Electronic Supplementary Material (ESI) for ChemComm.

Supporting Information

Carbene-Mediated Stereoselective Olefination of Vinyl Sulfoxonium Ylides with Diazo Compounds and Acetals

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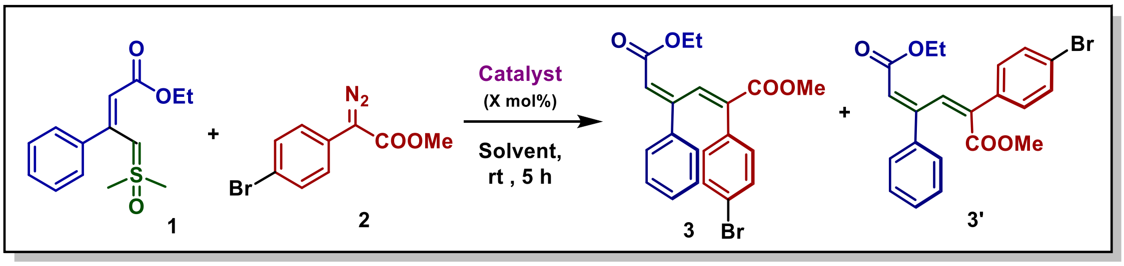
I. General Information

Commercial-grade reagents and solvents were purchased at the highest commercial quality and used without further purification unless otherwise stated. Phenyl propiolate is commercially available. Other starting materials like various substituted aldehydes, phenyl acetic acids were purchased from a commercial source and used as received. Reactions were carried out under argon in flame-dried or oven-dried glassware and reaction tubes unless otherwise specified. Synthesis-grade solvents were used as purchased. Chromatographic purification of products was accomplished using silica gel (230–400 mesh). For thin layer chromatography (TLC) analysis throughout this work, Merck pre-coated TLC plates (silica gel 60 GF254, 0.25 mm) were employed, using UV light as the visualizing agent and ethanol solution of phosphomolybdic acid or basic aqueous potassium permanganate (KMnO4) stain solutions and heat as developing agents. The NMR spectra were recorded at 400 MHz and 500 MHz for both ^{1}H-NMR and ^{13}C-NMR. The chemical shift (δ) for ^{1}H-NMR and ^{13}C-NMR are given in ppm relative to residual signals of the solvents ($CDCl_3$ @ 7.26 ppm ^{1}H-NMR and 77.16 ppm ^{13}C-NMR, and tetramethylsilane @ 0 ppm). Coupling constants are given in Hertz (Hz). The following abbreviations are used to indicate the multiplicity: s, singlet; d, doublet; t, triplet; q, quartet; p, pentet; sept, septet; m, multiplet. High-resolution mass spectra (HRMS) were obtained from the High-Resolution Mass Spectrometry using electrospray ionization time-of-flight (ESI-TOF) reflectron experiments. The single-crystal X-ray data were collected on Bruker D8 Quest diffractometer using graphite monochromated Mo Kα radiation (λ = 0.71073 Å).

II. Optimization Studies:

a) General procedure for the optimization: Dienoate (3)

To an oven-dried reaction tube purged with argon gas, vinyl sulfoxonium ylide **1** (54 mg, 0.2 mmol, 1 equiv.) was dissolved in solvent (2 mL), added the catalyst (X mol%) and allowed to stir at room temperature for 30 mins. Then, to the reaction mixture diazo ester **2** (36 mg, 0.2 mmol, 1 equiv.) dissolved in solvent (1 mL) was added dropwise and continued stirring at room temperature for 5 hours. Then, the reaction mixture was passed through a short plug of silica, eluted with dichloromethane, and concentrated in *vacuo*. The yield of the product was determined by ^{1}H-NMR analysis using CH_2Br_2 as the internal standard.



Catalyst screening and Solvent optimization:

We began our investigations using vinyl sulfoxonium ylide **1** (1 equiv.) and diazo ester **2** (1 equiv.) as the model substrates to determine the optimum reaction conditions. Various catalysts were tried for the present transformation. Among those catalysts, ruthenium catalyst and iridium catalyst served 84% and 86% of the desired product respectively (**Table 1, entry 1–2**). However, the iridium catalyst gave the better diastereoselectivity of the dienoate **3** (d.r. >20:1). The reaction with $RuCl_3$ and $Rh_2(OAc)_4$ didn't yield the desired product **3** (**Table 1, entry 3–4).** However, the $Pd(PPh_3)_4$ delivered the dienoate **3** in 23% yield with d.r. 1:1 (**Table 1, entry 5**). Expected product formation was not observed with the silver catalyst and some of the lewis acid catalysts like $Sc(OTf)_3$, $In(OTf)_3$ and $FeCl_2$ (**Table 1, entry 6–9**). In absence of the catalyst no product formation was observed (**Table 1, entry 10**). Thus, the catalyst optimisation concludes that iridium catalyst is the best for the present reaction. With this, we proceeded to the solvent optimisation using various solvents. The reaction in DCM and DCE solvent gave the desired product in 52-57% yield with less selectivity (**Table 1, entry 11–12**). When the reaction was carried out in ethanol, we observed only 43% yield of the dienoate with d.r. 1:1 (**Table 1, entry 13**). Toluene and THF gave similar yield of the product in 65-68% with d.r. >8:1 (**Table 1, entry 14–15**). However, the acetonitrile as solvent gave the good yield of dienoate **3** (75%) with d.r. >10:1 (**Table 1, entry 16**). Thus, the best yield of the product was delivered by the chloroform solvent. This optimisation studies showed that the $[Ir(COD)Cl]_2$ catalyst in chloroform solvent is the standard condition for the present transformation (**Table 1, entry 2**).

Table 1: Optimization studies for the synthesis of dienoate (3)

Entry[a-b]	**Catalyst 1 (X mol%)**	**Solvent**	**Yield (%)**[c]	**d.r. (3:3′)**
1.	[Ru(*p*-cymene)Cl_2]$_2$ (3)	$CHCl_3$	84	>10:1
2.	**$[Ir(COD)Cl]_2$ (3)**	**$CHCl_3$**	**86**	**>20:1**
3.	$RuCl_3$ (3)	$CHCl_3$	ND	--
4.	$Rh_2(OAc)_4$ (3)	$CHCl_3$	ND	--
5.	$Pd(PPh_3)_4$ (4)	$CHCl_3$	23	1:1
6.	$Ag(PF_6)$ (3)	$CHCl_3$	ND	--
7.	$Sc(OTf)_3$ (3)	$CHCl_3$	ND	--

8.	In(OTf)$_3$ (3)	CHCl$_3$	ND	--
9.	FeCl$_2$ (3)	CHCl$_3$	ND	--
10.	--	CHCl$_3$	ND	--
11.	[Ir(COD)Cl]$_2$ (3)	DCM	57	>10:1
12.	[Ir(COD)Cl]$_2$ (3)	DCE	52	>8:1
13.	[Ir(COD)Cl]$_2$ (3)	EtOH	43	1:1
14.	[Ir(COD)Cl]$_2$ (3)	Toluene	65	>8:1
15.	[Ir(COD)Cl]$_2$ (3)	THF	68	>8:1
16.	[Ir(COD)Cl]$_2$ (3)	CH$_3$CN	75	>10:1

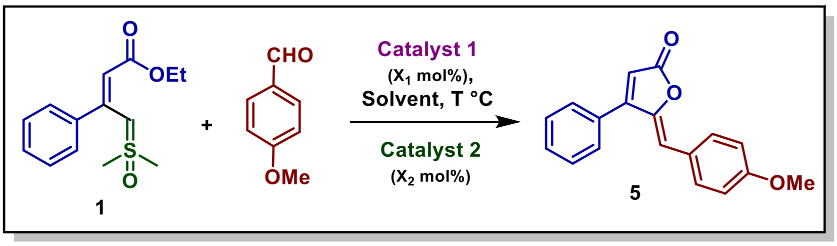
[a] Standard reaction conditions: **1** (0.2 mmol, 1 equiv.), **2** (0.2 mmol, 1 equiv.) *[b]* The yields were determined by ^{1}H NMR analysis of crude product using CH_2Br_2 as the internal standard *[c]* ND (Not Detected) DCE=dichloroethane, DCM=dichloromethane, EtOH=ethanol, THF=Tetrahydrofuran

b) General procedure for the optimization: Ylidene butenolide (5)

To an oven-dried reaction tube purged with argon gas, vinyl sulfoxonium ylide **1** (54 mg, 0.2 mmol) was dissolved in solvent (3 mL), added the catalyst-1 (X_1 mol%) and allowed to stir at room temperature for 20 mins. Then, the reaction mixture is cooled to 0 ºC and the aldehyde/acetal (0.2 mmol) was added. Catalyst-2 (X_2 mol%) was added to the cooled reaction mixture and stirring was continued at 0 ºC for 4 hours. The reaction mixture was passed through a short plug of silica, eluted with dichloromethane and concentrated in *vacuo*. The yield of the product was determined by ^{1}H-NMR analysis using CH_2Br_2 as the internal standard.

Catalyst screening and Solvent optimization:

With Aldehyde



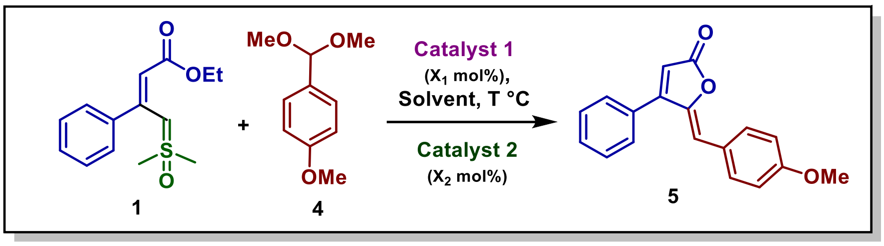
We began our investigations using vinyl sulfoxonium ylide **1** (1 equiv.) and 4-methoxy benzaldehyde (1 equiv.) as the model substrates to determine the optimum reaction conditions. The reaction involves two parts where the part-1 involves the generation of furan whereas part-2 involves the reaction of furan with aldehyde. The expected product was not observed when the reaction was carried out only with the ruthenium catalyst ***(Table 2, entry 1)***. Thus, we kept ruthenium catalyst as standard for the generation of furan and optimised the catalyst 2. When the reaction was performed with the Cu(OTf)$_2$ as catalyst-2, the product was obtained in 10% yield ***(Table 2, entry 2)***. On the otherhand, Sc(OTf)$_3$ as catalyst-2 yielded the product in 38% ***(Table 2, entry 3)***. Trace amount of product was observed with In(OTf)$_3$ ***(Table 2, entry 4)*** but TMSOTf served the best yield of the product **5** (42%, ***Table 2, entry 5***) with aldehyde. Other catalysts like ZnCl$_2$, FeBr$_3$ did not yield the expected product ***(Table 2, entry 6–7)***. When the reaction was carried out at room temperature the decrement in yield of the product was observed which confirms that the product formation was compatible at 0 ºC ***(Table 2, entry 8)***. The reaction was also working with iridium catalyst (as catalyst 1), but due to the ease availability, the reaction was carried out with ruthenium catalyst itself ***(Table 2, entry 9)***.

Table 2: Optimization studies for the synthesis of ylidene butenolides with aldehyde.

Entry[a-b]	**Catalyst 1 (X_1 mol%)**	**Catalyst 2 (X_2 mol%)**	**Solvent**	**T (°C)**	**Yield (%)**[c]
1.	[Ru(*p*-cymene)Cl$_2$]$_2$ (3)	--	DCE	0 ºC	ND
2.	[Ru(*p*-cymene)Cl$_2$]$_2$ (3)	Cu(OTf)$_2$ (10)	DCE	0 ºC	10
3.	[Ru(*p*-cymene)Cl$_2$]$_2$ (3)	Sc(OTf)$_3$ (10)	DCE	0 ºC	38
4.	[Ru(*p*-cymene)Cl$_2$]$_2$ (3)	In(OTf)$_3$ (10)	DCE	0 ºC	Trace
5.	**[Ru(*p*-cymene)Cl$_2$]$_2$ (3)**	**TMSOTf (30)**	**DCE**	**0 ºC**	**42**
6.	[Ru(*p*-cymene)Cl$_2$]$_2$ (3)	ZnCl$_2$ (10)	DCE	0 ºC	ND
7.	[Ru(*p*-cymene)Cl$_2$]$_2$ (3)	FeBr$_3$ (10)	DCE	0 ºC	ND
8.	[Ru(*p*-cymene)Cl$_2$]$_2$ (3)	TMSOTf (30)	DCE	25 ºC	12
9.	[Ir(COD)Cl]$_2$ (3)	TMSOTf (30)	DCE	0 ºC	ND

[a] Standard reaction conditions: **1** (0.02 mmol, 1 equiv.), anisaldehyde (0.02 mmol, 1 equiv.) [b] The yields were determined by ^{1}H NMR analysis of crude product using CH$_2$Br$_2$ as the internal standard, other diastereomer is not observed [c]ND (Not Detected). DCE=dichloroethane, DCM=dichloromethane, EtOH=ethanol, THF=Tetrahydrofuran

With Acetal



The expected product **5,** was obtained in 42% yield as the highest when the reaction was carried out with aldehyde. Further, to improve the yield of the reaction, we proceeded to the activated aldehydes like acetal. Here, we began our investigations using vinyl sulfoxonium ylide **1**(1 equiv.), and *p*-anisaldehyde dimethyl acetal **4**, as the model substrates to determine the optimum reaction conditions. The reaction afforded 82% of the desired ylidene butenolide (**5**) product with a dual catalytic system, ruthenium/TMSOTf in DCE solvent ***(Table 3, entry 1)***.

Table 3: Optimization studies for the synthesis of ylidene butenolides with acetal

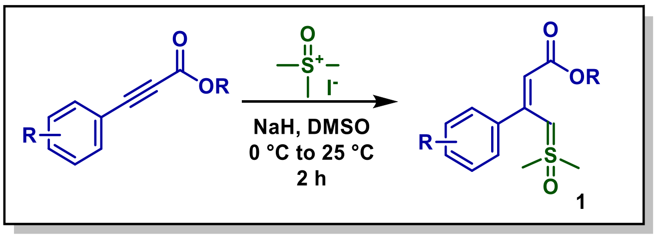
Entry[a-b]	**Catalyst 1 (X_1 mol%)**	**Catalyst 2 (X_2 mol%)**	**Solvent**	**T (°C)**	**Yield (%)**[c]
1.	**[Ru(*p*-cymene)Cl_2]$_2$(3)**	**TMSOTf (30)**	**DCE**	**0 ºC**	**82%**
2.	[Ir(COD)Cl]$_2$(3)	TMSOTf (30)	DCE	0 ºC	80%
3.	[Ru(*p*-cymene)Cl_2]$_2$(3)	Sc(OTf)$_3$ (10)	DCE	0 ºC	58%
4.	[Ru(*p*-cymene)Cl_2]$_2$(3)	In(OTf)$_3$ (10)	DCE	0 ºC	56%
5.	[Ru(*p*-cymene)Cl_2]$_2$(3)	Cu(OTf)$_2$ (10)	DCE	0 ºC	55%
6.	[Ru(*p*-cymene)Cl_2]$_2$(3)	$ZnCl_2$ (10)	DCE	0 ºC	61%
7.	[Ru(*p*-cymene)Cl_2]$_2$(3)	$FeBr_3$ (10)	DCE	0 ºC	21%
8.	[Ru(*p*-cymene)Cl_2]$_2$(3)	--	DCE	0 ºC	ND
9.	--	TMSOTf (30)	DCE	0 ºC	ND
10.	[Ru(*p*-cymene)Cl_2]$_2$(3)	TMSOTf (10)	DCE	0 ºC	36%
11.	[Ru(*p*-cymene)Cl_2]$_2$(3)	TMSOTf (30)	DCE	25 ºC	ND
12.	[Ru(*p*-cymene)Cl_2]$_2$(3)	TMSOTf (30)	DCM	0 ºC	77%
13.	[Ru(*p*-cymene)Cl_2]$_2$(3)	TMSOTf (30)	THF	0 ºC	68%
14.	[Ru(*p*-cymene)Cl_2]$_2$(3)	TMSOTf (30)	Toluene	0 ºC	65%
15.	[Ru(*p*-cymene)Cl_2]$_2$(3)	TMSOTf (30)	Dioxane	0 ºC	21%
16.	[Ru(*p*-cymene)Cl_2]$_2$(3)	TMSOTf (30)	ACN	0 ºC	34%
17.	[Ru(*p*-cymene)Cl_2]$_2$(3)	TMSOTf (30)	MeOH	0 ºC	28%

[a] Standard reaction conditions: **1** (1 equiv.), **4** (1 equiv.) [b] The yields were determined by ^1H NMR analysis of crude product using CH_2Br_2 as the internal standard, other diastereomer is not observed [c] ND (Not Detected) DCE=dichloroethane, DCM=dichloromethane, EtOH=ethanol, THF=Tetrahydrofuran

Iridium catalyst (as catalyst 1) gave the desired product in good yield ***(Table 3, entry 2)***. But, due to the cheap and easy availability of the ruthenium catalyst reactions were carried out with ruthenium. Further, optimization was carried out with various lewis acid catalysts. Among them, Sc(OTf)$_3$, In(OTf)$_3$, Cu(OTf)$_2$, and $ZnCl_2$ served moderate yields (55-61%) ***(Table 3, entry 3–6)***. However, in the case of $FeBr_3$, the yield of desired product was very less ***(Table 3, entry 7)***. No desired product was observed in absence of either of the catalyst ***(Table 3, entry 8–9)***. Also, the yield of the desired product decreased when we decreased the mol% of the lewis acid ***(Table 3, entry 10)***. When the reaction was carried out at room temperature using ruthenium catalyst and TMSOTf, we observed the decrease in yield of the desired product ***(Table 3, entry 11)***. In addition, we have proceeded to the solvent optimization which proved that DCE is the best solvent for the given reaction by providing 82% yield of the desired product. However, the desired product was observed in yield of 77% with DCM ***(Table 3, entry 12)***. Other solvents like THF, toluene, dioxane, acetonitrile, methanol served the less yield ***(Table 3, entry 13–17)***. From this optimization study, it is observed that the reaction yields 82% of the desired product **5** with dual catalysts ruthenium (3 mol%)/TMSOTf (30 mol%) in dichloroethane solvent ***(Table 3, entry 1)***.

III. Experimental Procedure:

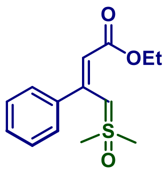
a) General procedure for the synthesis of vinyl sulfoxonium ylides (1): [1a-b]



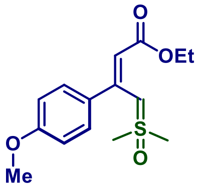
Vinyl sulfoxonium ylides were prepared using the reported procedure. [1a-b] To an oven-dried, Ar-purged 250 mL round-bottom flask equipped with a magnetic stir bar is added NaH (2 equiv., 21 mmol) and DMSO (0.5 M, 20 mL). Trimethylsulfoxonium iodide (recrystallized from water and dried at 70 °C under vacuum overnight) (1.4 equiv., 14 mmol), is added to the above turbid solution at 20 °C. The resulting suspension is stirred for 20 mins at rt, after which it becomes a clear, homogeneous solution of dimethylsulfoxonium methylide. To a separate, oven-dried, Ar-purged 100 mL round-bottom flask equipped with a stir bar, added the ynoate (1 equiv., 10 mmol) in 25 mL THF and the resulting solution is cooled to 0 °C (ice/water bath).

Figure 1: *Synthesis of vinyl sulfoxonium ylide.* ***(a)*** *Addition of electrophile at 0 °C.* ***(b)*** *reddish brown reaction mixture 15 mins after the addition of electrophile at rt.* ***(c)*** *After pouring the reaction in crushed ice.* ***(d)*** *Doing the vacuum filtration.* ***(e)*** *Drying the product after washing with cold ethanol and n-hexane.*

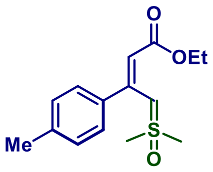
The pre-made methylide solution is added *via* cannula or syringe dropwise over 5 mins. The resulting mixture is stirred for 2 hours at rt and then poured into crushed ice (75 mL by volume) with vigorous stirring. The precipitate was collected and washed with cold ethanol and *n*-hexane (1:1) to give almost pure vinyl sulfoxonium ylide. Spectral data for some of the newly synthesized vinyl sulfoxonium ylides were provided below. The ylides mentioned below were prepared in the same way.



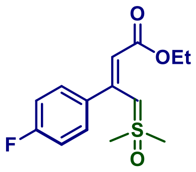
1a (93%)



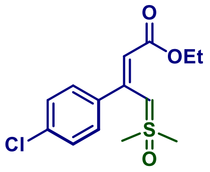
1b (78%)



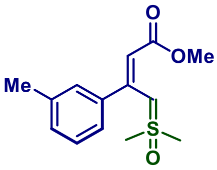
1c (88%)



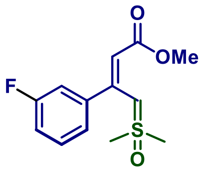
1d (77%)



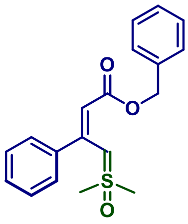
1e (79%)



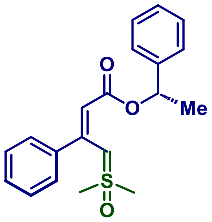
1f (73%)



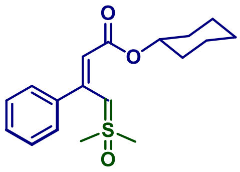
1g (75%)



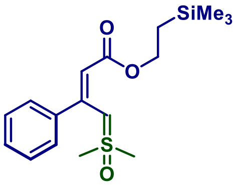
1h (80%)



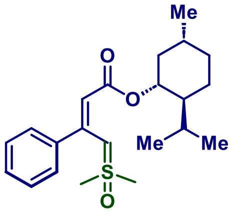
1i (79%)



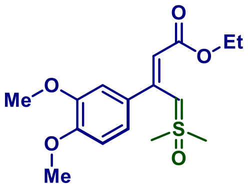
1j (86%)



1k (85%)

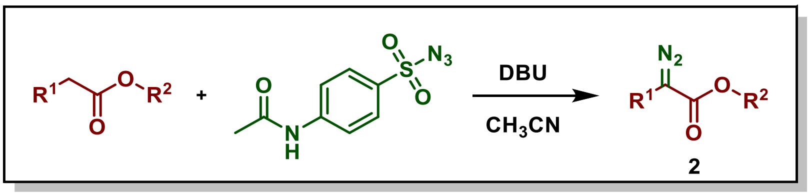


1l (80%)

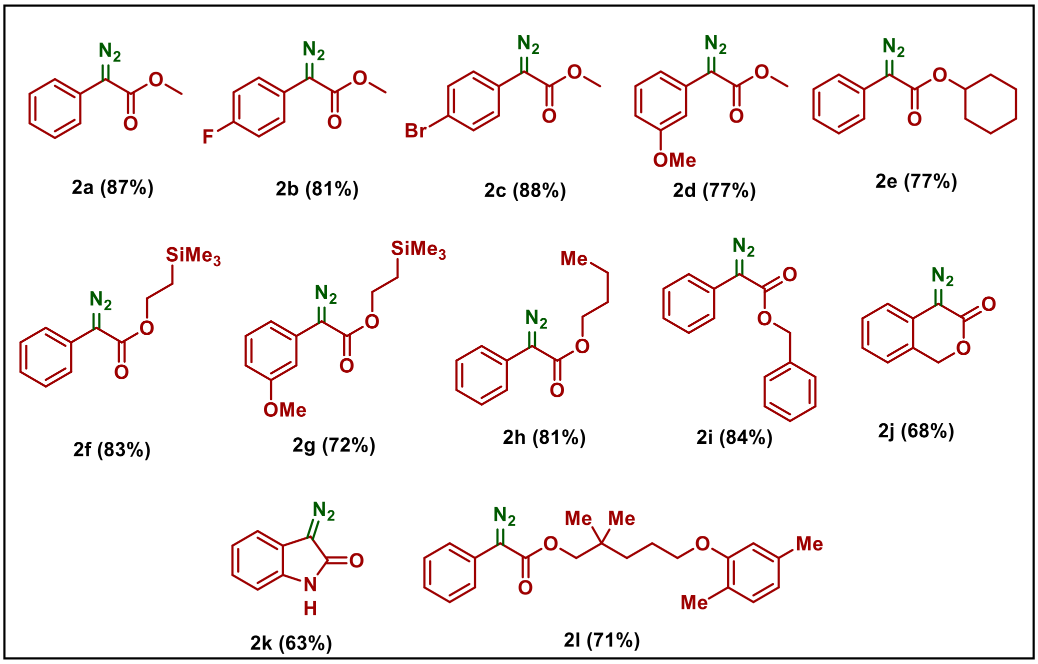


1m (69%)

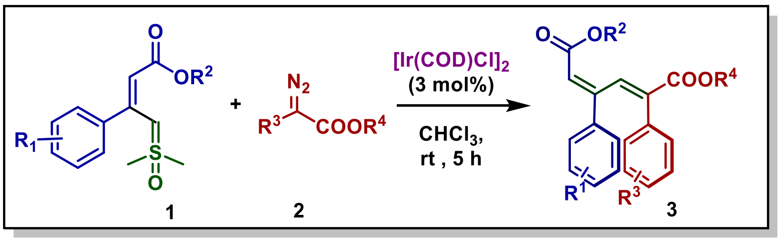
b) General procedure for the preparation of diazo ester (2): [2]



Diazo compounds were prepared using the reported procedure.[2] To an oven-dried, Ar-purged round-bottom flask equipped with a magnetic stir bar, ester (2 mmol, 1 equiv.) was dissolved in the dry acetonitrile solvent (0.2 M) and the reaction mixture is cooled to 0 °C. Then, the 4-acetamido benzenesulfonyl azide (3 mmol, 1.5 equiv.) dissolved in acetonitrile (0.1 M) solvent was added dropwise. To the reaction mixture, DBU (3 mmol, 1.5 equiv.) base was added, and the reaction mixture is allowed to warm to the room temperature. Stirring was continued at room temperature overnight. After the completion, reaction mixture was quenched with the aqueous NH_4Cl, extracted with DCM (3x10 mL) and dried over anhydrous sodium sulfate. The crude mixture was evaporated in *vacuo* and purified by flash column chromatography on silica gel to give the corresponding diazo esters, **2**. The diazo compounds mentioned below are synthesized using this procedure.

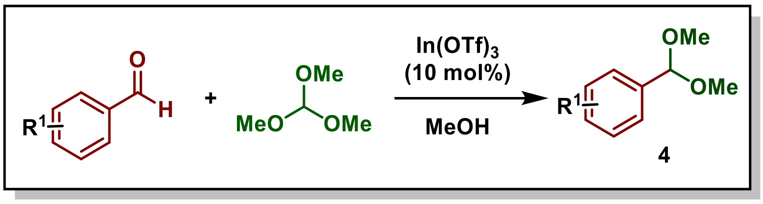


c) General procedure for the synthesis of dienoates (3):

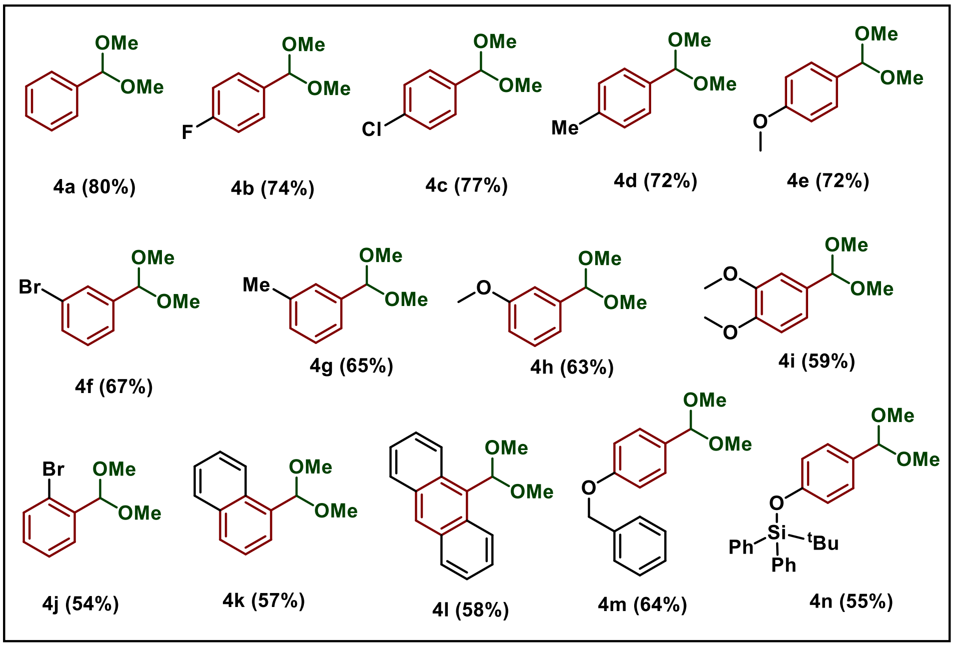


To an oven-dried, Ar-purged round-bottom flask equipped with a magnetic stir bar, vinyl sulfoxonium ylide **1** (0.4 mmol, 1 equiv.) was dissolved in $CHCl_3$ (2 mL) solvent. To the solution, 3 mol% $[Ir(COD)Cl]_2$ catalyst was added and stirred for 30 mins. Diazo ester **2** (0.4 mmol, 1 equiv.) was dissolved in $CHCl_3$ (1 mL) solvent added to the stirring solution dropwise at room temperature. The reaction mixture is allowed to stir for 5 hours. After the completion of reaction (monitored *via* TLC), reaction mixture is passed through a short plug of silica, eluted with dichloromethane. The crude mixture is concentrated in *vacuo* and purified using flash column chromatography on silica gel to yield the corresponding dienoates, **3**.

d) General procedure for the preparation of acetals (4): [3]



Acetals were prepared using the reported procedure.[3] To an oven-dried, Ar-purged round-bottom flask equipped with a magnetic stir bar, aldehyde (2 mmol, 1 equiv.) was dissolved in methanol (0.3 M). Trimethyl orthoformate (3 mmol, 1.5 equiv.) was added to the stirring solution along with $In(OTf)_3$ (0.01 mmol, 10 mol%) catalyst and stirring was continued for 4 hours. After the completion of reaction, the reaction mixture was evaporated in *vacuo*, passed through a silica gel, and obtained acetal **4** is used directly without further purification. The acetals shown below are prepared using this procedure and utilised directly.

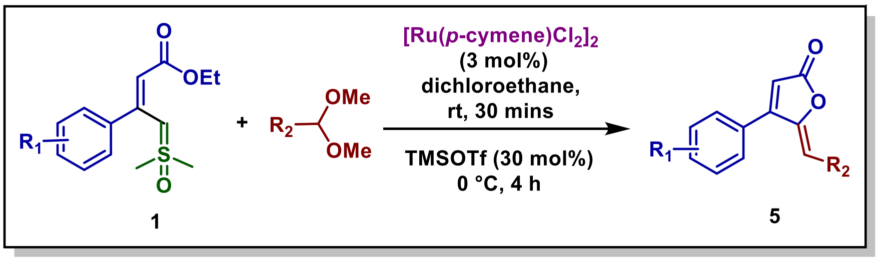


4a (80%) 4b (74%) 4c (77%) 4d (72%) 4e (72%)

4f (67%) 4g (65%) 4h (63%) 4i (59%)

4j (54%) 4k (57%) 4l (58%) 4m (64%) 4n (55%)

e) General procedure for the synthesis of ylidene butenolides (5):



To an oven-dried, Ar-purged round-bottom flask equipped with a magnetic stir bar, vinyl sulfoxonium ylide (0.4 mmol, 1 equiv.) is dissolved in dichloroethane (3 mL) solvent. To this solution, ruthenium catalyst (3 mol%) was added and allowed to stir for 30 mins at room temperature. Then, the reaction mixture was cooled to 0 ℃ and acetal (0.4 mmol, 1 equiv.) was added. To the stirring solution, trimethylsilyl trifluoromethanesulfonate (30 mol%) was added and continued to stir at 0 ℃ for 4 hours. After the completion of the reaction, reaction mixture was passed through a short plug of silica, eluted with DCM and concentrated in *vacuo*. Crude mixture was purified by flash column chromatography on silica gel to give the corresponding ylidene butenolides, **5**.

IV. X-ray crystallographic data

a) X-ray crystallographic data of 3j (CCDC 2313826):

Sample Preparation:

Single crystal of compound **3j** suitable for the X-ray diffraction studies were grown from its $CHCl_3$ solution at room temperature by slow evaporation of the solvent.

Molecular structure determination of compounds 3j:

Single crystal X-ray diffraction data for compound **3j** were collected using a Bruker D8 Quest diffractometer equipped with a 3- axis goniometer. The crystals were covered with Paratone–N and mounted using loop. The data were collected at room temperature using Mo Kα radiation (λ = 0.71073). Integration of data was performed using SAINT. Empirical absorption correction was applied using SADABS. Structure solutions were accomplished by directs methods and refine by full matrix leastsquare on F2 using OLEX2. All non-hydrogen atoms were refined anisotropically. The position of hydrogen atoms was fixed according to a riding model as well as fourier map and were refined isotropically. CCDC 2313826 (**3j**) contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from Data Centre *via* www.ccdc.cam.ac.uk/data_request/cif. The crystallographic refinement parameters are given below:

Table 1 Crystal data and structure refinement for 3j.

CCDC	2313826
Identification code	Dienoate
Empirical formula	$C_{21}H_{18}O_4$
Formula weight	334.35
Temperature/K	298
Crystal system	triclinic

Space group	P-1
a/Å	8.4870(10)
b/Å	10.1115(12)
c/Å	10.5324(11)
α/°	91.975(4)
β/°	93.296(4)
γ/°	108.179(4)
Volume/Å^3	856.01(17)
Z	2
ρ_{calc}g/cm^3	1.297
μ/mm^{-1}	0.089
F(000)	352.0
Crystal size/mm^3	0.21 × 0.14 × 0.11
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	4.246 to 64.608
Index ranges	$-12 \leq h \leq 12$, $-14 \leq k \leq 15$, $-15 \leq l \leq 15$
Reflections collected	42554
Independent reflections	6039 [$R_{int} = 0.0448$, $R_{sigma} = 0.0347$]
Data/restraints/parameters	6039/0/227
Goodness-of-fit on F^2	1.036
Final R indexes [I>=2σ (I)]	$R_1 = 0.0506$, $wR_2 = 0.1394$
Final R indexes [all data]	$R_1 = 0.0741$, $wR_2 = 0.1593$
Largest diff. peak/hole / e Å^{-3}	0.32/-0.17

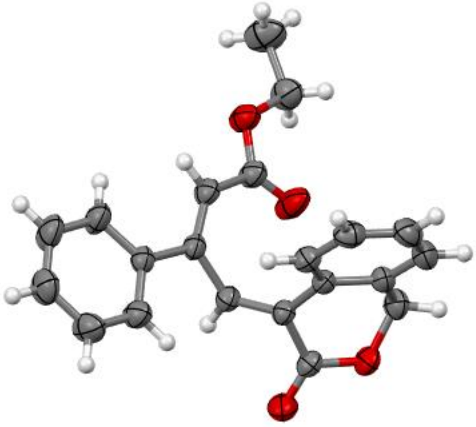


Figure 2: ***ORTEP representation of the X-ray structure of 3j with Thermal ellipsoid at 50% probability.***

b) X-ray crystallographic data of 5k (CCDC 2313823):

Sample Preparation:

Single crystal of compound **5k** suitable for the X-ray diffraction studies were grown from its $CHCl_3$ solution at room temperature by slow evaporation of the solvent.

Molecular structure determination of compounds 5k:

Single crystal X-ray diffraction data for compound **5k** were collected using a Bruker D8 Quest diffractometer equipped with a 3- axis goniometer. The crystals were covered with Paratone–N and mounted using loop. The data were collected at room temperature using Mo Kα radiation (λ = 0.71073). Integration of data was performed using SAINT. Empirical absorption correction was applied using SADABS. Structure solutions were accomplished by directs methods and refine by full matrix leastsquare on F2 using OLEX2. All non-hydrogen atoms were refined anisotropically. The position of hydrogen atoms was fixed according to a riding model as well as fourier map and were refined isotropically. CCDC 2313823 (**5k**) contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from Data Centre *via* www.ccdc.cam.ac.uk/data_request/cif. The crystallographic refinement parameters are given below:

Table 1 Crystal data and structure refinement for 5k.

CCDC	2313823
Identification code	Naphthylidene butenolide
Empirical formula	$C_{21}H_{14}O_2$
Formula weight	298.32
Temperature/K	298.00
Crystal system	monoclinic
Space group	$P2_1/c$
a/Å	8.1483(7)
b/Å	18.7780(15)
c/Å	9.9744(8)
α/°	90
β/°	98.770(3)
γ/°	90
Volume/Å^3	1508.3(2)
Z	4
ρ_{calc}g/cm^3	1.314
μ/mm^{-1}	0.084
F(000)	624.0
Crystal size/mm^3	0.21 × 0.15 × 0.12

Radiation	MoKα ($\lambda = 0.71073$)
2Θ range for data collection/°	4.338 to 51.998
Index ranges	$-10 \leq h \leq 10$, $-23 \leq k \leq 23$, $-12 \leq l \leq 12$
Reflections collected	47156
Independent reflections	2951 [$R_{int} = 0.1039$, $R_{sigma} = 0.0507$]
Data/restraints/parameters	2951/0/209
Goodness-of-fit on F^2	1.057
Final R indexes [$I>=2\sigma(I)$]	$R_1 = 0.0586$, $wR_2 = 0.1146$
Final R indexes [all data]	$R_1 = 0.1119$, $wR_2 = 0.1270$
Largest diff. peak/hole / e Å^{-3}	0.14/-0.15

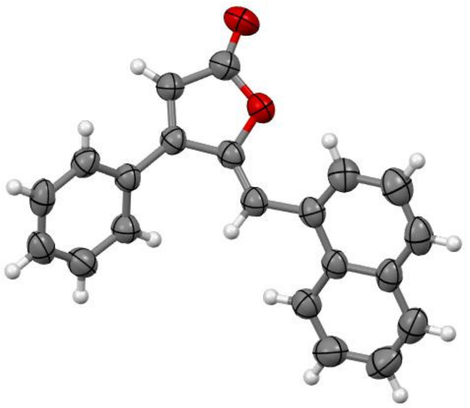


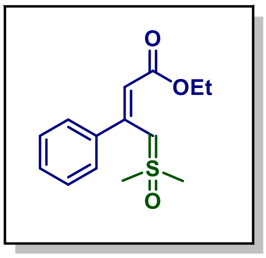
Figure 3: ***ORTEP representation of the X-ray structure of 5k with Thermal ellipsoid at 50% probability.***

V. Characterisation Data:

a) Vinyl Sulfoxonium ylide (1)

Ylides that are used in this work are synthesized using the reported procedure. However, the characterisation data for some ylides which are newly prepared are provided here.

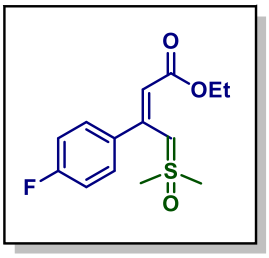
ethyl (Z)-4-(dimethyl(oxo)-l6-sulfaneylidene)-3-phenylbut-2-enoate (1a):



Following the general procedure (a), reaction of ethyl 3-phenylpropiolate (1.7 g, 10 mmol, 1 equiv.) in THF (25 mL) at 0 ºC with dimethylsulfoxonium methylide generated from trimethylsulfoxonium iodide (3.01 g, 14 mmol, 1 .4 equiv.) and sodium hydride (468 mg, 20 mmol, 2 equiv.) in DMSO (20 mL) yielded vinyl sulfoxonium ylide **1a** as yellow solid (2.4 g, 93%).

^{1}H NMR (400 MHz, CDCl$_3$) δ 7.48 – 7.21 (m, 5H), 6.16 (s, 1H), 4.61 (s, 1H), 4.04 – 3.96 (m, 2H), 2.86 (s, 6H), 1.18 – 1.10 (m, 3H). **^{13}C NMR (101 MHz, CDCl$_3$) δ** 168.3, 158.0, 140.9, 128.8, 128.1, 95.3, 70.5, 58.3, 44.0, 14.5. **HRMS (ESI) m/z:** [M+H]$^+$ calculated for $C_{14}H_{19}O_3S$, 267.1049; found 267.1053.

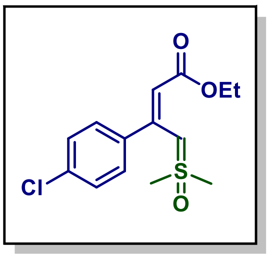
ethyl (Z)-4-(dimethyl(oxo)-l6-sulfaneylidene)-3-(4-fluorophenyl)but-2-enoate (1d):



Following the general procedure (a), reaction of ethyl 3-(4-fluorophenyl)propiolate (1.95 g, 10 mmol, 1 equiv.) in THF (25 mL) at 0 ºC with dimethylsulfoxonium methylide generated from trimethylsulfoxonium iodide (3.13 g, 14 mmol, 1.4 equiv.) and sodium hydride (487 mg, 20 mmol, 2 equiv.) in DMSO (20 mL) yielded vinyl sulfoxonium ylide **1d** as yellow solid (2.23 g, 77%).

^{1}H NMR (400 MHz, CDCl$_3$) δ 7.46 (dd, *J* = 8.7, 5.5 Hz, 2H), 7.03 (t, *J* = 8.7 Hz, 2H), 6.21 (s, 1H), 4.68 (s, 1H), 4.07 (q, *J* = 7.1 Hz, 2H), 2.97 (s, 6H), 1.22 (t, *J* = 7.1 Hz, 3H). **^{13}C NMR (101 MHz, CDCl$_3$) δ** 168.4, 162.96 (d, *J* = 248.4 Hz), 130.93 (d, *J* = 8.1 Hz), 115.22 (d, *J* = 21.3 Hz), 70.2, 58.6, 44.3, 14.7. **HRMS (ESI) m/z:** [M+Na]$^+$ calculated for $C_{14}H_{18}FO_3FS$, 285.0955; found 285.0960.

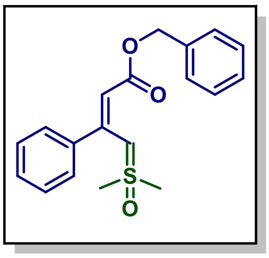
ethyl (Z)-3-(4-chlorophenyl)-4-(dimethyl(oxo)-l6-sulfaneylidene)but-2-enoate (1e):



Following the general procedure (a), reaction of ethyl 3-(4-chlorophenyl)propiolate (2.1 g, 10 mmol, 1 equiv.) in THF (25 mL) at 0 ºC with dimethylsulfoxonium methylide generated from trimethylsulfoxonium iodide (3.1 g, 14 mmol, 1 .4 equiv.) and sodium hydride (483 mg, 20 mmol, 2 equiv.) in DMSO (20 mL) yielded vinyl sulfoxonium ylide **1e** as yellow solid (2.4 g, 79%).

^{1}H NMR (400 MHz, CDCl$_3$) δ 7.47 – 7.28 (m, 4H), 6.21 (s, 1H), 4.69 (s, 1H), 4.12 – 4.03 (m, 2H), 2.99 (s, 6H), 1.25 – 1.16 (m, 3H). **^{13}C NMR (101 MHz, CHLOROFORM-*D*) δ** 168.4, 156.6, 139.4, 134.8, 130.5, 129.7, 128.5, 127.8, 96.2, 70.0, 58.7, 44.4, 14.6. **HRMS (ESI) m/z:** [M+Na]$^+$ calculated for $C_{14}H_{17}O_3NaClS$, 323.0479; found 323.0478.

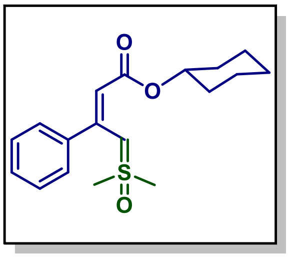
benzyl (Z)-4-(dimethyl(oxo)-l6-sulfaneylidene)-3-phenylbut-2-enoate (1h):



Following the general procedure (a), reaction of benzyl 3-phenylpropiolate (2.4 g, 10 mmol, 1 equiv.) in THF (25 mL) at 0 ºC with dimethylsulfoxonium methylide generated from trimethylsulfoxonium iodide (3.1 g, 14 mmol, 1 .4 equiv.) and sodium hydride (488 mg, 20 mmol, 2 equiv.) in DMSO (20 mL) yielded vinyl sulfoxonium ylide **1h** as yellow solid (2.67 g, 80%).

^{1}H NMR (400 MHz, CDCl$_3$) δ 7.53 – 7.19 (m, 10H), 6.25 (s, 1H), 5.10 (s, 2H), 4.80 (s, 1H), 2.89 (s, 6H). **^{13}C NMR (101 MHz, CDCl$_3$) δ** 168.1, 158.7, 141.0, 137.6, 137.6, 129.0, 128.8, 128.4, 128.3, 127.8, 127.7, 71.0, 64.5, 44.2, 44.2. **HRMS (ESI) m/z:** [M+Na]$^+$ calculated for $C_{19}H_{20}O_3NaS$, 351.1025; found 351.1023.

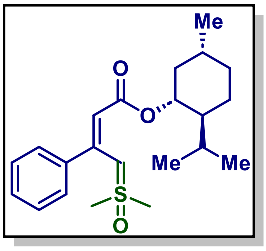
cyclohexyl (Z)-4-(dimethyl(oxo)-l6-sulfaneylidene)-3-phenylbut-2-enoate (1j):



Following the general procedure (a), reaction of cyclohexyl 3-phenylpropiolate (2.3 g, 10 mmol, 1 equiv.) in THF (25 mL) at 0 ºC with dimethylsulfoxonium methylide generated from trimethylsulfoxonium iodide (3.1 g, 14 mmol, 1 .4 equiv.) and sodium hydride (484 mg, 20 mmol, 2 equiv.) in DMSO (20 mL) yielded vinyl sulfoxonium ylide **1j** as yellow solid (2.78 g, 86%).

^{1}H NMR (400 MHz, CDCl$_3$) δ 7.50 – 7.28 (m, 5H), 6.23 (s, 1H), 4.70 (s, 2H), 2.91 (s, 6H), 1.88 – 1.62 (m, 4H), 1.50 (ddt, *J* = 12.6, 6.5, 3.1 Hz, 1H), 1.40 – 1.12 (m, 5H). **^{13}C NMR (101 MHz, CDCl$_3$) δ** 168.1, 157.8, 141.1, 129.0, 128.2, 70.6, 70.1, 44.2, 44.2, 40.9, 32.1, 25.5, 24.0. **HRMS (ESI) m/z:** [M+Na]$^+$ calculated for $C_{18}H_{24}O_3NaS$, 343.1338; found 343.1330.

(1R,2S,5R)-2-isopropyl-5-methylcyclohexyl (Z)-4-(dimethyl(oxo)-l6-sulfaneylidene)-3-phenylbut-2-enoate (1l):

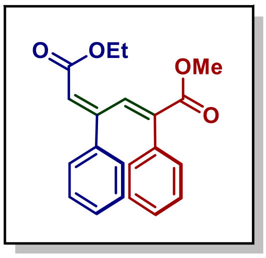


Following the general procedure (a), reaction of (1*R*,2*S*,5*R*)-2-isopropyl-5-methylcyclohexyl 3-phenylpropiolate (2.85 g, 10 mmol, 1 equiv.) in THF (25 mL) at 0 ºC with dimethylsulfoxonium methylide generated from trimethylsulfoxonium iodide (3.09 g, 14 mmol, 1.4 equiv.) and sodium hydride (481 mg, 20 mmol, 2 equiv.) in DMSO (20 mL) yielded vinyl sulfoxonium ylide **1l** as yellow solid (3.03 g, 80%).

^{1}H NMR (400 MHz, CDCl$_3$) δ 7.50 – 7.29 (m, 5H), 6.22 (d, *J* = 2.0 Hz, 1H), 4.67 (d, *J* = 1.3 Hz, 1H), 4.62 – 4.51 (m, 1H), 2.89 (dt, *J* = 21.7, 2.2 Hz, 6H), 2.06 – 1.84 (m, 2H), 1.65 – 1.55 (m, 2H), 1.49 – 1.38 (m, 1H), 1.34 – 1.23 (m, 1H), 1.07 – 0.86 (m, 1H), 0.82 (ddt, *J* = 9.3, 7.2, 1.9 Hz, 7H), 0.71 (dt, *J* = 7.0, 2.0 Hz, 4H). **^{13}C NMR (101 MHz, CDCl$_3$) δ** 168.2, 157.7, 141.1, 129.0, 128.7, 128.2, 96.4, 71.9, 70.1, 47.1, 44.2, 44.2, 41.6, 34.4, 31.4, 26.1, 23.6, 22.1, 20.8, 16.6. **HRMS (ESI) m/z:** [M+Na]$^+$ calculated for $C_{22}H_{32}O_3NaS$, 399.1964; found 399.1963.

b) Dienoate (3)

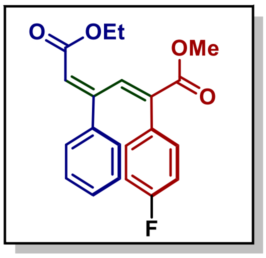
6-ethyl 1-methyl (*2E,4E*)-2,4-diphenylhexa-2,4-dienedioate (3a)



Following the general procedure (c), reaction of vinyl sulfoxonium ylide **1a** (107 mg, 0.4 mmol, 1 equiv.) is carried-out with iridium catalyst (8.1 mg, 3 mol%) and diazo ester **2a** (71 mg, 0.4 mmol, 1 equiv.) in chloroform (3 mL) as solvent. The reaction mixture was stirred at room temperature for 5 h to give **3a** in 85% yield (115 mg) as colourless viscous liquid after purification by the flash column chromatography (*n-Hexane*/EtOAc: 80:20, R$_f$ 0.42) with d.r. >20:1.

^{1}H NMR (500 MHz, CDCl$_3$) δ 8.33 (d, *J* = 1.9 Hz, 1H), 7.14 (d, *J* = 7.2 Hz, 3H), 7.11 (d, *J* = 7.2 Hz, 2H), 7.04 (d, *J* = 6.3 Hz, 3H), 6.98 (d, *J* = 7.9 Hz, 2H), 6.12 (d, *J* = 2.1 Hz, 1H), 4.30 (q, *J* = 7.2 Hz, 2H), 3.85 (s, 3H), 1.35 (t, *J* = 7.2 Hz, 3H). **^{13}C NMR (126 MHz, CDCl$_3$) δ** 167.4, 165.8, 152.8, 139.7, 138.6, 136.7, 134.9, 129.8, 128.9, 128.0, 127.6, 127.4, 120.8, 60.5, 52.5, 14.3. **HRMS (ESI) M/Z:** [M+Na]$^+$ calculated for $C_{21}H_{20}NaO_4$, 359.1254 ; found to be 359.1249.

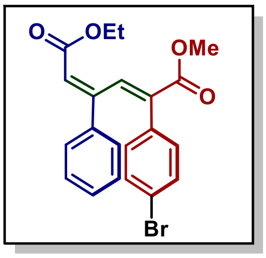
6-ethyl 1-methyl (*2E,4E*)-2-(4-fluorophenyl)-4-phenylhexa-2,4-dienedioate (3b)



Following the general procedure (c), reaction of vinyl sulfoxonium ylide **1a** (107 mg, 0.4 mmol, 1 equiv.) is carried-out with iridium catalyst (8.1 mg, 3 mol%) and diazo ester **2b** (78 mg, 0.4 mmol, 1 equiv.) in chloroform (3 mL) as solvent. The reaction mixture was stirred at room temperature for 5 h to give **3b** in 80% yield (114 mg) as colourless viscous liquid after purification by the flash column chromatography (n-Hexane/EtOAc: 80:20, R_f 0.4) with d.r. >20:1.

^{1}H NMR (400 MHz, CHLOROFORM-*D*) δ 8.46 (d, *J* = 1.7 Hz, 1H), 7.11 (d, *J* = 3.2 Hz, 1H), 7.10 – 7.08 (m, 3H), 7.08 – 7.05 (m, 1H), 7.04 – 6.98 (m, 1H), 6.88 (td, *J* = 7.4, 1.9 Hz, 1H), 6.80 (td, *J* = 7.5, 1.2 Hz, 1H), 6.65 (ddd, *J* = 9.5, 8.3, 1.2 Hz, 1H), 6.09 (d, *J* = 1.7 Hz, 1H), 4.26 (q, *J* = 7.1 Hz, 2H), 3.82 (s, 3H), 1.34 (t, *J* = 7.1 Hz, 3H). **^{13}C NMR (101 MHz, CHLOROFORM-*D*) δ** 166.6, 165.8, 159.57 (d, *J* = 247.8 Hz), 152.4, 141.7, 138.5, 132.1, 131.7, 131.7, 130.13 (d, *J* = 8.2 Hz), 129.0, 128.1, 127.5, 123.3, 123.3, 123.2, 123.1, 121.3, 114.86 (d, *J* = 21.6 Hz), 60.6, 52.7, 14.3. **^{19}F NMR (376 MHz, CHLOROFORM-*D*) δ** -111.72 – -111.84 (m). **HRMS (ESI) M/Z:** $[M+Na]^+$ calculated for $C_{21}H_{19}FNaO_4$, 377.1160 ; found to be 377.1148.

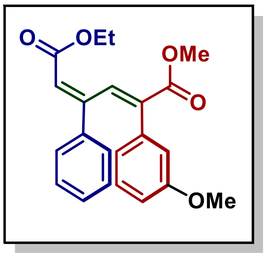
6-ethyl 1-methyl (*2E,4E*)-2-(4-bromophenyl)-4-phenylhexa-2,4-dienedioate (3c)



Following the general procedure (c), reaction of vinyl sulfoxonium ylide **1a** (107 mg, 0.4 mmol, 1 equiv.) is carried-out with iridium catalyst (8.1 mg, 3 mol%) and diazo ester **2c** (102 mg, 0.4 mmol, 1 equiv.) in chloroform (3 mL) as solvent. The reaction mixture was stirred at room temperature for 5 h to give **3c** in 86% yield (143 mg) as colourless viscous liquid after purification by the flash column chromatography (n-Hexane/EtOAc: 90:10, R_f 0.47) with d.r. >20:1.

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.31 (d, *J* = 1.8 Hz, 1H), 7.13 (d, *J* = 8.3 Hz, 3H), 7.09 (d, *J* = 4.4 Hz, 4H), 6.81 (d, *J* = 8.1 Hz, 2H), 6.10 (d, *J* = 1.8 Hz, 1H), 4.23 (q, *J* = 7.1 Hz, 2H), 3.81 (s, 3H), 1.31 (t, *J* = 7.1 Hz, 3H). **^{13}C NMR (126 MHz, $CDCl_3$) δ** 166.8, 165.6, 152.3, 140.3, 138.4, 135.4, 133.8, 131.3, 130.4, 129.0, 128.1, 127.5, 121.9, 120.9, 60.5, 52.5, 14.2. **HRMS (ESI) M/Z:** $[M+Na]^+$ calculated for $C_{21}H_{19}BrNaO_4$, 437.0359; found to be 437.0359.

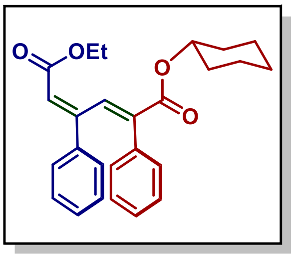
6-ethyl 1-methyl (*2E,4E*)-2-(3-methoxyphenyl)-4-phenylhexa-2,4-dienedioate (3d)



Following the general procedure (c), reaction of vinyl sulfoxonium ylide **1a** (107 mg, 0.4 mmol, 1 equiv.) is carried-out with iridium catalyst (8.1 mg, 3 mol%) and diazo ester **2d** (83 mg, 0.4 mmol, 1 equiv.) in chloroform (3 mL) as solvent. The reaction mixture was stirred at room temperature for 5 h to give **3d** in 78% yield (115 mg) as colourless viscous liquid after purification by the flash column chromatography (n-Hexane/EtOAc: 80:20, R_f 0.35) with d.r. >20:1.

^{1}H NMR (400 MHz,) δ 8.29 (s, 1H), 7.11 (q, *J* = 7.6, 6.3 Hz, 5H), 6.93 (t, *J* = 8.1 Hz, 1H), 6.56 (t, *J* = 10.5 Hz, 2H), 6.46 (s, 1H), 6.09 (s, 1H), 4.24 (q, *J* = 7.4, 7.0 Hz, 2H), 3.82 (s, 3H), 3.61 (s, 3H), 1.32 (t, *J* = 7.4 Hz, 3H). **^{13}C NMR (126 MHz, CDCl$_3$) δ** 167.4, 165.9, 158.6, 152.9, 139.9, 138.7, 136.5, 136.2, 128.9, 128.5, 128.0, 127.7, 122.4, 120.8, 115.3, 113.7, 60.6, 55.2, 52.6, 14.4. **HRMS (ESI) M/Z:** [M+Na]$^+$ calculated for $C_{22}H_{22}NaO_5$, 389.1359; found to be 389.1352.

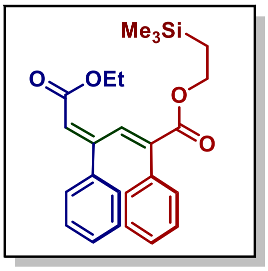
1-cyclohexyl 6-ethyl (*2E,4E*)-2,4-diphenylhexa-2,4-dienedioate (3e)



Following the general procedure (c), reaction of vinyl sulfoxonium ylide **1a** (107 mg, 0.4 mmol, 1 equiv.) is carried-out with iridium catalyst (8.1 mg, 3 mol%) and diazo ester **2e** (98 mg, 0.4 mmol, 1 equiv.) in chloroform (3 mL) as solvent. The reaction mixture was stirred at room temperature for 5 h to give **3e** in 74% yield (120 mg) as colourless viscous liquid after purification by the flash column chromatography (n-Hexane/EtOAc: 90:10, R$_f$ 0.52) with d.r. >20:1.

^{1}H NMR (400 MHz, CHLOROFORM-*D*) δ 8.28 (d, *J* = 1.7 Hz, 1H), 7.12 (dd, *J* = 7.9, 1.8 Hz, 2H), 7.10 – 7.07 (m, 2H), 7.06 – 7.04 (m, 1H), 7.01 – 6.95 (m, 5H), 6.09 (d, *J* = 1.7 Hz, 1H), 4.96 (dq, *J* = 8.7, 4.6, 4.2 Hz, 1H), 4.24 (q, *J* = 7.2 Hz, 2H), 1.92 – 1.86 (m, 2H), 1.68 (td, *J* = 6.8, 6.3, 3.1 Hz, 2H), 1.60 – 1.46 (m, 4H), 1.44 – 1.37 (m, 2H), 1.31 (d, *J* = 7.2 Hz, 3H). **^{13}C NMR (101 MHz, CHLOROFORM-*D*) δ** 166.3, 165.7, 152.7, 138.8, 138.7, 137.5, 135.0, 129.8, 128.7, 127.9, 127.6, 127.4, 127.1, 120.8, 73.4, 60.4, 31.4, 25.4, 23.4, 14.3. **HRMS (ESI) M/Z:** [M+Na]$^+$ calculated for $C_{26}H_{28}NaO_4$, 427.1880 ; found to be 427.1869.

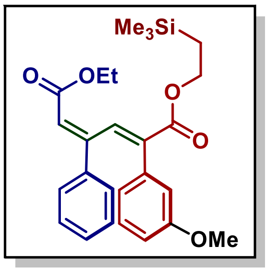
6-ethyl 1-(2-(trimethylsilyl)ethyl) (*2E,4E*)-2,4-diphenylhexa-2,4-dienedioate (3f)



Following the general procedure (c), reaction of vinyl sulfoxonium ylide **1a** (107 mg, 0.4 mmol, 1 equiv.) is carried-out with iridium catalyst (8.1 mg, 3 mol%) and diazo ester **2f** (105 mg, 0.4 mmol, 1 equiv.) in chloroform (3 mL) as solvent. The reaction mixture was stirred at room temperature for 5 h to give **3f** in 71% yield (121 mg) as colourless viscous liquid after purification by the flash column chromatography (n-Hexane/EtOAc: 90:10, R$_f$ 0.52) with d.r. >20:1.

^{1}H NMR (400 MHz, CHLOROFORM-*D*) δ 8.28 (d, *J* = 1.7 Hz, 1H), 7.14 – 7.12 (m, 1H), 7.11 (d, *J* = 1.9 Hz, 2H), 7.08 (dd, *J* = 5.3, 1.1 Hz, 2H), 7.06 (t, *J* = 2.1 Hz, 1H), 7.01 (d, *J* = 2.3 Hz, 1H), 6.99 (d, *J* = 3.6 Hz, 1H), 6.96 (d, *J* = 1.9 Hz, 1H), 6.94 (d, *J* = 4.4 Hz, 1H), 6.09 (d, *J* = 1.8 Hz, 1H), 4.37 – 4.32 (m, 2H), 4.24 (q, *J* = 7.1 Hz, 2H), 1.32 (t, *J* = 7.1 Hz, 3H), 1.10 – 1.06 (m, 2H), 0.02 (s, 9H). **^{13}C NMR (101 MHz, CHLOROFORM-*D*) δ** 167.1, 165.8, 152.9, 139.1, 138.7, 137.2, 135.0, 129.8, 128.8, 128.0, 127.6, 127.5, 127.2, 120.7, 63.6, 60.4, 17.4, 14.3, -1.4. **HRMS (ESI) M/Z:** [M+Na]$^+$ calculated for $C_{25}H_{30}NaO_4Si$, 445.1806 ; found to be 445.1799.

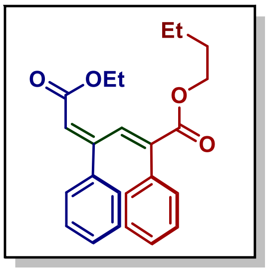
6-ethyl 1-(2-(trimethylsilyl)ethyl) (2E,4E)-2-(3-methoxyphenyl)-4-phenylhexa-2,4-dienedioate (3g)



Following the general procedure (c), reaction of vinyl sulfoxonium ylide **1a** (107 mg, 0.4 mmol, 1 equiv.) is carried-out with iridium catalyst (8.1 mg, 3 mol%) and diazo ester **2g** (117 mg, 0.4 mmol, 1 equiv.) in chloroform (3 mL) as solvent. The reaction mixture was stirred at room temperature for 5 h to give **3g** in 54% yield (98 mg) as colourless viscous liquid after purification by the flash column chromatography (n-Hexane/EtOAc: 90:10, R_f 0.4) with d.r. 14:1.

^{1}H NMR (400 MHz, CHLOROFORM-*D*) δ 8.25 (d, *J* = 2.3 Hz, 1H), 7.13 – 7.07 (m, 5H), 6.90 (d, *J* = 7.5 Hz, 1H), 6.57 – 6.51 (m, 2H), 6.46 – 6.42 (m, 1H), 6.07 (d, *J* = 1.8 Hz, 1H), 4.34 – 4.29 (m, 2H), 4.23 (d, *J* = 7.2 Hz, 2H), 3.59 (s, 3H), 1.31 (t, *J* = 7.2 Hz, 3H), 1.09 – 1.04 (m, 2H), 0.01 (s, 9H). **^{13}C NMR (101 MHz, CHLOROFORM-*D*) δ** 167.1, 165.8, 158.5, 152.9, 139.3, 138.8, 137.1, 136.3, 128.8, 128.4, 128.0, 127.7, 122.5, 120.7, 115.3, 113.6, 63.7, 60.5, 55.1, 17.4, 14.3, -1.4. **HRMS (ESI) M/Z:** $[M+Na]^+$ calculated for $C_{26}H_{32}NaO_5Si$, 475.1911; found to be 475.1902.

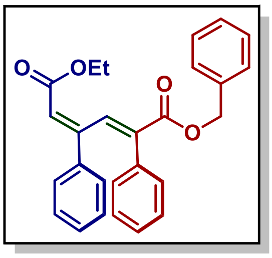
1-butyl 6-ethyl (*2E,4E*)-2,4-diphenylhexa-2,4-dienedioate (3h)



Following the general procedure (c), reaction of vinyl sulfoxonium ylide **1a** (107 mg, 0.4 mmol, 1 equiv.) is carried-out with iridium catalyst (8.1 mg, 3 mol%) and diazo ester **2h** (88 mg, 0.4 mmol, 1 equiv.) in chloroform (3 mL) as solvent. The reaction mixture was stirred at room temperature for 5 h to give **3h** in 79% yield (120 mg) as colourless viscous liquid after purification by the flash column chromatography (n-Hexane/EtOAc: 90:10, R_f 0.5) with d.r. >20:1.

^{1}H NMR (500 MHz, CDCl$_3$) δ 8.29 (d, *J* = 1.8 Hz, 1H), 7.13 – 7.11 (m, 2H), 7.11 – 7.04 (m, 3H), 7.01 (dd, *J* = 5.1, 2.1 Hz, 3H), 6.97 – 6.94 (m, 2H), 6.10 (d, *J* = 1.8 Hz, 1H), 4.24 (td, *J* = 6.9, 4.3 Hz, 4H), 1.71 – 1.65 (m, 2H), 1.40 (q, *J* = 7.5 Hz, 2H), 1.32 (t, *J* = 7.2 Hz, 3H), 0.94 (t, *J* = 7.4 Hz, 3H). **^{13}C NMR (126 MHz, CDCl$_3$) δ** 166.9, 165.7, 152.7, 139.2, 138.6, 137.0, 134.9, 129.7, 128.8, 127.9, 127.6, 127.5, 127.2, 120.7, 65.2, 60.4, 30.6, 19.2, 14.3, 13.7. **HRMS (ESI) M/Z:** $[M+Na]^+$ calculated for $C_{24}H_{26}NaO_4$, 401.1723; found to be 401.1715.

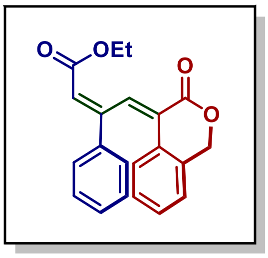
1-benzyl 6-ethyl (*2E,4E*)-2,4-diphenylhexa-2,4-dienedioate (3i)



Following the general procedure (c), reaction of vinyl sulfoxonium ylide **1a** (107 mg, 0.4 mmol, 1 equiv.) is carried-out with iridium catalyst (8.1 mg, 3 mol%) and diazo ester **2i** (101 mg, 0.4 mmol, 1 equiv.) in chloroform (3 mL) as solvent. The reaction mixture was stirred at room temperature for 5 h to give **3i** in 81% yield (134 mg) as colourless viscous liquid after purification by the flash column chromatography (n-Hexane/EtOAc: 90:10, R_f 0.4) with d.r. >20:1.

^{1}H NMR (400 MHz, CHLOROFORM-*D*) δ 8.38 (d, *J* = 1.7 Hz, 1H), 7.43 – 7.37 (m, 4H), 7.36 – 7.33 (m, 1H), 7.15 – 7.12 (m, 3H), 7.11 – 7.08 (m, 2H), 7.04 (dd, *J* = 5.0, 2.1 Hz, 3H), 7.01 – 6.98 (m, 2H), 6.13 (d, *J* = 1.8 Hz, 1H), 5.32 (s, 2H), 4.25 (t, *J* = 7.2 Hz, 2H), 1.32 (t, *J* = 7.2 Hz, 3H). **^{13}C NMR (101 MHz, CHLOROFORM-*D*) δ** 166.7, 165.8, 152.6, 139.9, 138.5, 136.6, 136.1, 134.8, 129.8, 128.8, 128.5, 128.1, 128.0, 127.6, 127.6, 127.3, 66.9, 60.5, 14.3. **HRMS (ESI) M/Z:** $[M+Na]^+$ calculated for $C_{27}H_{24}NaO_4$, 435.1567 ; found to be 435.1569.

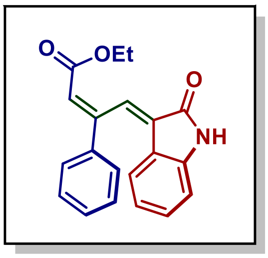
ethyl (*E*)-4-((*E*)-3-oxoisochroman-4-ylidene)-3-phenylbut-2-enoate (3j)



Following the general procedure (c), reaction of vinyl sulfoxonium ylide **1a** (107 mg, 0.4 mmol, 1 equiv.) is carried-out with iridium catalyst (8.1 mg, 3 mol%) and diazo ester **2j** (70 mg, 0.4 mmol, 1 equiv.) in chloroform (3 mL) as solvent. The reaction mixture was stirred at room temperature for 5 h to give **3j** in 62% yield (83 mg) as colourless solid after purification by the flash column chromatography (n-Hexane/EtOAc: 80:10, R_f 0.35) with d.r. 5:1.

^{1}H NMR (400 MHz, CHLOROFORM-*D*) δ 7.79 (d, *J* = 7.7 Hz, 1H), 7.75 (d, *J* = 1.9 Hz, 1H), 7.51 (dd, *J* = 6.3, 2.5 Hz, 2H), 7.43 (d, *J* = 7.6 Hz, 1H), 7.39 – 7.35 (m, 4H), 7.21 (d, *J* = 7.5 Hz, 1H), 6.27 (d, *J* = 1.9 Hz, 1H), 5.25 (s, 2H), 4.22 (d, *J* = 7.2 Hz, 2H), 1.32 (t, *J* = 7.1 Hz, 3H). **^{13}C NMR (101 MHz, CHLOROFORM-*D*) δ** 166.3, 164.5, 153.3, 139.3, 138.0, 133.0, 131.4, 129.5, 129.3, 128.7, 128.7, 128.4, 127.5, 124.4, 124.3, 118.2, 69.2, 60.4, 14.4. **HRMS (ESI) M/Z:** $[M+Na]^+$ calculated for $C_{21}H_{18}NaO_4$, 357.1097 ; found to be 357.1110.

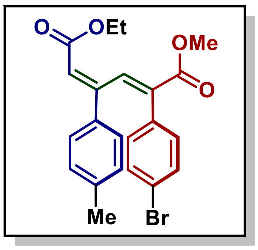
ethyl (*E*)-4-((*E*)-2-oxoindolin-3-ylidene)-3-phenylbut-2-enoate (3k)



Following the general procedure (c), reaction of vinyl sulfoxonium ylide **1a** (107 mg, 0.4 mmol, 1 equiv.) is carried-out with iridium catalyst (8.1 mg, 3 mol%) and diazo ester **2k** (64 mg, 0.4 mmol, 1 equiv.) in chloroform (3 mL) as solvent. The reaction mixture was stirred at room temperature for 5 h to give **3k** in 65% yield (82 mg) as orange solid after purification by the flash column chromatography (n-Hexane/EtOAc: 70:30, R_f 0.42) with d.r. 4:1 (inseparable).

^{1}H NMR (400 MHz, CHLOROFORM-*D*) δ 7.92 – 7.85 (m, 2H), 7.60 (d, *J* = 6.9 Hz, 1H), 7.54 (d, *J* = 1.7 Hz, 1H), 7.53 (d, *J* = 4.1 Hz, 1H), 7.34 (d, *J* = 1.8 Hz, 2H), 7.33 (d, *J* = 1.8 Hz, 1H), 7.22 (t, *J* = 7.7 Hz, 1H), 7.04 (t, *J* = 7.6 Hz, 1H), 6.75 (d, *J* = 7.0 Hz, 1H), 6.36 (d, *J* = 2.1 Hz, 1H), 4.19 (t, *J* = 7.2 Hz, 2H), 1.28 (d, *J* = 7.1 Hz, 3H). **^{13}C NMR (126 MHz, $CDCl_3$) δ** 167.1, 166.2, 152.2, 141.0, 139.1, 134.2, 129.9, 129.4, 128.5, 127.4, 123.4, 122.1, 120.8, 119.2, 109.9, 60.4, 14.4. **HRMS (ESI) M/Z:** $[M+Na]^+$ calculated for $C_{20}H_{17}NNaO_3$, 342.1101; found to be 342.1098.

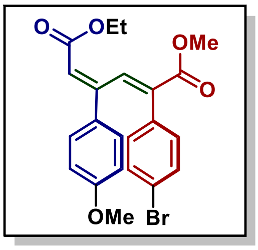
6-ethyl 1-methyl (2E,4E)-2-(4-bromophenyl)-4-(p-tolyl)hexa-2,4-dienedioate (3l)



Following the general procedure (c), reaction of vinyl sulfoxonium ylide **1c** (112 mg, 0.4 mmol, 1 equiv.) is carried-out with iridium catalyst (8.1 mg, 3 mol%) and diazo ester **2c** (102 mg, 0.4 mmol, 1 equiv.) in chloroform (3 mL) as solvent. The reaction mixture was stirred at room temperature for 5 h to give **3l** in 70% yield (120 mg) as colourless viscous liquid after purification by the flash column chromatography (n-Hexane/EtOAc: 90:10, R_f 0.4) with d.r. >20:1.

^{1}H NMR (400 MHz, CHLOROFORM-*D*) δ 8.26 (d, *J* = 1.8 Hz, 1H), 7.16 (d, *J* = 8.6 Hz, 2H), 7.03 (d, *J* = 8.3 Hz, 2H), 6.93 (d, *J* = 7.8 Hz, 2H), 6.83 (d, *J* = 8.1 Hz, 2H), 6.10 (d, *J* = 1.7 Hz, 1H), 4.21 (t, *J* = 7.2 Hz, 2H), 3.83 (s, 3H), 2.26 (s, 3H), 1.31 (t, *J* = 7.1 Hz, 3H). **^{13}C NMR (101 MHz, CHLOROFORM-*D*) δ** 167.0, 165.9, 152.2, 140.6, 139.5, 135.2, 135.1, 133.9, 131.4, 130.5, 129.0, 127.5, 121.9, 119.8, 60.5, 52.6, 21.2, 14.3. **HRMS (ESI) M/Z:** $[M+Na]^+$ calculated for $C_{22}H_{21}BrNaO_4$, 451.0515; found to be 451.0520.

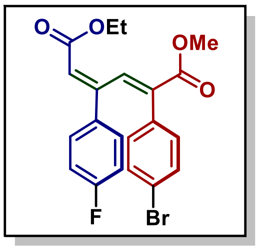
6-ethyl 1-methyl (*2E,4E*)-2-(4-bromophenyl)-4-(4-methoxyphenyl)hexa-2,4-dienedioate (3m)



Following the general procedure (c), reaction of vinyl sulfoxonium ylide **1b** (119 mg, 0.4 mmol, 1 equiv.) is carried-out with iridium catalyst (8.1 mg, 3 mol%) and diazo ester **2c** (102 mg, 0.4 mmol, 1 equiv.) in chloroform (3 mL) as solvent. The reaction mixture was stirred at room temperature for 5 h to give **3m** in 71% yield (127 mg) as colourless viscous liquid after purification by the flash column chromatography (n-Hexane/EtOAc: 80:20, R_f 0.35) with d.r. >20:1.

^{1}H NMR (400 MHz, CHLOROFORM-*D*) δ 8.24 (d, *J* = 1.7 Hz, 1H), 7.17 (d, *J* = 8.5 Hz, 2H), 7.10 (d, *J* = 8.9 Hz, 2H), 6.84 (d, *J* = 8.5 Hz, 2H), 6.66 (d, *J* = 8.9 Hz, 2H), 6.06 (d, *J* = 1.7 Hz, 1H), 4.21 (t, *J* = 7.1 Hz, 2H), 3.83 (s, 3H), 3.75 (s, 3H), 1.31 (t, *J* = 7.1 Hz, 3H). **^{13}C NMR (126 MHz, $CDCl_3$) δ** 166.9, 165.9, 160.5, 151.7, 140.8, 135.0, 133.9, 131.3, 130.5, 130.4, 129.0, 121.9, 118.6, 113.7, 60.4, 55.3, 52.5, 14.3. **HRMS (ESI) M/Z:** $[M+Na]^+$ calculated for $C_{22}H_{21}BrNaO_5$, 467.0465; found to be 467.0467.

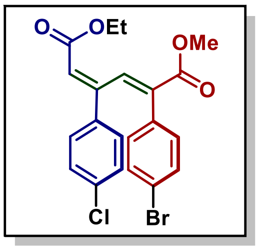
6-ethyl 1-methyl (*2E,4E*)-2-(4-bromophenyl)-4-(4-fluorophenyl)hexa-2,4-dienedioate (3n)



Following the general procedure (c), reaction of vinyl sulfoxonium ylide **1d** (114 mg, 0.4 mmol, 1 equiv.) is carried-out with iridium catalyst (8.1 mg, 3 mol%) and diazo ester **2c** (102 mg, 0.4 mmol, 1 equiv.) in chloroform (3 mL) as solvent. The reaction mixture was stirred at room temperature for 5 h to give **3n** in 76% yield (132 mg) as colourless viscous liquid after purification by the flash column chromatography (n-Hexane/EtOAc: 80:10, R_f 0.42) with d.r. >20:1.

^{1}H NMR (400 MHz, CHLOROFORM-*D*) δ 8.30 (d, *J* = 1.8 Hz, 1H), 7.17 (d, *J* = 8.7 Hz, 2H), 7.08 (dd, *J* = 9.0, 5.3 Hz, 2H), 6.80 (dd, *J* = 8.7, 4.7 Hz, 4H), 6.06 (d, *J* = 1.8 Hz, 1H), 4.23 (t, *J* = 7.2 Hz, 2H), 3.82 (s, 3H), 1.32 (t, *J* = 7.2 Hz, 3H). **^{13}C NMR (101 MHz, CHLOROFORM-*D*) δ** 166.9, 165.7, 163.18 (d, *J* = 250.0 Hz), 151.4, 140.3, 135.8, 134.6, 134.6, 133.8, 131.4, 130.7, 129.58 (d, *J* = 8.4 Hz), 122.2, 121.0, 121.0, 115.34 (d, *J* = 21.8 Hz), 60.7, 52.7, 14.3. **^{19}F NMR (376 MHz, CHLOROFORM-*D*) δ** -111.29 (tt, *J* = 8.3, 5.2 Hz). **HRMS (ESI) M/Z:** $[M+Na]^+$ calculated for $C_{21}H_{18}BrFNaO_4$, 455.0265 ; found to be 455.0265.

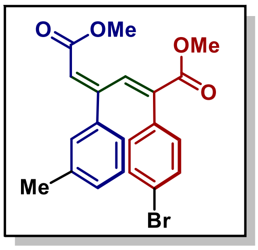
6-ethyl 1-methyl (*2E,4E*)-2-(4-bromophenyl)-4-(4-chlorophenyl)hexa-2,4-dienedioate (3o)



Following the general procedure (c), reaction of vinyl sulfoxonium ylide **1e** (120 mg, 0.4 mmol, 1 equiv.) is carried-out with iridium catalyst (8.1 mg, 3 mol%) and diazo ester **2c** (102 mg, 0.4 mmol, 1 equiv.) in chloroform (3 mL) as solvent. The reaction mixture was stirred at room temperature for 5 h to give **3o** in 74% yield (133 mg) as colourless viscous liquid after purification by the flash column chromatography (n-Hexane/EtOAc: 80:20, R_f 0.45) with d.r. >20:1.

^{1}H NMR (400 MHz, CHLOROFORM-*D*) δ 8.28 (d, *J* = 1.8 Hz, 1H), 7.19 – 7.16 (m, 2H), 7.10 – 7.07 (m, 2H), 7.02 (d, *J* = 8.8 Hz, 2H), 6.80 (d, *J* = 8.4 Hz, 2H), 6.08 (d, *J* = 1.8 Hz, 1H), 4.24 (q, *J* = 7.2 Hz, 2H), 3.82 (s, 3H), 1.32 (t, *J* = 7.2 Hz, 3H). **^{13}C NMR (126 MHz, CDCl$_3$) δ** 166.8, 165.5, 151.1, 139.9, 136.9, 135.8, 135.2, 133.7, 131.4, 130.7, 128.9, 128.4, 122.2, 121.4, 60.7, 52.7, 14.3. **HRMS (ESI) M/Z:** [M+Na]$^+$ calculated for $C_{21}H_{18}BrClNaO_4$, 470.9969 ; found to be 470.9972.

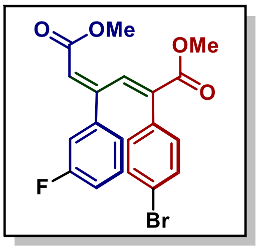
6-ethyl 1-methyl (*2E,4E*)-2-(4-bromophenyl)-4-(m-tolyl)hexa-2,4-dienedioate (3p)



Following the general procedure (c), reaction of vinyl sulfoxonium ylide **1f** (107 mg, 0.4 mmol, 1 equiv.) is carried-out with iridium catalyst (8.1 mg, 3 mol%) and diazo ester **2c** (102 mg, 0.4 mmol, 1 equiv.) in chloroform (3 mL) as solvent. The reaction mixture was stirred at room temperature for 5 h to give **3p** in 74% yield (123 mg) as colourless viscous liquid after purification by the flash column chromatography (n-Hexane/EtOAc: 80:20, R$_f$ 0.6) with d.r. >20:1.

^{1}H NMR (500 MHz, CDCl$_3$) δ 8.36 – 8.27 (m, 1H), 7.14 (d, *J* = 8.1 Hz, 2H), 7.02 – 6.96 (m, 2H), 6.90 (d, *J* = 7.4 Hz, 1H), 6.83 (s, 1H), 6.79 (d, *J* = 8.1 Hz, 2H), 6.13 – 6.04 (m, 1H), 3.82 (s, 3H), 3.76 (s, 3H), 2.20 (s, 3H). **^{13}C NMR (126 MHz, CDCl$_3$) δ** 166.9, 166.1, 152.9, 140.4, 138.3, 137.7, 135.6, 133.9, 131.3, 130.4, 129.7, 128.4, 128.1, 124.7, 121.9, 120.2, 52.6, 51.6, 21.2. **HRMS (ESI) M/Z:** [M+Na]$^+$ calculated for $C_{21}H_{19}BrNaO_4$, 437.0359; found to be 437.0355.

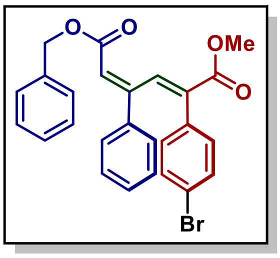
6-ethyl 1-methyl (*2E,4E*)-2-(4-bromophenyl)-4-(3-fluorophenyl)hexa-2,4-dienedioate (3q)



Following the general procedure (c), reaction of vinyl sulfoxonium ylide **1g** (108 mg, 0.4 mmol, 1 equiv.) is carried-out with iridium catalyst (8.1 mg, 3 mol%) and diazo ester **2c** (102 mg, 0.4 mmol, 1 equiv.) in chloroform (3 mL) as solvent. The reaction mixture was stirred at room temperature for 5 h to give **3q** in 72% yield (121 mg) as colourless viscous liquid after purification by the flash column chromatography (n-Hexane/EtOAc: 80:20, R$_f$ 0.6) with d.r. >20:1.

^{1}H NMR (500 MHz, CDCl$_3$) δ 8.33 – 8.26 (m, 1H), 7.19 – 7.14 (m, 2H), 7.09 – 7.05 (m, 1H), 6.87 (d, *J* = 7.7 Hz, 2H), 6.81 (d, *J* = 8.4 Hz, 3H), 6.11 (d, *J* = 1.8 Hz, 1H), 3.83 (s, 3H), 3.79 (s, 3H). **^{13}C NMR (126 MHz, CDCl$_3$) δ** 166.8, 165.9, 162.39 (d, *J* = 246.9 Hz), 151.4, 140.6, 139.5, 136.3, 133.7, 131.4, 130.7, 129.87 (d, *J* = 8.2 Hz), 123.5, 122.3, 121.6, 116.02 (d, *J* = 21.3 Hz), 114.75 (d, *J* = 22.8 Hz), 52.7, 51.9. **^{19}F NMR (376 MHz, CHLOROFORM-*D*) δ** -112.89 – -112.97 (m). **HRMS (ESI) M/Z:** [M+Na]$^+$ calculated for $C_{20}H_{16}BrFNaO_4$, 441.0108; found to be 441.0106.

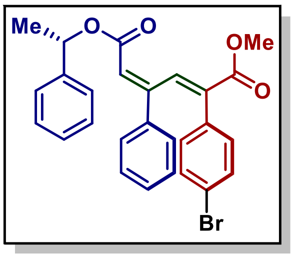
6-benzyl 1-methyl (*2E,4E*)-2-(4-bromophenyl)-4-phenylhexa-2,4-dienedioate (3s)



Following the general procedure (c), reaction of vinyl sulfoxonium ylide **1h** (132 mg, 0.4 mmol, 1 equiv.) is carried-out with iridium catalyst (8.1 mg, 3 mol%) and diazo ester **2c** (102 mg, 0.4 mmol, 1 equiv.) in chloroform (3 mL) as solvent. The reaction mixture was stirred at room temperature for 5 h to give **3s** in 80% yield (153 mg) as colourless viscous liquid after purification by the flash column chromatography (n-Hexane/EtOAc: 90:10, R_f 0.42) with d.r. >20:1.

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.34 (d, J = 1.8 Hz, 1H), 7.41 (d, J = 6.6 Hz, 4H), 7.38 – 7.34 (m, 1H), 7.20 – 7.15 (m, 2H), 7.13 (t, J = 4.2 Hz, 5H), 6.82 (d, J = 8.3 Hz, 2H), 6.18 (d, J = 1.8 Hz, 1H), 5.24 (s, 2H), 3.83 (s, 3H). **^{13}C NMR (126 MHz, $CDCl_3$) δ** 166.7, 165.4, 152.8, 140.2, 138.2, 135.8, 135.6, 133.7, 131.3, 130.5, 129.2, 128.6, 128.4, 128.3, 128.2, 127.6, 121.9, 120.4, 66.4, 52.5. **HRMS (ESI) M/Z:** $[M+Na]^+$ calculated for $C_{26}H_{21}BrNaO_4$, 499.0515 ; found to be 499.0513.

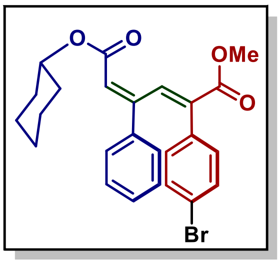
1-methyl 6-((S)-1-phenylethyl) (2E,4E)-2-(4-bromophenyl)-4-phenylhexa-2,4-dienedioate (3t)



Following the general procedure (c), reaction of vinyl sulfoxonium ylide **1i** (137 mg, 0.4 mmol, 1 equiv.) is carried-out with iridium catalyst (8.1 mg, 3 mol%) and diazo ester **2c** (102 mg, 0.4 mmol, 1 equiv.) in chloroform (3 mL) as solvent. The reaction mixture was stirred at room temperature for 5 h to give **3t** in 78% yield (155 mg) as colourless viscous liquid after purification by the flash column chromatography (n-Hexane/EtOAc: 90:10, R_f 0.5) with d.r. >20:1.

^{1}H NMR (400 MHz, CHLOROFORM-*D*) δ 8.33 – 8.31 (m, 1H), 7.43 (d, *J* = 1.9 Hz, 1H), 7.41 (dd, *J* = 2.6, 1.3 Hz, 2H), 7.39 (d, *J* = 1.0 Hz, 1H), 7.35 – 7.32 (m, 1H), 7.17 (dd, *J* = 4.7, 3.8 Hz, 1H), 7.14 (s, 1H), 7.13 (d, *J* = 0.9 Hz, 2H), 7.12 (s, 3H), 6.78 (d, *J* = 8.7 Hz, 2H), 6.17 (d, *J* = 1.8 Hz, 1H), 6.02 (q, *J* = 6.5 Hz, 1H), 3.82 (s, 3H), 1.62 (d, *J* = 6.6 Hz, 3H). **^{13}C NMR (126 MHz, $CDCl_3$) δ** 166.7, 164.8, 152.4, 141.5, 140.4, 138.3, 135.4, 133.7, 131.3, 130.5, 129.1, 128.5, 128.1, 128.0, 127.5, 126.2, 121.9, 120.9, 72.6, 52.5, 22.3. **HRMS (ESI) M/Z:** $[M+Na]^+$ calculated for $C_{27}H_{23}BrNaO_4$, 513.0672; found to be 513.0680.

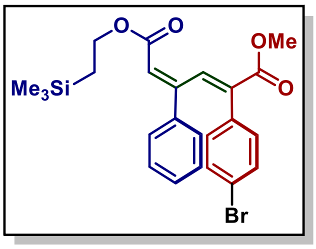
6-cyclohexyl 1-methyl (*2E,4E*)-2-(4-bromophenyl)-4-phenylhexa-2,4-dienedioate (3u)



Following the general procedure (c), reaction of vinyl sulfoxonium ylide **1j** (128 mg, 0.4 mmol, 1 equiv.) is carried-out with iridium catalyst (8.1 mg, 3 mol%) and diazo ester **2c** (102 mg, 0.4 mmol, 1 equiv.) in chloroform (3 mL) as solvent. The reaction mixture was stirred at room temperature for 5 h to give **3u** in 81% yield (152 mg) as colourless viscous liquid after purification by the flash column chromatography (n-Hexane/EtOAc: 90:10, R_f 0.53) with d.r. >20:1.

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.38 – 8.26 (m, 1H), 7.14 (d, *J* = 8.5 Hz, 3H), 7.10 (d, *J* = 4.3 Hz, 4H), 6.81 (d, *J* = 8.5 Hz, 2H), 6.10 (d, *J* = 2.0 Hz, 1H), 4.87 (dq, *J* = 8.8, 4.2 Hz, 1H), 3.82 (s, 3H), 1.91 (d, *J* = 9.3 Hz, 2H), 1.79 – 1.71 (m, 2H), 1.55 (d, *J* = 9.3 Hz, 1H), 1.49 (d, *J* = 9.8 Hz, 2H), 1.40 (dd, *J* = 10.2, 3.3 Hz, 2H), 1.31 – 1.26 (m, 1H). **^{13}C NMR (126 MHz, $CDCl_3$) δ** 166.9, 165.2, 151.9, 140.7, 138.5, 135.2, 133.9, 131.4, 130.5, 129.0, 128.2, 127.6, 122.0, 121.7, 73.0, 52.6, 31.7, 25.5, 23.8. **HRMS (ESI) M/Z:** $[M+Na]^+$ calculated for $C_{25}H_{25}BrNaO_4$, 491.0828; found to be 491.0828.

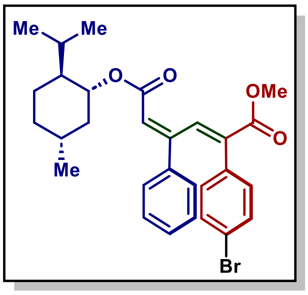
1-methyl 6-(2-(trimethylsilyl)ethyl) (*2E,4E*)-2-(4-bromophenyl)-4-phenylhexa-2,4-dienedioate (3v)



Following the general procedure (c), reaction of vinyl sulfoxonium ylide **1k** (136 mg, 0.4 mmol, 1 equiv.) is carried-out with iridium catalyst (8.1 mg, 3 mol%) and diazo ester **2c** (102 mg, 0.4 mmol, 1 equiv.) in chloroform (3 mL) as solvent. The reaction mixture was stirred at room temperature for 5 h to give **3v** in 78% yield (152 mg) as colourless viscous liquid after purification by the flash column chromatography (n-Hexane/EtOAc: 90:10, R_f 0.52) with d.r. >20:1.

^{1}H NMR (400 MHz, CHLOROFORM-*D*) δ 8.31 (d, *J* = 1.8 Hz, 1H), 7.12 (d, *J* = 8.5 Hz, 3H), 7.09 – 7.07 (m, 4H), 6.80 (d, *J* = 8.5 Hz, 2H), 6.07 (d, *J* = 1.7 Hz, 1H), 4.28 – 4.24 (m, 2H), 3.80 (s, 3H), 1.06 – 1.02 (m, 2H), 0.06 (s, 9H). **^{13}C NMR (101 MHz, CHLOROFORM-*D*) δ** 166.8, 165.9, 152.3, 140.4, 138.5, 135.4, 133.9, 131.4, 130.5, 129.0, 128.2, 127.6, 121.9, 121.1, 62.8, 52.5, 17.4, -1.4. **HRMS (ESI) M/Z:** $[M+Na]^+$ calculated for $C_{24}H_{27}BrNaO_4Si$, 509.0754; found to be 509.0748.

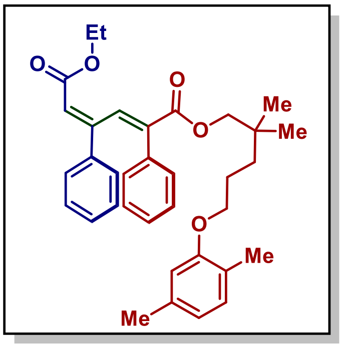
6-((1R,2S,5R)-2-isopropyl-5-methylcyclohexyl) 1-methyl (2E,4E)-2-(4-bromophenyl)-4-phenylhexa-2,4-dienedioate (3w)



Following the general procedure (c), reaction of vinyl sulfoxonium ylide **1l** (151 mg, 0.4 mmol, 1 equiv.) is carried-out with iridium catalyst (8.1 mg, 3 mol%) and diazo ester **2c** (102 mg, 0.4 mmol, 1 equiv.) in chloroform (3 mL) as solvent. The reaction mixture was stirred at room temperature for 5 h to give **3w** in 78% yield (165 mg) as colourless viscous liquid after purification by the flash column chromatography (n-Hexane/EtOAc: 90:10, R_f 0.52) with d.r. >20:1.

^{1}H NMR (400 MHz, CHLOROFORM-*D*) δ 8.31 (d, *J* = 1.8 Hz, 1H), 7.12 (d, *J* = 8.5 Hz, 3H), 7.09 (d, *J* = 3.9 Hz, 4H), 6.80 (d, *J* = 8.4 Hz, 2H), 6.08 (d, *J* = 1.8 Hz, 1H), 4.77 (td, *J* = 10.9, 4.4 Hz, 1H), 3.80 (s, 3H), 2.10 – 2.04 (m, 1H), 1.90 (td, *J* = 7.0, 2.7 Hz, 1H), 1.71 – 1.65 (m, 2H), 1.54 – 1.46 (m, 1H), 1.45 – 1.37 (m, 1H), 1.10 – 0.99 (m, 2H), 0.92 (d, *J* = 6.5 Hz, 3H), 0.89 (d, *J* = 7.0 Hz, 3H), 0.79 (d, *J* = 7.0 Hz, 3H). **^{13}C NMR (126 MHz, $CDCl_3$) δ** 166.8, 165.2, 152.1, 140.6, 138.4, 135.1, 133.8, 131.3, 130.5, 129.0, 128.1, 127.5, 121.9, 121.3, 52.5, 47.0, 41.0, 34.2, 31.4, 26.3, 23.5, 22.0, 20.8, 16.4. **HRMS (ESI) M/Z:** $[M+Na]^+$ calculated for $C_{29}H_{33}BrNaO_4$, 547.1454 ; found to be 547.1450.

1-(5-(2,6-dimethylphenoxy)-2,2-dimethylpentyl) 6-ethyl (*2E,4E*)-2,4-diphenylhexa-2,4-dienedioate (3x)

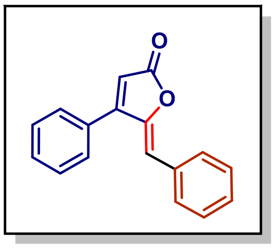


Following the general procedure (c), reaction of vinyl sulfoxonium ylide **1a** (107 mg, 0.4 mmol, 1 equiv.) is carried-out with iridium catalyst (8.1 mg, 3 mol%) and diazo ester **2l** (153 mg, 0.4 mmol, 1 equiv.) in chloroform (3 mL) as solvent. The reaction mixture was stirred at room temperature for 5 h to give **3x** in 67% yield (146 mg) as colourless viscous liquid after purification by the flash column chromatography (n-Hexane/EtOAc: 80:20, R_f 0.4) with d.r. >20:1.

^{1}H NMR (400 MHz, CHLOROFORM-*D*) δ 8.43 – 8.37 (m, 1H), 7.17 – 7.06 (m, 5H), 7.05 – 6.95 (m, 6H), 6.68 (d, *J* = 6.8 Hz, 1H), 6.64 (s, 1H), 6.13 (t, *J* = 1.7 Hz, 1H), 4.30 – 4.22 (m, 2H), 4.03 (s, 2H), 3.89 (t, *J* = 6.4 Hz, 2H), 2.34 (s, 3H), 2.20 (d, *J* = 1.7 Hz, 3H), 1.81 – 1.72 (m, 2H), 1.48 – 1.40 (m, 2H), 1.34 (t, *J* = 7.2 Hz, 3H), 0.97 (d, *J* = 1.7 Hz, 6H). **^{13}C NMR (101 MHz, CHLOROFORM-*D*) δ** 166.8, 165.6, 157.0, 152.7, 139.4, 138.6, 137.0, 136.3, 134.9, 130.2, 129.7, 128.8, 127.9, 127.6, 127.4, 127.1, 123.5, 120.9, 120.6, 111.9, 73.1, 68.3, 60.4, 35.4, 33.7, 24.3, 24.1, 21.4, 15.8, 14.3. **HRMS (ESI) M/Z:** [M+Na]$^+$ calculated for $C_{35}H_{40}NaO_5$, 563.2768; found to be 563.2766.

c) Ylidene Butenolide (5)

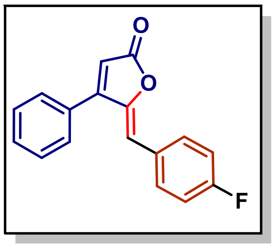
(*Z*)-5-benzylidene-4-phenylfuran-2(*5H*)-one (5a)



Following the general procedure (e), reaction of vinyl sulfoxonium ylide **1a** (107 mg, 0.4 mmol, 1 equiv.) is carried-out with ruthenium catalyst (7 mg, 3 mol%) and acetal **4a** (61 mg, 0.4 mmol, 1 equiv.) in presence of TMSOTf (22 µL, 30 mol%) with dichloroethane (3 mL) as solvent. The reaction mixture was stirred at 0 °C for 4 h to give **5a** in 79% yield (79 mg) as white viscous liquid after purification by the flash column chromatography (n-Hexane/EtOAc: 80:20, R_f 0.52).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.83 (d, *J* = 7.6 Hz, 2H), 7.55 (dd, *J* = 11.2, 3.7 Hz, 5H), 7.42 (t, *J* = 7.5 Hz, 2H), 7.37 (d, *J* = 7.1 Hz, 1H), 6.23 (s, 1H), 6.21 (s, 1H). **^{13}C NMR (126 MHz, $CDCl_3$) δ** 168.8, 158.8, 148.0, 133.0, 130.8, 130.5, 130.4, 129.3, 129.1, 128.8, 128.5, 114.5, 113.9. **HRMS (ESI) M/Z:** [M+Na]$^+$ calculated for $C_{17}H_{12}NaO_2$, 271.0730; found to be 271.0723.

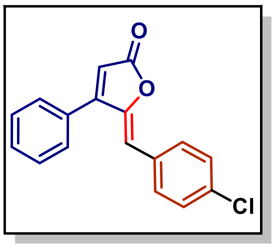
(*Z*)-5-(4-fluorobenzylidene)-4-phenylfuran-2(*5H*)-one (5b)



Following the general procedure (e), reaction of vinyl sulfoxonium ylide **1a** (107 mg, 0.4 mmol, 1 equiv.) is carried-out with ruthenium catalyst (7 mg, 3 mol%) and acetal **4b** (68 mg, 0.4 mmol, 1 equiv.) in presence of TMSOTf (22 µL, 30 mol%) with dichloroethane (3 mL) as solvent. The reaction mixture was stirred at 0 °C for 4 h to give **5b** in 72% yield (77 mg) as white viscous liquid after purification by the flash column chromatography (n-Hexane/EtOAc: 80:20, R$_f$ 0.47).

^{1}H NMR (500 MHz, CDCl$_3$) δ 7.80 (dd, *J* = 8.5, 5.4 Hz, 2H), 7.58 – 7.47 (m, 5H), 7.08 (t, *J* = 8.5 Hz, 2H), 6.21 (s, 1H), 6.14 (s, 1H). **^{13}C NMR (126 MHz, CDCl$_3$) δ** 168.8, 163.19 (d, *J* = 249.9 Hz), 158.8, 147.7, 132.87 (d, *J* = 8.2 Hz), 130.6, 130.4, 129.4, 129.2, 128.6, 116.10 (d, *J* = 21.3 Hz), 114.5, 112.7. **HRMS (ESI) M/Z:** [M+Na]$^+$ calculated for $C_{17}H_{11}FNaO_2$, 289.0635; found to be 289.0640.

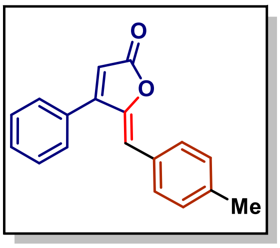
(*Z*)-5-(4-chlorobenzylidene)-4-phenylfuran-2(5*H*)-one (5c)



Following the general procedure (e), reaction of vinyl sulfoxonium ylide **1a** (107 mg, 0.4 mmol, 1 equiv.) is carried-out with ruthenium catalyst (7 mg, 3 mol%) and acetal **4c** (75 mg, 0.4 mmol, 1 equiv.) in presence of TMSOTf (22 µL, 30 mol%) with dichloroethane (3 mL) as solvent. The reaction mixture was stirred at 0 °C for 4 h to give **5c** in 70% yield (79 mg) as white viscous liquid after purification by the flash column chromatography (n-Hexane/EtOAc: 80:20, R$_f$ 0.52).

^{1}H NMR (500 MHz, CHLOROFORM-D) δ 7.74 (d, *J* = 8.2 Hz, 2H), 7.54 (d, *J* = 5.3 Hz, 3H), 7.51 (s, 2H), 7.36 (d, *J* = 8.2 Hz, 2H), 6.23 (s, 1H), 6.13 (s, 1H). **^{13}C NMR (101 MHz, CDCl$_3$) δ** 168.7, 158.8, 148.3, 135.3, 132.0, 131.5, 130.6, 130.3, 129.2, 129.1, 128.6, 114.8, 112.6. **HRMS (ESI) M/Z:** [M+Na]$^+$ calculated for $C_{17}H_{11}ClNaO_2$, 305.0340 ; found to be 305.0335.

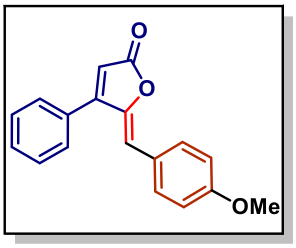
(*Z*)-5-(4-methylbenzylidene)-4-phenylfuran-2(5*H*)-one (5d)



Following the general procedure (e), reaction of vinyl sulfoxonium ylide **1a** (107 mg, 0.4 mmol, 1 equiv.) is carried-out with ruthenium catalyst (7 mg, 3 mol%) and acetal **4d** (67 mg, 0.4 mmol, 1 equiv.) in presence of TMSOTf (22 µL, 30 mol%) with dichloroethane (3 mL) as solvent. The reaction mixture was stirred at 0 °C for 4 h to give **5d** in 75% yield (78 mg) as white solid after purification by the flash column chromatography (n-Hexane/EtOAc: 80:20, R$_f$ 0.52).

^{1}H NMR (500 MHz, CDCl$_3$) δ 7.71 (d, *J* = 7.8 Hz, 2H), 7.54 – 7.49 (m, 5H), 7.21 (d, *J* = 7.9 Hz, 2H), 6.19 (s, 1H), 6.17 (s, 1H), 2.38 (s, 3H). **^{13}C NMR (126 MHz, CDCl$_3$) δ** 169.0, 158.8, 147.4, 139.8, 130.8, 130.5, 130.3, 130.2, 129.6, 129.0, 128.5, 114.1, 114.1, 21.5. **HRMS (ESI) M/Z:** [M+Na]$^+$ calculated for $C_{18}H_{14}NaO_2$, 285.0886; found to be 285.0877.

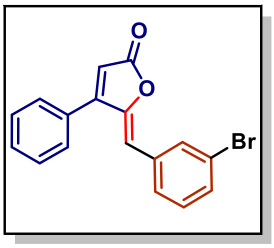
(*Z*)-5-(4-methoxybenzylidene)-4-phenylfuran-2(5*H*)-one (5e)



Following the general procedure (e), reaction of vinyl sulfoxonium ylide **1a** (107 mg, 0.4 mmol, 1 equiv.) is carried-out with ruthenium catalyst (7 mg, 3 mol%) and acetal **4e** (73 mg, 0.4 mmol, 1 equiv.) in presence of TMSOTf (22 µL, 30 mol%) with dichloroethane (3 mL) as solvent. The reaction mixture was stirred at 0 °C for 4 h to give **5e** in 82% yield (92 mg) as yellow solid after purification by the flash column chromatography (n-Hexane/EtOAc: 80:20, R*f* 0.45).

^{1}H NMR (500 MHz, CDCl$_3$) δ 7.77 (d, *J* = 9.0 Hz, 2H), 7.54 – 7.49 (m, 5H), 6.92 (d, *J* = 8.9 Hz, 2H), 6.15 (s, 1H), 6.14 (s, 1H), 3.84 (s, 3H). **^{13}C NMR (126 MHz, CDCl$_3$) δ** 169.2, 160.6, 158.8, 146.6, 132.7, 130.8, 130.4, 129.1, 128.6, 125.9, 114.4, 114.0, 113.6, 55.4. **HRMS (ESI) M/Z:** [M+H]$^+$ calculated for $C_{18}H_{15}O_3$, 279.1016; found to be 279.1014.

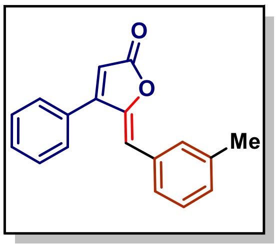
(*Z*)-5-(3-bromobenzylidene)-4-phenylfuran-2(*5H*)-one (5f)



Following the general procedure (e), reaction of vinyl sulfoxonium ylide **1a** (107 mg, 0.4 mmol, 1 equiv.) is carried-out with ruthenium catalyst (7 mg, 3 mol%) and acetal **4f** (93 mg, 0.4 mmol, 1 equiv.) in presence of TMSOTf (22 µL, 30 mol%) with dichloroethane (3 mL) as solvent. The reaction mixture was stirred at 0 °C for 4 h to give **5f** in 63% yield (83 mg) as pale yellow solid after purification by the flash column chromatography (n-Hexane/EtOAc: 80:20, R*f* 0.5).

^{1}H NMR (400 MHz, CHLOROFORM-*D*) δ 7.89 (t, *J* = 1.8 Hz, 1H), 7.76 (dt, *J* = 8.2, 1.6 Hz, 1H), 7.54 (d, *J* = 1.9 Hz, 1H), 7.53 – 7.52 (m, 1H), 7.49 (d, *J* = 1.9 Hz, 1H), 7.48 – 7.43 (m, 2H), 7.27 (d, *J* = 7.9 Hz, 1H), 7.24 (d, *J* = 4.2 Hz, 1H), 6.24 (d, *J* = 0.8 Hz, 1H), 6.09 (s, 1H). **^{13}C NMR (101 MHz, CHLOROFORM-*D*) δ** 168.5, 158.8, 148.8, 135.0, 133.3, 132.2, 130.7, 130.4, 130.2, 129.3, 128.6, 128.6, 128.6, 122.9, 115.2, 112.1. **HRMS (ESI) M/Z:** [M+H]$^+$ calculated for $C_{17}H_{12}BrO_2$, 327.0015; found to be 327.0009.

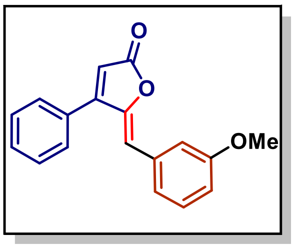
(*Z*)-5-(3-methylbenzylidene)-4-phenylfuran-2(*5H*)-one (5g)



Following the general procedure (e), reaction of vinyl sulfoxonium ylide **1a** (107 mg, 0.4 mmol, 1 equiv.) is carried-out with ruthenium catalyst (7 mg, 3 mol%) and acetal **4g** (67 mg, 0.4 mmol, 1 equiv.) in presence of TMSOTf (22 µL, 30 mol%) with dichloroethane (3 mL) as solvent. The reaction mixture was stirred at 0 °C for 4 h to give **5g** in 62% yield (65 mg) as white viscous liquid after purification by the flash column chromatography (n-Hexane/EtOAc: 80:20, R*f* 0.5).

^{1}H NMR (500 MHz, CDCl$_3$) δ 7.65 (s, 2H), 7.58 – 7.51 (m, 5H), 7.31 (t, *J* = 8.0 Hz, 1H), 7.18 (d, *J* = 7.5 Hz, 1H), 6.22 (s, 1H), 6.19 (s, 1H), 2.40 (s, 3H). **^{13}C NMR (101 MHz, CHLOROFORM-*D*) δ** 169.0, 158.9, 147.8, 138.5, 132.9, 131.4, 130.5, 130.3, 129.1, 128.7, 128.6, 128.1, 114.4, 114.3, 21.4. **HRMS (ESI) M/Z:** [M+Na]$^+$ calculated for $C_{18}H_{14}NaO_2$, 285.0886; found to be 285.0878.

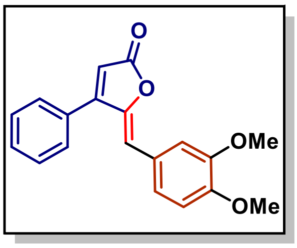
(*Z*)-5-(3-methoxybenzylidene)-4-phenylfuran-2(*5H*)-one (5h)



Following the general procedure (e), reaction of vinyl sulfoxonium ylide **1a** (107 mg, 0.4 mmol, 1 equiv.) is carried-out with ruthenium catalyst (7 mg, 3 mol%) and acetal **4h** (73 mg, 0.4 mmol, 1 equiv.) in presence of TMSOTf (22 µL, 30 mol%) with dichloroethane (3 mL) as solvent. The reaction mixture was stirred at 0 °C for 4 h to give **5h** in 68% yield (76 mg) as yellow viscous liquid after purification by the flash column chromatography (n-Hexane/EtOAc: 80:20, R_f 0.45).

^{1}H NMR (500 MHz, CDCl$_3$) δ 7.58 – 7.51 (m, 5H), 7.42 – 7.37 (m, 2H), 7.33 (d, *J* = 7.9 Hz, 1H), 6.92 (dd, *J* = 7.5, 2.2 Hz, 1H), 6.23 (s, 1H), 6.18 (s, 1H), 3.86 (s, 3H). **^{13}C NMR (126 MHz, CDCl$_3$) δ** 168.8, 159.8, 158.8, 148.1, 134.2, 130.5, 130.4, 129.8, 129.1, 128.6, 123.6, 115.7, 115.4, 114.7, 113.9, 55.4. **HRMS (ESI) M/Z:** $[M+H]^+$ calculated for $C_{18}H_{15}O_3$, 279.1016; found to be 279.1021.

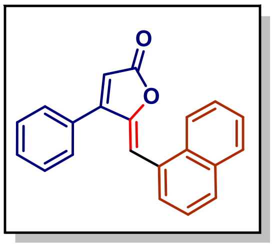
(*Z*)-5-(3,4-dimethoxybenzylidene)-4-phenylfuran-2(*5H*)-one (5i)



Following the general procedure (e), reaction of vinyl sulfoxonium ylide **1a** (107 mg, 0.4 mmol, 1 equiv.) is carried-out with ruthenium catalyst (7 mg, 3 mol%) and acetal **4i** (85 mg, 0.4 mmol, 1 equiv.) in presence of TMSOTf (22 µL, 30 mol%) with dichloroethane (3 mL) as solvent. The reaction mixture was stirred at 0 °C for 4 h to give **5i** in 80% yield (99 mg) as yellow solid after purification by the flash column chromatography (n-Hexane/EtOAc: 80:20, R_f 0.52).

^{1}H NMR (500 MHz, CDCl$_3$) δ 7.47 (q, *J* = 6.4, 6.0 Hz, 5H), 7.40 (t, *J* = 2.7 Hz, 1H), 7.27 (d, *J* = 6.1 Hz, 1H), 6.81 (dd, *J* = 8.5, 3.0 Hz, 1H), 6.08 (s, 2H), 3.87 (s, 3H), 3.86 (s, 3H). **^{13}C NMR (126 MHz, CDCl$_3$) δ** 169.0, 158.7, 150.3, 149.0, 146.6, 130.6, 130.3, 129.0, 128.5, 126.1, 125.0, 114.1, 113.4, 113.0, 111.0, 55.9, 55.9. **HRMS (ESI) M/Z:** $[M+Na]^+$ calculated for $C_{19}H_{16}NaO_4$, 331.0941; found to be 331.0933.

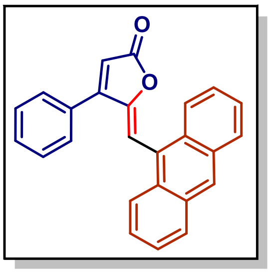
(*Z*)-5-(naphthalen-1-ylmethylene)-4-phenylfuran-2(*5H*)-one (5k)



Following the general procedure (e), reaction of vinyl sulfoxonium ylide **1a** (107 mg, 0.4 mmol, 1 equiv.) is carried-out with ruthenium catalyst (7 mg, 3 mol%) and acetal **4k** (81 mg, 0.4 mmol, 1 equiv.) in presence of TMSOTf (22 µL, 30 mol%) with dichloroethane (3 mL) as solvent. The reaction mixture was stirred at 0 °C for 4 h to give **5k** in 58% yield (69 mg) as yellow solid after purification by the flash column chromatography (n-Hexane/EtOAc: 80:20, R_f 0.42).

^{1}H NMR (400 MHz, CHLOROFORM-*D*) δ 8.36 (dd, *J* = 7.5, 3.6 Hz, 1H), 7.91 (d, *J* = 5.0 Hz, 1H), 7.87 – 7.84 (m, 2H), 7.59 (d, *J* = 2.2 Hz, 6H), 7.49 (d, *J* = 5.0 Hz, 2H), 6.99 (d, *J* = 3.7 Hz, 1H), 6.27 (d, *J* = 3.6 Hz, 1H). **^{13}C NMR (101 MHz, CHLOROFORM-*D*) δ** 169.1, 158.8, 149.0, 133.7, 131.8, 130.7, 130.6, 130.0, 129.3, 129.3, 129.2, 128.8, 128.7, 126.9, 126.0, 125.9, 123.0, 114.8, 109.9. **HRMS (ESI) M/Z:** $[M+H]^+$ calculated for $C_{21}H_{15}O_2$, 299.1067; found to be 299.1064.

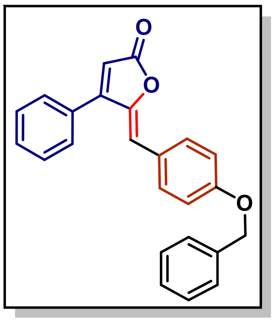
(*Z*)-5-(anthracen-9-ylmethylene)-4-phenylfuran-2(*5H*)-one (5l)



Following the general procedure (e), reaction of vinyl sulfoxonium ylide **1a** (107 mg, 0.4 mmol, 1 equiv.) is carried-out with ruthenium catalyst (7 mg, 3 mol%) and acetal **4l** (101 mg, 0.4 mmol, 1 equiv.) in presence of TMSOTf (22 µL, 30 mol%) with dichloroethane (3 mL) as solvent. The reaction mixture was stirred at 0 °C for 4 h to give **5l** in 54% yield (75 mg) as yellow solid after purification by the flash column chromatography (n-Hexane/EtOAc: 80:20, R$_f$ 0.5).

^{1}H NMR (400 MHz, CHLOROFORM-*D*) δ 8.50 (d, *J* = 0.9 Hz, 1H), 8.05 – 7.98 (m, 4H), 7.79 – 7.75 (m, 2H), 7.64 – 7.59 (m, 3H), 7.52 – 7.46 (m, 4H), 7.17 (s, 1H), 6.36 (d, *J* = 0.8 Hz, 1H). **^{13}C NMR (101 MHz, CHLOROFORM-*D*) δ** 168.4, 157.8, 157.3, 150.9, 150.3, 131.4, 130.9, 130.7, 129.8, 129.4, 129.0, 128.8, 128.5, 127.9, 126.4, 126.4, 126.3, 125.8, 125.4, 125.3, 125.2, 120.1, 116.2, 112.6, 110.9. **HRMS (ESI) M/Z:** [M+Na]$^+$ calculated for C$_{25}$H$_{16}$NaO$_2$, 371.1043 ; found to be 371.1037.

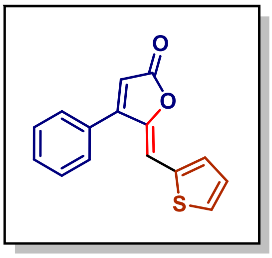
(*Z*)-5-(4-(benzyloxy)benzylidene)-4-phenylfuran-2(*5H*)-one (5m)



Following the general procedure (e), reaction of vinyl sulfoxonium ylide **1a** (107 mg, 0.4 mmol, 1 equiv.) is carried-out with ruthenium catalyst (7 mg, 3 mol%) and acetal **4m** (104 mg, 0.4 mmol, 1 equiv.) in presence of TMSOTf (22 µL, 30 mol%) with dichloroethane (3 mL) as solvent. The reaction mixture was stirred at 0 °C for 4 h to give **5m** in 83% yield (118 mg) as yellow viscous liquid after purification by the flash column chromatography (n-Hexane/EtOAc: 80:20, R$_f$ 0.4).

^{1}H NMR (500 MHz,) δ 7.78 (d, *J* = 8.9 Hz, 2H), 7.56 – 7.52 (m, 3H), 7.50 (d, *J* = 6.1 Hz, 2H), 7.44 (d, *J* = 7.2 Hz, 2H), 7.40 (t, *J* = 7.6 Hz, 3H), 7.00 (d, *J* = 8.9 Hz, 2H), 6.16 (s, 1H), 6.15 (s, 1H), 5.11 (s, 2H). **^{13}C NMR (126 MHz, CDCl$_3$) δ** 169.26, 159.83, 158.84, 146.74, 136.58, 132.73, 130.77, 130.45, 129.16, 128.78, 128.64, 128.27, 127.64, 126.21, 115.36, 114.00, 113.64, 70.18. **HRMS (ESI) M/Z:** [M+Na]$^+$ calculated for C$_{24}$H$_{18}$NaO$_3$, 377.1148; found to be 377.1150.

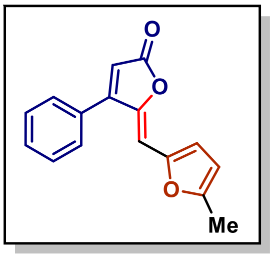
(*Z*)-4-phenyl-5-(thiophen-2-ylmethylene)furan-2(*5H*)-one (5n)



Reaction of vinyl sulfoxonium ylide **1a** (107 mg, 0.4 mmol, 1 equiv.) is carried-out with ruthenium catalyst (7 mg, 3 mol%) and thiophene-2-aldehyde (45 mg, 0.4 mmol, 1 equiv.) in presence of TMSOTf (22 µL, 30 mol%) with dichloroethane (3 mL) as solvent. The reaction mixture was stirred at 0 °C for 4 h to give **5n** in 75% yield (77 mg) as yellow viscous liquid after purification by the flash column chromatography (n-Hexane/EtOAc: 80:20, R$_f$ 0.5).

^{1}H NMR (500 MHz, CDCl$_3$) δ 7.57 – 7.51 (m, 6H), 7.42 (d, *J* = 3.7 Hz, 1H), 7.11 (dd, *J* = 5.1, 3.7 Hz, 1H), 6.50 (s, 1H), 6.23 (s, 1H). **^{13}C NMR (126 MHz, CDCl$_3$) δ** 168.3, 157.7, 146.2, 136.4, 131.5, 130.9, 130.6, 130.3, 129.2, 128.4, 127.8, 114.3, 107.5. **HRMS (ESI) M/Z:** [M+Na]$^+$ calculated for C$_{15}$H$_{10}$NaO$_2$S, 277.0294 ; found to be 277.0285.

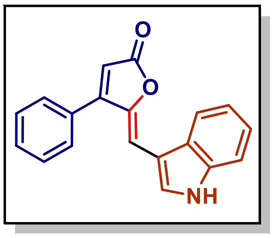
(*Z*)-5-((5-methylfuran-2-yl)methylene)-4-phenylfuran-2(*5H*)-one (5o)



Reaction of vinyl sulfoxonium ylide **1a** (107 mg, 0.4 mmol, 1 equiv.) is carried-out with ruthenium catalyst (7 mg, 3 mol%) and 5-methyl-2-furfural (44 mg, 0.4 mmol, 1 equiv.) in presence of TMSOTf (22 µL, 30 mol%) with dichloroethane (3 mL) as solvent. The reaction mixture was stirred at 0 °C for 4 h to give **5o** in 68% yield (69 mg) as yellow viscous liquid after purification by the flash column chromatography (n-Hexane/EtOAc: 80:20, R_f 0.5).

^{1}H NMR (400 MHz,) δ 7.48 (dtt, *J* = 6.0, 3.8, 1.9 Hz, 6H), 7.01 (d, *J* = 3.6 Hz, 1H), 6.18 (s, 1H), 6.17 – 6.15 (m, 1H), 6.12 (s, 1H), 2.33 (s, 3H). **^{13}C NMR (126 MHz, $CDCl_3$) δ** 168.8, 157.6, 155.0, 147.9, 144.9, 130.4, 130.3, 129.1, 128.3, 117.3, 113.4, 109.9, 102.6, 13.9. **HRMS (ESI) M/Z:** $[M+Na]^+$ calculated for $C_{16}H_{12}NaO_3$, 275.0679 ; found to be 275.0672.

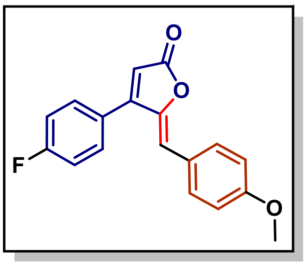
(*Z*)-5-((1H-indol-3-yl)methylene)-4-phenylfuran-2(*5H*)-one (5p)



Reaction of vinyl sulfoxonium ylide **1a** (107 mg, 0.4 mmol, 1 equiv.) is carried-out with ruthenium catalyst (7 mg, 3 mol%) and indole-3-aldehyde (58 mg, 0.4 mmol, 1 equiv.) in presence of TMSOTf (22 µL, 30 mol%) with dichloroethane (3 mL) as solvent. The reaction mixture was stirred at 0 °C for 4 h to give **5p** in 71% yield (82 mg) as yellow viscous liquid after purification by the flash column chromatography (n-Hexane/EtOAc: 70:30, R_f 0.45).

^{1}H NMR (500 MHz, $CDCl_3$) δ 9.18 (s, 1H), 8.22 (d, *J* = 2.8 Hz, 1H), 7.70 (d, *J* = 7.9 Hz, 1H), 7.62 – 7.57 (m, 5H), 7.51 – 7.47 (m, 1H), 7.30 (dd, *J* = 7.3, 1.3 Hz, 1H), 7.25 – 7.21 (m, 1H), 6.66 (s, 1H), 6.17 (s, 1H). **^{13}C NMR (126 MHz, $CDCl_3$) δ** 169.0, 158.0, 145.6, 135.9, 131.1, 130.4, 129.2, 129.2, 128.6, 126.8, 123.3, 121.2, 118.3, 112.0, 111.9, 110.6, 107.0. **HRMS (ESI) M/Z:** $[M+Na]^+$ calculated for $C_{19}H_{13}NNaO_2$, 310.0838; found to be 310.0830.

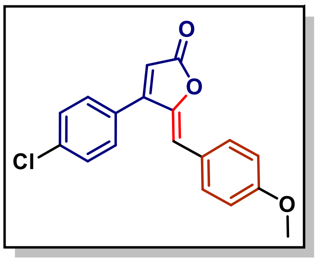
(*Z*)-4-(4-fluorophenyl)-5-(4-methoxybenzylidene)furan-2(*5H*)-one (5q)



Following the general procedure (e), reaction of vinyl sulfoxonium ylide **1d** (114 mg, 0.4 mmol, 1 equiv.) is carried-out with ruthenium catalyst (7 mg, 3 mol%) and acetal **4e** (73 mg, 0.4 mmol, 1 equiv.) in presence of TMSOTf (22 µL, 30 mol%) with dichloroethane (3 mL) as solvent. The reaction mixture was stirred at 0 °C for 4 h to give **5q** in 71% yield (84 mg) as pale yellow solid after purification by the flash column chromatography (n-Hexane/EtOAc: 80:20, R_f 0.52).

^{1}H NMR (400 MHz, CHLOROFORM-*D*) δ 7.77 – 7.74 (m, 2H), 7.50 – 7.47 (m, 2H), 7.23 – 7.18 (m, 2H), 6.93 – 6.90 (m, 2H), 6.13 (q, *J* = 0.8 Hz, 1H), 6.08 (d, *J* = 1.5 Hz, 1H), 3.84 (d, *J* = 1.8 Hz, 3H). **^{13}C NMR (101 MHz, CHLOROFORM-*D*) δ** 169.0, 164.03 (d, *J* = 251.3 Hz), 160.7, 157.6, 146.5, 132.7, 130.59 (d, *J* = 8.4 Hz), 126.7, 126.7, 125.8, 116.38 (d, *J* = 21.7 Hz), 114.4, 114.0, 113.5, 55.4. **HRMS (ESI) M/Z:** $[M+Na]^+$ calculated for $C_{18}H_{13}FNaO_3$, 319.0741 ; found to be 319.0753.

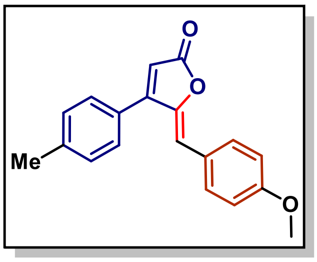
(*Z*)-4-(4-chlorophenyl)-5-(4-methoxybenzylidene)furan-2(5*H*)-one (5r)



Following the general procedure (e), reaction of vinyl sulfoxonium ylide **1e** (121 mg, 0.4 mmol, 1 equiv.) is carried-out with ruthenium catalyst (7 mg, 3 mol%) and acetal **4e** (73 mg, 0.4 mmol, 1 equiv.) in presence of TMSOTf (22 µL, 30 mol%) with dichloroethane (3 mL) as solvent. The reaction mixture was stirred at 0 °C for 4 h to give **5r** in 72% yield (89 mg) as yellow viscous liquid after purification by the flash column chromatography (n-Hexane/EtOAc: 80:20, R_f 0.45).

^{1}H NMR (500 MHz, CDCl$_3$) δ 7.76 (d, *J* = 8.4 Hz, 2H), 7.50 (d, *J* = 8.2 Hz, 2H), 7.44 (d, *J* = 8.4 Hz, 2H), 6.92 (d, *J* = 8.6 Hz, 2H), 6.15 (s, 1H), 6.08 (s, 1H), 3.84 (s, 3H). **^{13}C NMR (126 MHz, CDCl$_3$) δ** 168.9, 160.8, 157.5, 146.3, 136.7, 132.7, 129.9, 129.5, 129.1, 125.8, 114.5, 114.0, 113.8, 55.5. **HRMS (ESI) M/Z:** [M+H]$^+$ calculated for $C_{18}H_{14}ClO_3$, 313.0626; found to be 313.0627.

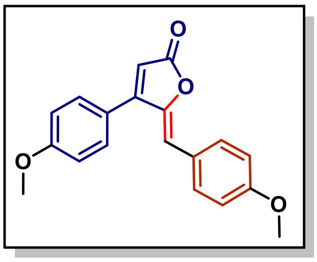
(*Z*)-5-(4-methoxybenzylidene)-4-(p-tolyl)furan-2(5*H*)-one (5s)



Following the general procedure (e), reaction of vinyl sulfoxonium ylide **1c** (112 mg, 0.4 mmol, 1 equiv.) is carried-out with ruthenium catalyst (7 mg, 3 mol%) and acetal **4e** (73 mg, 0.4 mmol, 1 equiv.) in presence of TMSOTf (22 µL, 30 mol%) with dichloroethane (3 mL) as solvent. The reaction mixture was stirred at 0 °C for 4 h to give **5s** in 76% yield (89 mg) as yellow viscous liquid after purification by the flash column chromatography (n-Hexane/EtOAc: 80:20, R_f 0.52).

^{1}H NMR (400 MHz, CHLOROFORM-*D*) δ 7.78 – 7.75 (m, 2H), 7.40 (d, *J* = 8.1 Hz, 2H), 7.32 (dd, *J* = 8.5, 0.8 Hz, 2H), 6.91 (d, *J* = 8.9 Hz, 2H), 6.15 (s, 1H), 6.12 (d, *J* = 0.8 Hz, 1H), 3.84 (s, 3H), 2.45 (s, 3H). **^{13}C NMR (101 MHz, CHLOROFORM-*D*) δ** 169.4, 160.5, 158.8, 146.7, 140.8, 132.6, 129.8, 128.5, 127.8, 126.0, 114.4, 113.9, 113.0, 55.4, 21.5. **HRMS (ESI) M/Z:** [M+Na]$^+$ calculated for $C_{19}H_{16}NaO_3$, 315.0992; found to be 315.0980.

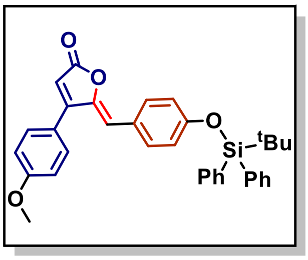
(*Z*)-5-(4-methoxybenzylidene)-4-(4-methoxyphenyl)furan-2(5*H*)-one (5t)



Following the general procedure (e), reaction of vinyl sulfoxonium ylide **1b** (119 mg, 0.4 mmol, 1 equiv.) is carried-out with ruthenium catalyst (7 mg, 3 mol%) and acetal **4e** (73 mg, 0.4 mmol, 1 equiv.) in presence of TMSOTf (22 µL, 30 mol%) with dichloroethane (3 mL) as solvent. The reaction mixture was stirred at 0 °C for 4 h to give **5t** in 73% yield (90 mg) as yellow liquid after purification by the flash column chromatography (n-Hexane/EtOAc: 80:20, R_f 0.3).

^{1}H NMR (500 MHz, CDCl$_3$) δ 7.77 (d, *J* = 8.4 Hz, 2H), 7.46 (d, *J* = 8.3 Hz, 2H), 7.03 (d, *J* = 8.3 Hz, 2H), 6.92 (d, *J* = 8.4 Hz, 2H), 6.16 (s, 1H), 6.10 (s, 1H), 3.89 (s, 3H), 3.85 (s, 3H). **^{13}C NMR (126 MHz, CDCl$_3$) δ** 169.5, 161.5, 160.6, 158.5, 146.8, 132.6, 130.1, 126.1, 123.1, 114.6, 114.4, 113.8, 112.4, 55.6, 55.5. **HRMS (ESI) M/Z:** [M+Na]$^+$ calculated for $C_{19}H_{16}NaO_4$, 331.0941; found to be 331.0950.

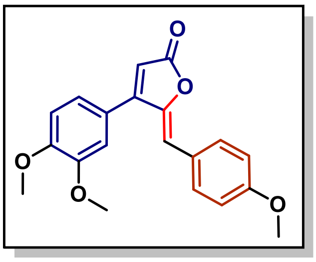
(*Z*)-5-(4-((tert-butyldiphenylsilyl)oxy)benzylidene)-4-(4-methoxyphenyl)furan-2(*5H*)-one (5u)



Following the general procedure (e), reaction of vinyl sulfoxonium ylide **1b** (59 mg, 0.2 mmol, 1 equiv.) is carried-out with ruthenium catalyst (4 mg, 3 mol%) and acetal **4n** (81 mg, 0.2 mmol, 1 equiv.) in presence of TMSOTf (11 µL, 30 mol%) with dichloroethane (3 mL) as solvent. The reaction mixture was stirred at 0 °C for 4 h to give **5u** in 70% yield (74 mg) as white viscous liquid after purification by the flash column chromatography (n-Hexane/EtOAc: 80:20, R_f 0.4).

^{1}H NMR (500 MHz, CDCl$_3$) δ 7.76 (d, *J* = 7.3 Hz, 3H), 7.62 (d, *J* = 8.4 Hz, 2H), 7.44 (dt, *J* = 20.2, 7.7 Hz, 9H), 7.04 (d, *J* = 8.3 Hz, 2H), 6.82 (d, *J* = 8.4 Hz, 2H), 6.12 (s, 1H), 6.09 (s, 1H), 3.89 (s, 3H), 1.16 (s, 9H). **^{13}C NMR (126 MHz, CDCl$_3$) δ** 169.3, 161.4, 158.4, 156.8, 146.7, 135.5, 132.5, 132.3, 130.1, 130.0, 127.9, 126.4, 122.9, 120.3, 114.5, 113.7, 112.3, 55.5, 26.5, 19.5. **HRMS (ESI) M/Z:** [M+Na]$^+$ calculated for $C_{34}H_{32}NaO_4Si$, 555.1962; found to be 555.1965.

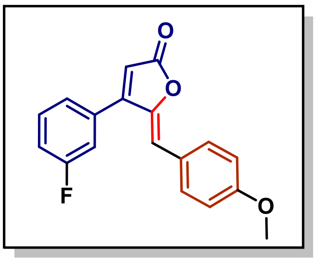
(*Z*)-4-(3,4-dimethoxyphenyl)-5-(4-methoxybenzylidene)furan-2(*5H*)-one (5v)



Following the general procedure (e), reaction of vinyl sulfoxonium ylide **1m** (98 mg, 0.3 mmol, 1 equiv.) is carried-out with ruthenium catalyst (6 mg, 3 mol%) and acetal **4e** (55 mg, 0.3 mmol, 1 equiv.) in presence of TMSOTf (16 µL, 30 mol%) with dichloroethane (3 mL) as solvent. The reaction mixture was stirred at 0 °C for 4 h to give **5v** in 73% yield (74 mg) as yellow solid after purification by the flash column chromatography (n-Hexane/EtOAc: 70:30, R_f 0.5).

^{1}H NMR (500 MHz, CDCl$_3$) δ 7.76 (d, *J* = 8.8 Hz, 2H), 7.10 (dd, *J* = 8.2, 2.1 Hz, 1H), 7.03 – 6.96 (m, 2H), 6.91 (d, *J* = 8.8 Hz, 2H), 6.19 (s, 1H), 6.09 (s, 1H), 3.96 (s, 3H), 3.94 (s, 3H), 3.84 (s, 3H). **^{13}C NMR (126 MHz, CDCl$_3$) δ** 169.2, 160.5, 158.5, 150.9, 149.3, 146.6, 132.5, 125.9, 123.1, 121.6, 114.3, 113.7, 112.4, 111.5, 111.3, 56.1, 56.0, 55.3. **HRMS (ESI) M/Z:** [M+Na]$^+$ calculated for $C_{20}H_{18}NaO_5$, 361.1046 ; found to be 361.1050.

(*Z*)-4-(3-fluorophenyl)-5-(4-methoxybenzylidene)furan-2(*5H*)-one (5w)

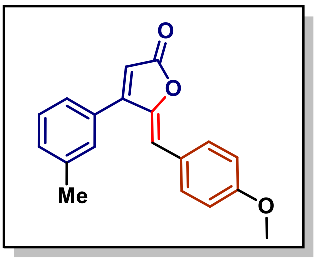


Following the general procedure (e), reaction of vinyl sulfoxonium ylide **1g** (108 mg, 0.4 mmol, 1 equiv.) is carried-out with ruthenium catalyst (7 mg, 3 mol%) and acetal **4e** (73 mg, 0.4 mmol, 1 equiv.) in presence of TMSOTf (22 µL, 30 mol%) with dichloroethane (3 mL) as solvent. The reaction mixture was stirred at 0 °C for 4 h to give **5w** in 63% yield (75 mg) as yellow viscous liquid after purification by the flash column chromatography (n-Hexane/EtOAc: 80:20, R_f 0.52).

^{1}H NMR (400 MHz, CHLOROFORM-*D*) δ 7.76 (d, *J* = 8.8 Hz, 2H), 7.52 – 7.45 (m, 1H), 7.27 (d, *J* = 7.7 Hz, 1H), 7.25 – 7.17 (m, 2H), 6.91 (d, *J* = 9.0 Hz, 2H), 6.16 (s, 1H), 6.11 (s, 1H), 3.84 (s, 3H). **^{13}C NMR (101 MHz, CHLOROFORM-*D*) δ** 168.9, 162.88 (d, *J* = 248.2 Hz), 160.8, 157.3, 157.3, 146.2, 132.8, 132.7, 132.6, 131.7, 130.95 (d, *J* = 8.4 Hz), 125.7, 124.44 (d, *J* = 3.1 Hz), 117.4, 117.2, 115.74 (d, *J* = 22.8 Hz), 114.5, 114.1, 114.1, 113.4, 55.4. **^{19}F NMR (376 MHz, CHLOROFORM-*D*)**

δ -111.09, -111.11 (d, *J* = 3.4 Hz), -111.13 (d, *J* = 2.7 Hz), -111.15. **HRMS (ESI) M/Z:** $[M+H]^+$ calculated for $C_{18}H_{14}FO_3$, 297.0921; found to be 297.0927.

(*Z*)-5-(4-methoxybenzylidene)-4-(*m*-tolyl)furan-2(*5H*)-one (5x)



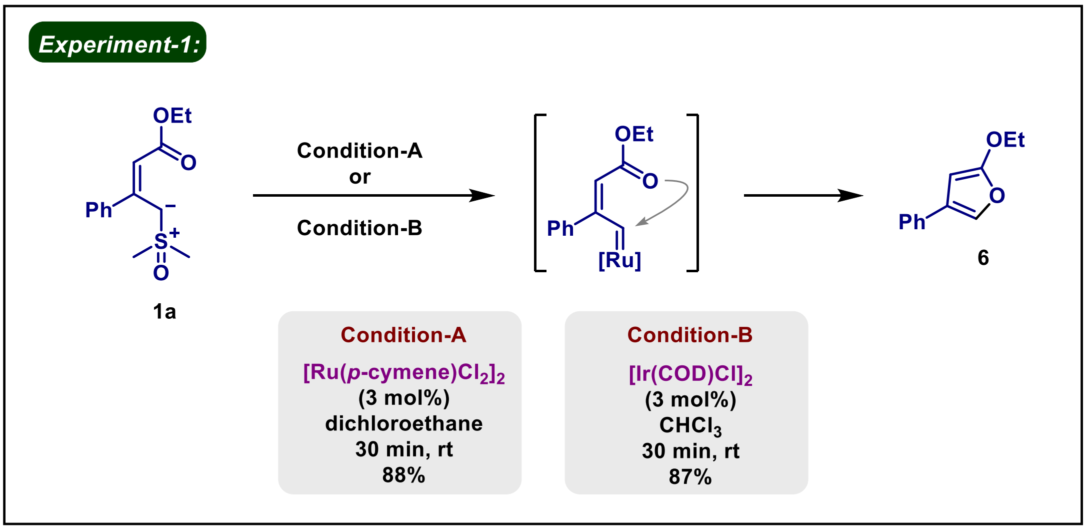
Following the general procedure (e), reaction of vinyl sulfoxonium ylide **1f** (107 mg, 0.4 mmol, 1 equiv.) is carried-out with ruthenium catalyst (7 mg, 3 mol%) and acetal **4e** (73 mg, 0.4 mmol, 1 equiv.) in presence of TMSOTf (22 µL, 30 mol%) with dichloroethane (3 mL) as solvent. The reaction mixture was stirred at 0 °C for 4 h to give **5x** in 66% yield (77 mg) as yellow viscous liquid after purification by the flash column chromatography (n-Hexane/EtOAc: 80:20, R_f 0.5).

^{1}H NMR (500 MHz,) δ 7.75 (d, *J* = 9.2 Hz, 2H), 7.39 (t, *J* = 7.6 Hz, 1H), 7.33 (d, *J* = 8.1 Hz, 1H), 7.28 (d, *J* = 7.6 Hz, 2H), 6.90 (d, *J* = 9.0 Hz, 2H), 6.14 (s, 1H), 6.10 (s, 1H), 3.82 (s, 3H), 2.44 (s, 3H). **^{13}C NMR (126 MHz, $CDCl_3$) δ** 169.2, 160.5, 158.9, 146.5, 138.9, 132.5, 131.1, 130.5, 129.0, 128.9, 125.8, 125.6, 114.3, 113.8, 113.2, 55.3, 21.4. **HRMS (ESI) M/Z:** $[M+Na]^+$ calculated for $C_{19}H_{16}NaO_3$, 315.0992; found to be 315.0985.

VI. Mechanistic studies:

a) Experiment-1: Isolation of intermediate

To an oven-dried, Ar-purged round-bottom flask equipped with a magnetic stir bar, vinyl sulfoxonium ylide **1** (107 mg, 0.4 mmol, 1 equiv.) is dissolved in dichloroethane solvent (3 mL). To this solution, ruthenium catalyst (7 mg, 3 mol%) was added and allowed to stir for 30 mins at room temperature (Condition-A). Then, the reaction mixture was passed through celite eluted with dichloromethane. The crude mixture is concentrated in *vacuo* and purified using flash column chromatography on silica gel to yield the furan, **6** in 88% (67 mg) yield.

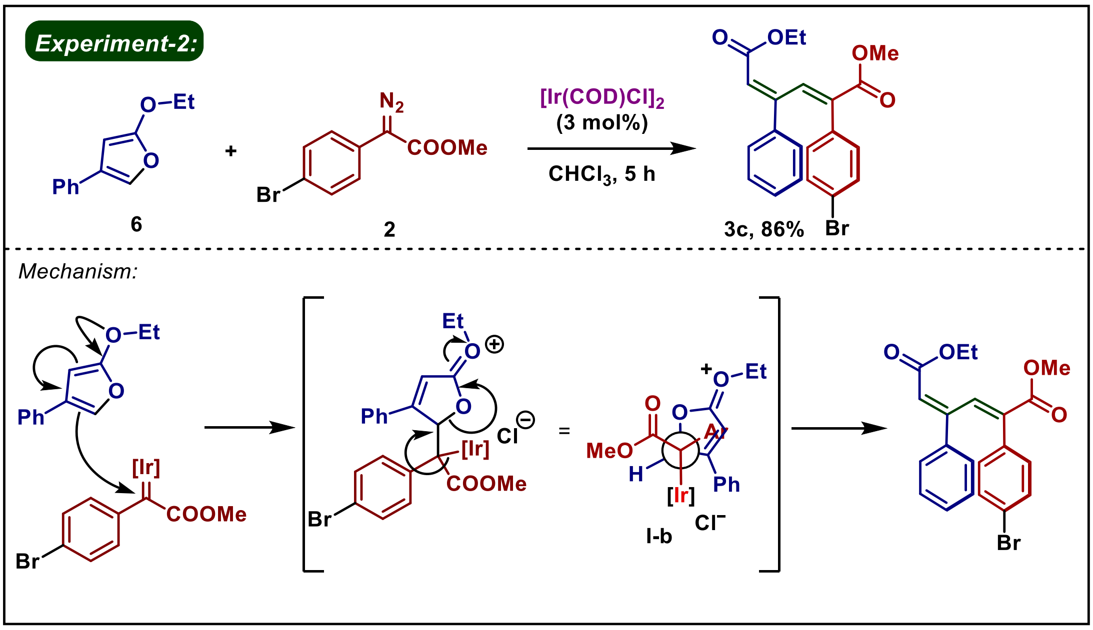


When the same procedure was carried out with iridium catalyst instead of ruthenium (Condition-2), we observed the same furan **6** as the product in 87% (66 mg) yield. Generation of furan from vinyl sulfoxonium ylide follows the mechanism as shown in the scheme 2.

^{1}H NMR (500 MHz, CDCl$_3$) δ 7.44 (d, *J* = 8.1 Hz, 2H), 7.35 (t, *J* = 7.8 Hz, 2H), 7.24 (d, *J* = 7.3 Hz, 1H), 7.19 (s, 1H), 5.49 (d, *J* = 1.4 Hz, 1H), 4.15 (q, *J* = 7.1 Hz, 2H), 1.44 (t, *J* = 7.1 Hz, 3H).

******The isolation of furan after 30 mins of standard reaction condition shows that furan can be one of the possible intermediate in both reactions.*

b) Experiment-2: Synthesis of dienoate from the isolated intermediate



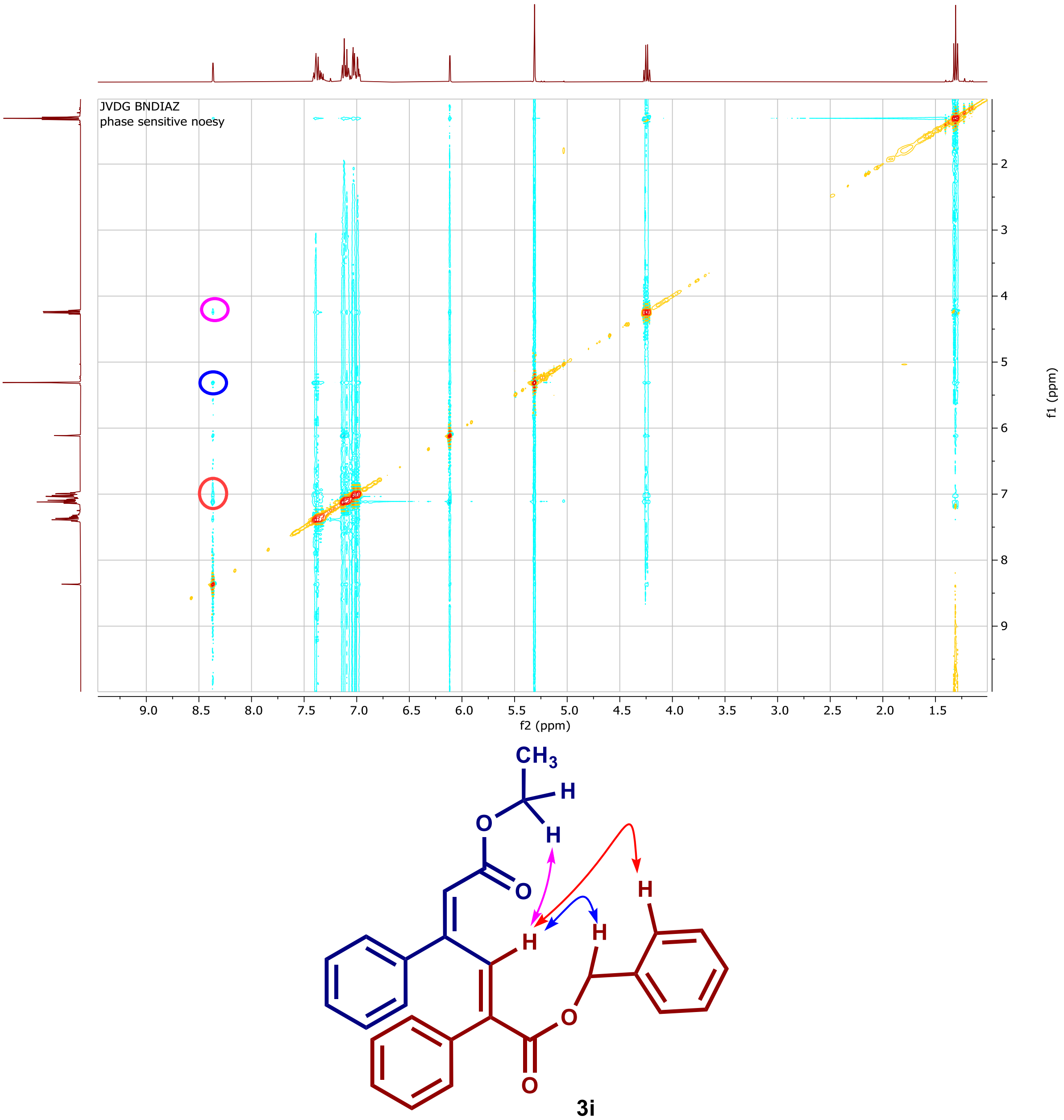
To an oven-dried, Ar-purged round-bottom flask equipped with a magnetic stir bar, furan **6** (67 mg, 0.36 mmol, 1 equiv.) was dissolved in CHCl$_3$ (2 mL). Then to the stirring solution, [Ir(COD)Cl]$_2$ (5 mg, 2 mol%) catalyst was added. The diazo ester **2c** (91 mg, 0.36 mmol, 1 equiv.) dissolved in CHCl$_3$ (1mL) is added dropwise to the reaction mixture at room temperature and stirring was continued for 5 hours. After the completion of reaction, mixture was passed through a short plug of silica, eluted with dichloromethane. The crude mixture is concentrated in *vacuo* and purified using flash column chromatography on silica gel to deliver the dienoate, **3c** in 86% (127 mg) yield.

^{1}H NMR (500 MHz, CDCl$_3$) δ 8.31 (d, *J* = 1.8 Hz, 1H), 7.13 (d, *J* = 8.3 Hz, 3H), 7.09 (d, *J* = 4.4 Hz, 4H), 6.81 (d, *J* = 8.1 Hz, 2H), 6.10 (d, *J* = 1.8 Hz, 1H), 4.23 (q, *J* = 7.1 Hz, 2H), 3.81 (s, 3H), 1.31 (t, *J* = 7.1 Hz, 3H). **^{13}C NMR (126 MHz, CDCl$_3$) δ** 166.8, 165.6, 152.3, 140.3, 138.4, 135.4, 133.8, 131.3, 130.4, 129.0, 128.1, 127.5, 121.9, 120.9, 60.5, 52.5, 52.4, 14.2. **HRMS (ESI) M/Z:** [M+Na]$^+$ calculated for $C_{21}H_{19}BrNaO_4$, 437.0359; found to be 437.0359.

This further proves that the isolated furan **6 is the potential intermediate involved in the synthesis of dienoate, **3c**. The mechanism involved in the conversion of furan to dienoate is shown in the scheme 2.*

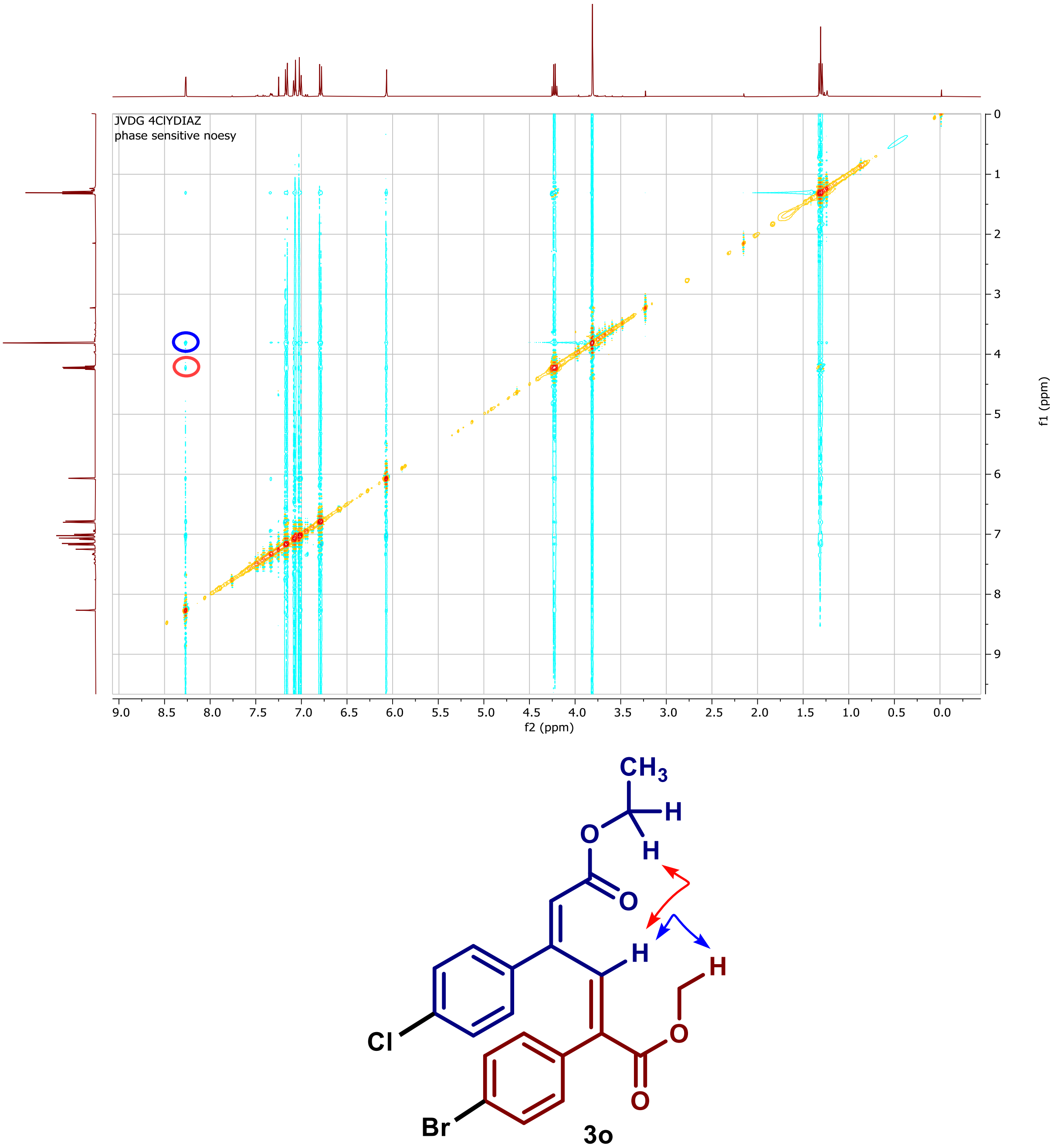
nOe:

To understand the configuration of the newly forming double bond between ylide carbon and diazo carbon, we performed nOe experiment for **3i** and **3o**. Here, the interaction present between the ylide hydrogen and benzyl hydrogen proves the *E*-configuration of the double bond. To further validate this assigned configuration, we carried out the same experiment with one more substrate, **3o**. Here, the presence of interaction between ylide hydrogen and methyl group of confirms the *E*-configuration of the double bond.



3i

^{1}H NOESY Spectra, (CDCl$_3$, 400 MHz)

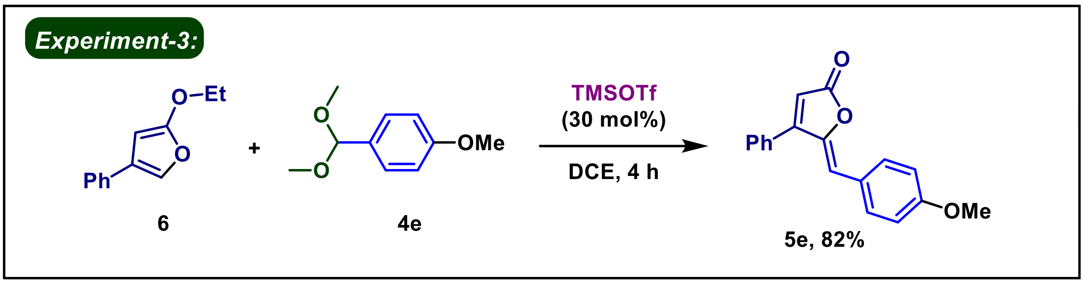


3o

^{1}H NOESY Spectra, ($CDCl_3$, 400 MHz)

c) Experiment-3: Synthesis of ylidene butenolide from the isolated intermediate

To an oven-dried, Ar-purged round-bottom flask equipped with a magnetic stir bar, furan **6** (66 mg, 0.35 mmol, 1 equiv.) was dissolved in dichloroethane. This solution is cooled to 0 °C and anisaldehyde acetal **4e** (64 mg, 0.35 mmol, 1 equiv.) was added with 30 mol% of TMSOTf (19 µL) and the stirring was continued at 0 °C for 4 hours. After the completion of reaction, mixture was passed through a short plug of silica, eluted with dichloromethane. The crude mixture is concentrated in *vacuo* and purified using flash column chromatography on silica gel to deliver the ylidene butenolide, **5e** in 82% (80 mg) yield.

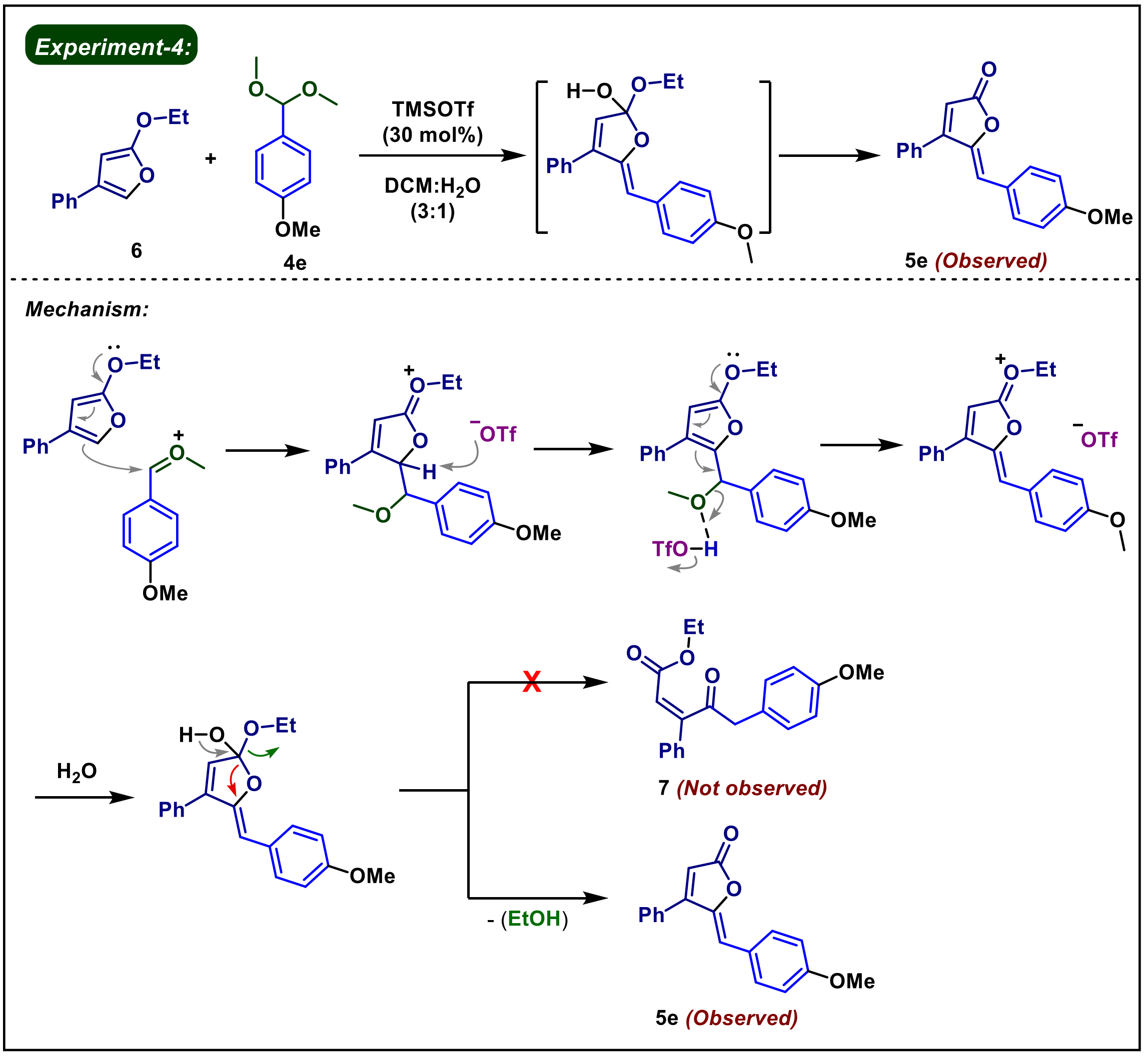


^{1}H NMR (500 MHz, CDCl$_3$) δ 7.77 (d, *J* = 9.0 Hz, 2H), 7.54 – 7.49 (m, 5H), 6.92 (d, *J* = 8.9 Hz, 2H), 6.15 (s, 1H), 6.14 (s, 1H), 3.84 (s, 3H). **^{13}C NMR (126 MHz, CDCl$_3$) δ** 169.2, 160.6, 158.8, 146.6, 132.7, 130.8, 130.4, 129.1, 128.6, 125.9, 114.4, 114.0, 113.6, 55.4. **HRMS (ESI) M/Z:** $[M+H]^+$ calculated for $C_{18}H_{15}O_3$, 279.1016; found to be 279.1014.

This confirms that the isolated furan is the potential intermediate involved in the synthesis of ylidene butenolide, **5e. The mechanism involved in the conversion of furan to ylidene butenolide is shown in the scheme 2.*

d) Experiment-4: Reaction in presence of water

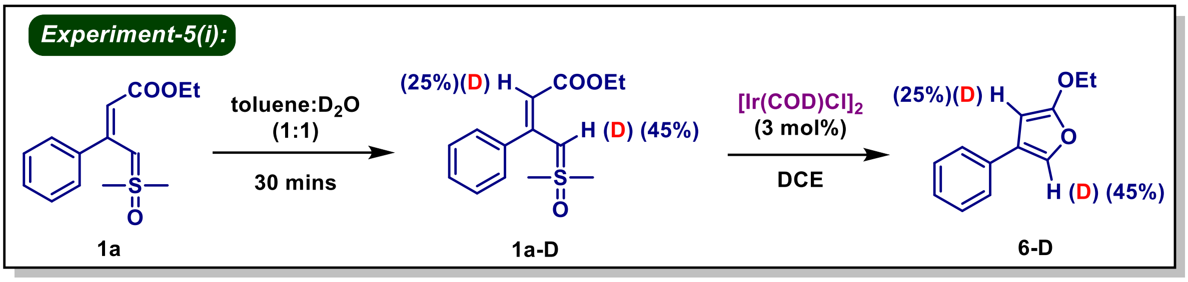
To an oven-dried, Ar-purged round-bottom flask equipped with a magnetic stir bar, furan **6** (66 mg, 0.35 mmol, 1 equiv.) was dissolved in DCM (2.1 mL). This solution is cooled to 0 °C and anisaldehyde acetal **4e** (64 mg, 0.35 mmol, 1 equiv.) was added with 30 mol% of TMSOTf (19 µL). To the same reaction mixture, water (0.7 mL) was added and the stirring was continued for 4 hours. After the completion of reaction, mixture was passed through a short plug of silica, eluted with dichloromethane. The crude mixture is concentrated in *vacuo* and purified using flash column chromatography on silica gel to deliver the ylidene butenolide, **5e** in 61% yield.



^{1}H NMR (500 MHz, CDCl$_3$) δ 7.77 (d, *J* = 9.0 Hz, 2H), 7.54 – 7.49 (m, 5H), 6.92 (d, *J* = 8.9 Hz, 2H), 6.15 (s, 1H), 6.14 (s, 1H), 3.84 (s, 3H). **^{13}C NMR (126 MHz, CDCl$_3$) δ** 169.2, 160.6, 158.8, 146.6, 132.7, 130.8, 130.4, 129.1, 128.6, 125.9, 114.4, 114.0, 113.6, 55.4. **HRMS (ESI) M/Z:** [M+H]$^+$ calculated for $C_{18}H_{15}O_3$, 279.1016; found to be 279.1014.

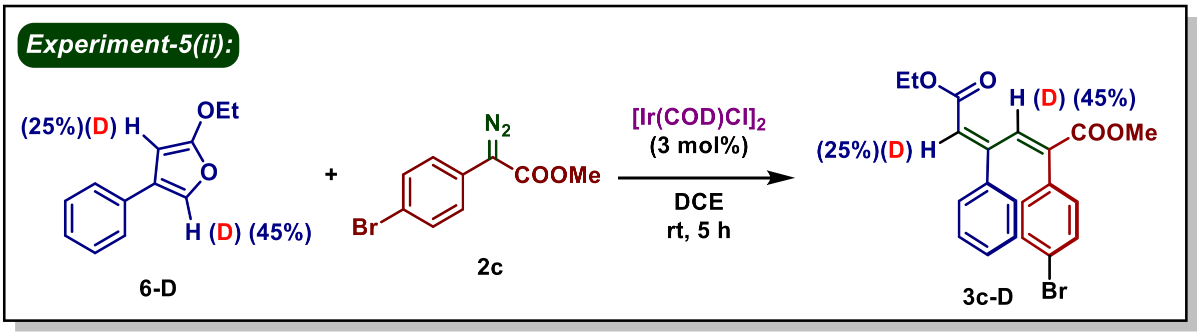
In presence of water, it is expected that the -OH can attack the oxonium ion and rearranges to generate **7 (Piancatelli rearrangement) as reported previously. But, in the present case, we observed **5e** instead of **7** which shows that the ethyl group is eliminated via S_N2 attack by the nucleophile rather than addition-elimination mechanism.*

e) Experiment-5: Deuterium Labelling Studies

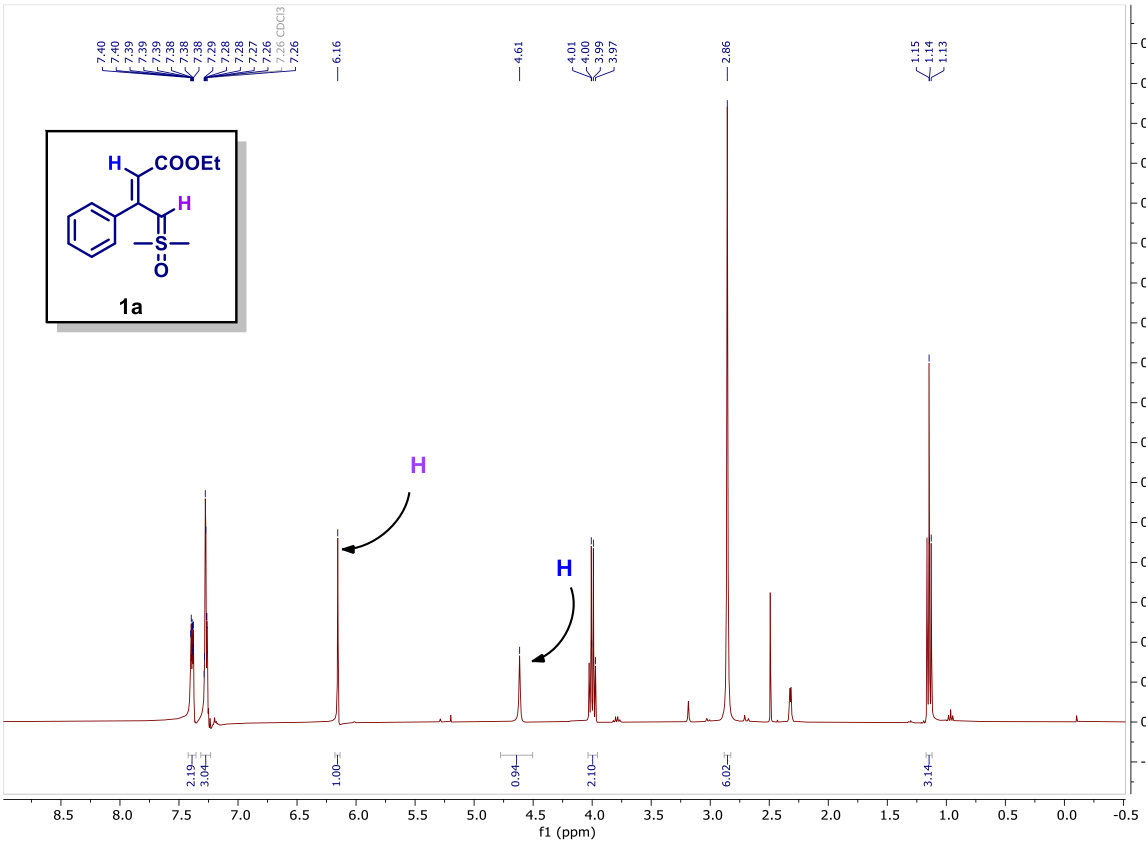


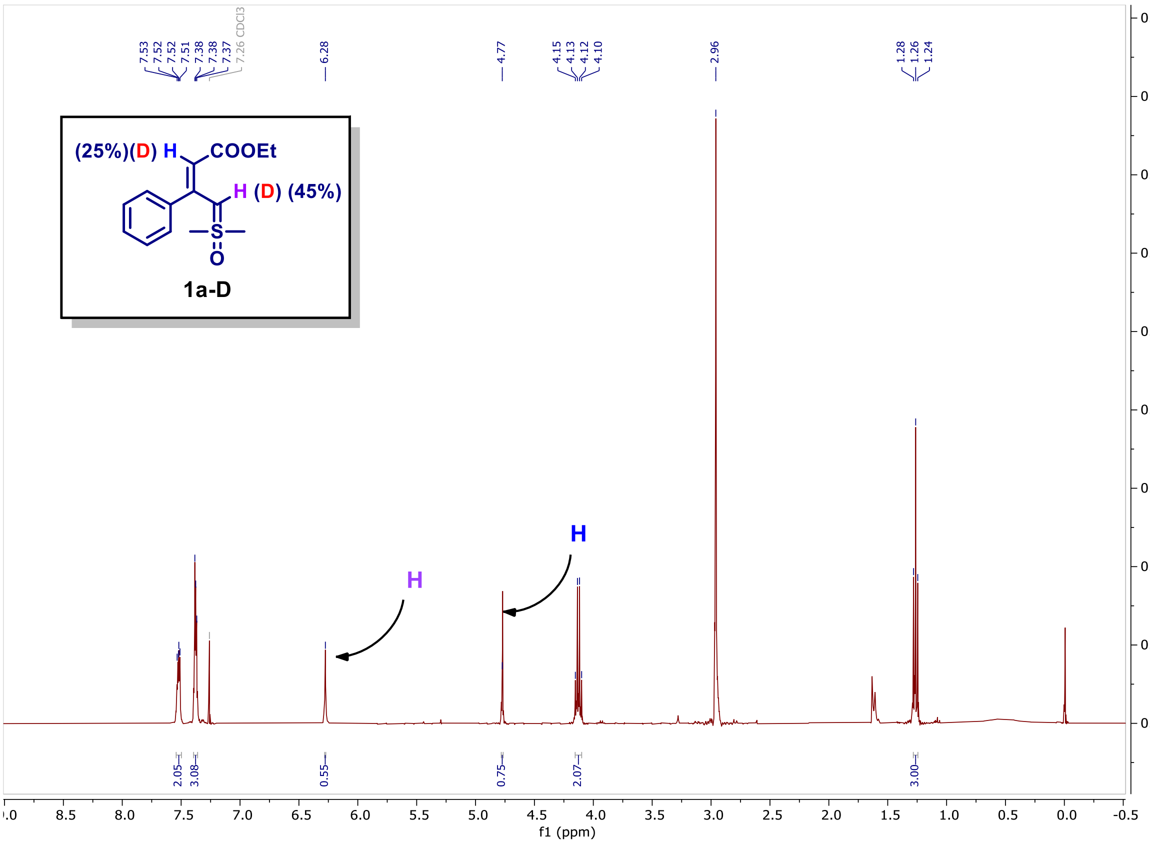
To an oven-dried argon purged 10 mL reaction tube equipped with a magnetic stir bar, was added vinyl sulfoxonium ylide **1a** (1 equiv., 0.5 mmol, 133 mg) in Toluene:D_2O (1:1) (0.5 M:0.5 M) as a solvent under argon atmosphere and allowed to stir for 30 minutes. Then, the mixture is added to the distilled hexane (6 mL) to generate the deuterated vinyl sulfoxonium ylide **1a-D** as white solid in 96% (128 mg) yield.

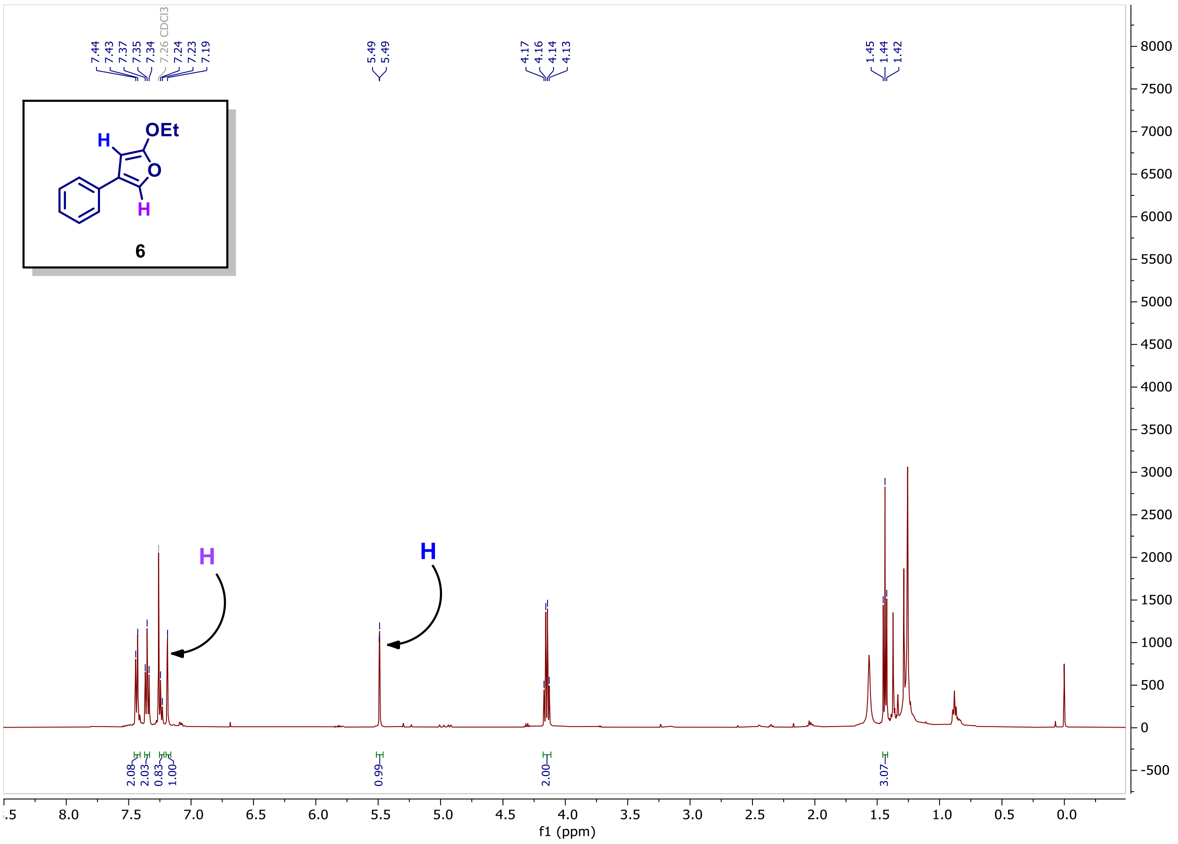
In a flame dried, argon purged reaction tube, Deuterated vinyl sulfoxonium ylide **1a-D** (1 equiv., 0.3 mmol, 81 mg) is dissolved in dichloroethane solvent (2 mL). To the solution iridium catalyst (3 mol%, 6 mg) was added and stirred for 30 minutes. After 30 minutes, the reaction mixture was concentrated under reduced pressure. The residue was purified using flash column chromatography. (Biotage flash chromatography gradient purification: n-Hexane:EtOAc = 95:5 (R_f 0.43) to give the product deuterated furan **6-D** in 87% yield (50 mg) as white solid.



Next, to an oven-dried, Ar-purged reaction tube equipped with a magnetic stir bar is added isolated Deuterated furan **6-D** (1 equiv., 0.2 mmol, 38 mg) and diazo compound **2c** (1 equiv., 0.2 mmol, 51 mg) with 3 mol% iridium catalyst (4 mg) and the mixture is stirred at room temperature for 5 hours. After the completion of reaction (monitored *via* TLC), reaction mixture is passed through a short plug of silica, eluted with dichloromethane. The crude mixture is concentrated in *vacuo* and purified using flash column chromatography on silica gel to give dienoate **3c-D** in 86% yield (72 mg) as colourless viscous liquid after purification by the flash column chromatography (n-Hexane/EtOAc: 90:10, R_f 0.4).


7.40
7.40
7.39
7.39
7.39
7.38
7.38
7.38
7.29
7.28
7.28
7.27
7.26
7.26 CDCl3
7.26
6.16
4.61
4.01
4.00
3.99
3.97
2.86
1.15
1.14
1.13
H
COOEt
H
S
O
1a
H
H
2.19
3.04
1.00
0.94
2.10
6.02
3.14
f1 (ppm)


7.53
7.52
7.52
7.51
7.38
7.38
7.37
7.26 CDCl3
6.28
4.77
4.15
4.13
4.12
4.10
2.96
1.28
1.26
1.24
(25%)(D) H
COOEt
H (D) (45%)
S
O
1a-D
H
H
2.05
3.08
0.55
0.75
2.07
3.00
f1 (ppm)



7.44
7.43
7.37
7.35
7.34
7.26 CDCl3
7.24
7.23
7.19
5.49
5.49
4.17
4.16
4.14
4.13
1.45
1.44
1.42
OEt
H
O
H
6
H
H
2.08
2.03
0.83
1.00
0.99
2.00
3.07
8000
7500
7000
6500
6000
5500
5000
4500
4000
3500
3000
2500
2000
1500
1000
500
0
-500
.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
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2.0
1.5
1.0
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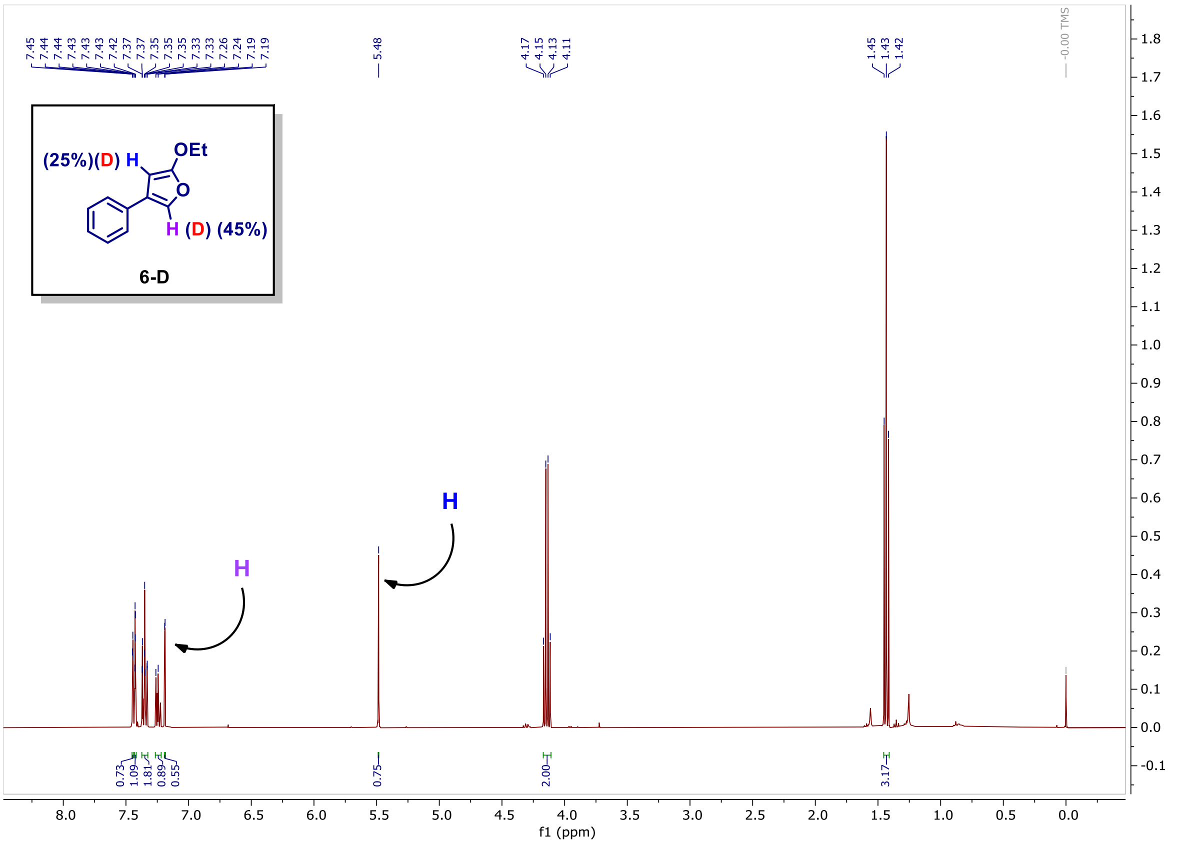
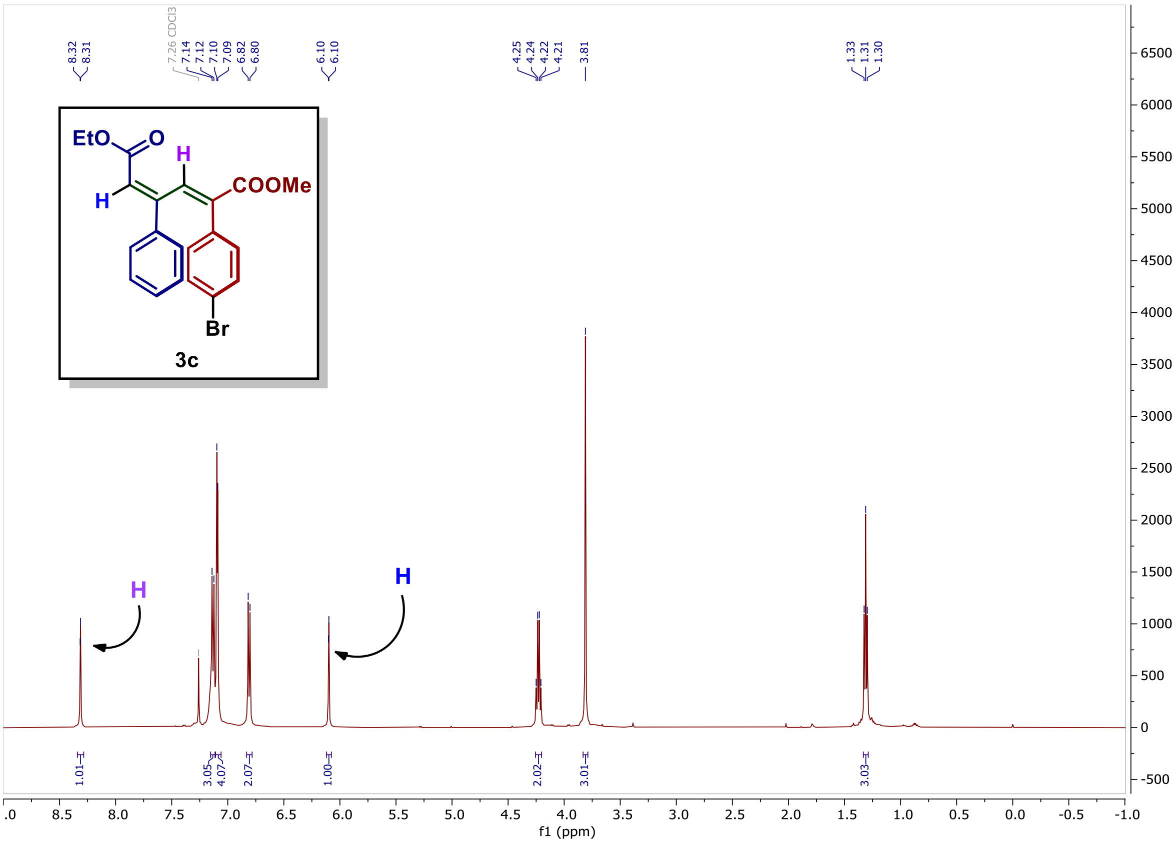
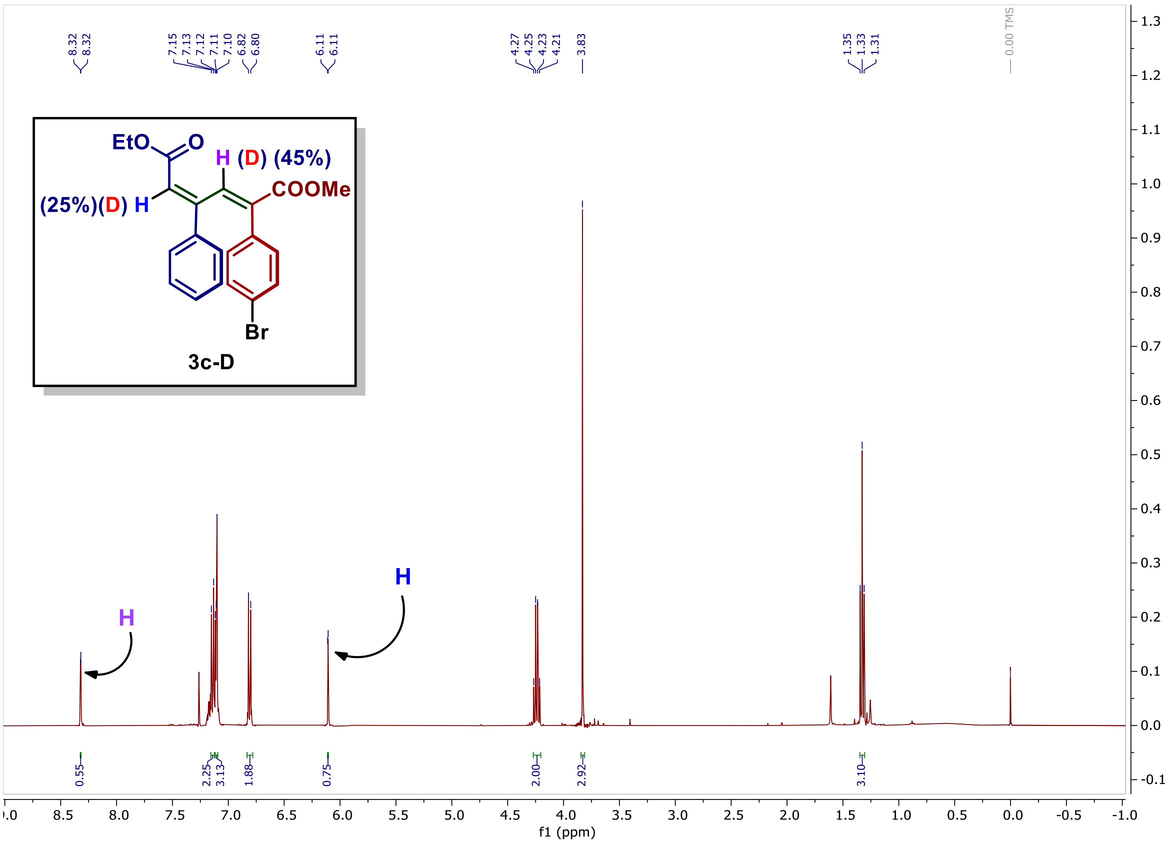
f1 (ppm)



7.45
7.44
7.44
7.43
7.43
7.43
7.42
7.37
7.37
7.35
7.35
7.33
7.33
7.26
7.24
7.19
7.19
5.48
4.17
4.15
4.13
4.11
1.45
1.43
1.42
-0.00 TMS
(25%)(D) H
OEt
O
H (D) (45%)
6-D
H
H
0.73
1.09
1.81
0.89
0.55
0.75
2.00
3.17
1.8
1.7
1.6
1.5
1.4
1.3
1.2
1.1
1.0
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0.0
-0.1
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)

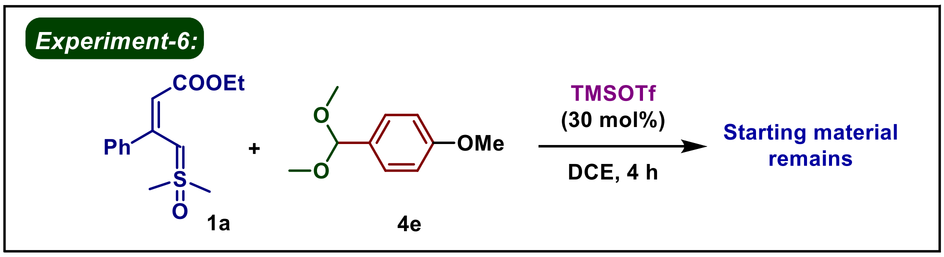




The percentage of deuterium present in the ylide **1a-D remains same in the final product. This further confirms that the protons in the starting material remains unaffected.*

f) Experiment-6: Reaction of ylide with acetal in presence of TMSOTf

To an oven-dried, Ar-purged round-bottom flask equipped with a magnetic stir bar, vinyl sulfoxonium ylide **1a** (107 mg, 0.4 mmol, 1 equiv.) is dissolved in dichloroethane (3 mL) solvent. The reaction mixture is cooled to 0 °C and acetal **4e** (73 mg, 0.4 mmol, 1 equiv.) with TMSOTf (22 μL, 30 mol%) was added and stirred for 4 hours. When the progress of the reaction was monitored using Thin Layer Chromatography (TLC), it is observed that the acetal and ylide was not consumed.

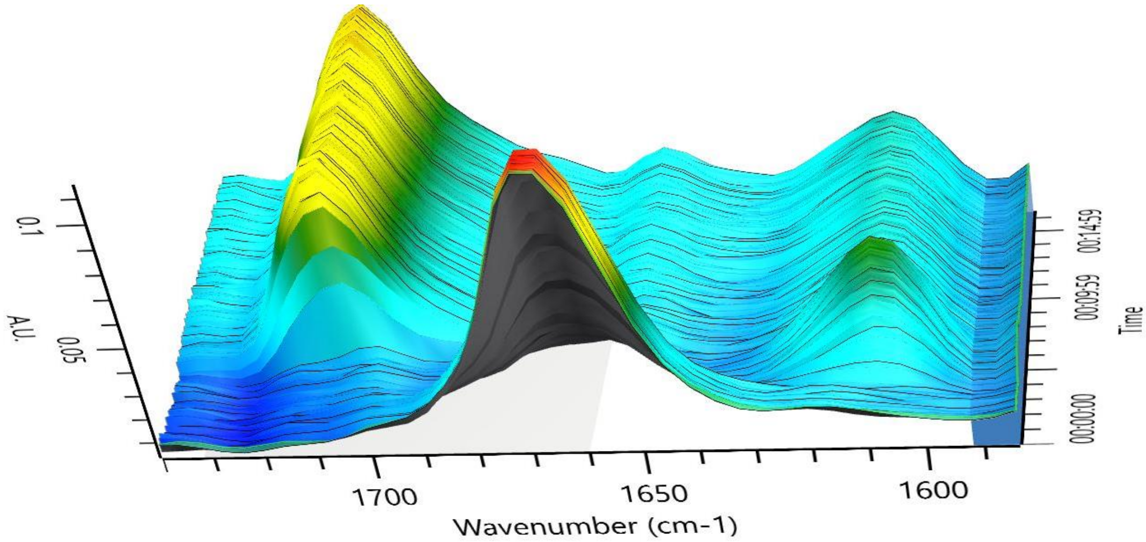


g) Experiment-7: React-IR studies to detect insitu generated furan

During the experimental investigation for the generation of dienoate **3** and ylidene butanolide **5**, it was proved that the reaction proceeds through the furan intermediate **6**. For further confirmation of the furan **6** intermediate in both transformations, we have performed *In-situ* IR studies.

➢ Synthesis of dienoate (3)

For the generation of dienoate **3**, we added ylide **1** and catalyst followed by the addition of diazo ester **2** after 3 mins in the flask and monitored the reaction through react-IR probe. During the reaction, we observed the formation of furan a peak at 1607 cm^{-1}. The gradual formation of the dienoate product **3** (peak at 1705 cm^{-1}) and consumption of furan was observed. This confirms that furan is the intermediate in this transformation.



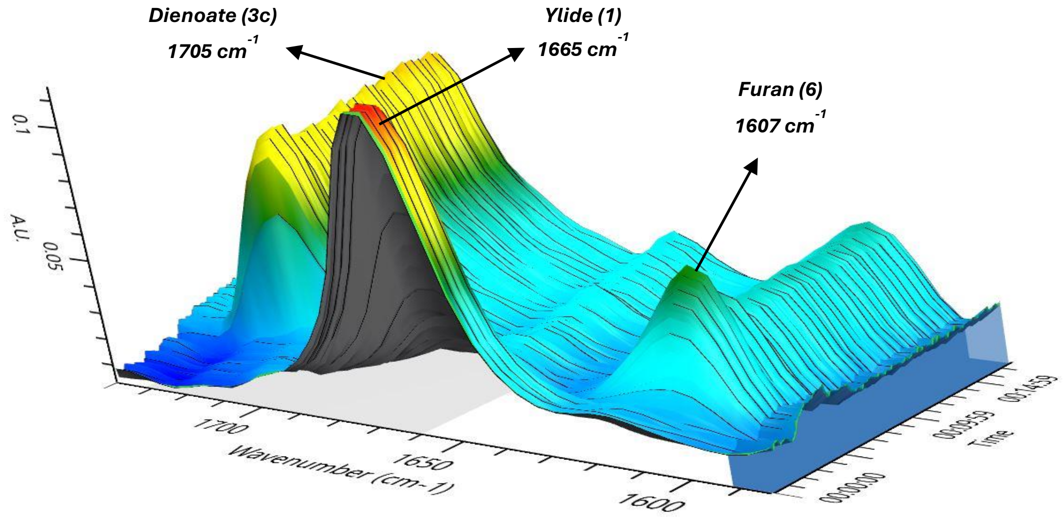
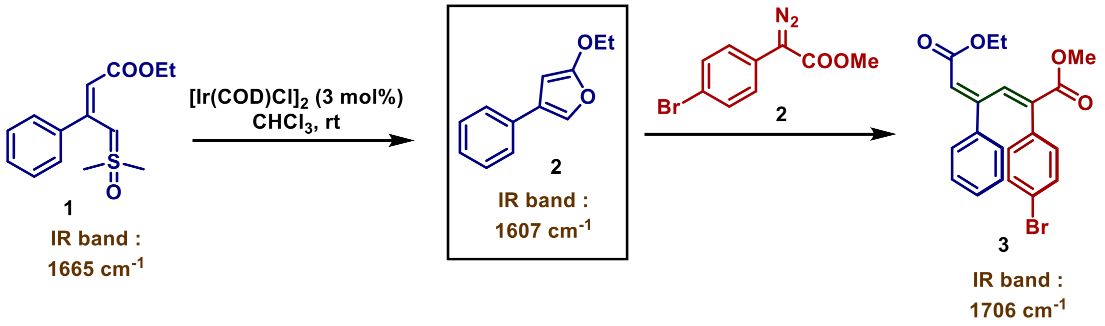


Figure 4: *3D Surface for the reaction analysis of dienoate synthesis.*



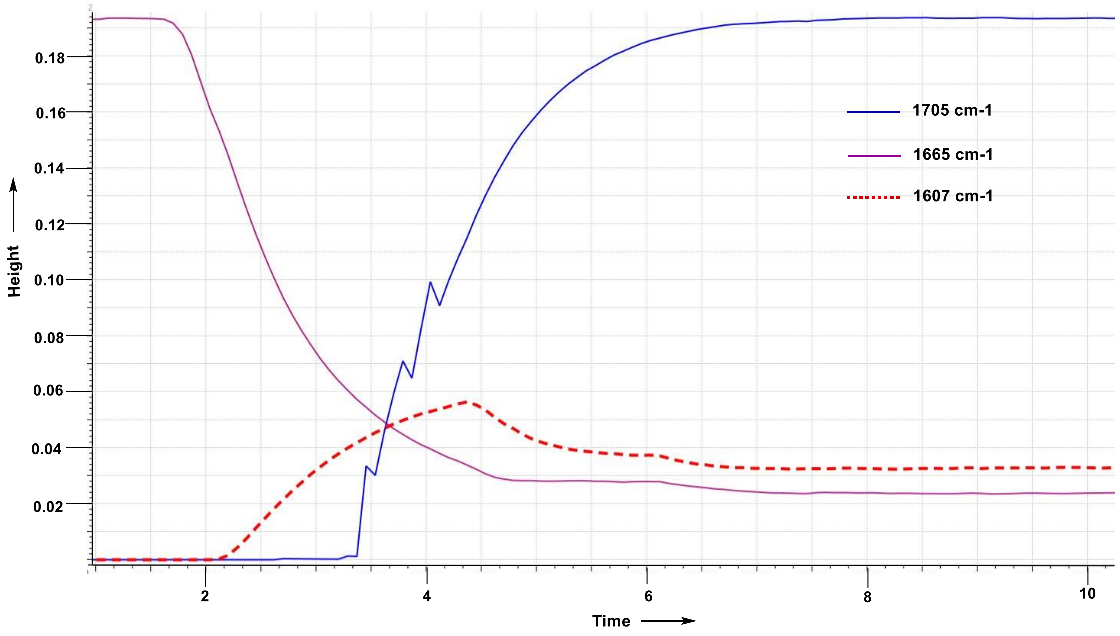


Figure 5: *2D React-IR spectra for the synthesis of Dienoate.*

➢ Synthesis of ylidene butenolide (5)

When the vinyl sulfoxonium ylide **1** was treated with the catalyst (either Iridium or Ruthenium complexes), the IR bands at 1665 cm^{-1} and 1607 cm^{-1} were observed in the spectra which correspond to ylide **1** and furan **6** respectively. On adding acetal **4** with TMSOTf for the synthesis of butenolide the peak at 1757 cm^{-1} confirmed the product generation **5**. This further proves that the furan **6** is the intermediate in this reaction.

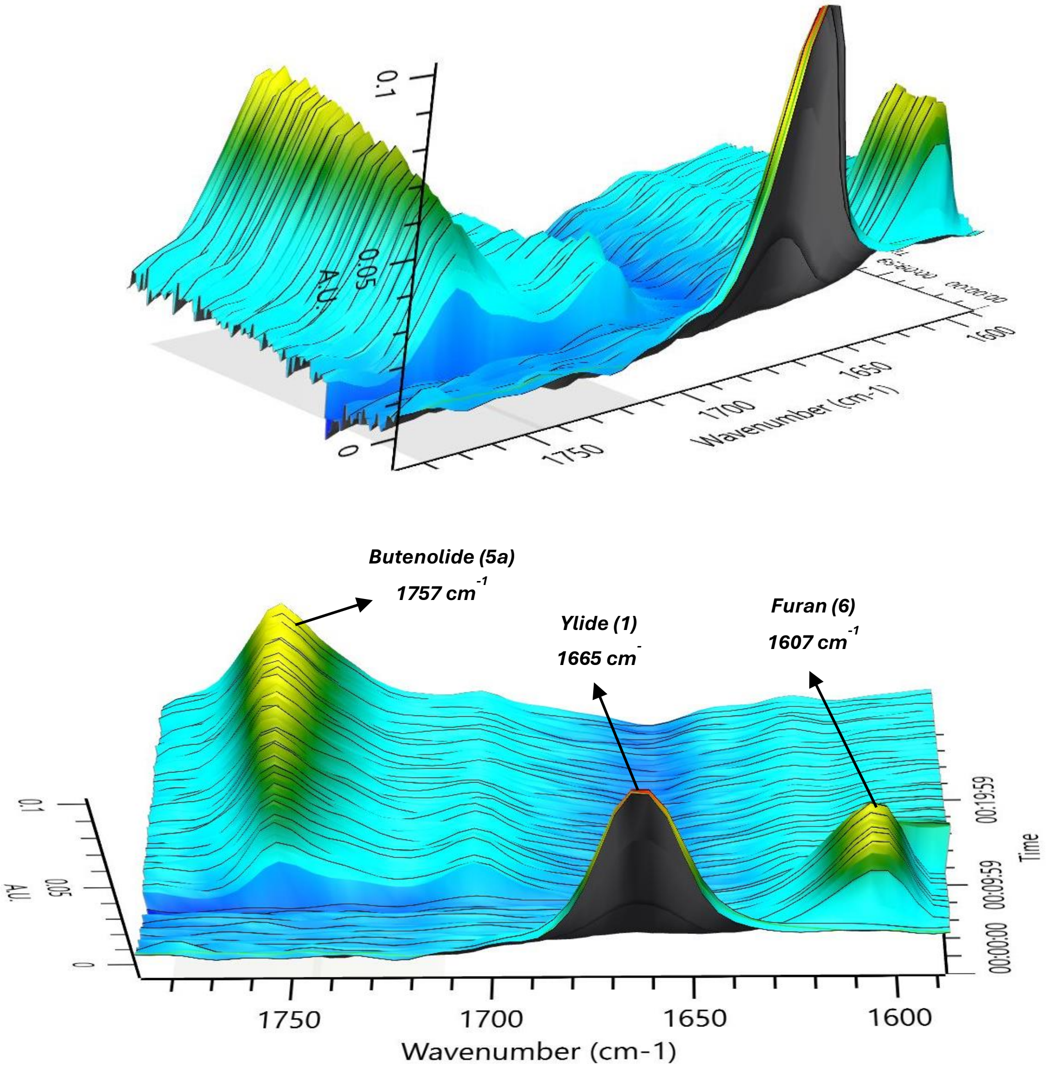
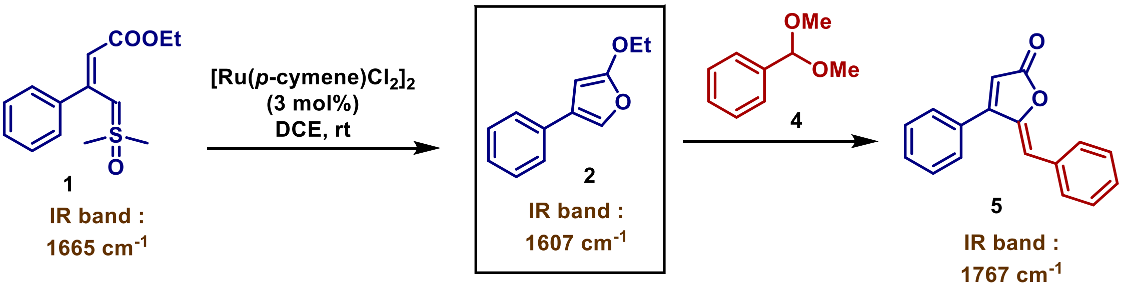


Figure 6: *3D Surface for the reaction analysis of ylidene butenolide synthesis.*



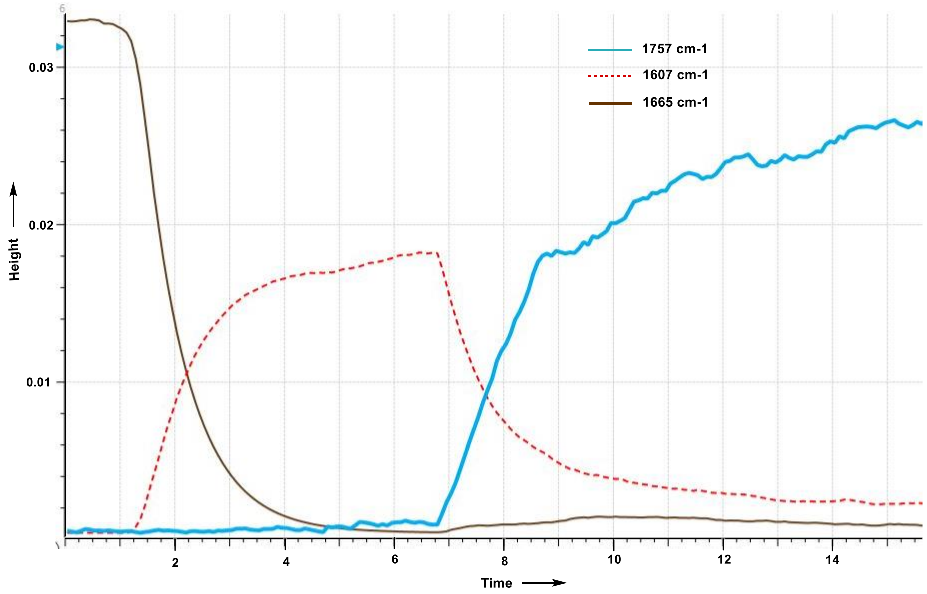


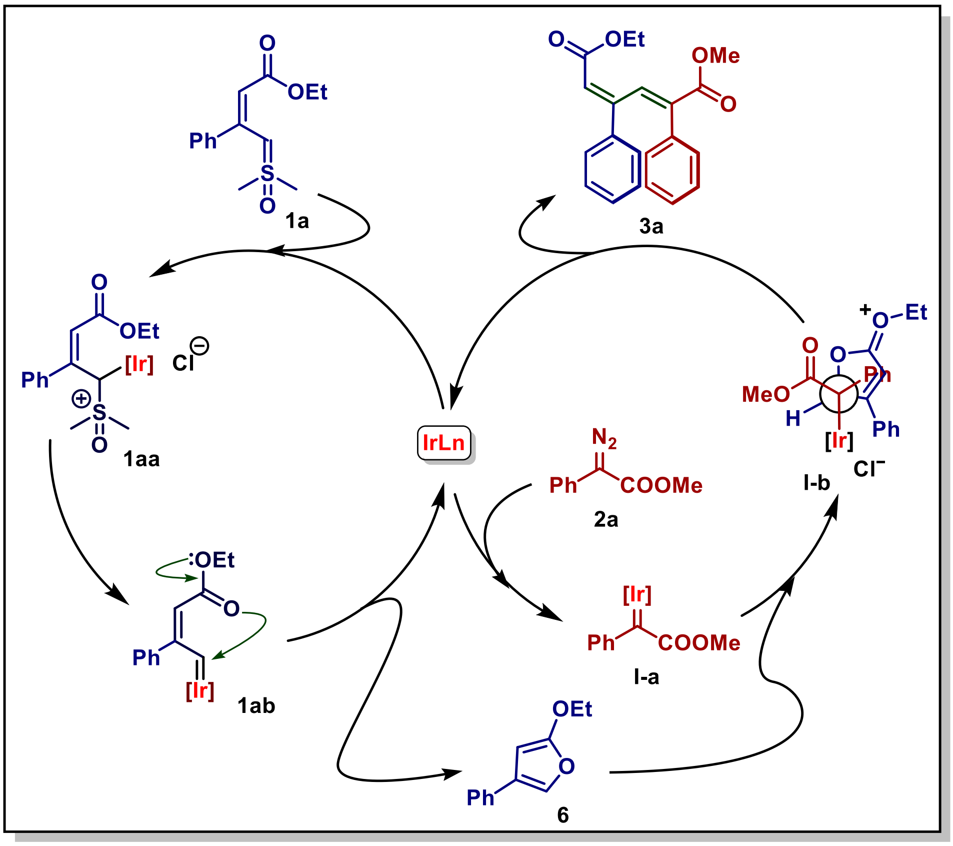
Figure 7: *2D React-IR spectra for the synthesis of ylidene butenolide.*

VII. Reaction Mechanism:

Based on the experimental mechanistic investigation and theoretical calculations, the mechanism for the synthesis of dienoate and ylidene butenolide were given here.

a) Synthesis of dienoate (3)

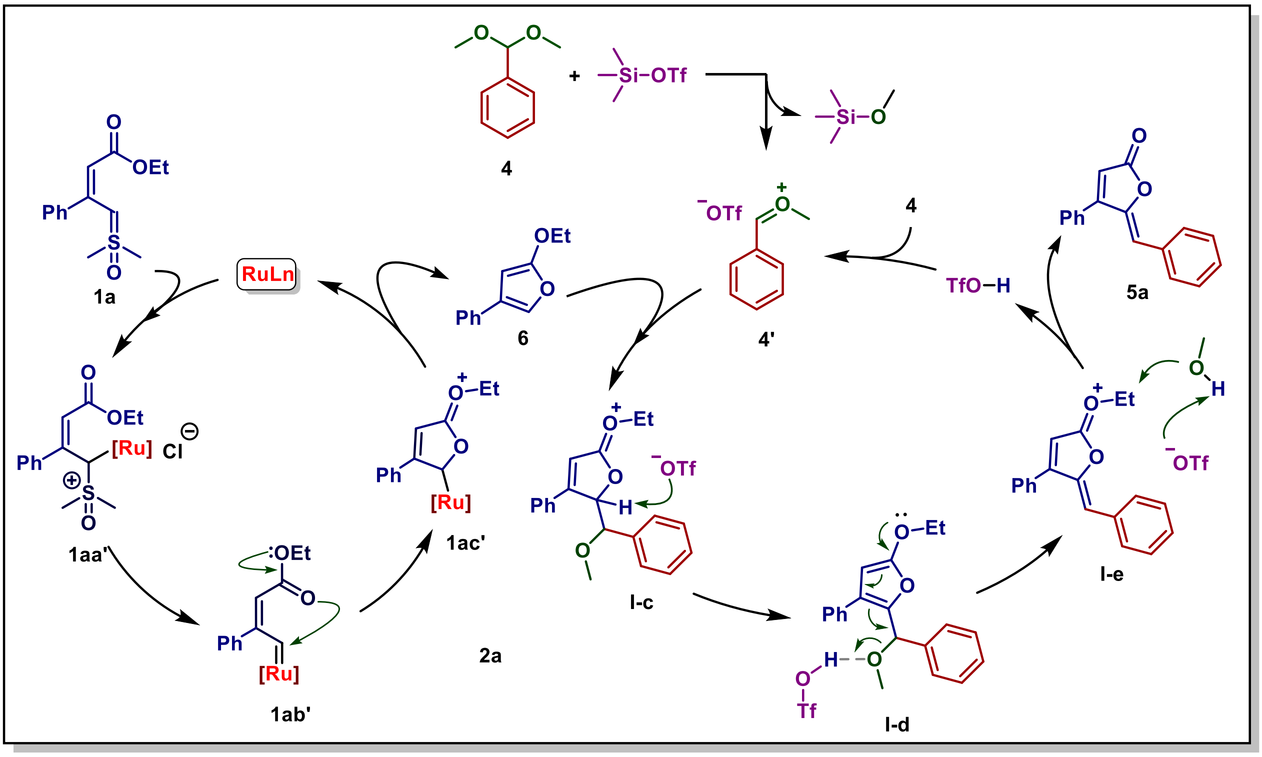
First, the vinyl sulfoxonium ylide generates vinyl carbene **1ab** through the metal carbenoid intermediate **1aa**. Intramolecular nucleophilic attack followed aromatisation regenerates the catalyst and releases furan intermediate **6,** which is isolated and confirmed. The regenerated Ir catalyst now reacts with the diazo ester **2a** and forms a metal carbene, **I-a**. Furan being a reactive species undergoes nucleophilic addition to the diazo derived metal carbene (**I-a**) which forms the carbenoid **I-b**. This can undergo the cyclopropanation as per previous reports. But, in the present methodology cyclopropanation is not observed which may be due to the steric of phenyl group. Thus, here **I-b** releases catalyst and rearranges to form the dienoate, **3a** (Scheme 1).



Scheme 1: Reaction mechanism for the synthesis of dienoate

b) Synthesis of ylidene butenolide (5):

For the synthesis of ylidene butenolides, the mechanism works as shown in the scheme 2. Here, vinyl sulfoxonium ylide **1** forms the furan as mentioned earlier. On the other hand, acetal **4** in presence of TMSOTf catalyst generates the oxonium ion **4′** *in-situ*. The reactive intermediate **6** undergoes nucleophilic addition with the oxonium ion to generate the species **I-c**. Triflate being the counter ion abstract the proton from the γ-position which aromatises **I-c** and releases TfOH. This TfOH protonates the methoxy group and removes as MeOH to form the intermediate **I-e**. The generated methanol can deprotect the ethyl group from the intermediate **I-e** to deliver the ylidene butenolide, **6**. Here the regenerated TfOH can proceed to the second catalytic cycle by generating the oxonium ion from the acetal directly.



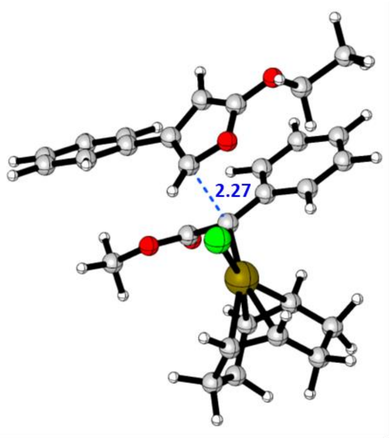
Scheme 2: Reaction mechanism for the synthesis of ylidene butenolide

VIII. Computational details:

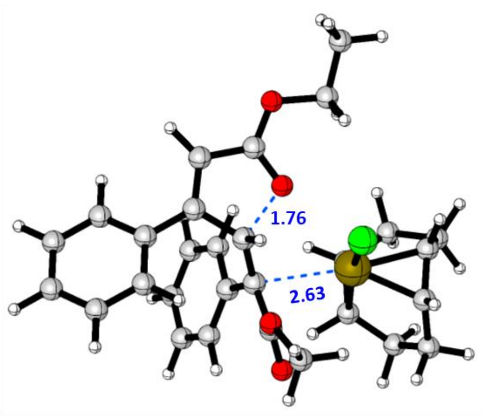
All the Density Functional Theory (DFT) calculations were performed using Gaussian 16 Revision C.01.[4] The geometry optimisation of all the stationary points in gas phase was performed using M06-2X[5] hybrid density functional, with a Karlsruhe double-zeta basis set def2-SVP for all atoms.[6] to confirm the nature of the stationary points, the harmonic vibrational frequencies of normal modes were computed using the same level of theory. From the vibrational frequency analysis, it was confirmed that all the intermediates are at minimum with no imaginary frequencies, whereas all the transition states were accompanied with exactly one imaginary frequency corresponding to the stretching of the bond involved which is expected to form or break during that step of the reaction. Further, the single point energy calculations were performed using triple-zeta basis set, def2-TZVPP.[7] To incorporate the effect of solvent, a continuum solvation model SMD[8] was used. All the 3D structures were illustrated using CYLview[9] software and 2D structure were obtained using ChemDraw software.

a) 3D structures of transition states:

(i) Synthesis of dienoate

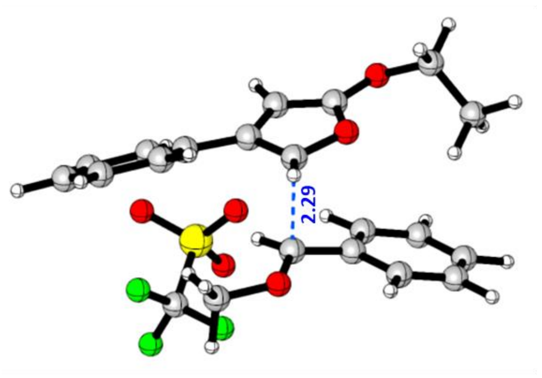


TS-1

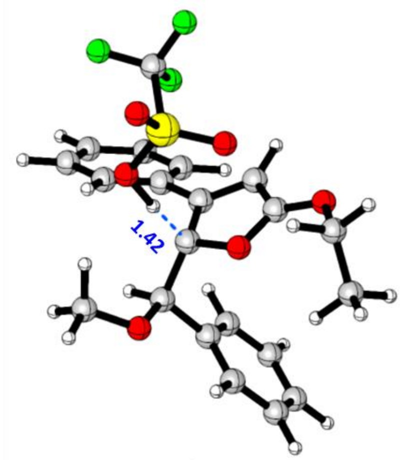


TS-2

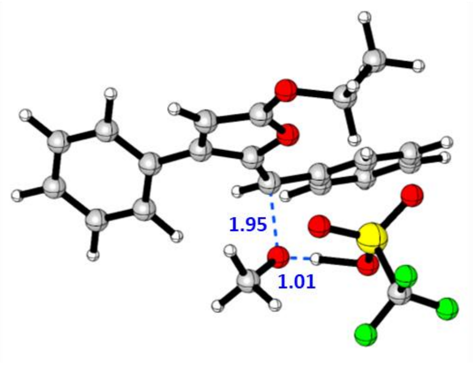
(ii) Synthesis of ylidene butenolides



TS-3



TS-4

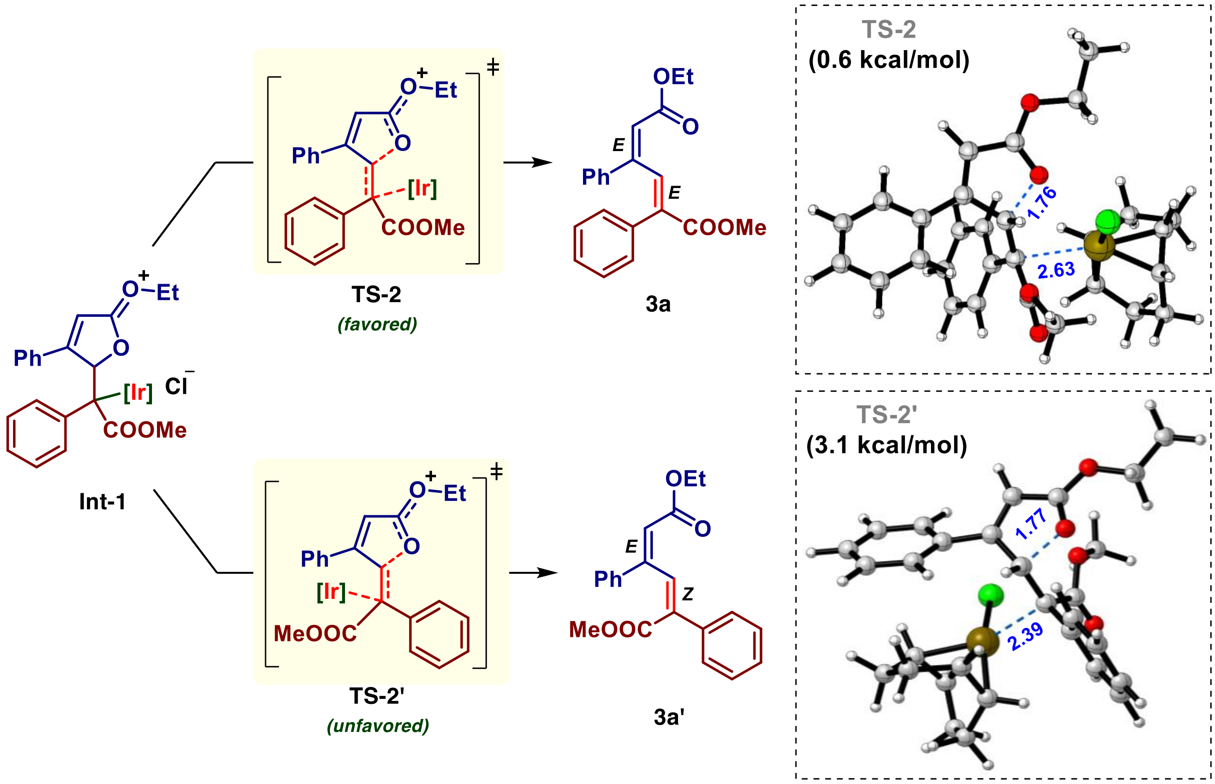


TS-5

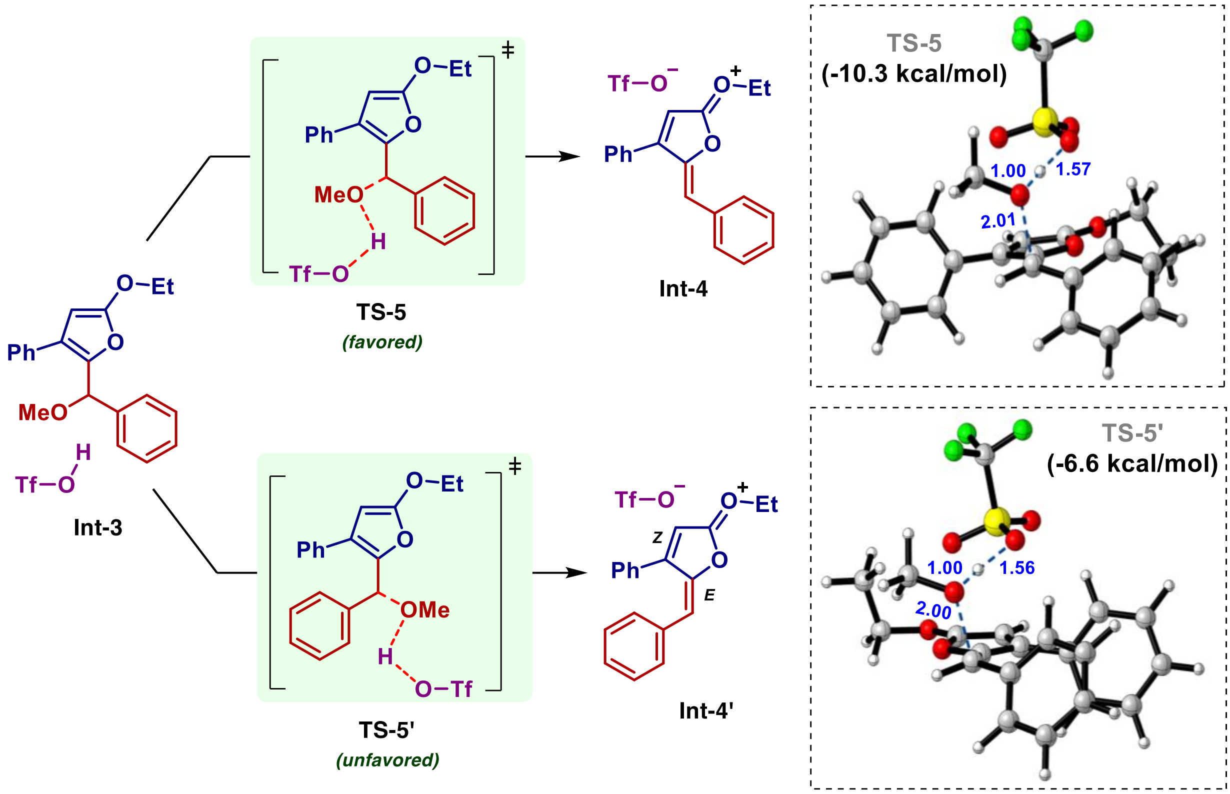
b) Stereoselectivity studies:

There are two possible ways that **int-1** can demetallize, resulting in two diastereomers for the dienoate **3a**. But experimentally only one diastereomer (*E*,*E*) is observed. To understand the energetics for the other possible diastereomer is analysed through DFT calculations. Here, **TS-2** (0.6 kcal/mol) for the formation of *(E,E)*-dienoate is more stable than the **TS-2′** (3.1 kcal/mol) which gives *(E,Z)*-dienoate.

This could be due to the steric repulsion between the catalyst and phenyl group of ylide in **TS-2′**. Thus, the **int-1** generates selectively *(E,E)*-dienoate via **TS-2**.



Similarly, the transition states for the possible diastereomers of **5** were analysed through computational methods. The results shows that **TS-5** is more stable (-10.3 kcal/mol) than the **TS-5′** (-6.6 kcal/mol). This could be due to the steric repulsion between the phenyl rings of ylide and acetal which destabilise the **TS-5′**. Thus, the **int-3** selectively generates (*Z*,*Z*) diastereomer (**int-4**) via **TS-5**.



c) Single Point Energy of stationary points:

Single point energy of all the transition states, intermediates and molecules involved in the reaction pathways are mentioned here.

No.	Stationary points/Molecule	Single Point Energy (Hartree)
1.	6	-614.915316
2.	TS-1	-1989.670969
3.	Int-1	-1989.70565
4.	TS-2	-1989.696752
5.	3a	-1989.750929
6.	TS-3	-1961.915390
7.	Int-2	-1961.960510
8.	TS-4	-1961.929704
9.	Int-3	-1961.948936
10.	TS-5	-1961.937873
11.	Int-4	-1961.955255
12.	5a	-805.477162

13.	I-a	-1374.754944
14.	1	-1168.105777
15.	Oxonium ion	-1871.423565
16.	TMSOMe	-524.414257
17.	TMSOTf	-1370.833271
18.	TS-2′	-1989.695309
19.	TS-5′	-1961.933359

d) Coordinates for Stationary Points:

6

C	0.25515700	0.22277200	-0.14946000
C	-0.70684000	-0.75572100	-0.59766800
C	-0.46608500	1.33406200	0.17426700
C	-1.91620700	-0.13626700	-0.52262400
H	-0.20250000	2.29609700	0.60037100
O	-1.79047100	1.12028000	-0.05701400
C	1.71315400	0.04889500	-0.03731900
C	2.26764100	-1.22959800	0.10902300
C	2.57686400	1.15346200	-0.07078700
C	3.64534700	-1.39913400	0.22632900
H	1.60832000	-2.09847800	0.14619600
C	3.95283700	0.98468100	0.05379800
H	2.16312300	2.15300200	-0.21724100
C	4.49347100	-0.29293000	0.20206500
H	4.05851400	-2.40236700	0.34194000
H	4.60926300	1.85577400	0.02345800
H	5.57239300	-0.42549500	0.29354500
C	-4.23570300	-0.01393800	-0.15489500
H	-5.11845800	-0.39723900	-0.68048300
H	-4.23203800	1.08294400	-0.24098600
C	-4.22789400	-0.44974200	1.29743600
H	-3.34709200	-0.05202800	1.82092500
H	-5.12587200	-0.07545700	1.80791000
H	-4.21435200	-1.54577800	1.36969400
H	-0.52940400	-1.76332800	-0.95764800
O	-3.12857300	-0.54864200	-0.87906900

TS-1

Ir	-1.72178500	-0.22578600	-0.30806900
C	-2.52017300	0.22841000	1.56756000
C	-2.41502900	-1.19001700	1.44337600
C	-3.61553800	-2.10903500	1.23355400
C	-3.89073700	-2.37924700	-0.25302200
C	-3.54955200	-1.20371700	-1.13889400
C	-3.88004400	0.11966600	-0.89315000
C	-4.69720100	0.58586700	0.29581100
C	-3.80376200	1.02619100	1.46579700
H	-1.77747800	0.70941900	2.21308200
H	-1.60002600	-1.65190400	2.00837400
H	-3.22879800	-1.44923100	-2.15444600
H	-3.77332700	0.81519500	-1.72903700
H	-3.42696300	-3.06444400	1.74315700
H	-4.49970700	-1.68026800	1.72796800
H	-3.26667800	-3.22283500	-0.58291800
H	-4.93942100	-2.68749400	-0.41082900

H	-5.33369900	1.42618400	-0.01494100
H	-5.38366000	-0.21352400	0.60740600
H	-3.51659200	2.08006200	1.32215800
H	-4.35815600	0.98473300	2.42033300
Cl	-1.15043900	0.28785200	-2.60895200
C	0.61517000	-1.41155900	0.90584000
C	0.13435400	-0.06772300	0.44067900
C	0.91906300	-3.64899300	0.33320800
H	1.88693400	-3.69571700	0.85216600
H	0.13246500	-4.01040500	1.01085500
O	0.85334200	-1.69992900	2.05464200
O	0.63532000	-2.32021900	-0.07511400
H	0.94525000	-4.25142200	-0.58006500
C	0.56512100	1.11997300	1.19083200
C	-0.07126500	2.35059700	0.91216300
C	1.60041100	1.12012500	2.14733700
C	0.29788500	3.51901100	1.56514600
H	-0.86929700	2.35595800	0.16510500
C	1.96414100	2.29234300	2.80843400
H	2.10022500	0.18342900	2.38897100
C	1.32269800	3.49364200	2.51558100
H	-0.21381500	4.45552400	1.33512700
H	2.76023900	2.26575000	3.55380800
H	1.61490100	4.41005700	3.03143200
C	2.89012800	-0.14692800	-0.61147600
C	3.47793800	1.08842100	-0.27656200
C	1.66277800	0.13389000	-1.22810800
C	2.61891900	2.04653400	-0.79484300
H	1.01793700	-0.45223300	-1.87832800
O	1.58879800	1.49502600	-1.41267200
C	3.47657200	-1.47572200	-0.37461000
C	3.40663500	-2.46694600	-1.36481500
C	4.14605900	-1.75485600	0.82372900
C	4.00536200	-3.70636900	-1.16241000
H	2.88770100	-2.25051400	-2.30009300
C	4.73467600	-3.00184800	1.02940300
H	4.19464500	-0.99117100	1.60253500
C	4.67040000	-3.97726800	0.03520200
H	3.95482600	-4.46617500	-1.94379000
H	5.24570900	-3.21094700	1.97006000
H	5.13831600	-4.95008200	0.19313800
C	1.75759800	4.12123500	-1.49490900
H	0.74932500	3.78374400	-1.21686900
H	1.89400300	3.91917700	-2.56836700
C	1.98803100	5.57129700	-1.15000500
H	3.00827700	5.87726900	-1.41665300
H	1.27690800	6.20272000	-1.69845600
H	1.84576700	5.73120300	-0.07241100
H	4.41619700	1.28195800	0.23245800
O	2.72117700	3.34964000	-0.76217000

Int-1

Ir	-1.67948300	-0.24637700	-0.14946200
C	-1.84201000	-0.58367900	1.89562500
C	-1.85186300	-1.82962700	1.21181400
C	-3.12001200	-2.65729500	1.03220200
C	-3.81356100	-2.33721400	-0.30148400
C	-3.56515700	-0.91275400	-0.75187700
C	-3.72487300	0.23785400	0.06036300
C	-4.23157400	0.16320700	1.49456700
C	-3.06477100	0.08956100	2.49056800
H	-0.90998500	-0.32057500	2.40329800
H	-0.91902300	-2.40203100	1.20525700
H	-3.62251200	-0.75260300	-1.83308200
H	-3.89321100	1.18095900	-0.46823000
H	-2.86240600	-3.72468600	1.06472000
H	-3.79896400	-2.48257300	1.88078000
H	-3.40926000	-2.99884100	-1.08210900
H	-4.89770500	-2.54252300	-0.24822600
H	-4.85152800	1.04462700	1.71145000

H	-4.89654700	-0.70626200	1.60583300
H	-2.76833600	1.11234900	2.77235100
H	-3.36844900	-0.41246500	3.42646900
Cl	-1.62704800	1.04385200	-2.25502900
C	0.57683900	-1.60965300	-1.06161500
C	0.68297100	-0.44814300	-0.15168800
C	-0.00948800	-2.18538900	-3.26523000
H	0.45829600	-3.17588200	-3.19330000
H	-1.08011200	-2.26976200	-3.02512800
O	0.44781400	-2.76883800	-0.73277500
O	0.60387900	-1.26827000	-2.37945300
H	0.10763900	-1.76897500	-4.27098800
C	1.34784900	-0.68617500	1.17550100
C	1.38131400	0.35979000	2.11762800
C	2.05530900	-1.85726800	1.49752200
C	2.11379300	0.26584500	3.29865300
H	0.79085800	1.26030700	1.93002400
C	2.78167900	-1.95574200	2.68374100
H	2.04198000	-2.69536100	0.80353900
C	2.82687400	-0.89627800	3.58808600
H	2.11255100	1.09976100	4.00323200
H	3.32669500	-2.87712800	2.89740800
H	3.39824700	-0.98006700	4.51367100
C	2.62130400	1.23581300	-0.57864000
C	2.64934800	2.54947700	-0.21482200
C	1.19663300	0.80025800	-0.82493900
C	1.28033200	2.95602000	-0.16705800
H	0.97727700	0.72833400	-1.90413200
O	0.45942700	2.01254100	-0.41979900
C	3.75109800	0.31663800	-0.66934300
C	3.71568900	-0.78063900	-1.54356600
C	4.85171300	0.49340500	0.18334400
C	4.77818700	-1.67863600	-1.56853600
H	2.85888800	-0.92422100	-2.20412800
C	5.90211500	-0.41673500	0.16366100
H	4.85507000	1.31920800	0.89681300
C	5.86678800	-1.50151700	-0.71394500
H	4.75057700	-2.52798100	-2.25180700
H	6.74526400	-0.28810400	0.84308900
H	6.68981300	-2.21766300	-0.72605300
C	-0.62159400	4.31160500	0.01408500
H	-1.04918000	3.79912600	0.88771600
H	-0.98368700	3.79358800	-0.88571400
C	-0.89100300	5.79280500	0.01418400
H	-0.43841700	6.27092800	-0.86416900
H	-1.97534200	5.95919800	-0.02129000
H	-0.49401500	6.26636000	0.92152100
H	3.49845100	3.19308200	-0.00566200
O	0.82931400	4.13109700	0.08304200

TS-2

Ir	-1.68482300	-0.20482700	-0.22662800
C	-1.82946200	-0.46471800	1.82970400
C	-1.85977100	-1.73609700	1.19836100
C	-3.13680600	-2.55556700	1.06134600
C	-3.80665300	-2.30115400	-0.29697200
C	-3.52787300	-0.90415400	-0.80912000
C	-3.68220200	0.29876800	-0.04822700
C	-4.20424900	0.30046500	1.38560000
C	-3.04834200	0.24072600	2.39721100
H	-0.88243200	-0.17962200	2.30122000
H	-0.93178600	-2.31560500	1.18889800
H	-3.59848300	-0.79235600	-1.89611800
H	-3.86851600	1.20861300	-0.62806100
H	-2.89395700	-3.62205000	1.15966600
H	-3.82051600	-2.31991800	1.89067800
H	-3.39490100	-3.00340300	-1.03670600
H	-4.89440200	-2.48729800	-0.25345400
H	-4.80175000	1.20684200	1.55617400
H	-4.89397600	-0.54513500	1.52616400

H	-2.74280700	1.26651500	2.65534400
H	-3.36832800	-0.23306700	3.34178200
Cl	-1.54974500	0.96995000	-2.36386100
C	0.56935900	-1.64981200	-1.25269100
C	0.90992100	-0.64631700	-0.22057200
C	0.09957500	-1.90918900	-3.53969000
H	0.36195200	-2.97422600	-3.51082500
H	-0.98660900	-1.78579900	-3.41936200
O	0.19552300	-2.78269600	-1.04415000
O	0.76857300	-1.19770600	-2.51254100
H	0.41590800	-1.45462900	-4.48400600
C	1.43358100	-1.10681600	1.09292200
C	1.60133100	-0.17692500	2.13559500
C	1.84424300	-2.43014000	1.33881700
C	2.17732000	-0.53461400	3.35266000
H	1.24951300	0.84666100	1.99707200
C	2.41229100	-2.78784500	2.55911300
H	1.71331500	-3.18305200	0.56400500
C	2.58969800	-1.84651700	3.57267400
H	2.29007700	0.21612300	4.13696600
H	2.72540400	-3.82158600	2.71625200
H	3.03568000	-2.13502200	4.52542800
C	2.58888100	1.32750400	-0.31731200
C	2.43928900	2.61153800	0.08793200
C	1.30184900	0.63865500	-0.68888700
C	1.02271800	2.89782100	0.15911400
H	1.02217100	0.80642100	-1.73956600
O	0.26493400	1.93893300	-0.08692300
C	3.85861400	0.61309300	-0.48913900
C	3.95985000	-0.44775600	-1.40330800
C	4.98156000	0.98281200	0.26710500
C	5.17273600	-1.11190000	-1.56437200
H	3.09202500	-0.74277500	-1.99688000
C	6.18645000	0.30835100	0.10900600
H	4.89558100	1.78072600	1.00659700
C	6.28414300	-0.73811000	-0.80985200
H	5.24765000	-1.93013200	-2.28132600
H	7.05059000	0.59152000	0.71100500
H	7.22961900	-1.26865200	-0.93194500
C	-0.88051800	4.23289100	0.36951400
H	-1.31364500	3.64368500	1.19094600
H	-1.22515700	3.78680400	-0.57459600
C	-1.18603000	5.70402100	0.48514800
H	-0.73001900	6.26118900	-0.34357000
H	-2.27274200	5.85392300	0.44752100
H	-0.80983300	6.11010300	1.43333100
H	3.21445100	3.34322200	0.29880100
O	0.56270900	4.07901900	0.43291700

3a

Ir	-1.99353400	0.05936200	0.00405400
C	-2.27666700	-0.24927900	2.03691600
C	-1.47463700	-1.29679500	1.50522300
C	-2.00264900	-2.70931300	1.27970700
C	-2.56896000	-2.88698700	-0.14099400
C	-3.00734200	-1.56964500	-0.75178200
C	-3.91905600	-0.67352600	-0.12122300
C	-4.55472300	-0.99025000	1.22979500
C	-3.74683400	-0.37952400	2.38592900
H	-1.74808500	0.54034500	2.58441300
H	-0.39282900	-1.22467100	1.67277900
H	-2.96878200	-1.52316400	-1.84506300
H	-4.49166400	-0.01010500	-0.77779000
H	-1.18369400	-3.42425800	1.43428100
H	-2.76446400	-2.93743900	2.04139100
H	-1.78187800	-3.31495700	-0.77593500
H	-3.40769600	-3.60511600	-0.14702800
H	-5.58358300	-0.60568100	1.24980200
H	-4.63503600	-2.08171200	1.34437800
H	-4.12419500	0.63307800	2.59411600

H	-3.88196200	-0.96022500	3.31496300
Cl	-2.01562000	1.16944900	-2.15155600
C	0.77206000	-1.91855600	-1.47468900
C	1.64046900	-0.98562600	-0.67535100
C	-0.66924600	-2.00385400	-3.35801200
H	-0.14758700	-2.49484300	-4.19177900
H	-1.20550200	-2.76124600	-2.77394000
O	0.56235000	-3.06733600	-1.17914100
O	0.26930000	-1.31632800	-2.54862300
H	-1.35970300	-1.23836500	-3.73109100
C	2.49322600	-1.57272300	0.38143200
C	2.58298400	-0.94927200	1.63384100
C	3.23330500	-2.74084400	0.15069400
C	3.41998100	-1.46081200	2.62263100
H	1.97370800	-0.06414200	1.83079400
C	4.07378500	-3.24706500	1.13765400
H	3.14632200	-3.25136700	-0.80894600
C	4.17335500	-2.60678100	2.37365100
H	3.47795100	-0.96661800	3.59353700
H	4.65294200	-4.15084900	0.94289000
H	4.83024500	-3.00882500	3.14648900
C	2.31997500	1.42594300	-0.30464400
C	1.69242600	2.51448900	0.20035700
C	1.52806600	0.33355700	-0.91862200
C	0.23357500	2.51950800	0.37522000
H	0.76788800	0.64601300	-1.64331600
O	-0.40950300	1.49273100	0.55560600
C	3.80155300	1.35236400	-0.35763100
C	4.44807000	0.63713000	-1.37551500
C	4.58003500	1.98970700	0.62005800
C	5.83825400	0.57835200	-1.42407400
H	3.85320500	0.12920800	-2.13591500
C	5.96874100	1.92418600	0.57408700
H	4.08872500	2.51156900	1.44308900
C	6.60221900	1.22083500	-0.45090700
H	6.32758600	0.02454600	-2.22631300
H	6.56001000	2.41376200	1.34910500
H	7.69126000	1.16637300	-0.48522200
C	-1.74696300	3.78734600	0.47126200
H	-2.05873000	3.26092200	1.38637900
H	-2.16982500	3.25327700	-0.39293800
C	-2.12521200	5.24805800	0.49260400
H	-1.78887800	5.74542500	-0.42649800
H	-3.21658300	5.34518000	0.56010200
H	-1.67382200	5.75875800	1.35382700
H	2.23224000	3.42104700	0.47352200
O	-0.31072600	3.71329100	0.37272100

TS-3

C	0.28521800	1.96098900	-0.38450100
C	0.92802100	1.61225400	-1.59536900
C	1.26227400	1.89338600	0.61306200
C	2.26323900	1.48453300	-1.27834900
H	1.29044100	2.29732600	1.62079600
O	2.48387000	1.68912100	0.02530600
C	-1.12628700	2.30563100	-0.17217200
C	-1.49217300	3.15427600	0.88633700
C	-2.12047800	1.77507900	-1.00396400
C	-2.83251600	3.43381400	1.12882200
H	-0.72014800	3.60805800	1.51219700
C	-3.46306200	2.04230000	-0.74632900
H	-1.85655700	1.09866900	-1.81453700
C	-3.82102900	2.86635400	0.31910300
H	-3.11050700	4.09864000	1.94812400
H	-4.21814200	1.56782800	-1.37400500
H	-4.87322700	3.07323600	0.52090600
C	4.60434900	1.56846900	-1.60405400
H	4.55944700	2.51824400	-1.05118900
H	5.17654300	1.72792200	-2.52563100
C	5.20931600	0.46639900	-0.76260100

H	5.24058000	-0.47449000	-1.32760600
H	6.23605700	0.74089600	-0.48239100
H	4.62630700	0.30626000	0.15426300
H	0.48704900	1.48790100	-2.57795500
O	3.28437800	1.23761600	-2.06070700
C	3.09697400	-2.30529100	-0.30320300
C	1.95782000	-1.52457100	-0.10227700
C	1.78385400	-0.87729500	1.13274500
C	2.74739500	-0.99789800	2.15057600
C	3.87388600	-1.77648800	1.93438500
C	4.04507100	-2.43443000	0.70823400
H	3.22874600	-2.82940300	-1.25043100
H	1.16494200	-1.45606700	-0.85307700
H	2.58527700	-0.49656100	3.10587300
H	4.62032600	-1.88793300	2.72183500
H	4.92761300	-3.05679000	0.54956300
C	0.53876300	-0.16180000	1.34814100
O	0.18931000	0.10875400	2.56978000
C	-1.17666200	0.44093900	2.84611500
H	-1.75175700	0.52806700	1.91620100
H	-1.58917900	-0.35949000	3.47226100
H	-1.18804800	1.39125600	3.39233500
H	-0.23802600	-0.25765600	0.57656800
O	-1.75676000	-3.04535900	-1.84162700
S	-2.03117700	-1.67641100	-1.44602900
C	-2.71123700	-1.84884600	0.27300400
F	-1.73100400	-2.13622900	1.14688600
F	-3.26462700	-0.70355900	0.68849500
F	-3.62318400	-2.79881600	0.35451300
O	-0.81840200	-0.85360300	-1.18929900
O	-3.08814500	-0.95186800	-2.14506900

Int-2

C	-1.18586400	-0.54435000	1.59397100
C	-0.76198200	0.58327200	2.21196600
C	0.01596100	-1.40667700	1.30147700
C	0.66564900	0.49911100	2.23994700
H	0.00510500	-2.37934500	1.81765000
O	1.11463200	-0.64717400	1.82742900
C	-2.54808700	-0.81008000	1.12943300
C	-3.09417600	-2.10264200	1.12576100
C	-3.30794100	0.27552700	0.66369600
C	-4.39875600	-2.30108500	0.68870200
H	-2.49387500	-2.94845400	1.46133600
C	-4.60754500	0.06276900	0.21062800
H	-2.84601000	1.26569800	0.61109000
C	-5.15528100	-1.21951000	0.23088300
H	-4.82761800	-3.30384400	0.69814000
H	-5.19083600	0.90299000	-0.16750100
H	-6.17538500	-1.38136500	-0.12101500
C	2.85919600	1.39075100	2.26241200
H	2.95375000	0.71267600	1.40571500
H	3.42149100	0.99611900	3.11918000
C	3.22691600	2.80923000	1.90913500
H	3.07531300	3.47935300	2.76545600
H	4.28717000	2.84151000	1.62370000
H	2.62115400	3.15472200	1.05995100
H	-1.32121400	1.47205600	2.48520200
O	1.45349500	1.39743400	2.66525700
C	3.89688500	-1.60060800	-1.21370700
C	2.59177800	-1.18237100	-0.95432700
C	1.63939900	-2.10952300	-0.51983700
C	1.99499100	-3.45174300	-0.36185100
C	3.30032600	-3.86511000	-0.62335700
C	4.25380800	-2.93881700	-1.04589700
H	4.63730400	-0.87705900	-1.55868700
H	2.29617300	-0.13786300	-1.08085100
H	1.23470300	-4.17126000	-0.05088100
H	3.57345800	-4.91463300	-0.50252500
H	5.27482800	-3.26273300	-1.25388700

C	0.22352200	-1.66803700	-0.20704900
O	-0.72319800	-2.65842900	-0.49579200
C	-1.15965300	-2.64728300	-1.83478900
H	-1.61481600	-1.67514400	-2.08812500
H	-0.32315200	-2.84394100	-2.52676200
H	-1.91015300	-3.43962800	-1.94090500
H	0.00482000	-0.72864900	-0.73952800
O	0.96623300	3.72268100	-0.71945300
S	0.16549700	2.54219600	-0.44072900
C	-0.51658100	2.02811200	-2.07536700
F	0.45623200	1.69106900	-2.91095300
F	-1.30524000	0.95636100	-1.91425800
F	-1.23769400	2.98987500	-2.62351100
O	0.95677400	1.33693300	-0.07098800
O	-1.03609000	2.72634100	0.37885100

TS-4

C	-0.12632500	0.80873600	-0.66272600
C	-0.14725200	0.01822100	-1.80022200
C	-0.56746100	0.02282700	0.45200700
C	-0.63339500	-1.22623000	-1.36957100
H	0.70856700	-0.27396800	1.02487400
O	-0.94309800	-1.22646300	-0.10336300
C	0.34809700	2.19439500	-0.55637300
C	1.02397000	2.62996200	0.59338600
C	0.13274500	3.09301300	-1.61059900
C	1.46618400	3.94709300	0.68546000
H	1.23688800	1.92228500	1.39771000
C	0.57086400	4.41029100	-1.51008900
H	-0.39935800	2.75593800	-2.50246300
C	1.23768100	4.83930200	-0.36204100
H	2.00125900	4.27550700	1.57726300
H	0.39143400	5.10570400	-2.33098600
H	1.58487200	5.87062600	-0.28595000
C	-1.04289400	-3.54195000	-1.37606500
H	-0.41724200	-3.57374900	-0.47431600
H	-0.70429100	-4.31876400	-2.07021600
C	-2.52179500	-3.66157000	-1.07543400
H	-3.11116300	-3.59892400	-2.00016700
H	-2.71830600	-4.63440100	-0.60436700
H	-2.85301200	-2.87118600	-0.38829700
H	0.23812700	0.23244500	-2.79162300
O	-0.74453300	-2.30880600	-2.06645000
C	-4.52517500	1.32515800	-0.90054600
C	-3.29793800	1.39376400	-0.24373800
C	-2.98651800	0.48250000	0.76956200
C	-3.91640200	-0.49793500	1.12092200
C	-5.14298400	-0.56738200	0.46011500
C	-5.45004100	0.34080600	-0.55212100
H	-4.76209600	2.04624500	-1.68432400
H	-2.57659100	2.16990200	-0.51479700
H	-3.66683900	-1.19522600	1.92045300
H	-5.86575700	-1.33517900	0.74153900
H	-6.41116700	0.28635200	-1.06547700
C	-1.62159300	0.53041300	1.43587100
O	-1.66917500	-0.21224000	2.61485800
C	-0.66052700	0.08662500	3.54482100
H	-0.67186100	1.16026400	3.80781400
H	-0.86738500	-0.49856500	4.44864800
H	0.34129500	-0.18130700	3.17359600
H	-1.36254100	1.58644600	1.64770500
O	1.79052400	-0.56032500	1.44737300
S	2.55877200	-1.59238100	0.60623500
C	3.65368000	-0.46577500	-0.35834300
F	4.37009700	-1.16692100	-1.21774500
F	2.91460200	0.41100000	-1.02910100
F	4.46377400	0.19249500	0.44953900
O	3.43168400	-2.40409100	1.41315300
O	1.69097500	-2.20746200	-0.38760500

Int-3

C	1.63331700	0.83727500	1.09070100
C	0.94204300	0.86192900	2.34906000
C	1.09149000	-0.18764200	0.36631000
C	0.02955800	-0.15213800	2.28092000
H	-1.12724500	-0.39363000	-1.33271800
O	0.10210400	-0.78713500	1.09857200
C	2.68077000	1.77391400	0.63982500
C	2.46715700	3.15543800	0.74694500
C	3.88644600	1.31445600	0.09284400
C	3.43336900	4.05544500	0.30390400
H	1.52453200	3.51341500	1.16636500
C	4.85020000	2.21695300	-0.35461300
H	4.07415300	0.23935900	0.04599500
C	4.62564600	3.58903700	-0.25121900
H	3.25325200	5.12822100	0.38855200
H	5.78688600	1.84632200	-0.77392300
H	5.38183500	4.29515100	-0.59717800
C	-1.51938800	-1.81909500	2.91649300
H	-1.94035800	-1.80356200	1.90249300
H	-2.35508400	-1.81984100	3.62570900
C	-0.60265700	-3.00712700	3.13457100
H	-0.17526900	-2.98523000	4.14640900
H	-1.17194900	-3.93993100	3.01767900
H	0.21610300	-3.01561900	2.40140700
H	1.11235600	1.52000900	3.19378300
O	-0.85052000	-0.57881000	3.16562000
C	0.32605700	-4.35495300	-1.05169100
C	0.21475700	-2.96852000	-0.97768500
C	1.34737400	-2.16450800	-1.15158900
C	2.58322800	-2.76650400	-1.39625800
C	2.69426300	-4.15487400	-1.46359100
C	1.56455600	-4.95165000	-1.29180600
H	-0.56211100	-4.97443900	-0.91878100
H	-0.75705200	-2.51267600	-0.77948400
H	3.46936600	-2.14287900	-1.53734200
H	3.66528800	-4.61308400	-1.65637700
H	1.64719800	-6.03803600	-1.34710400
C	1.26168800	-0.65959400	-1.03453500
O	0.18217400	-0.18401100	-1.87165900
C	0.34799800	1.16482000	-2.29802400
H	1.14508800	1.21173500	-3.05442600
H	-0.60405500	1.48321000	-2.73852800
H	0.58319900	1.81496800	-1.44307000
H	2.18871900	-0.21401800	-1.42404600
O	-2.08095400	-0.51683300	-0.90378600
S	-2.45739900	0.67910700	0.02515500
C	-3.74853900	1.46563100	-1.02908200
F	-4.19088400	2.55443700	-0.43130200
F	-3.21959300	1.79612100	-2.19895000
F	-4.75012100	0.63330500	-1.22683800
O	-3.13434800	0.20497400	1.20273500
O	-1.37434000	1.63560300	0.09564400

TS-5

C	-0.51843800	1.49874400	1.28425200
C	-0.76335500	0.67108800	2.37687700
C	0.64150800	1.01421100	0.64043700
C	0.24759600	-0.29209700	2.35012600
H	0.28661000	-0.36858300	-1.72041800
O	1.08041800	-0.09282800	1.34608600
C	-1.34640100	2.63514300	0.84538400
C	-2.71641900	2.43184700	0.63150500
C	-0.78699500	3.90099900	0.63167900
C	-3.51257200	3.48994300	0.20058200
H	-3.12357000	1.42628700	0.75470200
C	-1.59136100	4.95577200	0.20440000
H	0.27586000	4.06155800	0.82521900
C	-2.95341300	4.75082100	-0.01286400
H	-4.57622400	3.32667600	0.02206600

H	-1.15395500	5.94266700	0.04718400
H	-3.58169200	5.57670600	-0.34959300
C	1.33927100	-2.33915100	2.75448400
H	1.13751800	-2.53623200	1.69351900
H	0.98875100	-3.19862800	3.33607700
C	2.79015300	-2.01680100	3.04083400
H	2.93351500	-1.77665500	4.10306200
H	3.40822700	-2.89262400	2.79944400
H	3.13983600	-1.17288000	2.43120900
H	-1.57618000	0.71720500	3.09296000
O	0.46693000	-1.26318800	3.17174200
C	4.36182700	-0.73586500	-1.05224700
C	3.05384000	-0.36995600	-0.75144100
C	2.67115800	0.97763200	-0.84310900
C	3.60204700	1.93614700	-1.26094500
C	4.91407700	1.56479100	-1.54462000
C	5.29557200	0.22850600	-1.43762100
H	4.65396700	-1.78520700	-0.99352700
H	2.31049400	-1.12303600	-0.48233300
H	3.29739100	2.98051100	-1.35548000
H	5.63677300	2.31897200	-1.85848000
H	6.32062200	-0.06581700	-1.66781900
C	1.30435400	1.41577800	-0.51167300
O	0.43657000	0.54446700	-2.11326100
C	-0.81481400	1.09433100	-2.47454600
H	-0.64527600	1.89025800	-3.21229200
H	-1.45316400	0.31467600	-2.91493500
H	-1.34757000	1.49422500	-1.59816500
H	0.99464900	2.39184200	-0.88999500
O	0.03003900	-1.68521800	-0.90429400
S	-1.28183000	-1.77062800	-0.19807300
C	-2.19625800	-2.98560400	-1.23403600
F	-3.41102700	-3.18363400	-0.74698300
F	-2.30759600	-2.52303800	-2.47451800
F	-1.55744500	-4.14403300	-1.27111500
O	-1.19189000	-2.39152400	1.11914600
O	-2.07968400	-0.54836100	-0.30497500

Int-4

C	-2.10035600	-0.50265500	0.88338800
C	-1.61140800	-1.37611700	1.82562000
C	-1.09814900	0.52852100	0.71059100
C	-0.34408400	-0.87372500	2.20701500
H	-0.11125200	0.20030200	-2.25985600
O	-0.05623100	0.24850300	1.58711600
C	-3.42800300	-0.56782900	0.25614100
C	-3.65013000	-0.18589500	-1.07649100
C	-4.50335800	-1.03934700	1.02820500
C	-4.93306800	-0.27510600	-1.61421900
H	-2.80928500	0.12447000	-1.70358200
C	-5.78021400	-1.11725200	0.48456300
H	-4.33670800	-1.32069300	2.06941000
C	-5.99736000	-0.73392000	-0.83989900
H	-5.09591200	0.00865800	-2.65474300
H	-6.60942300	-1.47469200	1.09623100
H	-6.99854800	-0.79748100	-1.26875800
C	1.75249000	-0.81010600	3.33870800
H	2.24738000	-0.70030900	2.36530800
H	2.24237100	-1.60390200	3.91128300
C	1.68581500	0.48556100	4.11614900
H	1.13608700	0.35798200	5.05875100
H	2.71106800	0.79975300	4.35364200
H	1.21834700	1.28519300	3.52669900
H	-2.04857900	-2.29540100	2.20066700
O	0.42107000	-1.35561800	3.10239200
C	2.06228400	3.68070900	0.11034100
C	1.19600800	2.60787200	0.27794200
C	-0.13266600	2.70361800	-0.18289800
C	-0.55081700	3.88441300	-0.82724200
C	0.31831000	4.95681200	-0.98001200

C	1.62779800	4.85523400	-0.50783800
H	3.09418900	3.58693000	0.44985300
H	1.57423200	1.68523200	0.71275800
H	-1.57274000	3.95171000	-1.20584300
H	-0.01924600	5.86732600	-1.47599600
H	2.31833900	5.69039800	-0.63614400
C	-1.11765300	1.64821800	-0.04723800
O	-0.97931500	-0.11512500	-2.56830400
C	-0.93472300	-1.51081600	-2.40062300
H	-1.93387300	-1.91845600	-2.61759000
H	-0.21490700	-1.98668000	-3.08809000
H	-0.64849400	-1.79868800	-1.37228300
H	-2.04042100	1.77769600	-0.61586700
O	1.39397300	0.03688200	-1.31876500
S	2.07019300	-0.85439300	-0.36368000
C	3.12120500	-1.91669800	-1.43711900
F	3.80209100	-2.78332100	-0.70153300
F	2.36461900	-2.59233500	-2.29327900
F	3.97825900	-1.17756700	-2.12383000
O	3.02602300	-0.17169700	0.51762300
O	1.19173600	-1.82282100	0.31622600

5a

C	-1.35870200	0.92988600	0.04960600
C	-1.57597600	2.26225800	0.04862600
C	0.09856700	0.73007700	0.05978200
C	-0.27158800	2.94834900	0.09974600
O	0.69533900	1.95537500	0.11697100
C	-2.36743000	-0.14453800	0.02899800
C	-2.28136300	-1.23337100	0.90862800
C	-3.45324800	-0.06318200	-0.85316600
C	-3.26243100	-2.22202400	0.90011500
H	-1.45468700	-1.28777100	1.61899900
C	-4.42929900	-1.05607700	-0.86228300
H	-3.51651200	0.77896700	-1.54457600
C	-4.33526300	-2.13775400	0.01311100
H	-3.19180400	-3.05964300	1.59532600
H	-5.26590100	-0.98667300	-1.55878800
H	-5.10067800	-2.91499100	0.00592100
H	-2.52398300	2.79356500	0.05728100
O	0.01413500	4.10264600	0.13436200
C	4.53673100	0.05685400	0.01604400
C	3.18000600	0.36336600	0.05194500
C	2.21989000	-0.65942900	-0.06552700
C	2.66678500	-1.98410200	-0.21742500
C	4.02400800	-2.28473400	-0.25386200
C	4.96542600	-1.26246800	-0.13688000
H	5.26923200	0.86005900	0.10850200
H	2.85751600	1.39572100	0.17090400
H	1.93050400	-2.78557300	-0.30933800
H	4.34861300	-3.31929800	-0.37370900
H	6.03143500	-1.49290900	-0.16454300
C	0.77581400	-0.43063900	-0.03699500
H	0.14890900	-1.32044800	-0.11941800

I-a

Ir	0.60142100	-0.01180200	-0.28705100
C	0.79627300	-1.05847300	1.52540700
C	1.26111700	0.27669100	1.71841800
C	2.72963800	0.65584500	1.88919000
C	3.44408800	0.99659000	0.56984500
C	2.99766100	0.16562000	-0.60830900
C	2.75335500	-1.17561500	-0.60756800
C	2.95064200	-2.08922400	0.57928000
C	1.65780700	-2.29574800	1.38607000
H	-0.20015000	-1.28815400	1.91889600
H	0.56491000	0.95300700	2.22214800
H	2.96330400	0.67197800	-1.57665300
H	2.51443600	-1.63698400	-1.56945700
H	2.78660600	1.53220400	2.54915300

H	3.25360700	-0.14917000	2.42384300
H	3.24065900	2.04729800	0.31918800
H	4.53800500	0.91642500	0.69462900
H	3.30312600	-3.06537900	0.21776800
H	3.75094000	-1.69434100	1.21823400
H	1.04108900	-3.05762900	0.88410600
H	1.89374500	-2.69976600	2.38616900
Cl	0.44790500	0.02666700	-2.66585600
C	-1.38541500	1.87884600	0.48858600
C	-1.14686500	0.45608500	0.07632200
C	-1.69304100	4.07034000	-0.24262600
H	-2.60580700	4.21291500	0.35098200
H	-0.83688900	4.45069300	0.32985000
O	-1.44396400	2.22912900	1.64120200
O	-1.50846100	2.69378400	-0.54899200
H	-1.77337500	4.58659500	-1.20322800
C	-2.30053500	-0.44236600	0.12426900
C	-2.29414300	-1.61727400	-0.65430500
C	-3.41502200	-0.16281700	0.94000500
C	-3.37808200	-2.48624600	-0.61592900
H	-1.44371500	-1.80102000	-1.31391700
C	-4.48403300	-1.05081500	0.99106400
H	-3.41860800	0.73770000	1.55632400
C	-4.46843500	-2.20887800	0.21165500
H	-3.37609100	-3.38385800	-1.23538600
H	-5.33594100	-0.83826100	1.63812700
H	-5.31433200	-2.89752400	0.24580800

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C	-0.12347800	0.20683000	-0.14486200
C	-1.40435600	0.69491000	-0.11293900
H	-1.56670000	1.77133300	-0.13162100
C	-2.59423400	-0.14314000	-0.08412100
C	-4.94378500	-0.11979700	-0.02941100
C	-6.07244700	0.88573100	-0.00564700
H	-7.04255700	0.37085100	0.00925200
C	0.20223400	-1.18135000	-0.17049300
H	-0.57883800	-1.93146600	-0.27182200
C	2.58766800	-1.18138300	1.43013200
H	3.51120500	-1.76508400	1.52687100
C	1.40302300	-3.52205400	0.41331400
H	0.83581300	-3.93533000	-0.42903000
C	0.98897700	1.20425100	-0.13047700
C	1.04712900	2.17785400	0.87626500
C	1.99721100	1.16975200	-1.10372900
C	2.10428100	3.08434600	0.92376200
H	0.26084700	2.20271200	1.63307400
C	3.05054200	2.08203500	-1.05677800
H	1.96108400	0.41595800	-1.89061900
C	3.11125200	3.03590900	-0.04121700
H	2.14406300	3.82999200	1.71947900
H	3.82809300	2.04524700	-1.82113700
H	3.94027600	3.74431400	-0.00343700
S	1.72886200	-1.81828800	-0.01892900
H	1.93933600	-1.26551100	2.30932300
H	0.82809300	-3.58005900	1.34335500
H	2.38055200	-4.01163000	0.48734800
H	2.82686500	-0.13282900	1.21425300
O	-2.64224700	-1.35680400	-0.08667300
O	2.73048100	-1.81115500	-1.10212300
O	-3.72106100	0.60173400	-0.04929300
H	-4.99513400	-0.77373900	-0.91376900
H	-6.00085000	1.52388500	0.88559200
H	-6.03163100	1.53041400	-0.89404500
H	-4.96378900	-0.77999900	0.85172100

Oxonium ion

C	0.18756300	0.23803700	0.88973700
C	0.70266900	1.47468800	0.36360600
C	0.32950300	1.82364800	-0.94533200

C	1.55820400	2.29590200	1.12115100
C	0.83816000	2.99512700	-1.50052800
H	-0.36623600	1.17598900	-1.48835300
C	2.05864400	3.45726600	0.55394600
H	1.81305400	2.01342900	2.14358700
C	1.70054400	3.80055600	-0.75708500
H	0.55790400	3.28168100	-2.51421800
H	2.72447700	4.10445700	1.12528500
H	2.09793100	4.71634400	-1.19827600
O	1.64241300	-1.46277100	-0.09053300
O	0.44338500	-0.09390200	2.08254900
C	0.90619800	-2.09072400	-1.13072600
H	-0.12093800	-2.26041200	-0.78205100
H	0.85307200	-1.45123600	-2.02721500
H	1.36019100	-3.05780100	-1.40022400
C	-0.00361100	-1.39087700	2.54798100
H	-0.94418100	-1.65091100	2.04415800
H	0.78836400	-2.10158700	2.28388300
H	-0.11454400	-1.29848000	3.63128700
H	-0.48709300	-0.38241000	0.28995600
Si	3.29849200	-1.14185900	-0.22964500
C	4.16237000	-2.68674800	-0.84402500
H	3.90218400	-3.55738400	-0.22359500
H	3.89870000	-2.91691000	-1.88684300
H	5.25403600	-2.55328300	-0.79982100
C	3.83563400	-0.70979000	1.50906900
H	4.89573400	-0.41615900	1.53029500
H	3.24528600	0.12708300	1.90924800
H	3.70859200	-1.57160000	2.18112300
C	3.58296900	0.27867700	-1.41928800
H	3.19125300	1.22766100	-1.02336700
H	4.66020800	0.40640100	-1.60730800
H	3.09685600	0.08619600	-2.38797700
O	-2.17392200	-1.82091000	0.38023500
S	-2.79304800	-1.00848100	-0.69014700
C	-3.46323700	0.41330400	0.28122900
F	-2.46042100	0.98742100	0.97740000
F	-3.98455800	1.34162800	-0.50341600
F	-4.38042000	0.02517200	1.15116700
O	-1.77888200	-0.34266600	-1.53100900
O	-3.93924900	-1.57746900	-1.36461200

TMSOMe

O	1.05462400	0.00124200	-0.85533100
C	2.31639900	0.00052500	-0.25049600
H	3.08851000	0.00274500	-1.03275800
H	2.47358500	0.89255700	0.38226700
H	2.47448100	-0.89426500	0.37812300
Si	-0.38197200	-0.00008800	0.00682800
C	-0.46782000	-1.53807500	1.08215300
H	-0.35903900	-2.44682100	0.47156500
H	0.32244400	-1.54478200	1.84801100
H	-1.43516300	-1.59327100	1.60445400
C	-1.73477200	0.00025200	-1.27952400
H	-2.72990000	-0.00049100	-0.81050700
H	-1.65687900	0.89030100	-1.92058200
H	-1.65620500	-0.88864200	-1.92209000
C	-0.46943000	1.53643800	1.08412600
H	-0.36194500	2.44598900	0.47450700
H	-1.43665200	1.58987000	1.60682500
H	0.32111500	1.54326000	1.84969400

TMSOTf

Si	1.99732500	-0.19474400	0.01804500
C	1.68182800	-1.34196800	-1.41353000
H	1.00384800	-0.86663900	-2.13643800
H	2.62805800	-1.57503300	-1.92482600
H	1.23099600	-2.28593500	-1.07622700
C	2.72664300	1.43736600	-0.49934600
H	3.73272700	1.29695900	-0.92205700

H	2.08979600	1.90846100	-1.26147600
H	2.80837200	2.11905100	0.35981400
C	2.89728700	-1.00152100	1.43149200
H	2.36982400	-1.90735400	1.76264700
H	3.91501100	-1.28822700	1.12747500
H	2.97377100	-0.31432000	2.28597800
C	-1.92629300	-0.57625400	0.02430200
S	-0.78247000	0.87022900	0.06215600
F	-1.35055800	-1.57628600	-0.62383600
F	-2.21317800	-0.95977200	1.25059300
F	-3.03166800	-0.22820800	-0.60227100
O	0.44118800	0.16954600	0.74916000
O	-0.46646100	1.17972100	-1.31498000
O	-1.36392500	1.83678800	0.94833200

TS-2′

Ir	1.31164600	0.23334200	-0.45377200
C	1.95465600	1.10383300	1.32720700
C	2.18640300	1.99896500	0.24514400
C	3.58568300	2.26213800	-0.30287000
C	3.88944500	1.36049900	-1.50799500
C	3.15515200	0.03990000	-1.42063300
C	3.12666300	-0.79387900	-0.27189800
C	3.90917100	-0.48040700	0.99810900
C	3.08788500	0.35019000	2.00228700
H	1.10515300	1.34131400	1.98225100
H	1.48853300	2.83115800	0.13546000
H	2.95926500	-0.44748700	-2.38002200
H	2.89780000	-1.85237100	-0.44250200
H	3.66662900	3.31721800	-0.59832700
H	4.32942900	2.11547100	0.49530700
H	3.55041900	1.85955600	-2.42748100
H	4.97571800	1.19711100	-1.62249800
H	4.22241600	-1.42542300	1.46401600
H	4.83701100	0.04680500	0.72814300
H	2.66265600	-0.31204600	2.76926500
H	3.73745900	1.05948400	2.54474900
Cl	0.45951000	-1.42192800	-2.06373000
C	-1.52901600	0.67995800	-1.42228500
C	-0.97827000	0.79711400	-0.02873400
C	-2.78215400	-0.64622600	-2.88952400
H	-3.28381800	0.20406000	-3.37022300
H	-1.87873800	-0.90918100	-3.45549500
O	-1.27772500	1.41424200	-2.34016000
O	-2.42042200	-0.32482300	-1.55469900
H	-3.45909700	-1.50592600	-2.82190500
C	-1.09819000	2.19903700	0.52311200
C	-1.55844000	2.45720800	1.82633900
C	-0.77667900	3.31859900	-0.27032000
C	-1.65178700	3.75654200	2.32712300
H	-1.89664400	1.64657700	2.47156300
C	-0.88861400	4.61429700	0.22425500
H	-0.42967600	3.15758900	-1.28926000
C	-1.31650400	4.84644300	1.53130900
H	-2.01069500	3.91036200	3.34636900
H	-0.62797900	5.45367200	-0.42291100
H	-1.39604600	5.86295000	1.91896800
C	-1.25496100	-1.74465700	0.72624600
C	-2.47221800	-2.30275800	0.57260000
C	-1.30499000	-0.24441900	0.91588800
C	-3.47005400	-1.26006600	0.68540100
H	-1.01466900	0.02135400	1.93894000
O	-3.06605800	-0.15974800	1.11381400
C	-0.02837900	-2.53617300	0.93944100
C	0.85289100	-2.19869200	1.97213400
C	0.21318500	-3.68599300	0.17659500
C	1.95155700	-3.00972700	2.25109500
H	0.67513800	-1.30536800	2.57290900
C	1.32040700	-4.48205100	0.44466900
H	-0.44027400	-3.90997700	-0.66671000

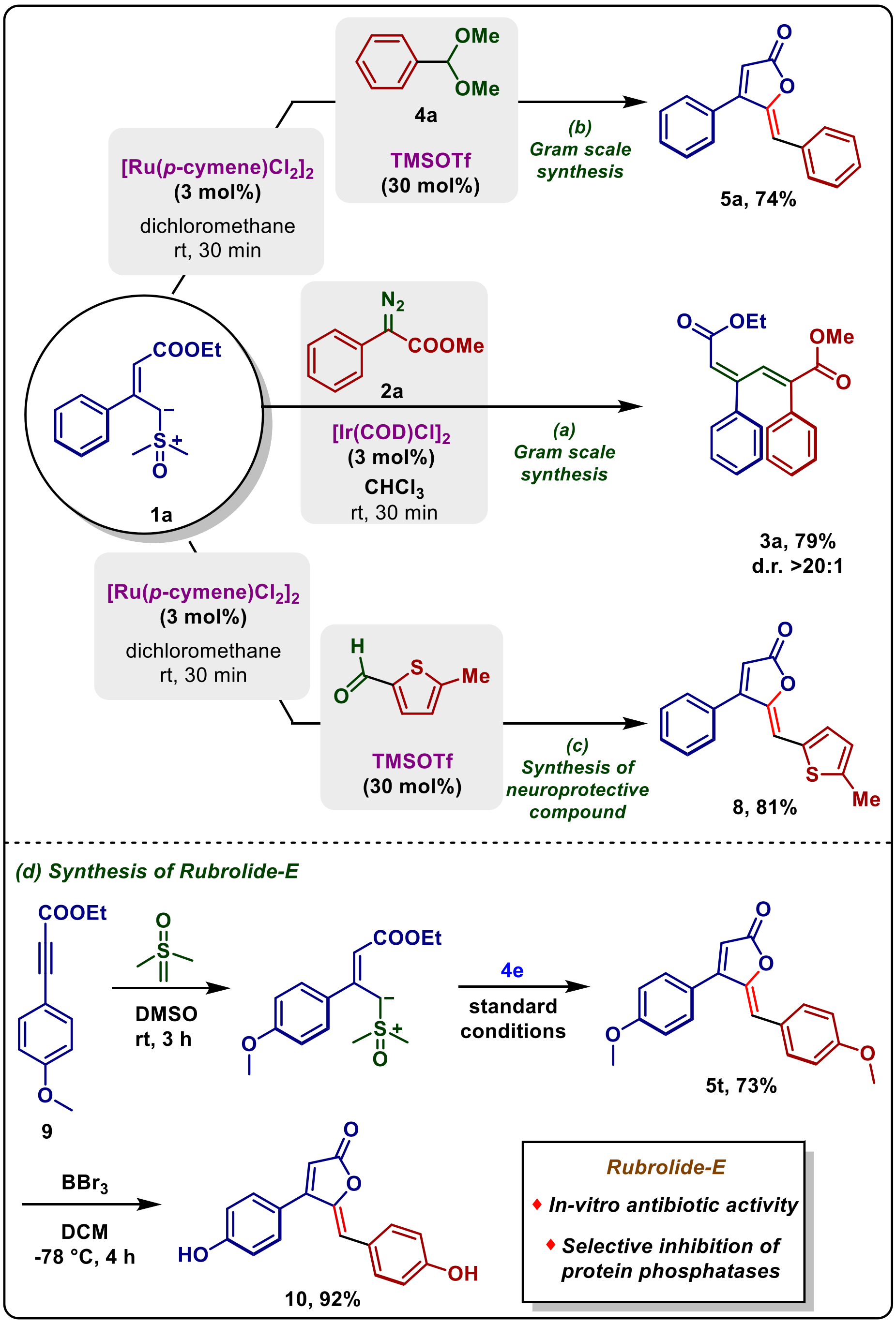
C	2.19021800	-4.14902500	1.48569100
H	2.62540400	-2.74486600	3.06783500
H	1.51438400	-5.36182600	-0.16991900
H	3.05712300	-4.77718800	1.69598200
C	-5.60536400	-0.33940500	0.43485500
H	-5.17248900	0.45655700	-0.18719000
H	-5.63314100	0.01965900	1.47325100
C	-6.95421000	-0.79796500	-0.05794000
H	-7.34605400	-1.60657300	0.57290900
H	-7.66078800	0.04150800	-0.02905500
H	-6.88524000	-1.15997900	-1.09208100
H	-2.70009300	-3.35808500	0.44835200
O	-4.71059300	-1.47221700	0.37470900

TS-5′

C	-0.64027500	0.84866300	-1.30630600
C	0.41594500	1.19326000	-2.14291000
C	-0.46170000	1.55914300	-0.09471000
C	1.18683700	2.10801000	-1.42146000
H	0.29993500	-0.35514300	1.71469700
O	0.67121200	2.35936600	-0.23949400
C	-1.76635000	-0.03679200	-1.66916200
C	-3.07248600	0.46870500	-1.67777300
C	-1.52673200	-1.37139700	-2.01347600
C	-4.13813200	-0.36059600	-2.01136300
H	-3.24823400	1.51172000	-1.40677000
C	-2.60276400	-2.19864800	-2.33451600
H	-0.50460200	-1.75596000	-1.99176500
C	-3.90454000	-1.69879200	-2.33237300
H	-5.15433900	0.03616000	-2.01265300
H	-2.41844000	-3.24378200	-2.58700200
H	-4.74072900	-2.35261900	-2.58548900
C	2.94594700	3.61248800	-0.90757400
H	2.20655800	4.15297300	-0.30079300
H	3.45140000	4.32907100	-1.56525200
C	3.92896700	2.84118600	-0.05505100
H	4.65509600	2.31790100	-0.69069500
H	4.46907800	3.53996500	0.59884500
H	3.41496700	2.08558000	0.55164600
H	0.62184000	0.83444100	-3.14528200
O	2.24892800	2.73796600	-1.81541300
C	-3.72194700	-1.11089100	1.48900600
C	-2.48299800	-0.51890300	1.26981400
C	-2.33429500	0.86383100	1.44170400
C	-3.42259000	1.63504000	1.86238500
C	-4.66667400	1.03868600	2.06109400
C	-4.81710900	-0.33408400	1.87223200
H	-3.83347300	-2.18696700	1.35030400
H	-1.62928000	-1.12316500	0.95619100
H	-3.30009400	2.70921700	2.01787600
H	-5.51622300	1.64686300	2.37450300
H	-5.78887700	-0.80282700	2.03482900
C	-1.05197800	1.54467400	1.16197100
O	0.10229300	0.40932600	2.34088200
C	1.31638300	1.01332700	2.73760200
H	1.63131300	1.78368300	2.01505500
H	1.17751500	1.46459400	3.72942500
H	2.11365000	0.25849000	2.78406400
H	-0.80816500	2.40408400	1.79289500
O	0.56754900	-1.43950300	0.61966500
S	1.80429000	-1.20721700	-0.18132400
C	3.00694500	-2.34022100	0.63093800
F	4.19981500	-2.22458400	0.06981200
F	3.11639900	-2.03091700	1.92095000
F	2.60694600	-3.59633900	0.53257500
O	1.72569700	-1.66612800	-1.55904100
O	2.38198100	0.12242700	0.05291200

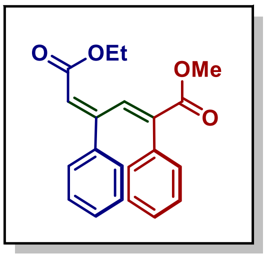
IX. Applications:

To extend the utility of the present strategy, we focussed on various applications as shown in the scheme 3. Mainly, we looked at the scaling up of the reaction and utilizing the method to synthesize molecules with biological activity.



Scheme 3: *Utility of the present approach*

a) Gram-scale synthesis of dienoate, 3a:

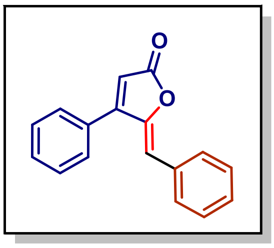


To an oven-dried, Ar-purged round-bottom flask equipped with a magnetic stir bar, vinyl sulfoxonium ylide **1** (1.07 g, 4 mmol, 1 equiv.) was dissolved in chloroform solvent (8 mL). To the solution, $[Ir(COD)Cl]_2$ (81 mg, 3 mol%) catalyst was added and stirred for 30 mins. Diazo ester **2a** (708 mg, 4 mmol, 1 equiv.) was dissolved in $CHCl_3$ (4 mL) solvent and added to the stirring solution dropwise at room temperature. The reaction mixture is allowed to stir for 5 hours. After the completion of reaction (monitored *via* TLC), reaction mixture is passed through a short plug of silica, eluted with dichloromethane. The crude mixture is concentrated in *vacuo* and purified using flash column chromatography on silica gel to yield the corresponding dienoates, **3a** in 79% (1.07 g) yield (Scheme 3, a).

^{1}H NMR (500 MHz, CDCl$_3$) δ 8.33 (d, *J* = 1.9 Hz, 1H), 7.14 (d, *J* = 7.2 Hz, 3H), 7.11 (d, *J* = 7.2 Hz, 2H), 7.04 (d, *J* = 6.3 Hz, 3H), 6.98 (d, *J* = 7.9 Hz, 2H), 6.12 (d, *J* = 2.1 Hz, 1H), 4.30 – 4.25 (m, 2H), 3.85 (s, 3H), 1.35 (t, *J* = 7.2 Hz, 3H). **^{13}C NMR (126 MHz, CDCl$_3$) δ** 167.3, 165.7, 152.7, 139.7, 138.6, 136.6, 134.8, 129.7, 128.8, 128.0, 127.6, 127.3, 120.7, 60.4, 52.4, 14.3. **HRMS (ESI) M/Z:** $[M+Na]^+$ calculated for $C_{21}H_{20}NaO_4$, 359.1254 ; found to be 359.1249.

b) Gram-scale synthesis of ylidene butenolide, 5a:

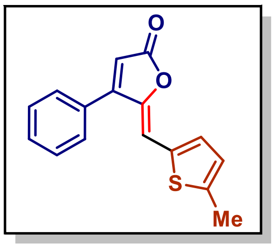
To an oven-dried, Ar-purged round-bottom flask equipped with a magnetic stir bar, vinyl sulfoxonium ylide **1** (1.5 g, 5.6 mmol, 1 equiv.) is dissolved in dichloroethane (15 mL) solvent. To this solution, ruthenium catalyst (103 mg, 3 mol%) was added and allowed to stir for 30 mins at room temperature. Then, the reaction mixture was cooled to 0 °C and acetal **4a** (857 mg, 5.6 mmol, 1 equiv.) was added. To the stirring solution, trimethylsilyl trifluoromethanesulfonate (307 μL, 30 mol%) was added and continued to stir at 0 °C for 4 hours. After the completion of the reaction, reaction mixture was passed through a short plug of silica, eluted with DCM and concentrated in *vacuo*. Crude mixture was purified by flash column chromatography on silica gel to give the corresponding ylidene butenolide, **5a** in 74% (1.04 g) yield (Scheme 3, b).



^{1}H NMR (500 MHz, CDCl$_3$) δ 7.83 (d, *J* = 7.6 Hz, 2H), 7.55 (dd, *J* = 11.2, 3.7 Hz, 5H), 7.42 (t, *J* = 7.5 Hz, 2H), 7.37 (d, *J* = 7.1 Hz, 1H), 6.23 (s, 1H), 6.21 (s, 1H). **^{13}C NMR (126 MHz, CDCl$_3$) δ** 168.8, 158.8, 148.0, 133.0, 130.8, 130.5, 130.4, 129.3, 129.1, 128.8, 128.5, 114.5, 113.9. **HRMS (ESI) M/Z:** $[M+Na]^+$ calculated for $C_{17}H_{12}NaO_2$, 271.0730; found to be 271.0723.

c) Synthesis of ylidene butenolide, 8 *(neuro-protective compound)*:

To an oven-dried, Ar-purged round-bottom flask equipped with a magnetic stir bar, vinyl sulfoxonium ylide **1** (107 mg, 0.4 mmol, 1 equiv.) is dissolved in dichloroethane (3 mL) solvent. To this solution, ruthenium catalyst (7 mg, 3 mol%) was added and allowed to stir for 30 mins at room temperature. Then, the reaction mixture was cooled to 0 °C and 5-methyl thiophene-2-aldehyde (51 mg, 0.4 mmol, 1 equiv.) was added. To the stirring solution, trimethylsilyl trifluoromethanesulfonate (22 µL, 30 mol%) was added and continued to stir at 0 °C for 4 hours. After the completion of the reaction, reaction mixture was passed through a short plug of silica, eluted with DCM and concentrated in *vacuo*. Crude mixture was purified by flash column chromatography on silica gel to give the corresponding ylidene butenolides, **8** in 80% (85 mg) yield as yellow liquid, which is a neuro protective compound (Scheme 3, c).



^{1}**H NMR (500 MHz, CDCl$_3$) δ** 7.54 (dd, *J* = 5.2, 2.1 Hz, 3H), 7.52 – 7.49 (m, 2H), 7.18 (d, *J* = 3.7 Hz, 1H), 6.76 (d, *J* = 2.5 Hz, 1H), 6.41 (s, 1H), 6.16 (s, 1H), 2.54 (s, 3H). ^{13}**C NMR (126 MHz, CDCl$_3$) δ** 168.4, 157.5, 146.7, 145.2, 134.4, 132.0, 130.4, 129.1, 128.3, 128.1, 126.3, 113.5, 108.0, 15.7. **HRMS (ESI) M/Z:** $[M+Na]^+$ calculated for $C_{16}H_{12}NaO_2S$, 291.0450; found to be 291.0442.

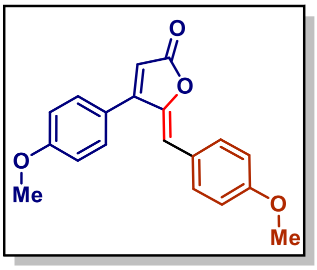
d) Synthesis of Rubrolide-E, 10:

Step-1: Synthesis of vinyl sulfoxonium ylide:

Vinyl sulfoxonium ylide **1b** is synthesized using the reported procedure.[1a-b] To an oven-dried, Ar-purged round-bottom flask equipped with a magnetic stir bar, trimethylsulfoxonium iodide (663 mg, 1.5 equiv., 3 mmol) (recrystallized from water and dried at 70 °C under vacuum overnight) is added and suspended in DMSO (4 mL, 0.5 M). To the resulting suspension sodium hydride (106 mg, 2.2 equiv., 4.4 mmol) is added and stirred for 20 mins at room temperature, after which it becomes a clear, homogeneous solution of dimethylsulfoxonium methylide. To a separate, oven dried, Ar-purged round-bottom flask equipped with a magnetic stir bar, added the aryl propiolate (**9**, 410 mg, 1 equiv., 2 mmol) in DMSO (2 mL, 1M) and the resulting solution is cooled to 0 °C (ice/water bath). The pre-made methylide solution is added *via* cannula or syringe dropwise over 5 mins. The resulting mixture is stirred for 2 hours at room temperature and then poured into crushed ice (75 mL by volume) with vigorous stirring. The precipitate was collected, washed with n-Hexane and used directly without further purification to yield vinyl sulfoxonium ylide **1b** in 79% (466 mg) yield as yellow solid.

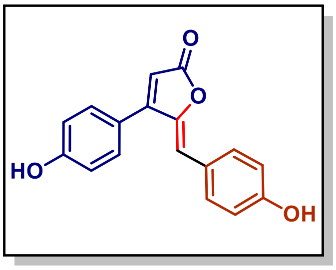
Step-2: Synthesis of ylidene butanolide (5t):

To an oven-dried, Ar-purged round-bottom flask equipped with a magnetic stir bar, vinyl sulfoxonium ylide (**1b**, 119 mg, 0.4 mmol, 1 equiv.) is dissolved in dichloroethane solvent (3 mL). To this solution, ruthenium catalyst (7 mg, 3 mol%) was added and allowed to stir for 30 mins at room temperature. Then, the reaction mixture was cooled to 0 °C and acetal (**4e**, 73 mg, 0.4 mmol, 1 equiv.) was added. To the stirring solution, trimethylsilyl trifluoromethanesulfonate (22 µL, 30 mol%) was added and continued to stir at 0 °C for 4 hours. After the completion of the reaction, mixture was passed through a short plug of silica, eluted with DCM and concentrated in *vacuo*. Crude mixture was purified by flash column chromatography on silica gel to give the corresponding ylidene butenolide, **5t** in 73% (90 mg) as yellow liquid.



^{1}H NMR (500 MHz, CDCl$_3$) δ 7.77 (d, *J* = 8.4 Hz, 2H), 7.46 (d, *J* = 8.3 Hz, 2H), 7.03 (d, *J* = 8.3 Hz, 2H), 6.92 (d, *J* = 8.4 Hz, 2H), 6.16 (s, 1H), 6.10 (s, 1H), 3.89 (s, 3H), 3.85 (s, 3H). **^{13}C NMR (126 MHz, CDCl$_3$) δ** 165.0, 152.1, 136.7, 136.0, 132.0, 129.2, 128.2, 120.3, 118.9, 65.5, 39.0, 29.8. **HRMS (ESI) M/Z:** [M+Na]$^+$ calculated for $C_{19}H_{16}NaO_4$, 331.0941; found to be 331.0950.

Step-3: Deprotection of 5t

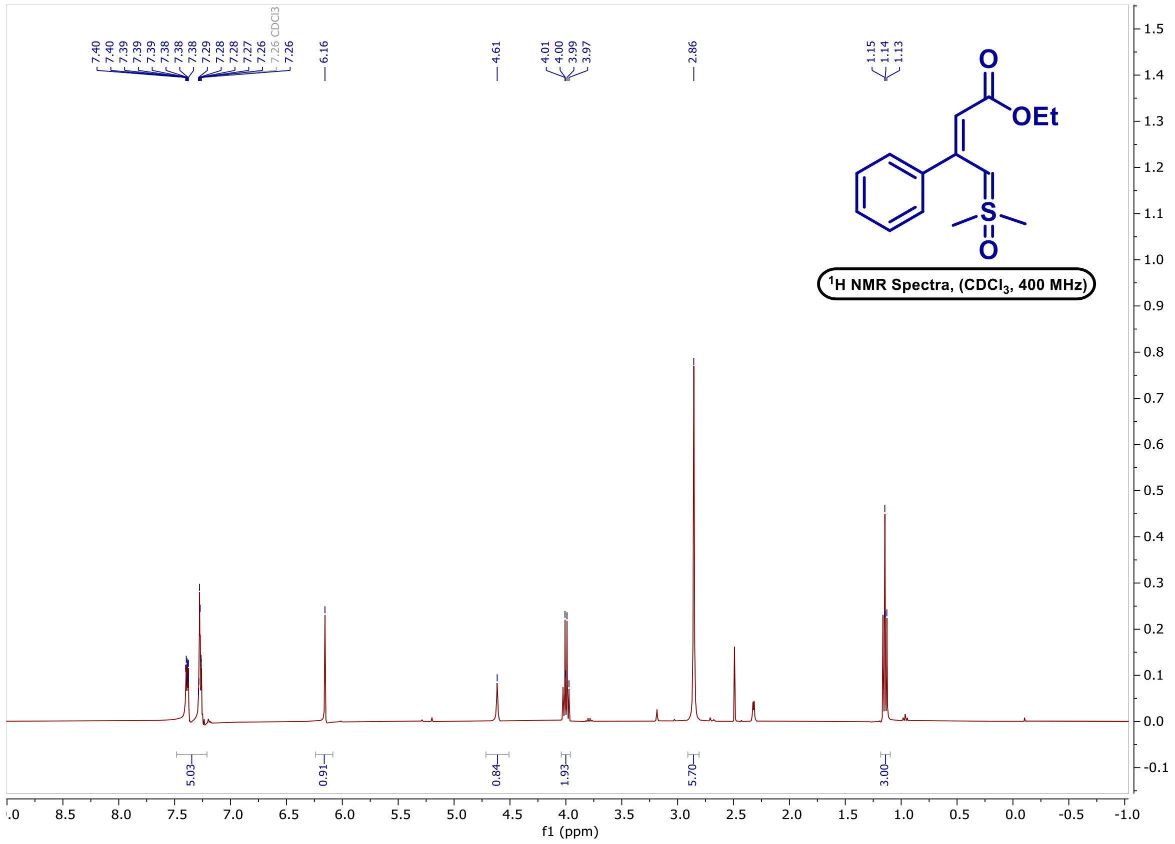


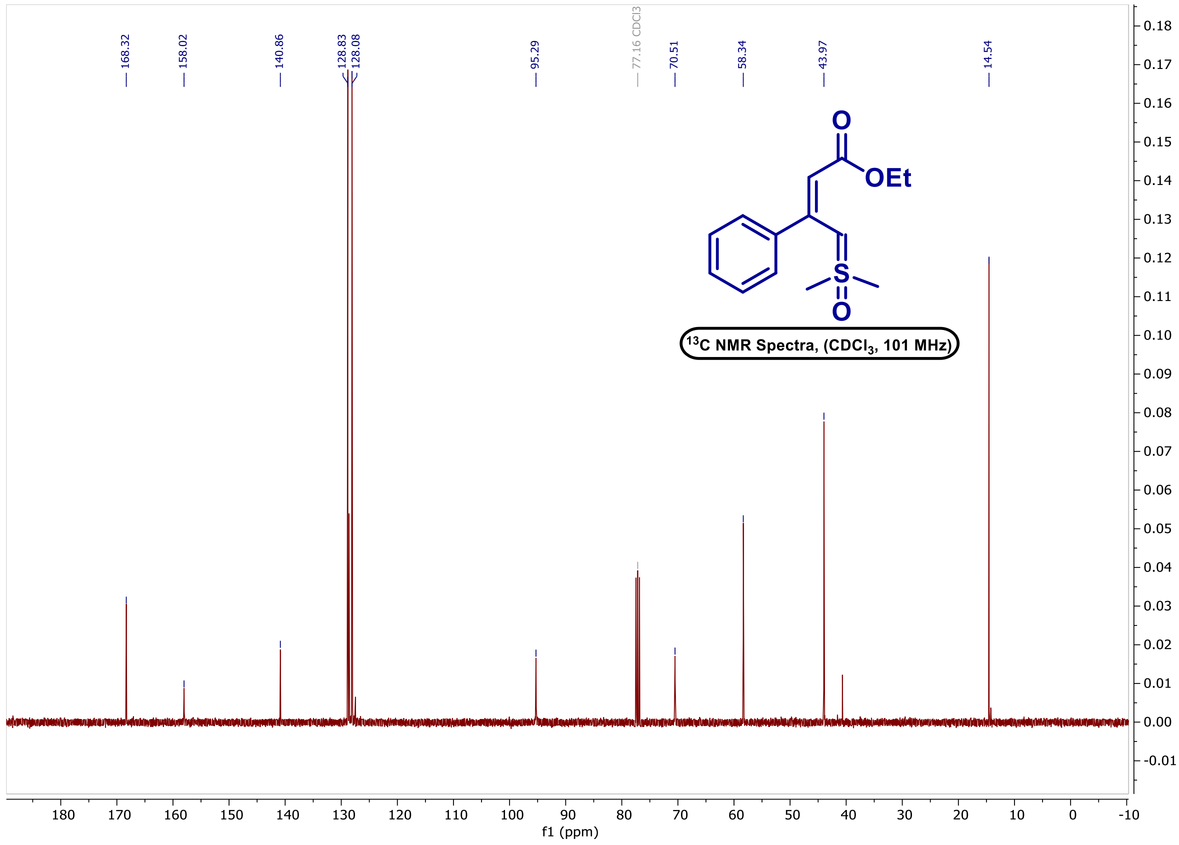
The deprotection of methoxy group was carried-out using the reported procedure.[10] To a stirred solution of **5t** (90 mg, 0.3 mmol, 1 equiv.) in anhydrous CH_2Cl_2 (4 mL) at –78 °C, was added a 1 M solution of BBr_3 in CH_2Cl_2 (876 µL, 3 equiv.) dropwise. The mixture was then allowed to warm up to room temperature and stirred for further 24 h. The reaction was quenched with H_2O (5 mL). The organic layer was separated, and the aqueous layer was extracted with EtOAc (3 × 5 mL). The combined organic layers were washed with H_2O, brine and dried (over Na_2SO_4) and concentrated in *vacuo*. Crude mixture was purified by flash column chromatography on silica gel to give the corresponding Rubrolide-E, **10** in 92% (64 mg) yield as yellow solid (Scheme 3, d).

^{1}H NMR (500 MHz, DMSO) δ 10.07 (s, 2H), 7.69 (d, *J* = 8.4 Hz, 2H), 7.49 (d, *J* = 8.2 Hz, 2H), 6.93 (d, *J* = 8.3 Hz, 2H), 6.84 (d, *J* = 8.3 Hz, 2H), 6.36 (s, 1H), 6.32 (s, 1H). **^{13}C NMR (126 MHz, DMSO) δ** 168.6, 159.7, 158.7, 158.1, 145.3, 132.6, 130.4, 124.2, 120.7, 115.9, 115.9, 113.4, 110.8. **HRMS (ESI) M/Z:** [M+Na]$^+$ calculated for $C_{17}H_{12}NaO_4$, 303.0628; found to be 303.0620.

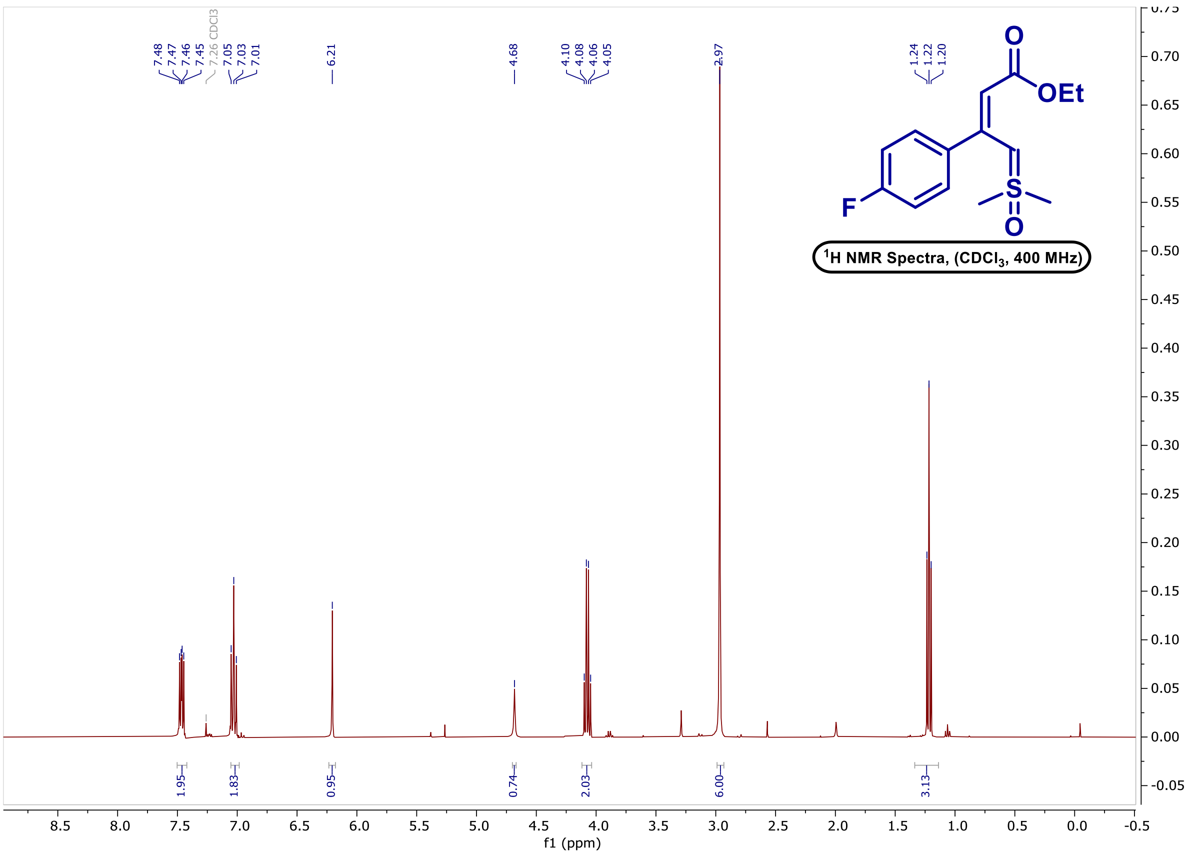
X. Spectral Data:

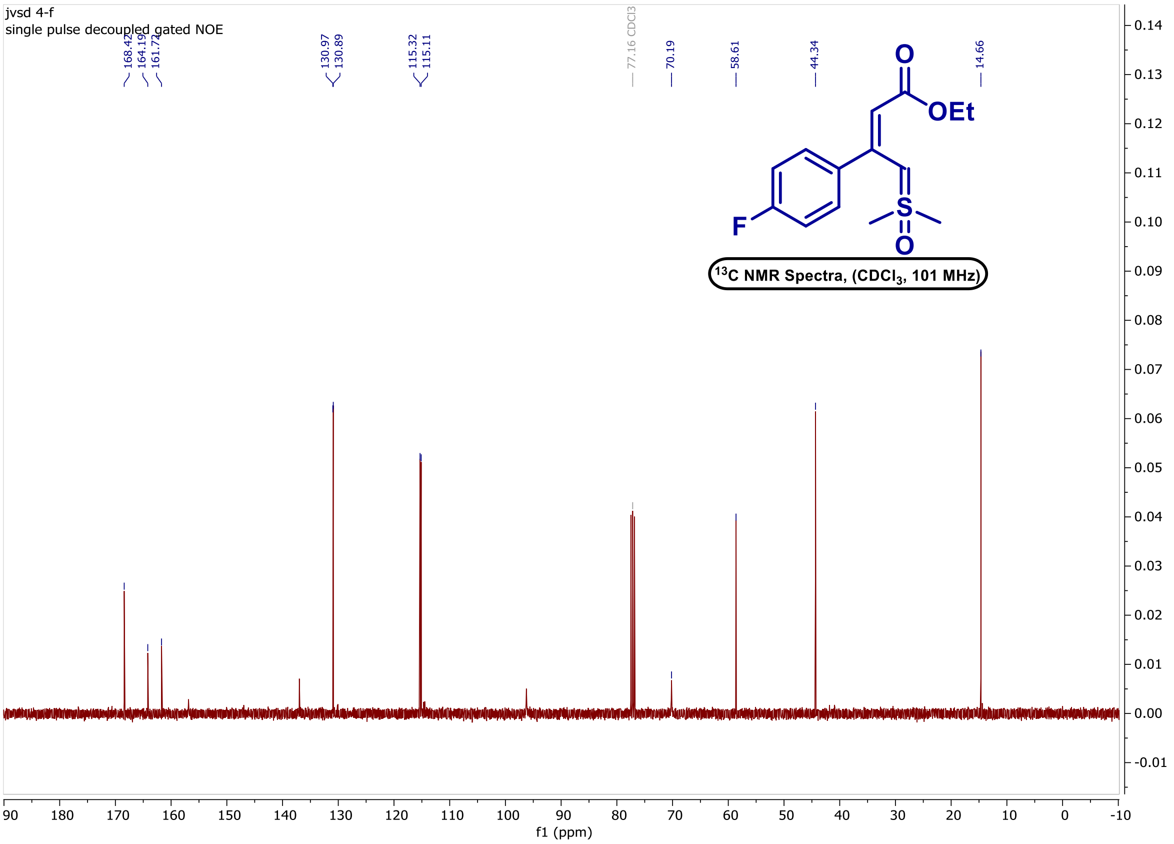
ethyl (Z)-4-(dimethyl(oxo)-l6-sulfaneylidene)-3-phenylbut-2-enoate (1a)



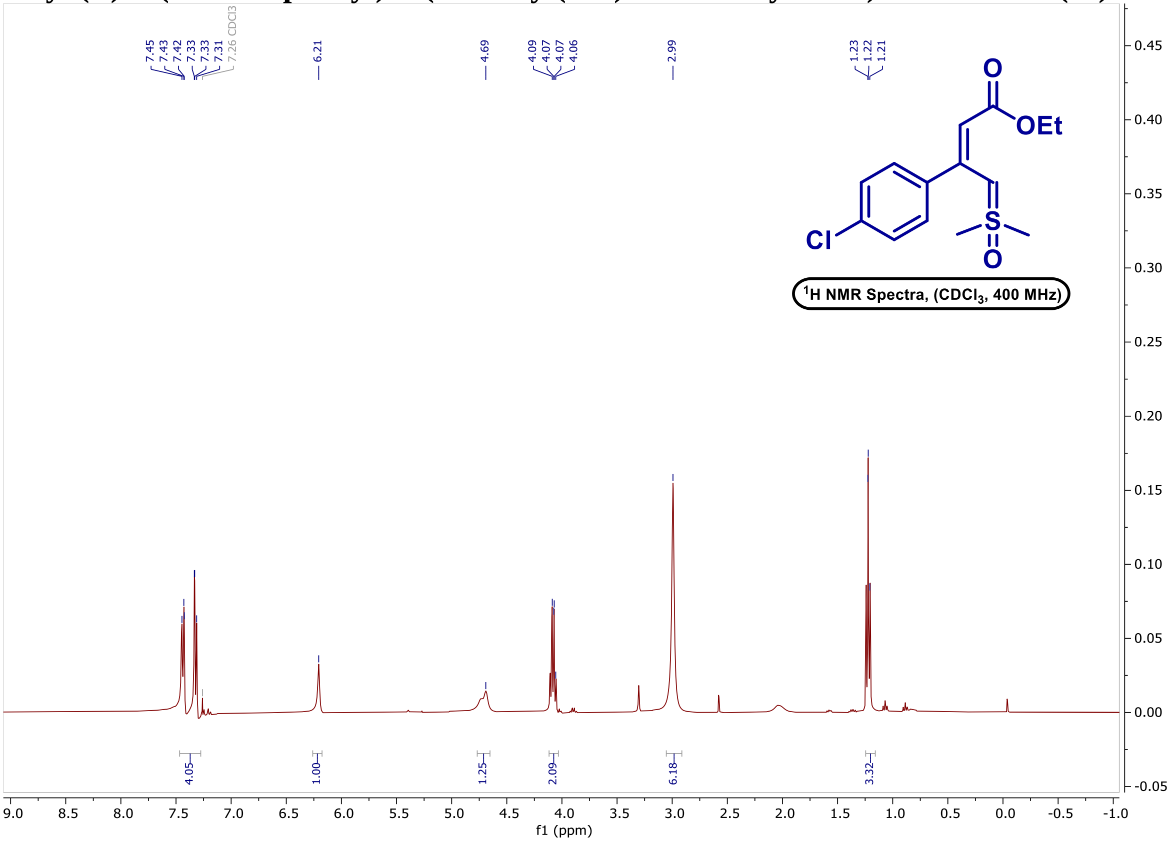


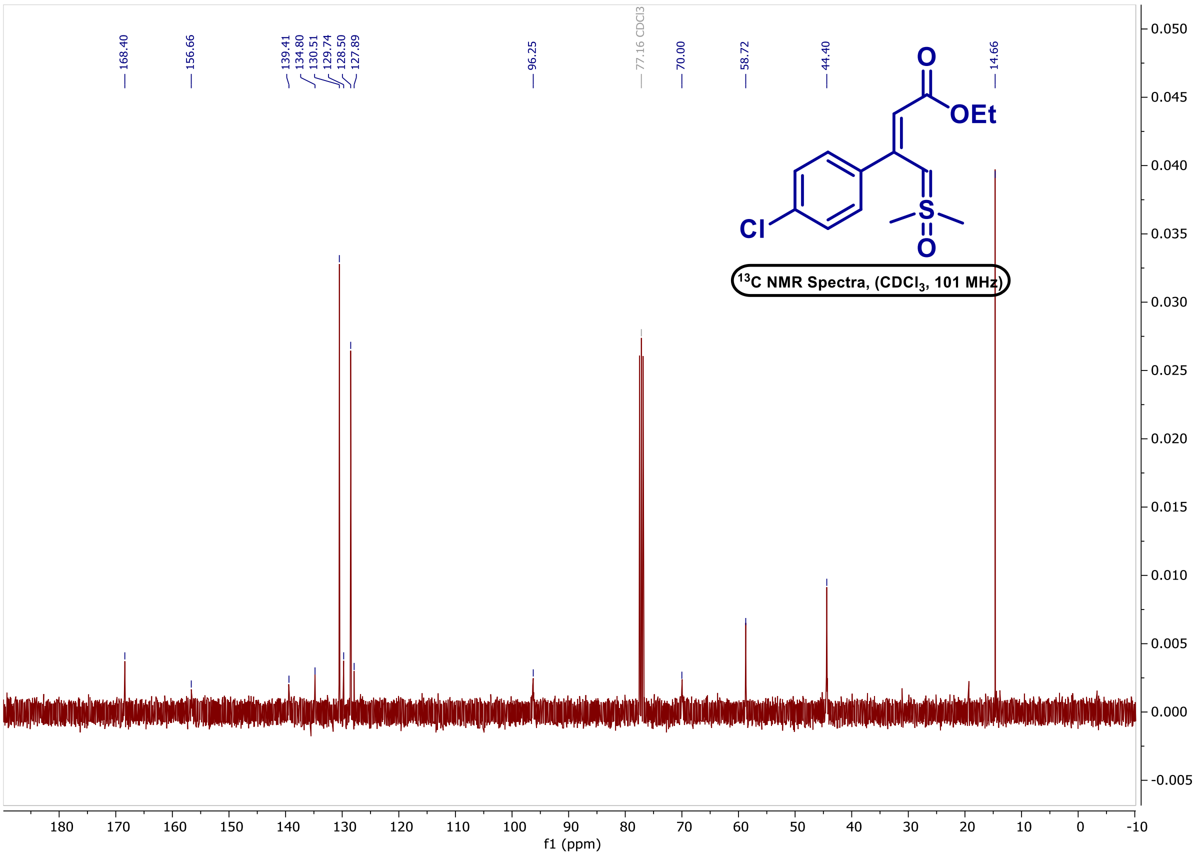
ethyl (Z)-4-(dimethyl(oxo)-l6-sulfaneylidene)-3-(4-fluorophenyl)but-2-enoate (1d)



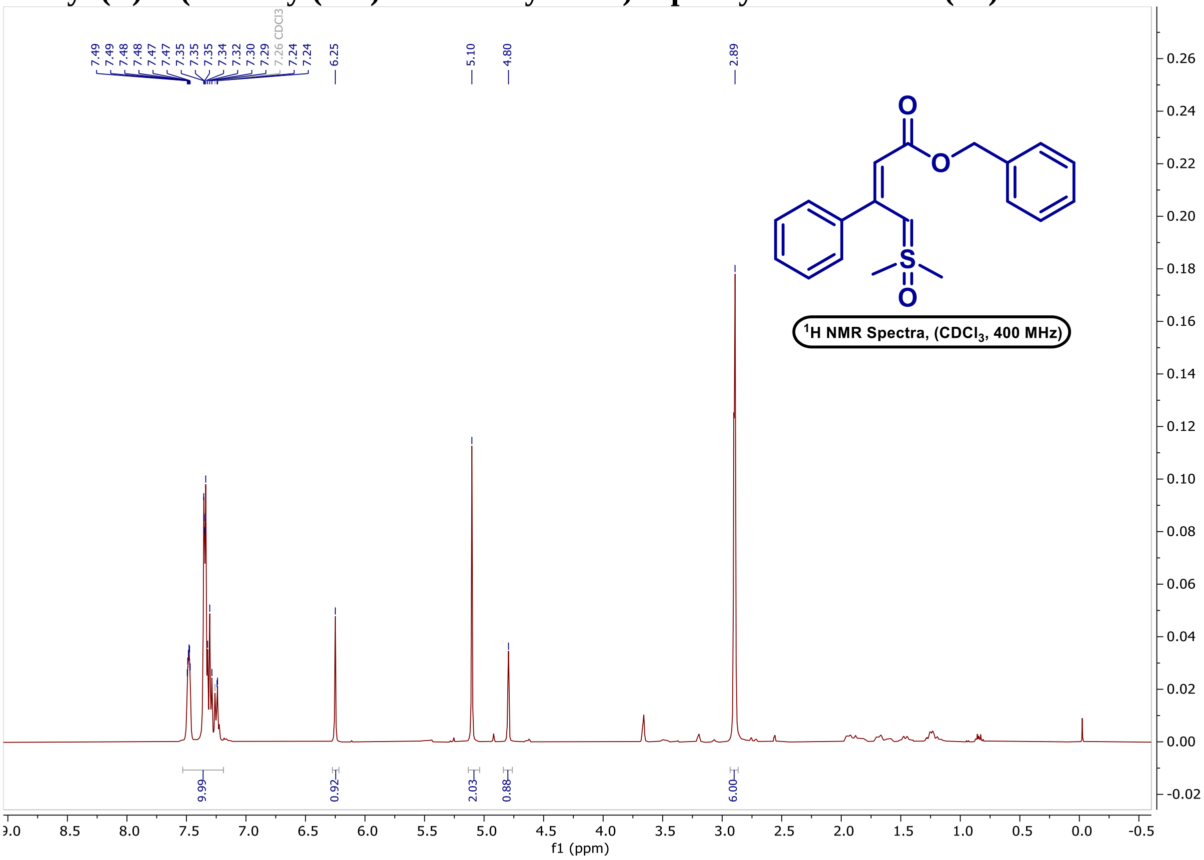


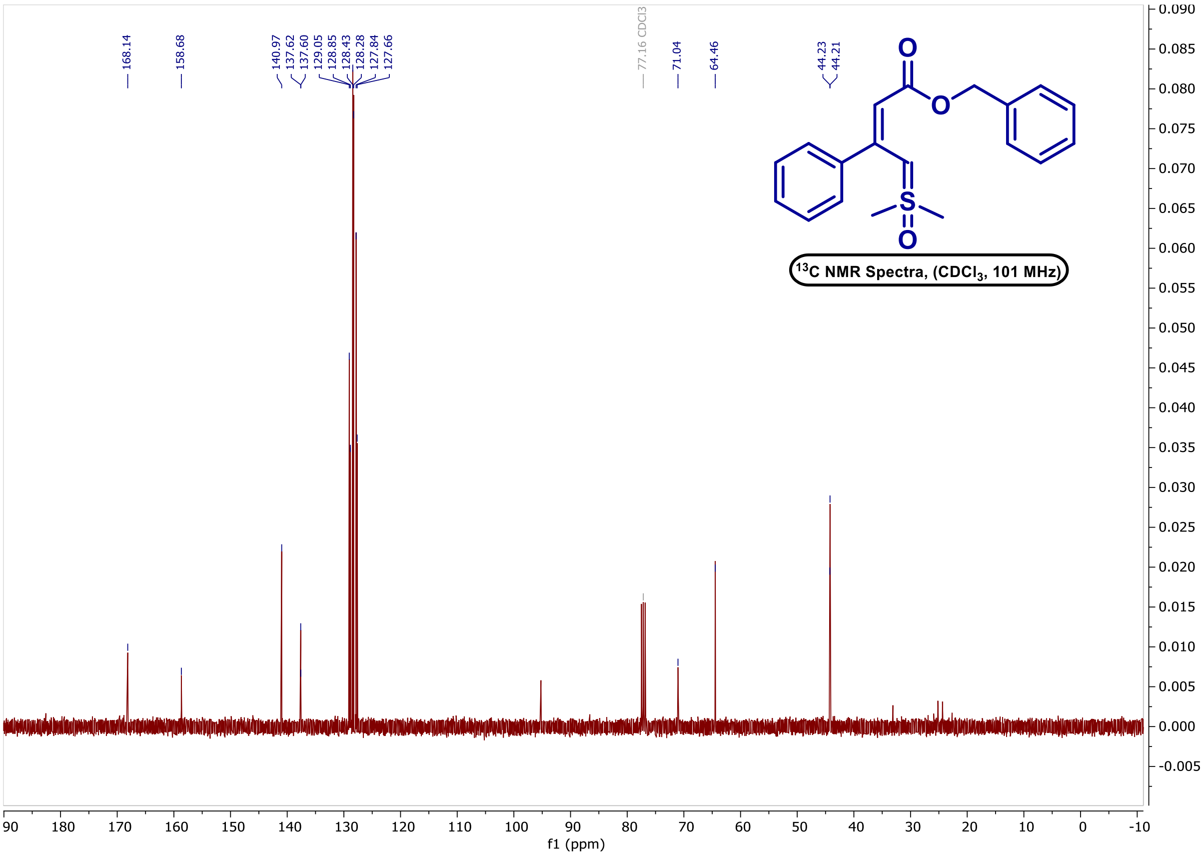
ethyl (Z)-3-(4-chlorophenyl)-4-(dimethyl(oxo)-l6-sulfaneylidene)but-2-enoate (1e):



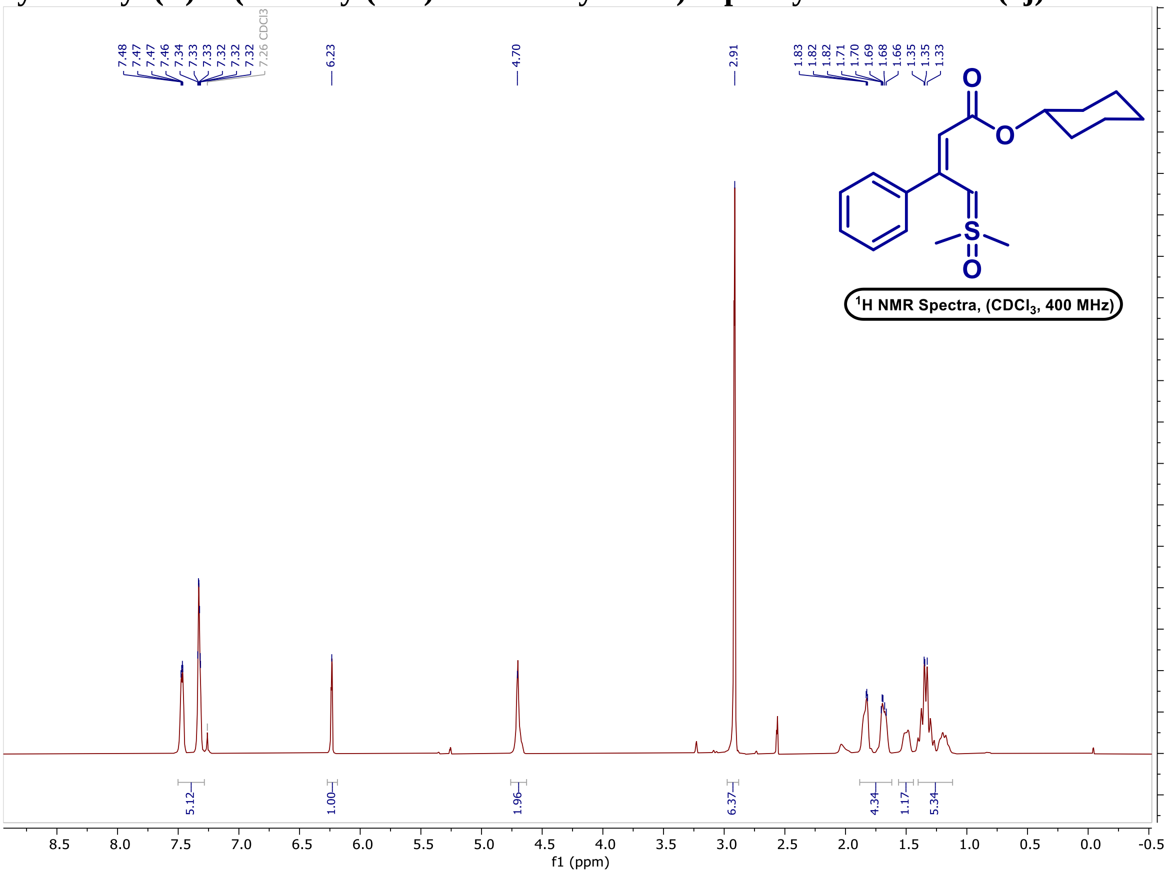


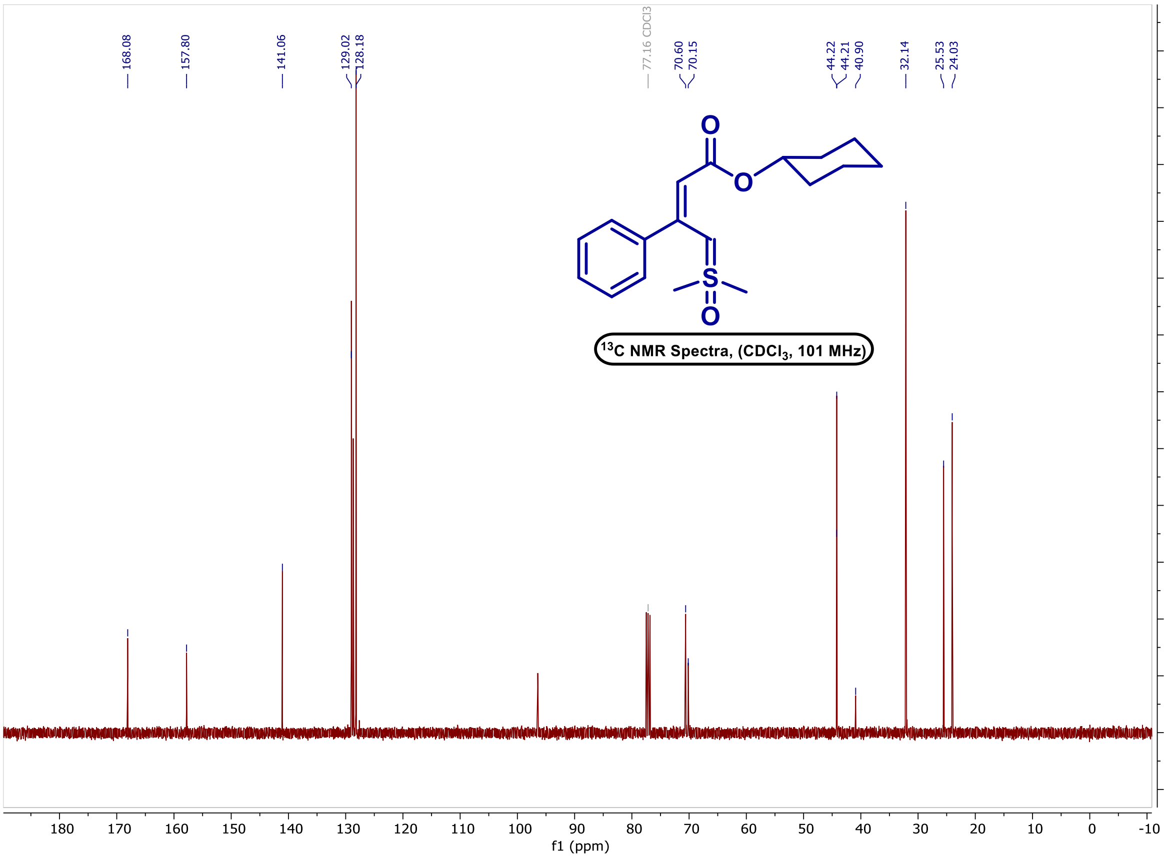
benzyl (Z)-4-(dimethyl(oxo)-l6-sulfaneylidene)-3-phenylbut-2-enoate (1h)



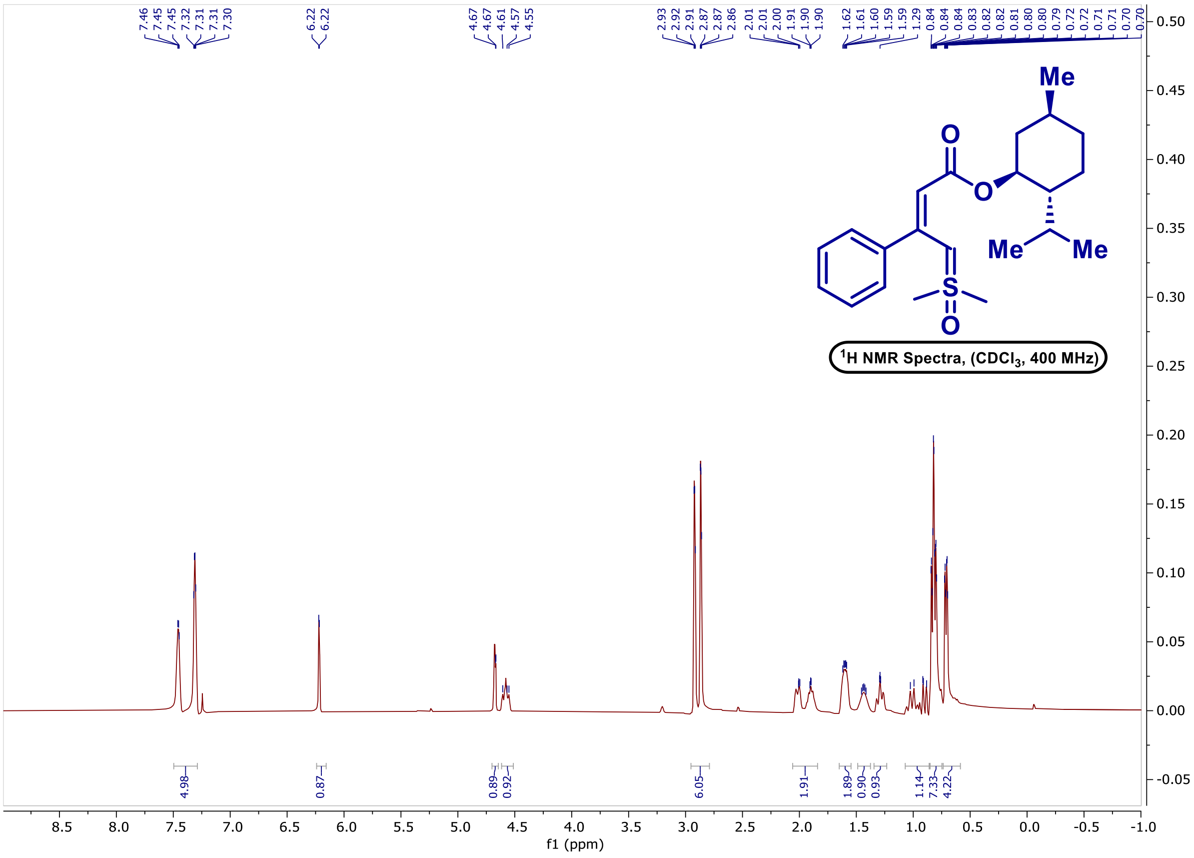


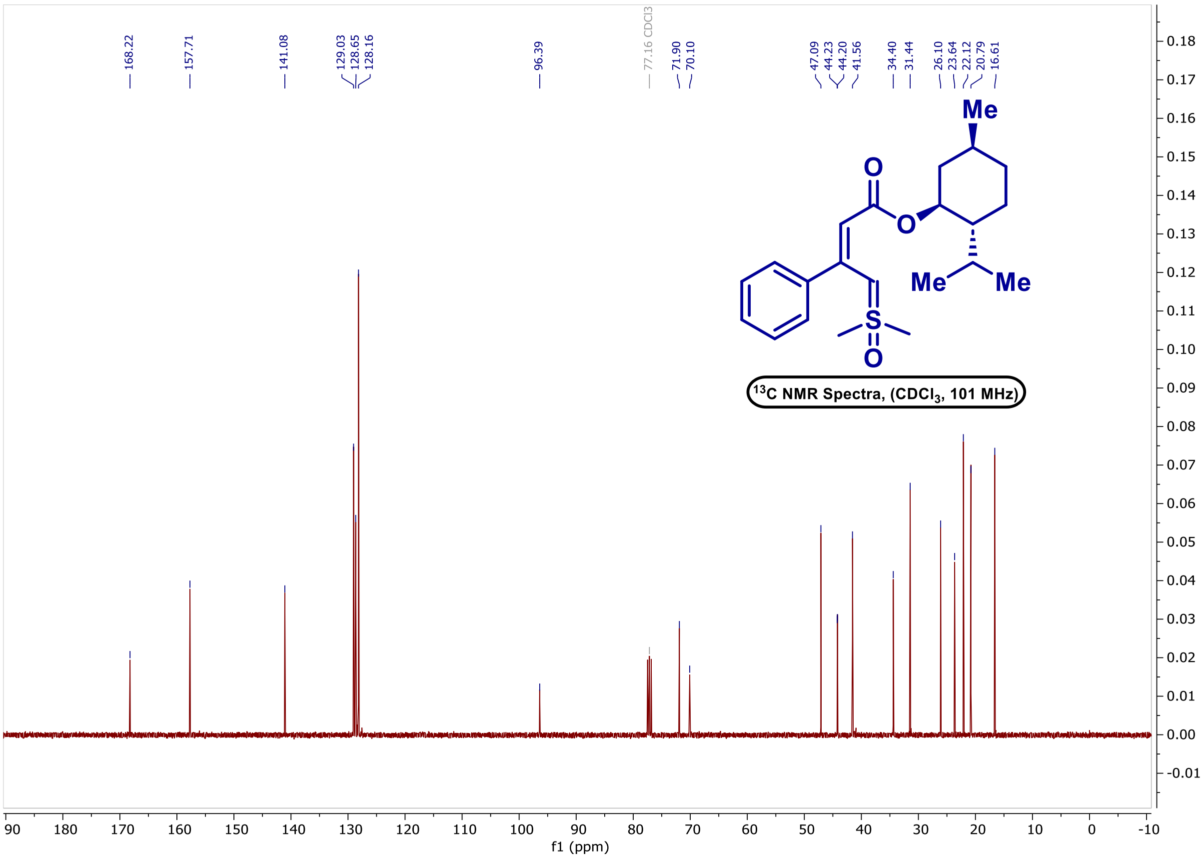
cyclohexyl (Z)-4-(dimethyl(oxo)-l6-sulfaneylidene)-3-phenylbut-2-enoate (1j)



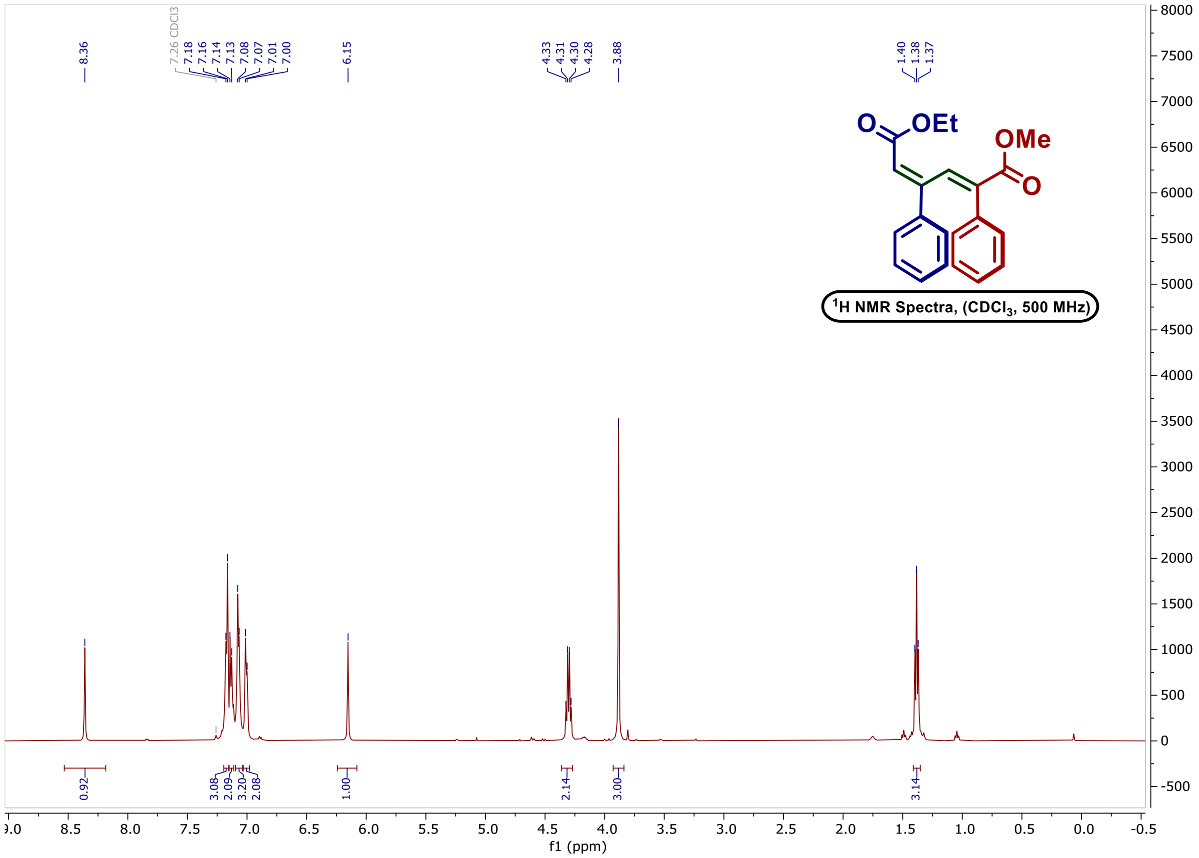


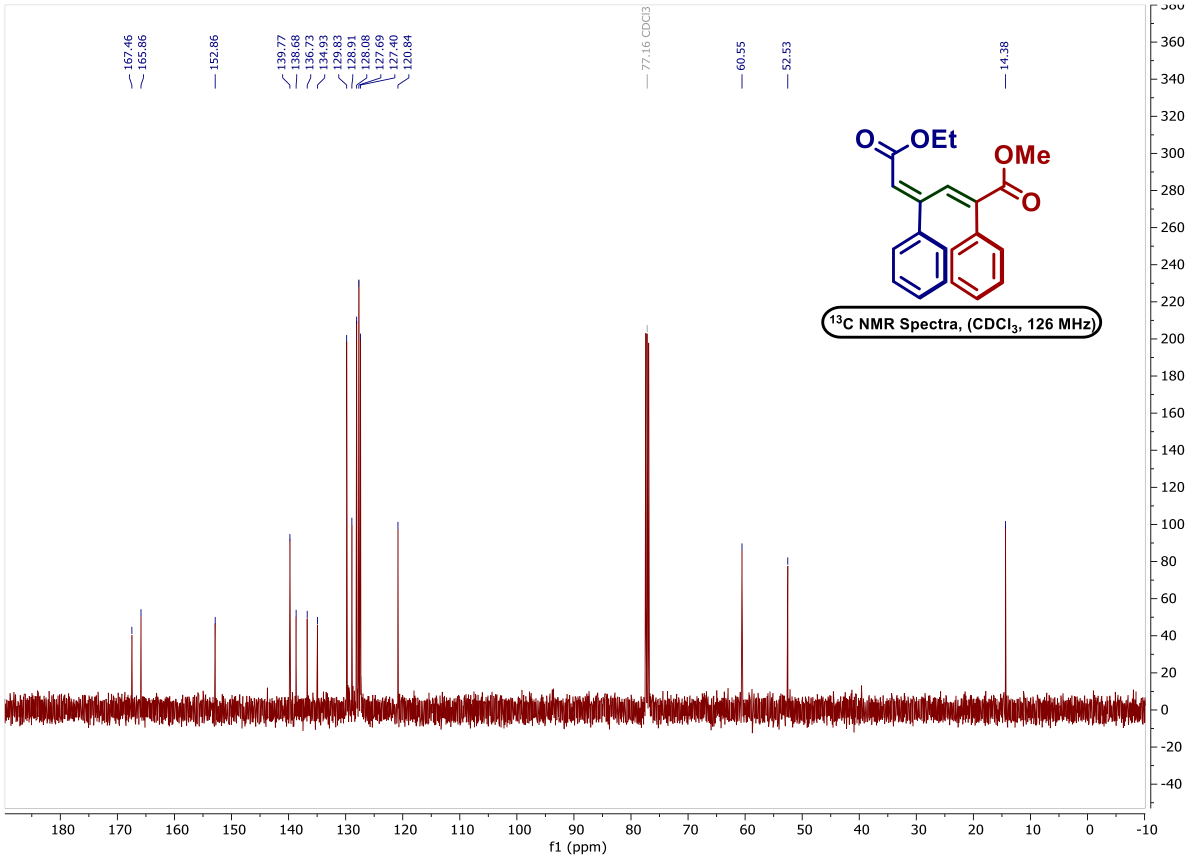
(1R,2S,5R)-2-isopropyl-5-methylcyclohexyl (Z)-4-(dimethyl(oxo)-l6-sulfaneylidene)-3-phenylbut-2-enoate (1l):



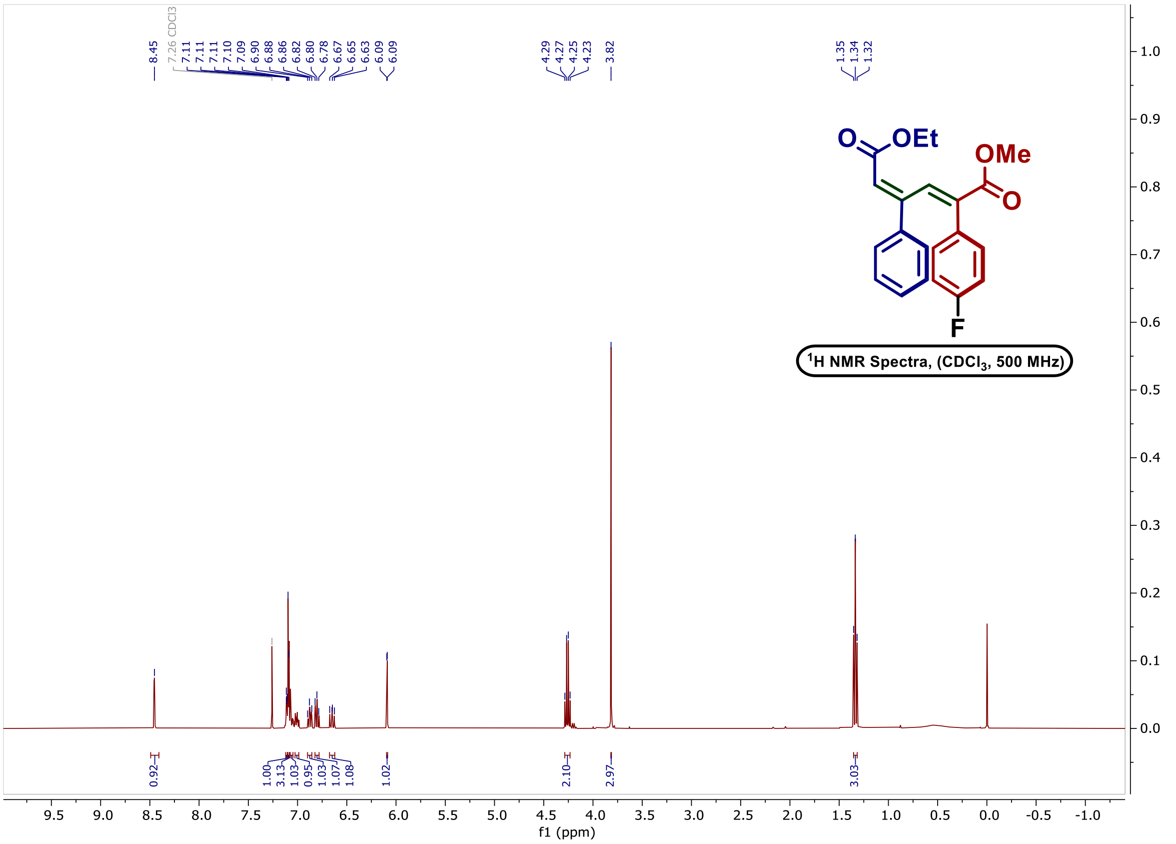


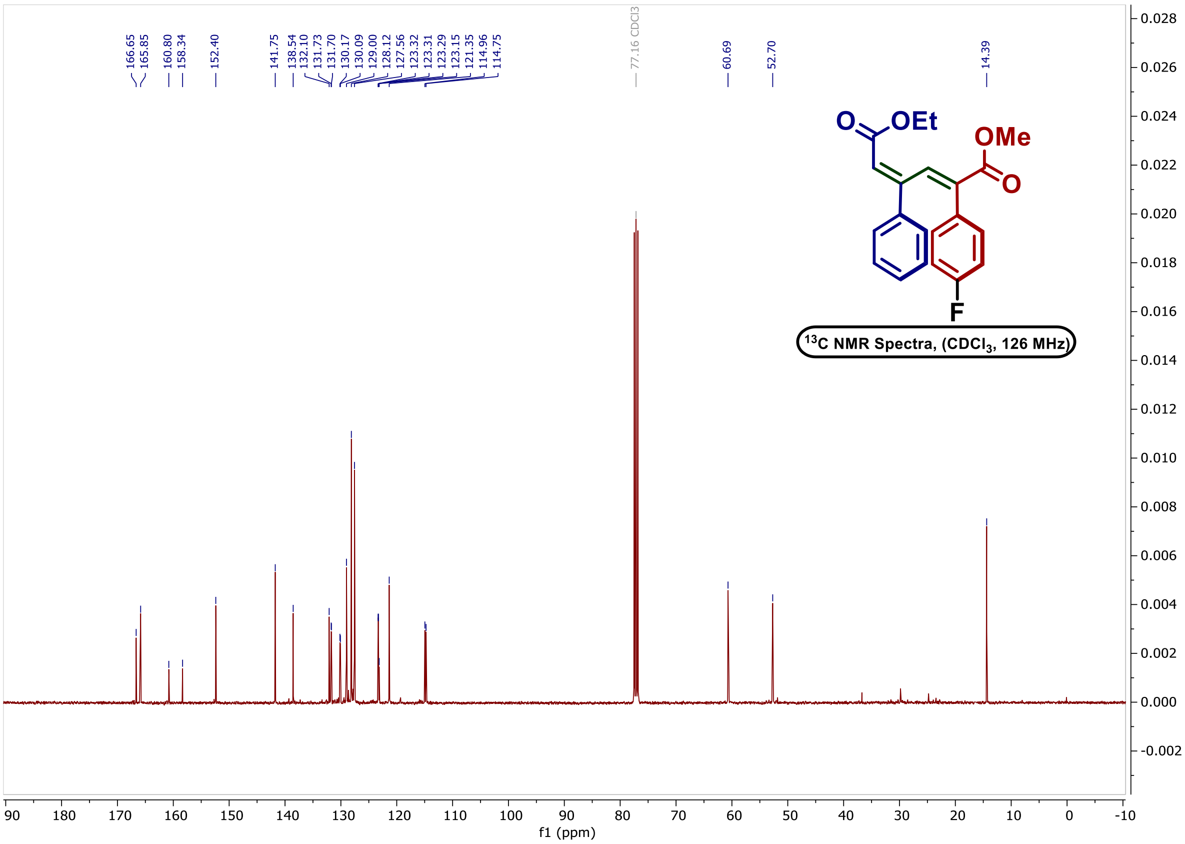
6-ethyl 1-methyl (*2E*,*4E*)-2,4-diphenylhexa-2,4-dienedioate (3a)

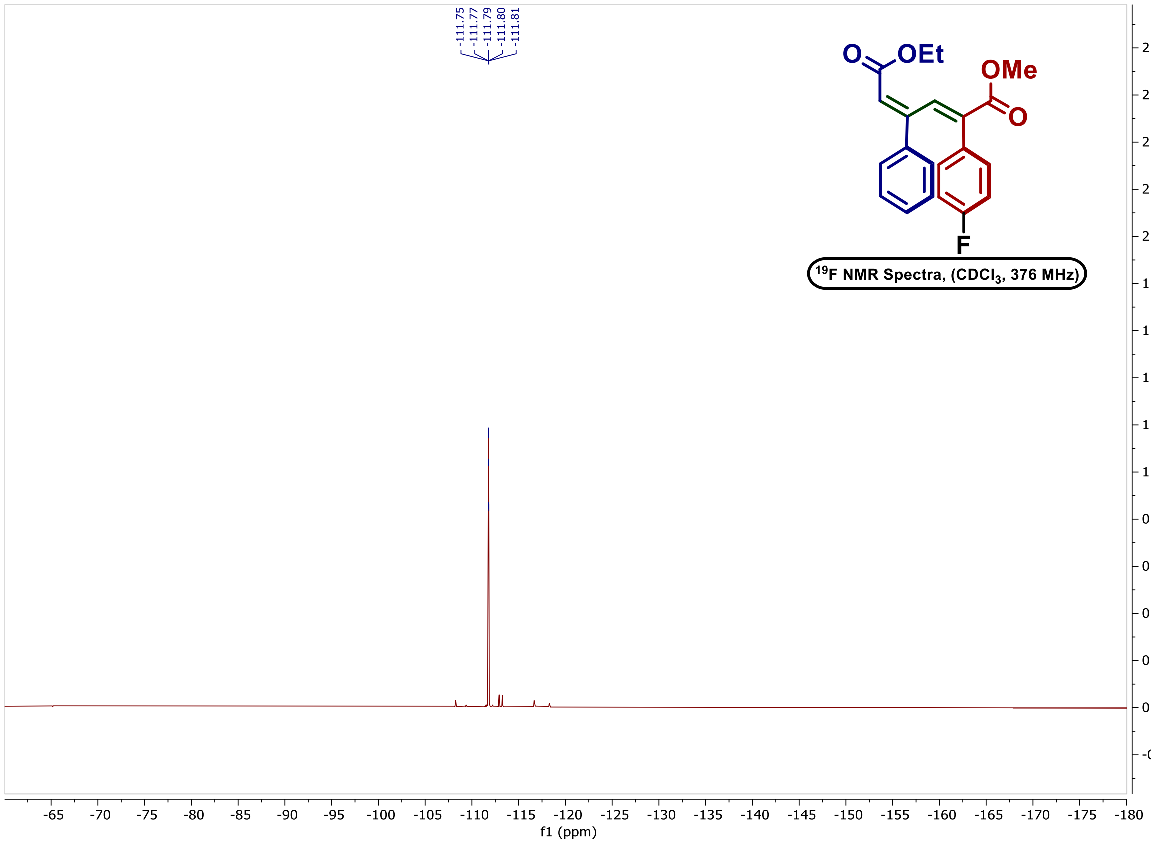




6-ethyl 1-methyl (*2E*,*4E*)-2-(4-fluorophenyl)-4-phenylhexa-2,4-dienedioate (3b)



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-111.81
O
OEt
OMe
O
F
19F NMR Spectra, (CDCl3, 376 MHz)
2.8
2.6
2.4
2.2
2.0
1.8
1.6
1.4
1.2
1.0
0.8
0.6
0.4
0.2
0.0
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-85
-90
-95
-100
-105
-110
-115
-120
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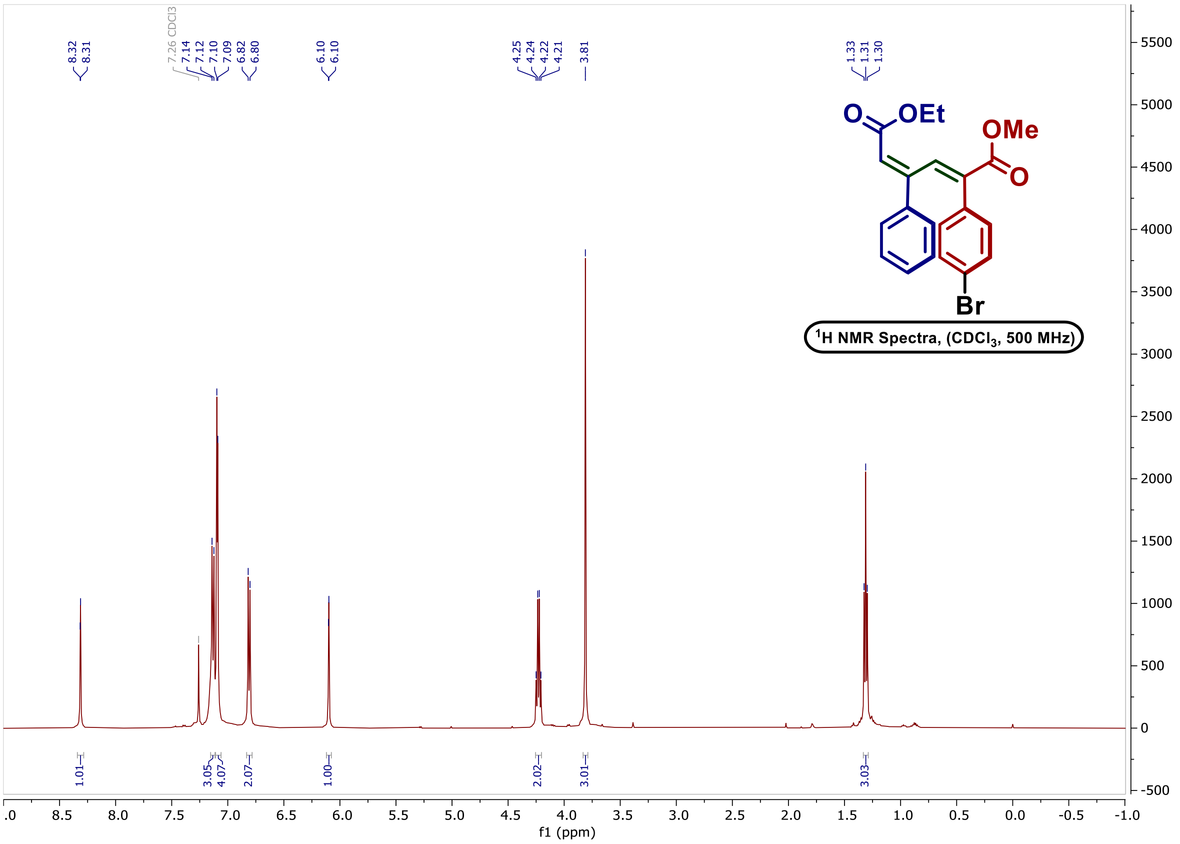
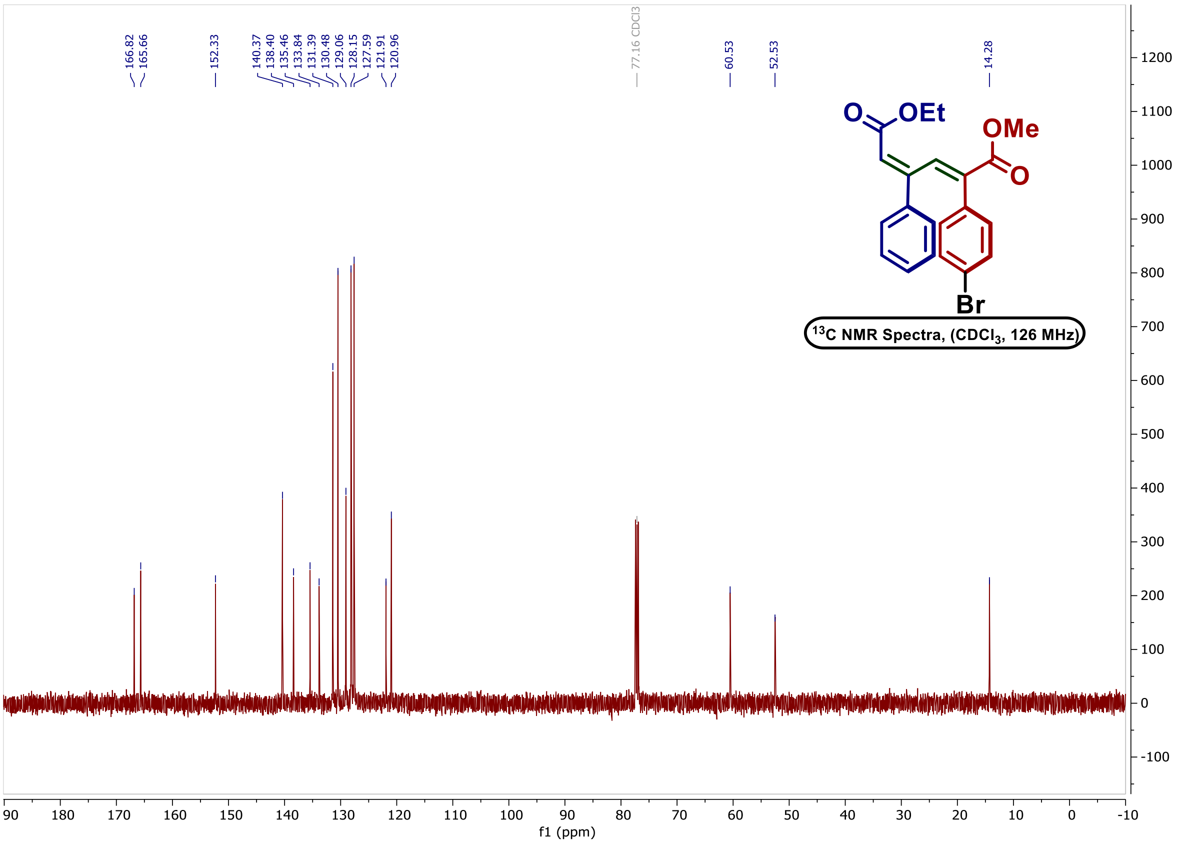
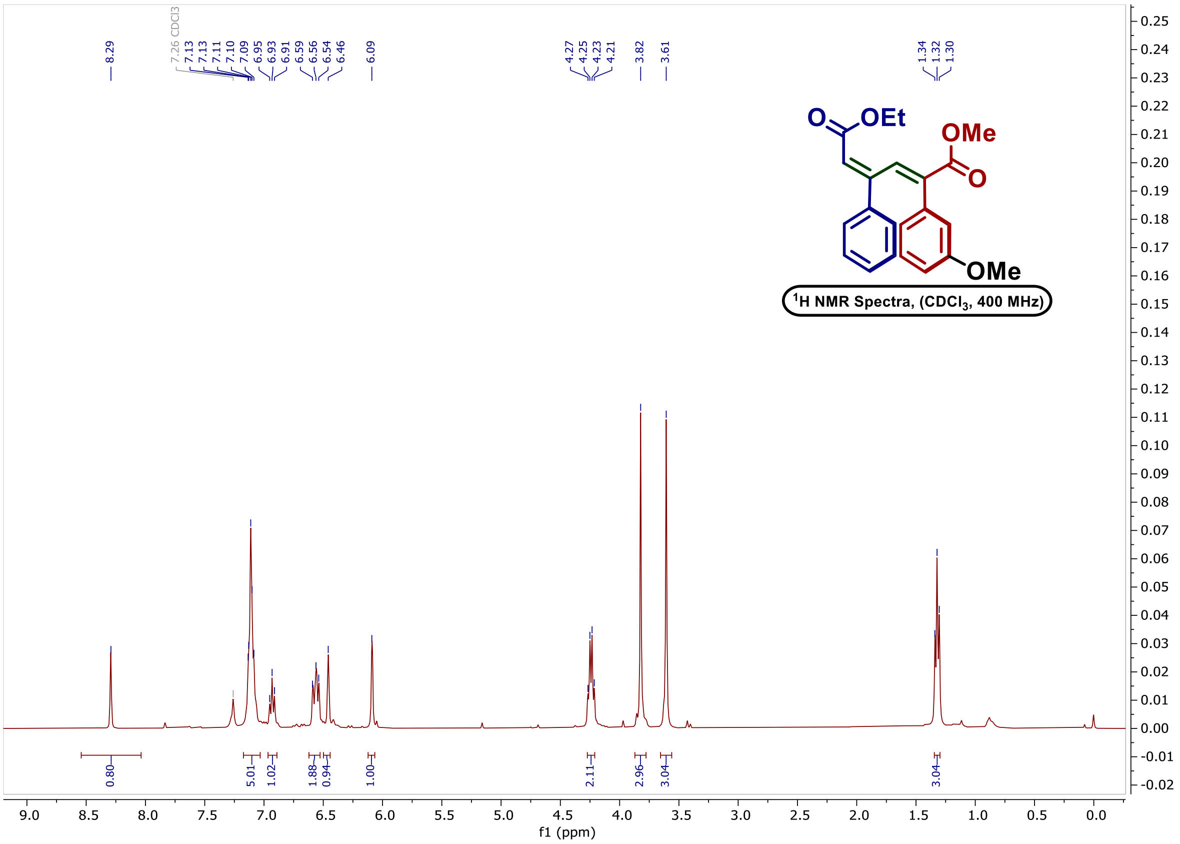
-135
-140
-145
-150
-155
-160
-165
-170
-175
-180
f1 (ppm)

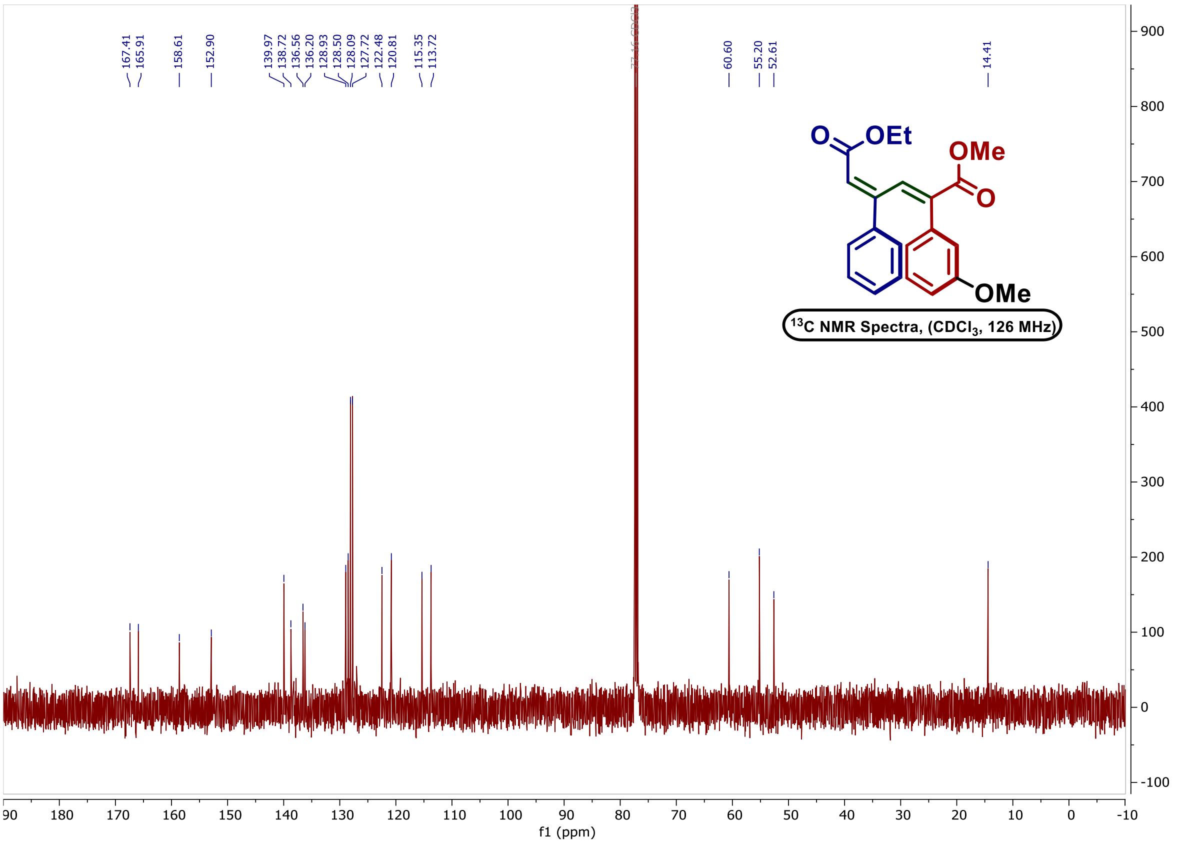
6-ethyl 1-methyl (*2E,4E*)-2-(4-bromophenyl)-4-phenylhexa-2,4-dienedioate (3c)



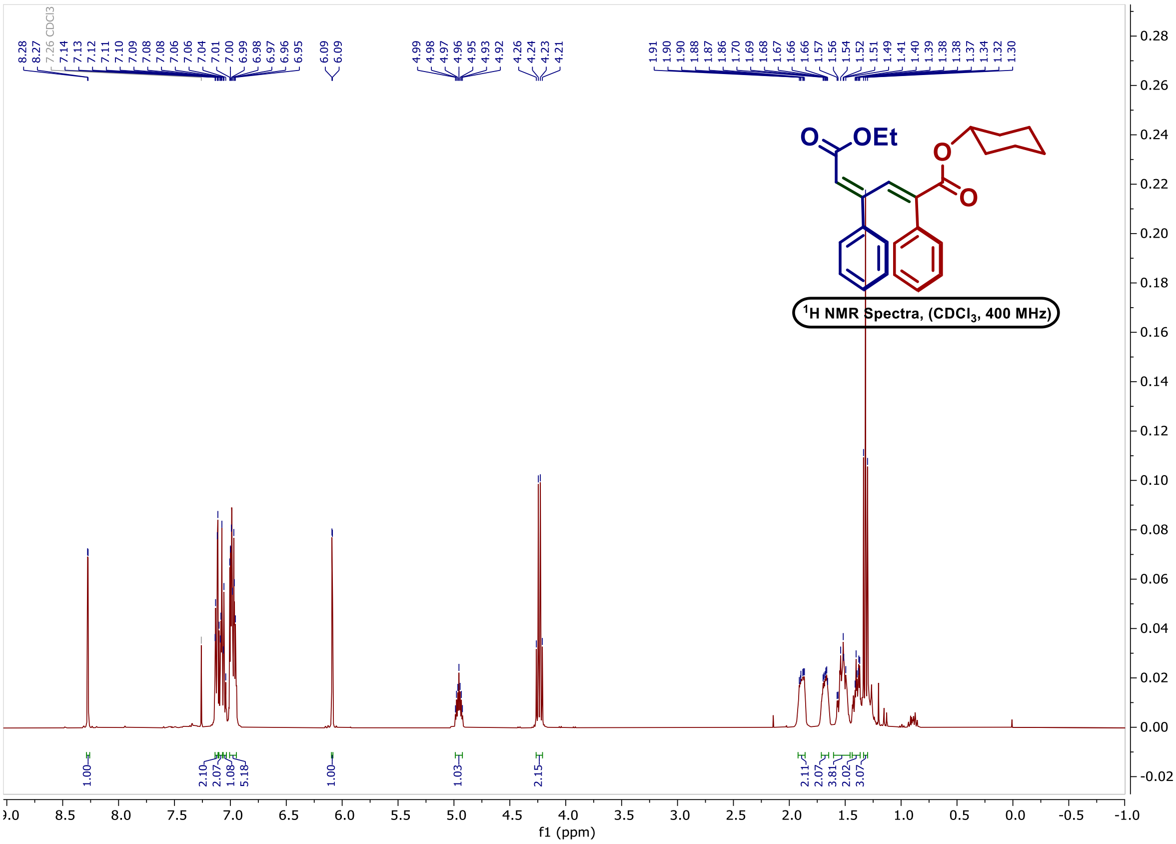


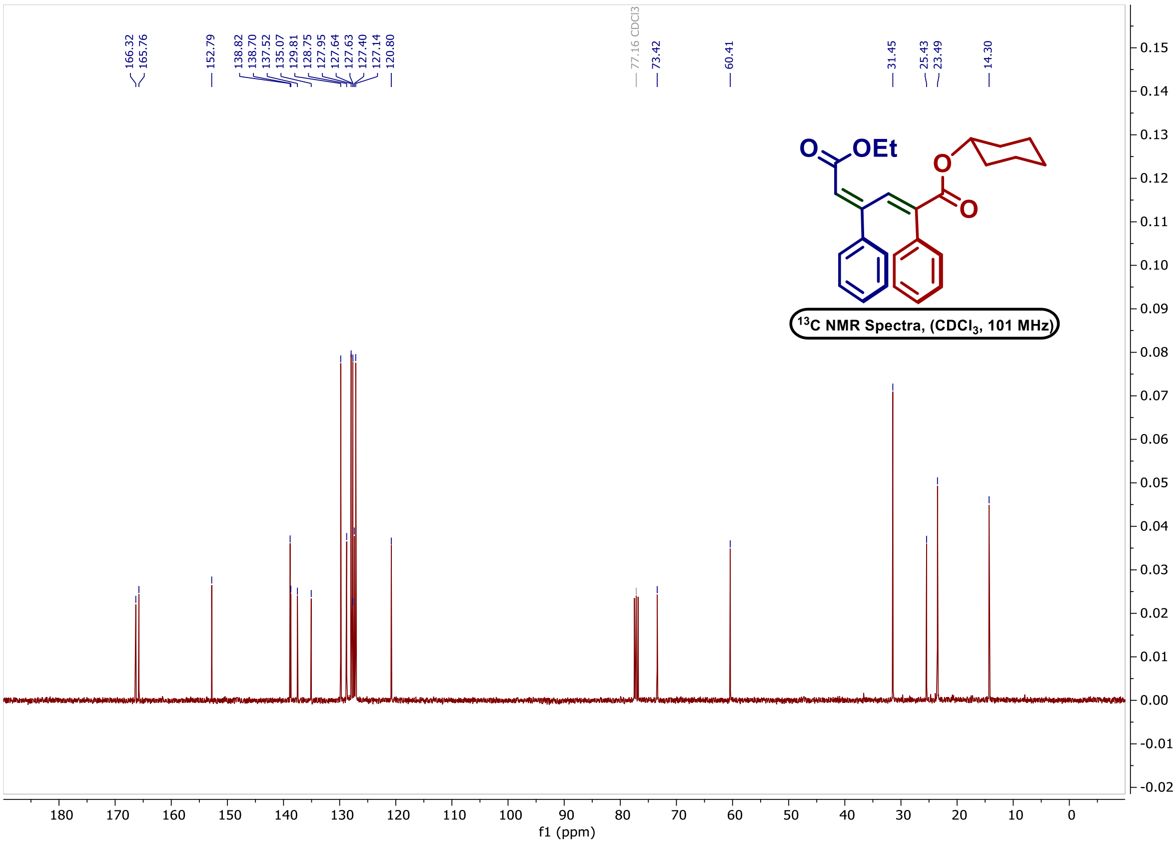
6-ethyl 1-methyl (*2E,4E*)-2-(3-methoxyphenyl)-4-phenylhexa-2,4-dienedioate (3d)



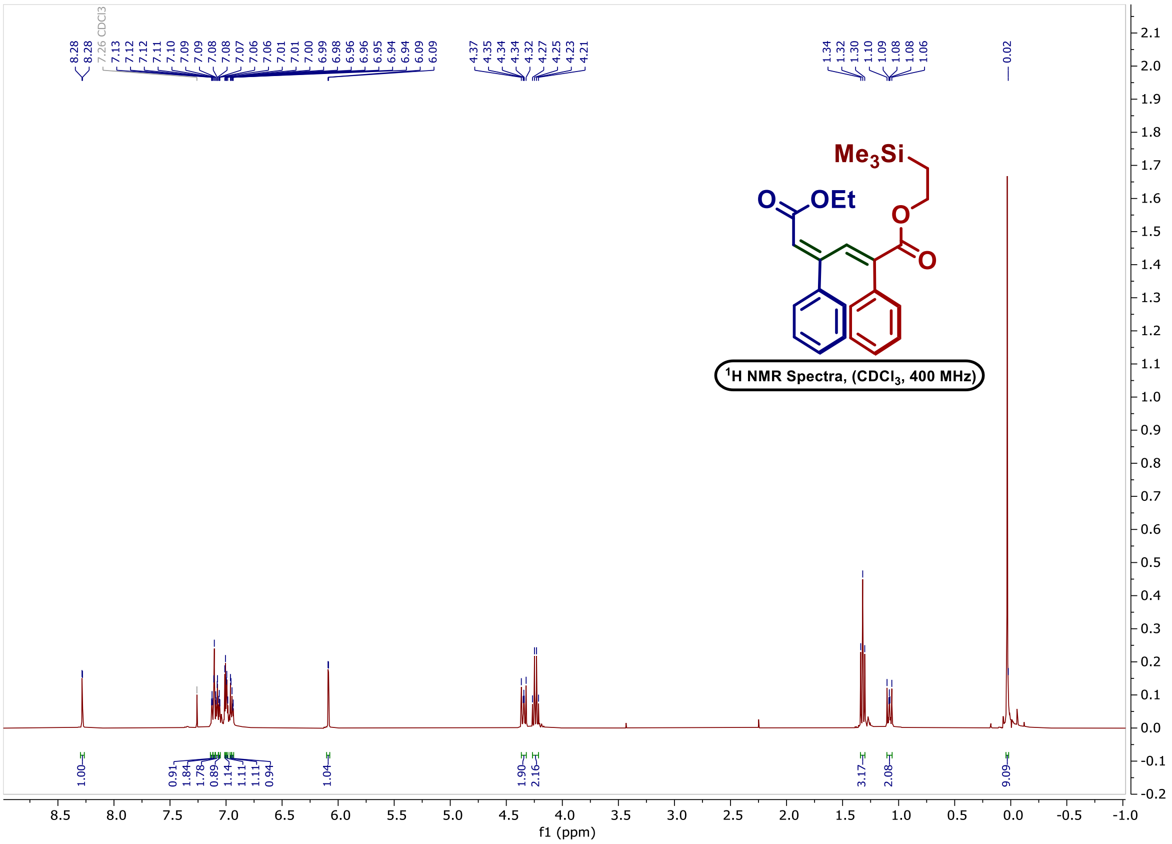


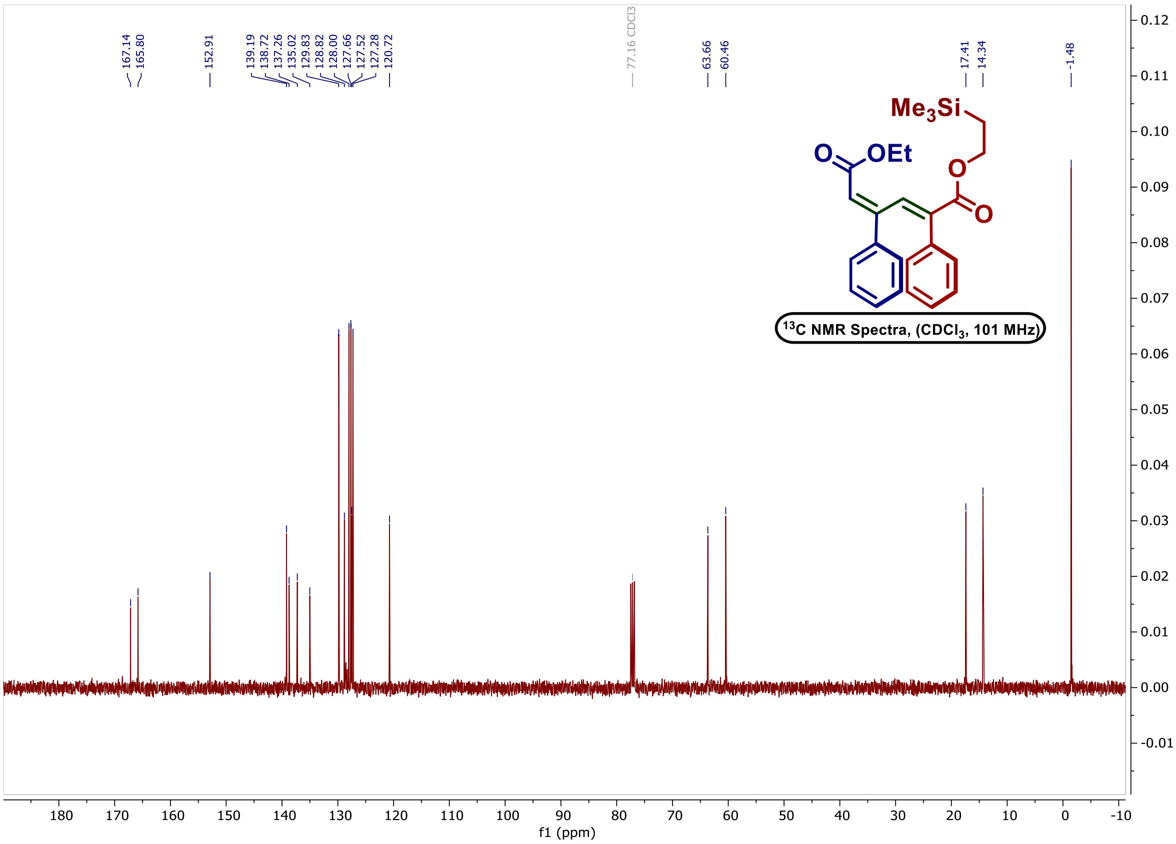
1-cyclohexyl 6-ethyl (*2E,4E*)-2,4-diphenylhexa-2,4-dienedioate (3e)





6-ethyl 1-(2-(trimethylsilyl)ethyl) (*2E*,*4E*)-2,4-diphenylhexa-2,4-dienedioate (3f)





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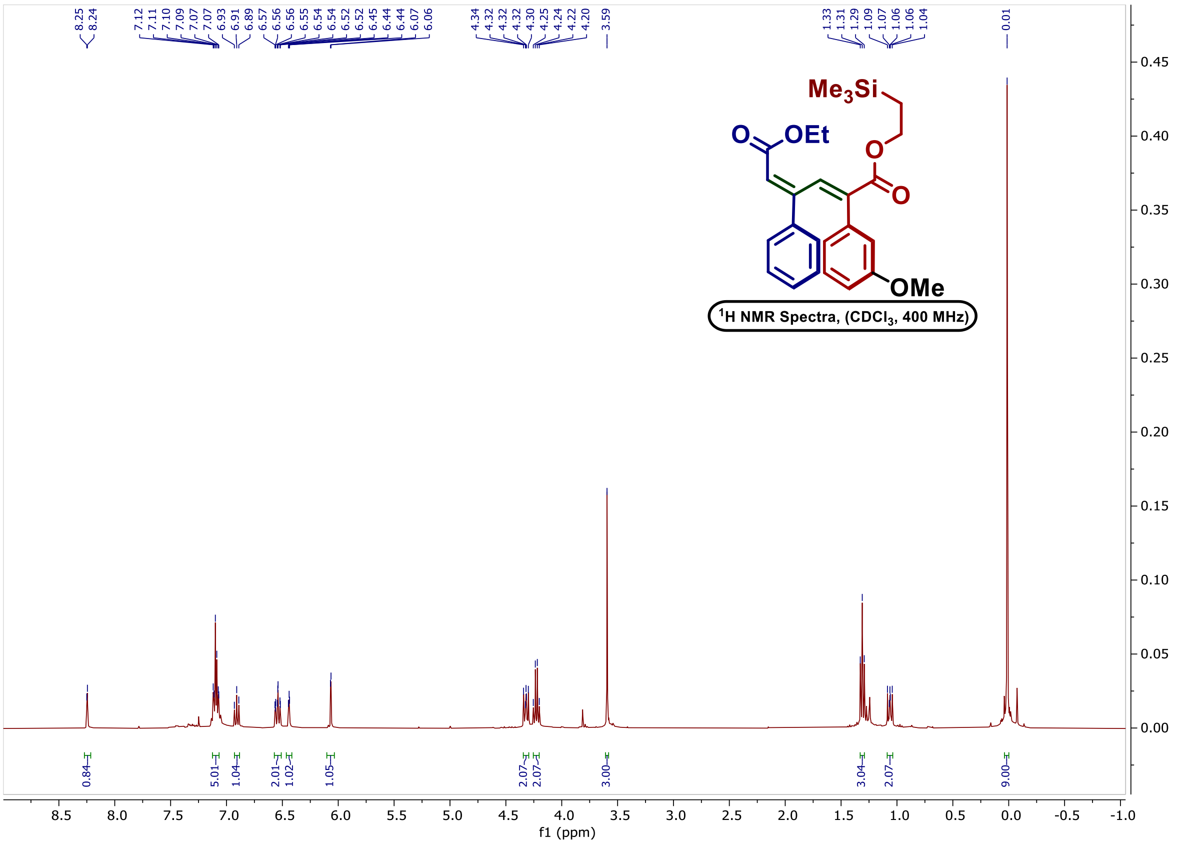
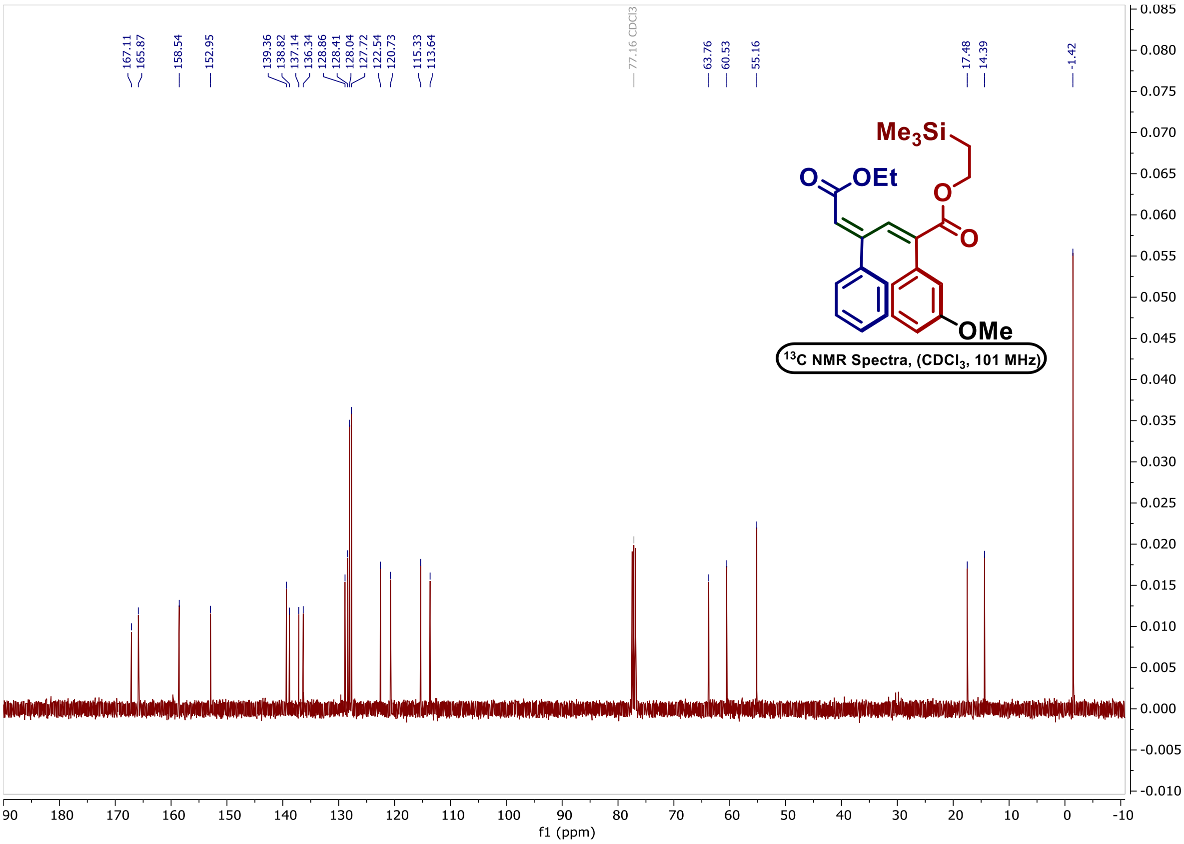
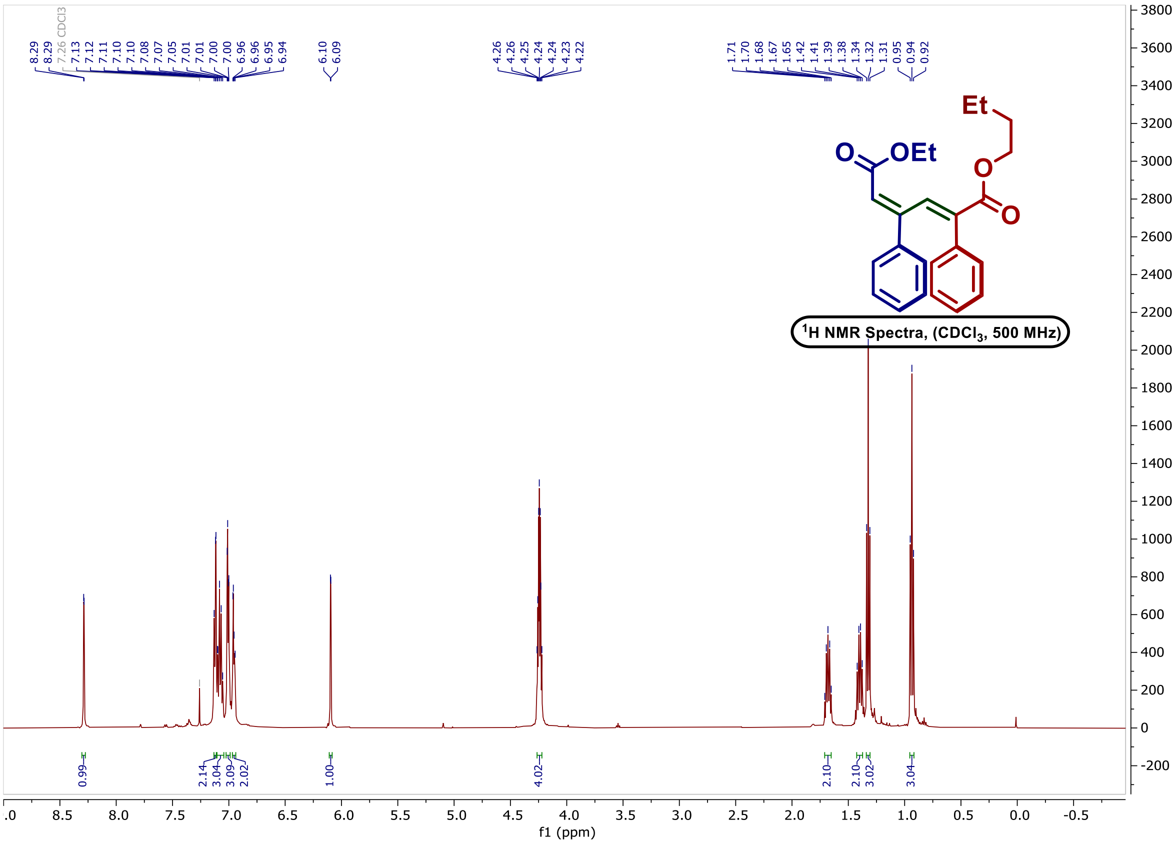
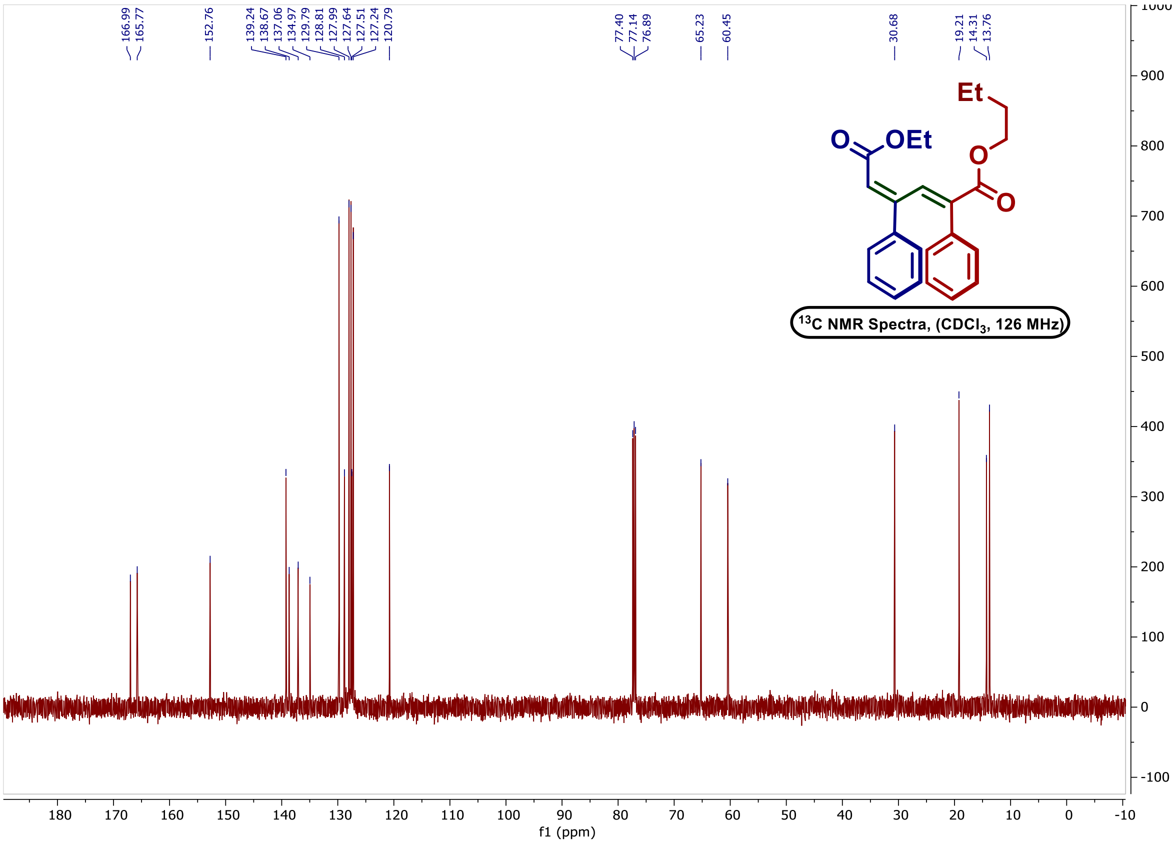


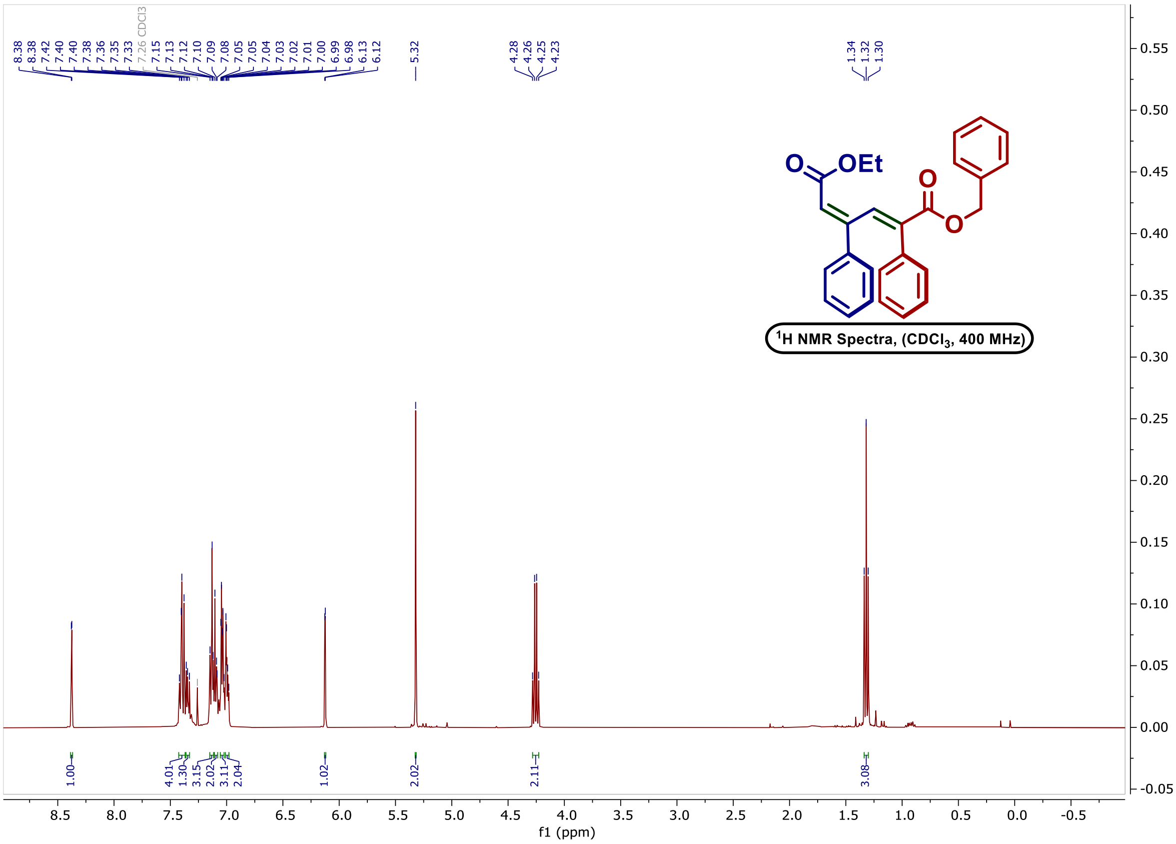


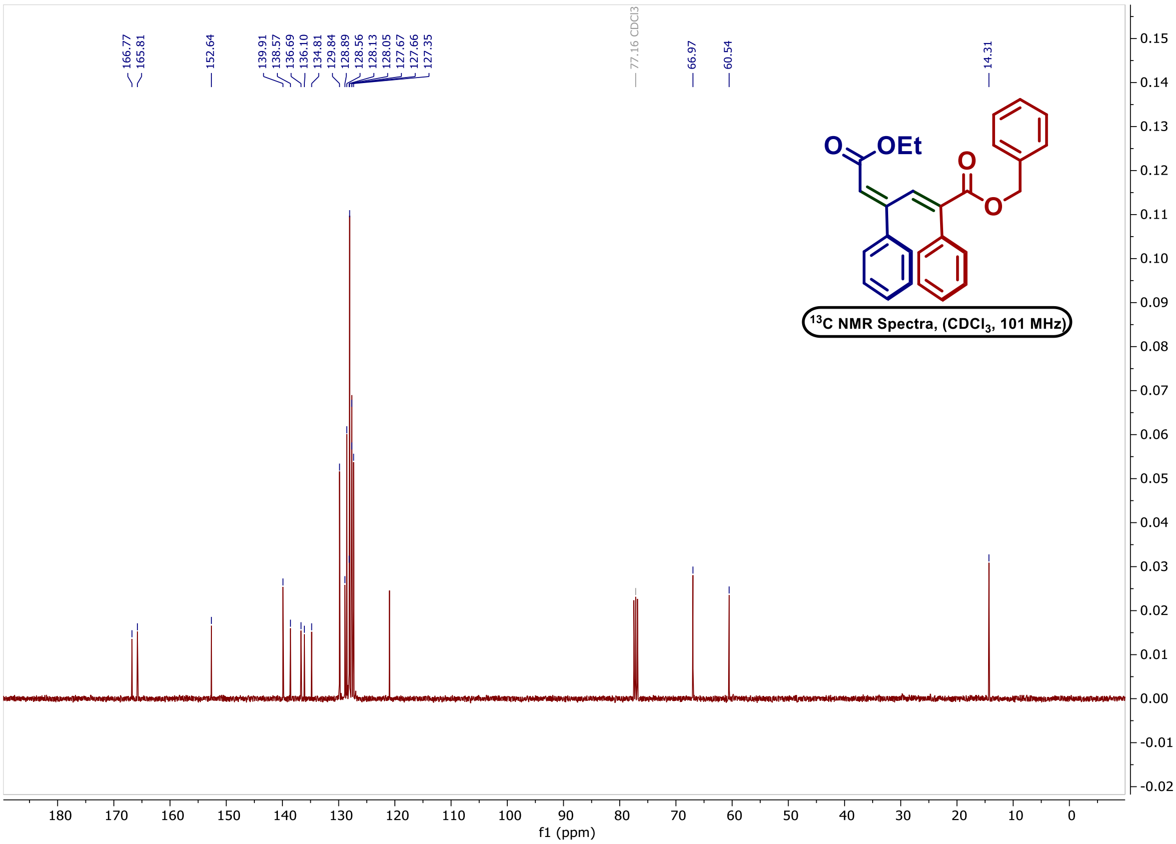
1-butyl 6-ethyl (*2E*,*4E*)-2,4-diphenylhexa-2,4-dienedioate (3h)



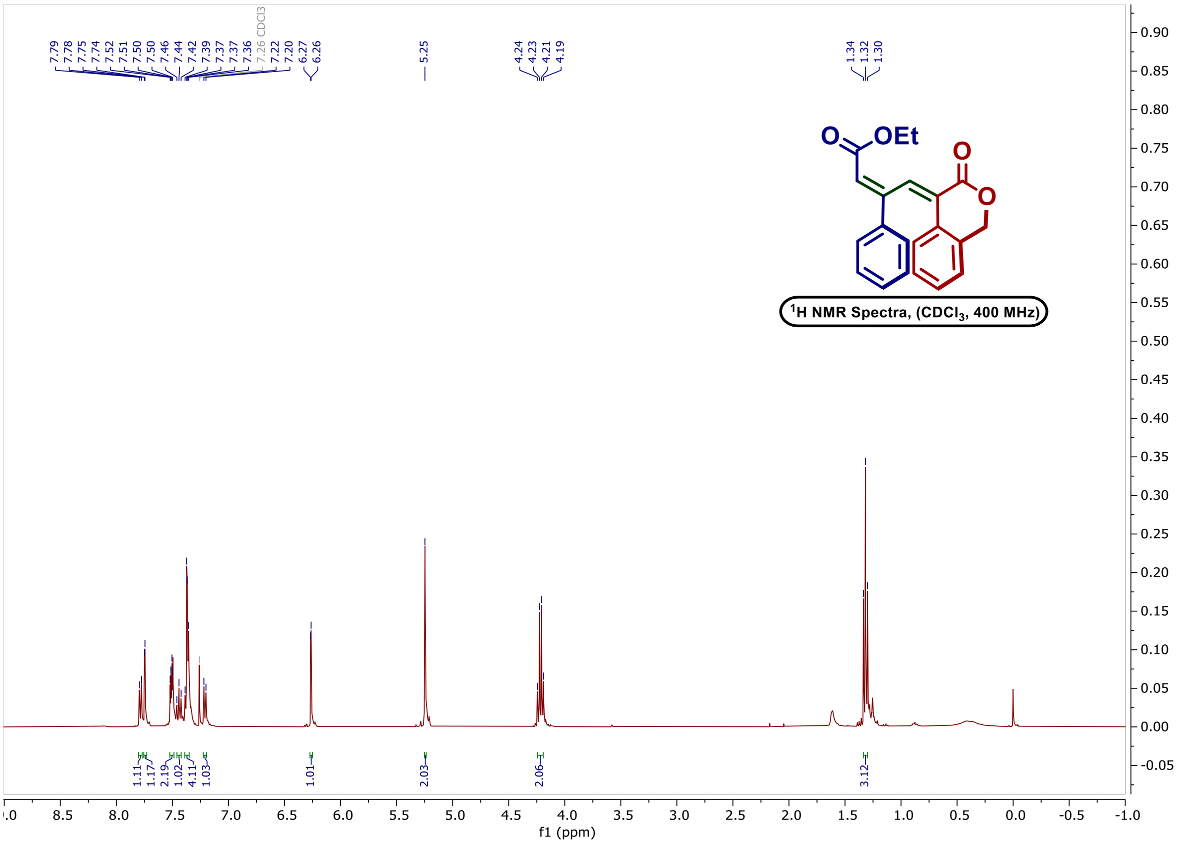


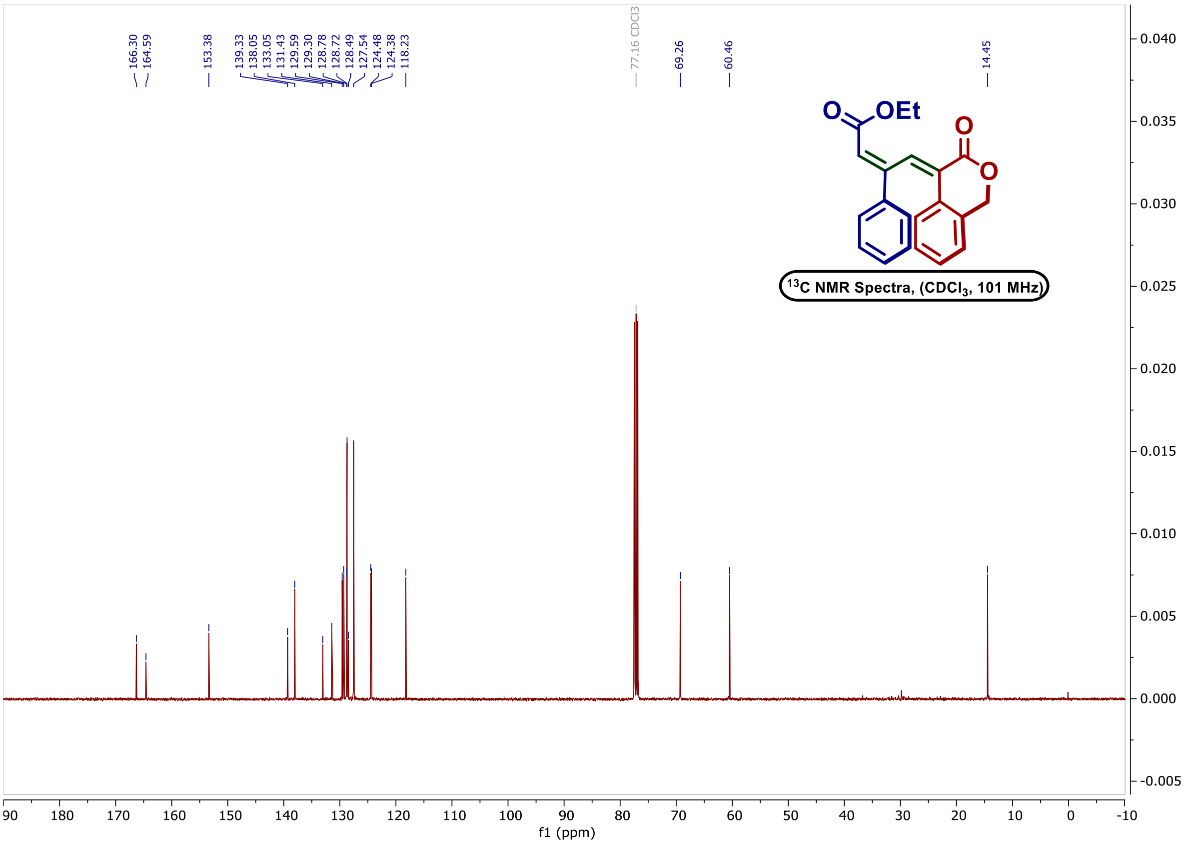
1-benzyl 6-ethyl (*2E*,*4E*)-2,4-diphenylhexa-2,4-dienedioate (3i)



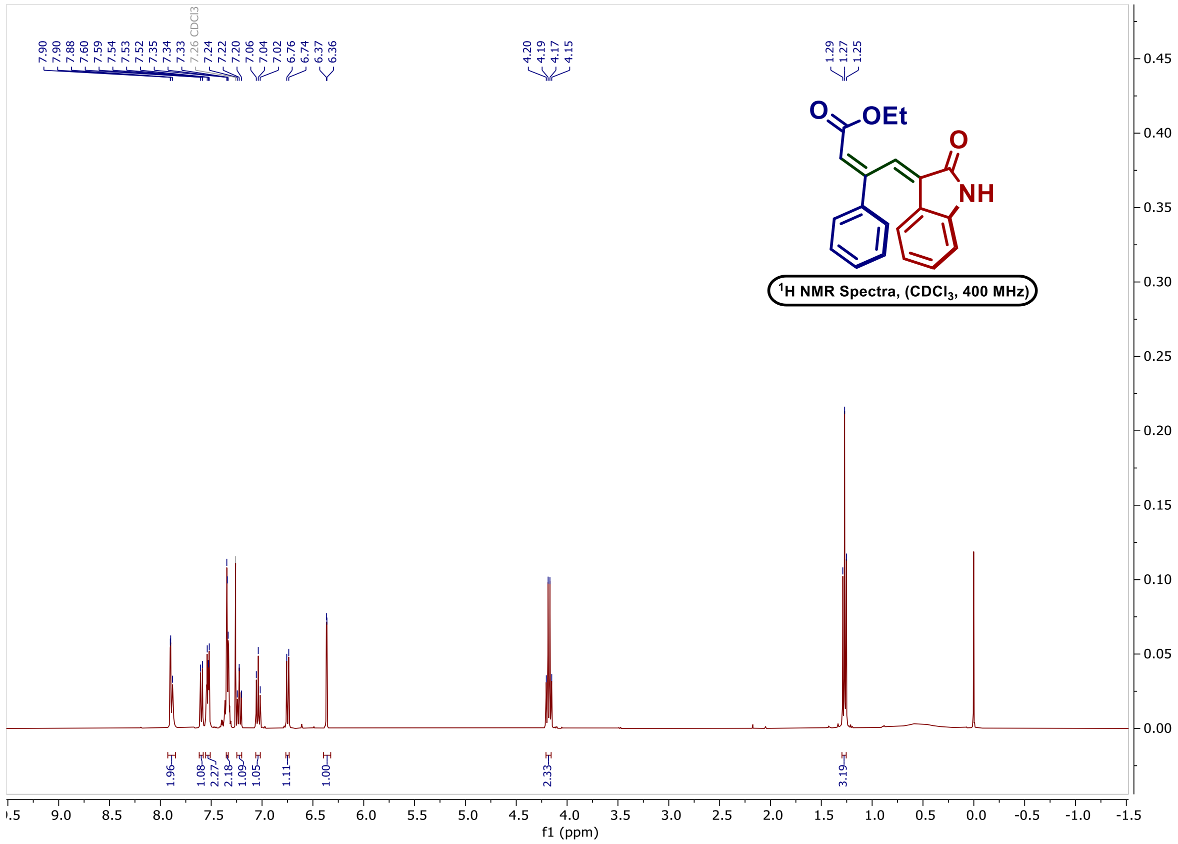


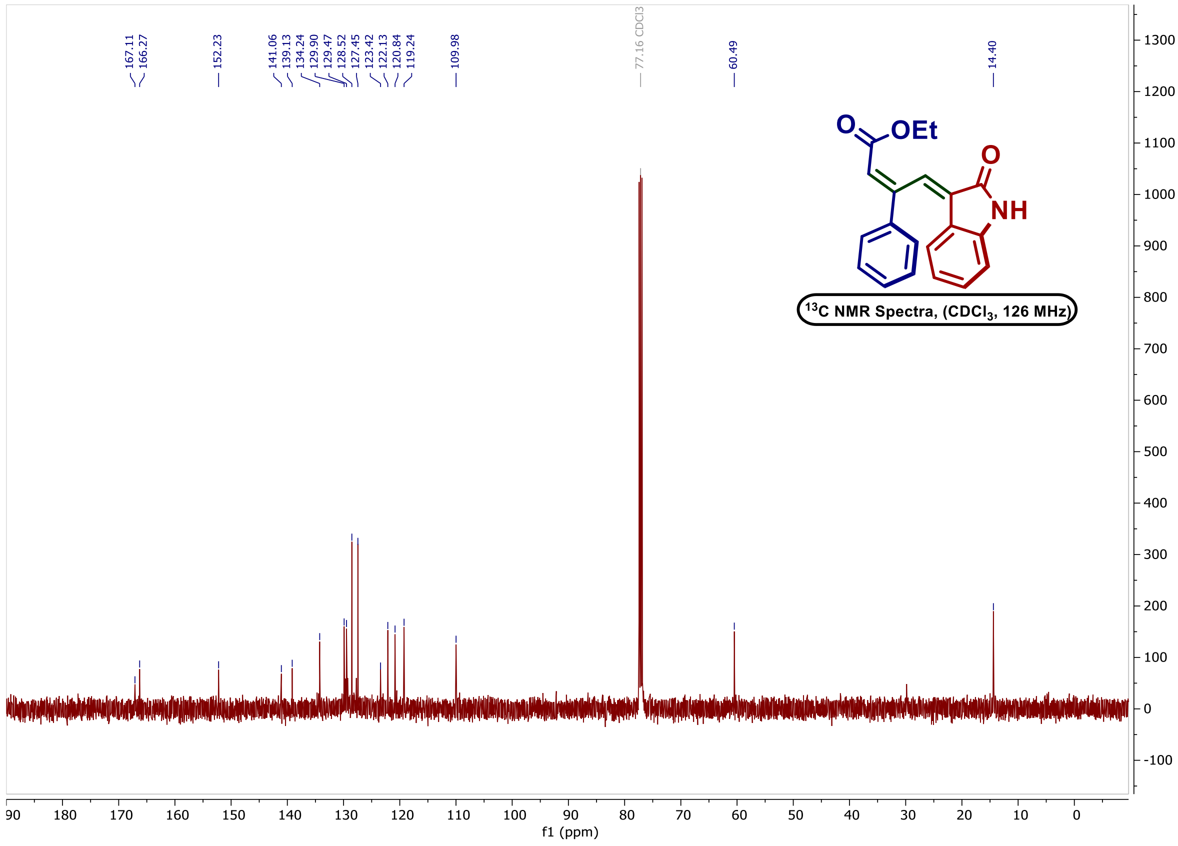
ethyl (*E*)-4-((*E*)-3-oxoisochroman-4-ylidene)-3-phenylbut-2-enoate (3j)



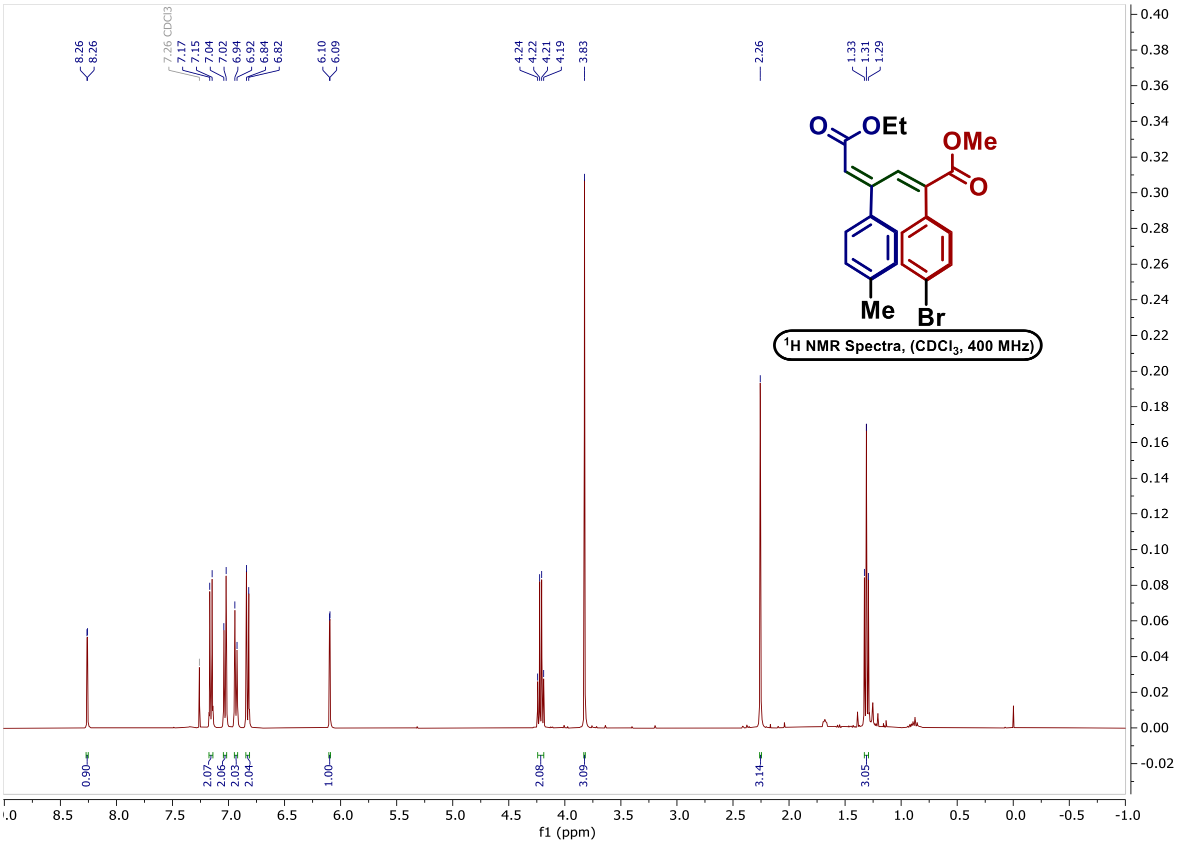


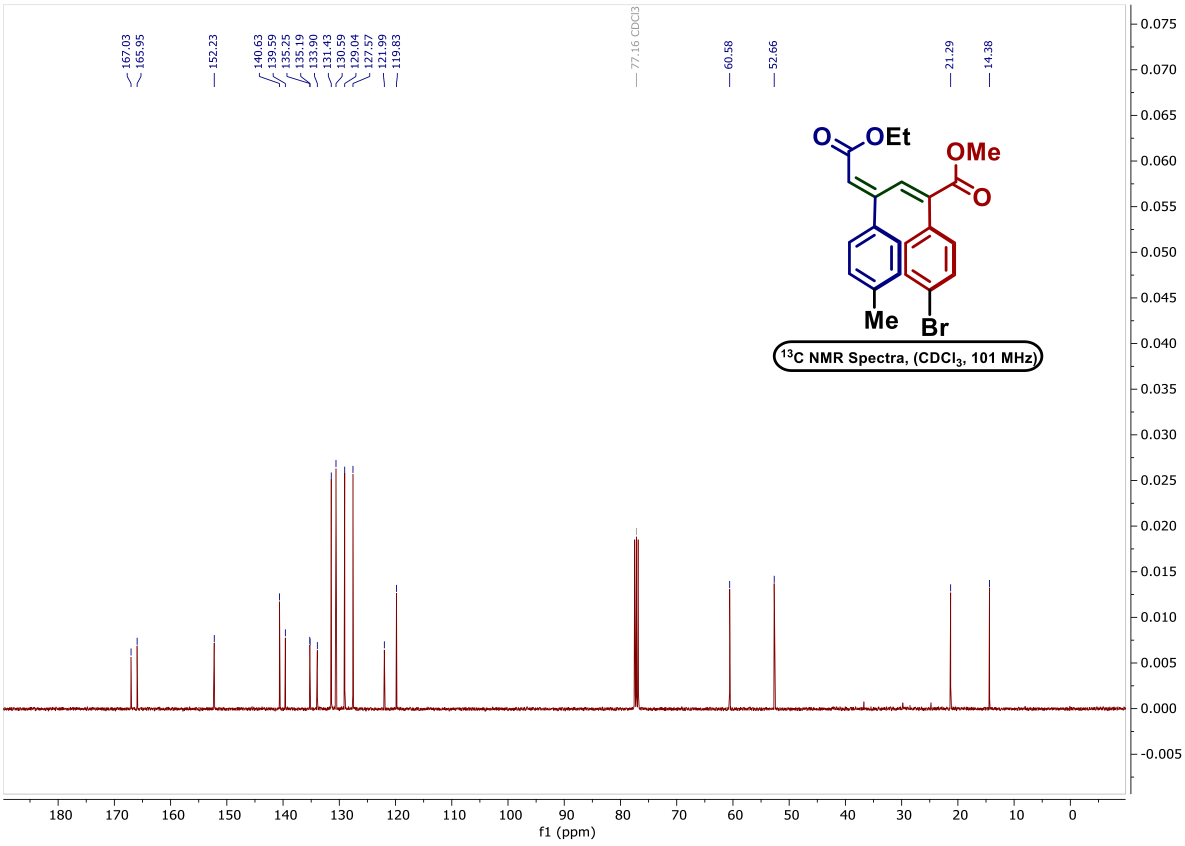
ethyl (*E*)-4-((*E*)-2-oxoindolin-3-ylidene)-3-phenylbut-2-enoate (3k)



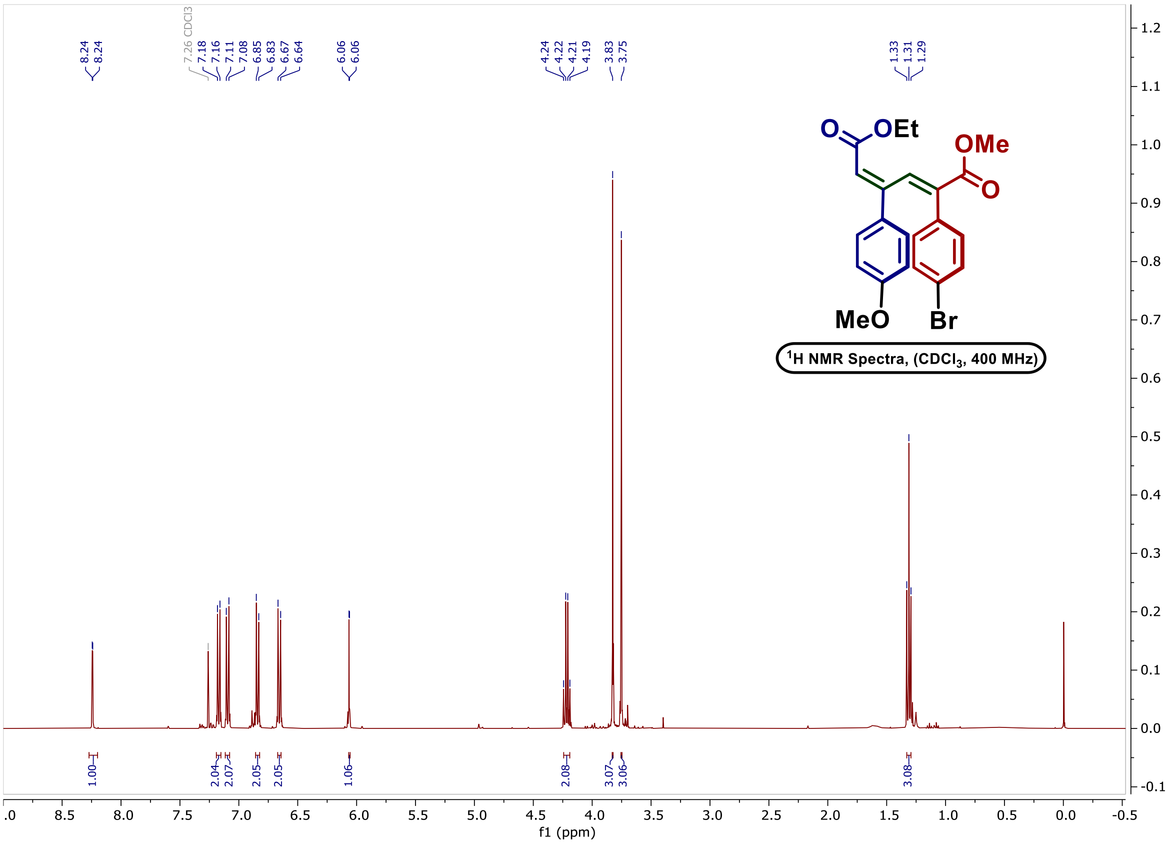


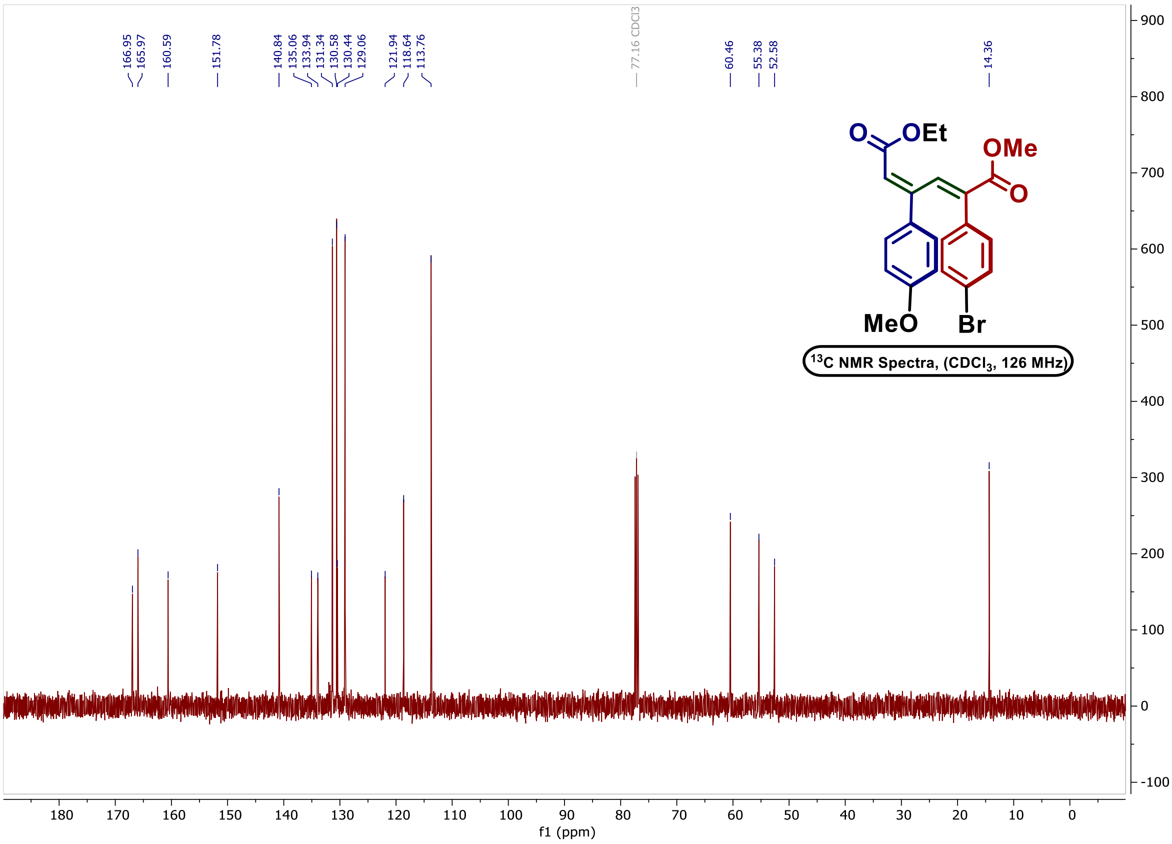
6-ethyl 1-methyl (2E,4E)-2-(4-bromophenyl)-4-(p-tolyl)hexa-2,4-dienedioate (3l)



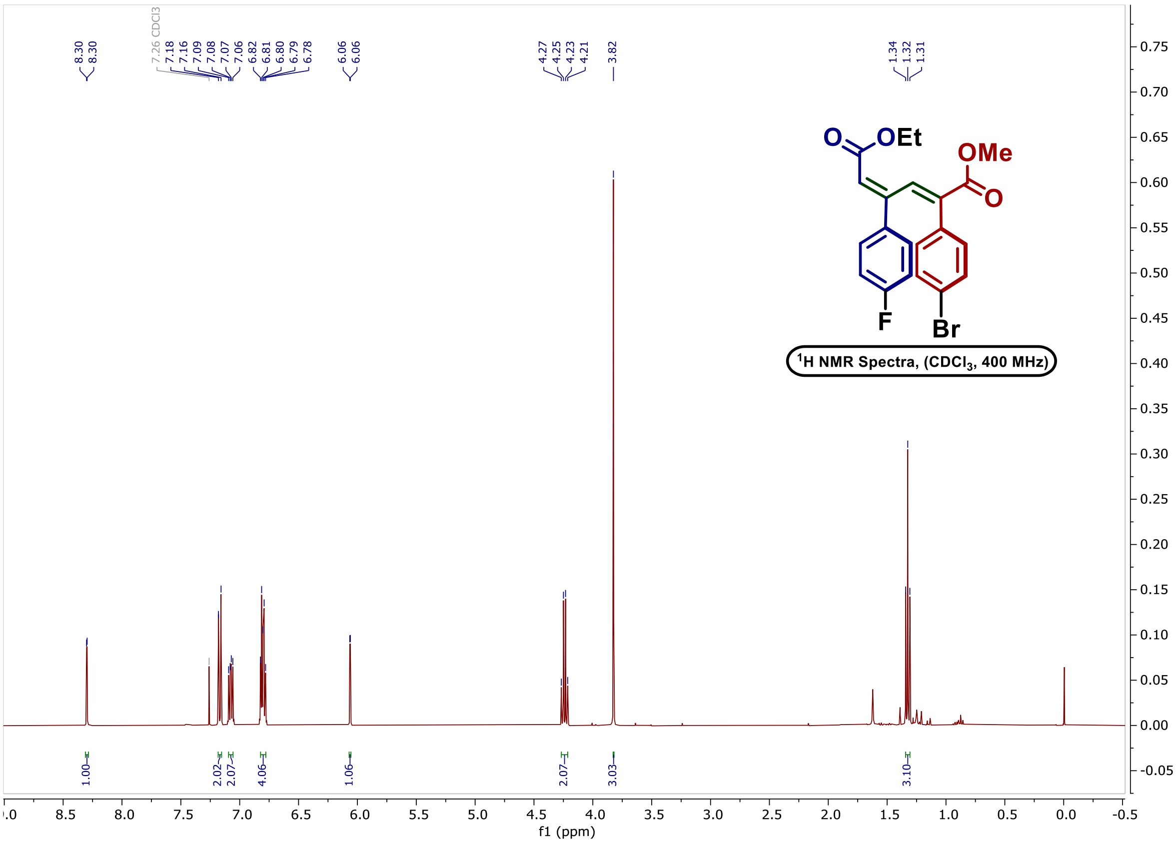


6-ethyl 1-methyl (*2E,4E*)-2-(4-bromophenyl)-4-(4-methoxyphenyl)hexa-2,4-dienedioate (3m)

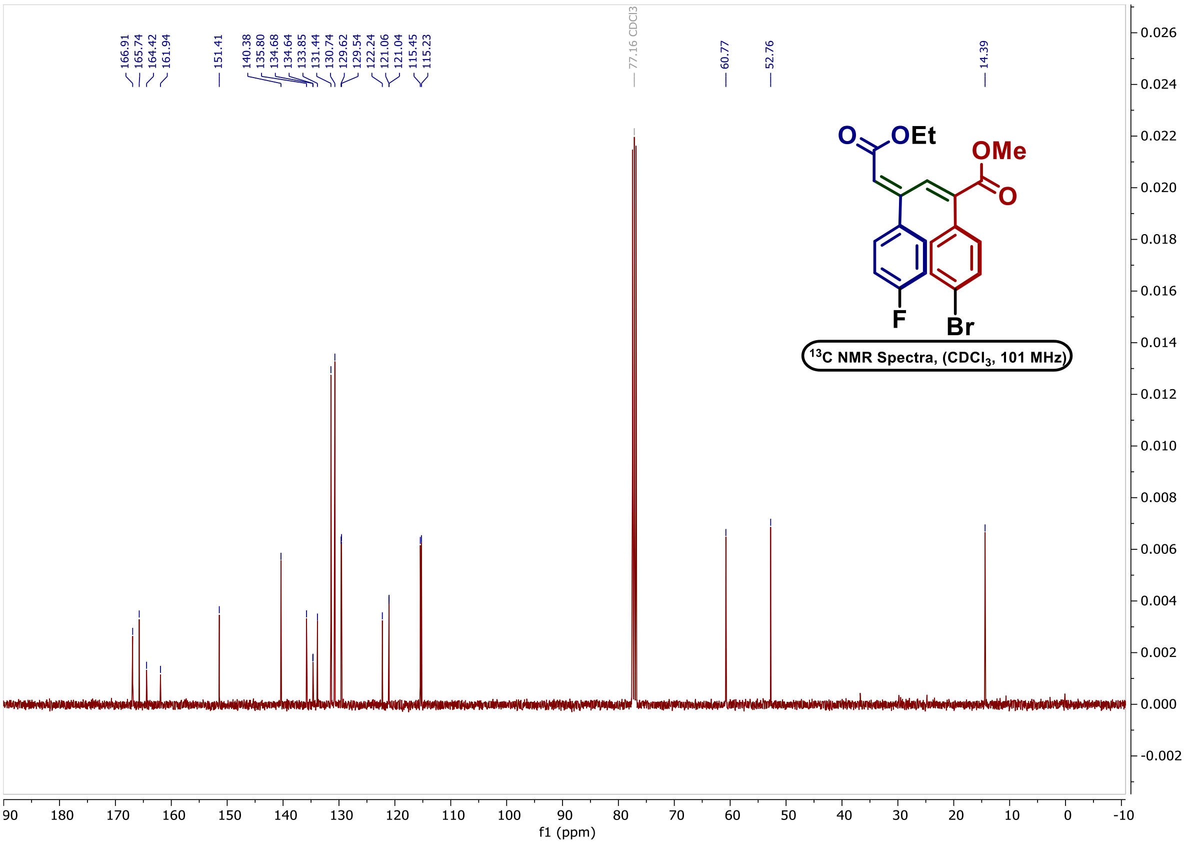




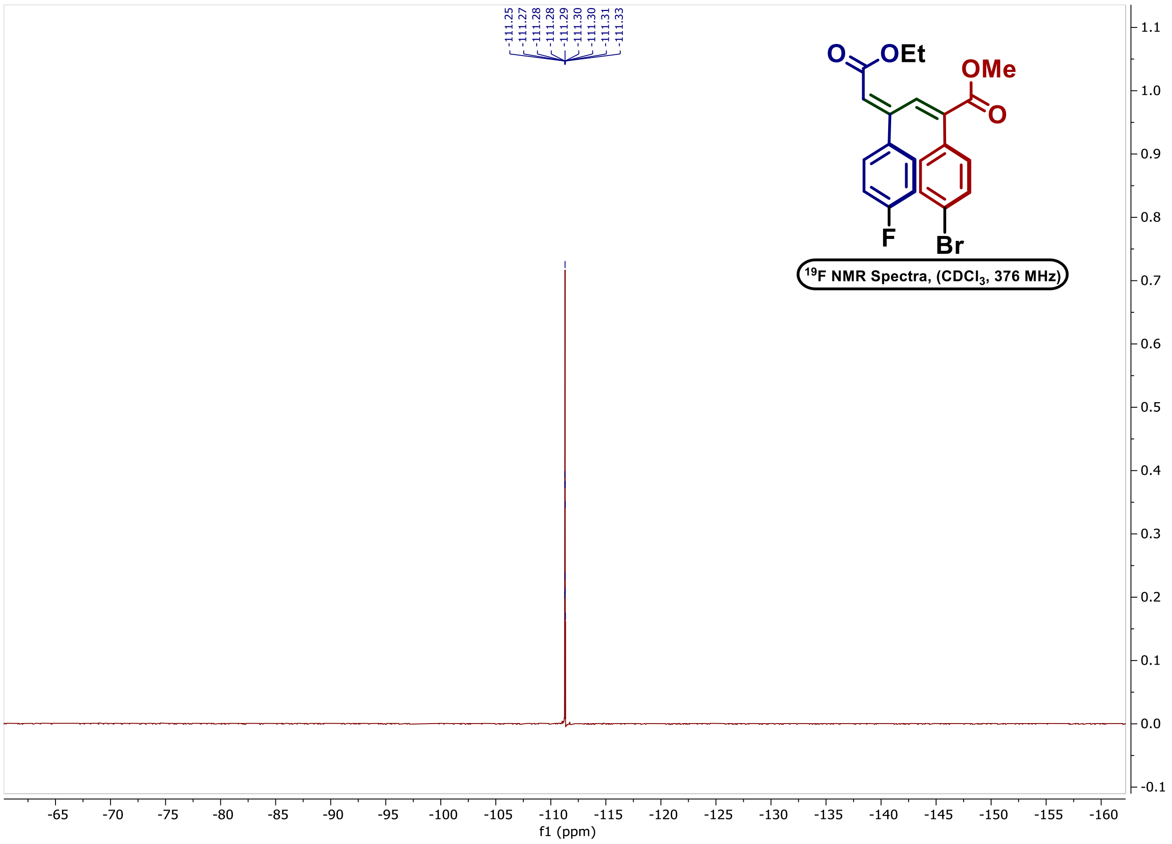
6-ethyl 1-methyl (*2E,4E*)-2-(4-bromophenyl)-4-(4-fluorophenyl)hexa-2,4-dienedioate (3n)



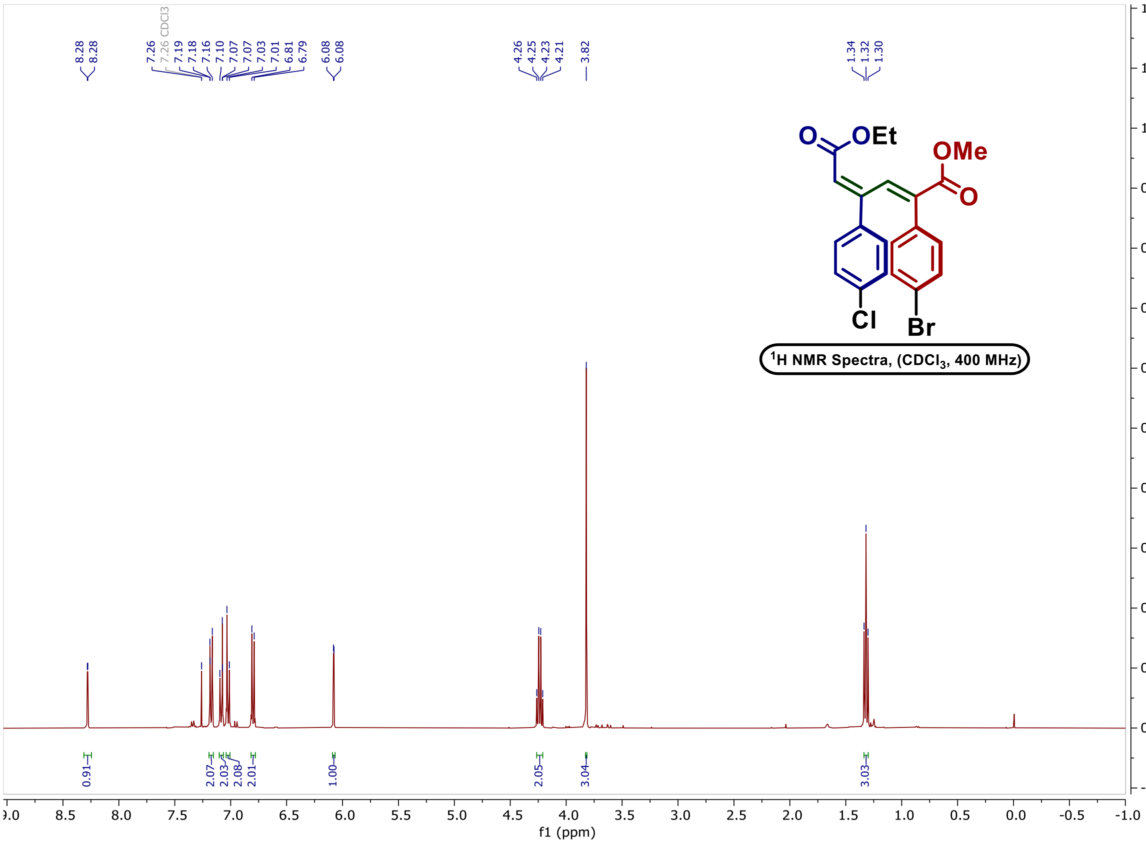
8.30
8.30
7.26 CDCl3
7.18
7.16
7.09
7.08
7.07
7.06
6.82
6.81
6.80
6.79
6.78
6.06
6.06
4.27
4.25
4.23
4.21
3.82
1.34
1.32
1.31
O
OEt
OMe
O
F
Br
1H NMR Spectra, (CDCl3, 400 MHz)
1.00
2.02
2.07
4.06
1.06
2.07
3.03
3.10
f1 (ppm)

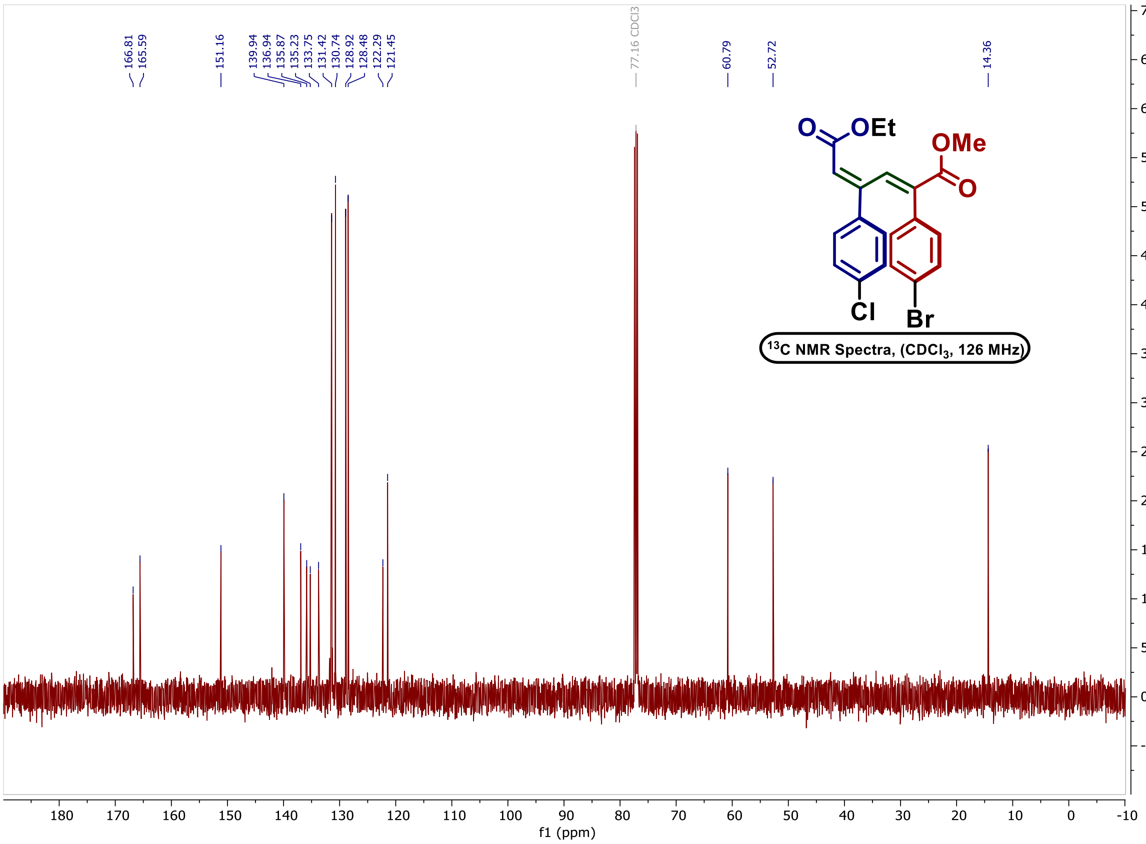


166.91
165.74
164.42
161.94
151.41
140.38
135.80
134.68
134.64
133.85
131.44
130.74
129.62
129.54
122.24
121.06
121.04
115.45
115.23
77.16 CDCl3
60.77
52.76
14.39
O
OEt
OMe
O
F
Br
13C NMR Spectra, (CDCl3, 101 MHz)
f1 (ppm)

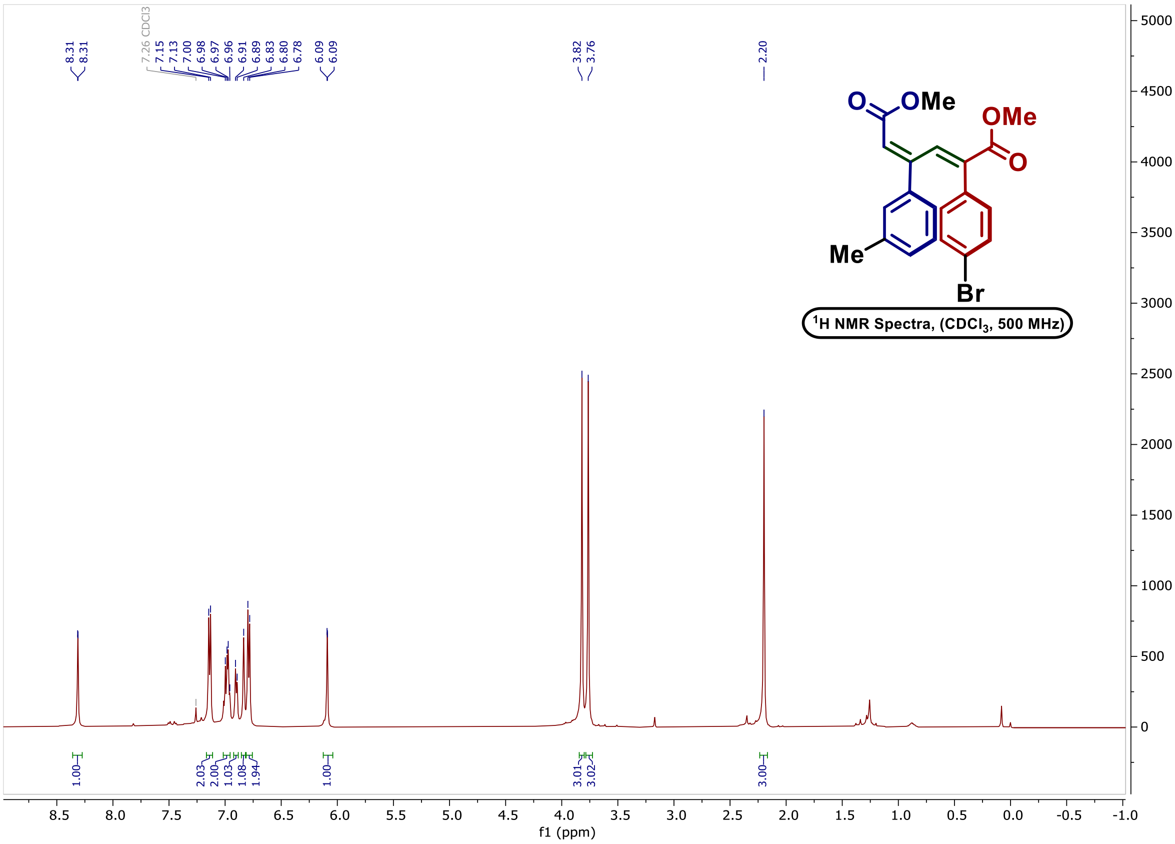

-111.25
-111.27
-111.28
-111.28
-111.29
-111.30
-111.30
-111.31
-111.33
O
OEt
OMe
O
F
Br
^{19}F NMR Spectra, (CDCl$_3$, 376 MHz)
1.1
1.0
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0.0
-0.1
-65
-70
-75
-80
-85
-90
-95
-100
-105
-110
-115
-120
-125
-130
-135
-140
-145
-150
-155
-160
f1 (ppm)

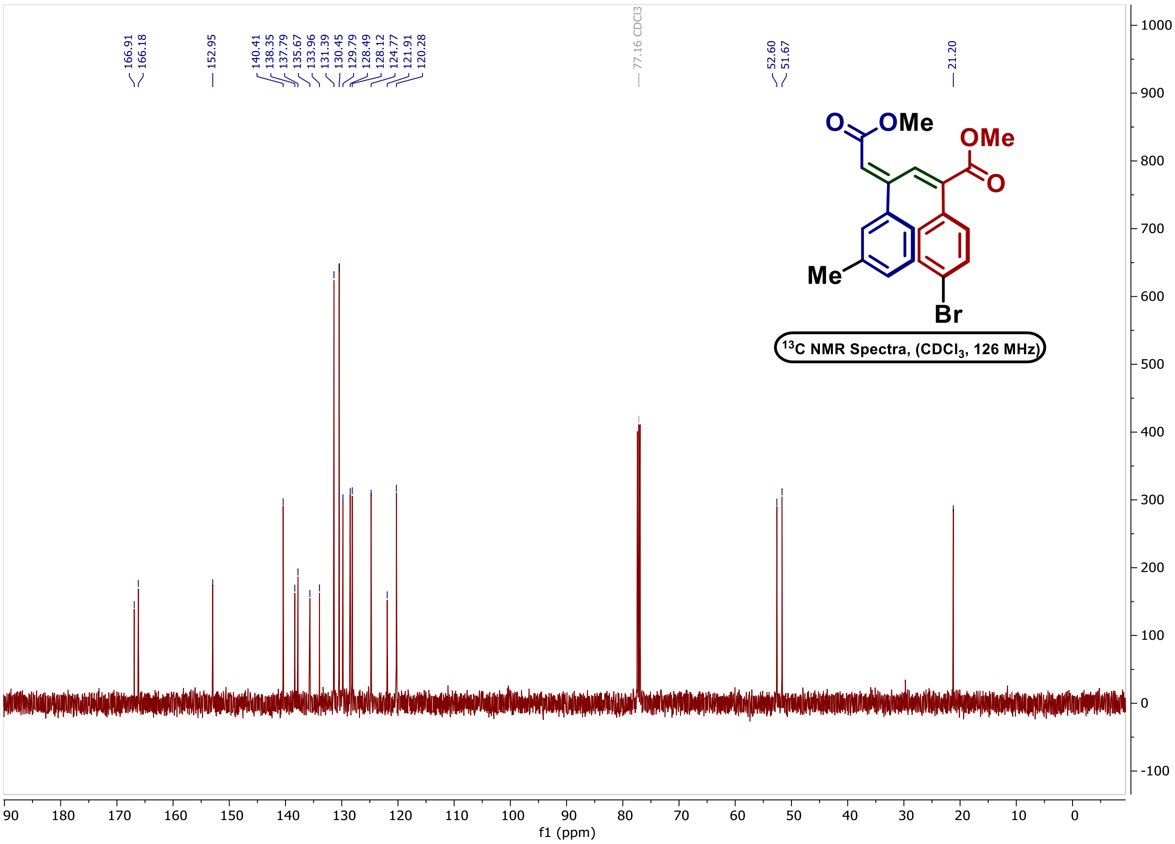
6-ethyl 1-methyl (*2E,4E*)-2-(4-bromophenyl)-4-(4-chlorophenyl)hexa-2,4-dienedioate (3o)



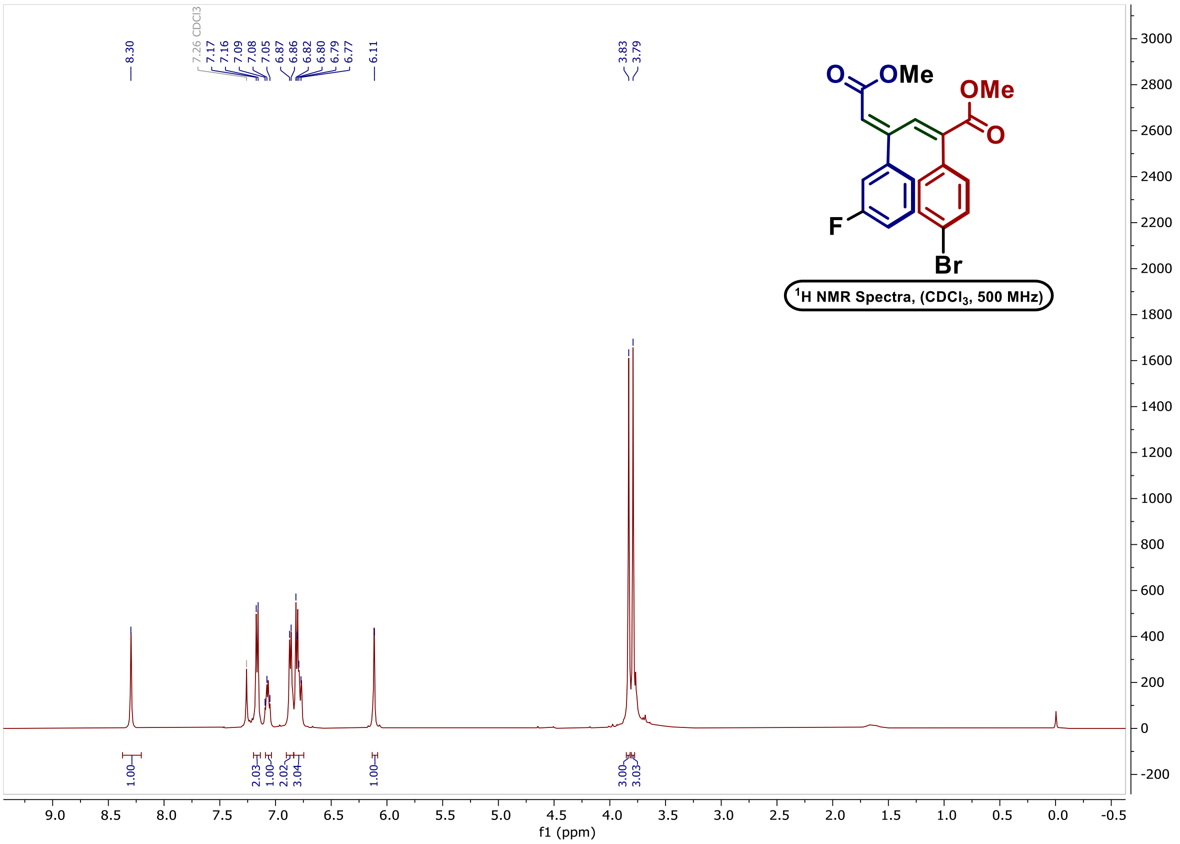


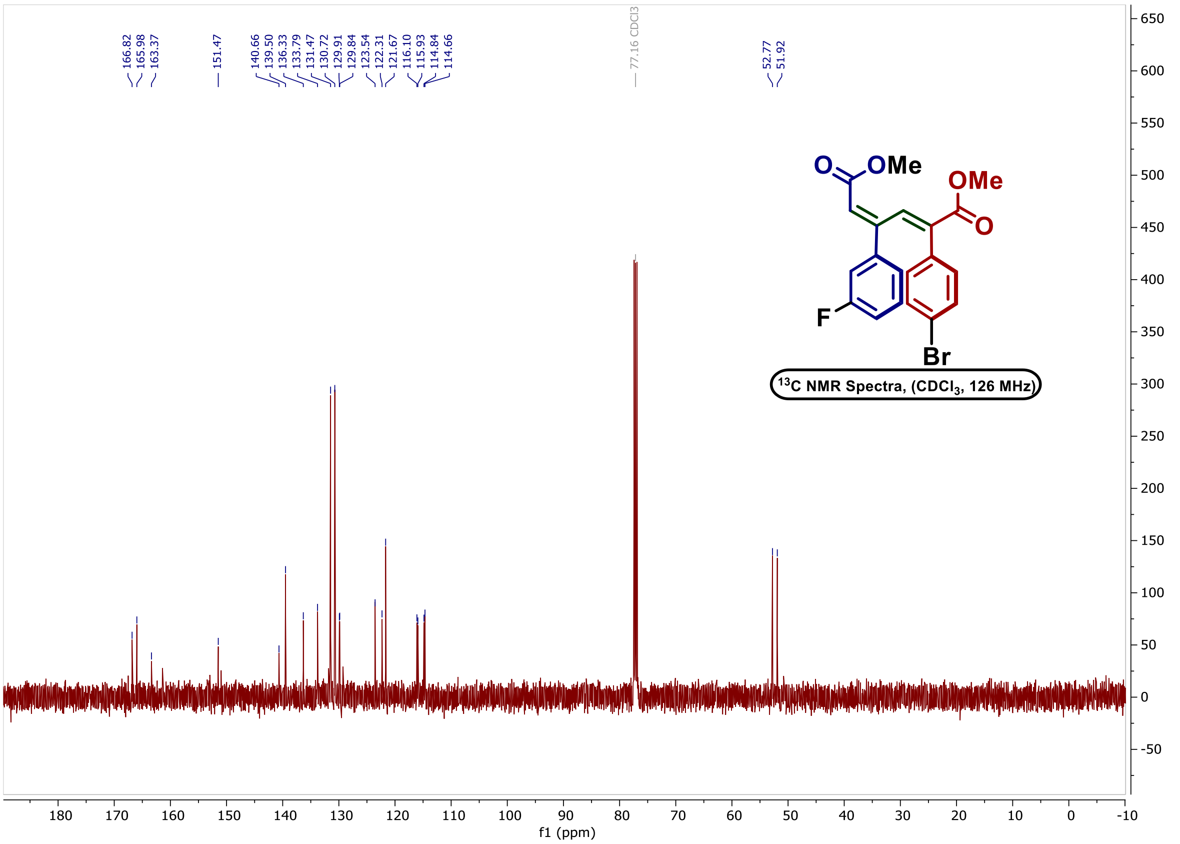
6-ethyl 1-methyl (*2E*,*4E*)-2-(4-bromophenyl)-4-(*m*-tolyl)hexa-2,4-dienedioate (3p)

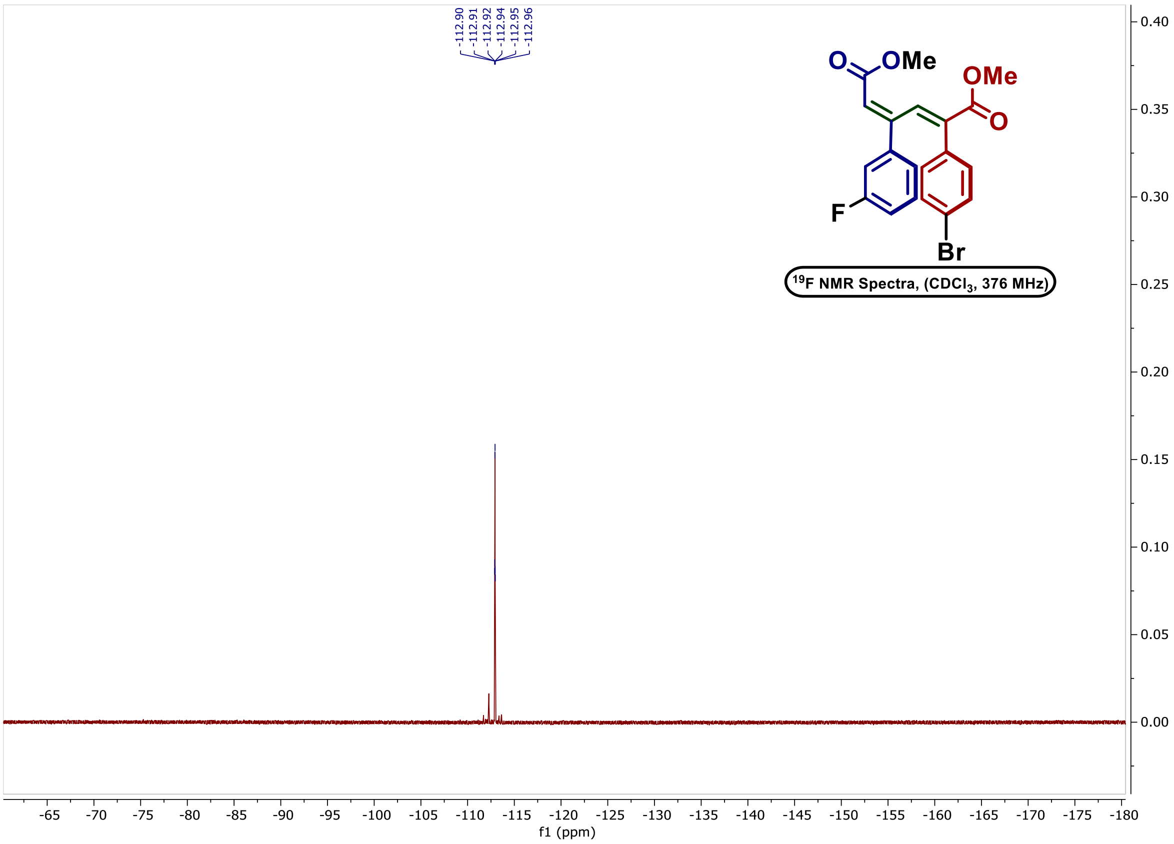




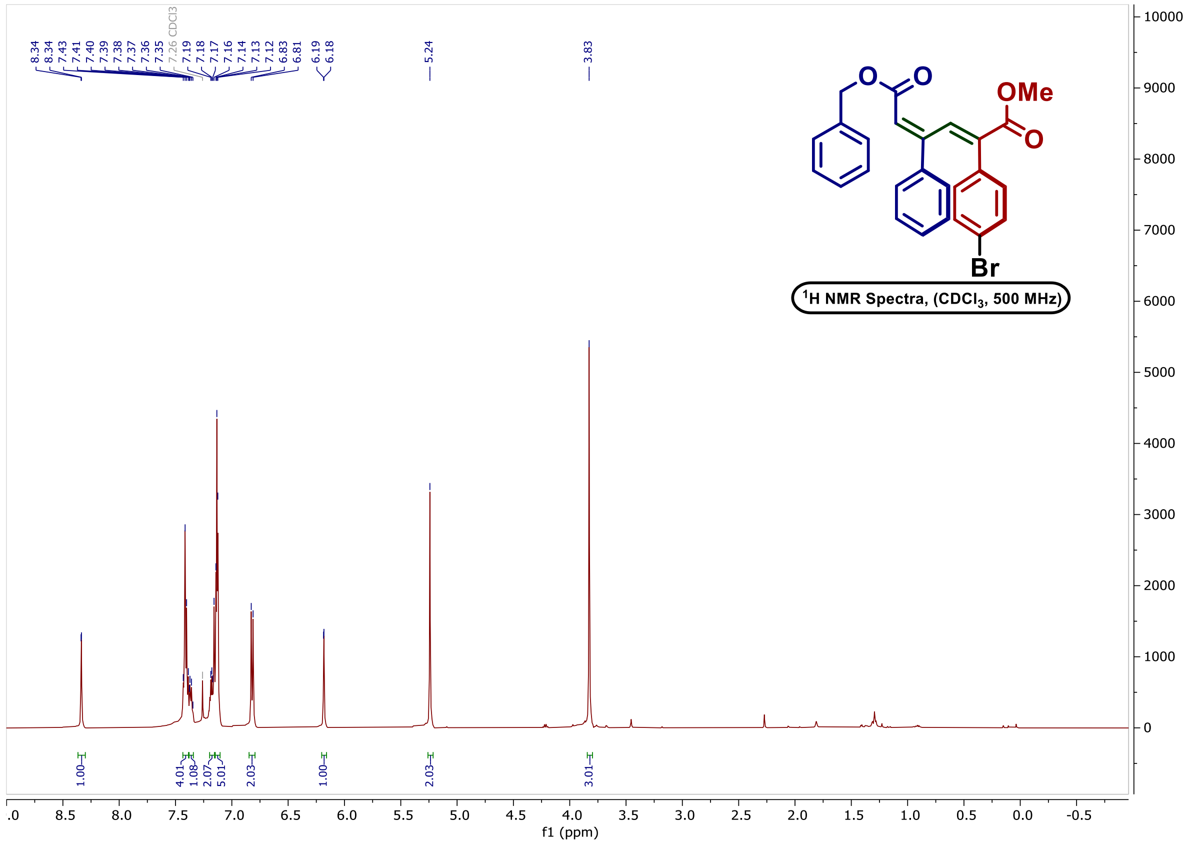
6-ethyl 1-methyl (*2E,4E*)-2-(4-bromophenyl)-4-(3-fluorophenyl)hexa-2,4-dienedioate (3q)

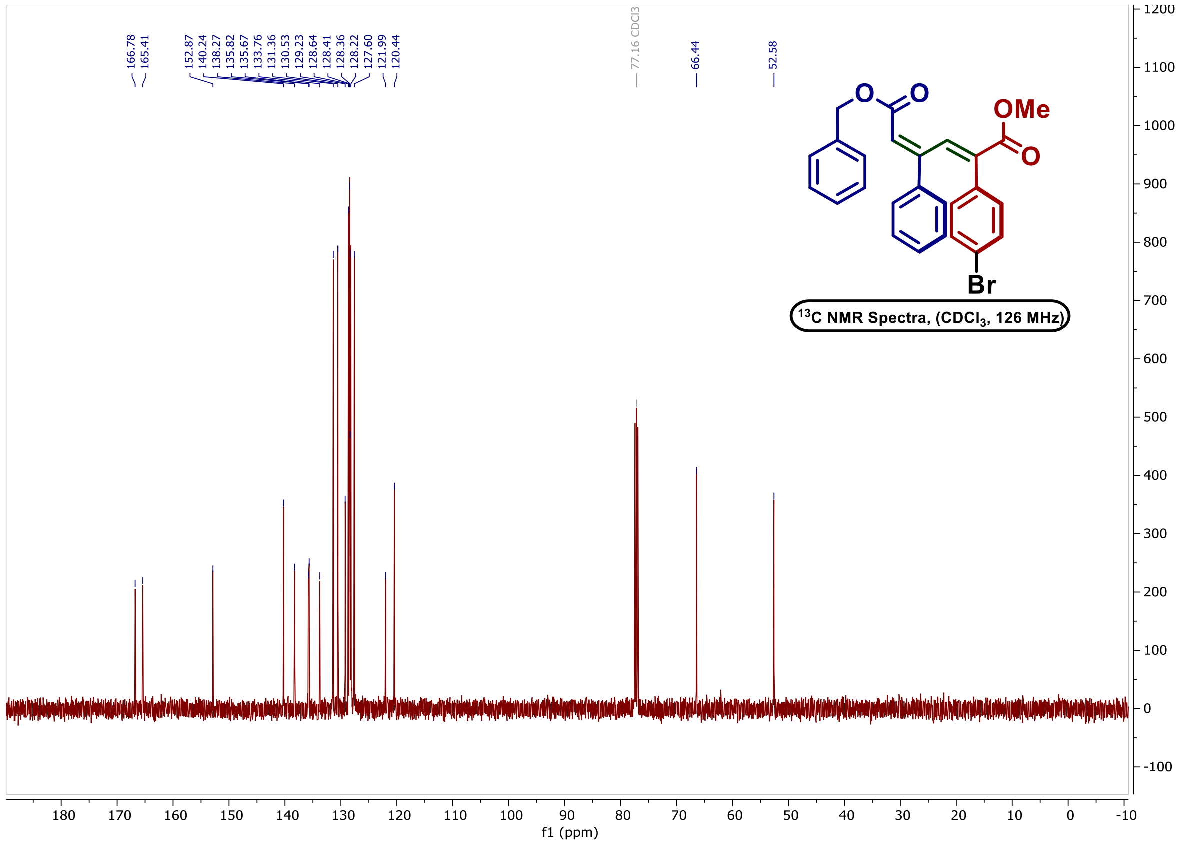




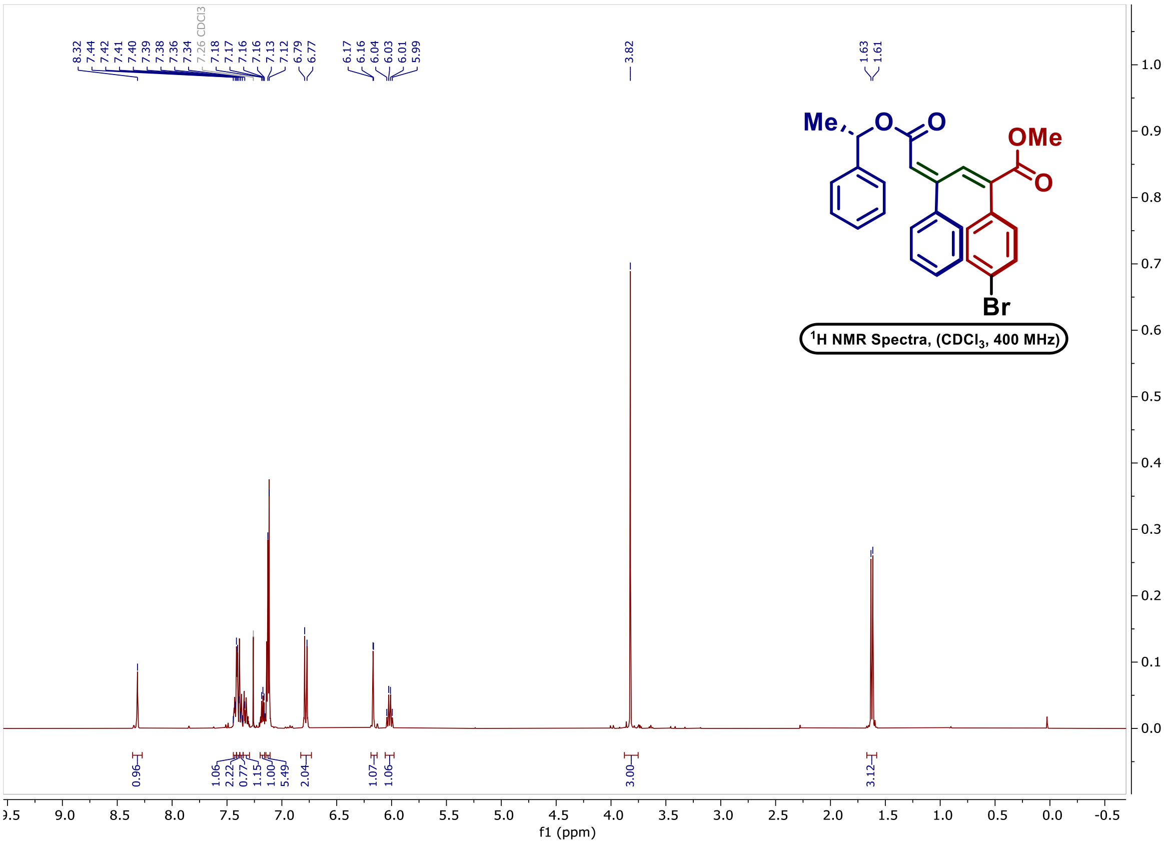

-112.90
-112.91
-112.92
-112.94
-112.95
-112.96
OMe
O
OMe
O
F
Br
^{19}F NMR Spectra, (CDCl$_3$, 376 MHz)
0.40
0.35
0.30
0.25
0.20
0.15
0.10
0.05
0.00
-65
-70
-75
-80
-85
-90
-95
-100
-105
-110
-115
-120
-125
-130
-135
-140
-145
-150
-155
-160
-165
-170
-175
-180
f1 (ppm)

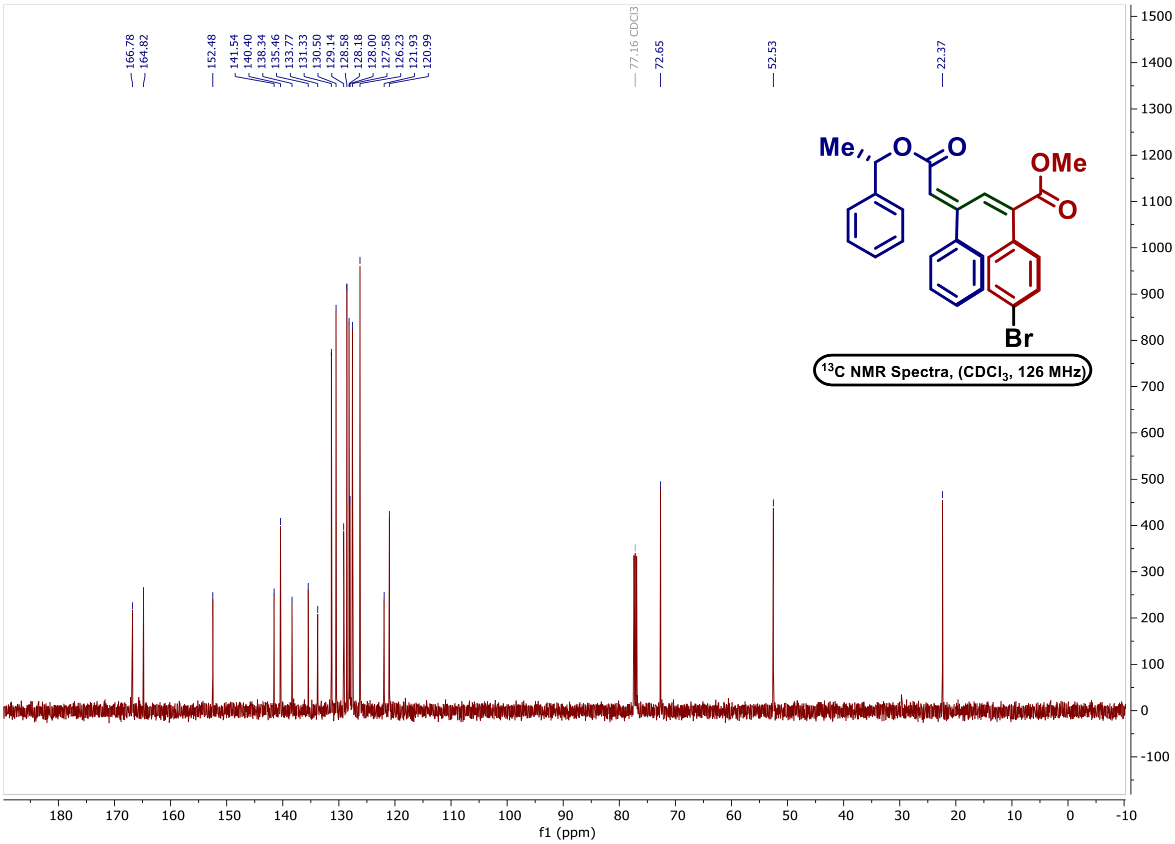
6-benzyl 1-methyl (2*E*,4*E*)-2-(4-bromophenyl)-4-phenylhexa-2,4-dienedioate (3s)



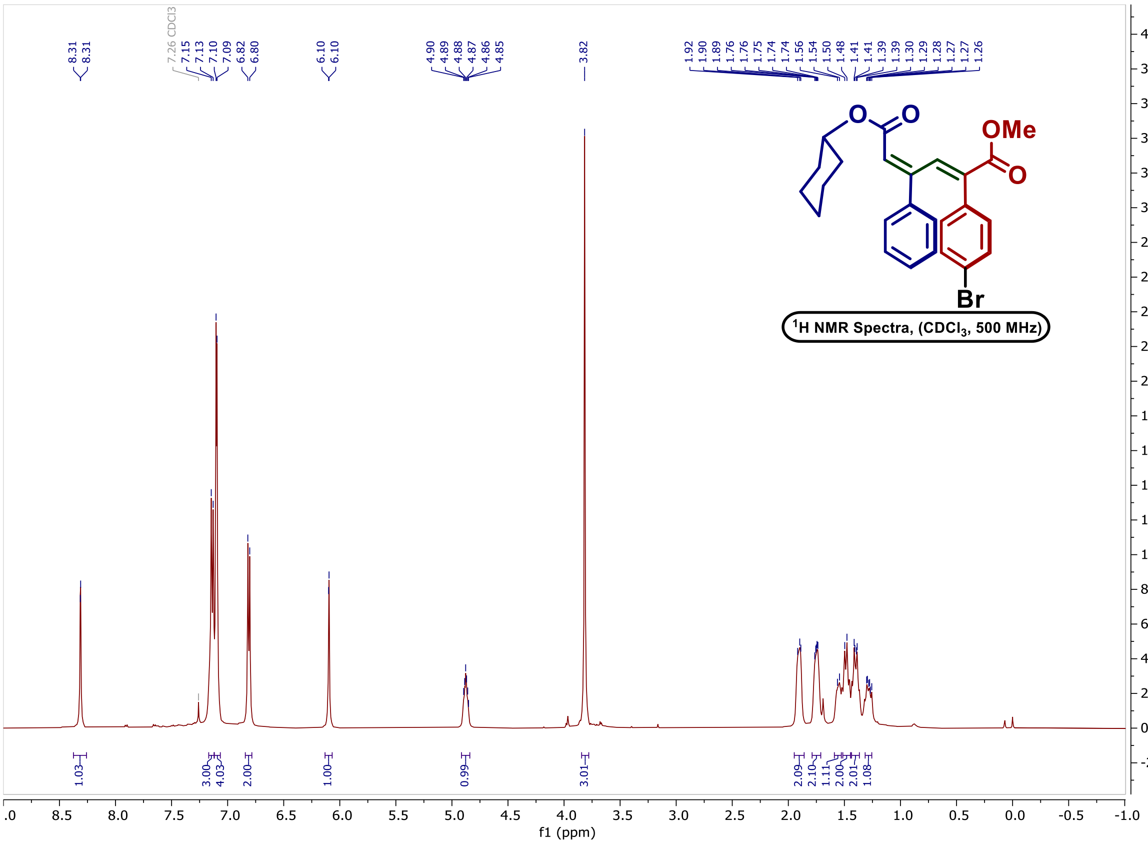


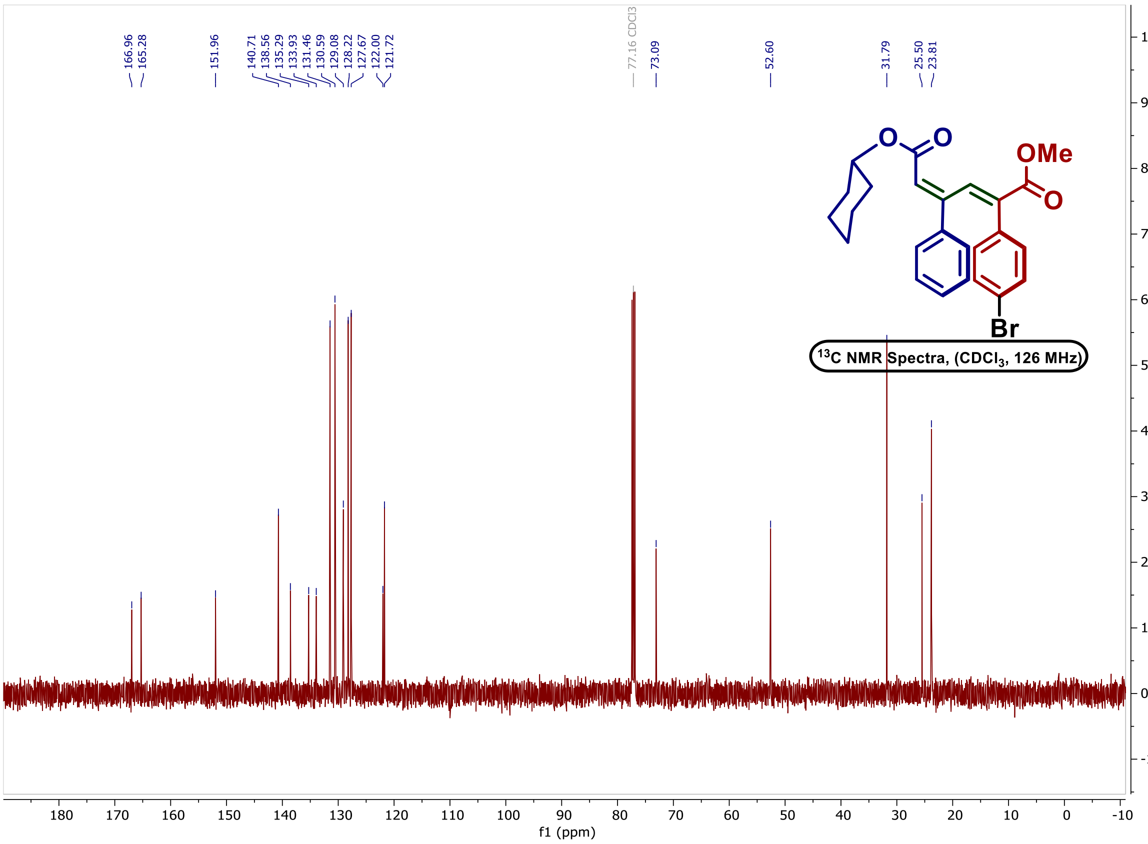
1-methyl 6-(1-phenylethyl) (*2E,4E*)-2-(4-bromophenyl)-4-phenylhexa-2,4-dienedioate (3t)



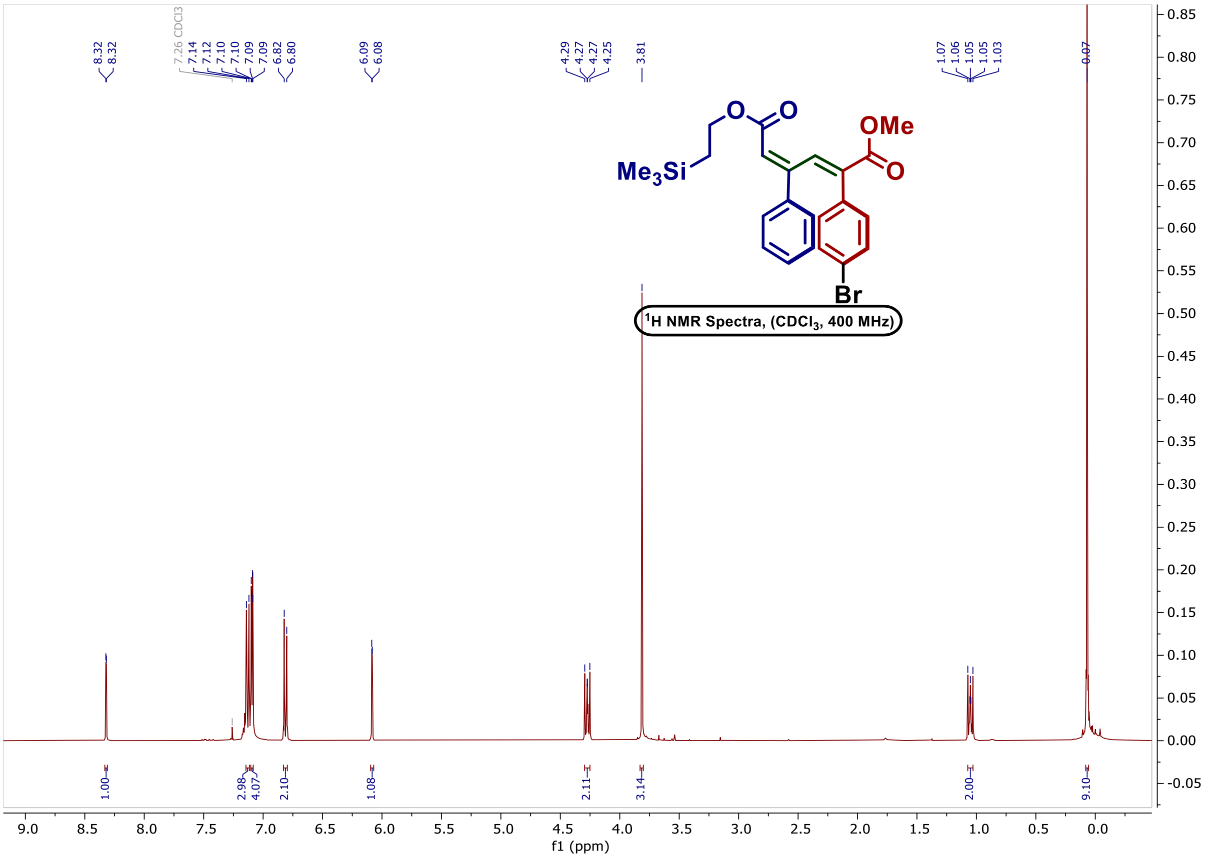


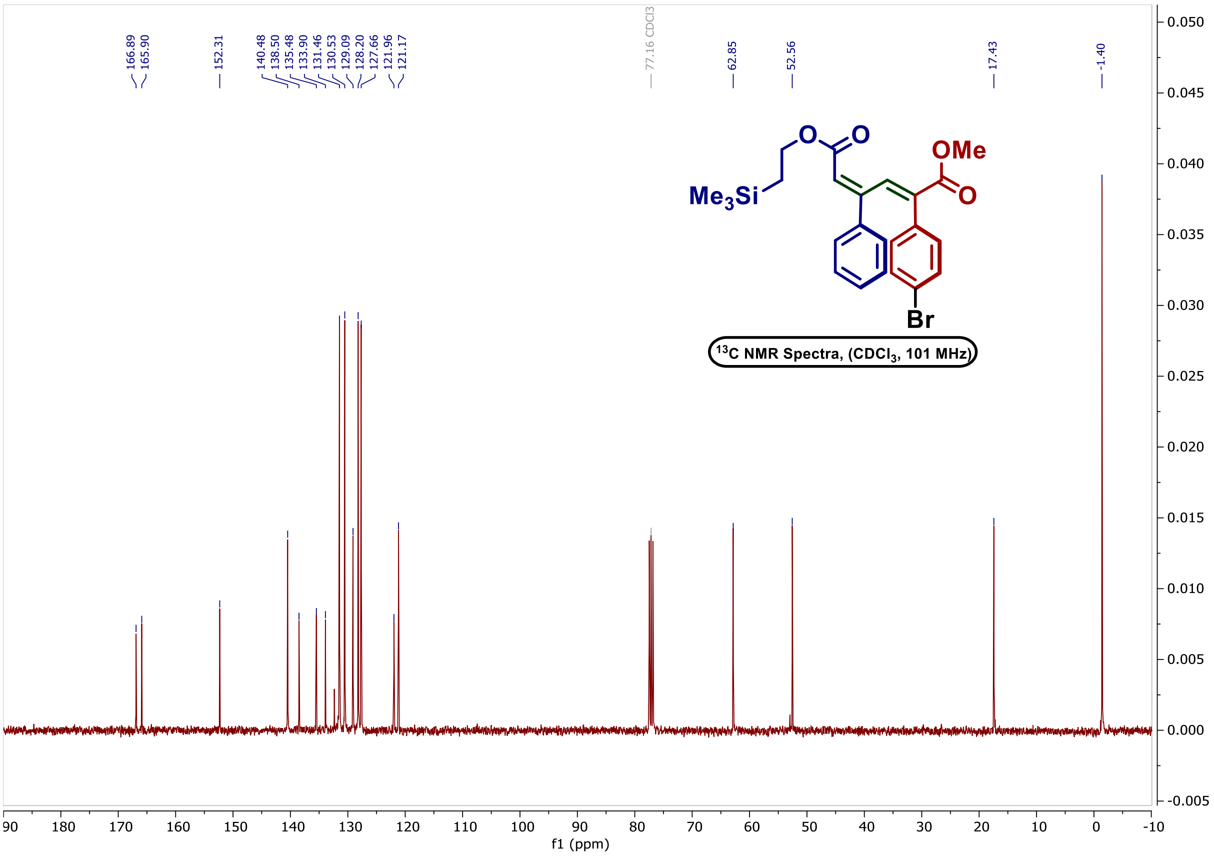
6-cyclohexyl 1-methyl (*2E,4E*)-2-(4-bromophenyl)-4-phenylhexa-2,4-dienedioate (3u)



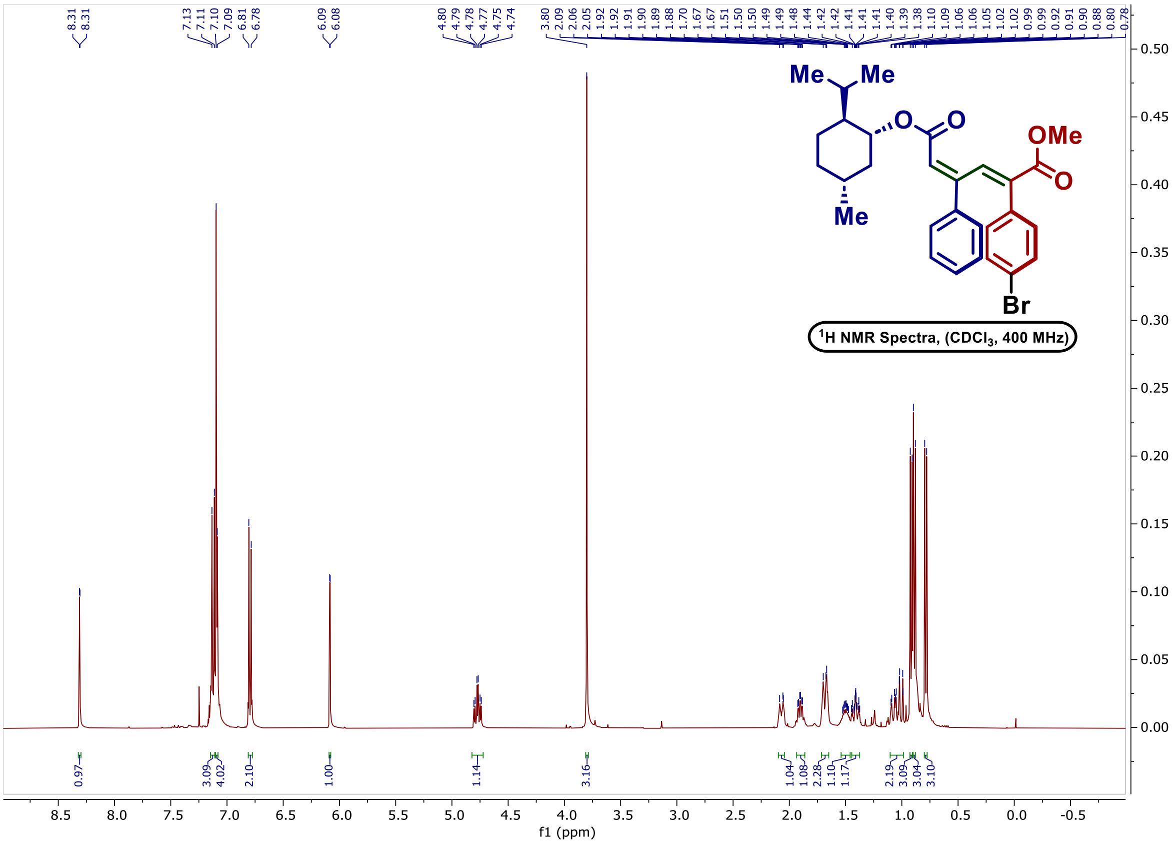


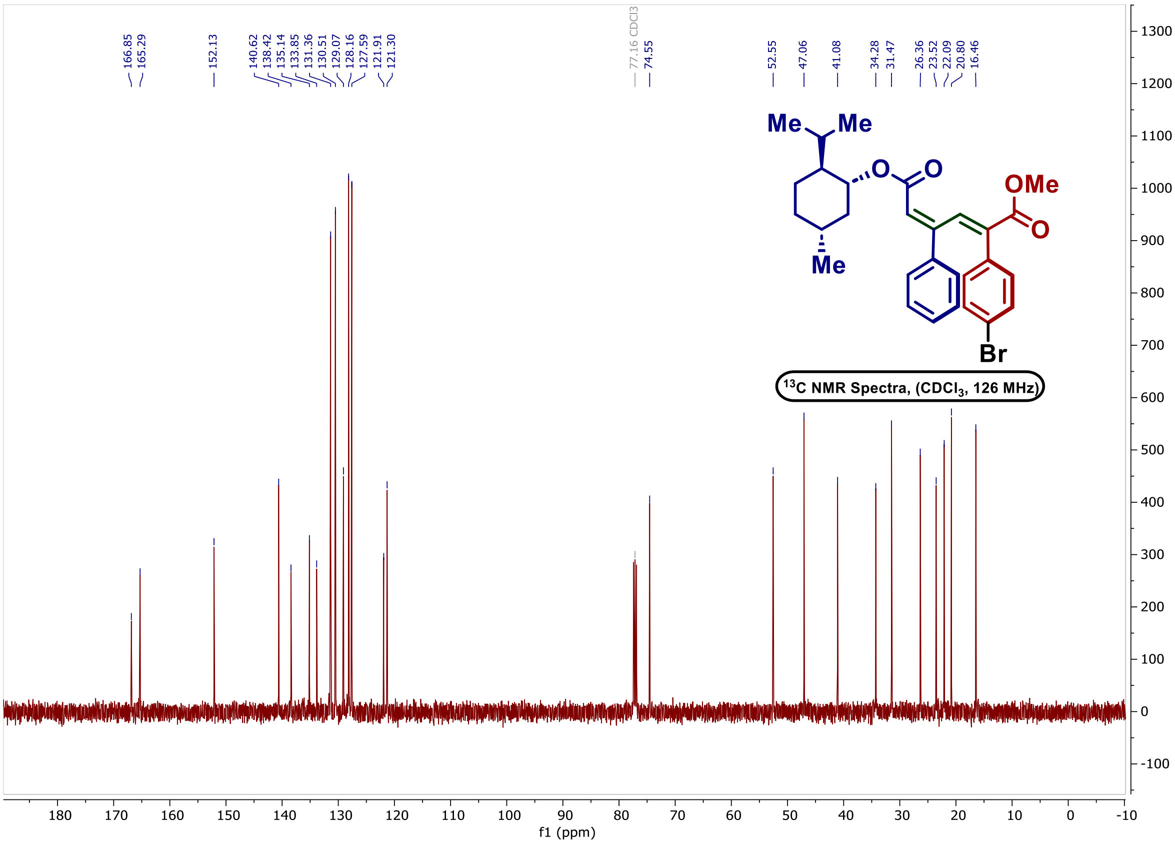
1-methyl 6-(2-(trimethylsilyl)ethyl) (*2E*,*4E*)-2-(4-bromophenyl)-4-phenylhexa-2,4-dienedioate (3v)



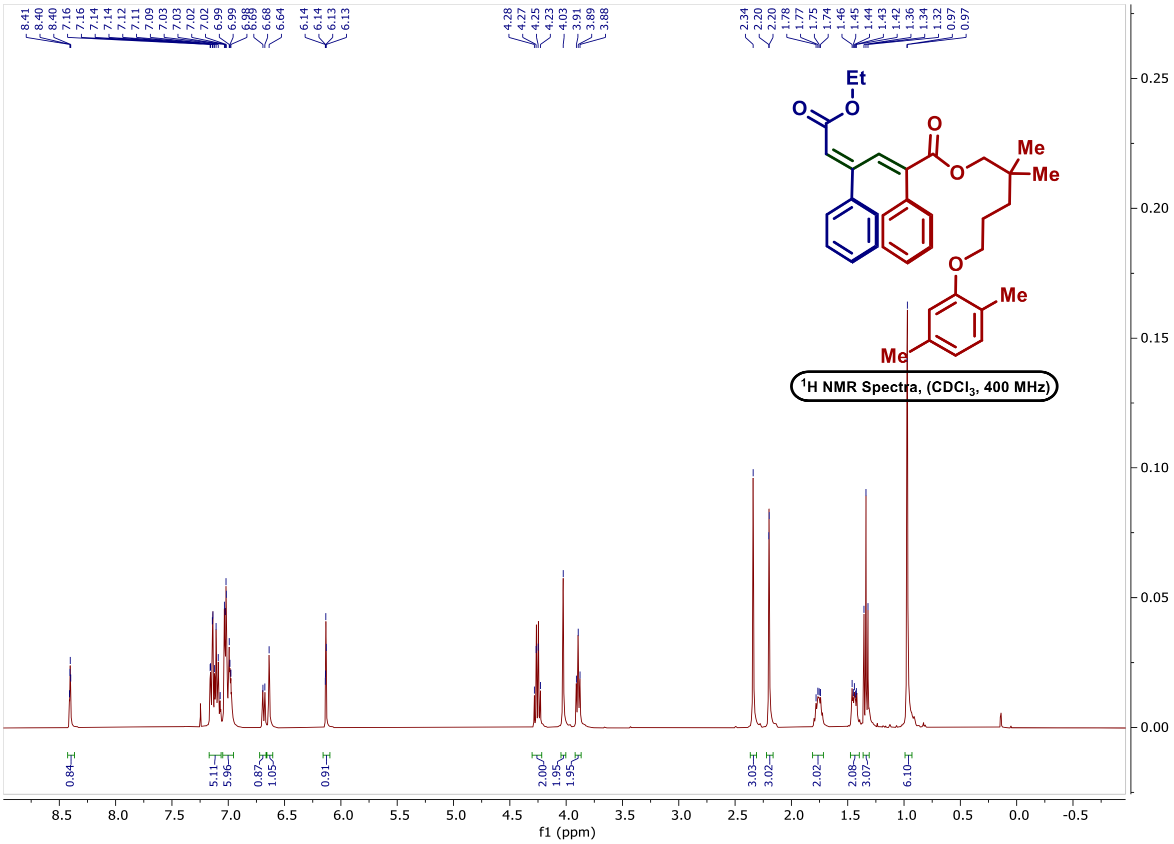


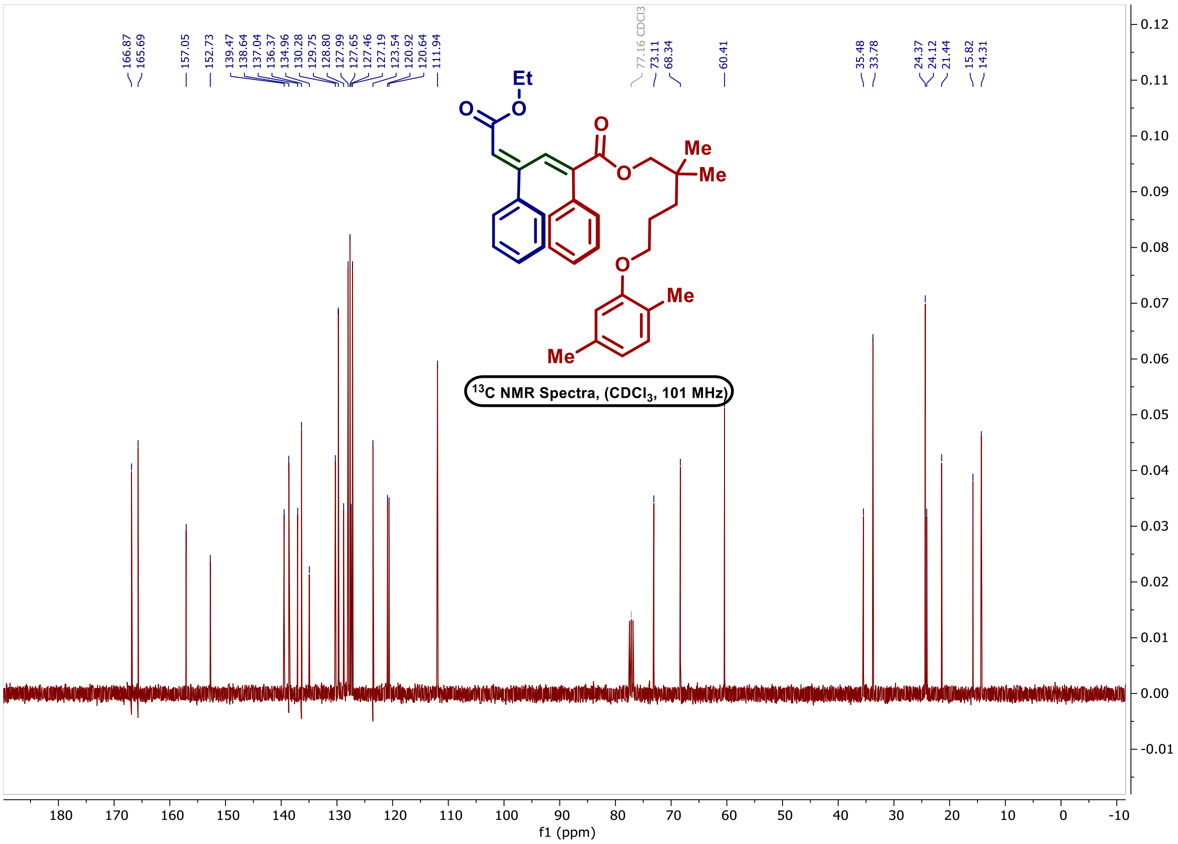
6-((1R,2S,5R)-2-isopropyl-5-methylcyclohexyl) 1-methyl (2E,4E)-2-(4-bromophenyl)-4-phenylhexa-2,4-dienedioate (3w)



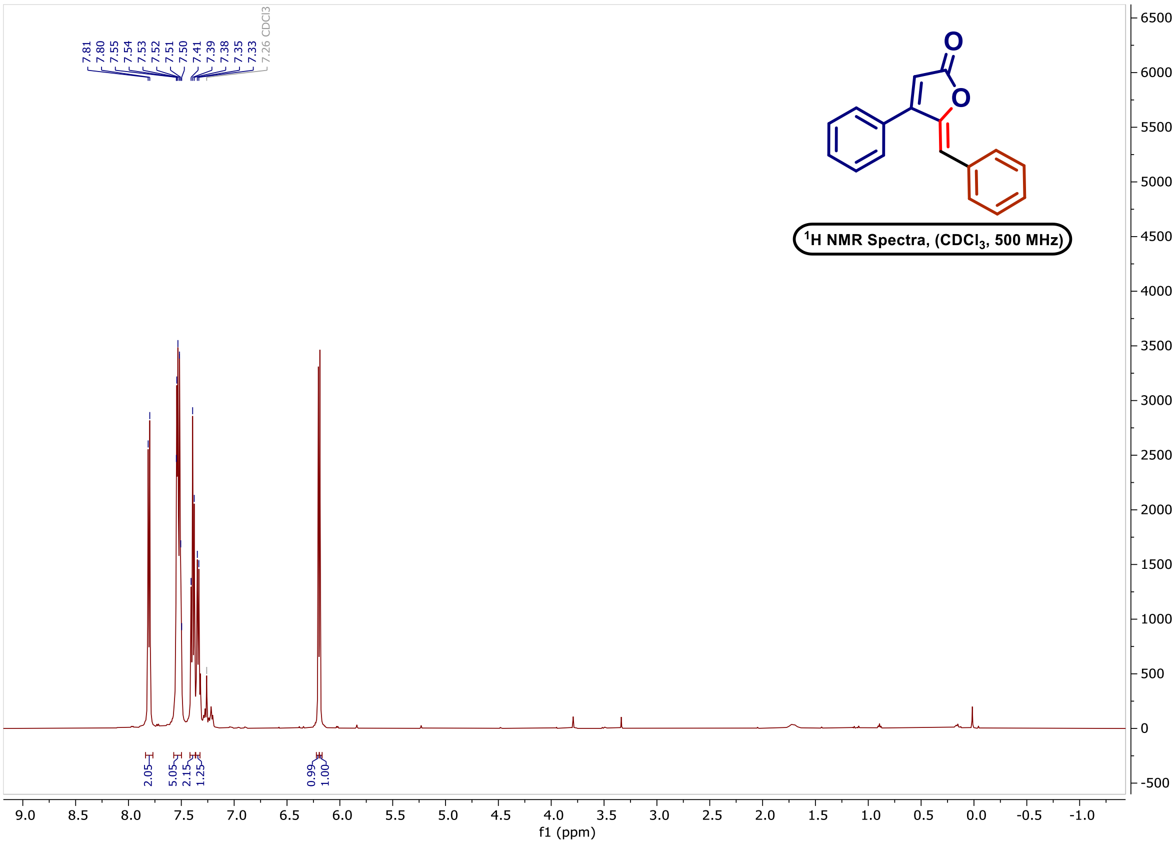


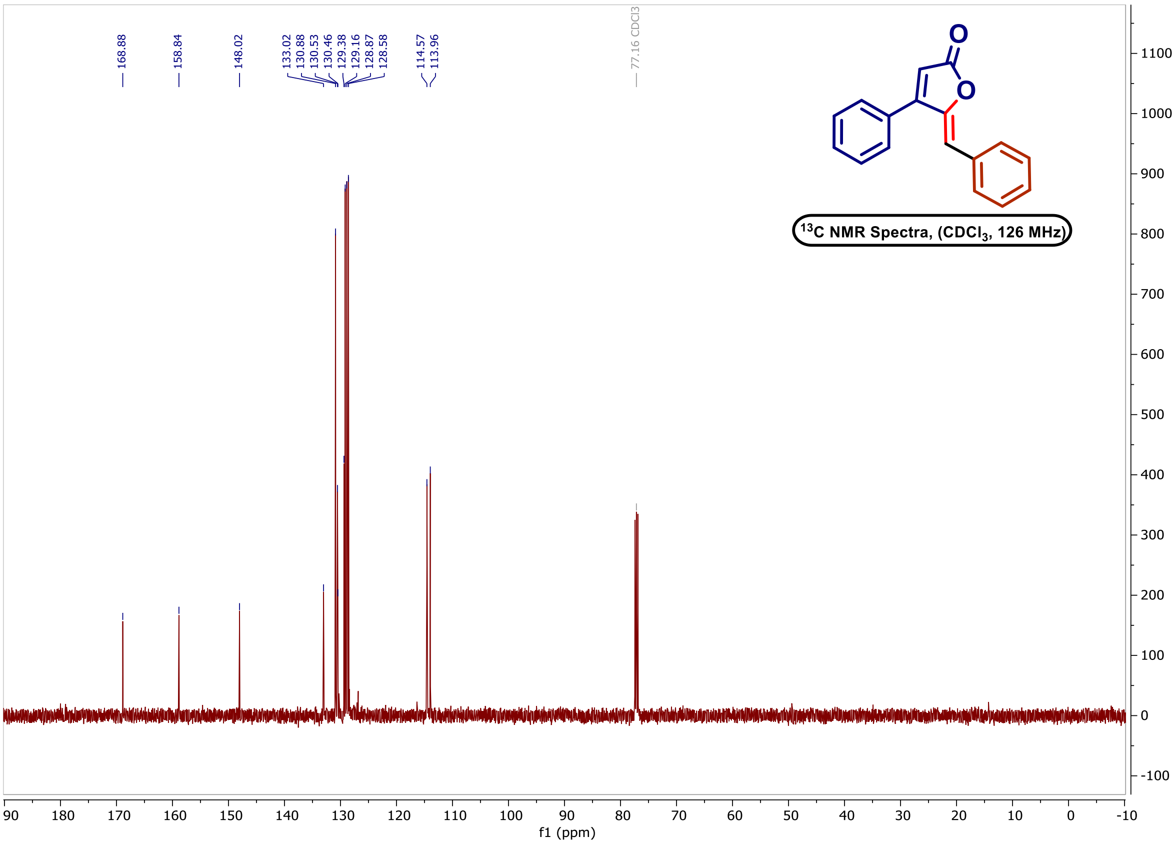
1-(5-(2,6-dimethylphenoxy)-2,2-dimethylpentyl) 6-ethyl (2*E*,4*E*)-2,4-diphenylhexa-2,4-dienedioate (3x)



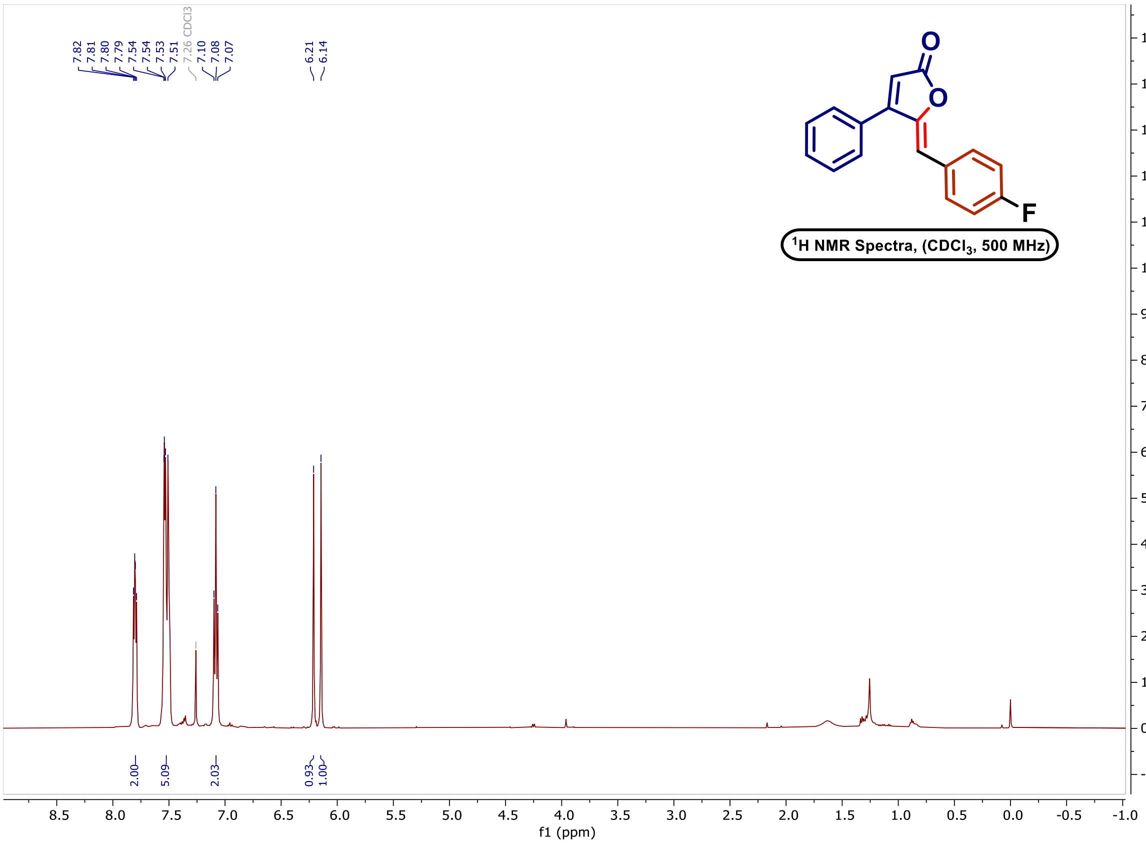


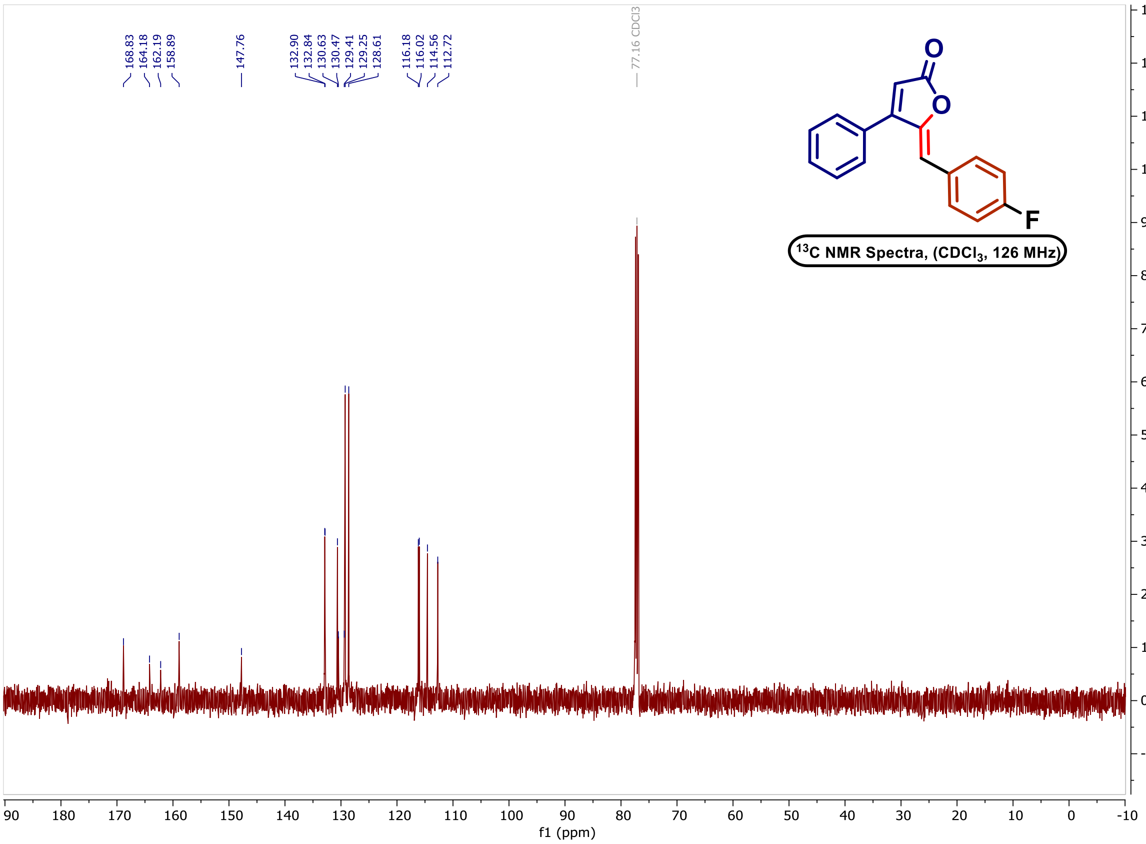
(*Z*)-5-benzylidene-4-phenylfuran-2(5*H*)-one (5a)



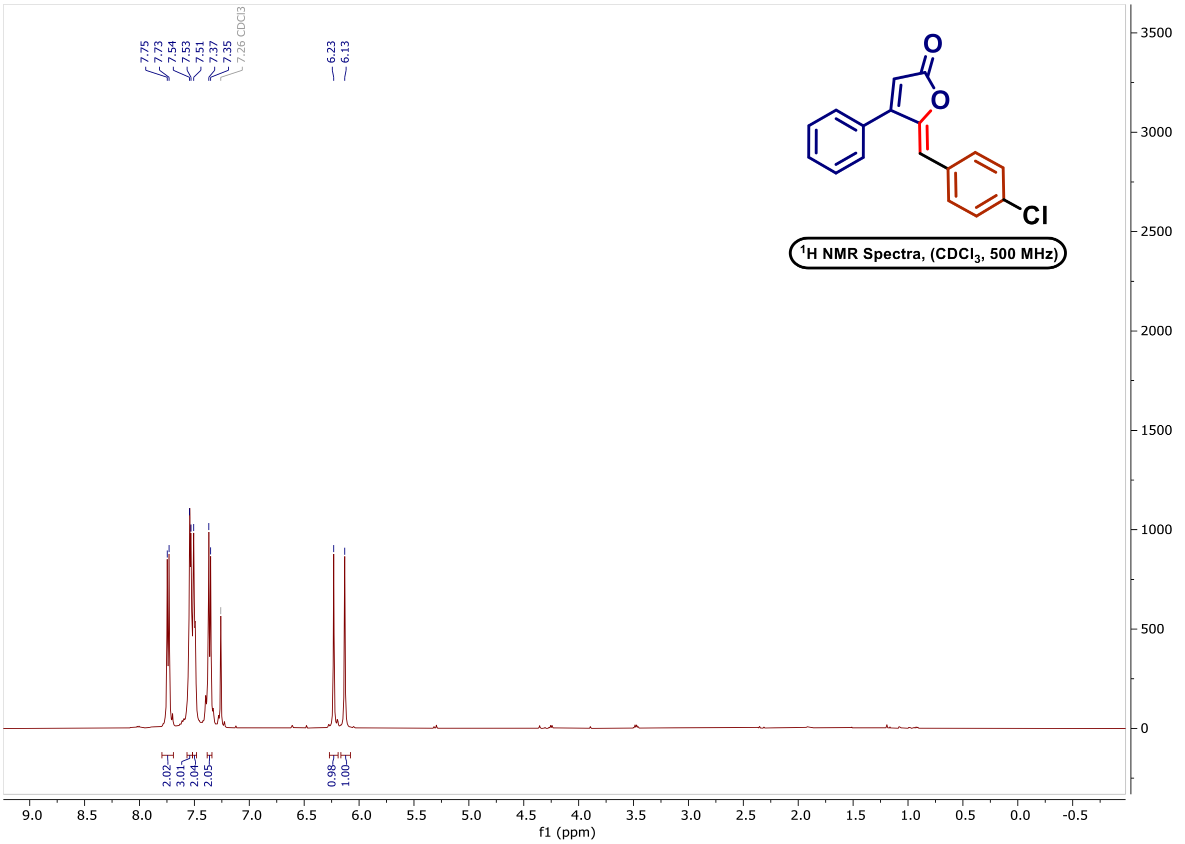


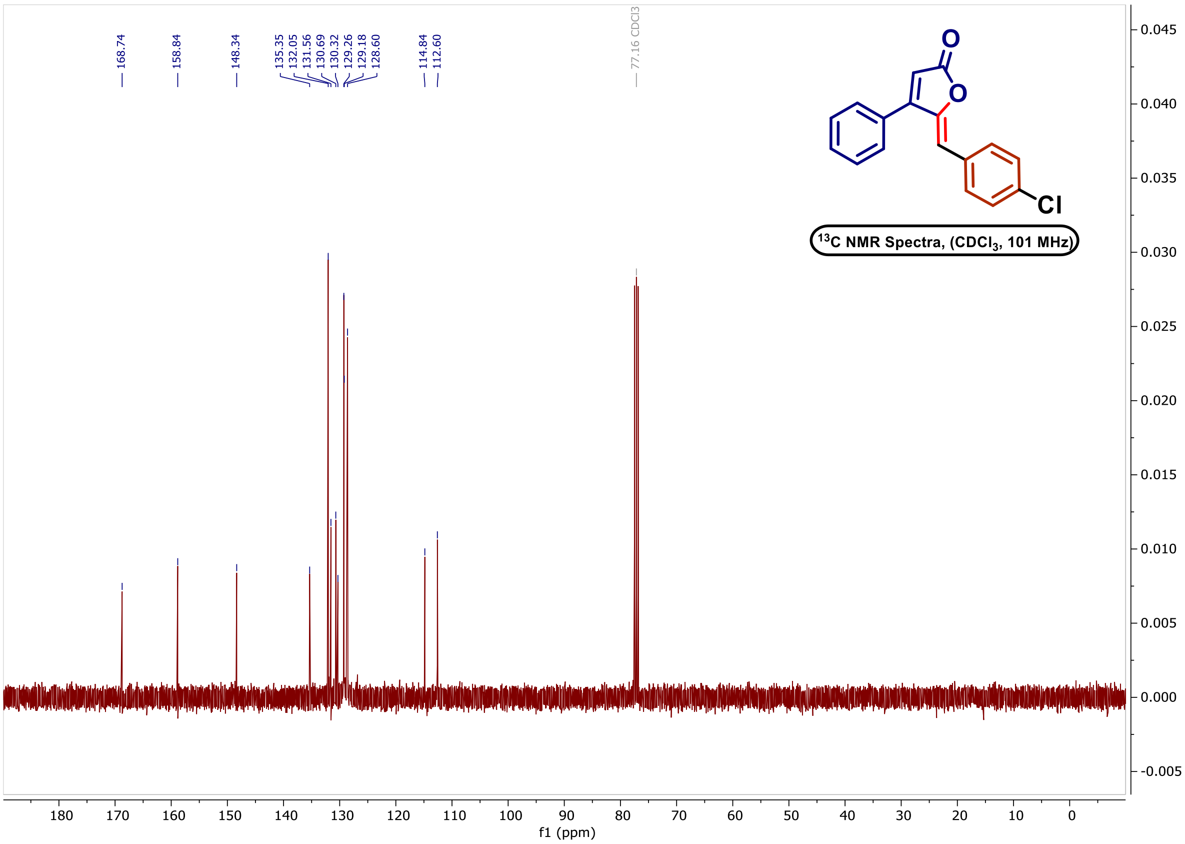
(*Z*)-5-(4-fluorobenzylidene)-4-phenylfuran-2(5*H*)-one (5b)



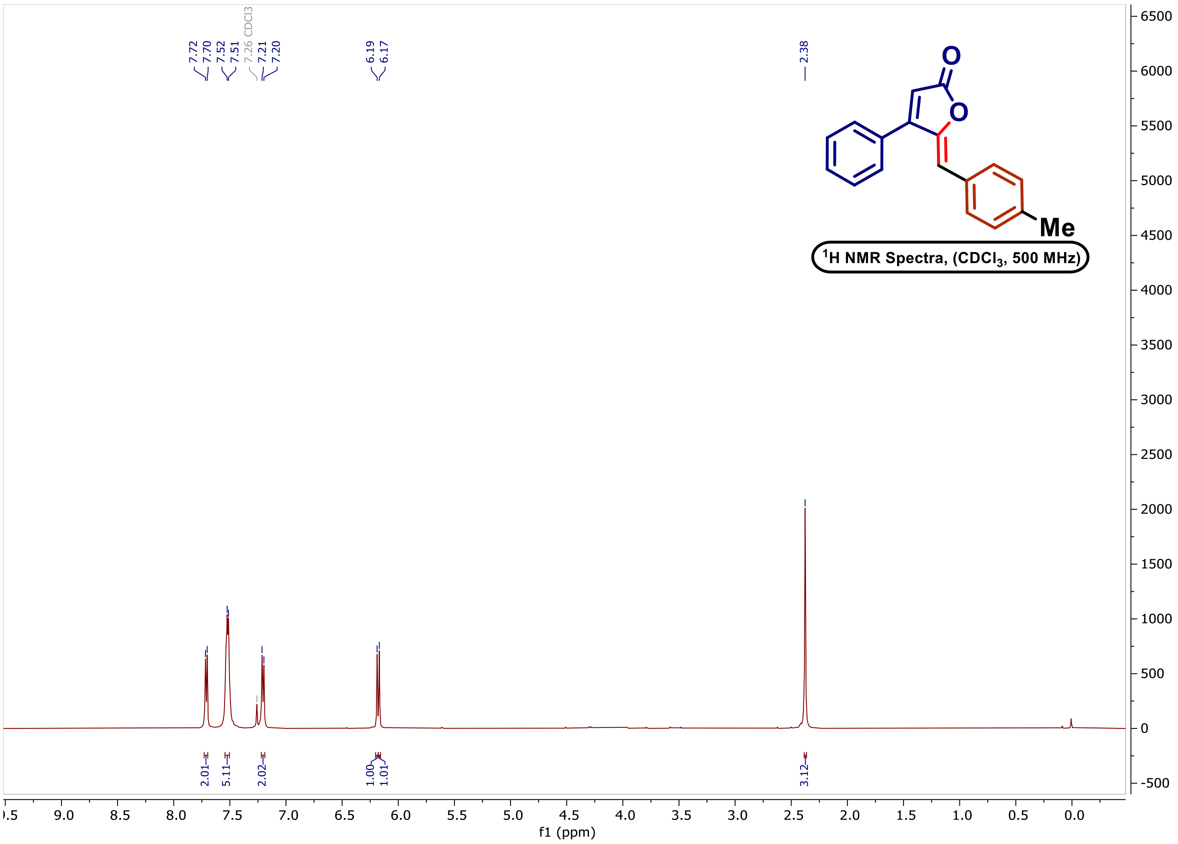


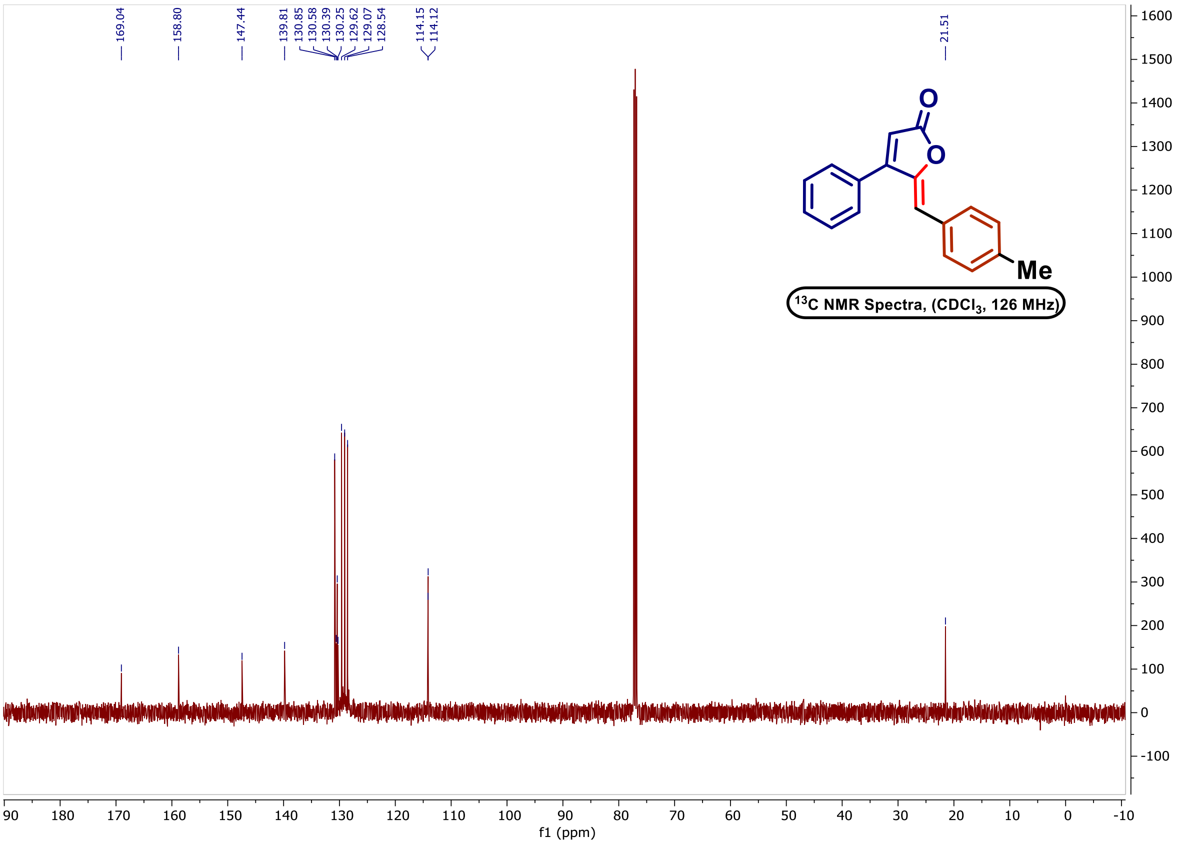
(*Z*)-5-(4-chlorobenzylidene)-4-phenylfuran-2(5*H*)-one (5c)



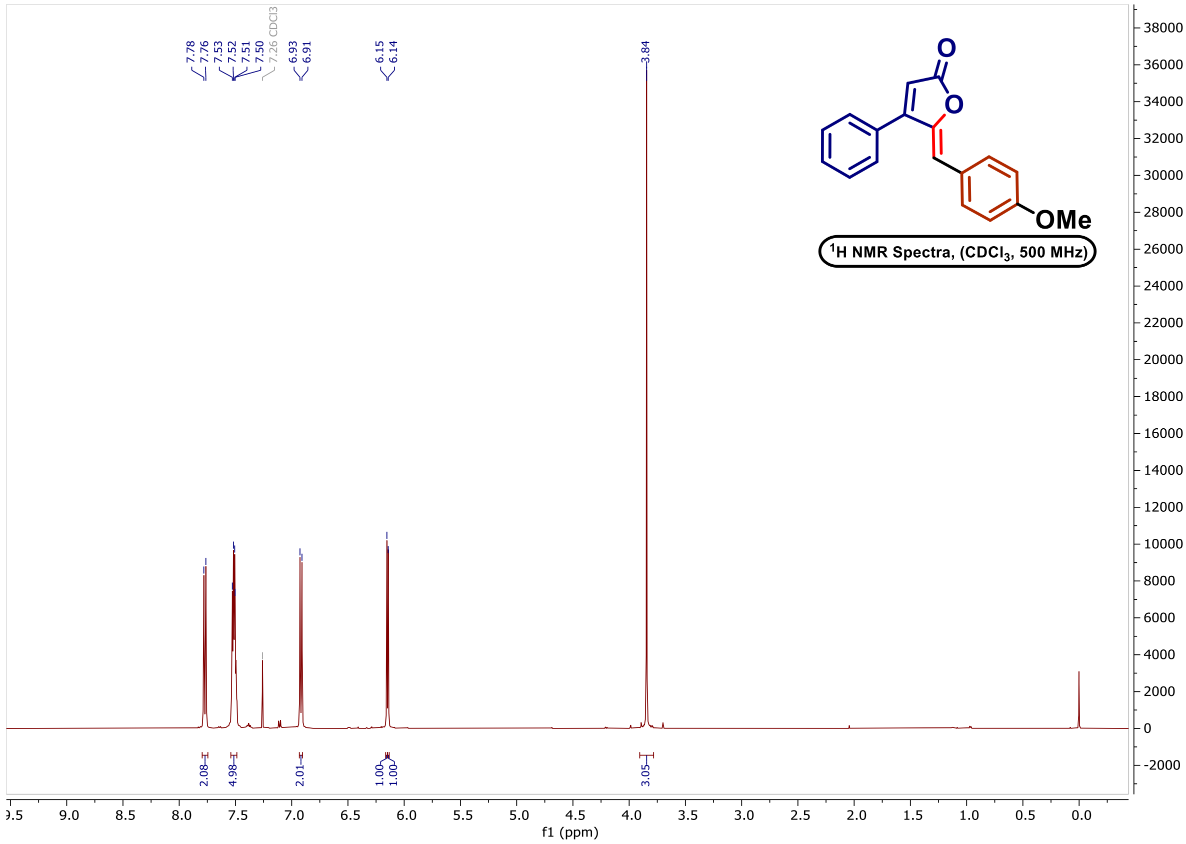


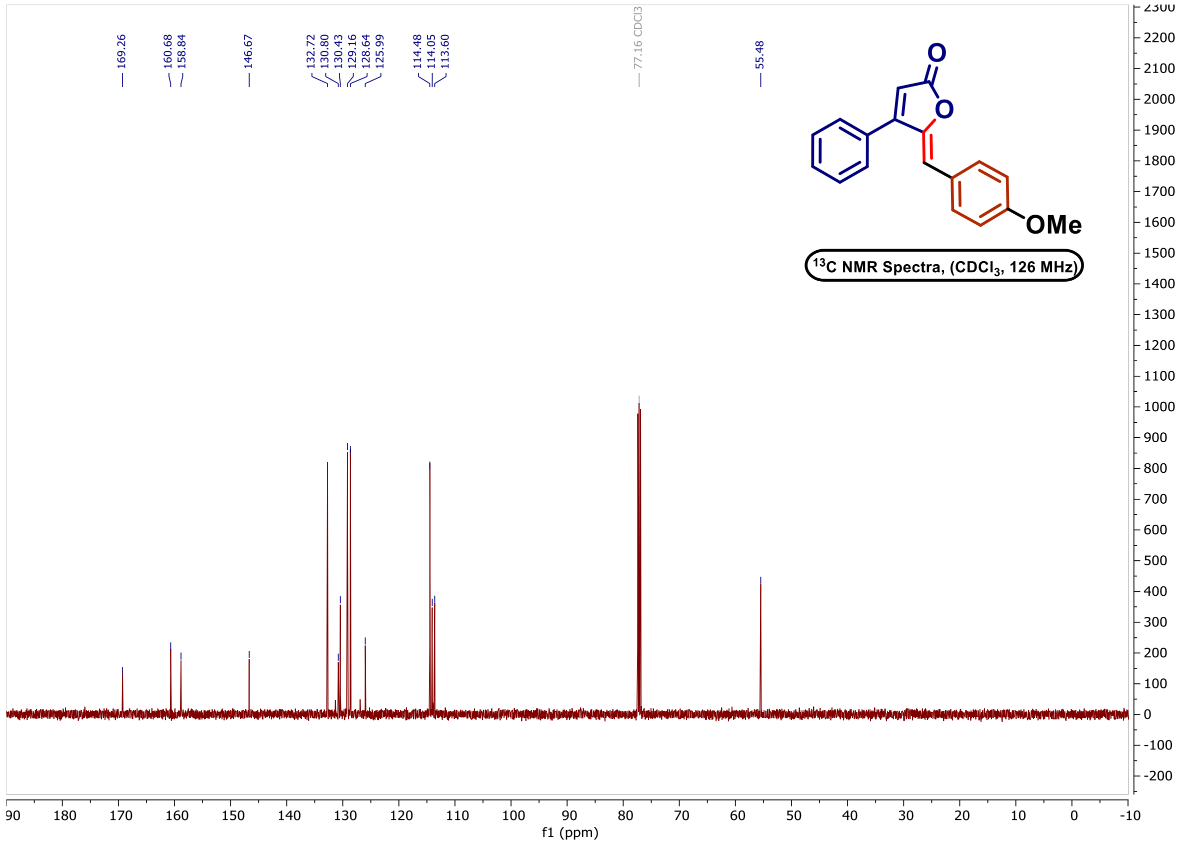
(*Z*)-5-(4-methylbenzylidene)-4-phenylfuran-2(5*H*)-one (5d)



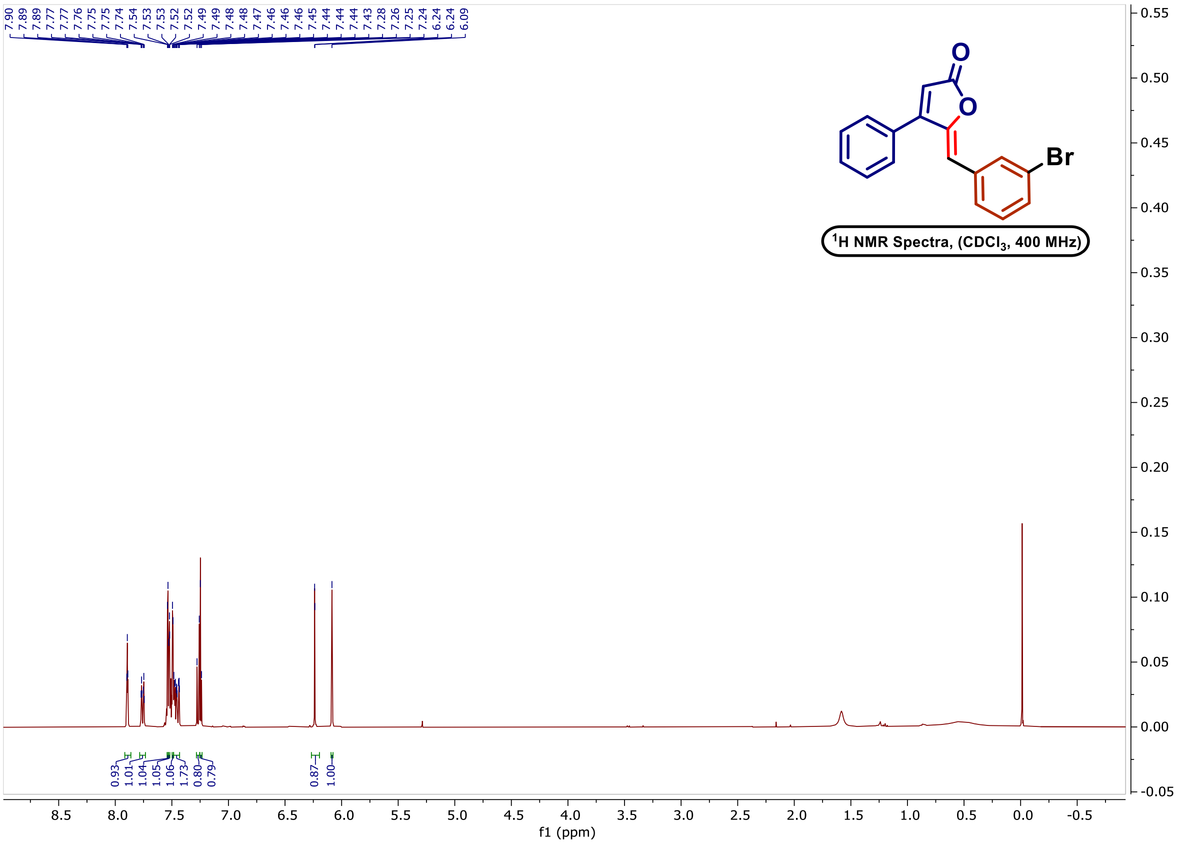


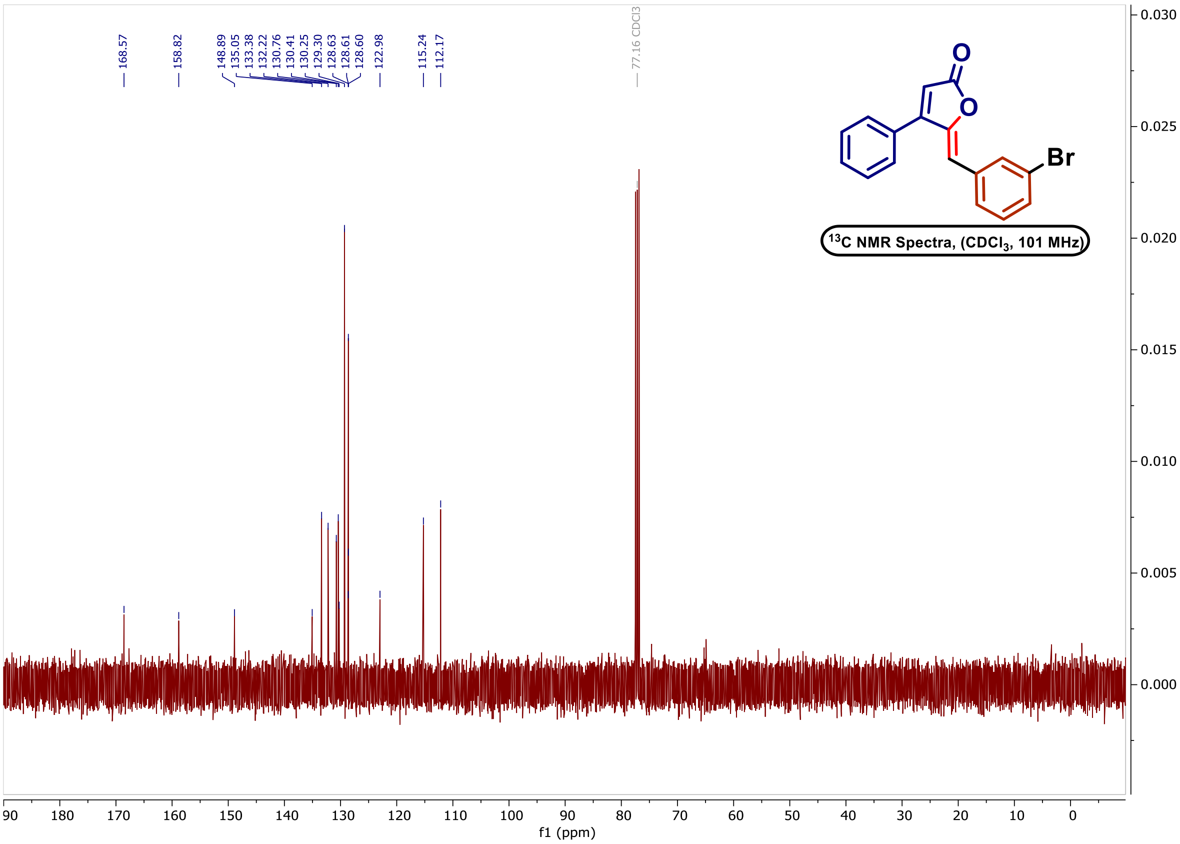
(*Z*)-5-(4-methoxybenzylidene)-4-phenylfuran-2(5*H*)-one (5e)



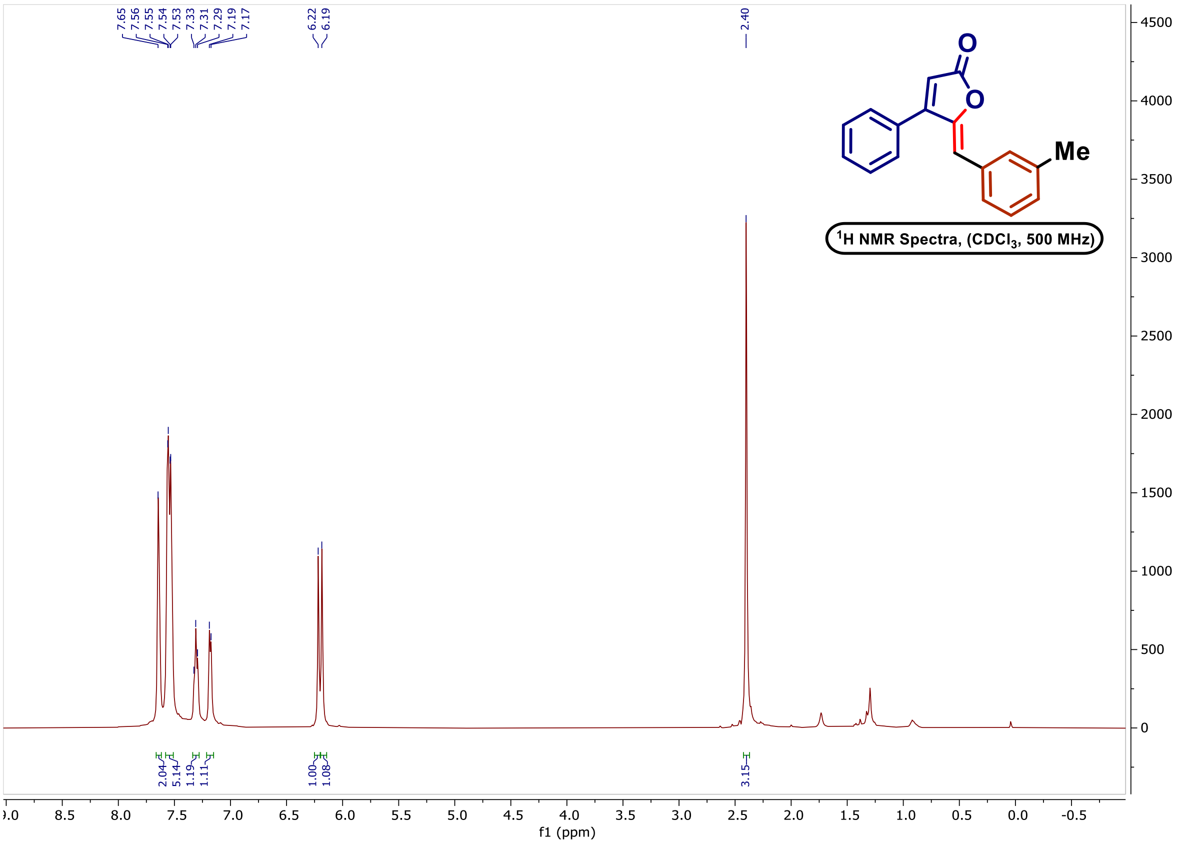


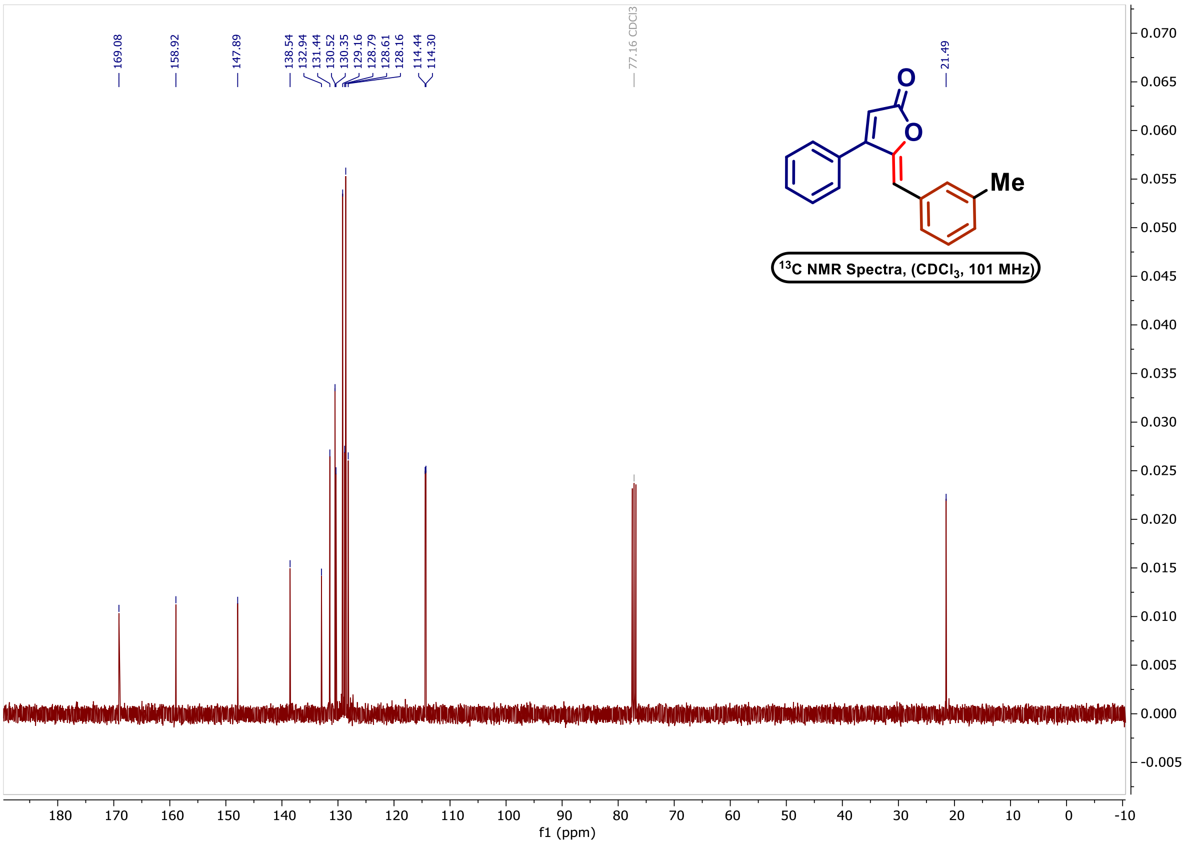
(*Z*)-5-(3-bromobenzylidene)-4-phenylfuran-2(5*H*)-one (5f)



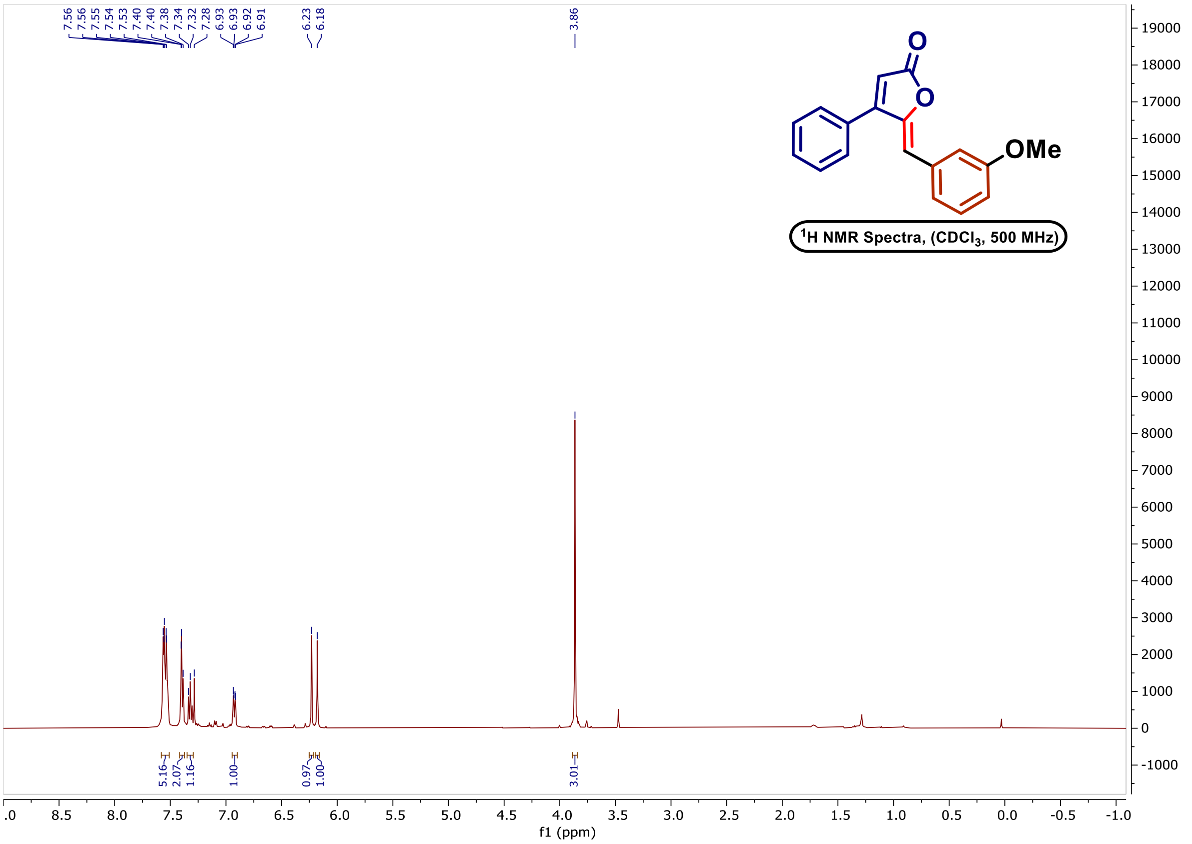


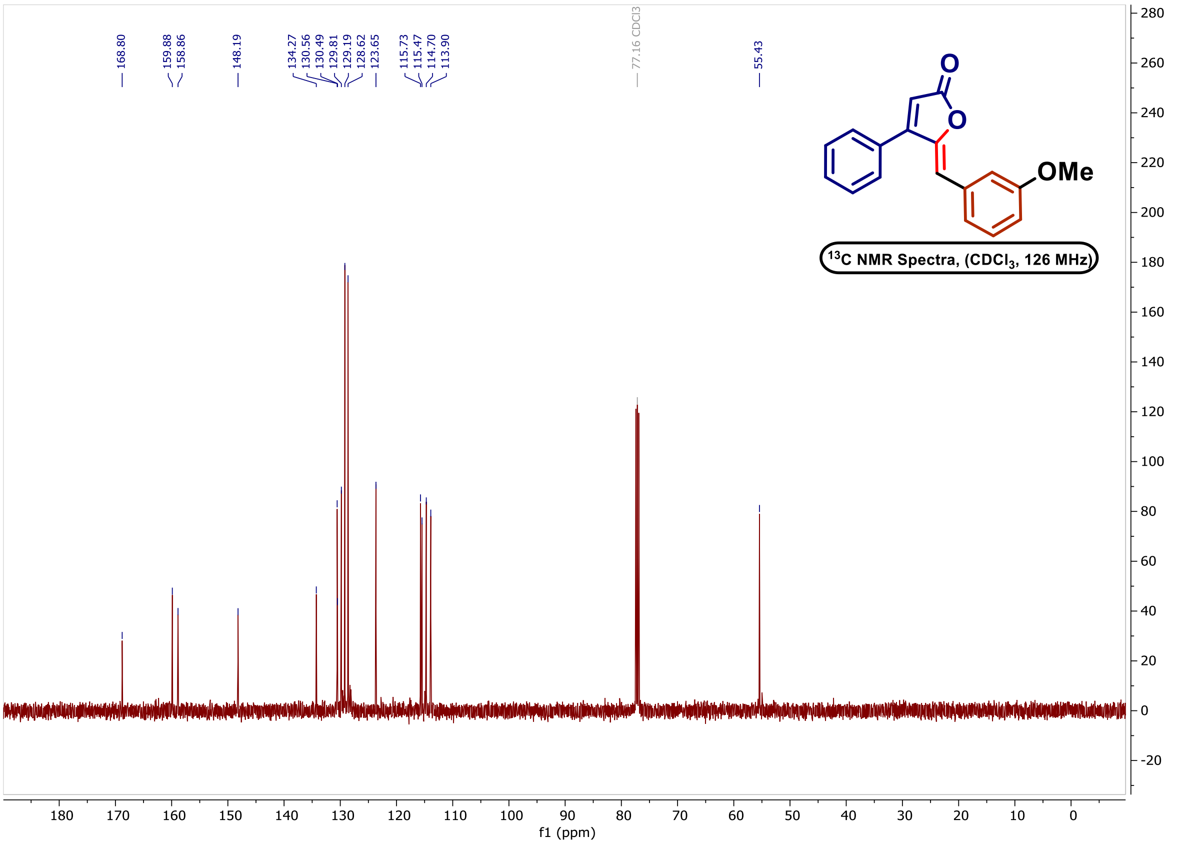
(*Z*)-5-(3-methylbenzylidene)-4-phenylfuran-2(5*H*)-one (5g)



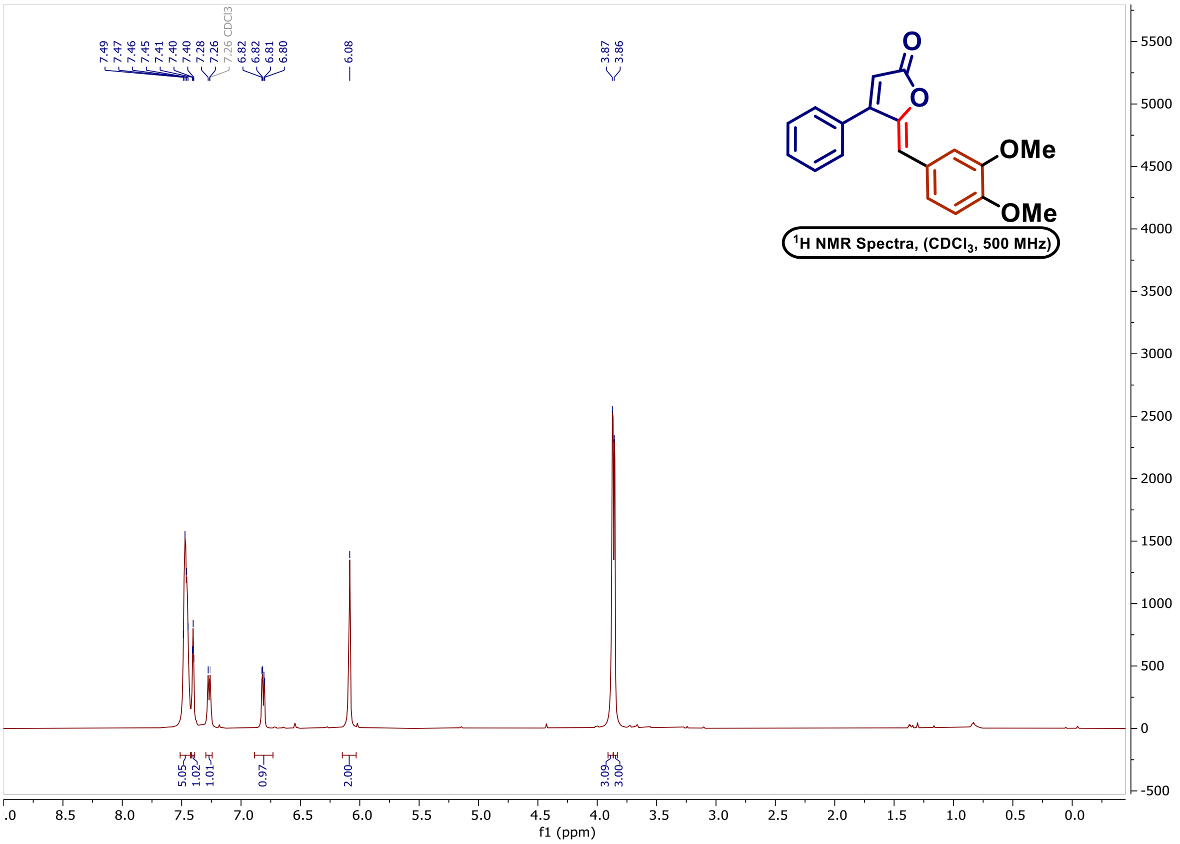


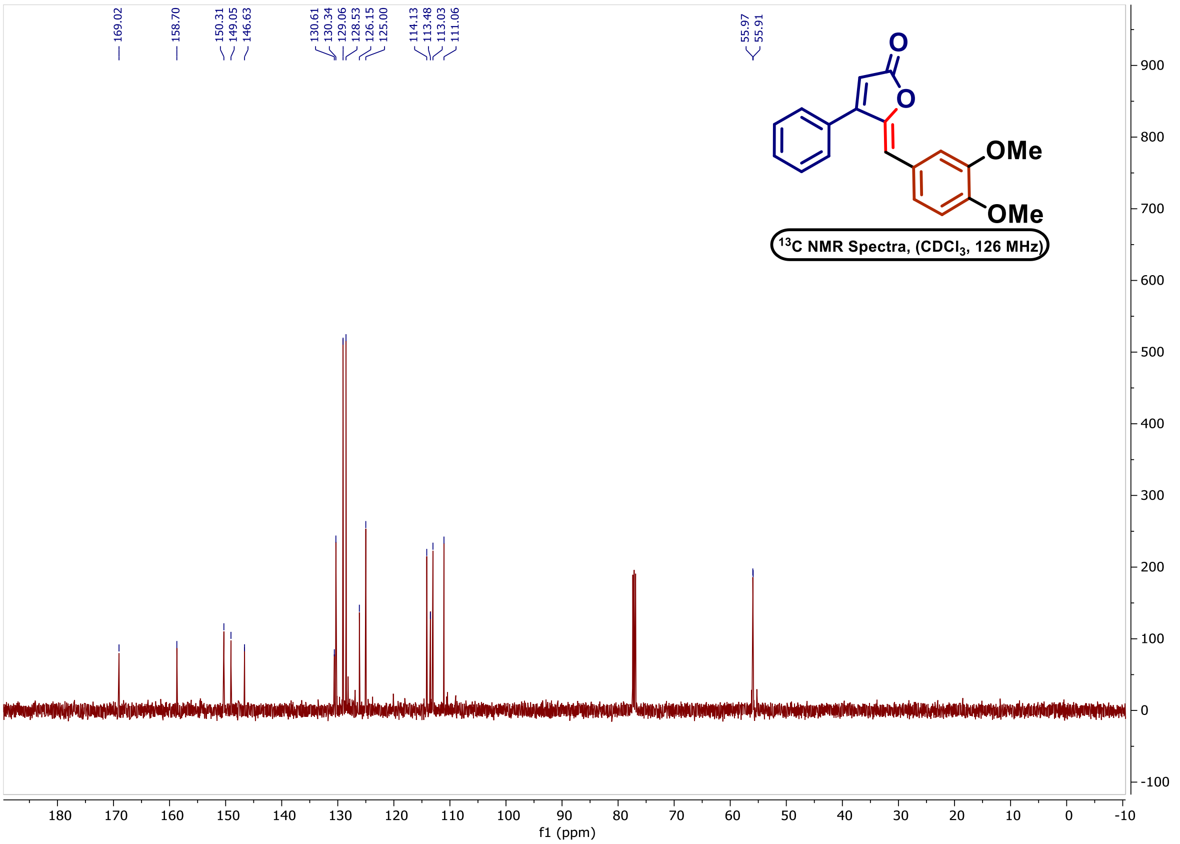
(*Z*)-5-(3-methoxybenzylidene)-4-phenylfuran-2(5*H*)-one (5h)



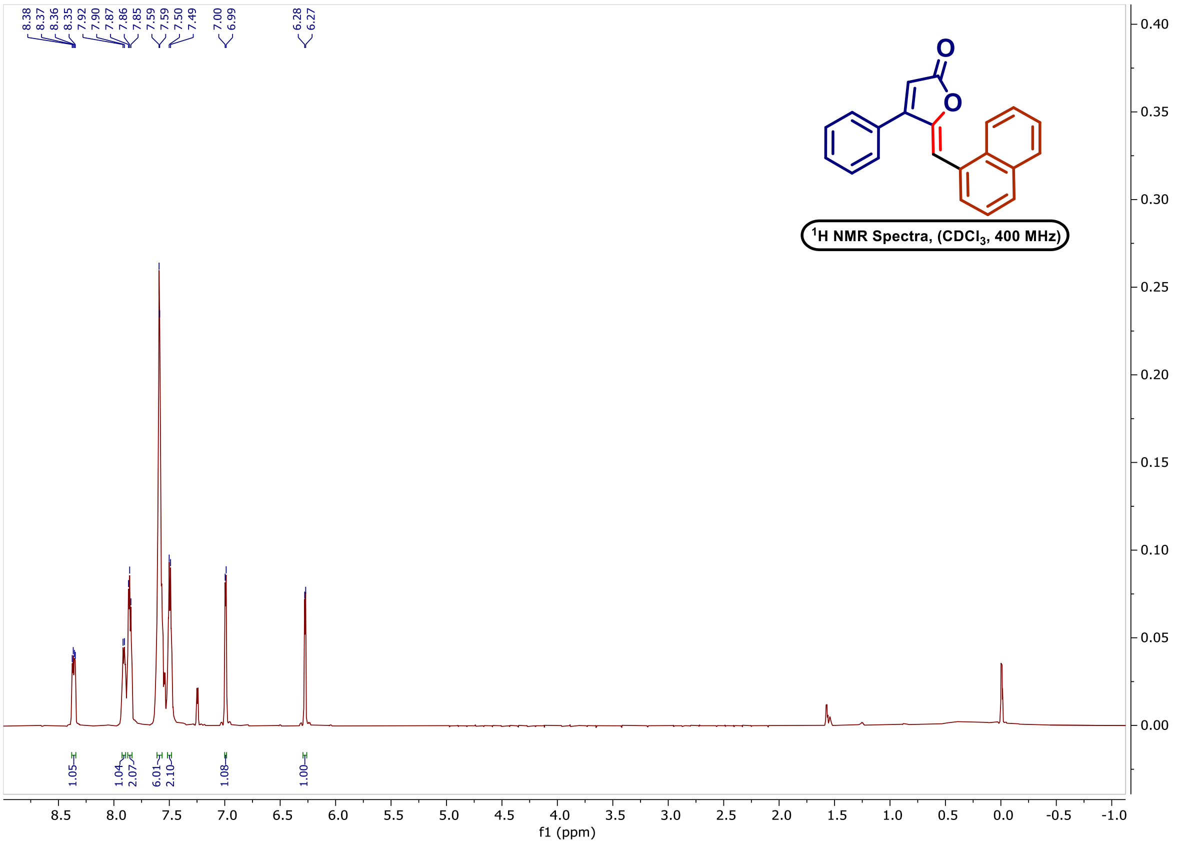


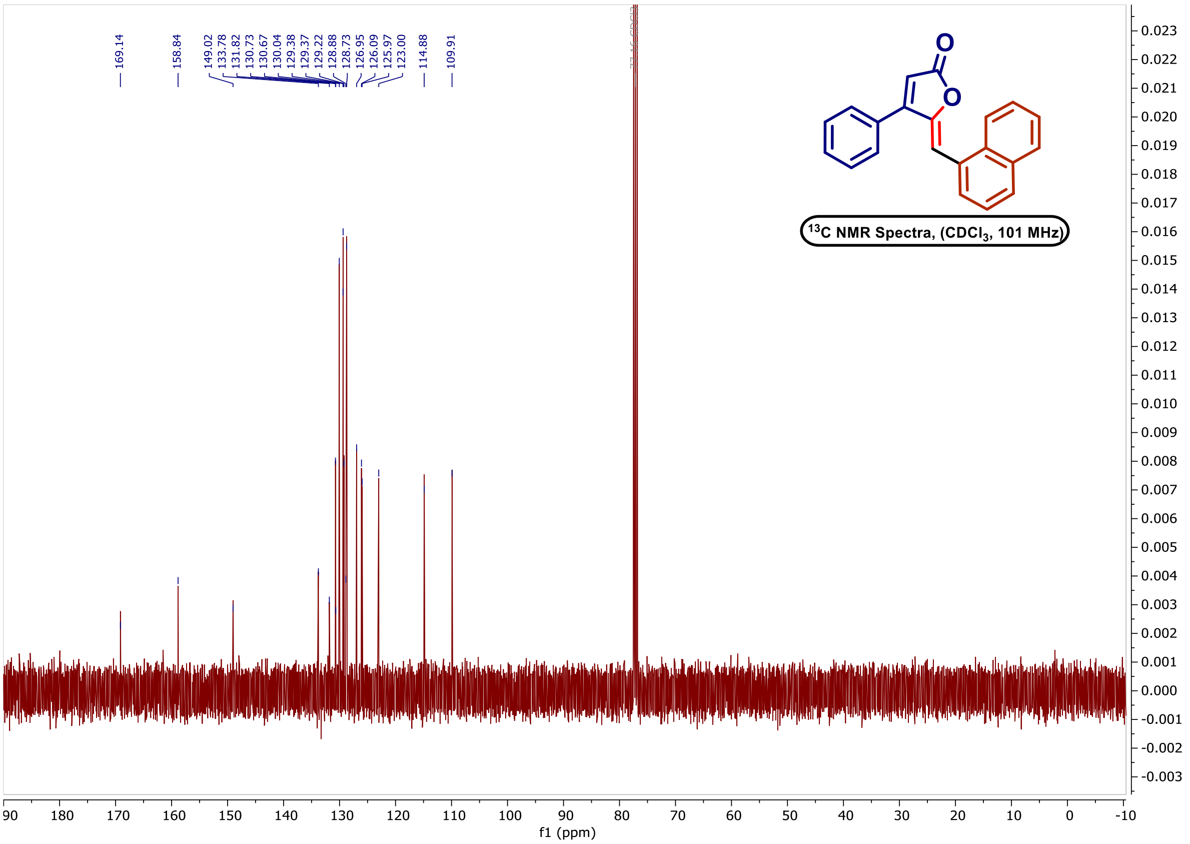
(*Z*)-5-(3,4-dimethoxybenzylidene)-4-phenylfuran-2(5*H*)-one (5i)



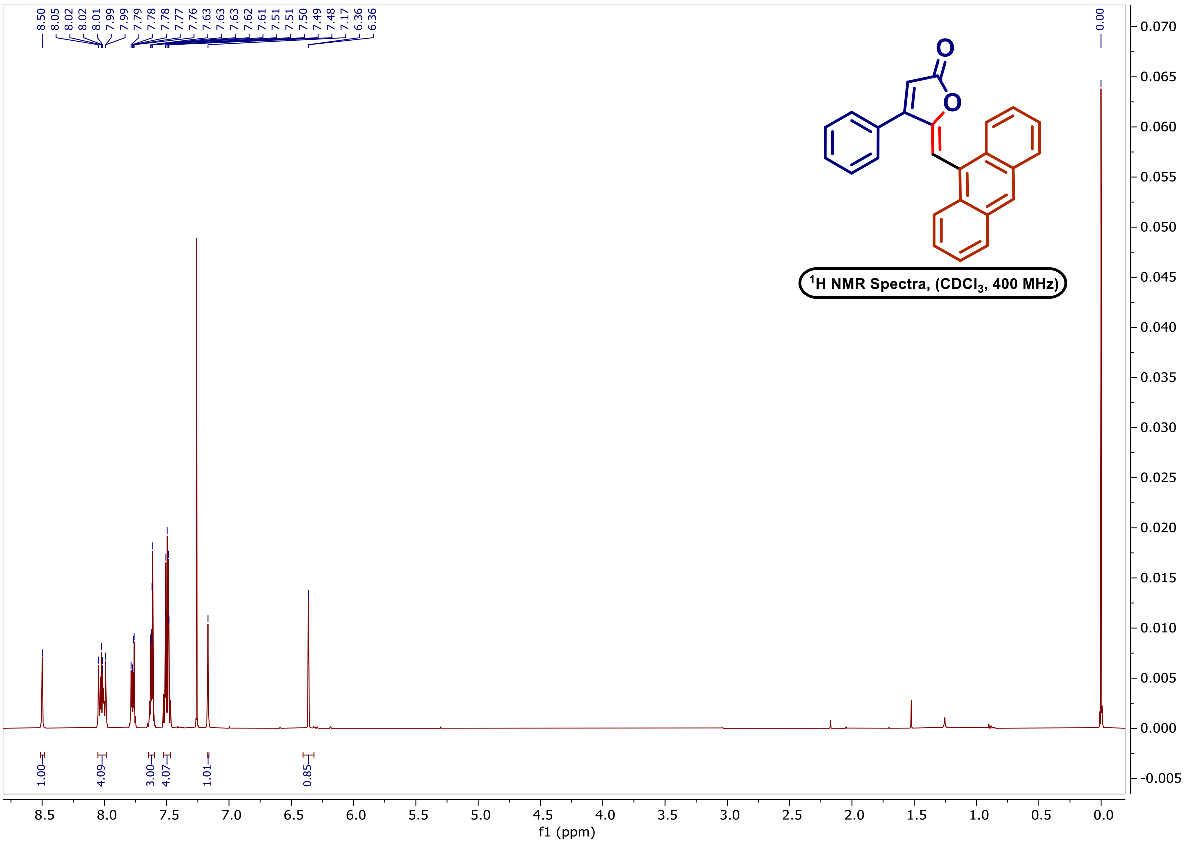


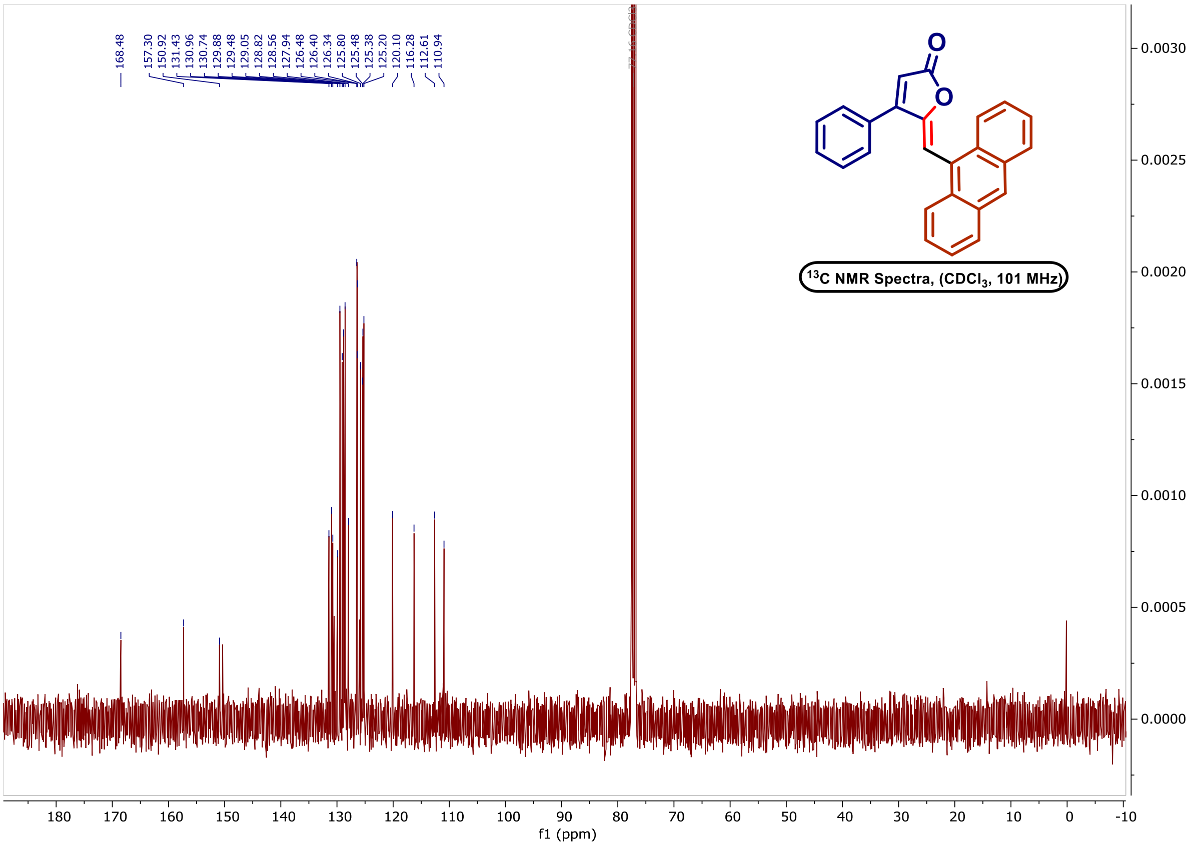
(*Z*)-5-(naphthalen-1-ylmethylene)-4-phenylfuran-2(*5H*)-one (5k)



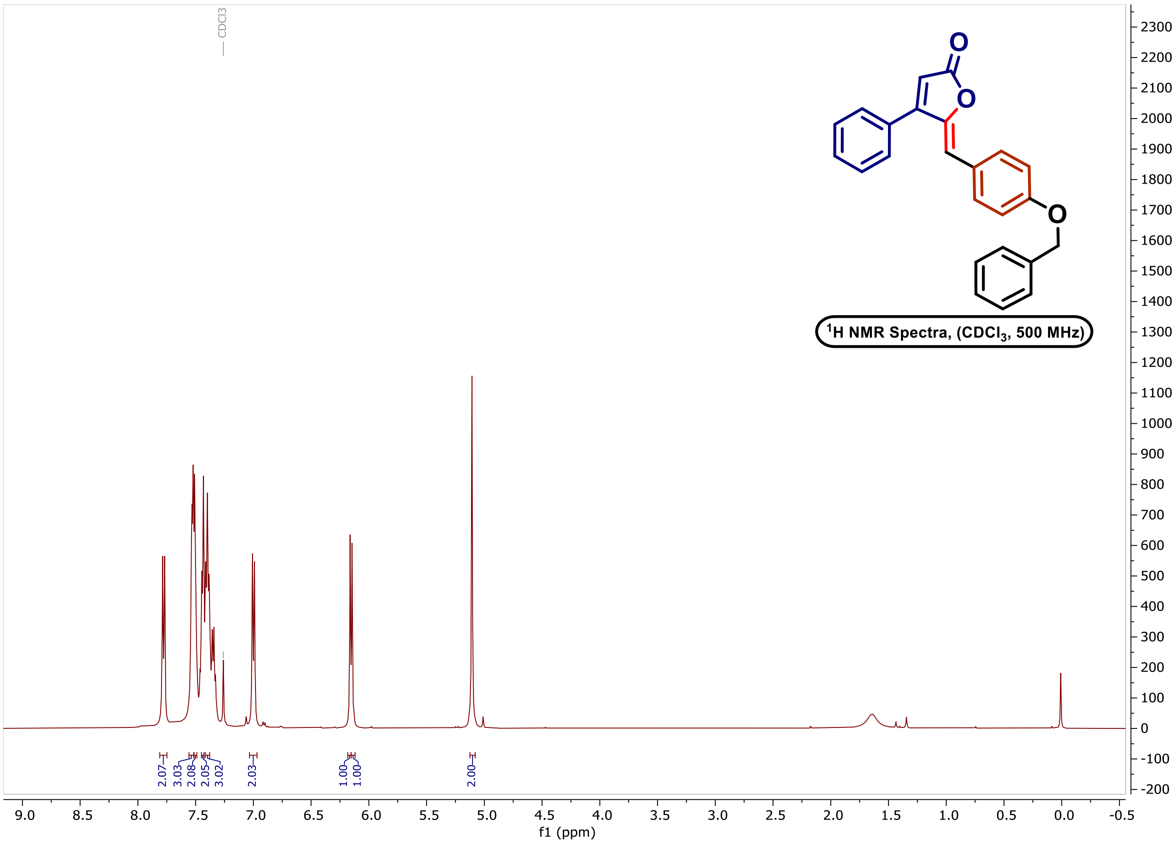


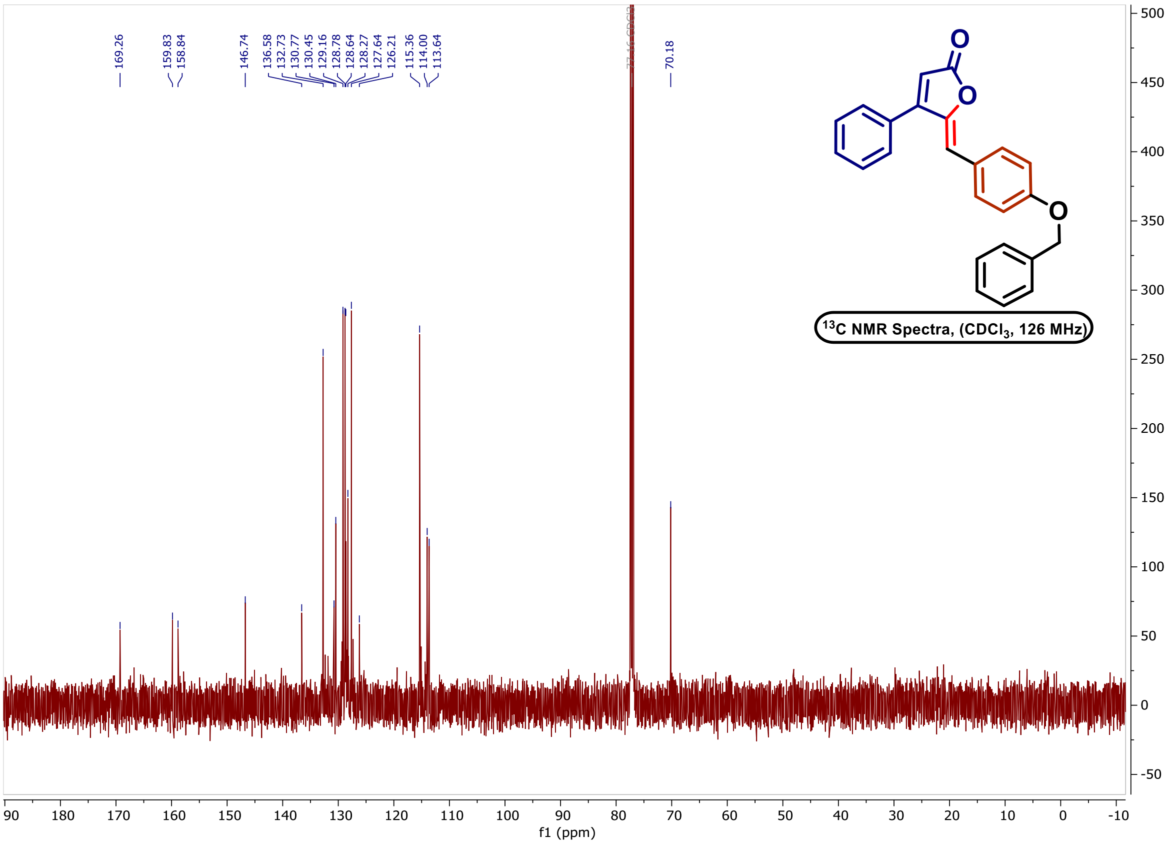
(*Z*)-5-(anthracen-9-ylmethylene)-4-phenylfuran-2(*5H*)-one (5l)



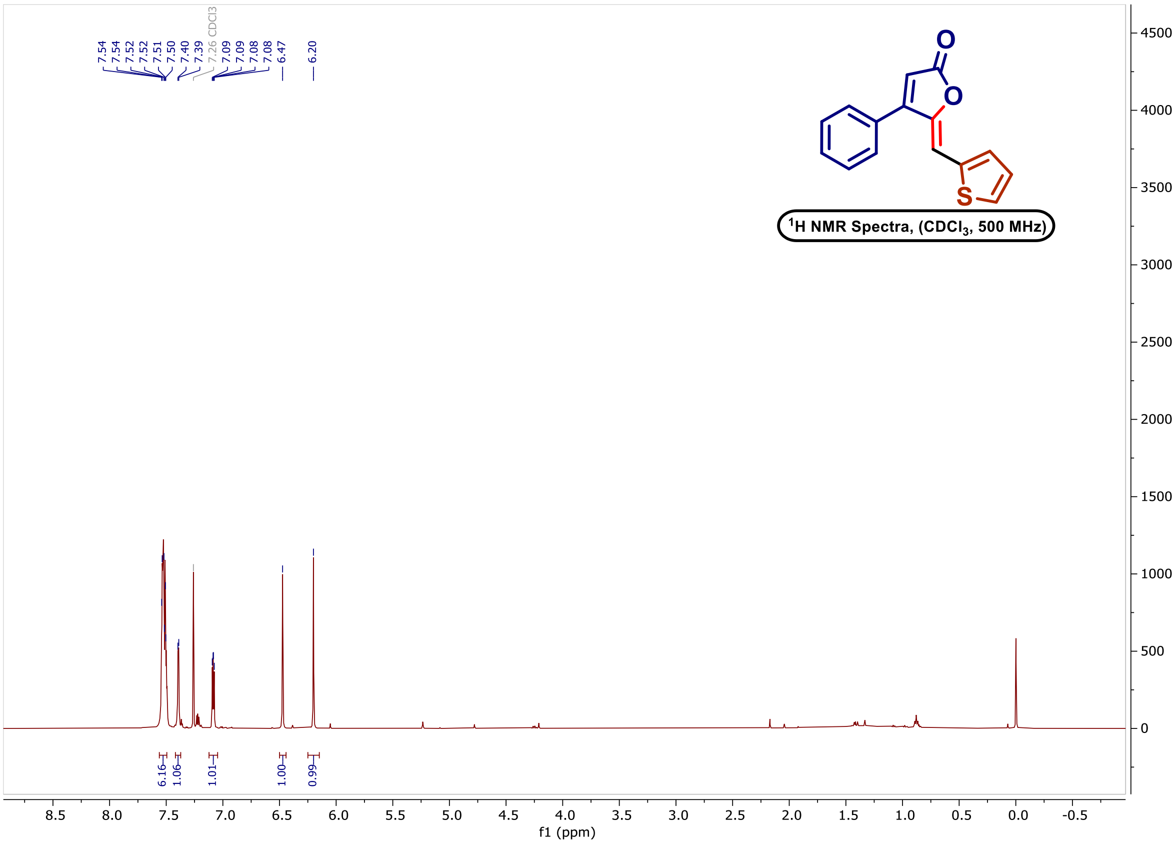


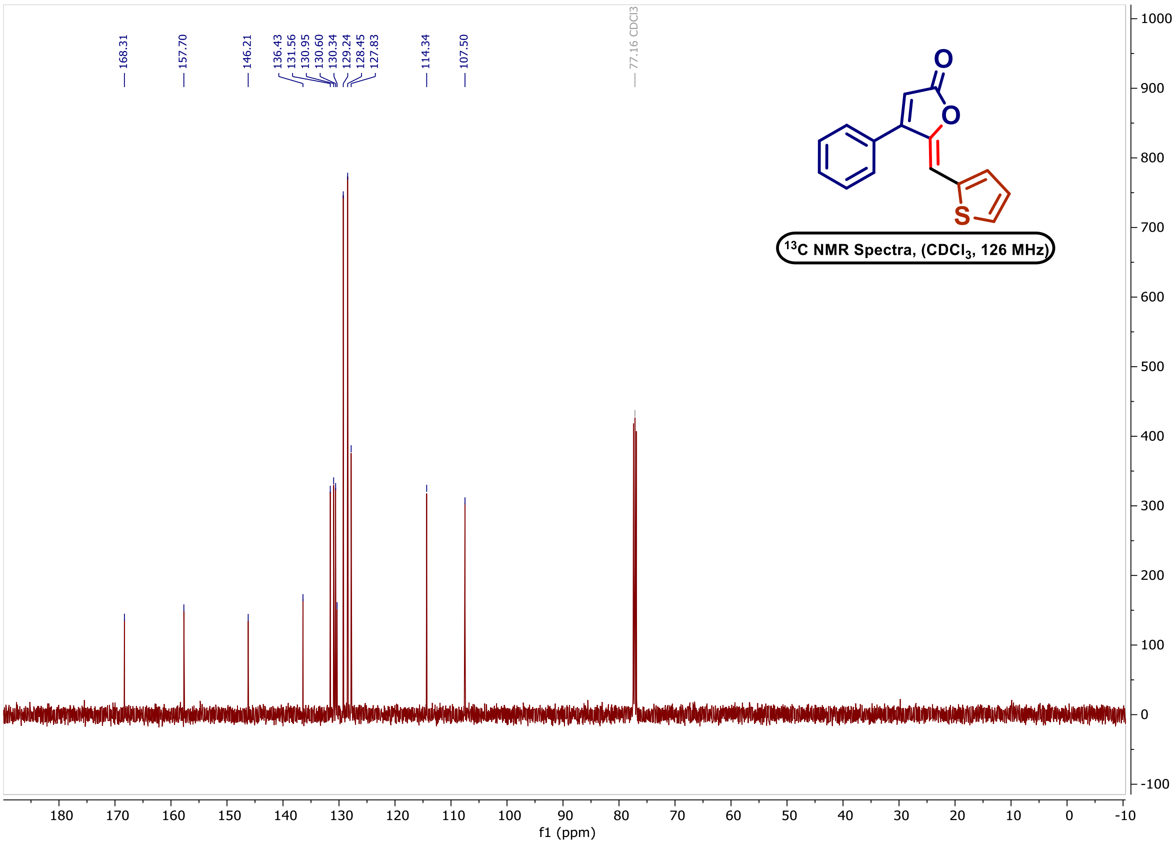
(*Z*)-5-(4-(benzyloxy)benzylidene)-4-phenylfuran-2(5*H*)-one (5m)



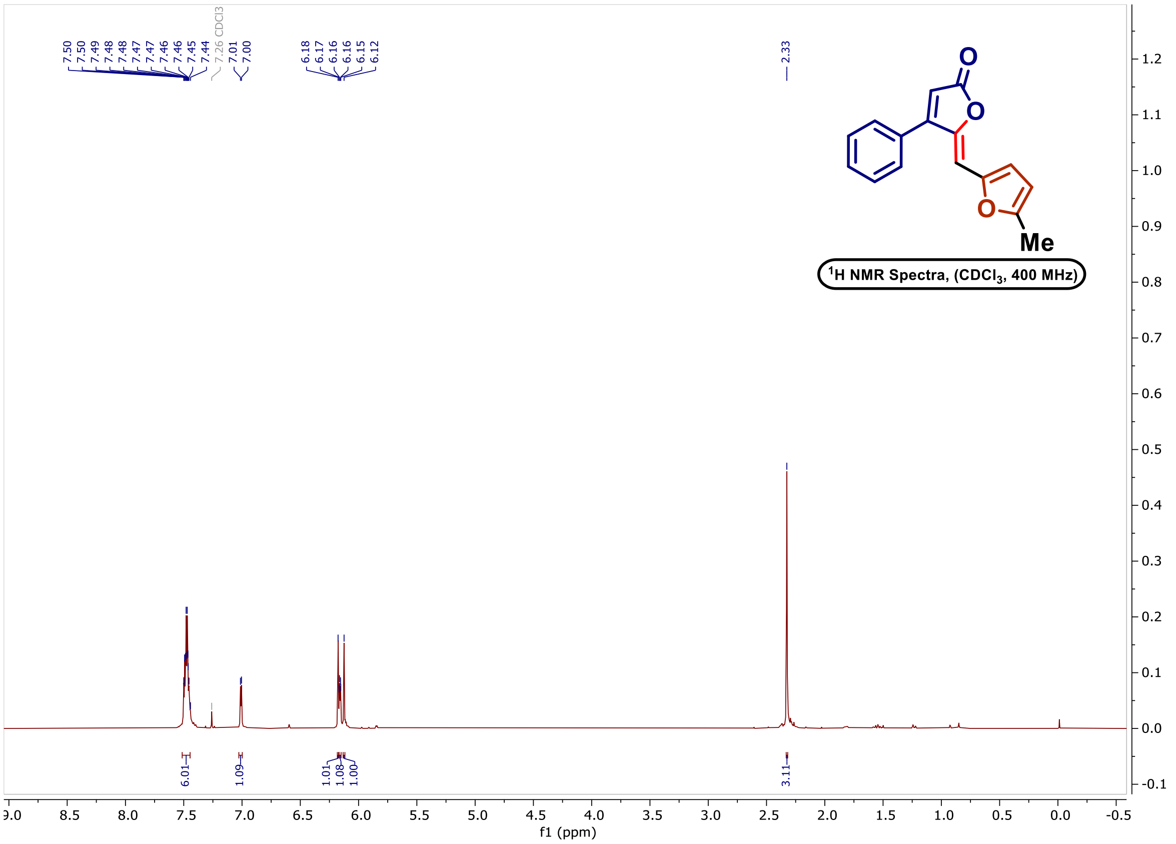


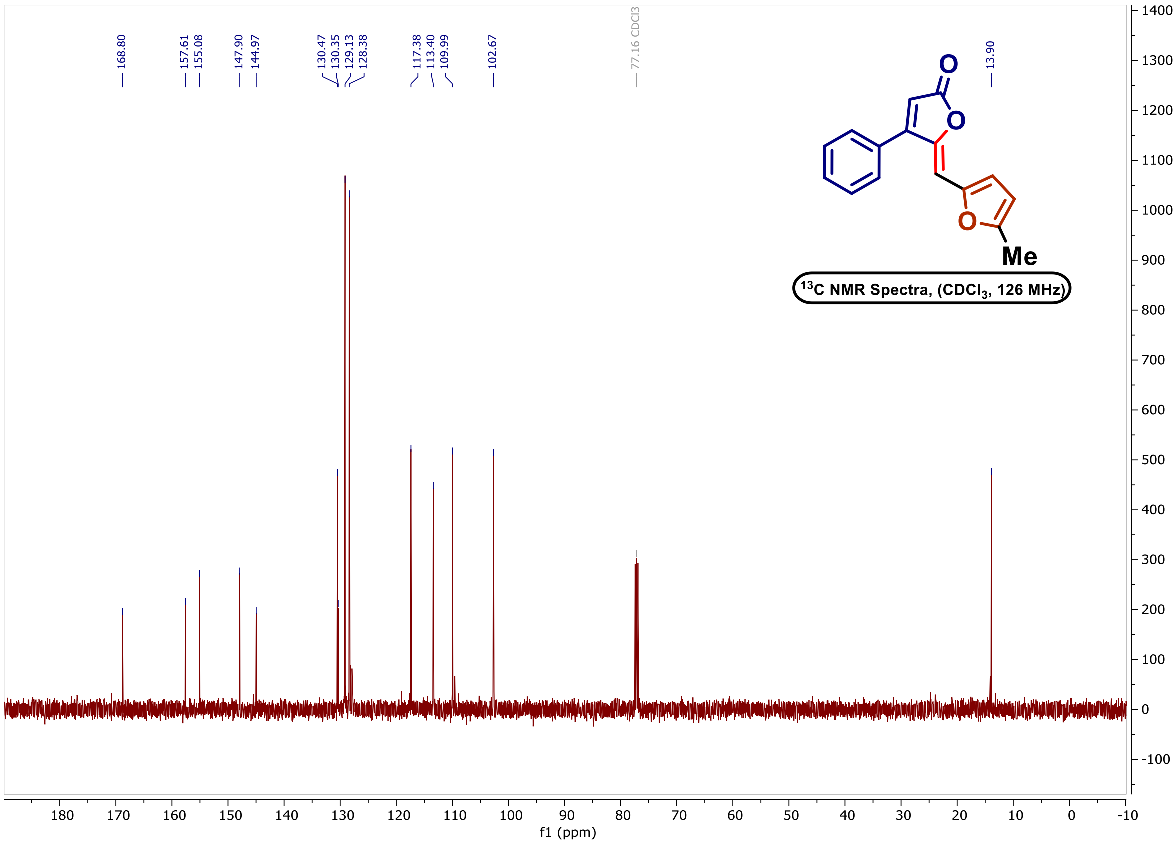
(*Z*)-4-phenyl-5-(thiophen-2-ylmethylene)furan-2(5*H*)-one (5n)



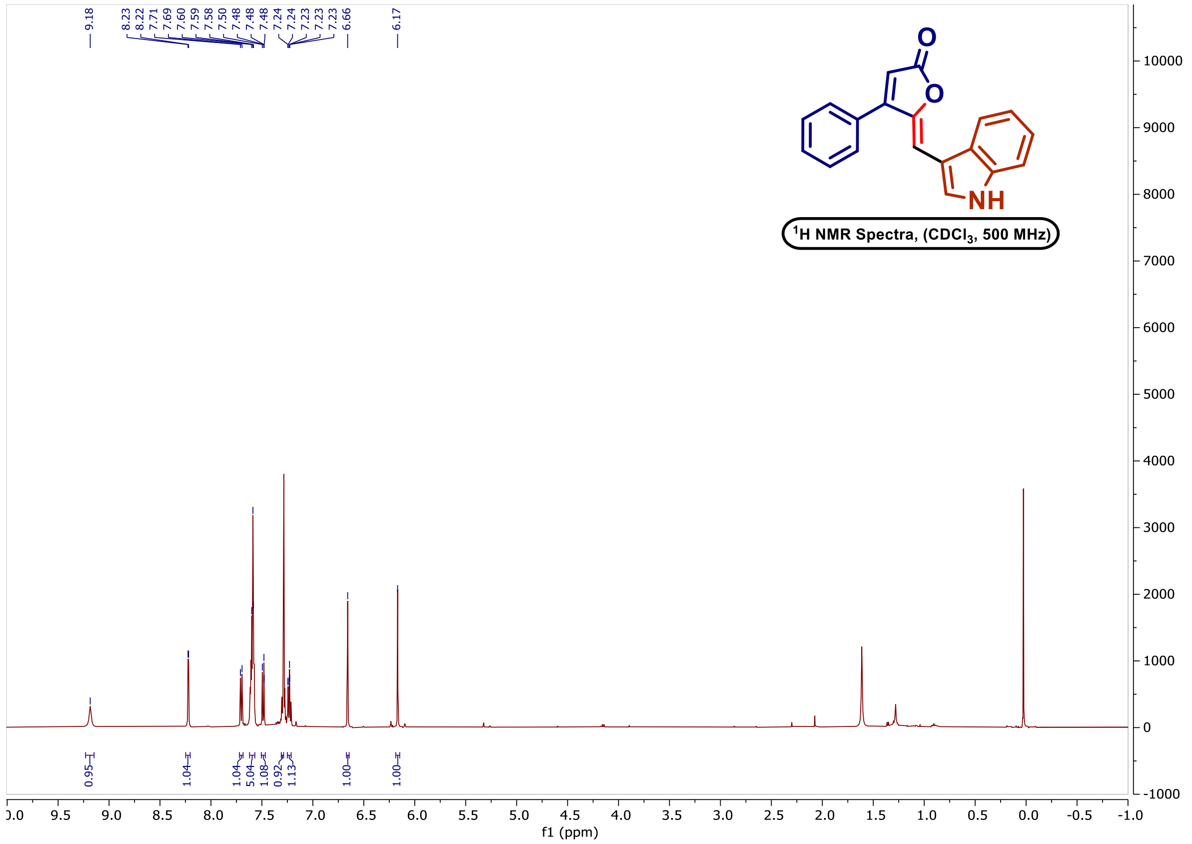


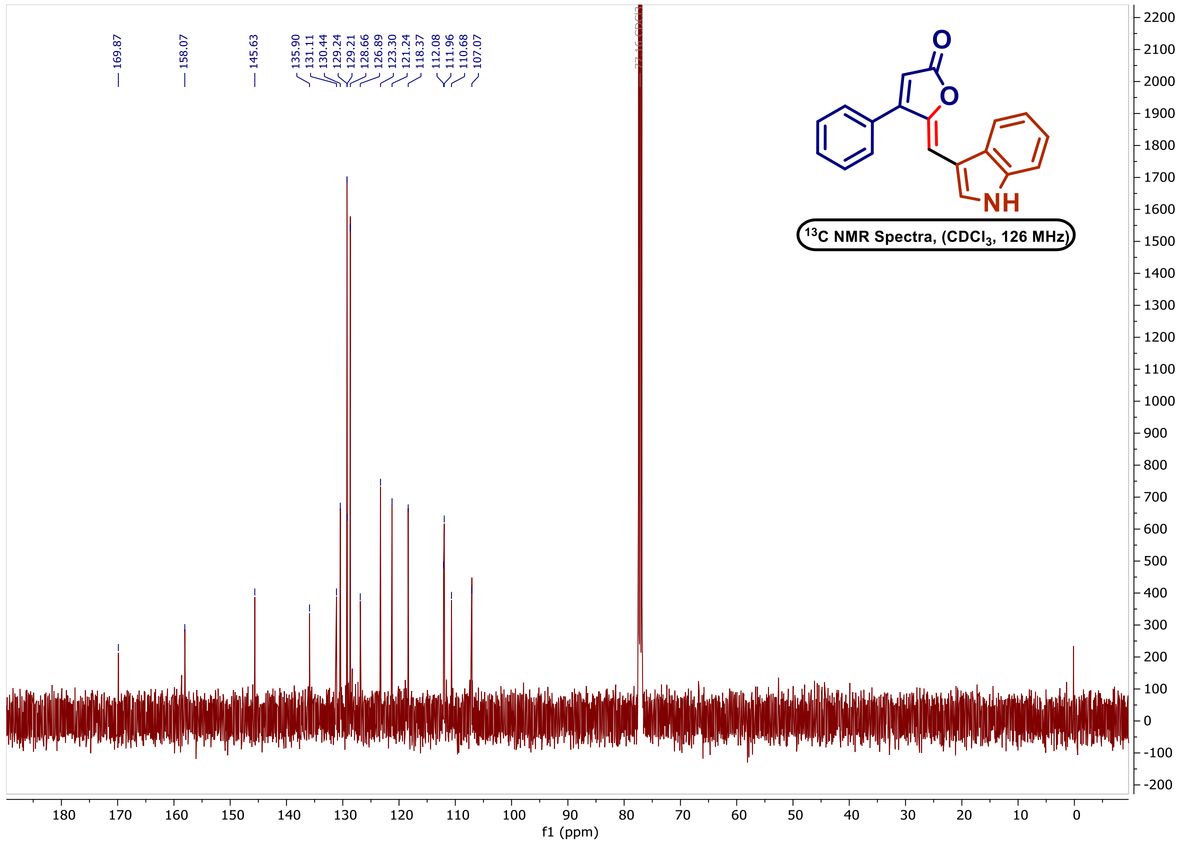
(*Z*)-5-((5-methylfuran-2-yl)methylene)-4-phenylfuran-2(5*H*)-one (5o)



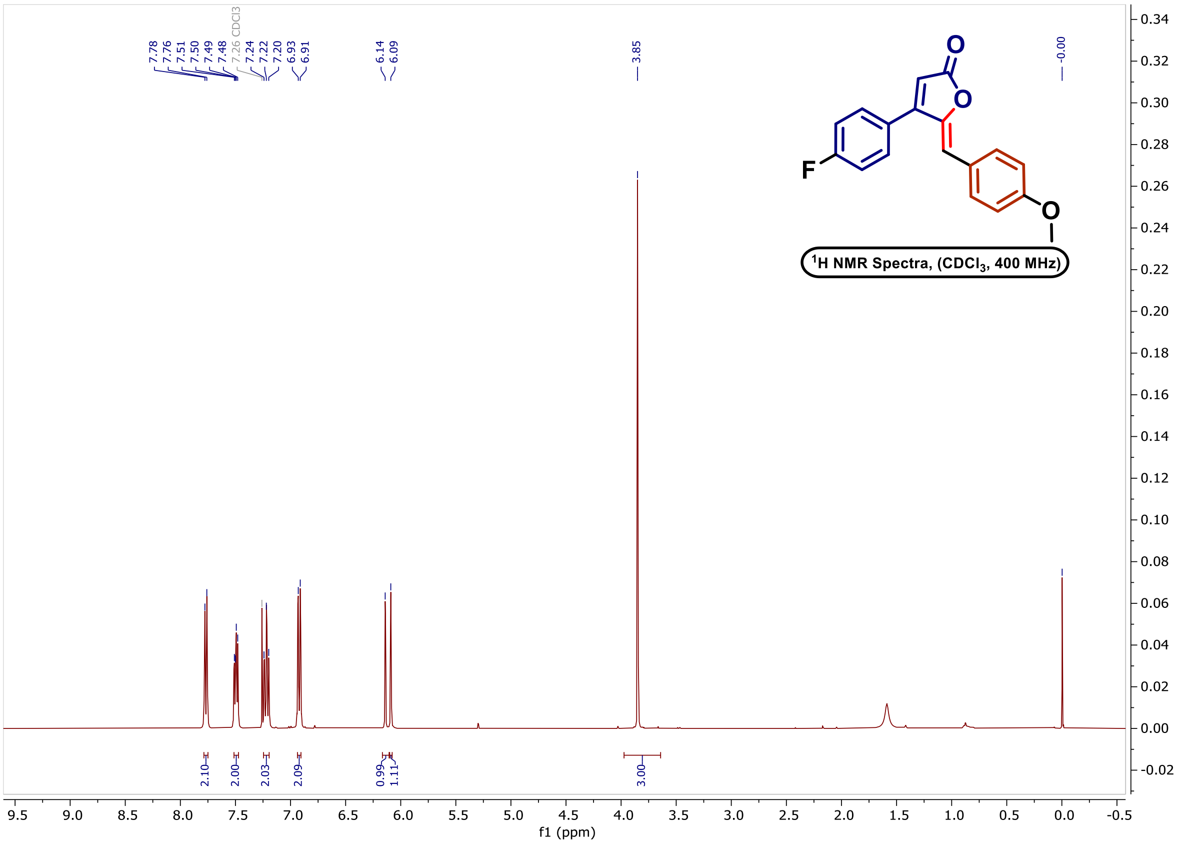


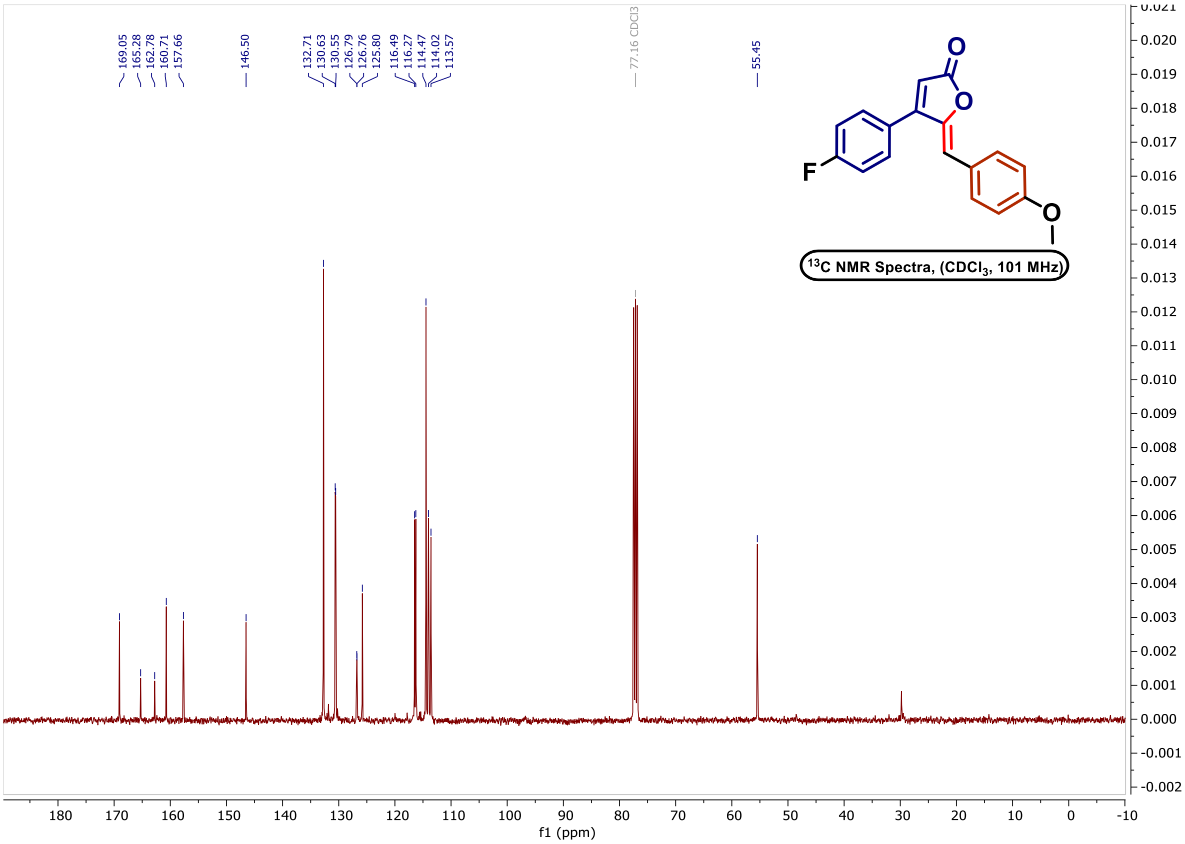
(*Z*)-5-((1H-indol-3-yl)methylene)-4-phenylfuran-2(*5H*)-one (5p)



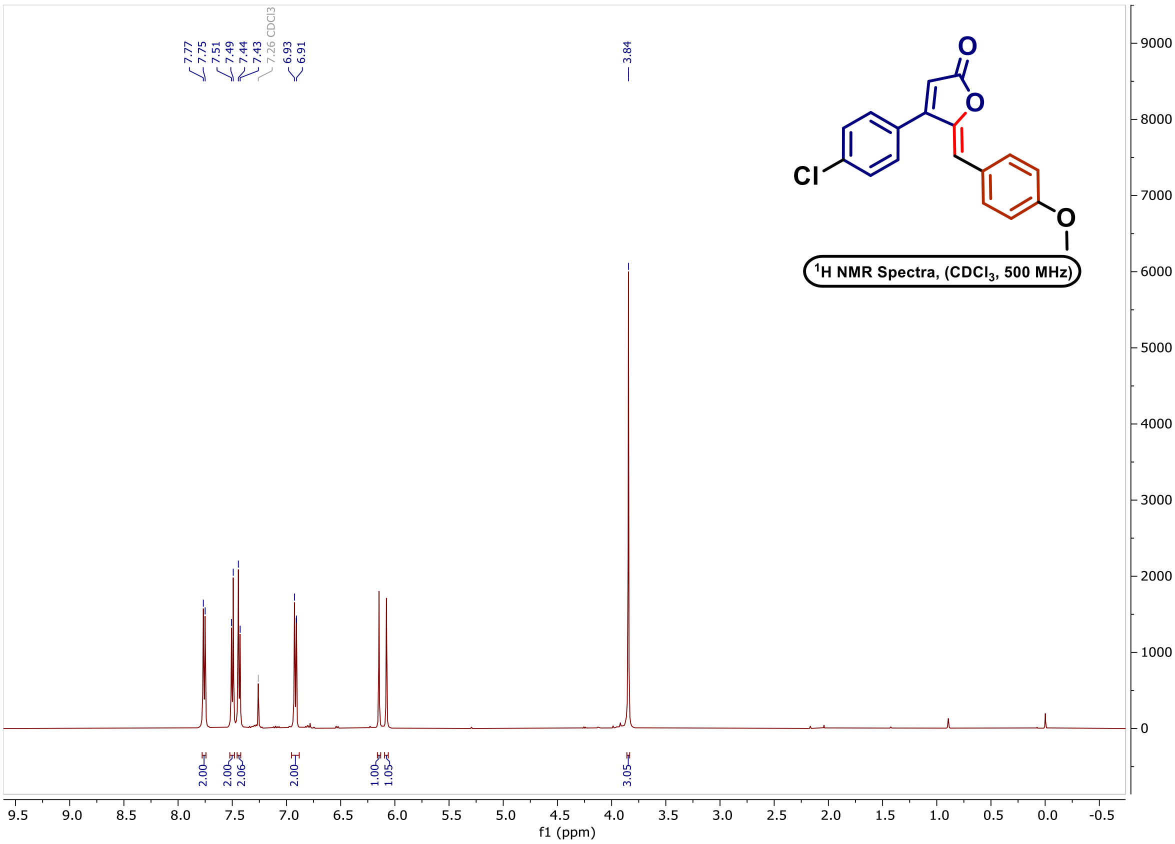


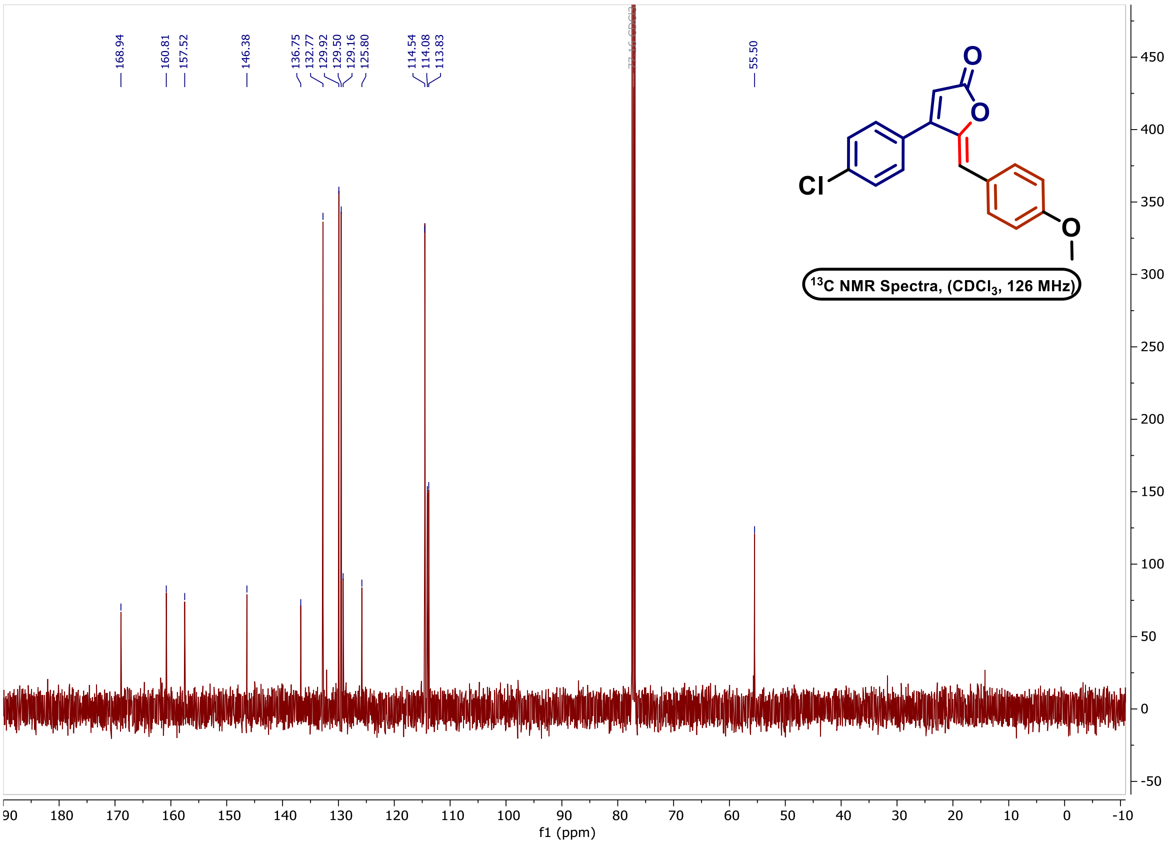
(*Z*)-4-(4-fluorophenyl)-5-(4-methoxybenzylidene)furan-2(*5H*)-one (5q)



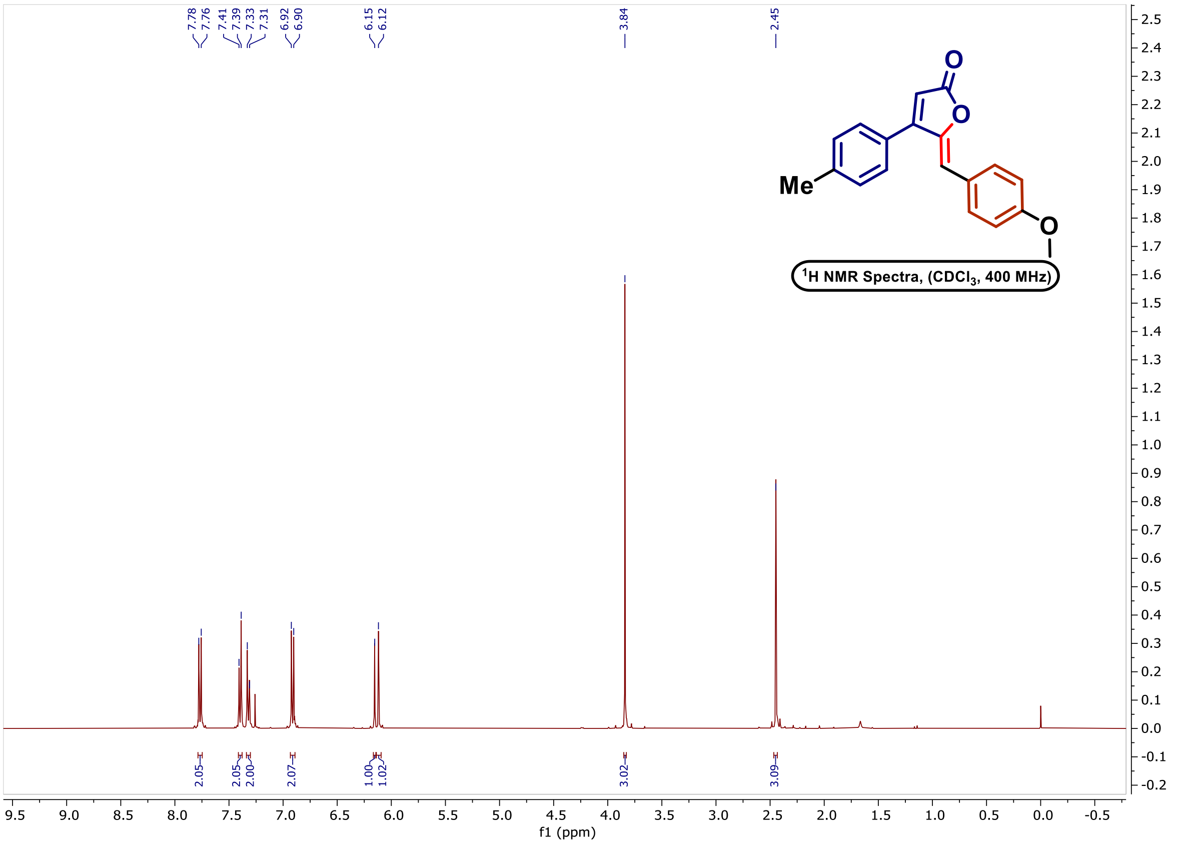


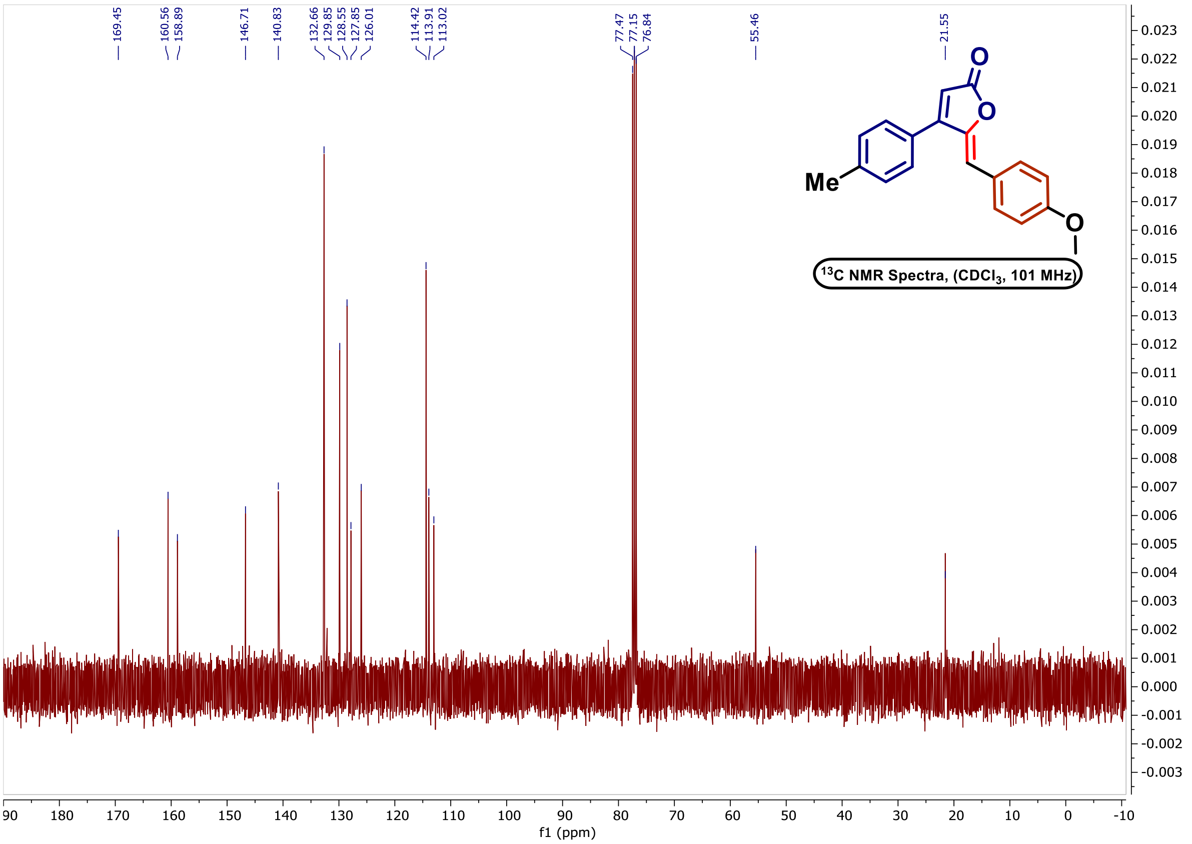
(*Z*)-4-(4-chlorophenyl)-5-(4-methoxybenzylidene)furan-2(5*H*)-one (5r)



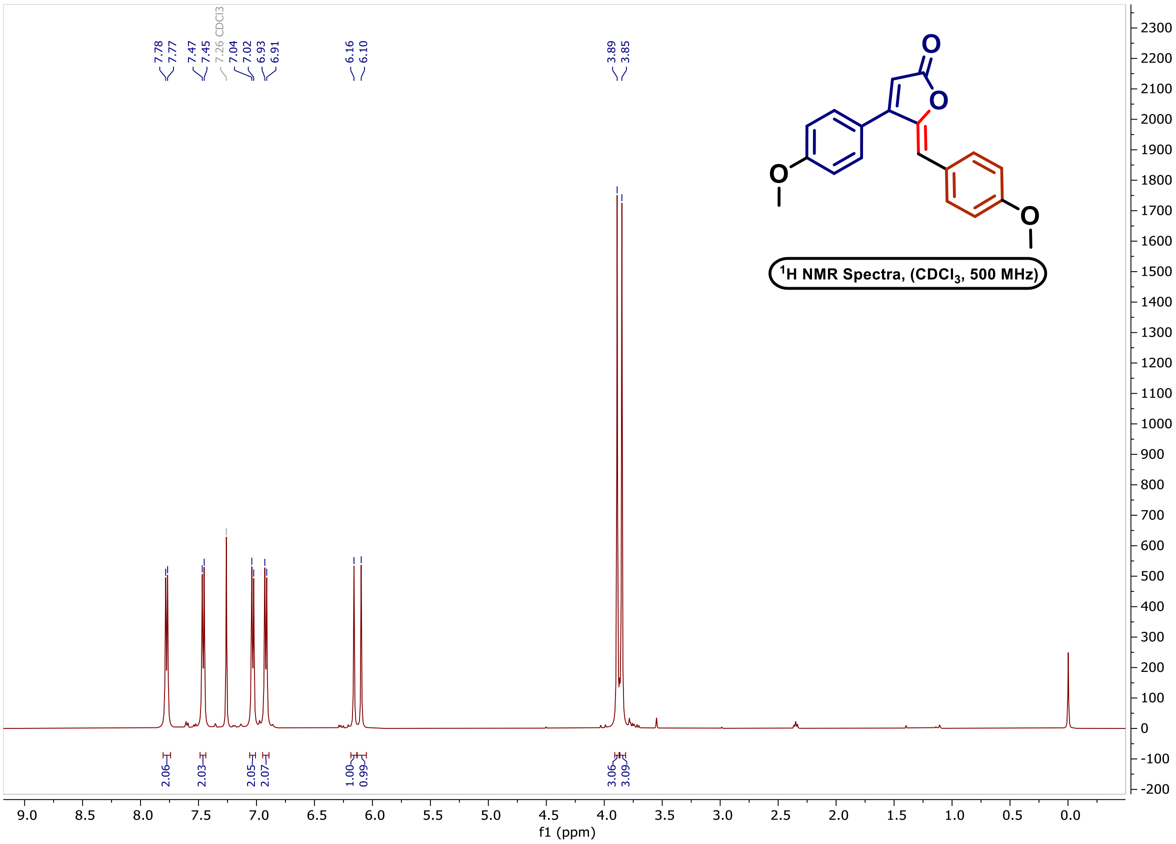


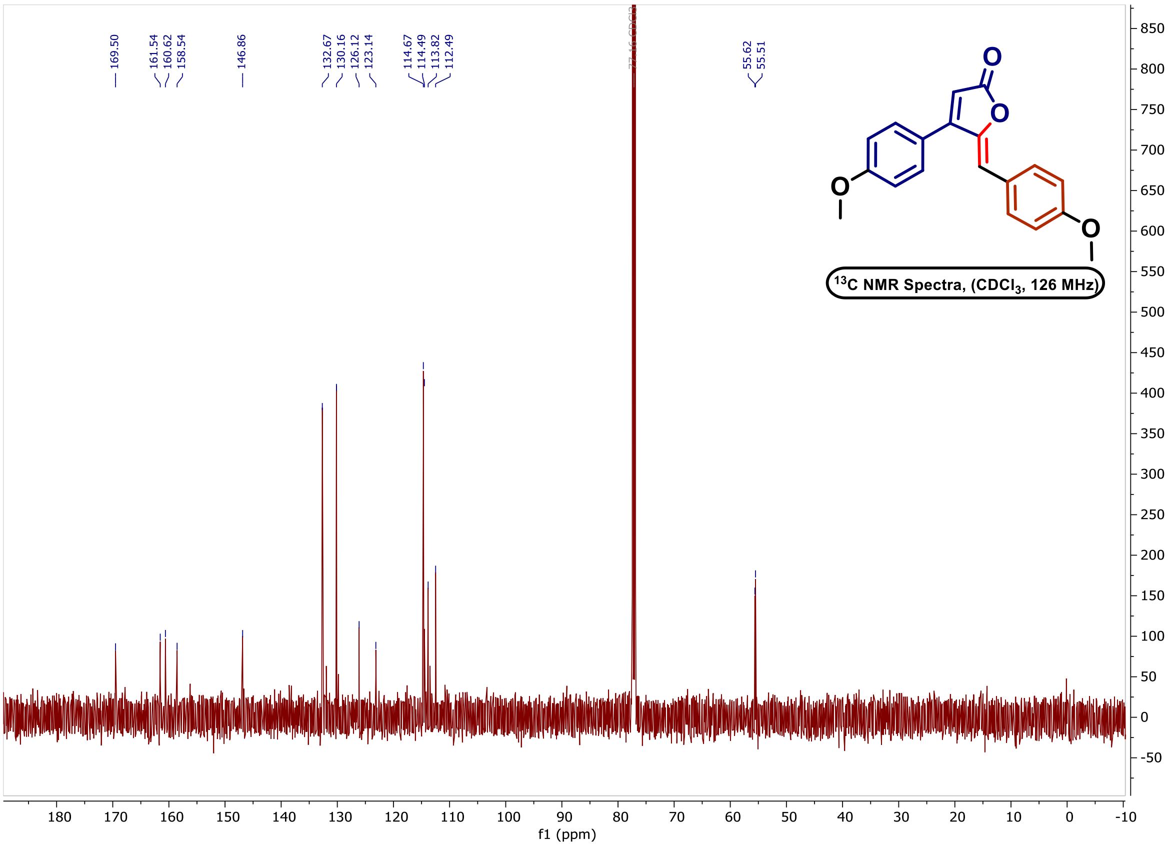
(*Z*)-5-(4-methoxybenzylidene)-4-(*p*-tolyl)furan-2(5*H*)-one (5s)



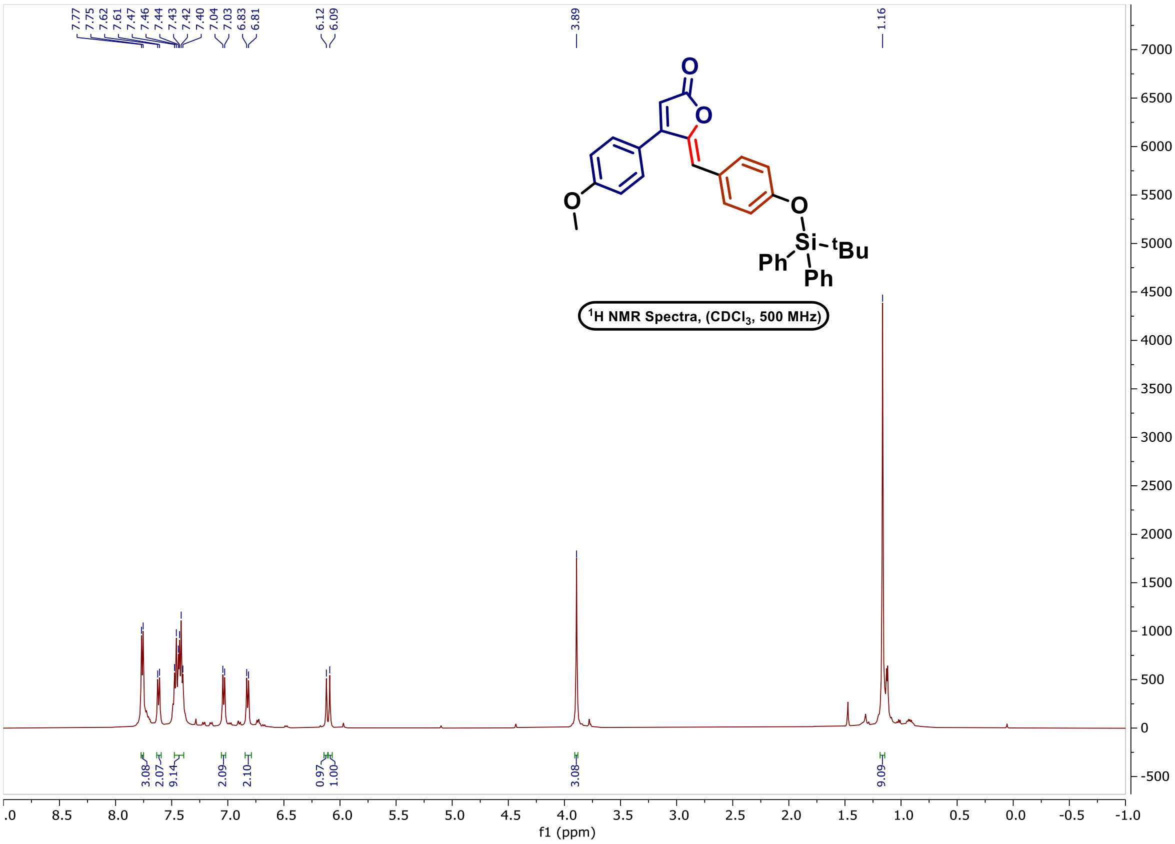


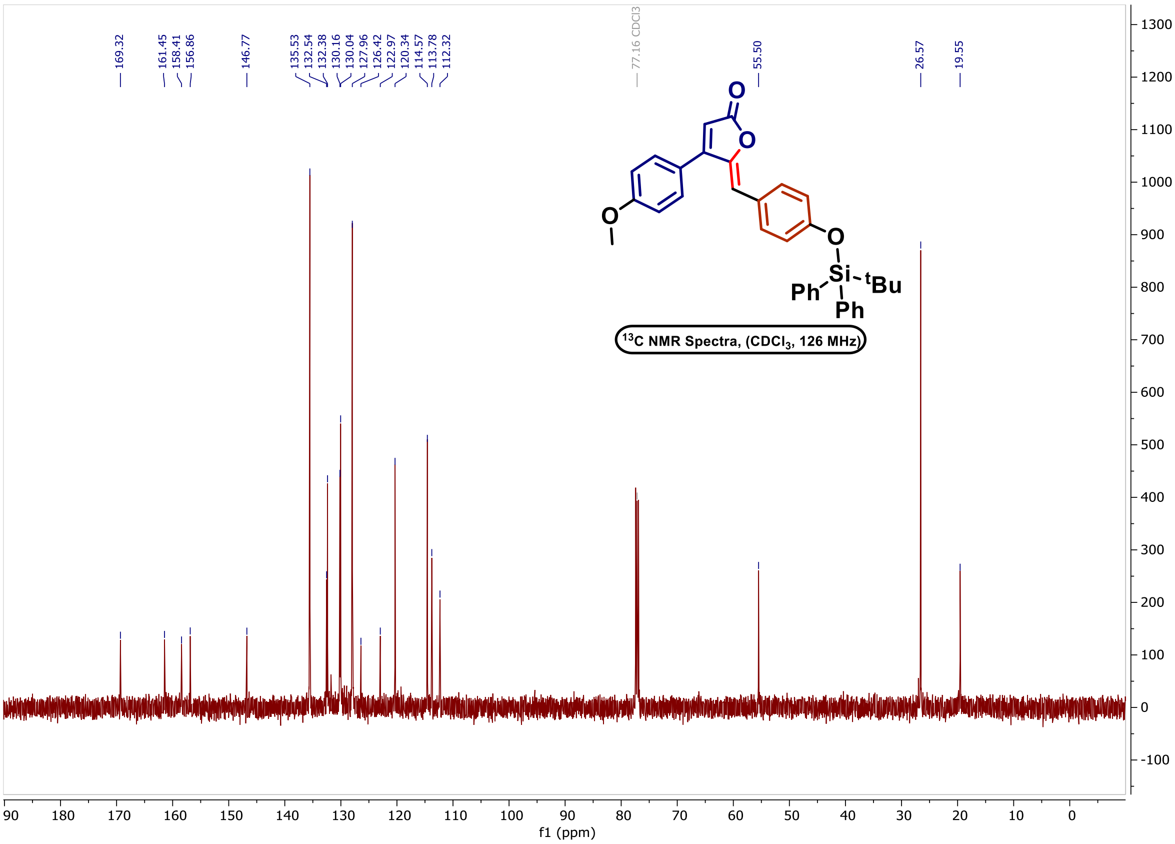
(*Z*)-5-(4-methoxybenzylidene)-4-(4-methoxyphenyl)furan-2(5*H*)-one (5t)



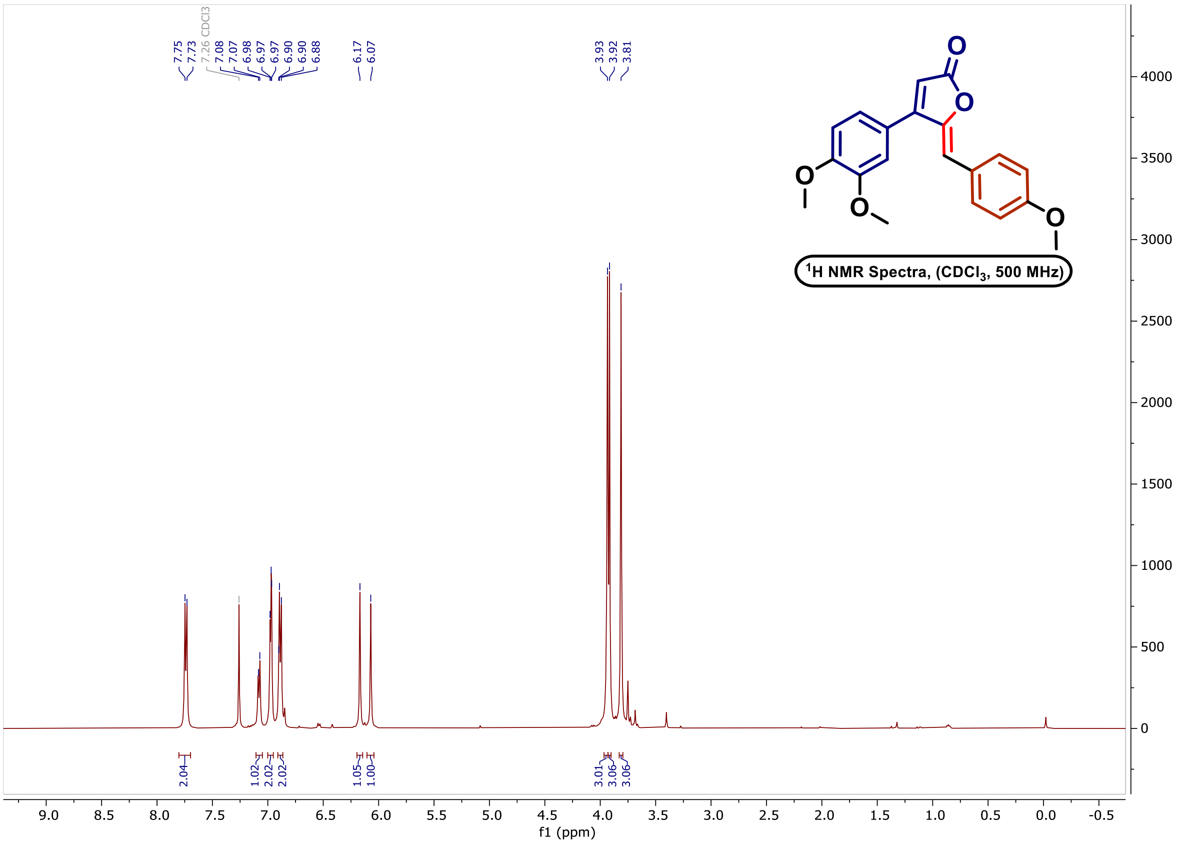


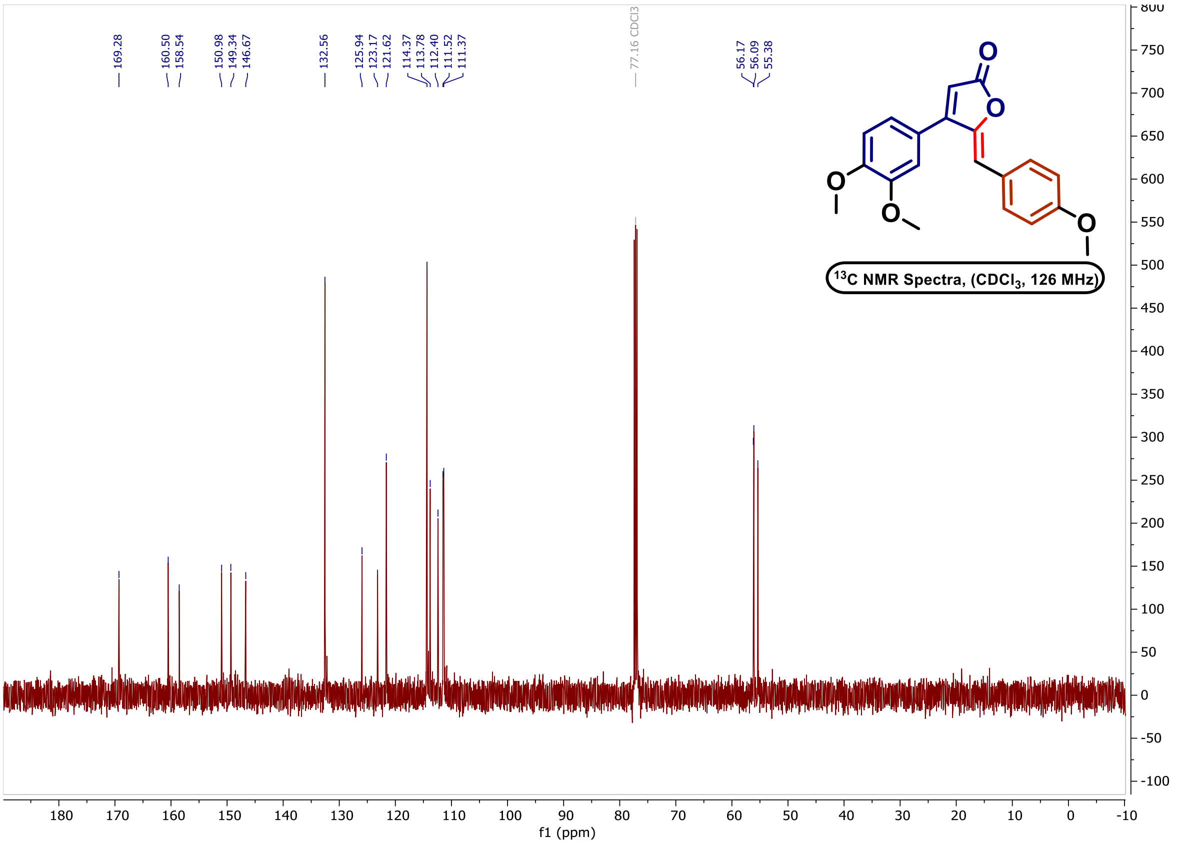
(*Z*)-5-(4-((tert-butyldiphenylsilyl)oxy)benzylidene)-4-(4-methoxyphenyl)furan-2(5*H*)-one (5u)



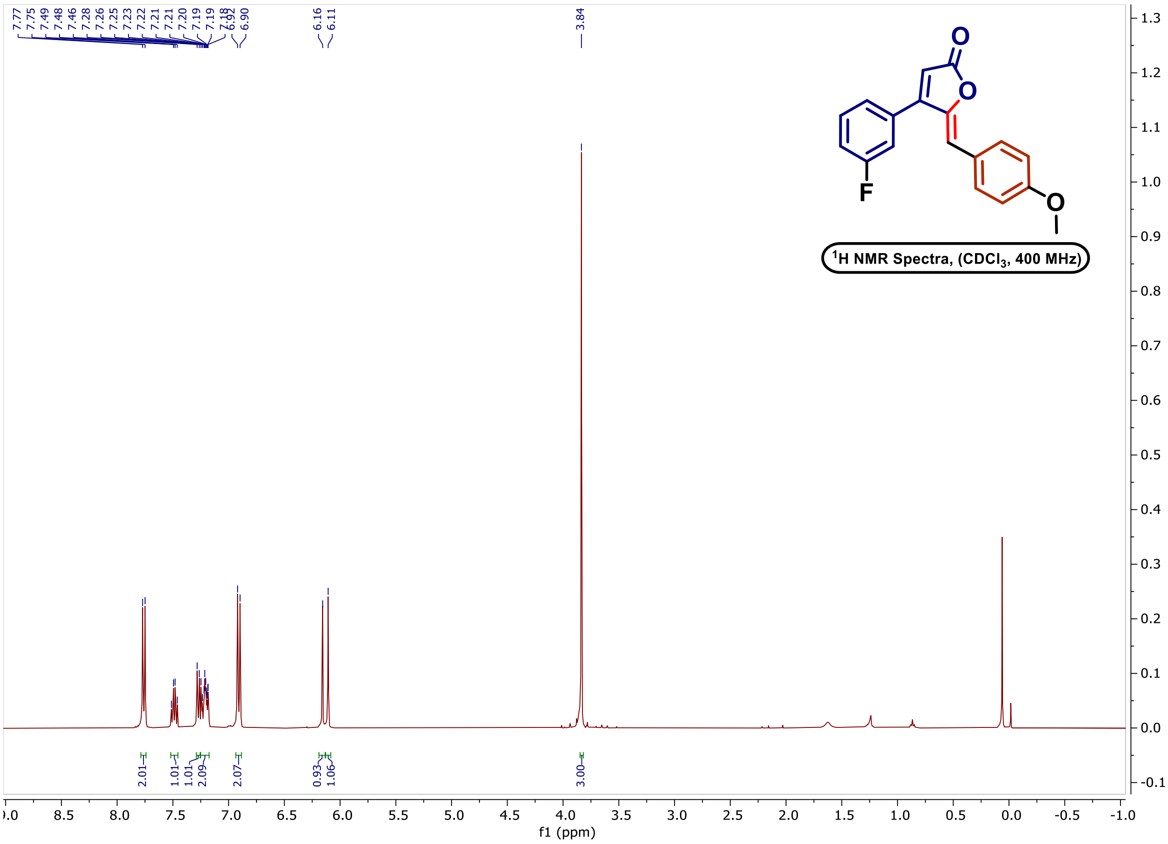


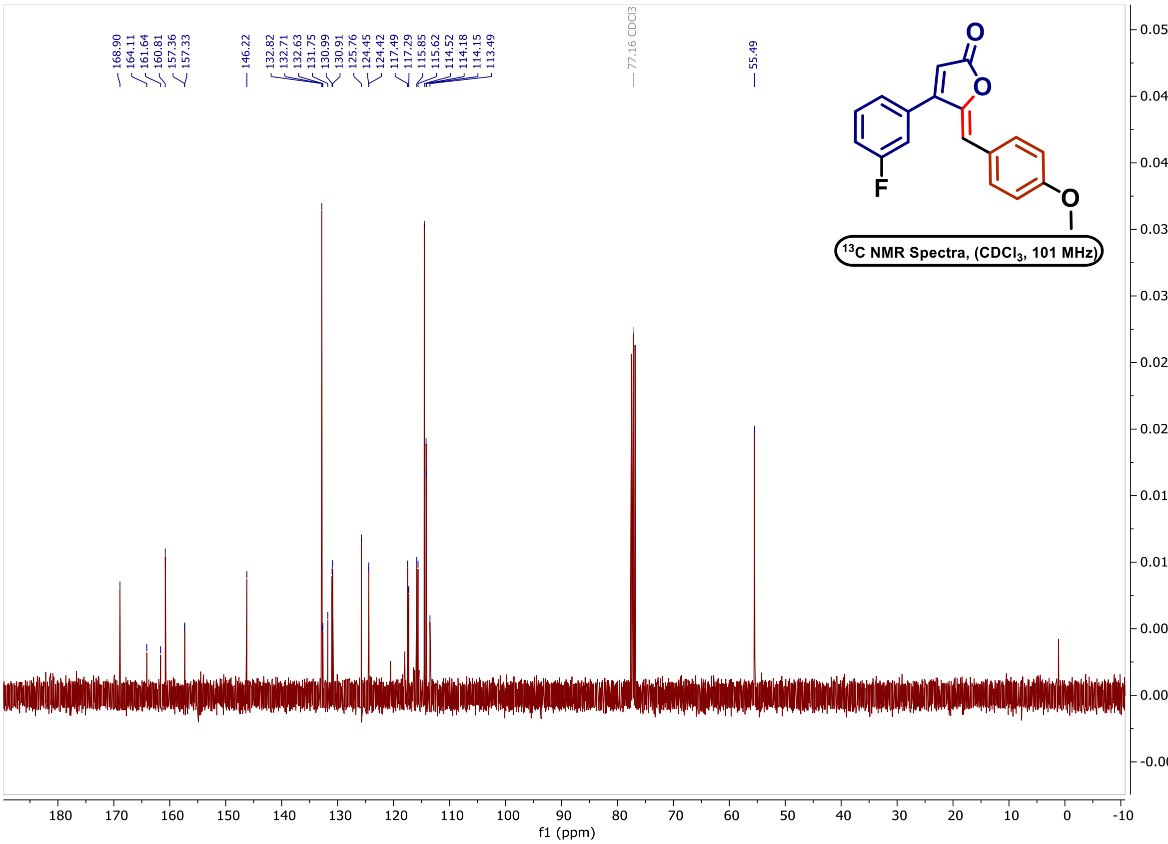
(*Z*)-4-(3,4-dimethoxyphenyl)-5-(4-methoxybenzylidene)furan-2(5*H*)-one (5v)

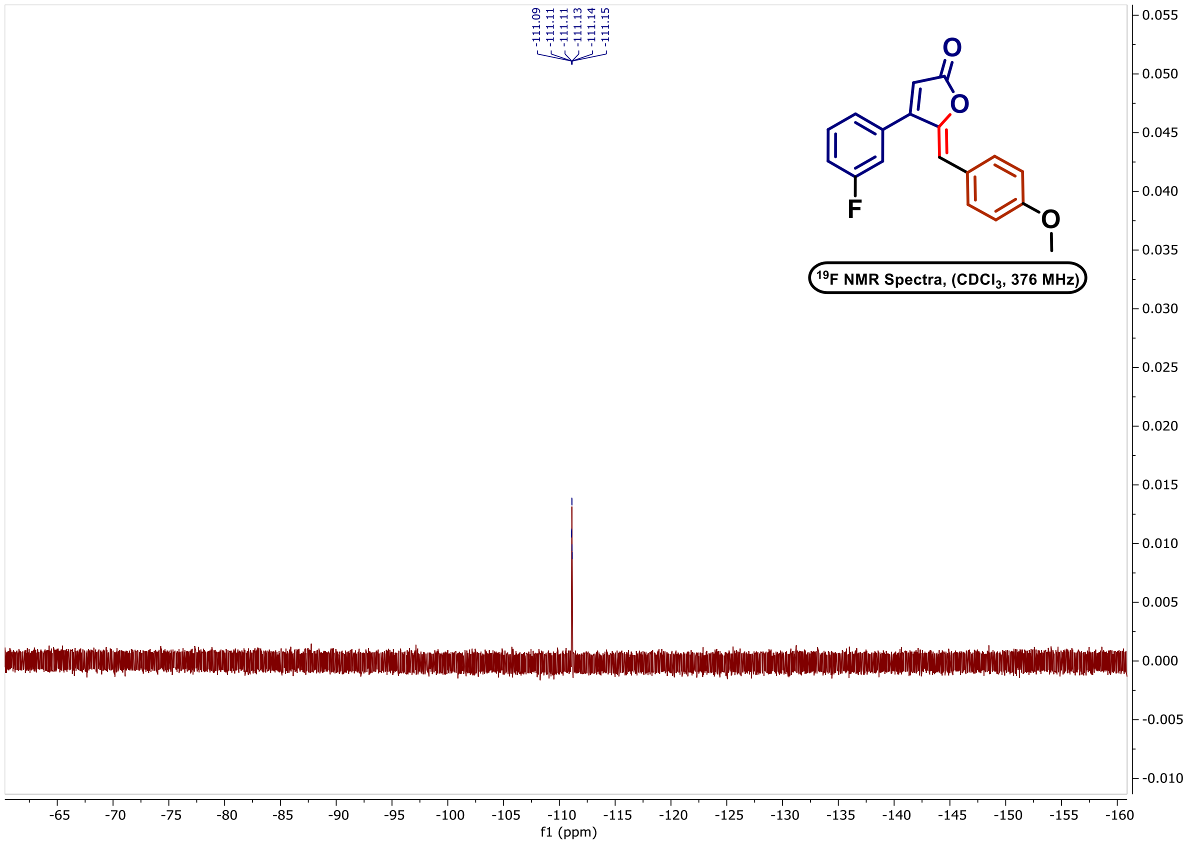




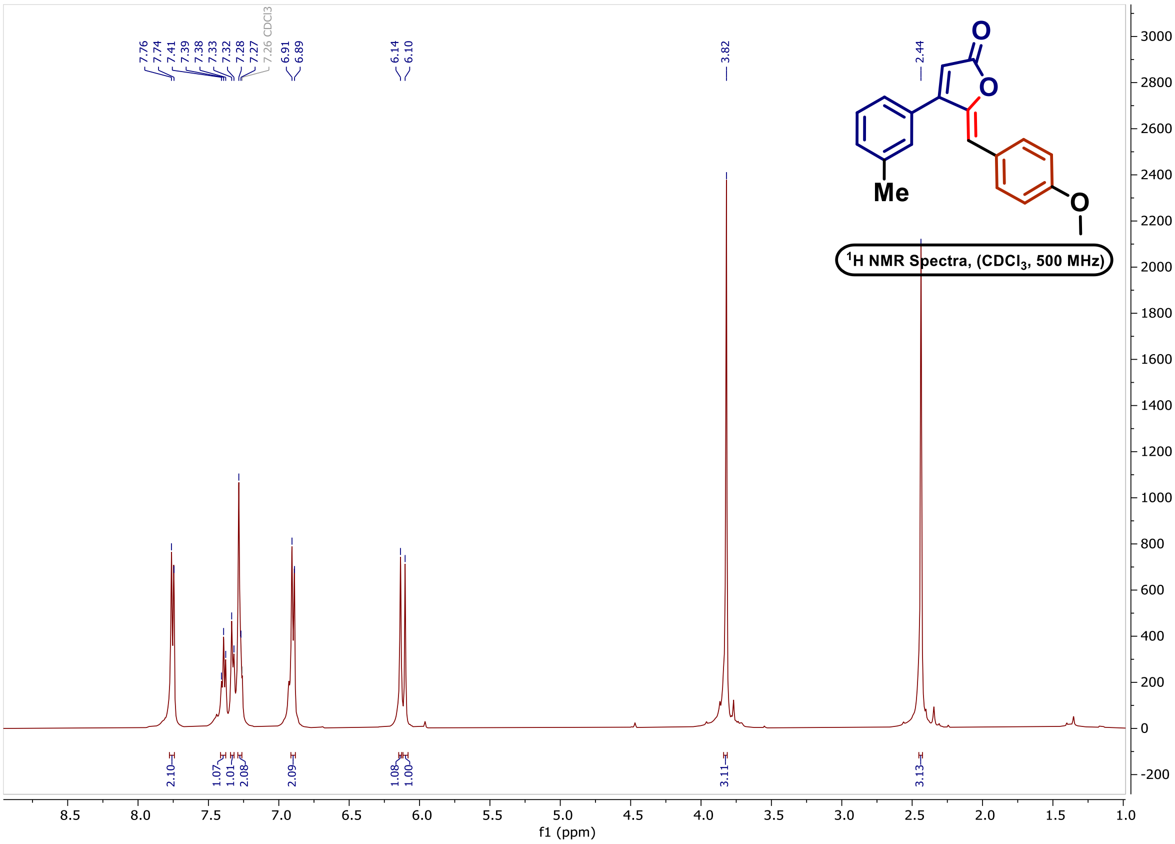
(*Z*)-4-(3-fluorophenyl)-5-(4-methoxybenzylidene)furan-2(*5H*)-one (5w)

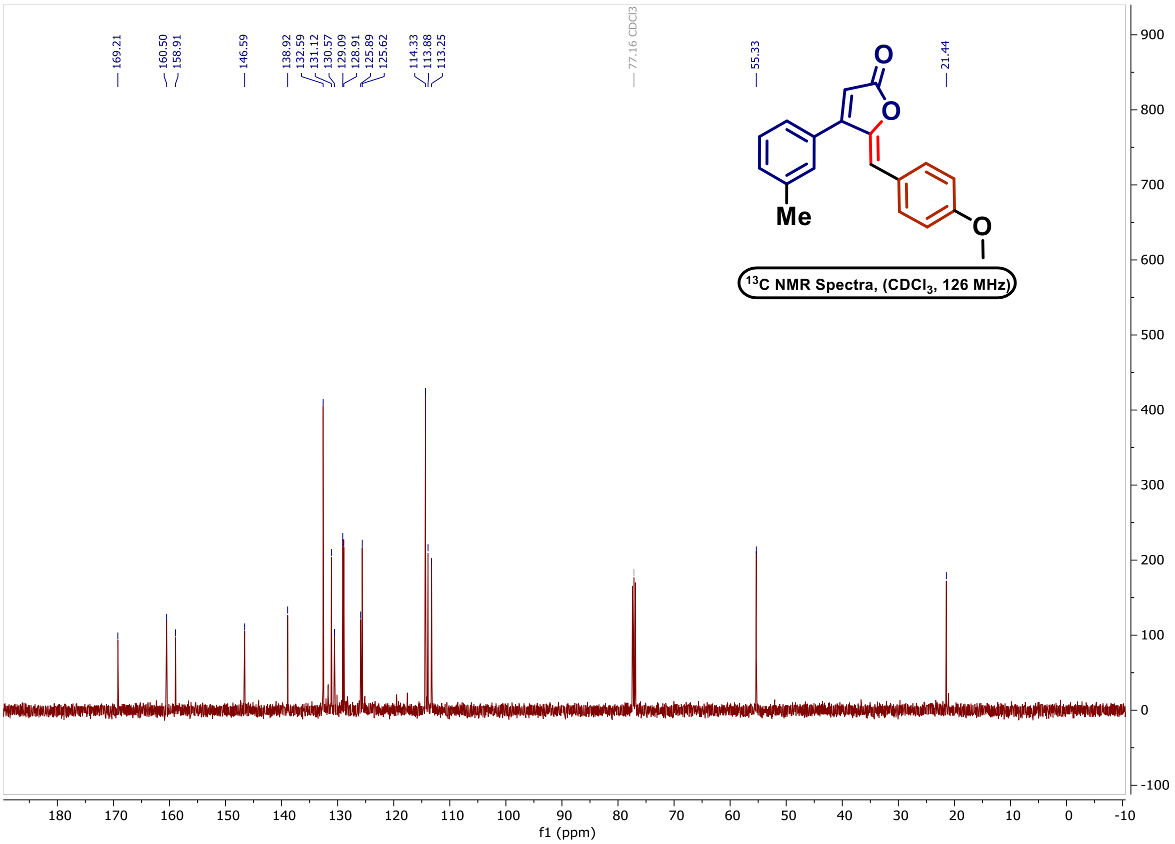




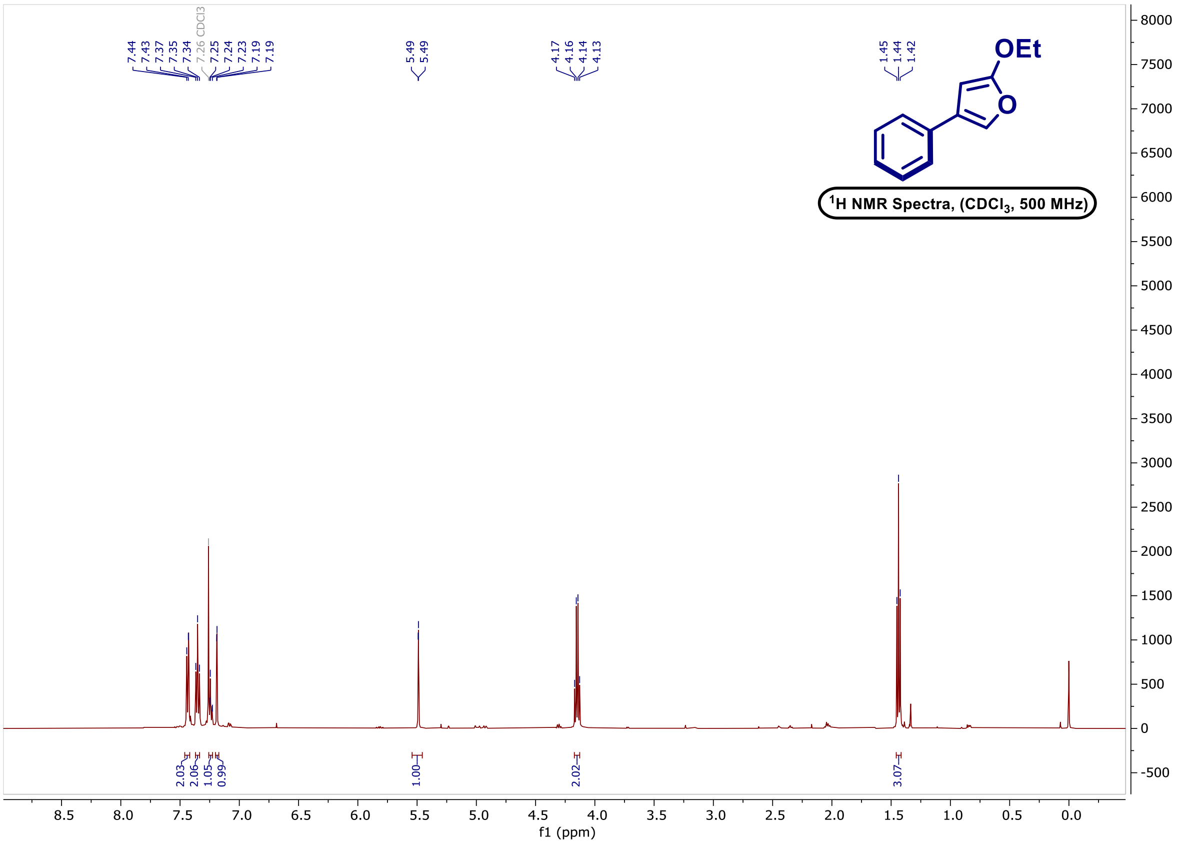

-111.09
-111.11
-111.11
-111.13
-111.14
-111.15
O
O
F
O
19F NMR Spectra, (CDCl3, 376 MHz)
0.055
0.050
0.045
0.040
0.035
0.030
0.025
0.020
0.015
0.010
0.005
0.000
-0.005
-0.010
-65
-70
-75
-80
-85
-90
-95
-100
-105
-110
-115
-120
-125
-130
-135
-140
-145
-150
-155
-160
f1 (ppm)

(*Z*)-5-(4-methoxybenzylidene)-4-(*m*-tolyl)furan-2(5H)-one (5x)

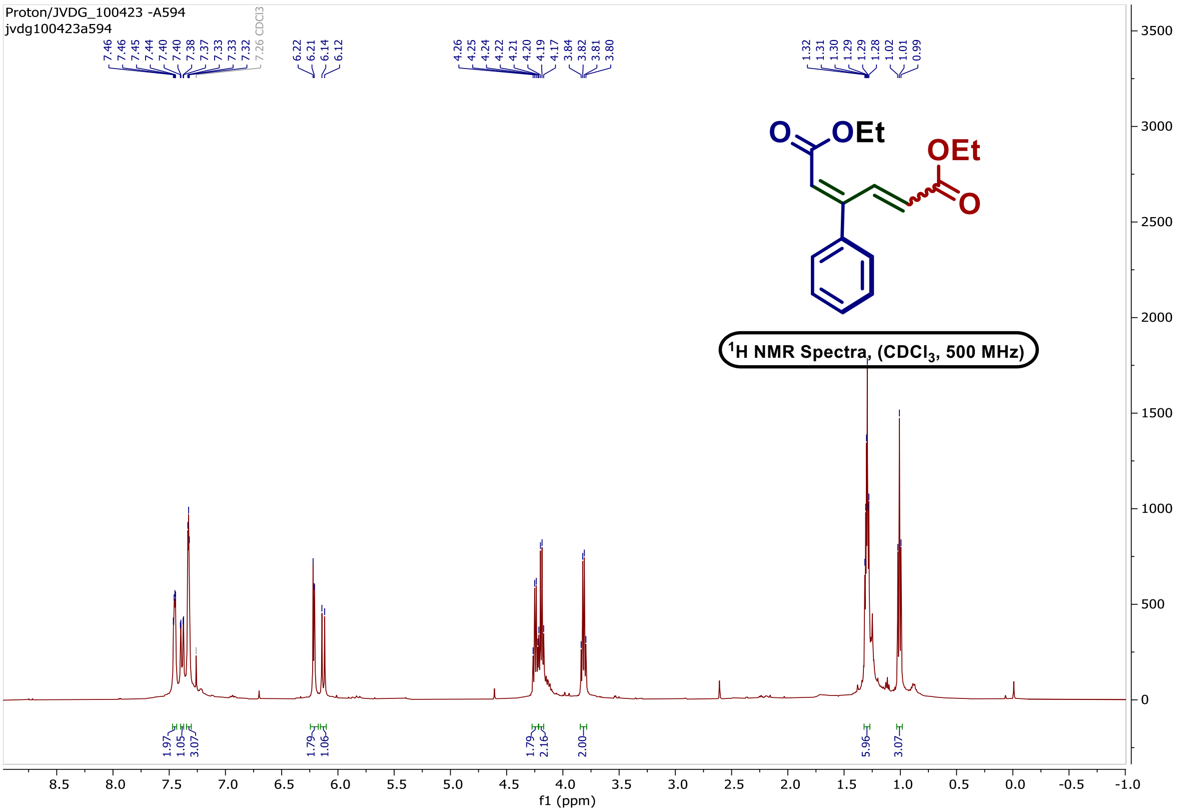




2-ethoxy-4-phenylfuran (6)

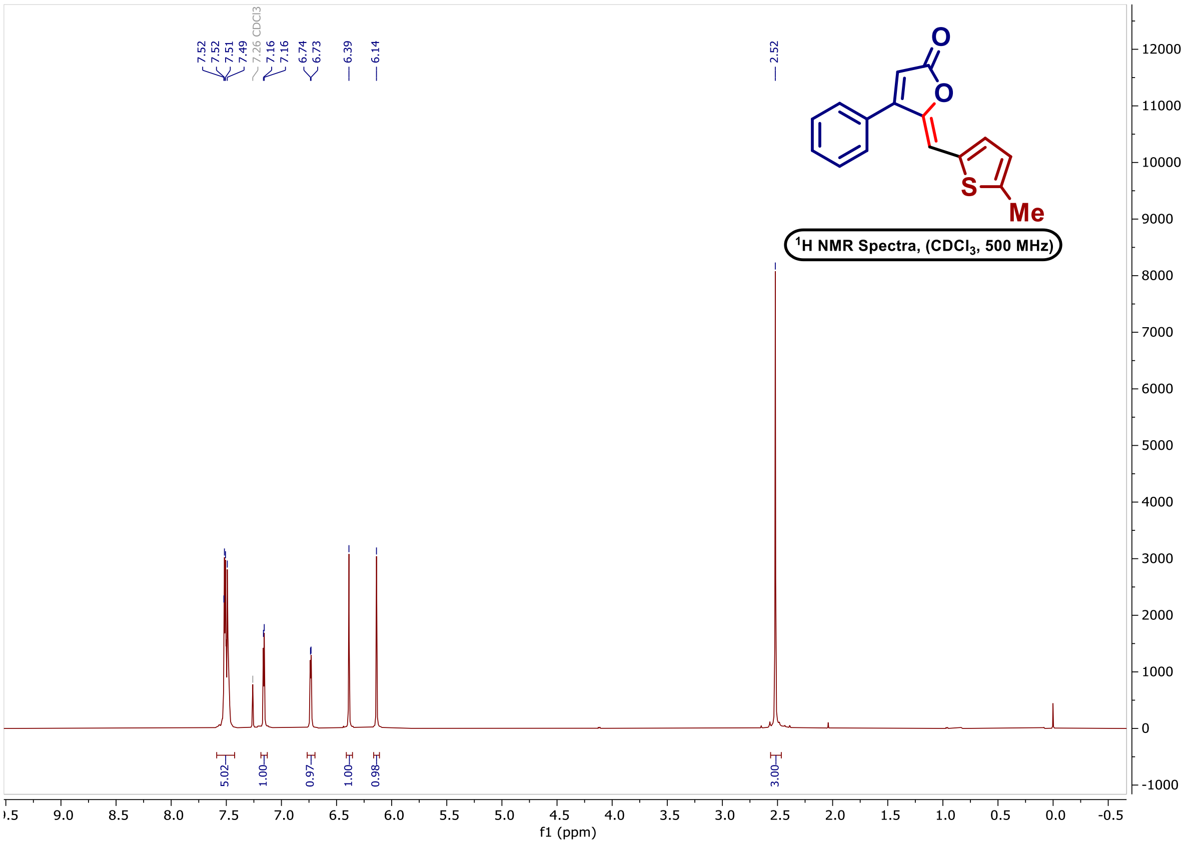


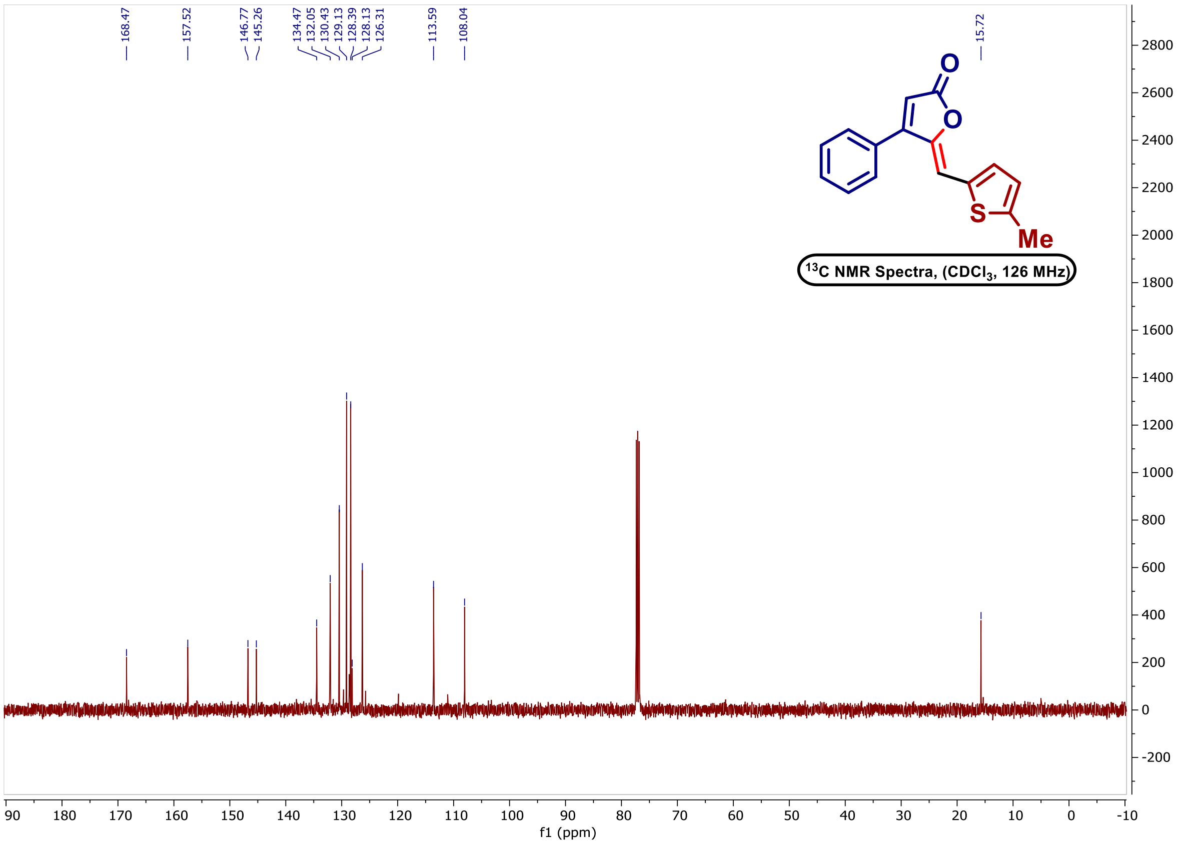
diethyl (2E)-3-phenylhexa-2,4-dienedioate



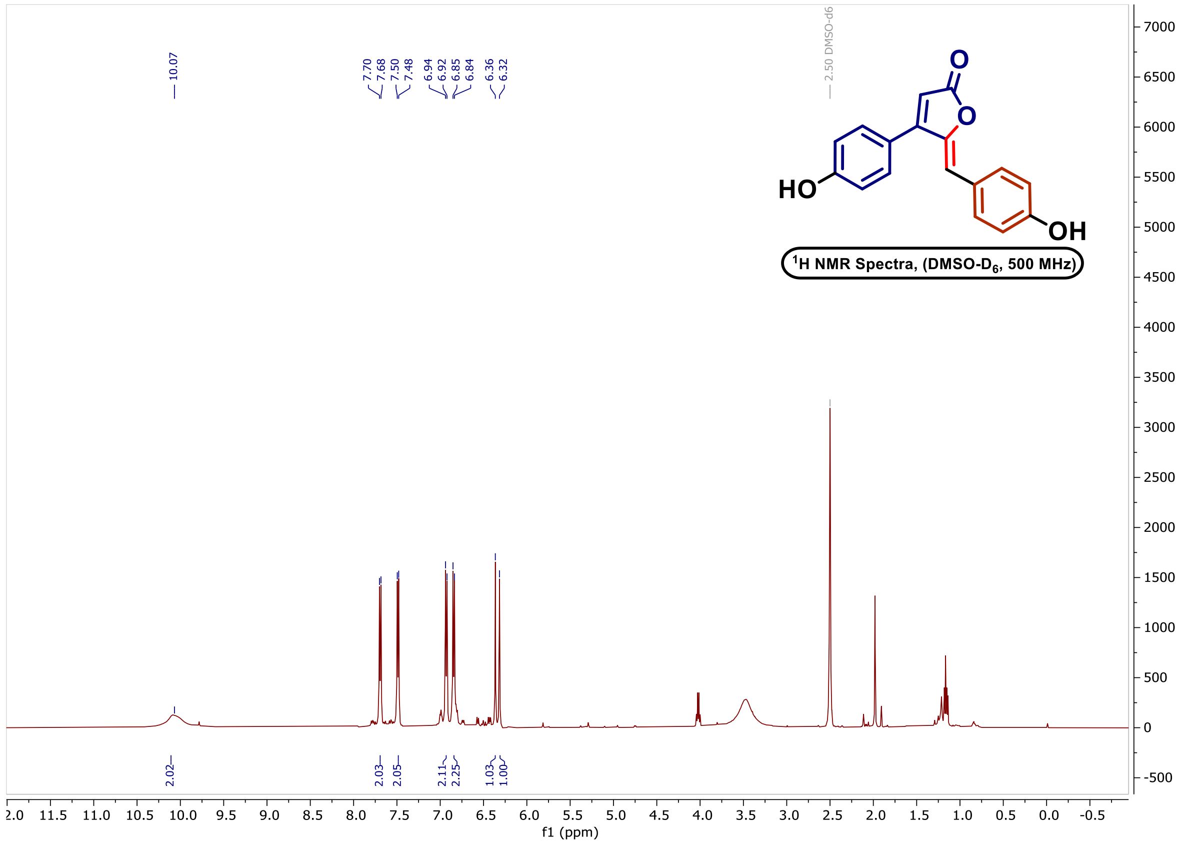
**Ethyl diazo acetate also delivered the dienoate in 62% yield but with 1:1 d.r. and diazo impurity.*

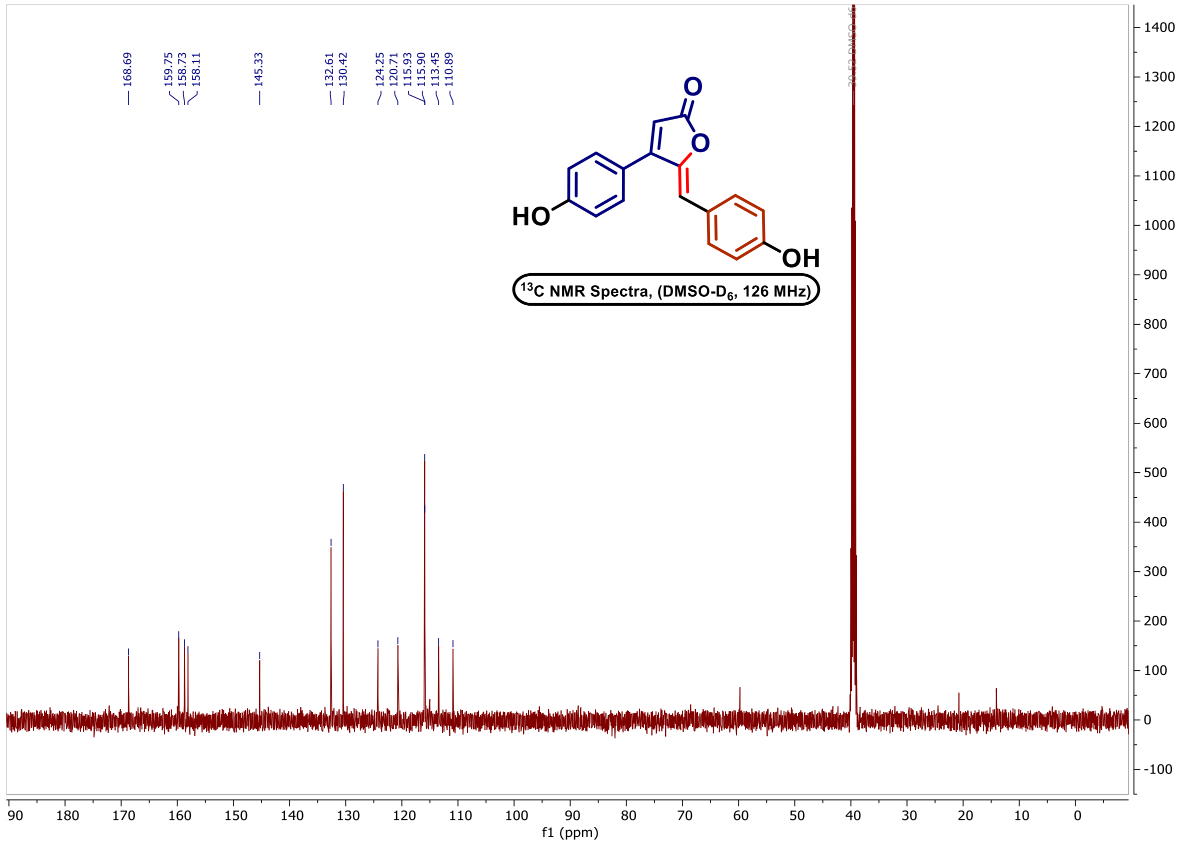
(*Z*)-5-((5-methylthiophen-2-yl)methylene)-4-phenylfuran-2(5*H*)-one (8)





(*Z*)-5-(4-hydroxybenzylidene)-4-(4-hydroxyphenyl)furan-2(5*H*)-one (10)





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