Efficient Preparation of Polyunsaturated and Functionalized Acetylenic Ketones from Alkynylmanganese Bromides

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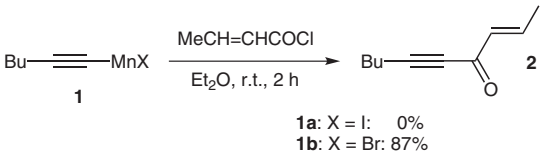
Abstract: α,β-Acetylenic ketones are efficiently prepared, under mild conditions, by reacting alkynylmanganese compounds with acyl chlorides. The procedure is especially useful for preparing polyfunctionalized and polyunsaturated α,β-acetylenic ketones.

Key words: organomanganese, acylation, acetylenic ketones, acyl chlorides

Acetylenic ketones are very useful synthetic intermediates and they are also present as subunits in several natural or bioactive products.[1] The main routes used to prepare these compounds are the oxidation of allylic alcohols or propargylic methylene groups,[2] and the acylation of various alkynylmetal derivatives.[3] The latter route has been extensively used, with the most efficient applications involving the acylation of alkynylsilanes,[4] owing to its large scope. The direct acylation of terminal alkynes in the presence of a strong base (Et_3N or *i*-Pr_2EtN) and a metal salt[5] (Cu, Zn, Pd) has also been recently developed, although it should be noted that only non-enolizable ketones can be obtained by the last procedure. Acylation of organomanganese reagents is a very efficient and simple method that can be used to prepare a vast array of simple and functionalized ketones.[6] The reaction was first developed by using organomanganese iodides in diethyl ether, it takes place under mild conditions and generally leads to high yields.[7] Later, we reported that organomanganese chlorides, prepared from manganese chloride in tetrahydrofuran (THF), can also be used sucessfully.[8] This is a clear improvement for preparative chemistry since, in contrast to manganese iodide, manganese chloride is a very common and inexpensive commercial material. In THF, aliphatic, vinylic, allylic, and aromatic organomanganese chlorides readily react with carboxylic acid chlorides, which are the most common acylating agents. However, in this solvent, alkynylmanganese halides react sluggishly and lead to poor yields. In fact, in this case, it is much more efficient to perform the acylation in diethyl ether and many simple acetylenic ketones were thus prepared in good yields from alkynylmanganese iodides.[7] Unfortunately, we have observed that the presence of iodides in the reaction mixture is sometimes very detrimental, for instance in preparing polyunsaturated acetylenic ketones. Thus, ketone **2** cannot be obtained from 1-hexynylmanganese iodide (**1a**; Equation 1). We have previously shown that this drawback can be avoided by using 1-hexynylmanganese bromide (**1b**) instead of **1a**.[9]

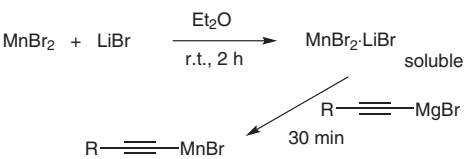


Equation 1 Acylation of hexynylmanganese iodide **1a** and bromide **1b** with crotyl chloride

Moreover, it is much more advantageous to use manganese bromide, which is less expensive and more readily available than manganese iodide. Until now, only one example of acylation of alkynylmanganese bromides by carboxylic acid chlorides has been described.[9] Herein, we report that such a reaction is a very general way to efficiently prepare various polyunsaturated and highly functionalized acetylenic ketones.

Alkyl- and arylethynylmanganese bromides are easily and quantitatively prepared in diethyl ether from alkyl- and arylacetylenes **3** by metallation with *n*-butyllithium (Bu-Li·LiBr prepared in diethyl ether) then transmetallation with manganese bromide (Table 1). The presence of lithium bromide in the reaction mixture is very important since it allows the $MnBr_2$ to be solubilized by forming the ate-complex $MnBr_2$·LiBr. Further acylation with acyl chlorides leads to conjugated alkynones **4** in good yields. It should be noted that functionalized (Table 1, entries 6 and 7) and conjugated ethylenic or dienic (entries 4 and 5) carboxylic acid chlorides were successfully employed.

Alkynylmanganese bromides can also be prepared from the corresponding Grignard reagents. However, in this case it is then necessary to use the soluble ate-complex $MnBr_2$·LiBr to perform the transmetallation (Scheme 1). It should be noted that the metallation of 1-alkyne with Grignard reagents is less efficient than with organolithium



Scheme 1 Preparation of alkynylmanganese bromides via the soluble ate-complex $MnBr_2$·LiBr

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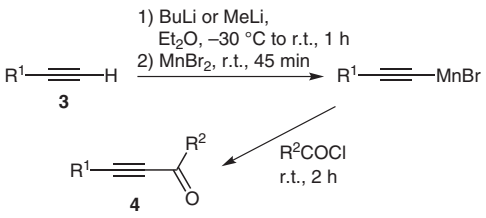
Table 1 Preparation of Akynyl Ketones from Alkynylmanganese Bromides



Entry	Alkynyl ketone **4**	Yield (%)[a]
1	**4a**	95
2	**4b**	90
3	**4c**	86
4	**4d**	97
5	**4e**	79
6	**4f**	83
7	**4g**	80
8	**4h**	76

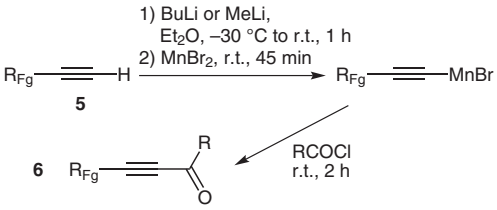
[a] All products were isolated by distillation.

compounds. Thus, the organolithium route is generally preferred.

Various alkoxy-, alkylthio-, chloro- and bromoalkynylmanganese compounds **6** were successfully prepared from the corresponding terminal alkynes **5**. They are stable at room temperature and react chemoselectively with various functionalized carboxylic acid chlorides to give, in satisfactory yields, a vast array of polyfunctionalyzed alkynyl ketones having functionality on both sides of the keto group (Table 2).

Acetylenic ketones, for example, 1-undecyn-8-one, cannot be lithiated, however, it is possible to use the corresponding ketal **7**. After a one-pot sequence involving lithiation–transmetallation–acylation, the expected acetylenic ketone **8** was obtained in satisfactory yield (Equation 2).

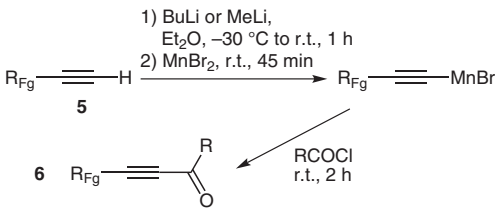
Table 2 Preparation of Functionalized Acetylenic Ketones **6**



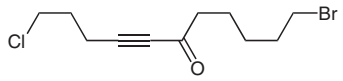
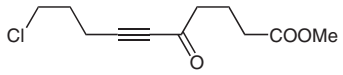
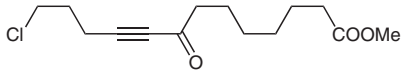
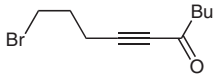
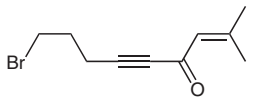
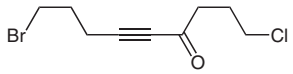
Fg = MeO, BuS, PhS, Cl, and Br.

Entry	Alkynyl ketone **6**	Yield (%)[a]
1	**6a**	80
2	**6b**	50
3	**6c**	49
4	**6d**	73
5	**6e**	41
6	**6f**	66
7	**6g**	73
8	**6h**	69
9	**6i**	63
10	**6j**	71
11	**6k**	82
12	**6l**	78
13	**6m**	56
14	**6n**	68

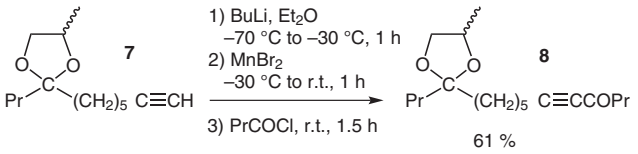
Table 2 Preparation of Functionalized Acetylenic Ketones **6** (continued)



Fg = MeO, BuS, PhS, Cl, and Br.

Entry	Alkynyl ketone **6**	Yield (%)[a]
15	**6o** 	61
16	**6p** 	45
17	**6q** 	73
18	**6r** 	79
19	**6s** 	77
20	**6t** 	53

[a] All products were isolated by distillation.



Equation 2 Preparation of akynyl ketones **8** from the ketal of 1-undecyn-8-one **7**

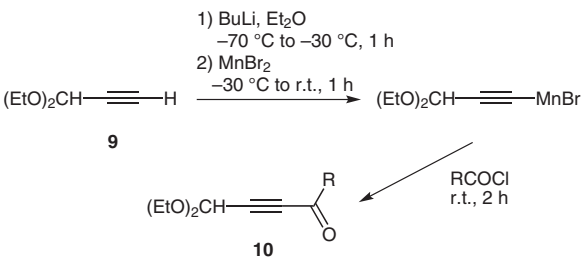
Similarly, the propargylaldehyde diethylacetal **9** was efficiently converted into a range of polyfunctionnalized acetylenic ketones **10** (Table 3).

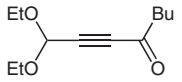
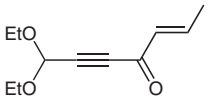
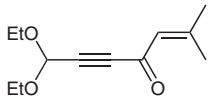
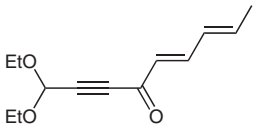
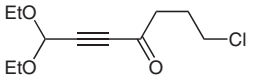
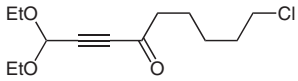
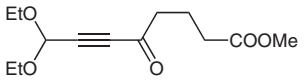
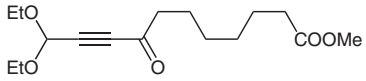
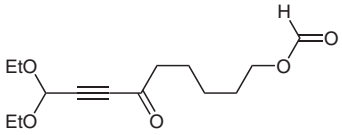
Acetylenic alcohols **11** can be protected before metallation, for instance as a methyl ether (Table 2, entries 1–5). However, it is also possible to convert them directly into the corresponding alkynylmanganese bromide alcoholate **12** (Table 4). The acylation of **12** readily takes place but the alcoholate group also reacts to give the acetylenic keto esters **13**.

In the same way, 1-ethynylcyclohexanol (**14**) can be efficiently converted into the acetylenic keto ester **15** (Scheme 2).

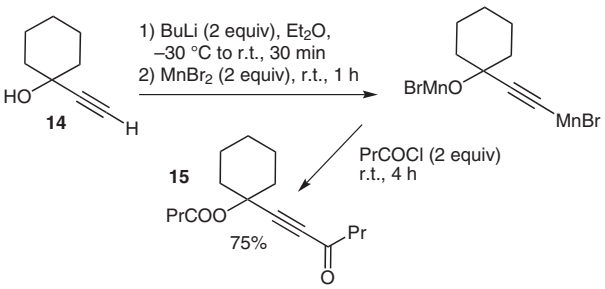
In conclusion, the acylation of alkynylmanganese bromides is a very efficient procedure that can be used to prepare various highly polyunsaturated or polyfunctionalized conjugated acetylenic ketones. The reaction can be easily

Table 3 Preparation of Acetylenic Ketones from Propargylaldehyde Diethyacetal **9**



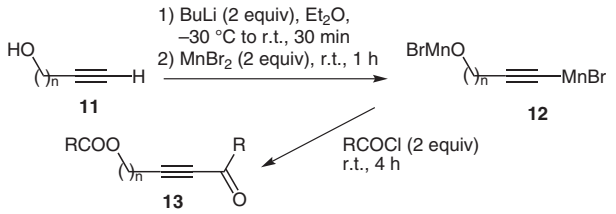
Entry	Alkynyl ketones **10**	Yield (%)[a]
1	**10a** 	80
2	**10b** 	75
3	**10c** 	87
4	**10d** 	78
5	**10e** 	53
6	**10f** 	71
7	**10g** 	71
8	**10h** 	65
9	**10i** 	82

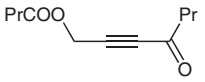
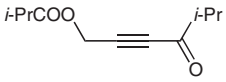
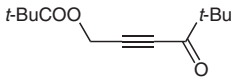
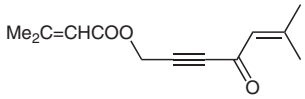
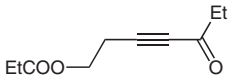
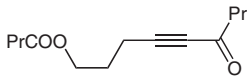
[a] All products were isolated by distillation.



Scheme 2 Preparation of a keto ester from 1-ethynylcyclohexan-1-ol

Table 4 Preparation of Acetylenic Keto Esters **13**



Entry	Alkynyl ketone **13**	Yield (%)[a]
1	**13a** 	77
2	**13b** 	76
3	**13c** 	70
4	**13d** 	78
5	**13e** 	52
6	**13f** 	71

[a] All products were isolated by distillation.

performed on a large scale because the simple and functionalized alkynylmanganeses are stable at room temperature and smoothly react with carboxylic acid chlorides without troublesome exothermic effects.

Et_2O was distilled from sodium/benzophenone under a nitrogen atmosphere before use. Manganese powder (Mn 99%, 20–50 mesh) was purchased from STREM.

All reactions were performed under a nitrogen atmosphere. Products were purified by distillation, purity >95% (GC analysis). All products gave satisfactory analyses, ^1H and ^{13}C NMR (Jeol MH100, Jeol FX90Q and Jeol GSX400 spectrometers), IR (Perkin-Elmer 457 spectrometer) and GC (capillary column OV1, 25 m × 0.53 mm, 0.5 mm film thickness).

$MnBr_2$

Anhydrous $MnBr_2$ can be obtained from commercial sources. However, in a very convenient procedure, the material can be prepared according to the following procedure:

To a suspension of manganese powder (20–50 mesh; 2 mol, 110 g) in anhydrous EtOAc (ethanol free; 1.5 L) was added dropwise under vigorous stirring, bromine (2.02 mol, 323.2 g). The reaction was exothermic and the temperature of the reaction mixture was kept below 35 °C with an ice bath. Stirring was then continued for 3 h at 30 °C. The precipitate was separated by filtration and washed several times with EtOAc until a colorless filtrate was obtained, then with Et_2O (200 mL). The solid was then dried under vacuo (0.01 torr) under progressive heating until 200 °C. It is then finely crushed and dried again under vacuo (200 °C, 6 h). The yield was generally better than 90% (>390 g). The product is hygroscopic and must be stored in the absence of moisture.

Preparation of RC≡CMnBr from RC≡CH; General Procedure

To a solution of RC≡CH (50 mmol) in Et_2O (40 mL), was added BuLi (1.2 M in Et_2O, 52 mmol), keeping the temperature between –50 to –20 °C (see Table 5). Stirring was continued at this temperature for 10 min, then the reaction mixture was allowed to warm to r.t. and stirred for 30 min to 1.5 h (see Table 5). After addition of $MnBr_2$ (55 mmol) at –30 °C, stirring was continued for 1–4 h (see Table 5) at r.t. The alkynylmanganese bromide RC≡CMnBr was generally obtained as a beige or brownish suspension.

Acylation of RC≡CMnBr; General Procedure

To a suspension of RC≡CMnBr (50 mmol) in Et_2O (80 mL) was added R′COCl (50 mmol) dropwise between –20 and –30 °C. The reaction mixture was then allowed to warm to r.t. and stirred for 1–4 h (the progress of the reaction was monitored by GC analysis, see Table 5) then quenched by addition of a 1 N HCl (100 mL) at –10 °C. After extraction with petroleum ether (2 × 50 mL) the combined organic layers were dried with $MgSO_4$ and the solvents were removed under vacuo. The alkynyl ketones were isolated by distillation (Table 6).

Table 5 Reaction Conditions (General Procedure)

RC≡CH to RC≡CCOR′	Metallation by BuLi Temp (°C)	Time (min)	Transmetallation Li/Mn Temp (°C)	Time (h)	Acylation Temp (°C)	Time (h)
3 to **4**	–30 then r.t.	60	0 then r.t.	1	–20 then r.t.	2
5 to **6a–e**	–70 then r.t.	45	–10 then r.t.	4	–30 then r.t.	1–3
5 to **6f–i**	–70 then r.t.	45	–10 then r.t.	2	–30 then r.t.	1–3
5 to **6j–q**	–80 then –30	90	–30 then r.t.	2	–30 then r.t.	1–4
5 to **6r–t**	–30 then r.t.	60	–30 then r.t.	2	–30 then r.t.	1–4
7 to **8**	–60 then –30	60	–50 then r.t.	1–3[a]	–30 then r.t.	2–3
9 to **10**	–60 then –30	60	–50 then r.t.	1–3	–30 then r.t.	2–3
11 to **12**	–50 then r.t.	30	–10 then r.t.	2	–30 then r.t.	4
14 to **15**	–50 then r.t.	30	–10 then r.t.	2	–30 then r.t.	4

[a] Until a solution was obtained.

Table 6 Physical and Spectral Data of Acetylenic Ketones

Product	Bp (°C/torr)	n_D^T	IR (cm^{-1})				^{13}C NMR (ppm)[d]
			C=O	C≡C	C=C	C-O-C	
2	55/0.1	1.4830[a]	1650	2200	1630		178.30, 148.90, 134.0, 94.25, 79.10, 30.00, 22.10, 18.65, 18.30, 13.55
4a	42/0.01	1.4480[a]	1670	2210			187.80, 93.60, 81.20, 45.40, 26.40, 22.30, 21.55, 20.95, 13.90, 13.50
4b	58/0.01	1.4819[a]	1675	2200			190.70, 94.20, 88.45, 52.30, 29.00, 28.50 (2C), 26.10, 25.60 (2C), 21.60, 13.55
4c	60/0.01	1.5430[a]	1640	2200	1450, 1580		177.95, 136.95, 133.85, 129.45 (2C), 128.50 (2C), 96.65, 79.75, 29.88, 22.10, 18.85, 13.55
4d	62/0.05	1.4940[a]	1650	2210	1615		176.40, 156.90, 126.25, 92.15, 83.46, 30.05, 27.70, 22.10, 20.90, 18.70, 13.60
4e	60/0.01	1.5380[a]	1625	2210	1580		178.30, 148.15, 141.70, 130.20, 130.05, 93.95, 79.40, 30.00, 22.05, 18.90, 18.65, 13.53
4f	88–89/0.05	1.4640[a]	1670, 1735	2210			186.60, 173.15, 94.10, 80.90, 51.40, 44.50, 32.80, 29.95, 22.10, 19.30, 18.60, 13.55
4g	53/0.01	1.5762[a]	1675	2200	1490, 1175		184.15, 133.00 (2C), 130.75, 128.65 (2C), 119.90, 90.05, 88.30, 32.60
4h	70/0.05	1.4473[c]	1680	2240			187.45, 102.30, 97.10, 45.30, 31.70, 29.00 (2C), 24.05, 22.65, 14.05, –0.75 (3C)
6a	65/11	1.4975[c]	1655	2220	1615	1110, 1150	175.50, 158.65, 125.65, 87.70, 85.85, 59.60, 57.85, 27.75, 21.10
6b	100/0.3	1.5440	1630	2220		1110, 1255	177.60, 149.10, 142.65, 130.10, 129.45, 87.70, 83.85, 59.60, 57.90, 18.90
6c	70/0.1	1.4798	1680	2220		1110	185.65, 88.15, 85.15, 59.50, 58.00, 43.95, 42.35, 26.60
6d	70/0.01	1.4727	1675	2200		1100	186.80, 87.70, 85.30, 59.50, 57.90, 45.10, 44.70, 32.35, 26.20, 23.15
6e	110/0.01	1.4598	1655, 1730	2205		1105	186.95, 173.90, 87.50, 85.40, 59.50, 57.85, 51.35, 45.25, 33.90, 28.80, 28.60, 24.75, 23.75
6f	95/0.01	1.4960[b]	1675	2220		1740 (C-S-C)	187.45, 88.60, 81.90, 45.30, 31.70, 31.10, 26.15, 22.15, 21.95, 19.35, 13.80, 13.70
6g	90/0.01	1.5740[b]	1675	2220	1480		187.65, 134.05, 130.85 (2C), 129.10 (2C), 127.50, 88.15, 82.15, 38.70, 22.85, 7.80
6h	115/0.01	1.4568	1670	2210	1435, 1480		191.55, 135.80, 129.50 (2C), 128.90 (2C), 126.20, 93.25, 80.35, 42.90, 32.60, 27.25, 17.90 (2C), 17.80
6i	150/0.01	1.5749	1640	2210	1435, 1475		178.10, 148.95, 135.80, 133.85, 129.45 (2C), 128.90 (2C), 126.15, 92.70, 79.60, 32.60, 27.25, 18.25, 17.80
6j	63/0.01	1.4719[a]	1670	2210			187.75, 91.50, 81.52, 45.30, 43.30, 30.65, 26.25, 22.20, 16.40, 13.80
6k	85/0.05	1.5074	1680	2210	1420		178.10, 149.25, 133.85, 92.00, 79.65, 43.45, 30.65, 18.30, 16.40
6l	80/0.01	1.5605	1620	2210	1585		178.20, 148.55, 142.15, 130.05, 129.75, 91.75, 79.90, 43.40, 30.55, 18.90, 16.45

Table 6 Physical and Spectral Data of Acetylenic Ketones (continued)

Product	Bp (°C/torr)	n_D^T	IR (cm^{-1})				^{13}C NMR (ppm)[d]
			C=O	C≡C	C=C	C-O-C	
6m	135/0.05	1.5664	1640	2190	1575, 1595		177.75, 136.75, 134.00, 129.45 (2C), 128.55 (2C), 94.25, 80.20, 43.40, 30.50, 16.60
6n	96/0.1	1.4900	1670	2200			187.25, 91.85, 81.35, 45.20, 44.70, 43.35, 32.35, 30.55, 26.20, 23.25, 16.40
6o	130/0.01	1.5072[a]	1670	2200			187.10, 91.75, 81.30, 45.15, 43.40, 33.55, 32.40, 30.45, 27.40, 23.05, 16.35
6p	110.0.05	1.4822	1670, 1735	2200			186.60, 173.15, 92.05, 81.10, 51.50, 44.40, 43.35, 32.80, 30.55, 19.20, 16.35
6q	120/0.01	1.4749	1670, 1735	2200			187.50, 173.80, 91.55, 81.45, 51.30, 45.40, 43.35, 33.90, 30.60, 28.80, 28.60, 24.75, 23.85, 16.40
6r	70/0.01	1.4879[a]	1670	2200			187.60, 91.25, 81.50, 45.25, 31.80, 30.65, 26.20, 22.15, 17.65, 13.80
6s	68/0.05	1.5273	1645	2200	1610		176.10, 157.55, 125.95, 89.70, 83.85, 31.95, 30.70, 27.70, 21.00, 17.70
6t	84/0.01	1.5065	1670	2205			186.00, 92.20, 81.25, 44.00, 42.35, 31.90, 30.50, 26.65, 17.65
8	105/0.05	1.4638	1670	2220		1090, 1170	187.75, 111.90, 93.75, 81.05, 72.15, 71.40, 47.40, (40.05, 40.35)[e], (37.55, 37.70)[e], 29.15, 27.80, (23.10, 23.45)[e], 18.85, 18.30, 17.65, (17.00, 17.35)[e], 14.40, 13.55
10a	80/0.01	1.4445[b]	1685	2200		1120	186.80, 91.20, 84.95, 82.70, 61.45 (2C), 45.25, 25.95, 22.15, 15.10 (2C), 13.80
10b	85/0.1	1.4680	1650	2220	1440	1250, 1050	177.20, 150.35, 133.65, 91.30, 85.80, 81.05, 61.55 (2C), 18.45, 15.10 (2C)
10c	79/0.01	1.4850	1660	2230	1620	1060, 1120	212.20, 175.25, 125.60, 91.30, 85.00, 83.40, 61.45 (2C), 27.80, 21.25, 15.10 (2C)
10d	114/0.01	1.5155	1630	2220	1590	1060, 1120	177.35, 149.25, 142.70, 130.15, 129.55, 91.35, 85.65, 81.45, 61.55 (2C), 18.95, 15.10 (2C)
10e	93/0.01	1.4625	1680	2220		1050, 1130	185.35, 91.15, 85.65, 82.40, 61.55 (2C), 42.45, 43.85, 26.50, 10.05 (2C)
10f	100/0.01	1.4615	1680	2220		1050	186.45, 91.10, 85.25, 82.55, 61.45 (2C), 45.20, 44.60, 32.35, 26.20, 23.05, 15.05 (2C)
10g	104/0.01	1.4554[a]	1680, 1740	2220		1050, 1140	185.85, 173.05, 91.20, 85.40, 82.55, 61.55 (2C), 51.50, 44.45, 32.70, 19.00, 15.10 (2C)
10h	115/0.01	1.4541[a]	1680, 1740	2220		1050, 1200	186.60, 173.70, 91.15, 85.10, 82.60, 61.45 (2C), 51.25, 45.35, 33.90, 28.85, 28.60, 24.75, 23.65, 15.05 (2C)
10i	100/0.01	1.4550[a]	1680, 1725	2220		1050, 1150	186.45, 160.95, 91.15, 85.20, 82.55, 63.50, 61.50 (2C), 45.25, 28.35, 25.30, 23.35, 15.05 (2C)
13a	88/0.01	1.4535[a]	1675, 1740	2220		1160	186.80, 172.40, 85.30, 84.85, 51.25, 47.15, 35.70, 18.40, 17.40, 13.60, 13.50

Table 6 Physical and Spectral Data of Acetylenic Ketones (continued)

Product	Bp (°C/torr)	n_D^T	IR (cm^{-1})				^{13}C NMR (ppm)[d]
			C=O	C≡C	C=C	C-O-C	
13b	77/0.01	1.4490	1675, 1740	2210		1140	190.70, 175.80, 86.50, 83.95, 51.40, 42.95, 33.80, 18.85 (2C), 17.75 (2C)
13c	85/0.01	1.4700	1680, 1740	2220		1140	192.70, 177.10, 87.35, 82.95, 51.50, 44.65, 38.75, 27.05 (3C), 25.80 (3C)
13d	140/0.2	1.5161	1650, 1720	2210	1610		175.25, 165.10, 159.00, 158.85, 125.55, 114.85, 86.90, 84.25, 50.70, 27.80, 27.40, 21.15, 20.30
13e	70/0.01	1.4555[a]	1680, 1740	2220		1180	188.00, 173.90, 89.15, 81.45, 61.10, 38.80, 27.45, 19.55, 9.10, 8.00
13f	80/0.01	1.4565	1670, 1735	2205		1175	186.75, 172.50, 85.35, 84.90, 51.30, 45.05, 33.60, 27.00, 26.00, 22.20, 22.30, 13.80 (2C)
15	135/0.1	1.4749	1675, 1740	2200			187.40, 171.45, 91.70, 85.20, 74.15, 47.60, 36.75, 36.50 (2C), 25.05, 22.40 (2C), 17.60, 17.55, 13.55 (2C)

[a] T = 20 °C.
[b] T = 22 °C.
[c] T = 25 °C.
[d] 25 MHz, $CDCl_3$, TMS.
[e] Stereoisomers.

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