Electronic Supplementary Information for

Regiodivergent formal [4+2] Cycloaddition of Nitrosoarenes with Furanyl Cyclopropane derivatives as 4π Components

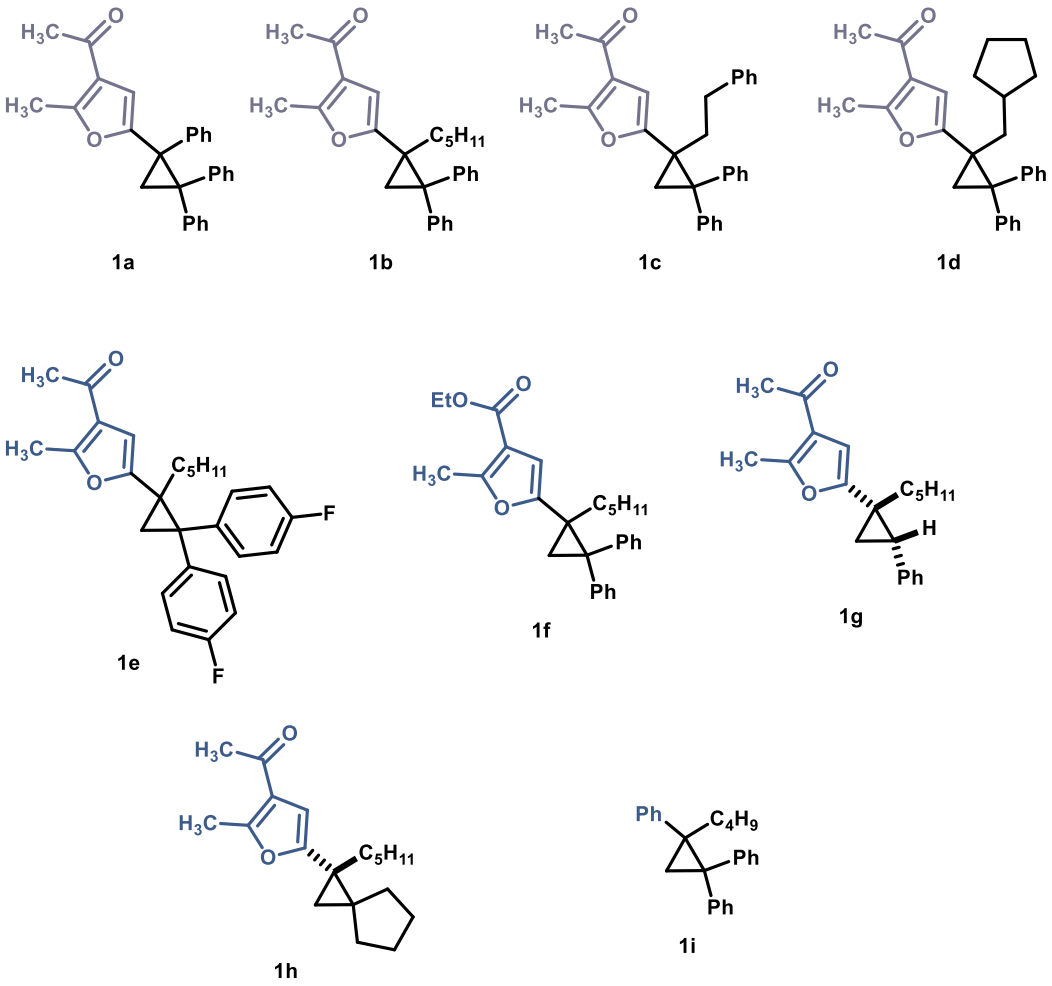
Darío Coto, Sergio Mata, Luis A. López* and Rubén Vicente*

TABLE OF CONTENTS

General Remarks

All reactions were carried out under Argon atmosphere using standard Schlenck techniques. 1,2-dichloroethane was distilled from CaH_2 under N_2 atmosphere. Solvents for column chromatography were obtained from commercial suppliers and used without further purification. TLC was performed on aluminium-backed plates coated with silica gel 60 with F_{254} indicator. Flash column chromatography was carried out on silica gel (230-240 mesh). ^{1}H-NMR (300, 400 MHz) and ^{13}C-NMR (75.5 and 100 MHz) spectra were recorded at room temperature in the indicated solvent on a Bruker DPX-300, or Bruker AVANCE-300 MHz and 400 MHz instruments. Chemical shifts (δ) are given in ppm relative to TMS (^{1}H, 0.0 ppm) or $CDCl_3$ (^{13}C, 77.0 ppm). Carbon multiplicities were assigned by DEPT experiments. 2D-NMR experiments were recorded on a Bruker AVANCE-400 MHz. High-resolution mass spectra were recorded in an Agilent 6520Q-TOF and a Finnigan Mat95 spectrometers. This study was carried out using cyclopropanes **1** and nitrosoarenes **2** (Scheme S1). Furanyl cyclopropanes **1** were prepared according to our previously reported procedure.[1] Nitrosobenzene **2a** was purchased from Aldrich and used as received. Nitrosoarenes **2b-i** are known compounds and were prepared from the corresponding anilines by oxidation according to reported procedures.[2] Commercially available catalysts were used as received and stored under Ar atmosphere.

[1] S. Mata, J. González, R. Vicente and L. A. López, *Eur. J. Org. Chem.*, 2016, **2016**, 2681–2687.
[2] J. Kubitschke, C. Naether and R. Herges, *Eur. J. Org. Chem.* 2010, 5041-5055.

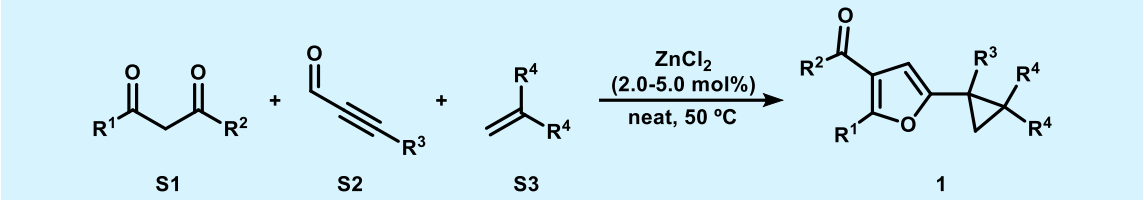


Scheme S1. Starting materials used in this work.

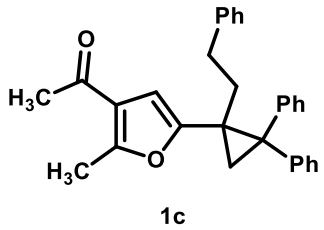
Synthesis and characterization of furanyl cyclopropanes 1.

Synthesis of furanyl cyclopropanes 1a-g.

Furanyl cyclopropanes **1** were prepared according to our previously reported procedure.[1] Compounds **1a**, **1b**, **1f** and **1g** are known compounds.[1]



Representative procedure A: To a mixture of 1,3-dicarbonyl compound **S1** (1.0 equiv.), alkynal **S2** (1.1 equiv.) and alkene **S3** (3.0 equiv.), $ZnCl_2$ (2.0 mol%) was added at ambient temperature under an inert gas. The Schlenk flask was sealed with a septum and placed in a preheated oil bath at 50 °C, and the reaction mixture was stirred at this temperature until the starting material was consumed (checked by TLC analysis). The excess of the alkene was removed under vacuum. The resulting residue was purified by flash column chromatography (SiO_2; hexane/EtOAc) to afford furanylcyclopropane **1**.



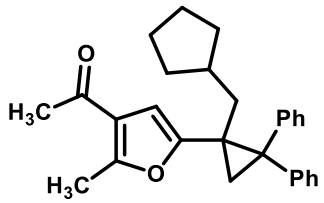
1-(2-Methyl-5-(1-phenethyl-2,2-diphenylcyclopropyl)furan-3-yl)ethan-1-one (**1c**): The representative procedure **A** was followed using 2,4-pentanedione (100 mg, 1.0 mmol), 5-phenylpent-2-ynal[3] (175 mg, 1.1 mmol) and 1,1-diphenylethene (540 mg, 3.0 mmol). After 24 h, analysis of the crude mixture (TLC) indicated the disappearance of starting materials. Purification by flash chromatography (SiO_2, hexanes:EtOAc = 40:1 to 20:1) afforded **1c** (311 mg, 74%) as a colourless oil.

[3] J.-M. I. A. Lawrence and P. E. Floreancig, *Org. Lett.* 2020, **22**, 9513–9517.

^{1}H NMR (300 MHz, $CDCl_3$): 1.13 – 1.37 (m, 1H), 1.64 (d, *J* = 5.3 Hz, 1H), 2.05 (d, *J* = 5.3 Hz, 1H), 2.30 (s, 3H), 2.57 (s, 3H), 2.61 – 2.83 (m, 3H), 6.13 (s, 1H), 7.05 – 7.36 (m, 13H), 7.56 (dd, *J* = 8.2, 1.3 Hz, 2H).

^{13}C NMR (75 MHz, $CDCl_3$): 14.4, 22.7, 29.1, 30.8, 33.9, 36.1, 44.3, 107.9, 121.9, 125.8, 126.2, 126.6, 127.9, 128.3, 128.5, 128.6, 129.56, 129.59, 142.0, 142.6, 143.5, 153.5, 157.0, 194.3.

HR-MS (ESI) calc. for $[C_{30}H_{28}O_2+H]^+$ 421.2162, found 421.2160.



1d

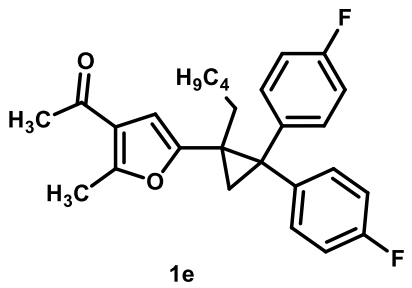
1-(5-(1-(Cyclopentylmethyl)-2,2-diphenylcyclopropyl)-2-methylfuran-3-yl)ethan-1-one (**1d**): The representative procedure **A** was followed using 2,4-pentanedione (500 mg, 5.0 mmol), 4-cyclopentylbut-2-ynal[4] (680 mg, 5.0 mmol) and 1,1-diphenylethene (2.70 g, 15.0 mmol). After 16 h, analysis of the crude mixture (TLC) indicated the disappearance of starting materials. Purification by flash chromatography (SiO_2, hexanes:EtOAc = 100:1 to 20:1) afforded **1d** (1.23 g, 62%) as a yellow oil.

^{1}H NMR (400 MHz, $CDCl_3$): 0.66 (dd, *J* = 14.1, 8.7 Hz, 1H), 0.84 – 0.96 (m, 2H), 1.37 – 1.62 (m, 5H), 1.69 (d, *J* = 5.3 Hz, 1H), 1.71 – 1.82 (m, 2H), 2.00 (dd, *J* = 5.3, 1.5 Hz, 1H), 2.25 (s, 3H), 2.45 – 2.50 (m, 1H, overlapped signal), 2.51 (s, 3H), 5.97 (s, 1H), 6.95 – 7.03 (m, 1H), 7.04 – 7.11 (m, 2H), 7.15 – 7.23 (m, 1H),.25 – 7.35 (m, 4H), 7.43 – 7.68 (m, 2H).

^{13}C NMR (101 MHz, $CDCl_3$): 14.5, 23.1, 24.6, 25.0, 29.2, 30.6, 32.7, 33.2, 39.6, 40.0, 43.3, 107.4, 121.9, 126.1, 126.5, 127.9, 128.5, 129.6, 129.7, 142.9, 143.8, 154.3, 156.9, 194.5.

HR-MS (ESI) calc. for $[C_{28}H_{30}O_2+H]^+$ 399.2319, found 399.2318.

[4] A. Kivrak and M. Zora, *Tetrahedron* 2014, **70**, 817–831.



1e

1-(5-(2,2-*bis*(4-Fluorophenyl)-1-pentylcyclopropyl)-2-methylfuran-3-yl)ethan-1-one (**1e**): The representative procedure **A** was followed using 2,4-pentanedione (160 mg, 1.6 mmol), 2-octyn-1-al (198 mg, 1.6 mmol) and 4,4'-(ethene-1,1-diyl)bis(fluorobenzene)[5] (1.04 g, 4.8 mmol). After 16 h, analysis of the crude mixture (TLC) indicated the disappearance of starting materials. Purification by flash chromatography (SiO_2, hexanes:EtOAc = 100:1 to 20:1) afforded **1e** (190 mg, 28%) as a yellow oil.

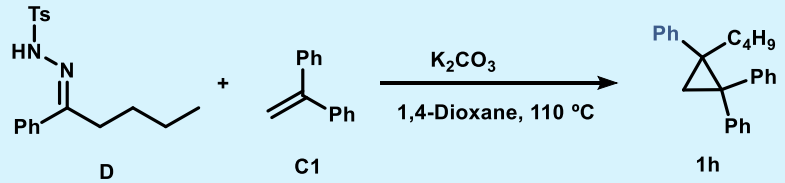
^{1}H NMR (400 MHz, $CDCl_3$): 0.59 – 0.72 (m, 1H), 0.79 (t, *J* = 6.8 Hz, 3H), 0.99 – 1.32 (m, 6H), 1.52 (d, *J* = 5.3 Hz, 1H), 1.92 (dd, *J* = 5.3, 1.4 Hz, 1H), 2.11 – 2.24 (m, 1H), 2.25 (s, 3H), 2.47 (s, 3H), 6.01 (s, 1H), 6.75 (t, *J* = 8.7 Hz, 2H), 6.96 (t, *J* = 8.7 Hz, 2H), 7.17 (dd, *J* = 8.6, 5.5 Hz, 2H), 7.40 (dd, *J* = 8.6, 5.5 Hz, 2H).

^{13}C NMR (101 MHz, $CDCl_3$): 14.0, 14.4, 22.6, 23.0, 27.2, 29.1, 31.2, 31.8, 34.2, 42.5, 107.6, 114.78 (d, *J* = 21.2 Hz), 115.45 (d, *J* = 21.2 Hz), 130.9 (d, *J* = 8.1 Hz), 131.0 (d, *J* = 8.1 Hz), 138.57 (d, *J* = 3.3 Hz), 139.39 (d, *J* = 3.4 Hz), 153.51, 156.96, 161.1 (d, *J* = 245.0 Hz), 161.5 (d, *J* = 245.6 Hz), 194.3.

^{19}F NMR (282 MHz, $CDCl_3$) δ = -116.03 (s), -116.46 (s).

HR-MS (ESI) calc. for $[C_{27}H_{28}F_2O_2+H]^+$ 423.2130, found 423.2132.

Synthesis of cyclopropane 1i.

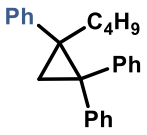


D C1 1h

Following a reported procedure,[6] a suspension of **D**[7] (330 mg, 1 mmol), 1,1-diphenylethene (**C1**, 360 mg, 2.0 mmol, 2.0 equiv.) and K_2CO_3 (207 mg, 1.5 mmol, 1.5 equiv.) in 1,4-dioxane (9 mL) was heated at 110 °C for 6 h. The solvent was removed under vacuum and the resulting mixture

[5] J. C. L. Walker and M. Oestreich, *Org. Lett.* 2018, **20**, 6411–6414.
[6] J. Barluenga, N. Quiñones, M. Tomás-Gamasa and M.-P. Cabal. *Eur. J. Org. Chem.* 2012, 2312–2317.
[7] A. R. Katritzky, G. N. Nikonov, E. L. Moyano, N. G. Akhmedov and P. J. Steel, *ARKIVOC*, 2003, **7**, 121–138.

was purified by flash column chromatography (hexanes) to afford cyclopropane **1h** along with **C1**. Most of the excess of the alkene could be removed using a high-vacuum pump and a subsequent flash column chromatography (hexanes) to afford **1h** (80 mg) as a colourless oil.



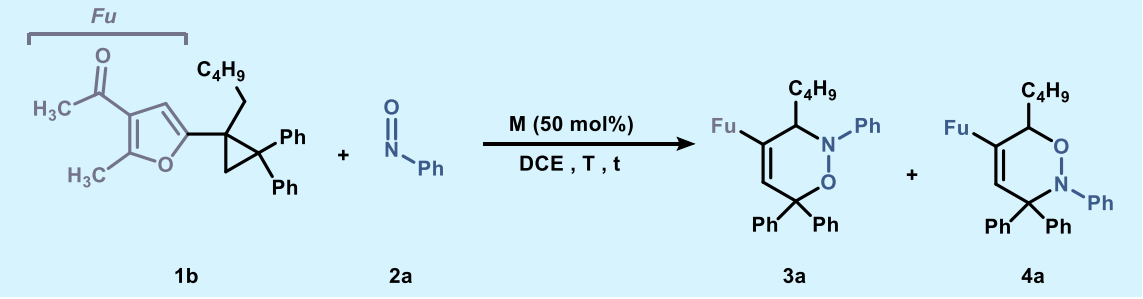
1i

(2-Butylcyclopropane-1,1,2-triyl)tribenzene (**1i**):

^{1}H NMR (300 MHz, $CDCl_3$): 0.70 – 0.83 (m, 3H), 0.85 – 1.02 (m, 1H), 1.11 – 1.31 (m, 4H), 1.46 – 1.60 (m, 1H), 2.12 – 2.37 (m, 2H), 6.86 – 7.01 (m, 3H), 7.05 – 7.13 (m, 3H), 7.14 – 7.29 (m, 5H), 7.35 – 7.49 (m, 2H), 7.54 – 7.66 (m, 2H).

^{13}C NMR (75 MHz, $CDCl_3$): 14.1, 22.8, 23.1, 29.9, 38.3, 38.9, 42.9, 125.2, 125.6, 126.2, 127.4, 127.7, 128.4, 129.4, 130.5, 141.2, 143.1, 143.9.

Screening for the reaction of furanyl cyclopropane 1b with nitrosobenzene (2a)



1b **2a** **3a** **4a**

1b:2a	M	solvent	T (º C)	t (h)	Conv.(%)	3a+4a (%)[a]	*r.r* [a]
1:1.5	$MgBr_2$	1,2-DCE	90	22	39	21	>20:1
1:4	$MgBr_2$	1,2-DCE	90	48	60	40	>20:1
1:4	$MgBr_2$	1,2-DCE	50	48	>95	71	>20:1
1:4	$MgBr_2$	1,2-DCE	r.t	96	32	31	>20:1
1:4	$MgBr_2$	THF	r.t	48	0	0	–
1:4	$MgBr_2$	Toluene	r.t	48	0	0	–
1:4	$MgBr_2$	AcOEt	r.t	48	0	0	–
1:4	$MgBr_2$	Et_2O	r.t	48	0	0	–
1:4	$MgBr_2$	1,2-DCE	50	48	32	71	>20:1
1:4	$Mg(ClO_4)_2$	1,2-DCE	r.t	48	31	18	>20:1
1:4	$Mg(OTf)_2$	1,2-DCE	r.t	48	34	27	>20:1
1:4	$MgBr_2{\cdot}OEt_2$	1,2-DCE	r.t	48	32	19	>20:1
1:4	$Zn(OTf)_2$	1,2-DCE	r.t	15	60	33	>20:1
1:4	$Zn(OTf)_2$	1,2-DCE	50	15	>95	93	7:1
1:4	$Yb(OTf)_3$	1,2-DCE	r.t	15	54	35	1.3:1
1:4	$FeCl_2$	1,2-DCE	r.t	15	42	22	1.2:1
1:4	$InCl_3$	1,2-DCE	r.t	15	25	15	1.5:1
1:4	$Sc(OTf)_3$	1,2-DCE	r.t	15	90	83	1.9:1
1:4	$Ca(OTf)_2$	1,2-DCE	r.t	15	>95	95	1.7:1
1:4	$Cu(OTf)_2$	1,2-DCE	r.t	15	>95	87	1.9:1
1:4	CuCl	1,2-DCE	r.t	15	10	3	-
1:4	CuBr	1,2-DCE	r.t	15	40	32	1:1
1:4	CuI	1,2-DCE	r.t	15	0	0	-
1:4	$Cu(MeCN)_4PF_6$	1,2-DCE	r.t	15	-	-	-
1:4	$In(OTf)_3$	1,2-DCE	r.t	15	>95	93	1:1.6
1:4	Ag(OTf)	1,2-DCE	r.t	15	>95	58	1:6.2
1:4	$Bi(OTf)_3$	1,2-DCE	r.t	15	>95	61	>1:20
1:4	$Fe(OTf)_3$	1,2-DCE	r.t	15	>95	99	>1:20
1:4	CF_3SO_3H	1,2-DCE	r.t	15	>95	80	1:7.9
1:4	$HBF_4{\cdot}OEt_2$	1,2-DCE	r.t	15	>95	41	1:2.5
1:4	*no catalyst*	1,2-DCE	r.t-90 °C	48	–	–	–

[a] From ^1H NMR of the reaction crude.

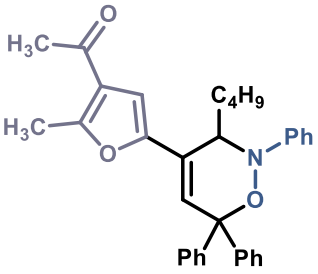
Synthesis and characterization of 1,2-oxazines 3 and 4.

Representative procedure B *(regioselective synthesis of 1,2-oxanizes **3**)*:

To a solution of the corresponding furanyl cyclopropane **1** (0.1-0.5 mmol) in 1,2-DCE (2-10 mL), nitrosoarene **2** (0.4-1.0 mmol, 4.0 equiv.) and $MgBr_2$ or $Zn(OTf)_2$ (50 mol%) were added under Ar atmosphere. The resulting mixture was heated at 50 °C overnight (15-16 h, at this time starting cyclopropane is consumed as indicated by TLC analysis). The solvent was removed under reduced pressure and the residue was purified by flash column chromatography (hexanes:EtOAc) to afford the corresponding oxazines **3** as major products.

Representative procedure C *(regioselective synthesis of 1,2-oxanizes **4**)*:

To a solution of the corresponding furanyl cyclopropane **1** (0.1-0.5 mmol) in 1,2-DCE (2-10 mL), nitrosoarene **2** (0.4-1.0 mmol, 4.0 equiv.) and $Fe(OTf)_3$ or $Bi(OTf)_3$ (50 mol%) were added under Ar atmosphere. The resulting mixture was heated at 50 °C overnight (15-16 h, at this time starting cyclopropane is consumed as indicated by TLC analysis). The solvent was removed under reduced pressure and the residue was purified by flash column chromatography (hexanes:EtOAc) to afford the corresponding oxazines **4** as major products.



3a

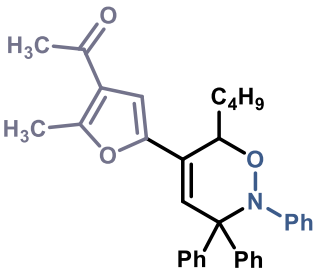
1-(5-(3-Butyl-2,6,6-triphenyl-3,6-dihydro-2*H*-1,2-oxazin-4-yl)-2-methylfuran-3-yl)ethan-1-one (**3a**): The representative procedure B was followed using cyclopropane **1b** (38.7 mg, 0.10 mmol), nitrosobenzene **2a** (43.0 mg, 0.4 mmol) and $Zn(OTf)_2$ (16.5 mg, 0.05 mmol). After 15 h, analysis of the crude mixture (TLC) indicated the disappearance of **1b**. Purification by flash chromatography (SiO_2, hexanes:EtOAc = 20:1) afforded **3a** (40.9 mg, 83%) as a pale yellow oil.

^{1}H NMR (300 MHz, $CDCl_3$): 0.73 (t, *J* = 7.0 Hz, 3H), 1.07 – 1.22 (m, 4H), 1.72 – 1.94 (m, 1H), 1.87 – 2.13 (m, 1H), 2.46 (s, 3H), 2.66 (s, 3H), 4.52 (t, *J* = 5.2 Hz, 1H), 6.58 (s, 1H), 6.89 (s, 1H), 6.96 (tt,

J = 7.2, 1.1 Hz, 1H), 7.13 – 7.23 (m, 3H), 7.24 – 7.35 (m, 5H), 7.35 – 7.40 (m, 2H), 7.41 – 7.66 (m, 4H).

^{13}C NMR (75 MHz, $CDCl_3$): 13.8, 14.6, 22.9, 29.2, 29.7, 30.2, 59.8, 84.7, 106.3, 116.0, 121.3, 122.9, 126.4, 127.2, 127.3, 127.7, 128.0, 128.3, 128.6, 129.0, 143.5, 144.2, 148.9, 150.1, 158.1, 193.9.

HR-MS (ESI) calc. for $[C_{33}H_{33}NO_3+H]^+$ 492.2533, found 492.2534.



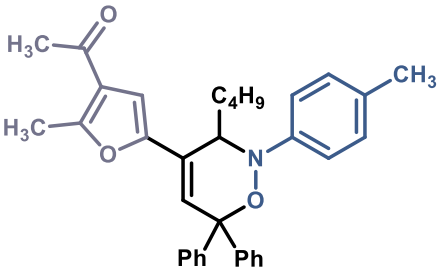
4a

1-(5-(6-Butyl-2,3,3-triphenyl-3,6-dihydro-2*H*-1,2-oxazin-5-yl)-2-methylfuran-3-yl)ethan-1-one (**4a**): The representative procedure C was followed using cyclopropane **1b** (38.7 mg, 0.10 mmol), nitrosobenzene **2b** (43.0 mg, 0.4 mmol) and $Fe(OTf)_3$ (22.5 mg, 0.05 mmol). After 15 h, analysis of the crude mixture (TLC) indicated the disappearance of **1b**. Purification by flash chromatography (SiO_2, hexanes:EtOAc = 20:1) afforded **4a** (43.3 mg, 88%) as a pale brown oil.

^{1}H NMR (300 MHz, $CDCl_3$): 0.93 (t, *J* = 7.0 Hz, 3H), 1.42 – 1.58 (m, 4H), 1.81 – 1.89 (m, 1H), 2.38-2.52 (bs, 1H), 2.45 (s, 3H, overlapped), 2.61 (s, 3H), 4.84 (d, *J* = 9.7 Hz, 1H), 6.25 (s, 1H), 6.49 (s, 1H), 6.77 – 6.84 (m, 2H), 6.85 – 6.94 (m, 1H), 6.97 – 7.05 (m, 2H), 7.16 – 7.30 (m, 5H), 7.33 – 7.42 (m, 3H), 7.63 (bs, 2H).

^{13}C NMR (75 MHz, $CDCl_3$): 14.0, 14.5, 22.4, 28.7, 29.2, 32.3, 74.0, 77.0, 106.1, 120.2, 122.9, 123.0, 126.3, 127.1, 127.4, 127.7, 128.1, 129.3, 129.8, 130.4, 149.0, 149.2, 158.0, 193.8.

HR-MS (ESI) calc. for $[C_{33}H_{33}NO_3+H]^+$ 492.2533, found 492.2534.



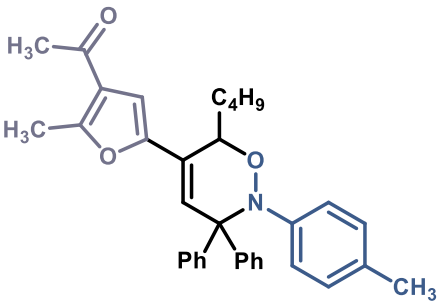
3b

1-(5-(3-Butyl-6,6-diphenyl-2-(*p*-tolyl)-3,6-dihydro-2*H*-1,2-oxazin-4-yl)-2-methylfuran-3-yl)ethan-1-one (**3b**): The representative procedure B was followed using cyclopropane **1b** (38.8 mg, 0.10 mmol), nitrosoarene **2b** (48.2 mg, 0.4 mmol) and $Zn(OTf)_2$ (16.5 mg, 0.05 mmol). After 48 h, analysis of the crude mixture (TLC) indicated the disappearance of **1b**. Purification by flash chromatography (SiO_2, hexanes:EtOAc = 20:1) afforded **3b** (28.9 mg, 59%) as a pale yellow oil.

^{1}H NMR (300 MHz, $CDCl_3$): 0.72 (t, *J* = 7.1 Hz, 3H), 1.11 – 1.18 (m, 2H), 1.56 – 1.60 (m, 2H), 1.74 – 1.81 (m, 1H), 1.95 – 1.99 (m, 1H), 2.31 (s, 3H), 2.44 (s, 3H), 2.65 (s, 3H), 4.44 (t, *J* = 5.1 Hz, 1H), 6.56 (s, 1H), 6.88 (s, 1H), 7.09 (s, 4H), 7.19 – 7.43 (m, 10H).

^{13}C NMR (75 MHz, $CDCl_3$): 13.7, 14.5, 20.7, 22.9, 29.2, 29.7, 30.0, 60.0, 84.6, 106.2, 116.2, 122.9, 126.5, 127.1, 127.2, 127.3, 127.6, 128.0, 128.2, 129.1, 129.2, 130.7, 143.6, 144.2, 146.5, 150.2, 158.0, 193.9.

HR-MS (ESI) calc. for $[C_{34}H_{35}NO_3+H]^+$ 506.2690, found 506.2693.



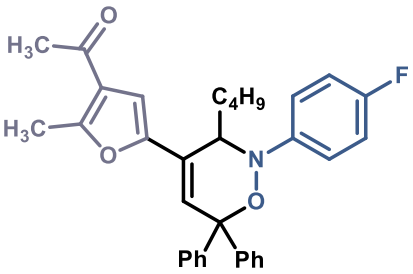
4b

1-(5-(6-Butyl-3,3-diphenyl-2-(*p*-tolyl)-3,6-dihydro-2*H*-1,2-oxazin-5-yl)-2-methylfuran-3-yl)ethan-1-one (**4b**): The representative procedure C was followed using cyclopropane **1b** (38.7 mg, 0.10 mmol), nitrosoarene **2b** (48.6 mg, 0.4 mmol) and $Bi(OTf)_3$ (29.5 mg, 0.05 mmol). After 15 h, analysis of the crude mixture (TLC) indicated the disappearance of **1b**. Purification by flash chromatography (SiO_2, hexanes:EtOAc = 20:1) afforded **4b** (28.5 mg, 56%) as a yellow oil.

^{1}H NMR (300 MHz, $CDCl_3$): 0.90 (t, *J* = 7.0 Hz, 3H), 1.34 – 1.54 (m, 5H), 1.78 – 1.84 (m, 1H), 2.20 (s, 3H), 2.43 (s, 3H), 2.58 (s, 3H), 4.79 (d, *J* = 9.4 Hz, 1H), 6.22 (s, 1H), 6.45 (s, 1H), 6.65 (d, *J* = 8.5 Hz, 2H), 6.79 (d, *J* = 8.5 Hz, 2H), 7.19 – 7.38 (m, 8H), 7.60 (bs, 2H).

^{13}C NMR (75 MHz, $CDCl_3$): 14.0, 14.5, 20.6, 22.4, 28.6, 29.2, 32.3, 73.9, 76.8, 106.0, 120.6, 122.9, 126.4, 127.0, 127.3, 127.4, 127.9, 128.2, 129.9, 130.5, 132.4, 146.3, 149.3, 157.9, 193.8.

HR-MS (ESI) calc. for $[C_{34}H_{35}NO_3+H]^+$ 506.2690, found 506.2693.



3c

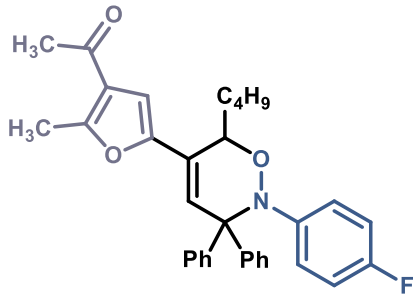
1-(5-(3-Butyl-2-(4-fluorophenyl)-6,6-diphenyl-3,6-dihydro-2*H*-1,2-oxazin-4-yl)-2-methylfuran-3-yl)ethan-1-one (**3c**): The representative procedure B was followed using cyclopropane **1b** (38.5 mg, 0.10 mmol), nitrosoarene **2c** (50.0 mg, 0.4 mmol) and $Zn(OTf)_2$ (16.5 mg, 0.05 mmol). After 15 h, analysis of the crude mixture (TLC) indicated the disappearance of **1b**. Purification by flash chromatography (SiO_2, hexanes:EtOAc = 20:1) afforded **3c** (34.3 mg, 67%) as a colourless oil.

^{1}H NMR (300 MHz, $CDCl_3$): 0.74 (t, *J* = 7.1 Hz, 3H), 1.12 – 1.19 (m, 4H), 1.73 – 1.80 (m, 1H), 1.98 – 2.05 (m, 1H) 2.45 (s, 3H), 2.66 (s, 3H), 4.41 (t, *J* = 5.1 Hz, 1H), 6.57 (s, 1H), 6.88 (s, 1H), 6.97 – 7.01 (m, 2H), 7.14 – 7.17 (m, 2H), 7.18 – 7.41 (m, 10H).

^{13}C NMR (75 MHz, $CDCl_3$): 13.7, 14.5, 22.9, 29.2, 29.8, 30.0, 60.5, 84.9, 106.3, 115.26 (d, *J* = 22.4 Hz), 117.68 (d, *J* = 7.7 Hz), 122.9, 126.4, 127.1, 127.2, 127.3, 127.8, 128.0, 128.3, 129.0, 143.3, 144.1, 145.1, 145.2, 150, 158.0, 158.1 (d, *J* = 239.9 Hz), 193.8.

^{19}F NMR (282 MHz, $CDCl_3$): -122.7 (s).

HR-MS (ESI) calc. for $[C_{33}H_{32}FNO_3+H]^+$ 510.2439, found 510.2440.



4c

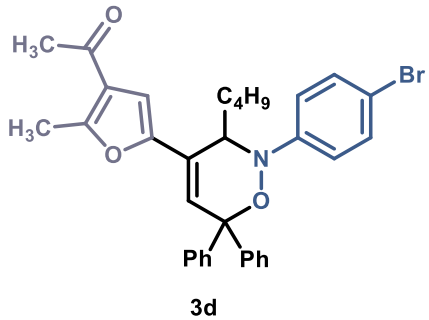
1-(5-(6-Butyl-2-(4-fluorophenyl)-3,3-diphenyl-3,6-dihydro-2*H*-1,2-oxazin-5-yl)-2-methylfuran-3-yl)ethan-1-one (**4c**): The representative procedure C was followed using cyclopropane **1b** (38.7 mg, 0.10 mmol), nitrosobenzene **2c** (50.0 mg, 0.4 mmol) and $Fe(OTf)_3$ (22.5 mg, 0.05 mmol). After 15 h, analysis of the crude mixture (TLC) indicated the disappearance of **1b**. Purification by flash chromatography (SiO_2, hexanes:EtOAc = 20:1) afforded **4c** (41.5 mg, 82%) as a pale yellow oil.

^{1}H NMR (300 MHz, $CDCl_3$): 0.89 (t, *J* = 7.1 Hz, 3H), 1.37 – 1.50 (m, 4H), 1.81 – 1.88 (m, 1H), 2.34 – 2.51 (bs, 1H), 2.44 (s, 3H, overlapped), 2.59 (s, 3H), 4.80 (d, *J* = 9.6 Hz, 1H), 6.20 (s, 1H), 6.47 (s, 1H), 6.66 –6.74 (m, 4H), 7.13 (bs, 2H), 7.18 – 7.30 (m, 3H), 7.30 – 7.42 (m, 3H), 7.61 (bs, 2H).

^{13}C NMR (75 MHz, $CDCl_3$): 14.0, 14.5, 22.4, 28.5, 29.2, 32.3, 74.4, 77.0, 106.1, 114.18 (d, *J* = 22.0 Hz), 122.66 (d, *J* = 7.8 Hz), 122.9, 126.5, 127.1, 127.5, 127.6, 128.0, 129.0, 129.9, 130.5, 145.0, 149.2, 158.0, 159.20 (d, *J* = 245.8 Hz, 193.7.

^{19}F NMR (282 MHz, $CDCl_3$): -120.0 (s).

HR-MS (ESI) calc. for $[C_{34}H_{35}NO_3+H]^+$ 506.2690, found 506.2694.



3d

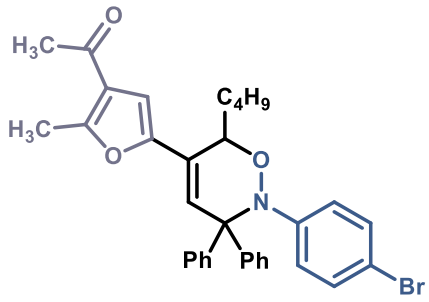
1-(5-(2-(4-Bromophenyl)-3-butyl-6,6-diphenyl-3,6-dihydro-2*H*-1,2-oxazin-4-yl)-2-methylfuran-3-yl)ethan-1-one (**3d**): The representative procedure B was followed using cyclopropane **1b** (38.5 mg, 0.10 mmol), nitrosoarene **2d** (74.5 mg, 0.4 mmol) and $Zn(OTf)_2$ (16.5 mg, 0.05 mmol). After 15 h, analysis of the crude mixture (TLC) indicated the disappearance of

1b. Purification by flash chromatography (SiO_2, hexanes:EtOAc = 20:1) afforded **3d** (44.0 mg, 77%) as a light brown oil.

^{1}H NMR (300 MHz, $CDCl_3$): 0.75 (t, *J* = 7.0 Hz, 3H), 1.15 – 1.30 (m, 4H), 1.80 – 1.85 (m, 1H), 1.98 – 2.06 (m, 1H) 2.48 (s, 3H), 2.66 (s, 3H), 4.50 (t, *J* = 5.1 Hz, 1H), 6.59 (s, 1H), 6.87 (s, 1H), 7.06 (d_{app}, *J* = 8.9 Hz, 2H), 7.20 – 7.28 (m, 3H), 7.29 – 7.42 (m, 9H).

^{13}C NMR (75 MHz, $CDCl_3$): 13.8, 14.6, 22.9, 29.2, 29.7, 30.3, 59.5, 85.0, 106.4, 113.5, 117.5, 123.0, 126.5, 127.3, 127.4, 127.8, 128.0, 128.3, 128.6, 131.5, 143.1, 143.9, 147.9, 149.9, 158.1, 193.8.

HR-MS (ESI) calc. for $[C_{33}H_{32}BrNO_3+H]^+$ 570.1638, found 570.1637.



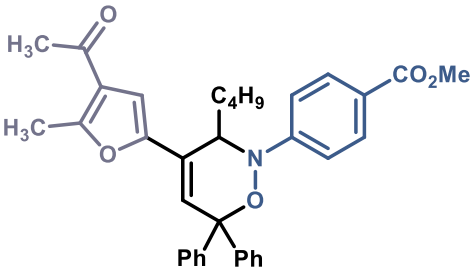
4d

1-(5-(2-(4-Bromophenyl)-6-butyl-3,3-diphenyl-3,6-dihydro-2H-1,2-oxazin-5-yl)-2-methylfuran-3-yl)ethan-1-one (**4d**): The representative procedure C was followed using cyclopropane **1b** (38.7 mg, 0.10 mmol), nitrosobenzene **2d** (74.5 mg, 0.4 mmol) and $Bi(OTf)_3$ (29.5 mg, 0.05 mmol). After 15 h, analysis of the crude mixture (TLC) indicated the disappearance of **1b**. Purification by flash chromatography (SiO_2, hexanes:EtOAc = 20:1) afforded **4c** (36.1 mg, 63%) as a yellow oil.

^{1}H NMR (300 MHz, $CDCl_3$): 0.90 (t, *J* = 7.2 Hz, 3H), 1.30 – 1.40 (m, 4H), 1.78 – 1.84 (m, 1H), 2.32 – 2.46 (bs, 1H), 2.42 (s, 3H, overlapped), 2.58 (s, 3H), 4.79 (d, *J* = 9.8 Hz, 1H), 6.20 (s, 1H), 6.46 (s, 1H), 6.66 (d_{ap}, *J* = 9.0 Hz, 2H), 7.10 (d_{ap}, *J* = 9.0 Hz, 2H), 7.20 – 7.28 (m, 5H), 7.29 – 7.38 (m, 3H), 7.58 (bs, 2H).

^{13}C NMR (75 MHz, $CDCl_3$): 14.0, 14.5, 22.3, 28.7, 29.2, 32.2, 74.0, 106.2, 115.8, 121.8, 122.9, 126.3, 127.2, 127.6, 127.7, 128.2, 128.9, 129.7, 130.3, 130.6, 148.0, 149.0, 158.0, 193.7.

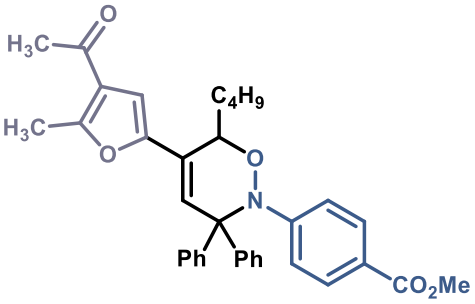
HR-MS (ESI) calc. for $[C_{33}H_{32}BrNO_3+H]^+$ 570.1638, found 570.1636.



3e

Methyl 4-(4-(4-acetyl-5-methylfuran-2-yl)-3-butyl-6,6-diphenyl-3,6-dihydro-2*H*-1,2-oxazin-2-yl)benzoate (**3e**): The representative procedure B was followed using cyclopropane **1b** (38.5 mg, 0.10 mmol), nitrosoarene **2e** (66.0 mg, 0.4 mmol) and $MgBr_2$ (8.5 mg, 0.05 mmol). After 15 h, analysis of the crude mixture (TLC) indicated the disappearance of **1b**. Purification by flash chromatography (SiO_2, hexanes:EtOAc = 10:1) afforded **3e** (33.0 mg, 60%) as a yellow oil.

^{1}H NMR (300 MHz, $CDCl_3$): 0.75 (t, *J* = 7.1 Hz, 3H), 1.15 – 1.28 (m, 4H), 1.87 – 1.92 (m, 1H), 2.02 – 2.07 (m, 1H) 2.46 (s, 3H), 2.66 (s, 3H), 3.88 (s, 3H), 4.70 (t, *J* = 5.2 Hz, 1H), 6.61 (s, 1H), 6.83 (s, 1H), 7.12 (d, *J* = 8.9 Hz, 2H), 7.21 – 7.27 (m, 3H), 7.33 – 7.44 (m, 7H), 7.92 (d, *J* = 8.9 Hz, 2H).
^{13}C NMR (75 MHz, $CDCl_3$): 13.7, 14.6, 22.9, 29.2, 29.4, 31.1, 51.8, 58.3, 85.3, 106.5, 113.9, 121.8, 123.0, 126.5, 127.1, 127.6, 127.8, 128.0, 128.2, 128.4, 130.6, 142.9, 143.5, 149.6, 152.4, 158.2, 167.1, 193.8.
HR-MS (ESI) calc. for $[C_{35}H_{35}NO_5+H]^+$ 550.2588, found 550.2592.



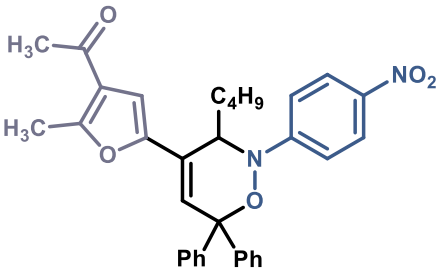
4e

Methyl 4-(5-(4-acetyl-5-methylfuran-2-yl)-6-butyl-3,3-diphenyl-3,6-dihydro-2*H*-1,2-oxazin-2-yl)benzoate (**4e**): The representative procedure C was followed using cyclopropane **1b** (38.7 mg, 0.10 mmol), nitrosobenzene **2e** (66.0 mg, 0.4 mmol) and $Fe(OTf)_3$ (22.5 mg, 0.05 mmol). After 15 h, analysis of the crude mixture (TLC) indicated the disappearance of **1b**. Purification by flash chromatography (SiO_2, hexanes:EtOAc = 10:1) afforded **4e** (31.5 mg, 57%) as a light yellow oil. *[Compound **3e** (14.5 mg, 26%) was also isolated]*.

^{1}H NMR (300 MHz, $CDCl_3$): 0.91 (t, *J* = 7.0 Hz, 3H), 1.36 – 1.61 (m, 4H), 1.83 – 1.88 (m, 1H), 2.33 – 2.38 (m, 1H), 2.43 (s, 3H), 2.58 (s, 3H), 3.83 (s, 3H), 4.85 (d, *J* = 9.6 Hz, 1H), 6.25 (s, 1H), 6.46 (s, 1H), 6.87 (d, *J* = 9.0 Hz, 2H), 7.18 – 7.31 (m, 5H), 7.32 – 7.42 (m, 3H), 7.58 (d, *J* = 7.2 Hz, 1H), 7.69 (d, *J* = 9.0 Hz, 2H).

^{13}C NMR (75 MHz, $CDCl_3$): 14.0, 14.5, 22.4, 28.9, 29.2, 32.3, 51.7, 73.6, 77.4, 106.3, 117.8, 123.0, 123.1, 125.9, 127.5, 127.8, 128.4, 128.9, 129.4, 129.7, 129.8, 148.8, 153.0, 158.1, 167.0, 193.7.

HR-MS (ESI) calc. for $[C_{35}H_{35}NO_5+H]^+$ 550.2588, found 550.2586.



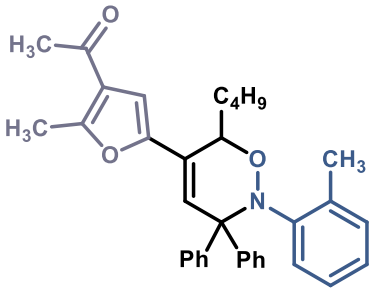
3f

1-(5-(3-Butyl-2-(4-nitrophenyl)-6,6-diphenyl-3,6-dihydro-2*H*-1,2-oxazin-4-yl)-2-methylfuran-3-yl)ethan-1-one (**3f**): The representative procedure B was followed using cyclopropane **1b** (38.5 mg, 0.10 mmol), nitrosoarene **2f** (61 mg, 0.4 mmol) and $Zn(OTf)_2$ (22.5 mg, 0.05 mmol). After 15 h, analysis of the crude mixture (TLC) indicated the disappearance of **1b**. Purification by flash chromatography (SiO_2, hexanes:EtOAc = 10:1) afforded **3f** (39.8 mg, 74%) as an orange oil. When the reaction was performed using $Bi(OTf)_3$ (28.5 mg, 0.05 mmol) under otherwise identical reaction conditions, **3f** (25.2 mg, 47%) was also obtained but the formation of the expected **4f** was not detected.

^{1}H NMR (400 MHz, $CDCl_3$): 0.79 (t, *J* = 7.0 Hz, 3H), 1.14 – 1.41 (m, 4H), 1.88 – 2.00 (m, 1H), 2.03 – 2.25 (m, 1H), 2.47 (s, 3H), 2.66 (s, 3H), 4.81 (t, *J* = 5.4 Hz, 1H), 6.65 (s, 1H), 6.77 (s, 1H), 7.02 (d, *J* = 9.3 Hz, 2H), 7.19 – 7.33 (m, 3H), 7.34 – 7.50 (m, 7H), 8.07 (d, *J* = 9.2 Hz, 2H).

^{13}C NMR (100 MHz, $CDCl_3$): 13.8, 14.6, 22.8, 29.2, 31.7, 57.4, 85.8, 106.8, 112.6, 123.1, 125.3, 126.3, 126.8, 127.5, 127.9, 128.0, 128.1, 128.5, 140.1, 142.3, 142.7, 149.1, 153.1, 158.4, 193.7.

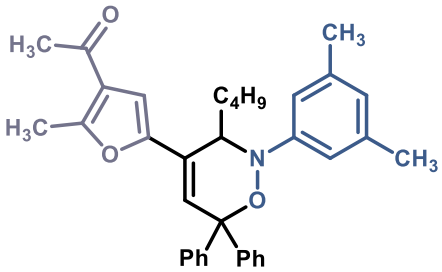
HR-MS (ESI) calc. for $[C_{33}H_{32}N_2O_5+H]^+$ 537.2384, found 537.2386.



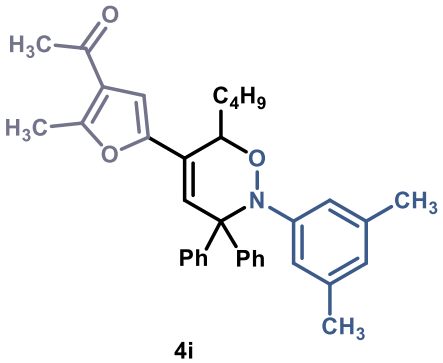
4h

1-(5-(6-Butyl-3,3-diphenyl-2-(o-tolyl)-3,6-dihydro-2*H*-1,2-oxazin-5-yl)-2-methylfuran-3-yl)ethan-1-one (**4h**): The representative procedure C was followed using cyclopropane **1b** (38.7 mg, 0.10 mmol), nitrosobenzene **2h** (48.9 mg, 0.4 mmol) and $Bi(OTf)_3$ (32.0 mg, 0.05 mmol). After 15 h, analysis of the crude mixture (TLC) indicated the disappearance of **1b**. Purification by flash chromatography (SiO_2, hexanes:EtOAc = 20:1 to 5:1) afforded **4h** (25.0 mg, 47%, inseparable mixture of regioisomers) as a pale yellow oil. A second flash chromatography (SiO_2, hexanes:EtOAc = 20:1 to 5:1) enabled the isolation of **4h** (13 mg) as single isomer.

^{1}H NMR (400 MHz, $CDCl_3$): 0.71 (t, *J* = 6.9 Hz, 3H), 1.03 – 1.20 (m, 4H), 1.63 – 1.73 (m, 1H), 1.79 (bs, 1H), 2.36 (bs, 3H), 2.40 (s, 3H), 2.65 (s, 3H), 4.39 (d, *J* = 7.1 Hz, 1H), 6.37 (s, 1H), 6.71 (td, *J* = 7.9, 1.6 Hz, 1H), 6.83 (dd, *J* = 8.2, 1.3 Hz, 1H), 6.91 (td, *J* = 7.3, 1.3 Hz, 1H), 7.04 – 7.20 (m, 2H), 7.16 – 7.24 (m, 3H), 7.25 – 7.36 (m, 3H), 7.45 (d, *J* = 7.1 Hz, 2H), 7.66 (d, *J* = 7.0 Hz, 2H).
^{13}C NMR (101 MHz, $CDCl_3$): 13.8, 14.6, 19.5, 22.5, 26.7, 29.2, 32.1, 68.3, 71.6, 106.4, 122.8, 124.3, 125.3, 126.2, 126.3, 126.8, 127.8, 127.9, 128.0, 128.08, 128.11, 130.9, 137.2, 142.0, 142.9, 149.1, 157.8, 193.9 (various aromatic CH-atoms appear at the same chemical shift).
HR-MS (ESI) calc. for $[C_{34}H_{35}NO_3+H]^+$ 506.2690, found 506.2693.



3i



4i

1-(5-(3-Butyl-2-(3,5-dimethylphenyl)-6,6-diphenyl-3,6-dihydro-2*H*-1,2-oxazin-4-yl)-2-methylfuran-3-yl)ethan-1-one (**3i**) and **1-(5-(6-butyl-2-(3,5-dimethylphenyl)-3,3-diphenyl-3,6-**

dihydro-2*H*-1,2-oxazin-5-yl)-2-methylfuran-3-yl)ethan-1-one (**4i**): The representative procedure B was followed using cyclopropane **1b** (38.5 mg, 0.10 mmol), nitrosoarene **2i** (49 mg, 0.4 mmol) and $In(OTf)_3$ (28.1 mg, 0.04 mmol). After 15 h, analysis of the crude mixture (TLC) indicated the disappearance of **1b** and the formation of **3i** (32% NMR yield) and **4i** (17% NMR yield) (49% combined, *rr* = 2:1). Purification by two consecutive flash chromatographies (SiO_2, hexanes:EtOAc = 10:1) enabled the isolation of both regioisomers: **3i** (12 mg) and **4i** (7.2 mg). *(Note: other fractions contain both regioisomers and residues arising from decomposition of nitrosoarene and starting cyclopropane).*

Characterization data for compound **3i**:

^{1}H NMR (300 MHz, $CDCl_3$): 0.72 (t, *J* = 7.0 Hz, 3H), 1.07 – 1.25 (m, 4H), 1.72 – 1.84 (m, 1H), 1.91 – 2.04 (m, 1H), 2.29 (s, 6H), 2.44 (s, 3H), 2.64 (s, 3H), 4.45 (t, *J* = 5.2 Hz, 1H), 6.56 (s, 1H), 6.59 (s, 1H), 6.79 (s, 2H), 6.85 (s, 1H), 7.18 – 7.44 (m, 10H).

^{13}C NMR (75 MHz, $CDCl_3$): 13.8, 14.6, 21.7, 22.9, 29.2, 29.7, 30.1, 59.8, 84.7, 106.2, 113.9, 122.9, 123.2, 126.5, 127.1, 127.2, 127.4, 127.7, 128.0, 128.2, 129.0, 138.1, 143.5, 144.2, 149.0, 150.2, 158.0, 193.9.

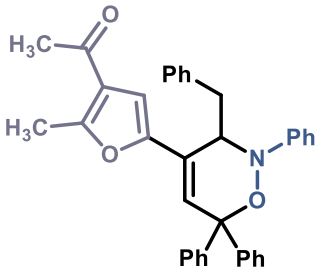
HR-MS (ESI) calc. for $[C_{35}H_{37}NO_3+H]^+$ 520.2846, found 520.2844.

Characterization data for compound **4i**:

^{1}H NMR (300 MHz, $CDCl_3$): 0.91 (t, *J* = 7.2 Hz, 3H), 1.25 – 1.59 (m, 5H), 1.74 – 1.89 (m, 1H), 2.04 (s, 6H), 2.42 (s, 3H), 2.57 (s, 3H), 4.78 (d, *J* = 9.5 Hz, 1H), 6.25 (s, 1H), 6.36 (s, 2H), 6.44 (s, 1H), 6.52 (s, 1H), 7.11 – 7.26 (m, 5H), 7.26 – 7.41 (m, 3H), 7.58 (bs, 2H).

^{13}C NMR (75 MHz, $CDCl_3$): 14.0, 14.5, 21.4, 22.4, 28.8, 29.2, 32.3, 73.6, 77.2, 106.0, 118.2, 122.9, 124.4, 126.3, 127.1, 127.35, 127.39, 127.9, 129.4, 129.6, 129.8, 130.4, 136.9, 148.6, 149.3, 158.0, 193.9.

HR-MS (ESI) calc. for $[C_{35}H_{37}NO_3+H]^+$ 520.2846, found 520.2847.



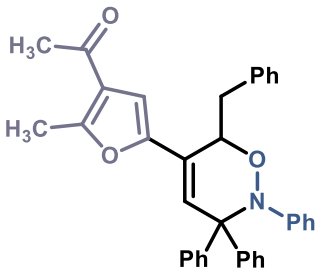
3j

1-(5-(3-Benzyl-2,6,6-triphenyl-3,6-dihydro-2*H*-1,2-oxazin-4-yl)-2-methylfuran-3-yl)ethan-1-one (**3j**): The representative procedure B was followed using cyclopropane **1c** (42.1 mg, 0.10 mmol), nitrosoarene **2a** (48.3 mg, 0.4 mmol) and $Zn(OTf)_2$ (16.5 mg, 0.05 mmol). After 15 h, analysis of the crude mixture (TLC) indicated the disappearance of **1b**. Purification by flash chromatography (SiO_2, hexanes:EtOAc = 20:1) afforded **3j** (31.5 mg, 60%) as a yellow oil.

^{1}H NMR (400 MHz, $CDCl_3$): 2.21 (s, 3H), 2.50 (s, 3H), 3.14 (dd, *J* = 13.6, 8.1 Hz, 1H), 3.28 (dd, *J* = 13.6, 3.7 Hz, 1H), 4.66 (ddd, *J* = 8.2, 3.7, 0.9 Hz, 1H), 5.86 (s, 1H), 6.88 (s, 1H), 6.94 – 7.01 (m, 3H), 7.05 – 7.12 (m, 2H), 7.19 – 7.30 (m, 6H), 7.31 – 7.41 (m, 7H), 7.43 – 7.47 (m, 2H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 14.3, 29.0, 37.0, 62.2, 85.0, 107.3, 116.0, 121.6, 122.4, 126.0, 126.4, 127.3, 127.3, 127.7, 128.0, 128.3, 128.6, 128.9, 129.7, 139.1, 143.3, 144.1, 148.5, 149.3, 157.8, 194.0.

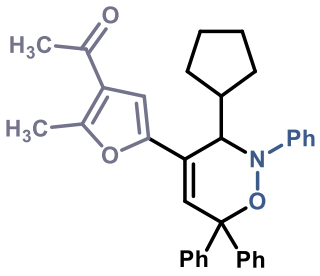
HR-MS (ESI) calc. for $[C_{36}H_{31}NO_3+H]^+$ 526.2377, found 526.2380.



4j

1-(5-(6-Benzyl-2,3,3-triphenyl-3,6-dihydro-2*H*-1,2-oxazin-5-yl)-2-methylfuran-3-yl)ethan-1-one (**4j**): The representative procedure C was followed using cyclopropane **1c** (42.0 mg, 0.10 mmol), nitrosobenzene **2a** (48.3 mg, 0.4 mmol) and $Fe(OTf)_3$ (22.5 mg, 0.05 mmol). After 15 h, analysis of the crude mixture (TLC) indicated the disappearance of **1b**. Purification by flash chromatography (SiO_2, hexanes:EtOAc = 10:1) afforded **4e** (38.6 mg, 73%) as a light yellow oil.

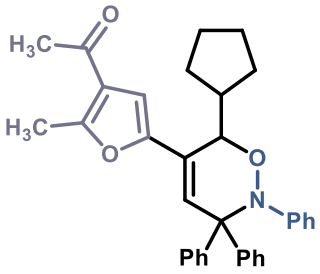
^{1}H NMR (400 MHz, $CDCl_3$): 2.43 (s, 3H), 2.61 (s, 3H), 3.21 (dd, *J* = 14.4, 2.8 Hz, 1H), 3.80 (bs, 1H), 5.04 (d, *J* = 8.7 Hz, 1H), 6.28 (s, 1H), 6.48 (s, 1H), 6.73 (dd, *J* = 8.3, 1.1 Hz, 2H), 6.88 – 6.93 (m, 2H), 6.98 (dd, *J* = 8.6, 6.8 Hz, 2H), 7.11 – 7.26 (m, 9H), 7.35 – 7.45 (m, 3H), 7.64 (s, 2H).
^{13}C NMR (101 MHz, $CDCl_3$): δ 14.5, 29.2, 39.1, 74.3, 78.5, 106.4, 120.9, 122.9, 123.3, 125.6, 126.3, 127.0, 127.5, 127.5, 127.6, 128.1, 128.2, 129.5, 129.9, 130.5, 139.0, 148.6, 149.0, 158.1, 193.8.
HR-MS (ESI) calc. for $[C_{36}H_{31}NO_3+H]^+$ 526.2377, found 526.2374.



3k

1-(5-(3-Cyclopentyl-2,6,6-triphenyl-3,6-dihydro-2*H*-1,2-oxazin-4-yl)-2-methylfuran-3-yl)ethan-1-one (**3k**): The representative procedure B was followed using cyclopropane **1d** (39.8 mg, 0.10 mmol), nitrosoarene **2a** (42.8 mg, 0.4 mmol) and $Zn(OTf)_2$ (18.2 mg, 0.05 mmol). After 15 h, analysis of the crude mixture (TLC) indicated the disappearance of **1b**. Purification by flash chromatography (SiO_2, hexanes:EtOAc = 20:1) afforded **3j** (35.0 mg, 70%) as a yellow oil.

^{1}H NMR (400 MHz, $CDCl_3$): 1.05 – 1.47 (m, 7H), 1.55 – 1.70 (m, 1H), 2.40 – 2.49 (m, 1H, overlapped signal), 2.45 (s, 3H, overlapped signal), 2.67 (s, 3H), 4.64 (s, 1H), 6.62 (s, 1H), 6.88 (s, 1H), 6.93 (t, *J* = 7.1 Hz, 1H), 7.15 – 7.36 (m, 8H), 7.35 – 7.43 (m, 4H), 7.47 (d, *J* = 7.7 Hz, 2H).
^{13}C NMR (101 MHz, $CDCl_3$): 14.6, 24.2, 24.4, 29.2, 30.5, 32.6, 42.7, 63.0, 84.7, 106.7, 115.7, 120.9, 123.0, 127.13 (two C atoms), 127.15, 127.4, 127.6, 128.0, 128.3, 128.6, 128.9, 143.4, 144.4, 149.1, 151.0, 157.8, 193.9.
HR-MS (ESI) calc. for $[C_{34}H_{33}NO_3+H]^+$ 504.2533, found 504.2531.



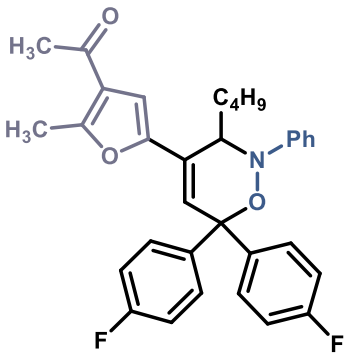
4k

1-(5-(6-Cyclopentyl-2,3,3-triphenyl-3,6-dihydro-2*H*-1,2-oxazin-5-yl)-2-methylfuran-3-yl)ethan-1-one (**4k**): The representative procedure C was followed using cyclopropane **1d** (39.5 mg, 0.10 mmol), nitrosobenzene **2a** (42.9 mg, 0.4 mmol) and $Fe(OTf)_3$ (22.5 mg, 0.05 mmol). After 15 h, analysis of the crude mixture (TLC) indicated the disappearance of **1b**. Purification by flash chromatography (SiO_2, hexanes:EtOAc = 10:1) afforded **4e** (29.2 mg, 58%) as a light yellow oil.

^{1}H NMR (300 MHz, $CDCl_3$): 1.42 – 1.83 (m, 8H), 2.43 (s, 3H), 2.61 (s, 3H), 2.79 (bs, 1H), 4.86 (bs, 1H), 6.23 (s, 1H), 6.51 (s, 1H), 6.79 (d, *J* = 7.6 Hz, 2H), 6.89 (t, *J* = 7.2 Hz, 1H), 7.01 (t, *J* = 7.7 Hz, 2H), 7.25 (bs, 4H), 7.34 (bs, 4H), 7.48 (bs, 2H).

^{13}C NMR (75 MHz, $CDCl_3$, due to broaden signals, relaxation time (d1) was 10s, however some peaks did not appear in ^{13}C NMR and were obtained by indirect measurement using ^{1}H/^{13}C-HSQC experiment): 14.5, 24.9 (broad signal), 25.9, 29.2, 29.8 (broad signal), 43.9 (CH detected via HSQC), 74.3, 80.0 (broad signal), 106.7, 120.2, 122.8, 122.9, 127.1, 127.4, 127.5, 127.7, 130.1, 131.6 (broad signal), 148.9, 149.8, 157.7, 194.0.

HR-MS (ESI) calc. for $[C_{34}H_{33}NO_3+H]^+$ 504.2533, found 504.2534.



3l

1-(5-(3-Butyl-6,6-*bis*(4-fluorophenyl)-2-phenyl-3,6-dihydro-2*H*-1,2-oxazin-4-yl)-2-methylfuran-3-yl)ethan-1-one (**3l**): The representative procedure B was followed using

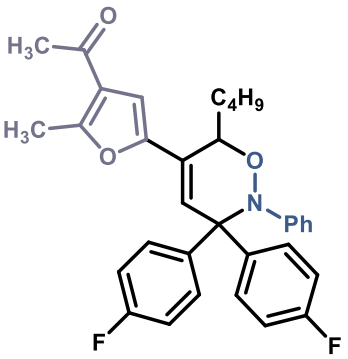
cyclopropane **1e** (42.5 mg, 0.10 mmol), nitrosoarene **2a** (48.3 mg, 0.4 mmol) and $Zn(OTf)_2$ (16.5 mg, 0.05 mmol). After 15 h, analysis of the crude mixture (TLC) indicated the disappearance of **1e**. Purification by flash chromatography (SiO_2, hexanes:EtOAc = 20:1) afforded **3l** (29.5 mg, 56%) as a yellow oil.

^{1}H NMR (300 MHz, $CDCl_3$): 0.71 (t, *J* = 7.0 Hz, 3H), 1.02 – 1.34 (m, 4H), 1.68 – 1.90 (m, 1H), 1.90 – 2.10 (m, 1H), 2.44 (s, 3H), 2.65 (s, 3H), 4.49 (t, *J* = 5.2 Hz, 1H), 6.58 (s, 1H), 6.76 (s, 1H), 6.87 – 6.99 (m, 3H), 7.04 (t, *J* = 8.8 Hz, 2H), 7.14 (d, *J* = 8.1 Hz, 2H), 7.28 (t, *J* = 8.0 Hz, 2H), 7.30 – 7.42 (m, 4H).

^{13}C NMR (75 MHz, $CDCl_3$): 13.8, 14.6, 22.9, 29.2, 29.7, 30.2, 59.8, 83.9, 106.6, 114.9 (d, *J* = 21.0 Hz), 115.2 (d, *J* = 20.9 Hz), 115.9, 121.6, 123.0, 125.8, 128.7, 129.0 (d, *J* = 8.2 Hz), 129.1 (d, *J* = 8.2 Hz), 129.2, 139.1 (d, *J* = 2.8 Hz), 139.7 (d, *J* = 3.1 Hz), 148.7, 149.7, 128.3, 162.0 (d, *J* = 246.1 Hz), 162.2 (d, *J* = 247.2 Hz), 193.9.

^{19}F NMR (282 MHz, $CDCl_3$): -115.2 (s), -114.3 (s).

HR-MS (ESI) calc. for $[C_{33}H_{31}F_2NO_3+H]^+$ 528.2345, found 528.2354.



4l

1-(5-(6-Butyl-3,3-*bis*(4-fluorophenyl)-2-phenyl-3,6-dihydro-2*H*-1,2-oxazin-5-yl)-2-methylfuran-3-yl)ethan-1-one (**4l**): The representative procedure C was followed using cyclopropane **1e** (42.0 mg, 0.10 mmol), nitrosobenzene **2a** (48.3 mg, 0.4 mmol) and $Bi(OTf)_3$ (32.5 mg, 0.05 mmol). After 15 h, analysis of the crude mixture (TLC) indicated the disappearance of **1e**. Purification by flash chromatography (SiO_2, hexanes:EtOAc = 10:1) afforded **4l** (28.0 mg, 53%) as a light yellow oil.

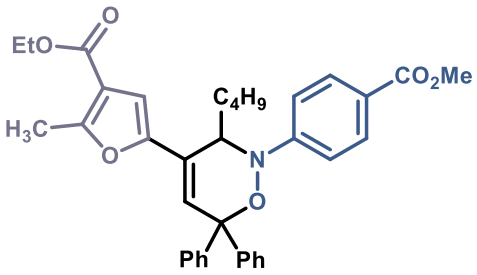
^{1}H NMR (300 MHz, $CDCl_3$): 0.88 (t, *J* = 7.0 Hz, 3H), 1.23 – 1.57 (m, 4H), 1.73 – 1.88 (m, 1H), 2.31 – 2.45 (m, 1H, overlapped), 2.43 (s, 3H, overlapped), 2.58 (s, 3H), 4.78 (d, *J* = 10.1 Hz, 1H), 6.11

(s, 1H), 6.46 (s, 1H), 6.73 (d, *J* = 7.9 Hz, 2H), 6.81 – 6.94 (m, 3H), 6.96 – 7.11 (m, 6H), 7.53 (bs, 2H).

^{13}C NMR (75 MHz, $CDCl_3$): 14.1, 14.7, 22.5, 28.7, 29.3, 32.4, 73.4, 77.4, 106.5, 114.1 (d, *J* = 21.2 Hz), 115.1 (d, *J* = 21.1 Hz), 120.8, 123.1, 123.6, 126.8, 127.9, 131.6 (d, *J* = 7.2 Hz), 132.1 (d, *J* = 7.7 Hz), 148.7, 149.0, 158.2, 162.2 (d, *J* = 247.7 Hz), 162.3 (d, *J* = 247.3 Hz), 193.9 (missing signals due to overlapping).

^{19}F NMR (282 MHz, $CDCl_3$): 114.61 (s), -114.64 (s).

HR-MS (ESI) calc. for $[C_{33}H_{31}F_2NO_3+H]^+$ 528.2345, found 528.2346.



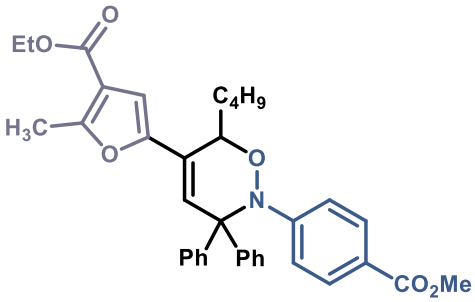
3m

Ethyl 5-(3-butyl-2-(4-(methoxycarbonyl)phenyl)-6,6-diphenyl-3,6-dihydro-2*H*-1,2-oxazin-4-yl)-2-methylfuran-3-carboxylate (**3m**): The representative procedure B was followed using cyclopropane **1f** (41.8 mg, 0.10 mmol), nitrosoarene **2e** (66.0 mg, 0.4 mmol) and $MgBr_2$ (8.5 mg, 0.05 mmol). After 15 h, analysis of the crude mixture (TLC) indicated the disappearance of **1b**. Purification by flash chromatography (SiO_2, hexanes:EtOAc = 10:1) afforded **3m** (41.7 mg, 72%) as a yellow oil.

^{1}H NMR (400 MHz, $CDCl_3$): 0.74 (t, *J* = 7.1 Hz, 3H), 1.17 – 1.29 (m, 4H), 1.39 (t, *J* = 7.1 Hz, 3H), 1.81 – 1.93 (m, 1H), 1.98 – 2.25 (m, 1H), 2.64 (s, 3H), 3.88 (s, 3H), 4.33 (qd, *J* = 7.2, 1.3 Hz, 2H), 4.68 (t, *J* = 5.2 Hz, 1H), 6.64 (s, 1H), 6.82 (s, 1H), 7.11 (d, *J* = 8.9 Hz, 2H), 7.18 – 7.27 (m, 3H), 7.31 – 7.60 (m, 7H), 7.92 (d, *J* = 9.0 Hz, 2H).

^{13}C NMR (101 MHz, $CDCl_3$): 13.7, 13.9, 14.4, 22.9, 29.4, 31.1, 51.7, 58.3, 60.3, 85.2, 107.0, 113.9, 115.2, 121.7, 126.1, 127.1, 127.6, 127.8, 128.0, 128.2, 128.3, 130.6, 142.9, 143.6, 149.6, 152.4, 158.9, 163.8, 167.1.

HR-MS (ESI) calc. for $[C_{36}H_{37}NO_6+H]^+$ 580.2694, found 580.2696.



4m

Methyl 4-(5-(4-acetyl-5-methylfuran-2-yl)-6-butyl-3,3-diphenyl-3,6-dihydro-2*H*-1,2-oxazin-2-yl)benzoate (**4m**): The representative procedure B was followed using cyclopropane **1f** (41.8 mg, 0.10 mmol), nitrosoarene **2e** (66.0 mg, 0.4 mmol) and $Bi(OTf)_3$ (32.5 mg, 0.05 mmol). After 15 h, analysis of the crude mixture (TLC) indicated the disappearance of **1b**. Purification by flash chromatography (SiO_2, hexanes:EtOAc = 10:1) afforded **3m** (20.3 mg, 35%) as a yellow oil. *[Compound **3m** (17.9 mg, 31%) was also isolated. The reaction in the presence of $Bi(OTf)_3$ or TfOH, under otherwise identical reaction conditions, led to the formation of **3m** and **4m** in 50% (rr = 1:1) and 40% (rr = 1:1.2)].*

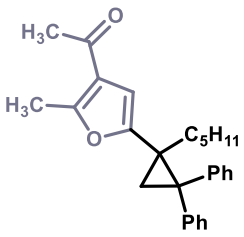
^{1}H NMR (300 MHz, $CDCl_3$): 0.89 (t, *J* = 7.2 Hz, 3H), 1.25 – 1.60 (m, 4H, overlapped signal), 1.36 (t, *J* = 7.1 Hz, 3H, overlapped signal), 1.75 – 2.02 (m, 1H), 2.25 – 2.42 (m, 1H), 2.55 (s, 3H), 3.82 (s, 3H), 4.30 (q, *J* = 7.1 Hz, 2H), 4.82 (d, *J* = 9.6 Hz, 1H), 6.22 (s, 1H), 6.49 (s, 1H), 6.86 (d, *J* = 9.0 Hz, 2H), 7.16 – 7.32 (m, 5H), 7.31 – 7.45 (m, 3H), 7.57 (d, *J* = 6.4 Hz, 2H), 7.68 (d, *J* = 9.0 Hz, 2H).

^{13}C NMR (75 MHz, $CDCl_3$): 13.9, 14.0, 14.4, 22.4, 29.0, 32.2, 51.7, 60.3, 73.5, 77.5, 106.8, 115.1, 117.7, 123.0, 125.9, 127.5, 127.7, 128.4, 129.4, 129.7, 129.8, 141.6, 148.8, 153.0, 158.8, 163.8, 167.0.

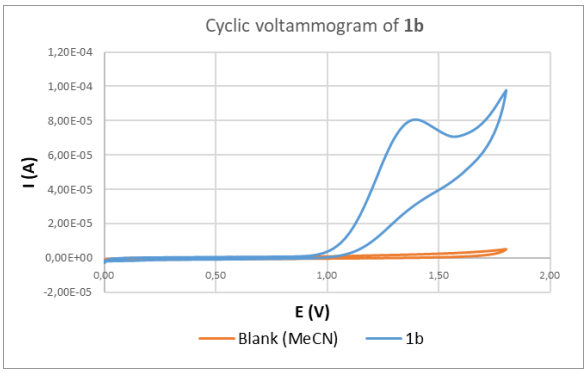
HR-MS (ESI) calc. for $[C_{36}H_{37}NO_6+H]^+$ 580.2694, found 580.2694.

Mechanistic experiments.

Cyclic voltammetry of 1b.



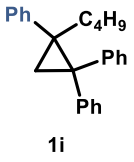
1b



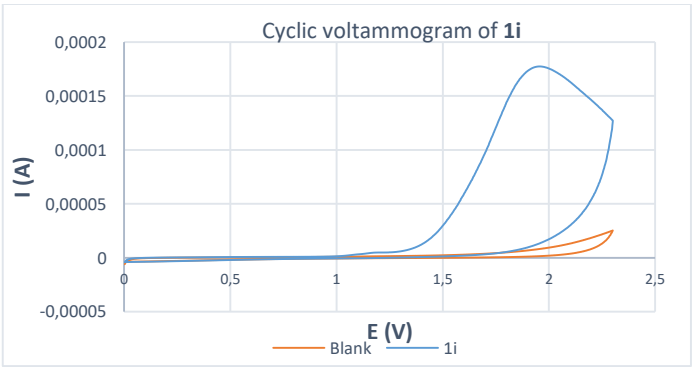
Cyclic voltammograms (CV) were accomplished at ambient temperature using an Eco Chemie BV Metrohm FRA2 Autolab Potentiostat/Galvanostat. A glassy carbon disc electrode, an Ag/AgCl electrode and a platinum sheet electrode were used. The electrolyte solution contained 5.0 mL of a 0.1 M tetrabutylammonium hexafluorophosphate and 300 μL of a 0.118 M solution of **1b** in MeCN (final concentration of **1b**: 6.68 mM). The scan rate was set at 50 mV/s in a potential window of 0.0 V to + 2.30 V.

The value obtained for E (**1b**/**1b**$^{+}$) is +1.35 V (vs Ag/AgCl).

Cyclic voltammetry of 1i.



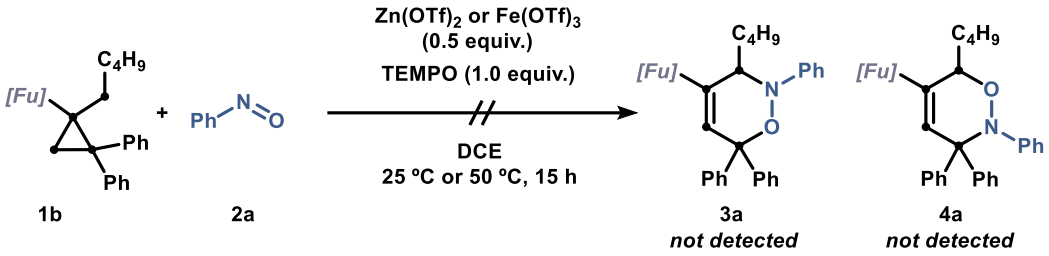
1i



Cyclic voltammograms (CV) were accomplished at ambient temperature using an Eco Chemie BV Metrohm FRA2 Autolab Potentiostat/Galvanostat. A glassy carbon disc electrode, an Ag/AgCl electrode and a platinum sheet electrode were used. The electrolyte solution contained 5.0 mL of a 0.1 M tetrabutylammonium hexafluorophosphate and 620 μL of a 0.078 M solution of **1i** in MeCN (final concentration of **1i**: 6.83 mM). The scan rate was set at 50 mV/s in a potential window of 0.0 V to + 2.30 V.

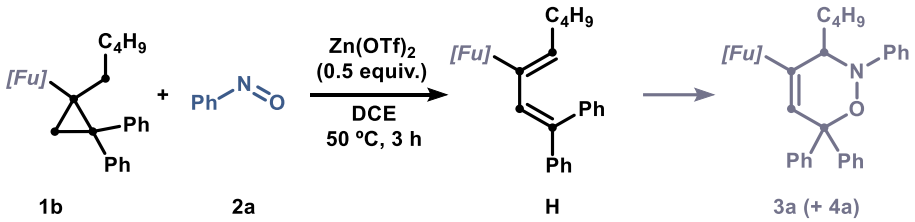
The value obtained for E (**1i**/**1i**$^{+}$) is +1.92 V (vs Ag/AgCl).

Radical inhibition experiment.



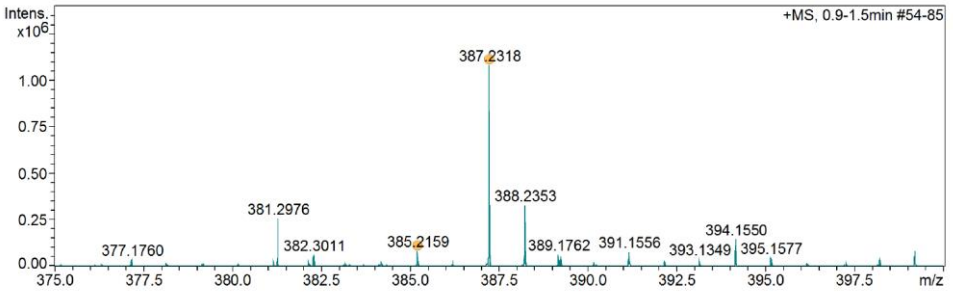
ESI-HRMS analysis.

From the reaction indicated in the scheme below, a sample for ESI-HRMS analysis was directly taken from the reaction crude mixture after 3 h and 15 h.

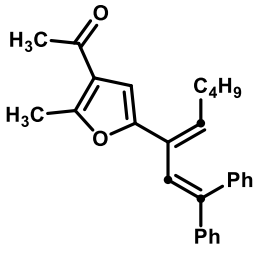


Acquisition Parameter

Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	2.4 Bar
Focus	Active	Set Capillary	3500 V	Set Dry Heater	250 °C
Scan Begin	50 m/z	Set End Plate Offset	-500 V	Set Dry Gas	6.0 l/min
Scan End	1500 m/z	Set Charging Voltage	2000 V	Set Divert Valve	Source
		Set Corona	0 nA	Set APCI Heater	0 °C

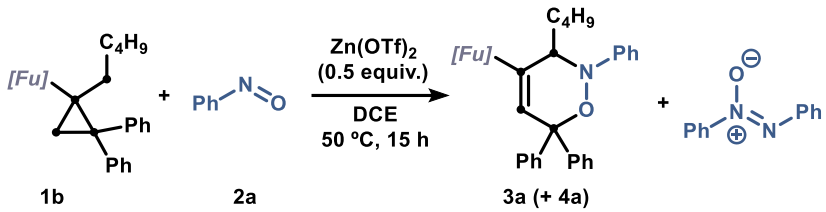


Meas. m/z	#	Ion Formula	m/z	err [ppm]	mSigma	# mSigma	Score	rdb	e⁻ Conf	N-Rule
199.0869	1	C12H11N2O	199.0866	-1.8	6.7	1	100.00	9.0	even	ok
385.2159	1	C27H29O2	385.2162	0.8	781.2	1	100.00	14.0	even	ok
387.2318	1	C27H31O2	387.2319	0.0	5.6	1	100.00	13.0	even	ok

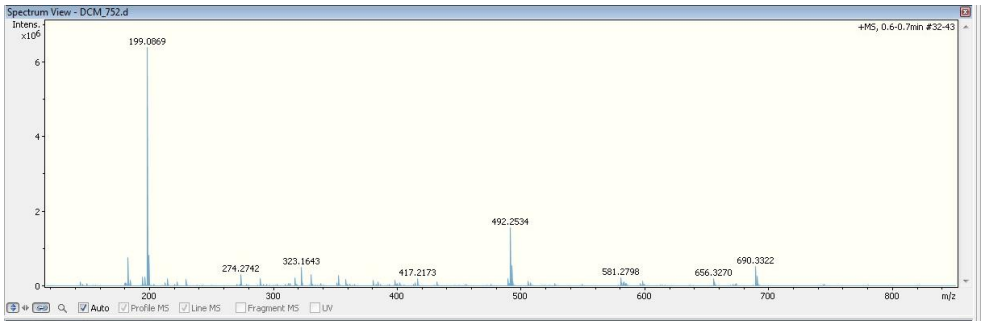


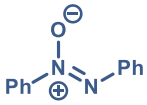
H

Chemical Formula: $C_{27}H_{28}O_2$
Exact Mass for $C_{27}H_{28}O_2$ $+H^+$**: 385.2162**
Exact Mass found $C_{27}H_{28}O_2$ $+H^+$**: 385.2159**

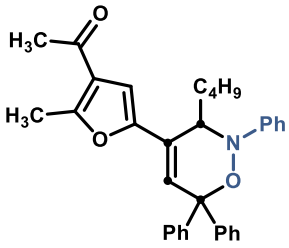


1b 2a 3a (+ 4a)





Chemical Formula: $C_{12}H_{10}N_2O$
Exact Mass calc. for $C_{12}H_{10}N_2O+H^+$**: 199.0866**
Exact Mass found $C_{12}H_{10}N_2O+H^+$**: 199.0869**

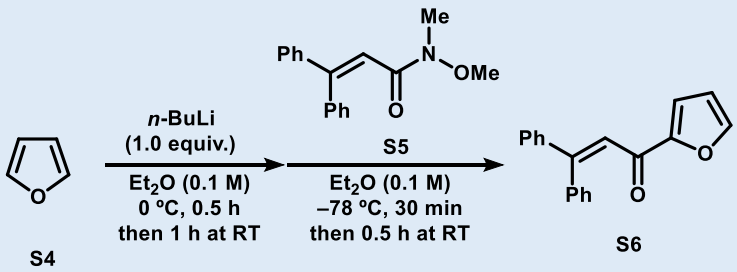


3a

Chemical Formula: $C_{33}H_{33}NO_3$
Exact Mass for $C_{33}H_{33}NO_3+H^+$**: 492.2533**
Exact Mass found $C_{33}H_{33}NO_3+H^+$**: 492.2534**

Synthesis of 1,3-diene S8 (related to intermediate H).

In order to gain additional information about the reaction mechanism, 1,3-diene **5** was prepared according to the procedure described below.[8]

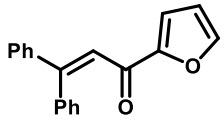


S4 **S6**

1-(Furan-2-yl)-3,3-diphenylprop-2-en-1-one (**S6**): To a solution of freshly distilled furan (**S4**, 140 µL, 1.0 equiv.) in Et_2O (0.1 M) at 0 °C, *n*-BuLi (1.2 mL, 1.0 equiv., 1.6 M in hexanes) was added

[8] In should be noticed that attempts to prepare the postulated 1,3-diene intermediate **H** were unsuccessful.

dropwise and the mixture was stirred at this temperature for 0.5 h and then at ambient temperature for 1 h. Then, the mixture was cooled to –78 °C and a solution of **S5**[9] (500 mg, 1.0 equiv.) in Et_2O (0.1 M) was added dropwise. After stirring at –78 °C for 0.5 h, the mixture was warmed to ambient temperature and allowed to stir for 1 h. A saturated aqueous solution of NH_4Cl (50 mL) was added and the phases were separated. The aqueous phase was extracted with Et_2O (3 x 20 mL). The collected organic phases were dried over Na_2SO_4, the solution was filtered and the solvent was removed under vacuum. The residue was purified by flash column chromatography (SiO_2, hexanes:AcOEt = 20:1 to 10:1) to yield ketone **S6** (376 mg, 73%) as a pale yellow oil.

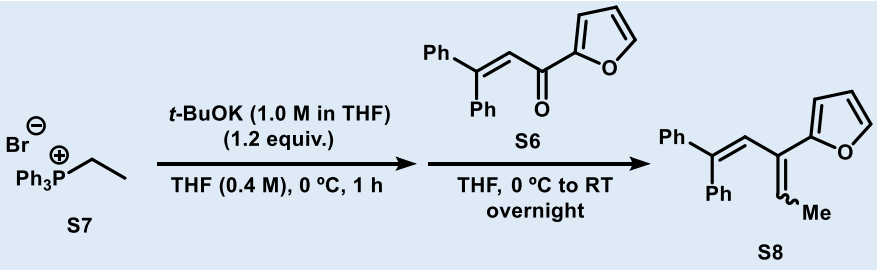


S6

^{1}H NMR (400 MHz, $CDCl_3$): δ 6.50 (dd, *J* = 3.5, 1.6 Hz, 1H), 7.15 (d, *J* = 3.5 Hz, 1H), 7.19 (s, 1H), 7.22 – 7.29 (m, 2H), 7.32 – 7.44 (m, 8H), 7.54 (dd, *J* = 1.7, 0.9 Hz, 1H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 112.3, 117.2, 121.4, 128.0, 128.3, 128.4, 128.7, 129.54, 129.58, 139.0, 141.5, 146.0, 154.1, 156.3, 178.9.

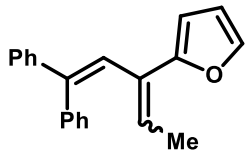
HR-MS (ESI) calc. for $[C_{19}H_{14}O_2+H]^+$ 275.1067, found 275.1071.



2-(1,1-Diphenylpenta-1,3-dien-3-yl)furan (**S8**): To a suspension of **S7** (600 mg, 1.2 equiv.) in THF (0.4 M) at 0 °C, a solution of *t*-BuOK (1.6 mL, 1.2 equiv., 1.6 M in hexanes) was added dropwise and the mixture was stirred at this temperature for 1.0 h. Then, a solution of **S6** (367 mg, 1.0 equiv.) in THF (5.0 mL) was added dropwise and the mixture was allowed to warm to ambient temperature and stirred overnight. A saturated aqueous solution of NH_4Cl (20 mL) was added and the phases were separated. The aqueous phase was extracted with Et_2O (3 x 20 mL). The collected organic phases were dried over Na_2SO_4, the solution was filtered and the solvent was

[9] K. H. Kim, S. Lee, S. H. Kim, C. H. Lim and J. N. Kim, *Tetrahedron Lett*. 2012, **53**, 5088 – 5093.

removed under vacuum. The residue was purified by flash column chromatography (SiO_2, hexanes:AcOEt = 60:1 to 40:1) to yield 1,3-diene **S8** (237 mg, 62%, 2:1 mixture of diasteroisomers) as a pale yellow oil.



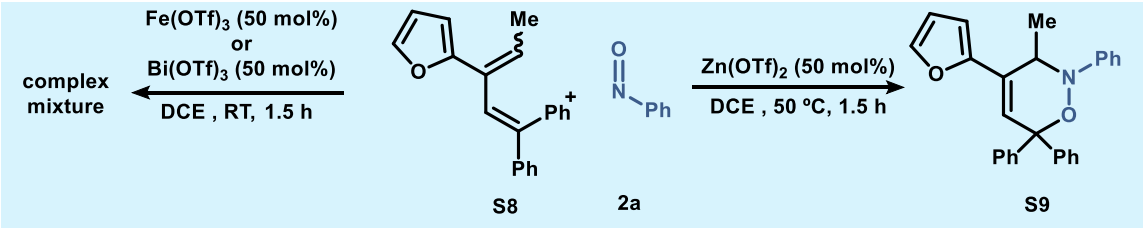
S8

^{1}H NMR (400 MHz, $CDCl_3$, *M*: major isomer, *m* = minor isomer): δ 1.52 (dd, *J* = 7.2, 1.2 Hz, 3H, *m*), 1.86 (dd, *J* = 7.4, 1.3 Hz, 3H, *M*), 5.67 (qd, *J* = 7.4, 1.2 Hz, 1H, *M*), 6.05 (q, *J* = 6.9 Hz, 1H, *m*), 6.21 – 6.25 (m, 1H, *M+m*), 6.33 (dd, *J* = 3.3, 1.8 Hz, 1H, *M*), 6.35 (dd, *J* = 3.3, 1.8 Hz, 1H, *m*), 6.50 – 6.61 (m, 0H, *m*), 6.65 – 6.81 (m, 1H, *M*), 7.10 – 7.48 (m, 11H, *M+m*).

^{13}C NMR (101 MHz, $CDCl_3$): δ 15.0, 15.5, 105.8, 109.2, 110.7, 111.1, 122.5, 122.9, 126.8, 127.3, 127.4, 127.8, 127.9, 128.0, 128.2, 128.2, 128.3, 128.3, 128.6, 129.6, 129.7, 130.2, 140.4, 141.2, 141.3, 143.0, 143.2, 143.5, 146.6, 152.9, 154.6.

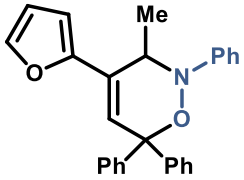
HR-MS (ESI) calc. for $[C_{21}H_{18}O+H]^+$ 287.1430, found 287.1425.

Reactivity of 1,3-diene S8 with nitrosobenzene (2a).



To a solution of the **S8** (30 mg, 0.11 mmol) in 1,2-DCE (2.0 mL), nitrosobenzene **2a** (43.5 mg, 0.45 mmol) and $Zn(OTf)_2$ (18.0 mg, 50 mol%) were added under Ar atmosphere. The resulting mixture was heated at 50 °C for 1.5 h (**S8** was consumed as indicated by TLC analysis). The solvent was removed under reduced pressure and the residue was purified by flash column chromatography (SiO_2, hexanes:EtOAc = 40:1 to 20:1) to afford oxazines **S9** (35 mg, 89%) as yellow oil.

A complex mixture was obtained when using $Fe(OTf)_3$ or $Bi(OTf)_3$ as Lewis acids.



S9

4-(Furan-2-yl)-3-methyl-2,6,6-triphenyl-3,6-dihydro-2*H*-1,2-oxazine (**S9**):

^{1}H NMR (400 MHz, CD_2Cl_2): δ 1.41 (d, *J* = 6.4 Hz, 3H), 4.67 (qd, *J* = 6.5, 1.0 Hz, 1H), 6.48 (d, *J* = 3.4 Hz, 1H), 6.53 (dd, *J* = 3.4, 1.8 Hz, 1H), 6.93 (s, 1H), 7.01 (tt, *J* = 7.2, 1.1 Hz, 1H), 7.20 – 7.28 (m, 2H), 7.26 – 7.32 (m, 1H), 7.33 – 7.43 (m, 7H), 7.46 – 7.50 (m, 2H), 7.51 (d, *J* = 1.5 Hz, 1H), 7.52 – 7.57 (m, 2H).

^{13}C NMR (101 MHz, CD_2Cl_2): δ 13.7, 55.4, 84.8, 106.2, 111.4, 115.7, 121.4, 124.8, 127.1, 127.3, 127.4, 127.6, 127.9, 128.3, 128.8, 130.1, 142.2, 143.6, 144.6, 148.7, 151.8.

HR-MS (ESI) calc. for $[C_{27}H_{23}NO_2+H]^+$ 394.1802, found 394.1799.

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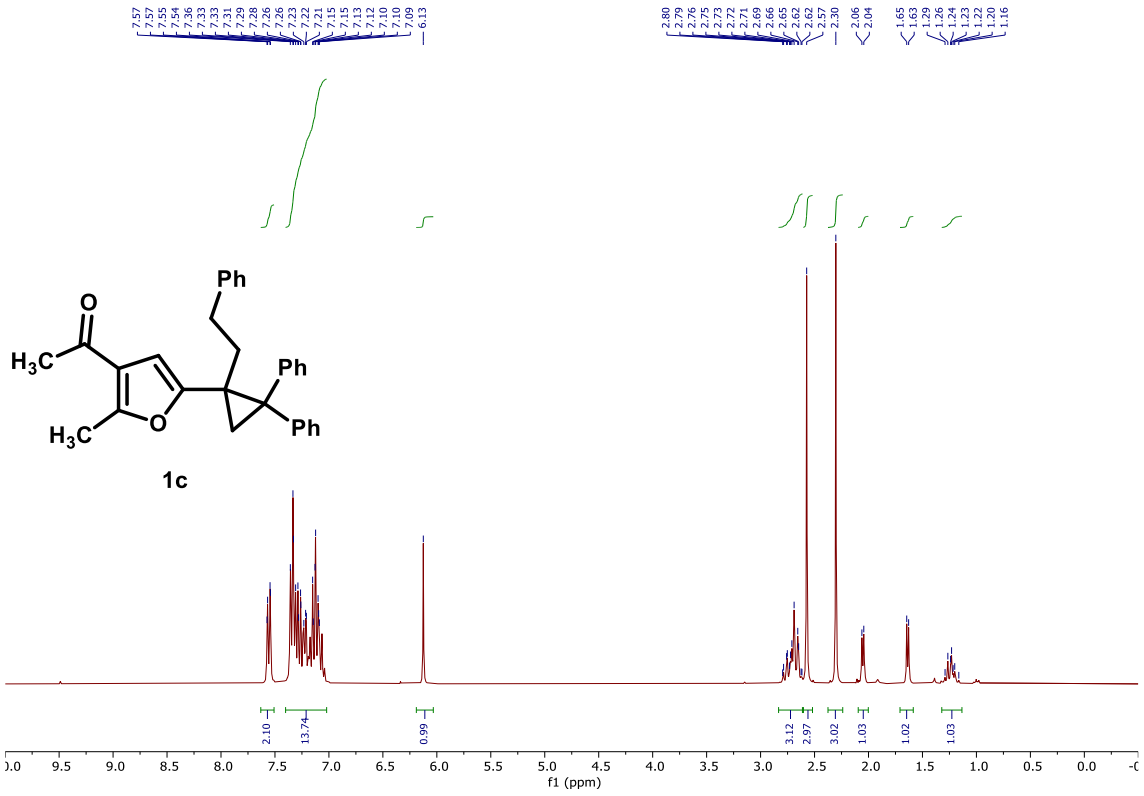
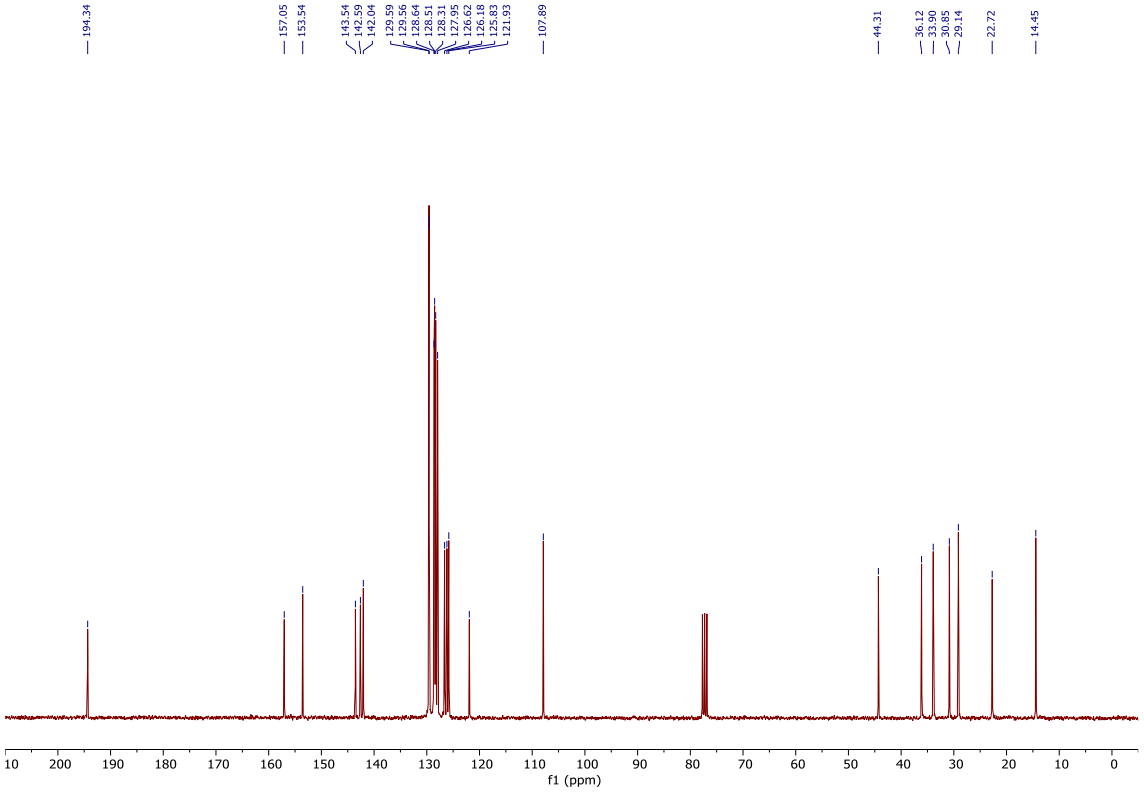
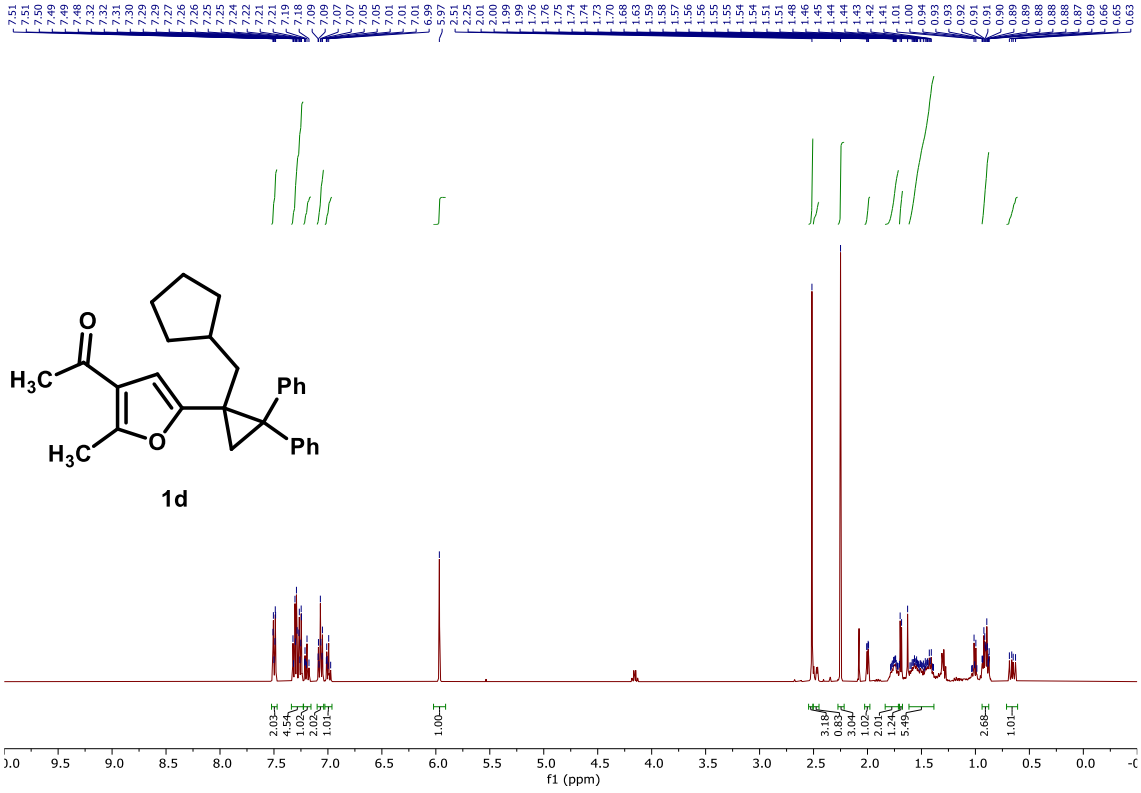
*These results point to the participation of 1,3-diene **H** as intermediate in the case of the zinc-mediated reaction. In the case of Fe and Bi, the substitution on the furanyl ring should have a crucial influence the reactivity*.

^{1}H, ^{13}C NMR and selected 2D-NMR spectra for new compounds



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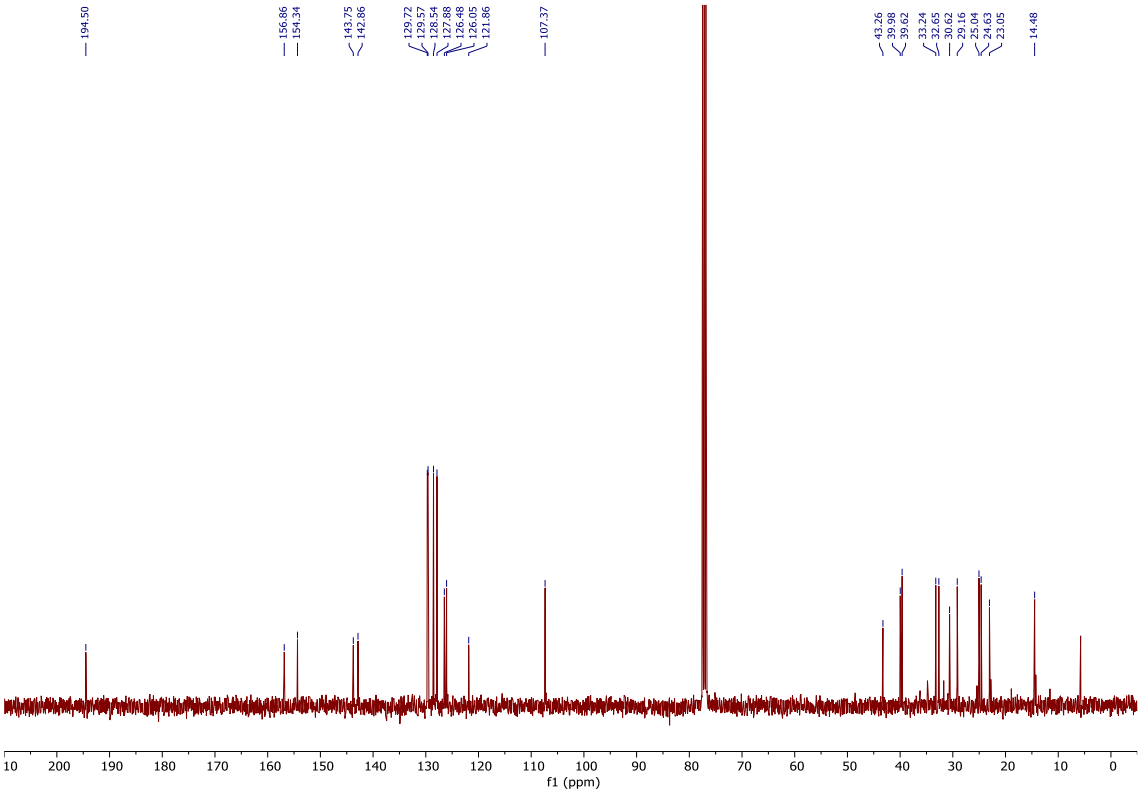
H3C
Ph
Ph
H3C
O
1d
f1 (ppm)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156.86
154.34
143.75
142.86
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129.57
128.54
127.88
126.48
126.05
121.86
107.37
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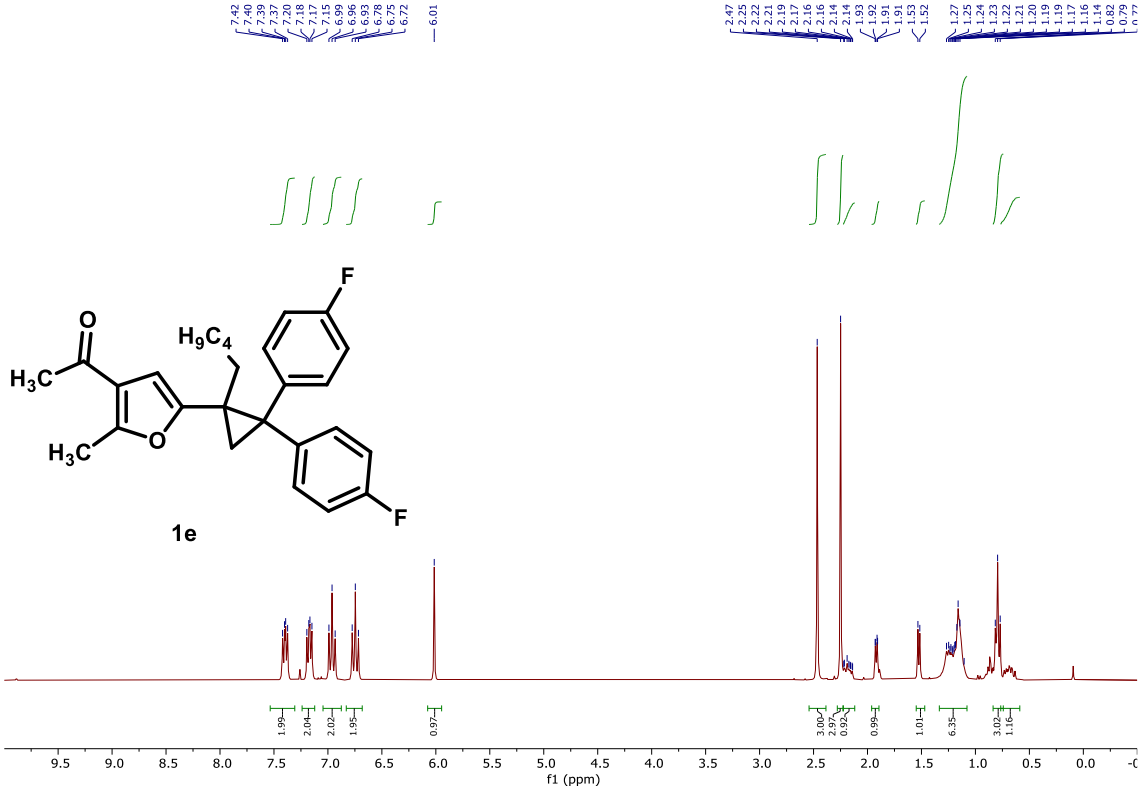
25.04
24.63
23.05
14.48
f1 (ppm)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7.39
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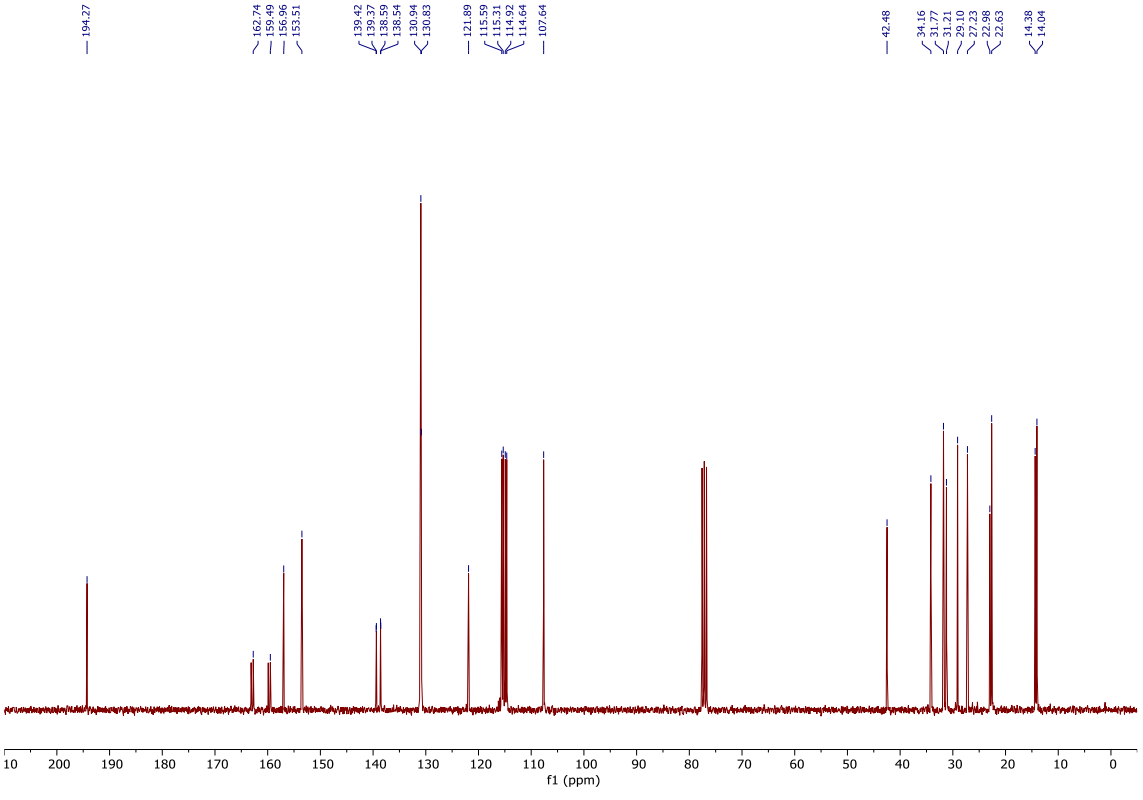
7.20
7.18
7.17
7.15
6.99
6.96
6.93
6.78
6.75
6.72
6.01
2.47
2.25
2.22
2.21
2.19
2.17
2.16
2.16
2.14
2.14
1.93
1.92
1.91
1.91
1.53
1.52
1.27
1.25
1.24
1.23
1.22
1.21
1.20
1.19
1.19
1.17
1.16
1.14
0.82
0.79
F
O
H_9C_4
H_3C
H_3C
O
F
1e
1.99
2.04
2.02
1.95
0.97
3.00
2.97
0.92
0.99
1.01
6.35
3.02
1.16
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)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138.59
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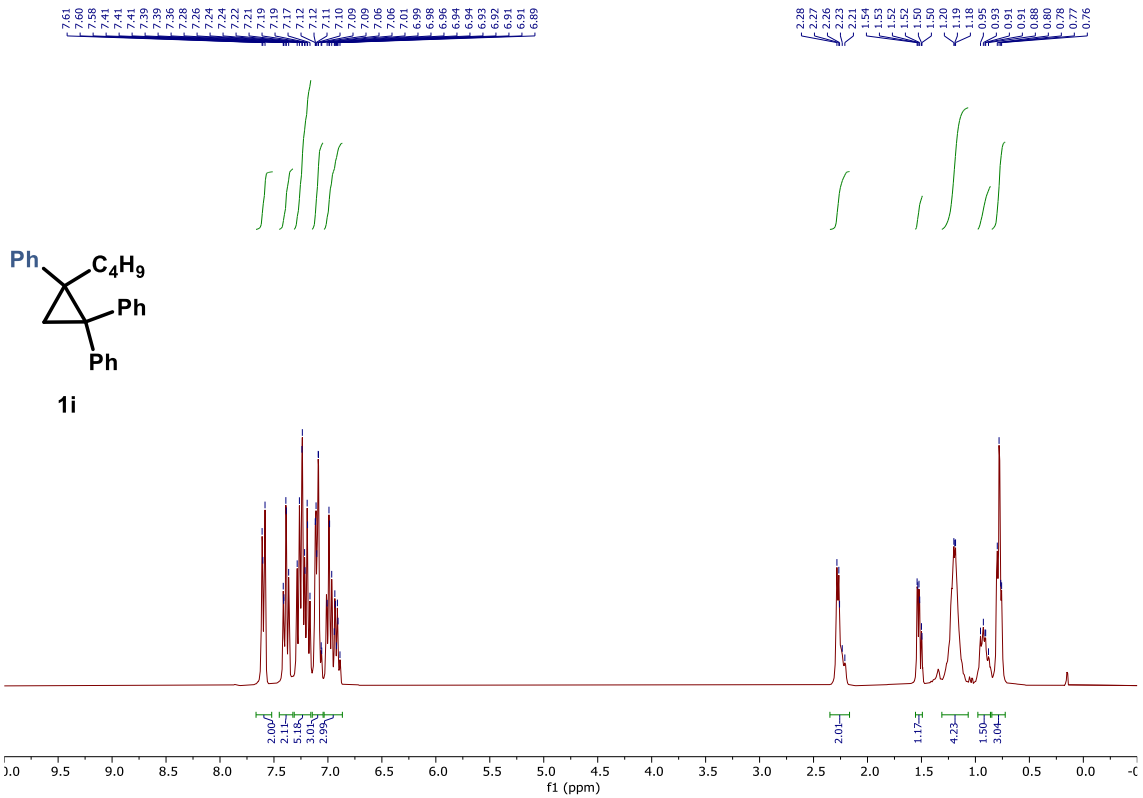
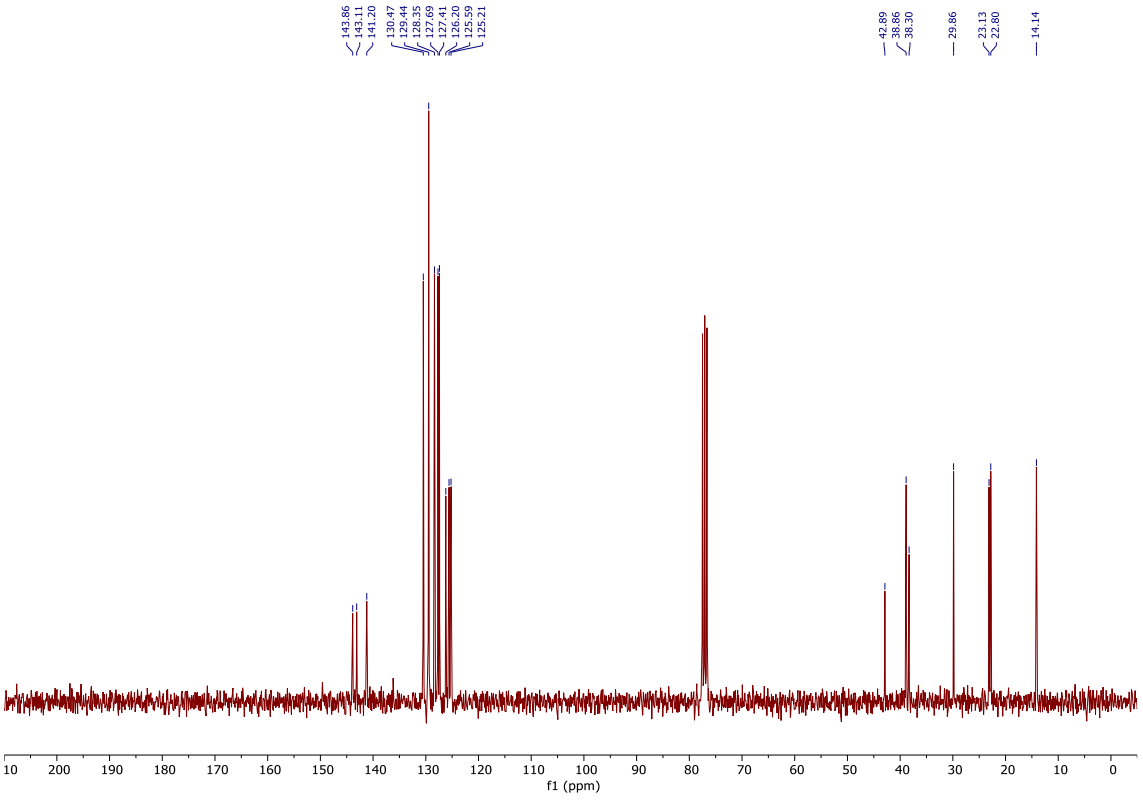
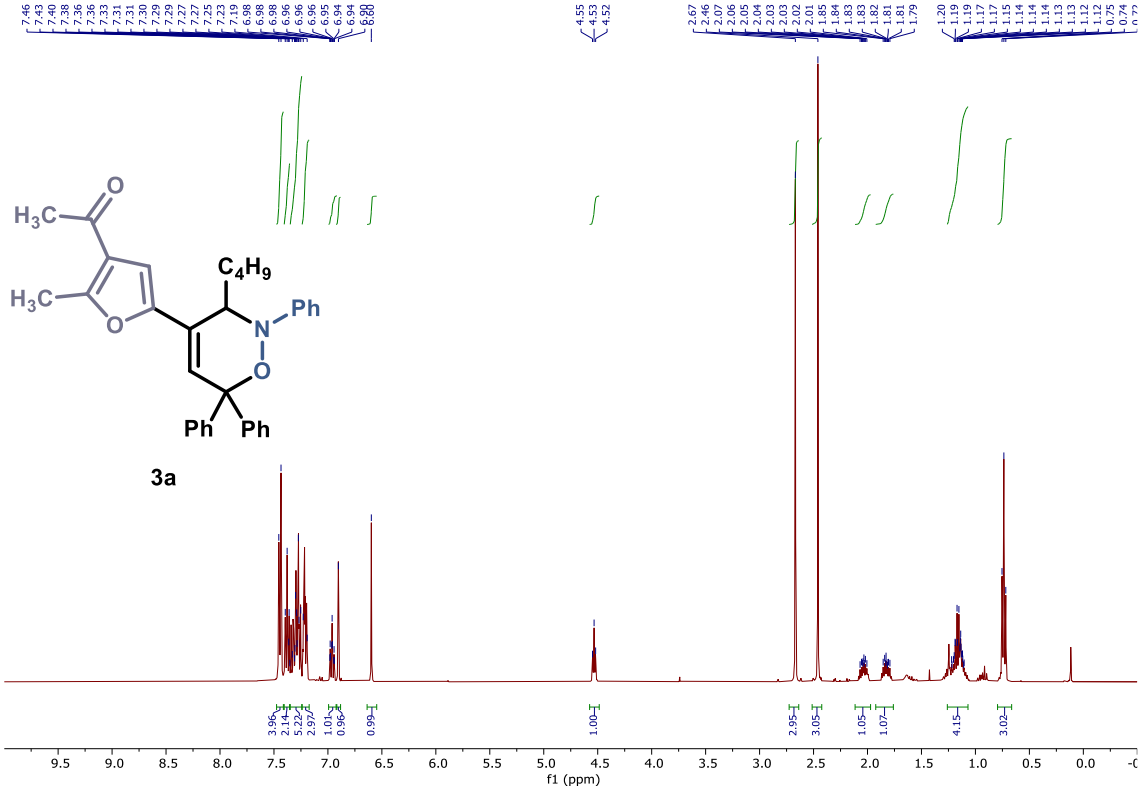
121.89
115.59
115.31
114.92
114.64
107.64
42.48
34.16
31.77
31.21
29.10
27.23
22.98
22.63
14.38
14.04
10 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


Ph
C4H9
Ph
Ph
1i
f1 (ppm)


f1 (ppm)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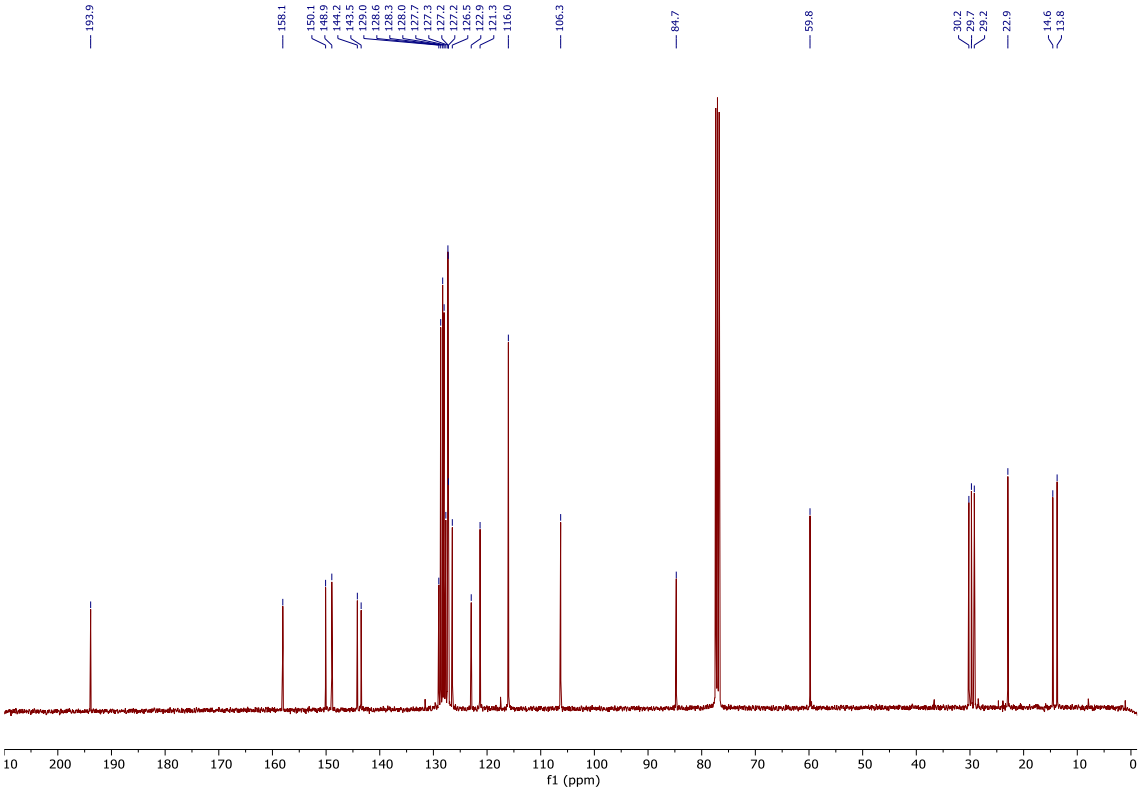
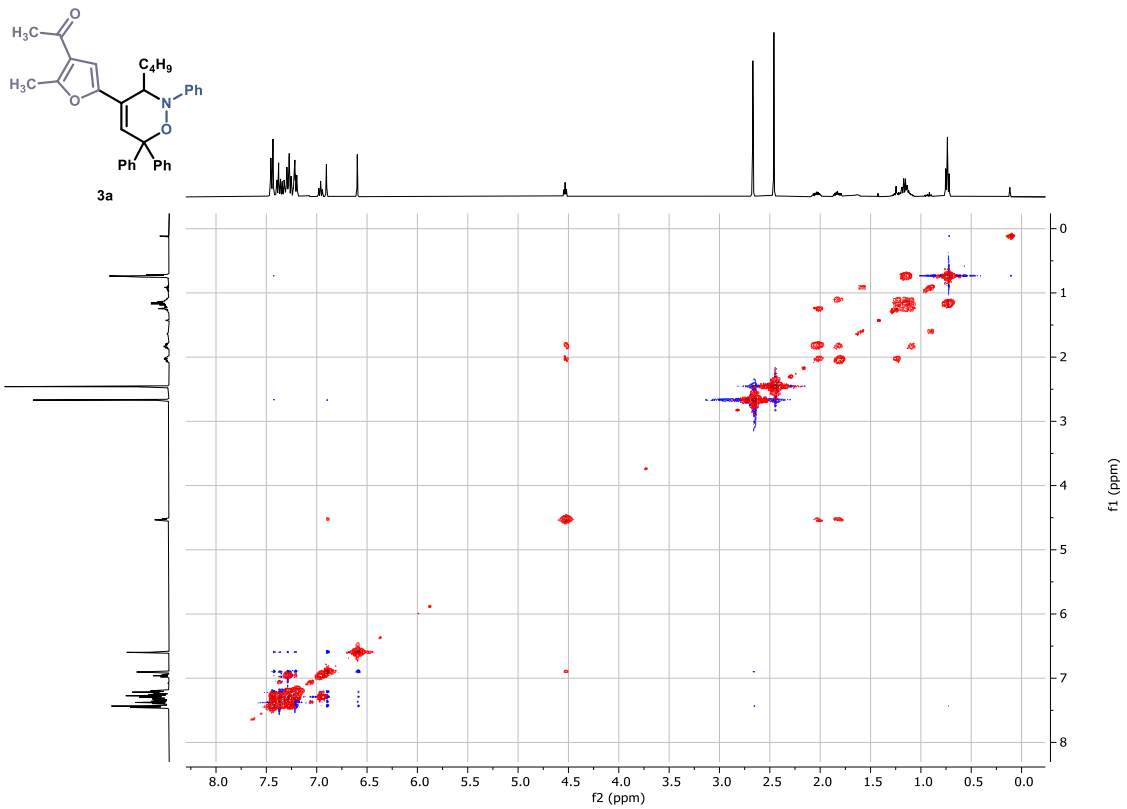
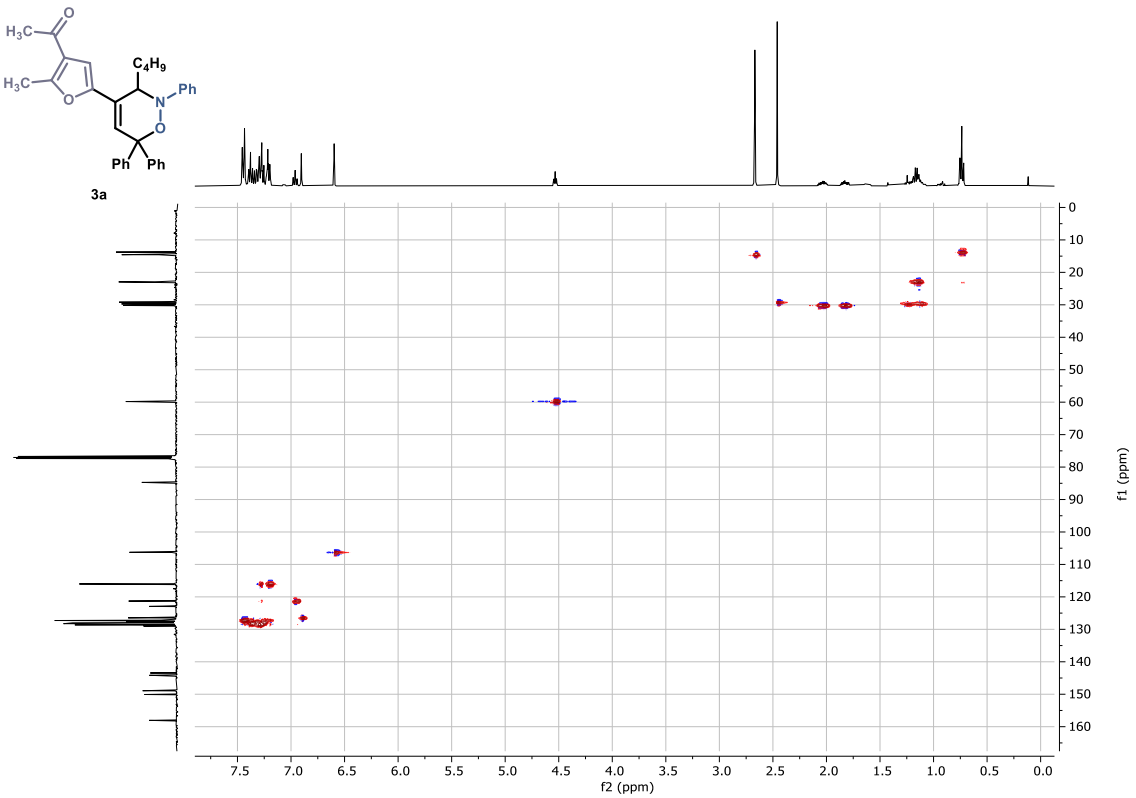
H3C
O
C4H9
N
Ph
O
Ph
Ph
3a
f1 (ppm)


f1 (ppm)

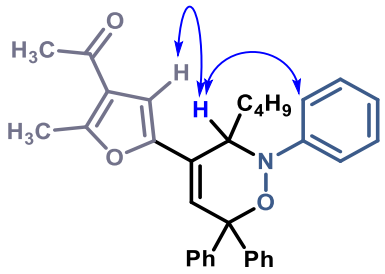
^{1}H-^{1}H COSY



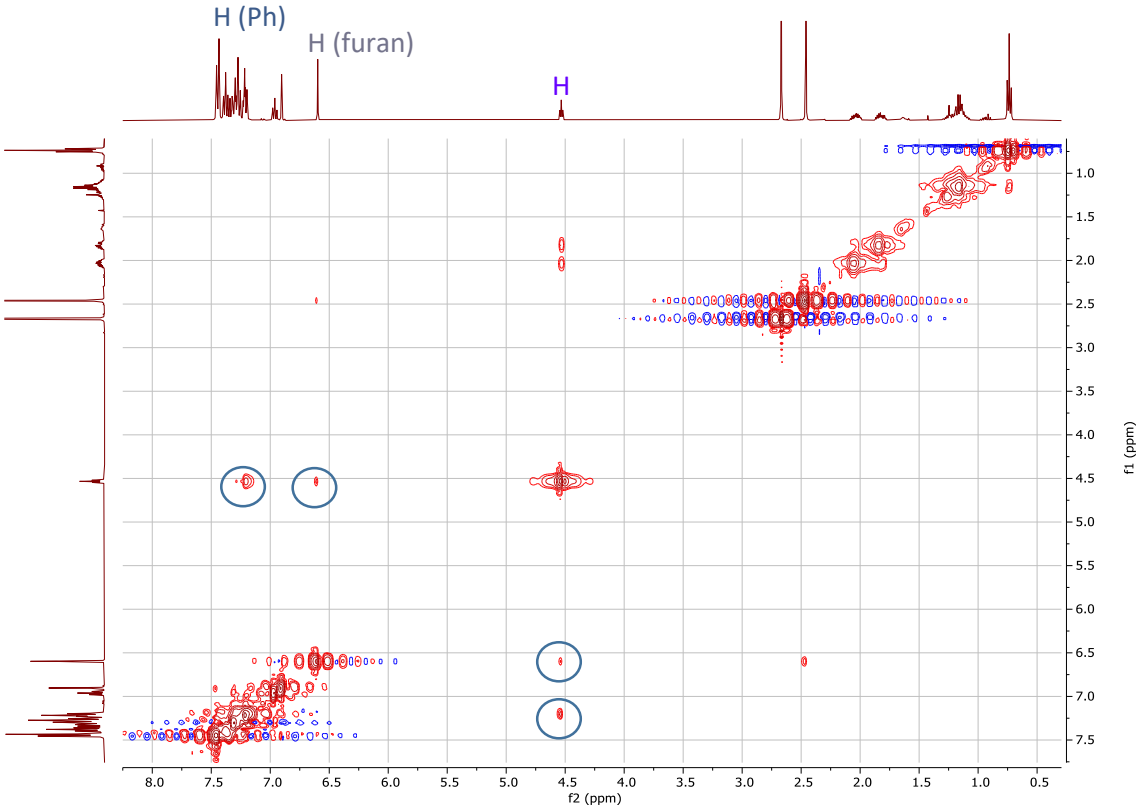
^{1}H-^{13}C HSQC



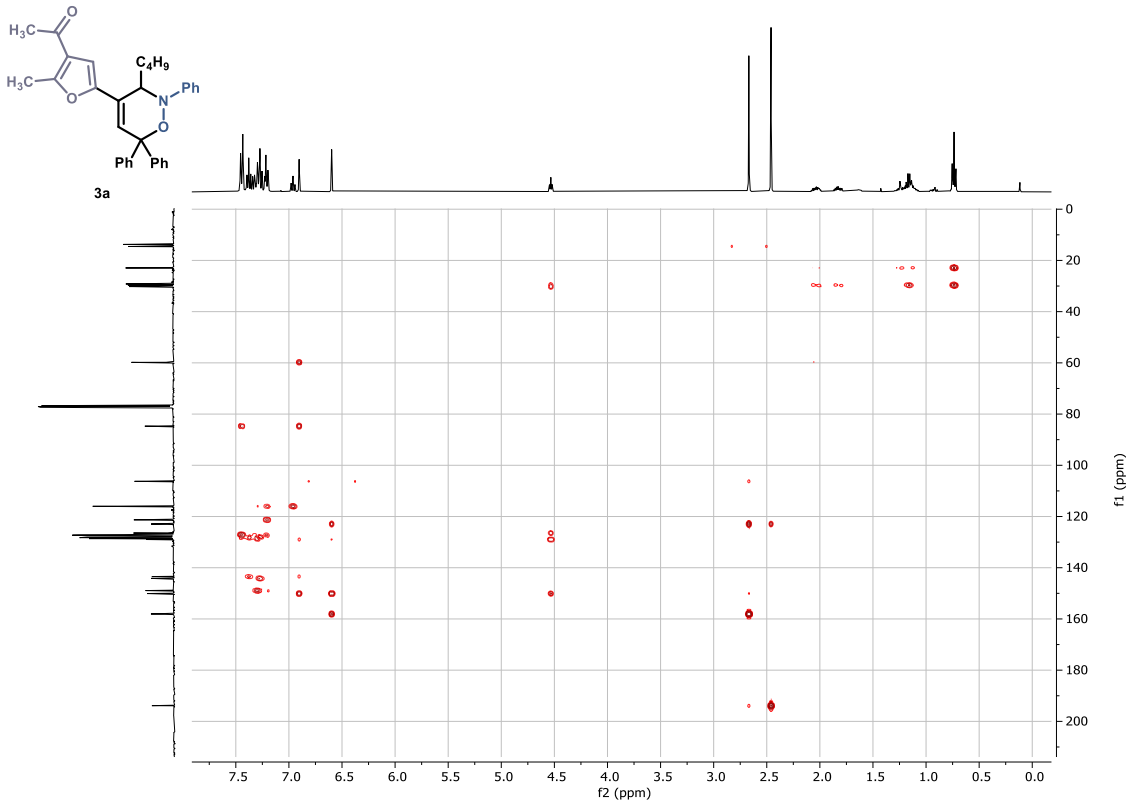
2D NOESY

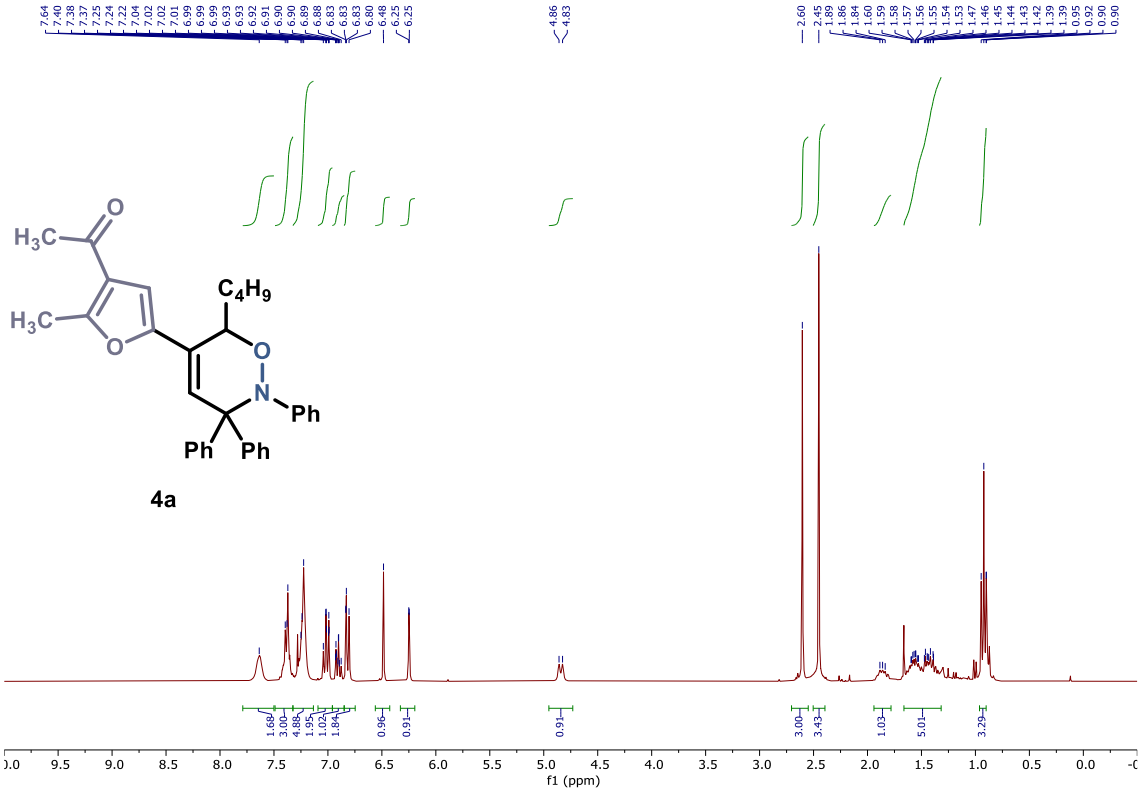


3a



^{1}H-^{13}C HMBC

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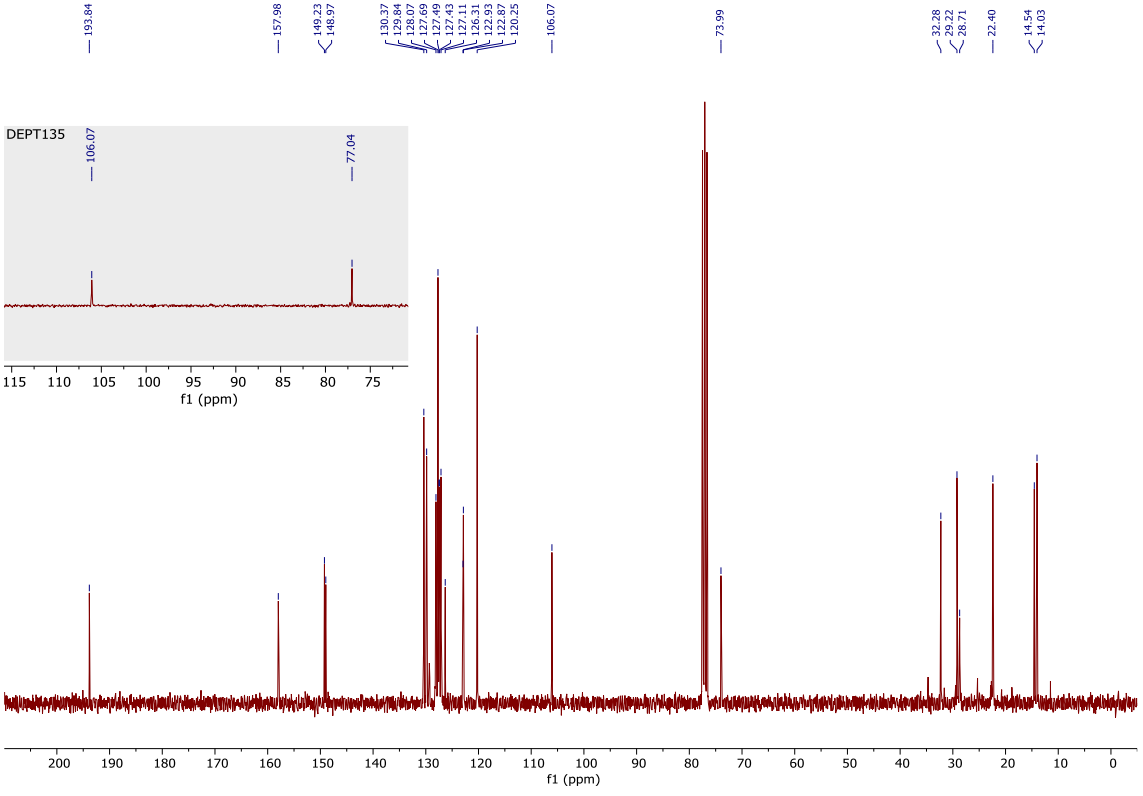
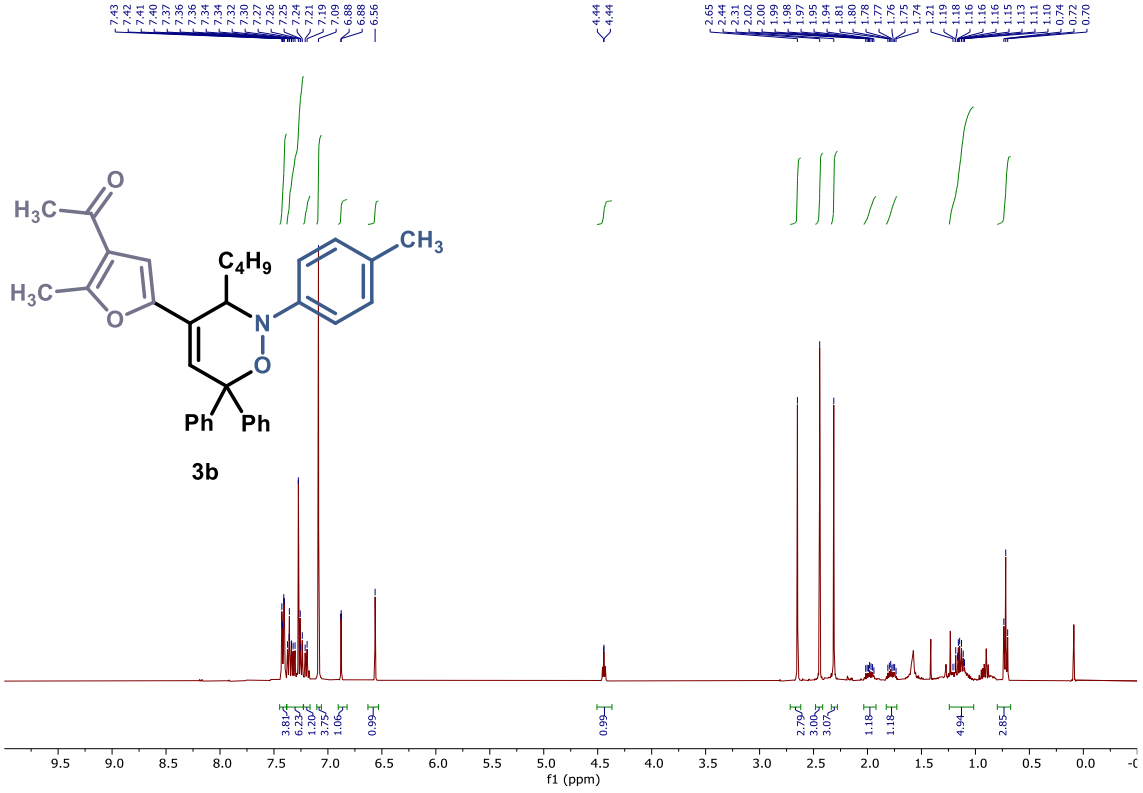
4.86 4.83
2.60 2.45 1.89 1.86 1.84 1.60 1.59 1.58 1.57 1.56 1.55 1.54 1.53 1.47 1.46 1.45 1.44 1.43 1.42 1.39 1.38 0.95 0.92 0.90 0.90
H3C
O
H3C
O
C4H9
O
N
Ph
Ph
Ph
4a
1.68 3.00 4.88 1.95 2.02 1.84 0.96 0.91 0.91 3.00 3.43 1.03 5.01 3.29
f1 (ppm)


193.84 157.98 149.23 148.97 130.37 129.84 128.07 127.69 127.49 127.43 127.11 126.31 122.93 122.87 120.25 106.07 73.99 32.28 29.22 28.71 22.40 14.54 14.03
DEPT135
106.07
77.04
f1 (ppm)
f1 (ppm)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Ph
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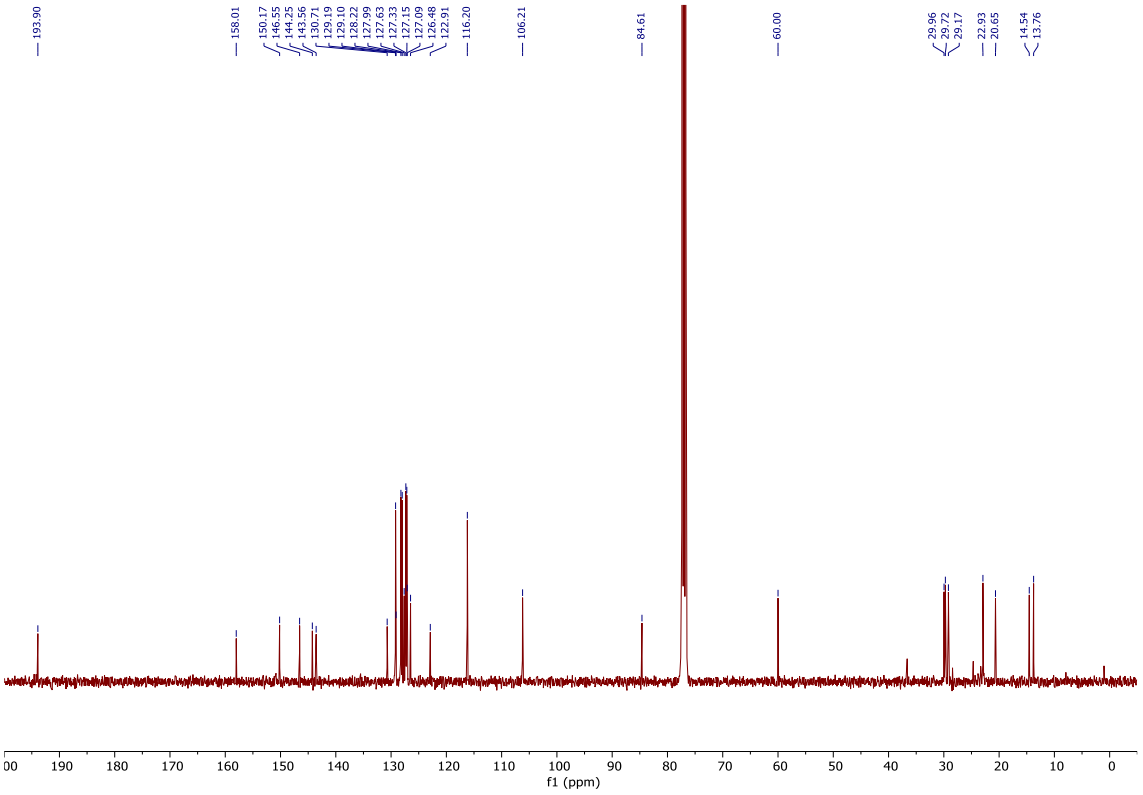
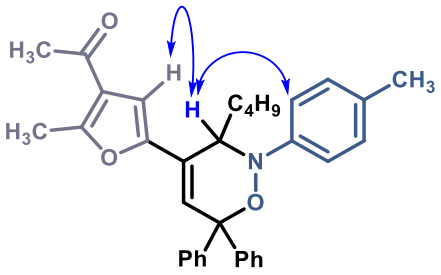
f1 (ppm)


f1 (ppm)

2D NOESY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CH3
H
C4H9
H3C
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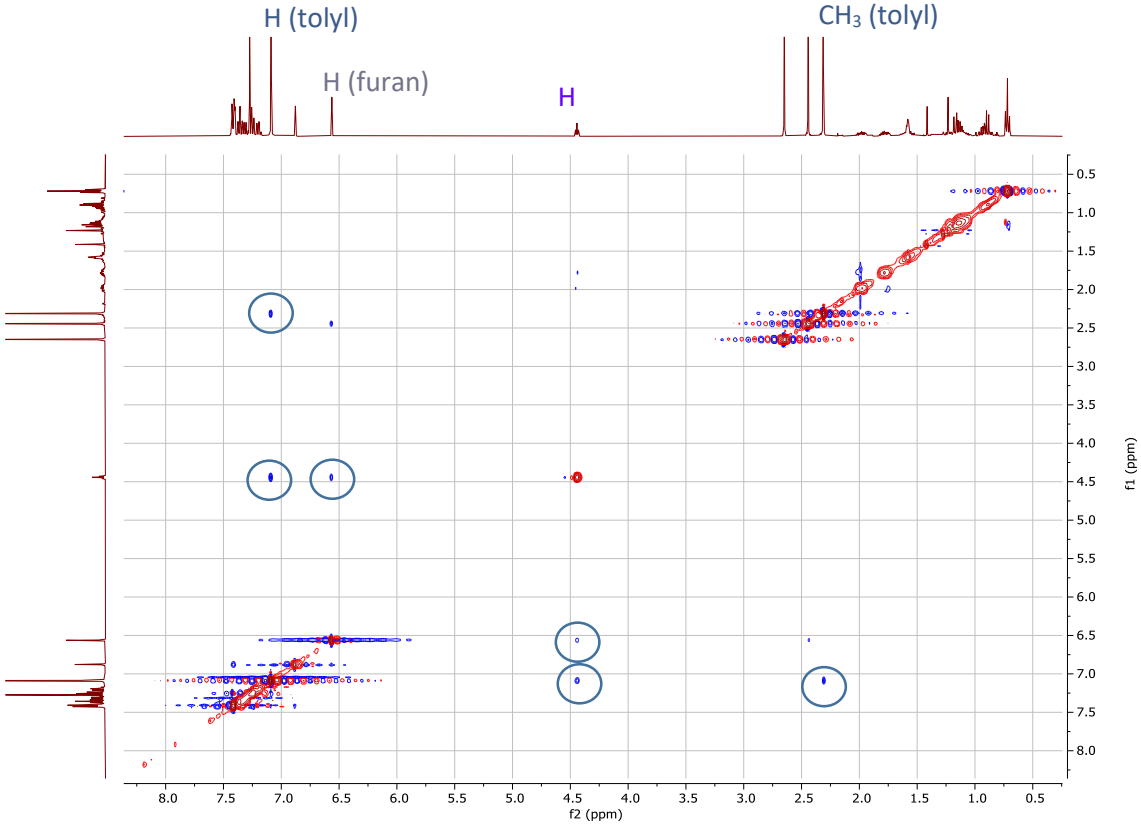
N
O
Ph
Ph

3b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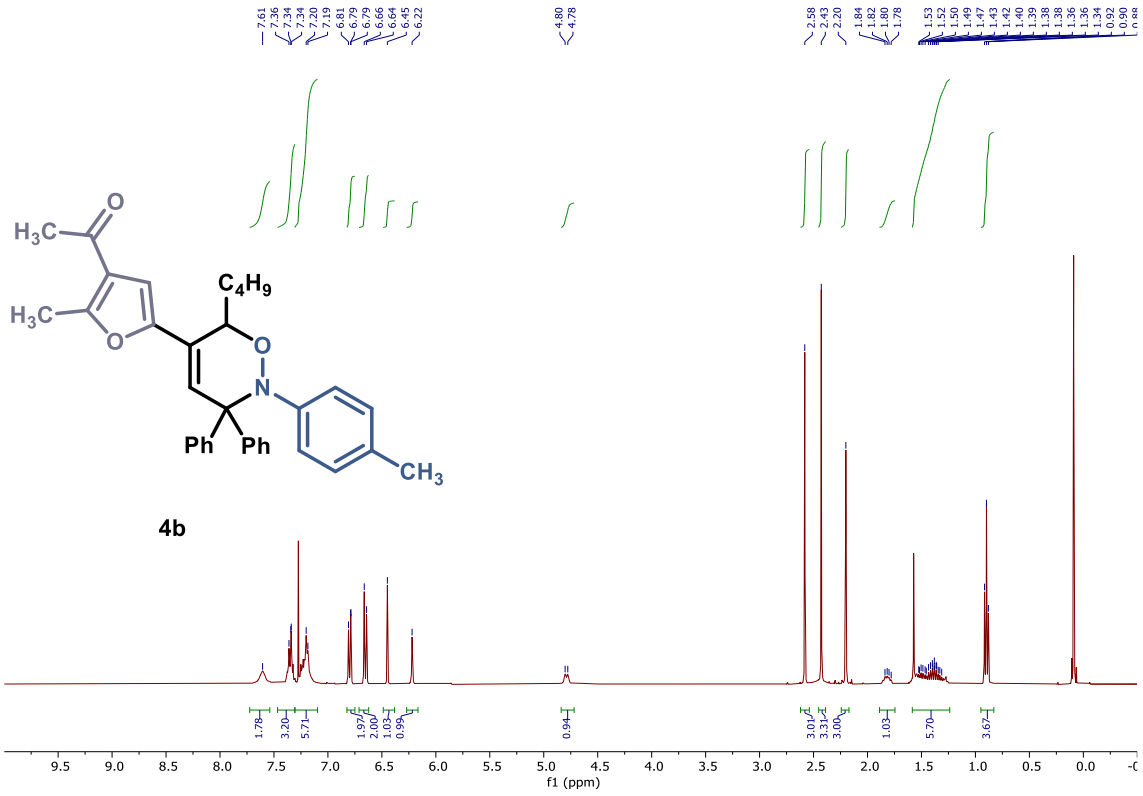
H (furan)
H
CH3 (tolyl)
f2 (ppm)
f1 (ppm)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6.22
4.80
4.78
2.58
2.43
2.20
1.84
1.82
1.80
1.78
1.53
1.52
1.50
1.49
1.47
1.43
1.42
1.40
1.39
1.38
1.38
1.36
1.36
1.34
0.92
0.90
H3C
O
H3C
O
C4H9
O
N
Ph
Ph
CH3
4b
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3.20
5.71
1.97
2.00
1.03
0.99
0.94
3.01
3.31
3.00
1.03
5.70
3.67
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
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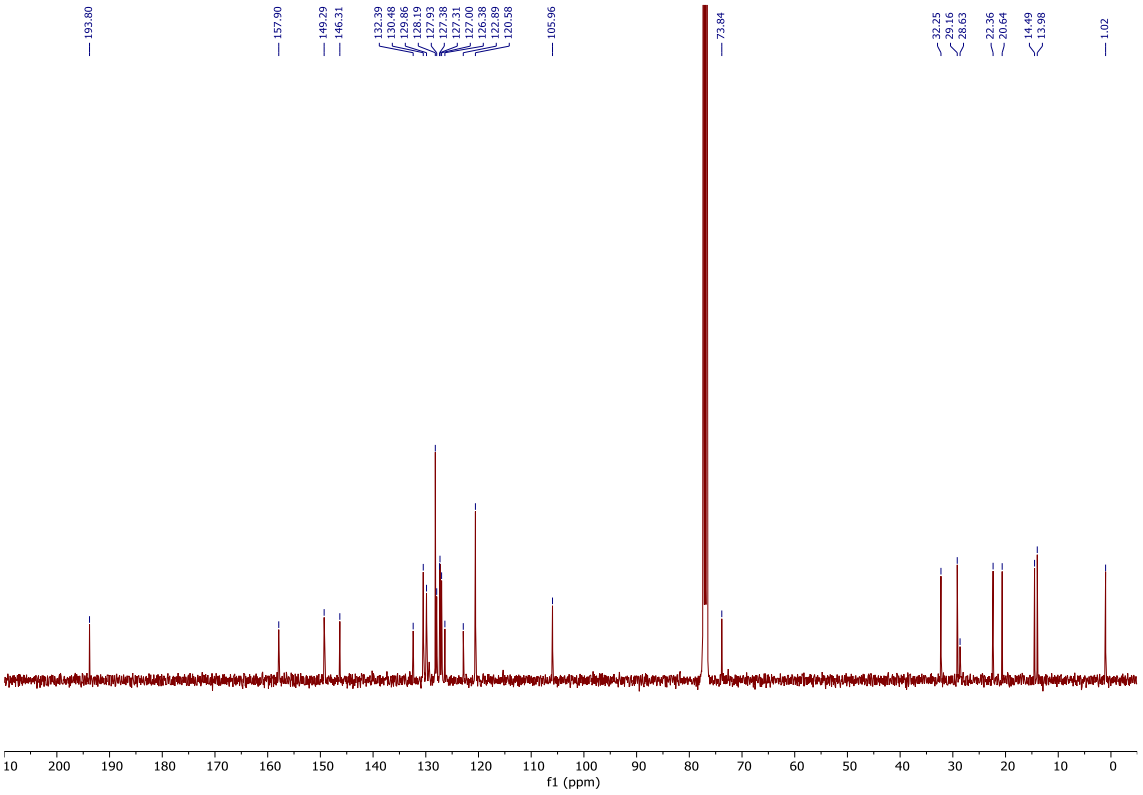
0.0
f1 (ppm)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14.49
13.98
1.02
10
200
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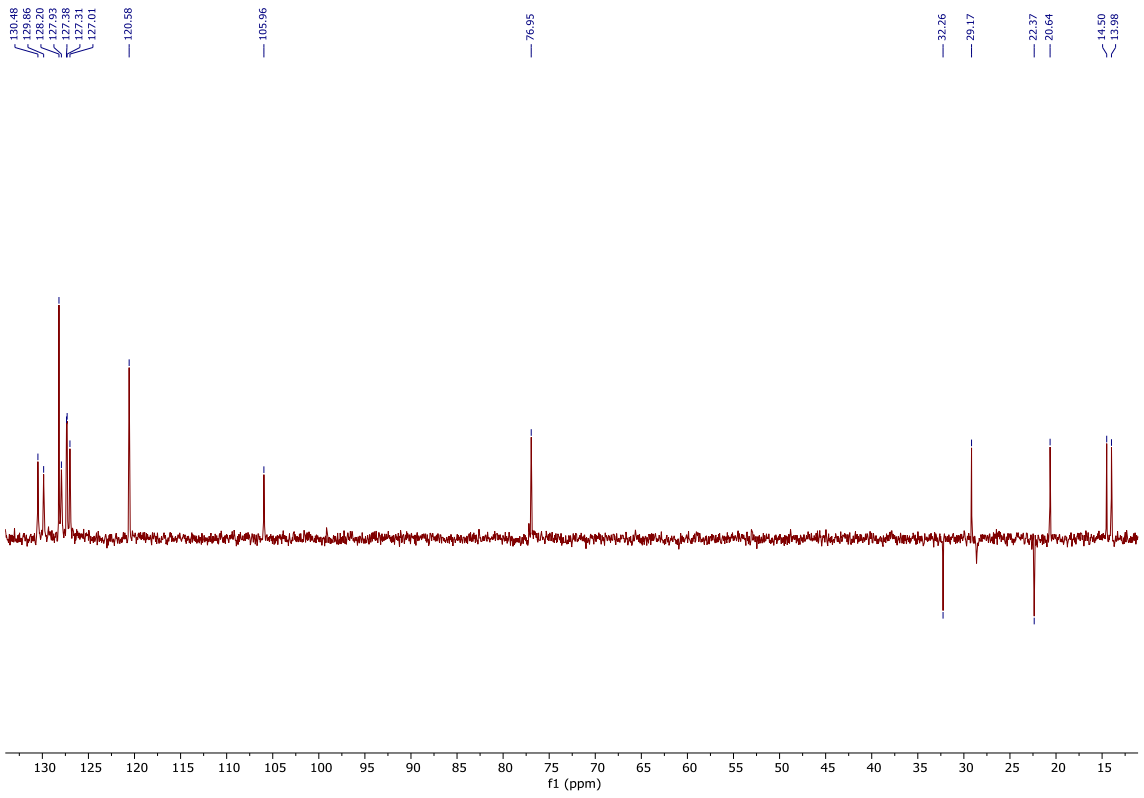
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

DEPT 135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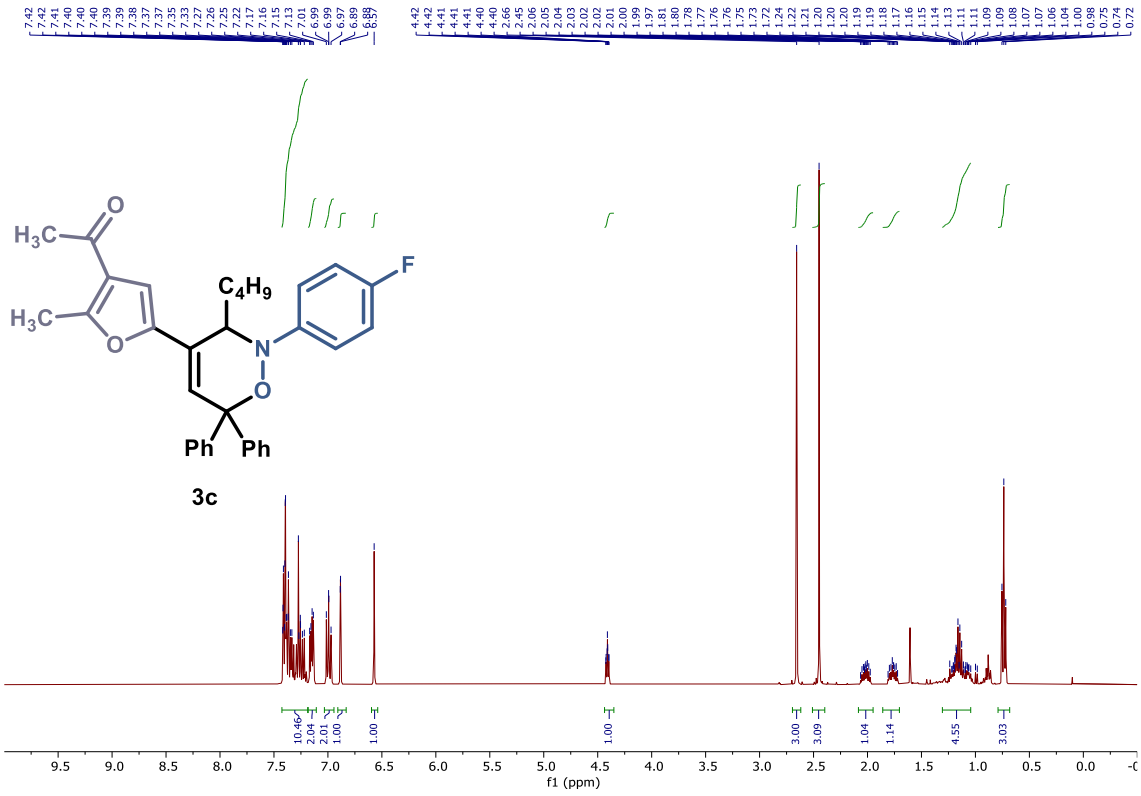
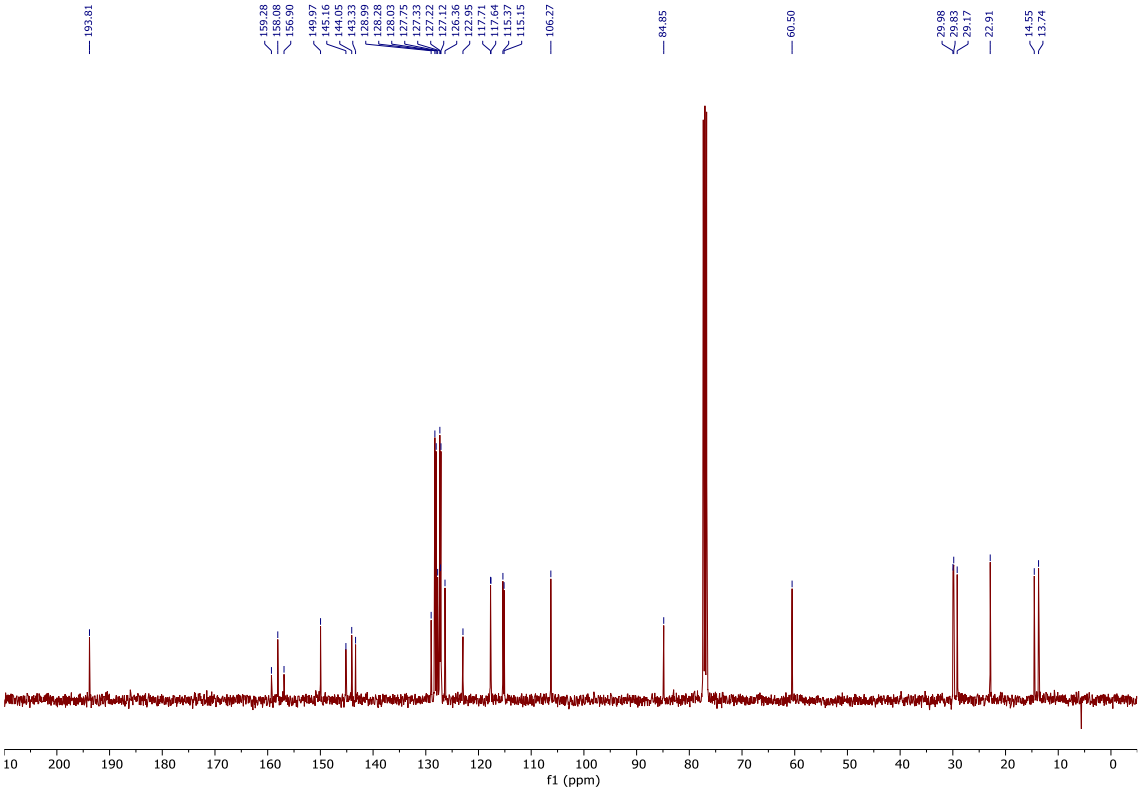
129.86
128.20
127.93
127.38
127.31
127.01
120.58
105.96
76.95
32.26
29.17
22.37
20.64
14.50
13.98
130 125 120 115 110 105 100 95 90 85 80 75 70 65 60 55 50 45 40 35 30 25 20 15
f1 (ppm)


H3C
O
H3C
O
C4H9
N
O
F
Ph
Ph
3c
f1 (ppm)


193.81
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158.08
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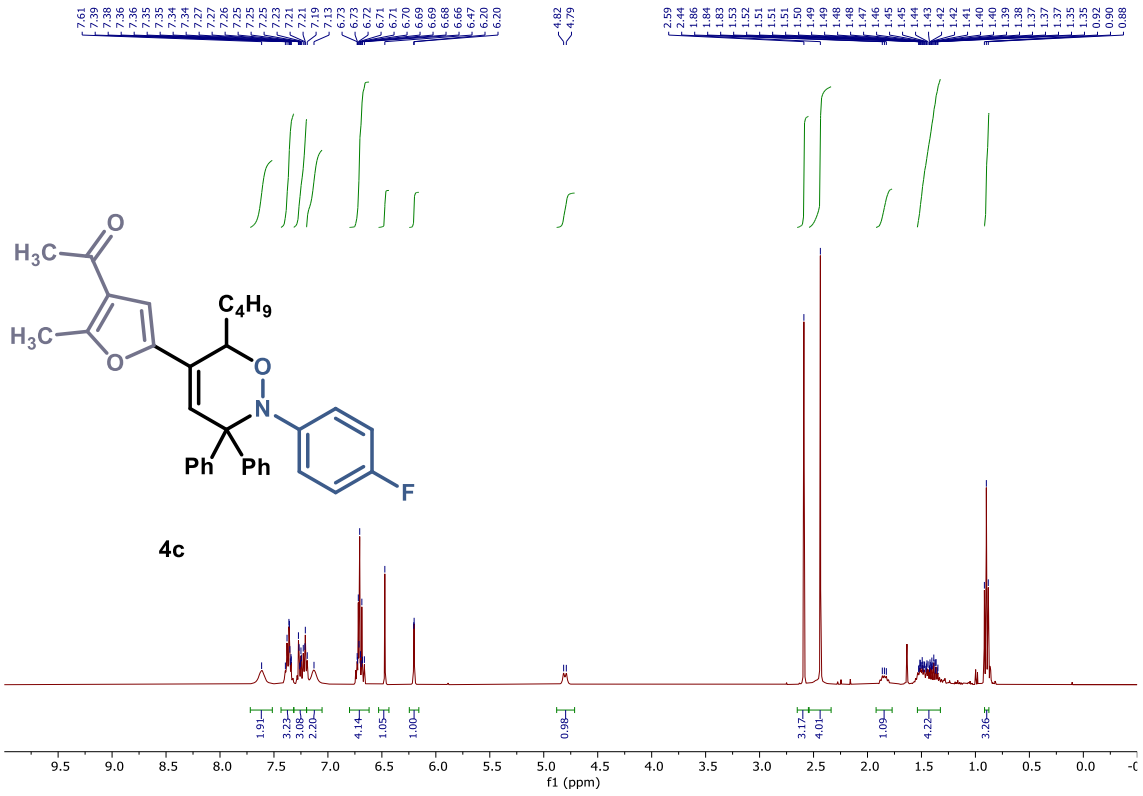
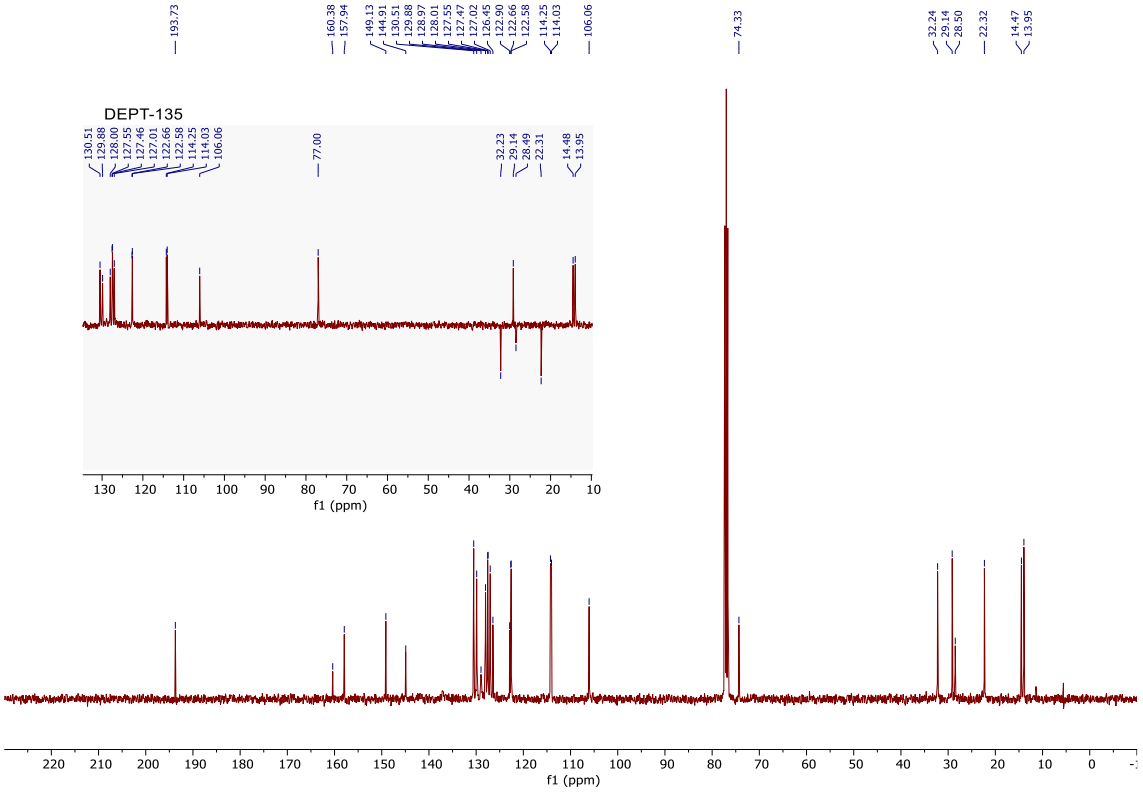
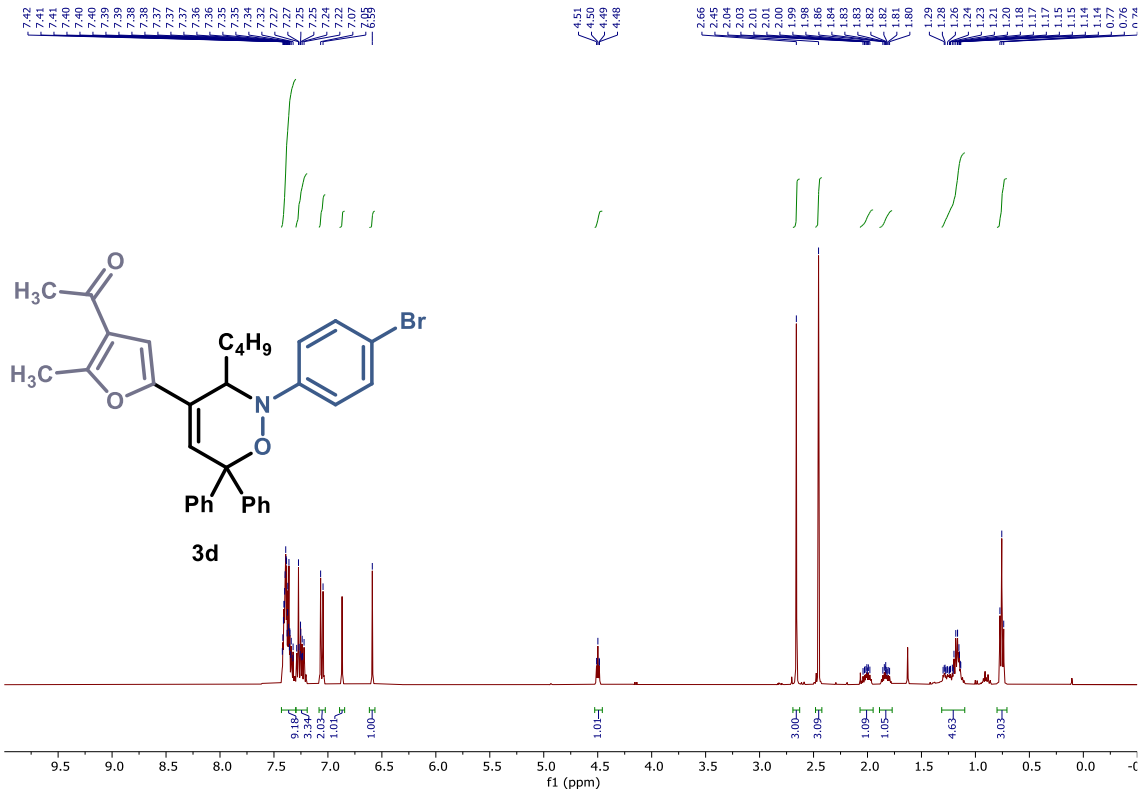
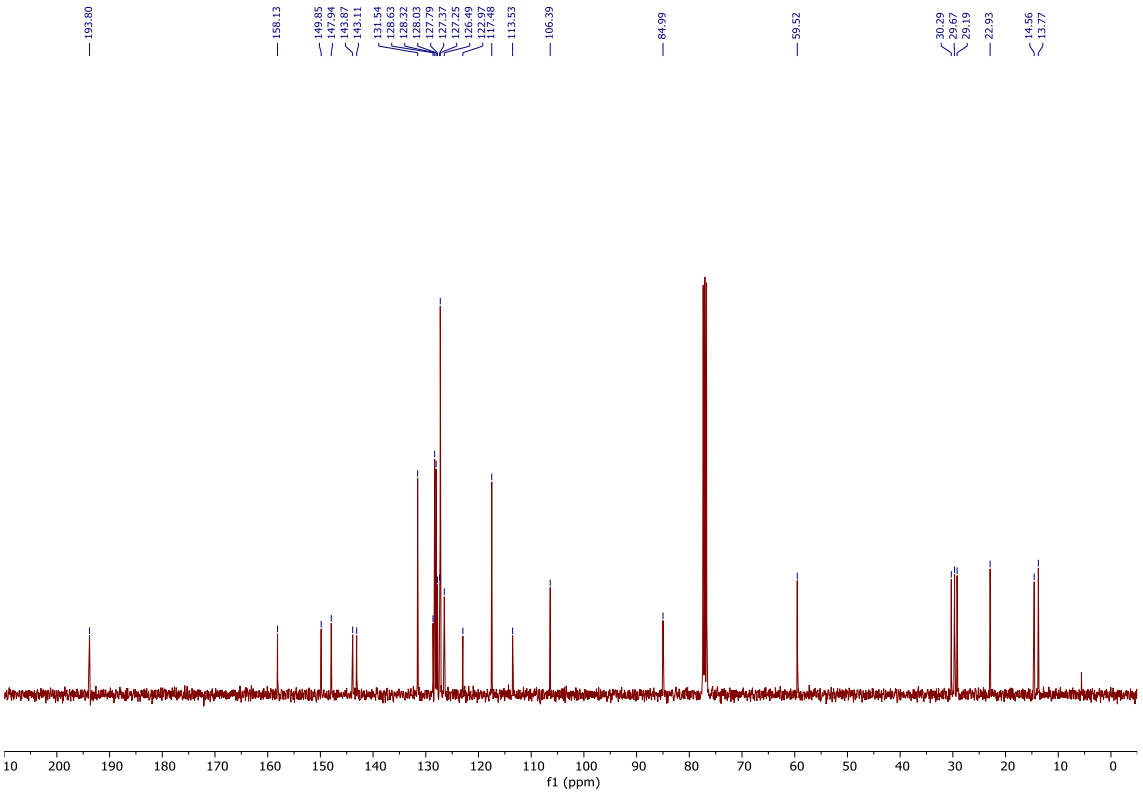
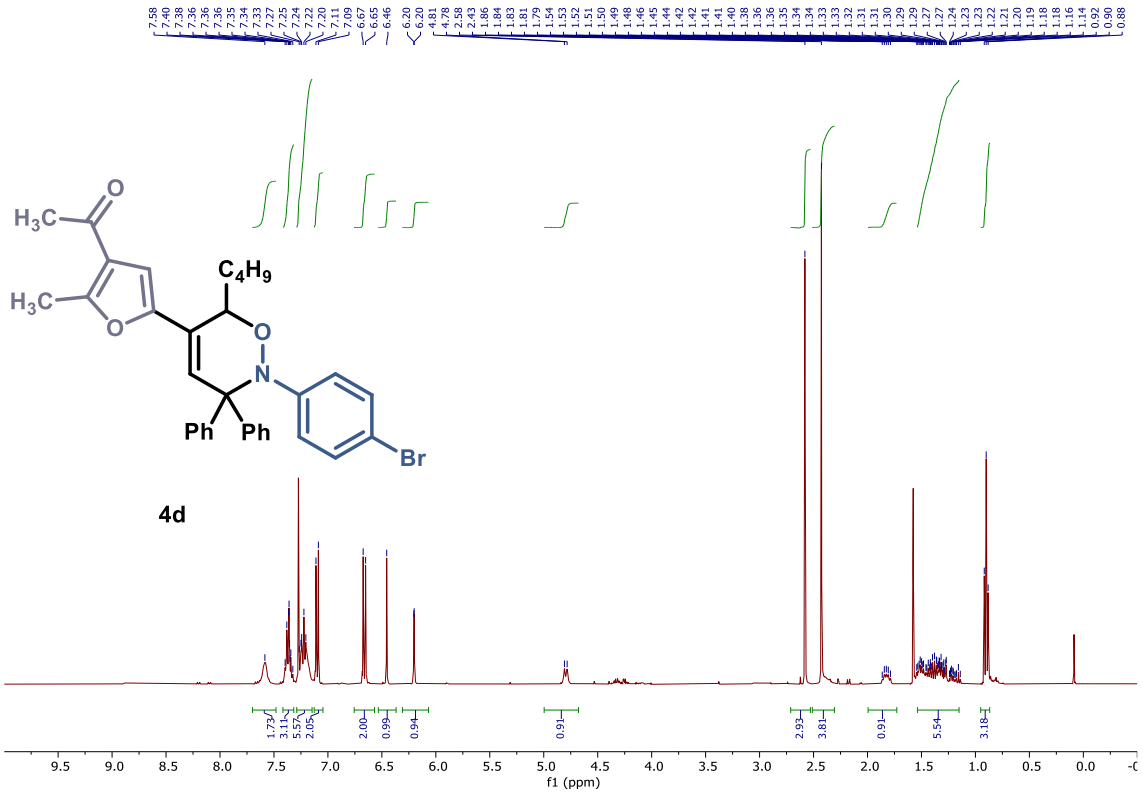
145.16
144.05
143.33
128.99
128.28
128.03
127.75
127.33
127.22
127.12
126.36
122.95
117.71
117.64
115.37
115.15
106.27
84.85
60.50
29.98
29.83
29.17
22.91
14.55
13.74
f1 (ppm)

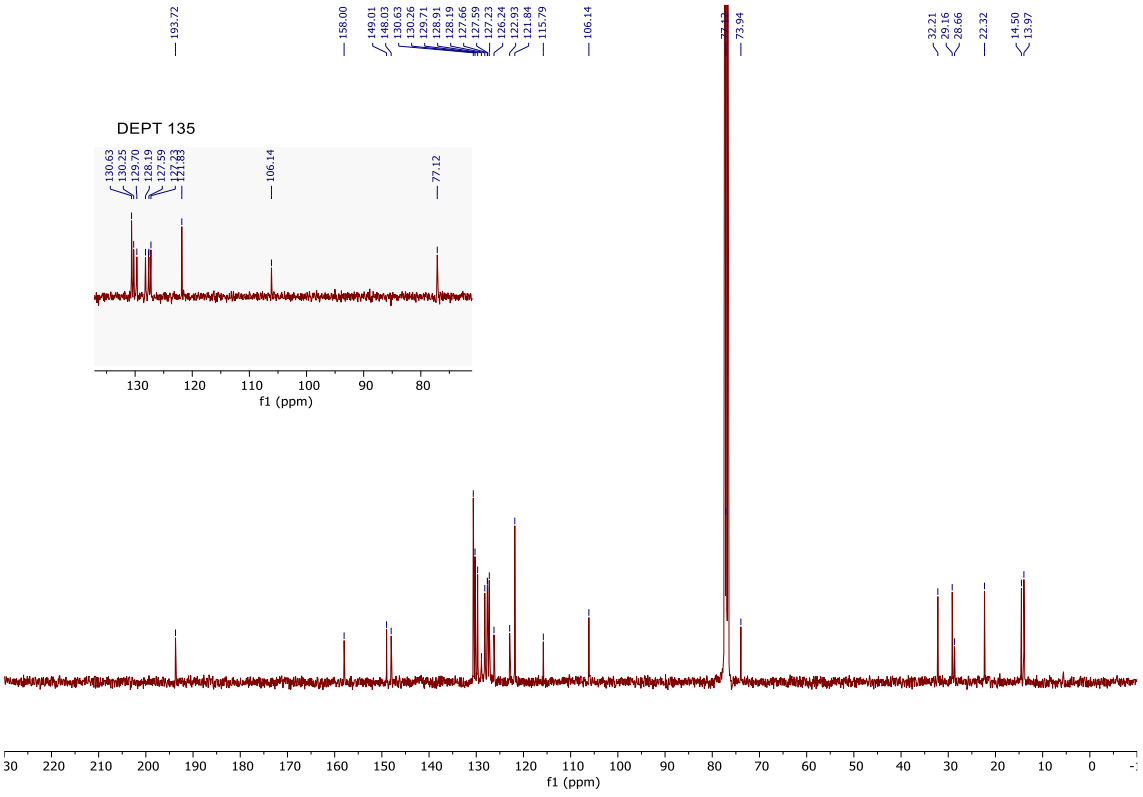

4c
f1 (ppm)

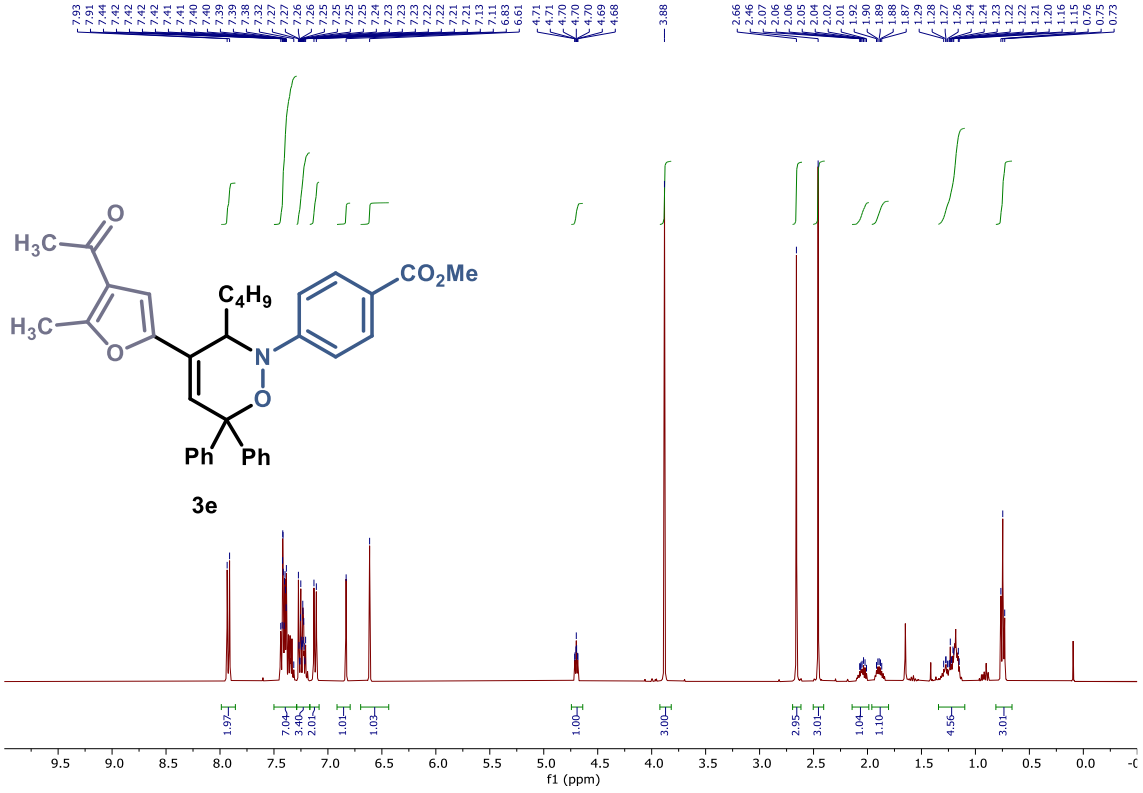

DEPT-135
f1 (ppm)

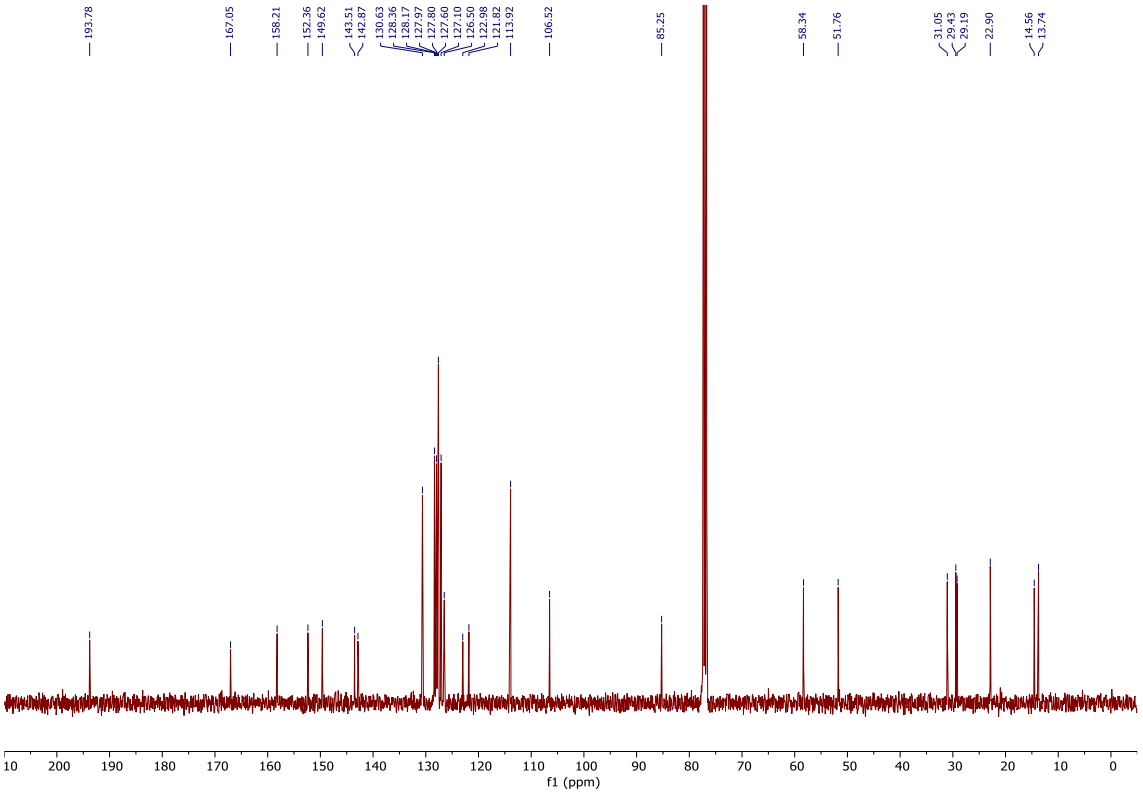

H3C
O
H3C
O
C4H9
N
O
Br
Ph
Ph
3d
f1 (ppm)


f1 (ppm)

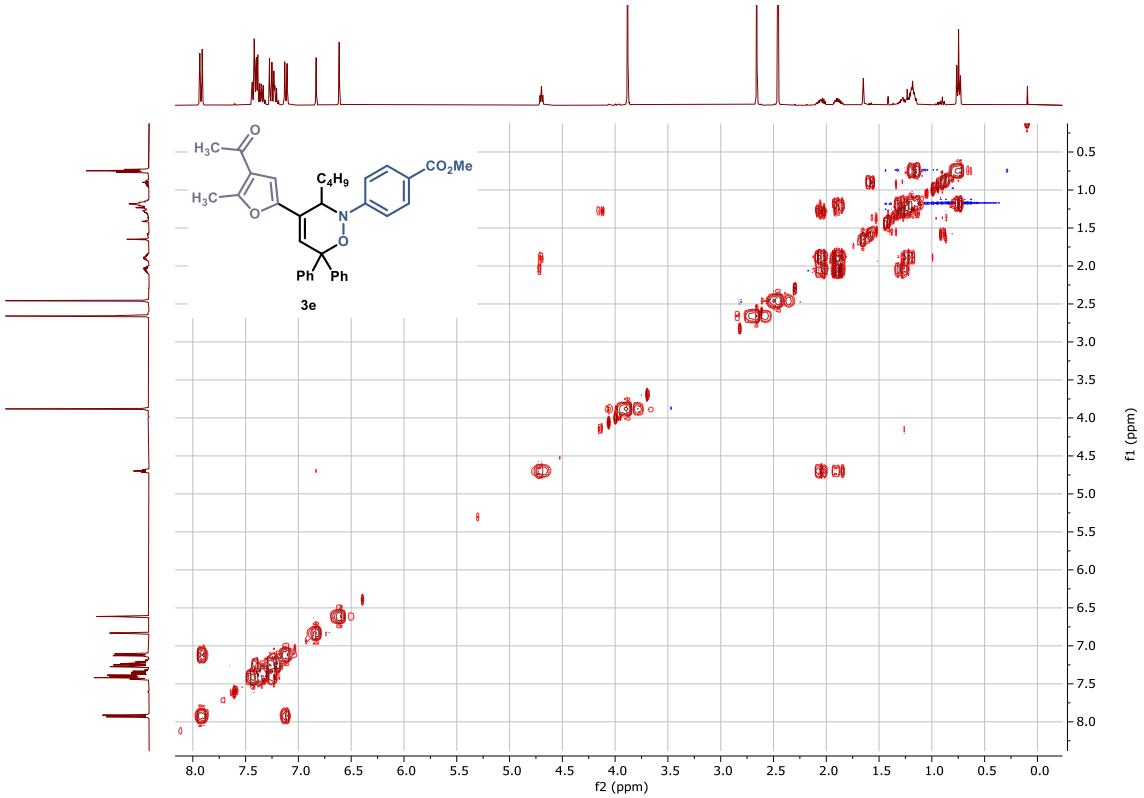

4d
f1 (ppm)


DEPT 135
f1 (ppm)
f1 (ppm)

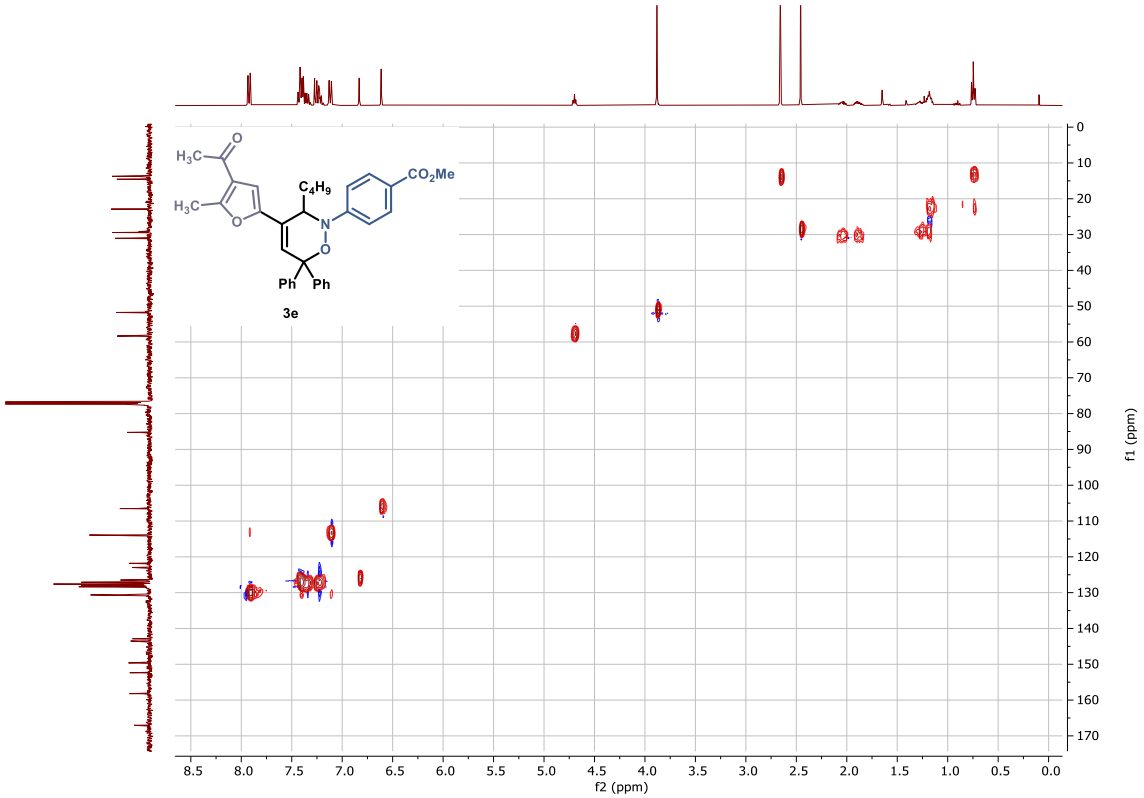

H3C
O
H3C
O
C4H9
N
O
CO2Me
Ph
Ph
3e
f1 (ppm)


f1 (ppm)

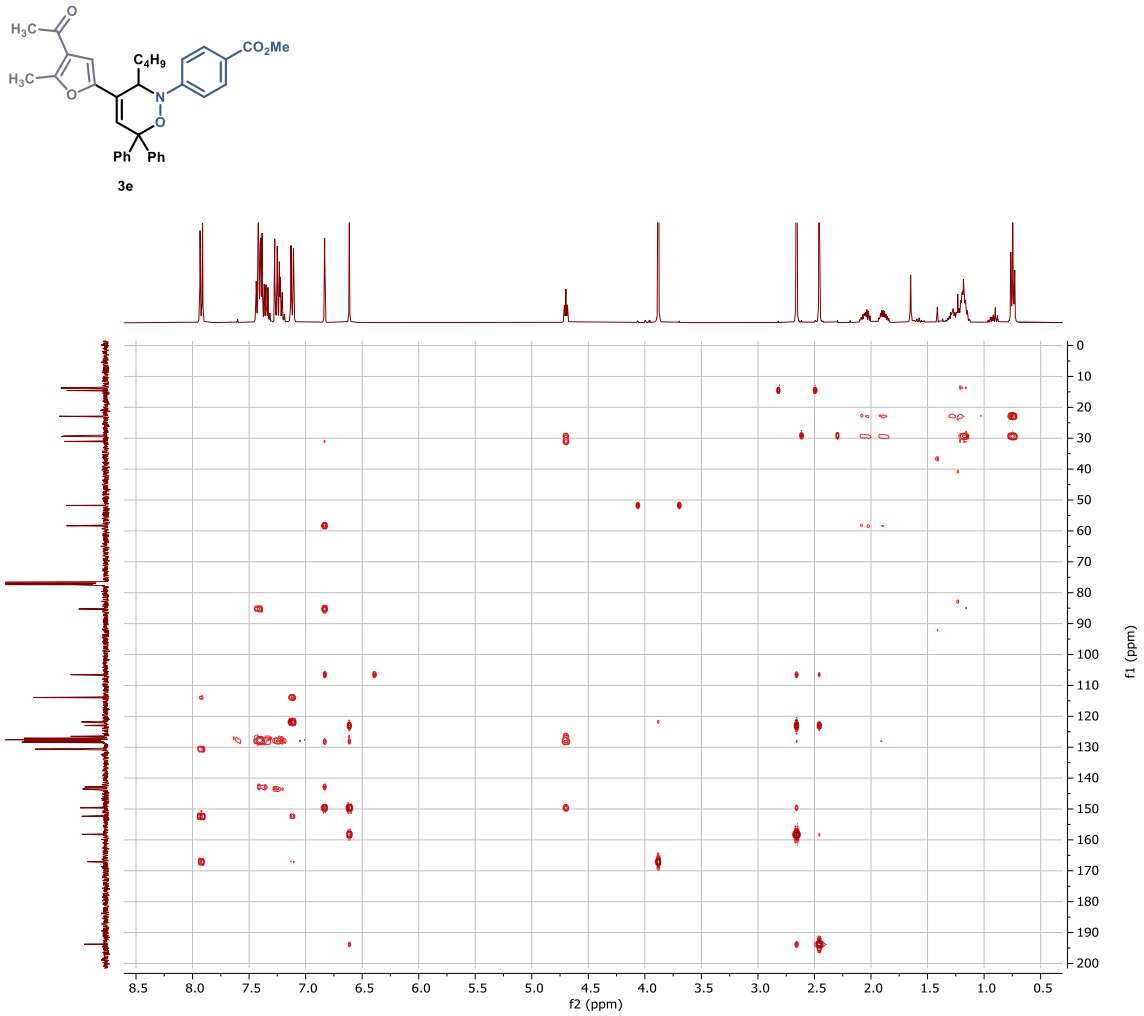
^{1}H-^{1}H COSY



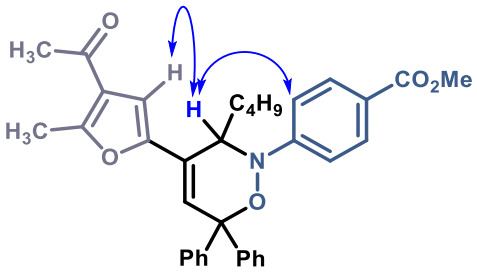
^{1}H-^{13}C HSQC



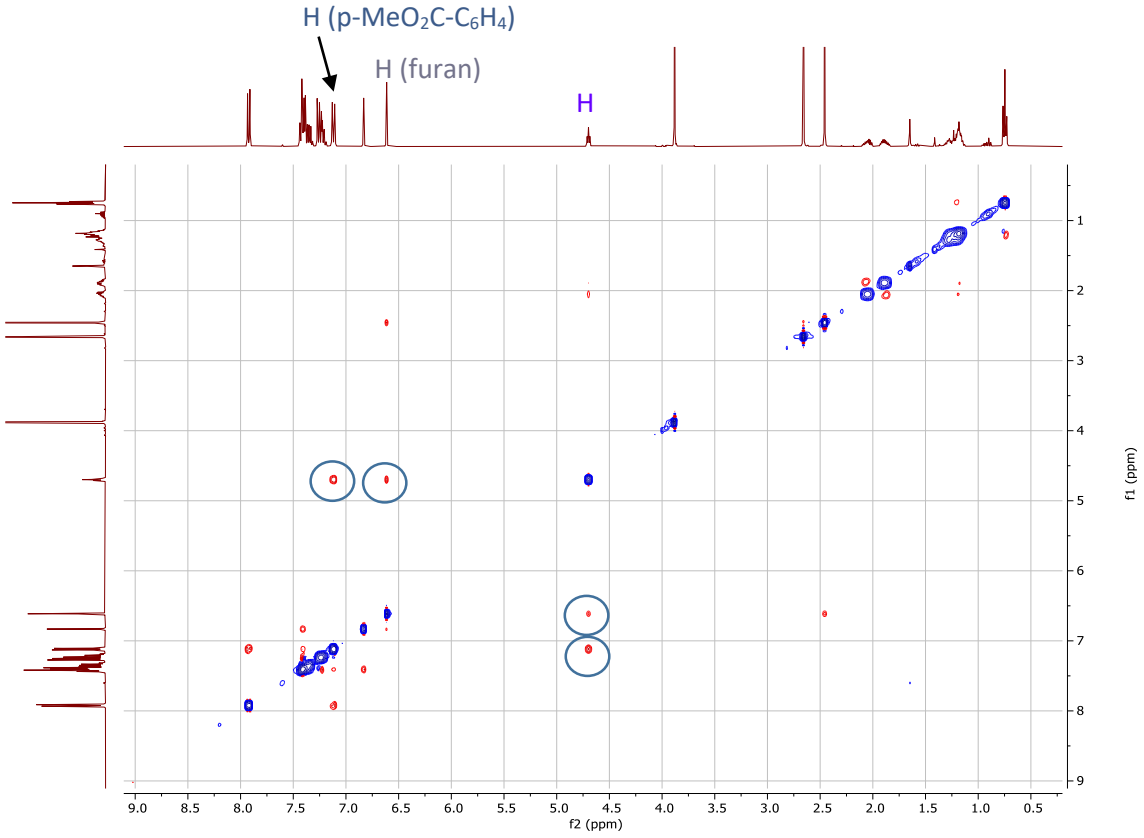
^{1}H-^{13}C HMBC

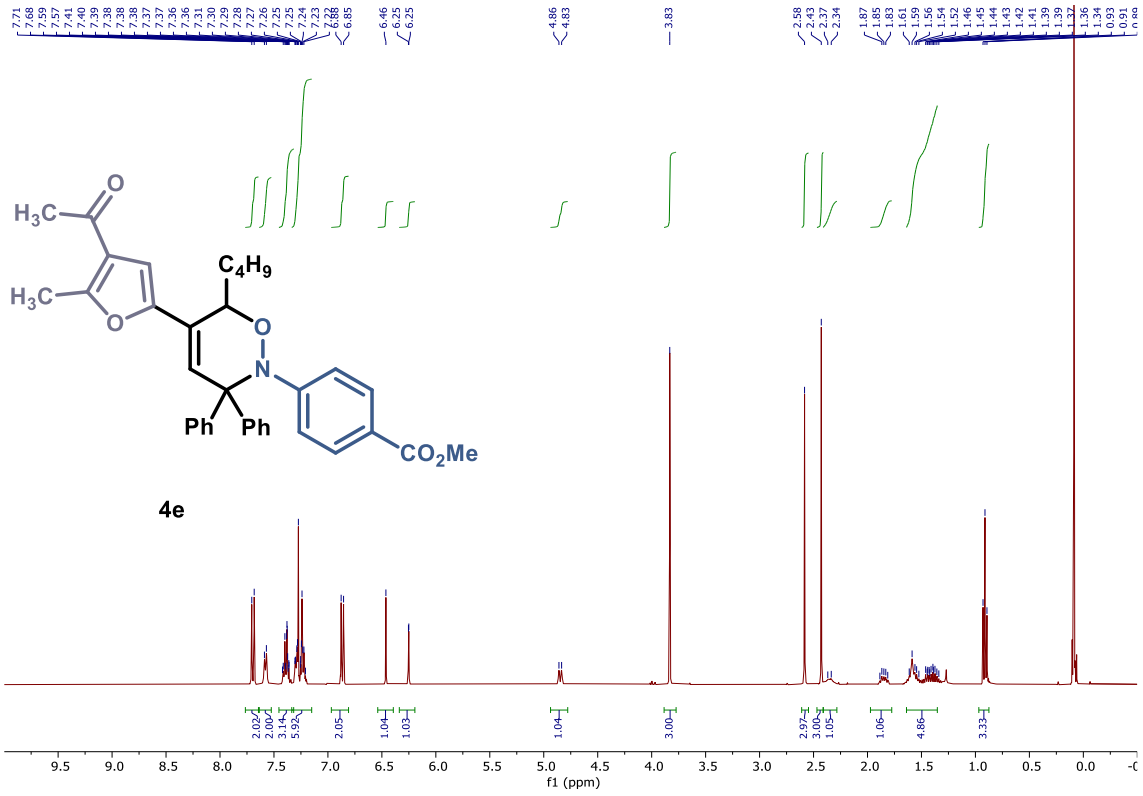


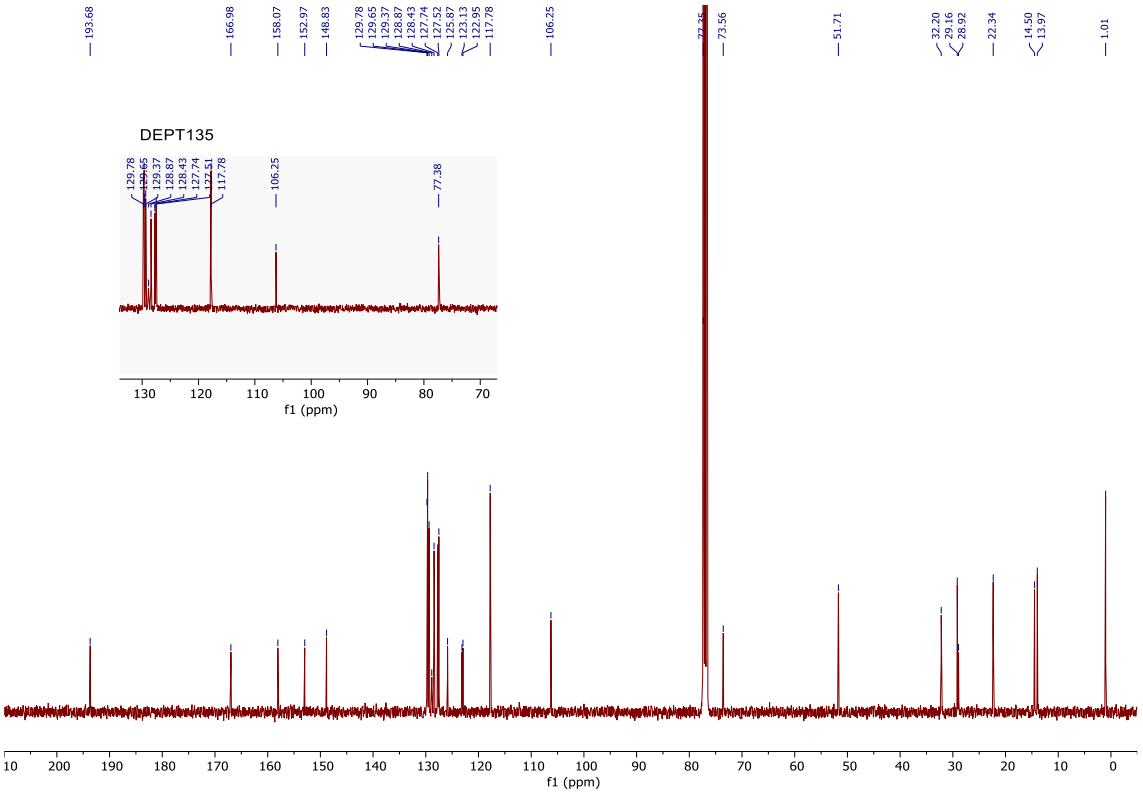
2D NOESY


H3C
O
H
H3C
O
H
C4H9
CO2Me
N
O
Ph
Ph

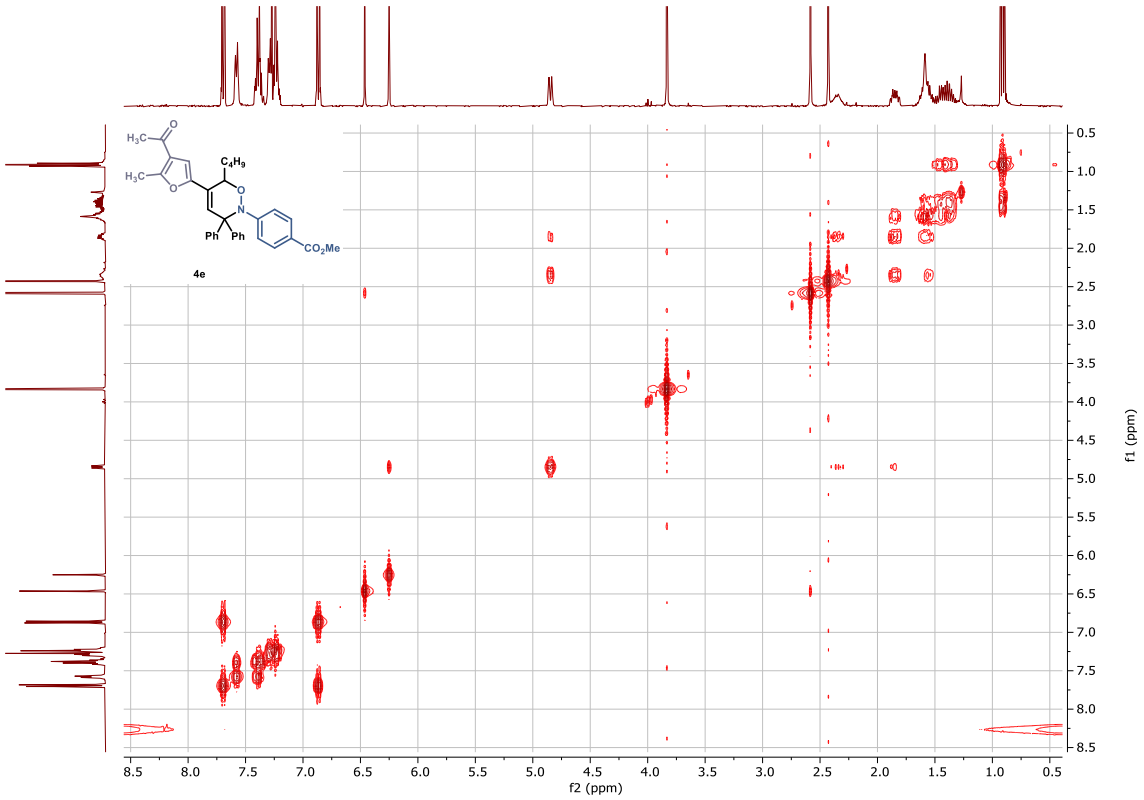
3e


H (p-MeO2C-C6H4)
H (furan)
H
f2 (ppm)
f1 (ppm)

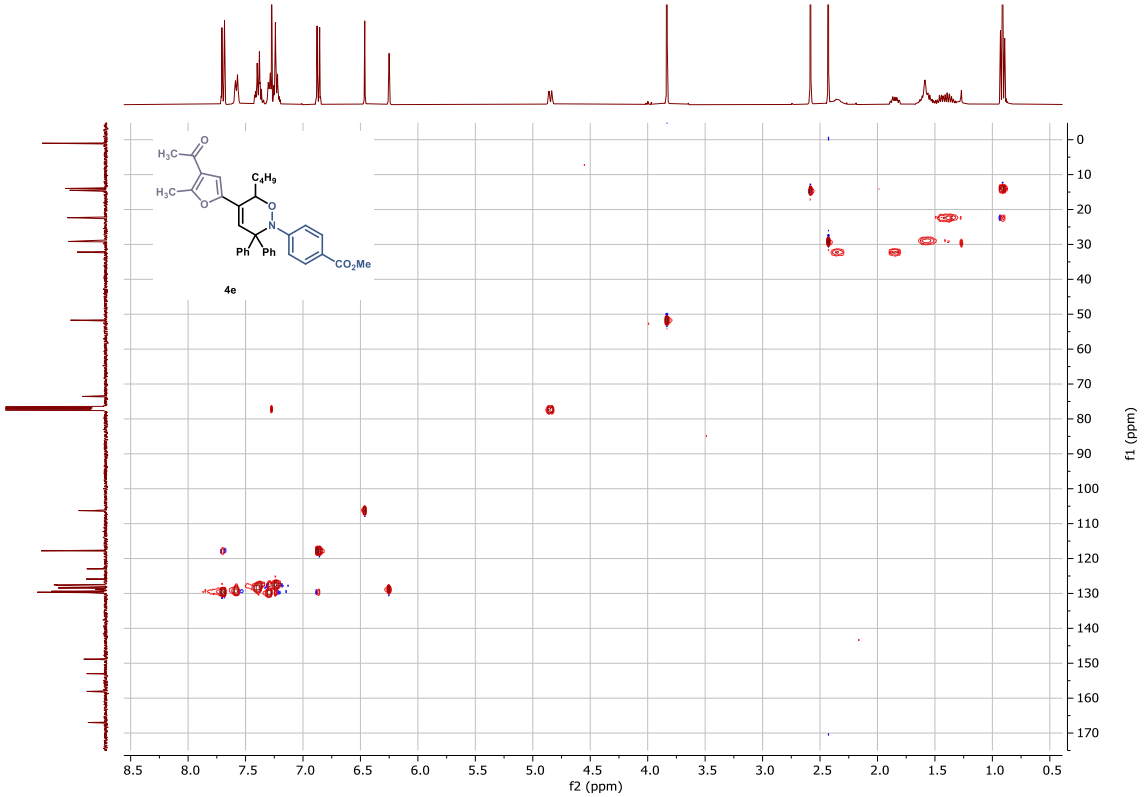

4e
f1 (ppm)


DEPT135
f1 (ppm)

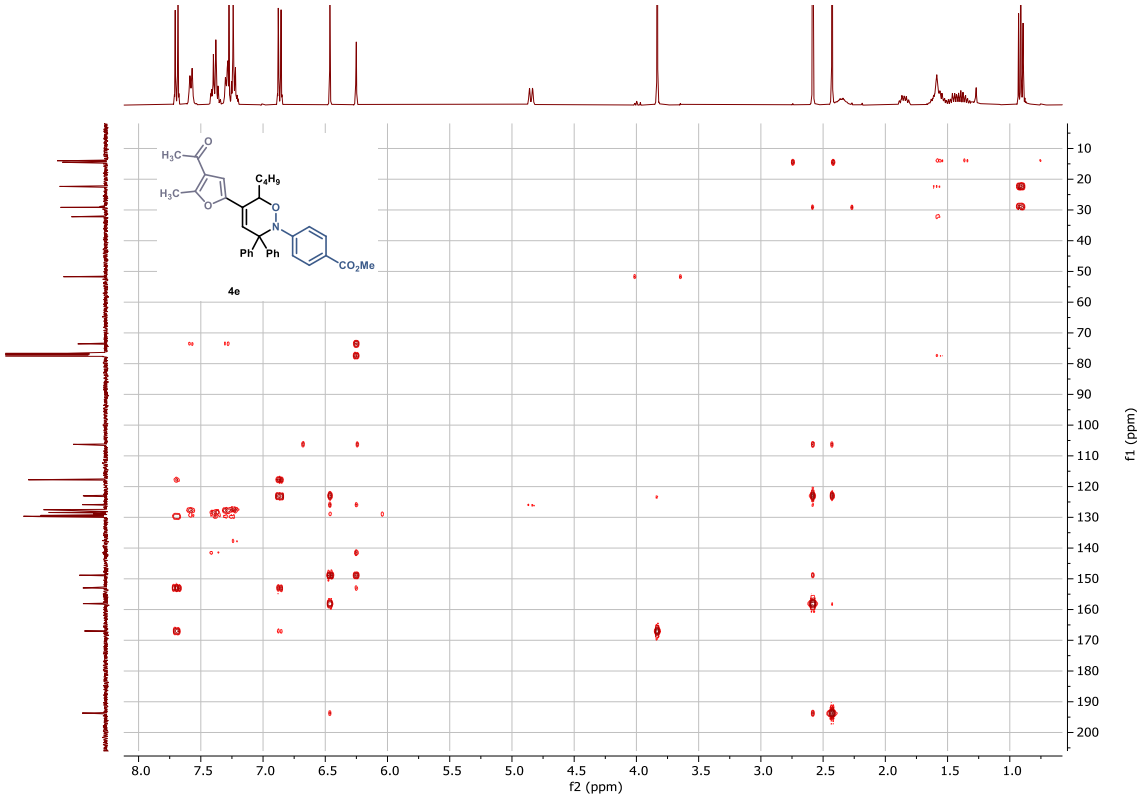
^{1}H-^{1}H COSY



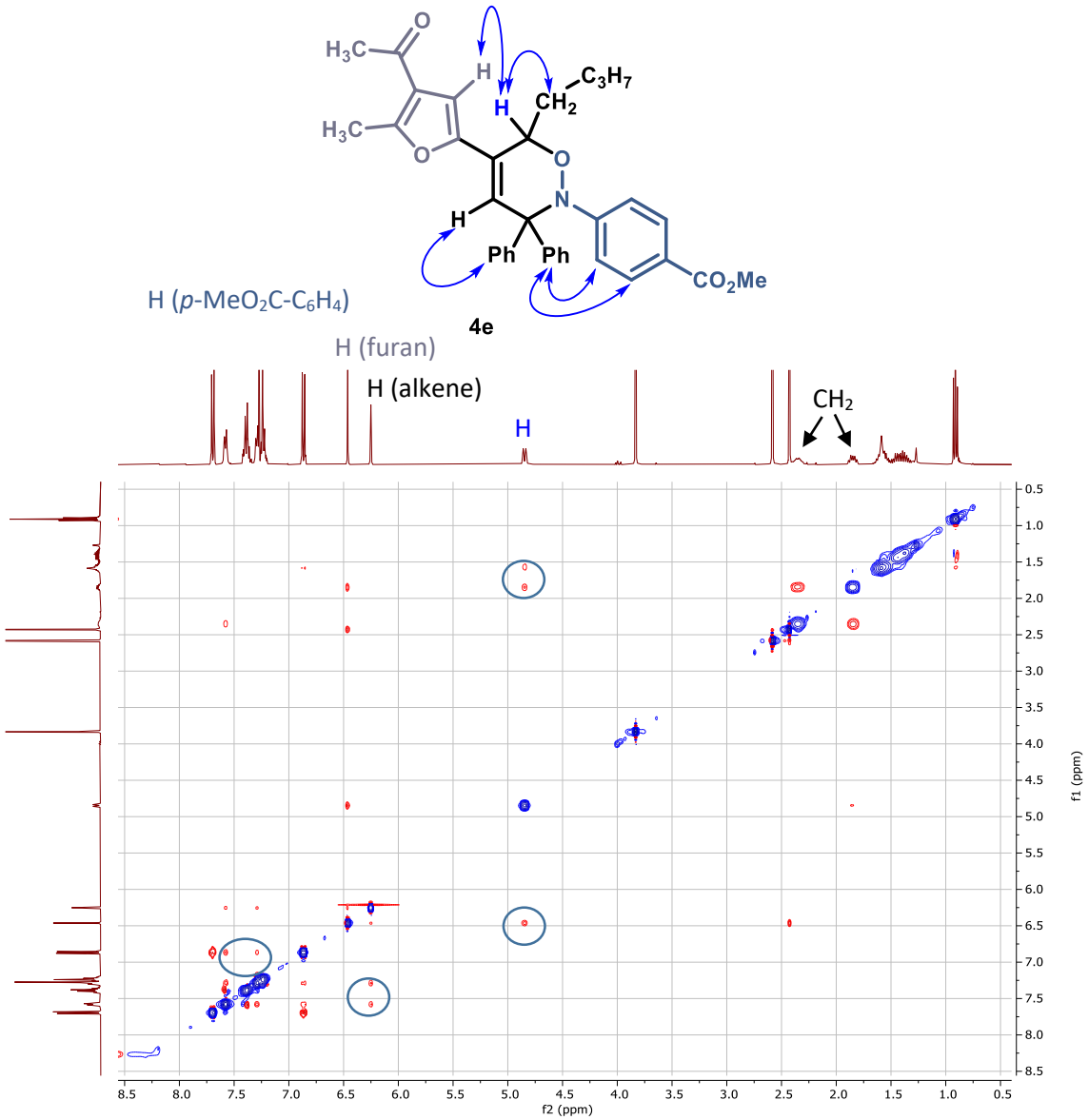
^{1}H-^{13}C HSQC

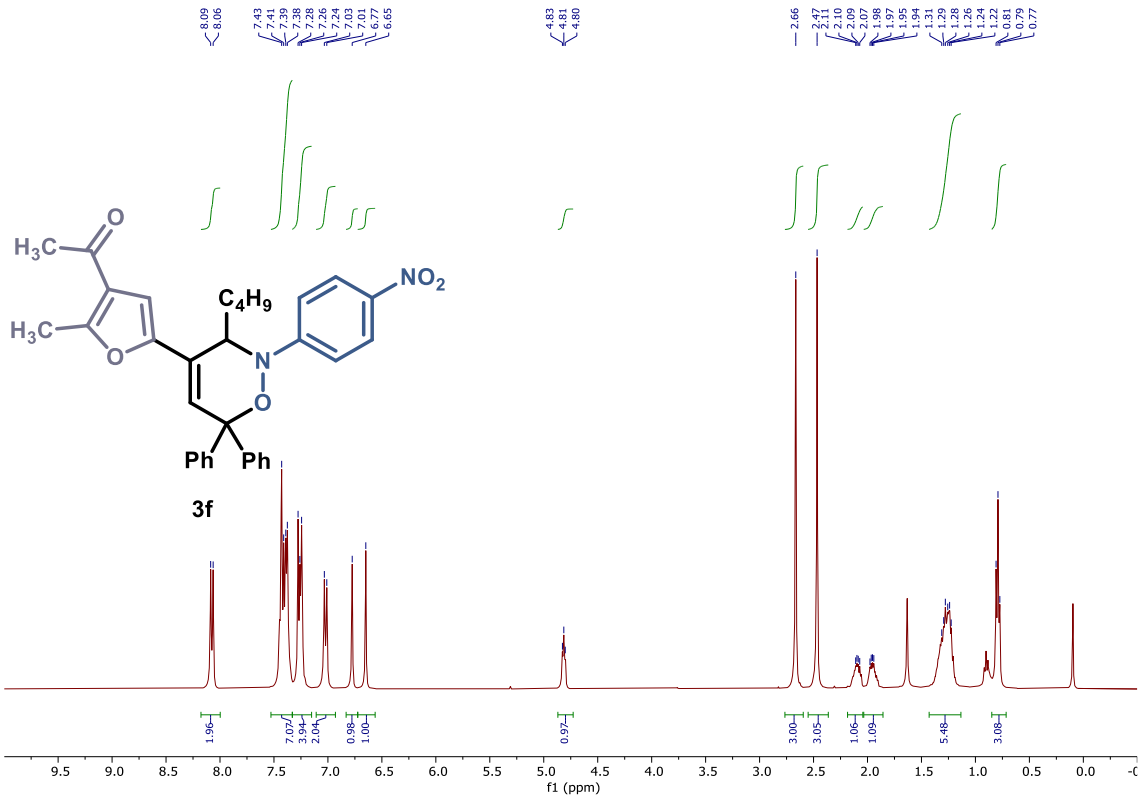


^{1}H-^{13}C HMBC



2D NOESY

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8.06
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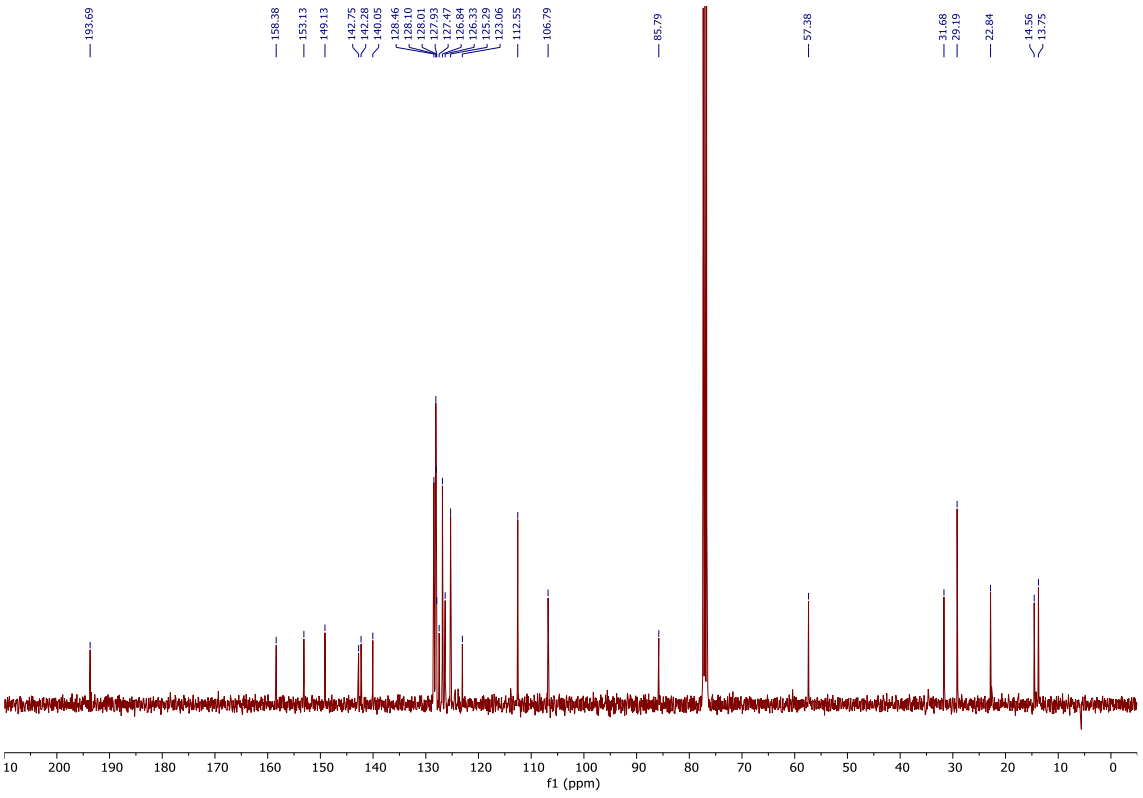
7.41
7.39
7.38
7.28
7.26
7.24
7.03
7.01
6.77
6.65
4.83
4.81
4.80
2.66
2.47
2.11
2.10
2.09
2.07
1.98
1.97
1.95
1.94
1.31
1.29
1.28
1.26
1.24
1.22
0.81
0.79
0.77
H3C
O
H3C
O
C4H9
N
O
NO2
Ph
Ph
3f
1.96
7.07
3.94
2.04
0.98
1.00
0.97
3.00
3.05
1.06
1.09
5.48
3.08
f1 (ppm)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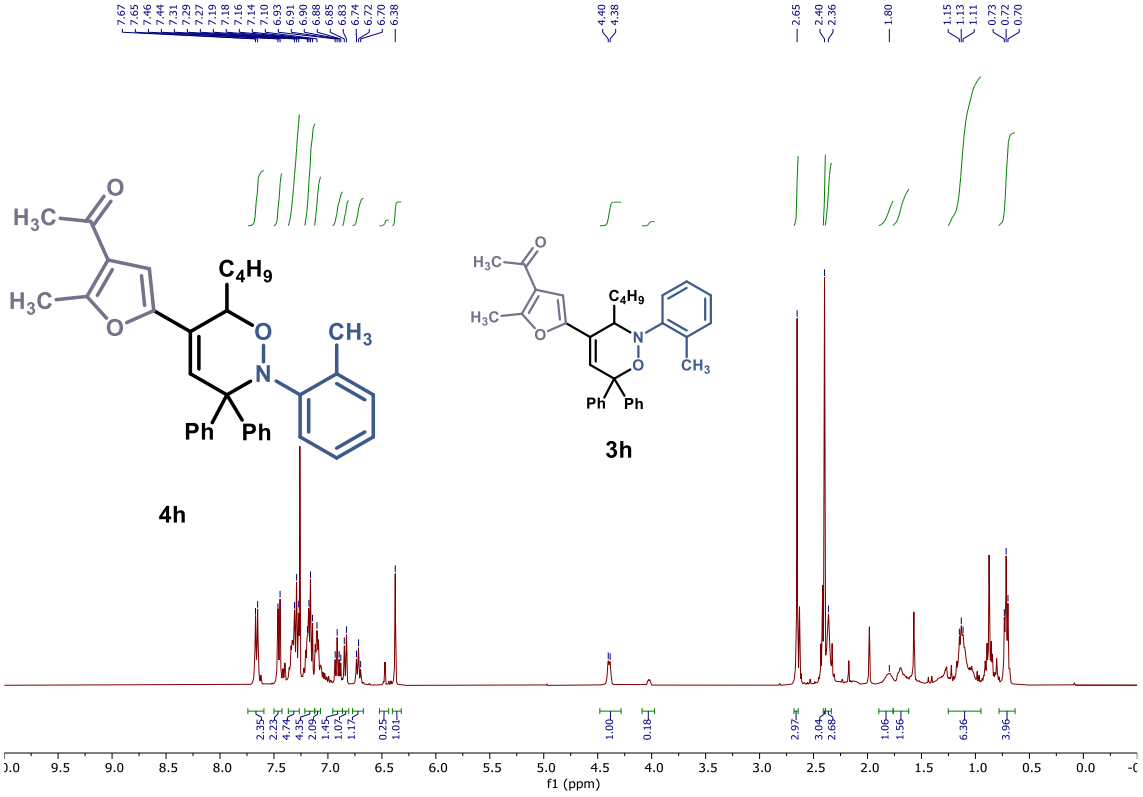
153.13
149.13
142.75
142.38
140.05
128.46
128.10
128.01
127.93
127.47
126.84
126.33
125.29
123.06
112.55
106.79
85.79
57.38
31.68
29.19
22.84
14.56
13.75
f1 (ppm)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7.29
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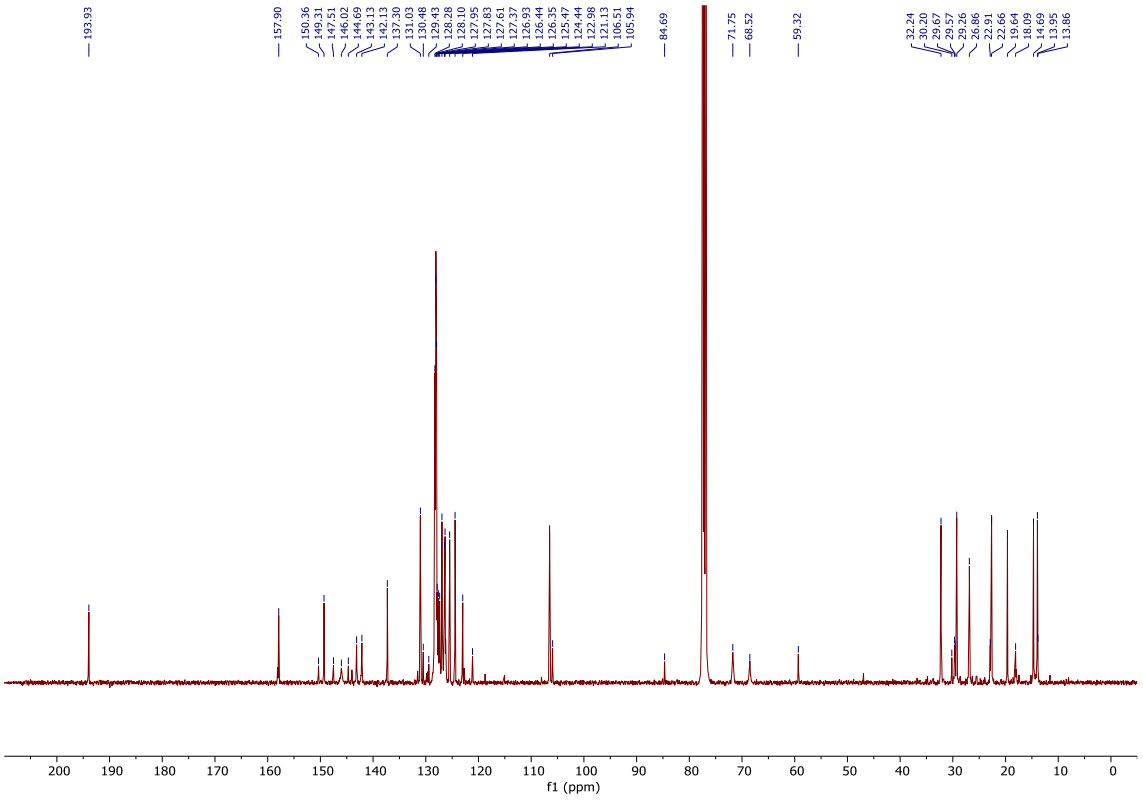
7.19
7.18
7.16
7.14
7.10
6.93
6.91
6.90
6.88
6.85
6.83
6.74
6.72
6.70
6.38
4.40
4.38
2.65
2.40
2.36
1.80
1.15
1.13
1.11
0.73
0.72
0.70
H3C
O
C4H9
CH3
N
Ph
Ph
4h
3h
2.35
2.23
4.74
4.35
2.09
1.45
1.07
1.17
0.25
1.01
1.00
0.18
2.97
3.04
2.68
1.06
1.56
6.36
3.96
f1 (ppm)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143.13
142.13
137.30
131.03
130.48
129.43
128.38
128.10
127.95
127.83
127.61
127.37
126.93
126.44
126.35
125.47
124.44
122.98
121.13
106.51
105.94
84.69
71.75
68.52
59.32
32.24
30.20
29.67
29.57
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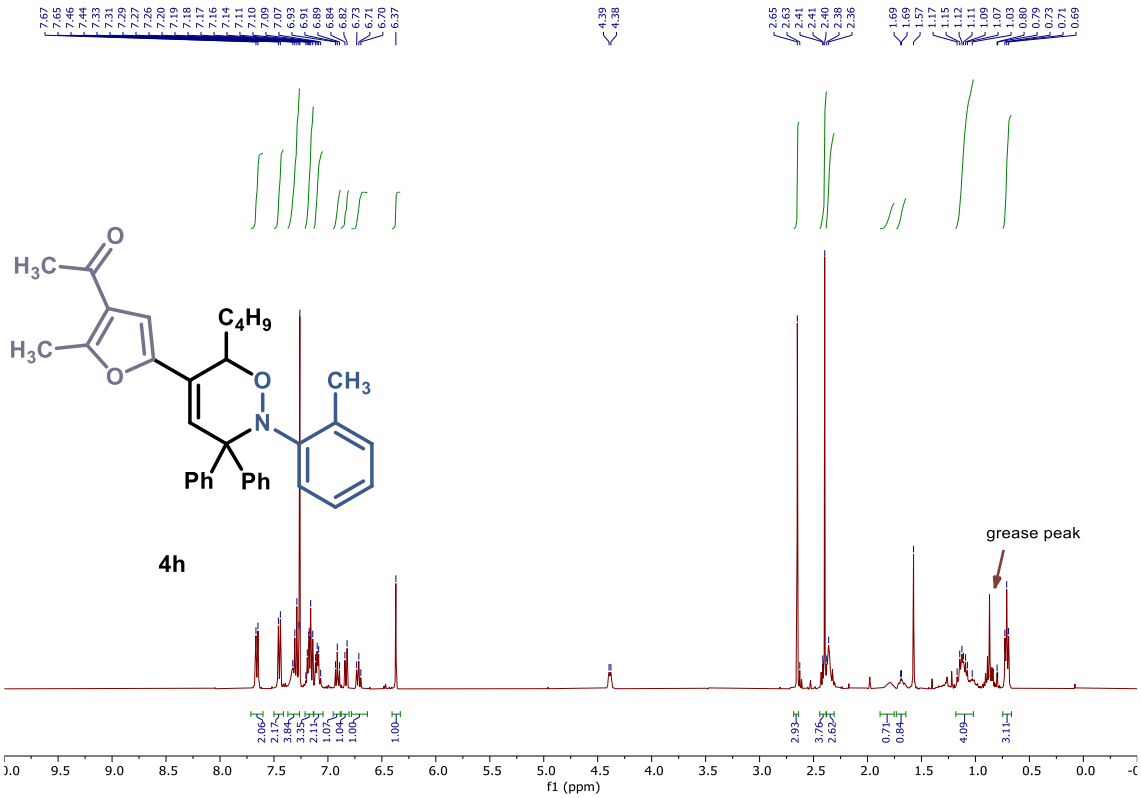
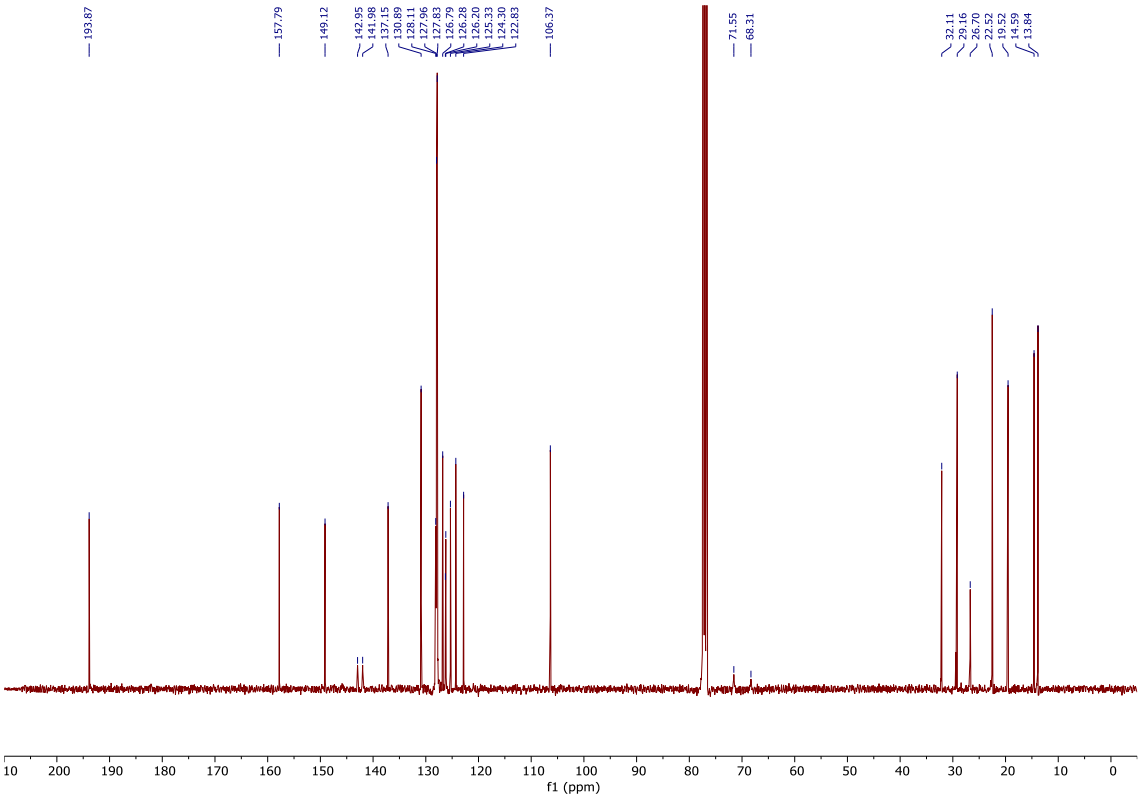
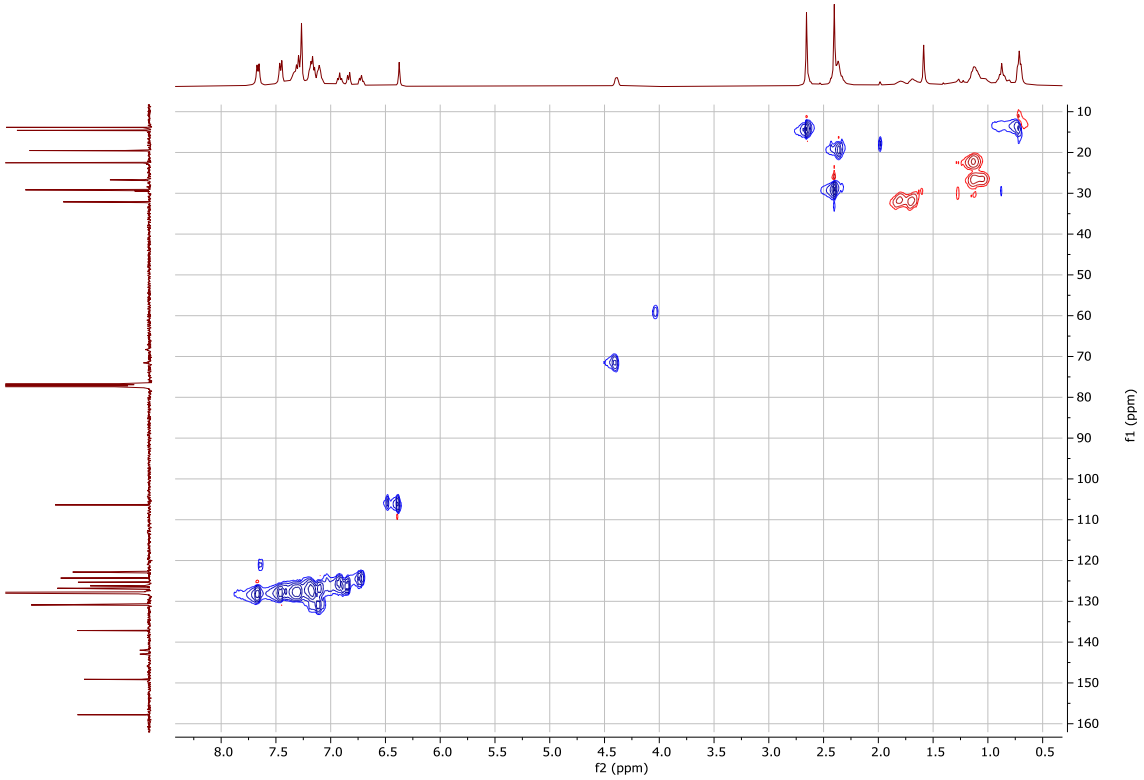
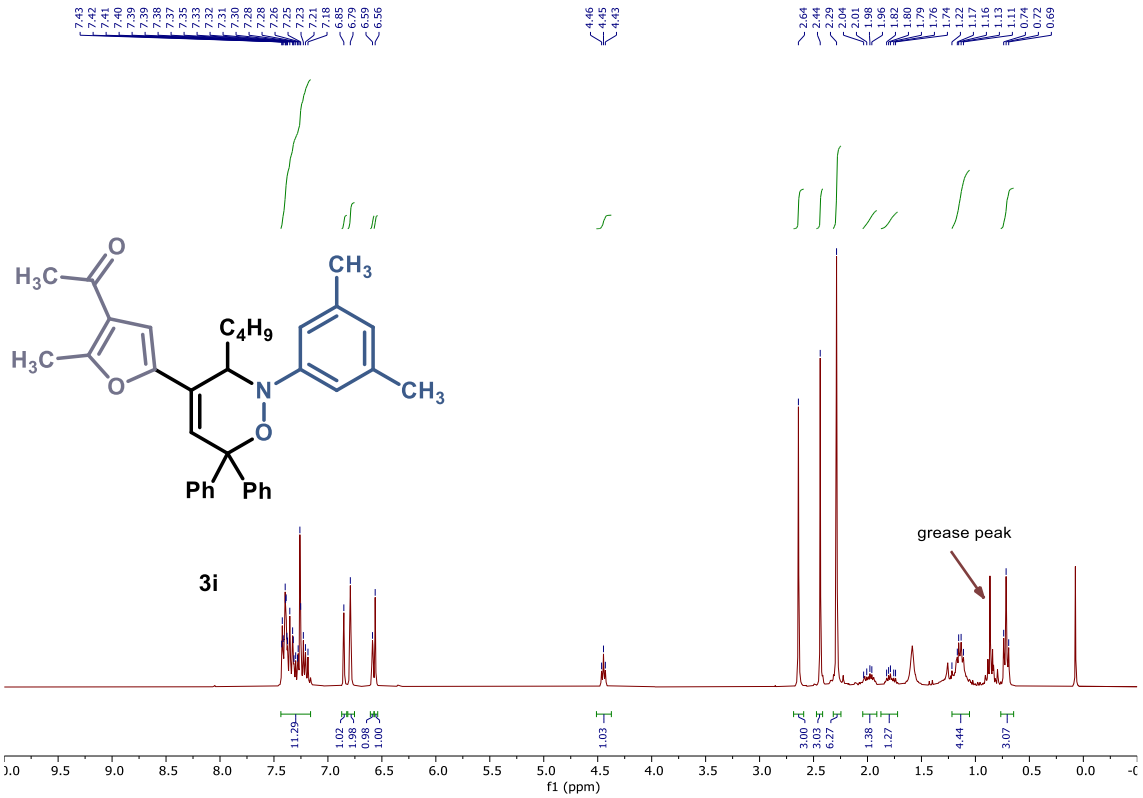
26.86
22.91
22.66
19.64
18.09
14.69
13.95
13.86
f1 (ppm)


4h
grease peak
f1 (ppm)


f1 (ppm)

^{1}H-^{13}C HSQC

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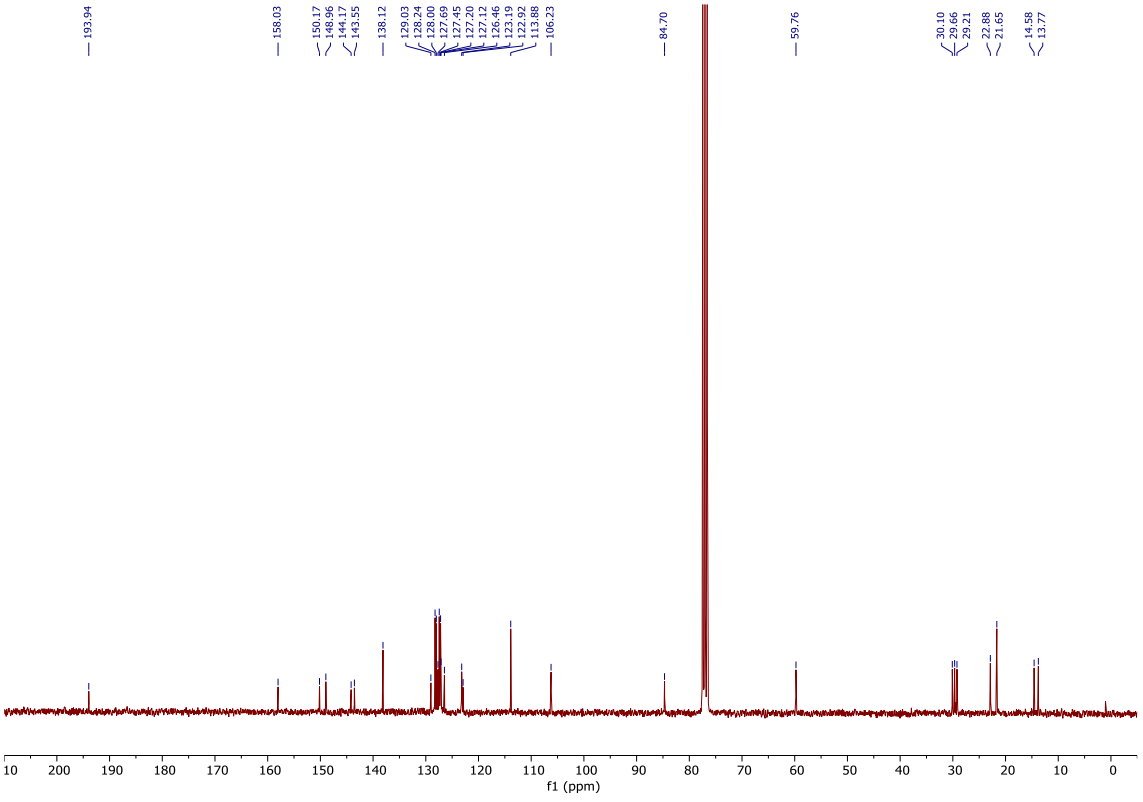
7.28
7.26
7.25
7.23
7.21
7.18
6.85
6.79
6.59
6.56
4.46
4.45
4.43
2.64
2.44
2.29
2.04
2.01
1.98
1.96
1.82
1.80
1.79
1.76
1.74
1.22
1.17
1.16
1.13
1.11
0.74
0.72
0.69
H3C
O
H3C
O
C4H9
CH3
N
O
CH3
Ph
Ph
3i
grease peak
11.29
1.02
1.98
0.98
1.00
1.03
3.00
3.03
6.27
1.38
1.27
4.44
3.07
f1 (ppm)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128.24
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127.69
127.45
127.20
127.12
126.46
123.19
122.92
113.88
106.23
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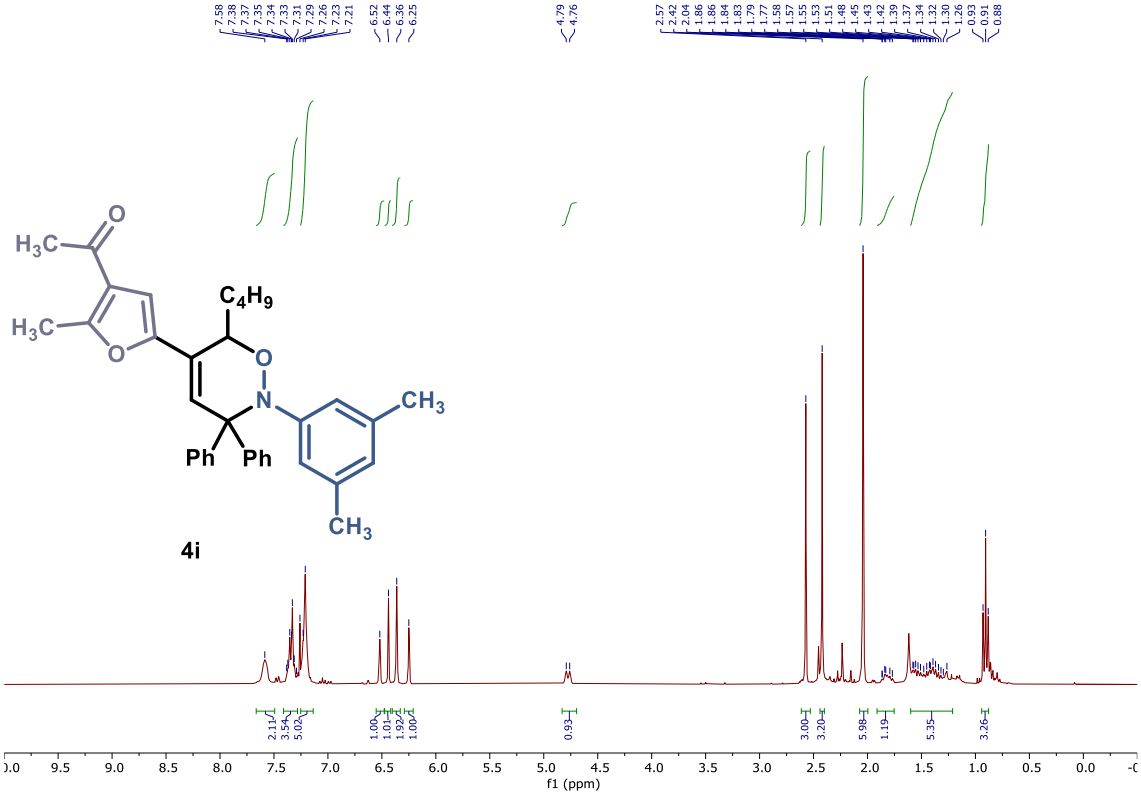
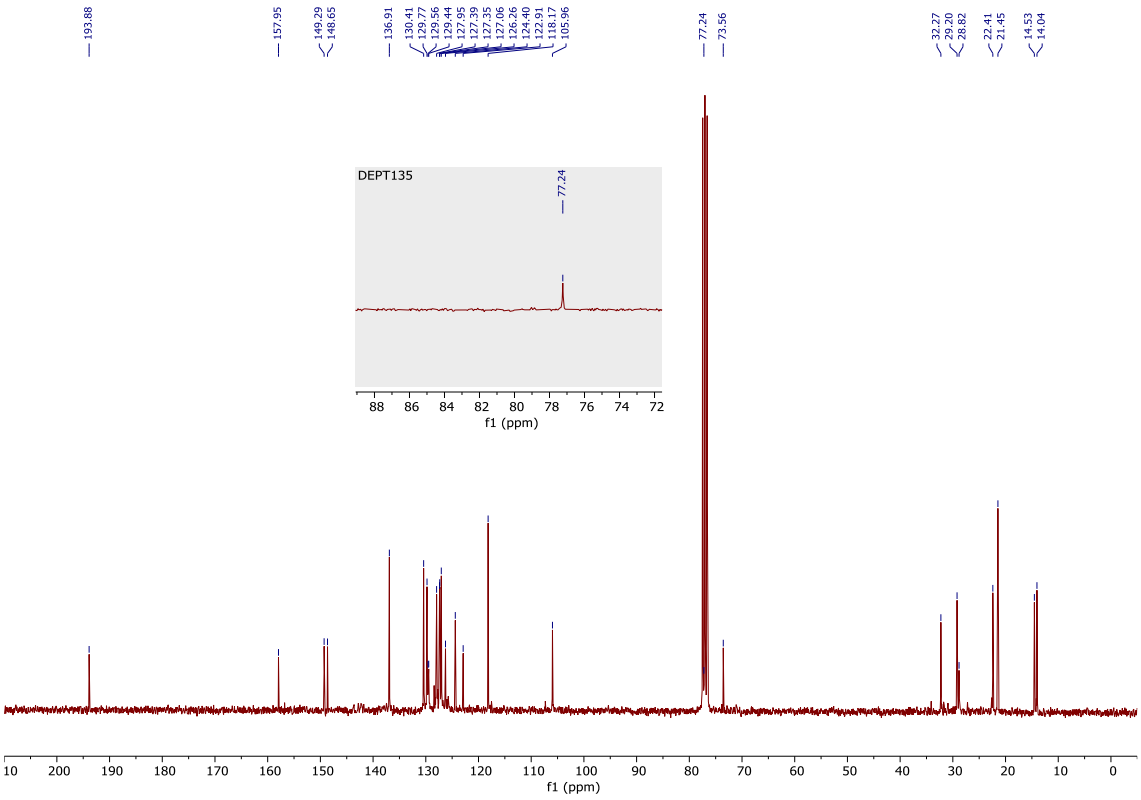
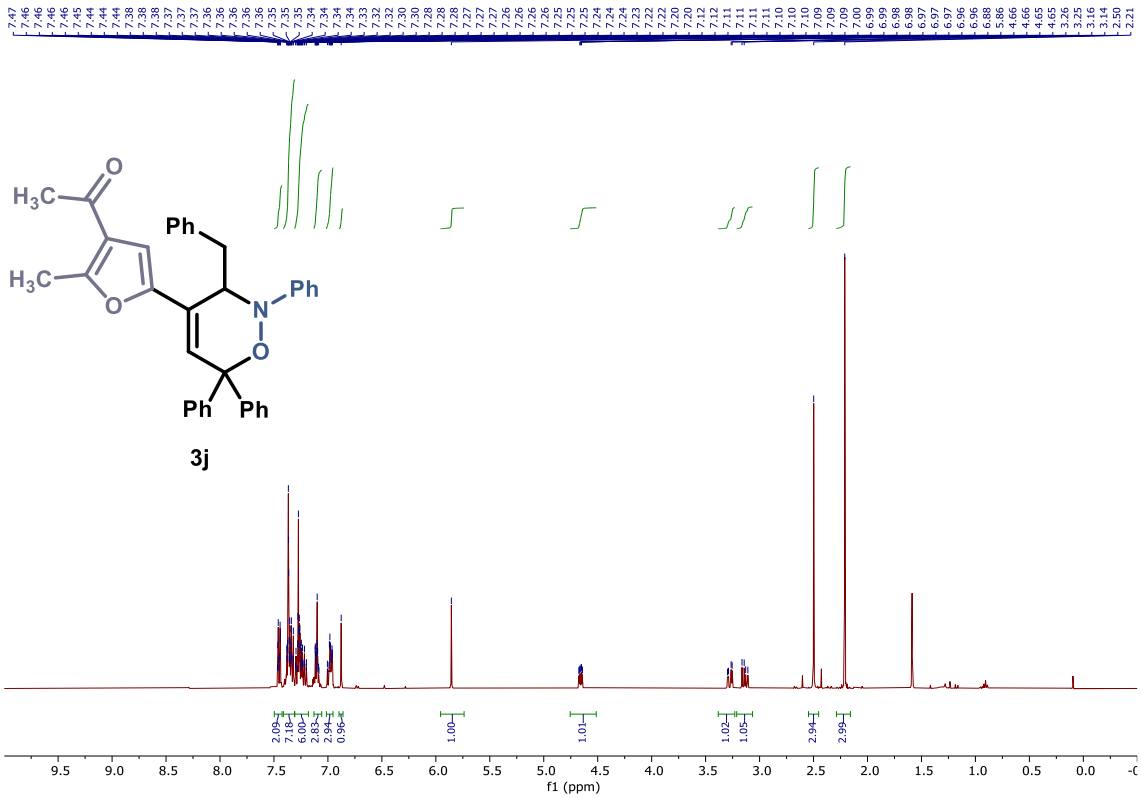
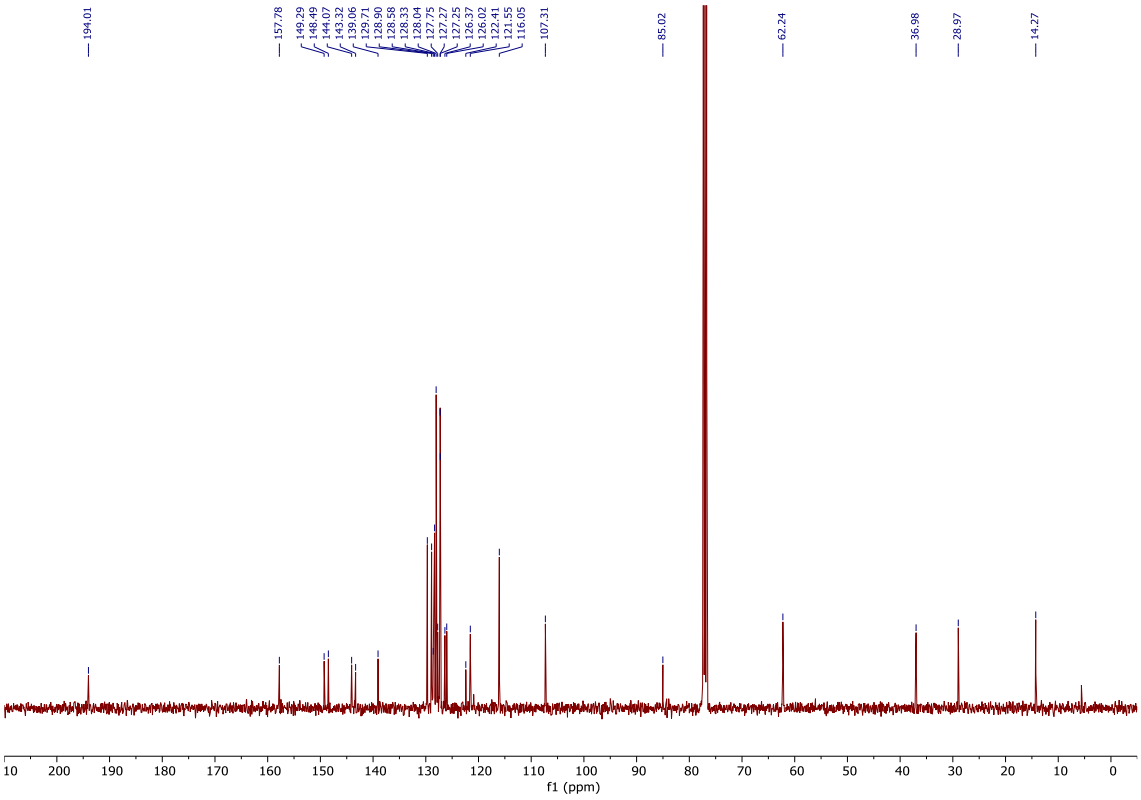
59.76
30.10
29.66
29.21
22.88
21.65
14.58
13.77
f1 (ppm)


4i
f1 (ppm)


DEPT135
f1 (ppm)
f1 (ppm)


H3C
O
Ph
H3C
O
N
Ph
O
Ph
Ph
3j
f1 (ppm)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128.58
128.33
128.04
127.75
127.27
127.25
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126.02
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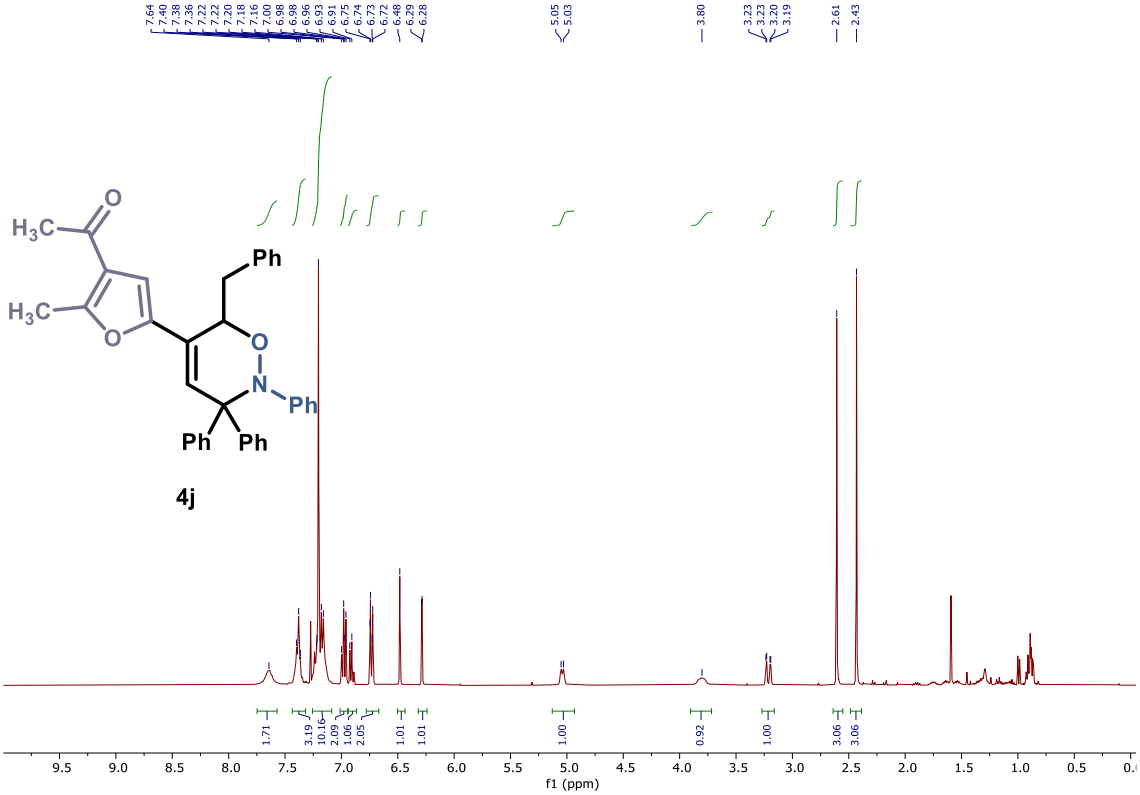
121.55
116.05
107.31
85.02
62.24
36.98
28.97
14.27
f1 (ppm)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7.18
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7.00
6.98
6.96
6.93
6.91
6.75
6.74
6.73
6.72
6.48
6.29
6.28
5.05
5.03
3.80
3.23
3.23
3.20
3.19
2.61
2.43
H3C
O
H3C
O
Ph
O
N
Ph
Ph
Ph
4j
1.71
3.19
10.16
2.09
1.06
2.05
1.01
1.01
1.00
0.92
1.00
3.06
3.06
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
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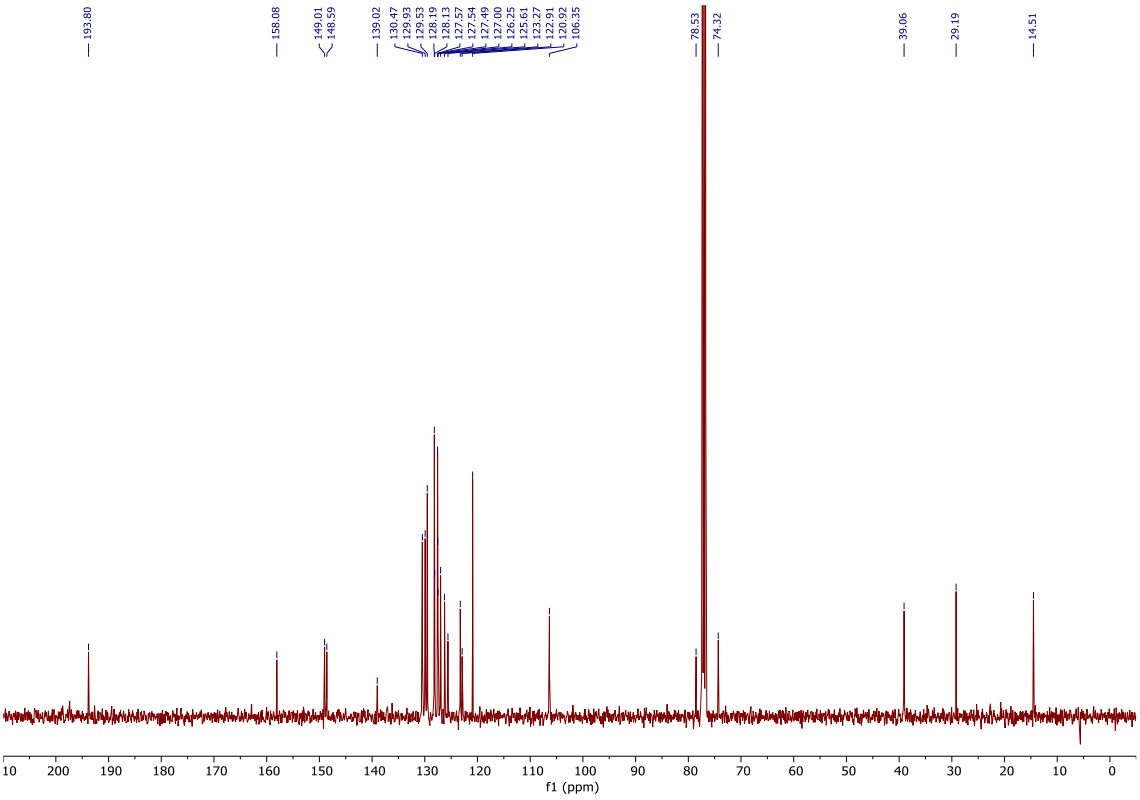
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)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127.49
127.00
126.25
125.61
123.27
122.91
120.92
106.35
78.53
74.32
39.06
29.19
14.51
10
200
190
180
170
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120
110
100
90
80
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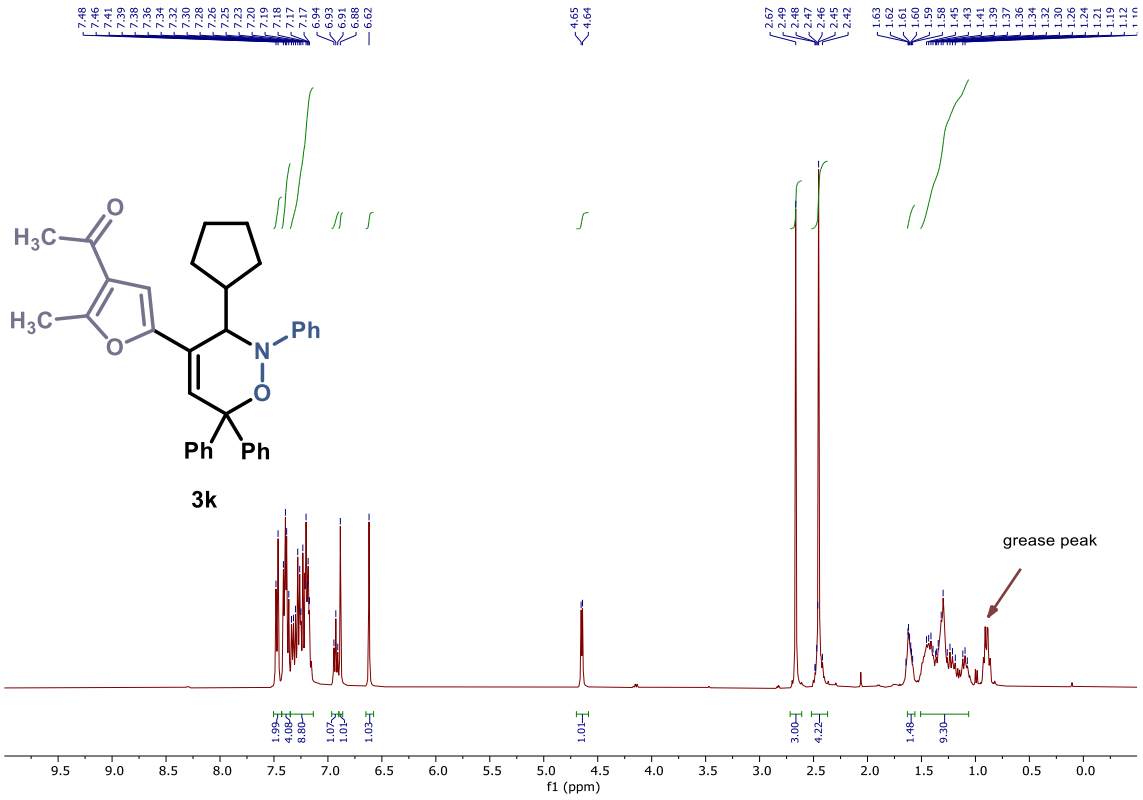
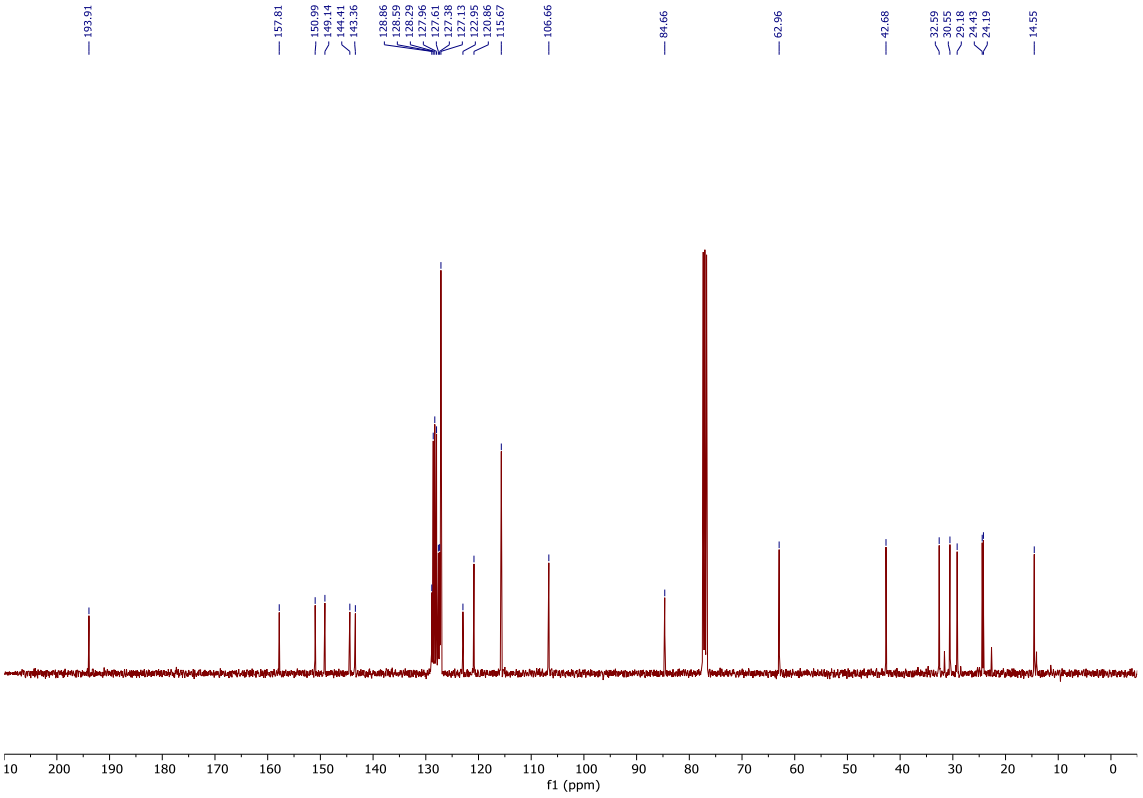
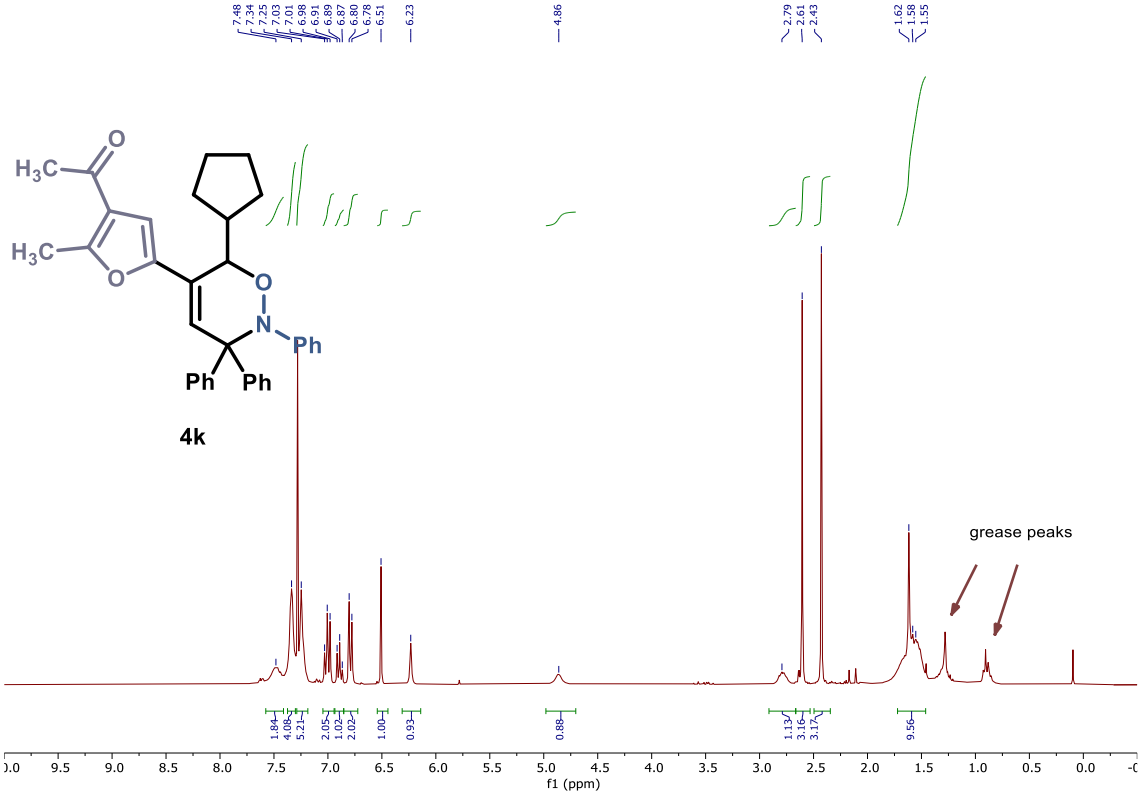
50
40
30
20
10
0
f1 (ppm)


3k
grease peak
f1 (ppm)


f1 (ppm)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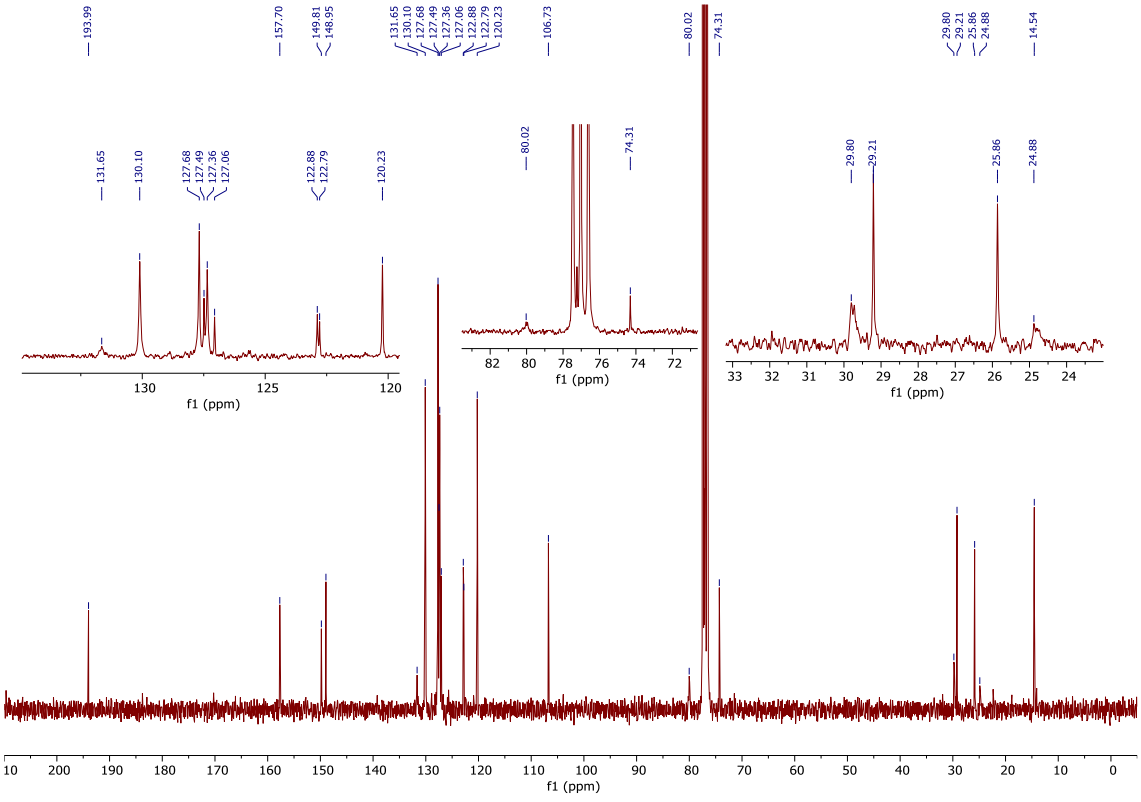
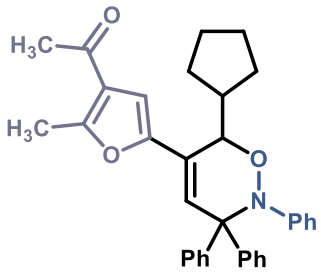
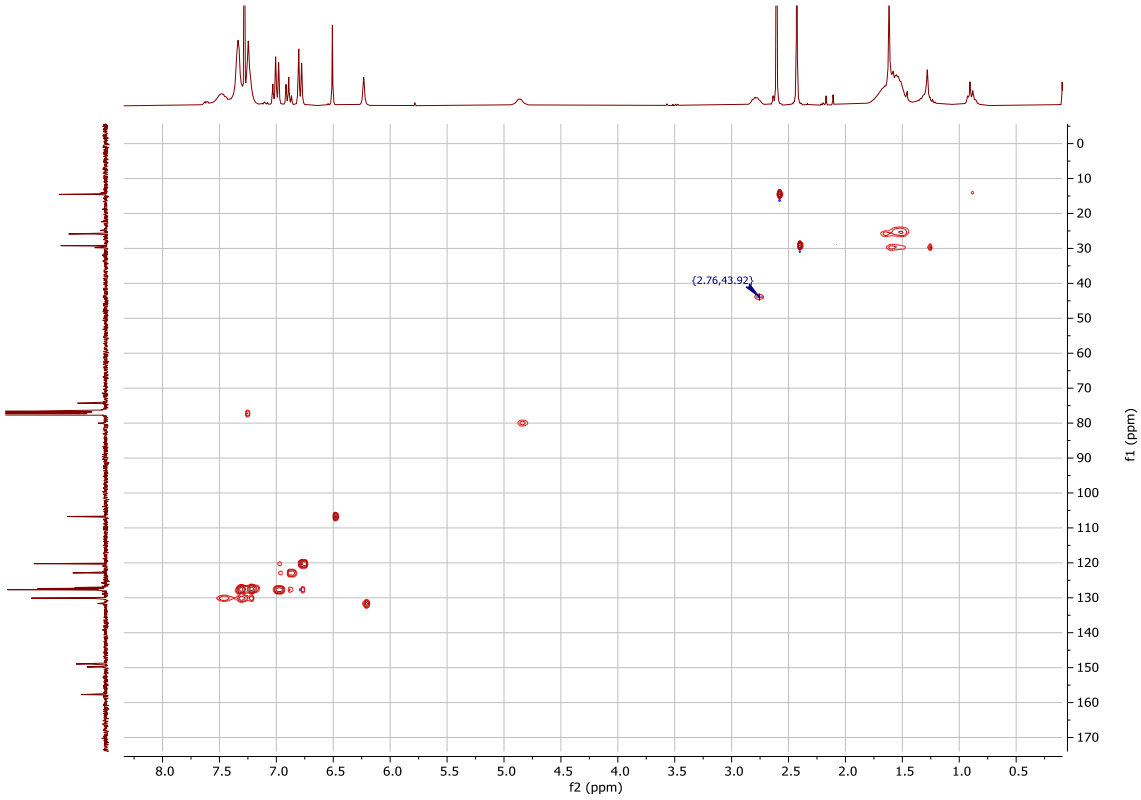
7.34
7.25
7.03
7.01
6.98
6.91
6.89
6.87
6.80
6.78
6.51
6.23
4.86
2.79
2.61
2.43
1.62
1.58
1.55
H3C
O
H3C
O
O
N
Ph
Ph
Ph
4k
grease peaks
1.84
4.08
5.21
2.05
1.02
2.02
1.00
0.93
0.88
1.13
3.16
3.17
9.56
f1 (ppm)

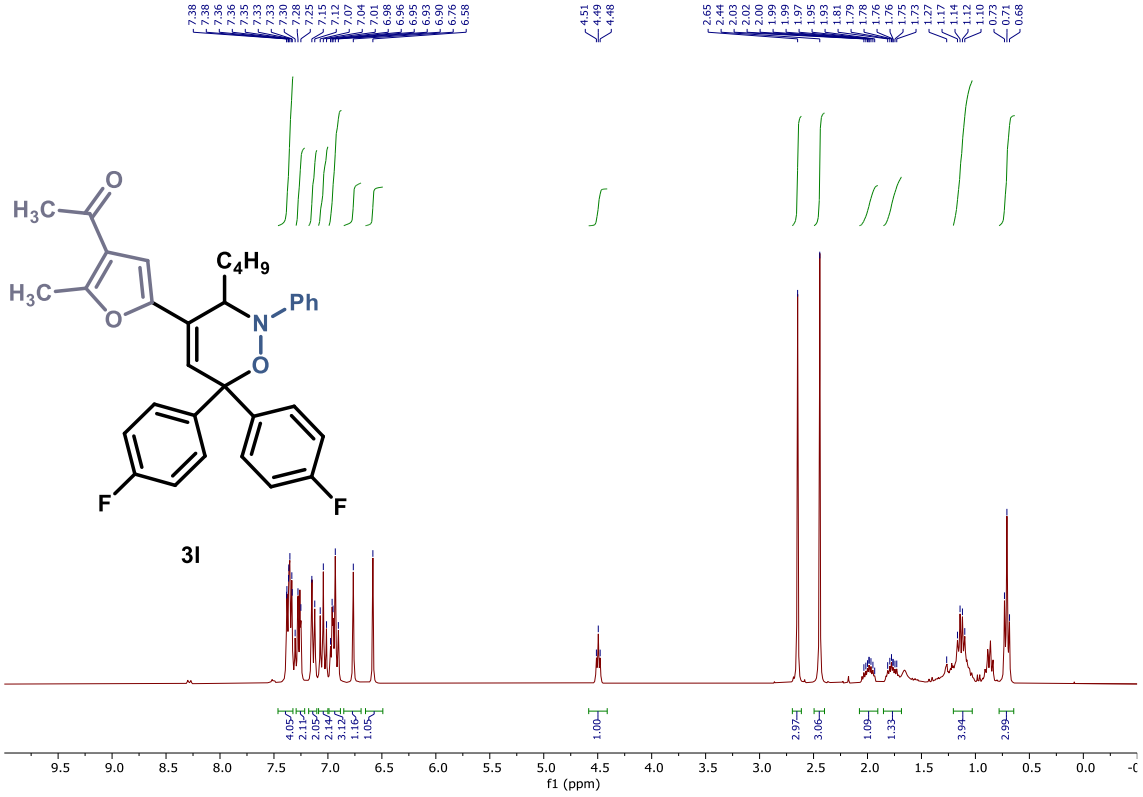

193.99
157.70
149.81
148.95
131.65
130.10
127.68
127.49
127.36
127.06
122.88
122.79
120.23
106.73
80.02
74.31
29.80
29.21
25.86
24.88
14.54
f1 (ppm)

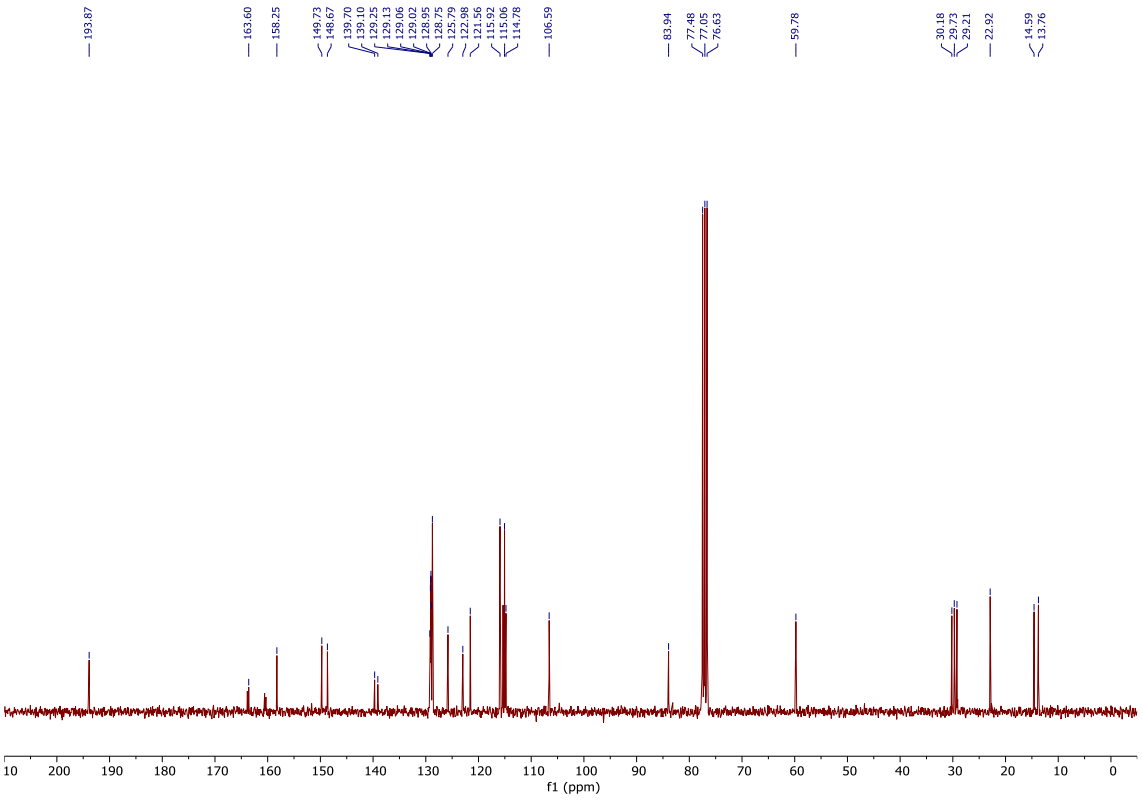
^{1}H-^{13}C HSQC

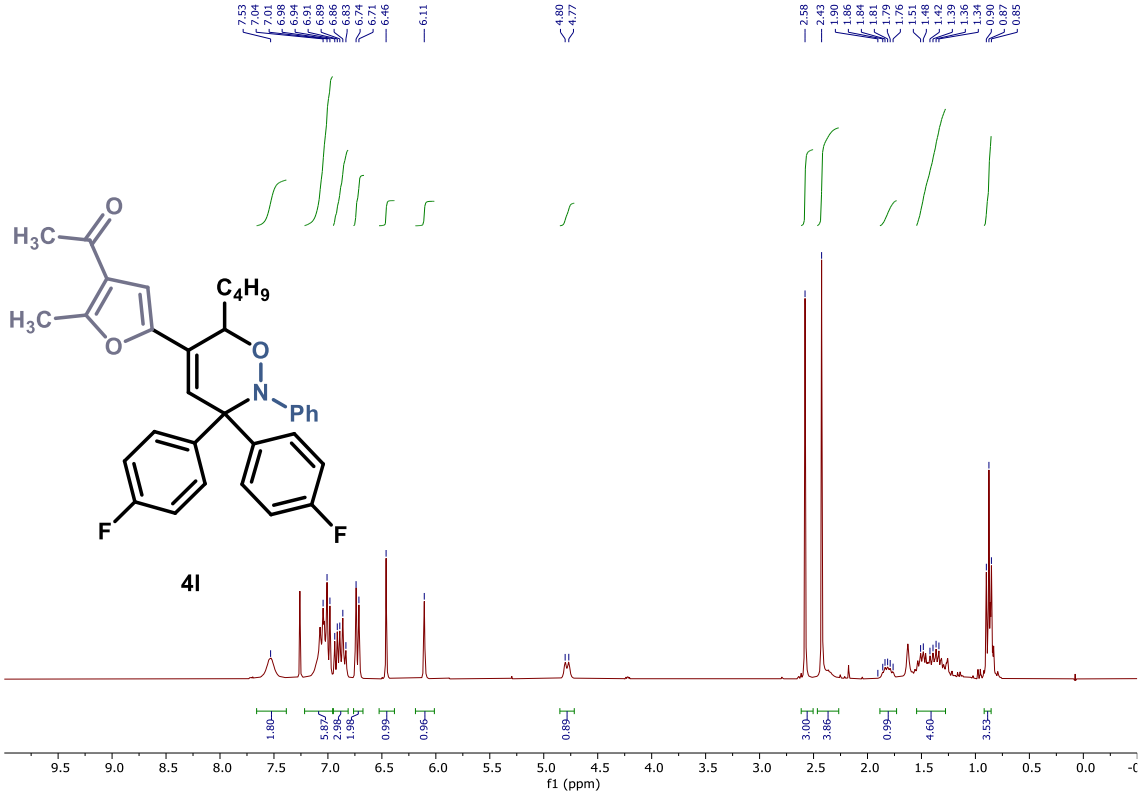


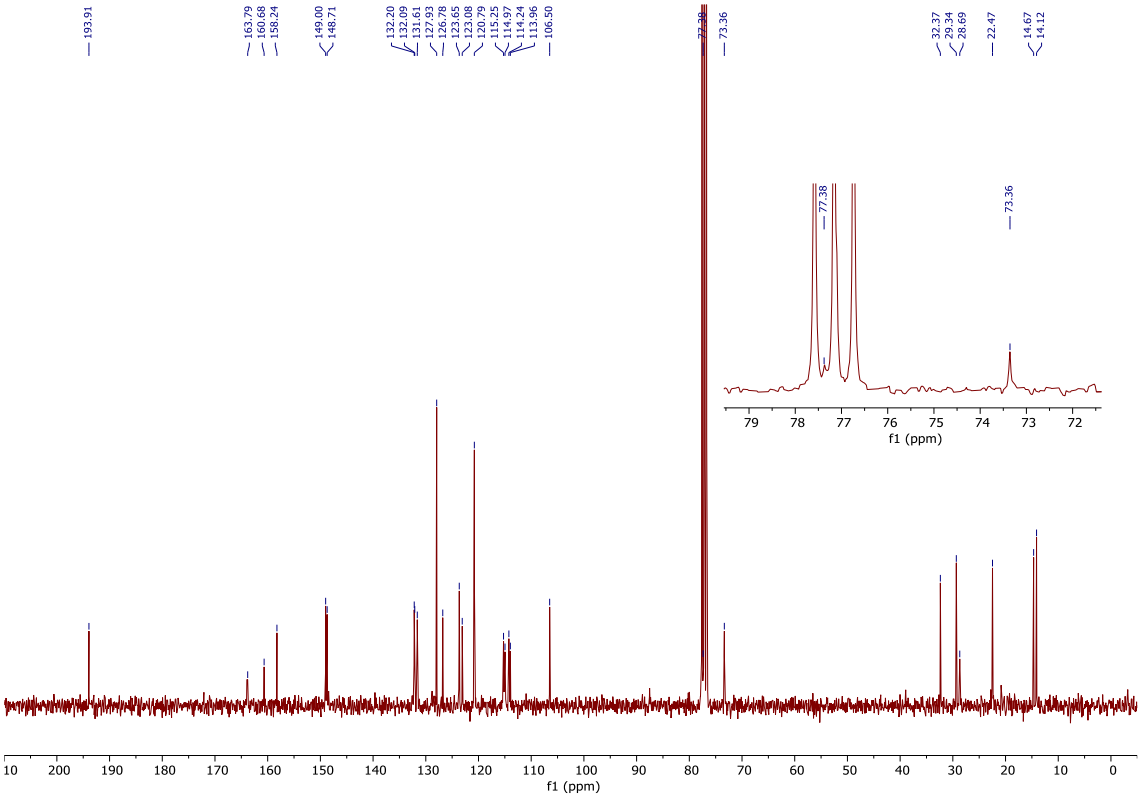
4k

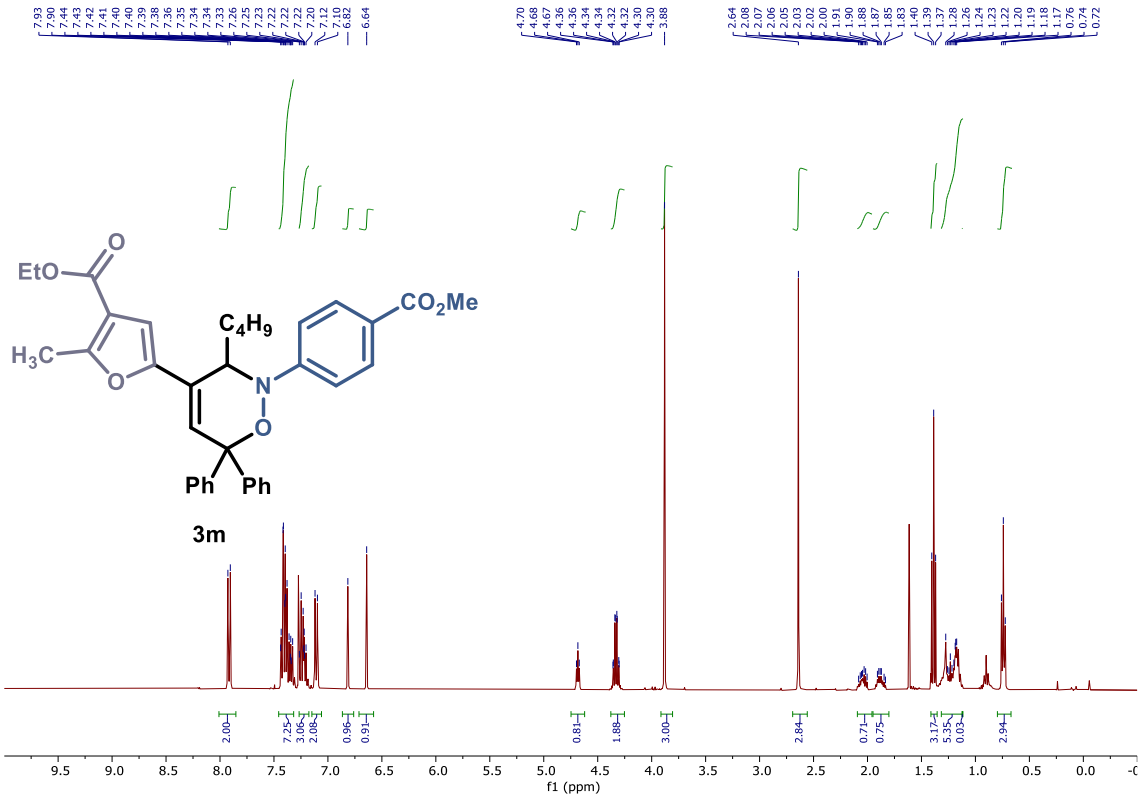


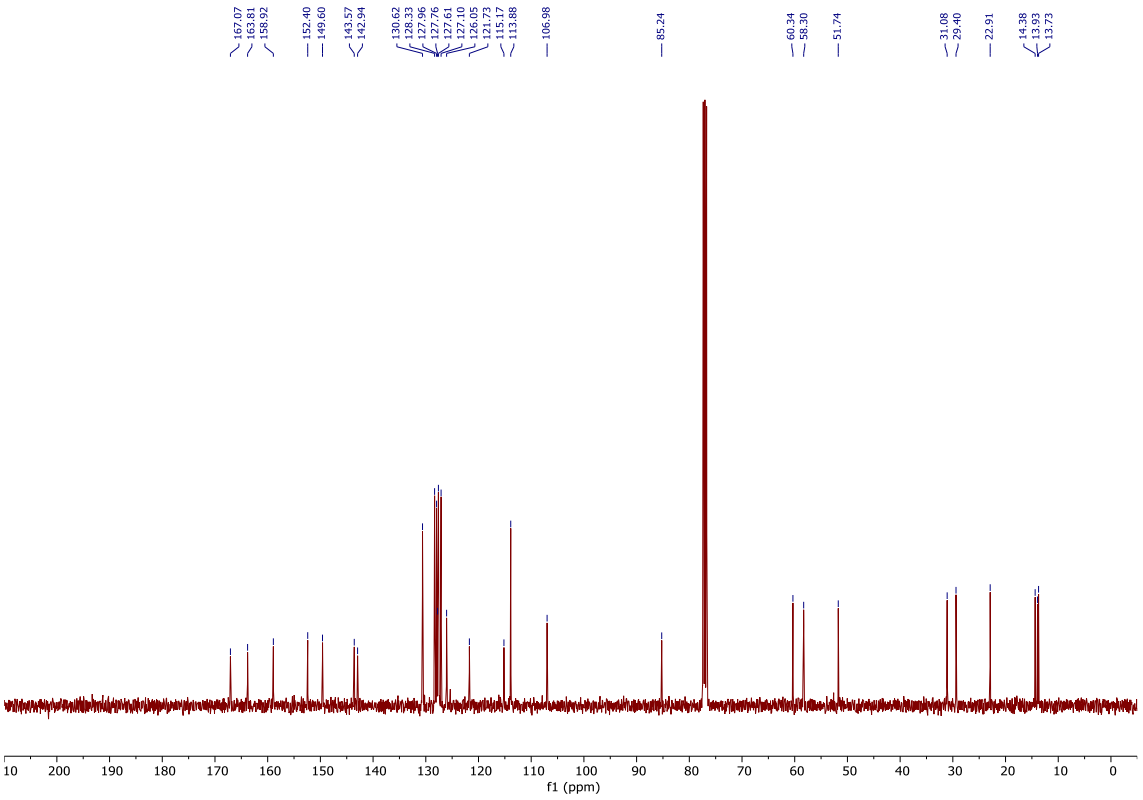

7.38
7.38
7.36
7.36
7.35
7.33
7.33
7.30
7.28
7.25
7.15
7.12
7.07
7.04
7.01
6.98
6.96
6.95
6.93
6.90
6.76
6.58
4.51
4.49
4.48
2.65
2.44
2.03
2.02
2.00
1.99
1.99
1.97
1.95
1.93
1.81
1.79
1.78
1.76
1.76
1.75
1.73
1.27
1.17
1.14
1.12
1.10
0.73
0.71
0.68
H3C
O
H3C
O
C4H9
N
Ph
O
F
F
3l
4.05
2.11
2.05
2.14
3.12
1.16
1.05
1.00
2.97
3.06
1.09
1.33
3.94
2.99
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

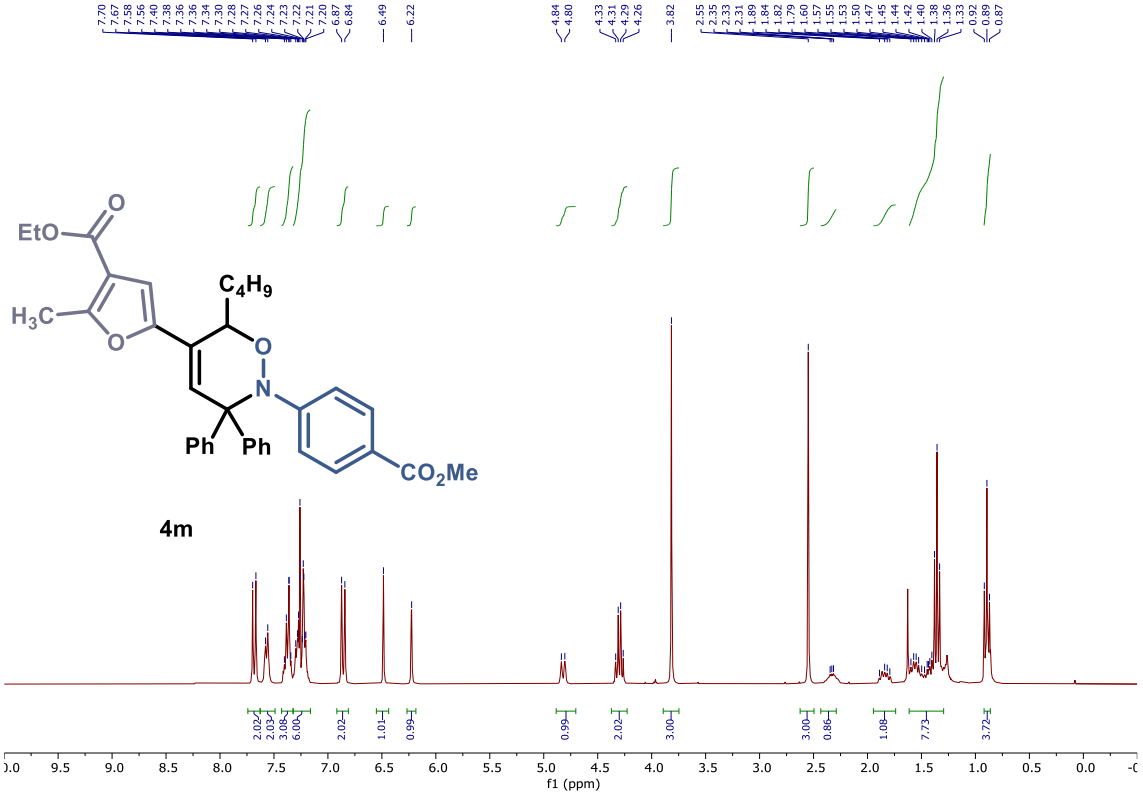

193.87
163.60
158.25
149.73
148.67
139.70
139.10
129.25
129.13
129.06
129.02
128.95
128.75
125.79
122.98
121.56
115.23
115.06
114.78
106.59
83.94
77.48
77.05
76.63
59.78
30.18
29.73
29.21
22.92
14.59
13.76
10
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

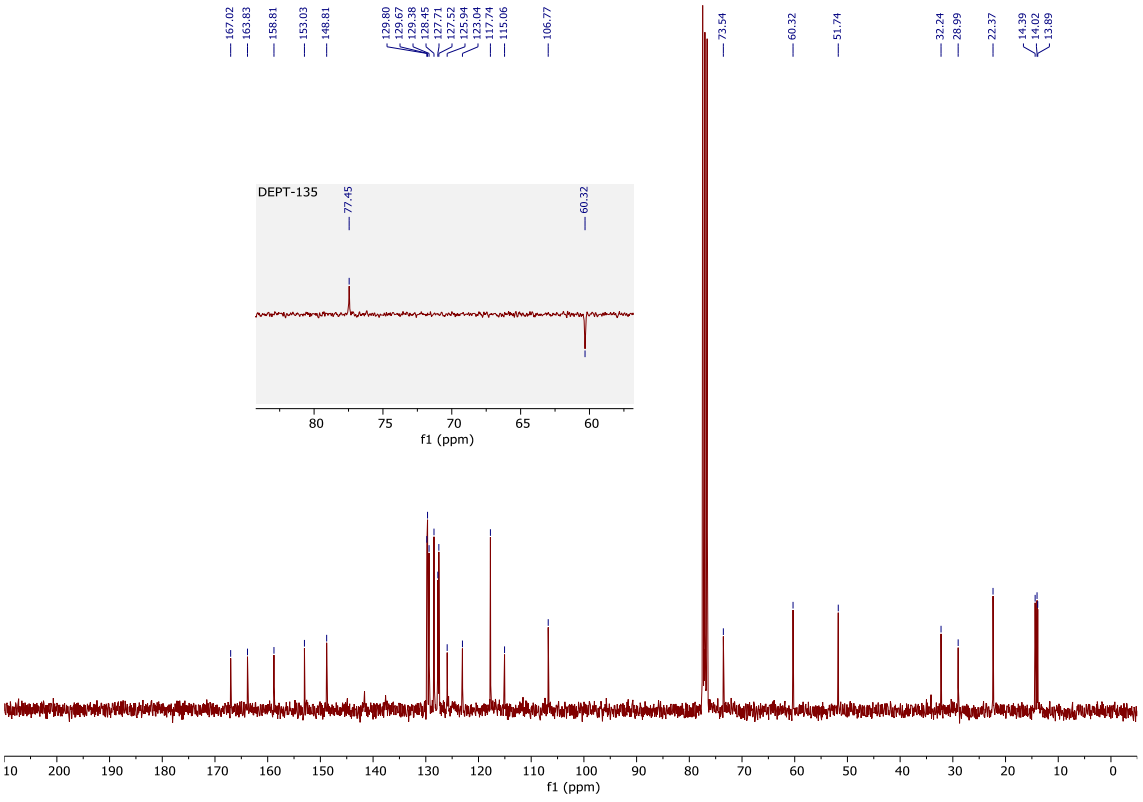

7.53
7.04
7.01
6.98
6.94
6.91
6.89
6.86
6.83
6.74
6.71
6.46
6.11
4.80
4.77
2.58
2.43
1.90
1.86
1.84
1.81
1.79
1.76
1.51
1.48
1.42
1.39
1.36
1.34
0.90
0.87
0.85
H3C
O
H3C
O
C4H9
O
N
Ph
F
F
4l
1.80
5.87
2.98
1.98
0.99
0.96
0.89
3.00
3.86
0.99
4.60
3.53
f1 (ppm)

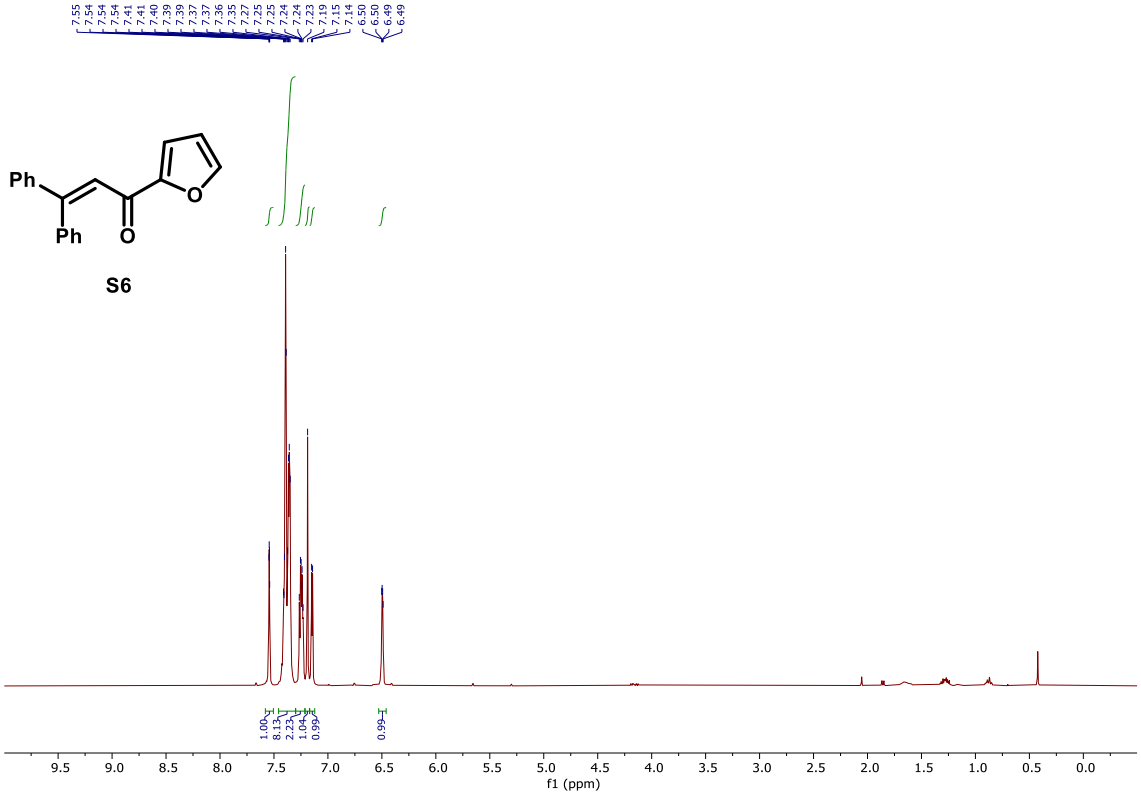

193.91
163.79
160.68
158.24
149.00
148.71
132.20
132.09
131.61
127.93
126.78
123.65
123.08
120.79
115.25
114.97
114.24
113.96
106.50
77.38
73.36
32.37
29.34
28.69
22.47
14.67
14.12
77.38
73.36
f1 (ppm)
f1 (ppm)


EtO
O
H3C
O
C4H9
N
O
CO2Me
Ph
Ph
3m
f1 (ppm)

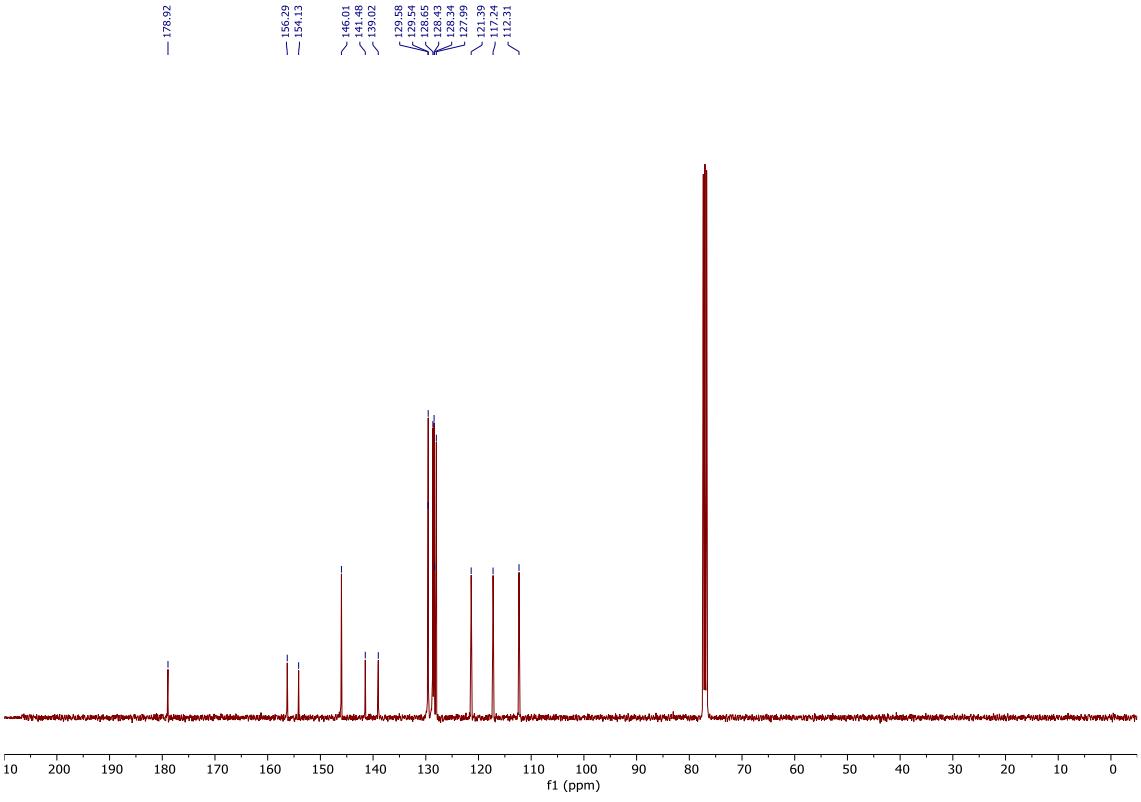

f1 (ppm)

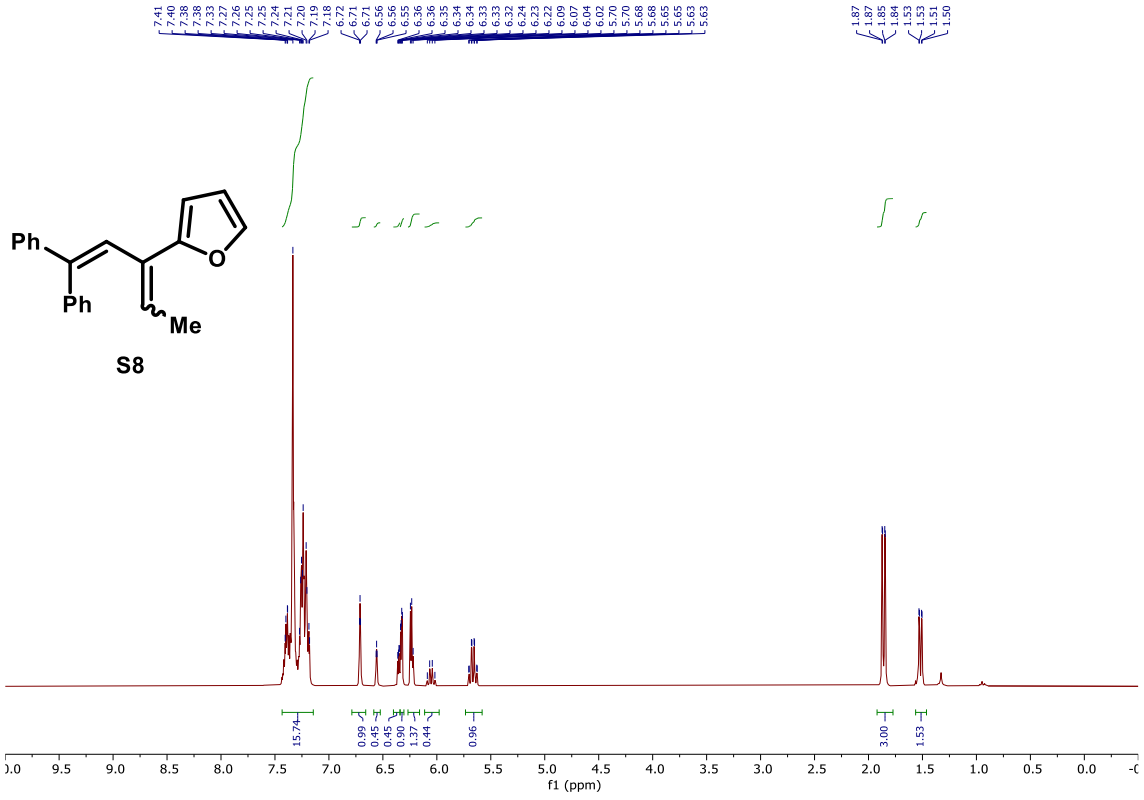

7.70 7.67 7.58 7.55 7.40 7.38 7.36 7.36 7.34 7.30 7.28 7.27 7.26 7.24 7.23 7.22 7.21 7.20 6.87 6.84 6.49 6.22
4.84 4.80 4.33 4.31 4.29 4.26 3.82
2.55 2.35 2.33 2.31 1.89 1.84 1.82 1.79 1.60 1.57 1.55 1.53 1.50 1.47 1.45 1.44 1.42 1.40 1.38 1.36 1.33 0.92 0.89 0.87
EtO
O
H_3C
O
C_4H_9
O
N
Ph
Ph
CO_2Me
4m
2.02 2.03 3.08 6.00 2.02 1.01 0.99 0.99 2.02 3.00 3.00 0.86 1.08 7.73 3.72
f1 (ppm)

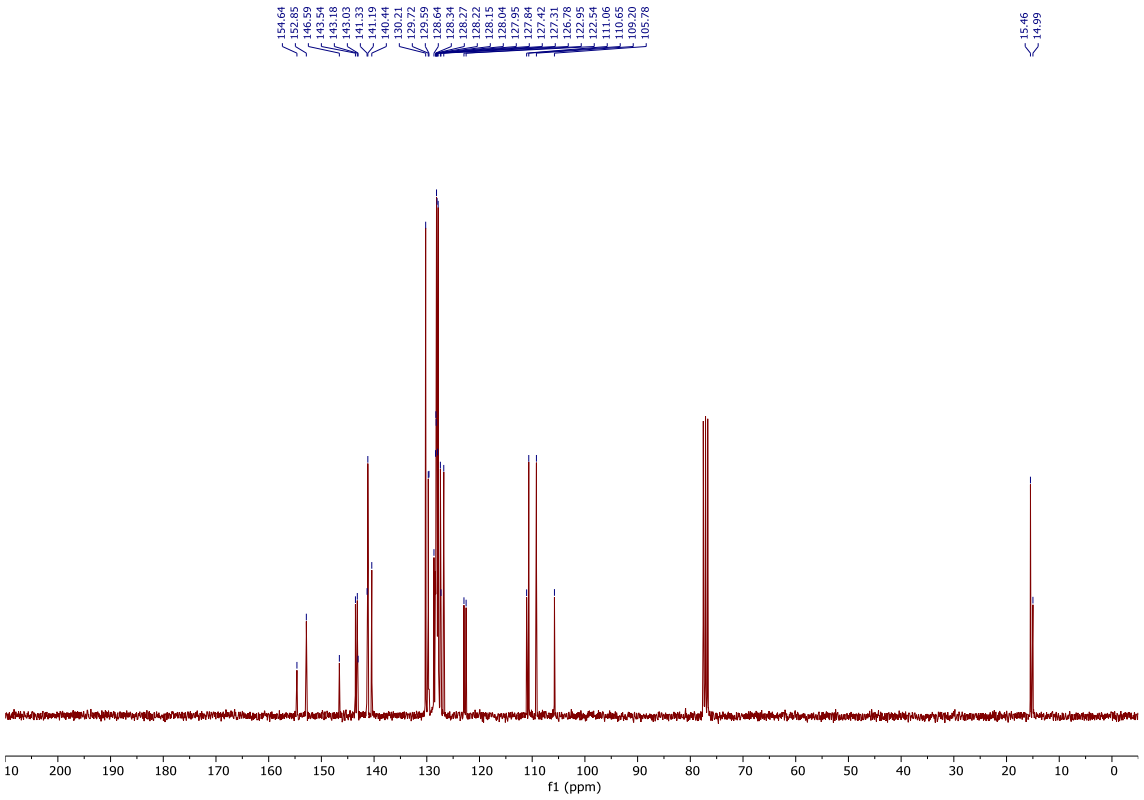

167.02 163.83 158.81 153.03 148.81 129.80 129.67 129.38 128.45 127.71 127.52 125.94 123.84 117.74 115.06 106.77 73.54 60.32 51.74 32.24 28.99 22.37 14.39 14.02 13.89
DEPT-135
77.45
60.32
f1 (ppm)

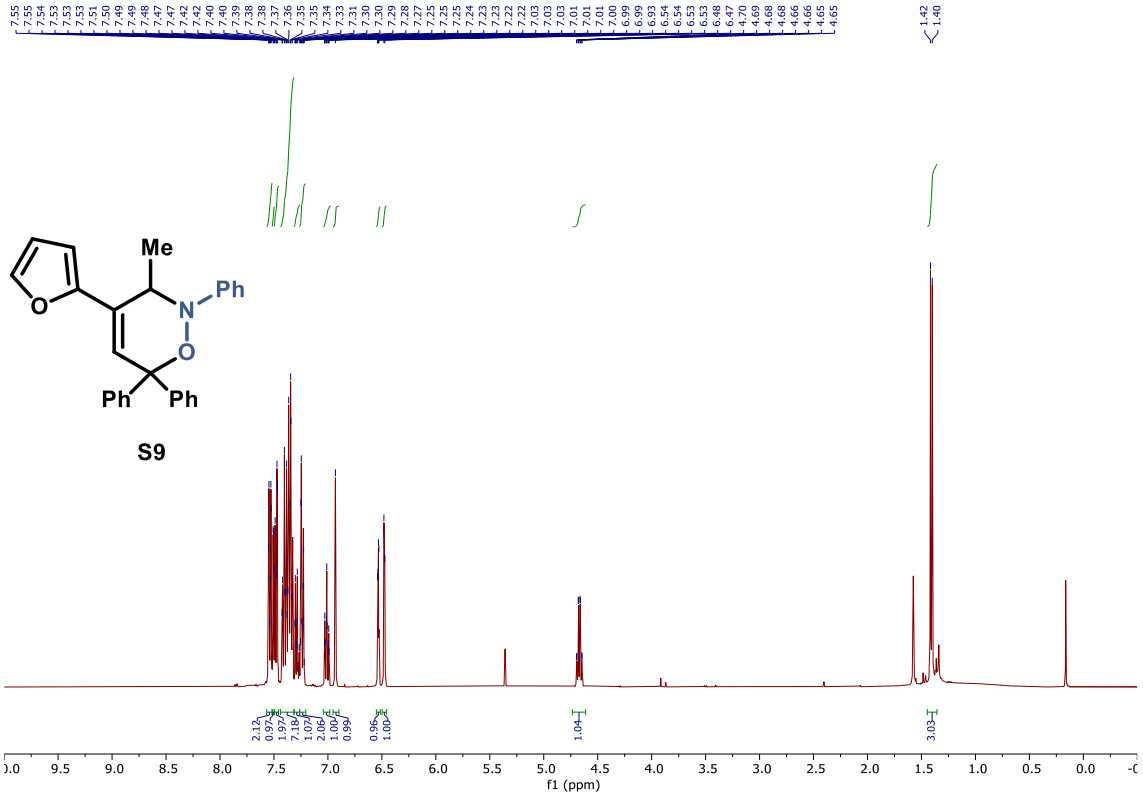

7.55
7.54
7.54
7.54
7.41
7.41
7.40
7.39
7.39
7.37
7.37
7.36
7.35
7.27
7.25
7.25
7.24
7.24
7.23
7.19
7.15
7.14
6.50
6.50
6.49
6.49
6.49
Ph
Ph
O
O
1.00
8.13
2.23
1.04
0.99
0.99
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

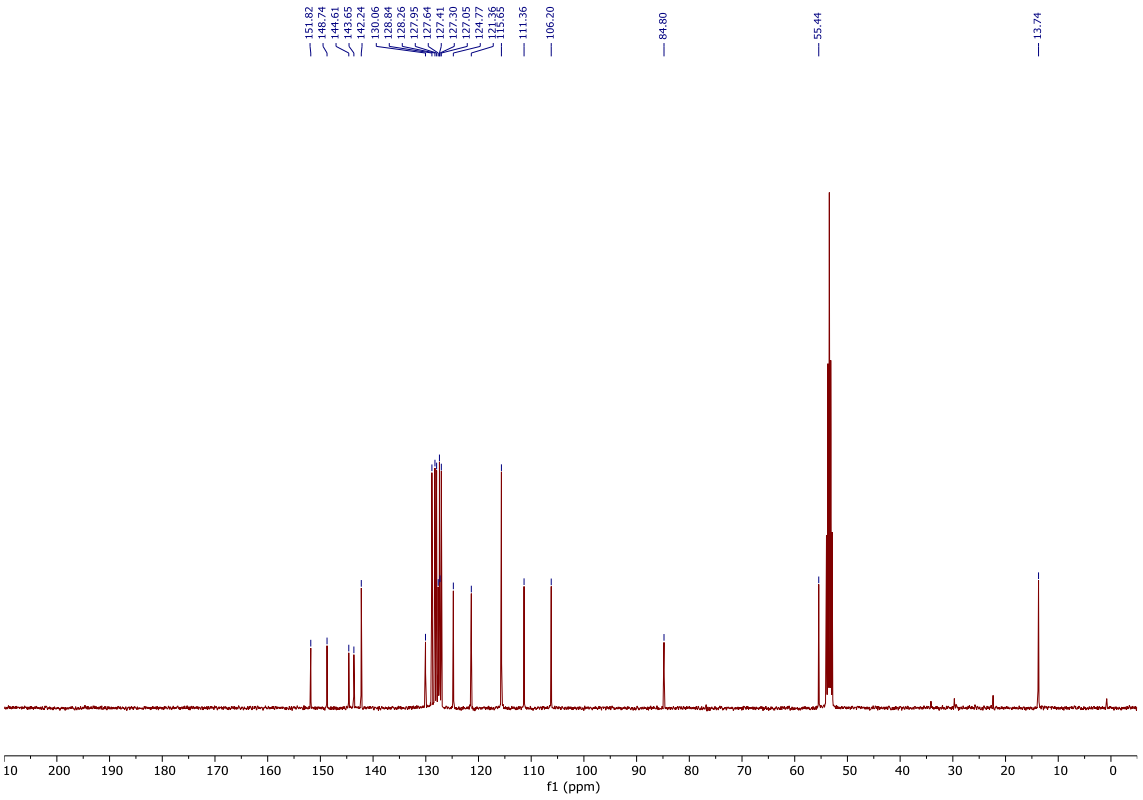
S6


178.92
156.29
154.13
146.01
141.48
139.02
129.58
129.54
128.65
128.43
128.34
127.99
121.39
117.24
112.31
10
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


Ph
Ph
O
Me
S8
f1 (ppm)


f1 (ppm)


Me
Ph
N
O
O
Ph
Ph
S9
f1 (ppm)


f1 (ppm)