Supporting Information for
Ligandless Nickel-Catalyzed Transfer Hydrogenation of Alkenes and Alkynes Using Water as the Hydrogen Donor

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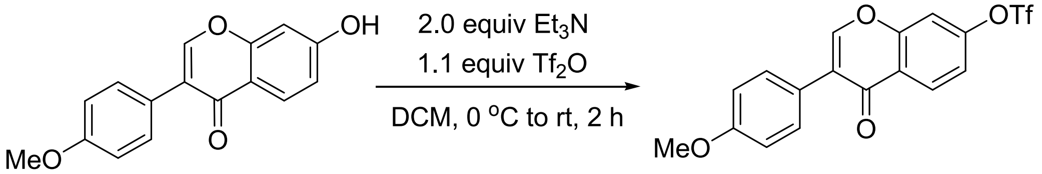
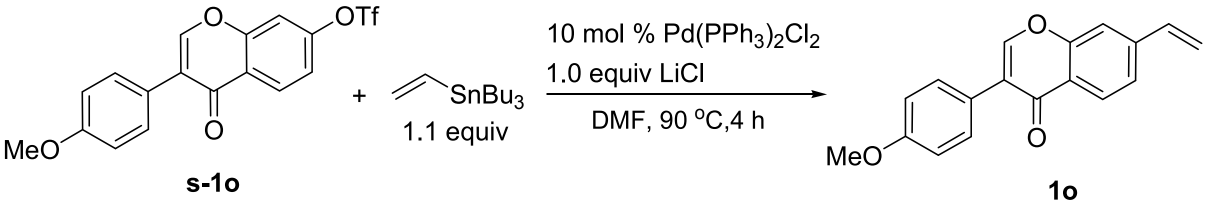
General Methods. Unless noted, all reactions were carried out using standard Schlenk technique under an argon atmosphere or a dry box technique under a nitrogen atmosphere. Tetrahydrofuran was distilled from sodium and benzophenone. 1,4-Dioxane was distilled from sodium. Acetonitrile was dried using Innovative Technology Solvent Purifier. Ni(COD)$_2$, NiI$_2$, Ni(acac)$_2$ and NiF$_2$ were purchased from Strem Chemicals Inc. NiCl$_2$(DME) was purchased from Sigma-Aldrich. NiCl$_2$·6H$_2$O and NiCl$_2$ were purchased from Alfa Aesar. Zinc powder (98%, -325 mesh) was purchased from Adamas. Zinc flake (99.8%, -325 mesh) and Mn powder (APS<10 micron, 99.6% metals basis) were purchased from Alfa Aesar. Al powder (200 mesh) and Mg turning (99.9+%) were purchased from Acros Organics. Before using, zinc powder and zinc flake were stirred with 1 M HCl aqueous solution, filtered and washed thoroughly with water, acetone and diethyl ether and dried under vacuum. The deionized water was deoxygenated by argon gas bubbling method prior to use. Unless noted, all commercial reagents were used without further purification. ^{1}H and ^{13}C NMR spectra were recorded at room temperature in CDCl$_3$ (containing 0.03% TMS) on Varian or Agilent XL-400 MHz spectrometer. ^{1}H NMR spectra was recorded with tetramethylsilane (δ = 0.00 ppm); ^{13}C NMR spectra was recorded with CDCl$_3$ (δ = 77.00 ppm) as internal reference. High-resolution mass spectra were obtained by using Waters Micromass GCT Premier mass spectrometer, Agilent Technologies 6224 TOF LC/MS or Thermo Fisher Scientific LTQ FT Ultra mass spectrometers. The IR spectra were measured on a ThermoFisher Nicolet FT-IR spectrometer. H$_2$ gas analysis was acquired on Agilent 6890Plus gas chromatograph equipped with a Thermal Conductivity Detector.

Alkenes were synthesized according to the published methods. The spectral data of known compounds were in agreement with the literature. For the synthesis of new alkenes **1o** and **5d**, see the following:

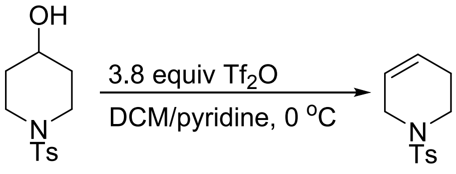


s-1o

To a solution of 7-hydroxy-3-(4-methoxyphenyl)-4*H*-chromen-4-one (2.68 g, 10 mmol) and Et_3N (2.02 g, 20 mmol) in DCM (50 mL) was added Tf_2O (3.10 g, 11 mmol) at 0 °C under Argon, then the mixture was warmed up to room temperature and stirred for another 2 h. The reaction was quenched with saturated NH_4Cl and extracted with DCM. The combined organic layers were dried over Na_2SO_4, filtered and concentrated in vacuum. The residue was purified by column chromatography on silica gel (eluent: dichloromethane/ petroleum ether = 2:1) to give 3-(4-methoxyphenyl)-4-oxo-4*H*-chromen-7-yl trifluoromethanesulfonate **(s-1o)** in 69% yield (2.76 g) as a white solid. M.p.: 125.0-126.3 °C. ^1H NMR (400 M, $CDCl_3$): δ 8.40 (d, J = 8.8 Hz, 1H), 8.01 (s, 1H), 7.49 (d, J = 8.8 Hz, 2H), 7.45 (d, J = 2.0 Hz, 1H), 7.33 (dd, J = 8.8, 2.4 Hz, 1H), 6.97 (d, J = 8.8 Hz, 2H), 3.84 (s, 3H). ^{13}C NMR (100 M, $CDCl_3$): δ 175.11, 159.86, 156.27, 152.80, 152.02, 130.00, 129.12, 125.62, 124.14, 123.08, 118.63 (q, $^1J_{C\text{-}F}$ = 321.3 Hz), 118.47, 114.04, 111.39, 55.26. IR (neat): 3097, 3076, 3058, 2954, 2907, 2836, 1644, 1612, 1568, 1516, 1424, 1400, 1292, 1250, 1212, 1182, 1168, 1132, 1095, 1029, 952, 883, 864, 824, 801, 788, 782, 689, 659 cm^{-1}. HRMS (ESI) calcd for $C_{17}H_{12}F_3O_6S$ $[M+H]^+$: 401.0301, found 401.0298.



To a solution of **s-1o** (1.20 g, 3 mmol), $Pd(PPh_3)_2Cl_2$ (210.6 mg, 0.3 mmol) and LiCl (127.2 mg, 3 mol) in DMF (18 mL) was added tributyl(vinyl)stannane (1.05 g, 3.3 mmol) dropwise under Argon. The mixture was heated at 90 °C for 4 h. After completion the reaction mixture was cooled down to room temperature and diluted with Et_2O and washed with 1 M HCl (aq.), then washed with saturated $NaHCO_3$(aq.) and brine. The combined aqueous layers were extracted once with Et_2O. The combined organic layers were dried over Na_2SO_4, filtered and concentrated in vacuum. The residue was purified by column chromatography on silica gel (eluent: petroleum ether/dichloromethane/ethyl acetate = 6:1:1) to give 3-(4-methoxyphenyl)-7-vinyl-4*H*-chromen-4-one **(1o)** in 76% yield (637.7 mg) as a white solid. M.p.: 154.0-155.1 °C**.** ^1H NMR (400 M, $CDCl_3$): δ 8.24 (d, J = 8.4 Hz, 1H), 7.96 (s, 1H), 7.52-7.46 (m, 3H), 7.41 (s, 1H), 6.98-6.96 (m, 2H), 6.79 (dd, *J* = 17.6, 11.2 Hz, 1H), 5.94 (d, *J* = 17.6, Hz, 1H), 5.48 (d, *J* = 11.2 Hz, 1H), 3.83 (s, 3H). ^{13}C NMR (100 M, CDCl$_3$): δ 176.06, 159.55, 156.44, 152.49, 142.89, 135.32, 130.02, 126.49, 124.97, 124.03, 123.62, 122.83, 117.81, 115.37, 113.91, 55.26. IR (neat): 3092, 3076, 3040, 3011, 2972, 2930, 2838, 1624, 1609, 1557, 1513, 1439, 1407, 1358, 1291, 1253, 1233, 1176, 1106, 1024, 985, 927, 901, 886, 878, 830, 821, 802, 791, 767, 717 cm^{-1}. HRMS (ESI) calcd for $C_{18}H_{15}O_3$ [M+H]$^+$: 279.1016, found 279.1007.



5d

To a solution of 1-tosylpiperidin-4-ol (1.79 g, 7 mmol) in DCM (50 mL) was added pyridine (12.5 mL). Then the mixture was cooled to 0 °C and Tf$_2$O (4.48 mL, 26.6 mmol) was slowly added. Then the mixture was stirred for 3 h at 0 °C. The reaction mixture was quenched by H$_2$O and extracted with DCM. The combined organic layers were dried over anhydrous Na$_2$SO$_4$. The mixture was filtered and the solvent was evaporated under the reduced pressure. The residue was purified by column chromatography on silica gel (eluent: petroleum ether/DCM = 1/1 to DCM) to afford 1-tosyl-1,2,3,6-tetrahydropyridine **(5d)** in 46% yield (762.3 mg) as a white solid. ^{1}H NMR (400 MHz, CDCl$_3$): δ 7.68 (d, *J* = 8.4 Hz, 2H), 7.32 (d, *J* = 8.0 Hz, 2H), 5.76-5.73 (m, 1H), 5.63-5.60 (m, 1H), 3.59-3.56 (m, 2H), 3.17 (t, *J* = 5.6 Hz, 2H), 2.43 (s, 3H), 2.24-2.18 (m, 2H). ^{13}C NMR (100 MHz, CDCl$_3$): δ 143.44, 133.18, 129.55, 127.59, 124.97, 122.65, 44.70, 42.56, 25.17, 21.43. The spectroscopic data are in agreement with that previously reported.[1]

Optimization studies for transfer hydrogenation of aryl alkenes.

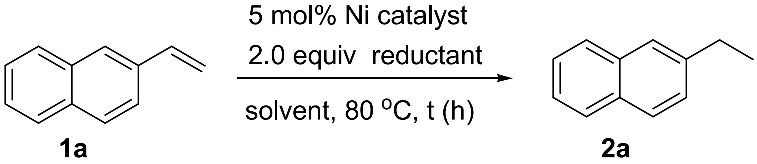
General procedure for optimization studies.

The reaction was conducted in an oven-dried screw-cap vial (4 mL) equipped with a magnetic stir bar. In a nitrogen-filled glove box, NiCl$_2$·6H$_2$O (3.6 mg, 0.015 mmol) [or other Ni(II) salts], Zinc powder (39.2 mg, 0.6 mmol) [or other reductants], 2-vinylnaphthalene (46.3

mg, 0.3 mmol), dioxane or other solvents (1.5 mL) were added sequentially to a screw-cap vial. The vial cap was then securely fitted and taken outside the glove box. Then H_2O (0.3 mL or x mL) was added to the vial. After the reaction mixture was stirred at 80 ^{o}C, the mixture was filtered through a pad of silica gel and washed with petroleum ether. The solvent was evaporated under the reduced pressure and the residue was dissolved in $CDCl_3$. The NMR yields were obtained by ^{1}H NMR analysis of the crude mixture using 1,3,5-trimethoxybenzene (50.5 mg, 0.3 mmol) as an internal standard.

Note: $NiCl_2 \cdot 6H_2O$ used in the optimization study was stored under air (outside of glove box), which was brought into the glove box and used immediately for every experiment.

Table 1. Optimization of the reaction conditions

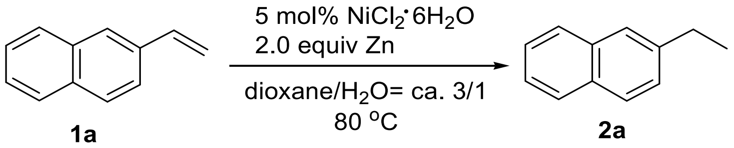


entry	catalyst	reductant	solvent	time (h)	yield (%)[a]
1	$NiCl_2 \cdot 6H_2O$	Zn	dioxane/H_2O (5/1)	10	88
2	$NiCl_2$	Zn	dioxane/H_2O (5/1)	10	89
3	$NiBr_2$	Zn	dioxane/H_2O (5/1)	10	89
4	NiI_2	Zn	dioxane/H_2O (5/1)	10	79 (7)
5	NiF_2	Zn	dioxane/H_2O (5/1)	10	2 (85)
6	$Ni(acac)_2$	Zn	dioxane/H_2O (5/1)	10	- (89)
7	$NiCl_2 \cdot 6H_2O$	Al	dioxane/H_2O (5/1)	10	24 (68)
8	$NiCl_2 \cdot 6H_2O$	Mn	dioxane/H_2O (5/1)	10	13 (81)
9	$NiCl_2 \cdot 6H_2O$	Mg	dioxane/H_2O (5/1)	10	- (96)
10	$NiCl_2 \cdot 6H_2O$	Zn	DMF/H_2O (5/1)	10	90 (1)
11	$NiCl_2 \cdot 6H_2O$	Zn	THF/H_2O (5/1)	10	95
12	$NiCl_2 \cdot 6H_2O$	Zn	CH_3CN/H_2O (5/1)	10	1 (58)
13	$NiCl_2 \cdot 6H_2O$	Zn	dioxane/H_2O (25/1)	10	33 (59)
14	$NiCl_2 \cdot 6H_2O$	Zn	dioxane/H_2O (3/1)	10	96
15	$NiCl_2 \cdot 6H_2O$	Zn	dioxane/H_2O (3/1)	5	95
16[b]	$NiCl_2 \cdot 6H_2O$	Zn	dioxane/H_2O (3/1)	5	48 (48)
17[c]	$NiCl_2 \cdot 6H_2O$	Zn	dioxane/H_2O (3/1)	5	32 (63)
18	-	Zn	dioxane/H_2O (3/1)	5	- (94)
19	$NiCl_2 \cdot 6H_2O$	-	dioxane/H_2O (3/1)	5	- (94)

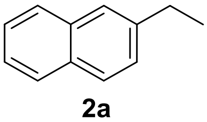
[a]Determined by ^1H NMR using 1,3,5-trimethoxybenzene as an internal standard. The yields of the unreacted **1a** are shown in parentheses. [b]1.0 equiv Zn was used. [c]50 °C.

Ni-Catalyzed transfer hydrogenation of aryl/heteroaryl alkenes, alkyl alkenes and heterocycles.

Typical procedure for the synthesis of 2a.

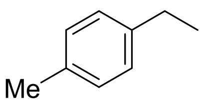


To an oven dried Schlenk tube (25 mL) were added NiCl$_2$·6H$_2$O (5.9 mg, 0.025 mmol), Zinc powder (65.4 mg, 1.0 mmol), and 2-vinylnaphthalene (77.1 mg, 0.5 mmol) under air. The Schlenk tube was capped with a rubber septum, evacuated and back filled with argon for three times. Then dioxane (2.5 mL) and H$_2$O (0.8 mL) were added sequentially under argon. (If the starting material is a liquild, after the NiCl$_2$·6H$_2$O and Zinc were added, the Schlenk tube was capped with a rubber septum, evacuated and back filled with argon for three times. Then dioxane, the alkene and H$_2$O were added sequentially under argon). The tube cap was then securely fitted and sealed with electrical tape, and the stopcock valve on the sidearm of the Schlenk tube was closed. After the reaction mixture was stirred at 80 °C for 10 h, it was filtered through a pad of silica gel and washed with petroleum ether. **Note: a stirring speed above 600 rpm is highly important for reproducibility.** The solvent was evaporated under the reduced pressure and the residue was purified by column chromatography on silica gel (eluent: petroleum ether) to give the desired product **2a** in 92% yield (72.0 mg) as a colorless oil.



2a

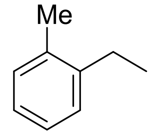
2-Ethylnaphthalene (2a). ^{1}H NMR (400 MHz, CDCl$_3$): δ 7.77-7.71 (m, 3H), 7.58 (s, 1H), 7.42-7.35 (m, 2H), 7.31-7.29 (m, 1H), 2.77 (q, J = 7.6 Hz, 2H), 1.29 (t, J = 7.6 Hz, 3H); ^{13}C NMR (100 MHz, CDCl$_3$): δ 141.69, 133.67, 131.90, 127.77, 127.56, 127.38, 127.04, 125.79, 125.50, 124.97, 29.01, 15.51. The spectroscopic data are in agreement with that previously reported.[2]



2b

1-Ethyl-4-methylbenzene (2b). NiCl$_2$·6H$_2$O (5.9 mg, 0.025 mmol), Zinc powder (65.4 mg, 1.0 mmol), dioxane (2.5 mL), 1-methyl-4-vinylbenzene (59.1 mg, 0.5 mmol) and H_2O (0.8 mL) were stirred at 80 °C for 11.5 h. Column chromatography on silica gel (eluent: petroleum ether) afforded the desired product **2b** in 44% yield (26.7 mg) as a colorless oil. ^1H NMR (400 MHz, $CDCl_3$): δ 7.09 (s, 4H), 2.61 (q, *J* = 7.2 Hz, 2H), 2.31 (s, 3H), 1.22 (t, *J* = 7.6 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 141.18, 134.96, 128.97, 127.71, 28.42, 20.96, 15.78. The spectroscopic data are in agreement with that previously reported.[3]

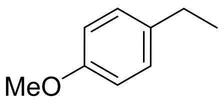
Due to the volatile nature of this compound, the NMR yield was determined. 86% NMR yield of the desired product **2b** was obtained.



2c

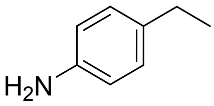
1-Ethyl-2-methylbenzene(2c). $NiCl_2 \cdot 6H_2O$ (5.9 mg, 0.025 mmol), Zinc powder (65.4 mg, 1.0 mmol), dioxane (2.5 mL), 1-methyl-2-vinylbenzene (59.1 mg, 0.5 mmol) and H_2O (0.8 mL) were stirred at 80 °C for 24 h. Column chromatography on silica gel (eluent: petroleum ether) afforded the desired product **2c** in 21% yield (12.5 mg) as a colorless oil. ^1H NMR (400 MHz, $CDCl_3$): δ 7.15-7.07 (m, 4H), 2.63 (q, *J* = 7.2 Hz, 2H), 2.31 (s, 3H), 1.21 (t, *J* = 7.6 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 142.29, 135.73, 129.99, 127.86, 125.98, 125.70, 26.15, 19.15, 14.36. The spectroscopic data are in agreement with that previously reported.[4]

Due to the volatile nature of this compound, the NMR yield was determined. 89% NMR yield of the desired product **2c** was obtained.



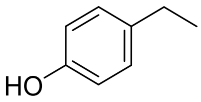
2d

1-Ethyl-4-methoxybenzene(2d). $NiCl_2 \cdot 6H_2O$ (5.9 mg, 0.025 mmol), Zinc powder (65.4 mg, 1.0 mmol), dioxane (2.5 mL), 1-methoxy-4-vinylbenzene (67.1 mg, 0.5 mmol) and H_2O (0.8 mL) were stirred at 80 °C for 10.5 h. Column chromatography on silica gel (eluent: petroleum ether to petroleum ether/ethyl ether = 50:1) afforded the desired product **2d** in 63% yield (42.6 mg) as a colorless oil. ^1H NMR (400 MHz, $CDCl_3$): δ 7.11 (d, *J* = 8.4 Hz, 2H), 6.82 (d, *J* = 8.8 Hz, 2H), 3.77 (s, 3H), 2.58 (q, *J* = 7.6 Hz, 2H), 1.20 (t, *J* = 7.6 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 157.56, 136.33, 128.65, 113.67, 55.18, 27.93, 15.87. The spectroscopic data are in agreement with that previously reported.[4]



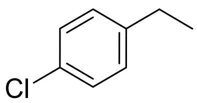
2e

4-Ethylaniline(2e). $NiCl_2·6H_2O$ (5.9 mg, 0.025 mmol), Zinc powder (65.4 mg, 1.0 mmol), dioxane (2.5 mL), 4-vinylaniline (59.6 mg, 0.5 mmol) and H_2O (0.8 mL) were stirred at 80 °C for 7 h. The mixture was filtered through a pad of silica gel and washed with ethyl ether. Column chromatography on silica gel (eluent: petroleum ether/ethyl ether = 1:1) afforded the desired product **2e** in 90% yield (54.8 mg) as a yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.98 (d, *J* = 8.0 Hz, 2H), 6.61 (d, *J* = 8.4 Hz, 2H), 3.46 (bs, 2H), 2.53 (q, *J* = 7.6 Hz, 2H), 1.18 (t, *J* = 7.6 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 143.97, 134.31, 128.48, 115.17, 27.88, 15.87. The spectroscopic data are in agreement with that previously reported.[5]



2f

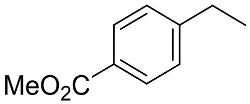
4-Ethylphenol (2f). $NiCl_2·6H_2O$ (5.9 mg, 0.025 mmol), Zinc powder (65.4 mg, 1.0 mmol), 4-vinylphenol (60.1 mg, 0.5 mmol), dioxane (2.5 mL) and H_2O (0.8 mL) were stirred at 80 °C for 7 h, the mixture was filtered through a pad of silica gel and washed with ethyl ether and ethyl acetate. Column chromatography on silica gel (eluent: petroleum ether/ethyl ether = 3:1) afforded the desired product **2f** in 86% yield (52.5 mg) as a colorless soild. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.05 (d, *J* = 8.0 Hz, 2H), 6.75 (d, *J* = 8.4 Hz, 2H), 5.39 (s, 1H), 2.57 (q, *J* = 8.0 Hz, 2H), 1.19 (t, *J* = 7.6 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 153.19, 136.56, 128.88, 115.13, 27.92, 15.83. The spectroscopic data are in agreement with that previously reported.[6]



2g

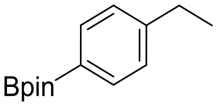
1-Chloro-4-ethylbenzene (2g). $NiCl_2·6H_2O$ (5.9 mg, 0.025 mmol), Zinc powder (65.4 mg, 1.0 mmol), dioxane (2.5 mL), 1-chloro-4-vinylbenzene (69.3 mg, 0.5 mmol) and H_2O (0.8 mL) were stirred at 80 °C for 20 h. Column chromatography on silica gel (eluent: petroleum ether) afforded the desired product **2g** in 35% yield (24.7 mg) as a colorless oil. ^1H NMR (400 MHz, $CDCl_3$): δ 7.24 (d, J = 8.4 Hz, 2H), 7.11 (d, J = 8.4 Hz, 2H), 2.61 (q, J = 8.0 Hz, 2H), 1.21 (t, J = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 142.60, 131.22, 129.18, 128.34, 28.23, 15.52. The spectroscopic data are in agreement with that previously reported.[7]

Due to the volatile nature of this compound, the NMR yield was determined. 62% NMR yield of the desired product **2g** was obtained.



2h

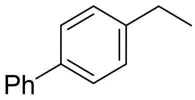
Methyl 4-ethylbenzoate (2h). $NiCl_2·6H_2O$ (5.9 mg, 0.025 mmol), Zinc powder (65.4 mg, 1.0 mmol), methyl 4-vinylbenzoate (81.1 mg, 0.5 mmol), dioxane (2.5 mL) and H_2O (0.8 mL) were stirred at 80 °C for 23.5 h, the mixture was filtered through a pad of silica gel and washed with ethyl acetate. Column chromatography on silica gel (eluent: petroleum ether/ethyl acetate = 15:1) afforded the desired product **2h** in 76% yield (62.8 mg) as a colorless oil. ^1H NMR (400 MHz, $CDCl_3$): δ 7.95 (d, J = 8.0 Hz, 2H), 7.25 (d, J = 8.0 Hz, 2H), 3.89 (s, 3H), 2.69 (q, J = 7.6 Hz, 2H), 1.25 (t, J = 7.6 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 167.10, 149.66, 129.63, 127.80, 127.55, 51.86, 28.86, 15.14. The spectroscopic data are in agreement with that previously reported.[8]



2i

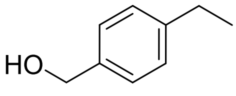
2-(4-Ethylphenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (2i). $NiCl_2·6H_2O$ (5.9 mg, 0.025 mmol), Zinc powder (65.4 mg, 1.0 mmol), 4,4,5,5-tetramethyl-2-(4-vinylphenyl)-1,3,2-dioxaborolane (115.1 mg, 0.5 mmol), dioxane (2.5 mL) and H_2O (0.8 mL) were stirred at 80 °C for 11 h, the mixture was filtered through a pad of silica gel and washed with ethyl acetate.

Column chromatography on silica gel (eluent: petroleum ether/ethyl acetate = 20:1) afforded the desired product **2i** in 72% yield (83.4 mg) as a colorless solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.74 (d, *J* = 8.0 Hz, 2H), 7.21 (d, *J* = 8.4 Hz, 2H), 2.65 (q, *J* = 7.6 Hz, 2H), 1.33 (s, 12H), 1.23 (t, *J* = 7.6 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 147.66, 134.87, 127.30, 83.54, 29.06, 24.80, 15.44. The spectroscopic data are in agreement with that previously reported.[9]



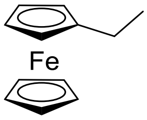
2j

4-Ethyl-1,1'-biphenyl (2j). $NiCl_2·6H_2O$ (5.9 mg, 0.025 mmol), Zinc powder (65.4 mg, 1.0 mmol), 4-vinyl-1,1'-biphenyl (90.1 mg, 0.5 mmol), dioxane (2.5 mL) and H_2O (0.8 mL) were stirred at 80 °C for 7.5 h. Column chromatography on silica gel (eluent: petroleum ether) afforded the desired product **2j** in 94% yield (85.3 mg) as a white solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.58 (d, *J* = 7.2 Hz, 2H), 7.52 (d, *J* = 8.0 Hz, 2H), 7.43 (t, *J* = 7.6 Hz, 2H), 7.34-7.27 (m, 3H), 2.70 (q, *J* = 7.6 Hz, 2H), 1.28 (t, *J* = 7.6 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 143.32, 141.14, 138.57, 128.67, 128.25, 127.04, 126.96, 126.92, 28.48, 15.57. The spectroscopic data are in agreement with that previously reported.[10]



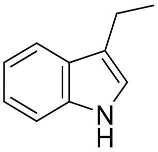
2k

(4-Ethylphenyl)methanol (2k). $NiCl_2·6H_2O$ (5.9 mg, 0.025 mmol), Zinc powder (65.4 mg, 1.0 mmol), dioxane (2.5 mL), (4-vinylphenyl)methanol (67.1 mg, 0.5 mmol) and H_2O (0.8 mL) were stirred at 80 °C for 12 h. Column chromatography on silica gel (eluent: petroleum ether : ether acetate = 5:1) afforded the desired product **2k** in 81% yield (55.2 mg) as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.24 (d, *J* = 8.0 Hz, 2H), 7.17 (d, *J* = 7.6 Hz, 2H), 4.57 (s, 2H), 2.63 (q, *J* = 7.6 Hz, 2H), 2.27 (s, 1H), 1.22 (t, *J* = 7.6 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 143.63, 138.10, 127.93, 127.10, 64.99, 28.49, 15.58. The spectroscopic data are in agreement with that previously reported.[11]



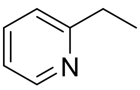
2l

1-Ethylferrocene (2l). $NiCl_2\cdot6H_2O$ (5.9 mg, 0.025 mmol), Zinc powder (65.4 mg, 1.0 mmol), 1-vinylferrocene (106.0 mg, 0.5 mmol), dioxane (2.5 mL) and H_2O (0.8 mL) were stirred at 80 °C for 17 h. The mixture was filtered through a pad of silica gel and washed with petroleum ether and ethyl acetate. Column chromatography on silica gel (eluent: petroleum ether) afforded the desired product **2l** in 97% yield (103.4 mg) as a yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 4.09-4.03 (m, 9H), 2.33 (q, J = 7.6 Hz, 2H), 1.16 (t, J = 7.6 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 91.03, 68.31, 67.36, 66.88, 22.17, 14.61. The spectroscopic data are in agreement with that previously reported.[12]



2m

3-Ethyl-1*H*-indole (2m). $NiCl_2\cdot6H_2O$ (5.9 mg, 0.025 mmol), Zinc powder (65.4 mg, 1.0 mmol), 3-vinyl-1*H*-indole (71.6 mg, 0.5 mmol), dioxane (2.5 mL) and H_2O (0.8 mL) were stirred at 80 °C for 8 h. The mixture was filtered through a pad of silica gel and washed with ethyl acetate. Column chromatography on silica gel (eluent: petroleum ether/ethyl acetate = 5:1) afforded the desired product **2m** in 98% yield (71.0 mg) as a colorless soild. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.60 (d, J = 7.6 Hz, 2H), 7.25-7.23 (m, 1H), 7.17 (t, J = 7.2 Hz, 1H), 7.12-7.08 (m, 1H), 6.84 (s, 1H), 2.76 (q, J = 7.6 Hz, 2H), 1.31 (t, J = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 136.28, 127.30, 121.78, 120.44, 118.98, 118.88, 118.60, 111.02, 18.27, 14.40. The spectroscopic data are in agreement with that previously reported.[13]

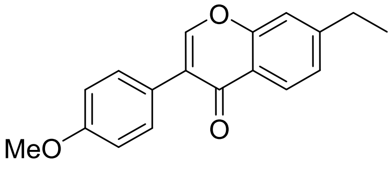


2n

2-Ethylpyridine (2n). $NiCl_2\cdot6H_2O$ (5.9 mg, 0.025 mmol), Zinc powder (65.4 mg, 1.0 mmol), dioxane (2.5 mL), 2-vinylpyridine (52.6 mg, 0.5 mmol) and H_2O (0.8 mL) were stirred at 80

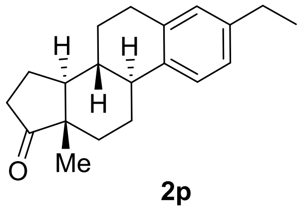
°C for 9 h. The mixture was filtered through a pad of silica gel and washed with ethyl ether. Column chromatography on silica gel (eluent: petroleum ether to petroleum ether/ethyl ether = 3:1) afforded the desired product **2n** in 25% yield (13.3 mg) as a colorless oil. The product contains small amount of stabilizer and solvent. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.53 (d, *J* = 4.4 Hz, 1H), 7.59 (td, *J* = 8.0, 1.6 Hz, 1H), 7.16 (d, *J* = 8.0 Hz, 1H), 7.11-7.08 (m, 1H), 2.83 (q, *J* = 7.6 Hz, 2H), 1.31 (t, *J* = 8.0 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 163.47, 149.10, 136.34, 122.00, 120.85, 31.33, 13.87. The spectroscopic data are in agreement with that previously reported.[14]

Due to the volatile nature of this compound, the NMR yield was determined. 92% NMR yield of the desired product **2n** was obtained.



2o

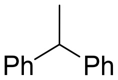
7-Ethyl-3-(4-methoxyphenyl)-4*H*-chromen-4-one (2o). $NiCl_2·6H_2O$ (7.1 mg, 0.03 mmol), Zinc powder (39.2 mg, 0.6 mmol), 3-(4-methoxyphenyl)-7-vinyl-4*H*-chromen-4-one (83.5 mg, 0.3 mmol), dioxane (1.5 mL) and H_2O (0.5 mL) were stirred at 80 °C for 20 h. the mixture was filtered through a pad of silica gel and washed with ethyl acetate. Column chromatography on silica gel (eluent: petroleum ether/ethyl acetate = 5:1) afforded the desired product **2o** in 86 % yield (72.4 mg) as a white soild. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.20 (d, *J* = 9.6 Hz, 1H), 7.93 (s, 1H), 7.50 (d, *J* = 8.4 Hz, 2H), 7.25-7.23 (m, 2H), 6.96 (d, *J* = 8.4 Hz, 2H), 3.82 (s, 3H), 2.77 (q, *J* = 8.0 Hz, 2H), 1.29 (t, *J* = 7.6 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 176.21, 159.43, 156.33, 152.21, 150.87, 129.98, 126.08, 125.44, 124.67, 124.17, 122.32, 116.33, 113.82, 55.19, 28.86, 14.88. IR (neat): 3082, 3063, 3032, 2961, 2928, 2870, 2852, 1726, 1633, 1622, 1607, 1575, 1559, 1511, 1461, 1439, 1372, 1358, 1289, 1246, 1225, 1194, 1178, 1105, 1027, 906, 885, 873, 836, 817, 803, 792, 761, 697 cm^{-1}. HRMS (ESI) calcd for $C_{18}H_{17}O_3$ $[M+H]^+$: 281.1172, found 281.1179.



2p

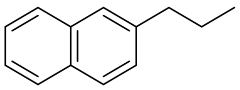
(8*R*,9*S*,13*S*,14*S*)-3-Ethyl-13-methyl-6,7,8,9,11,12,13,14,15,16-decahydro-17*H*-cyclopenta[*a*]phenanthren-17-one (2p). $NiCl_2 \cdot 6H_2O$ (7.1 mg, 0.03 mmol), Zinc powder (39.2 mg, 0.6 mmol), (8*R*,9*S*,13*S*,14*S*)-13-methyl-3-vinyl-6,7,8,9,11,12,13,14,15,16-decahydro-17*H*-cyclo-

penta[*a*]phenanthren-17-one (84.1 mg, 0.3 mmol), dioxane (1.5 mL) and H_2O (0.5 mL) were stirred at 80 °C for 13 h. The mixture was filtered through a pad of silica gel and washed with ethyl acetate. Column chromatography on silica gel (eluent: petroleum ether/ethyl acetate = 10:1) afforded the desired product **2p** in 80% yield (68.2 mg) as a white soild. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.21 (d, *J* = 7.6 Hz, 1H), 7.00 (d, *J* = 8.0 Hz, 1H), 6.94 (s, 1H), 2.90-2.88 (m, 2H), 2.59 (q, *J* = 7.6 Hz, 2H), 2.53-2.40 (m, 2H), 2.30-2.25 (m, 1H), 2.18-1.93 (m, 4H), 1.67-1.38 (m, 6H), 1.23 (t, *J* = 7.2 Hz, 3H), 0.89 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 220.80, 141.60, 136.88, 136.21, 128.40, 125.26, 125.23, 50.40, 47.91, 44.21, 38.16, 35.77, 31.53, 29.33, 28.21, 26.51, 25.66, 21.50, 15.53, 13.75. IR (neat): 2968, 2943, 2925, 2860, 1735, 1499, 1459, 1437, 1403, 1374, 1281, 1256, 1211, 1085, 1048, 1006, 910, 880, 823, 783, 711 cm^{-1}. HRMS (ESI) calcd for $C_{20}H_{27}O$ [M+H]$^+$: 283.2056, found 283.2060.



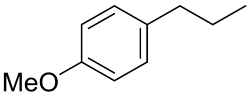
2q

Ethane-1,1-diyldibenzene (2q). $NiCl_2 \cdot 6H_2O$ (11.9 mg, 0.05 mmol), Zinc flake (65.4 mg, 1.0 mmol), dioxane (2.5 mL), ethene-1,1-diyldibenzene (90.1 mg, 0.5 mmol) and H_2O (0.8 mL) were stirred at 80 °C for 24 h. Column chromatography on silica gel (eluent: petroleum ether) afforded the desired product **2q** in 90% yield (81.8 mg) as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.27-7.11 (m, 10H), 4.13 (q, *J* = 7.2 Hz, 1H), 1.62 (d, *J* = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 146.30, 128.32, 127.58, 125.98, 44.70, 21.83. The spectroscopic data are in agreement with that previously reported.[15]



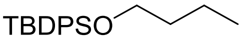
2r

2-Propylnaphthalene (2r). $NiCl_2 \cdot 6H_2O$ (5.9 mg, 0.025 mmol), Zinc powder (65.4 mg, 1.0 mmol), dioxane (2.5 mL), 2-allylnaphthalene (84.1 mg, 0.5 mmol) and H_2O (0.8 mL) were stirred at 80 °C for 10 h. The mixture was filtered through a pad of silica gel and washed with ethyl acetate. Column chromatography on silica gel (eluent: petroleum ether) afforded the desired product **2r** in 93% yield (79.1 mg) as a colorless oil. ^1H NMR (400 MHz, $CDCl_3$): δ 7.79-7.73 (m, 3H), 7.59 (s, 1H), 7.44-7.37 (m, 2H), 7.31 (d, J = 8.4 Hz, 1H), 2.73 (t, J = 7.6 Hz, 2H), 1.77-1.67 (m, 2H), 0.96 (t, J = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 140.14, 133.61, 131.94, 127.69, 127.57, 127.43, 127.38, 126.36, 125.76, 124.96, 38.17, 24.44, 13.85. The spectroscopic data are in agreement with that previously reported.[16]



2s

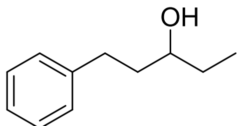
1-Methoxy-4-propylbenzene (2s). $NiCl_2 \cdot 6H_2O$ (5.9 mg, 0.025 mmol), Zinc powder (65.4 mg, 1.0 mmol), dioxane (2.5 mL), 1-allyl-4-methoxybenzene (74.1 mg, 0.5 mmol) and H_2O (0.8 mL) were stirred at 80 °C for 8 h. The mixture was filtered through a pad of silica gel and washed with ethyl acetate. Column chromatography on silica gel (eluent: petroleum ether/ethyl acetate = 50:1) afforded the desired product **2s** in 93% yield (70.2 mg) as a colorless oil. ^1H NMR (400 MHz, $CDCl_3$): δ 7.08 (d, J = 8.4 Hz, 2H), 6.81 (d, J = 8.8 Hz, 2H), 3.76 (s, 3H), 2.52 (t, J = 7.2 Hz, 2H), 1.64-1.55 (m, 2H), 0.92 (t, J = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 157.55, 134.72, 129.25, 113.53, 55.12, 37.09, 24.79, 13.74. The spectroscopic data are in agreement with that previously reported.[17]



2t

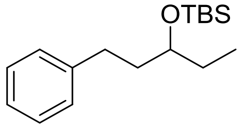
Butoxy(*tert*-butyl)diphenylsilane (2t). $NiCl_2 \cdot 6H_2O$ (11.9 mg, 0.05 mmol), Zinc powder

(65.4 mg, 1.0 mmol), dioxane (2.5 mL), (but-3-en-1-yloxy)(*tert*-butyl)diphenylsilane (155.3 mg, 0.5 mmol) and H_2O (0.8 mL) were stirred at 80 °C for 20 h. The mixture was filtered through a pad of silica gel and washed with ethyl acetate. Column chromatography on silica gel (eluent: petroleum ether/ethyl acetate = 50:1) afforded the desired product **2t** in 94% yield (147.0 mg) as a colorless oil. ^1H NMR (400 MHz, $CDCl_3$): δ 7.68 (d, J = 6.0 Hz, 4H), 7.42-7.35 (m, 6H), 3.66 (t, J = 6.4 Hz, 2H), 1.58-1.50 (m, 2H), 1.43-1.34 (m, 2H), 1.05 (s, 9H), 0.88 (t, J = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 135.57, 134.17, 129.47, 127.56, 63.69, 34.76, 26.86, 19.23, 19.01, 13.91. The spectroscopic data are in agreement with that previously reported.[18]



2u

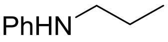
1-Phenylpentan-3-ol (2u). $NiCl_2·6H_2O$ (11.9 mg, 0.05 mmol), Zinc powder (65.4 mg, 1.0 mmol), dioxane (2.5 mL), 5-phenylpent-1-en-3-ol (81.1 mg, 0.5 mmol) and H_2O (0.8 mL) were stirred at 80 °C for 12 h. The mixture was filtered through a pad of silica gel and washed with ethyl acetate. Column chromatography on silica gel (eluent: petroleum ether/ethyl acetate = 8:1) afforded the desired product **2u** in 86% yield (71.0 mg) as a colorless oil. ^1H NMR (400 MHz, $CDCl_3$): δ 7.29-7.25 (m, 2H), 7.22-7.15 (m, 3H), 3.57-3.51 (m, 1H), 2.83-2.75 (m, 1H), 2.69-2.62 (m, 1H), 1.83-1.67 (m, 3H), 1.58-1.41 (m, 2H), 0.93 (t, J = 7.6 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 142.18, 128.34, 128.30, 125.69, 72.51, 38.49, 31.99, 30.18, 9.78. The spectroscopic data are in agreement with that previously reported.[19]



2v

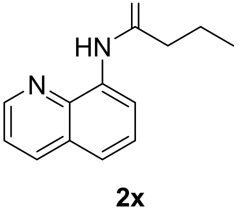
***tert*-Butyldimethyl((1-phenylpentan-3-yl)oxy)silane (2v).** $NiCl_2·6H_2O$ (11.9 mg, 0.05 mmol), Zinc powder (65.4 mg, 1.0 mmol), dioxane (2.5 mL), *tert*-butyldimethyl((5-phenylpent-1-en-3-yl)oxy)silane (138.3 mg, 0.5 mmol) and H_2O (0.8 mL) were stirred at 80 °C for 24 h. The mixture was filtered through a pad of silica gel and washed with ethyl acetate.

Column chromatography on silica gel (eluent: petroleum ether/ethyl acetate = 50:1) afforded the desired product **2v** in 96% yield (133.3 mg) as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.28-7.25 (m, 2H), 7.20-7.14 (m, 3H), 3.68-3.62 (m, 1H), 2.73-2.55 (m, 2H), 1.77-1.71 (m, 2H), 1.55-1.48 (m, 2H), 0.92-0.87 (m, 12H), 0.06 (s, 3H), 0.05 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 142.85, 128.32, 128.31, 125.60, 73.06, 38.49, 31.79, 29.69, 25.94, 18.17, 9.57, -4.36, -4.46. IR (neat): 3061, 3027, 2956, 2928, 2852, 1602, 1495, 1459, 1360, 1253, 1062, 1046, 1005, 833, 792, 772, 745, 697 cm^{-1}. HRMS (ESI) calcd for $C_{17}H_{31}OSi$ $[M+H]^+$: 279.2139, found 279.2136.



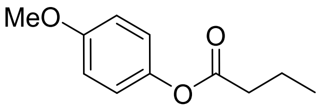
2w

***N*-Propylaniline (2w).** $NiCl_2·6H_2O$ (5.9 mg, 0.025 mmol), Zinc powder (65.4 mg, 1.0 mmol), dioxane (2.5 mL), *N*-allylaniline (66.6 mg, 0.5 mmol) and H_2O (0.8 mL) were stirred at 80 °C for 24 h. The mixture was filtered through a pad of silica gel and washed with ethyl acetate. Column chromatography on silica gel (eluent: petroleum ether/ethyl acetate = 20:1) afforded the desired product **2w** in 91% yield (61.3 mg) as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.16 (t, *J* = 8.4 Hz, 2H), 6.67 (t, *J* = 7.2 Hz, 1H), 6.59 (d, *J* = 8.0 Hz, 2H), 3.59 (bs, 1H), 3.06 (t, *J* = 6.8 Hz, 2H), 1.67-1.58 (m, 2H), 0.98 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 148.47, 129.16, 117.01, 112.63, 45.74, 22.68, 11.59. The spectroscopic data are in agreement with that previously reported.[17a]



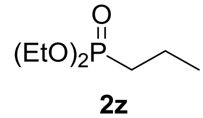
2x

***N*-(Quinolin-8-yl)butyramide (2x).** $NiCl_2·6H_2O$ (5.9 mg, 0.025 mmol), Zinc powder (65.4 mg, 1.0 mmol), dioxane (2.5 mL), *N*-(quinolin-8-yl)but-3-enamide (106.1 mg, 0.5 mmol) and H_2O (0.8 mL) were stirred at 80 °C for 9 h. The mixture was filtered through a pad of silica gel and washed with ethyl acetate. Column chromatography on silica gel (eluent: petroleum ether/ethyl acetate = 5:1) afforded the desired product **2x** in 92% yield (98.8 mg) as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.80 (s, 1H), 8.80-8.76 (m, 2H), 8.09 (d, J = 8.4 Hz, 1H), 7.52-7.38 (m, 3H), 2.53 (t, J = 7.2 Hz, 2H), 1.90-1.80 (m, 2H), 1.05 (t, J = 7.6 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 171.57, 147.91, 138.08, 136.14, 134.34, 127.70, 127.18, 121.38, 121.16, 116.15, 39.94, 18.96, 13.67. The spectroscopic data are in agreement with that previously reported.[20]



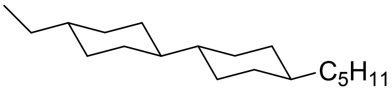
2y

4-Methoxyphenyl butyrate (2y). $NiCl_2·6H_2O$ (5.9 mg, 0.025 mmol), Zinc powder (65.4 mg, 1.0 mmol), dioxane (2.5 mL), 4-methoxyphenyl but-3-enoate (96.1 mg, 0.5 mmol) and H_2O (0.8 mL) were stirred at 80 °C for 10.5 h. The mixture was filtered through a pad of silica gel and washed with ethyl acetate. Column chromatography on silica gel (eluent: petroleum ether/ethyl acetate = 10:1) afforded the desired product **2y** in 78% yield (76.2 mg) as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.98 (d, J = 8.8 Hz, 2H), 6.87 (d, J = 8.8 Hz, 2H), 3.77 (s, 3H), 2.51 (q, J = 7.2 Hz, 2H), 1.81-1.72 (m, 2H), 1.03 (t, J = 7.6 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 172.41, 157.05, 144.12, 122.22, 114.28, 55.42, 36.03, 18.37, 13.53. The spectroscopic data are in agreement with that previously reported.[21]



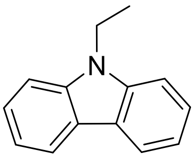
2z

Diethyl propylphosphonate (2z). $NiCl_2·6H_2O$ (5.9 mg, 0.025 mmol), Zinc powder (65.4 mg, 1.0 mmol), dioxane (2.5 mL), diethyl allylphosphonate (89.1 mg, 0.5 mmol) and H_2O (0.8 mL) were stirred at 80 °C for 21 h. Column chromatography on silica gel (eluent: petroleum ether to ethyl ether) afforded the desired product **2z** in 80% yield (71.7 mg) as a yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 4.15-4.04 (m, 4H), 1.75-1.60 (m, 4H), 1.33 (t, J = 7.2 Hz, 6H), 1.04-1.00 (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 61.09 (d, $J_{C\text{-}P}$ = 6.4 Hz), 27.46 (d, $J_{C\text{-}P}$ = 139.5 Hz), 16.23 (d, $J_{C\text{-}P}$ = 5.9 Hz), 15.90 (d, $J_{C\text{-}P}$ = 5.4 Hz), 15.06 (d, $J_{C\text{-}P}$ = 17.7 Hz). The spectroscopic data are in agreement with that previously reported.[22]



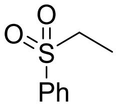
2za

4-Ethyl-4'-pentyl-1,1'-bi(cyclohexane) (2za). $NiCl_2 \cdot 6H_2O$ (11.9 mg, 0.05 mmol), Zinc powder (65.4 mg, 1.0 mmol), (*trans*,*trans*)-4-pentyl-4'-vinyl-1,1'-bi(cyclohexane) (131.2 mg, 0.5 mmol), dioxane (2.5 mL) and H_2O (0.8 mL) were stirred at 80 °C for 26 h. Column chromatography on silica gel (eluent: petroleum ether) afforded the desired product **2za** in 58% yield (77.1 mg) as a white solid. ^1H NMR (400 MHz, $CDCl_3$): δ 1.76-1.68 (m, 8H), 1.32-0.79 (m, 28H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 43.56, 39.77, 38.00, 37.56, 33.73, 33.29, 32.31, 30.16, 30.13, 30.10, 26.73, 22.76, 14.13, 11.54. IR (neat): 2958, 2916, 2848, 1459, 1447, 1378, 1219, 1213, 974, 894, 754, 720 cm^{-1}. HRMS (EI) calcd for $C_{19}H_{36}$ $[M]^+$: 264.2817, found 264.2812.



4a

9-Ethyl-9*H*-carbazole (4a). $NiCl_2 \cdot 6H_2O$ (5.9 mg, 0.025 mmol), Zinc powder (65.4 mg, 1.0 mmol), 9-vinyl-9*H*-carbazole (96.6 mg, 0.5 mmol), dioxane (2.5 mL) and H_2O (0.8 mL) were stirred at 80 °C for 12 h. The mixture was filtered through a pad of silica gel and washed with ethyl acetate. Column chromatography on silica gel (eluent: petroleum ether/ethyl acetate = 30:1) afforded the desired product **4a** in 89% yield (86.7 mg) as a white solid. ^1H NMR (400 MHz, $CDCl_3$): δ 8.08 (d, J = 8.0 Hz, 2H), 7.45-7.41 (m, 2H), 7.35-7.33 (m, 2H), 7.20 (t, J = 8.0 Hz, 2H), 4.26 (q, J = 7.2 Hz, 2H), 1.34 (t, J = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 139.82, 125.53, 122.83, 120.35, 118.67, 108.36, 37.36, 13.71. The spectroscopic data are in agreement with that previously reported.[23]



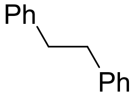
4b

(Ethylsulfonyl)benzene (4b). $NiCl_2·6H_2O$ (5.9 mg, 0.025 mmol), Zinc powder (65.4 mg, 1.0 mmol), (vinylsulfonyl)benzene (84.1 mg, 0.5 mmol), dioxane (2.5 mL) and H_2O (0.8 mL) were stirred at 80 °C for 21 h. The mixture was filtered through a pad of silica gel and washed with ethyl ether. The residue was purified by preparative TLC on silica gel (eluent: petroleum ether/ethyl ether = 1:1) to give the desired product **4b** in 88% yield (74.6 mg) as a colorless oil. ^1H NMR (400 MHz, $CDCl_3$): δ 7.91 (d, J = 7.2 Hz, 2H), 7.69-7.65 (m, 1H), 7.60-7.56 (m, 2H), 3.13 (q, J = 7.2 Hz, 2H), 1.28 (t, J = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 138.29, 133.58, 129.14, 128.03, 50.42, 7.31. The spectroscopic data are in agreement with that previously reported.[24]

4c

Ethyldimethyl(phenyl)silane (4c). $NiCl_2·6H_2O$ (5.9 mg, 0.025 mmol), Zinc powder (65.4 mg, 1.0 mmol), dioxane (2.5 mL), dimethyl(phenyl)(vinyl)silane (81.2 mg, 0.5 mmol) and H_2O (0.8 mL) were stirred at 80 °C for 12 h. Column chromatography on silica gel (eluent: petroleum ether) afforded the desired product **4c** in 78% yield (64.3 mg) as a colorless oil. ^1H NMR (400 MHz, $CDCl_3$): δ 7.52-7.49 (m, 2H), 7.34-7.33 (m, 3H), 0.95 (t, J = 8.0 Hz, 3H), 0.73 (q, J = 8.0 Hz, 2H), 0.25 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 139.43, 133.58, 128.75, 127.69, 7.41, 7.40, -3.56. IR (neat): 3069, 3048, 2954, 2907, 2873, 1426, 1247, 1112, 1012, 957, 832, 815, 774, 728, 698 cm^{-1}. HRMS (EI) calcd for $C_{10}H_{16}Si$ $[M]^+$: 164.1021, found 164.1027.

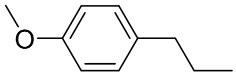
Due to the volatile nature of this compound, the NMR yield was determined. 93% NMR yield of the desired product **4c** was obtained.



6a

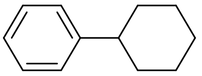
1,2-Diphenylethane (6a). $NiCl_2·6H_2O$ (11.9 mg, 0.05 mmol), Zinc powder (65.4 mg, 1.0 mmol), *E*-stilbene (90.1 mg, 0.5 mmol), dioxane (2.5 mL) and H_2O (0.8 mL) were stirred at 80 °C for 17 h. Column chromatography on silica gel (eluent: petroleum ether) afforded the desired product **6a** in 91% yield (82.8 mg) as a white solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.27-7.24 (m, 4H), 7.18-7.15 (m, 6H), 2.90 (s, 4H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 141.72, 128.41, 128.29, 125.88, 37.90. The spectroscopic data are in agreement with that previously reported.[25]

When *Z*-stilbene was used as the substrate, the desired product **6a** was obtained in 99% yield (90.5 mg) as a white solid.



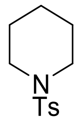
2s

1-Methoxy-4-propylbenzene (2s). $NiCl_2·6H_2O$ (5.9 mg, 0.025 mmol), Zinc powder (65.4 mg, 1.0 mmol), (*E*)-1-methoxy-4-(prop-1-en-1-yl)benzene (74.1 mg, 0.5 mmol), dioxane (2.5 mL) and H_2O (0.8 mL) were stirred at 80 °C for 24 h. The mixture was filtered through a pad of silica gel and washed with petroleum ether and ethyl acetate. Column chromatography on silica gel (eluent: petroleum ether/ethyl ether = 50:1) afforded the desired product **2s** in 93% yield (70.1 mg) as a colorless oil. The spectroscopic data are in agreement with that obtained from **1s**.



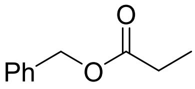
6c

Cyclohexylbenzene (6c). $NiCl_2·6H_2O$ (11.9 mg, 0.05 mmol), Zinc flake (98.1 mg, 1.5 mmol), dioxane (2.5 mL), 2,3,4,5-tetrahydro-1,1'-biphenyl (79.1 mg, 0.5 mmol) and H_2O (0.8 mL) were stirred at 80 °C for 24 h. Column chromatography on silica gel (eluent: petroleum ether) afforded the desired product **6c** in 89% yield (71.1 mg) as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.29-7.26 (m, 2H), 7.21-7.14 (m, 3H), 2.51-2.45 (m, 1H), 1.88-1.82 (m, 4H), 1.76-1.72 (m, 1H), 1.47-1.33 (m, 4H), 1.29-1.22 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 148.05, 128.25, 126.80, 125.74, 44.57, 34.44, 26.90, 26.15. The spectroscopic data are in agreement with that previously reported.[26]



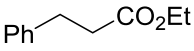
6d

1-Tosylpiperidine (6d). $NiCl_2 \cdot 6H_2O$ (11.9 mg, 0.05 mmol), Zinc powder (98.1 mg, 1.5 mmol), 1-tosyl-1,2,3,6-tetrahydropyridine (118.7 mg, 0.5 mmol), dioxane (2.5 mL) and H_2O (0.8 mL) were stirred at 80 °C for 23 h. The mixture was filtered through a pad of silica gel and washed with ethyl acetate. Column chromatography on silica gel (eluent: petroleum ether/ethyl ether = 5:1) afforded the desired product **6d** in 81% yield (96.5 mg) as a white soild. ^1H NMR (400 MHz, $CDCl_3$): δ 7.64 (d, J = 8.0 Hz, 2H), 7.32 (d, J = 8.0 Hz, 2H), 2.96 (t, J = 5.2 Hz, 4H), 2.43 (s, 3H), 1.66-1.60 (m, 4H), 1.43-1.38 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 143.20, 132.96, 129.41, 127.54, 46.80, 25.00, 23.33, 21.37. The spectroscopic data are in agreement with that previously reported.[27]



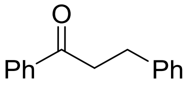
8a

Benzyl propionate (8a). $NiCl_2 \cdot 6H_2O$ (5.9 mg, 0.025 mmol), Zinc powder (65.4 mg, 1.0 mmol), dioxane (2.5 mL), benzyl acrylate (81.1 mg, 0.5 mmol) and H_2O (0.8 mL) were stirred at 80 °C for 8 h. Column chromatography on silica gel (eluent: petroleum ether/ ethyl acetate = 20:1) afforded the desired product **8a** in 91% yield (74.5mg) as a yellow oil. ^1H NMR (400 MHz, $CDCl_3$): δ 7.35-7.30 (m, 5H), 5.11 (s, 2H), 2.37 (q, J = 7.6 Hz, 2H), 1.15 (t, J = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 174.15, 136.02, 128.43, 128.06, 66.00, 27.46, 8.99. The spectroscopic data are in agreement with that previously reported.[28]



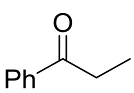
8b

Ethyl 3-phenylpropanoate (8b). $NiCl_2 \cdot 6H_2O$ (11.9 mg, 0.05 mmol), Zinc powder (65.4 mg, 1.0 mmol), dioxane (2.5 mL), ethyl cinnamate (88.1 mg, 0.5 mmol) and H_2O (0.8 mL) were stirred at 80 °C for 12 h. The mixture was filtered through a pad of silica gel and washed with petroleum ether and ethyl acetate. Column chromatography on silica gel (eluent: petroleum ether/ ethyl acetate = 20:1) afforded the desired product **8b** in 96% yield (85.6 mg) as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.29-7.26 (m, 2H), 7.22-7.17 (m, 3H), 4.11 (q, *J* = 7.2 Hz, 2H), 2.94 (t, *J* = 8.0 Hz, 2H), 2.61 (t, *J* = 8.4 Hz, 2H), 1.22 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 172.78, 140.45, 128.35, 128.19, 126.10, 60.27, 35.81, 30.84, 14.08. The spectroscopic data are in agreement with that previously reported.[29]



8c

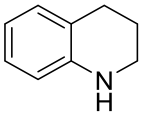
1,3-Diphenylpropan-1-one (8c). $NiCl_2·6H_2O$ (23.8 mg, 0.1 mmol), Al powder (53.9 mg, 2.0 mmol), (*E*)-chalcone (104.1 mg, 0.5 mmol), dioxane (2.5 mL) and H_2O (0.5 mL) were stirred at 80 °C for 10 h in Schlenk tube (10 mL). The mixture was filtered through a pad of silica gel and washed with petroleum ether and ethyl acetate. Column chromatography on silica gel (eluent: petroleum ether/ethyl ether = 30:1) afforded the desired product **8c** in 86% yield (89.9 mg) as a white soild. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.96 (d, *J* = 7.6 Hz, 2H), 7.55 (t, *J* = 7.6 Hz, 1H), 7.45 (t, *J* = 7.6 Hz, 2H), 7.32-7.24 (m, 4H), 7.22-7.19 (m, 1H), 3.30 (t, *J* = 7.2 Hz, 2H), 3.07 (t, *J* = 8.0 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 199.18, 141.25, 136.79, 133.03, 128.57, 128.49, 128.39, 128.00, 126.10, 40.42, 30.07. The spectroscopic data are in agreement with that previously reported.[30]



8d

Propiophenone (8d). $NiCl_2·6H_2O$ (23.8 mg, 0.1 mmol), Al powder (53.9 mg, 2.0 mmol), dioxane (2.5 mL), 1-phenylprop-2-en-1-one (66.1 mg, 0.5 mmol) and H_2O (0.5 mL) were stirred at 80 °C for 10 h in Schlenk tube (10 mL). The mixture was filtered through a pad of silica gel and washed with petroleum ether and ethyl acetate. Column chromatography on silica gel (eluent: petroleum ether/ethyl acetate = 30:1) afforded the desired product **8d** in 72%

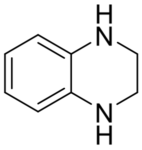
yield (48.0 mg) as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.96 (d, *J* = 8.0 Hz, 2H), 7.55 (t, *J* = 8.0 Hz, 1H), 7.45 (t, *J* = 7.2 Hz, 2H), 3.00 (q, *J* = 7.2 Hz, 2H), 1.23 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 200.76, 136.82, 132.81, 128.48, 127.90, 31.71, 8.16. The spectroscopic data are in agreement with that previously reported.[31]



10a

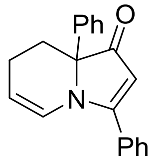
1,2,3,4-Tetrahydroquinoline (10a). To an oven dried sealable Schlenk tube (10 mL) were added $NiCl_2 \cdot 6H_2O$ (7.1 mg, 0.03 mmol), Zinc powder (58.9 mg, 0.9 mmol), dioxane (1.5 mL), quinoline (38.7 mg, 0.3 mmol), NEt_3 (30.4 mg, 0.3 mmol) and H_2O (0.3 mL) were added sequentially under argon. The tube was sealed with a teflon screwcap and the mixture was stirred at 100 °C for 10 h, then the mixture was filtered through a pad of silica gel and washed with ethyl acetate. **Note: the tube should be tightly sealed, which is highly important for reproducibility.** The solvent was evaporated under the reduced pressure and the residue was purified by column chromatography on silica gel (eluent: petroleum ether/ethyl acetate = 5:1) to give the desired product **10a** in 76% yield (30.4 mg) as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.97-6.93 (m, 2H), 6.59 (t, *J* = 7.6 Hz, 1H), 6.45 (d, *J* = 7.6 Hz, 1H), 3.74 (br, 1H), 3.28 (t, *J* = 5.6 Hz, 2H), 2.75 (t, *J* = 6.4 Hz, 2H), 1.96-1.90 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 144.71, 129.45, 126.65, 121.36, 116.85, 114.11, 41.90, 26.90, 22.10. The spectroscopic data are in agreement with that previously reported.[32]

When the reaction was carried out in a 25 mL sealable Schlenk tube, 55% yield of **10a** was obtained. The results indicated that the yield of the product **10a** was decreased by using a larger tube.



10b

1,2,3,4-Tetrahydroquinoxaline (10b). $NiCl_2 \cdot 6H_2O$ (7.1 mg, 0.03 mmol), Zinc powder (58.9 mg, 0.9 mmol), quinoxaline (39.0 mg, 0.3 mmol), dioxane (1.5 mL) and H_2O (0.5 mL) were stirred at 100 °C for 11 h in Schlenk tube (10 mL). The mixture was filtered through a pad of silica gel and washed with ethyl acetate. Column chromatography on silica gel (eluent: petroleum ether/ethyl ether = 2:1) to give the desired product **10b** in 52% yield (20.8 mg) as a white soild. ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.59-6.57 (m, 2H), 6.50-6.49 (m, 2H), 3.65 (bs, 2H), 3.42 (s, 4H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 133.62, 118.69, 114.64, 41.31. The spectroscopic data are in agreement with that previously reported.[33]

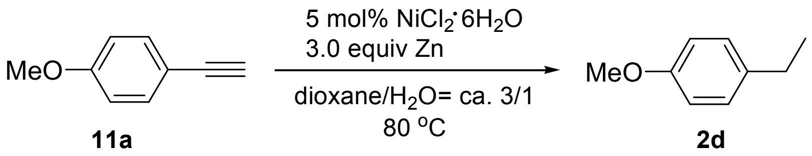


10c

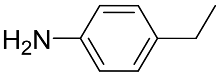
3,8a-Diphenyl-8,8a-dihydroindolizin-1(7*H*)-one (10c). To an oven dried sealable Schlenk tube (10 mL) were added $NiCl_2\cdot6H_2O$ (7.1 mg, 0.03 mmol), Zinc powder (39.2 mg, 0.6 mmol), 3,8a-diphenylindolizin-1(8a*H*)-one (85.6 mg, 0.3 mmol), dioxane (1.5 mL), NEt_3 (30.4 mg, 0.3 mmol) and H_2O (0.3 mL) were added sequentially under argon. The tube was sealed with a teflon screwcap and the mixture was stirred at 100 °C for 10 h, the mixture was filtered through a pad of silica gel and washed with ethyl acetate. **Note: the tube should be tightly sealed, which is highly important for reproducibility.** The solvent was evaporated under the reduced pressure and the residue was purified by column chromatography on silica gel (eluent: petroleum ether/ethyl acetate = 5:1) to give the desired product **10c** in 65% yield (55.9 mg) as a yellow soild. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.60-7.54 (m, 7H), 7.38 (t, J = 7.2 Hz, 2H), 7.32-7.28 (m, 1H), 6.73 (d, J = 7.6Hz, 1H), 5.36 (s, 1H), 4.96 (t, J = 6.0 Hz, 1H), 2.69-2.65 (m, 1H), 2.04-1.73 (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 200.86, 172.66, 136.79, 130.96, 129.81, 128.96, 128.60, 128.03, 127.56, 125.29, 123.71, 109.50, 101.60, 71.02, 31.16, 19.71. IR (neat): 3095, 3066, 3003, 2966, 2917, 2848, 1668, 1637, 1581, 1537, 1487, 1449, 1407, 1384, 1298, 1210, 1143, 1124, 1071, 1029, 1017, 994, 883, 828, 809, 775, 767, 734, 696, 669, 656 cm^{-1}. HRMS (ESI) calcd for $C_{20}H_{18}NO$ [M+H]$^+$: 288.1383, found 288.1386.

Ni-Catalyzed transfer hydrogenation of alkynes.

Typical procedure for the synthesis of 2d from alkyne 11a.

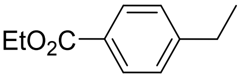


To an oven dried Schlenk tube (25 mL) were added $NiCl_2·6H_2O$ (5.9 mg, 0.025 mmol), Zinc powder (98.1 mg, 1.5 mmol). The Schlenk tube was capped with a rubber septum, evacuated and back filled with argon for three times. Then dioxane (2.5 mL), 1-ethynyl-4-methoxybenzene (66.1 mg, 0.5 mmol) and H_2O (0.8 mL) were added sequentially under argon. The tube cap was then securely fitted and sealed with electrical tape, and the stopcock valve on the sidearm of the Schlenk tube was closed. After the mixture was stirred at 80 °C for 16.5 h, it was filtered through a pad of silica gel and washed with petroleum ether and ethyl ether. **Note: a stirring speed above 600 rpm is highly important for reproducibility.** The solvent was evaporated under the reduced pressure and the residue was purified by column chromatography on silica gel (eluent: petroleum ether to petroleum ether/ethyl ether = 50:1) to give the desired product **2d** in 71% yield (48.1 mg) as a colorless oil. The spectroscopic data are in agreement with that obtained from **1d**.



2e

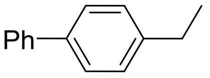
4-Ethylaniline (2e). $NiCl_2·6H_2O$ (5.9 mg, 0.025 mmol), Zinc powder (98.1 mg, 1.5 mmol), 4-ethynylaniline (58.6 mg, 0.5 mmol), dioxane (2.5 mL) and H_2O (0.8 mL) were stirred at 80 °C for 22 h. The mixture was filtered through a pad of silica gel and washed with ethyl ether. Column chromatography on silica gel (eluent: petroleum ether/ethyl ether = 1:1) afforded the desired product **2e** in 93% yield (56.4 mg) as a yellow oil. The spectroscopic data are in agreement with that obtained from **1e**.



12c

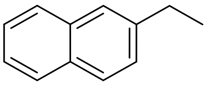
Ethyl 4-ethylbenzoate (12c). $NiCl_2·6H_2O$ (5.9 mg, 0.025 mmol), Zinc powder (98.1 mg, 1.5

mmol), ethyl 4-ethynylbenzoate (87.1 mg, 0.5 mmol), dioxane (2.5 mL) and H_2O (0.8 mL) were stirred at 80 °C for 24 h. The mixture was filtered through a pad of silica gel and washed with petroleum ether and ethyl acetate. Column chromatography on silica gel (eluent: petroleum ether/ethyl acetate = 20:1) afforded the desired product **12c** in 90% yield (80.5 mg) as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.96 (d, J = 8.4 Hz, 2H), 7.24 (d, J = 8.0 Hz, 2H), 4.36 (q, J = 6.8 Hz, 2H), 2.69 (q, J = 7.6 Hz, 2H), 1.38 (t, J = 7.2 Hz, 3H)， 1.24 (t, J = 7.6 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 166.58, 149.50, 129.57, 127.90, 127.73, 60.62, 28.84, 15.15, 14.25. The spectroscopic data are in agreement with that previously reported.[34]



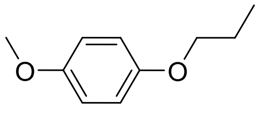
2j

4-Ethyl-1,1'-biphenyl (2j). $NiCl_2 \cdot 6H_2O$ (11.9 mg, 0.05 mmol), Zinc powder (98.1 mg, 1.5 mmol), 4-ethynyl-1,1'-biphenyl (89.1 mg, 0.5 mmol), dioxane (2.5 mL) and H_2O (0.8 mL) were stirred at 80 °C for 24 h. The mixture was filtered through a pad of silica gel and washed with petroleum ether and ethyl acetate. Column chromatography on silica gel (eluent: petroleum ether) afforded the desired product **2j** in 89% yield (80.7 mg) as a white soild. The spectroscopic data are in agreement with that obtained from **1j**.



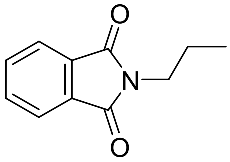
2a

2-Ethylnaphthalene (2a). $NiCl_2 \cdot 6H_2O$ (5.9 mg, 0.025 mmol), Zinc powder (98.1 mg, 1.5 mmol), 2-ethynylnaphthalene (76.1 mg, 0.5 mmol), dioxane (2.5 mL) and H_2O (0.8 mL) were stirred at 80 °C for 10 h. The mixture was filtered through a pad of silica gel and washed with petroleum ether. Column chromatography on silica gel (eluent: petroleum ether) afforded the desired product **2a** in 91% yield (71.3 mg) as a colorless oil. The spectroscopic data are in agreement with that obtained from **1a**.



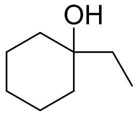
12f

1-Methoxy-4-propoxybenzene (12f). $NiCl_2 \cdot 6H_2O$ (5.9 mg, 0.025 mmol), Zinc powder (98.1 mg, 1.5 mmol), dioxane (2.5 mL), 1-methoxy-4-(prop-2-yn-1-yloxy)benzene (81.1 mg, 0.5 mmol) and H_2O (0.8 mL) were stirred at 80 °C for 22.5 h, the mixture was filtered through a pad of silica gel and washed with ethyl acetate. Column chromatography on silica gel (eluent: petroleum ether/ethyl acetate = 10:1) afforded the desired product **12f** in 68% yield (56.1 mg) as a colorless oil. ^1H NMR (400 MHz, $CDCl_3$): δ 6.82 (s, 4H), 3.85 (t, *J* = 6.8 Hz, 2H), 3.75 (s, 3H), 1.82-1.73 (m, 2H), 1.02 (t, *J* = 7.6 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 153.57, 153.21, 115.32, 114.51, 70.05, 55.62, 22.63, 10.48. The spectroscopic data are in agreement with that previously reported.[35]



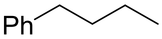
12g

2-Propylisoindoline-1,3-dione (12g). $NiCl_2 \cdot 6H_2O$ (11.9 mg, 0.05 mmol), Zinc powder (98.1 mg, 1.5 mmol), 2-(prop-2-yn-1-yl)isoindoline-1,3-dione (92.6 mg, 0.5 mmol), dioxane (2.5 mL) and H_2O (0.8 mL) were stirred at 80 °C for 23 h. The mixture was filtered through a pad of silica gel and washed with ethyl acetate. Column chromatography on silica gel (eluent: petroleum ether/ethyl acetate = 10:1) afforded the desired product **12g** in 86% yield (81.2 mg) as a white soild. ^1H NMR (400 MHz, $CDCl_3$): δ 7.85-7.83 (m, 2H), 7.73-7.71 (m, 2H), 3.66 (t, *J* = 7.2 Hz, 2H), 1.76-1.67 (m, 2H), 0.96 (t, *J* = 7.6 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 168.30, 133.69, 131.99, 122.98, 39.43, 21.77, 11.19. The spectroscopic data are in agreement with that previously reported.[36]



12h

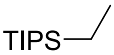
1-Ethylcyclohexan-1-ol (12h). $NiCl_2·6H_2O$ (11.9 mg, 0.05 mmol), Zinc powder (98.1 mg, 1.5 mmol), dioxane (2.5 mL), 1-ethynylcyclohexan-1-ol (62.0 mg, 0.5 mmol) and H_2O (0.8 mL) were stirred at 80 °C for 24 h, the mixture was filtered through a pad of silica gel and washed with petroleum ether and ethyl acetate. Column chromatography on silica gel (eluent: petroleum ether /ethyl acetate = 50:1) afforded the desired product **12h** in 67% yield (43.2 mg) as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.63-1.37 (m, 11H), 1.31-1.24 (m, 2H), 0.90 (t, *J* = 7.6 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 71.38, 36.81, 34.63, 25.82, 22.16, 7.17. The spectroscopic data are in agreement with that previously reported.[37]



12i

Butylbenzene (12i). $NiCl_2·6H_2O$ (11.9 mg, 0.05 mmol), Zinc powder (98.1 mg, 1.5 mmol), dioxane (2.5 mL), but-3-yn-1-ylbenzene (65.1 mg, 0.5 mmol) and H_2O (0.8 mL) were stirred at 80 °C for 24 h, the mixture was filtered through a pad of silica gel and washed with petroleum ether. Column chromatography on silica gel (eluent: petroleum ether) afforded the desired product **12i** in 47% yield (31.7 mg) as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.27 (t, *J* = 7.2 Hz, 2H), 7.20-7.14 (m, 3H), 2.60 (t, *J* = 7.6 Hz, 2H), 1.63-1.56 (m, 2H), 1.40-1.31 (m, 2H), 0.92 (t, *J* = 7.6 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 142.88, 128.39, 128.19, 125.52, 35.66, 33.68, 22.37, 13.96. The spectroscopic data are in agreement with that previously reported.[38]

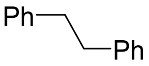
Due to the volatile nature of this compound, the NMR yield was determined. 87% NMR yield of the desired product **12i** was obtained.



12j

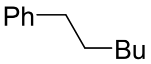
Ethyltriisopropylsilane (12j). $NiCl_2·6H_2O$ (11.9 mg, 0.05 mmol), Zinc powder (98.1 mg, 1.5

mmol), dioxane (2.5 mL), ethynyltriisopropylsilane (91.2 mg, 0.5 mmol) and H_2O (0.8 mL) were stirred at 80 °C for 22 h, the mixture was filtered through a pad of silica gel and washed with pentane. Column chromatography on silica gel (eluent: pentane) afforded the desired product **12j** in 64% yield (59.9 mg) as a white soild. ^1H NMR (400 MHz, $CDCl_3$): δ 1.04-0.97 (m, 24H), 0.60 (q, *J* = 8.0 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 18.84, 10.79, 8.21, 0.85. The spectroscopic data are in agreement with that previously reported.[39]



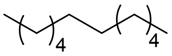
6a

1,2-Diphenylethane (6a). $NiCl_2\cdot 6H_2O$ (11.9 mg, 0.05 mmol), Zinc flake (98.1 mg, 1.5 mmol), 1,2-diphenylethyne (89.1 mg, 0.5 mmol), dioxane (2.5 mL) and H_2O (0.8 mL) were stirred at 80 °C for 24 h. The mixture was filtered through a pad of silica gel and washed with petroleum ether. Column chromatography on silica gel (eluent: petroleum ether) afforded the desired product **6a** in 94% yield (85.4 mg) as a white soild. The spectroscopic data are in agreement with that obtained from **5a**.



12l

Hexylbenzene (12l). $NiCl_2\cdot 6H_2O$ (11.9 mg, 0.05 mmol), Zinc powder (98.1 mg, 1.5 mmol), dioxane (2.5 mL), hex-1-yn-1-ylbenzene (79.1 mg, 0.5 mmol), and H_2O (0.8 mL) were stirred at 80 °C for 24 h. The mixture was filtered through a pad of silica gel and washed with petroleum ether. Column chromatography on silica gel (eluent: petroleum ether) afforded the desired product **12l** in 93% yield (75.3 mg) as a colorless oil. ^1H NMR (400 MHz, $CDCl_3$): δ 7.28-7.24 (m, 2H), 7.18-7.14 (m, 3H), 2.59 (t, *J* = 7.6 Hz, 2H), 1.64-1.57 (m, 2H), 1.36-1.30 (m, 6H), 0.88 (t, *J* = 6.0 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 142.92, 128.38, 128.19, 125.52, 36.00, 31.75, 31.52, 29.03, 22.63, 14.11. The spectroscopic data are in agreement with that previously reported.[10]



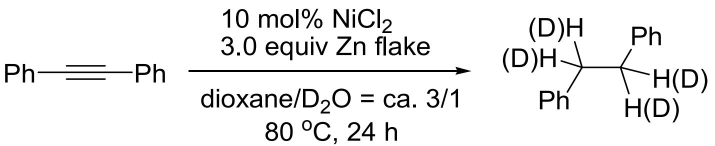
12m

Dodecane (12m). $NiCl_2·6H_2O$ (11.9 mg, 0.05 mmol), Zinc flake (98.1 mg, 1.5 mmol), dioxane (2.5 mL), dodec-6-yne (83.2 mg, 0.5 mmol), and H_2O (0.8 mL) were stirred at 80 °C for 24 h. Column chromatography on silica gel (eluent: petroleum ether) afforded the desired product **12m** in 75% yield (63.6 mg) as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.26 (s, 20H), 0.90-0.86 (m, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 31.99, 29.77, 29.72, 29.43, 22.74, 14.13. The spectroscopic data are in agreement with that previously reported.[41]

Control experiments.

(1) Deuterium labeling experiments.

$NiCl_2$-catalyzed deuterium labeling experiment of 11k with D_2O.

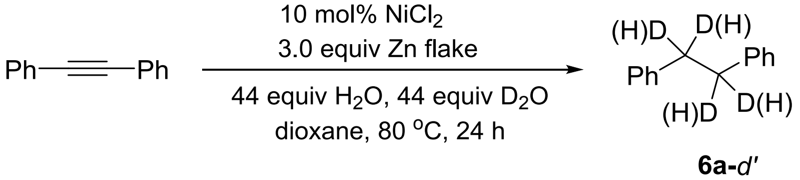


11k

6a-*d*, 86%, D = 91%

To an oven dried Schlenk tube were added $NiCl_2$ (6.5 mg, 0.05 mmol), Zinc flake (98.1 mg, 1.5 mmol), 1,2-diphenylethyne (89.1 mg, 0.5 mmol). The tube was evacuated and back filled with argon for three times, then dioxane (2.5 mL) and D_2O (0.8 mL) were added sequentially under argon. The tube was sealed and the mixture was stirred at 80 °C for 24 h, the mixture was filtered through a pad of silica gel and washed with petroleum ether. The solvent was evaporated under the reduced pressure and the residue was purified by column chromatography on silica gel (eluent: petroleum ether) to give the desired product **6a-*d*** in 86% yield (80.0 mg) as a white soild. ^{11}H NMR (400 MHz, $CDCl_3$): δ 7.28-7.24 (m, 4H), 7.19-7.15 (m, 6H), 2.87 (s, 0.36H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 141.64, 128.40, 128.29, 125.87, 37.77-36.63 (m). HRMS (EI) calcd for $C_{14}H_{10}D_4$ $[M]^+$: 186.1347, found 186.1351.

(2) KIE experiment.

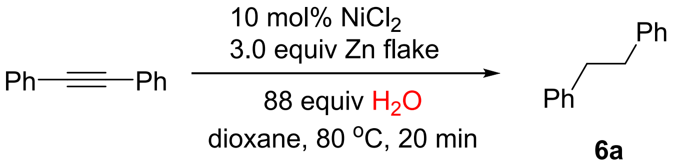


6a-*d'*

To an oven dried Schlenk tube were added $NiCl_2$ (6.5 mg, 0.05 mmol), Zinc flake (98.1

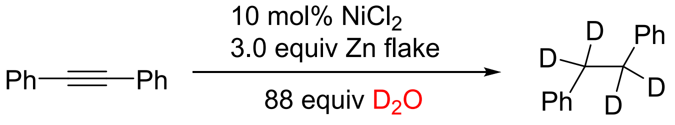
mg, 1.5 mmol), 1,2-diphenylethyne (89.1 mg, 0.5 mmol). The tube was evacuated and back filled with argon for three times, then dioxane (2.5 mL), H_2O (396 mg, 22 mmol, 44 equiv) and D_2O (440 mg, 22 mmol, 44 equiv) were added sequentially under argon. The tube was sealed and the mixture was stirred at 80 °C for 24 h, the mixture was filtered through a pad of silica gel and washed with petroleum ether. The solvent was evaporated under the reduced pressure and the residue was purified by column chromatography on silica gel (eluent: petroleum ether) to give the desired product **6a-*d’*** in 90% yield (82.4 mg) as a colorless oil. （目标产物 FW:183.5）^{1}H NMR (400 MHz, $CDCl_3$): δ 7.27-7.24 (m, 4H), 7.18-7.15 (m, 6H), 2.90-2.87 (m, 2.77H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 141.71, 141.68, 128.40, 128.28, 125.87, 37.90, 37.83, 37.76, 37.53 (t, $J_{C\text{-}D}$ = 19.5 Hz), 37.46 (t, $J_{C\text{-}D}$ = 19.5 Hz). HRMS (EI) calcd for $C_{14}H_{10}D_4$ $[M]^+$: 186.1347, found 186.1345.

Kinetic isotopic effect with individual reaction.



6a

(1)



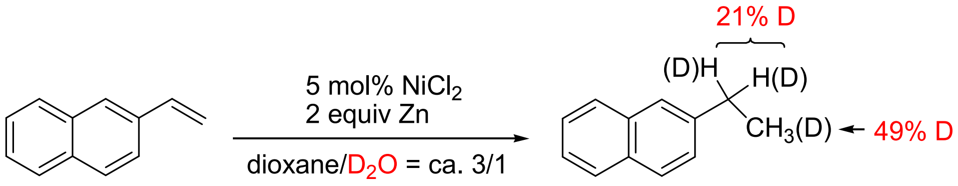
6a-*d*

(2)

Following the general procedure: (1) The reduction of diphenylacetylene with H_2O: $NiCl_2$ (6.5 mg, 0.05 mmol), Zinc flake (98.1 mg, 1.5 mmol), 1,2-diphenylethyne (89.1 mg, 0.5 mmol), dioxane (2.5 mL) and H_2O (792 mg, 44 mmol, 88 equiv) were stirred at 80 °C for 20 min. (2) The reduction of diphenylacetylene with D_2O: $NiCl_2$ (6.5 mg, 0.05 mmol), Zinc flake (98.1 mg, 1.5 mmol), 1,2-diphenylethyne (89.1 mg, 0.5 mmol), dioxane (2.5 mL) and D_2O (881 mg, 44 mmol, 88 equiv) were stirred at 80 °C for 20 min. After quenching the reactions, the mixture of the two reactions was combined and purified by preparative TLC on silica gel (eluent: hexane) to give a mixture of **6a** and **6a**-*d,* along with a byproduct of *E*-stilbene. The ratio of **6a** and **6a**-*d* was determined by ^{1}H NMR, and the KIE of k_H/k_D was found to be 3.0.

(3) Deuterium labeling experiment.

$NiCl_2$-catalyzed deuterium labeling experiment of 1a with D_2O.

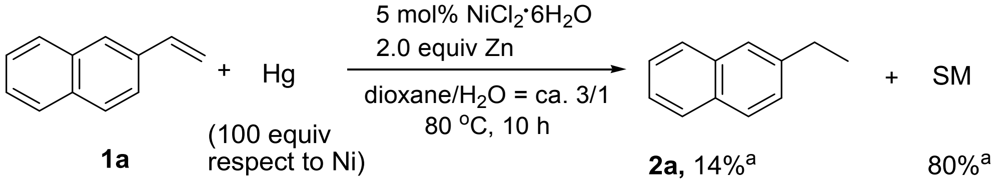


1a

2a-*d*, 92%

To an oven dried Schlenk tube were added $NiCl_2$ (3.2 mg, 0.05 mmol), Zinc powder (65.4 mg, 1.0 mmol), 2-vinylnaphthalene (77.1 mg, 0.5 mmol). The tube was evacuated and back filled with argon for three times, then dioxane (2.5 mL) and D_2O (0.8 mL) were added sequentially under argon. The tube was sealed and the mixture was stirred at 80 °C for 10 h, the mixture was filtered through a pad of silica gel and washed with petroleum ether. The solvent was evaporated under the reduced pressure and the residue was purified by column chromatography on silica gel (eluent: petroleum ether) to give the desired product **2a-*d*** in 92% yield (73.1 mg) as a colorless oil. ^1H NMR (400 MHz, $CDCl_3$): δ 7.77-7.71 (m, 3H), 7.58 (s, 1H), 7.43-7.35 (m, 2H), 7.30 (d, $J = 8.4$ Hz, 1H), 2.80-2.75 (m, 1.59H), 1.34-1.26 (m, 1.54H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 141.70, 133.66, 131.90, 127.76, 127.57, 127.38, 127.04, 125.79, 125.50, 124.96, 29.01, 28.84 (t, $J_{C\text{-}D} = 8.3$ Hz), 15.52, 15.44, 15.22 (t, $J_{C\text{-}D} = 19.4$ Hz). HRMS (EI) calcd for $C_{12}H_{10}D_2$ $[M]^+$: 158.1065, found 158.1060.

(4) Mercury poisoning experiment.



1a

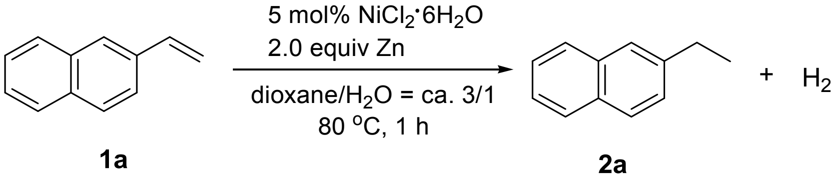
2a, 14%[a]

80%[a]

[a]NMR yield

To an oven dried Schlenk tube were added $NiCl_2 \cdot 6H_2O$ (5.9 mg, 0.025 mmol), Zn (65.4 mg, 1.0 mmol), **1a** (77.1 mg, 0.5 mmol). The tube was evacuated and back filled with argon for three times, then dioxane (2.5 mL), H_2O (0.8 mL) and Hg (501.5 mg, 2.5 mmol, 100 equiv respect to Ni) were added sequentially under argon. The tube was sealed and the mixture was stirred at 80 °C for 10 h, the mixture was filtered through a pad of silica gel and washed with petroleum ether. The solvent was evaporated under the reduced pressure and the residue was dissolved in $CDCl_3$. The NMR yields were obtained by ^1H NMR analysis of the crude mixture using 1, 3, 5-methoxybenzene (84.1 mg, 0.5 mmol) as an internal standard. 14% NMR yield of the desired product **2a** and 80% NMR yield of the **1a** was observed.

(5) Gas-chromatographic analysis of H_2 gas:



The reaction was conducted in an oven-dried screw-cap vial (12 mL) equipped with a magnetic stir bar. In a nitrogen-filled glove box, $NiCl_2·6H_2O$ (5.9 mg, 0.025 mmol), Zinc powder (65.4 mg, 1.0 mmol), 2-vinylnaphthalene (77.1 mg, 0.5 mmol), dioxane (2.5 mL) were added sequentially to a screw-cap vial. The vial cap was then securely fitted and taken outside the glove box, then H_2O (0.8 mL) was added to the vial. After the reaction mixture was stirred at 80 °C for 1 h. The gas in the vial is analyzed by the gas chromatography equipped with TCD detector using N_2 as the carrier gas, and H_2 was detected. H_2 was also detected in the absence of **1a**. See **Figure S1**.

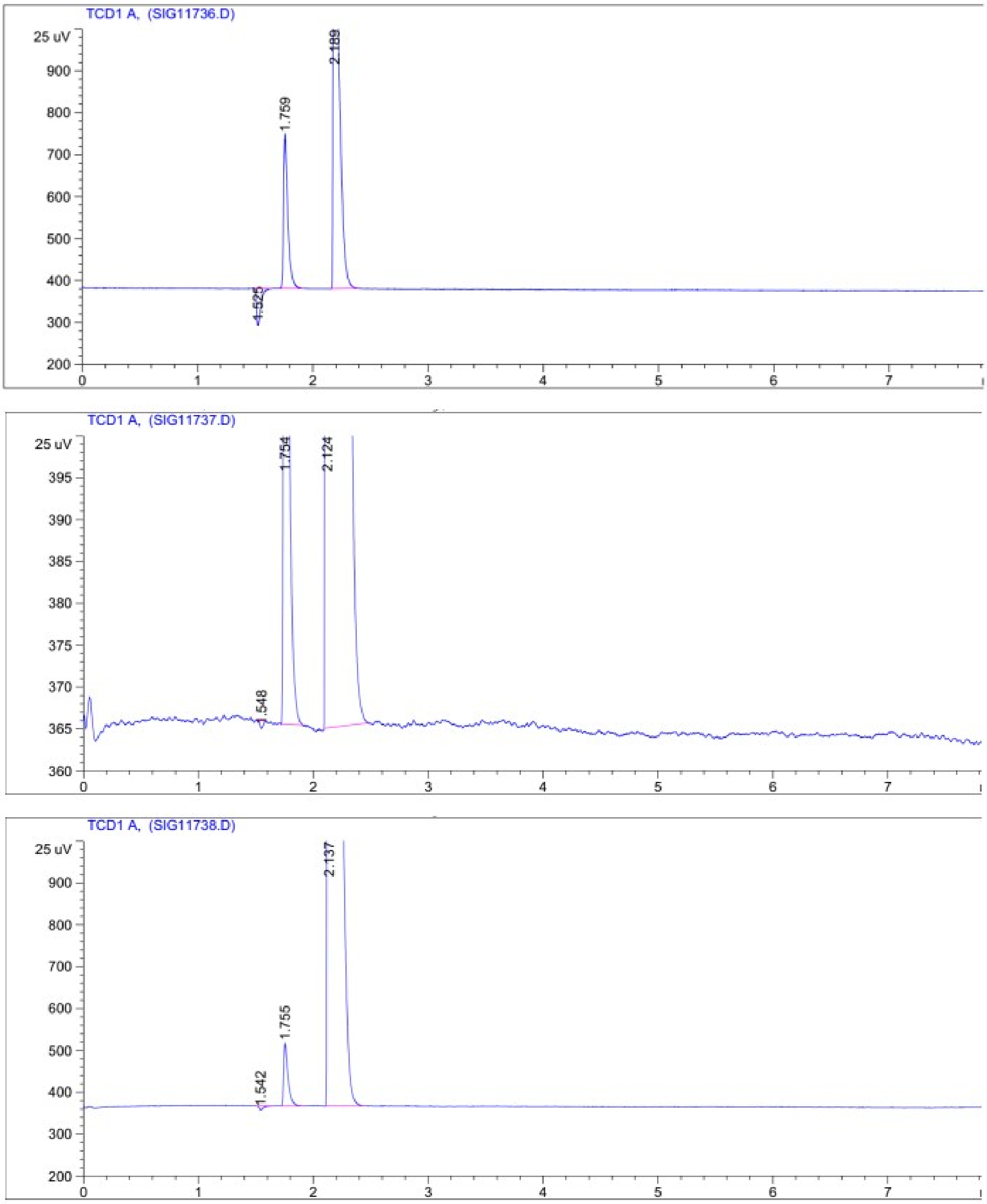
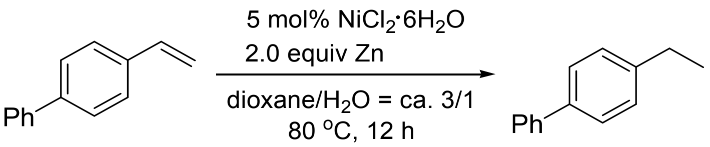


Figure S1. The gas chromatography of the H_2 standard (above). The gas chromatography of the gas in the reaction vial containing alkyne **1a** (middle). The gas chromatography of the gas under the reaction conditions without addition of alkyne **1a** (below). The results indicated that H_2 was formed during the reaction. The retention time of H_2 is around 1.5 min, O_2 is around 1.7 min, and N_2 is around 2.1 min.

1 mmol scale reaction



1j **2j**, 94%

To an oven dried Schlenk tube were added $NiCl_2·6H_2O$ (11.9 mg, 0.05 mmol), Zn (130.8 mg, 2 mmol), and **1j** (180.3 mg, 1 mmol) under air. The Schlenk tube was capped with a rubber septum, evacuated and back filled with argon for three times. Then dioxane (5 mL) and H_2O (1.6 mL) were added sequentially under argon. The tube cap was then securely fitted and sealed with electrical tape, and the stopcock valve on the sidearm of the Schlenk tube was closed. After the mixture was stirred at 80 °C for 12 h, it was filtered through a pad of silica gel and washed with petroleum ether. The solvent was evaporated under the reduced pressure and the residue was purified by column chromatography on silica gel (eluent: petroleum ether) to give the desired product **2j** in 94% yield (171.7 mg) as a white soild.

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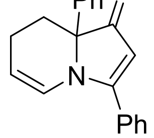
X-ray crystallographic structure and data for compound 10c.

The ellipsoid contour is 30%.



10c

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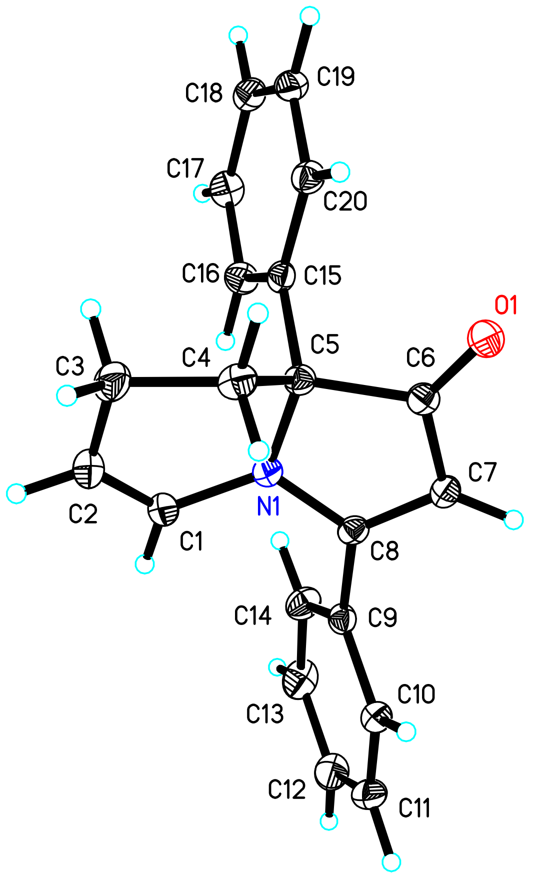


Figure S2. X-ray crystal structure of compound **10c**

Table S2. Crystal data and structure refinement for d8v19160.

Identification code	d8v19160	
Empirical formula	C20 H17 N O	
Formula weight	287.35	
Temperature	194(2) K	
Wavelength	0.71073 Å	
Crystal system	Orthorhombic	
Space group	P b c a	
Unit cell dimensions	a = 14.5964(5) Å	α= 90°.
	b = 13.9382(5) Å	β= 90°.

	c = 14.6669(5) Å	γ = 90°.
Volume	2983.94(18) Å^3	
Z	8	
Density (calculated)	1.279 Mg/m^3	
Absorption coefficient	0.078 mm^{-1}	
F(000)	1216	
Crystal size	0.180 x 0.160 x 0.130 mm^3	
Theta range for data collection	2.452 to 25.993°.	
Index ranges	-18<=h<=15, -17<=k<=15, -18<=l<=17	
Reflections collected	28649	
Independent reflections	2907 [R(int) = 0.0400]	
Completeness to theta = 25.242°	99.4 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.7456 and 0.6536	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	2907 / 0 / 200	
Goodness-of-fit on F^2	1.034	
Final R indices [I>2sigma(I)]	R1 = 0.0359, wR2 = 0.0880	
R indices (all data)	R1 = 0.0422, wR2 = 0.0931	
Extinction coefficient	0.018(2)	
Largest diff. peak and hole	0.254 and -0.156 e.Å^{-3}	

Table S3. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (Å^{2}x 10^3) for d8v19160. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
O(1)	4758(1)	7970(1)	3759(1)	36(1)
N(1)	5932(1)	6078(1)	2663(1)	27(1)
C(1)	5919(1)	5385(1)	1967(1)	32(1)
C(2)	5421(1)	5499(1)	1217(1)	40(1)
C(3)	4781(1)	6326(1)	1086(1)	40(1)
C(4)	4542(1)	6773(1)	2009(1)	33(1)
C(5)	5420(1)	6976(1)	2549(1)	26(1)
C(6)	5216(1)	7267(1)	3549(1)	27(1)
C(7)	5671(1)	6576(1)	4113(1)	28(1)
C(8)	6062(1)	5893(1)	3572(1)	25(1)
C(9)	6593(1)	5049(1)	3876(1)	26(1)
C(10)	6200(1)	4377(1)	4456(1)	29(1)
C(11)	6708(1)	3607(1)	4768(1)	37(1)
C(12)	7618(1)	3514(1)	4518(1)	42(1)
C(13)	8016(1)	4178(1)	3945(1)	42(1)
C(14)	7503(1)	4938(1)	3614(1)	35(1)
C(15)	6012(1)	7744(1)	2094(1)	26(1)
C(16)	6916(1)	7584(1)	1839(1)	32(1)
C(17)	7425(1)	8301(1)	1422(1)	35(1)
C(18)	7037(1)	9187(1)	1252(1)	33(1)
C(19)	6142(1)	9360(1)	1518(1)	32(1)
C(20)	5633(1)	8648(1)	1937(1)	30(1)

Table S4. Bond lengths [Å] and angles [°] for d8v19160.

O(1)-C(6)	1.2258(14)
N(1)-C(8)	1.3708(15)
N(1)-C(1)	1.4067(15)
N(1)-C(5)	1.4674(14)
C(1)-C(2)	1.3276(18)
C(1)-H(1)	0.9500
C(2)-C(3)	1.496(2)
C(2)-H(2)	0.9500
C(3)-C(4)	1.5302(18)
C(3)-H(3A)	0.9900
C(3)-H(3B)	0.9900
C(4)-C(5)	1.5337(16)
C(4)-H(4A)	0.9900
C(4)-H(4B)	0.9900
C(5)-C(15)	1.5289(15)
C(5)-C(6)	1.5513(16)
C(6)-C(7)	1.4325(16)
C(7)-C(8)	1.3634(16)
C(7)-H(7)	0.9500
C(8)-C(9)	1.4782(16)
C(9)-C(10)	1.3888(16)
C(9)-C(14)	1.3920(17)
C(10)-C(11)	1.3824(17)
C(10)-H(10)	0.9500
C(11)-C(12)	1.383(2)
C(11)-H(11)	0.9500
C(12)-C(13)	1.380(2)
C(12)-H(12)	0.9500

C(13)-C(14)	1.3839(18)
C(13)-H(13)	0.9500
C(14)-H(14)	0.9500
C(15)-C(16)	1.3897(17)
C(15)-C(20)	1.3944(16)
C(16)-C(17)	1.3880(17)
C(16)-H(16)	0.9500
C(17)-C(18)	1.3820(18)
C(17)-H(17)	0.9500
C(18)-C(19)	1.3854(19)
C(18)-H(18)	0.9500
C(19)-C(20)	1.3833(17)
C(19)-H(19)	0.9500
C(20)-H(20)	0.9500

C(8)-N(1)-C(1)	125.40(10)
C(8)-N(1)-C(5)	109.96(9)
C(1)-N(1)-C(5)	119.73(9)
C(2)-C(1)-N(1)	121.79(12)
C(2)-C(1)-H(1)	119.1
N(1)-C(1)-H(1)	119.1
C(1)-C(2)-C(3)	122.72(12)
C(1)-C(2)-H(2)	118.6
C(3)-C(2)-H(2)	118.6
C(2)-C(3)-C(4)	110.05(10)
C(2)-C(3)-H(3A)	109.7
C(4)-C(3)-H(3A)	109.7
C(2)-C(3)-H(3B)	109.7
C(4)-C(3)-H(3B)	109.7
H(3A)-C(3)-H(3B)	108.2

C(3)-C(4)-C(5)	109.94(10)
C(3)-C(4)-H(4A)	109.7
C(5)-C(4)-H(4A)	109.7
C(3)-C(4)-H(4B)	109.7
C(5)-C(4)-H(4B)	109.7
H(4A)-C(4)-H(4B)	108.2
N(1)-C(5)-C(15)	111.06(9)
N(1)-C(5)-C(4)	109.14(9)
C(15)-C(5)-C(4)	112.09(9)
N(1)-C(5)-C(6)	102.29(9)
C(15)-C(5)-C(6)	109.76(9)
C(4)-C(5)-C(6)	112.10(10)
O(1)-C(6)-C(7)	130.23(11)
O(1)-C(6)-C(5)	123.46(10)
C(7)-C(6)-C(5)	106.30(9)
C(8)-C(7)-C(6)	109.13(10)
C(8)-C(7)-H(7)	125.4
C(6)-C(7)-H(7)	125.4
C(7)-C(8)-N(1)	112.14(10)
C(7)-C(8)-C(9)	126.86(10)
N(1)-C(8)-C(9)	120.98(10)
C(10)-C(9)-C(14)	119.22(11)
C(10)-C(9)-C(8)	120.32(10)
C(14)-C(9)-C(8)	120.41(10)
C(11)-C(10)-C(9)	120.29(11)
C(11)-C(10)-H(10)	119.9
C(9)-C(10)-H(10)	119.9
C(10)-C(11)-C(12)	120.05(12)
C(10)-C(11)-H(11)	120.0
C(12)-C(11)-H(11)	120.0

C(13)-C(12)-C(11)	120.15(12)
C(13)-C(12)-H(12)	119.9
C(11)-C(12)-H(12)	119.9
C(12)-C(13)-C(14)	119.95(12)
C(12)-C(13)-H(13)	120.0
C(14)-C(13)-H(13)	120.0
C(13)-C(14)-C(9)	120.31(12)
C(13)-C(14)-H(14)	119.8
C(9)-C(14)-H(14)	119.8
C(16)-C(15)-C(20)	118.49(11)
C(16)-C(15)-C(5)	122.75(10)
C(20)-C(15)-C(5)	118.76(10)
C(17)-C(16)-C(15)	120.77(11)
C(17)-C(16)-H(16)	119.6
C(15)-C(16)-H(16)	119.6
C(18)-C(17)-C(16)	120.26(11)
C(18)-C(17)-H(17)	119.9
C(16)-C(17)-H(17)	119.9
C(17)-C(18)-C(19)	119.39(11)
C(17)-C(18)-H(18)	120.3
C(19)-C(18)-H(18)	120.3
C(20)-C(19)-C(18)	120.48(11)
C(20)-C(19)-H(19)	119.8
C(18)-C(19)-H(19)	119.8
C(19)-C(20)-C(15)	120.59(11)
C(19)-C(20)-H(20)	119.7
C(15)-C(20)-H(20)	119.7

Symmetry transformations used to generate equivalent atoms:

Table S5. Anisotropic displacement parameters ($Å^2$x 10^3) for d8v19160. The anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2 a^{*2}U^{11} + ... + 2 h k a^* b^* U^{12}]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
O(1)	36(1)	34(1)	37(1)	0(1)	7(1)	9(1)
N(1)	31(1)	25(1)	24(1)	1(1)	0(1)	2(1)
C(1)	41(1)	28(1)	28(1)	-2(1)	4(1)	0(1)
C(2)	53(1)	39(1)	28(1)	-5(1)	-2(1)	-4(1)
C(3)	45(1)	44(1)	30(1)	2(1)	-10(1)	-8(1)
C(4)	29(1)	36(1)	35(1)	5(1)	-5(1)	-3(1)
C(5)	27(1)	26(1)	26(1)	2(1)	0(1)	2(1)
C(6)	23(1)	28(1)	29(1)	0(1)	4(1)	-2(1)
C(7)	29(1)	31(1)	24(1)	1(1)	1(1)	-1(1)
C(8)	22(1)	27(1)	25(1)	3(1)	0(1)	-4(1)
C(9)	27(1)	27(1)	23(1)	-2(1)	-2(1)	0(1)
C(10)	30(1)	30(1)	28(1)	1(1)	1(1)	-1(1)
C(11)	47(1)	30(1)	35(1)	6(1)	3(1)	3(1)
C(12)	50(1)	39(1)	37(1)	3(1)	-1(1)	19(1)
C(13)	33(1)	54(1)	40(1)	2(1)	4(1)	14(1)
C(14)	31(1)	40(1)	35(1)	6(1)	6(1)	2(1)
C(15)	28(1)	29(1)	21(1)	-1(1)	-2(1)	-1(1)
C(16)	29(1)	30(1)	35(1)	0(1)	1(1)	3(1)
C(17)	28(1)	39(1)	38(1)	-2(1)	3(1)	-2(1)
C(18)	35(1)	35(1)	28(1)	2(1)	-2(1)	-9(1)
C(19)	39(1)	28(1)	30(1)	3(1)	-5(1)	1(1)
C(20)	29(1)	32(1)	28(1)	2(1)	-1(1)	4(1)

Table S6. Hydrogen coordinates (x 10^4) and isotropic displacement parameters ($Å^2$x 10 ^{3}) for d8v19160.

	x	y	z	U(eq)
H(1)	6277	4820	2034	39
H(2)	5473	5036	745	48
H(3A)	4215	6102	782	48
H(3B)	5073	6814	691	48
H(4A)	4145	6329	2358	40
H(4B)	4200	7378	1913	40
H(7)	5696	6590	4760	33
H(10)	5579	4446	4639	35
H(11)	6433	3142	5154	45
H(12)	7969	2991	4743	50
H(13)	8642	4115	3777	50
H(14)	7774	5385	3206	42
H(16)	7188	6976	1951	38
H(17)	8043	8182	1254	42
H(18)	7381	9674	954	40
H(19)	5875	9972	1413	38
H(20)	5020	8775	2119	35

Table S7. Torsion angles [°] for d8v19160.

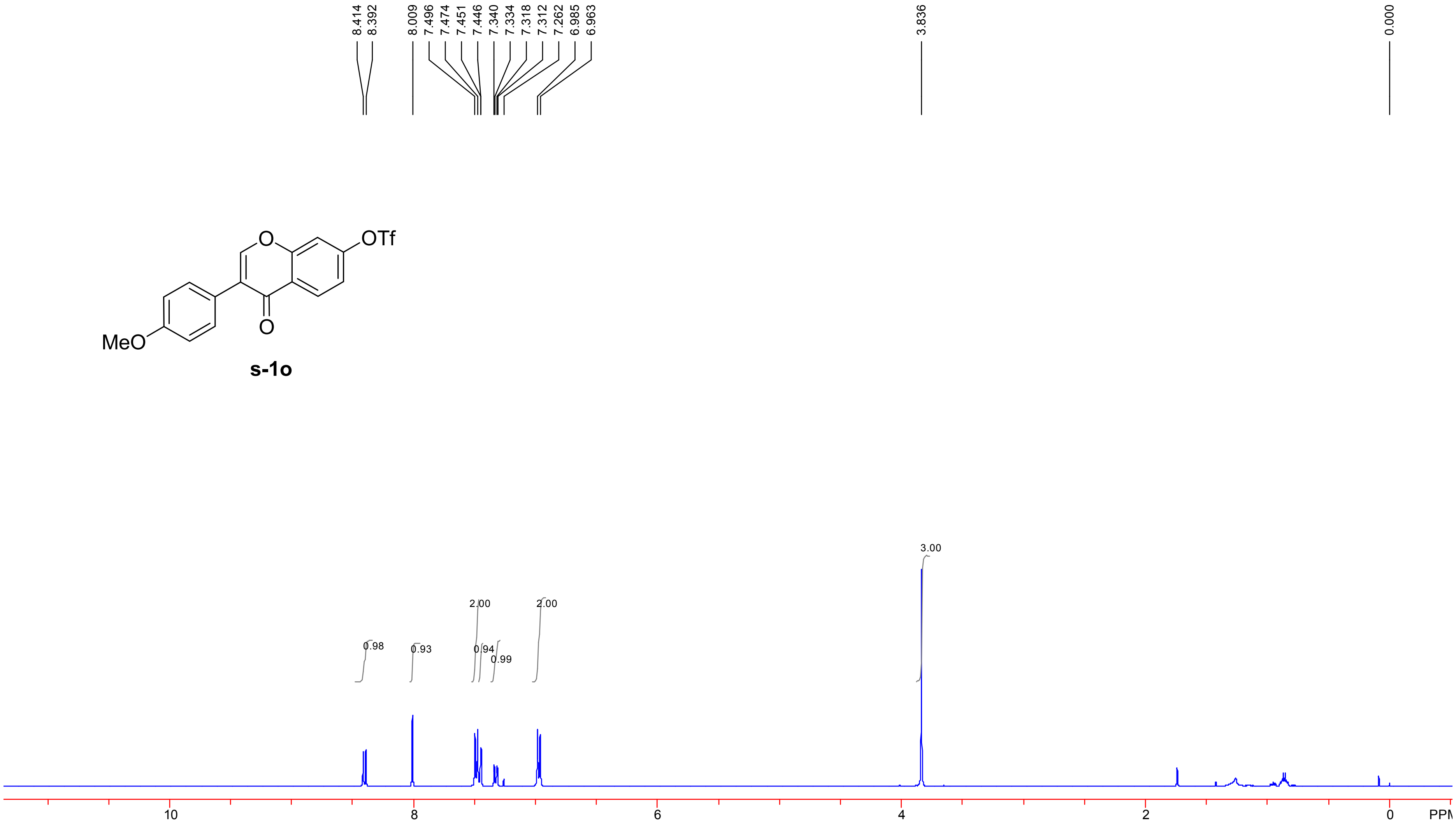
C(8)-N(1)-C(1)-C(2)	149.63(13)
C(5)-N(1)-C(1)-C(2)	-3.01(17)
N(1)-C(1)-C(2)-C(3)	-5.0(2)
C(1)-C(2)-C(3)-C(4)	-19.83(18)
C(2)-C(3)-C(4)-C(5)	50.40(14)
C(8)-N(1)-C(5)-C(15)	113.91(10)
C(1)-N(1)-C(5)-C(15)	-89.57(12)
C(8)-N(1)-C(5)-C(4)	-122.03(10)
C(1)-N(1)-C(5)-C(4)	34.49(14)
C(8)-N(1)-C(5)-C(6)	-3.14(12)
C(1)-N(1)-C(5)-C(6)	153.38(10)
C(3)-C(4)-C(5)-N(1)	-57.70(13)
C(3)-C(4)-C(5)-C(15)	65.75(13)
C(3)-C(4)-C(5)-C(6)	-170.29(10)
N(1)-C(5)-C(6)-O(1)	-176.88(10)
C(15)-C(5)-C(6)-O(1)	65.14(14)
C(4)-C(5)-C(6)-O(1)	-60.10(14)
N(1)-C(5)-C(6)-C(7)	4.09(11)
C(15)-C(5)-C(6)-C(7)	-113.89(10)
C(4)-C(5)-C(6)-C(7)	120.87(10)
O(1)-C(6)-C(7)-C(8)	177.32(12)
C(5)-C(6)-C(7)-C(8)	-3.74(12)
C(6)-C(7)-C(8)-N(1)	1.84(13)
C(6)-C(7)-C(8)-C(9)	-179.73(10)
C(1)-N(1)-C(8)-C(7)	-153.85(11)
C(5)-N(1)-C(8)-C(7)	1.02(13)
C(1)-N(1)-C(8)-C(9)	27.62(17)
C(5)-N(1)-C(8)-C(9)	-177.51(9)

C(7)-C(8)-C(9)-C(10)	58.47(16)
N(1)-C(8)-C(9)-C(10)	-123.23(12)
C(7)-C(8)-C(9)-C(14)	-118.95(14)
N(1)-C(8)-C(9)-C(14)	59.35(15)
C(14)-C(9)-C(10)-C(11)	-0.04(18)
C(8)-C(9)-C(10)-C(11)	-177.48(11)
C(9)-C(10)-C(11)-C(12)	1.36(19)
C(10)-C(11)-C(12)-C(13)	-1.2(2)
C(11)-C(12)-C(13)-C(14)	-0.3(2)
C(12)-C(13)-C(14)-C(9)	1.7(2)
C(10)-C(9)-C(14)-C(13)	-1.48(19)
C(8)-C(9)-C(14)-C(13)	175.96(12)
N(1)-C(5)-C(15)-C(16)	-0.36(15)
C(4)-C(5)-C(15)-C(16)	-122.72(12)
C(6)-C(5)-C(15)-C(16)	112.03(12)
N(1)-C(5)-C(15)-C(20)	-179.69(10)
C(4)-C(5)-C(15)-C(20)	57.95(14)
C(6)-C(5)-C(15)-C(20)	-67.31(13)
C(20)-C(15)-C(16)-C(17)	-1.09(17)
C(5)-C(15)-C(16)-C(17)	179.58(11)
C(15)-C(16)-C(17)-C(18)	-0.29(19)
C(16)-C(17)-C(18)-C(19)	1.40(18)
C(17)-C(18)-C(19)-C(20)	-1.14(18)
C(18)-C(19)-C(20)-C(15)	-0.25(18)
C(16)-C(15)-C(20)-C(19)	1.35(17)
C(5)-C(15)-C(20)-C(19)	-179.29(10)

Symmetry transformations used to generate equivalent atoms:

Table S8. Hydrogen bonds for d8v19160 [Å and °].

D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)


OTf
O
O
MeO

s-1o

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8.392
8.009
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7.451
7.446
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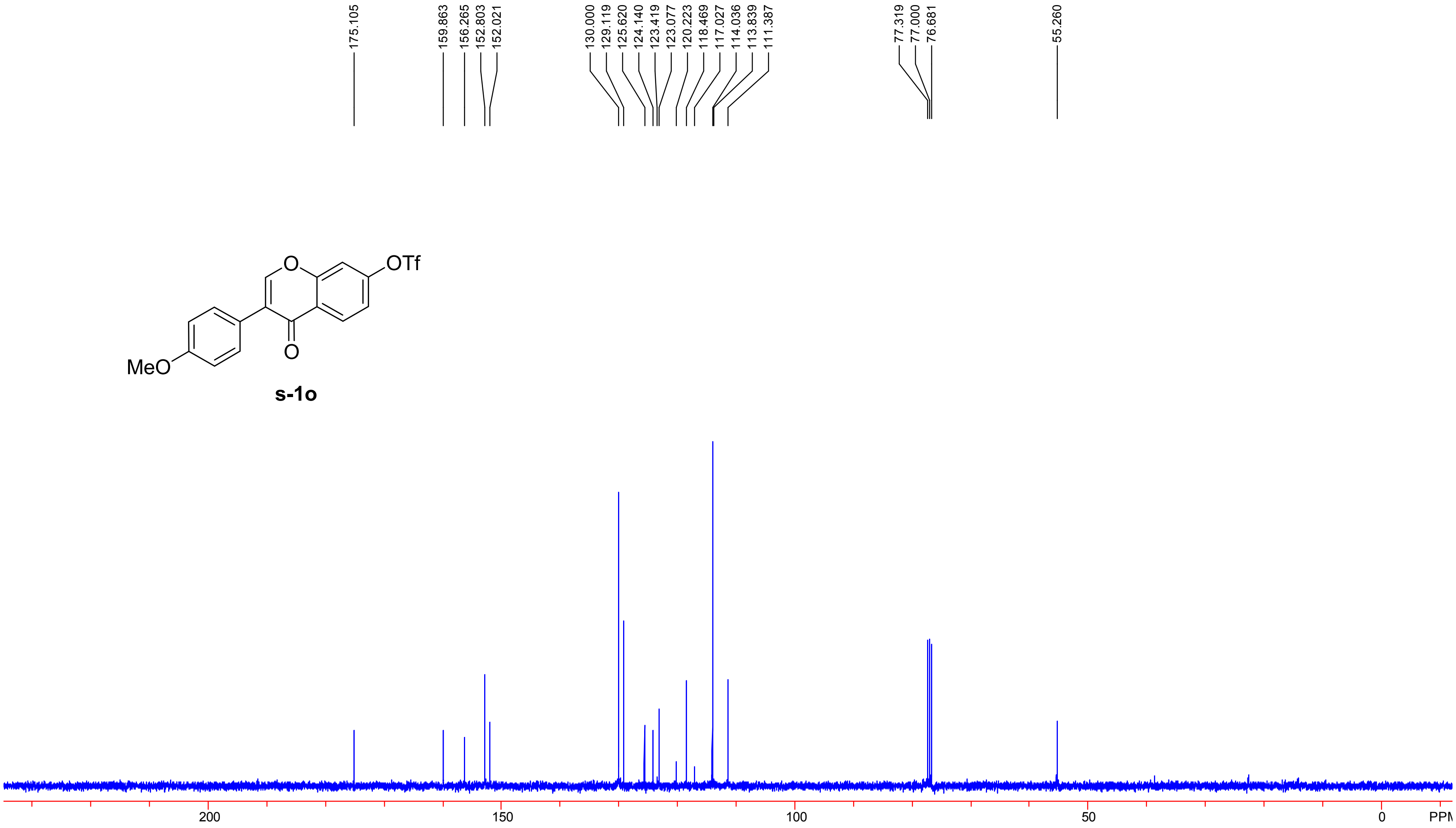
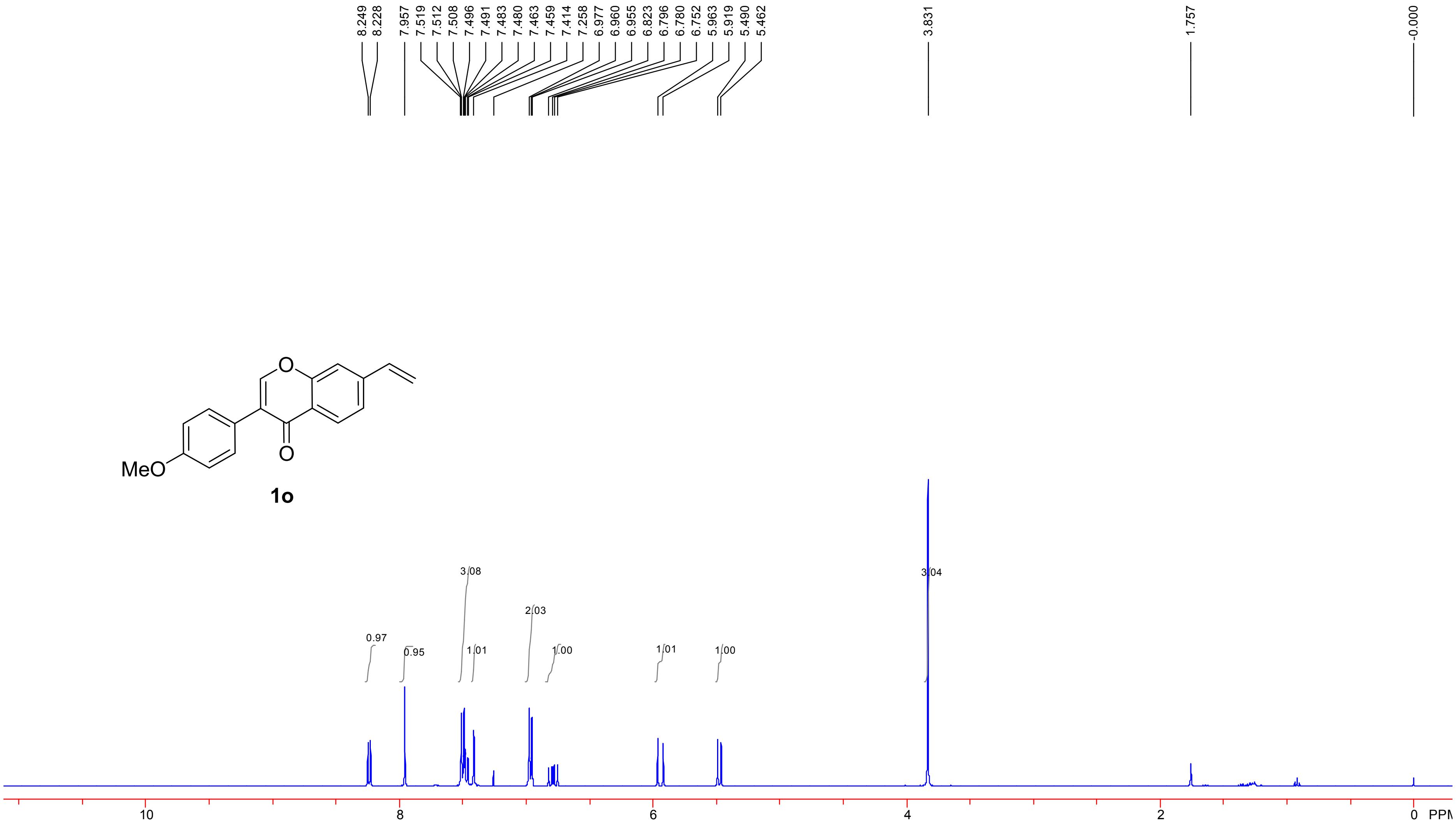
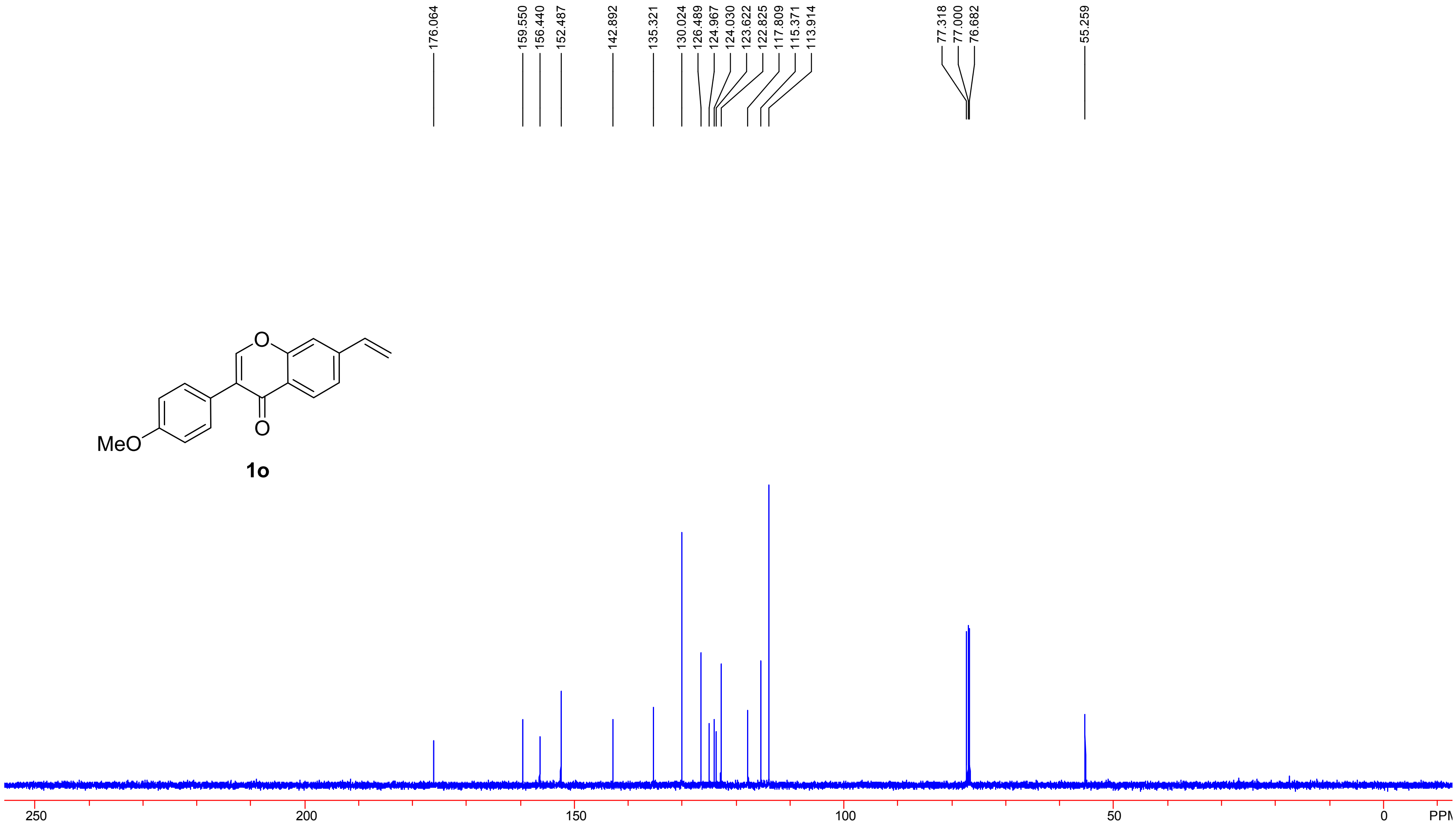
7.334
7.318
7.312
7.262
6.985
6.963
3.836
0.000
3.00
2.00
2.00
0.98
0.93
0.94
0.99
10
8
6
4
2
0
PPM



s-1o

175.105
159.863
156.265
152.803
152.021
130.000
129.119
125.620
124.140
123.419
123.077
120.223
118.469
117.027
114.036
113.839
111.387
77.319
77.000
76.681
55.260
200
150
100
50
0
PPM


8.249
8.228
7.957
7.519
7.512
7.508
7.496
7.491
7.483
7.480
7.463
7.459
7.414
7.258
6.977
6.960
6.955
6.823
6.796
6.780
6.752
5.963
5.919
5.490
5.462
3.831
1.757
-0.000
MeO
O
O
1o
0.97
0.95
3.08
1.01
2.03
1.00
1.01
1.00
3.04
10
8
6
4
2
0
PP

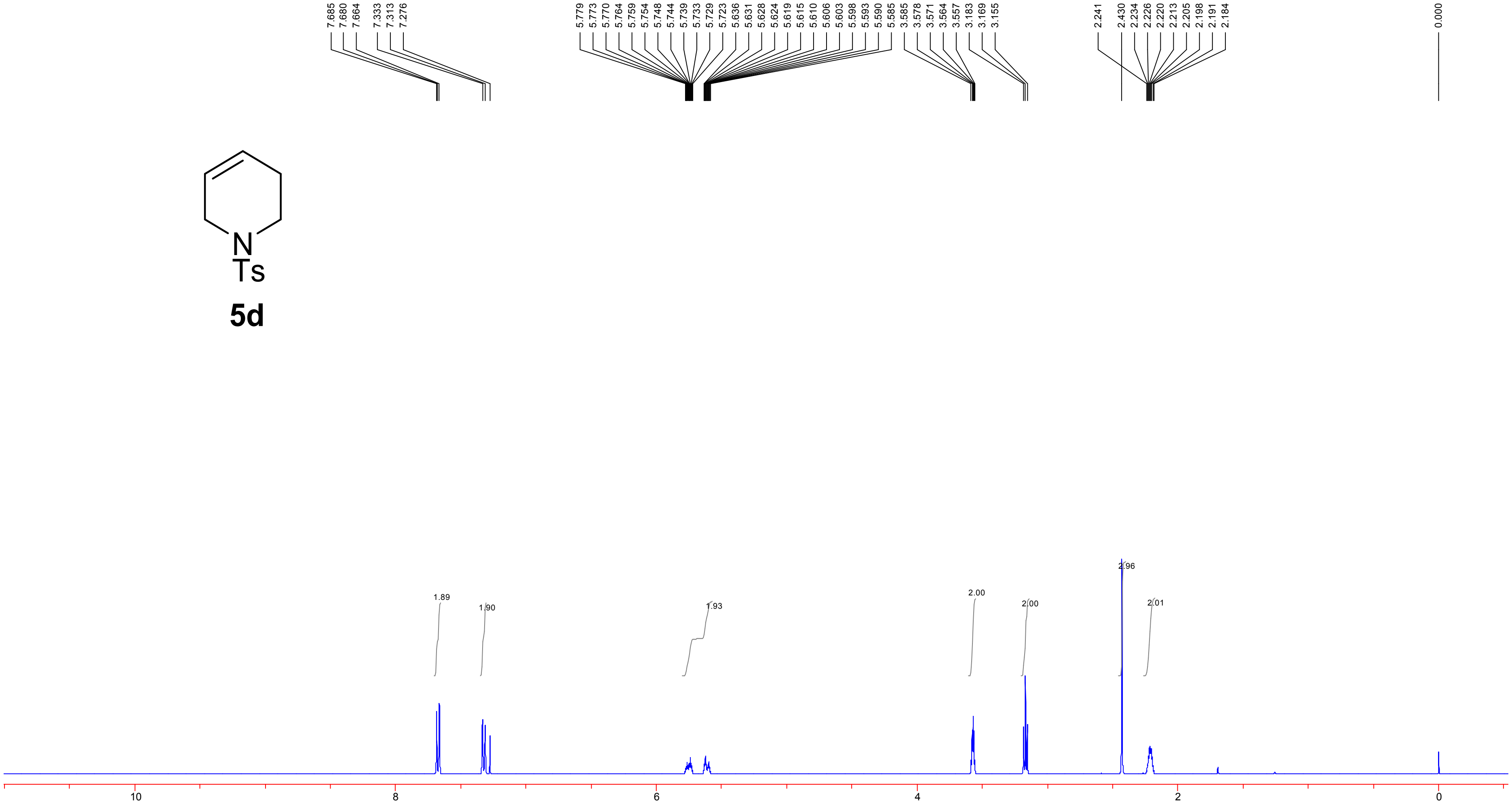


1o

MeO
O
O
176.064
159.550
156.440
152.487
142.892
135.321
130.024
126.489
124.967
124.030
123.622
122.825
117.809
115.371
113.914
77.318
77.000
76.682
55.259
250
200
150
100
50
0
PPM

N
Ts

5d


7.685
7.680
7.664
7.333
7.313
7.276
5.779
5.773
5.770
5.764
5.759
5.754
5.748
5.744
5.739
5.733
5.729
5.723
5.636
5.631
5.628
5.624
5.619
5.615
5.610
5.606
5.603
5.598
5.593
5.590
5.585
3.585
3.578
3.571
3.564
3.557
3.183
3.169
3.155
2.241
2.430
2.234
2.226
2.220
2.213
2.205
2.198
2.191
2.184
0.000
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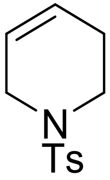
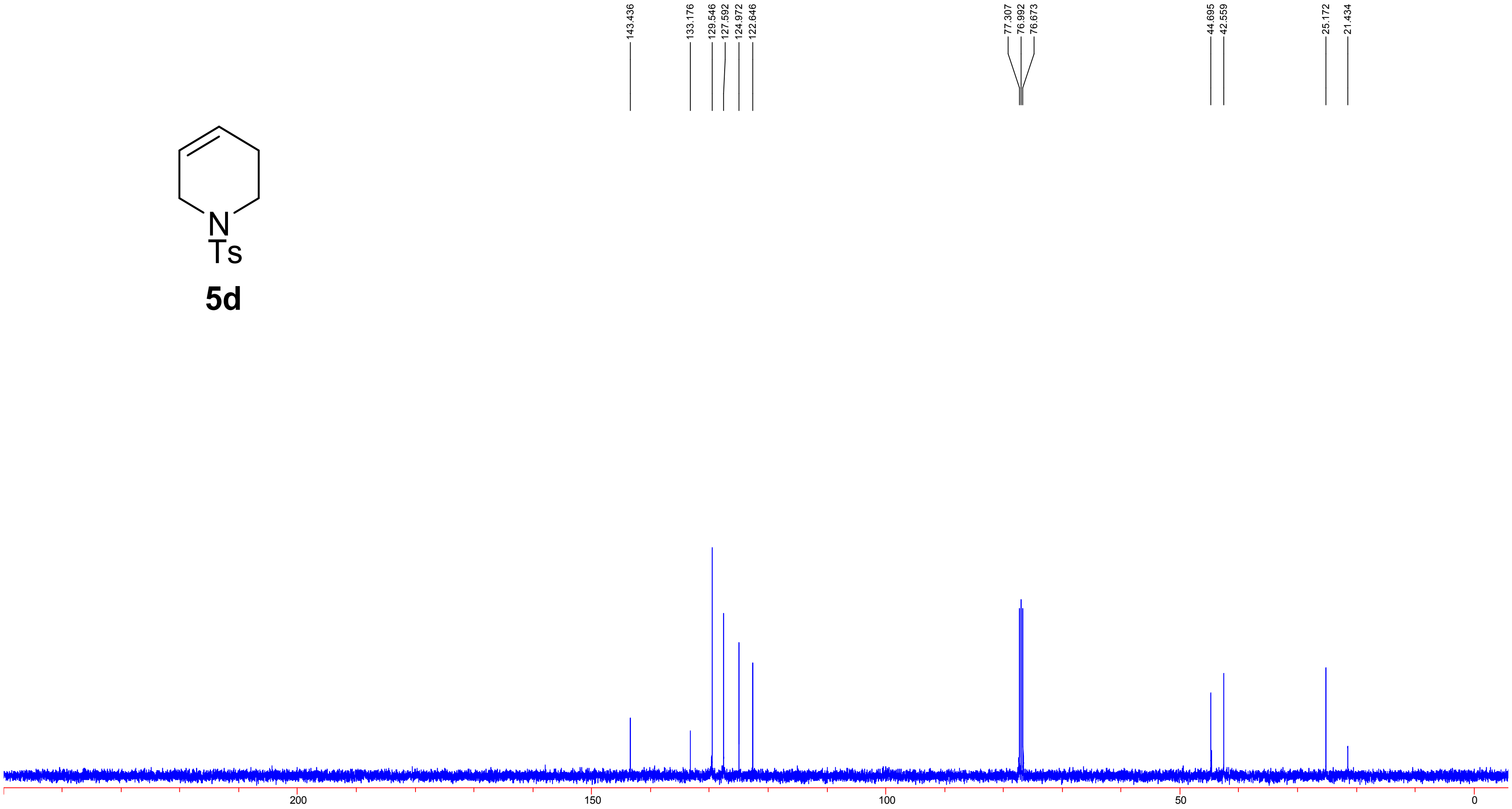
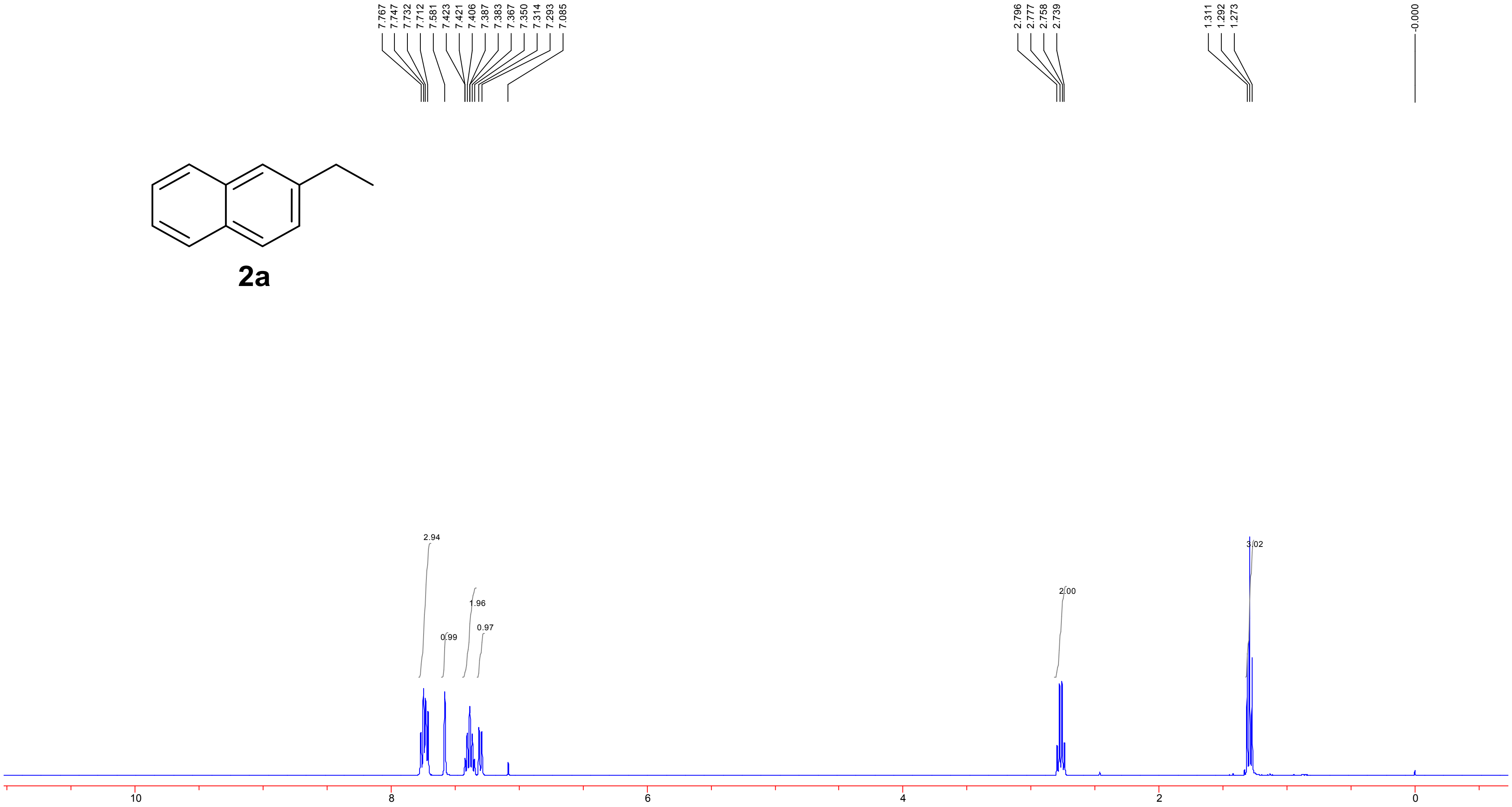
1.90
1.93
2.00
2.00
2.96
2.01
10
8
6
4
2
0


N
Ts

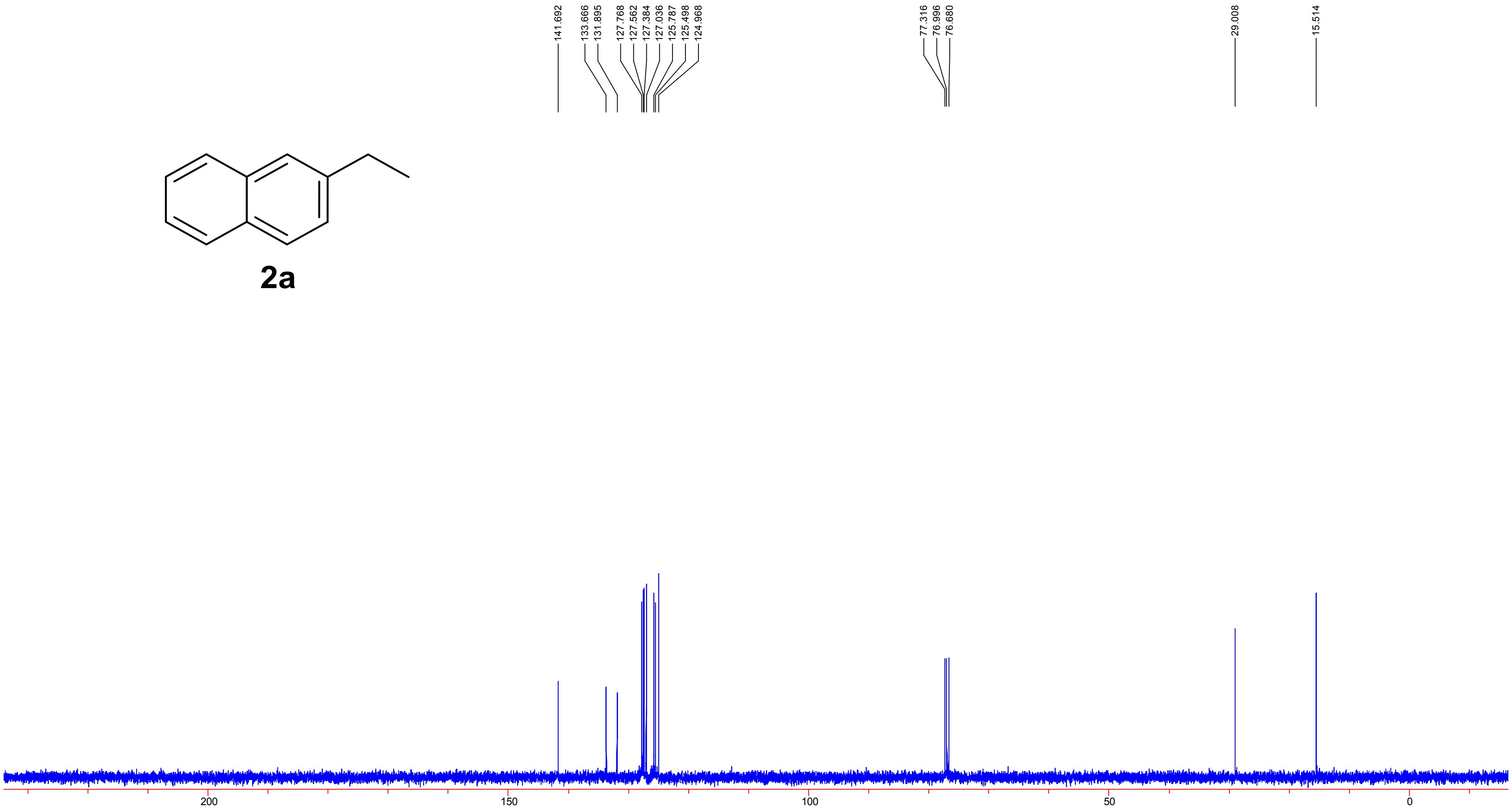
5d


143.436
133.176
129.546
127.592
124.972
122.646
77.307
76.992
76.673
44.695
42.559
25.172
21.434
200
150
100
50
0



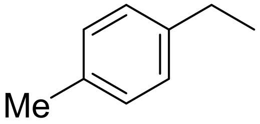
2a

7.767
7.747
7.732
7.712
7.581
7.423
7.421
7.406
7.387
7.383
7.367
7.350
7.314
7.293
7.085
2.796
2.777
2.758
2.739
1.311
1.292
1.273
-0.000
2.94
0.99
1.96
0.97
2.00
3.02
10
8
6
4
2
0

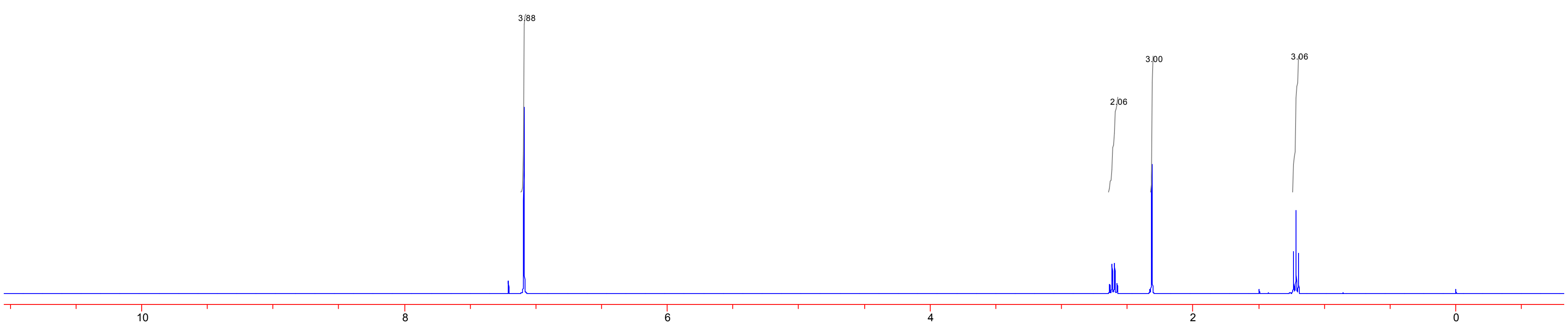


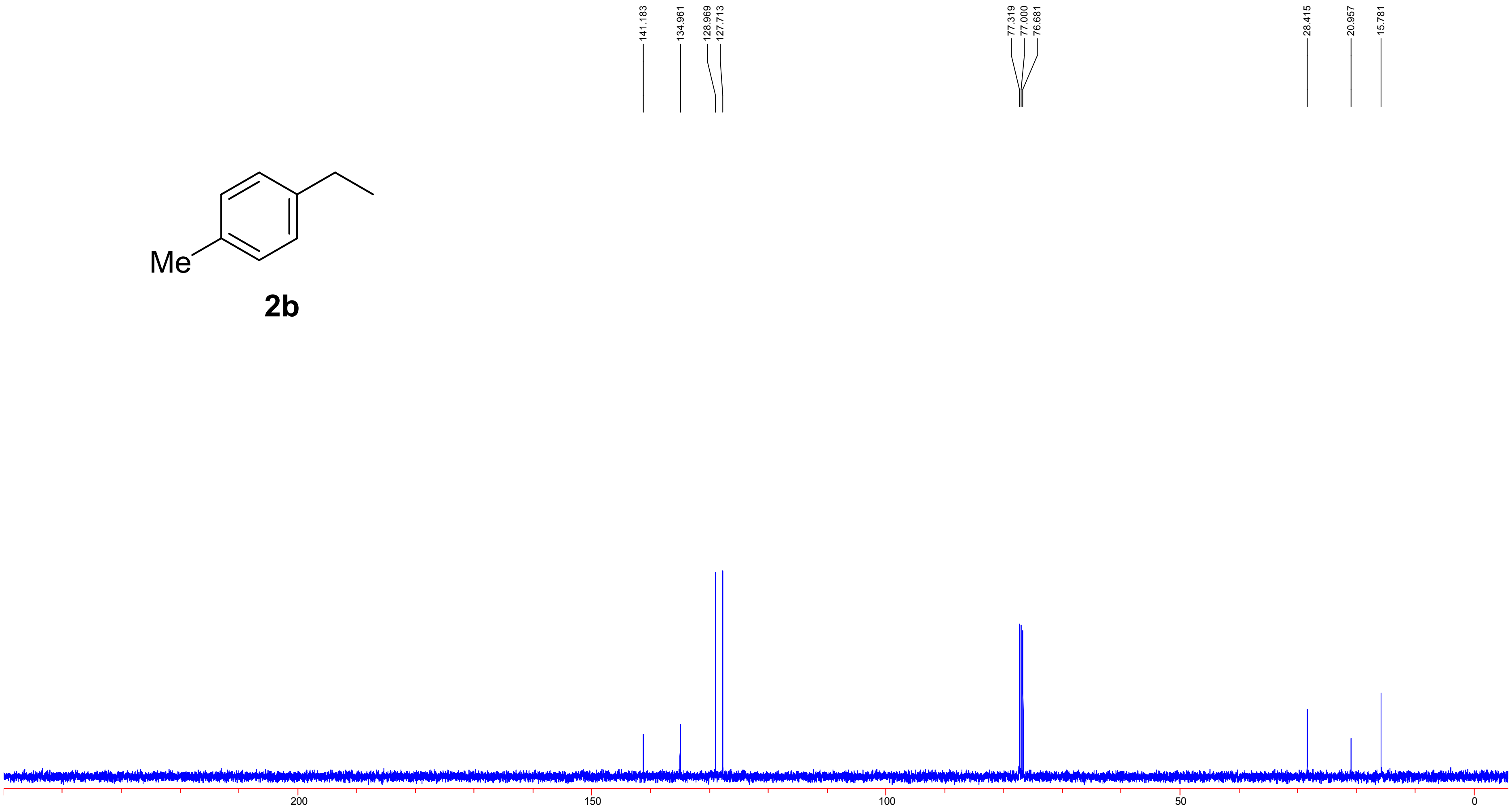
2a

141.692
133.666
131.895
127.768
127.562
127.384
127.036
125.787
125.498
124.968
77.316
76.996
76.680
29.008
15.514
200
150
100
50
0


Me

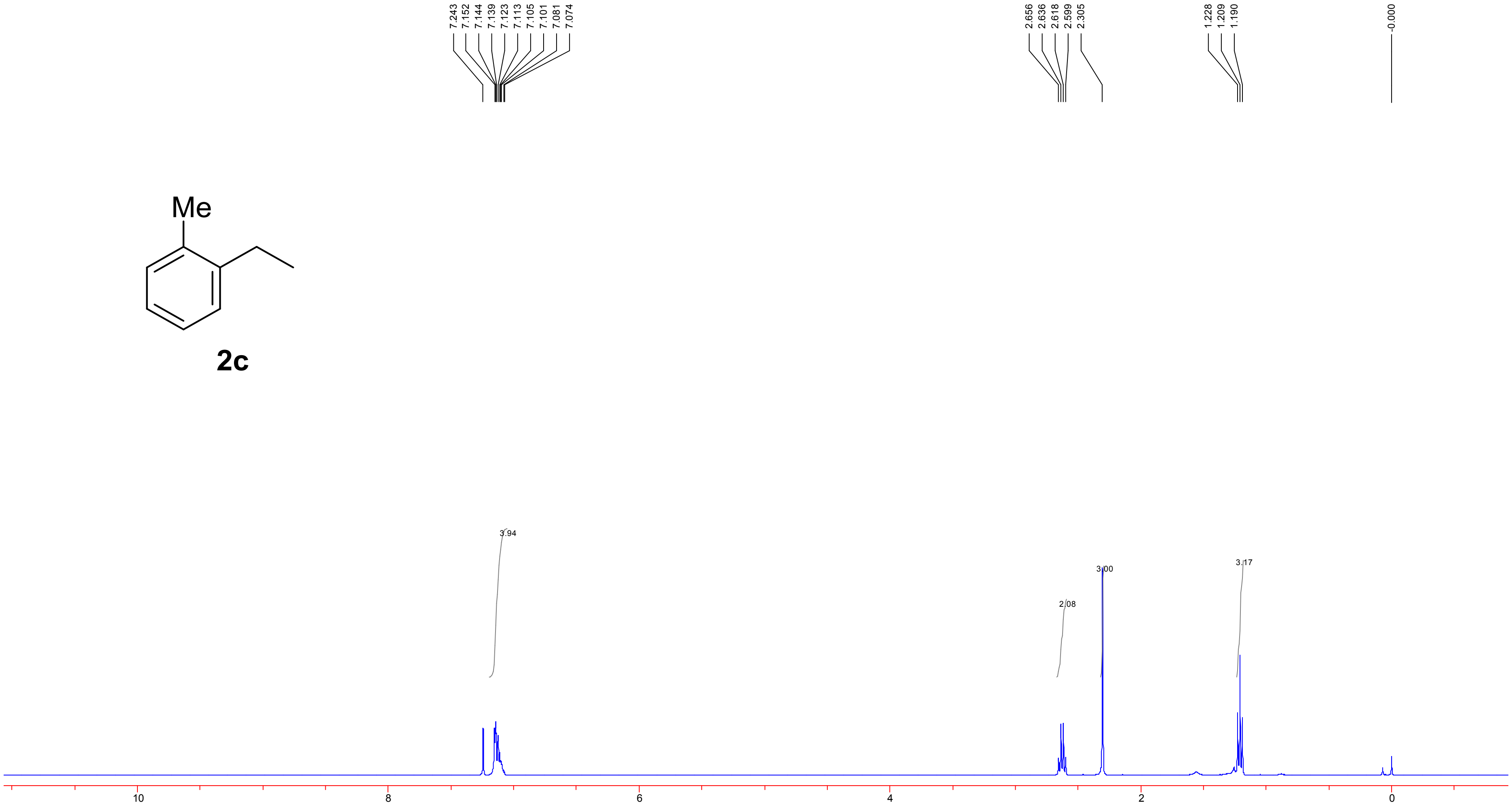
2b


7.208
7.090
2.633
2.614
2.596
2.577
2.313
1.235
1.216
1.197
3.88
2.06
3.00
3.06
10
8
6
4
2
0

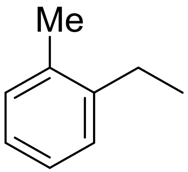


2b

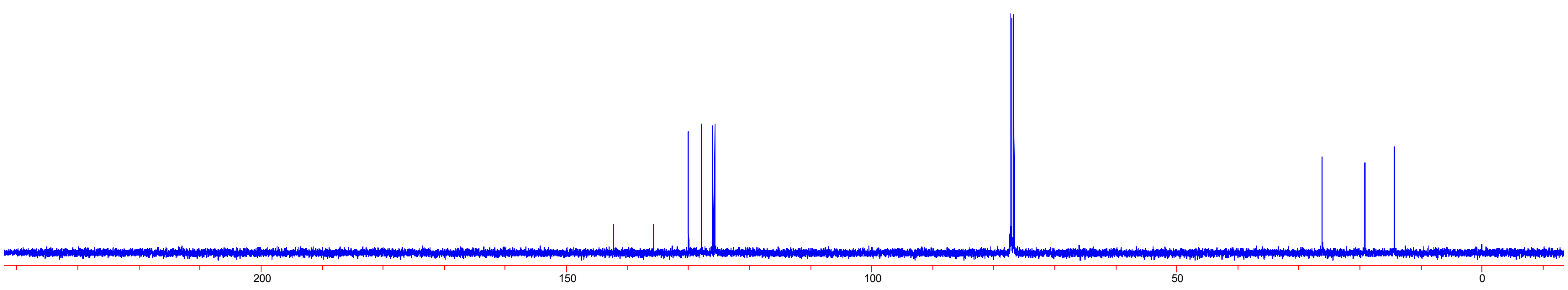
141.183
134.961
128.969
127.713
77.319
77.000
76.681
28.415
20.957
15.781
Me
200
150
100
50
0

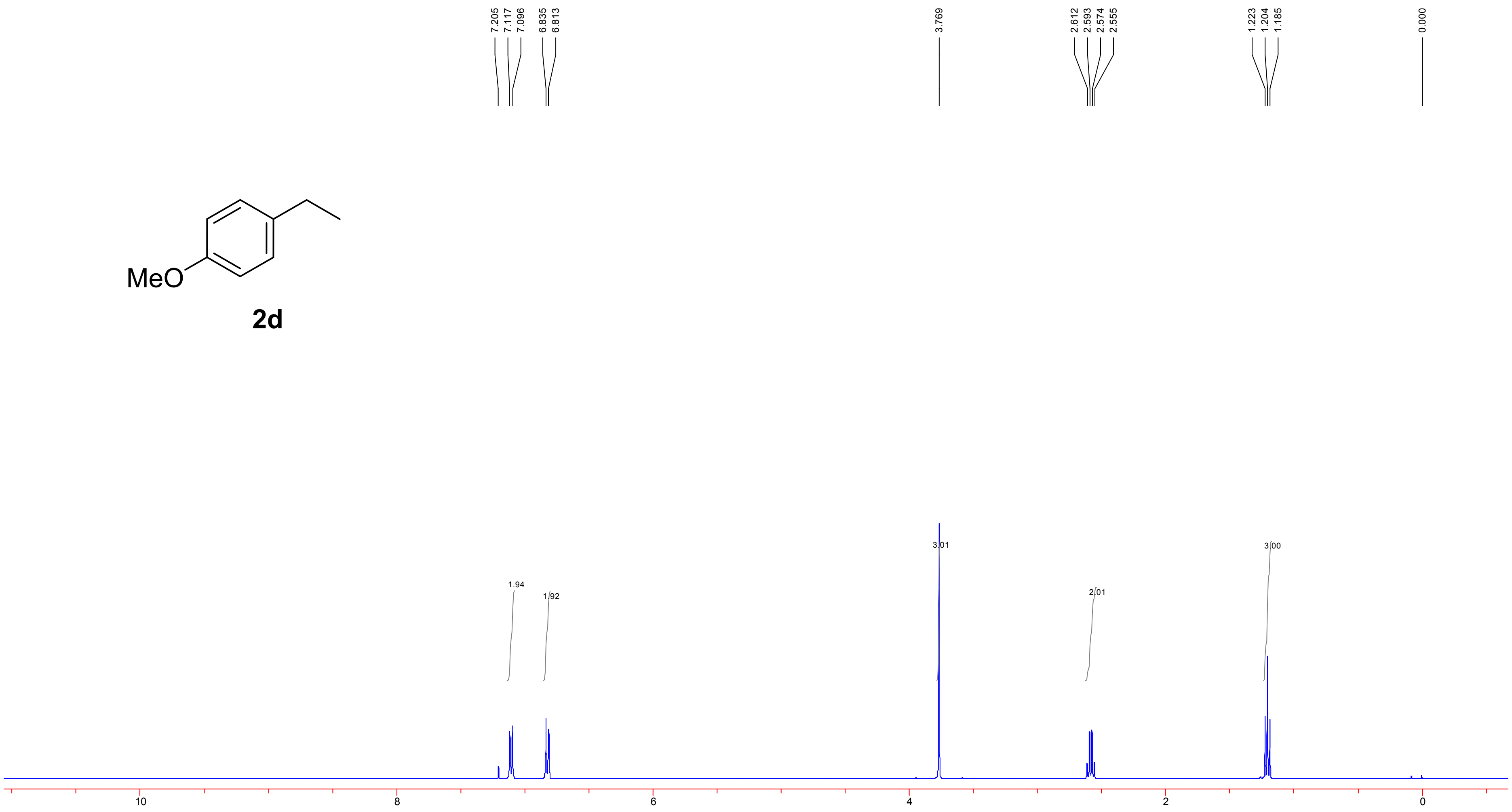

7.243
7.152
7.144
7.139
7.123
7.113
7.105
7.101
7.081
7.074
2.656
2.636
2.618
2.599
2.305
1.228
1.209
1.190
-0.000
Me
3.94
2.08
3.00
3.17
10
8
6
4
2
0

2c


Me

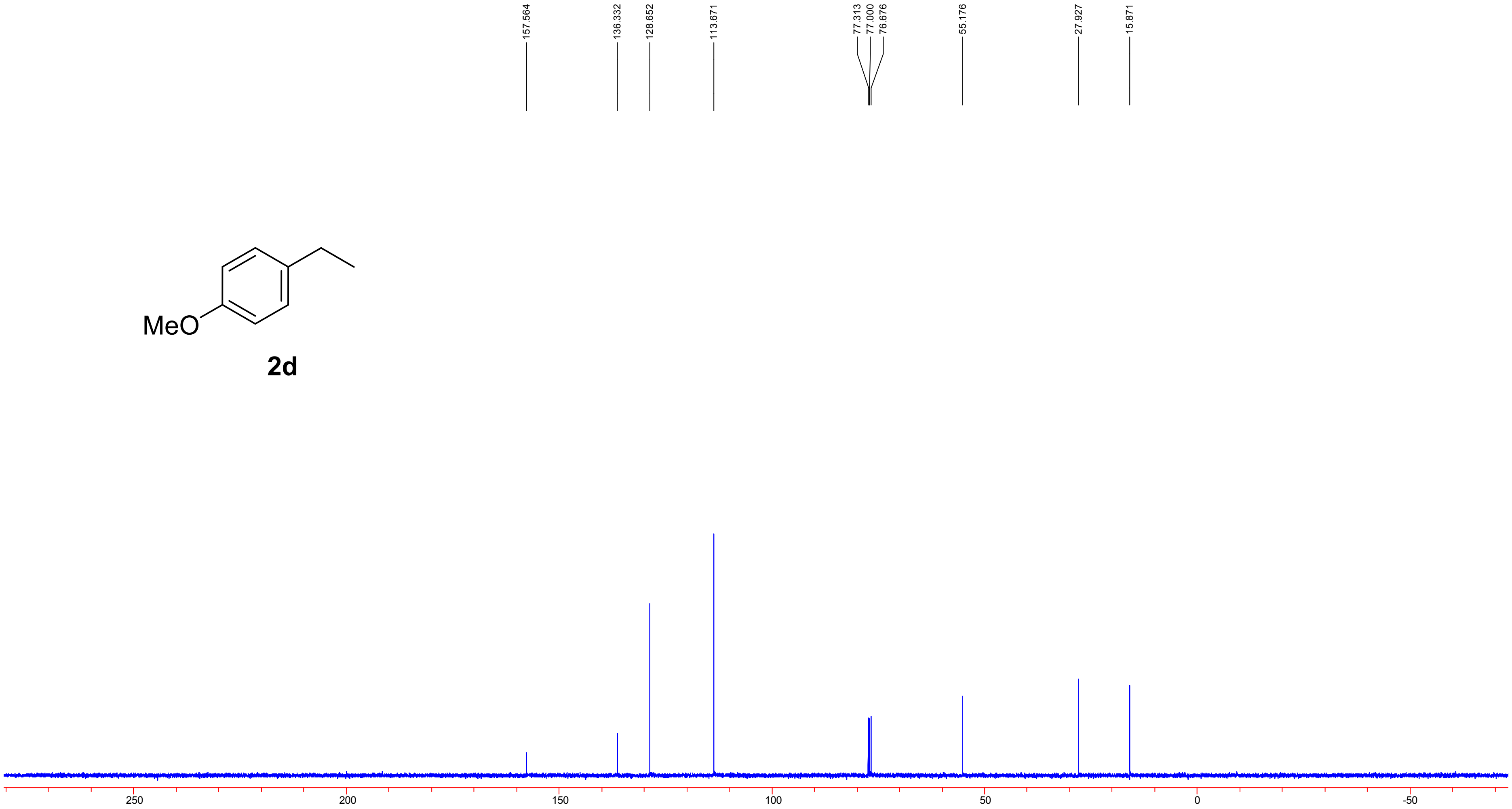
2c


142.291
135.731
129.986
127.856
125.979
125.697
77.319
77.206
77.000
76.685
26.153
19.149
14.355
200
150
100
50
0



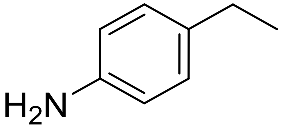
2d

7.205
7.117
7.096
6.835
6.813
3.769
2.612
2.593
2.574
2.555
1.223
1.204
1.185
0.000
MeO
1.94
1.92
3.01
2.01
3.00
10
8
6
4
2
0

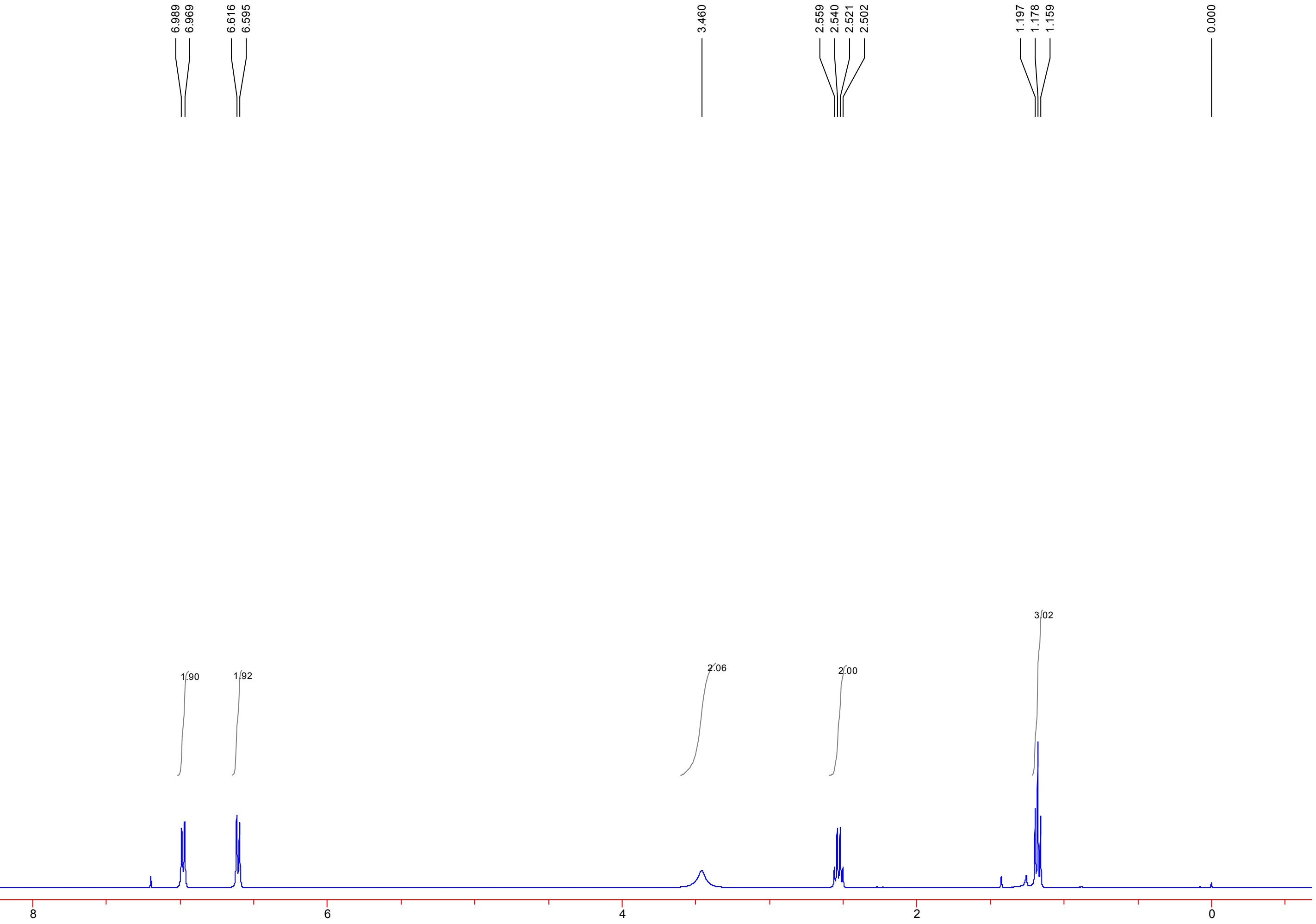


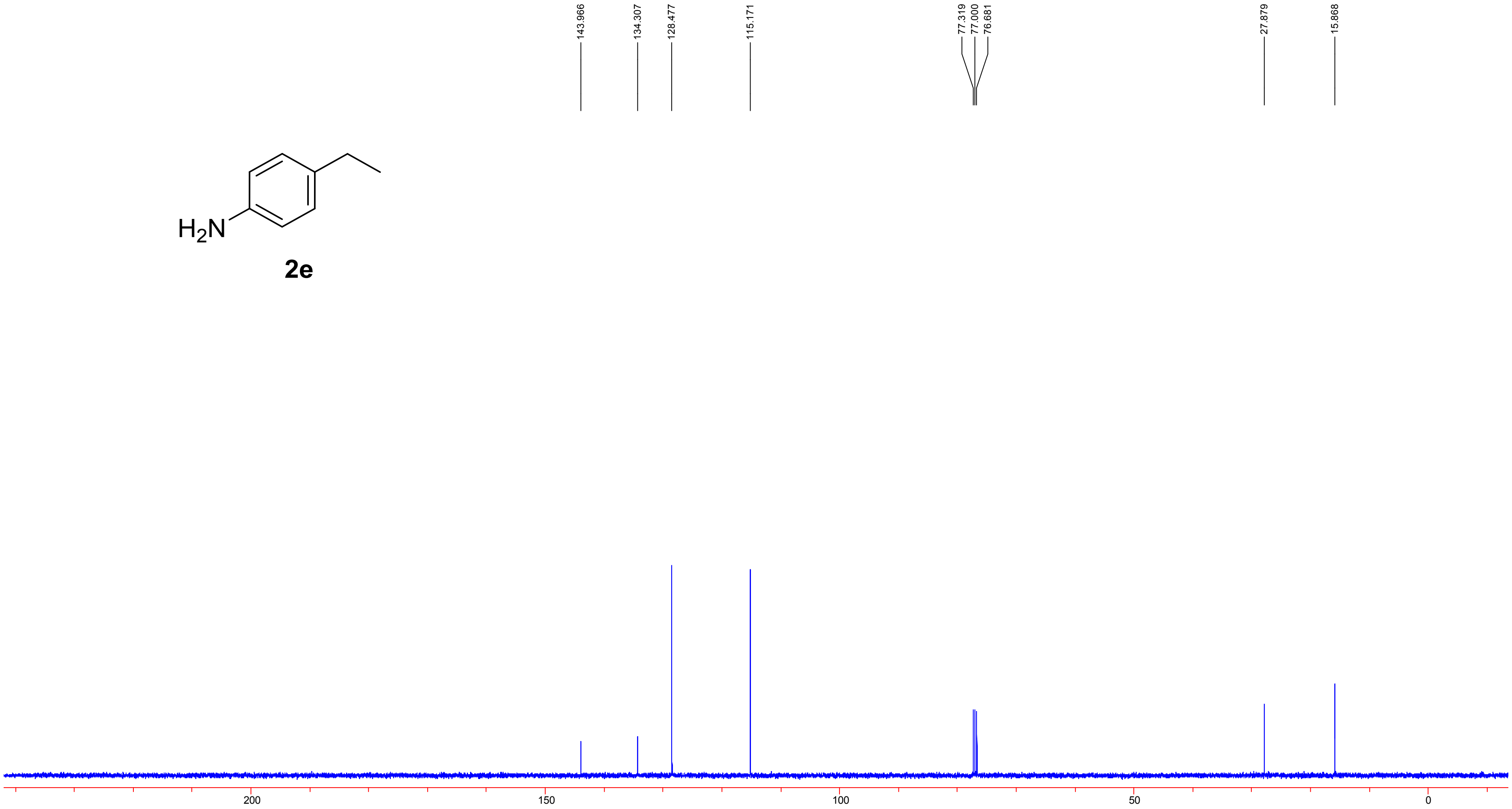
2d

157.564
136.332
128.652
113.671
77.313
77.000
76.676
55.176
27.927
15.871
MeO
250
200
150
100
50
0
-50


H2N

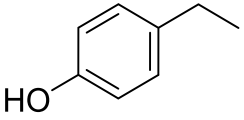
2e


6.989
6.969
6.616
6.595
3.460
2.559
2.540
2.521
2.502
1.197
1.178
1.159
0.000
1.90
1.92
2.06
2.00
3.02
10
8
6
4
2
0

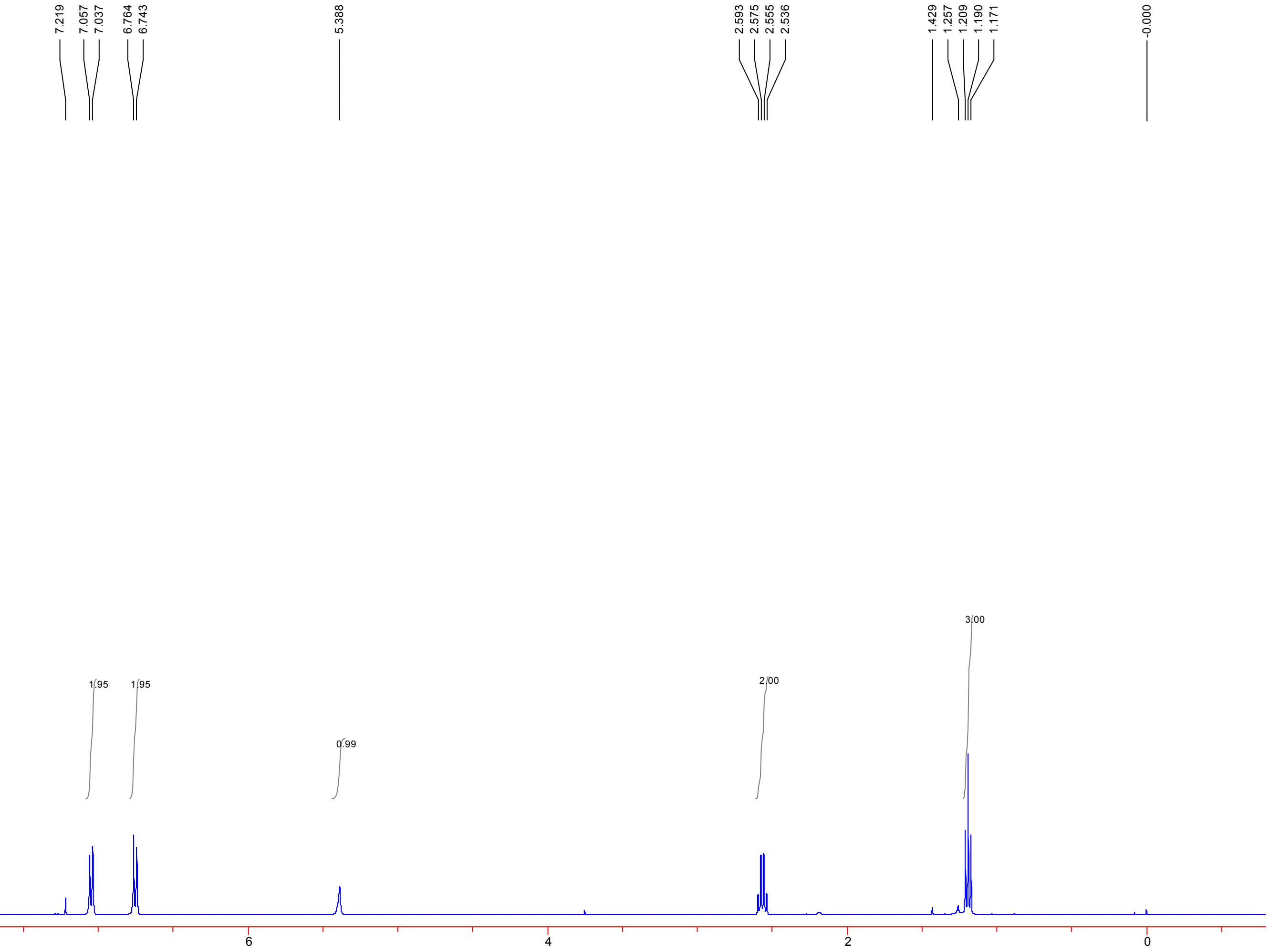


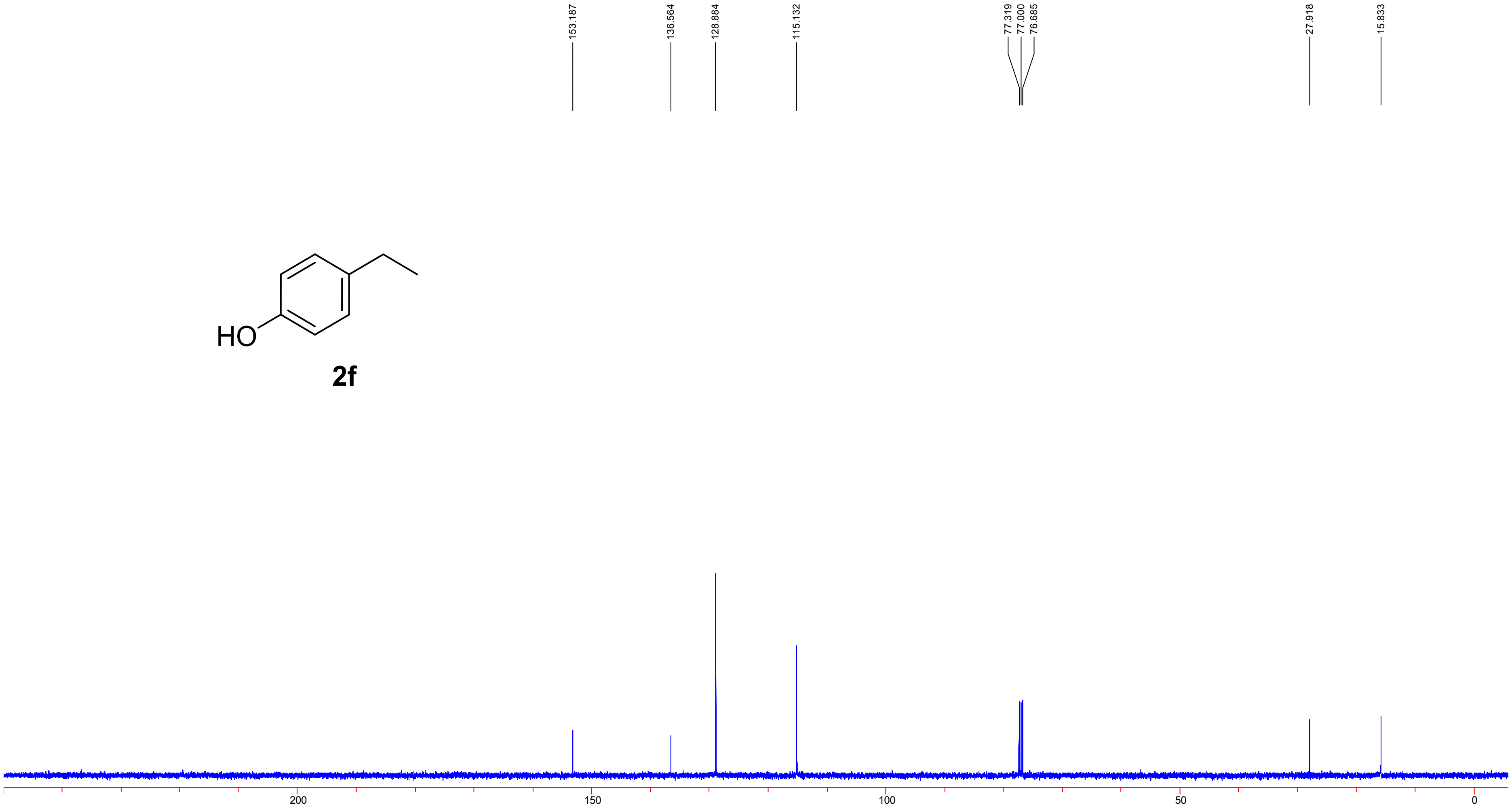
2e

143.966
134.307
128.477
115.171
77.319
77.000
76.681
27.879
15.868
200
150
100
50
0



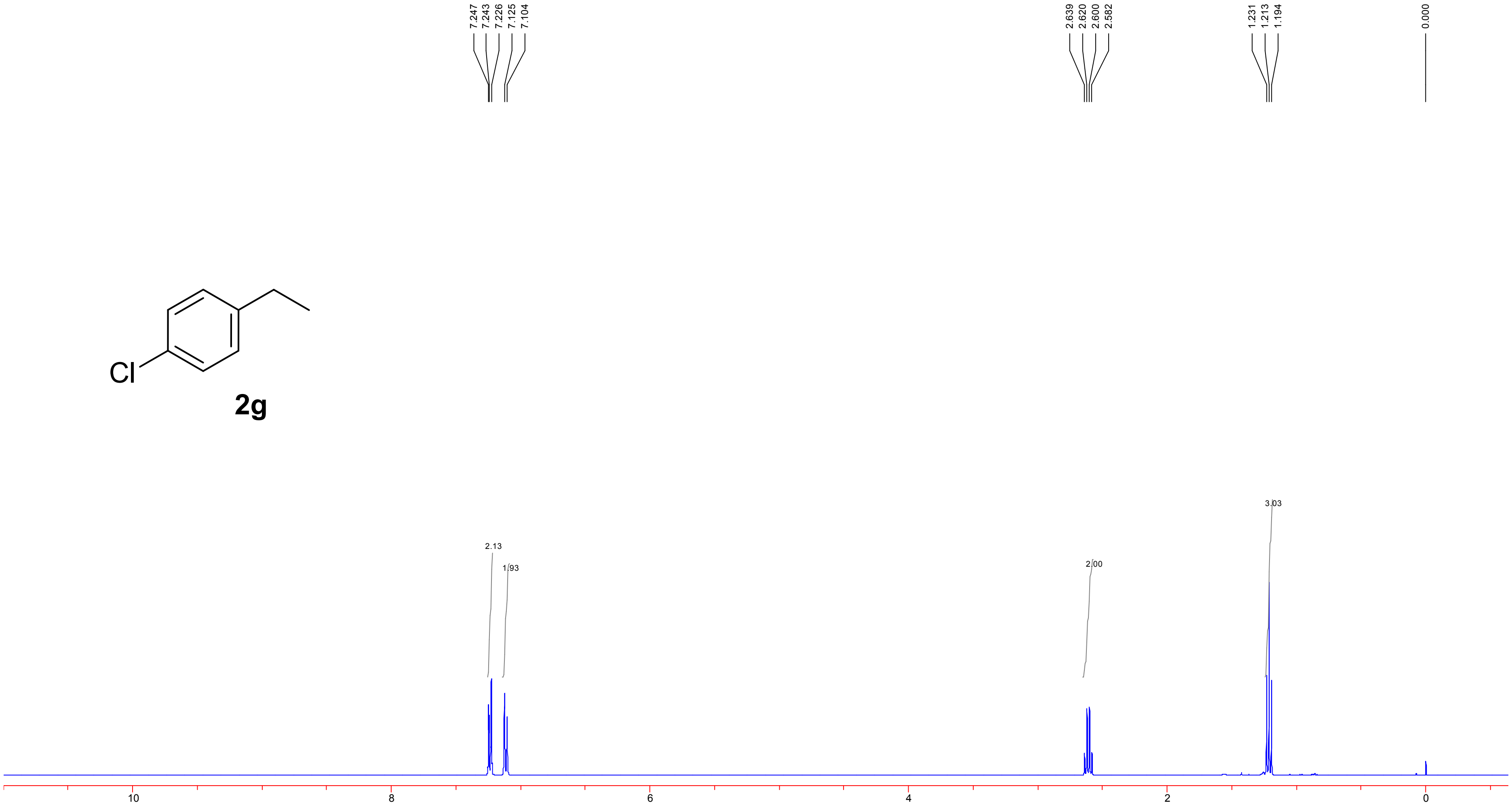
2f


7.219
7.057
7.037
6.764
6.743
5.388
2.593
2.575
2.555
2.536
1.429
1.257
1.209
1.190
1.171
-0.000
1.95
1.95
0.99
2.00
3.00
10
8
6
4
2
0

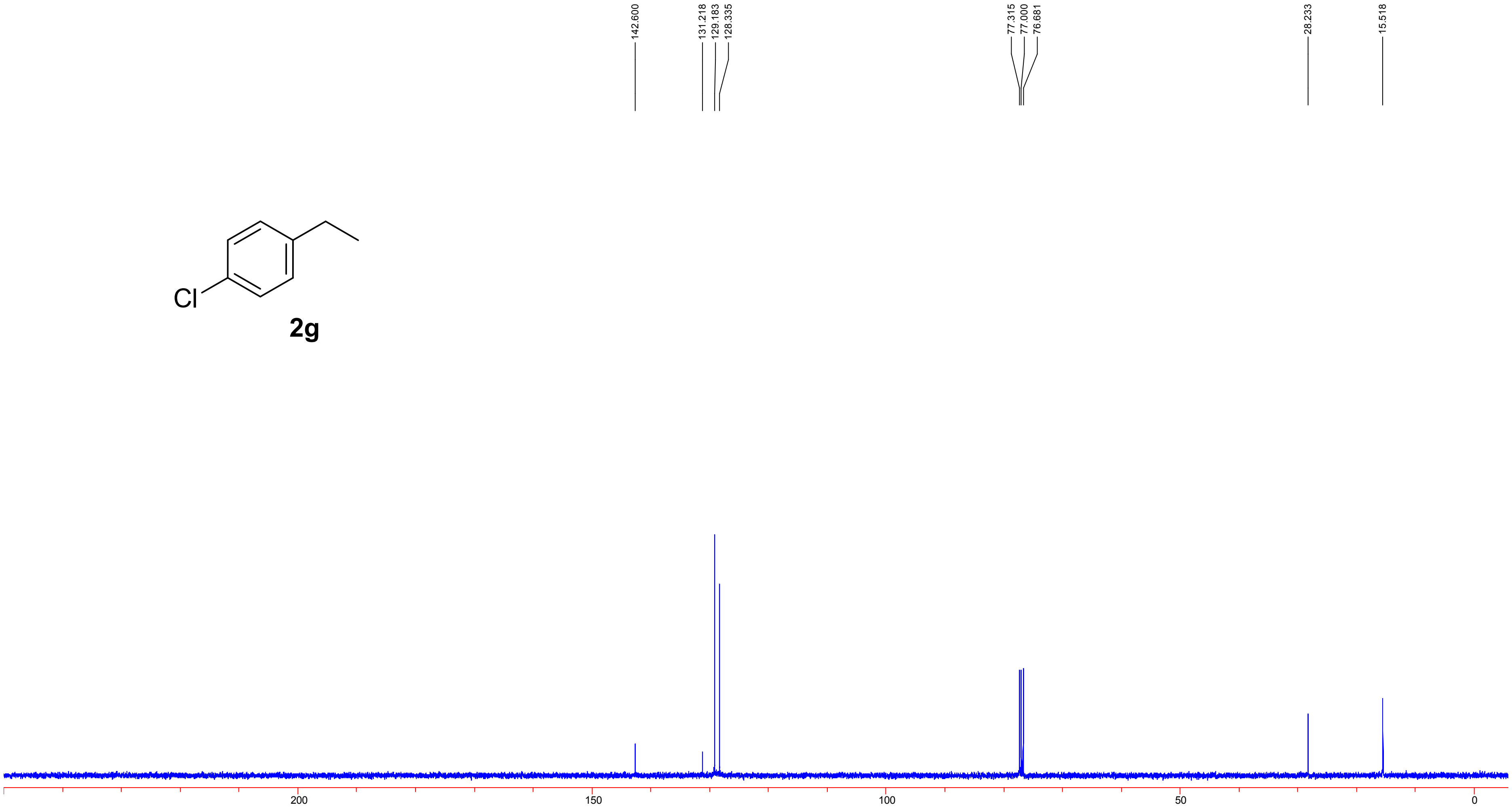


2f

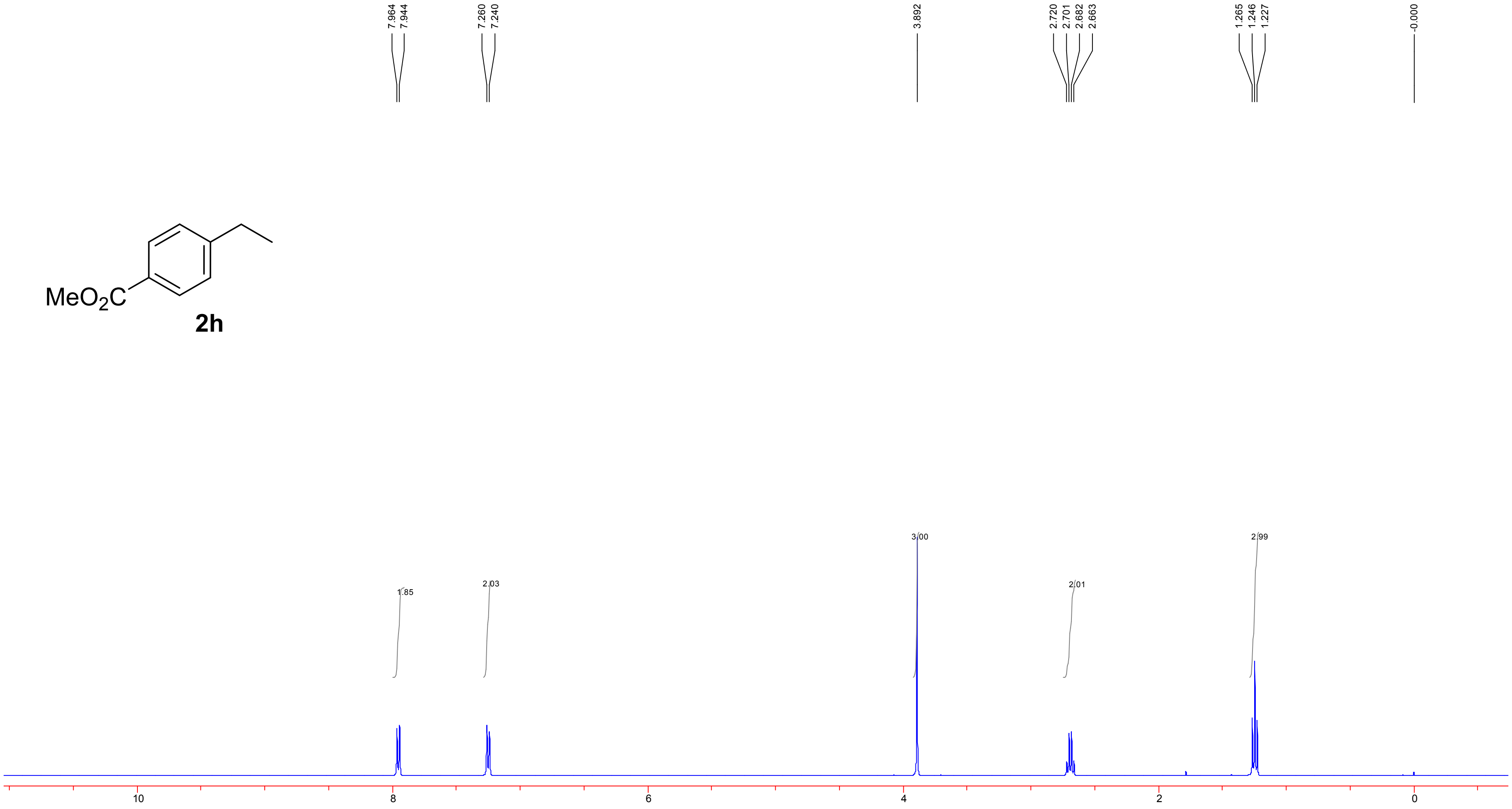
153.187
136.564
128.884
115.132
77.319
77.000
76.685
27.918
15.833
HO
200
150
100
50
0


7.247
7.243
7.226
7.125
7.104
2.639
2.620
2.600
2.582
1.231
1.213
1.194
0.000
2.13
1.93
2.00
3.03
Cl
10
8
6
4
2
0

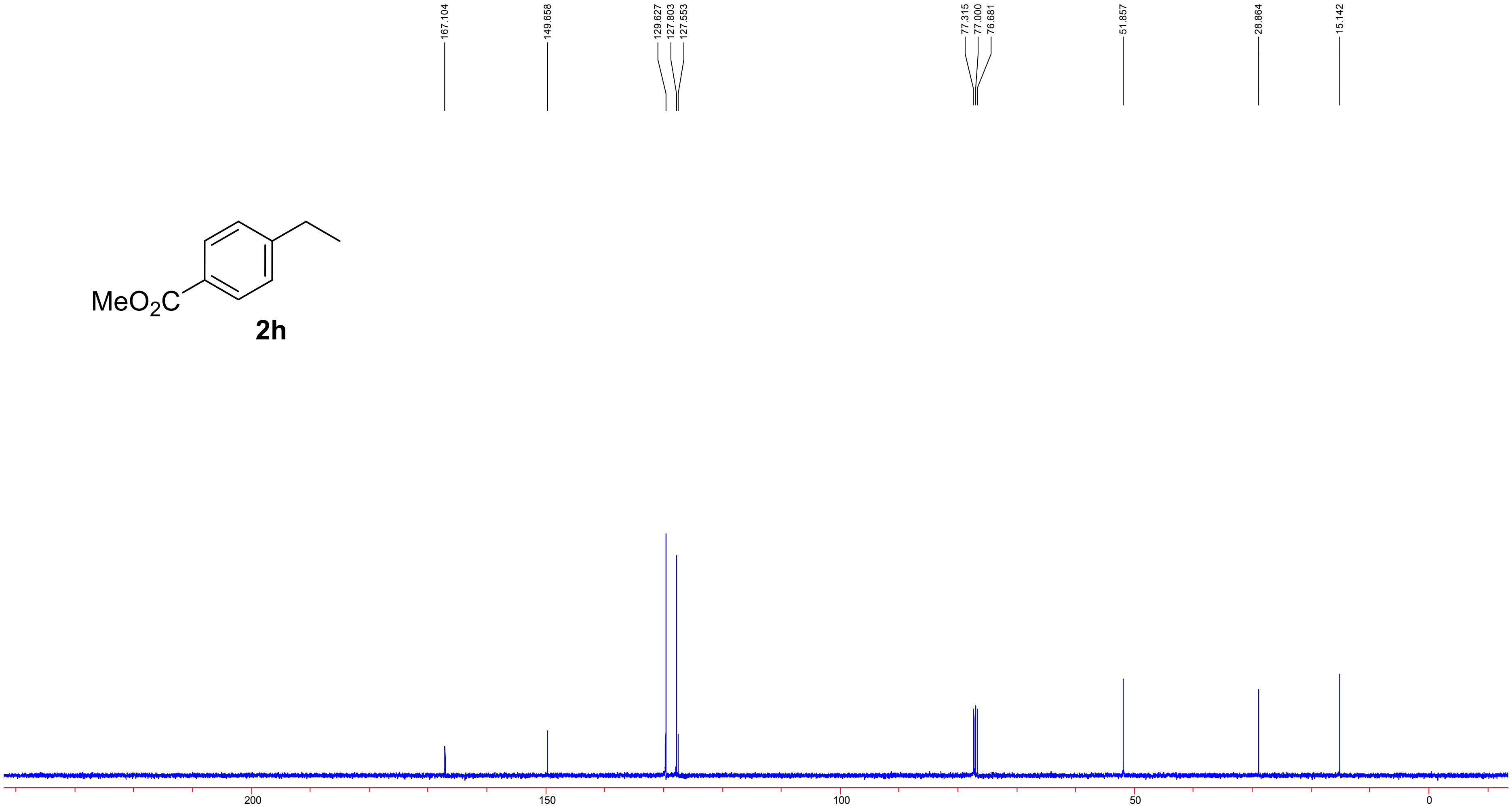
2g


142.600
131.218
129.183
128.335
77.315
77.000
76.681
28.233
15.518
Cl
200
150
100
50
0

2g

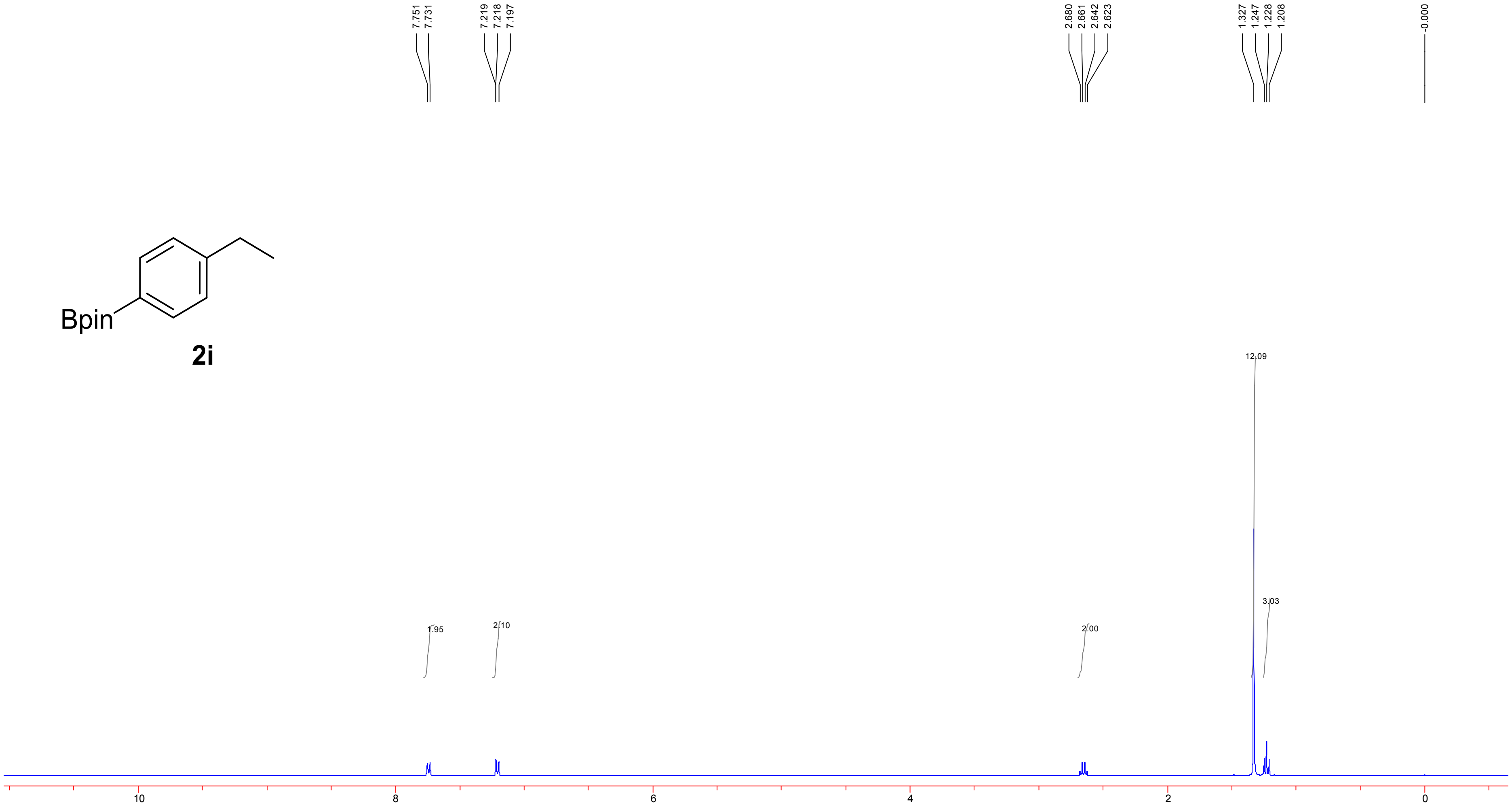

7.964
7.944
7.260
7.240
3.892
2.720
2.701
2.682
2.663
1.265
1.246
1.227
-0.000
MeO$_2$C
1.85
2.03
3.00
2.01
2.99
10
8
6
4
2
0

2h



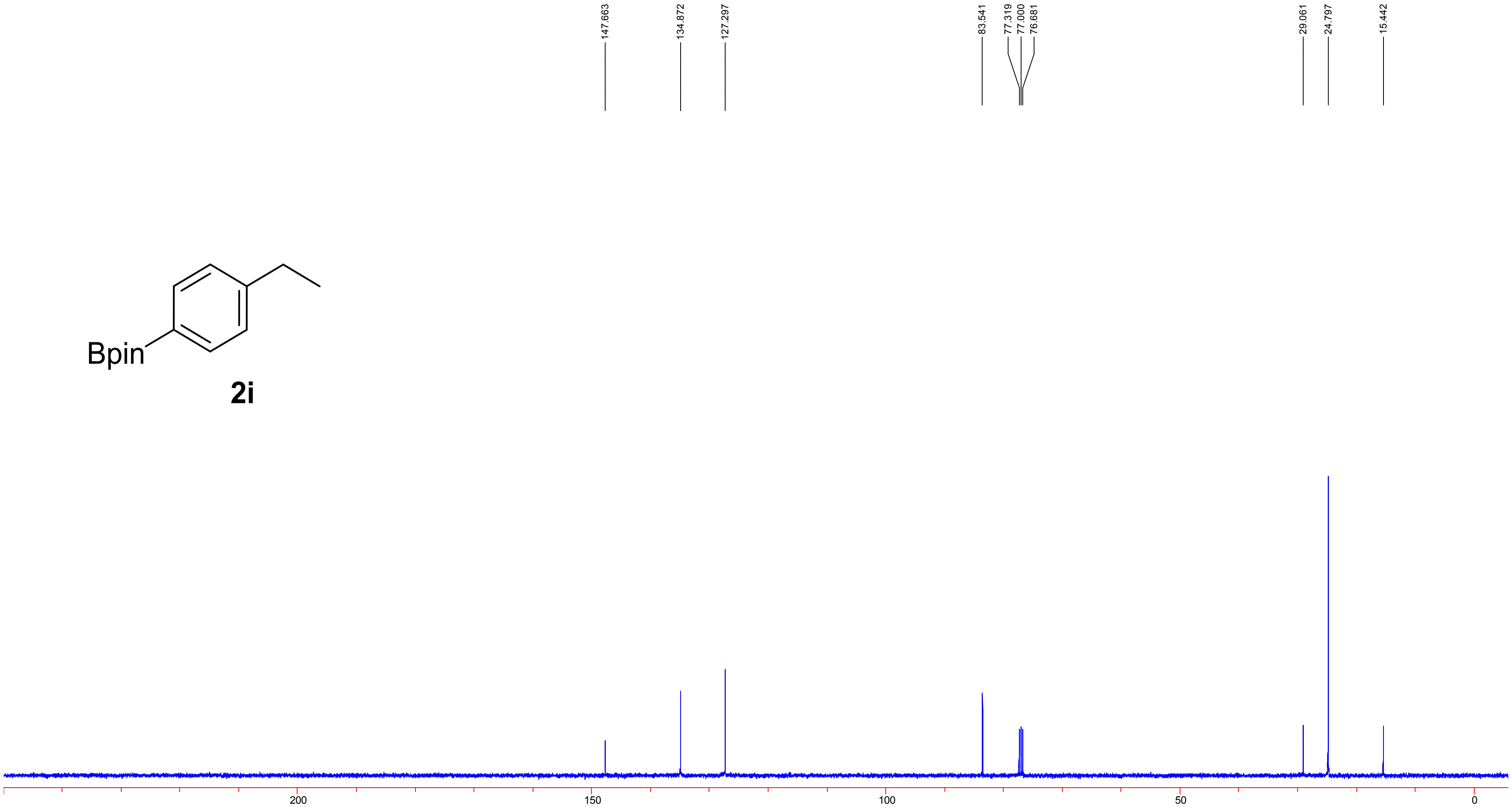
2h

167.104
149.658
129.627
127.803
127.553
77.315
77.000
76.681
51.857
28.864
15.142
200
150
100
50
0



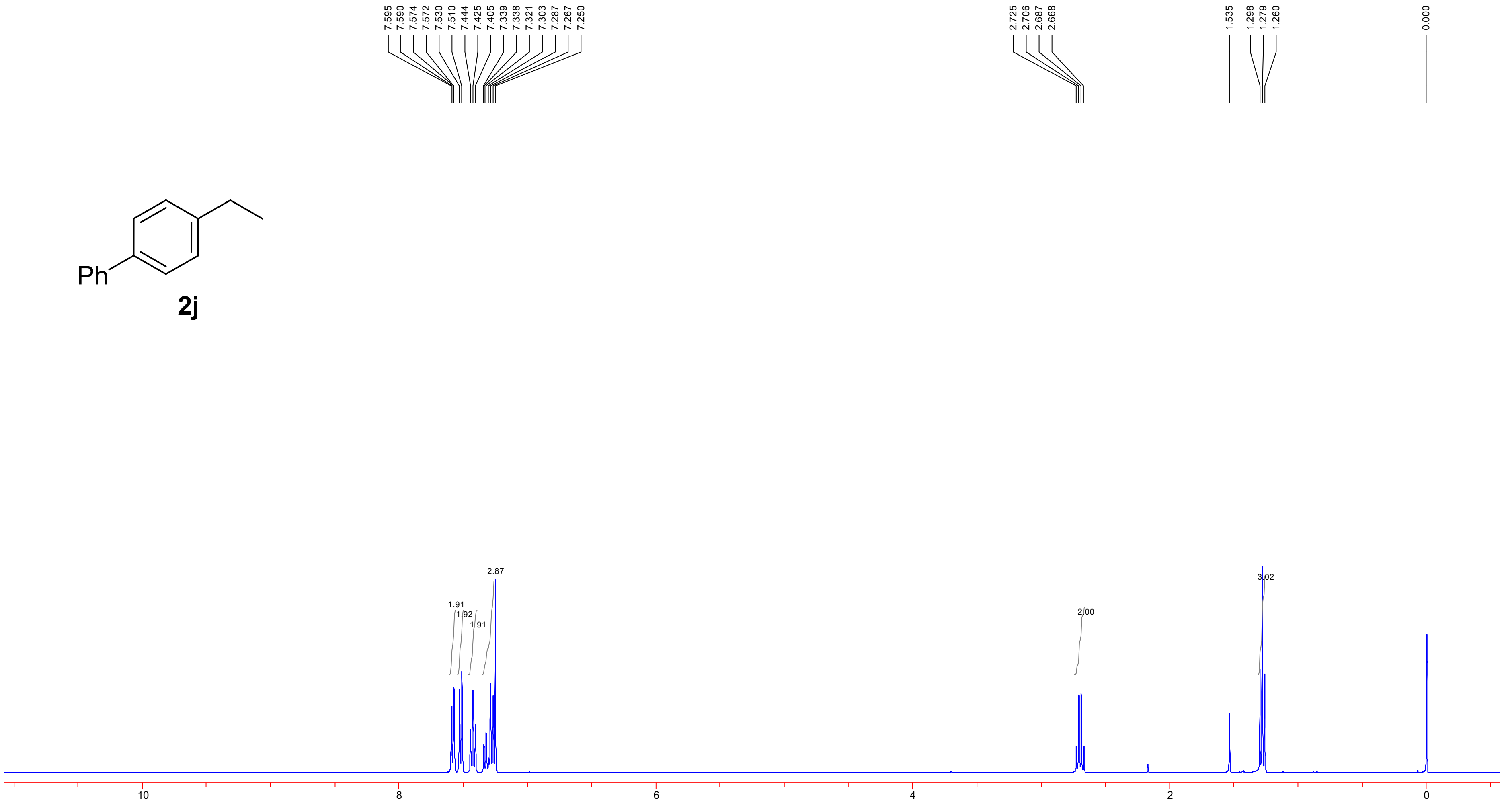
2i

7.751
7.731
7.219
7.218
7.197
2.680
2.661
2.642
2.623
1.327
1.247
1.228
1.208
-0.000
1.95
2.10
2.00
12.09
3.03
10
8
6
4
2
0



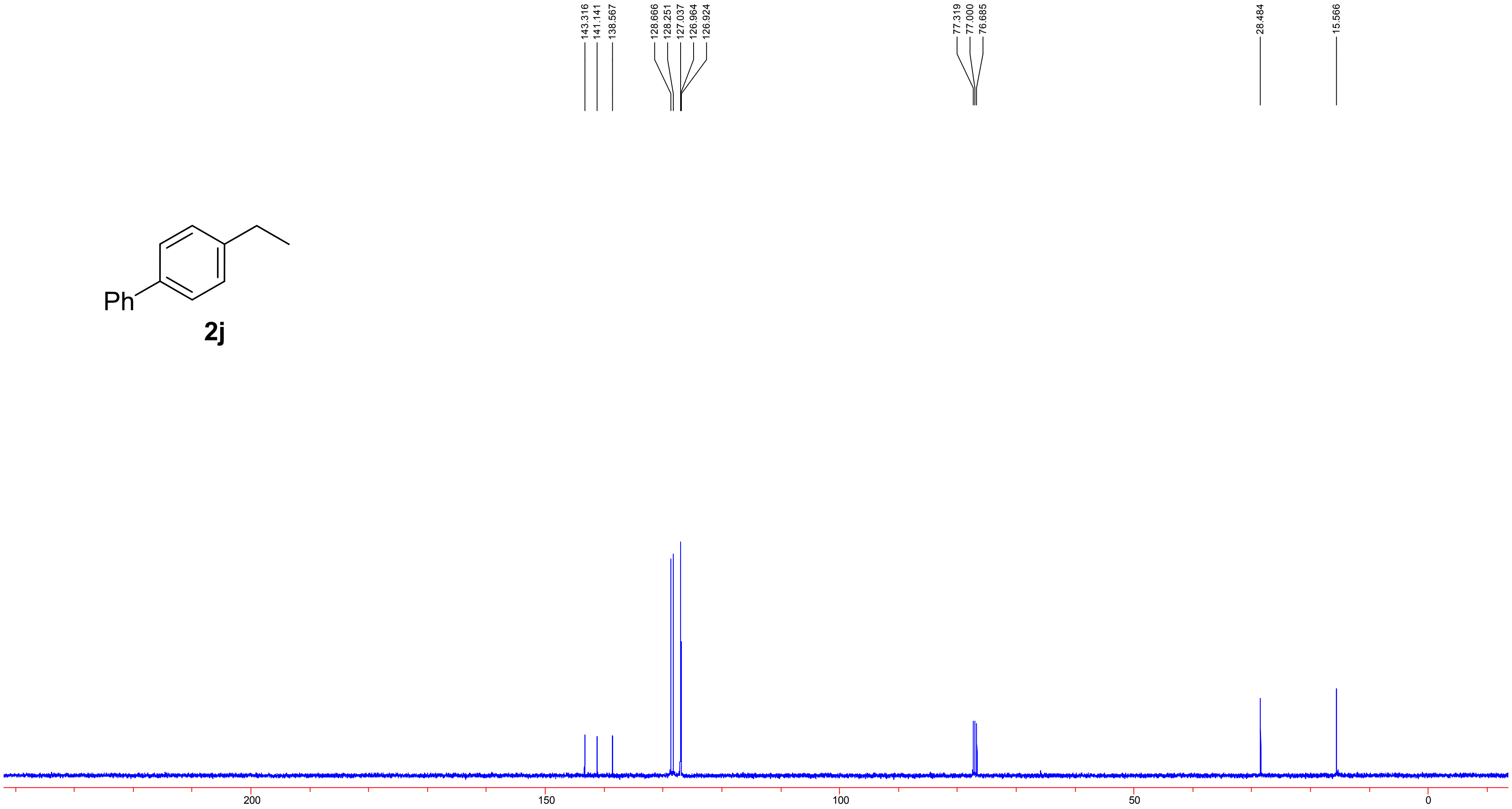
2i

147.663
134.872
127.297
83.541
77.319
77.000
76.681
29.061
24.797
15.442
200
150
100
50
0


Ph

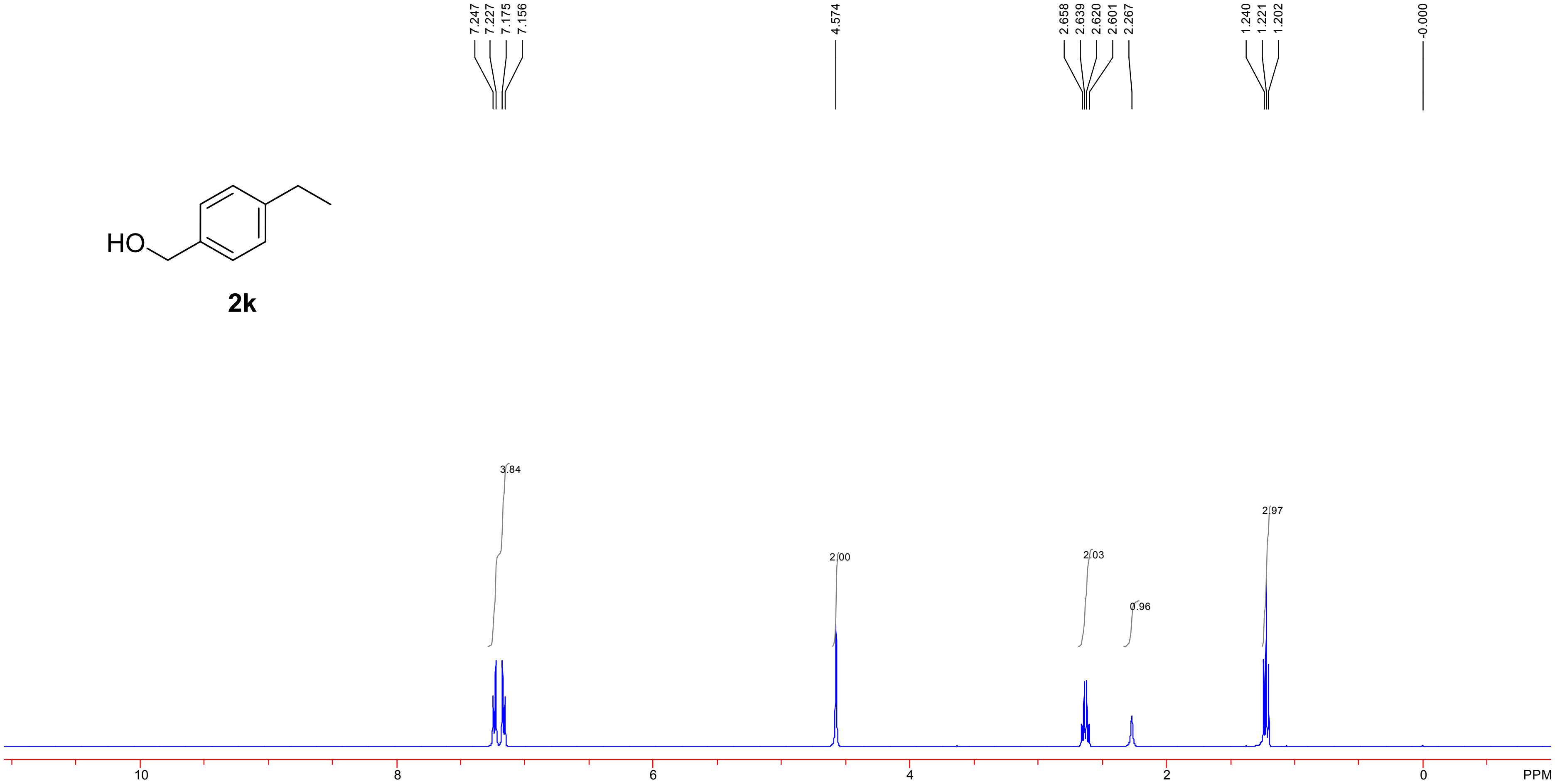
2j

7.595
7.590
7.574
7.572
7.530
7.510
7.444
7.425
7.405
7.339
7.338
7.321
7.303
7.287
7.267
7.250
2.725
2.706
2.687
2.668
1.535
1.298
1.279
1.260
0.000
1.91
1.92
1.91
2.87
2.00
3.02
10
8
6
4
2
0



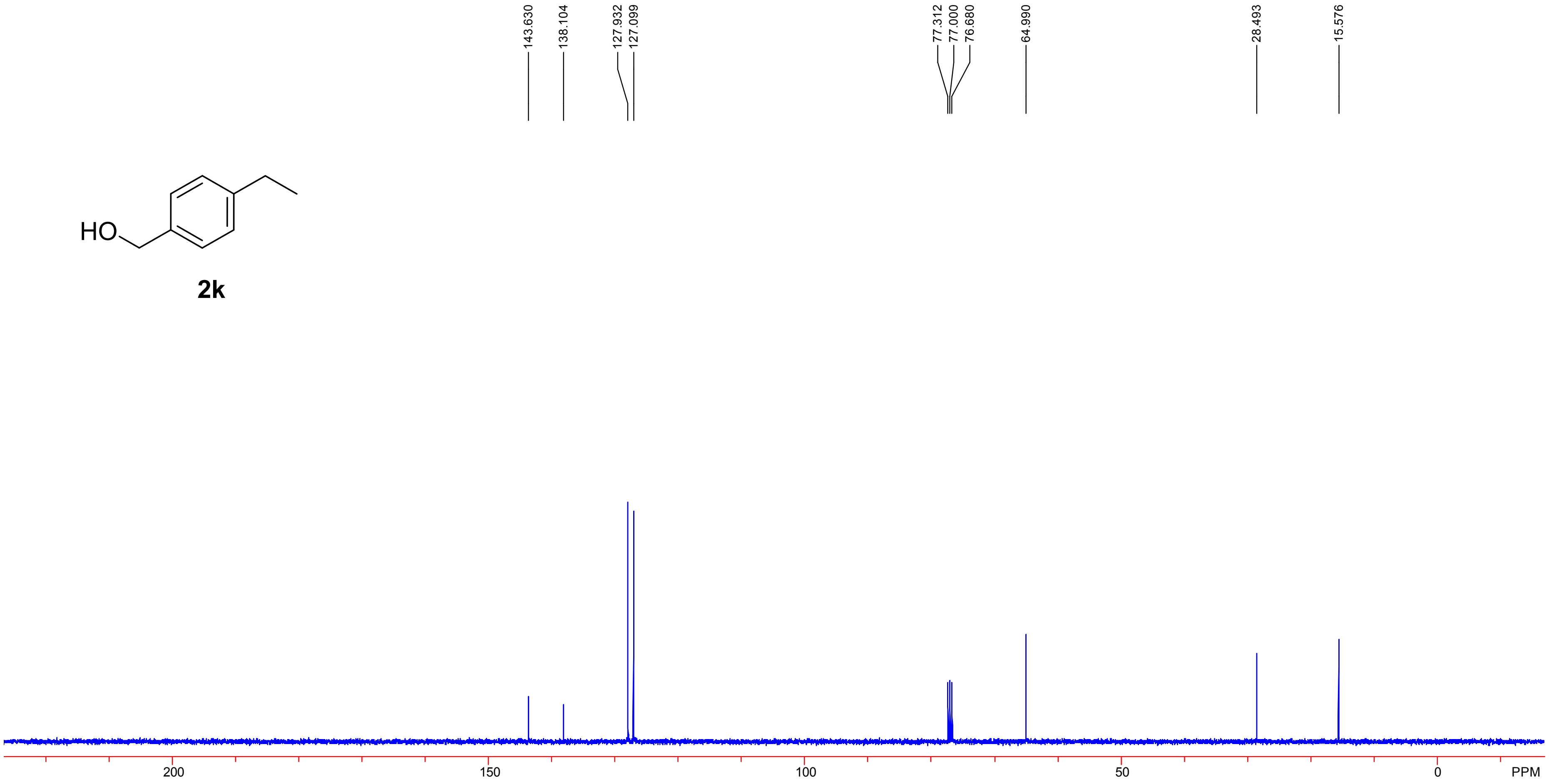
2j

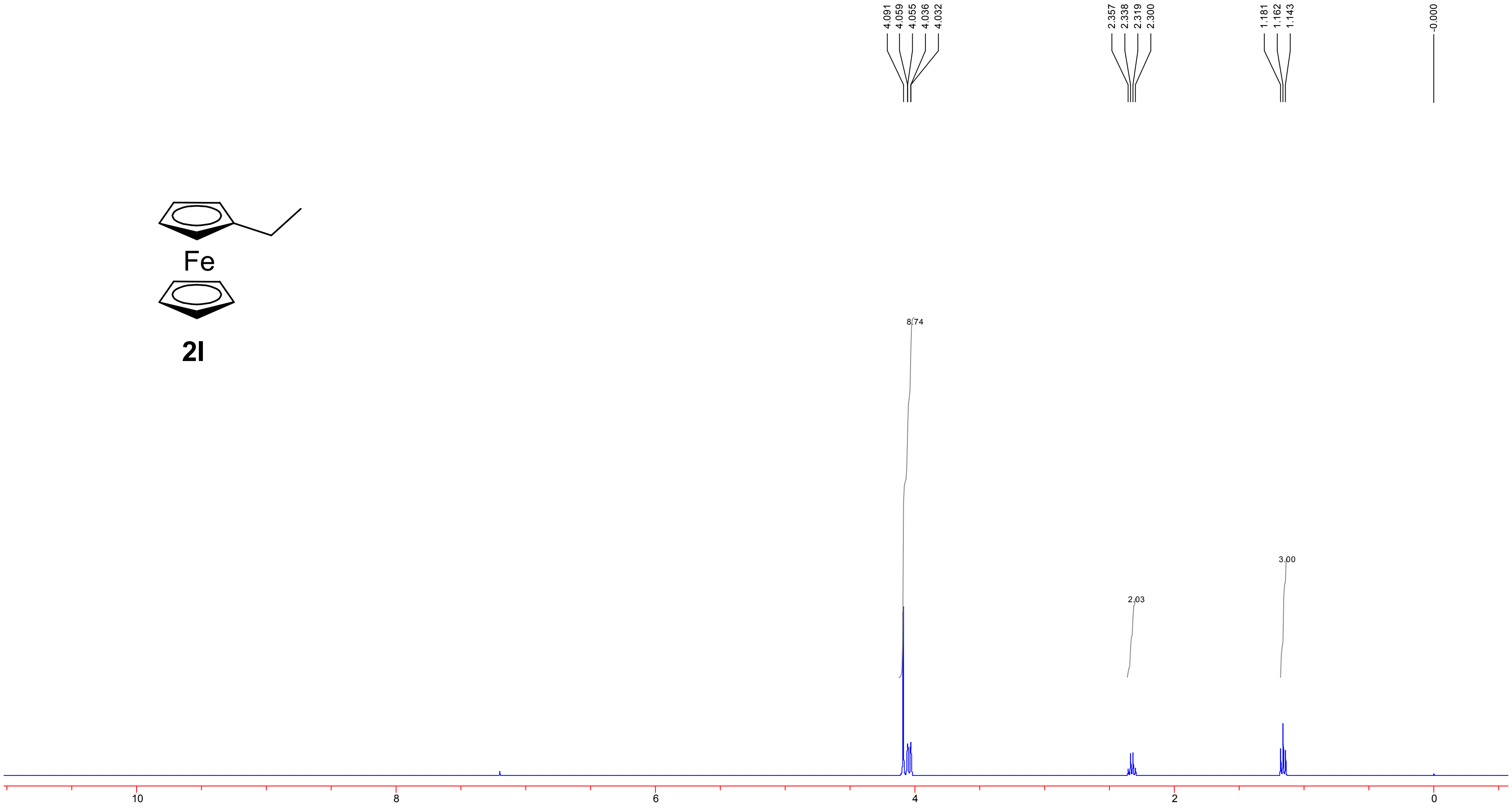
143.316
141.141
138.567
128.666
128.251
127.037
126.964
126.924
77.319
77.000
76.685
28.484
15.566
200
150
100
50
0



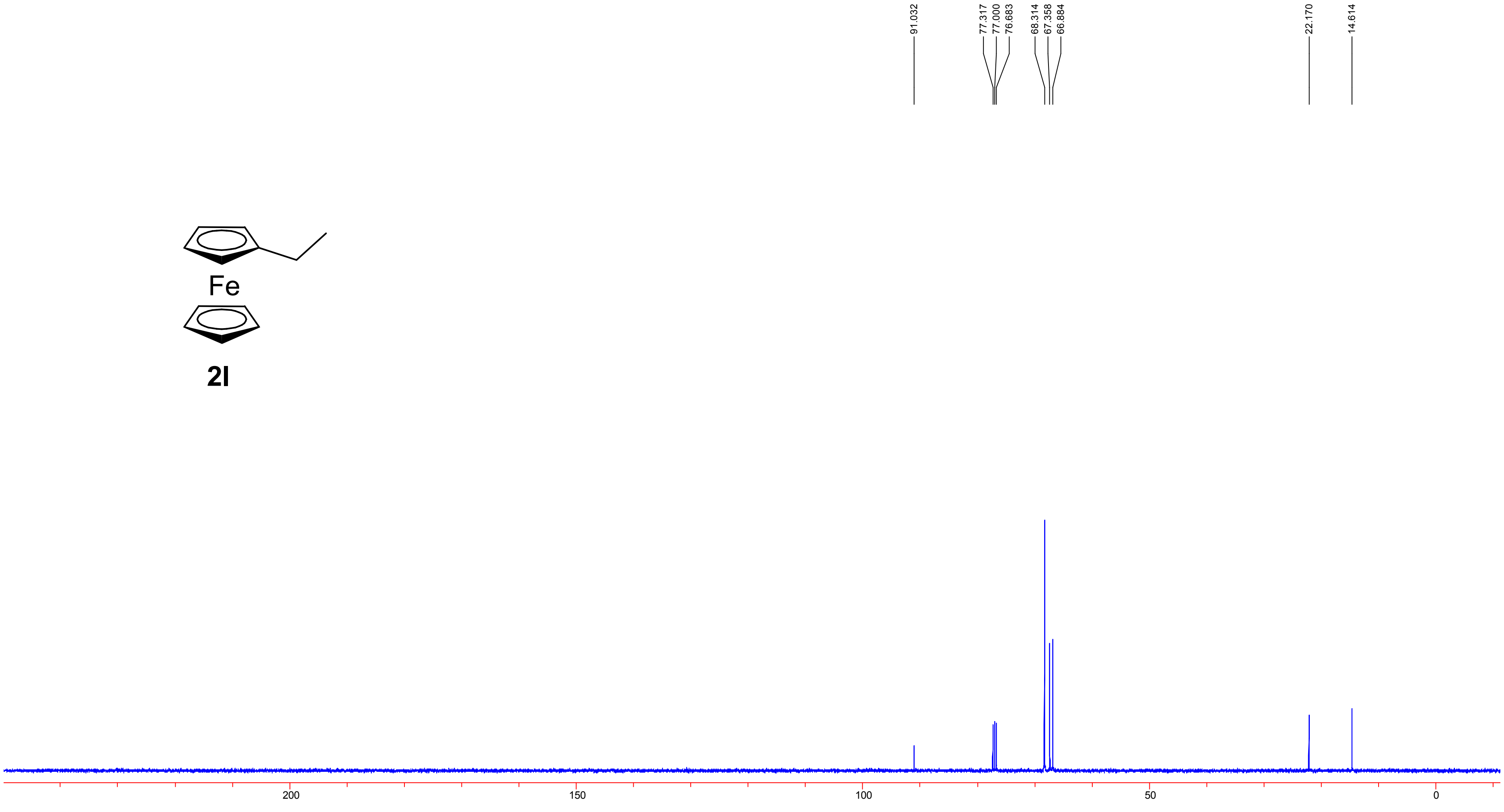
2k

7.247
7.227
7.175
7.156
4.574
2.658
2.639
2.620
2.601
2.267
1.240
1.221
1.202
-0.000
3.84
2.00
2.03
0.96
2.97
10
8
6
4
2
0
PPM


143.630
138.104
127.932
127.099
77.312
77.000
76.680
64.990
28.493
15.576
HO
2k
200
150
100
50
0
PPM

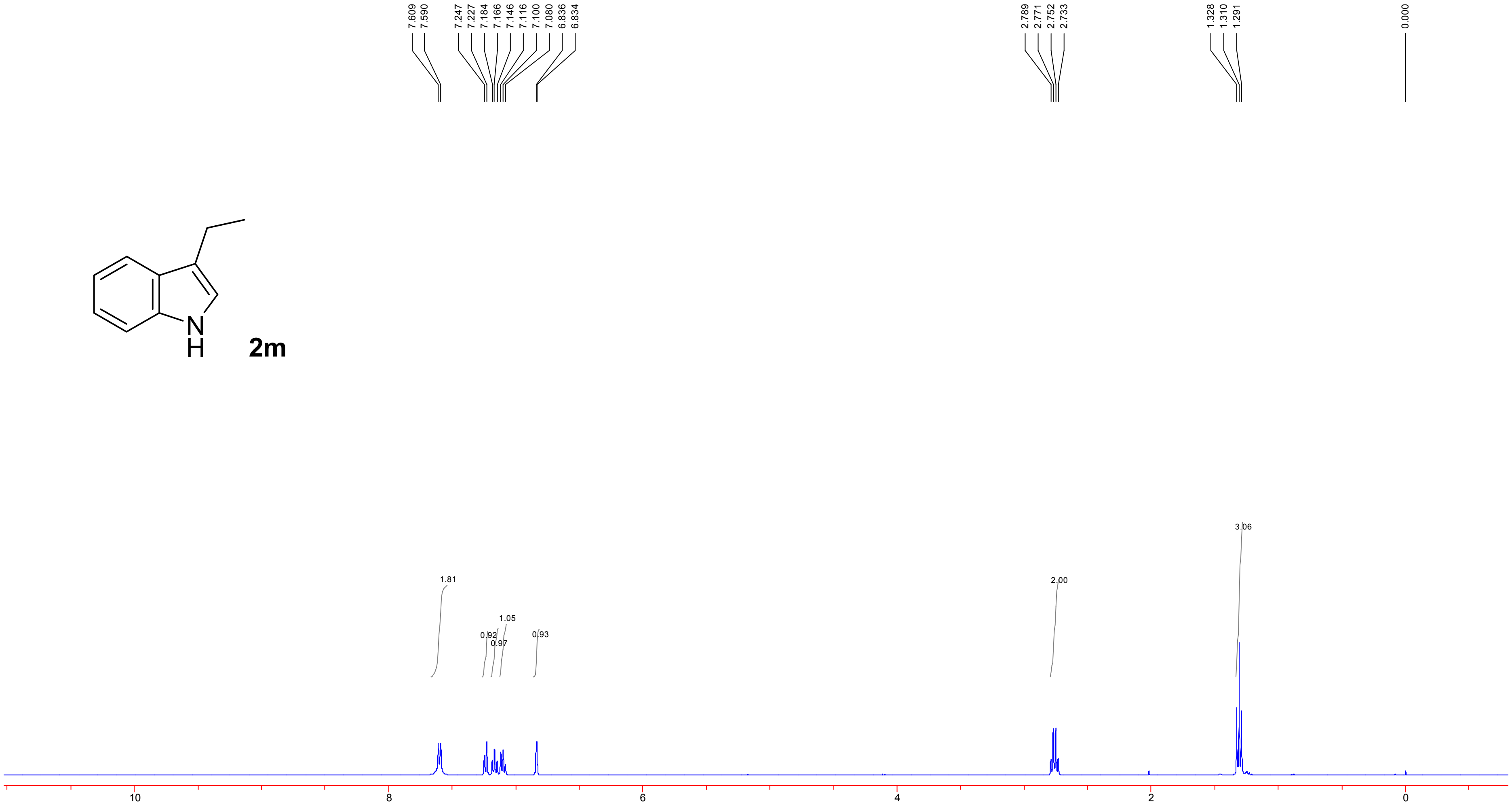

4.091
4.059
4.055
4.036
4.032
2.357
2.338
2.319
2.300
1.181
1.162
1.143
-0.000
Fe
8.74
2.03
3.00
10
8
6
4
2
0

2l

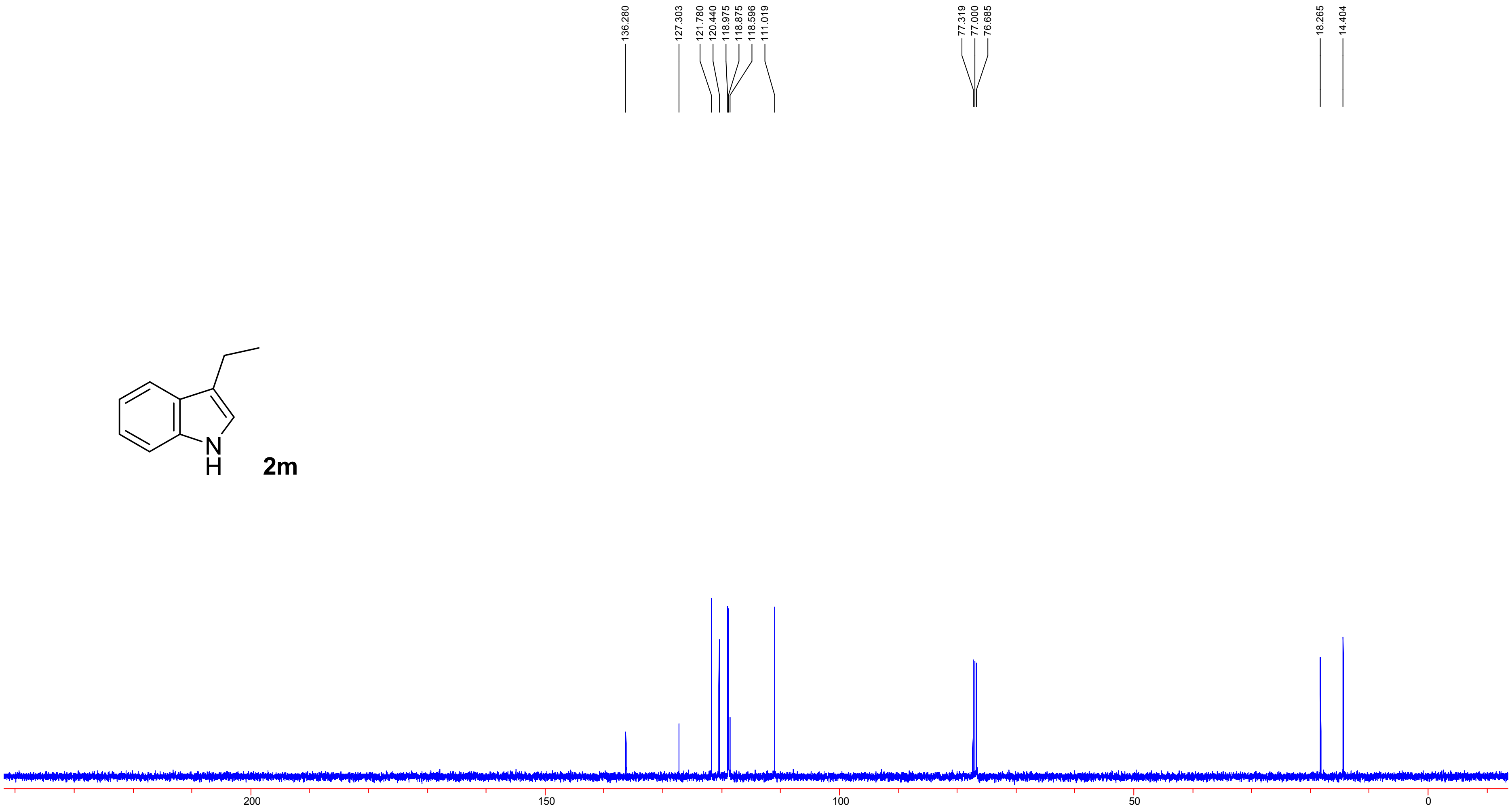


2l

91.032
77.317
77.000
76.683
68.314
67.358
66.884
22.170
14.614
200
150
100
50
0


7.609
7.590
7.247
7.227
7.184
7.166
7.146
7.116
7.100
7.080
6.836
6.834
2.789
2.771
2.752
2.733
1.328
1.310
1.291
0.000
N
H
1.81
0.92
0.97
1.05
0.93
2.00
3.06
10
8
6
4
2
0

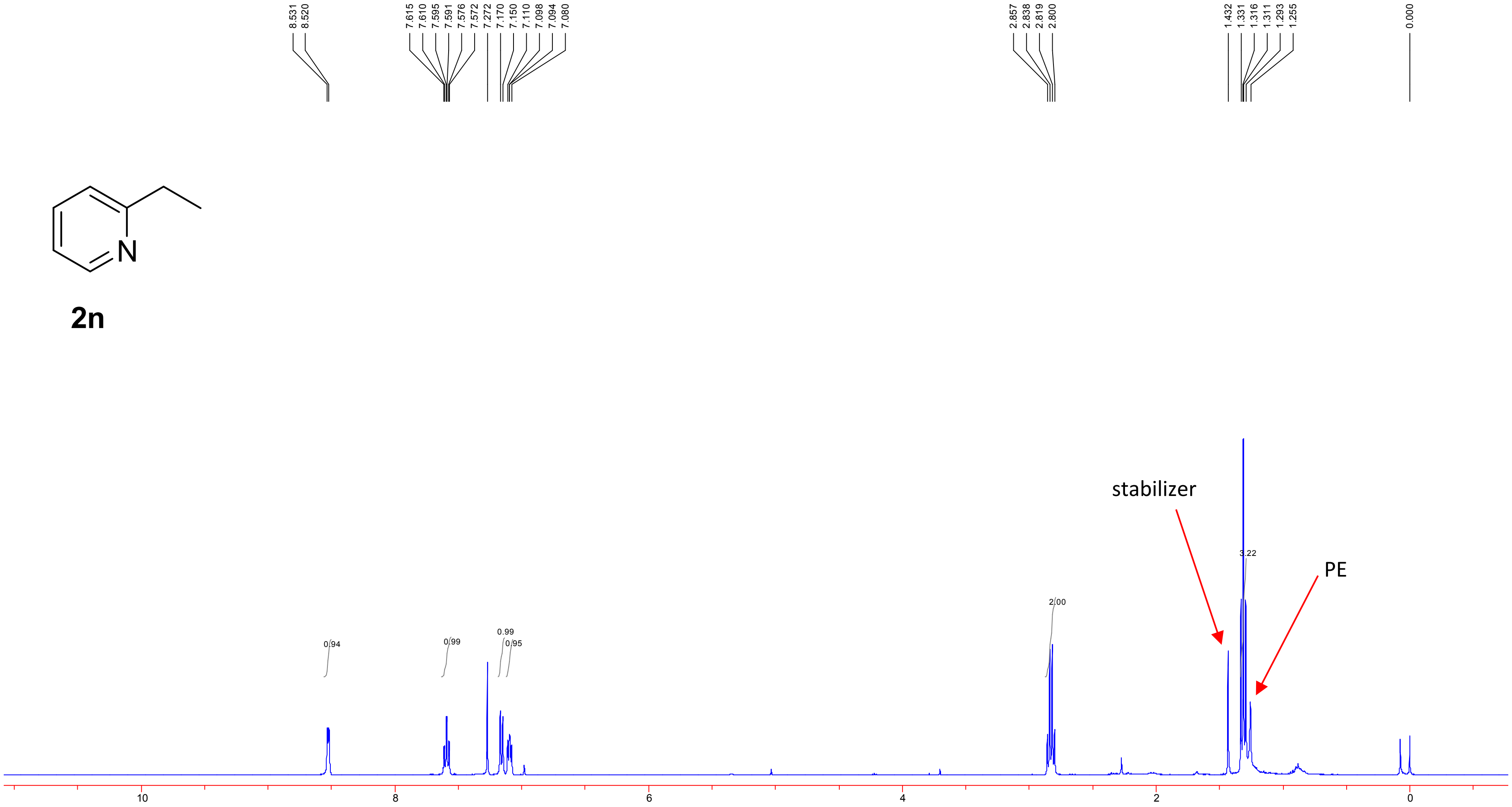
2m



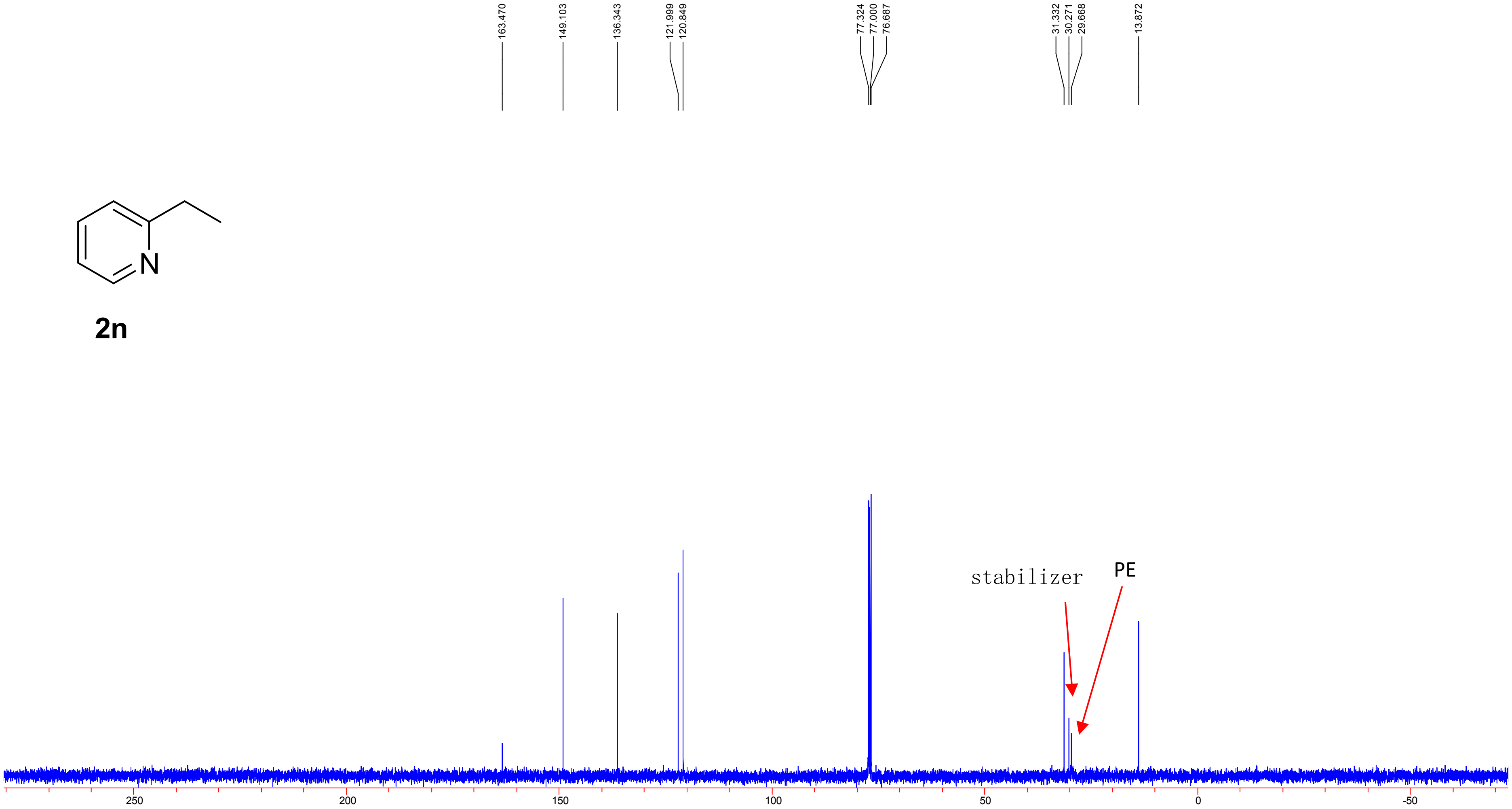
2m

136.280
127.303
121.780
120.440
118.975
118.875
118.596
111.019
77.319
77.000
76.685
18.265
14.404
200
150
100
50
0

Due to the volatile nature of this compound, not all the petroleum ether could be removed.

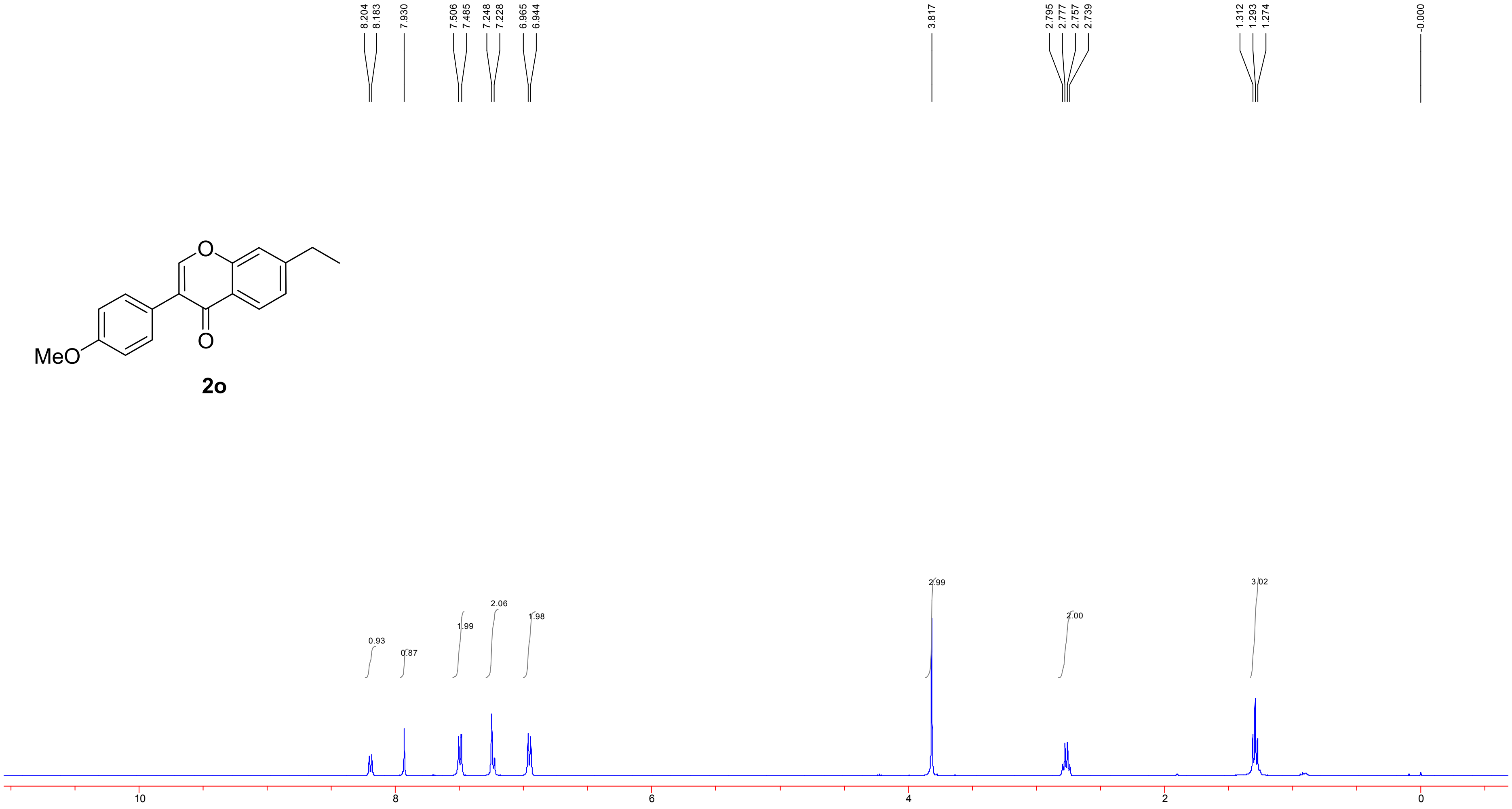


2n

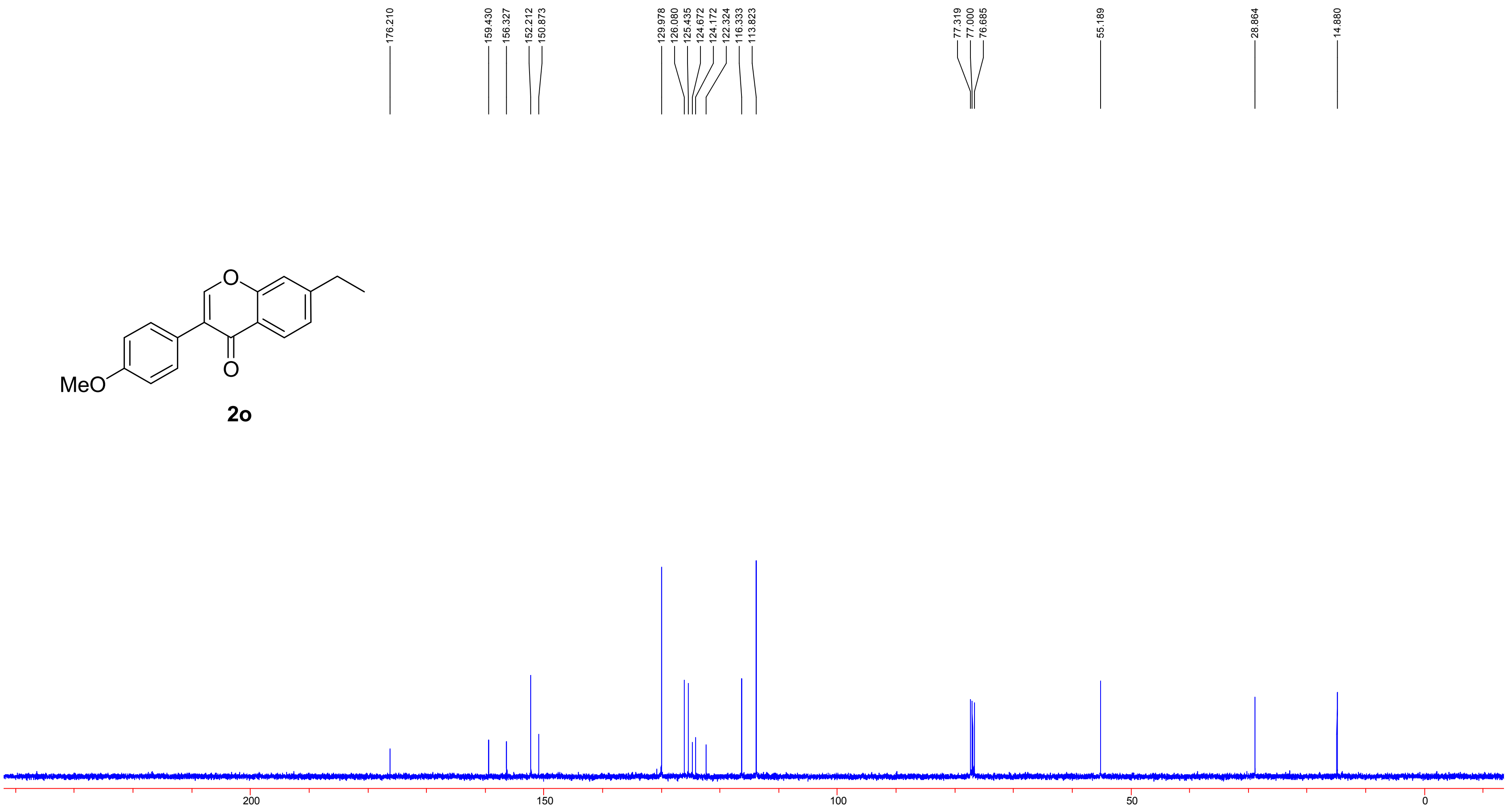


2n

163.470
149.103
136.343
121.999
120.849
77.324
77.000
76.687
31.332
30.271
29.668
13.872
stabilizer
PE
250
200
150
100
50
0
-50



2o
8.204
8.183
7.930
7.506
7.485
7.248
7.228
6.965
6.944
3.817
2.795
2.777
2.757
2.739
1.312
1.293
1.274
-0.000
0.93
0.87
1.99
2.06
1.98
2.99
2.00
3.02
10
8
6
4
2
0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O
MeO
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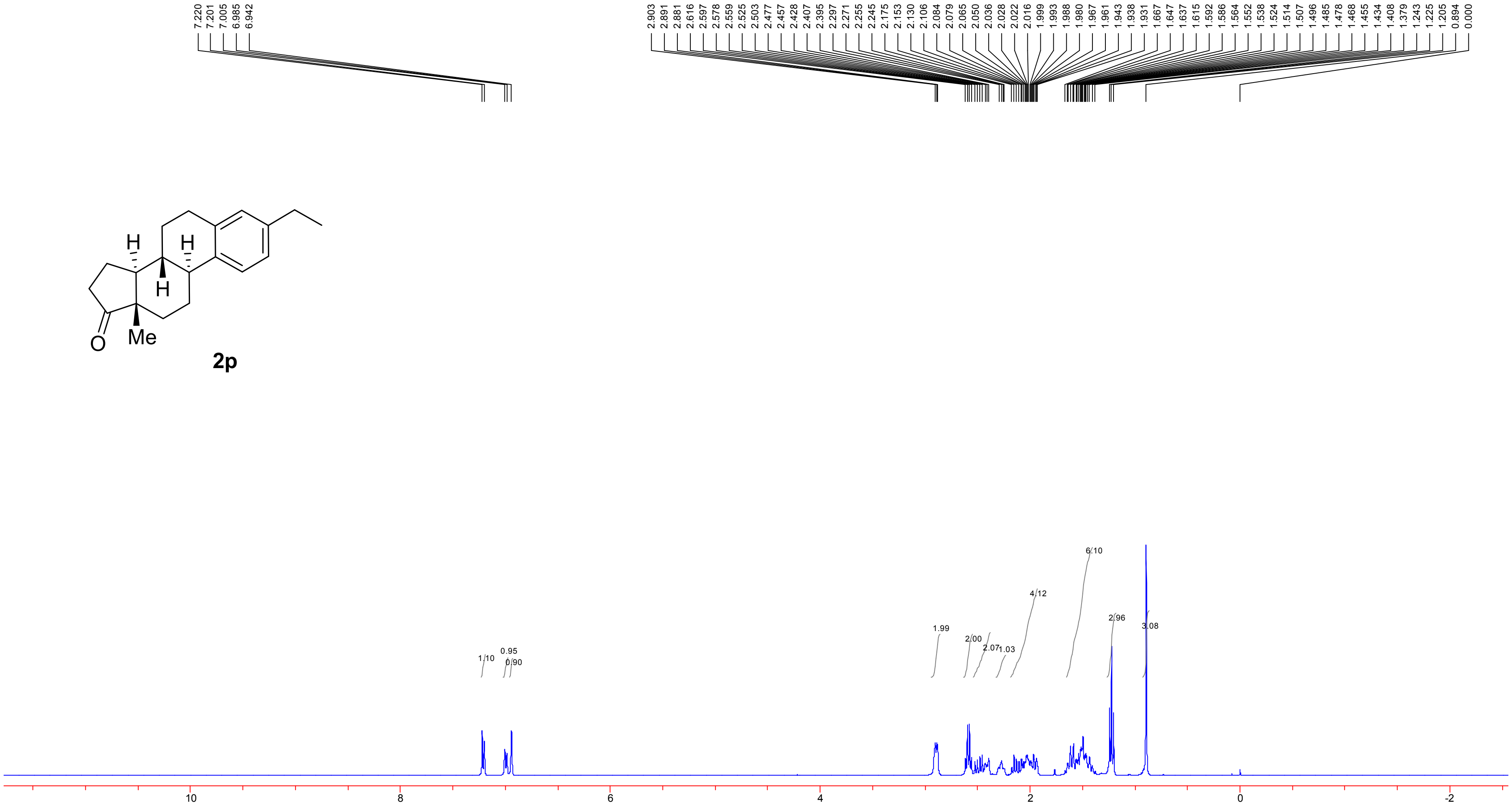
0

2o


H
H
H
Me
O

2p

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2.578
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2.525
2.503
2.477
2.457
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2.255
2.245
2.175
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2.130
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2.079
2.065
2.050
2.036
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2.016
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1.993
1.988
1.980
1.967
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1.943
1.938
1.931
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1.637
1.615
1.592
1.586
1.564
1.552
1.538
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1.455
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1.225
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0.000
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0.95
0.90
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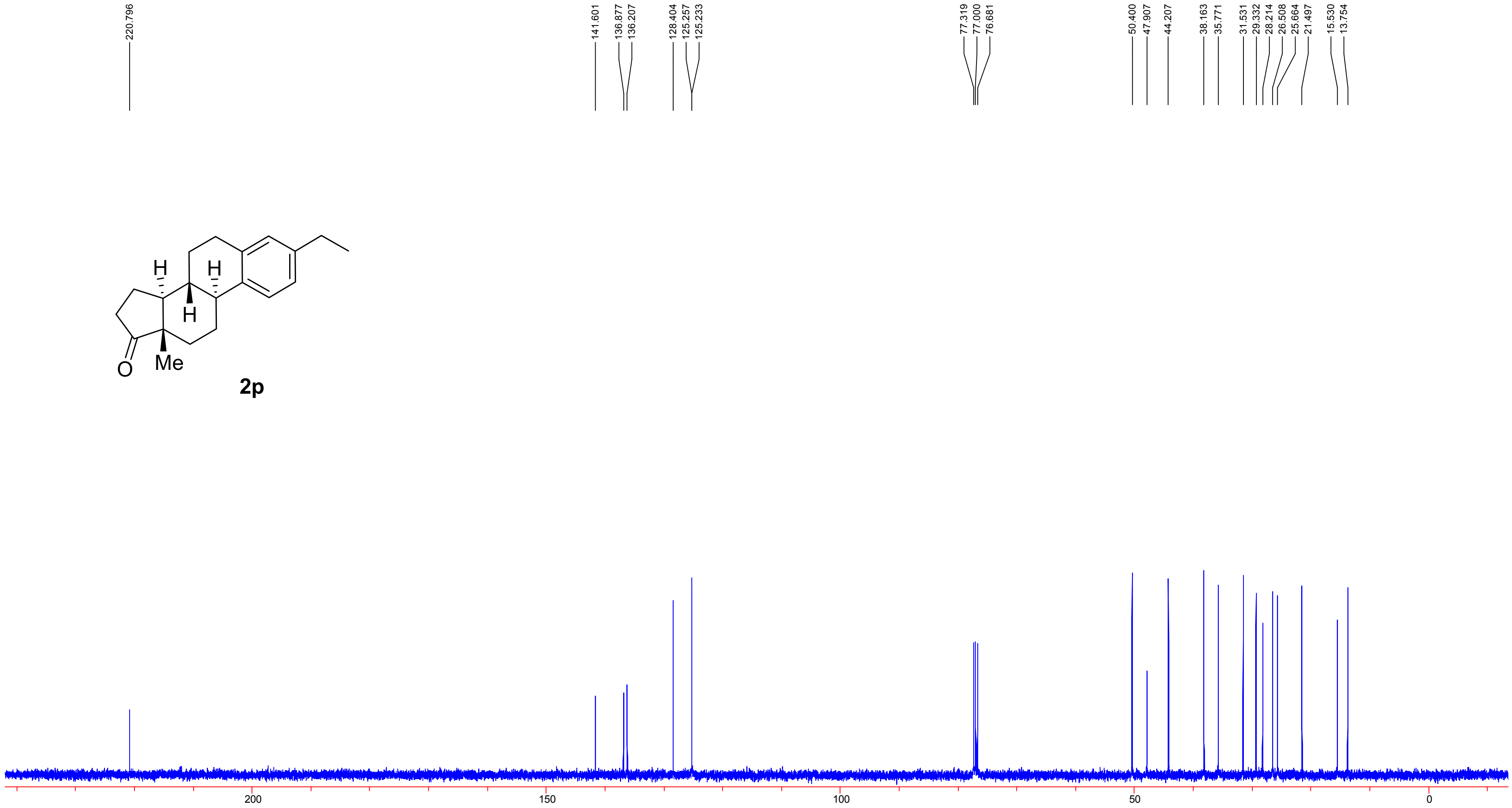
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38.163
35.771
31.531
29.332
28.214
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H
H
O
Me
2p
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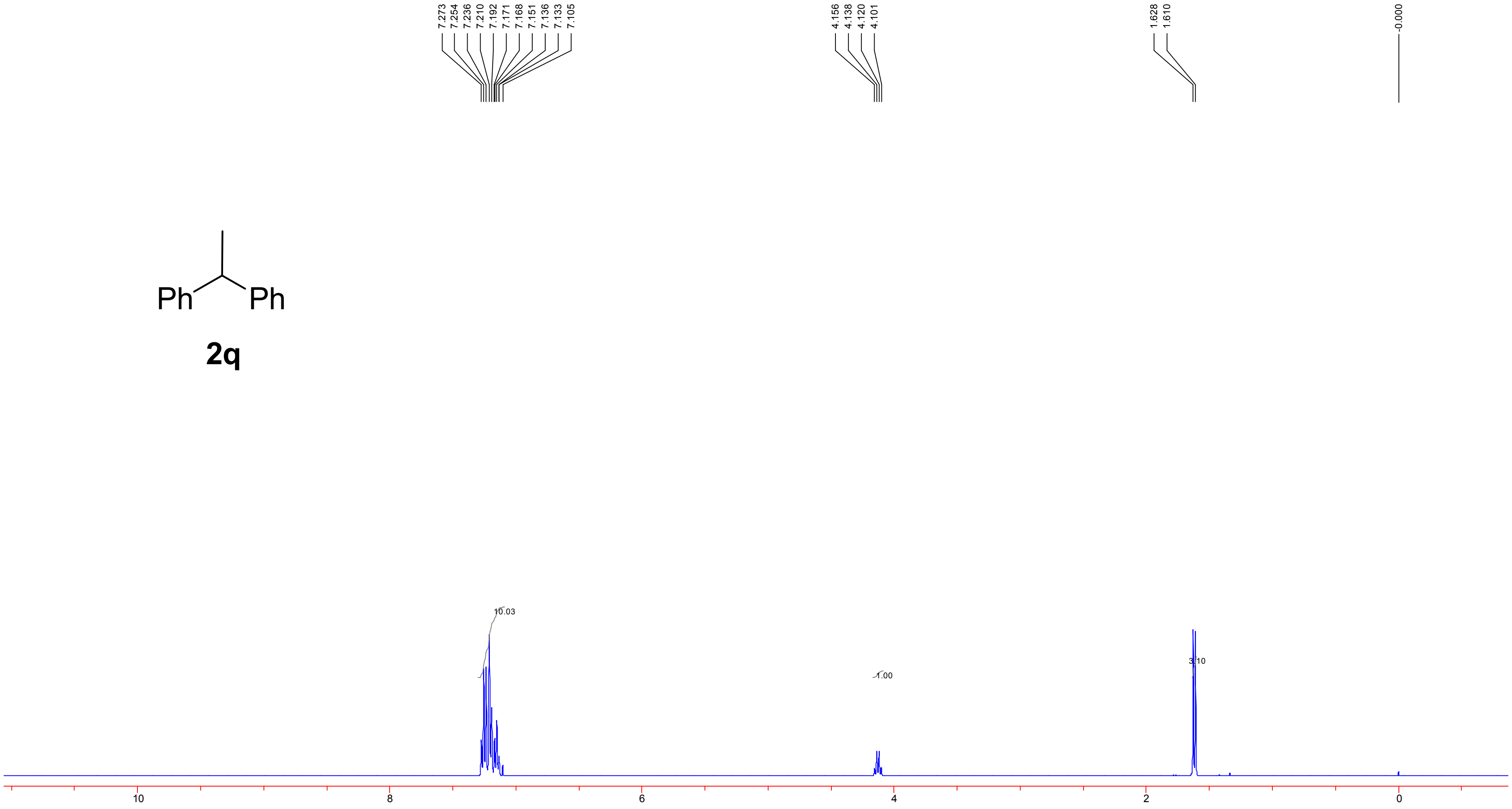

2q

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7.192
7.171
7.168
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7.136
7.133
7.105
4.156
4.138
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1.610
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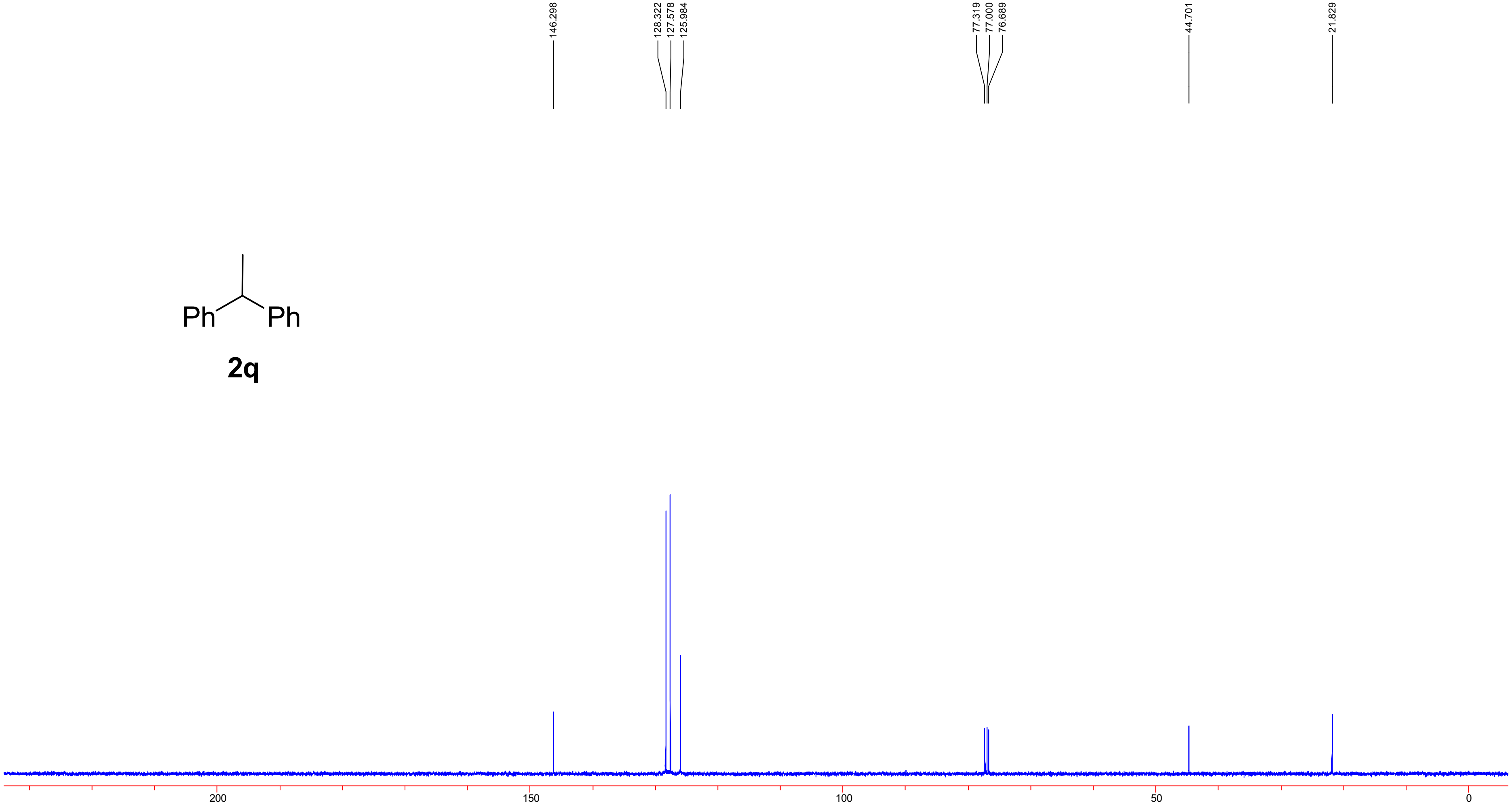

2q

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50
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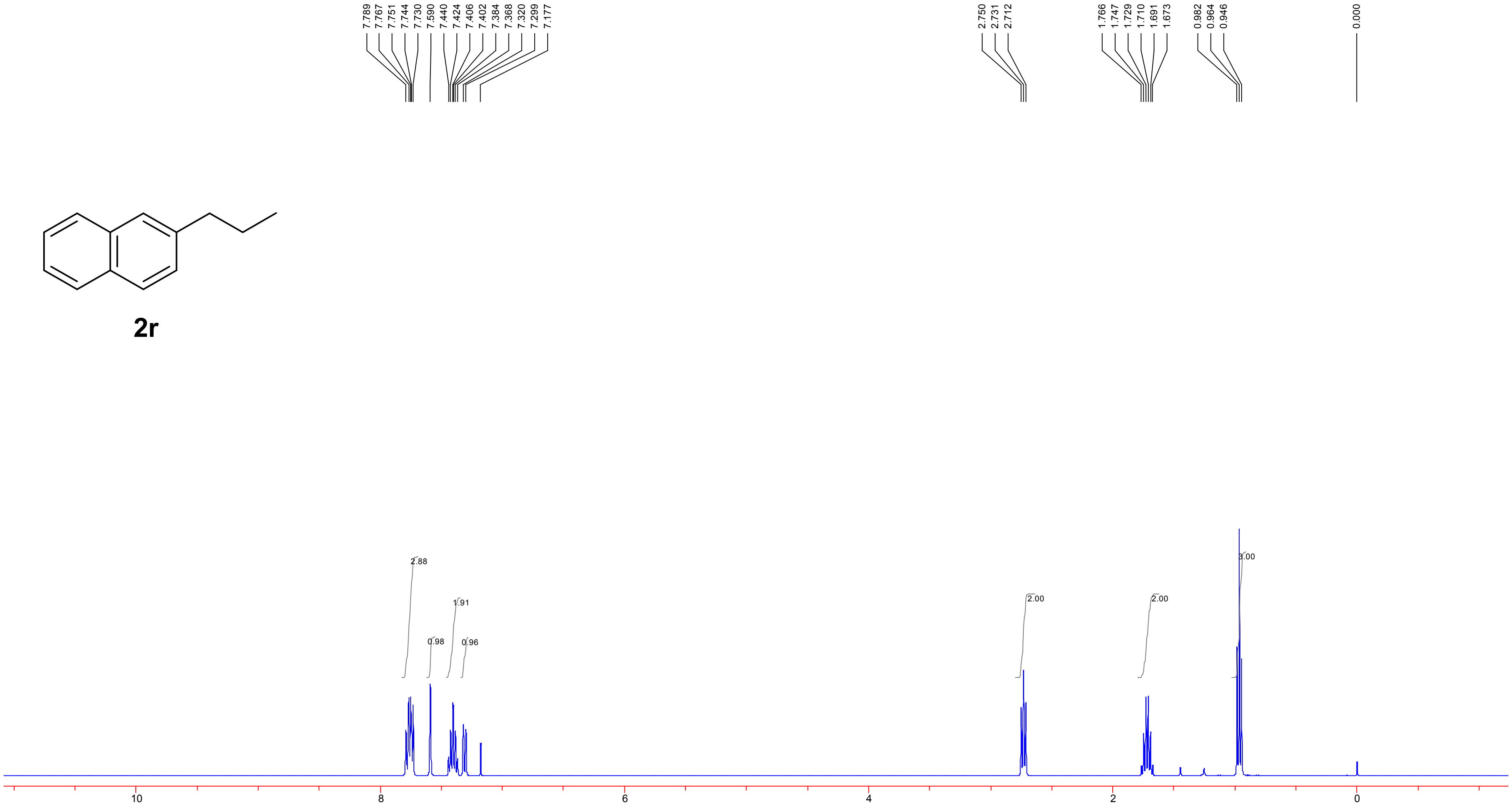

2r

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7.406
7.402
7.384
7.368
7.320
7.299
7.177
2.750
2.731
2.712
1.766
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1.729
1.710
1.691
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0.982
0.964
0.946
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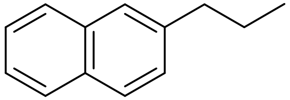
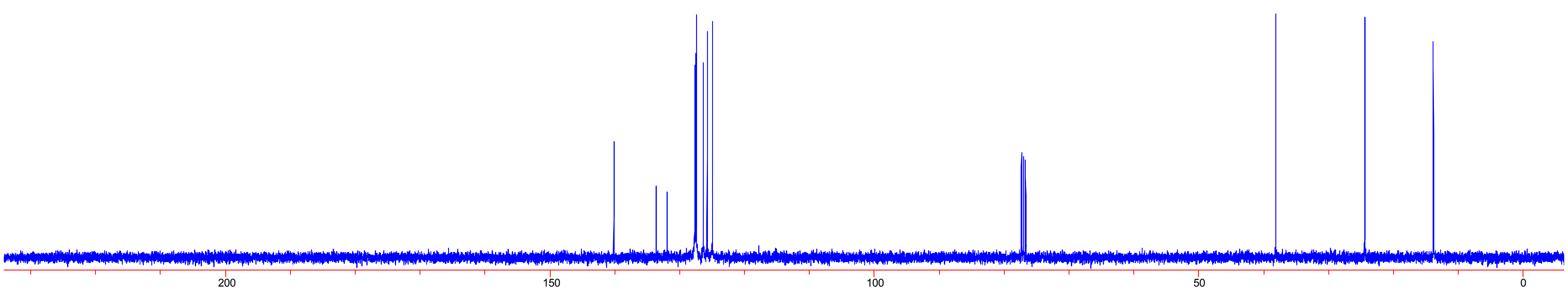


2r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76.681
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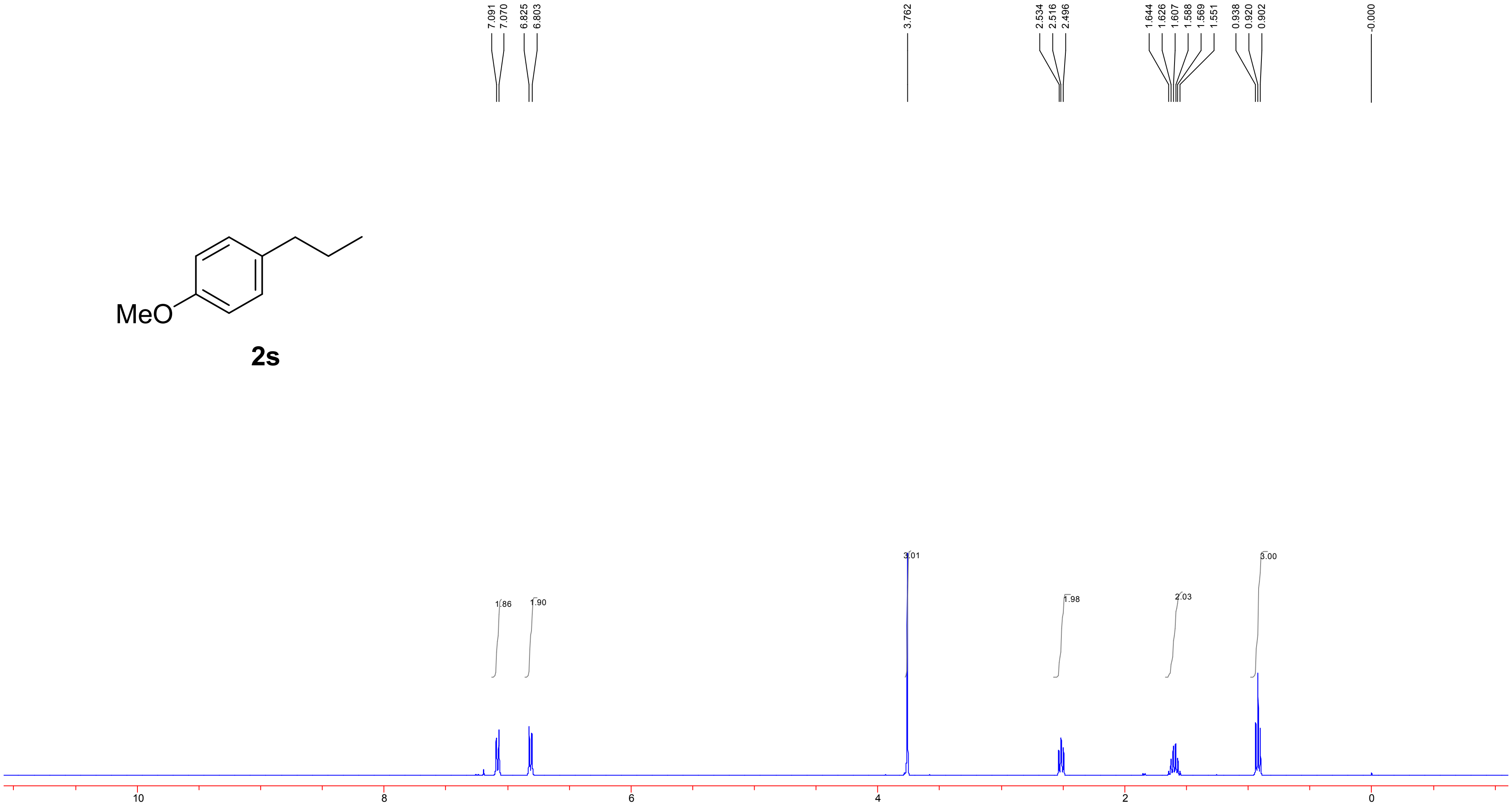

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7.070
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6.803
3.762
2.534
2.516
2.496
1.644
1.626
1.607
1.588
1.569
1.551
0.938
0.920
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1.86
1.90
3.01
1.98
2.03
3.00
10
8
6
4
2
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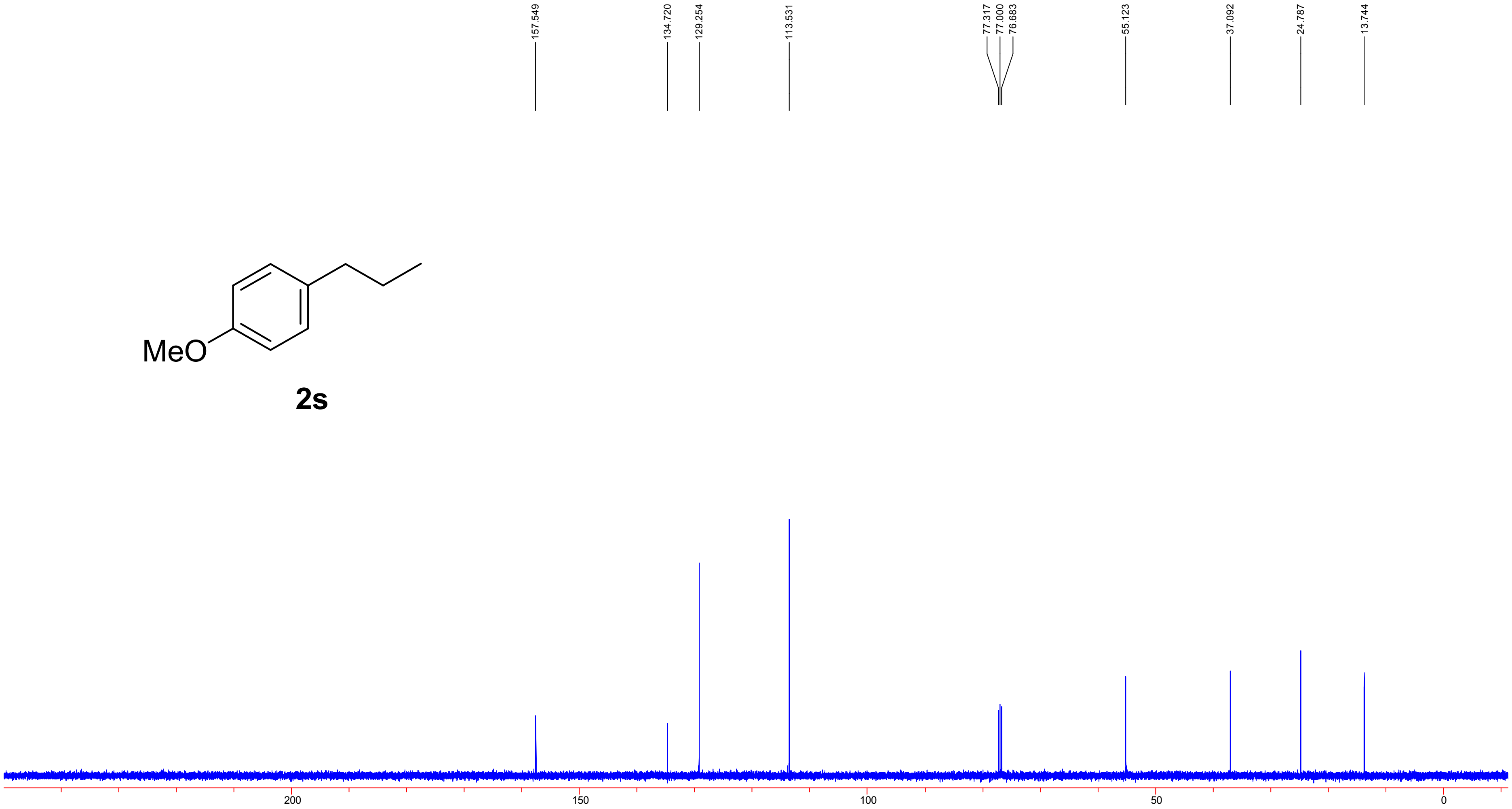
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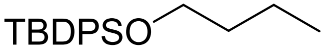
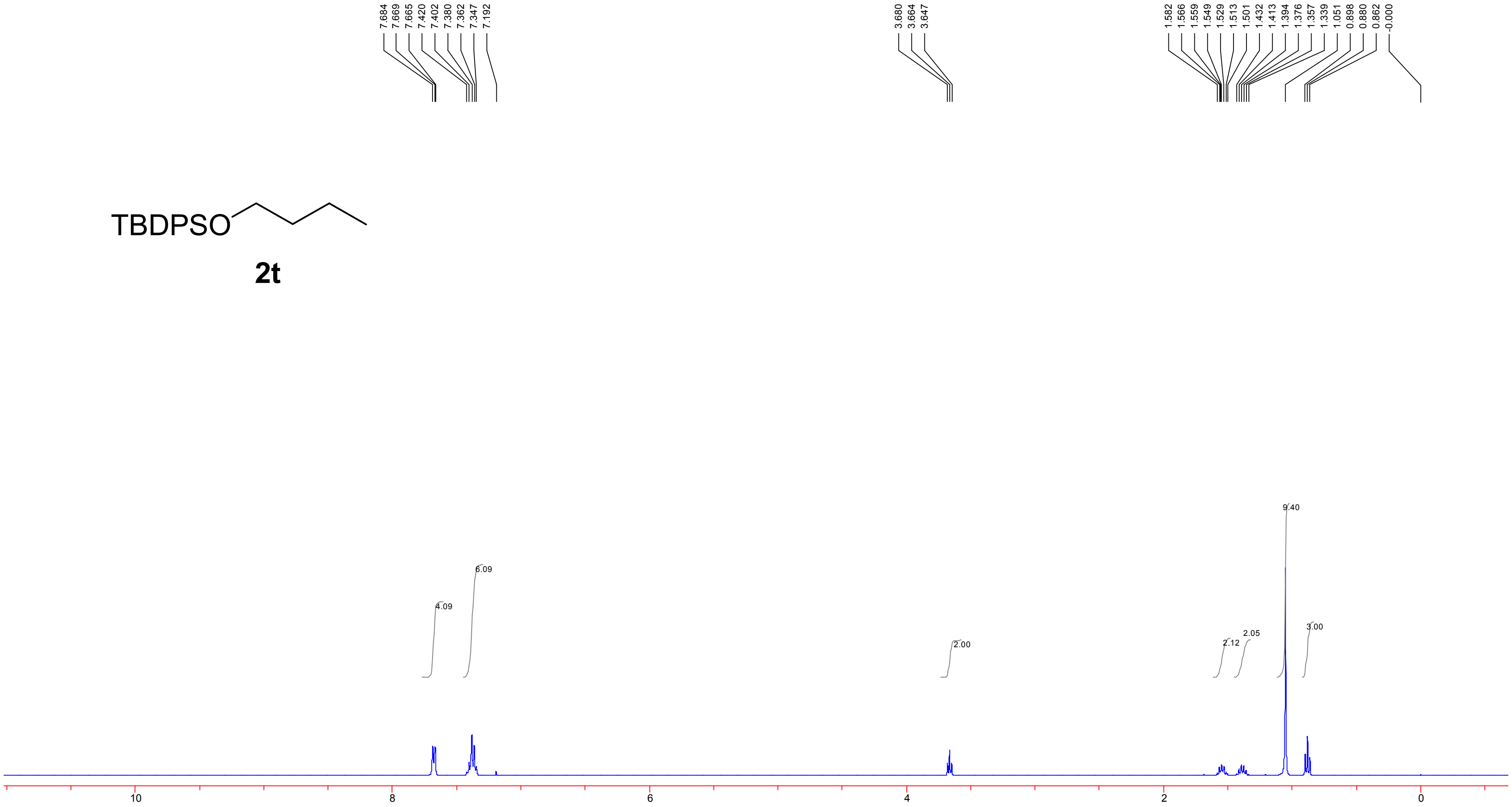
100
50
0

2s


TBDPSO

2t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7.347
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3.680
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3.647
1.582
1.566
1.559
1.549
1.529
1.513
1.501
1.432
1.413
1.394
1.376
1.357
1.339
1.051
0.898
0.880
0.862
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6.09
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3.00
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6
4
2
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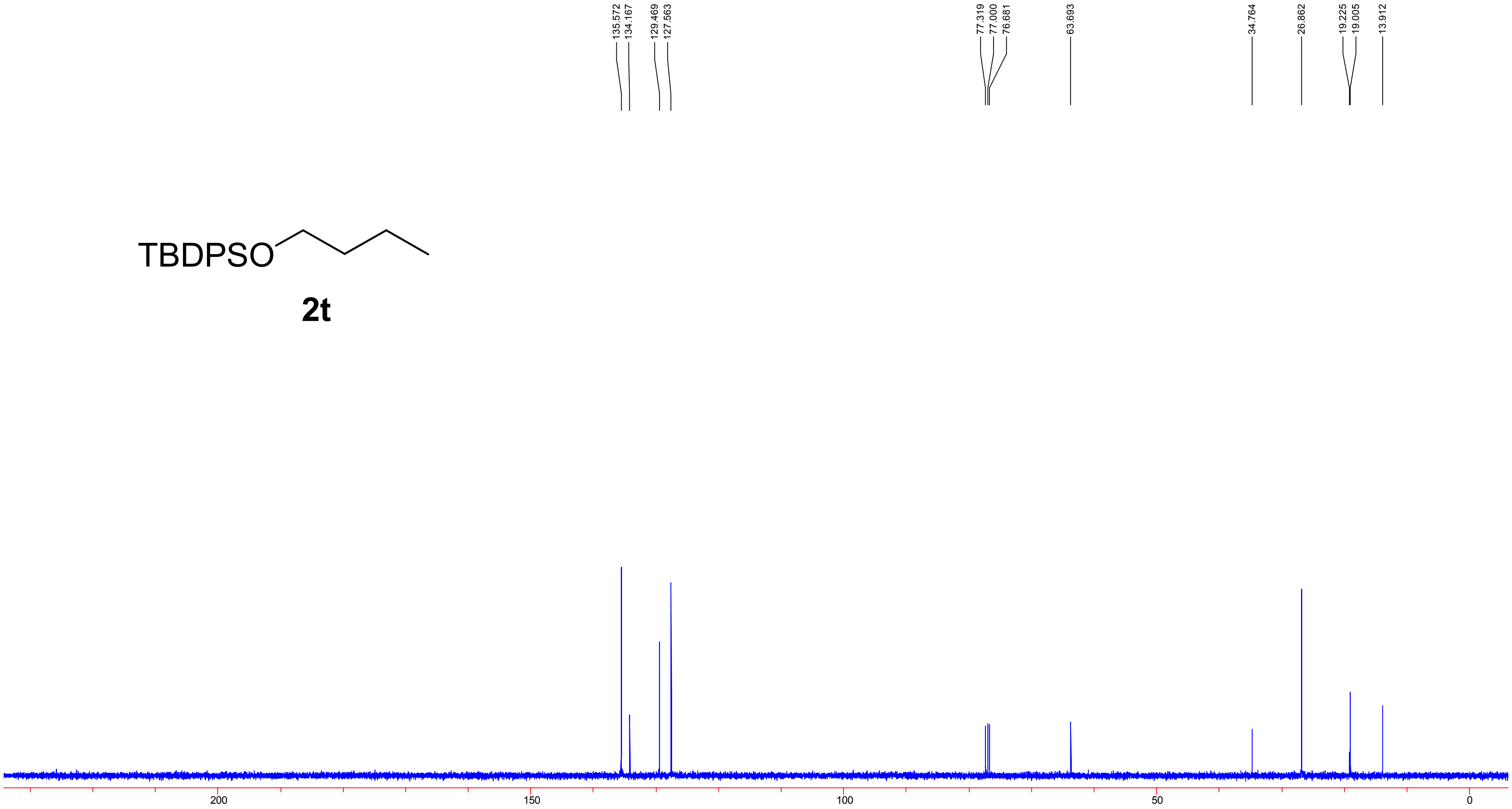

2t

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19.005
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150
100
50
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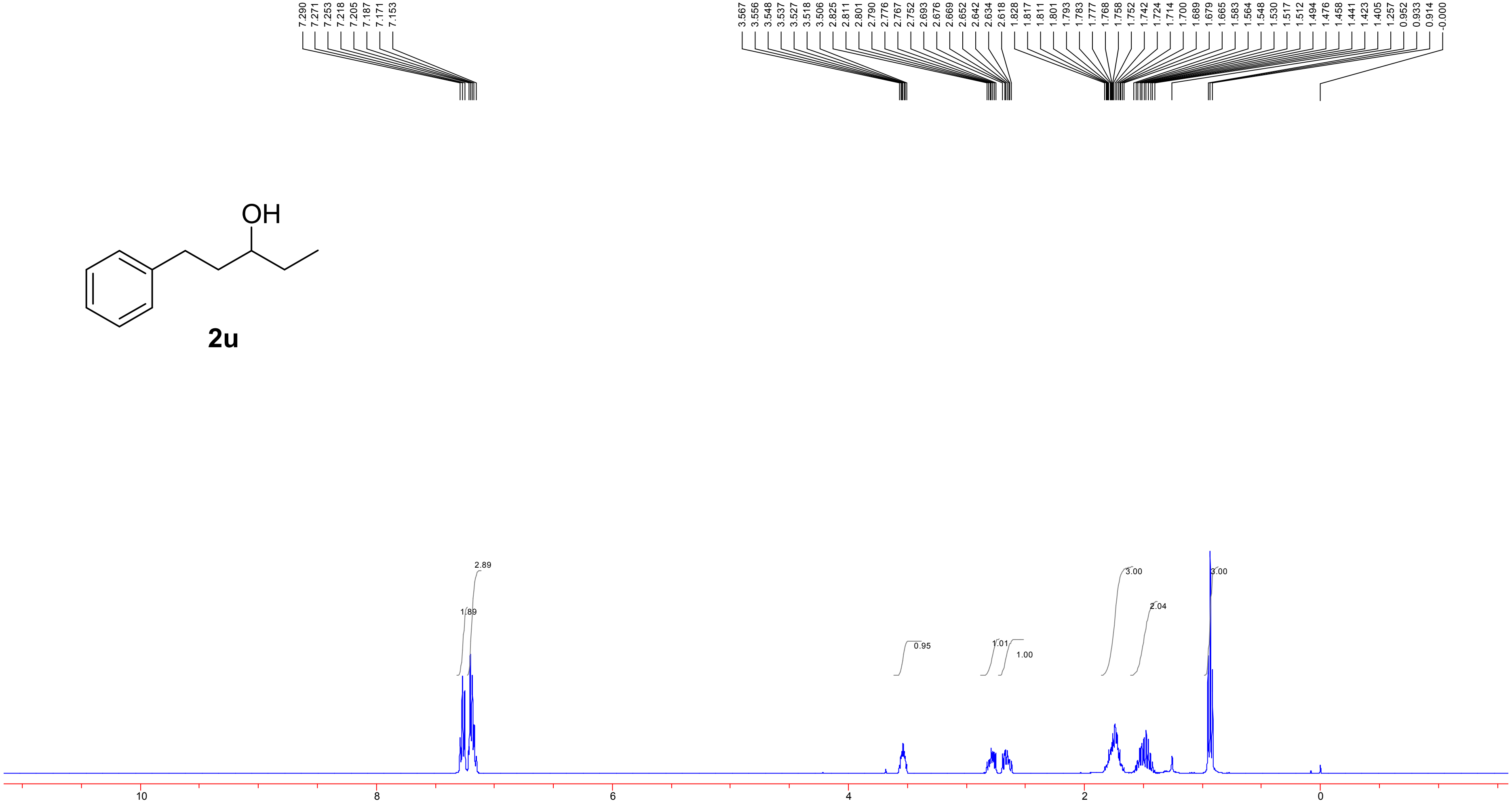

2u

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7.171
7.153
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3.556
3.548
3.537
3.527
3.518
3.506
2.825
2.811
2.801
2.790
2.776
2.767
2.752
2.693
2.676
2.669
2.652
2.642
2.634
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1.817
1.811
1.801
1.793
1.783
1.777
1.768
1.758
1.752
1.742
1.724
1.714
1.700
1.689
1.679
1.665
1.583
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1.548
1.530
1.517
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1.476
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0.914
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3.00
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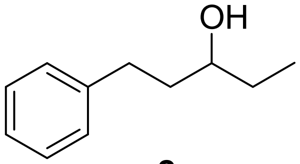

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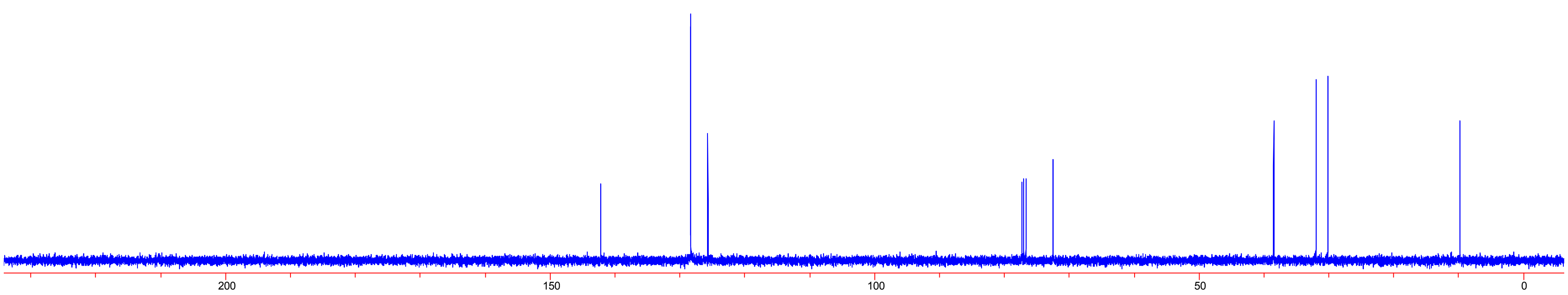

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72.514
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30.179
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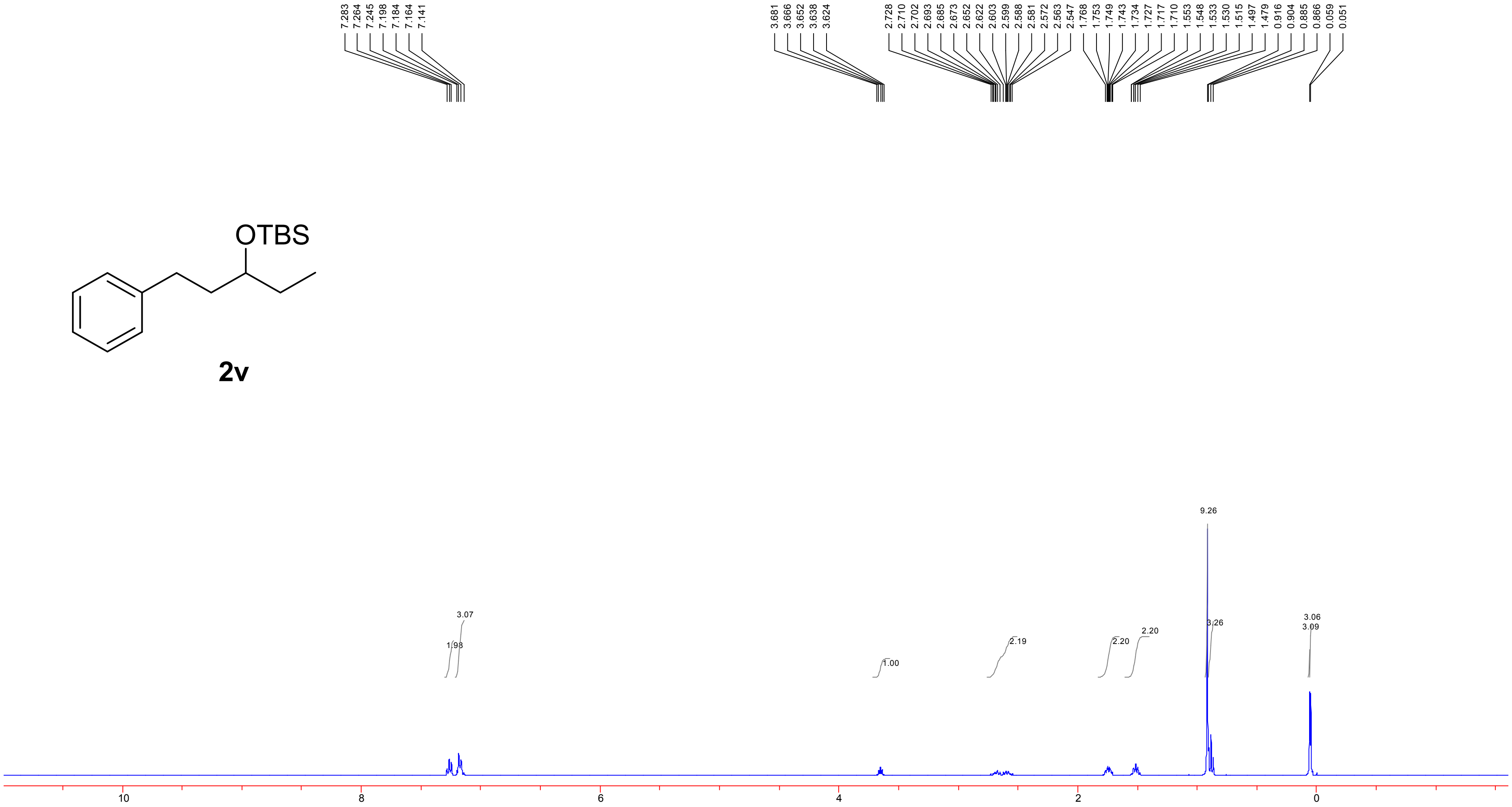
200
150
100
50
0

OTBS

2v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3.681
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3.638
3.624
2.728
2.710
2.702
2.693
2.685
2.673
2.652
2.622
2.603
2.599
2.588
2.581
2.572
2.563
2.547
1.768
1.753
1.749
1.743
1.734
1.727
1.717
1.710
1.553
1.548
1.533
1.530
1.515
1.497
1.479
0.916
0.904
0.885
0.866
0.059
0.051
9.26
3.07
1.98
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2.20
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3.06
3.09
10
8
6
4
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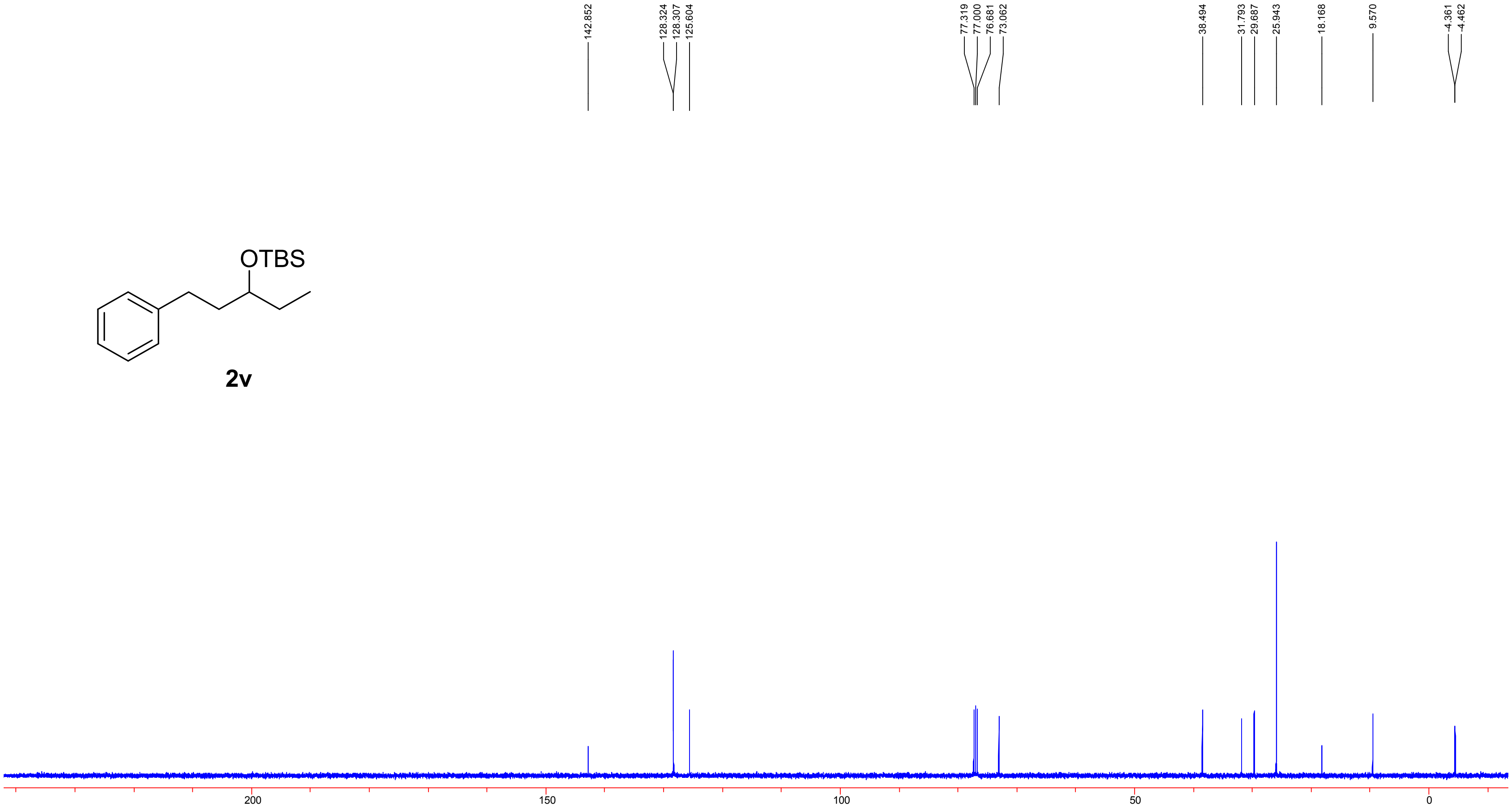
0

OTBS

2v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128.307
125.604
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77.000
76.681
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29.687
25.943
18.168
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150
100
50
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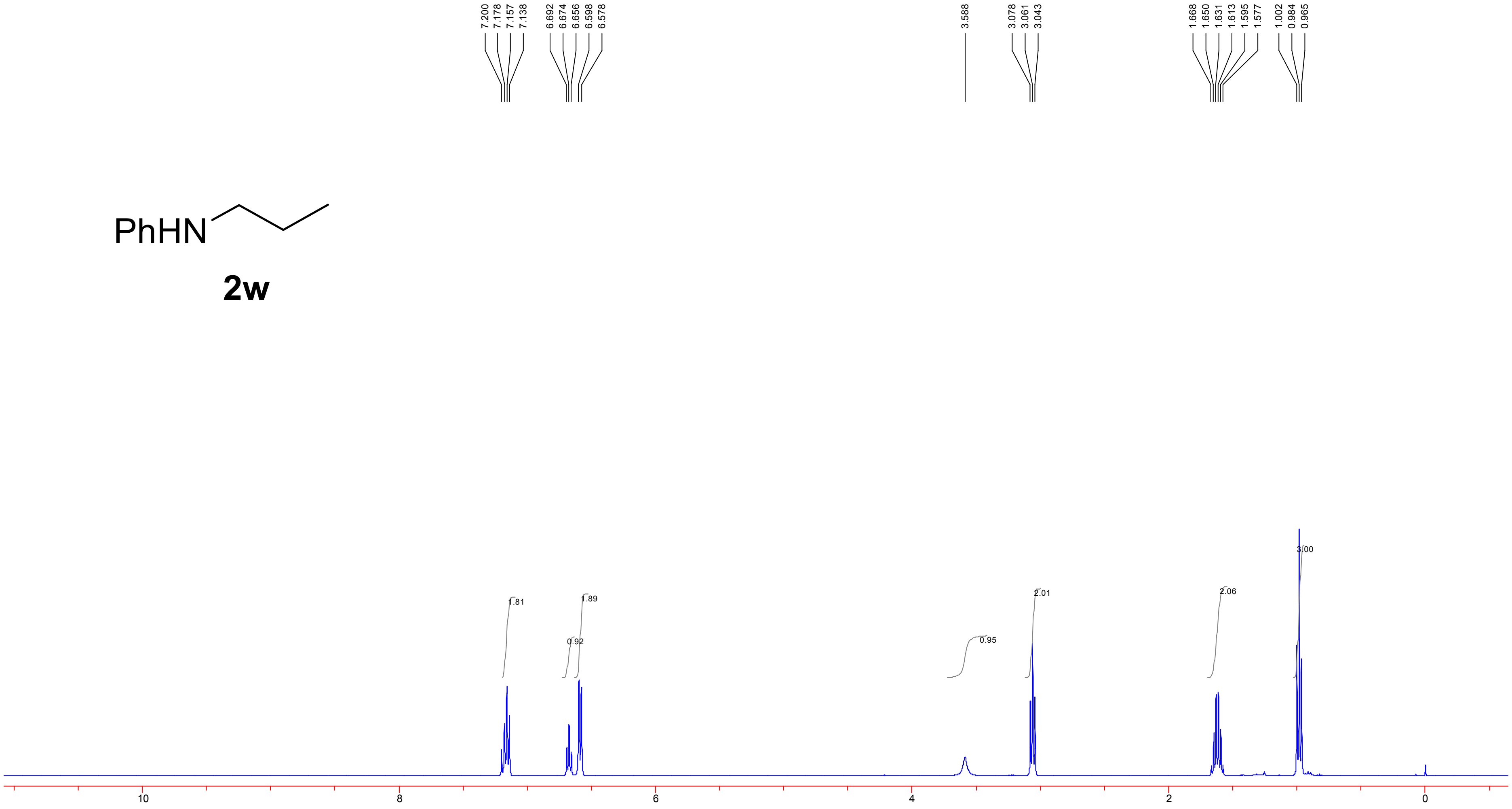
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6.674
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6.598
6.578
3.588
3.078
3.061
3.043
1.668
1.650
1.631
1.613
1.595
1.577
1.002
0.984
0.965
PhHN
1.81
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6
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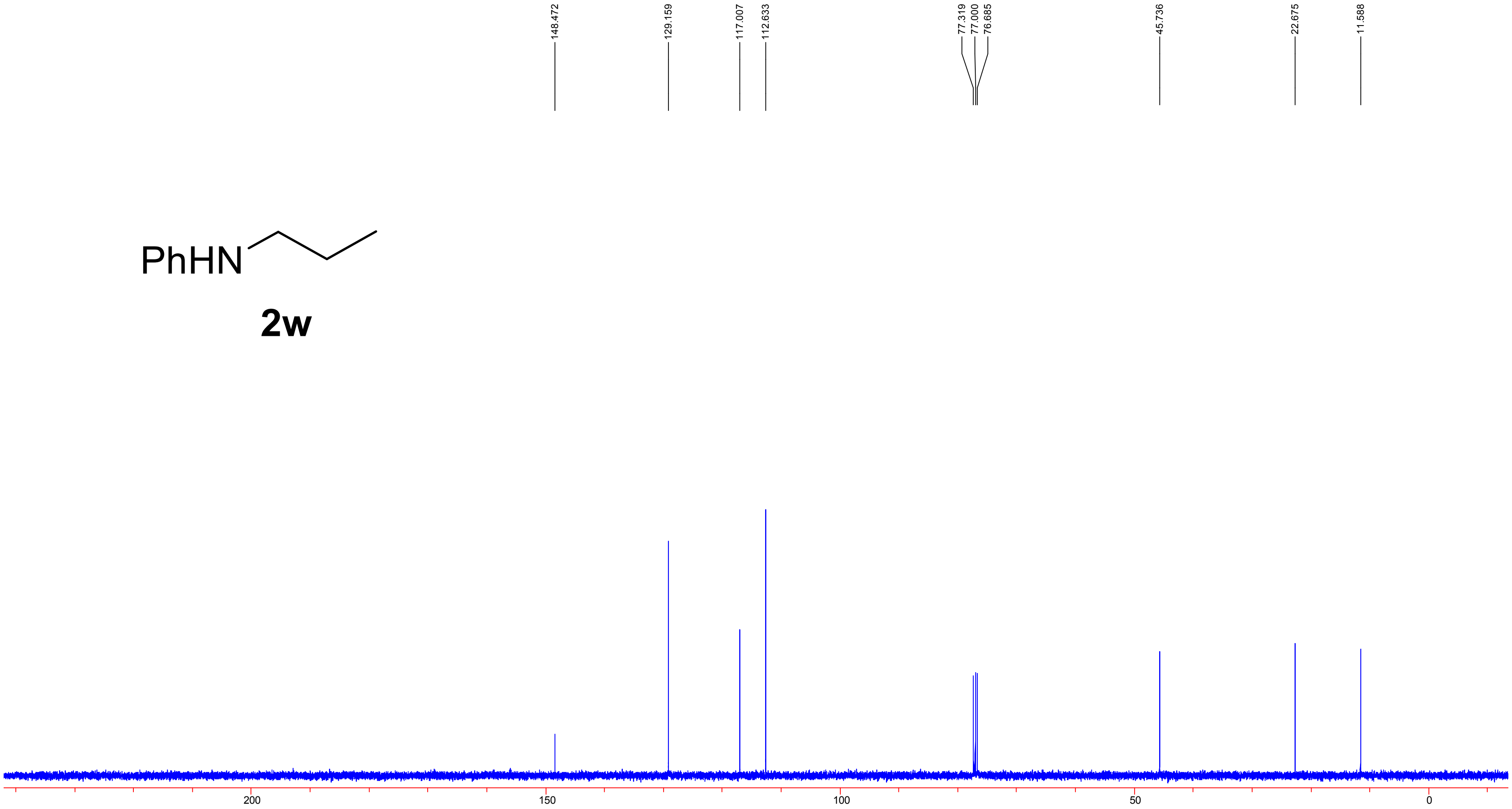
2w

PhHN

2w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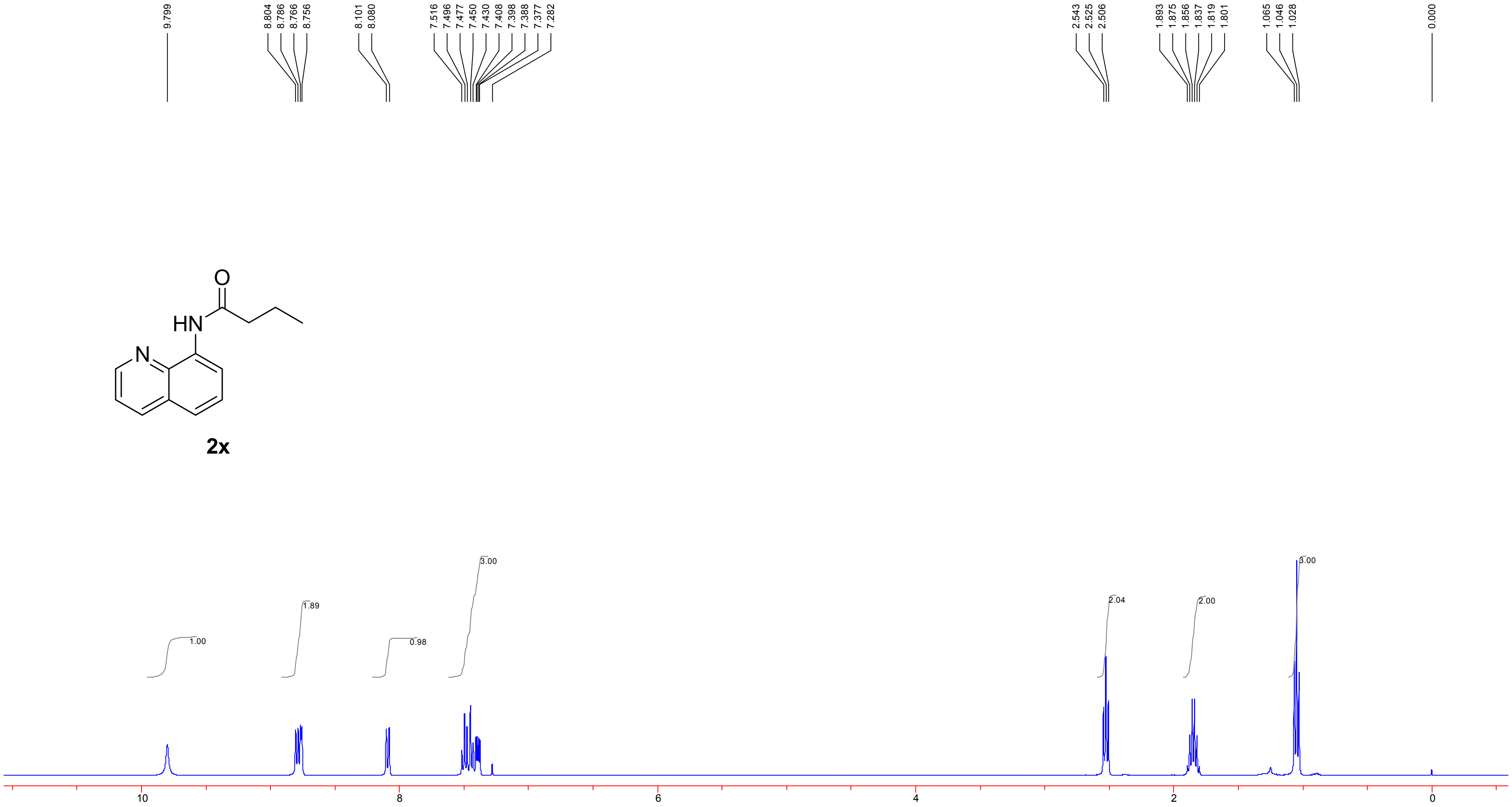
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7.377
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2.506
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1.046
1.028
0.000
O
HN
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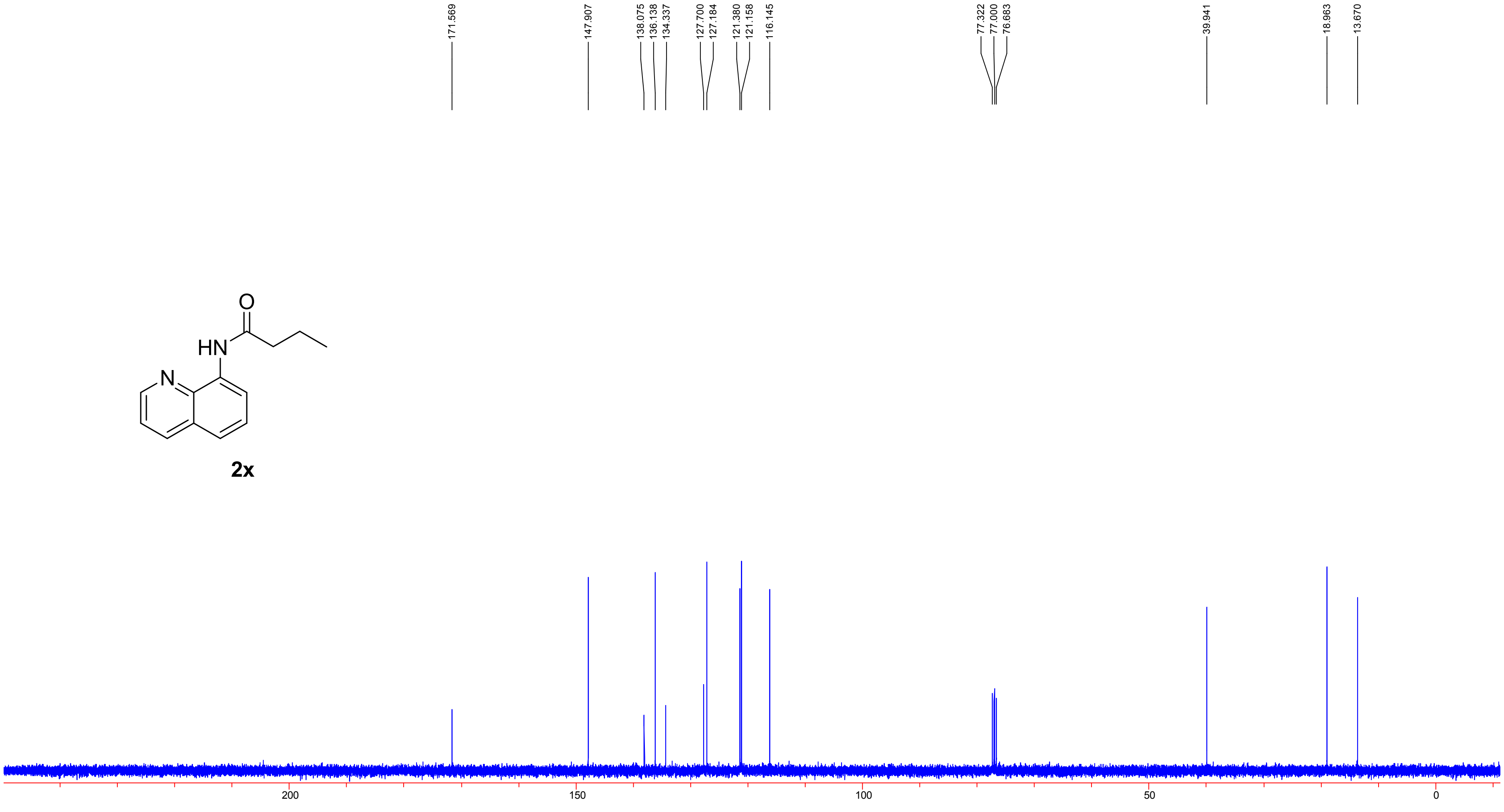

2x

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134.337
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127.184
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77.000
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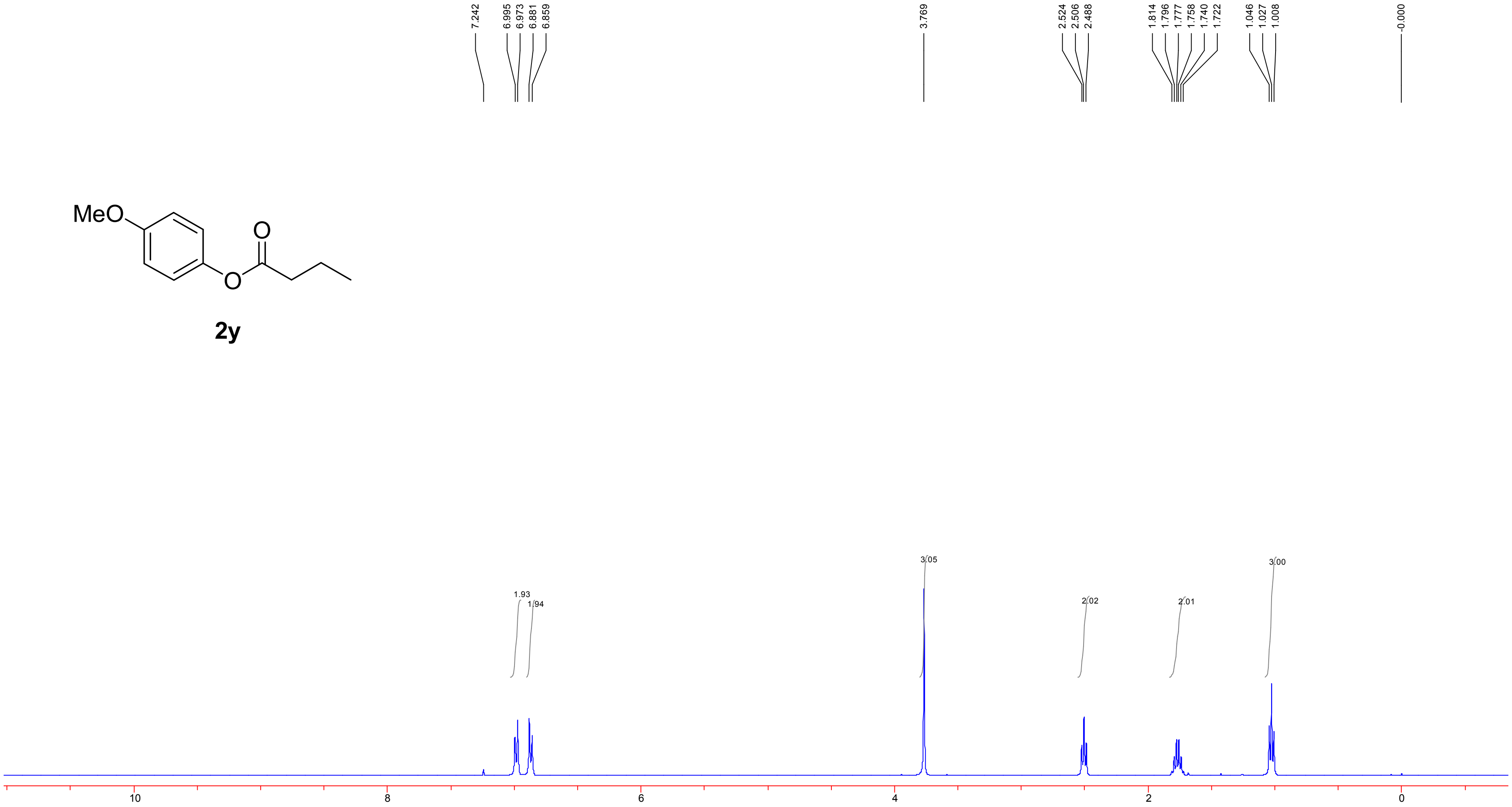
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1.777
1.758
1.740
1.722
1.046
1.027
1.008
-0.000
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O
O
2y
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1.94
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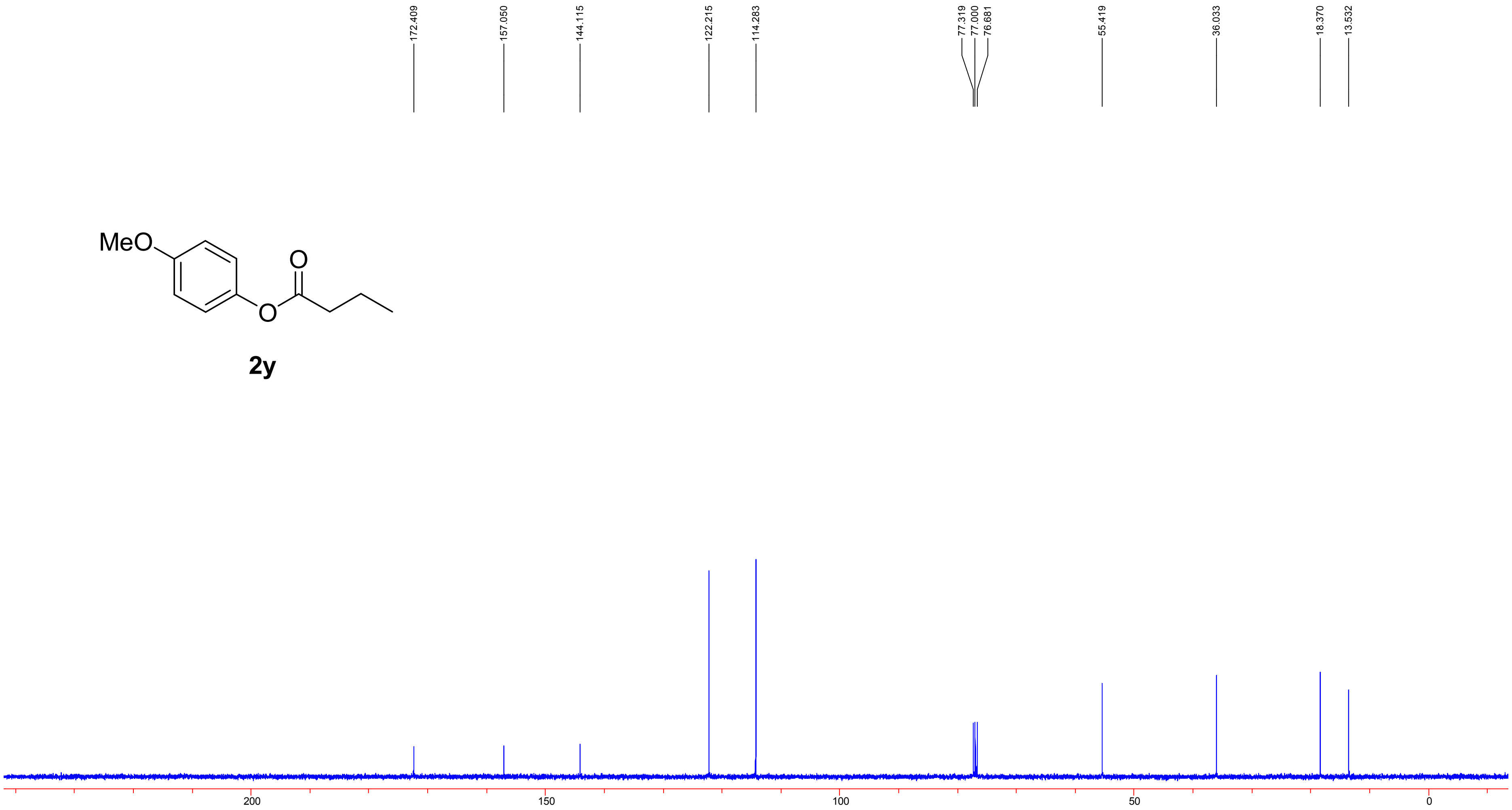
2.01
3.00
10
8
6
4
2
0



2y

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13.532
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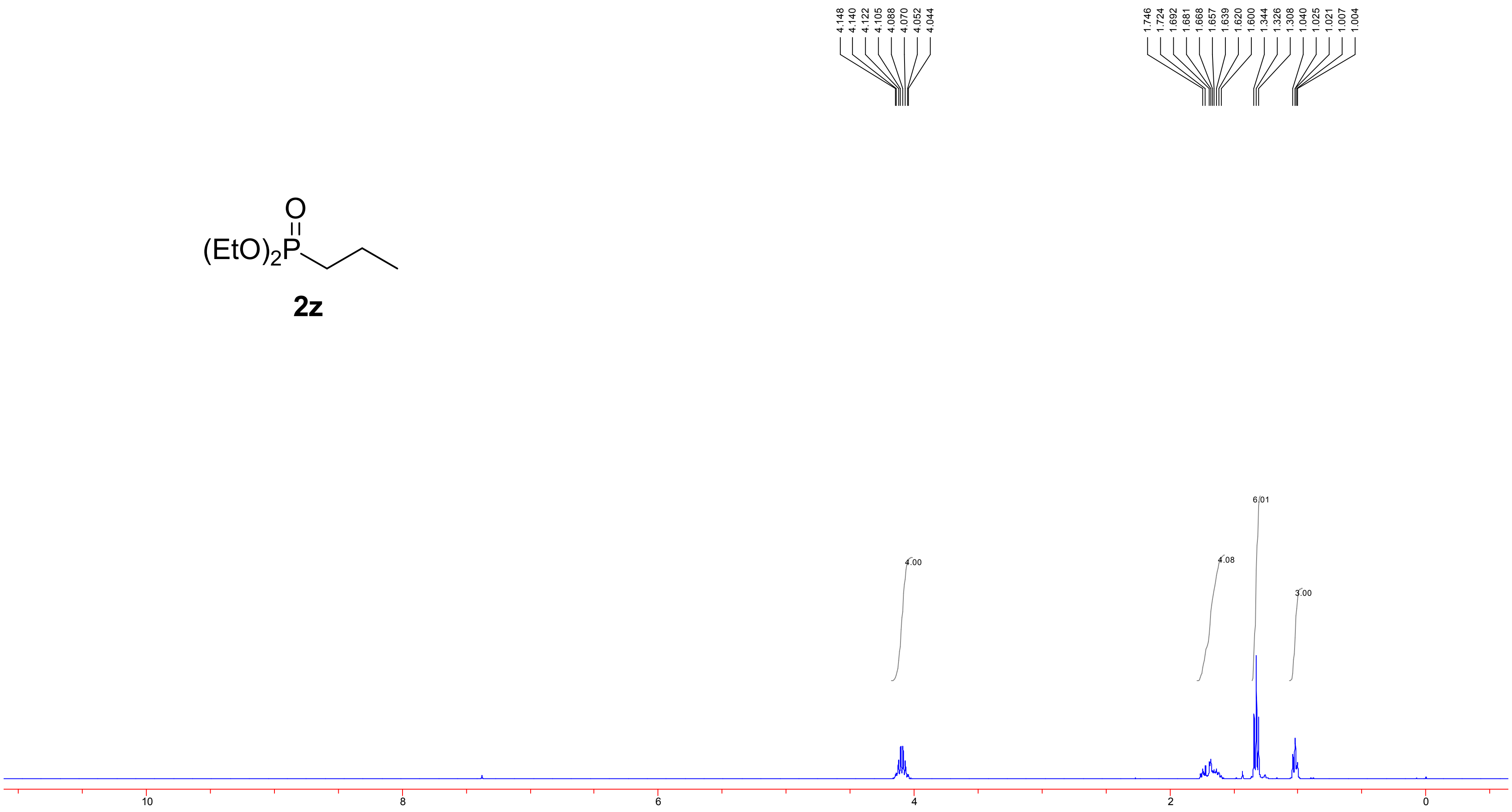
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1.681
1.668
1.657
1.639
1.620
1.600
1.344
1.326
1.308
1.040
1.025
1.021
1.007
1.004
O
(EtO)2P
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4.00
4.08
3.00
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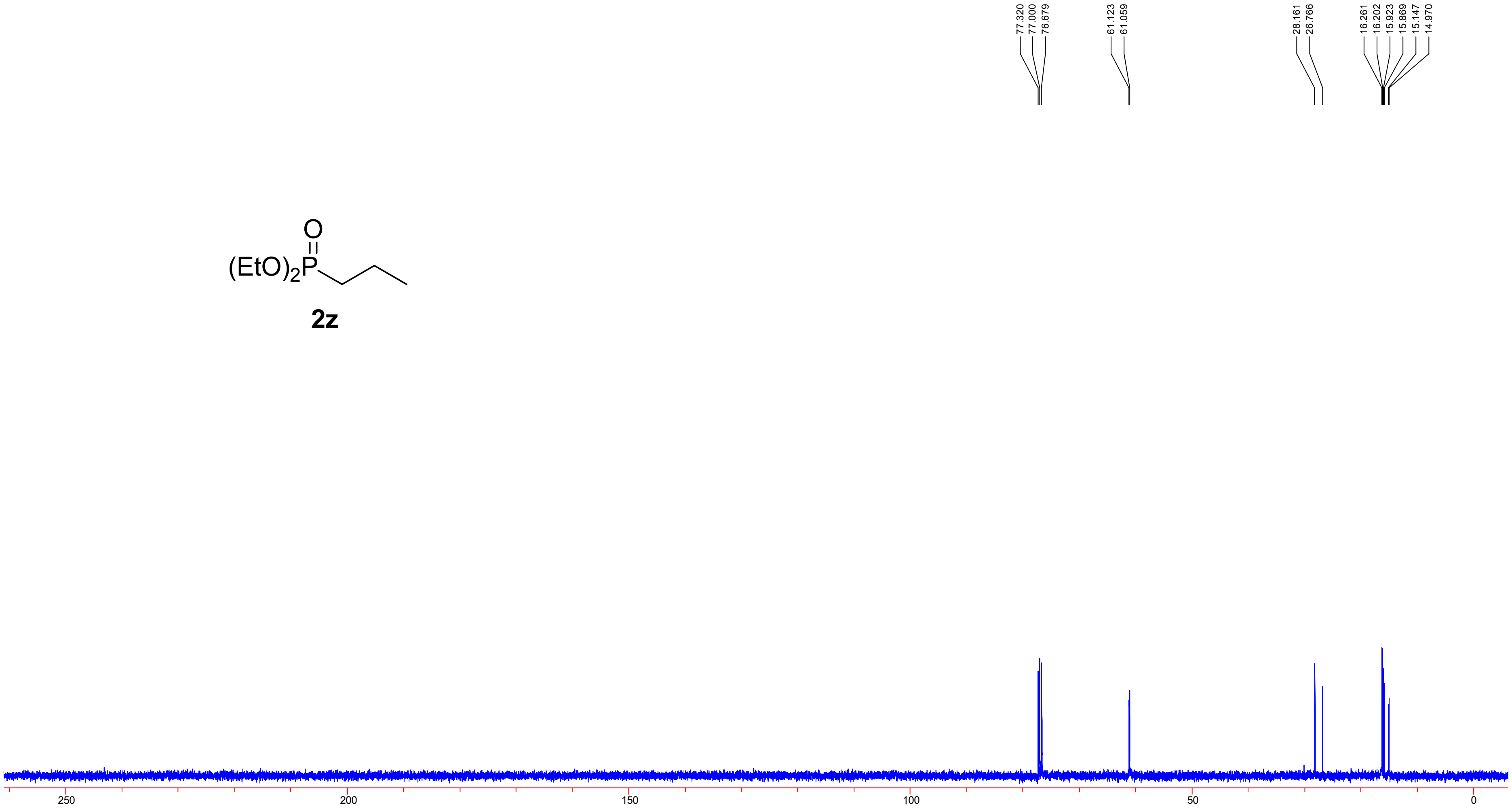
6
4
2
0

2z


O
(EtO)$_2$P

2z

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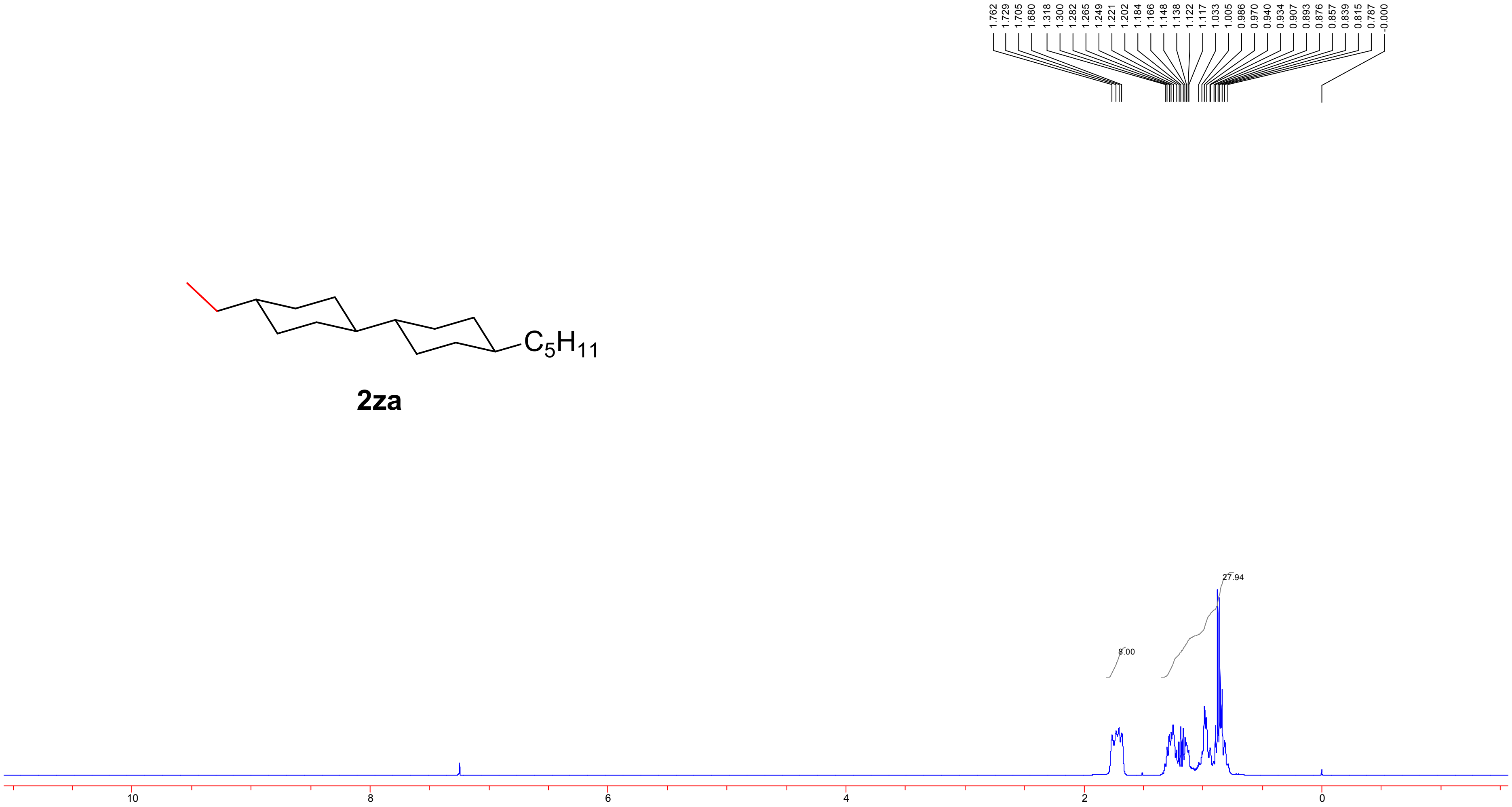
0

C5H11

2za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1.122
1.117
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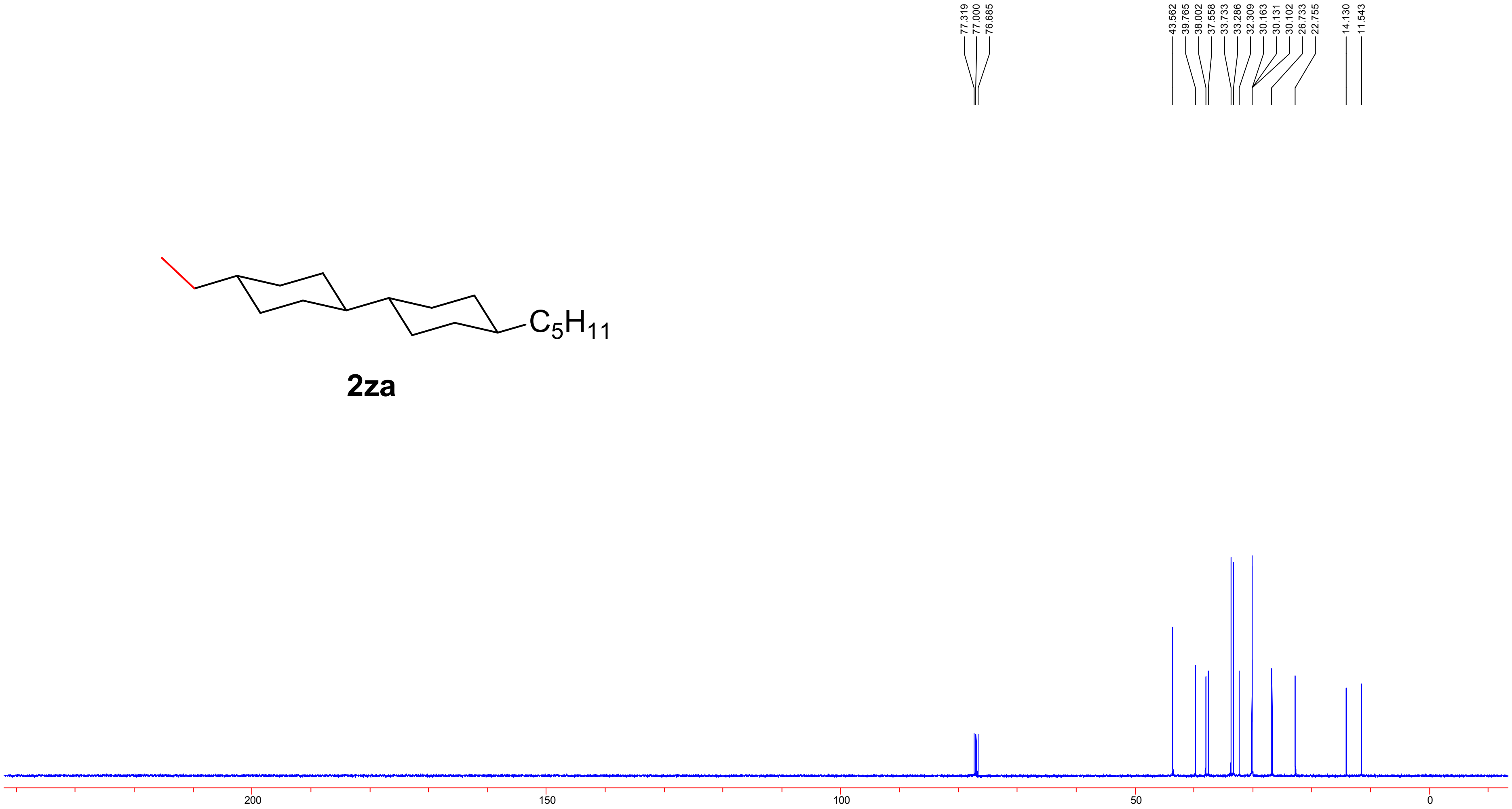

2za

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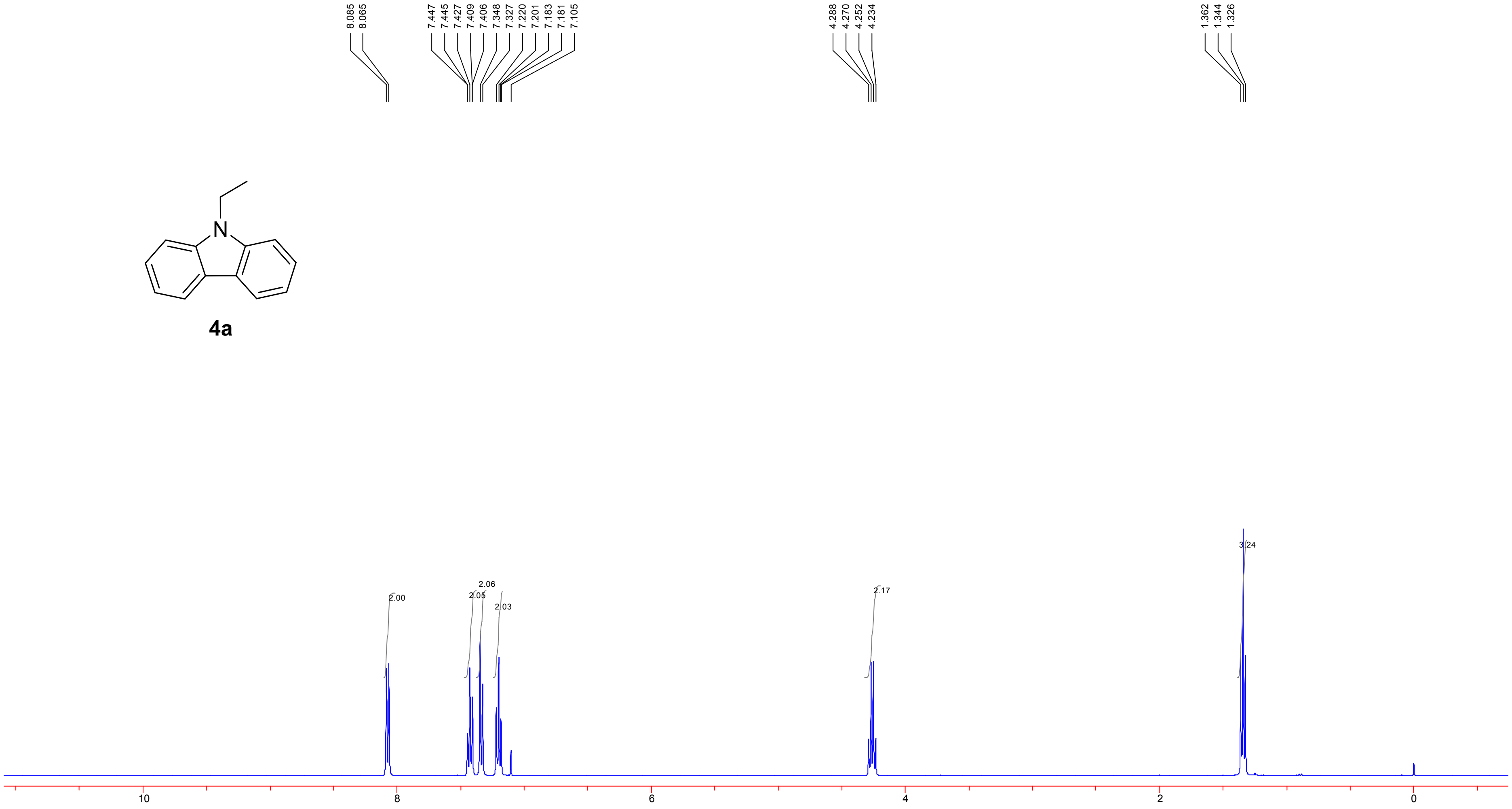
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7.220
7.201
7.183
7.181
7.105
4.288
4.270
4.252
4.234
1.362
1.344
1.326
N
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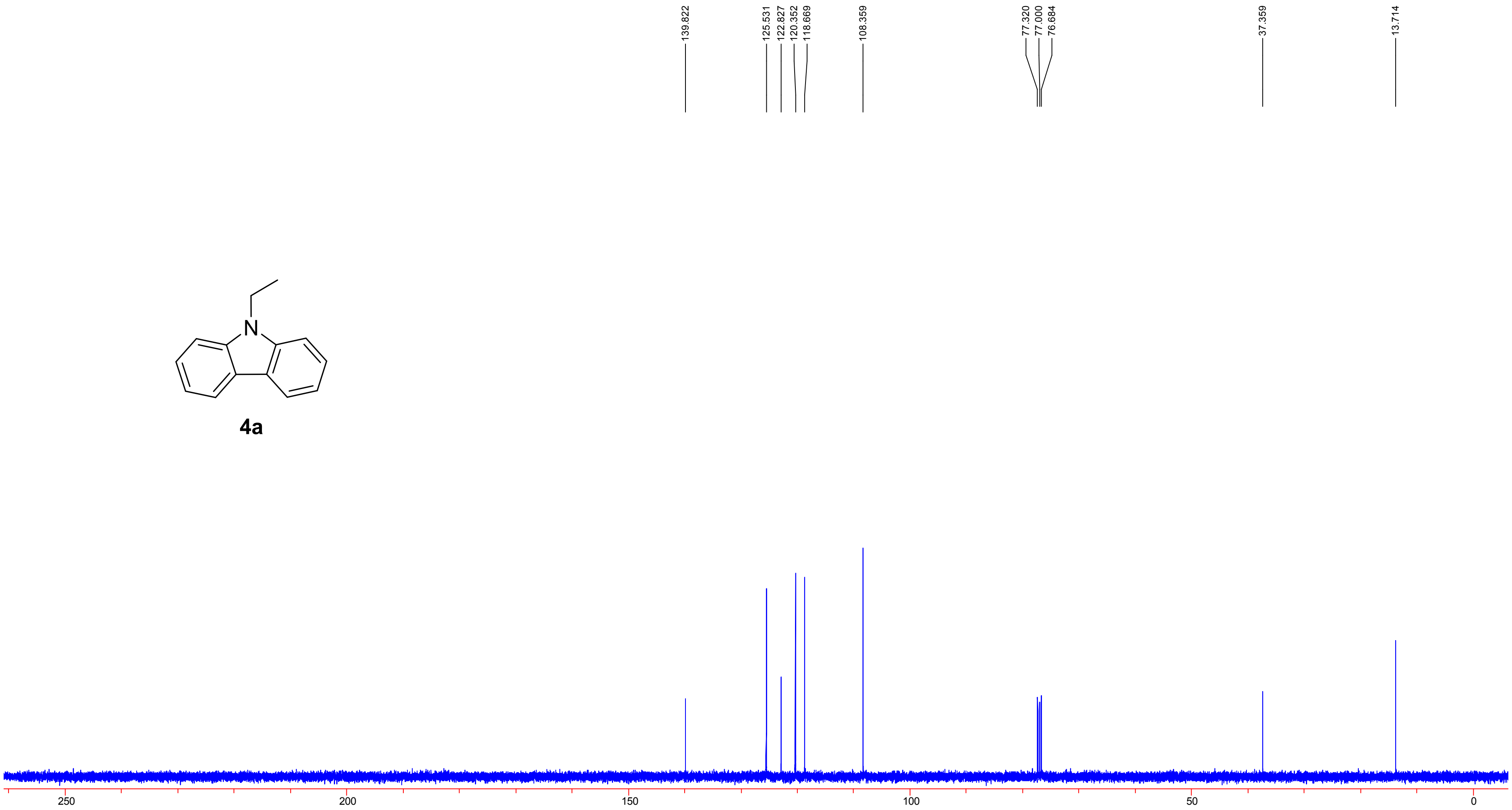
2.05
2.06
2.03
2.17
3.24
10
8
6
4
2
0

4a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122.827
120.352
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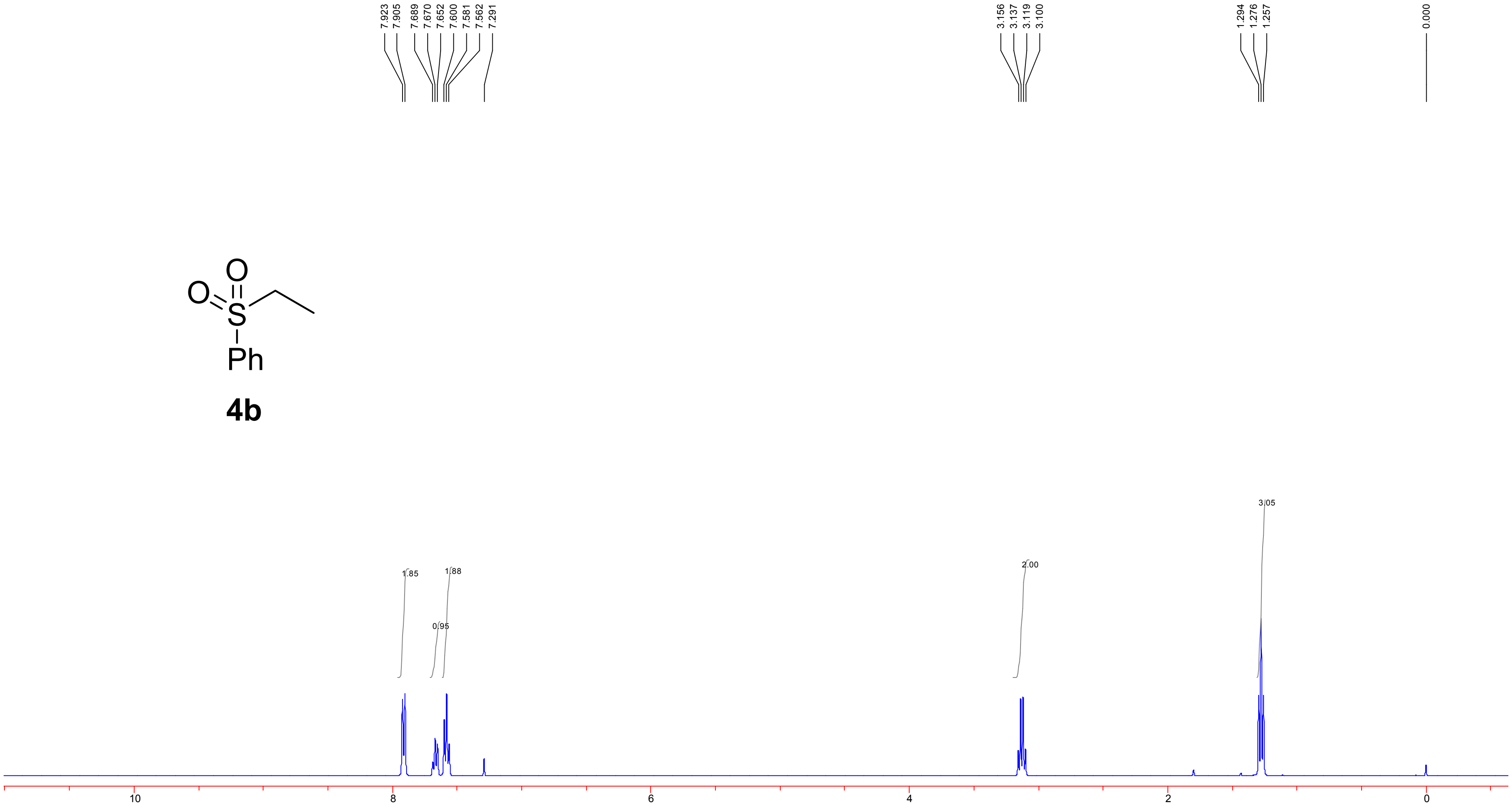
108.359
77.320
77.000
76.684
37.359
13.714
N
4a
250
200
150
100
50
0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7.600
7.581
7.562
7.291
3.156
3.137
3.119
3.100
1.294
1.276
1.257
0.000
O
O
S
Ph
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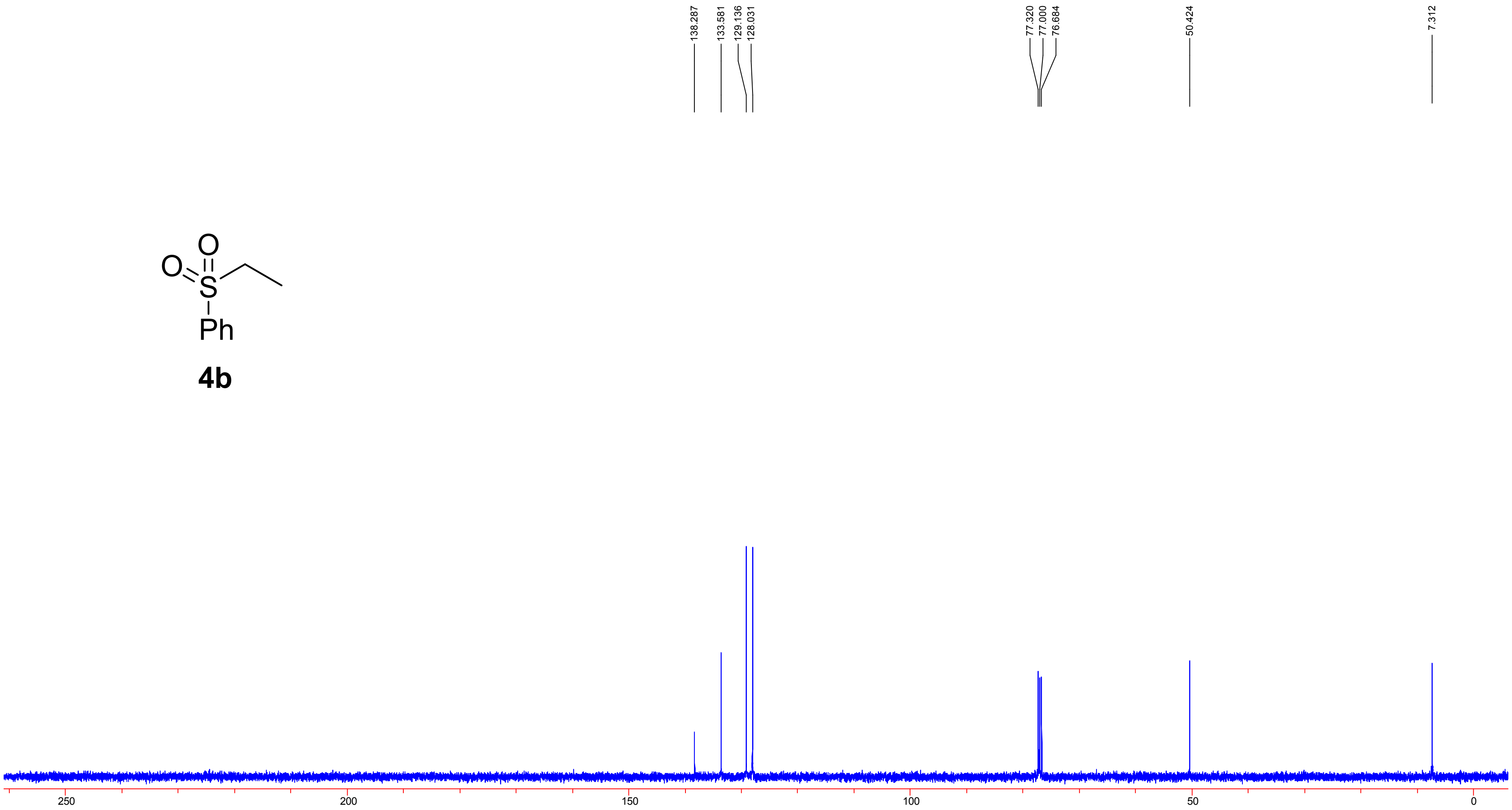
10
8
6
4
2
0

4b



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129.136
128.031
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76.684
50.424
7.312
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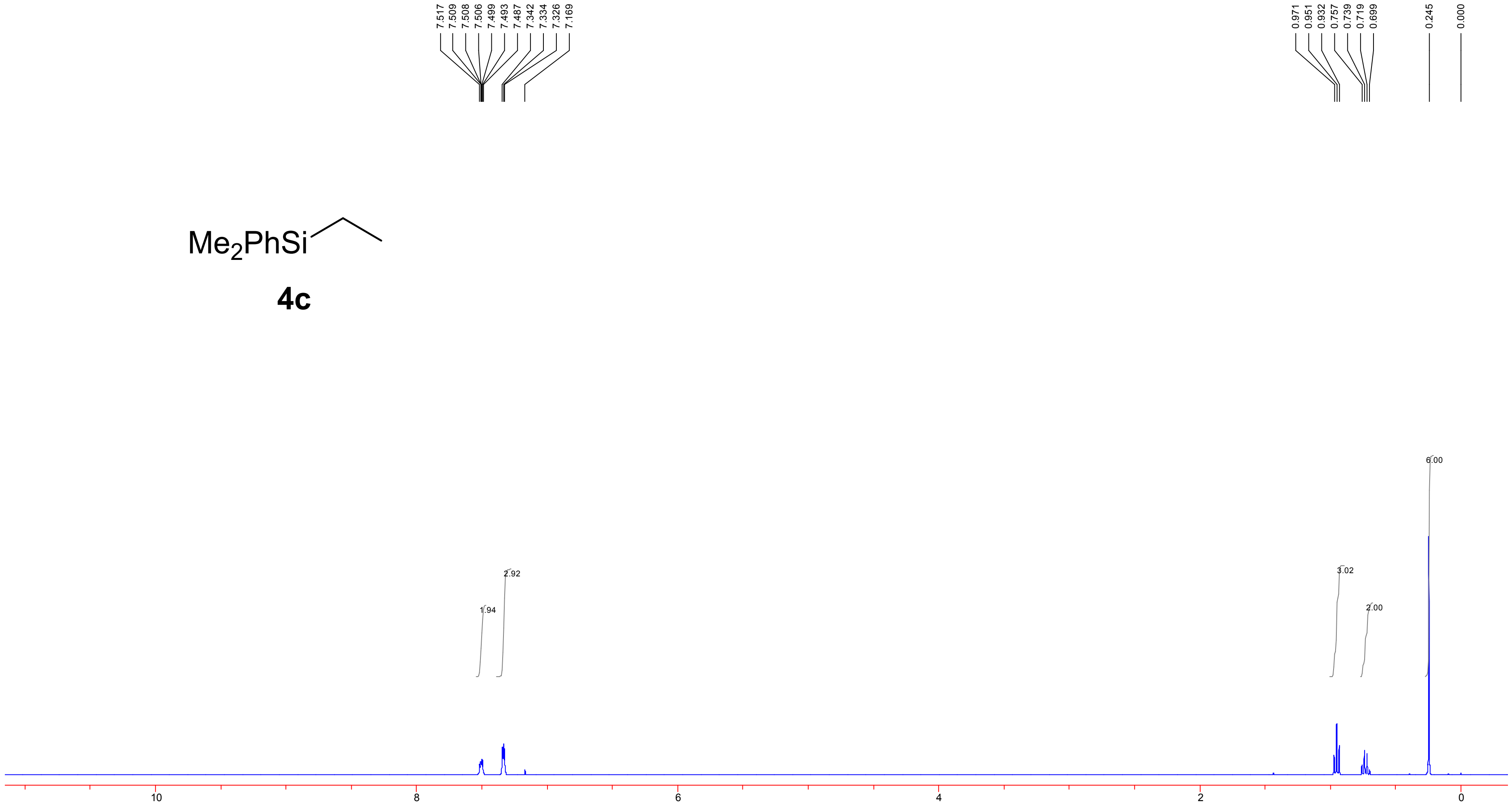
O
S
Ph
250
200
150
100
50
0

4b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7.326
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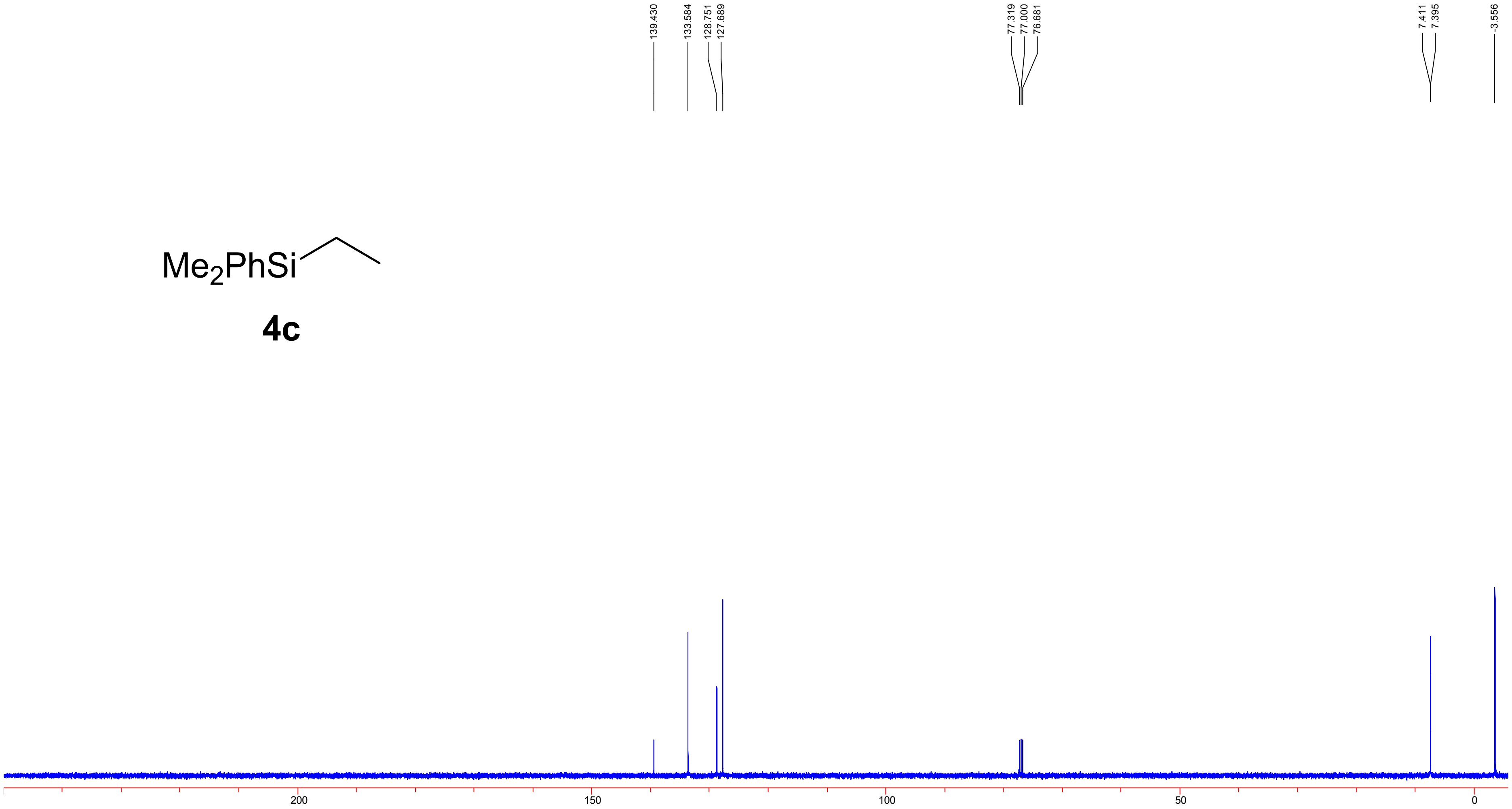
0.951
0.932
0.757
0.739
0.719
0.699
0.245
0.000
Me$_2$PhSi
1.94
2.92
3.02
2.00
6.00
10
8
6
4
2
0

4c

4c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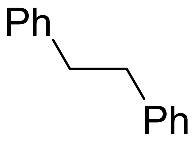
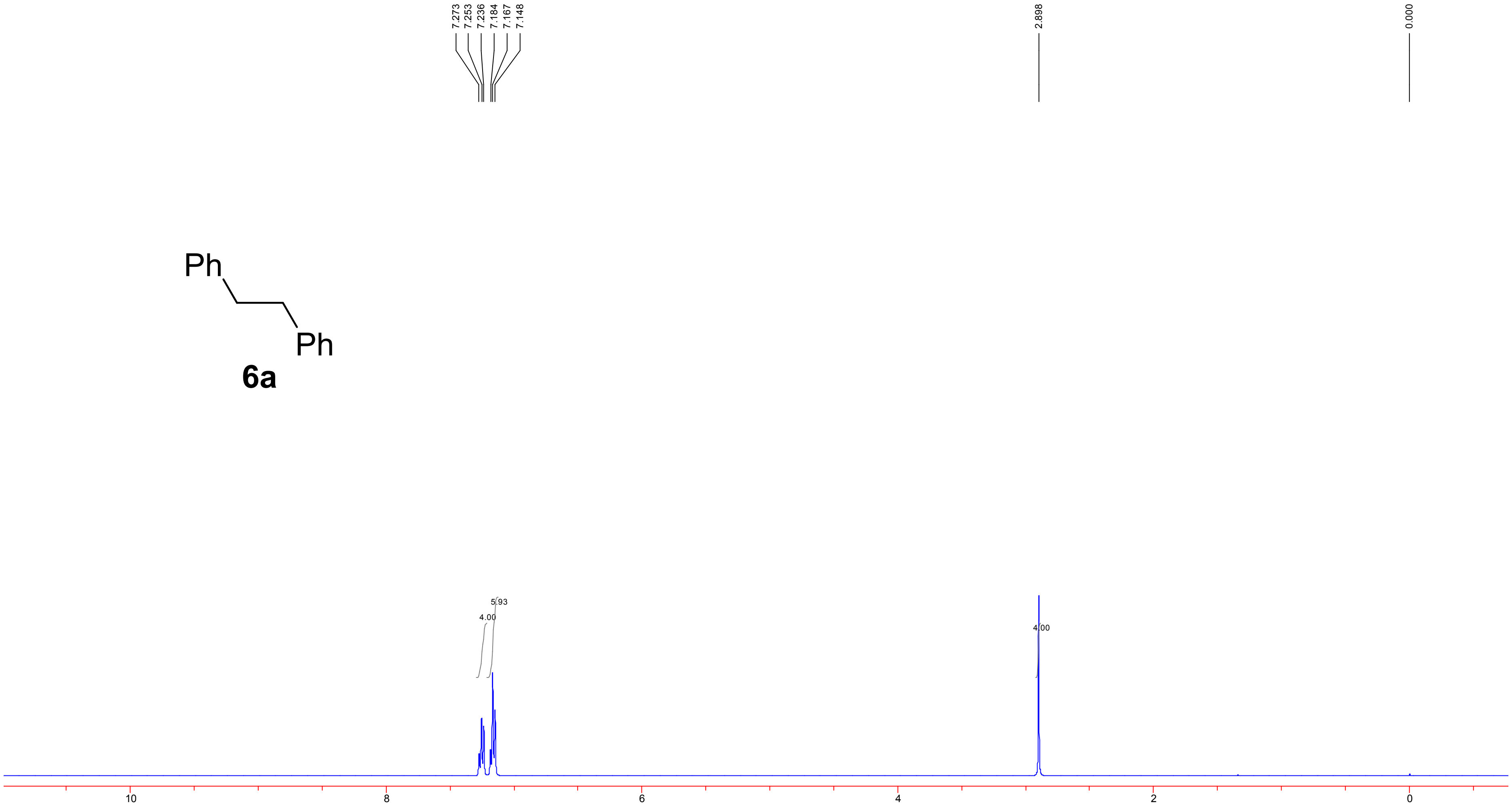
76.681
7.411
7.395
-3.556
200
150
100
50
0


Ph
Ph

6a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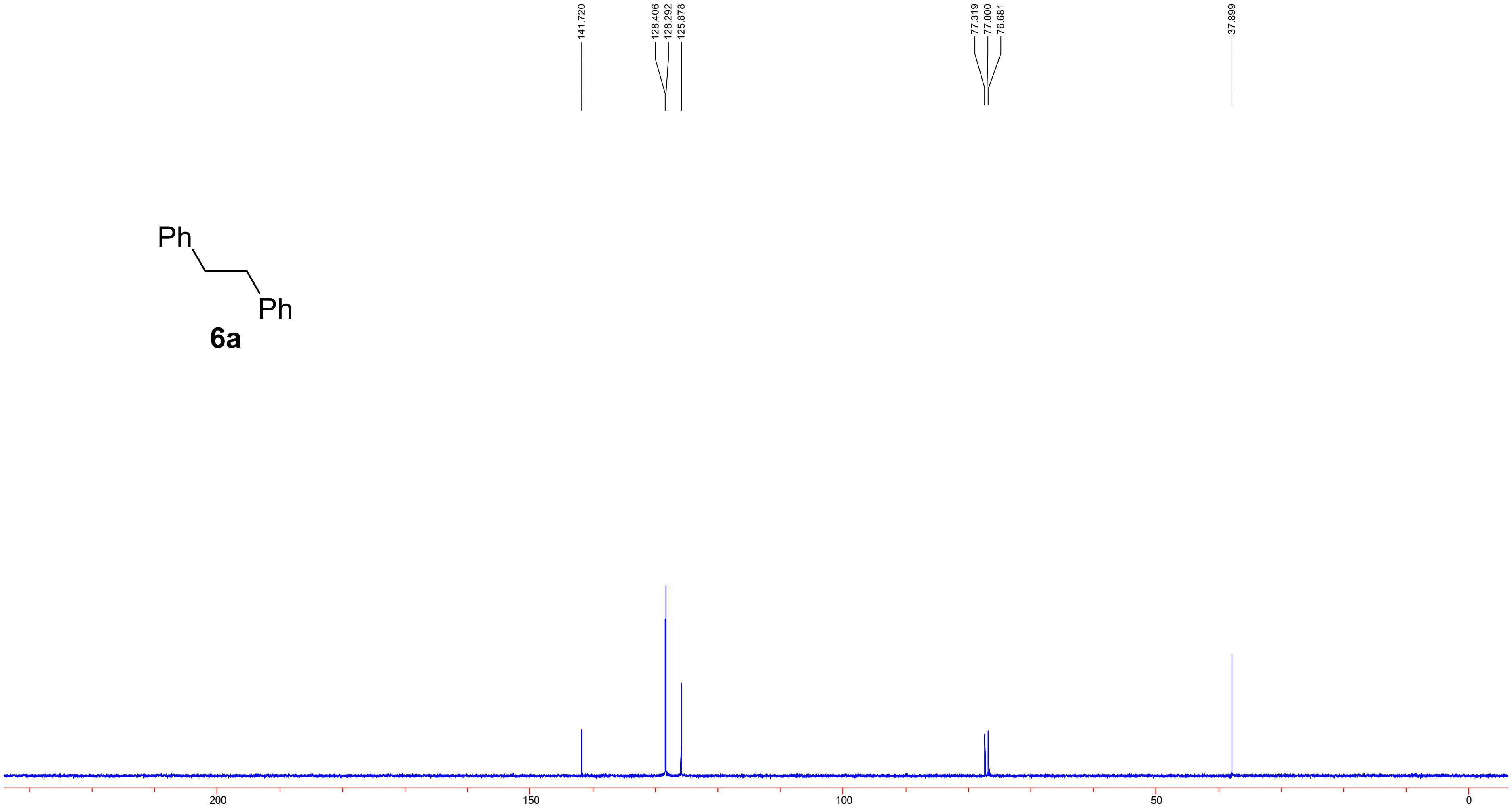
7.253
7.236
7.184
7.167
7.148
2.898
0.000
5.93
4.00
4.00
10
8
6
4
2
0

6a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77.319
77.000
76.681
37.899
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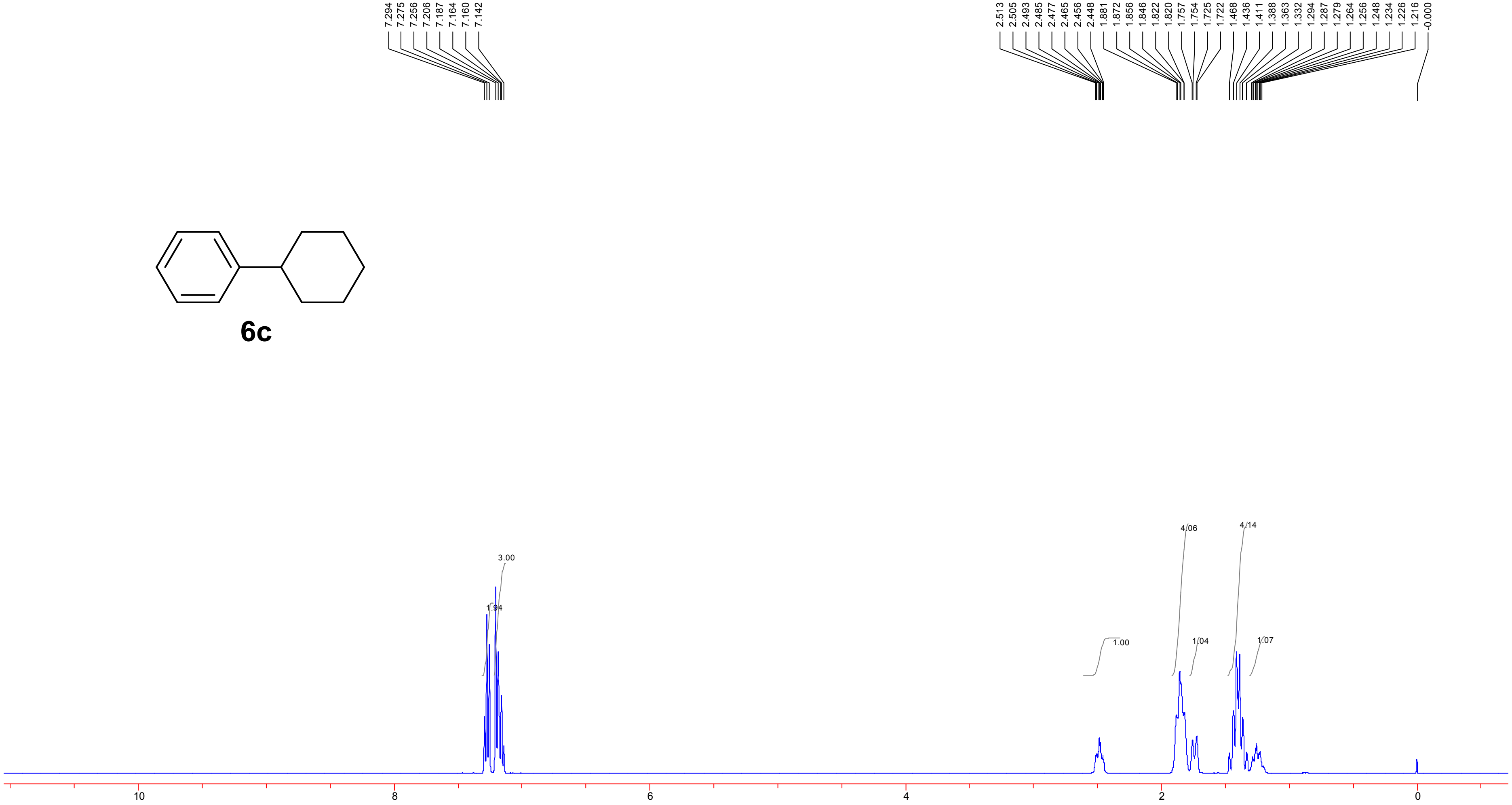
150
100
50
0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7.275
7.256
7.206
7.187
7.164
7.160
7.142
2.513
2.505
2.493
2.485
2.477
2.465
2.456
2.448
1.881
1.872
1.856
1.846
1.822
1.820
1.757
1.754
1.725
1.722
1.468
1.436
1.411
1.388
1.363
1.332
1.294
1.287
1.279
1.264
1.256
1.248
1.234
1.226
1.216
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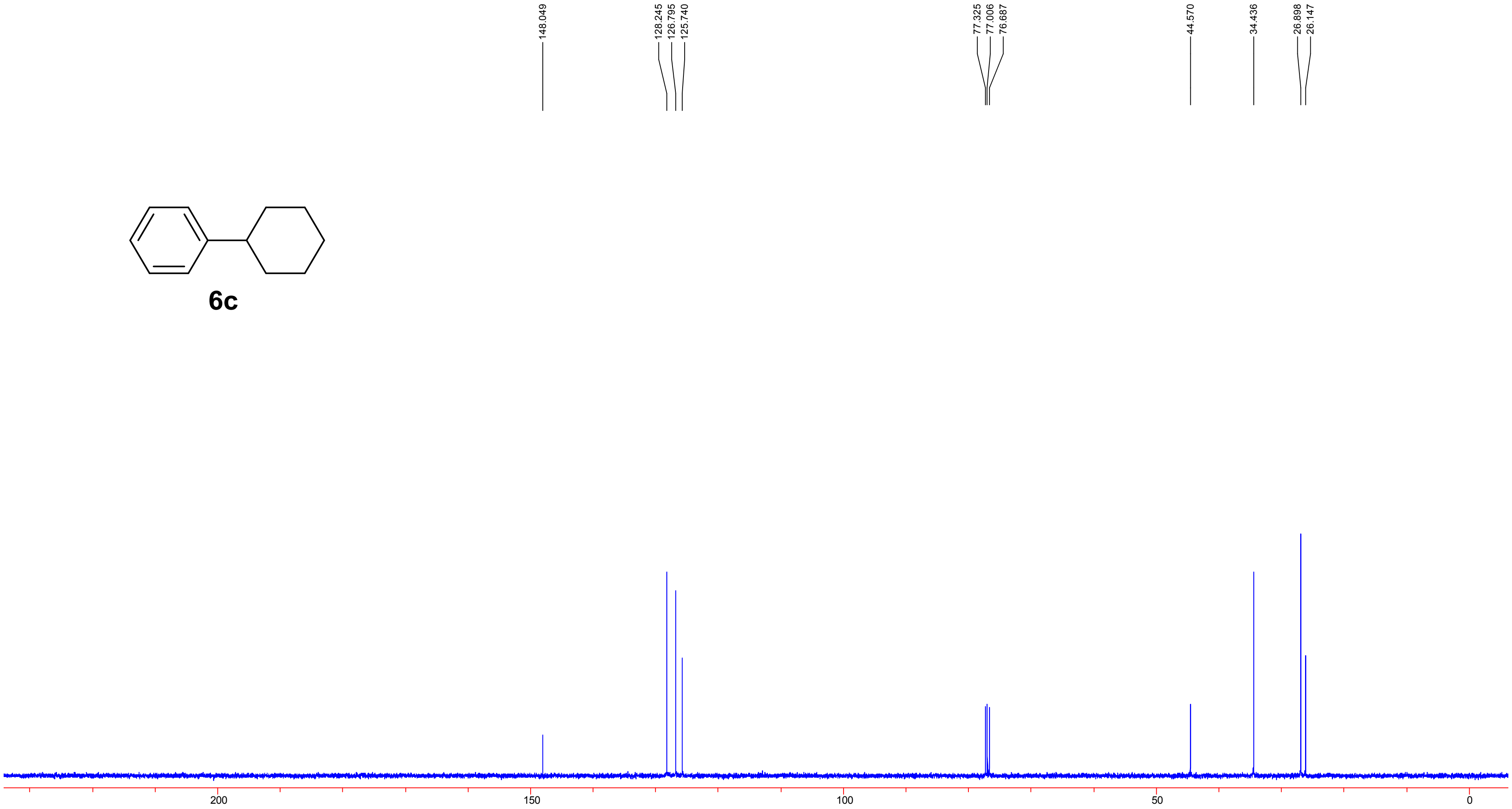
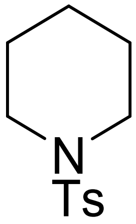
1.00
4.06
1.04
4.14
1.07
10
8
6
4
2
0

6c

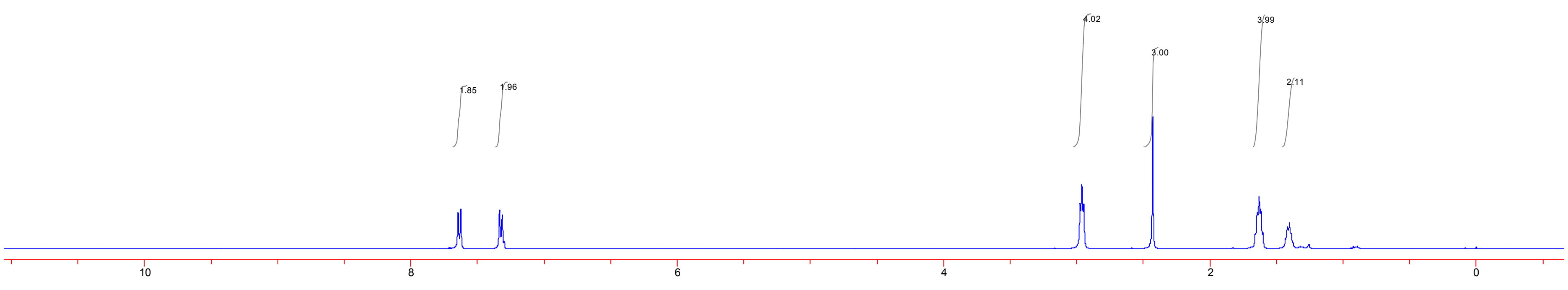


6c

148.049
128.245
126.795
125.740
77.325
77.006
76.687
44.570
34.436
26.898
26.147
200
150
100
50
0



6d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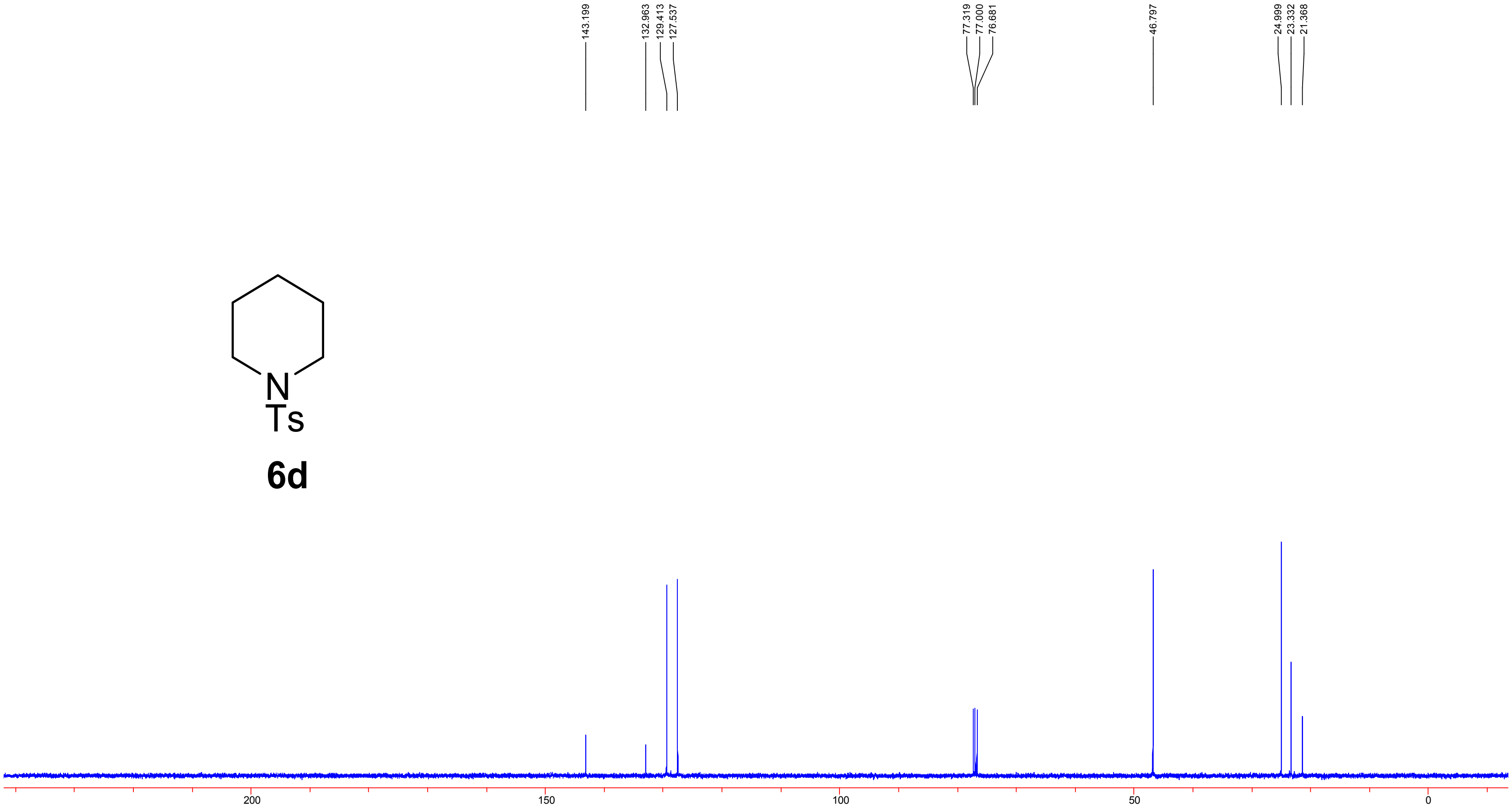
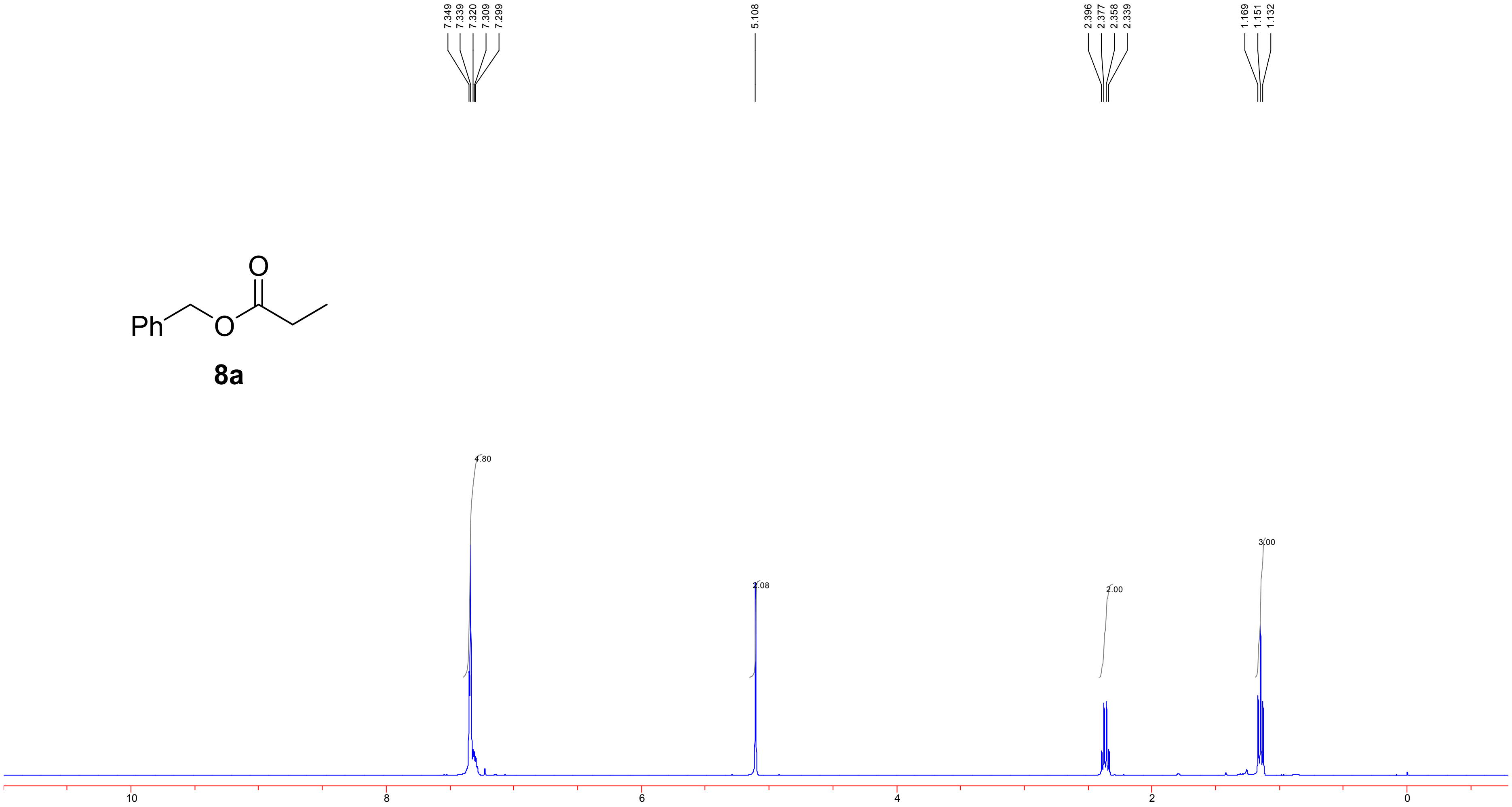
7.625
7.334
7.314
7.300
2.975
2.962
2.949
2.431
1.660
1.646
1.632
1.619
1.604
1.434
1.419
1.405
1.391
1.377
0.000
1.85
1.96
4.02
3.00
3.99
2.11
10
8
6
4
2
0



6d

143.199
132.963
129.413
127.537
77.319
77.000
76.681
46.797
24.999
23.332
21.368
N
Ts
200
150
100
50
0

8a


7.349
7.339
7.320
7.309
7.299
5.108
2.396
2.377
2.358
2.339
1.169
1.151
1.132
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10
8
6
4
2
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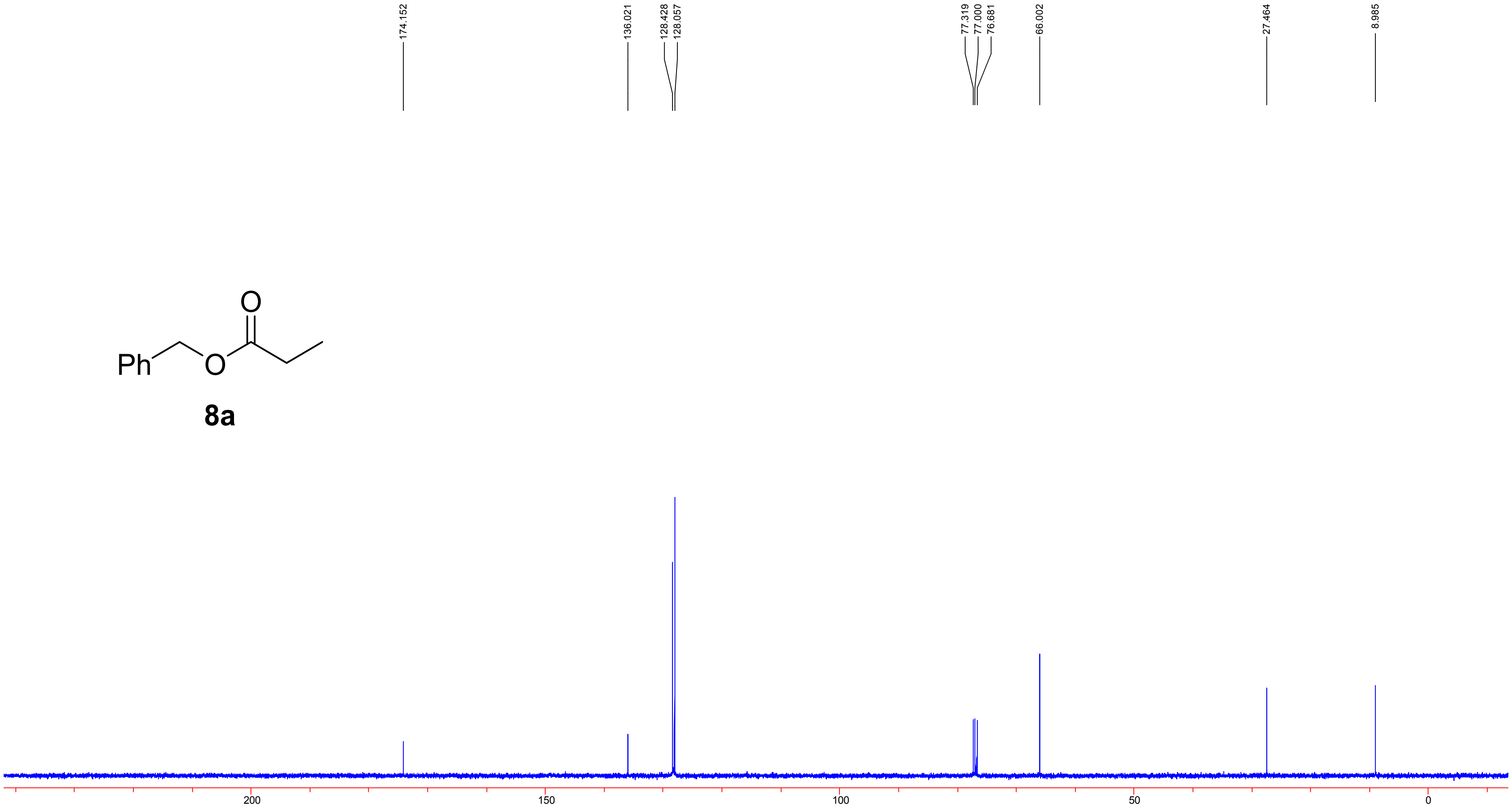
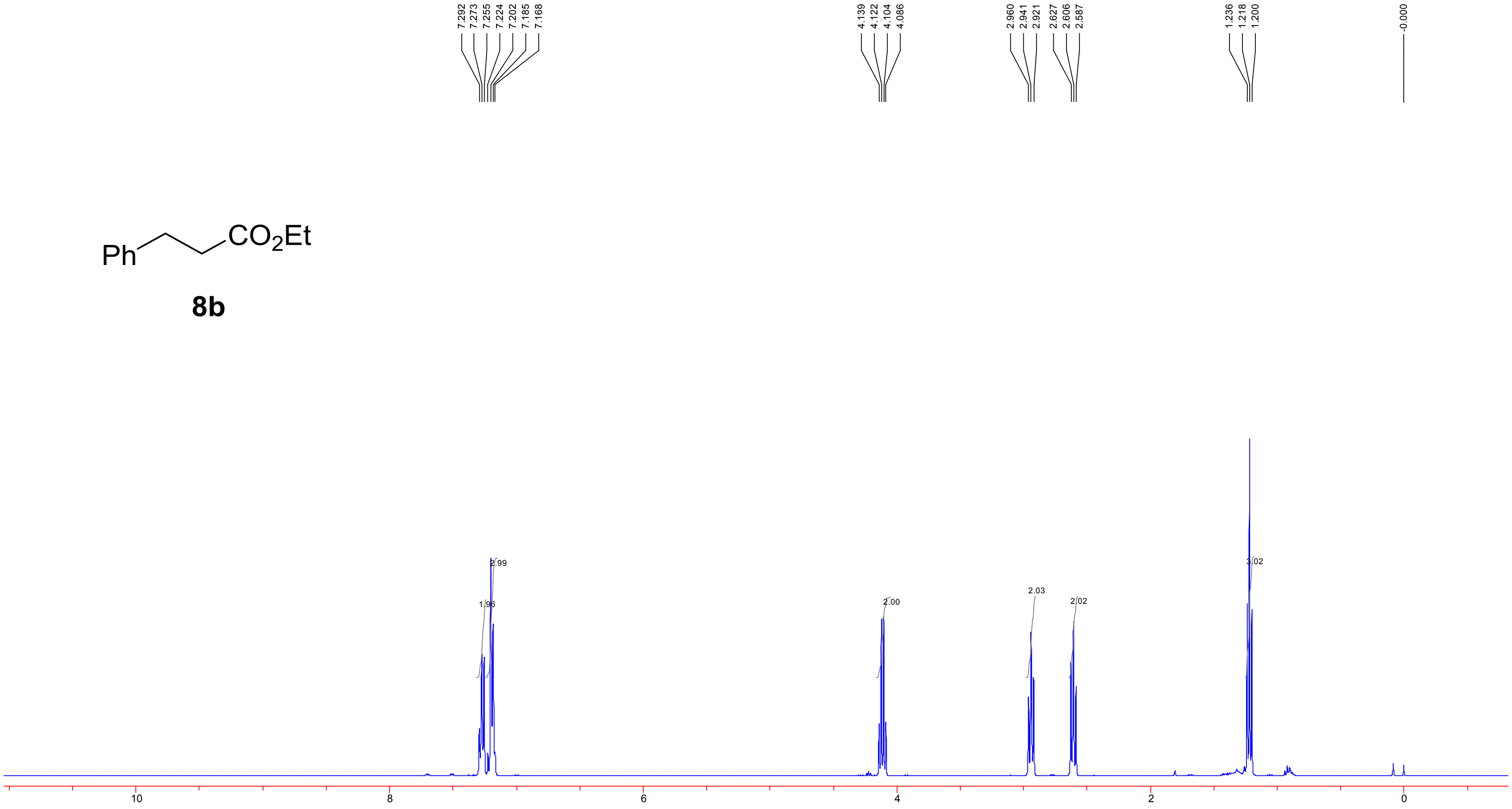
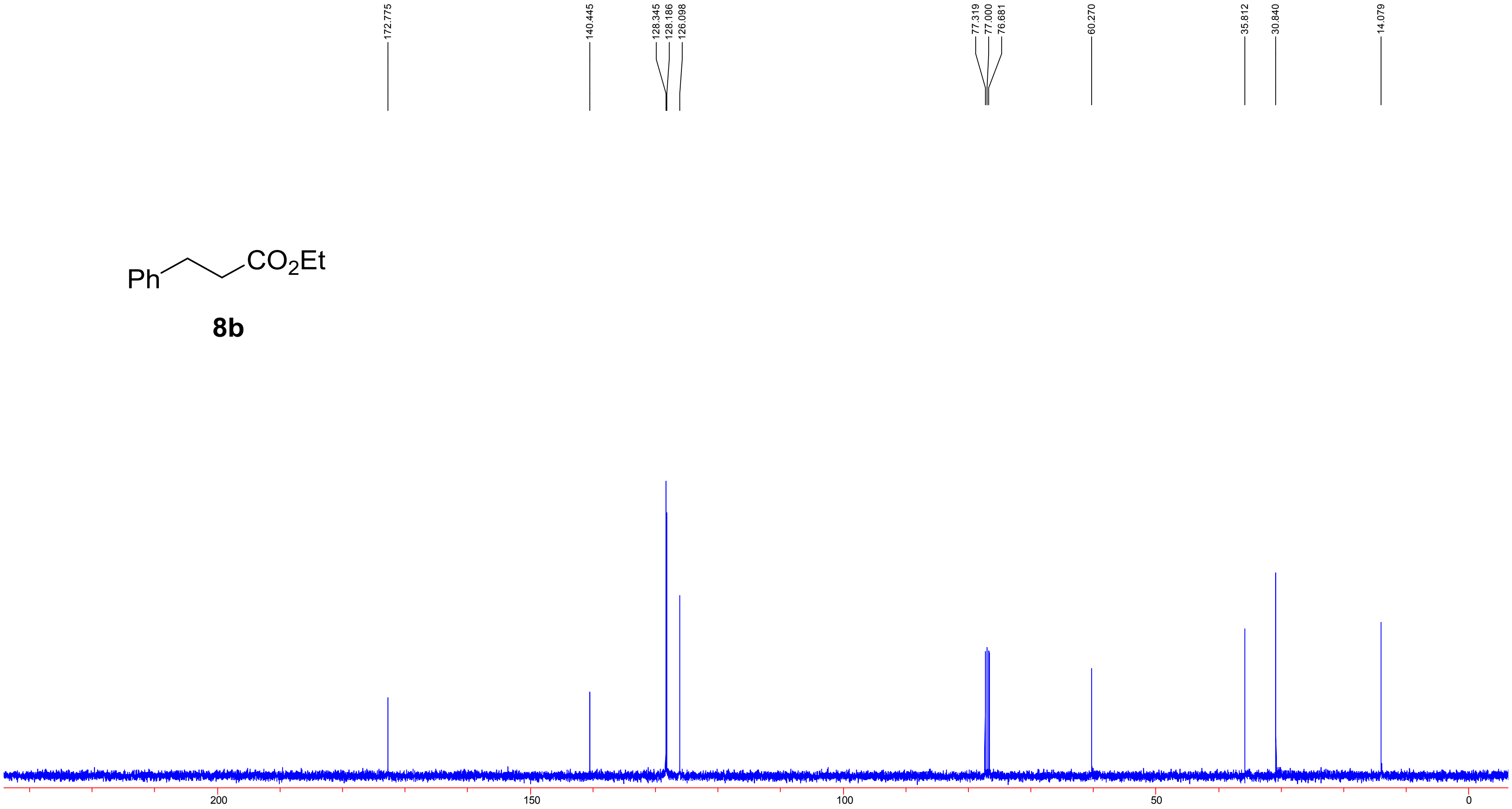

174.152
136.021
128.428
128.057
77.319
77.000
76.681
66.002
27.464
8.985
Ph
O
O
8a
200
150
100
50
0


7.292
7.273
7.255
7.224
7.202
7.185
7.168
4.139
4.122
4.104
4.086
2.960
2.941
2.921
2.627
2.606
2.587
1.236
1.218
1.200
-0.000
Ph
CO2Et
8b
1.96
2.99
2.00
2.03
2.02
3.02
10
8
6
4
2
0

Ph
CO$_2$Et

8b


172.775
140.445
128.345
128.186
126.098
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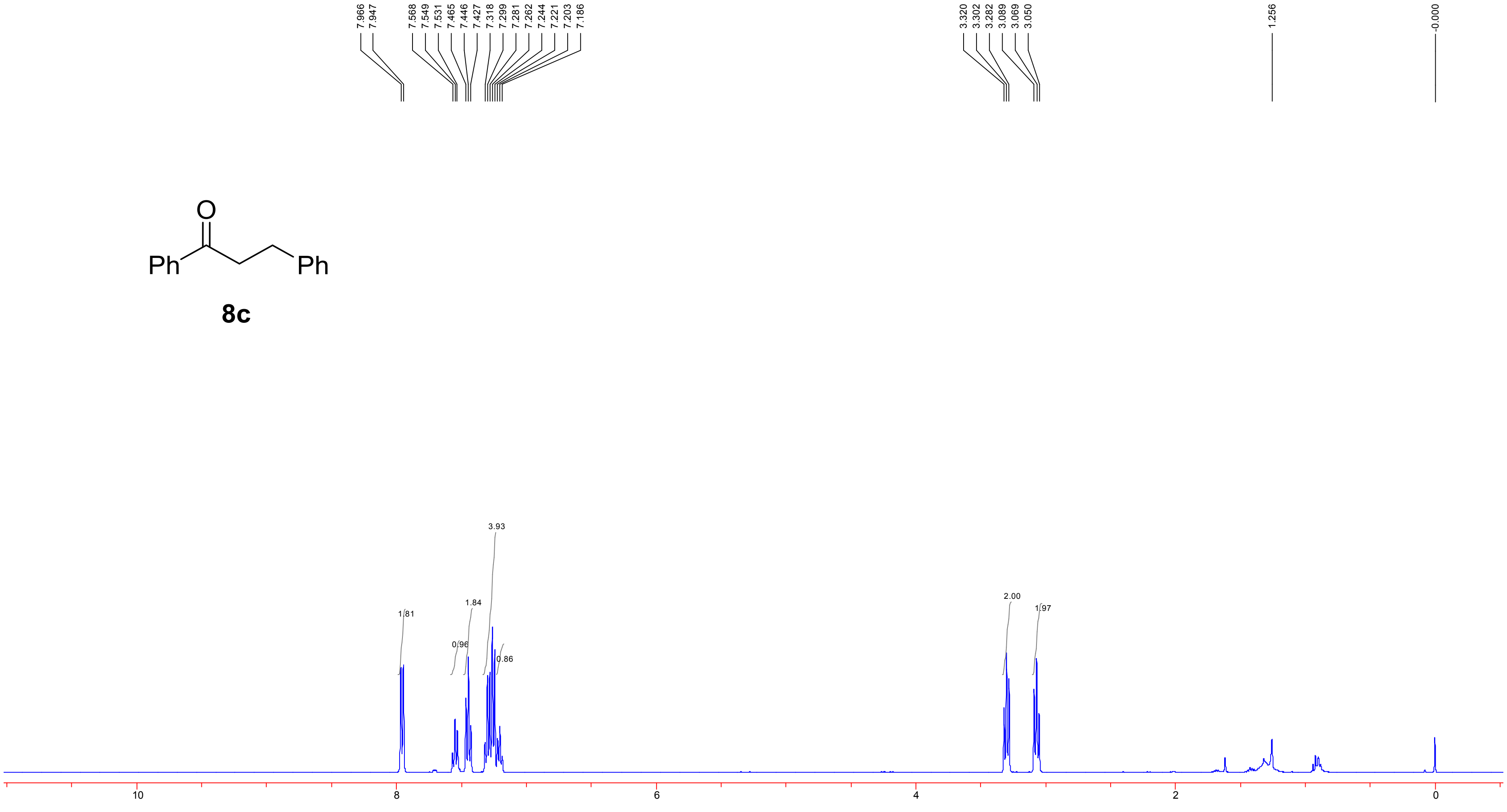
77.000
76.681
60.270
35.812
30.840
14.079
200
150
100
50
0

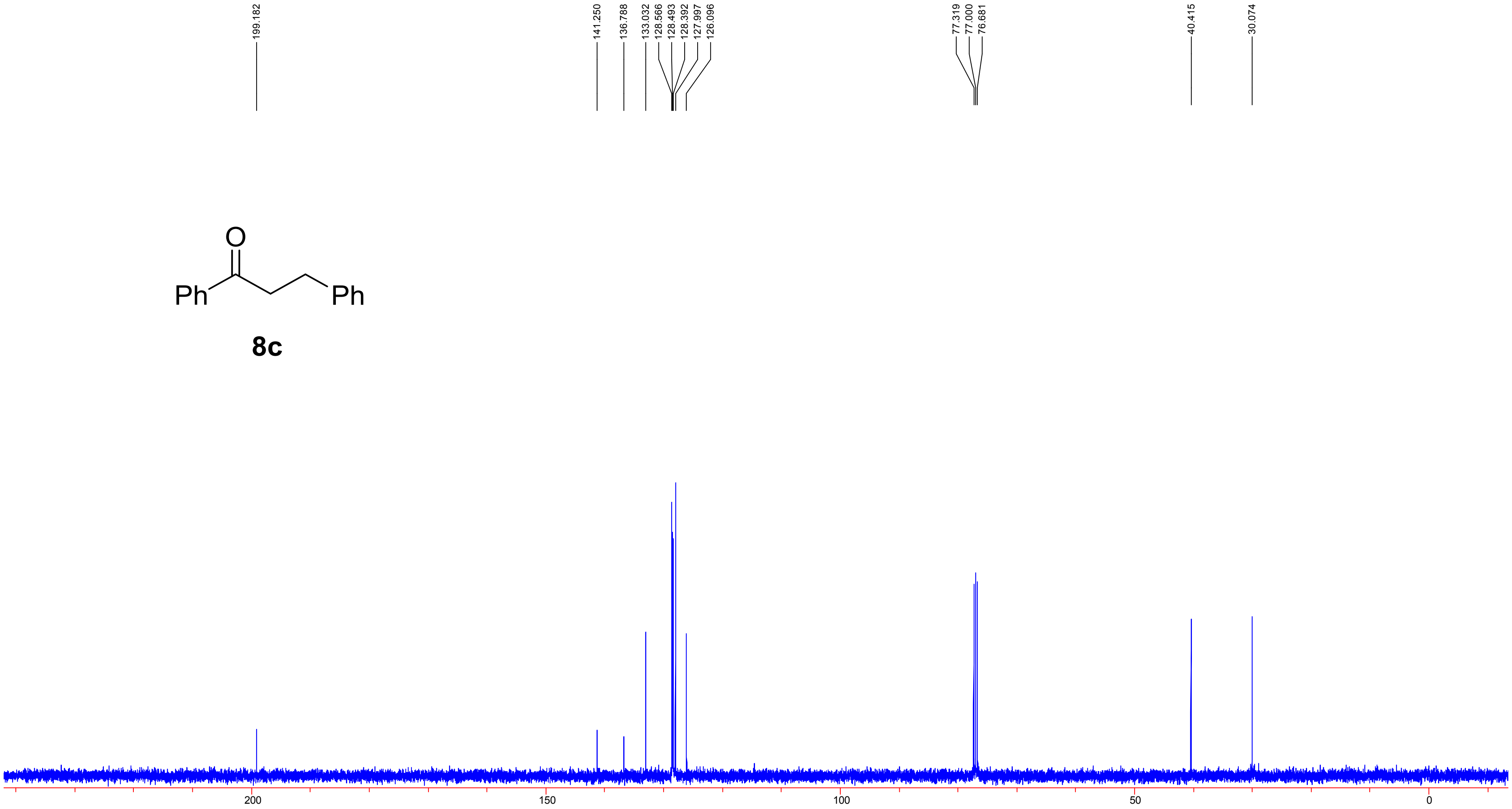
O
Ph
Ph

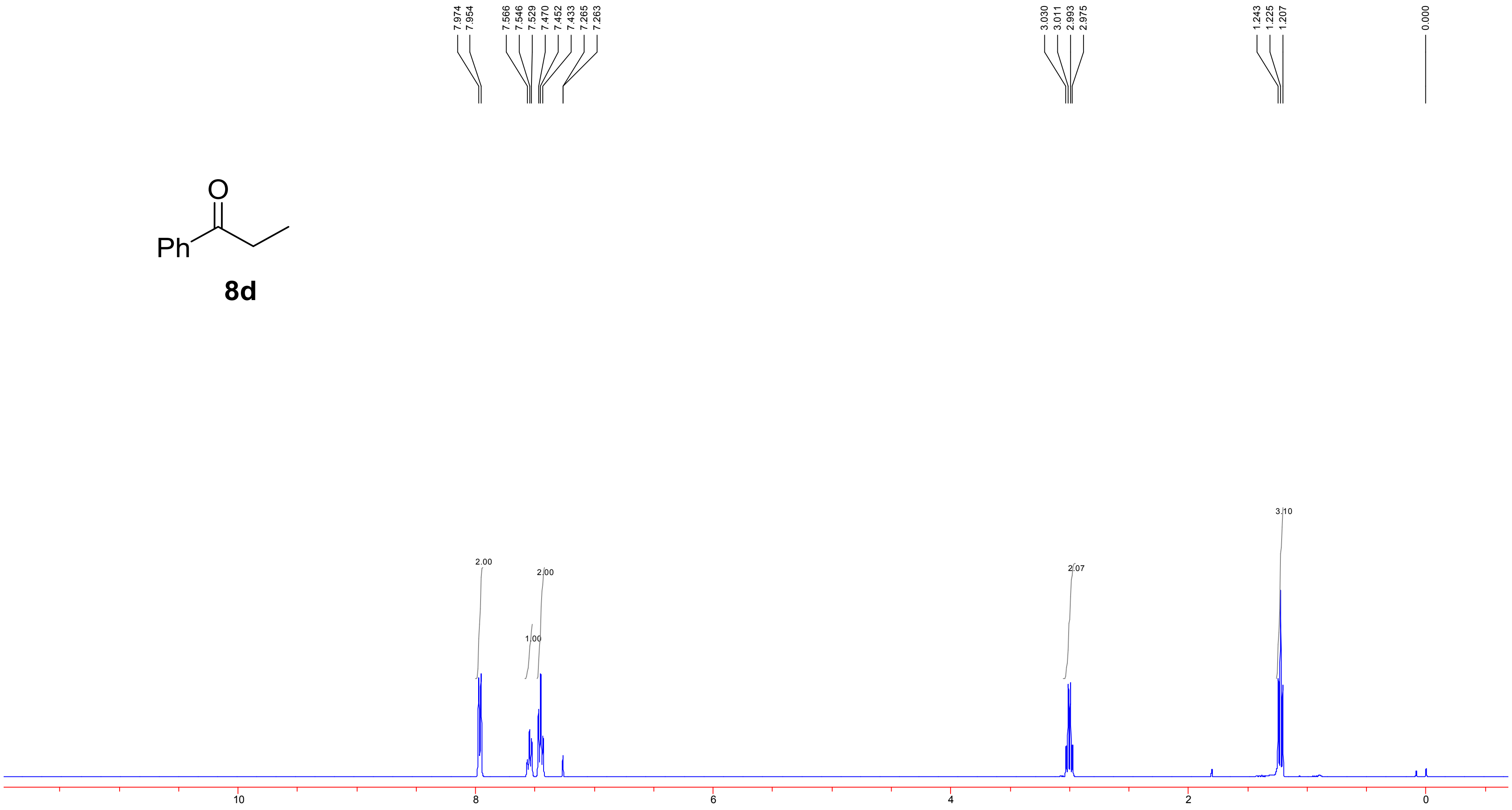
8c

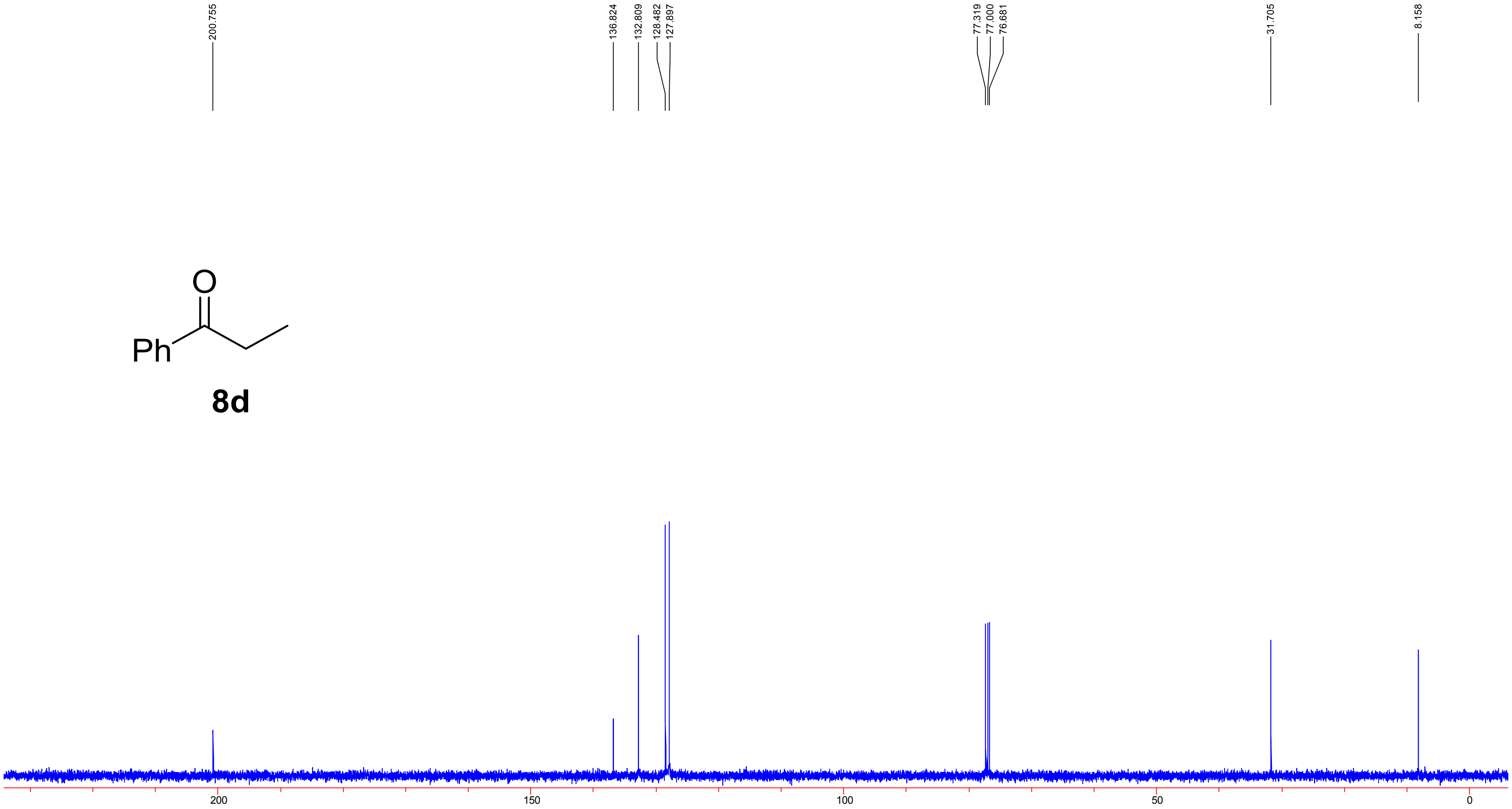

7.966
7.947
7.568
7.549
7.531
7.465
7.446
7.427
7.318
7.299
7.281
7.262
7.244
7.221
7.203
7.186
3.320
3.302
3.282
3.089
3.069
3.050
1.256
-0.000
1.81
0.96
1.84
3.93
0.86
2.00
1.97
10
8
6
4
2
0

O
Ph
Ph

8c


199.182
141.250
136.788
133.032
128.566
128.493
128.392
127.997
126.096
77.319
77.000
76.681
40.415
30.074
200
150
100
50
0


7.974
7.954
7.566
7.546
7.529
7.470
7.452
7.433
7.265
7.263
3.030
3.011
2.993
2.975
1.243
1.225
1.207
0.000
O
Ph
8d
2.00
1.00
2.00
2.07
3.10
10
8
6
4
2
0



8d

200.755
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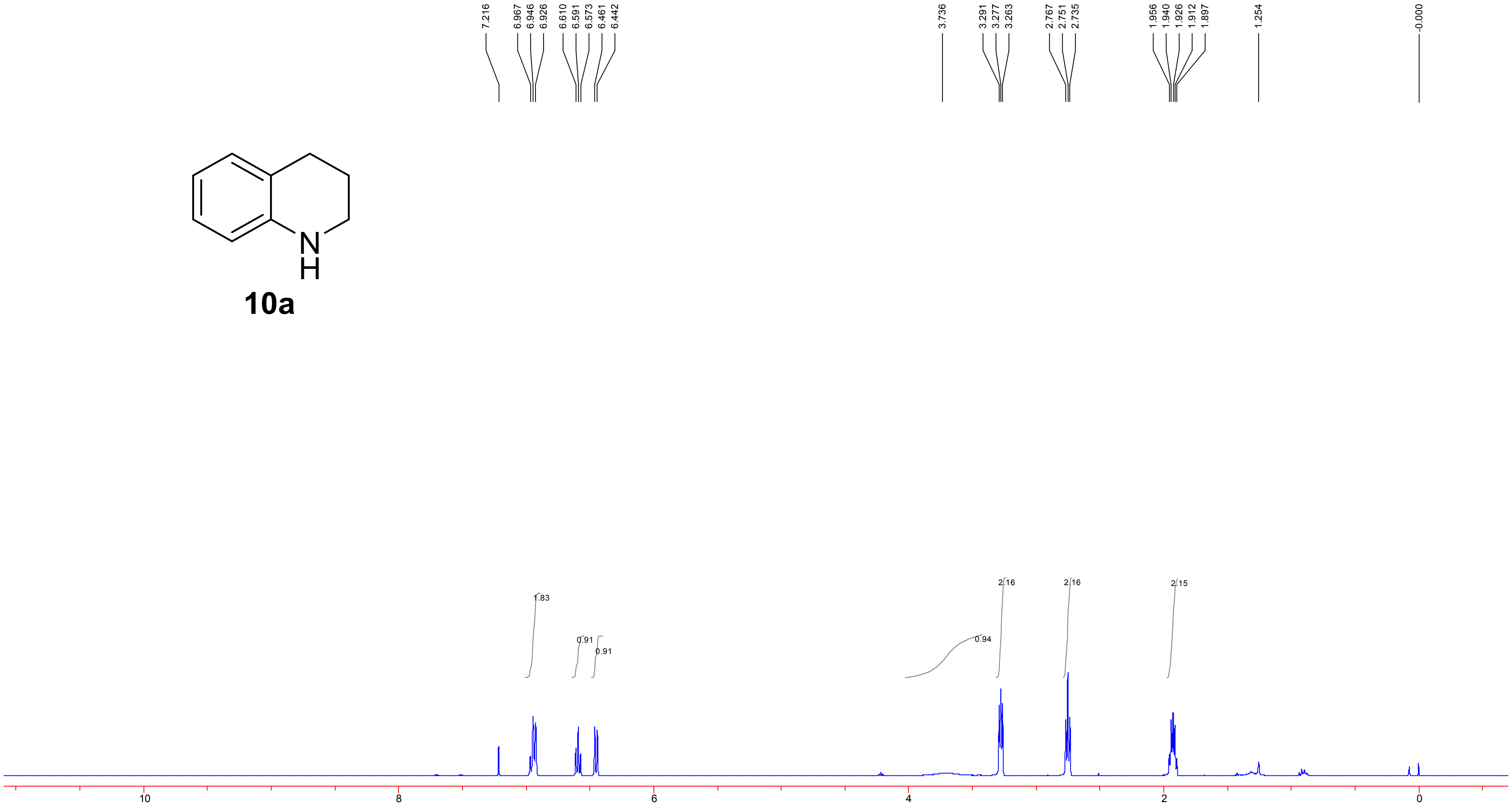
132.809
128.482
127.897
77.319
77.000
76.681
31.705
8.158
200
150
100
50
0



10a

7.216
6.967
6.946
6.926
6.610
6.591
6.573
6.461
6.442
3.736
3.291
3.277
3.263
2.767
2.751
2.735
1.956
1.940
1.926
1.912
1.897
1.254
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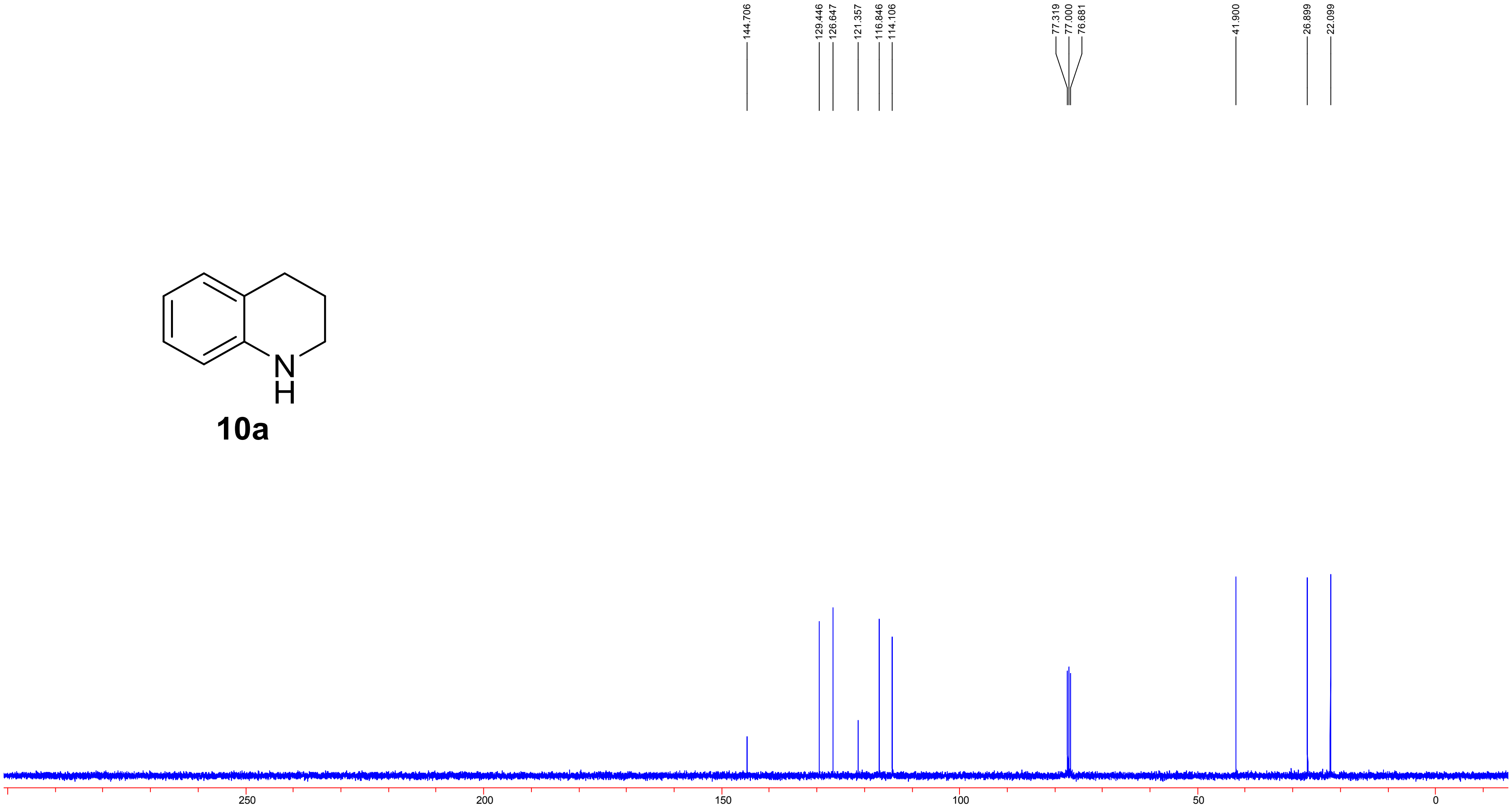
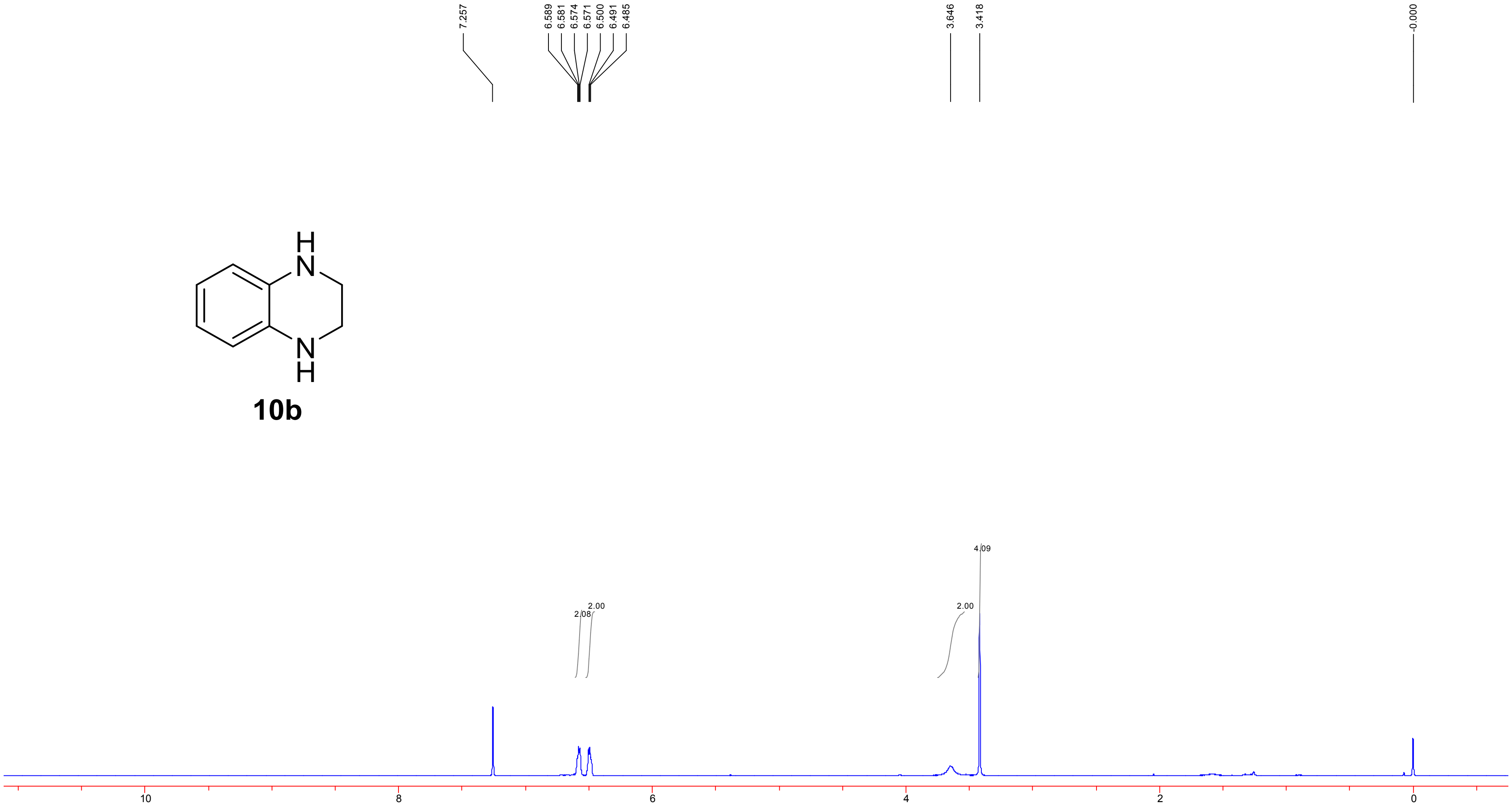
1.83
0.91
0.91
0.94
2.16
2.16
2.15
10
8
6
4
2
0

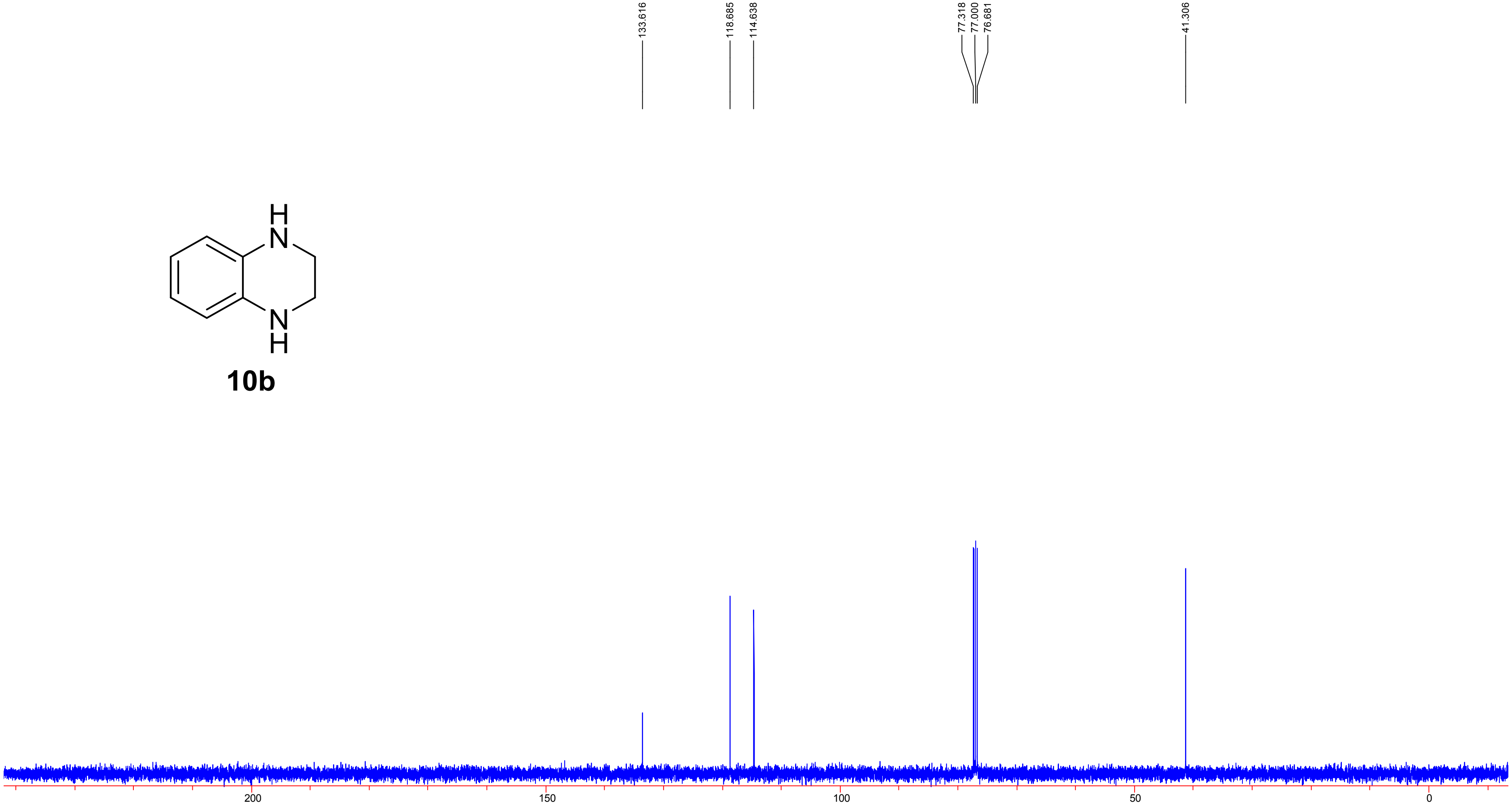


10a

144.706
129.446
126.647
121.357
116.846
114.106
77.319
77.000
76.681
41.900
26.899
22.099
250
200
150
100
50
0

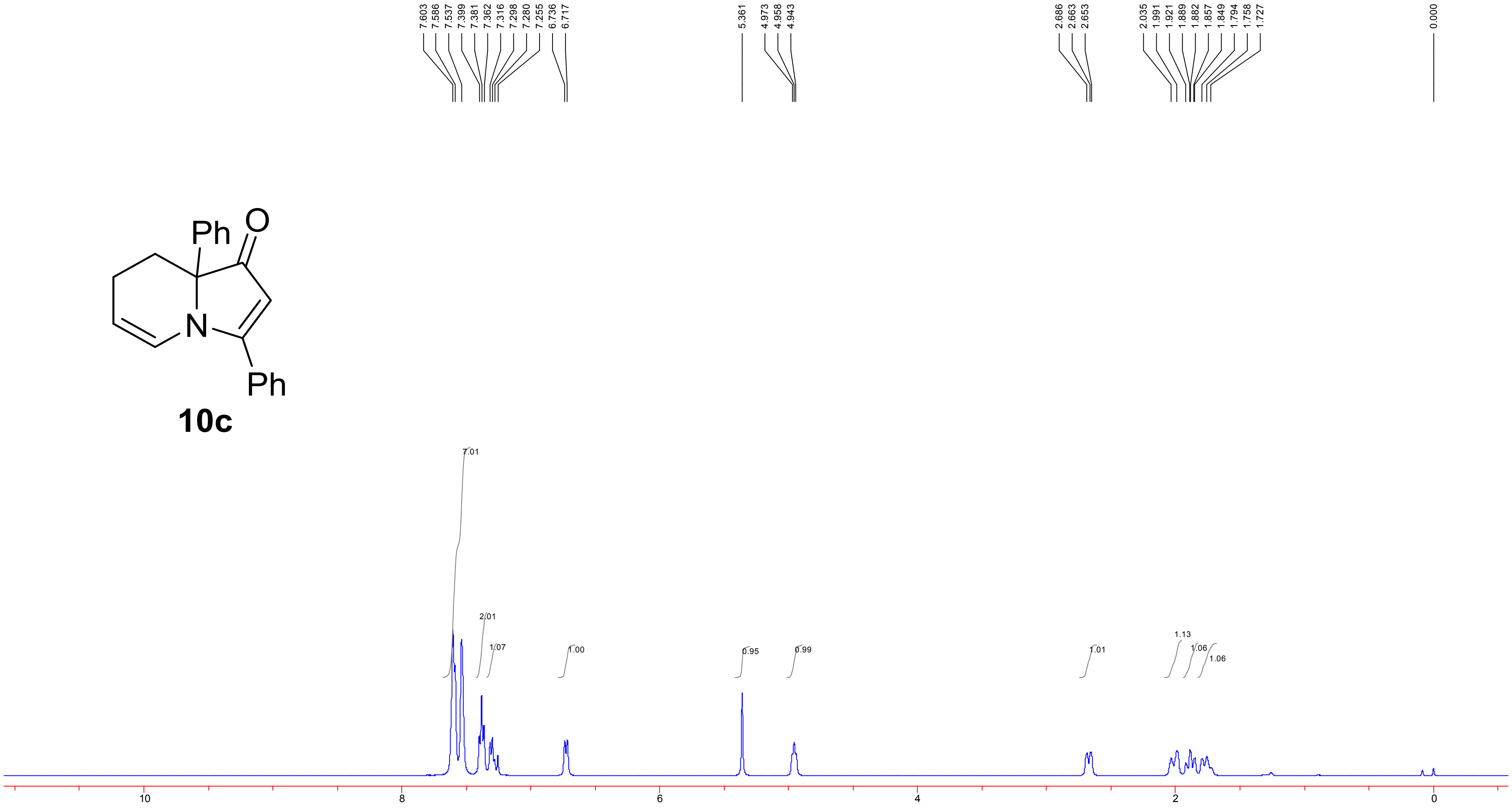

7.257
6.589
6.581
6.574
6.571
6.500
6.491
6.485
3.646
3.418
-0.000
H
N
N
H
2.08
2.00
2.00
4.09
10
8
6
4
2
0

10b

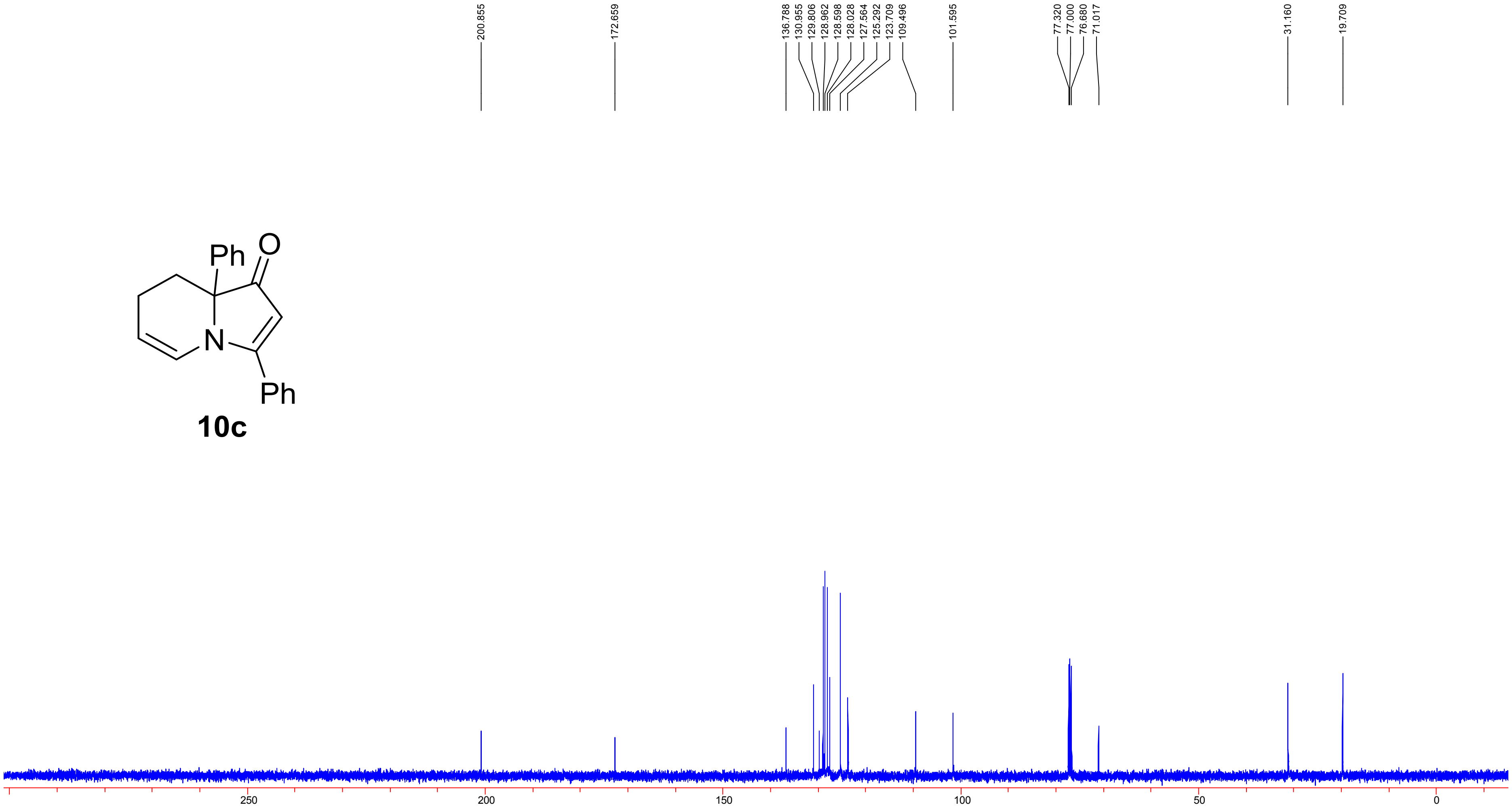


10b

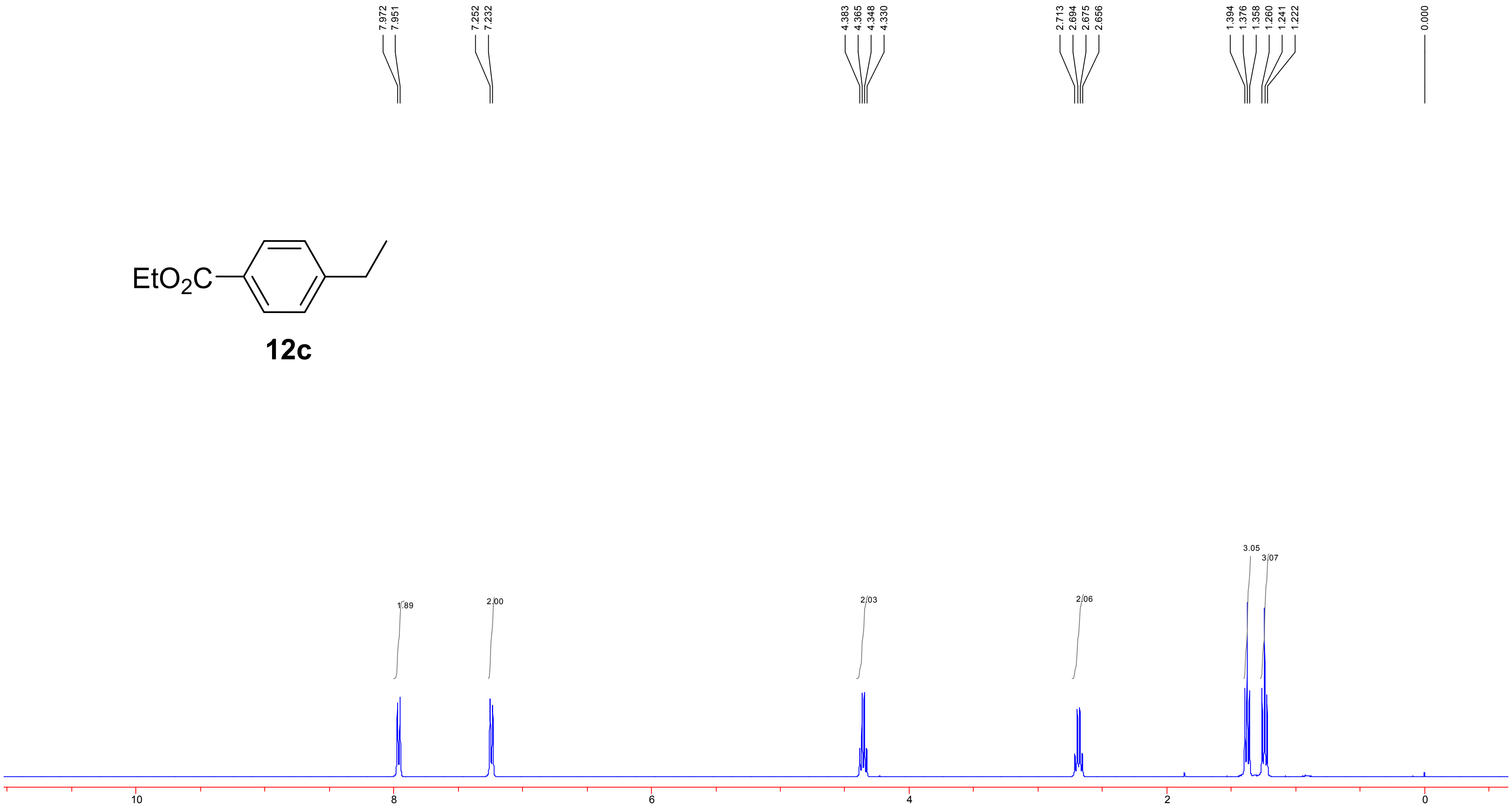
133.616
118.685
114.638
77.318
77.000
76.681
41.306
H
N
N
H
200
150
100
50
0


7.603
7.586
7.537
7.399
7.381
7.362
7.316
7.298
7.280
7.255
6.736
6.717
5.361
4.973
4.958
4.943
2.686
2.663
2.653
2.035
1.991
1.921
1.889
1.882
1.857
1.849
1.794
1.758
1.727
0.000
Ph
O
N
Ph
7.01
2.01
1.07
1.00
0.95
0.99
1.01
1.13
1.06
1.06
10
8
6
4
2
0

10c



10c
200.855
172.659
136.788
130.955
129.806
128.962
128.598
128.028
127.564
125.292
123.709
109.496
101.595
77.320
77.000
76.680
71.017
31.160
19.709
250
200
150
100
50
0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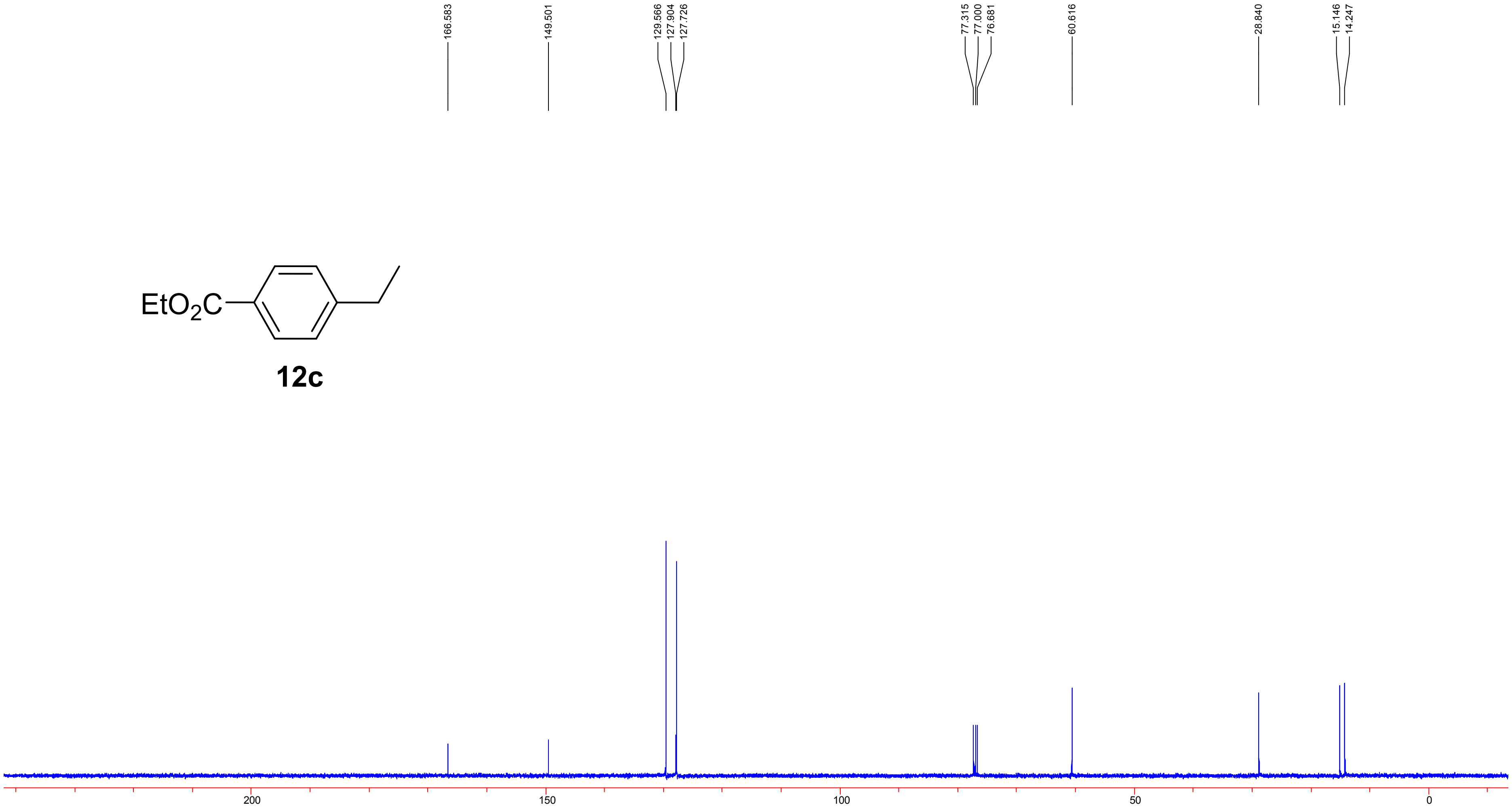
7.252
7.232
4.383
4.365
4.348
4.330
2.713
2.694
2.675
2.656
1.394
1.376
1.358
1.260
1.241
1.222
0.000
EtO$_2$C
1.89
2.00
2.03
2.06
3.05
3.07
10
8
6
4
2
0

12c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127.904
127.726
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77.000
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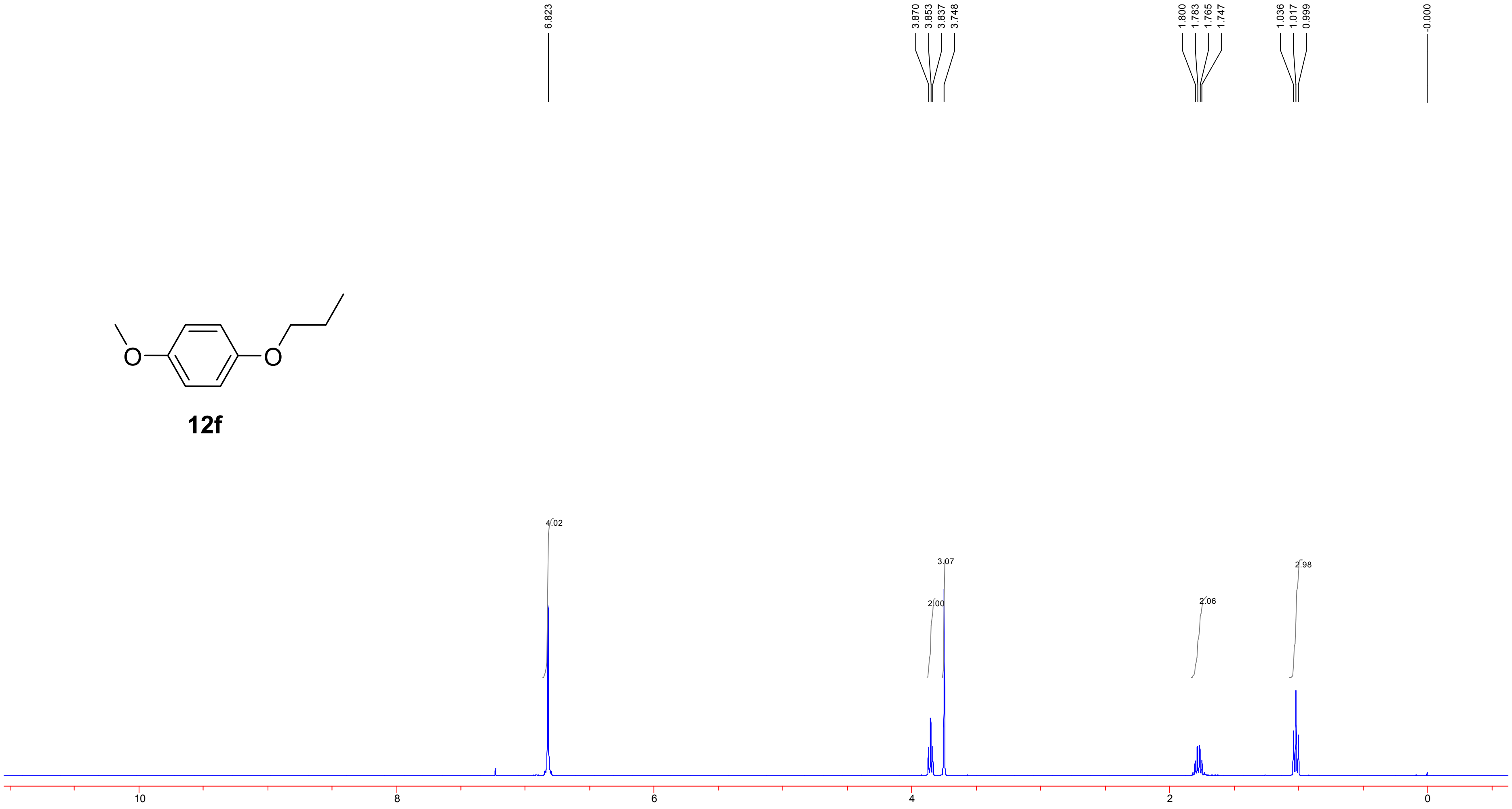
60.616
28.840
15.146
14.247
EtO$_2$C
12c
200
150
100
50
0


6.823
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3.853
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3.748
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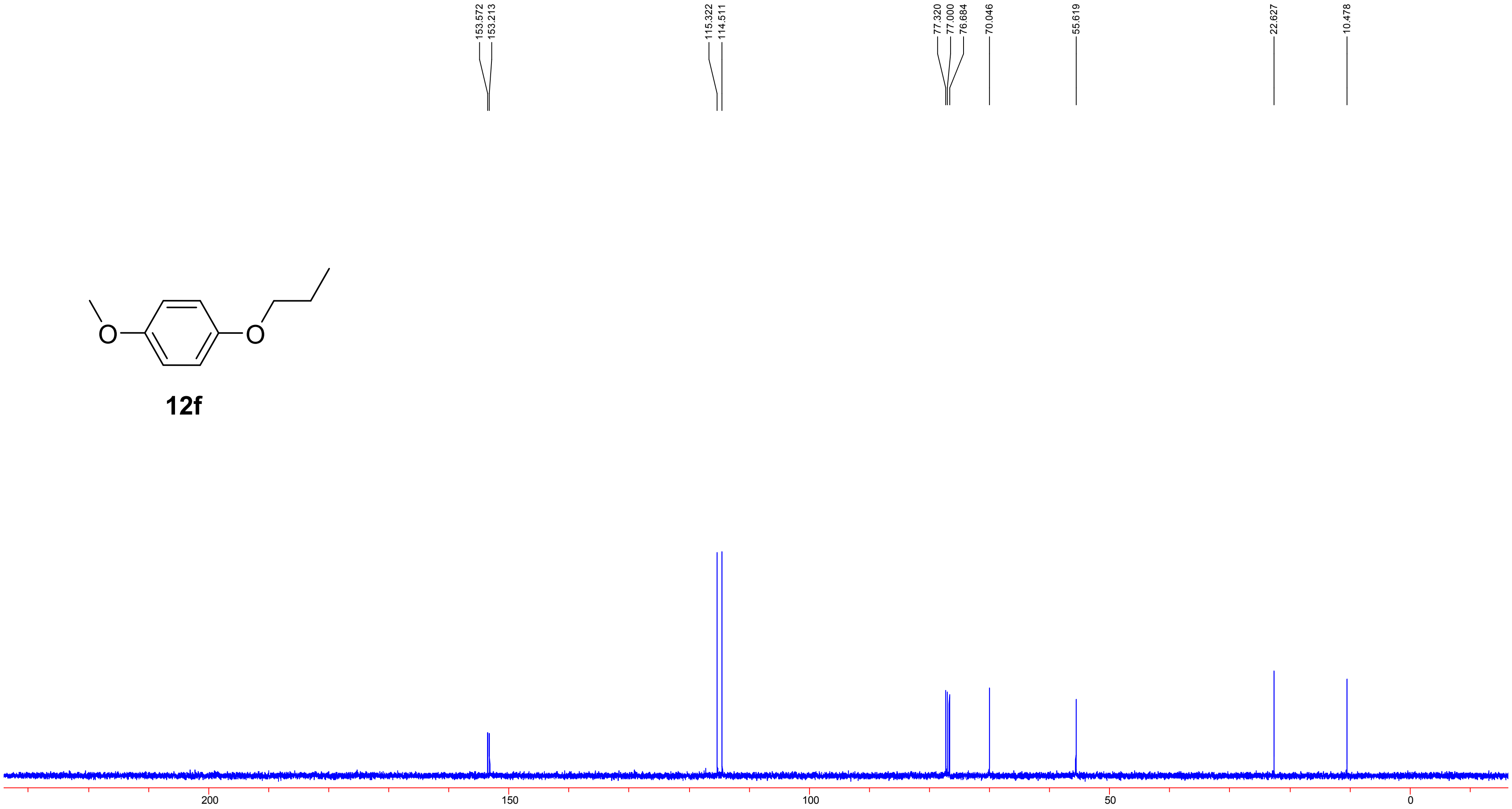
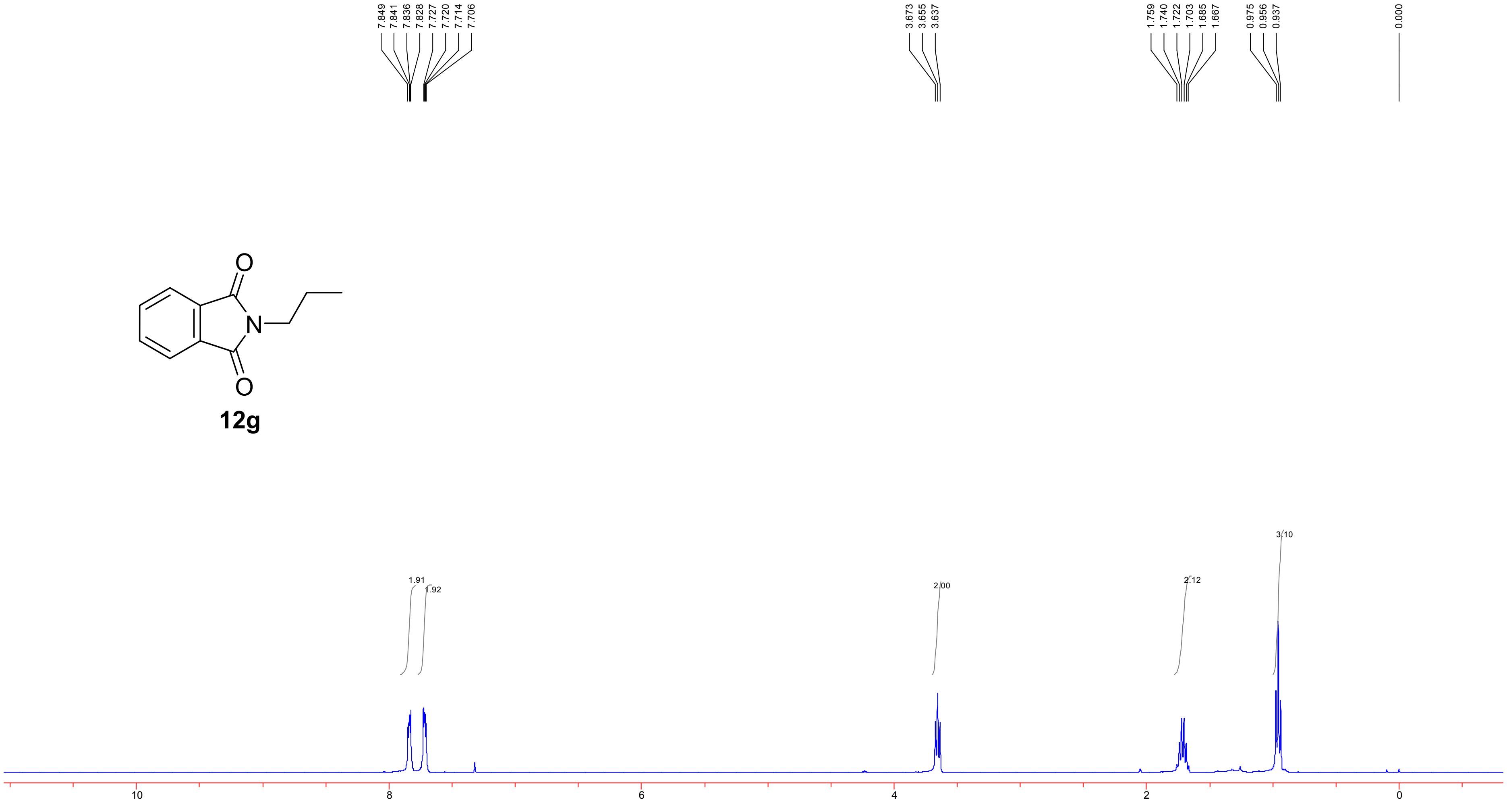
1.765
1.747
1.036
1.017
0.999
-0.000
4.02
3.07
2.00
2.06
2.98
10
8
6
4
2
0

12f


153.572
153.213
115.322
114.511
77.320
77.000
76.684
70.046
55.619
22.627
10.478
200
150
100
50
0

12f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7.836
7.828
7.727
7.720
7.714
7.706
3.673
3.655
3.637
1.759
1.740
1.722
1.703
1.685
1.667
0.975
0.956
0.937
0.000
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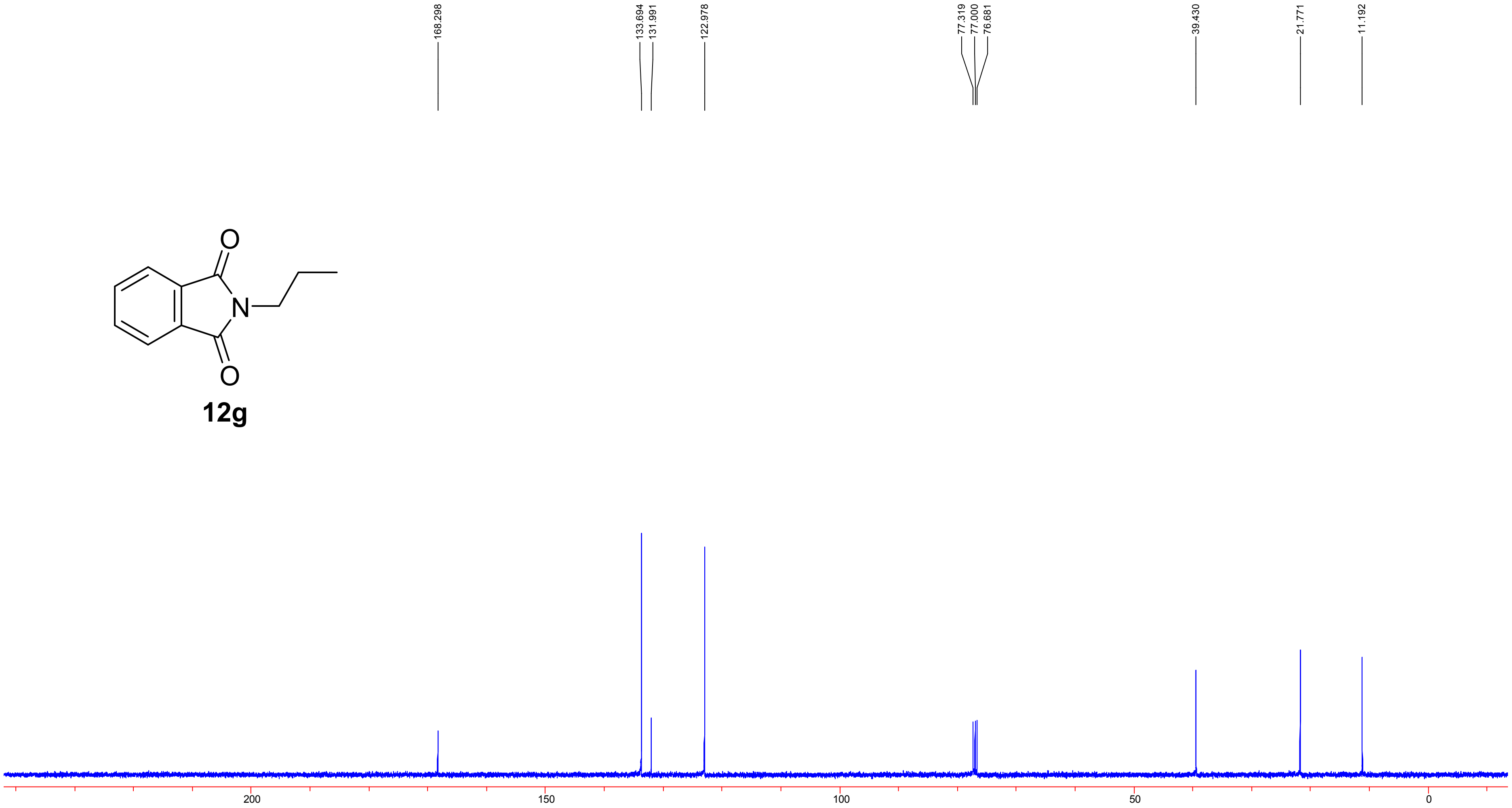
N
O
1.91
1.92
2.00
2.12
3.10
10
8
6
4
2
0

12g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131.991
122.978
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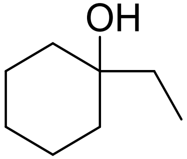
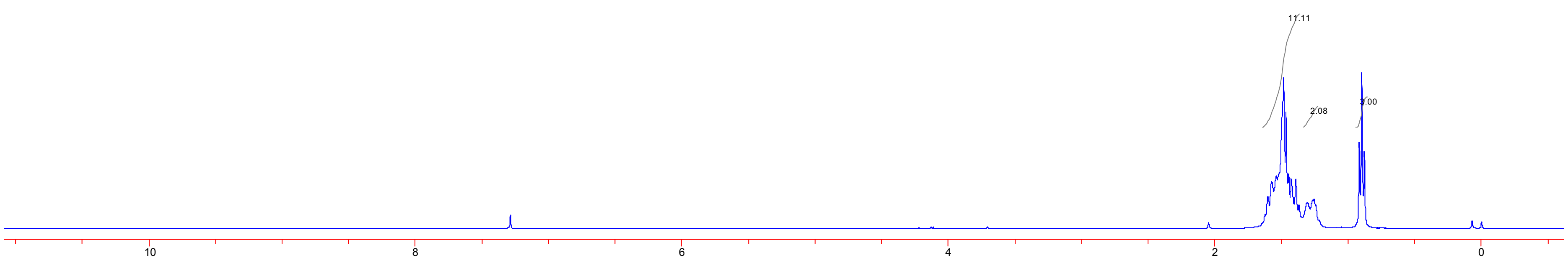
77.000
76.681
39.430
21.771
11.192
200
150
100
50
0
O
N
O

12g


OH

12h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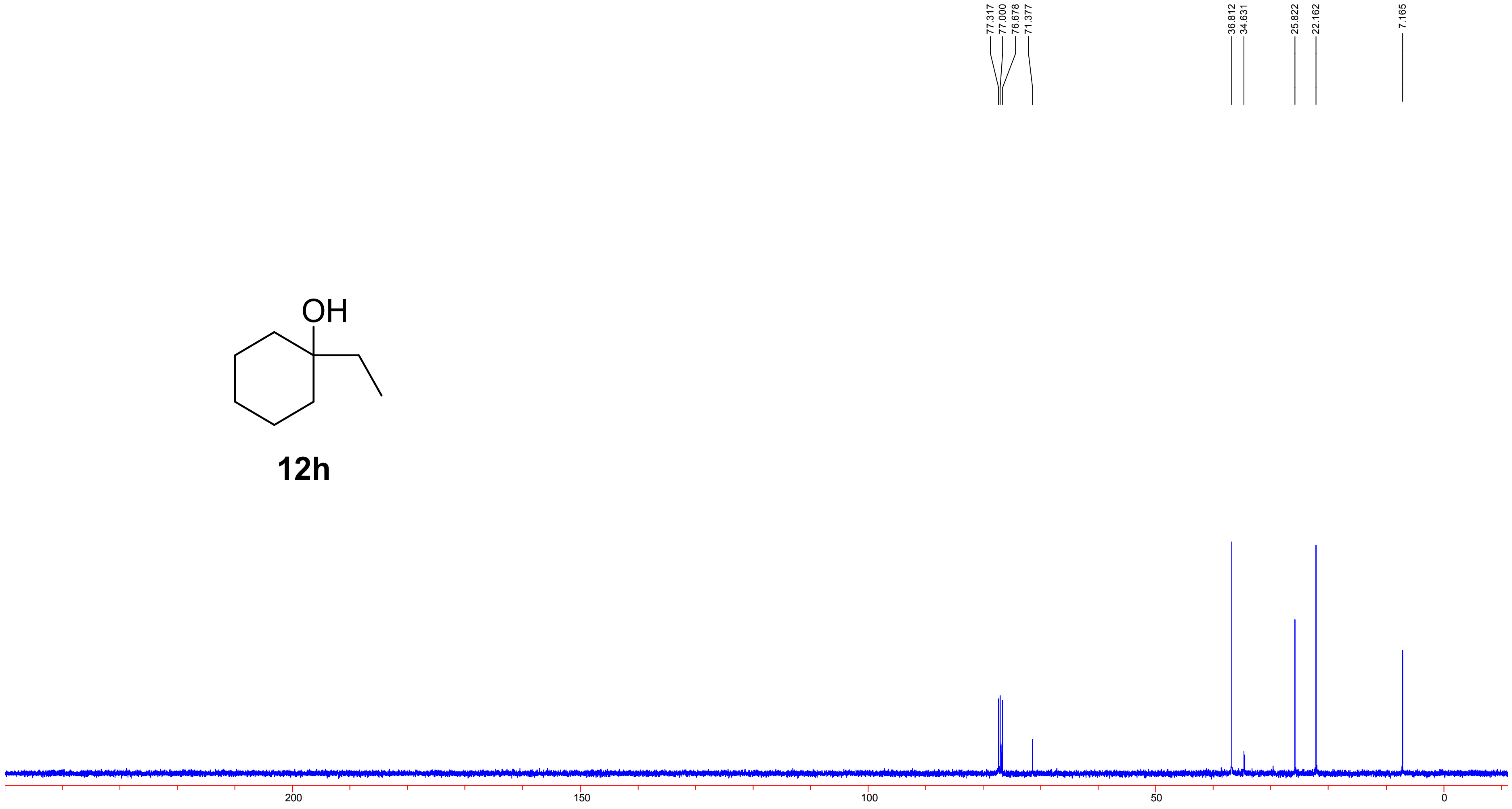
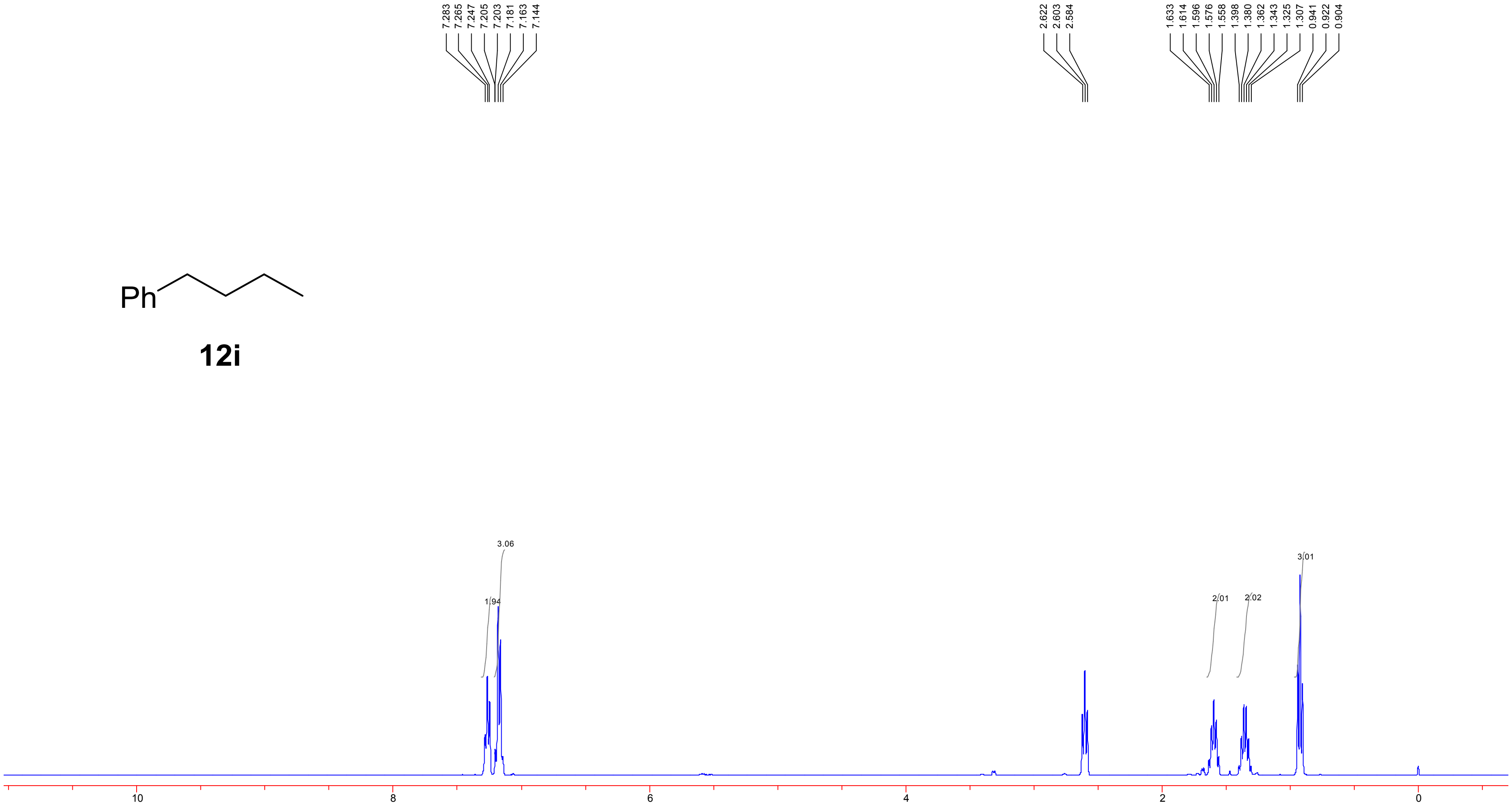
1.604
1.575
1.538
1.485
1.466
1.447
1.428
1.394
1.371
1.310
1.267
1.256
1.243
0.917
0.898
0.880
0.000
11.11
2.08
3.00
10
8
6
4
2
0


77.317
77.000
76.678
71.377
36.812
34.631
25.822
22.162
7.165
OH
12h
200
150
100
50
0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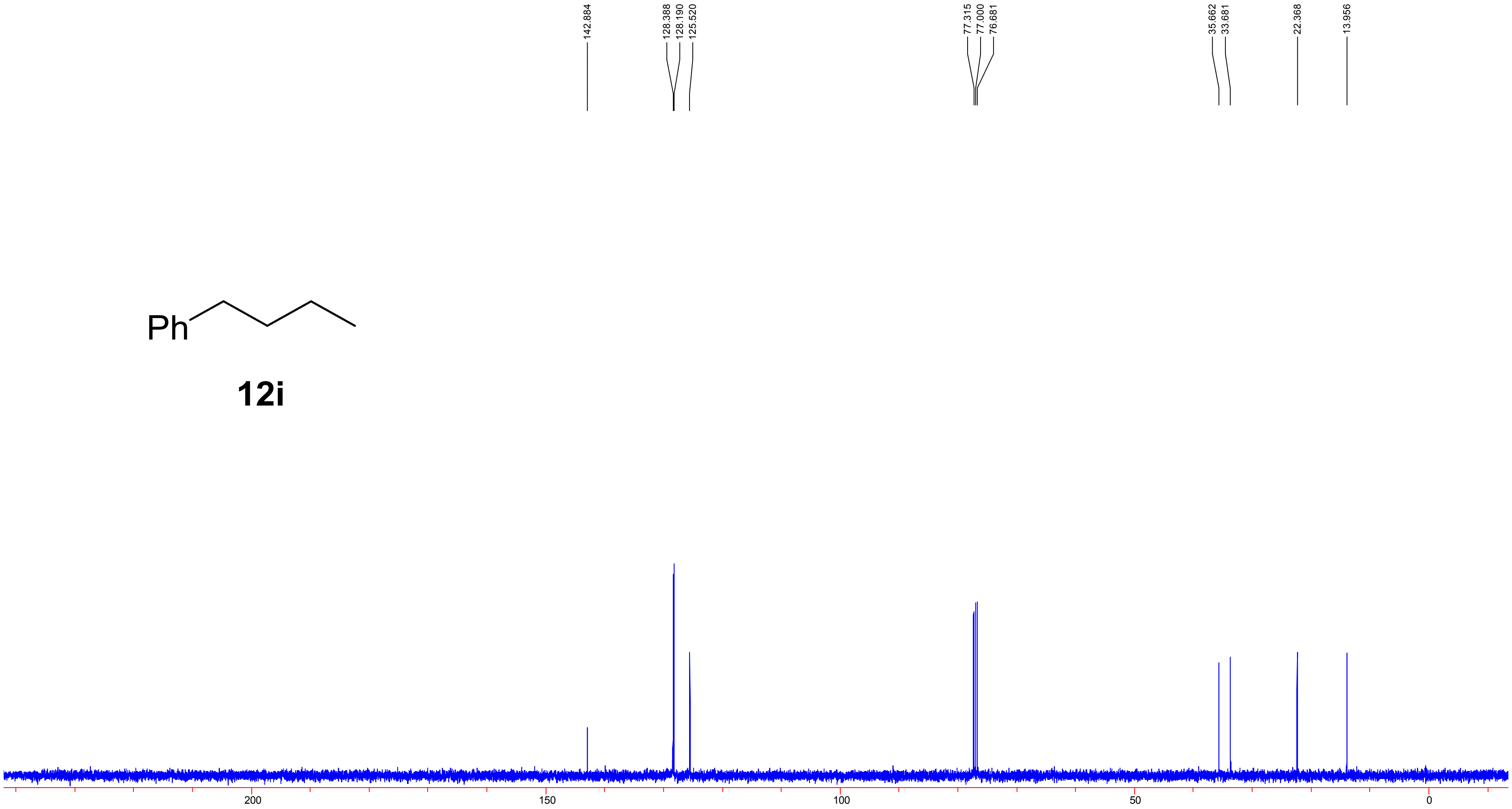
7.265
7.247
7.205
7.203
7.181
7.163
7.144
2.622
2.603
2.584
1.633
1.614
1.596
1.576
1.558
1.398
1.380
1.362
1.343
1.325
1.307
0.941
0.922
0.904
Ph
3.06
1.94
2.01
2.02
3.01
10
8
6
4
2
0

12i

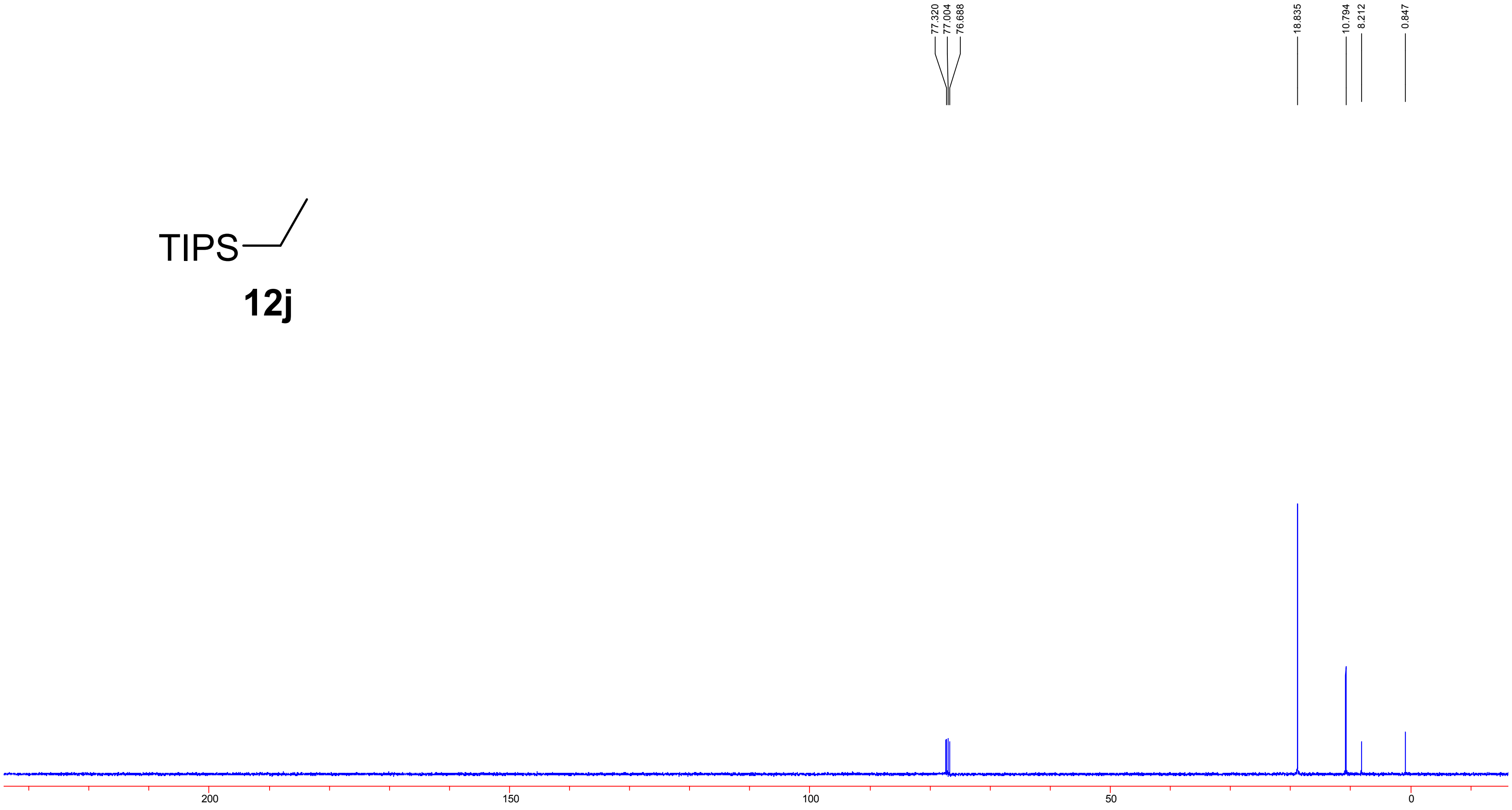


12i
142.884
128.388
128.190
125.520
77.315
77.000
76.681
35.662
33.681
22.368
13.956
200
150
100
50
0


TIPS

12j

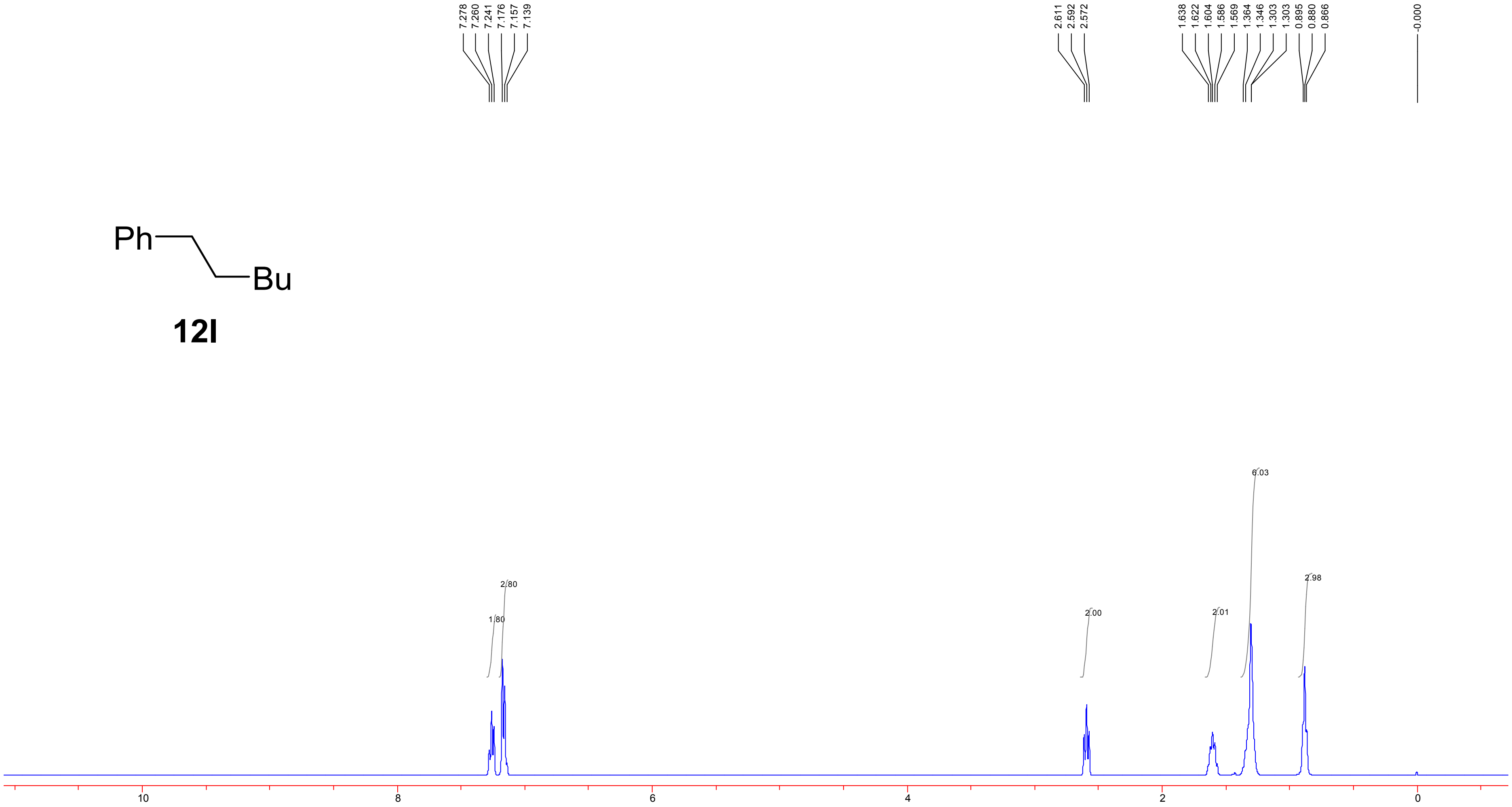

1.038
1.013
0.993
0.973
0.631
0.611
0.591
0.571
21.12
3.18
2.00
10
8
6
4
2
0



12j

Ph
Bu

12l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7.176
7.157
7.139
2.611
2.592
2.572
1.638
1.622
1.604
1.586
1.569
1.364
1.346
1.303
1.303
0.895
0.880
0.866
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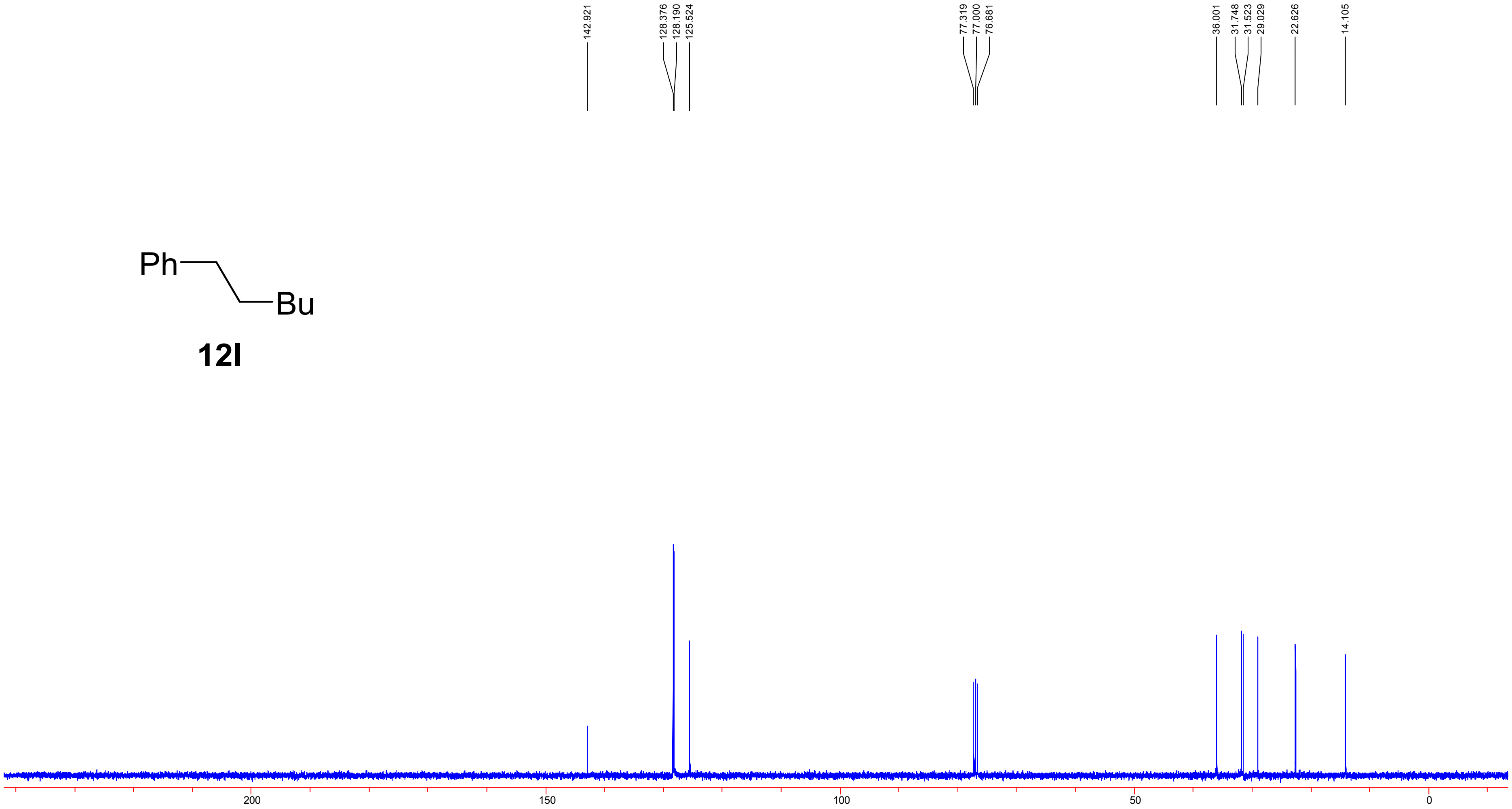
1.80
2.80
2.00
2.01
6.03
2.98
10
8
6
4
2
0


142.921
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125.524
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77.000
76.681
36.001
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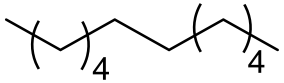
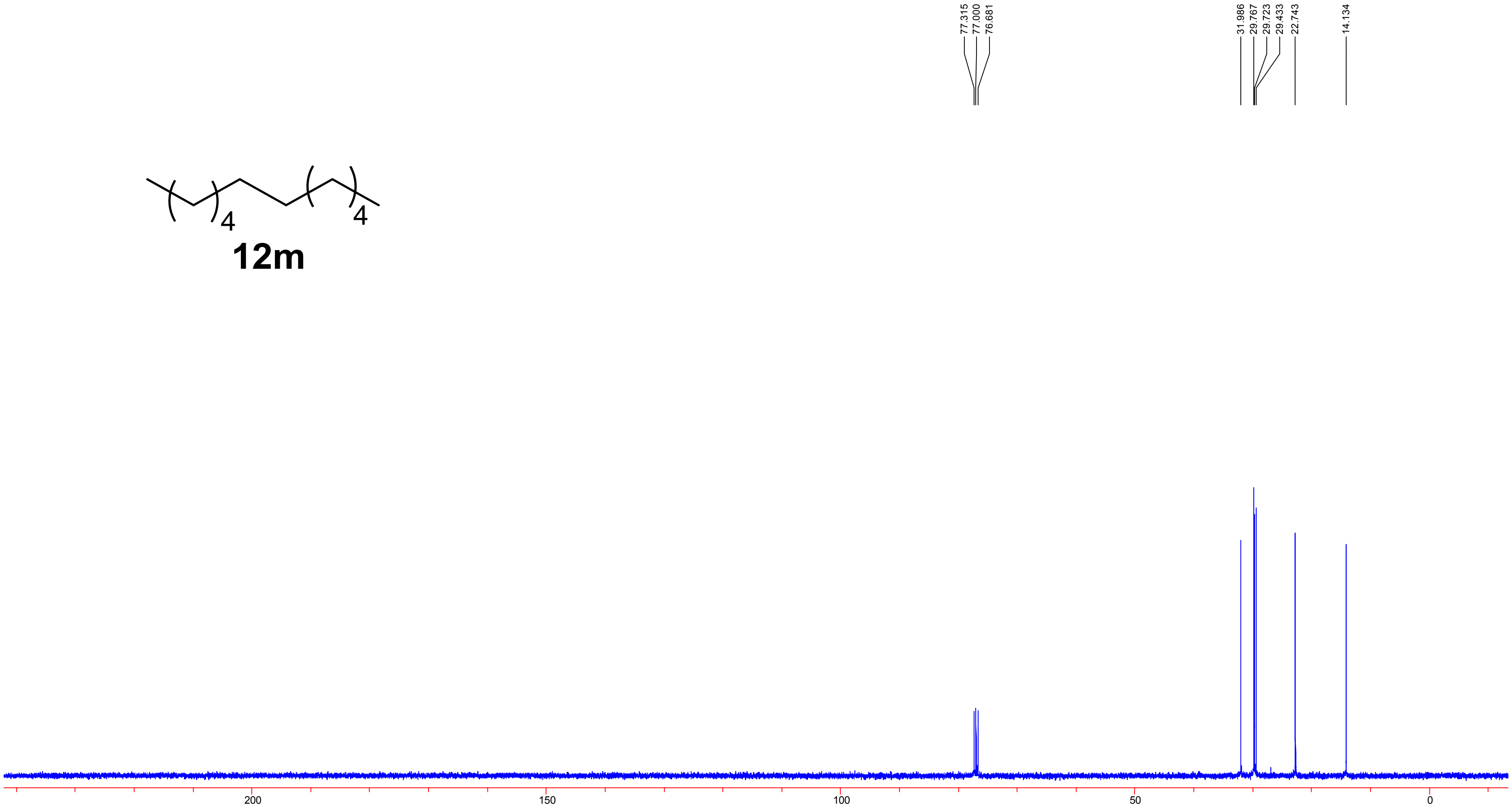
31.523
29.029
22.626
14.105
200
150
100
50
0

Ph
Bu

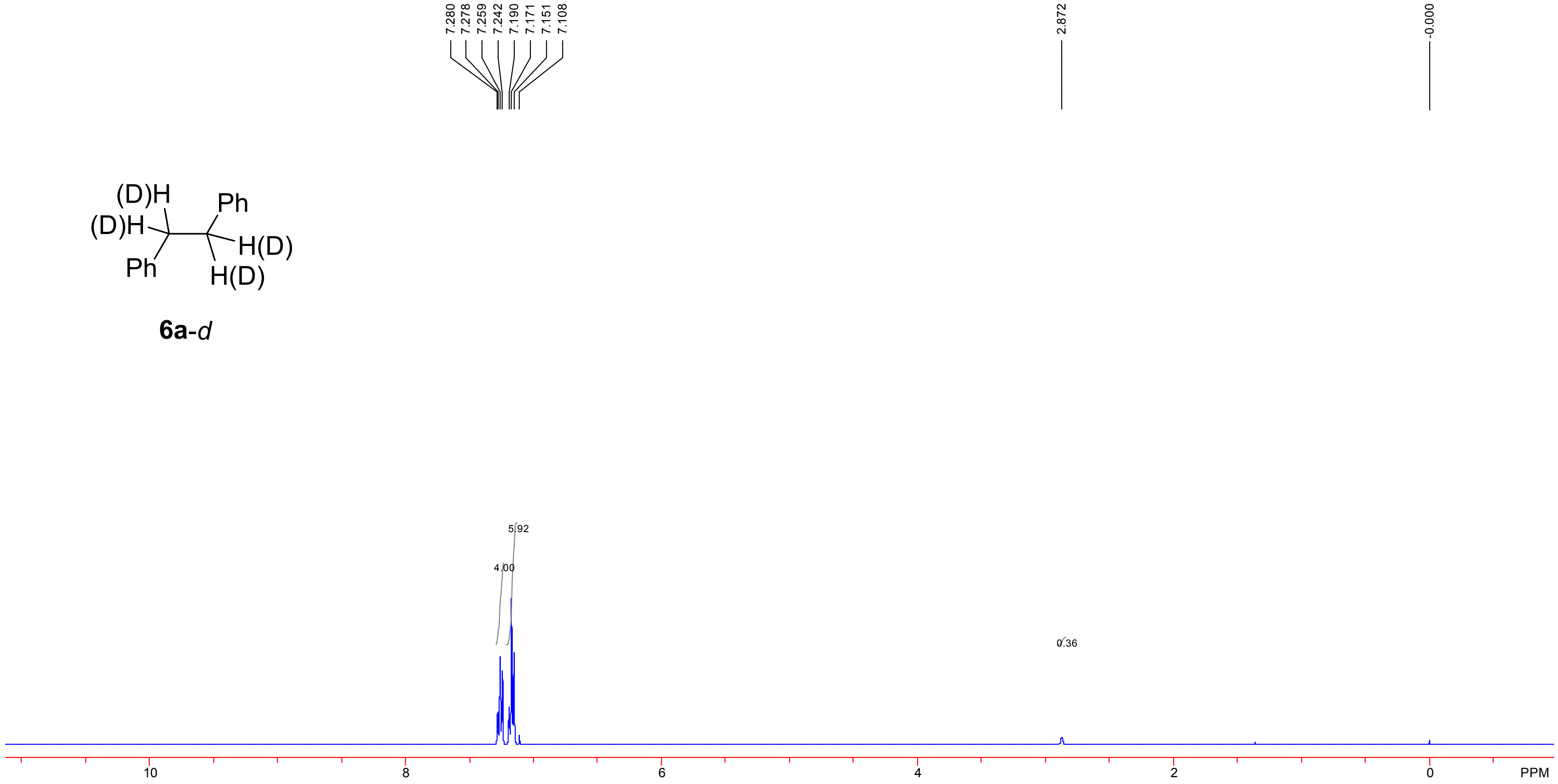
12l



12m


77.315
77.000
76.681
31.986
29.767
29.723
29.433
22.743
14.134
4
4
200
150
100
50
0

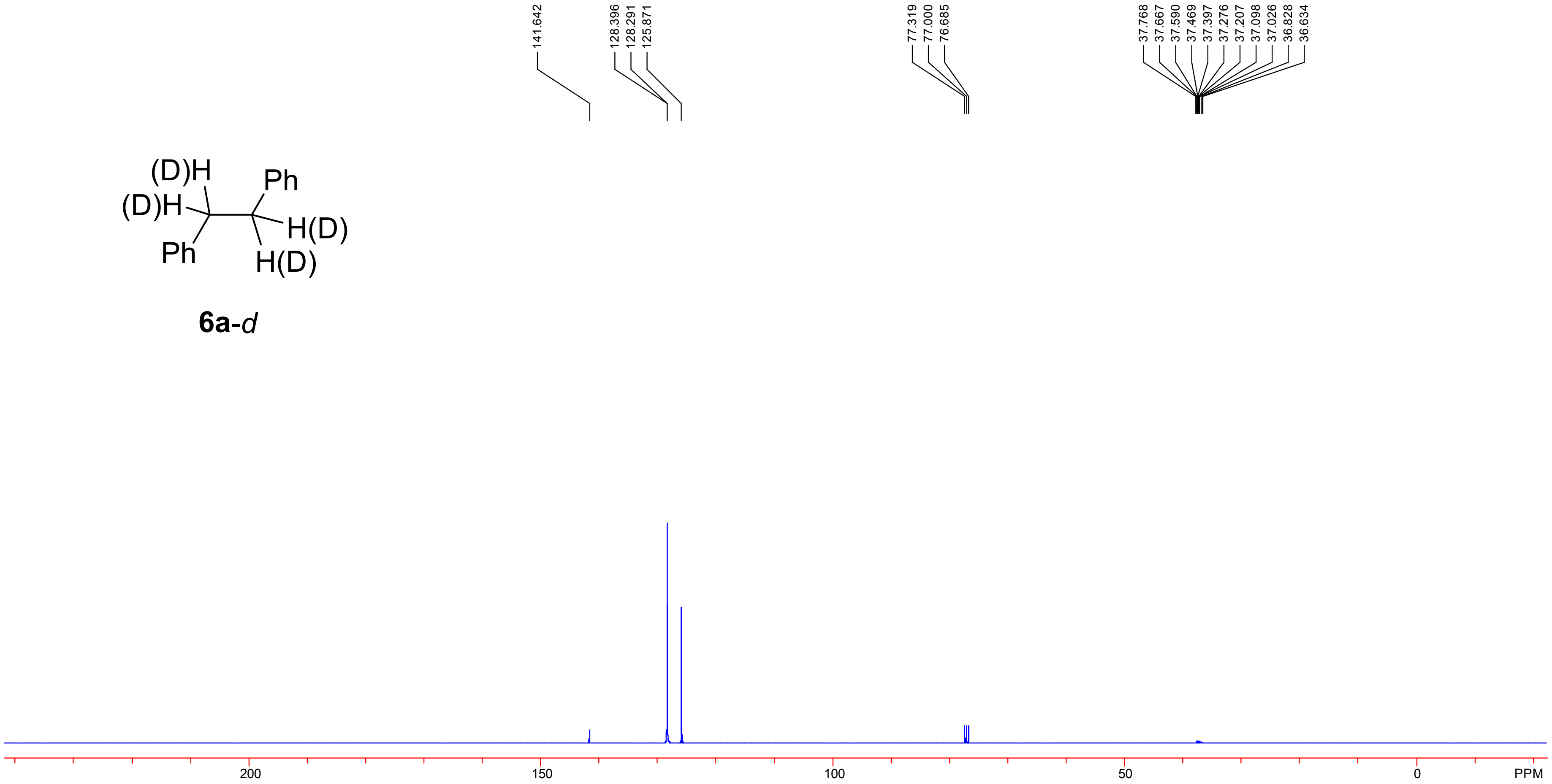
12m

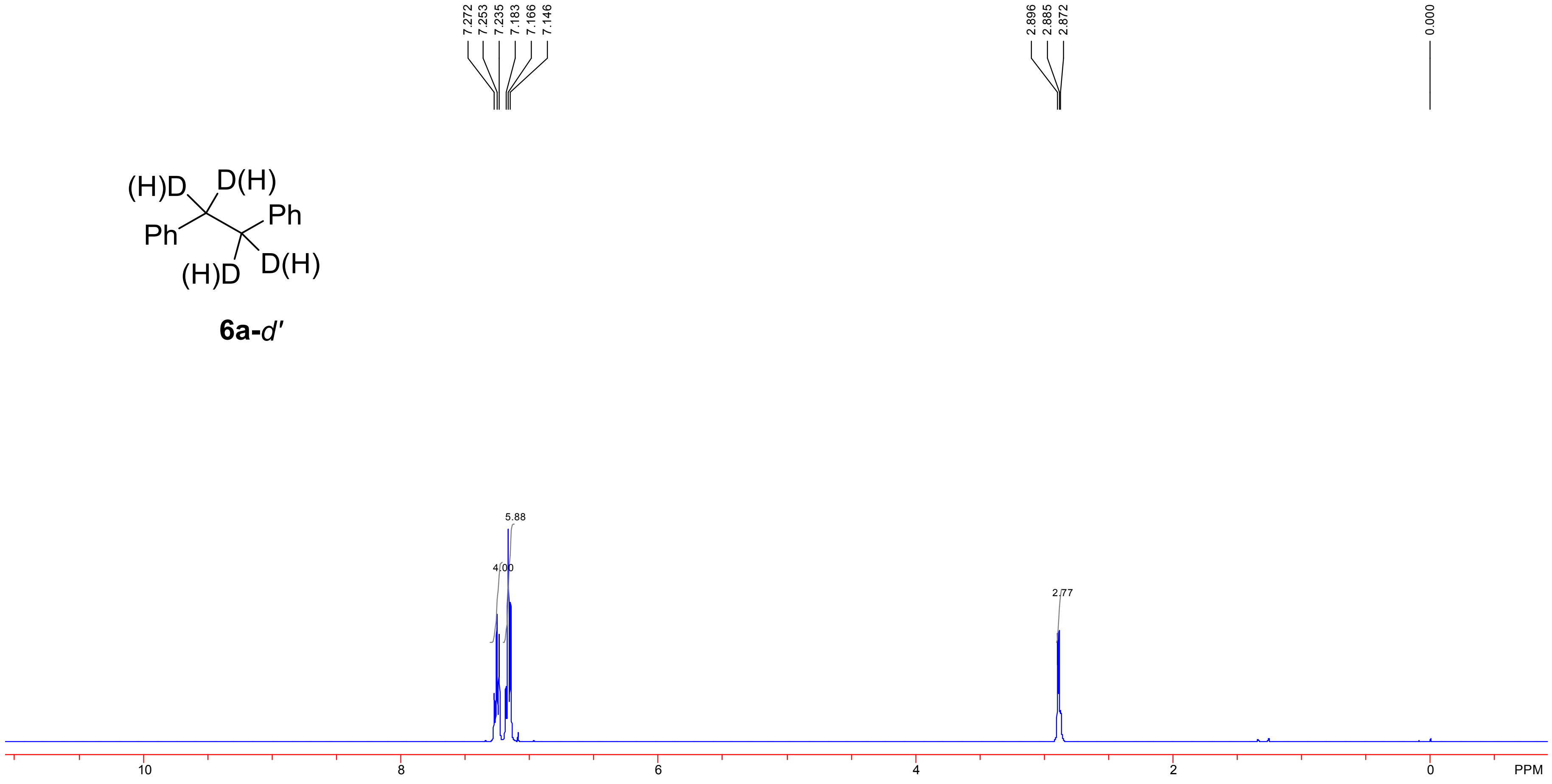

7.280
7.278
7.259
7.242
7.190
7.171
7.151
7.108
2.872
-0.000
(D)H
(D)H
Ph
Ph
H(D)
H(D)
5.92
4.00
0.36
10
8
6
4
2
0
PPM

6a-*d*

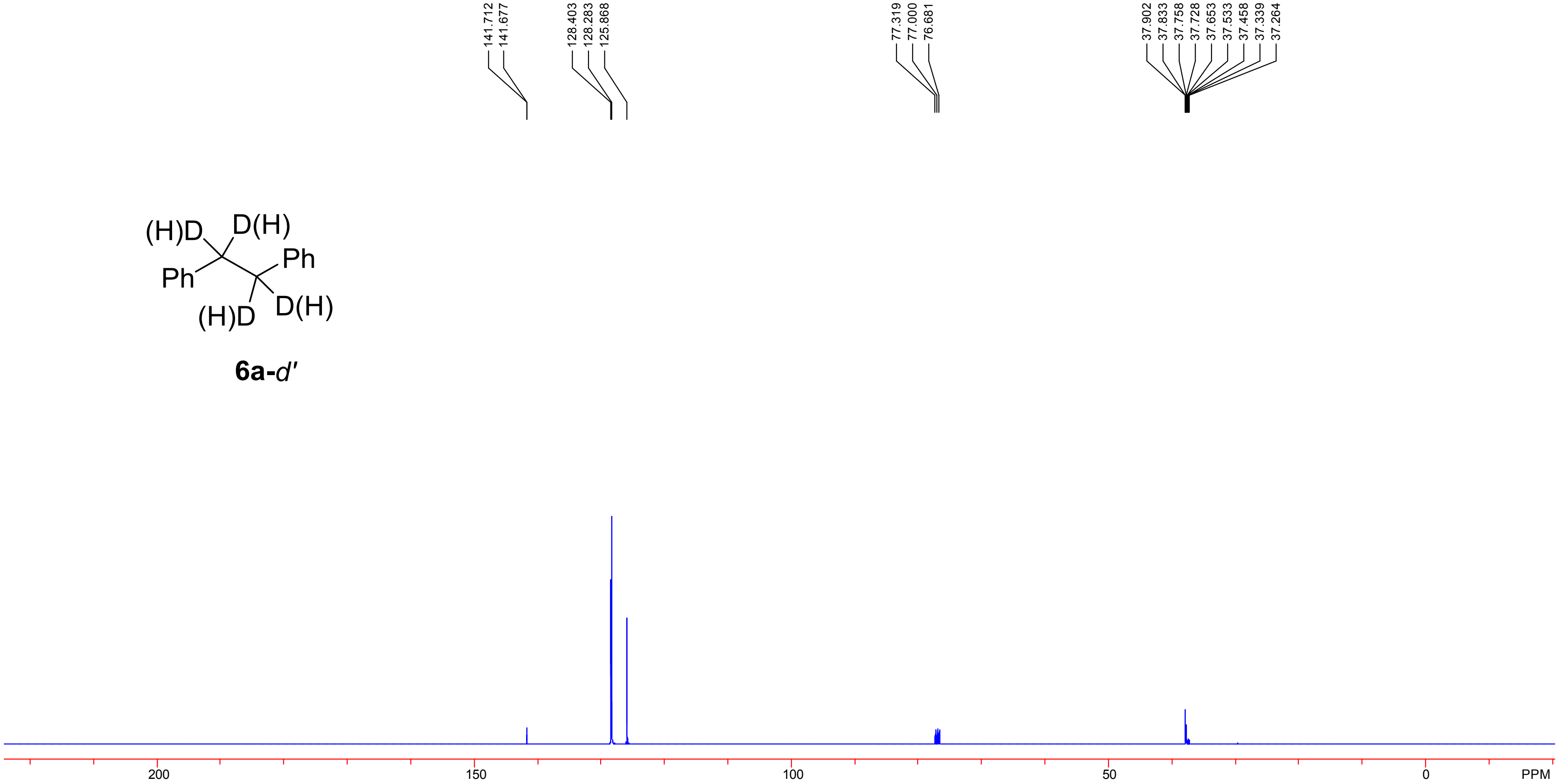
(D)H
(D)H
Ph
Ph
H(D)
H(D)

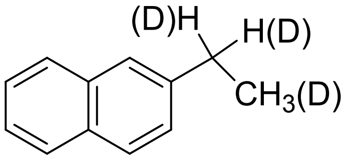
6a-*d*


141.642
128.396
128.291
125.871
77.319
77.000
76.685
37.768
37.667
37.590
37.469
37.397
37.276
37.207
37.098
37.026
36.828
36.634
200
150
100
50
0
PPM

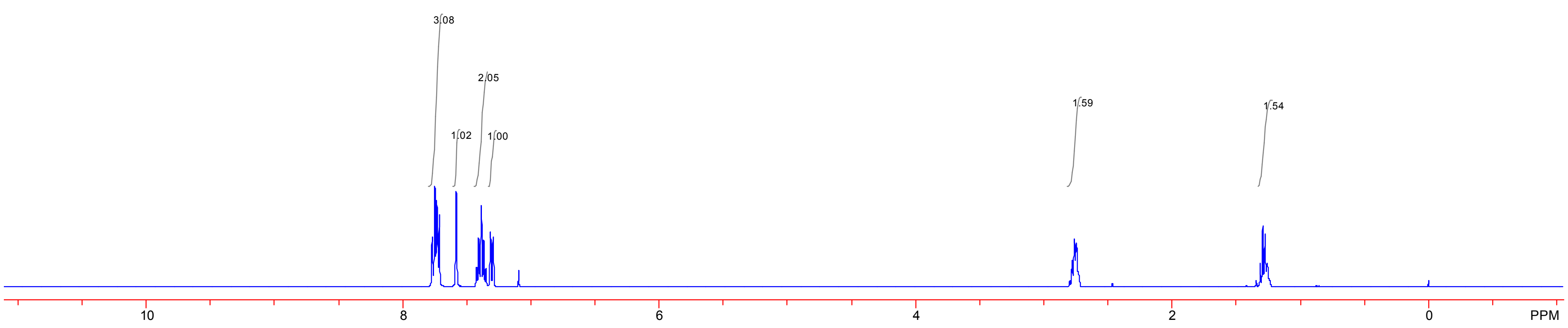

(H)D
D(H)
Ph
Ph
(H)D
D(H)
7.272
7.253
7.235
7.183
7.166
7.146
2.896
2.885
2.872
0.000
5.88
4.00
2.77
10
8
6
4
2
0
PPM

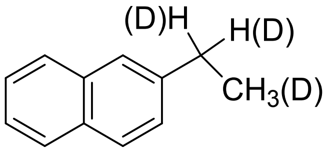
6a-*d′*


6a-_d′_
141.712
141.677
128.403
128.283
125.868
77.319
77.000
76.681
37.902
37.833
37.758
37.728
37.653
37.533
37.458
37.339
37.264
(H)D
D(H)
Ph
Ph
(H)D
D(H)
200
150
100
50
0
PPM

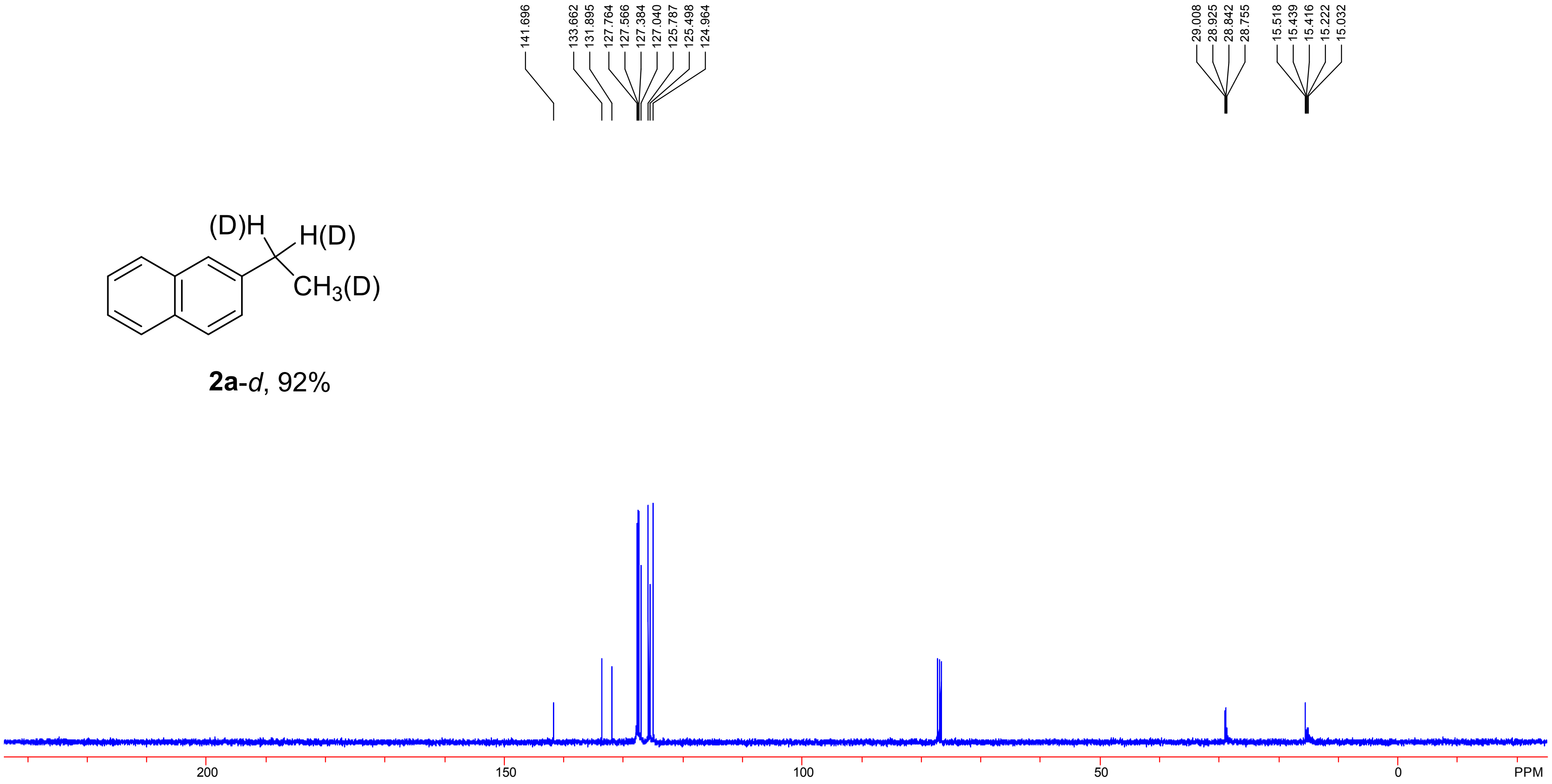

(D)H
H(D)
CH3(D)

2a-*d*, 92%


7.770
7.749
7.734
7.714
7.582
7.425
7.423
7.408
7.389
7.385
7.369
7.352
7.316
7.295
7.095
2.798
2.780
2.762
2.747
2.747
1.344
1.312
1.294
1.275
1.258
-0.000
3.08
2.05
1.02
1.00
1.59
1.54
10
8
6
4
2
0
PPM


(D)H
H(D)
CH3(D)

2a-*d*, 92%


141.696
133.662
131.895
127.764
127.566
127.384
127.040
125.787
125.498
124.964
29.008
28.925
28.842
28.755
15.518
15.439
15.416
15.222
15.032
200
150
100
50
0
PPM