

Supplementary Information

Zinc and manganese redox potentials in organic solvents and their influence on nickel-catalyzed cross-electrophile coupling

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1. General Experimental Considerations

Solvents and reagents

All reagents were purchased from commercial sources and used as received without further purification. Starting materials (amines and aryl halides) were purchased from MilliporeSigma, Alfa Aesar, Thermo Scientific, TCI America, and Combi-Blocks. Zn powder (average 4-7 micron) and Mn powder (~325 mesh) were purchased from Alfa Aesar. Electrolytes and additives (LiCl, LiBr, LiI, LiPF₆, NaBr, KPF₆, ⁿBu₄NCl, ⁿBu₄NBr, ⁿBu₄NI, ⁿBu₄NPF₆, ⁿBu₄NBF₄, ZnBr₂, MnBr₂, MgBr₂, FeBr₂, AlBr₃) were purchased from MilliporeSigma, TCI America, and Thermo Scientific and handled in a nitrogen-filled glove box, unless otherwise noted. Nickel salts and ligands were purchased from MilliporeSigma or Alfa Aesar. Anhydrous solvents (DMF, DMA, DMSO, NMP, MeCN, THF, DMPU, DMI) were purchased from MilliporeSigma and stored over activated 4 Å molecular sieves in a nitrogen-filled glove box.

Electrodes

All electrode materials were purchased from commercial sources and used as received. Ni foams (1.6 mm thickness, 80-110 pores per inch, average hole diameters 0.25 mm, > 99.9 wt% purity) were purchased from MTI. Fe rods (5 mm diameter, 99.8 wt% purity) were purchased from American-Scientific. Zn foil (99.99% metals basis) was purchased from MilliporeSigma. Mn pieces (99.95% metals basis) were purchased from Thermo Scientific. Mg plates (99.95% metals basis) and Al plates (99.95% metals basis) were purchased from American-Scientific. Glassy carbon working electrodes (MF-2012) and non-aqueous reference electrodes (MW-1085) were purchased from BASi. Pt wires (0.5 mm diameter, 99.99% metals basis) were purchased from MilliporeSigma and custom-made as Pt counter electrodes (~ 4 cm, 5-7 spiral coils).

Characterization of products

All proton (¹H), carbon (¹³C), and fluorine (¹⁹F) nuclear magnetic resonance (NMR) spectra were recorded on a Bruker 400 MHz at 25 °C (¹H 400.1 MHz, ¹³C 100.6 MHz, ¹⁹F 376.5 MHz) or a Bruker 500 MHz at 25 °C (¹H 500.1 MHz, ¹³C 125.7 MHz, ¹⁹F 470.6 MHz). Chemical shifts are given in parts per million (ppm) relative to residual solvent peaks in the ¹H and ¹³C NMR spectra or are referenced as noted. An absolute referencing method was used for ¹⁹F NMR chemical shifts, based on the frequency of solvent peaks in the ¹H NMR spectra. The following abbreviations (and their combinations) are used to label the multiplicities: s (singlet), d (doublet), t (triplet), m (multiplet) and br (broad). High-resolution mass spectra were obtained using a Thermo Q ExactiveTM Plus in the mass spectrometry facility at the University of Wisconsin (data were collected by facility staff). Automatic normal phase column chromatography was performed using reusable Silicycle SiliaSep premium cartridges (25 or 40 g, 25 µm) on a Biotage[®] Isolera. Thin-layer chromatography (TLC) was performed on Silicycle silica gel UV254 pre-coated plates (0.25 mm). Preparative TLC was performed using 20 cm × 20 cm glass-backed silica preparative thin-layer chromatography plates (1000 µm, layer thickness) from Miles Scientific. Visualization of the developed chromatogram was performed by using UV lamps (254 nm) or KMnO₄ stain.

Electrochemical experiments

Cyclic Voltammetry (CV) experiments: All CV experiments were performed using a Pine WaveNow PGstat without IR compensation under an N₂ atmosphere. The experiments were carried out in a three-electrode cell configuration with a glassy carbon (GC) working electrode, a platinum wire counter electrode, and a Ag/AgNO₃ non-aqueous reference electrode (internal solution, 0.1 M ⁿBu₄NPF₆ and 0.01 M AgNO₃

in DMF). The redox potential of ferrocene/ferrocenium (Fc/Fc^+) was measured (under same experimental conditions) and used to provide an internal reference. The potential values recorded versus Ag/AgNO_3 were then adjusted relative to Fc/Fc^+ , and electrochemical studies in organic solvents were reported accordingly. The GC working electrode was polished with alumina powder (5 μm) before each experiment. The resultant voltammograms were plotted following IUPAC convention.

Open-Circuit Potential (OCP) measurements: All OCP measurements were performed using a CH-600E potentiostat under an N_2 atmosphere. The experiments were carried out in a three-electrode cell configuration with a metal (Zn, Mn, Mg, Fe, or Al) as the working electrode, a platinum wire counter electrode, and a Ag/AgNO_3 reference electrode (internal solution, 0.1 M $^n\text{Bu}_4\text{NPF}_6$ and 0.01 M AgNO_3 in DMF). The redox potential of ferrocene/ferrocenium (Fc/Fc^+) was measured (under same experimental conditions; when bromide or iodide salts were used as the electrolyte, $^n\text{Bu}_4\text{NPF}_6$ was used instead for measuring Fc/Fc^+ potential, as Br_2/Br^- and I_2/I_3^- redox waves overlap with Fc/Fc^+ redox wave) and used to provide an internal reference. The potential values recorded versus Ag/AgNO_3 were then adjusted relative to Fc/Fc^+ , and electrochemical studies in organic solvents were reported accordingly. The working electrodes were polished using a smooth file before each experiment under nitrogen atmosphere. All solvents were rigorously purged with nitrogen for 15 min before preparation of the solutions for OCP analysis. The prepared solutions were stirred for 15 min under nitrogen atmosphere to allow full dissolution of all reagents.

Bulk Electrolysis: All bulk electrolysis experiments were performed using a Pine WaveNow PGstat. The experiments were performed in custom-built undivided cells, with Ni foam as a working electrode, Fe rod as a counter electrode and Ag/AgNO_3 (internal solution, 0.1 M $^n\text{Bu}_4\text{NPF}_6$ and 0.01 M AgNO_3 in DMF) as a reference electrode.

2. General Procedure for Open-Circuit Potential (OCP) Measurements

In a solution containing ZnBr_2 (11.2 mg, 10 mM), MnBr_2 (10.7 mg, 10 mM), MgBr_2 (9.2 mg, 10 mM), FeBr_2 (10.8 mg, 10 mM), or AlBr_3 (13.3 mg, 10 mM), electrolyte (0.2 M, or otherwise noted), and anhydrous solvent (5 mL), the corresponding metal electrode (polished using a smooth file before every experiment) was used as the working electrode for OCP measurements, with a Pt wire counter electrode and a Ag/AgNO_3 reference electrode. While stirring at 600 rpm, the open-circuit potential was measured and recorded after it remained stable (< 5 mV fluctuation over 1 min) (Supplementary Figs. 1 and 2). The measured potential versus Ag/AgNO_3 was then adjusted to be referenced versus Fc/Fc^+ and converted to the formal thermodynamic potential (E°) using the Nernst equation below.

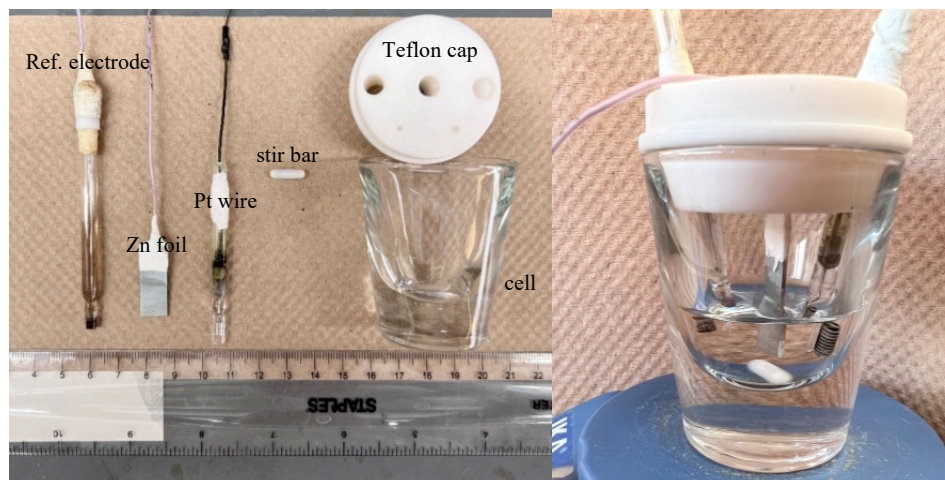
$$E = E^\circ + \frac{RT}{nF} \ln \left(\frac{[M^{n+}]}{[M^0]} \right)$$

Given that the measurements were made at room temperature ($T = 298$ K), and the number of electrons involved in the redox process is two for Zn, Mn, Mg, Fe ($n = 2$) and three for Al ($n = 3$), F is the Faraday constant (96485 C/mol), R is the universal gas constant (8.3145 J M^{-1} K^{-1}), $[M^0]$ is the activity of the reduced form (defined as 1 for solid state), $[M^{n+}]$ is the activity of the oxidized form (approximately equal to the concentration of the oxidized form in solution, 0.01 M), then the Nernst equation (with all potentials relative to Fc/Fc^+) becomes:

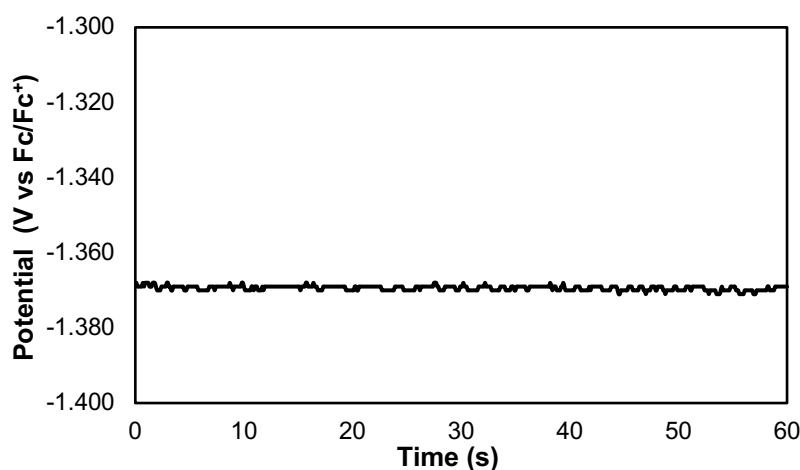
$$E^\circ = E + 59 \text{ mV} \quad T = 298 \text{ K (for Zn, Mn, Mg, Fe)}$$

$$E^{\circ'} = E + 39 \text{ mV} \quad T = 298 \text{ K (for Al)}$$

Note: Zn and Mn are the most common metal reductants used in Ni-catalyzed cross-electrophile coupling (XEC) reactions.⁸ Mg is seldom used as metal reductant, although an *in situ* Grignard reagent formation was proposed for the corresponding XEC reaction.^{54,55} Other common reducing metals, such as Fe and Al, were also studied in organic solvents. Mixed solvents have proven indispensable for achieving optimal outcomes in certain XEC reactions. Therefore, redox potentials of Zn and Mn in mixed solvents were also measured. The results are tabulated in Supplementary Tables 1 and 2.



Supplementary Fig. 1. Picture of the undivided cell for OCP and CV experiments before (left) and after (right) assembly (working electrode varies based on each experiment, shown is with Zn plate).



Supplementary Fig. 2. A typical trace obtained in OCP measurements (after conversion using the Nernst equation). Conditions: Zn working electrode, 10 mM ZnBr₂, 0.2 M ⁿBu₄NPF₆, DMF.

Supplementary Table 1. Formal thermodynamic potentials of Zn, Mn, Mg, Fe, and Al

Entry	Solvent	Metal	Additive	E° (V vs Fc/Fc ⁺)
1	DMF	Zn	ⁿ Bu ₄ NPF ₆	-1.37
2	DMA	Zn	ⁿ Bu ₄ NPF ₆	-1.36
3	DMSO	Zn	ⁿ Bu ₄ NPF ₆	-1.43
4	NMP	Zn	ⁿ Bu ₄ NPF ₆	-1.36
5	MeCN	Zn	ⁿ Bu ₄ NPF ₆	-1.07
6	THF	Zn	ⁿ Bu ₄ NPF ₆	-1.25
7	DMPU	Zn	ⁿ Bu ₄ NPF ₆	-1.32
8	DMI	Zn	ⁿ Bu ₄ NPF ₆	-1.33
9	DMF	Mn	ⁿ Bu ₄ NPF ₆	-1.55
10	DMA	Mn	ⁿ Bu ₄ NPF ₆	-1.56
11	DMSO	Mn	ⁿ Bu ₄ NPF ₆	-1.53
12	NMP	Mn	ⁿ Bu ₄ NPF ₆	-1.50
13	MeCN	Mn	ⁿ Bu ₄ NPF ₆	-1.19
14	THF	Mn	ⁿ Bu ₄ NPF ₆	-1.54
15	DMPU	Mn	ⁿ Bu ₄ NPF ₆	-1.48
16	DMI	Mn	ⁿ Bu ₄ NPF ₆	-1.50
17	DMF	Zn	LiCl	-1.65
18 ^b	DMF	Zn	LiCl	-1.68
19 ^c	DMF	Zn	LiCl	-1.72
20 ^d	DMF	Zn	LiCl	-1.72
21	DMF	Zn	LiBr	-1.53
22	DMF	Zn	LiI	-1.43
23	DMF	Zn	LiPF ₆	-1.36
24	DMF	Zn	NaBr	-1.52
25	DMF	Zn	KPF ₆	-1.36
26 ^a	DMA	Zn	KPF ₆	-1.31
27 ^a	DMF	Zn	ⁿ Bu ₄ NCl	-1.60
28	DMF	Zn	ⁿ Bu ₄ NCl	-1.64
29 ^b	DMF	Zn	ⁿ Bu ₄ NCl	-1.67
30 ^c	DMF	Zn	ⁿ Bu ₄ NCl	-1.70
31 ^d	DMF	Zn	ⁿ Bu ₄ NCl	-1.72
32 ^e	DMF	Zn	ⁿ Bu ₄ NCl	-1.72
33	DMF	Zn	ⁿ Bu ₄ NBr	-1.52
34	DMF	Zn	ⁿ Bu ₄ NI	-1.41
35	DMF	Zn	ⁿ Bu ₄ NPF ₆	-1.37
36	DMF	Zn	ⁿ Bu ₄ NBF ₄	-1.37
37	DMA	Zn	ZnBr ₂	-1.33
38 ^f	DMPU	Zn	ⁿ Bu ₄ NPF ₆	-1.46
39 ^g	DMPU	Zn	ⁿ Bu ₄ NPF ₆	-1.47
40	DMF	Mn	LiCl	-1.75
41	DMF	Mn	LiBr	-1.63
42	DMF	Mn	LiI	-1.59
43	DMF	Mn	LiPF ₆	-1.58

44	DMF	Mn	NaBr	-1.62
45	DMF	Mn	KPF ₆	-1.55
46 ^a	DMA	Mn	KPF ₆	-1.55
47	DMF	Mn	ⁿ Bu ₄ NCl	-1.76
48	DMF	Mn	ⁿ Bu ₄ NBr	-1.66
49	DMF	Mn	ⁿ Bu ₄ NI	-1.61
50	DMF	Mn	ⁿ Bu ₄ NPF ₆	-1.55
51	DMF	Mn	ⁿ Bu ₄ NBF ₄	-1.57
52 ^f	DMPU	Mn	ⁿ Bu ₄ NPF ₆	-1.65
53	DMF	Mg	ⁿ Bu ₄ NPF ₆	-2.19
54	MeCN	Mg	ⁿ Bu ₄ NPF ₆	-2.01
55	DMF	Mg	LiCl	-2.45
56	DMF	Mg	LiBr	-2.22
57	DMF	Mg	LiI	-2.14
58	DMF	Mg	ⁿ Bu ₄ NCl	-2.39
59	DMF	Fe	ⁿ Bu ₄ NPF ₆	-0.81
60	MeCN	Fe	ⁿ Bu ₄ NPF ₆	-0.54
61	DMF	Fe	LiCl	-1.04
62	DMF	Fe	LiBr	-0.95
63	DMF	Fe	LiI	-0.97
64	DMF	Fe	ⁿ Bu ₄ NCl	-1.00
65	DMF	Al	ⁿ Bu ₄ NPF ₆	-1.28
66	MeCN	Al	ⁿ Bu ₄ NPF ₆	-1.07
67	DMF	Al	LiCl	-1.47
68	DMF	Al	LiBr	-1.32
69	DMF	Al	LiI	-1.31
70	DMF	Al	ⁿ Bu ₄ NCl	-1.51
71	MeCN	Zn	ⁿ Bu ₄ NCl	-1.60
72	MeCN	Zn	ⁿ Bu ₄ NBr	-1.47
73	MeCN	Zn	ⁿ Bu ₄ NI	-1.34
74	MeCN	Mn	ⁿ Bu ₄ NCl	-1.64
75	MeCN	Mn	ⁿ Bu ₄ NBr	-1.52
76	MeCN	Mn	ⁿ Bu ₄ NI	-1.32
77	THF	Zn	LiCl	-1.62
78	THF	Zn	LiBr	-1.61
79	THF	Zn	LiI	-1.58
80	THF	Mn	LiCl	-1.72
81	THF	Mn	LiBr	-1.64
82	THF	Mn	LiI	-1.52

^a 0.1 M additive. ^b 0.4 M additive. ^c 0.8 M additive. ^d 1.0 M additive. ^e 1.2 M additive. ^f Added 10 mM Me₃SiCl. ^g Added 20 mM Me₃SiCl.

Supplementary Table 2. Formal thermodynamic potentials of Zn and Mn in mixed solvents

Entry	Solvent	Metal	Additive	E° (V vs Fc/Fc ⁺)
1	DMF/THF (1:1)	Zn	ⁿ Bu ₄ NPF ₆	−1.29
2	DMA/THF (1:1)	Zn	ⁿ Bu ₄ NPF ₆	−1.30
3	DMF/THF (1:1)	Mn	ⁿ Bu ₄ NPF ₆	−1.48
4	DMA/THF (1:1)	Mn	ⁿ Bu ₄ NPF ₆	−1.52

Note: Other common additives (NaCl, NaI, KCl, KBr, KI) were less soluble in DMF and not included in this study.

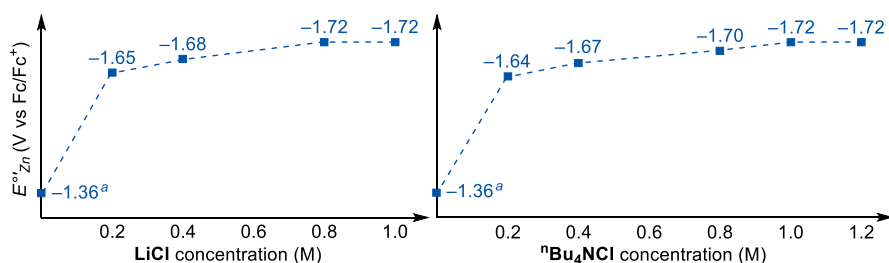
The OCP measurements can be sensitive to trace oxygen dissolved in the electrolyte solution (Supplementary Table 3). Therefore, rigorous N₂ purging of the solvents before the preparation of the electrolyte solution is required for OCP measurements.

Discussion: For a well-defined, fully reversible redox couple Fc/Fc⁺, Dempsey et al. determined its $E_{1/2}$ to be −0.003 V (vs. Fc/Fc⁺) in MeCN via OCP measurement, which is consistent with the theoretical value of 0 V. This $E_{1/2}$ was acquired by extracting the intercept value from the linear fit of the measured OCP data against $\ln \left(\frac{[Fc^+]}{[Fc]} \right)$ (see Nernst equation) for multiple solutions containing different concentrations of Fc and Fc⁺.⁴³ This corroborates the validity of OCP measurement in determining thermodynamic potentials of redox couples in organic solvents. However, this exact method was not applicable to this study as (a) limited solubility of the metal salts prevents measurements at high concentration, (b) the anions of the salts may affect the thermodynamic potentials in a non-Nernstian way (see discussions in the main text and Supplementary Fig. 3), and (c) the OCP measurement technique has a ± 5 mV inaccuracy while a ten-fold change in concentration only results in a theoretical change of E by 29 mV.

Supplementary Table 3. The impact of dissolved oxygen to measured OCP

Entry	Additive/Solvent	Metal	Treatment	Measured potential ^a (V vs Fc/Fc ⁺)
1	LiCl/DMF (0.2 M)	Zn	purged the solution with N ₂ for 15 min in glovebox, then measured OCP	−1.71
2	LiCl/DMF (0.2 M)	Zn	the same solution was brought out of glovebox, then measured OCP	−1.64
3	LiCl/DMF (0.2 M)	Zn	the same solution was left in ambient atmosphere for 1 h, then measured OCP	−1.53

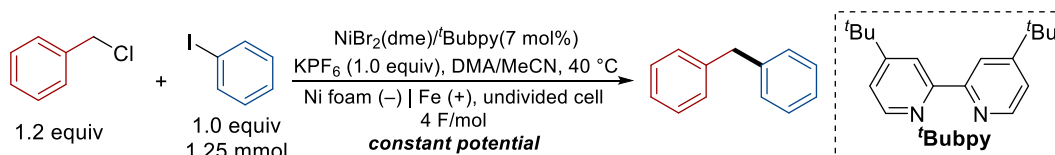
^a Note that a Nernstian conversion was not applied here.



Supplementary Fig. 3. Chloride concentration effect on Zn reduction potential in DMF. ^a 0.2 M nBu₄NPF₆ as electrolyte.

3. General Procedures for Reductive Coupling of Benzyl Chloride with Iodobenzene

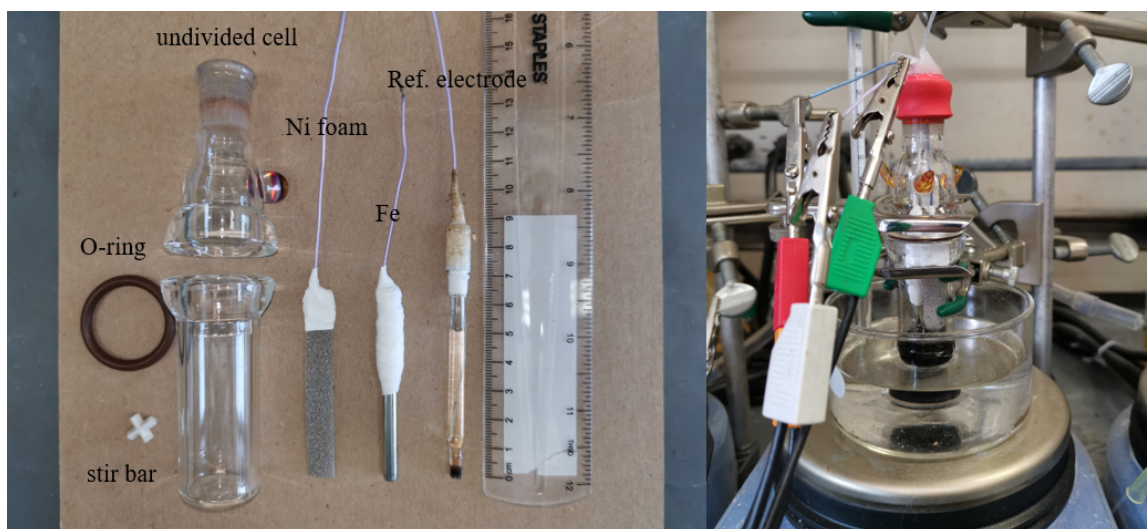
Electrochemical reductive coupling of benzyl chloride with iodobenzene



In a nitrogen-filled glove box, NiBr₂(dme) (27 mg, 7 mol%), tBubpy (23.5 mg, 7 mol%), and DMA or MeCN (5 mL) were added to a 2-dram vial. This solution was stirred at 800 rpm in the glove box for 30 min to allow complexation of Ni with the ligand. To an undivided cell (Supplementary Fig. 4) fitted with a cross-shaped stir bar was added KPF₆ (230 mg, 1.25 mmol, 1.0 equiv), iodobenzene (139 μ L, 1.25 mmol, 1.0 equiv), and benzyl chloride (172.5 μ L, 1.5 mmol, 1.2 equiv) under air. The cell was transferred into the glove box, followed by addition of the catalyst solution and installation of a Ni foam cathode, a Ag/AgNO₃ reference electrode, and an Fe rod anode. The cell was then sealed with a rubber septum before being removed from the glove box. A thin Teflon tube was introduced immediately into the cell to allow continuous nitrogen bubbling. The reaction mixture was stirred at 1000 rpm for 10 min to allow full dissolution of all reagents and exclusion of adventitious oxygen. After that, the Teflon tube was removed, and the top of the rubber septum was sealed with silicone gel. The reaction mixture was electrolyzed under a constant potential (−1.07 V to −1.40 V vs. Fc/Fc⁺) at the desired temperature (25 to 80 °C) until 4 F/mol of charge was passed or otherwise noted.

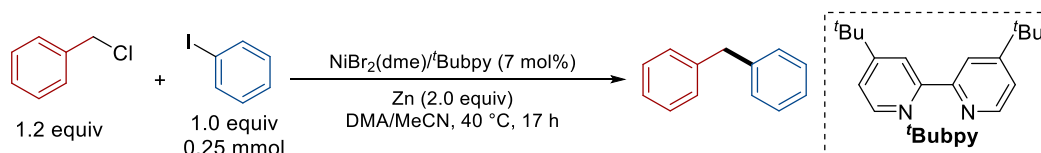
Work-up for condition screening: Upon completion of the reaction, the reaction mixture was cooled to room temperature and diluted with DMA or MeCN (10 mL). Mesitylene (57.9 μ L, 0.42 mmol, 0.33 equiv) was added to the crude material. Then a 100 μ L aliquot of the solution was filtered through a 2-cm silica gel plug in a Pasteur pipette into a vial. 400 μ L CDCl₃ was also added to the pipette and eluted into the same vial. The resultant sample was analyzed by ¹H NMR spectroscopy and yields were determined using mesitylene as the internal standard.

Work-up for product isolation: Upon reaction completion, the reaction mixture was cooled to room temperature and diluted with water (25 mL). The solution was extracted with ethyl acetate (50 mL $\times$ 2) and the organic layers were combined and washed with brine (50 mL). The resultant organic solution was dried over anhydrous Na₂SO₄, then concentrated *in vacuo*. The obtained residue was purified by flash column chromatography.



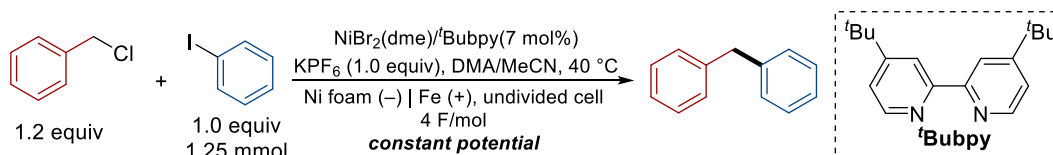
Supplementary Fig. 4. Picture of the undivided cell for bulk electrolysis before (left) and after (right) assembly.

Reductive coupling of benzyl chloride with iodobenzene using Zn reductant



In a nitrogen-filled glove box, $\text{NiBr}_2(\text{dme})$ (5.4 mg, 7 mol%), 'Bubpy (4.7 mg, 7 mol%), and DMA or MeCN (1 mL) were added to a 1-dram vial. This solution was stirred at 800 rpm in the glove box for 30 min to allow complexation of Ni with the ligand, followed by sequential addition of iodobenzene (27.8 μL , 0.25 mmol, 1.0 equiv), benzyl chloride (34.5 μL , 0.3 mmol, 1.2 equiv) and Zn powder (33 mg, 0.5 mmol, 2.0 equiv). The vial was capped with a screw cap fitted with a PTFE-faced silicone septum, then removed from the glove box and heated in a sand bath to 40 $^\circ\text{C}$ with stirring (1000 rpm) for 17 h. The reaction mixture was then cooled to room temperature and diluted with DMA or MeCN (2 mL). Mesitylene (19.3 μL , 0.083 mmol, 0.33 equiv) was added to the crude material. Then a 100 μL aliquot of the solution was filtered through a 2-cm silica gel plug in a Pasteur pipette into a vial. 400 μL CDCl_3 was also added to the pipette and eluted into the same vial. The resultant sample was analyzed by ^1H NMR spectroscopy and the yields were determined using mesitylene as the internal standard.

Supplementary Table 4. Optimization of (electro)chemical reductive coupling of benzyl chloride with iodobenzene^a



Entry	Solvent	Applied potential (V vs Fc/Fc ⁺)	Temp. (°C)	Yield (%)
1	MeCN	-1.20	80	34
2	MeCN	-1.30	80	40
3	MeCN	-1.35	80	58
4	MeCN	-1.40	80	50
5	MeCN	-1.35	40	78
6	MeCN	-1.35	25	74
7 ^b	MeCN	-1.07	80	11
8 ^c	MeCN	-1.07	40	23
9	DMA	-1.35	80	24
10	DMA	-1.35	60	28
11	DMA	-1.35	40	50
12 ^d	DMA	-1.35	25	50
13 ^e	DMA	-1.07	80	12
14 ^f	DMA	-1.07	40	0
15 ^g	MeCN	Zn instead of e-chem	40	12
16 ^g	DMA	Zn instead of e-chem	40	46

^a Yields were determined by ¹H NMR spectroscopy using mesitylene as the internal standard.

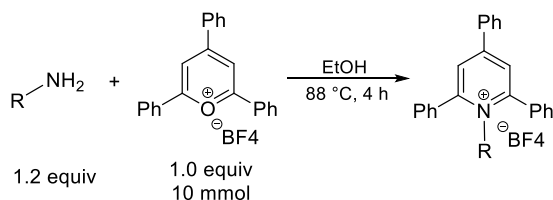
^b 88% iodobenzene remained unreacted. ^c 51% iodobenzene remained unreacted. ^d Reaction time = 72 h. ^e 71% iodobenzene remained unreacted. ^f >90% benzyl chloride and iodobenzene remained unreacted; the reaction was stopped after 36 h. ^g No KPF₆, the reaction was conducted at 0.25 mmol scale using Zn (2 equiv) as the reductant.

Discussion: The initial conditions are adapted from previous literature.²⁴ The thermochemical coupling of benzyl chloride with iodobenzene was conducted using 2 equiv of Zn reductant, which provide 4 equiv of e⁻ to the reaction medium. A total charge of 4 F/mol (of product) was chosen for electrolysis to mimic the thermochemical reaction, even though only 2 F/mol should be needed. We suspect that the surplus charge reduces Fe²⁺ ions (from the sacrificial anode oxidation) at the cathode, evident from the presence of iron precipitates at the bottom of the cell after reaction (stuck to the magnetic stir bar).

It is worth noting that the optimal yields under electrochemical conditions were obtained at 40 °C instead of 80 °C, as reported in the reaction using chemical reductants. This is attributed to fast reduction of Ni complexes at cathode surface, as indicated by the larger current observed during electrolysis at -1.35 V, 40 °C in MeCN (the current density was typically larger than 20 mA/cm², and the reaction completed in less than 5 h). At higher temperatures, homocouplings start to dominate, thus decreasing the cross-coupled product yields.

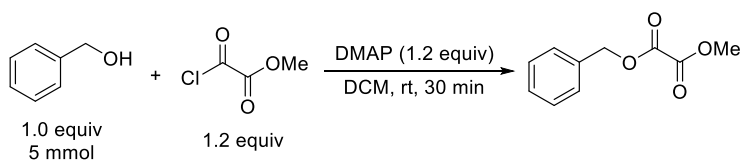
4. Synthesis of Substrates

Synthesis of Katritzky salts



The Katritzky salts were synthesized according to a procedure described previously in the literature.⁴⁹ To a 50 mL round bottom flask was added 2,4,6-triphenylpyrylium tetrafluoroborate (3.97 g, 10 mmol, 1.0 equiv) and absolute EtOH (10 mL). Subsequently, amine (12 mmol, 1.2 equiv) was added and the reaction mixture was refluxed at 88 °C for 4 h. Upon reaction completion, the mixture was cooled to room temperature and diluted with Et₂O (30 mL). The resulting precipitate was filtered off, washed with Et₂O (10 mL × 2), and dried *in vacuo* to afford the Katritzky salt.

Synthesis of benzyl methyl oxalate



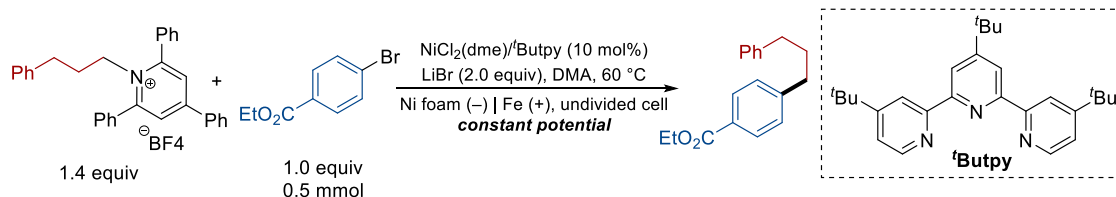
Benzyl methyl oxalate was synthesized according to a procedure described previously in the literature.⁵⁶ To a solution of DMAP (733 mg, 6 mmol, 1.2 equiv) in CH₂Cl₂ (20 mL) was dropwise added methyl chlorooxalate (552 μL, 6 mmol, 1.2 equiv) at 0 °C. After stirring at room temperature for 5 min, a solution of benzyl alcohol (519 μL, 5 mmol, 1.0 equiv) in CH₂Cl₂ (10 mL) was dropwise added and stirred for 30 min. Upon reaction completion, the reaction mixture was diluted with water (20 mL), extracted with CH₂Cl₂ (20 mL × 2) and the organic layers were combined and washed with brine (30 mL). The resultant organic solution was dried over anhydrous Na₂SO₄, then concentrated *in vacuo*. The obtained residue was purified by flash column chromatography (10:90 ethyl acetate:pentane) to afford the product as a white solid (892 mg, 92% yield). The spectroscopic data matched those reported in the literature.⁵⁷

5. Optimization of Electrochemical Reductive Coupling of Katritzky Salts with Aryl Halides

In a nitrogen-filled glove box, NiCl₂(dme), 'Butpy, and DMA (5 mL) were added to a 2-dram vial. This solution was stirred at 800 rpm in the glove box for 30 min to allow complexation of Ni with the ligand. To an undivided cell (Supplementary Fig. 4) fitted with a cross-shaped stir bar was added electrolyte, 2,4,6-triphenyl-1-(3-phenylpropyl)pyridin-1-ium tetrafluoroborate (360 mg, 0.7 mmol, 1.4 equiv), and aryl bromide (0.5 mmol, 1.0 equiv) under air. The cell was transferred into the glove box, followed by addition of the catalyst solution and installation of a Ni foam cathode, a Ag/AgNO₃ reference electrode, and a

sacrificial anode. The cell was then sealed with a rubber septum before removing from the glove box. A thin Teflon tube was introduced immediately into the cell to allow continuous nitrogen bubbling. The reaction mixture was stirred at 1000 rpm for 10 min to allow full dissolution of all reagents and exclusion of adventitious oxygen. After that, the Teflon tube was removed, and the top of the rubber septum was sealed with silicone gel. The reaction mixture was electrolyzed under constant potential for 10 – 17 h at 60 °C with stirring (800 rpm). The reaction was automatically stopped by the potentiostat after 2.5 F/mol of charge was passed to ensure full consumption of the aryl halides. The reaction mixture was then cooled to room temperature and diluted with DMA (10 mL). 1,3,5-Trimethoxybenzene (28 mg, 0.17 mmol, 0.33 equiv) was added to the crude material. Then a 100 μ L aliquot of the solution was filtered through a 2-cm silica gel plug in a Pasteur pipette into a vial. 400 μ L CDCl_3 was also added to the pipette and eluted into the same vial. The resultant sample was analyzed by ^1H NMR spectroscopy and the yields were determined using 1,3,5-trimethoxybenzene as the internal standard.

Supplementary Table 5. An example of optimization of electrochemical reductive coupling of Katritzky salts with aryl halides^a



Entry	Applied potential (V vs Fc/Fc ⁺)	Mass balance of ArBr (%)	Ar–Ar (%)	Yield (%)
1	–1.20	83	6	45
2	–1.25	103	14	75
3	–1.30	108	34	40
4	–1.50	100	33	33
5	–1.55	110	55	0
6 ^b	–1.25	110	12	70
7 ^c	–1.25	92	6	50
8 ^d	–1.25	110	9	20
9 ^e	–1.25	93	35	23
10^f	–1.25	102	7	81
11 ^g	–1.25	89	4	6

^a Yields were determined by ^1H NMR spectroscopy using 1,3,5-trimethoxybenzene as the internal standard.

^b 7 mol% Ni catalyst. ^c Al anode. ^d Zn anode. ^e Bu_4NPF_6 (1.0 equiv) instead of LiBr. ^f KPF_6 (1.0 equiv) instead of LiBr. ^g Divided cell with glass frit separator.

Discussion: The initial conditions were adapted from previous literature.⁴⁹ Note that although using LiBr gave a comparable yield as KPF_6 , bromide anions may participate in the catalytic process instead of just serving as the supporting electrolyte. KPF_6 is considered as a more appropriate electrolyte, due to its non-coordinating anion. For the coupling of secondary alkyl Katritzky salts with aryl halides, we continued using KPF_6 as the electrolyte.

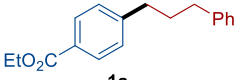
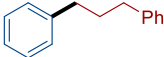
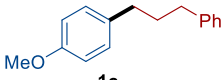
The optimization for the coupling of each pair of substrates generally proceeded according to the following sequence:

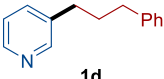
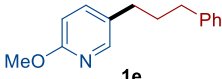
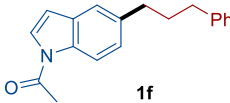
(1) Reactions were first performed at the applied potentials corresponding to $E^{\circ'}_{Zn}$ and $E^{\circ'}_{Mn}$, and the potential that led to the higher yield was then used as a starting point for further optimization (entries 1 and 2 in each table).

(2) Two experiments were then conducted, one 0.05–0.1 V above and one 0.05–0.1 V below, the $E^{\circ'}_{Zn}$ and $E^{\circ'}_{Mn}$ potential (whichever led to the higher yield in step 1) (entries 3 and 4 of each table, in most cases).

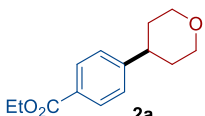
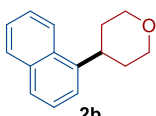
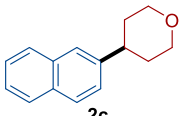
(3) The potential was incremented further in the direction that led to improved yield in step 2. Optimization efforts were discontinued after yields appeared to be optimized within ± 50 mV (entry 5, if present).

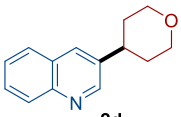
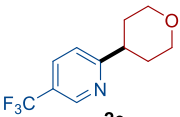
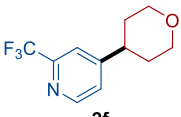
Optimization details for each of the products are summarized in Supplementary Figs. 5 and 6.

 1a			 1b			 1c		
Entry	Applied potential (V vs Fc/Fc ⁺)	Yield (%)	Entry	Applied potential (V vs Fc/Fc ⁺)	Yield (%)	Entry	Applied potential (V vs Fc/Fc ⁺)	Yield (%)
1	−1.31 ($E^{\circ'}_{Zn}$)	62	1	−1.31 ($E^{\circ'}_{Zn}$)	61	1	−1.31 ($E^{\circ'}_{Zn}$)	52
2	−1.55 ($E^{\circ'}_{Mn}$)	0	2	−1.55 ($E^{\circ'}_{Mn}$)	54	2	−1.55 ($E^{\circ'}_{Mn}$)	73
3	−1.25	81	3	−1.25	69	3	−1.50	92
4	−1.40	45	4	−1.35	76	4	−1.60	55
5	−1.20	62	5	−1.40	88	5	−1.45	75

 1d			 1e			 1f		
Entry	Applied potential (V vs Fc/Fc ⁺)	Yield (%)	Entry	Applied potential (V vs Fc/Fc ⁺)	Yield (%)	Entry	Applied potential (V vs Fc/Fc ⁺)	Yield (%)
1	−1.31 ($E^{\circ'}_{Zn}$)	0	1	−1.31 ($E^{\circ'}_{Zn}$)	61	1	−1.31 ($E^{\circ'}_{Zn}$)	57
2	−1.55 ($E^{\circ'}_{Mn}$)	35	2	−1.55 ($E^{\circ'}_{Mn}$)	54	2	−1.55 ($E^{\circ'}_{Mn}$)	50
3	−1.60	50	3	−1.25	51	3	−1.25	30
4	−1.65	67	4	−1.40	78	4	−1.40	90
5	−1.70	40	5	−1.45	72	5	−1.50	59

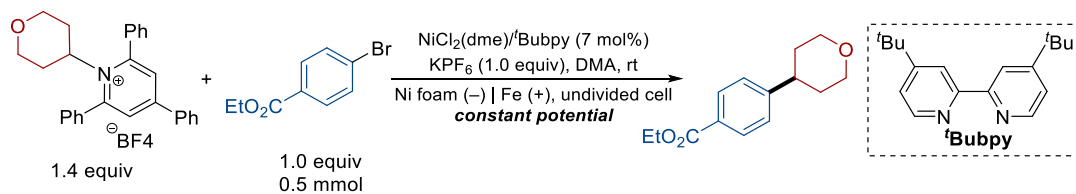
Supplementary Fig. 5. Optimization for electrochemical XEC reactions of alkyl Katritzky salt **1** with aryl bromides. Yields were determined by ¹H NMR spectroscopy using 1,3,5-trimethoxybenzene as the internal standard.

 2a			 2b			 2c		
Entry	Applied potential (V vs Fc/Fc ⁺)	Yield (%)	Entry	Applied potential (V vs Fc/Fc ⁺)	Yield (%)	Entry	Applied potential (V vs Fc/Fc ⁺)	Yield (%)
1	-1.31 (E°_{Zn})	99	1	-1.31 (E°_{Zn})	77	1	-1.31 (E°_{Zn})	82
2	-1.55 (E°_{Mn})	99	2	-1.55 (E°_{Mn})	64	2	-1.55 (E°_{Mn})	83
3	-1.30	99	3	-1.25	55	3	-1.50	92
			4	-1.40	84			
			5	-1.50	66			

 2d			 2e			 2f		
Entry	Applied potential (V vs Fc/Fc ⁺)	Yield (%)	Entry	Applied potential (V vs Fc/Fc ⁺)	Yield (%)	Entry	Applied potential (V vs Fc/Fc ⁺)	Yield (%)
1	-1.31 (E°_{Zn})	33	1	-1.31 (E°_{Zn})	19	1	-1.31 (E°_{Zn})	76
2	-1.55 (E°_{Mn})	9	2	-1.55 (E°_{Mn})	16	2	-1.55 (E°_{Mn})	56
3 ^a	-1.25	31	3	-1.25	46	3	-1.25	88
4	-1.40	38	4	-1.40	20	4	-1.15	92
5	-1.45	44	5	-1.20	26			

Supplementary Fig. 6. Optimization for electrochemical XEC reactions of alkyl Katritzky salt **2** with aryl bromides. Yields were determined by ¹H NMR spectroscopy using 1,3,5-trimethoxybenzene as the internal standard. ^a Current dropped to <20 μ A after 24 h of electrolysis, and the reaction was manually stopped; 2 F/mol of charge was passed.

Supplementary Table 6. Zn salt effects in the cross-coupling of Katritzky salts with aryl halides^a

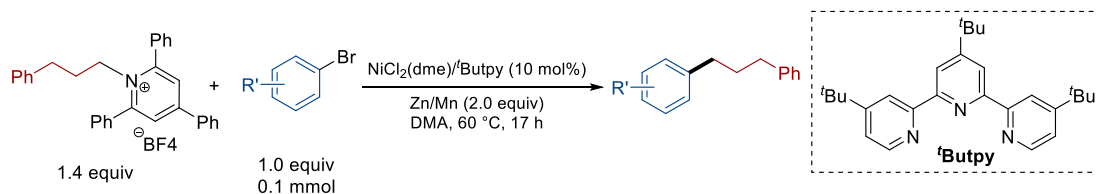


Entry	Applied potential (V vs Fc/Fc ⁺)	Mass balance of ArBr (%)	Ar-H (%)	Yield (%)
1	-1.31	102	0	99
2	-1.55	100	0	99
3 ^b	-1.55	98	56	42
4 ^c	Zn instead of e-chem	100	82	0
5 ^c	Mn instead of e-chem	103	0	99
6 ^{c,d}	Mn instead of e-chem	99	0	99
7 ^{b,c}	Mn instead of e-chem	101	52	44

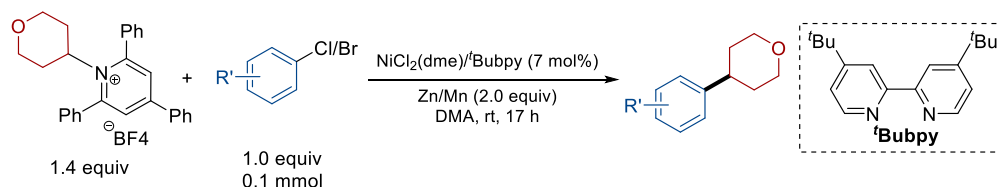
^a Yields were determined by ¹H NMR spectroscopy using 1,3,5-trimethoxybenzene as the internal standard. Ar-H represents the proto-dehalogenation byproduct. ^b ZnCl₂ (1.0 equiv) was added. ^c No KPF₆, the reaction was conducted at 0.1 mmol scale using Zn or Mn (2 equiv) as the reductant. ^d KPF₆ (1.0 equiv) was added.

6. General Procedures for Reductive Coupling of Katritzky Salts with Aryl Halides

Reductive coupling of Katritzky salts with aryl halides using Zn or Mn reductant

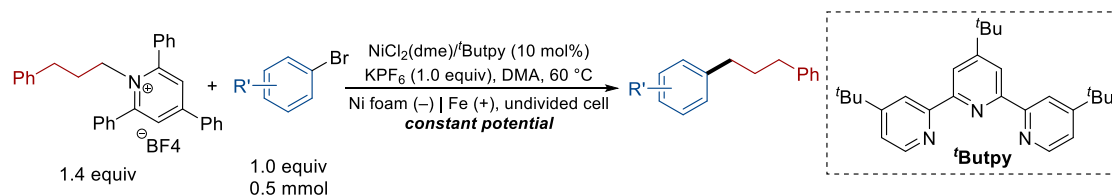


In a nitrogen-filled glove box, $\text{NiCl}_2(\text{dme})$ (2.2 mg, 10 mol%), tButpy (4.0 mg, 10 mol%), and DMA (1 mL) were added to a 1-dram vial. This solution was stirred at 800 rpm in the glove box for 30 min to allow complexation of Ni with the ligand, followed by sequential addition of 2,4,6-triphenyl-1-(3-phenylpropyl)pyridin-1-ium tetrafluoroborate (72 mg, 0.14 mmol, 1.4 equiv), aryl bromide (0.1 mmol, 1.0 equiv) and Zn powder (13 mg, 0.2 mmol, 2.0 equiv) or Mn powder (11 mg, 0.2 mmol, 2.0 equiv). The vial was capped with a screw cap fitted with a PTFE-faced silicone septum, then removed from the glove box and heated in a sand bath to 60 °C with stirring (1000 rpm) for 17 h. The reaction mixture was then cooled to room temperature and diluted with DMA (1 mL). 1,3,5-Trimethoxybenzene (5.6 mg, 0.033 mmol, 0.33 equiv) was added to the crude material. Then a 100 μL aliquot of the solution was filtered through a 2-cm silica gel plug in a Pasteur pipette into a vial. 400 μL CDCl_3 was also added to the pipette and eluted into the same vial. The resultant sample was analyzed by ^1H NMR spectroscopy and the yields were determined using 1,3,5-trimethoxybenzene as the internal standard.

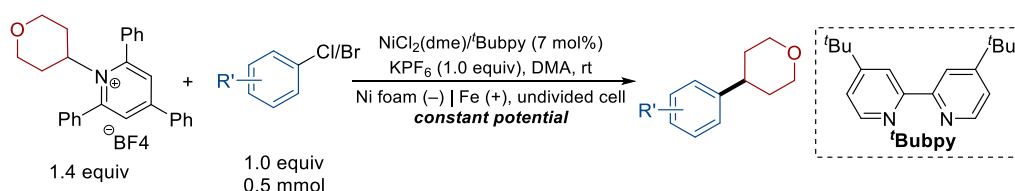


In a nitrogen-filled glove box, $\text{NiCl}_2(\text{dme})$ (1.54 mg, 7 mol%), tBubpy (1.88 mg, 7 mol%), and DMA (1 mL) were added to a 1-dram vial. This solution was stirred at 800 rpm in the glove box for 30 min to allow complexation of Ni with the ligand, followed by sequential addition of 2,4,6-triphenyl-1-(tetrahydro-2H-pyran-4-yl)pyridin-1-ium tetrafluoroborate (67 mg, 0.14 mmol, 1.4 equiv), aryl bromide or aryl chloride (0.1 mmol, 1.0 equiv) and Zn powder (13 mg, 0.2 mmol, 2.0 equiv) or Mn powder (11 mg, 0.2 mmol, 2.0 equiv). The vial was capped with a screw cap fitted with a PTFE-faced silicone septum, then removed from the glove box and stirred (1000 rpm) at room temperature for 17 h. The reaction mixture was then diluted with DMA (1 mL). 1,3,5-Trimethoxybenzene (5.6 mg, 0.033 mmol, 0.33 equiv) was added to the crude material. Then a 100 μL aliquot of the solution was filtered through a 2-cm silica gel plug in a Pasteur pipette into a vial. 400 μL CDCl_3 was also added to the pipette and eluted into the same vial. The resultant sample was analyzed by ^1H NMR spectroscopy and the yields were determined using 1,3,5-trimethoxybenzene as the internal standard.

Electrochemical reductive coupling of Katritzky salts with aryl halides



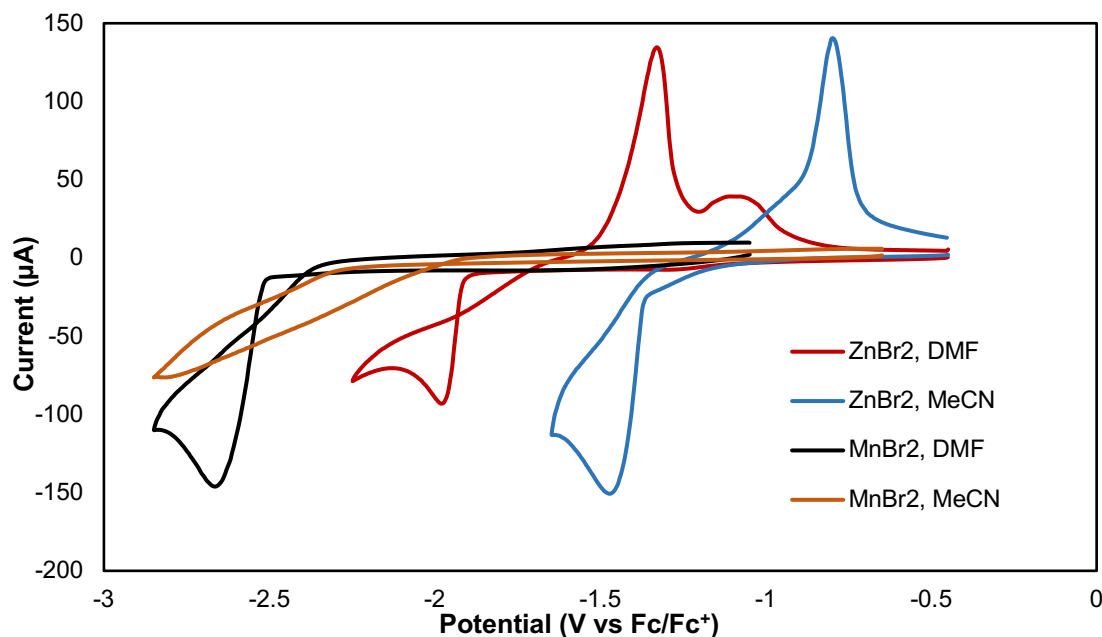
General Procedure 1 (GP 1): In a nitrogen-filled glove box, NiCl₂(dme) (11 mg, 10 mol%), *t*BuPy (20 mg, 10 mol%), and DMA (5 mL) were added to a 2-dram vial. This solution was stirred at 800 rpm in the glove box for 30 min to allow complexation of Ni with the ligand. To an undivided cell (Supplementary Fig. 4) fitted with a cross-shaped stir bar was added KPF₆ (92 mg, 0.5 mmol, 1.0 equiv, unless otherwise noted), 2,4,6-triphenyl-1-(3-phenylpropyl)pyridin-1-ium tetrafluoroborate (360 mg, 0.7 mmol, 1.4 equiv), and aryl bromide (0.5 mmol, 1.0 equiv) under air. The cell was transferred into the glove box, followed by addition of the catalyst solution and installation of a Ni foam cathode, a Ag/AgNO₃ reference electrode, and an Fe rod anode. The cell was then sealed with a rubber septum before removing from the glove box. A thin Teflon tube was introduced immediately into the cell to allow continuous nitrogen bubbling. The reaction mixture was stirred at 1000 rpm for 10 min to allow full dissolution of all reagents and exclusion of adventitious oxygen. After that, the Teflon tube was removed, and the top of the rubber septum was sealed with silicone gel. The reaction mixture was electrolyzed under the desired constant potential for 10 – 17 h at 60 °C with stirring (800 rpm). The reaction was automatically stopped by the potentiostat after the desired amount of charge (specified in Section 8 for each product) was passed. Upon reaction completion, the reaction mixture was cooled to room temperature and diluted with water (25 mL). The solution was extracted with ethyl acetate (50 mL × 2) and the organic layers were combined and washed with brine (50 mL). The resultant organic solution was dried over anhydrous Na₂SO₄, then concentrated *in vacuo*. The obtained residue was purified by flash column chromatography.



General Procedure 2 (GP 2): In a nitrogen-filled glove box, NiCl₂(dme) (7.7 mg, 7 mol%), *t*Bubpy (9.4 mg, 7 mol%), and DMA (5 mL) were added to a 2-dram vial. This solution was stirred at 800 rpm in the glove box for 30 min to allow complexation of Ni with the ligand. To an undivided cell (Supplementary Fig. 4) fitted with a cross-shaped stir bar was added KPF₆ (92 mg, 0.5 mmol, 1.0 equiv, unless otherwise noted), 2,4,6-triphenyl-1-(tetrahydro-2H-pyran-4-yl)pyridin-1-ium tetrafluoroborate (335 mg, 0.7 mmol, 1.4 equiv), and aryl bromide or chloride (0.5 mmol, 1.0 equiv) under air. The cell was transferred into the glove box, followed by addition of the catalyst solution and installation of a Ni foam cathode, a Ag/AgNO₃ reference electrode, and an Fe rod anode. The cell was then sealed with a rubber septum before removing from the glove box. A thin Teflon tube was introduced immediately into the cell to allow continuous nitrogen bubbling. The reaction mixture was stirred at 1000 rpm for 10 min to allow full dissolution of all reagents and exclusion of adventitious oxygen. After that, the Teflon tube was removed, and the top of rubber septum was sealed with silicone gel. The reaction mixture was electrolyzed under the desired constant potential for 10 – 17 h at room temperature with stirring (800 rpm). The reaction was automatically

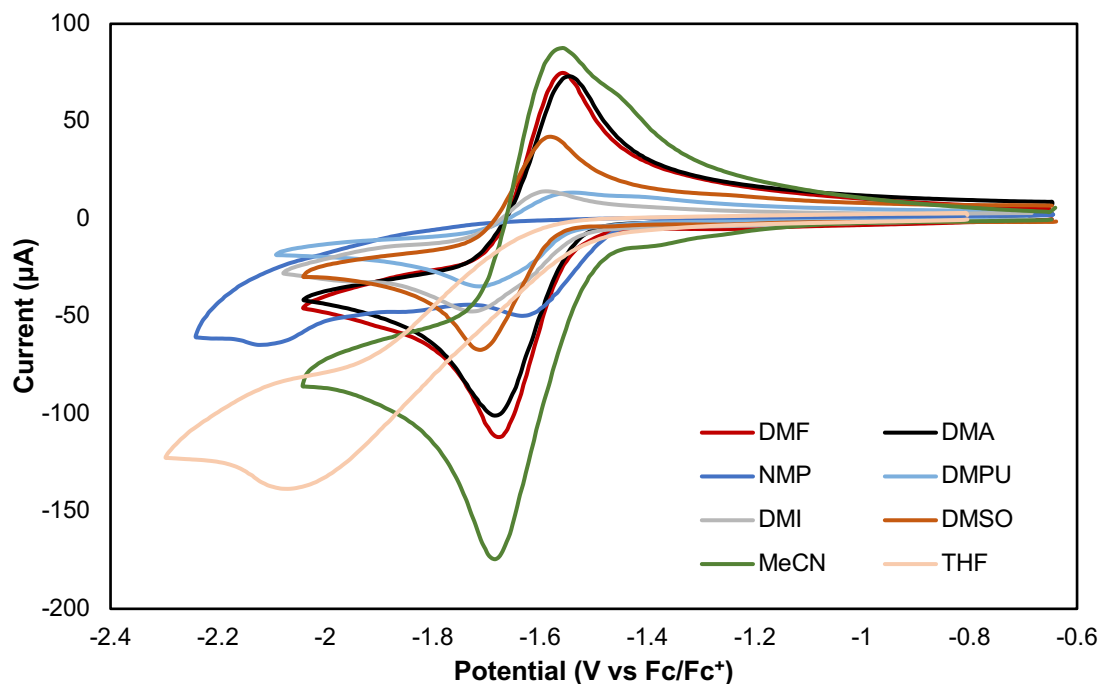
stopped by the potentiostat after the desired amount of charge (specified in Section 8 for each product) was passed. Upon reaction completion, the reaction mixture was diluted with water (25 mL) and extracted with ethyl acetate (50 mL $\times$ 2). The organic layers were combined and washed with brine (50 mL). The resultant organic solution was dried over anhydrous Na_2SO_4 , then concentrated *in vacuo*. The obtained residue was purified by flash column chromatography.

7. Cyclic Voltammetry Studies



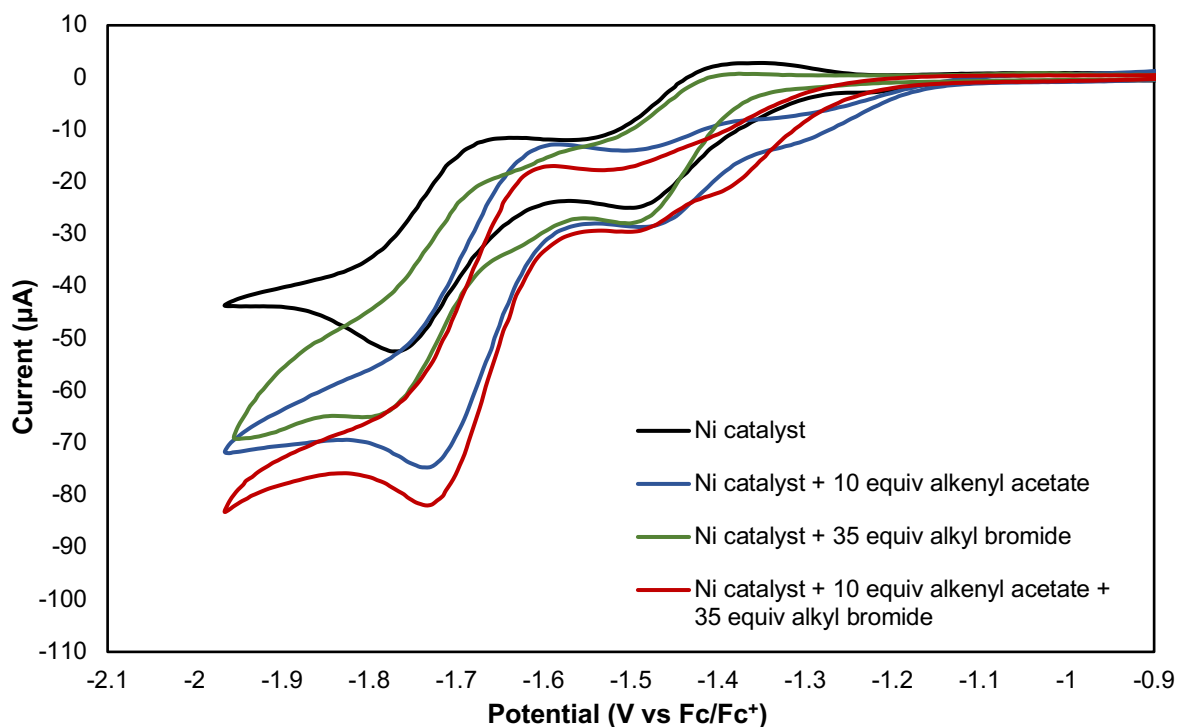
Supplementary Fig. 7. CVs of metal salts (10 mM) in DMF (5 mL) or MeCN (5 mL), with tBu_4NPF_6 (0.2 M) as supporting electrolyte, under N_2 atmosphere, at room temperature, scan rate = 20 mV/s, scanning towards a more negative potential.

Discussion: The CV of ZnBr_2 in DMF or MeCN displays an ill-defined redox couple with a large peak-to-peak separation and a sharp oxidation peak, indicating poor kinetics for the Zn redox and Zn electroplating on the working electrode during the sweep. The CV traces of MnBr_2 are fully irreversible, again indicating poor kinetics for Mn redox under CV conditions. Overall, these results suggest that CV is not a reliable tool for measuring the thermodynamic potentials of Zn and Mn, and the derived redox potentials thereby may not be appropriate for use in relevant studies.

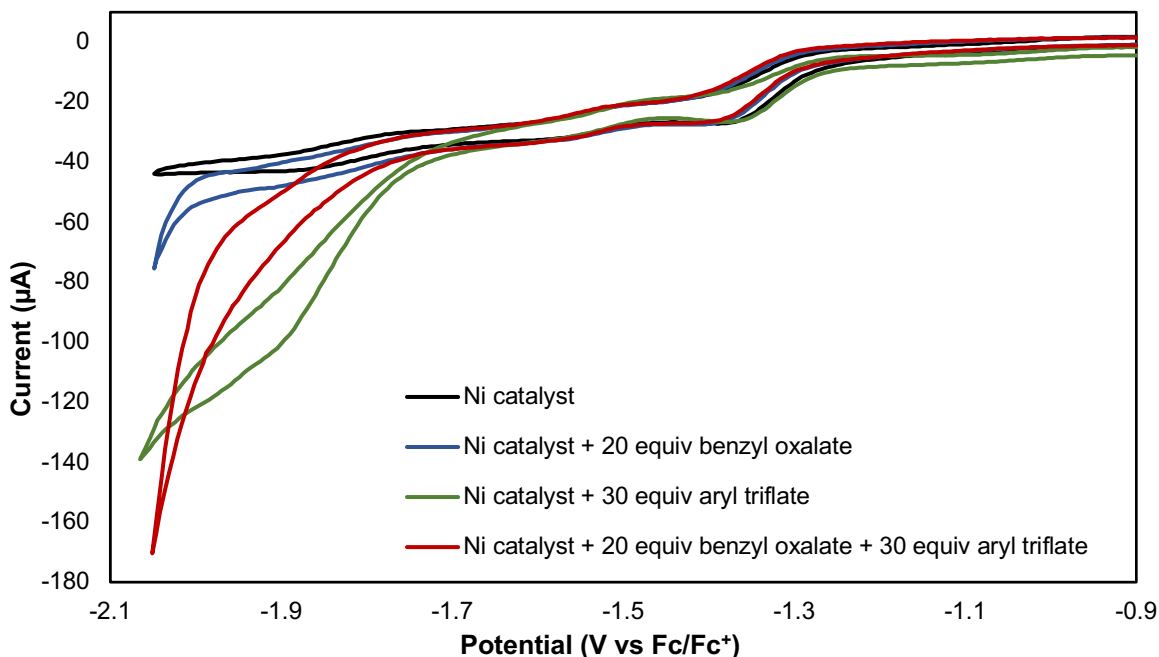


Supplementary Fig. 8. CVs of $[\text{Ni}(\text{bpy})_3]\text{Cl}_2$ (4 mM) in various organic solvents, with $^t\text{Bu}_4\text{NPF}_6$ (0.1 M) as supporting electrolyte, under N_2 atmosphere, at room temperature, scan rate = 100 mV/s, scanning towards a more negative potential.

Discussion: $[\text{Ni}(\text{bpy})_3]\text{Cl}_2$ displays a fully reversible 2-electron redox couple in DMF, DMA, and DMSO, but a slightly disrupted peak in DMPU, DMI, and MeCN, possibly due to solvent coordination to Ni center. CV traces in NMP and THF are not reversible, which can again be attributed to solvent coordination or a slow re-coordination process of chlorides and ligands back to Ni center. Therefore, no half potentials can be derived from CV traces of $[\text{Ni}(\text{bpy})_3]\text{Cl}_2$ in NMP and THF. Given these considerations, half-peak potentials instead of half potentials were reported in Fig. 2B for consistency.



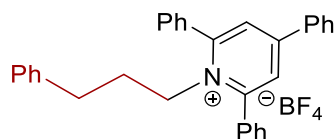
Supplementary Fig. 9. CVs of Ni/dmbpy catalyst in the presence or absence of substrates for cross-coupling of alkenyl acetate with alkyl bromide. Black trace: Ni catalyst [5 mM NiBr₂(dme) + 7.5 mM 5,5'-dimethyl-2,2'-bipyridine]. Blue trace: Ni catalyst + 10 equiv 1-phenylvinyl acetate. Green trace: Ni catalyst + 35 equiv ethyl 4-bromobutanoate. Red trace: Ni catalyst + 10 equiv 1-phenylvinyl acetate + 35 equiv ethyl 4-bromobutanoate. All CVs were recorded in DMA (5 mL), with KPF₆ (0.1 M) as supporting electrolyte, under N₂ atmosphere, at 40 °C, scan rate = 20 mV/s, scanning towards a more negative potential.



Supplementary Fig. 10. CVs of Ni/dppf/phen catalyst system in the presence or absence of substrates for cross-coupling of benzyl oxalate with aryl triflate. Black trace: Ni catalyst [2.5 mM NiCl₂(dppf) + 2.5 mM dppf + 0.5 mM 1,10-phenanthroline]. Blue trace: Ni catalyst + 20 equiv benzyl methyl oxalate. Green trace: Ni catalyst + 30 equiv methyl 4-(((trifluoromethyl)sulfonyl)oxy)benzoate. Red trace: Ni catalyst + 20 equiv benzyl methyl oxalate + 30 equiv methyl 4-(((trifluoromethyl)sulfonyl)oxy)benzoate. All CVs were recorded in DMF (5 mL), with KPF₆ (0.1 M) as supporting electrolyte, under N₂ atmosphere, at 80 °C, scan rate = 20 mV/s, scanning towards a more negative potential.

8. Compound Characterization Data

2,4,6-triphenyl-1-(3-phenylpropyl)pyridin-1-ium tetrafluoroborate (**1**)



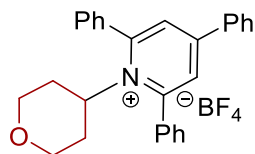
The spectroscopic data matched those reported in the literature.⁴⁹

¹H NMR (500 MHz, CDCl₃) δ 7.81 (s, 2H), 7.72 (td, *J* = 6.8, 1.3 Hz, 6H), 7.60 – 7.44 (m, 9H), 7.09 – 7.03 (m, 3H), 6.65 – 6.62 (m, 2H), 4.40 – 4.34 (m, 2H), 2.09 (t, *J* = 7.1 Hz, 2H), 1.84 – 1.74 (m, 2H).

¹³C NMR (126 MHz, CDCl₃) δ 156.4, 155.9, 138.8, 134.1, 132.6, 132.0, 131.0, 129.7, 129.3, 128.9, 128.5, 128.2, 127.7, 126.8, 126.2, 54.3, 32.3, 30.7.

HRMS (ESI⁺) Calc: [M]⁺ (C₃₂H₂₈N) 426.2216; measured: 426.2206 = 2.3 ppm difference.

2,4,6-triphenyl-1-(tetrahydro-2H-pyran-4-yl)pyridin-1-ium tetrafluoroborate (**2**)



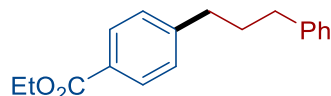
The spectroscopic data matched those reported in the literature.⁵⁸

¹H NMR (500 MHz, CDCl₃) δ 7.76 – 7.73 (m, 6H), 7.70 – 7.66 (m, 2H), 7.64 – 7.54 (m, 6H), 7.53 – 7.48 (m, 1H), 7.42 (dd, *J* = 8.5, 7.1 Hz, 2H), 4.87 (tt, *J* = 12.4, 3.2 Hz, 1H), 3.74 – 3.68 (m, 2H), 2.79 (td, *J* = 11.7, 1.8 Hz, 2H), 2.06 (dt, *J* = 12.5, 2.4 Hz, 2H), 1.87 (qd, *J* = 12.2, 4.3 Hz, 2H).

¹³C NMR (126 MHz, CDCl₃) δ 157.2, 155.3, 134.0, 133.8, 132.0, 131.1, 129.6, 129.4, 129.0, 128.3, 128.2, 69.1, 67.8, 33.8.

HRMS (ESI⁺) Calc: [M]⁺ (C₂₈H₂₆NO) 392.2009; measured: 392.2002 = 1.8 ppm difference.

ethyl 4-(3-phenylpropyl)benzoate (**1a**)



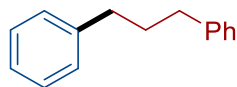
GP 1 was followed using ethyl 4-bromobenzoate (114 mg, 0.5 mmol, 1.0 equiv) under reductive electrolysis (−1.25 V vs Fc/Fc⁺, 2.5 F/mol), which furnished the title compound following purification by flash column chromatography (2:98 ethyl acetate:pentane) as a colorless oil (105 mg, 78% yield). The spectroscopic data matched those reported in the literature.¹⁷

¹H NMR (500 MHz, CDCl₃) δ 7.96 (d, *J* = 8.3 Hz, 2H), 7.31 – 7.14 (m, 7H), 4.36 (q, *J* = 7.1 Hz, 2H), 2.69 (t, *J* = 7.7 Hz, 2H), 2.64 (t, *J* = 7.7 Hz, 2H), 2.01 – 1.92 (m, 2H), 1.38 (t, *J* = 7.1 Hz, 3H).

¹³C NMR (126 MHz, CDCl₃) δ 166.7, 147.7, 141.9, 129.7, 128.45, 128.39, 125.9, 60.8, 35.44, 35.36, 32.6, 14.4.

HRMS (ESI⁺) Calc: [M+H]⁺ (C₁₈H₂₁O₂) 269.1536; measured: 269.1534 = 0.7 ppm difference.

1,3-diphenylpropane (**1b**)



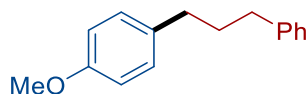
GP 1 was followed using bromobenzene (78 mg, 0.5 mmol, 1.0 equiv) under reductive electrolysis (−1.40 V vs Fc/Fc⁺, 2.5 F/mol), which furnished the title compound following purification by flash column chromatography (0:100 ethyl acetate:pentane) as a colorless oil (79 mg, 81% yield). This is the corrected yield that excluded the inseparable alkyl dimer byproduct (1.5% with respect to the product based on ¹H NMR). The spectroscopic data matched those reported in the literature.¹⁷

¹H NMR (500 MHz, CDCl₃) δ 7.26 (dd, *J* = 8.1, 6.8 Hz, 4H), 7.19 – 7.13 (m, 6H), 2.67 – 2.61 (m, 4H), 2.00 – 1.90 (m, 2H).

^{13}C NMR (126 MHz, CDCl_3) δ 142.4, 128.5, 128.4, 125.8, 35.5, 33.0.

HRMS (ESI $^+$) Calc: $[\text{M}+\text{H}]^+$ ($\text{C}_{16}\text{H}_{17}$) 197.1325; measured: 197.1323 = 1.0 ppm difference.

1-methoxy-4-(3-phenylpropyl)benzene (**1c**)



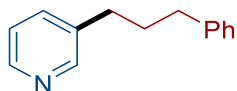
GP 1 was followed using 1-bromo-4-methoxybenzene (94 mg, 0.5 mmol, 1.0 equiv) under reductive electrolysis (-1.50 V vs Fc/Fc^+ , 2.5 F/mol), which furnished the title compound following purification by flash column chromatography (1:99 ethyl acetate:pentane) as a colorless oil (98 mg, 87% yield). The spectroscopic data matched those reported in the literature.¹⁷

^1H NMR (500 MHz, CDCl_3) δ 7.30 – 7.24 (m, 2H), 7.20 – 7.14 (m, 3H), 7.12 – 7.06 (m, 2H), 6.82 (d, J = 8.5 Hz, 2H), 3.78 (s, 3H), 2.63 (t, J = 7.7 Hz, 2H), 2.59 (t, J = 7.6 Hz, 2H), 1.92 (tt, J = 9.3, 6.8 Hz, 2H).

^{13}C NMR (126 MHz, CDCl_3) δ 157.8, 142.4, 134.4, 129.3, 128.5, 128.3, 125.7, 113.8, 55.3, 35.4, 34.5, 33.2.

HRMS (ESI $^+$) Calc: $[\text{M}+\text{H}]^+$ ($\text{C}_{16}\text{H}_{19}\text{O}$) 227.1430; measured: 227.1427 = 1.3 ppm difference.

3-(3-phenylpropyl)pyridine (**1d**)



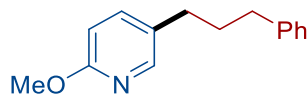
GP 1 was followed using 3-bromopyridine (79 mg, 0.5 mmol, 1.0 equiv), LiBr (87 mg, 1.0 mmol, 2.0 equiv) instead of KPF_6 as electrolyte, under reductive electrolysis (-1.65 V vs Fc/Fc^+ , 3.0 F/mol), which furnished the title compound following purification by flash column chromatography (20:80 ethyl acetate:pentane) as a pale-yellow oil (59 mg, 60% yield). The spectroscopic data matched those reported in the literature.⁵⁹

^1H NMR (500 MHz, CDCl_3) δ 8.44 (s, 2H), 7.46 (dt, J = 7.8, 2.0 Hz, 1H), 7.27 (dd, J = 8.2, 6.9 Hz, 2H), 7.21 – 7.14 (m, 4H), 2.63 (dt, J = 10.5, 7.7 Hz, 4H), 1.95 (tt, J = 9.3, 6.9 Hz, 2H).

^{13}C NMR (126 MHz, CDCl_3) δ 150.0, 147.3, 141.7, 137.5, 135.8, 128.4, 126.0, 123.3, 35.3, 32.6, 32.5.

HRMS (ESI $^+$) Calc: $[\text{M}+\text{H}]^+$ ($\text{C}_{14}\text{H}_{16}\text{N}$) 198.1277; measured: 198.1275 = 1.0 ppm difference.

2-methoxy-5-(3-phenylpropyl)pyridine (**1e**)



GP 1 was followed using 5-bromo-2-methoxypyridine (94 mg, 0.5 mmol, 1.0 equiv) under reductive electrolysis (-1.40 V vs Fc/Fc^+ , 3.0 F/mol), which furnished the title compound following purification by

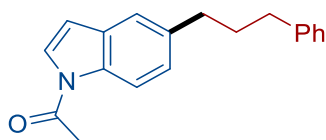
flash column chromatography (30:70 ethyl acetate:pentane) as a pale-yellow oil (85 mg, 75% yield). The spectroscopic data matched those reported in the literature.⁶⁰

¹H NMR (500 MHz, CDCl₃) δ 7.99 (d, J = 2.5 Hz, 1H), 7.41 (dd, J = 8.4, 2.5 Hz, 1H), 7.32 – 7.23 (m, 2H), 7.23 – 7.15 (m, 3H), 6.69 (d, J = 8.3 Hz, 1H), 3.93 (s, 3H), 2.65 (t, 2H), 2.57 (t, J = 7.6 Hz, 2H), 1.96 – 1.87 (m, 2H).

¹³C NMR (126 MHz, CDCl₃) δ 162.7, 146.0, 141.9, 139.0, 130.0, 128.44, 128.39, 125.9, 110.5, 53.4, 35.2, 32.8, 31.5.

HRMS (ESI⁺) Calc: [M+H]⁺ (C₁₅H₁₈NO) 228.1383; measured: 228.1379 = 1.8 ppm difference.

1-(5-(3-phenylpropyl)-1H-indol-1-yl)ethan-1-one (**1f**)



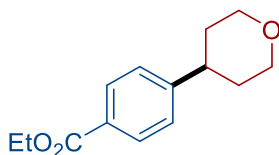
GP 1 was followed using 1-(5-bromo-1H-indol-1-yl)ethan-1-one (119 mg, 0.5 mmol, 1.0 equiv) under reductive electrolysis (−1.40 V vs Fc/Fc⁺, 2.5 F/mol), which furnished the title compound following purification by flash column chromatography (10:90 ethyl acetate:pentane) as a yellow oil (118 mg, 85% yield). The spectroscopic data matched those reported in the literature.¹⁷

¹H NMR (500 MHz, CDCl₃) δ 8.32 (d, J = 8.6 Hz, 1H), 7.38 (d, J = 3.7 Hz, 1H), 7.36 (s, 1H), 7.30 – 7.25 (m, 2H), 7.21 – 7.15 (m, 4H), 6.57 (d, J = 3.7 Hz, 1H), 2.74 (t, J = 7.7 Hz, 2H), 2.66 (t, J = 7.6 Hz, 2H), 2.61 (s, 3H), 2.03 – 1.96 (m, 2H).

¹³C NMR (126 MHz, CDCl₃) δ 168.5, 142.4, 137.8, 134.0, 130.7, 128.5, 128.3, 125.9, 125.8, 125.3, 120.3, 116.3, 109.1, 35.43, 35.37, 33.4, 23.9.

HRMS (ESI⁺) Calc: [M+H]⁺ (C₁₉H₁₉NONa) 300.1359; measured: 300.1354 = 1.7 ppm difference.

ethyl 4-(tetrahydro-2H-pyran-4-yl)benzoate (**2a**)



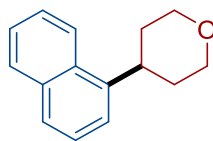
GP 2 was followed using ethyl 4-bromobenzoate (114 mg, 0.5 mmol, 1.0 equiv) under reductive electrolysis (−1.30 V vs Fc/Fc⁺, 2.5 F/mol), which furnished the title compound following purification by flash column chromatography (4:96 ethyl acetate:pentane) as a white solid (111 mg, 95% yield). The spectroscopic data matched those reported in the literature.¹⁸

¹H NMR (500 MHz, CDCl₃) δ 7.99 (d, J = 8.4 Hz, 2H), 7.29 (d, J = 8.4 Hz, 2H), 4.36 (q, J = 7.1 Hz, 2H), 4.12 – 4.05 (m, 2H), 3.53 (td, J = 11.6, 2.4 Hz, 3H), 2.82 (tt, J = 11.8, 4.2 Hz, 1H), 1.89 – 1.73 (m, 4H), 1.38 (t, J = 7.1 Hz, 3H).

¹³C NMR (126 MHz, CDCl₃) δ 166.5, 151.0, 129.9, 128.7, 126.8, 68.2, 60.8, 41.7, 33.6, 14.4.

HRMS (ESI⁺) Calc: [M+H]⁺ (C₁₄H₁₉O₃) 235.1329; measured: 235.1326 = 1.3 ppm difference.

4-(naphthalen-1-yl)tetrahydro-2H-pyran (**2b**)



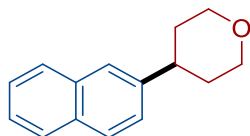
GP 2 was followed using ethyl 1-bromonaphthalene (104 mg, 0.5 mmol, 1.0 equiv) under reductive electrolysis (−1.40 V vs Fc/Fc⁺, 2.5 F/mol), which furnished the title compound following purification by flash column chromatography (5:95 ethyl acetate:pentane) as a white powder (87 mg, 82% yield). The spectroscopic data matched those reported in the literature.¹⁸

¹H NMR (500 MHz, CDCl₃) δ 8.12 (d, *J* = 8.4 Hz, 1H), 7.88 (dd, *J* = 8.0, 1.5 Hz, 1H), 7.74 (d, *J* = 8.0 Hz, 1H), 7.55 – 7.44 (m, 3H), 7.41 (dd, *J* = 7.2, 1.3 Hz, 1H), 4.20 – 4.13 (m, 2H), 3.71 (td, *J* = 11.5, 2.5 Hz, 2H), 3.60 (tt, *J* = 11.5, 4.0 Hz, 1H), 2.04 – 1.88 (m, 4H).

¹³C NMR (126 MHz, CDCl₃) δ 141.5, 134.0, 131.1, 129.1, 126.8, 125.9, 125.7, 125.4, 122.8, 122.6, 68.7, 36.7, 33.8.

HRMS (ESI⁺) Calc: [M+H]⁺ (C₁₅H₁₇O) 213.1274; measured: 213.1272 = 0.9 ppm difference.

4-(naphthalen-2-yl)tetrahydro-2H-pyran (**2c**)



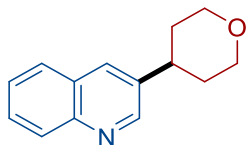
GP 2 was followed using ethyl 1-bromonaphthalene (104 mg, 0.5 mmol, 1.0 equiv) under reductive electrolysis (−1.50 V vs Fc/Fc⁺, 2.5 F/mol), which furnished the title compound following purification by flash column chromatography (10:90 ethyl acetate:pentane) as a white solid (94 mg, 89% yield). The spectroscopic data matched those reported in the literature.¹⁸

¹H NMR (500 MHz, CDCl₃) δ 7.79 (dd, *J* = 8.9, 2.9 Hz, 3H), 7.63 (s, 1H), 7.43 (dq, *J* = 8.0, 6.8, 1.5 Hz, 2H), 7.36 (dd, *J* = 8.5, 1.8 Hz, 1H), 4.14 – 4.08 (m, 2H), 3.56 (td, *J* = 11.7, 2.2 Hz, 2H), 2.90 (tt, *J* = 11.9, 4.0 Hz, 1H), 1.97 – 1.80 (m, 4H).

¹³C NMR (126 MHz, CDCl₃) δ 143.3, 133.7, 132.3, 128.1, 127.7, 127.6, 126.0, 125.7, 125.4, 124.8, 68.5, 41.7, 33.9.

HRMS (ESI⁺) Calc: [M+H]⁺ (C₁₅H₁₇O) 213.1274; measured: 213.1273 = 0.5 ppm difference.

3-(tetrahydro-2H-pyran-4-yl)quinoline (**2d**)



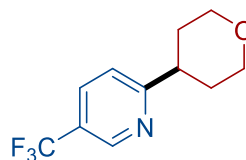
GP 2 was followed using 3-bromoquinoline (104 mg, 0.5 mmol, 1.0 equiv) under reductive electrolysis (-1.45 V vs Fc/Fc^+ , 2.5 F/mol), which furnished the title compound following purification by flash column chromatography (50:50 ethyl acetate:pentane) as a white solid (41 mg, 38% yield). This is the corrected yield that excluded the inseparable aryl dimer byproduct (6% with respect to the product based on ^1H NMR). The spectroscopic data matched those reported in the literature.⁶¹

^1H NMR (500 MHz, CDCl_3) δ 8.84 (d, $J = 2.2$ Hz, 1H), 8.09 (d, $J = 8.4$ Hz, 1H), 7.94 (d, $J = 2.2$ Hz, 1H), 7.80 (dd, $J = 8.1, 1.4$ Hz, 1H), 7.68 (ddd, $J = 8.5, 6.8, 1.4$ Hz, 1H), 7.54 (t, $J = 7.5$ Hz, 1H), 4.18 – 4.11 (m, 2H), 3.60 (td, $J = 11.5, 2.7$ Hz, 2H), 2.99 (tt, $J = 11.6, 4.4$ Hz, 1H), 2.00 – 1.85 (m, 4H).

^{13}C NMR (126 MHz, CDCl_3) δ 150.9, 147.2, 138.2, 132.5, 129.2, 128.9, 128.2, 127.6, 126.7, 68.2, 39.2, 33.6.

HRMS (ESI^+) Calc: $[\text{M}+\text{H}]^+$ ($\text{C}_{14}\text{H}_{16}\text{NO}$) 214.1226; measured: 214.1224 = 0.9 ppm difference.

2-(tetrahydro-2H-pyran-4-yl)-5-(trifluoromethyl)pyridine (**2e**)



GP 2 was followed using 2-bromo-5-(trifluoromethyl)pyridine (113 mg, 0.5 mmol, 1.0 equiv), LiBr (87 mg, 1.0 mmol, 2.0 equiv) instead of KPF_6 as electrolyte, under reductive electrolysis (-1.25 V vs Fc/Fc^+ , 2.5 F/mol), which furnished the title compound following purification by flash column chromatography (33:67 ethyl acetate:pentane) as a pale-yellow oil (39 mg, 42% yield).

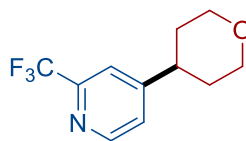
^1H NMR (400 MHz, CDCl_3) δ 8.83 – 8.79 (m, 1H), 7.89 – 7.84 (m, 1H), 7.30 (d, $J = 8.2$ Hz, 1H), 4.15 – 4.07 (m, 2H), 3.56 (td, $J = 11.5, 2.8$ Hz, 2H), 3.04 (tt, $J = 11.2, 4.5$ Hz, 1H), 1.98 – 1.83 (m, 4H).

^{13}C NMR (126 MHz, CDCl_3) δ 168.3 (d, $J = 1.5$ Hz), 146.3 (q, $J = 4.1$ Hz), 133.7 (q, $J = 3.5$ Hz), 124.6 (q, $J = 33.0$ Hz), 123.7 (q, $J = 272.1$ Hz), 120.6, 67.9, 43.5, 32.1.

^{19}F NMR (377 MHz, CDCl_3) δ -62.28.

HRMS (ESI^+) Calc: $[\text{M}+\text{H}]^+$ ($\text{C}_{11}\text{H}_{13}\text{F}_3\text{NO}$) 232.0944; measured: 232.0941 = 1.3 ppm difference.

4-(tetrahydro-2H-pyran-4-yl)-2-(trifluoromethyl)pyridine (**2f**)



GP 2 was followed using 4-chloro-2-(trifluoromethyl)pyridine (91 mg, 0.5 mmol, 1.0 equiv) under reductive electrolysis (-1.15 V vs Fc/Fc⁺, 2.5 F/mol), which furnished the title compound following purification by flash column chromatography (33:67 ethyl acetate:pentane) as a colorless oil (102 mg, 88% yield).

¹H NMR (400 MHz, CDCl₃) δ 8.65 (d, $J = 5.0$ Hz, 1H), 7.55 (s, 1H), 7.36 (d, $J = 5.1$ Hz, 1H), 4.16 – 4.07 (m, 2H), 3.62 – 3.49 (m, 2H), 2.95 – 2.82 (m, 1H), 1.90 – 1.77 (m, 4H).

¹³C NMR (126 MHz, CDCl₃) δ 156.4, 150.2, 148.5 (q, $J = 34.1$ Hz), 124.7, 121.6 (q, $J = 274.3$ Hz), 119.0 (q, $J = 2.8$ Hz), 67.8, 40.9, 32.8.

¹⁹F NMR (377 MHz, CDCl₃) δ -67.96.

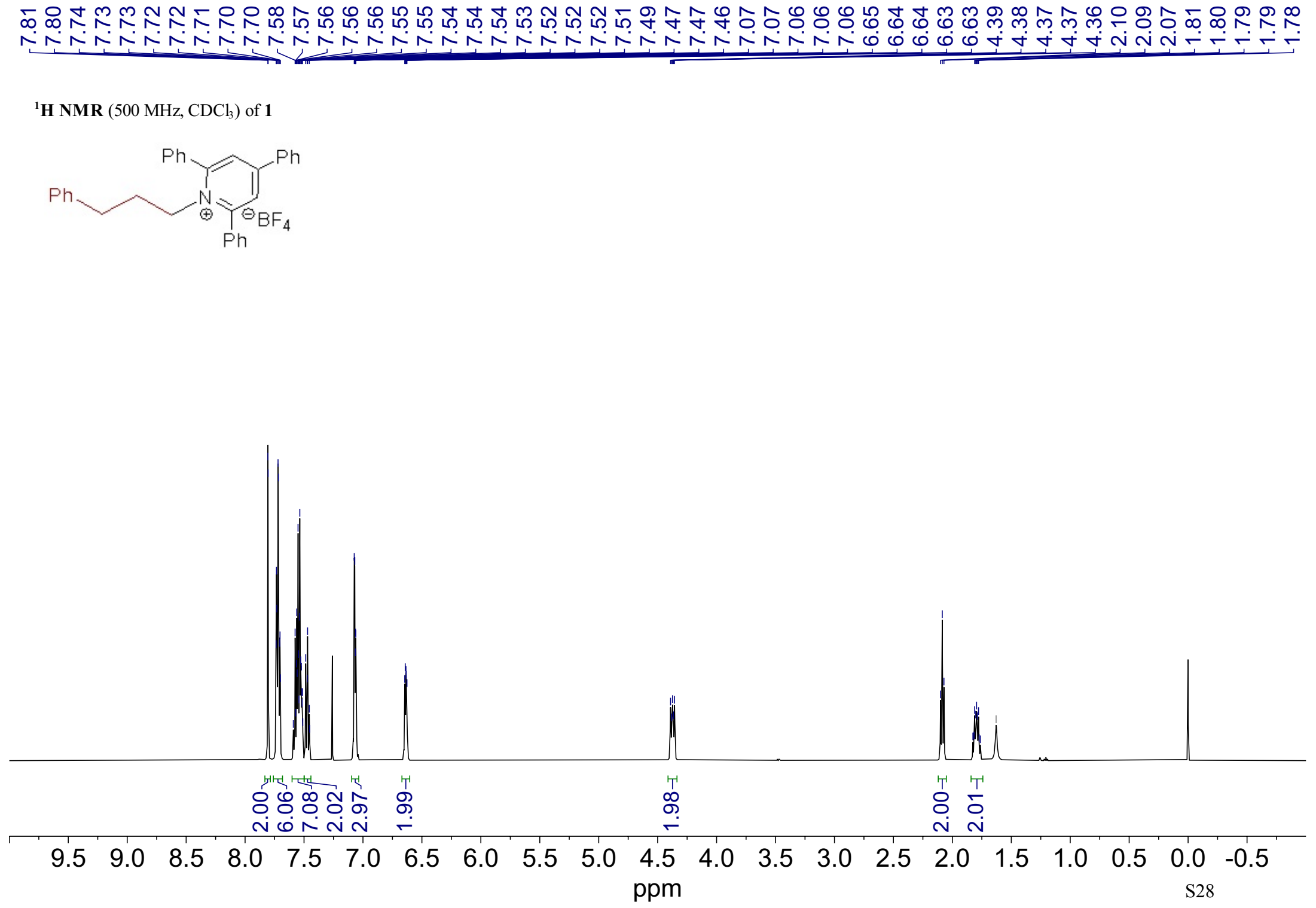
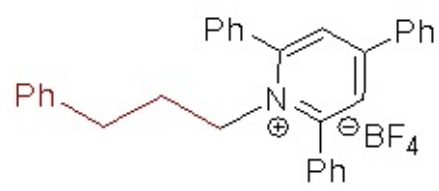
HRMS (ESI⁺) Calc: [M+H]⁺ (C₁₁H₁₃F₃NO) 232.0944; measured: 232.0941 = 1.3 ppm difference.

9. References

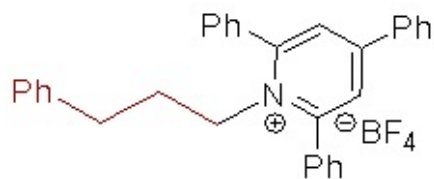
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10. NMR Spectra of Compounds

¹H NMR (500 MHz, CDCl₃) of **1**



^{13}C NMR (126 MHz, CDCl_3) of **1**

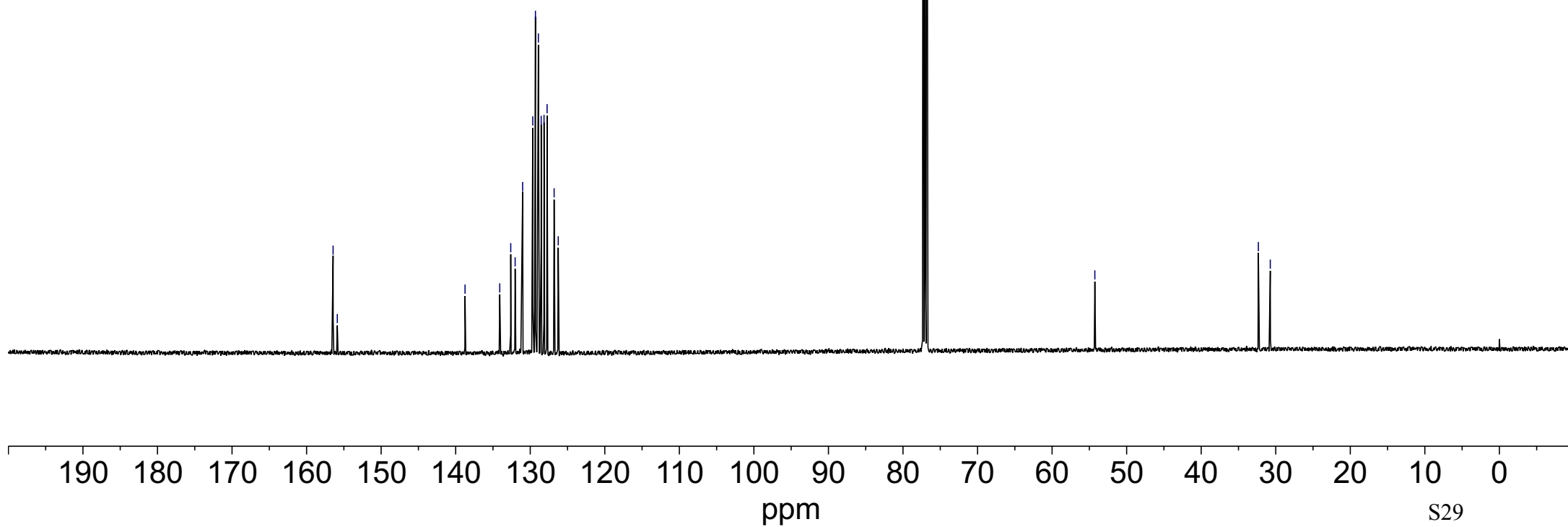


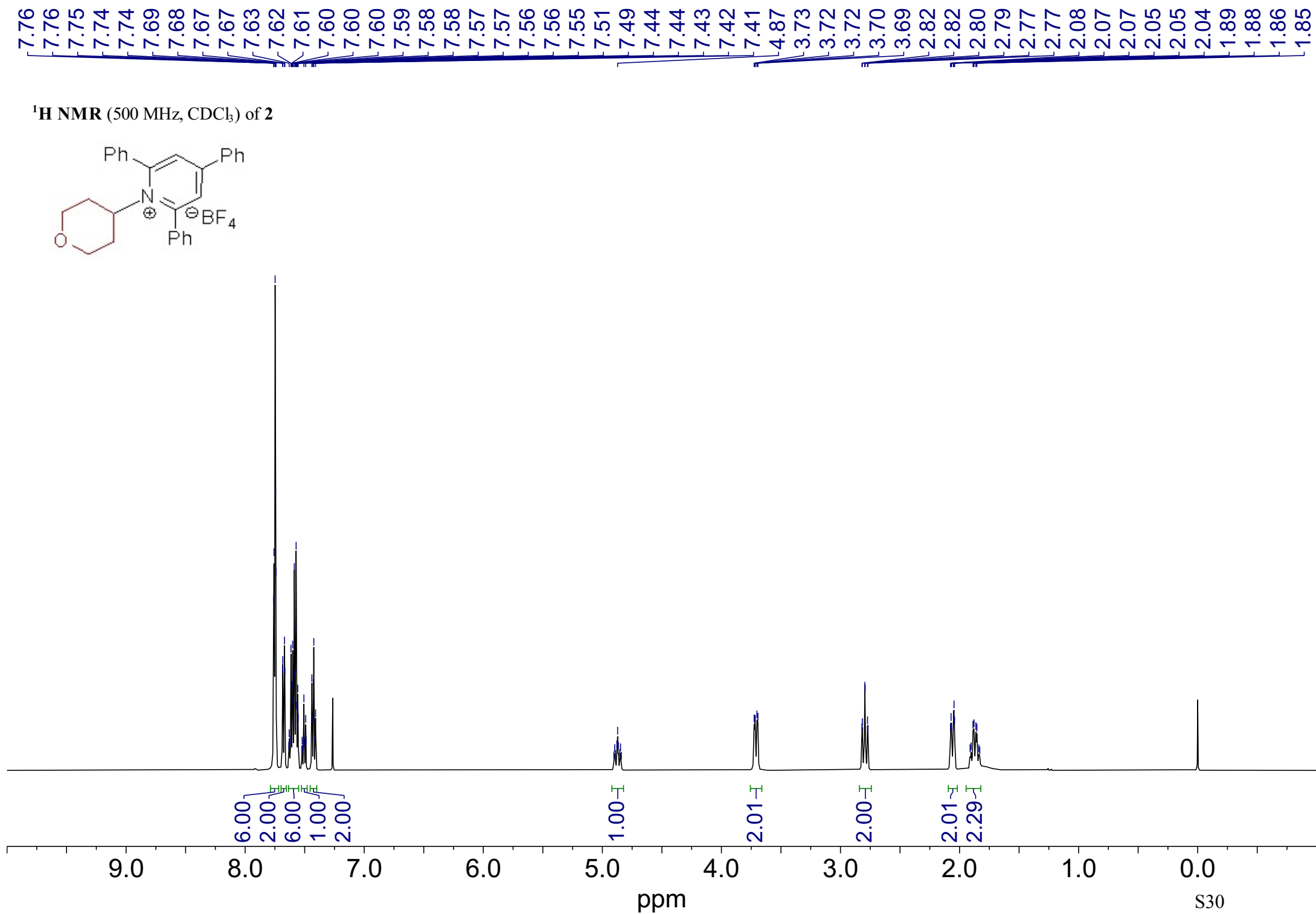
156.44
155.88
138.75
134.09
132.61
132.02
131.02
129.66
129.30
128.91
128.53
128.15
127.74
126.80
126.25

77.30 CDCl_3
77.05 CDCl_3
76.79 CDCl_3

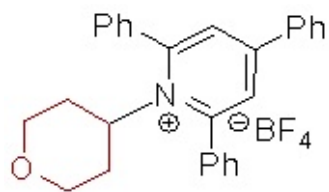
54.27

32.33
30.73





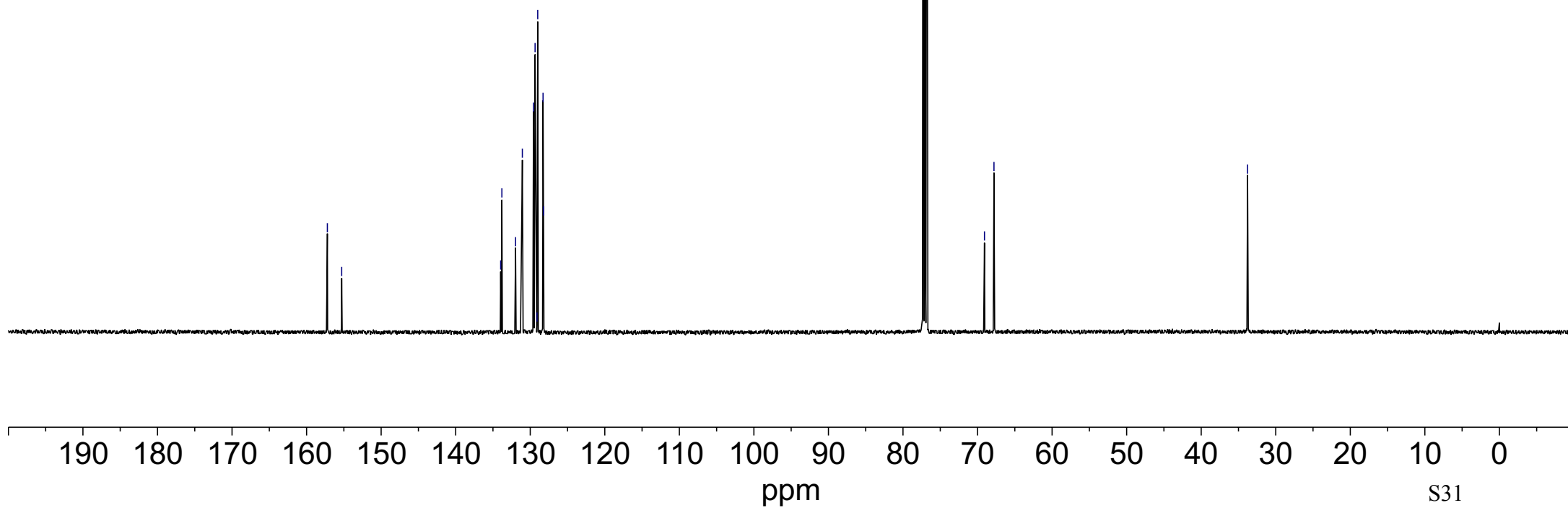
¹³C NMR (126 MHz, CDCl₃) of **2**



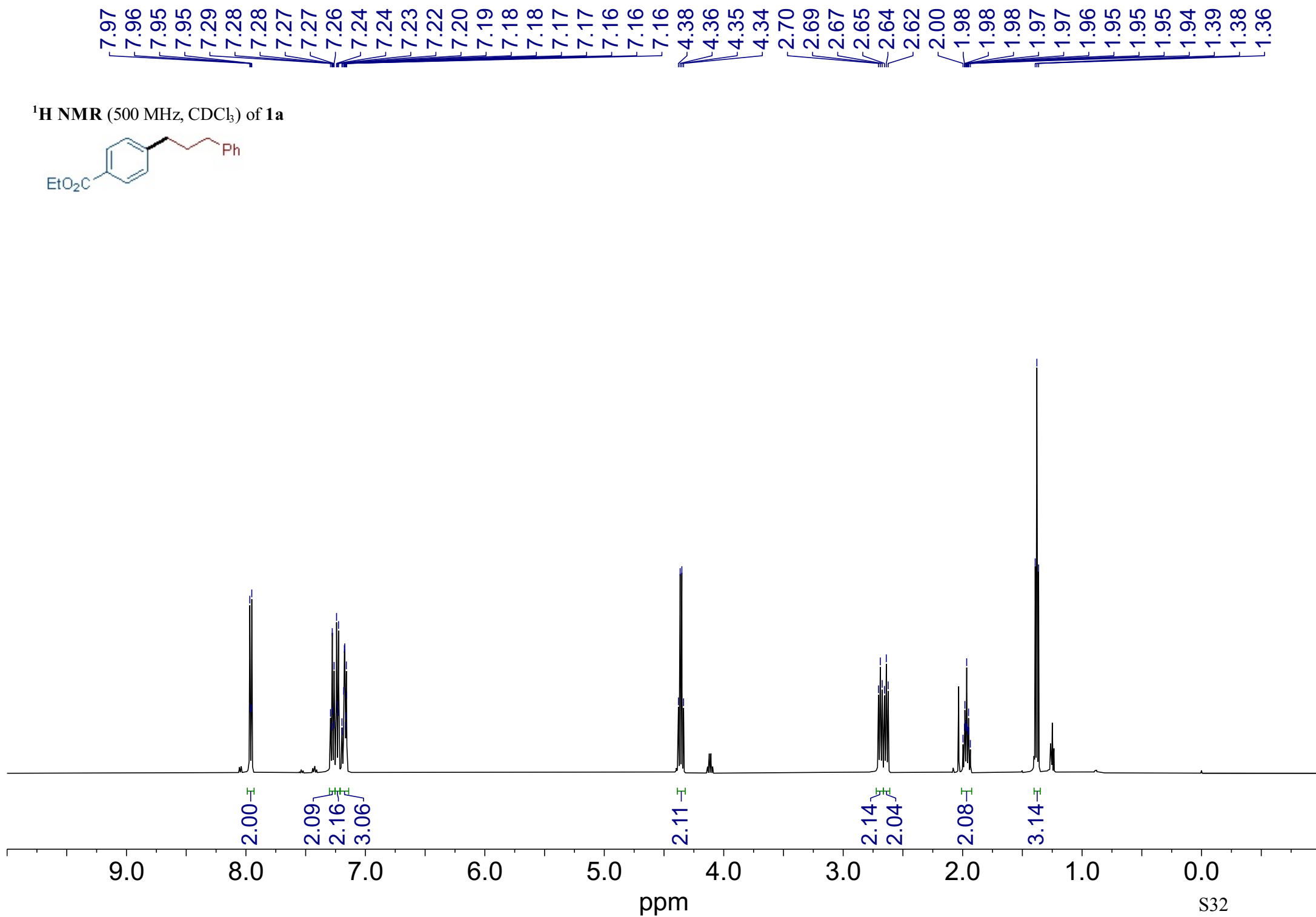
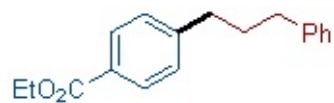
~157.21
~155.29
133.96
133.80
131.97
131.06
129.57
129.35
129.09
129.00
128.28
128.22

77.31 CDCl₃
77.05 CDCl₃
76.80 CDCl₃
~69.07
67.80

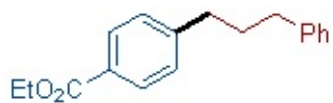
—33.78



¹H NMR (500 MHz, CDCl₃) of **1a**



^{13}C NMR (126 MHz, CDCl_3) of **1a**



—166.70

—147.72

—141.95

129.68

128.45

128.39

125.89

77.33 CDCl_3

77.07 CDCl_3

76.82 CDCl_3

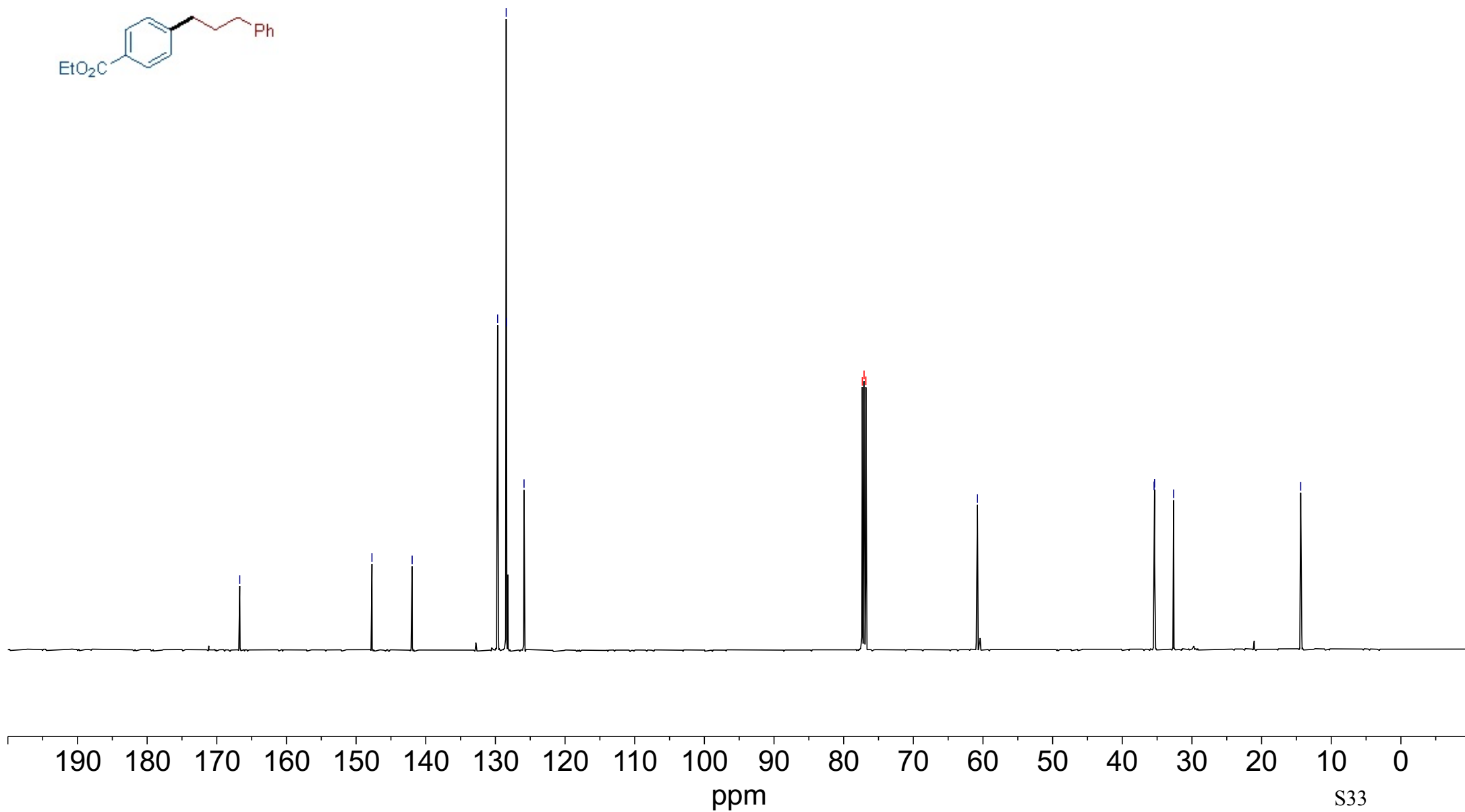
—60.79

35.44

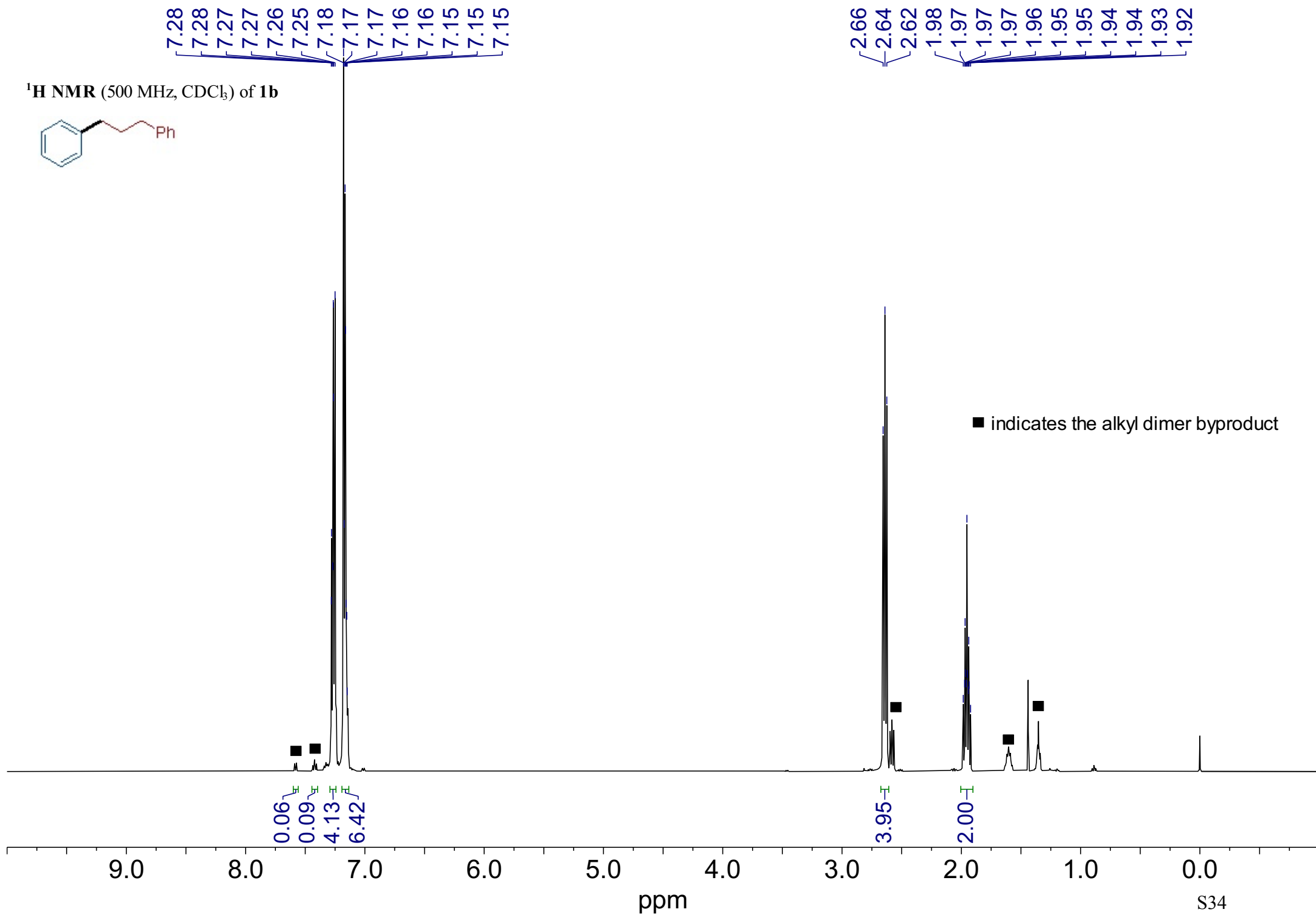
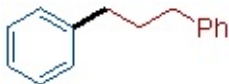
35.36

32.63

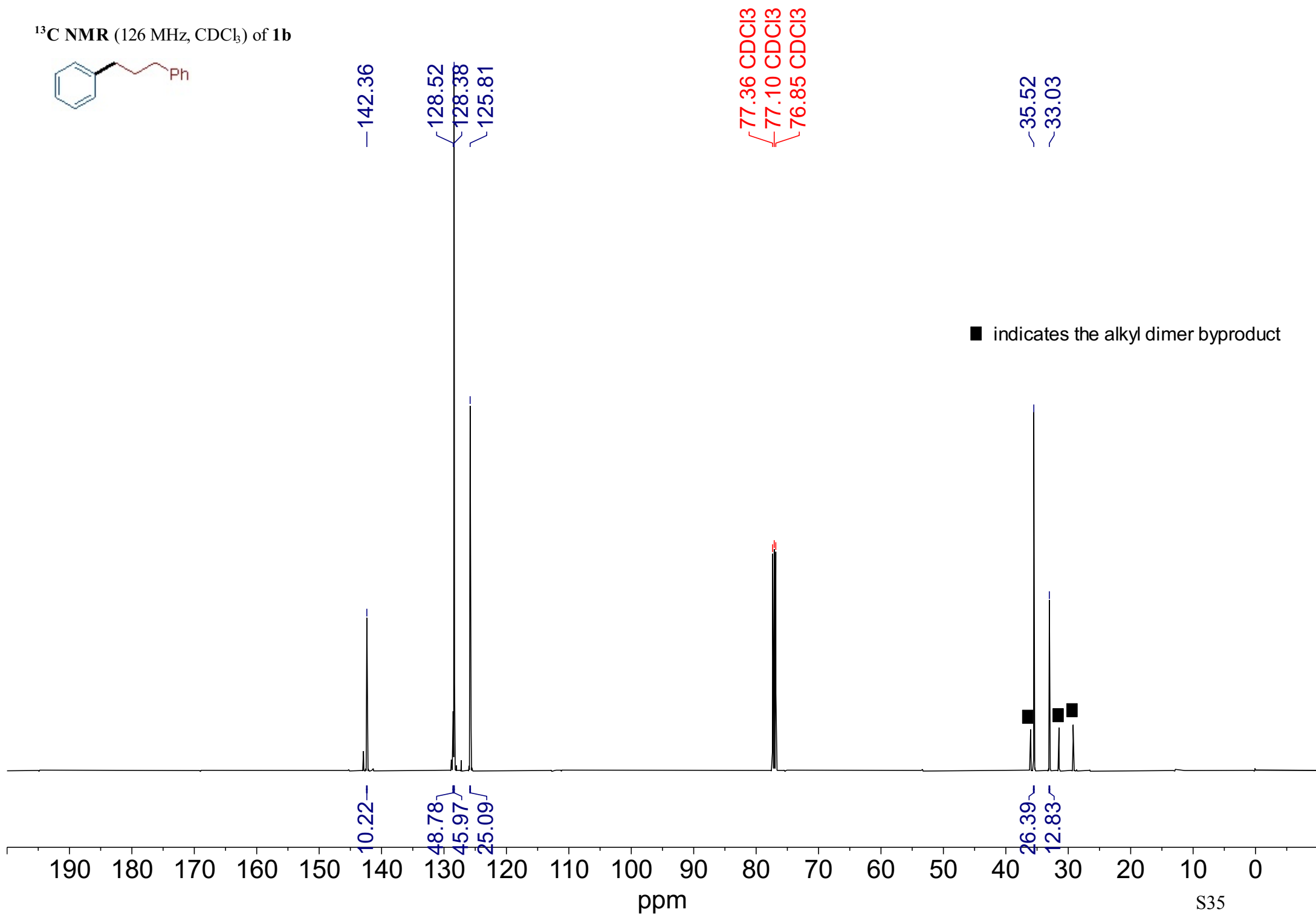
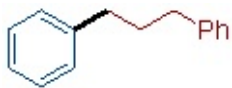
—14.39



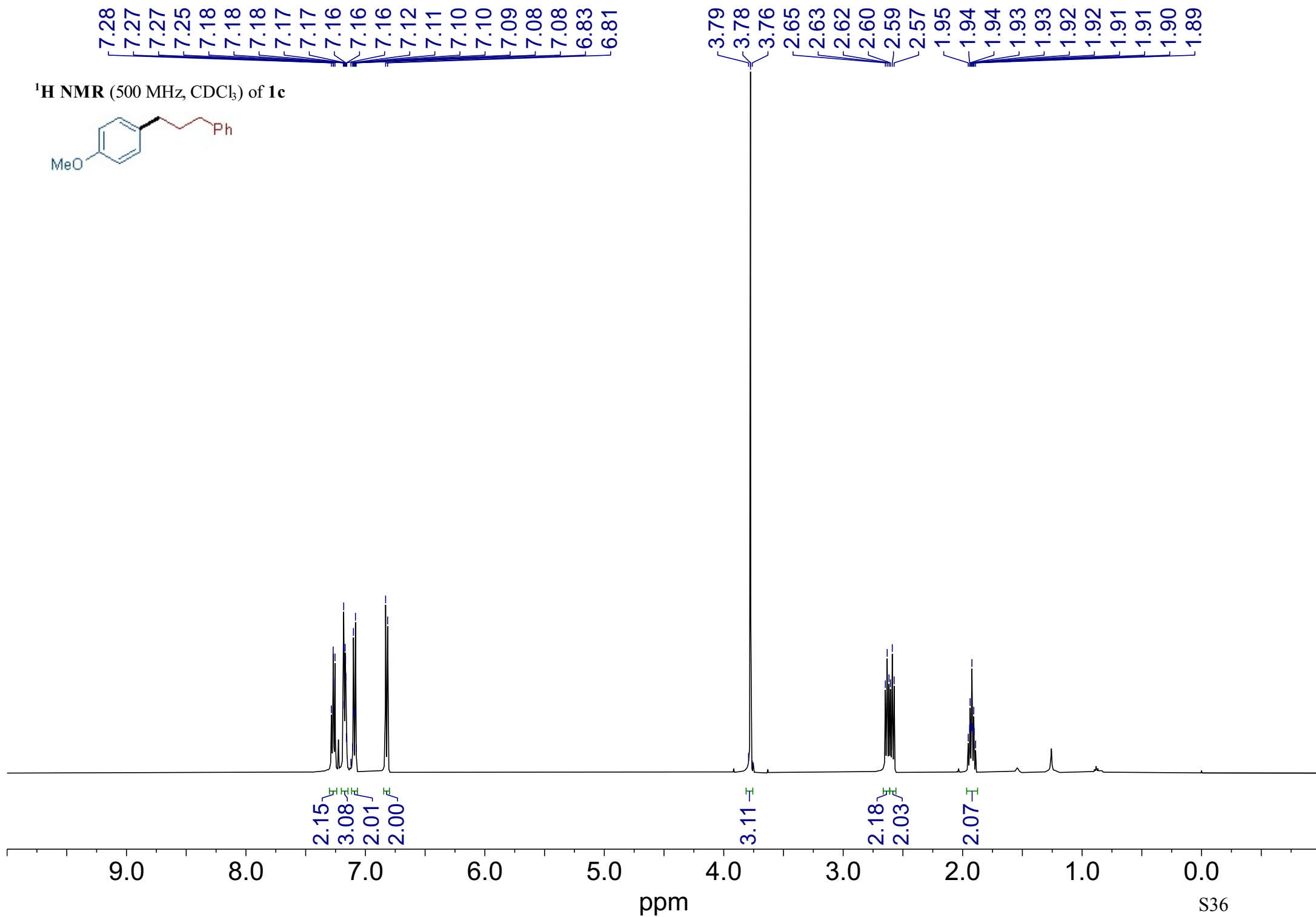
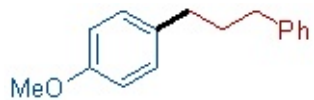
¹H NMR (500 MHz, CDCl₃) of **1b**



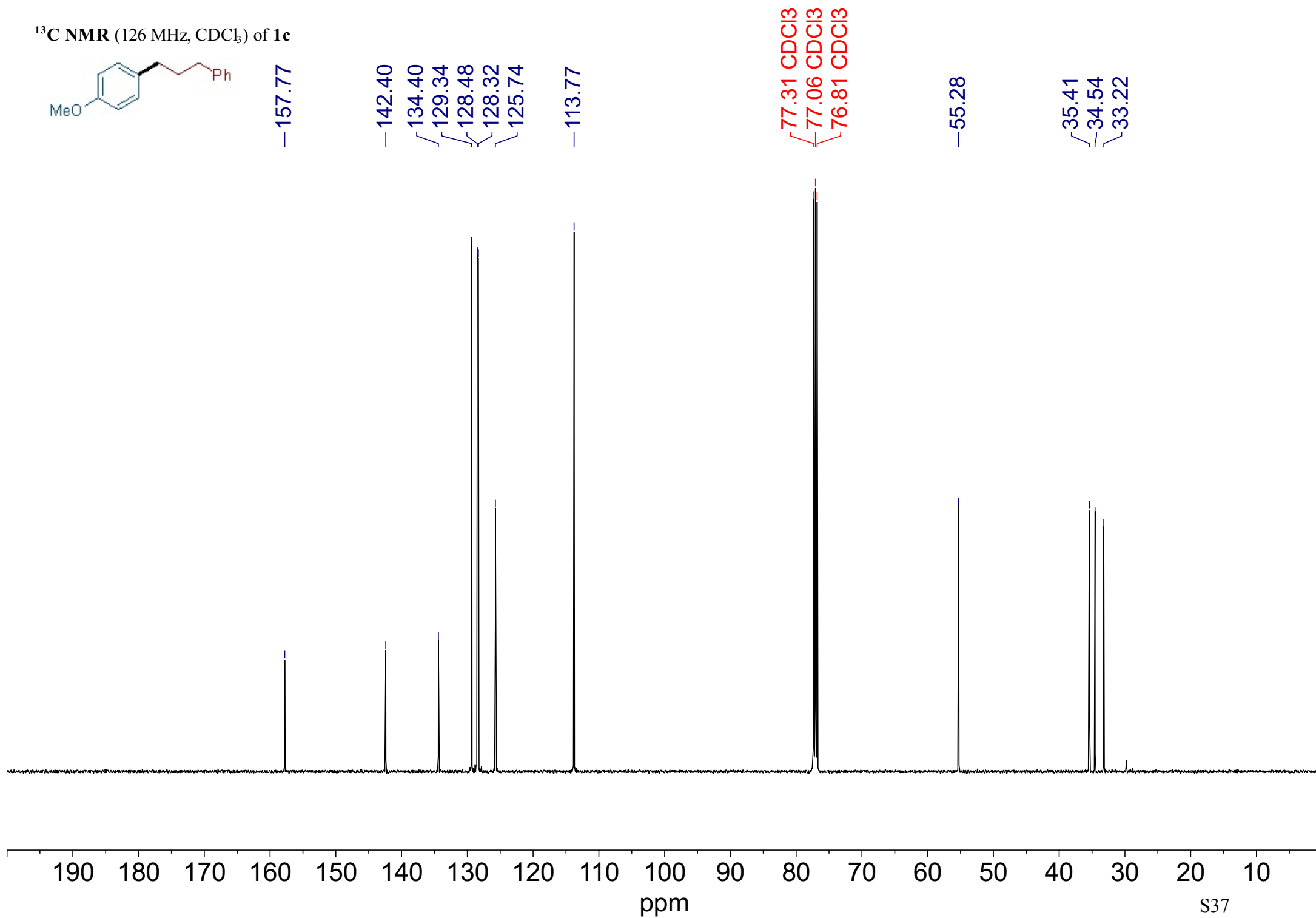
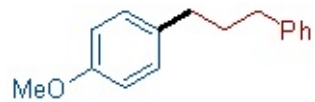
^{13}C NMR (126 MHz, CDCl_3) of **1b**



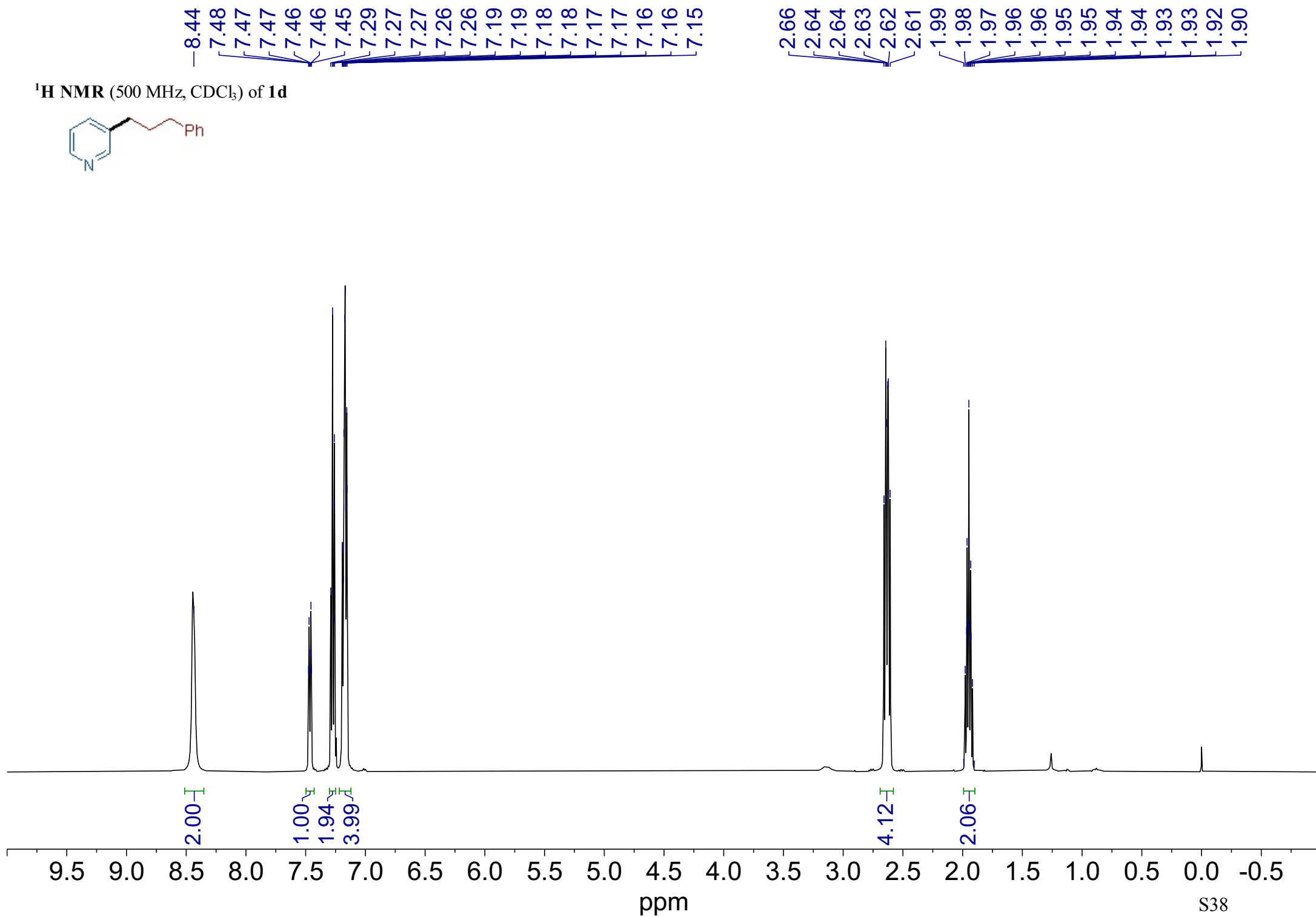
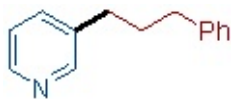
¹H NMR (500 MHz, CDCl₃) of **1c**



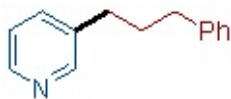
¹³C NMR (126 MHz, CDCl₃) of **1c**



¹H NMR (500 MHz, CDCl₃) of **1d**



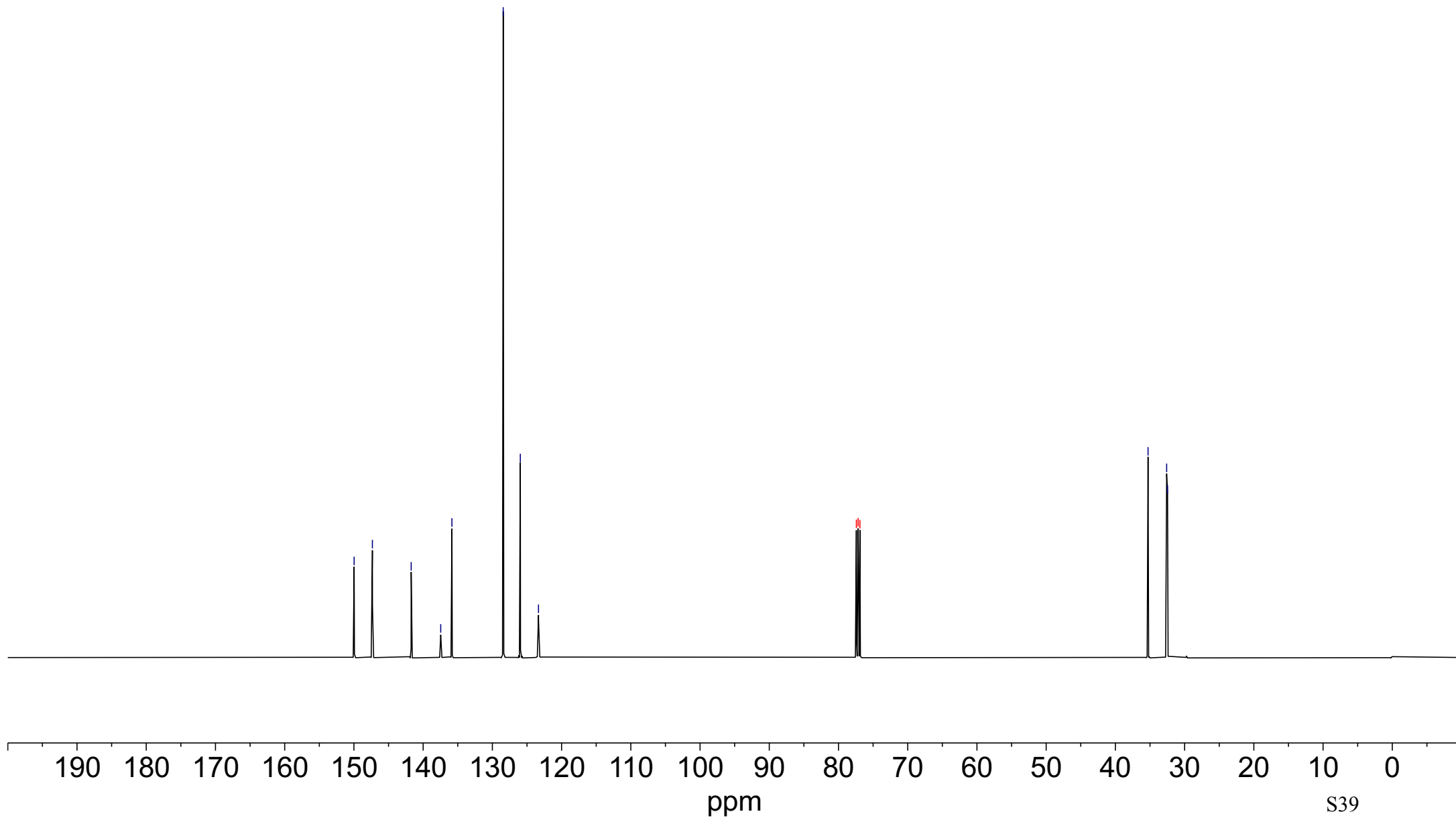
^{13}C NMR (126 MHz, CDCl_3) of **1d**



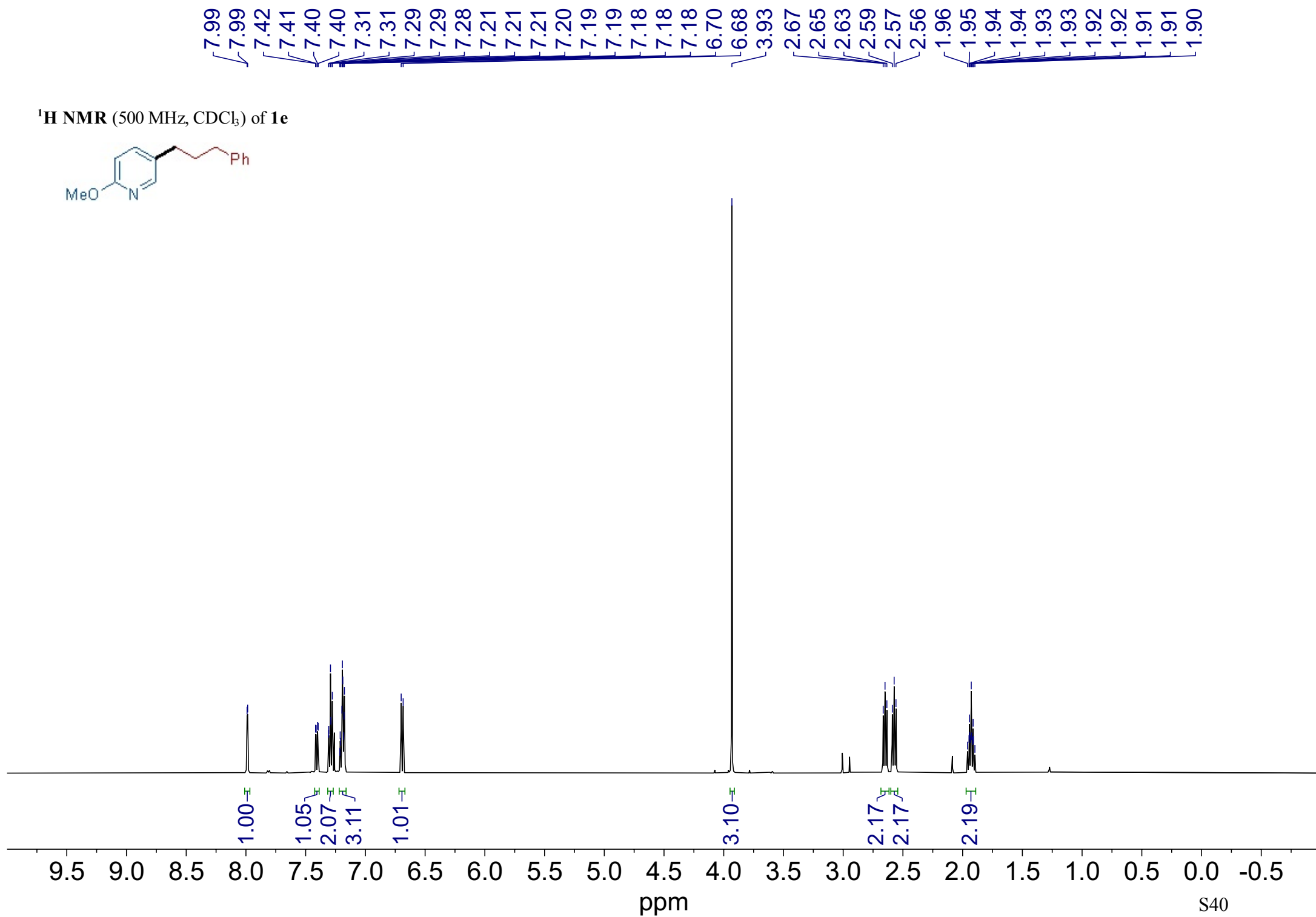
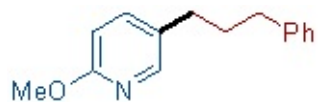
~149.97
~147.33
~141.73
~137.46
~135.84
~128.43
~125.96
~123.34

77.42 CDCl_3
77.16 CDCl_3
76.91 CDCl_3

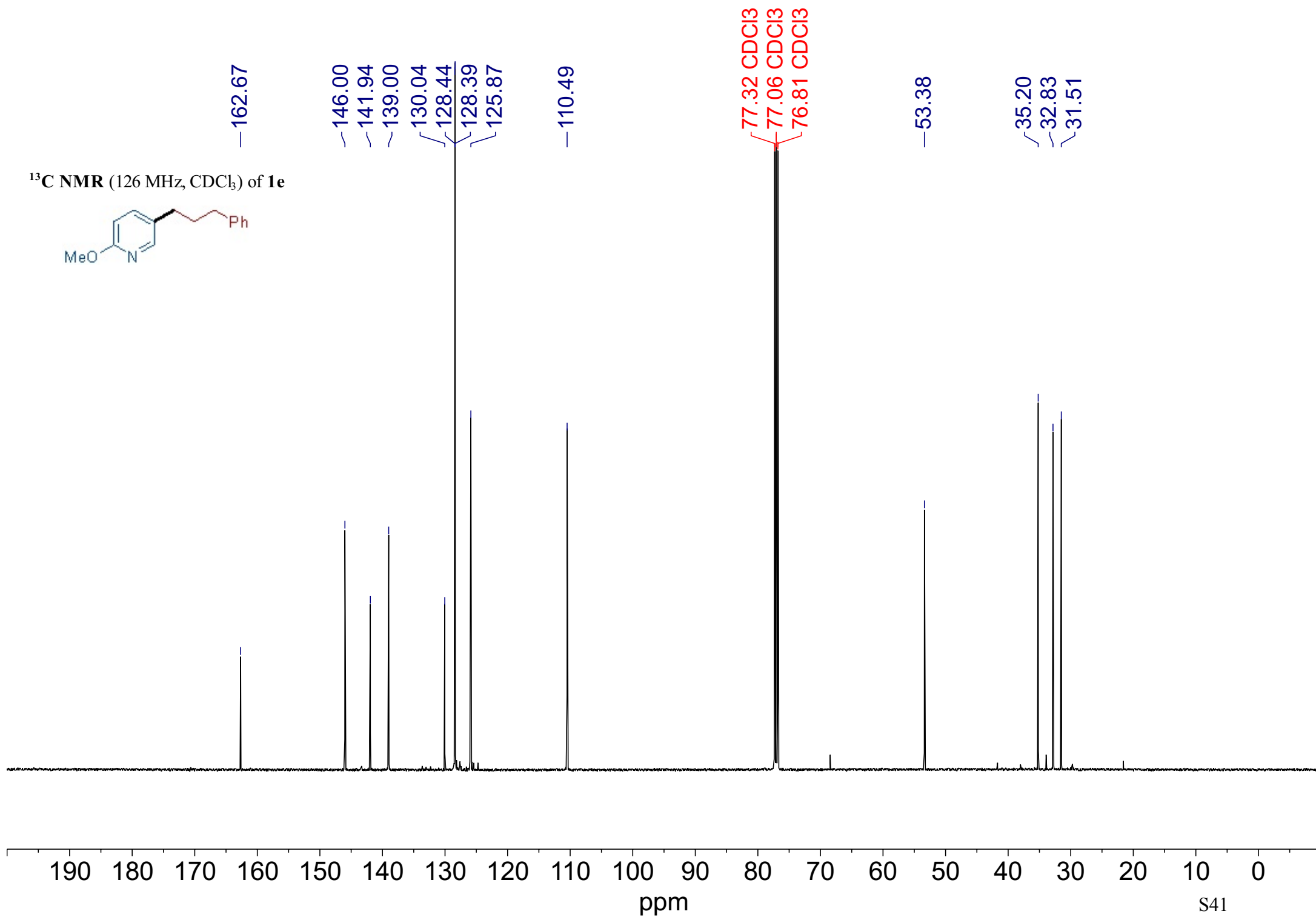
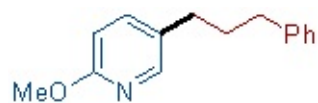
35.28
32.60
32.46



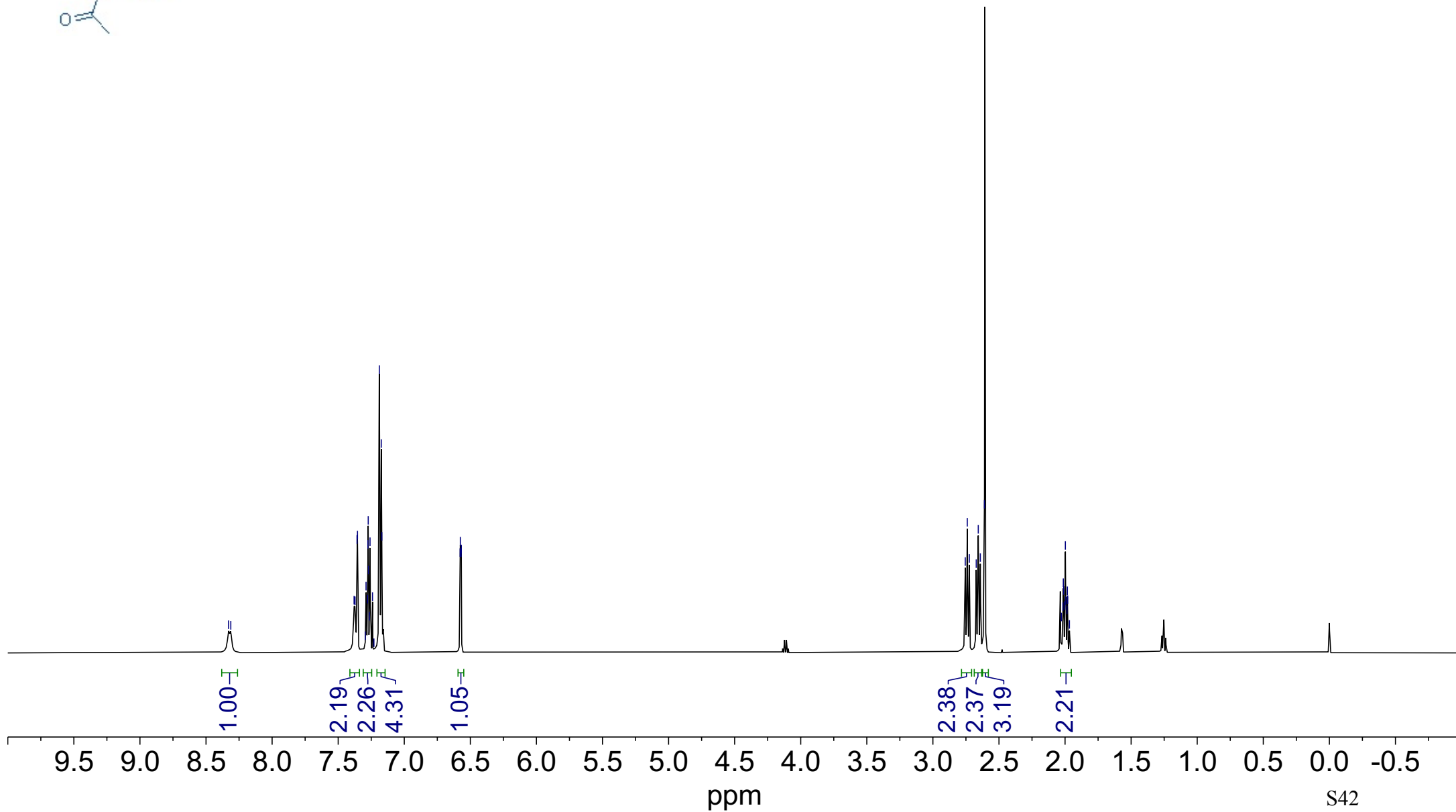
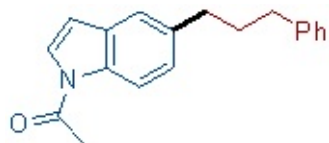
¹H NMR (500 MHz, CDCl₃) of **1e**



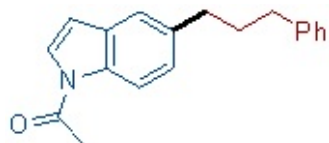
¹³C NMR (126 MHz, CDCl₃) of **1e**



¹H NMR (500 MHz, CDCl₃) of **1f**



¹³C NMR (126 MHz, CDCl₃) of **1f**



— 168.48

142.36

137.79

134.04

130.69

128.48

128.32

125.90

125.75

125.33

120.27

116.28

109.08

77.31 CDCl₃

77.05 CDCl₃

76.80 CDCl₃

35.43

35.37

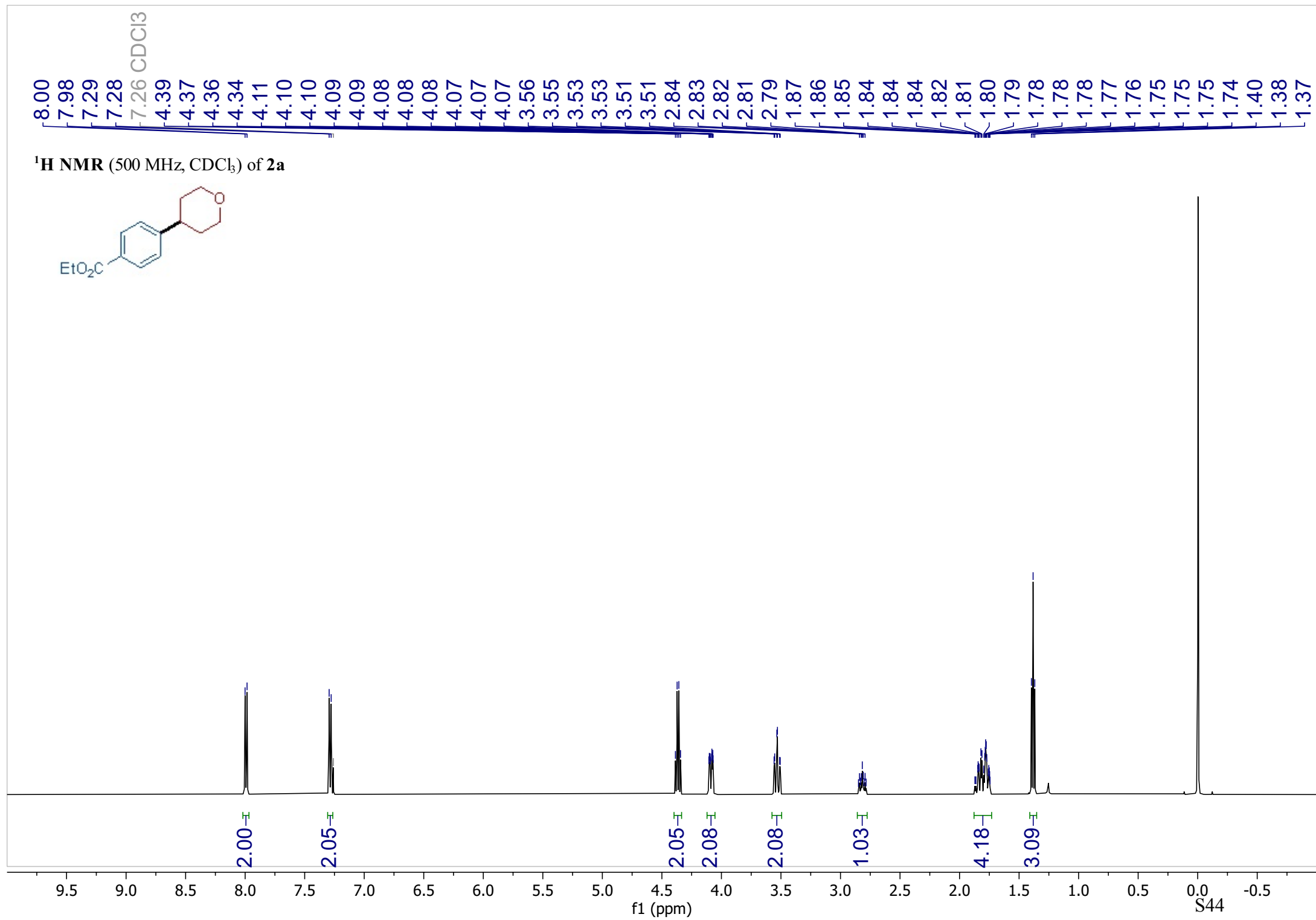
33.39

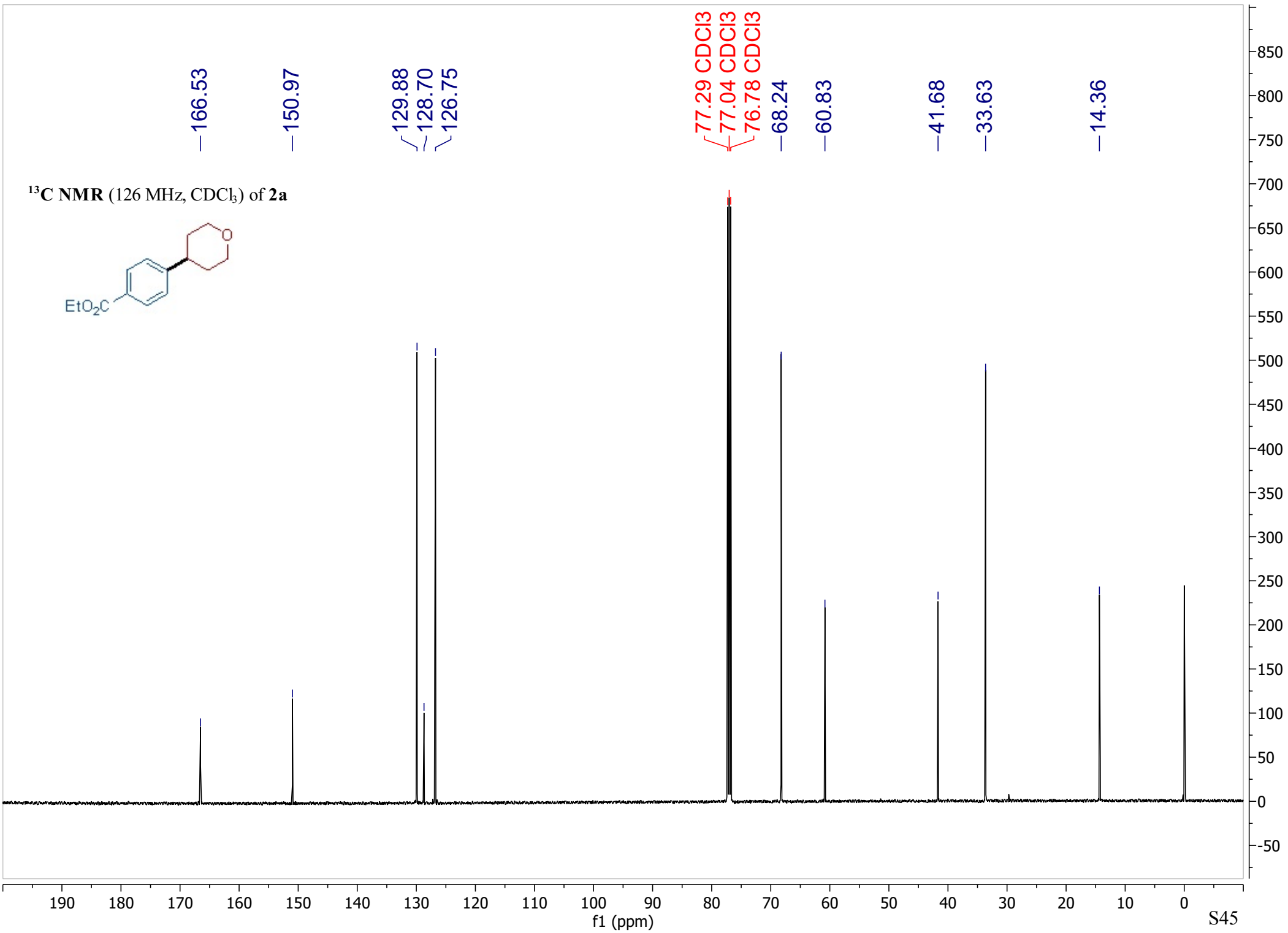
— 23.90

190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0

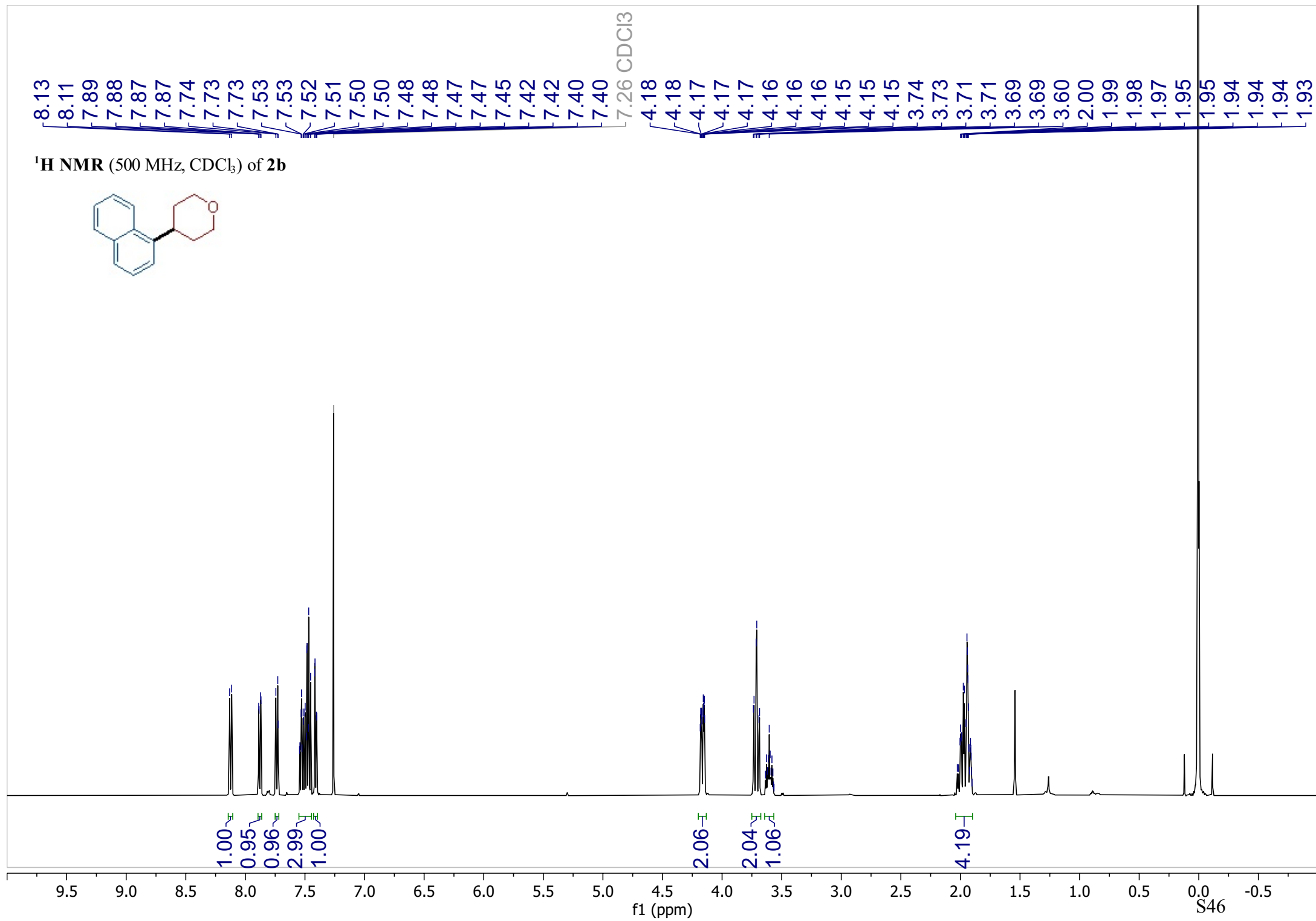
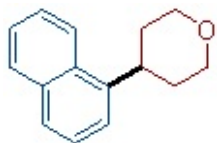
ppm

S43

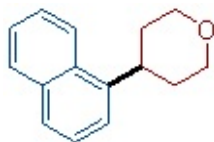




¹H NMR (500 MHz, CDCl₃) of **2b**



^{13}C NMR (126 MHz, CDCl_3) of **2b**



141.53
134.00
131.14
129.13
126.80
125.89
125.71
125.42
122.77
122.56

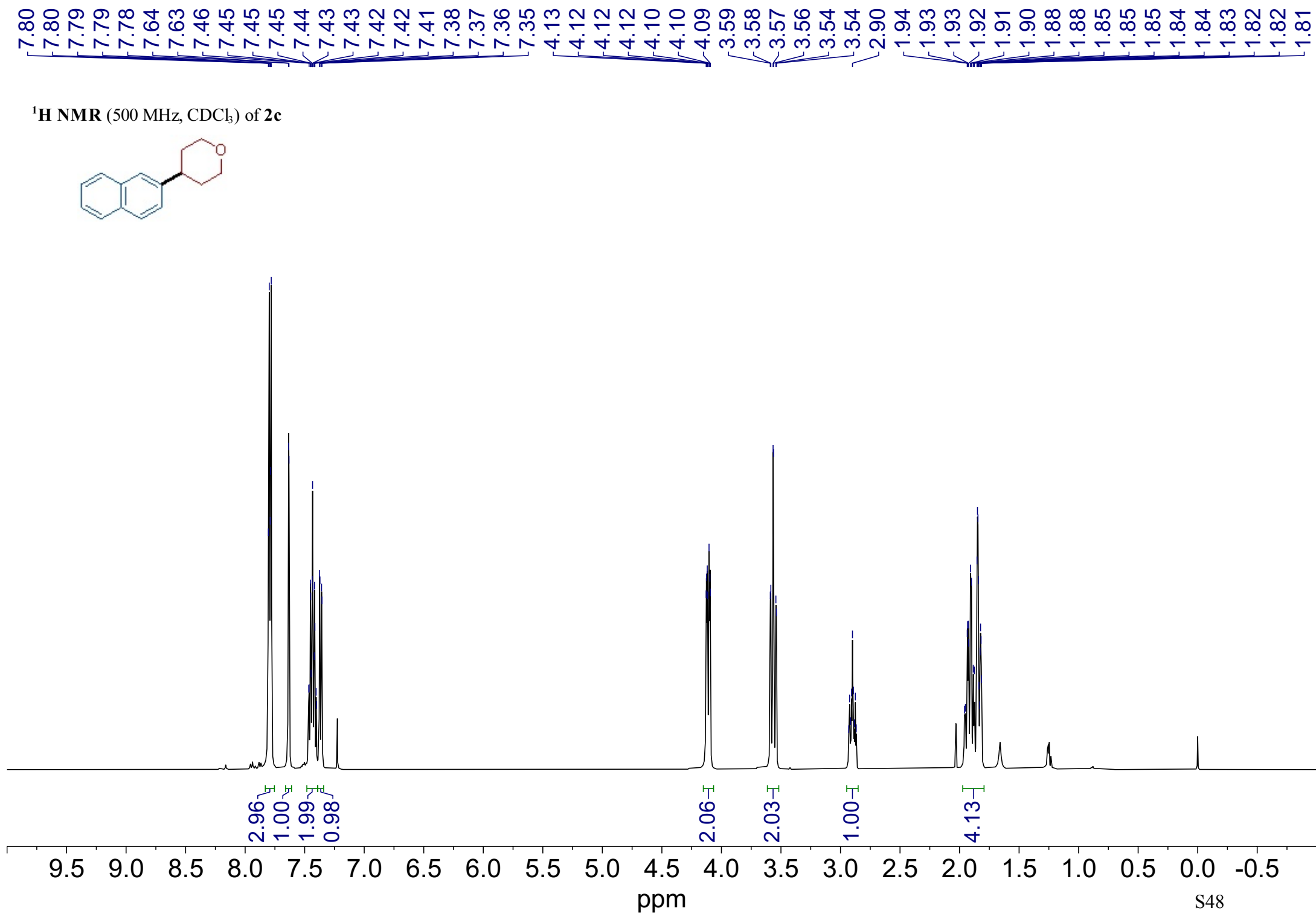
77.27 CDCl_3
77.02 CDCl_3
76.76 CDCl_3
-68.74

~36.70
~33.80

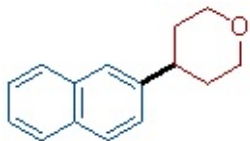
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0

f1 (ppm)

S47



^{13}C NMR (126 MHz, CDCl_3) of **2c**



143.33
133.67
132.33
128.12
127.67
127.63
126.04
125.73
125.41
124.75

77.34 CDCl_3
77.08 CDCl_3
76.83 CDCl_3

68.46

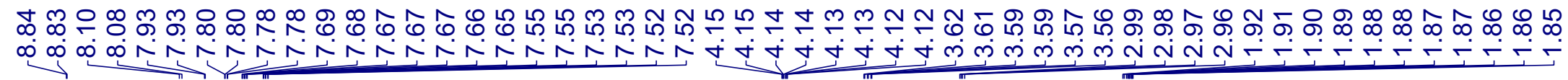
41.69

33.93

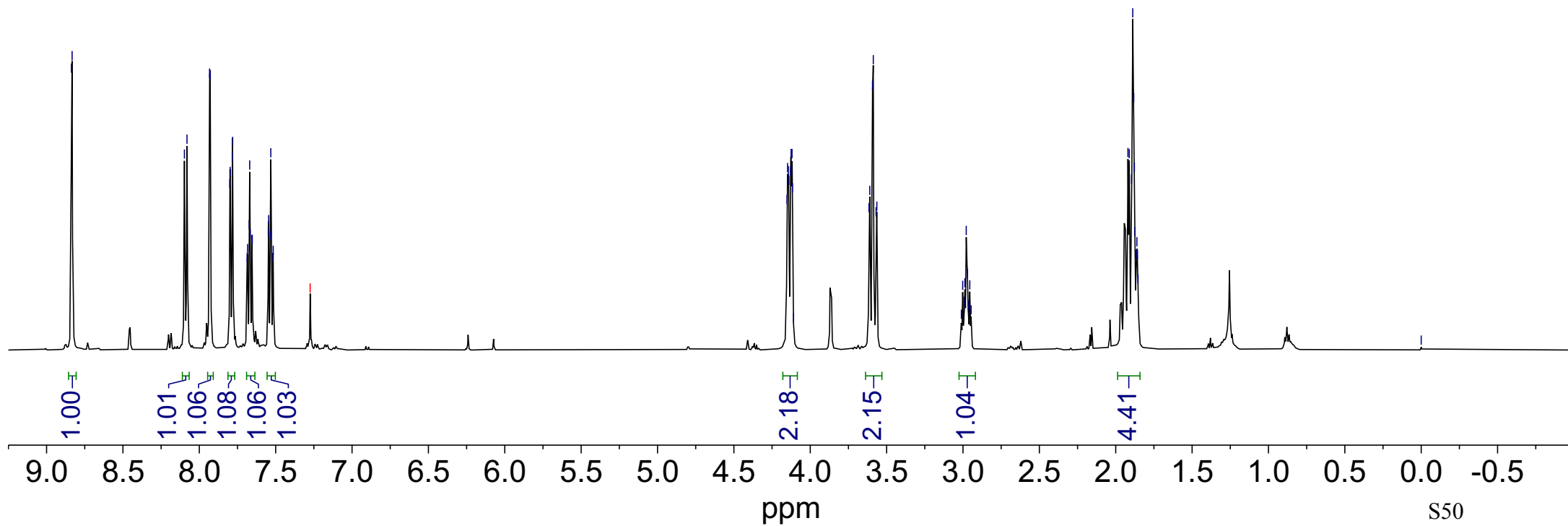
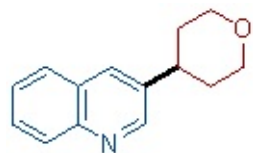
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0

ppm

S49



¹H NMR (500 MHz, CDCl₃) of **2d**

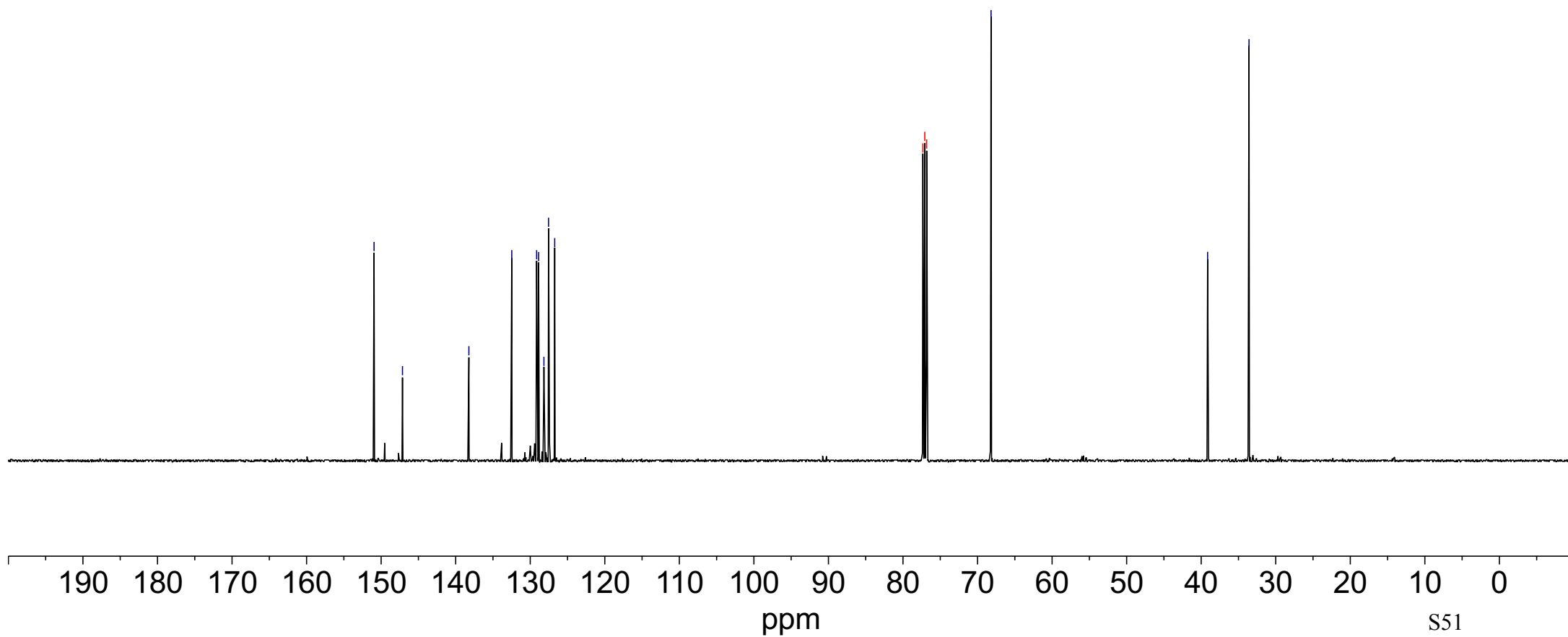


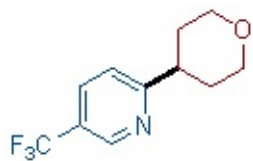

C1=CC=C2C(=C1)N=CC=C2C3=CC=CC=C3O3

—150.95
—147.14
138.23
132.48
129.14
128.87
128.16
127.54
126.72

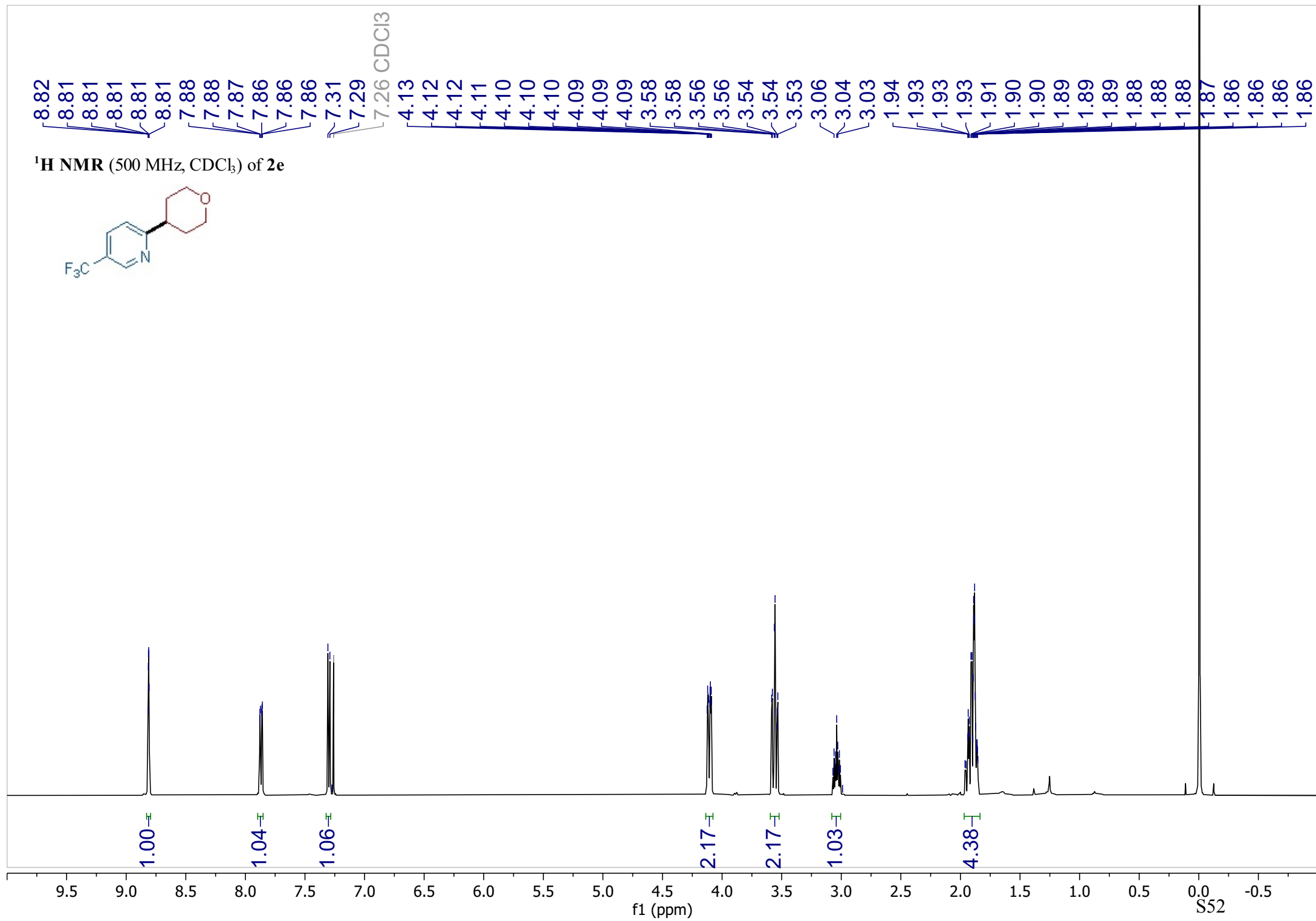
77.33 CDCI3
77.08 CDCI3
76.82 CDCI3
—68.19

—39.14
—33.59

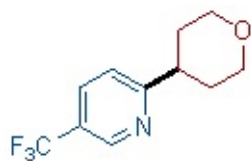




¹H NMR (500 MHz, CDCl₃) of **2e**



^{13}C NMR (126 MHz, CDCl_3) of **2e**



168.30
168.29

146.32
146.29
146.25
146.22
133.74
133.72
133.69
133.66
126.94
124.96
124.78
124.70
124.43
124.17
122.61
120.65
120.45

77.29 CDCl_3
77.03 CDCl_3
76.78 CDCl_3
67.93

43.50

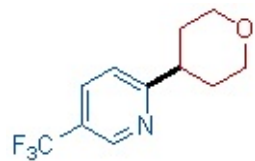
32.14

190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0

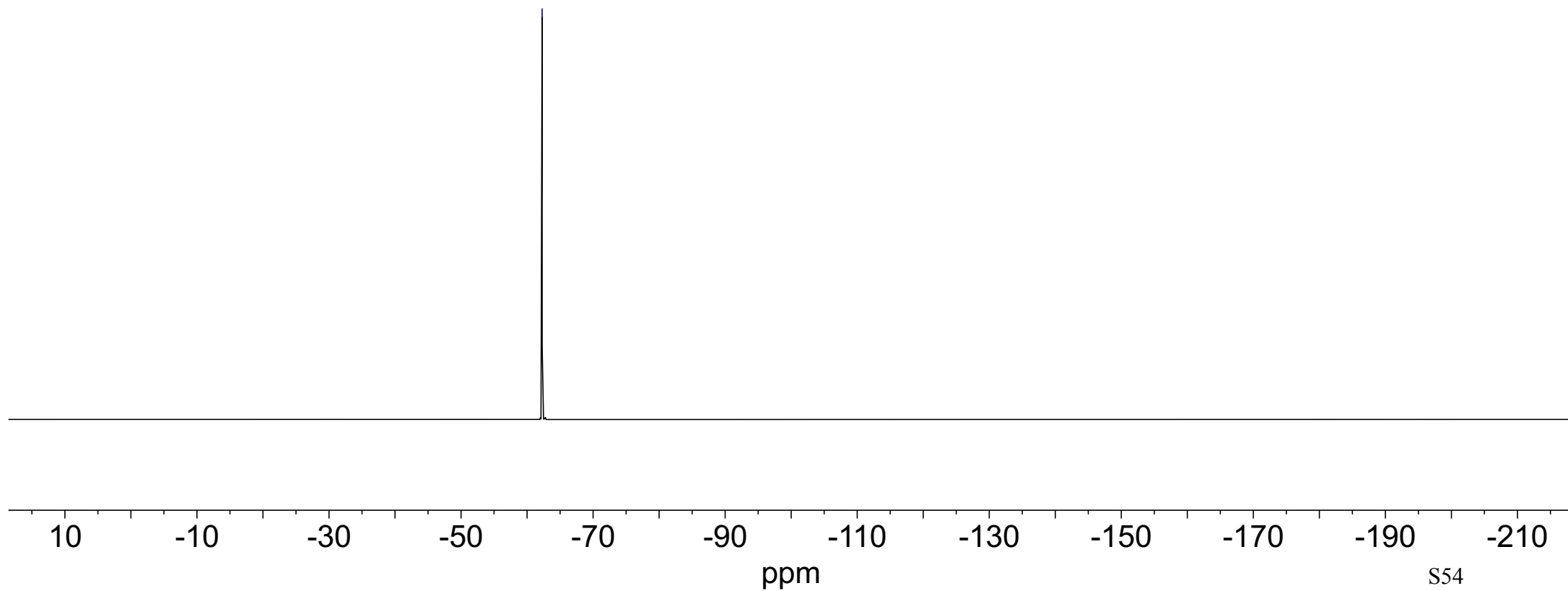
f1 (ppm)

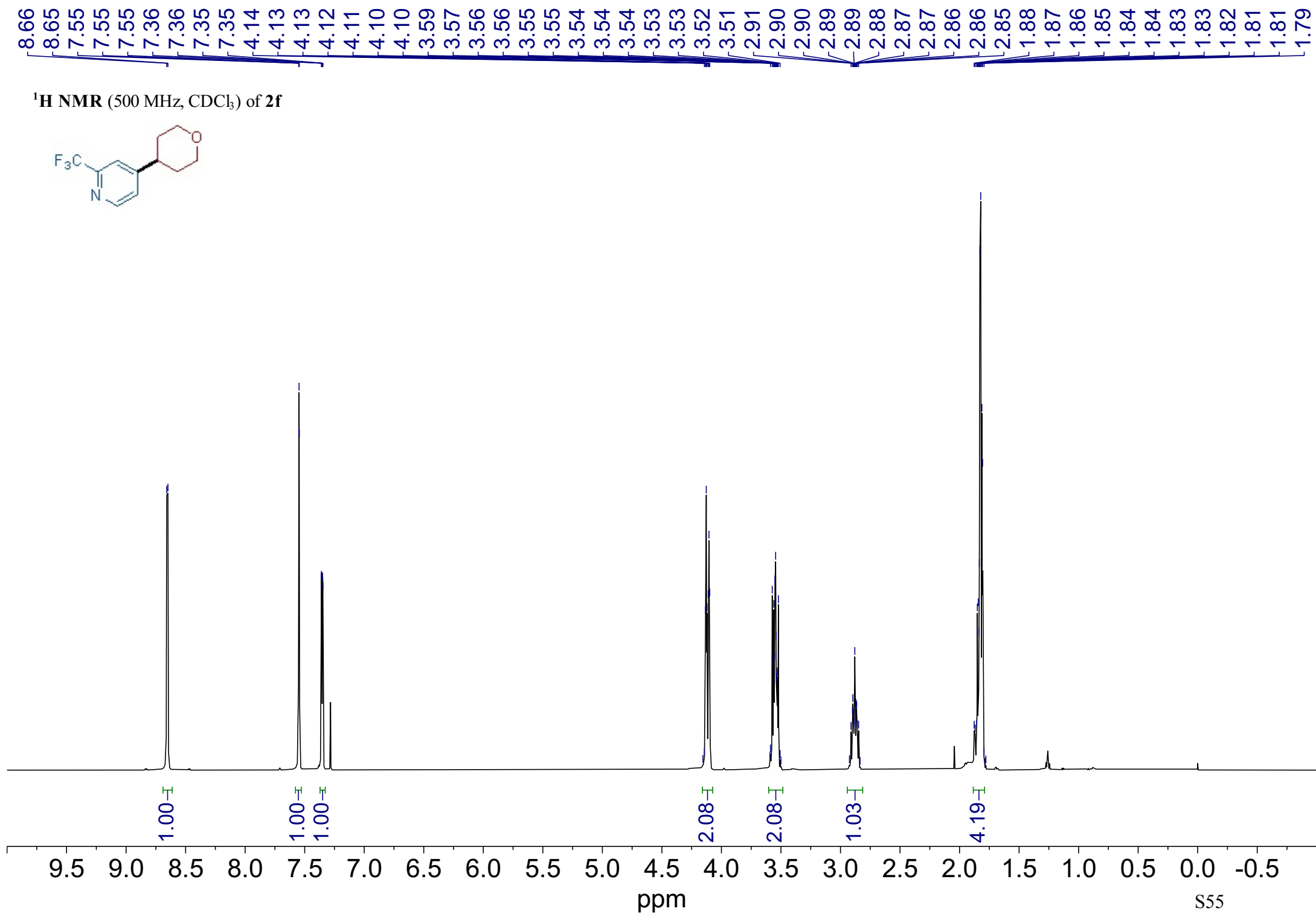
S53

¹⁹F NMR (377 MHz, CDCl₃) of **2e**

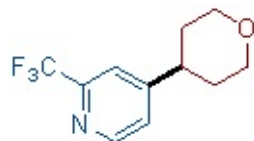


---62.28





¹³C NMR (126 MHz, CDCl₃) of **2f**

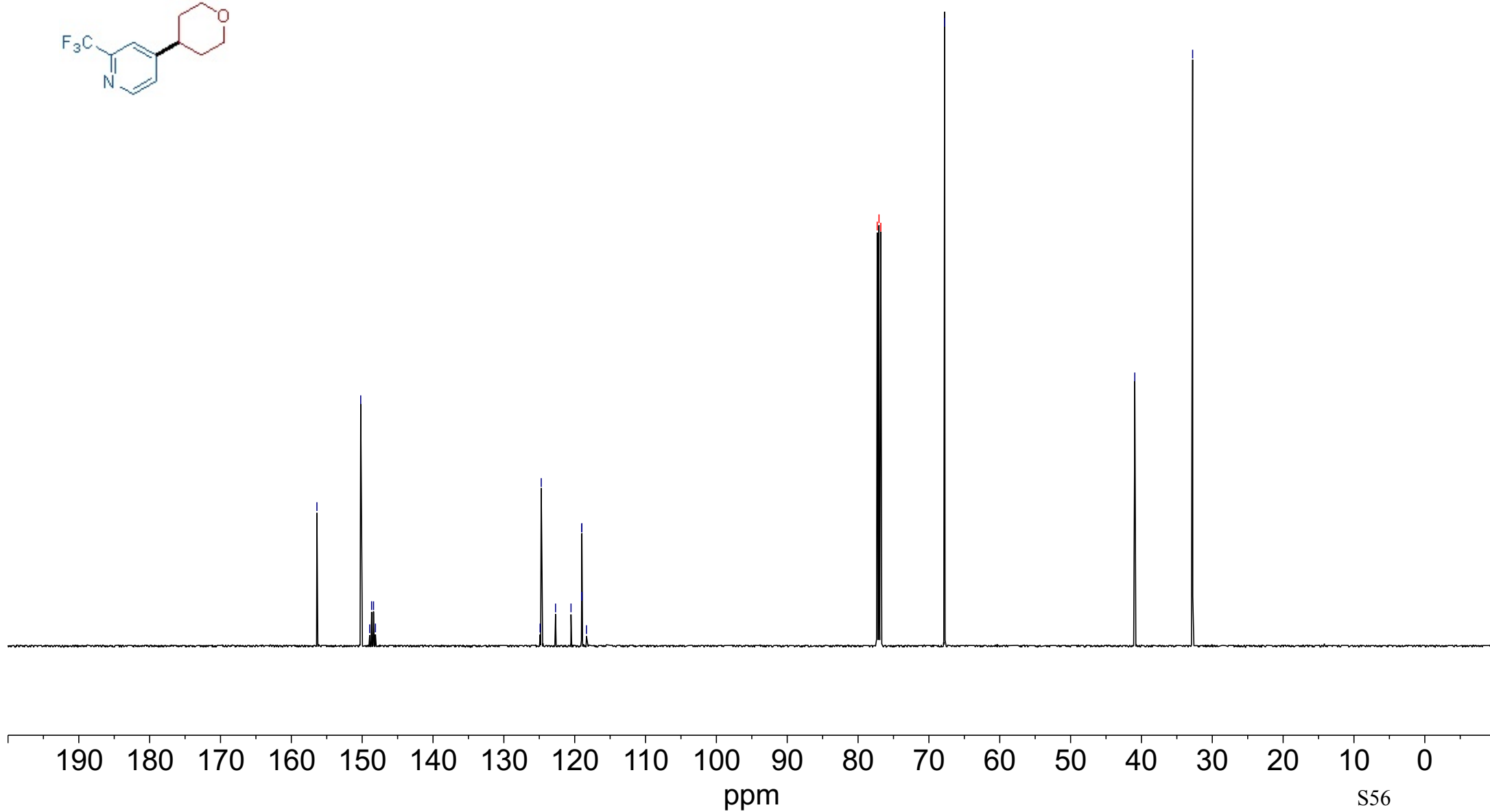


156.39
150.21
148.94
148.67
148.40
148.13
124.88
124.72
122.70
120.52
119.03
119.01
118.99
118.96
118.34

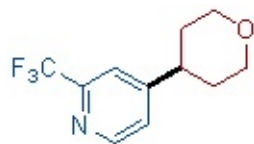
77.30 CDCl₃
77.05 CDCl₃
76.79 CDCl₃
67.78

40.94

32.77



¹⁹F NMR (377 MHz, CDCl₃) of **2f**



— -67.96

