Electronic supplementary materials *Mendeleev Commun.*, 2024, **34**, 581–583

The reaction of 1-alkyl-3-phenylpropynones with aromatic aldehydes: an update

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Table S1. Optimization of conditions for the reaction between cyclobutyl ynone **1b** and aldehyde **2a**

Entry[a]	Catalyst	Solvent	Amount of aldehyde 2a per 1b	*T*	*t*	Yield of 3b, %[b]
1	*t*-BuOK (100 mol%)	DMSO	1 equiv.	rt	2 h	10
2	*t*-BuOK (100 mol%)	DMSO	1 equiv.	90 °C	2 h	21
3	*t*-BuOK (150 mol%)	DMSO	2 equiv.	rt	5 min	0
4	*t*-BuOK (50 mol%)	DMSO	2 equiv.	rt	5 min	20
5	***t*-BuOK (25 mol%)**	**DMSO**	**2 equiv.**	**rt**	**5 min**	**21**
6	*t*-BuOK (15 mol%)	DMSO	2 equiv.	rt	5 min	6
7	*t*-BuOK (25 mol%)	DMSO	2 equiv.	90 °C	5 min	17
8	*t*-BuOK (100 mol%)	THF	2 equiv.	rt	5 min	traces
9	*t*-BuOK (100 mol%)	DMF	2 equiv.	rt	5 min	13
10	*t*-BuOK (100 mol%)	DMA	2 equiv.	rt	5 min	17
11	*t*-BuONa (100 mol%)	DMSO	2 equiv.	rt	5 min	10
12	$KOH \cdot 0.5H_2O$ (100 mol%)	DMSO	2 equiv.	rt	5 min	9
13	Cs_2CO_3 (100 mol%)	DMSO	2 equiv.	rt	5 min	0
14	Cs_2CO_3 (100 mol%)	DMSO	2 equiv.	rt	overnight	0
15	DBU (25 mol%)	DCM	2 equiv.	rt	overnight	0
16	PPh_3 (25 mol%)	DCM	2 equiv.	rt	19 h	24
17	PPh_3 (25 mol%)	1,2-DCE	2 equiv.	80 °C	7 h	32
18	PPh_3 (25 mol%)	THF	2 equiv.	rt	19 h	9
19	PPh_3 (25 mol%)	MeCN	2 equiv.	rt	19 h	46
20	PPh_3 (25 mol%)	MeCN	2 equiv.	rt	27 h	50
21	PPh_3 (25 mol%)	MeCN	2 equiv.	rt	48 h	60
22	PPh_3 (100 mol%)	MeCN	1 equiv.	rt	6 h	51
23	**PPh_3 (100 mol%)**	**MeCN**	**1 equiv.**	**rt**	**24 h**	**62**
24	PPh_3 (100 mol%)	MeCN	2 equiv.	rt	24 h	59

[a]Reaction conditions: **1b** (0.2 mmol), solvent (0.5 M). [b]Yields determined by ^{1}H NMR using durene as an internal standard.

General information

NMR spectra were recorded from solutions in $CDCl_3$ on Bruker DPX-400 and AV-400 spectrometers (400.1 MHz for ^1H and 100.6 MHz for ^{13}C). Chemical shifts (δ) are quoted in parts per million (ppm). The residual solvent peak, δ_H 7.26 and δ_C 77.16, was used as a reference. Coupling constants (J) are reported in Hertz (Hz). Melting points were measured on a digital melting point apparatus Electrothermal IA 9200. Elemental analysis was performed on a Flash EA 1112 Series analyzer. Thin layer chromatography was carried out on Merck silica gel 60 F_{254} pre-coated aluminium foil sheets and were visualized using UV light (254 nm). Column chromatography was carried out using slurry packed Sigma Aldrich silica gel (SiO_2), 70-230 mesh, pore size 60 Å.

Characterization data for products 3

(*Z*)-7-Benzylidene-5-(4-chlorophenyl)-6-oxaspiro[3.4]octan-8-one (3b)

Following the typical procedure, **3b** was prepared from 1-cyclobutyl-3-phenylprop-2-yn-1-one **1b** (184 mg, 1 mmol) and 4-chlorobenzaldehyde **2a** (141 mg, 1 mmol), isolated as a light yellow oil (71 mg, 22% yield), R_f = 0.49 (hexane/diethyl ether, 3/1, v/v). The ^1H NMR yield was 62%. ^1H NMR (400.1 MHz, $CDCl_3$): δ = 7.79 (d, J = 7.3 Hz, 2H), 7.43-7.28 (m, 7H), 6.46 (s, 1H), 5.44 (s, 1H), 2.56-2.49 (m, 1H), 2.22-2.10 (m, 2H), 2.04-1.99 (m, 1H), 1.74-1.64 (m, 2H). $^{13}C\{^1H\}$ NMR (100.6 MHz, $CDCl_3$): δ = 202.52, 146.63, 136.29, 134.64, 133.88, 130.43, 129.13, 128.76, 128.46, 127.86, 106.02, 88.29, 52.21, 29.41, 27.37, 15.62. Found (%): C 73.96, H 5.28.Calc. for $C_{20}H_{17}ClO_2$: C 74.19, H 5.33.

(*Z*)-3-Benzylidene-1-(4-chlorophenyl)-2-oxaspiro[4.4]nonan-4-one (3c)

Following the typical procedure, **3c** was prepared from 1-cyclopentyl-3-phenylprop-2-yn-1-one **1c** (198 mg, 1 mmol) and 4-chlorobenzaldehyde **2a** (141 mg, 1 mmol), isolated as a colorless oil (20 mg, 6% yield), Rf = 0.61 (hexane/diethyl ether, 3/1, v/v). The ^1H NMR yield was 44%. ^1H NMR (400.1 MHz, $CDCl_3$): δ = 7.81 (d, J = 7.7 Hz, 2H), 7.40-7.35 (m, 4H), 7.30-7.28 (m, 3H), 6.45 (s, 1H), 5.41 (s, 1H), 2.22-2.15 (m, 1H), 1.89-1.81 (m, 2H), 1.73-1.54 (m, 3H), 1.36-1.27 (m, 2H). $^{13}C\{^1H\}$ NMR (100.6 MHz, $CDCl_3$): δ = 204.06, 146.83, 136.26, 134.50, 133.91, 130.42, 128.95, 128.77, 128.46, 127.93, 106.12, 88.71, 58.59, 35.65, 32.49, 25.83, 25.78. Found (%): C 74.44, H 5.65. Calc. for $C_{21}H_{19}ClO_2$: C 74.29, H 5.51.

(*Z*)-3-Benzylidene-1-(4-chlorophenyl)-2-oxaspiro[4.5]decan-4-one (3d)

Following the typical procedure, **3d** was prepared from 1-cyclohexyl-3-phenylprop-2-yn-1-one **1d** (212 mg, 1 mmol) and 4-chlorobenzaldehyde **2a** (141 mg, 1 mmol), isolated as a light yellow powder (222 mg, 63% yield), mp 128-130 °C, R_f = 0.68 (hexane/diethyl ether, 3/1, v/v). The ^1H NMR yield was 63%. ^1H NMR (400.1 MHz, $CDCl_3$): δ = 7.81 (d, J = 8.9 Hz, 2H), 7.38-7.34 (m, 4H), 7.30-7.28 (m, 3H), 6.44

(s, 1H), 5.34 (s, 1H), 2.07-2.01 (m, 1H), 1.83-1.77 (m, 1H), 1.66-1.50 (m, 5H), 1.33-1.18 (m, 2H), 0.97-0.89 (m, 1H). $^{13}C\{^{1}H\}$ NMR (100.6 MHz, $CDCl_3$): δ = 203.30, 146.94, 135.91, 134.45, 133.89, 130.32, 128.78, 128.69, 128.31, 128.22, 105.72, 88.90, 50.38, 32.55, 28.58, 25.25, 21.92, 21.00. Found (%): C 74.89, H 6.00. Calc. for $C_{22}H_{21}ClO_2$: C 75.05, H 6.15.

(*Z*)-2-Benzylidene-5-(4-chlorophenyl)-4,4-dimethyltetrahydrofuran-3-one (3e)

Following the typical procedure, **3e** was prepared from 4-methyl-1-phenylpent-1-yn-3-one **1e** (172 mg, 1 mmol) and 4-chlorobenzaldehyde **2a** (141 mg, 1 mmol), isolated as a light yellow oil (77 mg, 25% yield), R_f = 0.5 (hexane/diethyl ether, 3/1, v/v). The ^{1}H NMR yield was 27%. ^{1}H NMR (400.1 MHz, $CDCl_3$): δ = 7.75 (d, *J* = 8.5 Hz, 2H), 7.34-7.22 (m, 7H), 6.40 (s, 1H), 5.17 (s, 1H), 1.24 (s, 3H), 0.65 (s, 3H). $^{13}C\{^{1}H\}$ NMR (100.6 MHz, $CDCl_3$): δ = 203.74, 146.40, 135.26, 134.34, 133.77, 130.50, 128.85, 128.78, 128.58, 127.48, 106.86, 88.74, 47.28, 21.34, 20.26. Found (%): C 72.96, H 5.48. Calc. for $C_{19}H_{17}ClO_2$: C 73.09, H 5.63.

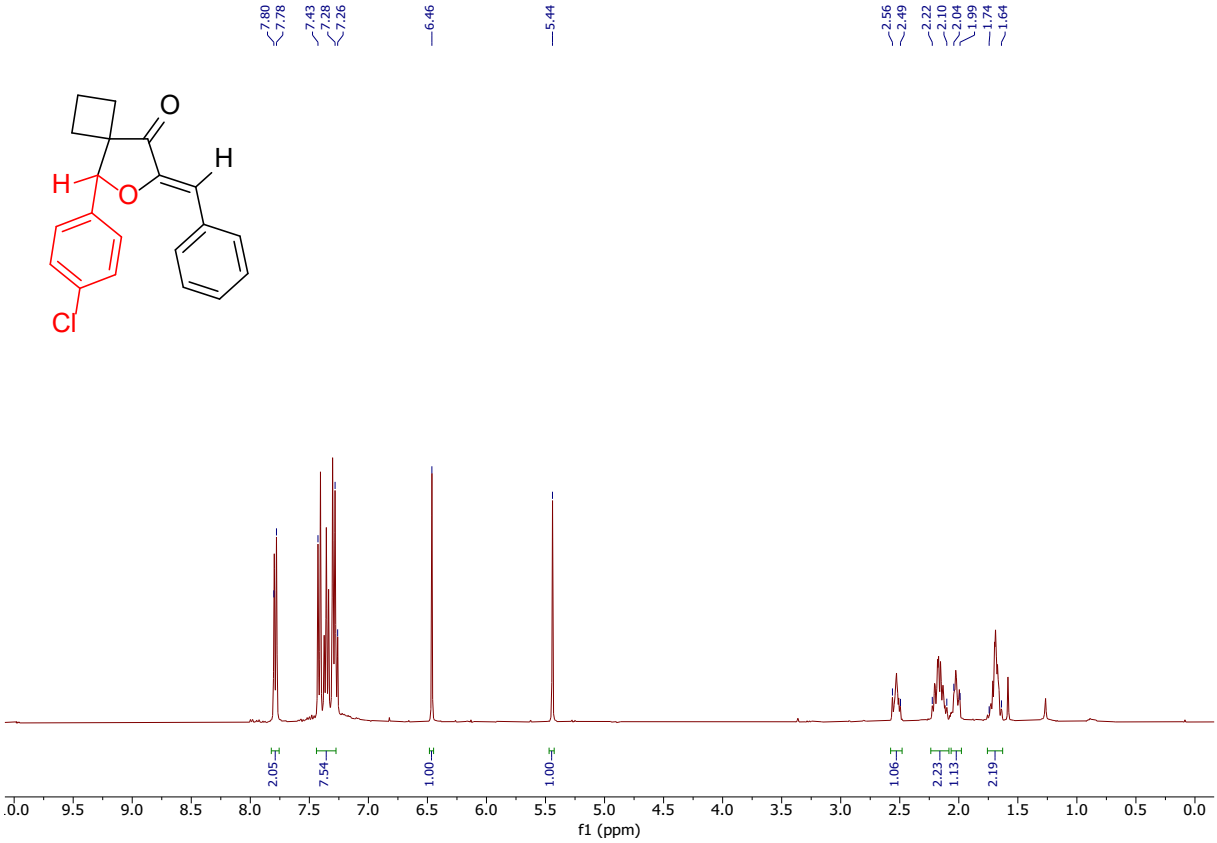
(*Z*)-2-Benzylidene-5-(4-chlorophenyl)-4-ethyltetrahydrofuran-3-one (3f)

Following the typical procedure, **3f** was prepared from 1-phenylhex-1-yn-3-one **1f** (172 mg, 1 mmol) and 4-chlorobenzaldehyde **2a** (141 mg, 1 mmol), isolated as a light yellow oil (132 mg, 42% yield), R_f = 0.63 (hexane/diethyl ether, 3/1, v/v). The ^{1}H NMR yield was 42%. ^{1}H NMR (400.1 MHz, $CDCl_3$): δ = 7.80 (d, *J* = 8.7 Hz, 2H), 7.43-7.35 (m, 6H), 7.31-7.29 (m, 1H), 6.44 (s, 1H), 5.29 (d, *J* = 7.7 Hz, 1H), 2.58-2.53 (m, 1H), 1.97-1.86 (m, 1H), 1.84-1.74 (m, 1H), 1.07-1.03 (m, 3H). $^{13}C\{^{1}H\}$ NMR (100.6 MHz, $CDCl_3$): δ = 200.70, 147.29, 138.78, 134.60, 133.68, 130.38, 129.19, 128.68, 128.42, 127.63, 105.61, 84.47, 54.53, 21.69, 11.32. Found (%): C 72.96, H 5.48. Calc. for $C_{19}H_{17}ClO_2$: C 73.06, H 5.57.

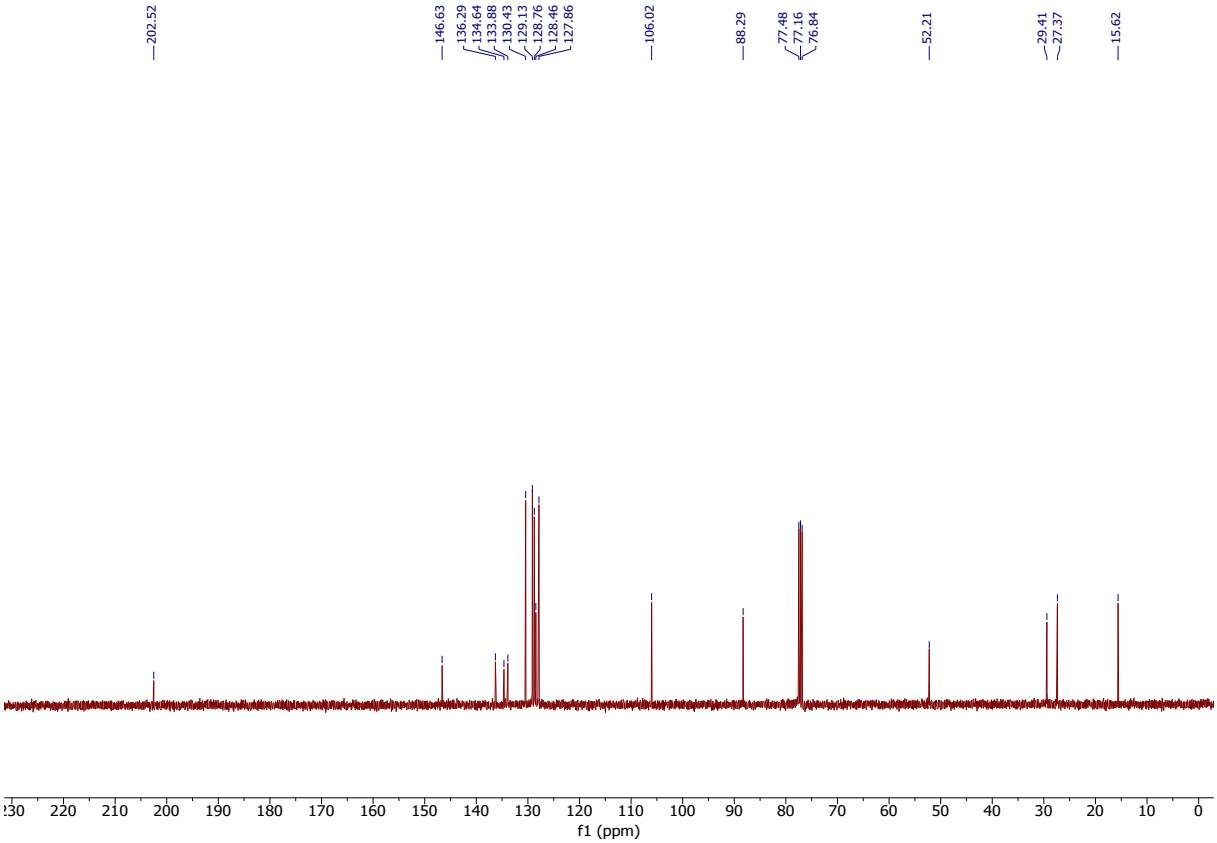
(*Z*)-2-Benzylidene-4-ethyl-5-(4-nitrophenyl)tetrahydrofuran-3-one (3h)

Following the typical procedure, **3h** was prepared from 1-phenylhex-1-yn-3-one **1h** (172 mg, 1 mmol) and 4-nitrobenzaldehyde **2b** (151 mg, 1 mmol), isolated as an yellow oil (142 mg, 44% yield), R_f = 0.16 (hexane/diethyl ether, 3/1, v/v). The ^{1}H NMR yield was 93%. ^{1}H NMR (400.1 MHz, $CDCl_3$): δ = 8.27 (d, *J* = 8.9 Hz, 2H), 7.79 (d, *J* = 7.5 Hz, 2H), 7.60 (d, *J* = 8.4 Hz, 2H), 7.38-7.35 (m, 2H), 7.32-7.28 (m, 1H), 6.45 (s, 1H), 5.44 (d, *J* = 7.4 Hz, 1H), 2.58-2.53 (m, 1H), 1.99-1.80 (m, 2H), 1.10-1.06 (m, 3H). $^{13}C\{^{1}H\}$ NMR (100.6 MHz, $CDCl_3$): δ = 199.80, 148.09, 147.49, 146.80, 133.41, 130.46, 128.78, 128.72, 126.88, 124.29, 106.38, 83.80, 54.61, 21.96, 11.28. Found (%): C 70.58, H 5.30. Calc. for $C_{19}H_{17}NO_4$: C 70.72, H 5.39.

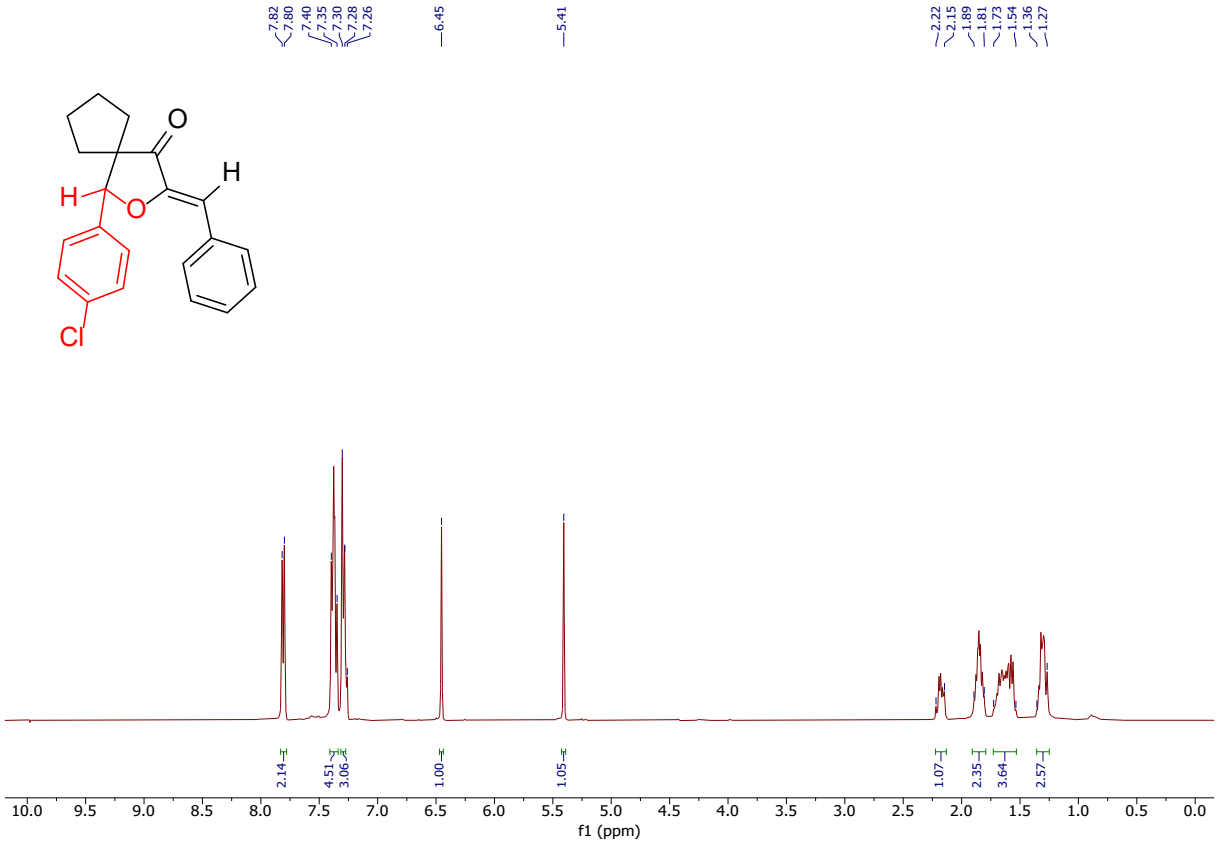
^{1}H and ^{13}C Spectra for products 3



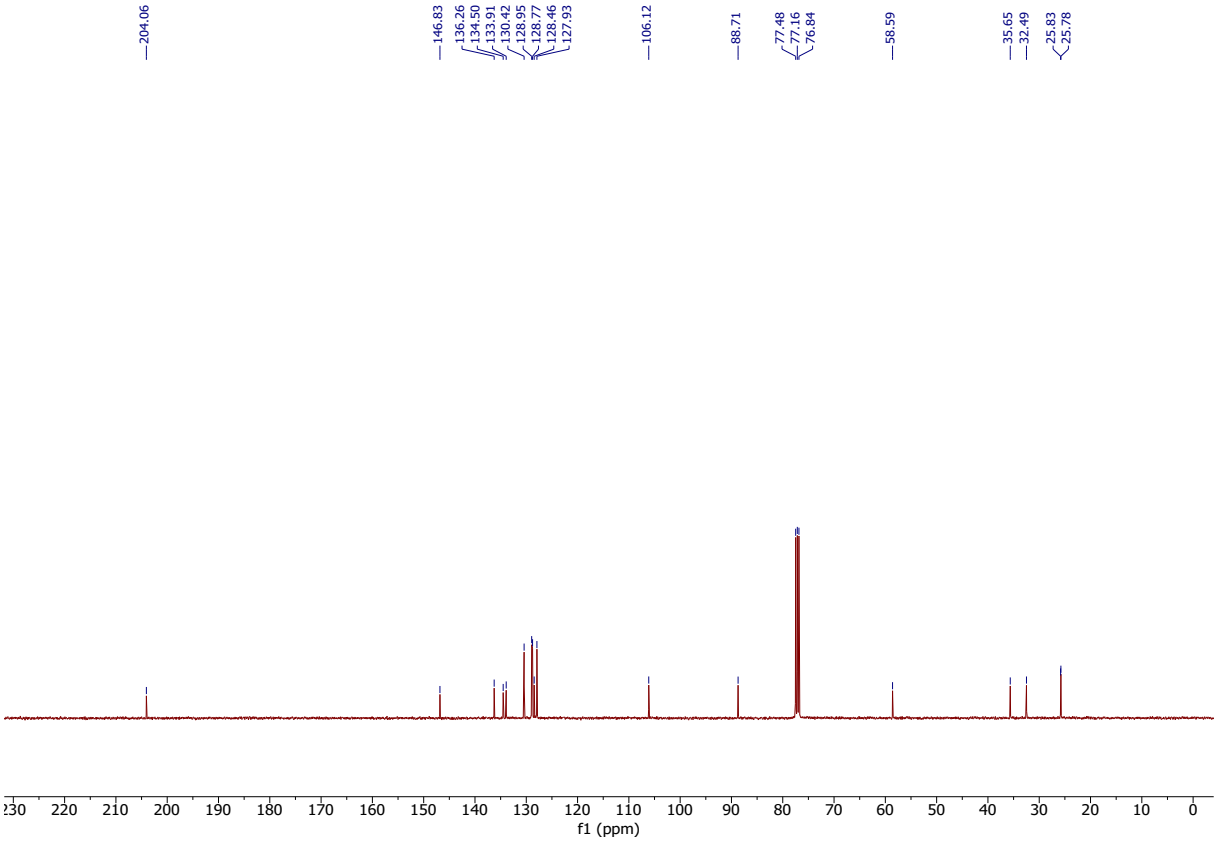
^{1}H NMR spectrum of **3b** (400.1 MHz, $CDCl_3$)



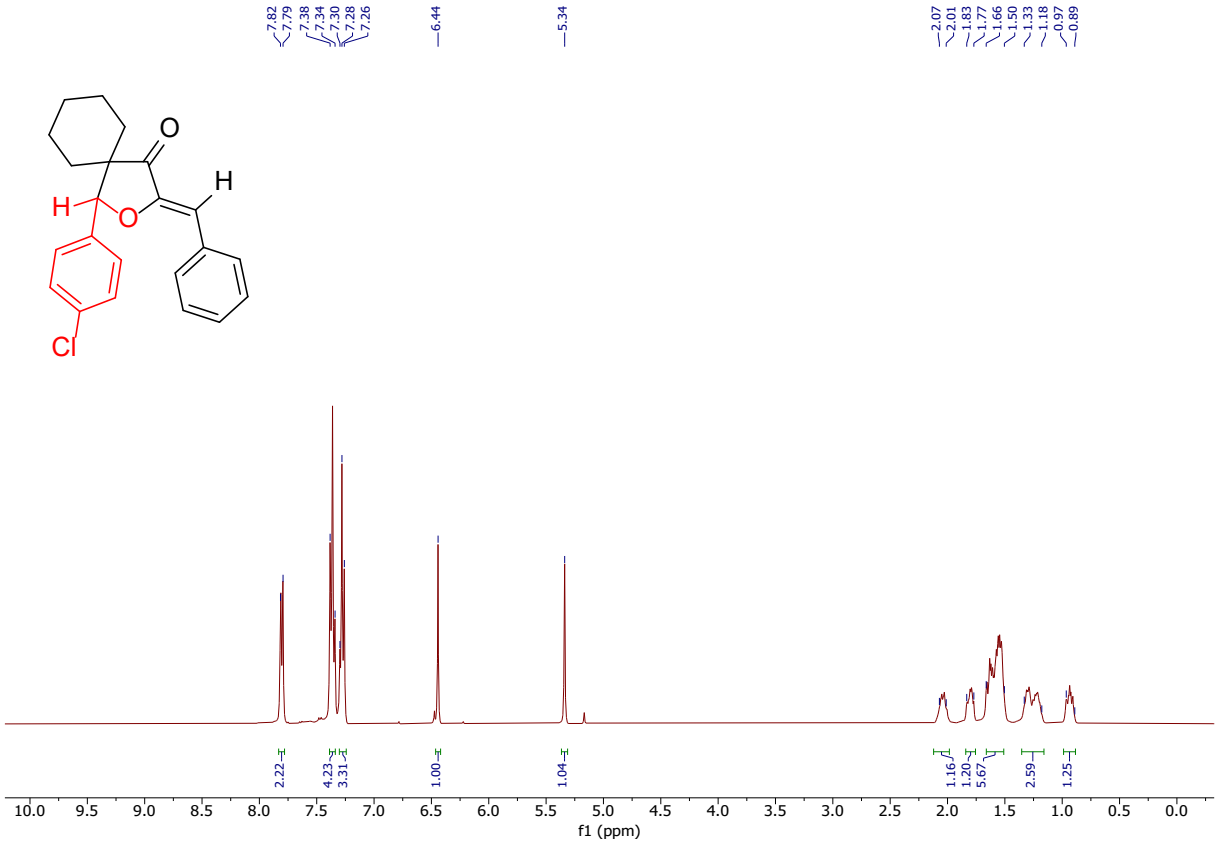
^{13}C NMR spectrum of **3b** (100.6 MHz, $CDCl_3$)



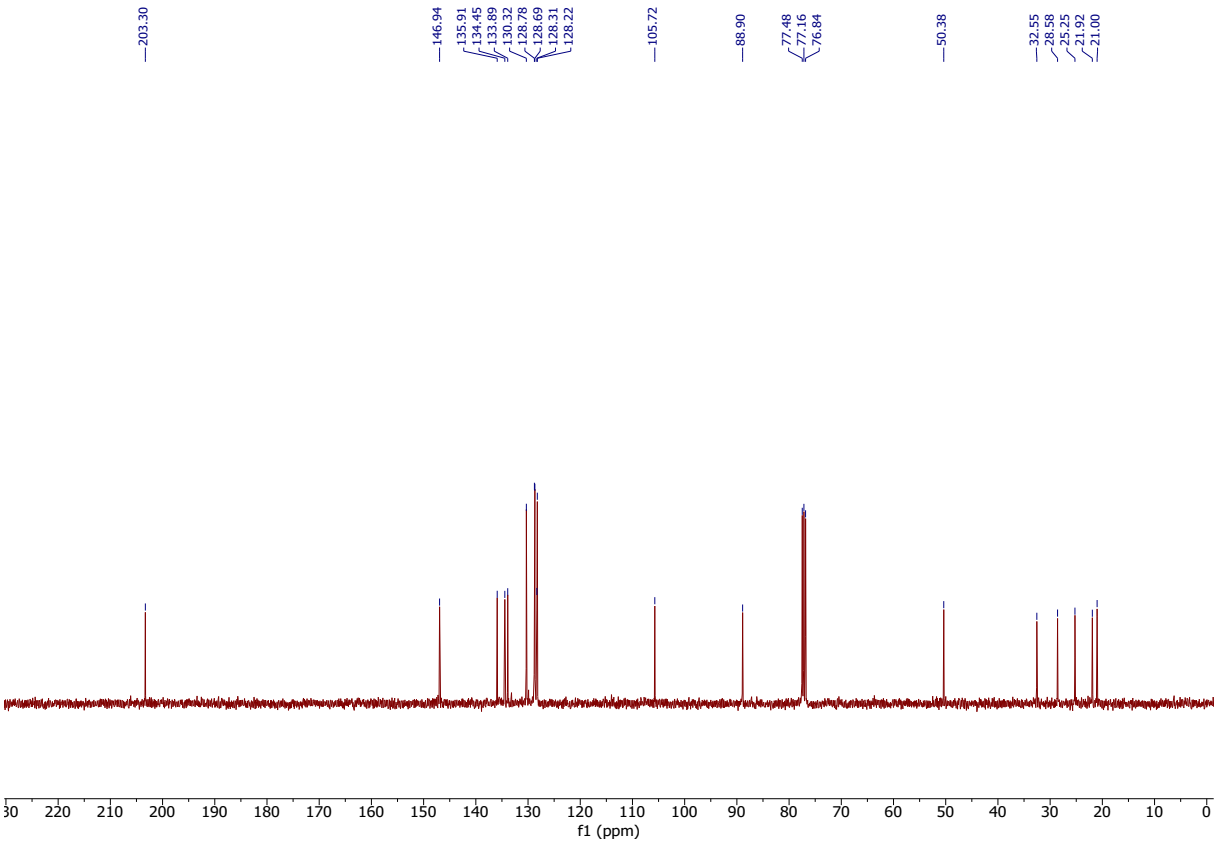
^{1}H NMR spectrum of **3c** (400.1 MHz, $CDCl_3$)



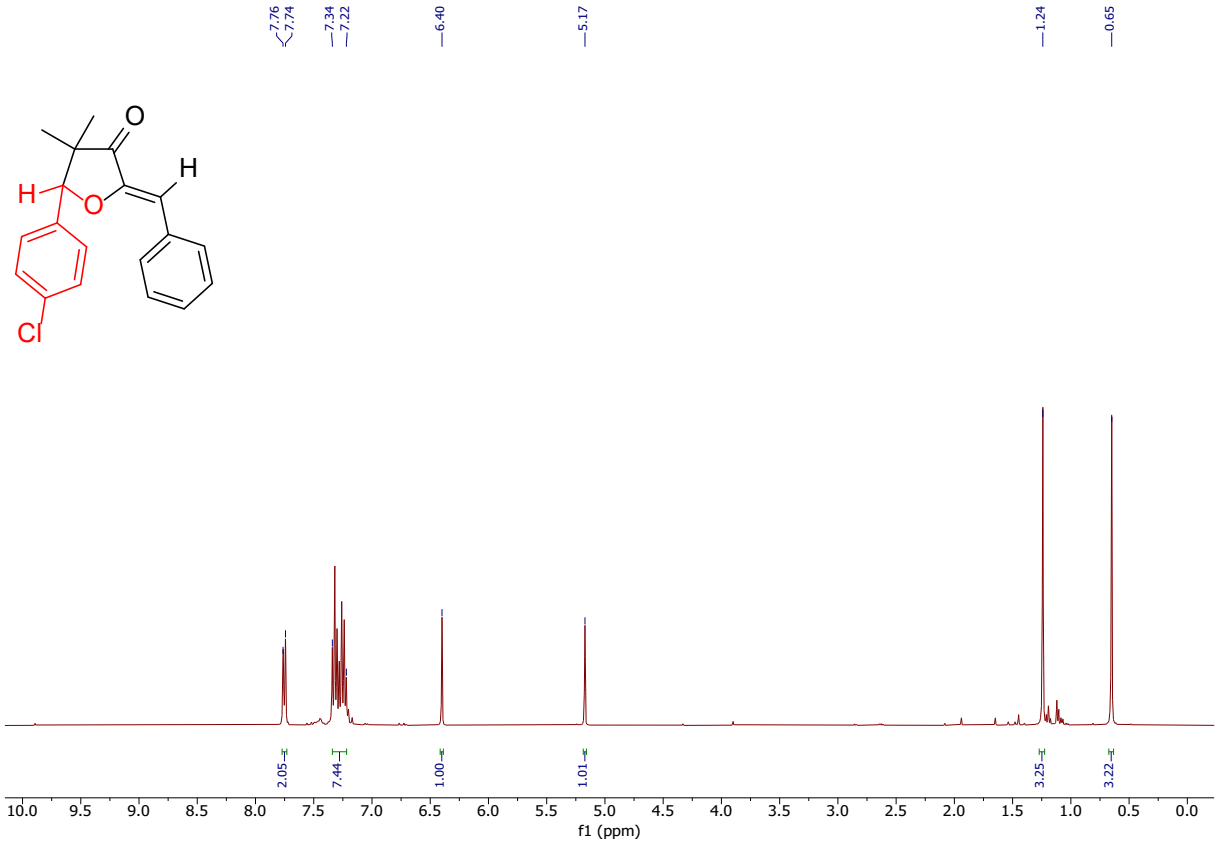
^{13}C NMR spectrum of **3c** (100.6 MHz, $CDCl_3$)



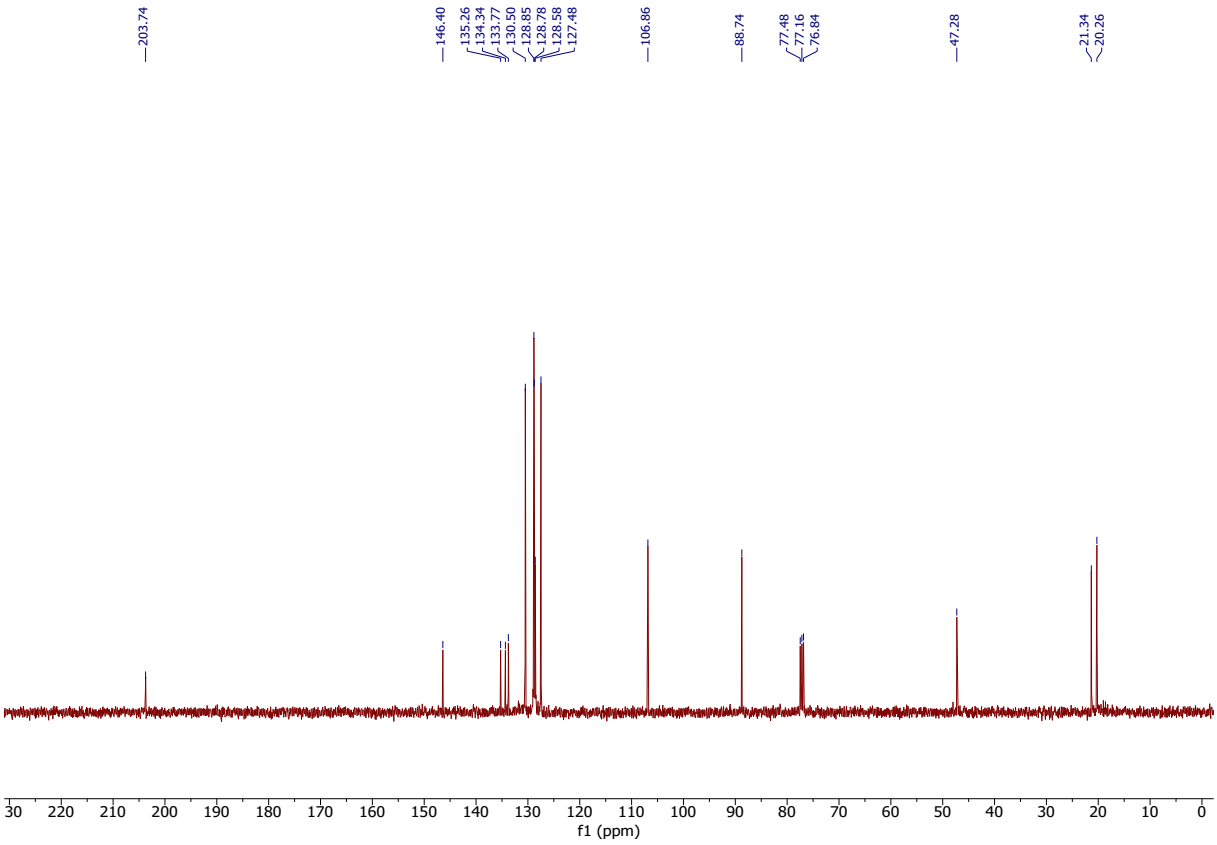
^{1}H NMR spectrum of **3d** (400.1 MHz, $CDCl_3$)



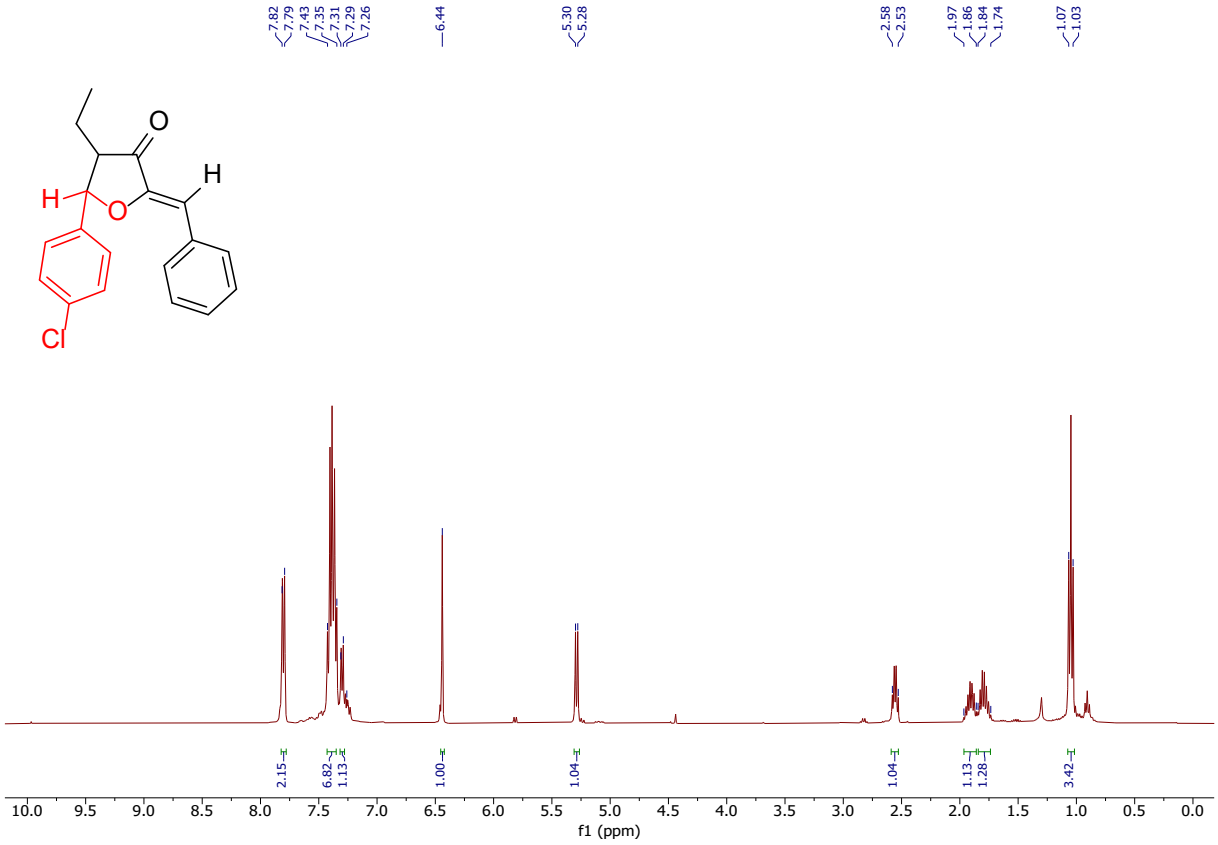
^{13}C NMR spectrum of **3d** (100.6 MHz, $CDCl_3$)



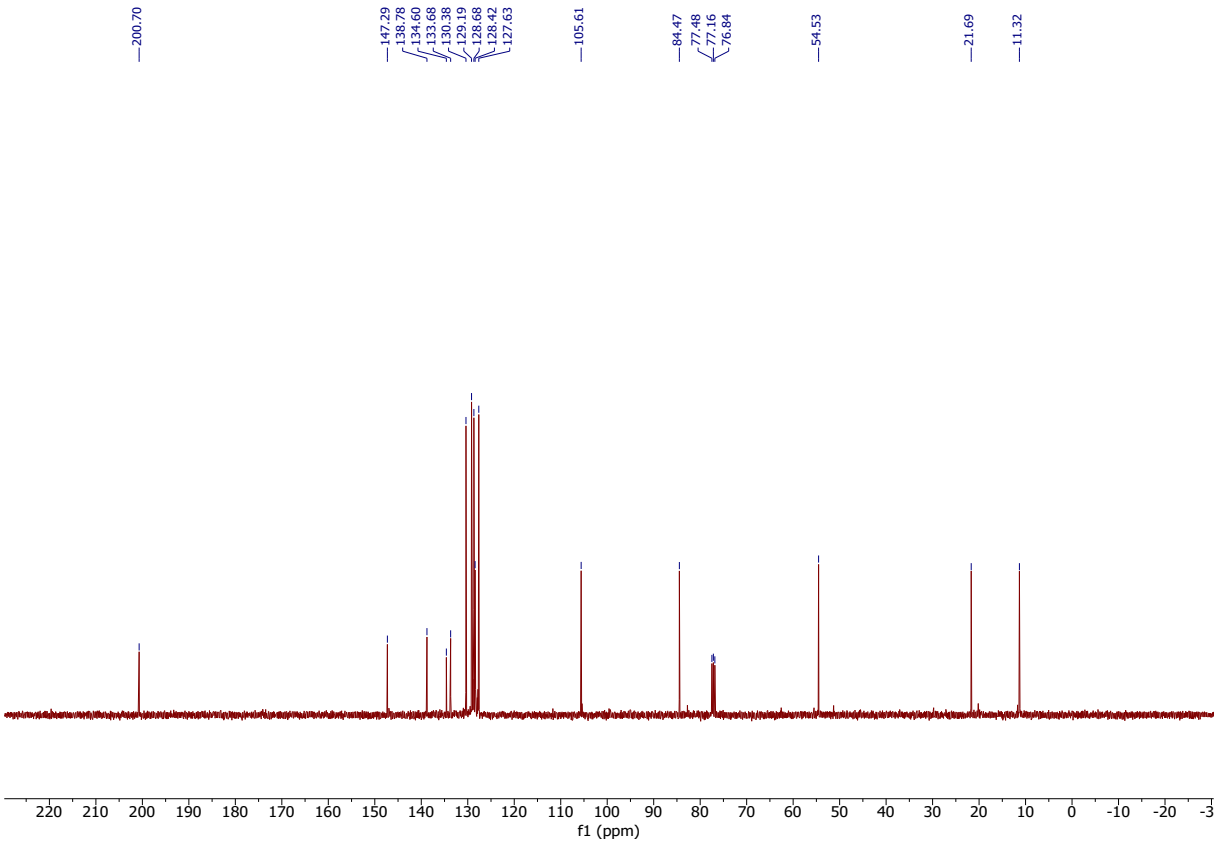
^{1}H NMR spectrum of **3e** (400.1 MHz, $CDCl_3$)



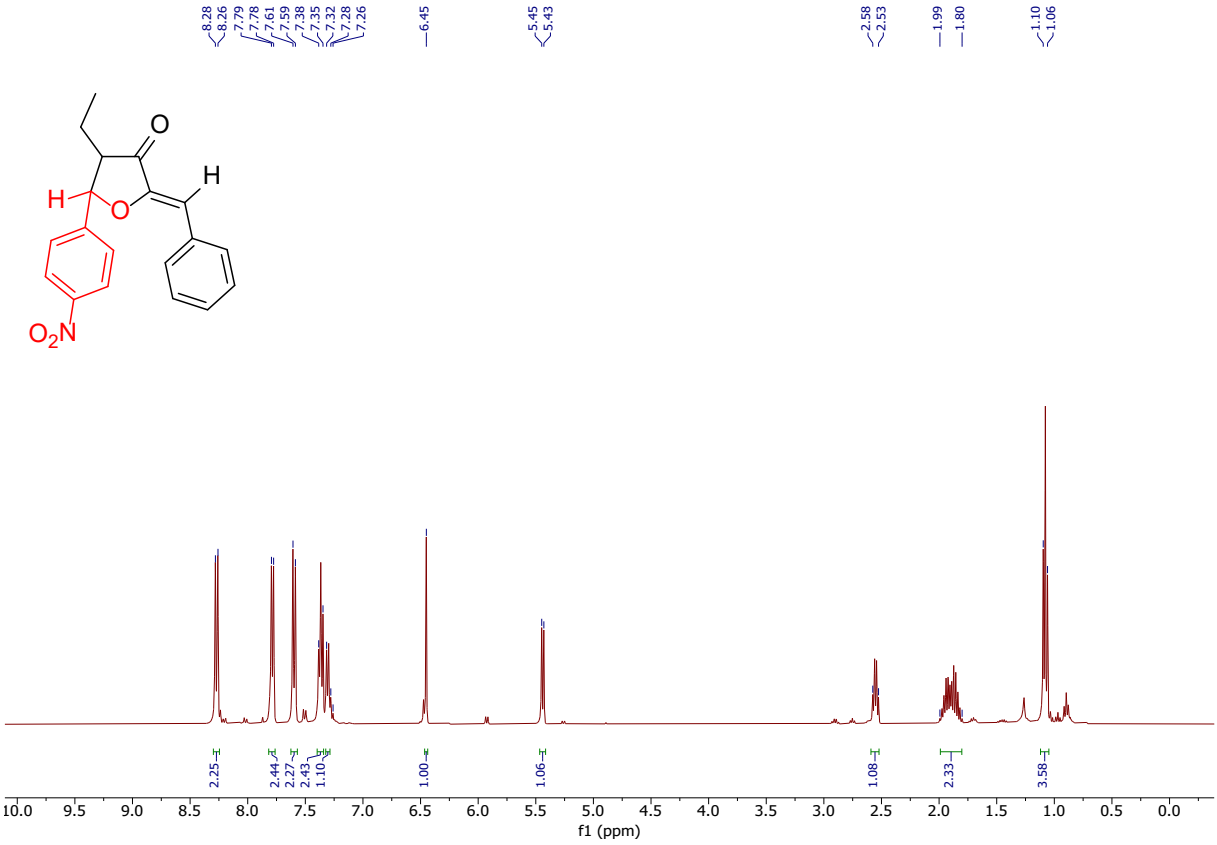
^{13}C NMR spectrum of **3e** (100.6 MHz, $CDCl_3$)



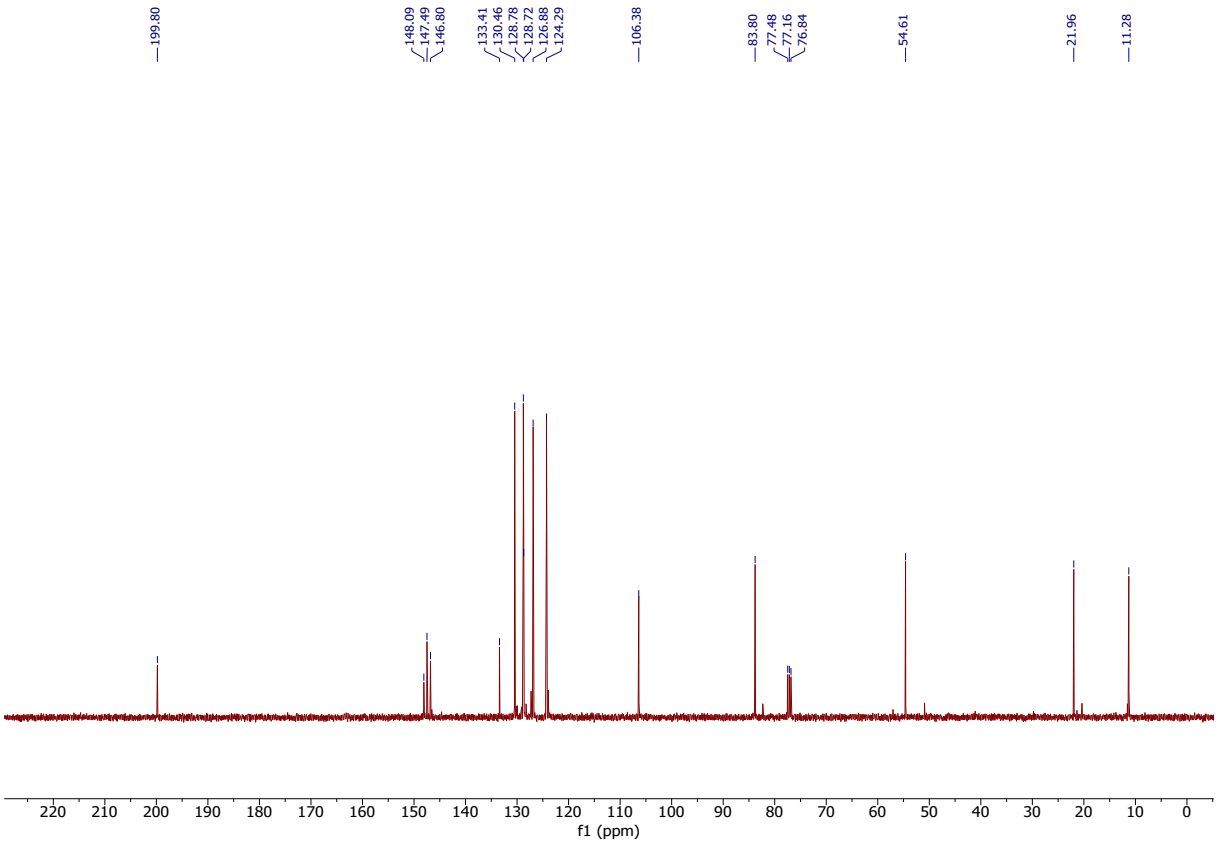
^{1}H NMR spectrum of **3f** (400.1 MHz, $CDCl_3$)



^{13}C NMR spectrum of **3f** (100.6 MHz, $CDCl_3$)



^{1}H NMR spectrum of **3h** (400.1 MHz, $CDCl_3$)



^{13}C NMR spectrum of **3h** (100.6 MHz, $CDCl_3$)