Supplementary Material

Sonogashira-Hagihara and Buchwald-Hartwig cross-coupling reactions with sydnone and sydnone imine derived catalysts

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Experimental Section

General Bruker Avance 400 MHz was used to measure the nuclear magnetic resonance (NMR) spectra. The ^{1}H NMR spectra were recorded at 400 MHz, and the ^{13}C NMR spectra were recorded at 100 MHz. The solvent peaks or tetramethylsilane were used as the internal references. Multiplicities are described using the following abbreviations: s = singlet, d = doublet, t = triplet, q = quartet, and m = multiplet.

General Procedure for the preparation of compounds 10-19 Under an inert atmosphere (N_2) the halogen compound was dissolved in 15 mL of triethylamine at rt and 10 mol-% of the corresponding catalyst and 0.010 g (0.05 mmol) of Cu(I)I as co-catalyst was added. After the acetylene was carefully added, the mixture was stirred at reflux temperature over a period of 5 h - 72 h. After cooling to rt, the mixture was treated with 15 mL of distilled water and subsequently extracted with $CHCl_3$ or CH_2Cl_2. The organic phase was dried over $MgSO_4$, and then the solvent was removed under reduced pressure. The resulting crude product was finally purified by column chromatography.

2-Methyl-4-phenylbut-3-yn-2-ol (10)
Samples of 0.400 g (2.5 mmol) of bromobenzene and 0.6 mL (6.0 mmol) of 2-methyl-but-3-yn-2-ol were used. Column chromatography was performed with (petroleum ether : ethyl acetate = 2:1). Brownish solid. Reaction conditions and yields are summarized in Table 1.

Table 1: Variation of the reaction conditions and corresponding yields of **10**

Entry	Cat.	Yield [g]	Yield [%]	Reaction time [h]
1	**cat. 1**	0.351	85	5
2	**cat. 2**	0.408	100	7
3	**cat. 4**	0.336	82	5
4	**cat. 8**	0.364	88	48
5	**cat. 9**	0.355	86	48
6	**cat. 10**	0.305	75	48
7	**cat. 11**	0.292	71	48
8	**cat. 12**	0.352	87	48
9	**cat. 13**	0.331	82	48

^{1}H-NMR (400 MHz, $CDCl_3$): δ = 7.43-7.40 (m, 2 H), 7.32-7.29 (m, 3 H), 1.99 (br s, 1 H), 1.62 (s, 6 H) ppm.
2-Methyl-4-(thiophen-3-yl)but-3-yn-2-ol (11)
Samples of 0.400 g (2.5 mmol) of 1-bromothiophene and 0.6 mL (6.0 mmol) of 2-methyl-but-3-yn-2-ol were used. Column chromatography was performed with (petroleum ether : ethyl acetate = 2:1). Yellowish solid. Reaction conditions and yields are summarized in Table 2.

Table 2: Variation of the reaction conditions and corresponding yields of **11**

Entry	cat.	Yield [g]	Yield [%]	Reaktion time [h]
32	**cat. 1**	0.311	75	5
33	**cat. 2**	0.391	95	5
34	**cat. 8**	0.262	64	48
35	**cat. 9**	0.294	72	48
36	**cat. 12**	0.283	69	48
37	**cat. 13**	0.322	78	48

^{1}H-NMR (400 MHz, $CDCl_3$): δ = 7.33 (d, $J_{H,H}$ = 7.8 Hz, 1 H), 7.18-7.15 (m, 1 H), 7.01 (d, $J_{H,H}$ = 7.8 Hz, 1 H), 2.19 (br s, 1 H), 1.53 (s, 6 H), ppm.

Methyl 4-(3-hydroxy-3-methylbut-1-yn-1-yl)benzoate (12)

Samples of 1.000 g (4.0 mmol) of ethyl-4-bromobenzoate and 1.2 mL (12.0 mmol) of 2--methyl-but-3-yn-2-ol were used. Column chromatography was performed with (petroleum ether : ethyl acetate = 2:1). Yellowish solid. Reaction conditions and yields are summarized in Table 3.

Table S3: Variation of the reaction conditions and corresponding yields of **12**

Entry.	Cat.	Yield [g]	Yield [%]	Reaktion time [h]
50	**Kat. 1**	0.92	91	5
51	**Kat. 2**	0.98	97	5
52	**Kat. 6**	0.96	95	5

^{1}H-NMR (400 MHz, $CDCl_3$): δ = 8.01-7.97 (m, 2 H), 7.50-7.46 (m, 2 H), 3.91 (s, 3 H),), 2.29 (s, 1 H), 1.63 (s, 6 H) ppm.

2-Methyl-4-(naphtho-1-yl)but-3-yn-2-ol (13)

Samples of 0.500 g (2.5 mmol) of 1-bromonaphthalene and 0.6 mL (6.0 mmol) of 2-methyl-but-3-yn-2-ol were used. Column chromatography was performed with (petroleum ether : ethyl acetate = 2:1). Brownish solid. Reaction conditions and yields are summarized in Table 4.

Table 4: Variation of the reaction conditions and corresponding yields of **13**

Entry	Cat.	Yield [g]	Yield [%]	Reaktion time [h]
10	**cat. 1**	0.218	42	5
11	**cat. 2**	0.436	83	5
12	**cat. 4**	0.393	61	48
13	**cat. 8**	0.436	76	48
14	**cat. 9**	0.312	85	48
15	**cat. 10**	0.269	63	48
16	**cat. 11**	0.307	51	48
17	**cat. 12**	0.324	60	48
18	**cat. 13**	0.269	63	48

^{1}H-NMR (400 MHz, $CDCl_3$): δ = 8.28 (d, $J_{H,H}$ = 7.8 Hz, 1 H)), 7.80-7.74 (m, 2 H), 7.60 (d, $J_{H,H}$ = 7.8 Hz, 1 H), 7.55-7.52 (m, 1 H), 7.48-7.47 (m, 1 H), 7.36-7.33 (m, 1 H), 2.72 (br s, 1 H), 1.71 (s, 6 H) ppm.

4-(3,5-Dimethylphenyl)-2-methylbut-3-yn-2-ol (14)

Samples of 0.500 g (2.7 mmol) of 1-bromo-2,5-dimethylbenzole and 0.6 mL (6.0 mmol) of 2-methyl-but-3-yn-2-ol were used. Column chromatography was performed with (petroleum ether : ethyl acetate = 4:1). Brownish solid. Reaction conditions and yields are summarized in Table 5.

Table 5: Variation of the reaction conditions and corresponding yields of **14**

Entry.	Cat.	Yield [g]	Yield [%]	Reaction time [h]
38	**cat. 1**	0.310	75	5
39	**cat. 2**	0.392	95	5
40	**cat. 8**	0.263	64	48
41	**cat. 9**	0.291	72	48
42	**cat. 12**	0.280	69	48
43	**cat. 13**	0.322	78	48

^{1}H-NMR (400 MHz, $CDCl_3$): δ = 7.04 (s, 2 H), 6.93 (s, 1 H), 2.27 (s, 6 H), 2.27 (br s, 1 H), 1.60 (s, 6 H) ppm.

2-Methyl-4-(pyridin-3-yl)but-3-yn-2-ol (15)

Samples of 0.500 g (3.1 mmol) of 3-bromopyridine and 0.6 mL (6.0 mmol) of 2-methyl-but-3-yn-2-ol were used. Column chromatography was performed with (petroleum ether : ethyl acetate = 5:1). Brownish solid. Reaction conditions and yields are summarized in Table 6.

Table 6: Variation of the reaction conditions and corresponding yields of **15**

Entry	Cat.	Yield [g]	Yield [%]	Reaktion time[h]
19	**cat. 1**	0.091	25	5
20	**cat. 2**	0.213	59	5
21	**cat. 12**	0.174	48	48
22	**cat. 13**	0.161	46	48

^{1}H-NMR (400 MHz, $CDCl_3$): δ = 8.76 (br. s, 1 H), 8.51 (br. s, 1 H), 7.72-7.70 (m, 1 H), 7.27-7.24 (m, 1 H), 4.11 (br. s, 1 H), 1.63 (s, 6 H) ppm.

2-Methyl-4-(phenanthrene-9-yl)but-3-yn-2-ol (16)

Samples of 0.500 g (1.9 mmol) of 9-bromophenanthrene and 0.6 mL (6.0 mmol) of 2-methyl-but-3-yn-2-ol were used. Column chromatography was performed with (petroleum ether : ethyl acetate = 2:1). Brownish solid. Reaction conditions and yields are summarized in Table 7.

Table 7: Variation of the reaction conditions and corresponding yields of **16**

Entry	Cat.	Yield [g]	Yield [%]	Reaction time [h]
27	**cat. 1**	0.184.	35	5
28	**cat. 2**	0.405	80	5
29	**cat. 9**	0.234	45	72
30	**cat. 12**	0.316	61	72
31	**cat. 13**	0.283	56	72

^{1}H-NMR (400 MHz, $CDCl_3$): δ = 8.70-8.64 (m, 3 H) 8.40-8.38 (m, 1 H), 7.98 (s, 1 H), 7.83-7.85 (m, 2 H), 7.70-7.66 (m, 1 H), 7.65-7.60 (m, 1 H), 2.00 (br s, 1 H), 1.76 (s, 6 H) ppm.

2-Methyl-4-(quinolin-2-yl)but-3-yn-2-ol (17)

Samples of 0.500 g (2.4 mmol) of 2-bromochinoline and 0.6 mL (6.0 mmol) of 2--methyl-but-3-yn-2-ol were used. Column chromatography was performed with (petroleum ether : ethyl acetate = 2:1). Brownish solid. Reaction conditions and yields are summarized in Table 8.

Table 8: Variation of the reaction conditions and corresponding yields of **17**

Entry	Cat.	Yield [g]	Yield [%]	Reaction time [h]
47	**cat. 1**	0.42	85	5
48	**cat. 2**	0.49	97	5
49	**cat. 6**	0.48	95	5

^{1}H-NMR (400 MHz, $CDCl_3$): δ = 9.07-9.06 (m, 1 H), 8.15-8.10 (m, 2 H), 7.72-7.66 (m, 2 H), 7.54-7.50 (m, 1 H), 5.58 (br. s, 1 H), 1.69 (s, 6 H) ppm.

4-(Anthracen-9-yl)-2-methylbut-3-yn-2-ol (18)

Samples of 0.500 g (1.9 mmol) of 9-bromoanthracene and 0.6 mL (6.0 mmol) of 2-methyl-but-3-yn-2-ol were used. Column chromatography was performed with (petroleum ether : ethyl acetate = 2:1). Yellowish solid. Reaction conditions and yields are summarized in Table 9.

Table 9: Variation of the reaction conditions and corresponding yields of **18**

Entry	Cat.	Yield [g]	Yield [%]	Reaction time [h]
23	**cat. 1**	0.081	15	5
24	**cat. 2**	0.332	65	5
25	**cat. 12**	0.296	58	72
26	**cat. 13**	0.284	56	72

^{1}H-NMR (400 MHz, $CDCl_3$): δ = 8.48 (d, $J_{H,H}$ = 8.6 Hz, 2 H), 8.41 (s, 1 H), 7.98 (d, $J_{H,H}$ = 8.6 Hz, 2 H), 7.58-7.55 (m, 2 H), 7.51-7.47 (m, 2H), 2.30 (br s, 1H), 1.85 (s, 6 H), ppm.

4,4'-([1,1'-Biphenyl]-4,4'-diyl)bis(2-methylbut-3-yn-2-ol) (19)

Samples of 0.200 g (0.64 mmol) of 4,4'-dibromo-1,1'-biphenyl and 0.3 mL (3.0 mmol) of 2-methyl-but-3-yn-2-ol were used. Column chromatography was performed with (petroleum ether : ethyl acetate = 8:1). Brownish solid. Reaction conditions and yields are summarized in Table 10.

Table 10: Variation of the reaction conditions and corresponding yields of **19**

Entry	cat.	Yield [g]	Yield [%]	Reaction time [h]
44	**cat. 1**	0.047	23	5
45	**cat. 2**	0.195	95	5
46	**cat. 8**	0.069	34	48

^{1}H-NMR (400 MHz, DMSO-d_6): δ = 7.70 (d, $J_{H,H}$ = 8.4 Hz, 4 H), 7.48 (d, $J_{H,H}$ = 8.4 Hz, 4 H), 5.51 (bs, 2 H), 1.49 (s, 12 H), ppm.

General Procedure for the preparation of compounds 20-24

Under an inert atmosphere (N2) the halogen compound were dissolved in 20 ml of dry toluene and 10 mol-% of the corresponding catalyst was added. After stirring the mixture for 10 min at rt 0.075 g (0.4 mmol) diphenylamine and 0.424 g (2.0 mmol) potassium phosphate were added. Then the mixture was stirred at 100 °C for 12 h. After cooling the mixture down to room temperature, the solvent was removed under reduced pressure. The resulting crude product was finally purified by column chromatography which was performed with (petroleum ether : dichloromethane = 1:1).

***N,N,N*-Triphenylamine (20)**

0.150 g (1.0 mmol) of bromobenzene was used. The product was isolated as brownish solid. The yields achieved with the various catalysts are summarized in table S11.

Table S11: Variation of the catalysts and corresponding yields of **20**

Entry	Cat.	Yield [g]	Yield [%]
1	**cat. 1**	0.050	45
2	**cat. 2**	0.109	98
3	**cat. 5**	0.099	88

^{1}H-NMR (400 MHz, $CDCl_3$): δ = 7.47 (d, $J_{H,H}$ = 8.5 Hz, 6 H), 7.20-7.29 (m, 9 H) ppm.

***N,N*-Diphenylnaphthalene-1-amine (21)**

0.150 g (0.9 mmol) of 1-bromonaphthalene was used. The product was isolated as brownish solid. The yields achieved with the various catalysts are summarized in table S12.

Table S12: Variation of the catalysts and corresponding yields of **21**

Entry	Cat.	Yield [g]	Yield [%]
4	**cat. 1**	0.061	48
5	**cat. 2**	0.122	95
6	**cat. 5**	0.106	82

^{1}H-NMR (400 MHz, $CDCl_3$): δ = 8.20 (d, $J_{H,H}$ = 8.5 Hz, 2 H), 7.72-7.78 (m, 5 H), 7.56-7.52 (m, 2 H), 7.50-7.45 (m, 2 H), 7.26-7.20 (m, 3 H), 7.01 (d, $J_{H,H}$ = 8.5 Hz, 2 H), 6.88 (t, $J_{H,H}$ = 8.5 Hz, 1 H) ppm.

***N,N*-Diphenylphenanthren-9-amine (22)**

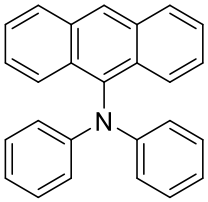
Sample of 0.150 g (0.8 mmol) 9-Bromophenanthrene was used. Brownish solid. The yields achieved with the various catalysts are summarized in table S13.

Table S13: Variation of the catalysts and corresponding yields of **22**

Entry.	Cat.	Yield [g]	Yield [%]
7	**cat. 1**	0.031	20
8	**cat. 2**	0.107	70
9	**cat. 5**	0.095	62

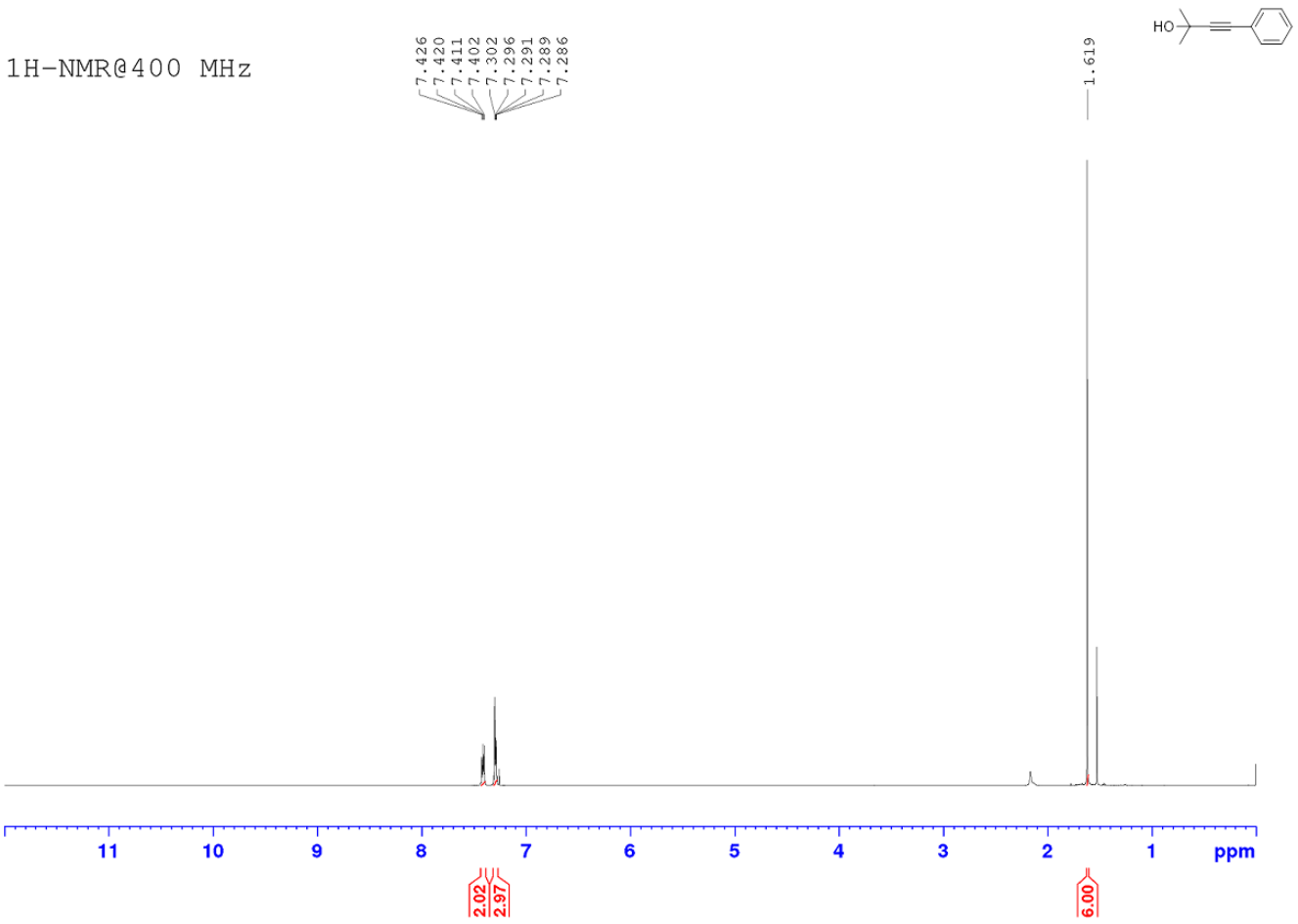
^{1}H-NMR (400 MHz, $CDCl_3$): δ = 8.62-8.56 (m, 4 H), 8.28-8.230 (m, 2 H), 8.03 (s, 2 H), 7.71 (d, $J_{H,H}$ = 8.5 Hz, 2 H), 7.65-7.53 (m, 7 H), 7.51 (t, $J_{H,H}$ = 8.5 Hz, 2 H) ppm.

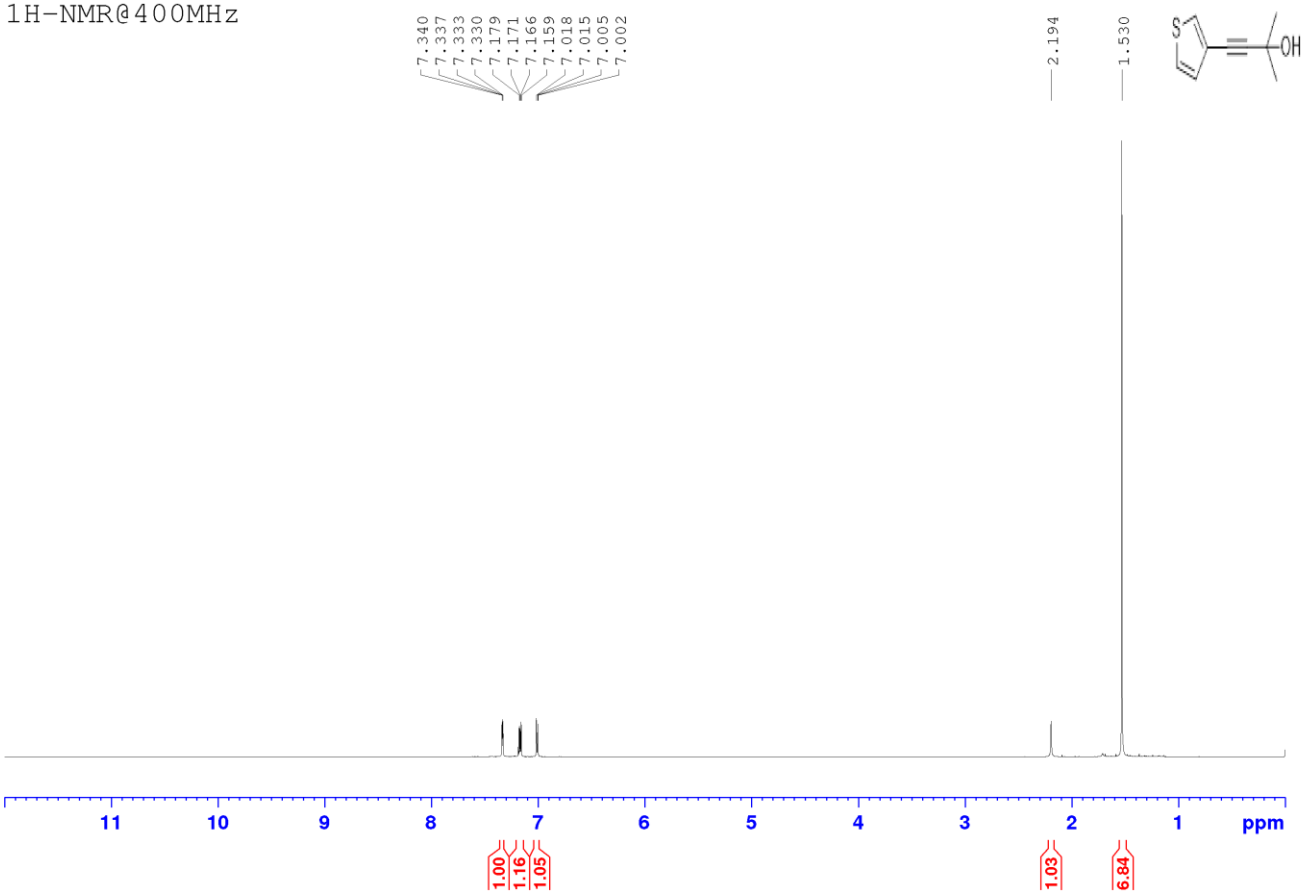
***N,N*-Diphenylanthracen-9-amine (23)**



Sample of 0.150 g (0.8 mmol) 9-bromoanthracene was used. No product could be synthesized using **cat. 1**, **cat. 2** and **cat. 5**.

^{1}H-NMR data for compound 10-19

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7.005
7.002
2.194
1.530
OH
11
10
9
8
7
6
5
4
3
2
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ppm
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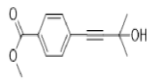
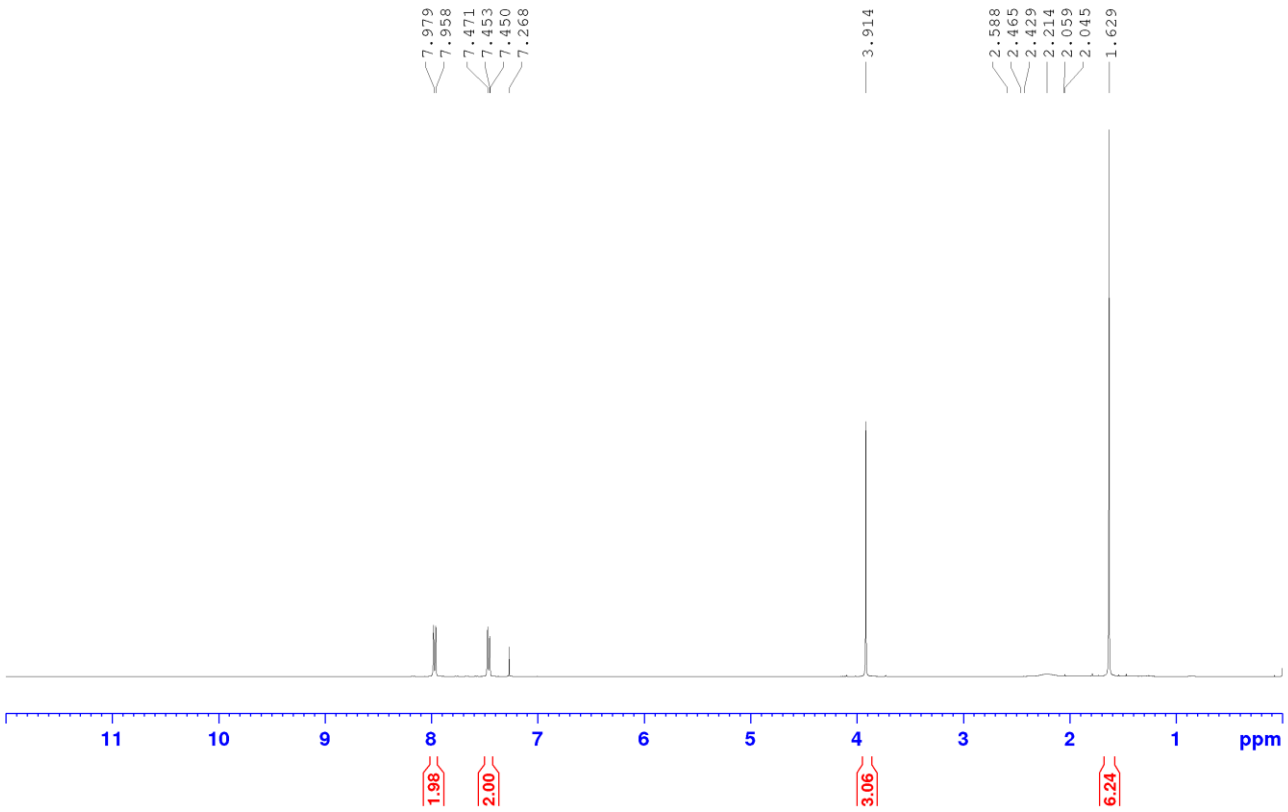
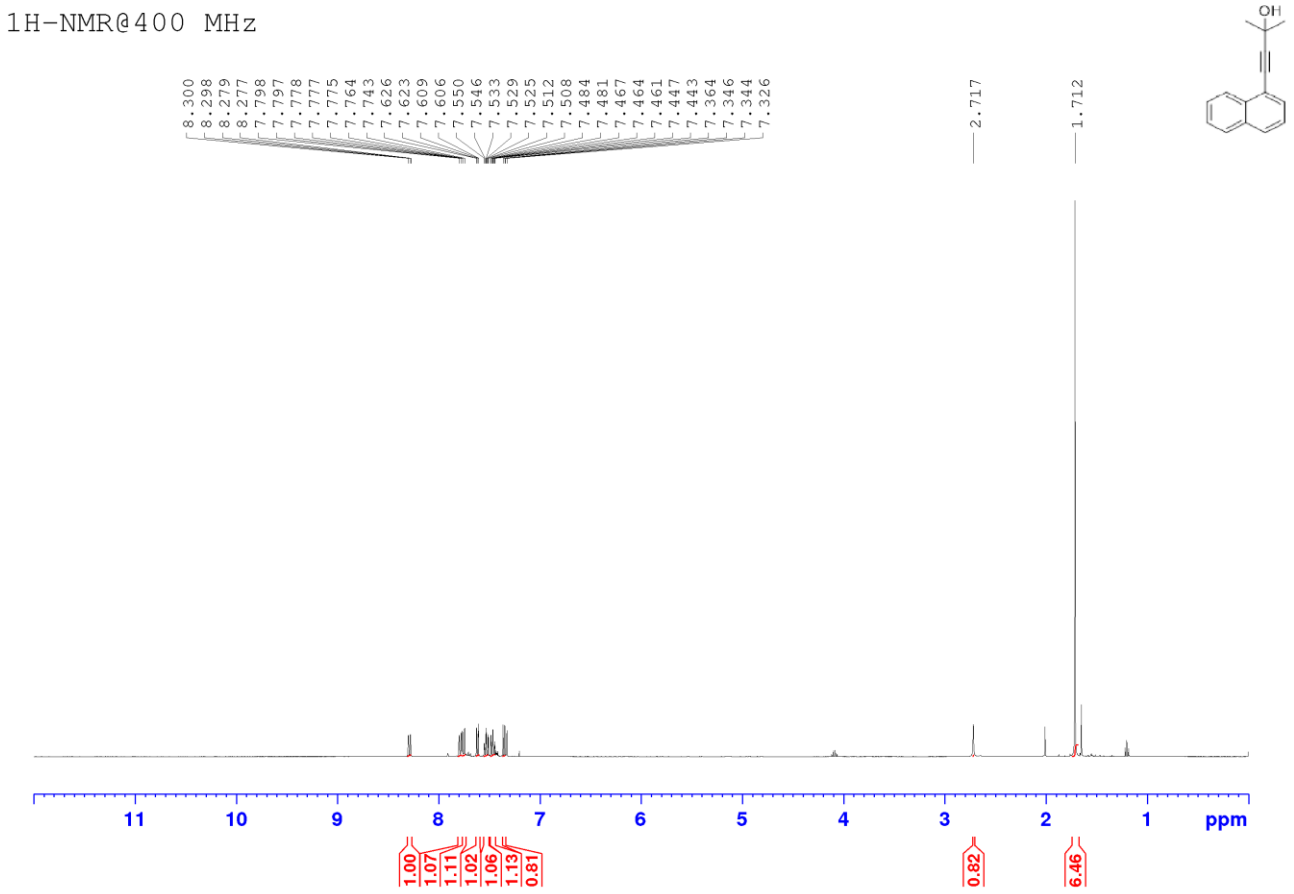
1.16
1.05
1.03
6.84

1H-NMR@400MHz



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7.626
7.623
7.609
7.606
7.550
7.546
7.533
7.529
7.525
7.512
7.508
7.484
7.481
7.467
7.464
7.461
7.447
7.443
7.364
7.346
7.344
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9
8
7
6
5
4
3
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1.06
1.13
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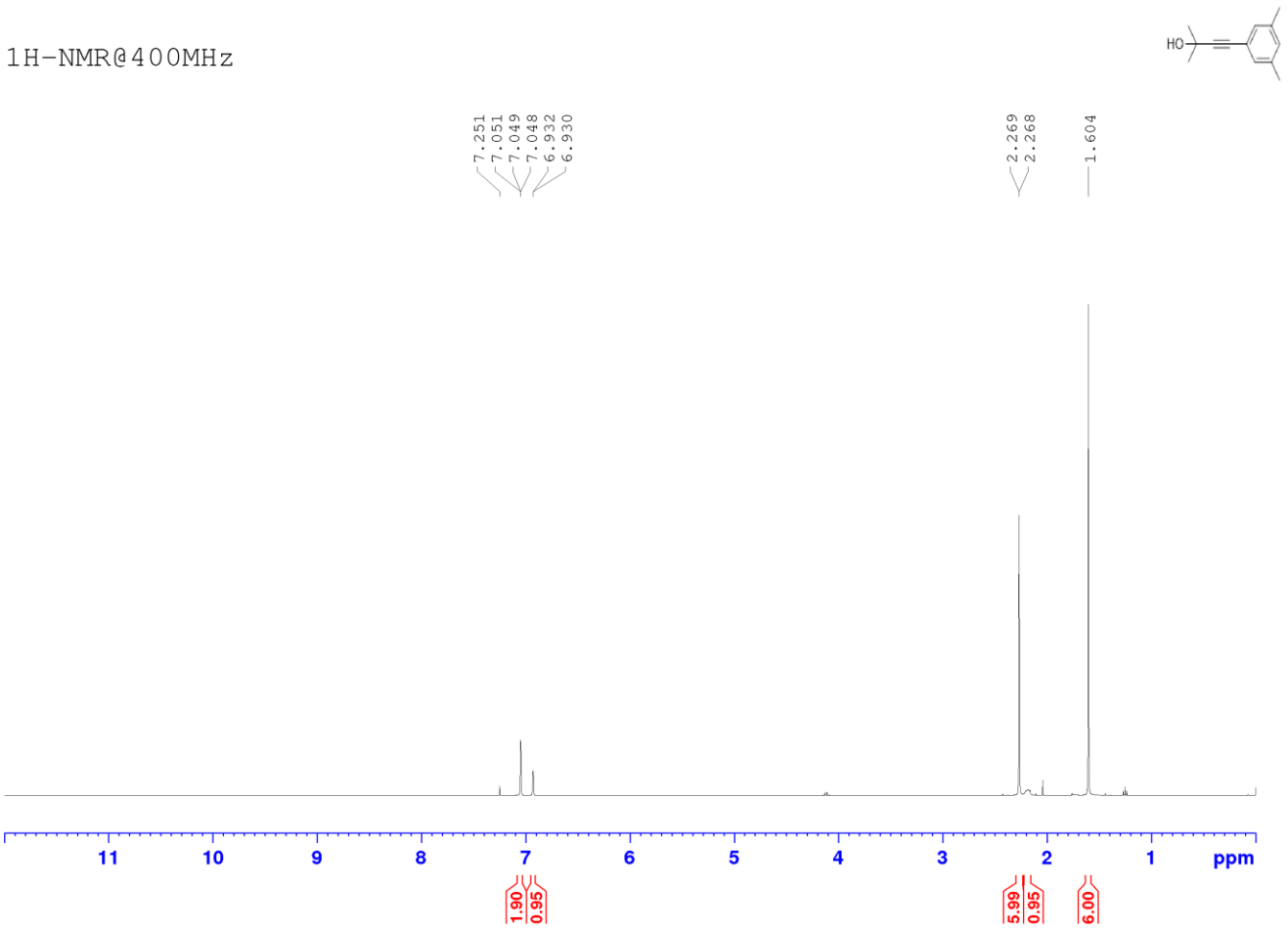
0.82
6.46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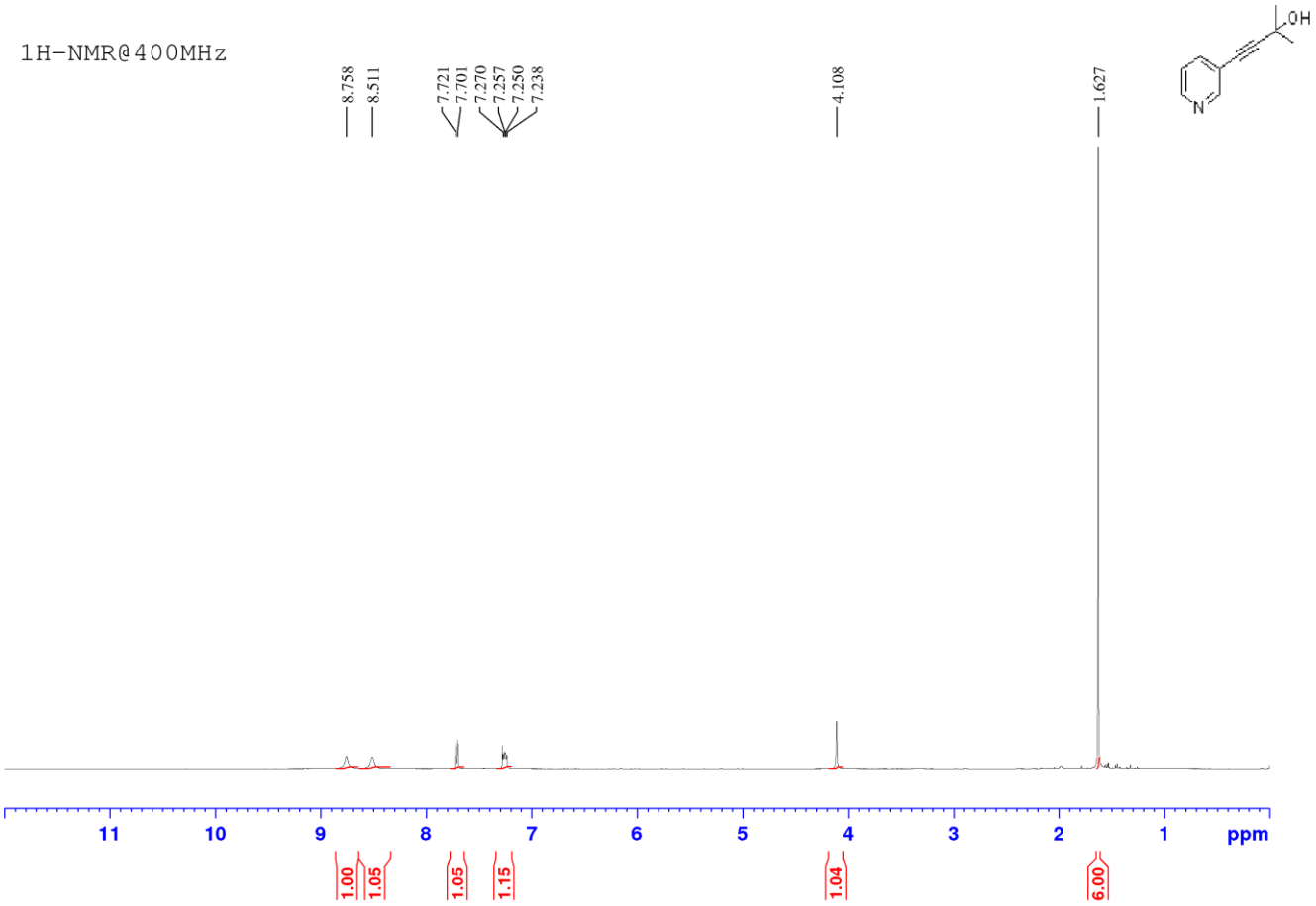
0.95
6.00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N
11
10
9
8
7
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5
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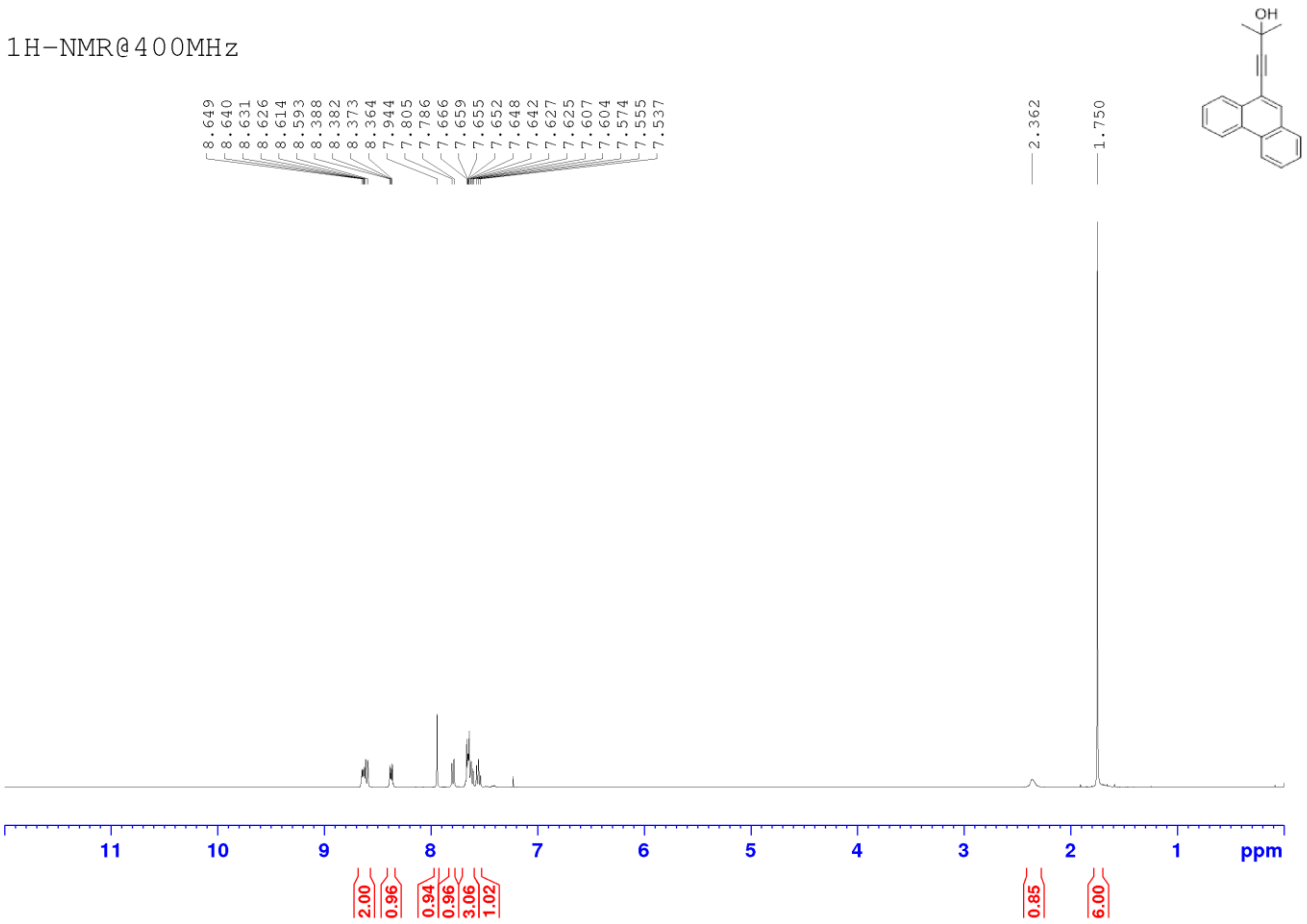
1.15
1.04
6.00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7.805
7.786
7.666
7.659
7.655
7.652
7.648
7.642
7.627
7.625
7.607
7.604
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2.362
1.750
OH
11
10
9
8
7
6
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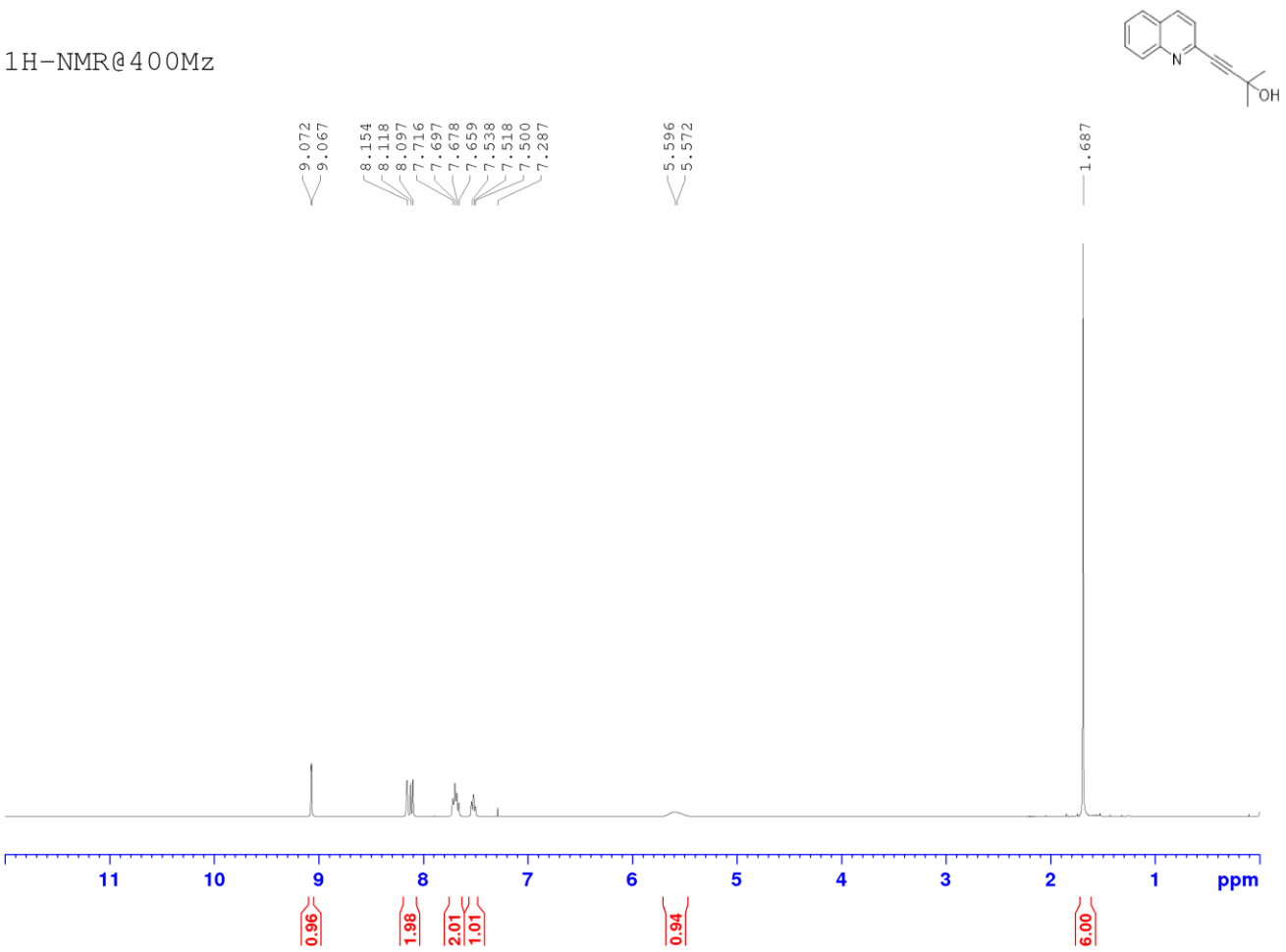
6.00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N
OH
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8.154
8.118
8.097
7.716
7.697
7.678
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7.538
7.518
7.500
7.287
5.596
5.572
1.687
11
10
9
8
7
6
5
4
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2
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1.01
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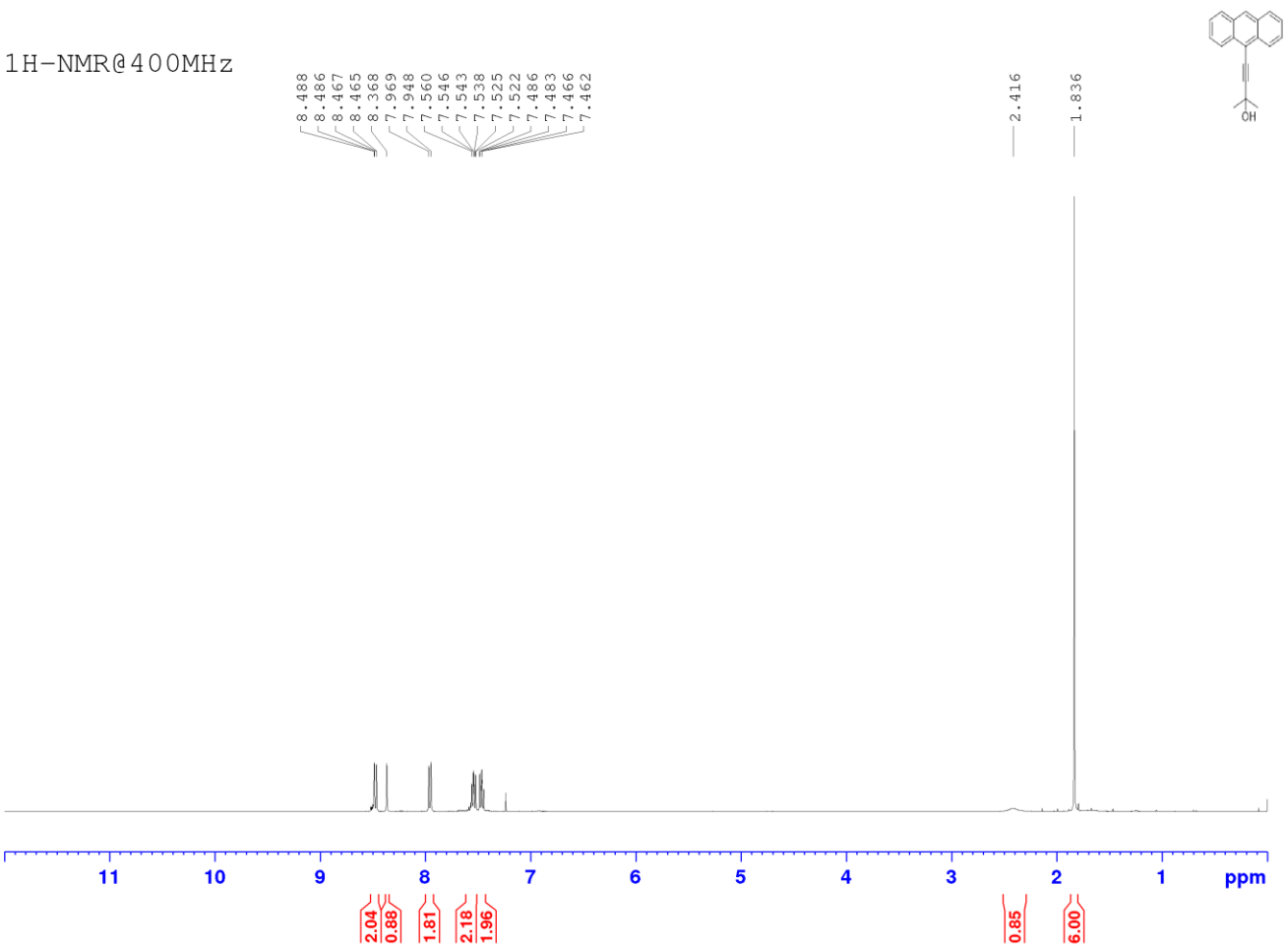
6.00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7.486
7.483
7.466
7.462
2.416
1.836
OH
11
10
9
8
7
6
5
4
3
2
1
ppm
2.04
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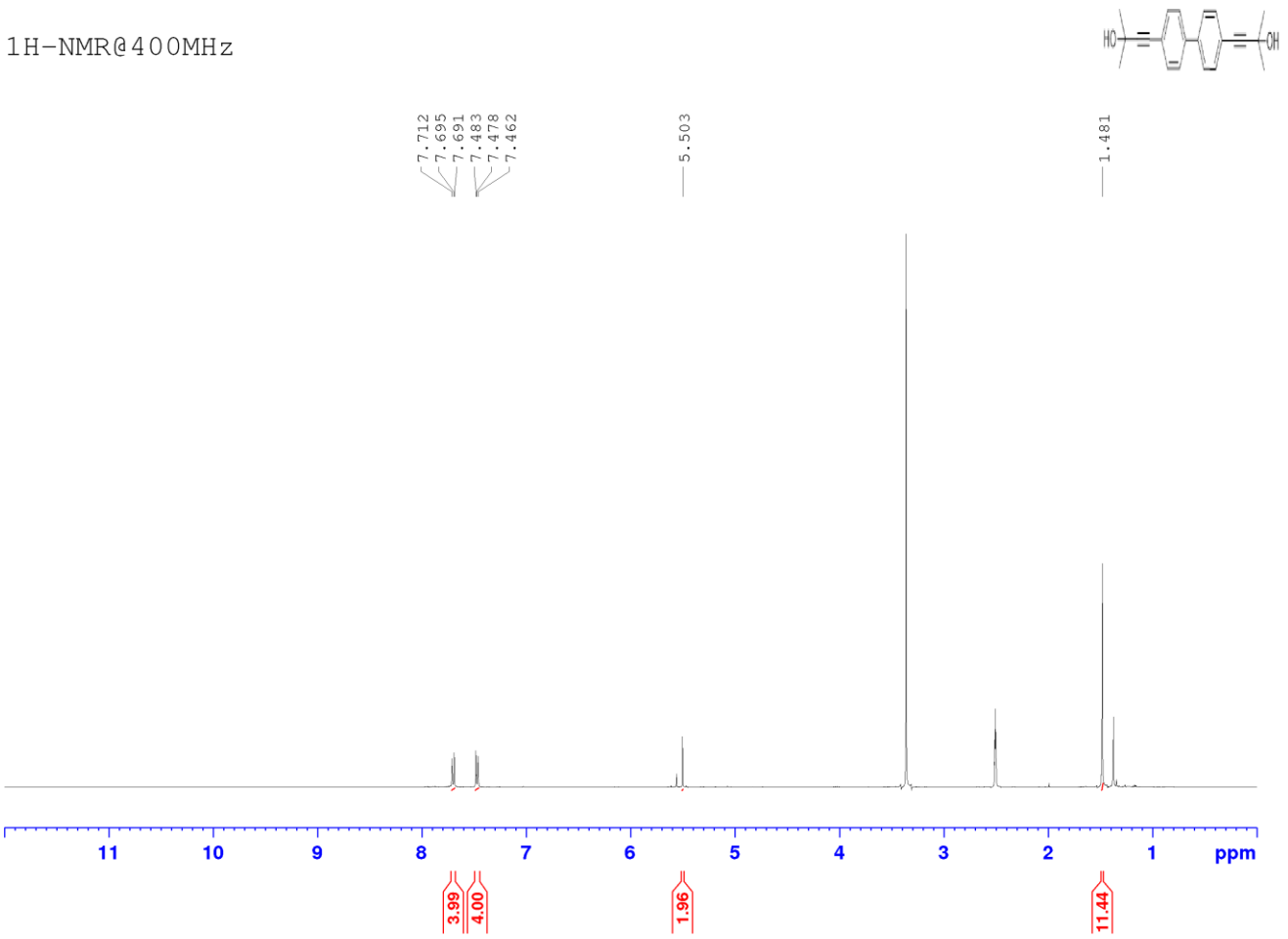
0.85
6.00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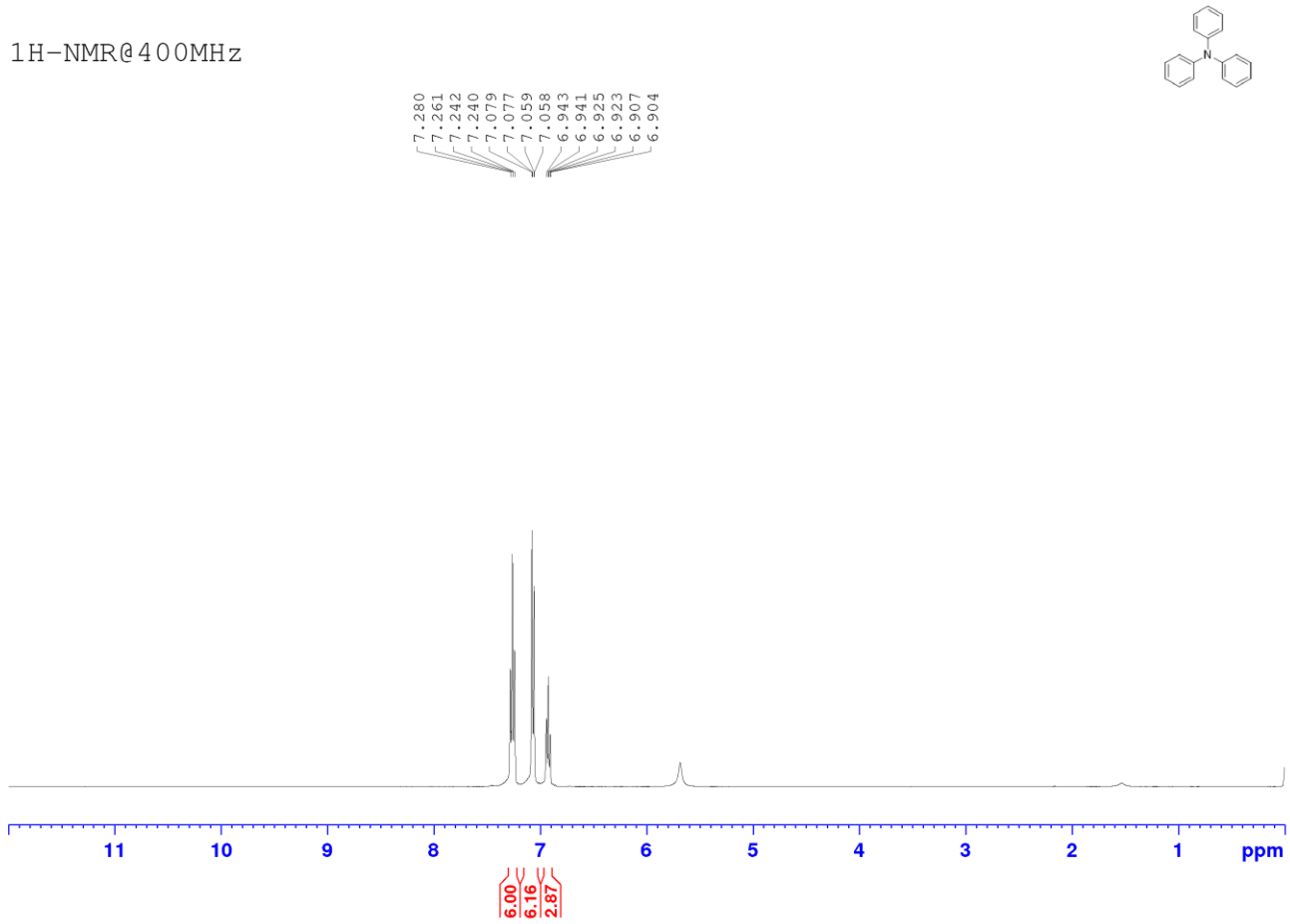
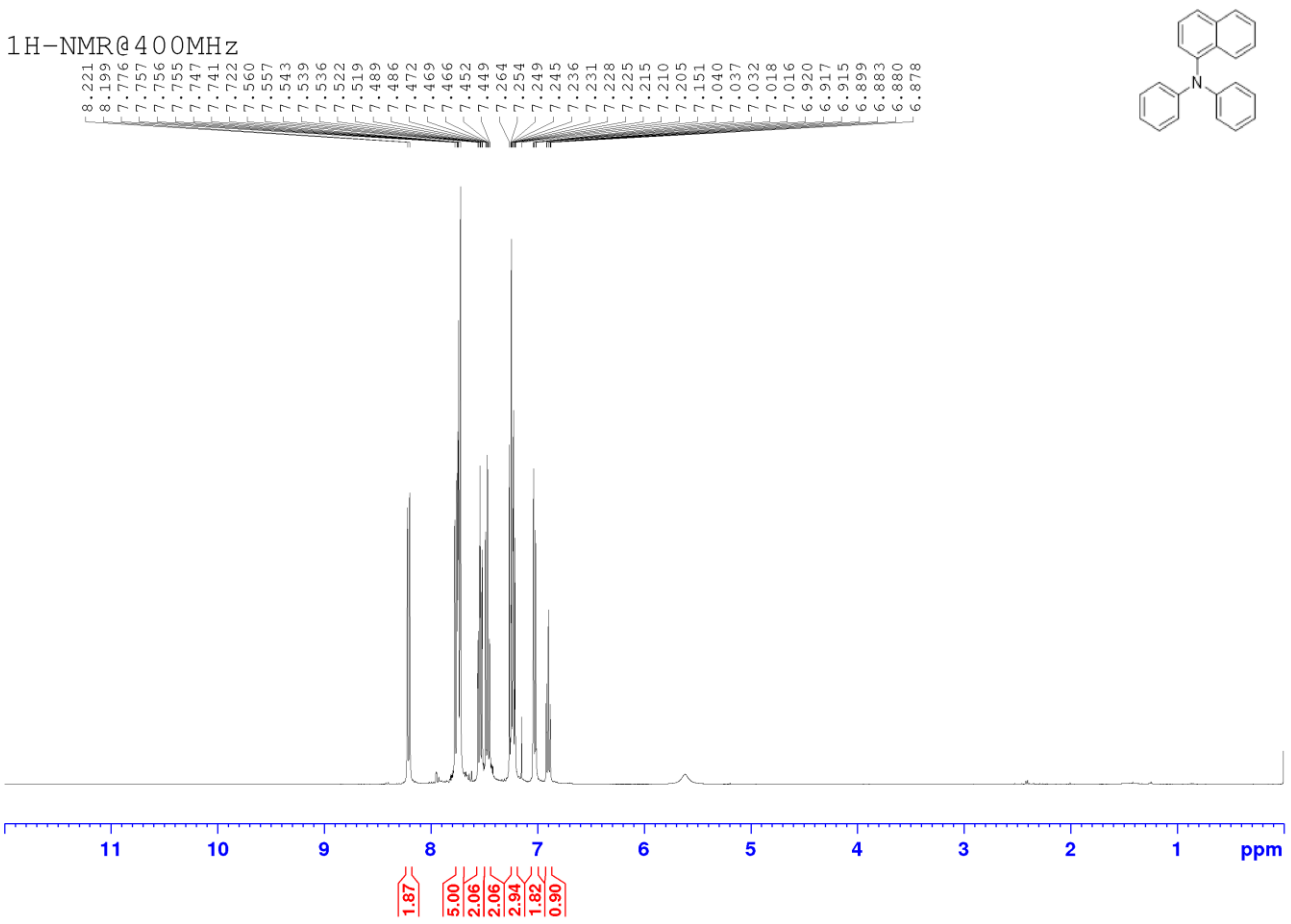
7.691
7.483
7.478
7.462
5.503
1.481
11
10
9
8
7
6
5
4
3
2
1
ppm
3.99
4.00
1.96
11.44

^{1}H-NMR data for compound 20-23

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7.757
7.756
7.755
7.747
7.741
7.722
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7.543
7.539
7.536
7.522
7.519
7.489
7.486
7.472
7.469
7.466
7.452
7.449
7.264
7.254
7.249
7.245
7.236
7.231
7.228
7.225
7.215
7.210
7.205
7.151
7.040
7.037
7.032
7.018
7.016
6.920
6.917
6.915
6.899
6.883
6.880
6.878
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11
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9
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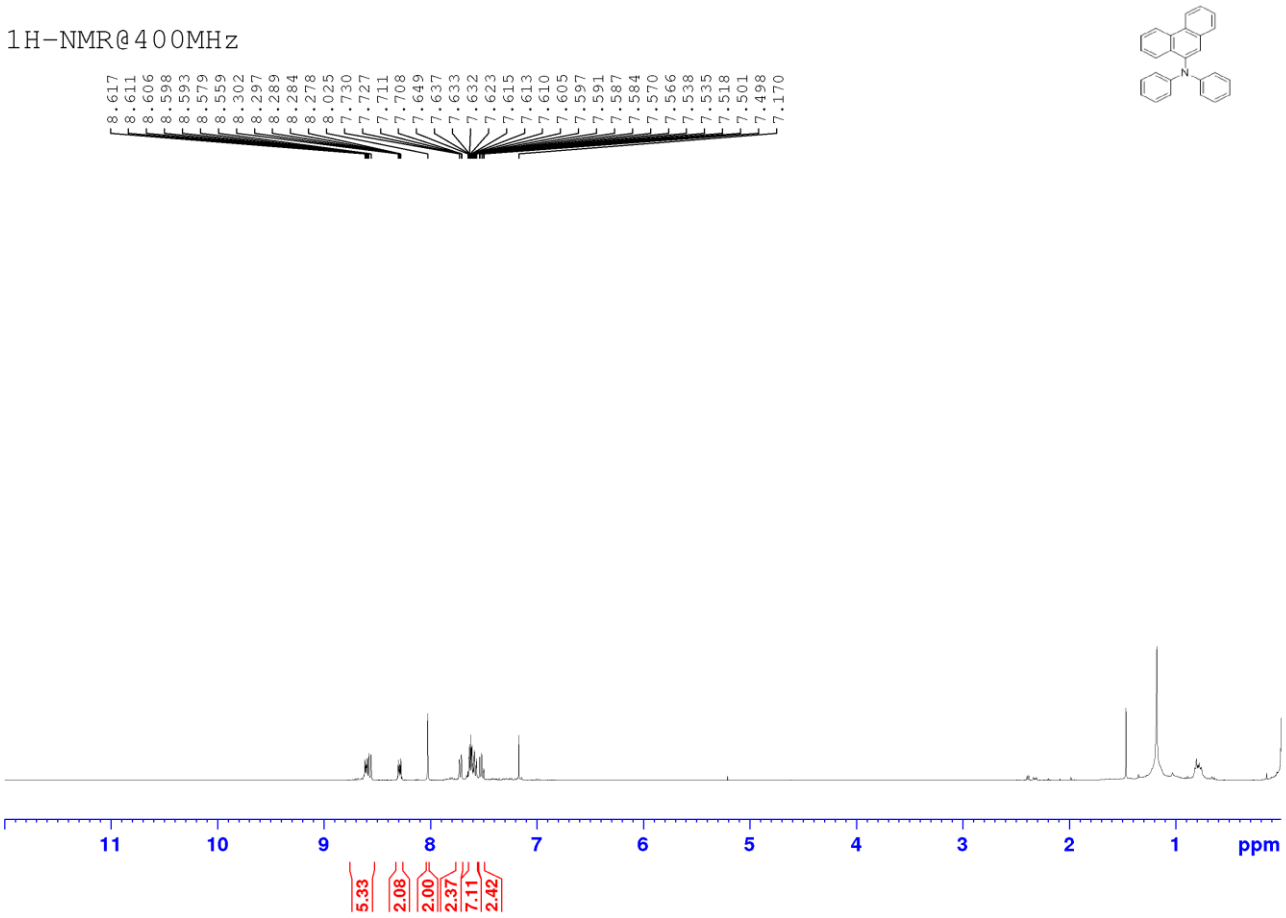
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11
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