

Supporting Information

Chemoselective Transfer Hydrogenation of α,β -Unsaturated Ketones Catalyzed by Pincer-Pd Complexes Using Alcohol as Hydrogen Source

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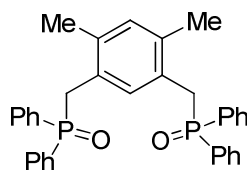
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1. General Details

All reactions were carried out without precaution to exclude air and moisture and the workup was carried out in air, unless otherwise noted. Column chromatographic purification of products was carried out using silica gel 60 (200~300 mesh). The reagents were used without further purification. The NMR spectra were recorded on a Varian MERCURY plus-400 (400 MHz, ^1H ; 100 MHz, ^{13}C ; 162 MHz, ^{31}P) spectrometer with chemical shifts reported in ppm relative to the residual deuterated solvents or the internal standard tetramethylsilane. Mass spectrometry analysis was carried out using an electrospray spectrometer Waters 4 micro quadrupole. Melting points were measured with SGW X-4 micro melting point apparatus. ^1H and ^{13}C NMR data for the known compounds **2a**¹, **2b**², **2c**³, **2d**⁴, **2e**², **2f**⁵, **2g**⁶, **2h**⁶, **2i**⁷, **2j**⁸, **2k**⁹, **2l**¹⁰, **2m**¹⁰, **2n**², **2o**¹⁰, **2p**¹⁰, **2q**³, **2r**⁸, **2s**¹⁰, **2t**¹⁰, **2u**², **2v**², **2w**¹, **2x**¹¹, **2y**¹², **2aa+2ab**^{1,13}, **2ac**¹ were consistent with the literature reported values.

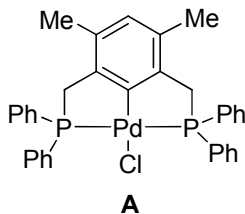
2. Preparation of Catalysts



1A

1,5-Bis((diphenylphosphinoyl)methyl)-3,5-dimethylbenzene (1A) A 250 mL, three-necked round-bottomed flask was charged with diphenylphosphine oxide (16.2 g, 80.1 mmol, 1.0 equiv), sodium hydride (60% in mineral oil, 3.50 g, 87.5 mmol, 1.1 equiv), and dry THF (90 mL). After stirring for 2 h under nitrogen at room temperature, a solution of 1,5-bis(chloromethyl)-2,4-dimethylbenzene (7.84 g, 38.6 mmol, 0.5 equiv) in dry THF (40 mL) was added slowly and the reaction mixture was then allowed to stir at room temperature for 18 h. The reaction was quenched carefully with water (10 mL), and the mixture was extracted with CH₂Cl₂ (3 × 60 mL), dried with MgSO₄, and concentrated to dryness. The crude product was triturated with a mixture of petroleum ether (100 mL) and ethyl acetate (1 mL). The product was collected by filtration to give 17.5 g (85% yield) of **1A** as white solid. Mp: 127.9-128.9 °C.

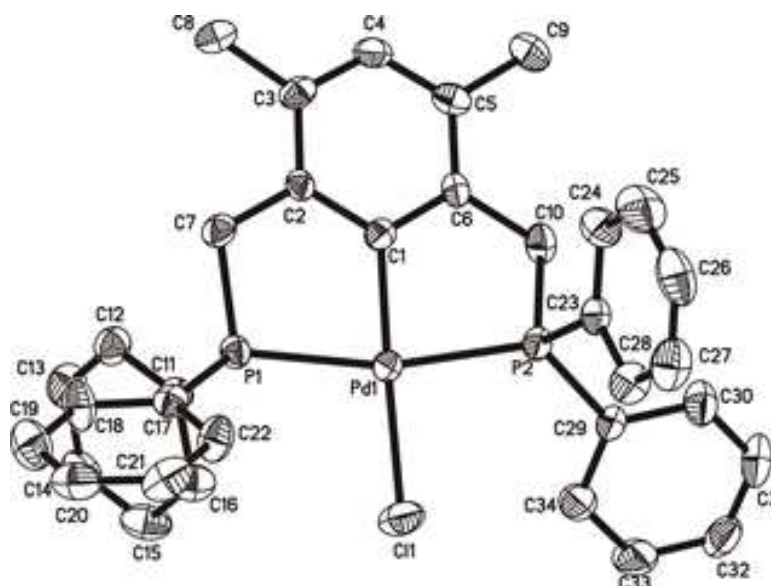
¹H NMR (400 MHz, CDCl₃): δ 7.62-7.57 (m, 8H), 7.52-7.48 (m, 4H), 7.44-7.39 (m, 8H), 6.79 (s, 1H), 6.48 (vt, *J*_{PH} = 2.4 Hz, 1H), 3.43 (d, *J*_{PH} = 14.0 Hz, 4H), 2.00 (s, 6H); ³¹P NMR (162 MHz, CDCl₃): δ 30.4 (s); ¹³C NMR (100 MHz, CDCl₃): δ 136.2 (t, *J*_{PC} = 4.4 Hz), 133.5 (t, *J*_{PC} = 4.4 Hz), 132.8 (t, *J*_{PC} = 2.5 Hz), 132.7 (d, *J*_{PC} = 97.1 Hz), 132.0, 131.4 (d, *J*_{PC} = 9.0 Hz), 128.6 (d, *J*_{PC} = 11.6 Hz), 127.0-126.9 (m), 34.9 (d, *J*_{PC} = 67.0 Hz), 19.7; HRMS (ESI): calcd. for C₃₄H₃₃O₂P₂ [M+H]⁺ 535.1956, found 535.1947, calcd. for C₃₄H₃₂O₂P₂Na [M+Na]⁺ 557.1775, found 557.1760.



(2,6-Bis((diphenylphosphino)methyl)-3,5-dimethylphenyl)palladium(II) chloride (A) A suspension of **1A** (0.267 g, 0.5 mmol, 1.0 equiv), triethylamine (1.01 g, 10.0 mmol, 20 equiv), trichlorosilane (1.36 g, 10.0 mmol, 20 equiv) in toluene (35 mL) was stirred at reflux for 18 h. The excess trichlorosilane was removed under vacuum. A solution of sodium hydroxide (4.0 g, 100 mmol) in degassed water (50 mL) was added and the reaction mixture was stirred for 15 min. The organic layer was separated and the aqueous layer was extracted with toluene (3 × 30 mL). The combined organic layers were dried over Na₂SO₄ and concentrated to give a light yellow sticky solid, which was used directly for palladation. The sticky solid was dissolved in dry toluene (10 mL), and the solution was transferred to a suspension of bis(acetonitrile)dichloropalladium(II) (0.13 g, 0.5 mmol, 1.0 equiv) in toluene (2 mL). The mixture was heated at reflux for 10 h. The crude reaction mixture was then subjected to silica gel chromatography (petroleum ether/ethyl acetate 10/1-3/1) affording **A** as a yellow solid (0.21 g, 65% overall yield). Mp: 313-315 °C.

¹H NMR (400 MHz, CDCl₃): δ 7.88- 7.84 (m, 8H), 7.41-7.26 (m, 12H), 6.74 (s, 1H), 3.84 (vt, *J*_{PH} = 4.4 Hz, 4H), 2.29 (s, 6H); ³¹P NMR (162 MHz, CDCl₃): δ 33.9 (s); ¹³C NMR (100 MHz, CDCl₃): δ 161.4, 144.7 (t, *J*_{PC} = 10.6 Hz), 133.2 (t, *J*_{PC} = 7.1 Hz), 133.0 (t, *J*_{PC} = 10.9 Hz), 132.6 (t, *J*_{PC} = 20.9 Hz), 130.7, 129.4, 129.0 (t, *J*_{PC} = 4.8 Hz), 40.7 (t, *J*_{PC} = 15.0 Hz), 22.7; HRMS (ESI): calcd for C₃₄H₃₁P₂Pd [M-Cl]⁺ 607.0936, found 607.0923.

Crystal Data for Complex A:



A

Bond precision: C-C = 0.0069 Å Wavelength=0.71073
 Cell: a=11.7377(2) b=15.1357(3) c=16.2481(3)
 alpha=90 beta=90 gamma=90
 Temperature: 293 K

	Calculated	Reported
Volume	2886.61(9)	2886.59(11)
Space group	P 21 21 21	P 21 21 21
Hall group	P 2ac 2ab	P 2ac 2ab
Moiety formula	C34 H31 Cl P2 Pd	C34 H31 Cl P2 Pd
Sum formula	C34 H31 Cl P2 Pd	C34 H31 Cl P2 Pd
Mr	643.38	643.38
Dx, g cm ⁻³	1.480	1.480
Z	4	4
Mu (mm ⁻¹)	0.869	0.869
F000	1312.0	1312.0
F000'	1309.76	
h,k,lmax	14, 18, 19	14, 18, 19

Nref	2985[5291]	5210
Tmin,Tmax	0.805, 0.840	0.812, 0.845
Tmin'	0.805	

Correction method= MULTI-SCAN

Data completeness= 1.75/0.98

Theta(max)= 25.350

R(reflections)= 0.0286(4651)

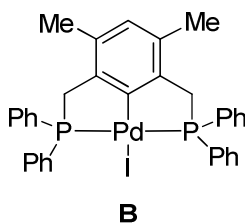
wR2(reflections)= 0.0689(5210)

S = 1.094

Npar= 345

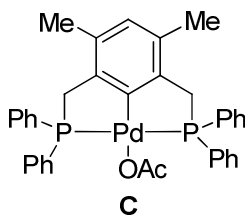
Selected Bond Lengths and Bond Angles for Complex A:

bond length	Å	bond angle	deg
Pd1- C1	2.042 (4)	C1- Pd1- P2	82.83 (11)
Pd1- P2	2.2751 (11)	C1- Pd1- P1	82.70 (11)
Pd1- P1	2.2812 (11)	P2- Pd1- P1	165.53 (4)
Pd1- Cl1	2.3861 (11)	C1- Pd1- Cl1	177.63 (11)
		P2- Pd1- Cl1	95.31 (4)
		P1- Pd1- Cl1	99.16 (4)



(2,6-Bis((diphenylphosphino)methyl)-3,5-dimethylphenyl)palladium(II) iodide (B) A mixture of **A** (64.3 mg, 0.1 mmol, 1.0 equiv) and potassium iodide (331.8 mg, 2.0 mmol, 20 equiv) was stirred in MeOH/CH₂Cl₂ (2/3 v/v, 5 mL) at room temperature until TLC confirmed the consumption of **A**. The reaction mixture was filtered through celite and the solvent was removed under reduced pressure. The residue was purified by silica gel chromatography (petroleum ether/ethyl acetate 10/1) affording of **B** as a yellow solid (62.4 mg, 85% yield). Mp: 289-291 °C.

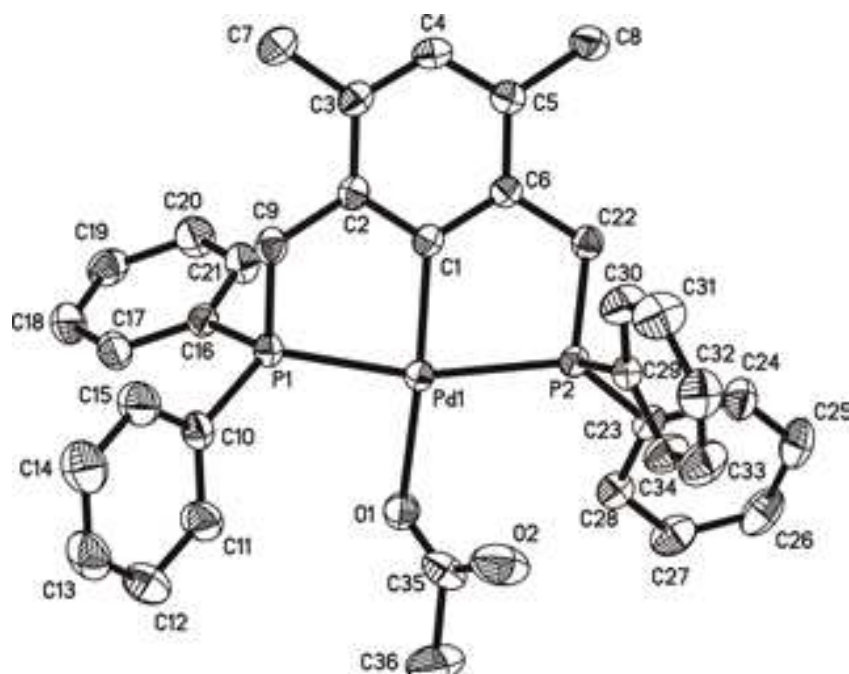
¹H NMR (400 MHz, CDCl₃): δ 7.84-7.79 (m, 8H), 7.43-7.38 (m, 12H), 6.76, (s, 1H), 3.92 (vt, *J*_{PH} = 4.4 Hz, 4H), 2.30 (s, 6H); ³¹P NMR (162 MHz, CDCl₃): δ 38.0 (s); ¹³C NMR (100 MHz, CDCl₃): δ 168.7, 144.8 (t, *J*_{PC} = 10.8 Hz), 133.6 (t, *J*_{PC} = 7.3 Hz), 132.9 (t, *J*_{PC} = 10.8 Hz), 132.5 (t, *J*_{PC} = 23.1 Hz), 130.8, 129.4, 128.9 (t, *J*_{PC} = 5.1 Hz), 42.9 (t, *J*_{PC} = 14.5 Hz), 22.9; HRMS (ESI): calcd for C₃₄H₃₁P₂Pd [M-I]⁺ 607.0936, found 607.0963.



Acetoxy(2,6-bis((diphenylphosphino)methyl)-3,5-dimethylphenyl)palladium (C) Silver acetate (117.0 mg, 0.70 mmol, 1.05 equiv) was added to a stirred solution of **A** (429.0 mg, 0.67 mmol, 1.0 equiv) in CH₂Cl₂ (30 mL) under nitrogen, and the resulting mixture was stirred in dark at room temperature for 24 h. The reaction mixture was filtered through celite and concentrated under vacuum, affording the product **C** as a yellow solid (427.0 mg, 96% yield). Mp: 212-214 °C.

¹H NMR (400 MHz, C₆D₆): δ 7.94-7.90 (m, 8H), 7.03-6.99 (m, 8H), 6.95-6.92 (m, 4H), 6.59 (s, 1H), 3.35 (vt, *J*_{PH} = 4.4 Hz, 4H), 2.22 (s, 3H), 2.03 (s, 6H); ³¹P NMR (162 MHz, C₆D₆): δ 35.6 (s); ¹³C NMR (100 MHz, C₆D₆): δ 175.7, 158.2, 144.6 (t, *J*_{PC} = 10.5 Hz), 133.3 (t, *J*_{PC} = 6.7 Hz), 133.2 (t, *J*_{PC} = 21.8 Hz), 132.0 (t, *J*_{PC} = 10.0 Hz), 130.3, 129.2, 128.7 (t, *J*_{PC} = 5.1 Hz), 39.7 (t, *J*_{PC} = 14.6 Hz), 24.5, 22.1; HRMS (ESI): calcd for C₃₄H₃₁P₂Pd [M-OAc]⁺ 607.0936, found 607.0989.

Crystal Data for Complex C.CHCl₃:



C

Bond precision:	C-C = 0.0065 Å	Wavelength=0.71073
Cell:	a=15.6441(8)	b=11.9037(4) c=20.3524(11)
	alpha=90	beta=111.491(6) gamma=90
Temperature:	293 K	

	Calculated	Reported
Volume	3526.6(3)	3526.6(3)
Space group	P 21/c	P 21/c
Hall group	-P 2ybc	-P 2ybc
Moiety formula	C36 H34 O2 P2 Pd, C H Cl3	C36 H34 O2 P2 Pd, C H Cl3
Sum formula	C37 H35 Cl3 O2 P2 Pd	C37 H35 Cl3 O2 P2 Pd
Mr	786.34	786.34
Dx, g cm ⁻³	1.481	1.481
Z	4	4
Mu (mm ⁻¹)	0.876	0.876

F000	1600.0	1600.0
F000'	1599.07	
h,k,lmax	18, 14, 24	18, 14, 24
Nref	6467	6455
Tmin,Tmax	0.763, 0.796	0.767, 0.804
Tmin'	0.748	

Correction method= MULTI-SCAN

Data completeness= 0.998

Theta(max)= 25.350

R(reflections)= 0.0387(5140)

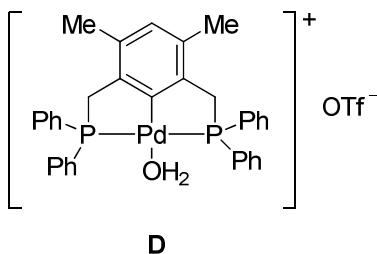
wR2(reflections)= 0.1046(6455)

S = 1.057

Npar= 409

Selected Bond Lengths and Bond Angles for Complex C.CHCl₃:

bond length	Å	bond angle	deg
Pd1- C1	2.029 (3)	C1- Pd1- O1	171.60 (12)
Pd1- O1	2.121 (3)	C1- Pd1- P1	82.56 (10)
Pd1- P1	2.2831 (9)	O1- Pd1- P1	95.05 (8)
Pd1- P2	2.2869 (9)	C1- Pd1- P2	81.64 (9)
O1- C35	1.181 (5)	O1- Pd1- P2	101.26 (8)
		P1- Pd1- P2	163.49 (4)
		C35- O1- Pd1	120.6 (3)



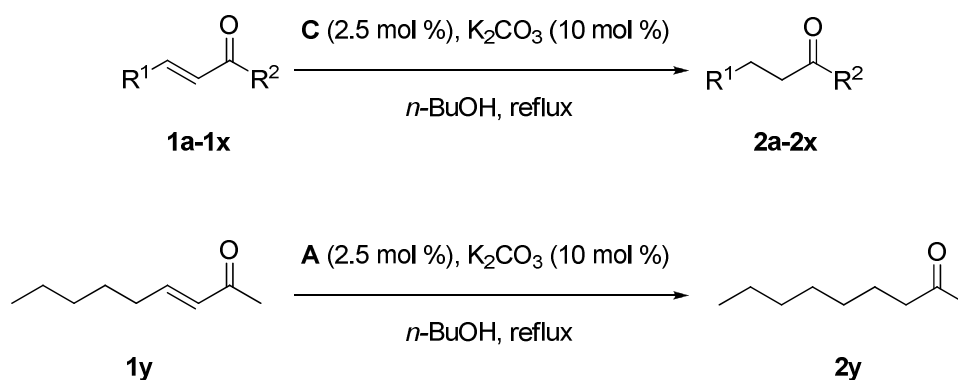
1-(Aqua-2,6-bis((diphenylphosphino)methyl)-3,5-dimethylbenzene

trifluoromethylsulfonate (D) Silver triflate (52.4 mg, 0.20 mmol, 1.0 equiv) dissolved in wet acetone (1 mL) was added to a stirred solution of **A** (128.7 mg, 0.20 mmol, 1.0 equiv) in wet acetone (5 mL). The mixture was stirred in dark at room temperature for 2 h. Subsequently, the reaction mixture was filtered and the filtrate was reduced to a volume of 1 mL. Hexane (10 mL) was added, resulting in the precipitation of a white solid, which was collected, washed with hexane (3 × 10 mL) and dried in vacuo (139.5 mg, 90% yield). Mp: 238-240 °C. ¹H NMR (400 MHz, CDCl₃): δ 7.75-7.70 (m, 8H), 7.49-7.42 (m, 12H), 6.73 (s, 1H), 3.74 (vt, *J*_{PH} = 4.4 Hz, 4H), 2.25 (s, 6H); ³¹P NMR (162 MHz, CDCl₃): δ 36.8; ¹⁹F NMR (376 MHz, CDCl₃): δ -78.7; ¹³C NMR (100 MHz, DMSO-*d*₆): δ 154.5, 144.3 (t, *J*_{PC} = 9.7 Hz), 133.9-133.6 (m), 132.2, 131.2 (t, *J*_{PC} = 21.7 Hz), 130.5, 130.0 (t, *J*_{PC} = 4.1 Hz), 121.1 (q, *J*_{FC} = 319.8 Hz), 38.2 (t, *J*_{PC} = 15.3 Hz), 22.2; HRMS (ESI): calcd for C₃₄H₃₁P₂Pd [M-OTf- H₂O]⁺ 607.0936, found 607.0960. The structure was deduced according to the related literature.¹⁴

3. General Procedure for Synthesis of α,β -Unsaturated Ketones¹⁵

To a solution of NaOH (2.2 g, 55 mmol, 1.3 equiv) in H₂O (20 mL) and aromatic ketone (43 mmol, 1.0 equiv) in 12 mL ethanol at 0 °C was added gradually aromatic aldehyde (43 mmol, 1.0 equiv). The mixture was then allowed to warm to room temperature and stirred for 4 h after which a precipitate of the product formed. The product was collected by suction filtration on a Buchner funnel and washed repeatedly with cold water. Recrystallization from ethanol or purification by silica gel chromatography for liquid products afforded α,β -unsaturated ketones **1a-1x**. **1y** was prepared according to literature^{15o}. All spectroscopic data of α -enones **1a-1y** are in good agreement with the literature reported data.

4. General Procedure for Conjugate Reduction

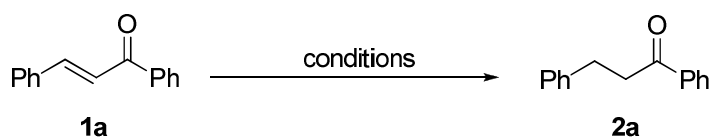


A mixture of catalyst **C** (8.34 mg, 0.0125 mmol, 2.5 mol %), enone (0.50 mmol, 1.0 equiv), and K₂CO₃ (6.91 mg, 0.05 mmol, 10 mol %) in *n*-BuOH (5 mL) was stirred for the allotted time at reflux. After evaporation of the solvent, the crude product was purified by silica gel chromatography.

4.1 Screening of Temperatures

In order to examine the effect of temperature on the reaction outcome, the reaction was carried out at different temperatures ranging from 65 °C to reflux (the boiling point of *n*-BuOH is 117 °C) (Table S1). It was observed that higher temperatures led to a faster rate of reaction (entries 1-4). At 65 °C, the complete consumption of **1a** with a yield of 72% required 36 h (entry 1). When the reaction was performed under reflux conditions for 1.5 h, the yield of **2a** increased to 83% only using 1.5 h (entry 4).

Table S1. Influence of Different Temperatures^a



entry	temperature (°C)	time (h)	yield (%) ^b
1	65	36	72
2	85	13	77
3	105	2.5	80
4	reflux	1.5	83


^a Reaction conditions: **1a** (0.50 mmol), **A** (5 mol %), NaOH (25 mol %), *n*-BuOH (5 mL).

^b Isolated yields.

4.2 Screening of Bases

We then examined the influence of different bases on the reaction (Table S2). It took 0.5-2.5 h to complete the reaction with commonly used bases (entries 1-6). However, the reaction ran considerably slower with Na₂CO₃ as base (entry 7) and was almost unsuccessful using DIPEA (diisopropylethylamine) (entry 8). K₂CO₃ was found to be optimal for the conjugate reduction of α,β -unsaturated ketones with the highest yield of 89% (entry 6). Increasing the quantity of the K₂CO₃ to 50 mol % did not improve the yield (entry 9), while reducing the amount to 10 mol % gave a higher yield of 93% (entry 10). Further reduction of the quantity of K₂CO₃ to 5 mol % did not increase the yield further, and a slightly longer reaction time was needed (entry 11).

Table S2. Influence of Different Bases



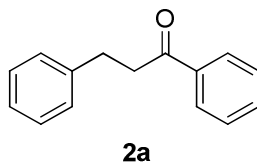
1a 2a

entry ^a	base (mol %)	time (h)	yield (%) ^b
1	NaOH (25)	1.5	83
2	KOH (25)	0.5	76
3	LiOH (25)	1.5	57
4	NaO <i>n</i> -Bu (25)	1	76
5	Cs ₂ CO ₃ (25)	0.5	78
6	K ₂ CO ₃ (25)	2.5	89
7	Na ₂ CO ₃ (25)	18	16 ^c
8	DIPEA (25)	18	trace
9	K ₂ CO ₃ (50)	2	86
10	K ₂ CO ₃ (10)	2.5	93
11	K ₂ CO ₃ (5)	3.5	88

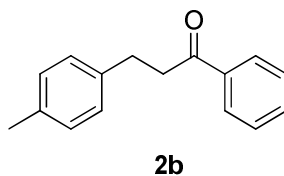
^a Reaction conditions: **1a** (0.50 mmol), **A** (5 mol %), base, *n*-BuOH (5 mL), at reflux.

^b Isolated yields. ^c GC yield based on recovered **1a**.

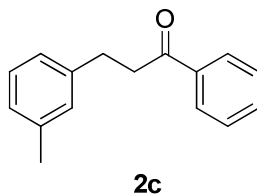
5. Data of NMR



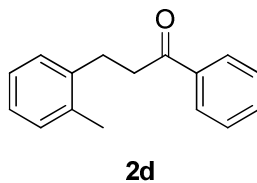
1,3-Diphenylpropan-1-one (2a)¹ 100.9 mg, 96% yield. ¹H NMR (400 MHz, CDCl₃): δ 7.97-7.95 (m, 2H), 7.58-7.54 (m, 1H), 7.47-7.44 (m, 2H), 7.32-7.19 (m, 5H), 3.33-3.29 (m, 2H), 3.09-3.06 (m, 2H).



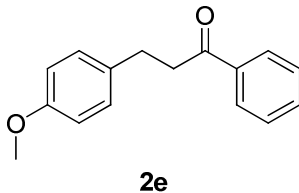
1-Phenyl-3-*p*-tolylpropan-1-one (2b)² 105.9 mg, 94% yield. ¹H NMR (400 MHz, CDCl₃): δ 7.97-7.95 (m, 2H), 7.57-7.53 (m, 1H), 7.48-7.43 (m, 2H), 7.16-7.10 (m, 4H), 3.30-3.27 (m, 2H), 3.05-3.02 (m, 2H), 2.33 (s, 3H).



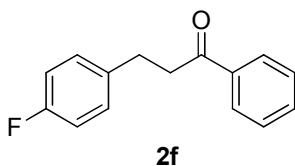
1-Phenyl-3-*m*-tolylpropan-1-one (2c)³ 108.1 mg, 96% yield. ¹H NMR (400 MHz, CDCl₃): δ 7.99-7.96 (m, 2H), 7.58-7.54 (m, 1H), 7.48-7.44 (m, 2H), 7.20 (t, *J* = 7.6 Hz, 1H), 7.08-7.02 (m, 3H), 3.32-3.28 (m, 2H), 3.06-3.02 (m, 2H), 2.34 (s, 3H).



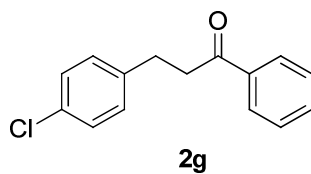
1-Phenyl-3-*o*-tolylpropan-1-one (2d)⁴ 102.1 mg, 91% yield. ¹H NMR (400 MHz, CDCl₃): δ 8.03-8.00 (m, 2H), 7.61-7.57 (m, 1H), 7.51-7.47 (m, 2H), 7.26-7.17 (m, 4H), 3.31-3.27 (m, 2H), 3.12- 3.08 (m, 2H), 2.40 (s, 3H).



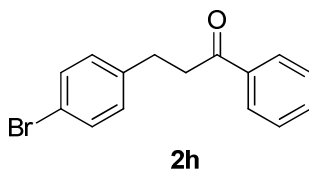
3-(4-Methoxyphenyl)-1-phenylpropan-1-one (2e)² 113.2 mg, 94% yield. ¹H NMR (400 MHz, CDCl₃): δ 7.98-7.95 (m, 2H), 7.58-7.53 (m, 1H), 7.48-7.43 (m, 2H), 7.20-7.16 (m, 2H), 6.87-6.83 (m, 2H), 3.79 (s, 3H), 3.29-3.25 (m, 2H), 3.04-3.00 (m, 2H).



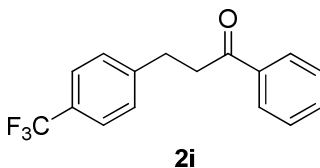
3-(4-Fluorophenyl)-1-phenylpropan-1-one (2f)⁵ 105.7 mg, 93% yield. ¹H NMR (400 MHz, CDCl₃): δ 7.97-7.94 (m, 2H), 7.58-7.54 (m, 1H), 7.47-7.44 (m, 2H), 7.22-7.18 (m, 2H), 7.00-6.95 (m, 2H), 3.31-3.26 (m, 2H), 3.05 (t, *J* = 8.0 Hz, 2H).



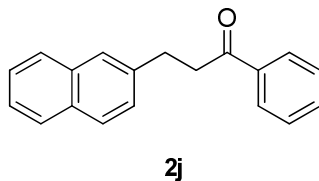
3-(4-Chlorophenyl)-1-phenylpropan-1-one (2g)⁶ 112.9 mg, 92% yield. ¹H NMR (400 MHz, CDCl₃): δ 7.95-7.93 (m, 2H), 7.57-7.53 (m, 1H), 7.47-7.43 (m, 2H), 7.26-7.24 (m, 2H), 7.19-7.17 (m, 2H), 3.29-3.26 (m, 2H), 3.06-3.02 (m, 2H).



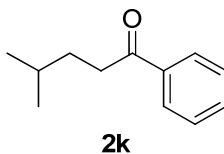
3-(4-Bromophenyl)-1-phenylpropan-1-one (2h)⁶ 127.8 mg, 88% yield. ¹H NMR (400MHz, CDCl₃): δ 7.96-7.93 (m, 2H), 7.58-7.54 (m, 1H), 7.47-7.40 (m, 4H), 7.14-7.12 (m, 2H), 3.30-3.26 (m, 2H), 3.03 (t, *J* = 8.0 Hz, 2H).



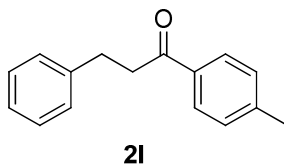
1-Phenyl-3-(4-(trifluoromethyl)phenyl)propan-1-one (2i)⁷ 135.4 mg, 97% yield. ¹H NMR (400 MHz, CDCl₃): δ 7.96-7.94 (m, 2H), 7.59-7.54 (m, 3H), 7.48-7.44 (m, 2H), 7.37 (d, *J* = 7.6 Hz, 2H), 3.35-3.31 (m, 2H), 3.14 (t, *J* = 7.6 Hz, 2H).



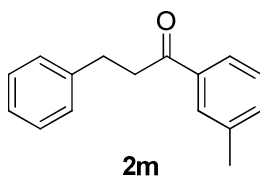
3-(Naphthalen-2-yl)-1-phenylpropan-1-one (2j)⁸ 124.0 mg, 95% yield. ¹H NMR (400 MHz, CDCl₃): δ 8.00-7.97 (m, 2H), 7.82-7.78 (m, 3H), 7.70 (s, 1H), 7.58-7.54 (m, 1H), 7.48-7.39 (m, 5H), 3.42-3.38 (m, 2H), 3.26-3.22 (m, 2H).



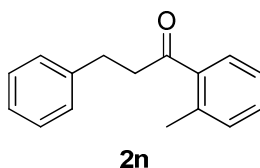
4-Methyl-1-phenylpentan-1-one (2k)⁹ 74.9 mg, 76.3 mg, 87% yield. ¹H NMR (400 MHz, CDCl₃): δ 7.97-7.95 (m, 2H) 7.57-7.53 (m, 1H), 7.48-7.43 (m, 2H), 2.98-2.94 (m, 2H), 1.68-1.60 (m, 3H), 0.94 (d, *J* = 6.0 Hz, 6H).



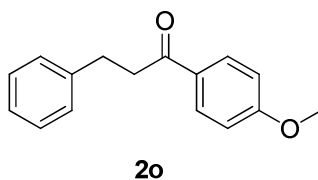
3-Phenyl-1-*p*-tolylpropan-1-one (2l)¹⁰ 103.7 mg, 92% yield. ¹H NMR (400 MHz, CDCl₃): δ 7.88-7.85 (m, 2H), 7.32-7.18 (m, 7H), 3.30-3.26 (m, 2H), 3.08-3.04 (m, 2H), 2.41 (s, 3H).



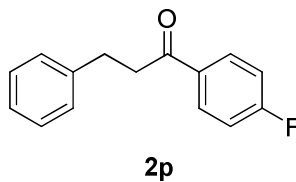
3-Phenyl-1-*m*-tolylpropan-1-one (2m)¹⁰ 106.2 mg, 95% yield. ¹H NMR (400MHz, CDCl₃): δ 7.77-7.74 (m, 2H), 7.38-7.19 (m, 7H), 3.31-3.27 (m, 2H), 3.09-3.05 (m, *J* = 7.7 Hz, 2H), 2.40 (s, 3H).



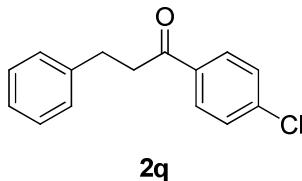
3-Phenyl-1-*o*-tolylpropan-1-one (2n)² 103.7 mg, 92% yield. ¹H NMR (400 MHz, CDCl₃): δ 7.61-7.59 (m, 1H), 7.38-7.19 (m, 8H), 3.25-3.21 (m, 2H), 3.05 (t, *J* = 8.0 Hz, 2H), 2.47 (s, 3H).



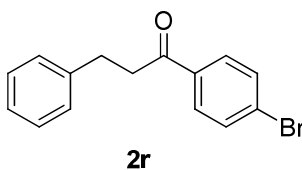
1-(4-Methoxyphenyl)-3-phenylpropan-1-one (2o)¹⁰ 116.3 mg, 97% yield. ¹H NMR (400 MHz, CDCl₃): δ 7.97-7.93 (m, 2H), 7.32-7.19 (m, 5H), 6.95-6.91 (m, 2H), 3.86 (s, 3H), 3.27-3.23 (m, 2H), 3.08-3.04 (m, 2H).



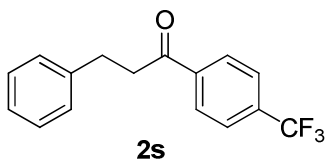
1-(4-Fluorophenyl)-3-phenylpropan-1-one (2p)¹⁰ 104.6 mg, 92% yield. ¹H NMR (400 MHz, CDCl₃): δ 8.01-7.96 (m, 2H), 7.33-7.19 (m, 5H), 7.15-7.09 (m, 2H), 3.30-3.26 (m, 2H), 3.09-3.05 (m, 2H).



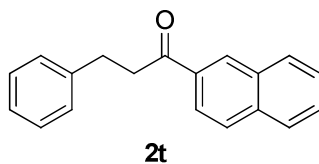
1-(4-Chlorophenyl)-3-phenylpropan-1-one (2q)³ 111.2 mg, 91% yield. ¹H NMR (400 MHz, CDCl₃): δ 7.91-7.87 (m, 2H), 7.44-7.41 (m, 2H), 7.32-7.19 (m, 5H), 3.29-3.25 (m, 2H), 3.08-3.04 (m, 2H).



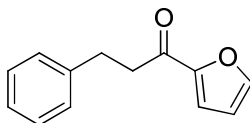
1-(4-Bromophenyl)-3-phenylpropan-1-one (2r)⁸ 124.7 mg, 86% yield. ¹H NMR (400 MHz, CDCl₃): δ 7.83-7.80 (m, 2H), 7.61-7.57 (m, 2H), 7.33-7.20 (m, 5H), 3.29-3.25 (m, 2H), 3.08-3.04 (m, 2H).



3-Phenyl-1-(4-(trifluoromethyl)phenyl)propan-1-one (2s)¹⁰ 129.1 mg, 93% yield. ¹H NMR (400 MHz, CDCl₃): δ 8.05 (d, *J* = 8.4 Hz, 2H), 7.72 (d, *J* = 8.4 Hz, 2H), 7.33-7.20 (m, 5H), 3.34-3.31 (m, 2H), 3.10-3.07 (m, 2H).

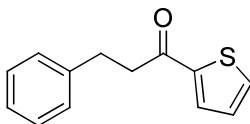


1-(Naphthalen-2-yl)-3-phenylpropan-1-one (2t)¹⁰ 128.0 mg, 98% yield. ¹H NMR (400 MHz, CDCl₃): δ 8.46 (s, 1H), 8.04 (dd, *J* = 8.8, 2.0 Hz, 1H), 7.95-7.86 (m, 3H), 7.62-7.53 (m, 2H), 7.34-7.21 (m, 5H), 3.47-3.43 (m, 2H), 3.15-3.12 (m, 2H).



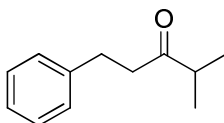
2u

3-(Furan-2-yl)-1-phenylpropan-1-one (2u)² 93.3 mg, 93% yield. ¹H NMR (400 MHz, CDCl₃): δ 7.57-7.56 (m, 1H), 7.31-7.16 (m, 6H), 6.52-6.51 (m, 1H), 3.18-3.14 (m, 2H), 3.06-3.04 (m, 2H).



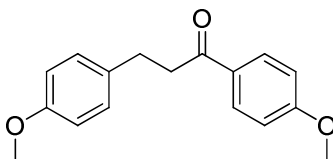
2v

3-Phenyl-1-(thiophen-2-yl)propan-1-one (2v)² 100.1 mg, 93% yield. ¹H NMR (400 MHz, CDCl₃): δ 7.69 (dd, *J* = 3.6, 1.2 Hz, 1H), 7.62 (dd, *J* = 5.2, 1.2 Hz, 1H), 7.32-7.19 (m, 5H), 7.12-7.10 (m, 1H), 3.26-3.21 (m, 2H), 3.09-3.05 (m, 2H).



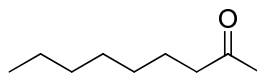
2w

4-Methyl-1-phenylpentan-3-one (2w)¹ 71.3 mg, 81% yield. ¹H NMR (400 MHz, CDCl₃): δ 7.30-7.25 (m, 2H), 7.20-7.17 (m, 3H), 2.91-2.87 (m, 2H), 2.79-2.75 (m, 2H), 2.57 (sept, *J* = 6.8 Hz, 1H), 1.07 (d, *J* = 6.8 Hz, 6H).



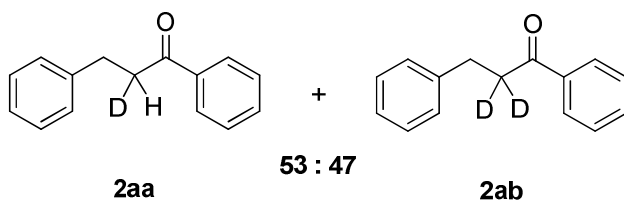
2x

1,3-Bis(4-methoxyphenyl)propan-1-one (2x)¹¹ 132.6 mg, 98% yield. ¹H NMR (400 MHz, CDCl₃): δ 7.95-7.92 (m, 2H), 7.18-7.15 (m, 2H), 6.94-6.90 (m, 2H), 6.86-6.82 (m, 2H), 3.86 (s, 3H), 3.78 (s, 3H), 3.23-3.19 (m, 2H), 3.01-2.97 (m, 2H).

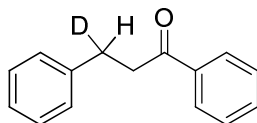


2y

Nonan-2-one 2y¹² 68% yield (determined by GC based on n-dodecane as an internal standard). ¹H NMR (CDCl₃, 400MHz): δ 2.41 (t, *J* = 7.6Hz, 2H), 2.13 (s, 3H), 1.58-1.54 (m, 2H), 1.31-1.26 (m, 8H), 0.89-0.84 (m, 3H).



2-Deuterio-1,3-diphenyl-1-propanone (2aa) and 2,2-bisDeuterio-1,3-diphenyl-1-propanone (2ab)^{1,13} The solvent is CH₃OD for **2aa** (8.5 mg, 8% GC yield based on recovered **1a**). ¹H NMR spectra showed that there are 53% **2aa** and 47% **2ab**. ¹H NMR (CDCl₃, 400MHz): 53% **2aa**: δ 7.99-7.96 (m, 2H), 7.59-7.54 (m, 1H), 7.48-7.43 (m 2H), 7.33-7.20 (m, 5H), 3.32-3.27 (m, 1H), 3.08 (d, *J* = 7.6 Hz, 2H). 47% **2ab**: δ 7.99-7.96 (m, 2H), 7.59-7.54 (m, 1H), 7.48-7.43 (m 2H), 7.33-7.20 (m, 5H), 3.07 (s, 2H).



2ac

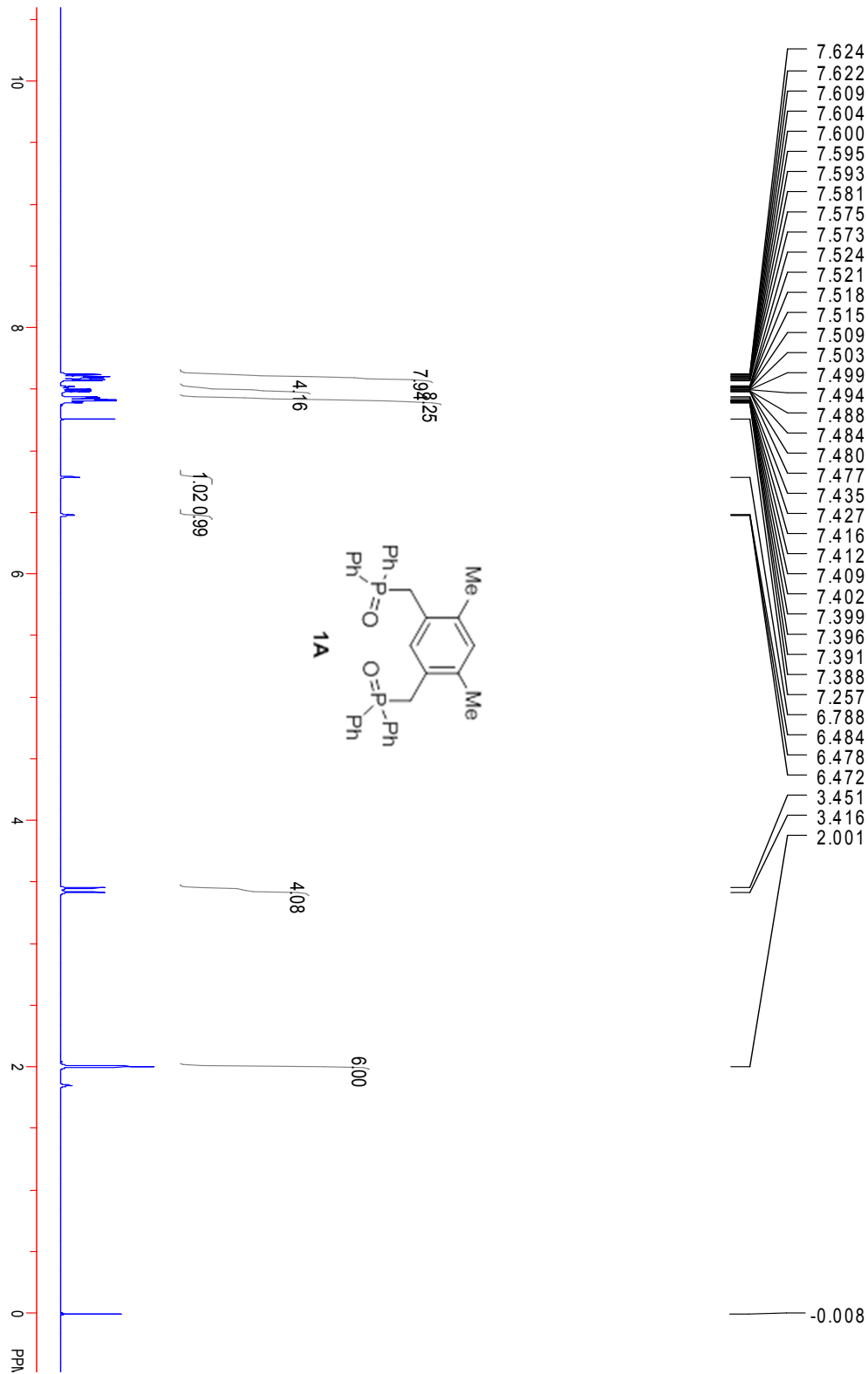
3-Deuterio-1,3-diphenyl-1-propanone (2ac)¹ The solvent is CH₃CD₂OH for **2ac** (47.5 mg, 45%). ¹H NMR (CDCl₃, 400MHz): δ 7.99-7.96 (m, 2H), 7.59-7.55 (m, 1H), 7.49-7.45 (m, 2H), 7.34-7.20 (m, 5H), 3.32 (d, *J* = 7.6 Hz, 2H), 3.11-3.05 (m, 1H).

6. References

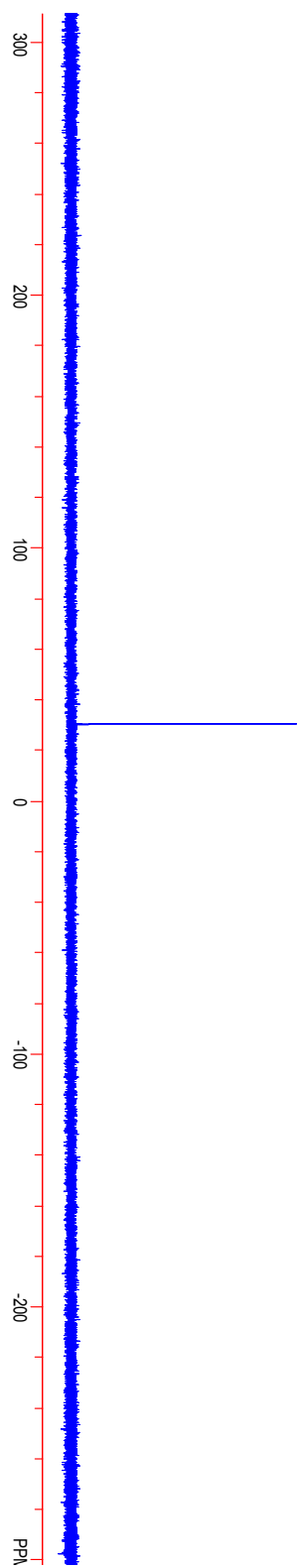
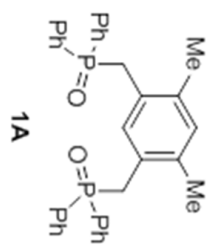
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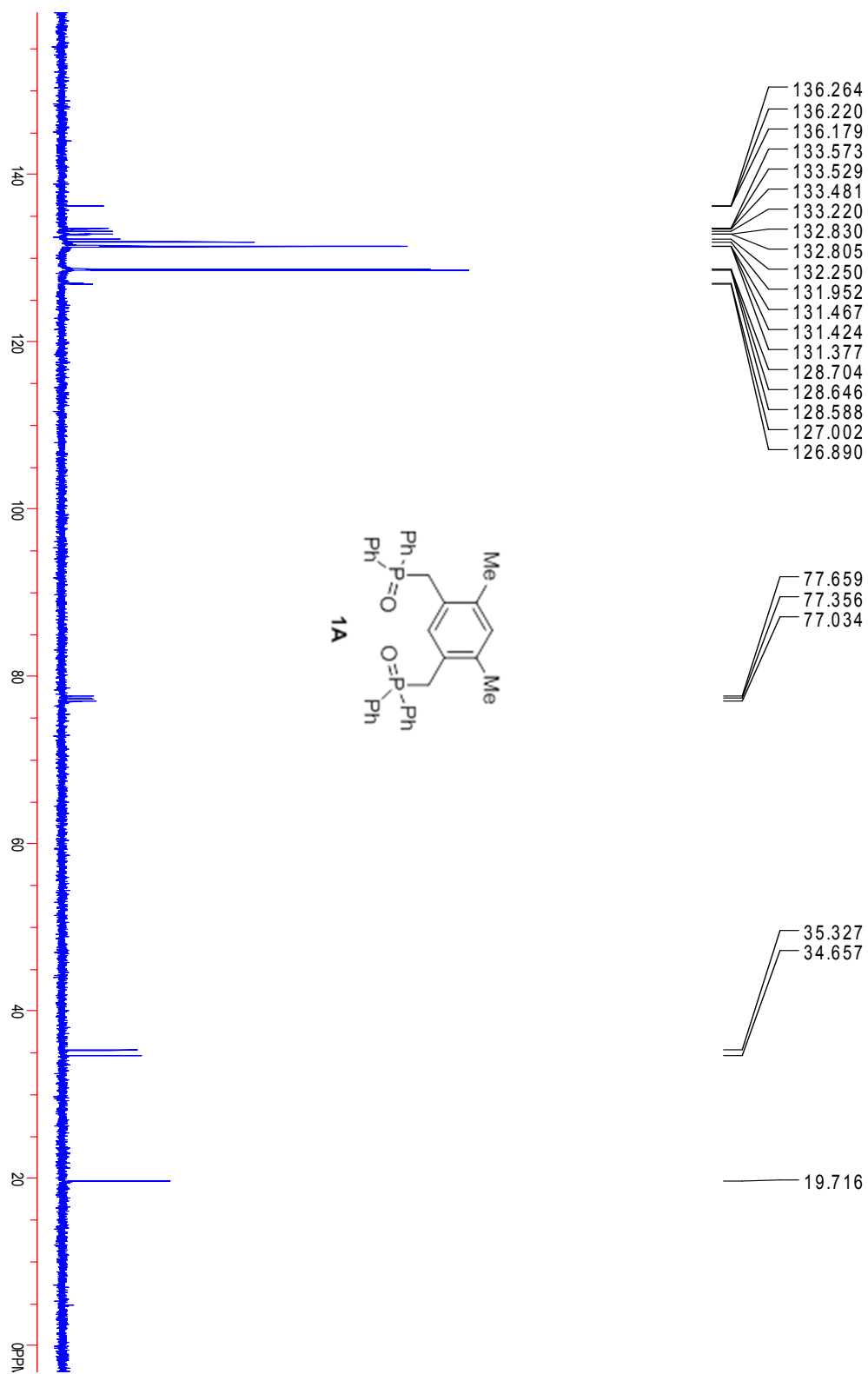
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7. Spectra of Products



30.412





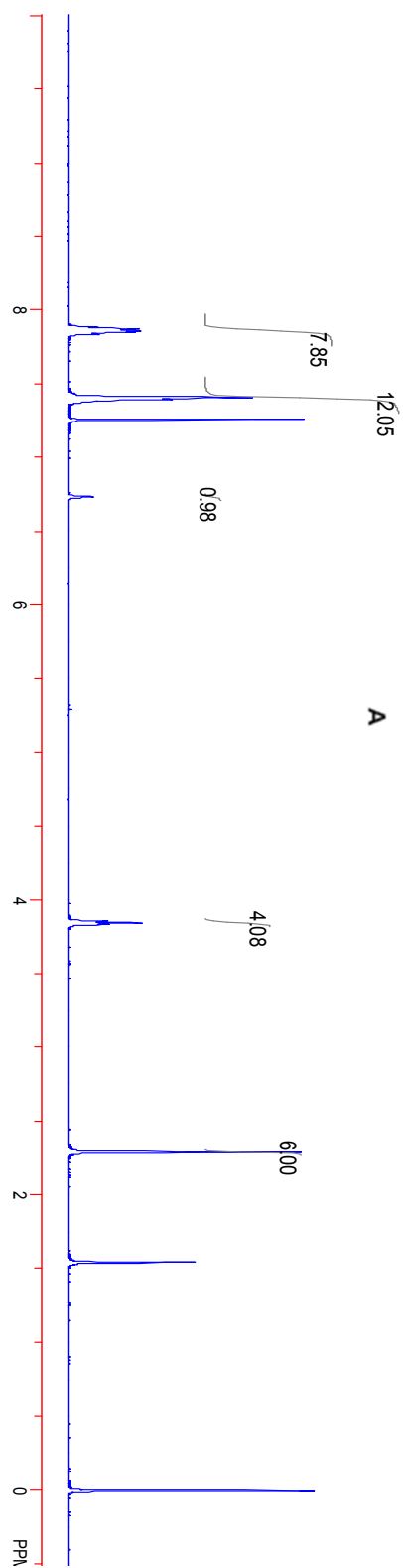
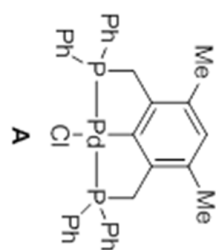
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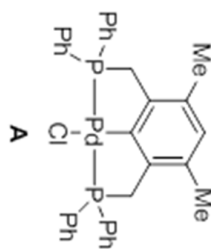
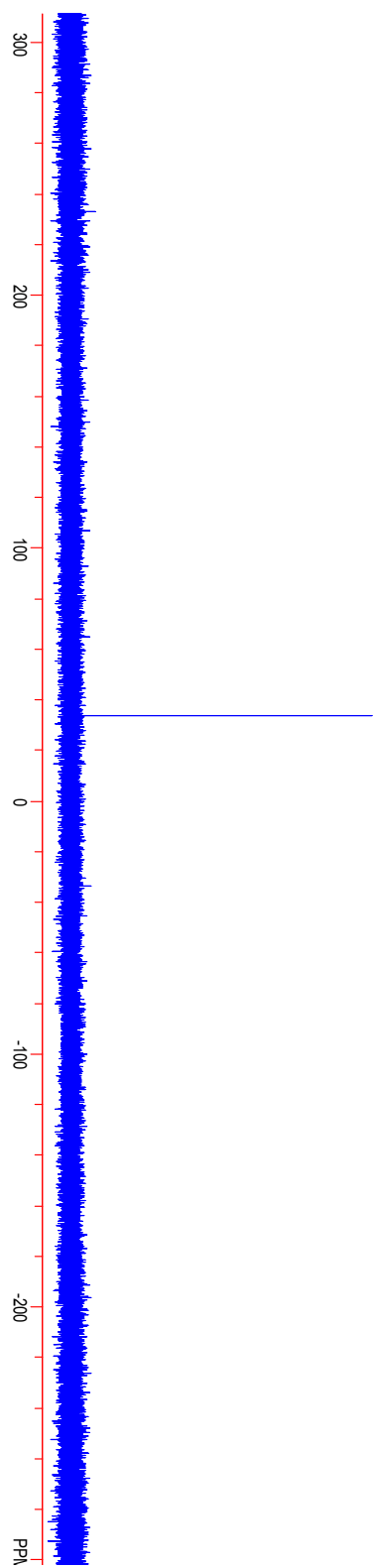
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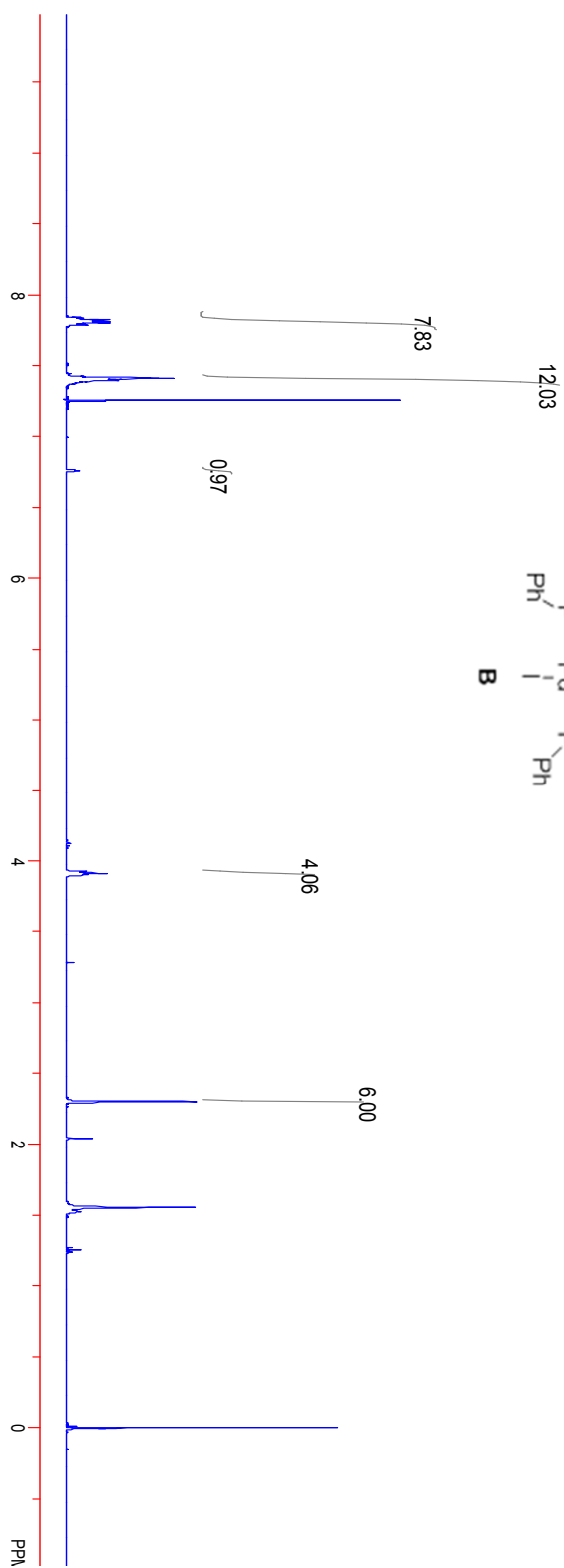
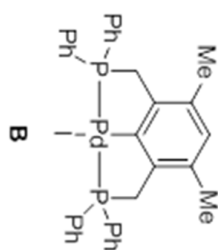
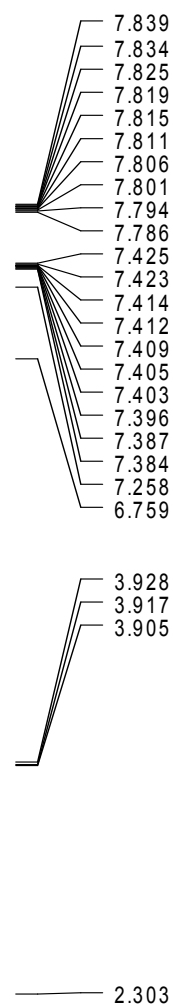
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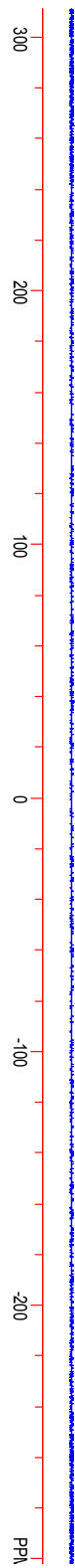
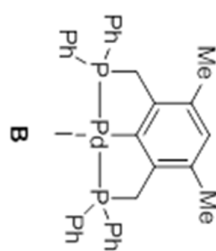


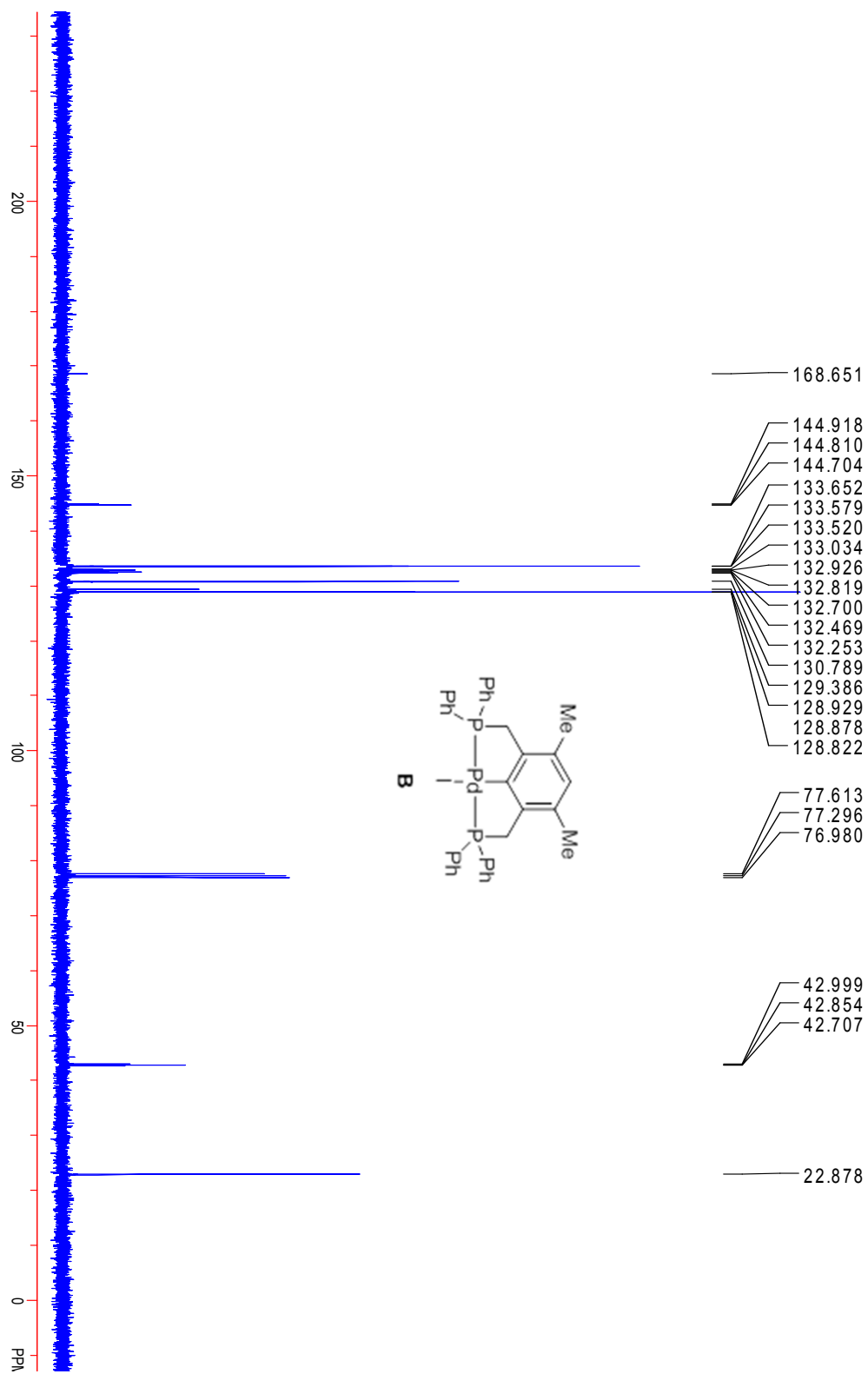


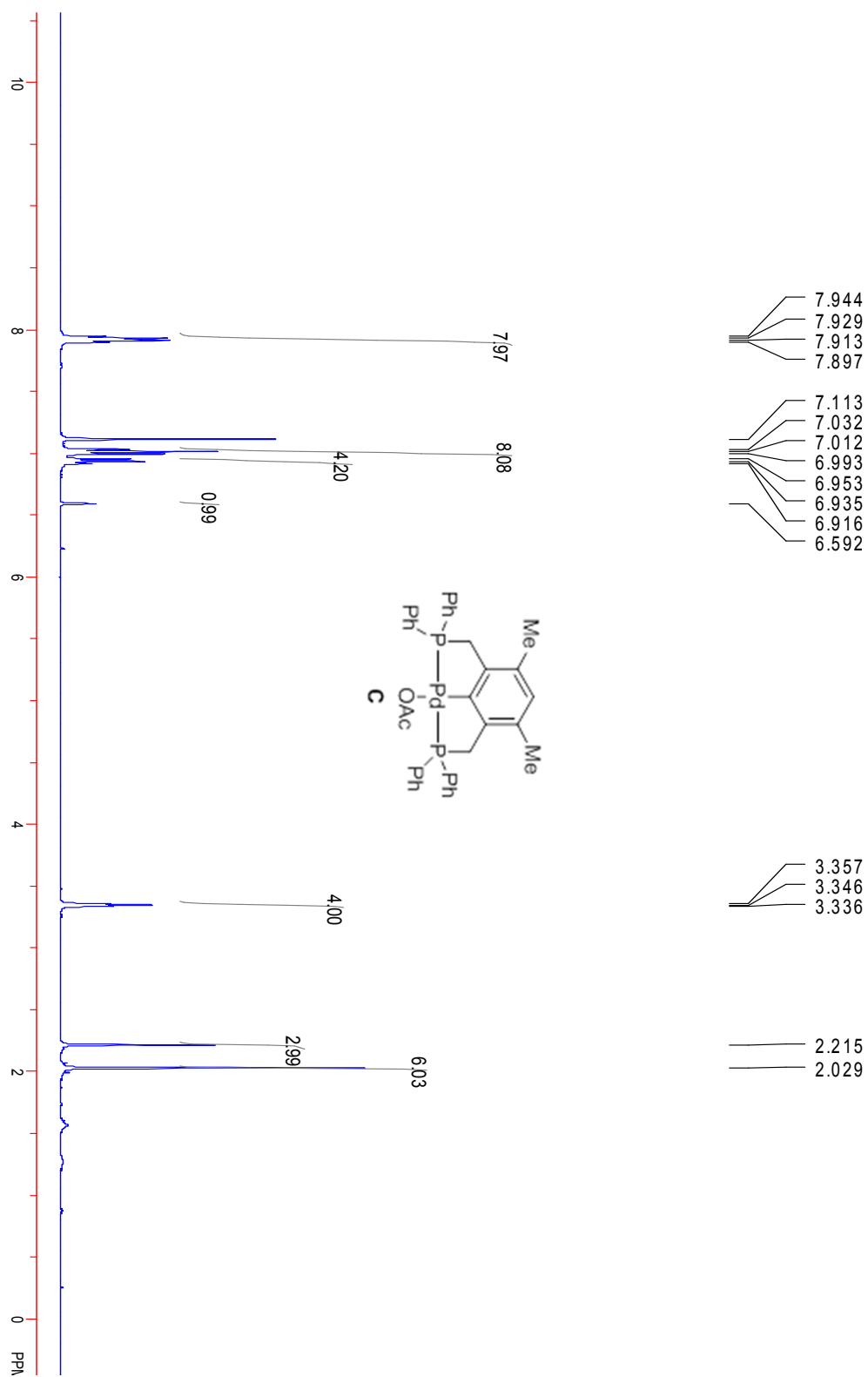
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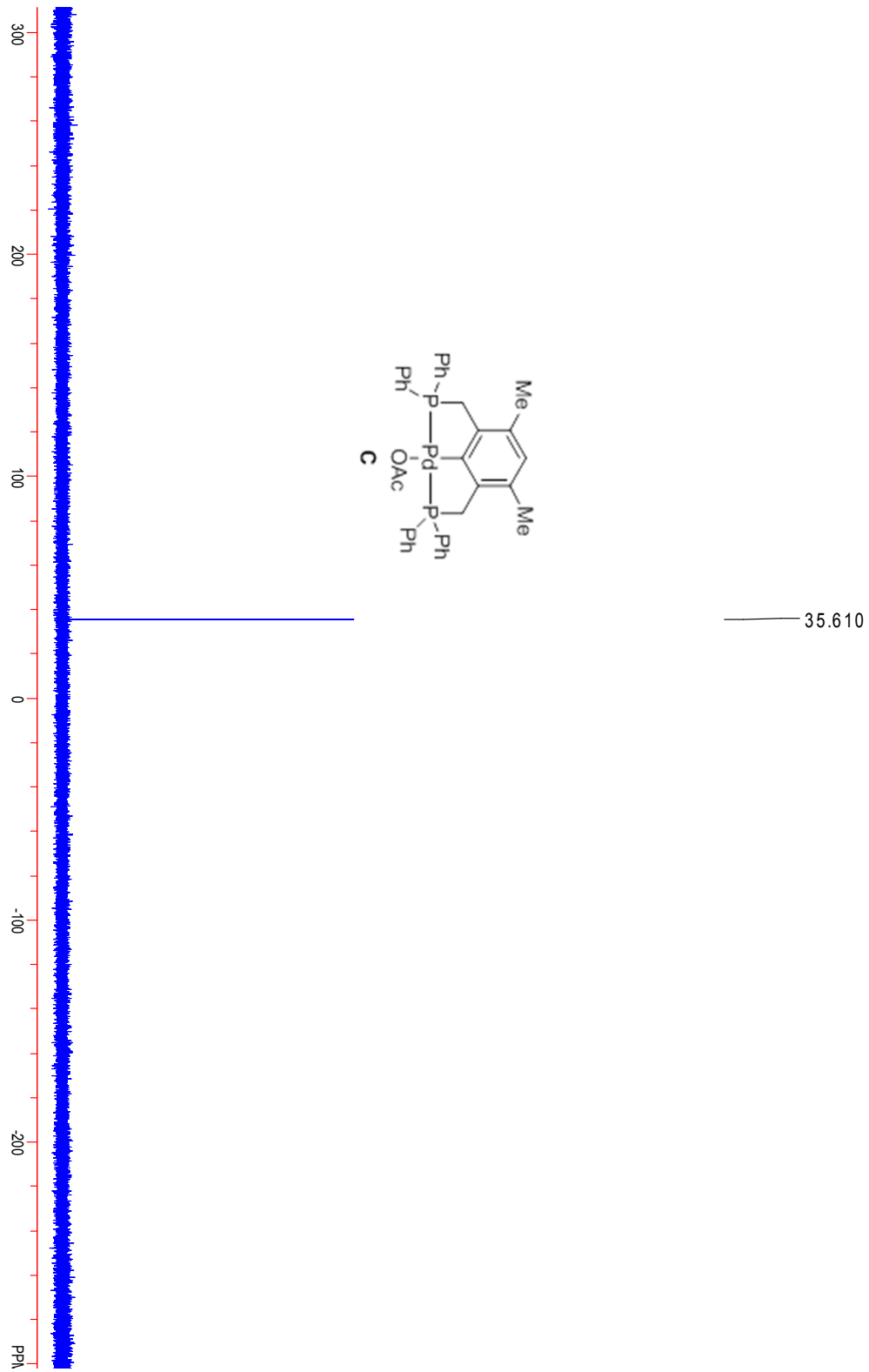


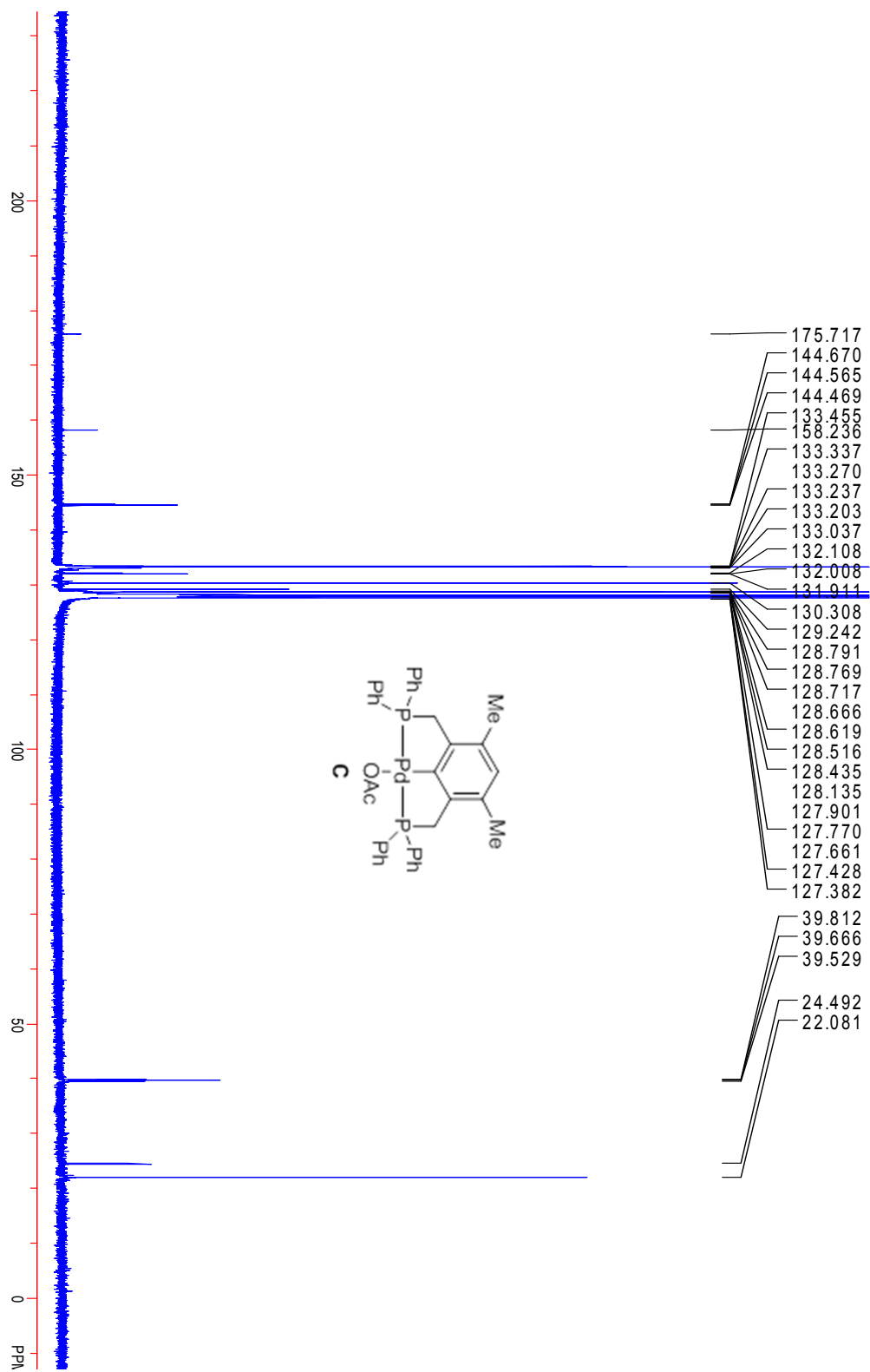
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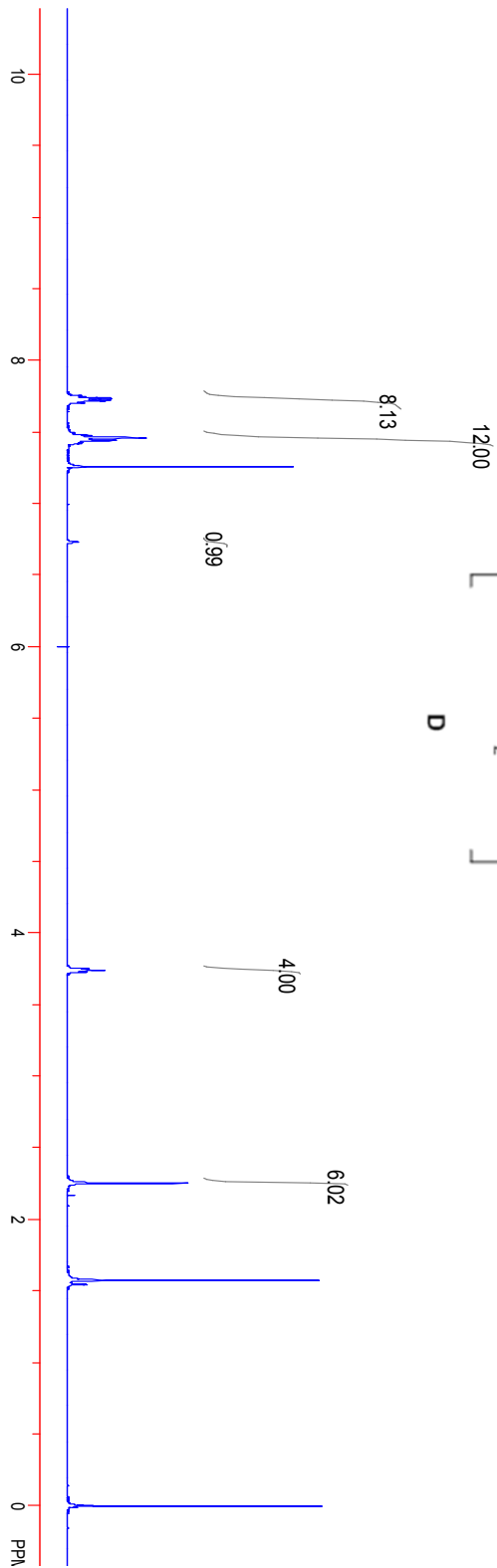
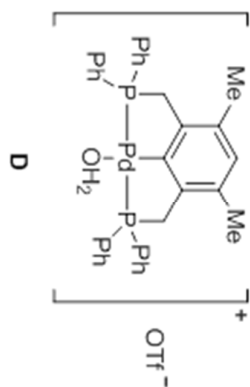
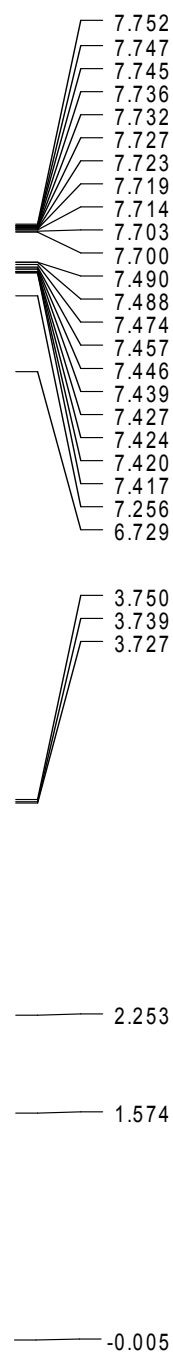




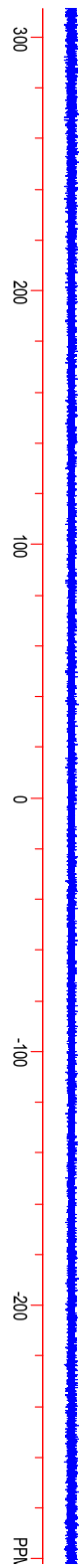
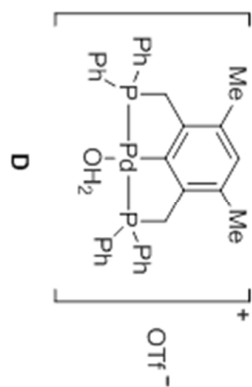




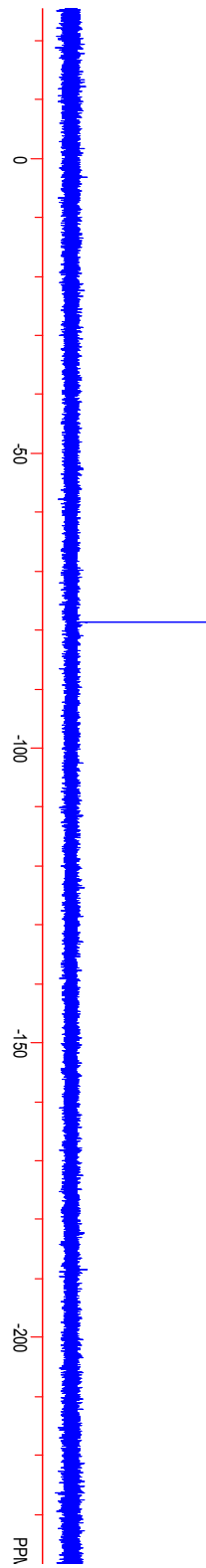
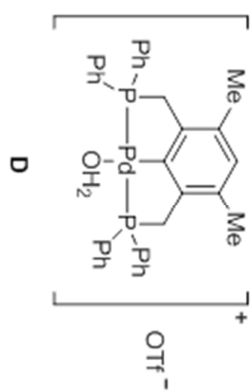


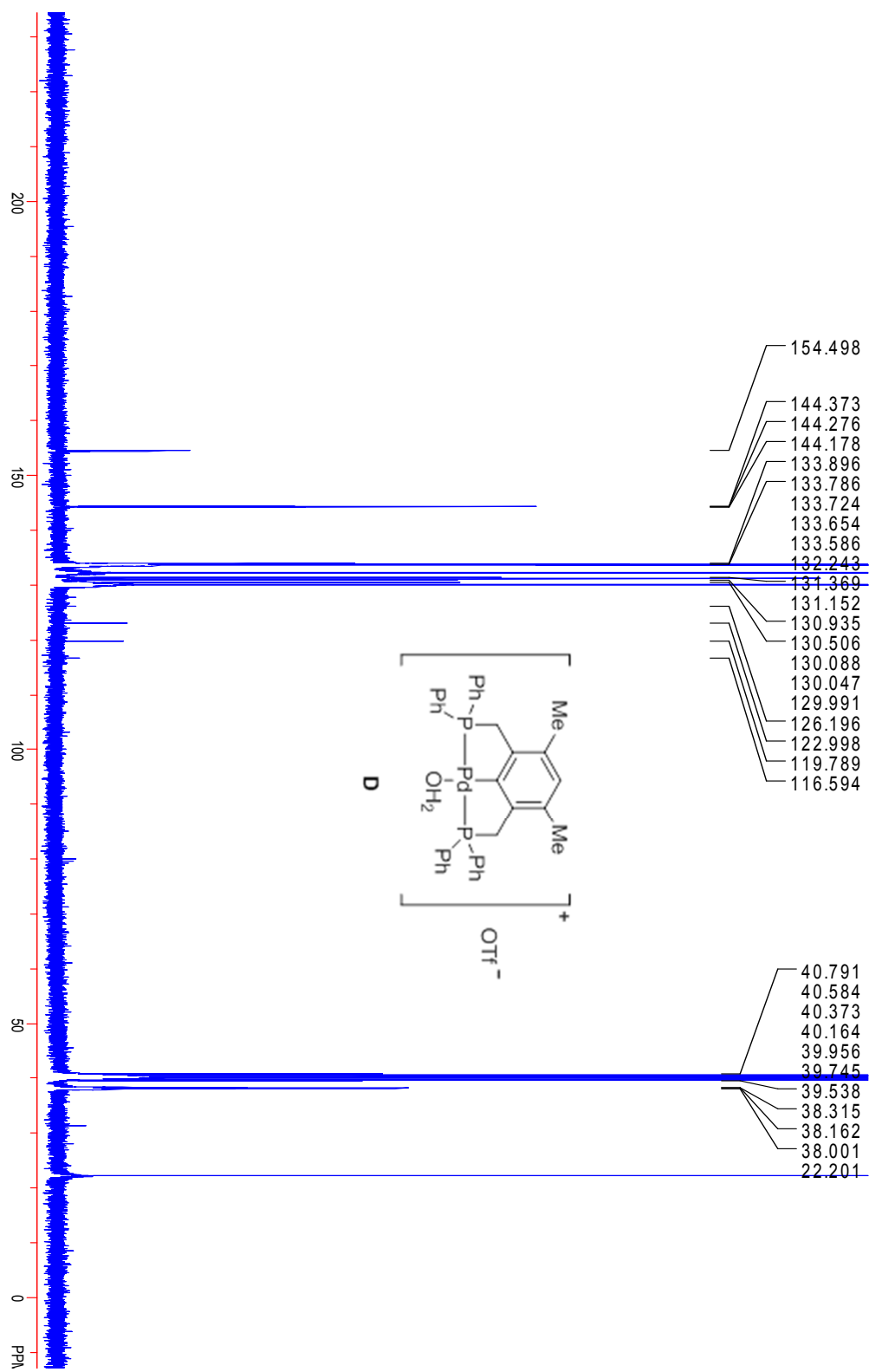


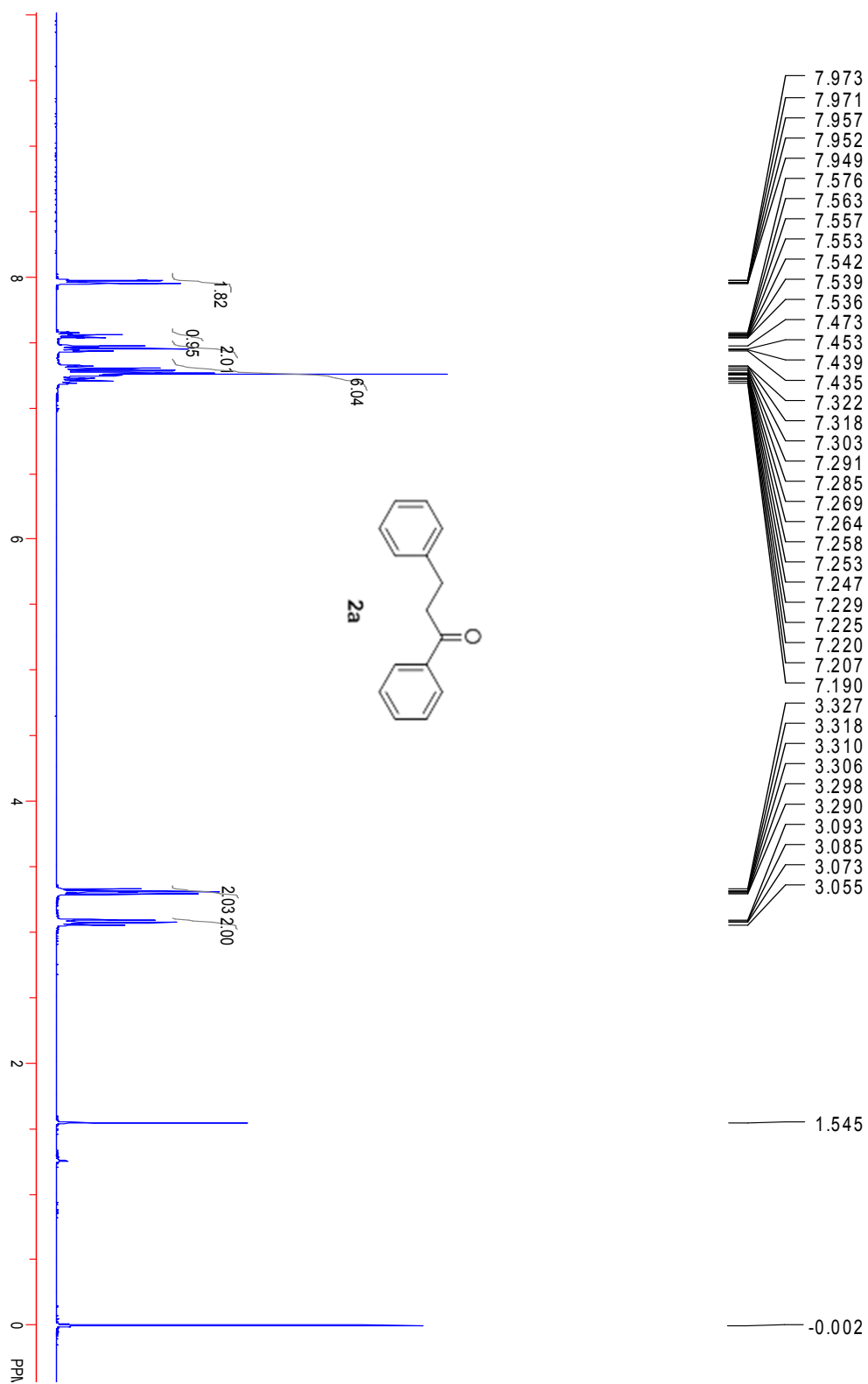
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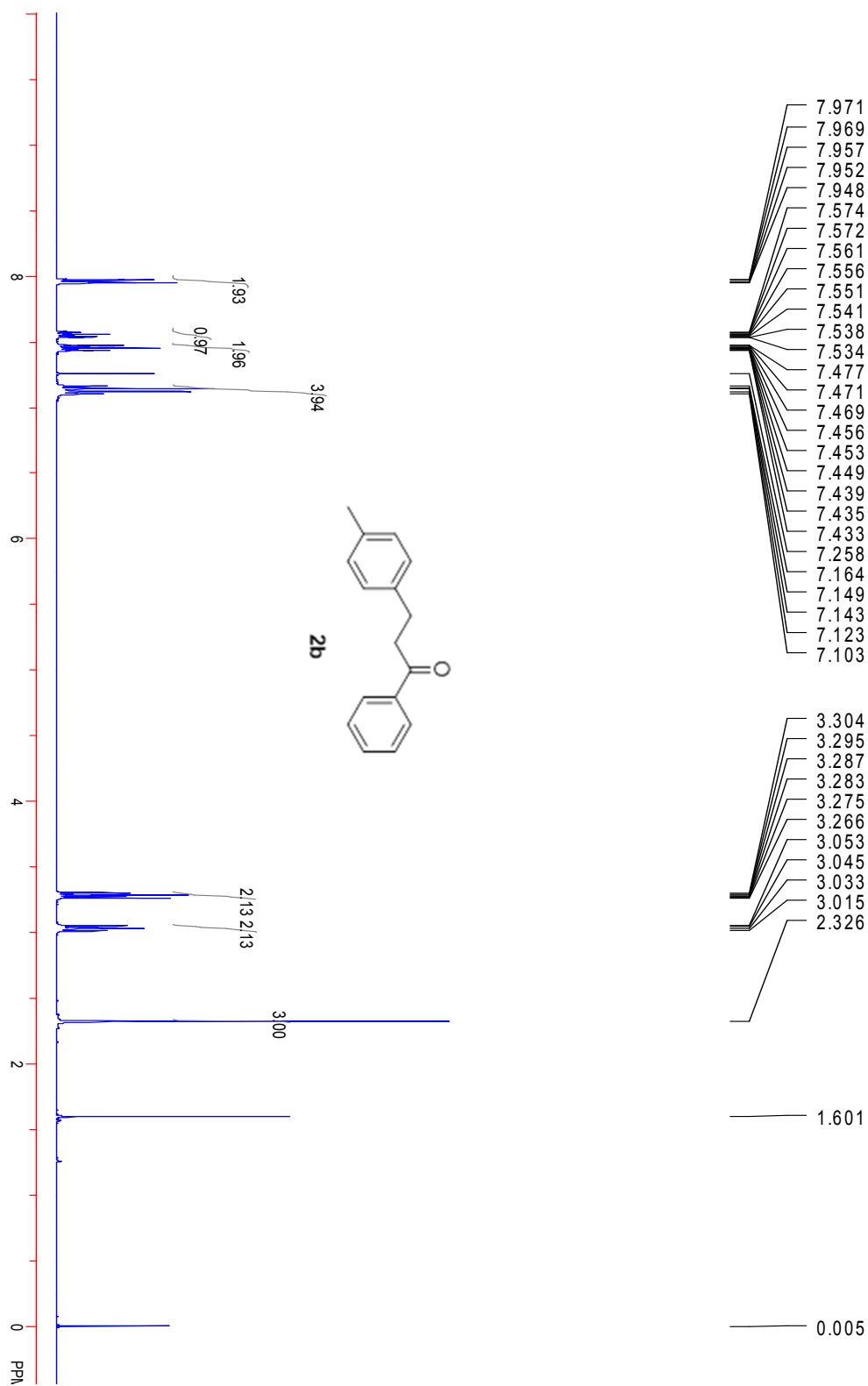


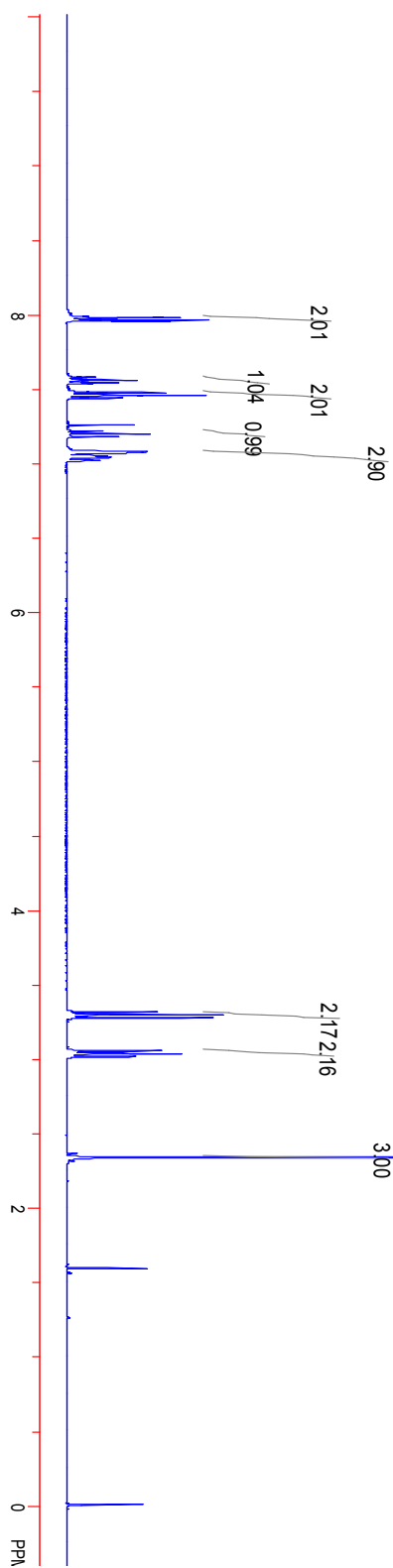
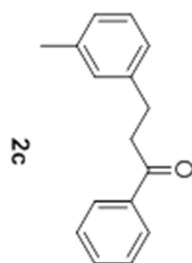
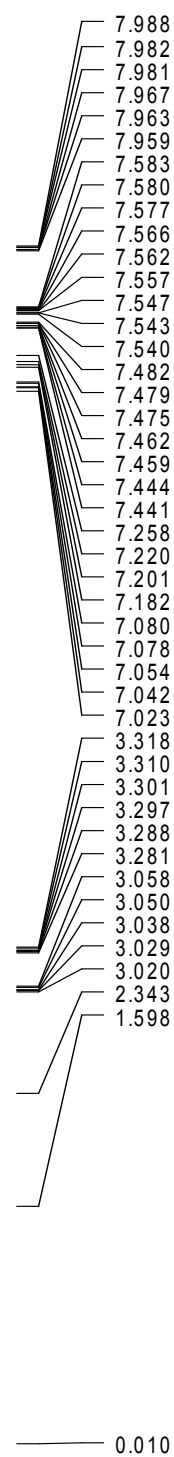
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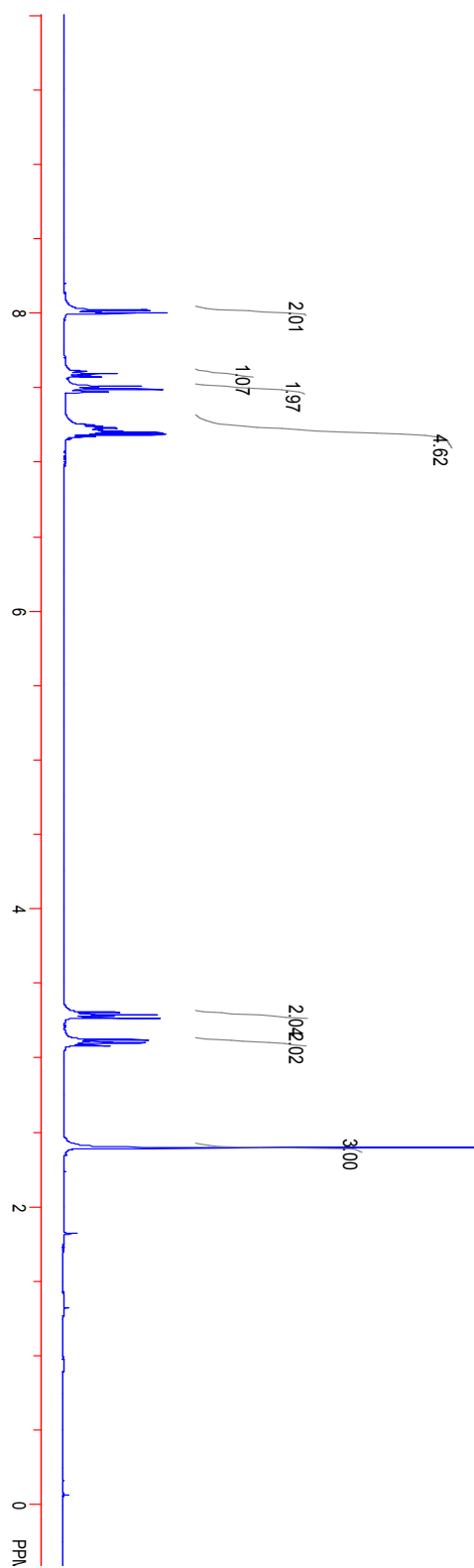
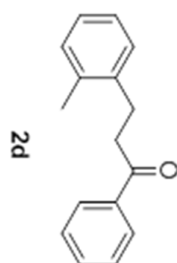
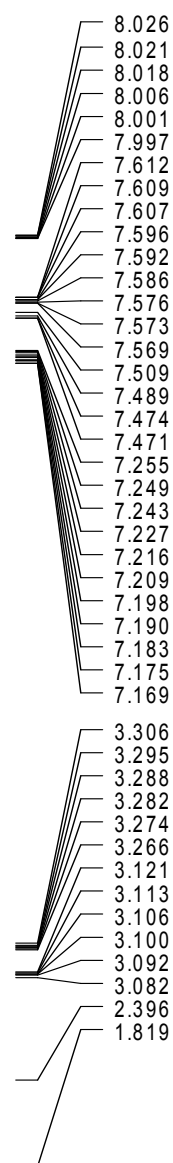


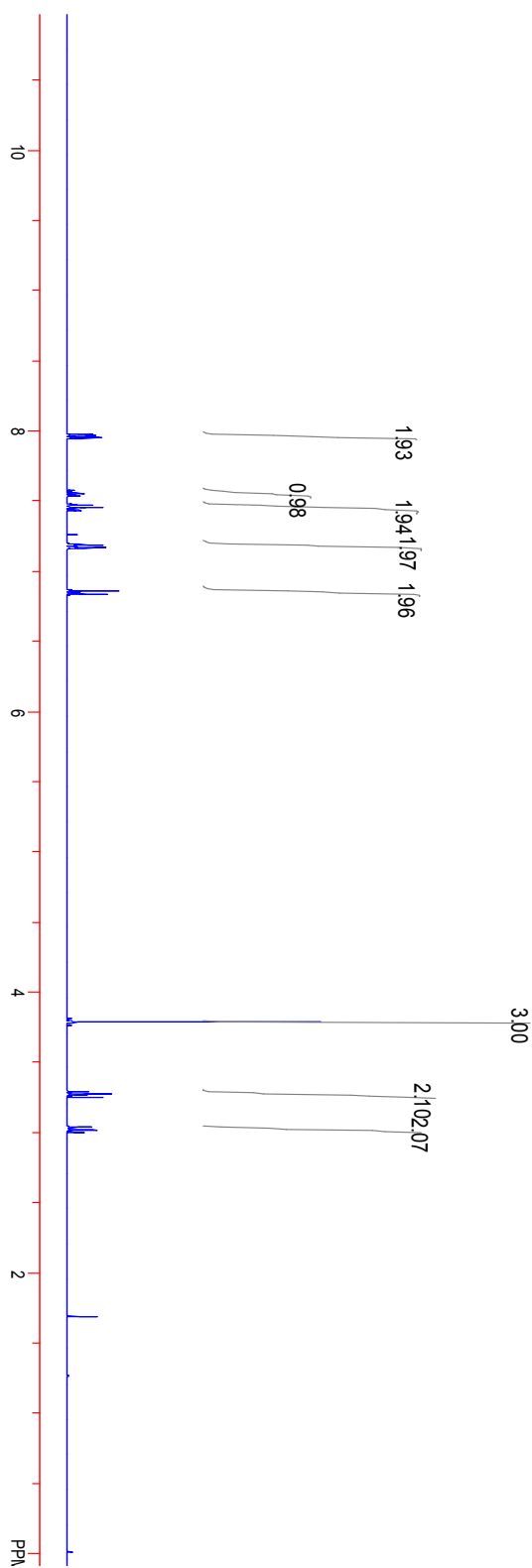
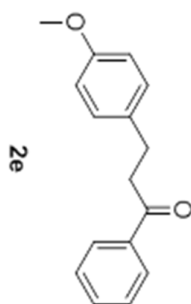
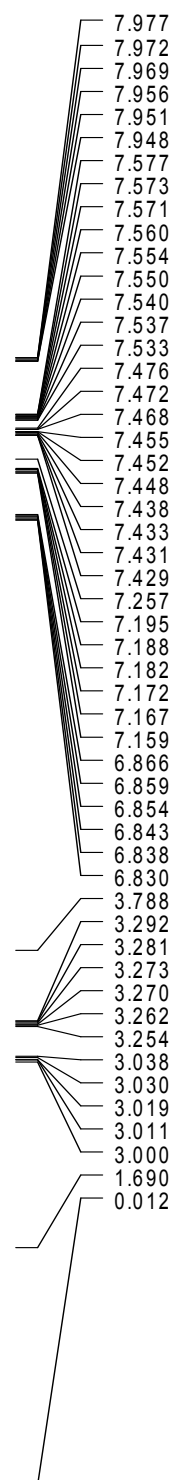


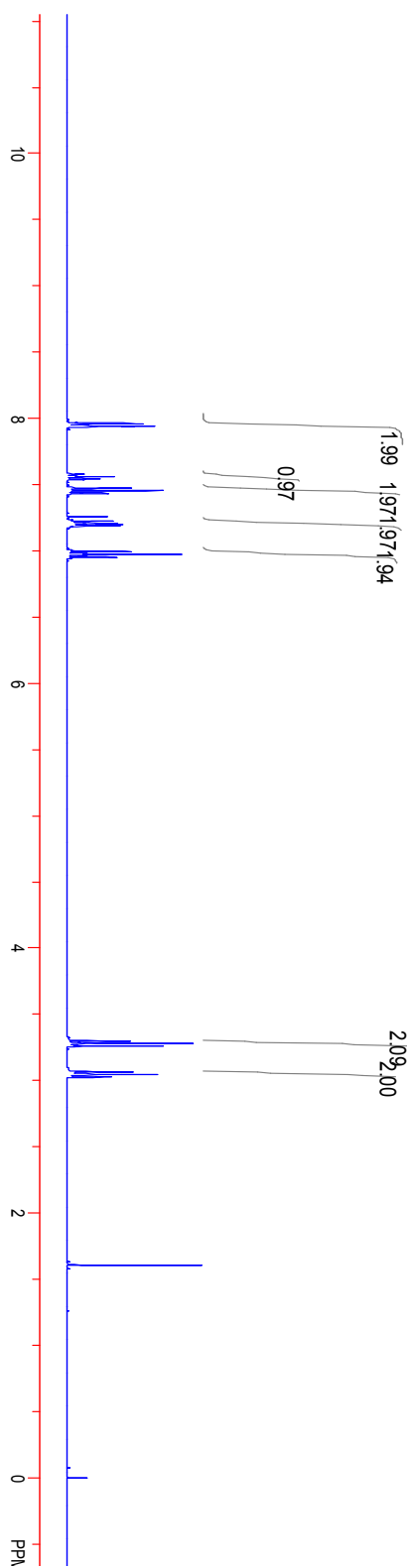
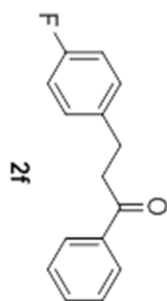
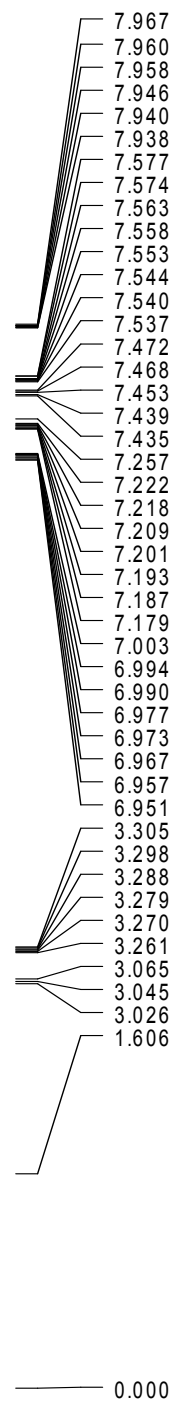


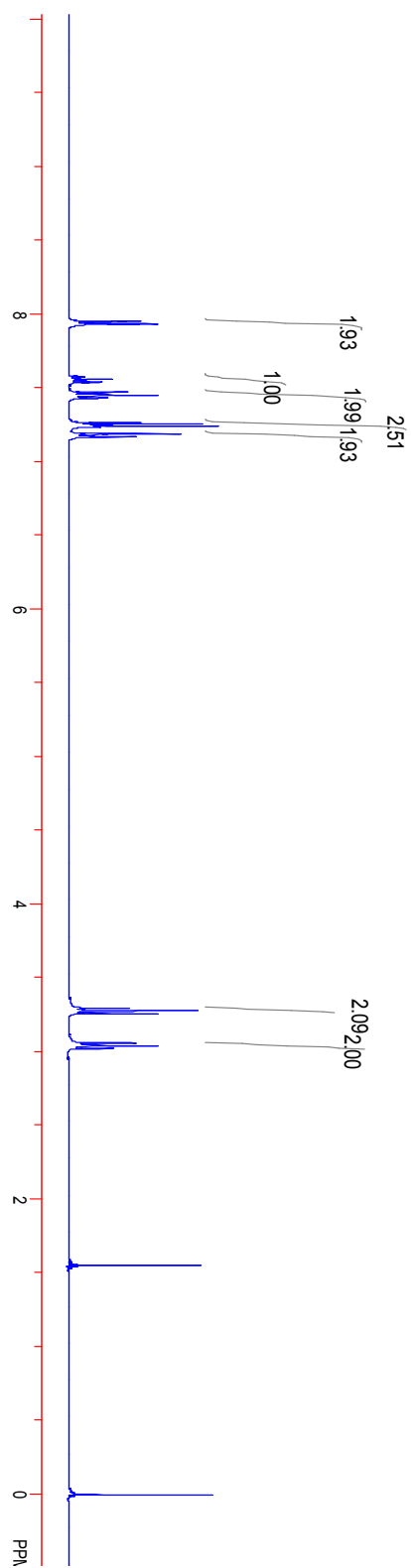
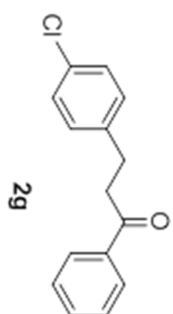
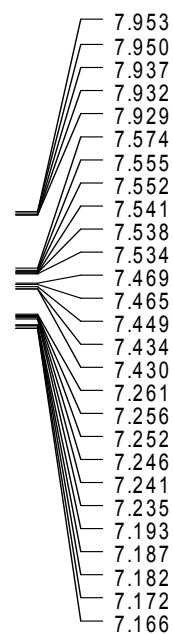










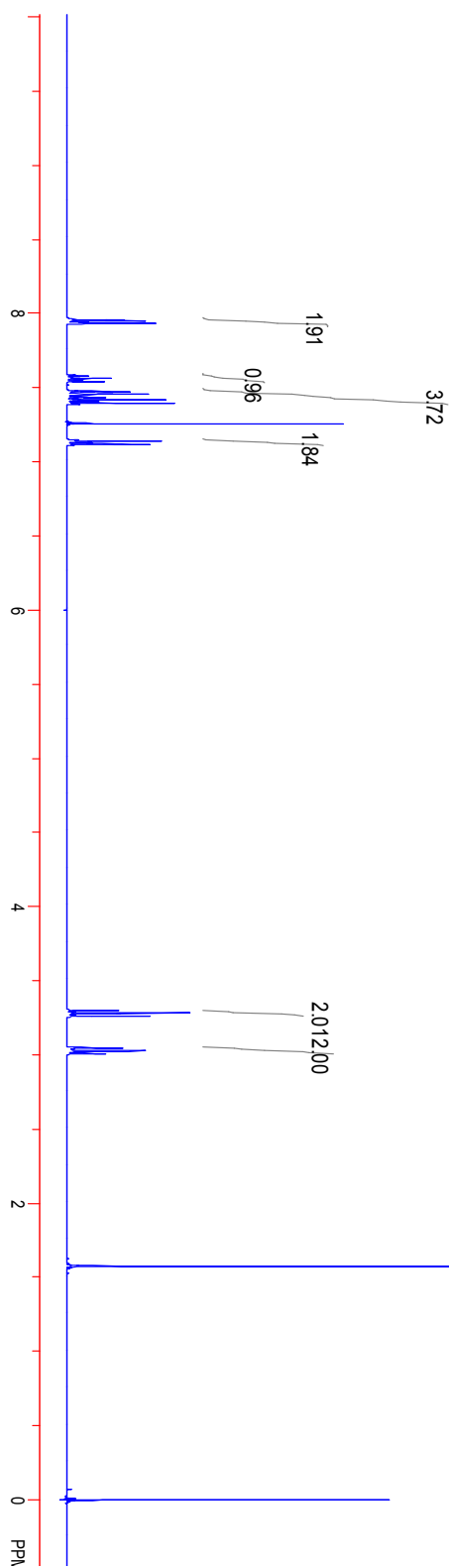
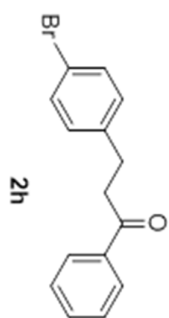


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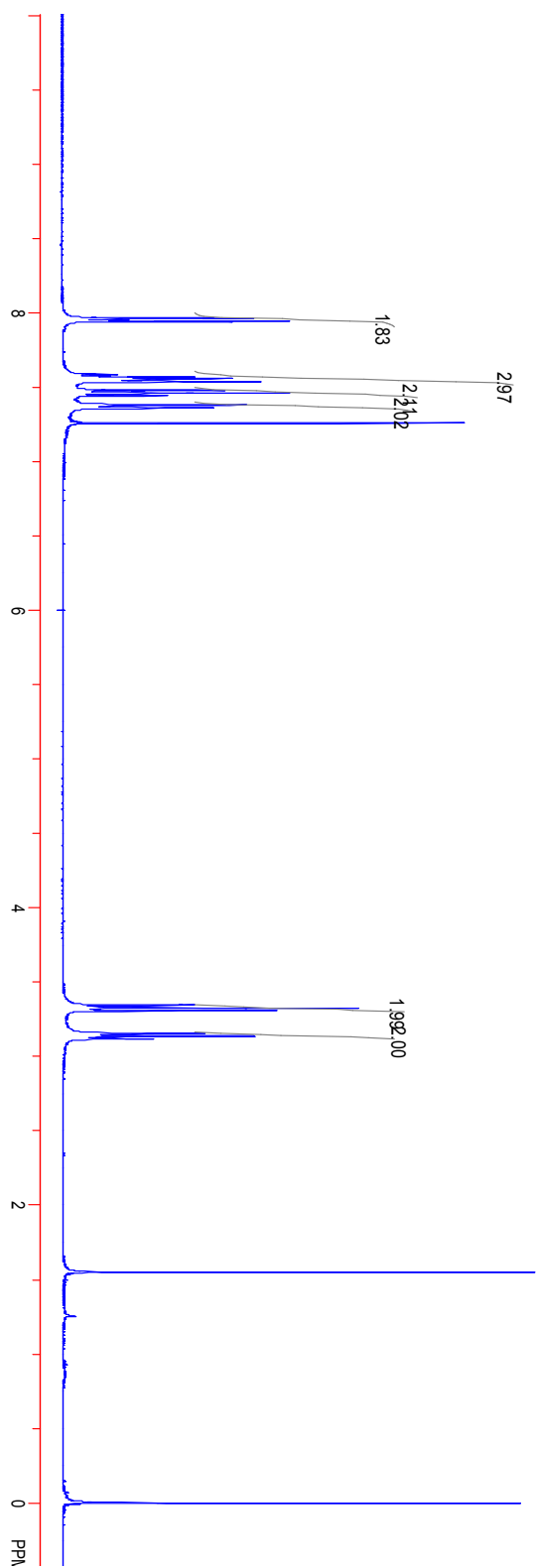
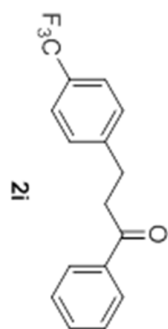


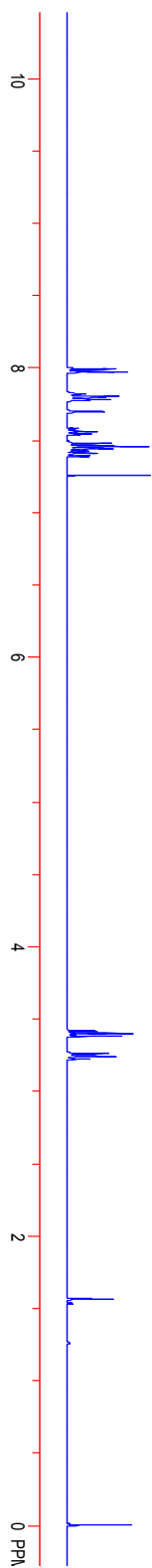
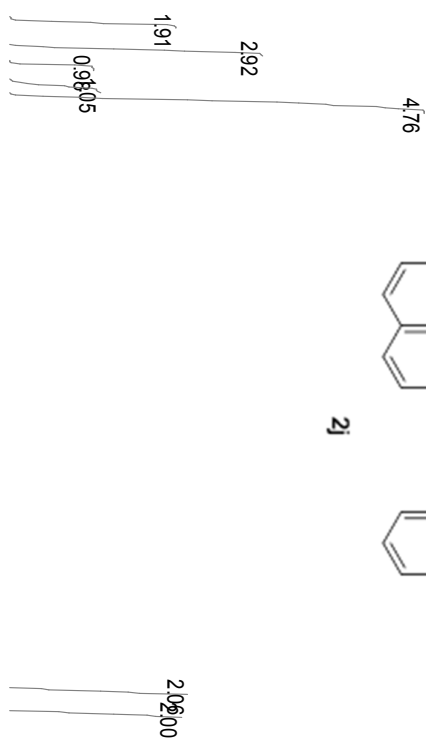
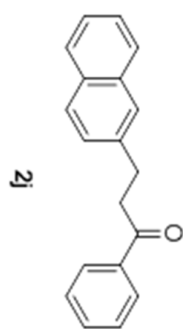
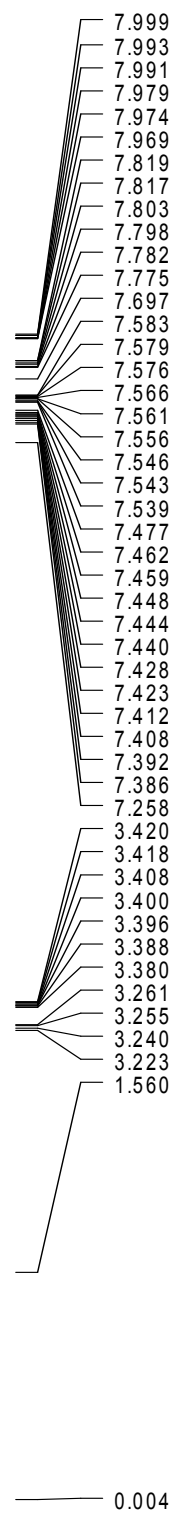
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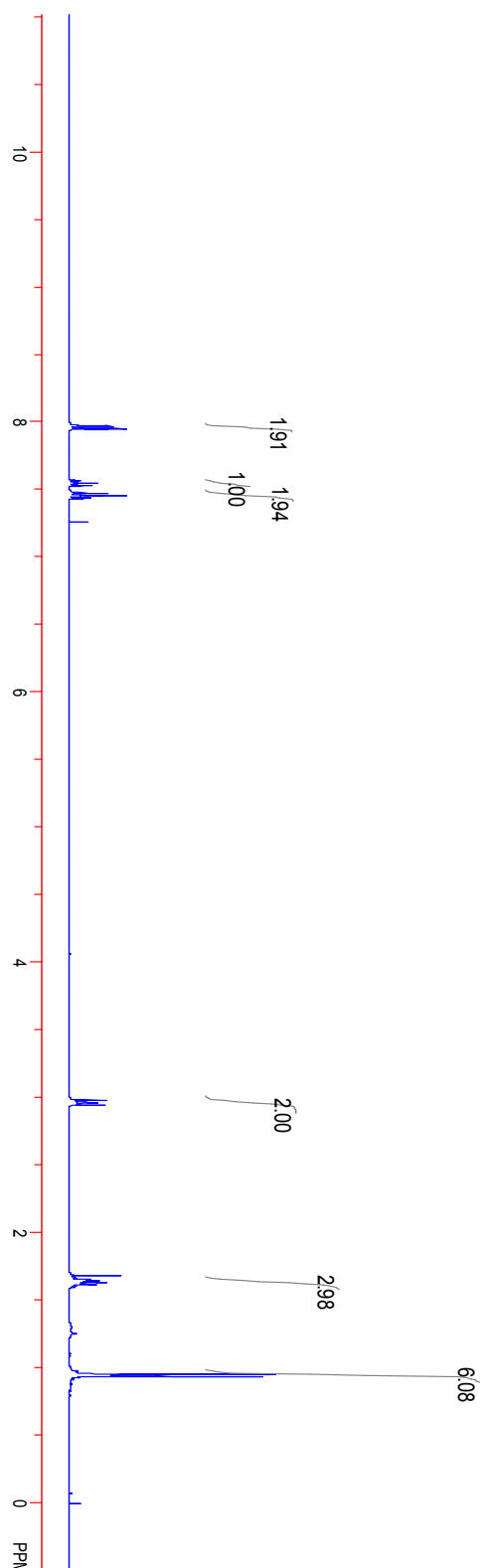
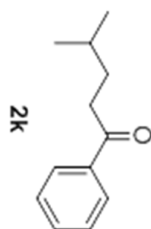
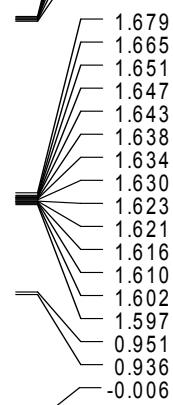
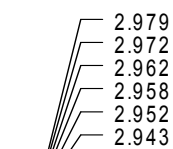
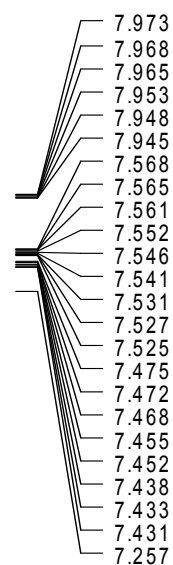
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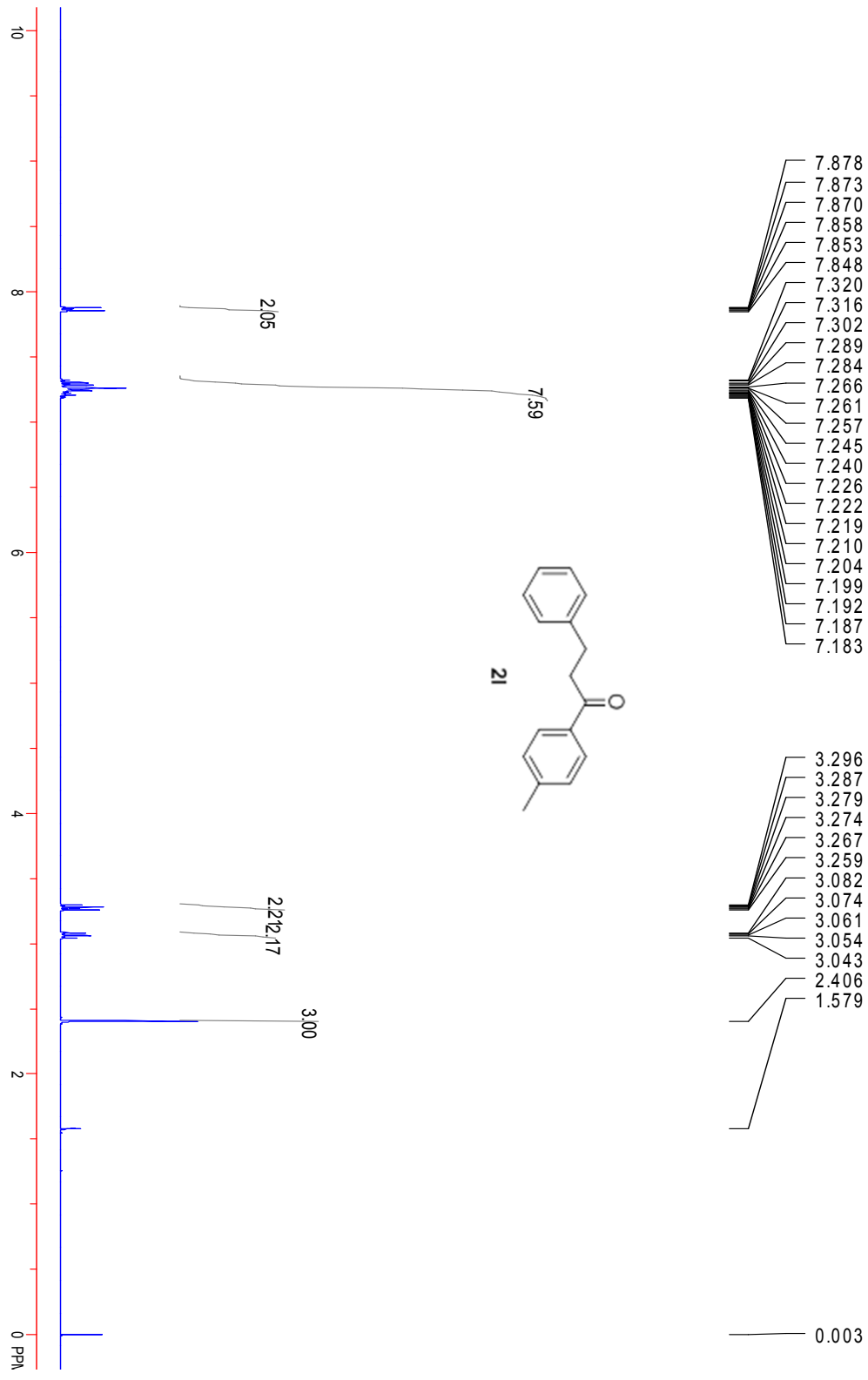
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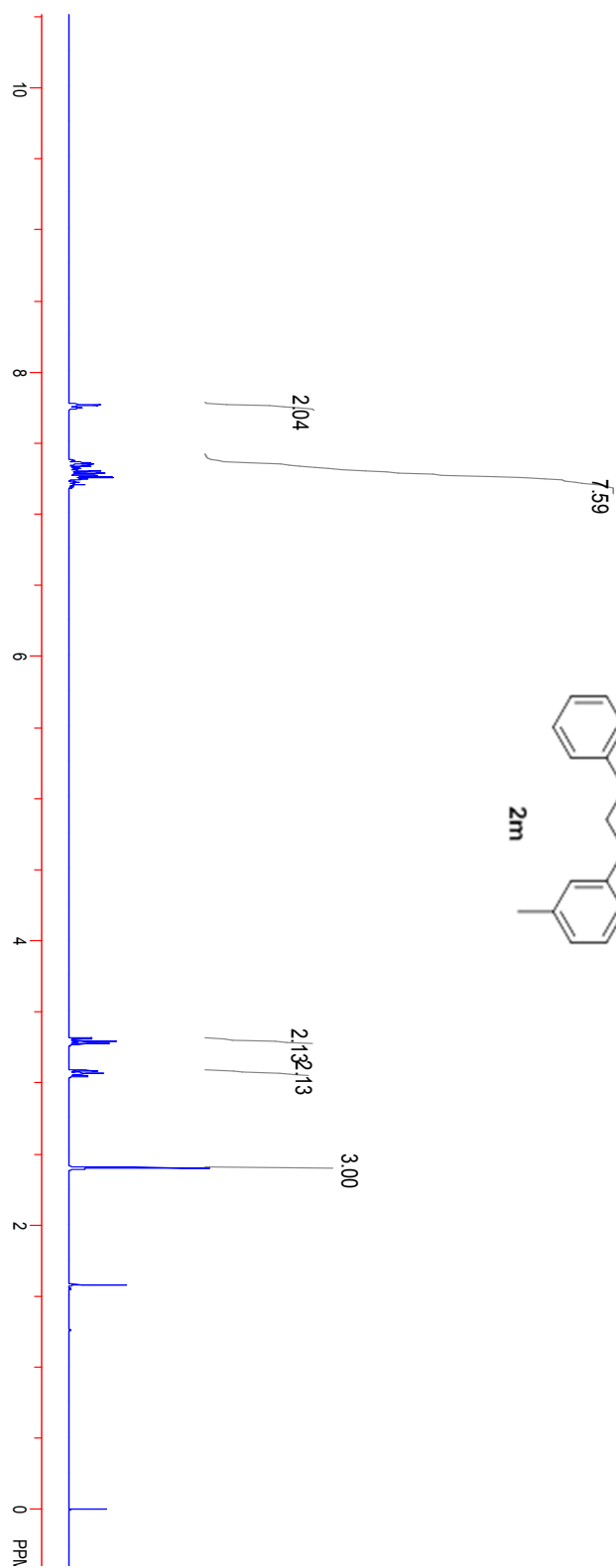
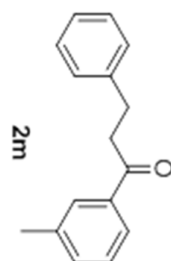
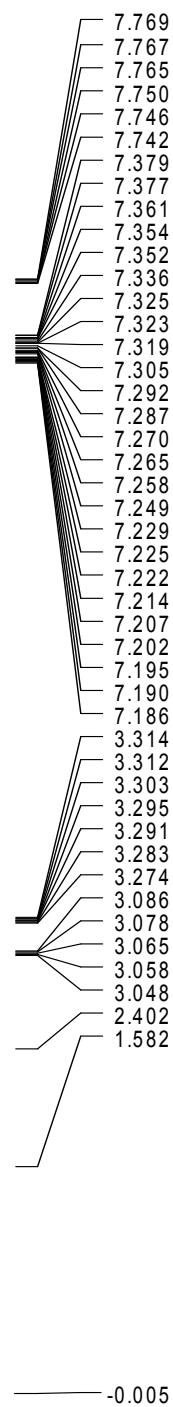
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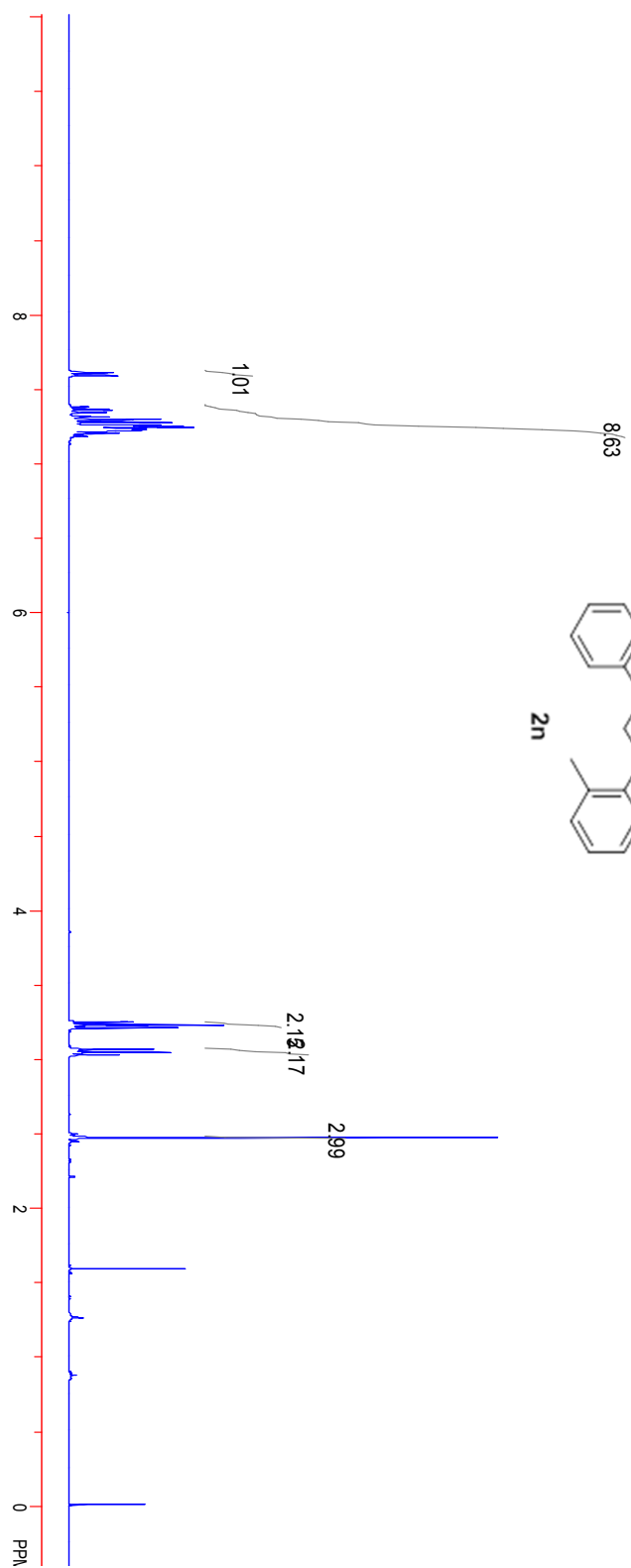
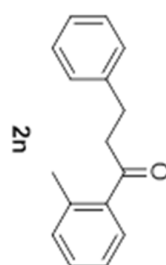
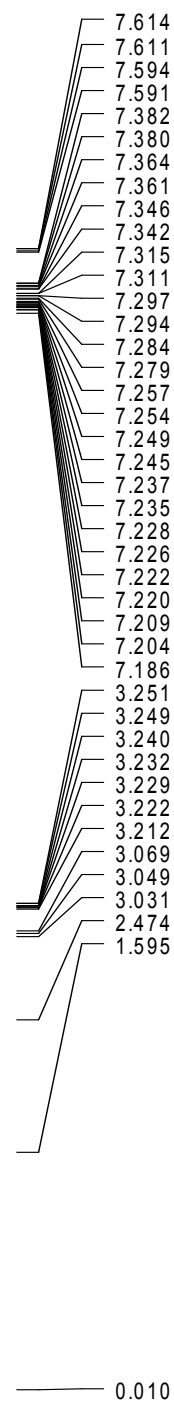


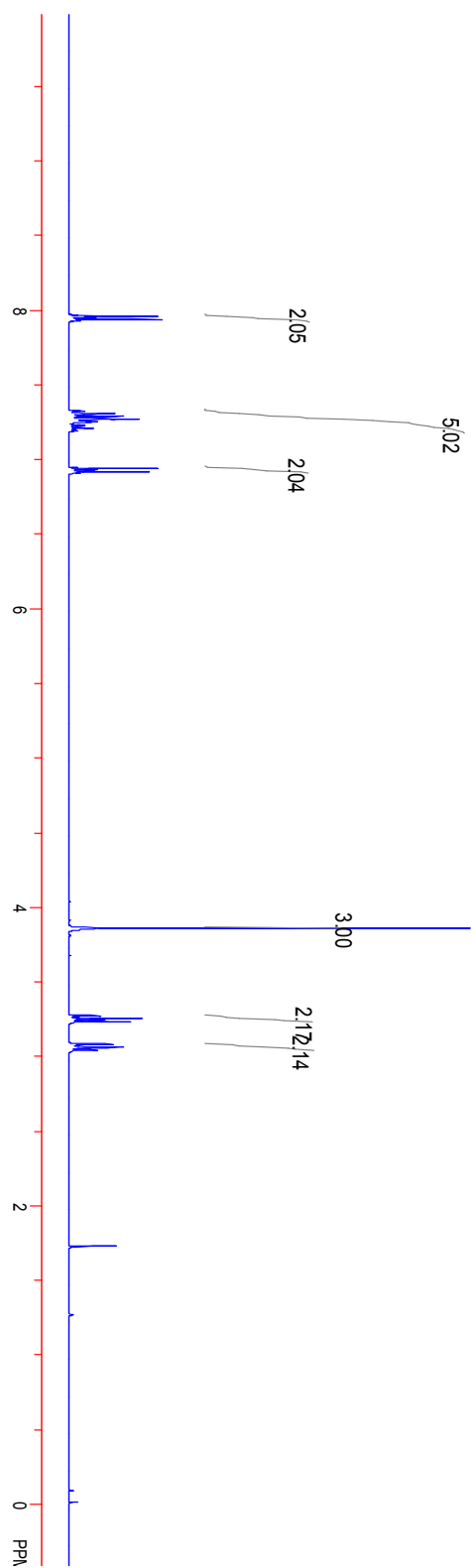
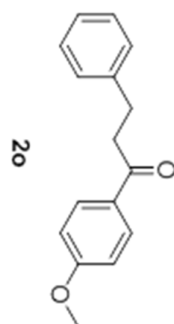
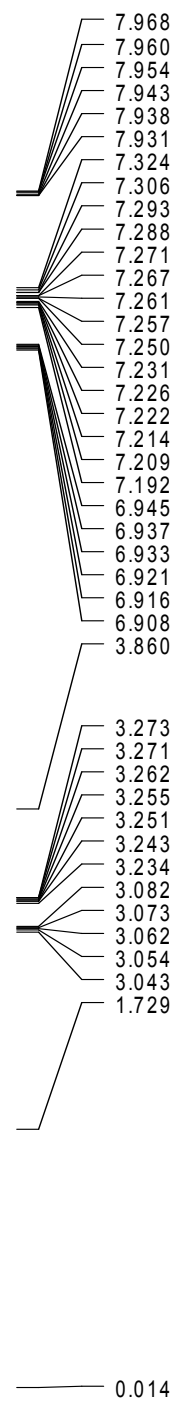


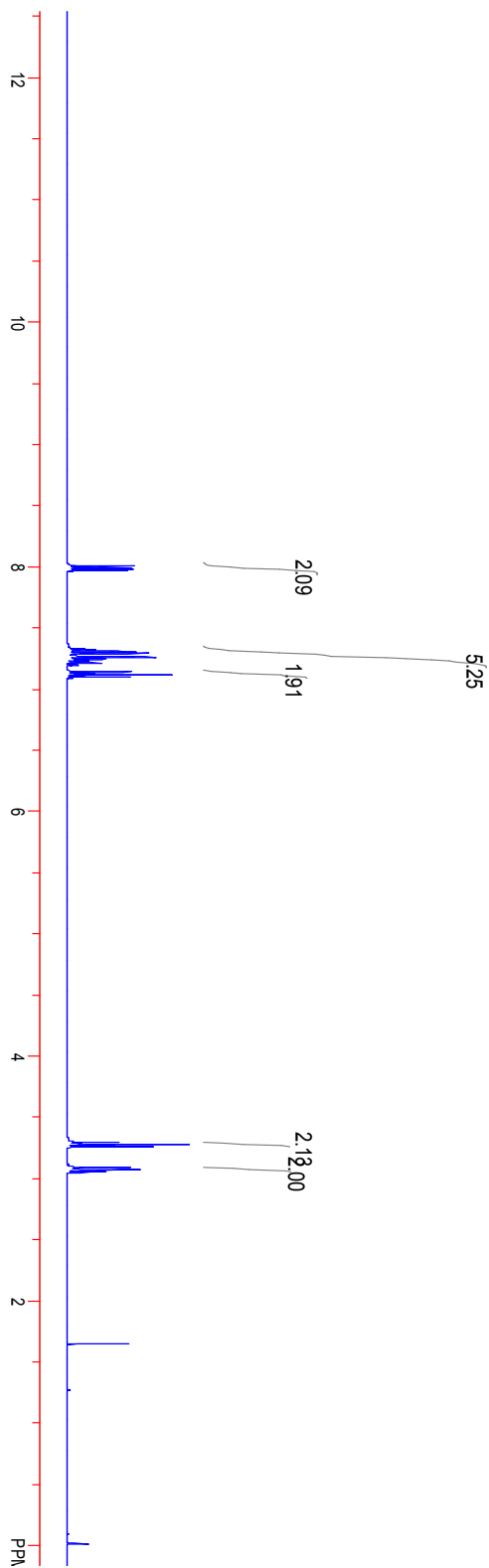
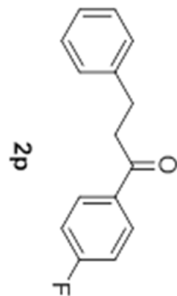
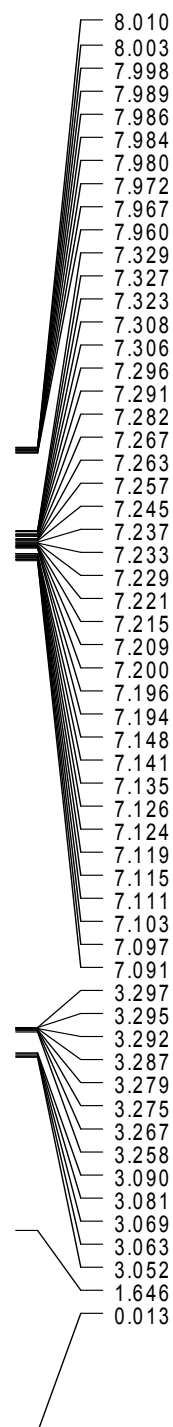


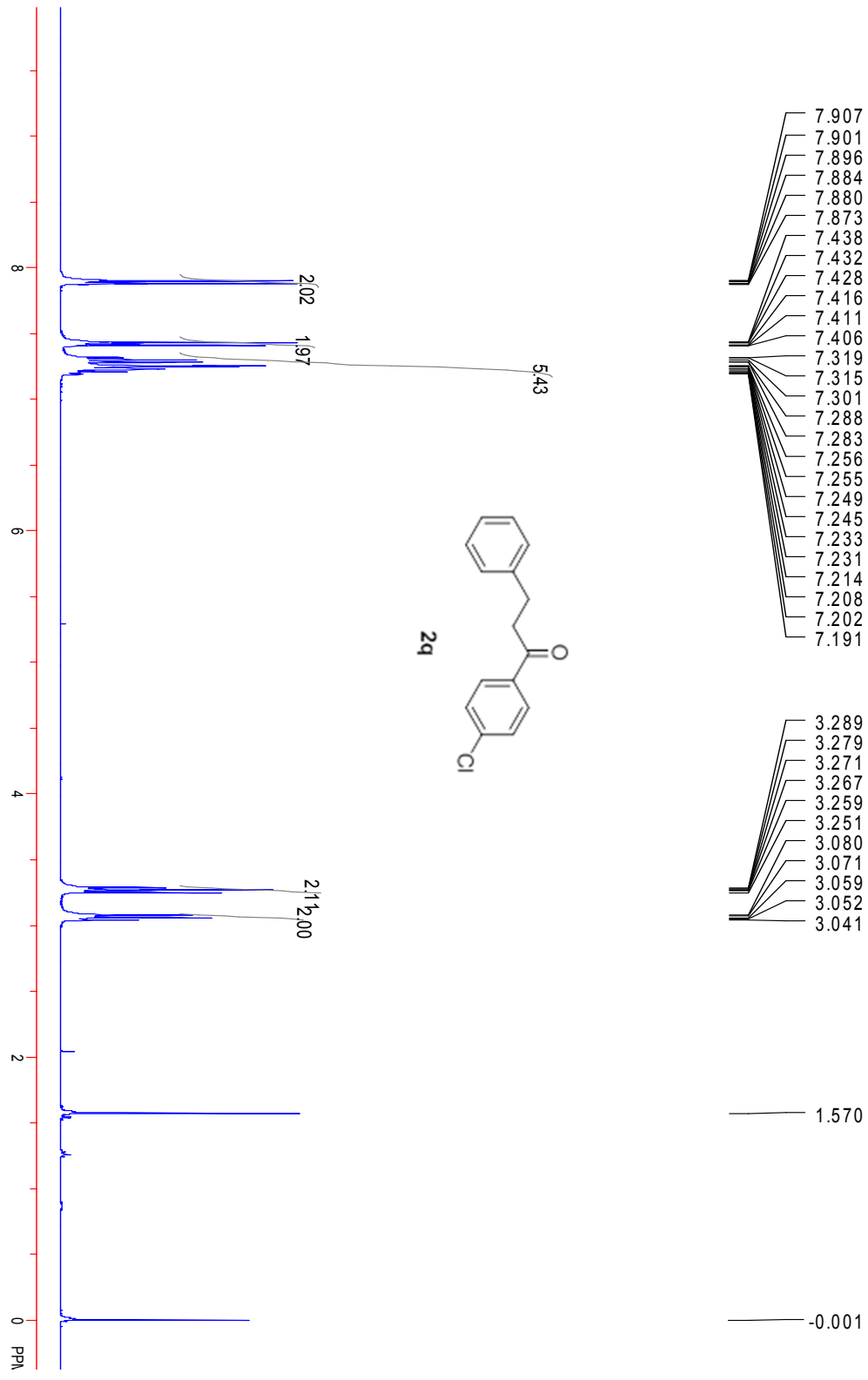


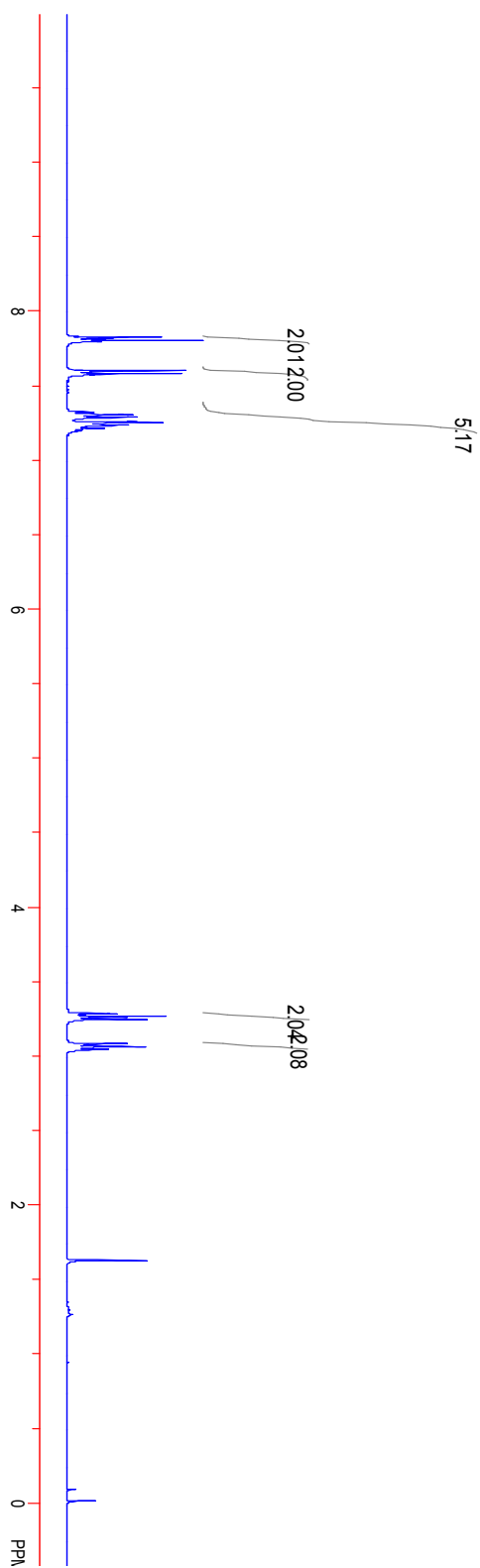
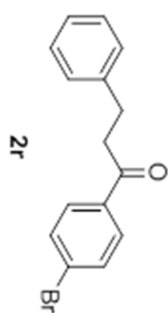
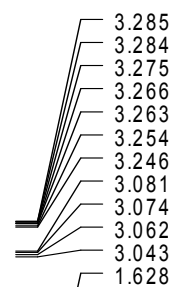
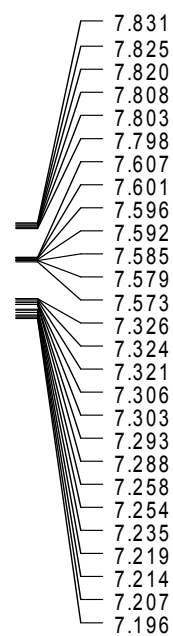


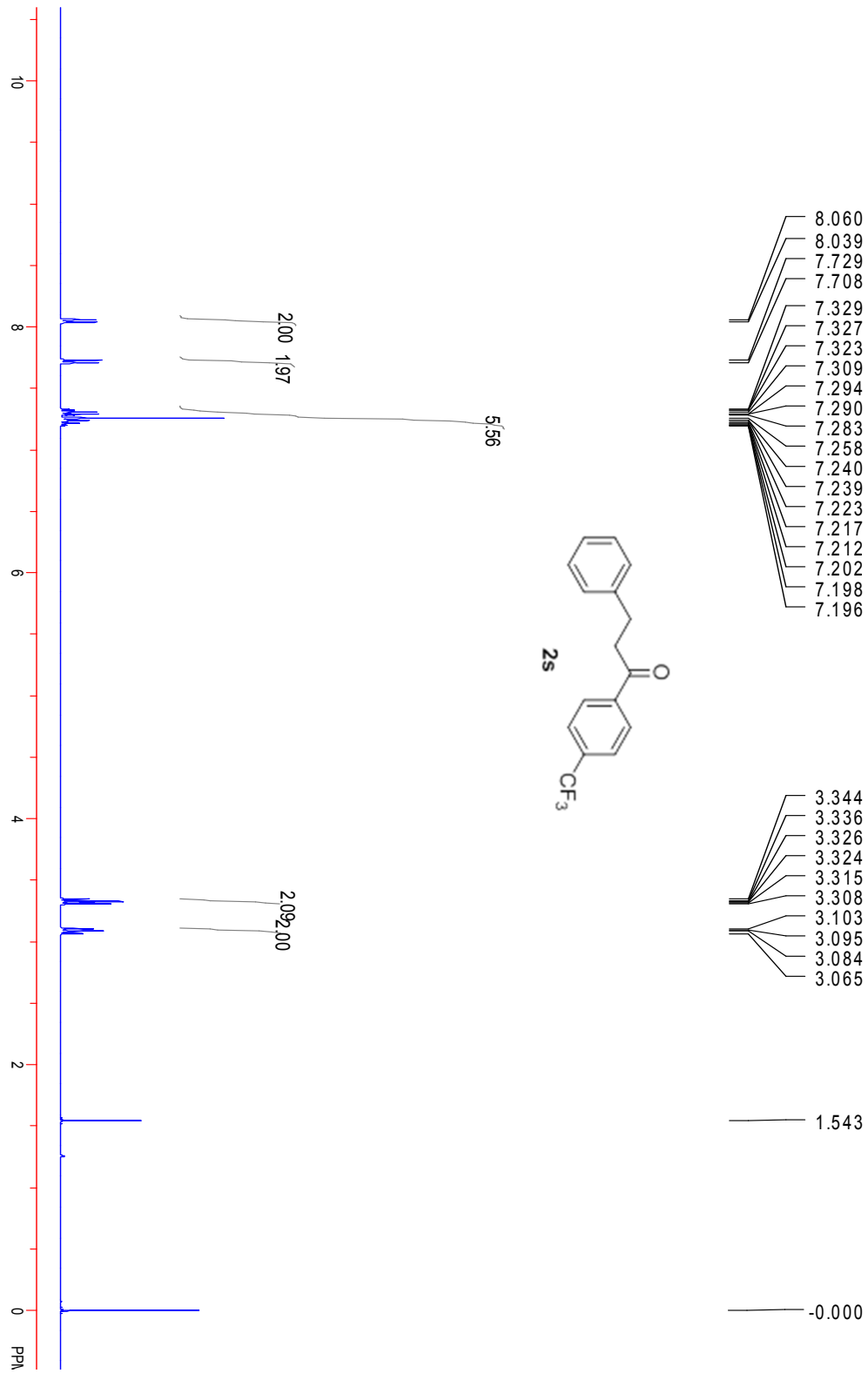


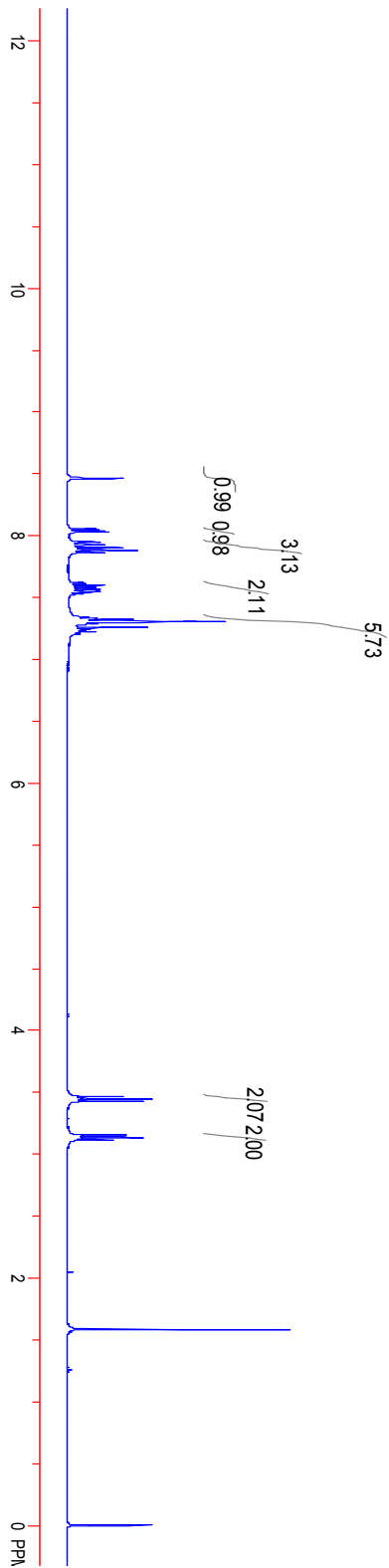
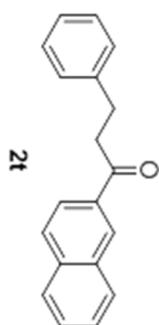
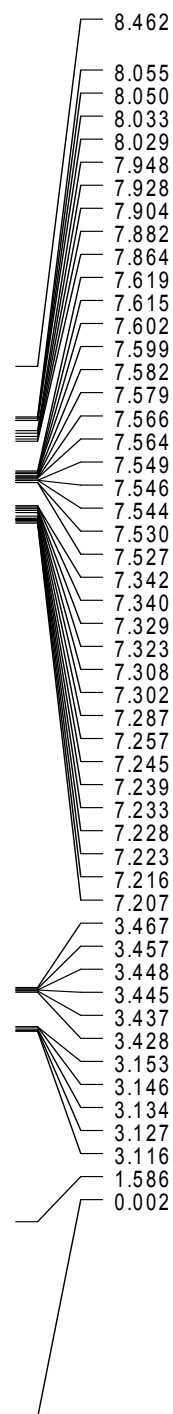


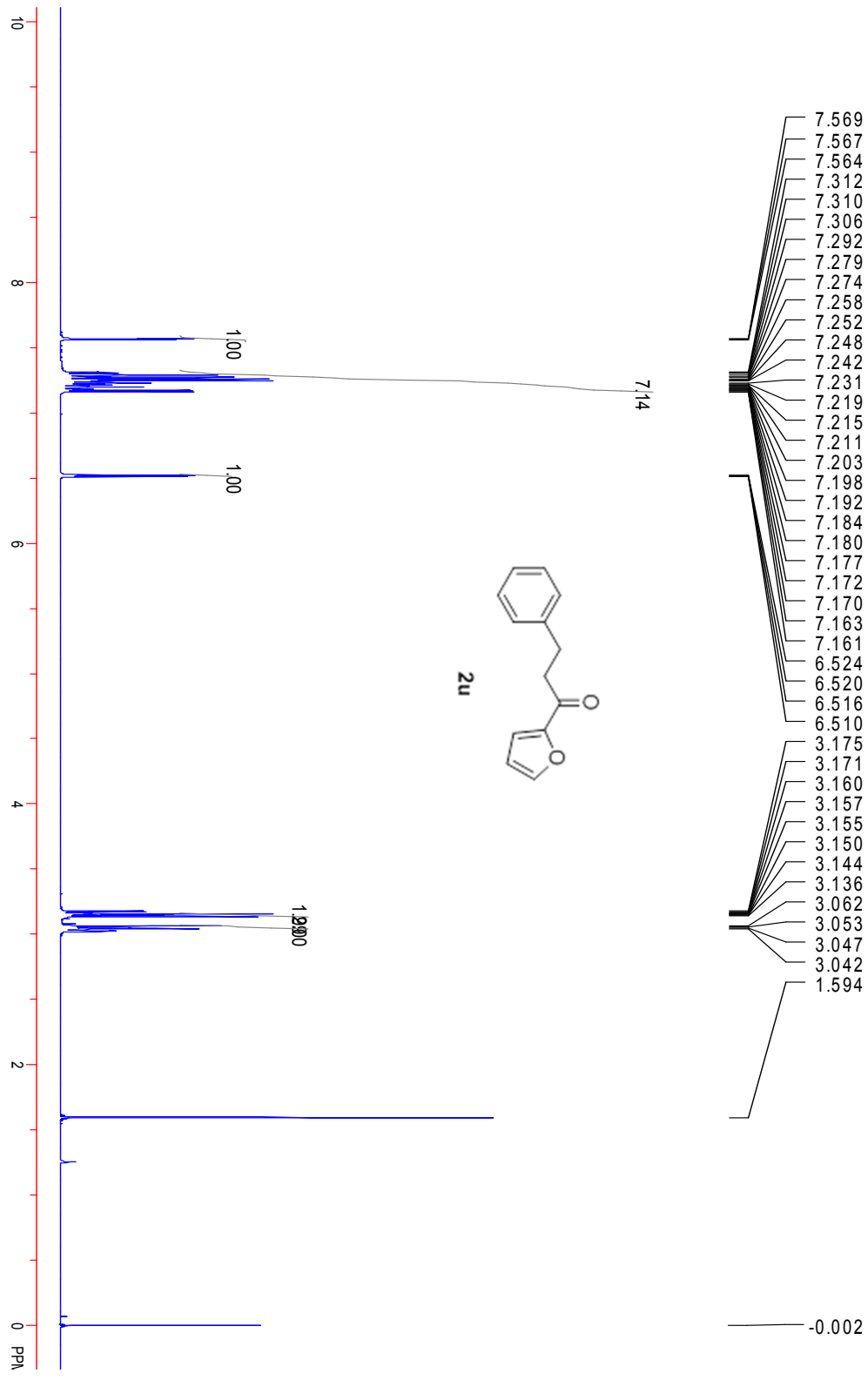


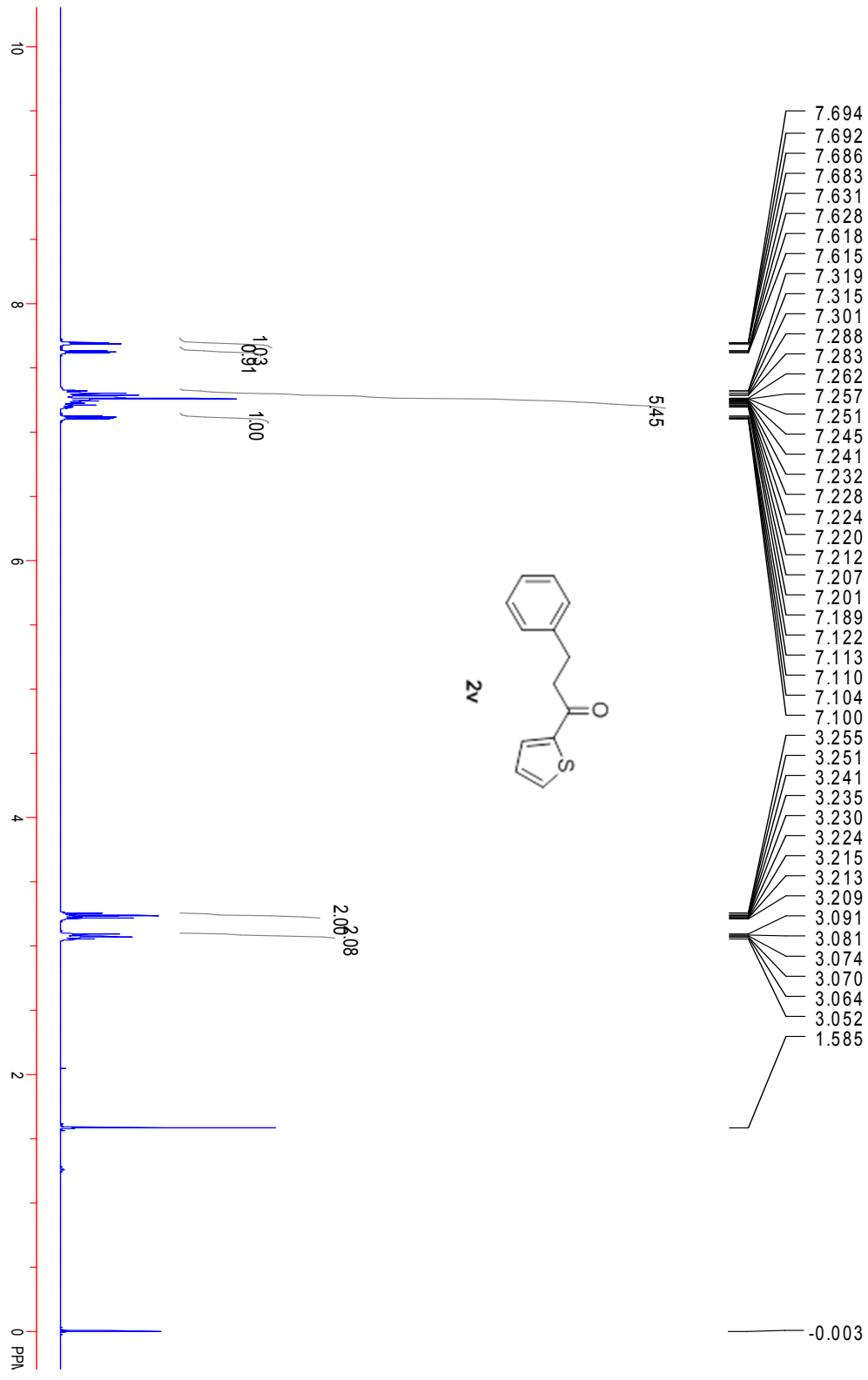


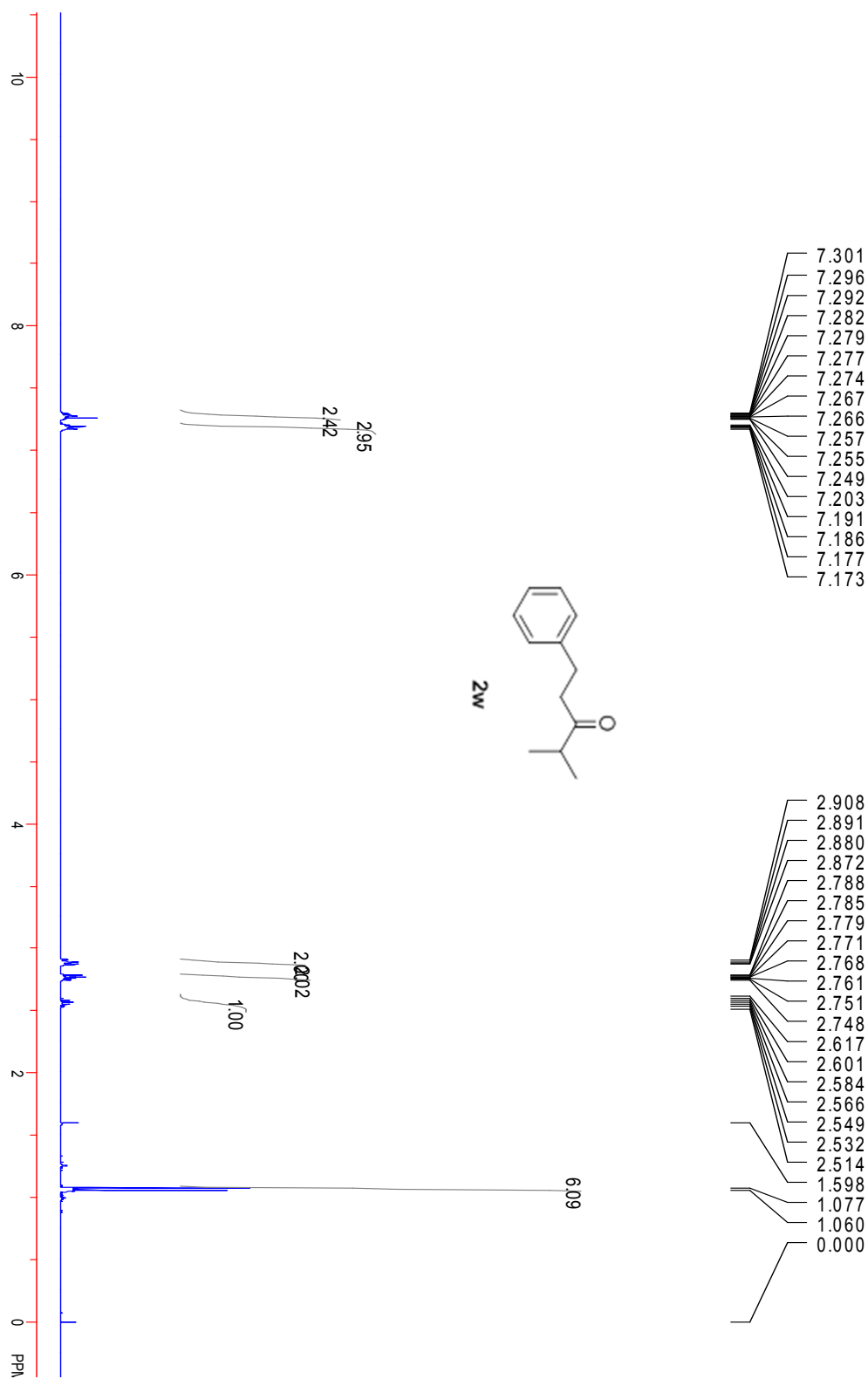




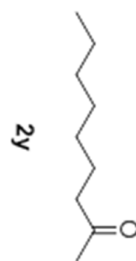












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