Supporting Information:

Synthesis of Aliphatic Nitriles from Cyclobutanone Oxime Mediated by Sulfuryl Fluoride (SO_2F_2)

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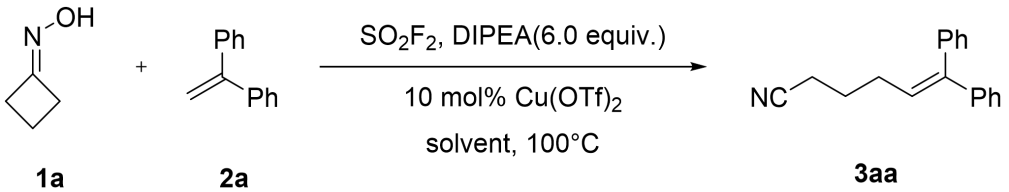
Table of Content

1. General information

All reactions were carried out in dried glassware. All reagents were purchased from commercial sources and used without further purification. Unless otherwise specified, NMR spectra were recorded in $CDCl_3$ on a 500 MHz (for ^{1}H), 471 MHz (for ^{19}F), 126 MHz (for ^{13}C) Bruker Avance spectrometer, and were internally referenced to solvent residual signals (note: $CDCl_3$: δ H = 7.264 ppm, δ C = 77.16 ppm). The HPLC experiments were carried out on a Waters e2695 instrument (column: J&K, RP-C18, 5 μm, 4.6 × 150 mm), and the yields of the products were determined by using the corresponding pure compounds as the external standards. The coupling constants were reported in Hertz (Hz). The following abbreviations were used to explain the multiplicities: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, br = broad.

2. Optimization of the reaction conditions

Table S1 Screening the Solvent[a]



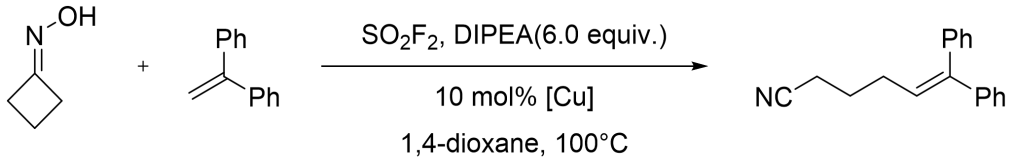
1a **2a** **3aa**

Entry	Solvent	Yield (**3aa**,%)[b]
1	**1,4-dioxane**	**47**
2	$PhCF_3$	N.D.
3	DMF	13
4	NMP	23
5	$PhCH_3$	12
6	CH_3CN	N.D.
7	CH_2Cl_2	39
8	THF	N.D.
9	CH_2ClCH_2Cl	N.D.
10	Acetone	N.D.
11	Dioxane/DMSO(1:1)	21
12	Dioxane/$PhCF_3$(1:1)	24
13	Dioxane/NMP(1:1)	32
14	Dioxane/CH_2Cl_2(1:1)	46

[a] Reaction conditions: A mixture of cyclobutanone (**1a**, 1.5 mmol, 3.0 equiv.), 1,1-Diphenylethylene (**2a**, 0.5 mmol), $Cu(OTf)_2$ (0.05 mmol, 10 mol%) and DIPEA (6.0 equiv.) in anhydrous solvent (0.1 M) was stirred at 100℃ with a SO_2F_2 balloon for 12h.

[b] The yield was determined by HPLC using pure **3aa** as the external standard (t_R = 5.0 min, λ_{max} = 250.0 nm, water / methanol = 20 : 80 (v / v)). N.D. = Not detectable.

Table S2 Screening the Copper Catalyst[a]



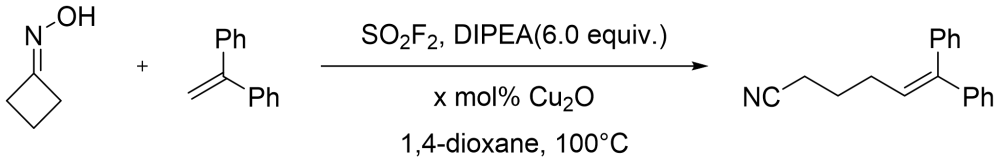
1a **2a** **3aa**

Entry	[Cu]	Yield (**3aa**,%)[b]
1	$Cu(OTf)_2$	47
2	CuO	N.D.
3	CuF_2	15
4	CuI	41
5	$Cu(CH_3CN)_4PF_6$	38
6	Cu power	16
7	Zu Cu alloy	16
8	CuCl	34
9	CuBr	9
10	**Cu_2O**	**55**
11	CuCN	40
12	/	N.D.
13	$CuSO_4$	35

[a] Reaction conditions: A mixture of cyclobutanone (**1a**, 1.5 mmol, 3.0 equiv.), 1,1-Diphenylethylene (**2a**, 0.5 mmol), copper catalyst (0.05 mmol, 10 mol%) and DIPEA (3.0 mmol, 6.0 equiv.) in anhydrous 1,4-Dioxane (0.1 M) was stirred at 100℃ with a SO_2F_2 balloon for 12h.

[b] The yield was determined by HPLC using pure **3aa** as the external standard (t_R = 5.0 min, λ_{max} = 250.0 nm, water / methanol = 20 : 80 (v / v)). N.D. = Not detectable.

Table S3 Screening the Loading of Copper Catalyst[a]



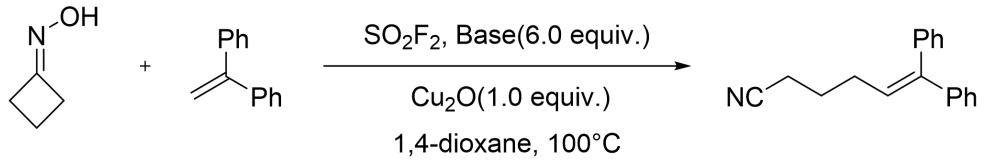
1a **2a** **3aa**

Entry	Cu_2O(x mol%)	Yield (**3aa**,%)[b]
1	10	55
2	30	48
3	50	61
4	**100**	**72**
5	120	71
6	150	66
7	200	46

[a] Reaction conditions: A mixture of cyclobutanone (**1a**, 1.5 mmol, 3.0 equiv.), 1,1-Diphenylethylene (**2a**, 0.5 mmol), Cu_2O (x mol%) and DIPEA (3.0 mmol, 6.0 equiv.) in anhydrous 1,4-Dioxane (0.1 M) was stirred at 100℃ with a SO_2F_2 balloon for 12h.

[b] The yield was determined by HPLC using pure **3aa** as the external standard (t_R = 5.0 min, λ_{max} = 250.0 nm, water / methanol = 20 : 80 (v / v)).

Table S4 Screening the Base[a]



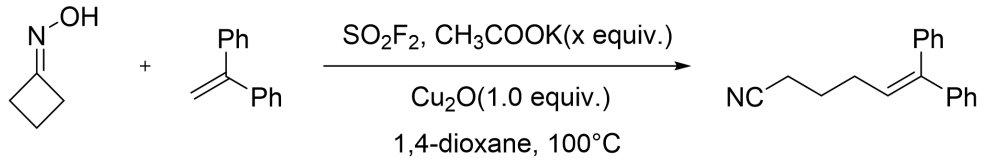
1a **2a** **3aa**

Entry	Base	Yield (**3aa**,%)[b]
1	K_2CO_3	40
2	Et_3N	37
3	DBU	N.D.
4	DIPEA	72
5	Na_2CO_3	62
6	Cs_2CO_3	29
7	$NaHCO_3$	N.D.
8	TMEDA	51
9	Li_2CO_3	N.D.
10	CH_3OK	11
11	KF	N.D.
12	**CH_3COOK**	**75**
13	t-BuONa	N.D.
14	PMDETA	7

[a] Reaction conditions: A mixture of cyclobutanone (**1a**, 1.5 mmol, 3.0 equiv.), 1,1-Diphenylethylene (**2a**, 0.5 mmol), Cu_2O (0.5 mmol, 1.0 equiv.) and Base (3.0 mmol, 6.0 equiv.) in anhydrous 1,4-Dioxane (0.1 M) was stirred at 100 ℃ with a SO_2F_2 balloon for 12h.

[b] The yield was determined by HPLC using pure **3aa** as the external standard (t_R = 5.0 min, λ_{max} = 250.0 nm, water / methanol = 20 : 80 (v / v)). N.D. = Not detectable.

Table S5 Screening the Loading of Base[a]



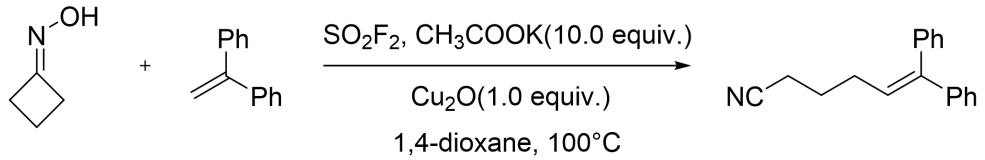
1a **2a** **3aa**

Entry	CH_3COOK(x equiv.)	Yield (**3aa**,%)[b]
1	2.0	21
2	3.0	24
3	4.0	23
4	5.0	55
5	6.0	75
6	7.0	65
7	8.0	72
8	9.0	79
9	**10.0**	**83**
10	11.0	83
11	12.0	84

[a] Reaction conditions: A mixture of cyclobutanone (**1a**, 1.5 mmol, 3.0 equiv.), 1,1-Diphenylethylene (**2a**, 0.5 mmol), Cu_2O (0.5 mmol, 1.0 equiv.) and CH_3COOK (x equiv.) in anhydrous 1,4-Dioxane (0.1 M) was stirred at 100℃ with a SO_2F_2 balloon for 12h.

[b] The yield was determined by HPLC using pure **3aa** as the external standard (t_R = 5.0 min, λ_{max} = 250.0 nm, water / methanol = 20 : 80 (v / v)). N.D. = Not detectable.

Table S6 Screening the Loading of 1a[a]



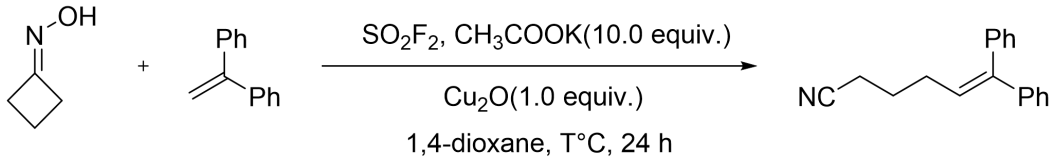
1a x equiv. **2a** **3aa**

Entry	**1a**(x equiv.)	Yield (**3aa**,%)[b]
1	0.33	N.D.
2	0.5	N.D.
3	1.0	15
4	1.5	35
5	2.0	50
6	**3.0**	**83**
7	5.0	76

[a] Reaction conditions: A mixture of cyclobutanone (**1a**, x equiv.), 1,1-Diphenylethylene (**2a**, 0.5 mmol), Cu_2O (0.5 mmol, 1.0 equiv.) and CH_3COOK (5.0 mmol, 10.0 equiv.) in anhydrous 1,4-Dioxane (0.1 M) was stirred at 100℃ with a SO_2F_2 balloon for 12h.

[b] The yield was determined by HPLC using pure **3aa** as the external standard (t_R = 5.0 min, λ_{max} = 250.0 nm, water / methanol = 20 : 80 (v / v)). N.D. = Not detectable.

Table S7 Screening the Reaction Temperature[a]



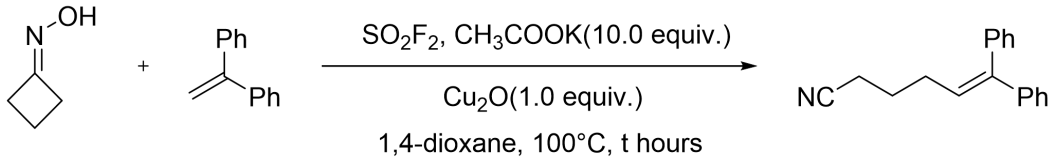
1a **2a** **3aa**

Entry	Temperature (°C)	Yield (**3aa**,%)[b]
1	80	54
2	**100**	**83**
3	120	64

[a] Reaction conditions: A mixture of cyclobutanone (**1a**, 1.0 mmol, 3.0 equiv.), 1,1-Diphenylethylene (**2a**, 0.5 mmol), Cu_2O (0.5 mmol, 1.0 equiv.) and CH_3COOK (5.0 mmol, 10.0 equiv.) in anhydrous 1,4-Dioxane (0.1 M) was stirred at T℃ with a SO_2F_2 balloon for 12h.

[b] The yield was determined by HPLC using pure **3aa** as the external standard (t_R = 5.0 min, λ_{max} = 250.0 nm, water / methanol = 20 : 80 (v / v)).

Table S8 Screening the Reaction Time[a]



1a **2a** **3aa**

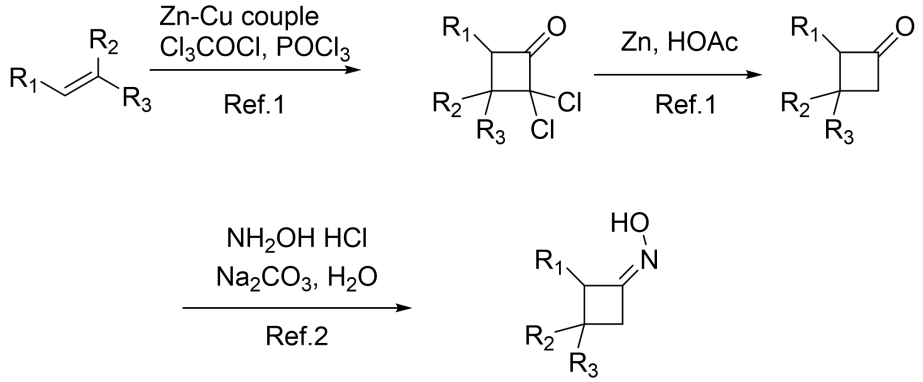
Entry	Time (h)	Yield (**3aa**,%)[b]
1	8	60
2	**12**	**83**
3	16	79
4	24	81

[a] Reaction conditions: A mixture of cyclobutanone (**1a**, 1.0 mmol, 3.0 equiv.), 1,1-Diphenylethylene (**2a**, 0.5 mmol), Cu_2O (100 mol%) and CH_3COOK (10.0 equiv.) in anhydrous 1,4-Dioxane (0.1 M) was stirred at 100℃ with a SO_2F_2 balloon for t hours.

[b] The yield was determined by HPLC using pure **3aa** as the external standard (t_R = 5.0 min, λ_{max} = 250.0 nm, water / methanol = 20 : 80 (v / v)).

3. General procedures

3.1 General procedures for synthesis of the compounds 1[1,2]



Cyclobutanone derivatives, which were commercial available or produced by the reduction of 2,2-dichlorocyclobutanones synthesized from the corresponding alkenes by the reported procedure[2]. The following experimental procedure is typical: To a 50 mL three-necked flask under argon were added alkene derivative (5.0 mmol, 1.0 equiv.), zinc-copper couple (960 mg, 15.0 mmol, 3.0 equiv.), and anhydrous ether (10 mL). To this was added a solution of trichloroacetyl chloride (1.12 mL, 10.0 mmol, 2.0 equiv.) and phosphorus oxychloride (0.51 mL, 5.5 mmol, 1.1 equiv.) in ether (10 mL) over 1 h through an addition funnel. The suspension was stirred overnight at reflux. The resulting mixture was filtered through a pad of Celite and was washed with ether (20 mL). The organic solution was successively washed with water (30 mL), a saturated aqueous solution of $NaHCO_3$ (30 mL) and brine (30 mL), and dried over $MgSO_4$. Then the solution was filtered, concentrated and used in the next step without further purification.

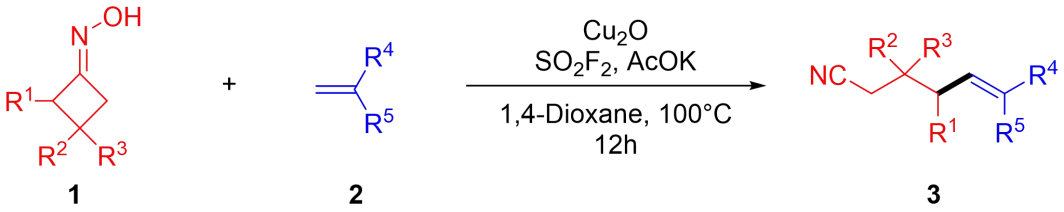
A mixture of 2,2-dichlorocyclobutanones (1.0 equiv.) and zinc dust (4.0 equiv.) in acetic acid (10 mL) was stirred at room temperature for 2 h and then heated at 80 °C for 5 h. The resulting mixture was allowed to cool to room temperature, then, the solution was diluted with water (30 mL) and extracted with ether (3*20 mL). The organic phase was washed successively with a saturated solution of aqueous $NaHCO_3$ (3*30 mL), water (30 mL) and brine (30 mL), then dried over MgSO4 and concentrated in vacuum. The crude material was then purified by flash

chromatography with a mixture of petroleum ether and ethyl acetate to afford various cyclobutanones.

To a stirred solution of cyclobutanones (1.0 equiv.) in H_2O (0.5 M) was added hydroxylamine hydrochloride (2.0 equiv) and Na_2CO_3 (0.5 equiv) at 45℃. After stirring for 3 h. The residue was diluted with water and extracted with EtOAc. The aqueous layer was extracted with EtOAc and the combined organic extracts were washed with brine, dried over MgSO4, and evaporated under reduced pressure to give the crude material, which were used in the next step without further purification.

3.2 General procedures for synthesis of the compounds 3

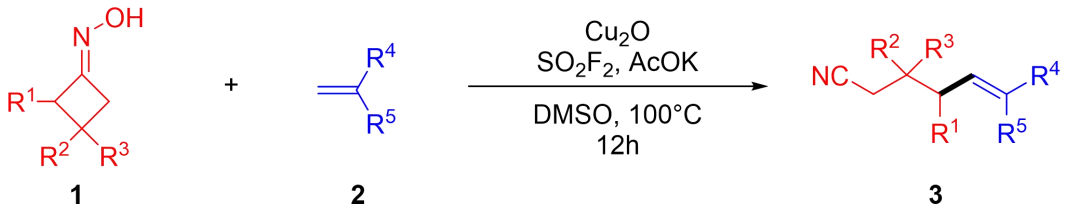
Method A:



1 **2** **3**

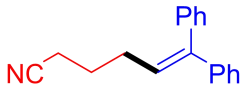
Cu_2O (1.0 mmol), AcOK (10.0 mmol), cyclobutanone oxime derivative (3.0 mmol), alkene (1.0 mmol) and extra dry 1,4-Dioxane (10 mL) were added to a 50 mL oven-dried round-bottom flask that was equipped with a stirrer bar. The tube was fitted with a plastic stopper and SO_2F_2 gas was introduced into the stirring reaction mixture by bubbling from a SO_2F_2 balloon. The mixture was stirred strongly at 100℃ for 12 h, then cooled to room temperature upon completion. After that, the reaction filtered with diatomite to remove insoluble substances such as copper catalyst and excessive base, washed by ethyl acetate. Then the reaction mixture was diluted with water and extracted with ethyl acetate (3×15 mL) and the combined organic layers were dried over anhydrous sodium sulfate, filtered and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel to afford the desired nitriles.

Method B:



Some substances with low yields have higher yields using Method B. Cu_2O (1.0 mmol), AcOK (10.0 mmol), cyclobutanone oxime derivative (3.0 mmol), alkene (1.0 mmol) and extra dry DMSO (10 mL) were added to a 50 mL oven-dried round-bottom flask that was equipped with a stirrer bar. The tube was fitted with a plastic stopper and SO_2F_2 gas was introduced into the stirring reaction mixture by bubbling from a SO_2F_2 balloon. The mixture was stirred strongly at 100℃ for 12 h, then cooled to room temperature upon completion. After that, the reaction diluted with water and filtered with diatomite, washed by ethyl acetate. Then the reaction mixture was extracted with ethyl acetate (3×15 mL) and the combined organic layers were dried over anhydrous sodium sulfate, filtered and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel to afford the desired nitriles.

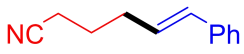
Product Characterization



3aa

6,6-diphenylhex-5-enenitrile **(3aa)**

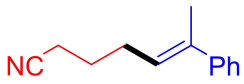
General procedures for synthesis of the compounds 3, Method A: **3aa** (206 mg, 83%), yellow oil. The NMR data is identical to that reported in literature.[3] **^{1}H NMR (500 MHz, $CDCl_3$)** δ 7.41 – 7.38 (m, 2H), 7.35 – 7.32 (m, 1H), 7.29 – 7.22 (m, 5H), 7.17 – 7.16 (m, 2H), 6.02 (t, J = 7.5 Hz, 1H), 2.33 – 2.25 (m, 4H), 1.84 – 1.78 (m, 2H);



3ab

(E)-6-phenylhex-5-enenitrile **(3ab)**

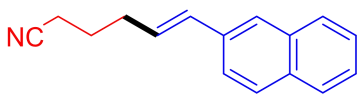
General procedures for synthesis of the compounds 3, Method B: **3ab** (117 mg, 68%), yellow oil. The NMR data is identical to that reported in literature. [3] **^{1}H NMR (500 MHz, $CDCl_3$)** δ 7.36 – 7.30 (m, 5H), 6.47 (d, J = 16.0 Hz, 1H), 6.17 – 6.11 (m, 1H), 2.41 – 2.38 (m, 4H), 1.89 – 1.83 (m, 2H);



3ac

(E)-6-phenylhept-5-enenitrile **(3ac)**

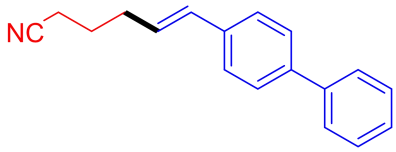
General procedures for synthesis of the compounds 3, Method A: **3ac** (121 mg, 66%), yellow oil. The NMR data is identical to that reported in literature. [3] **^{1}H NMR (500 MHz, $CDCl_3$)** δ 7.38 – 7.37 (m, 2H), 7.34 – 7.31 (m, 2H), 7.25 – 7.22 (m, 1H), 5.71 – 5.68 (m, 1H), 2.42 – 2.37 (m, 4H), 2.07 (s, 3H), 1.87 – 1.81 (m, 2H);



3ad

***(E)-6-(naphthalen-2-yl)hex-5-enenitrile* (3ad)**

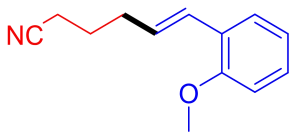
General procedures for synthesis of the compounds 3, Method A: **3ad** (125 mg, 56%), white solid. The NMR data is identical to that reported in literature.[4] **^{1}H NMR (500 MHz, $CDCl_3$)** δ 7.81 – 7.78 (m, 3H), 7.70 (s, 1H), 7.57 (dd, J_1 = 8.5 Hz, J_2 = 1.5 Hz, 1H), 7.47 – 7.44 (m, 2H), 6.63 (d, J = 16.0 Hz, 1H), 6.30 – 6.24 (m, 1H), 2.47 – 2.41 (m, 4H), 1.92 – 1.86 (m, 2H);



3ae

***(E)-6-([1,1'-biphenyl]-4-yl)hex-5-enenitrile* (3ae)**

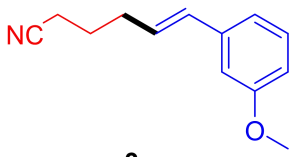
General procedures for synthesis of the compounds 3, Method A: **3ae** (153 mg, 62%), yellow solid. The NMR data is identical to that reported in literature.[5] **^{1}H NMR (500 MHz, $CDCl_3$)** δ 7.60 (d, *J* = 7.5 Hz, 2H), 7.56 (d, *J* = 8.0 Hz, 2H), 7.46 – 7.43 (m, 4H), 7.35 (t, *J* = 7.5 Hz, 1H), 6.51 (d, *J* = 15.5 Hz, 1H), 6.22 – 6.16 (m, 1H), 2.44 – 2.40 (m, 4H), 1.90 – 1.85 (m, 2H);



3af

***(E)-6-(4-methoxyphenyl)hex-5-enenitrile* (3af)**

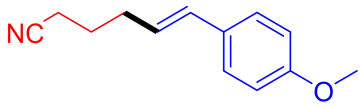
General procedures for synthesis of the compounds 3, Method B: **3af** (125 mg, 62%), yellow oil. The NMR data is identical to that reported in literature.[5] **^{1}H NMR (500 MHz, $CDCl_3$)** δ 7.42 – 7.40 (m, 1H), 7.24 – 7.20 (m, 1H), 6.93 (t, J = 7.5 Hz, 1H), 6.87 (d, J = 8.0 Hz, 1H), 6.78 (d, J = 16.0 Hz, 1H), 6.17 – 6.11 (m, 1H), 3.85 (s, 3H), 2.42 – 2.38 (m, 4H), 1.89-1.83 (m, 2H).



3ag

***(E)-6-(3-methoxyphenyl)hex-5-enenitrile* (3ag)**

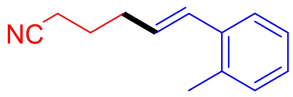
General procedures for synthesis of the compounds 3, Method B: **3ag** (106 mg, 52%), yellow oil. The NMR data is identical to that reported in literature.[5] **^{1}H NMR (500 MHz, $CDCl_3$)** δ 7.23 (t, J = 8.0 Hz, 1H), 6.95 (d, J = 7.5 Hz,1H), 6.89 (s , 1H), 6.80 – 6.78 (m, 1H), 6.44 (d, J = 16.0 Hz, 1H), 6.16 – 6.10 (m, 1H), 3.82 (s, 3H), 2.41 – 2.37 (m, 4H), 1.88 – 1.83 (m, 2H).



3ah

***(E)-6-(4-methoxyphenyl)hex-5-enenitrile* (3ah)**

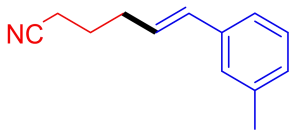
General procedures for synthesis of the compounds 3, Method B: **3ah** (128 mg, 63%), yellow oil. The NMR data is identical to that reported in literature.[5] **^{1}H NMR (500 MHz, $CDCl_3$)** δ 7.29 – 7.28 (m, 2H), 6.87 – 6.84 (m, 2H), 6.40 (d, J = 16.0 Hz, 1H), 6.01 – 5.95 (m, 1H), 3.80 (s, 3H), 2.40 – 2.34 (m, 4H), 1.86 – 1.81 (m, 2H).



3ai

***(E)- 6-(2-methylphenyl)hex-5-enenitrile* (3ai)**

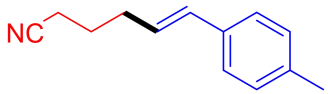
General procedures for synthesis of the compounds 3, Method B: **3ai** (118 mg, 64%), yellow oil. The NMR data is identical to that reported in literature.[5] **^{1}H NMR (500 MHz, $CDCl_3$)** δ 7.41 – 7.40 (m, 1H), 7.16 – 7.04 (m, 3H), 6.68 (d, J = 16.0 Hz, 1H), 6.03 – 5.97 (m, 1H), 2.43 – 2.40 (m, 4H), 2.35 (s, 3H), 1.90 – 1.84 (m, 2H);



3aj

***(E)- 6-(3-methylphenyl)hex-5-enenitrile* (3aj)**

General procedures for synthesis of the compounds 3, Method B: **3aj** (102 mg, 55%), yellow oil. The NMR data is identical to that reported in literature.[5] **^{1}H NMR (500 MHz, $CDCl_3$)** δ 7.10 (t, J = 7.5 Hz, 1H), 7.07 – 7.04(m, 2H), 6.96 – 6.93 (m, 1H), 6.34 (d, J = 15.5 Hz, 1H), 6.05 – 5.99 (m, 1H), 2.30 – 2.28 (m, 4H), 2.25 (s, 3H), 1.78 – 1.72 (m, 2H);



3ak

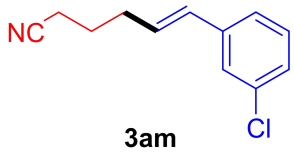
***(E)- 6-(4-methylphenyl)hex-5-enenitrile* (3ak)**

General procedures for synthesis of the compounds 3, Method B: **3ak** (67 mg, 36%), yellow oil. The NMR data is identical to that reported in literature.[5] **^{1}H NMR (500 MHz, $CDCl_3$)** δ 7.24 (d, J = 8.0 Hz, 2H), 7.10 (d, J = 10.0 Hz, 2H), 6.43 (d, J = 16.0 Hz, 1H), 6.10 – 6.04 (dt, J_1 = 15.5 Hz, J_2 = 7.5 Hz, 1H), 2.40 – 2.37 (m, 4H), 2.33 (s, 3H), 1.87 – 1.82 (m, 2H);

3al

***(E)-6-(2-chlorophenyl)hex-5-enenitrile* (3al)**

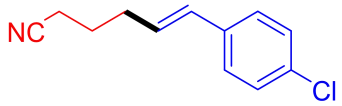
General procedures for synthesis of the compounds 3, Method B: **3al** (41 mg, 20%), yellow oil. The NMR data is identical to that reported in literature.[5] **^{1}H NMR (500 MHz, $CDCl_3$)** δ 7.49 (dd, J_1 = 8.0 Hz, J_2 = 2.0 Hz, 1H), 7.36 – 7.35 (m, 1H), 7.21 – 7.15 (m, 2H), 6.83 (d, J = 16.0 Hz, 1H), 6.12 (dt, J_1 = 16.0 Hz, J_2 = 7.0 Hz, 1H), 2.44 – 2.40 (m, 4H), 1.90 – 1.87 (m, 2H);



3am

***(E)-6-(3-chlorophenyl)hex-5-enenitrile* (3am)**

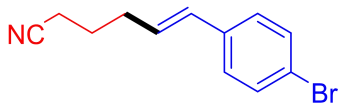
General procedures for synthesis of the compounds 3, Method B: **3am** (66 mg, 32%), yellow oil. The NMR data is identical to that reported in literature.[5] **^{1}H NMR (500 MHz, $CDCl_3$)** δ 7.33 (s, 1H), 7.25 – 7.17 (m, 3H), 6.41 (d, J = 16.0 Hz, 1H), 6.15 (dt, J_1 = 15.5 Hz, J_2 = 7.0 Hz, 1H), 2.42 – 2.37 (m, 4H), 1.88 – 1.82 (m, 2H);



3an

***(E)-6-(4-chlorophenyl)hex-5-enenitrile* (3an)**

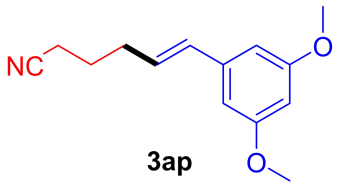
General procedures for synthesis of the compounds 3, Method B: **3an** (98 mg, 48%), yellow oil. The NMR data is identical to that reported in literature.[5] **^{1}H NMR (500 MHz, $CDCl_3$)** δ 7.31 – 7.24 (m, 4H), 6.42 (d, *J* = 16.0 Hz, 1H), 6.14 – 6.10 (m, 1H), 2.41 – 2.37 (m, 4H), 1.88 – 1.84 (m, 2H);



3ao

***(E)-6-(4-bromophenyl)hex-5-enenitrile* (3ao)**

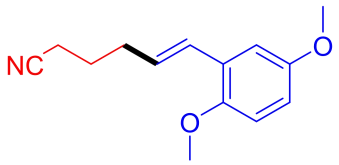
General procedures for synthesis of the compounds 3, Method B: **3ao** (105 mg, 42%), yellow oil. The NMR data is identical to that reported in literature.[5] **^{1}H NMR (500 MHz, $CDCl_3$)** δ 7.46 – 7.39 (m, 2H), 7.23 – 7.18 (m, 2H), 6.40 (d, *J* = 16.0 Hz, 1H), 6.16 – 6.09 (m, 1H), 2.41 – 2.36 (m, 4H), 1.87 – 1.84 (m, 2H);



3ap

***(E)-6-(3,5-dimethoxyphenyl)hex-5-enenitrile* (3ap)**

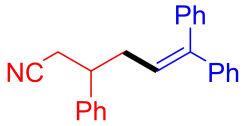
General procedures for synthesis of the compounds 3, Method B: **3ap** (144 mg, 62%), yellow oil. The NMR data is identical to that reported in literature.[6] **^{1}H NMR (500 MHz, $CDCl_3$)** 6.98 (s, 2H), 6.89 (s, 1H), 6.41 (d, *J* = 16.0 Hz, 1H), 6.14 – 6.08 (m, 1H), 2.41 – 2.36 (m, 4H), 2.31 (s, 6H), 1.88 – 1.82 (m, 2H);



3aq

***(E)-6-(2,5-dimethoxyphenyl)hex-5-enenitrile* (3aq)**

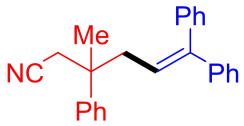
General procedures for synthesis of the compounds 3, Method B: **3aq** (119 mg, 51%), yellow oil. The NMR data is identical to that reported in literature.[6] **^{1}H NMR (500 MHz, $CDCl_3$)** 6.96 (d, *J* = 3.0 Hz, 1H), 6.81 – 6.73 (m, 3H), 6.16 – 6.10 (m, 1H), 3.81 (s, 3H), 3.79 (s, 3H),2.42 – 2.38 (m, 4H), 1.89 – 1.83 (m, 2H);



3ba

***3,6,6-triphenylhex-5-enenitrile* (3ba)**

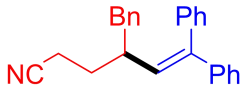
General procedures for synthesis of the compounds 3, Method A: **3ba** (243 mg, 75%), yellow oil. The NMR data is identical to that reported in literature.[3] **^{1}H NMR (500 MHz, $CDCl_3$)** δ 7.43 – 7.37 (m, 5H), 7.33 – 7.25 (m, 4H), 7.20 – 7.15 (m, 4H), 7.11 – 7.10 (m, 2H), 5.96 (t, *J* = 7.5 Hz, 1H), 3.16 – 3.13 (m, 1H), 2.68 – 2.56 (m, 4H);



3ca

3-methyl-3,6,6-triphenylhex-5-enenitrile **(3ca)**

General procedures for synthesis of the compounds 3, Method A: **3ca** (236 mg, 70%), yellow oil. The NMR data is identical to that reported in literature.[3] **^{1}H NMR (500 MHz, $CDCl_3$)** δ 7.41 – 7.35 (m, 5H), 7.32 – 7.29 (m, 3H), 7.22 – 7.21 (m, 3H), 7.11 – 7.06 (m, 4H), 5.78 (t, J = 7.0 Hz, 1H), 2.70 – 2.67 (m, 2H), 2.61 – 2.57 (m, 2H), 1.55 (s, 3H);



3da

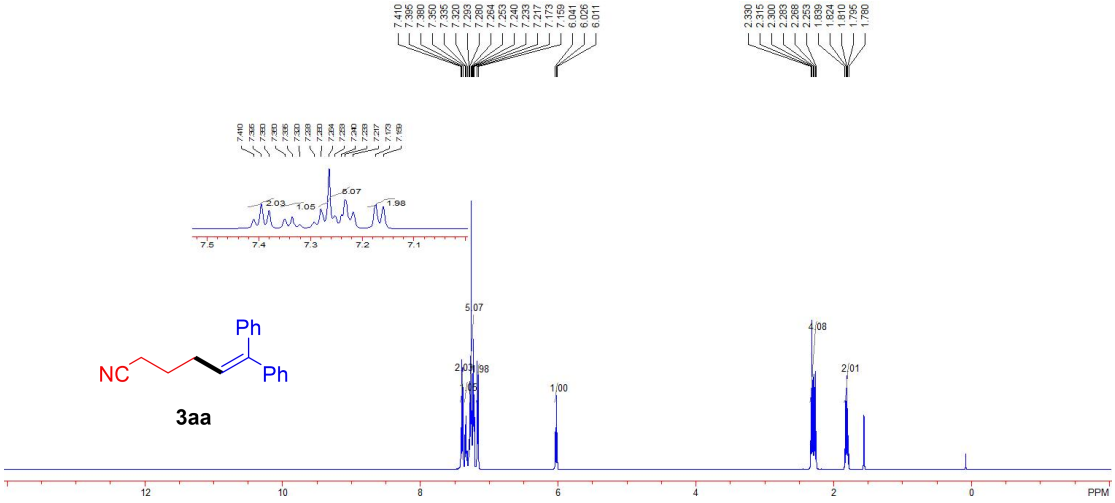
4-benzyl-6,6-diphenylhex-5-enenitrile **(3da)**

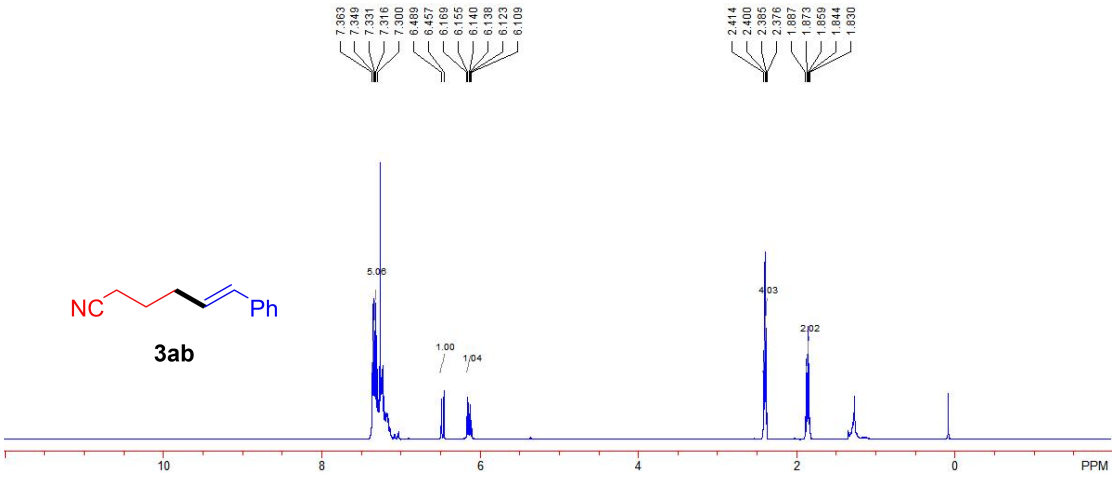
General procedures for synthesis of the compounds 3, Method A: **3da** (273 mg, 81%), yellow oil. The NMR data is identical to that reported in literature.[3] **^{1}H NMR (500 MHz, $CDCl_3$)** δ7.35 – 7.28 (m, 5H), 7.26 – 7.15 (m, 4H), 7.05 – 7.03 (m, 2H), 6.81 – 6.79 (m, 2H), 5.83 (d, J = 10.0 Hz, 1H), 2.76 – 2.66 (m, 2H), 2.55 – 2.51 (m, 1H), 2.38 – 2.32 (m, 1H), 2.19 – 2.12 (m, 1H), 1.85 – 1.81 (m, 1H), 1.71 – 1.65 (m, 1H).

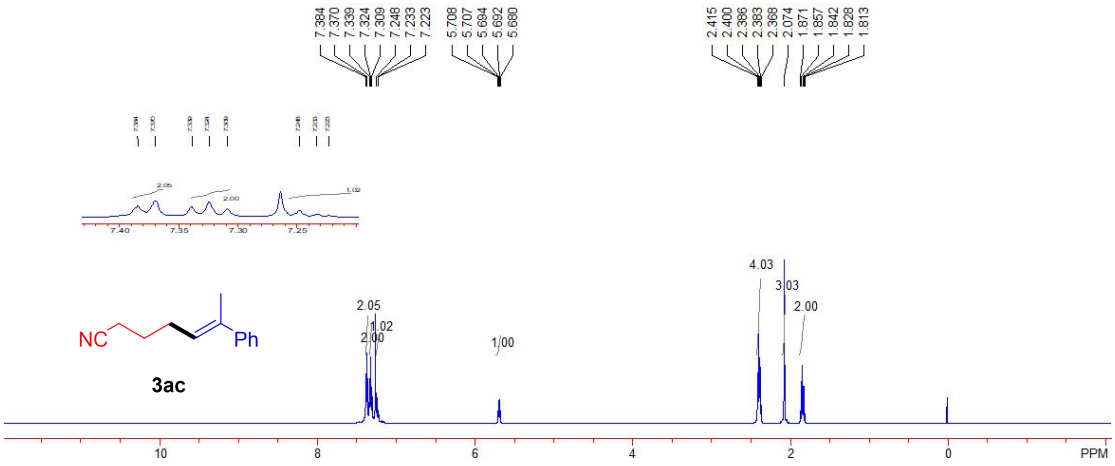
References

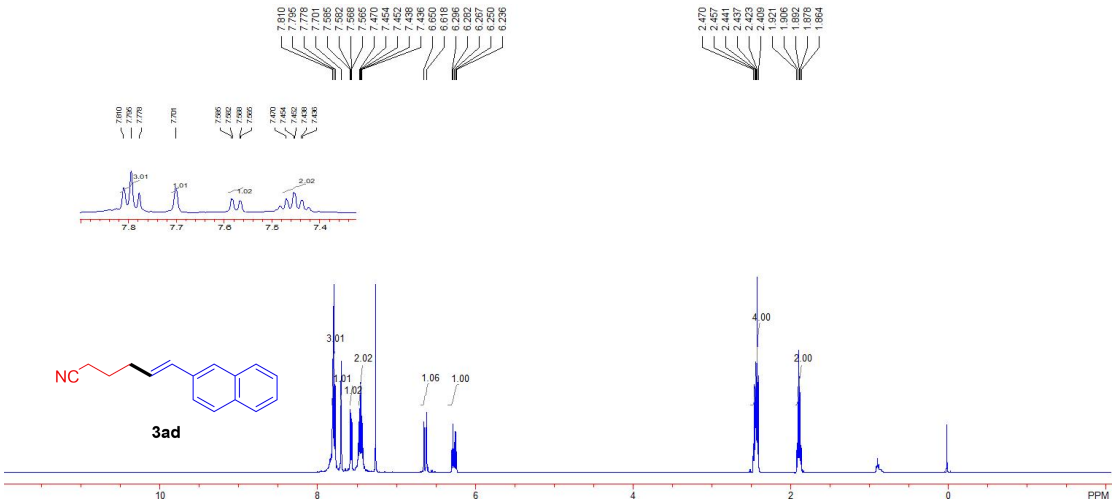
1. Cho H; Iwama Y; Sugimoto K; Mori S; Tokuyama H. *J Org Chem.* **2010**; *75*: 627.
2. Xu H-J; Zhu F-F; Shen Y-Y; Wan X; Feng Y-S. *Tetrahedron.* **2012**; *68*: 4145.
3. Zhao B; Shi Z. *Angew. Chem. Int. Edit.* **2017**; *56*: 12727.
4. Lu X Y; Xia Z J; Gao A; Liu Q L; Jiang R C; Liu C C. *J Org Chem.* **2021**; *86*: 8829.
5. Gao J; Ye Z P; Liu Y F; He X C; Guan J P; Liu F; Chen K; Xiang H Y; Chen X Q; Yang H. *Org Lett.* **2022**; *24*: 4640.
6. Gigant N; Backvall J E. *Org Lett.* **2014**; *16*: 4432.

NMR spectra





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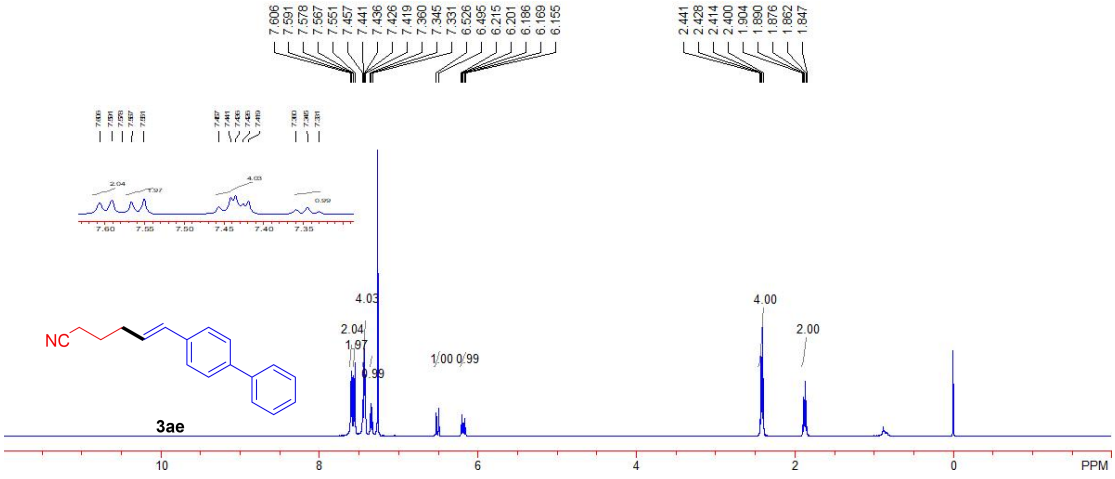
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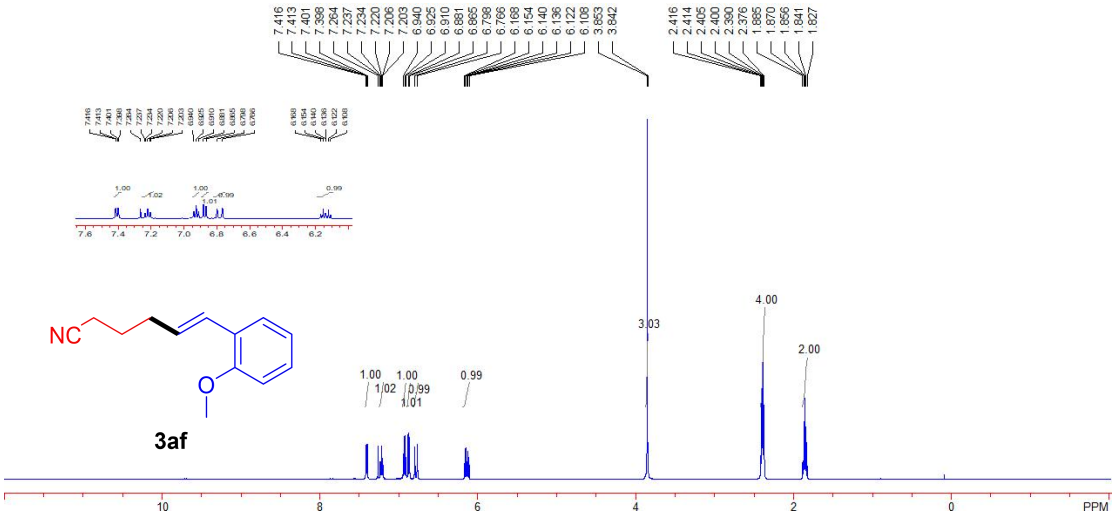
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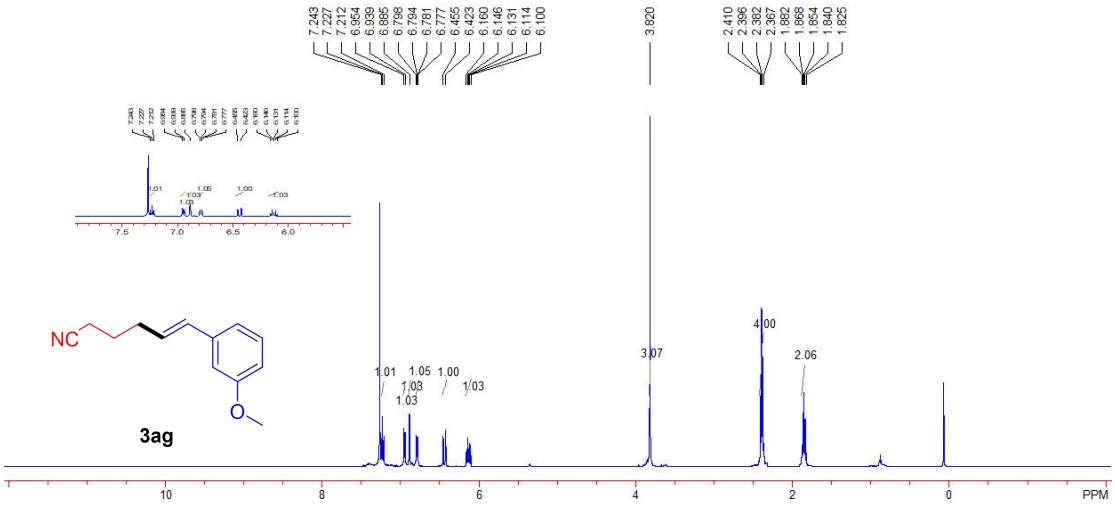
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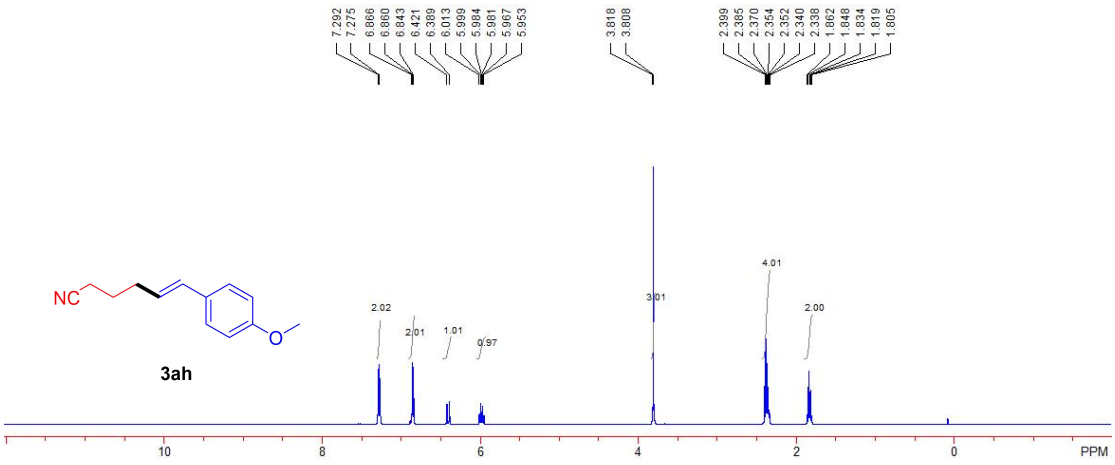
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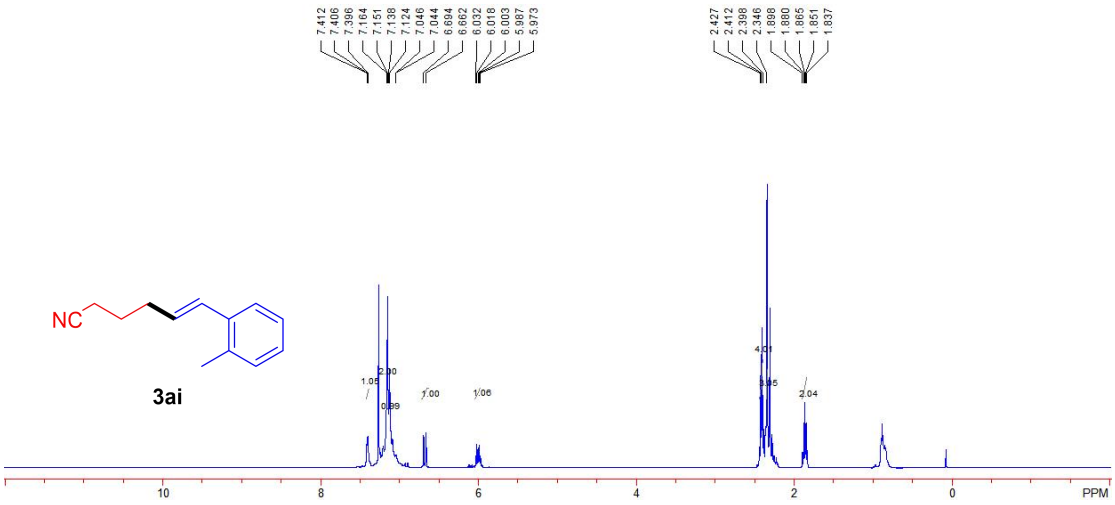
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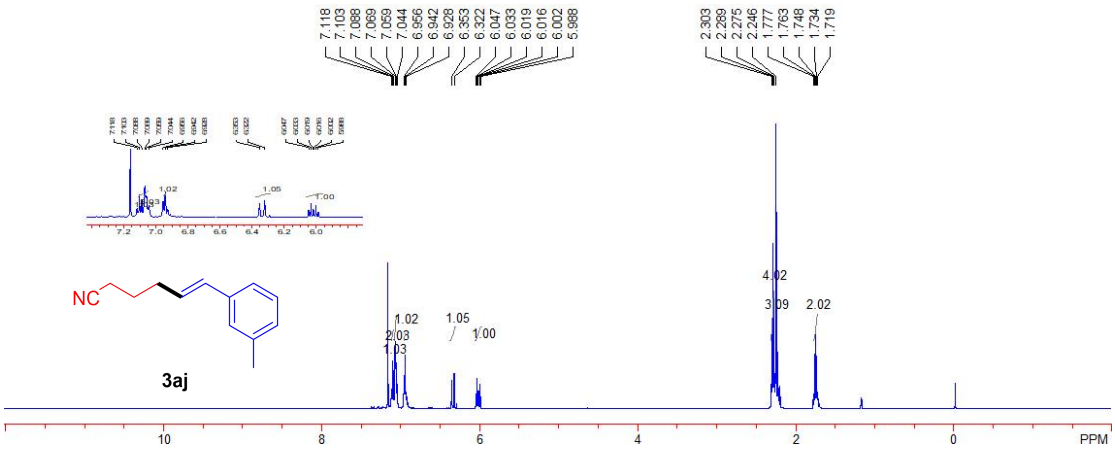
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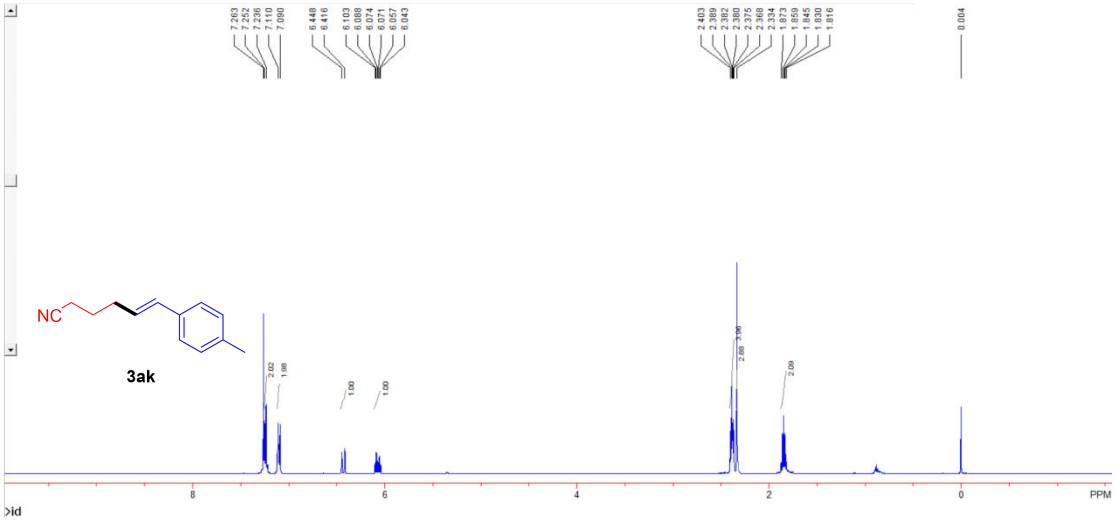
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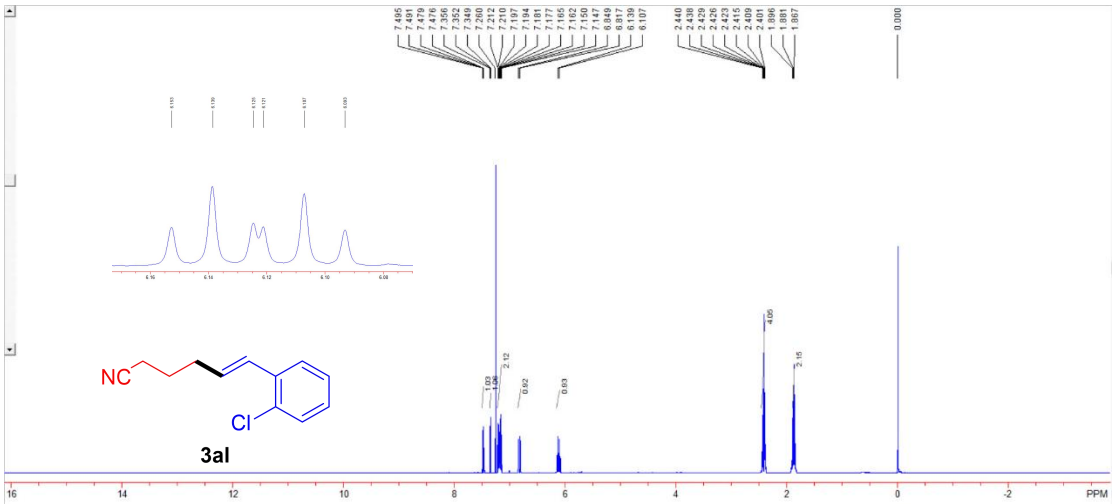
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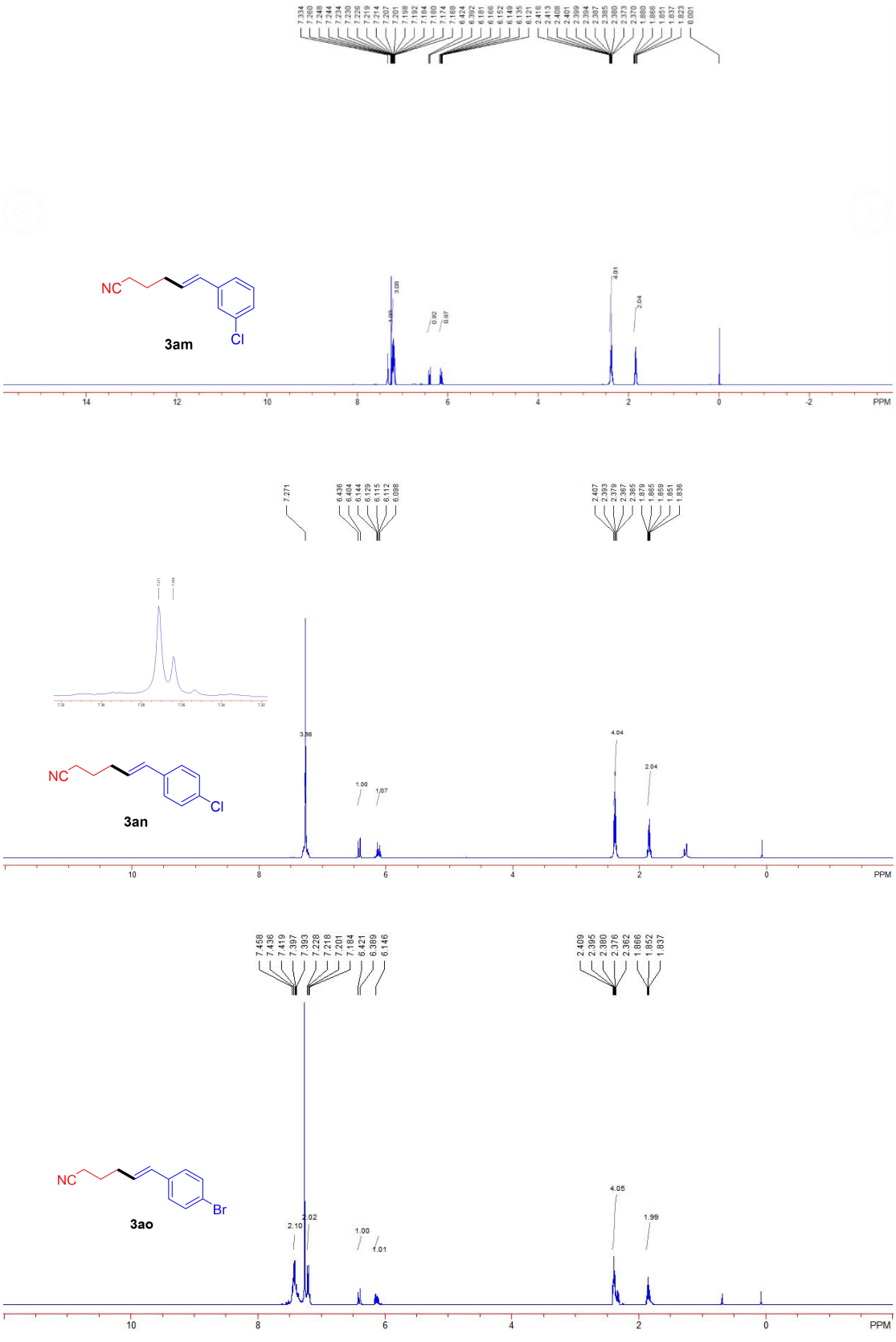
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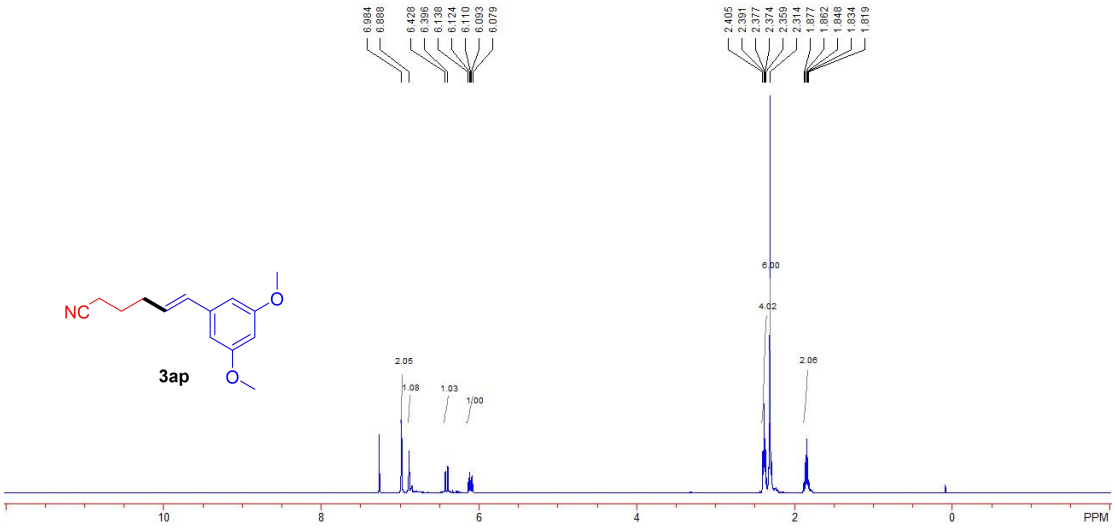
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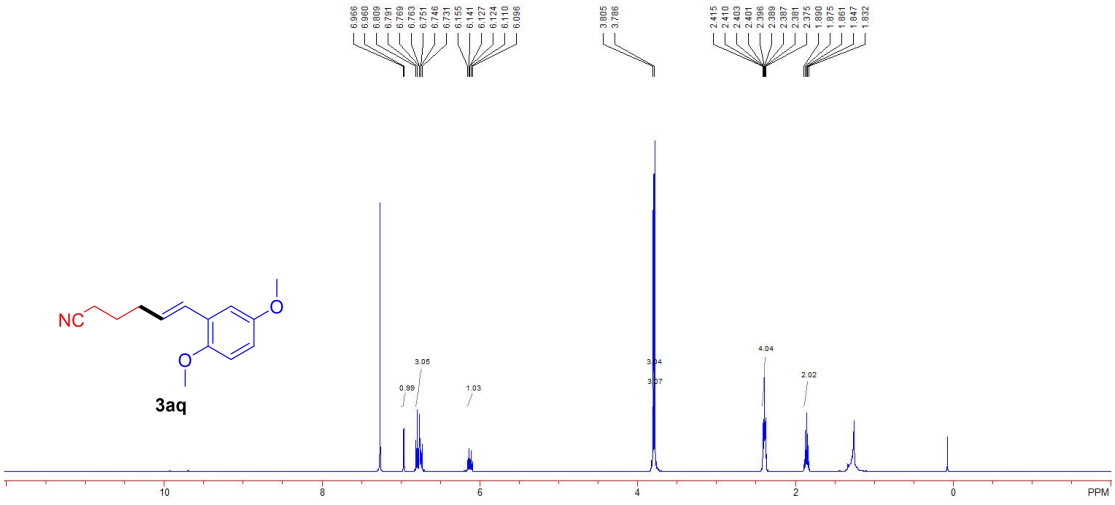
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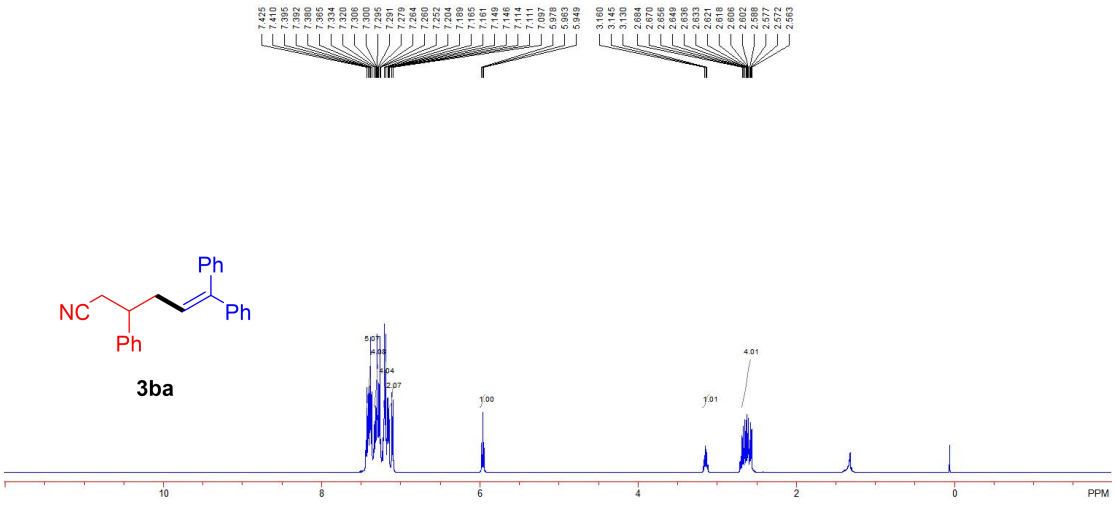
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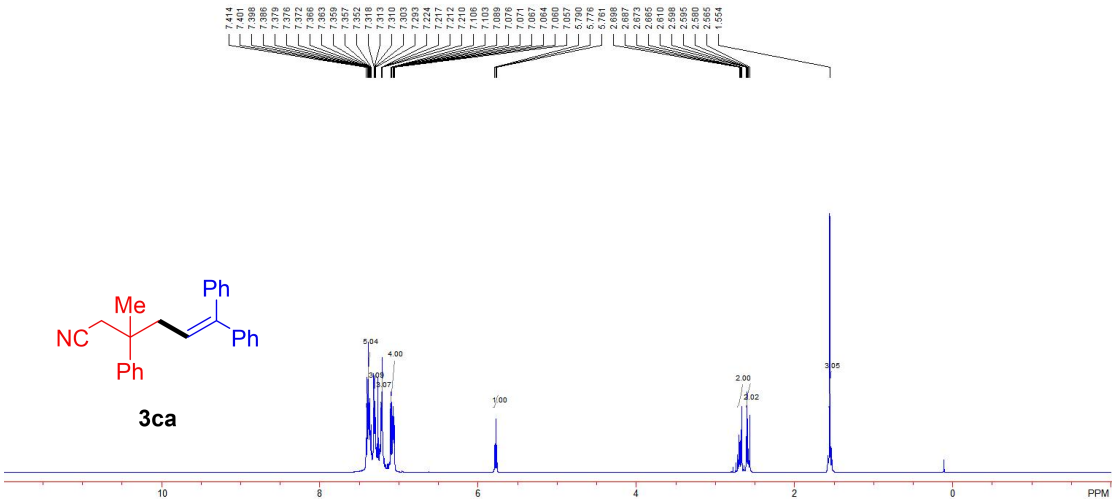
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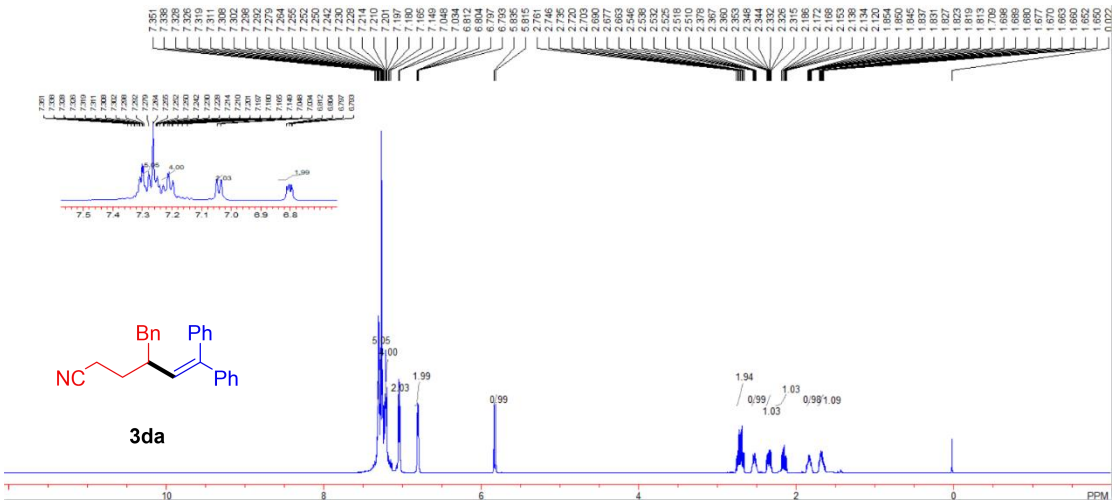
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NC
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6
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PPM