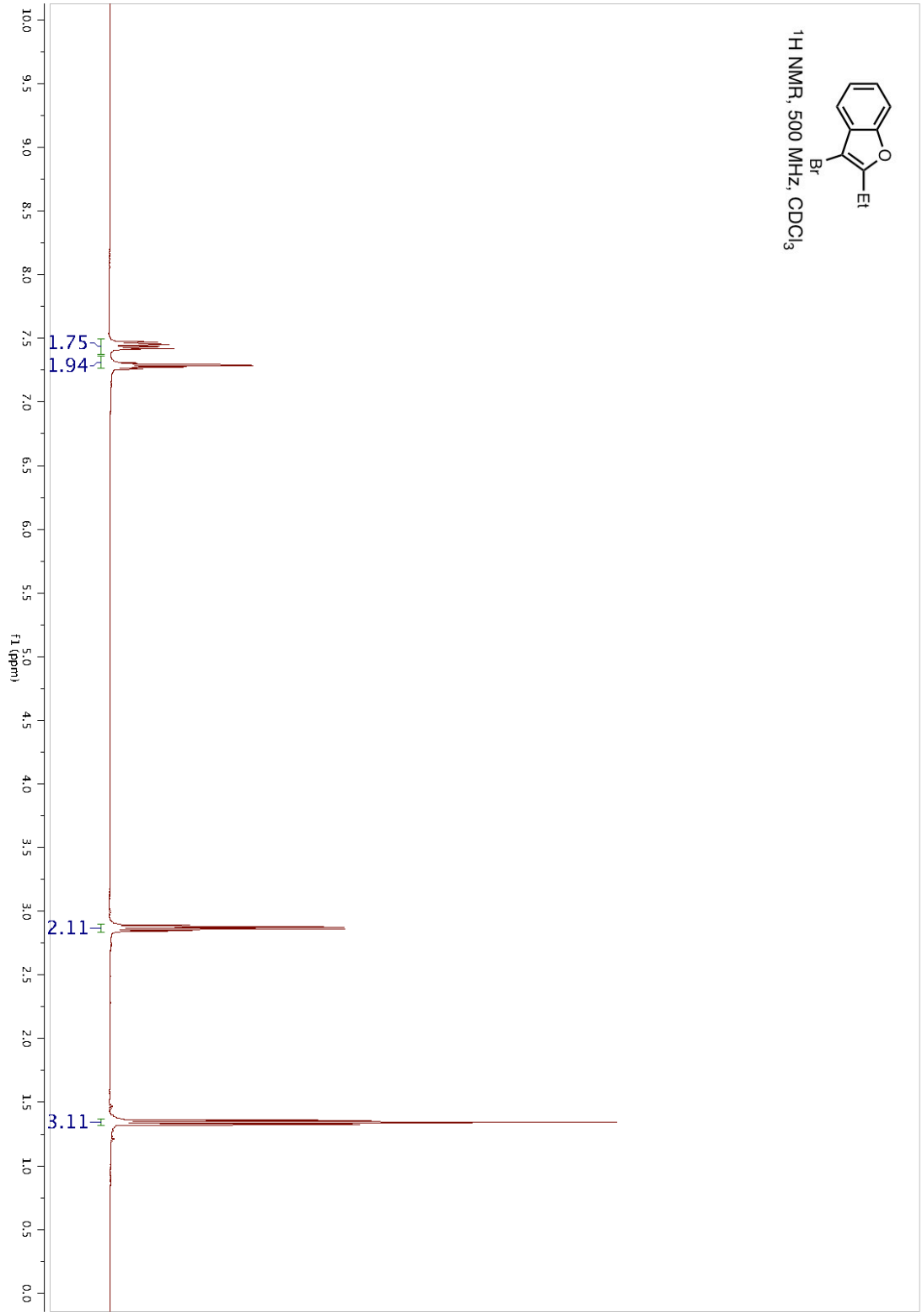

^{13}C NMR, 125 MHz, $CDCl_3$
Ph
S
Br
f1 (ppm)
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0

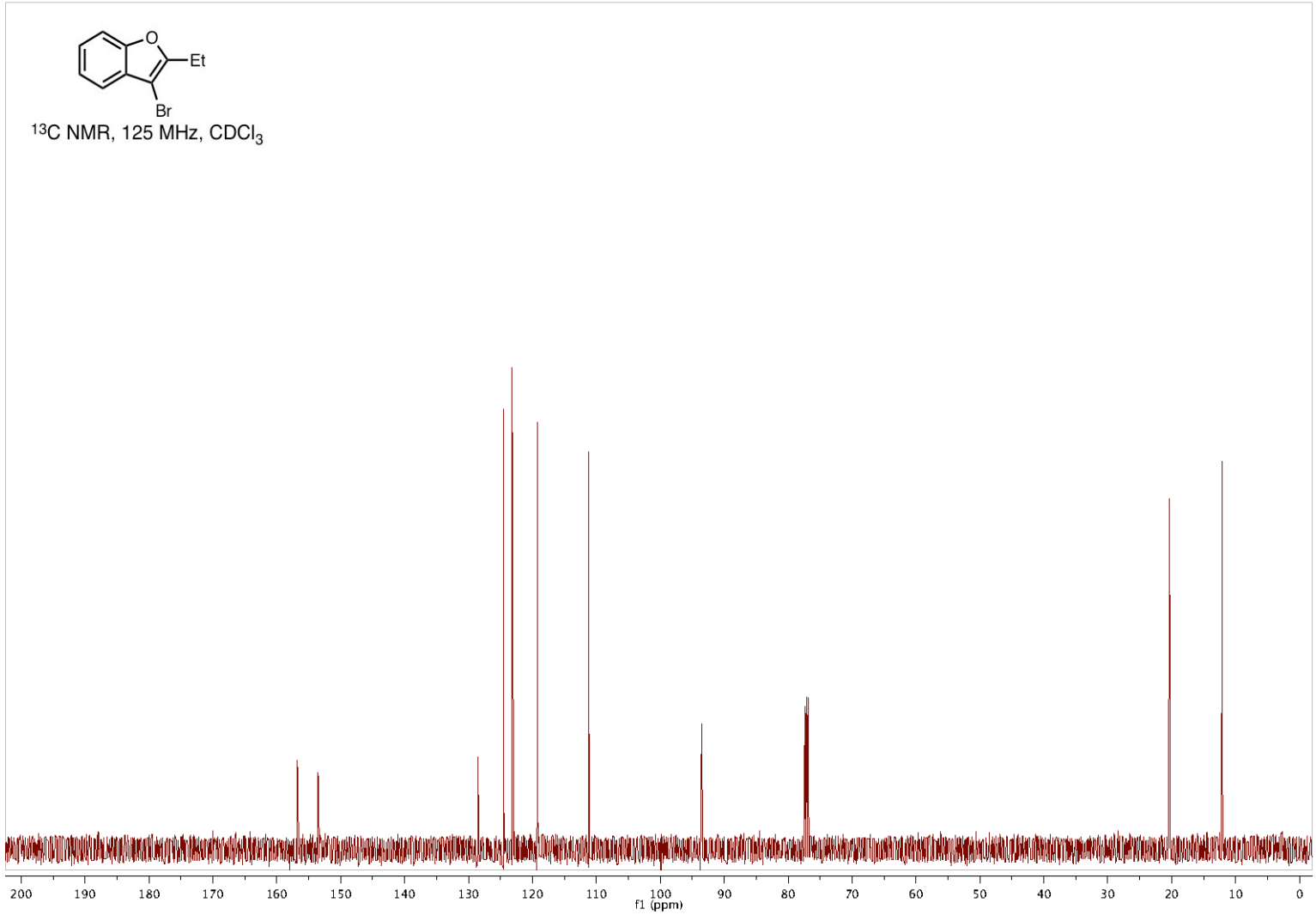

^{1}H NMR, 500 MHz, $CDCl_3$
MeO_2C
O
Br
Ph
2.00
2.21
1.11
0.92
3.48
f1 (ppm)

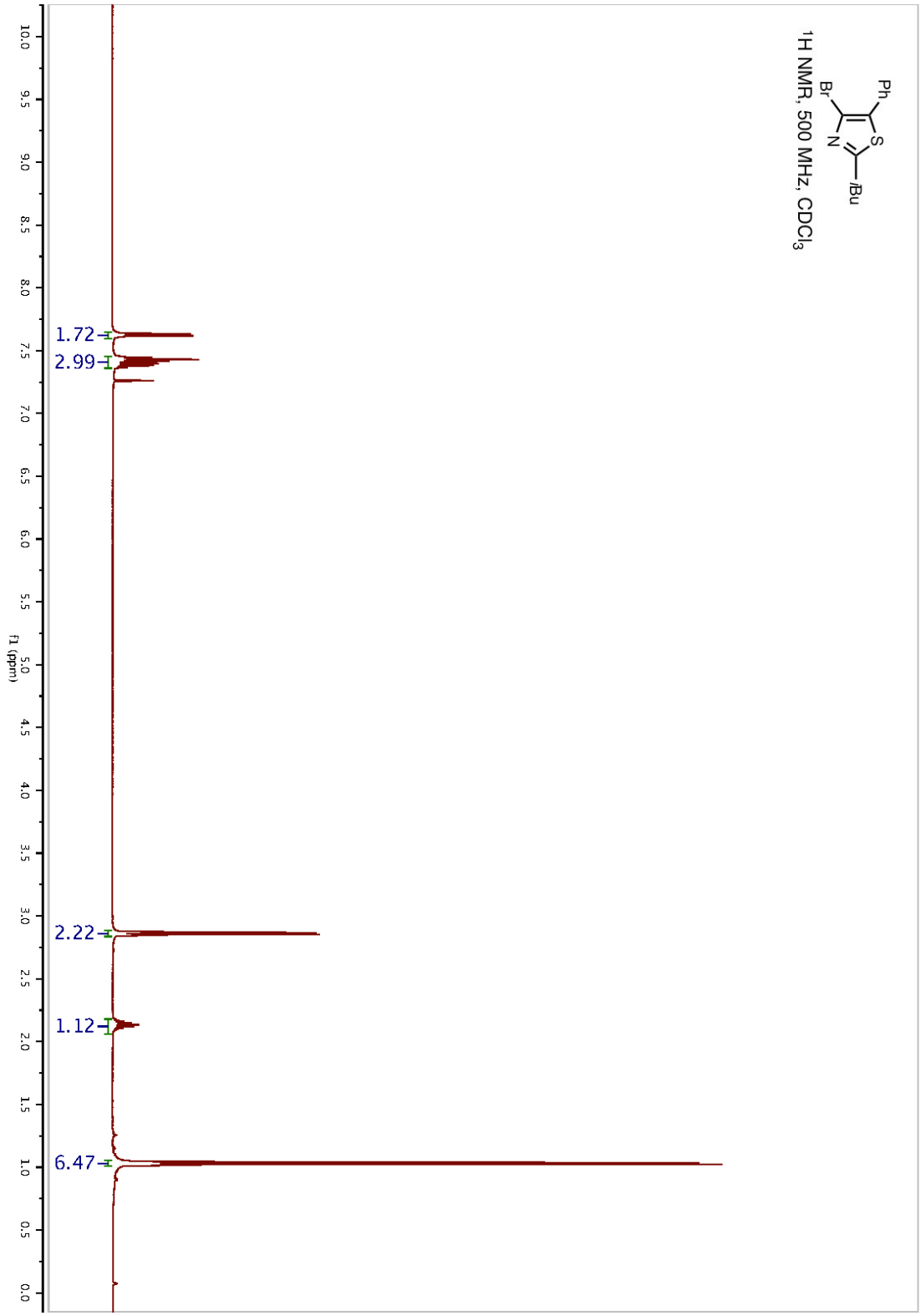

MeO2C
O
Ph
Br
13C NMR, 125 MHz, CDCl3
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

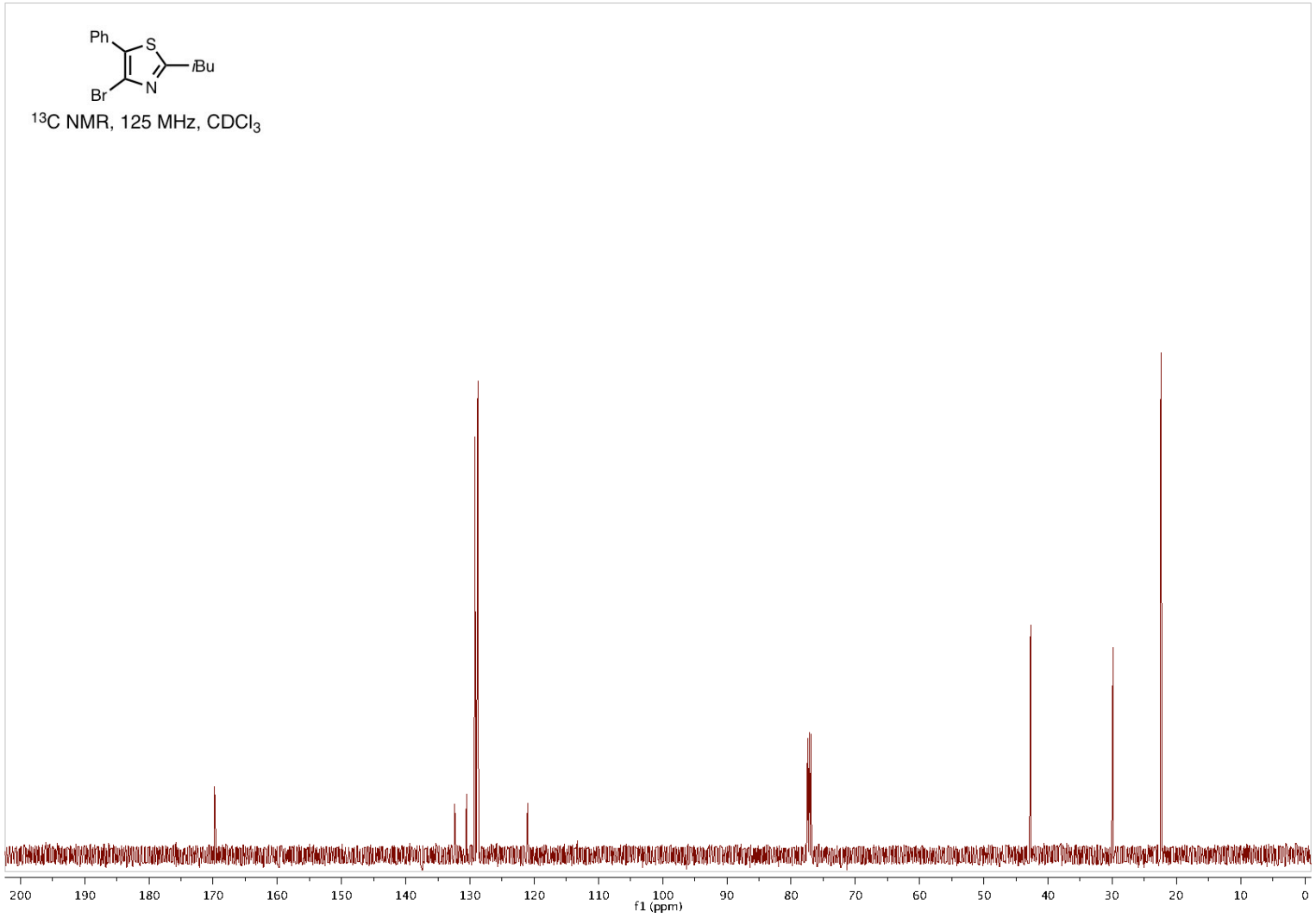

1H NMR, 500 MHz, CDCl3
Ph
O
Br
Ph
1.90
2.13
4.22
2.15
1.21
f1 (ppm)

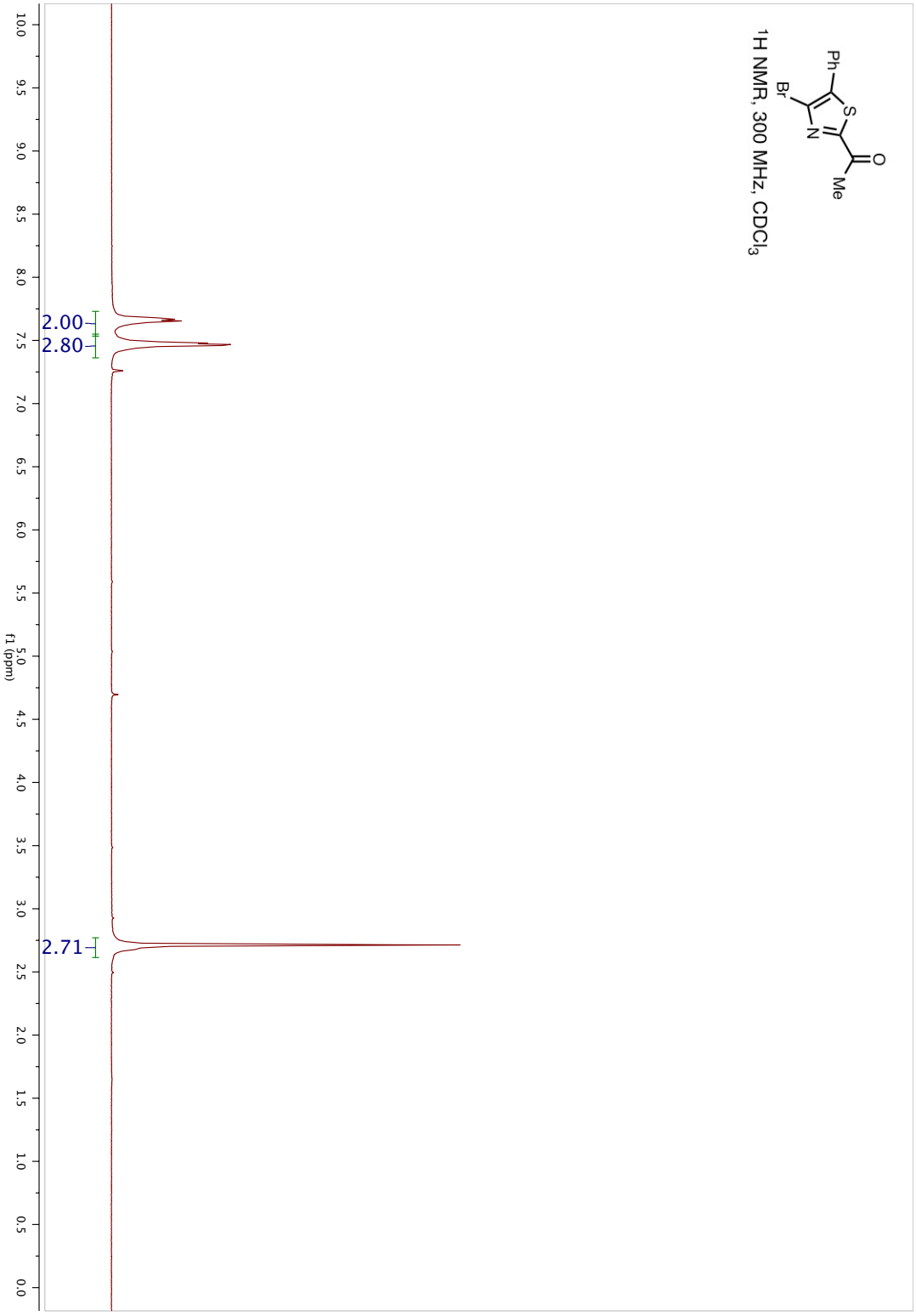

Ph
O
Br
Ph
^{13}C NMR, 125 MHz, $CDCl_3$
f1 (ppm)
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0

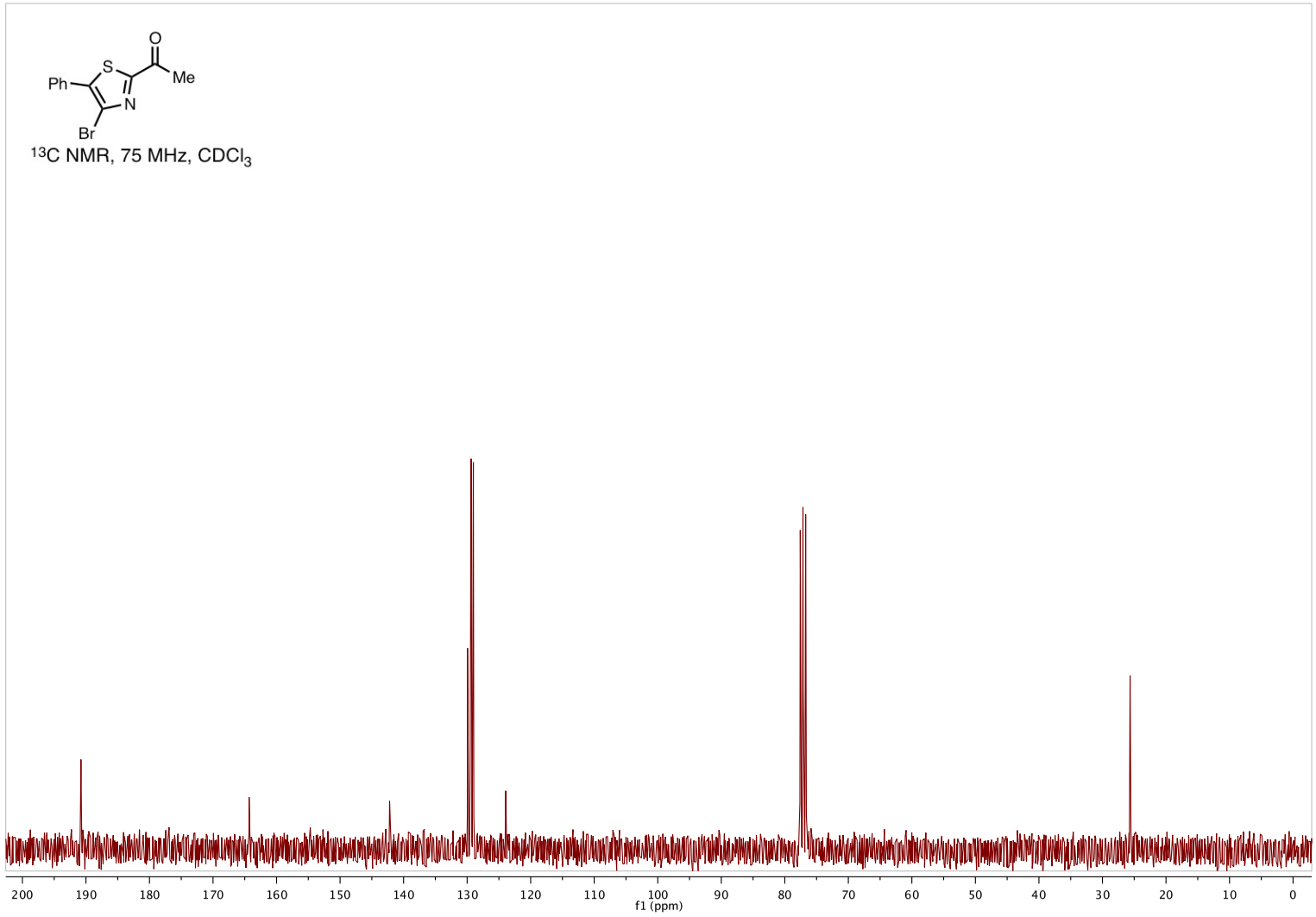

^{1}H NMR, 500 MHz, CDCl$_3$
Br
O
Et
1.75
1.94
2.11
3.11
f1 (ppm)

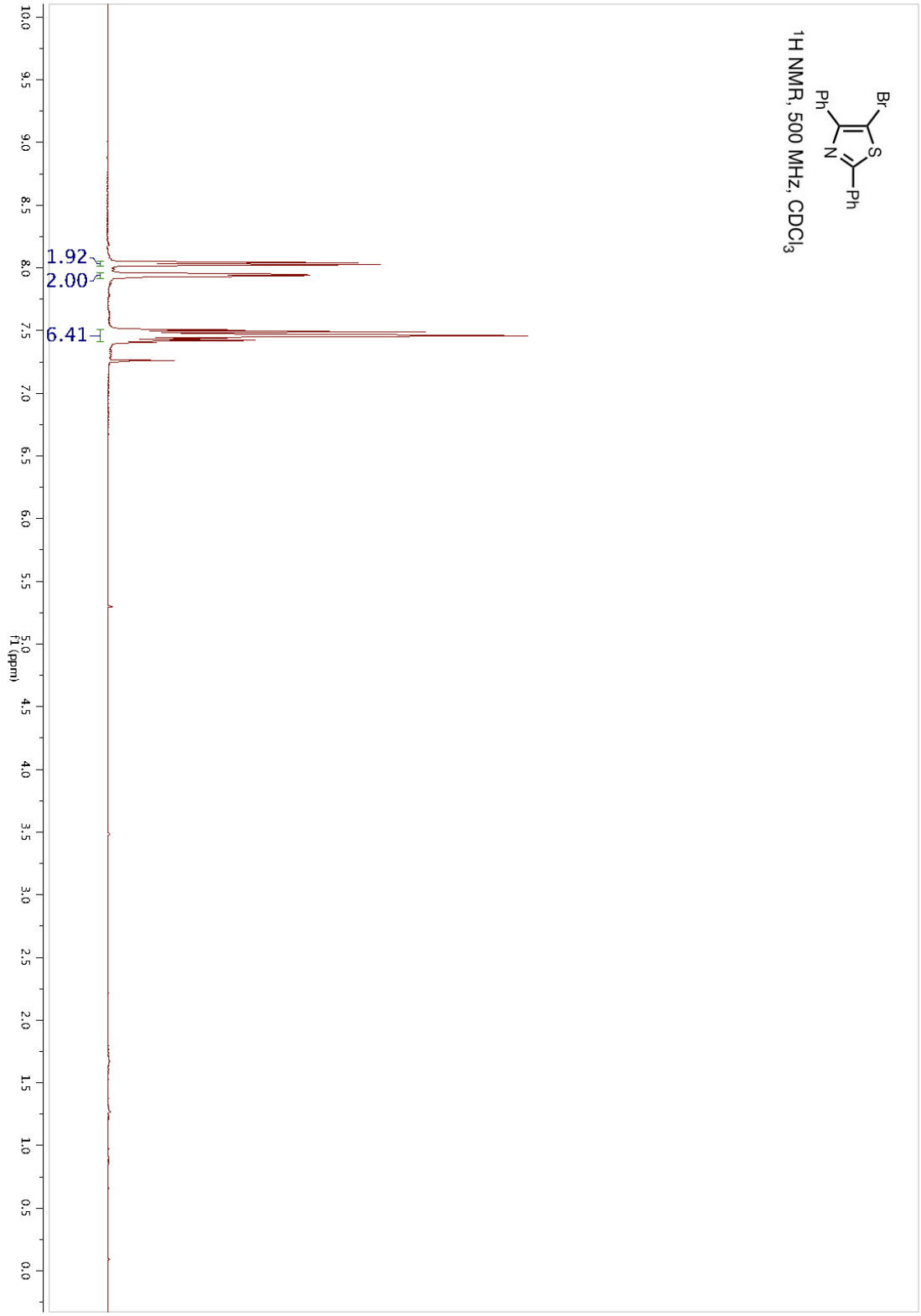

O
Et
Br
^{13}C NMR, 125 MHz, $CDCl_3$
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

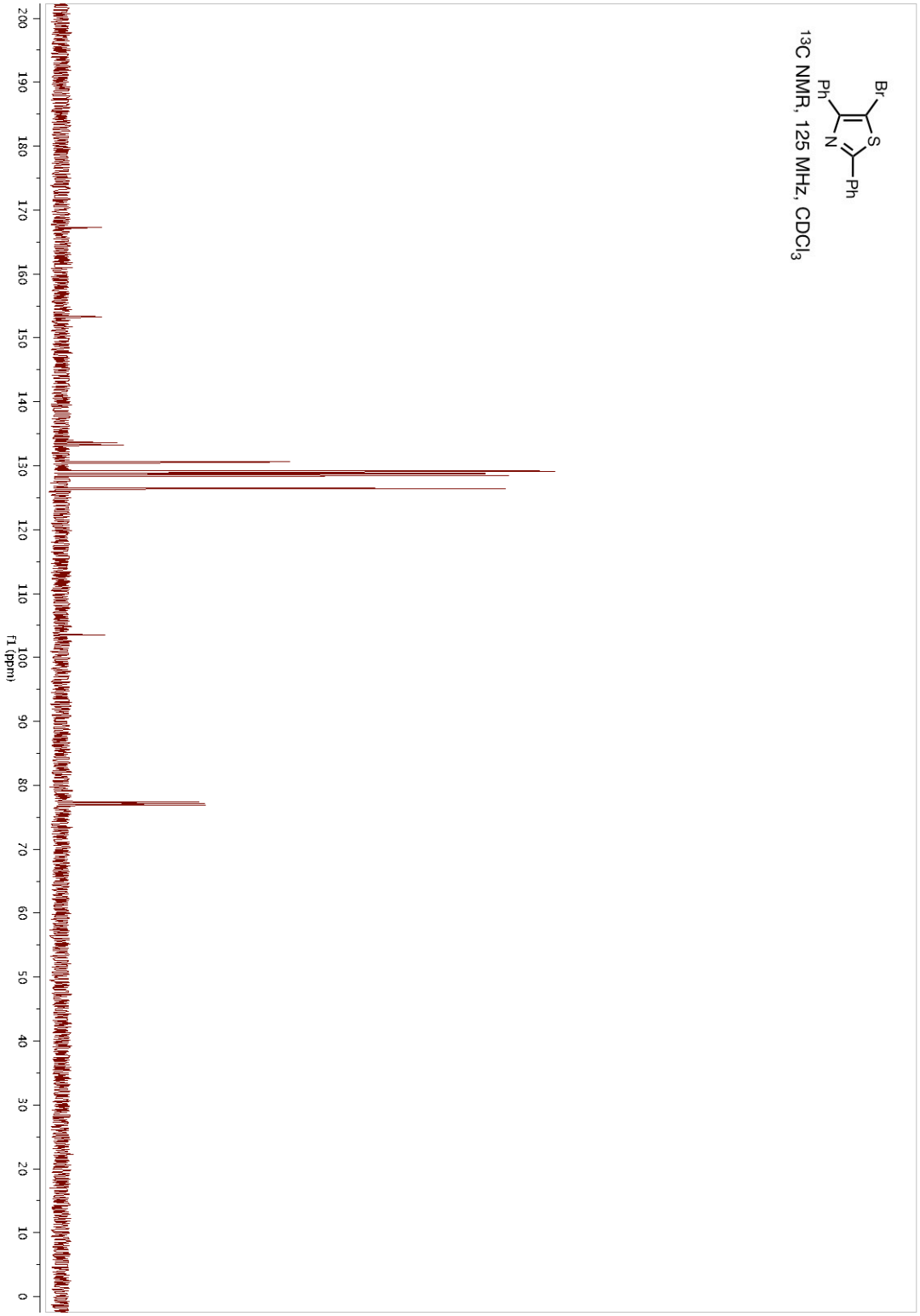

1H NMR, 500 MHz, CDCl3
Br
N
S
Ph
tBu
1.72
2.99
2.22
1.12
6.47
f1 (ppm)

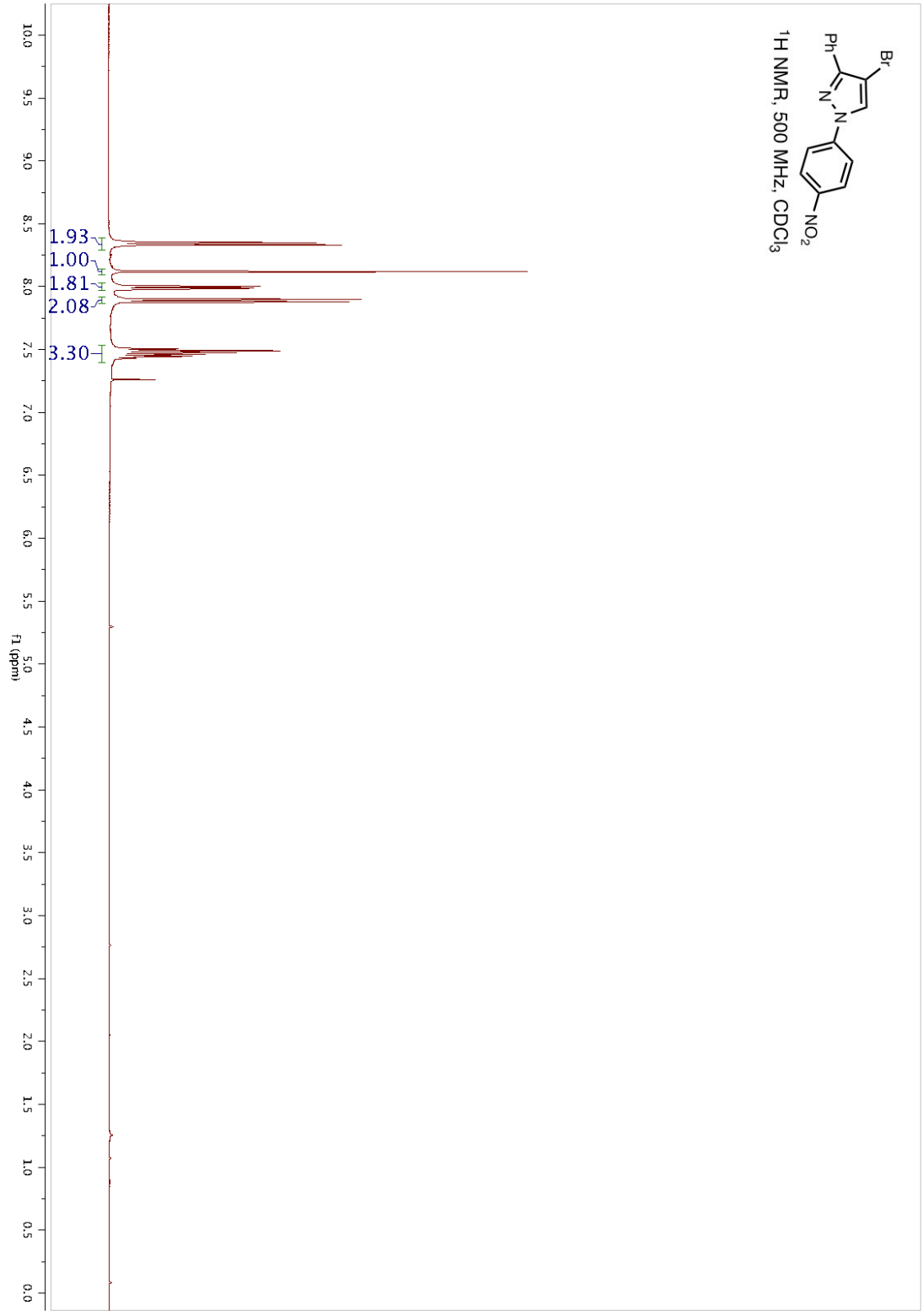

Ph
S
iBu
N
Br
13C NMR, 125 MHz, CDCl3
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

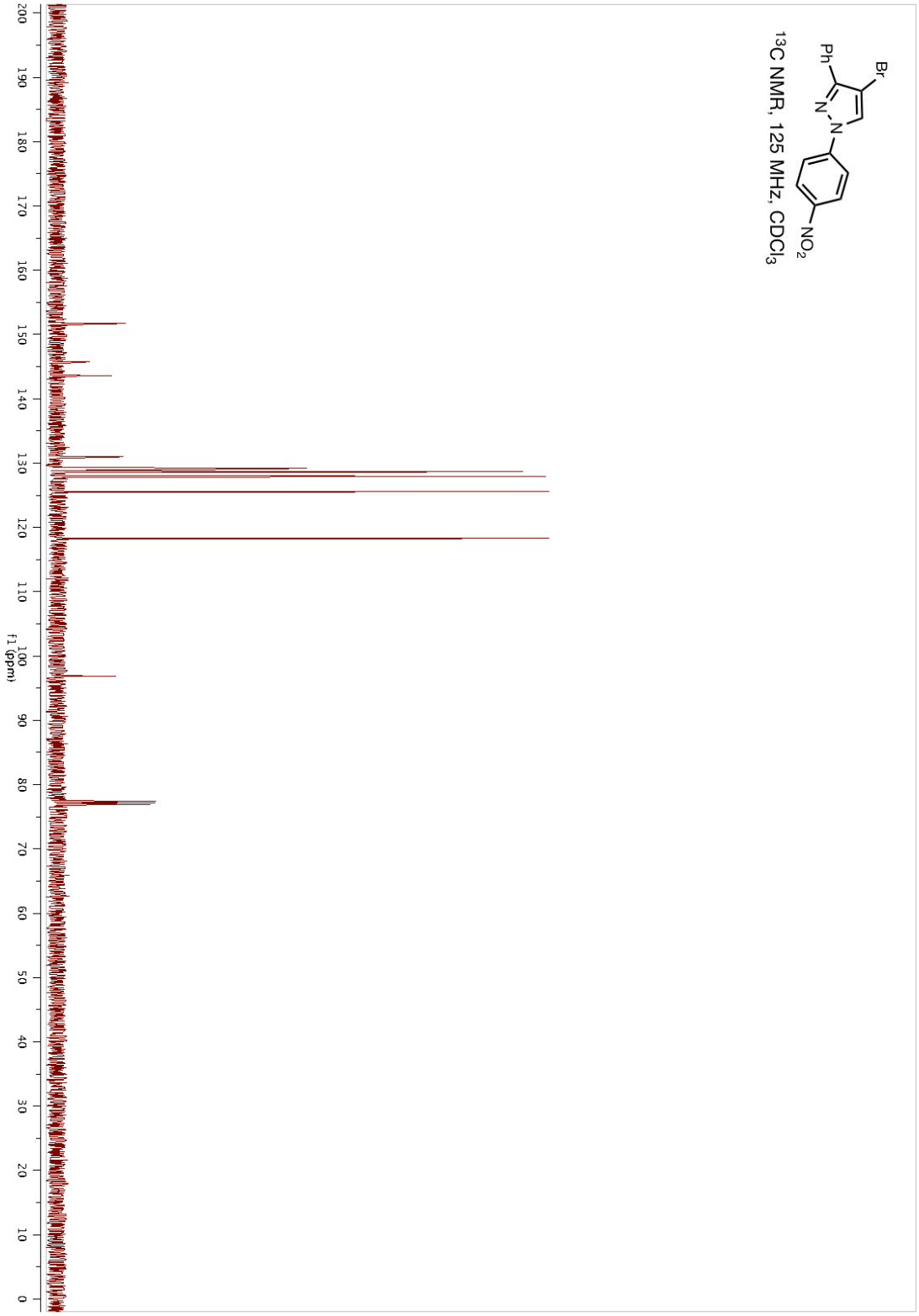

1H NMR, 300 MHz, CDCl3
Ph
Br
S
N
O
Me
2.00
2.80
2.71
f1 (ppm)

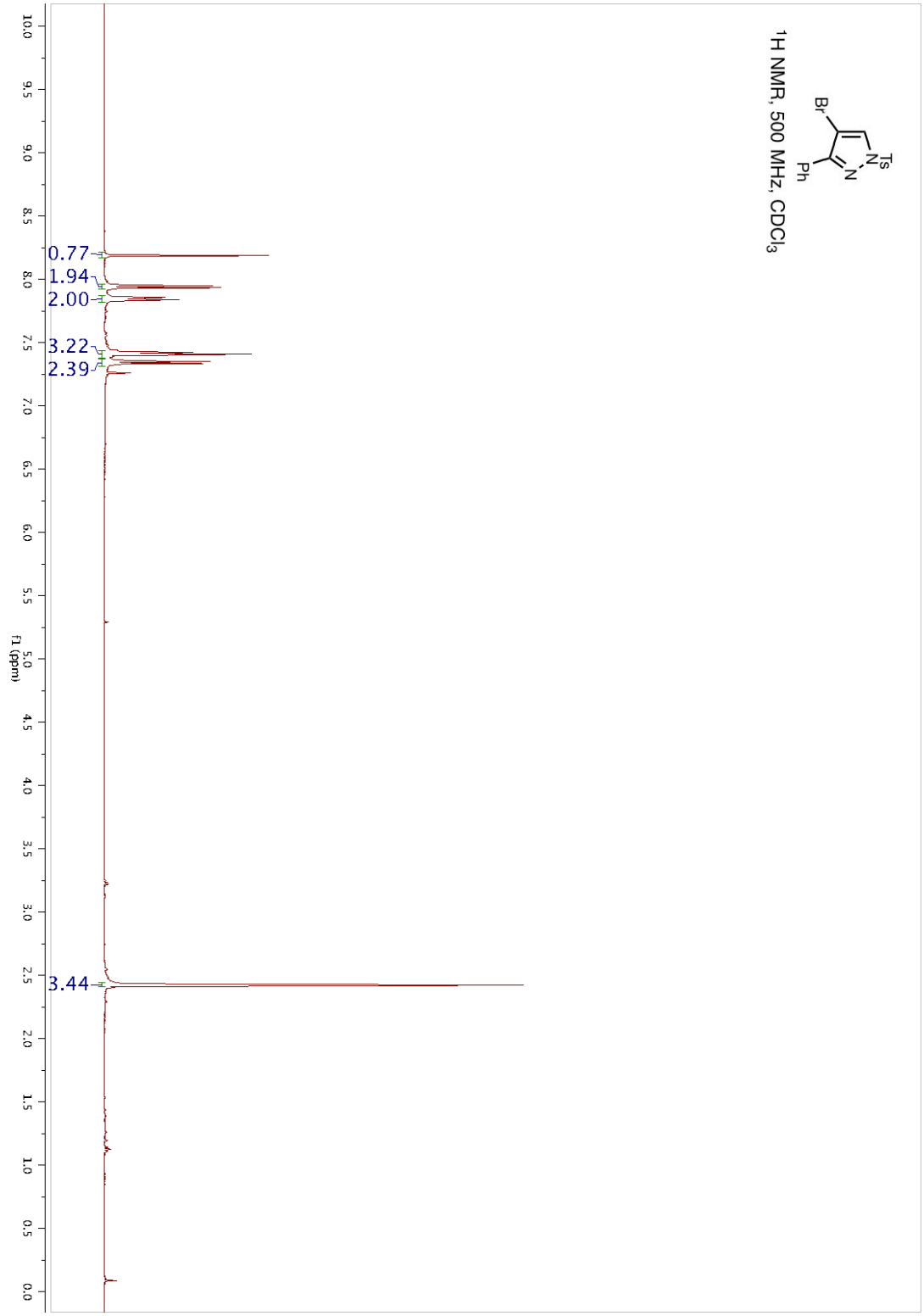

O
S
Me
Ph
N
Br
^{13}C NMR, 75 MHz, $CDCl_3$
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

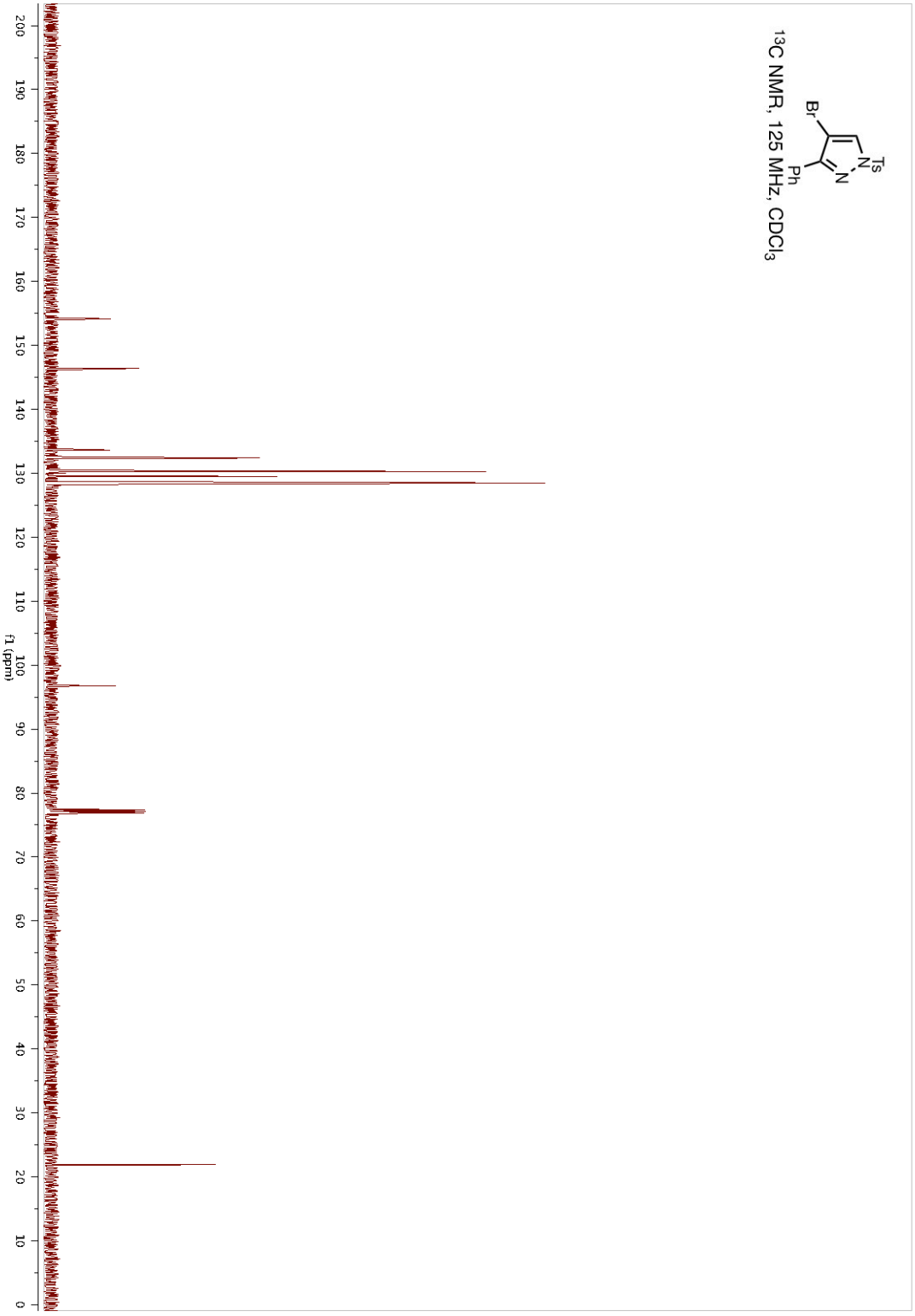

1H NMR, 500 MHz, CDCl3
Br
S
N
Ph
Ph
1.92
2.00
6.41
f1 (ppm)

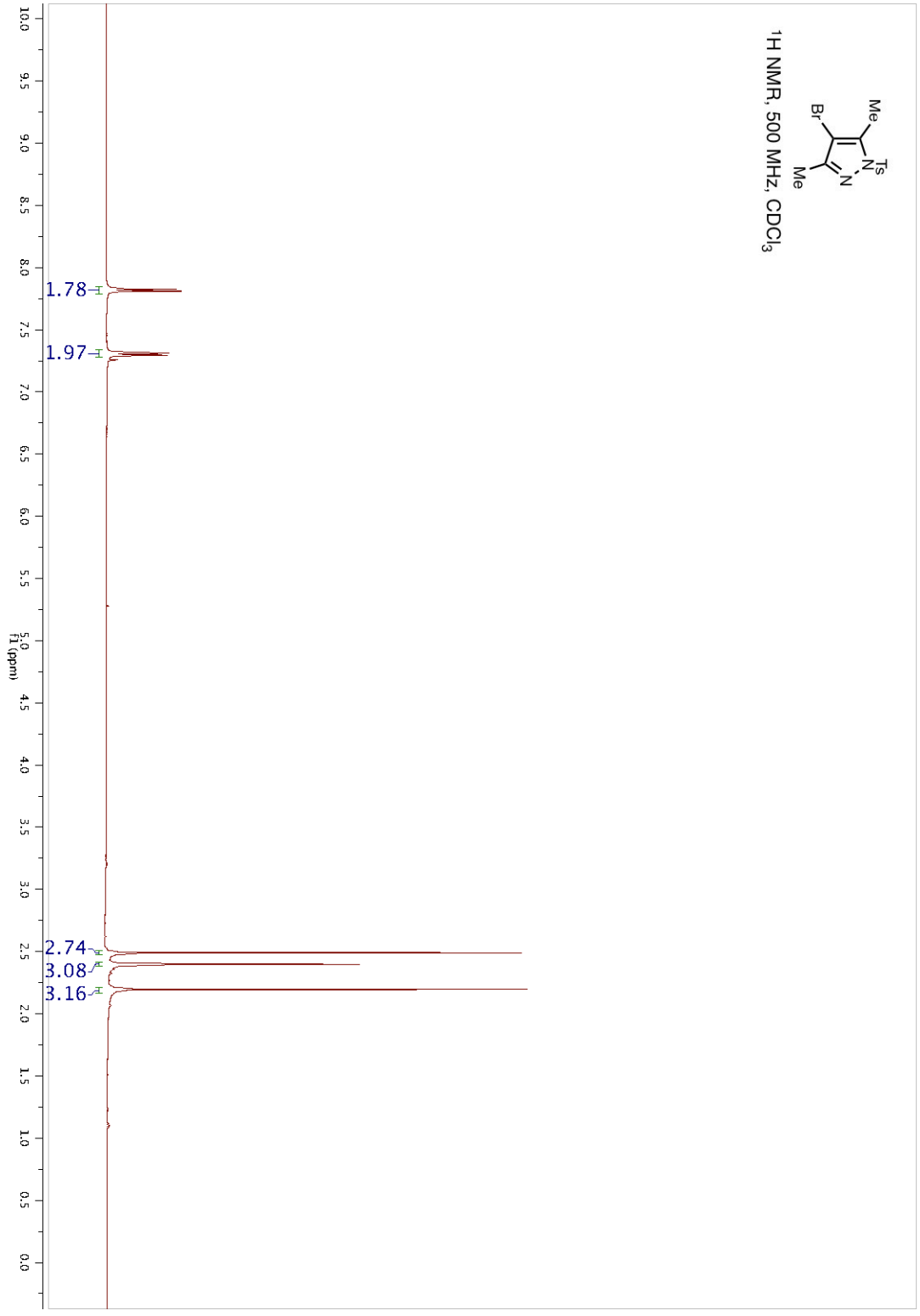

Br
S
Ph
N
Ph
^{13}C NMR, 125 MHz, CDCl$_3$
f1 (ppm)
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0

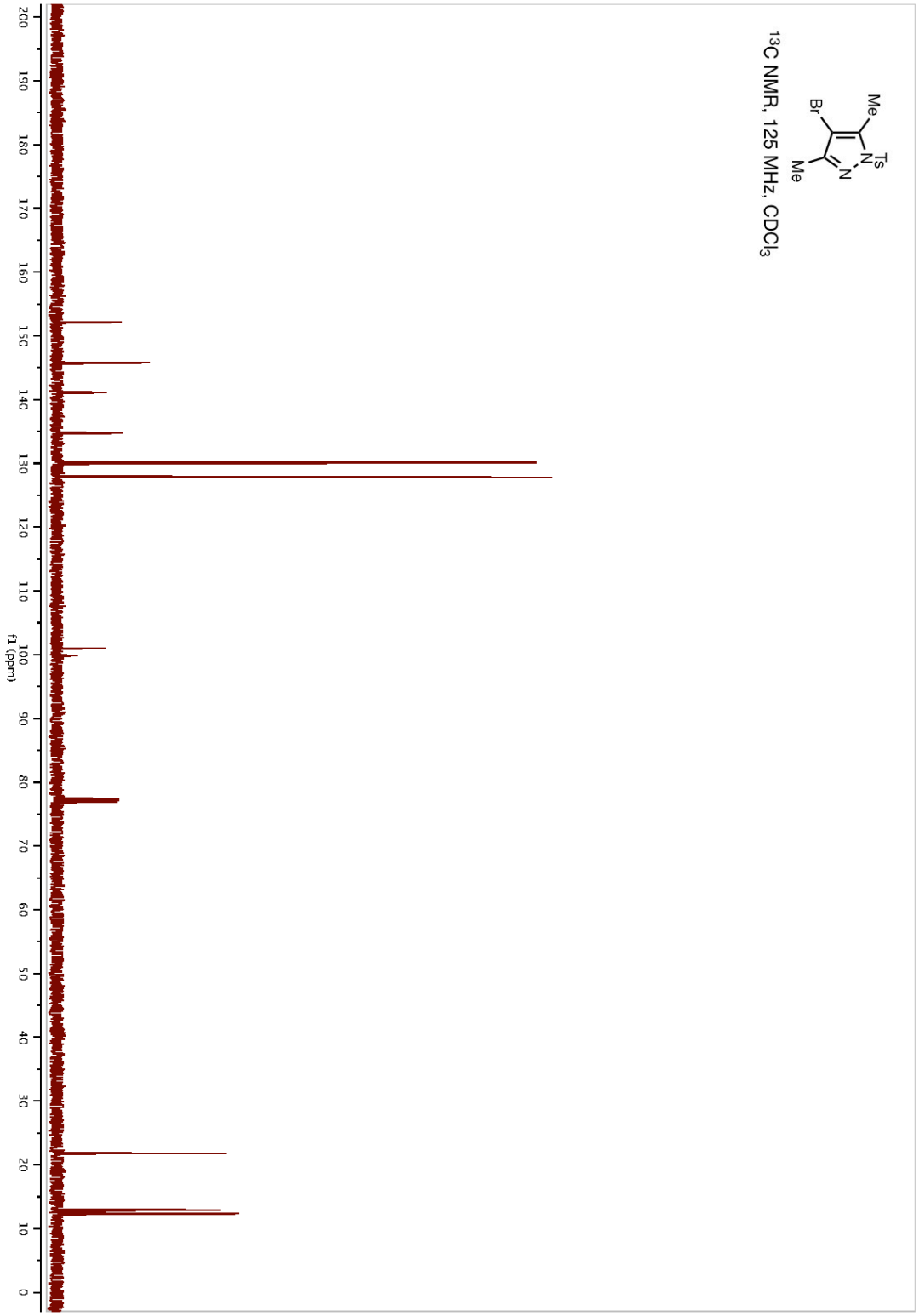

1.93
1.00
1.81
2.08
3.30
f1 (ppm)
Br
Ph
N
N
NO2
1H NMR, 500 MHz, CDCl3

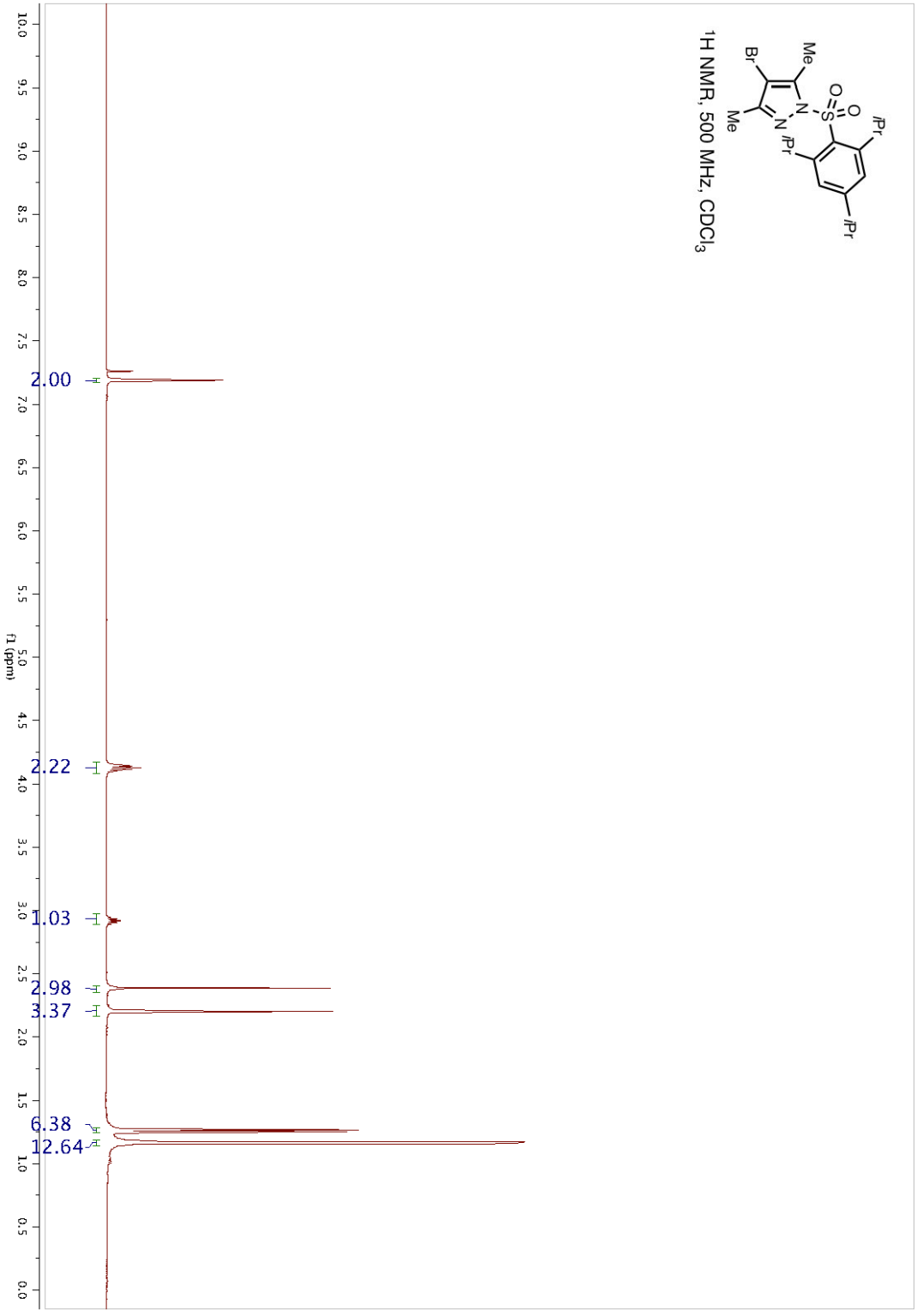

Br
Ph
N
N
NO2
13C NMR, 125 MHz, CDCl3
f1 (ppm)
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0

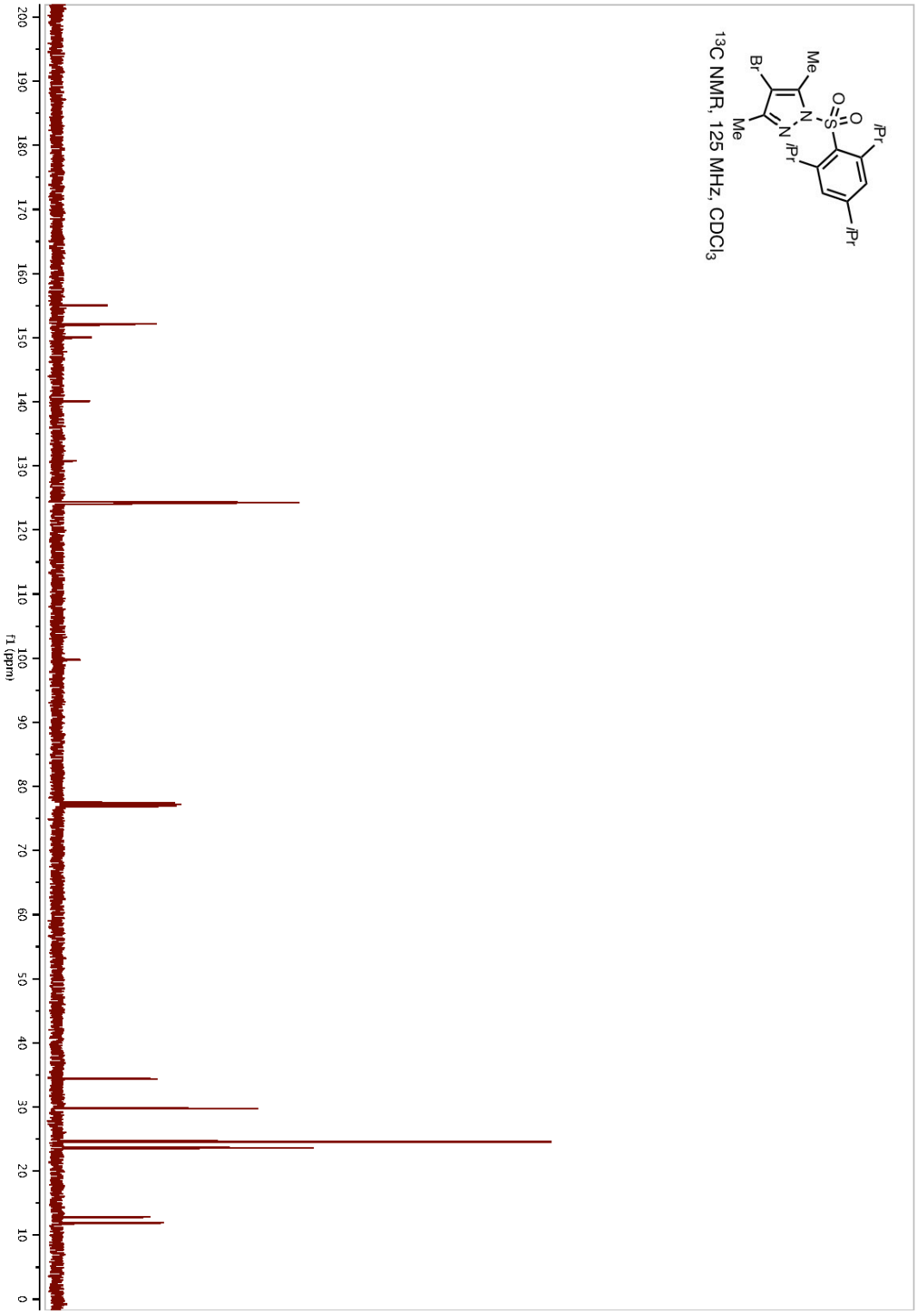

0.77
1.94
2.00
3.22
2.39
3.44
f1 (ppm)
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
^{1}H NMR, 500 MHz, CDCl$_3$
Br
Ph
N
N
Ts

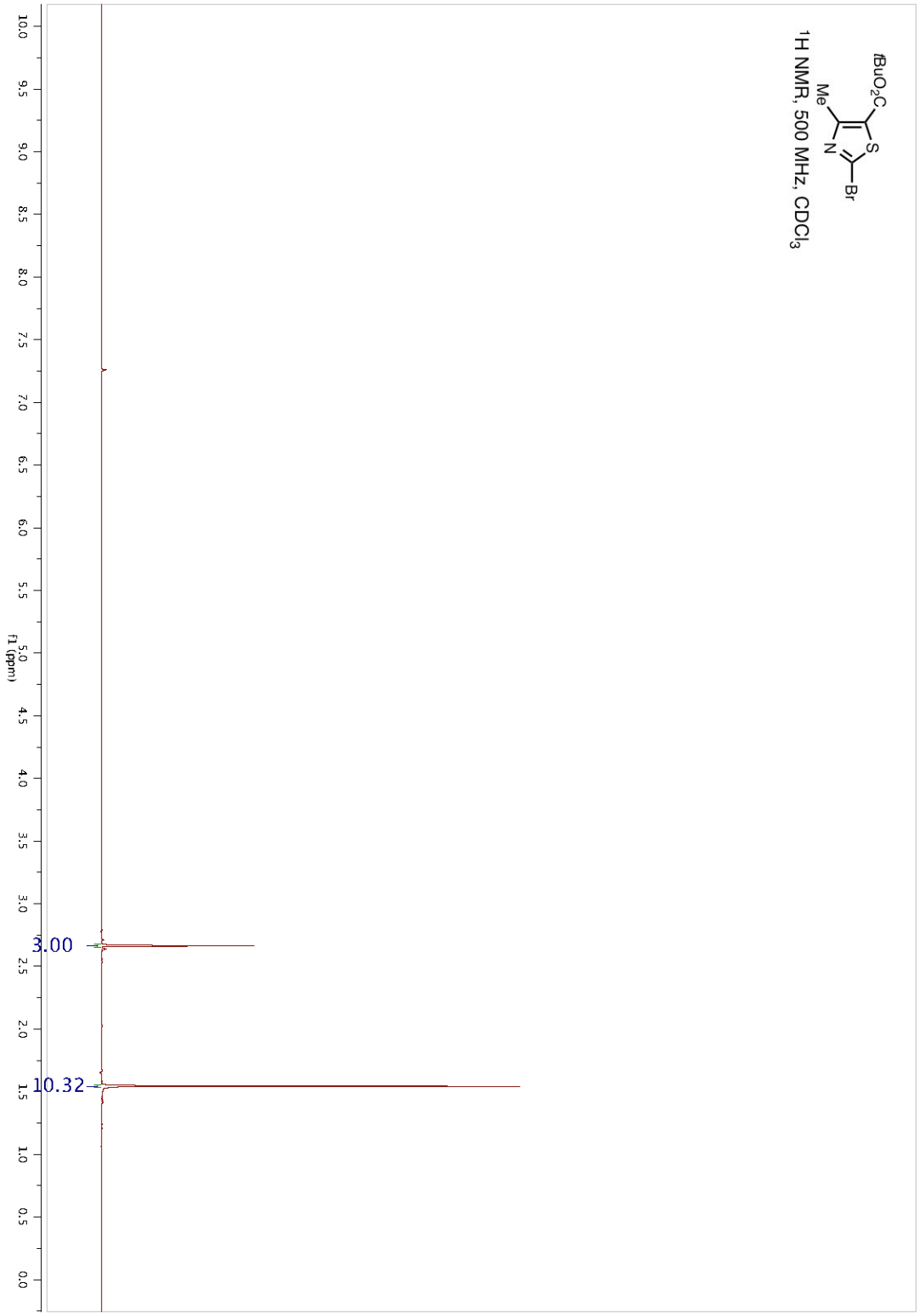

Br
Ts
N
N
Ph
^{13}C NMR, 125 MHz, CDCl$_3$
f1 (ppm)
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0

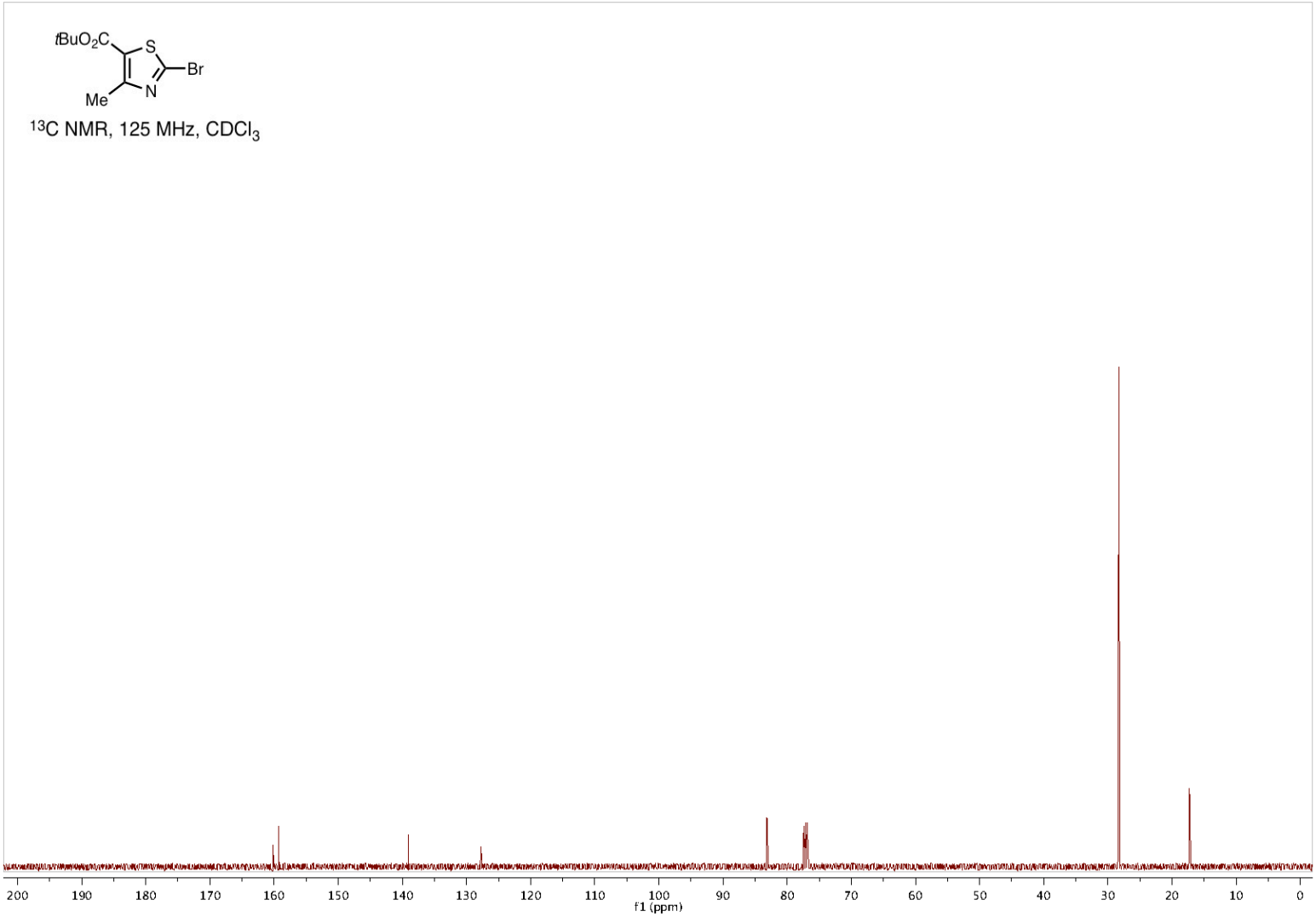

1H NMR, 500 MHz, CDCl3
Me
Br
Ts
N
N
Me
1.78
1.97
2.74
3.08
3.16
f1 (ppm)

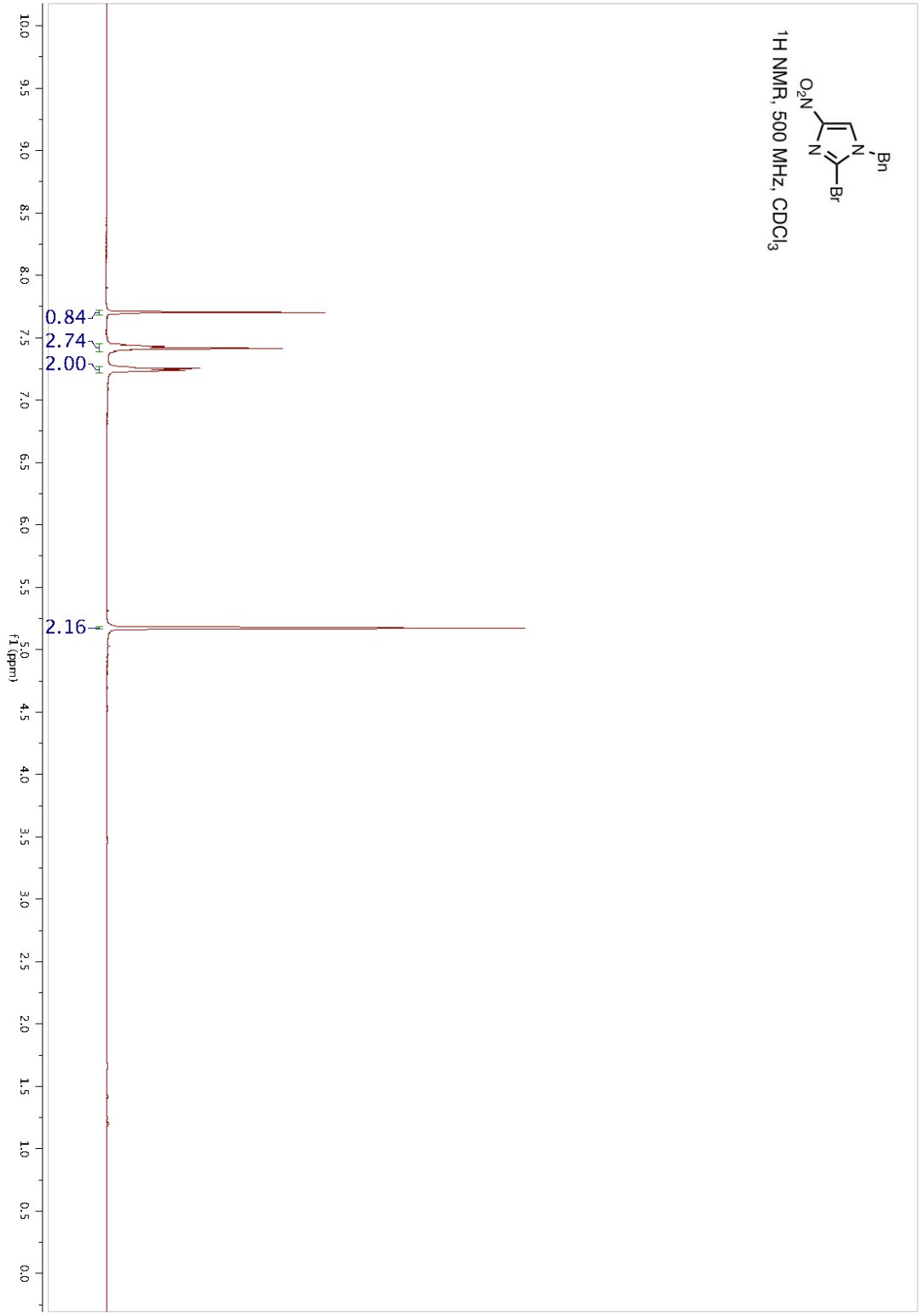

^{13}C NMR, 125 MHz, $CDCl_3$
Me
Br
Ts
N
N
Me
f1 (ppm)
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0

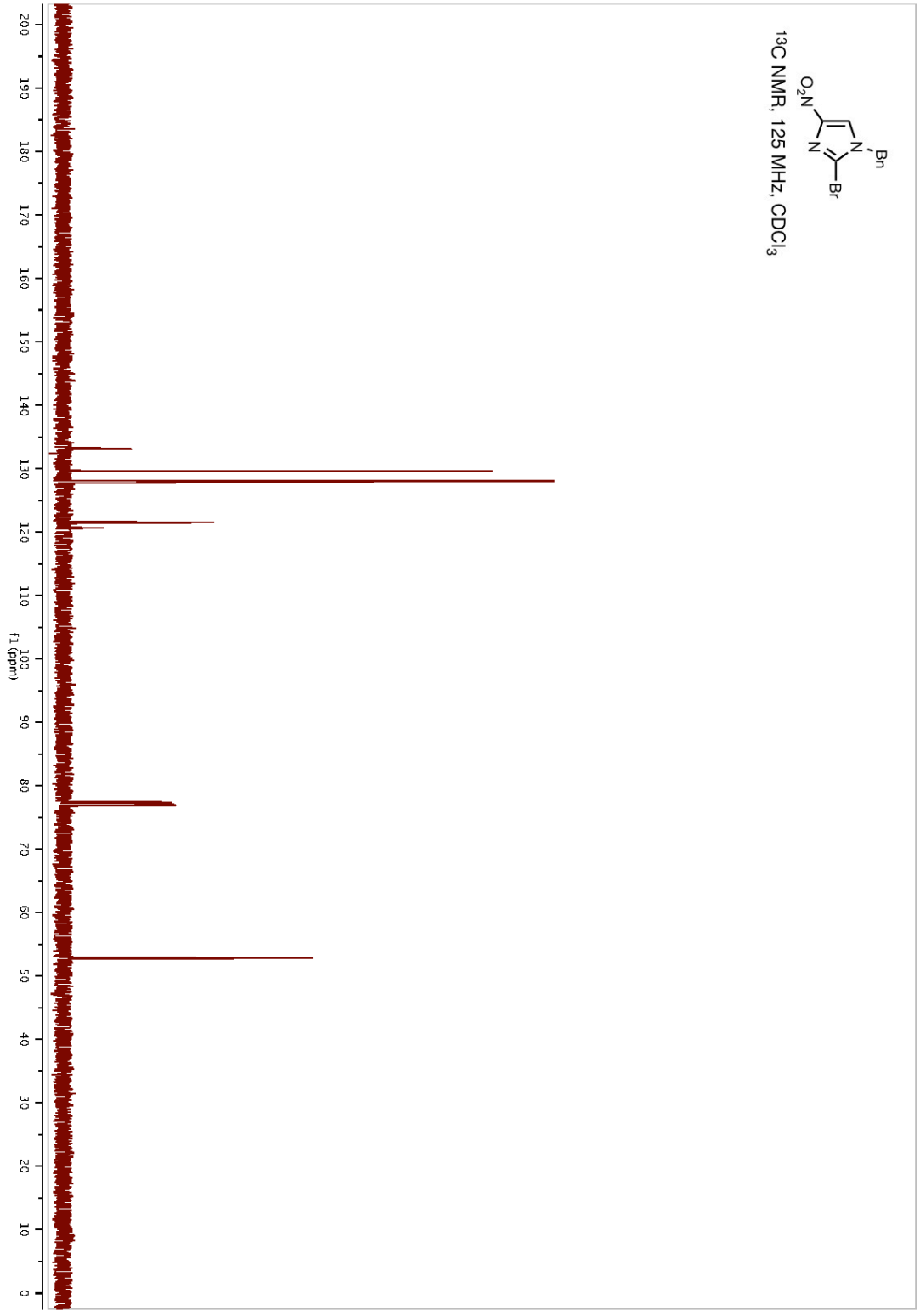

^{1}H NMR, 500 MHz, CDCl$_3$
Br
Me
Me
N
N
O
O
S
iPr
iPr
iPr
f1 (ppm)
2.00
2.22
1.03
2.98
3.37
6.38
12.64

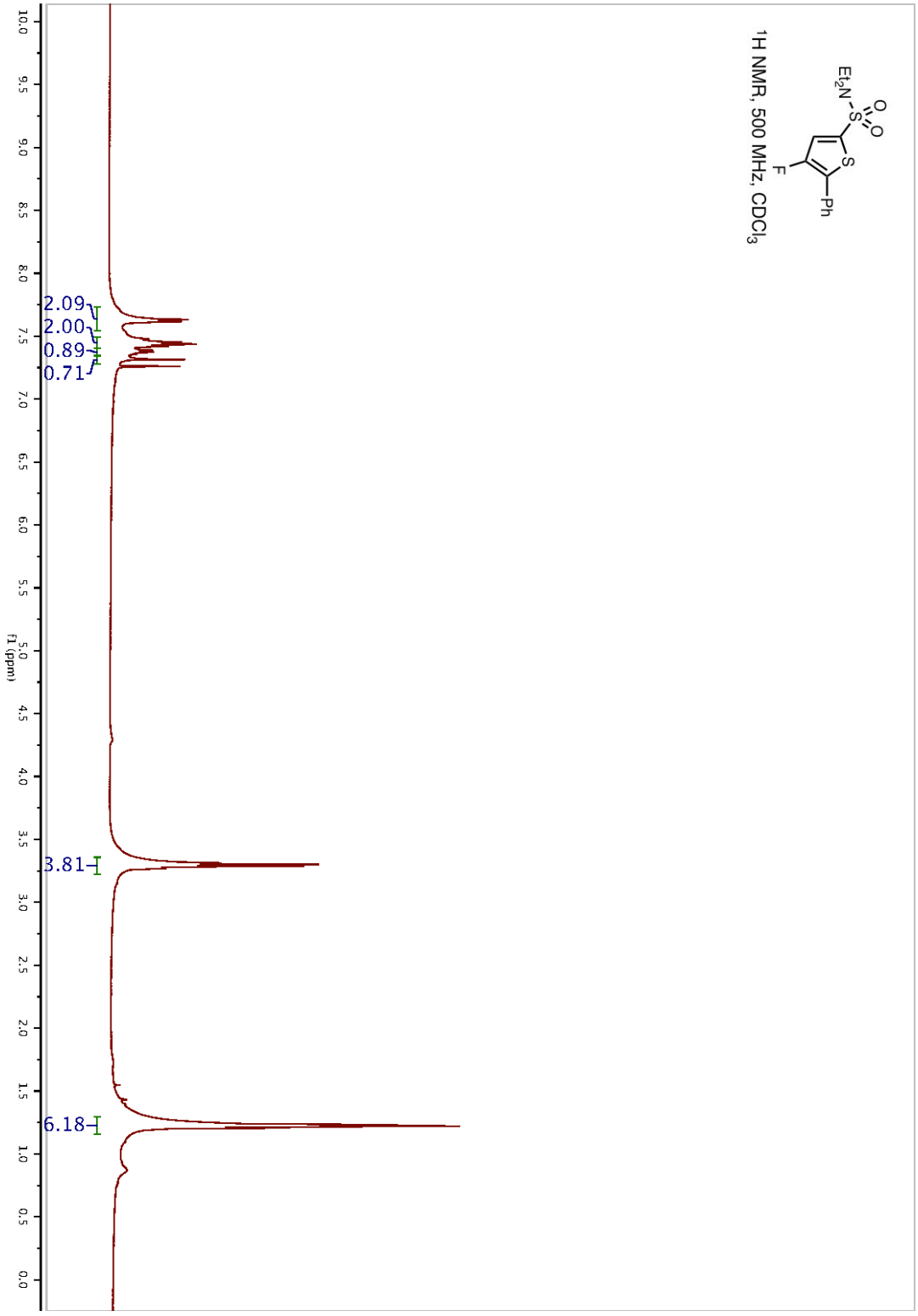

^{13}C NMR, 125 MHz, $CDCl_3$
Br
Me
Me
N
N
O
O
S
iPr
iPr
iPr
f1 (ppm)
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0

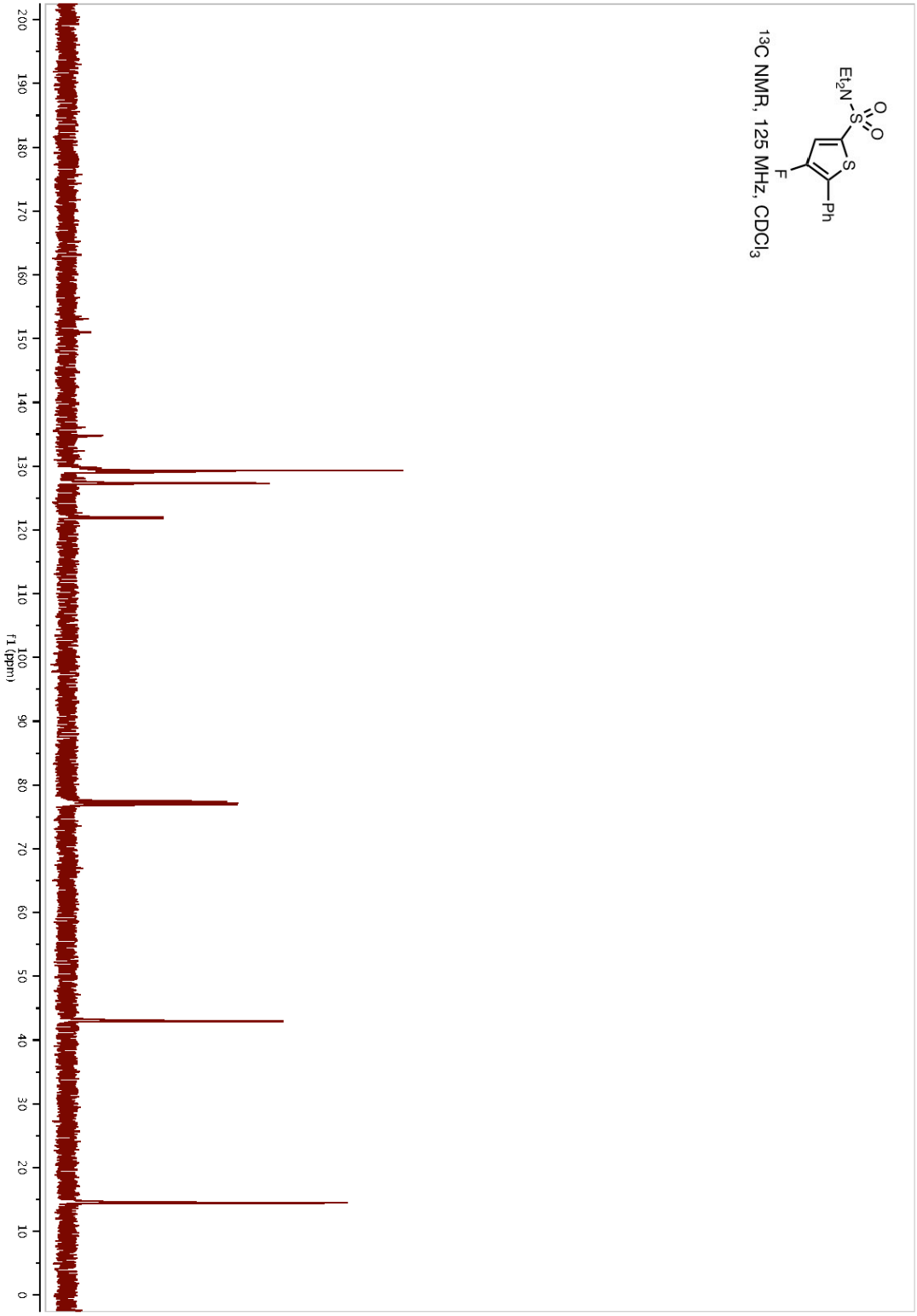

tBuO2C
Me
N
S
Br
1H NMR, 500 MHz, CDCl3
f1 (ppm)
3.00
10.32

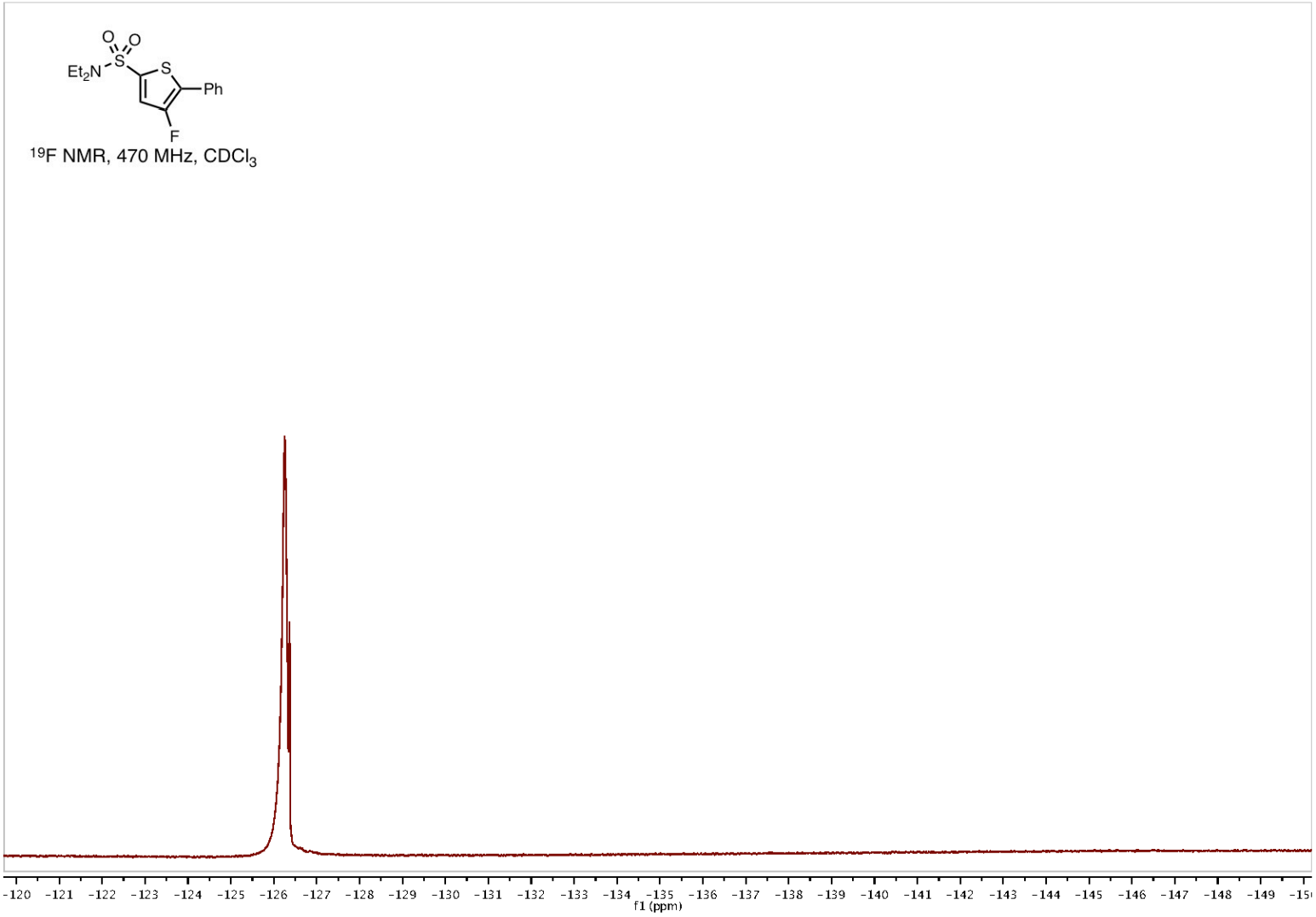

tBuO2C
S
Br
N
Me
13C NMR, 125 MHz, CDCl3
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

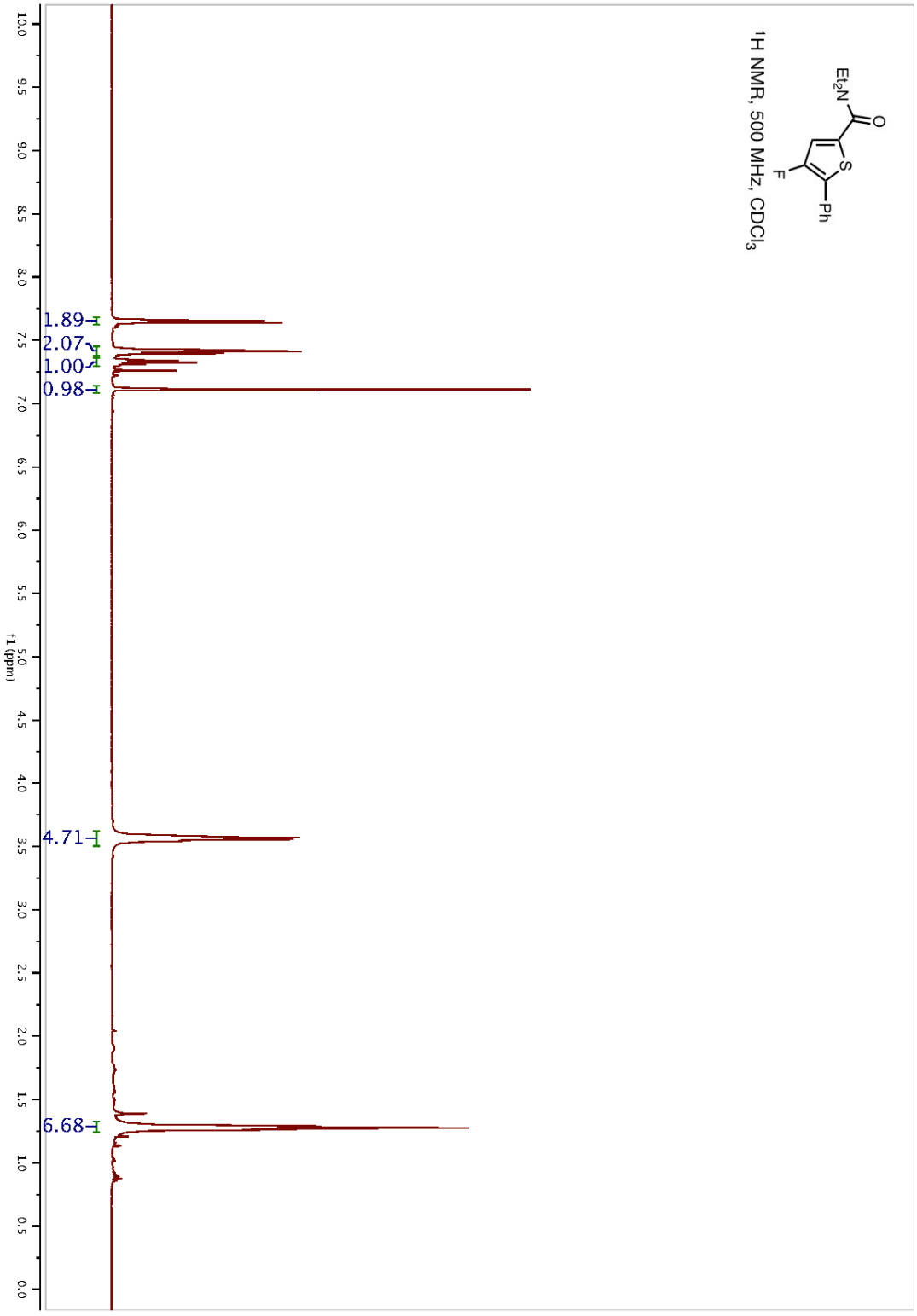

^{1}H NMR, 500 MHz, CDCl$_3$
O$_2$N
N
N
Bn
Br
0.84
2.74
2.00
2.16
f1 (ppm)
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0

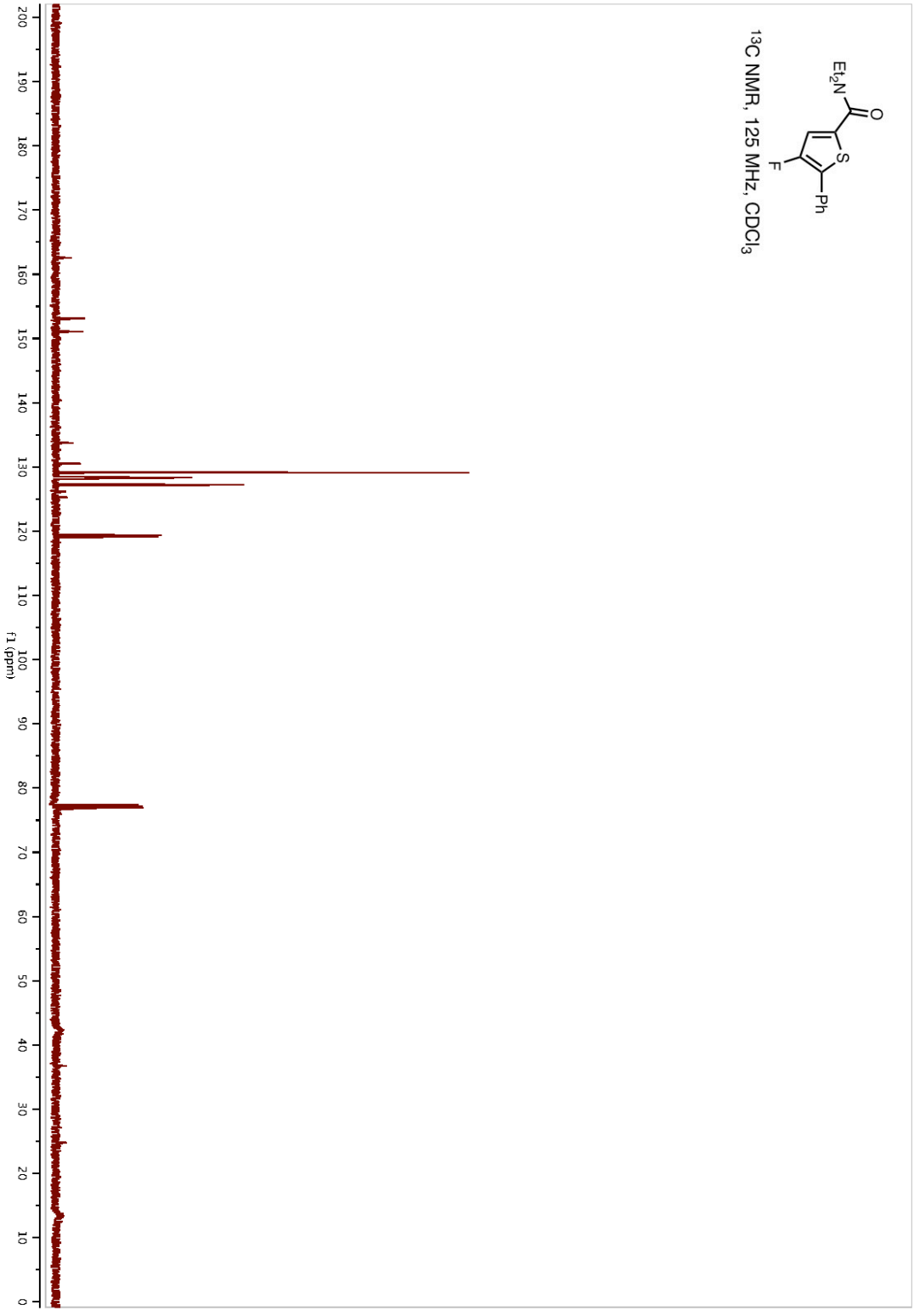

^{13}C NMR, 125 MHz, CDCl$_3$
O$_2$N
N
N
Bn
Br
f1 (ppm)
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0

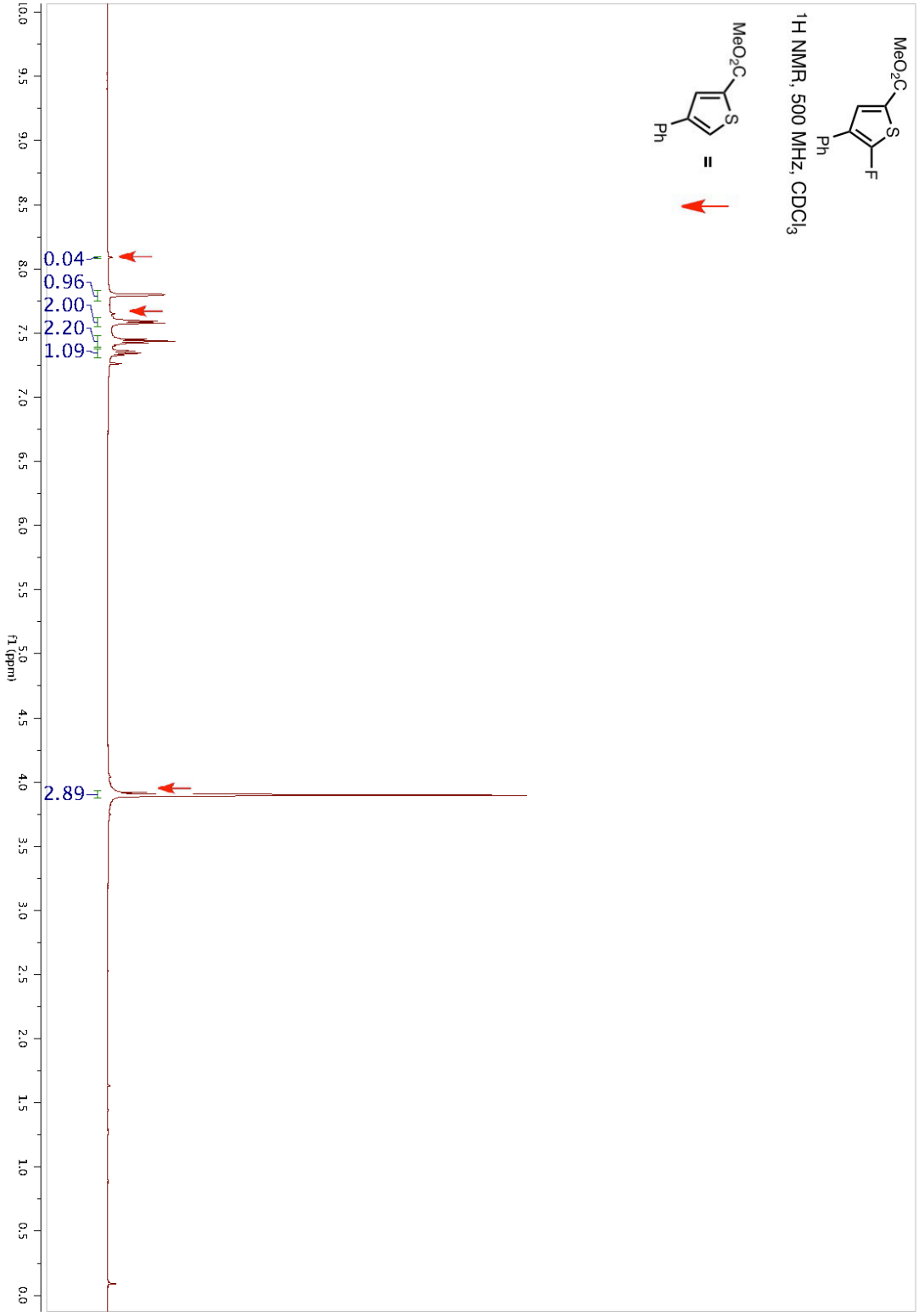

^{1}H NMR, 500 MHz, CDCl$_3$
Et$_2$N
S
O
O
S
F
Ph
2.09
2.00
0.89
0.71
3.81
6.18
f1 (ppm)

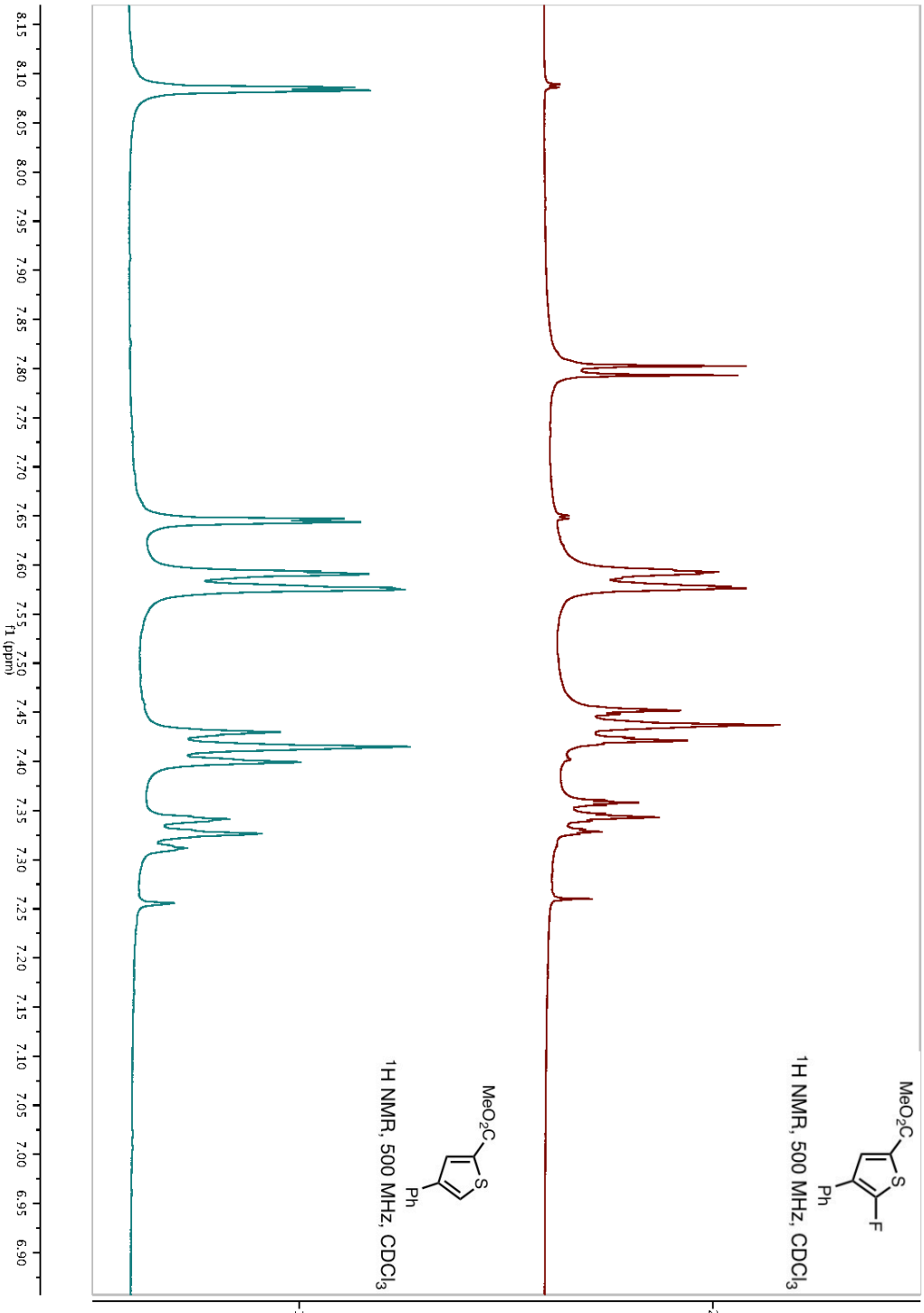

^{13}C NMR, 125 MHz, $CDCl_3$
Et_2N
S
O
O
S
F
Ph
f1 (ppm)
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0

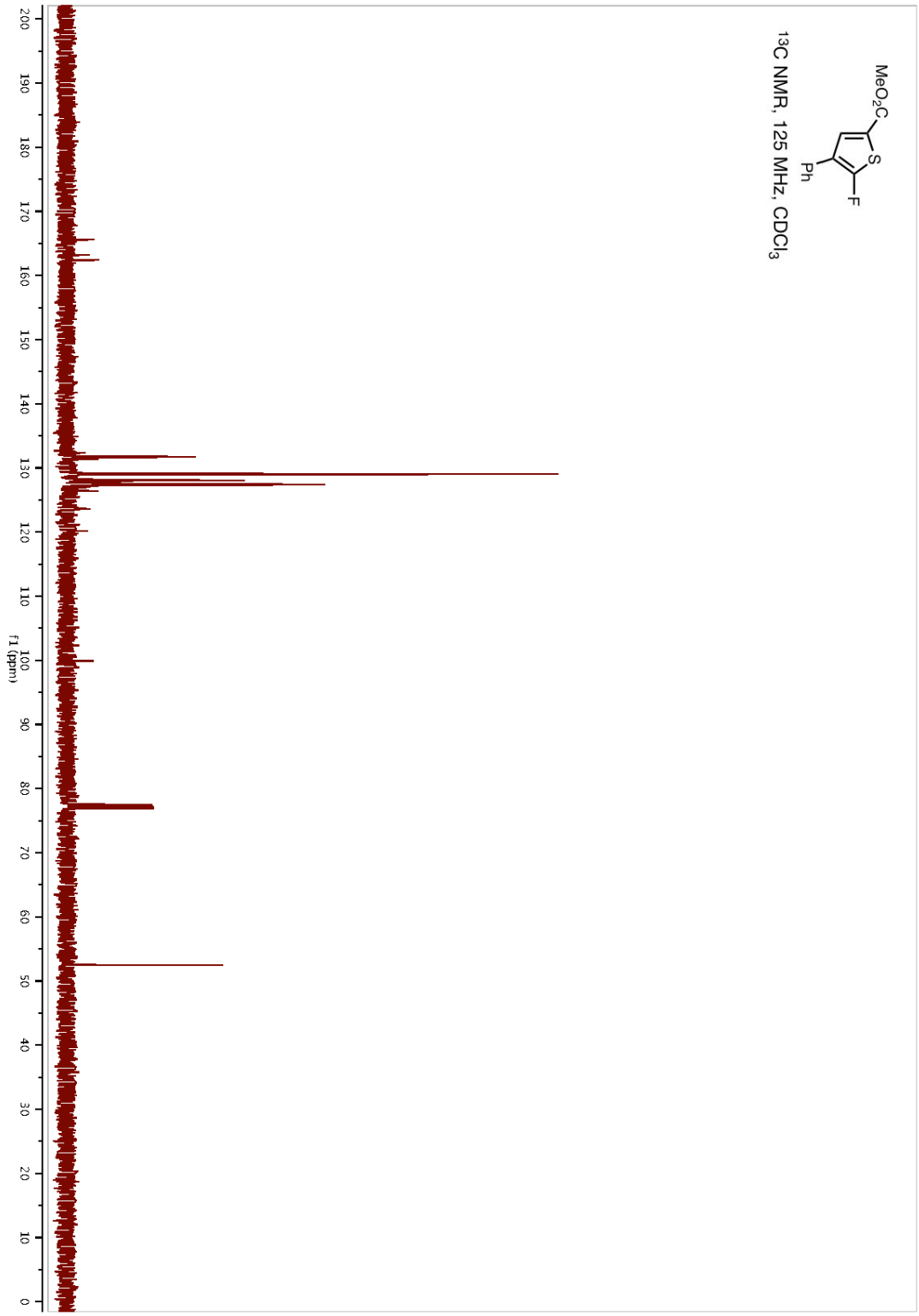

Et2N
S
O
O
S
Ph
F
19F NMR, 470 MHz, CDCl3
-120 -121 -122 -123 -124 -125 -126 -127 -128 -129 -130 -131 -132 -133 -134 -135 -136 -137 -138 -139 -140 -141 -142 -143 -144 -145 -146 -147 -148 -149
f1 (ppm)

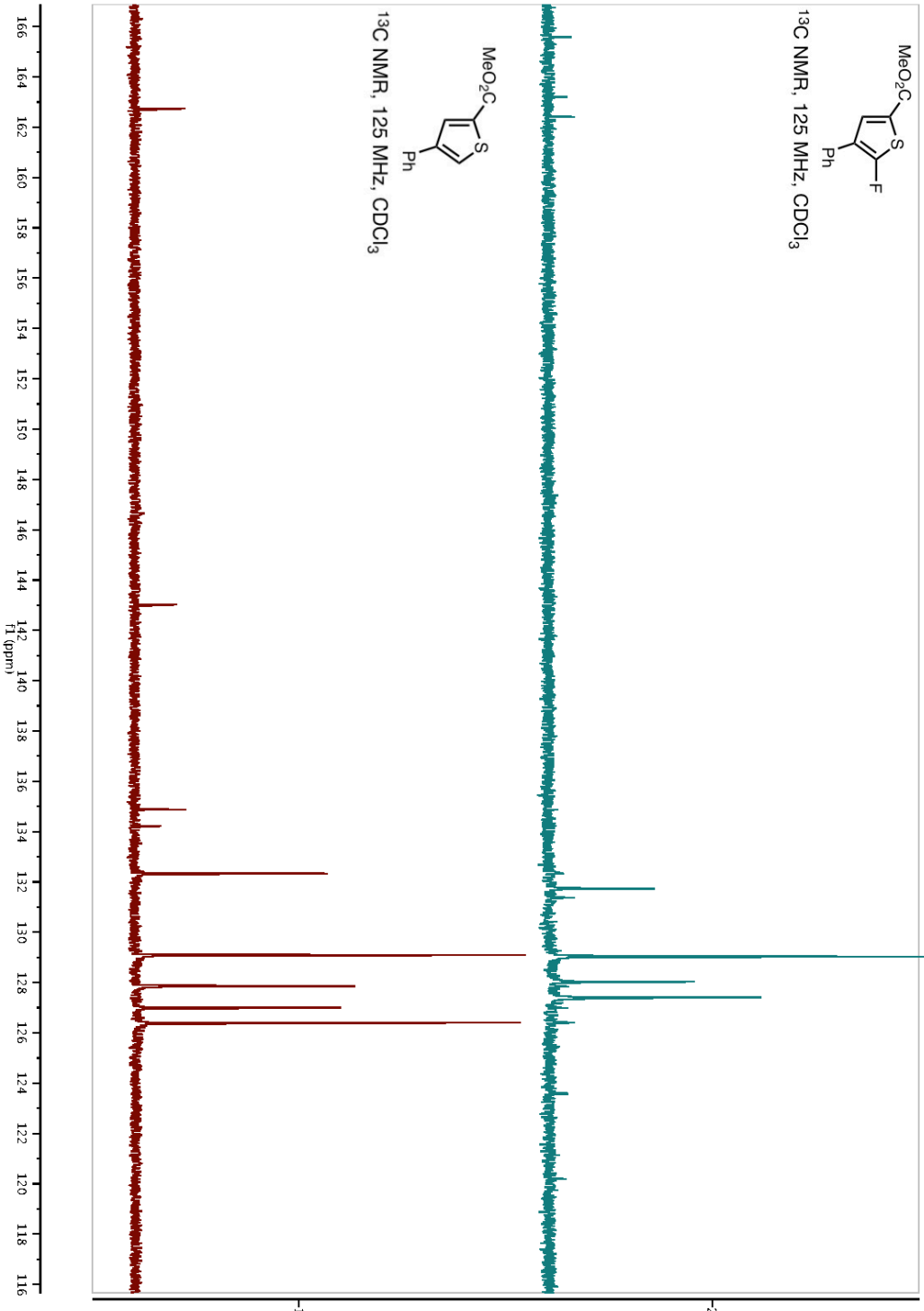

1H NMR, 500 MHz, CDCl3
Et2N
O
S
F
Ph
1.89
2.07
1.00
0.98
4.71
6.68
f1 (ppm)

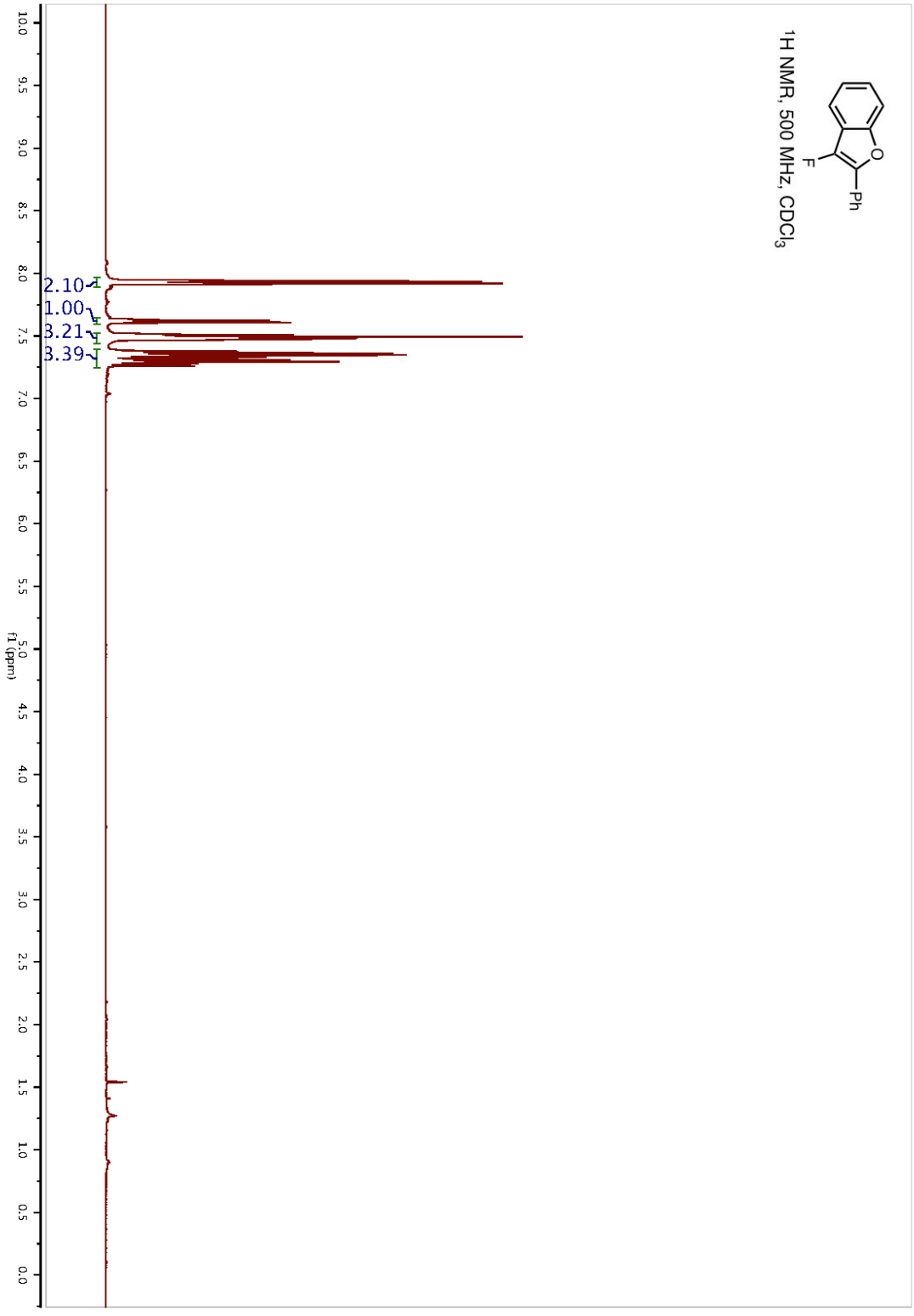

Et2N
O
S
F
Ph
13C NMR, 125 MHz, CDCl3
f1 (ppm)
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0

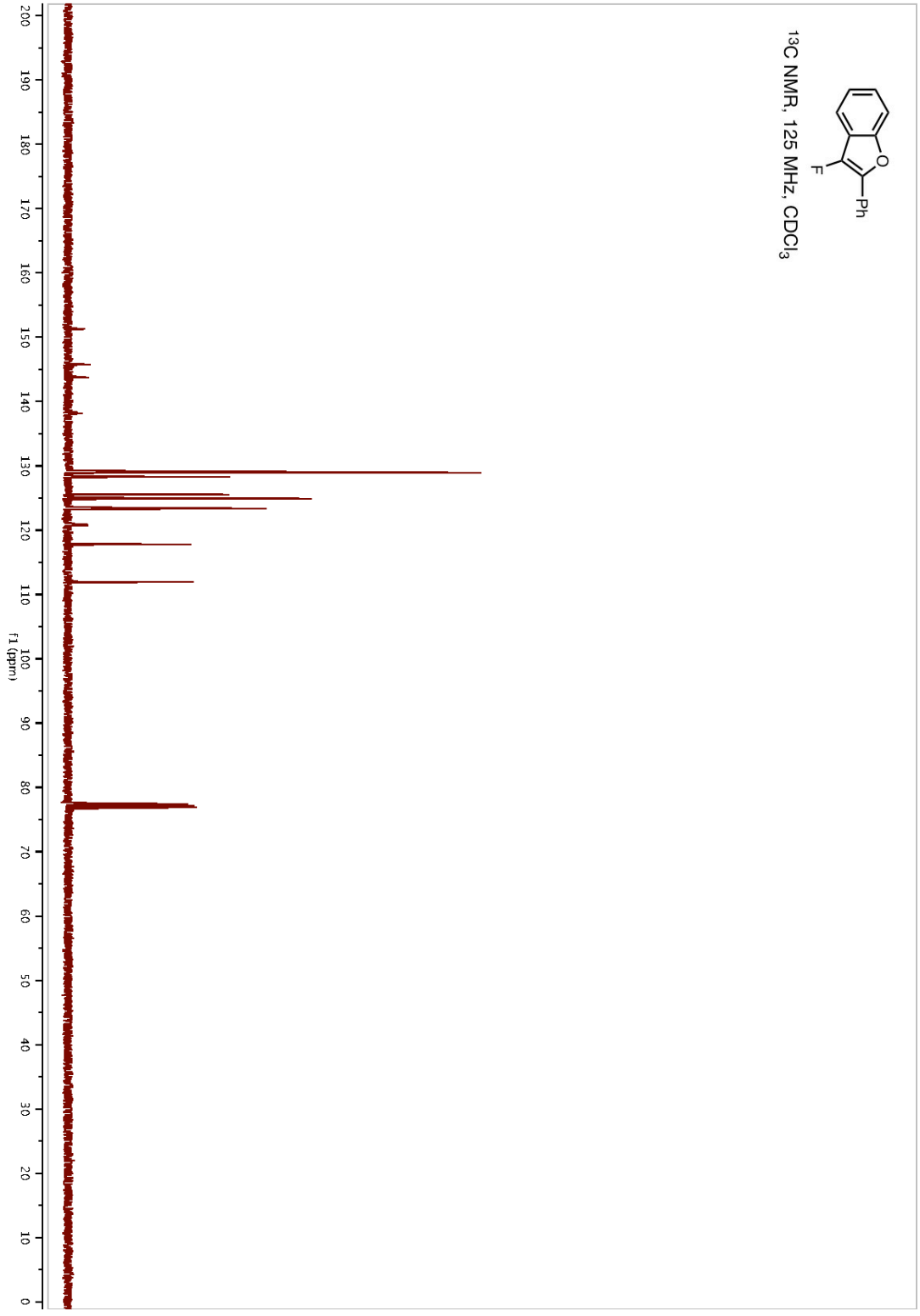

MeO2C
S
Ph
F
1H NMR, 500 MHz, CDCl3
MeO2C
S
Ph
=
0.04
0.96
2.00
2.20
1.09
2.89
f1 (ppm)

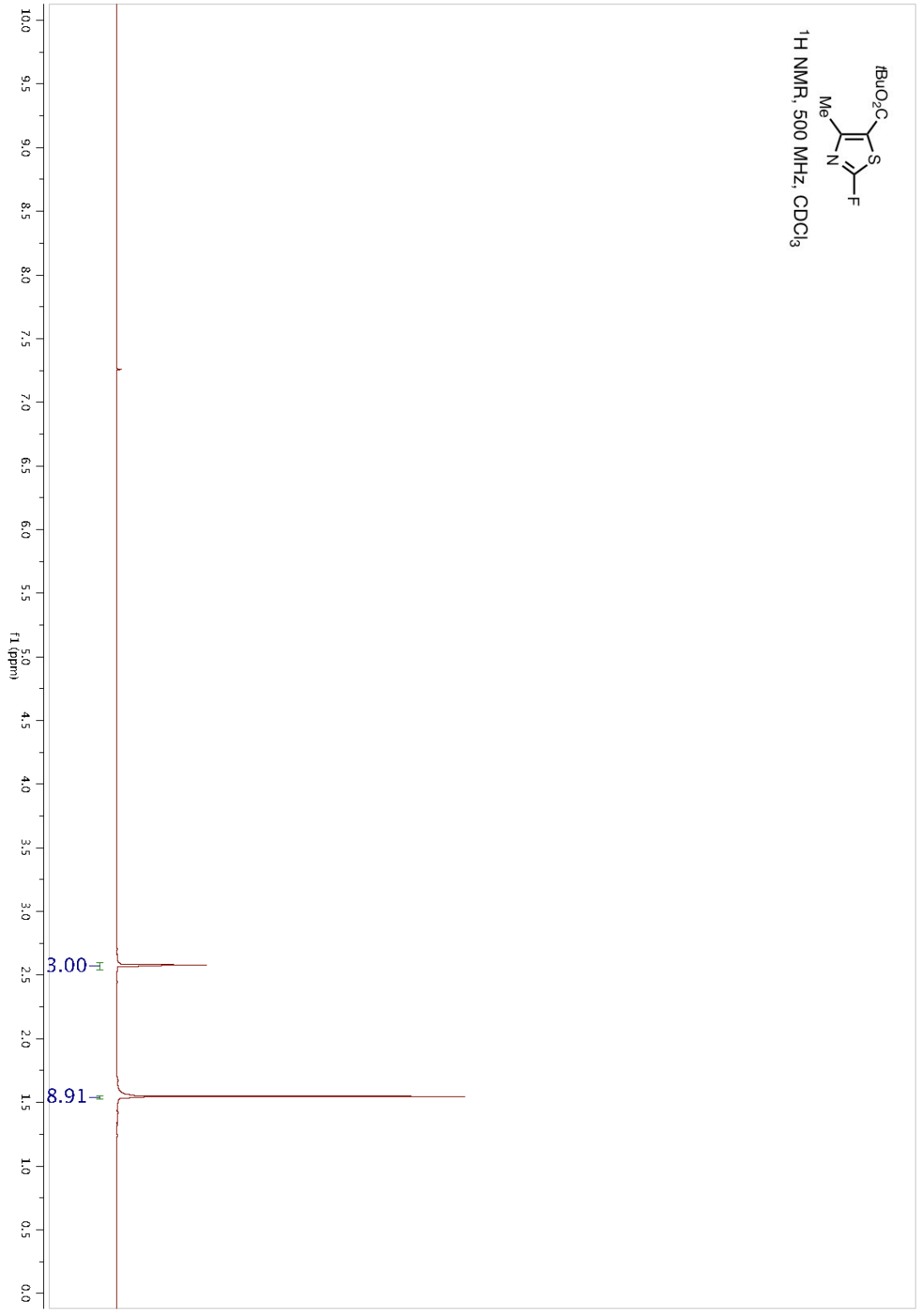

MeO2C
S
Ph
1H NMR, 500 MHz, CDCl3
MeO2C
S
F
Ph
1H NMR, 500 MHz, CDCl3
f1 (ppm)

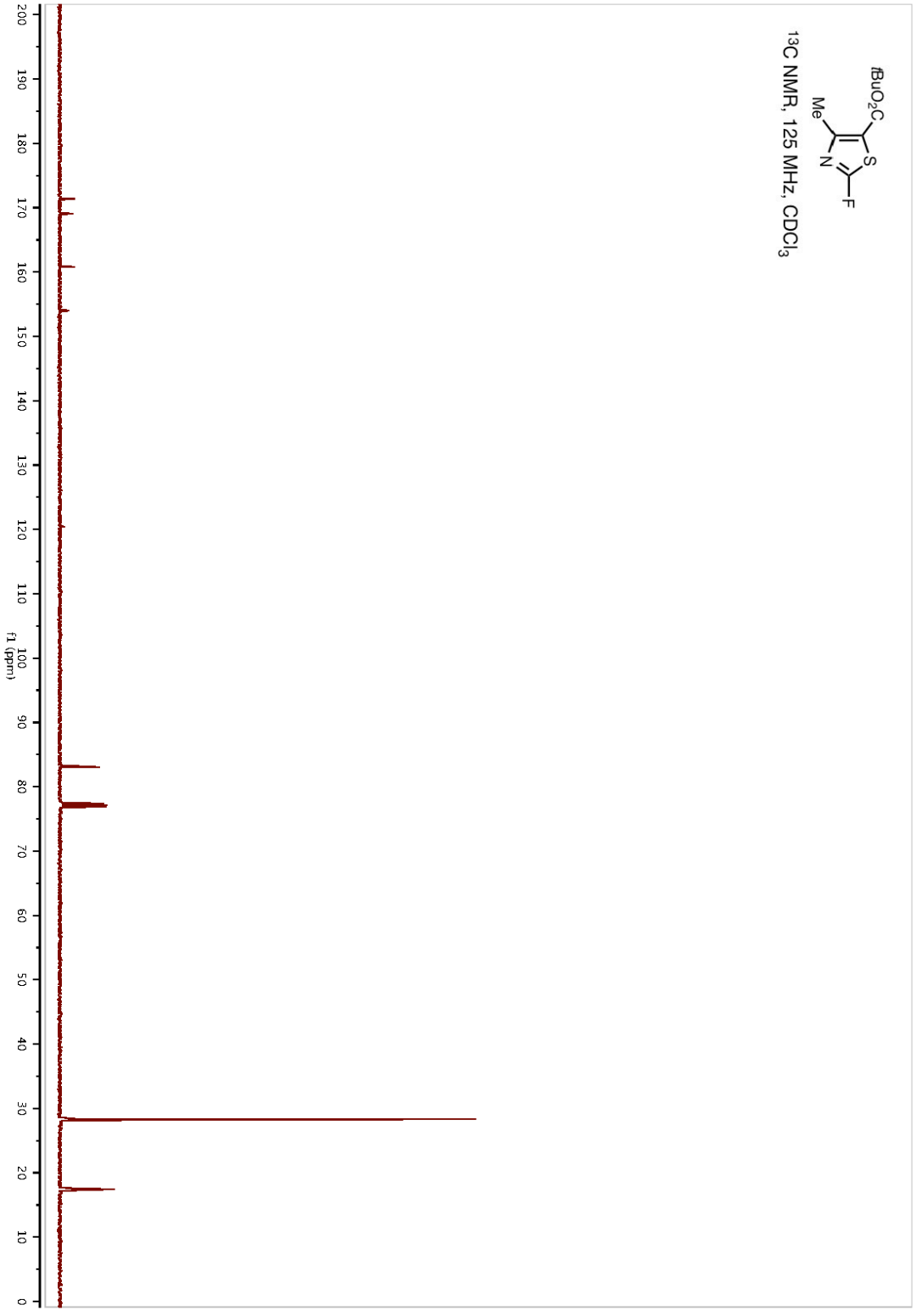

MeO2C
S
F
Ph
13C NMR, 125 MHz, CDCl3
f1 (ppm)
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0

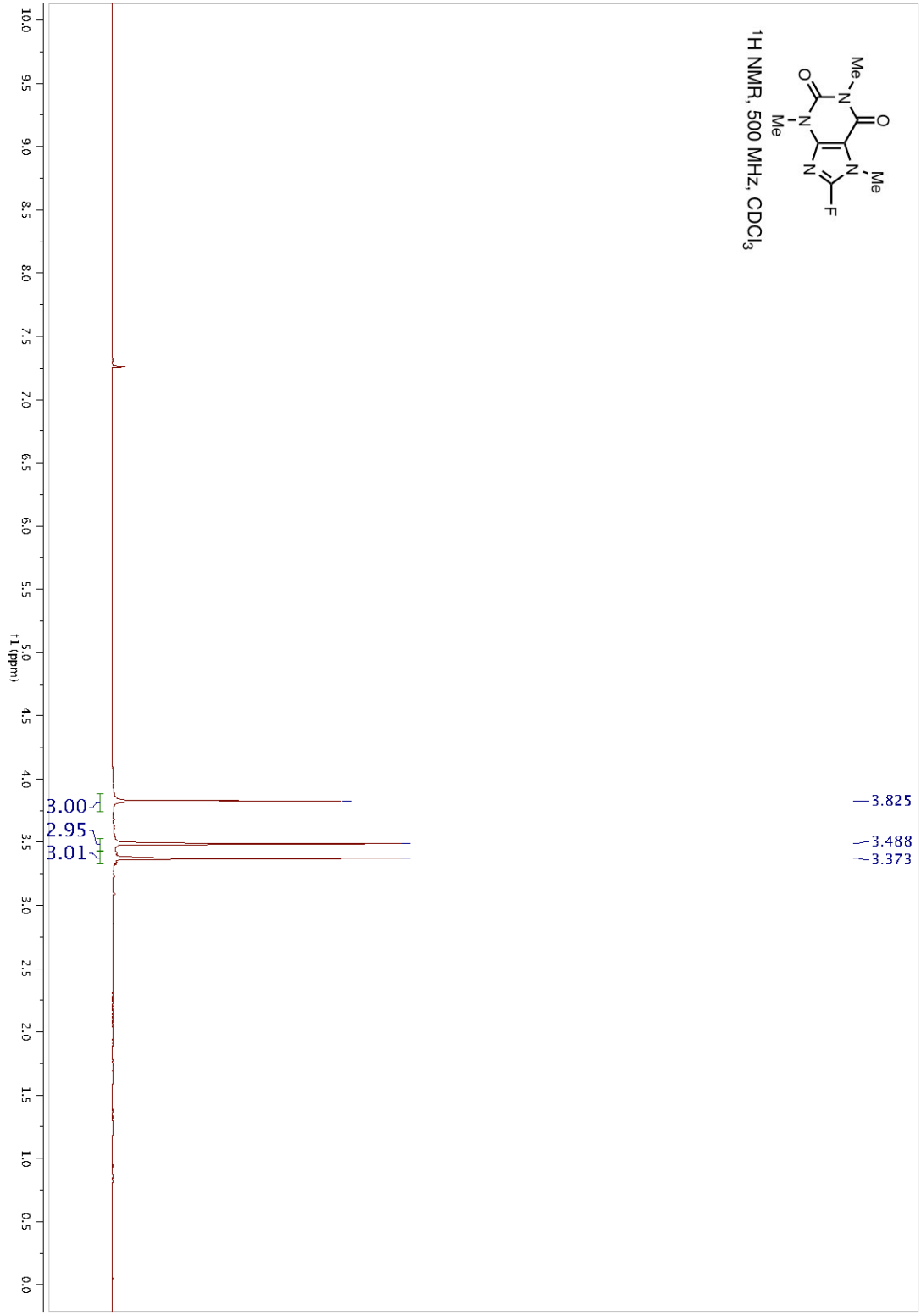

MeO2C
S
F
Ph
13C NMR, 125 MHz, CDCl3
MeO2C
S
Ph
13C NMR, 125 MHz, CDCl3
166
164
162
160
158
156
154
152
150
148
146
144
142
140
138
136
134
132
130
128
126
124
122
120
118
116
f1 (ppm)

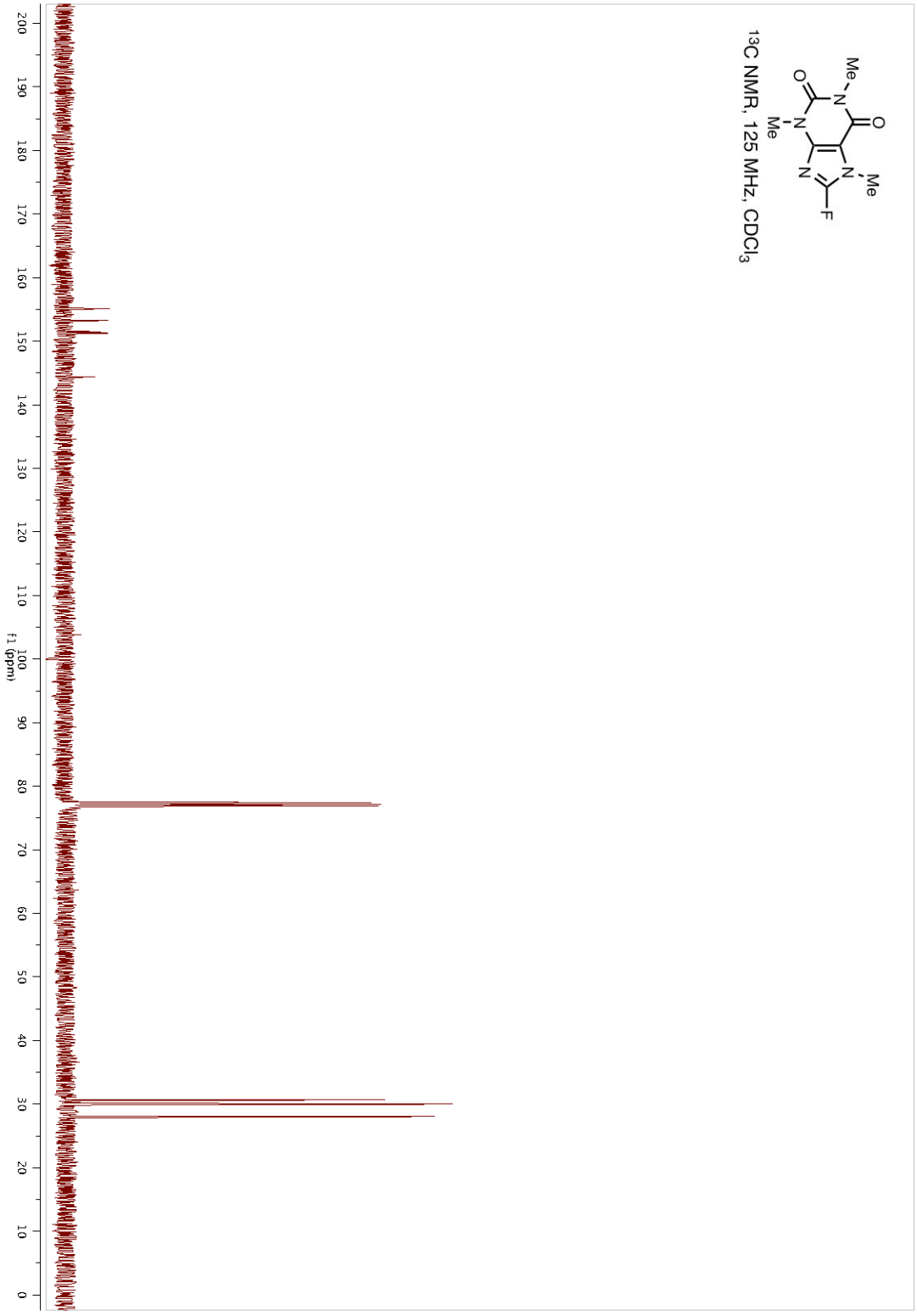

^{1}H NMR, 500 MHz, $CDCl_3$
F
O
Ph
2.10
1.00
3.21
3.39
f1 (ppm)
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0

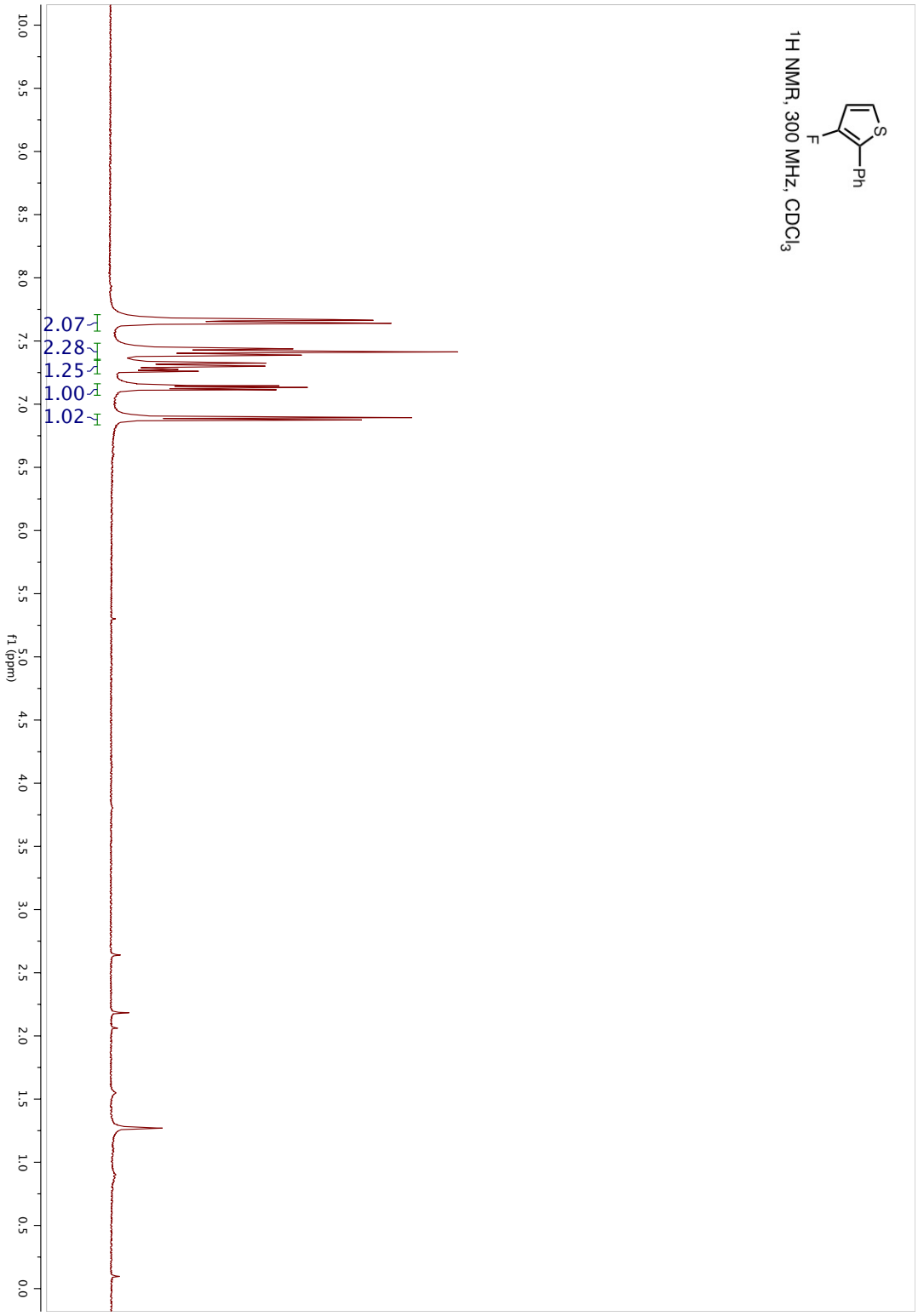

^{13}C NMR, 125 MHz, $CDCl_3$
O
F
Ph
f1 (ppm)
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0

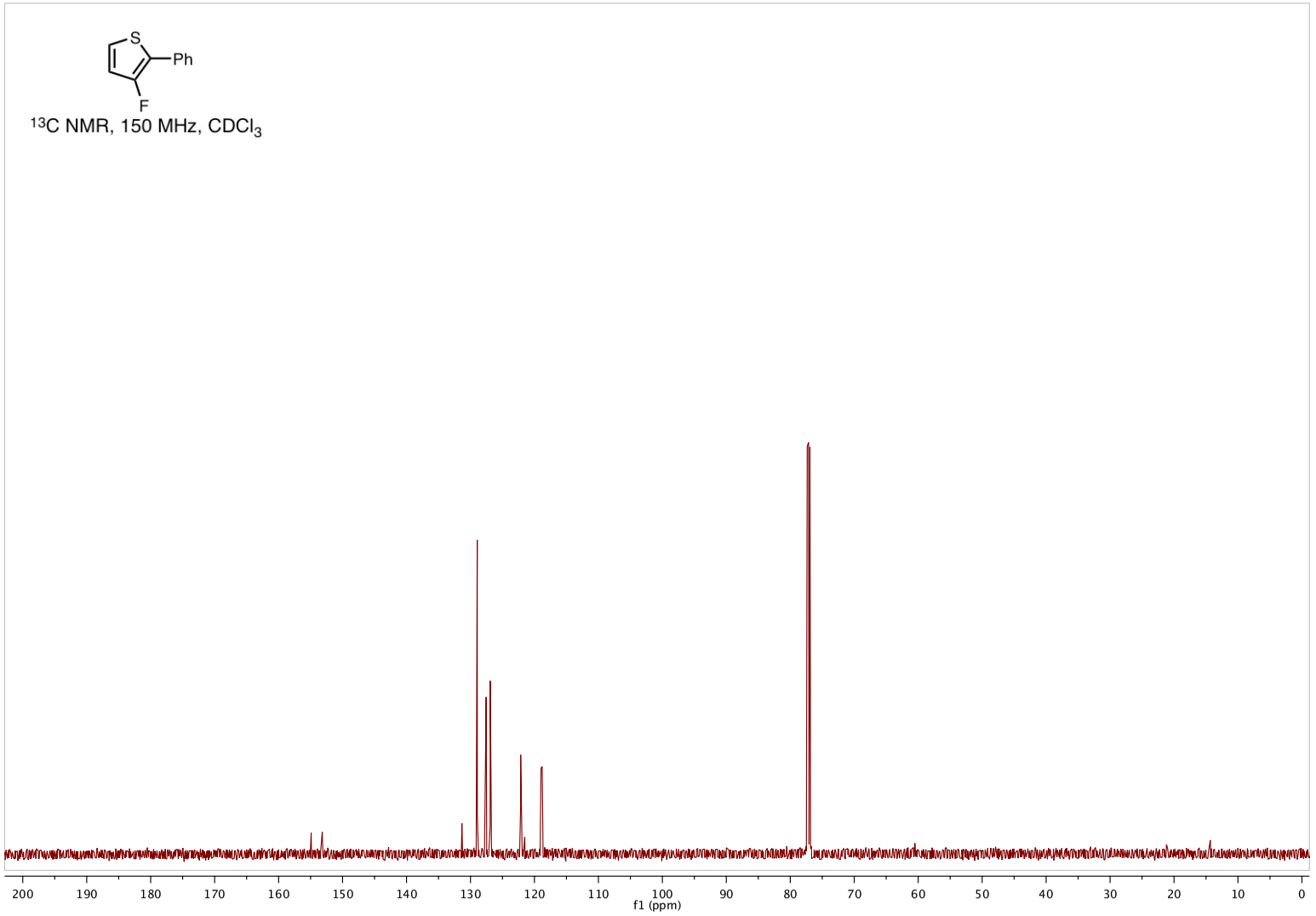

tBuO2C
Me
N
S
F
1H NMR, 500 MHz, CDCl3
f1 (ppm)
3.00
8.91

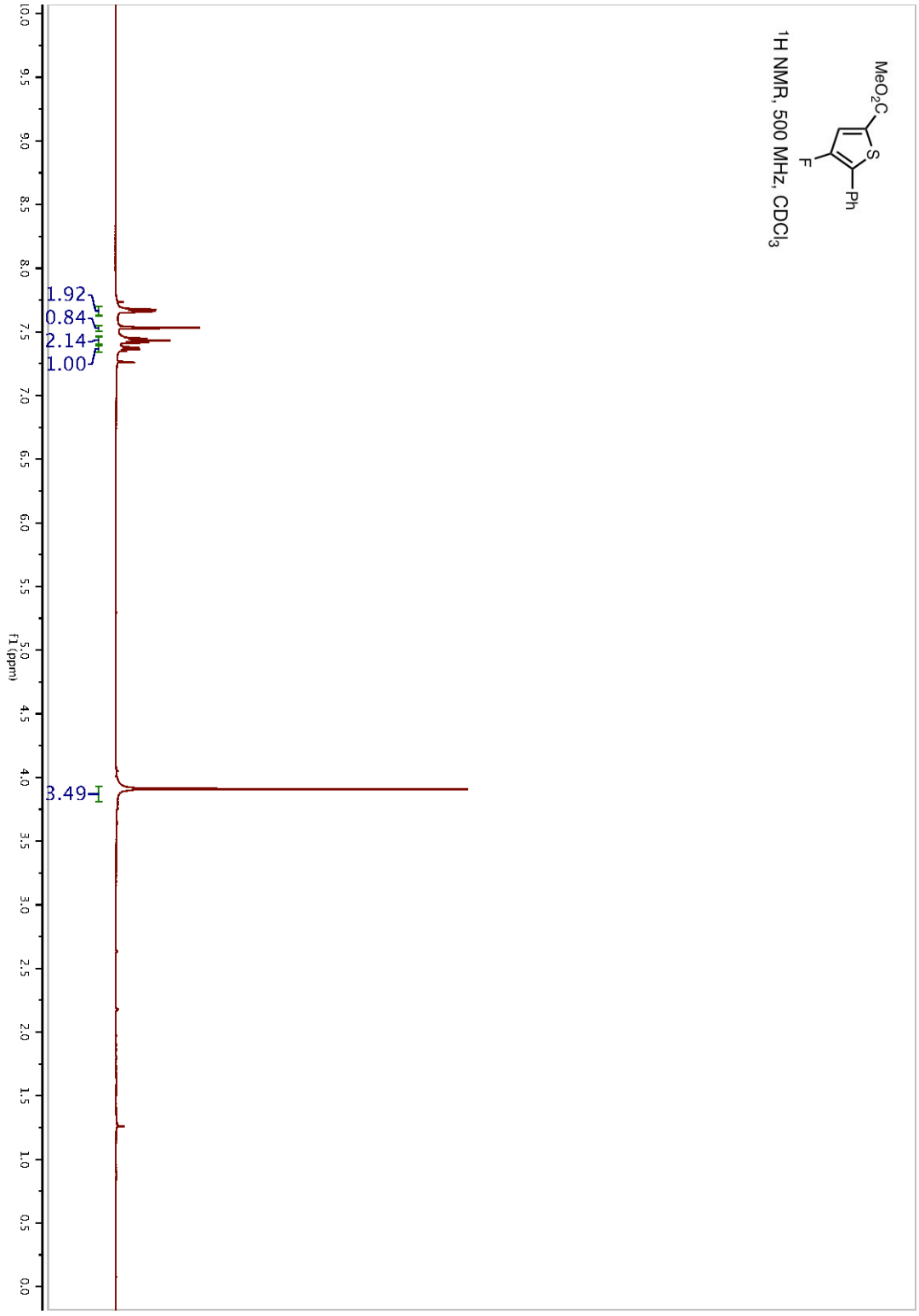

tBuO2C
Me
N
S
F
13C NMR, 125 MHz, CDCl3
f1 (ppm)

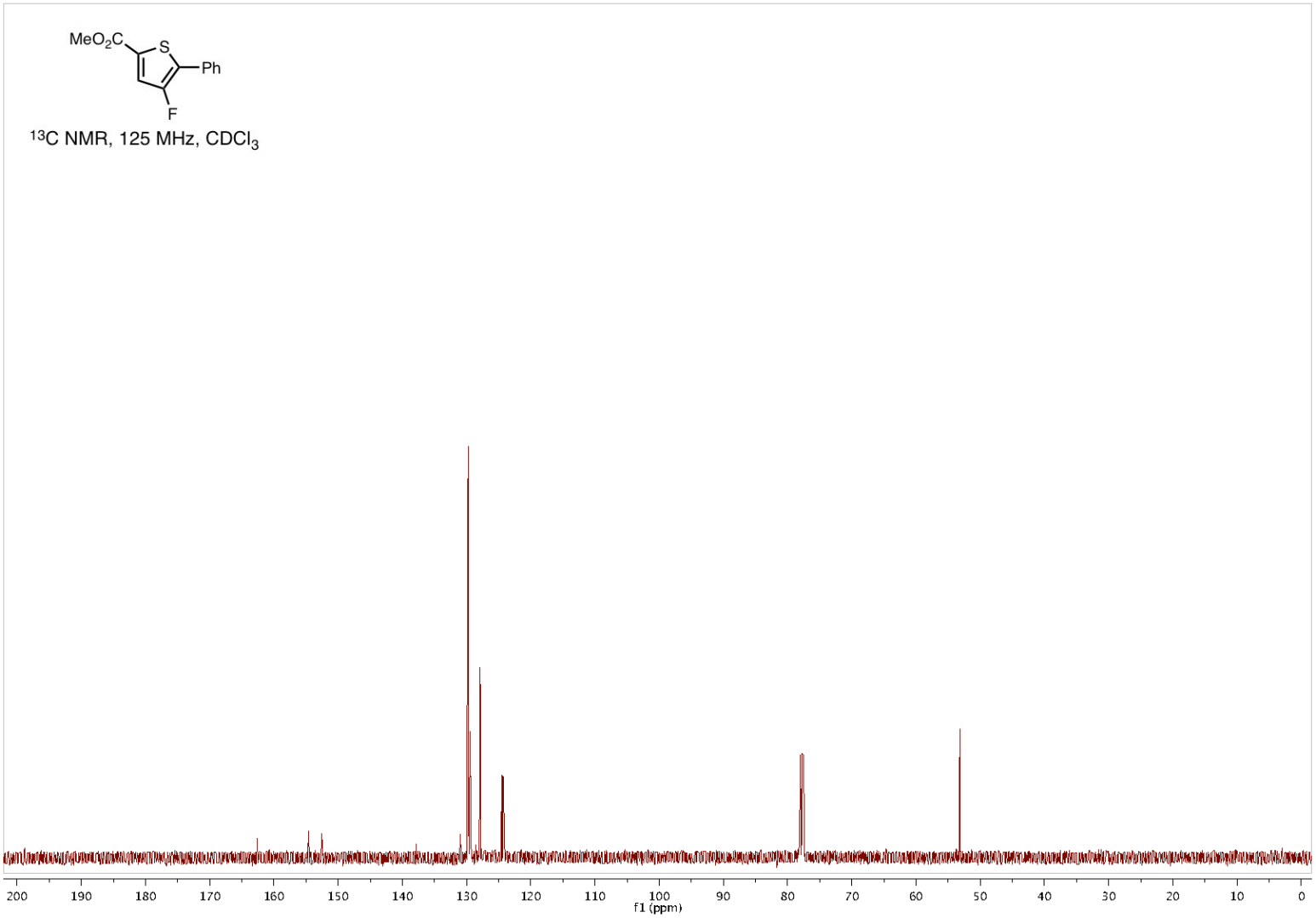

1H NMR, 500 MHz, CDCl3
Me
N
O
N
Me
O
N
N
Me
F
f1 (ppm)
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
3.00
2.95
3.01
3.825
3.488
3.373

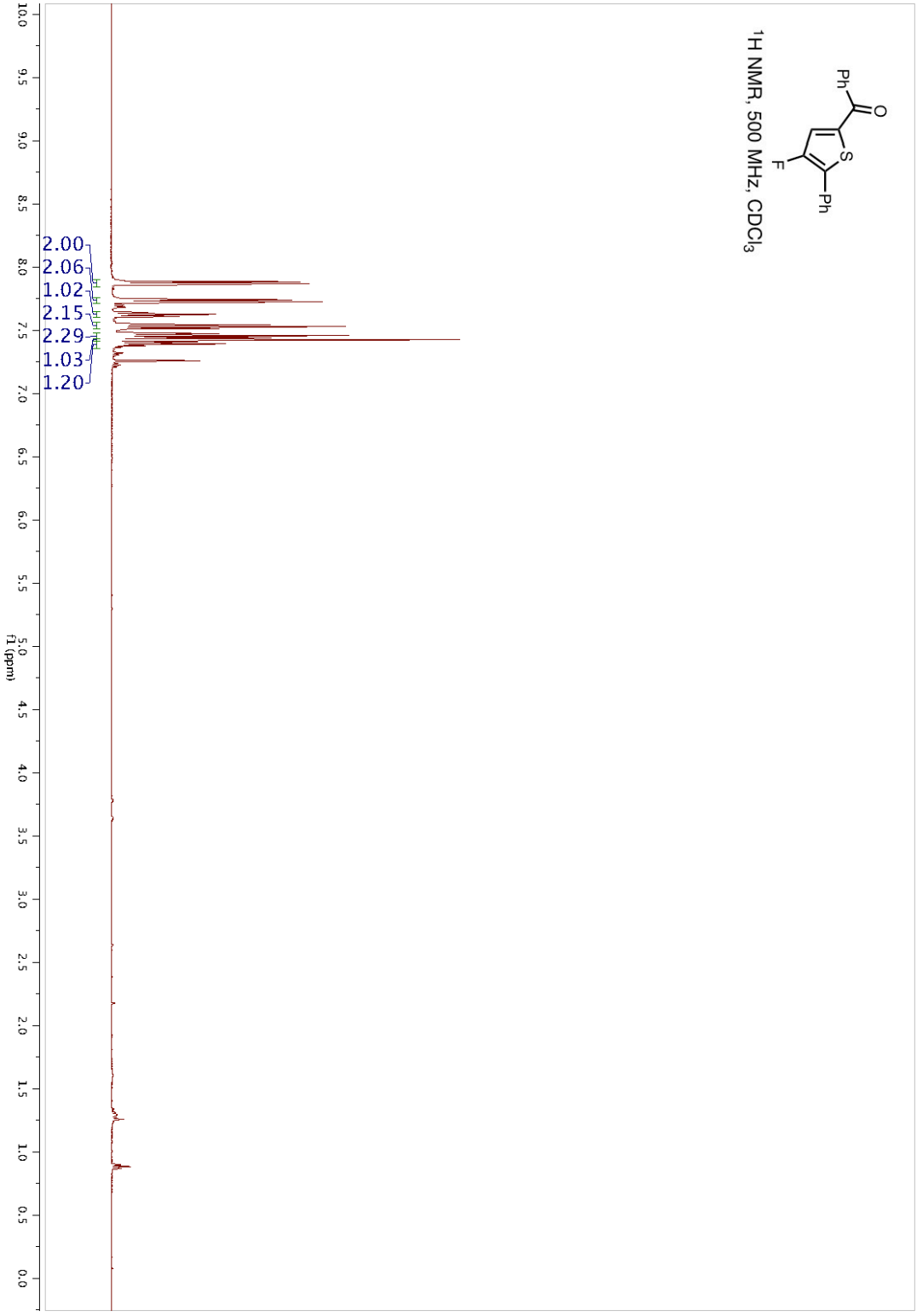

^{13}C NMR, 125 MHz, $CDCl_3$
f1 (ppm)
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0

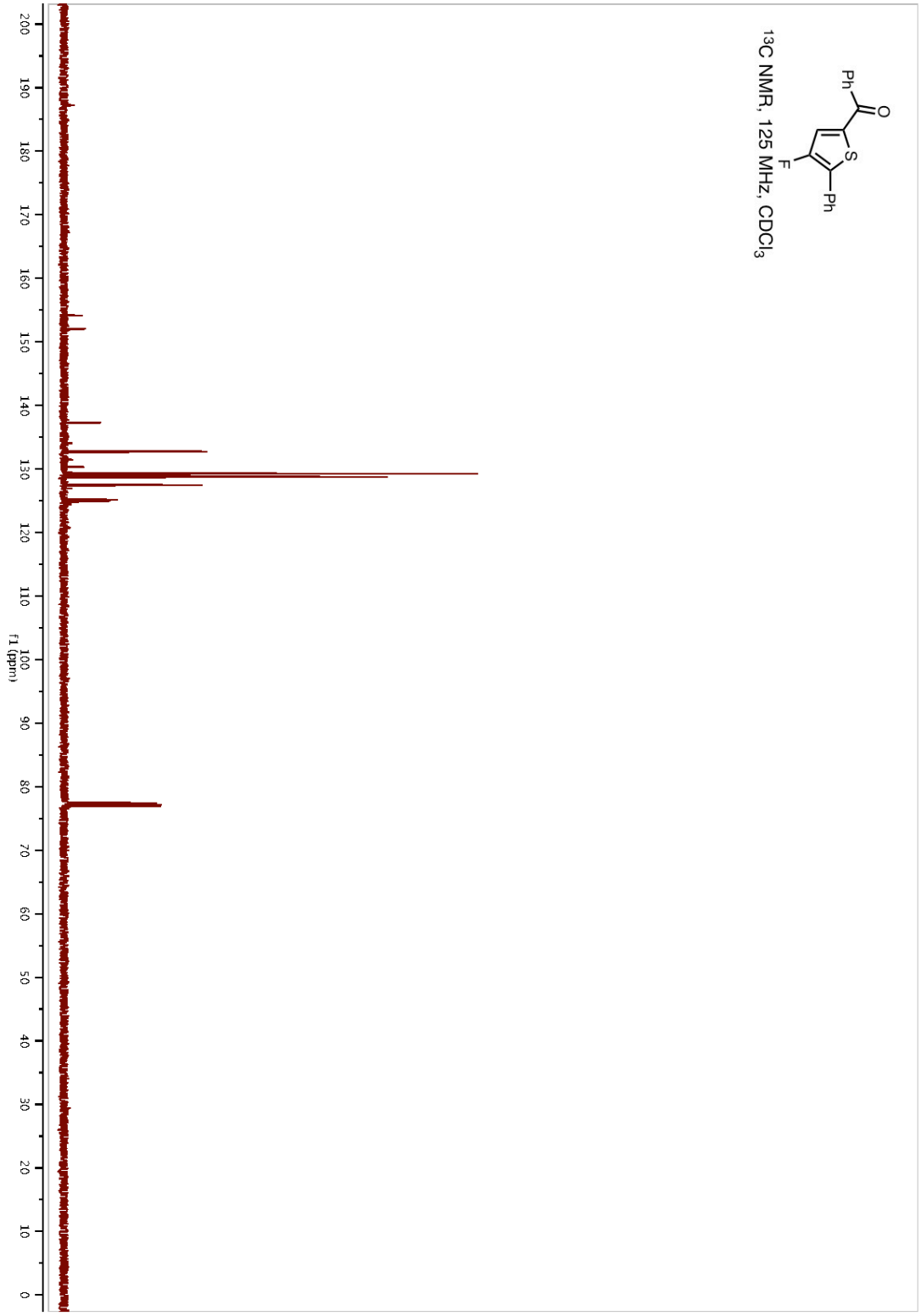

1H NMR, 300 MHz, CDCl3
S
F
Ph
2.07
2.28
1.25
1.00
1.02
f1 (ppm)

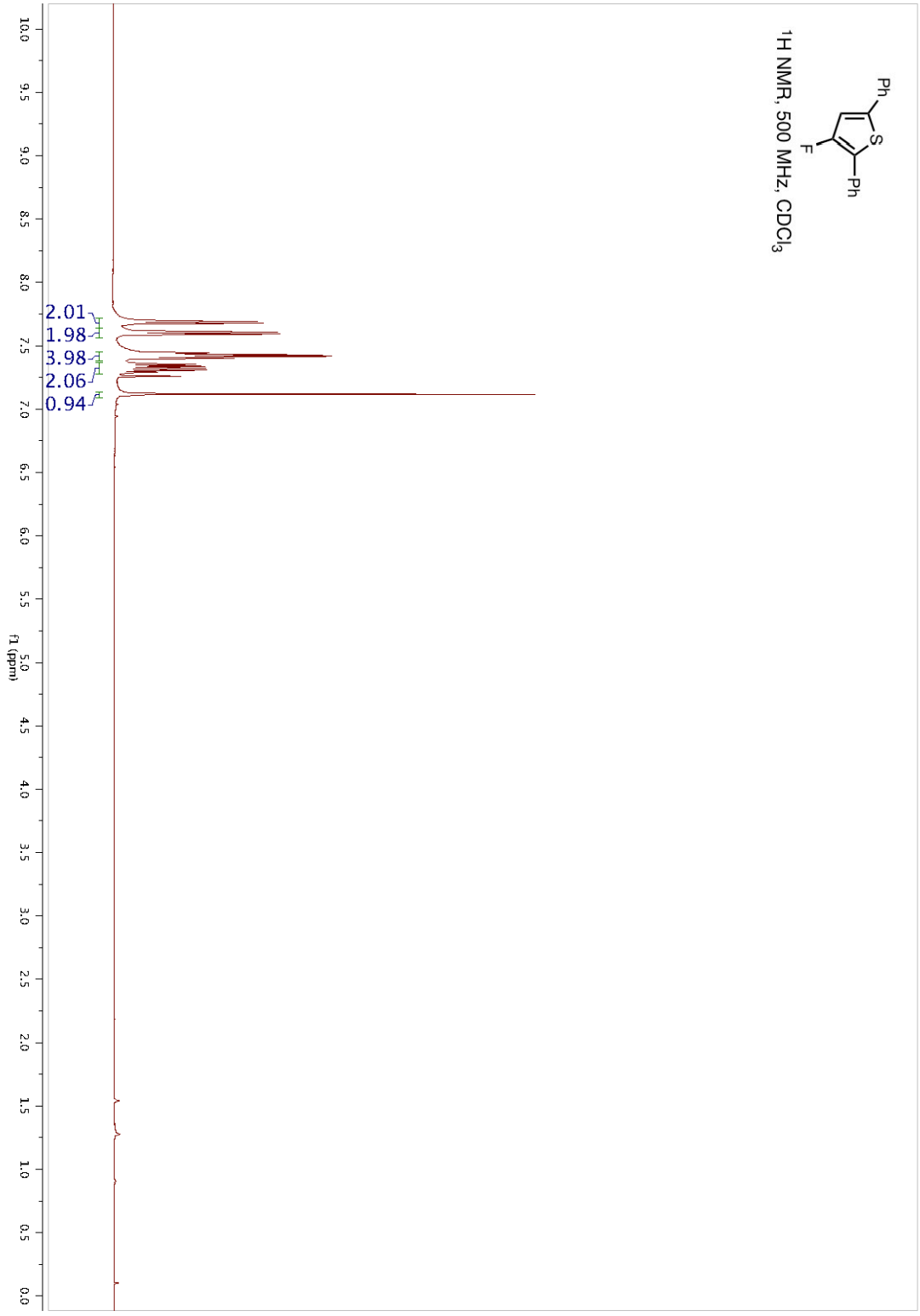

S
Ph
F
^{13}C NMR, 150 MHz, $CDCl_3$
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

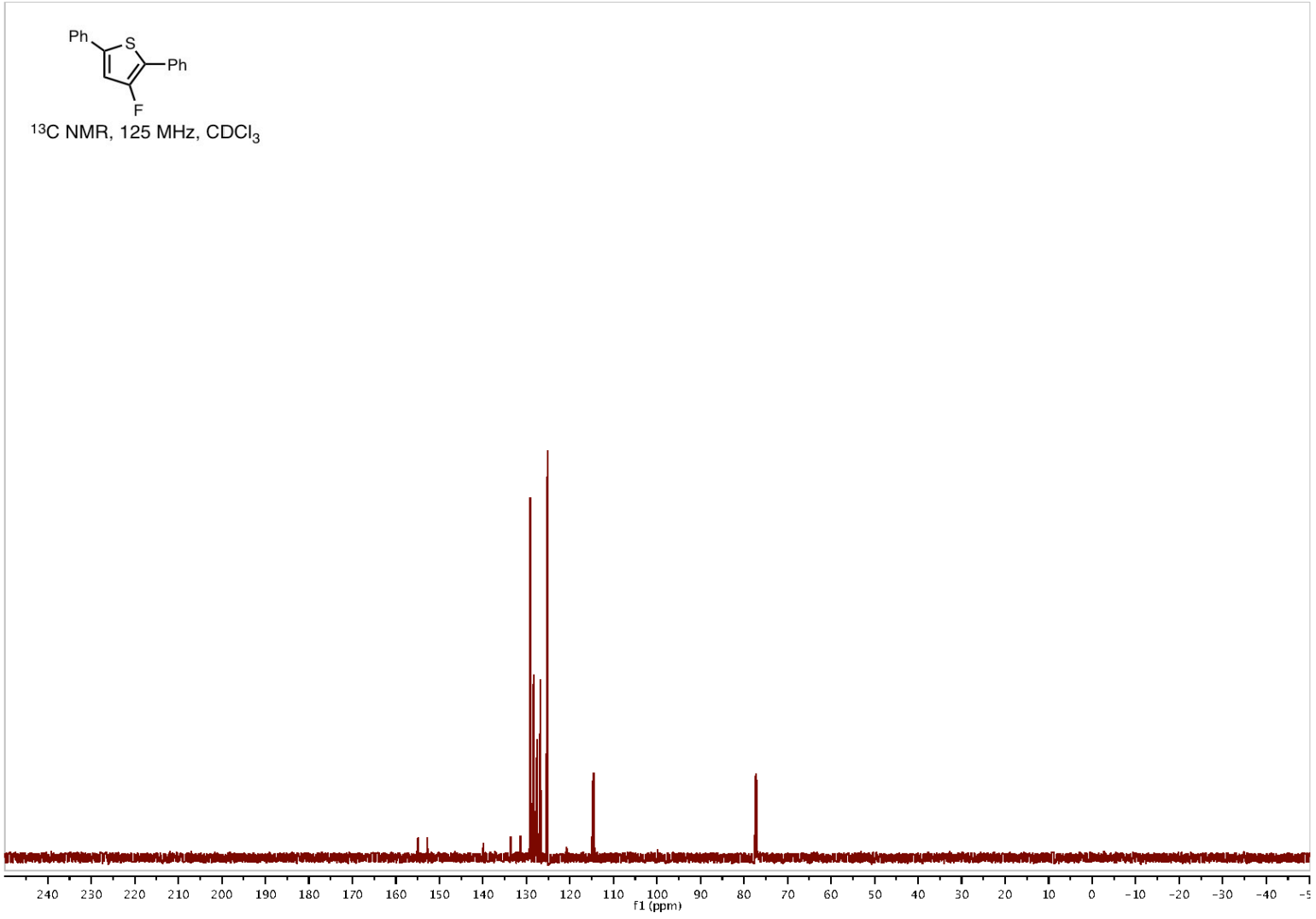

^{1}H NMR, 500 MHz, CDCl$_3$
MeO$_2$C
S
F
Ph
1.92
0.84
2.14
1.00
3.49
f1 (ppm)

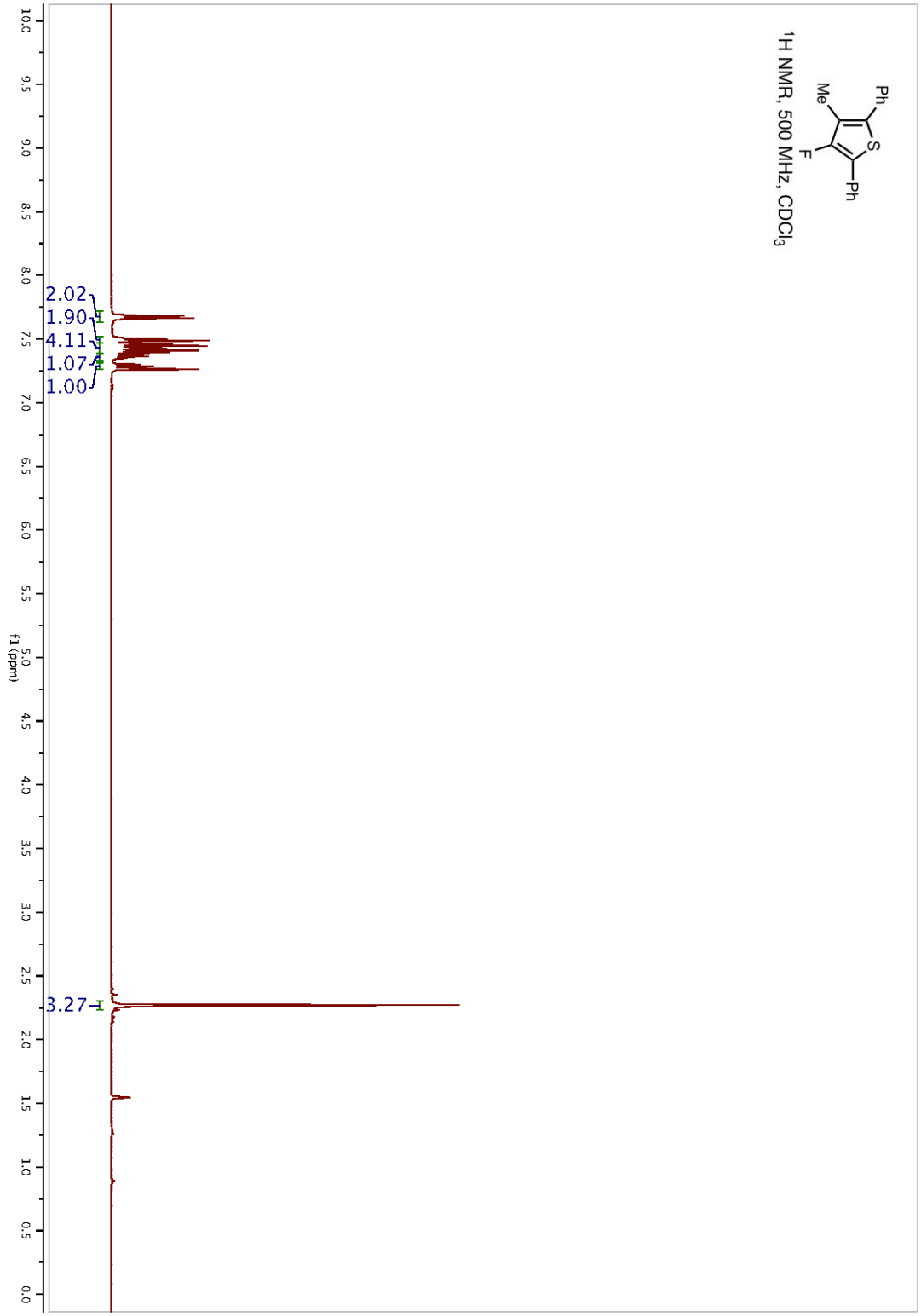

MeO2C
S
Ph
F
13C NMR, 125 MHz, CDCl3
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

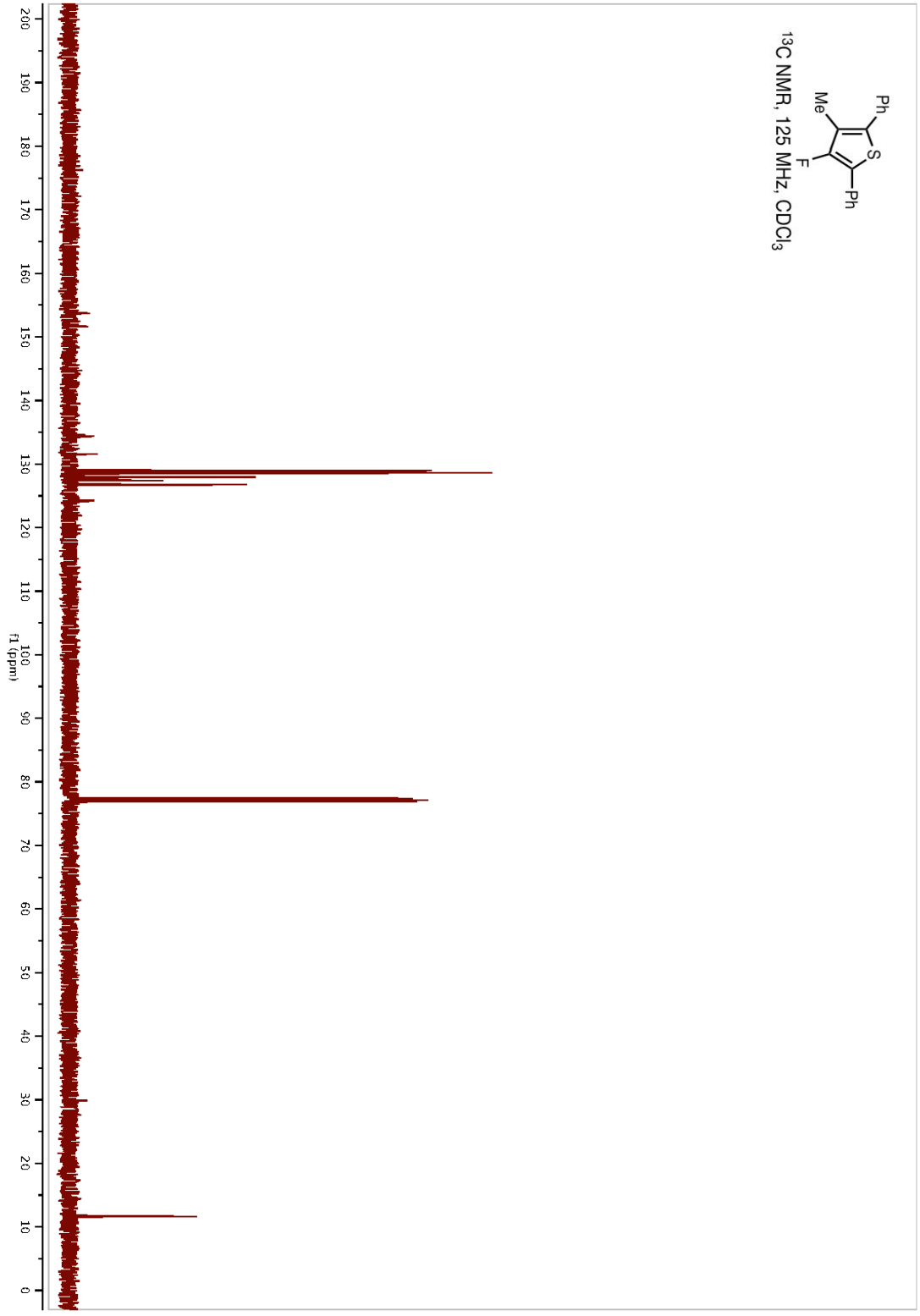

1H NMR, 500 MHz, CDCl3
Ph
O
S
F
Ph
2.00
2.06
1.02
2.15
2.29
1.03
1.20
f1 (ppm)

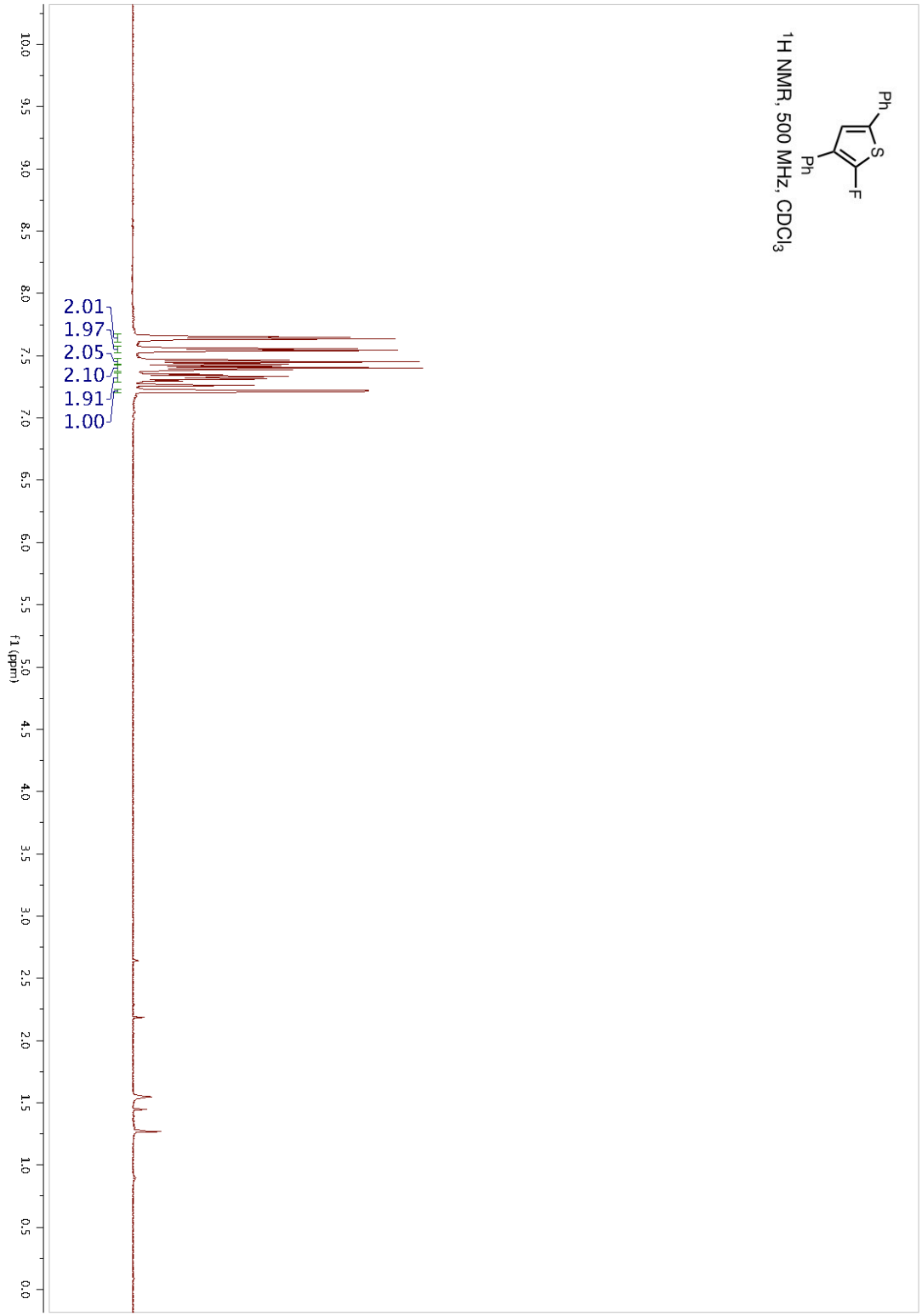

Ph
O
S
F
Ph
^{13}C NMR, 125 MHz, $CDCl_3$
f1 (ppm)
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0

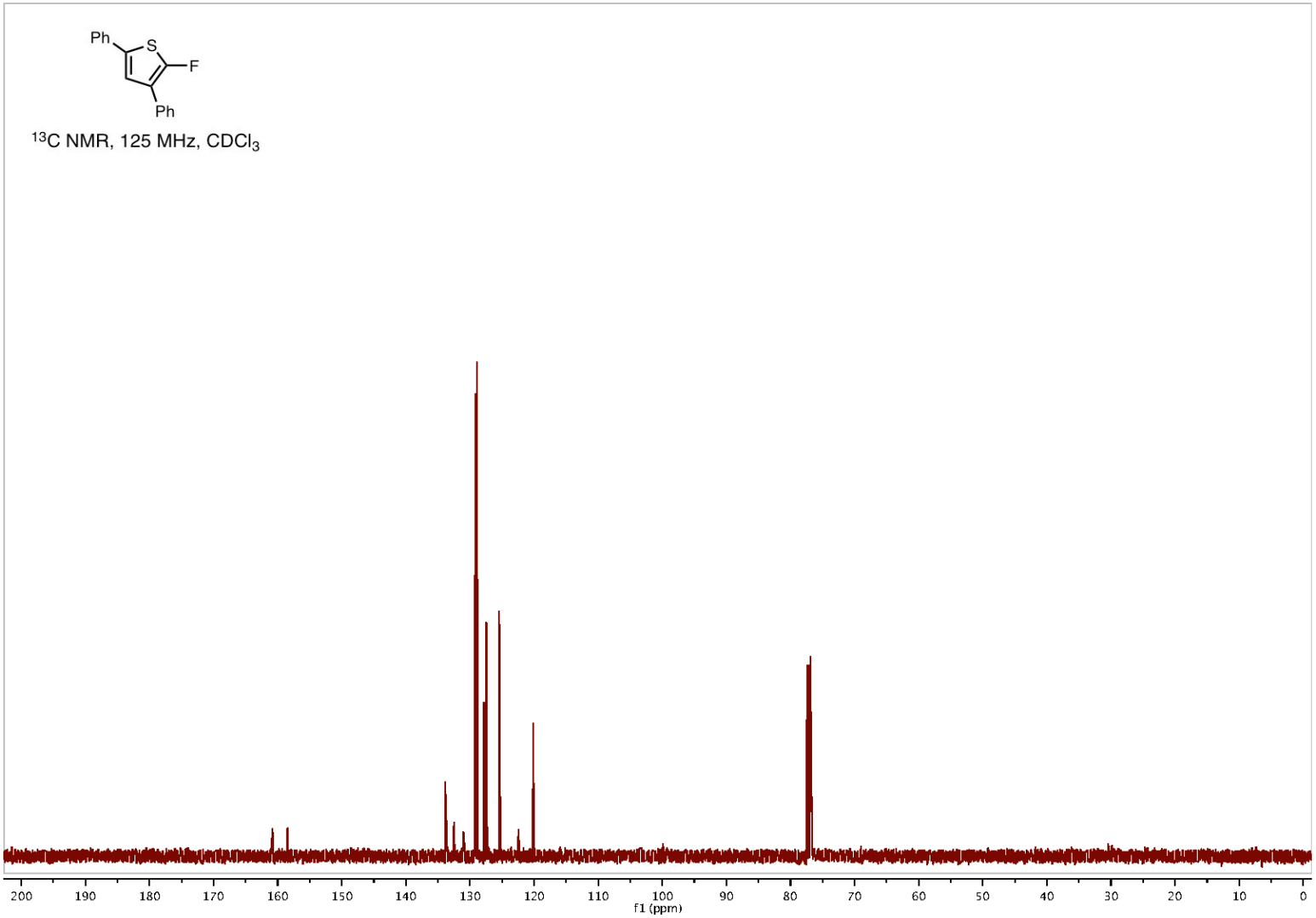

Ph
S
F
Ph
^{1}H NMR, 500 MHz, $CDCl_3$
2.01
1.98
3.98
2.06
0.94
f1 (ppm)

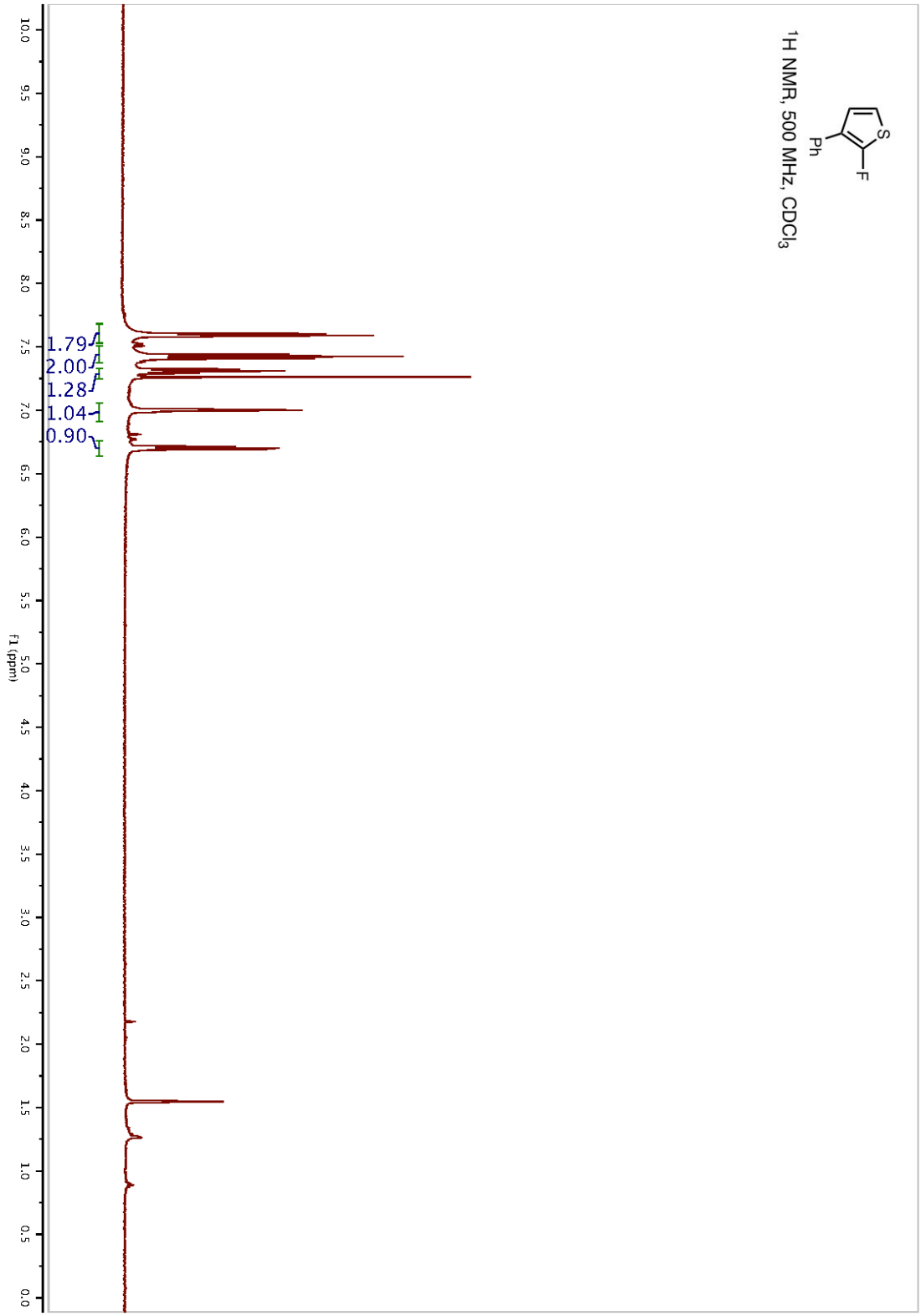

Ph
S
Ph
F
^{13}C NMR, 125 MHz, $CDCl_3$
240 230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20 -30 -40
f1 (ppm)

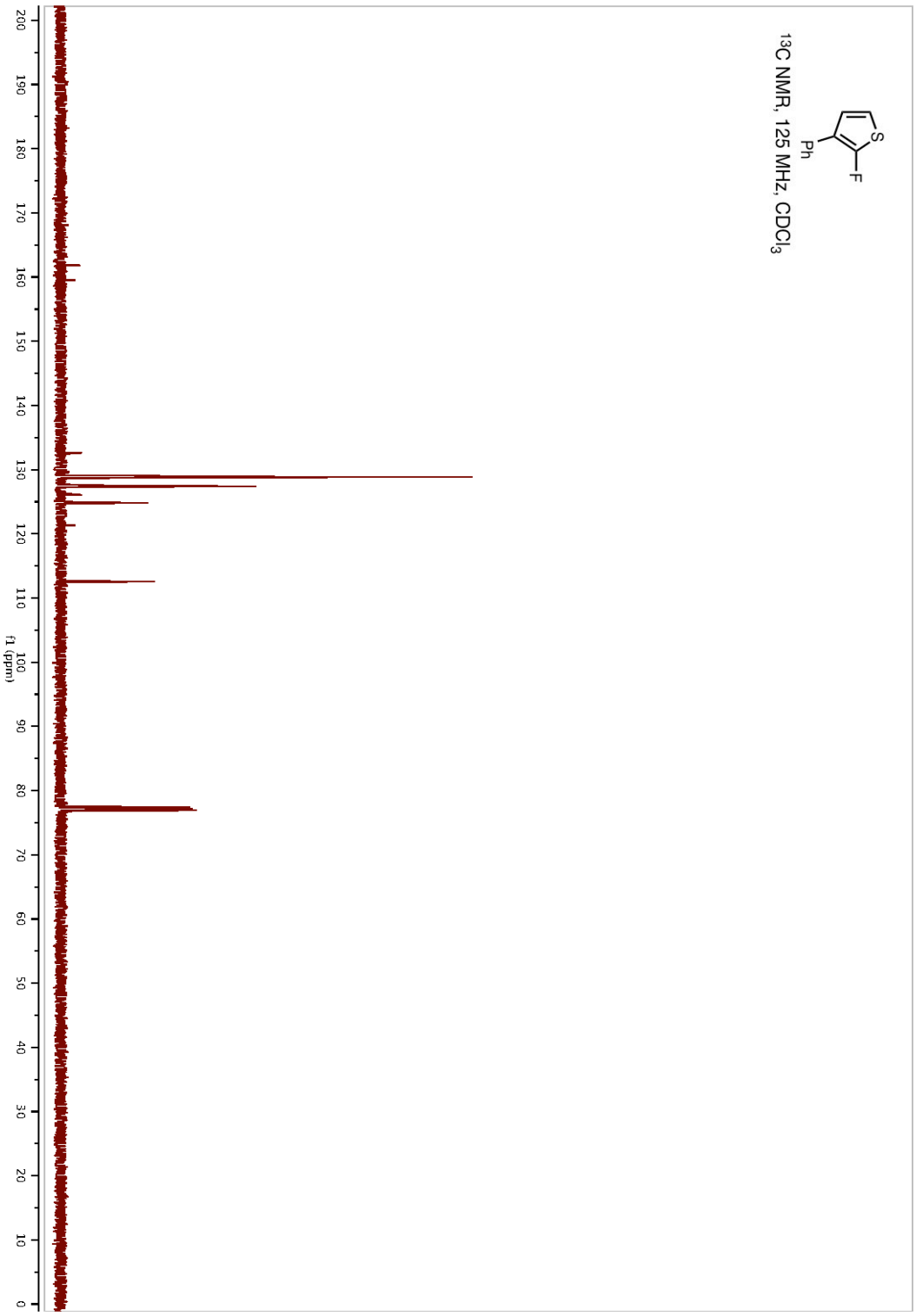

^{1}H NMR, 500 MHz, $CDCl_3$
Ph
Me
S
F
Ph
2.02
1.90
4.11
1.07
1.00
3.27
f1 (ppm)

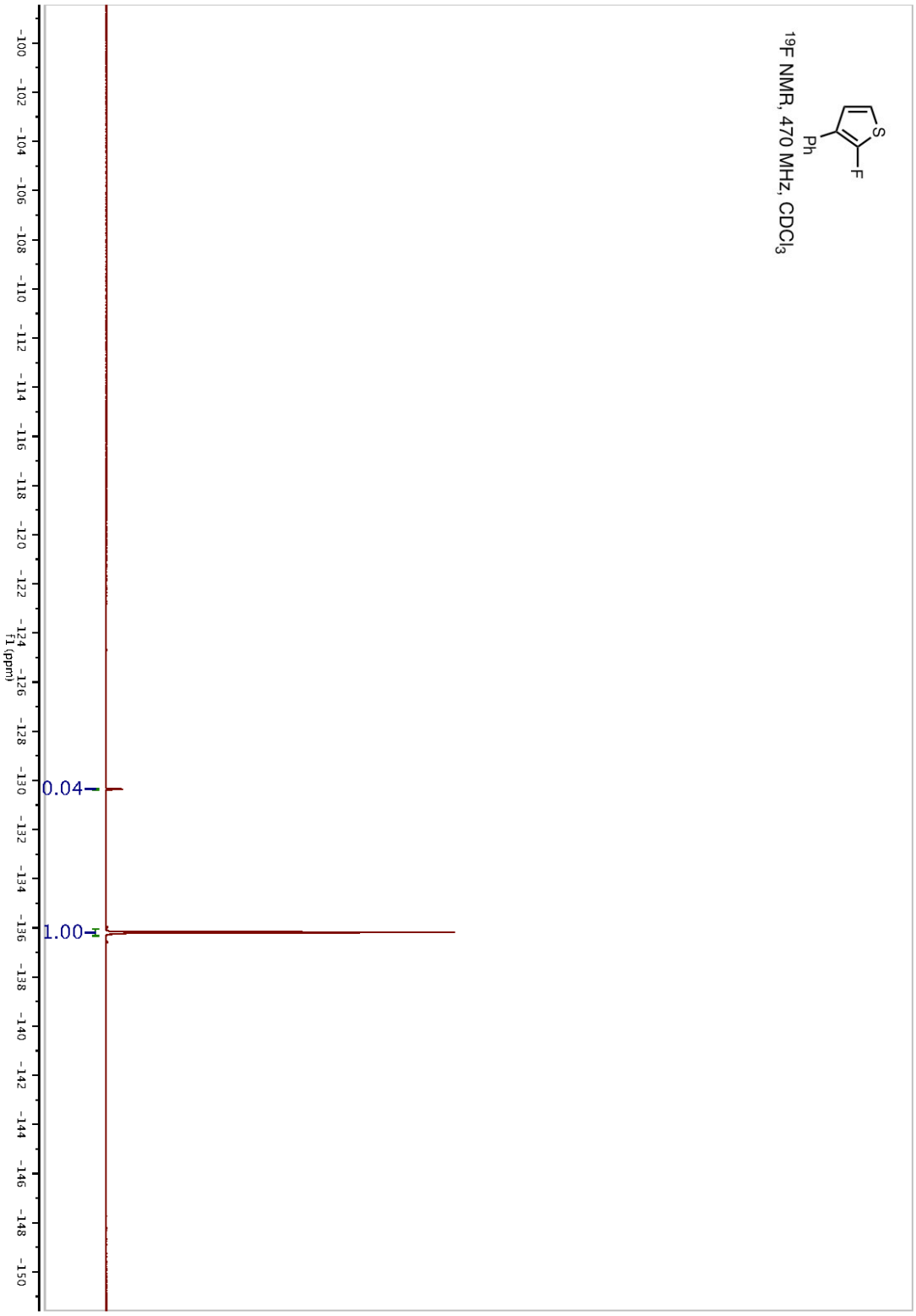

Ph
Me
S
F
Ph
^{13}C NMR, 125 MHz, $CDCl_3$
f1 (ppm)
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0

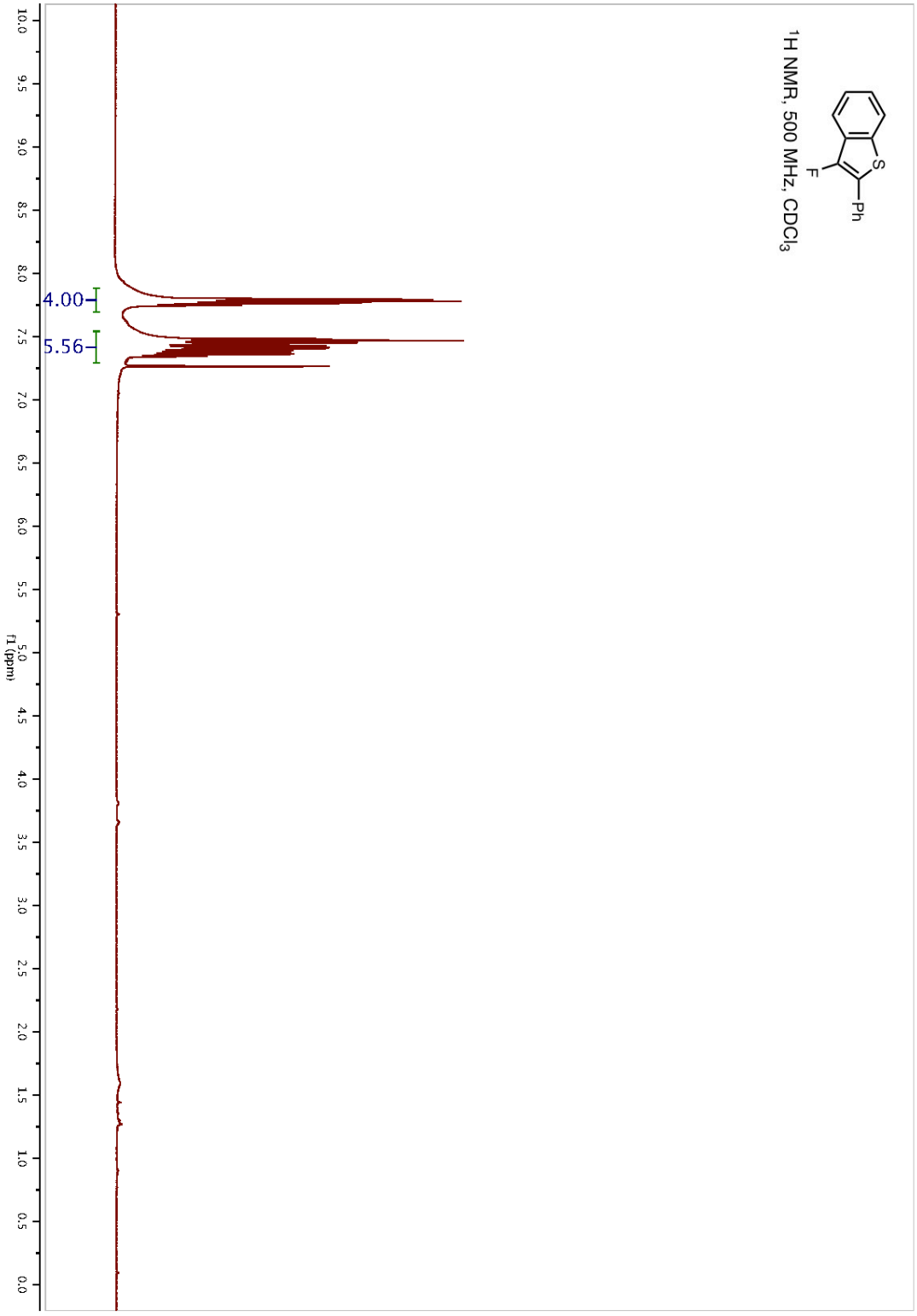

^{1}H NMR, 500 MHz, $CDCl_3$
Ph
S
F
Ph
2.01
1.97
2.05
2.10
1.91
1.00
f1 (ppm)
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0

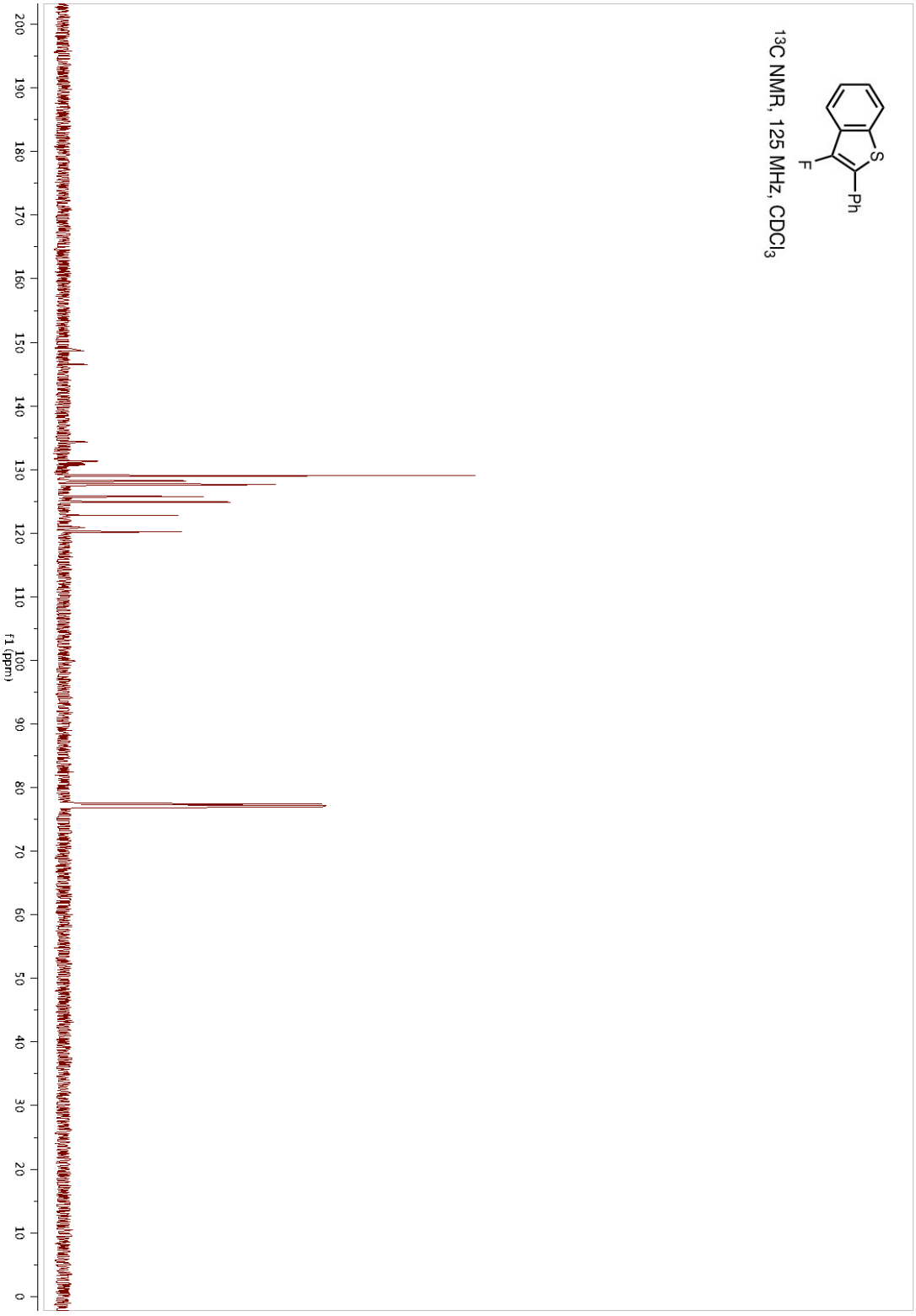

Ph
S
F
Ph
^{13}C NMR, 125 MHz, $CDCl_3$
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

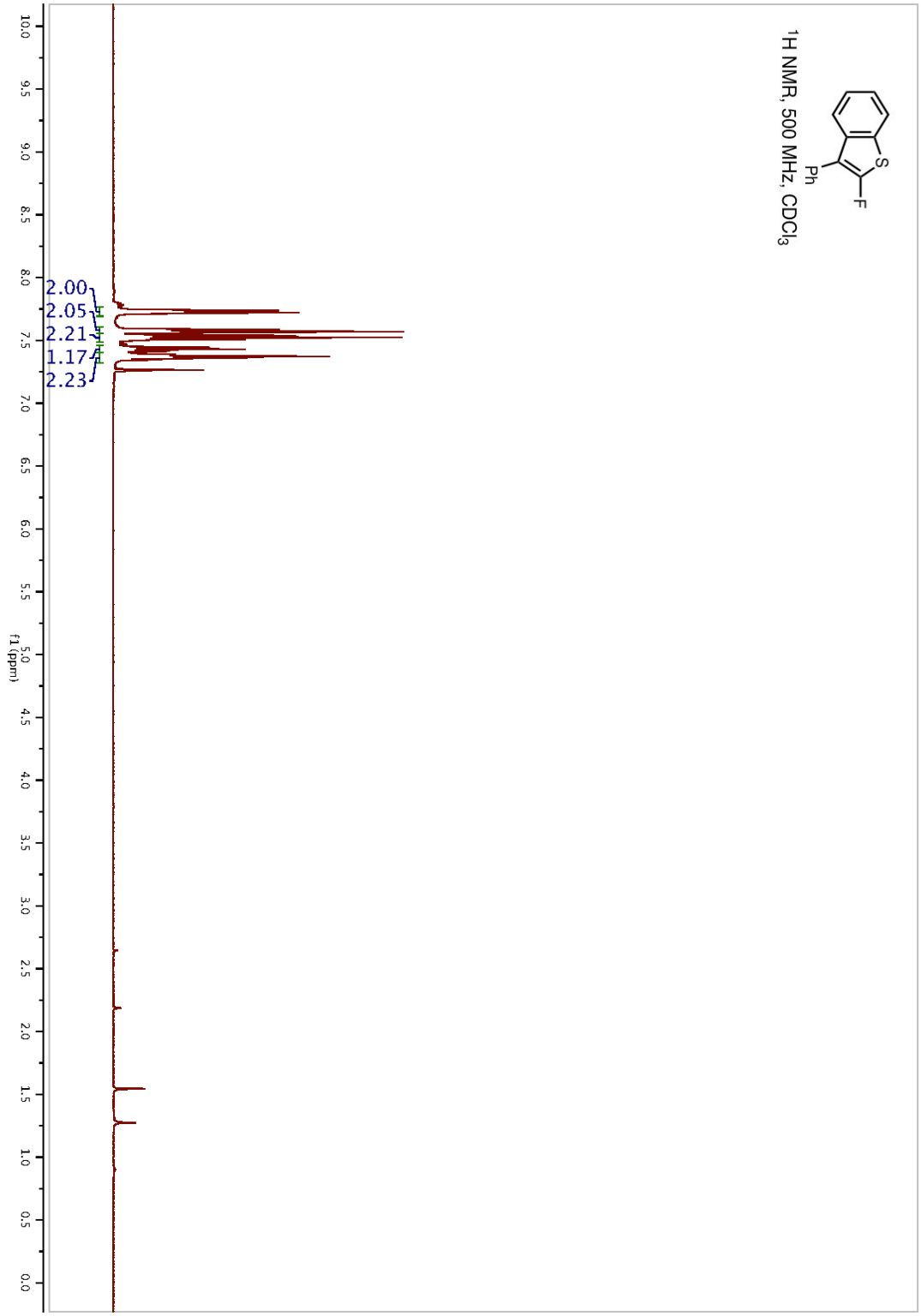

^{1}H NMR, 500 MHz, CDCl$_3$
Ph
S
F
1.79
2.00
1.28
1.04
0.90
f1 (ppm)
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0

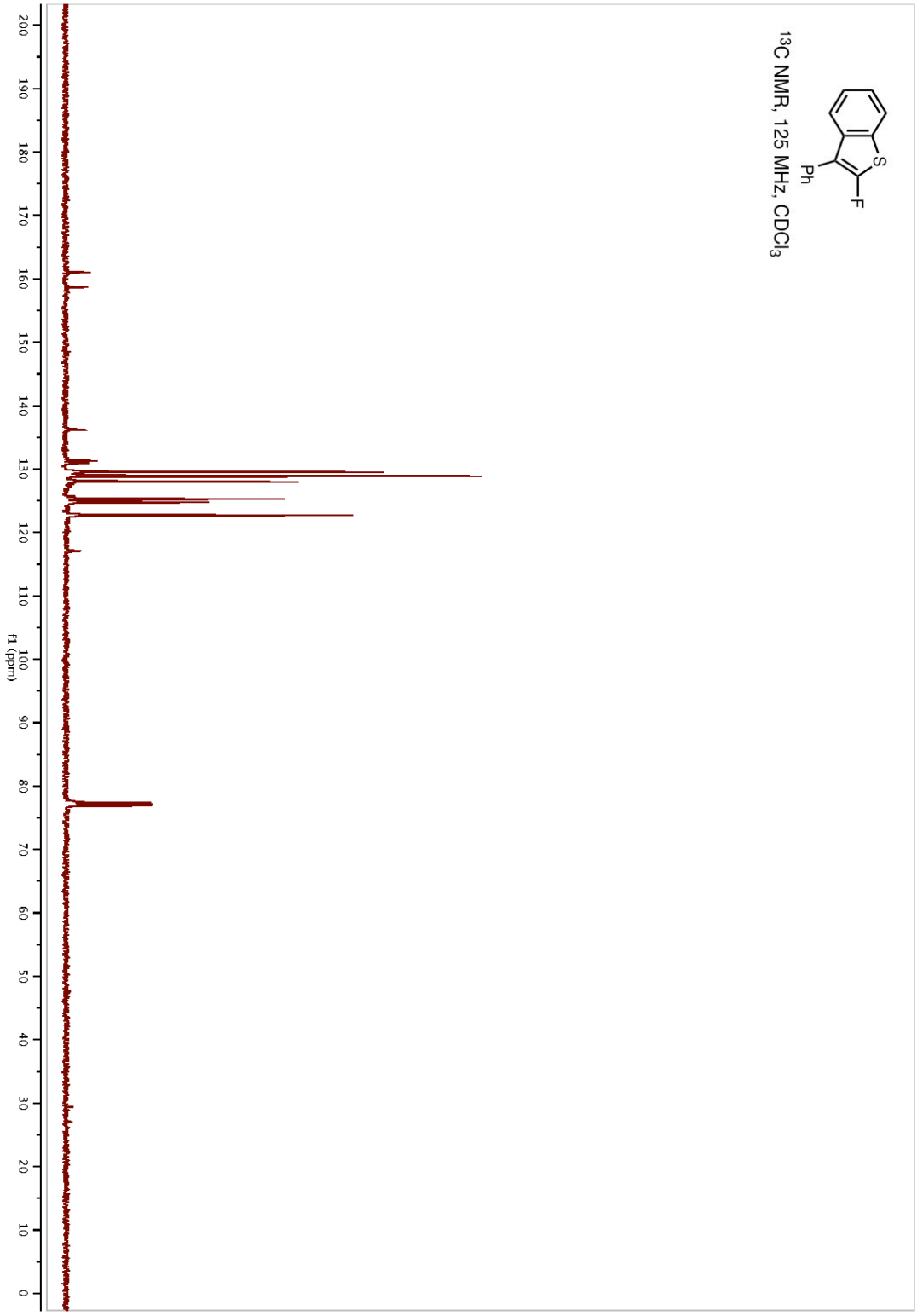

S
Ph
F
^{13}C NMR, 125 MHz, $CDCl_3$
f1 (ppm)
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0

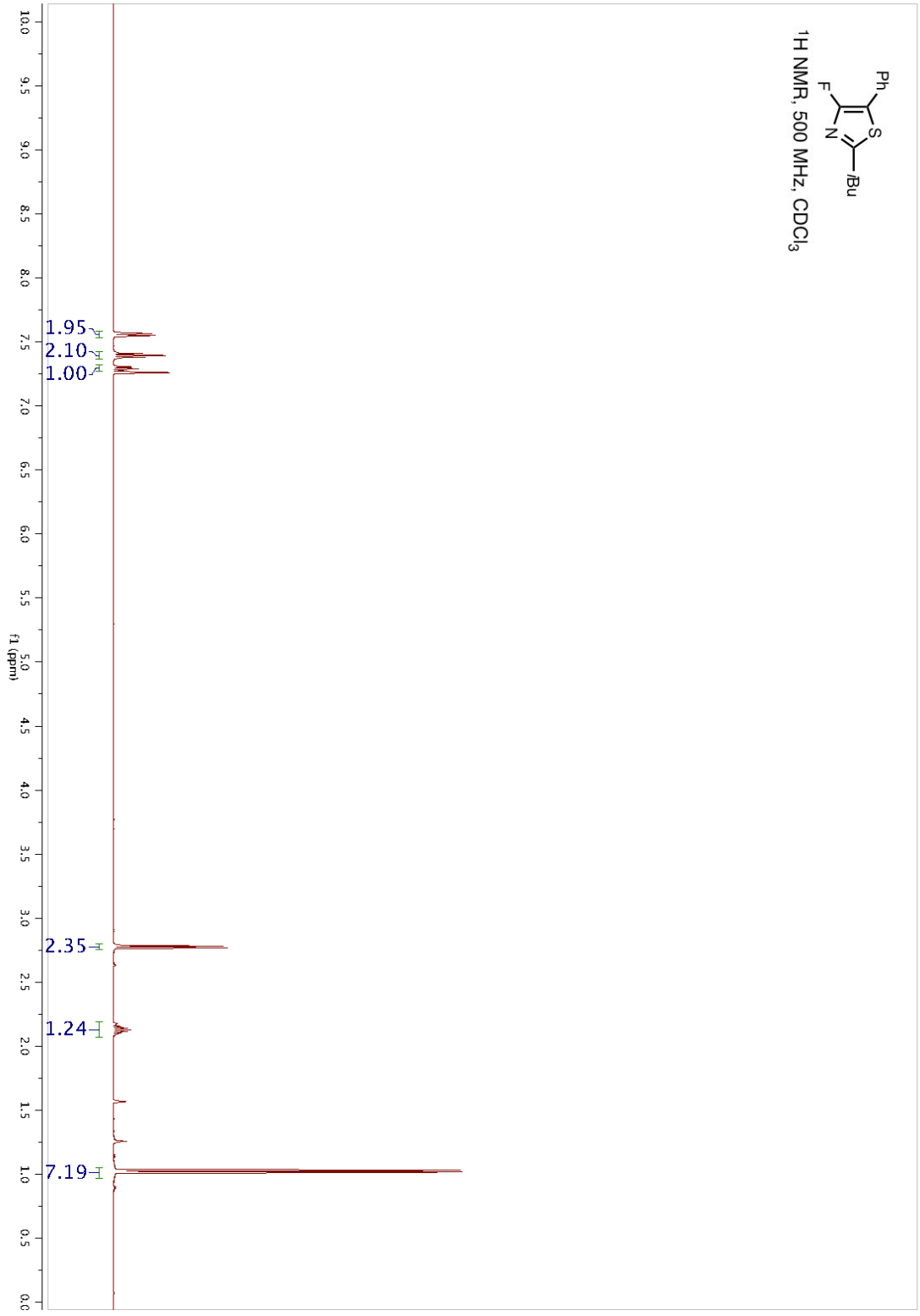

^{19}F NMR, 470 MHz, CDCl$_3$
Ph
S
F
f1 (ppm)
0.04
1.00

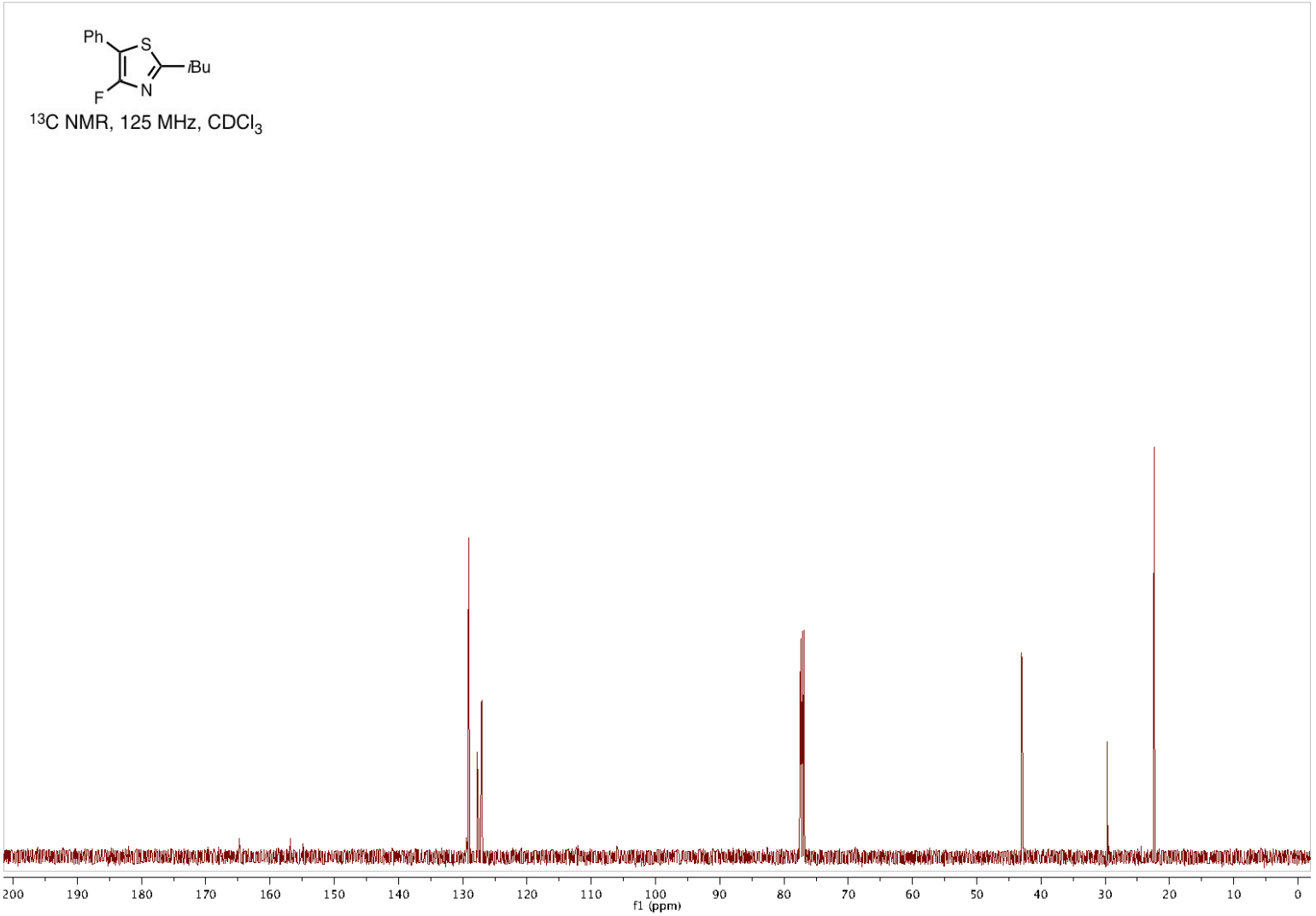

^{1}H NMR, 500 MHz, CDCl$_3$
F
S
Ph
4.00
5.56
f1 (ppm)
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0

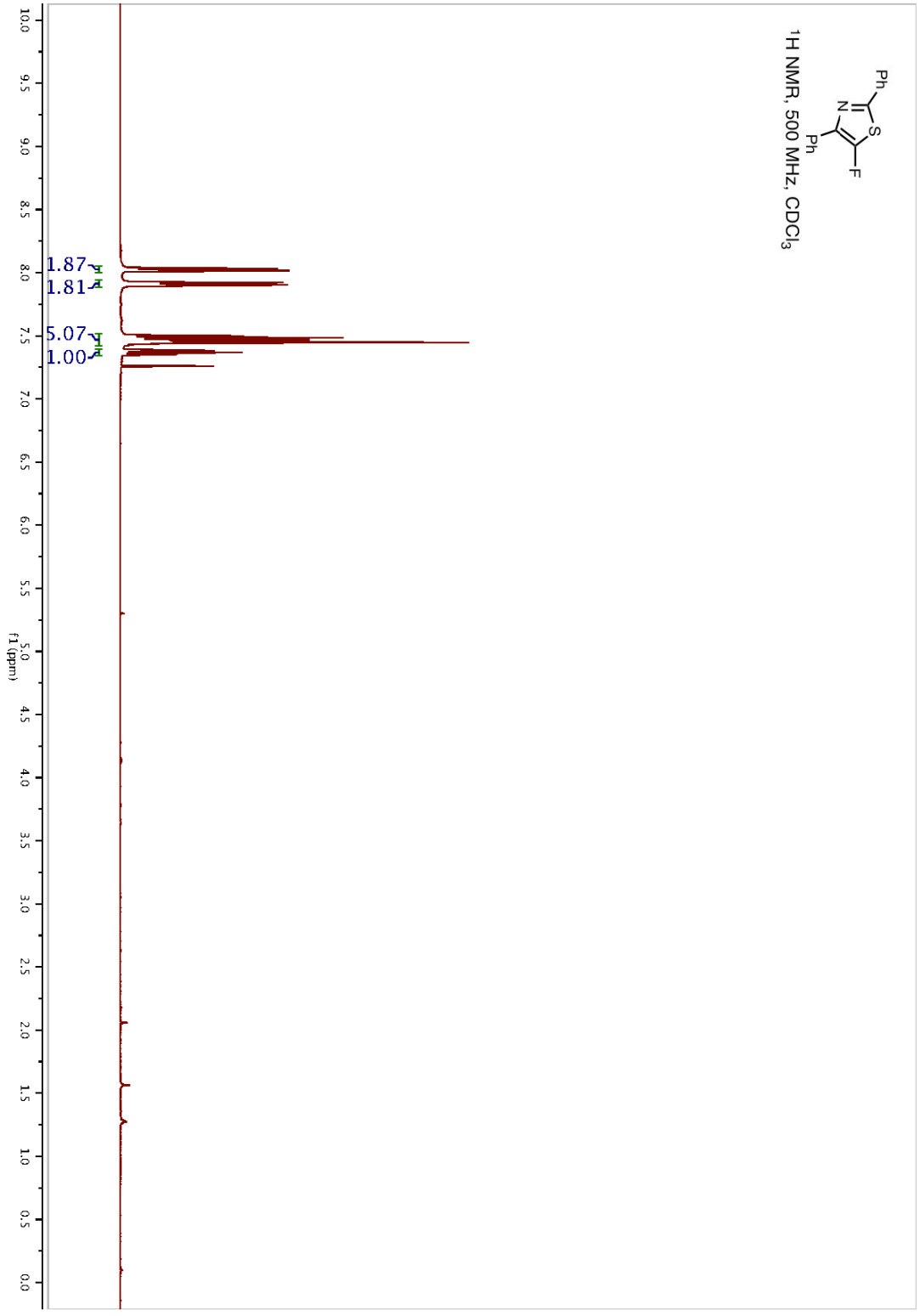

^{13}C NMR, 125 MHz, $CDCl_3$
S
F
Ph
f1 (ppm)
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0

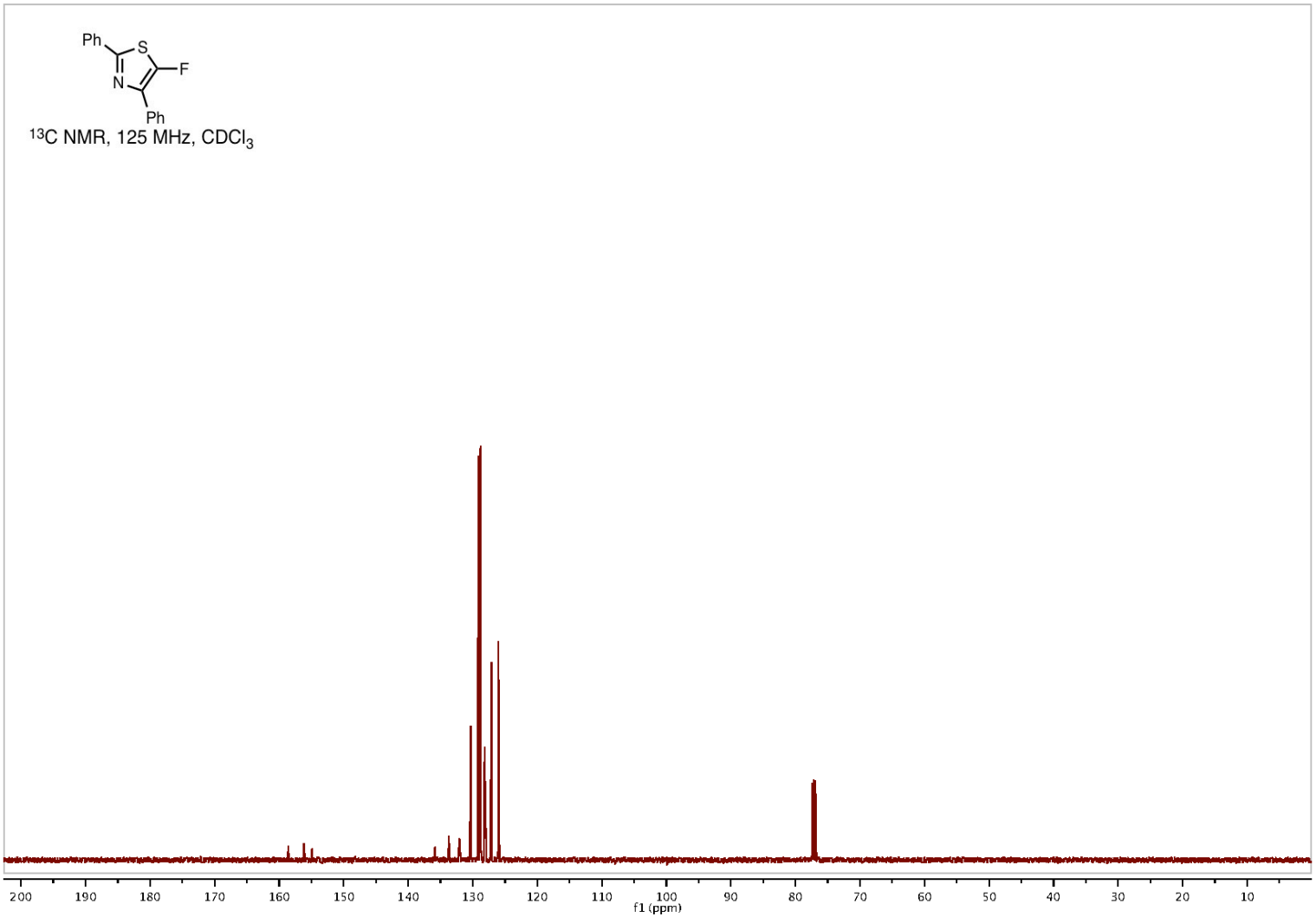

^{1}H NMR, 500 MHz, $CDCl_3$
Ph
S
F
2.00
2.05
2.21
1.17
2.23
f1 (ppm)

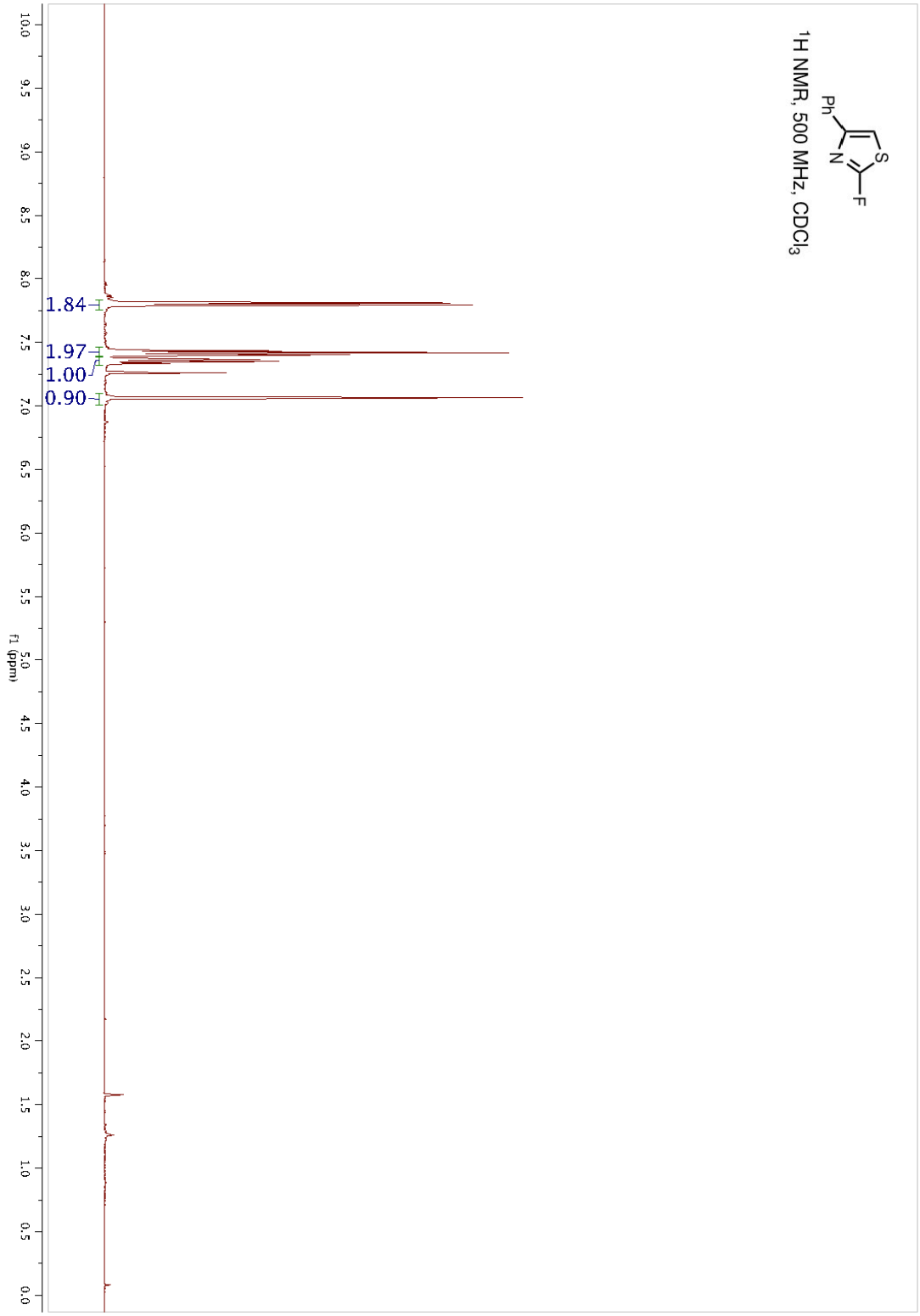

^{13}C NMR, 125 MHz, $CDCl_3$
Ph
S
F
f1 (ppm)
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0

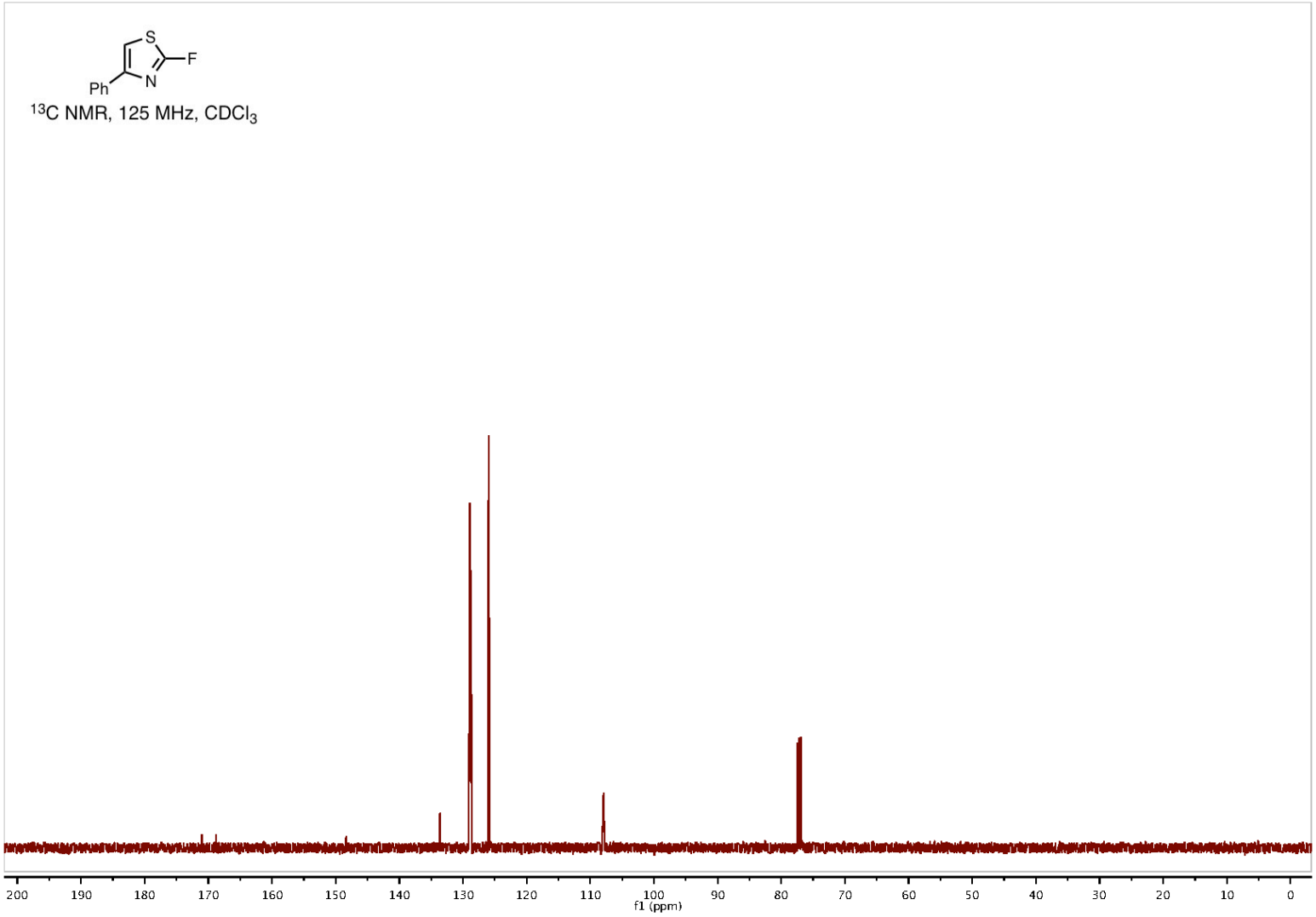

1H NMR, 500 MHz, CDCl3
Ph
F
N
S
tBu
1.95
2.10
1.00
2.35
1.24
7.19
f1 (ppm)


Ph
S
iBu
N
F
13C NMR, 125 MHz, CDCl3
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


1H NMR, 500 MHz, CDCl3
Ph
N
S
Ph
F
1.87
1.81
5.07
1.00
f1 (ppm)


Ph
S
F
N
Ph
^{13}C NMR, 125 MHz, $CDCl_3$
200
190
180
170
160
150
140
130
120
110
100
f1 (ppm)
90
80
70
60
50
40
30
20
10


^{1}H NMR, 500 MHz, CDCl$_3$
Ph
N
S
F
1.84
1.97
1.00
0.90
f1 (ppm)


S
F
N
Ph
^{13}C NMR, 125 MHz, $CDCl_3$
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)