Supplementary Materials

Oxidative coupling of tetraalkynyltin with aldehydes leading to alkynyl ketones

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[c]*Peoples Friendship University Russia, 6 Miklukho Maklaya St, Moscow 117198, Russia*

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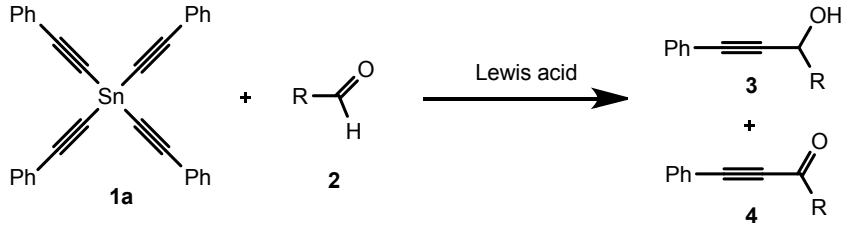
Supplementary Table 1. The results of the optimization experiments



A 2-mL sealable Wheaton vial was charged with 0.05 mmol of Lewis acid ($ZnCl_2$, $SnCl_4$), 0.123 mmol of $(PhC{\equiv}C)_4Sn$ **1a** and 0.5 ml of a dry solvent. Then the vial was flushed with a stream of dry argon, and 0.492 mmol (or 0.984 mmol if the ratio **1a** : **2a** was set as 1 : 8) of benzaldehyde **2c** was added subsequently through a syringe. The mixture was stirred for the indicated time (see Table below). The progress of the reaction was monitored by GC-MS (before the analysis, samples taken at regular intervals were quenched with saturated aqueous NH4Cl).

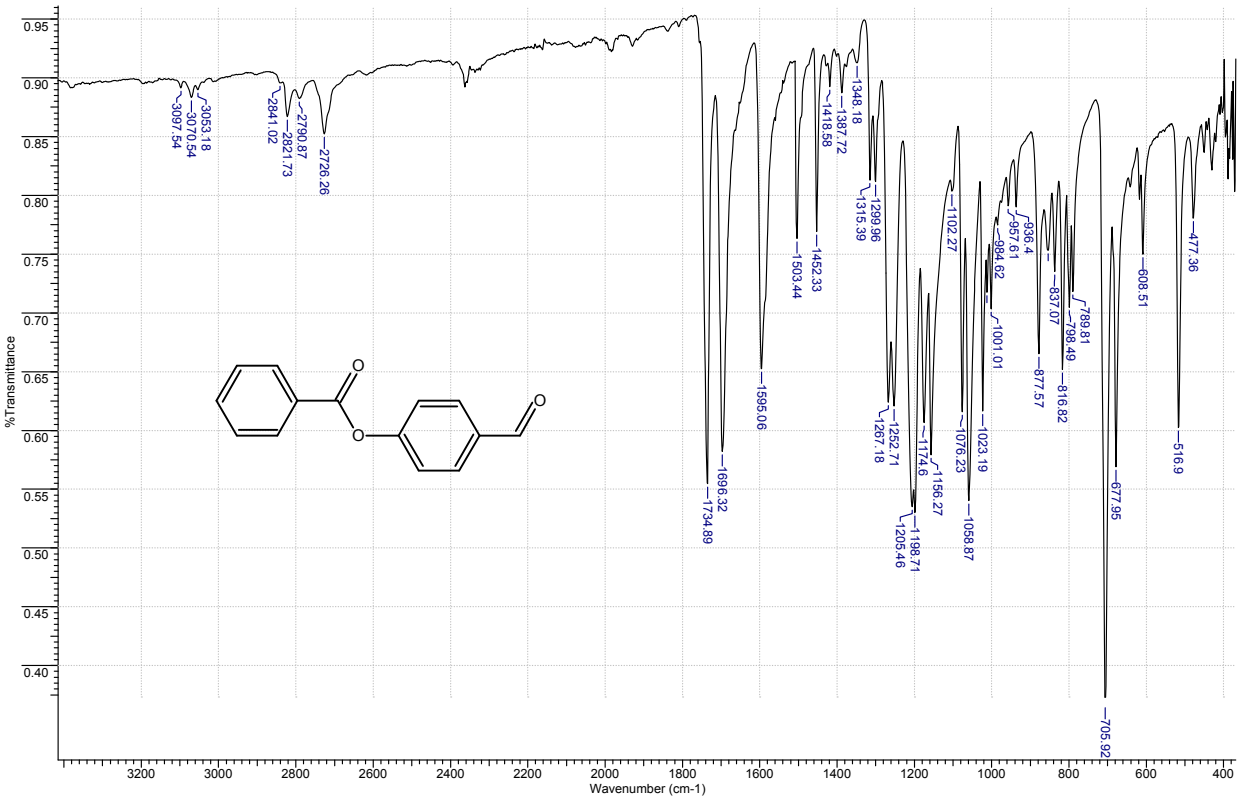
No	Ratio **1a** : **2c**	Solvent	Temperature, °C	Catalyst (mol %)	Time, h	Yield of **4**, (or **3** + **4**) %
1	1:4	DCE*	60	$SnCl_4$ (10)	1	**87**
					3	**99**
2	1:4	DCE	60	$ZnCl_2$ (10)	1	**77**
					3	**100**
3	1:4	DCE	60	$ZnCl_2$ (10) Et_3N 2 equv	1	**10 + 80**
4	1:8	DCE	60	$SnCl_4$ (10)	1	**13**
					3	**11**
					5	**69**
5	1:8	DCE	60	$SnCl_4$ (25)	0,75	**36**
					3	**28**
					5	**67**
6	1:4	PhMe	60	$SnCl_4$ (10)	3	**2 + 98**
7	1:4	PhMe	60	$SnCl_4$ (10) Acetone 4ч equv	1	**100**
					3	**100**
8	1:4	PhMe	60	$ZnCl_2$ (10)	1	**100**
					3	**100**
9	1:4	PhMe	60	$ZnCl_2$ (10) Acetone 4ч equv	0,5	**2 + 56**
					1	**86**
					3	**99**
10	1:8	PhMe	60	$SnCl_4$ (10)	1	**49**
					3	**86**
11	1:8	PhMe	60	$SnCl_4$ (25)	5	**82**
12	1:8	PhMe	60	$ZnCl_2$ (10)	2	**76**
					4	**84**
13	1:8	PhMe	40	$ZnCl_2$ (10)	2	**6 + 34**
					3	**89**
					5	**100**
14	1:8	PhMe	80	$ZnCl_2$ (10)	2	**75**
					3	**81**

					5	**78**
15	1:8	PhMe	25	$ZnCl_2$ (10)	5	**0**
16	1:4	dioxane	60	$ZnCl_2$ (10)	1	**1+5**
					3	**2**
					24	**4**
17	1:4	dioxane	60	$SnCl_4$ (10)	1	**1**
					3	**0,1+2**
					5	**2**
18	1:4	DMF	60	$ZnCl_2$ (10)	1	**0**
					3	**0**
					24	**1**
19	1:4	DMF	60	$SnCl_4$ (10)	1	**0**
					3	**0**
20	1:4	THF	60	$ZnCl_2$ (10)	1	**0,5**
					3	**7**

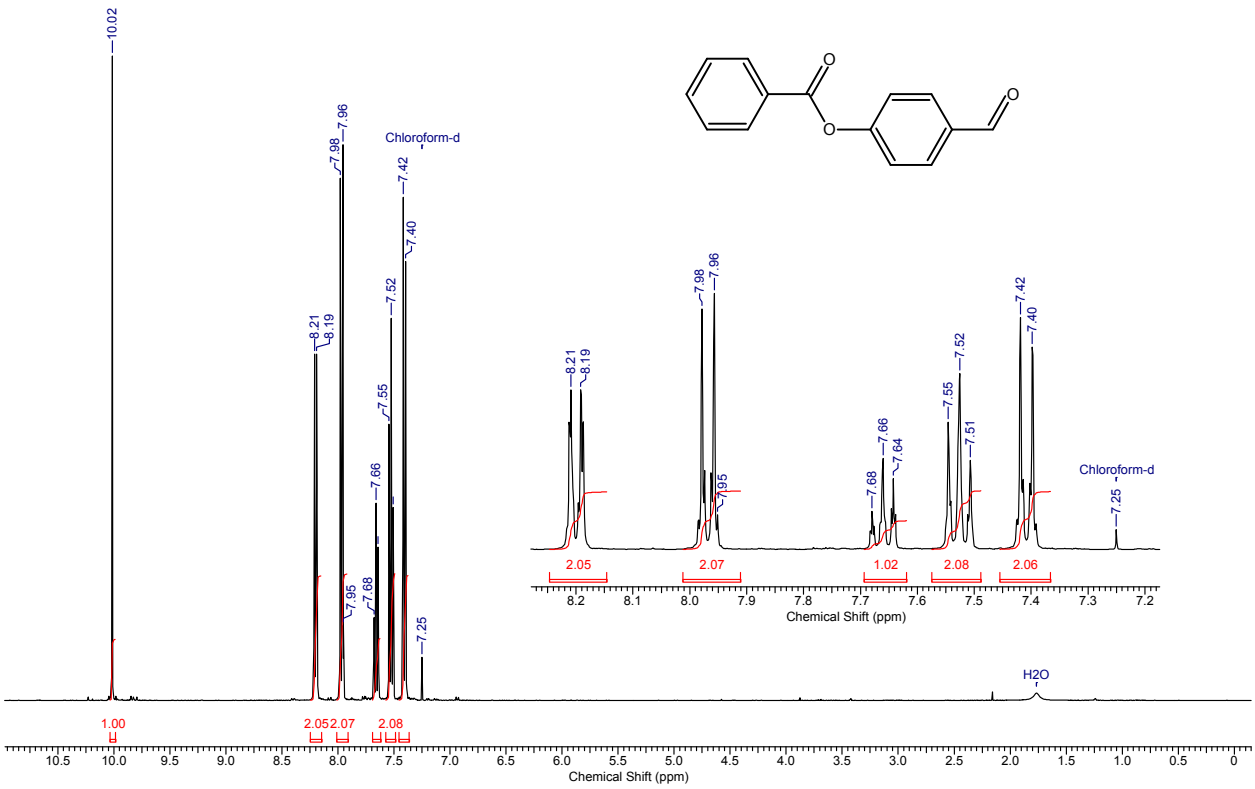
DCE = 1,2-dichloroethane

Spectra of starting reagents and alkynyl ketones **4**

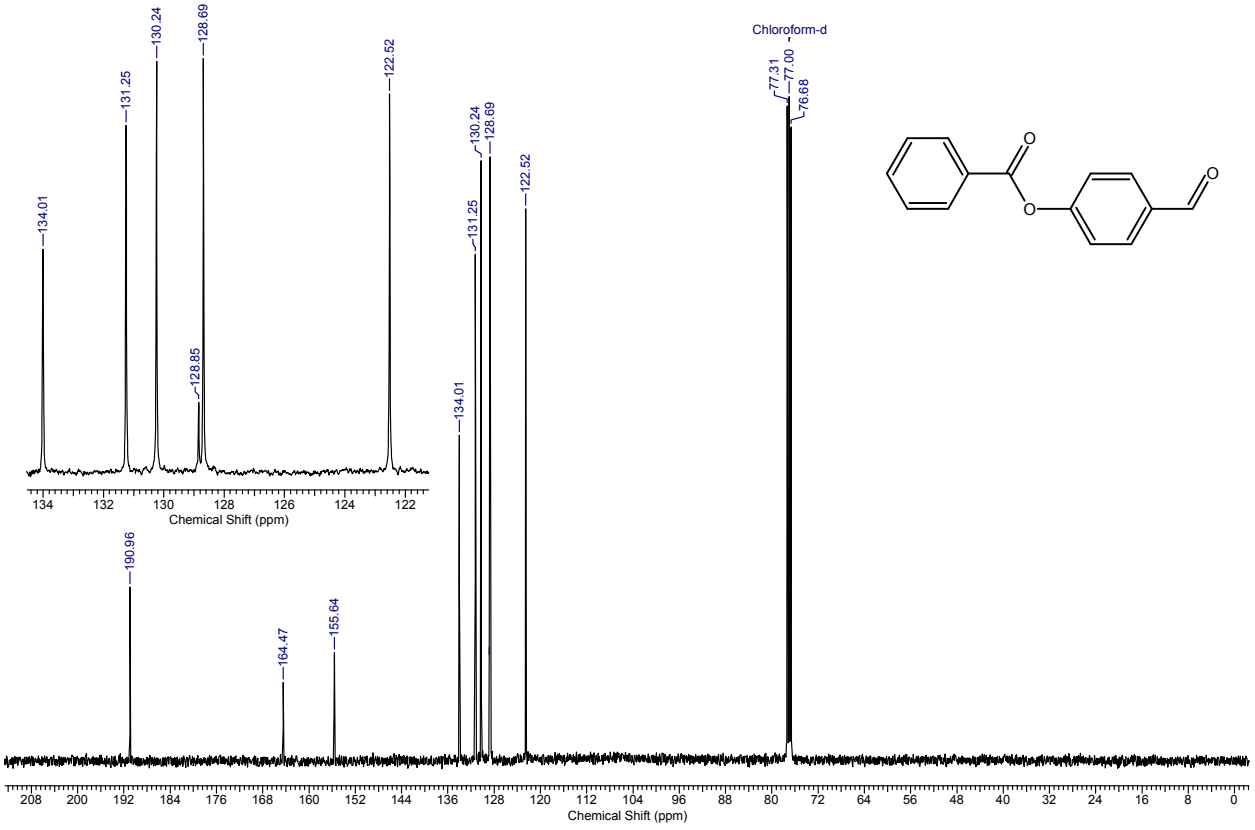
IR spectrum (KBr) of 4-formylphenyl benzoate (**2i**)



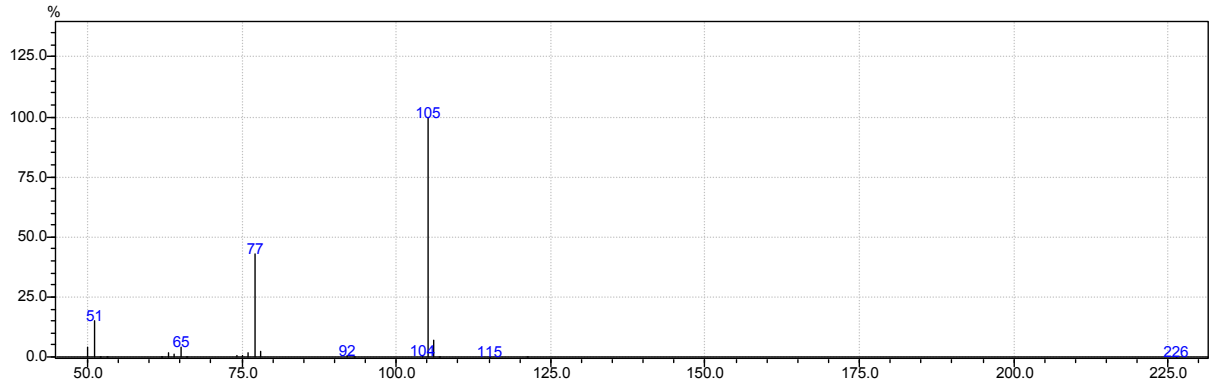
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of 4-formylphenyl benzoate (**2i**)



^{13}C NMR spectrum (100 MHz, $CDCl_3$) of 4-formylphenyl benzoate (**2i**)



Mass-spectrum (EI, 70 eV) of 4-formylphenyl benzoate (**2i**)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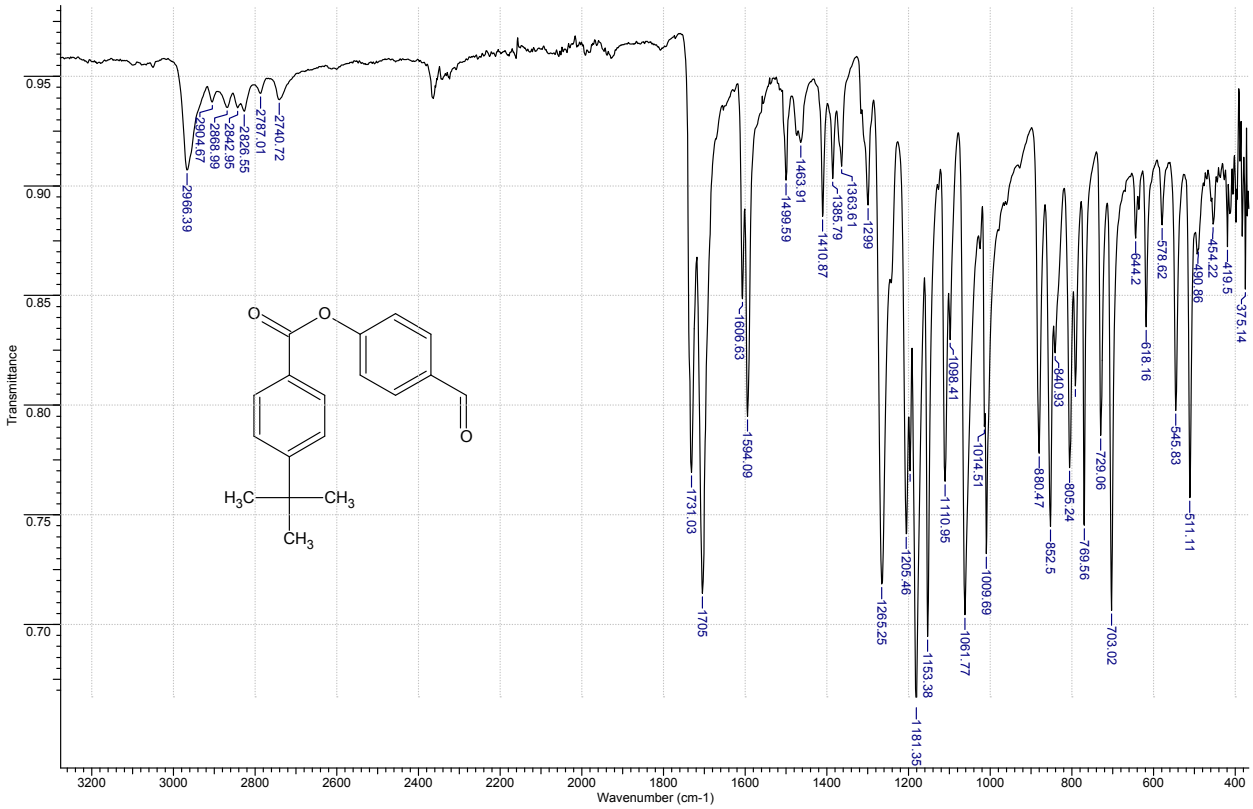
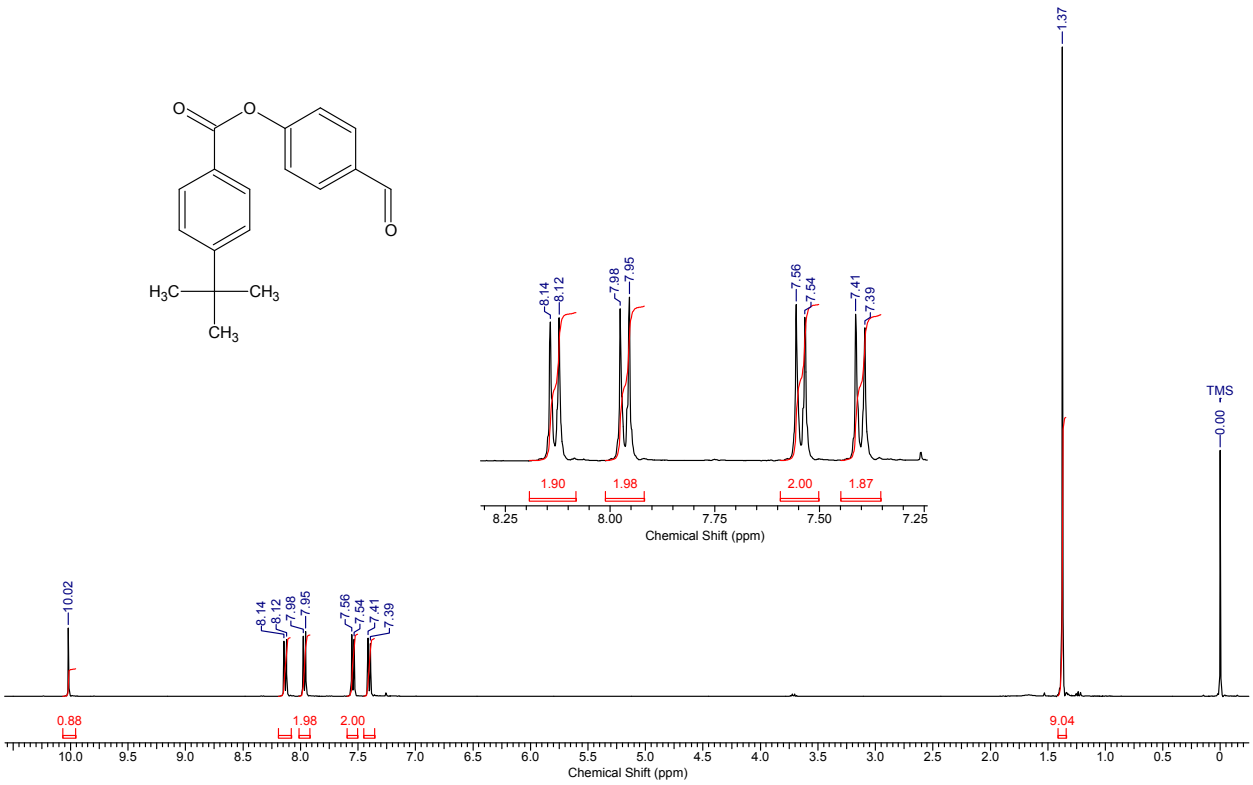
100.0
75.0
50.0
25.0
0.0
105
77
51
65
92
104
115
226
50.0
75.0
100.0
125.0
150.0
175.0
200.0
225.0

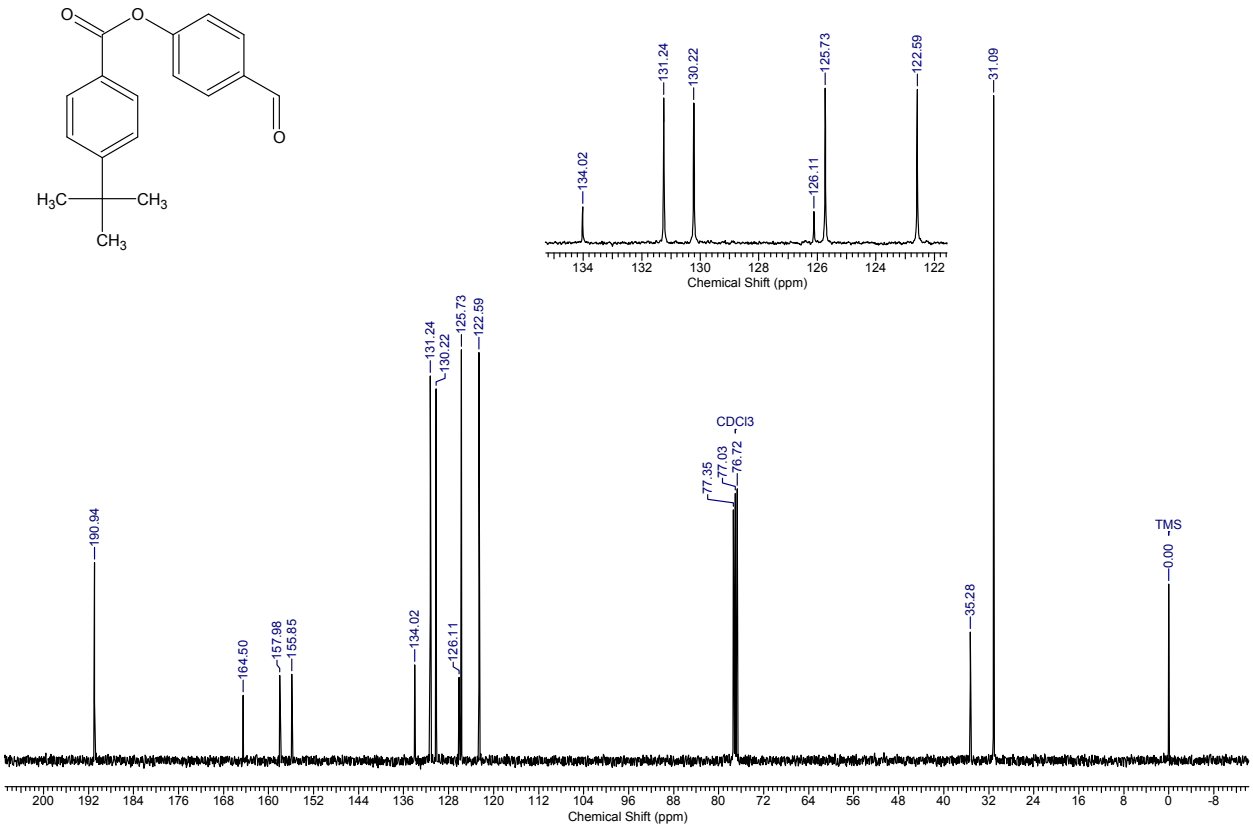
IR spectrum (KBr) of 4-formylphenyl 4-*tert*-butylbenzoate (**2j**)



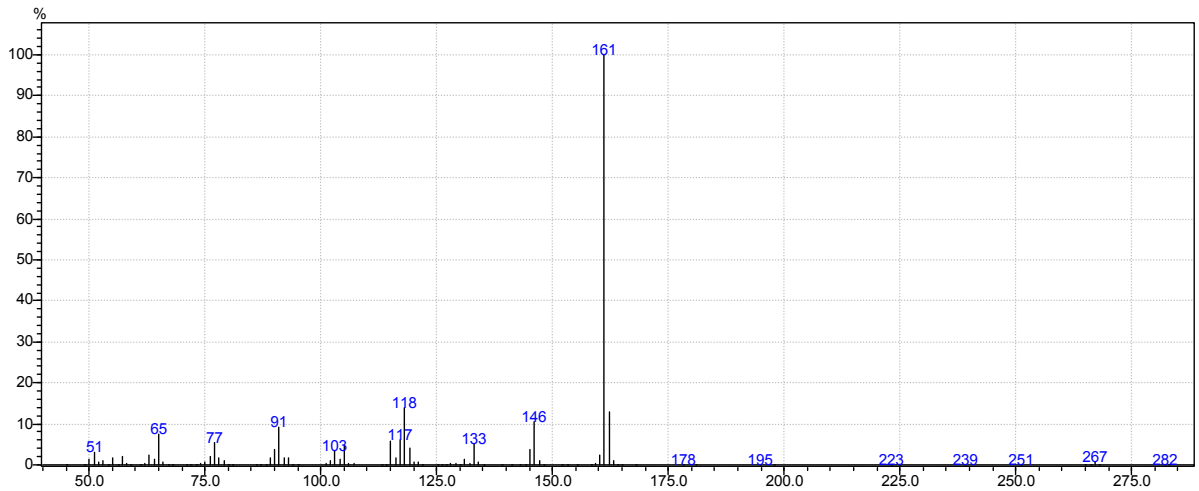
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of 4-formylphenyl 4-*tert*-butylbenzoate (**2j**)



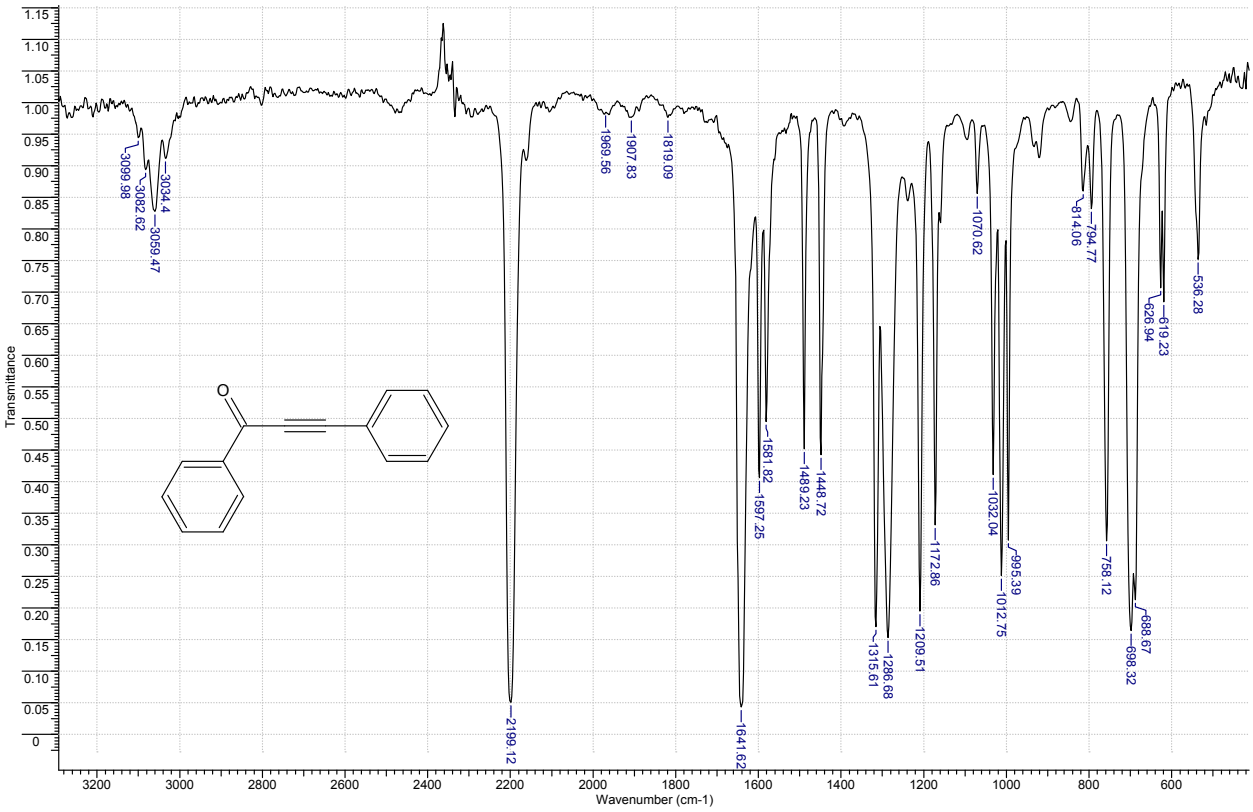
^{13}C NMR spectrum (100 MHz, $CDCl_3$) of 4-formylphenyl 4-*tert*-butylbenzoate (**2j**)



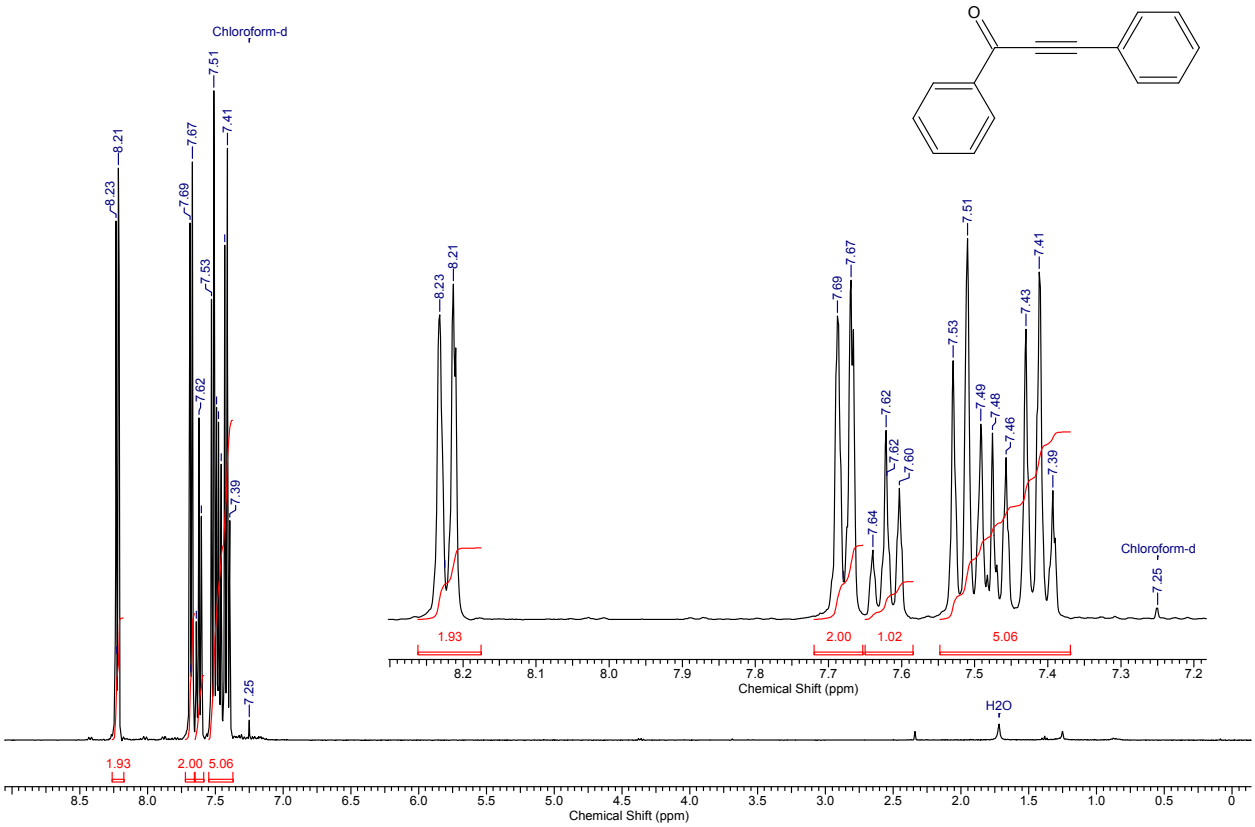
Mass-spectrum (EI, 70 eV) of 4-formylphenyl 4-*tert*-butylbenzoate (**2j**)



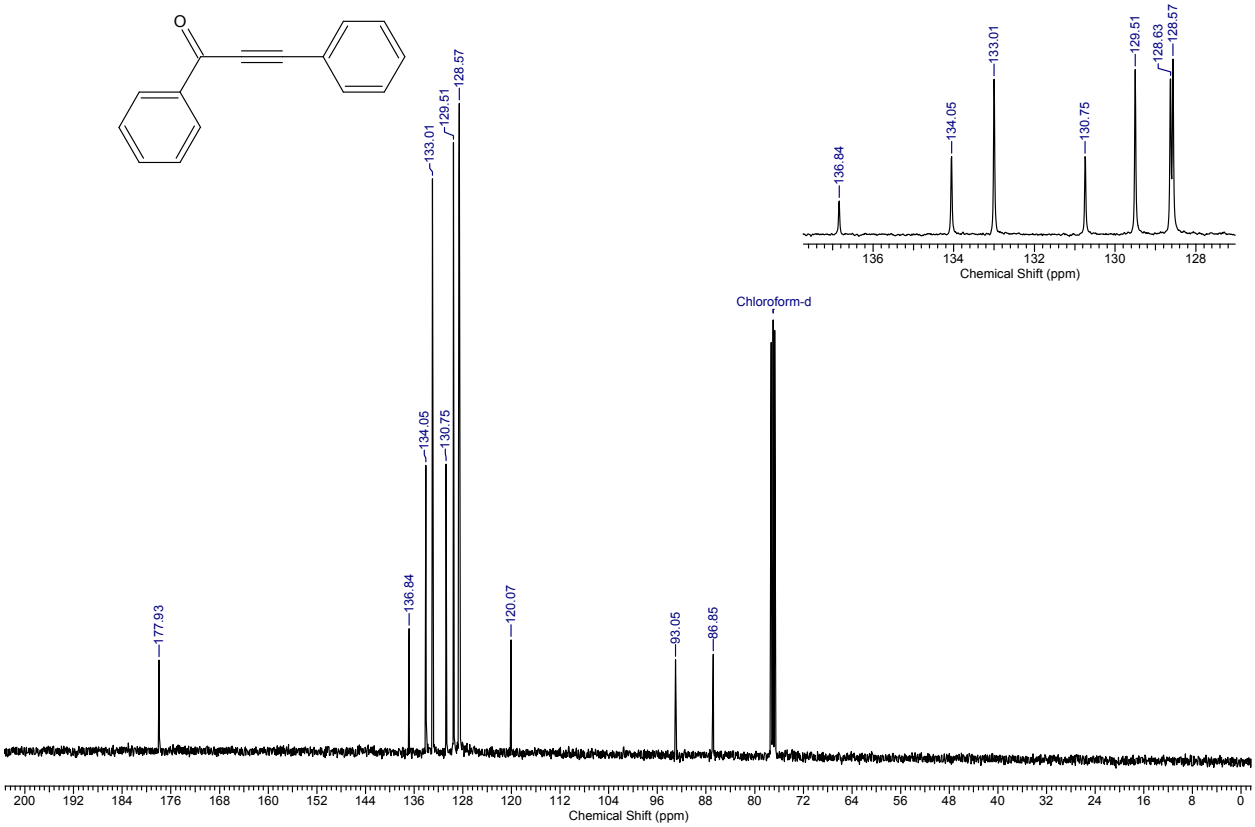
IR spectrum (liquid film) of 1,3-diphenylprop-2-yn-1-one (**4ac**)



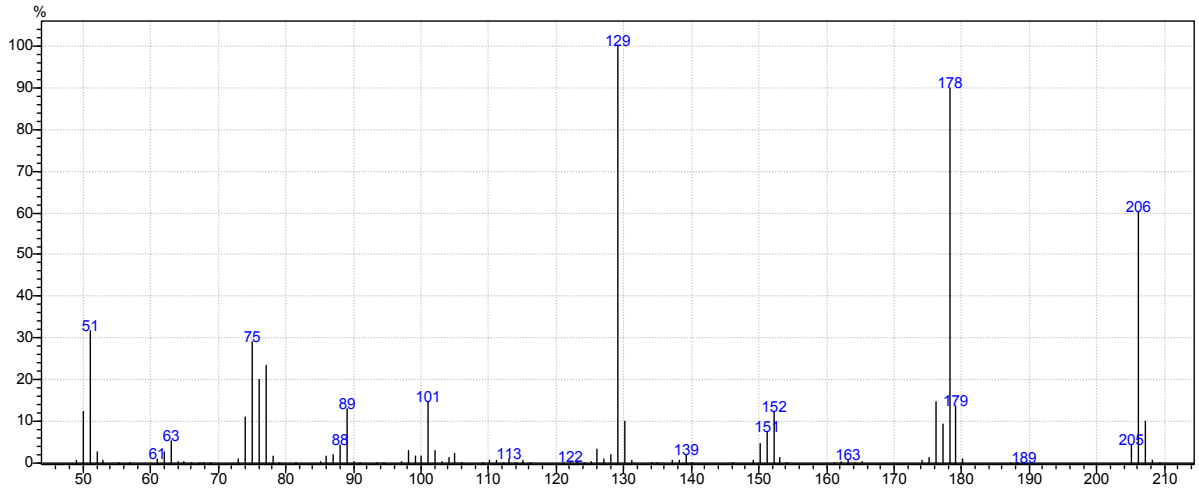
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of 1,3-diphenylprop-2-yn-1-one (**4ac**)



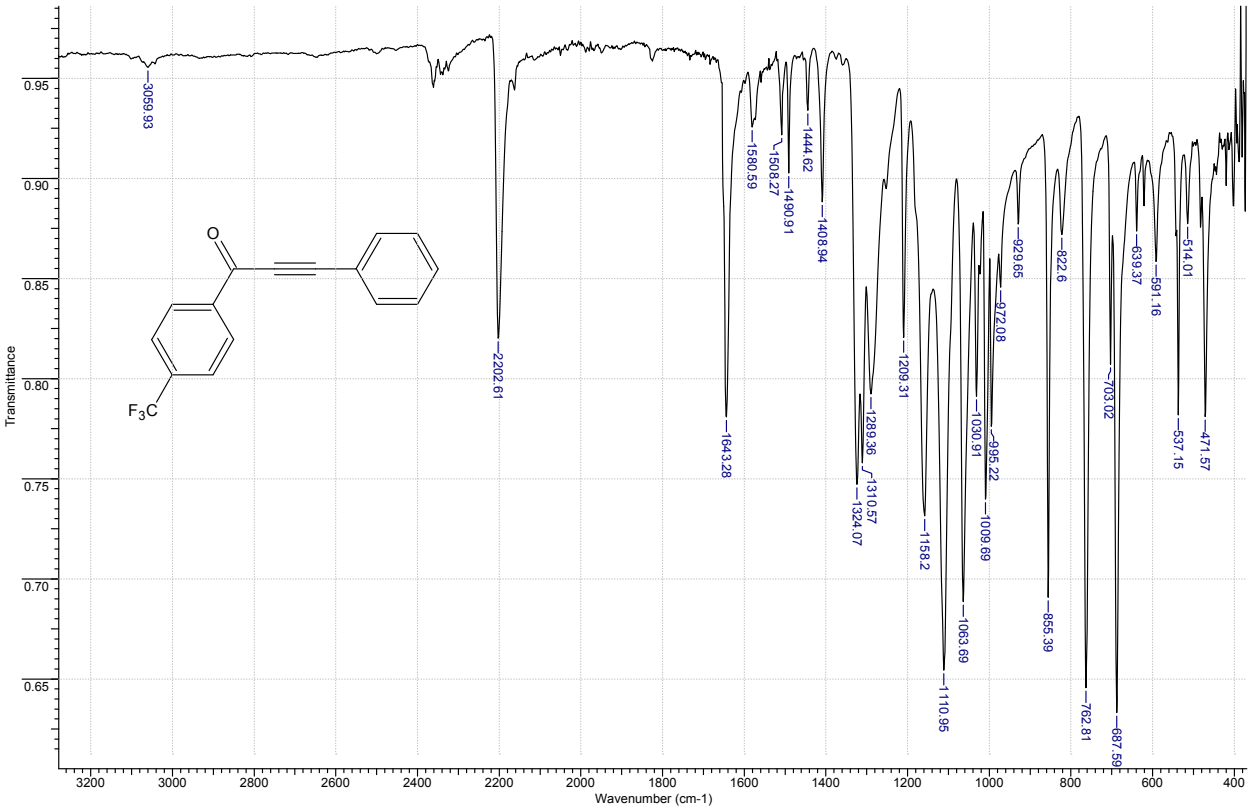
^{13}C NMR spectrum (100 MHz, $CDCl_3$) of 1,3-diphenylprop-2-yn-1-one (**4ac**)



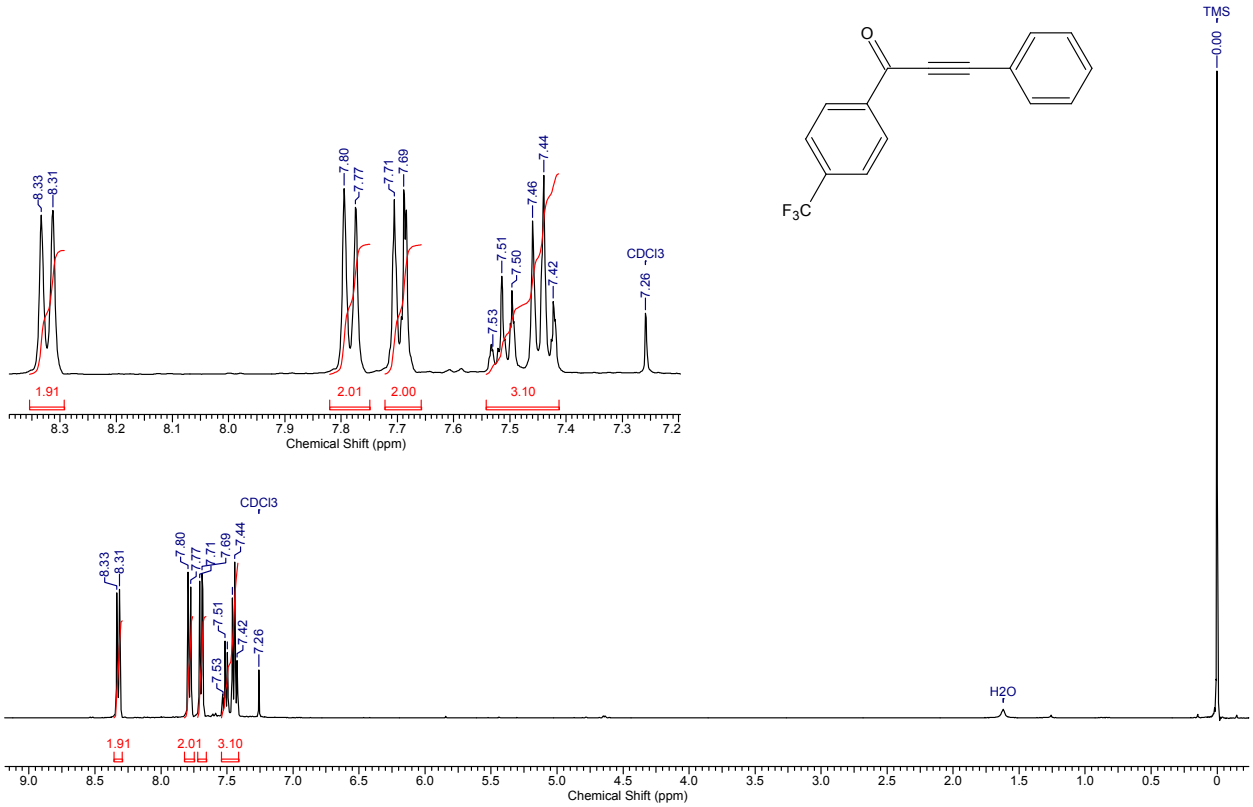
Mass-spectrum (EI, 70 eV) of 1,3-diphenylprop-2-yn-1-one (**4ac**)



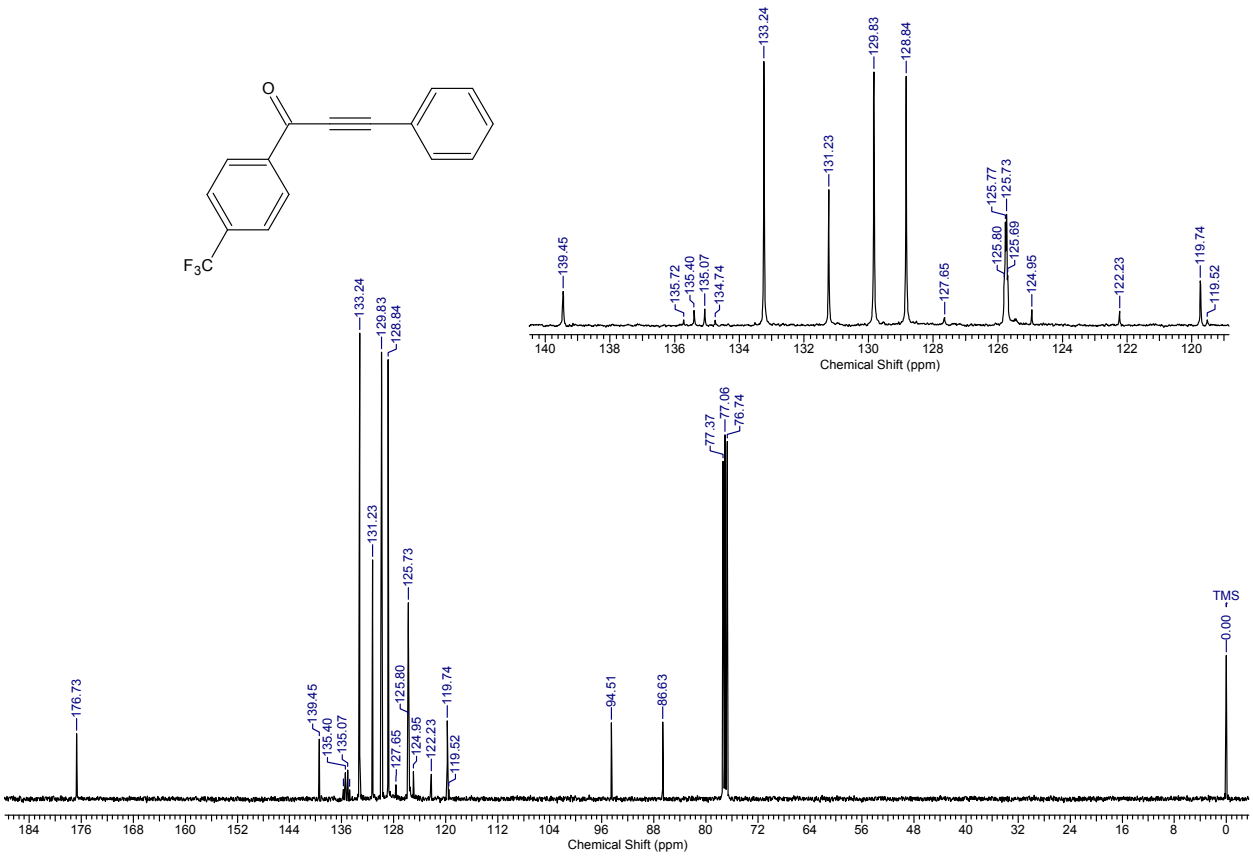
IR spectrum (KBr) of 3-phenyl-1-[4-(trifluoromethyl)phenyl]prop-2-yn-1-one (**4ad**)



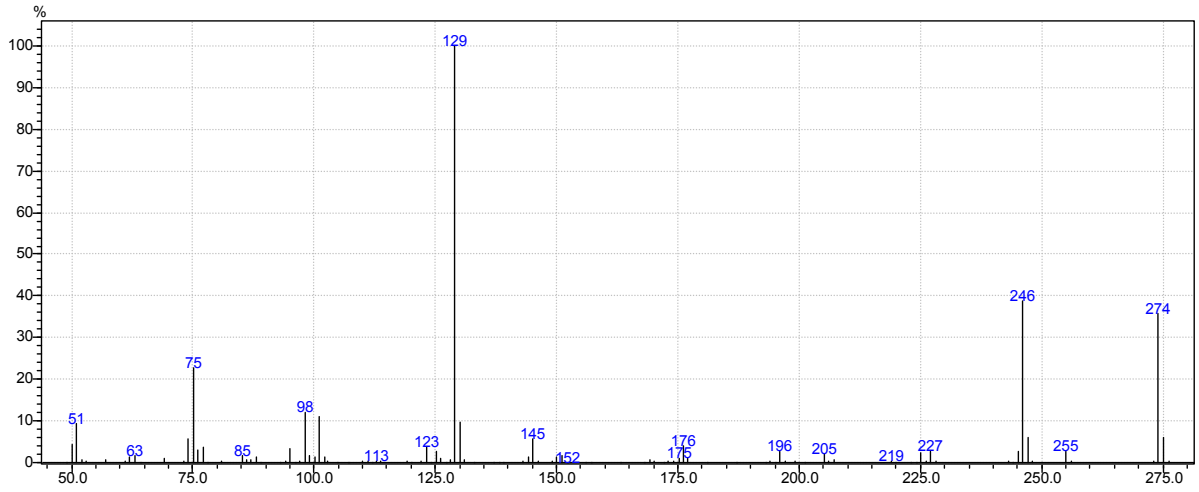
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of 3-phenyl-1-[4-(trifluoromethyl)phenyl]prop-2-yn-1-one (**4ad**)



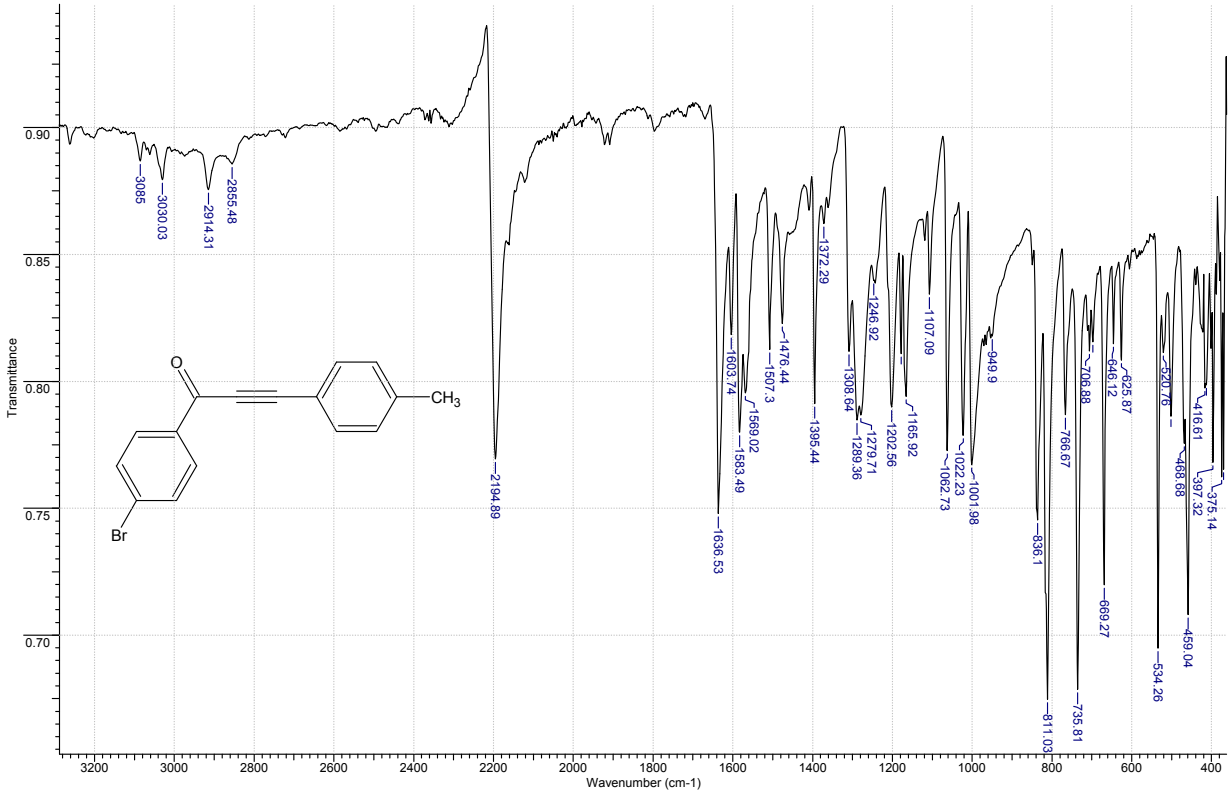
^{13}C NMR spectrum (100 MHz, $CDCl_3$) of 3-phenyl-1-[4-(trifluoromethyl)phenyl]prop-2-yn-1-one (**4ad**)



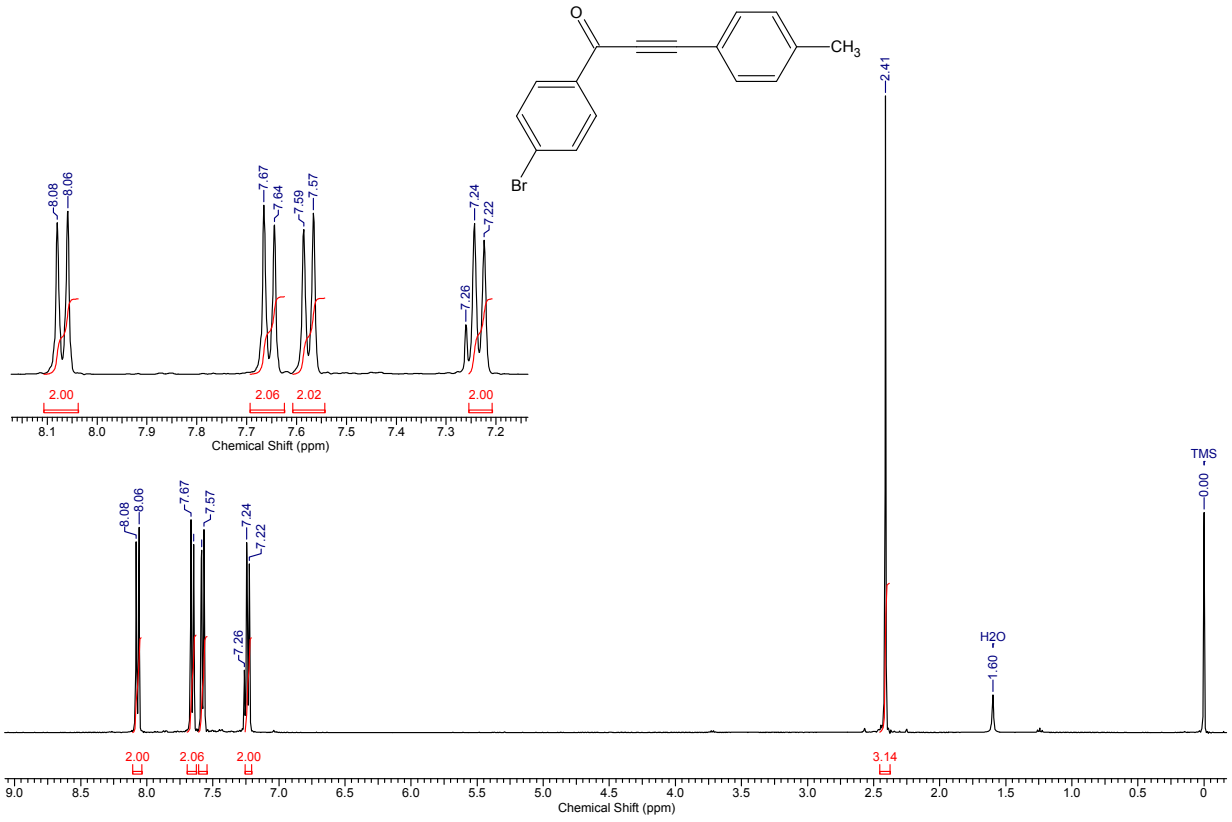
Mass-spectrum (EI, 70 eV) of 3-phenyl-1-[4-(trifluoromethyl)phenyl]prop-2-yn-1-one (**4ad**)



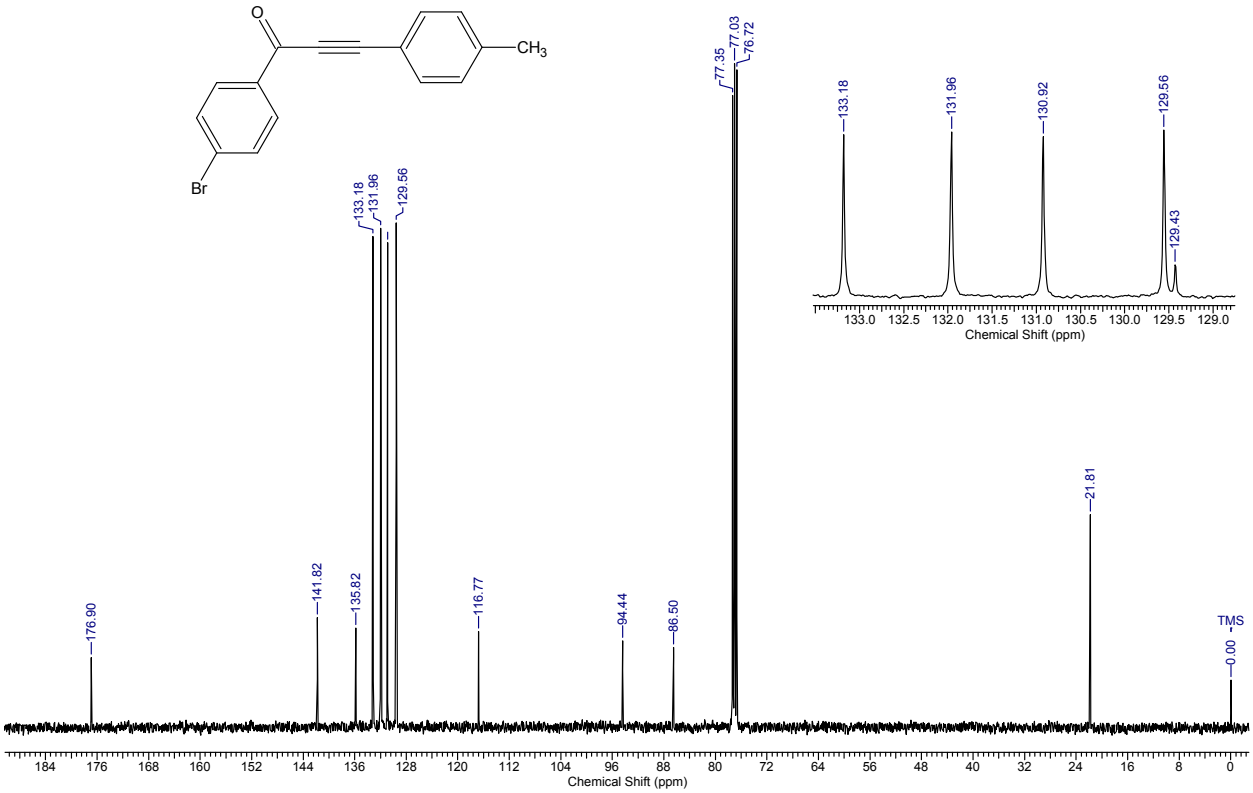
IR spectrum (KBr) of 1-(4-bromophenyl)-3-(4-methylphenyl)prop-2-yn-1-one (**4be**)



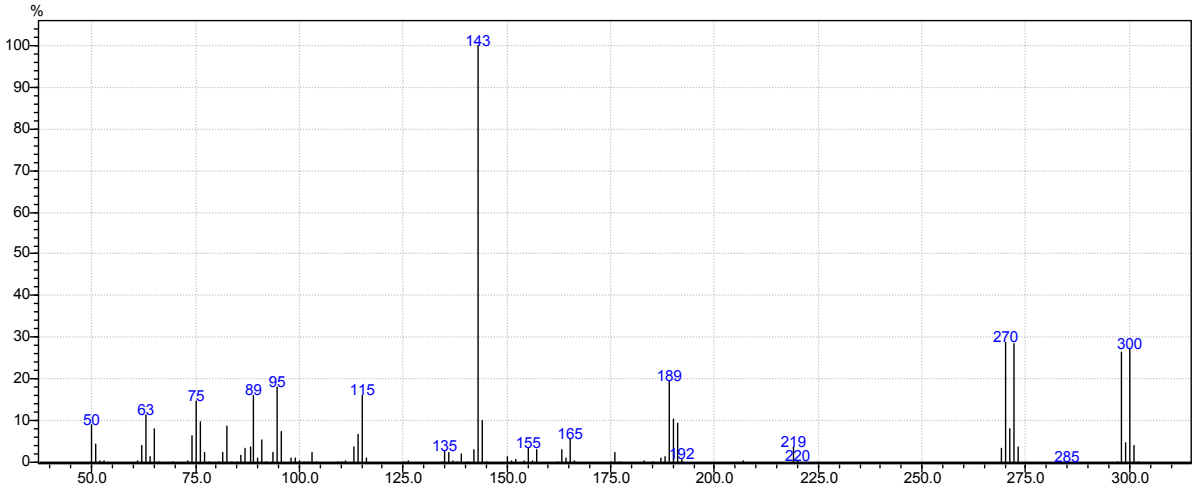
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of 1-(4-bromophenyl)-3-(4-methylphenyl)prop-2-yn-1-one (**4be**)



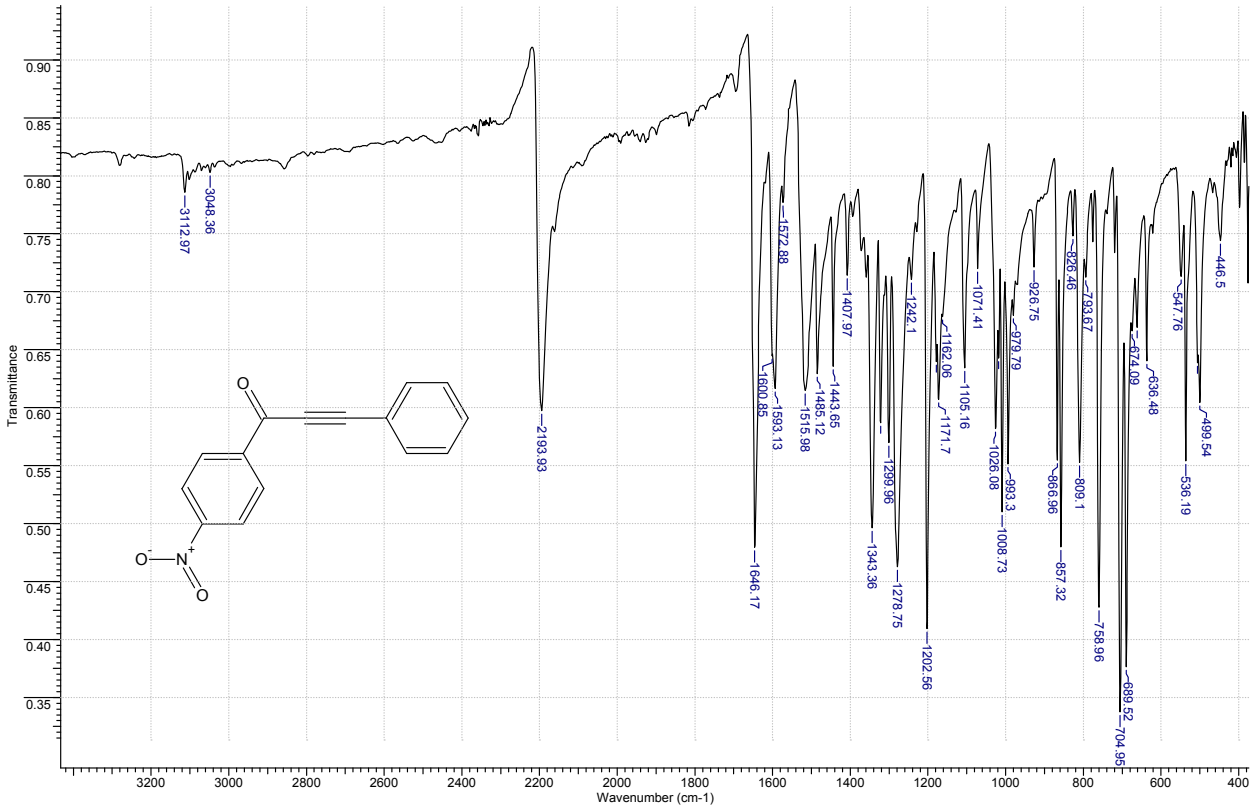
^{13}C NMR spectrum (100 MHz, $CDCl_3$) of 1-(4-bromophenyl)-3-(4-methylphenyl)prop-2-yn-1-one (**4be**)



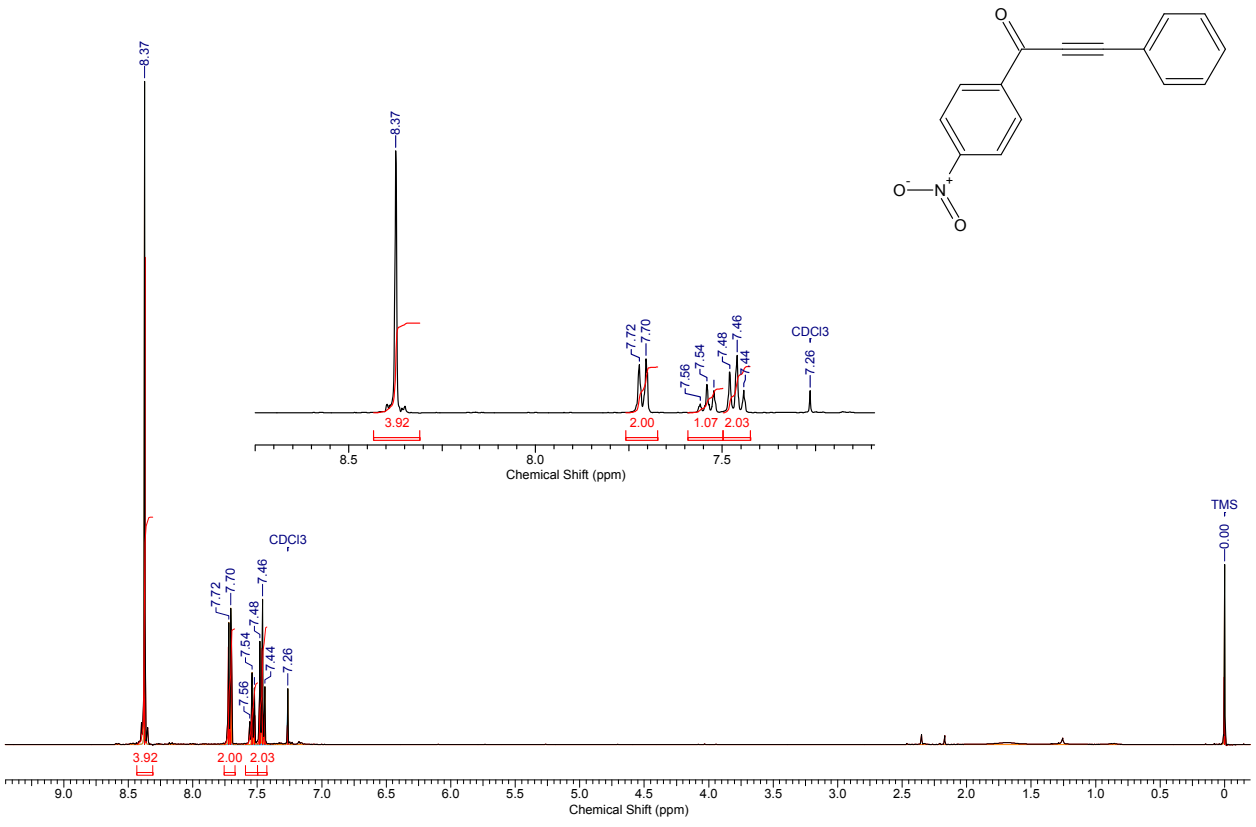
Mass-spectrum (EI, 70 eV) of 1-(4-bromophenyl)-3-(4-methylphenyl)prop-2-yn-1-one (**4be**)



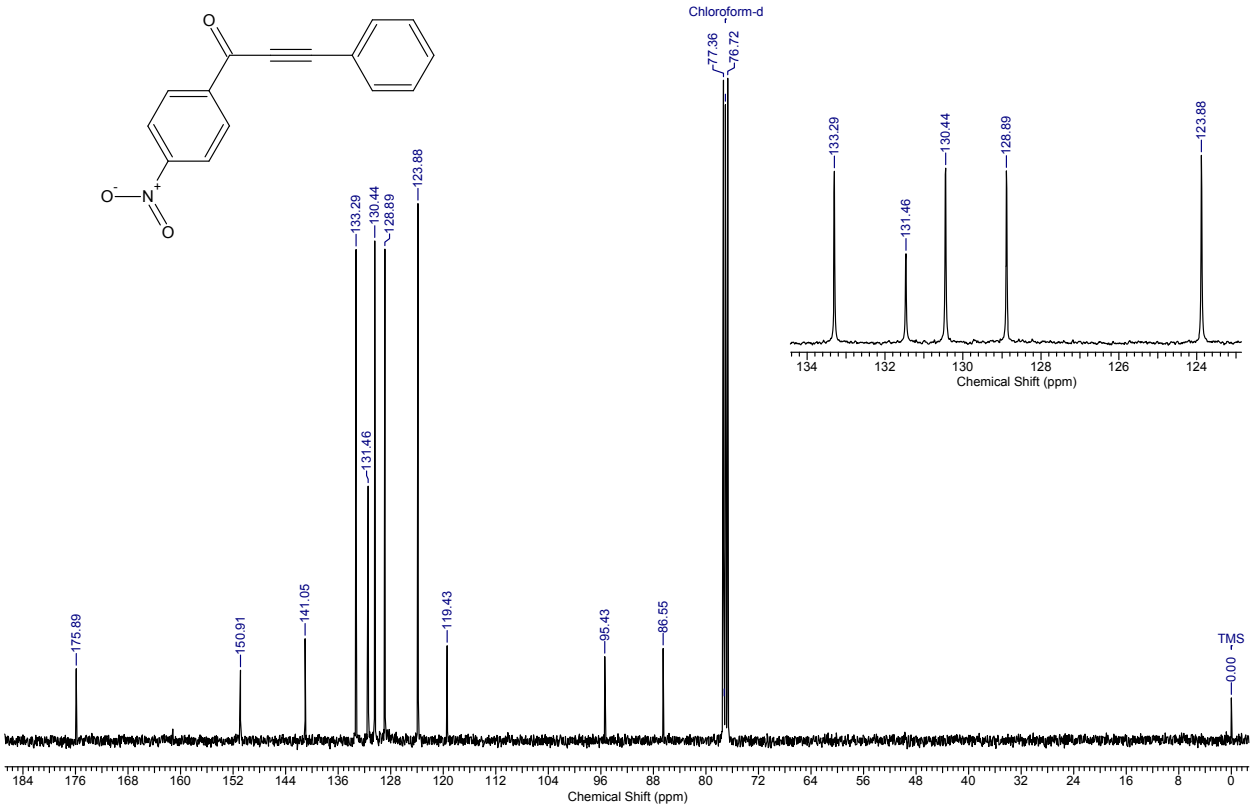
IR spectrum (KBr) of 1-(4-nitrophenyl)-3-phenylprop-2-yn-1-one (**4af**)



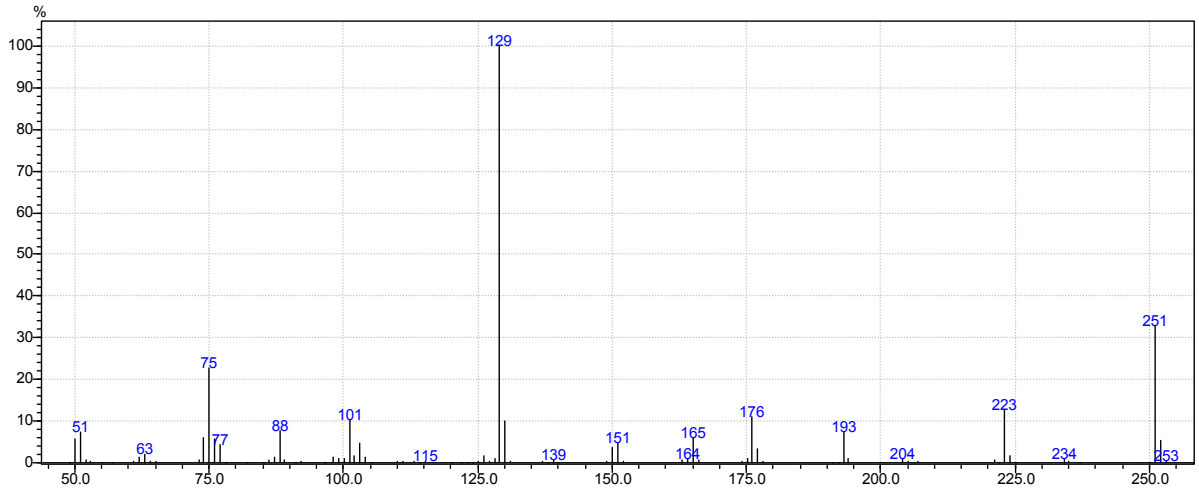
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of 1-(4-nitrophenyl)-3-phenylprop-2-yn-1-one (**4af**)



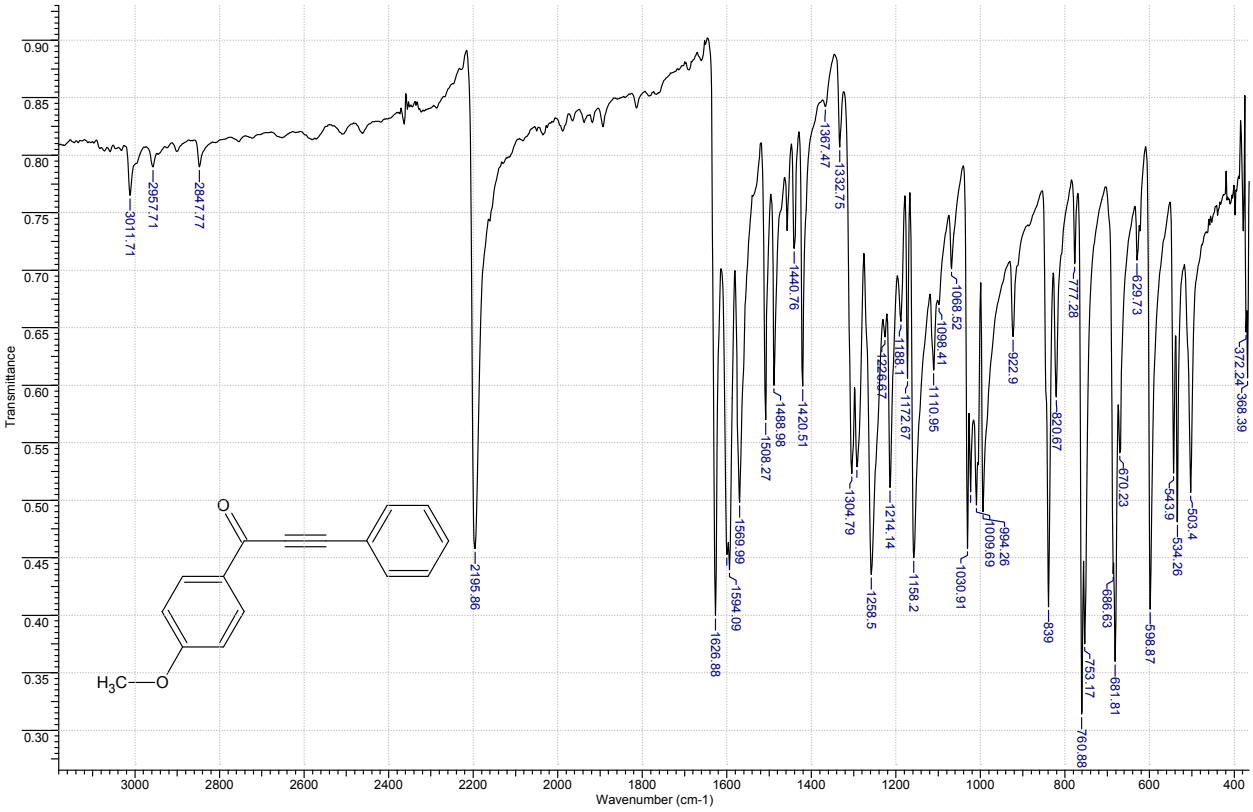
^{13}C NMR spectrum (100 MHz, $CDCl_3$) of 1-(4-nitrophenyl)-3-phenylprop-2-yn-1-one (**4af**)



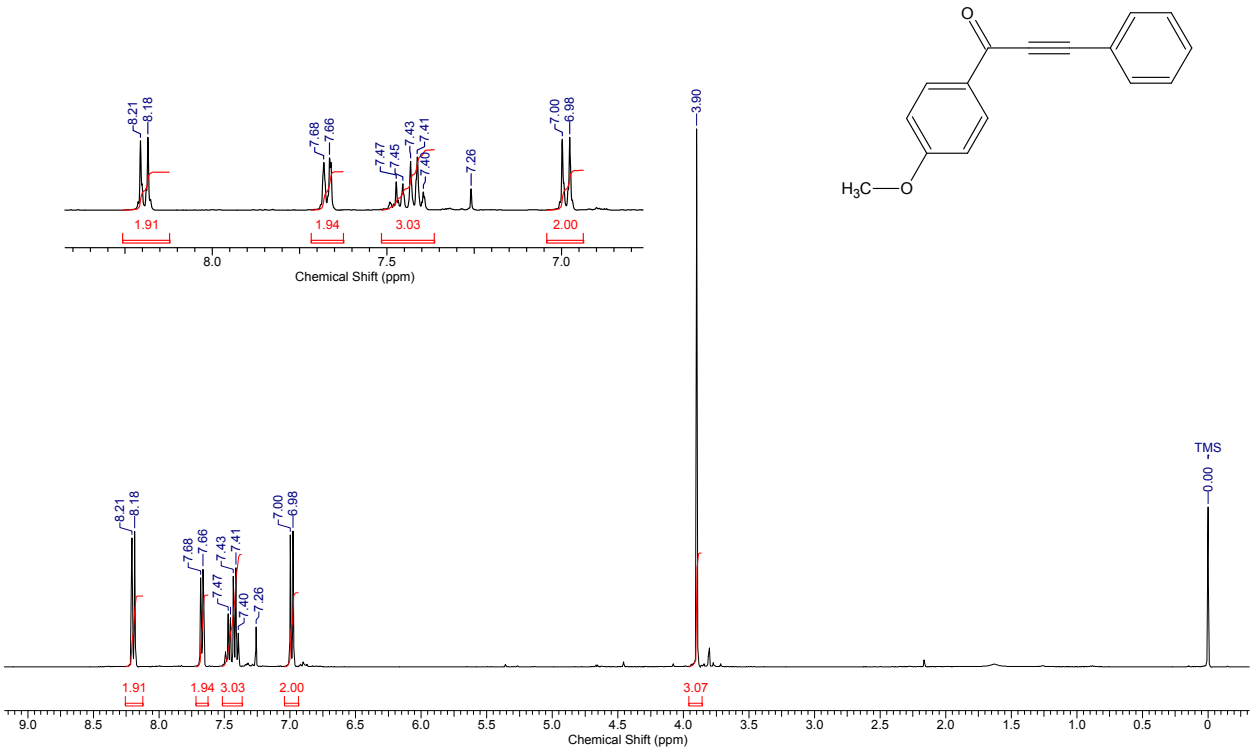
Mass-spectrum (EI, 70 eV) of 1-(4-nitrophenyl)-3-phenylprop-2-yn-1-one (**4af**)



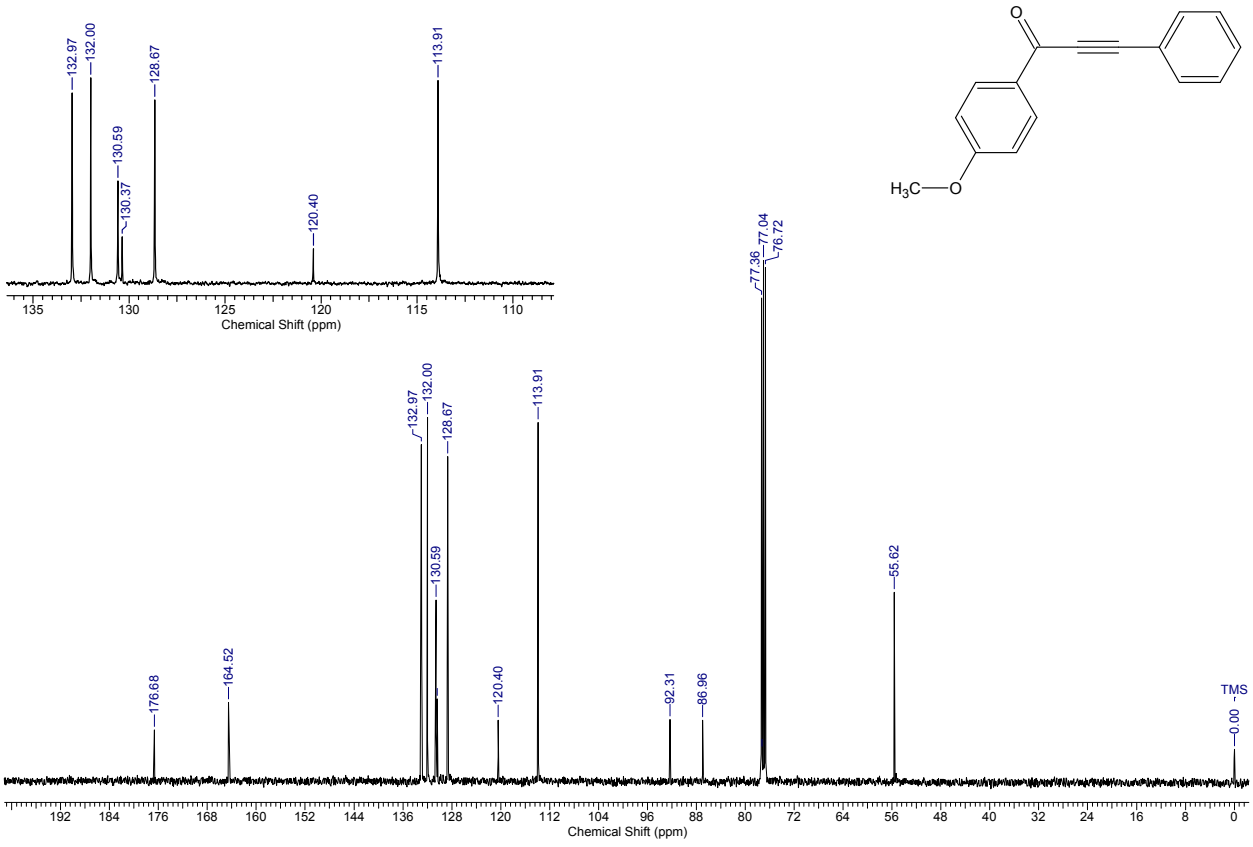
IR spectrum (KBr) of 1-(4-methoxyphenyl)-3-phenylprop-2-yn-1-one (**4ag**)



^{1}H NMR spectrum (400 MHz, $CDCl_3$) of 1-(4-methoxyphenyl)-3-phenylprop-2-yn-1-one (**4ag**)



^{13}C NMR spectrum (100 MHz, $CDCl_3$) of 1-(4-methoxyphenyl)-3-phenylprop-2-yn-1-one (**4ag**)



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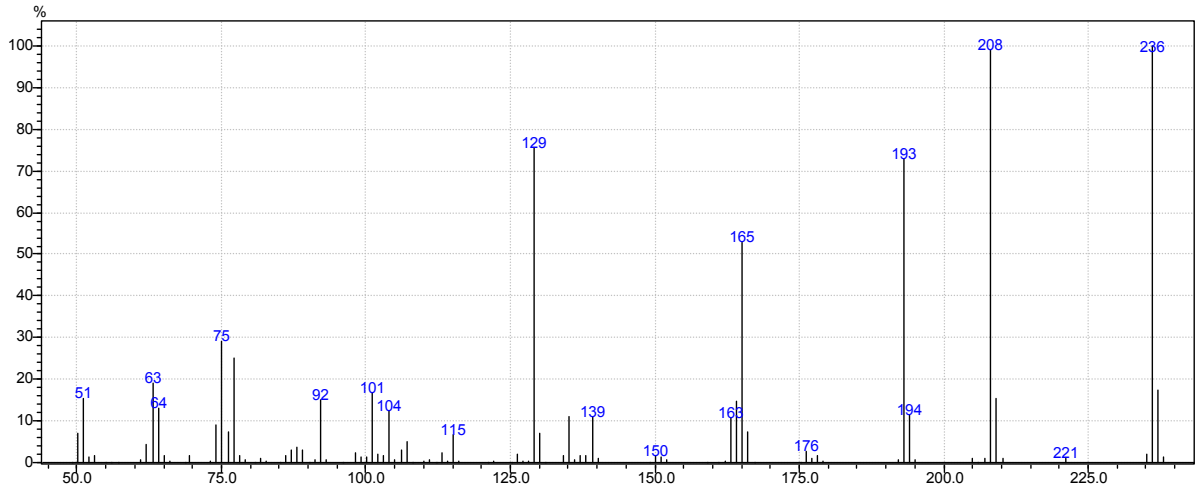
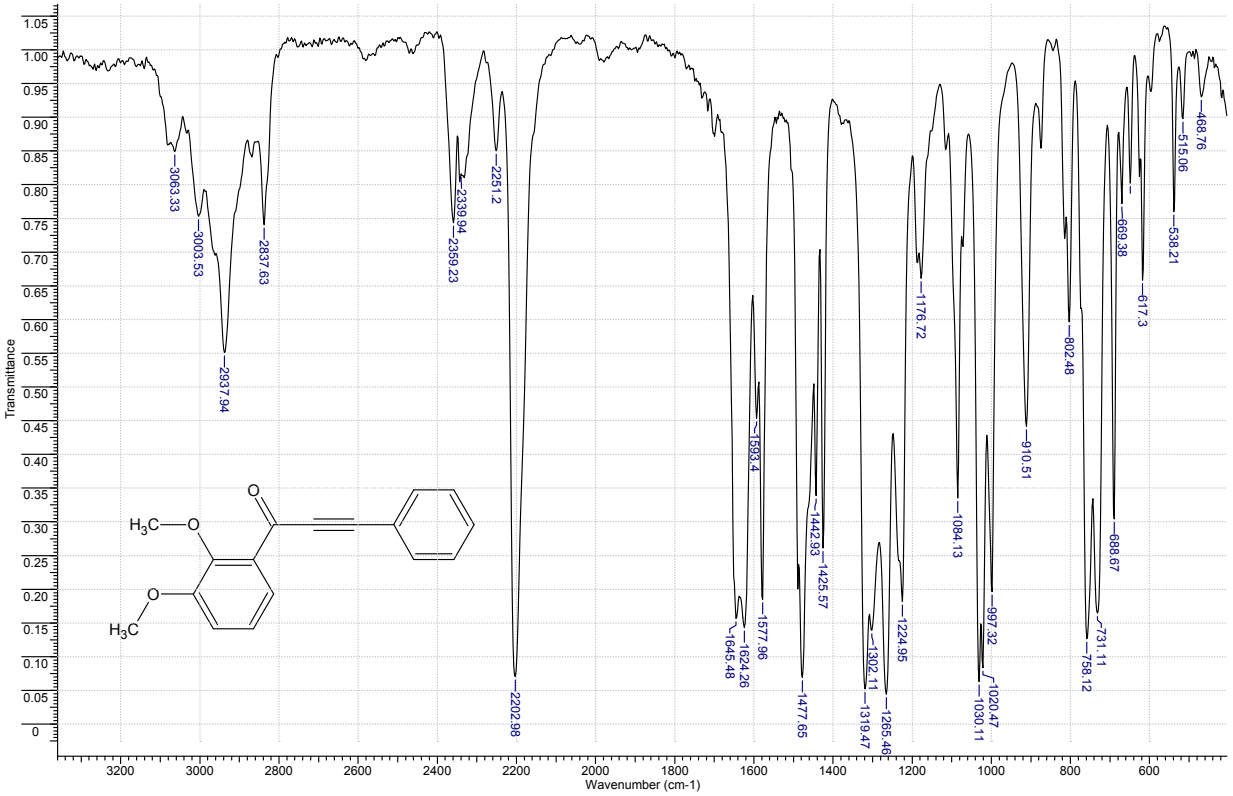
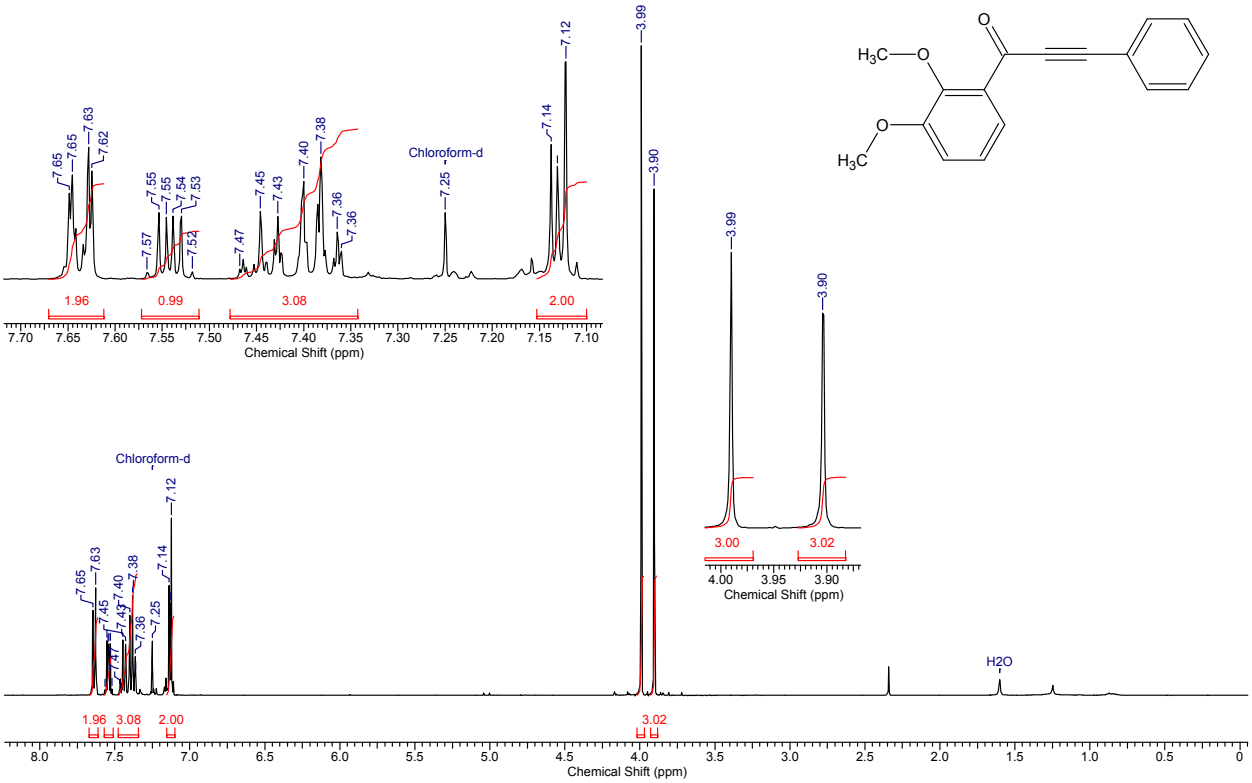


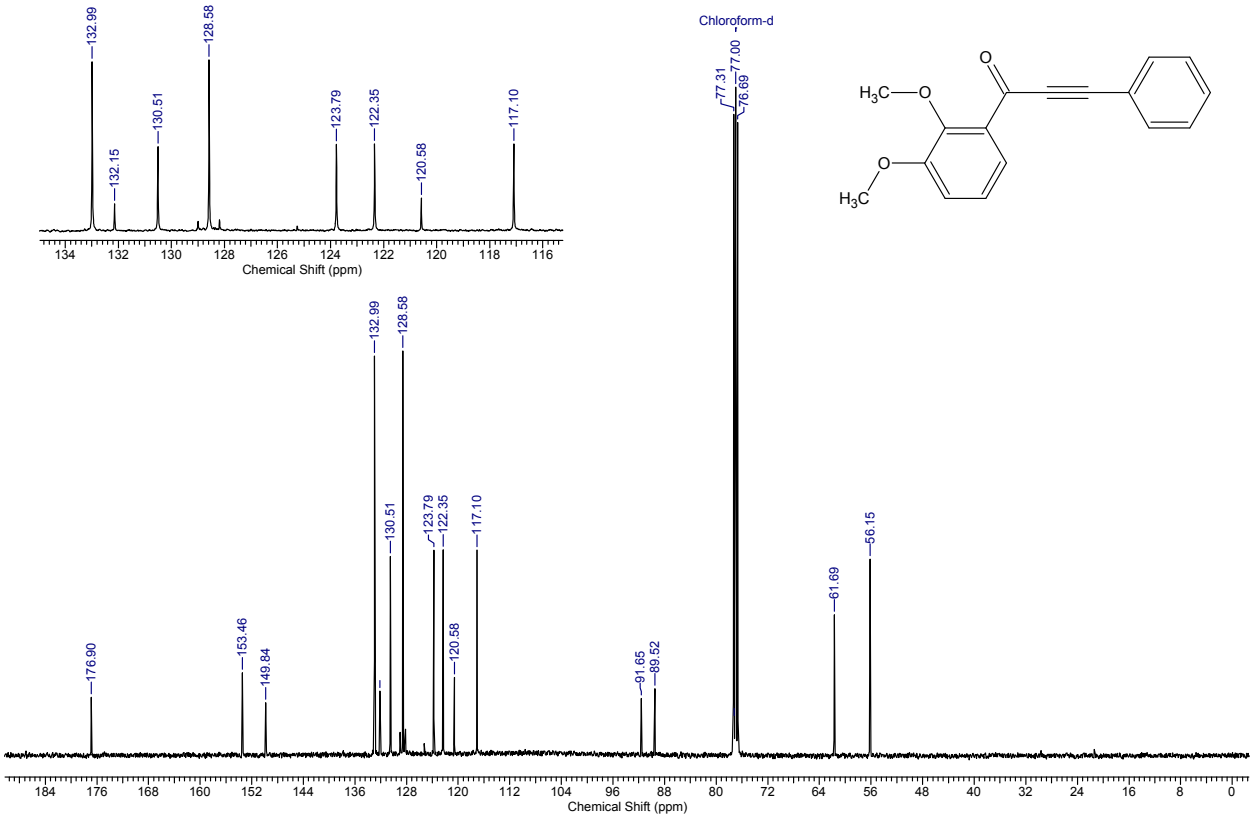
IR spectrum (KBr) of 1-(2,3-dimethoxyphenyl)-3-phenylprop-2-yn-1-one (**4ah**)



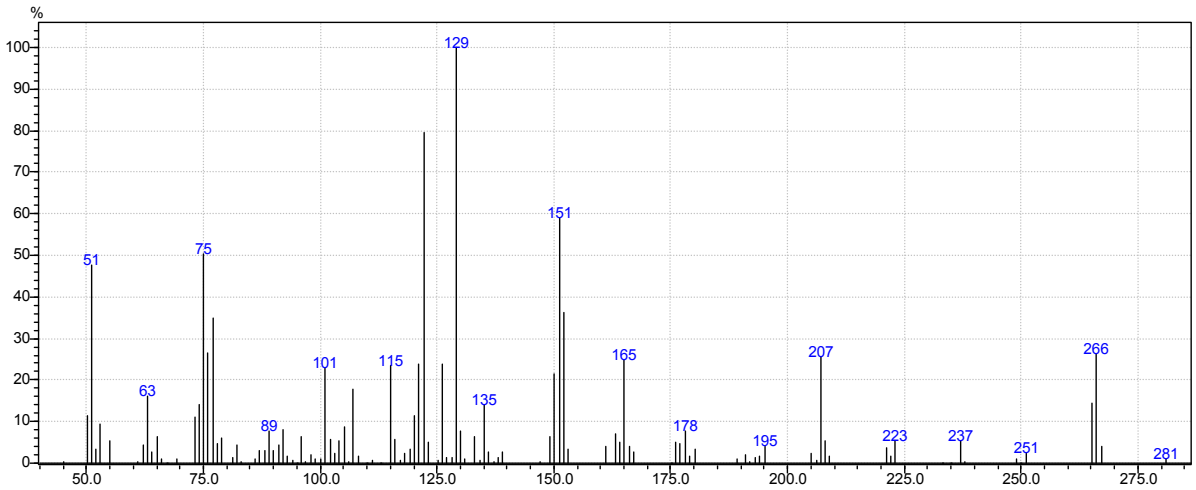
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of 1-(2,3-dimethoxyphenyl)-3-phenylprop-2-yn-1-one (**4ah**)



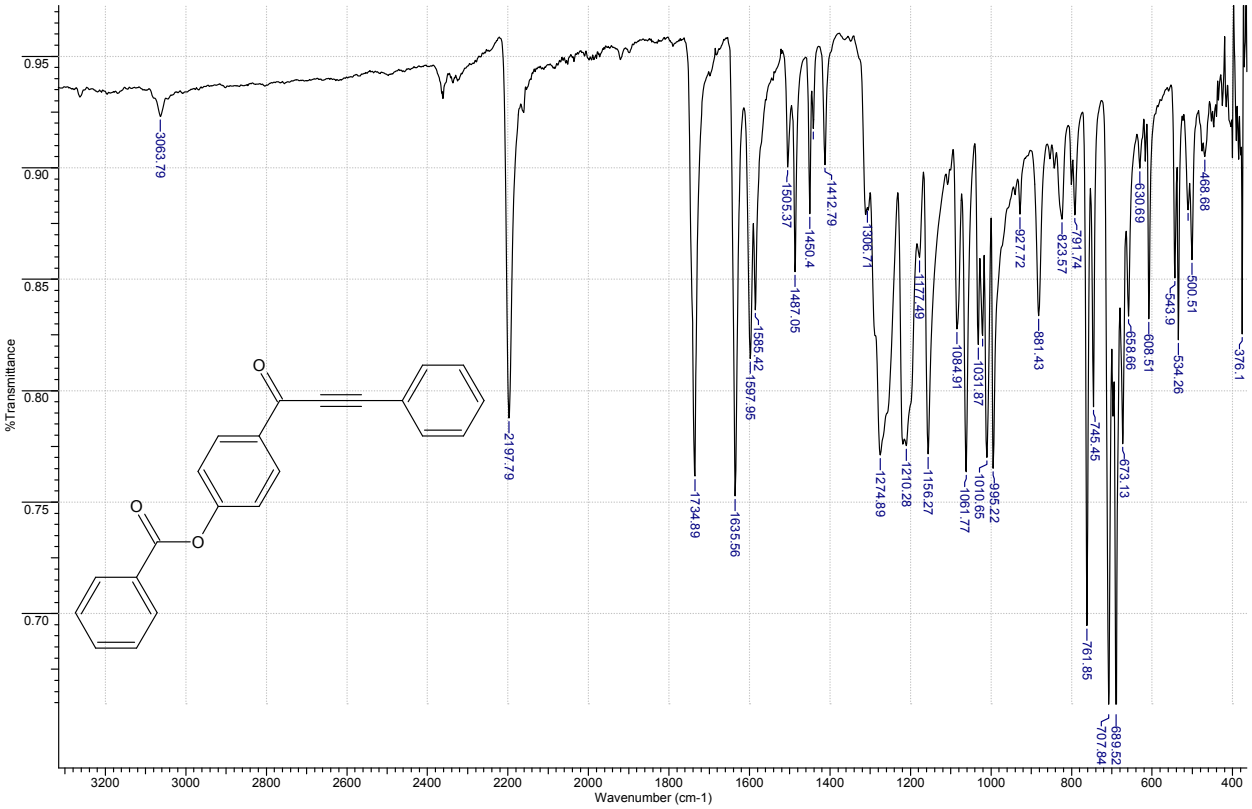
^{13}C NMR spectrum (100 MHz, $CDCl_3$) of 1-(2,3-dimethoxyphenyl)-3-phenylprop-2-yn-1-one (**4ah**)



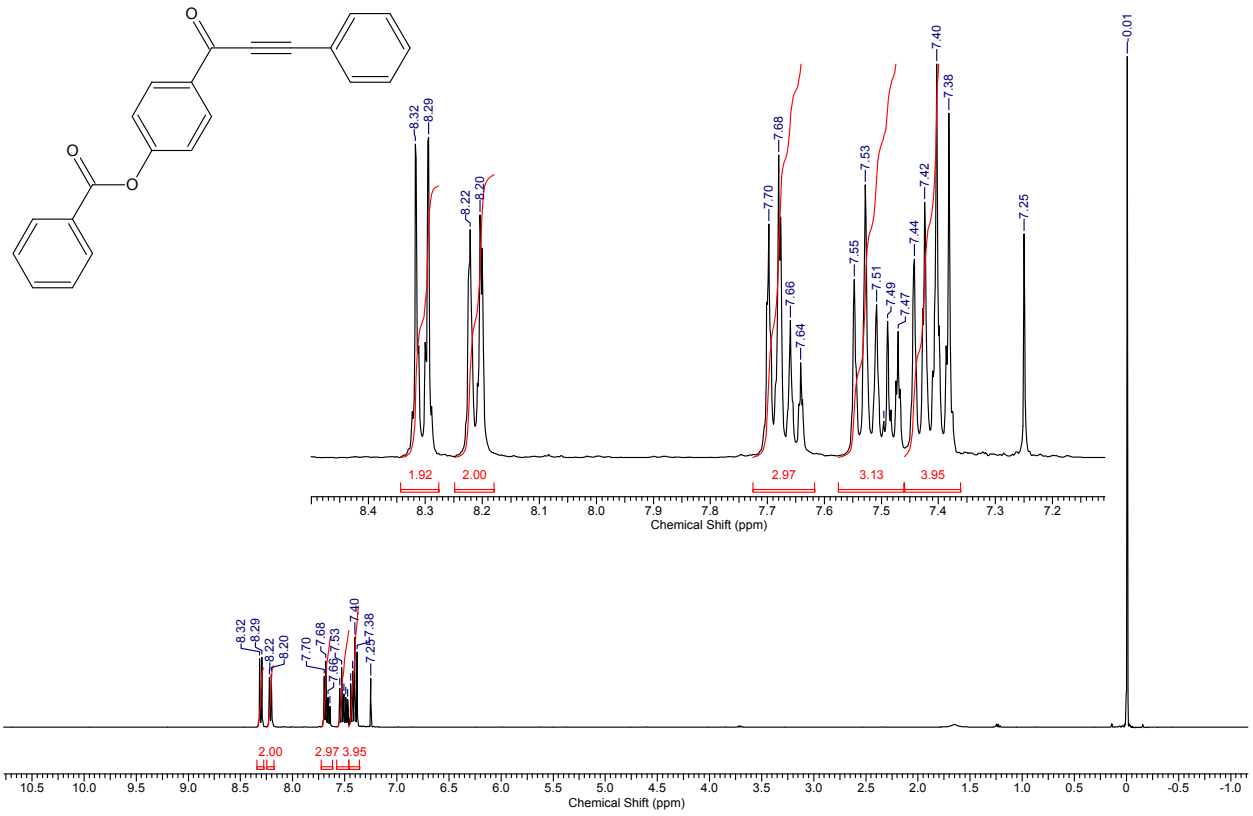
Mass-spectrum (EI, 70 eV) of1 -(2,3-dimethoxyphenyl)-3-phenylprop-2-yn-1-one (**4ah**)



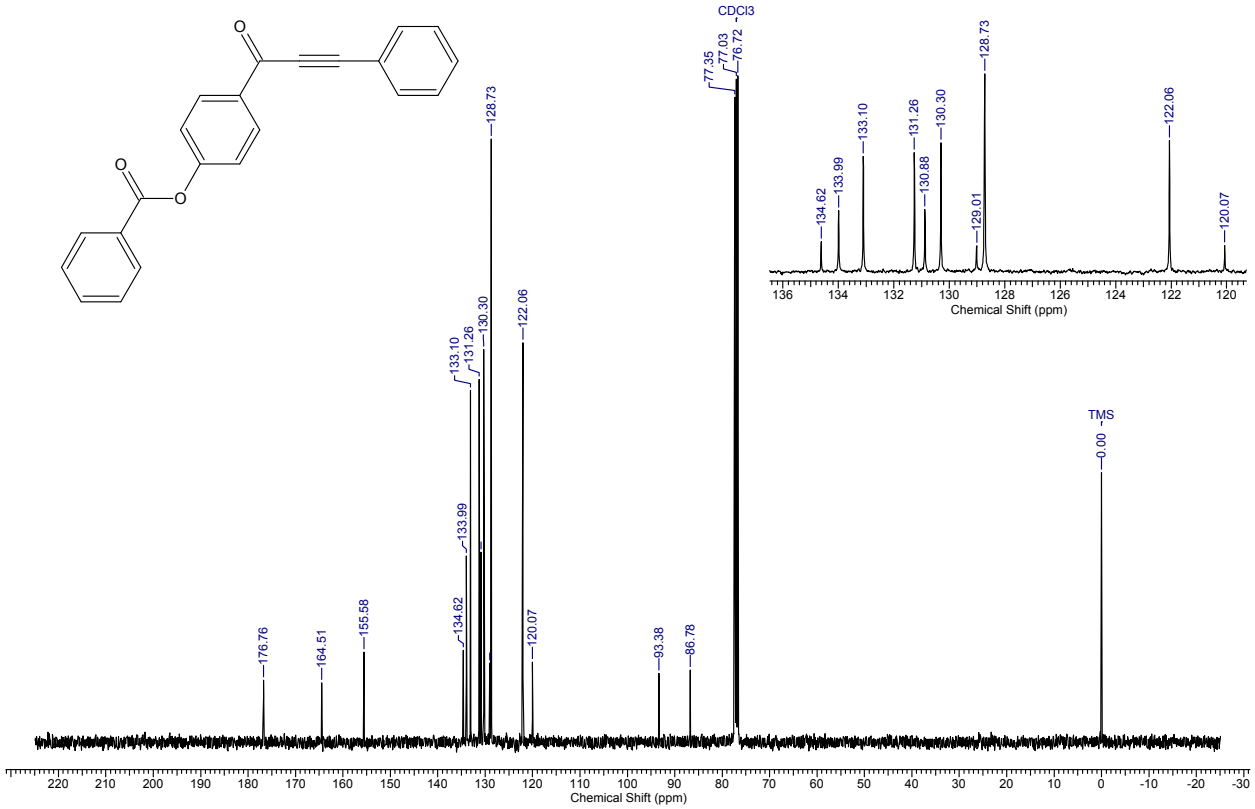
IR spectrum (KBr) of 4-(3-phenylprop-2-ynoyl)phenyl benzoate (**4ai**)



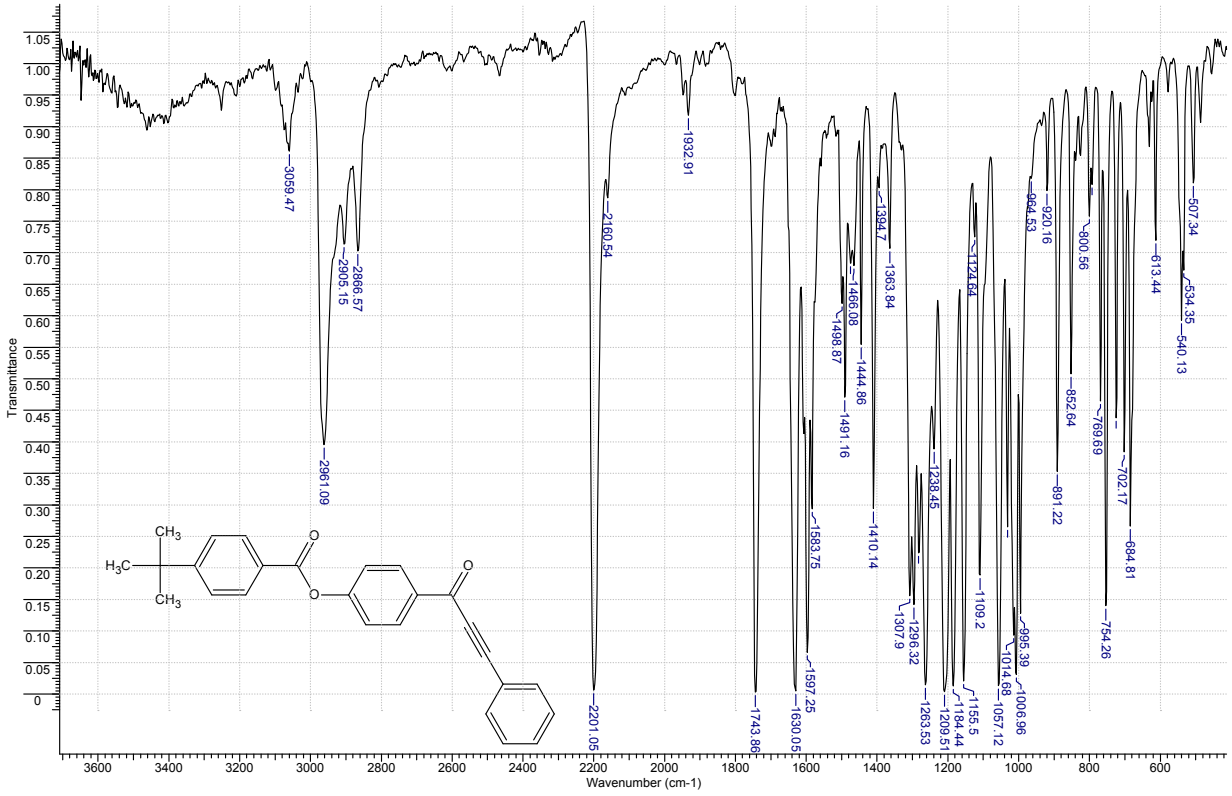
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of 4-(3-phenylprop-2-ynoyl)phenyl benzoate (**4ai**)



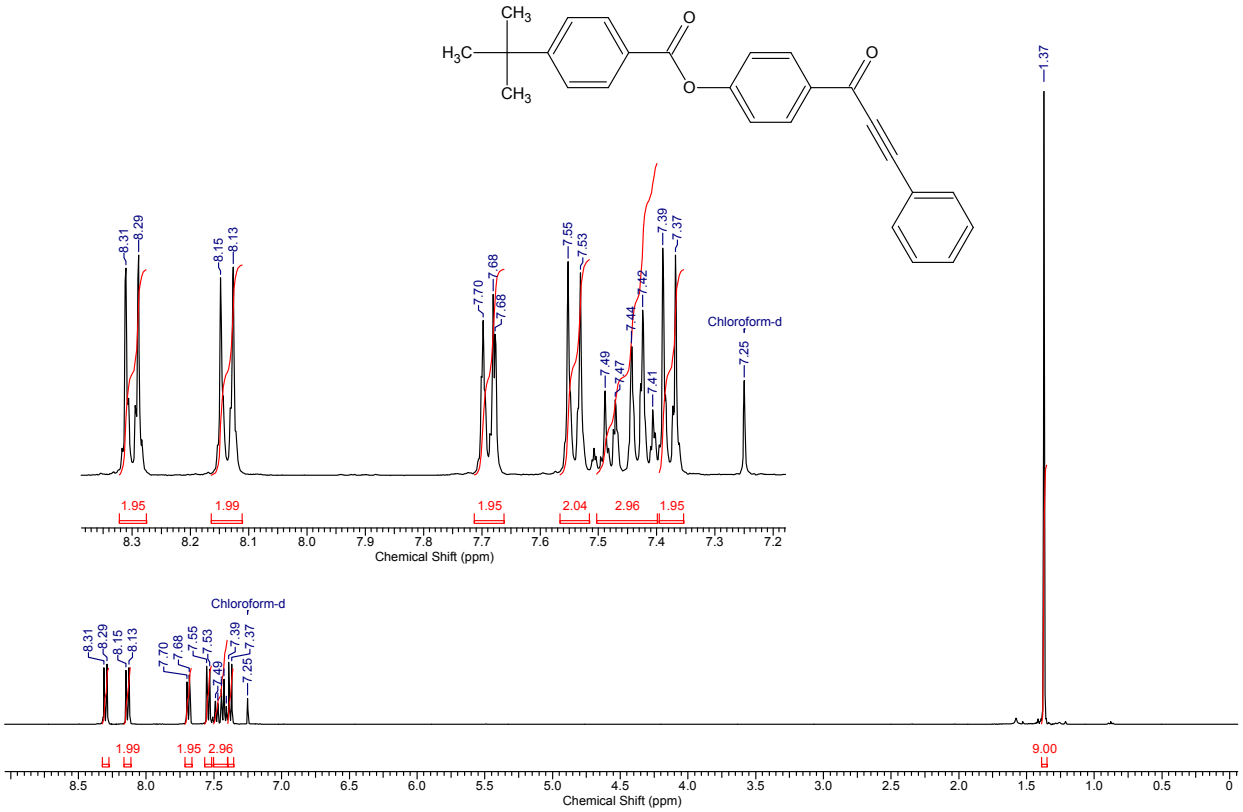
^{13}C NMR spectrum (100 MHz, $CDCl_3$) of 4-(3-phenylprop-2-ynoyl)phenyl benzoate (**4ai**)



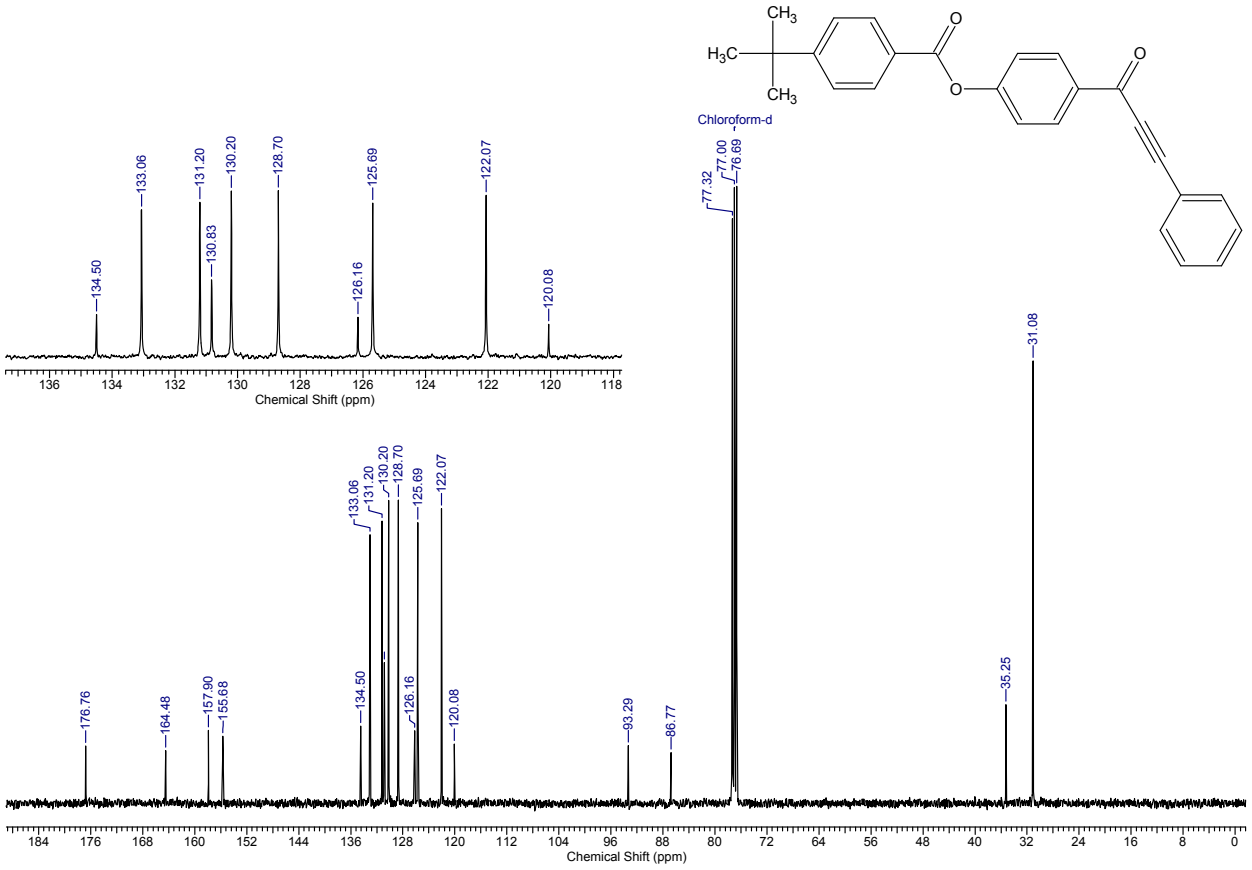
IR spectrum (KBr) of 4-(3-phenylprop-2-ynoyl)phenyl 4-*tert*-butylbenzoate (**4aj**)



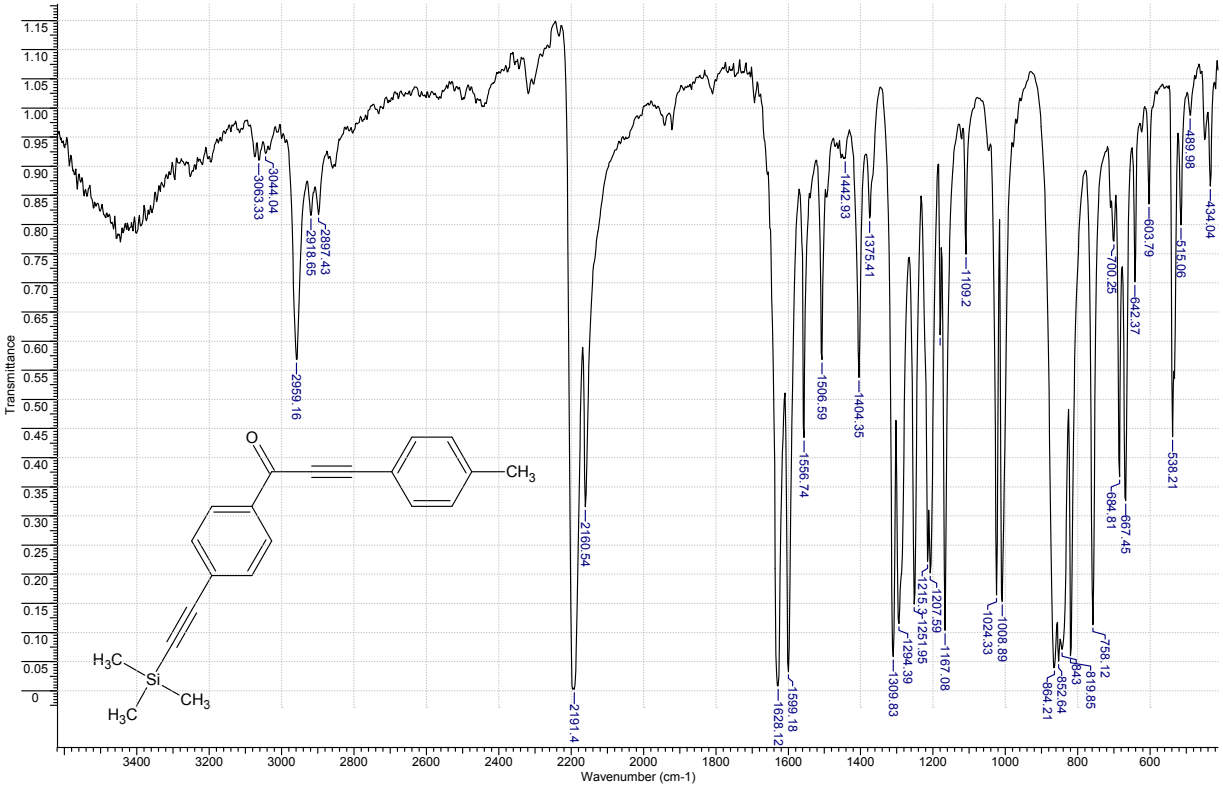
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of 4-(3-phenylprop-2-ynoyl)phenyl 4-*tert*-butylbenzoate (**4aj**)



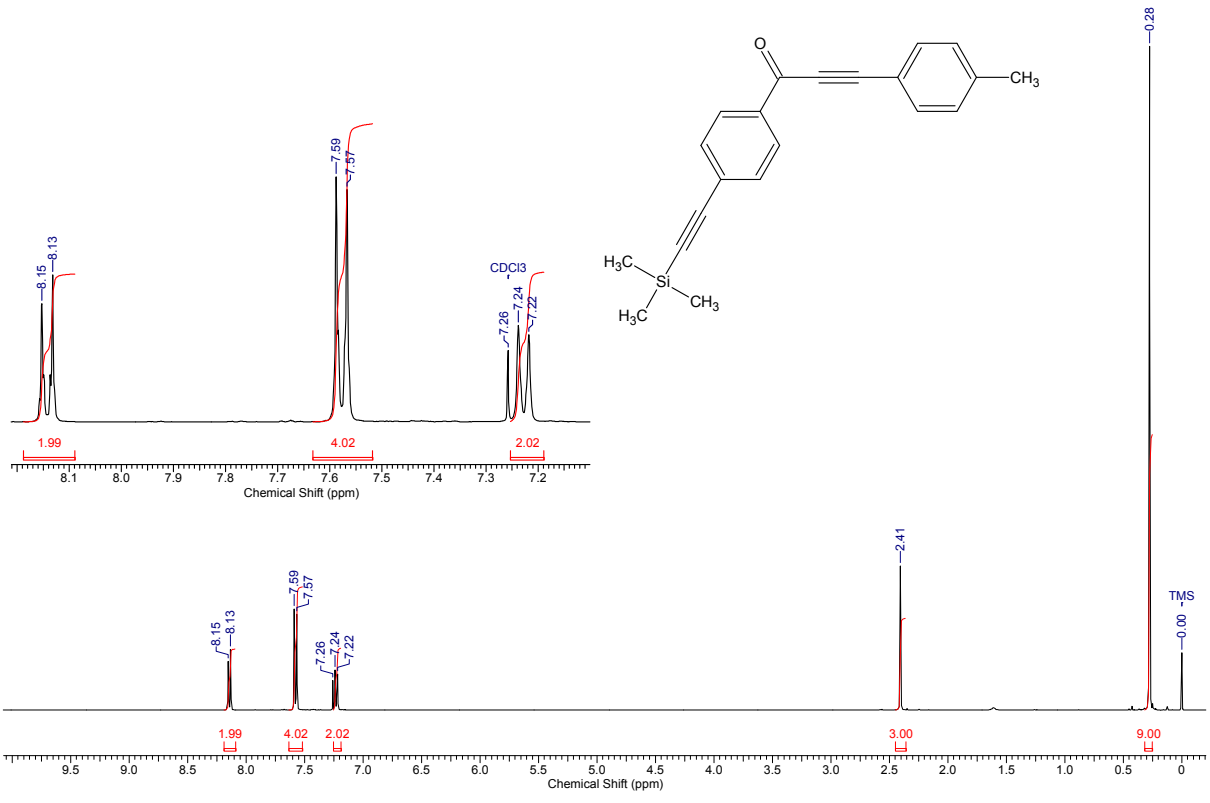
^{13}C NMR spectrum (100 MHz, $CDCl_3$) of 4-(3-phenylprop-2-ynoyl)phenyl 4-*tert*-butylbenzoate (**4aj**)



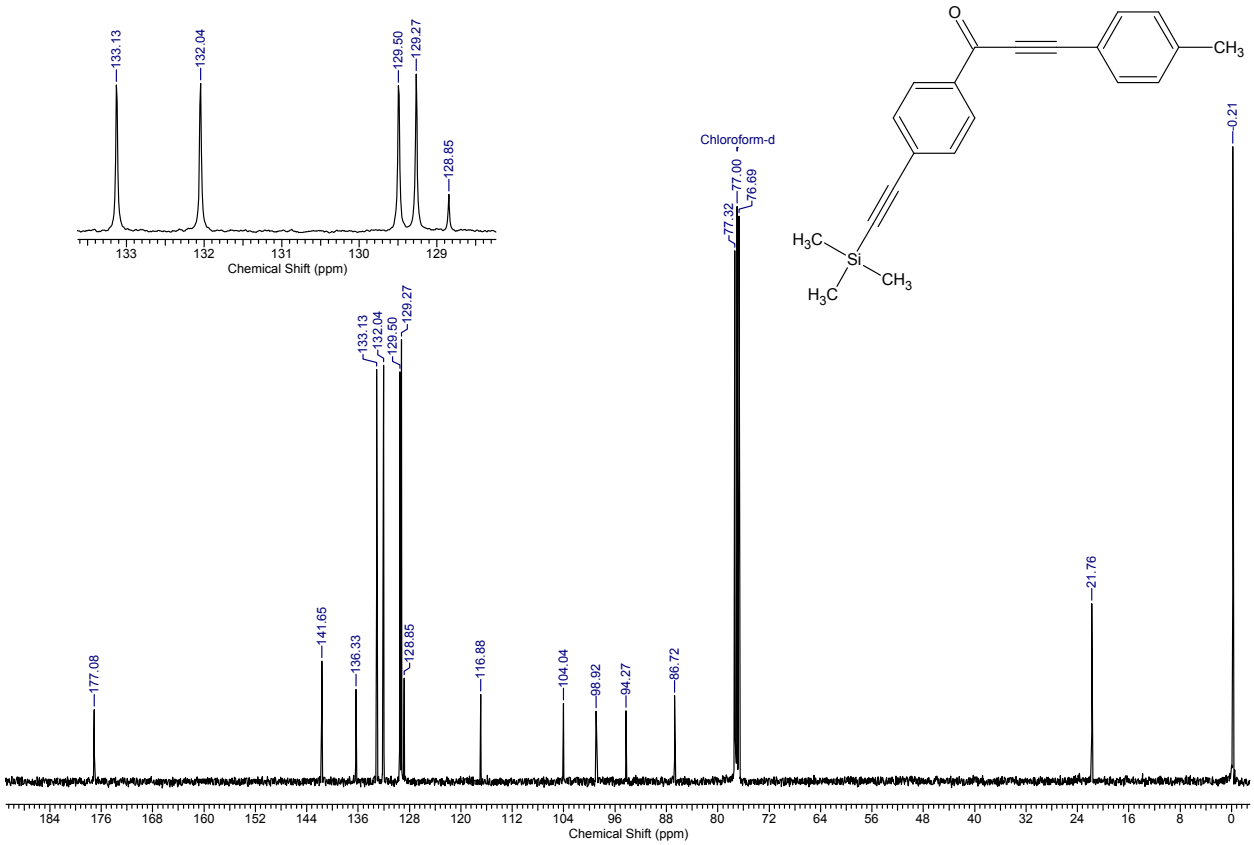
IR spectrum (KBr) of 3-phenyl-1-{4-[(trimethylsilyl)ethynyl]phenyl}prop-2-yn-1-one (**4bk**)



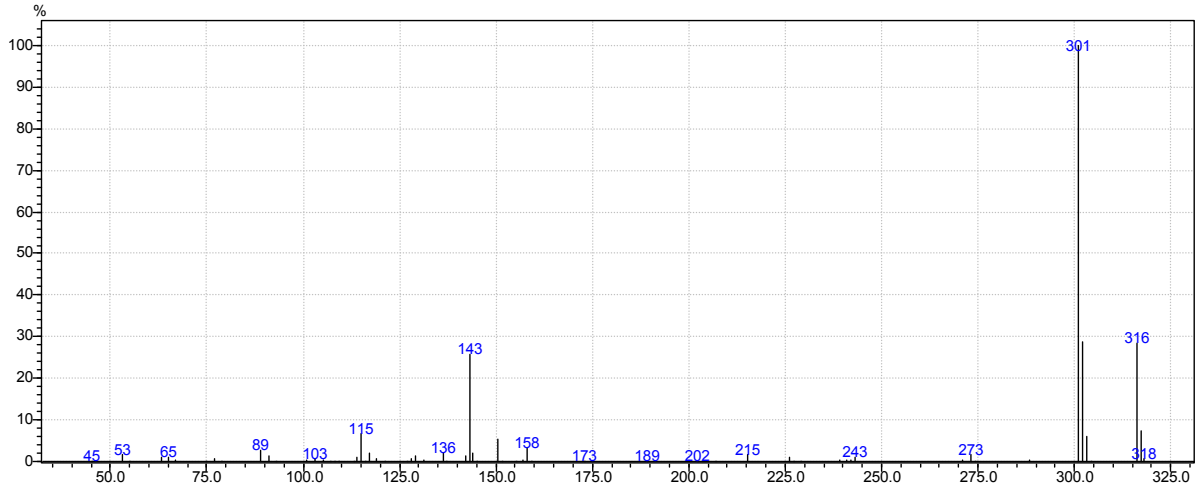
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of 3-phenyl-1-{4-[(trimethylsilyl)ethynyl]phenyl}prop-2-yn-1-one (**4bk**)



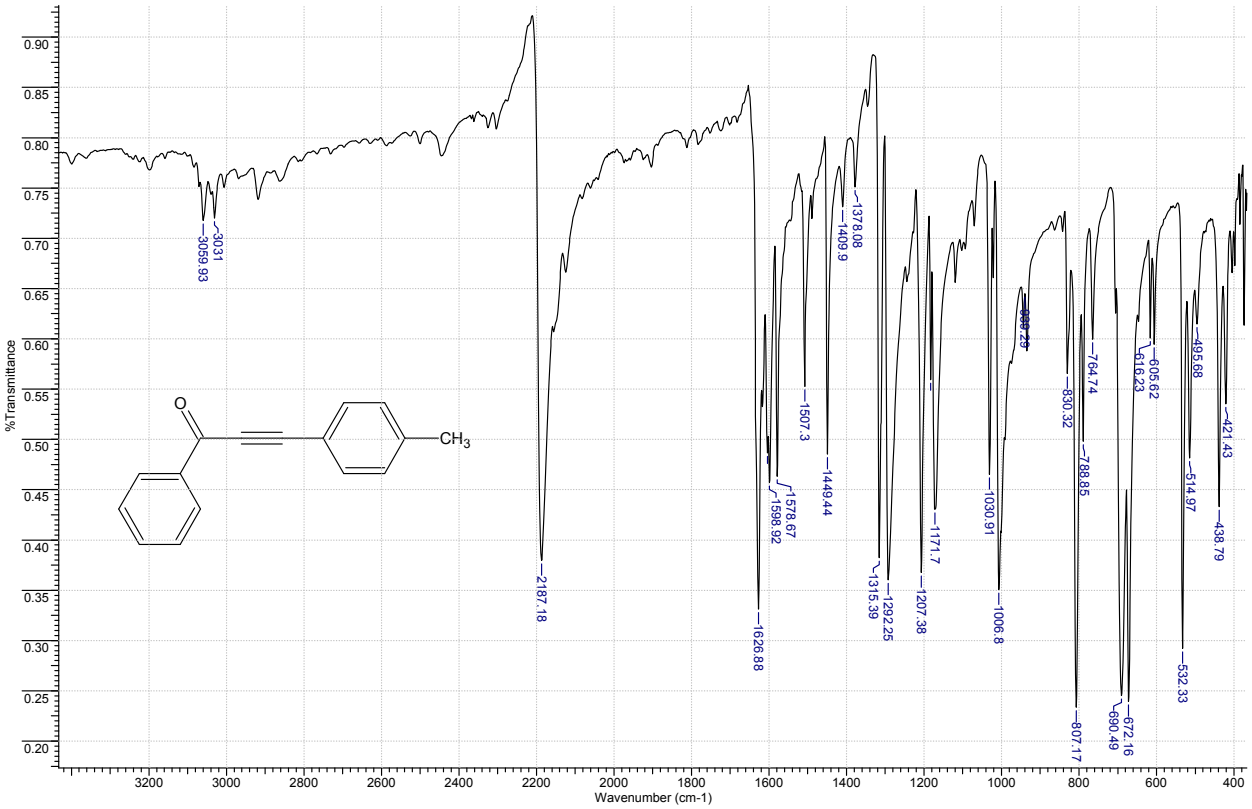
^{13}C NMR spectrum (100 MHz, $CDCl_3$) of 3-phenyl-1-{4-[(trimethylsilyl)ethynyl]phenyl}prop-2-yn-1-one (**4bk**)



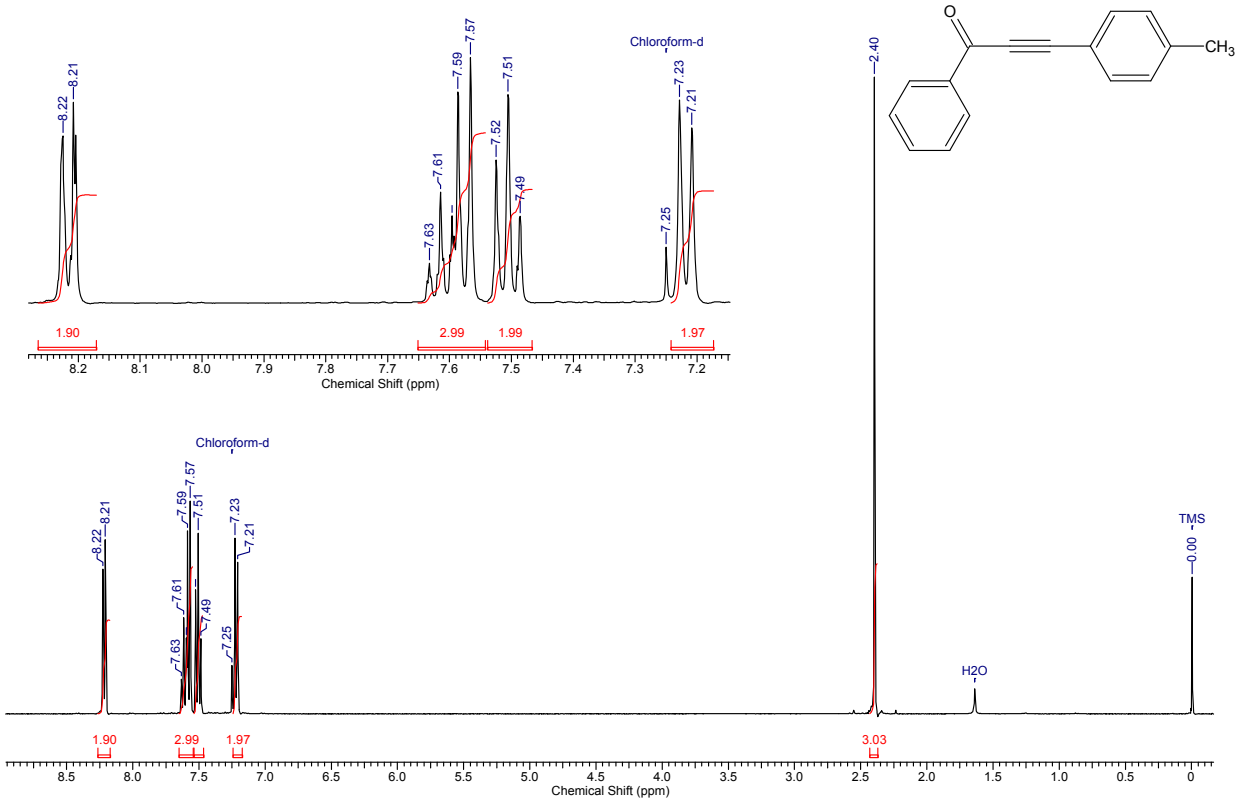
Mass-spectrum (EI, 70 eV) of 3-phenyl-1-{4-[(trimethylsilyl)ethynyl]phenyl}prop-2-yn-1-one (**4bk**)



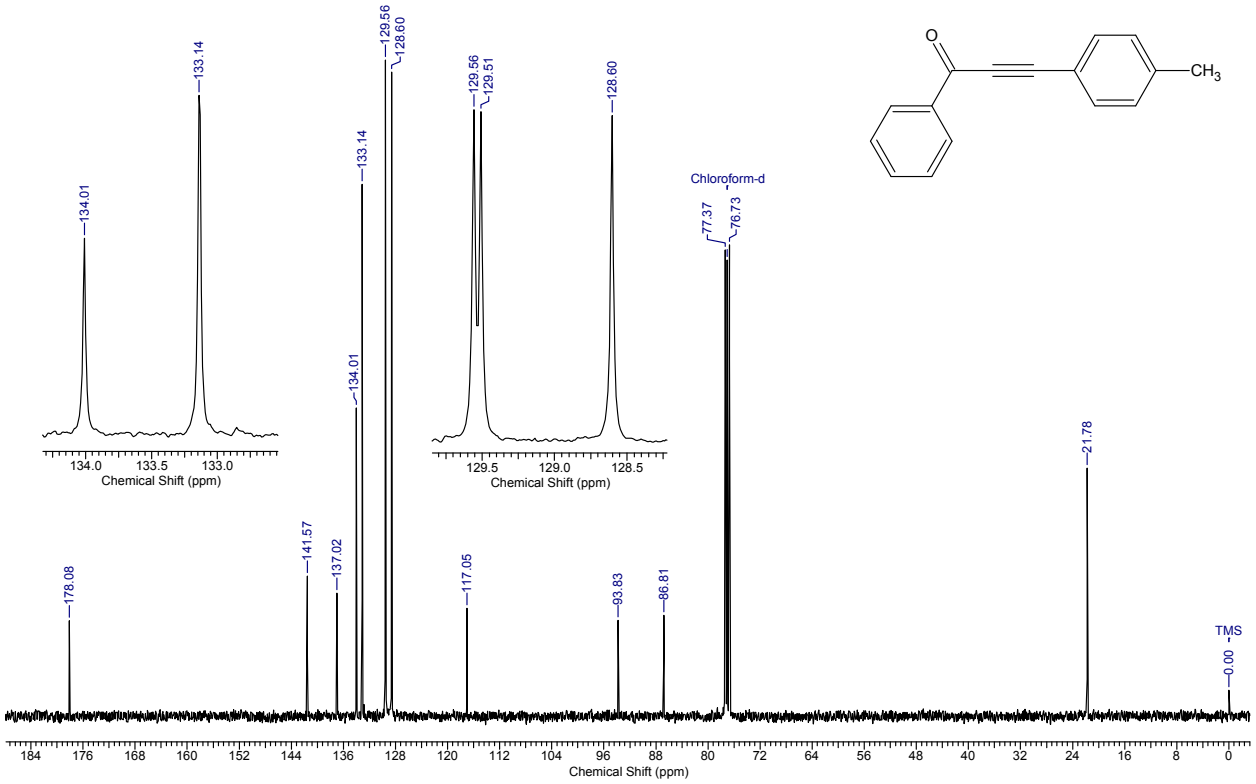
IR spectrum (KBr) of 3-(4-methylphenyl)-1-phenylprop-2-yn-1-one (**4bc**)



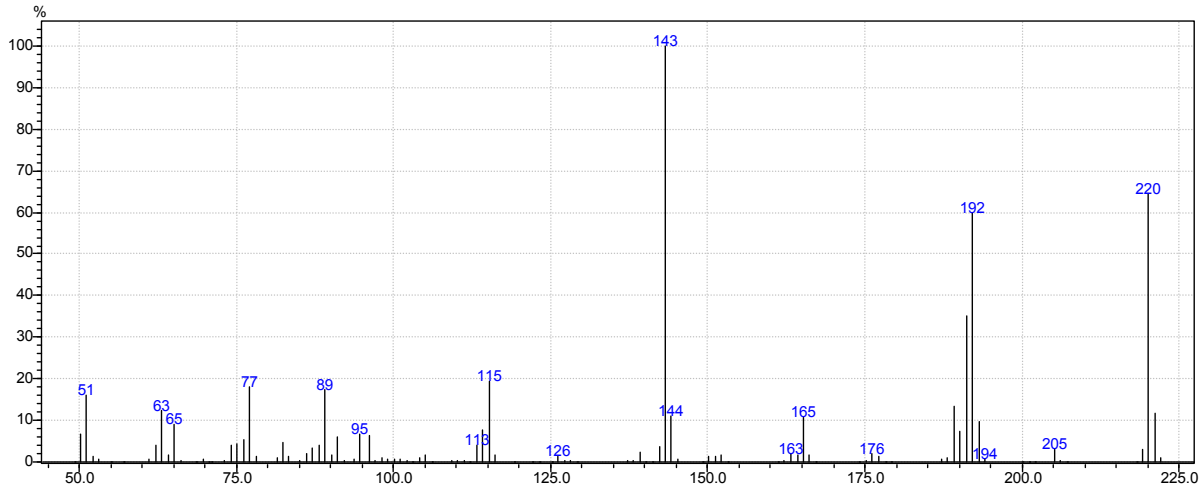
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of 3-(4-methylphenyl)-1-phenylprop-2-yn-1-one (**4bc**)



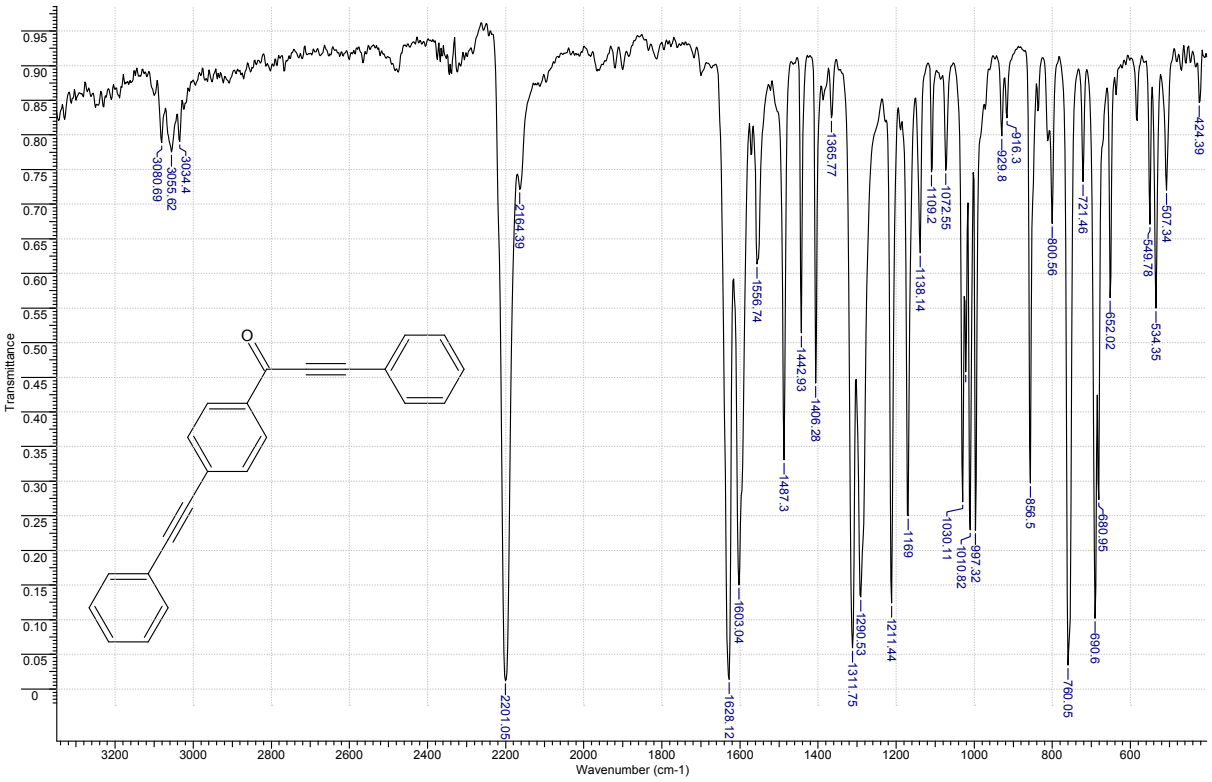
^{13}C NMR spectrum (100 MHz, $CDCl_3$) of 3-(4-methylphenyl)-1-phenylprop-2-yn-1-one (**4bc**)



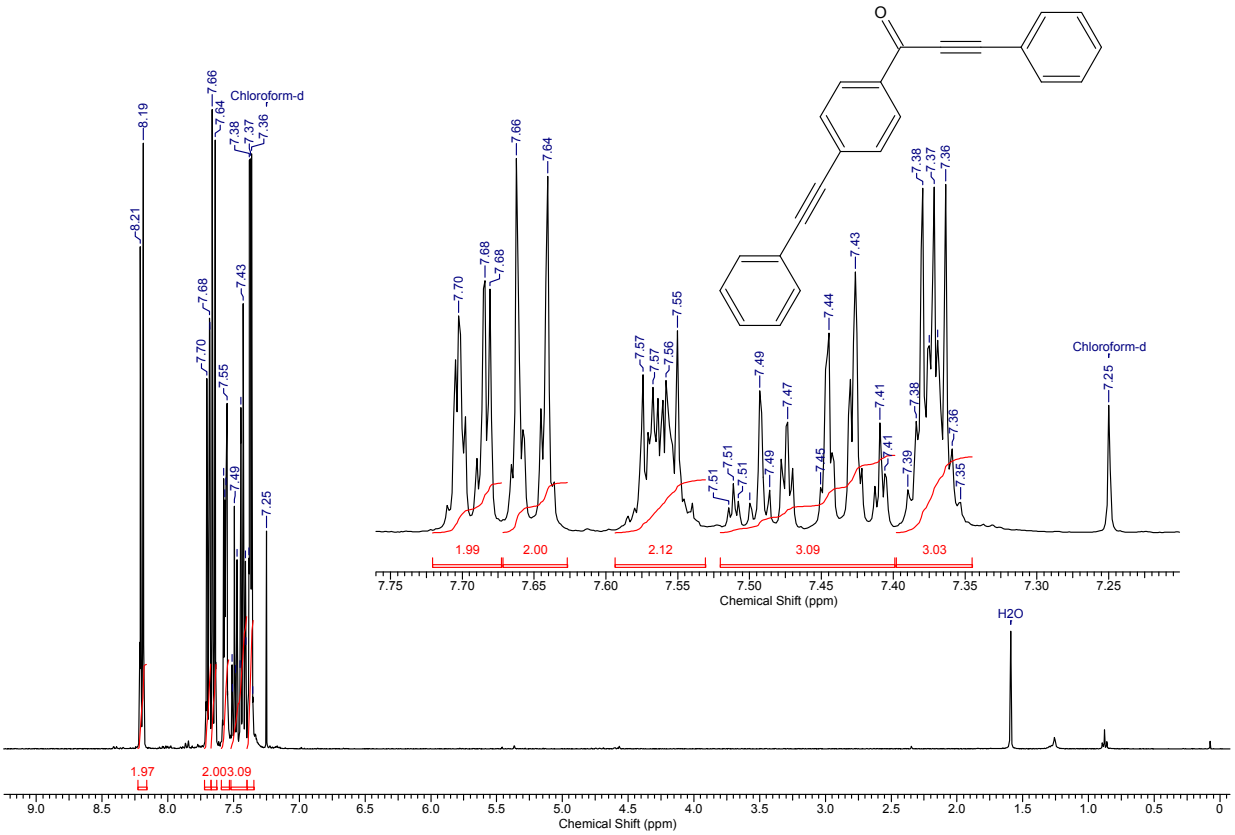
Mass-spectrum (EI, 70 eV) of 3-(4-methylphenyl)-1-phenylprop-2-yn-1-one (**4bc**)



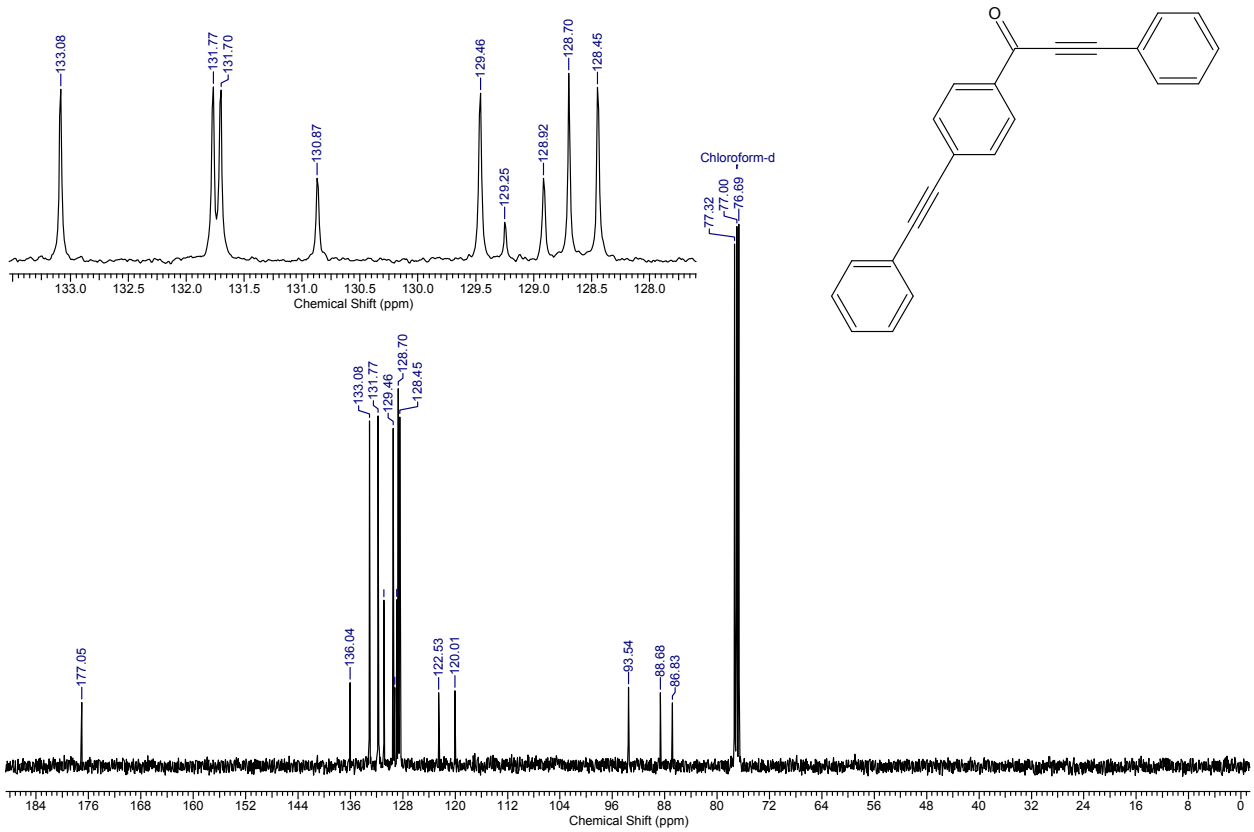
IR spectrum (KBr) of 3-phenyl-1-[4-(phenylethynyl)phenyl]prop-2-yn-1-one (**4al**)



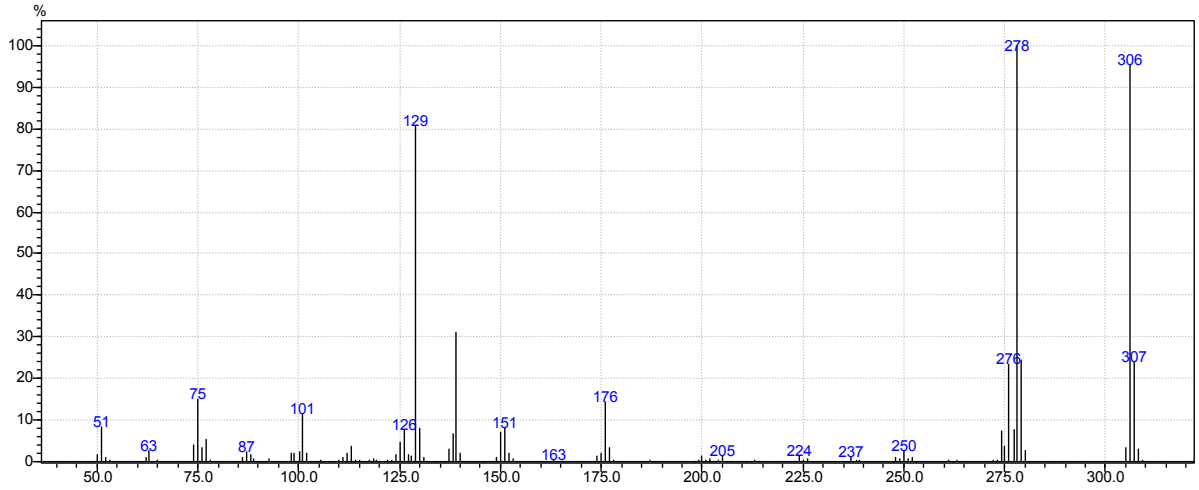
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of 3-phenyl-1-[4-(phenylethynyl)phenyl]prop-2-yn-1-one (**4al**)



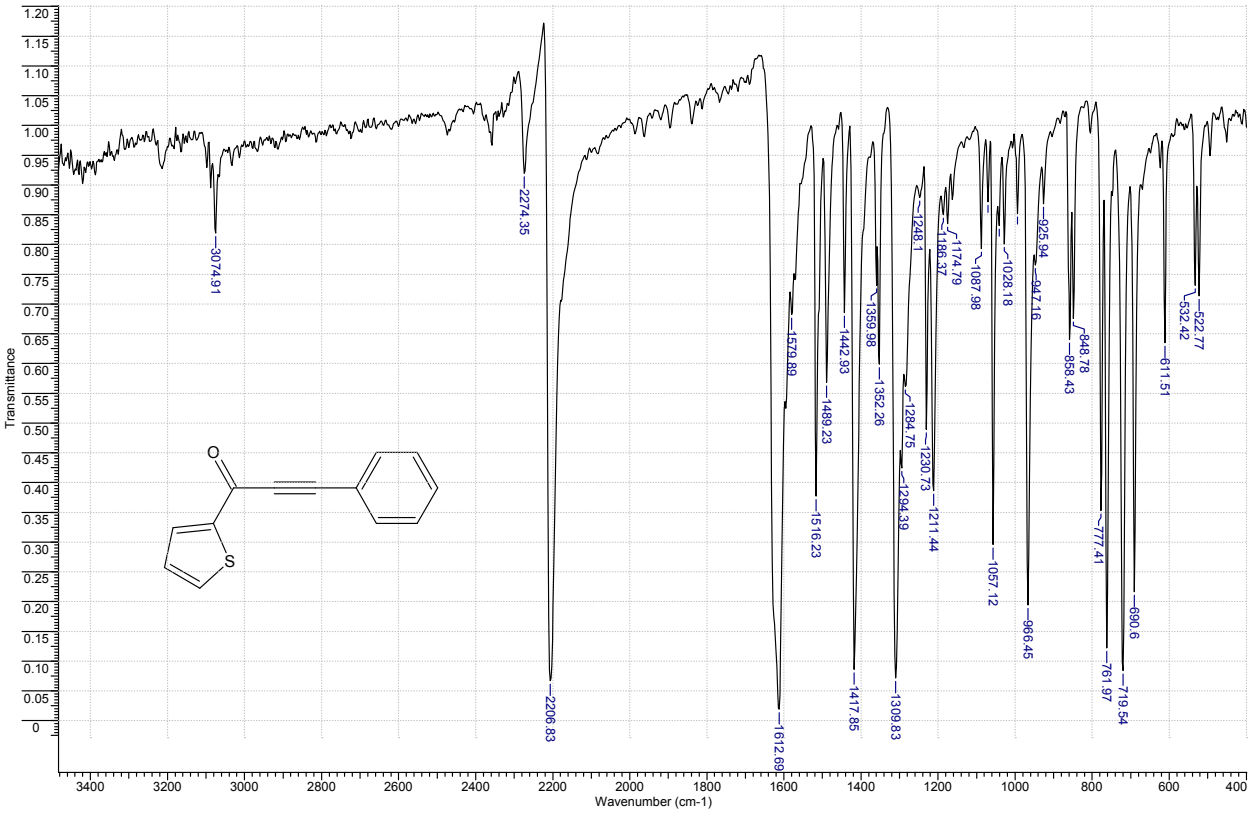
^{13}C NMR spectrum (100 MHz, $CDCl_3$) of 3-phenyl-1-[4-(phenylethynyl)phenyl]prop-2-yn-1-one (**4al**)



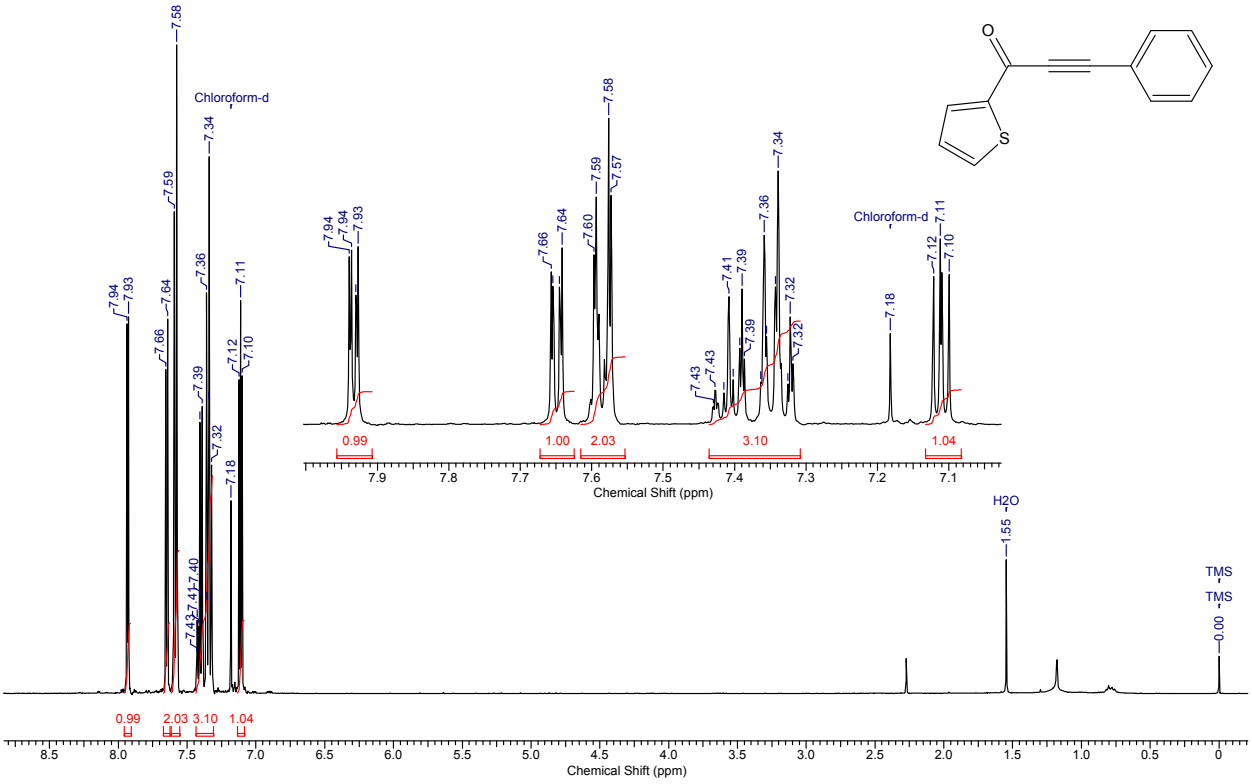
Mass-spectrum (EI, 70 eV) of 3-phenyl-1-[4-(phenylethynyl)phenyl]prop-2-yn-1-one (**4al**)



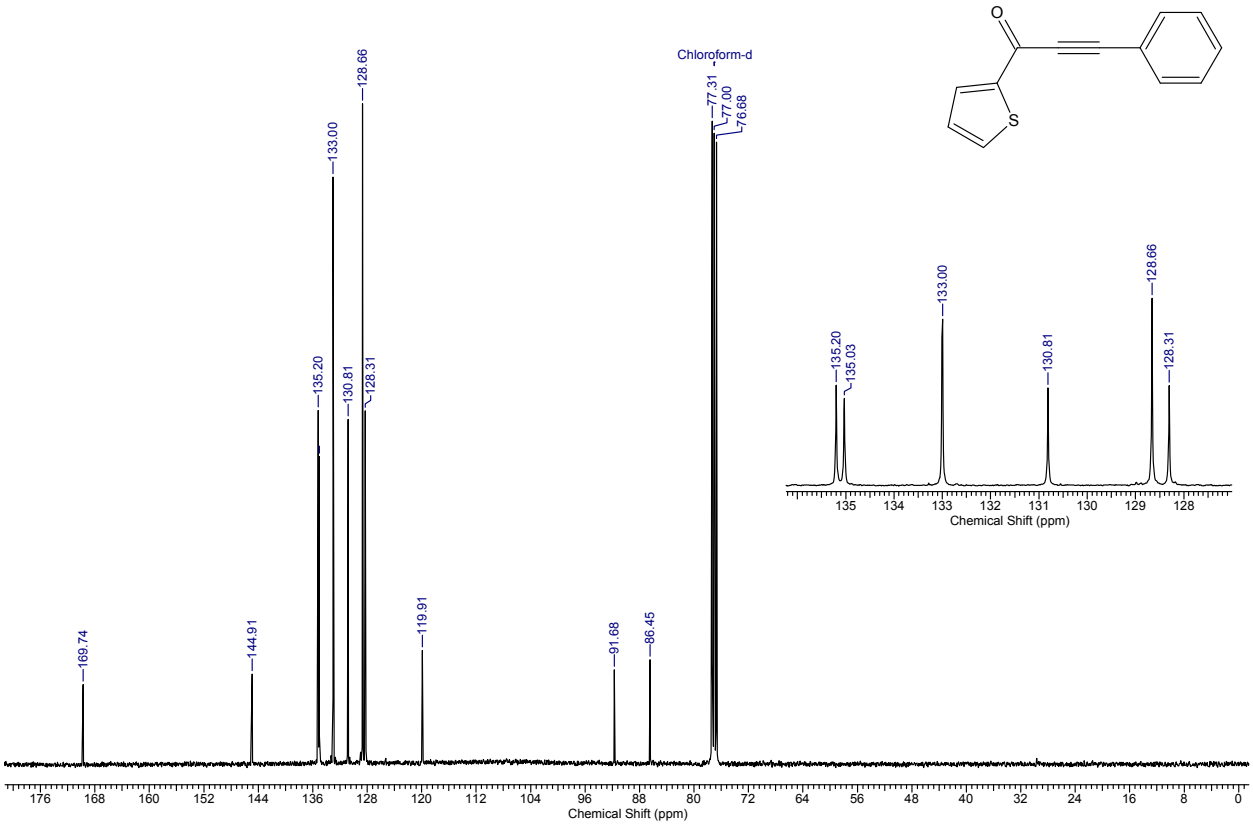
IR spectrum (KBr) of 3-phenyl-1-(2-thienyl)prop-2-yn-1-one (**4am**)



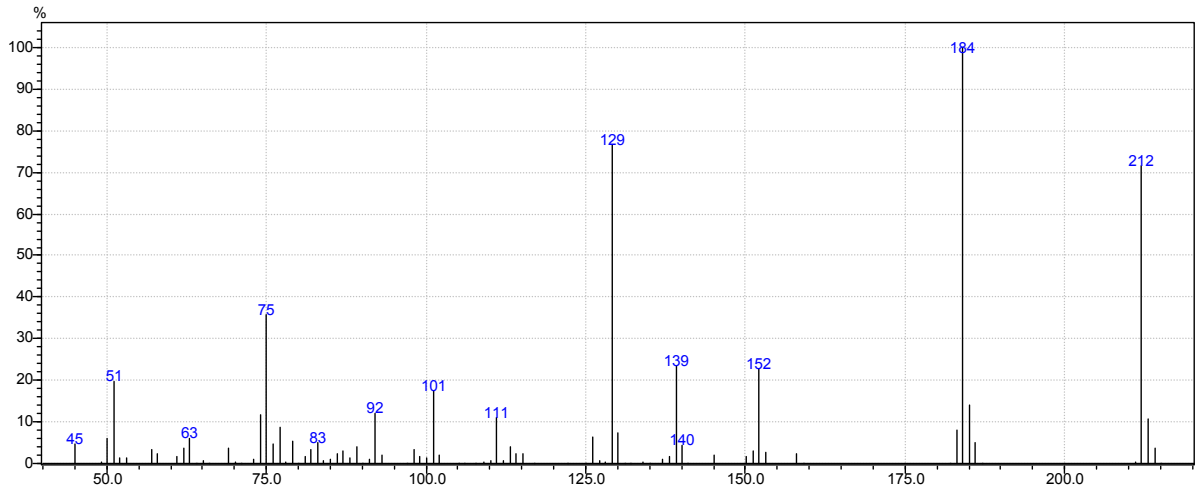
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of 3-phenyl-1-(2-thienyl)prop-2-yn-1-one (**4am**)



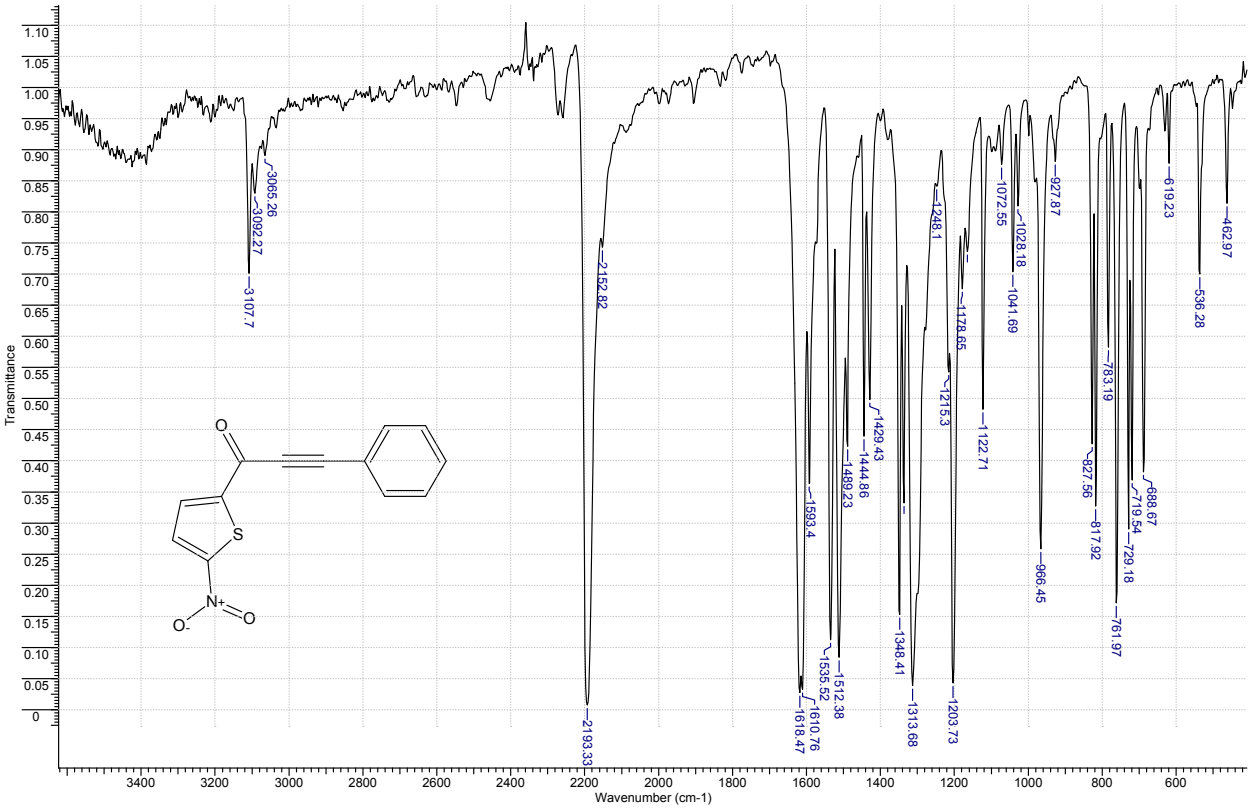
^{13}C NMR spectrum (100 MHz, $CDCl_3$) of 3-phenyl-1-(2-thienyl)prop-2-yn-1-one (**4am**)



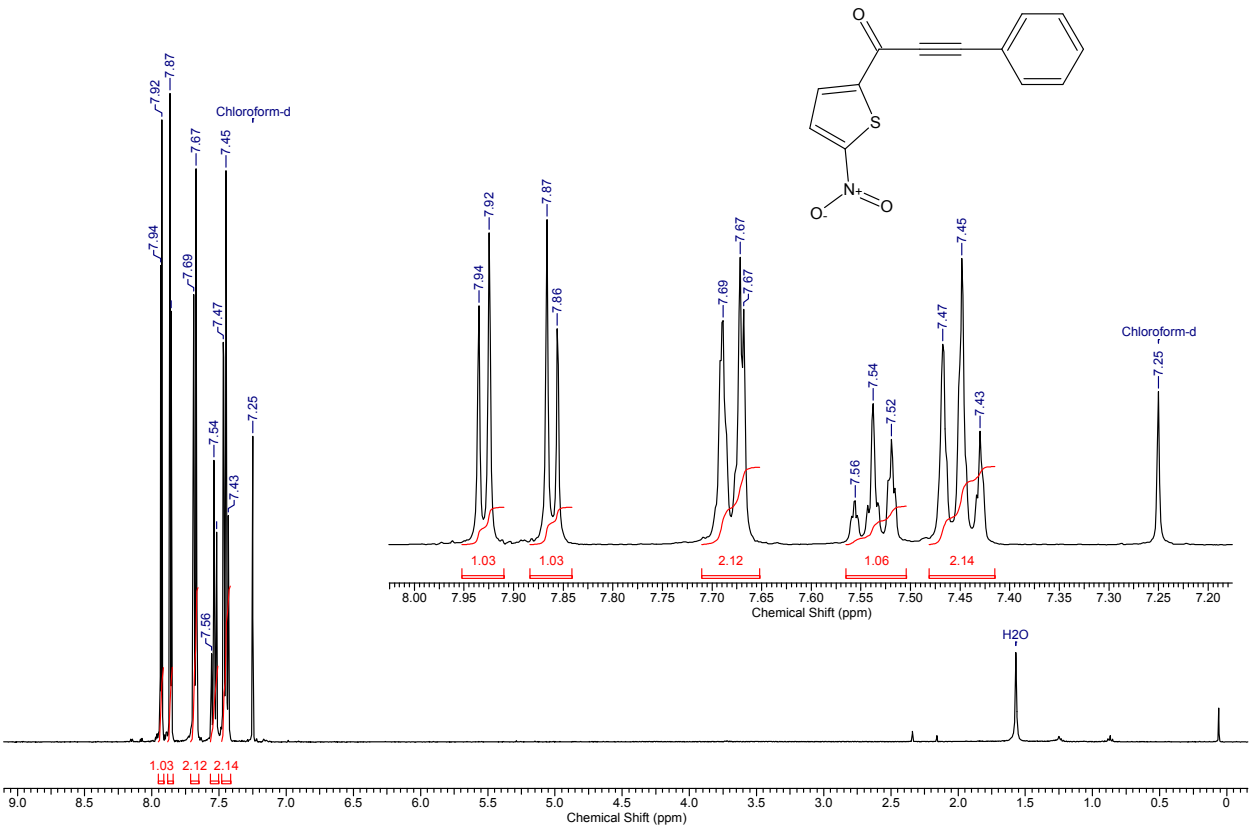
Mass-spectrum (EI, 70 eV) of 3-phenyl-1-(2-thienyl)prop-2-yn-1-one (**4am**)



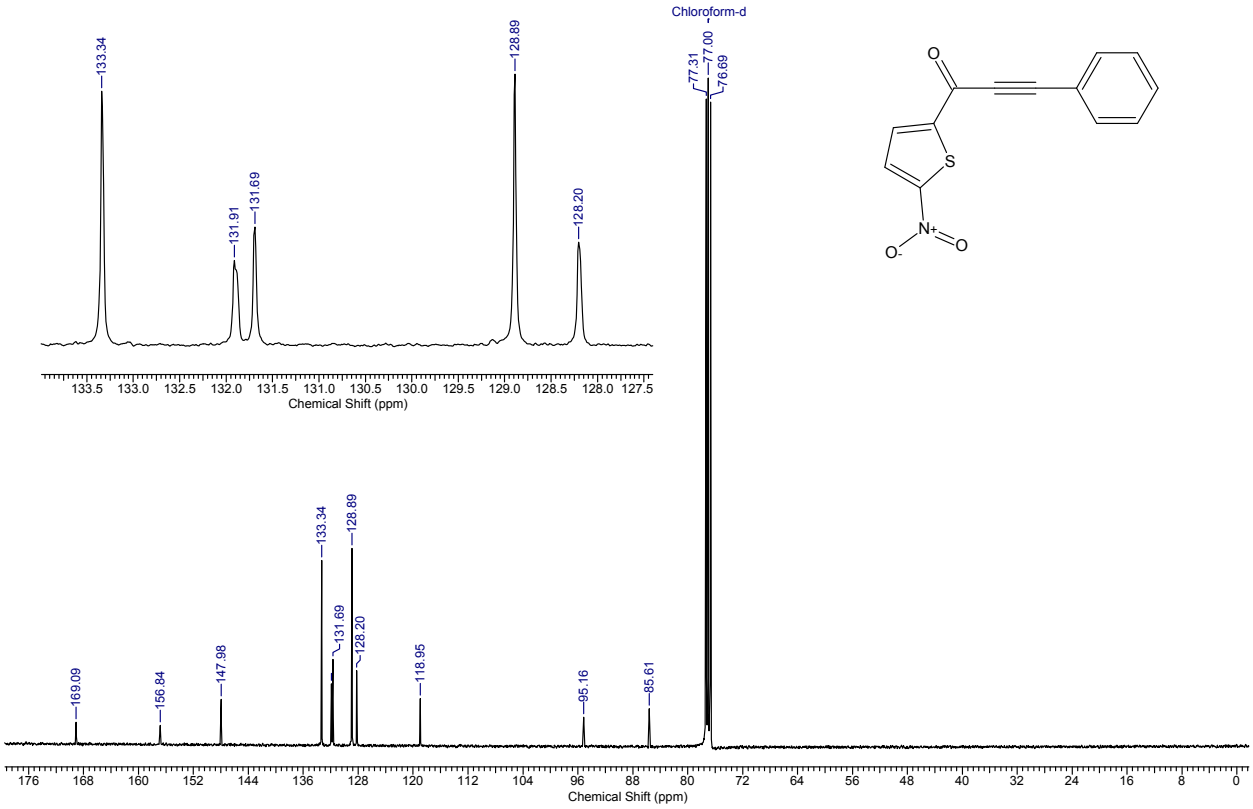
IR spectrum (KBr) of 1-(5-nitro-2-thienyl)-3-phenylprop-2-yn-1-one (**4an**)



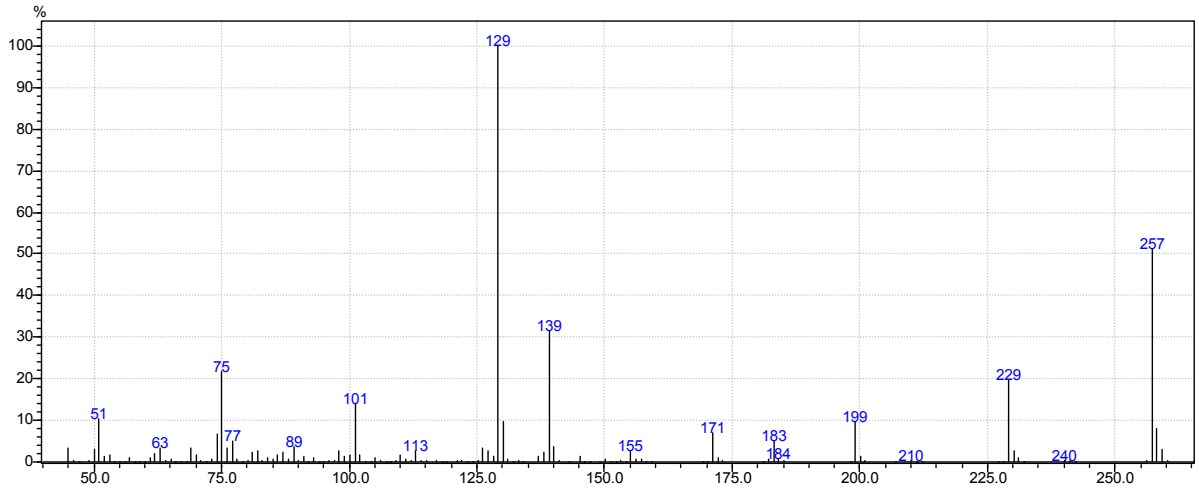
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of 1-(5-nitro-2-thienyl)-3-phenylprop-2-yn-1-one (**4an**)



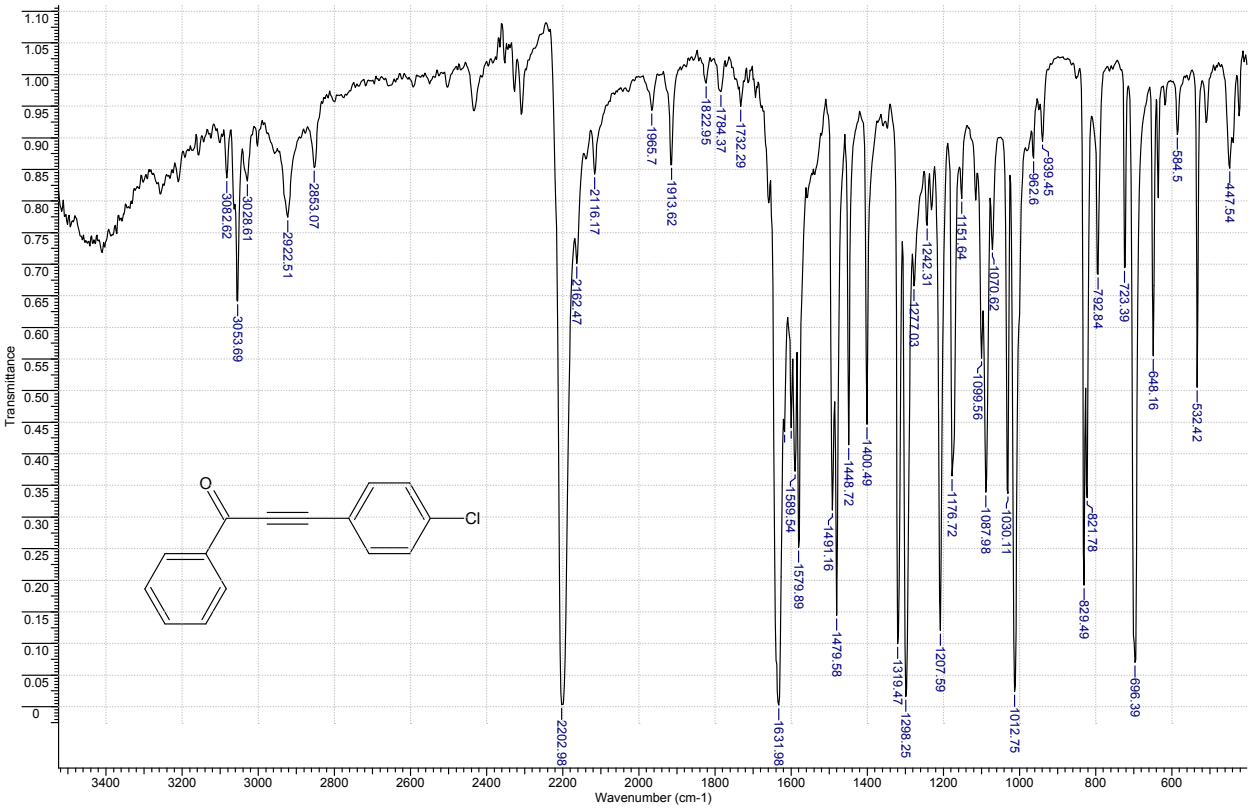
^{13}C NMR spectrum (100 MHz, $CDCl_3$) of 1-(5-nitro-2-thienyl)-3-phenylprop-2-yn-1-one (**4an**)



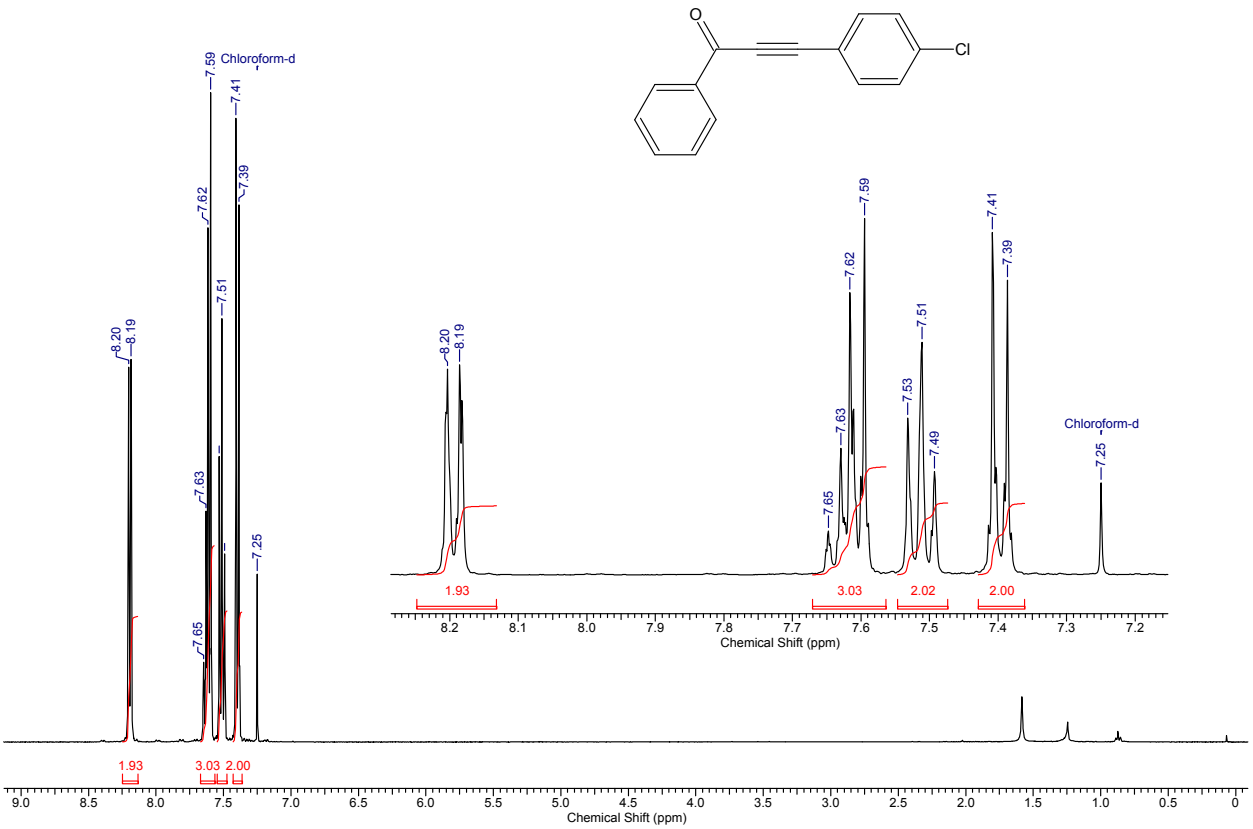
Mass-spectrum (EI, 70 eV) of 1-(5-nitro-2-thienyl)-3-phenylprop-2-yn-1-one (**4an**)



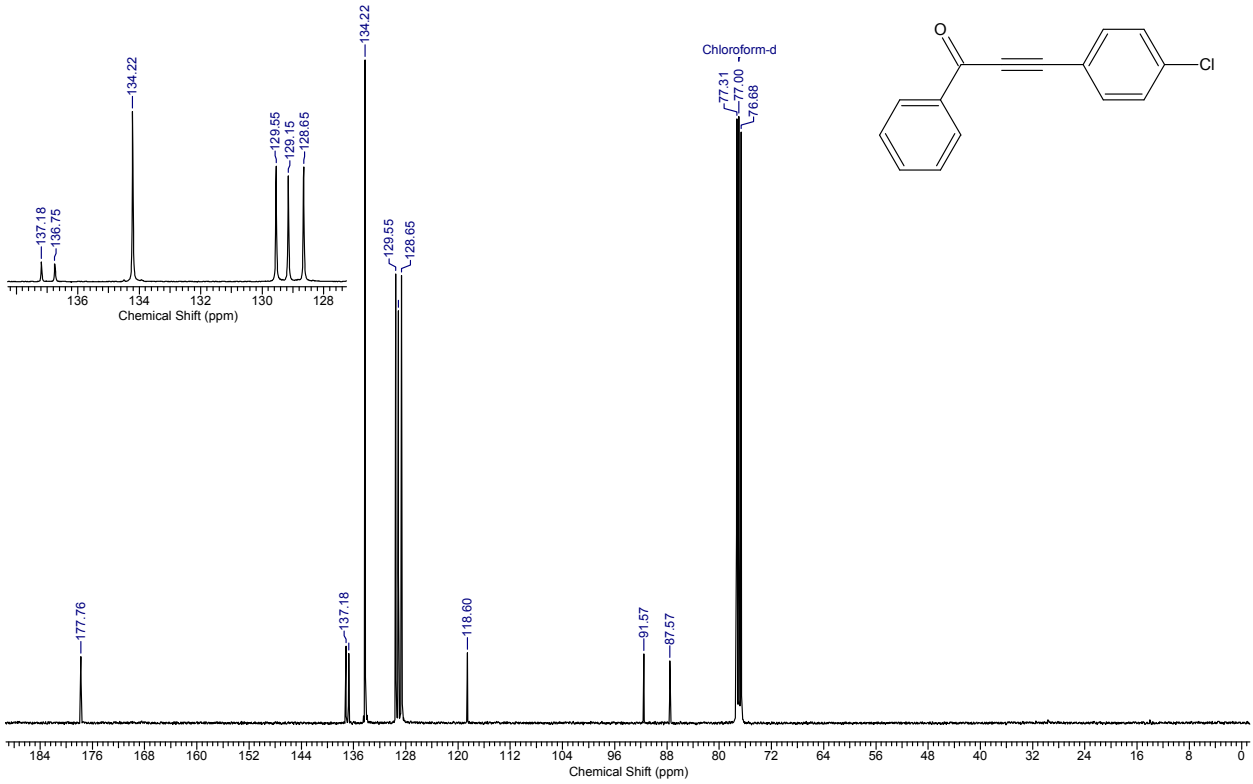
IR spectrum (KBr) of 3-(4-chlorophenyl)-1-phenylprop-2-yn-1-one (**4cc**)



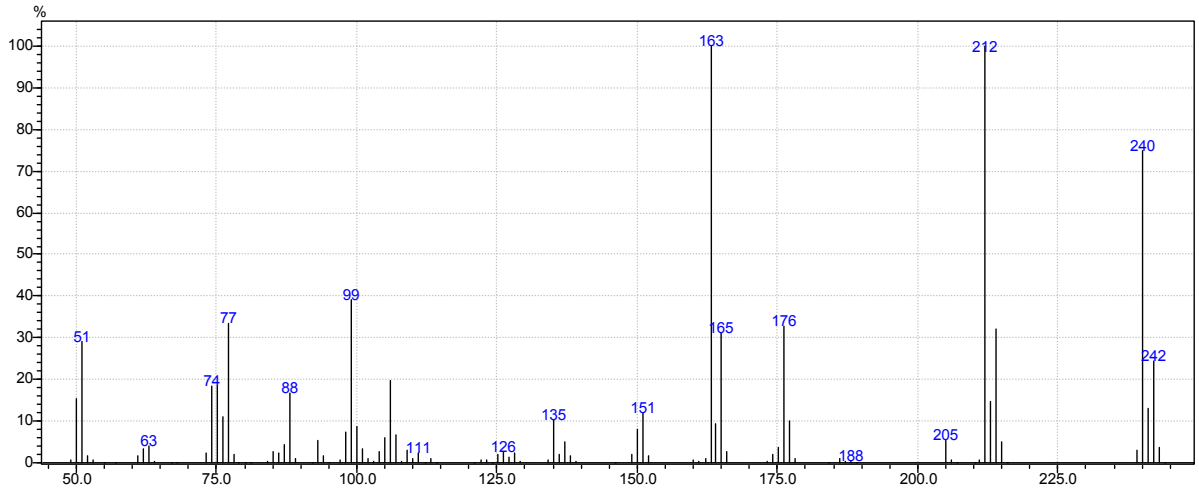
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of 3-(4-chlorophenyl)-1-phenylprop-2-yn-1-one (**4cc**)



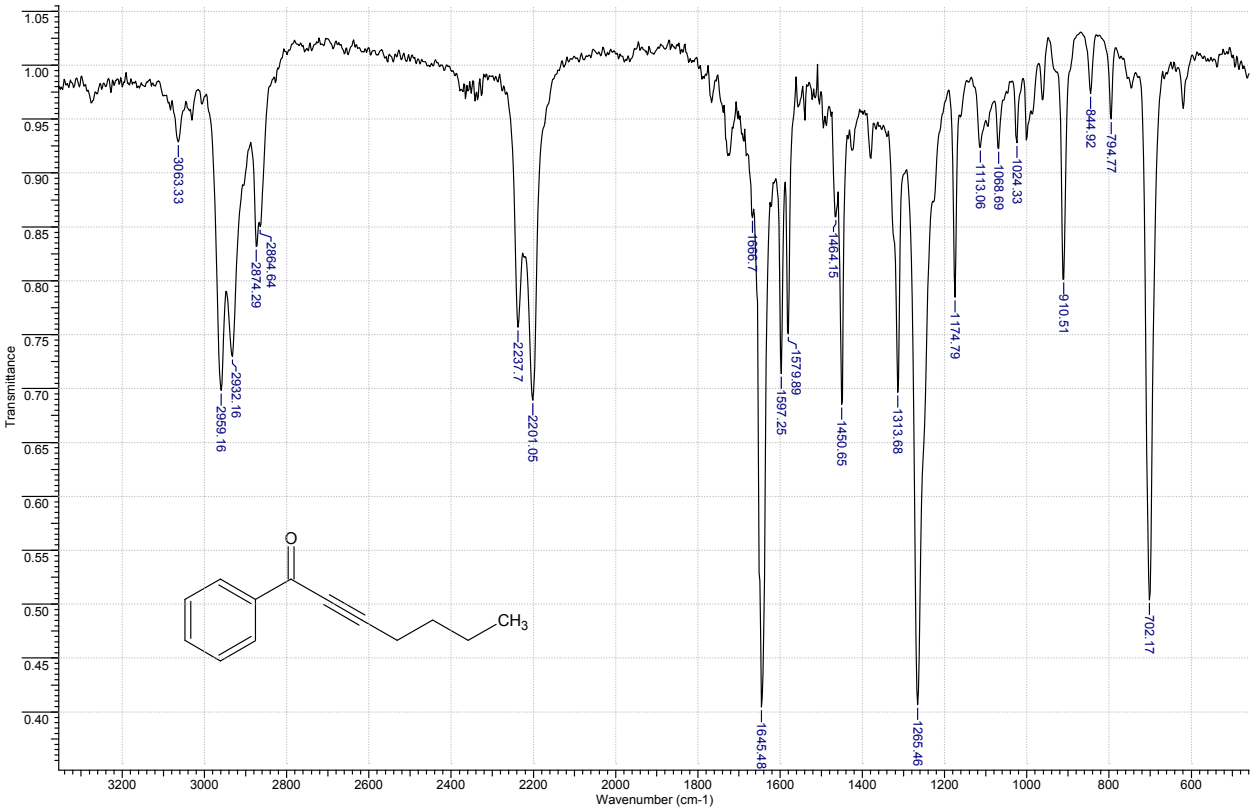
^{13}C NMR spectrum (100 MHz, $CDCl_3$) of 3-(4-chlorophenyl)-1-phenylprop-2-yn-1-one (**4cc**)



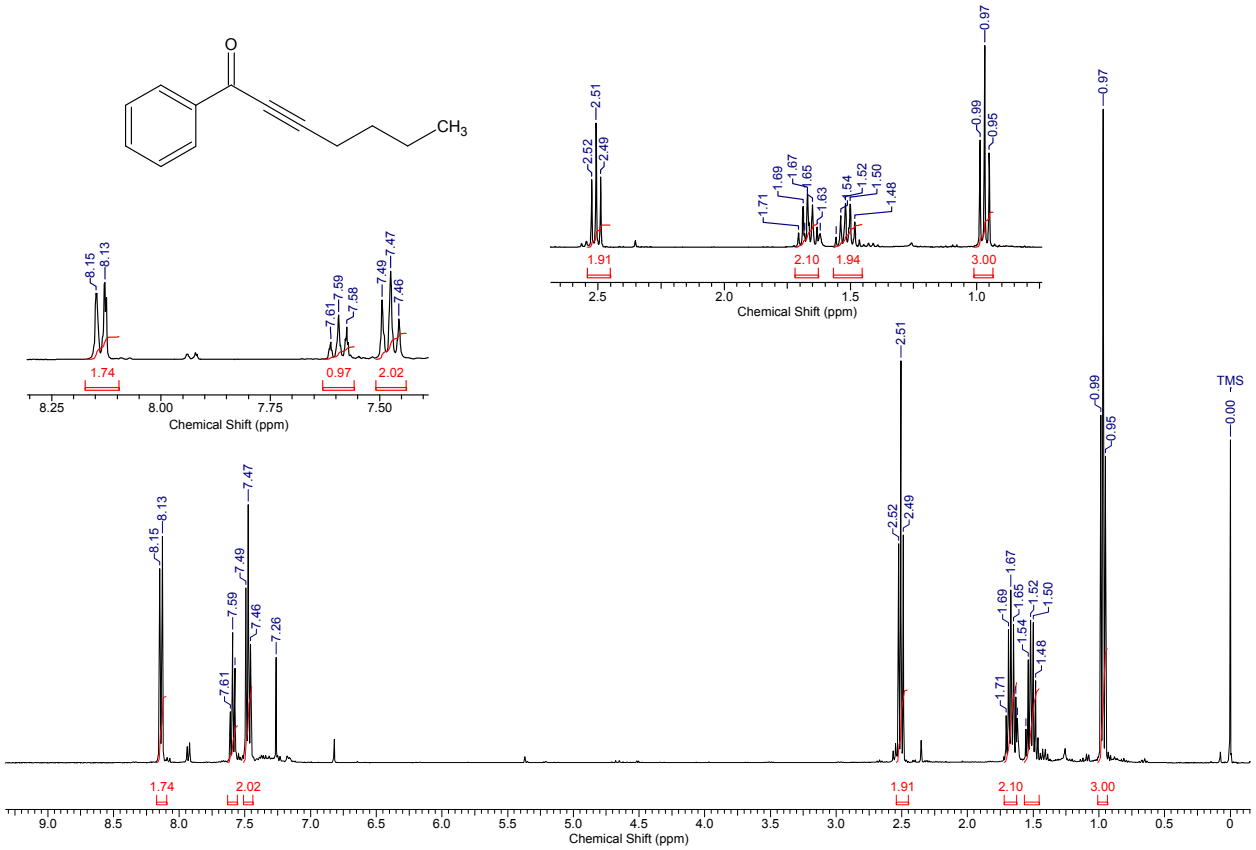
Mass-spectrum (EI, 70 eV) of 3-(4-chlorophenyl)-1-phenylprop-2-yn-1-one (**4cc**)



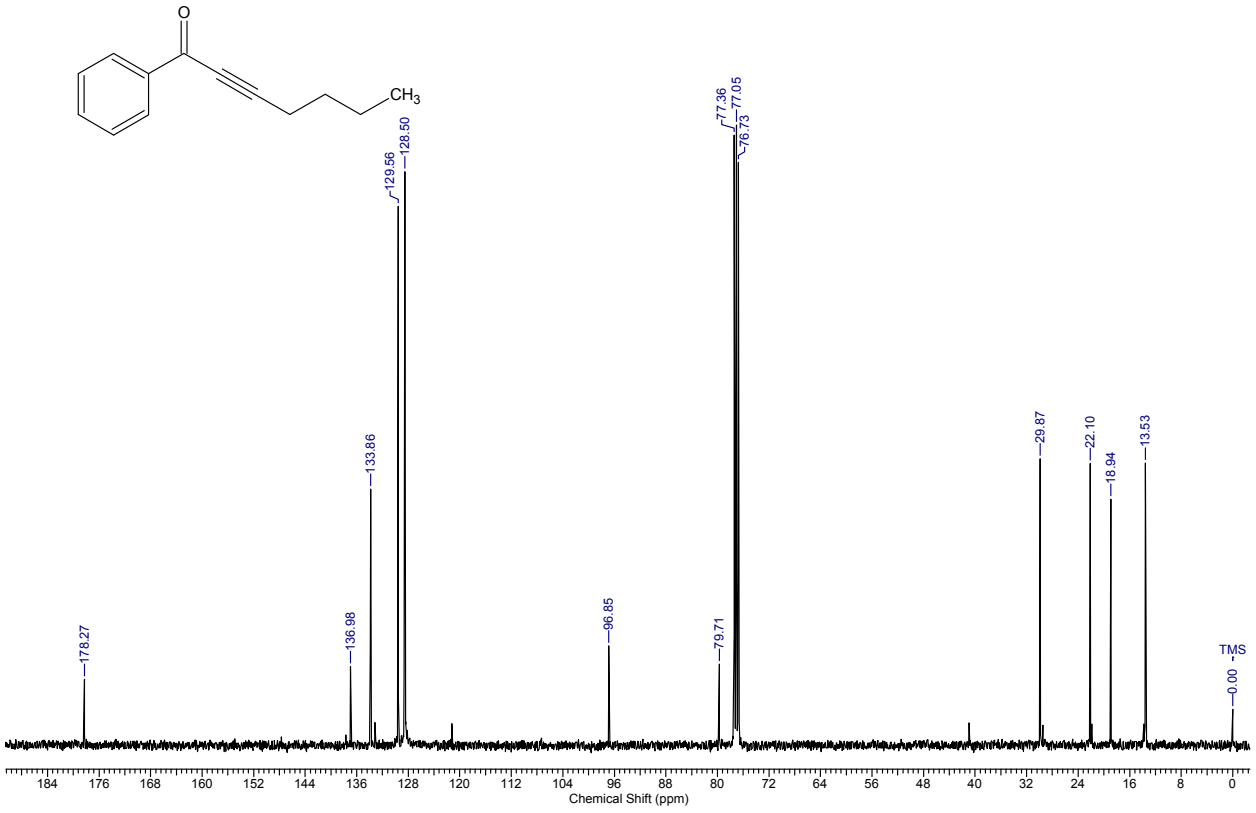
IR spectrum (KBr) of 1-phenylhept-2-yn-1-one (**4dc**)



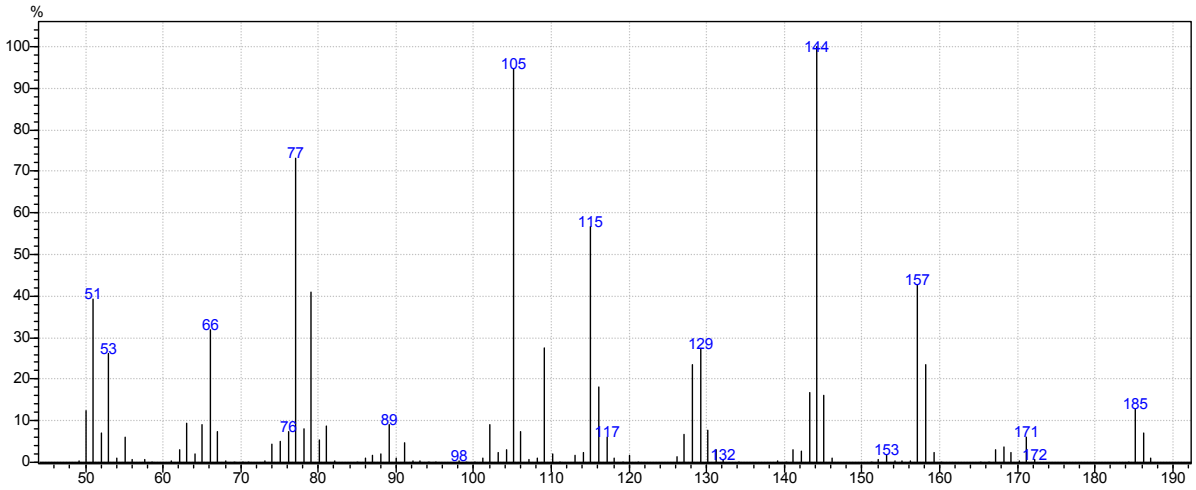
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of 1-phenylhept-2-yn-1-one (**4dc**)



^{13}C NMR spectrum (100 MHz, $CDCl_3$) of 1-phenylhept-2-yn-1-one (**4dc**)



Mass-spectrum (EI, 70 eV) of 1-phenylhept-2-yn-1-one (**4dc**)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