SUPPORTING INFORMATION

Rh(I)-Catalyzed [4+2]-annulation of furan-fused cyclobutanones with alkynes and synthetic applications

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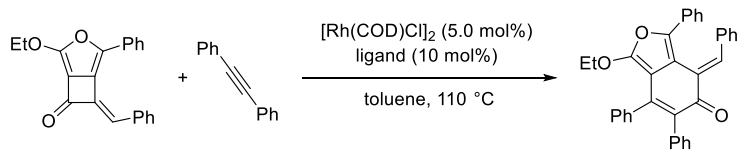
General Information

All reactions were carried out in oven-dried glassware. Solvents were purified and distilled by following the standard methods. Flash column chromatography was performed using silica gel (300-400 mesh). Analytical thin-layer chromatography was performed using glass plates pre-coated with 200-300 mesh silica gel impregnated with a fluorescent indicator (254 nm). The ^{1}H NMR, ^{13}C NMR, and ^{19}F NMR spectra were recorded in $CDCl_3$ on 400 MHz and 500 MHz spectrometer; chemical shifts were reported in ppm with the solvent signal as reference, and coupling constants (*J*) were given in Hertz. The peak information was described as: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, comp = composite. All substrates whose syntheses were not described herein were either obtained from commercial suppliers or prepared using the referenced literature procedures.[1] Unless stated otherwise, all commercially available compounds (Energy Chemical, Bidepharmatech) were used as received.

Optimization of the Intermolecular Reaction Conditions

Table S1 Optimization of reaction conditions[a]

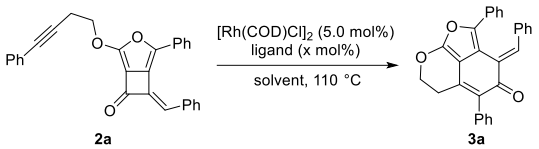


2s **4a** **5a**

Entry	Ligand (10 mol%)	Yield (%)[b]
1	DPEPhos	30[c]
2	dppf	15[c]
3	dppm	20[c]
4	PPh_3	80
5	P(2-furyl)$_3$	27
6	P(4-OMeC_6H_4)$_3$	25[c]
7	**P(4-$CF_3C_6H_4$)$_3$**	**85[d]**

[a][Rh(cod)Cl]$_2$ (1.23 mg, 5.0 mol%), ligand (10 mol%), furan-fused cyclobutanone **2s** (24.7 mg, 0.06 mmol), diphenylacetylene **4a** (24.7 mg, 0.09 mmol, 1.5 equiv.), and toluene (1.5 mL) were added in sequence under an argon atmosphere, and the reaction mixture was stirred for 2.0 h at 110 °C. [b]Determined by ^{1}H NMR analysis of the crude reaction mixture based on limited reagent **2s** with mesitylene as internal standard. [c]Most of the furan-fused cyclobutanone remains. [d]Isolated yield. DPEPhos = Bis(2-diphenylphosphinophenyl)ether. dppf = 1,1'-Bis(diphenylphosphino)ferrocene. dppm = Bis(diphenylphosphino)methane.

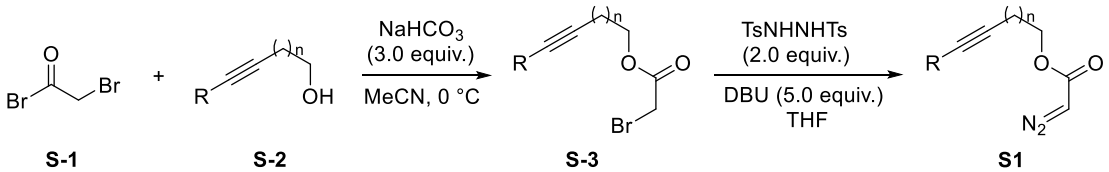
Table S2 Optimization of the reaction conditions[a]



Entry	Ligand (x mol%)	Solvent	Yield (%)[b]
1	PPh_3 (15)	toluene	45
2	P(c-Hex)$_3$ (15)	toluene	22[c]
3	DPEPhos (15)	toluene	56
4	dppf (15)	toluene	74
5	dppm (15)	toluene	63
6	dppp (15)	toluene	87
7	dppp (15)	p-xylene	60
8	dppp (15)	PhCl	13[c]
9	dppp (15)	$PhCF_3$	36
10	dppp (15)	1,4-dioxane	31[c]
11	dppp (15)	MeCN	trace
12[d]	dppp (15)	toluene	N.R.
13	dppp (10)	toluene	95[e]
14	dppp (5.0)	toluene	56[c]

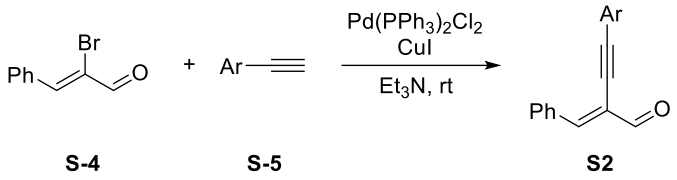
[a]Reaction conditions: $[Rh(COD)Cl]_2$ (1.23 mg, 5.0 mol%), ligand (5.0-20 mol%), FCB **2a** (22.7 mg, 0.06 mmol), and toluene (1.5 mL) were added in sequence under an argon atmosphere, and the reaction mixture was stirred for at 110 °C 4 h. [b]Determined by ^{1}H NMR analysis of the crude reaction mixture with mesitylene as internal standard. [c]The conversion of **2a** was low to moderate. [d]$Ni(COD)_2$ was used as catalyst instead of $[Rh(COD)Cl]_2$. [e] Isolated yield. DPEPhos = bis(2-diphenylphosphinophenyl)ether. dppf = 1,1'-bis(diphenylphosphino)ferrocene. dppm = bis(diphenylphosphino)methane. dppp = 1,3-bis(diphenylphosphanyl)propane. N.R. = No reaction.

General Procedure for the Synthesis of Diazo Compounds 1.[1]



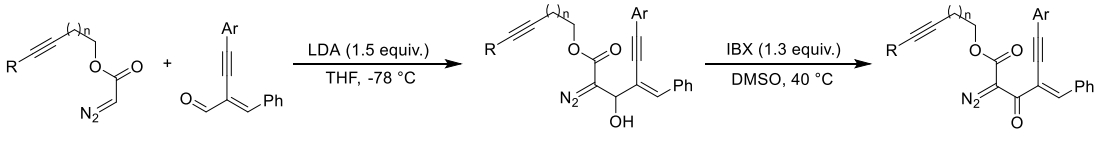
Synthesis of S1:[1a] To a 100-mL oven-dried round-bottom flask containing a magnetic stirring bar, alcohol **S-2** (10 mmol) and $NaHCO_3$ (2.52 g, 30 mmol) were dissolved in acetonitrile (20.0 mL) and bromoacetyl bromide **S-1** (1.32 mL, 15 mmol) was added slowly at 0 °C. After stirring 10 min at the temperarture, the reaction was quenched with H_2O. The solution was extracted with DCM three times. The organic phase was

washed with brine and dried over $MgSO_4$. The solvent was evaporated, and the residue was used in the next reaction without purification. The bromoacetate **S-3** thus obtained and N,N'-ditosylhydrazine (6.81 g, 20 mmol) were dissolved in THF (30.0 mL) and cooled to 0 °C. DBU (7.5 mL, 50 mmol) was added dropwise and stirred at the temperature for 10 minutes. After the quenching of the reaction by the addition of saturated $NaHCO_3$ solution, this was extracted with EtOAc three times. The organic phase was washed with brine, dried over $MgSO_4$ and evaporated to give the crude diazoacetate. Purification of the crude diazoacetate was performed with neutral silicagel (eluent: petroleum ether/EtOAc = 20:1) to give diazo compounds **S1** as a pale yellow oil (>72 % yields in two steps).



S-4 **S-5** **S2**

Synthesis of S2:[1b] To a 50-mL oven-dried flask containing a magnetic stirring bar, the commercially available α-bromocinnamaldehyde **S-4** (2.11 g, 10 mmol), $Pd(PPh_3)_2Cl_2$ (1.0 mol%, 70.2 mg), and CuI (1.0 mol%, 19 mg) in Et_3N (30.0 mL), was added a solution of alkyne **S-5** (12 mmol) in Et_3N (5.0 mL) slowly at room temperature. The reaction mixture was stirred 2.0 h. Upon completion (monitored by TLC), the solvent was evaporated under vacuum after filtering through Celite, and the resulting residues was purified by column chromatography on silica gel (eluent: petroleum ether/EtOAc = 30:1) to give the pure **S2** (>80 % yields)



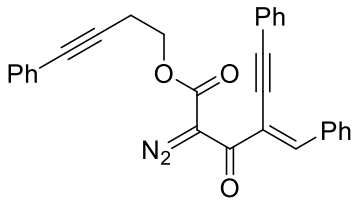
S1 **S2** **S3** **1**

Synthesis of S3:[1c] To a 50-mL oven-dried round-bottom flask containing a magnetic stirring bar, disopropyl amine (DIPA, 1.52 g, 15.0 mmol) in THF (20.0 mL), was added *n*-BuLi (6.0 mL, 2.5 M solution in hexane, 15.0 mmol) at -78 ˚C and stirred for 30 minutes under these conditions, Then, a solution of diazo compounds **S1** (15.0 mmol) in THF (10.0 mL) was added dropwise to the above reaction mixture at -78 ˚C,

and the reaction mixture was allowed to stir for 30 minutes. Subsequently, the solution of **S2** (10.0 mmol) in THF (10.0 mL) was added and the reaction mixture stirred for additional 30 minutes. After the completion of reaction (monitored by TLC), the reaction was quenched with saturated aqueous NH_4Cl (20.0 mL), and extracted with EtOAc (2 × 20.0 mL). The combined organic phase was dried over anhydrous Na_2SO_4 and the solvent was evaporated under vacuum after filtration. The crude product was purified by column chromatography on silica gel (eluent: petroleum ethers : ethyl acetate = 20:1 - 5:1) to give the pure products **S3.**

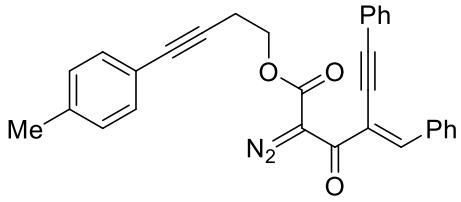
Synthesis of 1[1c]: To a 50-mL oven-dried flask containing a magnetic stirring bar, the above obtained product **S3** (5.0 mmol) in DMSO (10.0 mL), was added 2-iodoxybenzoic acid (IBX, 1.70 g, 6.0 mmol) slowly at 40 ˚C. The reaction mixture was stirred for 15 minutes under these conditions. Upon completion (monitored by TLC), the reaction was quenched with 20 mL water and extracted with ethyl acetate (2 × 20.0 mL). The combined organic phase was dried over anhydrous Na_2SO_4 and the solvent was evaporated under vacuum after filtration. The residue was purified by column chromatography on silica gel (eluent: petroleum ethers : ethyl acetate = 20:1 - 10:1) to give the pure products **1** in generally good yields.

The alkyne-tethered diazo compounds **1a**, **1s**, **1u**, **1w**, and **1x** are known compounds with identical characterization data as reported in the literature.[1c] Characterization of new diazo compounds **1b - 1r**, **1t**, and **1v** have been listed below.

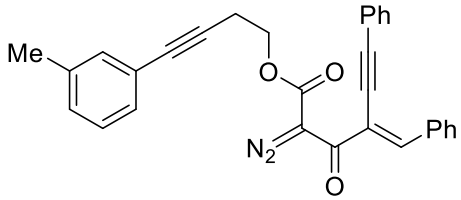


4-Phenylbut-3-yn-1-yl (*E*)-4-benzylidene-2-diazo-3-oxo-6-phenylhex-5-ynoate (1a).[1] ^{1}H NMR (500 MHz, $CDCl_3$) (δ, ppm) 8.04 - 8.02 (m, 2H), 7.51 - 7.48 (m, 2H), 7.45 (s, 1H), 7.43 - 7.40 (comp, 3H), 7.37 - 7.34 (comp, 5H), 7.27 - 7.24 (comp, 3H), 4.43 (t, *J* = 6.9 Hz, 2H), 2.79 (t, *J* = 6.9 Hz, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) (δ,

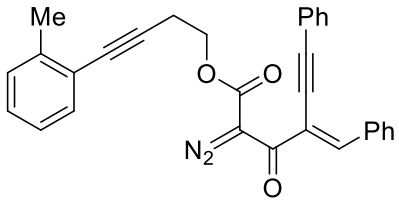
ppm) 182.7, 161.0, 143.7, 141.9, 134.6, 131.7, 131.5, 130.7, 130.4, 129.2, 128.7, 128.3, 128.1, 123.2, 122.6, 119.9, 100.3, 85.1, 84.9, 82.5, 75.0, 63.5, 20.1.



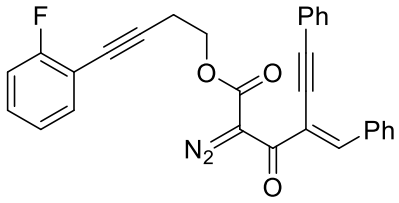
4-(*p*-Tolyl)but-3-yn-1-yl (*E*)-4-benzylidene-2-diazo-3-oxo-6-phenylhex-5-ynoate (1b) Yellow oil; 1.67 g, 73% yield; ^{1}H NMR (500 MHz, $CDCl_3$) (δ, ppm) 8.07 - 8.03 (m, 2H), 8.00 (d, *J* = 7.8 Hz, 1H), 7.51 - 7.49 (m, 2H), 7.45 - 7.42 (comp, 4H), 7.38 - 7.37 (m, 2H), 7.24 (s, 1H), 7.21 - 7.18 (m, 1H)7.07 (d, *J* = 7.8 Hz, 2H), 4.43 (t, *J* = 6.9 Hz, 2H), 2.79 (t, *J* = 6.9 Hz, 2H), 2.33 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) (δ, ppm) 182.8, 161.1, 143.7, 142.0, 138.2, 133.6, 131.63, 131.61, 130.5, 129.2, 129.1, 128.72, 128.70, 128.2, 122.7, 120.2, 120.0, 100.3, 85.2, 84.1, 62.6, 63.6, 21.6, 20.2. HRMS (TOF MS ESI$^+$) calculated for $C_{30}H_{22}N_2O_3Na$ $[M+Na]^+$: 481.1523, found 481.1525.



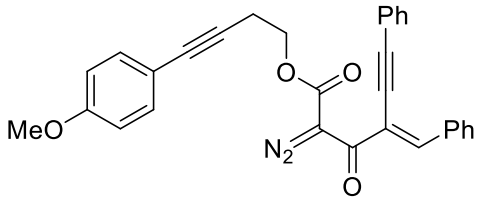
4-(*m*-Tolyl)but-3-yn-1-yl (*E*)-4-benzylidene-2-diazo-3-oxo-6-phenylhex-5-ynoate (1c). Yellow oil; 1.47 g, 64% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.03 (dd, *J* = 6.4, 2.7 Hz, 2H), 7.50 (dd, *J* = 6.5, 2.9 Hz, 2H), 7.44 (s, 1H), 7.42 - 7.41 (m, 2H), 7.37 - 7.36 (m, 2H), 7.26 (s, 1H), 7.21 - 7.18 (m, 2H), 7.16 - 7.15 (m, 2H), 7.11 - 7.09 (m, 1H), 4.43 (t, *J* = 6.9 Hz, 2H), 2.79 (t, *J* = 6.9 Hz, 2H), 2.29 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 182.8, 161.1, 143.7, 138.1, 134.6, 132.4, 131.6, 130.8, 130.5, 129.2, 129.0, 128.8, 128.7, 128.7, 128.3, 123.1, 122.6, 120.0, 100.3, 85.2, 84.5, 82.6, 63.6, 21.3, 20.2. HRMS (TOF MS ESI$^+$) calculated for $C_{30}H_{22}N_2O_3Na$ $[M+Na]^+$: 481.1523, found 481.1524.



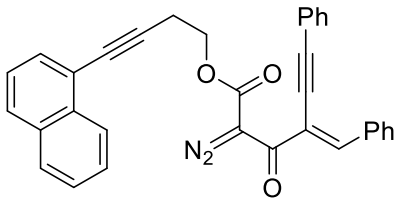
4-(*o*-Tolyl)but-3-yn-1-yl (*E*)-4-benzylidene-2-diazo-3-oxo-6-phenylhex-5-ynoate (1d). Yellow oil; 1.37 g, 60% yield; ^{1}H NMR (500 MHz, $CDCl_3$) (δ, ppm) 8.05 - 8.03 (m, 2H), 7.51 - 7.49 (m, 2H), 7.46 (s, 1H), 7.44 - 7.41 (comp, 3H), 7.39 - 7.35 (comp, 3H), 7.33 (d, *J* = 7.5 Hz, 1H), 7.20 - 7.15 (m, 2H), 7.11 - 7.08 (m, 1H), 4.46 (t, *J* = 6.8 Hz, 2H), 2.85 (t, *J* = 6.8 Hz, 2H), 2.38 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) (δ, ppm) 182.7, 161.0, 143.7, 140.2, 134.6, 132.0, 131.6, 130.8, 130.5, 129.5, 129.2, 128.71, 128.69, 128.1, 125.6, 123.0, 122.6, 120.0, 100.3, 88.8, 85.2, 81.4, 63.7, 20.7, 20.3. HRMS (TOF MS ESI$^+$) calculated for $C_{30}H_{22}N_2O_3Na$ $[M+Na]^+$: 481.1523, found 481.1525.



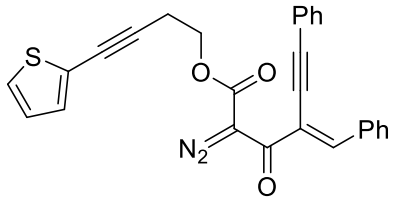
4-(2-Fluorophenyl)but-3-yn-1-yl (*E*)-4-benzylidene-2-diazo-3-oxo-6-phenylhex-5-ynoate (1e). Yellow oil; 1.36 g, 58.9% yield; ^{1}H NMR (400 MHz, $CDCl_3$) (δ, ppm) 8.04 - 8.02 (m, 2H), 7.50 (dd, *J* = 6.6, 3.0 Hz, 2H), 7.46 (s, 1H), 7.43 - 7.41 (comp, 3H), 7.39 - 7.34 (comp, 4H), 7.26 - 7.23 (m, 1H), 7.05 - 7.01 (m, 2H), 4.45 (t, *J* = 6.8 Hz, 2H), 2.84 (t, *J* = 6.8 Hz, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) (δ, ppm) 182.7, 162.9 (d, *J* = 250.7 Hz), 160.9, 143.7, 134.5, 133.6, 132.65 (d, *J* = 143.0 Hz), 131.5, 130.7, 130.42, 129.8 (d, *J* = 7.9 Hz), 129.2, 128.6, 123.95 (d, *J* = 3.7 Hz), 122.6, 119.9, 115.5 (d, *J* = 21.0 Hz), 111.71 (d, *J* = 15.7 Hz), 100.3, 90.35 (d, *J* = 3.2 Hz), 85.1, 75.8, 63.3, 20.3.^{19}F NMR (376 MHz, $CDCl_3$) (δ, ppm) -110.63. HRMS (TOF MS ESI$^+$) calculated for $C_{29}H_{19}FN_2O_3Na$ $[M+Na]^+$: 485.1272, found 485.1274.



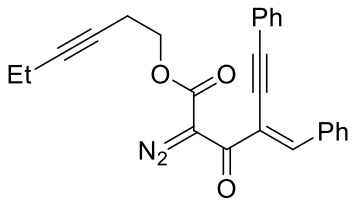
4-(4-Methoxyphenyl)but-3-yn-1-yl (*E*)-4-benzylidene-2-diazo-3-oxo-6-phenylhex-5-ynoate (1f). Yellow oil; 1.78 g, 75% yield; ^{1}H NMR (500 MHz, CDCl3) (δ, ppm) 8.05 - 8.02 (m, 2H), 8.00 (d, *J* = 7.8 Hz, 1H), 7.51 - 7.49 (m, 2H), 7.45 - 7.44 (m, 1H), 7.43 - 7.42 (m, 2H), 7.38 - 7.37 (m, 2H), 7.25 (d, *J* = 8.8 Hz, 2H), 7.20 (t, *J* = 7.6 Hz, 1H), 7.07 (d, *J* = 7.8 Hz, 2H), 4.43 (t, *J* = 6.9 Hz, 2H), 3.84 (s, 3H), 2.79 (t, *J* = 6.9 Hz, 2H); ^{13}C NMR (126 MHz, $CDCl_3$) (δ, ppm) 182.8, 161.1, 143.7, 142.0, 138.2, 133.6, 132.1, 131.63, 131.61, 130.5, 129.1, 128.7, 128.7, 128.6, 122.7, 120.2, 120.0, 100.3, 85.2, 84.1, 82.6, 63.6, 55.3, 20.2. HRMS (TOF MS ESI^{+}) calculated for $C_{30}H_{22}N_2O_4Na$ [M+Na]$^{+}$: 497.1472, found 497.1472.



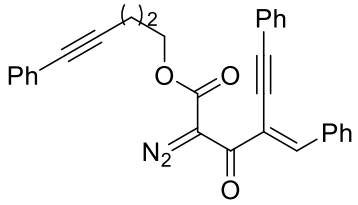
4-(Naphthalen-1-yl)but-3-yn-1-yl (*E*)-4-benzylidene-2-diazo-3-oxo-6-phenylhex-5-ynoate (1g). Yellow oil; 1.73 g, 70% yield; ^{1}H NMR (400 MHz, $CDCl_3$) (δ, ppm) 8.26 (d, *J* = 8.2 Hz, 1H), 8.02 - 8.00 (m, 2H), 7.84 - 7.77 (comp, 4H), 7.58 (d, *J* = 7.1 Hz, 1H), 7.53 - 7.51 (m, 1H), 7.50 - 7.49 (m, 1H), 7.48 - 7.46 (m, 2H), 7.44 (s, 1H), 7.40 - 7.38 (comp, 3H), 7.34 - 7.32 (m, 2H), 4.53 (t, *J* = 6.8 Hz, 2H), 2.95 (t, *J* = 6.8 Hz, 2H); ^{13}C NMR (126 MHz, $CDCl_3$) (δ, ppm) 174.4, 149.1, 137.9, 136.4, 133.8, 133.6, 133.2, 130.6, 130.0, 129.7, 129.3, 129.0, 128.7, 128.6, 128.3, 128.2, 128.0, 127.8, 126.9, 126.5, 126.3, 125.3, 122.2, 120.8, 117.2, 89.3, 81.1, 71.9, 20.7. HRMS (TOF MS ESI^{+}) calculated for $C_{33}H_{22}N_2O_3Na$ [M+Na]$^{+}$: 517.1523, found 517.1520.



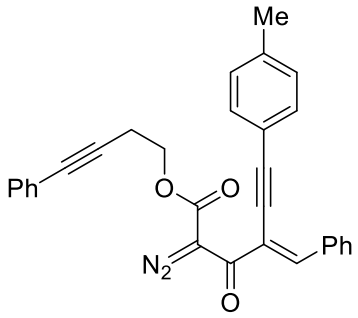
4-(Thiophen-2-yl)but-3-yn-1-yl (*E*)-4-benzylidene-2-diazo-3-oxo-6-phenylhex-5-ynoate (1h). Yellow oil; 1.58 g, 70% yield; ^{1}H NMR (400 MHz, $CDCl_3$) (δ, ppm) 8.04 - 8.01 (m, 2H), 7.51 - 7.48 (m, 2H), 7.44 (s, 1H), 7.41 - 7.40 (m, 2H), 7.37 - 7.35 (m, 2H), 7.18 - 7.16 (m, 2H), 7.10 (d, *J* = 3.6 Hz, 1H), 6.93 - 6.89 (m, 2H), 4.41 (t, *J* = 6.8 Hz, 2H), 2.80 (t, *J* = 6.8 Hz, 2H); ^{13}C NMR (126 MHz, $CDCl_3$) (δ, ppm) 182.6, 160.9, 143.7, 134.5, 131.7, 131.6, 131.5, 130.7, 130.4, 129.2, 128.6, 126.90, 126.89, 126.6, 126.5, 122.5, 119.9, 100.3, 89.0, 85.1, 75.7, 63.2, 20.3. HRMS (TOF MS ESI$^+$) calculated for $C_{27}H_{18}N_2O_3SNa$ [M+Na]$^+$: 473.0930, found 473.0929.



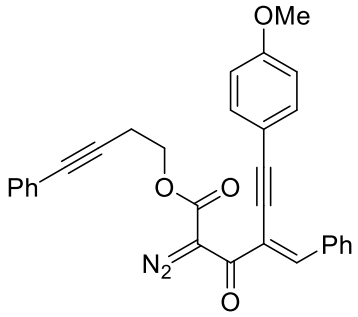
Hex-3-yn-1-yl (*E*)-4-benzylidene-2-diazo-3-oxo-6-phenylhex-5-ynoate (1i). Yellow oil; 1.50 g, 76% yield; ^{1}H NMR (400 MHz, $CDCl_3$) (δ, ppm) 8.05 - 8.03 (m, 2H), 7.52 - 7.50 (m, 2H), 7.45 (s, 1H), 7.43 - 7.40 (comp, 3H), 7.38 - 7.36 (comp, 3H), 4.31 (t, *J* = 7.0 Hz, 2H), 2.53 (t, *J* = 7.0 Hz, 2H), 2.10 (q, *J* = 7.5 Hz, 2H), 1.08 (t, *J* = 7.5 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) (δ, ppm) 182.6, 160.8, 143.5, 134.5, 131.4, 130.6, 130.3, 129.1, 128.57, 128.56, 122.5, 119.9, 100.1, 85.1, 83.8, 74.3, 63.9, 19.3, 14.1, 12.3. HRMS (TOF MS ESI$^+$) calculated for $C_{25}H_{20}N_2O_3Na$ [M+Na]$^+$: 419.1366, found 419.1369.



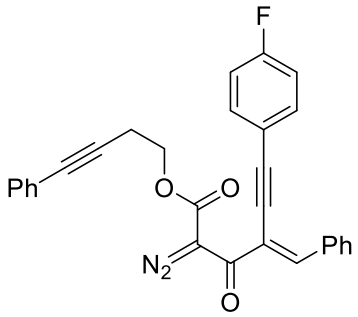
5-Phenylpent-4-yn-1-yl (*E*)-4-benzylidene-2-diazo-3-oxo-6-phenylhex-5-ynoate (1j). Yellow oil; 1.33 g, 60% yield; ^{1}H NMR (400 MHz, $CDCl_3$) (δ, ppm) 8.05 - 8.03 (m, 2H), 7.50 (dd, *J* = 6.6, 3.0 Hz, 2H), 7.43 - 7.40 (comp, 4H), 7.36 - 7.33 (comp, 5H), 7.26 - 7.25 (comp, 3H), 4.42 (t, *J* = 6.2 Hz, 2H), 2.49 (t, *J* = 6.9 Hz, 2H), 1.96 (p, *J* = 6.6 Hz, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) (δ, ppm) 182.8, 161.5, 143.4, 134.6, 131.7, 131.6, 130.7, 130.4, 129.2, 128.7, 128.7, 128.3, 127.9, 123.7, 122.6, 120.2, 100.3, 88.4, 85.2, 81.6, 64.7, 28.0, 16.3. HRMS (TOF MS ESI$^+$) calculated for $C_{30}H_{22}N_2O_3Na$ $[M+Na]^+$: 481.1523, found 481.1526.



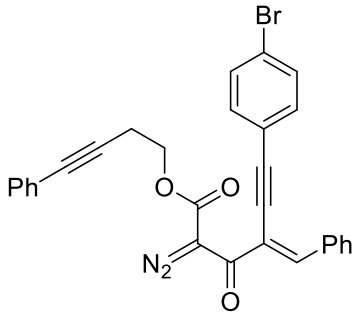
4-Phenylbut-3-yn-1-yl (*E*)-4-benzylidene-2-diazo-3-oxo-6-(*p*-tolyl)hex-5-ynoate (1k). Yellow oil; 1.40 g, 61% yield; ^{1}H NMR (500 MHz, $CDCl_3$) (δ, ppm) 8.03 - 8.02 (m, 2H), 7.43 (s, 1H), 7.39 - 7.38 (comp, 5H), 7.36 - 7.34 (m, 2H), 7.24 - 7.22 (comp, 3H), 7.14 (d, *J* = 8.0 Hz, 2H), 4.41 (t, *J* = 6.9 Hz, 2H), 2.77 (t, *J* = 6.9 Hz, 2H), 2.34 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) (δ, ppm) 182.5, 160.9, 143.1, 139.4, 134.5, 131.6, 131.3, 130.5, 130.3, 129.3, 128.5, 128.2, 128.0, 123.2, 120.0, 119.4, 100.6, 84.9, 84.6, 82.3, 63.4, 21.6, 20.0. HRMS (TOF MS ESI$^+$) calculated for $C_{30}H_{22}N_2O_3Na$ $[M+Na]^+$: 481.1523, found 481.1525.



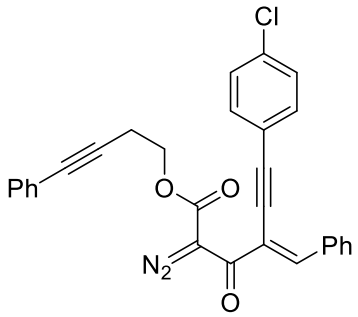
4-Phenylbut-3-yn-1-yl (*E*)-4-benzylidene-2-diazo-6-(4-methoxyphenyl)-3-oxohex-5-ynoate (1l). Yellow oil; 1.59 g, 67% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.04 - 8.02 (m, 2H), 7.44 (s, 1H), 7.42 (s, 1H), 7.40 - 7.39 (comp, 3H), 7.37 - 7.35 (m, 2H), 7.29 - 7.25 (comp, 4H), 6.88 (d, *J* = 8.7 Hz, 2H), 4.42 (t, *J* = 6.9 Hz, 2H), 3.82 (s, 3H), 2.79 (t, *J* = 6.9 Hz, 2H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 182.7, 160.4, 142.8, 134.7, 133.1, 131.8, 131.7, 130.6, 130.4, 128.7, 128.4, 128.1, 123.2, 120.2, 114.4, 100.7, 84.9, 84.1, 82.4, 63.5, 55.5, 20.1. HRMS (TOF MS ESI$^+$) calculated for $C_{30}H_{22}N_2O_4Na$ $[M+Na]^+$: 497.1472, found 497.1473.



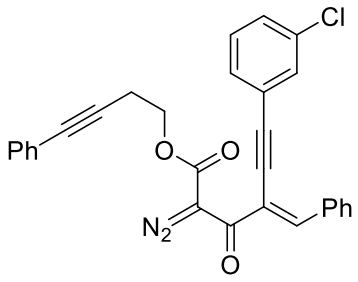
4-Phenylbut-3-yn-1-yl (*E*)-4-benzylidene-2-diazo-6-(4-fluorophenyl)-3-oxohex-5-ynoate (1m). Yellow oil; 1.48 g, 64% yield; ^{1}H NMR (400 MHz, $CDCl_3$) (δ, ppm) 8.01 (dd, *J* = 6.6, 2.9 Hz, 2H), 7.49 - 7.45 (m, 2H), 7.43 - 7.40 (comp, 4H), 7.37 - 7.34 (m, 2H), 7.28 - 7.26 (comp, 3H), 7.07 - 7.02 (m, 2H), 4.43 (t, *J* = 6.8 Hz, 2H), 2.79 (t, *J* = 6.8 Hz, 2H); ^{13}C NMR (101 MHz, CDCl3) (δ, ppm) 182.8, 163.0 (d, *J* = 251.3 Hz), 160.9, 143.7, 134.5, 133.6 (d, *J* = 8.6 Hz), 131.7, 130.8, 130.4, 128.7, 128.4, 128.2, 123.2, 119.9, 118.8 (d, *J* = 3.5 Hz), 116.1 (d, *J* = 22.2 Hz), 99.0, 84.9, 82.5, 63.5, 20.2. ^{19}F NMR (376 MHz, $CDCl_3$) (δ, ppm) -109.30. HRMS (TOF MS ESI$^+$) calculated for $C_{29}H_{19}FN_2O_3Na$ $[M+Na]^+$: 485.1272, found 485.1276.



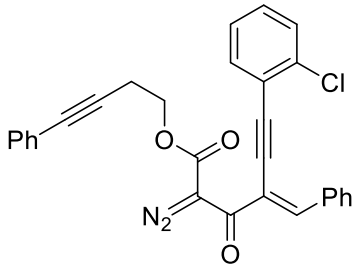
4-Phenylbut-3-yn-1-yl (*E*)-4-benzylidene-6-(4-bromophenyl)-2-diazo-3-oxohex-5-ynoate (1n). Yellow oil; 1.70 g, 65% yield; ^{1}H NMR (500 MHz, $CDCl_3$) (δ, ppm) 7.99 (dd, *J* = 6.5, 2.7 Hz, 2H), 7.47 (s, 1H), 7.45 (d, *J* = 4.3 Hz, 2H), 7.40 - 7.39 (comp, 3H), 7.36 - 7.33 (comp, 3H), 7.31 (s, 1H), 7.27 - 7.24 (comp, 3H), 4.41 (t, *J* = 6.8 Hz, 2H), 2.78 (t, *J* = 6.8 Hz, 2H); ^{13}C NMR (126 MHz, $CDCl_3$) (δ, ppm) 182.5, 160.8, 143.9, 134.4, 132.8, 131.9, 131.6, 130.8, 130.3, 128.6, 128.3, 128.1, 123.5, 123.1, 121.5, 119.7, 98.7, 86.2, 84.8, 82.4, 63.4, 20.1. HRMS (TOF MS ESI$^+$) calculated for $C_{29}H_{19}N_2BrO_3Na$ $[M+Na]^+$: 545.0471, found 545.0474.



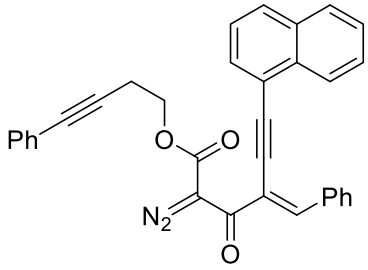
4-Phenylbut-3-yn-1-yl (*E*)-4-benzylidene-6-(4-chlorophenyl)-2-diazo-3-oxohex-5-ynoate (1o). Yellow oil; 1.67 g, 70% yield;^{1}H NMR (400 MHz, $CDCl_3$) (δ, ppm) 7.99 (dd, *J* = 6.8, 2.7 Hz, 2H), 7.44 (s, 1H), 7.42 - 7.38 (comp, 5H), 7.36 - 7.34 (m, 2H), 7.32 - 7.29 (m, 2H), 7.27 - 7.25 (m, 2H), 7.24 (s, 1H), 4.42 (t, *J* = 6.8 Hz, 2H), 2.78 (t, *J* = 6.8 Hz, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) (δ, ppm) 182.6, 160.8, 143.9, 135.2, 134.4, 132.7, 131.6, 130.8, 130.3, 129.0, 128.7, 128.3, 128.1, 123.2, 121.0, 119.7, 98.7, 86.1, 84.8, 82.4, 63.5, 20.1. HRMS (TOF MS ESI$^+$) calculated for $C_{29}H_{19}N_2ClO_3Na$ $[M+Na]^+$: 501.0976, found 501.0976.



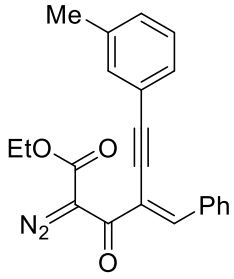
4-Phenylbut-3-yn-1-yl (*E*)-4-benzylidene-6-(3-chlorophenyl)-2-diazo-3-oxohex-5-ynoate (1p). Yellow oil; 1.70 g, 71% yield; ^{1}H NMR (400 MHz, $CDCl_3$) (δ, ppm) 7.86 (dd, *J* = 6.5, 2.8 Hz, 2H), 7.33 (s, 2H), 7.28 - 7.26 (comp, 3H), 7.24 - 7.22 (comp, 3H), 7.18 (dd, *J* = 6.8, 1.7 Hz, 1H), 7.13 - 7.10 (comp, 4H), 4.29 (t, *J* = 6.8 Hz, 2H), 2.65 (t, *J* = 6.8 Hz, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) (δ, ppm) 182.4, 160.6, 144.2, 134.3, 134.2, 131.5, 131.1, 130.8, 130.2, 129.8, 129.5, 129.2, 128.6, 128.2, 128.0, 124.1, 123.1, 119.4, 98.1, 86.2, 84.8, 82.4, 63.4, 20.0. HRMS (TOF MS ESI$^+$) calculated for $C_{29}H_{19}N_2ClO_3Na$ $[M+Na]^+$: 501.0976, found 501.0974.



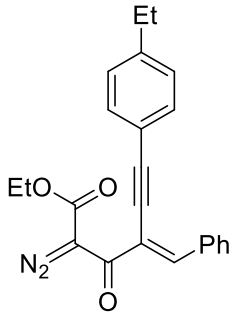
4-Phenylbut-3-yn-1-yl (*E*)-4-benzylidene-6-(2-chlorophenyl)-2-diazo-3-oxohex-5-ynoate (1q). Yellow oil; 1.58 g, 66% yield; ^{1}H NMR (400 MHz, $CDCl_3$) (δ, ppm) 8.11 - 8.10 (m, 2H), 7.49 (dd, *J* = 7.4, 1.3 Hz, 1H), 7.46 (s, 1H), 7.41 - 7.39 (comp, 4H), 7.35 - 7.33 (m, 2H), 7.28 - 7.22 (comp, 5H), 4.42 (t, *J* = 6.8 Hz, 2H), 2.78 (t, *J* = 6.8 Hz, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) (δ, ppm) 182.9, 160.8, 143.9, 135.8, 134.3, 133.4, 131.7, 130.8, 130.5, 130.1, 129.6, 128.6, 128.3, 128.0, 126.7, 123.2, 122.6, 119.9, 97.0, 89.9, 84.9, 82.4, 63.5, 20.0. HRMS (TOF MS ESI$^+$) calculated for $C_{29}H_{19}N_2ClO_3Na$ $[M+Na]^+$: 501.0976, found 501.0976



4-Phenylbut-3-yn-1-yl (*E*)-4-benzylidene-2-diazo-6-(naphthalen-1-yl)-3-oxohex-5-ynoate (1r). Yellow oil; 1.63 g, 66% yield; ^{1}H NMR (400 MHz, $CDCl_3$) (δ, ppm) 8.33 (d, *J* = 8.2 Hz, 1H), 8.12 - 8.10 (m, 2H), 7.86 (d, *J* = 8.2 Hz, 2H), 7.72 (dd, *J* = 7.1, 0.7 Hz, 1H), 7.58 - 7.50 (m, 2H), 7.48 - 7.45 (m, 2H), 7.43 - 7.40 (comp, 3H), 7.34 - 7.32 (m, 2H), 7.26 - 7.23 (comp, 3H), 4.41 (t, *J* = 6.9 Hz, 2H), 2.76 (t, *J* = 6.9 Hz, 2H); ^{13}C NMR (126 MHz, $CDCl_3$) (δ, ppm) 183.2, 160.9, 143.4, 134.7, 133.3, 133.2, 131.7, 131.0, 130.8, 130.4, 129.7, 128.7, 128.5, 128.3, 128.1, 127.2, 126.8, 126.1, 125.4, 123.2, 120.4, 120.4, 98.5, 89.7, 84.9, 82.5, 63.5, 20.1. HRMS (TOF MS ESI$^+$) calculated for $C_{33}H_{22}N_2O_3Na$ $[M+Na]^+$: 517.1523, found 517.1526.

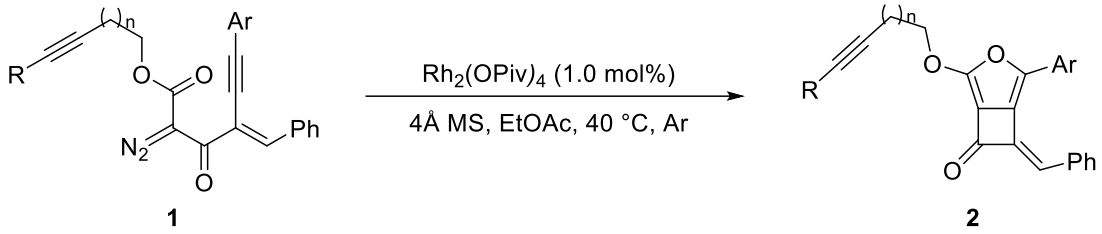


Ethyl (*E*)-4-benzylidene-2-diazo-3-oxo-6-(*m*-tolyl)hex-5-ynoate (1t). Yellow oil; 2.72 g, 76% yield; ^{1}H NMR (400 MHz, $CDCl_3$) (δ, ppm) 8.05 – 8.03 (m, 2H), 7.43 – 7.41 (comp, 4H), 7.32 – 7.29 (m, 2H), 7.27 – 7.25 (m, 1H), 7.20 – 7.19 (m, 1H), 4.32 (q, *J* = 7.1 Hz, 2H), 2.37 (s, 3H), 1.31 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) (δ, ppm) 182.8, 161.4, 143.2, 138.4, 134.6, 132.0, 130.6, 130.4, 130.0, 128.6, 128.5, 122.4, 120.2, 100.5, 84.8, 75.0, 62.0, 21.3, 14.4; HRMS (TOF MS ESI$^+$) calculated for $C_{22}H_{18}N_2O_3Na$ $[M+Na]^+$: 381.1210, found 381.1213.



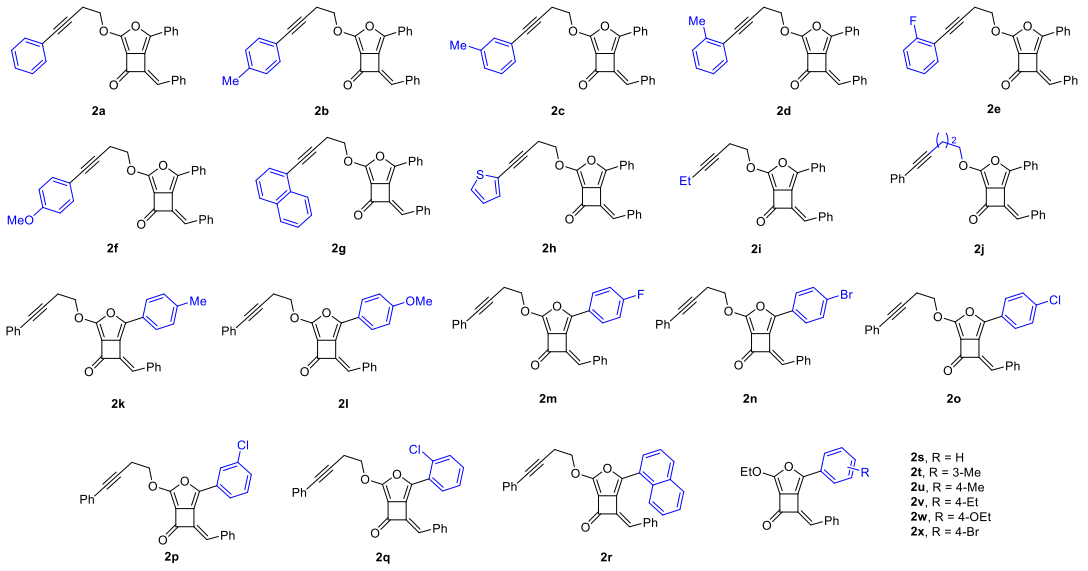
Ethyl (*E*)-4-benzylidene-2-diazo-6-(4-ethylphenyl)-3-oxohex-5-ynoate (1v). Yellow oil; 2.61 g, 70% yield; ^{1}H NMR (400 MHz, $CDCl_3$) (δ, ppm) 8.05 – 8.03 (m, 2H), 7.44 – 7.41 (comp, 6H), 7.21 (d, *J* = 8.0 Hz, 2H), 4.31 (q, *J* = 7.1 Hz, 2H), 2.68 (q, *J* = 7.6 Hz, 2H), 1.31 (t, *J* = 7.1 Hz, 3H), 1.25 (t, *J* = 7.6 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) (δ, ppm) 182.7, 161.3, 145.6, 142.9, 134.6, 131.4, 130.5, 130.3, 128.5, 128.1, 120.2, 119.7, 100.6, 84.5, 74.8, 61.9, 28.9, 15.3, 14.3; HRMS (TOF MS ESI^{+}) calculated for $C_{23}H_{20}N_2O_3Na$ $[M+Na]^{+}$: 395.1366, found 395.1369.

General Procedure for the Synthesis of Furan-fused Cyclobutanones 2.[1]

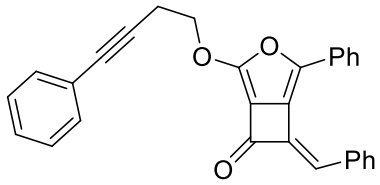


1 **2**

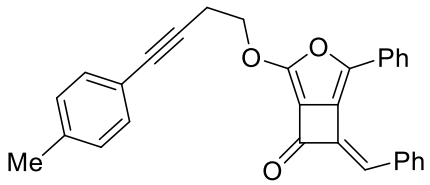
To a 10-mL oven-dried vial containing a magnetic stirring bar, $Rh_2(OPiv)_4$ (6.0 mg, 1.0 mol%), and 4Å MS (300 mg) in EtOAc (4.0 mL), was added as a solution of diazo compounds **1** (1.0 mmol) in the EtOAc (1.0 mL) slowly *via* a syringe under argon atmosphere at 40 °C. After addition, the reaction mixture was stirred for additional 1.0 h under these conditions. Until consumption of the material (monitored by TLC), the reaction mixture was purified by column chromatography on silica gel without any additional treatment (Hexanes : EtOAc = 15:1 to 5:1) or recrystallized from MeOH to give the pure products **2** in good to high yields.



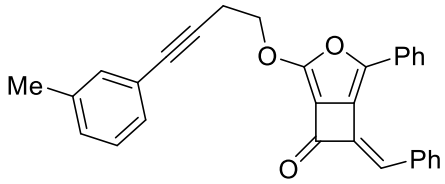
The furan-fused cyclobutanones **2a**, **2s**, **2u**, **2w**, and **2x** are known compounds with identical characterization data as reported in the literature.[1] Characterization of new furan-fused cyclobutanones **2b** - **2r**, **2t**, and **2v** have been listed below.



(*E*)-7-Benzylidene-2-phenyl-4-((4-phenylbut-3-yn-1-yl)oxy)-3-oxabicyclo[3.2.0] hepta-1,4-dien-6-one (2a).[1] ^{1}H NMR (400 MHz, $CDCl_3$) (δ, ppm) 7.43 - 7.41 (m, 2H), 7.37 - 7.30 (comp, 4H), 7.29 - 7.26 (comp, 7H), 7.25 - 7.23 (m, 2H), 7.10 (s, 1H), 4.56 (t, *J* = 6.6 Hz, 2H), 3.03 (t, *J* = 6.6 Hz, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) (δ, ppm) 174.4, 149.0, 137.8, 136.3, 133.8, 131.9, 130.0, 129.6, 129.3, 128.9, 128.6, 128.4, 128.2, 128.0, 127.7, 123.2, 122.2, 117.2, 84.3, 82.9, 71.8, 20.4.

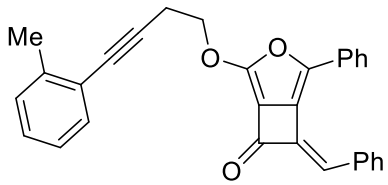


(*E*)-7-Benzylidene-2-phenyl-4-((4-(*p*-tolyl)but-3-yn-1-yl)oxy)-3-oxabicyclo[3.2.0] hepta-1,4-dien-6-one (2b). Yellow solid, mp = 161.8 - 163.4 °C; 322.6 mg, 75% yield. ^{1}H NMR (500 MHz, $CDCl_3$) (δ, ppm) 7.41 (d, *J* = 7.6 Hz, 1H), 7.39 - 7.33 (comp, 4H), 7.33 - 7.31 (m, 1H), 7.30 - 7.28 (comp, 5H), 7.23 - 7.19 (m, 2H), 7.14 - 7.11 (m, 2H), 4.60 (t, *J* = 6.5 Hz, 2H), 3.10 (t, *J* = 6.5 Hz, 2H), 2.45 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) (δ, ppm) 174.4, 149.1, 140.4, 137.8, 136.3, 133.8, 132.1, 130.0, 129.6, 129.5, 129.3, 128.9, 128.6, 128.2, 128.0, 127.7, 125.6, 123.0, 122.2, 117.2, 88.2, 81.8, 72.0, 20.8, 20.5. HRMS (TOF MS ESI$^+$) calculated for $C_{30}H_{22}O_3Na$ $[M+Na]^+$: 453.1461, found 453.1460.

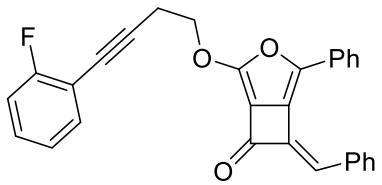


(*E*)-7-Benzylidene-2-phenyl-4-((4-(*m*-tolyl)but-3-yn-1-yl)oxy)-3-oxabicyclo[3.2.0] hepta-1,4-dien-6-one (2c). Yellow solid, mp = 128.6 - 130.5 °C; 331.2 mg, 77%

yield. ^{1}H NMR (400 MHz, $CDCl_3$) (δ, ppm) 7.36 - 7.31 (comp, 3H), 7.29 - 7.21 (comp, 9H), 7.16 (t, *J* = 7.5 Hz, 1H), 7.10 - 7.08 (m, 2H), 4.54 (t, *J* = 6.6 Hz, 2H), 3.01 (t, *J* = 6.6 Hz, 2H), 2.29 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) (δ, ppm) 174.4, 149.0, 138.0, 137.9, 136.3, 133.8, 132.5, 130.0, 129.6, 129.3, 129.1, 128.93, 128.91, 128.6, 128.25, 128.19, 128.0, 127.7, 123.0, 122.1, 117.2, 83.9, 83.0, 71.8, 21.3, 20.4. HRMS (TOF MS ESI$^+$) calculated for $C_{30}H_{22}O_3Na$ $[M+Na]^+$: 453.1461, found 453.1461.

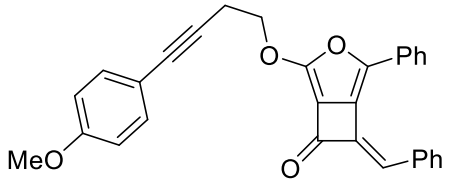


(*E*)-7-Benzylidene-2-phenyl-4-((4-(*o*-tolyl)but-3-yn-1-yl)oxy)-3-oxabicyclo[3.2.0] hepta-1,4-dien-6-one (2d).Yellow solid, mp = 154.2 - 157.1 °C; 331.2 mg, 77% yield. ^{1}H NMR (500 MHz, $CDCl_3$) (δ, ppm) 7.38 (d, *J* = 7.6 Hz, 1H), 7.36 - 7.30 (comp, 4H), 7.30 - 7.29 (m, 1H), 7.27 - 7.25 (comp, 5H), 7.20 - 7.16 (m, 2H), 7.11 - 7.08 (m, 2H), 4.57 (t, *J* = 6.5 Hz, 2H), 3.07 (t, *J* = 6.5 Hz, 2H), 2.42 (s, 3H).; ^{13}C NMR (126 MHz, $CDCl_3$) (δ, ppm) 174.3, 148.9, 140.3, 137.7, 136.2, 133.6, 132.0, 129.9, 129.5, 129.3, 129.2, 128.8, 128.5, 128.1, 127.9, 127.6, 125.4, 122.8, 122.0, 117.0, 88.0, 81.7, 71.8, 20.6, 20.4. HRMS (TOF MS ESI$^+$) calculated for $C_{30}H_{22}O_3Na$ $[M+Na]^+$: 453.1461, found 453.1465.

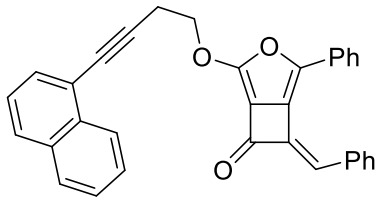


(*E*)-7-Benzylidene-4-((4-(2-fluorophenyl)but-3-yn-1-yl)oxy)-2-phenyl-3-oxabicyclo[3.2.0]hepta-1,4-dien-6-one (2e). Yellow oil; 303.9 mg, 70% yield. ^{1}H NMR (400 MHz, $CDCl_3$) (δ, ppm) 7.42 (dd, *J* = 7.3, 5.9 Hz, 1H), 7.36 - 7.31 (comp, 3H), 7.29 (d, *J* = 3.1 Hz, 1H), 7.27 - 7.22 (comp, 7H), 7.10 (s, 1H), 7.07 - 7.02 (m,

2H), 4.57 (t, *J* = 6.6 Hz, 2H), 3.07 (t, *J* = 6.6 Hz, 2H); ^{13}C NMR (126 MHz, $CDCl_3$) (δ, ppm) 174.4, 163.0 (d, *J* = 251.2 Hz), 149.0, 137.8, 136.4, 133.9 (d, *J* = 1.1 Hz), 133.8, 130.0, 129.9 (d, *J* = 7.9 Hz), 129.6, 129.3, 128.9, 128.6, 128.2, 128.0, 127.8, 124.0 (d, *J* = 3.7 Hz), 122.2, 117.2, 115.6 (d, *J* = 21.0 Hz), 111.8, 111.6, 111.7 (d, *J* = 15.6 Hz), 89.7 (d, *J* = 3.2 Hz), 76.3, 71.6, 20.5. HRMS (TOF MS ESI$^+$) calculated for $C_{30}H_{22}O_3FNa$ $[M+Na]^+$: 457.1210, found 457.1212.

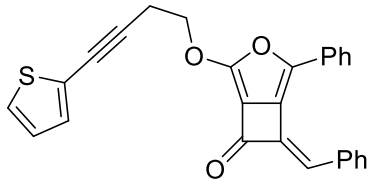


(*E*)-7-Benzylidene-4-((4-(4-methoxyphenyl)but-3-yn-1-yl)oxy)-2-phenyl-3-oxabicyclo[3.2.0]hepta-1,4-dien-6-one (2f). Yellow solid, mp = 112.2 - 116.6 °C; 303.4 mg, 68% yield. ^{1}H NMR (500 MHz, $CDCl_3$) (δ, ppm) 7.43 - 7.41 (m, 2H), 7.36 - 7.31 (comp, 3H), 7.29 - 7.25 (comp, 5H), 7.23 - 7.20 (m, 2H), 7.06 (s, 1H), 6.82 (d, *J* = 8.7 Hz, 2H), 4.54 (t, *J* = 6.6 Hz, 2H), 3.84 (s, 3H), 3.03 (t, *J* = 6.6 Hz, 2H); ^{13}C NMR (126 MHz, $CDCl_3$) (δ, ppm) 174.6, 159.7, 148.6, 137.9, 136.5, 133.9, 131.9, 129.9, 129.4, 129.2, 128.7, 128.4, 128.2, 128.1, 123.2, 121.9, 121.6, 116.8, 113.7, 84.4, 82.9, 71.7, 55.5, 20.4. HRMS (TOF MS ESI$^+$) calculated for $C_{30}H_{22}O_4Na$ $[M+Na]^+$: 469.1410, found 469.1411.

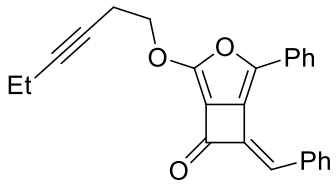


(*E*)-7-Benzylidene-4-((4-(naphthalen-1-yl)but-3-yn-1-yl)oxy)-2-phenyl-3-oxabicyclo[3.2.0]hepta-1,4-dien-6-one (2g). Yellow oil; 335.6 mg, 72% yield. ^{1}H NMR (500 MHz, $CDCl_3$) (δ, ppm) 8.33 (d, *J* = 8.3 Hz, 1H), 7.81 (d, *J* = 8.1 Hz, 1H), 7.79 (d, *J* = 8.3 Hz, 1H), 7.65 (d, *J* = 6.9 Hz, 1H), 7.56 - 7.52 (m, 1H), 7.50 - 7.46 (m, 1H), 7.40 - 7.34 (comp, 2H), 7.33 - 7.29 (comp, 4H), 7.27 - 7.25 (comp, 4H), 7.24 (d,

J = 7.6 Hz, 1H), 7.10 (s, 1H), 4.66 (t, *J* = 6.5 Hz, 2H), 3.19 (t, *J* = 6.5 Hz, 2H); ^{13}C NMR (126 MHz, $CDCl_3$) (δ, ppm) 174.4, 149.1, 137.9, 136.4, 133.8, 133.6, 133.2, 130.6, 130.0, 129.7, 129.3, 129.0, 128.7, 128.6, 128.3, 128.2, 128.0, 127.8, 126.9, 126.5, 126.3, 125.3, 122.2, 120.8, 117.2, 89.3, 81.1, 71.9, 20.7. HRMS (TOF MS ESI$^+$) calculated for $C_{33}H_{22}O_3Na$ $[M+Na]^+$: 489.1461, found 489.1460.

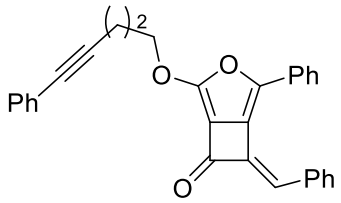


(*E*)-7-Benzylidene-2-phenyl-4-((4-(thiophen-2-yl)but-3-yn-1-yl)oxy)-3-oxabicyclo [3.2.0]hepta-1,4-dien-6-one (2h). Yellow solid, mp = 160.8 - 162.7 °C; 299.7 mg, 71% yield. (δ, ppm) ^{1}H NMR (500 MHz, $CDCl_3$) (δ, ppm) 7.39 - 7.35 (comp, 3H), 7.33 - 7.28 (comp, 7H), 7.23 (d, *J* = 5.2 Hz, 1H), 7.21 (d, *J* = 3.6 Hz, 1H),7.13 (s, 1H), 6.98 - 6.95 (m, 1H), 4.57 (t, *J* = 6.5 Hz, 2H), 3.08 (t, *J* = 6.5 Hz, 2H); ^{13}C NMR (126 MHz, $CDCl_3$) (δ, ppm) 174.4, 148.9, 137.8, 136.4, 133.8, 132.1, 130.0, 129.7, 129.3, 128.9, 128.7, 128.2, 128.1, 127.8, 127.0, 126.9, 123.2, 122.2, 117.2, 88.4, 76.2, 71.5, 20.6. HRMS (TOF MS ESI$^+$) calculated for $C_{27}H_{18}O_3SNa$ $[M+Na]^+$: 445.0869, found 445.0869.

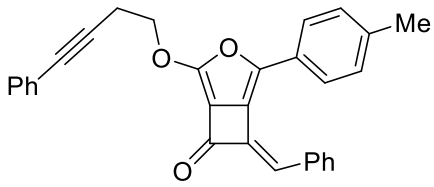


(*E*)-7-Benzylidene-4-(hex-3-yn-1-yloxy)-2-phenyl-3-oxabicyclo[3.2.0]hepta-1,4-dien-6-one (2i). Yellow solid, mp = 95.3 - 98.5 °C; 276.1 mg, 75% yield. ^{1}H NMR (500 MHz, $CDCl_3$) (δ, ppm) 7.36 - 7.32 (comp, 3H), 7.29 - 7.24 (comp, 7H), 7.10 (s, 1H), 4.44 (t, *J* = 6.6 Hz, 2H), 2.76 (t, *J* = 6.4 Hz, 2H), 2.18 (dd, *J* = 14.7, 7.3 Hz, 2H), 1.12 (t, *J* = 7.5 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) (δ, ppm) 174.4, 149.2, 138.0, 136.2, 133.8, 130.0, 129.6, 129.3, 129.0, 128.6, 128.2, 128.0, 127.7, 122.1, 117.1,

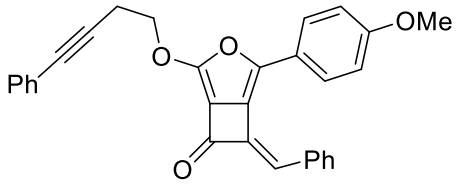
84.5, 73.8, 72.3, 19.7, 14.1, 12.6. HRMS (TOF MS ESI$^+$) calculated for $C_{25}H_{20}O_3Na$ $[M+Na]^+$: 391.1305, found 391.1301.



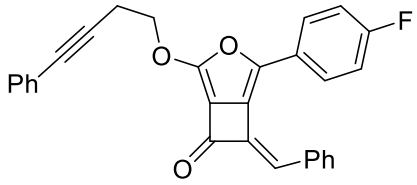
(*E*)-7-Benzylidene-2-phenyl-4-((5-phenylpent-4-yn-1-yl)oxy)-3-oxabicyclo[3.2.0] hepta-1,4-dien-6-one (2j). Yellow solid, mp = 149.8 - 151.2 °C; 316.3 mg, 76% yield. ^{1}H NMR (500 MHz, $CDCl_3$) (δ, ppm) 7.42 - 7.40 (m, 2H), 7.36 - 7.32 (comp, 3H), 7.30 - 7.27 (comp, 5H), 7.26 - 7.23 (comp, 5H), 7.09 (s, 1H), 4.57 (t, *J* = 6.0 Hz, 2H), 2.67 (t, *J* = 6.9 Hz, 2H), 2.22 - 2.16 (m, 2H); ^{13}C NMR (126 MHz, $CDCl_3$) (δ, ppm) 174.5, 149.5, 137.9, 136.1, 133.8, 131.8, 130.0, 129.6, 129.3, 129.0, 128.6, 128.4, 128.2, 127.94, 127.92, 127.7, 123.6, 122.0, 117.1, 88.0, 81.9, 72.9, 28.0, 16.1. HRMS (TOF MS ESI$^+$) calculated for $C_{30}H_{22}O_3Na$ $[M+Na]^+$: 453.1461, found 453.1464.



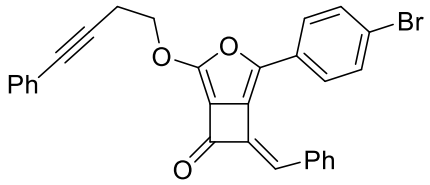
(*E*)-7-Benzylidene-4-((4-phenylbut-3-yn-1-yl)oxy)-2-(*p*-tolyl)-3-oxabicyclo[3.2.0] hepta-1,4-dien-6-one (2k). Yellow solid, mp = 112.6 - 114.6 °C; 322.6 mg, 75% yield. ^{1}H NMR (500 MHz, $CDCl_3$) (δ, ppm) 7.4 5 -7.43 (m, 2H), 7.38 - 7.34 (comp, 3H), 7.30 - 7.27 (comp, 5H), 7.19 (d, *J* = 8.1 Hz, 2H), 7.11 (d, *J* = 8.6 Hz, 3H), 4.56 (t, *J* = 6.6 Hz, 2H), 3.04 (t, *J* = 6.6 Hz, 2H), 2.40 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) (δ, ppm) 174.6, 148.8, 138.1, 137.9, 136.7, 133.8, 131.9, 130.0, 129.3, 128.9, 128.6, 128.4, 128.2, 127.8, 126.3, 123.2, 121.9, 117.0, 84.4, 82.9, 71.8, 21.5, 20.4. HRMS (TOF MS ESI$^+$) calculated for $C_{30}H_{22}O_3Na$ $[M+Na]^+$: 453.1461, found 453.1463.



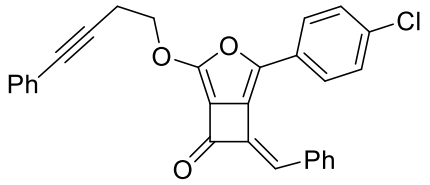
(*E*)-7-Benzylidene-2-(4-methoxyphenyl)-4-((4-phenylbut-3-yn-1-yl)oxy)-3-oxabicyclo[3.2.0]hepta-1,4-dien-6-one (2l). Yellow solid, mp = 145.6 - 148.9 °C; 361.4 mg, 81% yield. ^{1}H NMR (500 MHz, $CDCl_3$) (δ, ppm) 7.46 - 7.44 (m, 2H), 7.38 - 7.34 (comp, 3H), 7.31 - 7.28 (comp, 5H), 7.24 (d, *J* = 8.7 Hz, 2H), 7.09 (s, 1H), 6.85 (d, *J* = 8.7 Hz, 2H), 4.57 (t, *J* = 6.6 Hz, 2H), 3.87 (s, 3H), 3.05 (t, *J* = 6.6 Hz, 2H); ^{13}C NMR (126 MHz, $CDCl_3$) (δ, ppm) 174.6, 159.6, 148.6, 137.9, 136.5, 133.9, 131.9, 129.9, 129.4, 129.2, 128.7, 128.4, 128.2, 128.1, 123.2, 121.9, 121.6, 116.8, 113.7, 84.4, 82.9, 71.7, 55.5, 20.4. HRMS (TOF MS ESI$^+$) calculated for $C_{30}H_{22}O_4Na$ $[M+Na]^+$: 469.1410, found 469.1414.



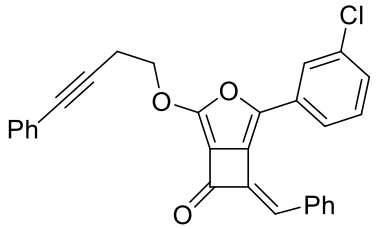
(*E*)-7-Benzylidene-2-(4-fluorophenyl)-4-((4-phenylbut-3-yn-1-yl)oxy)-3-oxabicyclo[3.2.0]hepta-1,4-dien-6-one (2m). Yellow solid, mp = 117.8 - 120.9 °C; 329.9 mg, 76% yield. ^{1}H NMR (400 MHz, $CDCl_3$) (δ, ppm) 7.42 (dd, *J* = 6.6, 3.0 Hz, 2H), 7.35 (t, *J* = 7.1 Hz, 1H), 7.30 - 7.25 (comp, 7H), 7.23 - 7.19 (m, 2H), 7.09 (s, 1H), 6.98-6.94 (m, 2H), 4.54 (t, *J* = 6.6 Hz, 2H), 3.02 (t, *J* = 6.6 Hz, 2H); 13C NMR (126 MHz, $CDCl_3$) (δ, ppm) 174.2, 162.5 (d, *J* = 248.8 Hz), 149.0, 137.8, 135.2, 133.8, 131.9, 129.9, 129.6 (d, *J* = 8.2 Hz), 129.4, 129.3 (d, *J* = 1.0 Hz), 128.7, 128.4, 128.2, 125.3 (d, *J* = 3.2 Hz), 123.2, 122.2, 117.1, 115.4, 115.2, 84.3, 82.9, 71.9, 20.3. ^{19}F NMR (376 MHz, $CDCl_3$) (δ, ppm) -112.69. HRMS (TOF MS ESI$^+$) calculated for $C_{29}H_{19}FO_3Na$ $[M+Na]^+$: 457.1210, found 457.1215.



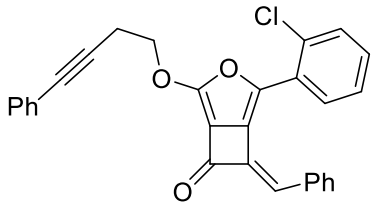
(*E*)-7-Benzylidene-2-(4-bromophenyl)-4-((4-phenylbut-3-yn-1-yl)oxy)-3-oxabicyclo[3.2.0]hepta-1,4-dien-6-one (2n). Yellow solid, mp = 148.5 - 140.2 °C; 396.0 mg, 80% yield. ^{1}H NMR (500 MHz, $CDCl_3$) (δ, ppm) 7.42 (dd, *J* = 6.6, 3.0 Hz, 2H), 7.40 - 7.37 (comp, 3H), 7.32 - 7.28 (comp, 7H), 7.12 (s, 1H), 7.09 (d, *J* = 8.5 Hz, 2H), 4.55 (t, *J* = 6.5 Hz, 2H), 3.03 (t, *J* = 6.5 Hz, 2H); ^{13}C NMR (126 MHz, $CDCl_3$) (δ, ppm) 174.0, 149.2, 137.8, 135.1, 133.8, 131.9, 131.4, 130.3, 129.9, 129.5, 128.9, 128.8, 128.4, 128.3, 127.8, 123.1, 122.6, 122.0, 117.4, 84.2, 82.9, 72.0, 20.4. HRMS (TOF MS ESI$^+$) calculated for $C_{29}H_{19}BrO_3Na$ $[M+Na]^+$: 517.0410, found 517.0413.



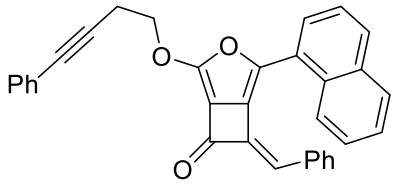
(*E*)-7-Benzylidene-2-(4-chlorophenyl)-4-((4-phenylbut-3-yn-1-yl)oxy)-3-oxabicyclo[3.2.0]hepta-1,4-dien-6-one (2o). Yellow solid, mp = 138.5 - 140.2 °C; 328.6 mg, 73% yield. ^{1}H NMR (500 MHz, $CDCl_3$) (δ, ppm) 7.42 (dd, *J* = 6.7, 3.0 Hz, 2H), 7.40 - 7.36 (m, 1H), 7.32 - 7.30 (comp, 4H), 7.29 - 7.27 (comp, 3H), 7.24 - 7.22 (m, 2H), 7.17 - 7.15 (m, 2H), 7.12 (s, 1H), 4.56 (t, *J* = 6.5 Hz, 2H), 3.03 (t, *J* = 6.5 Hz, 2H); ^{13}C NMR (126 MHz, $CDCl_3$) (δ, ppm) 174.1, 149.2, 137.8, 135.1, 133.8, 131.9, 130.2, 129.9, 129.5, 128.8, 128.7, 128.5, 128.4, 128.3, 127.4, 123.2, 122.6, 117.4, 84.2, 83.0, 72.0, 20.4. HRMS (TOF MS ESI$^+$) calculated for $C_{29}H_{19}ClO_3Na$ $[M+Na]^+$: 473.0915, found 473.0919.



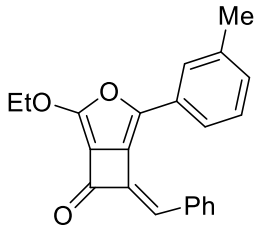
(*E*)-7-Benzylidene-2-(3-chlorophenyl)-4-((4-phenylbut-3-yn-1-yl)oxy)-3-oxabicyclo[3.2.0]hepta-1,4-dien-6-one (2p). Yellow oil; 342.1 mg, 76% yield. ^{1}H NMR (500 MHz, $CDCl_3$) (δ, ppm) δ 7.43 - 7.41 (m, 2H), 7.38 (t, *J* = 7.0 Hz, 1H), 7.33 - 7.31 (comp, 3H), 7.29 - 7.28 (comp, 4H), 7.25 (s, 1H), 7.22 - 7.18 (m, 2H), 7.14 - 7.12 (m, 2H), 4.56 (t, *J* = 6.5 Hz, 2H), 3.03 (t, *J* = 6.5 Hz, 2H); ^{13}C NMR (126 MHz, $CDCl_3$) (δ, ppm) 174.0, 149.3, 137.6, 134.6, 134.3, 133.6, 131.9, 130.8, 130.6, 129.8, 129.6, 129.5, 128.8, 128.4, 128.3, 127.8, 127.4, 125.5, 123.2, 122.9, 117.5, 84.2, 83.0, 72.0, 20.4. HRMS (TOF MS ESI$^+$) calculated for $C_{29}H_{19}ClO_3Na$ $[M+Na]^+$: 473.0915, found 473.0919.



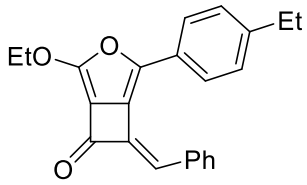
(*E*)-7-Benzylidene-2-(2-chlorophenyl)-4-((4-phenylbut-3-yn-1-yl)oxy)-3-oxabicyclo[3.2.0]hepta-1,4-dien-6-one (2q). Yellow oil; 333.1 mg, 74% yield. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.43 - 7.41 (m, 2H), 7.39 - 7.38 (m, 1H), 7.36 - 7.33 (comp, 3H), 7.28 - 7.26 (comp, 3H), 7.24 - 7.21 (comp, 4H), 7.03 - 6.99 (m, 2H), 4.55 (t, *J* = 6.6 Hz, 2H), 3.02 (t, *J* = 6.6 Hz, 2H); ^{13}C NMR (126 MHz, $CDCl_3$) (δ, ppm) 173.9, 149.3, 137.4, 134.5, 133.8, 133.2, 132.5, 132.4, 131.8, 131.7, 130.3, 130.0, 129.3, 128.3, 128.3, 128.2, 126.4, 123.1, 122.5, 116.9, 84.3, 82.9, 71.8, 20.3. HRMS (TOF MS ESI$^+$) calculated for $C_{29}H_{19}ClO_3Na$ $[M+Na]^+$: 473.0915, found 473.0914.



(*E*)-7-Benzylidene-2-(naphthalen-1-yl)-4-((4-phenylbut-3-yn-1-yl)oxy)-3-oxabicyclo[3.2.0]hepta-1,4-dien-6-one (2r). Yellow oil, 356.9 mg, 80% yield. ^{1}H NMR (500 MHz, $CDCl_3$) (δ, ppm) 8.11 (d, *J* = 8.5 Hz, 1H), 7.90 (d, *J* = 7.9 Hz, 1H), 7.85 (d, *J* = 8.2 Hz, 1H), 7.44 - 7.38 (comp, 5H), 7.28 - 7.26 (comp, 3H), 7.24 - 7.23 (m, 1H), 7.09 (d, *J* = 7.6 Hz, 2H), 7.03 - 6.97 (m, 2H), 6.73 (t, *J* = 7.7 Hz, 2H), 4.59 (t, *J* = 6.6 Hz, 2H), 3.05 (t, *J* = 6.6 Hz, 2H); ^{13}C NMR (126 MHz, $CDCl_3$) (δ, ppm) 174.3, 149.4, 137.6, 135.0, 133.5, 133.3, 132.6, 132.1, 131.9, 129.69, 129.67, 129.4, 129.2, 128.4, 128.2, 128.1, 128.0, 126.6, 126.4, 126.3, 125.9, 124.8, 123.2, 122.3, 117.0, 84.4, 82.9, 71.8, 20.4. HRMS (TOF MS ESI$^+$) calculated for $C_{33}H_{22}O_3Na$ $[M+Na]^+$: 489.1461, found 489.1467.

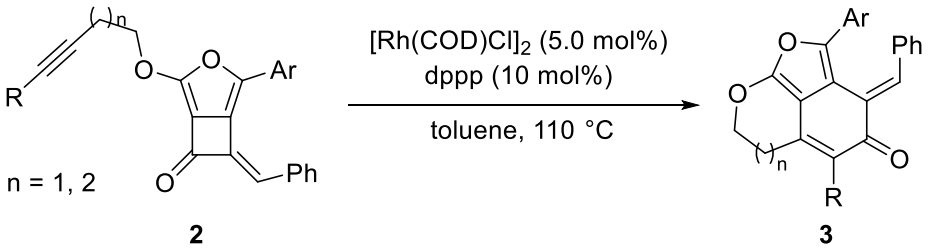


(*E*)-7-Benzylidene-4-ethoxy-2-(*m*-tolyl)-3-oxabicyclo[3.2.0]hepta-1,4-dien-6-one (2t). Yellow oil, 274.2 mg, 83% yield. ^{1}H NMR (400 MHz, $CDCl_3$) (δ, ppm) 7.35 – 7.32 (comp, 3H), 7.26 – 7.22 (m, 2H), 7.19 – 7.16 (m, 1H), 7.12 – 7.07 (comp, 3H), 6.97 (s, 1H), 4.44 (q, *J* = 7.1 Hz, 2H), 2.18 (s, 3H), 1.53 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) (δ, ppm) 174.6, 149.6, 138.0, 137.7, 136.1, 133.8, 130.0, 129.3, 129.1, 128.9, 128.64, 128.60, 128.56, 128.1, 124.4, 121.8, 116.7, 70.3, 21.3, 14.5; HRMS (TOF MS ESI$^+$) calculated for $C_{22}H_{18}O_3Na$ $[M+Na]^+$: 353.1148, found 353.1146.



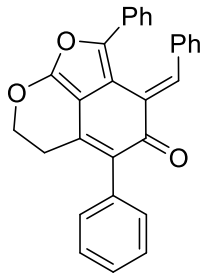
(*E*)-7-Benzylidene-4-ethoxy-2-(4-ethylphenyl)-3-oxabicyclo[3.2.0]hepta-1,4-dien-6-one (2v). Yellow oil, 292.7 mg, 85% yield. ^{1}H NMR (400 MHz, $CDCl_3$) (δ, ppm) 7.32 – 7.26 (comp, 3H), 7.21 – 7.17 (m, 2H), 7.12 – 7.10 (m, 2H), 7.06 – 7.04 (m, 2H), 7.01 (s, 1H), 4.39 (q, *J* = 7.1 Hz, 2H), 2.64 (q, *J* = 7.6 Hz, 2H), 1.49 (t, *J* = 7.1 Hz, 3H), 1.23 (t, *J* = 7.6 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) (δ, ppm) 174.5, 149.3, 144.1, 137.8, 136.1, 133.7, 129.9, 129.0, 128.7, 128.4, 127.6, 127.5, 126.4, 121.4, 116.6, 70.1, 28.7, 15.6, 14.4; HRMS (TOF MS ESI$^+$) calculated for $C_{23}H_{20}O_3Na$ $[M+Na]^+$: 367.1305, found 367.1308.

General Procedure for the Intramolecular [4+2] Cycloaddition Reaction

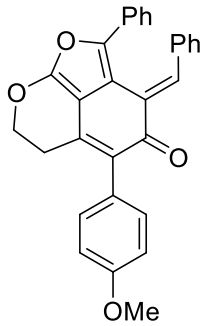


2 **3**

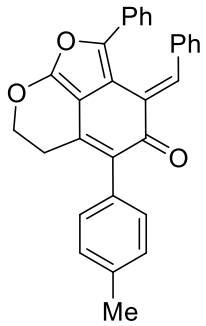
To a 10-mL oven-dried vial containing a magnetic stirring bar, [Rh (cod)Cl]$_2$ (1.23 mg, 5.0 mol%), 1,3-bis(diphenylphosphino)propane (dppp, 8.2 mg, 10 mol%), toluene (3.0 mL), and compound **2** (0.2 mmol) were added in sequence under an argon atmosphere, and the reaction mixture was stirred for 4 h at 110 ^{o}C. Until consumption of the material **2** (monitored by TLC), the reaction mixture was purified by column chromatography on silica gel without any additional treatment (hexane : EtOAc = 30:1 to 15:1) to give the pure products **3** in good to high yields.



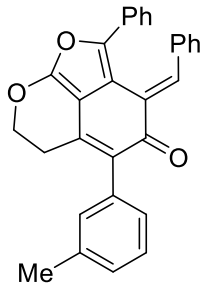
(*E*)-3-Benzylidene-2,5-diphenyl-6,7-dihydrofuro[4,3,2-*ij*]isochromen-4(3*H*)-one (3a). Red solid, mp = 88.7 - 90.3 °C; 79.1 mg, 95% yield; ^{1}H NMR (500 MHz, $CDCl_3$) (δ, ppm) 7.95 (s, 1H), 7.44 - 7.41 (m, 2H), 7.35 - 7.32 (comp, 3H), 7.14 (d, *J* = 7.3 Hz, 2H), 7.03 - 6.92 (comp, 4H), 6.87 - 6.81 (comp, 4H), 4.64 (t, *J* = 5.2 Hz, 2H), 2.92 (t, *J* = 5.2 Hz, 2H); ^{13}C NMR (126 MHz, $CDCl_3$) (δ, ppm) 188.3, 158.7, 143.0, 140.1, 138.9, 136.1, 134.9, 130.8, 130.4, 128.8, 128.6, 128.20, 128.15, 127.38,127.36, 127.3, 127.1, 127.0, 125.6, 112.9, 97.2, 72.2, 27.0. HRMS (TOF MS ESI^{+}) calculated for $C_{29}H_{20}O_3Na$ $[M+Na]^{+}$: 439.1305, found 439.1306.



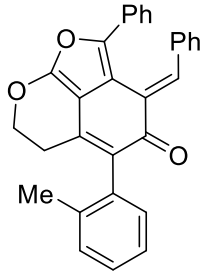
(*E*)-3-Benzylidene-5-(4-methoxyphenyl)-2-phenyl-6,7-dihydrofuro[4,3,2-ij]isochromen-4(3*H*)-one (3b). Red solid, mp = 235.9 - 239.9 °C; 83.9 mg, 94% yield; ^{1}H NMR (500 MHz, $CDCl_3$) (δ, ppm) 7.93 (s, 1H), 7.26 - 7.24 (m, 2H), 7.14 - 7.12 (m, 2H), 7.02 - 6.95 (comp, 4H), 6.93 - 6.91 (m, 2H), 6.86 - 6.80 (comp, 4H), 4.64 (t, *J* = 5.9 Hz, 2H), 3.85 (s, 3H), 2.93 (t, *J* = 6.0 Hz, 2H); ^{13}C NMR (126 MHz, $CDCl_3$) (δ, ppm) 188.7, 158.9, 158.5, 142.9, 139.7, 138.9, 136.2, 131.5, 130.9, 128.8, 128.6, 128.3, 127.4, 127.3, 127.1, 126.6, 125.6, 113.7, 112.9, 97.3, 72.2, 55.4, 27.0. HRMS (TOF MS ESI$^+$) calculated for $C_{30}H_{22}O_4Na$ $[M+Na]^+$: 469.1410, found 469.1410.



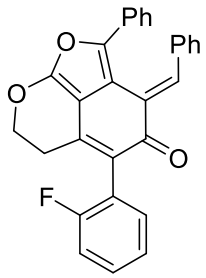
(*E*)-3-Benzylidene-2-phenyl-5-(*p*-tolyl)-6,7-dihydrofuro[4,3,2-*ij*]isochromen-4(3*H*)-one (3c). Red solid, mp = 221.5 - 224.9 °C; 81.7 mg, 95% yield; ^{1}H NMR (400 MHz, $CDCl_3$) (δ, ppm) 7.94 (s, 1H), 7.23 - 7.22 (comp, 3H), 7.13 (d, *J* = 7.6 Hz, 2H), 7.02 - 6.92 (comp, 5H), 6.86 - 6.80 (comp, 4H), 4.64 (t, *J* = 6.0 Hz, 2H), 2.93 (t, *J* = 6.0 Hz, 2H), 2.39 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) 188.5, 158.6, 142.9, 139.8, 138.8, 137.1, 136.2, 131.8, 130.9, 130.2, 128.9, 128.8, 128.6, 128.3, 127.4, 127.3, 127.1, 127.0, 125.6, 112.9, 97.3, 72.2, 27.0, 21.4. HRMS (TOF MS ESI$^+$) calculated for $C_{30}H_{22}O_3Na$ $[M+Na]^+$: 453.1461, found 453.1461.



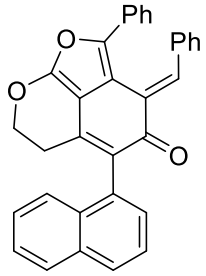
(*E*)-3-Benzylidene-2-phenyl-5-(*m*-tolyl)-6,7-dihydrofuro[4,3,2-*ij*]isochromen-4(3*H*)-one (3d). Red solid, mp = 199.9 - 202.5 °C; 80.0 mg, 93% yield; ^{1}H NMR (400 MHz, $CDCl_3$) (δ, ppm) 7.95 (s, 1H), 7.31 (t, *J* = 7.9 Hz, 1H), 7.16 - 7.09 (comp, 5H), 7.03 - 6.92 (comp, 4H), 6.87 - 6.80 (comp, 4H), 4.64 (t, *J* = 6.0 Hz, 2H), 2.92 (t, *J* = 6.0 Hz, 2H), 2.40 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) (δ, ppm) 188.4, 158.6, 143.0, 140.0, 138.8, 137.7, 136.2, 134.8, 131.0, 130.8, 128.8, 128.6, 128.2, 128.2, 128.1, 127.4, 127.3, 127.2, 127.09, 125.6, 112.9, 97.2, 72.2, 27.0, 21.7. HRMS (TOF MS ESI$^+$) calculated for $C_{30}H_{22}O_3Na$ $[M+Na]^+$: 453.1461, found 453.1464.



(*E*)-3-Benzylidene-2-phenyl-5-(*o*-tolyl)-6,7-dihydrofuro[4,3,2-*ij*]isochromen-4(3*H*)-one (3e). Red oil; 51.6 mg, 60% yield; ^{1}H NMR (500 MHz, DMSO-d_6) (δ, ppm) 7.79 (s, 1H), 7.28 - 7.19 (comp, 3H), 7.16 - 7.12 (comp, 3H), 7.06 - 6.99 (m, 2H), 6.91 - 6.84 (comp, 6H), 4.77 - 4.66 (m, 2H), 2.86 - 2.80 (m, 1H), 2.58 - 2.52 (m, 1H), 2.10 (s, 3H); ^{13}C NMR (126 MHz, DMSO-d_6) (δ, ppm) 186.8, 159.1, 142.5, 142.2, 138.3, 137.6, 135.8, 135.3, 130.63, 130.59, 130.1, 129.2, 128.9, 127.94, 127.92, 127.9, 127.8, 127.6, 126.5, 125.9, 125.5, 113.1, 96.9, 79.6, 73.1, 26.5, 20.1. HRMS (TOF MS ESI$^+$) calculated for $C_{30}H_{22}O_3Na$ $[M+Na]^+$: 453.1461, found 453.1463.

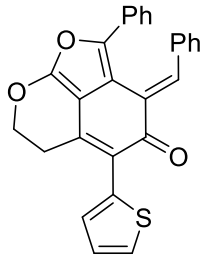


(*E*)-3-Benzylidene-5-(2-fluorophenyl)-2-phenyl-6,7-dihydrofuro[4,3,2-*ij*]isochromen-4(3*H*)-one (3f). Red solid, mp = 177.8 - 179.9 °C; 56.4 mg, 65% yield; ^{1}H NMR (400 MHz, $CDCl_3$) (δ, ppm) δ 7.81 (s, 1H), 7.45 - 7.34 (comp, 3H), 7.27 - 7.23 (m, 2H), 7.15 (d, *J* = 7.7 Hz, 2H), 7.07 - 7.04 (m, 1H), 7.01 (t, *J* = 7.4 Hz, 1H), 6.90 - 6.88 (comp, 3H), 6.87 - 6.84 (m, 2H), 4.75 (s, 2H), 2.85 (d, *J* = 73.3 Hz, 2H).; ^{13}C NMR (126 MHz, DMSO-d_6) (δ, ppm) 185.6, 160.0 (d, *J* = 244.5 Hz), 159.1, 142.9, 142.2, 138.0, 135.3, 132.4 (d, *J* = 3.7 Hz), 130.0, 129.6 (d, *J* = 8.3 Hz), 128.8, 128.5, 127.5, 127.4, 127.11, 127.07, 125.1, 124.0 (d, *J* = 3.1 Hz), 122.4 (d, *J* = 16.5 Hz), 120.1, 115.3 (d, *J* = 22.2 Hz), 112.4, 96.4, 72.7, 26.0; ^{19}F NMR (376 MHz, DMSO-d_6) (δ, ppm) -112.30. HRMS (TOF MS ESI$^+$) calculated for $C_{29}H_{19}FO_3Na$ $[M+Na]^+$: 457.1210, found 457.1207.

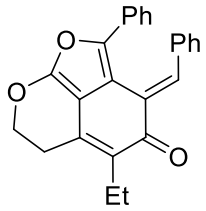


(*E*)-3-Benzylidene-5-(naphthalen-1-yl)-2-phenyl-6,7-dihydrofuro[4,3,2-*ij*]isochromen-4(3*H*)-one (3g). Red solid, mp = 113.1 - 115.2 °C; 83.9 mg, 90% yield; ^{1}H NMR (500 MHz, $CDCl_3$) (δ, ppm) 7.99 (s, 1H), 7.91 - 7.87 (m, 2H), 7.78 - 7.76 (m, 1H), 7.55 - 7.52 (m, 1H), 7.50 - 7.43 (m, 2H), 7.38 - 7.37 (m, 1H), 7.18 - 7.16 (m, 2H), 7.05 - 7.02 (m, 1H), 7.00 - 6.96 (comp, 3H), 6.89 - 6.82 (comp, 4H), 4.65 - 4.56 (m, 2H), 2.78 – 2.72 (m, 1H), 2.60 – 2.54 (m, 1H); ^{13}C NMR (126 MHz, $CDCl_3$) (δ, ppm) 188.4, 158.9, 143.2, 142.1, 139.1, 136.1, 133.9, 133.0, 132.6, 130.8, 128.9, 128.7, 128.6, 128.3, 128.1, 127.4, 127.4, 127.1, 126.2, 125.9, 125.7, 125.6, 113.2, 97.4, 72.2,

26.8. HRMS (TOF MS ESI$^+$) calculated for $C_{33}H_{22}O_3Na$ [M+Na]$^+$: 489.1461, found 489.1462.

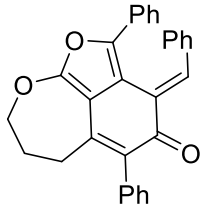


(*E*)-3-Benzylidene-2-phenyl-5-(thiophen-2-yl)-6,7-dihydrofuro[4,3,2-*ij*]isochromen-4(3*H*)-one (3h). Red solid, mp = 230.2 - 232.5 °C; 77.7 mg, 92% yield; ^{1}H NMR (500 MHz, $CDCl_3$) (δ, ppm) 7.97 (s, 1H), 7.42 - 7.41 (m, 1H), 7.11 - 7.10 (comp, 4H), 7.01 (t, *J* = 7.3 Hz, 1H), 6.96 (d, *J* = 7.3 Hz, 1H), 6.92 - 6.90 (m, 2H), 6.86 - 6.81 (comp, 4H), 4.68 (t, *J* = 6.0 Hz, 2H), 3.18 (t, *J* = 6.0 Hz, 2H); ^{13}C NMR (126 MHz, $CDCl_3$) (δ, ppm) 188.0, 159.0, 143.0, 139.9, 139.2, 136.0, 135.6, 130.7, 128.8, 128.7, 127.8, 127.45, 127.42, 127.4, 127.1, 126.5, 126.1, 125.7, 120.1, 112.4, 97.5, 72.0, 27.4. HRMS (TOF MS ESI$^+$) calculated for $C_{27}H_{18}O_3SNa$ [M+Na]$^+$: 445.0869, found 445.0868.

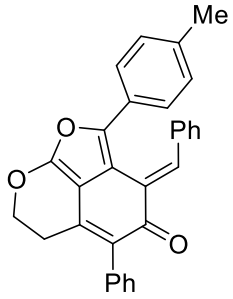


(*E*)-3-Benzylidene-2,5-diphenyl-7,8-dihydro-3*H*-oxepino[2,3,4-*cd*]isobenzofuran-4(6*H*)-one (3i). Red oil; 69.9 mg, 95% yield; ^{1}H NMR (400 MHz, $CDCl_3$) (δ, ppm) 7.92 (s, 1H), 7.11 (d, *J* = 7.6 Hz, 2H), 7.00 - 6.93 (m, 2H), 6.90 - 6.88 (m, 2H), 6.84 - 6.78 (comp, 4H), 4.68 (t, *J* = 6.0 Hz, 2H), 2.95 (t, *J* = 6.0 Hz, 2H), 2.45 (q, *J* = 7.5 Hz, 2H), 1.10 (t, *J* = 7.5 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) (δ, ppm) 189.1, 157.7, 142.6, 138.6, 138.2, 136.2, 130.9, 128.8, 128.5, 128.0, 127.9, 127.3, 127.2, 127.0,

125.5, 113.1, 97.1, 71.8, 25.8, 19.4, 13.8. HRMS (TOF MS ESI$^+$) calculated for $C_{25}H_{20}O_3Na$ [M+Na]$^+$: 391.1305, found 391.1304.

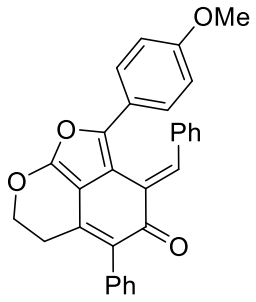


(*E*)-3-Benzylidene-5-ethyl-2-phenyl-6,7-dihydrofuro[4,3,2-*ij*]isochromen-4(3*H*)-one (3j). Red oil; 76.6 mg, 89% yield; ^{1}H NMR (400 MHz, $CDCl_3$) (δ, ppm) 7.62 (s, 1H), 7.45 - 7.41 (m, 2H), 7.35 (d, *J* = 7.2 Hz, 1H), 7.24 - 7.21 (m, 2H), 7.18 (d, *J* = 7.7 Hz, 2H), 7.11 (d, *J* = 8.2 Hz, 2H), 6.99 - 6.92 (m, 2H), 6.89 - 6.82 (comp, 4H), 4.52 - 4.50 (m, 2H), 2.79 - 2.76 (m, 2H), 2.11 (d, *J* = 3.0 Hz, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) (δ, ppm) 188.8, 157.6, 145.2, 141.7, 136.9, 136.8, 136.2, 132.4, 130.6, 130.5, 129.0, 128.6, 128.3, 127.9, 127.5, 127.3, 125.6, 114.5, 96.3, 73.2, 34.2, 26.5. HRMS (TOF MS ESI$^+$) calculated for $C_{30}H_{22}O_3Na$ [M+Na]$^+$: 453.1461, found 453.1463.

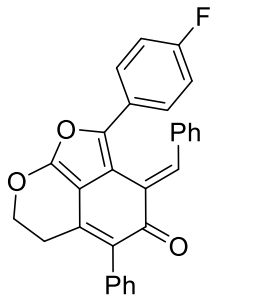


(*E*)-3-Benzylidene-5-phenyl-2-(*p*-tolyl)-6,7-dihydrofuro[4,3,2-*ij*]isochromen-4(3*H*)-one (3k). Red solid, mp = 218.4 - 221.9 °C; 81.7 mg, 95% yield; ^{1}H NMR (500 MHz, $CDCl_3$) (δ, ppm) 7.93 (s, 1H), 7.43 - 7.4 (m, 2H), 7.34 - 7.3 (comp, 3H), 7.11 (d, *J* = 7.6 Hz, 2H), 6.94 (t, *J* = 7.3 Hz, 1H), 6.83 - 6.80 (comp, 4H), 6.66 (d, *J* = 7.9 Hz, 2H), 4.63 (s, 2H), 2.91 (s, 2H), 2.22 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) (δ, ppm) 188.4, 158.5, 143.4, 140.1, 138.4, 137.7, 136.1, 135.0, 130.4, 128.8, 128.5, 128.3, 128.1, 128.1, 127.8, 127.4, 127.3, 126.9, 125.6, 112.2, 97.2, 72.7, 27.0, 21.5.

HRMS (TOF MS ESI$^+$) calculated for $C_{30}H_{22}O_3Na$ [M+Na]$^+$: 453.1461, found 453.1463.

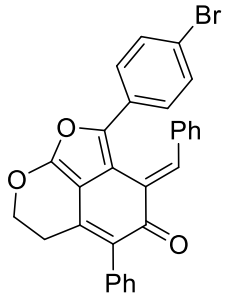


(*E*)-3-Benzylidene-2-(4-methoxyphenyl)-5-phenyl-6,7-dihydrofuro[4,3,2-*ij*]isochromen-4(3*H*)-one (3l). Red solid, mp = 231.6 - 235.5 °C; 82.1 mg, 92% yield; ^{1}H NMR (400 MHz, $CDCl_3$) (δ, ppm) 7.95 (s, 1H), 7.44 - 7.40 (m, 2H), 7.33 - 7.31 (m, 3H), 7.10 (d, *J* = 7.5 Hz, 2H), 7.01 (t, *J* = 7.4 Hz, 1H), 6.85 - 6.81 (comp, 4H), 6.39 (d, *J* = 8.8 Hz, 2H), 4.63 (t, *J* = 6.0 Hz, 2H), 3.70 (s, 3H), 2.91 (t, *J* = 6.0 Hz, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 188.4, 159.6, 158.4, 143.2, 140.1, 137.7, 136.1, 135.0, 130.4, 129.0, 128.5, 128.2, 128.1, 127.3, 127.2, 127.1, 126.8, 123.8, 112.7, 111.5, 97.1, 72.2, 55.5, 27.0. HRMS (TOF MS ESI$^+$) calculated for $C_{30}H_{22}O_4Na$ [M+Na]$^+$: 469.1410, found 469.1411.

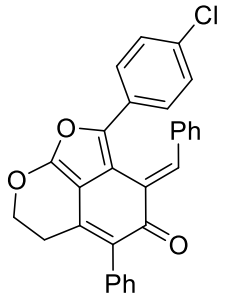


(*E*)-3-Benzylidene-2-(4-fluorophenyl)-5-phenyl-6,7-dihydrofuro[4,3,2-*ij*]isochromen-4(3*H*)-one (3m). Red solid, mp = 241.5 - 243.7 °C; 71.2 mg, 82% yield; ^{1}H NMR (400 MHz, $CDCl_3$) (δ, ppm) 7.95 (s, 1H), 7.44 - 7.40 (m, 2H), 7.35 - 7.30 (comp, 3H), 7.13 (d, *J* = 7.7 Hz, 2H), 7.05 - 7.01 (m, 1H), 6.91 - 6.85 (comp, 4H), 6.56 (t, *J* = 8.8 Hz, 2H), 4.63 (t, *J* = 6.0 Hz, 2H), 2.92 (t, *J* = 6.0 Hz, 2H); ^{13}C

NMR (126 MHz, $CDCl_3$) (δ, ppm) 188.1, 162.3 (d, *J* = 248.7 Hz), 158.6, 142.0, 140.0, 138.8, 136.0, 134.8, 130.4, 128.9, 128.8, 128.18, 128.15, 127.5, 127.4, 127.3 (d, *J* = 8.4 Hz), 127.2 (d, *J* = 3.2 Hz), 127.1, 114.2 (d, *J* = 22.0 Hz), 112.7, 97.2, 72.2, 27.0; ^{19}F NMR (376 MHz, $CDCl_3$) (δ, ppm) -113.20. HRMS (TOF MS ESI^+) calculated for $C_{29}H_{19}O_3FNa$ $[M+Na]^+$: 457.1210, found 457.1213.

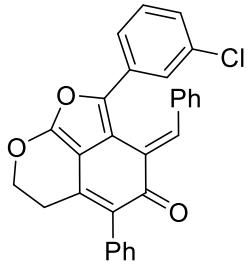


(*E*)-3-Benzylidene-2-(4-bromophenyl)-5-phenyl-6,7-dihydrofuro[4,3,2-*ij*]isochromen-4(3*H*)-one (3n). Red solid, mp = 249.5 - 251.2 °C; 87.9 mg, 89% yield; ^1H NMR (400 MHz, $CDCl_3$) (δ, ppm) 7.95 (s, 1H), 7.44 - 7.40 (m, 2H), 7.35 - 7.30 (comp, 3H), 7.13 (d, *J* = 7.7 Hz, 2H), 7.04 (t, *J* = 7.4 Hz, 1H), 6.98 (d, *J* = 8.5 Hz, 2H), 6.91 - 6.87 (m, 2H), 6.77 (d, *J* = 8.5 Hz, 2H), 4.64 (t, *J* = 6.0 Hz, 2H), 2.92 (t, *J* = 6.0 Hz, 2H); ^{13}C NMR (126 MHz, $CDCl_3$) (δ, ppm) 188.1, 158.8, 141.7, 139.9, 139.3, 136.0, 134.7, 130.4, 130.2, 129.6, 129.2, 128.7, 128.3, 128.2, 127.7, 127.5, 127.2, 126.9, 121.3, 113.5, 97.4, 72.3, 26.9. HRMS (TOF MS ESI^+) calculated for $C_{29}H_{19}O_3BrNa$ $[M+Na]^+$: 517.0410, found 517.0409.

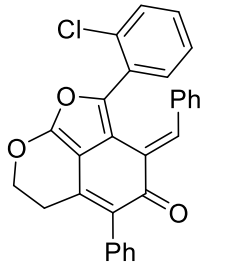


(*E*)-3-Benzylidene-2-(4-chlorophenyl)-5-phenyl-6,7-dihydrofuro[4,3,2-*ij*]isochromen-4(3*H*)-one (3o). Red solid, mp = 244.2 - 247.8 °C; 81.0 mg, 90% yield;

^{1}H NMR (400 MHz, $CDCl_3$) (δ, ppm) 7.95 (s, 1H), 7.44 - 7.40 (m, 2H), 7.35 - 7.29 (comp, 3H), 7.12 (d, *J* = 7.7 Hz, 2H), 7.04 (t, *J* = 7.4 Hz, 1H), 6.97 (d, *J* = 8.5 Hz, 2H), 6.91 - 6.87 (m, 2H), 6.77 (d, *J* = 8.5 Hz, 2H), 4.63 (t, *J* = 6.0 Hz, 2H), 2.92 (t, *J* = 6.0 Hz, 2H); ^{13}C NMR (126 MHz, $CDCl_3$) (δ, ppm) 188.1, 158.7, 141.7, 139.9, 139.3, 136.0, 134.7, 133.2, 130.4, 129.2, 129.1, 128.8, 128.2, 128.2, 127.6, 127.5, 127.3, 127.2, 126.6, 113.4, 97.3, 72.3, 27.0. HRMS (TOF MS ESI$^+$) calculated for $C_{29}H_{19}O_3ClNa$ $[M+Na]^+$: 473.0915, found 473.0917.

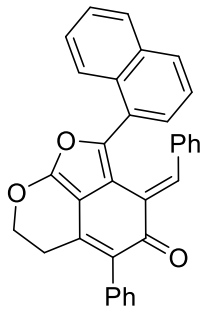


(*E*)-3-Benzylidene-2-(3-chlorophenyl)-5-phenyl-6,7-dihydrofuro[4,3,2-*ij*]isochromen-4(3*H*)-one (3p). Red solid, mp = 209.9 - 211.6 °C; 79.2 mg, 88% yield; ^{1}H NMR (500 MHz, $CDCl_3$) (δ, ppm) 7.96 (s, 1H), 7.43 (t, *J* = 7.5 Hz, 2H), 7.35 - 7.30 (comp, 3H), 7.17 (d, *J* = 7.7 Hz, 2H), 7.02 - 6.96 (m, 2H), 6.91 - 6.85 (comp, 4H), 6.81 (t, *J* = 7.8 Hz, 1H), 4.65 (t, *J* = 6.0 Hz, 2H), 2.93 (t, *J* = 6.0 Hz, 2H); ^{13}C NMR (126 MHz, $CDCl_3$) (δ, ppm) 188.2, 158.8, 141.2, 139.9, 139. 9, 136.1, 134.7, 133.4, 132.4, 130.4, 128.7, 128.6, 128.3, 128.22, 128.16, 127.8, 127.5, 127.3, 125. 9, 123.6, 113.9, 97.3, 72.1, 27.0. HRMS (TOF MS ESI$^+$) calculated for $C_{29}H_{19}O_3ClNa$ $[M+Na]^+$: 473.0915, found 473.0912.



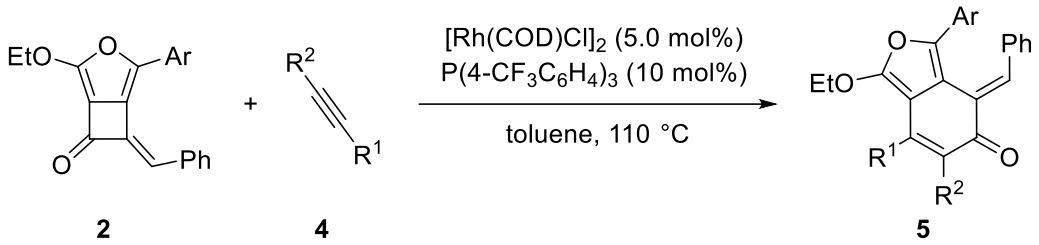
(*E*)-3-Benzylidene-2-(2-chlorophenyl)-5-phenyl-6,7-dihydrofuro[4,3,2-*ij*]isochromen-4(3*H*)-one (3q). Red oil; 77.4 mg, 86% yield; ^{1}H NMR (400 MHz,

$CDCl_3$) (δ, ppm) 8.12 (s, 1H), 7.43 (t, *J* = 7.4 Hz, 2H), 7.35 - 7.31 (comp, 3H), 7.15 - 7.13 (m, 1H), 7.02 - 6.98 (comp, 3H), 6.95 - 6.84 (comp, 3H), 6.78 (t, *J* = 7.6 Hz, 2H), 4.64 (t, *J* = 6.0 Hz, 2H), 2.92 (t, *J* = 6.0 Hz, 2H); ^{13}C NMR (126 MHz, $CDCl_3$) (δ, ppm) 187.3, 158.7, 141.9, 140.0, 139.9, 135.7, 134.8, 132.7, 131.4, 130.4, 120.0, 129.5, 129.3, 128.7, 128.13, 128.06, 127.8, 127.4, 127.2, 126.9, 125.6, 115.6, 96.8, 72.2, 26.9. HRMS (TOF MS ESI$^+$) calculated for $C_{29}H_{19}O_3ClNa$ [M+Na]$^+$: 473.0915, found 473.0913.

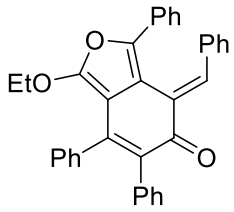


(*E*)-3-Benzylidene-2-(naphthalen-1-yl)-5-phenyl-6,7-dihydrofuro[4,3,2-*ij*]isochromen-4(3*H*)-one (3r). Red solid, mp = 95.2 - 97.6°C; 81.1 mg, 87% yield; ^{1}H NMR (500 MHz, $CDCl_3$) (δ, ppm) 7.99 (s, 1H), 7.60 - 7.55(m, 2H), 7.53 - 7.51 (m, 1H), 7.46 - 7.43 (m, 2H), 7.38 - 7.34 (comp, 6H), 7.17 - 7.14 (m, 1H), 6.58 (t, *J* = 7.4 Hz, 1H), 6.54 (d, *J* = 7.6 Hz, 2H), 6.28 (t, *J* = 7.7 Hz, 2H), 4.68 (t, *J* = 6.0 Hz, 2H), 2.97 (t, *J* = 6.0 Hz, 2H); ^{13}C NMR (126 MHz, $CDCl_3$) (δ, ppm) 187.5, 158.9, 141.7, 140.8, 140.2, 135.2, 135.0, 133.1, 130.4, 130.2, 129.8, 129.4, 129.1, 128.6, 128.2, 127.44, 127.39, 127.2, 126.98, 126.95, 126.4, 126.1, 125.8, 125.7, 124.2, 115.1, 97.0, 72.2, 27.0. HRMS (TOF MS ESI$^+$) calculated for $C_{33}H_{22}O_3Na$ [M+Na]$^+$: 489.1461, found 489.1462.

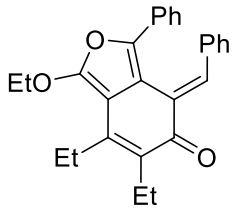
General Procedure for the Intermolecular [4+2] Cycloaddition Reaction



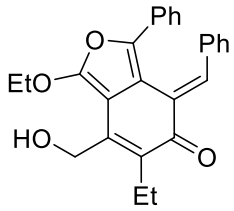
To a 10-mL oven-dried vial containing a magnetic stirring bar, $[Rh(cod)Cl]_2$ (1.23 mg, 5.0 mol%), tris(4-(trifluoromethyl)phenyl)phosphane (9.3 mg, 10 mol%), toluene (3.0 mL), compound **2** (0.2 mmol), and alkyne **4** (0.3 mmol) were added in sequence under an argon atmosphere, and the reaction mixture was stirred for 2 h at 110 ºC. Until consumption of the material (monitored by TLC), the reaction mixture was purified by column chromatography on silica gel without any additional treatment (hexane : EtOAc = 50:1 to 20:1) to give the pure products **5** in good to high yields.



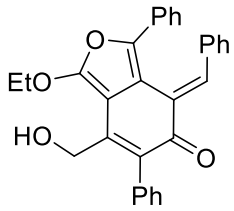
(*E*)-4-Benzylidene-1-ethoxy-3,6,7-triphenylisobenzofuran-5(4*H*)-one (5a). Red oil; 84.0 mg, 85% yield; ^{1}H NMR (400 MHz, $CDCl_3$) (δ, ppm) 7.70 (s, 1H), 7.24 (d, *J* = 2.7 Hz, 2H), 7.22 (s, 1H), 7.20 - 7.18 (comp, 3H), 7.17 - 7.13 (comp, 4H), 7.11 - 7.09 (comp, 4H), 7.00 - 6.93 (m, 2H), 6.91 - 6.84 (comp, 4H), 4.06 (q, *J* = 7.1 Hz, 2H), 0.99 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) (δ, ppm) 189.5, 156.6, 146.3, 141.5, 137.5, 136.7, 136.2, 135.6, 132.8, 131.4, 130.9, 129.3, 129.0, 128.7, 128.3, 127.6, 127.50, 127.46, 127.44, 127.38, 127.35, 126.6, 125.5, 114.5, 98.7, 68.5, 14.6. HRMS (TOF MS ESI$^+$) calculated for $C_{35}H_{26}O_3Na$ $[M+Na]^+$: 517.1774, found 517.1775.



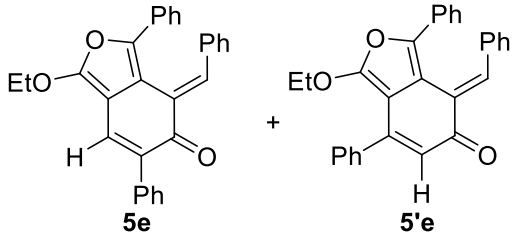
(*E*)-4-Benzylidene-1-ethoxy-6,7-diethyl-3-phenylisobenzofuran-5(4*H*)-one (5b). Red oil; 70.1 mg, 88% yield; ^{1}H NMR (400 MHz, $CDCl_3$) (δ, ppm) 7.63 (s, 1H), 7.14 (d, *J* = 7.4 Hz, 2H), 7.04 (d, *J* = 7.2 Hz, 2H), 6.97 - 6.91 (m, 2H), 6.89 - 6.79 (comp, 4H), 4.50 (q, *J* = 7.1 Hz, 2H), 2.76 (q, *J* = 7.5 Hz, 2H), 2.54 (q, *J* = 7.4 Hz, 2H), 1.51 (t, *J* = 7.1 Hz, 3H), 1.26 (t, *J* = 7.5 Hz, 3H), 1.11 (t, *J* = 7.4 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) (δ, ppm) 190.1, 154.5, 148.0, 140.9, 136.6, 136.5, 132.8, 131.1, 128.9, 128.3, 128.2, 127.4, 127.3, 127.1, 125.4, 114.9, 97.3, 67.7, 23.2, 19.3, 15.3, 14.6, 14.0. HRMS (TOF MS ESI$^+$) calculated for $C_{27}H_{26}O_3Na$ $[M+Na]^+$: 421.1774, found 421.1775.



(*E*)-4-Benzylidene-1-ethoxy-6-ethyl-7-(hydroxymethyl)-3-phenylisobenzofuran-5(4*H*)-one (5c). Red oil; 68.0 mg, 85% yield; ^{1}H NMR (400 MHz, $CDCl_3$) (δ, ppm) 7.69 (s, 1H), 7.12 (d, *J* = 7.6 Hz, 2H), 7.02 - 6.99 (m, 2H), 6.97 - 6.91 (m, 2H), 6.88 - 6.79 (comp, 4H), 4.57 (d, *J* = 4.5 Hz, 2H), 4.56 - 4.51 (m, 2H), 3.18 (s, 1H), 2.85 (q, *J* = 7.5 Hz, 2H), 1.51 (t, *J* = 7.1 Hz, 3H), 1.26 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) (δ, ppm) 191.4, 156.0, 151.5, 141.2, 137.4, 136.1, 130.8, 128.9, 128.73, 128.67, 127.45, 127.35, 127.3, 125.4, 114.7, 96.8, 67.8, 57.8, 23.0, 15.3, 14.4. HRMS (TOF MS ESI$^+$) calculated for $C_{26}H_{24}O_3Na$ $[M+Na]^+$: 423.1567, found 423.1566.

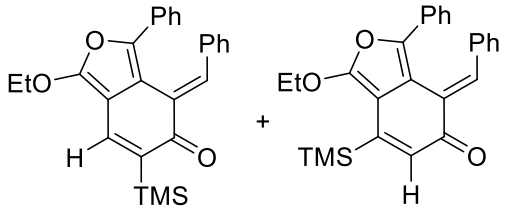


(*E*)-4-Benzylidene-1-ethoxy-7-(hydroxymethyl)-3,6-diphenylisobenzofuran-5(4*H*)-one (5d). Red oil; 73.5 mg, 82% yield; ^{1}H NMR (400 MHz, $CDCl_3$) (δ, ppm) 7.82 - 7.77 (m, 2H), 7.46 - 7.43 (m, 2H), 7.42 - 7.39 (m, 2H), 7.19 (d, *J* = 7.6 Hz, 2H), 7.03 (d, *J* = 7.3 Hz, 2H), 6.99 - 6.94 (m, 2H), 6.89 - 6.83 (comp, 4H), 4.32 (s, 2H), 4.07 (q, *J* = 7.0 Hz, 2H), 3.17 (s, 1H), 1.01 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) (δ, ppm) 191.9, 157.0, 147.8, 141.7, 137.8, 136.0, 135.5, 132.7, 132.6, 130.8, 129.6, 129.0, 128.9, 128.48, 128.46, 128.1, 127.6, 127.5, 127.4, 127.3, 125.6, 114.3, 98.3, 68.4, 59.2, 14.6. HRMS (TOF MS ESI$^+$) calculated for $C_{30}H_{24}O_3Na$ $[M+Na]^+$: 471.1567, found 471.1566.



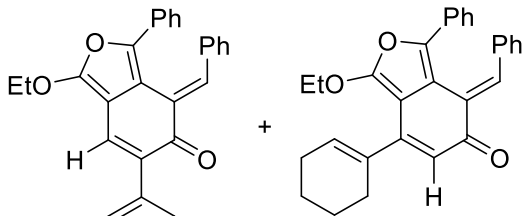
(*E*)-4-Benzylidene-1-ethoxy-3,6-diphenylisobenzofuran-5(4*H*)-one (5e) and (*E*)-4-benzylidene-1-ethoxy-3,7-diphenylisobenzofuran-5(*4H*)-one (5'e). (5e): Red oil; 66.2 mg, 79% yield; ^{1}H NMR (500 MHz, $CDCl_3$) (δ, ppm) 7.74 (s, 1H), 7.59 - 7.57 (m, 2H), 7.45 - 7.42 (comp, 3H), 7.22 (d, *J* = 7.6 Hz, 2H), 7.09 (d, *J* = 8.0 Hz, 2H), 7.00 - 6.95 (m, 2H), 6.90 - 6.84 (comp, 4H), 6.21 (s, 1H), 4.21 (q, *J* = 7.0 Hz, 2H), 1.15 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) (δ, ppm) 190.4, 156.0, 150.2, 141.8, 137.2, 136.8, 136.1, 130.8, 129.4, 129.1, 128.8, 128.3, 128.0, 127.6, 127.54, 127.51, 127.4, 125.5, 122.7, 115.4, 97.3, 68.4, 14.8. HRMS (TOF MS ESI$^+$) calculated for $C_{29}H_{22}O_3Na$ $[M+Na]^+$: 441.1461, found 441.1462. **(5'e)**: Red oil; 6.6 mg, 8% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.76 (s, 1H), 7.58 - 7.55 (m, 2H), 7.42 - 7.39 (m, 2H), 7.33 (d, *J* = 7.3 Hz, 1H), 7.17 (d, *J* = 7.6 Hz, 2H), 7.04 (d, *J* = 7.4 Hz,

2H), 7.00 - 6.92 (comp, 3H), 6.89 - 6.81 (comp, 4H), 4.52 (q, *J* = 7.1 Hz, 2H), 1.51 (t, *J* = 7.1 Hz, 3H).



5f **5'f**

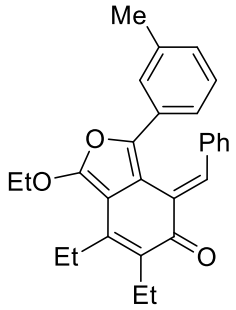
(*E*)-4-Benzylidene-1-ethoxy-3-phenyl-6-(trimethylsilyl)isobenzofuran-5(4*H*)-one (5f) and (*E*)-4-benzylidene-1-ethoxy-3-phenyl-7-(trimethylsilyl)isobenzofuran-5(*4H*)-one (5'f). (5f): Red oil; 64.5mg, 85.5% yield; ^{1}H NMR (400 MHz, $CDCl_3$) (δ, ppm) 7.37 (s, 1H), 7.35 (s, 1H), 6.85 (d, *J* = 7.6 Hz, 2H), 6.73 (d, *J* = 7.3 Hz, 2H), 6.66 (dd, *J* = 17.6, 7.4 Hz, 2H), 6.60 - 6.52 (comp, 4H), 4.24 (q, *J* = 7.1 Hz, 2H), 1.25 (t, *J* = 7.1 Hz, 3H), 0.00 (s, 9H); ^{13}C NMR (126 MHz, $CDCl_3$) (δ, ppm) 194.8, 156.6, 142.7, 142.0, 138.5, 137.4, 135.1, 132.0, 129.9, 129.6, 129.4, 128.5, 128.4, 128.3, 126.5, 116.7, 99.3, 69.2, 16.4, 0.0. HRMS (TOF MS ESI$^+$) calculated for $C_{26}H_{27}O_3Si$ $[M+H]^+$: 415.1724, found 415.1725. **(5'f)**: Red oil; 7.2mg, 9.5% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.10 (s, 1H), 6.73 (d, *J* = 7.5 Hz, 2H), 6.68 - 6.65 (comp, 4H), 6.60 (t, *J* = 7.4 Hz, 1H), 6.55 - 6.51 (m, 2H), 6.48 (t, *J* = 7.6 Hz, 2H), 4.35 (q, *J* = 7.1 Hz, 2H), 1.24 (t, *J* = 7.1 Hz, 3H), 0.00 (s, 9H).



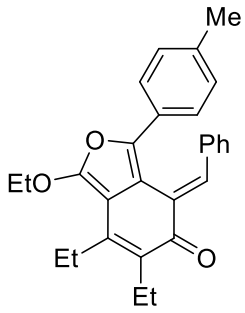
5g **5'g**

(*E*)-4-Benzylidene-6-(cyclohex-1-en-1-yl)-1-ethoxy-3-phenylisobenzofuran-5(4*H*)-one (5g) and (*E*)-4-benzylidene-7-(cyclohex-1-en-1-yl)-1-ethoxy-3-phenylisobenzofuran-5(*4H*)-one (5'g). (5g): Red oil; 58.2 mg, 69% yield; ^{1}H NMR

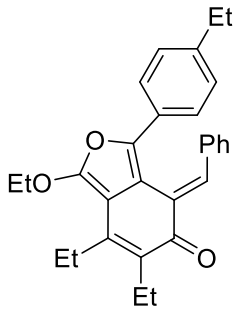
(500 MHz, $CDCl_3$) (δ, ppm) 7.65 (s, 1H), 7.18 (d, *J* = 7.5 Hz, 2H), 7.05 (d, *J* = 7.2 Hz, 2H), 6.97 - 6.91 (m, 2H), 6.88 - 6.81 (comp, 4H), 6.05 - 6.04 (m, 1H), 6.01 (s, 1H), 4.42 (q, *J* = 7.1 Hz, 2H), 2.33 - 2.31 (m, 2H), 2.23 - 2.20 (m, 2H), 1.80 - 1.76 (m, 2H), 1.72 - 1.67 (m, 2H), 1.44 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) (δ, ppm) 190.9, 155.3, 153.0, 141.4, 136.5, 136.2, 135.3, 130.9, 129.0, 128.9, 128.6, 127.8, 127.5, 127.4, 127.3, 125.4, 119.8, 115.6, 97.1, 68.1, 27.5, 25.7, 22.8, 22.1, 15.2. HRMS (TOF MS ESI$^+$) calculated for $C_{30}H_{26}O_3Na$ $[M+Na]^+$: 445.1774, found 445.1774. **(5'g)**: Red oil; 12.8 mg, 15% yield; ^1H NMR (400 MHz, $CDCl_3$) δ 7.62 (s, 1H), 7.31 (s, 1H), 7.13 (d, *J* = 7.4 Hz, 2H), 7.01 (d, *J* = 7.3 Hz, 2H), 6.96 - 6.90 (m, 2H), 6.87 - 6.79 (comp, 4H), 6.06 - 6.04 (m, 1H), 4.48 (q, *J* = 7.1 Hz, 2H), 2.33 - 2.31 (m, 2H), 2.23 - 2.18 (m, 2H), 1.77 - 1.72 (m, 2H), 1.69 - 1.63 (m, 2H), 1.50 (t, *J* = 7.1 Hz, 3H).



(*E*)-4-Benzylidene-1-ethoxy-6,7-diethyl-3-(*m*-tolyl)isobenzofuran-5(4*H*)-one (5h). Red oil; 73.4 mg, 89% yield; ^1H NMR (400 MHz, $CDCl_3$) (δ, ppm) 7.63 (s, 1H), 7.14 (d, *J* = 7.4 Hz, 2H), 7.00 (d, *J* = 7.8 Hz, 1H), 6.92 - 6.88 (m, 1H), 6.87 - 6.79 (comp, 3H), 6.76 (d, *J* = 7.5 Hz, 1H), 6.66 (s, 1H), 4.49 (q, *J* = 7.1 Hz, 2H), 2.75 (q, *J* = 7.5 Hz, 2H), 2.54 (q, *J* = 7.4 Hz, 2H), 1.96 (s, 3H), 1.50 (t, *J* = 7.1 Hz, 3H), 1.25 (t, *J* = 7.5 Hz, 3H), 1.11 (t, *J* = 7.4 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) (δ, ppm) 190.1, 154.4, 148.0, 141.0, 136.7, 136.5, 136.4, 132.6, 130.9, 128.5, 128.2, 128.0, 127.23, 127.15, 126.4, 122.3, 114.6, 97.2, 67.7, 23.2, 21.2, 19.3, 15.3, 14.6, 14.0. HRMS (TOF MS ESI$^+$) calculated for $C_{28}H_{28}O_3Na$ $[M+Na]^+$: 435.1931, found 435.1932.

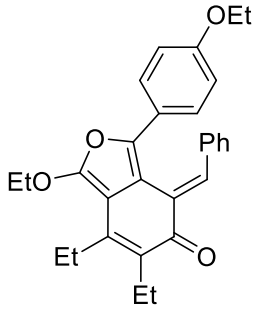


(*E*)-4-Benzylidene-1-ethoxy-6,7-diethyl-3-(p-tolyl)isobenzofuran-5(4*H*)-one (5i). Red oil; 71.8 mg, 87.2% yield; ^{1}H NMR (400 MHz, $CDCl_3$) (δ, ppm) 7.62 (s, 1H), 7.13 - 7.11 (m, 2H), 6.92 - 6.87 (comp, 3H), 6.81 (dd, *J* = 10.2, 4.6 Hz, 2H), 6.66 (d, *J* = 7.9 Hz, 2H), 4.48 (q, *J* = 7.1 Hz, 2H), 2.75 (q, *J* = 7.5 Hz, 2H), 2.54 (q, *J* = 7.4 Hz, 2H), 2.18 (s, 3H), 1.50 (t, *J* = 7.1 Hz, 3H), 1.25 (t, *J* = 7.5 Hz, 3H), 1.11 (t, *J* = 7.4 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) (δ, ppm) 190.1, 154.4, 148.0, 141.2, 137.4, 136.5, 136.1, 132.7, 128.9, 128.3, 128.2, 127.9, 127.3, 125.3, 114.3, 97.3, 67.7, 23.2, 21.3, 19.3, 15.3, 14.6, 14.0. HRMS (TOF MS ESI$^+$) calculated for $C_{28}H_{28}O_3Na$ $[M+Na]^+$: 435.1931, found 435.1934.

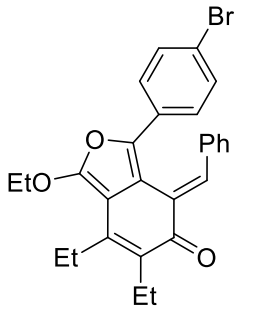


(*E*)-4-Benzylidene-1-ethoxy-6,7-diethyl-3-(4-ethylphenyl)isobenzofuran-5(4*H*)-one (5j). Red oil; 75.0 mg, 88% yield; ^{1}H NMR (400 MHz, $CDCl_3$) (δ, ppm) 7.63 (s, 1H), 7.11 (d, *J* = 7.5 Hz, 2H), 6.93 - 6.87 (comp, 3H), 6.81 - 6.77 (m, 2H), 6.67 (d, *J* = 7.6 Hz, 2H), 4.51 - 4.45 (m, 2H), 2.75 (q, *J* = 7.2 Hz, 2H), 2.54 (q, *J* = 7.2 Hz, 2H), 2.45 (q, *J* = 7.5 Hz, 2H), 1.50 (td, *J* = 7.0, 0.8 Hz, 3H), 1.25 (t, *J* = 7.1 Hz, 3H), 1.11 (t, *J* = 7.4 Hz, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) (δ, ppm) 190.0, 154.4, 148.0, 144.1, 141.2, 136.5, 136.1, 132.6, 128.9, 128.6, 128.2, 127.2, 126.8, 125.4, 114.2, 97.2, 67.7,

28.8, 23.2, 19.3, 16.2, 15.3, 14.6, 14.0. HRMS (TOF MS ESI$^+$) calculated for $C_{29}H_{30}O_3Na$ [M+Na]$^+$: 449.2087, found 449.2088.



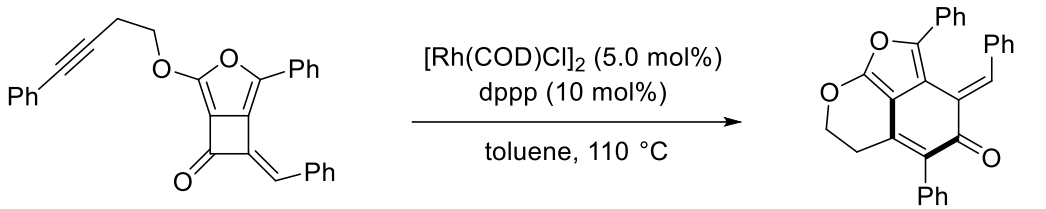
(*E*)-4-Benzylidene-1-ethoxy-3-(4-ethoxyphenyl)-6,7-diethylisobenzofuran-5(4*H*)-one (5k). Red oil; 74.3 mg, 84% yield; ^{1}H NMR (400 MHz, $CDCl_3$) (δ, ppm) 7.63 (s, 1H), 7.12 (d, *J* = 7.6 Hz, 2H), 6.92 - 6.96 (comp, 3H), 6.84 - 6.81 (m, 2H), 6.38 (d, *J* = 8.7 Hz, 2H), 4.48 (q, *J* = 7.1 Hz, 2H), 3.88 (q, *J* = 7.0 Hz, 2H), 2.75 (q, *J* = 7.5 Hz, 2H), 2.54 (q, *J* = 7.4 Hz, 2H), 1.49 (t, *J* = 7.1 Hz, 3H), 1.35 (t, *J* = 7.0 Hz, 3H), 1.29 - 1.25 (m, 3H), 1.11 (t, *J* = 7.4 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) (δ, ppm) 190.1, 158.6, 154.2, 148.0, 141.1, 136.4, 135.5, 132.6, 129.0, 128.3, 127.2, 126.9, 123.9, 113.4, 97.2, 67.8, 63.6, 23.2, 19.4, 15.3, 14.8, 14.6, 14.1. HRMS (TOF MS ESI$^+$) calculated for $C_{29}H_{30}O_4Na$ [M+Na]$^+$: 465.2036, found 465.2037.



(*E*)-4-Benzylidene-3-(4-bromophenyl)-1-ethoxy-6,7-diethylisobenzofuran-5(4*H*)-one (5l). Red oil; 76.2 mg, 80% yield; ^{1}H NMR (400 MHz, $CDCl_3$) (δ, ppm) 7.64 (s, 1H), 7.13 (d, *J* = 7.5 Hz, 2H), 7.00 - 6.95 (comp, 3H), 6.89 - 6.85 (comp, 4H), 4.49 (q, *J* = 7.1 Hz, 2H), 2.74 (q, *J* = 7.5 Hz, 2H), 2.53 (q, *J* = 7.4 Hz, 2H), 1.50 (t, *J* = 7.1 Hz, 3H), 1.24 (t, *J* = 7.5 Hz, 3H), 1.10 (t, *J* = 7.4 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) (δ,

ppm) 189.7, 154.6, 147.9, 139.6, 137.0, 136.4, 132.9, 130.4, 129.8, 128.9, 128.7, 128.2, 127.7, 126.7, 120.9, 115.59, 97.4, 67.8, 23.2, 19.3, 15.3, 14.6, 14.0. HRMS (TOF MS ESI$^+$) calculated for $C_{27}H_{25}BrO_3Na$ $[M+Na]^+$: 499.0879, found 499.0884.

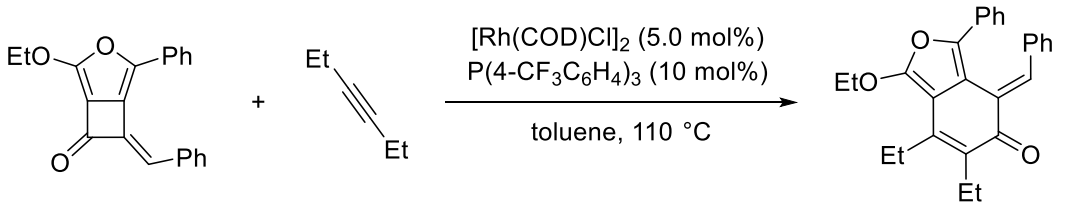
General Procedure for Scale Up and Synthetic Applications



2a, 2.5 mmol, 1.04 g

3a, 0.75 g, 72% yield

To a 25-mL oven-dried vial containing a magnetic stirring bar, $[Rh(cod)Cl]_2$ (61.6 mg, 5.0 mol%), 1,3-bis(diphenylphosphino)propane (dppp, 103.1 mg, 10 mol%), toluene (6 mL), and compounds **2a** (1.04 g, 2.5 mmol) were added in sequence under an argon atmosphere, and the reaction mixture was stirred for 4 h at 110 °C. Until consumption of the material (monitored by TLC), the reaction mixture was purified by column chromatography on silica gel after evaporation of the solvent under vacuo (hexane : EtOAc = 30:1 to 15:1) to give 0.75 g of pure product **3a** in 72% yield.

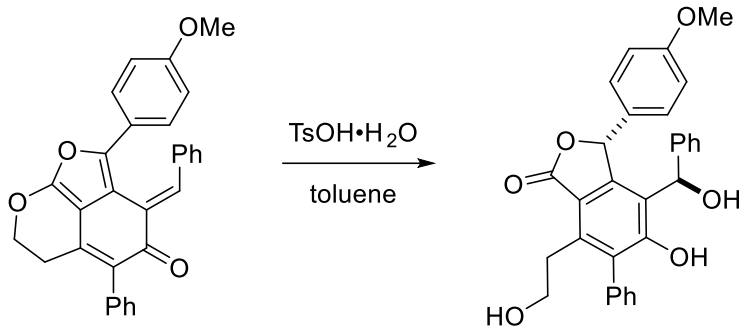


2s
3.2 mmol, 1.01 g

4b
4.8 mmol, 393.6 mg

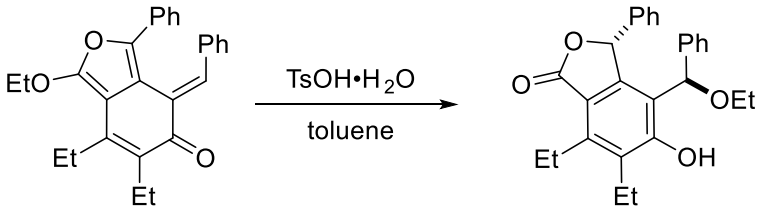
5b, 1.04 g, 82.0% yield

To a 25-mL oven-dried vial containing a magnetic stirring bar, $[Rh(cod)Cl]_2$ (78.9 mg, 5.0 mol%), tris(4-(trifluoromethyl)phenyl)phosphane (132.0 mg, 10 mol%), toluene (8 mL), compound **4b** (393.6 mg, 4.8 mmol), and compound **2s** (1.01 g, 3.2 mmol) were added in sequence under an argon atmosphere, and the reaction mixture was stirred for 2 h at 110 °C. Until consumption of the material (monitored by TLC), the reaction mixture was purified by column chromatography on silica gel after evaporation of the solvent under vacuo (hexane : EtOAc = 50:1 to 20:1) to give 1.04 g pure product **5b** in 82% yield.



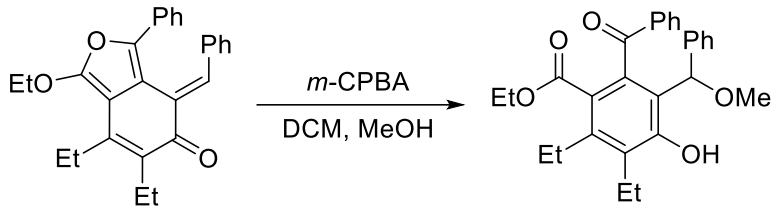
3l **6**, 82% yield, >20:1 *dr*

***Synthesis of 6*:** To a 10-mL oven-dried vial containing a magnetic stirring bar, *p*-toluene sulfonic acid ($TsOH \cdot H_2O$, 26.9 mg, 0.3 mmol, 1.5 equiv.) in toluene (1.5 mL), was added a solution of compound **3l** (93.2 mg, 0.2 mmol, 1.0 equiv.) in toluene (2.0 mL) slowly *via* a syringe at 40 °C. The reaction mixture was stirred for additional 1.0 h under these conditions. Until consumption of the material (monitored by TLC), the reaction mixture was quenched with saturated aqueous $NaHCO_3$ (10 mL), and extracted with EtOAc (2 × 10 mL). The combined organic phase was dried over anhydrous Na_2SO_4 and the solvent was evaporated under vacuum after filtration. The residues were purified by column chromatography on aluminum oxide (eluent: dichloromethane / methanol = 200:1 - 100:1) to give 79.1 mg pure product **6** in 82% yield with > 20:1 *dr*; Yellow oil, ^{1}H NMR (500 MHz, DMSO-d_6) (δ, ppm) 7.46 (t, *J* = 7.0 Hz, 2H), 7.41 - 7.38 (m, 1H), 7.32 - 7.26 (comp, 6H), 7.25 - 7.22 (m, 1H), 7.07 (d, *J* = 8.6 Hz, 2H), 6.77 (d, *J* = 8.6 Hz, 2H), 6.56 (s, 1H), 6.30 (s, 1H), 4.31 - 4.29 (m, 1H), 4.17 - 4.12 (m, 1H), 3.69 (s, 3H), 2.94 - 2.87 (m, 1H), 2.37 (d, *J* = 17.1 Hz, 1H); ^{13}C NMR (126 MHz, DMSO-d_6) (δ, ppm) 162.6, 158.4, 153.4, 145.7, 142.2, 141.0, 134.5, 134.0, 130.5, 129.3, 129.3, 128.6, 128.99, 127.95, 127.8, 127.7, 127.6, 113.1, 112.1, 9.12, 83.3, 66.4, 55.0, 27.0. HRMS (TOF MS ESI$^+$) calculated for $C_{30}H_{27}O_6$ $[M+H]^+$: 483.1802, found 483.1803.



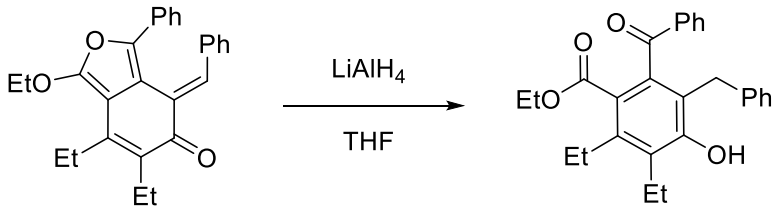
5b **7**, 86% yield, >20:1 *dr*

***Synthesis of 7*:** To a 10-mL oven-dried vial containing a magnetic stirring bar, *p*-toluene sulfonic acid ($TsOH \cdot H_2O$, 26.9 mg, 0.3 mmol, 1.5 equiv.), in toluene (1.5 mL), was added a solution of compound **5b** (79.6 mg, 0.2 mmol, 1.0 equiv.) in toluene (1.0 mL) slowly *via* a syringe at 40 °C. The reaction mixture was stirred for additional 1.0 h under these conditions. Until consumption of the material (monitored by TLC), the reaction mixture was quenched with saturated aqueous $NaHCO_3$ (10 mL), and extracted with EtOAc (2 × 10 mL). The combined organic phase was dried over anhydrous Na_2SO_4 and the solvent was evaporated under vacuum after filtration. The residues were purified by column chromatography on silica gel (eluent: petroleum ethers / ethyl acetate = 100:1 - 50:1) to give 71.9 mg the pure product **7** in 86% yield with > 20:1 *dr* ; Brown solid; ^{1}H NMR (400 MHz, $CDCl_3$) (δ, ppm) 9.48 (s, 1H), 7.42 - 7.39 (comp, 3H), 7.36 - 7.32 (comp, 3H), 7.26 - 7.23 (m, 2H), 7.21 - 7.19 (m, 2H), 5.83 (s, 1H), 5.14 (s, 1H), 3.23 - 3.15 (m, 3H), 3.00 - 2.92 (m, 1H), 2.78 (q, *J* = 7.4 Hz, 2H), 1.28 (t, *J* = 7.5 Hz, 3H), 1.21 (t, *J* = 7.4 Hz, 3H), 0.98 (t, *J* = 7.0 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) (δ, ppm) 170.2, 159.9, 147.1, 144.8, 138.6, 136.2, 133.3, 130.0, 129.2, 129.0, 128.9, 128.6, 127.4, 116.2, 114.7, 80.4, 79.8, 65.4, 20.6, 19.0, 15.7, 14.7, 14.4. HRMS (TOF MS ESI$^+$) calculated for $C_{27}H_{29}O_4$ $[M+H]^+$: 417.2061, found 417.2063.



5b **8**, 74% yield

***Synthesis of 8*:** To a 10-mL oven-dried vial containing a magnetic stirring bar, 3-chloroperbenzoic acid (*m*-CPBA, 46.9 mg, 0.3 mmol, 1.5 equiv.) in DCM (1.5 mL), was added a solution of compound **5b** (79.6 mg, 0.2 mmol, 1.0 equiv.) and MeOH (19.2 mg, 0.6 mmol, 3.0 equiv.) in DCM (1.0 mL) slowly *via* a syringe at room temperature. The reaction mixture was stirred for additional 0.5 h under these conditions. Until consumption of the material (monitored by TLC), the reaction mixture was quenched with saturated aqueous $NaHCO_3$ (10 mL), and extracted with EtOAc (2 × 10 mL). The combined organic phase was dried over anhydrous Na_2SO_4 and the solvent was evaporated under vacuum after filtration. The residues were purified by column chromatography on silica gel (eluent: petroleum ethers / ethyl acetate = 80:1 - 40:1) to give 66.0 mg pure product **8** in 74% yield; Yellow oil; ^{1}H NMR (500 MHz, $CDCl_3$) (δ, ppm) 8.88 (s, 1H), 7.69 (d, *J* = 4.9 Hz, 2H), 7.48 (t, *J* = 7.2 Hz, 1H), 7.32 (t, *J* = 7.4 Hz, 2H), 7.18 (s, 5H), 5.37 (s, 1H), 3.81 (q, *J* = 7.1 Hz, 2H), 3.34 (s, 3H), 2.91 - 2.84 (m, 1H), 2.83 - 2.75 (m, 3H), 1.24 (t, *J* = 7.4 Hz, 3H), 1.19 (t, *J* = 7.4 Hz, 3H), 0.95 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) (δ, ppm) 197.3, 168.2, 156.2, 143.2, 138.8, 138.4, 137.5, 133.5, 132.8, 129.6, 128.4, 128.4, 128.2, 127.3, 123.0, 119.1, 83.1, 61.2, 57.6, 23.5, 19.4, 16.0, 14.2, 13.4. HRMS (TOF MS ESI$^+$) calculated for $C_{28}H_{31}O_5$ $[M+H]^+$: 447.2166, found 447.2158.



5b **9**, 73% yield

***Synthesis of 9*:** To a 10-mL oven-dried vial containing a magnetic stirring bar, lithium aluminum hydride ($LiAlH_4$, 8.3 mg, 0.22 mmol, 1.1 equiv.) in THF (1.5 mL) was added a solution of compound **5b** (79.6 mg, 0.2 mmol, 1.0 equiv.) in THF (1.0 mL) slowly *via* a syringe at room temperature. The reaction mixture was stirred for additional 0.5 h under these conditions. Until consumption of the material (monitored by TLC), the reaction mixture was quenched with saturated aqueous NH_4Cl (10 mL), and extracted with EtOAc (2 × 10 mL). The combined organic phase was dried over anhydrous Na_2SO_4 and the solvent was evaporated under vacuum after filtration. The residues were purified by column chromatography on silica gel (eluent: petroleum ethers / ethyl acetate = 80:1 - 40:1) to give 60.76 mg pure product **9** in 73% yield, Colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) (δ, ppm) 7.78 (d, *J* = 7.4 Hz, 2H), 7.51 (t, *J* = 7.4 Hz, 1H), 7.38 (t, *J* = 7.7 Hz, 2H), 7.23 - 7.19 (m, 2H), 7.17 - 7.13 (comp, 3H), 5.08 (s, 1H), 3.87 (q, *J* = 7.1 Hz, 2H), 3.82 (s, 2H), 2.82 (q, *J* = 7.4 Hz, 2H), 2.71 (q, *J* = 7.5 Hz, 2H), 1.23 (d, *J* = 7.5 Hz, 3H), 1.16 (t, *J* = 7.5 Hz, 3H), 0.96 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) (δ, ppm) 197.8, 168.3, 154.6, 142.0, 139.3, 138.1, 137.7, 133.44, 131.1, 129.7, 129.0, 128.6, 128.5, 127.0, 124.0, 121.4, 61.2, 33.8, 23.6, 19.6, 16.2, 14.2, 13.5. HRMS (TOF MS ESI$^+$) calculated for $C_{27}H_{28}O_4Na$ $[M+Na]^+$: 439.1880, found 439.1878.

1D-NOE NMR Analysis of 5f

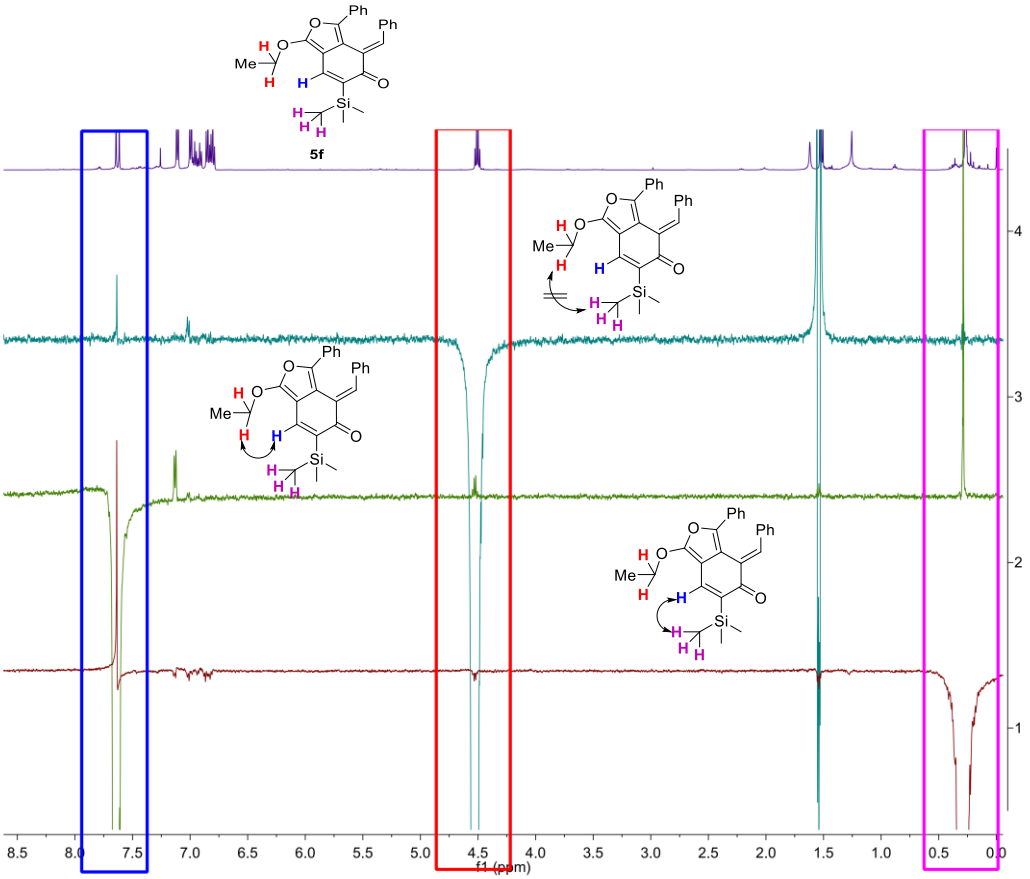
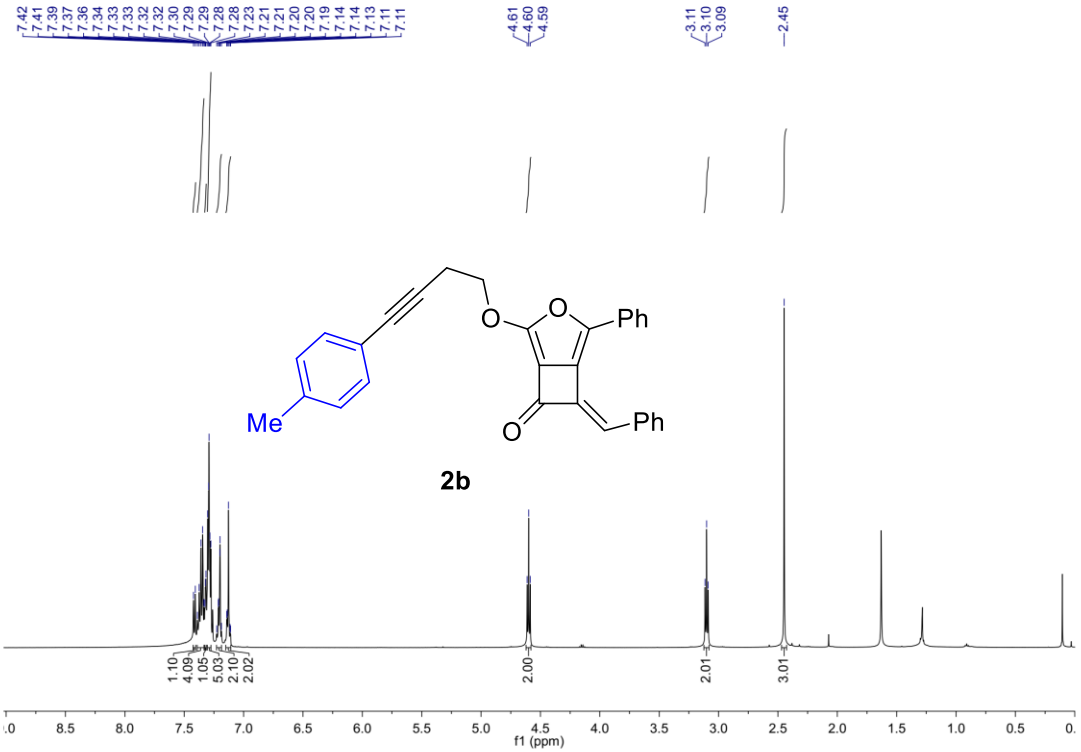


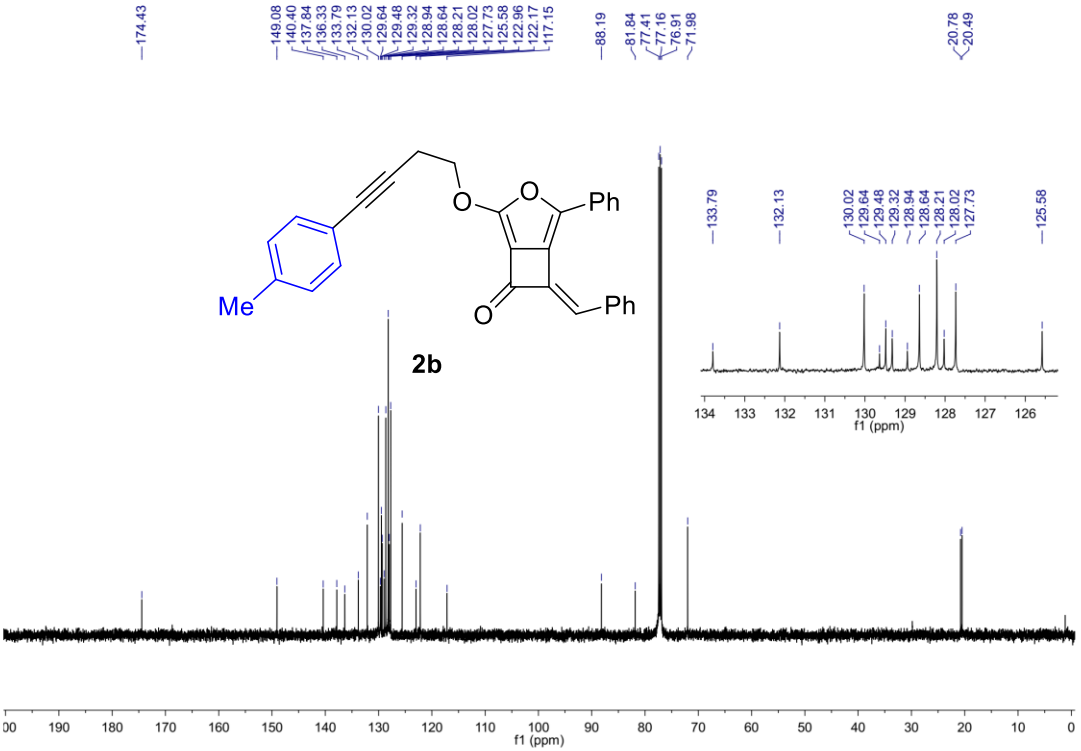
Figure S1. NOE NMR Spectra of **5f**.

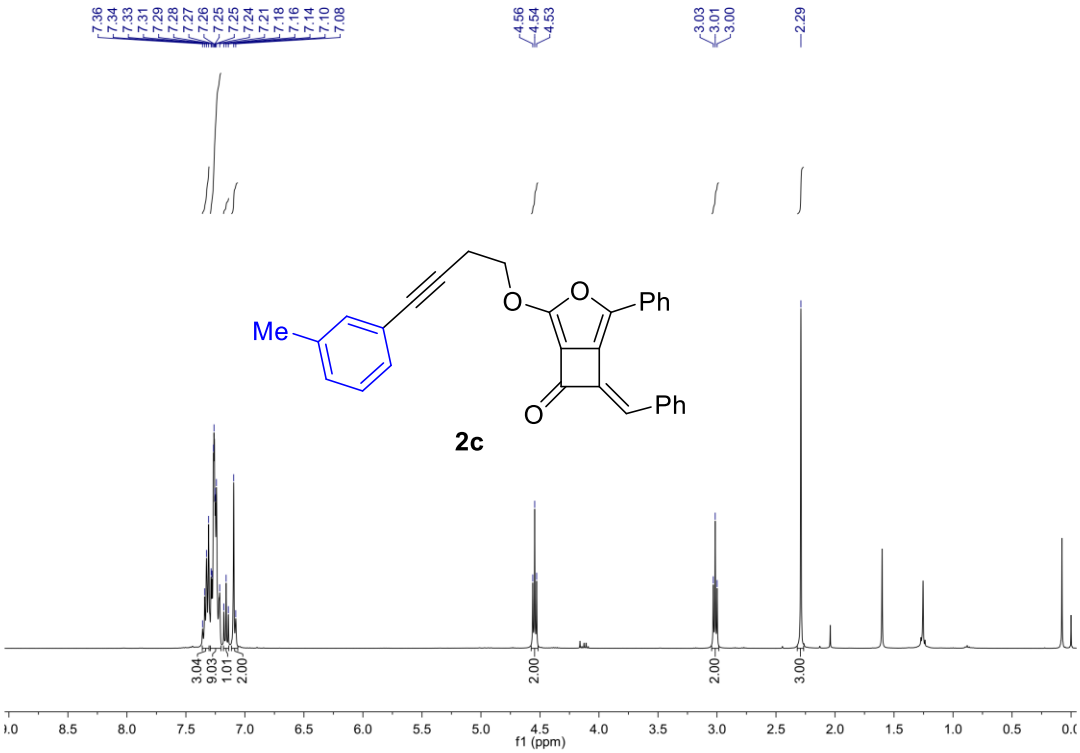
References

1. (a) T. Toma, J. Shimokawa and T. Fukuyama, *Org. Lett.*, 2007, **9**, 3195–3197; (b) R. D. Kardile, T.-H. Chao, M.-J. Cheng and R.-S. Liu, *Angew. Chem. Int. Ed.*, 2020, **59**, 10396–10400; (c) K. Hong, Y. Zhou, H. Yuan, Z. Zhang, J. Huang, S. Dong, W. Hu, Z.-X. Yu and X. Xu, *Nat. Commun.*, 2023, **14**, 6378.

NMR Spectra of New Compounds 2 - 3, and 5 - 9



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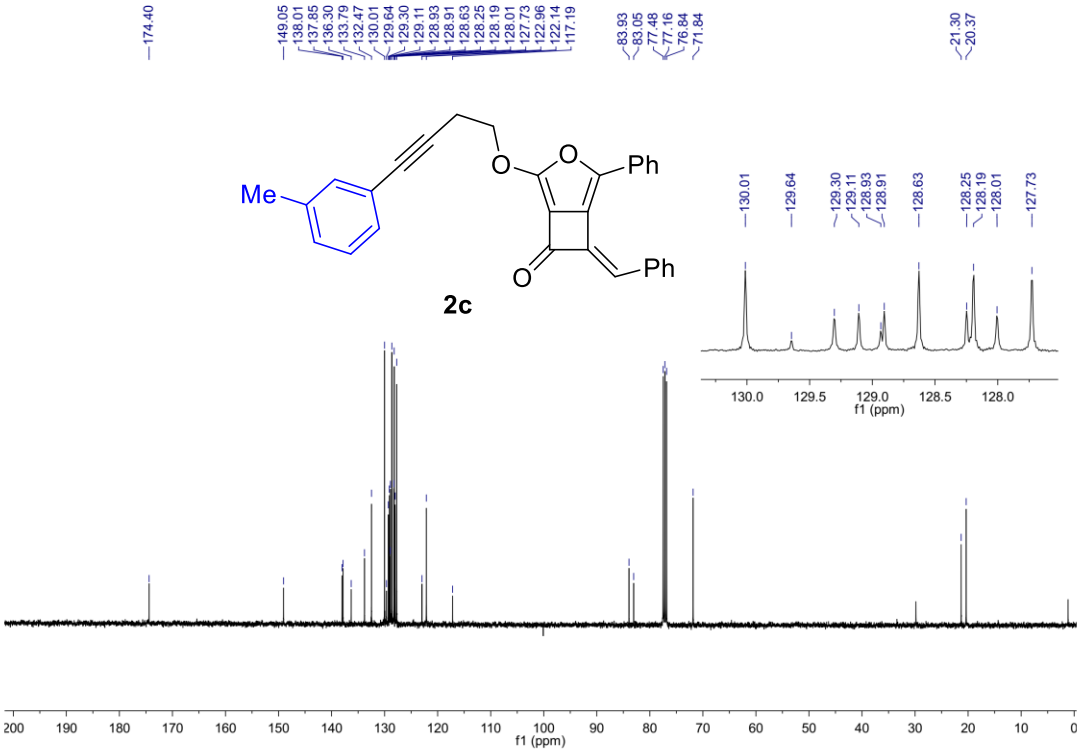
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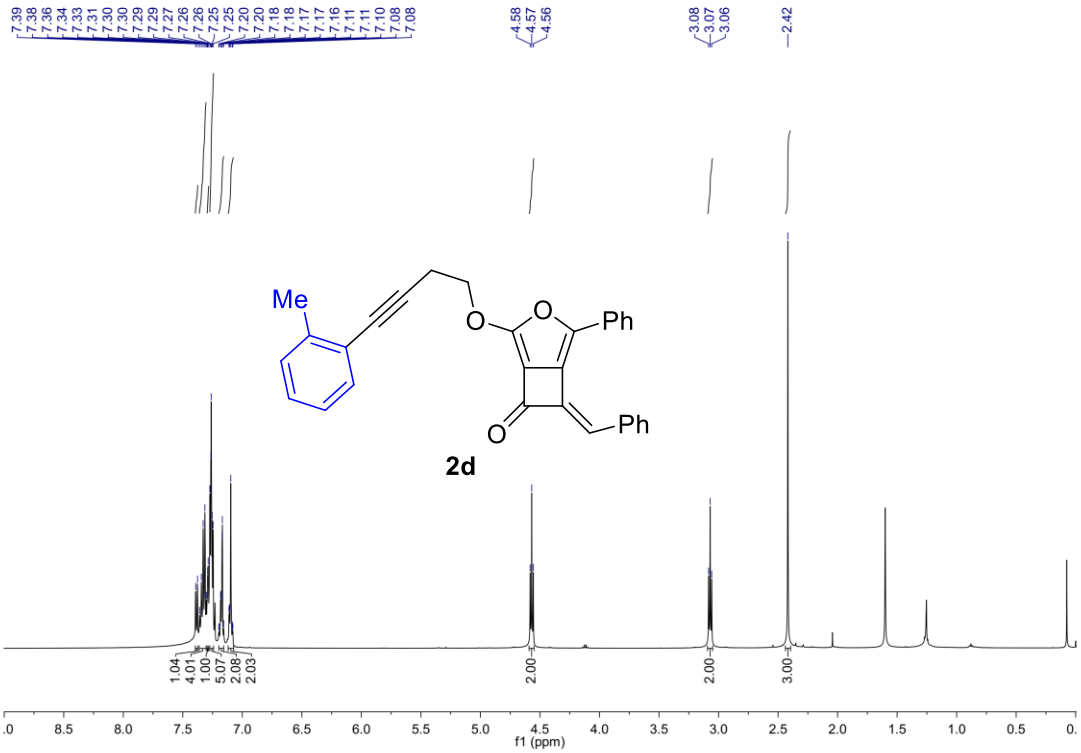
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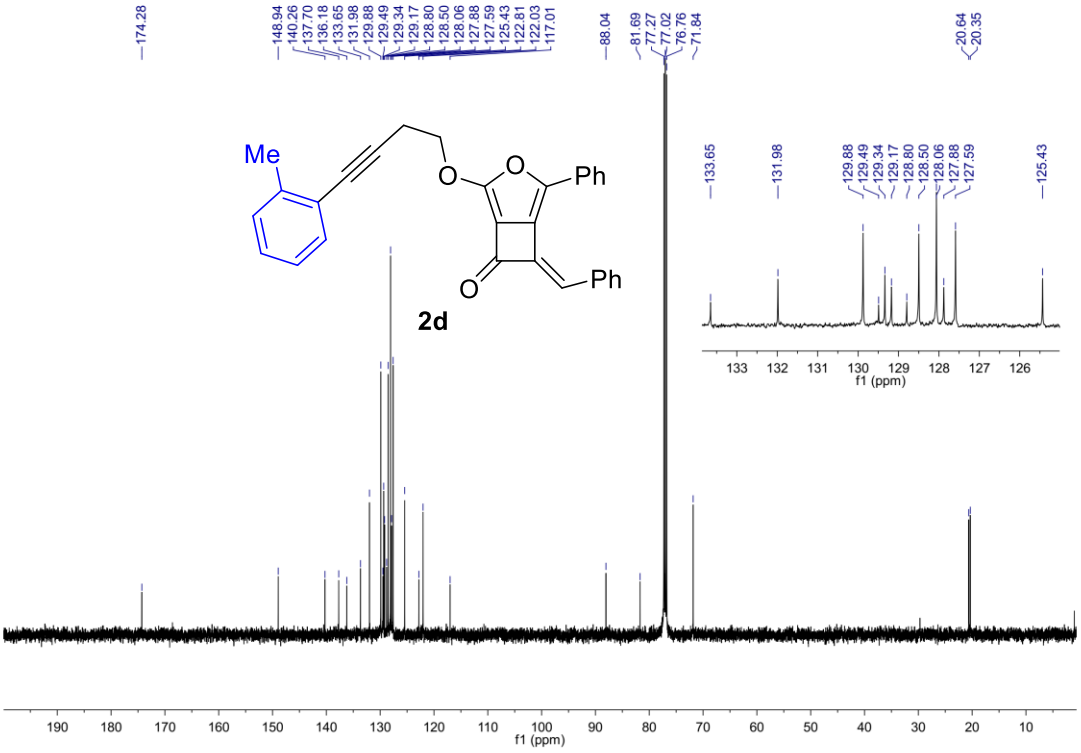
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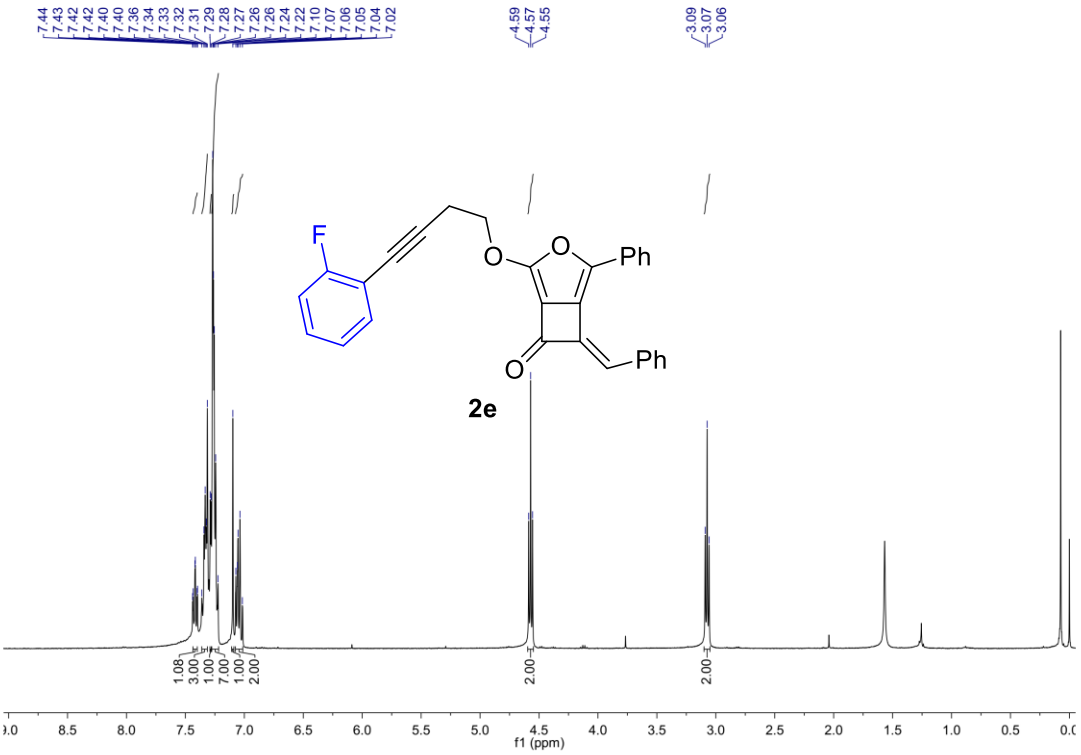
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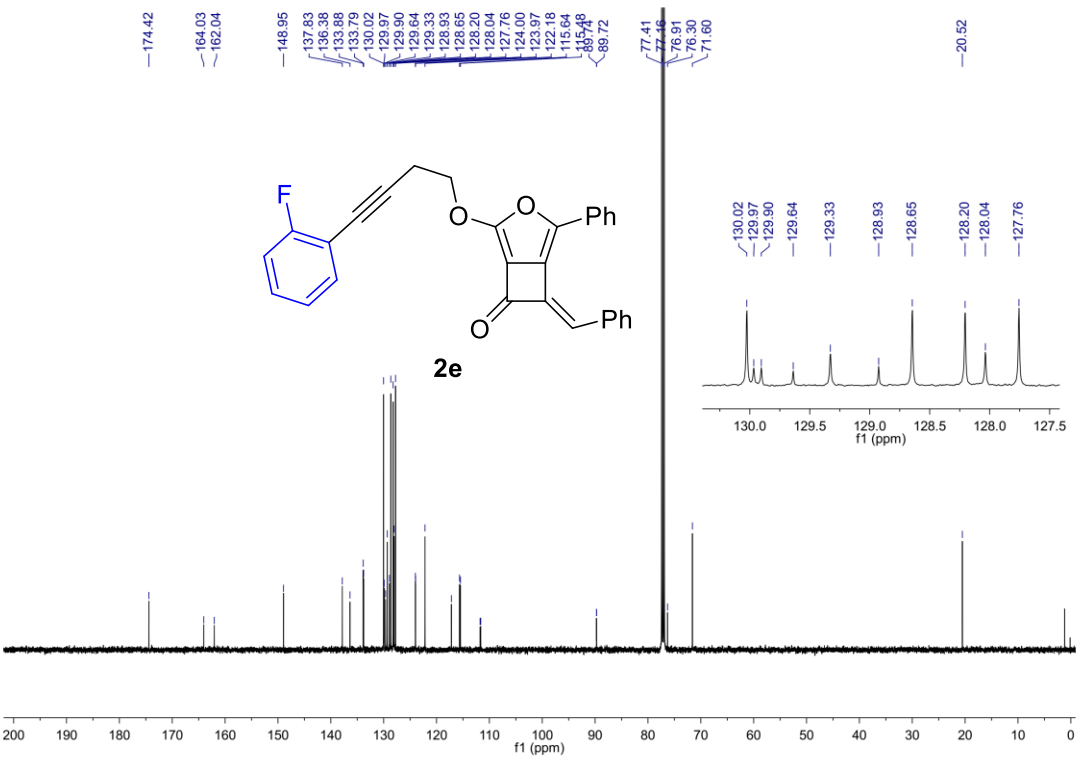
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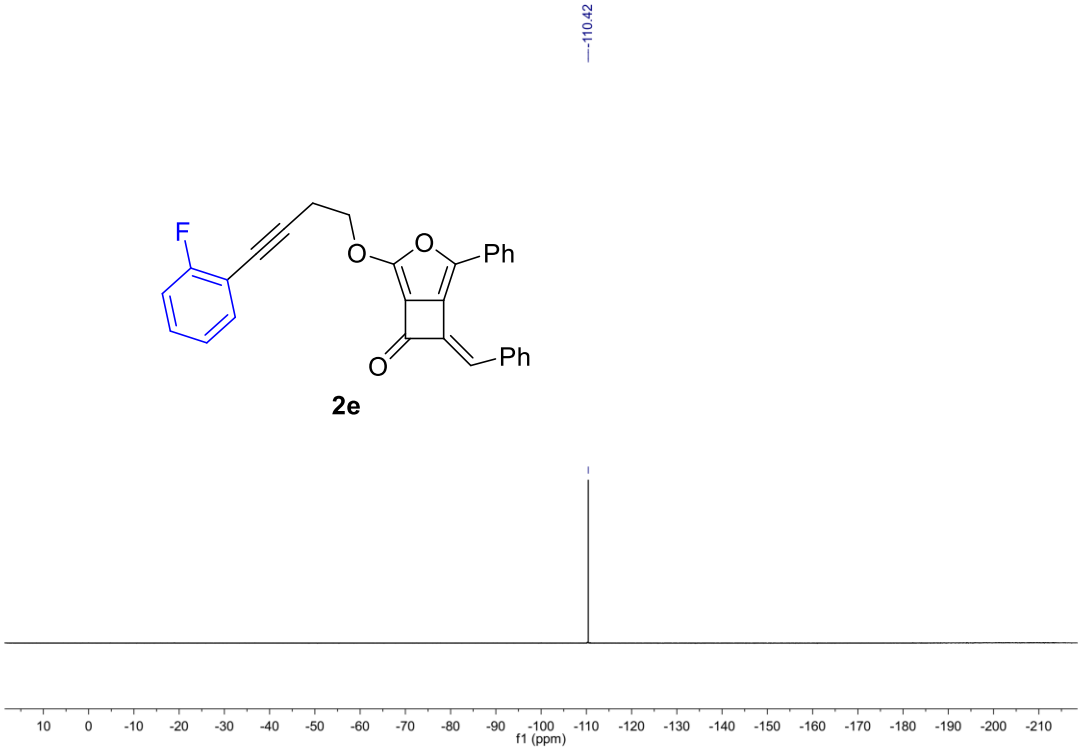
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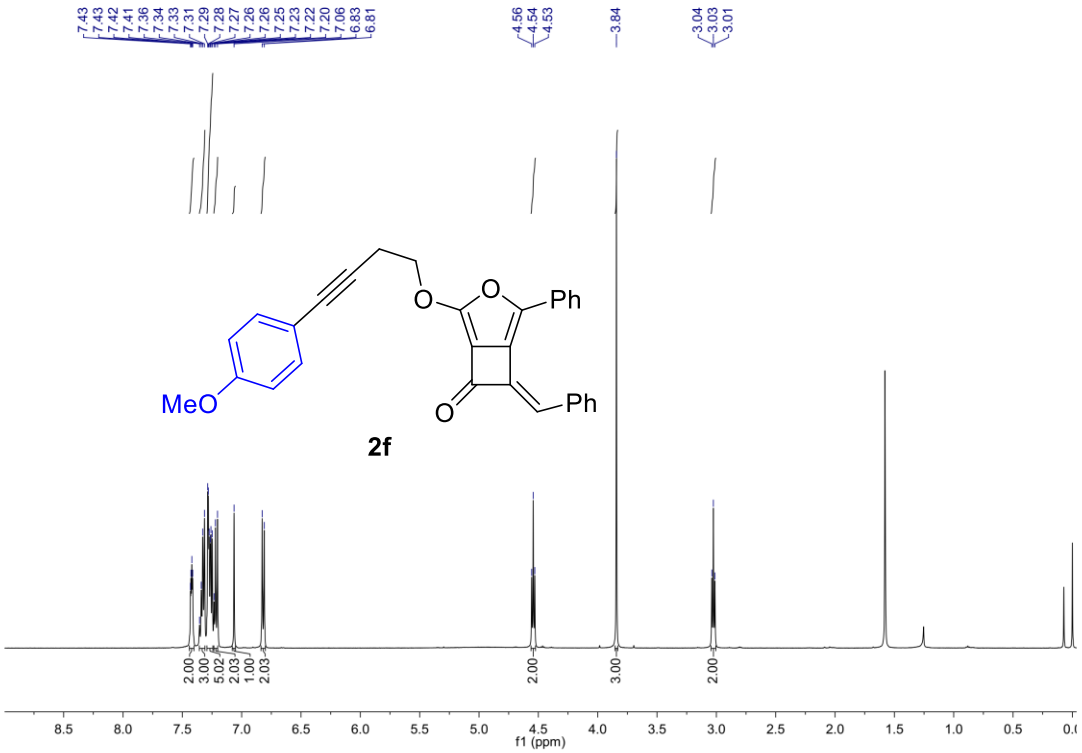
f1 (ppm)

2e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1.00
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3.00
2.00
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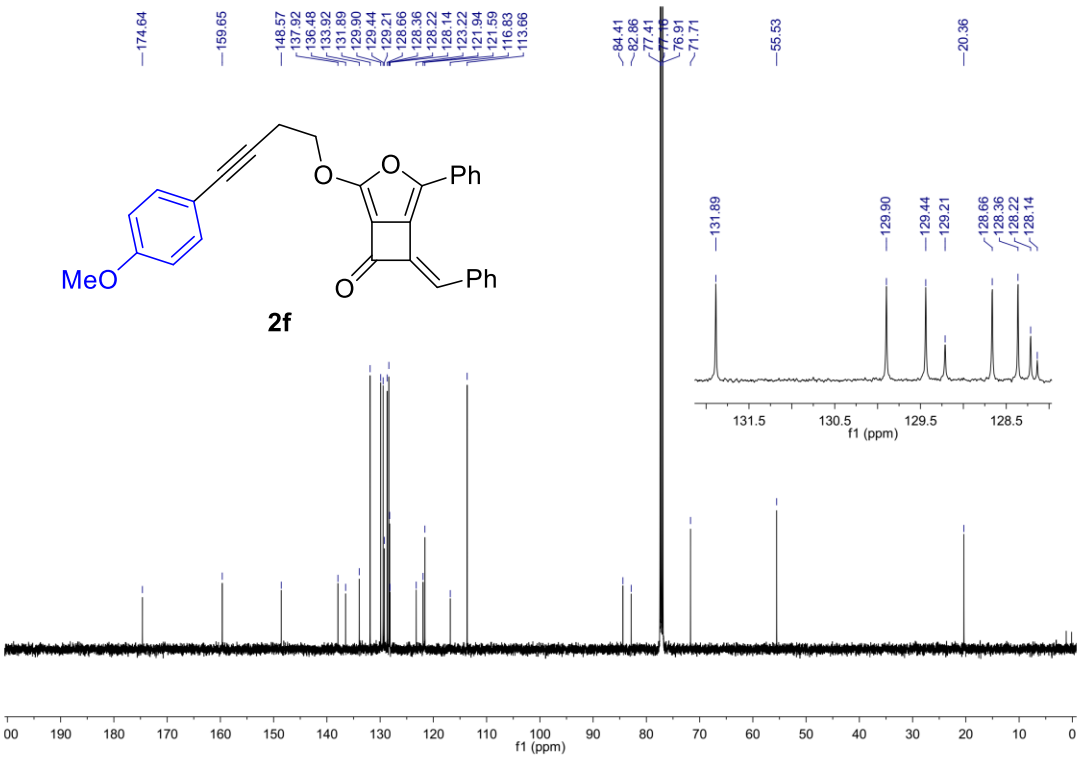
f1 (ppm)

2f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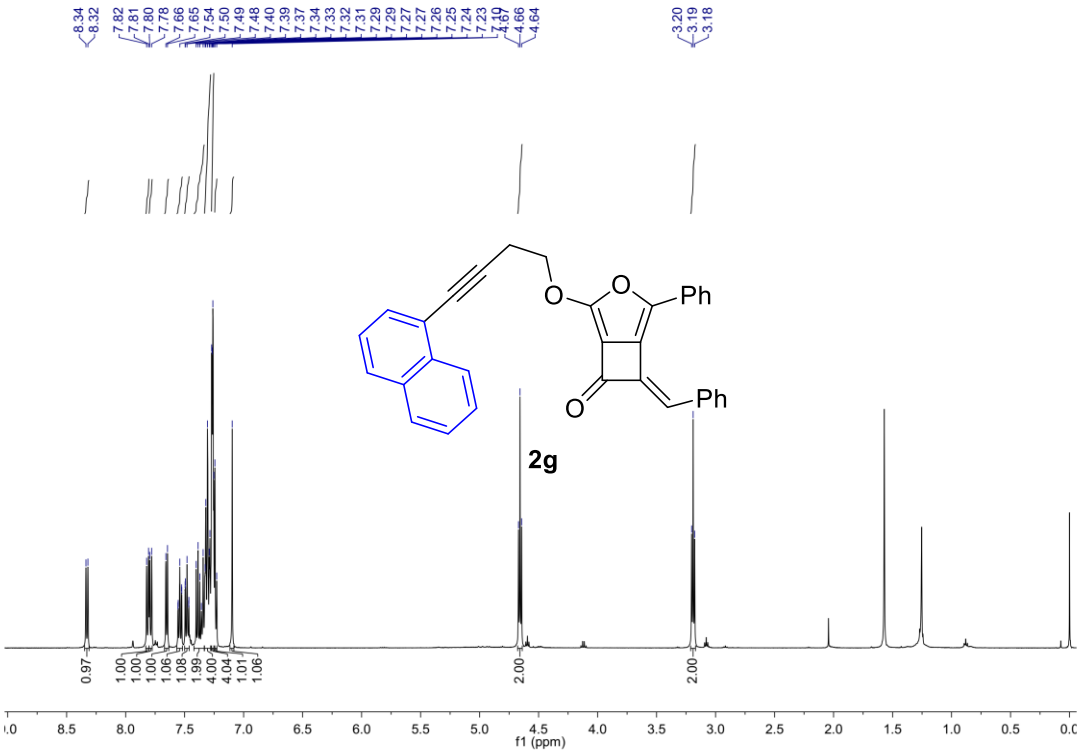
f1 (ppm)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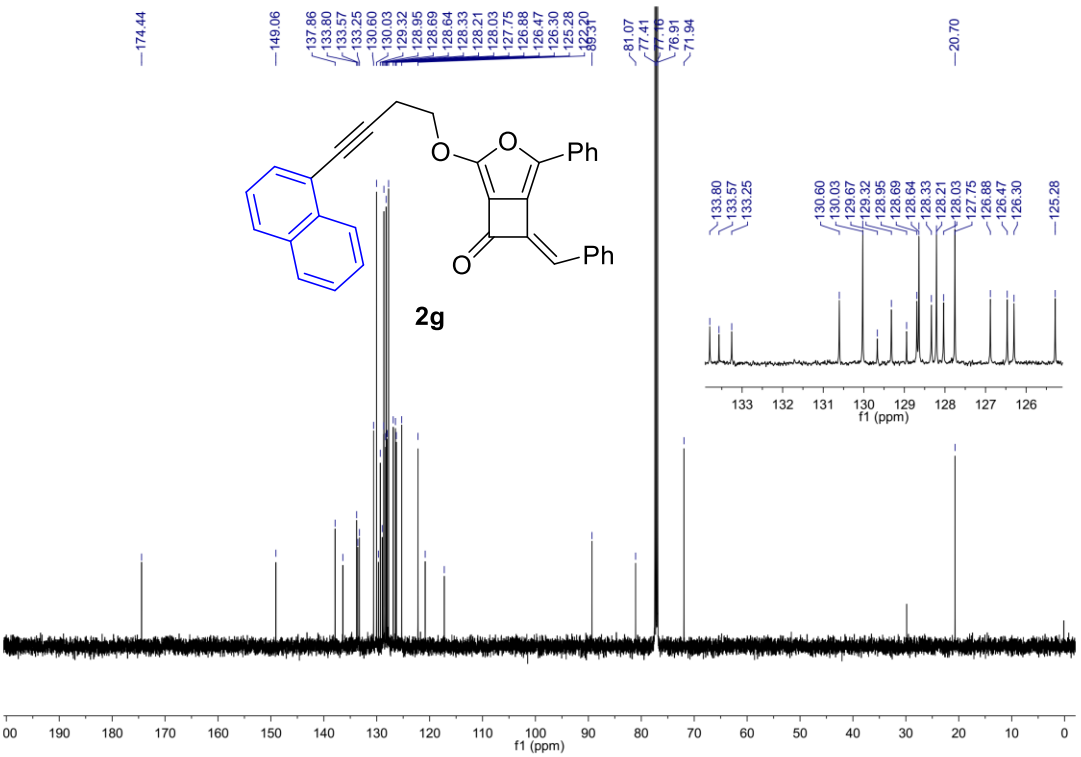
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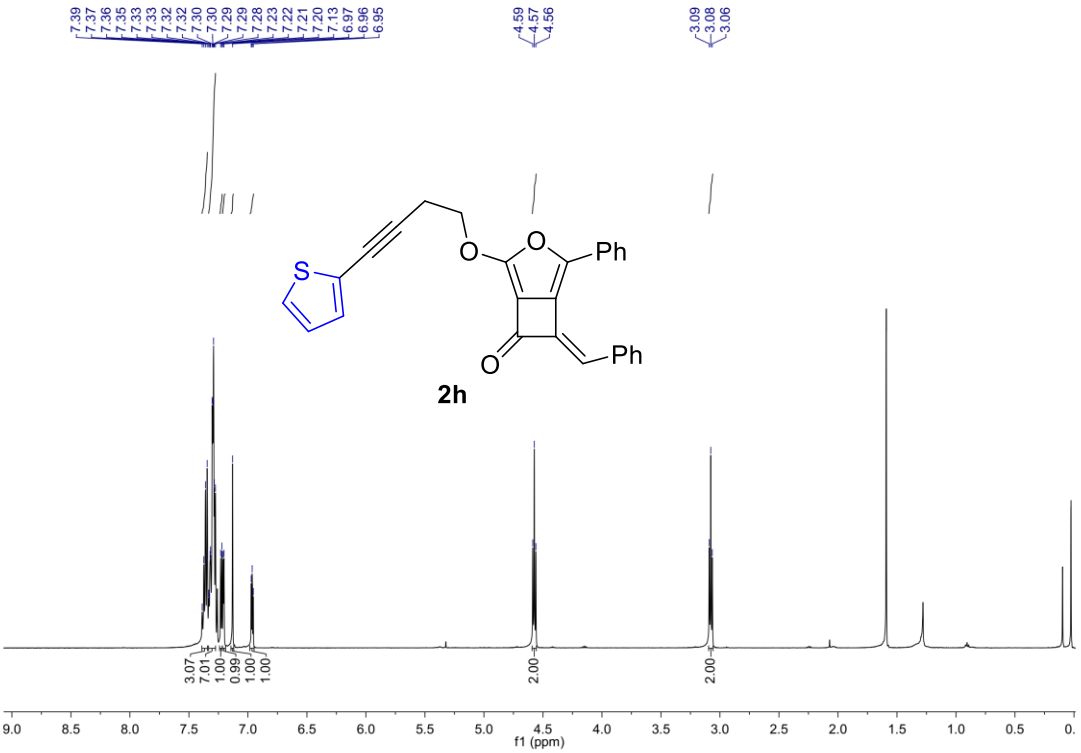
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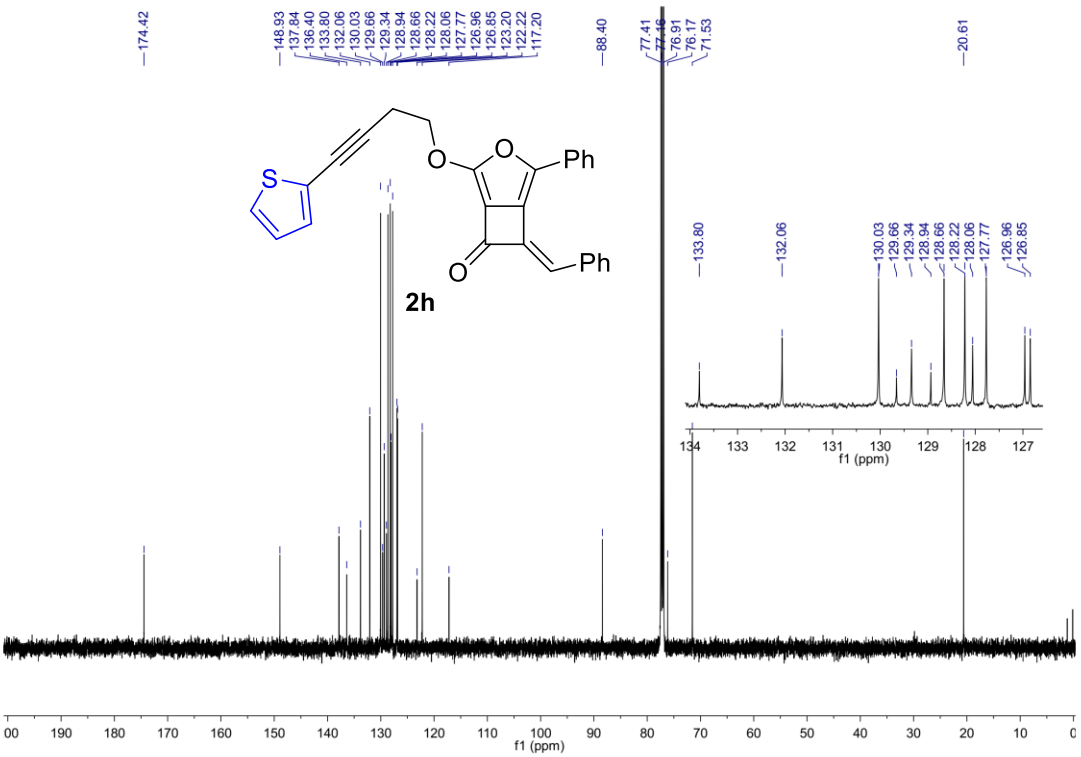
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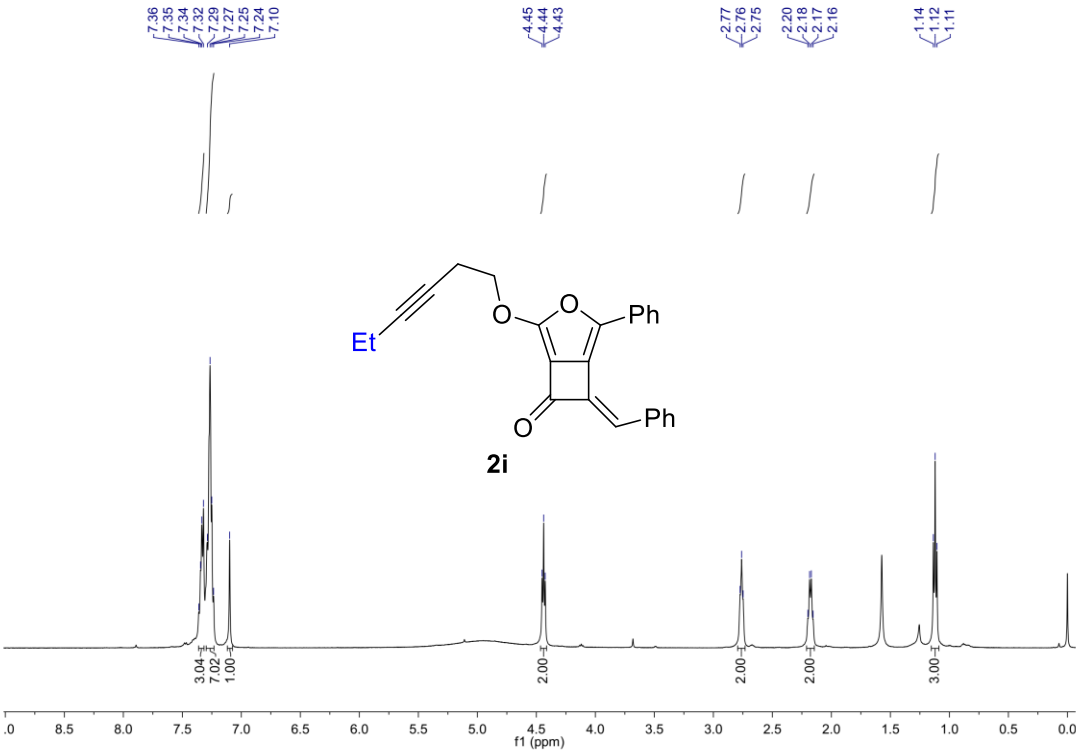
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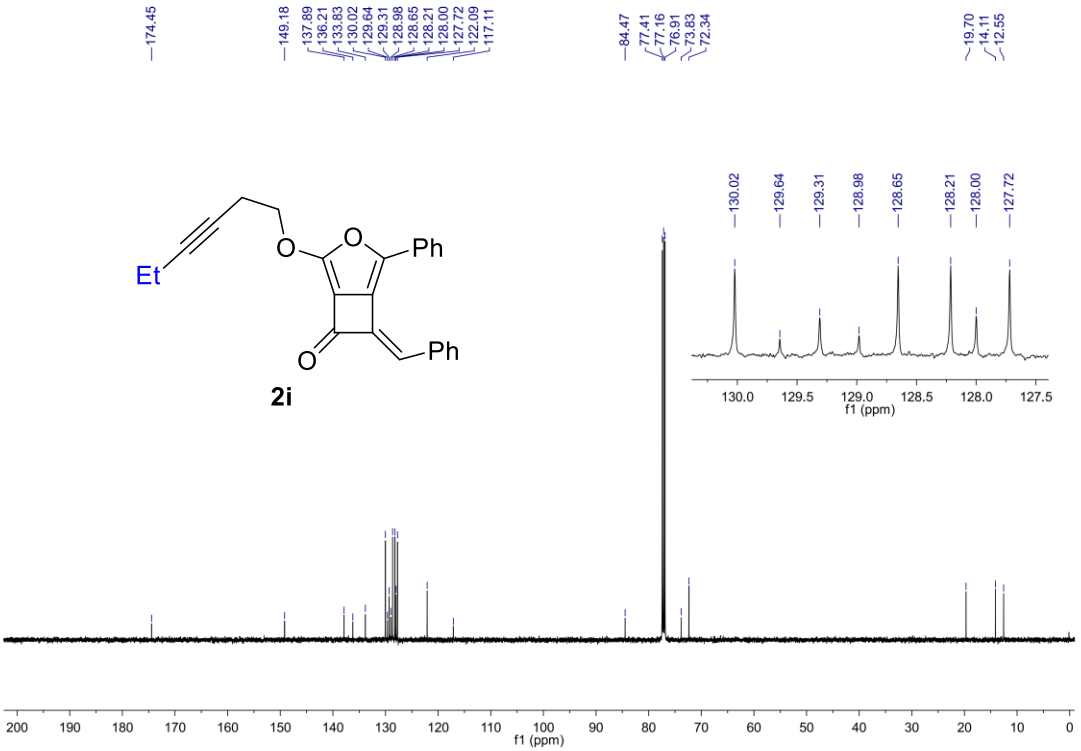
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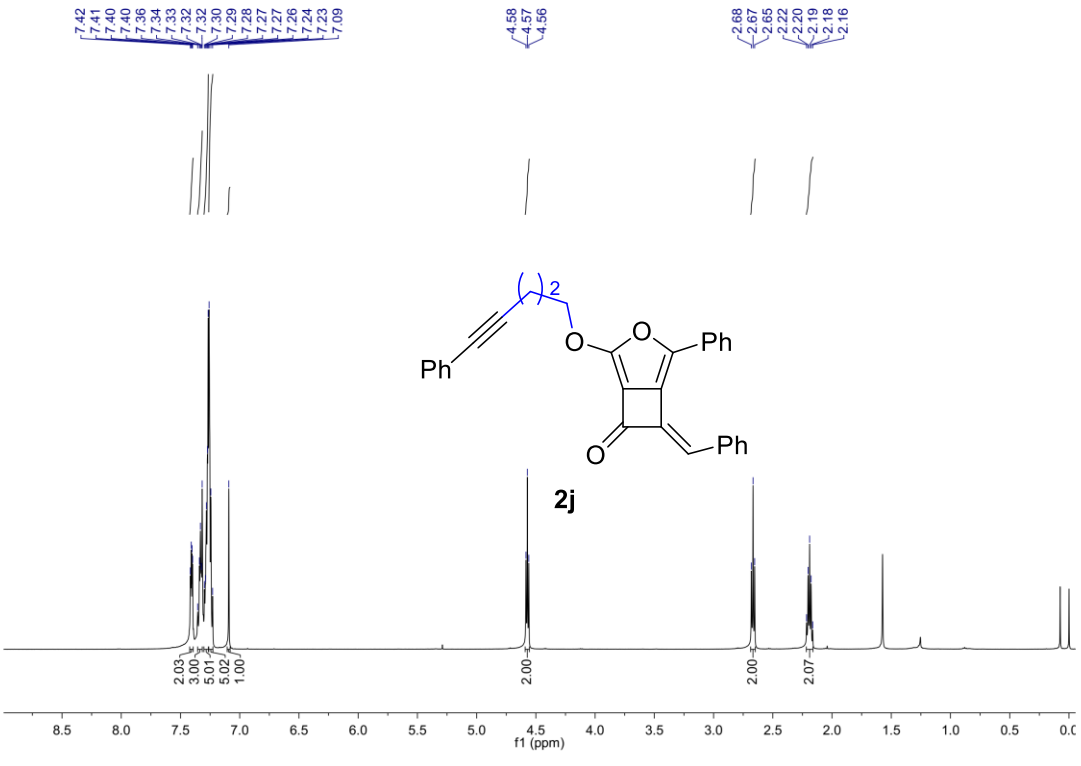
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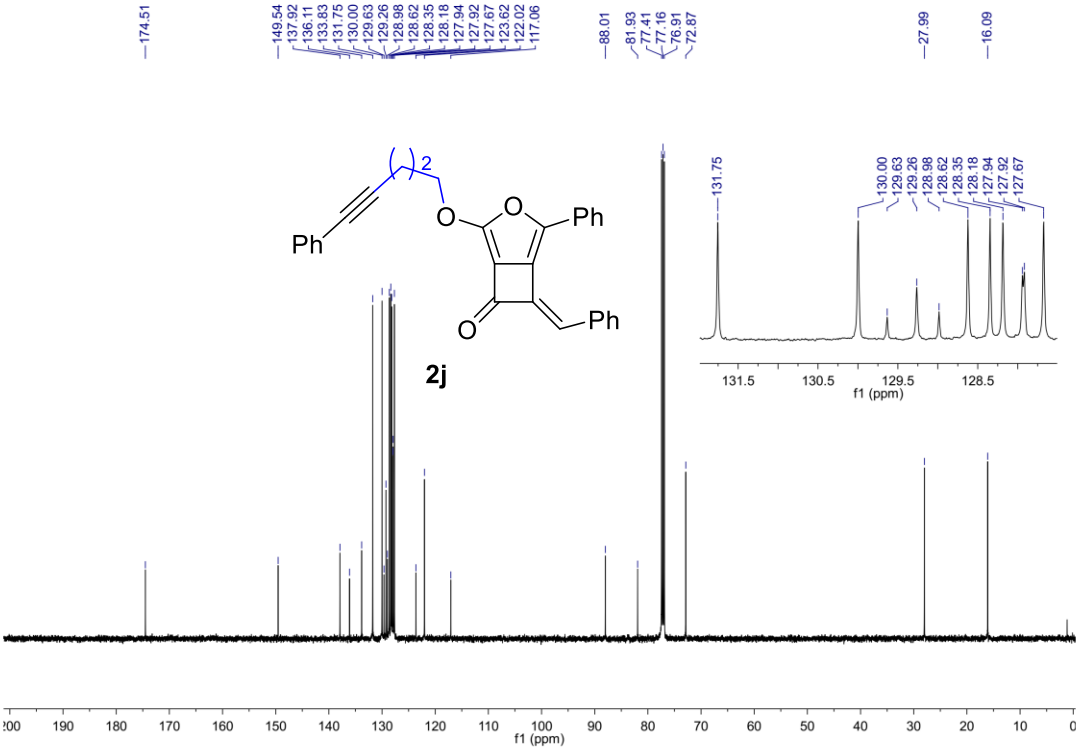
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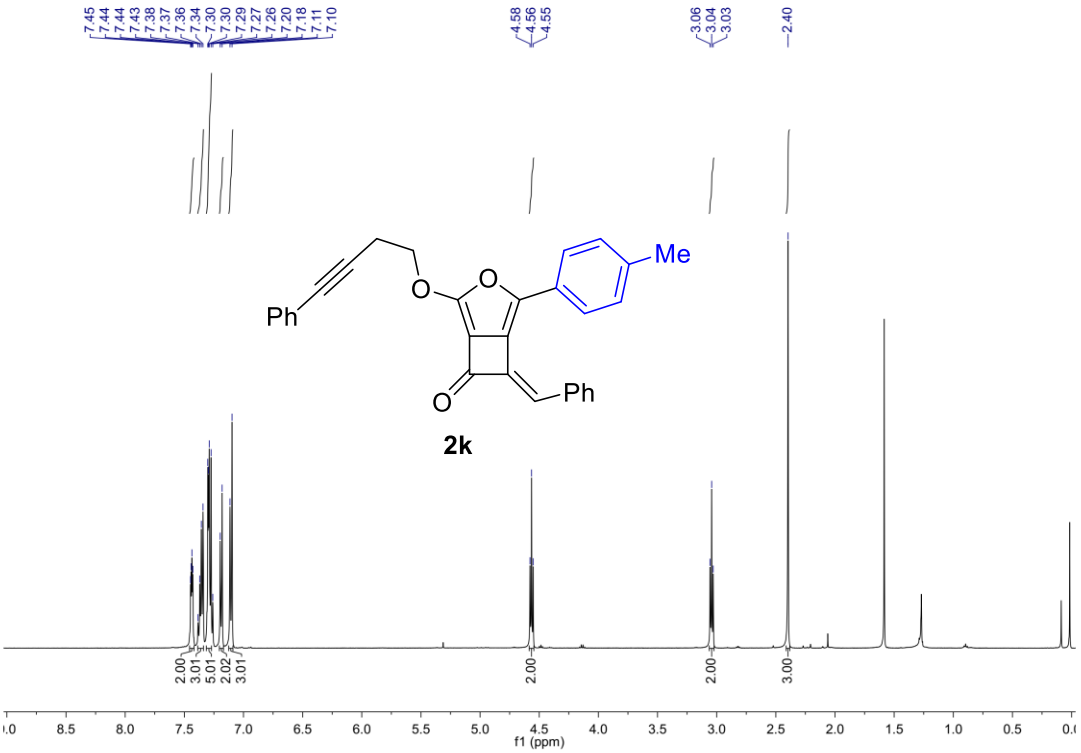
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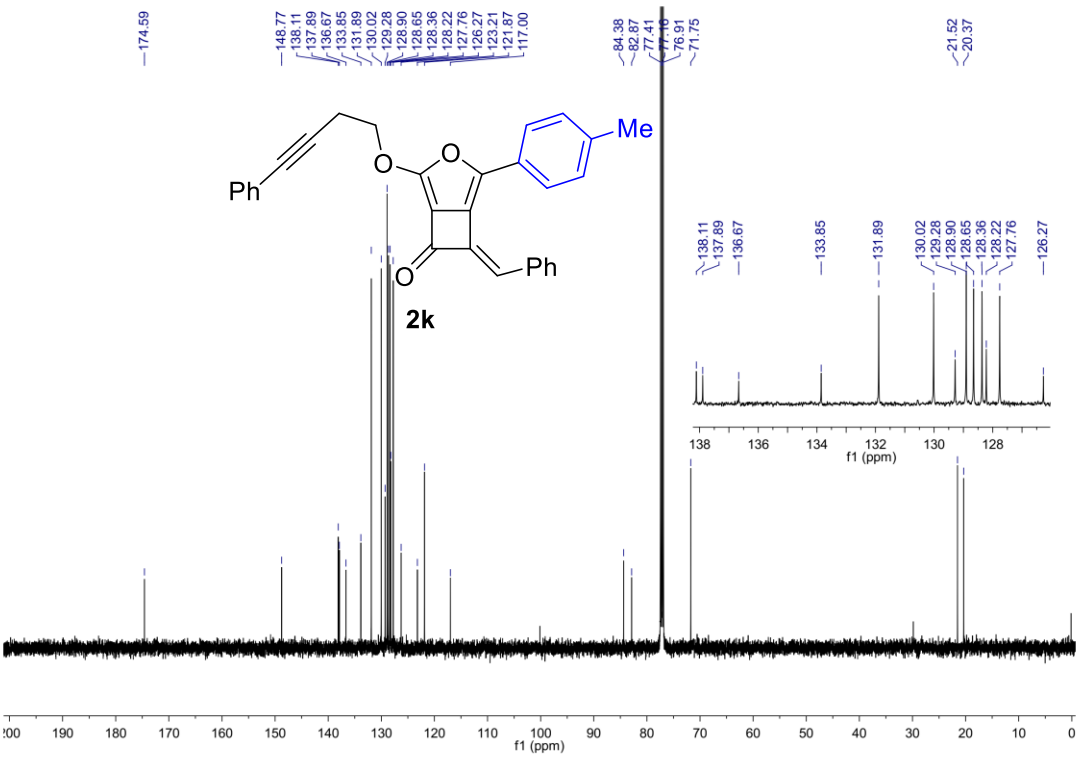
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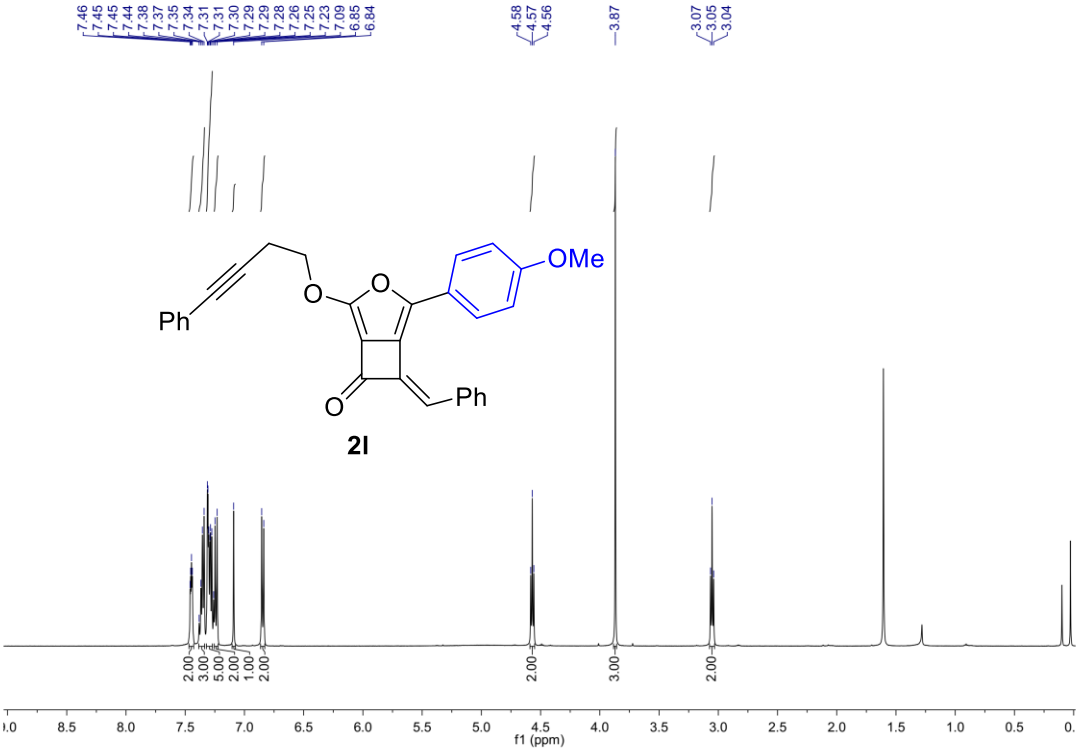
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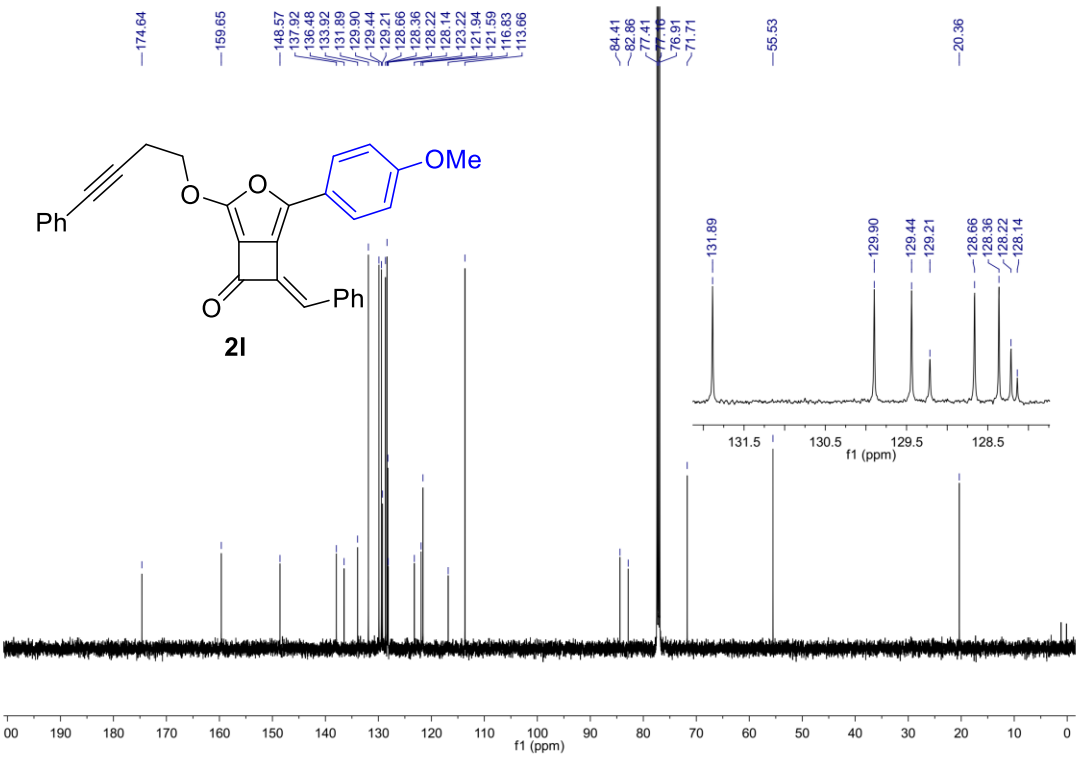
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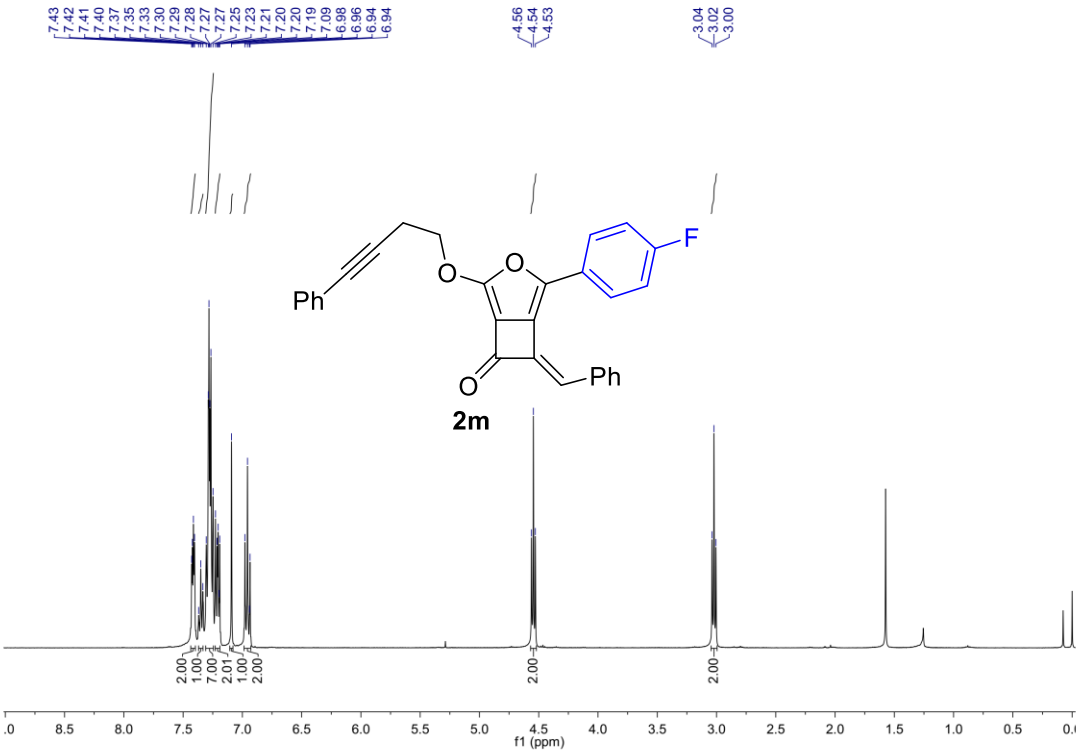
f1 (ppm)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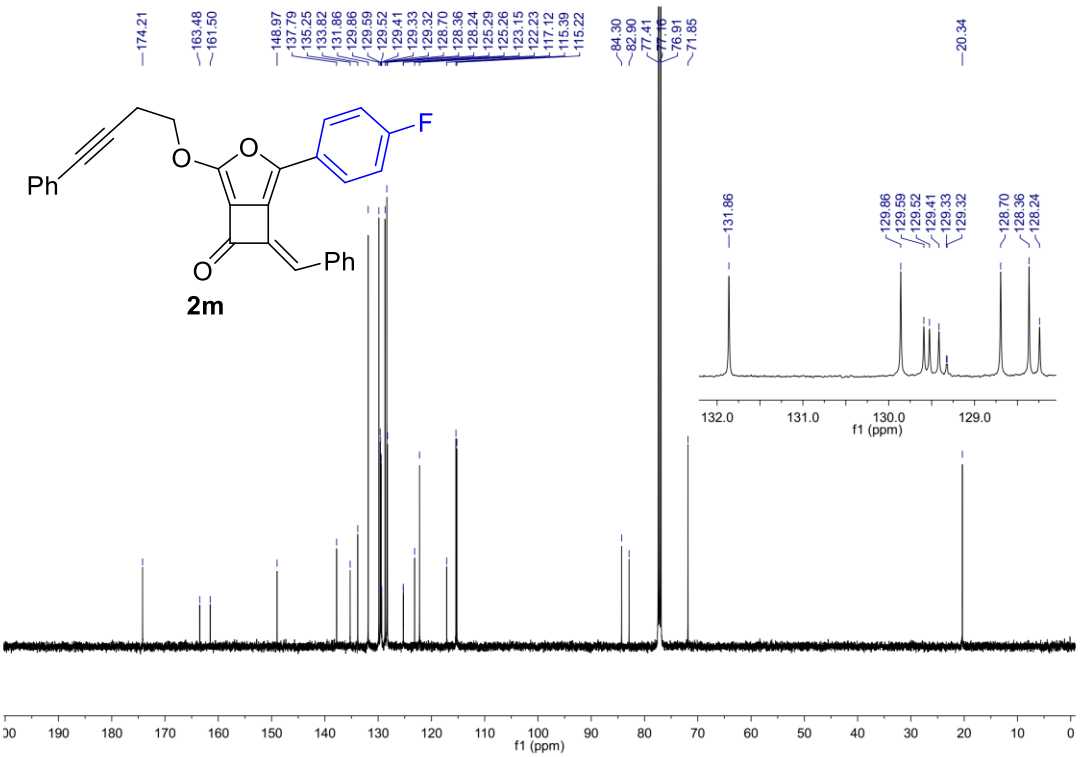
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161.50
148.97
137.79
135.25
133.82
131.86
129.86
129.59
129.52
129.41
129.33
129.32
128.70
128.36
128.24
125.29
125.26
123.15
122.23
117.12
115.39
115.22
84.30
82.90
77.41
77.16
76.91
71.85
20.34
F
O
O
Ph
O
Ph
2m
131.86
129.86
129.59
129.52
129.41
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128.70
128.36
128.24
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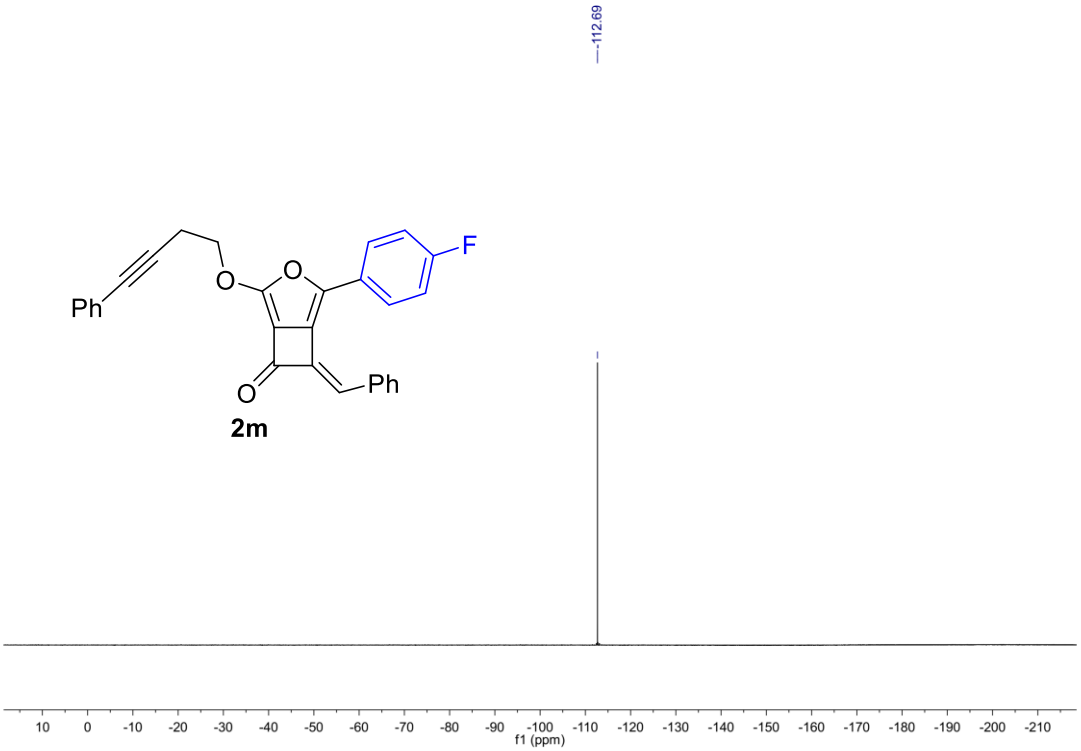
131.0
130.0
129.0
f1 (ppm)
f1 (ppm)


112.69
F
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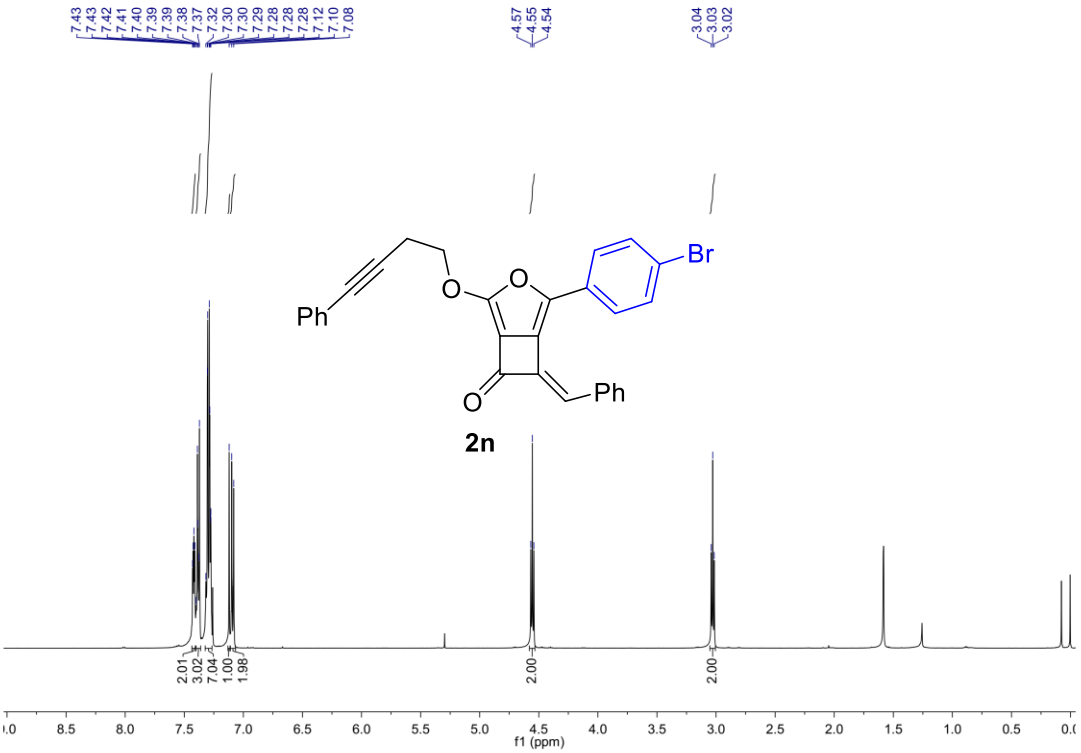
O
Ph
O
Ph
2m
f1 (ppm)


7.43
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7.39
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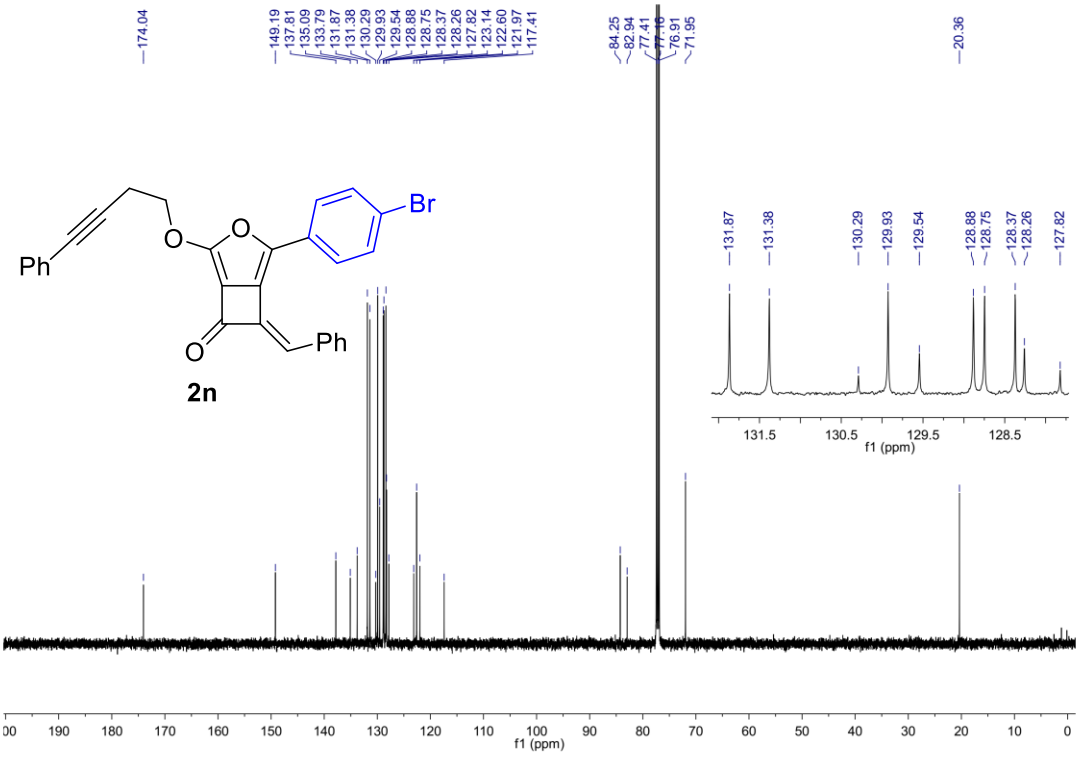
7.38
7.37
7.32
7.30
7.30
7.29
7.28
7.28
7.12
7.10
7.08
4.57
4.55
4.54
3.04
3.03
3.02
Br
Ph
O
O
O
Ph
2n
2.01
3.02
7.04
1.00
1.98
2.00
2.00
f1 (ppm)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129.54
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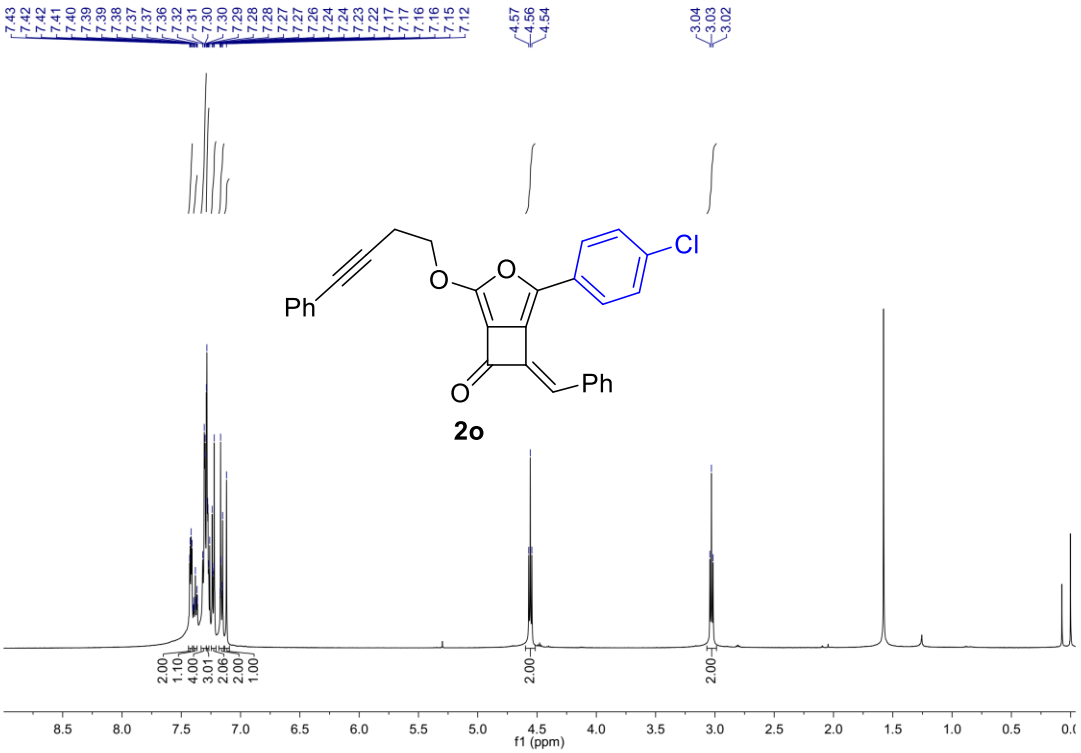
128.75
128.37
128.26
127.82
123.14
122.60
121.97
117.41
84.25
82.94
77.41
77.16
76.91
71.95
20.36
Br
Ph
O
O
O
Ph
2n
131.87
131.38
130.29
129.93
129.54
128.88
128.75
128.37
128.26
127.82
131.5
130.5
129.5
128.5
f1 (ppm)
f1 (ppm)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7.31
7.30
7.30
7.29
7.28
7.28
7.27
7.27
7.26
7.24
7.24
7.23
7.22
7.17
7.17
7.16
7.16
7.15
7.12
4.57
4.56
4.54
3.04
3.03
3.02
Cl
Ph
O
O
O
Ph
2o
2.00
1.10
4.00
3.01
2.06
2.00
1.00
2.00
2.00
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
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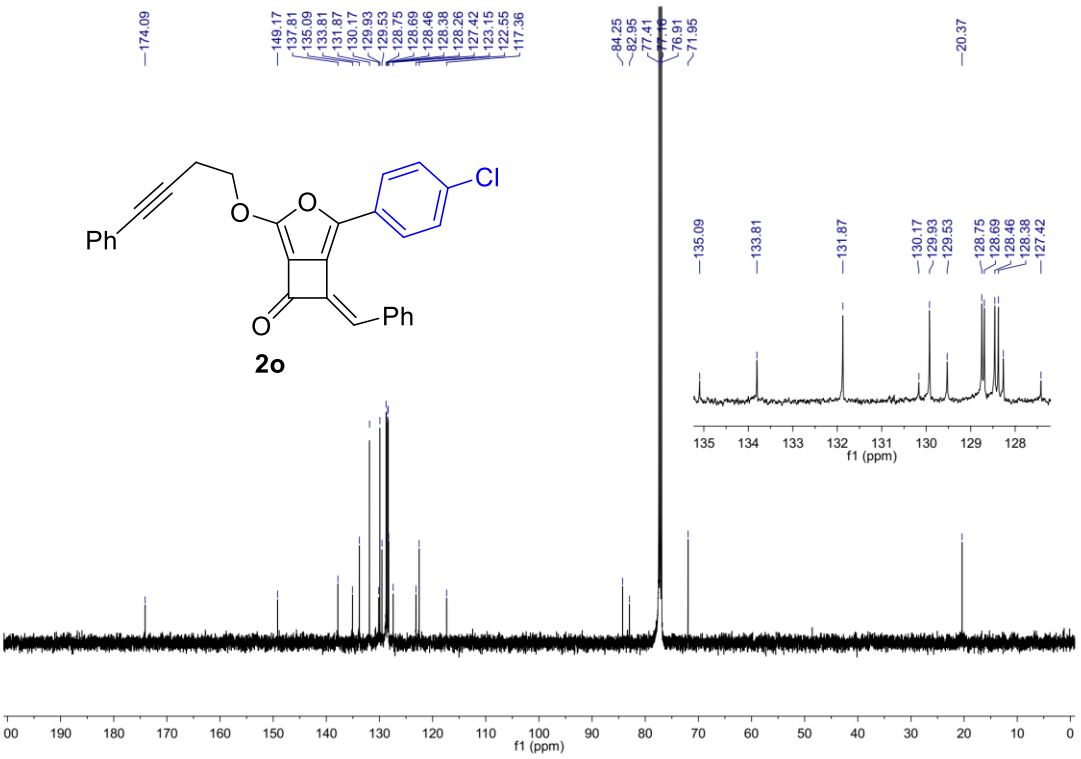
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)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149.17
137.81
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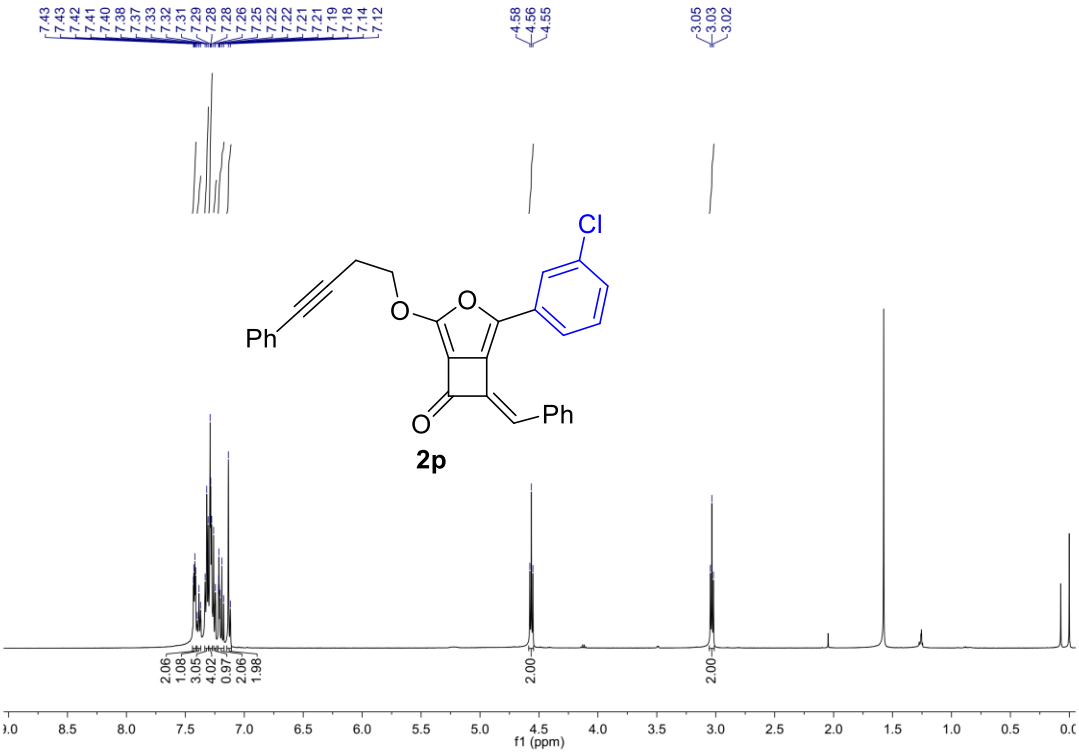
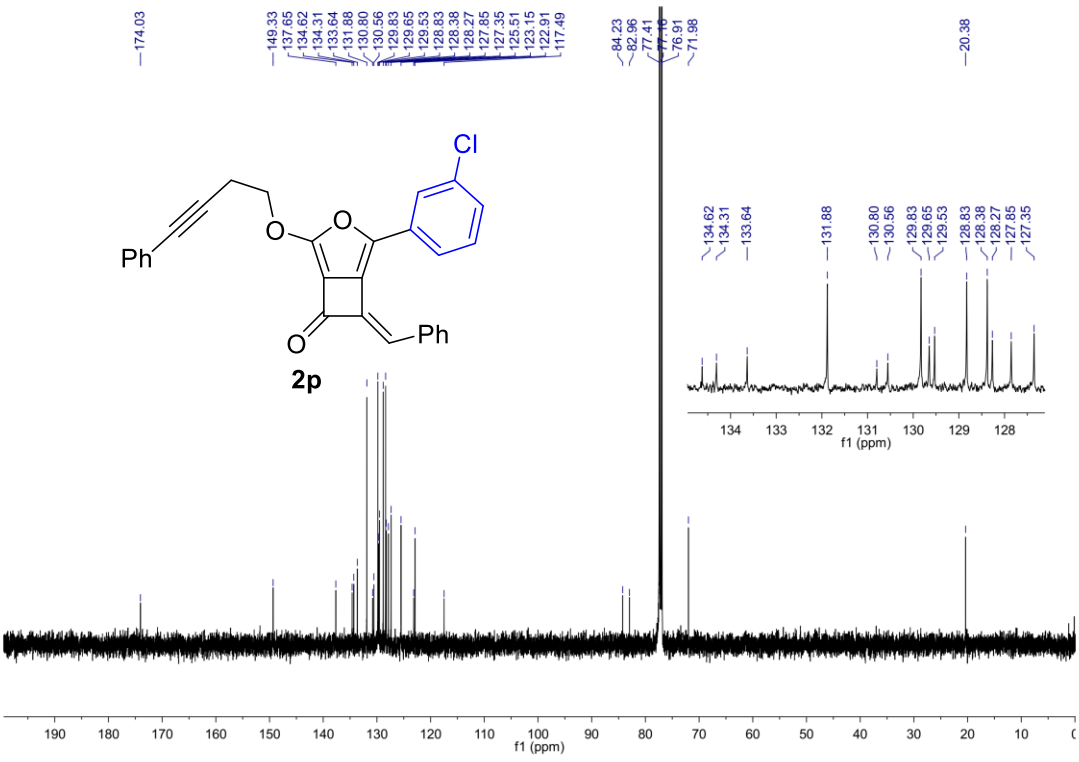
133.81
131.87
130.17
129.93
129.53
128.75
128.69
128.46
128.38
128.26
127.42
123.15
122.55
117.36
84.25
82.95
77.41
77.10
76.91
71.95
20.37
Cl
Ph
O
O
O
Ph
2o
135.09
133.81
131.87
130.17
129.93
129.53
128.75
128.69
128.46
128.38
127.42
135
134
133
132
131
130
129
128
f1 (ppm)
00
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


7.43
7.43
7.42
7.41
7.40
7.38
7.37
7.33
7.32
7.31
7.29
7.28
7.28
7.26
7.25
7.22
7.22
7.21
7.21
7.19
7.18
7.14
7.12
4.58
4.56
4.55
3.05
3.03
3.02
Cl
Ph
O
O
O
Ph
2p
2.06
1.08
3.05
4.02
0.97
2.06
1.98
2.00
2.00
f1 (ppm)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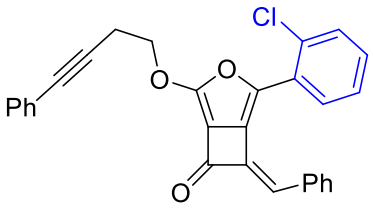
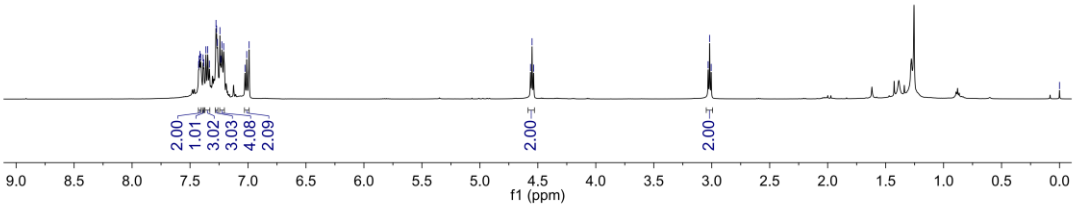
137.65
134.62
134.31
133.64
131.88
130.80
130.56
129.83
129.65
129.53
128.83
128.38
128.27
127.85
127.35
125.51
123.15
122.91
117.49
84.23
82.96
77.41
77.16
76.91
71.98
20.38
Cl
Ph
O
O
O
Ph
2p
134.62
134.31
133.64
131.88
130.80
130.56
129.83
129.65
129.53
128.83
128.38
128.27
127.85
127.35
f1 (ppm)
f1 (ppm)


7.43
7.42
7.41
7.41
7.39
7.38
7.36
7.35
7.33
7.28
7.27
7.26
7.24
7.24
7.23
7.21
7.03
7.01
6.99
4.56
4.55
4.54
3.03
3.02
3.00
0.00


Cl
O
O
Ph
O
Ph

2q


2.00
1.01
3.02
3.03
4.08
2.09
2.00
2.00
9.0
8.5
8.0
7.5
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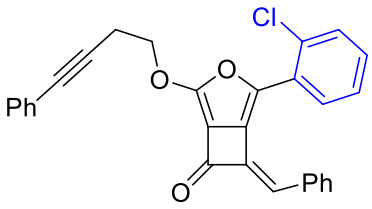
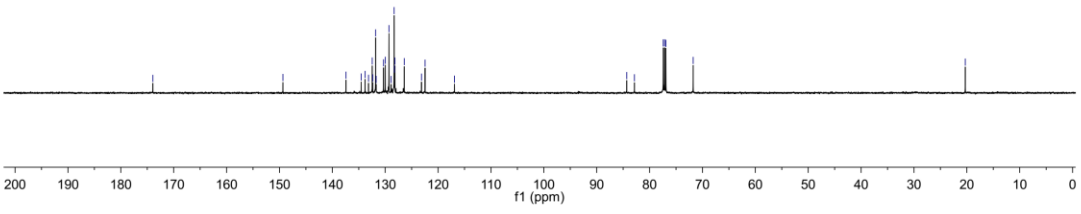
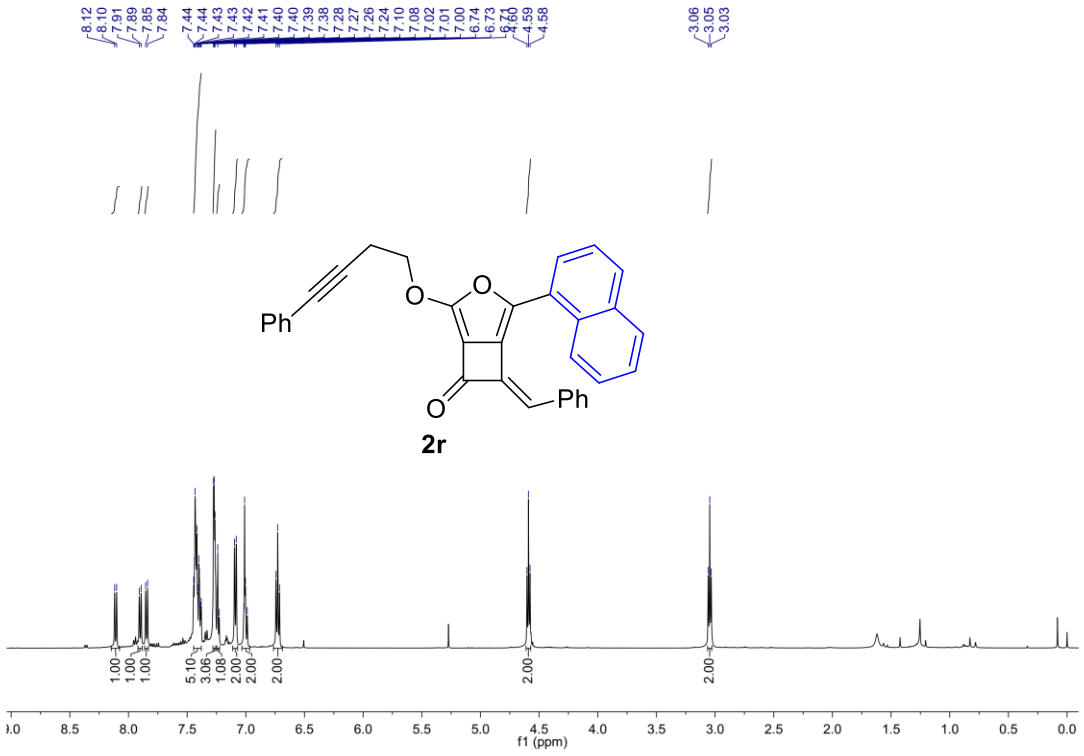
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

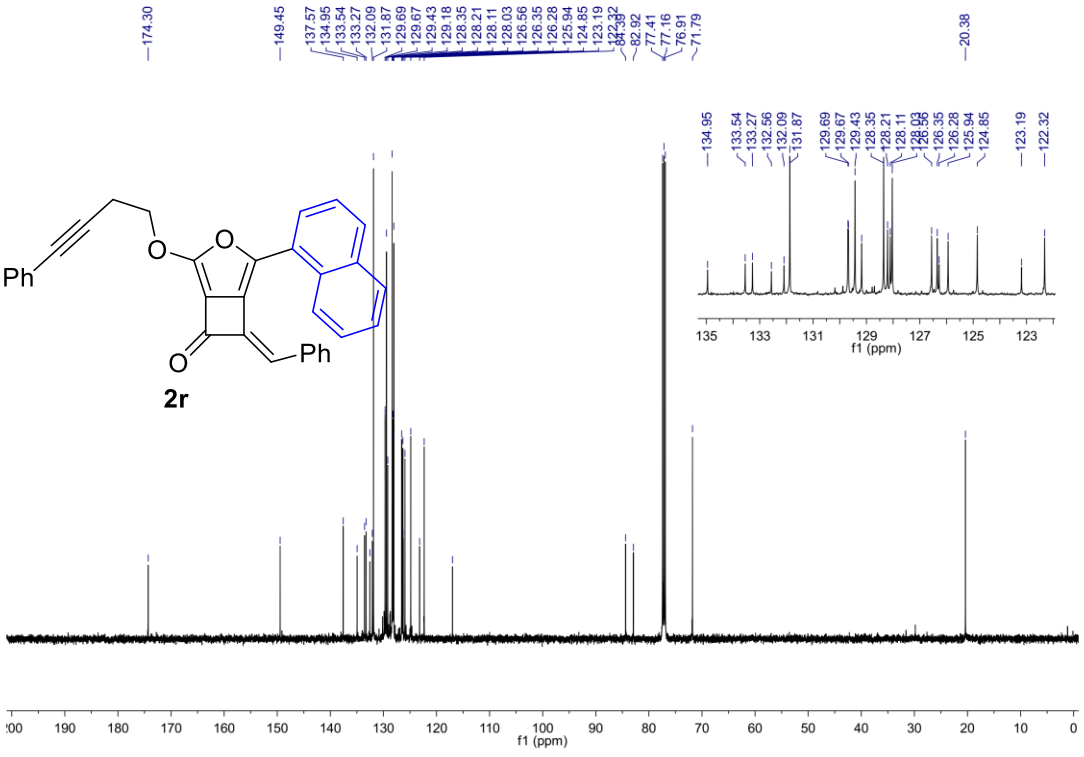

173.94
149.34
137.42
134.53
133.80
133.16
132.46
132.35
131.82
131.71
130.32
129.97
129.30
128.90
128.31
128.26
128.17
126.40
123.14
122.46
116.89
84.32
82.86
77.41
77.16
76.91
71.76
20.30


Cl
O
O
Ph
O
Ph

2q


200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


8.12
8.10
7.91
7.89
7.85
7.84
7.44
7.44
7.43
7.43
7.42
7.41
7.40
7.40
7.39
7.38
7.28
7.27
7.26
7.24
7.10
7.08
7.02
7.01
7.00
6.74
6.73
4.59
4.58
3.06
3.05
3.03
Ph
O
O
O
Ph
2r
1.00
1.00
1.00
5.10
3.06
1.08
2.00
2.00
2.00
2.00
2.00
f1 (ppm)


174.30
149.45
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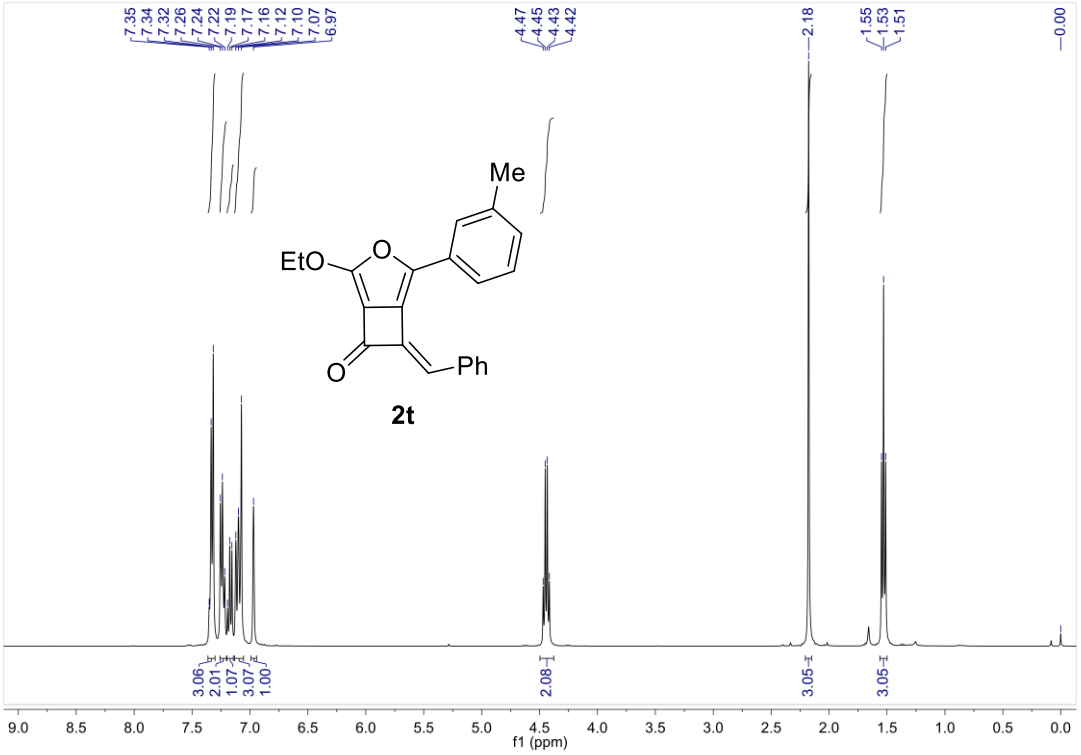
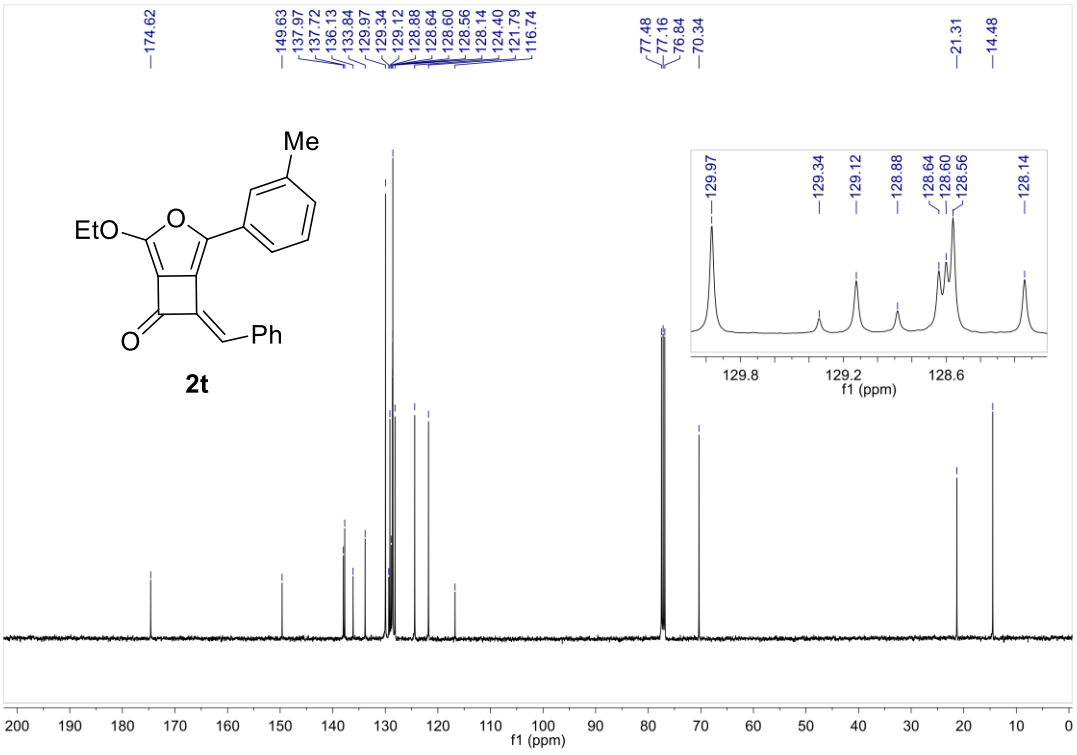
132.09
131.87
129.69
129.67
129.43
129.18
128.35
128.21
128.11
128.03
126.56
126.35
126.28
125.94
124.85
123.19
122.32
84.39
82.92
77.41
77.16
76.91
71.79
20.38
134.95
133.54
133.27
132.56
132.09
131.87
129.69
129.67
129.43
128.35
128.21
128.11
126.35
126.28
125.94
124.85
123.19
122.32
135
133
131
129
127
125
123
f1 (ppm)
Ph
O
O
O
Ph
2r
f1 (ppm)


7.35
7.34
7.32
7.26
7.24
7.22
7.19
7.17
7.16
7.12
7.10
7.07
6.97
4.47
4.45
4.43
4.42
2.18
1.55
1.53
1.51
0.00
Me
EtO
O
O
Ph
2t
3.06
2.01
1.07
3.07
1.00
2.08
3.05
3.05
f1 (ppm)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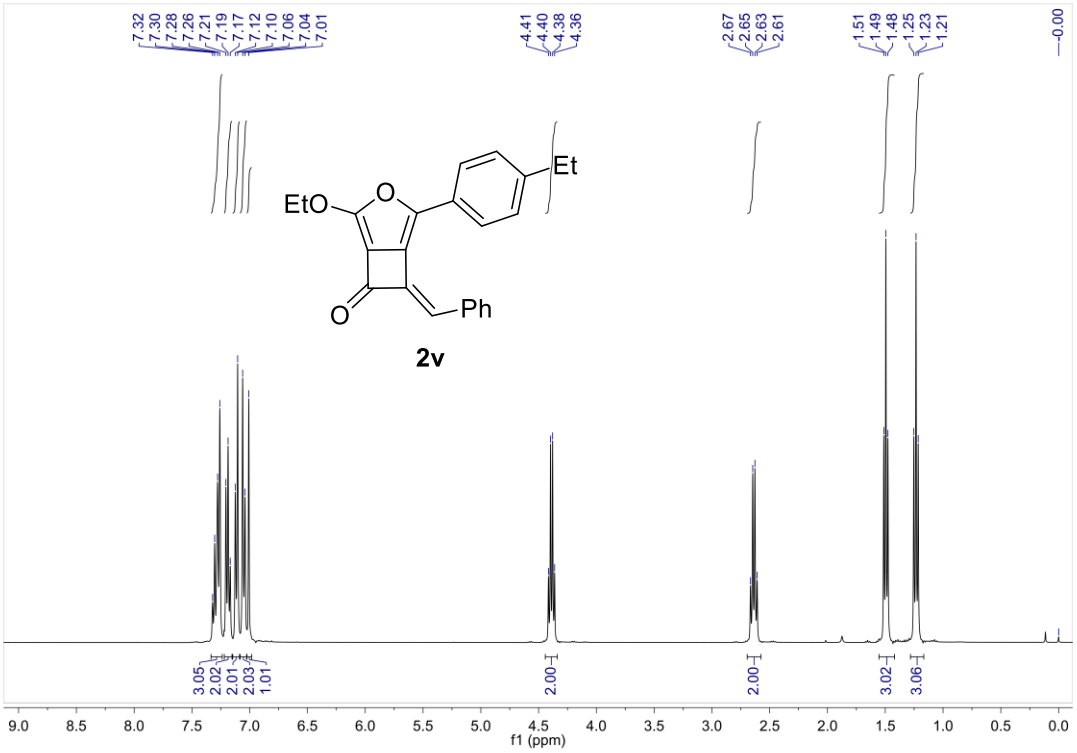
133.84
129.97
129.34
129.12
128.88
128.64
128.60
128.56
128.14
124.40
121.79
116.74
77.48
77.16
76.84
70.34
21.31
14.48
Me
EtO
O
O
Ph
2t
129.97
129.34
129.12
128.88
128.64
128.60
128.56
128.14
129.8
129.2
128.6
f1 (ppm)
f1 (ppm)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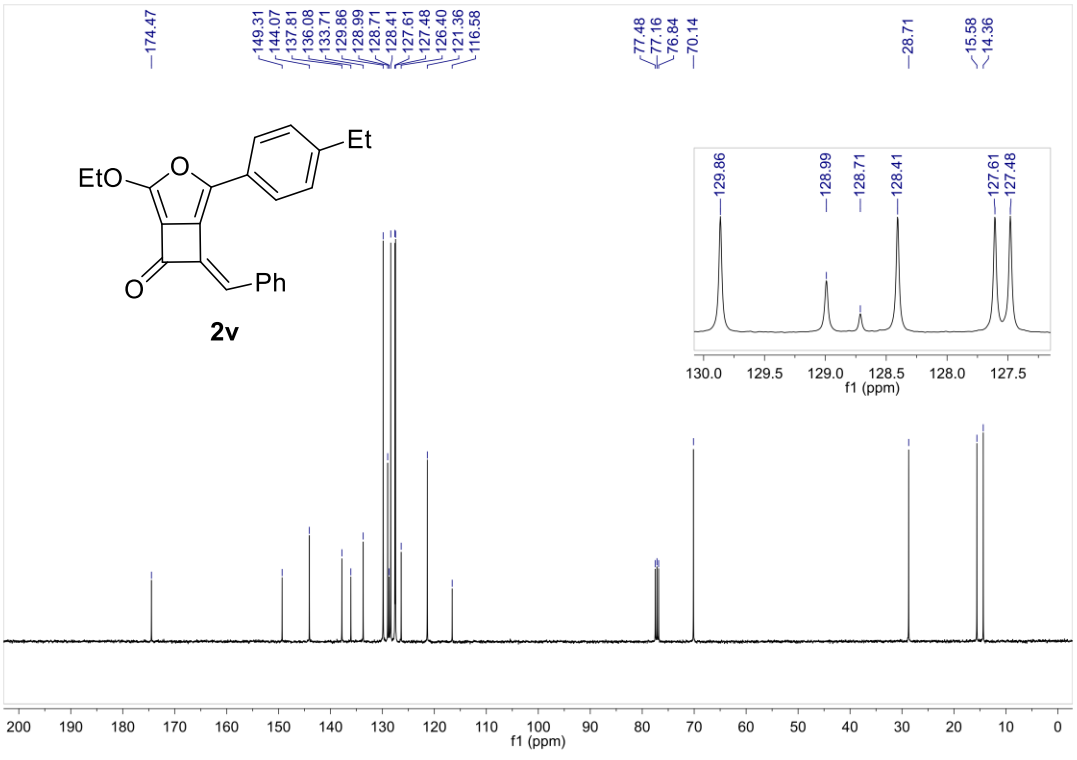
7.21
7.19
7.17
7.12
7.10
7.06
7.04
7.01
4.41
4.40
4.38
4.36
2.67
2.65
2.63
2.61
1.51
1.49
1.48
1.25
1.23
1.21
0.00
EtO
O
Et
O
Ph
2v
3.05
2.02
2.01
2.03
1.01
2.00
2.00
3.02
3.06
f1 (ppm)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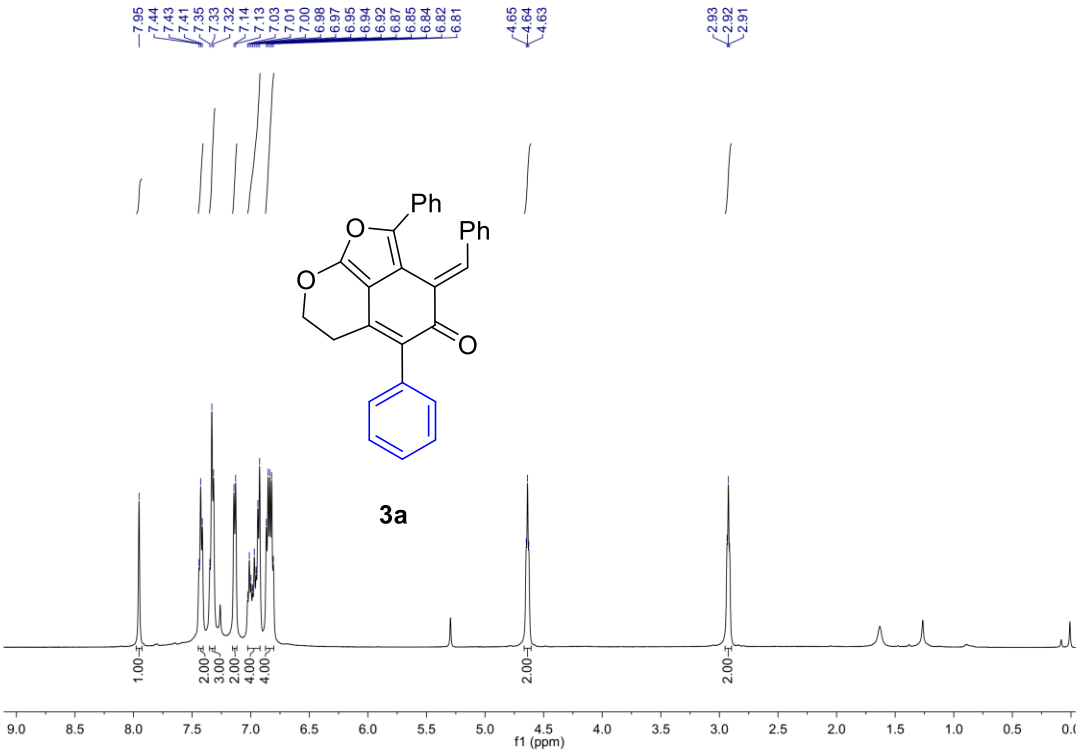
129.86
128.99
128.71
128.41
127.61
127.48
126.40
121.36
116.58
77.48
77.16
76.84
70.14
28.71
15.58
14.36
EtO
O
Et
O
Ph
2v
129.86
128.99
128.71
128.41
127.61
127.48
f1 (ppm)
f1 (ppm)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7.44
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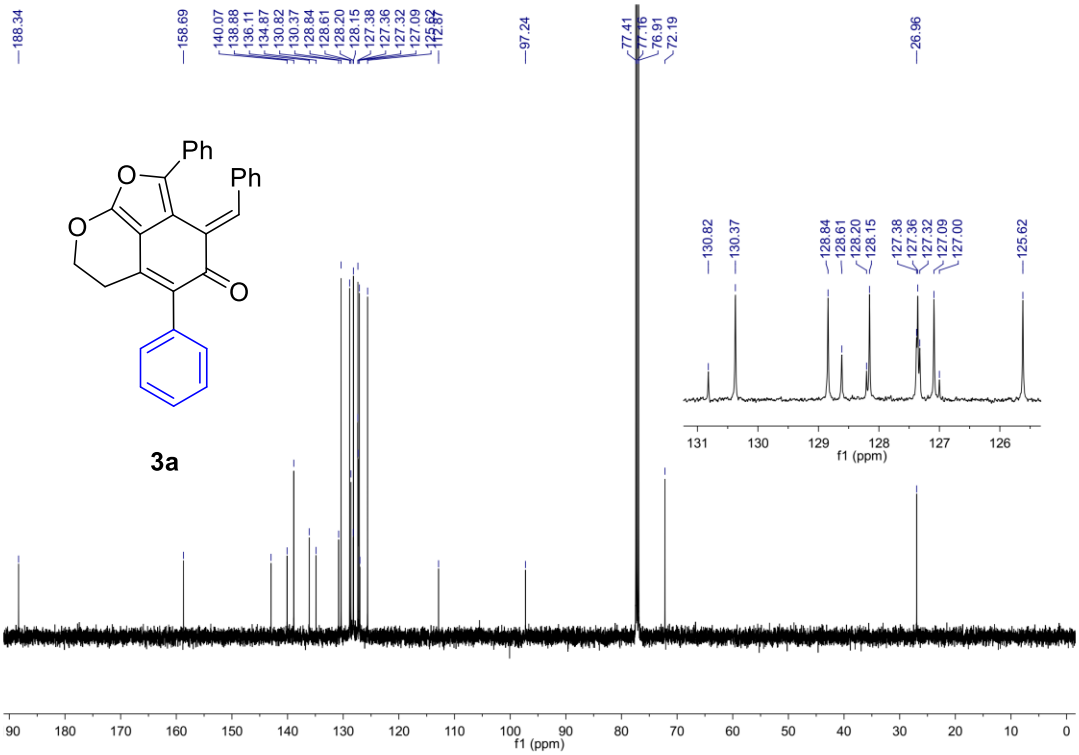
7.33
7.32
7.14
7.13
7.03
7.01
7.00
6.98
6.97
6.95
6.94
6.92
6.87
6.85
6.84
6.82
6.81
4.65
4.64
4.63
2.93
2.92
2.91
Ph
Ph
O
O
O
3a
1.00
2.00
3.00
2.00
4.00
4.00
2.00
2.00
f1 (ppm)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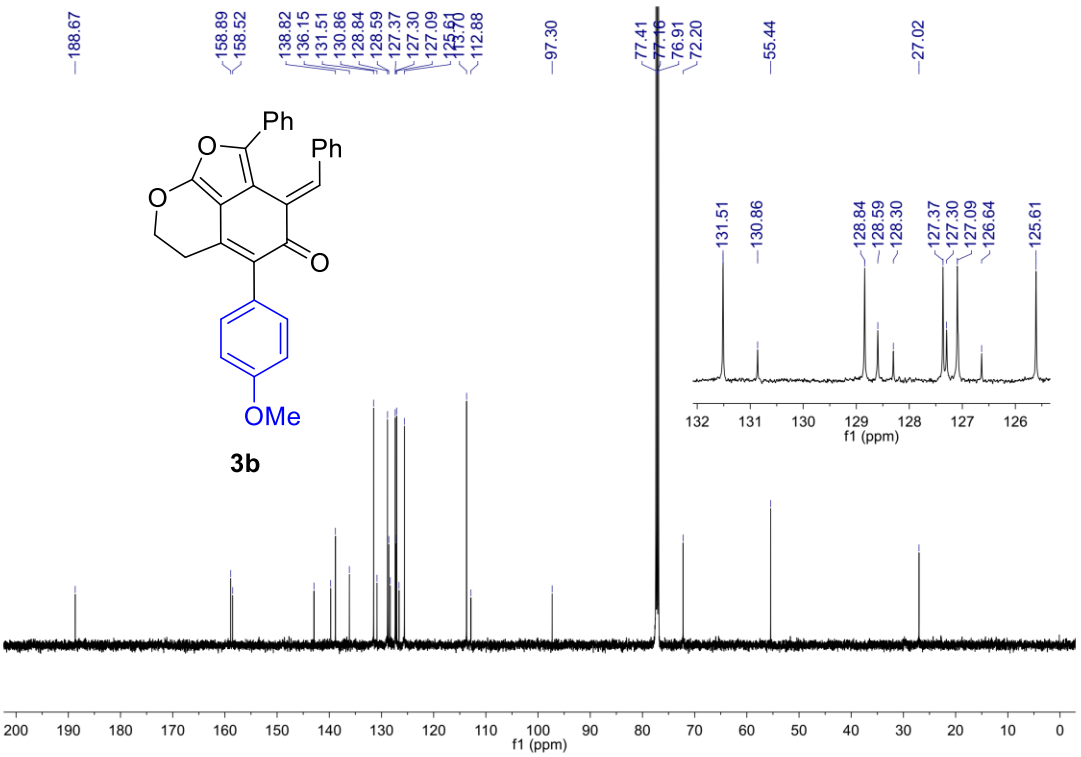
130.37
128.84
128.61
128.20
128.15
127.38
127.36
127.32
127.09
97.24
77.41
77.16
76.91
72.19
26.96
130.82
130.37
128.84
128.61
128.20
128.15
127.38
127.36
127.32
127.09
127.00
125.62
Ph
Ph
O
O
O
3a
f1 (ppm)
f1 (ppm)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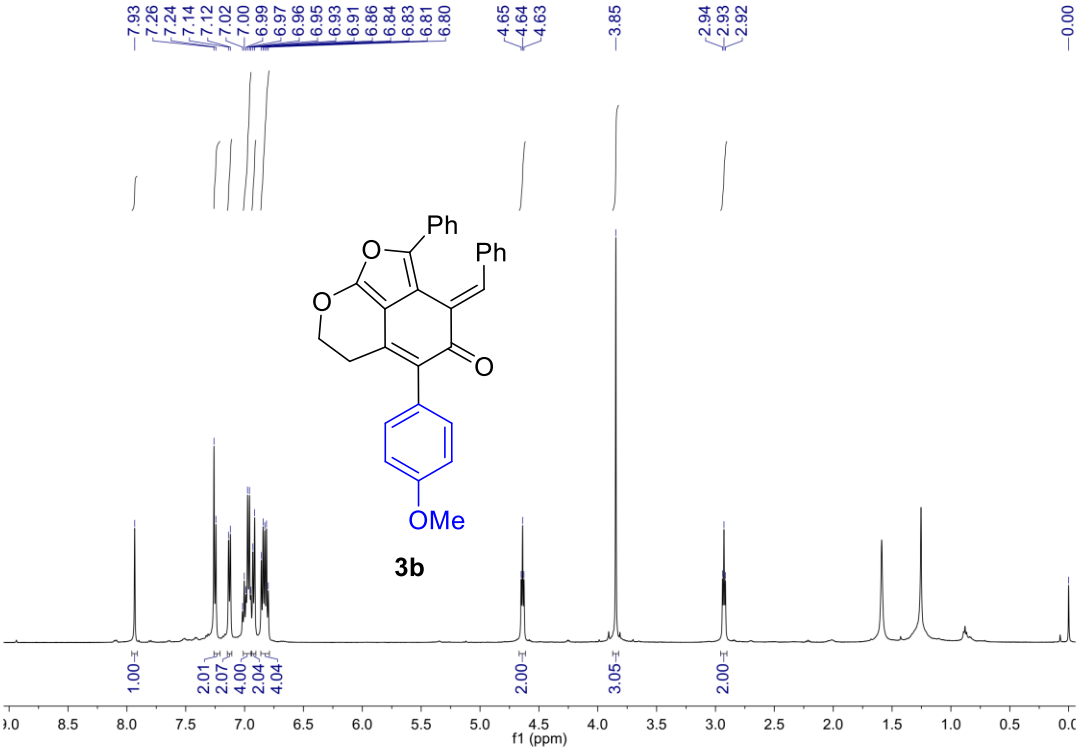
130.86
128.84
128.59
127.37
127.30
127.09
125.61
113.70
112.88
97.30
77.41
77.16
76.91
72.20
55.44
27.02
Ph
Ph
O
O
O
OMe
3b
131.51
130.86
128.84
128.59
128.30
127.37
127.30
127.09
126.64
125.61
132 131 130 129 128 127 126
f1 (ppm)
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


7.93
7.26
7.24
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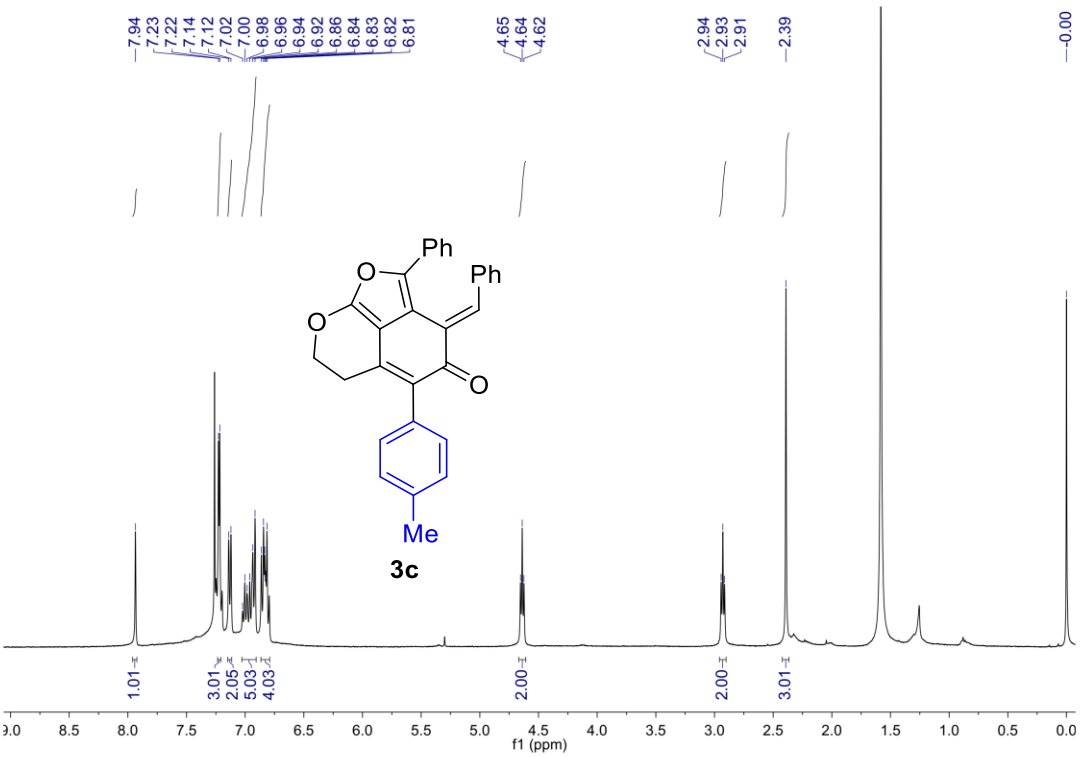
7.02
7.00
6.99
6.97
6.96
6.95
6.93
6.91
6.86
6.84
6.83
6.81
6.80
4.65
4.64
4.63
3.85
2.94
2.93
2.92
0.00
Ph
Ph
O
O
O
OMe
3b
1.00
2.01
2.07
4.00
2.04
4.04
2.00
3.05
2.00
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
f1 (ppm)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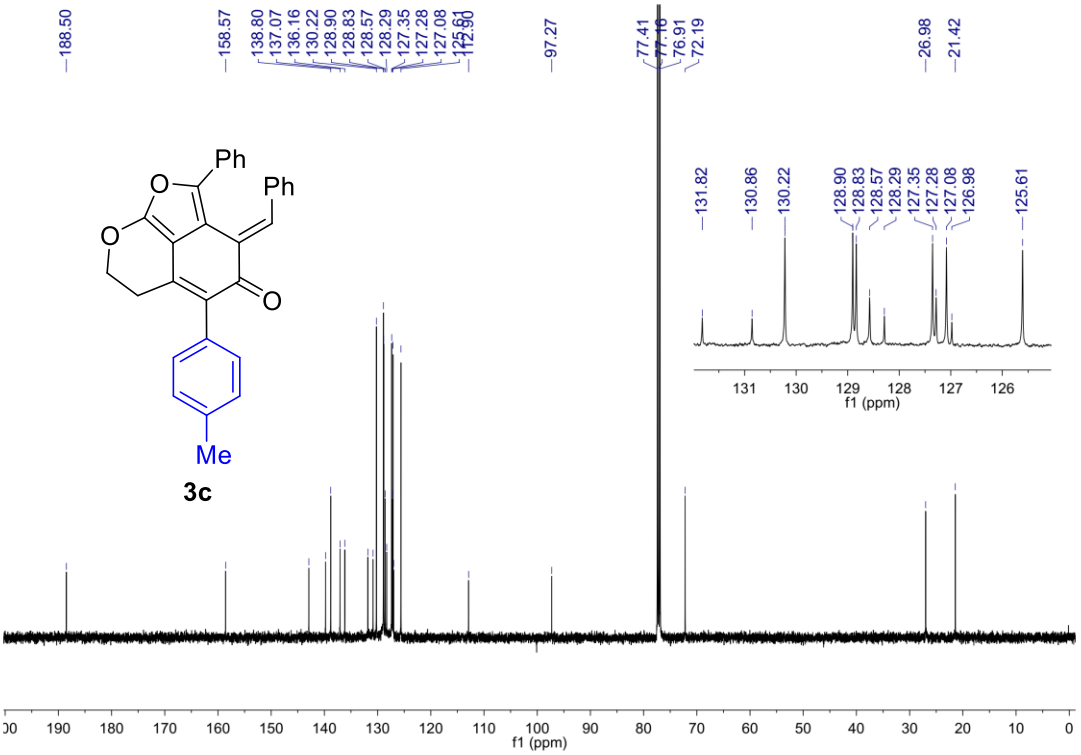
7.23
7.22
7.14
7.12
7.02
7.00
6.98
6.96
6.94
6.92
6.86
6.84
6.83
6.82
6.81
4.65
4.64
4.62
2.94
2.93
2.91
2.39
0.00
Ph
Ph
O
O
O
Me
3c
1.01
3.01
2.05
5.03
4.03
2.00
2.00
3.01
f1 (ppm)


188.50
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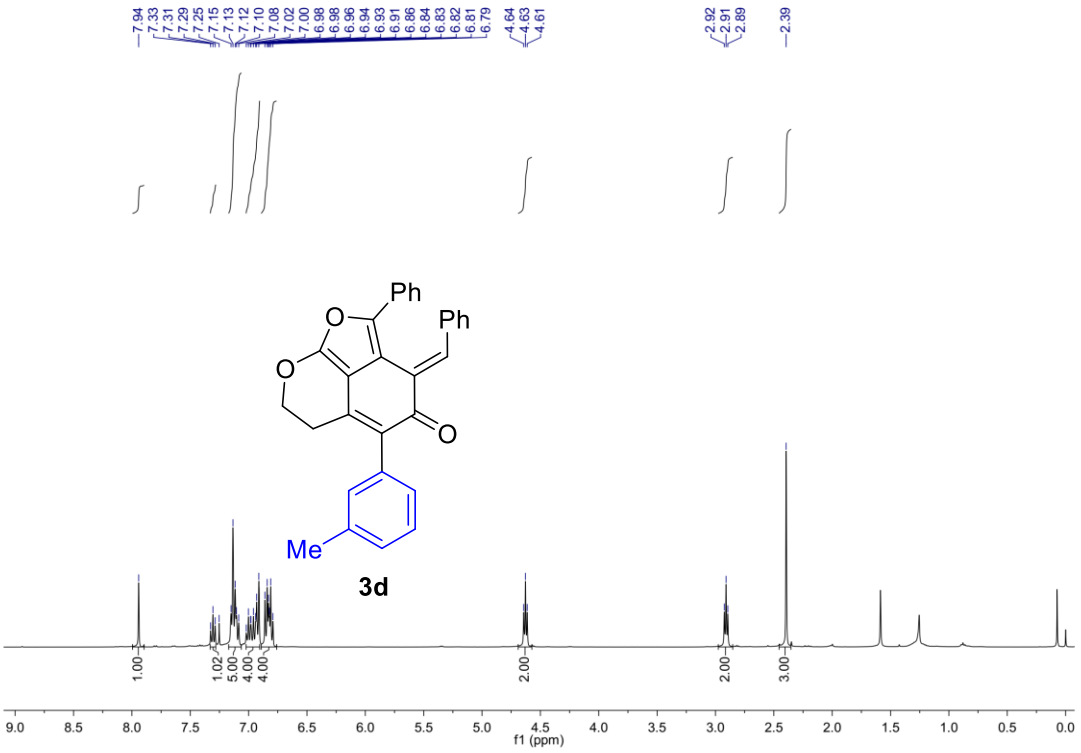
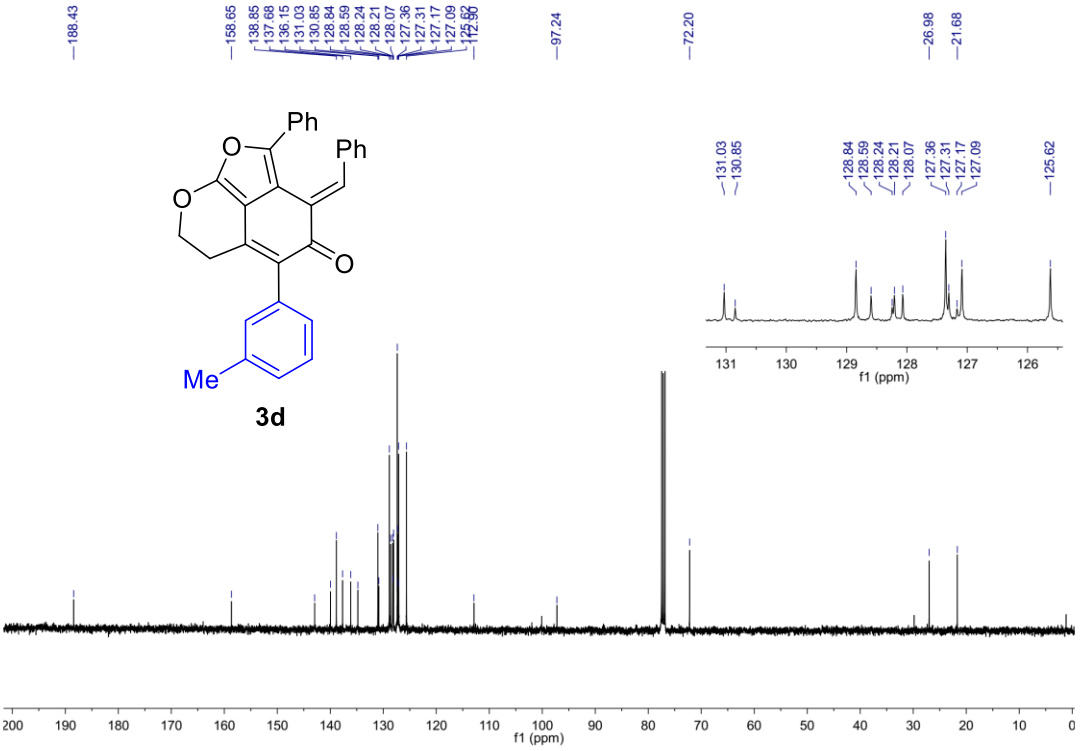
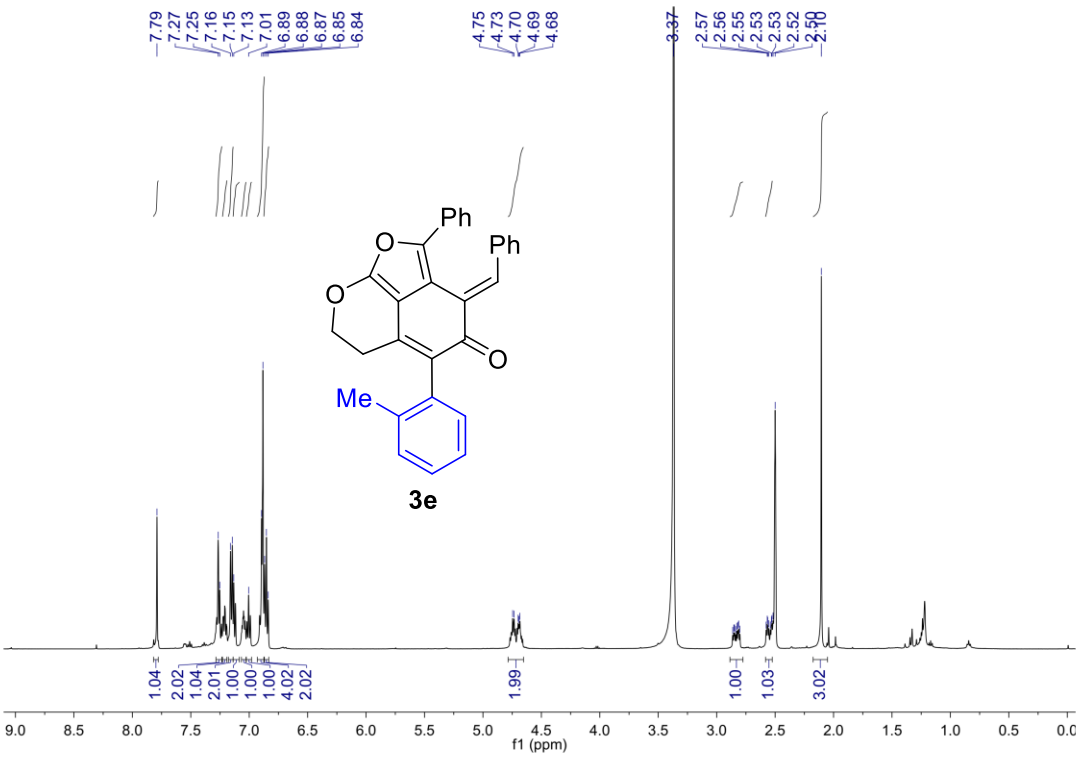
128.57
128.29
127.35
127.28
127.08
97.27
77.41
76.91
72.19
26.98
21.42
131.82
130.86
130.22
128.90
128.83
128.57
128.29
127.35
127.28
127.08
126.98
125.61
131
130
129
128
127
126
f1 (ppm)
Ph
Ph
O
O
O
Me
3c
f1 (ppm)


Ph
Ph
O
O
O
Me
3d
f1 (ppm)


Ph
Ph
O
O
O
Me
3d
f1 (ppm)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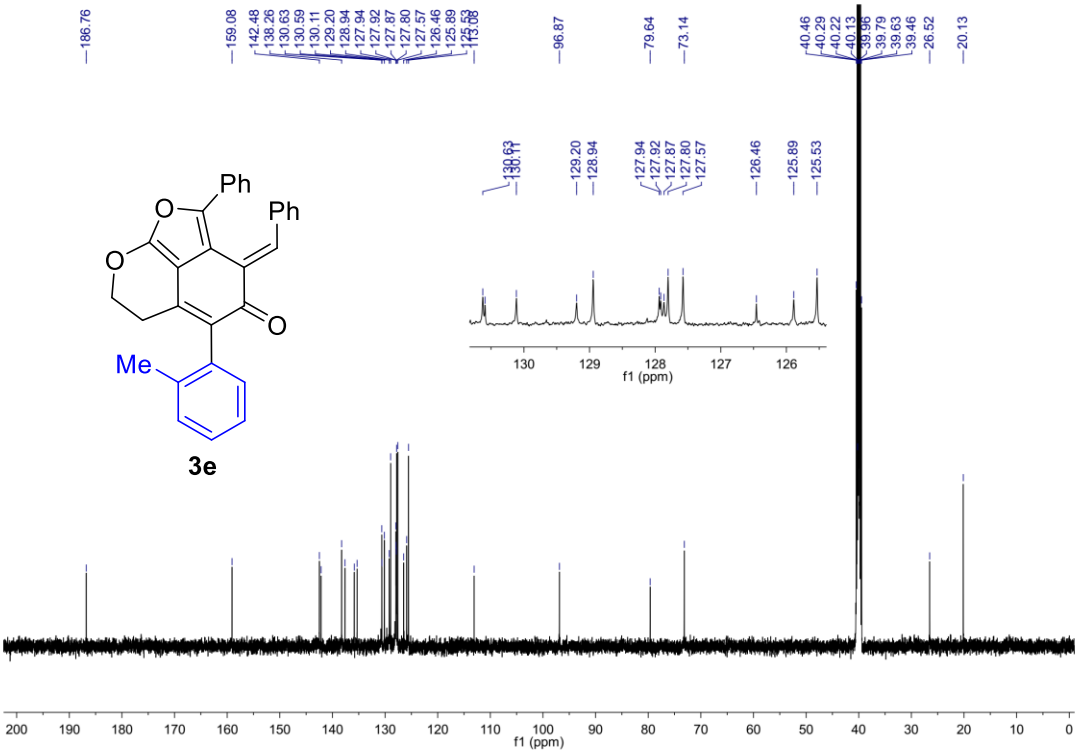
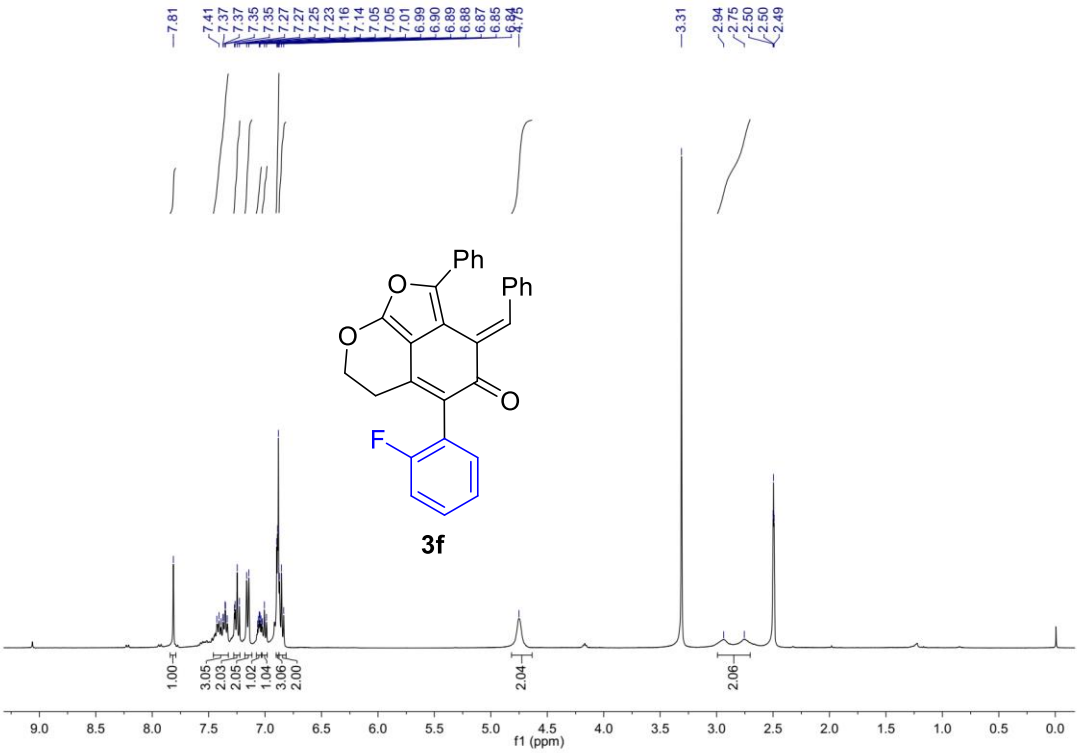
7.27
7.25
7.16
7.15
7.13
7.01
6.89
6.88
6.87
6.85
6.84
4.75
4.73
4.70
4.69
4.68
3.37
2.57
2.56
2.55
2.53
2.53
2.52
2.10
Ph
Ph
O
O
O
Me
3e
1.04
2.02
1.04
2.01
1.00
1.00
1.00
4.02
2.02
1.99
1.00
1.03
3.02
f1 (ppm)


186.76
159.08
142.48
138.26
130.63
130.59
130.11
129.20
128.94
127.94
127.92
127.87
127.80
127.57
126.46
125.89
125.53
113.08
96.87
79.64
73.14
40.46
40.29
40.22
40.13
39.96
39.79
39.63
39.46
26.52
20.13
Ph
Ph
O
O
O
Me
3e
f1 (ppm)
f1 (ppm)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7.41
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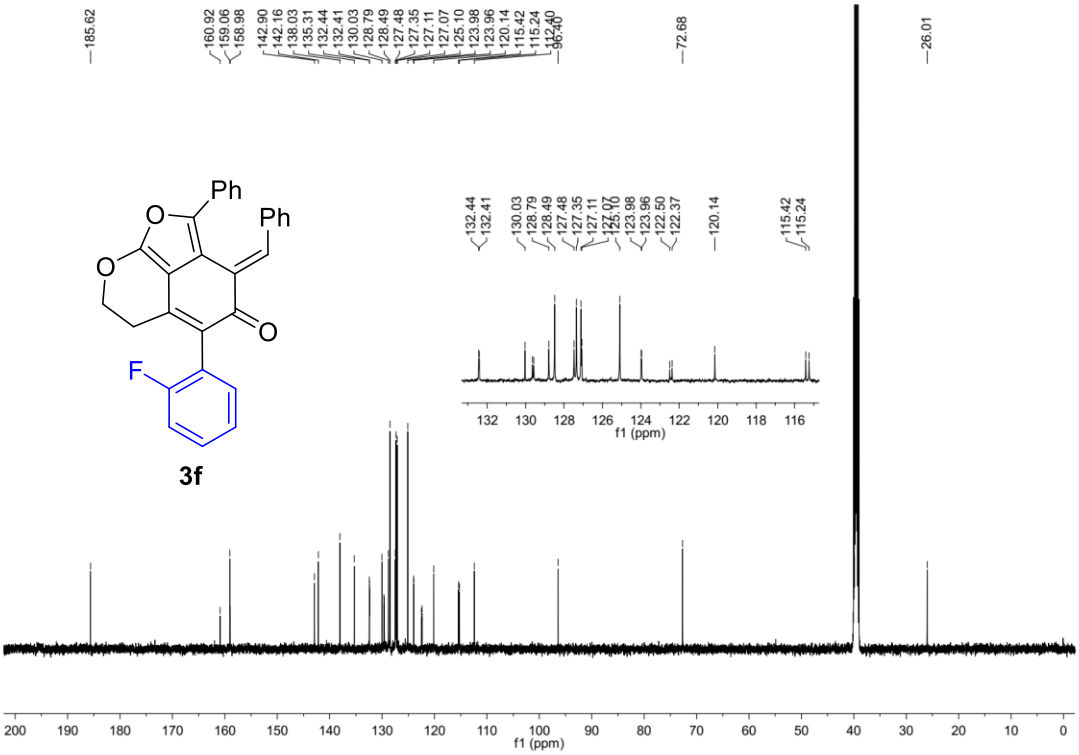
7.35
7.27
7.27
7.25
7.23
7.16
7.14
7.05
7.05
7.01
6.99
6.90
6.89
6.88
6.87
6.85
6.84
4.75
3.31
2.94
2.75
2.50
2.50
2.49
Ph
Ph
O
O
O
F
3f
1.00
3.05
2.03
2.05
1.02
1.04
3.06
2.00
2.04
2.06
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)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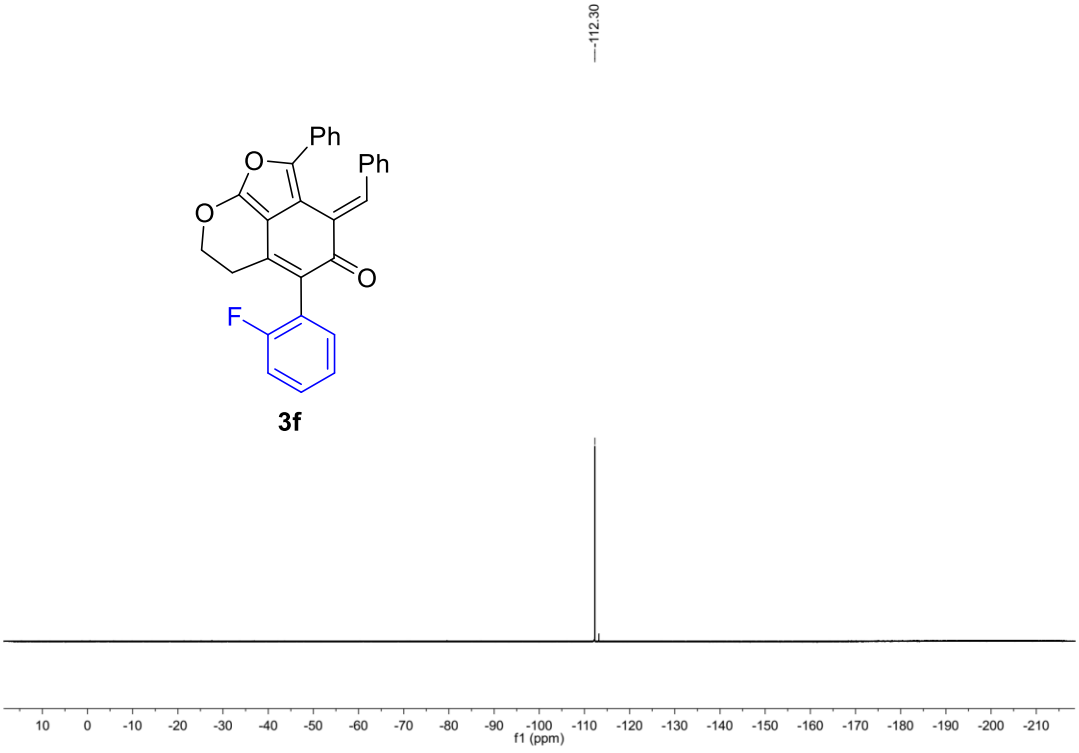
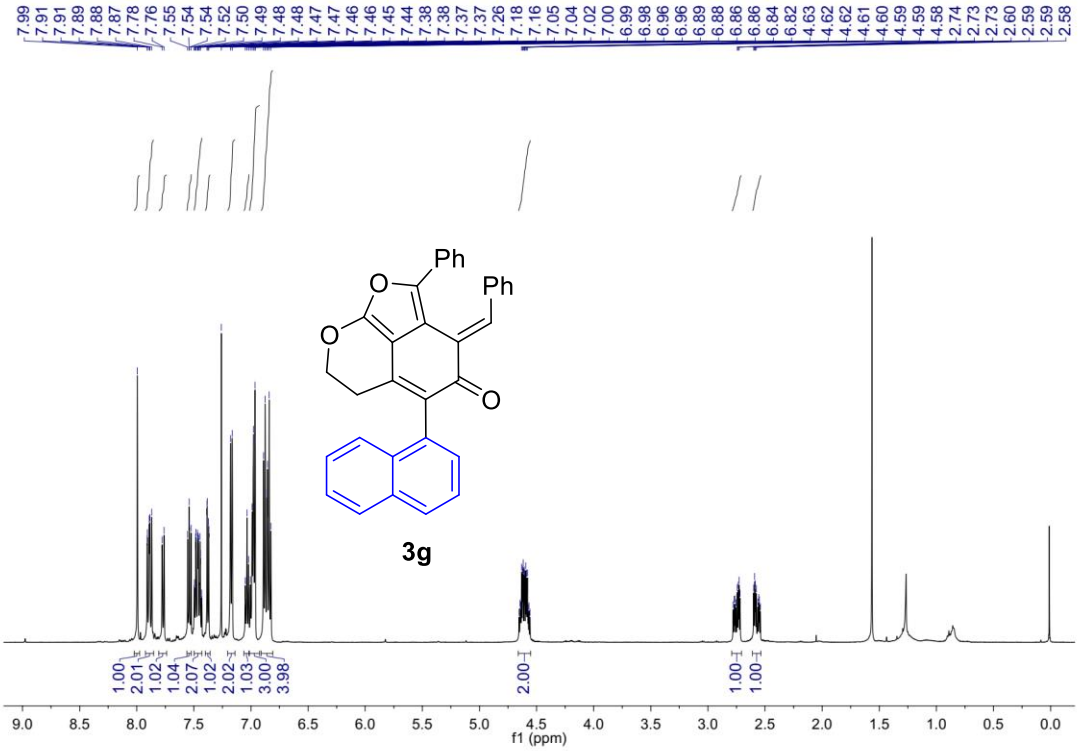
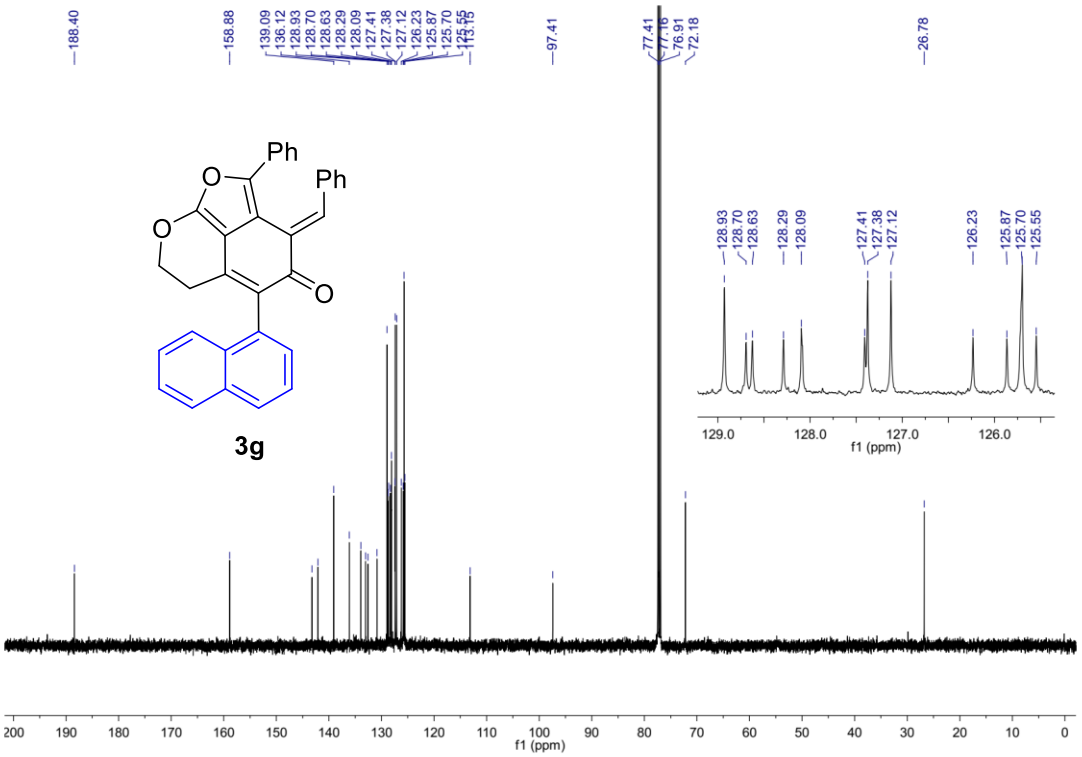
160.92
159.06
158.98
142.90
142.16
138.03
135.31
132.44
132.41
130.03
128.79
128.49
127.48
127.35
127.11
127.07
125.10
123.98
123.96
120.14
115.42
115.24
112.40
96.40
72.68
26.01
Ph
Ph
O
O
O
F
3f
132.44
132.41
130.03
128.79
128.49
127.48
127.35
127.11
127.07
125.10
123.98
123.96
122.50
122.37
120.14
115.42
115.24
132
130
128
126
124
122
120
118
116
f1 (ppm)
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

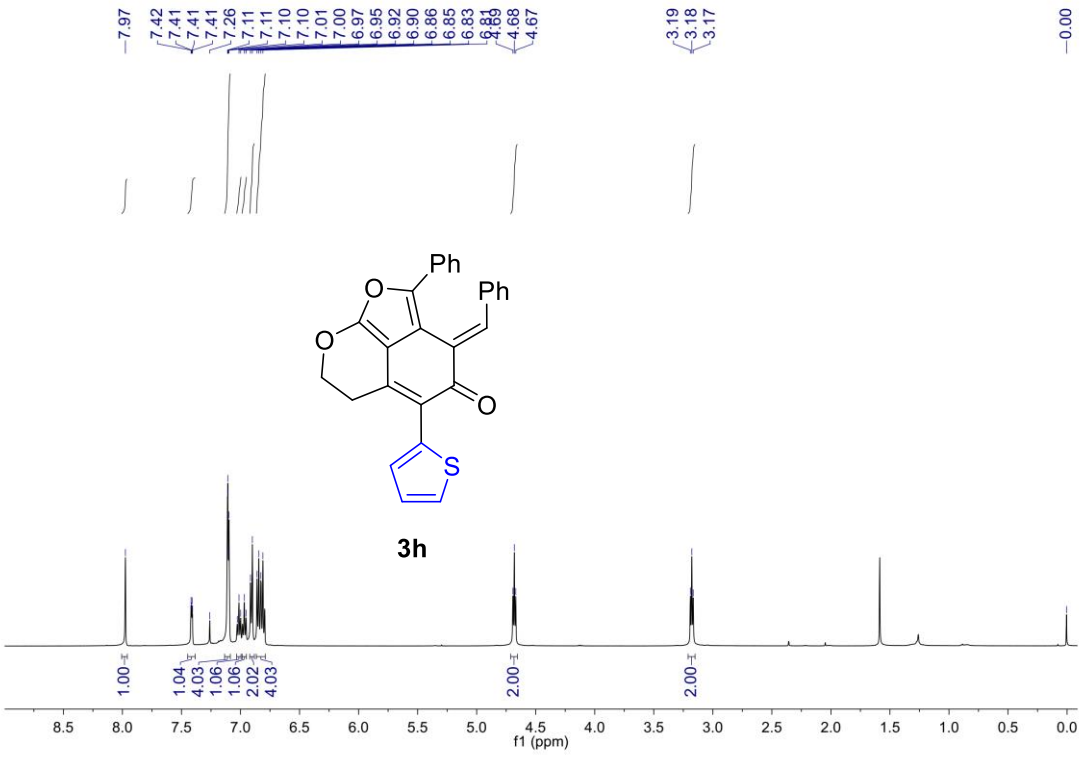

-112.30
Ph
Ph
O
O
O
F
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)

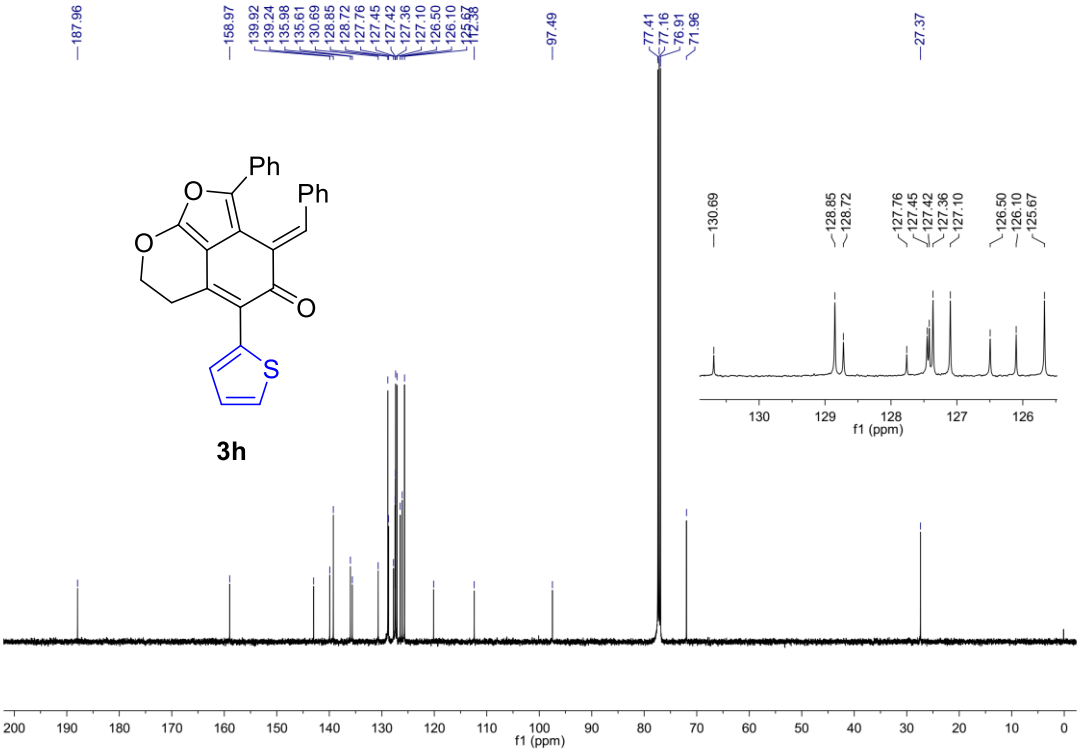
3f

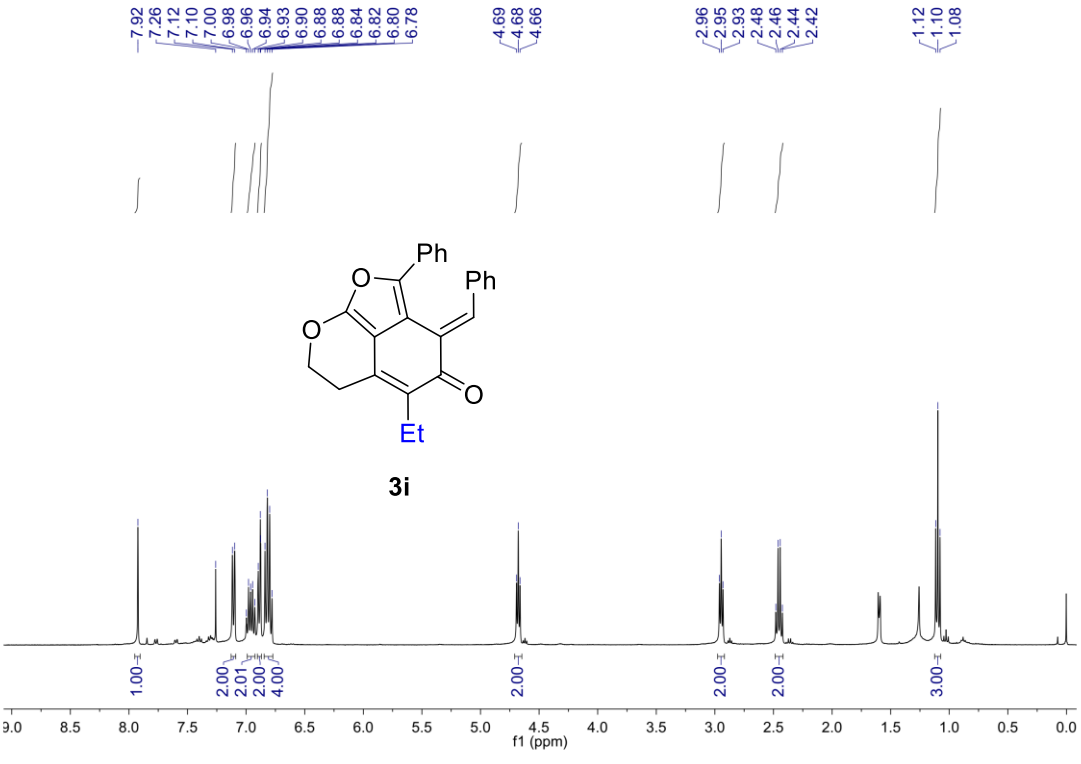

7.99 7.91 7.91 7.89 7.88 7.87 7.78 7.76 7.55 7.54 7.54 7.52 7.50 7.49 7.48 7.48 7.47 7.47 7.46 7.46 7.45 7.44 7.38 7.38 7.37 7.37 7.26 7.18 7.16 7.05 7.04 7.02 7.00 6.99 6.98 6.96 6.96 6.89 6.88 6.86 6.86 6.84 6.82 4.63 4.62 4.62 4.61 4.60 4.59 4.59 4.58 2.74 2.73 2.73 2.60 2.59 2.59 2.58
Ph
Ph
O
O
O
1.00 2.01 1.02 1.04 2.07 1.02 2.02 1.03 3.00 3.98
2.00
1.00 1.00
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)

3g


188.40
158.88
139.09
136.12
128.93
128.70
128.63
128.29
128.09
127.41
127.38
127.12
126.23
125.87
125.70
97.41
77.41
77.16
76.91
72.18
26.78
Ph
Ph
O
O
O
3g
128.93
128.70
128.63
128.29
128.09
127.41
127.38
127.12
126.23
125.87
125.70
125.55
129.0
128.0
127.0
126.0
f1 (ppm)
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


7.97
7.42
7.41
7.41
7.41
7.26
7.11
7.11
7.10
7.10
7.01
7.00
6.97
6.95
6.92
6.90
6.86
6.85
6.83
6.81
6.69
4.68
4.67
3.19
3.18
3.17
0.00
Ph
Ph
O
O
O
S
3h
1.00
1.04
4.03
1.06
1.06
2.02
4.03
2.00
2.00
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)


187.96
158.97
139.92
139.24
135.98
135.61
130.69
128.85
128.72
127.76
127.45
127.42
127.36
127.10
126.50
126.10
125.67
112.38
97.49
77.41
77.16
76.91
71.96
27.37
Ph
Ph
O
O
O
S
3h
130.69
128.85
128.72
127.76
127.45
127.42
127.36
127.10
126.50
126.10
125.67
130
129
128
127
126
f1 (ppm)
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)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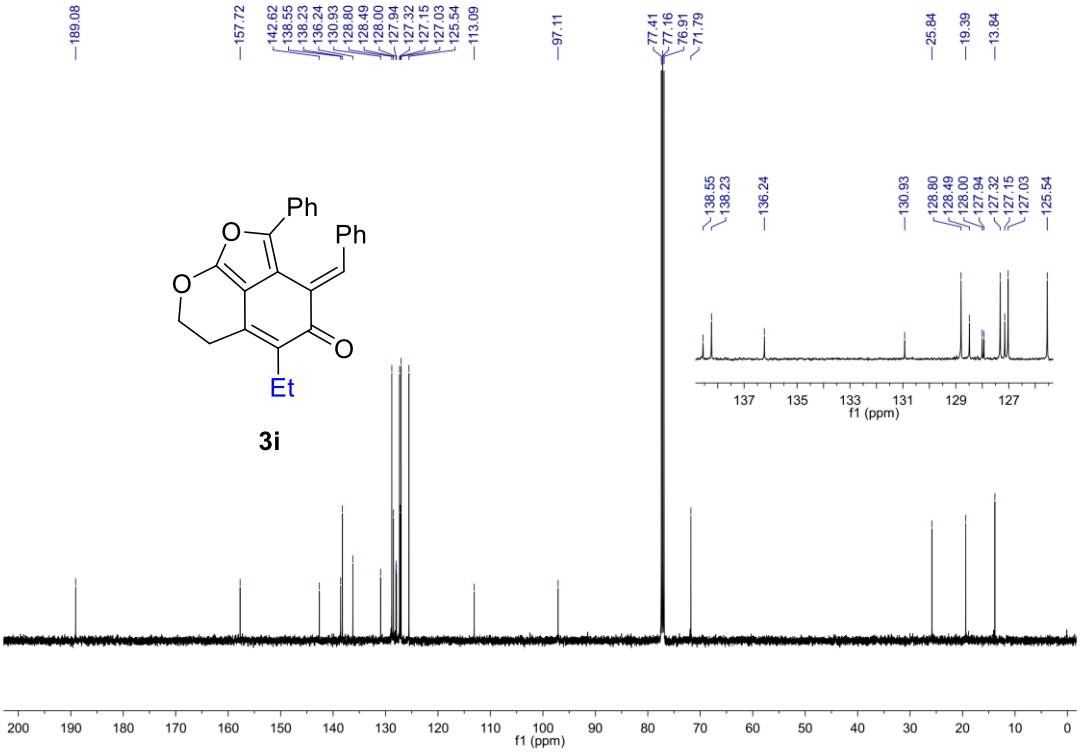
7.26
7.12
7.10
7.00
6.98
6.96
6.94
6.93
6.90
6.88
6.88
6.84
6.82
6.80
6.78
4.69
4.68
4.66
2.96
2.95
2.93
2.48
2.46
2.44
2.42
1.12
1.10
1.08
Ph
Ph
O
O
O
Et
3i
1.00
2.00
2.01
2.00
4.00
2.00
2.00
2.00
3.00
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)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157.72
142.62
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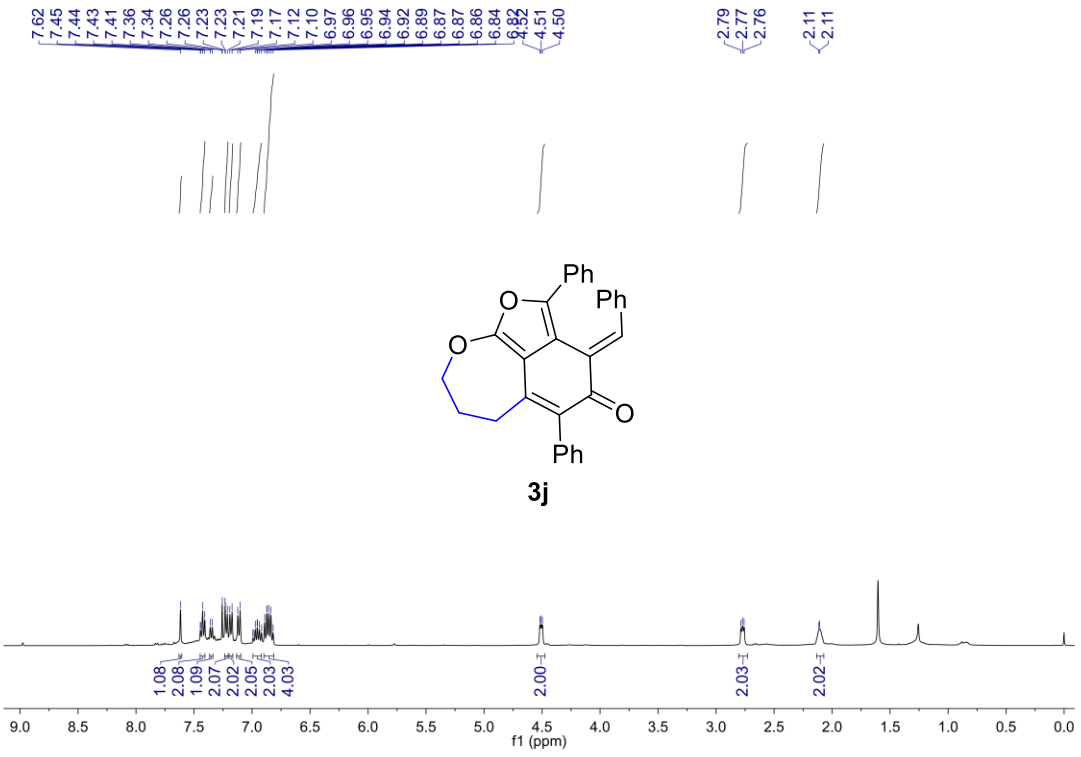
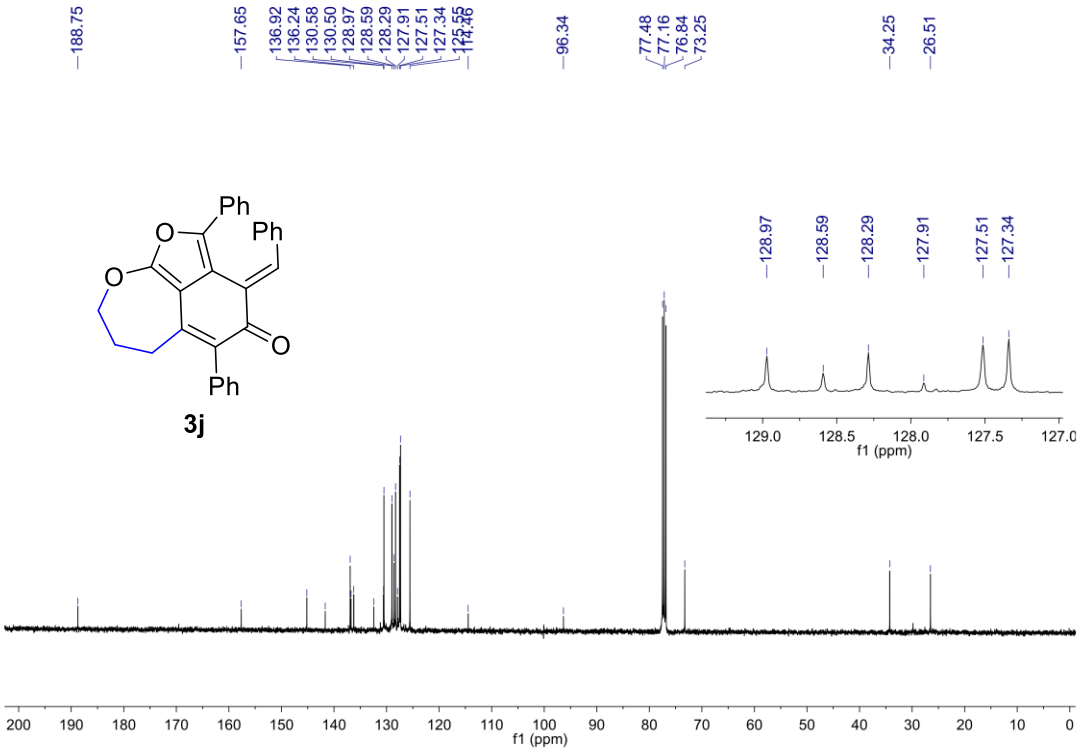
138.23
136.24
130.93
128.80
128.49
128.00
127.94
127.32
127.15
127.03
125.54
113.09
97.11
77.41
77.16
76.91
71.79
25.84
19.39
13.84
Ph
Ph
O
O
O
Et
3i
f1 (ppm)


7.62
7.45
7.44
7.43
7.41
7.36
7.34
7.26
7.26
7.23
7.23
7.21
7.19
7.17
7.12
7.10
6.97
6.96
6.95
6.94
6.92
6.89
6.87
6.87
6.86
6.84
4.51
4.50
2.79
2.77
2.76
2.11
2.11
Ph
Ph
O
O
O
Ph
3j
1.08
2.08
1.09
2.07
2.02
2.05
2.03
4.03
2.00
2.03
2.02
f1 (ppm)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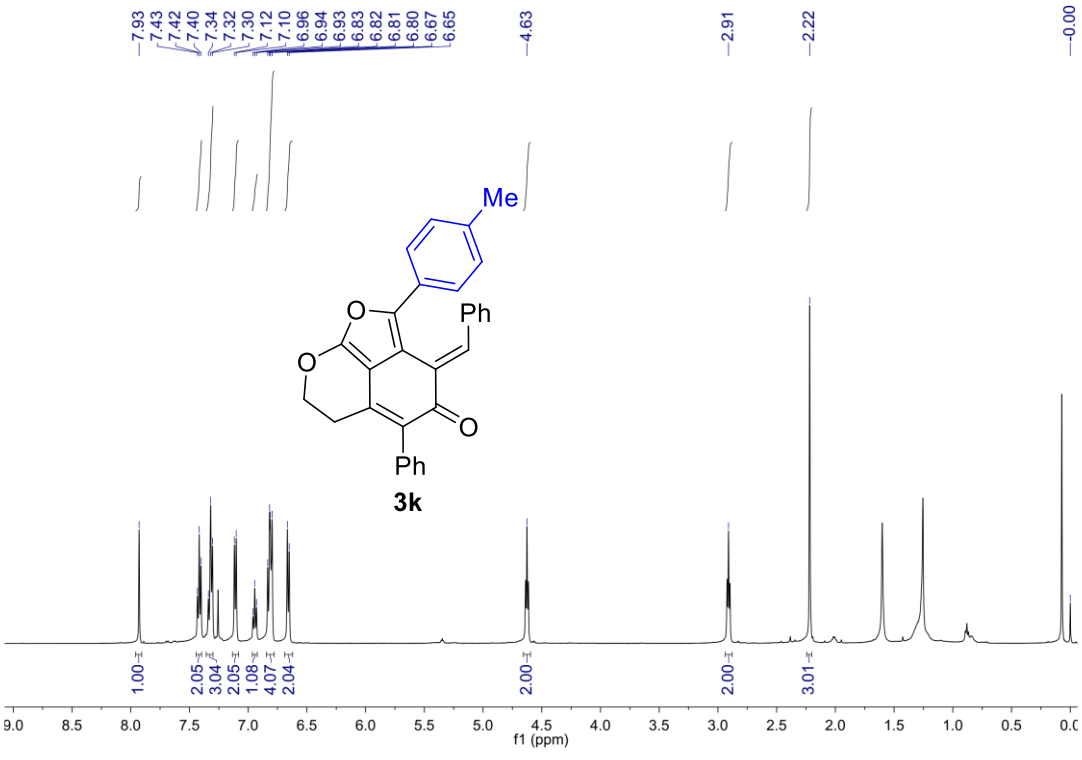
130.58
130.50
128.97
128.59
128.29
127.91
127.51
127.34
125.55
114.46
96.34
77.48
77.16
76.84
73.25
34.25
26.51
Ph
Ph
O
O
O
Ph
3j
128.97
128.59
128.29
127.91
127.51
127.34
129.0
128.5
128.0
127.5
127.0
f1 (ppm)
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)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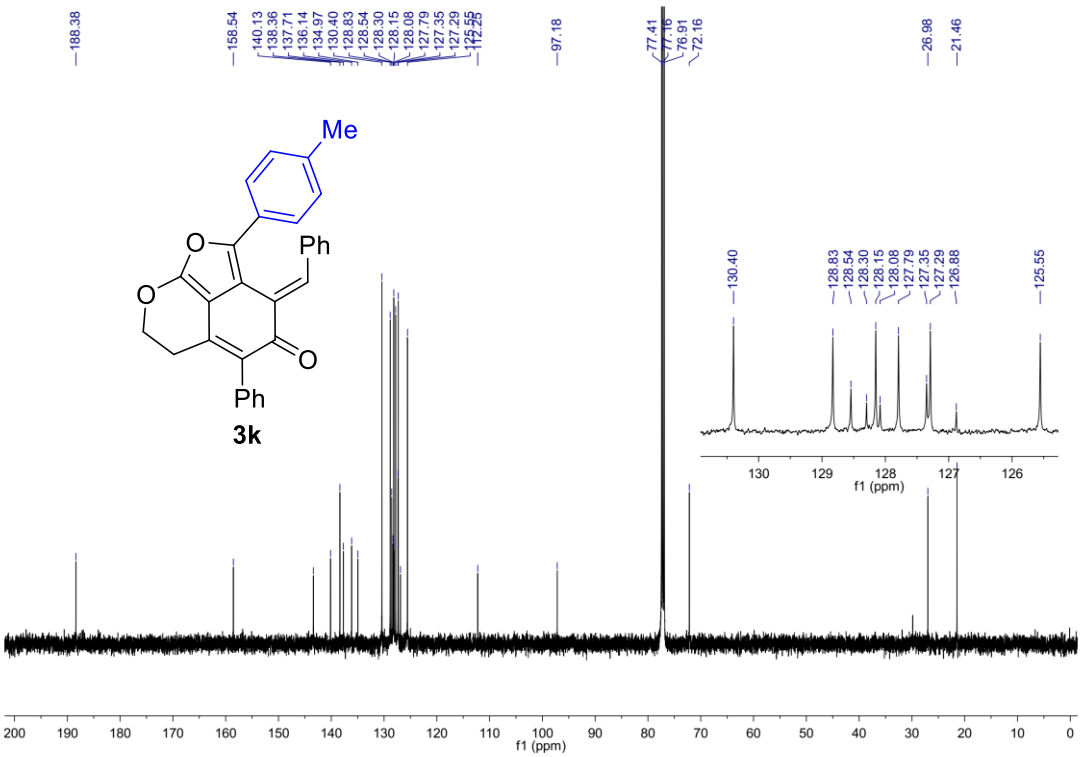
7.43
7.42
7.40
7.34
7.32
7.30
7.12
7.10
6.96
6.94
6.93
6.83
6.82
6.81
6.80
6.67
6.65
4.63
2.91
2.22
0.00
Me
O
O
Ph
O
Ph
3k
1.00
2.05
3.04
2.05
1.08
4.07
2.04
2.00
2.00
3.01
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)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137.71
136.14
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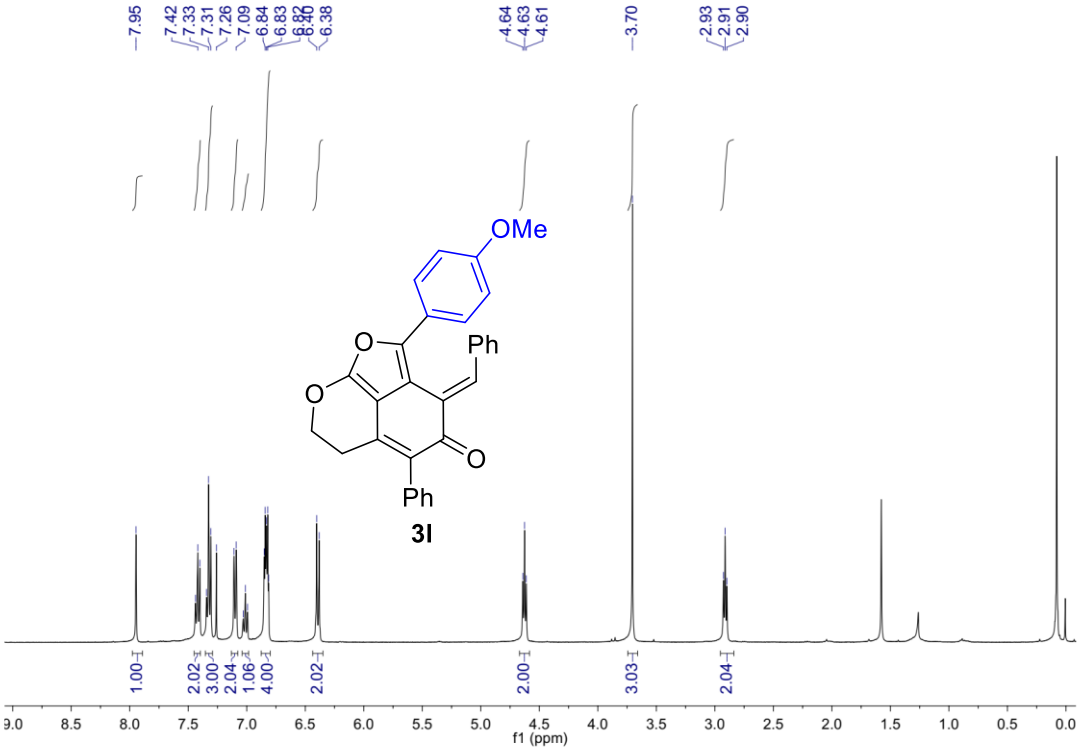
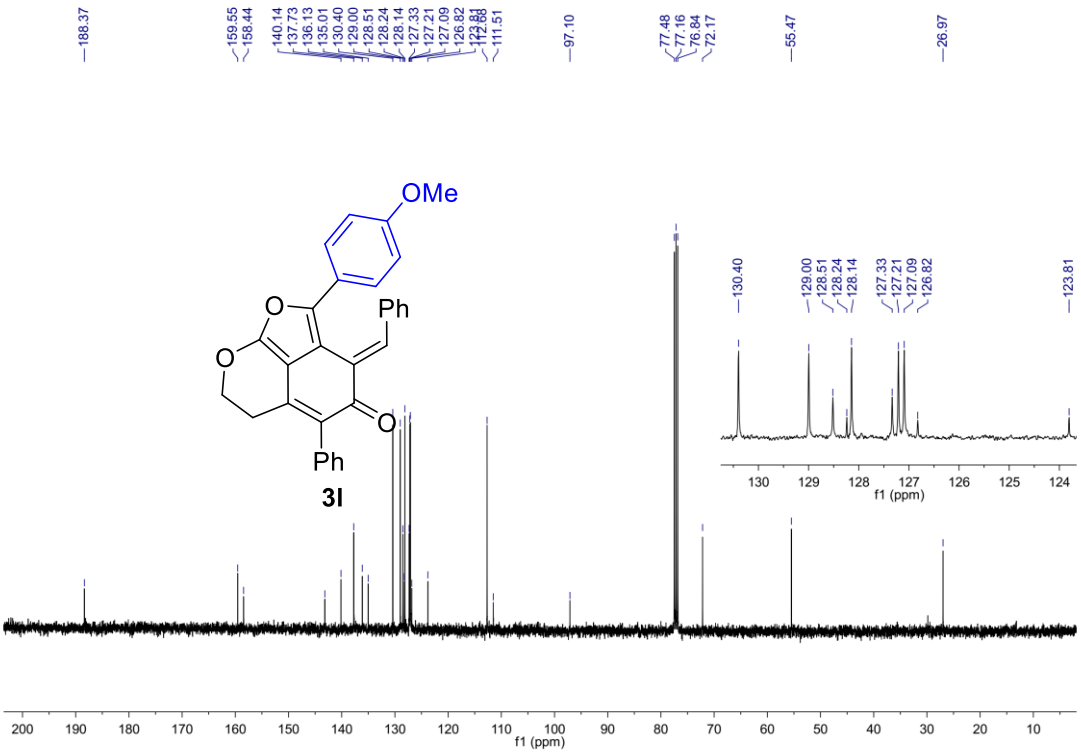
130.40
128.83
128.54
128.30
128.15
128.08
127.79
127.35
127.29
125.55
112.25
97.18
77.41
77.16
76.91
72.16
26.98
21.46
Me
O
O
Ph
Ph
O
3k
130.40
128.83
128.54
128.30
128.15
128.08
127.79
127.35
127.29
126.88
125.55
130
129
128
127
126
f1 (ppm)
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


7.95
7.42
7.33
7.31
7.26
7.09
6.84
6.83
6.82
6.40
6.38
4.64
4.63
4.61
3.70
2.93
2.91
2.90
OMe
O
O
Ph
Ph
O
3l
1.00
2.02
3.00
2.04
1.06
4.00
2.02
2.00
3.03
2.04
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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136.13
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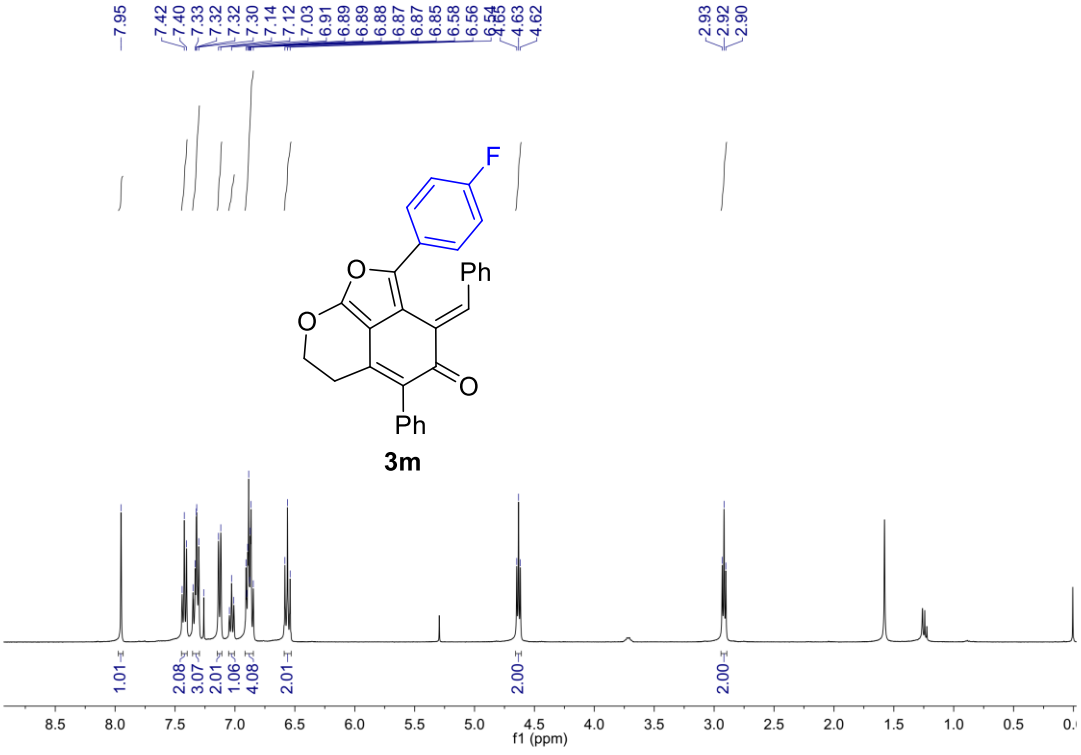
130.40
129.00
128.51
128.24
128.14
127.33
127.21
127.09
126.82
122.84
111.51
97.10
77.48
77.16
76.84
72.17
55.47
26.97
OMe
O
O
Ph
O
Ph
3l
130.40
129.00
128.51
128.24
128.14
127.33
127.21
127.09
126.82
123.81
130 129 128 127 126 125 124
f1 (ppm)
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
f1 (ppm)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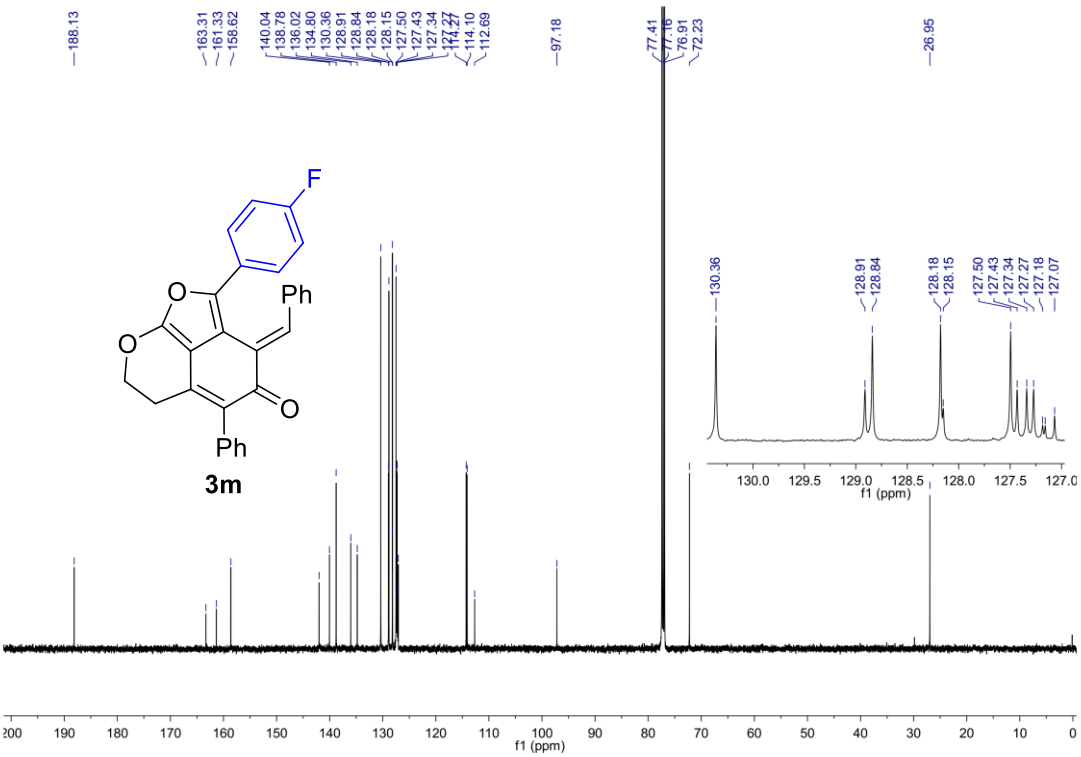
7.42
7.40
7.33
7.32
7.32
7.30
7.14
7.12
7.03
6.91
6.89
6.89
6.88
6.87
6.87
6.85
6.58
6.56
4.63
4.62
2.93
2.92
2.90
F
O
O
Ph
O
Ph
3m
1.01
2.08
3.07
2.01
1.06
4.08
2.01
2.00
2.00
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
f1 (ppm)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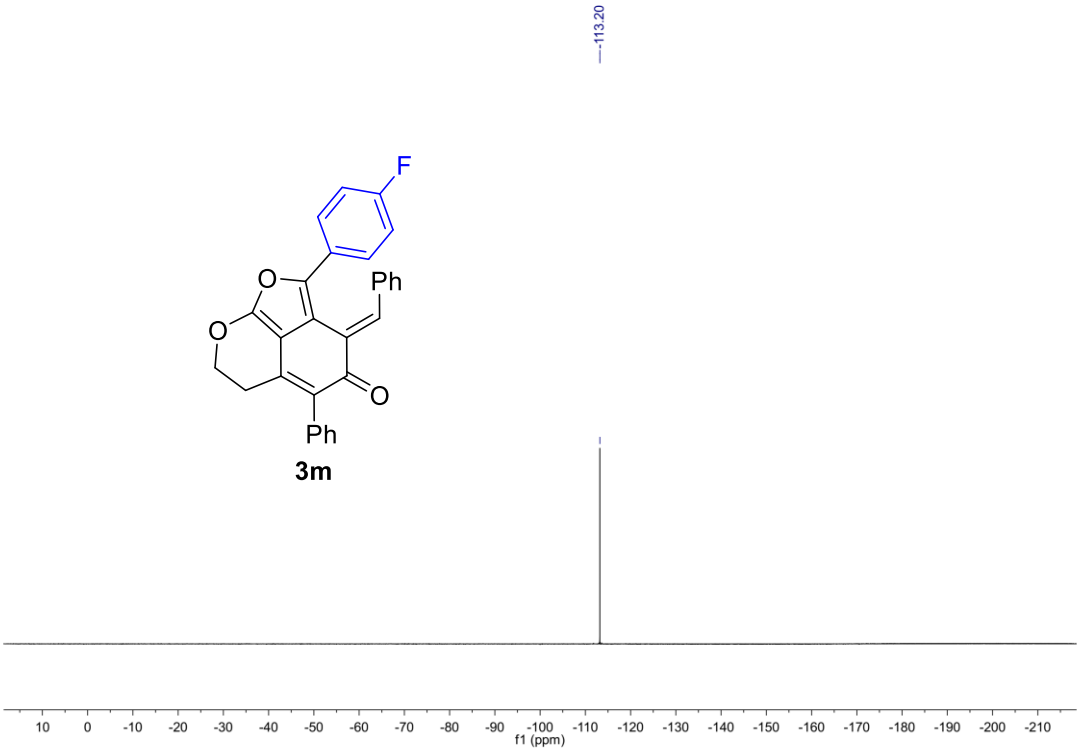
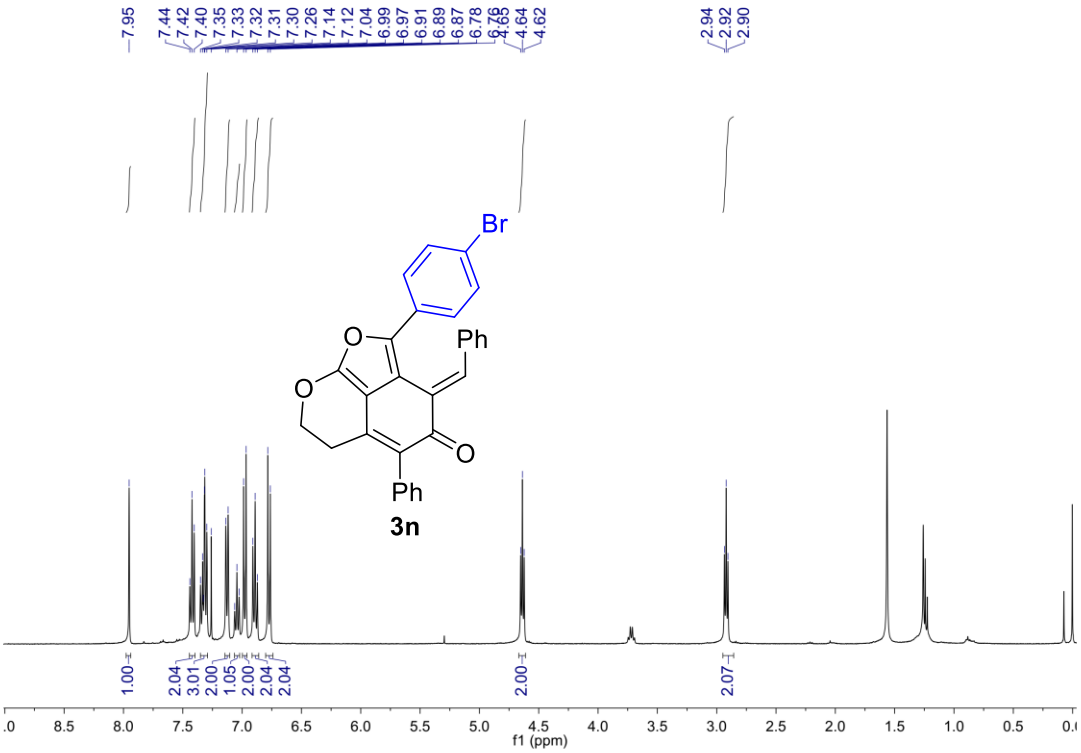
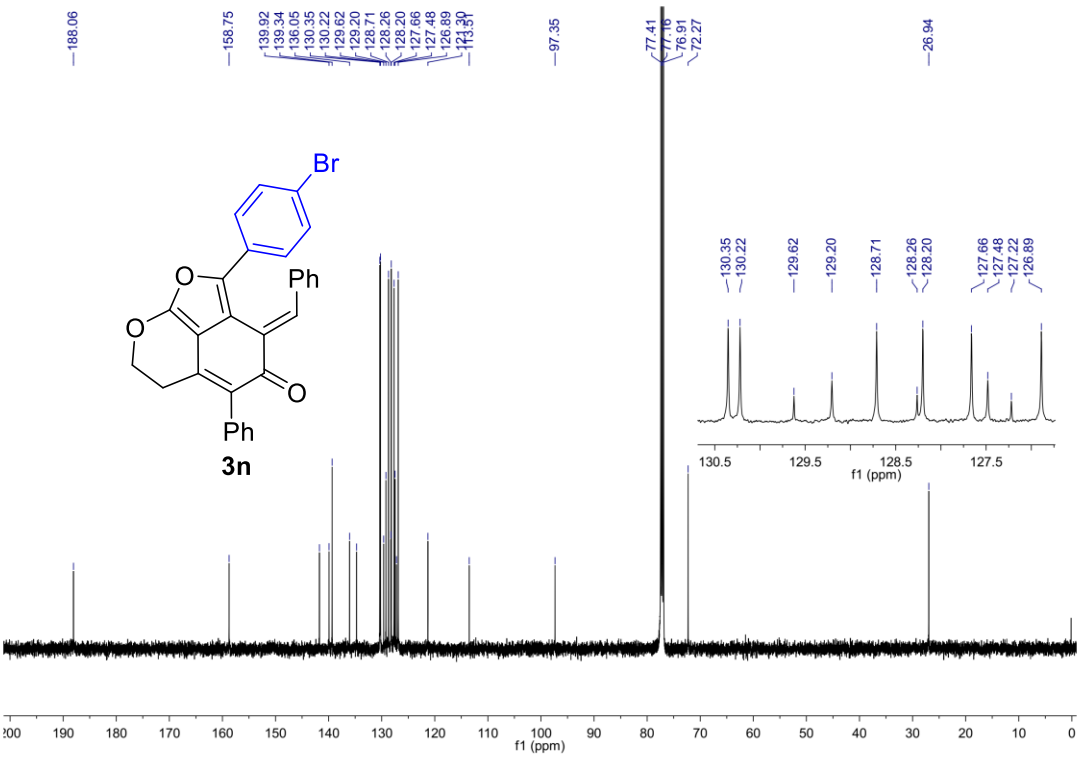
163.31
161.33
158.62
140.04
138.78
136.02
134.80
130.36
128.91
128.84
128.18
128.15
127.50
127.43
127.34
114.10
112.69
97.18
77.41
76.91
72.23
26.95
F
O
O
Ph
O
Ph
3m
130.36
128.91
128.84
128.18
128.15
127.50
127.43
127.34
127.27
127.18
127.07
f1 (ppm)
f1 (ppm)


113.20
F
O
O
Ph
O
Ph
3m
f1 (ppm)


7.95
7.44
7.42
7.40
7.35
7.33
7.32
7.31
7.30
7.26
7.14
7.12
7.04
6.99
6.97
6.91
6.89
6.87
6.78
4.64
4.62
2.94
2.92
2.90
Br
O
O
Ph
O
Ph
3n
1.00
2.04
3.01
2.00
1.05
2.00
2.04
2.04
2.00
2.07
f1 (ppm)


188.06
158.75
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139.34
136.05
130.35
130.22
129.62
129.20
128.71
128.26
128.20
127.66
127.48
126.89
97.35
77.41
77.16
76.91
72.27
26.94
Br
O
O
Ph
O
Ph
3n
130.35
130.22
129.62
129.20
128.71
128.26
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127.48
127.22
126.89
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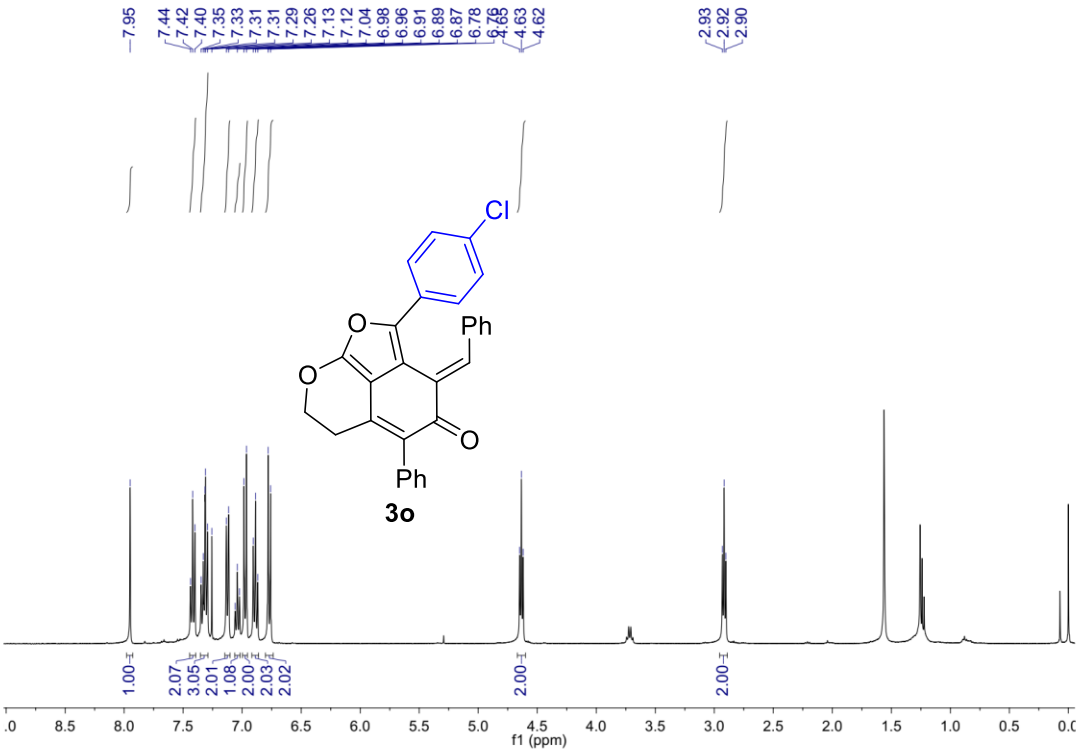
129.5
128.5
127.5
f1 (ppm)
f1 (ppm)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7.31
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7.26
7.13
7.12
7.04
6.98
6.96
6.91
6.89
6.87
6.78
4.63
4.62
2.93
2.92
2.90
Cl
O
O
Ph
O
Ph
3o
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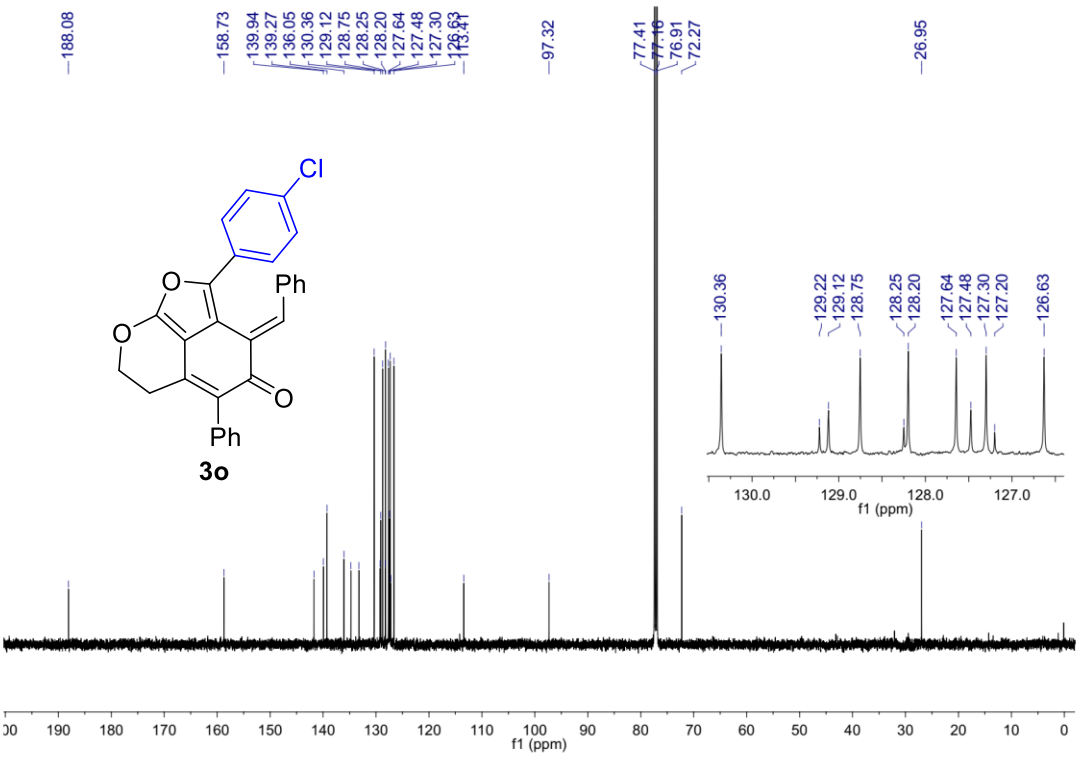
3.05
2.01
1.08
2.00
2.03
2.02
2.00
2.00
f1 (ppm)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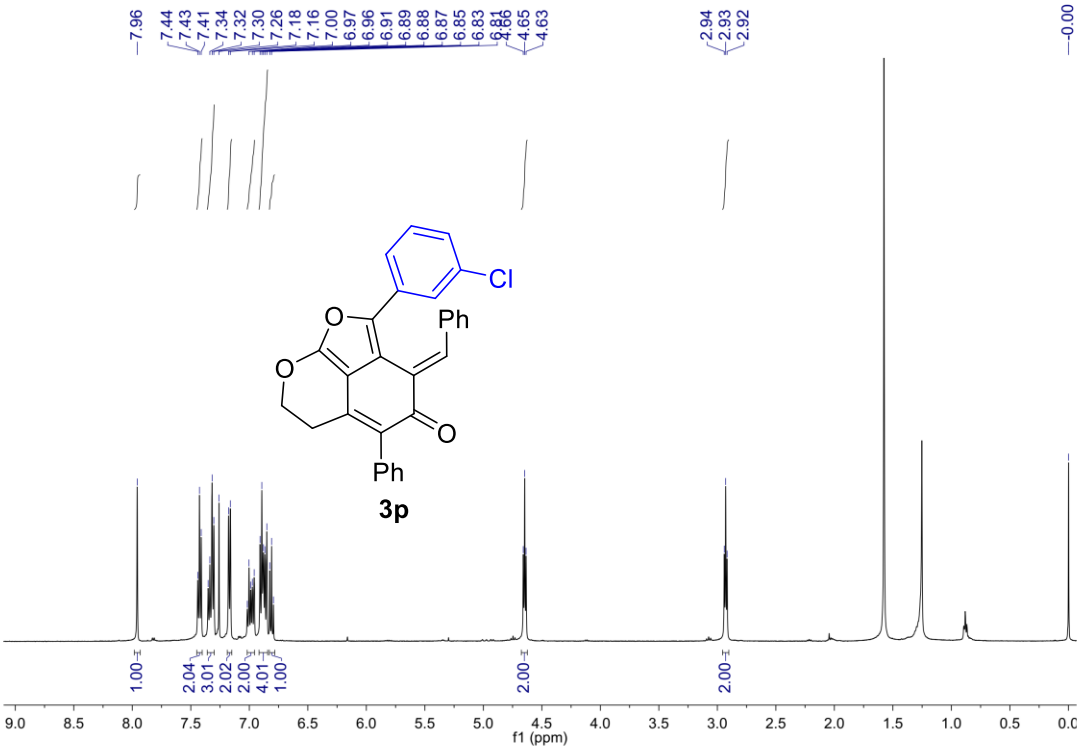
139.94
139.27
136.05
130.36
129.12
128.75
128.25
128.20
127.64
127.48
127.30
97.32
77.41
76.91
72.27
26.95
Cl
O
O
Ph
O
Ph
3o
130.36
129.22
129.12
128.75
128.25
128.20
127.64
127.48
127.30
127.20
126.63
f1 (ppm)
f1 (ppm)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7.34
7.32
7.30
7.26
7.18
7.16
7.00
6.97
6.96
6.91
6.89
6.88
6.87
6.85
6.83
4.65
4.63
2.94
2.93
2.92
0.00
Cl
O
O
Ph
O
Ph
3p
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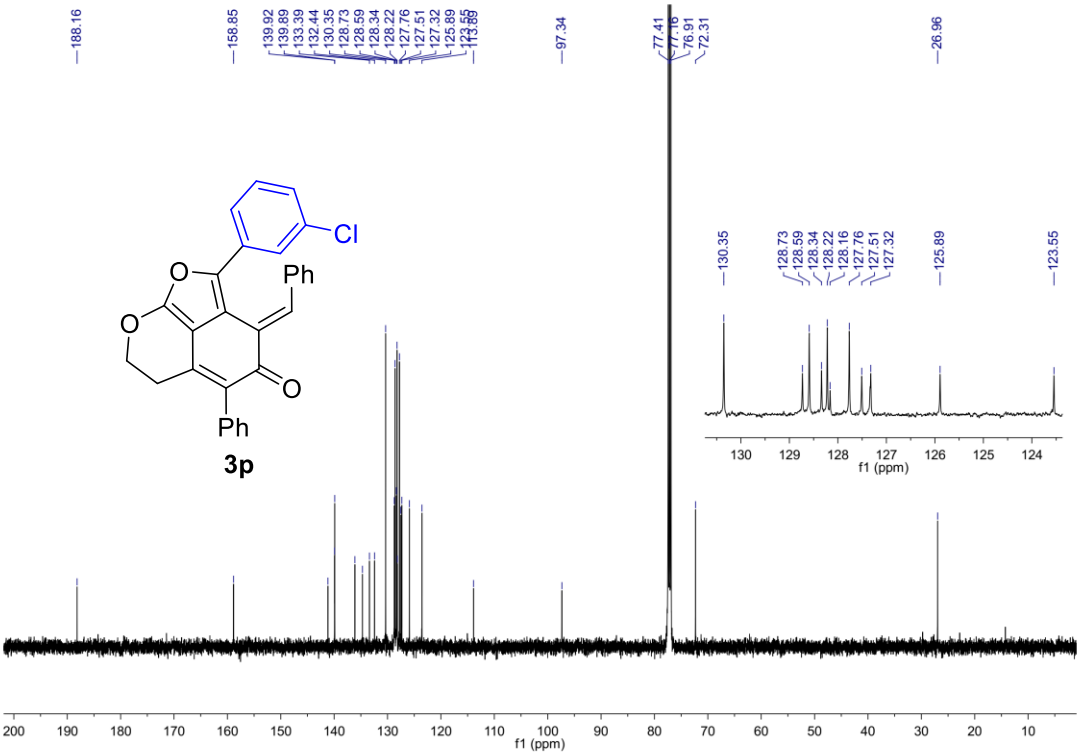
3.01
2.02
2.00
4.01
1.00
2.00
2.00
f1 (ppm)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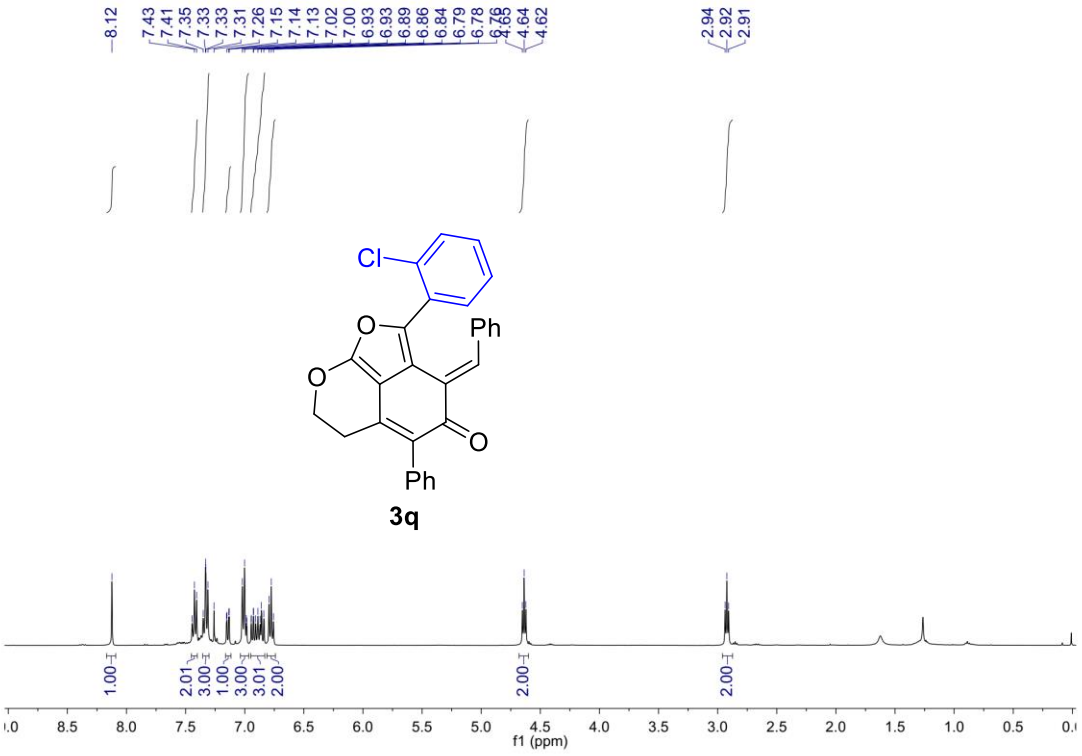
127.76
127.51
127.32
125.89
123.55
97.34
77.41
77.16
76.91
72.31
26.96
Cl
O
O
Ph
O
Ph
3p
130.35
128.73
128.59
128.34
128.22
128.16
127.76
127.51
127.32
125.89
123.55
f1 (ppm)
f1 (ppm)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7.31
7.26
7.15
7.14
7.13
7.02
7.00
6.93
6.93
6.89
6.86
6.84
6.79
6.78
4.65
4.64
4.62
2.94
2.92
2.91
Cl
O
O
Ph
O
Ph
3q
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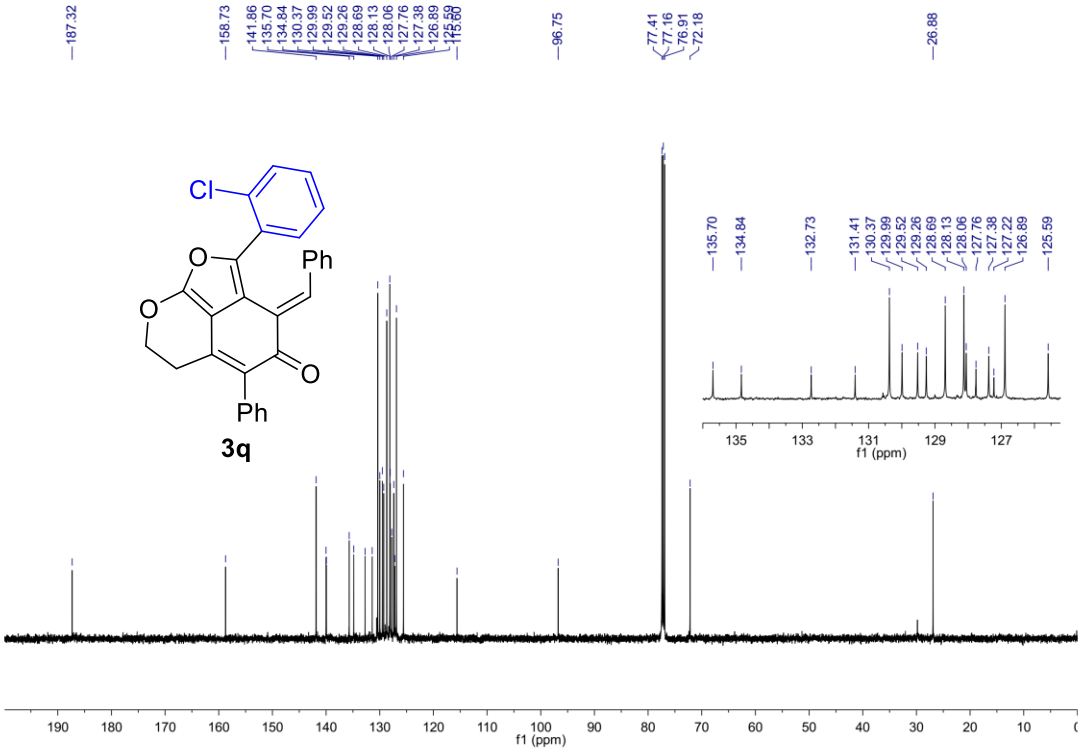
2.01
3.00
1.00
3.00
3.01
2.00
2.00
2.00
f1 (ppm)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129.52
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128.69
128.13
128.06
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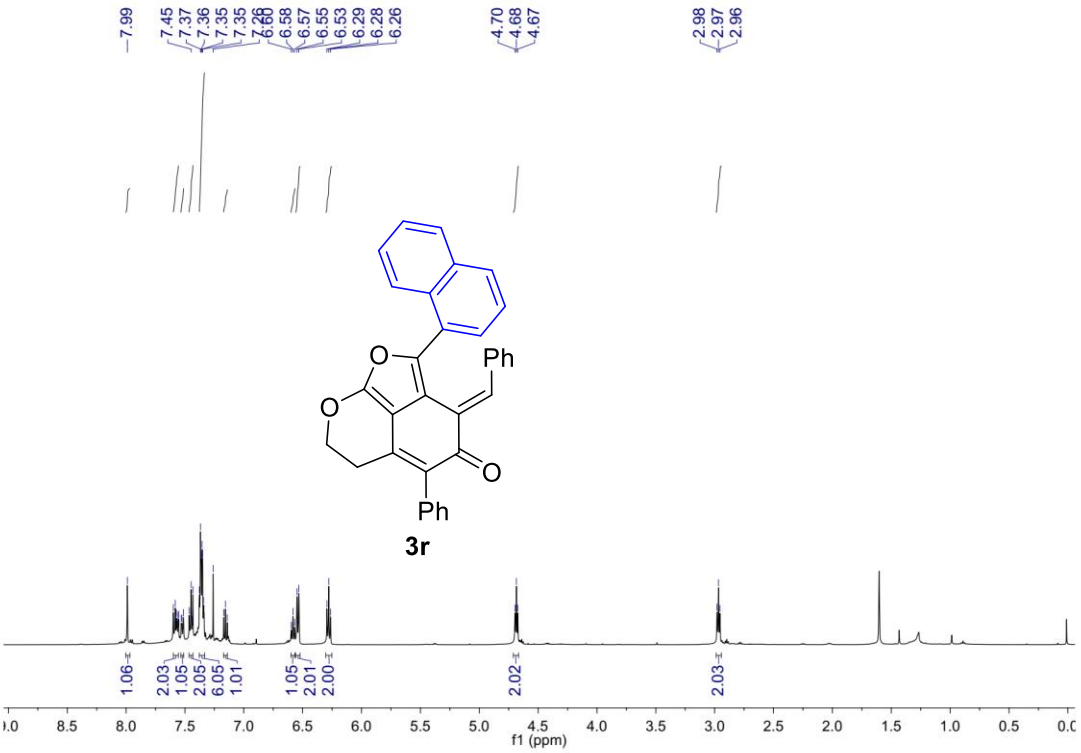
127.38
126.89
96.75
77.41
77.16
76.91
72.18
26.88
135.70
134.84
132.73
131.41
130.37
129.99
129.52
129.26
128.69
128.13
128.06
127.76
127.38
127.22
126.89
125.59
Cl
O
O
Ph
O
Ph
3q
f1 (ppm)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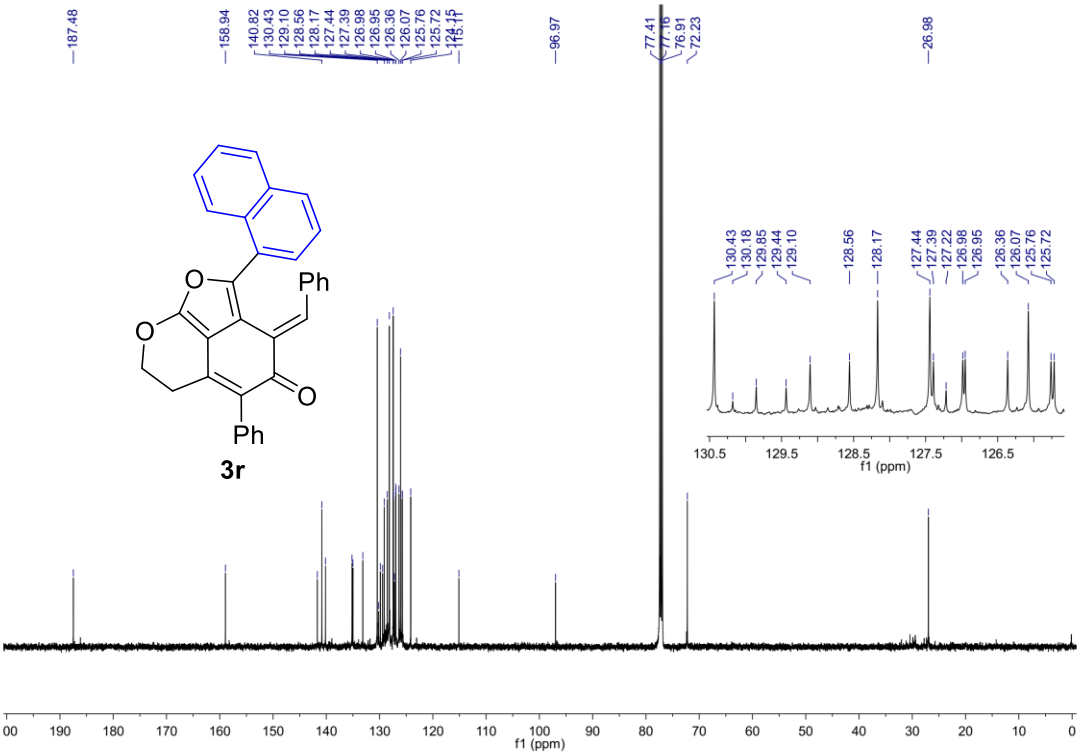
7.36
7.35
7.35
6.58
6.57
6.55
6.53
6.29
6.28
6.26
4.70
4.68
4.67
2.98
2.97
2.96
O
O
Ph
O
Ph
3r
1.06
2.03
1.05
2.05
6.05
1.01
1.05
2.01
2.00
2.02
2.03
f1 (ppm)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127.44
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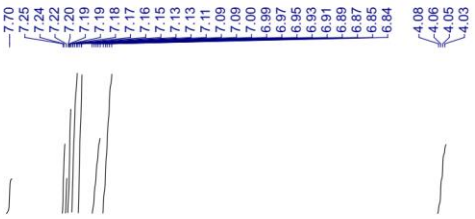
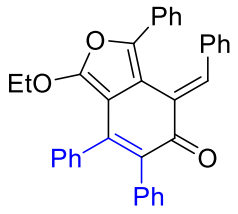
126.98
126.95
126.36
126.07
125.76
125.72
96.97
77.41
77.16
76.91
72.23
26.98
130.43
130.18
129.85
129.44
129.10
128.56
128.17
127.44
127.39
127.22
126.98
126.95
126.36
126.07
125.76
125.72
O
O
Ph
O
Ph
3r
f1 (ppm)





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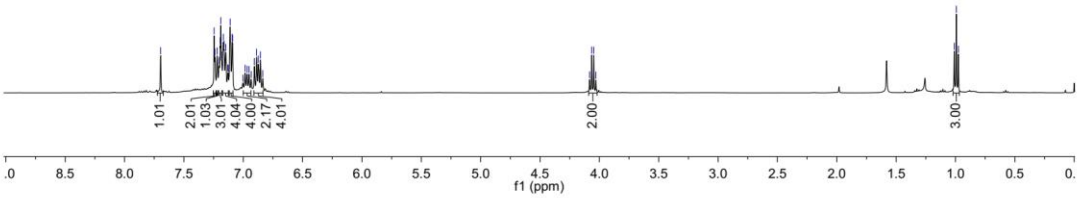
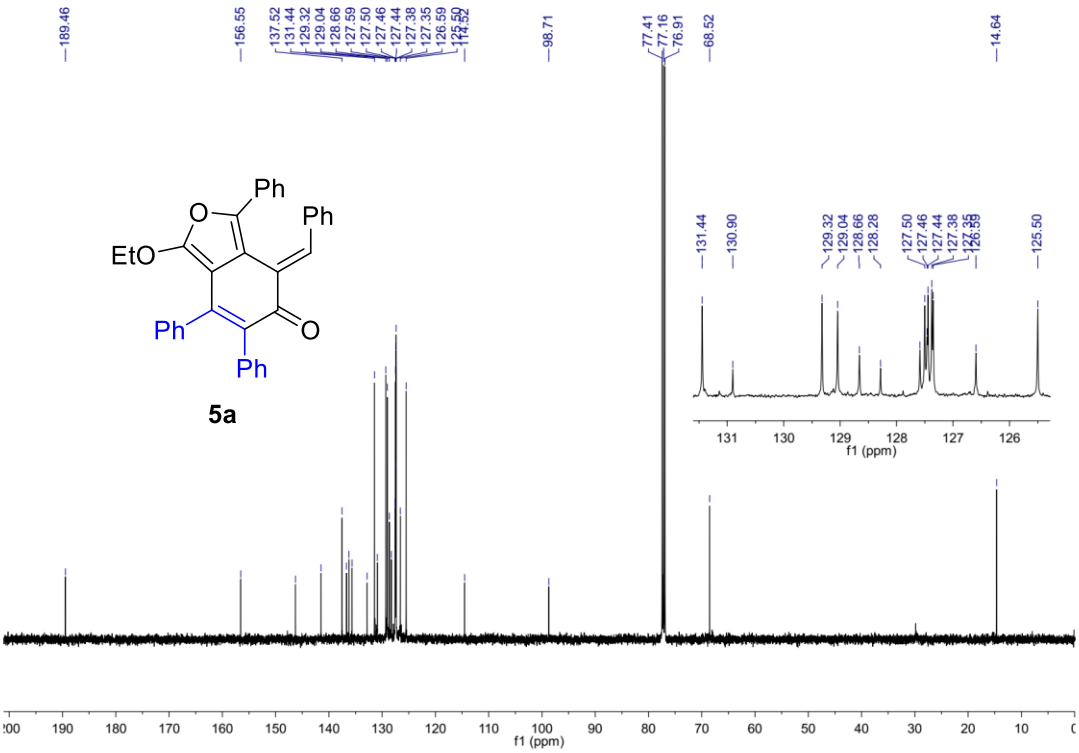
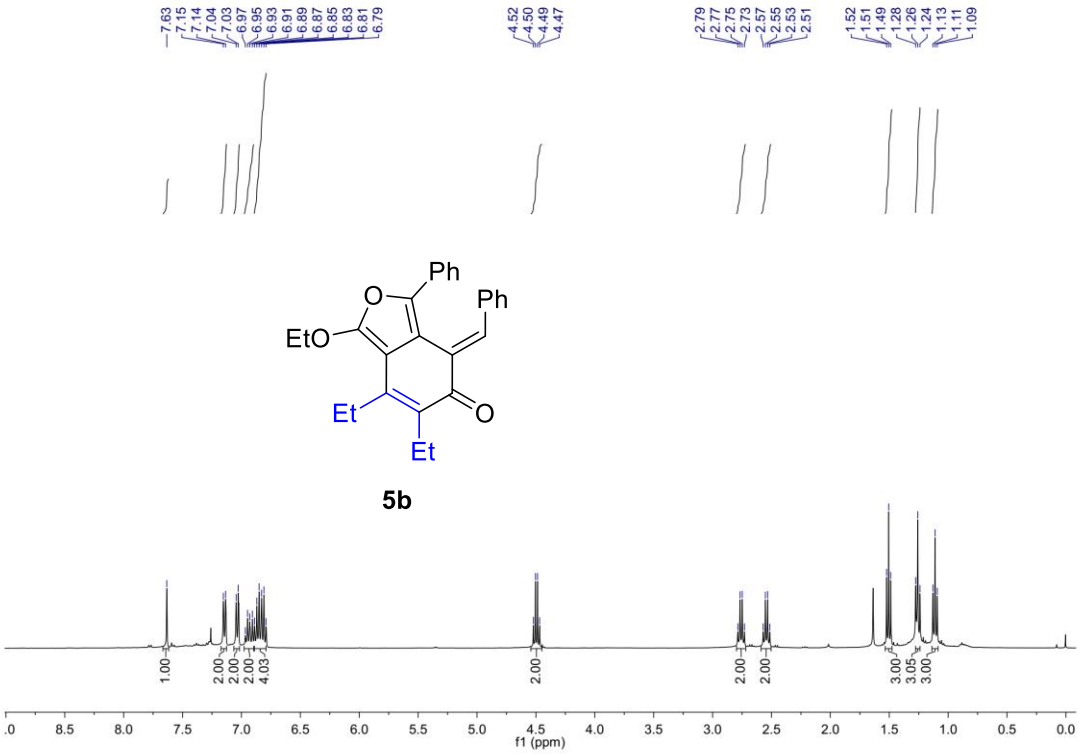




5a


7.63
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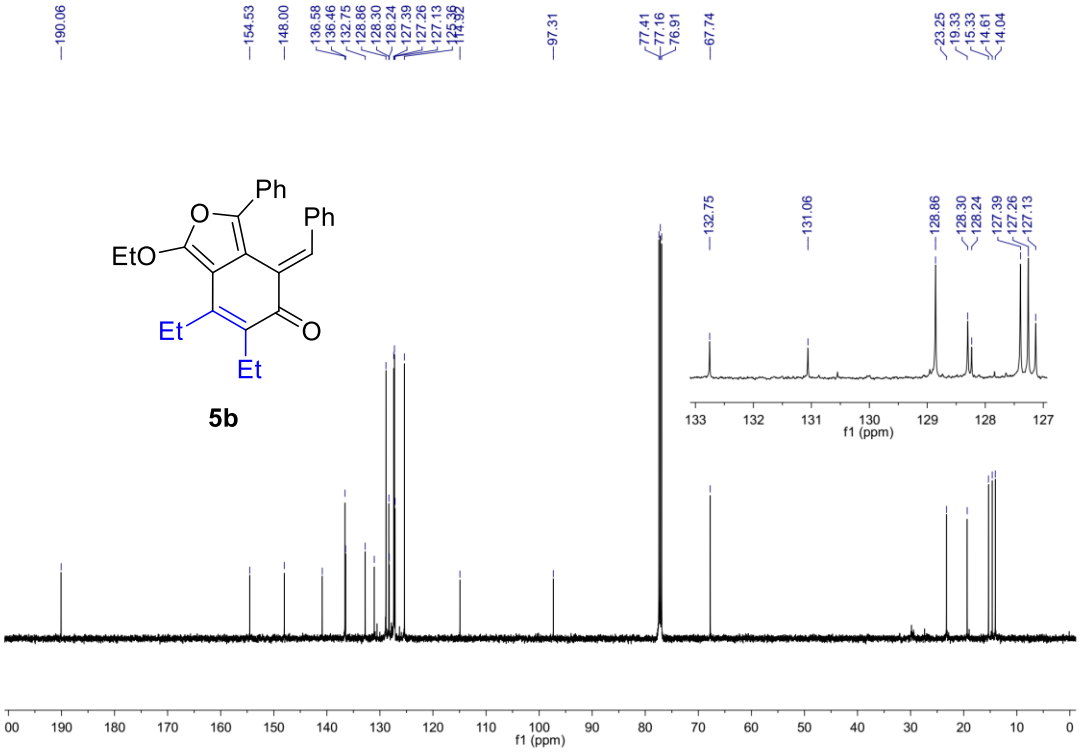
7.04
7.03
6.97
6.95
6.93
6.91
6.89
6.87
6.85
6.83
6.81
6.79
4.52
4.50
4.49
4.47
2.79
2.77
2.75
2.73
2.57
2.55
2.53
2.51
1.52
1.51
1.49
1.28
1.26
1.24
1.13
1.11
1.09
Ph
O
Ph
EtO
Et
O
Et
1.00
2.00
2.00
2.00
4.03
2.00
2.00
2.00
3.00
3.05
3.00
f1 (ppm)

5b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154.53
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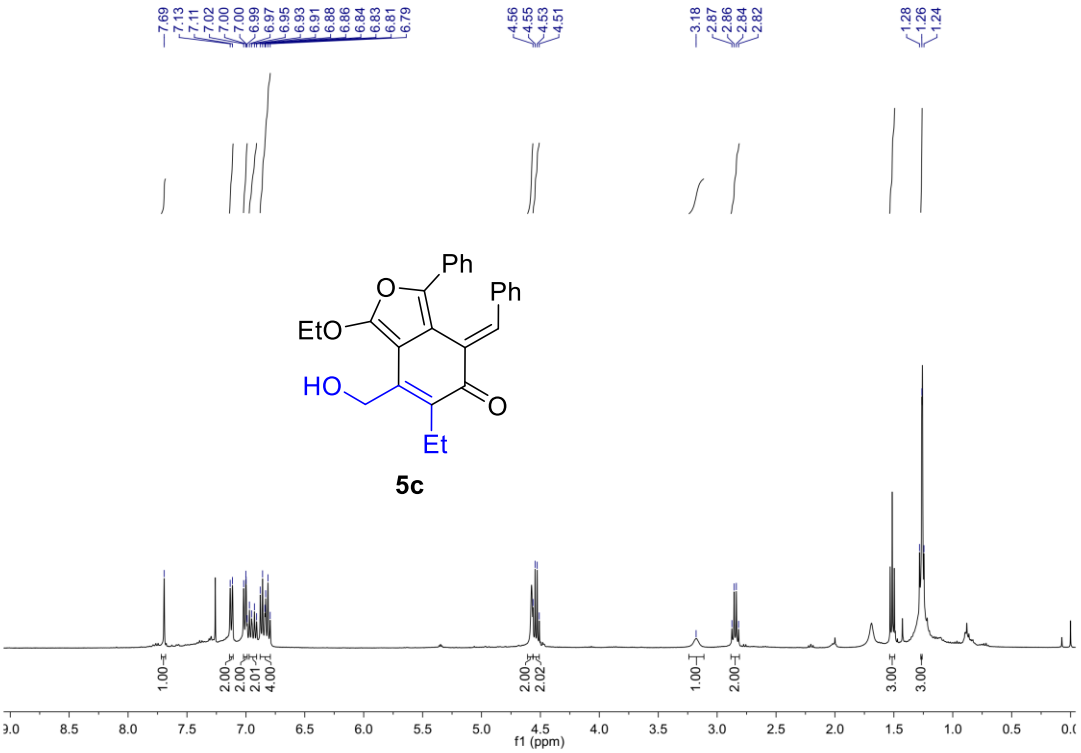
136.46
132.75
128.86
128.30
128.24
127.39
127.26
127.13
97.31
77.41
77.16
76.91
67.74
23.25
19.33
15.33
14.61
14.04
Ph
O
Ph
EtO
Et
O
Et
132.75
131.06
128.86
128.30
128.24
127.39
127.26
127.13
f1 (ppm)

5b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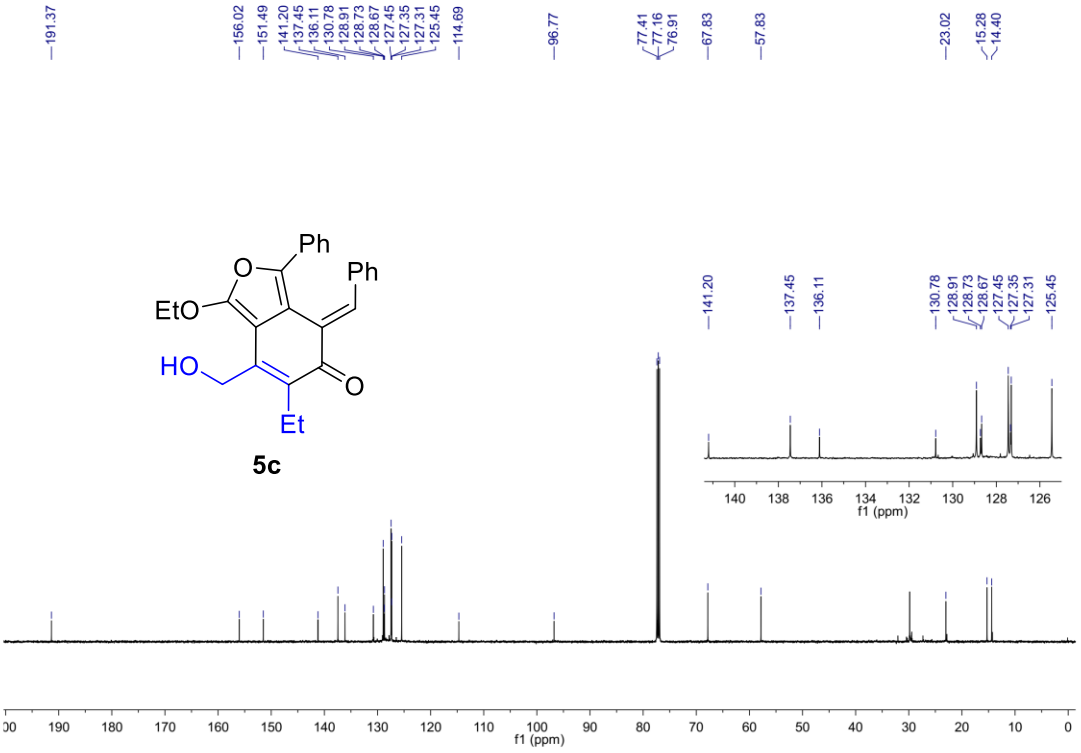
7.00
6.99
6.97
6.95
6.93
6.91
6.88
6.86
6.84
6.83
6.81
6.79
4.56
4.55
4.53
4.51
3.18
2.87
2.86
2.84
2.82
1.28
1.26
1.24
Ph
O
Ph
EtO
HO
O
Et
1.00
2.00
2.00
2.01
4.00
2.00
2.02
1.00
2.00
3.00
3.00
f1 (ppm)

5c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141.20
137.45
136.11
130.78
128.91
128.73
128.67
127.45
127.35
127.31
125.45
114.69
96.77
77.41
77.16
76.91
67.83
57.83
23.02
15.28
14.40
Ph
O
Ph
EtO
HO
O
Et
141.20
137.45
136.11
130.78
128.91
128.73
128.67
127.45
127.35
127.31
125.45
f1 (ppm)
f1 (ppm)

5c


7.84
7.82
7.79
7.79
7.77
7.46
7.44
7.43
7.42
7.41
7.40
7.39
7.20
7.18
7.04
7.02
6.99
6.97
6.96
6.94
6.89
6.87
6.87
6.85
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4.32
4.10
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4.06
4.04
3.17
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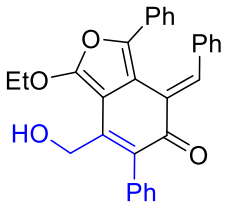
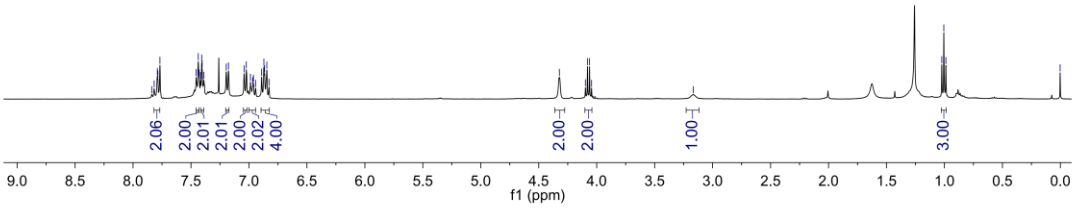
1.01
0.99
0.00


Ph
O
Ph
EtO
HO
O
Ph

5d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2.00
2.02
4.00
2.00
2.00
1.00
3.00
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)


191.94
157.00
147.75
137.77
129.05
128.88
128.48
128.46
128.10
127.61
127.52
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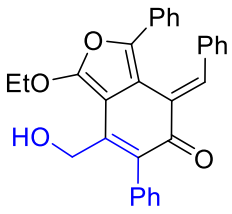
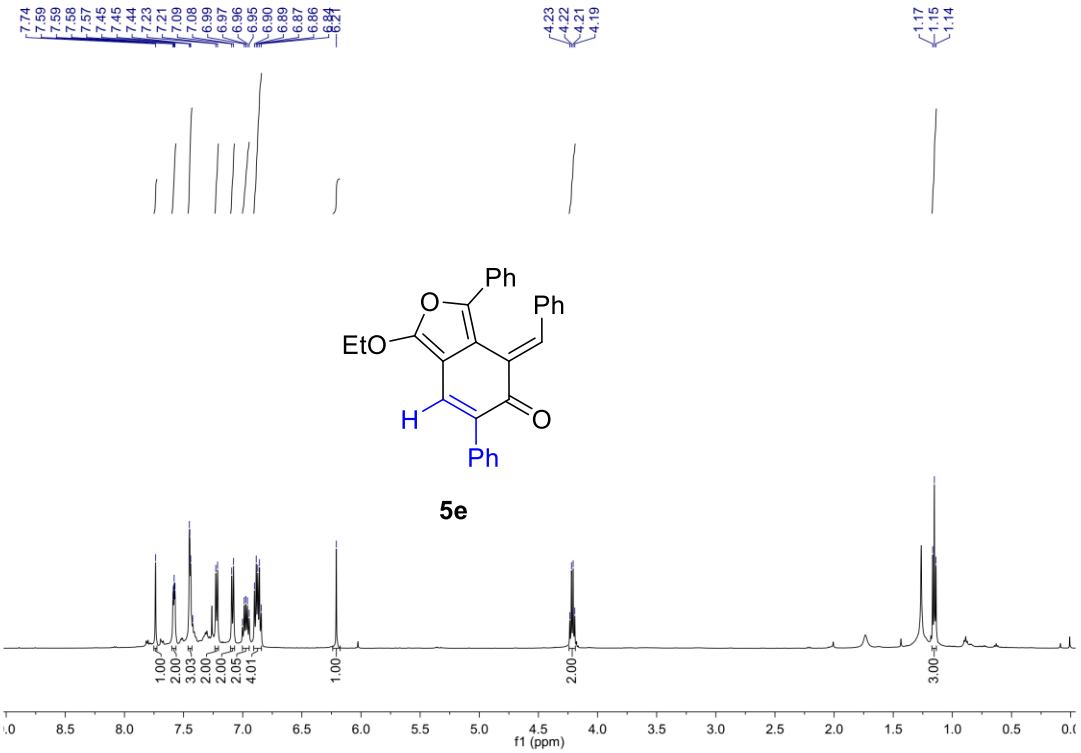
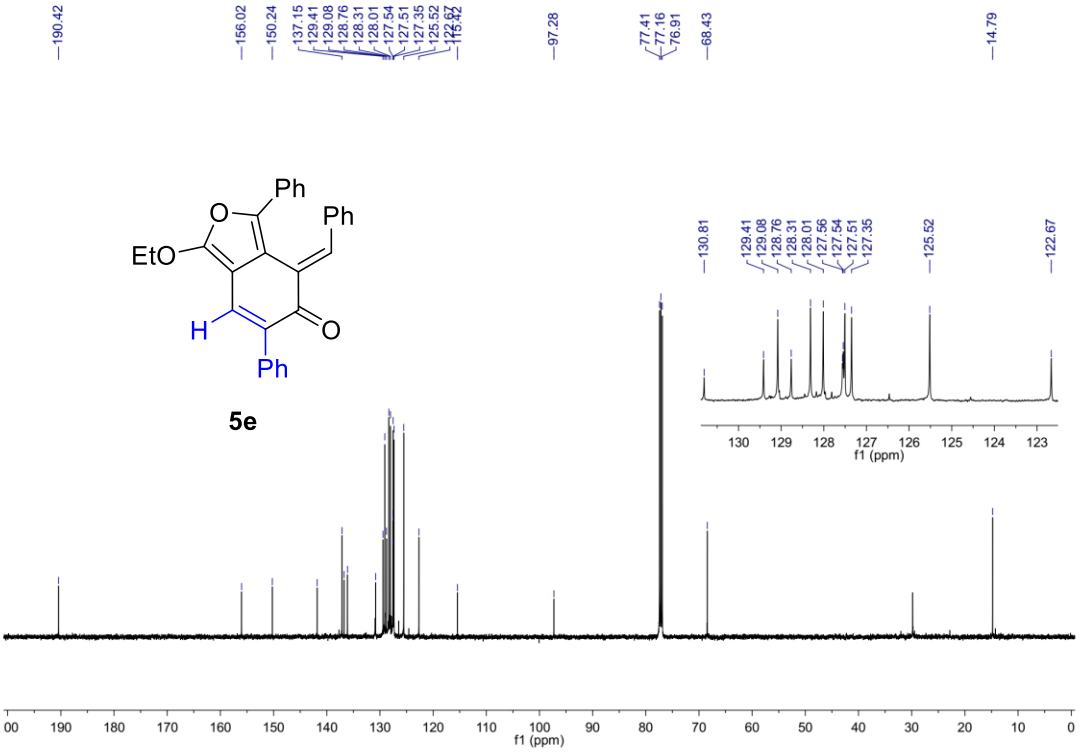
77.41
77.16
76.91
68.40
59.23
14.63

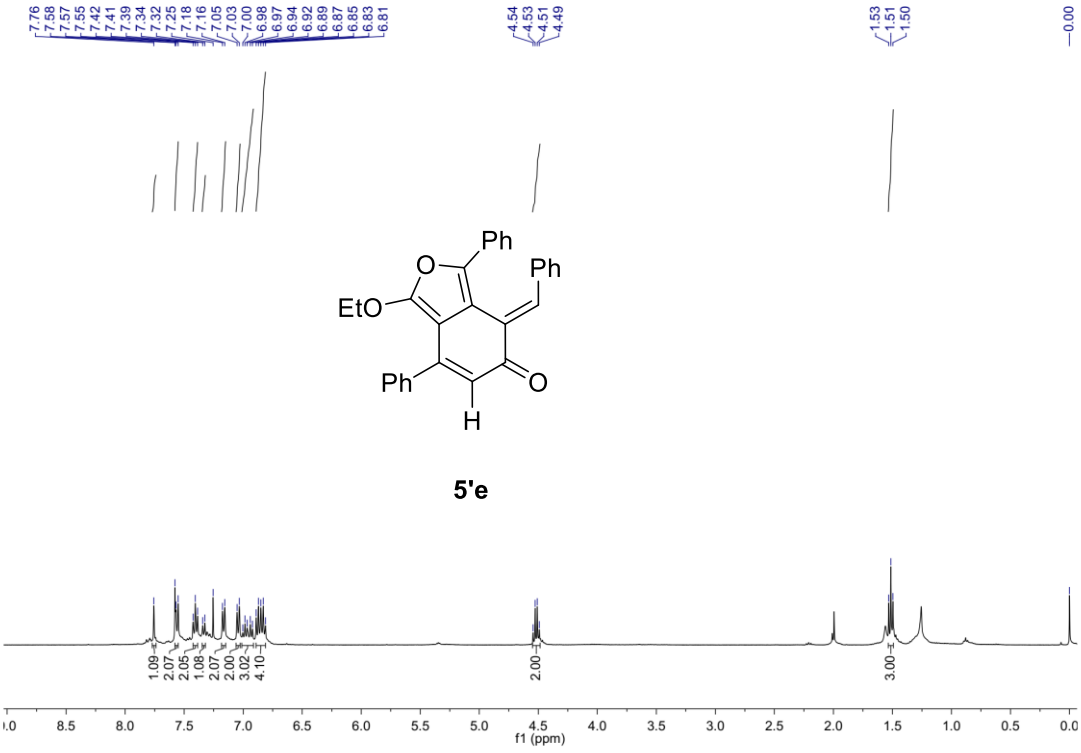

Ph
O
Ph
EtO
HO
O
Ph

5d

129.59
129.05
128.88
128.48
128.46
128.10
127.61
127.52
127.39
127.34
129.5
129.0
128.5
128.0
127.5
f1 (ppm)
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
EtO
H
O
Ph
5e
f1 (ppm)


Ph
Ph
O
EtO
H
O
Ph
5e
f1 (ppm)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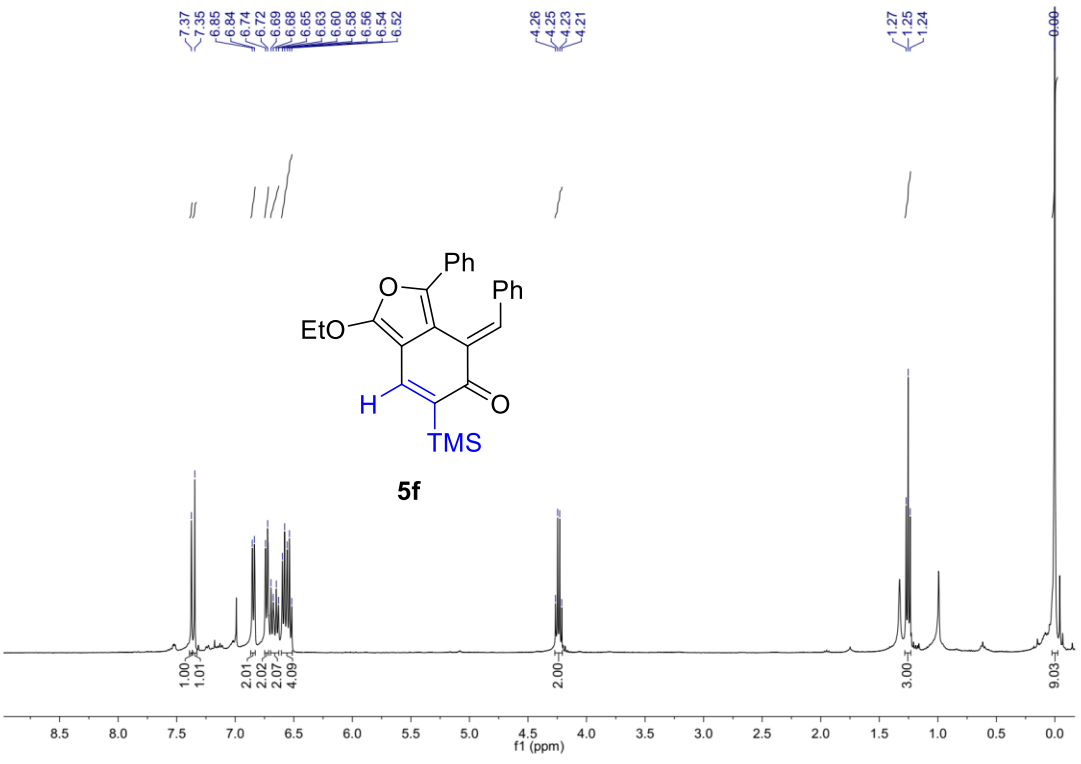
7.41
7.39
7.34
7.32
7.25
7.18
7.16
7.05
7.03
7.00
6.98
6.97
6.94
6.92
6.89
6.87
6.85
6.83
6.81
4.54
4.53
4.51
4.49
1.53
1.51
1.50
0.00
Ph
O
Ph
EtO
Ph
O
H
1.09
2.07
2.05
1.08
2.07
2.00
3.02
4.10
2.00
3.00
f1 (ppm)

5'e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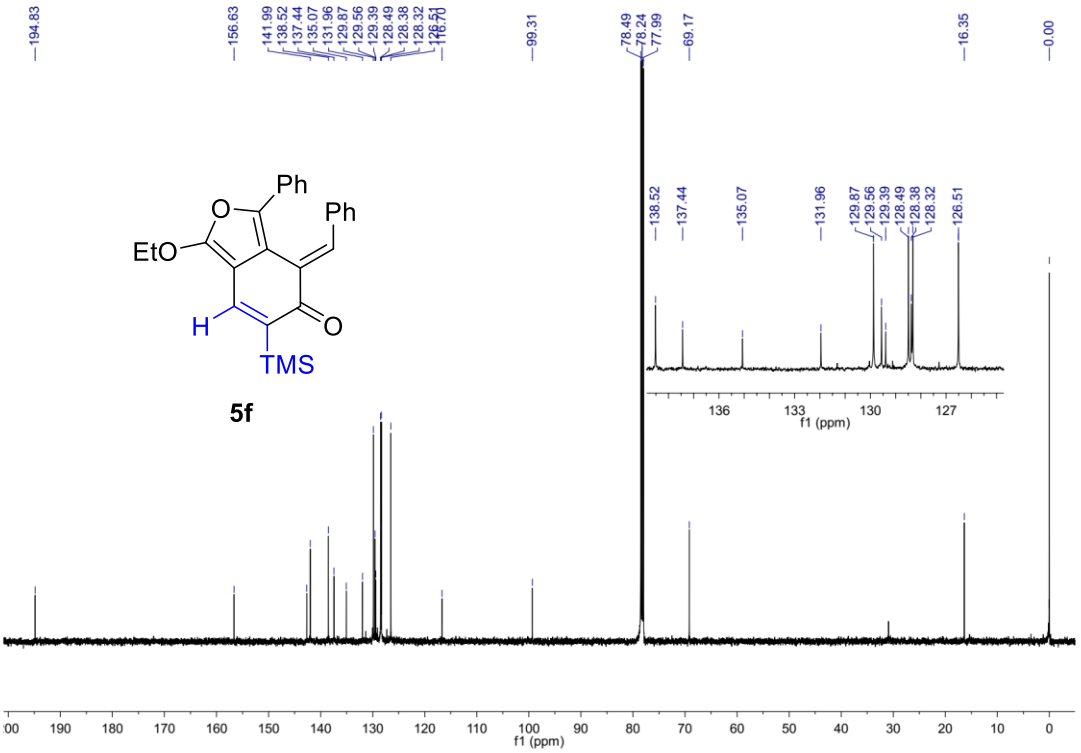
6.84
6.74
6.72
6.69
6.68
6.65
6.63
6.60
6.58
6.56
6.54
6.52
4.26
4.25
4.23
4.21
1.27
1.25
1.24
0.00
Ph
O
Ph
EtO
H
O
TMS
1.00
1.01
2.01
2.02
2.07
4.09
2.00
3.00
9.03
f1 (ppm)

5f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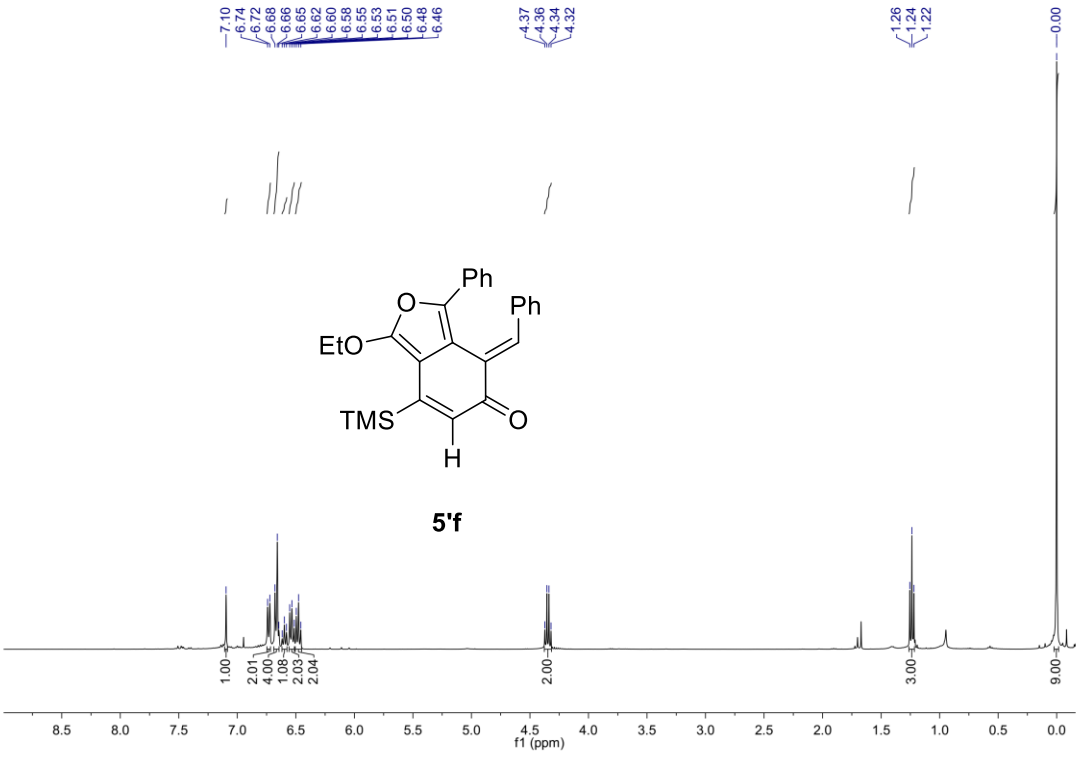
135.07
131.96
129.87
129.56
129.39
128.49
128.38
128.32
126.51
116.70
99.31
78.49
78.24
77.99
69.17
16.35
0.00
Ph
O
Ph
EtO
H
O
TMS
5f
138.52
137.44
135.07
131.96
129.87
129.56
129.39
128.49
128.38
128.32
126.51
136
133
130
127
f1 (ppm)
f1 (ppm)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6.74
6.72
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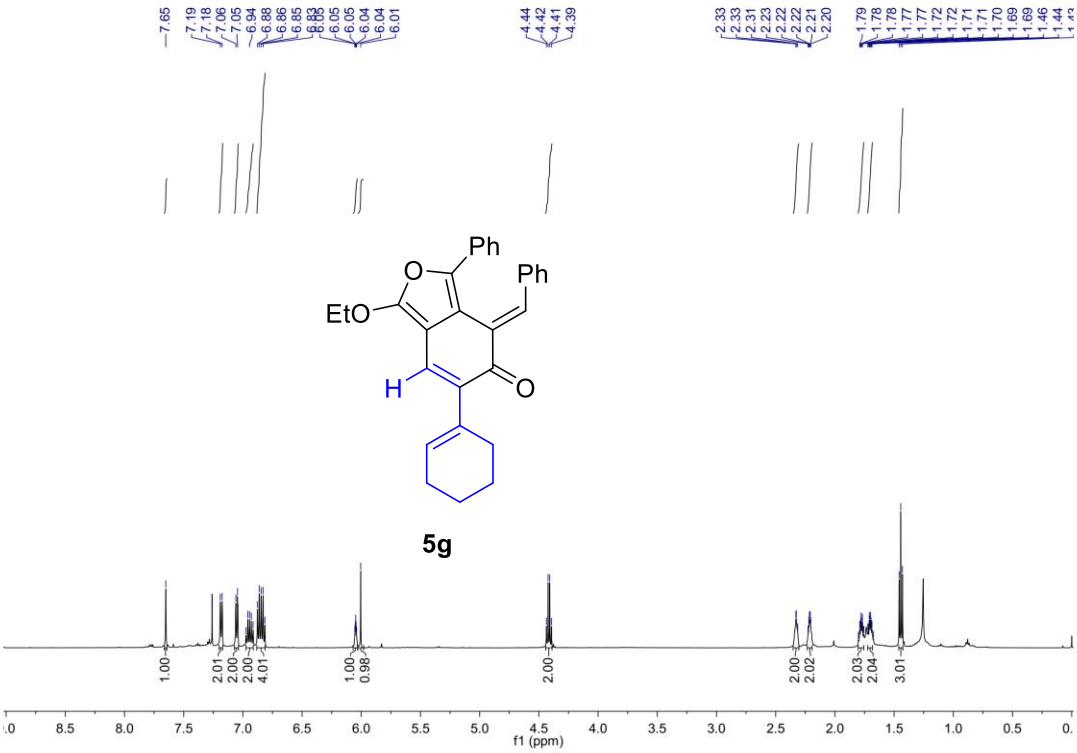
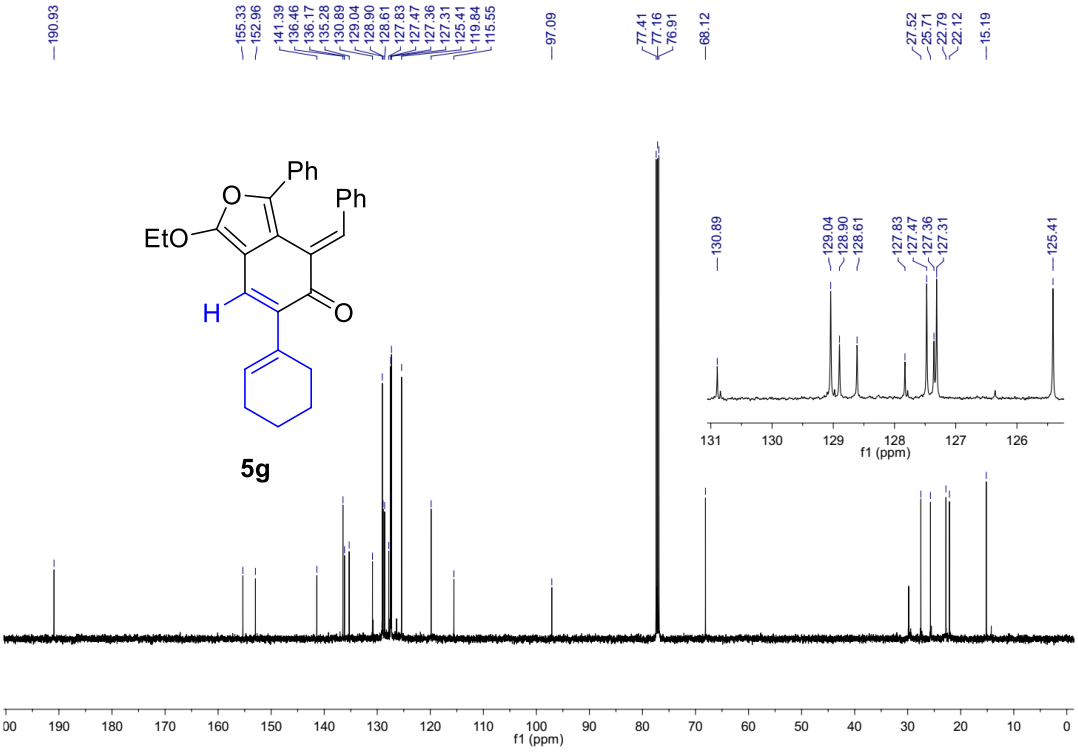
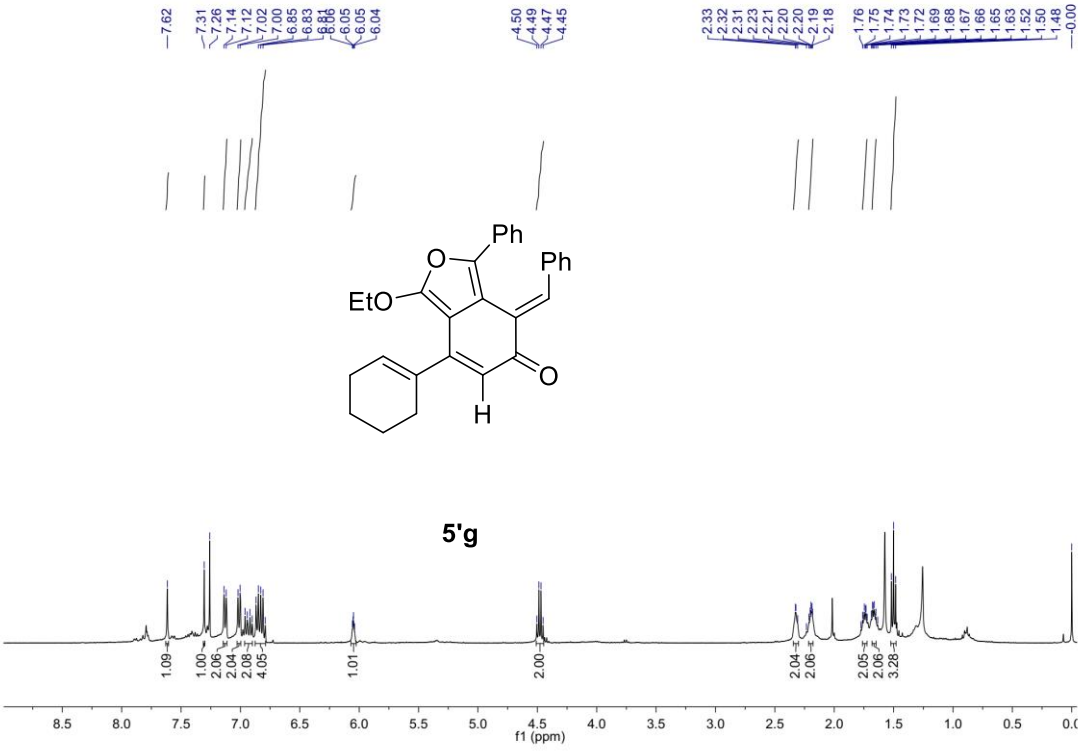
6.66
6.65
6.62
6.60
6.58
6.55
6.53
6.51
6.50
6.48
6.46
4.37
4.36
4.34
4.32
1.26
1.24
1.22
0.00
Ph
O
Ph
EtO
TMS
O
H
5'f
1.00
2.01
4.00
1.08
2.03
2.04
2.00
3.00
9.00
f1 (ppm)

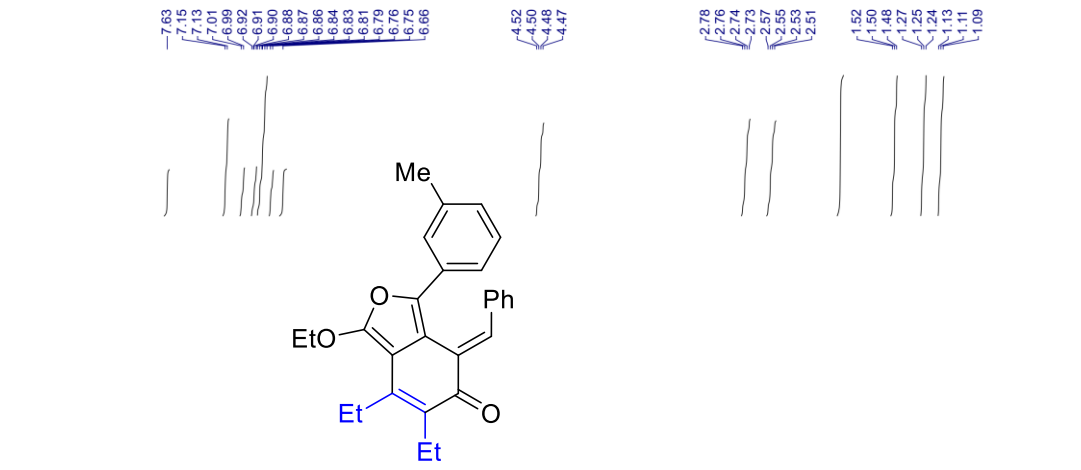

Ph
O
Ph
EtO
H
O
5g
f1 (ppm)


Ph
O
Ph
EtO
H
O
5g
f1 (ppm)

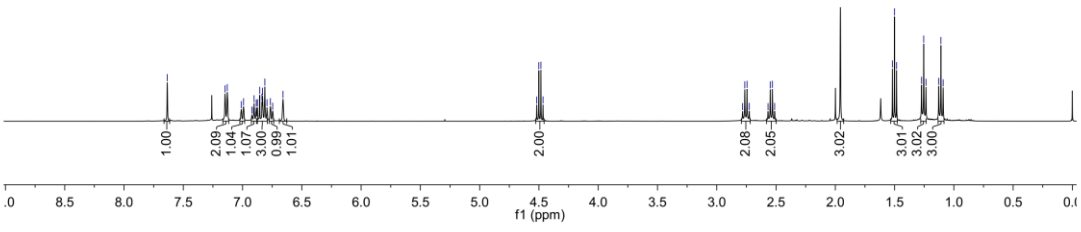

Ph
O
Ph
EtO
O
H

5'g

1.09
1.00
2.06
2.04
2.08
4.05
1.01
2.00
2.04
2.06
2.05
2.06
3.28
f1 (ppm)


Me
O
Ph
EtO
Et
O
Et

5h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2.09
1.04
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2.00
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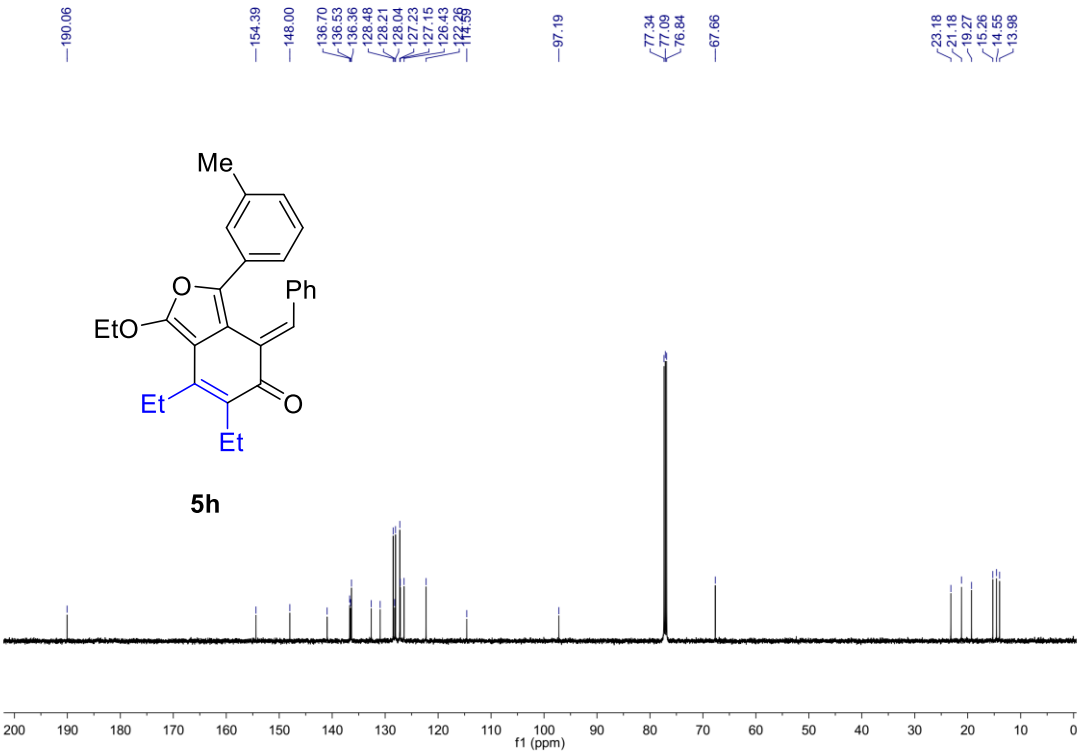
2.05
3.02
3.01
3.02
3.00
f1 (ppm)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136.53
136.36
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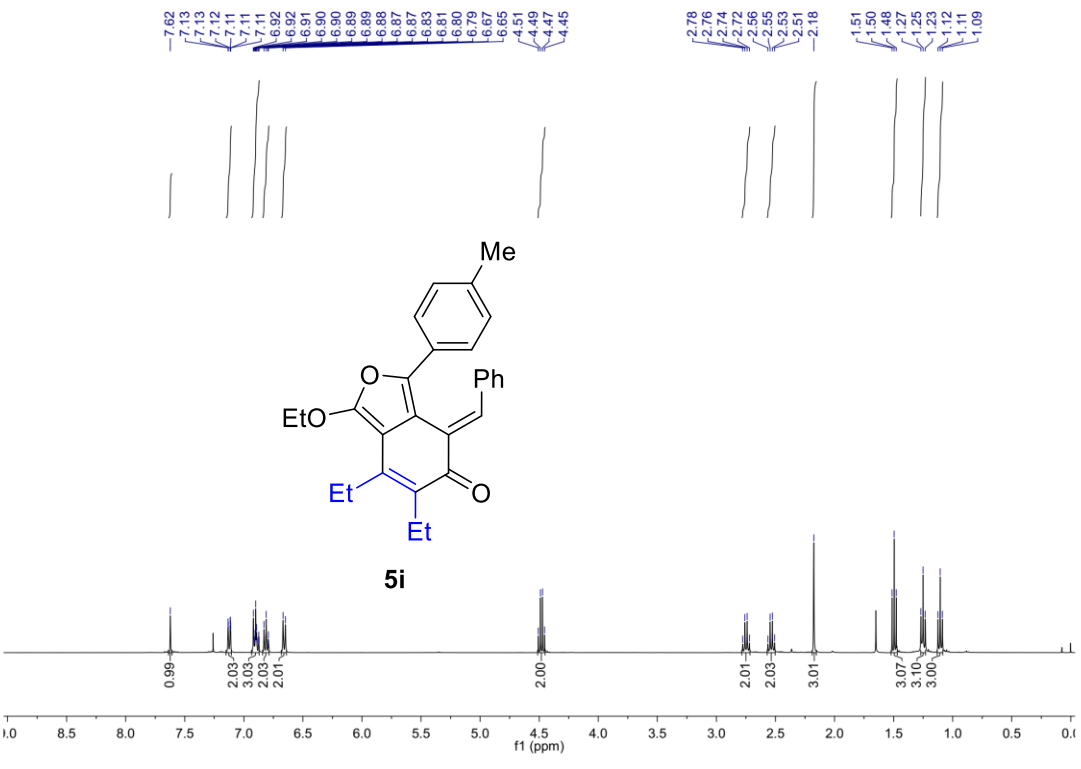
128.21
128.04
127.23
127.15
126.43
122.26
114.59
97.19
77.34
77.09
76.84
67.66
23.18
21.18
19.27
15.26
14.55
13.98
Me
O
Ph
EtO
Et
O
Et
5h
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)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7.13
7.12
7.11
7.11
7.11
6.92
6.92
6.91
6.90
6.90
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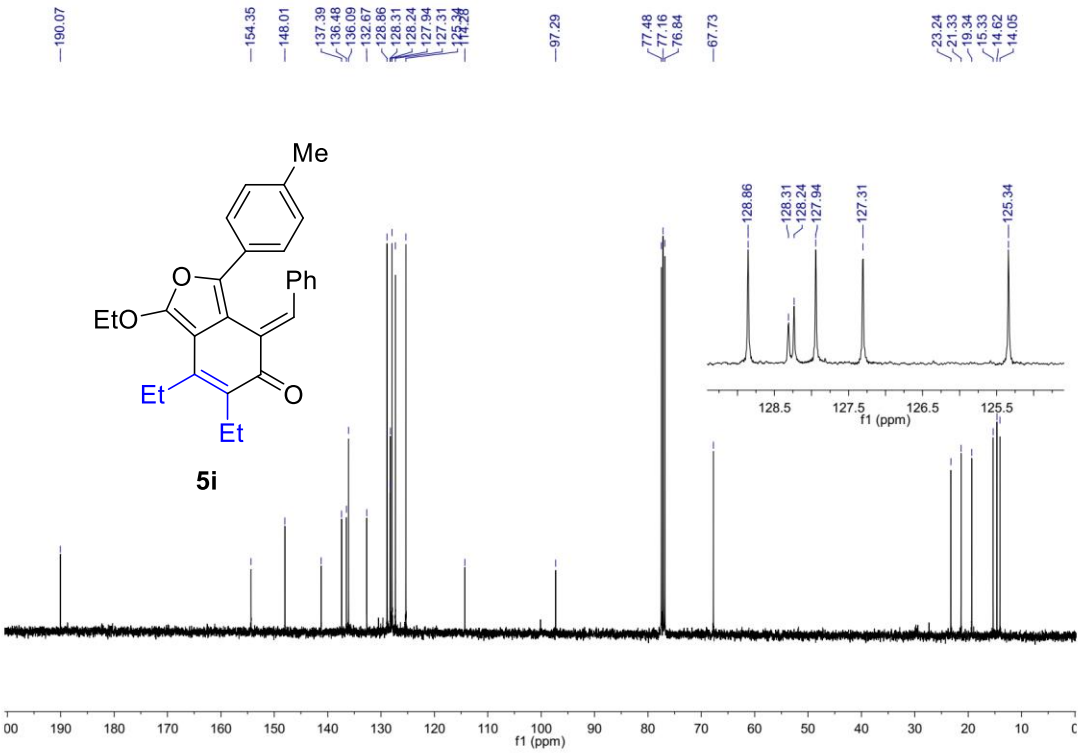
6.89
6.88
6.87
6.87
6.83
6.81
6.80
6.79
6.67
6.65
4.51
4.49
4.47
4.45
2.78
2.76
2.74
2.72
2.56
2.55
2.53
2.51
2.18
1.51
1.50
1.48
1.27
1.25
1.23
1.12
1.11
1.09
Me
O
Ph
EtO
Et
O
Et
5i
0.99
2.03
3.03
2.03
2.01
2.00
2.01
2.03
3.01
3.07
3.10
3.00
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)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154.35
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136.09
132.67
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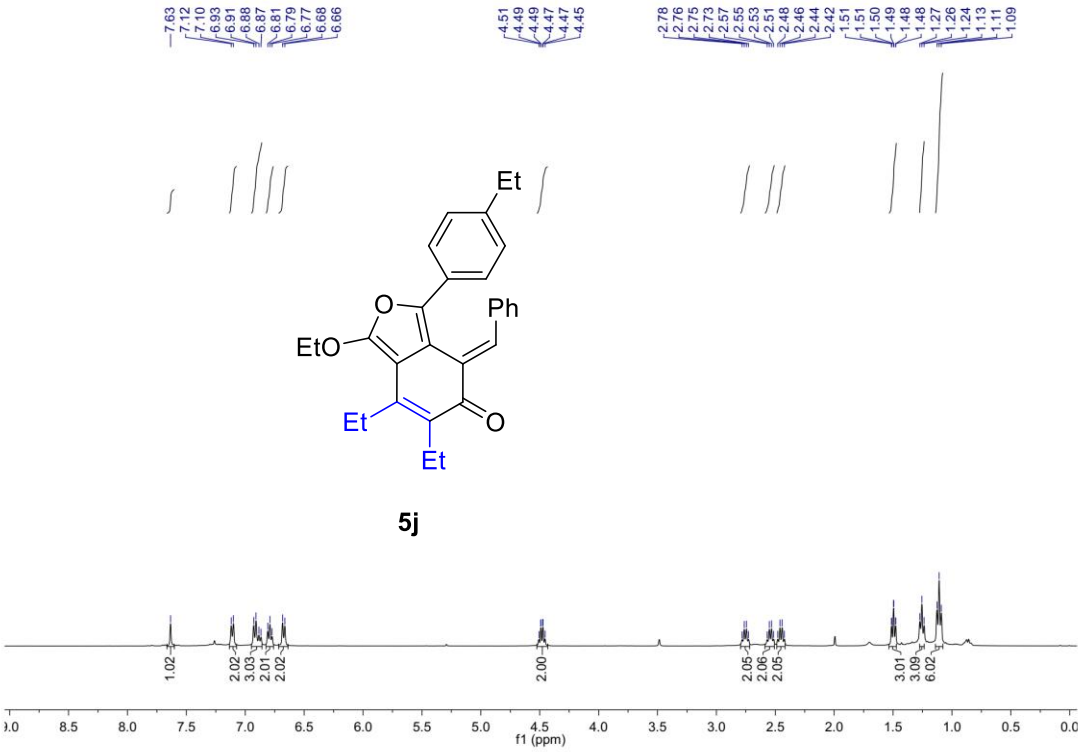
127.31
125.34
114.28
97.29
77.48
77.16
76.84
67.73
23.24
21.33
19.34
15.33
14.62
14.05
Me
O
Ph
EtO
Et
O
Et
128.86
128.31
128.24
127.94
127.31
125.34
128.5
127.5
126.5
125.5
f1 (ppm)
00 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

5i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7.10
6.93
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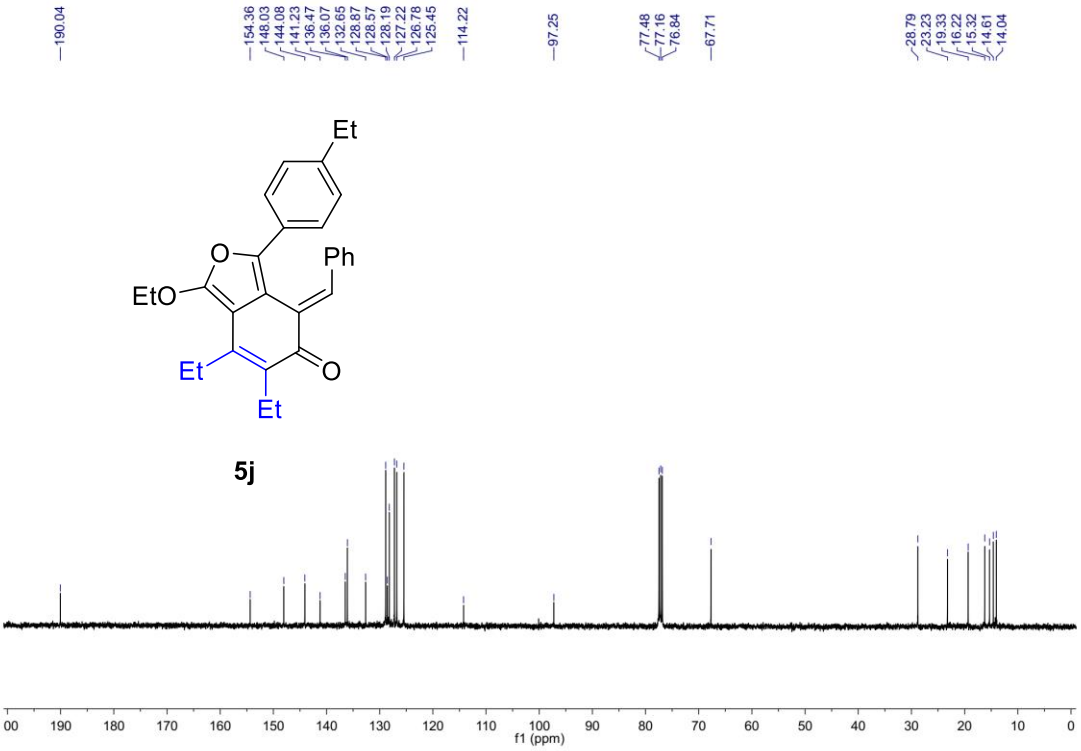
6.87
6.81
6.79
6.77
6.68
6.66
4.51
4.49
4.49
4.47
4.47
4.45
2.78
2.76
2.75
2.73
2.57
2.55
2.53
2.51
2.48
2.46
2.44
2.42
1.51
1.51
1.50
1.49
1.48
1.48
1.27
1.26
1.24
1.13
1.11
1.09
Et
O
Ph
EtO
Et
O
Et
1.02
2.02
3.03
2.01
2.02
2.00
2.05
2.06
2.05
3.01
3.09
6.02
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

5j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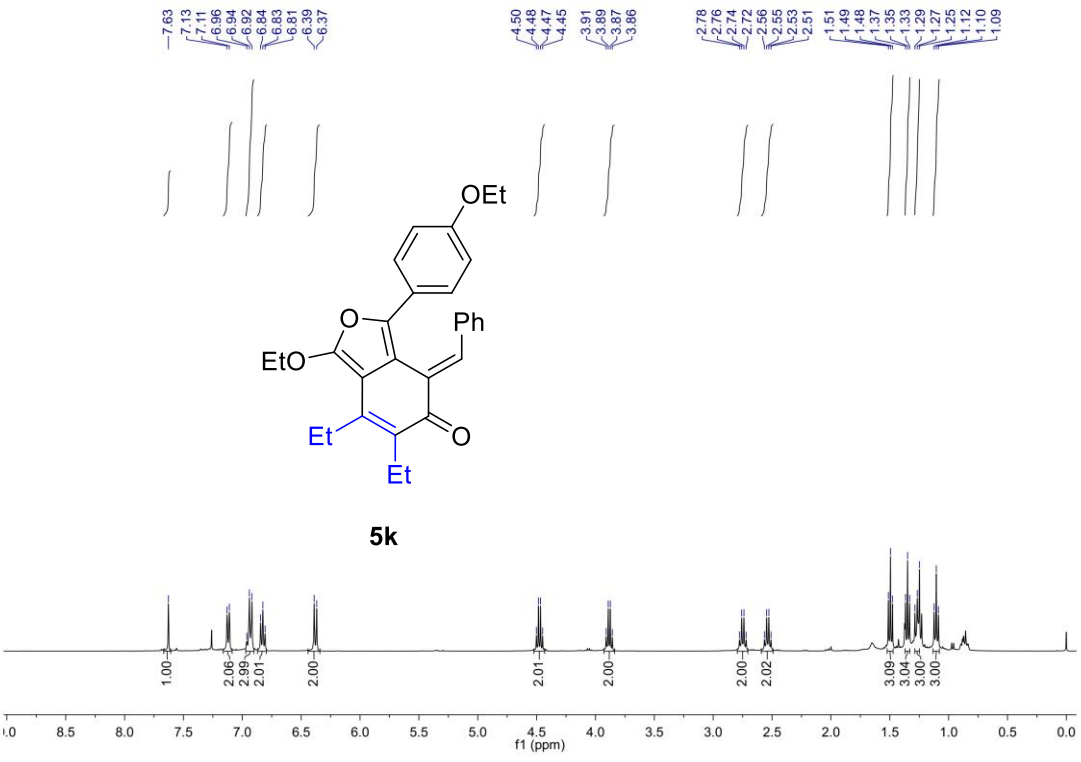
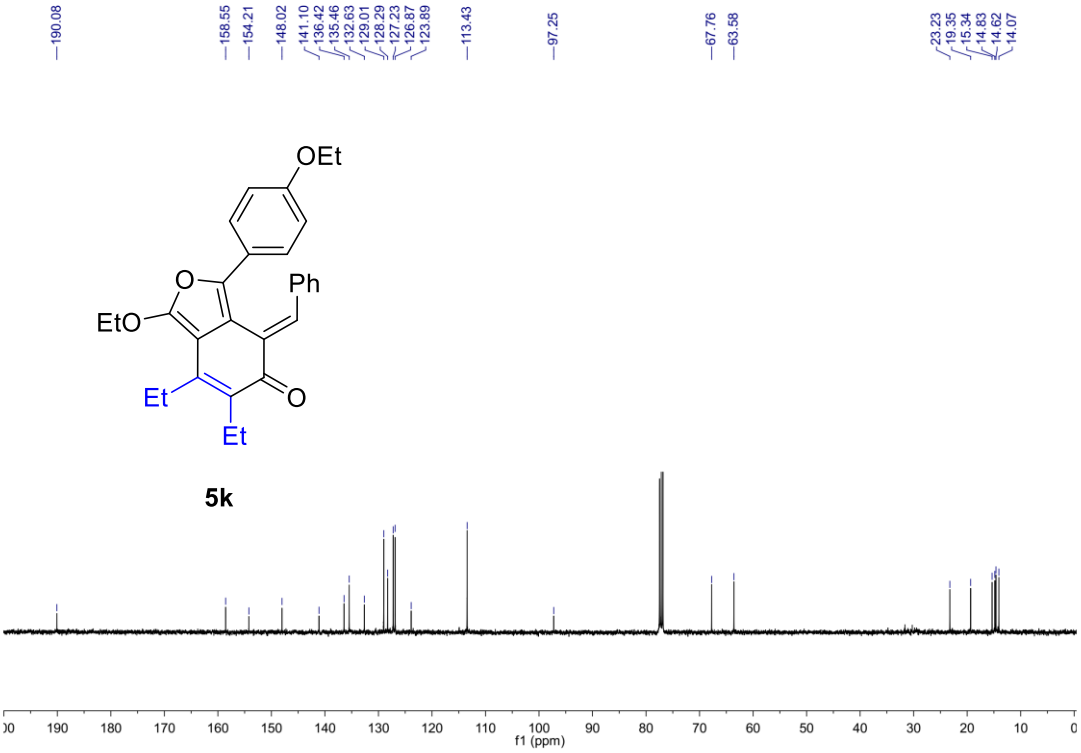
154.36
148.03
144.08
141.23
136.47
136.07
132.65
128.87
128.57
128.19
127.22
126.78
125.45
114.22
97.25
77.48
77.16
76.84
67.71
28.79
23.23
19.33
16.22
15.32
14.61
14.04
Et
O
Ph
EtO
Et
O
Et
5j
f1 (ppm)


7.63
7.13
7.11
6.96
6.94
6.92
6.84
6.83
6.81
6.39
6.37
4.50
4.48
4.47
4.45
3.91
3.89
3.87
3.86
2.78
2.76
2.74
2.72
2.56
2.55
2.53
2.51
1.51
1.49
1.48
1.37
1.35
1.33
1.29
1.27
1.25
1.12
1.10
1.09
OEt
O
Ph
EtO
Et
O
Et
5k
1.00
2.06
2.99
2.01
2.00
2.01
2.00
2.00
2.02
3.09
3.04
3.00
3.00
f1 (ppm)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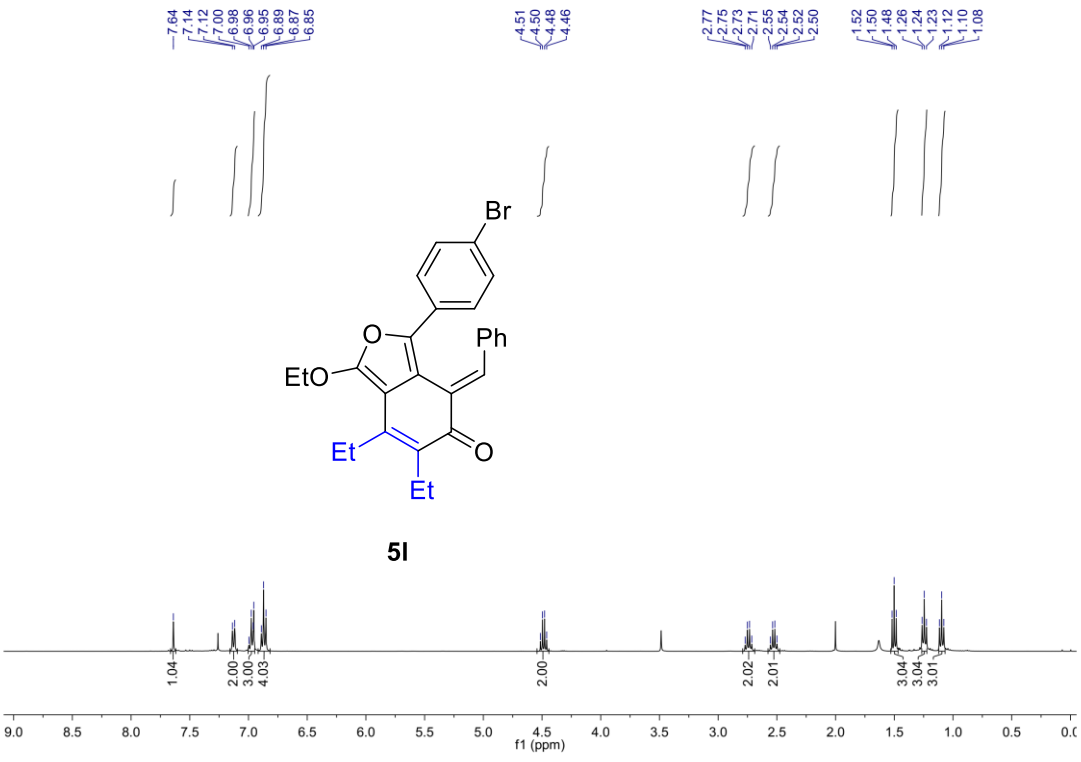
148.02
141.10
136.42
135.46
132.63
129.01
128.29
127.23
126.87
123.89
113.43
97.25
67.76
63.58
23.23
19.35
15.34
14.83
14.62
14.07
OEt
O
Ph
EtO
Et
O
Et
5k
f1 (ppm)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6.96
6.95
6.89
6.87
6.85
4.51
4.50
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4.46
2.77
2.75
2.73
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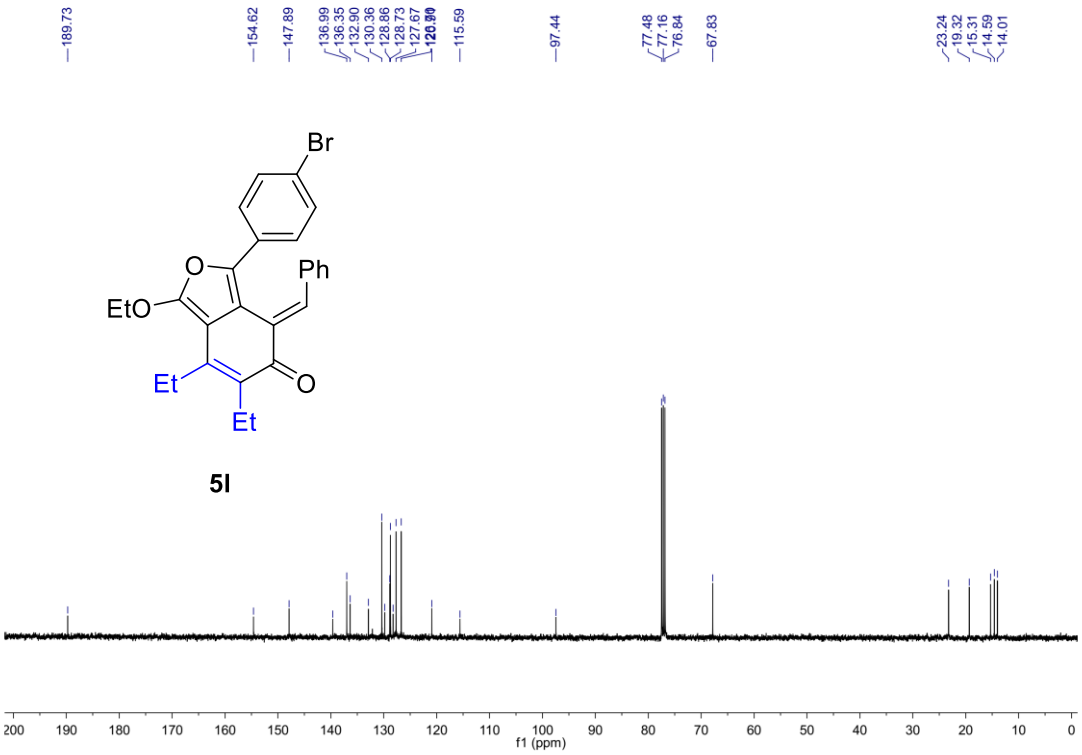
2.55
2.54
2.52
2.50
1.52
1.50
1.48
1.26
1.24
1.23
1.12
1.10
1.08
Br
O
Ph
EtO
Et
O
Et
5l
1.04
2.00
3.00
4.03
2.00
2.02
2.01
3.04
3.04
3.01
f1 (ppm)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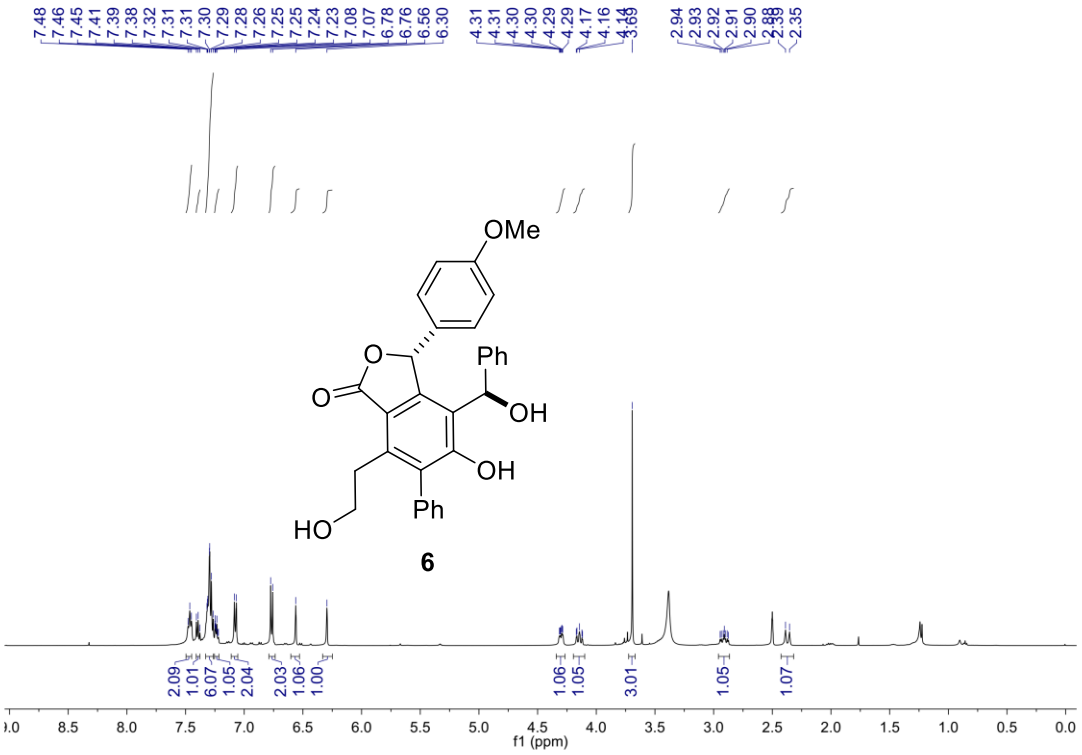
136.99
136.35
132.90
130.36
128.86
128.73
127.67
115.59
97.44
77.48
77.16
76.84
67.83
23.24
19.32
15.31
14.59
14.01
Br
O
Ph
EtO
Et
O
Et
5l
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)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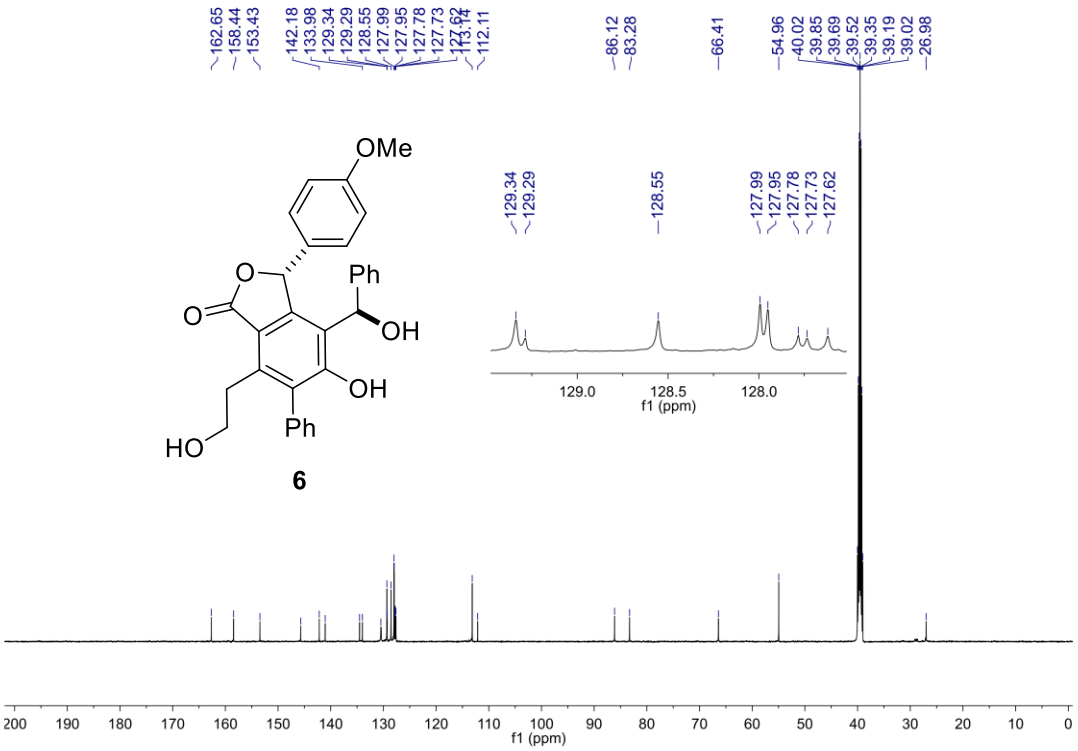
7.39
7.38
7.32
7.31
7.31
7.30
7.29
7.28
7.26
7.25
7.25
7.24
7.23
7.08
7.07
6.78
6.76
6.56
6.30
4.31
4.31
4.30
4.30
4.29
4.29
4.17
4.16
3.69
2.94
2.93
2.92
2.91
2.90
2.35
OMe
O
Ph
O
OH
OH
Ph
HO
6
2.09
1.01
6.07
1.05
2.04
2.03
1.06
1.00
1.06
1.05
3.01
1.05
1.07
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)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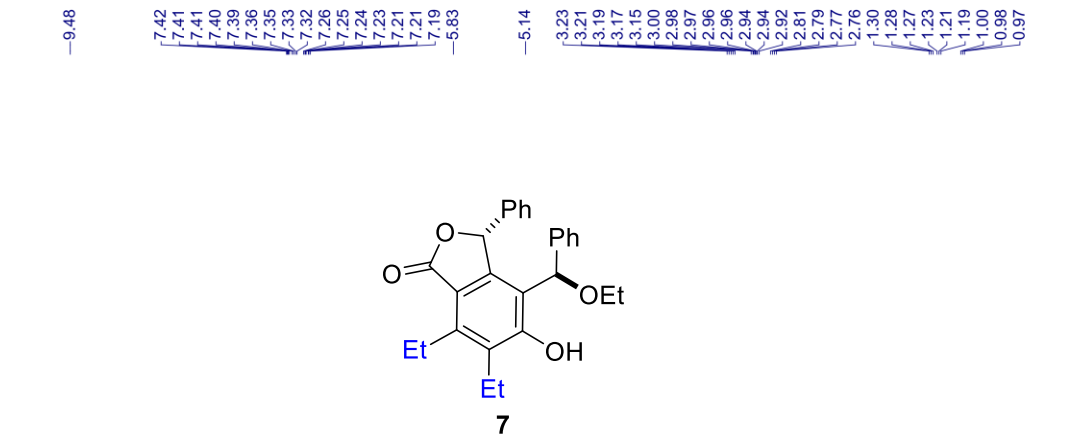
158.44
153.43
142.18
133.98
129.34
129.29
128.55
127.99
127.95
127.78
127.73
127.62
113.14
112.11
86.12
83.28
66.41
54.96
40.02
39.85
39.69
39.52
39.35
39.19
39.02
26.98
OMe
O
Ph
OH
O
OH
Ph
HO
129.34
129.29
128.55
127.99
127.95
127.78
127.73
127.62
129.0
128.5
128.0
f1 (ppm)
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

6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7.39
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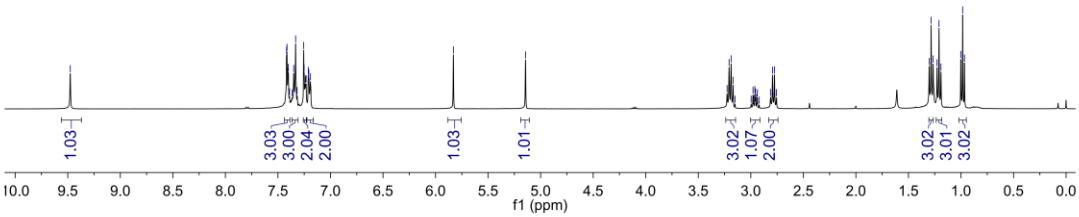
7.35
7.33
7.32
7.26
7.25
7.24
7.23
7.21
7.21
7.19
5.83
5.14
3.23
3.21
3.19
3.17
3.15
3.00
2.98
2.97
2.96
2.96
2.94
2.94
2.92
2.81
2.79
2.77
2.76
1.30
1.28
1.27
1.23
1.21
1.19
1.00
0.98
0.97

Ph
O
Ph
O
OEt
Et
OH
Et

7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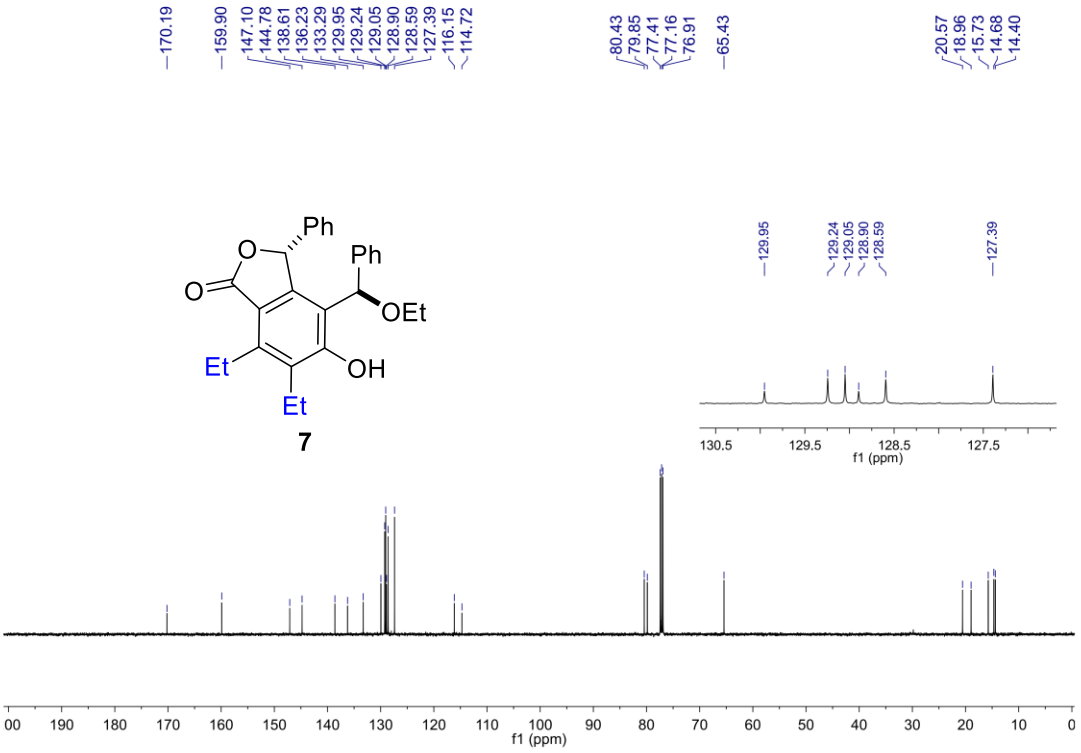
3.00
2.04
2.00
1.03
1.01
3.02
1.07
2.00
3.02
3.01
3.02
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)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159.90
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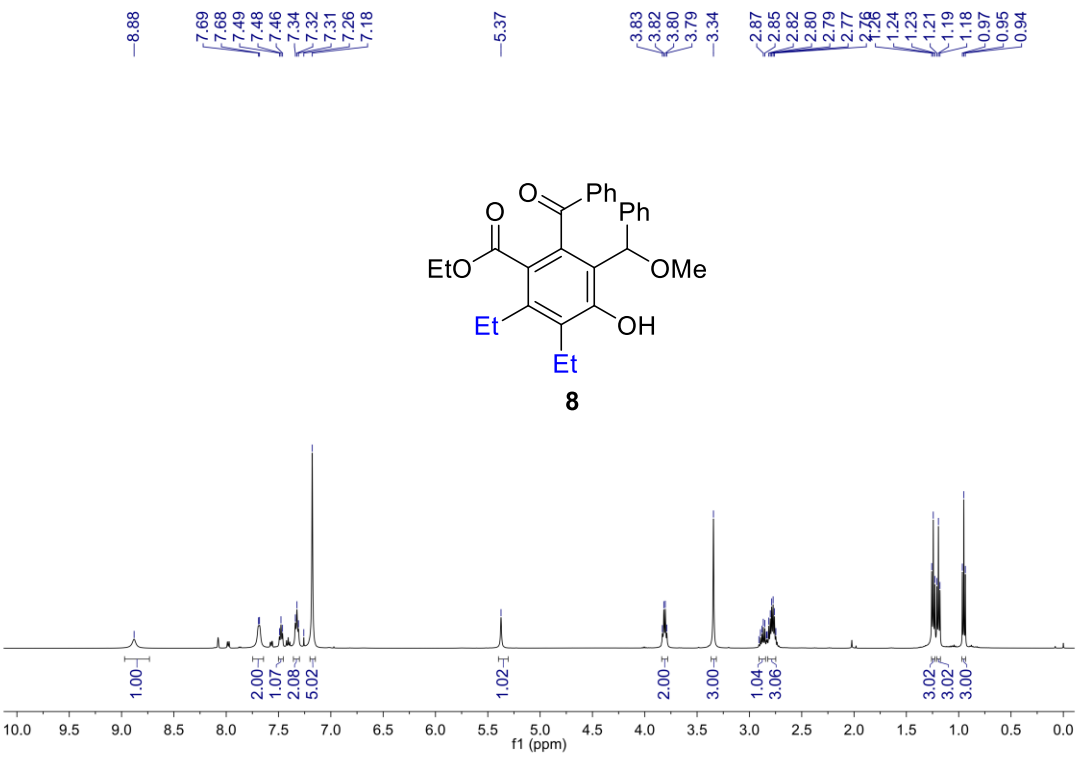
144.78
138.61
136.23
133.29
129.95
129.24
129.05
128.90
128.59
127.39
116.15
114.72
80.43
79.85
77.41
77.16
76.91
65.43
20.57
18.96
15.73
14.68
14.40
Ph
O
O
Ph
OEt
Et
OH
Et
7
129.95
129.24
129.05
128.90
128.59
127.39
130.5
129.5
128.5
127.5
f1 (ppm)
00
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)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7.69
7.68
7.49
7.48
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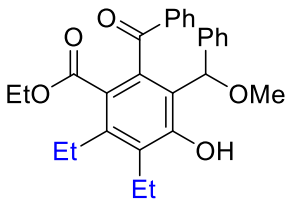
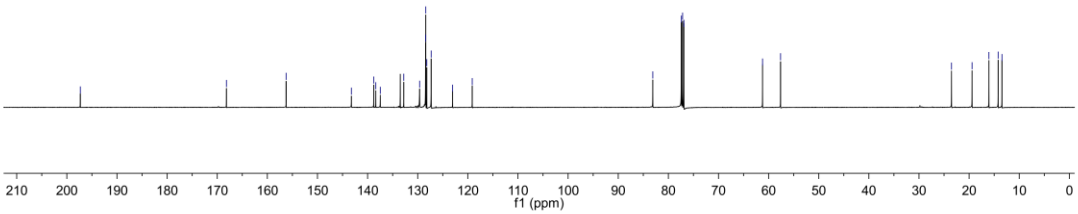
7.32
7.31
7.26
7.18
5.37
3.83
3.82
3.80
3.79
3.34
2.87
2.85
2.82
2.80
2.79
2.77
1.24
1.23
1.21
1.19
1.18
0.97
0.95
0.94
O
Ph
O
Ph
EtO
OMe
Et
OH
Et
8
1.00
2.00
1.07
2.08
5.02
1.02
2.00
3.00
1.04
3.06
3.02
3.02
3.00
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

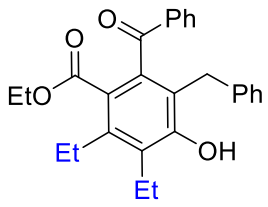

197.31
168.16
156.25
143.23
138.77
138.36
137.47
132.78
129.62
128.43
128.40
128.19
127.31
123.04
119.12
83.10
77.41
77.16
76.91
61.21
57.62
23.51
19.41
16.05
14.20
13.45


O
Ph
O
Ph
EtO
OMe
Et
OH
Et

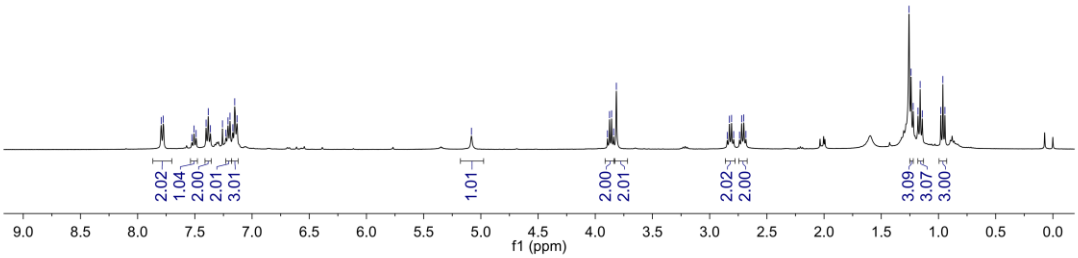
8

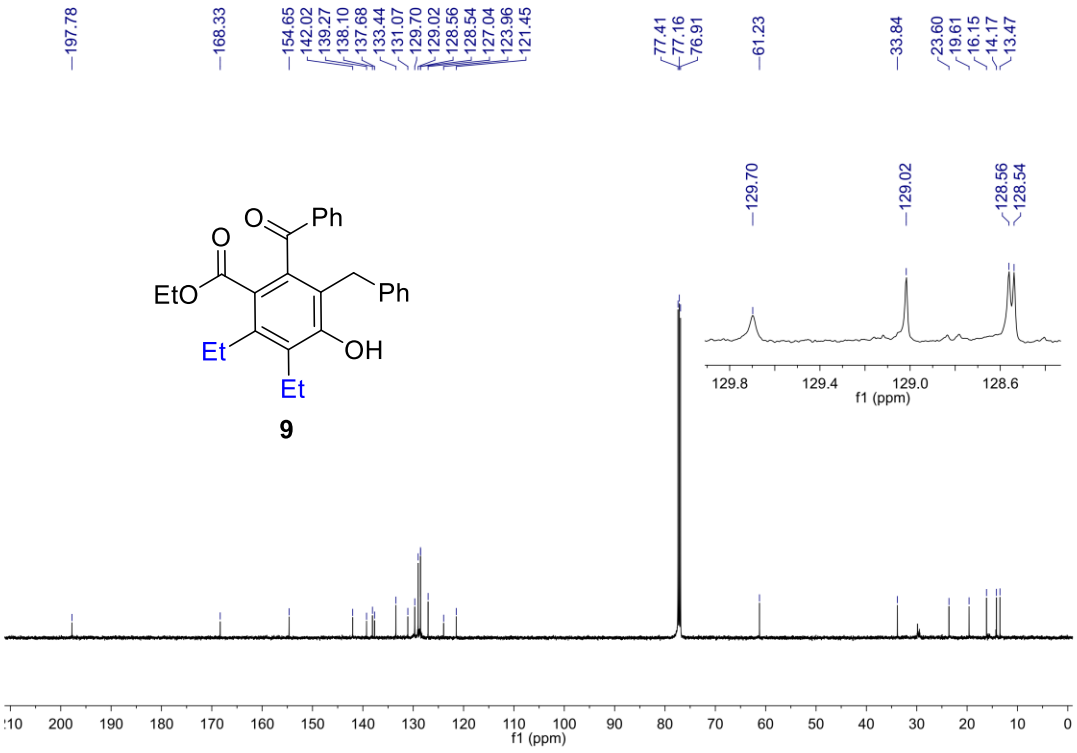

210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


7.79
7.78
7.53
7.51
7.49
7.40
7.38
7.36
7.26
7.23
7.21
7.19
7.17
7.15
7.13
5.08
3.89
3.88
3.86
3.84
3.82
2.85
2.83
2.81
2.79
2.74
2.72
2.70
2.68
1.26
1.24
1.22
1.18
1.16
1.14
0.98
0.96
0.94

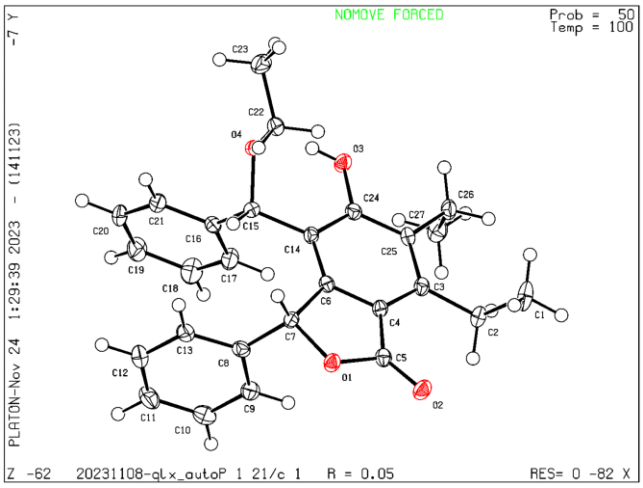

O
Ph
O
EtO
Ph
Et
OH
Et

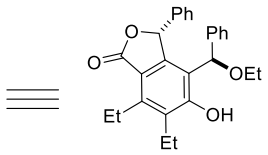
9


2.02
1.04
2.00
2.01
3.01
1.01
2.00
2.01
2.02
2.00
3.09
3.07
3.00
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)


197.78
168.33
154.65
142.02
139.27
138.10
137.68
133.44
131.07
129.70
129.02
128.56
128.54
127.04
123.96
121.45
77.41
77.16
76.91
61.23
33.84
23.60
19.61
16.15
14.17
13.47
O
Ph
O
EtO
Ph
Et
OH
Et
9
129.70
129.02
128.56
128.54
129.8
129.4
129.0
128.6
f1 (ppm)
f1 (ppm)

Single-Crystal X-ray Diffraction Analysis of 7





7

CCDC: 2310717

```
Bond precision:   C-C = 0.0024 A          Wavelength=1.54184

Cell:             a=17.4561(1)     b=11.6840(1)        c=10.9091(1)
                  alpha=90         beta=97.527(1)      gamma=90
Temperature:      100 K

                  Calculated                  Reported
Volume            2205.82(3)                  2205.82(3)
Space group       P 21/c                      P 1 21/c 1
Hall group        -P 2ybc                     -P 2ybc
Moiety formula    C27 H28 O4                  C27 H28 O4
Sum formula       C27 H28 O4                  C27 H28 O4
Mr                416.49                      416.49
Dx,g cm-3         1.254                       1.254
Z                 4                           4
Mu (mm-1)         0.664                       0.664
F000              888.0                       888.0
F000'             890.64
h,k,lmax                                      21,14,13
Nref                                          4330
Tmin,Tmax         0.887,0.967                 0.432,1.000
Tmin'             0.876

Correction method= # Reported T Limits: Tmin=0.432 Tmax=1.000
AbsCorr = MULTI-SCAN

Data completeness=                 Theta(max)= 75.785

R(reflections)= 0.0451( 3931)                 wR2(reflections)=
                                              0.1036( 4330)
S = 1.157                  Npar= 285
```

General Procedure for the *in vitro* Anti-tumor Activity Study

Cell viability was measured by CCK-8 assay

Human cancer cell lines HCT116 and A549 were obtained from Cell Cook. Cells were cultured in RPMI1640 medium containing 10% fetal bovine serum and 1% penicillin/streptomycin (Gibco) in a humidified incubator containing 5% CO_2 at 37 °C. Human cancer cell lines MCF-7 was obtained from Procell and cells were cultured in MEM medium containing 10% fetal bovine serum, 1% penicillin/streptomycin (Gibco) and 0.01 mg/mL insulin (Procell) in a humidified incubator containing 5% CO_2 at 37 °C. For cell viability, cells were seeded in 96-well plates at 5000 cells per well. After 24 hours, serially diluted compounds were added and cells were cultured for another 48 hours. Cell viability was measured using a Cell Counting Kit-8 (CCK-8) assay according to the manufacturer's instructions (Yeasen Biotechnology, China).

These representative products **3a**, **3d**, **3h**, **3i**, **3l**, **3m**, **3p**, **3r**, **5a**, **5b**, **5c**, **5d**, **5f**, **5g**, and **7** on cell viability was evaluated *via* CCK8 assay in HCT116 (colon cancer), MCF-7 (breast cancer), and A549 (lung adenocarcinoma) human cancer cell lines, and the *in vitro* anti-tumor activity results are listed in Table S3 and Table S4.

Most of these fully-substituted furan-fused *o*-QMs precursors, such as **3d** and **5f** showed significant anti-cancer activity (Figure S2 and S3), The results show that compound **3d** show the highest anticancer potency against human breast cancer cells (MCF-7 cells, IC_{50} = 1.87 ± 0.33 μM), compound **5f** show the highest anticancer potency against human colon cancer cells (HCT-116 cells, IC_{50} = 1.35 ± 0.15 μM). The results were presented as percentages and vehicle-treated cells set at 5000. All data were presented as mean values ± SD, n = 3.

Table S3. Anti-tumor activities of compounds **3a**, **3d**, **3h**, **3i**, **3l**, **3m**, **3p**, **3r**, **5a**, **5b**, **5c**, **5d**, **5f**, **5g**, and **7** (Inhibition rate at 20 μM)

Compound	HCT-116（%）	MCF-7（%）	A549（%）
3a	33.76±2.55	55.23±5.29	21.94±4.05
3d	56.78±9.64	96.63±1.26	92.66±1.08
3h	45.55±4.30	93.57±1.23	96.94±0.55
3i	45.02±3.42	97.45±0.39	98.74±0.57
3l	58.18±13.13	92.20±5.95	95.75±0.45
3m	56.37±7.98	55.79±6.56	71.82±0.57
3p	100.20±0.33	96.09±1.49	85.46±5.05
3r	98.73±0.48	97.08±0.88	98.44±0.14
5a	97.76±0.98	81.60±3.88	92.64±0.91
5b	97.93±1.22	92.31±0.25	97.85±0.31
5c	62.50±6.74	92.35±4.22	98.38±1.01
5d	70.46±7.23	63.14±3.11	98.65±0.08
5f	94.95±1.46	94.22±1.87	84.45±5.98
5g	77.85±3.32	86.42±6.71	96.20±0.34
7	76.49±10.60	71.77±2.14	68.98±3.43

Table S4. Anti-tumor activities of compounds **3a**, **3d**, **3h**, **3i**, **3l**, **3m**, **3p**, **3r**, **5a**, **5b**, **5c**, **5d**, **5f**, **5g**, and **7** (IC_{50}, μM)[a]

Compound	HCT-116	MCF-7	A549
3a	-	-	-
3d	-	**1.87±0.33**	8.55±0.69
3h	-	2.49±0.24	6.51±0.82
3i	-	1.99±0.24	3.61±0.84
3l	-	2.08±0.24	4.78±1.17
3m	-	-	-
3p	3.96±0.34	6.64±1.16	-
3r	1.44±0.05	2.84±0.23	3.67±0.39
5a	1.73±0.46	-	6.97±1.27
5b	1.47±0.35	5.86±0.83	6.30±1.37
5c	-	2.63±0.42	5.07±0.34
5d	-	-	7.71±1.49
5f	**1.35±0.15**	3.72±0.32	-
5g	-	-	8.90±2.41
7	-	-	-

[a]IC_{50} is the half maximal inhibitory concentration; All data were presented as mean values ± SD, n = 3.

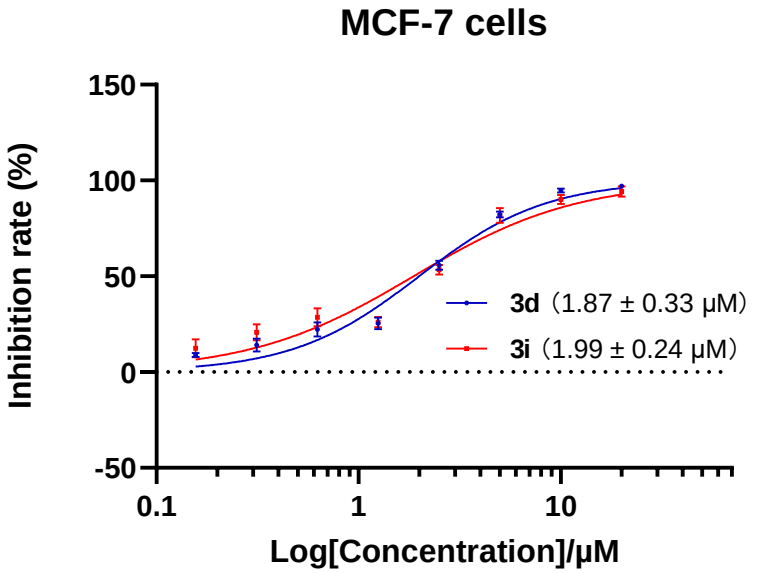


Figure S2. Compounds **3d** and **3i** on the inhibition of MCF-7 cells, data were presented as mean values ± SD, n = 3.

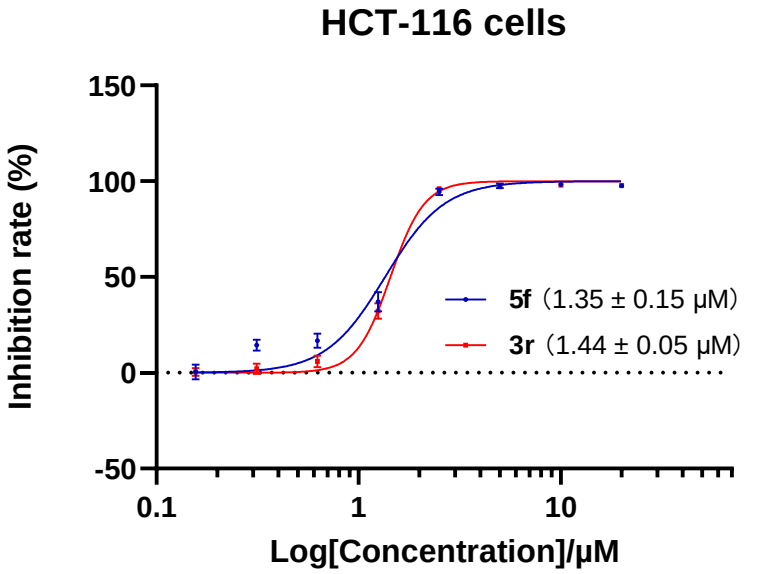


Figure S3. Compounds **5f** and **3r** on the inhibition of HCT-116 cells, data were presented as mean values ± SD, n = 3.

Hippocampal neuronal cell line, HT22, a sub-line derived from parent HT4 cells that were originally immortalized from primary mouse hippocampal neuronal culture. Cells were cultured in RPMI1640 medium containing 10% fetal bovine serum and 1% penicillin/streptomycin (Gibco) in a humidified incubator containing 5% CO_2 at 37 °C.

For cell viability, cells were seeded in 96-well plates at 5000 cells per well. After 24 hours, serially diluted compound was added and cells were cultured for another 48 hours. Cell viability was measured using a Cell Counting Kit-8 (CCK-8) assay according to the manufacturer's instructions (Yeasen Biotechnology, China). The compound **5f** on cell viability was evaluated via CCK8 assay in HT22 (hippocampal neuronal) mouse normal cell line. The results show that compound **5f** exhibits obvious cytotoxicity against mouse hippocampal neuronal cells (HT22 cells, **5f**: IC50 = 1.62 ± 0.01 μM;). The results were presented as percentages and vehicle-treated cells set at 100 (**Figure S4**).

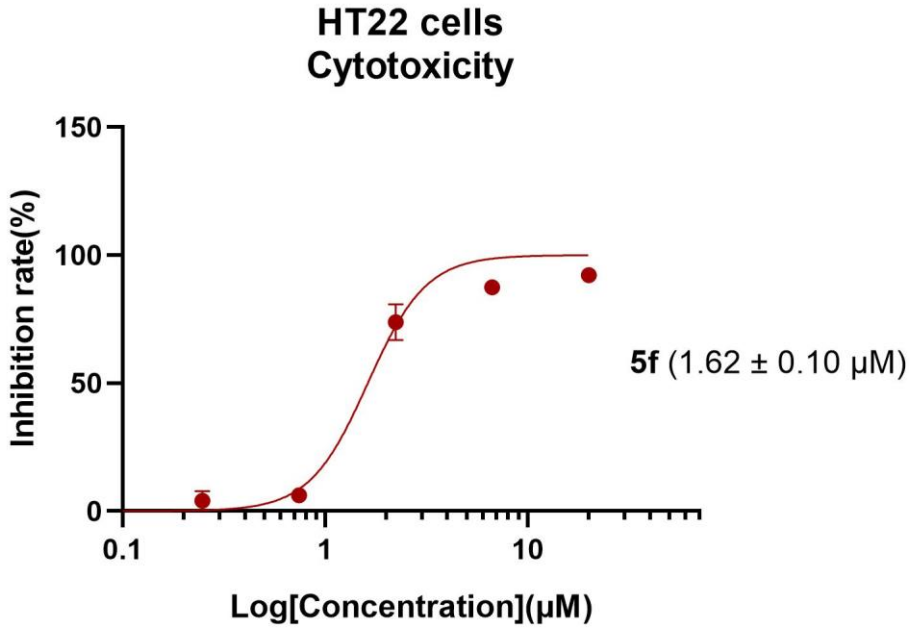


Figure S4. Compound **5f** on the inhibition of HT22 cells were presented as mean values ± SD, n = 3.

Embryonic kidney cell line, 293T, a sub-line derived from parent 293 cells that were originally immortalized from primary human embryonic kidney culture. Cells were cultured in RPMI1640 medium containing 10% fetal bovine serum and 1% penicillin/streptomycin (Gibco) in a humidified incubator containing 5% CO_2 at 37 °C. For cell viability, cells were seeded in 96-well plates at 5000 cells per well. After 24 hours, serially diluted compound was added and cells were cultured for another 48 hours. Cell viability was measured using a Cell Counting Kit-8 (CCK-8) assay

according to the manufacturer's instructions (Yeasen Biotechnology, China). The compound **3d** on cell viability was evaluated via CCK8 assay in 293T (embryonic kidney) human normal cell line. The results show that compound **3d** exhibits obvious cytotoxicity against human embryonic kidney cells (293T cells, **3d**: IC_{50} = 1.10 ± 0.05 μM). The results were presented as percentages and vehicle-treated cells set at 100 (**Figure S5**).

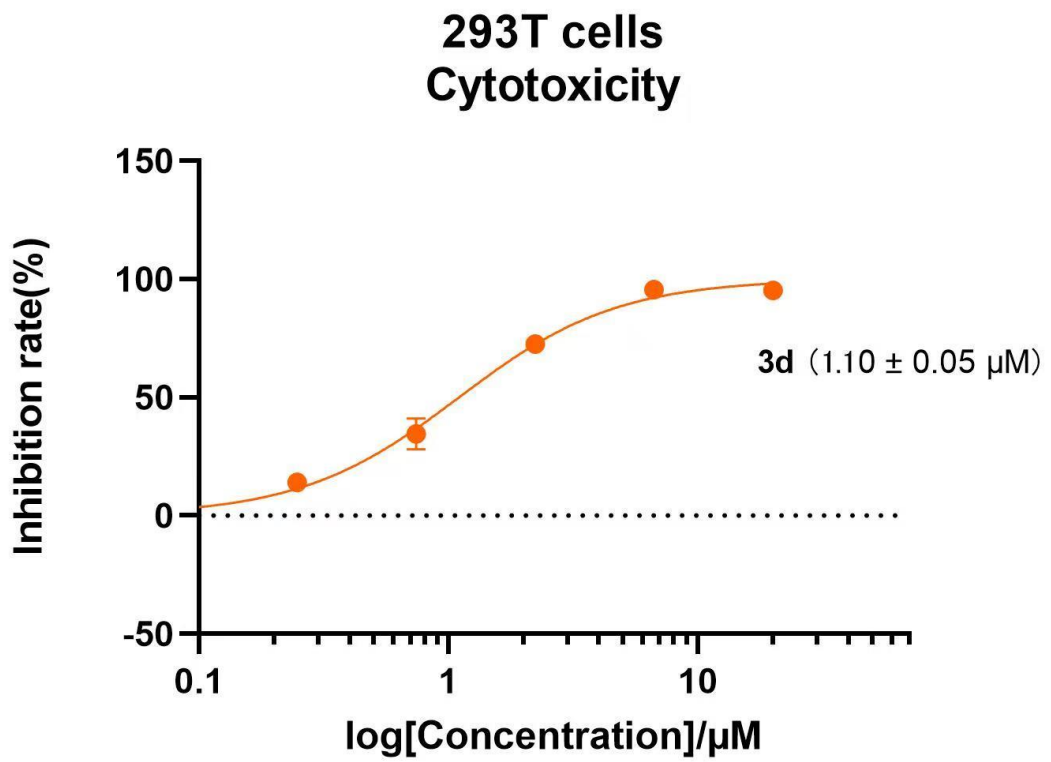


Figure S5. Compound **3d** on the inhibition of 293T cells were presented as mean values ± SD, n = 3.