

SUPPORTING INFORMATION

Transition-Metal Free Superbase-Promoted Stereoselective α -Vinylolation of Ketones with Arylacetylenes: A General Strategy for Synthesis of β,γ -Unsaturated Ketones

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Instrumental Techniques ^1H and ^{13}C NMR spectra were recorded at 400.13 and 100.61 MHz respectively equipped with an inverse gradient 5 mm probe in CDCl_3 with hexamethyldisiloxane (HMDS) as an internal standard. Coupling constants are given in Hertz. All 2D NMR spectra were recorded by using a standard gradient Bruker pulse programs. Standard COSY spectra with a 90° , 45° pulse sequence were recorded.¹ The NOESY spectra were recorded in the phase-sensitive TPPI mode with amixing time of 1-1.4 s.² HSQC spectra via double INEPT transfer in the phase sensitive TPPI mode with GARP decoupling during acquisition were recorded.³ HMBC spectra were obtained with the inverse technique and processed in the magnitude mode.⁴ IR spectra were taken with FT-IR. The geometries for all structures presented here were calculated at the MP2 level of theory⁵ without symmetry constraints using the GAUSSIAN 09 program package.⁶ The triple split-valence 6-311++G (d,p) basis set of Pople which included a set of diffuse functions as well as d-type polarization functions on all nonhydrogen atoms and p-type polarization functions on hydrogen atom were adopted in the calculations.^{7, 8} The energy minima with respect to the nuclear coordinates were obtained by the simultaneous relaxation of all the geometrical parameters of the molecules using the gradient method of Pulay.⁹

Materials: All chemicals and solvents are commercially available from Sigma Aldrich Chemie and were used without further purification. The elaborated procedure does not require degassing of DMSO and use of inert atmosphere and the benefit of DMSO as a solvent is that it is stable up to 150°C for a long time (24 h, weight lost 0.1-1.0%).¹⁰

(1) Nagayama, K.; Kumar, A.; Wutrich, K.; Ernst, R. R. *J. Magn. Reson.* **1980**, *40*, 321.

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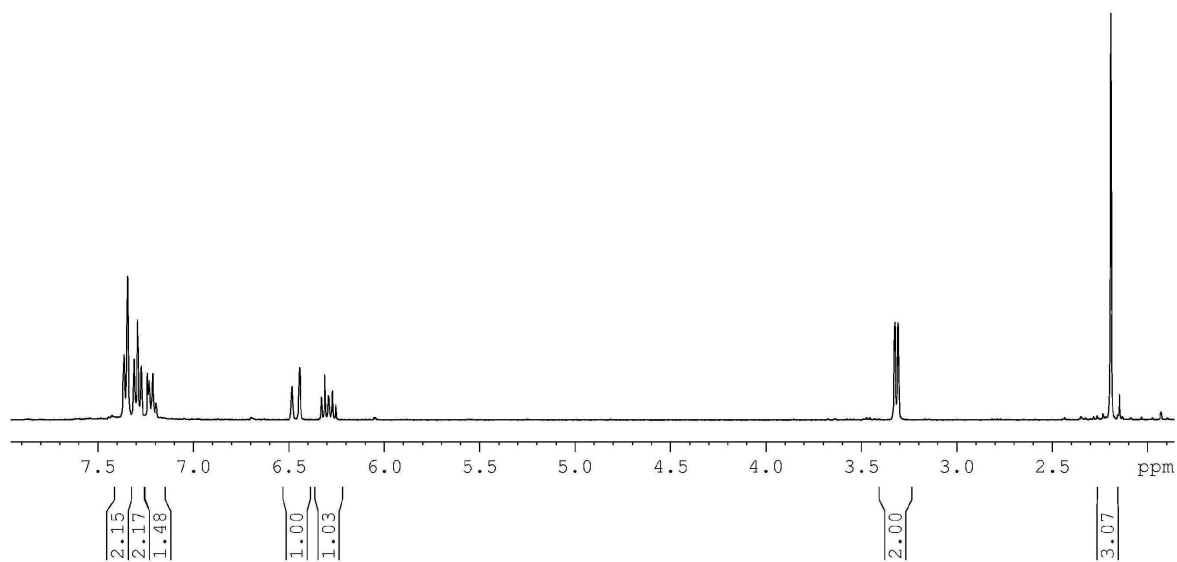
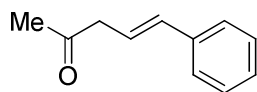
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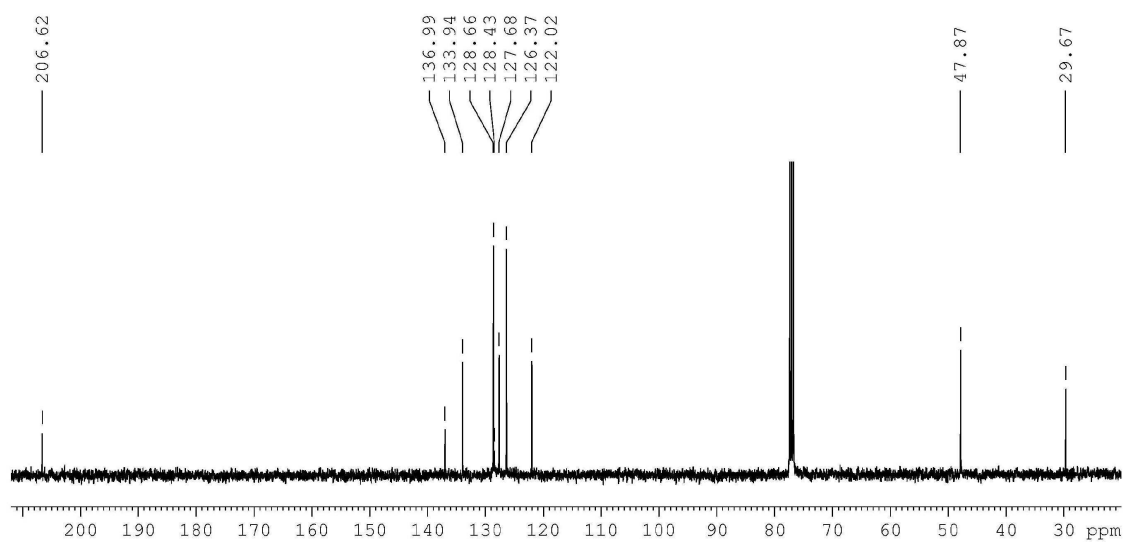
(10) *Dimethyl sulfoxide (DMSO). Technical Bulletin.* Crown Zellerbach Chemical Products Division, Vancouver (Orchards), WA 98662, **1985**.

^1H , ^{13}C Spectra

(*E*)-5-Phenylpent-4-en-2-one (**21**)

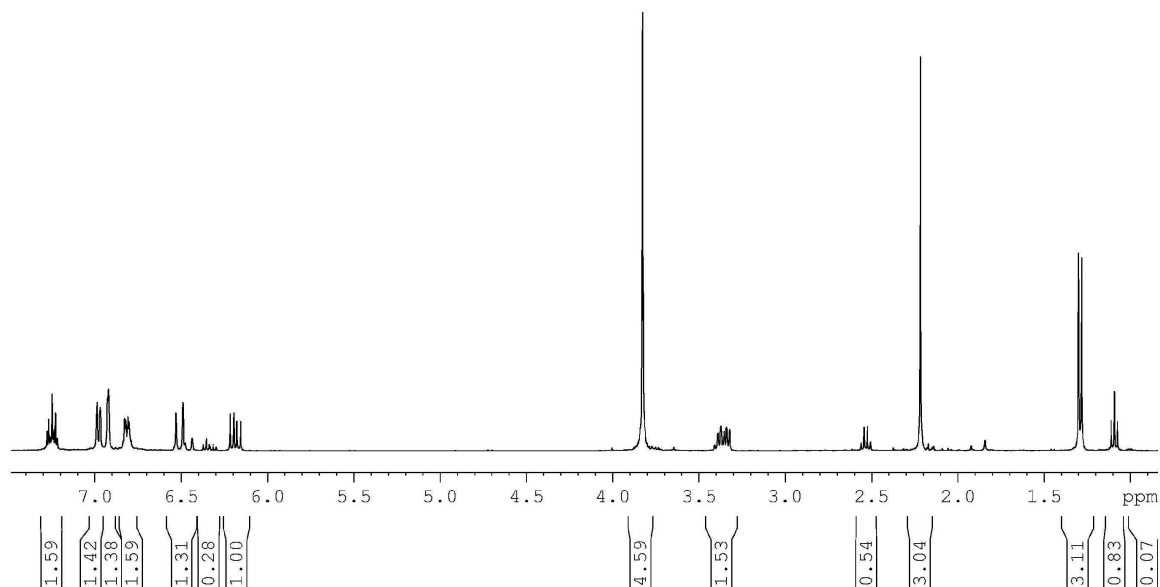
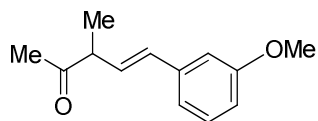


^1H NMR spectrum of **21** (400.13 MHz, CDCl_3)

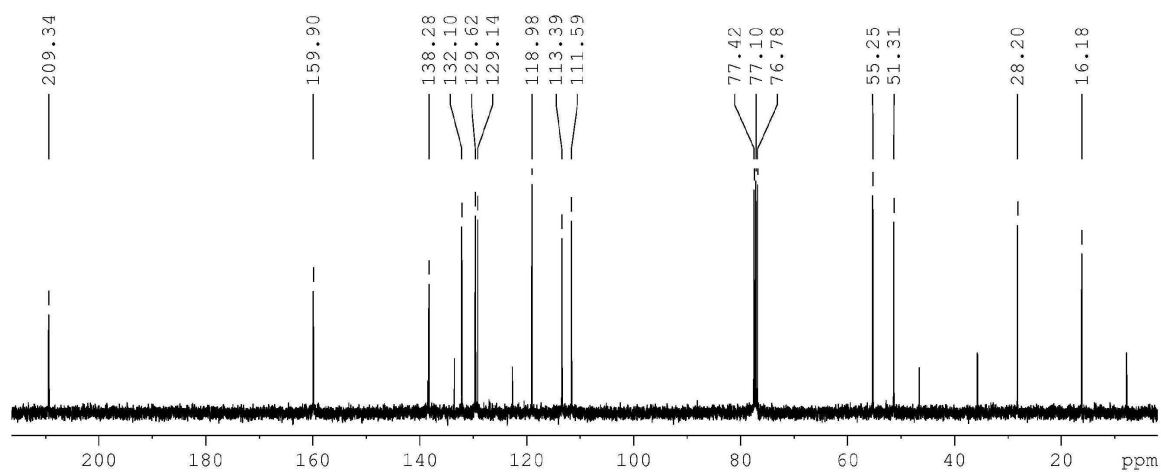


^{13}C NMR spectrum of **21** (100.61 MHz, CDCl_3)

(*E*)-5-(3-Methoxyphenyl)-3-methylpent-4-en-2-one (22**)**

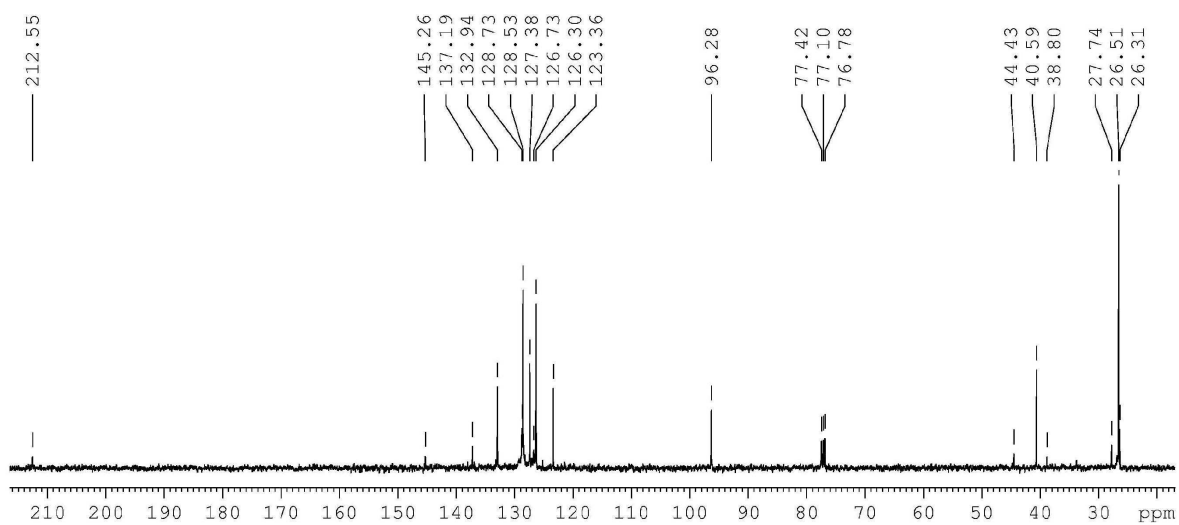
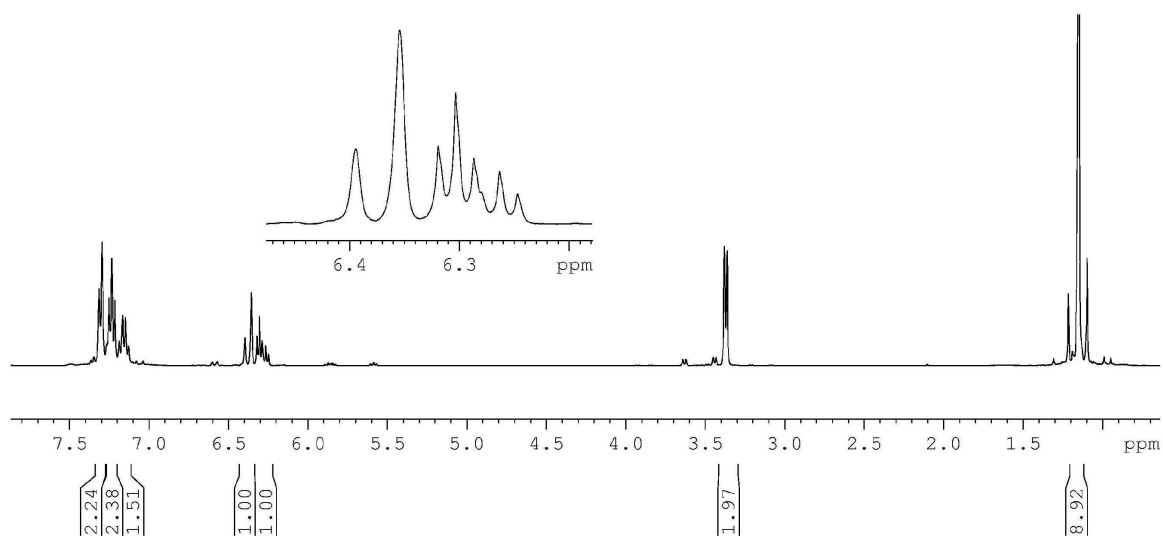
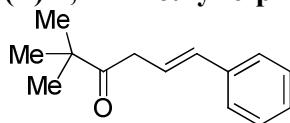


¹H NMR spectrum of **22** (400.13 MHz, CDCl₃)

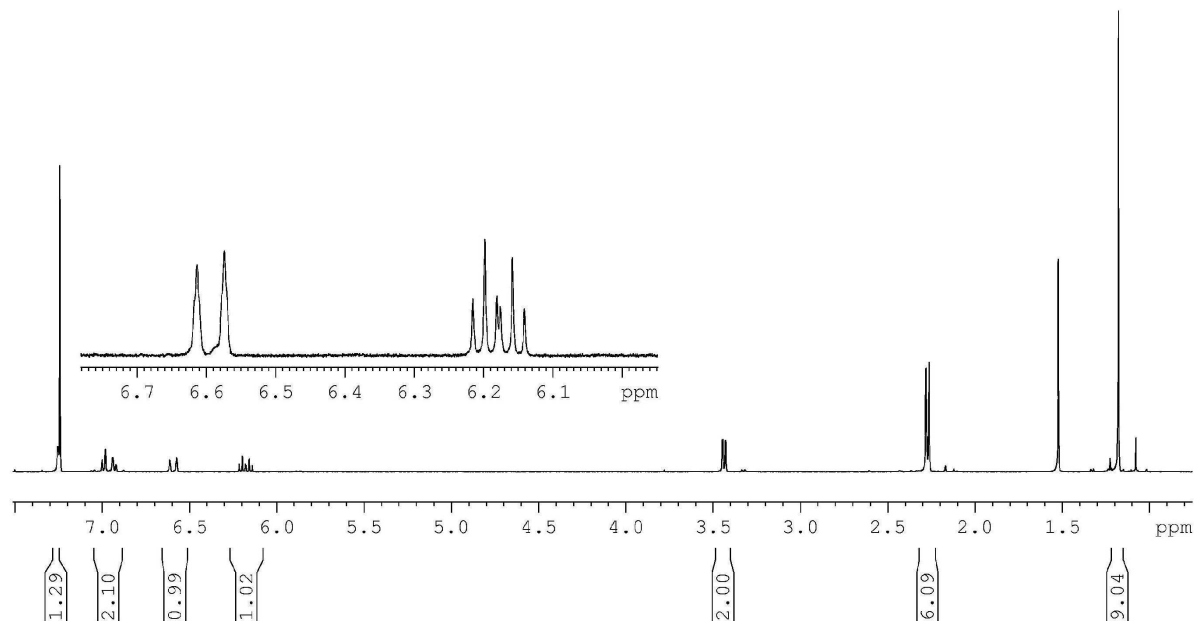
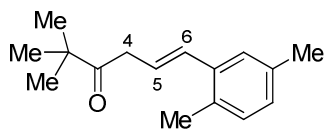


¹³C NMR spectrum of **22** (100.61 MHz, CDCl₃)

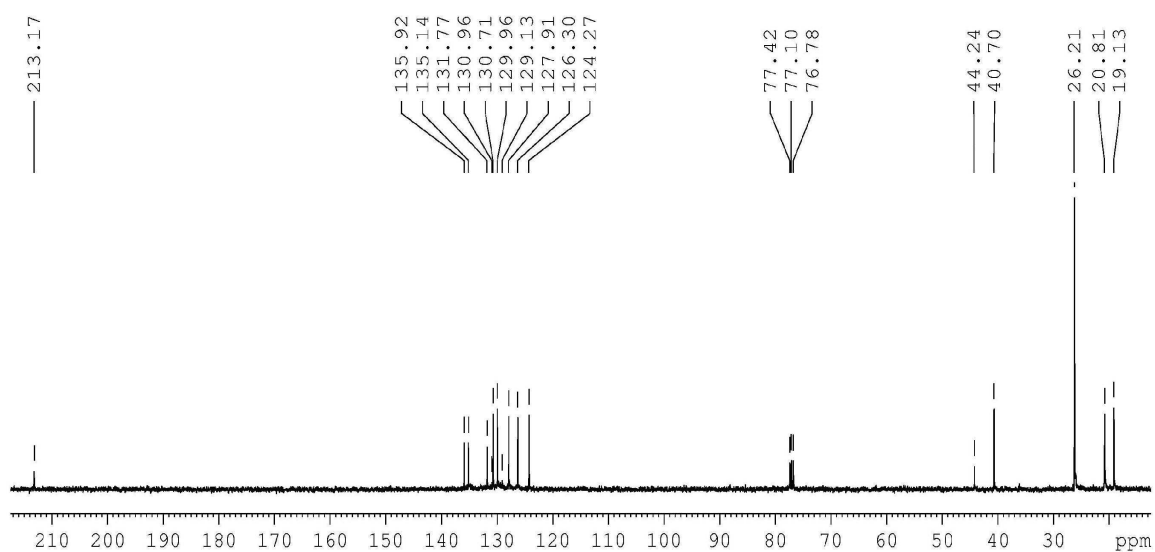
(*E*)-2,2-Dimethyl-6-phenylhex-5-en-3-one (23)



(*E*)-6-(2,5-Dimethylphenyl)-2,2-dimethylhex-5-en-3-one (24)

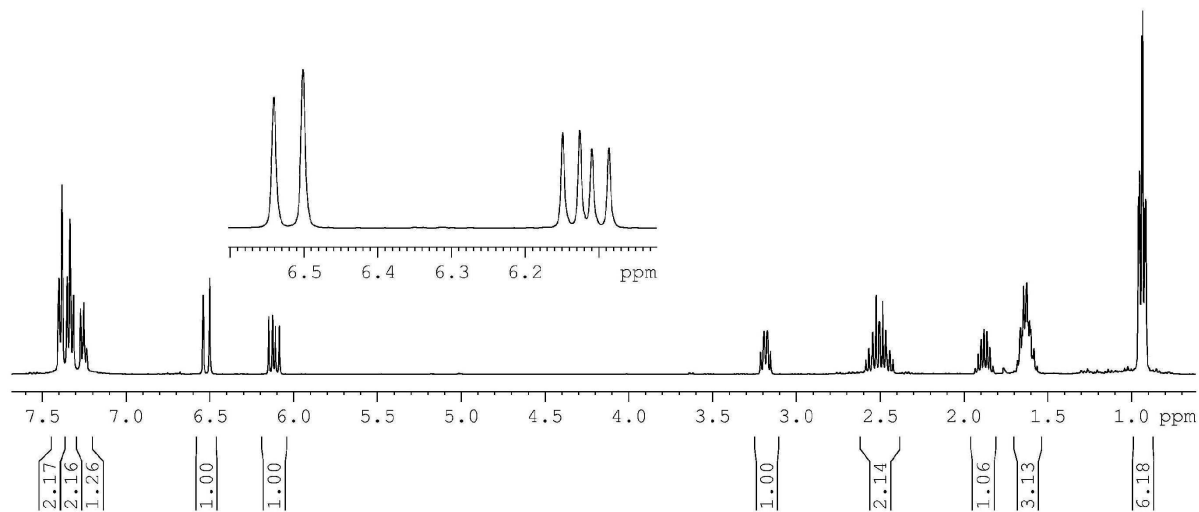
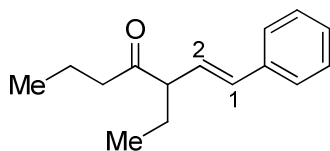


¹H NMR spectrum of **24** (400.13 MHz, CDCl₃)

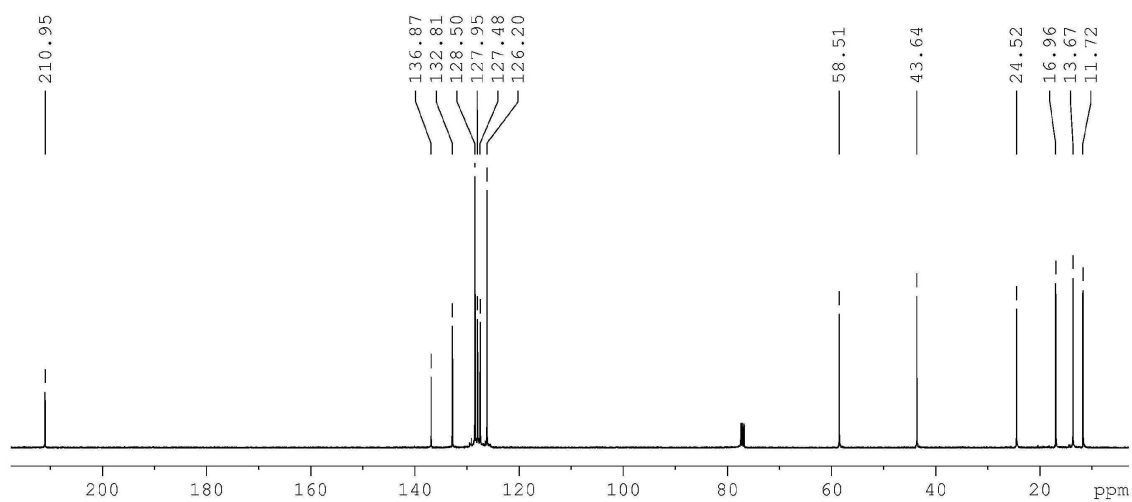


¹³C NMR spectrum of **24** (100.61 MHz, CDCl₃)

(E)-3-Ethyl-1-phenylhept-1-en-4-one (25)

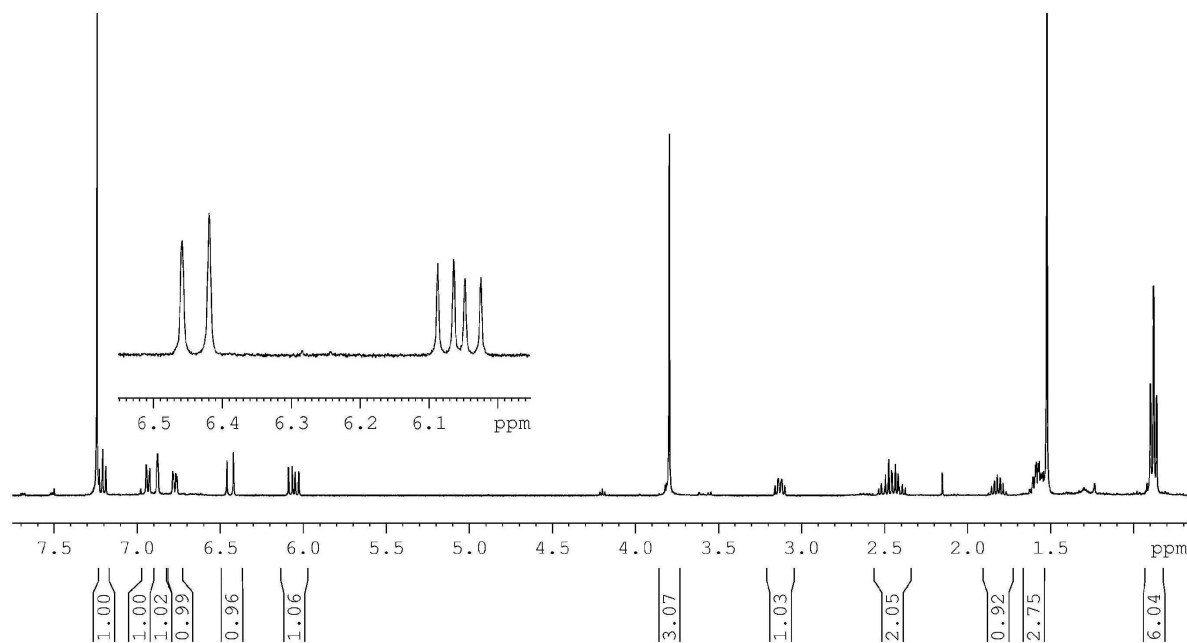
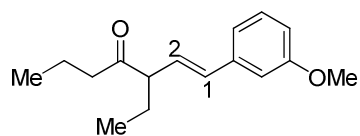


¹H NMR spectrum of **25** (400.13 MHz, CDCl₃)

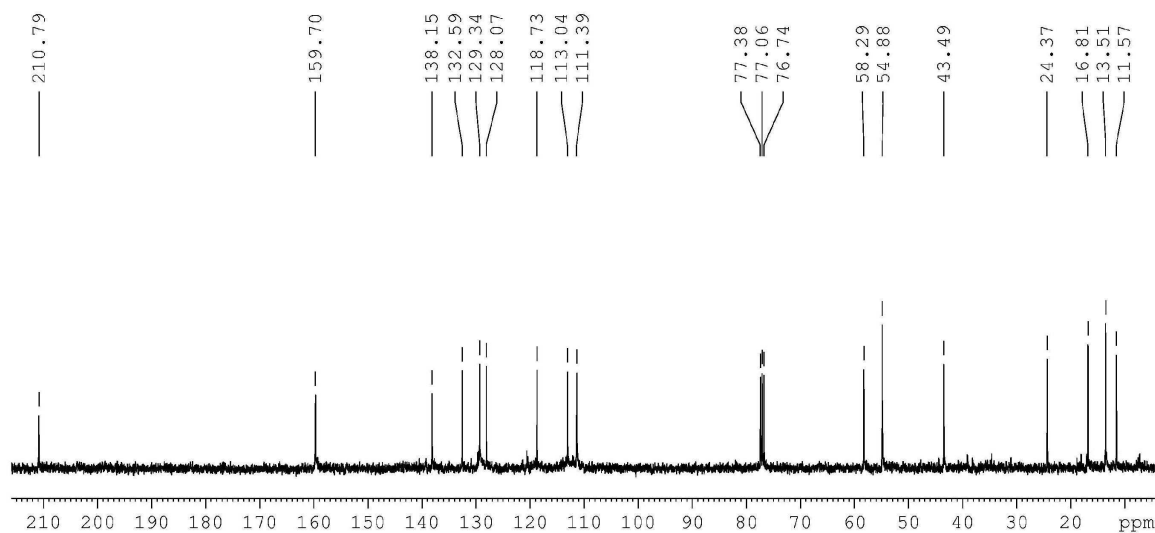


¹³C NMR spectrum of **25** (100.61 MHz, CDCl₃)

(*E*)-3-Ethyl-1-(3-methoxyphenyl)hept-1-en-4-one (26)

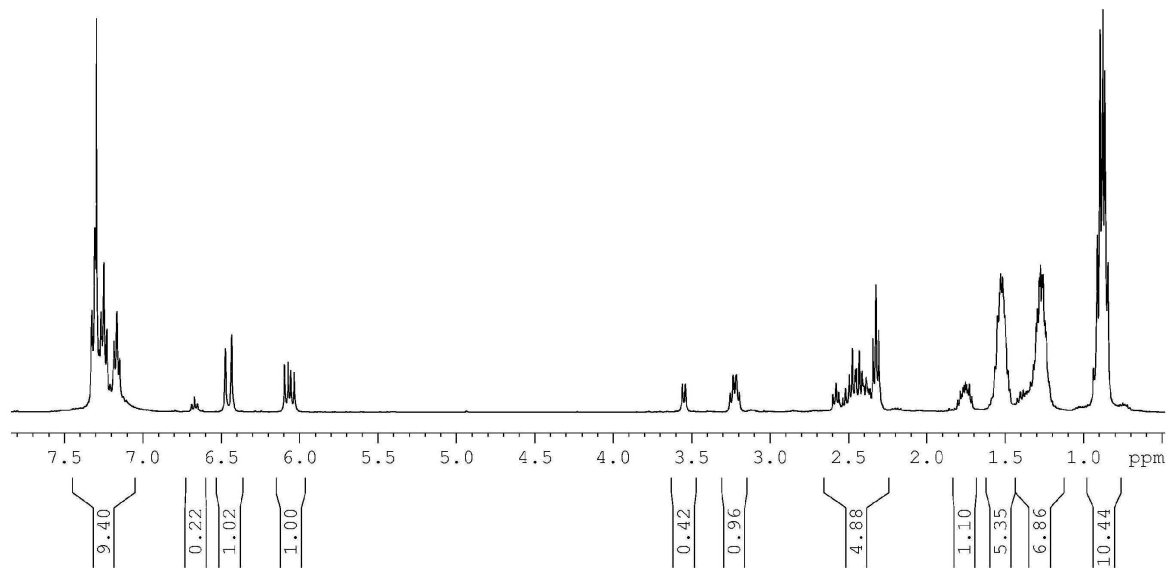
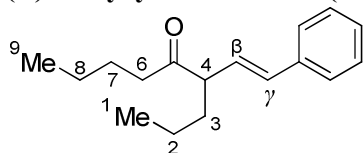


^1H NMR spectrum of **26** (400.13 MHz, CDCl_3)

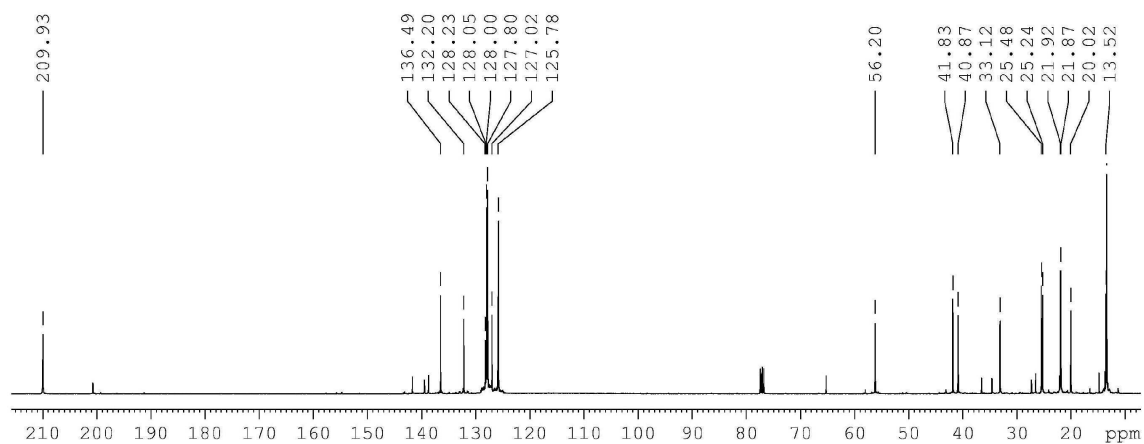


^{13}C NMR spectrum of **26** (100.61 MHz, CDCl_3)

(*E*)-4-Styrylnonan-5-one (27)

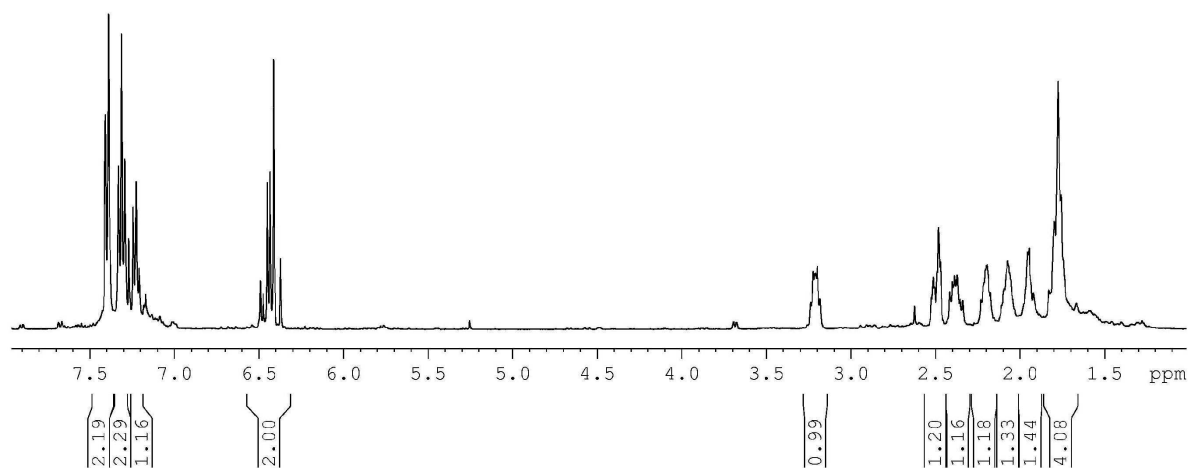
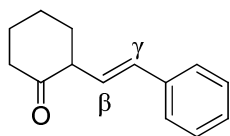


^1H NMR spectrum of **27** (400.13 MHz, CDCl_3)

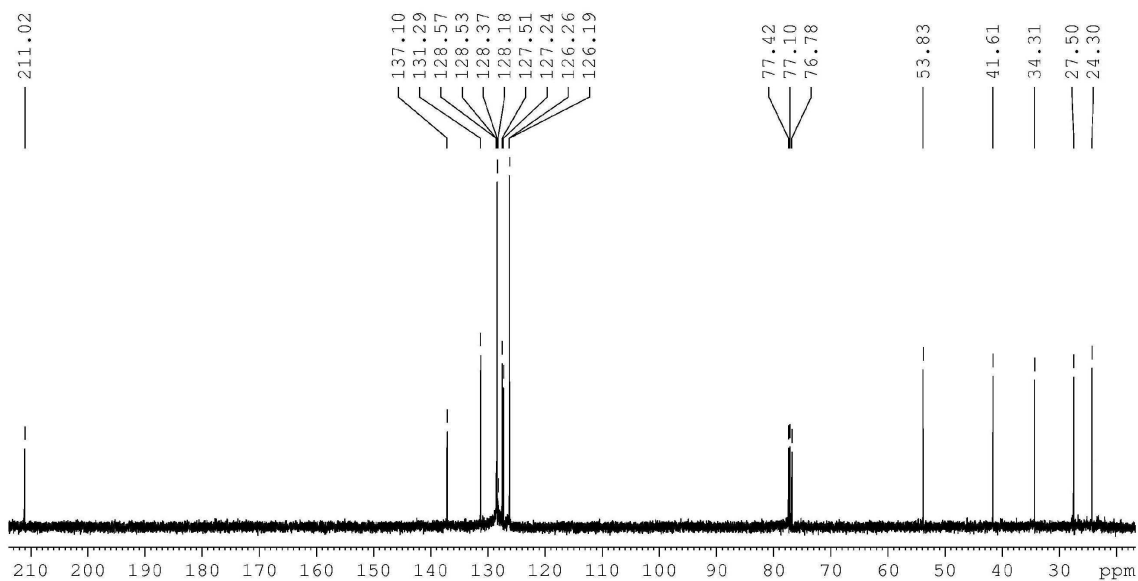


^{13}C NMR spectrum of **27** (100.61 MHz, CDCl_3)

(E)-2-Styrylcyclohexanone (28)

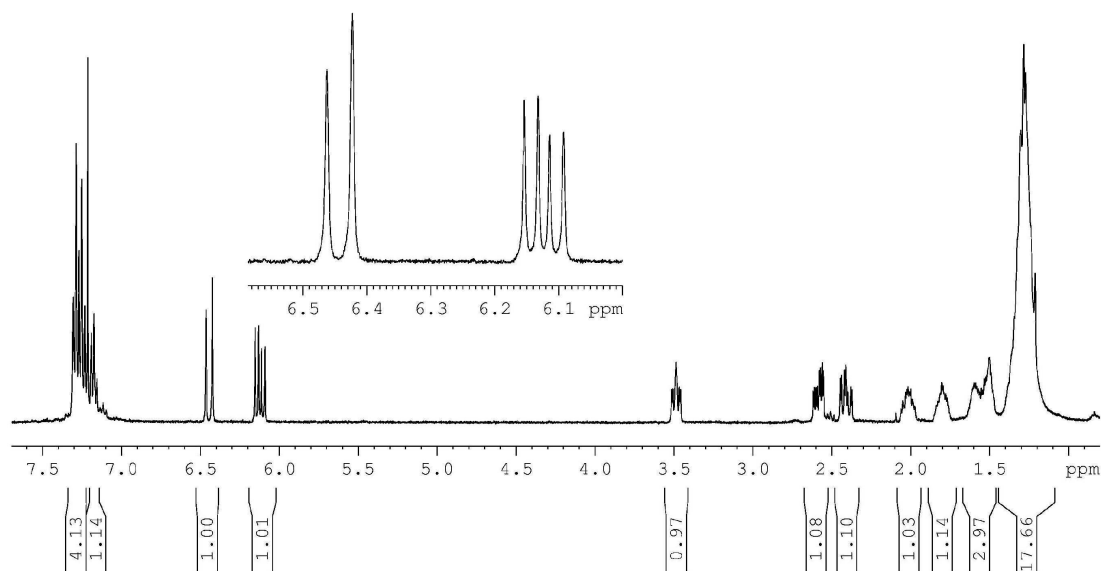
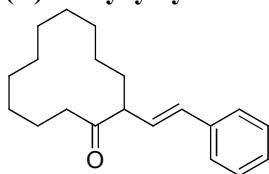


^1H NMR spectrum of **28** (400.13 MHz, CDCl_3)

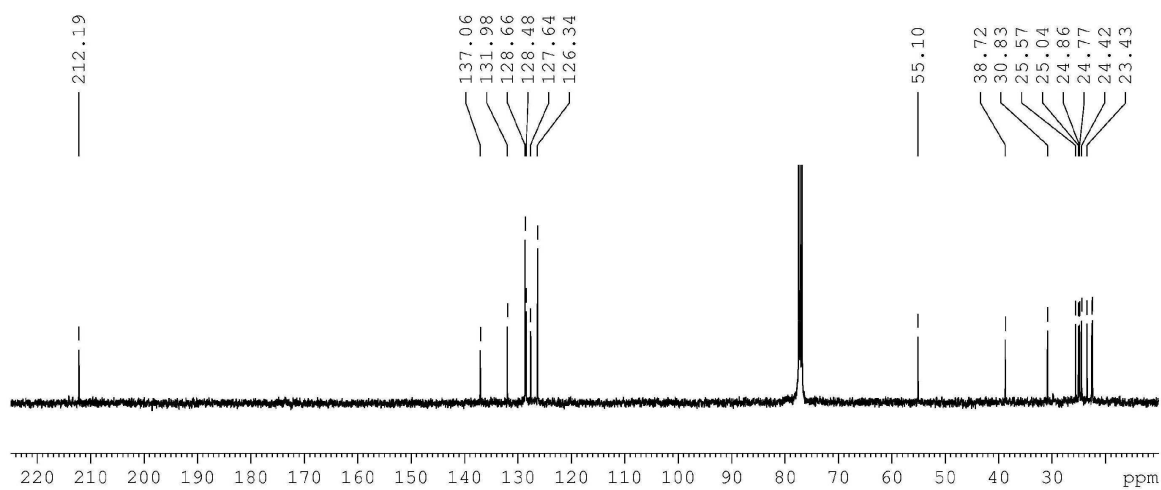


^{13}C NMR spectrum of **28** (100.61 MHz, CDCl_3)

(E)-2-Styrylcyclododecanone (29)

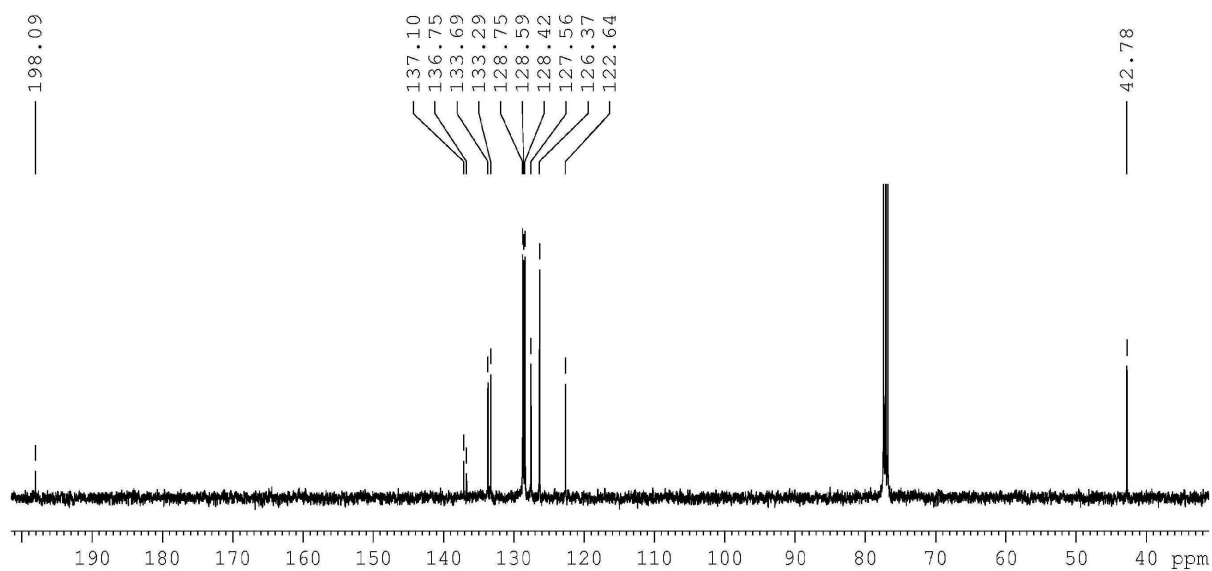
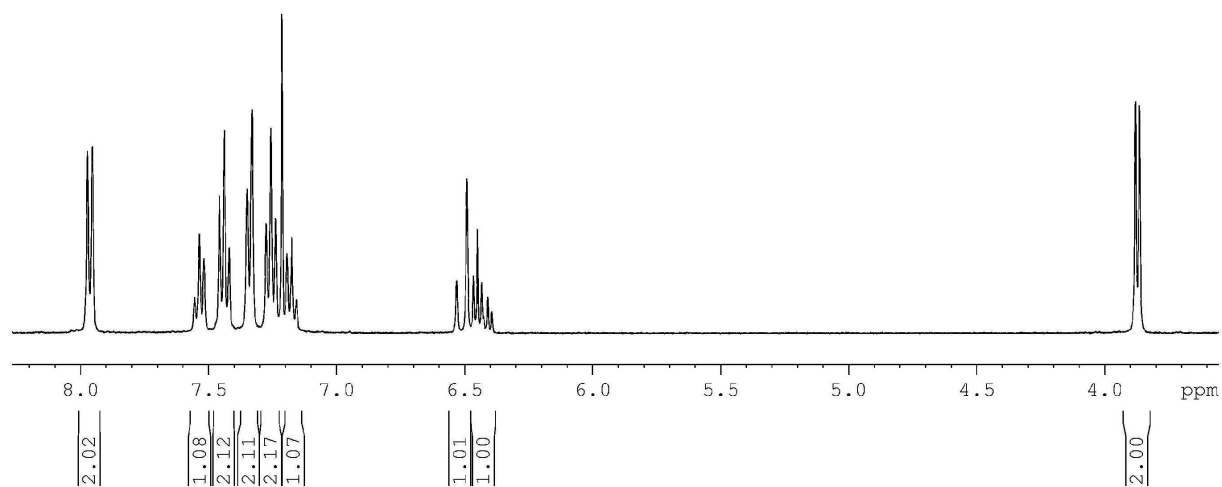
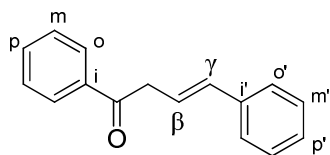


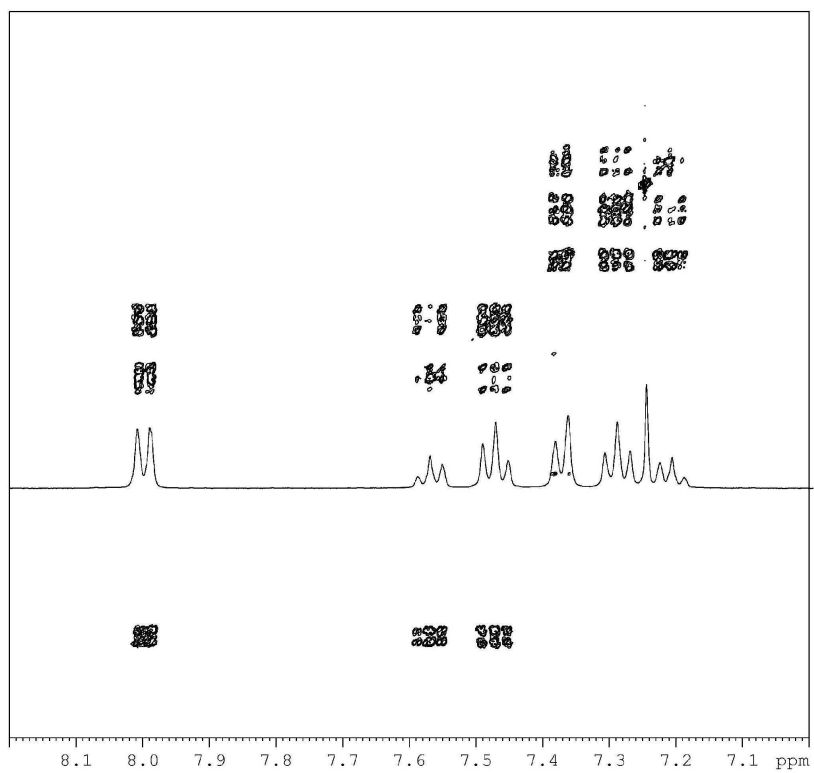
¹H NMR spectrum of **29** (400.13 MHz, CDCl₃)



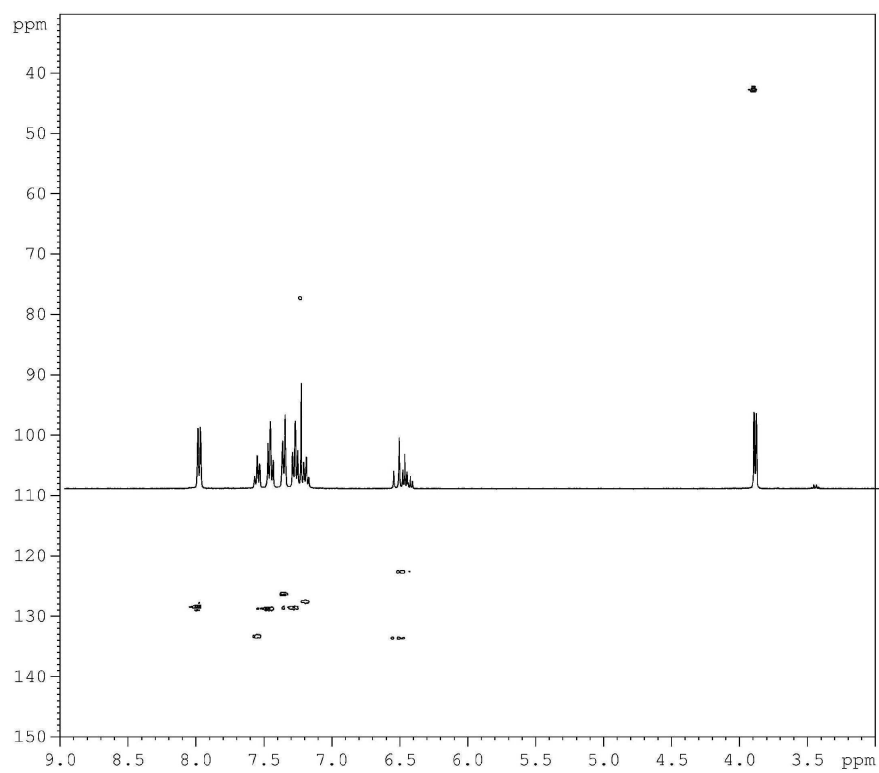
¹³C NMR spectrum of **29** (100.61 MHz, CDCl₃)

(*E*)-1,4-Diphenyl-3-buten-1-one (30)



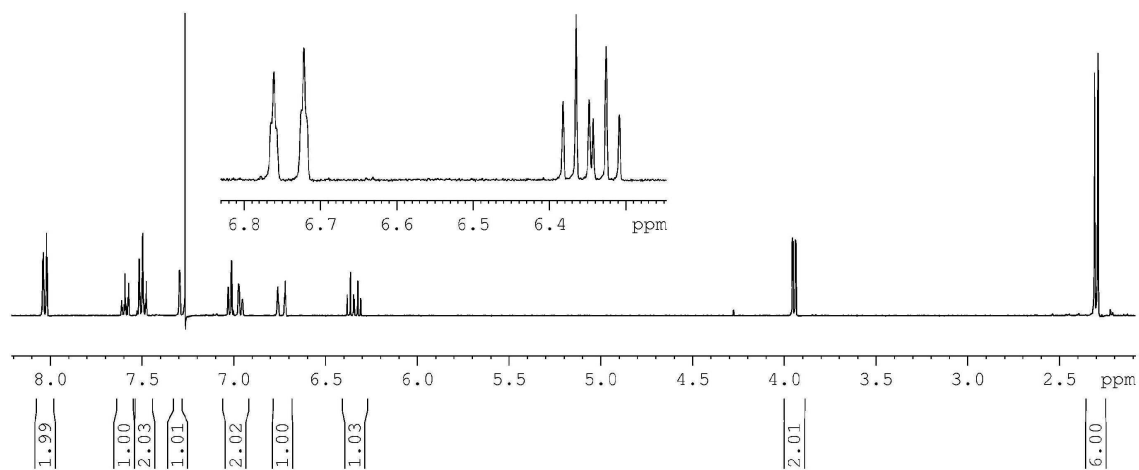
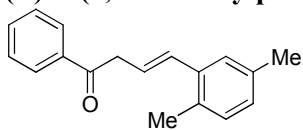


2D COSY spectrum of **30** (aromatic region), 400.13 MHz, CDCl_3

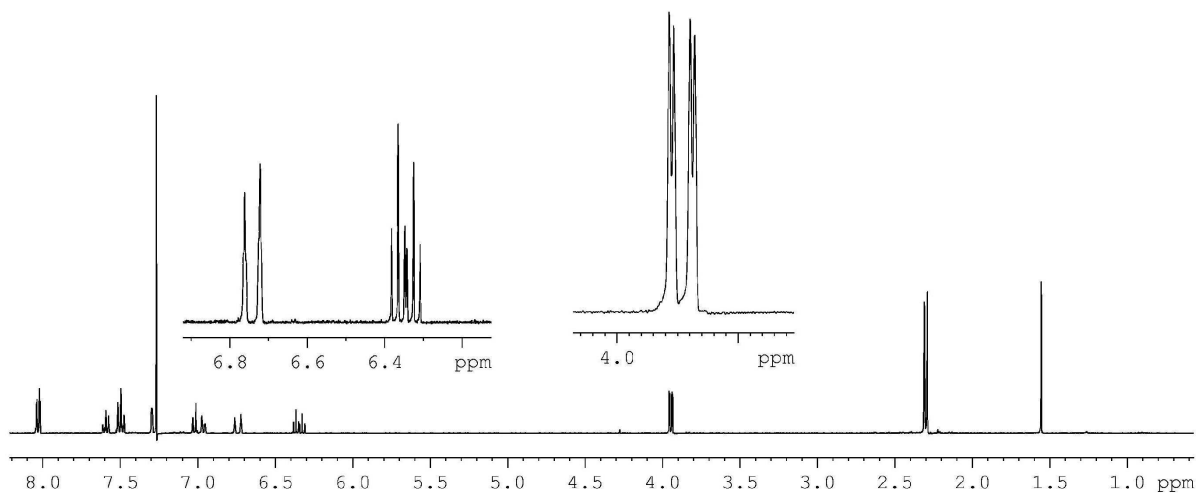


2D ^1H - ^{13}C HSQC spectrum of **30** (CDCl_3)

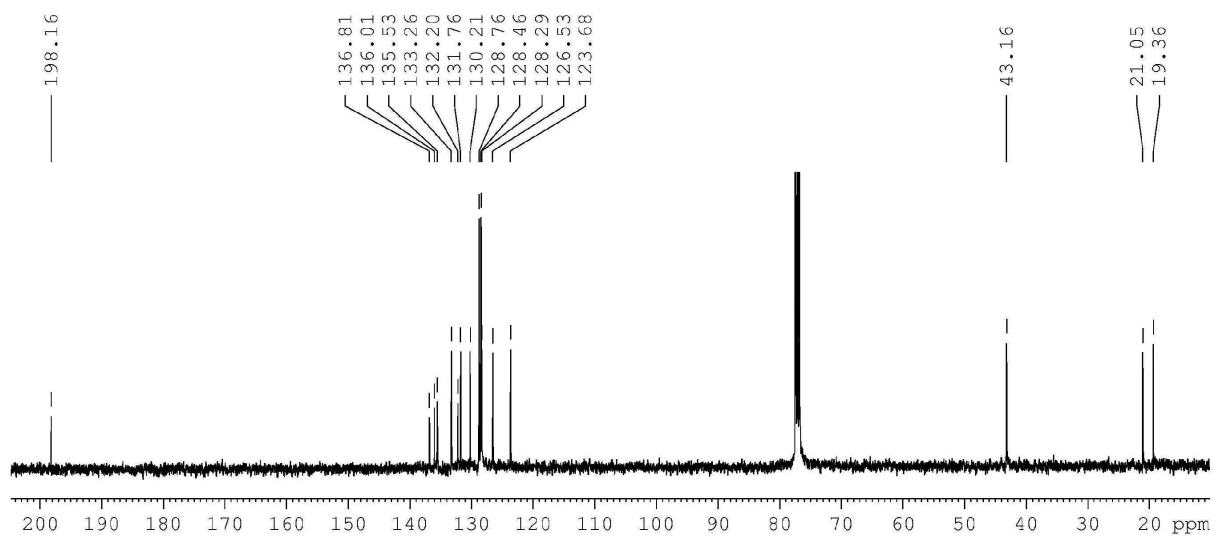
(*E*)-4-(2,5-Dimethylphenyl)-1-phenylbut-3-en-1-one (31)



¹H NMR spectrum of **31** (400.13 MHz, CDCl₃)

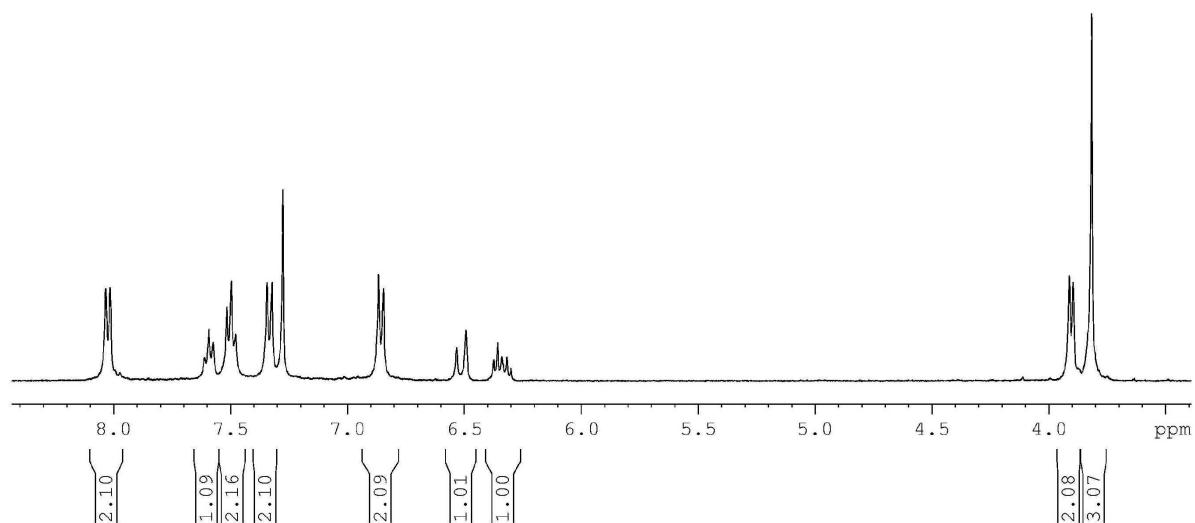
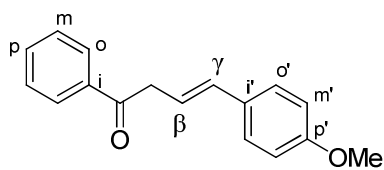


¹H NMR spectrum of **31** (low concentration) (400.13 MHz, CDCl₃)

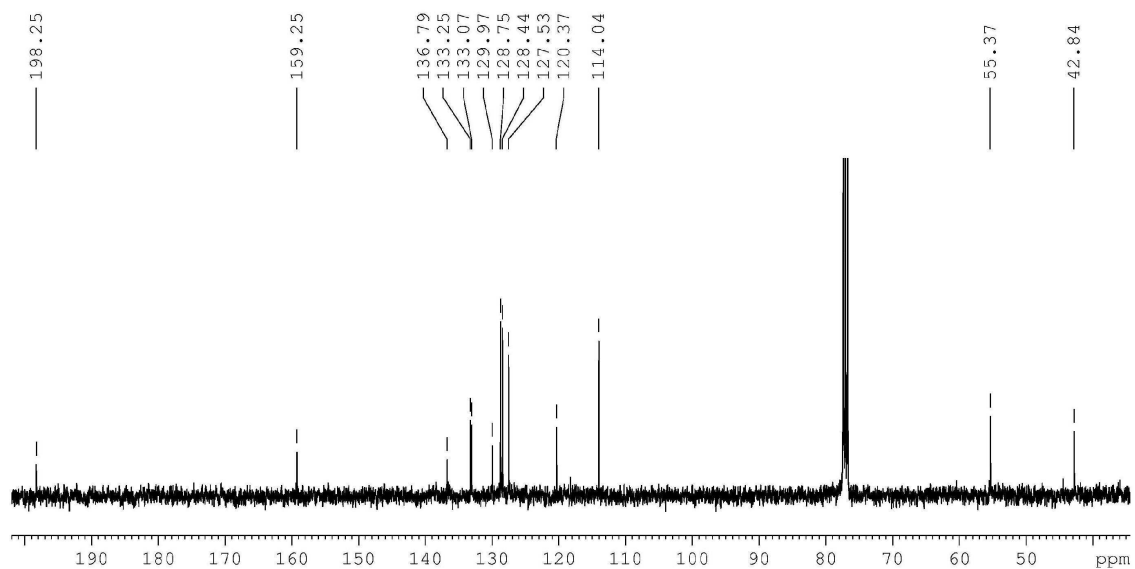


^{13}C NMR spectrum of **31** (100.61 MHz, CDCl_3)

(*E*)-4-(4-Methoxyphenyl)-1-phenylbut-3-en-1-one (32)

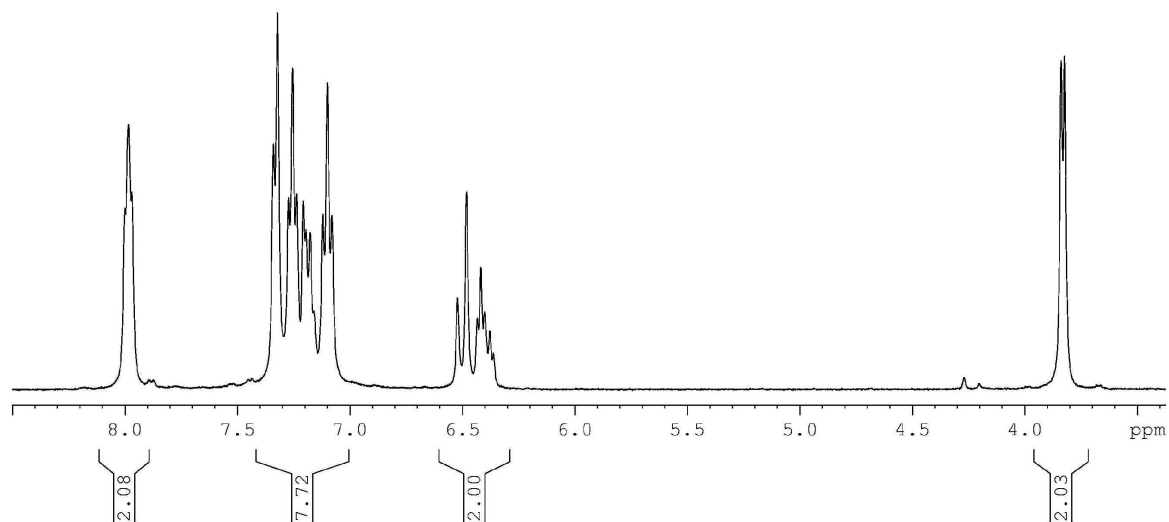
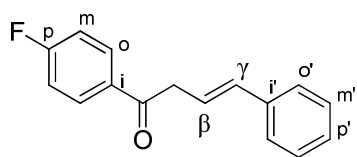


^1H NMR spectrum of **32** (400.13 MHz, CDCl_3)

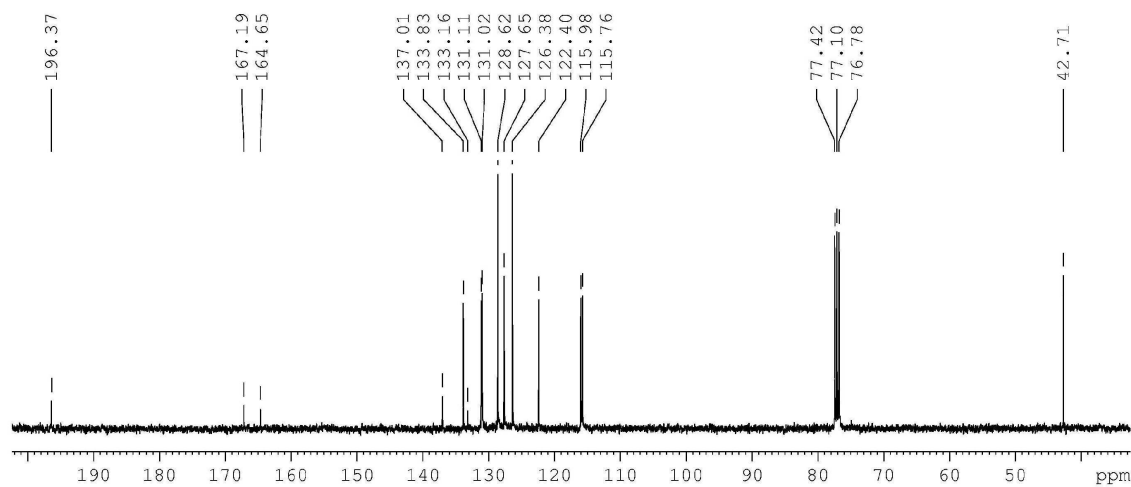


^{13}C NMR spectrum of **32** (100.61 MHz, CDCl_3)

(*E*)-1-(4-Fluorophenyl)-4-phenylbut-3-en-1-one (33)

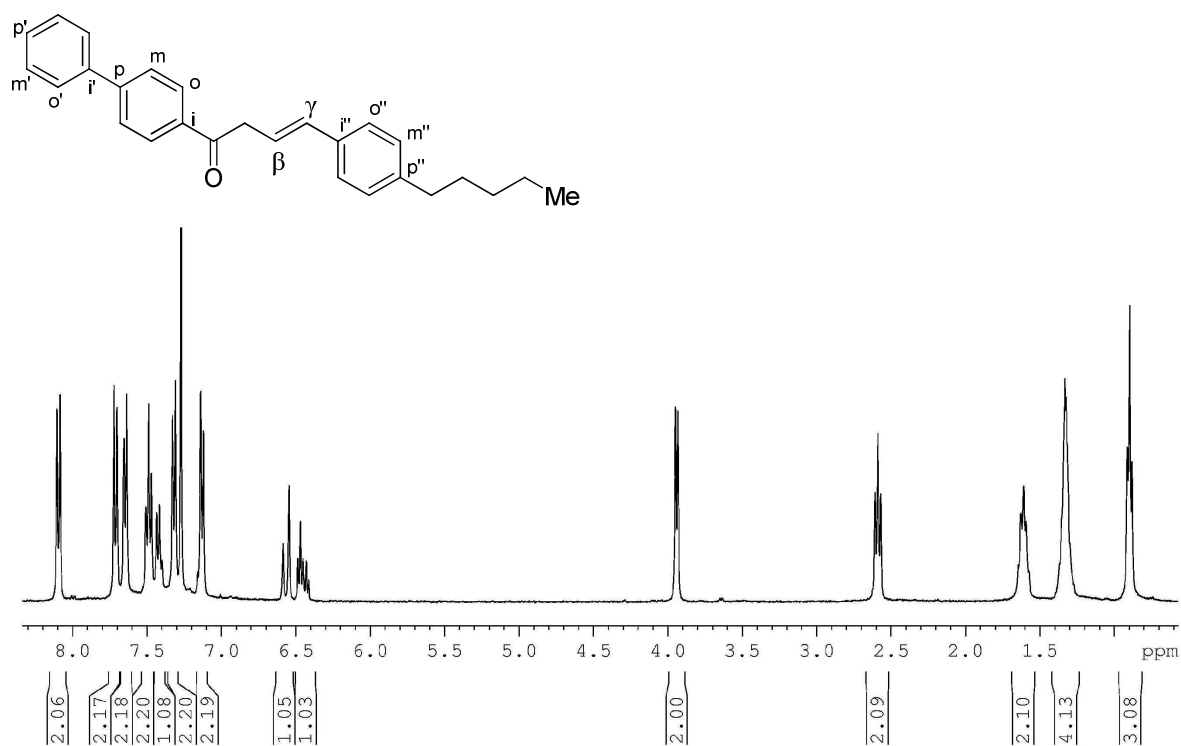


^1H NMR spectrum of **33** (400.13 MHz, CDCl_3)

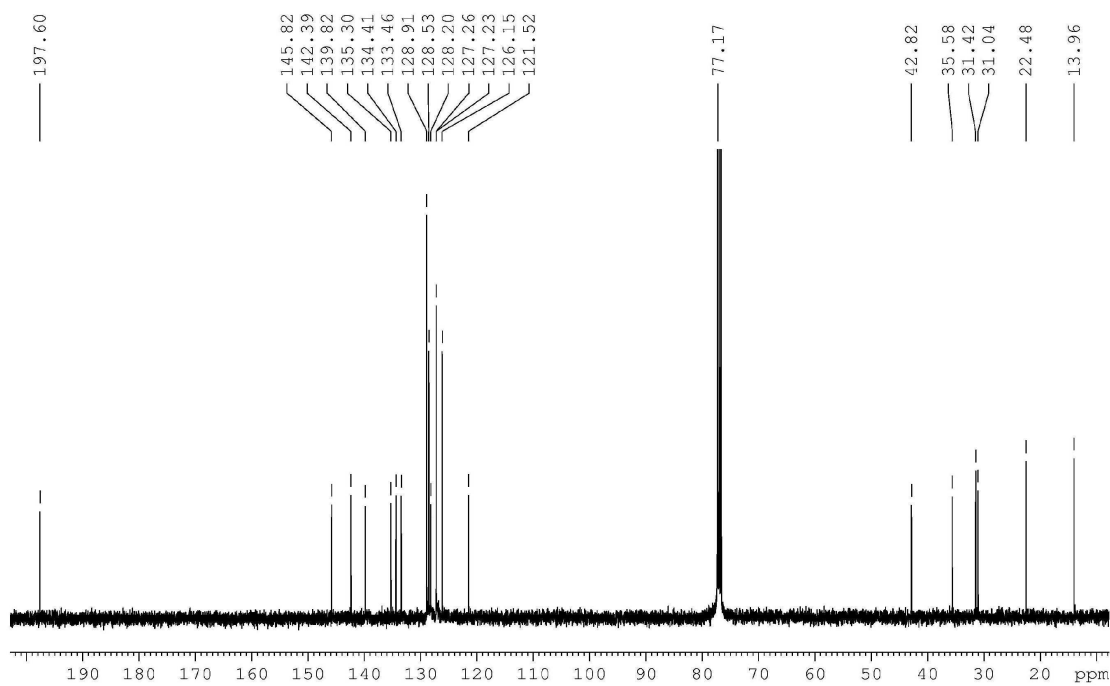


^{13}C NMR spectrum of **33** (100.61 MHz, CDCl_3)

(*E*)-1-[1,1'-Biphenyl]-4-yl-4-(4-pentylphenyl)-3-buten-1-one (34)

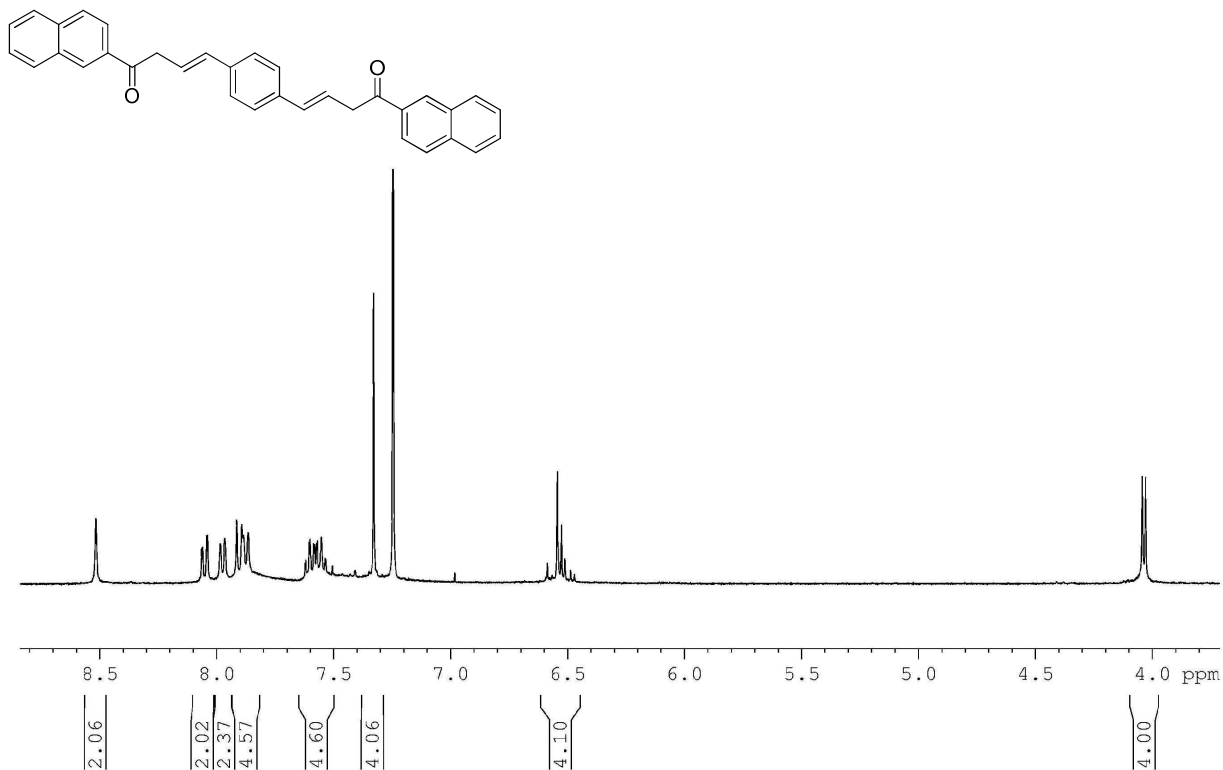


^1H NMR spectrum of **34** (400.13 MHz, CDCl_3)

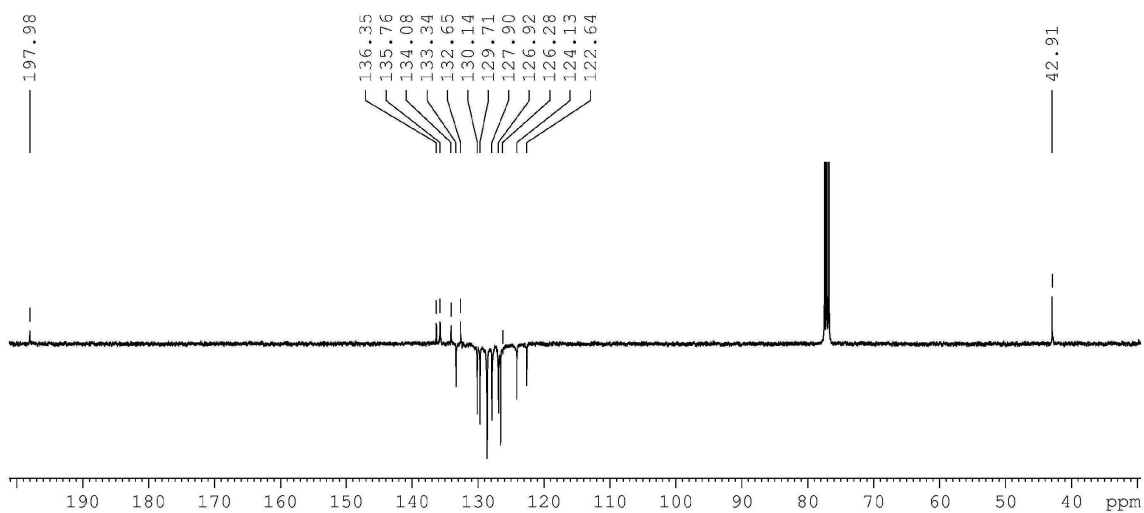


^{13}C NMR spectrum of **34** (100.61 MHz, CDCl_3)

(3*E*, 3'*E*)-4,4'-(1,4-phenylene)bis(1-(naphthalen-2-yl)but-3-en-1-one) (35**)**

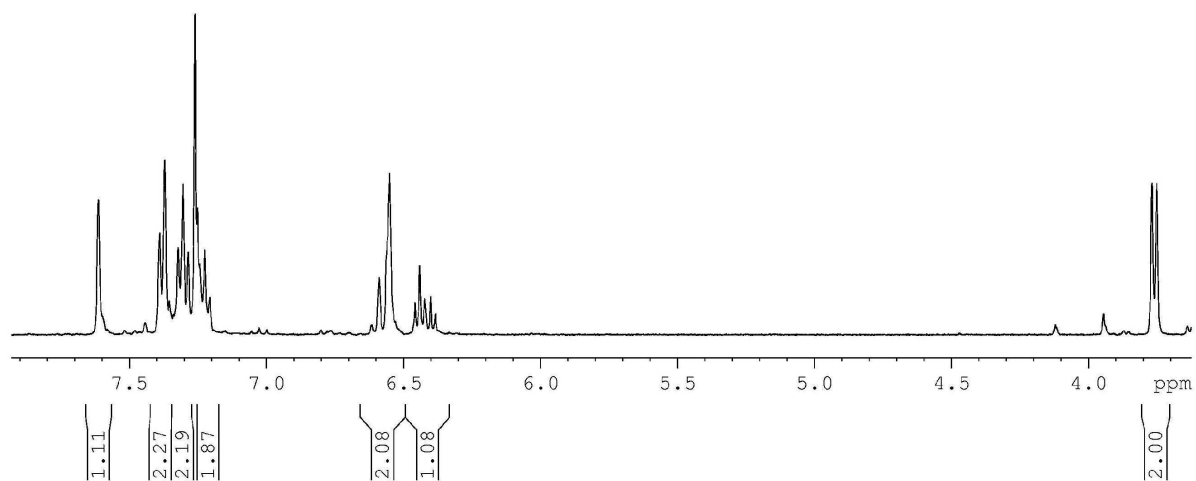
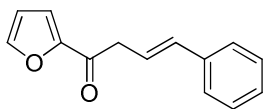


¹H NMR spectrum of **35** (400.13 MHz, CDCl₃)

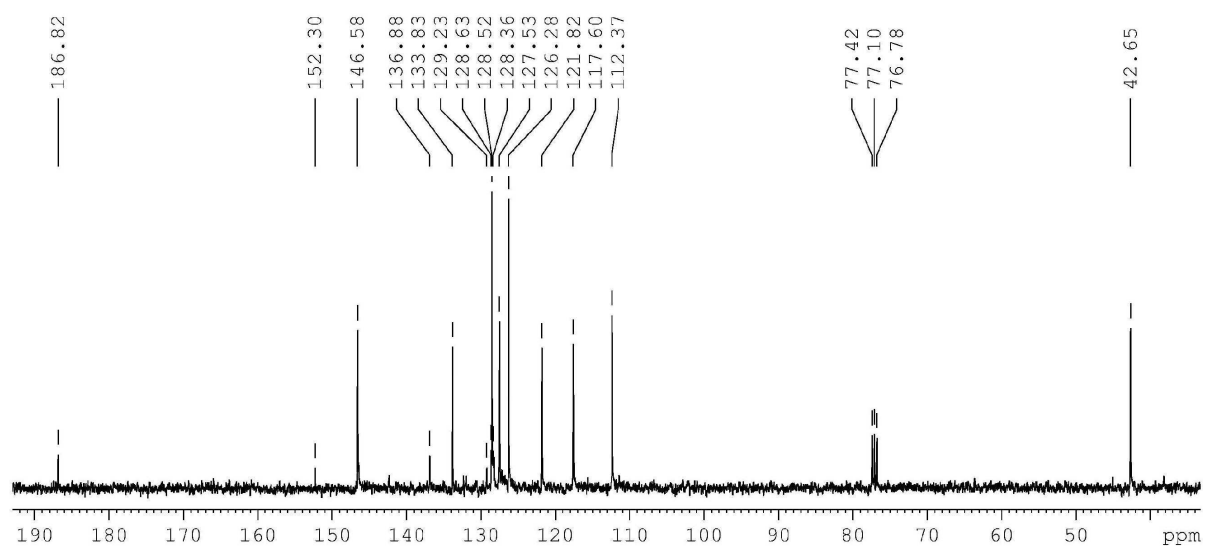


¹³Cjmod NMR spectrum of **35** (100.61 MHz, CDCl₃)

(*E*)-1-(Furan-2-yl)-4-phenylbut-3-en-1-one (36)

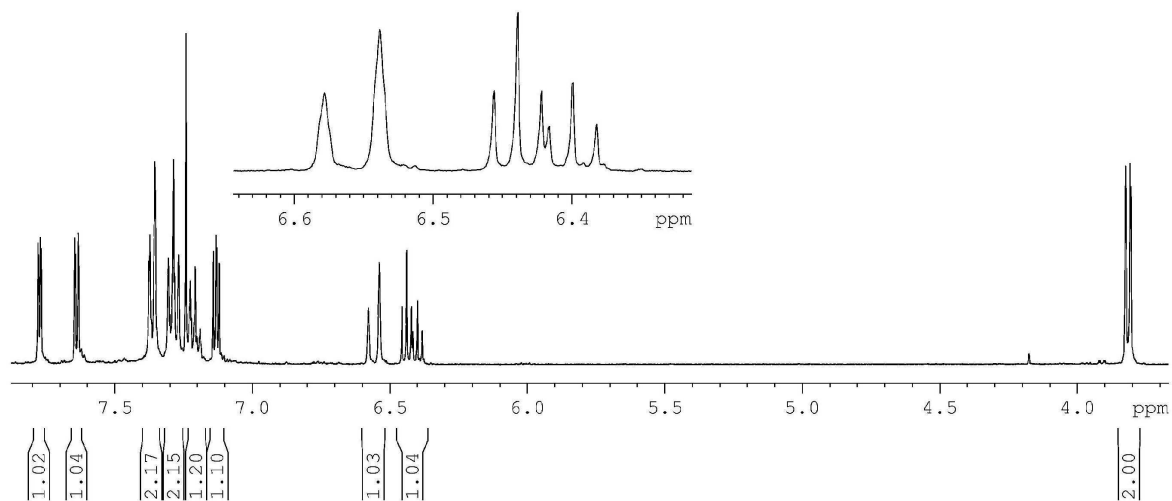
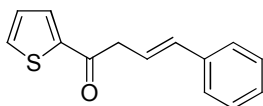


^1H NMR spectrum of **36** (400.13 MHz, CDCl_3)

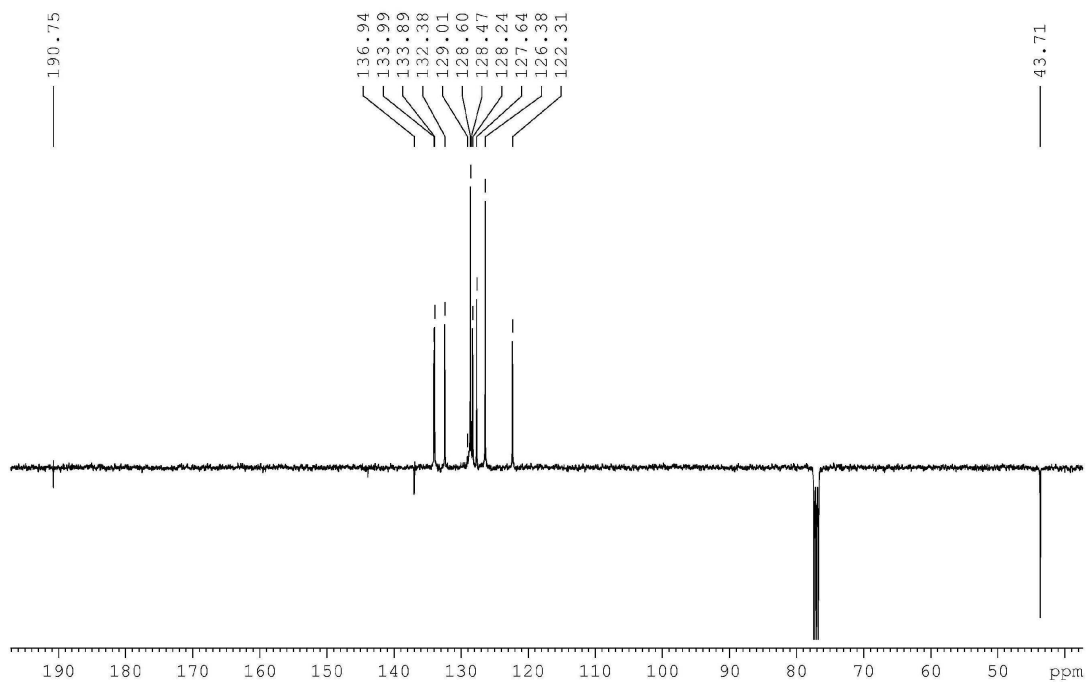


^{13}C NMR spectrum of **36** (100.61 MHz, CDCl_3)

(E)-4-Phenyl-1-thiophen-2-yl-3-buten-1-one (37)

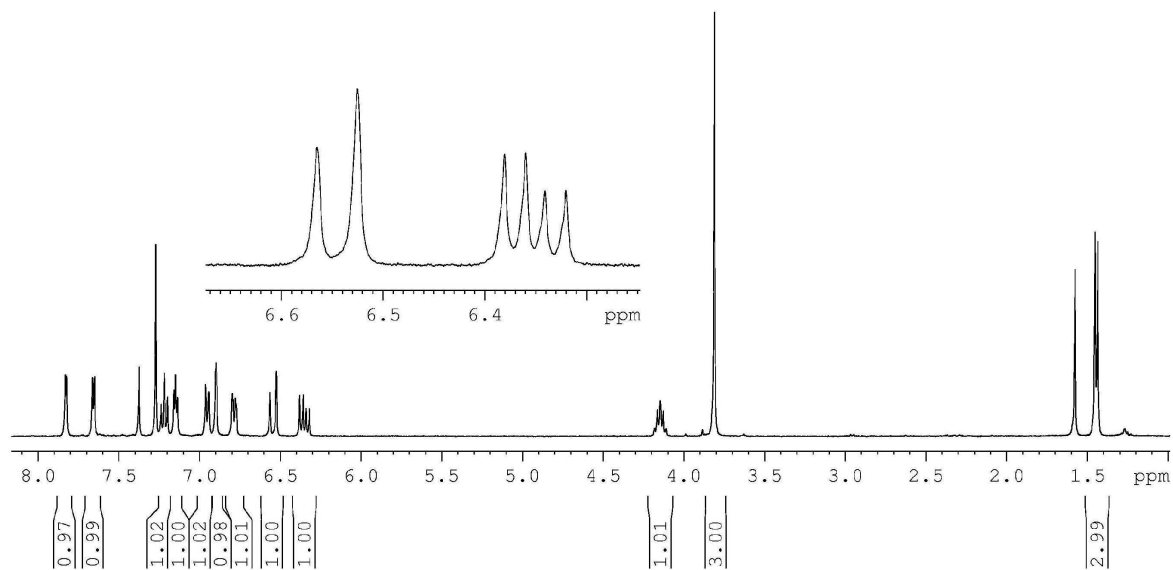
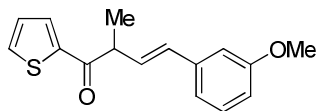


^1H NMR spectrum of **37** (400.13 MHz, CDCl_3)

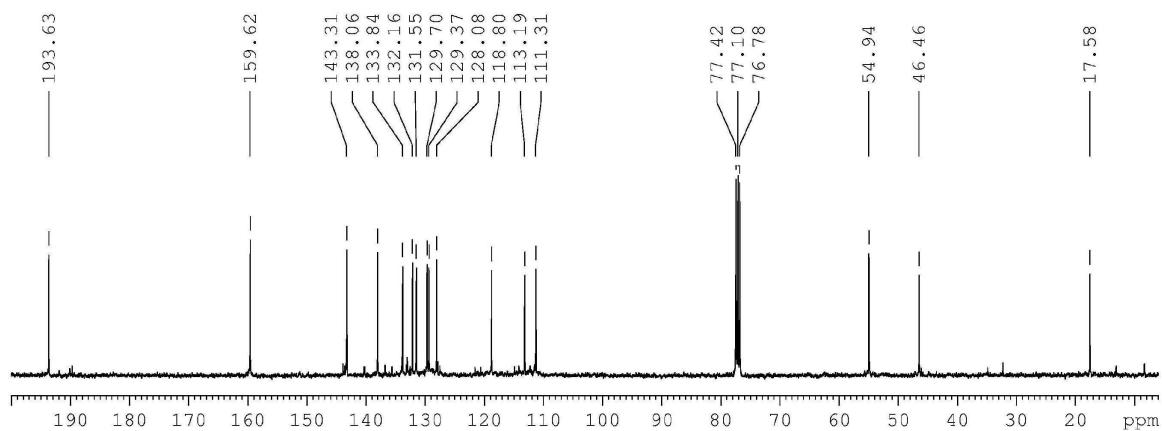


^{13}C NMR spectrum of **37** (100.61 MHz, CDCl_3)

(*E*)-4-(3-Methoxyphenyl)-2-methyl-1-(thiophen-2-yl)but-3-en-1-one (38)

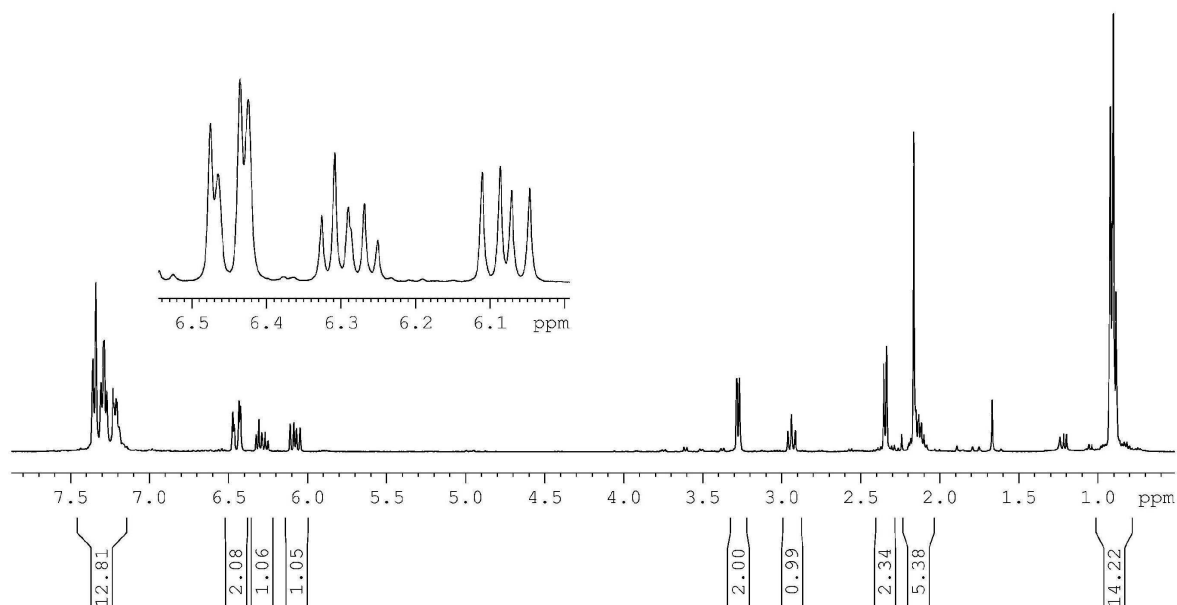
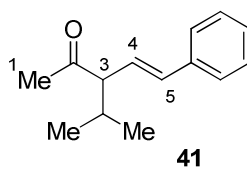
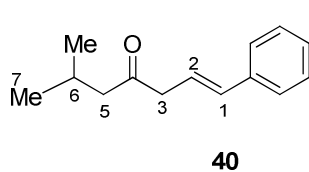


¹H NMR spectrum of **38** (400.13 MHz, CDCl₃)

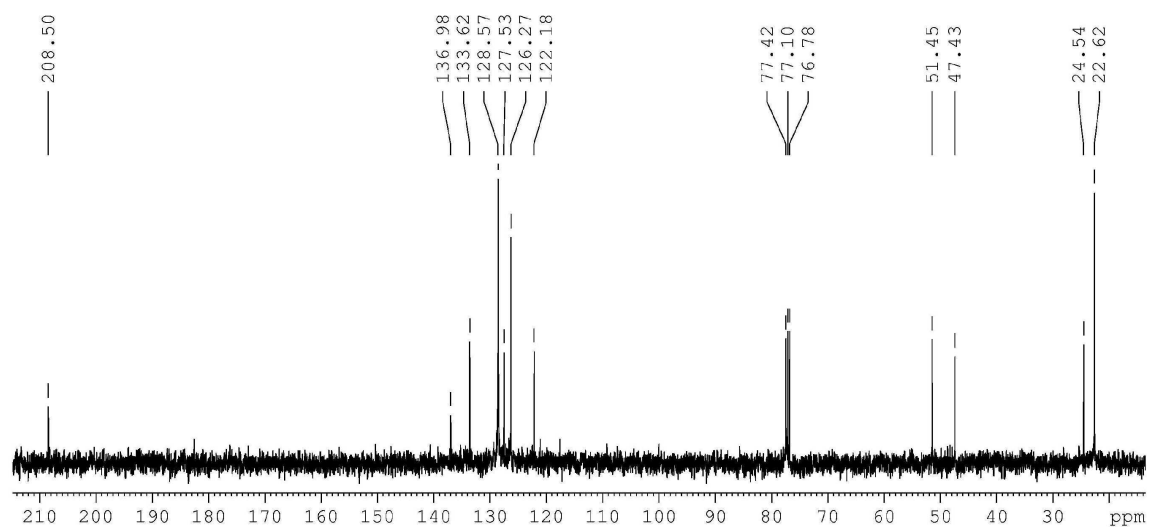


¹³C NMR spectrum of **38** (100.61 MHz, CDCl₃)

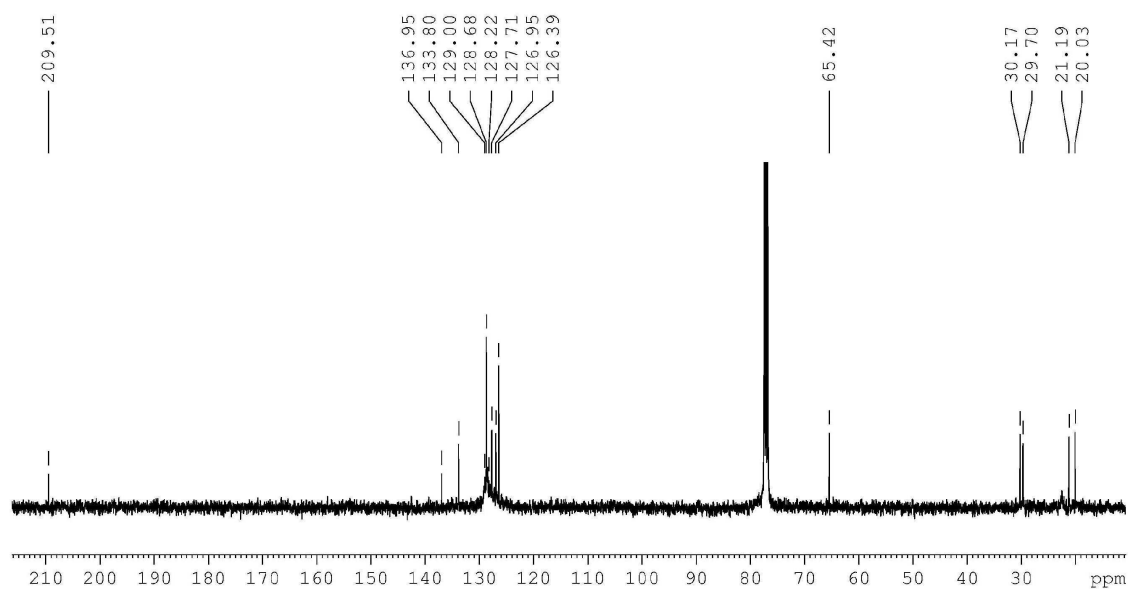
(*E*)-6-Methyl-1-phenylhept-1-en-4-one (40) and (*E*)-3-isopropyl-5-phenylpent-4-en-2-one (41) in mixture (1:1 ratio)



¹H NMR spectrum of **40** and **41** in a mixture (400.13 MHz, CDCl₃)

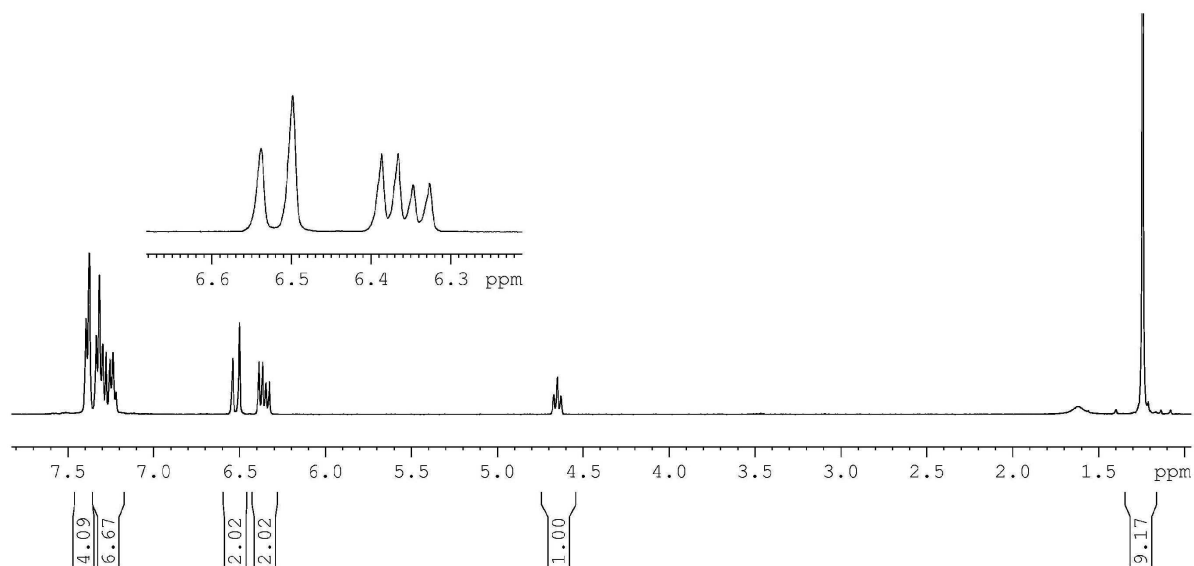
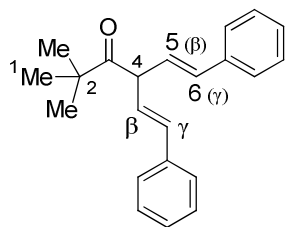


¹³C NMR spectrum of **40** (100.61 MHz, CDCl₃)

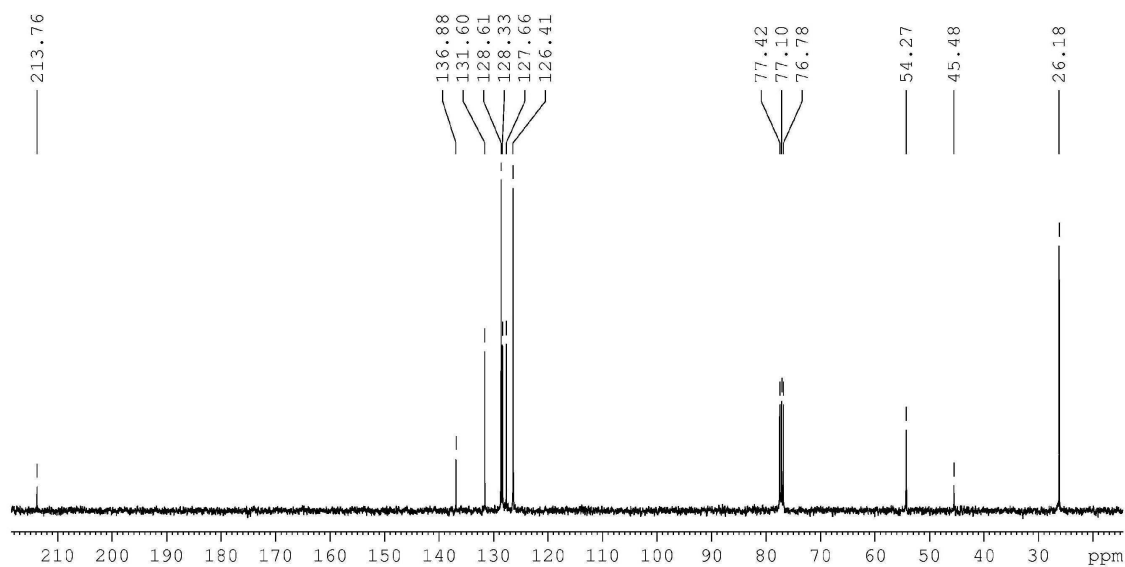


^{13}C NMR spectrum of **41** (100.61 MHz, CDCl_3)

(*E*)-2,2-Dimethyl-6-phenyl-4-styrylhex-5-en-3-one (42)



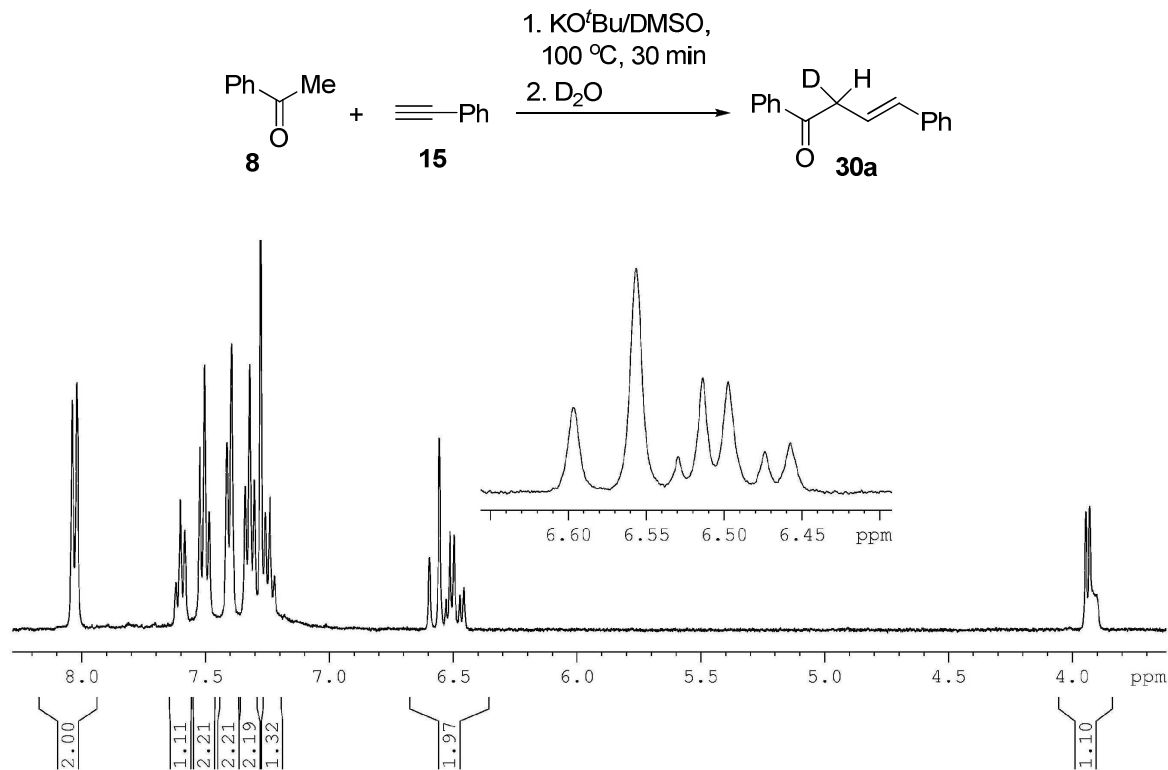
^1H NMR spectrum of **42** (400.13 MHz, CDCl_3)



^{13}C NMR spectrum of **42** (100.61 MHz, CDCl_3)

The isotope exchange during the synthesis of ketone 30 (synthesis of ketone 30a).

A mixture of acetophenone **8** (120 mg, 1.0 mmol), phenylacetylene **15** (112 mg, 1.0 mmol) and KO^tBu (112 mg, 4.0 mmol) in DMSO (4 mL) was stirred upon heating (100 °C) for 30 min. The reaction mixture, after cooling (20-25 °C), was quenched with D₂O (4 mL), neutralized with CO₂ and extracted with Et₂O (3 mL x 4). The organic extract was washed with D₂O (2 mL x 3) and dried (MgSO₄). After removal of Et₂O, a crude (178 mg) was analyzed by ¹H NMR.



¹H NMR spectrum of **30a** (400.13 MHz, CDCl₃)