

Transition-Metal-Free Alkynylation of 2-Oxindoles through Radical-Radical Coupling

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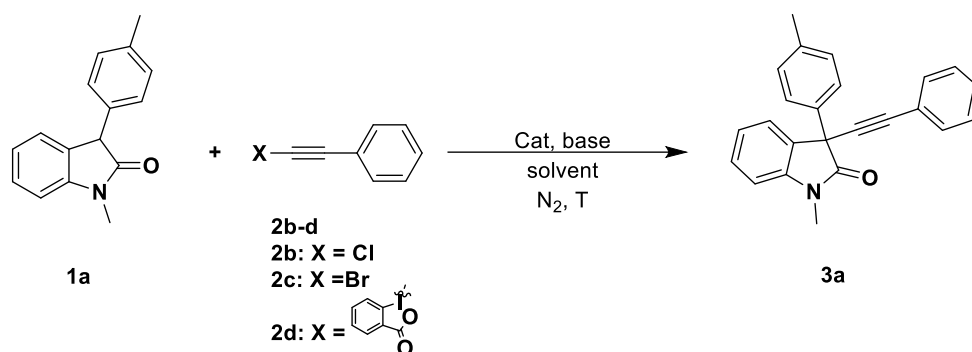
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General Information

All chemicals were obtained from commercial sources and were used as received unless otherwise noted. TLC analysis was performed on pre-coated, glass-backed silica gel plates and visualized with UV light. Column chromatography was performed on silica gel (200-300 mesh) using ethyl acetate (EA)/petroleum ether (PE). ^1H , ^{13}C and 2D-NMR Spectra were obtained on a Bruker 300 MHz, 400 MHz or 500 MHz NMR spectrometer in the deuterated solvents indicated. Chemical shifts are reported in ppm from tetramethylsilane with the solvent resonance as the internal standard. The following abbreviations were used to designate chemical shift multiplicities: s= singlet, d= doublet, t= triplet, q= quartet, h= heptet, m= multiplet. All first-order splitting patterns were assigned on the basis of the appearance of the multiplet. Splitting patterns that could not be easily interpreted are designated as multiplet (m) or broad (br). Melting points were measured on Beijing Tech X-4 apparatus without correction. IR spectra were recorded on a Nicolet 6700 FT-IR spectrometer. HRMS were obtained using electrospray ionization (ESI)-Orbitrap.

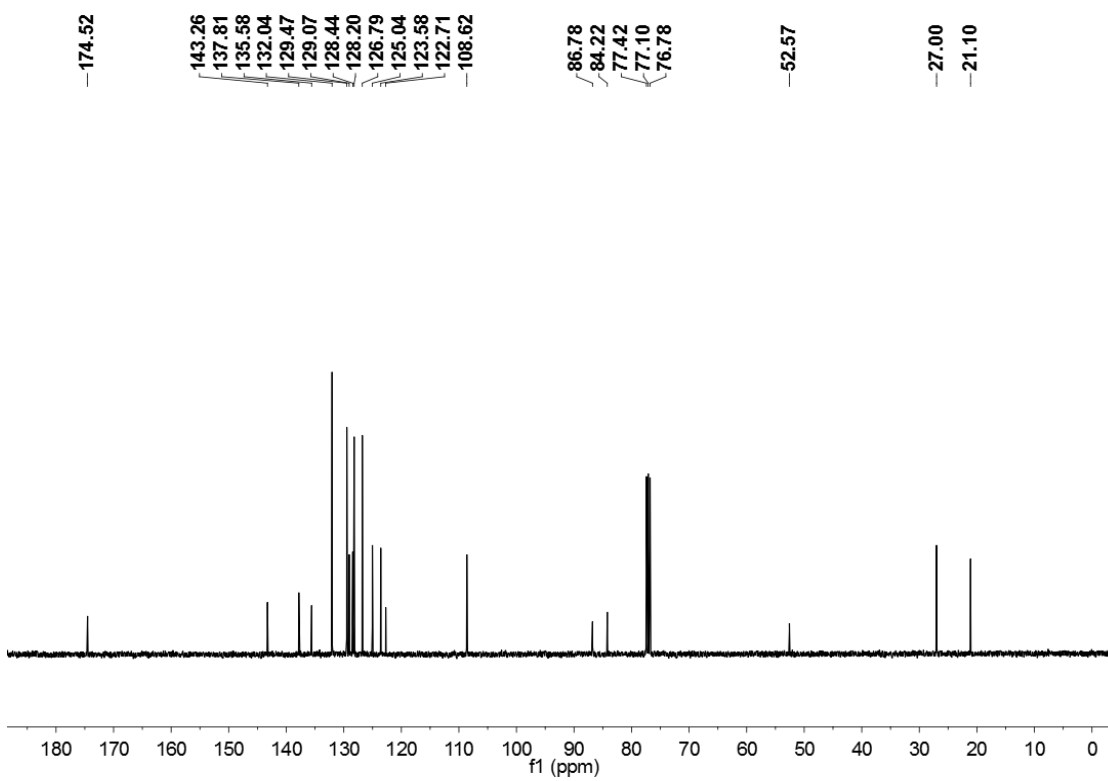
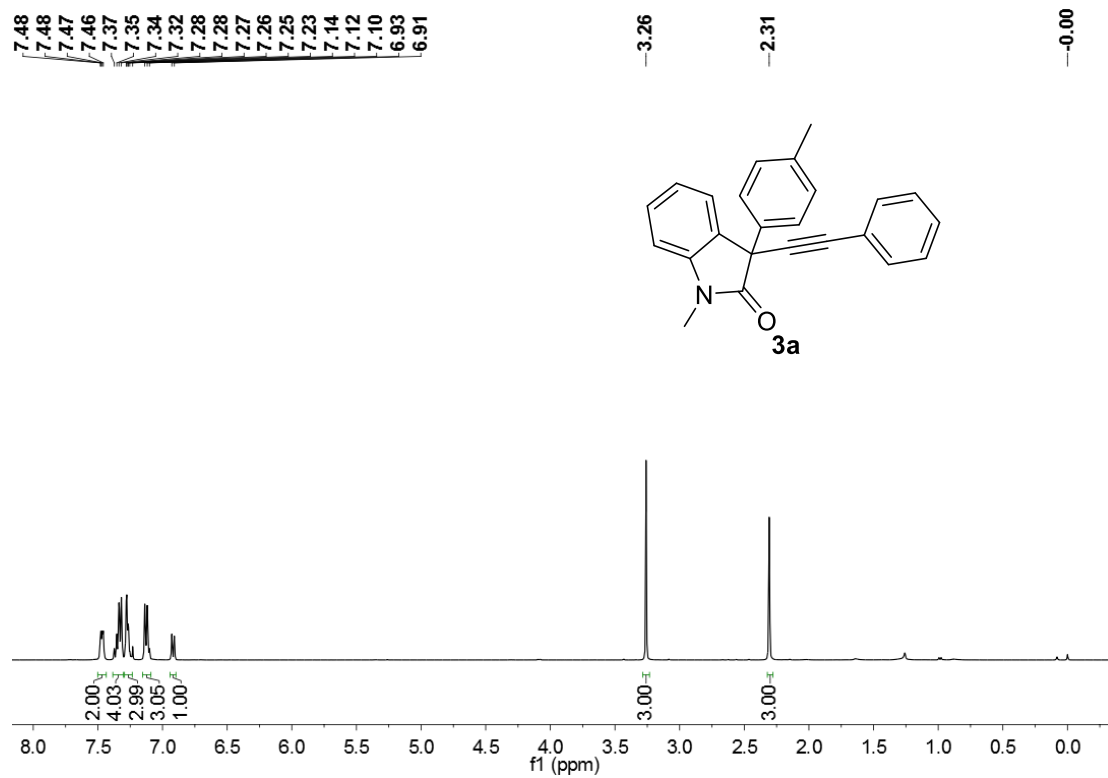
Table S1 Reactions of 2-oxindole with other kinds of alkynylation reagents^a



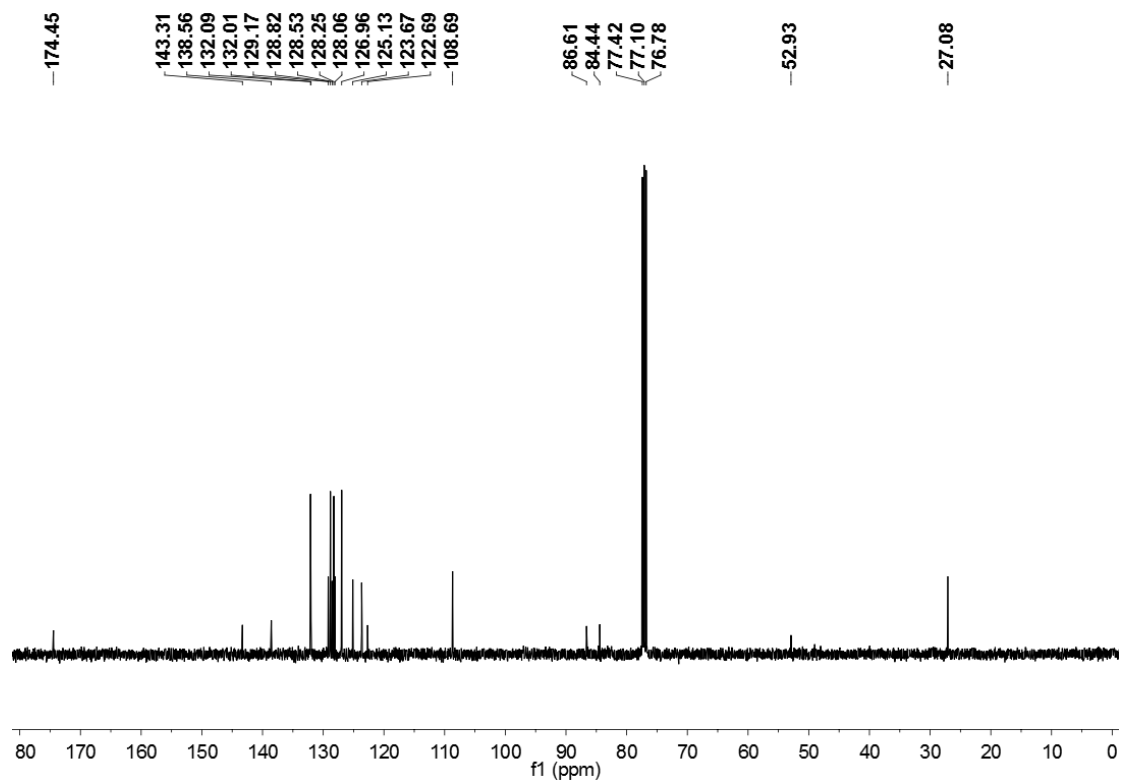
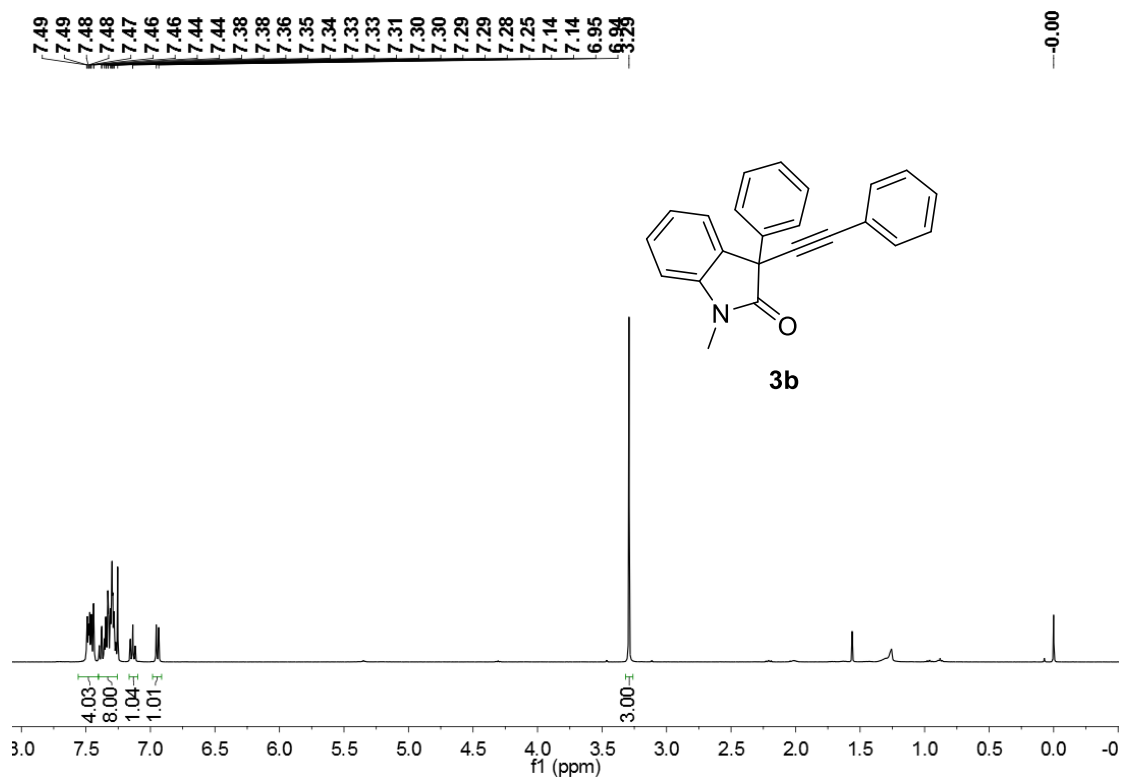
Entry	2	1a:2	Cat.	base	solvent	T/°C	t/h	Yield of 3a / % ^b
1	2b	1:1.5	Sc(OTf) ₃ (0.2)	Na ₂ CO ₃ (2.0)	DCM	r.t.	24	N.R. ^e
2	2b	1:1.5	n-Bu ₄ N ⁺ I ⁻ (0.2)	KF (33%w) ^c	oxylene/CHCl ₃ (7:1) ^d	r.t.	12	N.R.
3	2b	1:3	--	NaOAc (2.0)	PhCl	120 °C	24	N.P. ^f
4	2c	1:1.5	Sc(OTf) ₃ (0.2)	Na ₂ CO ₃ (2.0)	DCM	r.t.	12	N.R.
5	2c	1:1.5	n-Bu ₄ N ⁺ I ⁻ (0.2)	KF (33%w) ^c	oxylene/CHCl ₃ (7:1) ^d	r.t.	24	N.R.
6	2c	1:3	--	NaOAc (2.0)	PhCl	120 °C	12	N.P.
7	2d	1:1.5	DABCO (0.2)	--	DMF	r.t.	24	38
8	2d	1:3	--	NaOAc (2.0)	PhCl	120 °C	12	9

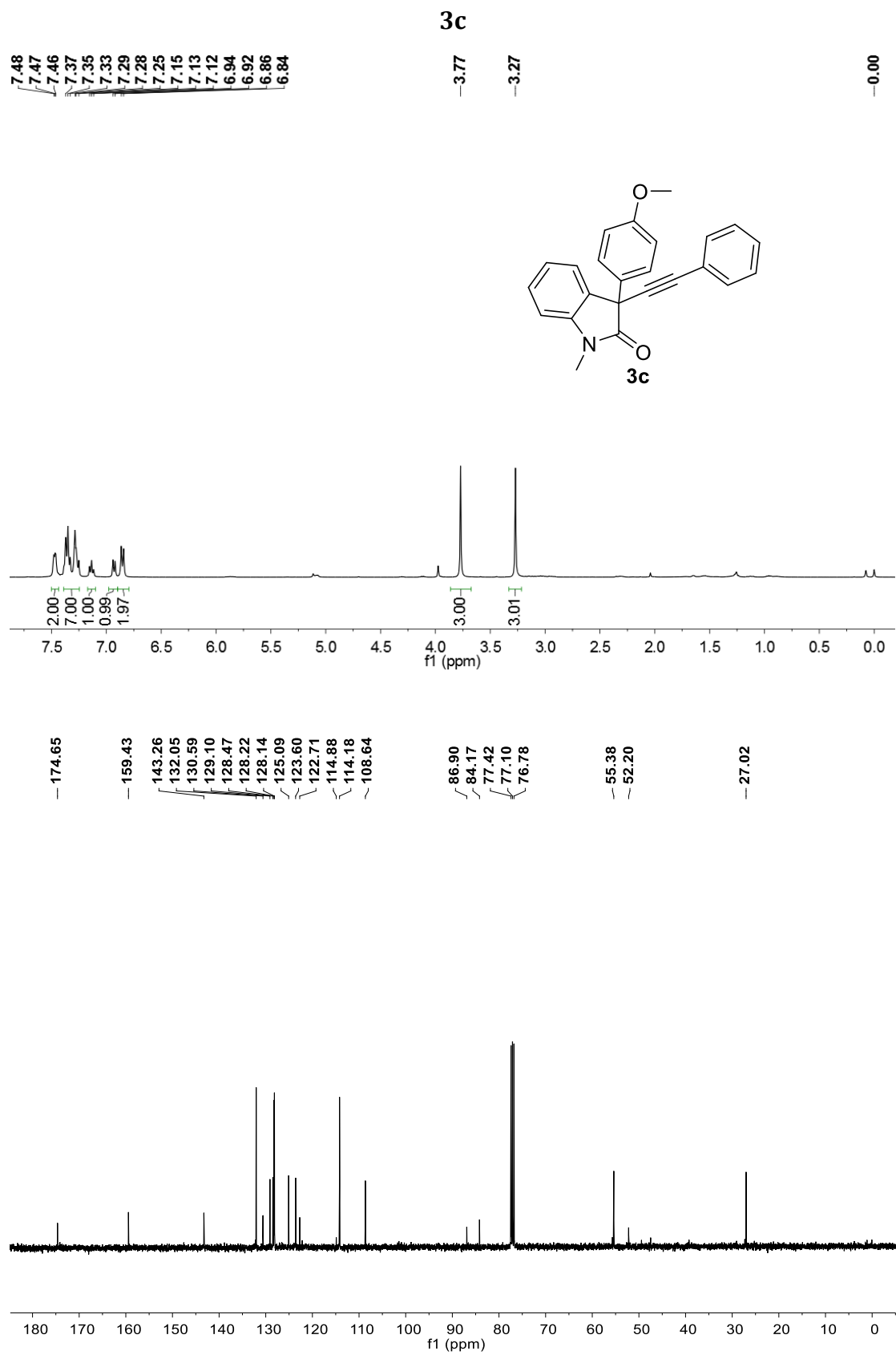
^aUnless noted, the reaction was carried out with **1a** (0.1 mmol), **2** (x mmol), catalyst (y mol %), base (2.0 equiv) in 2 mL of solvent under N₂. ^bIsolated yields. ^c1ml of aqueous solution. ^d1ml of solvents. ^eN.P. = no product. ^fN.R. = no reaction.

3a

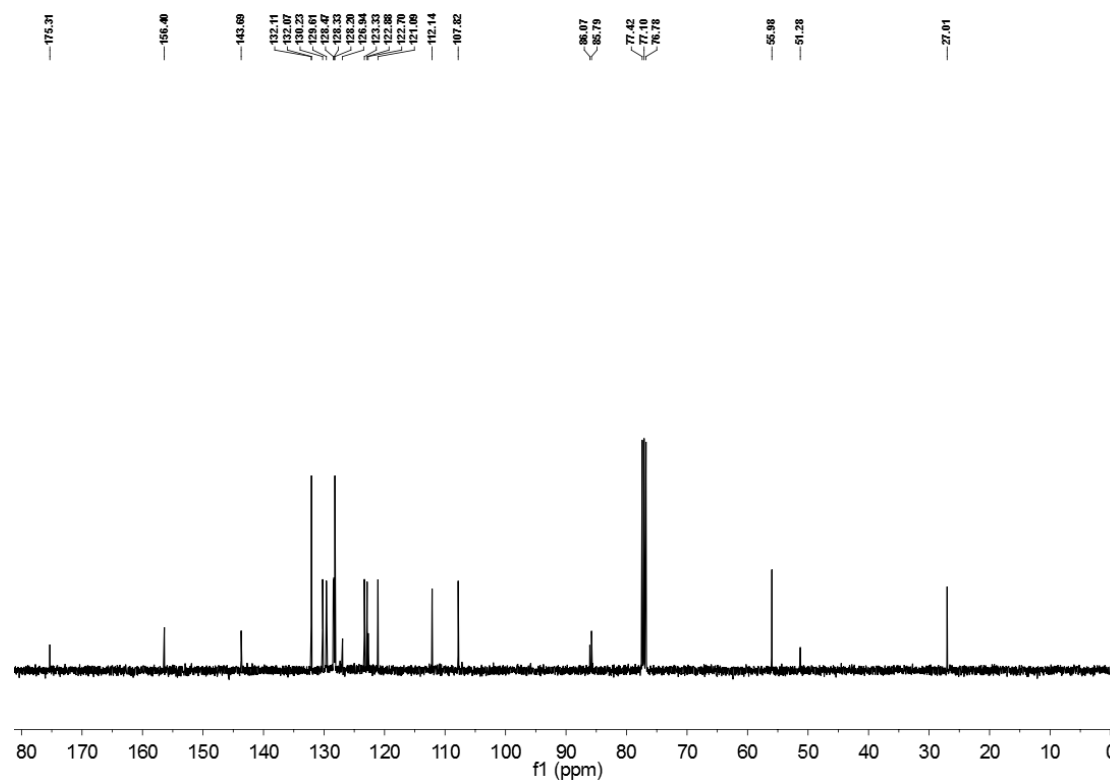
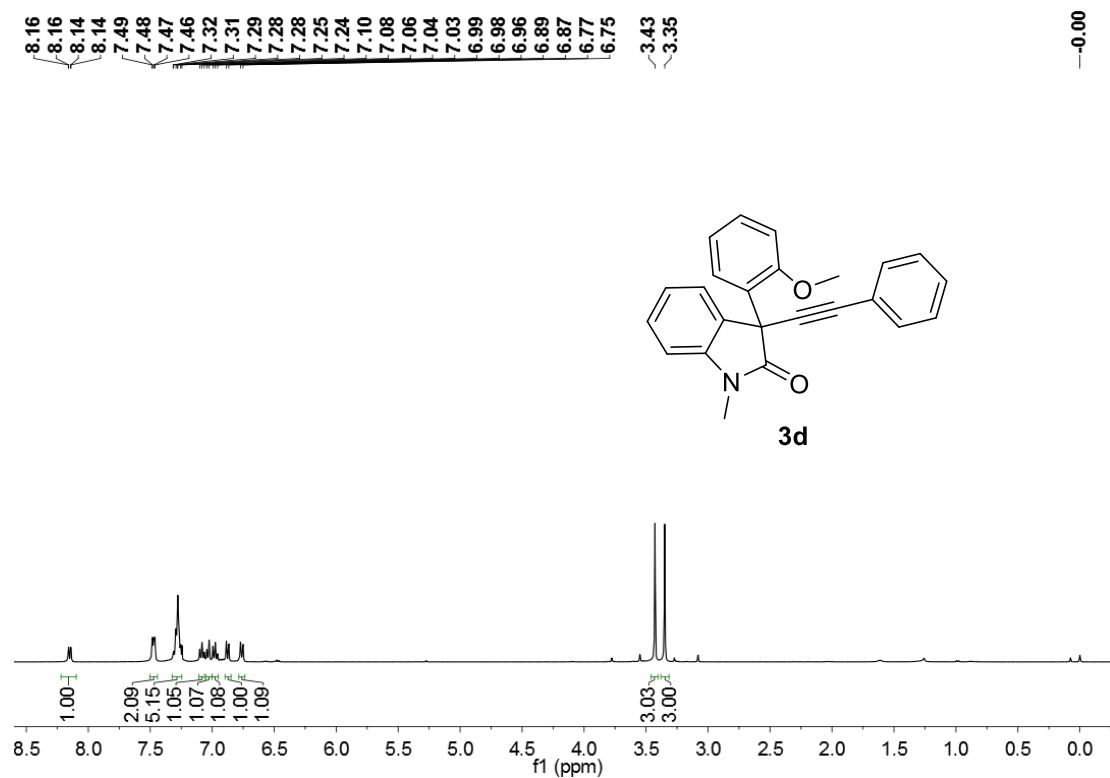


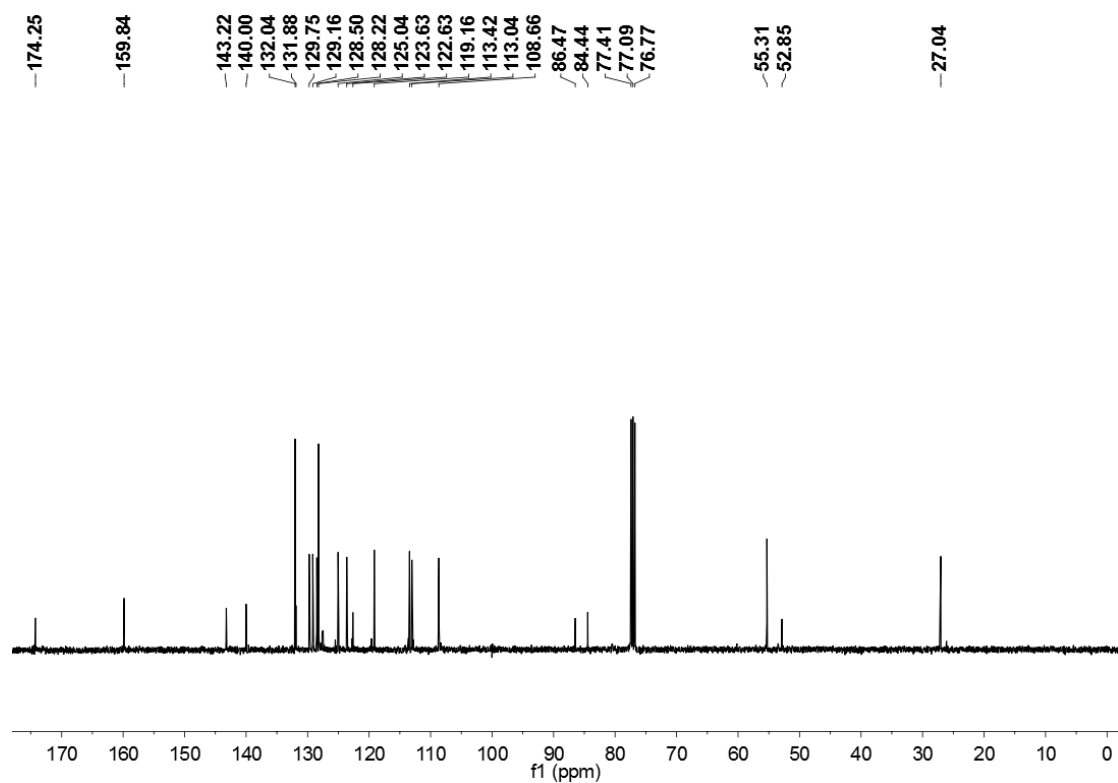
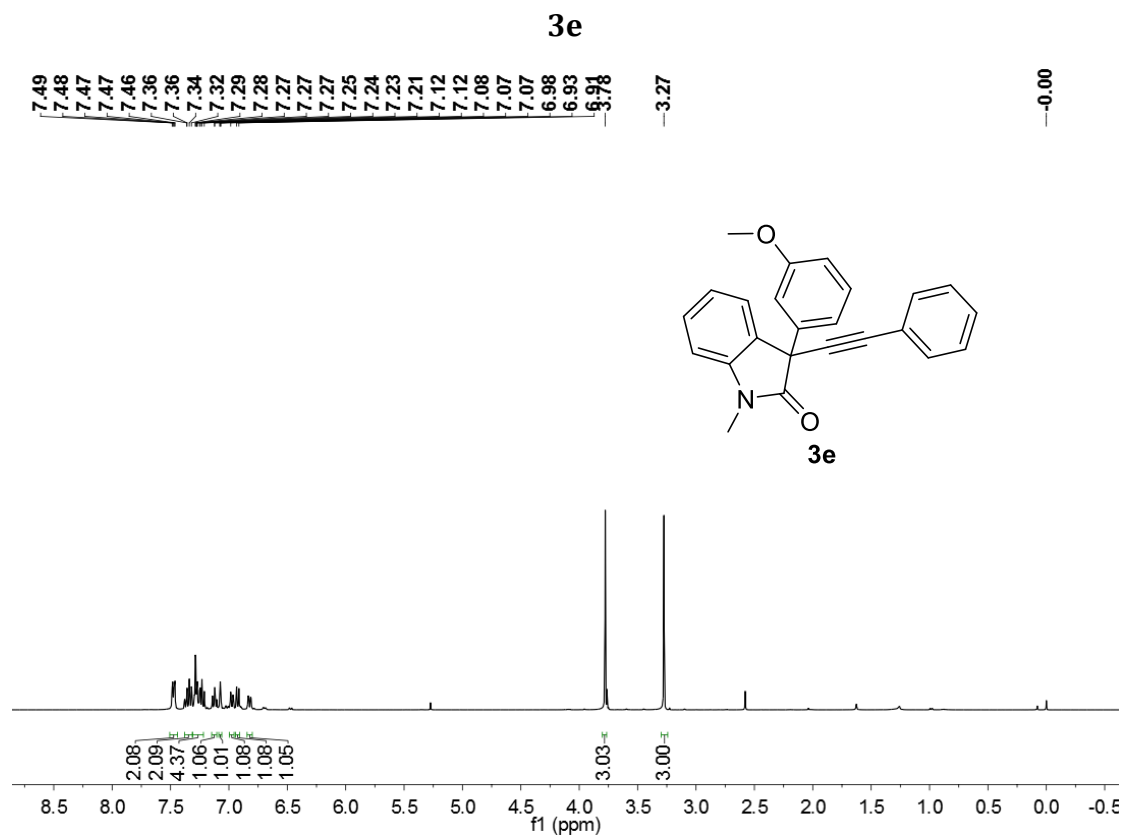
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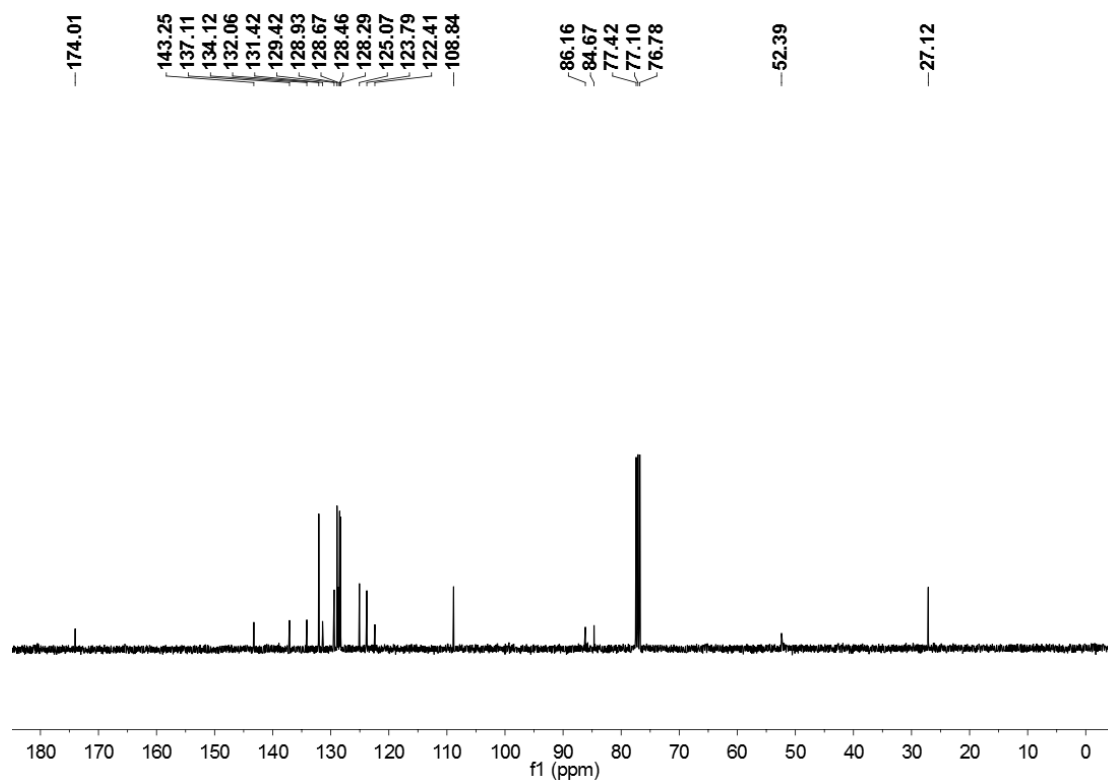
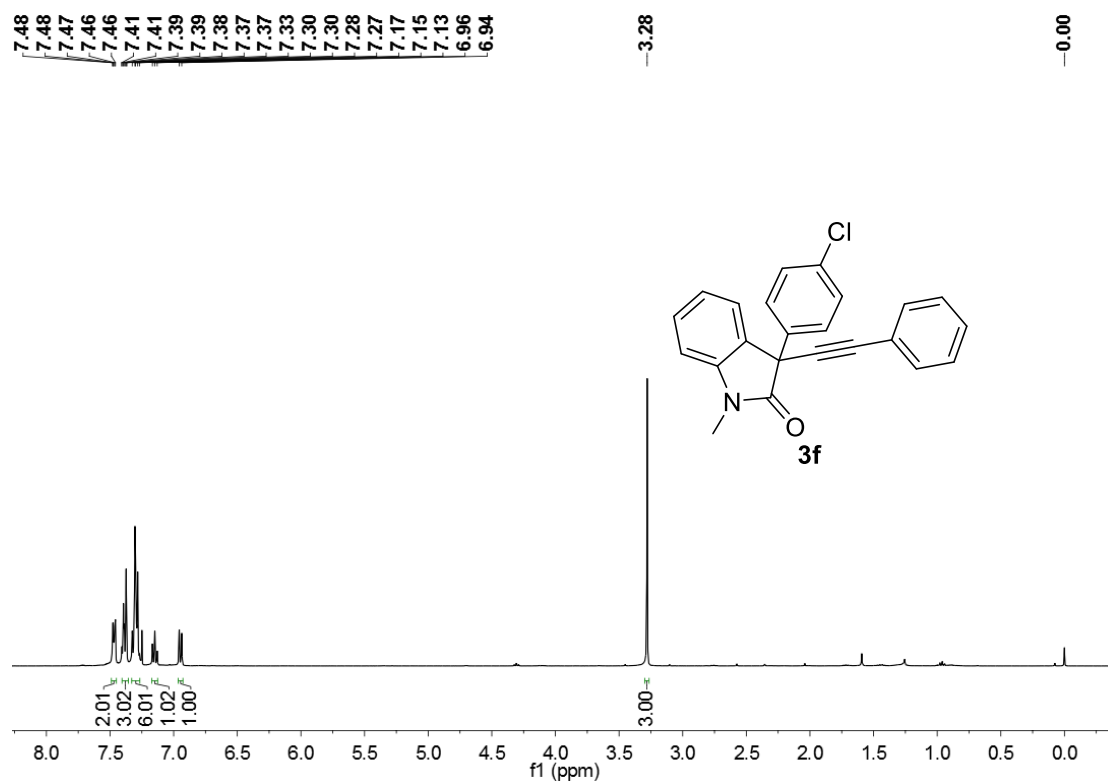


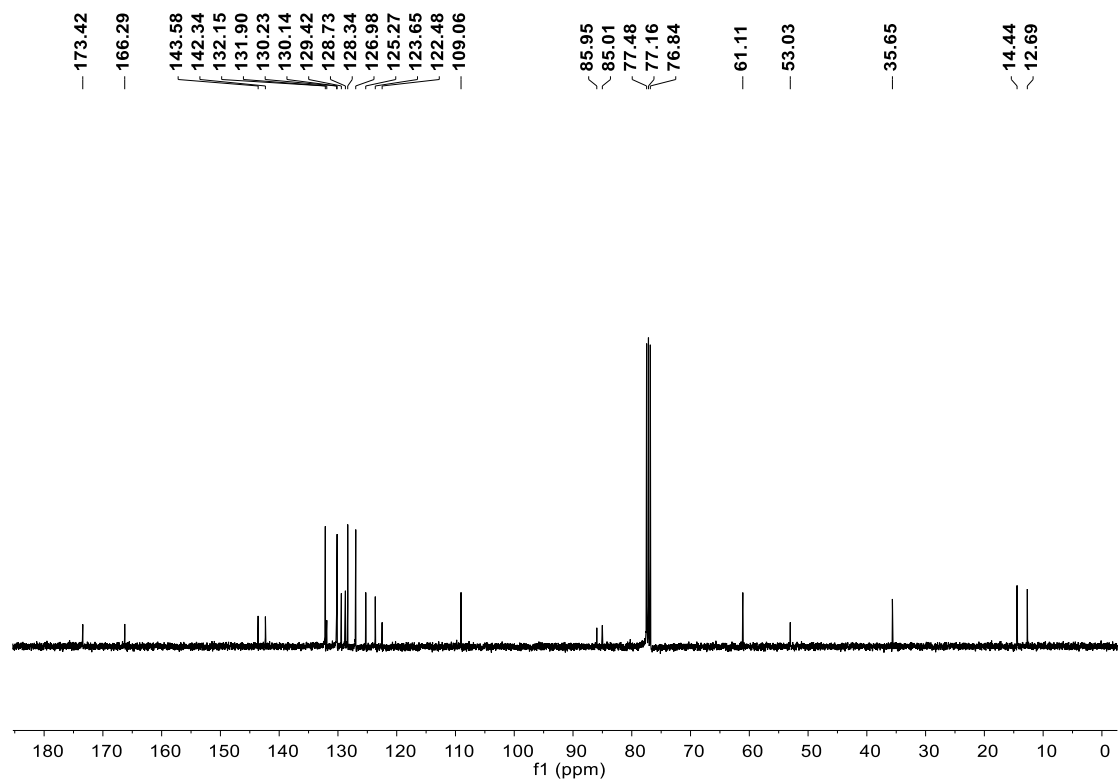
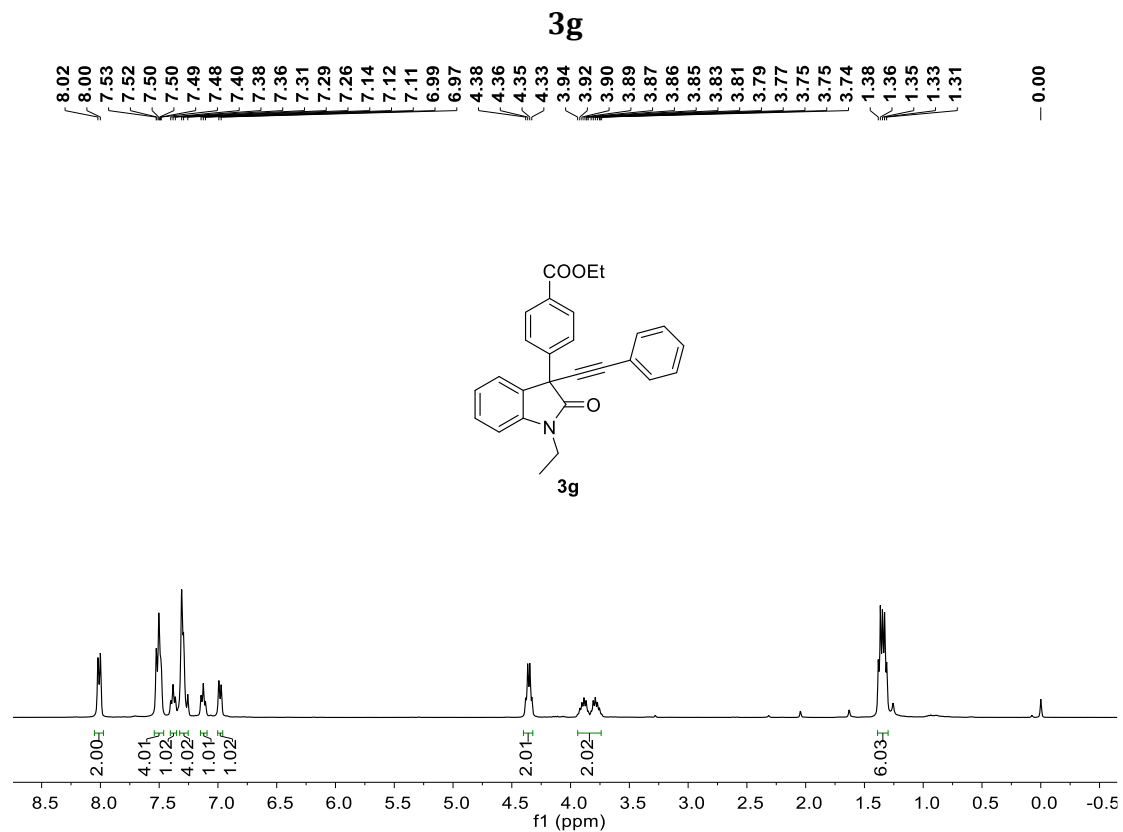
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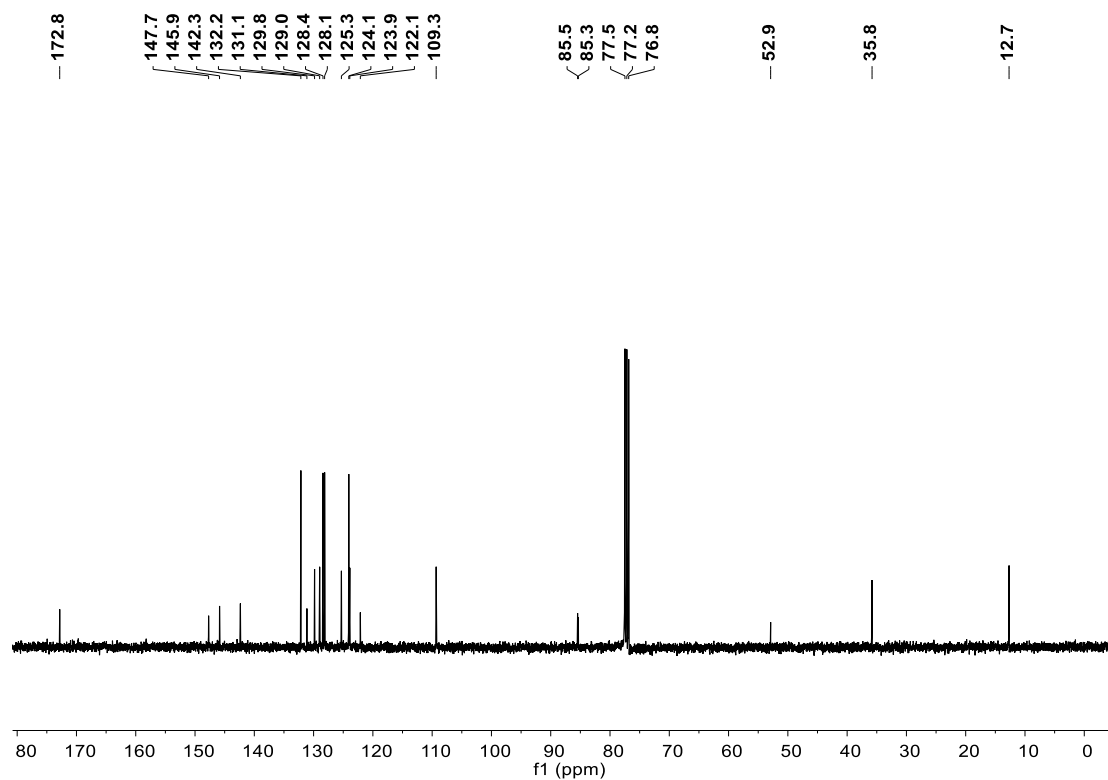
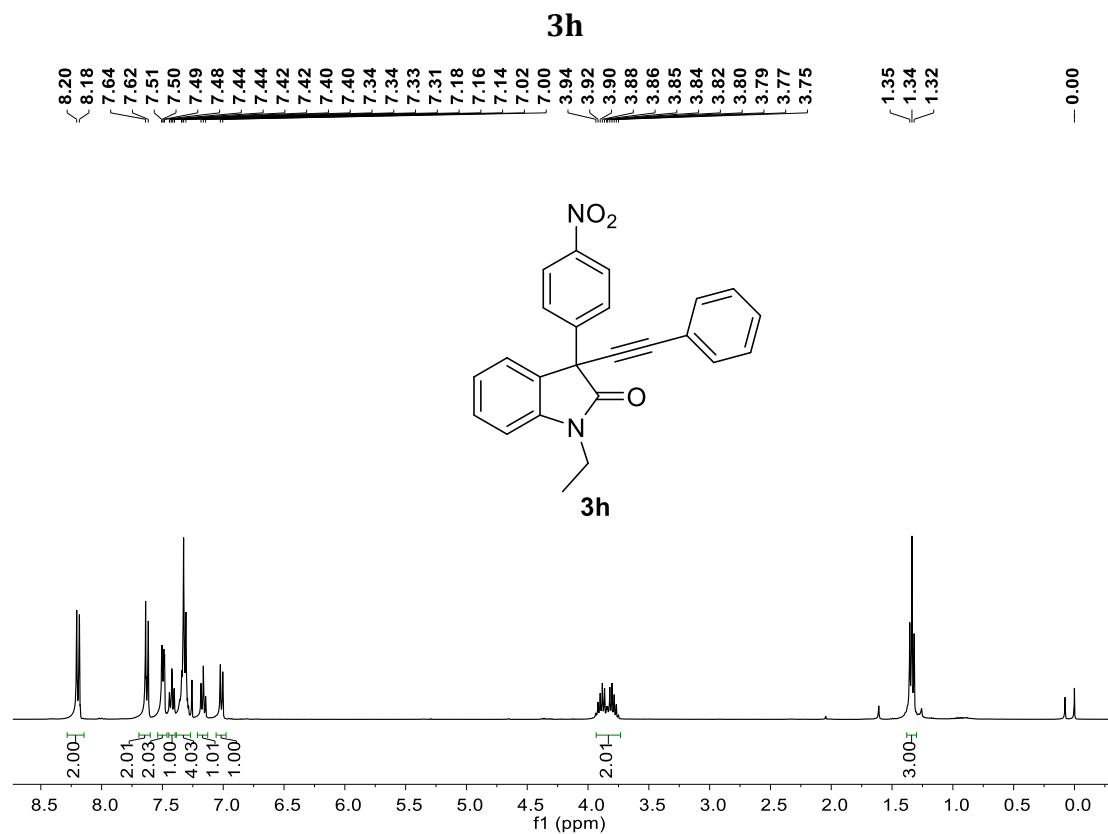


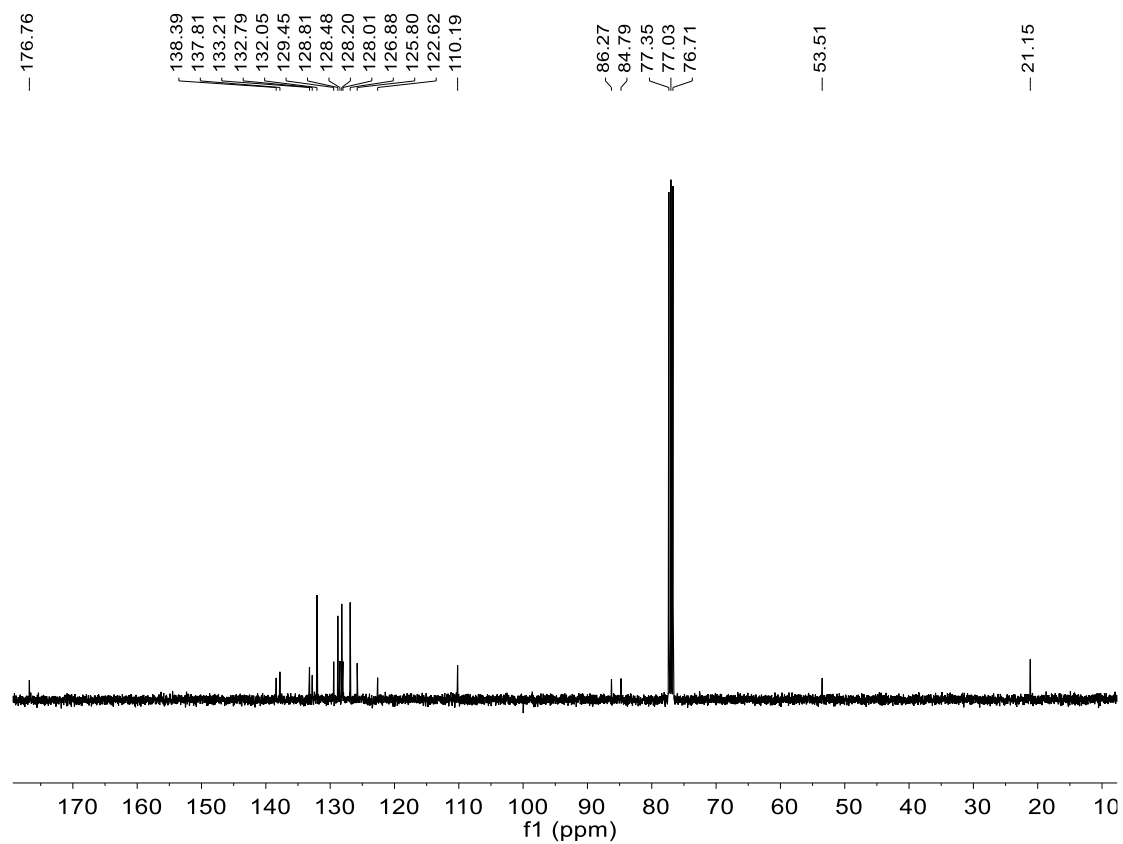
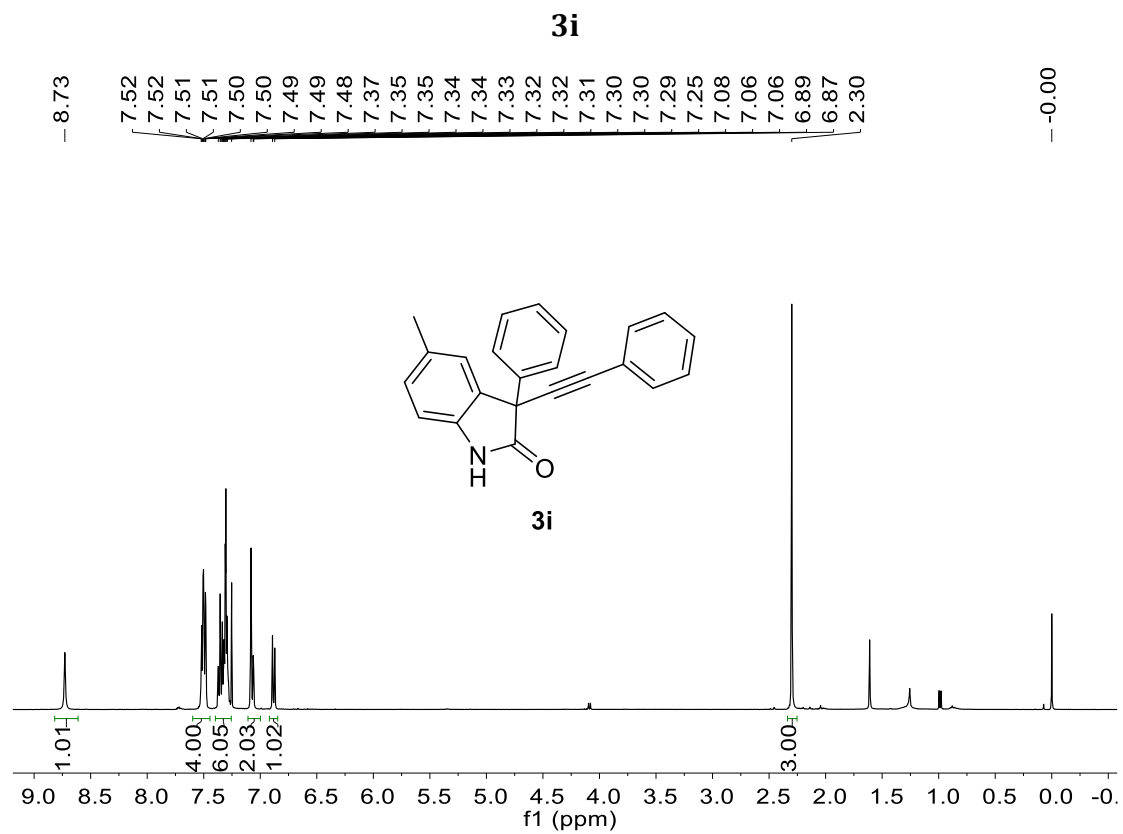


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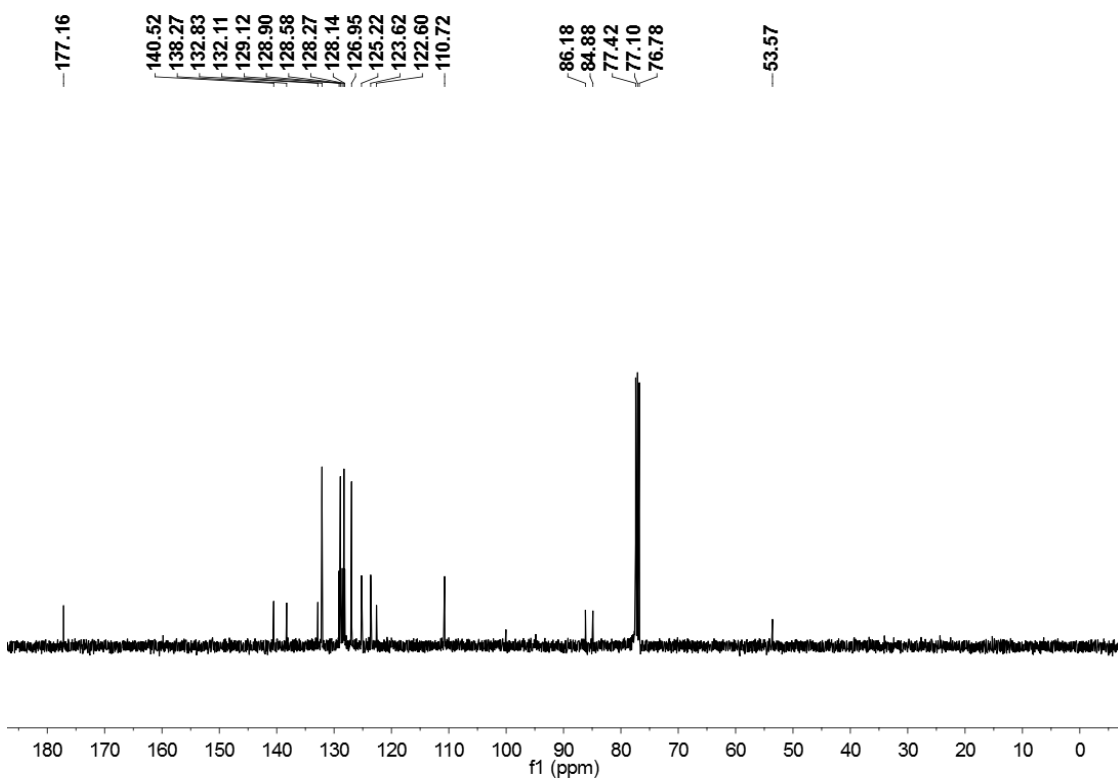
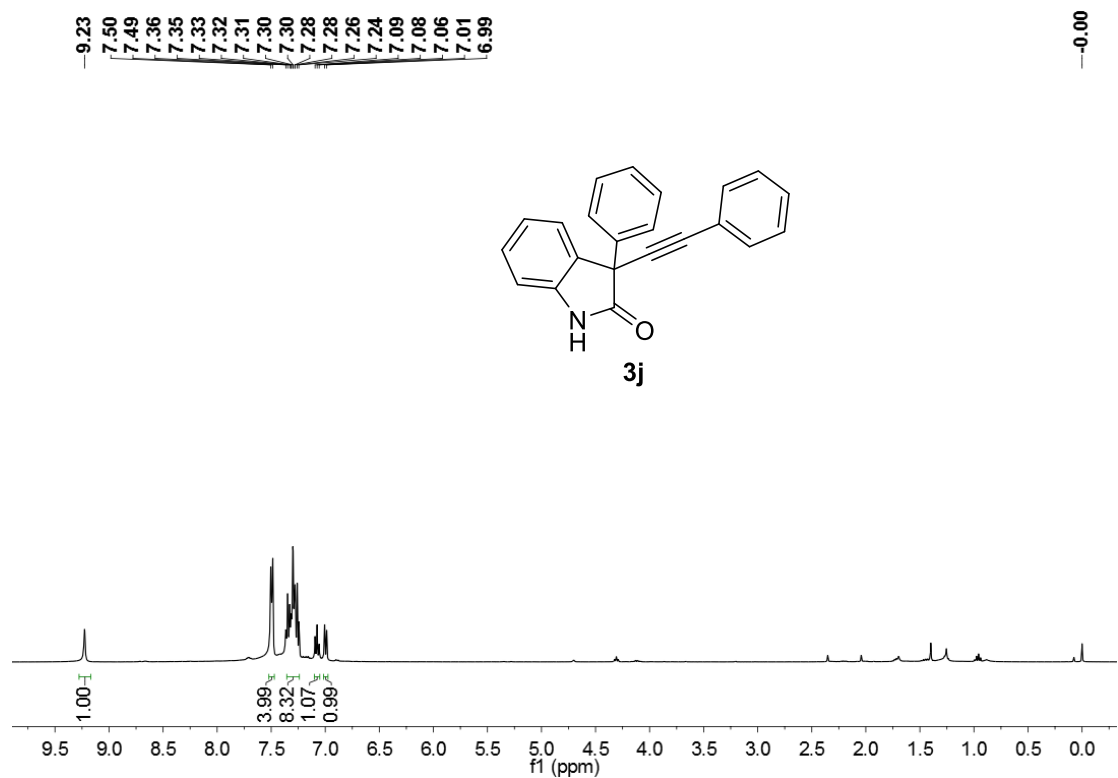


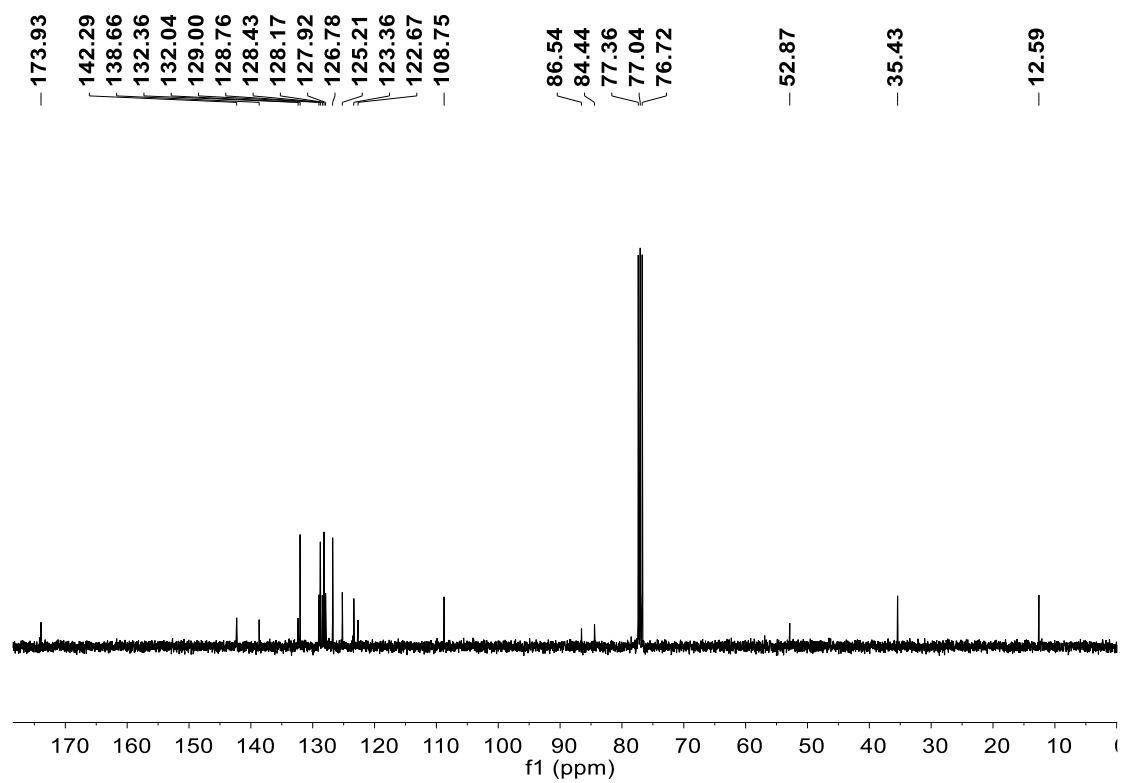
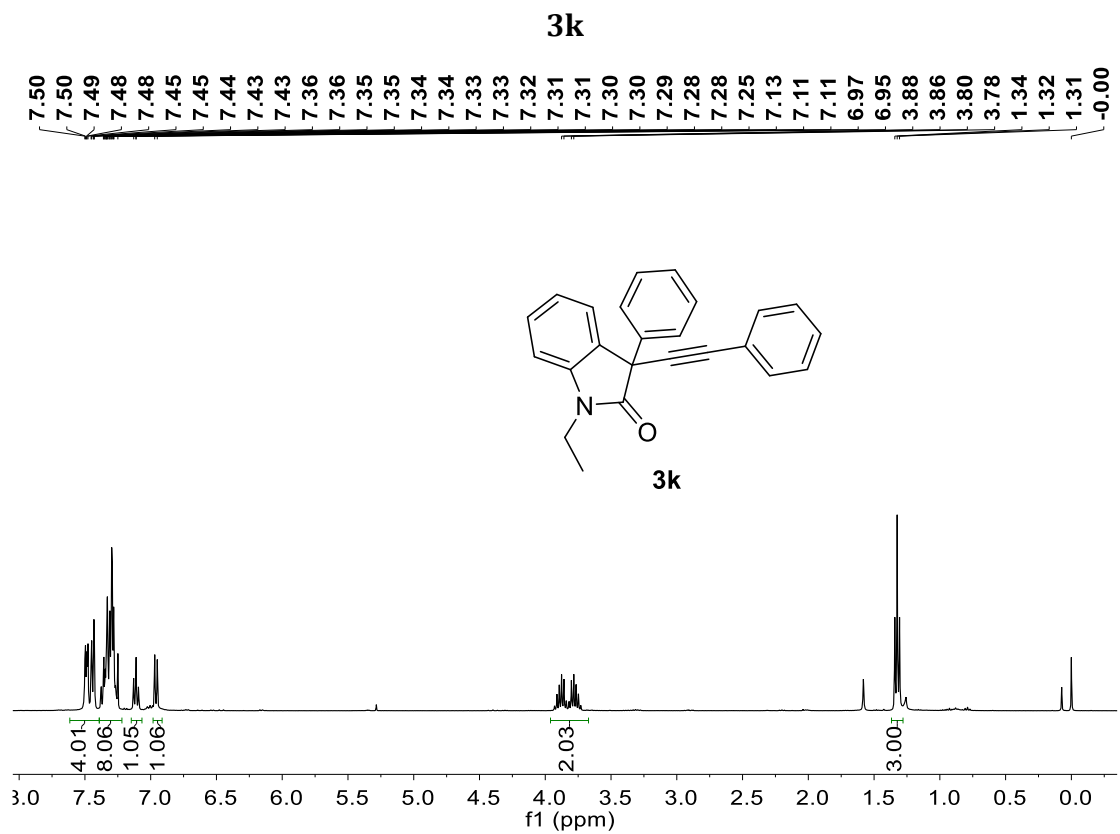




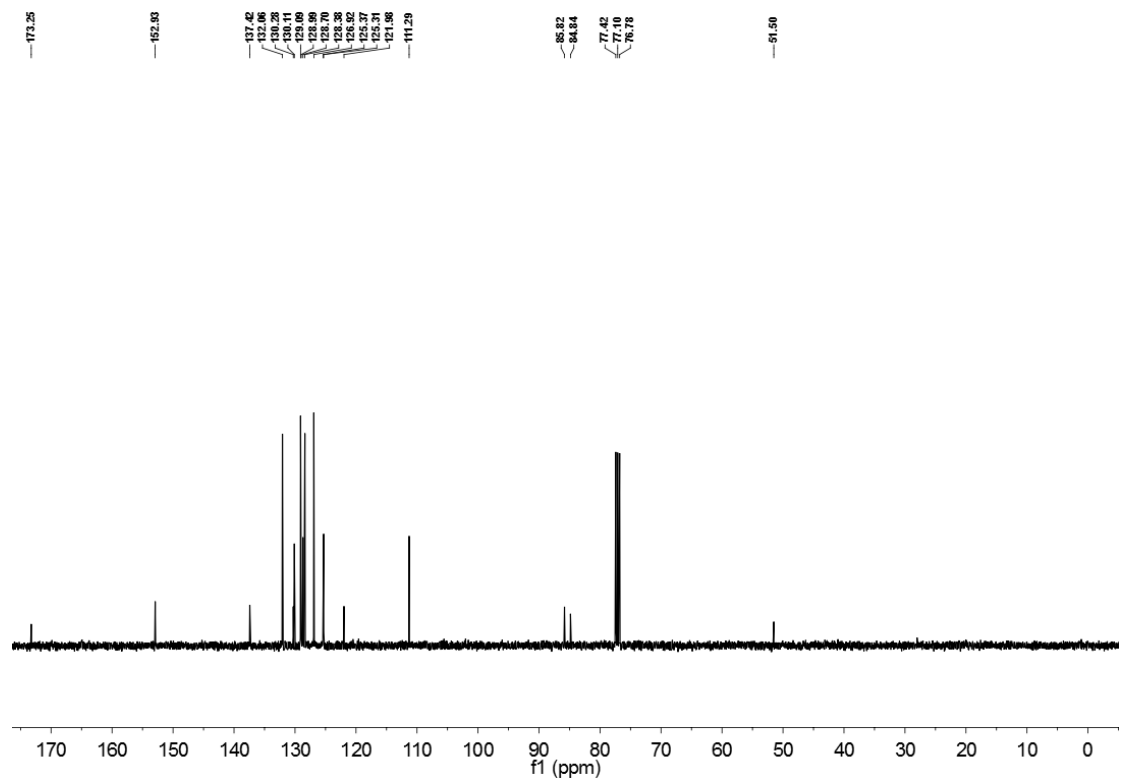
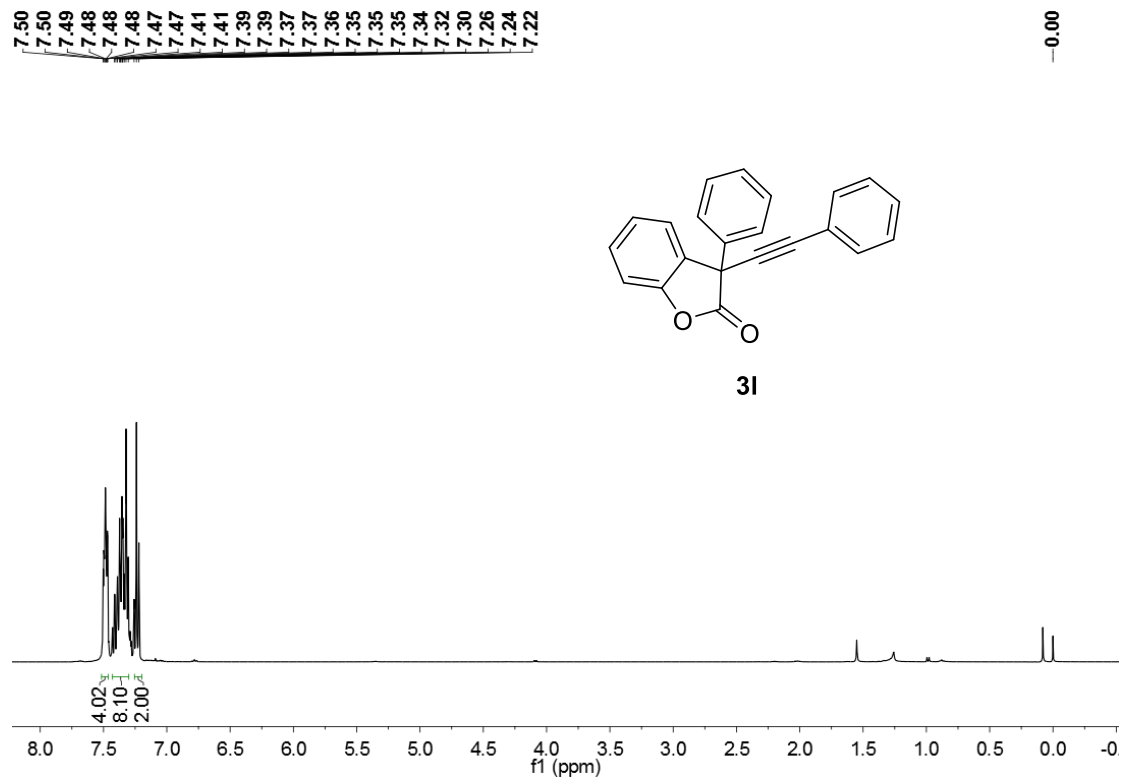
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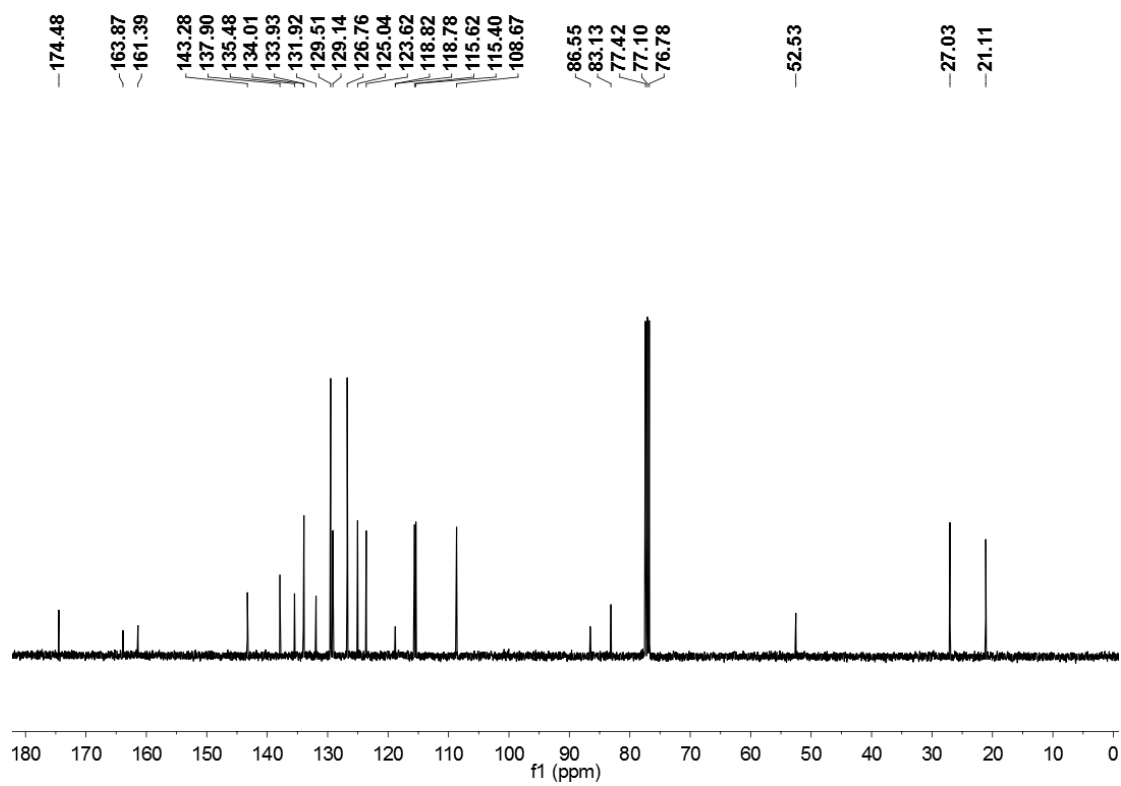
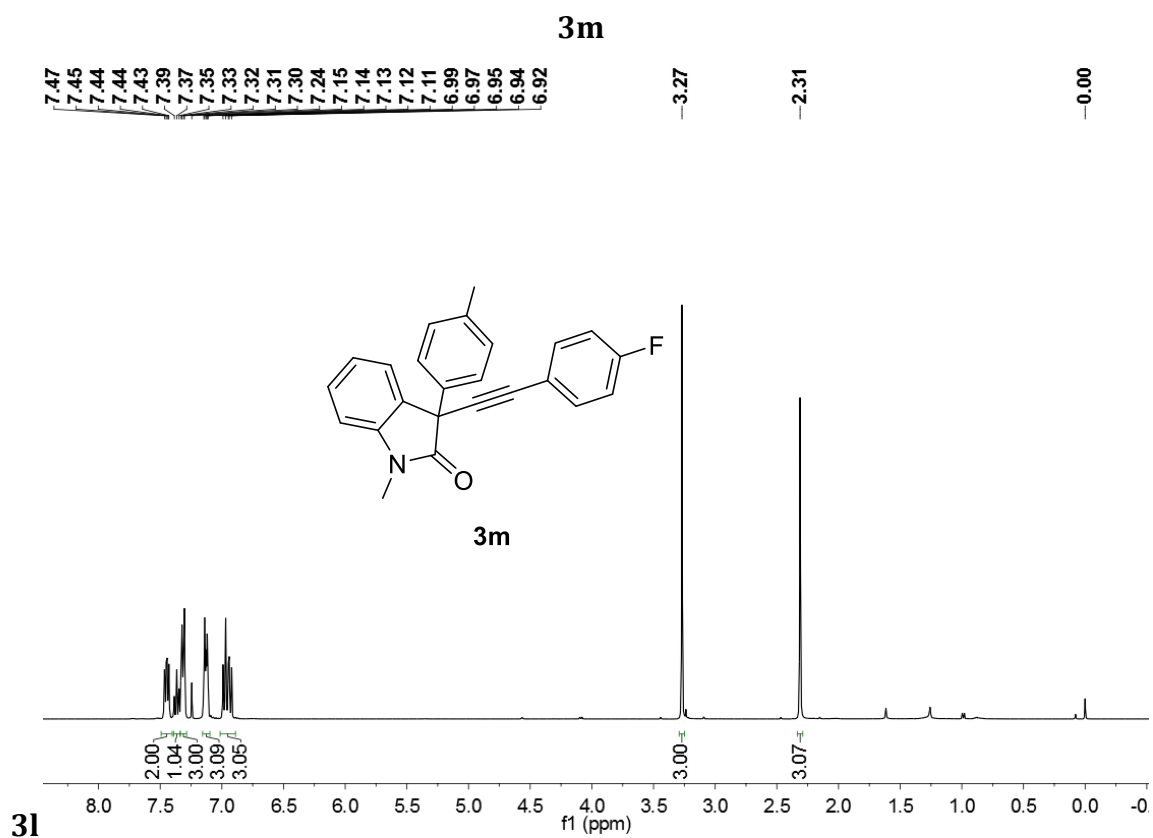
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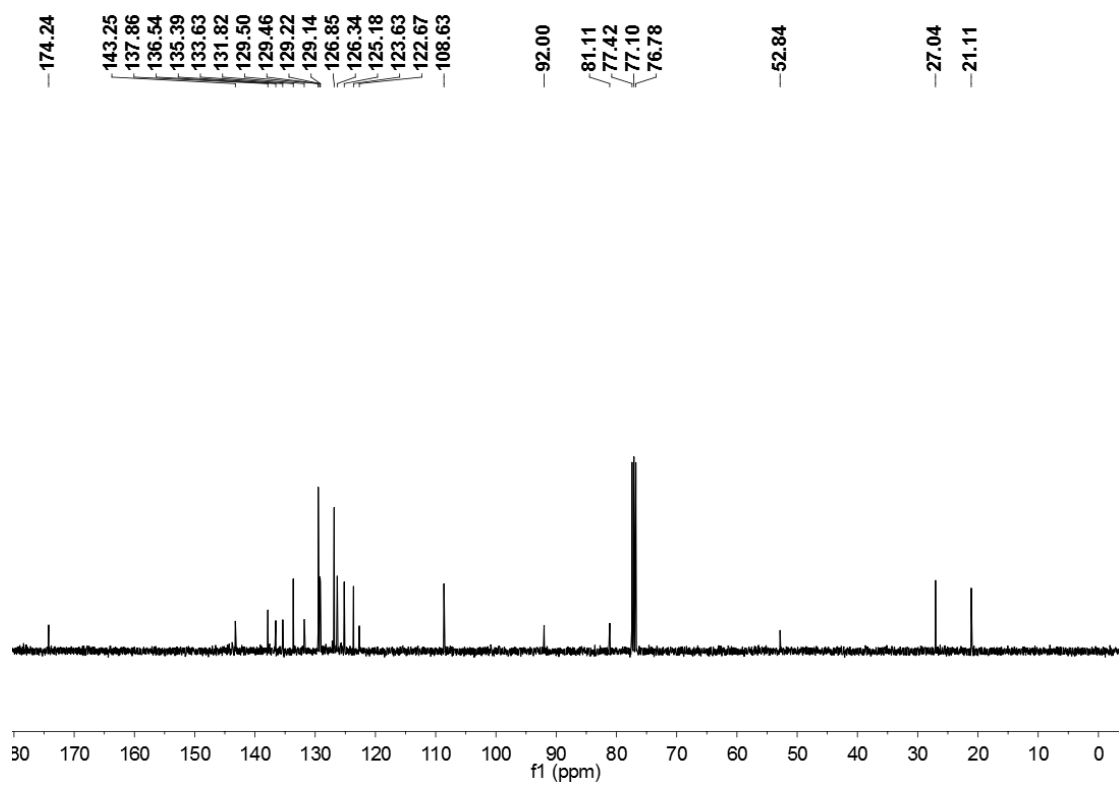
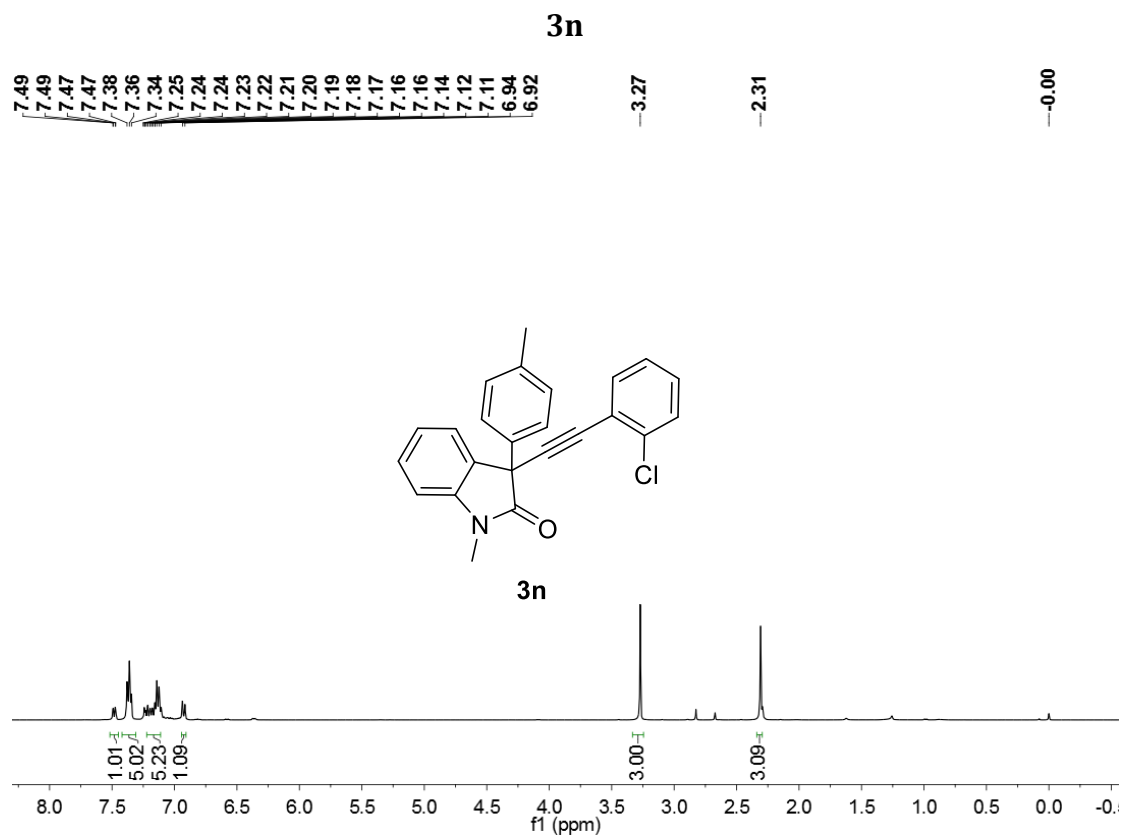




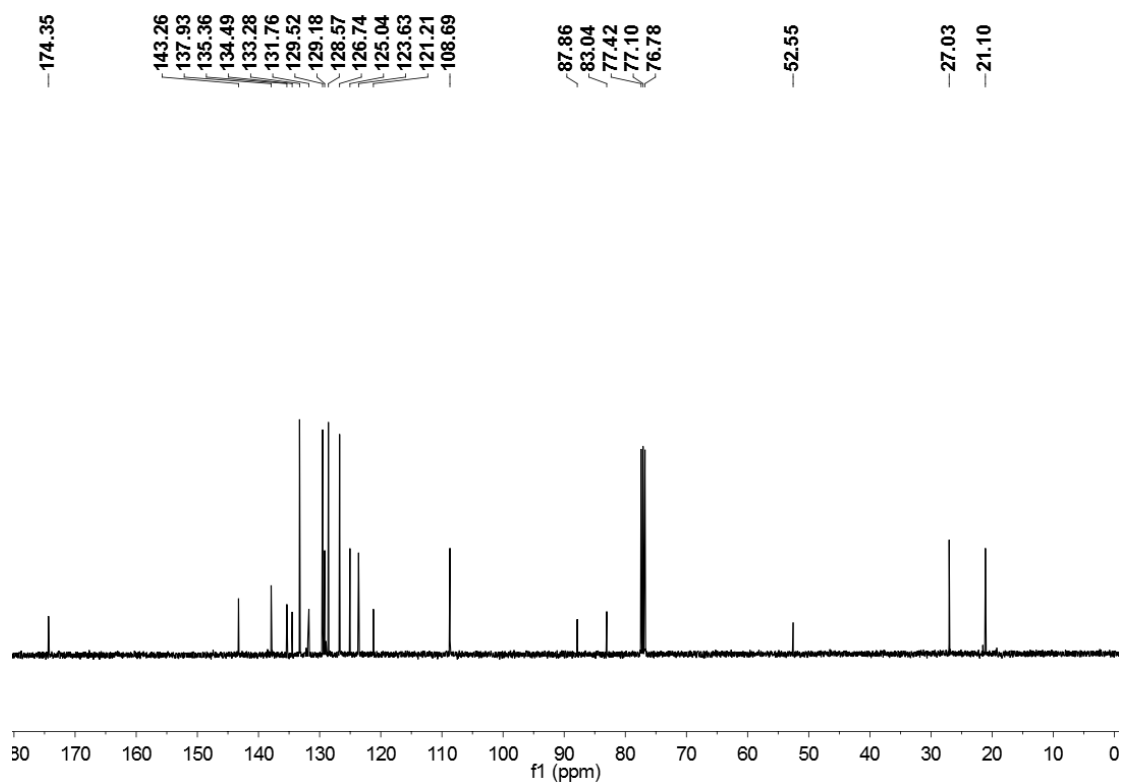
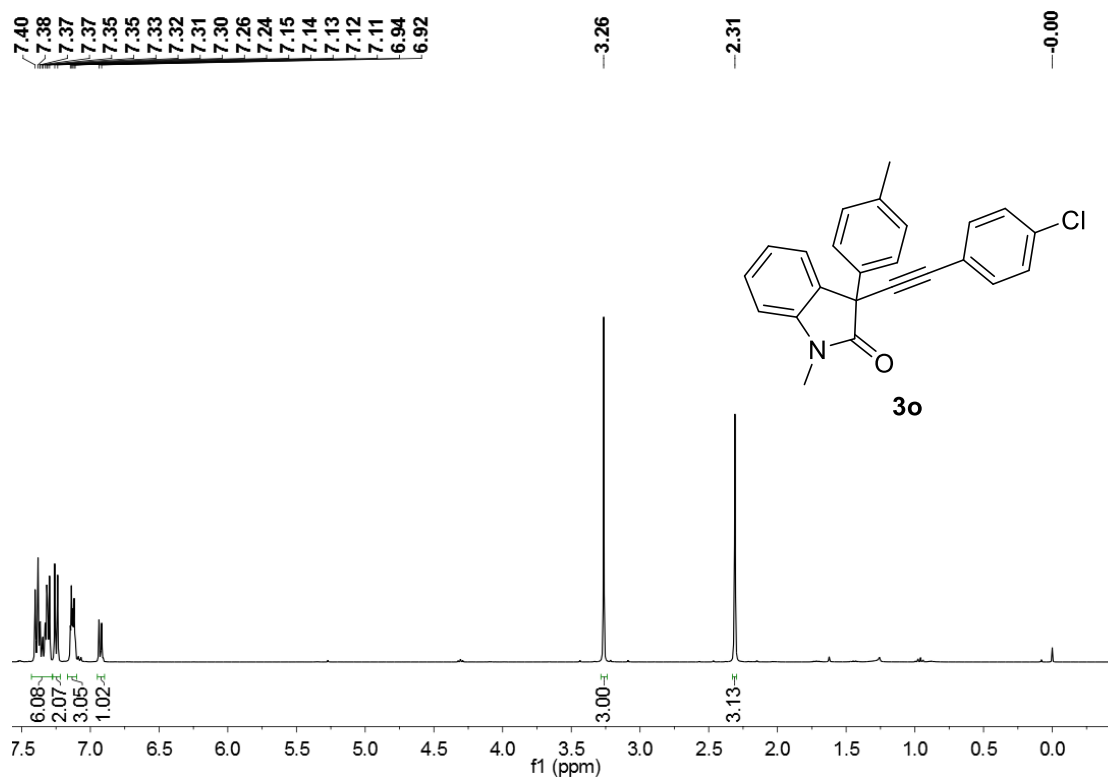
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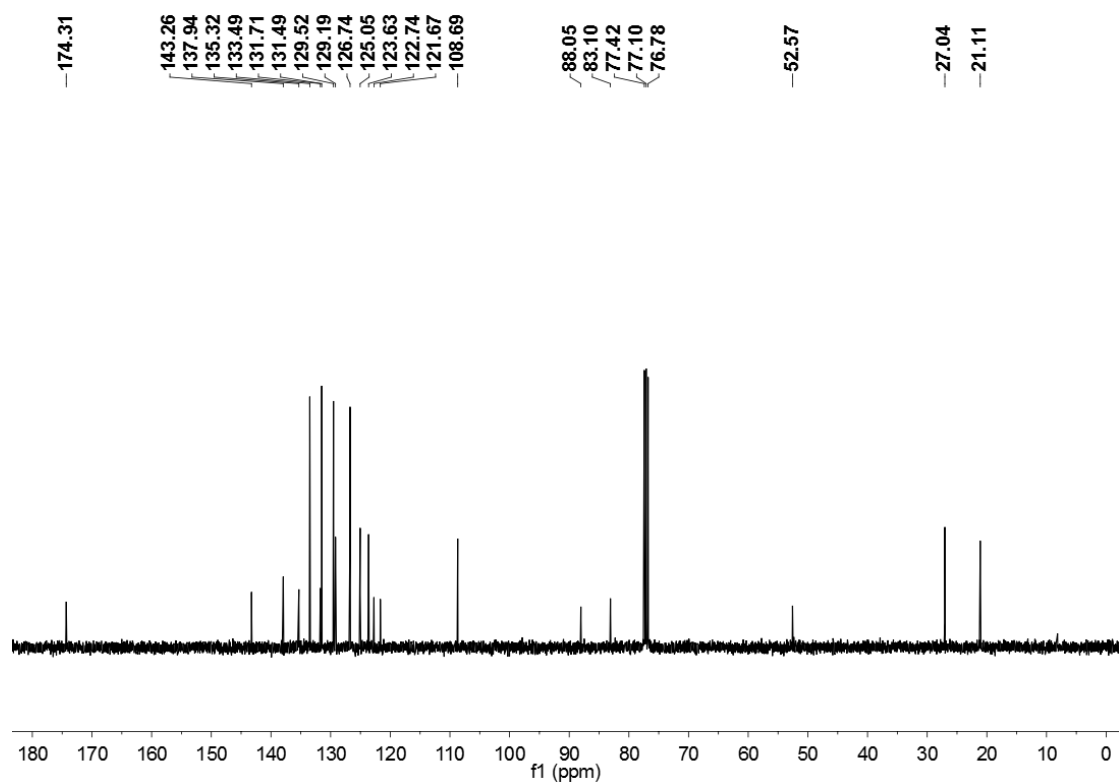
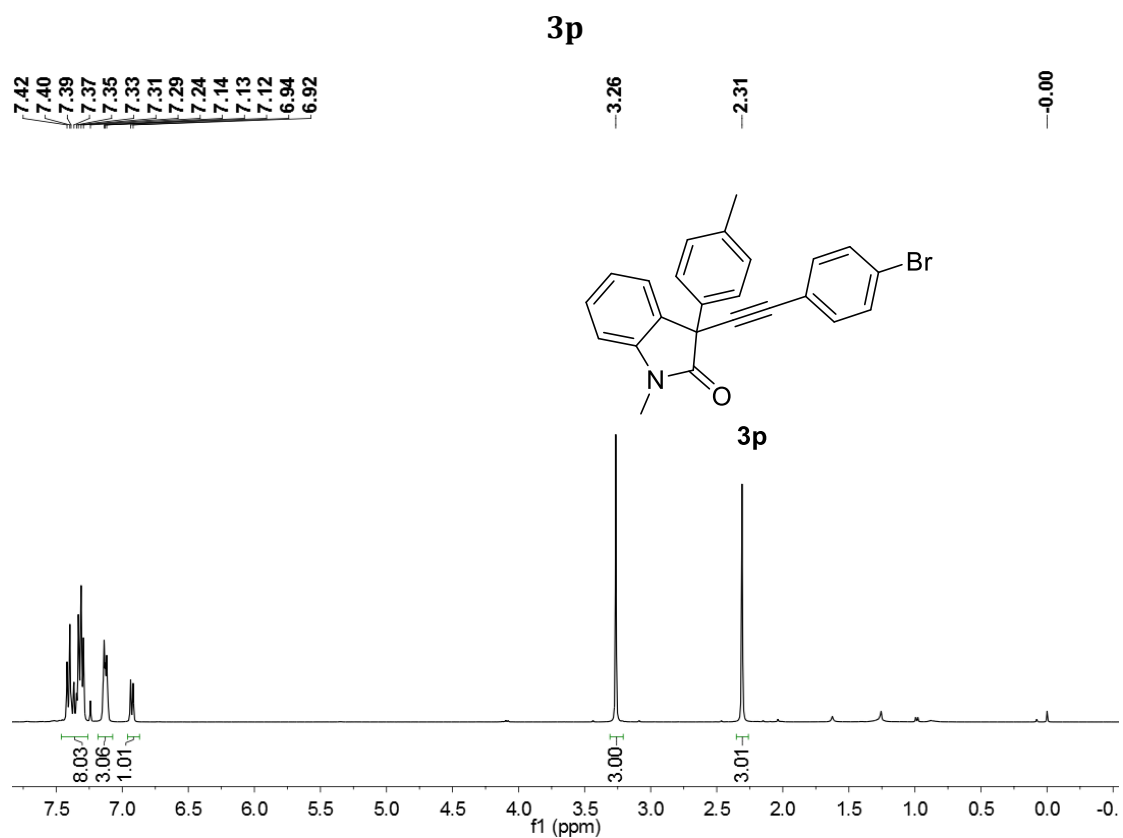


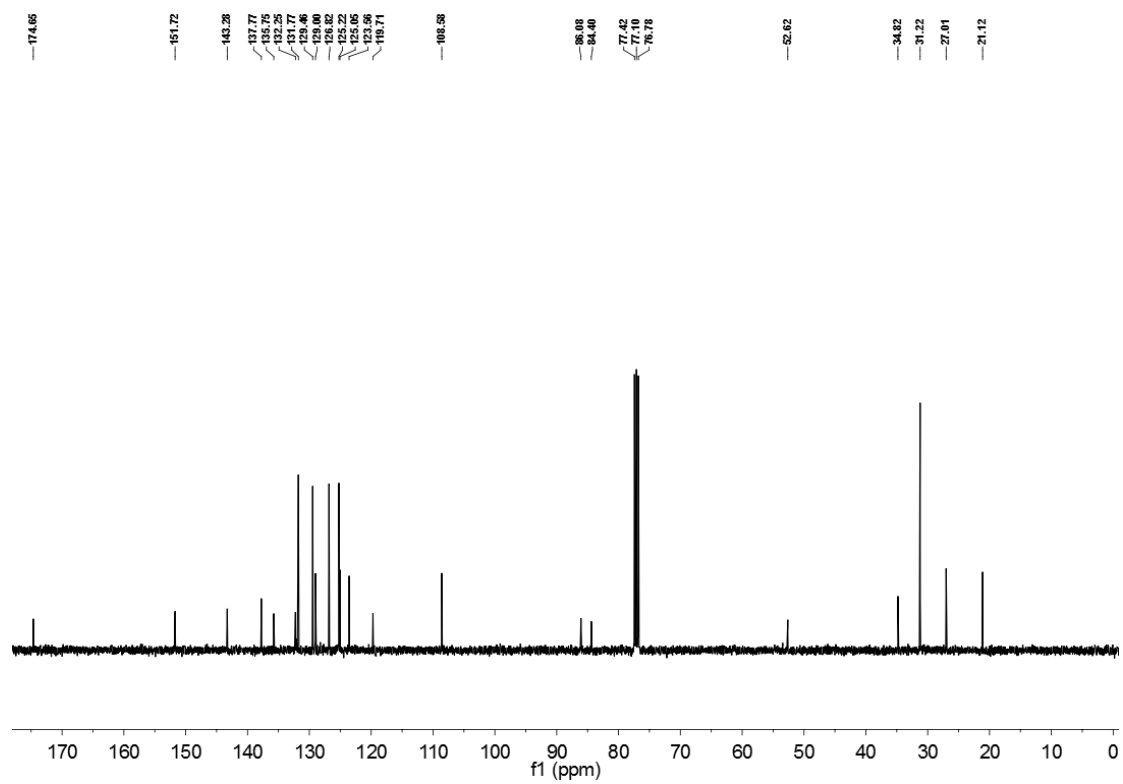
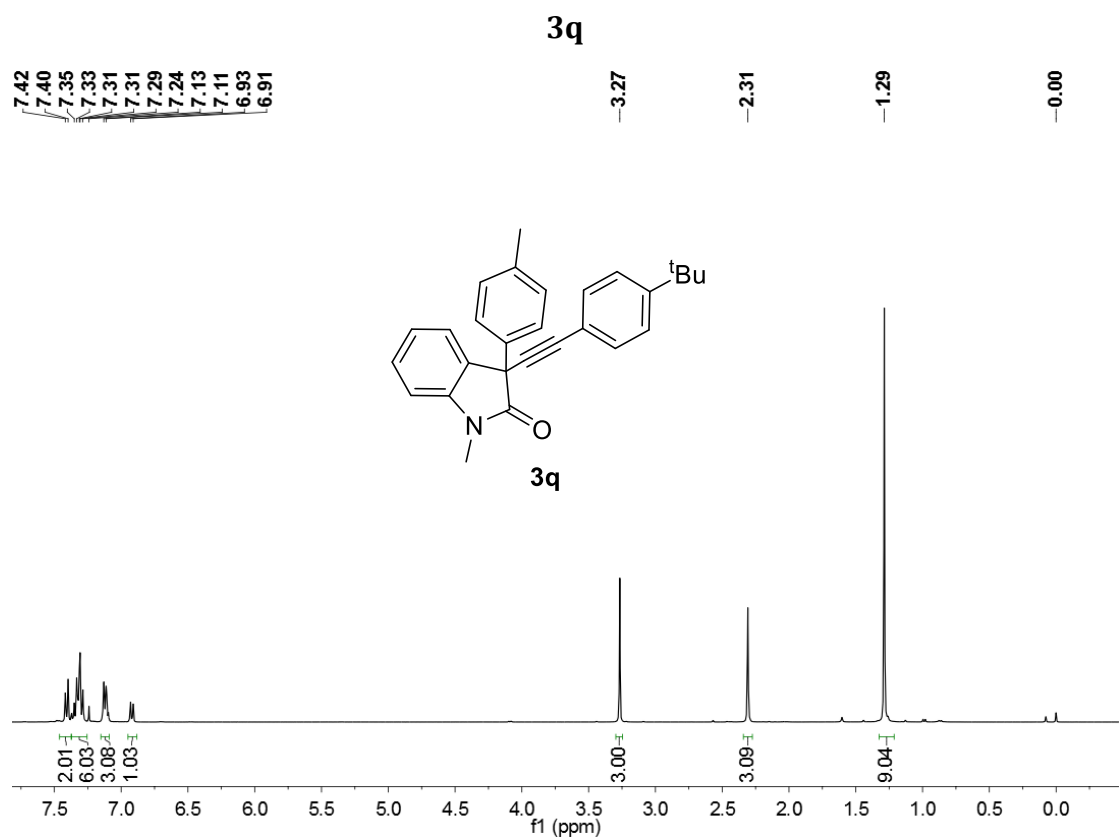


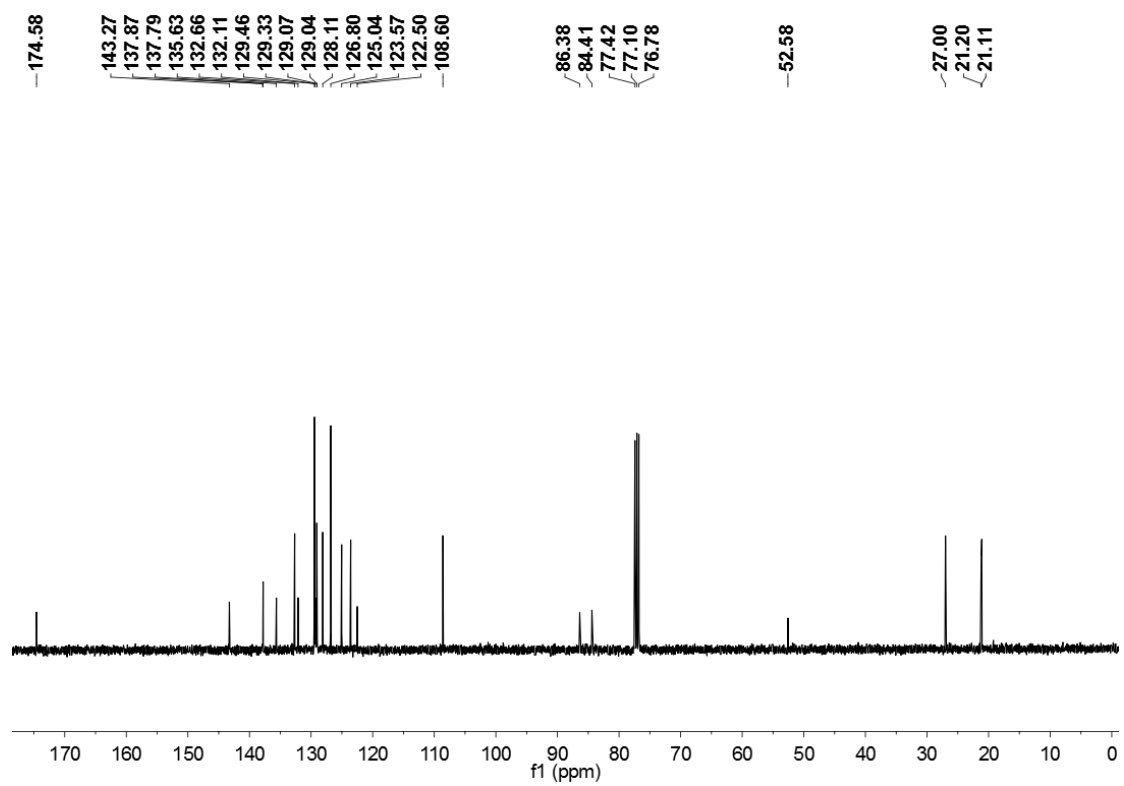
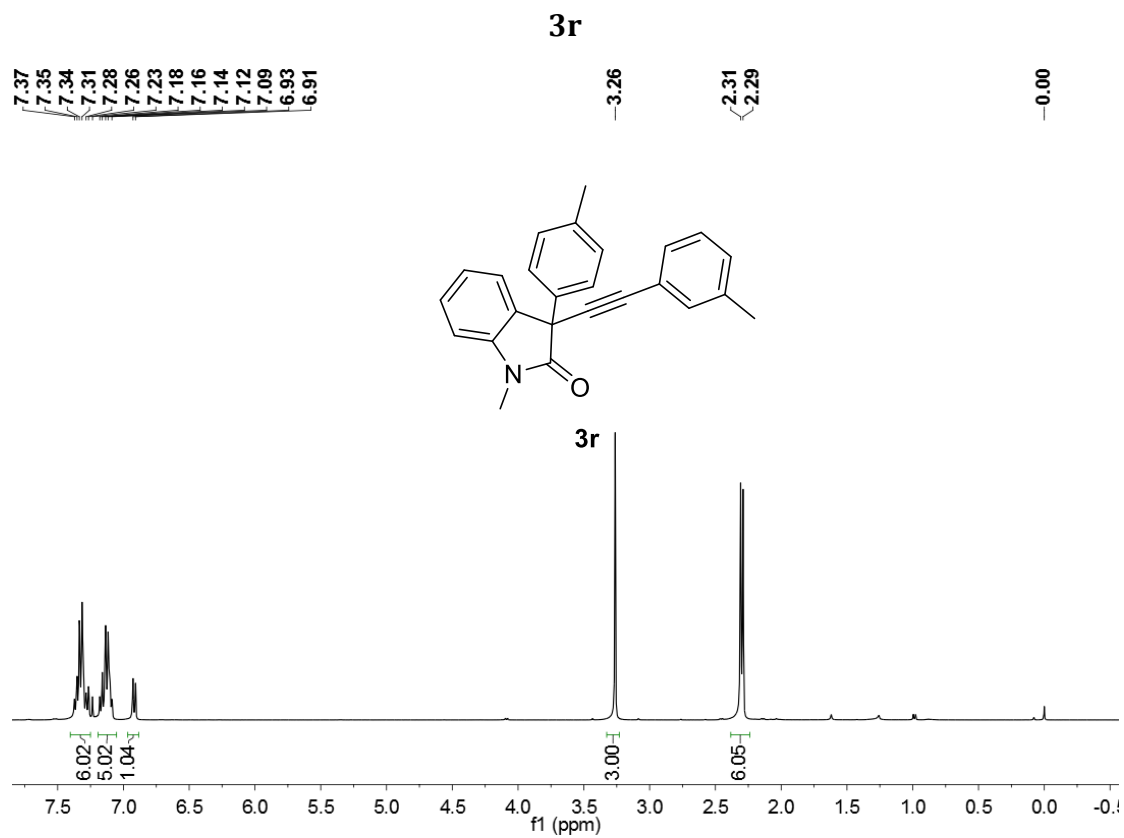


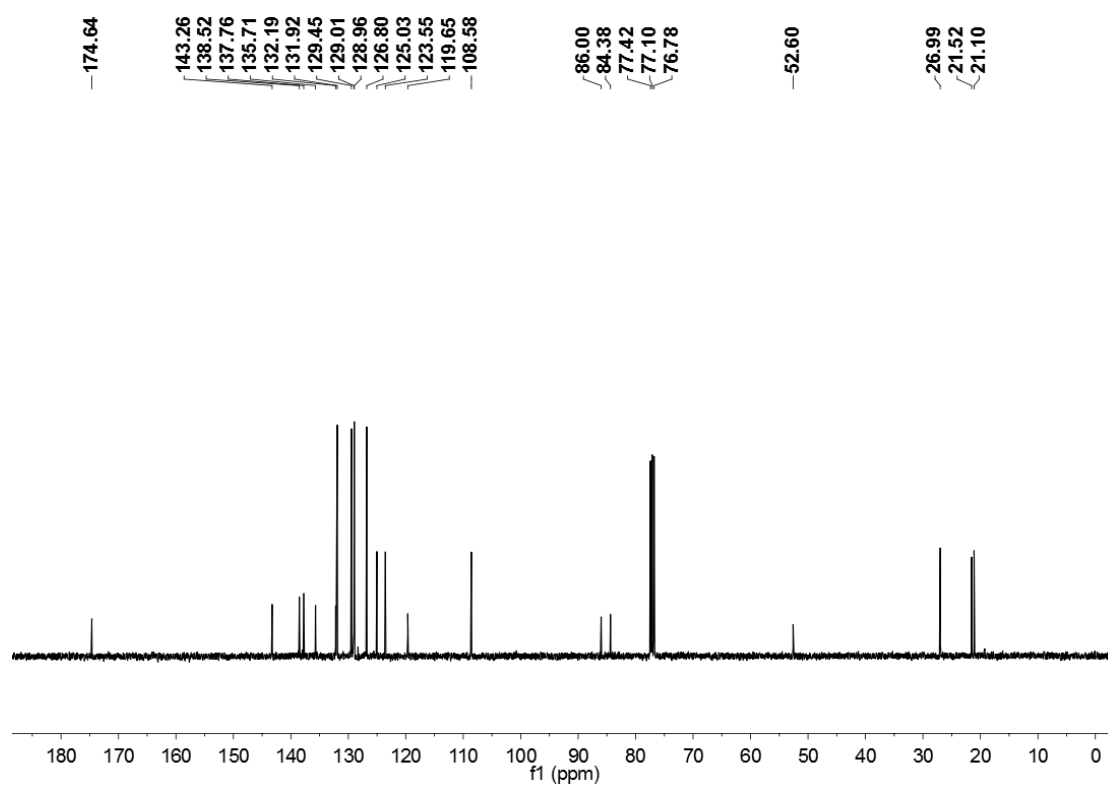
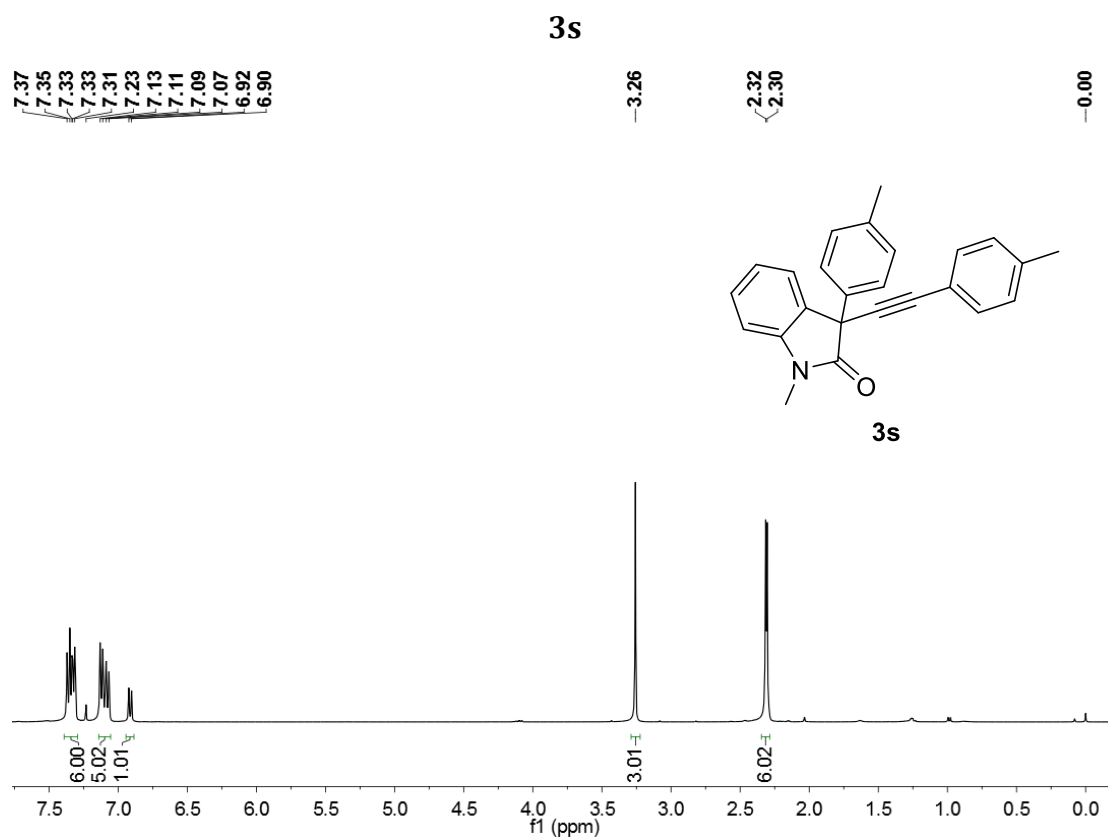
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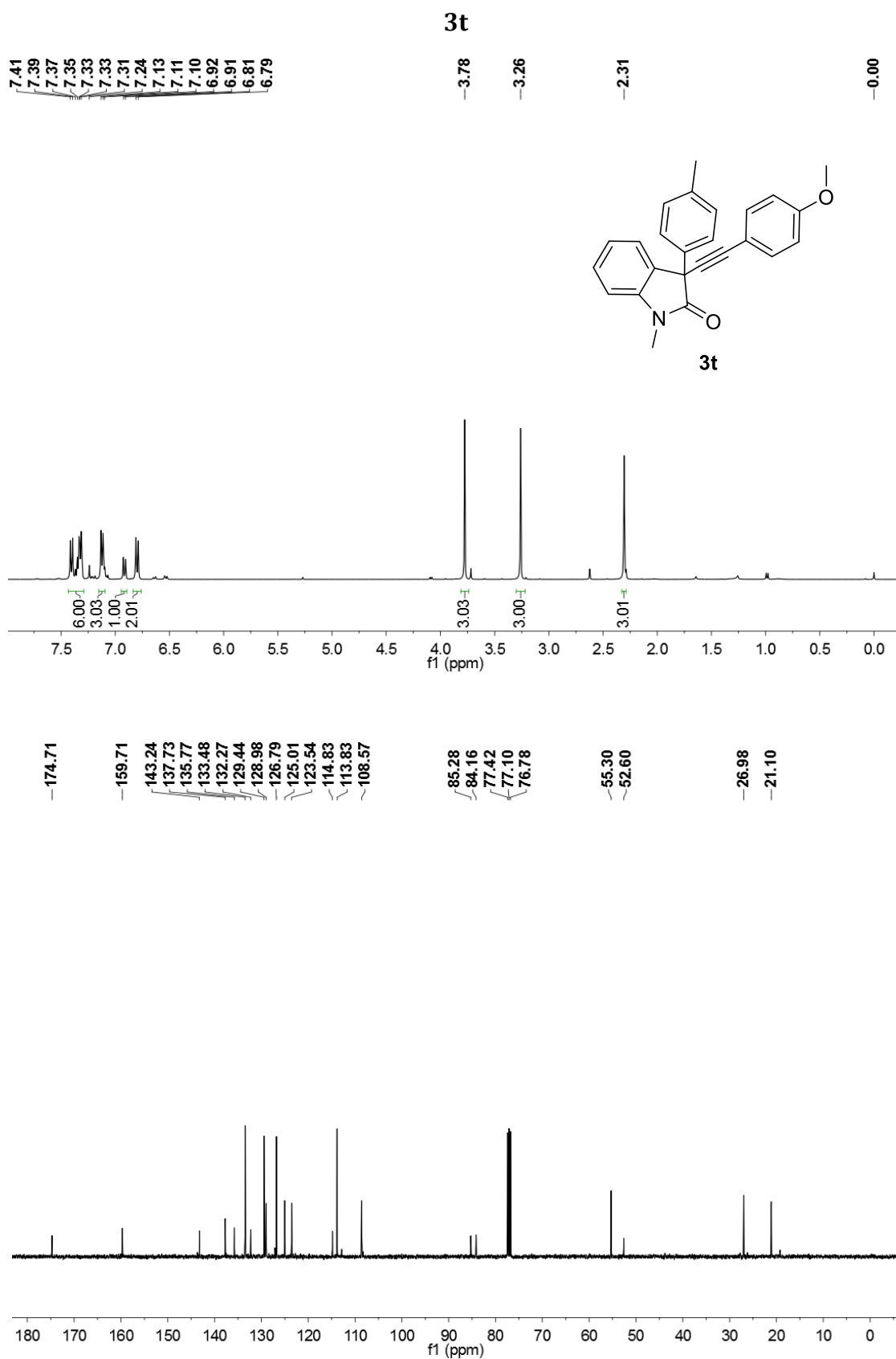


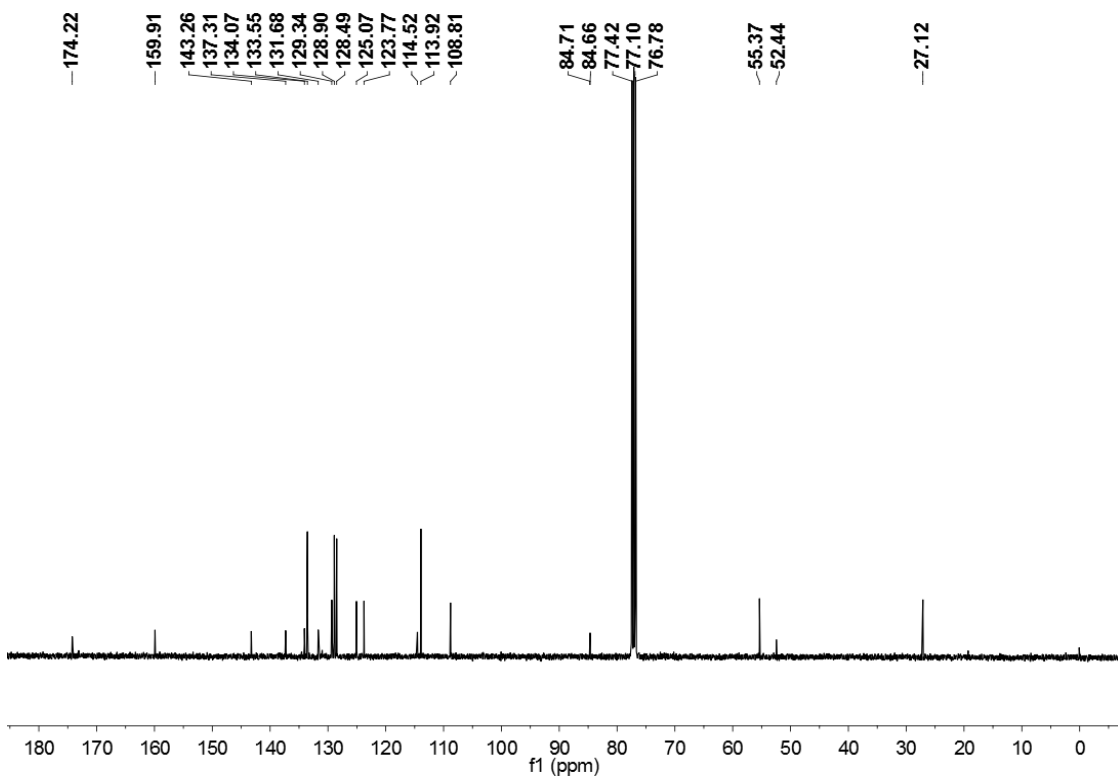
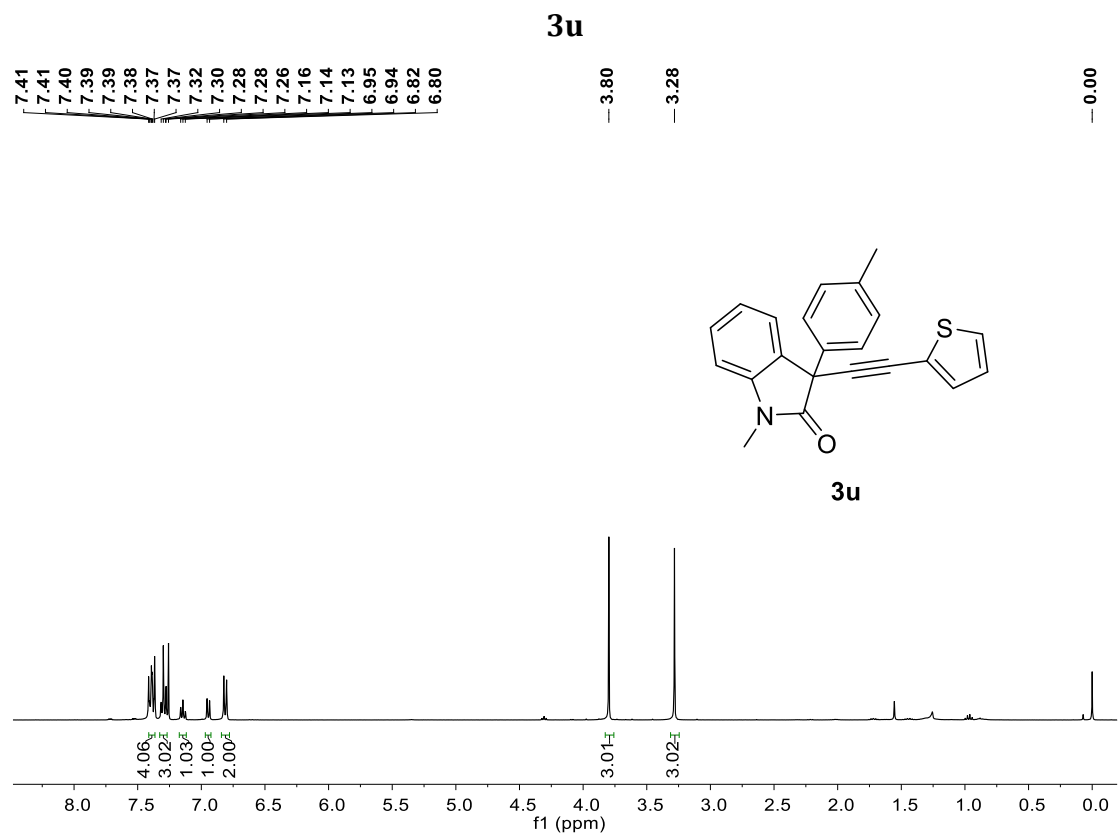




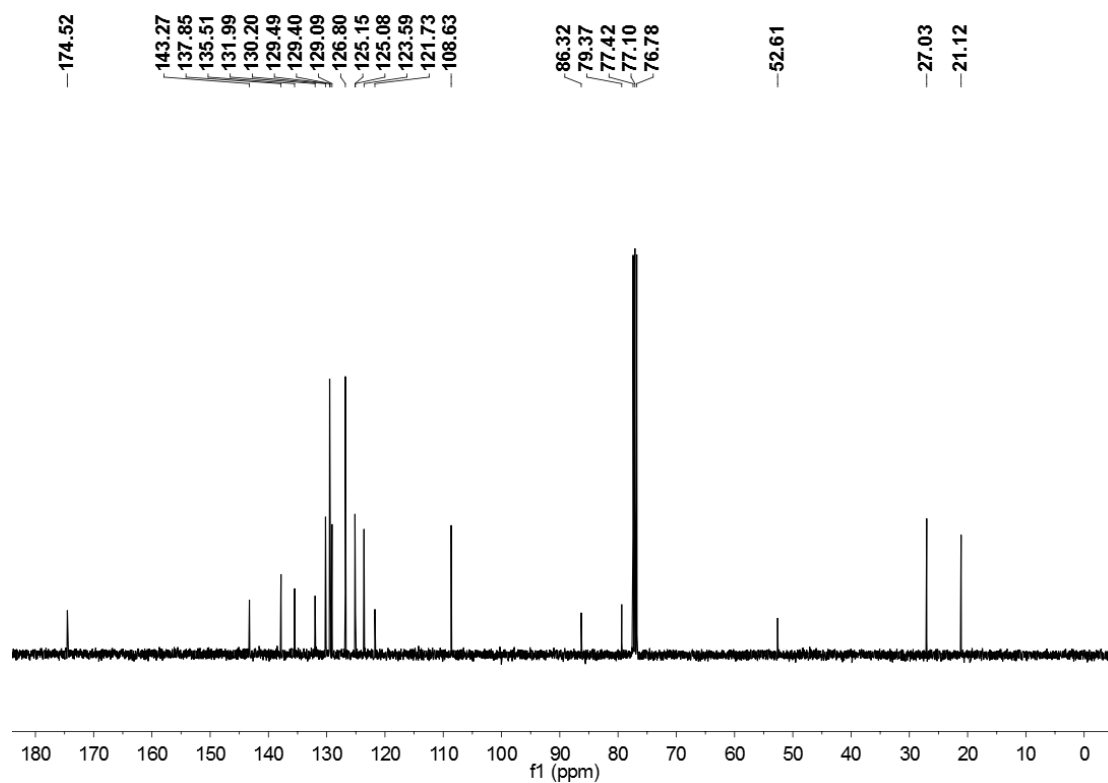
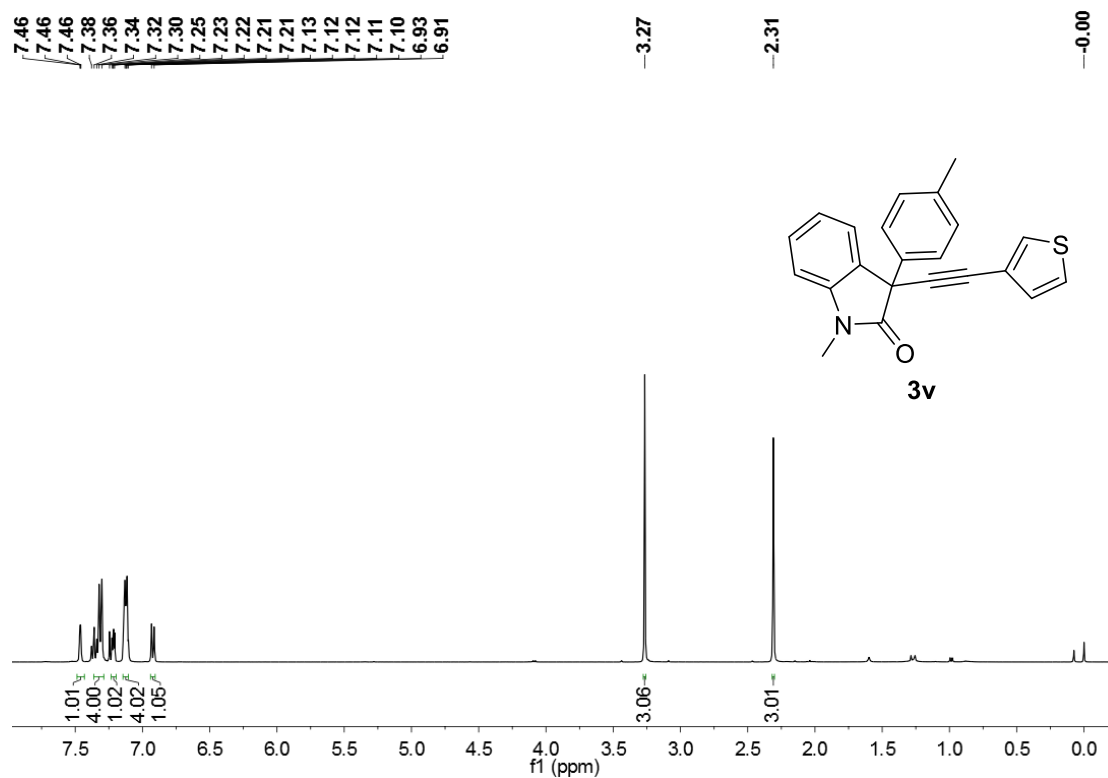


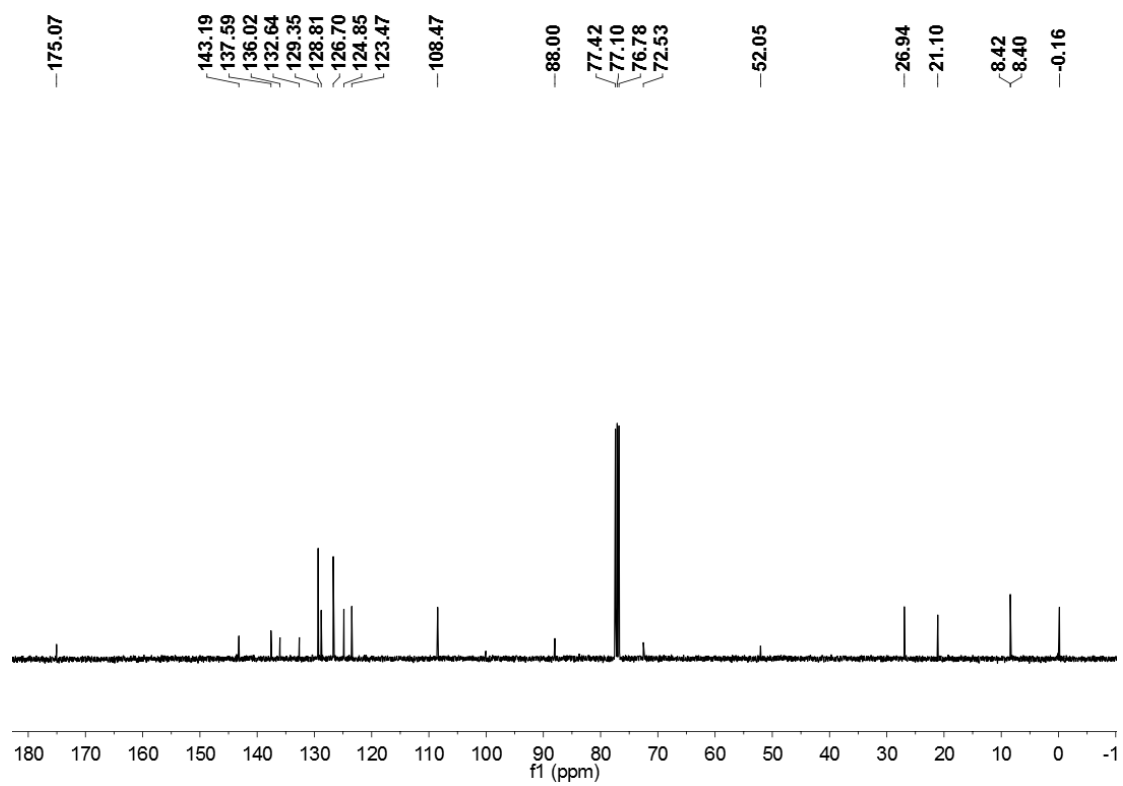
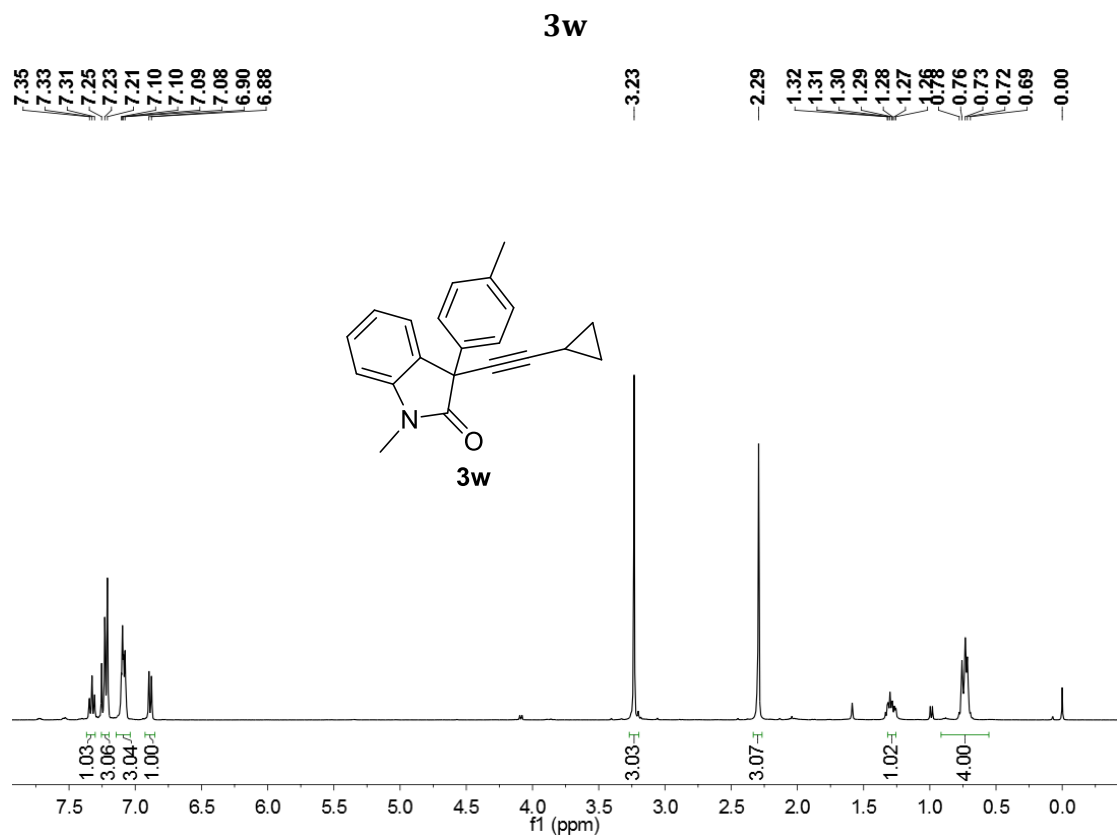




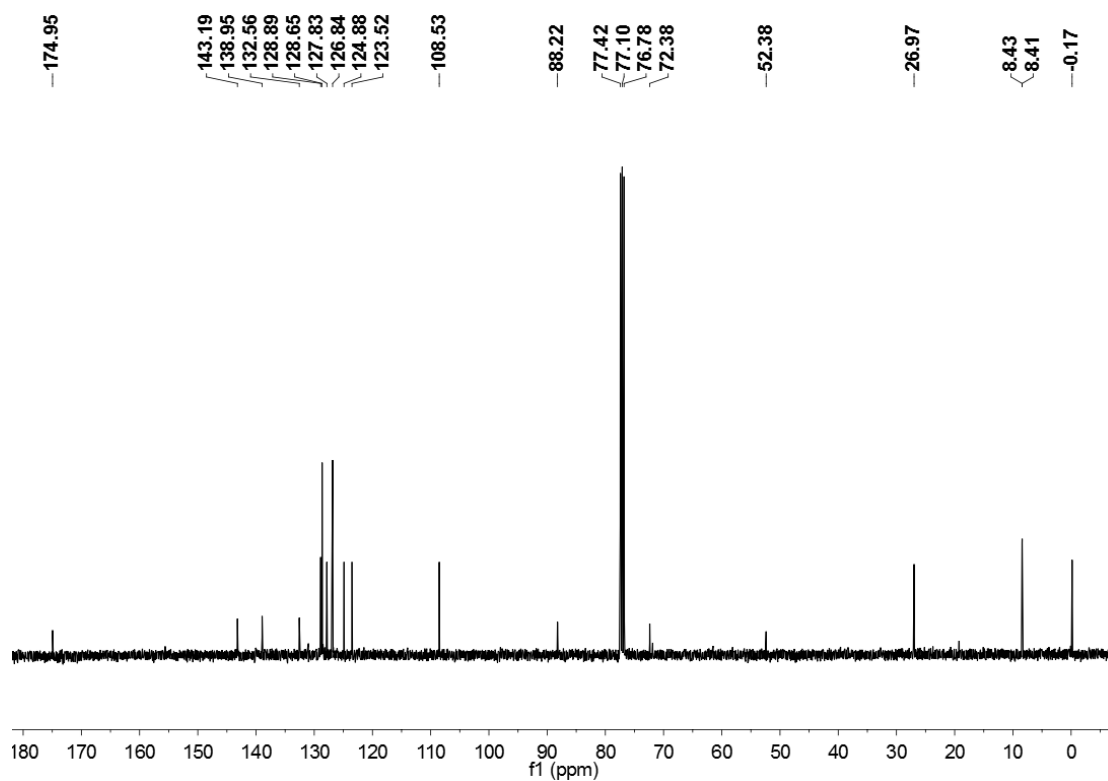
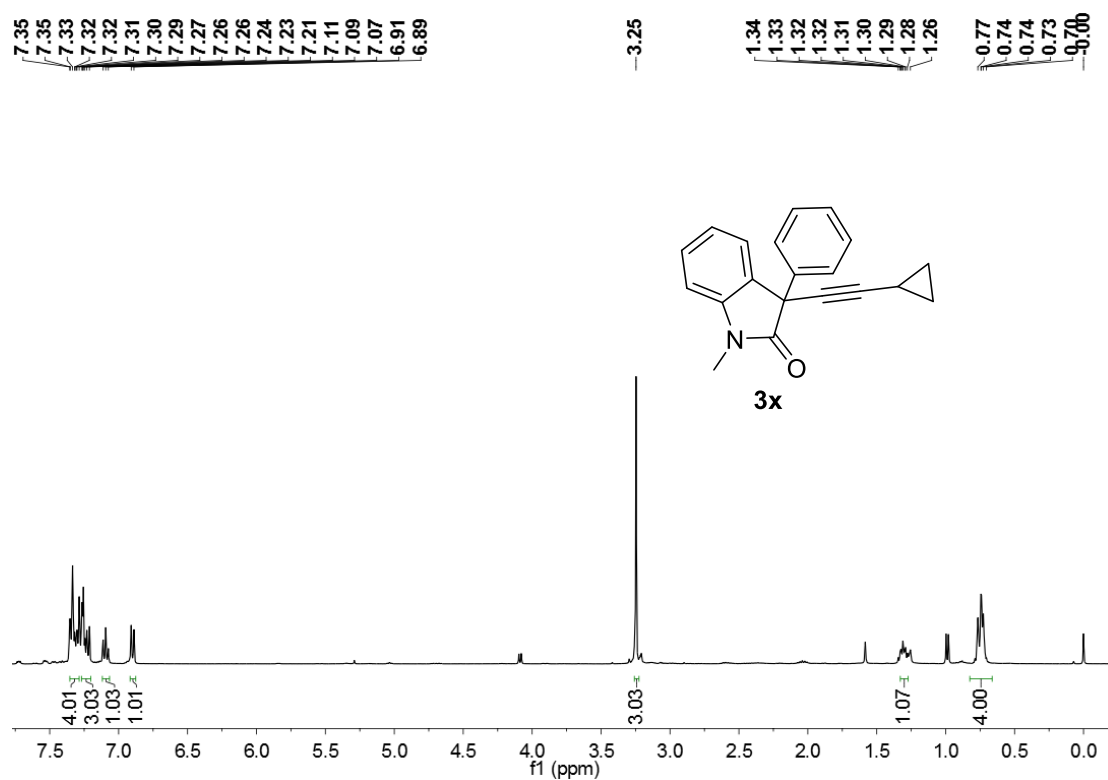


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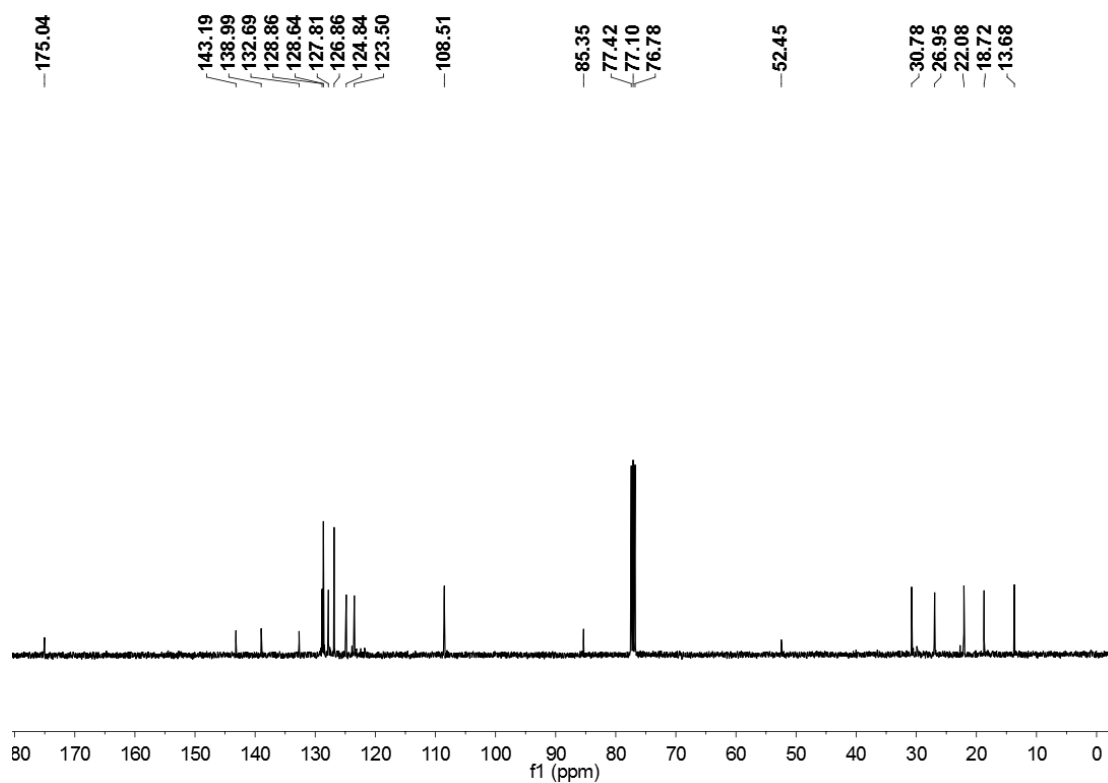
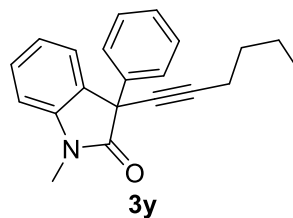
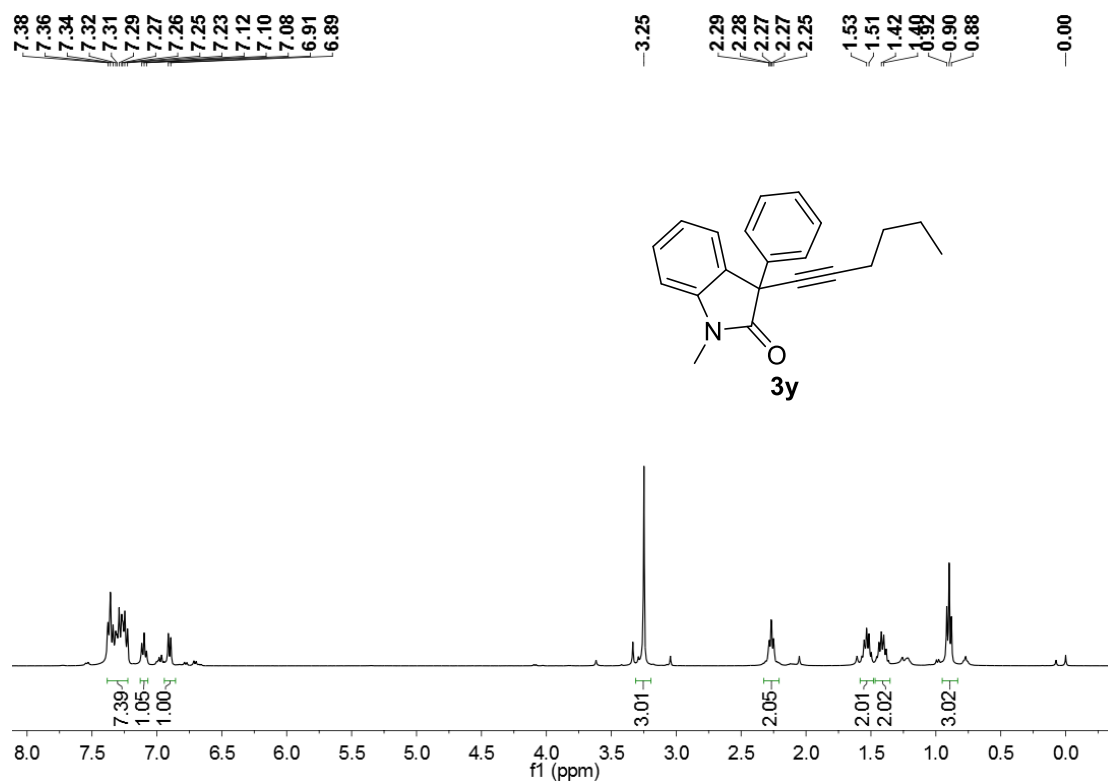




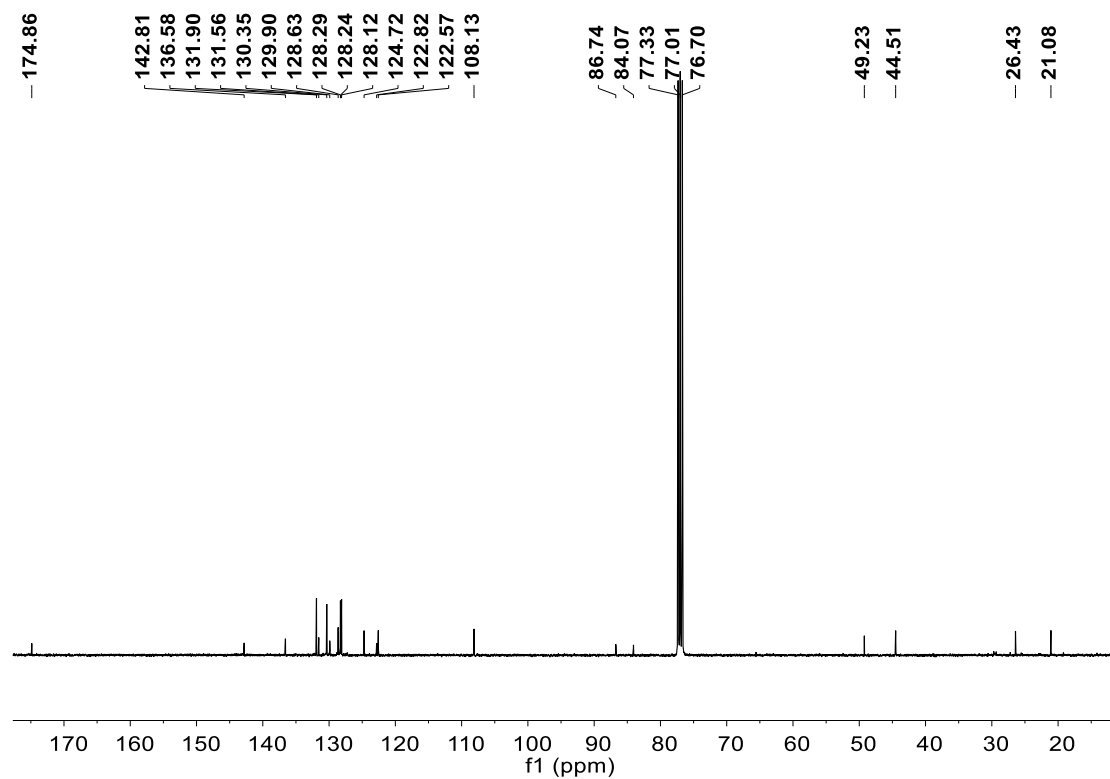
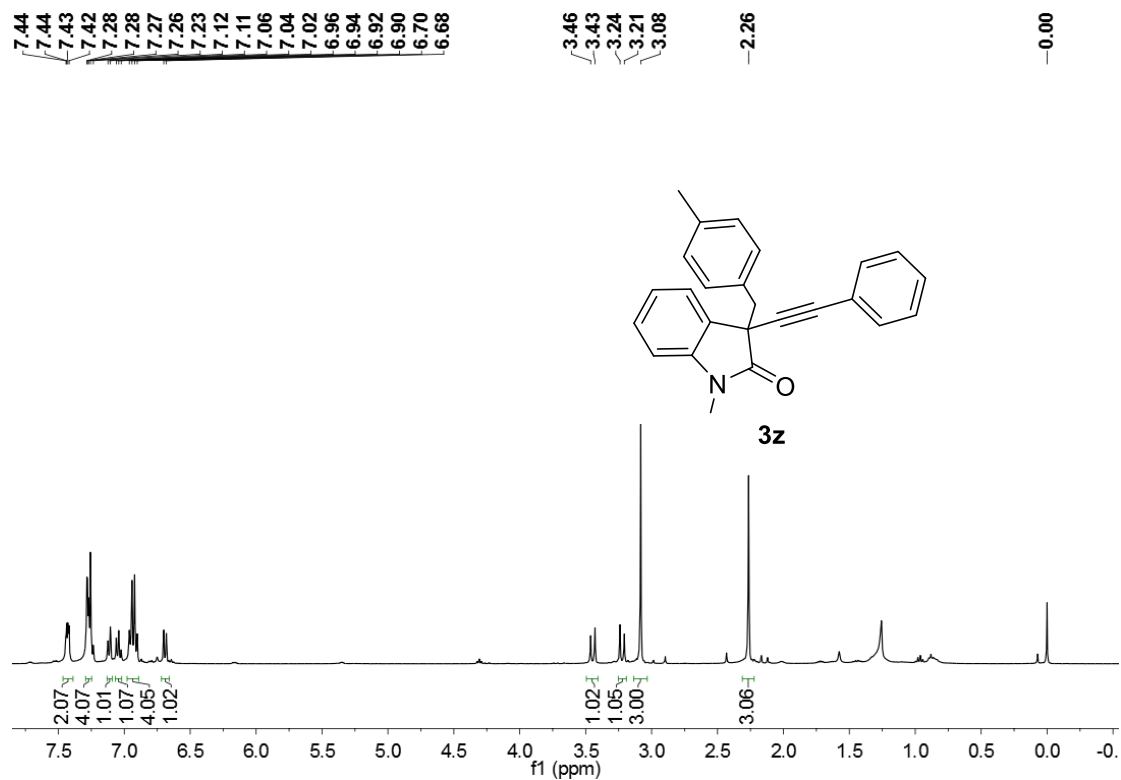
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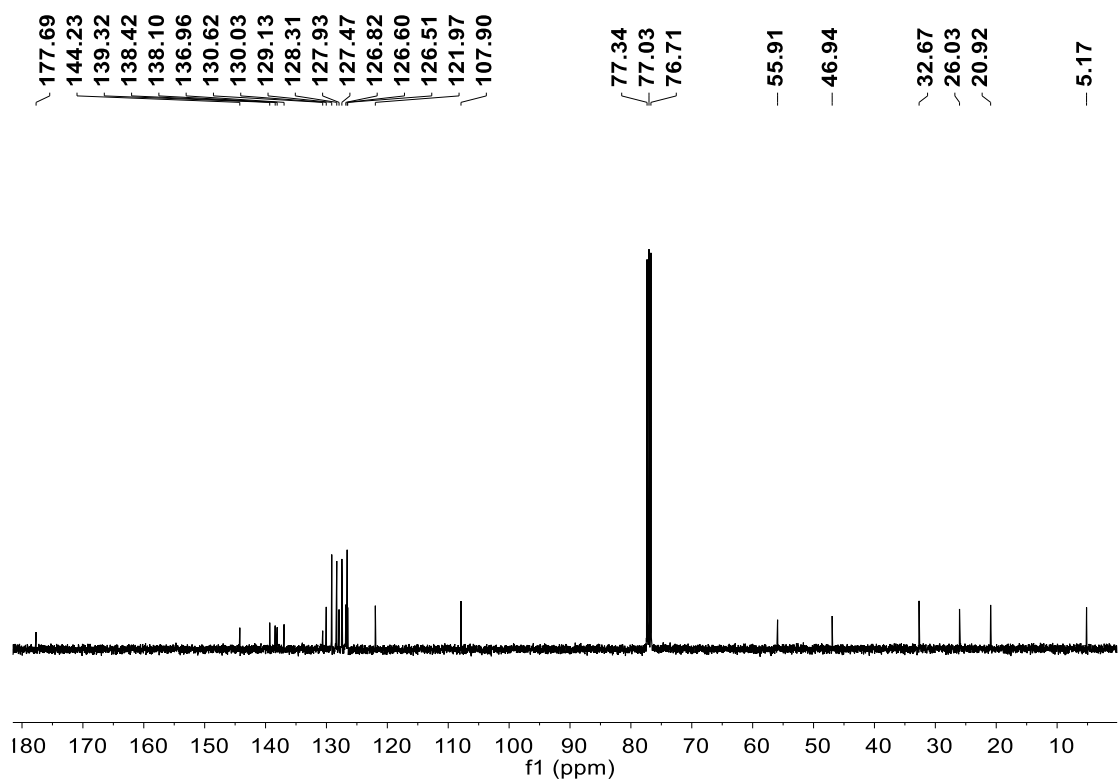
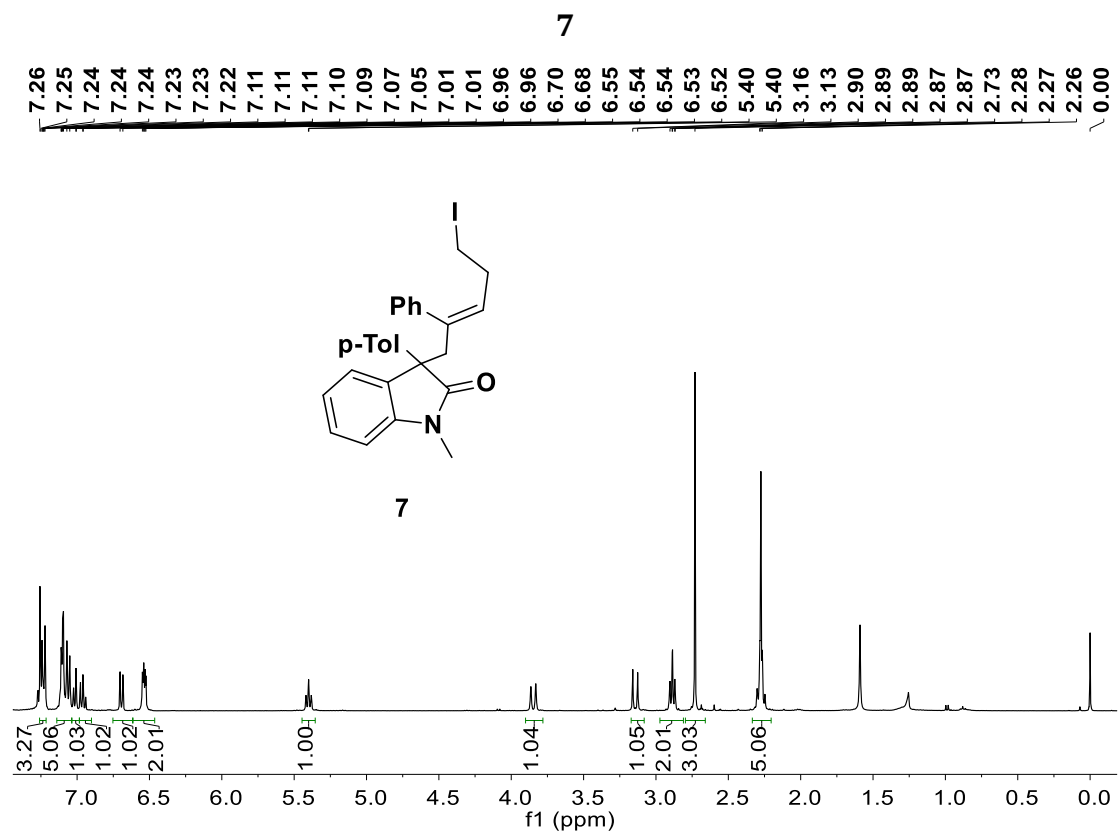


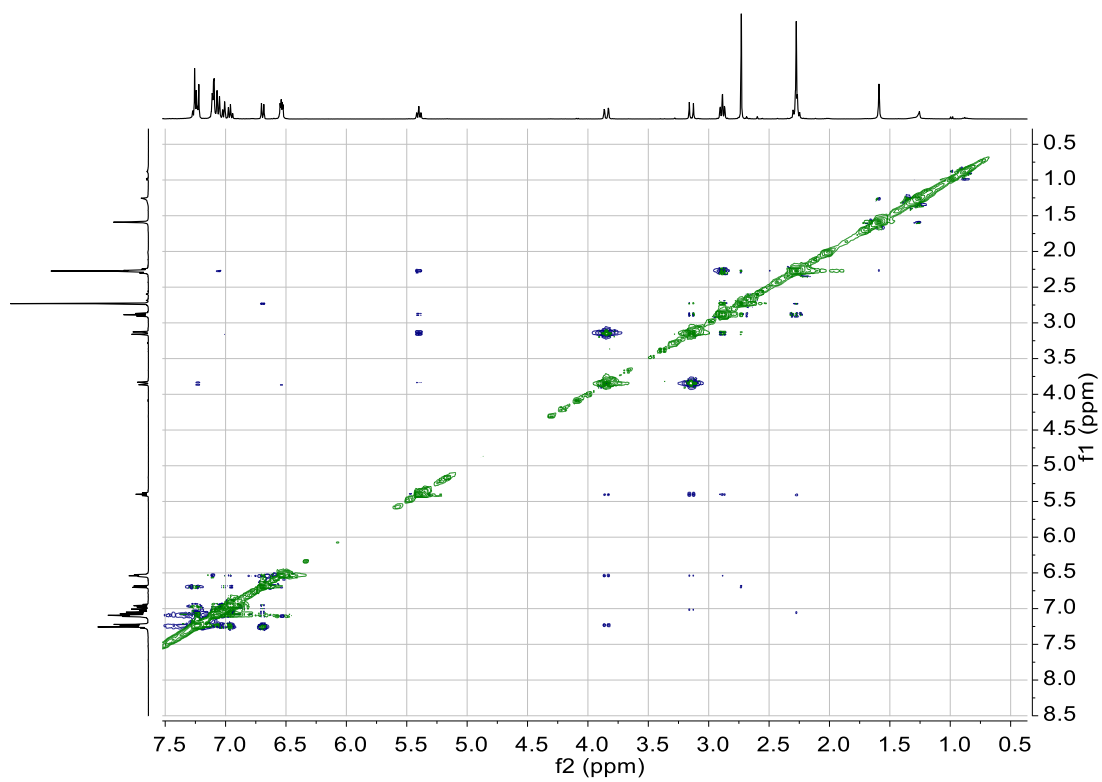
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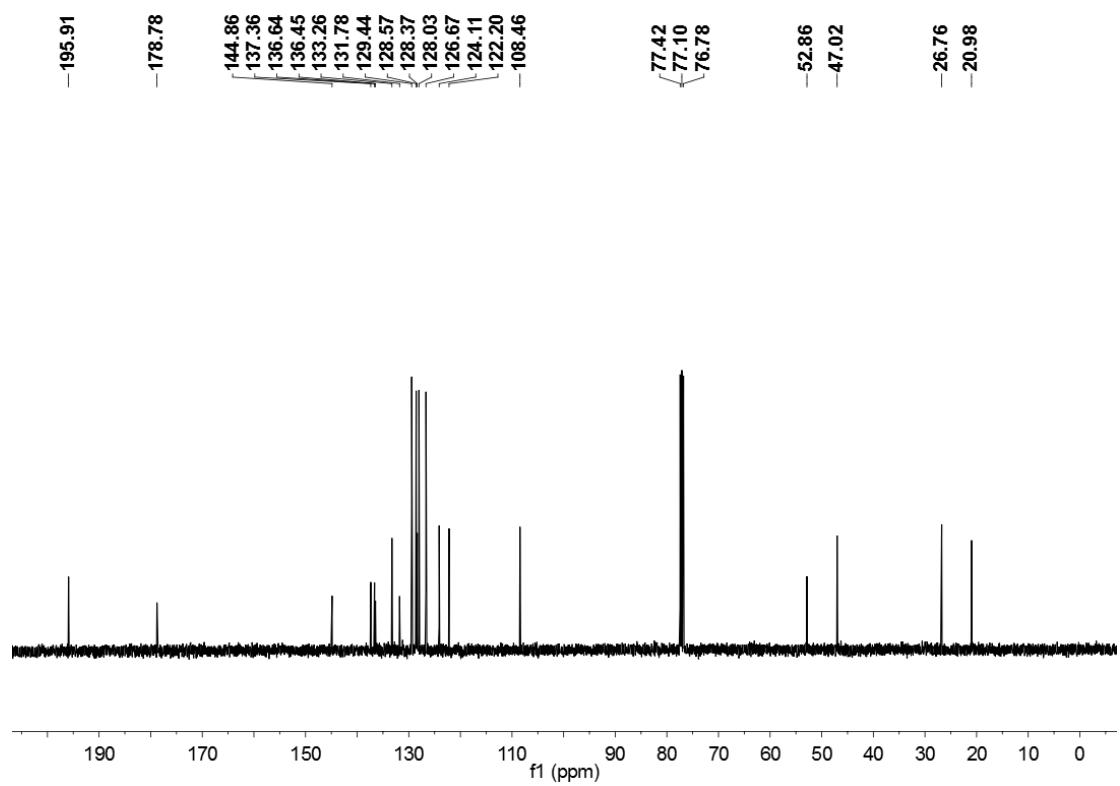
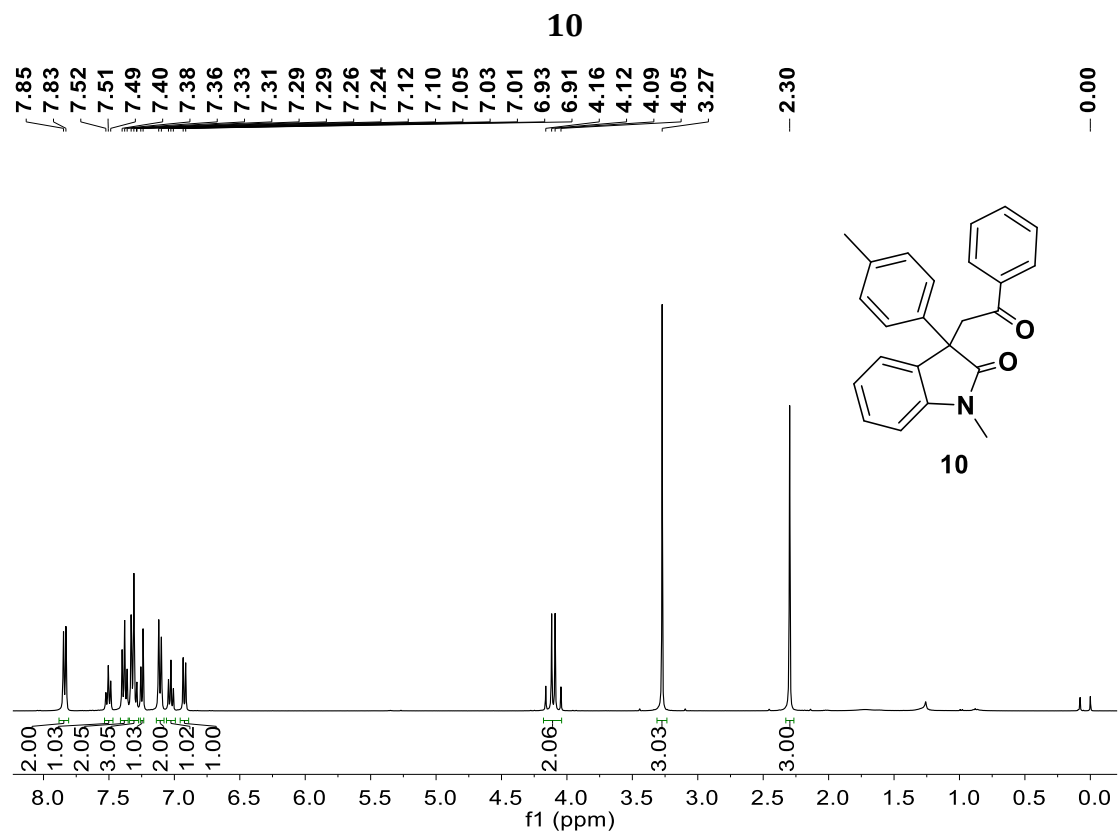


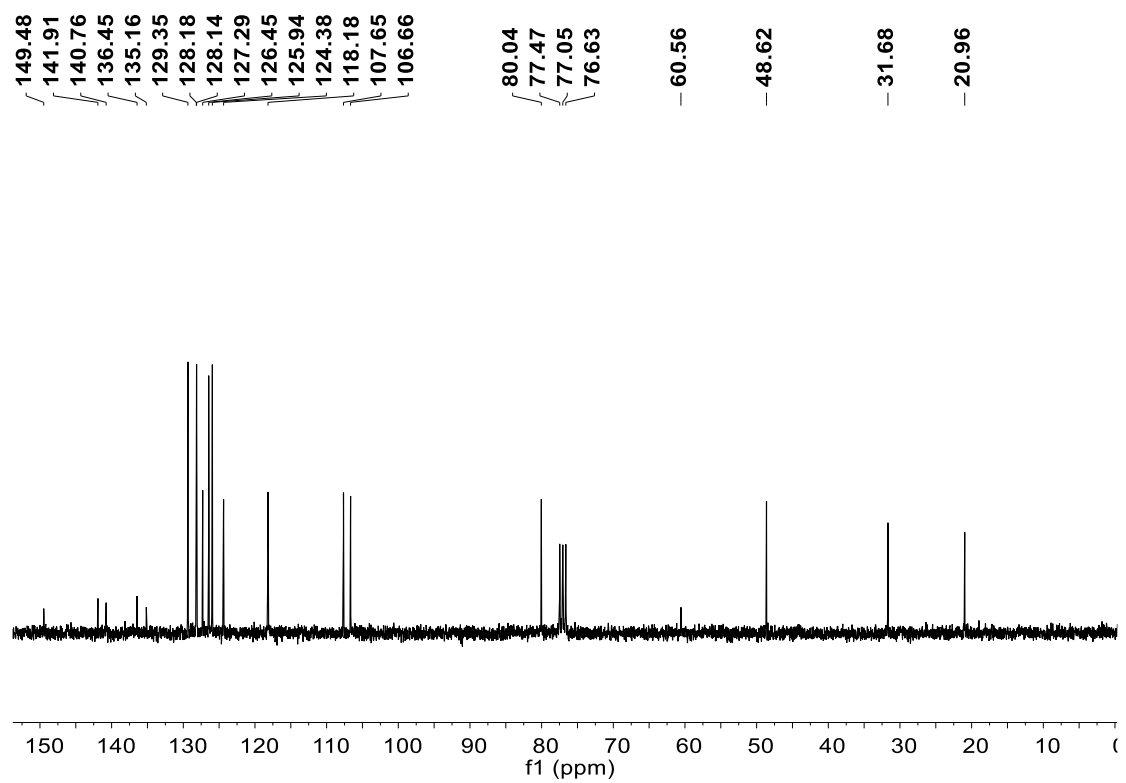
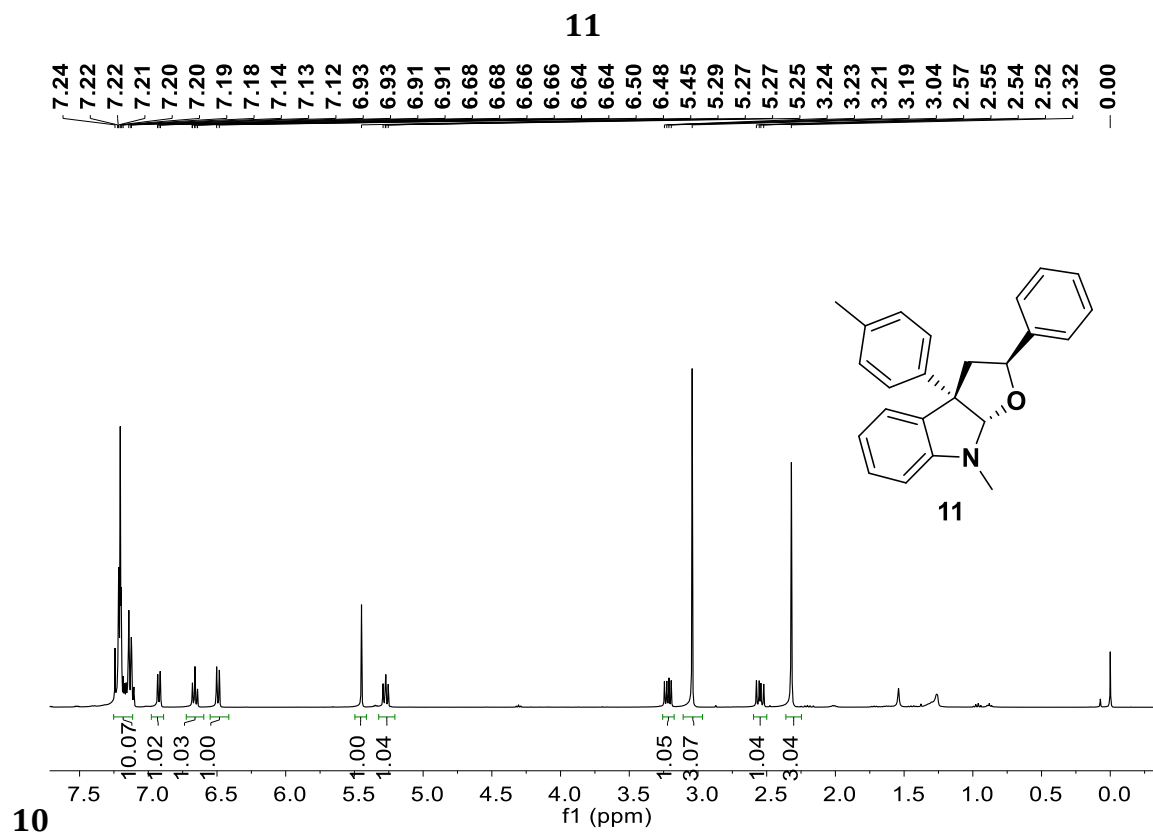
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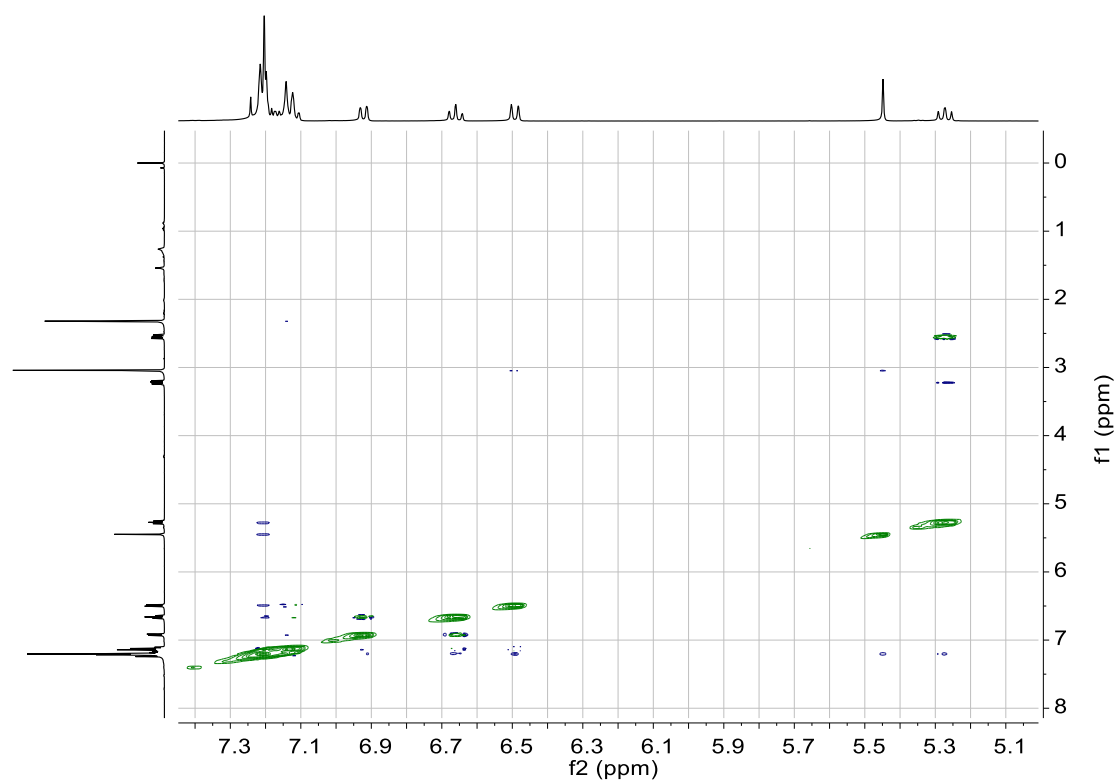












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