Supporting Information

# Diastereoselective Cyclopropanation of α,β- Unsaturated Carbonyl Compounds with Vinyl Sulfoxonium Ylides

*Shalu Deshwal,[a] Dinesh Kumar Gopalakrishnan,[a] Alok Purohit,[a] Tarak Karmakar*[a] and Janakiram Vaitla*[a]*

*Department of Chemistry, Indian Institute of Technology Delhi, Hauz Khas, New Delhi, 110016, India*

*E-mail: vaitla@chemistry.iitd.ac.in*

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## 1. General Information

Commercial grade reagents, solvents, and starting materials were purchased of pure analytical grades from TCI chemicals, sigma aldrich and Fisher chemicals and used as purchased without further purification, unless otherwise stated. Dichloroethane, Dichloromethane, DMSO and THF (after distilling from sodium) were dried from 4Å molecular sieves. Vinyl sulfoxonium ylide was prepared according to the literature. Moisture-sensitive reactions were performed under an atmosphere of argon and glassware was dried in an oven at 100 °C prior to use. Purification of reactions was carried out by Flash chromatography using a Biotage® SNAP Ultra Samplet 10 g and 25 g, 230- 400 mesh silica gel was used for flash column chromatography. For thin-layer chromatography (TLC) analysis throughout this work, Merck pre-coated TLC plates (silica gel 60 $GF_{254}$, 0.25 mm) were used and visualized with UV light. Organic solutions were concentrated under vacuum pressure using a rotary evaporator. The $^{1}H$ (400 MHz and 500 MHz) and $^{13}C$ (101 MHz and 126 MHz) nuclear magnetic resonance spectra were recorded on 400 MHz and 500 MHz spectrometers. Chemical shifts (δ) for $^{1}H$ and $^{13}C$ are reported in parts per million (ppm) relative to internal standard tetramethylsilane (tetramethylsilane @ 0 ppm) and residual solvent peak in the NMR solvent (for $CHCl_3$ @ 7.26 ppm), for $^{13}C$ NMR ($CHCl_3$ @ 77.16 ppm). Coupling constants are given in Hertz (Hz). The following abbreviations are used to indicate the multiplicity: s, singlet; d, doublet; q, quartet; p, pentet; sept, septet; m, multiplet; br, broad signal. High-resolution mass spectra (HRMS) were recorded on a Mass Spectrometry Unit 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).

## 2. Commercially available starting materials

### 2.1 Aldehydes

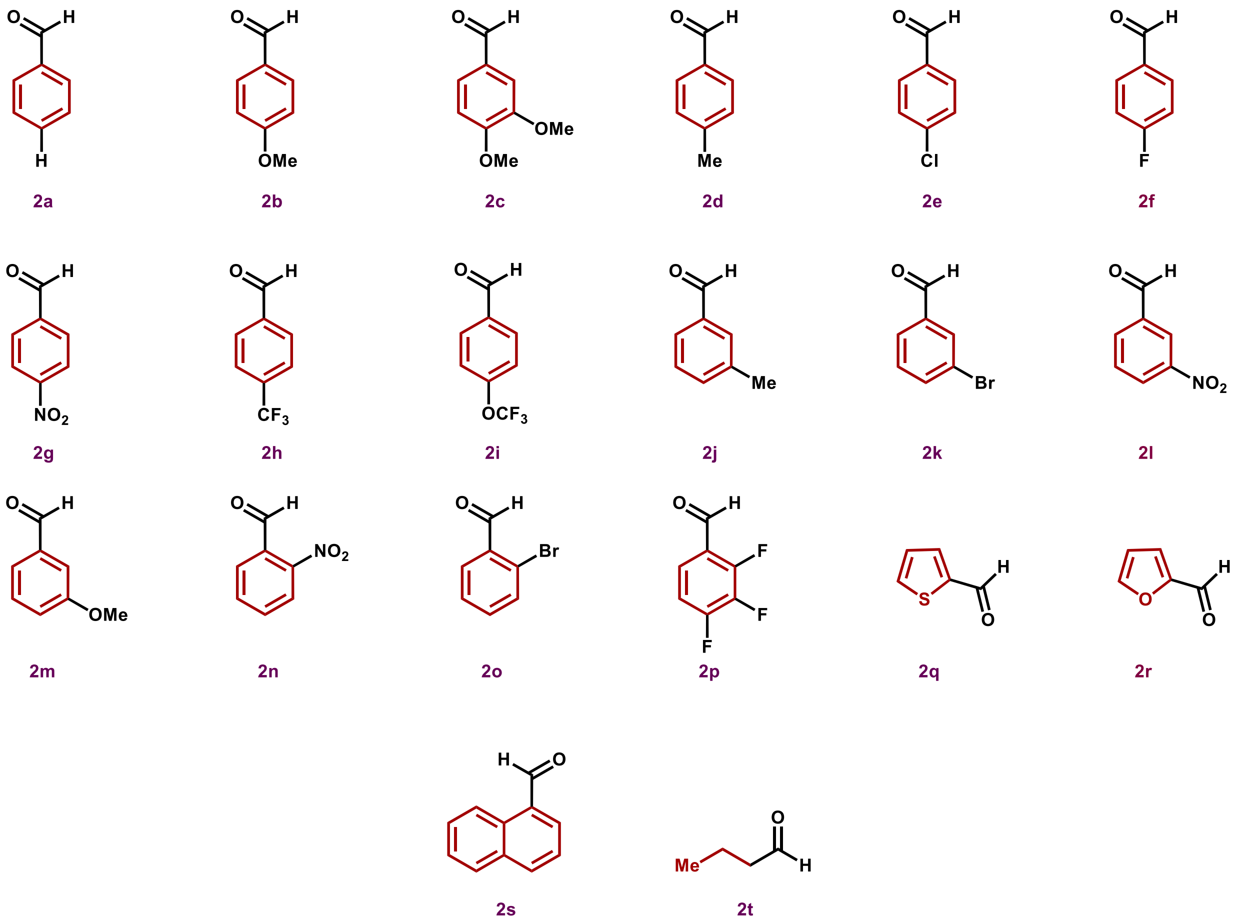



***Figure 1***: Commercially available aldehydes used in this study.

### 2.2 Ketones

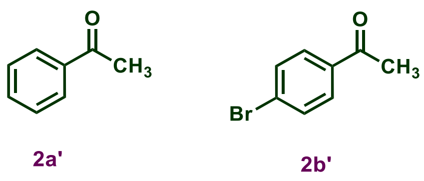
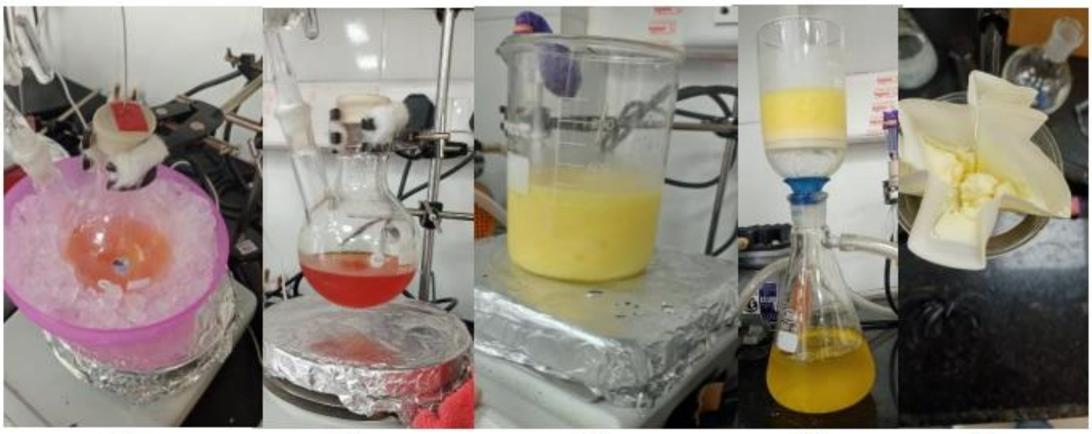



***Figure 2***: Commercially available ketones used in this study.

## 3. General Procedure for the synthesis of vinyl sulfoxonium ylide:[1]

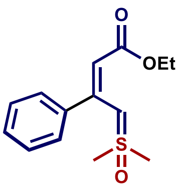
Ylides, we prepared according to the literature, to an oven-dried, Ar-purged 250 mL round-bottomed flask equipped with a magnetic stir bar is added NaH (2 equiv., 21 mmol) and DMSO (20 mL). Trimethylsulfoxonium iodide (1.4 equiv., 14 mmol) recrystallized from water and dried at 70 ºC under vacuum overnight, is added to the above turbid solution at 20 ºC. The resulting suspension is stirred for 20 min 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 alkyne (1 equiv., 10 mmol) in 25 mL THF and the resulting solution is cooled to 0 ºC (ice bath). The pre-made methylide solution is added via cannula or syringe dropwise over 5 min. The resulting mixture is stirred for 1 hour 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.

*"Caution! The thermal decomposition of NaH/DMSO is known. Care should be taken when handling DMSO in the presence of a base to limit personal exposure."*



**(a)** **(b)** **(c)** **(d)** **(e)**

***Figure 3*****:** 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.



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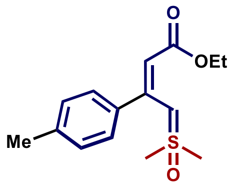

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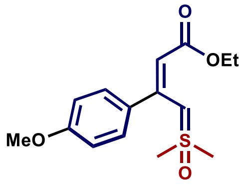

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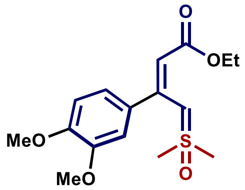

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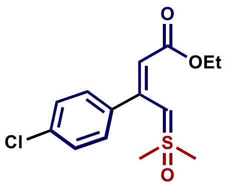

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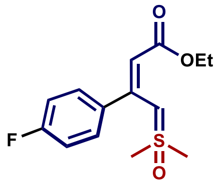

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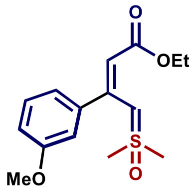

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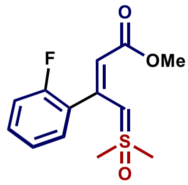

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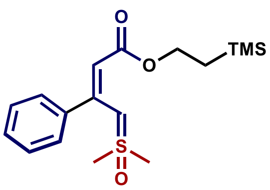

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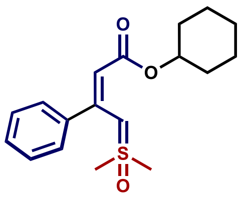

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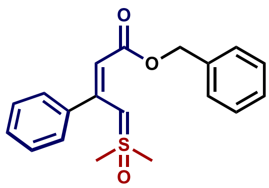

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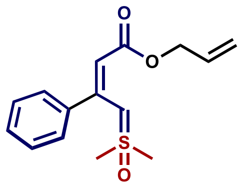

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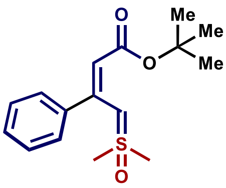

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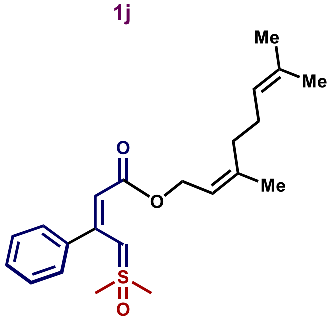

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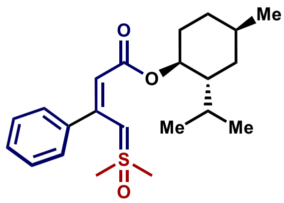
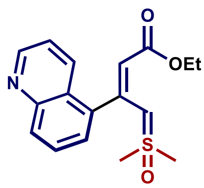


**1o**



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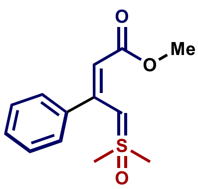
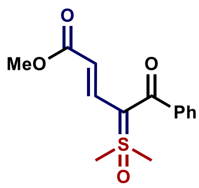


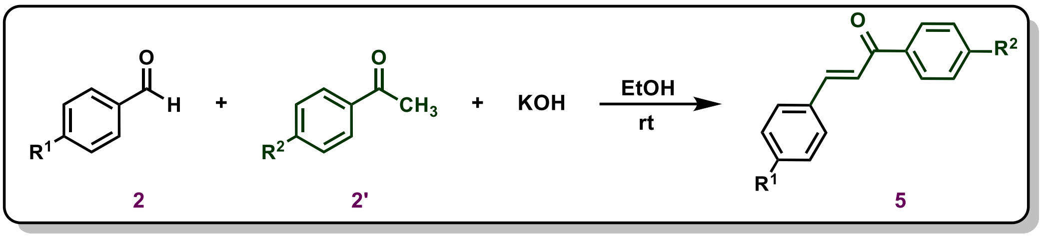
**1q**



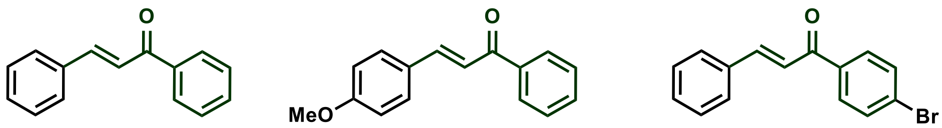
**1r***

***Figure 4.*** Vinyl sulfoxonium ylide used in this study.[1] Prepared by separate method. *

## 4. General Procedure for the Synthesis of *α*, *β*-Unsaturated Ketones (Enones, 5):[2]

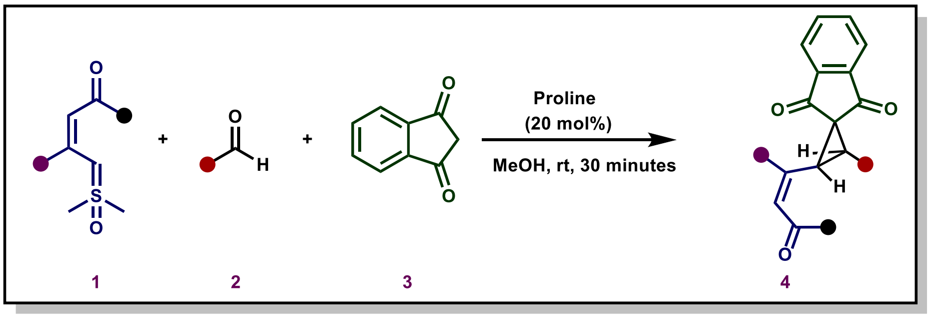



To a mixture of aldehyde (1.88 mmol, 1.0 equiv.) and ketone (1.88 mmol, 1 equiv.) in the ethanol solvent (0.6 M), KOH (2.26 mmol, 1.2 equiv.) was added at room temperature. The reaction was monitored by TLC, and on completion, solid was precipitated (in case of **5a** and **5c**). HCl solution (1 M) was used to neutralize the system, and the solid was filtered out and washed twice with water and once with cold ethanol. The enone **5a** and **5c** thus obtained were used without any purification. In the case of **5b** no solid precipitation was observed, and the reaction mixture was extracted three times with EtOAc after neutralizing the system with 1 M HCl. The combined organic layer was dried on $Na_2SO_4$, concentrated under reduced pressure and the residue was purified using flash column chromatography (Biotage flash chromatography gradient purification: EtOAc/*n*-Hexane = 1:5, $R_f$ 0.51) to give the product **5b** as yellow liquid.




5a 5b 5c

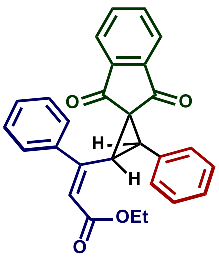
## 5. General procedure for the synthesis of spiro[cyclopropane-1,2'-indene]-1',3'-dione



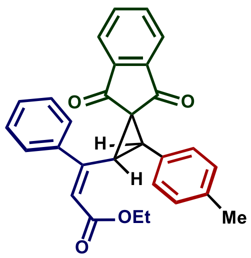

To an oven-dried, 25 mL round bottom flask equipped with a magnetic stir bar was added 1,3-Indanedione **3** (0.30 mmol, 1 equiv.) and aldehyde **2** (0.33 mmol, 1.1 equiv.) in methanol (0.1 M). To the stirring solution was added catalytic amount of L-proline (7 mg, 20 mol%) and Ylide **1** (0.42 mmol, 1.4 equiv.). After stirring for 30 minutes at room temperature, spiro[cyclopropane-1,2'-indene]-1',3'-dione precipitated at the bottom of the round bottom flask. The precipitate was filtered and washed with cold methanol to yield chromatographically and spectroscopically pure product.

**(a)** **(b)**

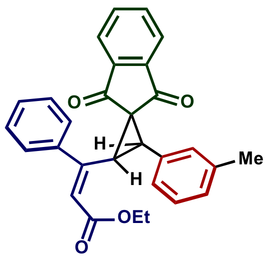
***Figure 5***: Representative example of **4j** **(a)** Reaction mixture containing precipitate of spiro[cyclopropane-1,2'-indene]-1',3'-dione. **(b)** Drying the product after washing with cold methanol.



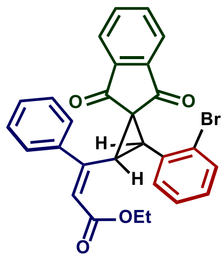
**4a** (87%)
(d.r.>20:1)



**4b** (90%)
(d.r.>20:1)



**4c** (89%)
(d.r.>20:1)



**4d** (80%)
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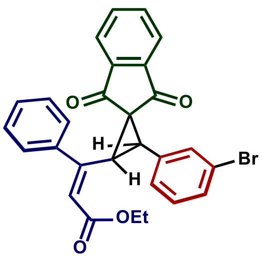
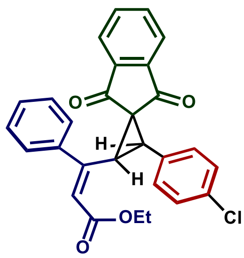
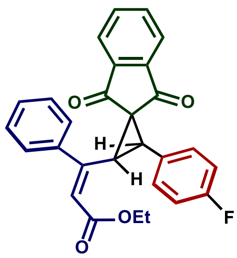


**4e** (83%)
(d.r.>20:1)



**4f** (86%)
(d.r.>20:1)



**4g** (85%)
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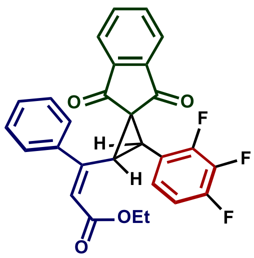
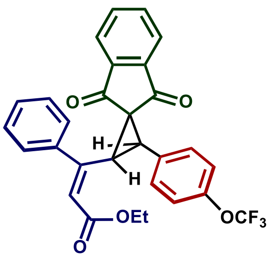
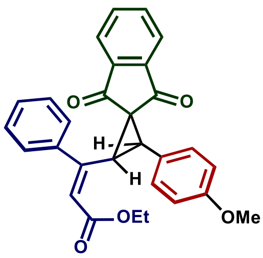


**4h** (80%)
(d.r.>20:1)



**4i** (82%)
(d.r.>20:1)



**4j** (91%)
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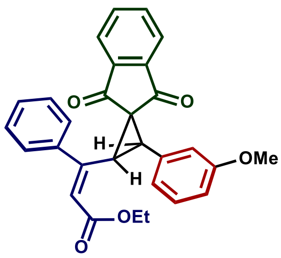
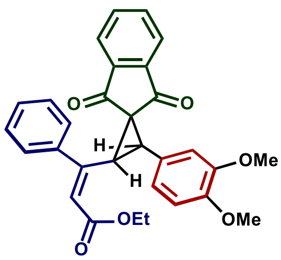


**4k** (88%)
(d.r.>20:1)



**4l** (93%)
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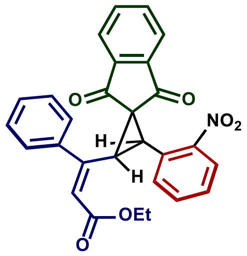

**4m** (79%)
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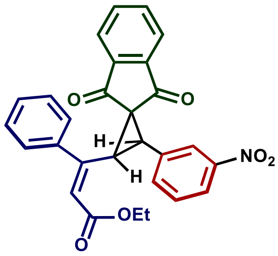

**4n** (81%)
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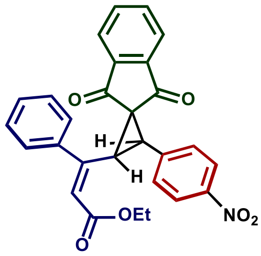

**4o** (83%)
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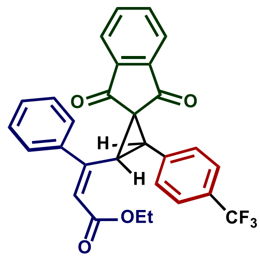

**4p** (84%)
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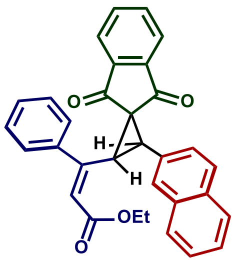

**4q** (81%)
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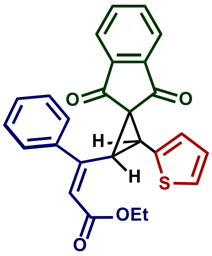

**4r** (89%)
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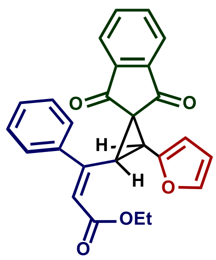
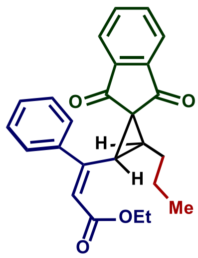
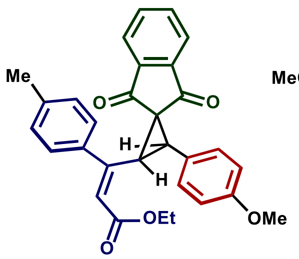


**4s** (87%)
(d.r.= 9:1)



**4t** (85%)
(d.r.= 5:1)



**4u** (89%)
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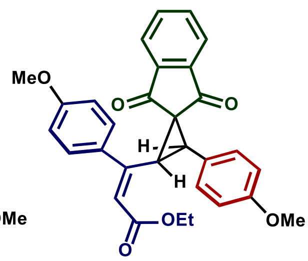

**4v** (90%)
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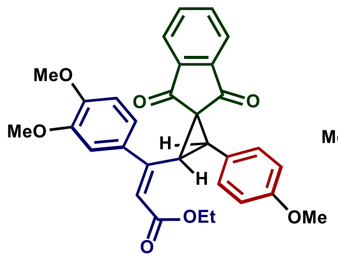

**4w** (92%)
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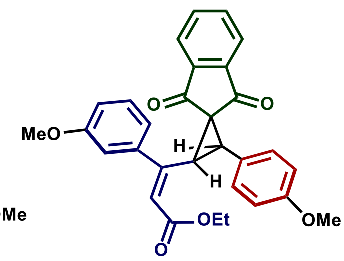

**4x** (86%)
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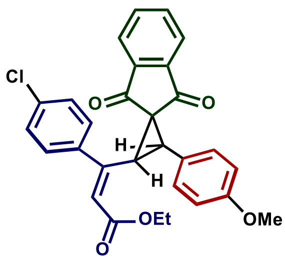

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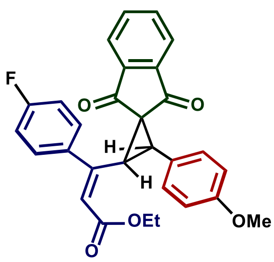

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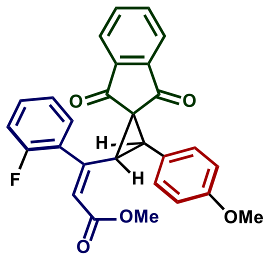

**4aa** (83%)
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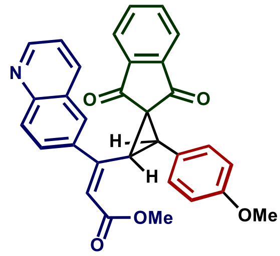

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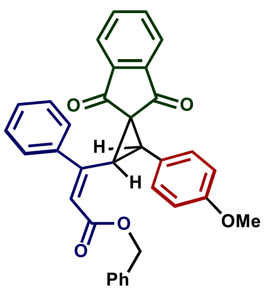

**4ac** (87%)
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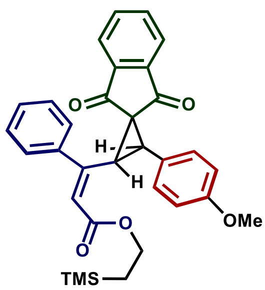

**4ad** (88%)
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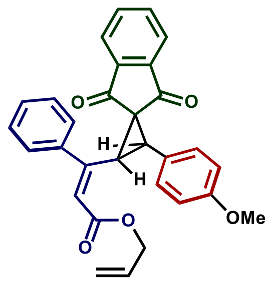
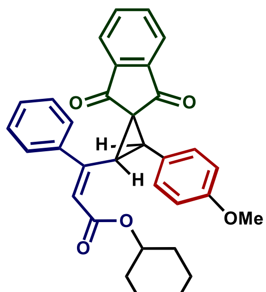
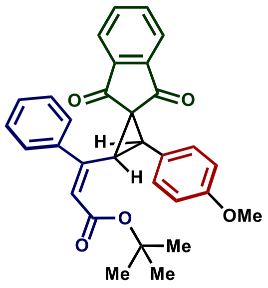


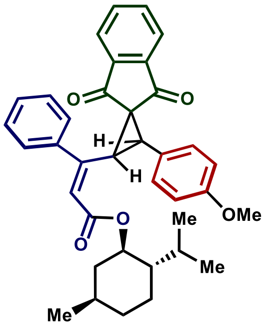
**4ae** (84%)
(d.r.>20:1)



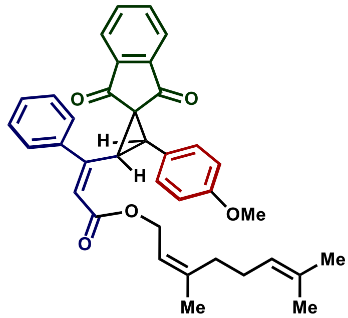
**4af** (86%)
(d.r.>20:1)



**4ag** (77%)
(d.r.>20:1)

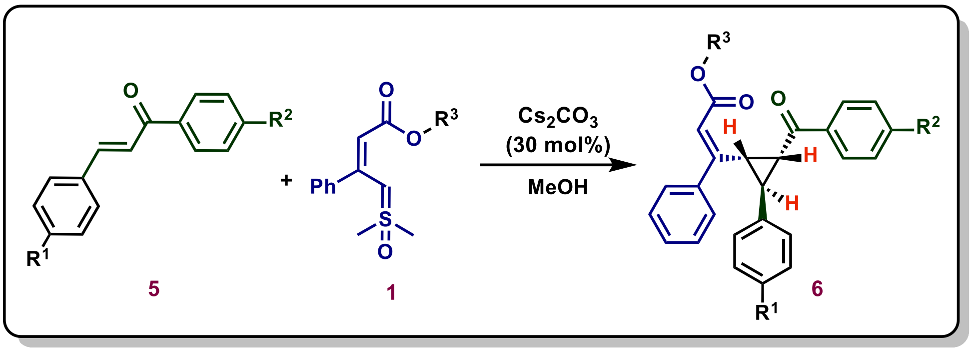


**4ah** (85%)
(d.r.= 1:1)

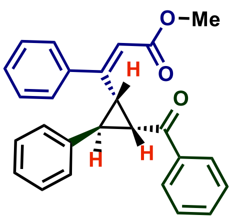


**4ai** (83%)
(d.r.>20:1)

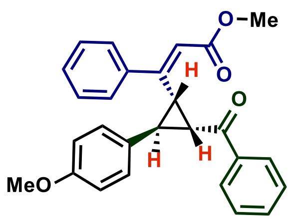
## 6. General procedure for the synthesis of 2-benzoyl-3-phenylcyclopropyl)-3-phenylacrylate



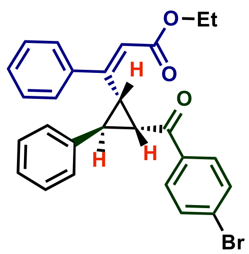
To an oven-dried, Ar-purged 25 mL round bottom flask equipped with a magnetic stir bar was added α, β-Unsaturated Ketone **5** (0.30 mmol, 1 equiv.) in methanol (0.1 M) under argon atmosphere. To the stirring solution was then added catalytic amount of cesium carbonate (28 mg, 30 mol%) and ylide **1** (0.40 mmol, 1.4 equiv.). After stirring for 2 hours at room temperature, the reaction mixture was concentrated under reduced pressure. The residue was purified using flash column chromatography (Biotage flash chromatography gradient purification: EtOAc/*n*-Hexane = 1:5) to give the product **6.**



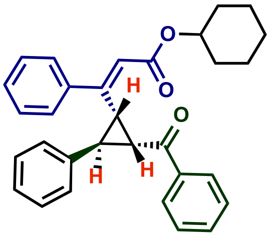
**6a** (79%)
(d.r.>20:1)



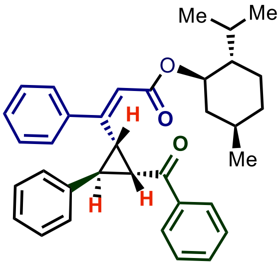
**6b** (76%)
(d.r.>20:1)



**6c** (78%)
(d.r.>20:1)



**6d** (77%)
(d.r.>20:1)



**6e** (74%)
(d.r.=1:1)

# 7. X-ray crystallographic data of 4l and 6a:

### 7.1 X-ray crystallographic data of 4l (CCDC number 2349128)

**Sample preparation**: Single crystal of compound **4l** suitable for the X-ray diffraction studies were grown from methanol at room temperature by slow evaporation of the solvent.

**Molecular structure determination of compound 4l:** Single crystal X-ray diffraction data for compound **4l** were collected using a Bruker SMART APEX 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 2349128 (**4l**) contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from Data Centre via http://www.ccdc.cam.ac.uk/data_request/cif.The crystallographic refinement parameters are given below:

**Table 1 Crystal data and structure refinement for cp_ome_0m_a.**

| | |
|---|---|
| CCDC | 2349128 |
| Identification code | cp_ome_0m_a |
| Empirical formula | $C_{30}H_{26}O_6$ |
| Formula weight | 482.51 |
| Temperature/K | 299.00 |
| Crystal system | triclinic |
| Space group | P-1 |
| a/Å | 8.6562(6) |
| b/Å | 11.0892(6) |
| c/Å | 13.6698(9) |
| α/° | 71.649(2) |
| β/° | 79.384(3) |
| γ/° | 83.229(2) |
| Volume/Å$^3$ | 1221.60(14) |
| Z | 2 |
| $\rho_{calc}$g/cm$^3$ | 1.312 |
| μ/mm$^{-1}$ | 0.091 |
| F(000) | 508.0 |
| Crystal size/mm$^3$ | 0.23 × 0.19 × 0.16 |

| | |
|---|---|
| Radiation | MoKα (λ = 0.71073) |
| 2Θ range for data collection/° | 3.878 to 52.888 |
| Index ranges | $-10 \le h \le 10, -13 \le k \le 13, -17 \le l \le 17$ |
| Reflections collected | 54112 |
| Independent reflections | 5015 [$R_{int}$ = 0.0931, $R_{sigma}$ = 0.0585] |
| Data/restraints/parameters | 5015/18/349 |
| Goodness-of-fit on $F^2$ | 0.866 |
| Final R indexes [I>=2σ (I)] | $R_1$ = 0.0482, $wR_2$ = 0.1281 |
| Final R indexes [all data] | $R_1$ = 0.0703, $wR_2$ = 0.1551 |
| Largest diff. peak/hole / e Å$^{-3}$ | 0.18/-0.19 |

This crystal data contains the distortion in the two carbons of ethoxy group of ylide moiety, which may be due to the rotation or vibration of the carbon atoms in the room temperature. Thus, the data was solved with the distortion treatment for the ethoxy group. The occupancy was 65% and 35% for each part. For the better understanding, the major occupancy structure is provided in the manuscript.

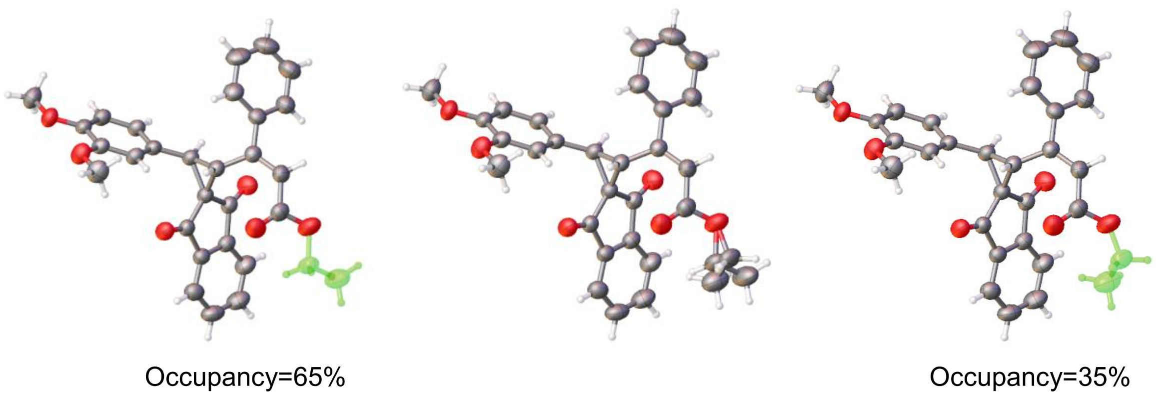



***Figure 6.*** ORTEP representation for the X-ray structure of **4l** with distortion treatment and corresponding occupancies

**7.2 X-ray crystallographic data of 6a (CCDC number 2349131)**

**Sample preparation**: Single crystal of compound **6a** suitable for the X-ray diffraction studies were grown from methanol at room temperature by slow evaporation of the solvent.

**Molecular structure determination of compound 6a:** Single crystal X-ray diffraction data for compound **6a** were collected using a Bruker SMART APEX 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 2349131 (**6a**) contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from Data Centre via http://www.ccdc.cam.ac.uk/data_request/cif.The crystallographic refinement parameters are given below:

**Table 2 Crystal data and structure refinement for 6a.**

| | |
|---|---|
| CCDC | 2349131 |
| Identification code | cis_cyclopropane |
| Empirical formula | $C_{26}H_{22}O_3$ |
| Formula weight | 382.43 |
| Temperature/K | 297.00 |
| Crystal system | orthorhombic |
| Space group | $Pca2_1$ |
| a/Å | 18.8323(8) |
| b/Å | 10.3176(4) |
| c/Å | 10.7363(4) |
| α/° | 90 |
| β/° | 90 |
| γ/° | 90 |
| Volume/Å$^3$ | 2086.11(14) |
| Z | 4 |
| $\rho_{calc}$g/cm$^3$ | 1.218 |
| μ/mm$^{-1}$ | 0.079 |
| F(000) | 808.0 |
| Crystal size/mm$^3$ | 0.22 × 0.18 × 0.15 |
| Radiation | MoKα (λ = 0.71073) |
| 2Θ range for data collection/° | 3.948 to 56.6 |
| Index ranges | $-25 \le h \le 25, -13 \le k \le 13, -14 \le l \le 14$ |
| Reflections collected | 21786 |
| Independent reflections | 5159 [$R_{int}$ = 0.0415, $R_{sigma}$ = 0.0427] |
| Data/restraints/parameters | 5159/1/264 |
| Goodness-of-fit on F$^2$ | 1.056 |
| Final R indexes [I>=2σ (I)] | $R_1$ = 0.0466, $wR_2$ = 0.1011 |
| Final R indexes [all data] | $R_1$ = 0.0668, $wR_2$ = 0.1112 |
| Largest diff. peak/hole / e Å$^{-3}$ | 0.16/-0.14 |
| Flack parameter | 0.7(6) |

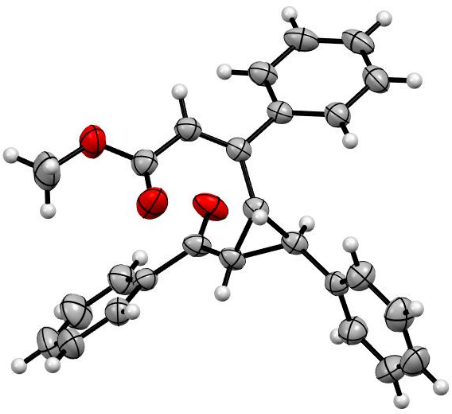
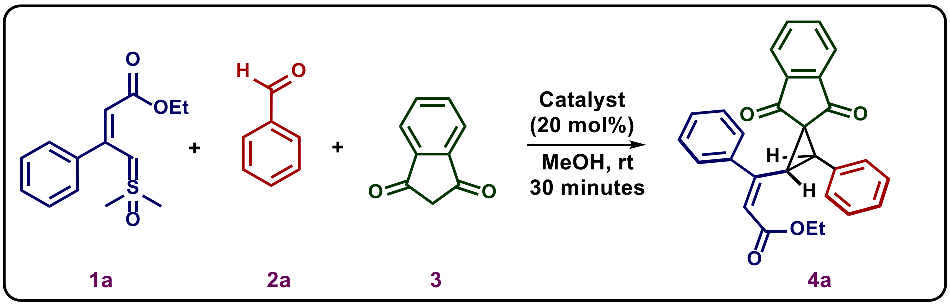


***Figure 7.*** ORTEP representation of the X-ray structure of **6a** with Thermal

ellipsoid at 40% probability.

# 8. Optimization Studies

### 8.1 General procedure for optimization study (investigation of catalyst):




To an oven-dried, 25 mL round bottom flask equipped with a magnetic stir bar was added 1,3-Indanedione (13 mg, 0.10 mmol, 1 equiv.) and aldehyde **2a** (11 µL, 0.11 mmol, 1.1 equiv.) in methanol (0.1 M). To the stirring solution was added Ylide **1a** (37 mg, 0.14 mmol, 1.4 equiv.). After stirring the solution for 30 minutes, solvent evaporated under reduced pressure. The analysis was done using crude $^{1}H$ NMR by taking $CH_2Br_2$ as the internal standard.

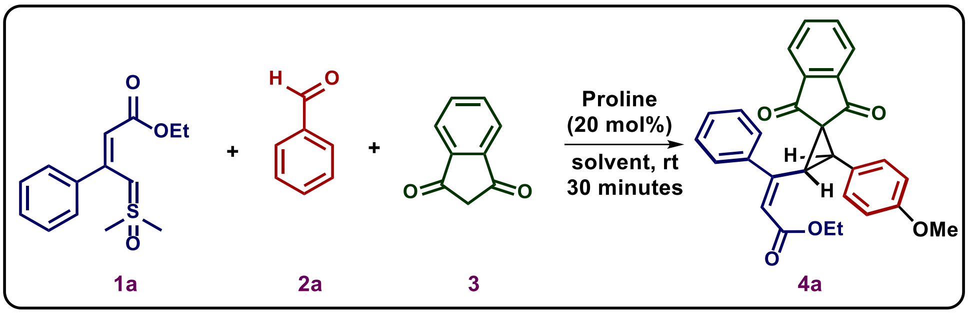
### 8.2 Optimization Table 3[a]: (Investigation of catalyst)

| Entry | Catalyst (20 mol%) | Yield[b] (d.r.)[c] |
|---|---|---|
| 1 | No catalyst | ND* |
| 2 | Piperidine | 43 (>20:1) |
| 3 | Triethyl amine | 34 (>20:1) |
| 4 | TMSOTf | 45 (>20:1) |
| 5 | $In(OTf)_3$ | 15 (>20:1) |
| 6 | $Sc(OTf)_3$ | 22 (>20:1) |
| 7 | $HBF_4.Et_2O$ | 85 (>20:1) |
| 8 | Acetic acid | ND* |
| 9 | L-proline | 92 (87)[d] (>20:1) |
| 10[e] | L-proline | 92 (>20:1) |
| 11[f] | L-proline | 91 (>20 :1) |

[a]Standard condition: Indane 1,3-dione (0.10 mmol), **1a** (0.14 mmol), **2a** (0.11 mmol), catalyst (20 mol%), methanol (0.1 M), 30 minutes. [b]The yield was determined by $^{1}H$ NMR analysis of crude products using dibromomethane as the internal standard.[c]Determined by crude NMR. [d]Isolated yield of the major diastereomer. [e]30 mol% of the catalyst were used. [f]Reaction was run for one hour. *ND-Not detected.

Initially, the optimization was carried out using Indane 1,3-dione, benzaldehyde (**2a**) and vinyl sulfoxonium ylide **2a** as model substrate**.** When the reaction was carried out in absence of catalyst, no desired product was detected (**Table 3, entry 1**). Then catalysts with different properties were screened. Firstly, screening was carried out with base catalyst such as piperidine and triethyl amine and product were detected in quantitative yield of 43% and 34% (**Table 3, entry 2 and 3 respectively**). With the excellent selectivity obtained, motivated to screen other catalyst. To further improve the yield optimization was carried out with lewis acid catalyst. When screening was done in presence of TMSOTf and $In(OTf)_3$, surprisingly low yield of product was obtained (**Table 3, entry 4 and 5**). When the reaction was carried out in the presence of $Sc(OTf)_3$, no improvement in yield was observed (**Table 3, entry 6**). But, when $HBF_4.Et_2O$ was used as a catalyst in desired transformation, a notable improvement in the yield was observed (**Table 3, entry 7**). Acetic acid failed to produce the product, Instead, the reaction resulted in the insertion of vinyl sulfoxonium ylides into the O−H bond of carboxylic acid (**Table 3, Entry 8**).[3] Further screening revealed L-proline as the most effective catalyst in this multicomponent [2+1] annulation (**Table 3, entry 9**). Further increasing the amount of catalyst and extending the reaction time did not have a significant impact on the yield (**Table 3, entry 10 and 11 respectively**).

### 8.3 General procedure for optimization study (investigation of solvent):




To an oven-dried, 25 mL round bottom flask equipped with a magnetic stir bar was added 1,3-Indanedione (13 mg, 0.10 mmol, 1 equiv.) and aldehyde **2a** (11 µL, 0.11 mmol, 1.1 equiv.) in solvent (0.1 M). To the stirring solution was added Ylide **1a** (37 mg, 0.14 mmol, 1.4 equiv.). After stirring the solution for 30 minutes, solvent evaporated under reduced pressure. The analysis was done using crude $^1$H NMR by taking $CH_2Br_2$ as the internal standard.

### 8.4 Optimization Table 4$^a$: (Investigation of solvent)

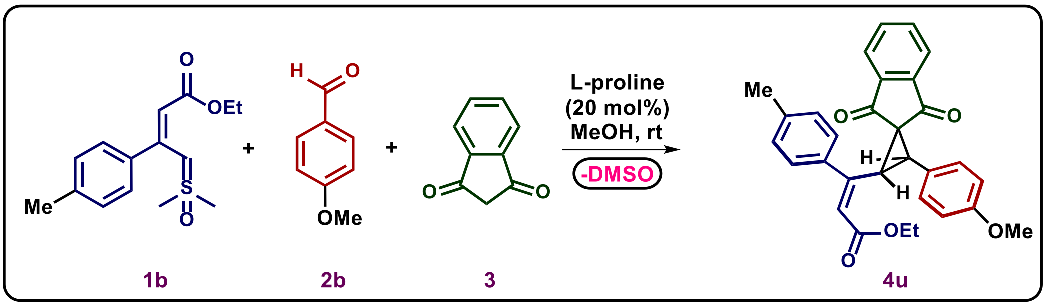
| Entry | Solvent (0.1 M) | Yield$^b$ (d.r.)$^c$ |
|---|---|---|
| 1 | Dichloromethane | 73 (>20:1) |
| 2 | 1,2-Dichloroethane | 67 (>20:1) |
| 3 | Acetonitrile | 78 (>20:1) |
| 4 | Diethyl ether | 63 (>20:1) |
| 5 | Ethyl acetate | 65 (>20:1) |
| 6 | Chloroform | 75 (>20:1) |
| 7 | Tetrahydrofuran | 64 (>20:1) |
| 8 | Dimethyl sulfoxide | 80 (>20:1) |
| 9 | Ethanol | 88 (>20:1) |

$^a$Standard condition: Indane 1,3-dione (0.10 mmol), **1a** (0.14 mmol), **2a** (0.11 mmol), L-proline (20 mol%), Solvent (0.1 M), 30 minutes. $^b$The yield was determined by $^1$H NMR analysis of crude products using dibromomethane as the internal standard.$^c$Determined by crude NMR.

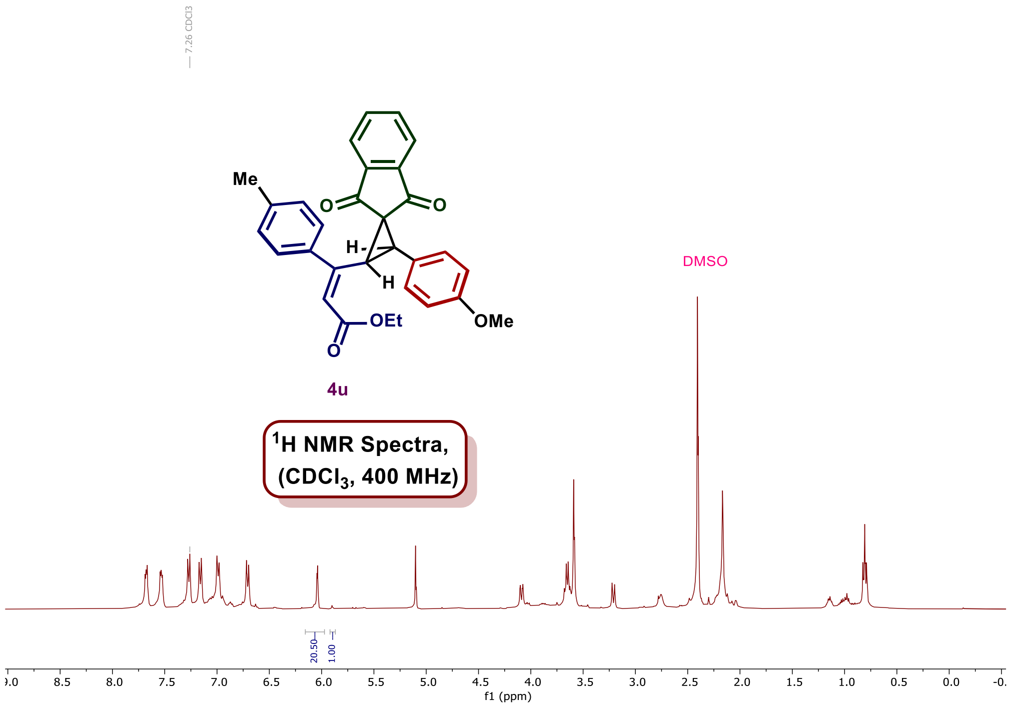
To further improve the yield, we continued our optimization with various solvents. A comprehensive screening of various solvents, including chlorinated, alcohol-based, aprotic, and protic solvents, was conducted (**Table 4, entry 1-9**). Among the tested solvents, ethanol (**Table 4, entry 9**) was found to be the most effective, yielding product in 88% yield, but we can conclude methanol is best solvent after overall comparison of optimization studies (**Table 1, entry 9**) for the present annulation approach.

## 9. Determination of diastereomeric ratio

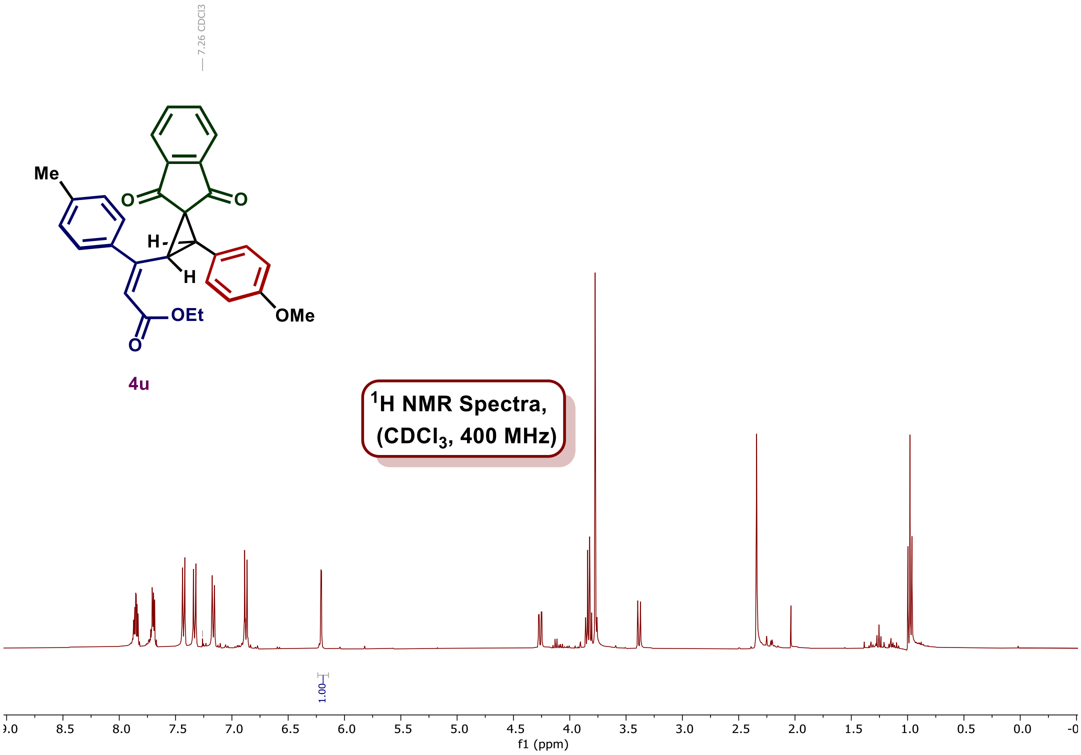
To an oven-dried, 25 mL round bottom flask equipped with a magnetic stir bar was added 1,3-Indanedione (44 mg, 0.30 mmol, 1 equiv.) and aldehyde **2b** (40 µL, 0.33 mmol, 1.1 equiv.) in methanol (0.1 M). To the stirring solution was added Ylide **1b** (118 mg, 0.42 mmol, 1.4 equiv.). After stirring the solution for 30 minutes, solvent evaporated under reduced pressure. The analysis was done using crude $^{1}$H NMR.




**$^{1}$H NMR spectrum of crude reaction mixture**



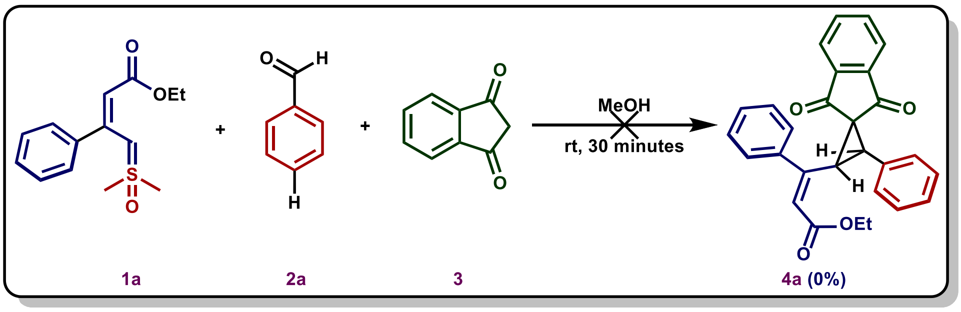

**$^{1}$H NMR spectrum of 4u**




# 10. Mechanistic Investigation:

## 10.1 Control experiment 1.

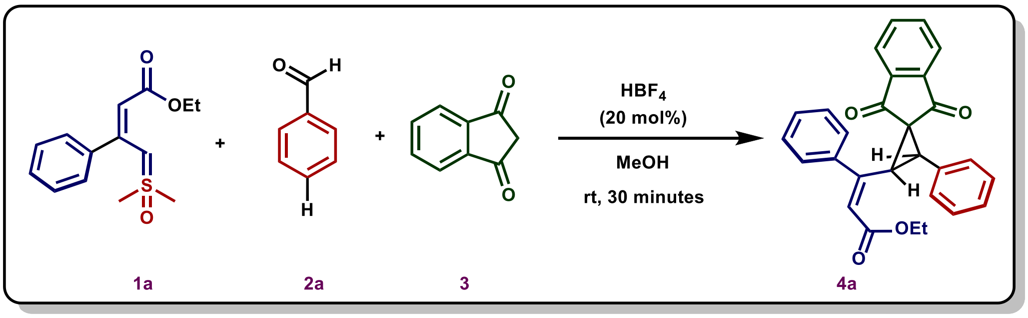
To an oven-dried, 25 mL round bottom flask equipped with a magnetic stir bar was added 1,3-Indanedione (44 mg, 0.30 mmol, 1 equiv.) and aldehyde **2a** (35 µL, 0.33 mmol, 1.1 equiv.) in methanol (0.1 M). To the stirring solution was added Ylide **1a** (112 mg, 0.42 mmol, 1.4 equiv.). After stirring the solution at room temperature for 30 minutes, there was no change in the reaction mixture and product **4a** was not detected.




*'The above control experiment suggests the role of the catalyst in product formation.'*

## 10.2 Control experiment 2.

To an oven-dried, 25 mL round bottom flask equipped with a magnetic stir bar was added 1,3-Indanedione (44 mg,0.30 mmol, 1 equiv.) and aldehyde **2a** (35 µL, 0.33 mmol, 1.1 equiv.) in methanol (0.1 M). To the stirring solution was added catalytic amount of $HBF_4$ (20 mol%) and Ylide **1a** (112 mg, 0.42 mmol, 1.4 equiv.). After stirring the solution at room temperature for 30 minutes, **4a** precipitated at the bottom of the round bottom flask. The precipitate was then filtered and washed with cold methanol to yield chromatographically and spectroscopically pure product.



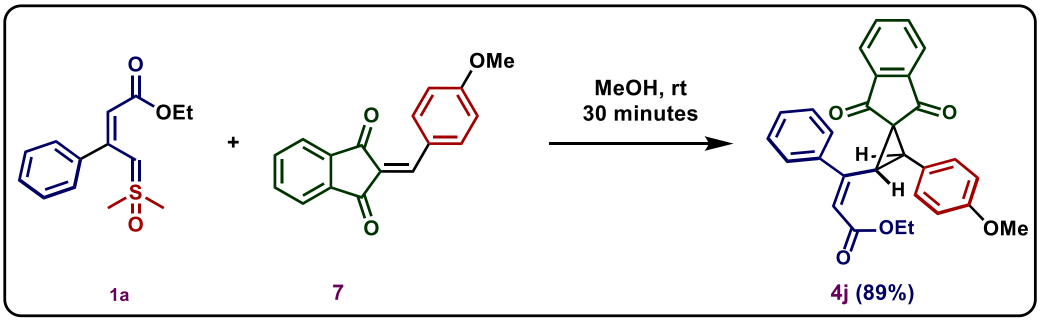

*'The above control experiment suggest that acid source is sufficient for generation of product.'*

# 11.Scale up experiment

## 11.1 Gram scale synthesis from intermediate

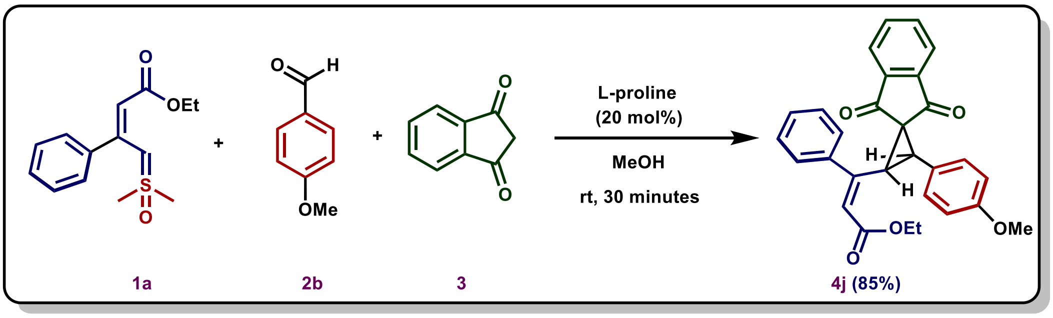
To an oven-dried, 250 mL round bottom flask equipped with a magnetic stir bar was added **7** (1 g, 3.78 mmol, 1 equiv.) and ylide **1a** (1.41 g, 5.30 mmol, 1.4 equiv.) in methanol (0.1 M). After stirring the solution at room temperature for 30 minutes, **4j** precipitated at the bottom of the round bottom flask. The precipitate was then filtered and washed with cold methanol to give **4j** in 89% yield (1.53 g, 3.36 mmol) as white solid.

*'7 was prepared according to the literature reports.'*[4]




*'The above result confirms that 2-benzylidene-1H-indene-1,3(2H)-dione (7) is the intermediate in this multicomponent [2+1] annulation and also confirms the exact role of catalyst i.e. catalyst role is up to intermediate formation after that there is no activation required for the interaction of ylide and intermediate.'*

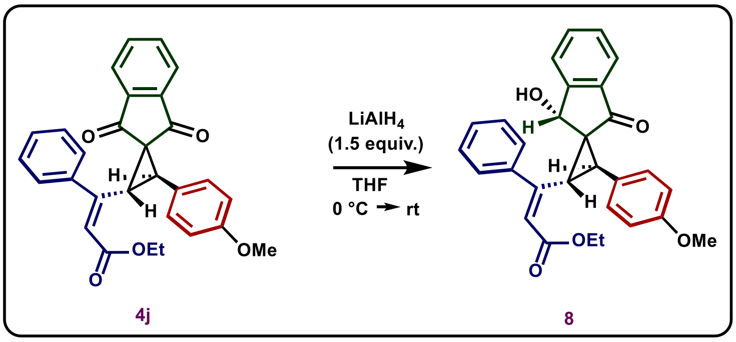
## 11.2 Gram scale synthesis via multicomponent approach



To an oven-dried, 250 mL round bottom flask equipped with a magnetic stir bar was added 1,3-Indanedione **3** (550 mg, 3.76 mmol, 1 equiv.) and aldehyde **2b** (503 μL, 4.41 mmol, 1.1 equiv.) in methanol (0.1 M). To the stirring solution was added catalytic amount of L-proline (87 mg, 20 mol%) and Ylide **1a** (1.4 g, 5.3 mmol, 1.4 equiv.). After stirring for 30 minutes at room temperature, spiro[cyclopropane-1,2'-indene]-1',3'-dione **4j** precipitated at the bottom of the round bottom flask. The precipitate was filtered and washed with cold methanol to give **4j** in 85% yield (1.45 g, 3.2 mmol) as white solid.

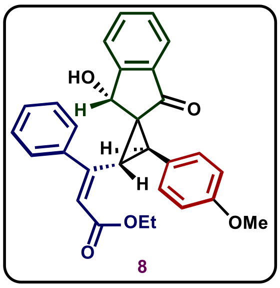
# 12. Synthetic utility

### 12.1 Selective reduction of keto group in cyclopropane




To an oven-dried, 25 mL round bottom flask equipped with a magnetic stir bar was added spiro[cyclopropane-1,2'-indene]-1',3'-dione **4j** (140 mg, 0.3 mmol, 1 equiv.) in THF (0.1M). To the stirring solution was added lithium aluminum hydride at 0 ºC. After adding reducing reagent, reaction was stirred at rt for 3 hours. After completion of reaction, quenched with methanol at 0 ºC. The reaction mixture was extracted three times with EtOAc. The combined organic layer was dried on $Na_2SO_4$, concentrated under reduced pressure and the residue was purified using flash column chromatography (Biotage flash chromatography gradient purification: EtOAc/*n*-Hexane = 1:4, $R_f$ 0.51) to give the product **8** in 71% yield (100 mg, 0.22 mmol) as yellow liquid with diastereomeric ratio >7:1.

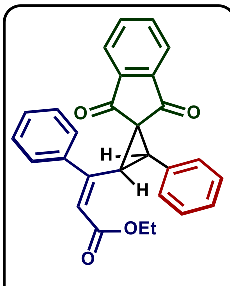
**ethyl (*E*)-3-(1'-hydroxy-2-(4-methoxyphenyl)-3'-oxo-1',3'-dihydrospiro[cyclopropane-1,2'-inden]-3-yl)-3-phenylacrylate (8):**




**$^1$H NMR (400 MHz, CHLOROFORM-*D*) δ** 7.72 (d, *J* = 0.9 Hz, 1H), 7.62 (d, *J* = 1.7 Hz, 2H), 7.53 – 7.49 (m, 2H), 7.38 – 7.34 (m, 3H), 7.28 – 7.23 (m, 3H), 6.91 (d, *J* = 8.8 Hz, 2H), 6.18 (d, *J* = 2.2 Hz, 1H), 5.14 (d, *J* = 11.7 Hz, 1H), 4.71 (d, *J* = 11.7 Hz, 1H), 3.81 (s, 5H), 3.70 – 3.66 (m, 1H), 2.86 (d, *J* = 8.5 Hz, 1H), 0.98 (t, *J* = 7.1 Hz, 3H). **$^{13}$C NMR (101 MHz, CHLOROFORM-*D*)** δ 199.5, 166.9, 158.9, 156.9, 155.1, 141.5, 136.2, 134.8, 129.1, 129.0, 128.9, 128.6, 128.5, 128.0, 126.3, 122.3, 120.4, 114.3, 69.3, 60.6, 55.4, 53.8, 40.5, 34.6, 13.9. **HRMS (ESI) m/z:** $[M+Na]^+$ calculated for $C_{29}H_{24}O_4Na$, 459.1567; found 459.1570.

# 13. Synthesis and characterization data of spiro[cyclopropane-1,2'-indene]-1',3'-dione

**ethyl (*E*)-3-(1',3'-dioxo-2-phenyl-1',3'-dihydrospiro[cyclopropane-1,2'-inden]-3-yl)-3-phenylacrylate (4a):**

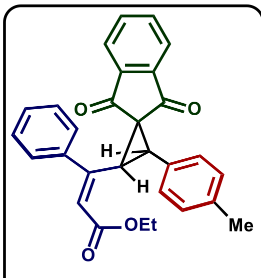


4a

Following the general procedure 5, reaction of 1*H*-indene-1,3(2*H*)-dione (44 mg, 0.30 mmol, 1 equiv.), aldehyde **2a** (34 µL, 0.33 mmol, 1.1 equiv.) and ylide **1a** (112 mg, 0.42 mmol, 1.4 equiv.) using catalytic amount (7 mg, 20 mol%) of L-proline in methanol (0.1 M) at room temperature for 30 minutes furnished **4a** in 87% (113 mg, 0.26 mmol,) as yellow solid with diastereomeric ratio >20:1.

**$^1$H NMR (500 MHz, CHLOROFORM-*D*) δ** 7.86 (s, 2H), 7.77 – 7.67 (m, 2H), 7.55 – 7.48 (m, 2H), 7.42 – 7.31 (m, 7H), 7.31 – 7.27 (m, 1H), 6.21 (s, 1H), 4.29 (d, *J* = 9.6 Hz, 1H), 3.84 (q, *J* = 7.1 Hz, 2H), 3.40 (d, *J* = 9.6 Hz, 1H), 0.99 (t, *J* = 7.1 Hz, 3H). **$^{13}$C NMR (101 MHz, CHLOROFORM-*D*) δ** 195.7, 194.7, 165.5, 141.8, 140.7, 136.0, 135.0, 134.6, 132.3, 131.1, 129.9, 129.2, 128.7, 127.8, 123.0, 122.5, 122.5, 122.4, 60.3, 50.7, 44.9, 38.3, 14.1. **IR (neat, cm$^{-1}$):** 3432, 3059, 2982, 1710, 1620, 1495, 1446, 1337, 1287, 1219, 1174, 1095, 1039, 875, 697, 617, 562, 534, 483.

**ethyl (*E*)-3-(1',3'-dioxo-2-(p-tolyl)-1',3'-dihydrospiro[cyclopropane-1,2'-inden]-3-yl)-3-phenylacrylate (4b):**

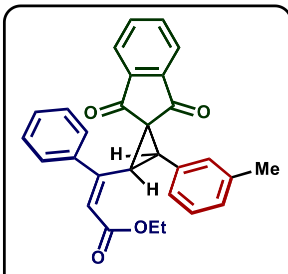


4b

Following the general procedure 5, reaction of 1*H*-indene-1,3(2*H*)-dione (44 mg, 0.30 mmol, 1 equiv.), aldehyde **2d** (39 µL, 0.33 mmol, 1.1 equiv.) and ylide **1a** (112 mg, 0.42 mmol, 1.4 equiv.) using catalytic amount (7 mg, 20 mol%) of L-proline in methanol (0.1 M) at room temperature for 30 minutes furnished **4b** in 90% (118 mg, 0.27 mmol,) as yellow with diastereomeric ratio >20:1.

**$^1$H NMR (500 MHz, CHLOROFORM-*D*) δ** 7.87 (d, *J* = 1.9 Hz, 2H), 7.72 (dd, *J* = 6.0, 2.9 Hz, 2H), 7.54 (t, *J* = 3.6 Hz, 2H), 7.40 – 7.33 (m, 3H), 7.25 – 7.19 (m, 3H), 7.12 (s, 1H), 6.22 (s, 1H), 4.31 (d, *J* = 9.6 Hz, 1H), 3.85 (q, *J* = 7.1 Hz, 2H), 3.40 (d, *J* = 9.6 Hz, 1H), 2.35 (s, 3H), 1.00 (t, *J* = 7.1 Hz, 3H).**$^{13}$C NMR (101 MHz, CHLOROFORM-*D*) δ** 196.0, 194.7, 165.3, 153.1, 142.4, 141.6, 140.7, 137.5, 134.6, 134.3, 130.4, 129.0, 128.9, 128.9, 128.4, 127.6, 122.6, 122.1, 122.0, 60.0, 51.0, 46.0, 38.2, 21.2, 13.9. **HRMS (ESI) m/z:** [M+Na]$^+$ calculated for $C_{29}H_{24}O_4Na$, 459.1567; found 459.1570. **IR (neat, cm$^{-1}$):** 3432, 2925, 2857, 1710, 1620, 1518, 1448, 1339, 1289, 1220, 1174, 1092, 1039, 876, 813, 774, 744, 699, 614, 562, 535, 485.

**ethyl (*E*)-3-(1',3'-dioxo-2-(m-tolyl)-1',3'-dihydrospiro[cyclopropane-1,2'-inden]-3-yl)-3-phenylacrylate (4c):**

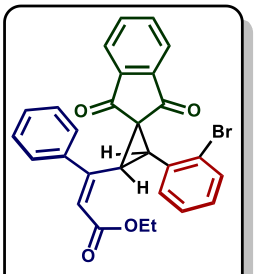


4c

Following the general procedure 5, reaction of 1*H*-indene-1,3(2*H*)-dione (44 mg, 0.30 mmol, 1 equiv.), aldehyde **2j** (39 µL, 0.33 mmol, 1.1 equiv.) and ylide **1a** (112 mg, 0.42 mmol, 1.4 equiv.) using catalytic amount (7 mg, 20 mol%) of L-proline in methanol (0.1 M) at room temperature for 30 minutes furnished **4c** in 89% (117 mg, 0.27 mmol,) as white solid with diastereomeric ratio >20:1.

**$^1$H NMR (500 MHz, CHLOROFORM-*D*) δ** 7.87 (d, *J* = 1.9 Hz, 2H), 7.72 (dd, *J* = 6.0, 2.9 Hz, 2H), 7.54 (t, *J* = 3.6 Hz, 2H), 7.40 – 7.33 (m, 3H), 7.25 – 7.19 (m, 3H), 7.12 (s, 1H), 6.22 (s, 1H), 4.31 (d, *J* = 9.6 Hz, 1H), 3.85 (q, *J* = 7.1 Hz, 2H), 3.40 (d, *J* = 9.6 Hz, 1H), 2.35 (s, 3H), 1.00 (s, *J* = 7.1 Hz, 3H).**$^{13}$C NMR (101 MHz, CHLOROFORM-*D*) δ** 196.0, 194.7, 165.4, 153.2, 142.5, 141.7, 140.7, 137.8, 134.7, 134.3, 133.4, 129.8, 129.0, 128.7, 128.5, 128.2, 127.7, 126.1, 122.7, 122.1, 122.1, 60.1, 51.0, 46.1, 38.3, 21.4, 13.9. **HRMS (ESI) m/z:** [M+Na]$^+$ calculated for $C_{29}H_{24}O_4Na$, 459.1567; found 459.1564. **IR (neat, cm$^{-1}$):** 3431, 2925, 2857, 1711, 1620, 1518, 1448, 1339, 1289, 1220, 1174, 1092, 1039, 876, 813, 774, 744, 700, 614, 562, 535, 485.

**ethyl (*E*)-3-(2-(2-bromophenyl)-1',3'-dioxo-1',3'-dihydrospiro[cyclopropane-1,2'-inden]-3-yl)-3-phenylacrylate (4d):**

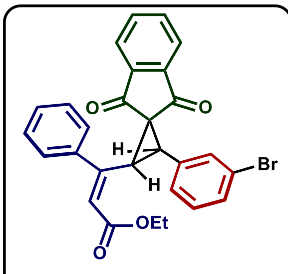



4d

Following the general procedure 5, reaction of 1*H*-indene-1,3(2*H*)-dione (44 mg, 0.30 mmol, 1 equiv.), aldehyde **2o** (34 µL, 0.33 mmol, 1.1 equiv.) and ylide **1a** (112 mg, 0.42 mmol, 1.4 equiv.) using catalytic amount (7 mg, 20 mol%) of L-proline in methanol (0.1 M) at room temperature for 30 minutes furnished **4d** in 80% (121 mg, 0.24 mmol,) as yellow solid with diastereomeric ratio >20:1.

**$^{1}$H NMR (500 MHz, CHLOROFORM-*D*) δ** 7.87 (s, 2H), 7.78 – 7.69 (m, 2H), 7.54 – 7.45 (m, 2H), 7.42 – 7.27 (m, 7H), 6.21 (d, *J* = 2.1 Hz, 1H), 4.24 (d, *J* = 9.5 Hz, 1H), 3.84 (q, *J* = 7.1 Hz, 2H), 3.33 (d, *J* = 9.5 Hz, 1H), 0.99 (t, *J* = 7.1 Hz, 3H). **$^{13}$C NMR (101 MHz, CHLOROFORM-*D*) δ** 195.6, 194.6, 165.4, 152.6, 142.4, 141.7, 140.6, 135.9, 134.9, 134.6, 132.1, 131.0, 129.8, 129.1, 128.6, 127.7, 127.7, 122.9, 122.4, 122.3, 122.3, 60.2, 50.6, 44.8, 38.2, 14.0. **HRMS (ESI) m/z:** $[M+Na]^+$ calculated for $C_{28}H_{21}O_4BrNa$, 523.0515; found 523.0515. **IR (neat, cm$^{-1}$):** 3432, 3060, 2982, 1710, 1622, 1598, 1446, 1407, 1341, 1278, 1220, 1175, 1094, 1039, 880, 767, 736, 698, 622, 567, 496.

**ethyl (*E*)-3-(2-(3-bromophenyl)-1',3'-dioxo-1',3'-dihydrospiro[cyclopropane-1,2'-inden]-3-yl)-3-phenylacrylate (4e):**

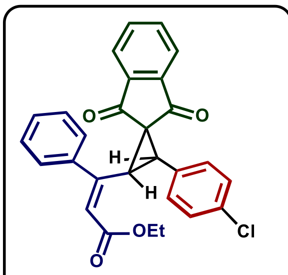



4e

Following the general procedure 5, reaction of 1*H*-indene-1,3(2*H*)-dione (44 mg, 0.30 mmol, 1 equiv.), aldehyde **2k** (34 µL, 0.33 mmol, 1.1 equiv.) and ylide **1a** (112 mg, 0.42 mmol, 1.4 equiv.) using catalytic amount (7 mg, 20 mol%) of L-proline in methanol (0.1 M) at room temperature for 30 minutes furnished **4e** in 83% (126 mg, 0.25 mmol,) as orange solid with diastereomeric ratio >20:1.

**$^{1}$H NMR (500 MHz, CHLOROFORM-*D*) δ** 7.90 – 7.81 (m, 2H), 7.76 – 7.67 (m, 2H), 7.53 – 7.47 (m, 2H), 7.41 – 7.31 (m, 5H), 7.02 (t, *J* = 8.5 Hz, 2H), 6.21 (s, 1H), 4.25 (d, *J* = 9.6 Hz, 1H), 3.84 (q, *J* = 7.1 Hz, 2H), 3.36 (d, *J* = 9.6 Hz, 1H), 0.99 (t, *J* = 7.1 Hz, 3H). **$^{13}$C NMR (101 MHz, CHLOROFORM-*D*) δ** 195.1, 194.6, 165.4, 152.1, 147.4, 142.3, 141.7, 141.3, 140.5, 135.1, 134.9, 130.0, 129.2, 128.7, 128.6, 127.6, 123.9, 123.5, 122.9, 122.5, 122.4, 60.3, 50.6, 44.2, 38.5, 14.0. **HRMS (ESI) m/z:** $[M+Na]^+$ calculated for $C_{28}H_{21}O_4BrNa$, 523.0515; found 523.0513. **IR (neat, cm$^{-1}$):** 3432, 3060, 2982, 1710, 1621, 1598, 1446, 1407, 1341, 1278, 1218, 1175, 1094, 1039, 880, 767, 736, 698, 624, 567, 496.

**ethyl (*E*)-3-(2-(4-chlorophenyl)-1',3'-dioxo-1',3'-dihydrospiro[cyclopropane-1,2'-inden]-3-yl)-3-phenylacrylate (4f):**

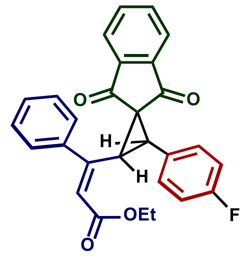



4f

Following the general procedure 5, reaction of 1*H*-indene-1,3(2*H*)-dione (44 mg, 0.30 mmol, 1 equiv.), aldehyde **2e** (46 mg, 0.33 mmol, 1.1 equiv.) and ylide **1a** (112 mg, 0.42 mmol, 1.4 equiv.) using catalytic amount (7 mg, 20 mol%) of L-proline in methanol (0.1 M) at room temperature for 30 minutes furnished **4f** in 86% (118 mg, 0.26 mmol) as yellow solid with diastereomeric ratio >20:1.

**$^{1}$H NMR (500 MHz, CHLOROFORM-*D*) δ** 7.87 (s, 2H), 7.78 – 7.69 (m, 2H), 7.54 – 7.45 (m, 2H), 7.42 – 7.27 (m, 7H), 6.21 (d, *J* = 2.1 Hz, 1H), 4.24 (d, *J* = 9.5 Hz, 1H), 3.84 (q, *J* = 7.1 Hz, 2H), 3.33 (d, *J* = 9.5 Hz, 1H), 0.99 (t, *J* = 7.1 Hz, 3H). **$^{13}$C NMR (101 MHz, CHLOROFORM-*D*) δ** 195.7, 194.8, 165.4, 152.7, 142.4, 141.7, 140.7, 134.9, 134.6, 133.7, 132.1, 130.4, 129.1, 128.6, 128.6, 127.6, 122.8, 122.3, 60.2, 50.7, 45.1, 38.4, 14.0. **HRMS (ESI) m/z:** $[M+Na]^+$ calculated for $C_{28}H_{21}O_4ClNa$, 479.1021; found 479.1018. **IR (neat, cm$^{-1}$):** 3427, 3060, 2987, 1708, 1605, 1494, 1446, 1400, 1339, 1294, 1214, 1165, 1091, 1036, 1016, 872, 817, 775, 735, 701, 622, 563, 530, 483.

**ethyl (*E*)-3-(2-(4-fluorophenyl)-1',3'-dioxo-1',3'-dihydrospiro[cyclopropane-1,2'-inden]-3-yl)-3-phenylacrylate (4g):**

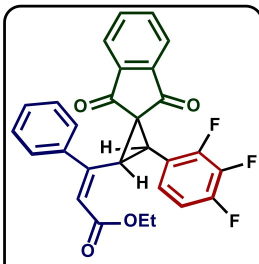


4g

Following the general procedure 5, reaction of 1*H*-indene-1,3(2*H*)-dione (44 mg, 0.30 mmol, 1 equiv.), aldehyde **2f** (34 µL, 0.33 mmol, 1.1 equiv.) and ylide **1a** (112 mg, 0.42 mmol, 1.4 equiv.) using catalytic amount (7 mg, 20 mol%) of L-proline in methanol (0.1 M) at room temperature for 30 minutes furnished **4g** in 85% (113 mg, 0.26 mmol,) as orange solid with diastereomeric ratio >20:1.

**$^1$H NMR (500 MHz, CHLOROFORM-*D*) δ** 7.90 – 7.81 (m, 2H), 7.76 – 7.67 (m, 2H), 7.53 – 7.47 (m, 2H), 7.41 – 7.31 (m, 5H), 7.02 (t, *J* = 8.5 Hz, 2H), 6.21 (s, 1H), 4.25 (d, *J* = 9.6 Hz, 1H), 3.84 (q, *J* = 7.1 Hz, 2H), 3.36 (d, *J* = 9.6 Hz, 1H), 0.99 (t, *J* = 7.1 Hz, 3H). **$^{13}$C NMR (101 MHz, CHLOROFORM-*D*) δ** 195.9, 194.9, 165.4, 161.1, 142.1 (d, *J* = 68.2 Hz), 140.7, 134.7 (d, *J* = 32.6 Hz), 130.7 (d, *J* = 8.1 Hz), 129.1, 128.6, 127.7, 122.8, 122.3, 115.4 (d, *J* = 21.7 Hz), 60.2, 50.8, 45.2, 38.6, 14.0. **$^{19}$F NMR (376 MHz, CHLOROFORM-*D*) δ** -113.85. **HRMS (ESI) m/z:** [M+Na]$^+$ calculated for $C_{28}H_{21}O_4FNa$, 463.1316; found 463.1313. **IR (neat, cm$^{-1}$):** 3431, 3059, 2981, 2928, 2856, 1710, 1604, 1514, 1448, 1340, 1288, 1223, 1175, 1088, 1038, 878, 828, 738, 699, 612, 537.

**ethyl (*E*)-3-(1',3'-dioxo-2-(2,3,4-trifluorophenyl)-1',3'-dihydrospiro[cyclopropane-1,2'-inden]-3-yl)-3-phenylacrylate (4h):**

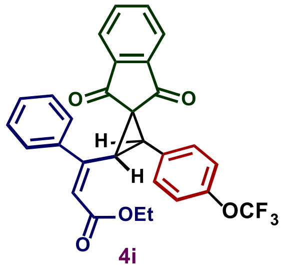


4h

Following the general procedure 5, reaction of 1*H*-indene-1,3(2*H*)-dione (44 mg, 0.30 mmol, 1 equiv.), aldehyde **2p** (38 µL, 0.33 mmol, 1.1 equiv.) and ylide **1a** (112 mg, 0.42 mmol, 1.4 equiv.) using catalytic amount (7 mg, 20 mol%) of L-proline in methanol (0.1 M) at room temperature for 30 minutes furnished **4h** in 80% (115 mg, 0.24 mmol,) as white solid with diastereomeric ratio >20:1.

**$^1$H NMR (500 MHz, CHLOROFORM-*D*) δ** δ 7.85 (s, 2H), 7.79 – 7.72 (m, 2H), 7.50 (dd, *J* = 7.5, 2.0 Hz, 2H), 7.38 (dd, *J* = 5.0, 2.5 Hz, 3H), 7.31 (q, *J* = 8.1, 7.3 Hz, 1H), 7.08 – 6.99 (m, 1H), 6.21 (s, 1H), 4.12 (d, *J* = 9.3 Hz, 1H), 3.85 (q, *J* = 7.1 Hz, 2H), 3.28 (d, *J* = 9.3 Hz, 1H), 1.00 (t, *J* = 7.1 Hz, 3H). **$^{13}$C NMR (101 MHz, CHLOROFORM-*D*) δ** 195.4, 194.8, 165.5, 152.4, 142.0 (d, *J* = 31.1 Hz), 140.7, 134.9 (d, *J* = 23.9 Hz), 129.2, 128.7, 127.7, 123.0, 122.9 (d, *J* = 22.6 Hz), 60.4, 48.9, 37.9, 29.8, 14.1. **$^{19}$F NMR (376 MHz, CHLOROFORM-*D*) δ** -133.98 (dt, *J* = 21.9, 7.7 Hz), -135.88 (dt, *J* = 20.8, 7.4 Hz), -160.07 (td, *J* = 20.6, 7.0 Hz). **HRMS (ESI) m/z:** [M+Na]$^+$ calculated for $C_{28}H_{19}O_4F_3Na$, 499.1128; found 499.1125. **IR (neat, cm$^{-1}$):** 3436, 3059, 2981, 2928, 2856, 1711, 1604, 1514, 1448, 1340, 1288, 1223, 1175, 1088, 1038, 878, 828, 738, 699, 612, 537.

**ethyl (*E*)-3-(1',3'-dioxo-2-(4-(trifluoromethoxy)phenyl)-1',3'-dihydrospiro[cyclopropane-1,2'-inden]-3-yl)-3-phenylacrylate (4i):**



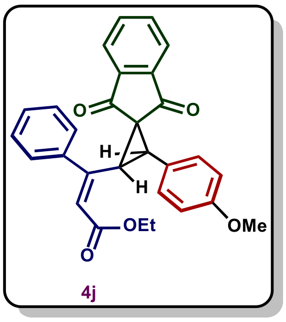
4i

Following the general procedure 5, reaction of 1*H*-indene-1,3(2*H*)-dione (44 mg, 0.30 mmol, 1 equiv.), aldehyde **2i** (63 mg, 0.33 mmol, 1.1 equiv.) and ylide **1a** (112 mg, 0.42 mmol, 1.4 equiv.) using catalytic amount (7 mg, 20 mol%) of L-proline in methanol (0.1 M) at room temperature for 30 minutes furnished **4i** in 82% (125 mg, 0.24 mmol,) as white solid with diastereomeric ratio >20:1.

**$^1$H NMR (500 MHz, CHLOROFORM-*D*) δ** 7.87 (s, 2H), 7.78 – 7.69 (m, 2H), 7.54 – 7.45 (m, 2H), 7.42 – 7.27 (m, 7H), 6.21 (d, *J* = 2.1 Hz, 1H), 4.24 (d, *J* = 9.5 Hz, 1H), 3.84 (q, *J* = 7.1 Hz, 2H), 3.33 (d, *J* = 9.5 Hz, 1H), 0.99 (t, *J* = 7.1 Hz, 3H). **$^{13}$C NMR (126 MHz, CHLOROFORM-*D*) δ** 195.6, 194.8, 165.5, 152.6, 142.1 (d, *J* = 85.0 Hz), 140.7, 134.9 (d, *J* = 39.6 Hz),129.5, 129.2, 128.2 (d, *J* = 126.5 Hz), 125.4 (q, *J* = 3.7 Hz), 123.0, 122.5 (d, *J* = 9.2 Hz).60.3, 50.7, 44.9, 38.5, 14.1. **$^{19}$F NMR (376 MHz, CHLOROFORM-*D*) δ** -62.42. **HRMS**

**(ESI) m/z:** [M+Na]$^+$ calculated for $C_{29}H_{21}O_5F_3Na$, 529.1233; found 529.1229. **IR (neat, cm$^{-1}$):** 3436, 2927, 1711, 1621, 1447, 1409, 1326, 1291, 1220, 1171, 1123, 1069, 1037, 877, 772, 744, 698, 609, 531.

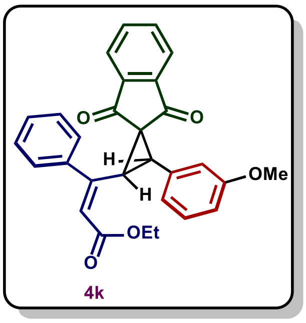
**ethyl (*E*)-3-(2-(4-methoxyphenyl)-1',3'-dioxo-1',3'-dihydrospiro[cyclopropane-1,2'-inden]-3-yl)-3-phenylacrylate (4j):**




Following the general procedure 5, reaction of 1*H*-indene-1,3(2*H*)-dione (44 mg, 0.30 mmol, 1 equiv.), aldehyde **2b** (41 µL, 0.33 mmol, 1.1 equiv.) and ylide **1a** (112 mg, 0.42 mmol, 1.4 equiv.) using catalytic amount (7 mg, 20 mol%) of L-proline in methanol (0.1 M) at room temperature for 30 minutes furnished **4j** in 91% (124 mg, 0.27 mmol,) as white solid with diastereomeric ratio >20:1.

**$^1$H NMR (500 MHz, CHLOROFORM-*D*) δ** $^1$H NMR (500 MHz, $CDCl_3$) δ 7.90 – 7.81 (m, 2H), 7.76 – 7.68 (m, 2H), 7.54 – 7.49 (m, 2H), 7.39 – 7.29 (m, 5H), 6.90 – 6.84 (m, 2H), 6.21 (d, *J* = 2.2 Hz, 1H), 4.26 (d, *J* = 9.7 Hz, 1H), 3.84 (q, *J* = 7.1 Hz, 2H), 3.80 (s, 3H), 3.35 (d, *J* = 9.7 Hz, 1H), 0.99 (t, *J* = 7.1 Hz, 3H). **$^{13}$C NMR (101 MHz, CHLOROFORM-*D*) δ** 195.9, 194.8, 165.3, 159.1, 153.1, 142.3, 141.6, 140.7, 134.6, 134.3, 130.1, 128.9, 128.4, 127.6, 125.3, 122.6, 122.0, 122.0, 113.7, 60.0, 55.1, 51.1, 46.0, 38.4, 13.9. **HRMS (ESI) m/z:** [M+Na]$^+$ calculated for $C_{29}H_{24}O_5Na$, 475.1516; found 475.1517. **IR (neat, cm$^{-1}$):** 3423, 3051, 2981, 2960, 2935, 2838, 1710, 1614, 1519, 1445, 1331, 1274, 1254, 1226, 1177, 1087, 1034, 869, 824, 775, 747, 696, 565, 541, 489.

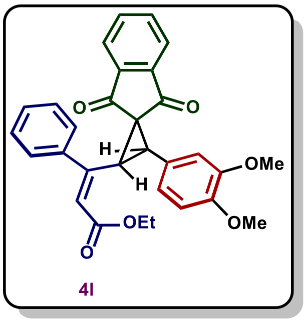
**ethyl (*E*)-3-(2-(3-methoxyphenyl)-1',3'-dioxo-1',3'-dihydrospiro[cyclopropane-1,2'-inden]-3-yl)-3-phenylacrylate (4k):**




Following the general procedure 5, reaction of 1*H*-indene-1,3(2*H*)-dione (44 mg, 0.30 mmol, 1 equiv.), aldehyde **2m** (41 µL, 0.33 mmol, 1.1 equiv.) and ylide **1a** (112 mg, 0.42 mmol, 1.4 equiv.) using catalytic amount (7 mg, 20 mol%) of L-proline in methanol (0.1 M) at room temperature for 30 minutes furnished **4k** in 88% (120 mg, 0.27 mmol,) as white solid with diastereomeric ratio >20:1.

**$^1$H NMR (500 MHz, CHLOROFORM-*D*) δ** 7.89 – 7.81 (m, 2H), 7.74 – 7.69 (m, 2H), 7.54 – 7.49 (m, 2H), 7.36 (dd, *J* = 5.2, 2.0 Hz, 3H), 7.33 – 7.30 (m, 2H), 6.87 (d, *J* = 8.7 Hz, 2H), 6.20 (d, *J* = 2.2 Hz, 1H), 4.25 (d, *J* = 9.7 Hz, 1H), 3.84 (q, *J* = 7.1 Hz, 2H), 3.80 (s, 3H), 3.35 (d, *J* = 9.7 Hz, 1H), 0.99 (t, *J* = 7.1 Hz, 3H). **$^{13}$C NMR (101 MHz, CHLOROFORM-*D*) δ** 195.9, 194.8, 165.3, 159.1, 153.1, 142.3, 141.6, 140.7, 134.6, 134.3, 130.1, 128.9, 128.4, 127.6, 125.3, 122.6, 122.0, 122.0, 113.7, 60.0, 55.1, 51.1, 46.0, 38.4, 13.9. **HRMS (ESI) m/z:** [M+Na]$^+$ calculated for $C_{29}H_{24}O_5Na$, 475.1516; found 475.1516. **IR (neat, cm$^{-1}$):** 3429, 3051, 2981, 2960, 2935, 2838, 1711, 1614, 1519, 1445, 1331, 1274, 1254, 1226, 1177, 1087, 1034, 869, 824, 775, 747, 696, 565, 541, 489.

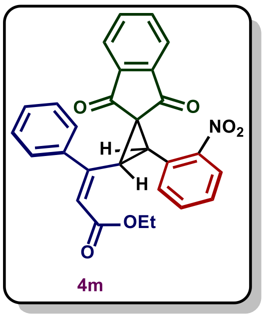
**ethyl (*E*)-3-(2-(3,4-dimethoxyphenyl)-1',3'-dioxo-1',3'-dihydrospiro[cyclopropane-1,2'-inden]-3-yl)-3-phenylacrylate (4l):**




Following the general procedure 5, reaction of 1*H*-indene-1,3(2*H*)-dione (44 mg, 0.30 mmol, 1 equiv.), aldehyde **2c** (55 mg, 0.33 mmol, 1.1 equiv.) and ylide **1a** (112 mg, 0.42 mmol, 1.4 equiv.) using catalytic amount (7 mg, 20 mol%) of L-proline in methanol (0.1 M) at room temperature for 30 minutes furnished **4l** in 93% (135 mg, 0.28 mmol,) as white solid with diastereomeric ratio >20:1.

**$^{1}$H NMR (500 MHz, CHLOROFORM-*D*) δ** 7.87 – 7.78 (m, 2H), 7.74 – 7.64 (m, 2H), 7.52 – 7.47 (m, 2H), 7.33 (d, *J* = 1.5 Hz, 3H), 6.98 (d, *J* = 8.3 Hz, 1H), 6.91 (s, 1H), 6.86 – 6.81 (m, 1H), 6.20 (s, 1H), 4.26 (d, *J* = 9.6 Hz, 1H), 3.86 – 3.79 (m, 8H), 3.33 (d, *J* = 9.6 Hz, 1H), 0.96 (t, *J* = 7.1 Hz, 3H). **$^{13}$C NMR (101 MHz, CHLOROFORM-*D*) δ** 195.9, 194.8, 165.3, 153.0, 148.6, 148.5, 142.4, 141.6, 140.6, 134.6, 134.3, 128.9, 128.4, 127.6, 125.8, 122.6, 122.0, 121.9, 121.3, 112.0, 110.6, 60.0, 55.8, 55.7, 51.3, 46.5, 38.5, 13.9. **HRMS (ESI) m/z:** $[M+Na]^+$ calculated for $C_{30}H_{26}O_6Na$, 505.1622; found 505.1624. **IR (neat, cm$^{-1}$):** 3420, 3071, 3009, 2932, 2841, 1710, 1623, 1596, 1523, 1465, 1444, 1334, 1305, 1272, 1238, 1214, 1177, 1091, 1040, 873, 809, 768, 740, 703, 634, 500, 634, 463.

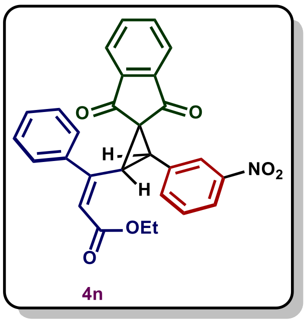
**ethyl (*E*)-3-(2-(2-nitrophenyl)-1',3'-dioxo-1',3'-dihydrospiro[cyclopropane-1,2'-inden]-3-yl)-3-phenylacrylate (4m):**




Following the general procedure 5, reaction of 1*H*-indene-1,3(2*H*)-dione (44 mg, 0.30 mmol, 1 equiv.), aldehyde **2n** (50 mg, 0.33 mmol, 1.1 equiv.) and ylide **1a** (112 mg, 0.42 mmol, 1.4 equiv.) using catalytic amount (7 mg, 20 mol%) of L-proline in methanol (0.1 M) at room temperature for 30 minutes furnished **4m** in 79% (111 mg, 0.24 mmol,) as yellow solid with diastereomeric ratio >20:1.

**$^{1}$H NMR (500 MHz, CHLOROFORM-*D*) δ** 8.18 (d, *J* = 8.7 Hz, 2H), 7.86 (s, 2H), 7.76 (dd, *J* = 5.9, 2.6 Hz, 2H), 7.58 (d, *J* = 8.5 Hz, 2H), 7.47 (dd, *J* = 6.7, 3.0 Hz, 2H), 7.38 – 7.32 (m, 3H), 6.22 (s, 1H), 4.29 (d, *J* = 9.5 Hz, 1H), 3.83 (q, *J* = 7.1 Hz, 2H), 3.41 (d, *J* = 9.5 Hz, 1H), 0.99 (t, *J* = 7.1 Hz, 3H). **$^{13}$C NMR (101 MHz, CHLOROFORM-*D*) δ** 195.7, 194.7, 165.5, 141.8, 140.7, 136.0, 135.0, 134.6, 132.3, 131.1, 129.9, 129.2, 128.7, 127.8, 123.0, 122.5, 122.5, 122.4, 60.3, 50.7, 44.9, 38.3, 14.1. **HRMS (ESI) m/z:** $[M+Na]^+$ calculated for $C_{28}H_{21}O_6NNa$, 490.1261; found 490.1263. **IR (neat, cm$^{-1}$):** 3434, 3061, 2984, 1712, 1601, 1521, 1448, 1404, 1344, 1288, 1220, 1178, 1090, 1037, 920, 878, 852, 770, 735, 699, 631, 562, 533.

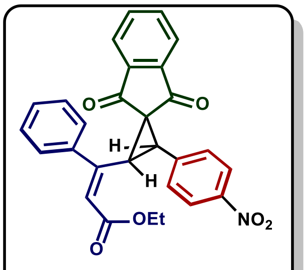
**ethyl (*E*)-3-(2-(3-nitrophenyl)-1',3'-dioxo-1',3'-dihydrospiro[cyclopropane-1,2'-inden]-3-yl)-3-phenylacrylate (4n):**




Following the general procedure 5, reaction of 1*H*-indene-1,3(2*H*)-dione (44 mg, 0.30 mmol, 1 equiv.), aldehyde **2l** (50 mg, 0.33 mmol, 1.1 equiv.) and ylide **1a** (112 mg, 0.42 mmol, 1.4 equiv.) using catalytic amount (7 mg, 20 mol%) of L-proline in methanol (0.1 M) at room temperature for 30 minutes furnished **4n** in 81% (114 mg, 0.24 mmol,) as yellow solid with diastereomeric ratio >20:1.

**$^{1}$H NMR (500 MHz, CHLOROFORM-*D*) δ** 7.90 – 7.81 (m, 2H), 7.76 – 7.67 (m, 2H), 7.53 – 7.47 (m, 2H), 7.41 – 7.31 (m, 5H), 7.02 (t, *J* = 8.5 Hz, 2H), 6.21 (s, 1H), 4.25 (d, *J* = 9.6 Hz, 1H), 3.84 (q, *J* = 7.1 Hz, 2H), 3.36 (d, *J* = 9.6 Hz, 1H), 0.99 (t, *J* = 7.1 Hz, 3H). **$^{13}$C NMR (126 MHz, CHLOROFORM-*D*) δ** 195.2, 194.8, 165.4, 152.2, 148.3, 142.3, 141.8, 140.6, 135.9, 135.2, 135.1, 134.9, 129.3, 129.2, 128.7, 127.6, 124.2, 123.0, 123.0, 122.6, 122.5, 60.3, 50.3, 44.1, 38.5, 14.0. **HRMS (ESI) m/z:** $[M+Na]^+$ calculated for $C_{28}H_{21}O_6NNa$, 490.1261; found 490.1260. **IR (neat, cm$^{-1}$):** 3431, 3061, 2984, 1711, 1601, 1521, 1448, 1404, 1344, 1288, 1220, 1178, 1090, 1037, 920, 878, 852, 770, 735, 699, 631, 562, 533.

**ethyl (*E*)-3-(2-(4-nitrophenyl)-1',3'-dioxo-1',3'-dihydrospiro[cyclopropane-1,2'-inden]-3-yl)-3-phenylacrylate (4o):**

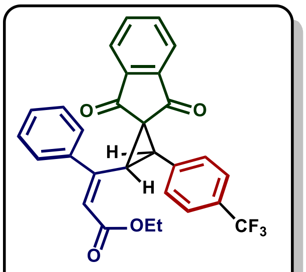


4o

Following the general procedure 5, reaction of 1*H*-indene-1,3(2*H*)-dione (44 mg, 0.30 mmol, 1 equiv.), aldehyde **2g** (50 mg, 0.33 mmol, 1.1 equiv.) and ylide **1a** (112 mg, 0.42 mmol, 1.4 equiv.) using catalytic amount (7 mg, 20 mol%) of L-proline in methanol (0.1 M) at room temperature for 30 minutes furnished **4o** in 83% (117 mg, 0.25 mmol,) as orange solid with diastereomeric ratio >20:1.

**$^1$H NMR (500 MHz, CHLOROFORM-*D*) δ** 8.18 (d, *J* = 8.7 Hz, 2H), 7.86 (s, 2H), 7.76 (dd, *J* = 5.9, 2.6 Hz, 2H), 7.58 (d, *J* = 8.5 Hz, 2H), 7.47 (dd, *J* = 6.7, 3.0 Hz, 2H), 7.38 – 7.32 (m, 3H), 6.22 (s, 1H), 4.29 (d, *J* = 9.5 Hz, 1H), 3.83 (q, *J* = 7.1 Hz, 2H), 3.41 (d, *J* = 9.5 Hz, 1H), 0.99 (t, *J* = 7.1 Hz, 3H). **$^{13}$C NMR (101 MHz, CHLOROFORM-*D*) δ** 195.1, 194.6, 165.4, 152.1, 147.4, 142.3, 141.7, 141.3, 140.5, 135.1, 134.9, 130.0, 129.2, 128.7, 128.6, 127.6, 123.9, 123.5, 122.9, 122.5, 122.4, 60.3, 50.6, 44.2, 38.5, 14.0. **HRMS (ESI) m/z:** $[M+Na]^+$ calculated for $C_{28}H_{21}O_6NNa$, 490.1261; found 490.1253. **IR (neat, cm$^{-1}$):** 3432, 3061, 2984, 1710, 1601, 1521, 1448, 1404, 1344, 1288, 1220, 1178, 1090, 1037, 920, 878, 852, 770, 735, 699, 631, 562, 533.

**ethyl (*E*)-3-(1',3'-dioxo-2-(4-(trifluoromethyl)phenyl)-1',3'-dihydrospiro[cyclopropane-1,2'-inden]-3-yl)-3-phenylacrylate (4p):**

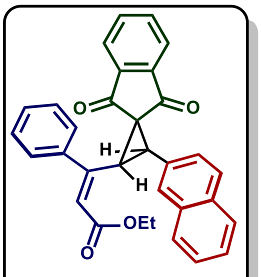


4p

Following the general procedure 5, reaction of 1*H*-indene-1,3(2*H*)-dione (44 mg, 0.30 mmol, 1 equiv.), aldehyde **2h** (44 µL, 0.33 mmol, 1.1 equiv.) and ylide **1a** (112 mg, 0.42 mmol, 1.4 equiv.) using catalytic amount (7 mg, 20 mol%) of L-proline in methanol (0.1 M) at room temperature for 30 minutes furnished **4p** in 84% (124 mg, 0.25 mmol,) as white solid with diastereomeric ratio >20:1.

**$^1$H NMR (500 MHz, CHLOROFORM-*D*) δ** 7.88 (s, 2H), 7.79 – 7.70 (m, 2H), 7.59 (s, 2H), 7.54 (s, 4H), 7.38 – 7.34 (m, 3H), 6.23 (s, 1H), 4.30 (d, *J* = 9.5 Hz, 1H), 3.84 (q, *J* = 7.1 Hz, 2H), 3.40 (d, *J* = 9.5 Hz, 1H), 0.99 (t, *J* = 7.1 Hz, 3H). **$^{13}$C NMR (101 MHz, CHLOROFORM-*D*) δ** 195.5, 194.7, 165.4, 152.5, 142.0 (d, *J* = 67.9 Hz),140.6, 134.8 (d, *J* = 31.1 Hz), 129.5, 129.2, 128.1 (d, *J* = 100.7 Hz), 125.3 (q, *J* = 3.9 Hz), 122.9, 122.4 (d, *J* = 2.9 Hz),60.2, 50.6, 44.8, 38.4, 14.0. **$^{19}$F NMR (376 MHz, CHLOROFORM-*D*) δ** -62.35. **HRMS (ESI) m/z:** $[M+Na]^+$ calculated for $C_{29}H_{21}O_4F_3Na$, 513.1284; found 513.1290. **IR (neat, cm$^{-1}$):** 3435, 2927, 1711, 1621, 1447, 1409, 1326, 1291, 1220, 1171, 1123, 1069, 1037, 877, 772, 744, 698, 609, 531.

**ethyl (*E*)-3-(2-(naphthalen-2-yl)-1',3'-dioxo-1',3'-dihydrospiro[cyclopropane-1,2'-inden]-3-yl)-3-phenylacrylate (4q):**

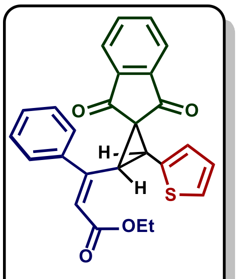


4q

Following the general procedure 5, reaction of 1*H*-indene-1,3(2*H*)-dione (44 mg, 0.30 mmol, 1 equiv.), aldehyde **2s** (43 µL, 0.33 mmol, 1.1 equiv.) and ylide **1a** (112 mg, 0.42 mmol, 1.4 equiv.) using catalytic amount (7 mg, 20 mol%) of L-proline in methanol (0.1 M) at room temperature for 30 minutes furnished **4q** in 81% (115 mg, 0.24 mmol,) as white solid with diastereomeric ratio >20:1.

**$^1$H NMR (500 MHz, CHLOROFORM-*D*) δ** 7.93 (d, *J* = 7.5 Hz, 1H), 7.88 – 7.82 (m, 2H), 7.82 – 7.79 (m, 1H), 7.71 (d, *J* = 18.0 Hz, 3H), 7.62 (d, *J* = 7.3 Hz, 3H), 7.43 – 7.39 (m, 1H), 7.38 – 7.28 (m, 4H), 7.18 – 7.14 (m, 1H), 6.27 (s, 1H), 4.45 (d, *J* = 9.5 Hz, 1H), 3.84 (q, *J* = 7.1 Hz, 2H), 3.76 (d, *J* = 9.5 Hz, 1H), 0.99 (t, *J* = 7.1 Hz, 3H). **$^{13}$C NMR (101 MHz, CHLOROFORM-*D*) δ** 196.6, 194.2, 165.6, 153.3, 142.2, 140.9, 134.9, 134.4, 133.6, 130.1, 129.1, 129.0, 128.9, 128.7, 127.8, 126.7, 126.6, 125.8, 125.5, 122.9, 122.8, 122.7, 122.3, 60.3, 50.6, 43.5, 38.4, 14.1. **HRMS (ESI) m/z:** $[M+Na]^+$ calculated for $C_{32}H_{24}O_4Na$, 495.1567; found 495.1568. **IR (neat, cm$^{-1}$):** 3434, 2926, 1709, 1620, 1446, 1337, 1293, 1271, 1174, 1097, 1028, 867, 777, 738, 698.

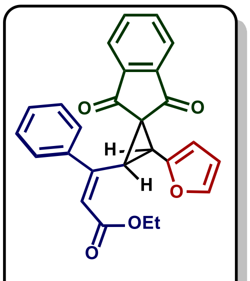
**ethyl (*E*)-3-(1',3'-dioxo-2-(thiophen-2-yl)-1',3'-dihydrospiro[cyclopropane-1,2'-inden]-3-yl)-3-phenylacrylate (4r):**


4r

Following the general procedure 5, reaction of 1*H*-indene-1,3(2*H*)-dione (44 mg, 0.30 mmol, 1 equiv.), aldehyde **2q** (31 µL, 0.33 mmol, 1.1 equiv.) and ylide **1a** (112 mg, 0.42 mmol, 1.4 equiv.) using catalytic amount (7 mg, 20 mol%) of L-proline in methanol (0.1 M) at room temperature for 30 minutes furnished **4r** in 89% (115 mg, 0.27 mmol) as orange solid with diastereomeric ratio 4:1.

**Major product: $^1$H NMR (500 MHz, CHLOROFORM-*D*) δ** 7.94 – 7.90 (m, 1H), 7.86 – 7.83 (m, 1H), 7.76 – 7.73 (m, 2H), 7.53 (d, *J* = 1.7 Hz, 2H), 7.40 – 7.37 (m, 2H), 7.25 – 7.22 (m, 2H), 7.14 (d, *J* = 3.5 Hz, 1H), 7.01 (dd, *J* = 5.2, 3.5 Hz, 1H), 6.19 (s, 1H), 4.18 (d, *J* = 9.3 Hz, 1H), 3.84 (q, *J* = 7.1 Hz, 2H), 3.41 (d, *J* = 9.3 Hz, 1H), 0.99 (t, *J* = 7.1 Hz, 3H).**$^{13}$C NMR (101 MHz, CHLOROFORM-*D*) δ** 195.4, 194.0, 165.2, 152.4, 142.3, 141.4, 140.6, 136.7, 134.8, 134.4, 129.0, 128.5, 127.6, 127.4, 127.0, 125.5, 122.8, 122.1, 121.9, 60.1, 50.7, 40.3, 39.8, 13.9. **HRMS (ESI) m/z:** $[M+Na]^+$ calculated for $C_{26}H_{20}O_4SNa$, 451.0975; found 451.0970. **IR (neat, cm$^{-1}$):** 3432, 3073, 2926, 1709, 1620, 1446, 1337, 1293, 1271, 1174, 1097, 1028, 867, 777, 738, 698.

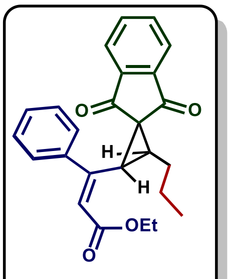
**ethyl (*E*)-3-(2-(furan-2-yl)-1',3'-dioxo-1',3'-dihydrospiro[cyclopropane-1,2'-inden]-3-yl)-3-phenylacrylate (4s):**


4s

Following the general procedure 5, reaction of 1*H*-indene-1,3(2*H*)-dione (44 mg, 0.30 mmol, 1 equiv.), aldehyde **2r** (44 µL, 0.33 mmol, 1.1 equiv.) and ylide **1a** (112 mg, 0.42 mmol, 1.4 equiv.) using catalytic amount (7 mg, 20 mol%) of L-proline in methanol (0.1 M) at room temperature for 30 minutes furnished **4s** in 87% (116 mg, 0.26 mmol,) as white solid with diastereomeric ratio 9:1.

**$^1$H NMR (500 MHz, CHLOROFORM-*D*) δ** 7.77 (s, 1H), 7.69 (d, *J* = 1.6 Hz, 1H), 7.63 – 7.55 (m, 2H), 7.41 – 7.37 (m, 2H), 7.26 – 7.18 (m, 4H), 6.35 (d, *J* = 3.3 Hz, 1H), 6.28 – 6.21 (m, 1H), 6.05 (d, *J* = 2.2 Hz, 1H), 3.99 (d, *J* = 9.3 Hz, 1H), 3.68 (q, *J* = 7.1 Hz, 2H), 3.08 (d, *J* = 9.3 Hz, 1H), 0.83 (t, *J* = 7.1 Hz, 3H). **$^{13}$C NMR (101 MHz, CHLOROFORM-*D*) δ** 195.4, 194.2, 165.4, 152.2, 148.4, 142.7, 142.4, 141.8, 140.8, 134.9, 134.5, 129.1, 128.6, 127.7, 122.9, 122.3, 122.2, 110.8, 109.4, 60.2, 49.4, 37.6, 37.5, 14.0. **HRMS (ESI) m/z:** $[M+Na]^+$ calculated for $C_{26}H_{20}O_5Na$, 435.1203; found 435.1198. **IR (neat, cm$^{-1}$):** 3436, 2928, 1710, 1621, 1446, 1341, 1293, 1175, 1094, 1037, 879, 775, 739, 698, 598, 525.

**ethyl (*E*)-3-(1',3'-dioxo-2-propyl-1',3'-dihydrospiro[cyclopropane-1,2'-inden]-3-yl)-3-phenylacrylate (4t):**

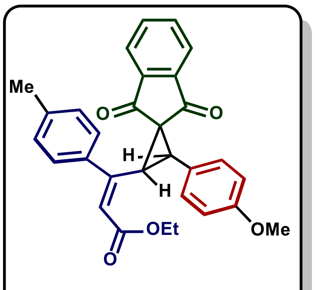

4t

Following the general procedure 5, reaction of 1*H*-indene-1,3(2*H*)-dione (44 mg, 0.30 mmol, 1 equiv.), aldehyde **2t** (30 µL, 0.33 mmol, 1.1 equiv.) and ylide **1a** (112 mg, 0.42 mmol, 1.4 equiv.) using catalytic amount (7 mg, 20 mol%) of L-proline in methanol (0.1 M) at room temperature for 30 minutes furnished **4t** in 85% (99 mg, 0.25 mmol,) as white solid with diastereomeric ratio 5:1.

**Major product:$^1$H NMR (500 MHz, CHLOROFORM-*D*) δ** 7.98 (d, *J* = 7.4 Hz, 1H), 7.82 – 7.71 (m, 3H), 7.47 – 7.42 (m, 2H), 7.37 (dd, *J* = 11.6, 7.2 Hz, 3H), 6.07 (s, 1H), 3.83 – 3.77 (m, 2H), 3.60 (d, *J* = 7.0 Hz, 1H), 2.16 (dt, *J* = 9.1, 4.5

Hz, 1H), 2.07 – 1.99 (m, 1H), 1.95 (d, $J$ = 5.8 Hz, 1H), 1.25 (s, 2H), 0.96 (t, $J$ = 7.1 Hz, 3H), 0.80 (t, $J$ = 7.4 Hz, 3H). **$^{13}$C NMR (126 MHz, CHLOROFORM-*D*) δ** 197.3, 197.1, 165.4, 153.8, 142.4, 141.6, 141.4, 134.6, 134.4, 128.8, 128.4, 128.4, 127.8, 126.9, 122.5, 122.1, 122.0, 60.1, 48.4, 43.5, 42.3, 28.6, 22.6, 14.0, 13.7. **HRMS (ESI) m/z:** [M+Na]$^+$ calculated for $C_{25}H_{24}O_4Na$, 411.1567; found 411.1566. **IR (neat, cm$^{-1}$):** 3428, 3059, 2961, 2928, 2870, 1709, 1620, 1449, 1368, 1334, 1276, 1209, 1173, 1103, 1038, 878, 769, 746, 699, 612, 562, 531.

**ethyl (*E*)-3-(2-(4-methoxyphenyl)-1',3'-dioxo-1',3'-dihydrospiro[cyclopropane-1,2'-inden]-3-yl)-3-(p-tolyl)acrylate (4u):**

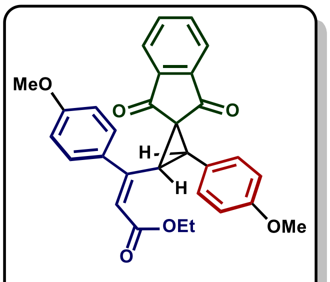


4u

Following the general procedure 5, reaction of 1*H*-indene-1,3(2*H*)-dione (44 mg, 0.30 mmol, 1 equiv.), aldehyde **2b** (40 µL, 0.33 mmol, 1.1 equiv.) and ylide **1b** (118 mg, 0.42 mmol, 1.4 equiv.) using catalytic amount (7 mg, 20 mol%) of L-proline in methanol (0.1 M) at room temperature for 30 minutes furnished **4u** in 89% (125 mg, 0.27 mmol,) as yellow solid with diastereomeric ratio >20:1.

**$^1$H NMR (400 MHz, CHLOROFORM-*D*) δ** 7.90 – 7.83 (m, 2H), 7.73 – 7.67 (m, 2H), 7.43 (d, $J$ = 8.2 Hz, 2H), 7.37 – 7.29 (m, 2H), 7.19 – 7.13 (m, 2H), 6.88 (d, $J$ = 8.7 Hz, 2H), 6.21 (d, $J$ = 2.1 Hz, 1H), 4.26 (d, $J$ = 9.6, 2.1 Hz, 1H), 3.83 (q, $J$ = 7.1 Hz, 2H), 3.77 (s, 3H), 3.38 (d, $J$ = 9.6 Hz, 1H), 2.34 (s, 3H), 0.98 (t, $J$ = 7.1 Hz, 3H). **$^{13}$C NMR (101 MHz, CHLOROFORM-*D*) δ** 195.9, 194.8, 165.4, 159.1, 153.0, 142.3, 141.6, 139.0, 137.8, 134.6, 134.2, 130.1, 129.1, 127.5, 125.4, 122.5, 122.0, 121.1, 113.6, 59.9, 55.1, 51.1, 46.0, 38.4, 21.2, 13.9. **HRMS (ESI) m/z:** [M+Na]$^+$ calculated for $C_{30}H_{26}O_5Na$, 489.1672; found 489.1674. **IR (neat, cm$^{-1}$):** 3429, 2981, 2933, 2838, 1709, 1611,1515, 1457, 1336, 1290, 1251, 1221, 1171, 1091, 1038, 876, 822, 740, 620, 579, 528, 501.

**ethyl (*E*)-3-(4-methoxyphenyl)-3-(2-(4-methoxyphenyl)-1',3'-dioxo-1',3'-dihydrospiro[cyclopropane-1,2'-inden]-3-yl)acrylate (4v):**

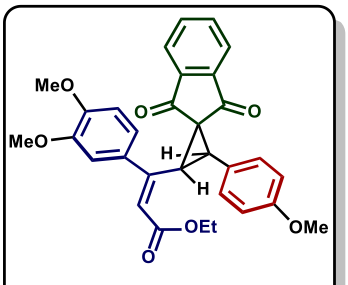


4v

Following the general procedure 5, reaction of 1*H*-indene-1,3(2*H*)-dione (44 mg, 0.30 mmol, 1 equiv.), aldehyde **2b** (40 µL, 0.33 mmol, 1.1 equiv.) and ylide **1c** (124 mg, 0.42 mmol, 1.4 equiv.) using catalytic amount (7 mg, 20 mol%) of L-proline in methanol (0.1 M) at room temperature for 30 minutes furnished **4v** in 90% (131 mg, 0.27 mmol,) as yellow solid with diastereomeric ratio >20:1.

**$^1$H NMR (500 MHz, CHLOROFORM-*D*) δ** 7.89 – 7.79 (m, 2H), 7.71 (dd, $J$ = 6.0, 2.8 Hz, 2H), 7.46 (d, $J$ = 8.7 Hz, 2H), 7.33 (d, $J$ = 8.6 Hz, 2H), 6.88 (dd, $J$ = 8.8, 2.8 Hz, 4H), 6.16 (s, 1H), 4.22 (d, $J$ = 9.6 Hz, 1H), 3.83 – 3.74 (m, 8H), 3.38 (d, $J$ = 9.6 Hz, 1H), 0.97 (t, $J$ = 7.1 Hz, 3H). **$^{13}$C NMR (101 MHz, CHLOROFORM-*D*) δ** 196.1, 195.1, 165.6, 160.4, 159.3, 152.7, 142.5, 141.8, 134.7, 134.3, 133.2, 130.2, 129.1, 125.5, 122.7, 122.2, 120.4, 114.0, 113.8, 60.1, 55.4, 55.3, 51.2, 46.2, 38.6, 14.0. **HRMS (ESI) m/z:** [M+Na]$^+$ calculated for $C_{30}H_{26}O_6Na$, 505.1622; found 505.1621. **IR (neat, cm$^{-1}$):** 3429, 2960, 2935, 2838, 1708, 1604, 1514, 1460, 1336, 1292, 1251, 1169, 1091, 1037, 874, 833, 739, 535.

**ethyl (*E*)-3-(3,4-dimethoxyphenyl)-3-(2-(4-methoxyphenyl)-1',3'-dioxo-1',3'-dihydrospiro[cyclopropane-1,2'-inden]-3-yl) acrylate (4w):**

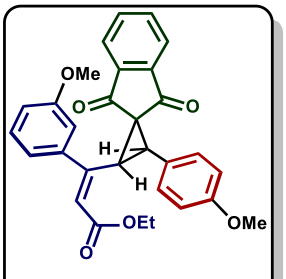


4w

Following the general procedure 5, reaction of 1*H*-indene-1,3(2*H*)-dione (44 mg, 0.30 mmol, 1 equiv.), aldehyde **2b** (40 µL, 0.33 mmol, 1.1 equiv.) and ylide **1d** (137 mg, 0.42 mmol, 1.4 equiv.) using catalytic amount (7 mg, 20 mol%) of L-proline in methanol (0.1 M) at room temperature for 30 minutes furnished **4w** in 92% (139 mg, 0.28mmol) as yellow solid with diastereomeric ratio >20:1.

**$^1$H NMR (500 MHz, CHLOROFORM-*D*) δ** 7.88 – 7.80 (m, 2H), 7.73 – 7.66 (m, 2H), 7.11 (d, *J* = 2.1 Hz, 1H), 7.01 (d, *J* = 2.2 Hz, 1H), 6.89 – 6.81 (m, 3H), 6.20 (d, *J* = 2.2 Hz, 1H), 4.18 (d, *J* = 9.7 Hz, 1H), 3.87 (s, 3H), 3.83 – 3.79 (m, 2H), 3.78 (s, 3H), 3.71 (s, 3H), 3.36 (d, *J* = 9.7 Hz, 1H), 0.97 (t, *J* = 7.1 Hz, 3H). **$^{13}$C NMR (101 MHz, CHLOROFORM-*D*) δ** 195.9, 195.0, 165.4, 159.1, 152.3, 149.8, 148.6, 142.3, 141.6, 134.6, 134.2, 133.3, 130.0, 125.3, 122.5, 122.0, 120.3, 120.1, 113.6, 110.8, 110.6, 59.9, 55.8, 55.6, 55.1, 51.1, 46.3, 38.3, 13.9. **HRMS (ESI) m/z:** [M+Na]$^+$ calculated for $C_{31}H_{28}O_7Na$, 535.727; found 535.720. **IR (neat, cm$^{-1}$):** 3427, 3048, 2943, 2841, 2037, 1706, 1601, 1518, 1463, 1338, 1259, 1224, 1161, 1031, 844, 812, 750, 561, 539.

**ethyl (*E*)-3-(3-methoxyphenyl)-3-(2-(4-methoxyphenyl)-1',3'-dioxo-1',3'-dihydrospiro[cyclopropane-1,2'-inden]-3-yl)acrylate (4x):**

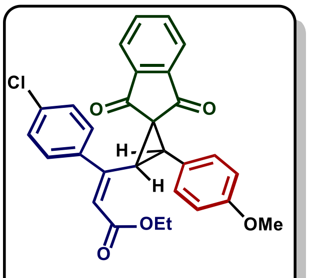


4x

Following the general procedure 5, reaction of 1*H*-indene-1,3(2*H*)-dione **1a** (44 mg, 0.30 mmol, 1 equiv.), aldehyde **2b** (40 µL, 0.33 mmol, 1.1 equiv.) and ylide **1g** (124 mg, 0.42 mmol, 1.4 equiv.) using catalytic amount (7 mg, 20 mol%) of L-proline in methanol (0.1 M) at room temperature for 30 minutes furnished **4x** in 86% (125 mg, 0.26 mmol,) as orange solid with diastereomeric ratio >20:1.

**$^1$H NMR (500 MHz, CHLOROFORM-*D*) δ** 7.88 – 7.78 (m, 2H), 7.70 (dd, *J* = 5.9, 2.6 Hz, 2H), 7.31 (d, *J* = 8.5 Hz, 2H), 7.24 (s, 1H), 7.09 (d, *J* = 7.7 Hz, 1H), 6.85 (d, *J* = 8.5 Hz, 3H), 6.22 (s, 1H), 4.21 (d, *J* = 9.7 Hz, 1H), 3.81 (q, *J* = 7.1 Hz, 2H), 3.77 (s, 3H), 3.70 (s, 3H), 3.35 (d, *J* = 9.7 Hz, 1H), 0.97 (t, *J* = 7.1 Hz, 3H). **$^{13}$C NMR (101 MHz, CHLOROFORM-*D*) δ** 195.9, 194.9, 165.4, 159.5, 159.2, 152.8, 142.4, 142.1, 141.7, 134.7, 134.3, 130.1, 129.5, 125.4, 122.6, 122.1, 122.0, 120.0, 115.1, 113.7, 112.7, 60.1, 55.2, 51.1, 46.1, 38.3, 13.9. **HRMS (ESI) m/z:** [M+Na]$^+$ calculated for $C_{30}H_{26}O_6Na$, 505.1622; found 505.1619. **IR (neat, cm$^{-1}$):** 3422, 2999, 2967, 2930, 2838, 1709, 1613, 1578, 1515, 1490, 1468, 1338, 1286, 1217, 1182, 1092, 1042, 871, 835, 785, 750, 689, 567, 541, 468.

**ethyl (*E*)-3-(4-chlorophenyl)-3-(2-(4-methoxyphenyl)-1',3'-dioxo-1',3'-dihydrospiro[cyclopropane-1,2'-inden]-3-yl) acrylate (4y):**

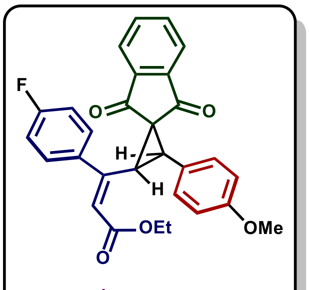


4y

Following the general procedure 5, reaction of 1*H*-indene-1,3(2*H*)-dione (44 mg, 0.30 mmol, 1 equiv.), aldehyde **2b** (40 µL, 0.33 mmol, 1.1 equiv.) and ylide **1e** (126 mg, 0.42 mmol, 1.4 equiv.) using catalytic amount (7 mg, 20 mol%) of L-proline in methanol (0.1 M) at room temperature for 30 minutes furnished **4y** in 87% (128 mg, 0.26 mmol,) as white solid with diastereomeric ratio >20:1.

**$^1$H NMR (500 MHz, CHLOROFORM-*D*) δ** 7.85 (ddd, *J* = 8.5, 6.0, 3.7 Hz, 2H), 7.74 – 7.68 (m, 2H), 7.44 (d, *J* = 8.6 Hz, 2H), 7.35 – 7.28 (m, 4H), 6.87 (d, *J* = 8.6 Hz, 2H), 6.18 (s, 1H), 4.24 (d, *J* = 9.7 Hz, 1H), 3.84 (q, *J* = 7.1 Hz, 2H), 3.78 (s, 3H), 3.31 (d, *J* = 9.7 Hz, 1H), 0.98 (t, *J* = 7.1 Hz, 3H). **$^{13}$C NMR (101 MHz, CHLOROFORM-*D*) δ** 195.9, 194.8, 165.3, 159.1, 153.1, 142.3, 141.6, 140.7, 134.6, 134.3, 130.1, 128.9, 128.4, 127.6, 125.3, 122.6, 122.0, 122.0, 113.7, 60.0, 55.1, 51.1, 46.0, 38.4, 13.9. **HRMS (ESI) m/z:** [M+Na]$^+$ calculated for $C_{29}H_{23}O_5ClNa$, 509.1126; found 509.1131. **IR (neat, cm$^{-1}$):** 3427, 2969, 2841, 1710, 1614, 1517, 1451, 1331, 1285, 1256, 1174, 1092, 1036, 872, 829, 745, 671, 568, 500.

**ethyl (*E*)-3-(4-fluorophenyl)-3-(2-(4-methoxyphenyl)-1',3'-dioxo-1',3'-dihydrospiro[cyclopropane-1,2'-inden]-3-yl) acrylate (4z):**

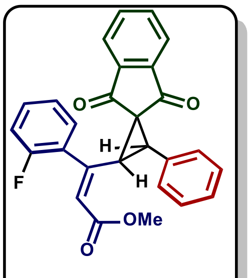


4z

Following the general procedure 5, reaction of 1*H*-indene-1,3(2*H*)-dione (44 mg, 0.30 mmol, 1 equiv.), aldehyde **2b** (40 µL, 0.33 mmol, 1.1 equiv.) and ylide **1f** (119 mg, 0.42 mmol, 1.4 equiv.) using catalytic amount (7 mg, 20 mol%) of L-proline in methanol (0.1 M) at room temperature for 30 minutes furnished **4z** in 85% (120 mg, 0.26 mmol,) as orange solid with diastereomeric ratio >20:1.

**$^{1}$H NMR (500 MHz, CHLOROFORM-*D*) δ** 7.88 – 7.81 (m, 2H), 7.75 – 7.69 (m, 2H), 7.49 (dd, *J* = 8.4, 5.3 Hz, 2H), 7.31 (d, *J* = 8.2 Hz, 2H), 7.05 (t, *J* = 8.4 Hz, 2H), 6.87 (d, *J* = 8.3 Hz, 2H), 6.16 (s, 1H), 4.23 (d, *J* = 9.6 Hz, 1H), 3.84 (q, *J* = 7.1 Hz, 2H), 3.79 (s, 3H), 3.31 (d, *J* = 9.6 Hz, 1H), 0.99 (t, *J* = 7.1 Hz, 3H). **$^{13}$C NMR (101 MHz, CHLOROFORM-*D*) δ** 196.0, 194.6, 165.2, 164.3, 161.8, 159.2, 152.0, 141.9 (d, *J* = 75.9 Hz), 136.8, 136.8, 134.5 (d, *J* = 36.2 Hz) 130.1, 129.5 (d, *J* = 8.2 Hz), 125.1, 122.4 (d, *J* = 58.2 Hz), 121.9, 115.5 (d, *J* = 21.9 Hz).113.7, 60.1, 55.1, 51.2, 45.9, 38.2, 13.9. **$^{19}$F NMR (376 MHz, CHLOROFORM-*D*) δ** -111.94. **HRMS (ESI) m/z:** [M+Na]$^{+}$ calculated for $C_{29}H_{23}O_5FNa$, 493.1422; found 493.1426. **IR (neat, cm$^{-1}$):** 3423, 3066, 2975, 2842, 2051, 1894, 1711, 1607, 1513, 1454, 1329, 1280, 1171, 1092, 1032, 870, 832, 743, 572, 525.

**methyl (*E*)-3-(1',3'-dioxo-2-phenyl-1',3'-dihydrospiro[cyclopropane-1,2'-inden]-3-yl)-3-(2-fluorophenyl) acrylate (4aa):**

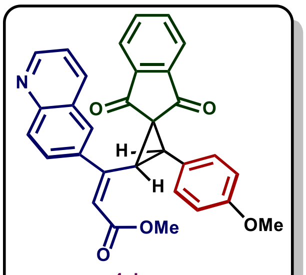


4aa

Following the general procedure 5, reaction of 1*H*-indene-1,3(2*H*)-dione (44 mg, 0.30 mmol, 1 equiv.), aldehyde **2b** (40 µL, 0.33 mmol, 1.1 equiv.) and ylide **1h** (114 mg, 0.42 mmol, 1.4 equiv.) using catalytic amount (7 mg, 20 mol%) of L-proline in methanol (0.1 M) at room temperature for 30 minutes furnished **4aa** in 83% (114 mg, 0.25 mmol,) as orange solid with diastereomeric ratio >20:1.

**$^{1}$H NMR (400 MHz, CHLOROFORM-*D*) δ** 7.85 (s, 2H), 7.78 – 7.68 (m, 2H), 7.53 – 7.45 (m, 2H), 7.36 (td, *J* = 5.1, 3.2 Hz, 5H), 7.02 (t, *J* = 8.7 Hz, 2H), 6.22 (s, 1H), 4.23 (d, *J* = 9.5 Hz, 1H), 3.38 (s, 4H). **$^{13}$C NMR (101 MHz, CHLOROFORM-*D*) δ** 195.8, 194.9, 165.9, 153.2, 142.12 (d, *J* = 64.1 Hz), 140.7, 134.73 (d, *J* = 28.3 Hz), 130.73 (d, *J* = 8.2 Hz),129.2, 127.7, 122.56 (d, *J* = 46.2 Hz), 121.9, 115.38 (d, *J* = 21.4 Hz) , 51.4, 50.8, 45.3, 38.7. **NMR (376 MHz, CHLOROFORM-*D*) δ** -113.88. **HRMS (ESI) m/z:** [M+Na]$^{+}$ calculated for $C_{28}H_{21}O_5FNa$, 479.1265; found 479.1262. **IR (neat, cm$^{-1}$):** 3425, 3066, 2975, 2842, 2051, 1894, 1710, 1607, 1513, 1454, 1329, 1280, 1171, 1092, 1032, 870, 832, 743, 572, 525.

**methyl (*E*)-3-(2-(4-methoxyphenyl)-1',3'-dioxo-1',3'-dihydrospiro[cyclopropane-1,2'-inden]-3-yl)-3-(quinolin-6-yl)acrylate (4ab):**



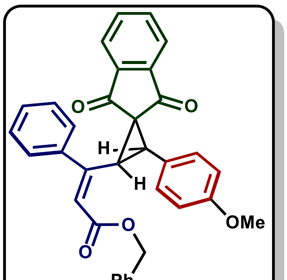
4ab

Following the general procedure 5, reaction of 1*H*-indene-1,3(2*H*)-dione (44 mg, 0.30 mmol, 1 equiv.), aldehyde **2b** (40 µL mg, 0.33 mmol, 1.1 equiv.) and ylide **1p** (128 mg, 0.42 mmol, 1.4 equiv.) using catalytic amount (7 mg, 20 mol%) of L-proline in methanol (0.1 M) at room temperature for 30 minutes furnished **4ab** in 35% (53 mg, 0.10 mmol,) as green solid with diastereomeric ratio >20:1.

**$^{1}$H NMR (400 MHz, CHLOROFORM-*D*) δ** 8.94 – 8.86 (m, 1H), 8.15 – 8.05 (m, 2H), 7.98 (s, 1H), 7.86 (dq, *J* = 4.9, 1.8, 1.4 Hz, 1H), 7.84 – 7.80 (m, 2H), 7.74 – 7.68 (m, 2H), 7.41 – 7.36 (m, 1H), 7.35 – 7.30 (m, 2H), 6.87 (d, *J* = 9.0 Hz, 2H), 6.33

(s, 1H), 4.31 (d, $J$ = 9.7 Hz, 1H), 3.77 (s, 3H), 3.39 (s, 3H), 3.34 (d, $J$ = 9.7 Hz, 1H). **$^{13}$C NMR (101 MHz, CHLOROFORM-*D*) δ** 196.0, 194.7, 165.6, 159.3, 152.7, 151.1, 148.2, 142.4, 141.7, 138.9, 136.7, 134.8, 134.5, 130.1, 129.7, 128.8, 128.0, 127.2, 125.1, 122.8, 122.7, 122.2, 121.7, 113.8, 55.2, 51.5, 51.3, 46.1, 38.3. **HRMS (ESI) m/z:** $[M+Na]^+$ calculated for $C_{31}H_{23}O_5NNa$, 512.1468; found 512.1466. **IR (neat, cm$^{-1}$):** 3427, 3054, 2951, 2840, 1710, 1612, 1516, 1458, 1436, 1291, 1251, 1168, 1121, 1090, 1038, 888, 838, 800, 738, 615, 566, 530, 480.

**benzyl (*E*)-3-(2-(4-methoxyphenyl)-1',3'-dioxo-1',3'-dihydrospiro[cyclopropane-1,2'-inden]-3-yl)-3-phenylacrylate (4ac):**

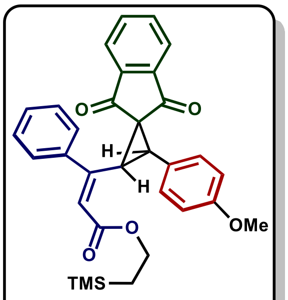


4ac

Following the general procedure 5, reaction of 1*H*-indene-1,3(2*H*)-dione (44 mg, 0.30 mmol, 1 equiv.), aldehyde **2b** (40 µL, 0.33 mmol, 1.1 equiv.) and ylide **1k** (138 mg, 0.42 mmol, 1.4 equiv.) using catalytic amount (7 mg, 20 mol%) of L-proline in methanol (0.1 M) at room temperature for 30 minutes furnished **4ac** in 87 % (135 mg, 0.26 mmol,) as yellow solid with diastereomeric ratio >20:1.

**$^1$H NMR (400 MHz, CHLOROFORM-*D*) δ** 7.87 (s, 1H), 7.81 (s, 1H), 7.72 (s, 2H), 7.52 (d, $J$ = 2.3 Hz, 2H), 7.38 – 7.34 (m, 4H), 7.33 (s, 1H), 7.25 (d, $J$ = 2.3 Hz, 3H), 7.14 (d, $J$ = 2.4 Hz, 2H), 6.89 (d, $J$ = 8.7 Hz, 2H), 6.28 (s, 1H), 4.87 (s, 2H), 4.30 (d, $J$ = 9.6 Hz, 1H), 3.80 (s, 3H), 3.38 (d, $J$ = 9.6 Hz, 1H). **$^{13}$C NMR (101 MHz, CHLOROFORM-*D*) δ** 196.0, 194.9, 165.1, 159.2, 154.3, 142.4, 141.7, 140.7, 135.9, 134.7, 134.3, 130.2, 129.1, 128.5, 128.4, 128.2, 128.1, 127.7, 125.4, 122.7, 122.2, 121.4, 113.8, 65.8, 55.2, 51.3, 46.1, 38.4. **HRMS (ESI) m/z:** $[M+Na]^+$ calculated for $C_{34}H_{26}O_5Na$, 537.1672; found 537.1670. **IR (neat, cm$^{-1}$):** 3428, 3060, 3033, 2935, 2838, 1709, 1613, 1516, 1452, 1341, 1291, 1251, 1160, 1089, 1036, 877, 826, 739, 699, 621, 564, 539.

**2-(trimethylsilyl)ethyl (*E*)-3-(2-(4-methoxyphenyl)-1',3'-dioxo-1',3'-dihydrospiro[cyclopropane-1,2'-inden]-3-yl)-3-phenylacrylate (4ad):**

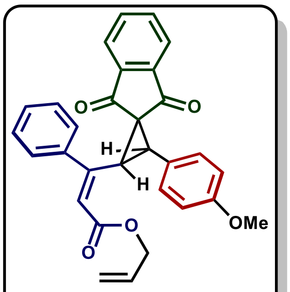


4ad

Following the general procedure 5, reaction of 1*H*-indene-1,3(2*H*)-dione (44 mg, 0.30 mmol, 1 equiv.), aldehyde **2b** (40 µL, 0.33 mmol, 1.1 equiv.) and ylide **1i** (142 mg, 0.42 mmol, 1.4 equiv.) using catalytic amount (7 mg, 20 mol%) of L-proline in methanol (0.1 M) at room temperature for 30 minutes furnished **4ad** in 88% (139 mg, 0.26 mmol,) as orange solid with diastereomeric ratio >20:1.

**$^1$H NMR (500 MHz, CHLOROFORM-*D*) δ** 7.86 (d, $J$ = 1.2 Hz, 2H), 7.77 – 7.66 (m, 2H), 7.51 (dd, $J$ = 7.1, 2.5 Hz, 2H), 7.40 – 7.28 (m, 5H), 6.87 (d, $J$ = 8.7 Hz, 2H), 6.19 (d, $J$ = 2.1 Hz, 1H), 4.26 (d, $J$ = 9.6, Hz, 1H), 3.93 – 3.84 (m, 2H), 3.80 (s, 3H), 3.35 (d, $J$ = 9.6 Hz, 1H), 0.75 (ddd, $J$ = 13.7, 11.1, 5.9 Hz, 1H), 0.62 (ddd, $J$ = 13.7, 11.1, 5.9 Hz, 1H), -0.08 (s, 9H). **$^{13}$C NMR (101 MHz, CHLOROFORM-*D*) δ** 195.8, 194.8, 165.5, 159.1, 152.8, 142.4, 141.7, 140.8, 137.2, 135.0, 134.5, 134.2, 130.1, 128.9, 128.4, 127.6, 125.3, 123.0, 123.0, 122.6, 122.2, 122.0, 114.3, 113.7, 62.2, 55.1, 51.1, 46.0, 38.5, 17.0, -1.6. **HRMS (ESI) m/z:** $[M+Na]^+$ calculated for $C_{32}H_{32}O_5SiNa$, 547.1911; found 547.1909. **IR (neat, cm$^{-1}$):** 3431, 2954, 2840, 1711, 1686, 1585, 1589, 1514, 1435, 1347, 1315, 1270, 1250, 1163, 1082, 1034, 862, 837, 775, 737, 698, 564, 532.

**allyl (*E*)-3-(2-(4-methoxyphenyl)-1',3'-dioxo-1',3'-dihydrospiro[cyclopropane-1,2'-inden]-3-yl)-3-phenylacrylate (4ae):**

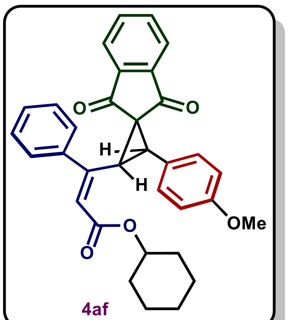


4ae

Following the general procedure 5, reaction of 1*H*-indene-1,3(2*H*)-dione (44 mg, 0.30 mmol, 1 equiv.), aldehyde **2b** (40 µL, 0.33 mmol, 1.1 equiv.) and ylide **1l** (117 mg, 0.42 mmol, 1.4 equiv.) using catalytic amount (7 mg, 20 mol%) of L-proline in methanol (0.1 M) at room temperature for 30 minutes furnished **4ae** in 84% (118 mg, 0.25 mmol,) as white solid with diastereomeric ratio >20:1.

**$^{1}$H NMR (400 MHz, CHLOROFORM-*D*) δ** 7.91 – 7.80 (m, 2H), 7.71 (d, *J* = 8.5 Hz, 2H), 7.58 – 7.50 (m, 2H), 7.34 (dd, *J* = 12.0, 7.9 Hz, 5H), 6.88 (s, 2H), 6.26 (d, *J* = 2.1 Hz, 1H), 5.64 (dd, *J* = 17.2, 10.4 Hz, 1H), 5.14 – 4.97 (m, 2H), 4.35 – 4.26 (m, 3H), 3.78 (d, *J* = 0.9 Hz, 3H), 3.37 (d, *J* = 9.6 Hz, 1H). **$^{13}$C NMR (101 MHz, CHLOROFORM-*D*)** δ 195.9, 194.7, 164.9, 159.2, 153.8, 142.4, 141.6, 140.7, 134.6, 134.3, 131.9, 130.1, 129.0, 128.5, 127.6, 125.3, 122.6, 122.1, 121.5, 118.0, 113.7, 64.7, 55.1, 51.1, 46.0, 38.3. **HRMS (ESI) m/z:** $[M+Na]^+$ calculated for $C_{30}H_{24}O_5Na$, 487.1516; found 487.1511. **IR (neat, cm$^{-1}$):** 3429, 2954, 2840, 1710, 1686, 1585, 1589, 1514, 1435, 1347, 1315, 1270, 1250, 1163, 1082, 1034, 862, 837, 775, 737, 698, 564, 532.

**cyclohexyl (*E*)-3-(2-(4-methoxyphenyl)-1',3'-dioxo-1',3'-dihydrospiro[cyclopropane-1,2'-inden]-3-yl)-3-phenylacrylate (4af):**

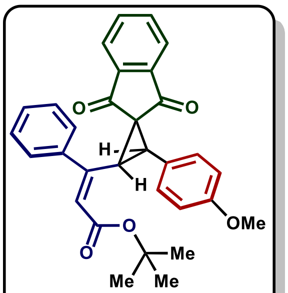


4af

Following the general procedure 5, reaction of 1*H*-indene-1,3(2*H*)-dione (44 mg, 0.30 mmol, 1 equiv.), aldehyde **2b** (40 µL, 0.33 mmol, 1.1 equiv.) and ylide **1j** (135 mg, 0.42 mmol, 1.4 equiv.) using catalytic amount (7 mg, 20 mol%) of L-proline in methanol (0.1 M) at room temperature for 30 minutes furnished **4af** in 86% (131 mg, 0.26 mmol,) as orange solid with diastereomeric ratio >20:1.

**$^{1}$H NMR (400 MHz, CHLOROFORM-*D*)** δ 7.89 – 7.82 (m, 2H), 7.70 (d, *J* = 3.2 Hz, 2H), 7.56 – 7.51 (m, 2H), 7.37 – 7.31 (m, 5H), 6.87 (d, *J* = 8.7 Hz, 2H), 6.22 (d, *J* = 2.1 Hz, 1H), 4.45 (dt, *J* = 9.1, 4.9 Hz, 1H), 4.31 (d, *J* = 9.7 Hz, 1H), 3.78 (s, 3H), 3.36 (d, *J* = 9.7 Hz, 1H), 1.72 – 1.58 (m, 2H), 1.54 – 1.48 (m, 1H), 1.42 (s, 1H), 1.30 (s, 1H), 1.27 – 1.20 (m, 2H), 1.14 – 1.05 (m, 3H). **$^{13}$C NMR (101 MHz, CHLOROFORM-*D*)** δ 196.0, 194.8, 164.8, 159.1, 152.7, 142.4, 141.6, 140.8, 134.6, 134.1, 130.1, 128.9, 128.4, 127.6, 125.4, 122.7, 122.4, 122.0, 113.7, 72.2, 55.1, 51.1, 46.0, 38.5, 31.4, 31.0, 25.2, 23.7, 23.6. **HRMS (ESI) m/z:** $[M+Na]^+$ calculated for $C_{33}H_{30}O_5Na$, 529.1985; found 529.1980. **IR (neat, cm$^{-1}$):** 3429, 3058, 2936, 2858, 1708, 1614, 1516, 1450, 1346, 1290, 1251, 1176, 1121, 1090, 1038, 968, 928, 882, 824, 738, 699, 621, 564, 539.

***tert*-butyl (*E*)-3-(2-(4-methoxyphenyl)-1',3'-dioxo-1',3'-dihydrospiro[cyclopropane-1,2'-inden]-3-yl)-3-phenylacrylate (4ag):**

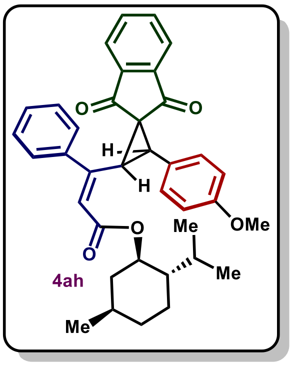


4ag

Following the general procedure 5, reaction of 1*H*-indene-1,3(2*H*)-dione (44 mg, 0.30 mmol, 1 equiv.), aldehyde **2b** (40 µL, 0.33 mmol, 1.1 equiv.) and ylide **1m** (124mg, 0.42 mmol, 1.4 equiv.) using catalytic amount (7 mg, 20 mol%) of L-proline in methanol (0.1 M) at room temperature for 30 minutes furnished **4ag** in 77% (112 mg, 0.23 mmol,) as white solid with diastereomeric ratio >20:1.

**$^{1}$H NMR (400 MHz, CHLOROFORM-*D*) δ** 7.84 (d, *J* = 10.6 Hz, 2H), 7.69 (d, *J* = 1.9 Hz, 2H), 7.52 (s, 2H), 7.34 (d, *J* = 3.1 Hz, 5H), 6.88 (dd, *J* = 8.4, 1.4 Hz, 2H), 6.16 (s, 1H), 4.29 (d, *J* = 9.7 Hz, 1H), 3.80 (s, 3H), 3.32 (d, *J* = 9.7 Hz, 1H), 1.10 (s, 9H). **$^{13}$C NMR (101 MHz, CHLOROFORM-*D*) δ** 196.3, 195.2, 164.9, 159.2, 151.8, 142.7, 141.7, 140.9, 134.6, 134.1, 130.2, 128.9, 128.6, 127.7, 125.7, 123.5, 122.7, 122.1, 113.8, 80.1, 55.3, 51.0, 45.9, 38.9, 27.7. **HRMS (ESI) m/z:** $[M+Na]^+$ calculated for $C_{31}H_{28}O_5Na$, 503.1829; found 503.1823. **IR (neat, cm$^{-1}$):** 3430, 3058, 2975, 2930, 1708, 1613, 1517, 1454, 1348, 1251, 1220, 1150, 1090, 1037, 869, 824, 775, 739, 698, 564, 539.

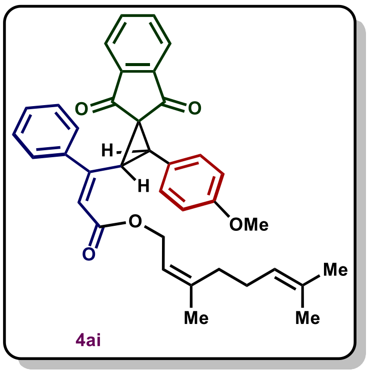
**(1*R*,2*S*,4*R*)-2-isopropyl-4-methylcyclohexyl (*E*)-3-(2-(4-methoxyphenyl)-1',3'-dioxo-1',3'-dihydrospiro[cyclopropane-1,2'-inden]-3-yl)-3-phenylacrylate (4ah):**




Following the general procedure 5, reaction of 1*H*-indene-1,3(2*H*)-dione (44 mg, 0.30 mmol, 1 equiv.), aldehyde **2b** (40 µL, 0.33 mmol, 1.1 equiv.) and ylide **1o** (159 mg, 0.42 mmol, 1.4 equiv.) using catalytic amount (7 mg, 20 mol%) of L-proline in methanol (0.1 M) at room temperature for 30 minutes furnished **4ah** in 85% (for both the diastereomers) (144 mg, 0.26 mmol,) as white solid with diastereomeric ratio 1:1.

**$^1$H NMR (500 MHz, CHLOROFORM-*D*)) δ**7.82 (s, 2H), 7.77 – 7.67 (m, 2H), 7.53 (dt, *J* = 5.3, 2.8 Hz, 2H), 7.39 – 7.28 (m, 5H), 6.87 (d, *J* = 8.2 Hz, 2H), 6.20 (d, *J* = 20.1 Hz, 1H), 4.49 – 4.35 (m, 1H), 4.32 (d, *J* = 9.5 Hz, 1H), 3.80 (s, 3H), 3.33 (d, *J* = 9.5 Hz, 1H), 1.83 – 1.70 (m, 1H), 1.61 – 1.49 (m, 3H), 1.37 – 1.12 (m, 3H), 0.89 – 0.58 (m, 10H), 0.23 (d, *J* = 6.9 Hz, 1H). **$^{13}$C NMR (101 MHz, CHLOROFORM-*D*) δ** 196.2, 195.0, 165.1, 165.0, 159.3, 152.9, 141.8, 140.9, 134.7, 134.3, 130.3, 129.1, 128.6, 127.9, 127.7, 125.6, 122.9, 122.3, 122.1, 113.8, 74.1, 55.3, 51.1, 46.7, 46.3, 40.0, 38.7, 34.3, 31.2, 26.4, 23.6, 22.1, 20.7, 16.5. **HRMS (ESI) m/z:** $[M+Na]^+$ calculated for $C_{37}H_{38}O_5Na$, 585.2611; found 585.2605. **IR (neat, cm$^{-1}$):** 3428, 2952, 2869, 1709, 1621, 1517, 1453, 1350, 1331, 1290, 1251, 1221, 1173, 1089, 1040, 988, 882, 826, 775, 746, 697, 620, 564, 538.

**(*Z*)-3,7-dimethylocta-2,6-dien-1-yl (*E*)-3-(2-(4-methoxyphenyl)-1',3'-dioxo-1',3'-dihydrospiro[cyclopropane-1,2'-inden]-3-yl)-3-phenylacrylate (4ai):**

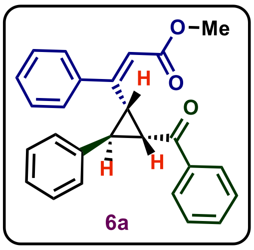



Following the general procedure 5, reaction of 1*H*-indene-1,3(2*H*)-dione (44 mg, 0.30 mmol, 1 equiv.), aldehyde **2b** (40 µL, 0.33 mmol, 1.1 equiv.) and ylide **1n** (158 mg, 0.42 mmol, 1.4 equiv.) using catalytic amount (7 mg, 20 mol%) of L-proline in methanol (0.1 M) at room temperature for 30 minutes furnished **4ai** in 83% (140 mg, 0.25 mmol,) as orange solid with diastereomeric ratio >20:1.

**$^1$H NMR (400 MHz, CHLOROFORM-*D*) δ** 7.86 (d, *J* = 1.8 Hz, 2H), 7.72 (s, 2H), 7.52 (s, 2H), 7.35 (s, 5H), 6.91 – 6.84 (m, 2H), 6.23 (s, 1H), 5.13 – 4.99 (m, 2H), 4.35 – 4.24 (m, 3H), 3.79 (s, 3H), 3.37 (d, *J* = 9.8 Hz, 1H), 1.97 (s, 3H), 1.66 (d, *J* = 4.9 Hz, 6H), 1.57 (s, 3H), 1.33 – 1.28 (m, 1H). **$^{13}$C NMR (101 MHz, CHLOROFORM-*D*) δ** 196.0, 194.9, 165.4, 159.2, 153.3, 142.5, 142.2, 142.1, 141.8, 140.8, 134.6, 134.3, 132.0, 130.2, 129.0, 128.5, 127.7, 125.5, 123.7, 122.7, 122.1, 122.0, 119.1, 113.8, 60.8, 55.2, 51.2, 46.1, 38.4, 32.0, 26.6, 25.7, 23.5, 17.7. **HRMS (ESI) m/z:** $[M+Na]^+$ calculated for $C_{37}H_{36}O_5Na$, 583.2455; found 583.2459. **IR (neat, cm$^{-1}$):** 3432, 2927, 1709, 1614, 1516, 1447, 1335, 1252, 1222, 1165, 1089, 1037, 965, 879, 827, 749, 699, 618, 563, 539.

## 13. Synthesis and characterization data of 2-benzoyl-3-phenylcyclopropyl)-3-phenylacrylate

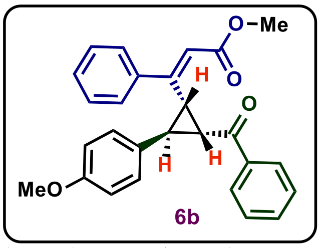
**methyl (*E*)-3-(-2-benzoyl-3-phenylcyclopropyl)-3-phenylacrylate (6a):**



Following the general procedure 6, reaction of chalcone **5a** (63 mg, 0.30 mmol, 1 equiv.) and ylide **1q** (106 mg, 0.42 mmol, 1.4 equiv.) using catalytic amount (29 mg, 30 mol%) of cesium carbonate in methanol (0.1 M) at room temperature for 2 hours furnished **6a** in 79% (92 mg, 0.24 mmol,) as white solid with diastereomeric ratio >20:1.

**$^1$H NMR (500 MHz, CHLOROFORM-*D*) δ** 7.98 (d, *J* = 7.5 Hz, 2H), 7.44 (dd, *J* = 20.8, 7.7 Hz, 6H), 7.37 – 7.31 (m, 5H), 7.23 (d, *J* = 6.5 Hz, 2H), 6.11 (s, 1H), 3.67 (dd, *J* = 9.2, 5.3 Hz, 1H), 3.52 (ddd, *J* = 9.4, 7.7, 1.9 Hz, 1H), 3.46 (s, 3H), 2.82 (dd, *J* = 7.8, 5.3 Hz, 1H). **$^{13}$C NMR (101 MHz, CHLOROFORM-*D*) δ** 196.4, 166.4, 156.3, 141.9, 139.7, 138.3, 132.7, 128.8, 128.8, 128.5, 128.4, 128.3, 127.8, 126.9, 126.4, 120.4, 51.1, 38.9, 35.9, 35.6. **HRMS (ESI) m/z:** $[M+Na]^+$ calculated for $C_{26}H_{22}O_3Na$, 405.1461; found 405.1459. **IR (neat, cm$^{-1}$):** 3406, 3061, 3029, 2944, 1711, 1660, 1609, 1492, 1446, 1429, 1374, 1337, 1275, 1226, 1170, 1078, 999, 914, 862, 772, 743, 697, 582, 529, 483.

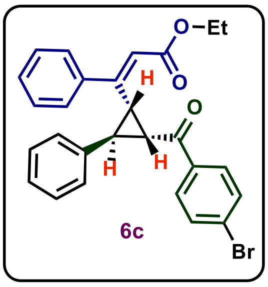
**methyl (*E*)-3-(-2-benzoyl-3-(4-methoxyphenyl) cyclopropyl)-3-phenylacrylate (6b):**



Following the general procedure 6, reaction of chalcone **5b** (73 mg, 0.30 mmol, 1 equiv.) and ylide **1q** (108 mg, 0.42 mmol, 1.4 equiv.) using catalytic amount (29 mg, 30 mol%) of cesium carbonate in methanol (0.1 M) at room temperature for 2 hours furnished **6b** in 76% (96 mg, 0.23 mmol,) as white solid with diastereomeric ratio >20:1.

**$^1$H NMR (500 MHz, CHLOROFORM-*D*) δ** 8.07 – 8.02 (m, 2H), 7.52 (s, 3H), 7.45 (s, 2H), 7.38 (s, 3H), 7.21 (s, 2H), 6.94 – 6.91 (m, 2H), 6.17 (d, *J* = 2.1 Hz, 1H), 3.81 (s, 3H), 3.70 – 3.65 (m, 1H), 3.54 (t, *J* = 8.5 Hz, 1H), 3.50 (s, 3H), 2.88 – 2.83 (m, 1H). **$^{13}$C NMR (126 MHz, CHLOROFORM-*D*) δ** 196.2, 166.2, 158.6, 156.2, 141.8, 138.3, 132.5, 131.6, 128.6, 128.3, 128.3, 128.2, 127.7, 127.4, 120.2, 114.1, 55.2, 50.9, 38.8, 35.3, 35.2. **HRMS (ESI) m/z:** $[M+Na]^+$ calculated for $C_{27}H_{24}O_4Na$, 435.1567; found 435.1571. **IR (neat, cm$^{-1}$):** 3404, 3061, 3029, 2944, 1705, 1660, 1609, 1492, 1446, 1429, 1374, 1337, 1275, 1226, 1170, 1078, 999, 914, 862, 772, 743, 697, 582, 529, 483.

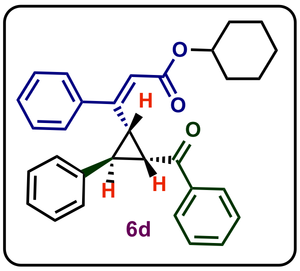
**ethyl (*E*)-3-(-2-(4-bromobenzoyl)-3-phenylcyclopropyl)-3-phenylacrylate (6c):**



Following the general procedure 6, reaction of chalcone **5c** (88 mg, 0.30 mmol, 1 equiv.) and ylide **1a** (114 mg, 0.42 mmol, 1.4 equiv.) using catalytic amount (29 mg, 30 mol%) of cesium carbonate in methanol (0.1 M) at room temperature for 2 hours furnished **6c** in 78% (110 mg, 0.24 mmol,) as orange solid with diastereomeric ratio >20:1.

**$^1$H NMR (500 MHz, CHLOROFORM-*D*) δ** 7.86 (d, *J* = 8.4 Hz, 2H), 7.54 (d, *J* = 8.4 Hz, 2H), 7.43 (d, *J* = 1.9 Hz, 2H), 7.38 – 7.30 (m, 5H), 7.28 – 7.19 (m, 3H), 6.10 (s, 1H), 3.98 (d, *J* = 7.1 Hz, 1H), 3.91 (d, *J* = 7.1 Hz, 1H), 3.61 (dd, *J* = 9.2, 5.3 Hz, 1H), 3.53 (t, *J* = 7.8 Hz, 1H), 2.85 – 2.78 (m, 1H), 1.09 (t, *J* = 7.1 Hz, 3H). **$^{13}$C NMR (126 MHz, CHLOROFORM-*D*) δ** 195.2, 165.8, 155.8, 141.7, 139.5, 137.0, 131.6, 130.0, 128.8, 128.7, 128.3, 127.8, 127.7, 127.0, 126.3, 120.9, 59.9, 38.8, 35.9, 35.7, 14.1. **HRMS (ESI) m/z:** $[M+Na]^+$ calculated for $C_{27}H_{23}O_3BrNa$, 497.0723; found 497.0720. **IR (neat, cm$^{-1}$):** 3394, 3090, 3059, 2983, 1706, 1662, 1611, 1582, 1490, 1434, 1374, 1271, 1222, 1174, 1070, 1022, 860, 809, 766, 697, 621, 582, 533, 481, 582.

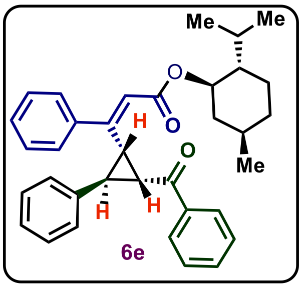
**cyclohexyl (*E*)-3-(-2-benzoyl-3-phenylcyclopropyl)-3-phenylacrylate (6d):**




Following the general procedure 6, reaction of chalcone **5a** (63 mg, 0.30 mmol, 1 equiv.) and ylide **1j** (135 mg, 0.42 mmol, 1.4 equiv.) using catalytic amount (29 mg, 30 mol%) of cesium carbonate in methanol (0.1 M) at room temperature for 2 hours furnished **6d** in 77% (120 mg, 0.23 mmol,) as white solid with diastereomeric ratio >20:1.

**$^1$H NMR (500 MHz, CHLOROFORM-*D*) δ** 7.91 (d, *J* = 7.2 Hz, 2H), 7.37 (d, *J* = 7.1 Hz, 3H), 7.29 (s, 2H), 7.23 (dd, *J* = 14.1, 7.2 Hz, 5H), 7.14 (s, 3H), 6.00 (s, 1H), 4.45 (s, 1H), 3.60 (ddd, *J* = 8.4, 5.3, 2.2 Hz, 1H), 3.47 (s, 1H), 2.74 (s, 1H), 1.68 (d, *J* = 5.7 Hz, 1H), 1.60 – 1.52 (m, 1H), 1.45 – 1.32 (m, 2H), 1.17 (s, 3H), 1.04 – 0.94 (m, 2H), 0.77 (dt, *J* = 15.1, 7.8 Hz, 1H). **$^{13}$C NMR (126 MHz, CHLOROFORM-*D*) δ** 196.1, 165.3, 155.6, 141.9, 139.8, 138.1, 132.6, 128.7, 128.6, 128.5, 128.5, 128.5, 128.3, 128.3, 128.3, 128.2, 128.2, 127.7, 126.8, 126.3, 121.4, 72.2, 38.8, 35.8, 35.7, 31.7, 31.3, 25.4, 23.8, 23.7. **HRMS (ESI) m/z:** $[M+Na]^+$ calculated for $C_{31}H_{30}O_3Na$, 473.2087; found 473.2085. **IR (neat, cm$^{-1}$):** 3441, 3060, 3029, 2933, 2857, 1706, 1668, 1614, 1495, 1449, 1371, 1266, 1219, 1173, 1078, 1018, 872, 750, 697, 534.

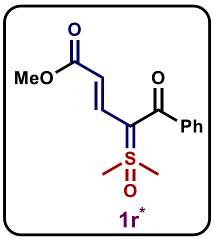
**(1*R*,2*S*,5*R*)-2-isopropyl-5-methylcyclohexyl (*E*)-3-(-2-benzoyl-3-phenylcyclopropyl)-3-phenylacrylate (6e):**




Following the general procedure 6, reaction of chalcone **5a** (63 mg, 0.30 mmol, 1 equiv.) and ylide **1o** (159 mg, 0.42 mmol, 1.4 equiv.) using catalytic amount (29 mg, 30 mol%) of cesium carbonate in methanol (0.1 M) at room temperature for 2 hours furnished **6e** in 74% (114 mg, 0.22 mmol,) as white solid with diastereomeric ratio 1:1.

**HRMS (ESI) m/z:** $[M+Na]^+$ calculated for $C_{35}H_{38}O_3Na$, 529.2713; found 529.2713.

**methyl (E)-4-(dimethyl(oxo)-l6-sulfaneylidene)-5-oxo-5-phenylpent-2-enoate (1r):**

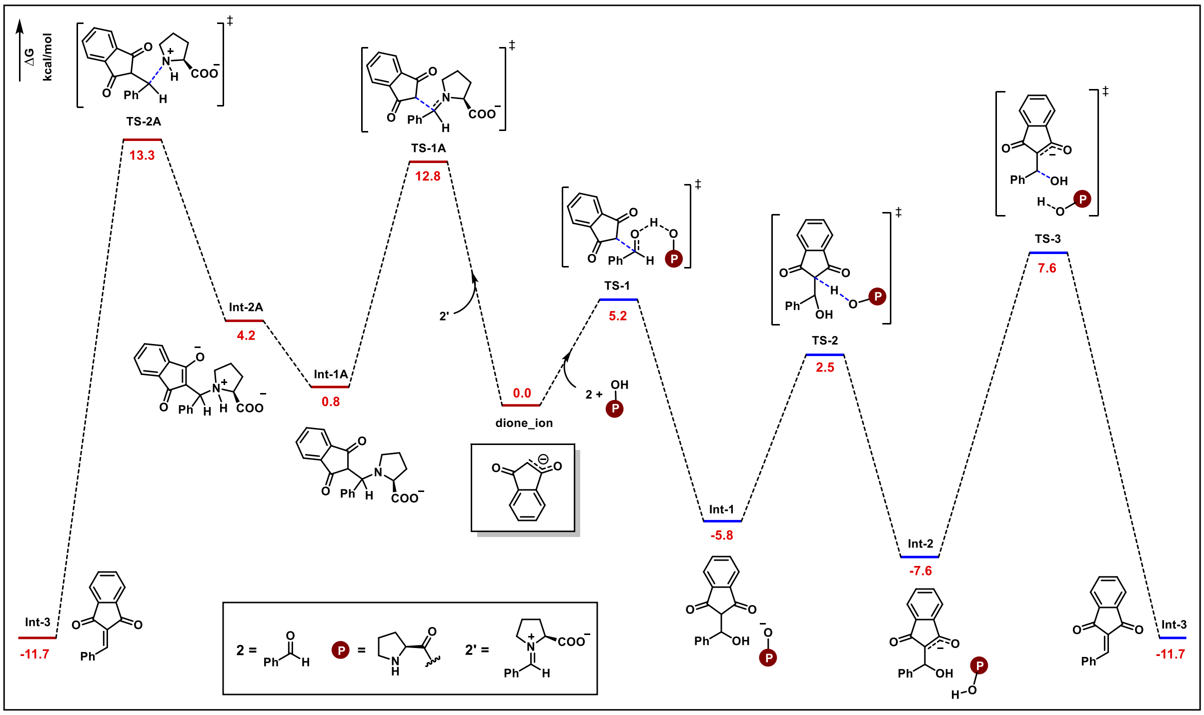



**$^1$H NMR (500 MHz, $CDCl_3$) δ** 7.64 (d, *J* = 15.7 Hz, 1H), 7.57 – 7.52 (m, 2H), 7.44 – 7.39 (m, 2H), 5.60 (d, *J* = 15.7 Hz, 1H), 3.69 – 3.57 (m, 9H). **$^{13}$C NMR (101 MHz, CHLOROFORM-*D*)** δ 187.9, 169.1, 139.7, 138.0, 131.0, 128.6, 128.1, 103.2, 88.5, 51.1, 43.5. **HRMS (ESI) m/z:** $[M+H]^+$ calculated for $C_{14}H_{17}O_4S$, 281.0842; found 281.0841.

## 14. Computational Details:

All the Density Functional Theory (DFT) calculations were performed using Gaussian 16 Revision C.01.[4] The geometry optimization 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 and SMD solvent model was incorporated at the optimization 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 structures were obtained using ChemDraw software. Non-covalent interactions were studied using NCIplot software.[10]

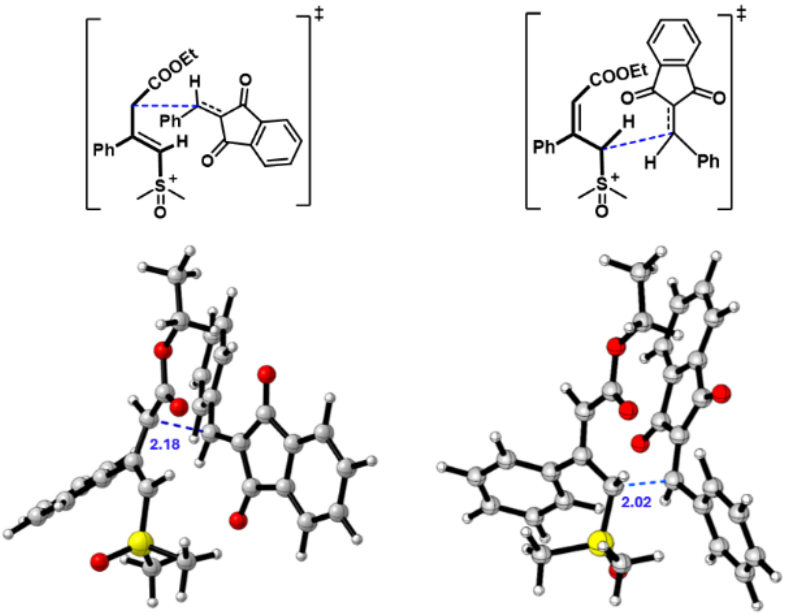
**Role of L-proline in the mechanism:**




L-Proline being a amino acid can catalyze the reaction either acting as Bronsted acid or by generating the iminium ion. In the present case, initially we believed that the mechanism proceeds through the iminium intermediate. But, in our DFT studies, we observed the less energy barrier of 5.2 kcal/mol in the case of carbonyl activation with proton which is significantly lower than iminium formation route with 12.8 kcal/mol energy barrier. In addition to this, a previous report[13] which states that the hydrogen-bonding ability of L-proline makes it a good facilitator for activation of the electrophile instead of the reactant to form an iminium intermediate supports the observed results. Although the iminium mechanism cannot be ruled out completely, in the present case, proline preferably acts as Bronsted acid catalyst.

**$\alpha$- versus $\gamma$-attack transition states:**

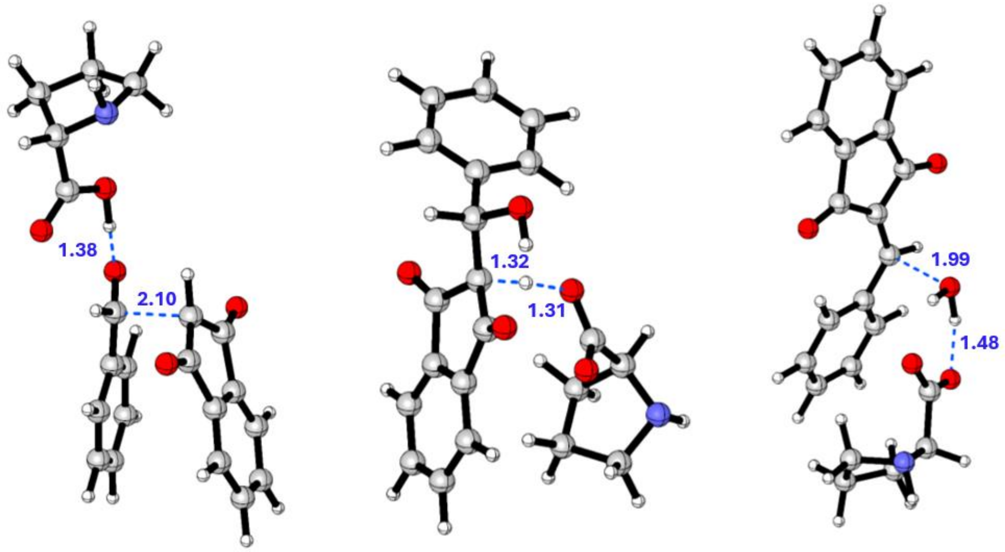
Experimental observations shows that the $\alpha$-attack of vinyl sulfoxonium ylide to arylidene is much favourable compared to the $\gamma$-attack. Computational calculations in gas phase proved that the $\alpha$-attack transition state is more stable than the $\gamma$-attack transition state by 4.8 kcal/mol (shown below). Thus, the int-3 undergoes $\alpha$-attack via TS-4a.



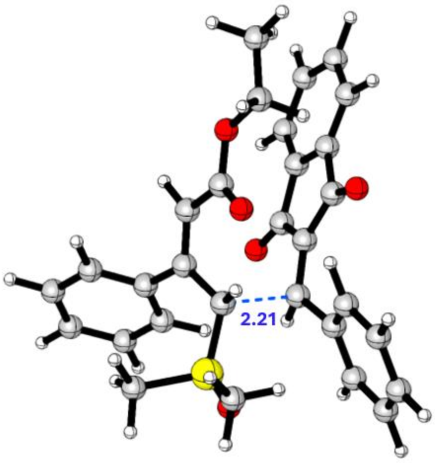

γ-attack TS (unfavored)
0.0 kcal/mol

α-attack TS (favored)
-4.8 kcal/mol

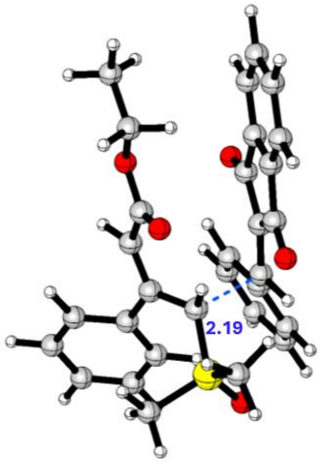
**3D structures of transition states:**



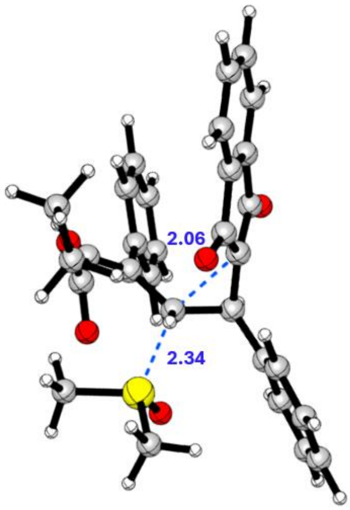

TS-1 TS-2 TS-3



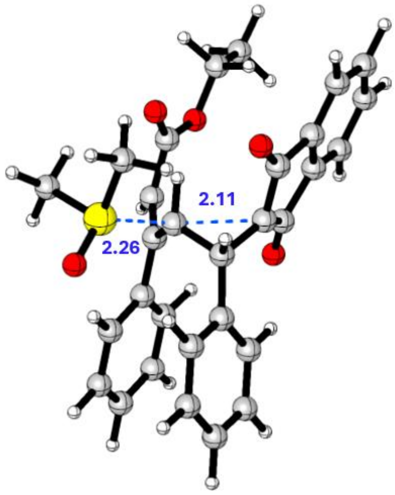

TS-4a



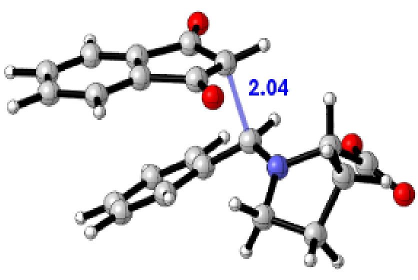

TS-4b



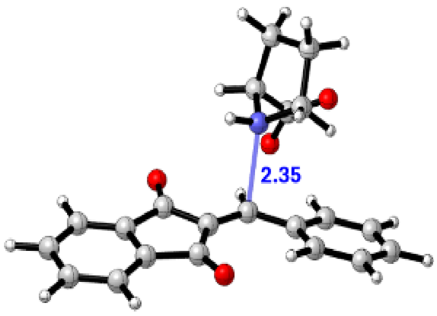

TS-5a




TS-5b




TS-1A




TS-2A

**Single Point Energies (SPE) of stationary points:**

Single point energy (SPE) of all the transition states, intermediates and molecules involved in the reaction mechanism are mentioned here.

| No. | Stationary Points | SPE (Hartree) |
|---|---|---|
| 1. | 2+3+proline | -1243.31469 |
| 2. | TS-1 | -1243.30629 |
| 3. | Int-1 | -1243.331583 |
| 4. | TS-2 | -1243.31249 |
| 5. | Int-2 | -1243.333362 |
| 6. | TS-3 | -1243.304821 |
| 7. | Int-3 | -1934.288428 |
| 8. | TS-4a | -1934.274464 |
| 9. | TS-4b | -1934.27037 |
| 10. | Int-4a | -1934.302724 |
| 11. | Int-4b | -1934.292263 |
| 12. | TS-5a | -1934.277962 |
| 13. | TS-5b | -1934.272423 |
| 14. | 4 (*trans*) | -1934.333454 |
| 15. | 4 (*cis*) | -1934.322334 |
| 16. | Ylide | -1168.109596 |
| 17. | L-proline_$H_2O$ | -477.157883 |
| 18. | TS-1A | -1166.569629 |
| 19. | Int-1A | -1166.587629 |
| 20. | Int-2A | -1243.020122 |
| 21. | TS-2A | -1166.567847 |

**Co-ordinates of stationary points:**

Co-ordinates of some stationary points were taken from the previous literatures[11] for further calculations and non-covalent interaction analysis.

**2+3+proline**

| | | | |
|---|---|---|---|
| C | 4.49641300 | -0.43923800 | 1.23751900 |
| C | 3.93237700 | -0.53169700 | -1.02833600 |
| C | 4.88593700 | -1.71775400 | -0.81337400 |
| C | 5.08720200 | -1.77345900 | 0.71534900 |
| H | 5.17391600 | 0.09442600 | 1.91714300 |
| H | 3.56028200 | -0.62221200 | 1.78345100 |
| H | 4.07270200 | -0.02534600 | -1.99167800 |
| H | 4.49998600 | -2.65519800 | -1.23603600 |
| H | 5.83372400 | -1.48636400 | -1.31975300 |
| H | 4.56467100 | -2.63068600 | 1.16071300 |
| H | 6.15216500 | -1.86796900 | 0.96753400 |
| N | 4.20875500 | 0.40390200 | 0.06816800 |
| H | 5.05279800 | 0.91766200 | -0.18381900 |
| C | 2.45901200 | -0.90346000 | -0.95830000 |
| O | 1.59764000 | -0.27095700 | -1.53656100 |
| O | 2.19755000 | -1.94482400 | -0.19714400 |
| H | 1.20289200 | -2.06201100 | -0.12143300 |
| C | -3.42770100 | -0.59890400 | -1.03973100 |
| C | -4.81669900 | -0.70840800 | -1.00745900 |
| C | -5.40946600 | -1.80878600 | -0.38742000 |
| C | -4.62058900 | -2.80227500 | 0.20415500 |
| C | -3.23510000 | -2.69478000 | 0.17678900 |
| C | -2.63823500 | -1.58935600 | -0.44582900 |
| H | -2.94702900 | 0.26032700 | -1.51482700 |
| H | -5.43746200 | 0.06479100 | -1.46276900 |
| H | -6.49748100 | -1.89563100 | -0.36168400 |
| H | -5.09392800 | -3.65894100 | 0.68681300 |
| H | -2.60076300 | -3.45677100 | 0.63399300 |
| C | -1.17240100 | -1.45168100 | -0.48577900 |
| O | -0.40686000 | -2.27465200 | -0.00793200 |
| H | -0.77537000 | -0.56734800 | -1.02270900 |
| C | -1.23509600 | 2.39763500 | 0.38160800 |
| C | 0.08281600 | 1.95049400 | 0.49537600 |
| C | 1.12603500 | 2.60752300 | -0.13094000 |
| C | 0.81391600 | 3.75050400 | -0.89033600 |
| C | -0.50222900 | 4.19749700 | -1.00557700 |
| C | -1.55424300 | 3.51691100 | -0.36490600 |
| C | -2.12392000 | 1.46056900 | 1.18009600 |

| | | | |
|---|---|---|---|
| C | -1.26819200 | 0.47910800 | 1.75455700 |
| C | 0.08208800 | 0.70839200 | 1.36784800 |
| H | 2.15015500 | 2.23434800 | -0.04703000 |
| H | 1.61149700 | 4.29525900 | -1.39962100 |
| H | -0.71737500 | 5.08635900 | -1.60216000 |
| H | -2.58803500 | 3.85955000 | -0.45111000 |
| H | -1.60314000 | -0.35229200 | 2.37325300 |
| O | -3.35349500 | 1.59448400 | 1.24151300 |
| O | 1.10928300 | 0.06441400 | 1.62296100 |

**TS-1**

| | | | |
|---|---|---|---|
| C | -5.86705300 | -0.43058600 | 1.35639100 |
| C | -4.83780600 | -0.64189700 | -0.75715300 |
| C | -5.90834500 | 0.45895700 | -0.89899800 |
| C | -6.11857400 | 0.87267100 | 0.56007300 |
| H | -6.80459500 | -0.86662200 | 1.72933600 |
| H | -5.23212400 | -0.22972400 | 2.23254800 |
| H | -4.80002200 | -1.30238800 | -1.63399500 |
| H | -5.59964700 | 1.28344700 | -1.55660400 |
| H | -6.82050000 | 0.00481400 | -1.31490200 |
| H | -5.38165600 | 1.63964900 | 0.84201400 |
| H | -7.11763800 | 1.29037600 | 0.74397800 |
| N | -5.20729400 | -1.38430700 | 0.44164800 |
| H | -5.88887600 | -2.08542200 | 0.16076400 |
| C | -3.47113600 | 0.02117500 | -0.65988200 |
| O | -2.93585100 | 0.48256000 | -1.65736700 |
| O | -2.96249700 | 0.09914600 | 0.53734700 |
| H | -2.03892500 | 0.64871200 | 0.53160500 |
| C | 2.14742700 | 1.26353000 | -1.52144700 |
| C | 3.44273200 | 1.77661200 | -1.56407300 |
| C | 3.93390600 | 2.52413500 | -0.49081000 |
| C | 3.12191400 | 2.76760900 | 0.61936600 |
| C | 1.82710600 | 2.25400400 | 0.66446500 |
| C | 1.33705900 | 1.49123400 | -0.40295800 |
| H | 1.76103000 | 0.66781200 | -2.35331000 |
| H | 4.07349600 | 1.59023700 | -2.43545200 |
| H | 4.94967200 | 2.92301900 | -0.52324000 |
| H | 3.50255200 | 3.35806500 | 1.45509900 |
| H | 1.18533400 | 2.42803400 | 1.52991300 |
| C | -0.02031800 | 0.88474000 | -0.31697900 |
| O | -0.82464800 | 1.30831500 | 0.56844200 |
| H | -0.41752100 | 0.49176700 | -1.26992300 |
| C | 2.62624800 | -1.60531200 | -0.31074300 |
| C | 2.64296500 | -1.06189500 | 0.97528100 |
| C | 3.83620400 | -0.78955200 | 1.62683900 |
| C | 5.02834900 | -1.09372400 | 0.95456300 |
| C | 5.01036900 | -1.65097400 | -0.32894700 |
| C | 3.79955100 | -1.91083000 | -0.98417300 |
| C | 1.19735300 | -1.69264600 | -0.77383100 |
| C | 0.38018000 | -1.09682900 | 0.26755200 |
| C | 1.22108700 | -0.80983800 | 1.41101800 |
| H | 3.84253600 | -0.34860200 | 2.62606000 |
| H | 5.98697900 | -0.89478300 | 1.43755900 |
| H | 5.95509600 | -1.87890900 | -0.82625000 |
| H | 3.77544500 | -2.32802600 | -1.99315600 |
| H | -0.68721900 | -1.29973100 | 0.35276100 |
| O | 0.85096100 | -2.11099800 | -1.87316800 |
| O | 0.90107700 | -0.35215800 | 2.50228700 |

**Int-1**

| | | | |
|---|---|---|---|
| C | 4.25532100 | -1.27095100 | 1.13885200 |
| C | 3.65053000 | -0.88048600 | -1.08225900 |
| C | 4.40308500 | -2.21980700 | -1.10996300 |
| C | 4.60877400 | -2.57384300 | 0.37740600 |
| H | 5.01426600 | -0.98602400 | 1.88042600 |
| H | 3.30180800 | -1.39105700 | 1.67175000 |
| H | 3.86110700 | -0.24425500 | -1.95226200 |
| H | 3.85700500 | -2.99555900 | -1.66414700 |
| H | 5.37285100 | -2.06933700 | -1.60746100 |
| H | 3.95090400 | -3.39583800 | 0.69009700 |
| H | 5.64475600 | -2.88503200 | 0.57186300 |
| N | 4.11279800 | -0.20259000 | 0.14086600 |
| H | 5.03996100 | 0.17364300 | -0.05799200 |
| C | 2.12442700 | -1.04072200 | -0.98787100 |
| O | 1.41514000 | -0.13485800 | -1.46628200 |
| O | 1.69215800 | -2.06707800 | -0.38905000 |

| | | | |
|---|---|---|---|
| H | 0.17988400 | -1.96931600 | 0.08870700 |
| C | -3.66537800 | -0.62134700 | -1.21730900 |
| C | -5.03008800 | -0.89221300 | -1.32741100 |
| C | -5.66278300 | -1.69211400 | -0.37545100 |
| C | -4.92460300 | -2.22128900 | 0.68543600 |
| C | -3.56181000 | -1.94770400 | 0.79482400 |
| C | -2.92305500 | -1.14192800 | -0.15403500 |
| H | -3.16856700 | 0.00191400 | -1.96515700 |
| H | -5.59969200 | -0.48112300 | -2.16318900 |
| H | -6.72954600 | -1.90752000 | -0.46207900 |
| H | -5.41348700 | -2.85309900 | 1.42974600 |
| H | -2.97997400 | -2.36926000 | 1.61732900 |
| C | -1.44486700 | -0.84270700 | -0.01599800 |
| O | -0.76797500 | -1.97674600 | 0.43089700 |
| H | -1.05983900 | -0.50813200 | -0.99372700 |
| C | 0.54133200 | 1.96090200 | 0.54578900 |
| C | -0.66448000 | 2.56876100 | 0.19876100 |
| C | -0.69854400 | 3.84571200 | -0.35983500 |
| C | 0.52022800 | 4.48819900 | -0.56930800 |
| C | 1.73575400 | 3.86760400 | -0.23181400 |
| C | 1.76390800 | 2.59374100 | 0.33320500 |
| C | 0.27181600 | 0.62767100 | 1.15158200 |
| C | -1.21531300 | 0.33342500 | 0.99614800 |
| C | -1.79699300 | 1.65774400 | 0.52079400 |
| H | -1.64724500 | 4.31641700 | -0.62394100 |
| H | 0.53668500 | 5.48795100 | -1.00682000 |
| H | 2.67168200 | 4.39675300 | -0.42026900 |
| H | 2.69836800 | 2.08286400 | 0.57534600 |
| H | -1.65325700 | 0.02700800 | 1.95895700 |
| O | 1.08318800 | -0.07617500 | 1.70577500 |
| O | -2.97136400 | 1.92926300 | 0.41584800 |

**TS-2**

| | | | |
|---|---|---|---|
| C | 4.23395000 | 1.82604900 | 0.11475400 |
| C | 2.06321300 | 2.69527700 | -0.13884000 |
| C | 2.41065600 | 2.00923700 | -1.47617600 |
| C | 3.54164000 | 1.07001200 | -1.04713100 |
| H | 5.21580000 | 2.22194400 | -0.18144500 |
| H | 4.40015200 | 1.14697500 | 0.96458600 |
| H | 1.50369300 | 3.63071000 | -0.27739300 |
| H | 1.55567200 | 1.49206600 | -1.93508000 |
| H | 2.77553100 | 2.77166100 | -2.18180500 |
| H | 3.11901800 | 0.12210100 | -0.68077700 |
| H | 4.23319300 | 0.82893100 | -1.86654200 |
| N | 3.34851000 | 2.94066700 | 0.50604500 |
| H | 3.72351500 | 3.79750400 | 0.10434400 |
| C | 1.19100200 | 1.73496600 | 0.66703300 |
| O | -0.02168900 | 1.64197700 | 0.24695100 |
| O | 1.66193100 | 1.06549700 | 1.58796800 |
| H | -1.49715300 | -0.47206200 | 2.94679900 |
| C | -4.26239000 | -0.80943100 | -0.38232200 |
| C | -5.17998400 | -0.16256200 | -1.21133000 |
| C | -5.15924300 | 1.22771400 | -1.32469000 |
| C | -4.21796000 | 1.96680500 | -0.60485000 |
| C | -3.29917600 | 1.31865100 | 0.21968600 |
| C | -3.31279600 | -0.07625200 | 0.33334900 |
| H | -4.28047500 | -1.89848000 | -0.29158600 |
| H | -5.91653000 | -0.74633600 | -1.76701100 |
| H | -5.87784900 | 1.73604200 | -1.97058600 |
| H | -4.19957800 | 3.05542700 | -0.68745700 |
| H | -2.56153600 | 1.89502900 | 0.78157600 |
| C | -2.29979600 | -0.77229200 | 1.21555600 |
| O | -2.24091200 | -0.08559500 | 2.45524300 |
| H | -2.64820600 | -1.80917000 | 1.38275800 |
| C | 1.23509000 | -1.88974400 | 0.47919800 |
| C | 0.78372500 | -1.72109600 | -0.82951000 |
| C | 1.58074900 | -2.05237800 | -1.91830000 |
| C | 2.85572600 | -2.56406500 | -1.65456100 |
| C | 3.31027300 | -2.72832400 | -0.33913000 |
| C | 2.50242200 | -2.38884200 | 0.75148900 |
| C | 0.15080900 | -1.44560800 | 1.41224900 |
| C | -0.90458100 | -0.81123300 | 0.60229700 |
| C | -0.61652700 | -1.17130200 | -0.80116000 |
| H | 1.21864700 | -1.92019500 | -2.93986800 |
| H | 3.51023000 | -2.83928300 | -2.48369300 |
| H | 4.31143400 | -3.12763400 | -0.16652400 |

| | | | |
|---|---|---|---|
| H | 2.84949100 | -2.51241800 | 1.77913900 |
| H | -0.48720100 | 0.44374900 | 0.53147900 |
| O | 0.15589800 | -1.59605100 | 2.62585900 |
| O | -1.30875500 | -1.01766700 | -1.79213200 |

**Int-2**

| | | | |
|---|---|---|---|
| C | -3.25731900 | 2.44793300 | -1.13664000 |
| C | -1.39970400 | 2.79525100 | 0.27643300 |
| C | -2.49124800 | 2.12703100 | 1.13766400 |
| C | -3.35050700 | 1.47045700 | 0.05640000 |
| H | -4.16442200 | 3.06235500 | -1.22784000 |
| H | -3.14287400 | 1.89490800 | -2.08131500 |
| H | -0.85754400 | 3.58499100 | 0.81436500 |
| H | -2.09519100 | 1.41975700 | 1.88027600 |
| H | -3.04584200 | 2.91693200 | 1.66619100 |
| H | -2.91412100 | 0.49804500 | -0.21723900 |
| H | -4.38595000 | 1.29070300 | 0.37665000 |
| N | -2.08873400 | 3.31993300 | -0.89218000 |
| H | -2.41782800 | 4.25336200 | -0.65886000 |
| C | -0.39080700 | 1.73851000 | -0.12420500 |
| O | 0.40477300 | 1.40541900 | 0.88851400 |
| O | -0.32579800 | 1.21576200 | -1.21275500 |
| H | 2.29957300 | -2.28455300 | -1.89881500 |
| C | 3.39227400 | 0.26912400 | 1.25179900 |
| C | 3.68672900 | 1.63167800 | 1.34368200 |
| C | 3.61073500 | 2.44153800 | 0.21076000 |
| C | 3.24589800 | 1.88386100 | -1.01813400 |
| C | 2.95212700 | 0.52453800 | -1.11058300 |
| C | 3.01668400 | -0.29196600 | 0.02641700 |
| H | 3.43571600 | -0.36503400 | 2.14084300 |
| H | 3.97492900 | 2.06132100 | 2.30518100 |
| H | 3.83699200 | 3.50706300 | 0.28266600 |
| H | 3.18504000 | 2.51468300 | -1.90734600 |
| H | 2.64824400 | 0.08775300 | -2.06514400 |
| C | 2.56589500 | -1.74425300 | -0.05577700 |
| O | 3.01814800 | -2.36495900 | -1.24424000 |
| H | 3.01703200 | -2.27775400 | 0.79874800 |
| C | -1.22019400 | -1.94056200 | -0.51667300 |
| C | -1.14941300 | -1.80011300 | 0.87299900 |
| C | -2.28836200 | -1.81870600 | 1.65541700 |
| C | -3.52658500 | -1.99932200 | 1.00819700 |
| C | -3.59477800 | -2.14810000 | -0.37542400 |
| C | -2.42841000 | -2.11410300 | -1.16418000 |
| C | 0.19227600 | -1.91429500 | -1.05803000 |
| C | 1.06605500 | -1.81974600 | 0.05490700 |
| C | 0.31522200 | -1.69834900 | 1.25933200 |
| H | -2.22725700 | -1.71115600 | 2.74079000 |
| H | -4.44504200 | -2.02575100 | 1.59794200 |
| H | -4.56599500 | -2.28872700 | -0.85401000 |
| H | -2.47432900 | -2.23003100 | -2.24921900 |
| H | 1.01672100 | 0.69997800 | 0.59973100 |
| O | 0.47113600 | -1.98749600 | -2.27040100 |
| O | 0.71472800 | -1.53007900 | 2.41832100 |

**TS-3**

| | | | |
|---|---|---|---|
| C | -4.87661800 | 0.40132300 | 1.86720200 |
| C | -4.45533200 | -1.37909700 | 0.46784500 |
| C | -4.88519200 | -0.20826000 | -0.47160100 |
| C | -5.35919200 | 0.89481100 | 0.49540000 |
| H | -5.46728800 | 0.78988000 | 2.70821700 |
| H | -3.82583200 | 0.69264400 | 2.02771200 |
| H | -4.87734400 | -2.33647500 | 0.12962900 |
| H | -4.04097600 | 0.11846900 | -1.09498800 |
| H | -5.68931200 | -0.52168500 | -1.15110400 |
| H | -4.96687800 | 1.88898300 | 0.23653400 |
| H | -6.45807100 | 0.96037600 | 0.49665300 |
| N | -4.94332600 | -1.05902000 | 1.80681000 |
| H | -5.92874200 | -1.32188900 | 1.84343000 |
| C | -2.93032100 | -1.55659100 | 0.42501000 |
| O | -2.46907300 | -1.85863500 | -0.72271100 |
| O | -2.24319400 | -1.40524000 | 1.44746300 |
| H | -0.06824900 | -1.67605100 | 0.64552500 |
| C | -0.94777800 | 0.94758900 | -2.31496700 |
| C | -1.99747600 | 1.86380700 | -2.35481000 |
| C | -2.46010500 | 2.44031400 | -1.17215200 |
| C | -1.87835000 | 2.08788900 | 0.04887900 |

| | | | |
|---|---|---|---|
| C | -0.81436500 | 1.18953300 | 0.08848100 |
| C | -0.32733600 | 0.62474700 | -1.09955000 |
| H | -0.59058900 | 0.48454900 | -3.23762300 |
| H | -2.45930200 | 2.12069100 | -3.30975300 |
| H | -3.28354000 | 3.15697800 | -1.19865600 |
| H | -2.25216600 | 2.52398300 | 0.97747000 |
| H | -0.36448400 | 0.91545300 | 1.04176700 |
| C | 0.82080000 | -0.30584600 | -1.14414100 |
| O | 0.00545800 | -1.91313700 | -0.29451400 |
| H | 0.88337800 | -0.88727300 | -2.06809600 |
| C | 3.98978600 | 0.54927200 | 0.67728200 |
| C | 4.38052700 | -0.50354900 | -0.14999100 |
| C | 5.68989500 | -0.96171900 | -0.17049800 |
| C | 6.61126800 | -0.32806600 | 0.67258200 |
| C | 6.21984300 | 0.72900500 | 1.50212100 |
| C | 4.89538000 | 1.18423900 | 1.51452800 |
| C | 2.51882100 | 0.82125000 | 0.48994300 |
| C | 2.05766200 | -0.12121700 | -0.52623000 |
| C | 3.18447000 | -0.96128500 | -0.93109300 |
| H | 5.98670700 | -1.78605500 | -0.82189000 |
| H | 7.65070400 | -0.66081800 | 0.68497700 |
| H | 6.96040300 | 1.20357100 | 2.14855600 |
| H | 4.58140200 | 2.00819100 | 2.15842700 |
| H | -0.99894100 | -1.93549300 | -0.56026000 |
| O | 1.92072000 | 1.69518300 | 1.09981300 |
| O | 3.18534800 | -1.86489200 | -1.75375600 |

**Int-3**

| | | | |
|---|---|---|---|
| C | 0.72156000 | -1.31604700 | 0.79534100 |
| C | -0.62428400 | -1.37559300 | 1.12420800 |
| H | -1.16690500 | -2.30562300 | 0.95620100 |
| C | -1.37186200 | -0.28577400 | 1.69938900 |
| C | -3.47786600 | 0.38216700 | 2.54607100 |
| C | -4.83766000 | -0.22211500 | 2.79690500 |
| H | -5.49780100 | 0.52482800 | 3.25910200 |
| C | 1.52877700 | -0.17451700 | 0.95685500 |
| H | 1.13017800 | 0.76539200 | 1.32925600 |
| C | 3.69073300 | 1.40535600 | 1.41007700 |
| H | 4.70839900 | 1.61407300 | 1.05696500 |
| C | 4.16215300 | -1.34821800 | 1.25299200 |
| H | 3.98892300 | -2.26255500 | 0.67305700 |
| C | 1.33950700 | -2.56990600 | 0.26152900 |
| C | 1.38037200 | -3.71566900 | 1.06755300 |
| C | 1.91081100 | -2.61056600 | -1.01738900 |
| C | 2.00436000 | -4.87588700 | 0.61211400 |
| H | 0.93742400 | -3.68579100 | 2.06535700 |
| C | 2.52580300 | -3.77683900 | -1.47353600 |
| H | 1.86965900 | -1.72861500 | -1.65625400 |
| C | 2.58161000 | -4.90785100 | -0.65863200 |
| H | 2.04231700 | -5.75821800 | 1.25370400 |
| H | 2.96322700 | -3.80004000 | -2.47335200 |
| H | 3.07067500 | -5.81627000 | -1.01524400 |
| S | 3.15831800 | -0.05148000 | 0.54314800 |
| H | 3.66290100 | 1.20937500 | 2.48892800 |
| H | 3.88931400 | -1.47566200 | 2.30735600 |
| H | 5.20258500 | -1.01627800 | 1.13686600 |
| H | 3.00304500 | 2.21734300 | 1.13930900 |
| O | -0.95973500 | 0.83716300 | 1.97264800 |
| O | 3.54699700 | 0.05911200 | -0.88847200 |
| O | -2.66080200 | -0.61730400 | 1.93259200 |
| H | -3.00313800 | 0.70800600 | 3.48404100 |
| H | -5.29616700 | -0.55923000 | 1.85616200 |
| H | -4.75848000 | -1.08388600 | 3.47517800 |
| H | -3.53278000 | 1.26012500 | 1.88260100 |
| C | -2.68159400 | -0.52533800 | -1.59553800 |
| C | -3.19773800 | 0.62984400 | -1.00398800 |
| C | -4.55034800 | 0.74367000 | -0.70194900 |
| C | -5.37171700 | -0.34787700 | -0.99362100 |
| C | -4.84884300 | -1.51414600 | -1.57162100 |
| C | -3.49199700 | -1.61658100 | -1.88637700 |
| C | -1.22310800 | -0.34109800 | -1.84039900 |
| C | -0.85631200 | 0.99980800 | -1.29628700 |
| C | -2.10599900 | 1.62686800 | -0.77803600 |
| H | -4.95008000 | 1.65393400 | -0.25061100 |
| H | -6.43821500 | -0.29716800 | -0.76699600 |
| H | -5.51745300 | -2.35031600 | -1.78323900 |

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|---|---|---|---|
| H | -3.07732100 | -2.51536200 | -2.34614300 |
| O | -0.48379300 | -1.12608100 | -2.39627800 |
| O | -2.26952200 | 2.72496300 | -0.28828100 |
| C | 0.42451900 | 1.42765300 | -1.38699400 |
| C | 1.09094800 | 2.63316600 | -0.89661200 |
| C | 0.63797600 | 3.37859800 | 0.20708700 |
| C | 2.29376700 | 3.00539400 | -1.52496900 |
| C | 1.36147300 | 4.48429600 | 0.64614100 |
| H | -0.26441400 | 3.07020800 | 0.73224800 |
| C | 3.00306200 | 4.12281900 | -1.09395200 |
| H | 2.66754200 | 2.40612500 | -2.35755800 |
| C | 2.53693800 | 4.86499400 | -0.00730600 |
| H | 1.00913900 | 5.05105200 | 1.50963300 |
| H | 3.92772900 | 4.40868100 | -1.59806000 |
| H | 3.09672600 | 5.73528500 | 0.34040600 |
| H | 1.08446900 | 0.74779400 | -1.94129500 |

**TS-4a**

| | | | |
|---|---|---|---|
| C | 0.73740700 | -1.25561700 | 0.75432100 |
| C | -0.55090800 | -1.33497500 | 1.21345000 |
| H | -1.08803600 | -2.27980300 | 1.12060300 |
| C | -1.29561800 | -0.24659200 | 1.84363000 |
| C | -3.43455300 | 0.40568900 | 2.61894000 |
| C | -4.81025500 | -0.19916000 | 2.74853400 |
| H | -5.49598100 | 0.53209400 | 3.19815900 |
| C | 1.42164200 | 0.00670700 | 0.68082400 |
| H | 1.10747800 | 0.78139500 | 1.38010800 |
| C | 3.62998200 | 1.55477100 | 1.36808300 |
| H | 4.71093800 | 1.65169700 | 1.20404200 |
| C | 4.02024500 | -1.19323200 | 1.38642100 |
| H | 3.94351200 | -2.12260800 | 0.81128200 |
| C | 1.37747900 | -2.49978700 | 0.23782900 |
| C | 1.37171100 | -3.65056200 | 1.03950600 |
| C | 2.02858800 | -2.53853500 | -1.00399800 |
| C | 2.01908100 | -4.81050500 | 0.61840000 |
| H | 0.87721400 | -3.62300800 | 2.01257900 |
| C | 2.67186300 | -3.70199900 | -1.42378700 |
| H | 2.02333100 | -1.66245900 | -1.65147000 |
| C | 2.67522300 | -4.83777600 | -0.61291200 |
| H | 2.01671300 | -5.69452200 | 1.25864200 |
| H | 3.17052800 | -3.72069100 | -2.39446400 |
| H | 3.18604300 | -5.74453900 | -0.94201800 |
| S | 3.14692800 | 0.08666100 | 0.49629500 |
| H | 3.39035900 | 1.42924500 | 2.43168800 |
| H | 3.58294400 | -1.29007200 | 2.38845300 |
| H | 5.06393000 | -0.85311000 | 1.43300800 |
| H | 3.08947900 | 2.40347200 | 0.93251800 |
| O | -0.85918900 | 0.82899000 | 2.21996500 |
| O | 3.64144500 | 0.12617000 | -0.89695600 |
| O | -2.58662800 | -0.57143800 | 2.00160600 |
| H | -3.01314000 | 0.67342500 | 3.59934900 |
| H | -5.20350000 | -0.48724400 | 1.76291000 |
| H | -4.78295000 | -1.09160800 | 3.39000200 |
| H | -3.43708800 | 1.31298800 | 1.99511600 |
| C | -2.71430300 | -0.60031700 | -1.61509200 |
| C | -3.17756600 | 0.54978600 | -0.97664500 |
| C | -4.53133000 | 0.76452700 | -0.76743500 |
| C | -5.42111600 | -0.22364200 | -1.21099500 |
| C | -4.95519000 | -1.38082800 | -1.84392800 |
| C | -3.58521900 | -1.58342300 | -2.05913300 |
| C | -1.22001000 | -0.51753900 | -1.71296500 |
| C | -0.80599900 | 0.73193700 | -1.06929200 |
| C | -2.00843700 | 1.42051600 | -0.59795100 |
| H | -4.88780600 | 1.67118000 | -0.27362300 |
| H | -6.49424700 | -0.09114800 | -1.06078300 |
| H | -5.67169800 | -2.13352400 | -2.17772900 |
| H | -3.21350600 | -2.48019100 | -2.55864600 |
| O | -0.50664300 | -1.34447500 | -2.26188400 |
| O | -2.13851200 | 2.48321400 | -0.00697300 |
| C | 0.55054800 | 1.07481200 | -1.04710100 |
| C | 1.11091000 | 2.42501400 | -0.79856400 |
| C | 0.71031800 | 3.23817600 | 0.27359300 |
| C | 2.12790100 | 2.87997600 | -1.65212000 |
| C | 1.30144800 | 4.48419300 | 0.46984700 |
| H | -0.05209600 | 2.87694600 | 0.96285200 |
| C | 2.71404800 | 4.12999600 | -1.45620400 |

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|---|---|---|---|
| H | 2.46340300 | 2.24254100 | -2.47284100 |
| C | 2.30168000 | 4.93598900 | -0.39490000 |
| H | 0.98572100 | 5.10427100 | 1.31088200 |
| H | 3.50035500 | 4.47175200 | -2.13167800 |
| H | 2.76455000 | 5.91163600 | -0.23522300 |
| H | 1.15148900 | 0.48001200 | -1.74264900 |

**TS-4b**

| | | | |
|---|---|---|---|
| C | -1.02374800 | 1.13640900 | 0.31592600 |
| C | 0.08614700 | 1.78116700 | -0.16811100 |
| H | -0.02369000 | 2.45740000 | -1.01667800 |
| C | 1.43527700 | 1.73138600 | 0.40203000 |
| C | 3.65872500 | 2.47381200 | 0.06479500 |
| C | 4.48278300 | 3.07468800 | -1.04646200 |
| H | 5.51662100 | 3.22006600 | -0.70328500 |
| C | -0.86839700 | 0.02771600 | 1.22336800 |
| H | 0.07269900 | -0.00917400 | 1.77239800 |
| C | -1.16291300 | -1.06991800 | 3.72008500 |
| H | -1.89190300 | -1.52384900 | 4.40311900 |
| C | -3.02984300 | 0.89899600 | 3.00225100 |
| H | -3.69557800 | 1.26283200 | 2.21024300 |
| C | -2.36520400 | 1.54657400 | -0.18923500 |
| C | -2.62100900 | 2.90904500 | -0.41641000 |
| C | -3.40256400 | 0.62577900 | -0.40751900 |
| C | -3.87098000 | 3.33686500 | -0.85777500 |
| H | -1.83718200 | 3.64270800 | -0.22058200 |
| C | -4.65269700 | 1.05593600 | -0.84930300 |
| H | -3.23889800 | -0.43873700 | -0.24409500 |
| C | -4.89199200 | 2.41115600 | -1.07722700 |
| H | -4.05065900 | 4.40097300 | -1.02103600 |
| H | -5.44188400 | 0.32140900 | -1.02075900 |
| H | -5.87262200 | 2.74599800 | -1.42029200 |
| S | -2.09635000 | -0.46708600 | 2.33985800 |
| H | -0.63094700 | -0.23073700 | 4.18615100 |
| H | -2.32911400 | 1.67591800 | 3.33325300 |
| H | -3.61020500 | 0.48811700 | 3.83983800 |
| H | -0.45760700 | -1.81389700 | 3.32583300 |
| O | 1.76140700 | 1.33590800 | 1.50929200 |
| O | -3.03094800 | -1.51472300 | 1.87637800 |
| O | 2.33073800 | 2.27237300 | -0.43662800 |
| H | 3.60516100 | 3.14031700 | 0.93936100 |
| H | 4.49702500 | 2.41065700 | -1.92274500 |
| H | 4.07593000 | 4.04948900 | -1.35167800 |
| H | 4.06817900 | 1.51129900 | 0.40292000 |
| C | 3.34255200 | -0.86637700 | -0.86795800 |
| C | 3.40022300 | -1.18433500 | 0.48824100 |
| C | 4.59407200 | -1.14623000 | 1.19345400 |
| C | 5.74774700 | -0.77343800 | 0.49095200 |
| C | 5.69148800 | -0.45722200 | -0.87154600 |
| C | 4.47966500 | -0.50331200 | -1.57391900 |
| C | 1.91972600 | -0.96794100 | -1.35755200 |
| C | 1.12198000 | -1.38089200 | -0.20283700 |
| C | 2.01503100 | -1.51630400 | 0.94535500 |
| H | 4.62909100 | -1.39432200 | 2.25596100 |
| H | 6.70627700 | -0.72815900 | 1.01105000 |
| H | 6.60708900 | -0.16939000 | -1.39181700 |
| H | 4.42547600 | -0.25731300 | -2.63637300 |
| O | 1.61516800 | -0.75668700 | -2.52349200 |
| O | 1.70029600 | -1.81126100 | 2.09168200 |
| C | -0.23772200 | -1.68015200 | -0.01099700 |
| C | -1.25712700 | -1.80261800 | -1.06935100 |
| C | -1.30111900 | -0.96047300 | -2.19181000 |
| C | -2.25064400 | -2.78520600 | -0.91947000 |
| C | -2.31238200 | -1.10444300 | -3.13962300 |
| H | -0.54950100 | -0.18400700 | -2.31316700 |
| C | -3.25849200 | -2.92830000 | -1.86914600 |
| H | -2.23354400 | -3.43148100 | -0.03948600 |
| C | -3.29267500 | -2.08477700 | -2.98209000 |
| H | -2.34052300 | -0.43770800 | -4.00351600 |
| H | -4.02191000 | -3.69758700 | -1.73987100 |
| H | -4.08497800 | -2.19217900 | -3.72552500 |
| H | -0.41992600 | -2.33568800 | 0.84653200 |

**Int-4a**

| | | | |
|---|---|---|---|
| C | -0.64984600 | 1.49894900 | -0.25748100 |
| C | 0.00322900 | 2.39943700 | 0.49893800 |

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|---|---|---|---|
| H | 0.40375700 | 3.30482600 | 0.03653400 |
| C | 0.28768100 | 2.24575800 | 1.95049400 |
| C | 1.90086900 | 2.59344000 | 3.62680300 |
| C | 3.28681300 | 3.17518700 | 3.73488000 |
| H | 3.65322600 | 3.06396800 | 4.76435300 |
| C | -1.09460400 | 0.18147100 | 0.35291800 |
| H | -0.75808900 | 0.12535600 | 1.39459500 |
| C | -3.39174600 | -0.75675900 | 1.93841700 |
| H | -4.44516400 | -0.50205300 | 2.11820000 |
| C | -3.36923300 | 1.84981500 | 0.98894900 |
| H | -3.22947900 | 2.48829600 | 0.10895700 |
| C | -0.99743000 | 1.85394900 | -1.66772900 |
| C | -1.58446300 | 3.11103800 | -1.89720700 |
| C | -0.73638000 | 1.03005500 | -2.77537200 |
| C | -1.92361700 | 3.52433300 | -3.18377200 |
| H | -1.78506600 | 3.77135400 | -1.05049300 |
| C | -1.07368500 | 1.44922500 | -4.06167400 |
| H | -0.23054400 | 0.07339100 | -2.66316700 |
| C | -1.67364100 | 2.69031400 | -4.27238900 |
| H | -2.38561900 | 4.50187700 | -3.33212300 |
| H | -0.85248200 | 0.79658400 | -4.90802000 |
| H | -1.93871400 | 3.00843000 | -5.28224100 |
| S | -2.91984500 | 0.20342600 | 0.51902200 |
| H | -2.75693200 | -0.45403400 | 2.78264200 |
| H | -2.72512700 | 2.15004300 | 1.82785100 |
| H | -4.42832700 | 1.80595300 | 1.27589700 |
| H | -3.28315100 | -1.81929600 | 1.69384300 |
| O | -0.47245300 | 1.76188100 | 2.76437400 |
| O | -3.59578000 | -0.23233800 | -0.71308700 |
| O | 1.46638600 | 2.75355700 | 2.26600800 |
| H | 1.18317400 | 3.10277700 | 4.28628100 |
| H | 3.97812100 | 2.65166300 | 3.05947600 |
| H | 3.28254700 | 4.24415400 | 3.47945100 |
| H | 1.88477100 | 1.51974800 | 3.86518700 |
| C | 2.96594200 | -1.38592700 | -1.54281200 |
| C | 3.16149100 | -0.80336500 | -0.28804300 |
| C | 4.42823300 | -0.51998200 | 0.18462500 |
| C | 5.52177200 | -0.84052200 | -0.64255300 |
| C | 5.32645200 | -1.42198100 | -1.89376300 |
| C | 4.02978100 | -1.70359900 | -2.36467600 |
| C | 1.47651400 | -1.55155400 | -1.74896200 |
| C | 0.83354200 | -1.04478000 | -0.57982900 |
| C | 1.80599900 | -0.58978600 | 0.35322700 |
| H | 4.57534900 | -0.06420200 | 1.16630500 |
| H | 6.53711000 | -0.63183200 | -0.29992000 |
| H | 6.19093300 | -1.66173400 | -2.51586700 |
| H | 3.86900400 | -2.15831700 | -3.34461300 |
| O | 0.96581600 | -2.02060400 | -2.77314000 |
| O | 1.66333000 | -0.09619000 | 1.48497600 |
| C | -0.65639200 | -1.09815300 | -0.39121000 |
| C | -1.12596000 | -2.34503600 | 0.34284400 |
| C | -0.61945400 | -2.65365700 | 1.61299600 |
| C | -2.09608000 | -3.17530600 | -0.22608400 |
| C | -1.09660800 | -3.76012700 | 2.31138300 |
| H | 0.14732200 | -2.01207100 | 2.05607700 |
| C | -2.57182600 | -4.28758000 | 0.47285700 |
| H | -2.49376400 | -2.93898600 | -1.21597200 |
| C | -2.07905200 | -4.57750900 | 1.74458600 |
| H | -0.70154100 | -3.98800800 | 3.30321300 |
| H | -3.33178300 | -4.92778400 | 0.02082700 |
| H | -2.45435900 | -5.44325900 | 2.29339000 |
| H | -1.13585700 | -1.11617900 | -1.38023800 |

**Int-4b**

| | | | |
|---|---|---|---|
| C | -1.03820500 | 1.18974300 | 0.08699200 |
| C | 0.03352700 | 1.90404200 | -0.31910000 |
| H | -0.08363100 | 2.62898000 | -1.12705800 |
| C | 1.40789700 | 1.86379500 | 0.25124800 |
| C | 3.65702100 | 2.42960700 | -0.20003800 |
| C | 4.47441400 | 2.88121800 | -1.38319200 |
| H | 5.51990400 | 3.02036000 | -1.07473700 |
| C | -0.78726700 | 0.02293100 | 1.01411600 |
| H | 0.05462000 | 0.28932500 | 1.66970000 |
| C | -1.11686800 | -0.83760000 | 3.68455100 |
| H | -1.86374700 | -1.12913400 | 4.43478400 |
| C | -2.69550400 | 1.30742200 | 2.81914600 |

| | | | |
|---|---|---|---|
| H | -3.41246200 | 1.64812900 | 2.06235000 |
| C | -2.39880400 | 1.54358700 | -0.40412800 |
| C | -2.67761100 | 2.88896500 | -0.70581800 |
| C | -3.44188000 | 0.60916600 | -0.51656500 |
| C | -3.94227900 | 3.28080500 | -1.13391300 |
| H | -1.90142600 | 3.64432700 | -0.57508700 |
| C | -4.70937000 | 1.00510200 | -0.94142300 |
| H | -3.28175900 | -0.44103700 | -0.28222700 |
| C | -4.96461900 | 2.33860800 | -1.25678300 |
| H | -4.13337700 | 4.33170400 | -1.35756800 |
| H | -5.50028900 | 0.25804300 | -1.02757300 |
| H | -5.95887600 | 2.64558300 | -1.58610600 |
| S | -2.05304300 | -0.26049400 | 2.29583300 |
| H | -0.47624500 | -0.02113100 | 4.04202200 |
| H | -1.85469700 | 2.00541600 | 2.93588600 |
| H | -3.19552700 | 1.11721100 | 3.77892400 |
| H | -0.51575400 | -1.69323400 | 3.35205400 |
| O | 1.69574300 | 1.63643500 | 1.40810300 |
| O | -3.11377600 | -1.22082600 | 1.95494500 |
| O | 2.30762600 | 2.21990800 | -0.65683800 |
| H | 3.63361500 | 3.18711900 | 0.59747200 |
| H | 4.44488100 | 2.13052600 | -2.18552600 |
| H | 4.09645200 | 3.83500400 | -1.77817100 |
| H | 4.03618300 | 1.49258400 | 0.23199000 |
| C | 3.28953000 | -0.91610900 | -0.78438200 |
| C | 3.39324400 | -1.13057400 | 0.58938300 |
| C | 4.61446700 | -1.10208300 | 1.23715500 |
| C | 5.75820600 | -0.84757000 | 0.45766300 |
| C | 5.65556500 | -0.63906600 | -0.91793700 |
| C | 4.40510900 | -0.67281600 | -1.56266200 |
| C | 1.82386000 | -0.94299900 | -1.18054900 |
| C | 1.09160300 | -1.24835700 | 0.01114300 |
| C | 1.99692000 | -1.33447700 | 1.11445300 |
| H | 4.68687400 | -1.26385900 | 2.31475500 |
| H | 6.73986900 | -0.81283400 | 0.93406100 |
| H | 6.55865600 | -0.44352200 | -1.49971000 |
| H | 4.31431600 | -0.50267900 | -2.63779900 |
| O | 1.47564100 | -0.70082400 | -2.34191500 |
| O | 1.71737000 | -1.49865600 | 2.30981700 |
| C | -0.37398200 | -1.34583800 | 0.33658400 |
| C | -1.29930300 | -1.85079400 | -0.75367200 |
| C | -1.40967800 | -1.22916100 | -2.00461200 |
| C | -2.10168600 | -2.96837200 | -0.48971400 |
| C | -2.30678200 | -1.70832100 | -2.95832500 |
| H | -0.78948800 | -0.36489200 | -2.23382400 |
| C | -3.00245900 | -3.44743200 | -1.44121100 |
| H | -2.03114700 | -3.45998000 | 0.48341300 |
| C | -3.11006500 | -2.81476900 | -2.67960300 |
| H | -2.38299100 | -1.20745000 | -3.92546200 |
| H | -3.62133000 | -4.31708400 | -1.21213400 |
| H | -3.81481600 | -3.18516700 | -3.42661200 |
| H | -0.42994100 | -2.08462500 | 1.15313200 |

## TS-5a

| | | | |
|---|---|---|---|
| C | -0.16566600 | 0.58000400 | 1.22767400 |
| C | -0.44349800 | 1.90147300 | 1.31397800 |
| H | -1.12023500 | 2.25952700 | 2.09267500 |
| C | 0.10253700 | 2.94199500 | 0.41047200 |
| C | -0.26443600 | 5.09409100 | -0.47589400 |
| C | -1.31228300 | 6.17345100 | -0.38617900 |
| H | -1.01946800 | 7.02164000 | -1.01967000 |
| C | 0.68467500 | 0.06696100 | 0.13141600 |
| H | 0.87265100 | 0.78914600 | -0.66534600 |
| C | 4.02125200 | 0.95094000 | -0.17470000 |
| H | 4.95639500 | 1.17615200 | 0.35625300 |
| C | 2.88585600 | 1.76380900 | 2.23017400 |
| H | 2.11844800 | 1.56149700 | 2.98920900 |
| C | -0.74783900 | -0.37048800 | 2.20822800 |
| C | -2.11952100 | -0.33493700 | 2.49110400 |
| C | 0.06572700 | -1.31914100 | 2.84207500 |
| C | -2.67402300 | -1.25315000 | 3.38013300 |
| H | -2.75603900 | 0.39550800 | 1.98624000 |
| C | -0.49241600 | -2.22847200 | 3.73894500 |
| H | 1.13884100 | -1.34556400 | 2.63392300 |
| C | -1.86247000 | -2.20317000 | 4.00207100 |
| H | -3.74640100 | -1.23153000 | 3.58227500 |

| | | | |
|---|---|---|---|
| H | 0.14730000 | -2.96314400 | 4.23093300 |
| H | -2.29895800 | -2.92553500 | 4.69422800 |
| S | 2.81327200 | 0.43485200 | 1.03778300 |
| H | 3.62591900 | 1.83315800 | -0.69536000 |
| H | 2.70034800 | 2.71773100 | 1.72231700 |
| H | 3.88966200 | 1.72655000 | 2.67519500 |
| H | 4.15543600 | 0.10872100 | -0.86679000 |
| O | 1.15261200 | 2.86848200 | -0.19766000 |
| O | 3.31522600 | -0.80850300 | 1.72376200 |
| O | -0.68539600 | 4.00485800 | 0.36456500 |
| H | 0.71917700 | 5.44109000 | -0.12703700 |
| H | -2.28601600 | 5.79982300 | -0.73262200 |
| H | -1.41642500 | 6.53047900 | 0.64800400 |
| H | -0.14837200 | 4.71416400 | -1.50125200 |
| C | -2.99324600 | -1.48725700 | -0.98989500 |
| C | -2.67456900 | -0.45244200 | -1.86967700 |
| C | -3.65187700 | 0.18952700 | -2.61229600 |
| C | -4.97758200 | -0.24049300 | -2.45028300 |
| C | -5.29597100 | -1.27716000 | -1.56867100 |
| C | -4.29818000 | -1.92028000 | -0.82105300 |
| C | -1.72491800 | -1.96097500 | -0.34057500 |
| C | -0.64149000 | -1.15340700 | -0.88462900 |
| C | -1.18894600 | -0.19871200 | -1.82594400 |
| H | -3.39572100 | 0.99970800 | -3.29785200 |
| H | -5.77447700 | 0.24151000 | -3.01955900 |
| H | -6.33668200 | -1.58840400 | -1.46160000 |
| H | -4.53685300 | -2.72992800 | -0.12845900 |
| O | -1.65274100 | -2.87430000 | 0.47111400 |
| O | -0.64936700 | 0.70587500 | -2.46365300 |
| C | 0.75688800 | -1.33277800 | -0.34530100 |
| C | 1.91910900 | -1.64114500 | -1.26099900 |
| C | 2.09173100 | -0.97545400 | -2.48132600 |
| C | 2.88328900 | -2.56785400 | -0.84867700 |
| C | 3.21567500 | -1.22693600 | -3.26817500 |
| H | 1.34340400 | -0.25351100 | -2.81326400 |
| C | 4.00809600 | -2.81723600 | -1.63547700 |
| H | 2.75609100 | -3.08864300 | 0.10246500 |
| C | 4.17926700 | -2.14425300 | -2.84553800 |
| H | 3.33918400 | -0.70163600 | -4.21711800 |
| H | 4.75343400 | -3.54111900 | -1.30061800 |
| H | 5.05988700 | -2.33823600 | -3.46082300 |
| H | 0.69341200 | -2.07714600 | 0.45821900 |

**TS-5b**

| | | | |
|---|---|---|---|
| C | 0.53613100 | 0.13458200 | 1.18759000 |
| C | -0.54530000 | 0.13568300 | 1.99616700 |
| H | -0.53957300 | -0.47269800 | 2.90326700 |
| C | -1.85464600 | 0.76985100 | 1.67960400 |
| C | -4.18440700 | 0.47003600 | 1.86557500 |
| C | -5.13604500 | -0.51735600 | 2.49054100 |
| H | -6.16973700 | -0.22837700 | 2.25556700 |
| C | 0.49487000 | 0.91266200 | -0.08620100 |
| H | -0.29307400 | 1.66582200 | -0.11877300 |
| C | 1.16739500 | 3.83113600 | -0.92747900 |
| H | 1.53983800 | 4.83398300 | -0.67941600 |
| C | 1.15825600 | 3.36040700 | 1.82566500 |
| H | 1.55247200 | 2.73091000 | 2.63499100 |
| C | 1.69899800 | -0.73396700 | 1.52744300 |
| C | 1.46537400 | -2.02366900 | 2.03038500 |
| C | 3.02454700 | -0.30930400 | 1.35431900 |
| C | 2.52780600 | -2.86935000 | 2.34187900 |
| H | 0.44003000 | -2.38084700 | 2.13509900 |
| C | 4.08536400 | -1.15588500 | 1.67035500 |
| H | 3.25495600 | 0.68415900 | 0.97075000 |
| C | 3.84212700 | -2.43977200 | 2.15971300 |
| H | 2.32507700 | -3.87399800 | 2.71710600 |
| H | 5.10972900 | -0.80671900 | 1.52736300 |
| H | 4.67540700 | -3.10436000 | 2.39518000 |
| S | 1.81784200 | 2.71155700 | 0.30114300 |
| H | 0.07005300 | 3.79332200 | -0.91492600 |
| H | 0.06114100 | 3.30184700 | 1.78223900 |
| H | 1.50894600 | 4.39616000 | 1.92831500 |
| H | 1.55872800 | 3.50186100 | -1.89916200 |
| O | -2.03275200 | 1.80027300 | 1.06467700 |
| O | 3.31256300 | 2.83691200 | 0.30602500 |
| O | -2.84483100 | 0.03308900 | 2.15873400 |

| | | | |
|---|---|---|---|
| H | -4.31497400 | 1.48465800 | 2.26915400 |
| H | -4.95989800 | -1.52950900 | 2.09936200 |
| H | -5.01834300 | -0.53475700 | 3.58338300 |
| H | -4.29539300 | 0.52012800 | 0.77147400 |
| C | -2.71874200 | -1.24296000 | -1.06376400 |
| C | -2.97511300 | -0.05051100 | -1.74075700 |
| C | -4.26473600 | 0.34137200 | -2.05770900 |
| C | -5.31438700 | -0.50747200 | -1.66977300 |
| C | -5.05926100 | -1.69631800 | -0.98231900 |
| C | -3.74577900 | -2.08162100 | -0.66613200 |
| C | -1.22806900 | -1.38500900 | -0.85117600 |
| C | -0.61436800 | -0.23687400 | -1.47310400 |
| C | -1.65924000 | 0.63630900 | -1.97043500 |
| H | -4.45620000 | 1.27783400 | -2.58536900 |
| H | -6.34503200 | -0.23323600 | -1.90228400 |
| H | -5.89479400 | -2.33329000 | -0.68548500 |
| H | -3.53847000 | -3.00762500 | -0.12553400 |
| O | -0.73955500 | -2.32250900 | -0.22180500 |
| O | -1.52491800 | 1.76459400 | -2.43871900 |
| C | 0.78470200 | 0.33245000 | -1.43284700 |
| C | 2.03691700 | -0.48372600 | -1.63883200 |
| C | 2.07453100 | -1.87859400 | -1.56491400 |
| C | 3.22452400 | 0.21566900 | -1.89206500 |
| C | 3.28655900 | -2.55755400 | -1.70811400 |
| H | 1.15803900 | -2.43364300 | -1.36681600 |
| C | 4.43374500 | -0.46140300 | -2.03692600 |
| H | 3.20834200 | 1.30707000 | -1.96065100 |
| C | 4.46841400 | -1.85350000 | -1.93883700 |
| H | 3.30416600 | -3.64701900 | -1.63751100 |
| H | 5.35045600 | 0.09940900 | -2.22880800 |
| H | 5.41391000 | -2.38806000 | -2.04875800 |
| H | 0.78366100 | 1.16132000 | -2.15645800 |

**4 (*trans*)**

| | | | |
|---|---|---|---|
| C | -0.98411100 | -0.96601000 | 0.86577900 |
| C | -0.54729600 | -2.21201500 | 0.58587900 |
| H | -1.01355100 | -3.06913400 | 1.07619300 |
| C | 0.46434100 | -2.60829600 | -0.41839800 |
| C | 2.32277800 | -1.96235900 | -1.74536600 |
| C | 3.50537400 | -2.62928800 | -1.07781000 |
| H | 4.31122800 | -2.76958700 | -1.81230500 |
| C | -0.48340700 | 0.24121600 | 0.13820200 |
| H | -0.52788200 | 0.17940700 | -0.95281200 |
| C | -2.35843700 | -1.33438000 | -4.06530300 |
| H | -3.43633900 | -1.50255900 | -4.19138300 |
| C | -2.54563000 | -3.25105000 | -2.13619200 |
| H | -2.44660400 | -3.50043700 | -1.07183400 |
| C | -2.03163800 | -0.77540700 | 1.90120900 |
| C | -3.08849200 | 0.12298900 | 1.68702800 |
| C | -1.98293000 | -1.49780200 | 3.10195700 |
| C | -4.08744800 | 0.27462200 | 2.64620000 |
| H | -3.13383100 | 0.69246600 | 0.75615600 |
| C | -2.97823200 | -1.33553400 | 4.06396500 |
| H | -1.14459900 | -2.17172700 | 3.29021600 |
| C | -4.03472800 | -0.45269000 | 3.83679600 |
| H | -4.91123700 | 0.96688500 | 2.46343500 |
| H | -2.92382800 | -1.89631000 | 4.99879100 |
| H | -4.81406400 | -0.32575000 | 4.59051200 |
| S | -1.94913900 | -1.56667200 | -2.33052700 |
| H | -1.76769200 | -2.03117100 | -4.67501800 |
| H | -1.92852300 | -3.92786100 | -2.74235500 |
| H | -3.59970300 | -3.28286600 | -2.44345400 |
| H | -2.09624500 | -0.29853900 | -4.31691500 |
| O | 0.52213700 | -3.73666200 | -0.86164800 |
| O | -2.94736700 | -0.69472500 | -1.56516200 |
| O | 1.30265300 | -1.64211000 | -0.78426700 |
| H | 1.88416300 | -2.59494200 | -2.52929700 |
| H | 3.88841800 | -2.00443600 | -0.25653500 |
| H | 3.22682100 | -3.61349000 | -0.67611900 |
| H | 2.59997600 | -0.99625100 | -2.18683200 |
| C | 3.01919600 | 0.35161200 | 1.36420500 |
| C | 3.17144400 | 0.82937600 | 0.05876800 |
| C | 4.42045400 | 0.88975400 | -0.54995000 |
| C | 5.52149900 | 0.45730100 | 0.19217100 |
| C | 5.36912300 | -0.02366100 | 1.50126900 |
| C | 4.11195600 | -0.08420000 | 2.10639100 |

| | | | |
|---|---|---|---|
| C | 1.57713600 | 0.37507600 | 1.74347500 |
| C | 0.83193300 | 0.88922600 | 0.55722200 |
| C | 1.83625700 | 1.16932200 | -0.51171000 |
| H | 4.52860100 | 1.25899100 | -1.57145900 |
| H | 6.51836800 | 0.48925700 | -0.25077300 |
| H | 6.25015100 | -0.35690100 | 2.05237000 |
| H | 3.98464300 | -0.46025400 | 3.12297300 |
| O | 1.09652300 | 0.02379700 | 2.79772400 |
| O | 1.60712800 | 1.54265100 | -1.64007100 |
| C | -0.50345500 | 1.60468300 | 0.69951300 |
| C | -0.82734800 | 2.78787400 | -0.15677600 |
| C | -0.31202600 | 4.04771400 | 0.17124800 |
| C | -1.65789200 | 2.65642700 | -1.27508200 |
| C | -0.62097600 | 5.16038800 | -0.60876700 |
| H | 0.33835500 | 4.15210000 | 1.04331000 |
| C | -1.96799600 | 3.77247100 | -2.05427600 |
| H | -2.06577900 | 1.67458400 | -1.53272200 |
| C | -1.45035800 | 5.02476400 | -1.72443800 |
| H | -0.21240800 | 6.13809500 | -0.34622600 |
| H | -2.61875100 | 3.66085500 | -2.92366300 |
| H | -1.69258600 | 5.89636700 | -2.33539700 |
| H | -0.79400800 | 1.68361600 | 1.75371800 |

**4 (*cis*)**

| | | | |
|---|---|---|---|
| C | 0.13363000 | 1.39522200 | -0.90834600 |
| C | -0.97808800 | 2.03221100 | -1.33124700 |
| H | -0.94644800 | 3.10104100 | -1.54669700 |
| C | -2.29920100 | 1.40019300 | -1.52272700 |
| C | -4.59496100 | 1.84354000 | -1.82943700 |
| C | -5.49499300 | 3.04523300 | -1.96658700 |
| H | -6.53326700 | 2.71392000 | -2.10368700 |
| C | 0.15769600 | -0.08404200 | -0.65214100 |
| H | 0.17162100 | -0.68090700 | -1.57358800 |
| C | 1.95331300 | -2.95860200 | -2.73636500 |
| H | 2.16020900 | -4.02077800 | -2.92518400 |
| C | 4.63064900 | -2.88425100 | -2.20857400 |
| H | 5.42462400 | -2.64135900 | -1.49098000 |
| C | 1.40443200 | 2.14852100 | -0.74163400 |
| C | 1.40070700 | 3.49856400 | -0.35911500 |
| C | 2.63603700 | 1.50167500 | -0.91992600 |
| C | 2.59799500 | 4.17947000 | -0.15145700 |
| H | 0.45373800 | 4.01080500 | -0.17889900 |
| C | 3.83282800 | 2.18396500 | -0.71527900 |
| H | 2.66022900 | 0.44688300 | -1.20018900 |
| C | 3.81814000 | 3.52386300 | -0.32434800 |
| H | 2.57715400 | 5.22414700 | 0.16390800 |
| H | 4.78187700 | 1.66242900 | -0.85361900 |
| H | 4.75576300 | 4.05467300 | -0.14940000 |
| S | 3.07743100 | -2.38149900 | -1.45866600 |
| H | 2.08719700 | -2.35495800 | -3.64412100 |
| H | 4.78037700 | -2.32543400 | -3.14212100 |
| H | 4.59010500 | -3.96680200 | -2.38914300 |
| H | 0.93890700 | -2.83277100 | -2.33475100 |
| O | -2.53365200 | 0.20987300 | -1.57278900 |
| O | 2.86624500 | -3.34854200 | -0.28993700 |
| O | -3.25320000 | 2.32079200 | -1.64900400 |
| H | -4.62256700 | 1.20293100 | -2.72309100 |
| H | -5.44582600 | 3.67298800 | -1.06574100 |
| H | -5.20495100 | 3.65112100 | -2.83657500 |
| H | -4.86472400 | 1.22383800 | -0.96087800 |
| C | -2.89830000 | -0.91001100 | 1.40710500 |
| C | -2.68614000 | -2.09783900 | 0.70600500 |
| C | -3.63526400 | -3.11447600 | 0.69490000 |
| C | -4.81146100 | -2.90427500 | 1.41711300 |
| C | -5.02634200 | -1.70920600 | 2.11972100 |
| C | -4.07109900 | -0.69054300 | 2.12139400 |
| C | -1.74057700 | 0.01406600 | 1.22253300 |
| C | -0.72842100 | -0.72526200 | 0.39688200 |
| C | -1.36842900 | -2.03180000 | 0.02310800 |
| H | -3.46163700 | -4.03811700 | 0.14023200 |
| H | -5.57984600 | -3.67902300 | 1.43568600 |
| H | -5.95809300 | -1.57618200 | 2.67212600 |
| H | -4.23205800 | 0.24407300 | 2.66153400 |
| O | -1.69576200 | 1.15435000 | 1.62609600 |
| O | -0.88417300 | -2.86692500 | -0.70622400 |
| C | 0.79769600 | -0.74659100 | 0.52606800 |

| | | | |
|---|---|---|---|
| C | 1.64271200 | -0.08967500 | 1.56825200 |
| C | 1.35689200 | 1.13800600 | 2.18238400 |
| C | 2.85781400 | -0.72490900 | 1.86554200 |
| C | 2.27746900 | 1.72223700 | 3.05103700 |
| H | 0.42216700 | 1.65272100 | 1.96519800 |
| C | 3.77573800 | -0.13917200 | 2.73734000 |
| H | 3.08784000 | -1.67986100 | 1.38486400 |
| C | 3.49148100 | 1.09093700 | 3.32890100 |
| H | 2.04374500 | 2.68433400 | 3.51149700 |
| H | 4.71889600 | -0.64643200 | 2.94964900 |
| H | 4.21020800 | 1.55583900 | 4.00637300 |
| H | 1.15847600 | -1.75379500 | 0.29452300 |

**Bq_TS**

| | | | |
|---|---|---|---|
| C | -0.41853300 | -0.70303100 | -0.39322600 |
| C | 0.93838100 | -0.99379000 | 0.03910300 |
| H | 1.05308900 | -2.00271900 | 0.44069600 |
| C | 2.04503700 | -0.71974700 | -0.93000700 |
| C | 4.28267100 | -1.28588900 | -1.38208000 |
| C | 5.34741800 | -2.10226700 | -0.68913600 |
| H | 6.32894900 | -1.90567700 | -1.14086800 |
| C | -0.66812300 | 0.50447600 | -0.97276200 |
| H | 0.14381800 | 1.14587000 | -1.32084700 |
| C | -3.06334200 | 1.26504700 | 0.43641100 |
| H | -4.04200800 | 1.71165700 | 0.21698200 |
| C | -1.82494400 | 2.94444100 | -1.40955100 |
| H | -1.15049900 | 2.97416300 | -2.27371300 |
| C | -1.50183700 | -1.59819100 | 0.06822100 |
| C | -1.48939100 | -2.09369900 | 1.38192000 |
| C | -2.56393000 | -1.94001600 | -0.78305500 |
| C | -2.54142000 | -2.87860900 | 1.84643700 |
| H | -0.66256100 | -1.84208200 | 2.04818100 |
| C | -3.60738100 | -2.73654600 | -0.31547100 |
| H | -2.56934400 | -1.58146500 | -1.81250200 |
| C | -3.60444400 | -3.19846500 | 1.00038000 |
| H | -2.53050700 | -3.24340100 | 2.87432400 |
| H | -4.42508100 | -3.00011900 | -0.98748700 |
| H | -4.42522800 | -3.81758900 | 1.36512200 |
| S | -2.23397200 | 1.23569600 | -1.14148000 |
| H | -2.44793700 | 1.89098000 | 1.11223100 |
| H | -1.37432400 | 3.33798100 | -0.48005900 |
| H | -2.77823800 | 3.43236600 | -1.64655500 |
| H | -3.17835100 | 0.23054300 | 0.77853400 |
| O | 2.08881200 | 0.18209700 | -1.73258700 |
| O | -3.11959900 | 0.73845900 | -2.20224300 |
| O | 3.03643800 | -1.58725100 | -0.74963700 |
| H | 4.20210800 | -1.51817800 | -2.45504900 |
| H | 5.38167800 | -1.82741000 | 0.37330500 |
| H | 5.13229300 | -3.17626600 | -0.77207800 |
| H | 4.46848600 | -0.20717700 | -1.28342700 |
| C | 2.55948200 | 0.78510900 | 1.21674200 |
| C | 1.24528500 | 0.11370300 | 1.56128700 |
| C | 0.15492900 | 0.98982800 | 1.87735100 |
| C | 0.10151900 | 2.31626800 | 1.41882300 |
| C | 1.34535900 | 2.86404600 | 0.77883000 |
| C | 2.48197700 | 2.16356100 | 0.67683200 |
| H | 1.43460800 | -0.70946800 | 2.25795100 |
| H | -0.72028100 | 0.60185100 | 2.40476600 |
| H | 1.27493800 | 3.89881800 | 0.43171700 |
| H | 3.40241700 | 2.57015700 | 0.25386800 |
| O | 3.62040800 | 0.21442900 | 1.34735100 |
| O | -0.88690300 | 3.08834700 | 1.50165200 |

**TS-1A**

| | | | |
|---|---|---|---|
| C | 1.91639500 | -0.57808400 | -1.71337600 |
| C | 3.09474100 | -0.45671400 | 0.40509000 |
| C | 3.66696800 | -1.58332300 | -0.44666100 |
| C | 3.34269100 | -1.10536300 | -1.86015500 |
| H | 1.19230900 | -1.39564600 | -1.84306500 |
| H | 1.67678700 | 0.22050700 | -2.42969100 |
| H | 2.80864000 | -0.80110000 | 1.41334800 |
| H | 4.73606900 | -1.72894100 | -0.25935200 |
| H | 3.12866300 | -2.51900100 | -0.23161200 |
| H | 4.02527300 | -0.28725900 | -2.13872400 |
| H | 3.41240500 | -1.89083700 | -2.62352300 |

| | | | |
|---|---|---|---|
| N | 1.89018100 | -0.06417700 | -0.33615300 |
| C | 4.06145800 | 0.75067700 | 0.61055500 |
| O | 3.52644100 | 1.84491900 | 0.88943500 |
| O | 5.28476500 | 0.52203400 | 0.52072100 |
| C | -0.69779100 | 2.45223700 | 0.04348300 |
| C | -1.79407000 | 3.08624700 | -0.54000800 |
| C | -2.44419500 | 2.49972100 | -1.62542400 |
| C | -1.98964000 | 1.27771600 | -2.12453600 |
| C | -0.89183900 | 0.64506400 | -1.54494600 |
| C | -0.22720800 | 1.22766500 | -0.45360500 |
| H | -0.19994700 | 2.90657500 | 0.90257000 |
| H | -2.14236300 | 4.04042700 | -0.14078600 |
| H | -3.30627900 | 2.99118200 | -2.08025300 |
| H | -2.49906500 | 0.80549300 | -2.96668800 |
| H | -0.58246100 | -0.32602700 | -1.92898000 |
| C | 0.88672800 | 0.57534000 | 0.28768400 |
| H | 1.22330400 | 1.15270800 | 1.15064300 |
| C | -2.37211600 | -0.49378800 | 1.13282800 |
| C | -1.92697900 | -1.57291800 | 0.36478700 |
| C | -2.75723700 | -2.19370900 | -0.55710000 |
| C | -4.05861000 | -1.69454300 | -0.69775800 |
| C | -4.49955600 | -0.60509300 | 0.06231500 |
| C | -3.65571800 | 0.01255000 | 0.99527500 |
| C | -1.23387200 | -0.00755100 | 1.98630600 |
| C | -0.04771800 | -0.73741600 | 1.55452300 |
| C | -0.47144500 | -1.80653800 | 0.66410000 |
| H | -2.40076100 | -3.03150700 | -1.16000100 |
| H | -4.73991400 | -2.15559500 | -1.41531700 |
| H | -5.51670500 | -0.23377700 | -0.07617500 |
| H | -3.98880600 | 0.86749700 | 1.58754900 |
| H | 0.80135000 | -0.87169900 | 2.22659300 |
| O | -1.31331100 | 0.88829900 | 2.81491300 |
| O | 0.21889300 | -2.68610300 | 0.16321500 |

## Int-1A

| | | | |
|---|---|---|---|
| C | 1.88427800 | -0.30003300 | -1.92579500 |
| C | 2.63504500 | -1.49357200 | -0.01110400 |
| C | 3.37978800 | -2.01920200 | -1.25999600 |
| C | 3.24286200 | -0.88769000 | -2.28471300 |
| H | 1.07375700 | -0.94308400 | -2.33162500 |
| H | 1.72008700 | 0.71789700 | -2.31440800 |
| H | 1.93057300 | -2.27520300 | 0.34567700 |
| H | 4.42018800 | -2.28188300 | -1.03029800 |
| H | 2.88539300 | -2.92435500 | -1.64149900 |
| H | 4.02385000 | -0.12738200 | -2.12977600 |
| H | 3.29999400 | -1.23620800 | -3.32481100 |
| N | 1.92891100 | -0.30575500 | -0.47524000 |
| C | 3.56474300 | -1.22355900 | 1.19695600 |
| O | 3.49561400 | -0.11454200 | 1.77140300 |
| O | 4.30246300 | -2.18084600 | 1.52686500 |
| C | 1.60616500 | 2.44130400 | 0.04836500 |
| C | 1.44067700 | 3.82467800 | 0.11069700 |
| C | 0.19224200 | 4.37285100 | 0.40665100 |
| C | -0.88715800 | 3.52296500 | 0.64555700 |
| C | -0.71957300 | 2.13911400 | 0.57890600 |
| C | 0.52633600 | 1.57821000 | 0.27282900 |
| H | 2.58217600 | 2.00518300 | -0.16526600 |
| H | 2.29573200 | 4.47887100 | -0.07176900 |
| H | 0.06141100 | 5.45554600 | 0.45380200 |
| H | -1.86896600 | 3.93535700 | 0.88577200 |
| H | -1.58591300 | 1.50570000 | 0.78459900 |
| C | 0.75682900 | 0.06924800 | 0.27121700 |
| H | 0.97711100 | -0.20290200 | 1.31738700 |
| C | -2.81829500 | -1.06359500 | 0.62317200 |
| C | -2.85629400 | -0.56900800 | -0.68226100 |
| C | -4.06196400 | -0.39731800 | -1.35641600 |
| C | -5.23257300 | -0.74708100 | -0.68231500 |
| C | -5.19389000 | -1.24417400 | 0.63001100 |
| C | -3.98321800 | -1.40563000 | 1.30434600 |
| C | -1.40630700 | -1.11427100 | 1.09315500 |
| C | -0.50429400 | -0.76373800 | -0.08458400 |
| C | -1.47306800 | -0.25900100 | -1.14699800 |

| | | | |
|---|---|---|---|
| H | -4.08329000 | -0.00374300 | -2.37411400 |
| H | -6.19733300 | -0.63011200 | -1.17892000 |
| H | -6.12910700 | -1.50418800 | 1.12884200 |
| H | -3.94318100 | -1.78552500 | 2.32663400 |
| H | -0.14340600 | -1.74561600 | -0.45235300 |
| O | -1.03214300 | -1.38439100 | 2.20953800 |
| O | -1.18786400 | 0.29714600 | -2.18121500 |

**Int-2A**

| | | | |
|---|---|---|---|
| C | 1.95571900 | -1.02623700 | -1.36449300 |
| C | 2.02670500 | -1.84863100 | 0.87709500 |
| C | 2.57690200 | -2.97244900 | 0.00191600 |
| C | 2.65312600 | -2.38930100 | -1.42838200 |
| H | 1.26028800 | -0.82450000 | -2.18753900 |
| H | 2.67783400 | -0.20965200 | -1.27787700 |
| H | 1.37265000 | -2.18962400 | 1.68846300 |
| H | 3.55339700 | -3.30568000 | 0.37367000 |
| H | 1.88843300 | -3.82763400 | 0.02806900 |
| H | 3.68999500 | -2.25617300 | -1.75987000 |
| H | 2.14913400 | -3.05271300 | -2.14246600 |
| N | 1.16755400 | -1.08027700 | -0.09321600 |
| C | 3.11730100 | -0.91387500 | 1.45807000 |
| O | 2.89600100 | -0.45636700 | 2.59920900 |
| O | 4.10164900 | -0.67876900 | 0.72832200 |
| C | 2.23151800 | 2.08465800 | 0.61449000 |
| C | 2.85266200 | 3.23005800 | 0.11090200 |
| C | 2.47053800 | 3.74837200 | -1.12478100 |
| C | 1.45720400 | 3.12145300 | -1.85452500 |
| C | 0.83192500 | 1.98370900 | -1.34981300 |
| C | 1.21938900 | 1.44937100 | -0.11306300 |
| H | 2.53307200 | 1.67809300 | 1.58235600 |
| H | 3.63756500 | 3.71856000 | 0.69145400 |
| H | 2.95634500 | 4.64310500 | -1.51885300 |
| H | 1.14883400 | 3.52499300 | -2.82087000 |
| H | 0.03865800 | 1.49808800 | -1.92191400 |
| C | 0.54325000 | 0.20869500 | 0.44968700 |
| H | 0.75151300 | 0.18551600 | 1.52837000 |
| C | -3.23161400 | 0.30047800 | 0.89209000 |
| C | -3.16307100 | -0.05250400 | -0.45769900 |
| C | -4.30575600 | -0.25554800 | -1.20776900 |
| C | -5.54704700 | -0.09125900 | -0.56447800 |
| C | -5.61485500 | 0.26157800 | 0.78217000 |
| C | -4.44298600 | 0.46311700 | 1.53567200 |
| C | -1.81527400 | 0.43344100 | 1.40647500 |
| C | -0.94286800 | 0.16398100 | 0.29848700 |
| C | -1.70545600 | -0.14724000 | -0.85165200 |
| H | -4.24587800 | -0.53205600 | -2.26264100 |
| H | -6.47038500 | -0.24174900 | -1.12721300 |
| H | -6.59001900 | 0.38263600 | 1.25769400 |
| H | -4.48806800 | 0.73792900 | 2.59172800 |
| H | -1.27303000 | -3.28360800 | -0.57978600 |
| O | -1.52542600 | 0.71319600 | 2.57023200 |
| O | -1.33437600 | -0.48060700 | -1.99714400 |
| O | -0.54029300 | -3.03572100 | -1.16262100 |
| H | 0.38263500 | -1.72966100 | -0.31034600 |
| H | -0.93016200 | -2.35900600 | -1.74629100 |

**TS-2A**

| | | | |
|---|---|---|---|
| C | -2.14905200 | -0.55082300 | 1.81561000 |
| C | -1.82916300 | -2.27897500 | 0.25362600 |
| C | -2.61790800 | -2.91929700 | 1.40479000 |
| C | -3.01514200 | -1.73537200 | 2.31145000 |
| H | -1.61499200 | -0.03094900 | 2.62249100 |
| H | -2.77910300 | 0.19156400 | 1.30048700 |
| H | -1.05206400 | -2.93108300 | -0.16588800 |
| H | -3.48433800 | -3.49057000 | 1.04437100 |
| H | -1.95759700 | -3.61217200 | 1.94711300 |
| H | -4.08216300 | -1.49583400 | 2.21467200 |
| H | -2.81771900 | -1.96040900 | 3.36853200 |
| N | -1.18893100 | -1.09702300 | 0.85527100 |
| C | -2.72291100 | -1.78950500 | -0.90998300 |
| O | -2.21261700 | -1.80969100 | -2.05645500 |
| O | -3.86245300 | -1.36135800 | -0.62158300 |

| | | | |
|---|---|---|---|
| C | -2.32188700 | 1.42122200 | -1.34928800 |
| C | -3.32612800 | 2.37872800 | -1.22785000 |
| C | -3.22849600 | 3.37032200 | -0.25111400 |
| C | -2.12457800 | 3.39806700 | 0.60485300 |
| C | -1.11393700 | 2.44851300 | 0.48122400 |
| C | -1.19584100 | 1.45239400 | -0.50666800 |
| H | -2.40463200 | 0.62597300 | -2.09308300 |
| H | -4.19193900 | 2.34427500 | -1.89145600 |
| H | -4.01720500 | 4.11851200 | -0.15025300 |
| H | -2.05316300 | 4.16524700 | 1.37803700 |
| H | -0.25867500 | 2.47155200 | 1.15366100 |
| C | -0.20346000 | 0.38826200 | -0.68024400 |
| H | -0.52459100 | -0.40203800 | -1.36314800 |
| C | 3.43211200 | 0.61922000 | 0.20989600 |
| C | 3.32650000 | -0.63266200 | -0.39628100 |
| C | 4.43332000 | -1.45431100 | -0.56191400 |
| C | 5.66575600 | -0.97953200 | -0.09997600 |
| C | 5.77268500 | 0.27809600 | 0.50721900 |
| C | 4.65080000 | 1.09819300 | 0.67100100 |
| C | 2.07987500 | 1.27468800 | 0.26959000 |
| C | 1.14249100 | 0.34566700 | -0.37970700 |
| C | 1.89779400 | -0.85511300 | -0.77943000 |
| H | 4.34007600 | -2.43298100 | -1.03634700 |
| H | 6.55936400 | -1.59599700 | -0.21259200 |
| H | 6.74791300 | 0.62036900 | 0.85812600 |
| H | 4.72472800 | 2.07873300 | 1.14521600 |
| O | 1.89502300 | 2.37350700 | 0.76567800 |
| O | 1.45493400 | -1.86189600 | -1.30669200 |
| H | -0.32745000 | -1.37619600 | 1.32475200 |

**L-proline_$H_2O$**

| | | | |
|---|---|---|---|
| C | -2.09998800 | -1.04916200 | 0.08374700 |
| C | -0.69295600 | 0.66875000 | -0.69553100 |
| C | -1.31962100 | 1.18726800 | 0.61353700 |
| C | -1.76979100 | -0.11808300 | 1.27838100 |
| H | -3.18144900 | -1.22034600 | -0.01606100 |
| H | -1.62822800 | -2.03275900 | 0.22565700 |
| H | -0.61999400 | 1.45318300 | -1.46181500 |
| H | -0.61994300 | 1.77666000 | 1.22258400 |
| H | -2.18706200 | 1.82130500 | 0.37087200 |
| H | -0.94535500 | -0.54060800 | 1.87157000 |
| H | -2.62644900 | 0.02023600 | 1.95247400 |
| N | -1.58618000 | -0.40068700 | -1.13768800 |
| H | -2.37177000 | 0.04732300 | -1.60556300 |
| C | 0.73400300 | 0.18285700 | -0.39273900 |
| O | 1.59211800 | 1.10014300 | -0.26298800 |
| O | 0.94447500 | -1.03822200 | -0.24117100 |
| O | 3.71005800 | -0.41470100 | 0.44586400 |
| H | 3.04459900 | 0.27326800 | 0.20594700 |
| H | 3.15582400 | -1.20099000 | 0.34013800 |

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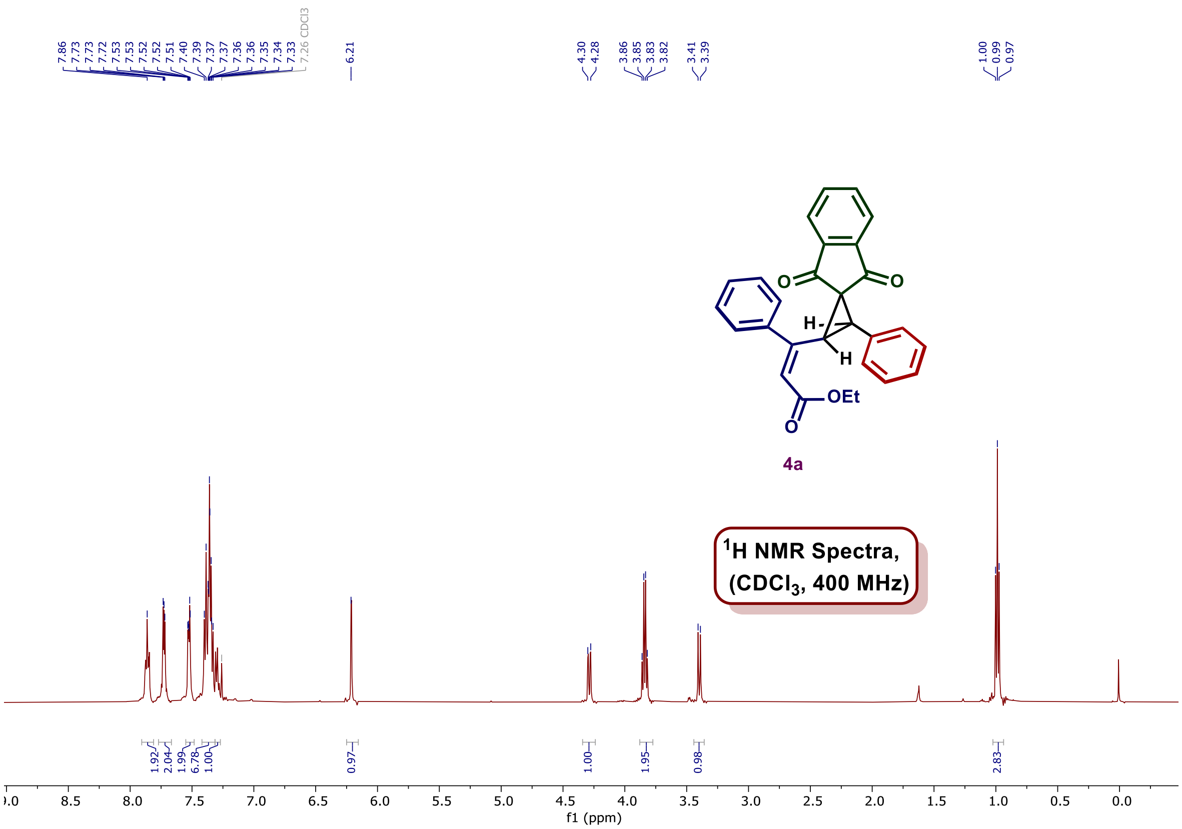
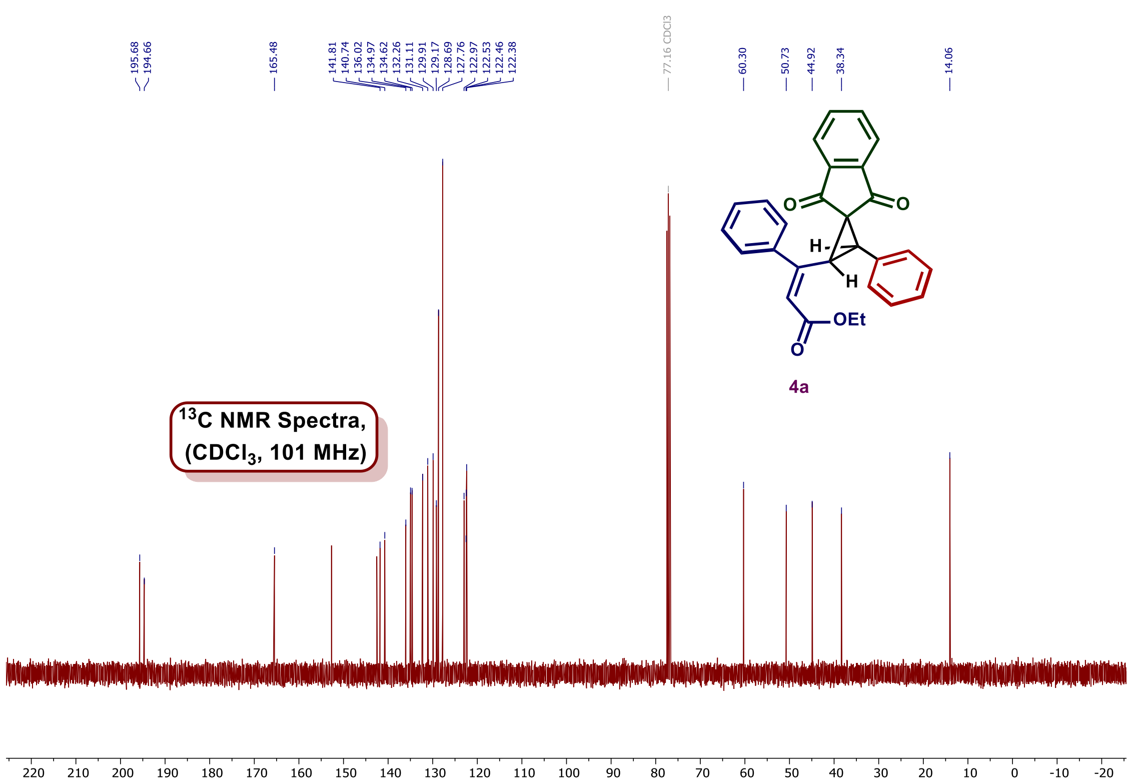
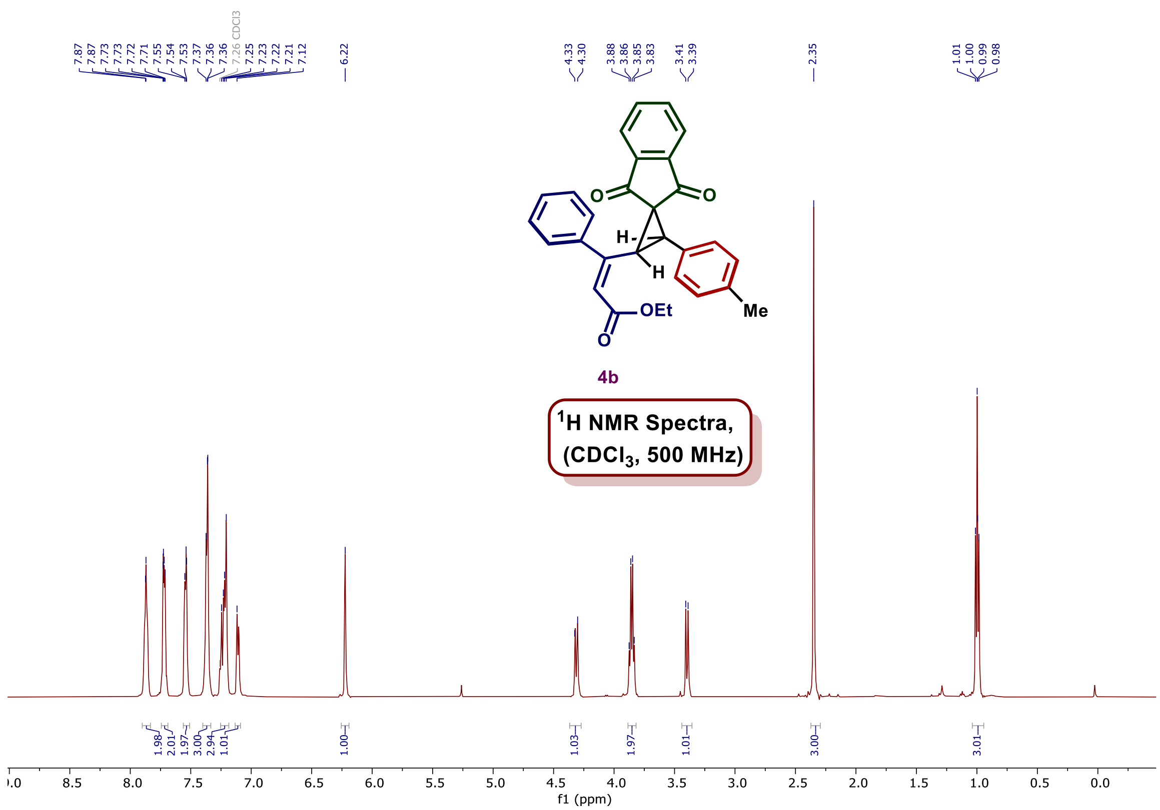
## 16. Spectral data

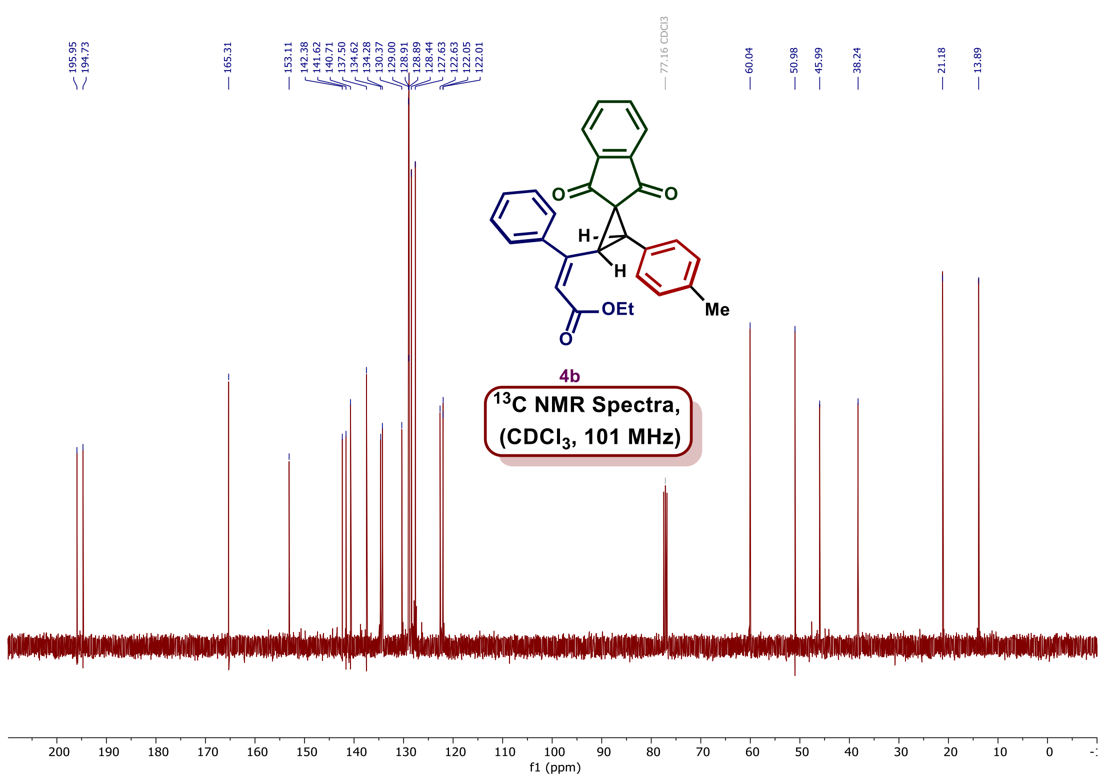
**ethyl (*E*)-3-(1',3'-dioxo-2-phenyl-1',3'-dihydrospiro[cyclopropane-1,2'-inden]-3-yl)-3-phenylacrylate (4a):**


7.86 7.73 7.73 7.72 7.53 7.53 7.52 7.52 7.51 7.40 7.39 7.37 7.37 7.36 7.36 7.35 7.34 7.33
7.26 CDCl3
6.21
4.30 4.28
3.86 3.85 3.83 3.82
3.41 3.39
1.00 0.99 0.97
O
O
H
H
OEt
O
4a
1H NMR Spectra,
(CDCl3, 400 MHz)
1.92 2.04 1.99 6.78 1.00
0.97
1.00
1.95
0.98
2.83
f1 (ppm)

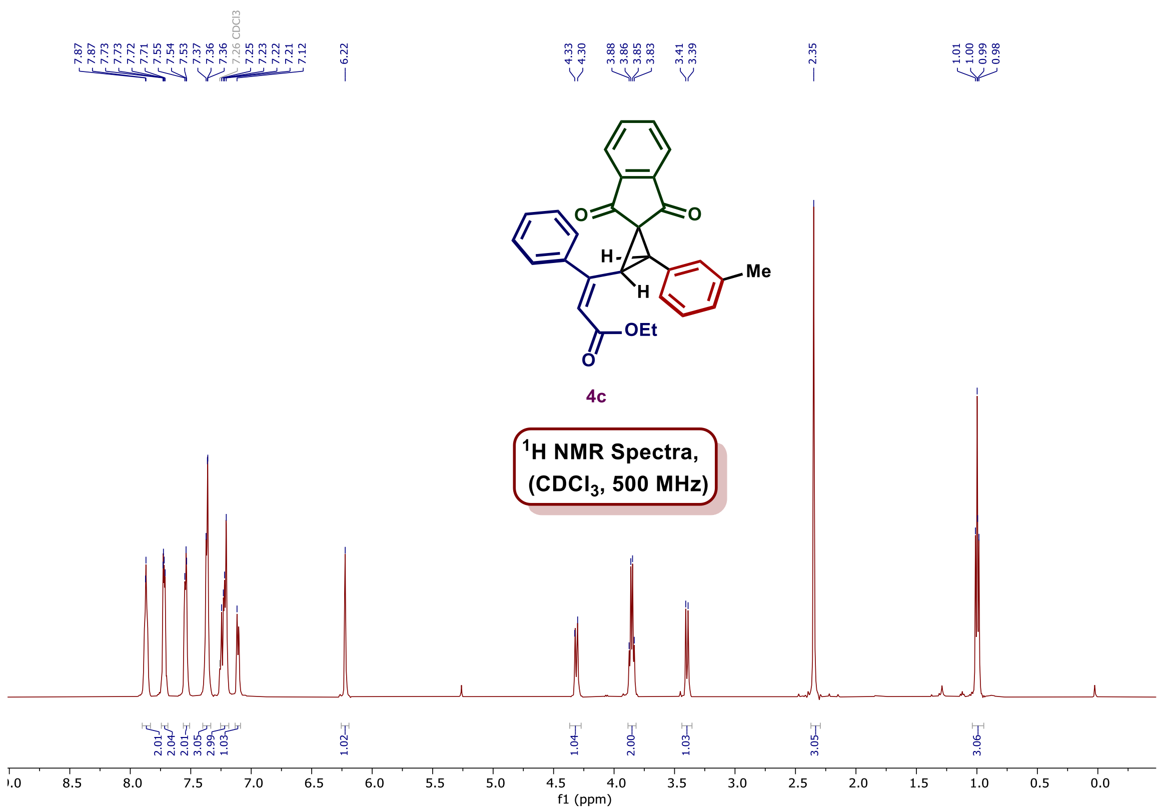

195.68 194.66
165.48
141.81 140.74 136.02 134.97 134.62 132.26 131.11 129.91 129.17 128.69 127.76 122.97 122.53 122.46 122.38
77.16 CDCl3
60.30
50.73
44.92
38.34
14.06
O
O
H
H
OEt
O
4a
13C NMR Spectra,
(CDCl3, 101 MHz)
f1 (ppm)

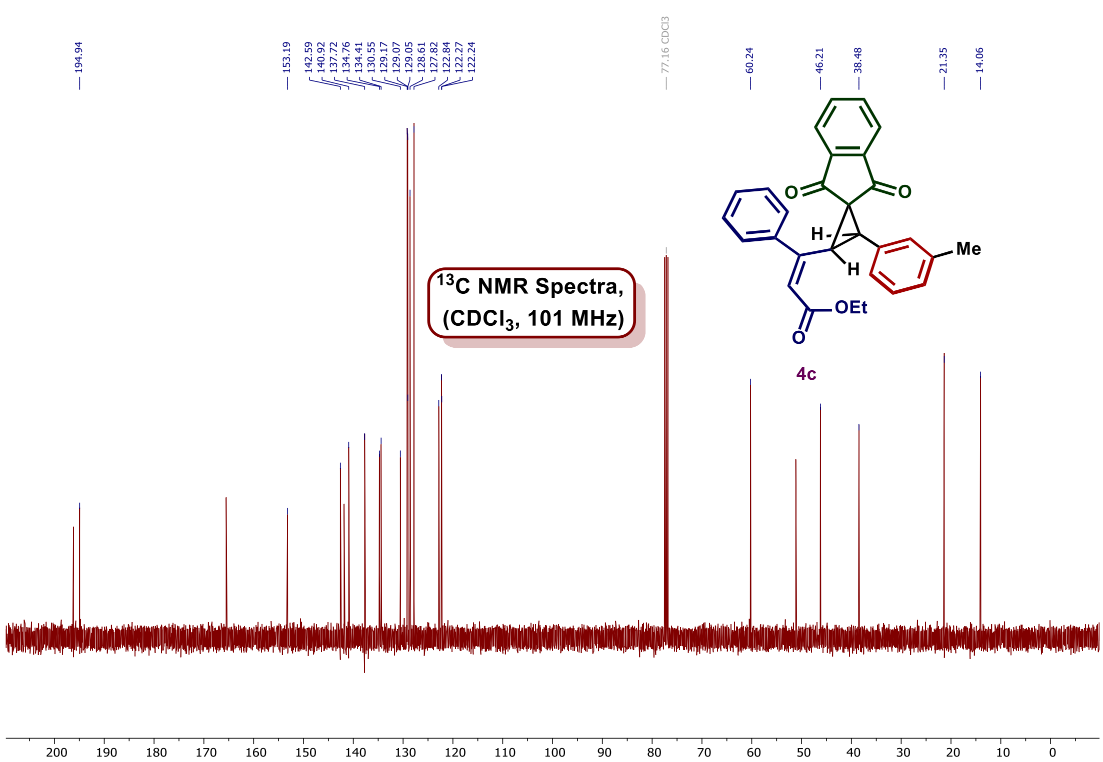
**ethyl (*E*)-3-(1',3'-dioxo-2-(p-tolyl)-1',3'-dihydrospiro[cyclopropane-1,2'-inden]-3-yl)-3-phenylacrylate (4b):**



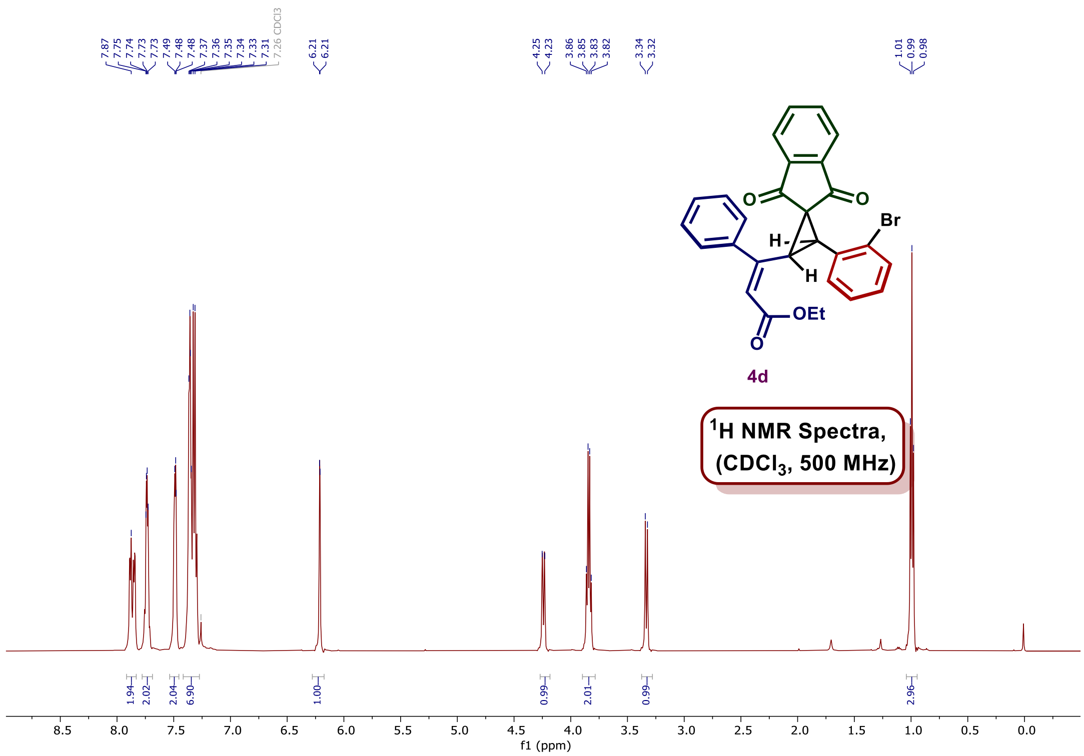



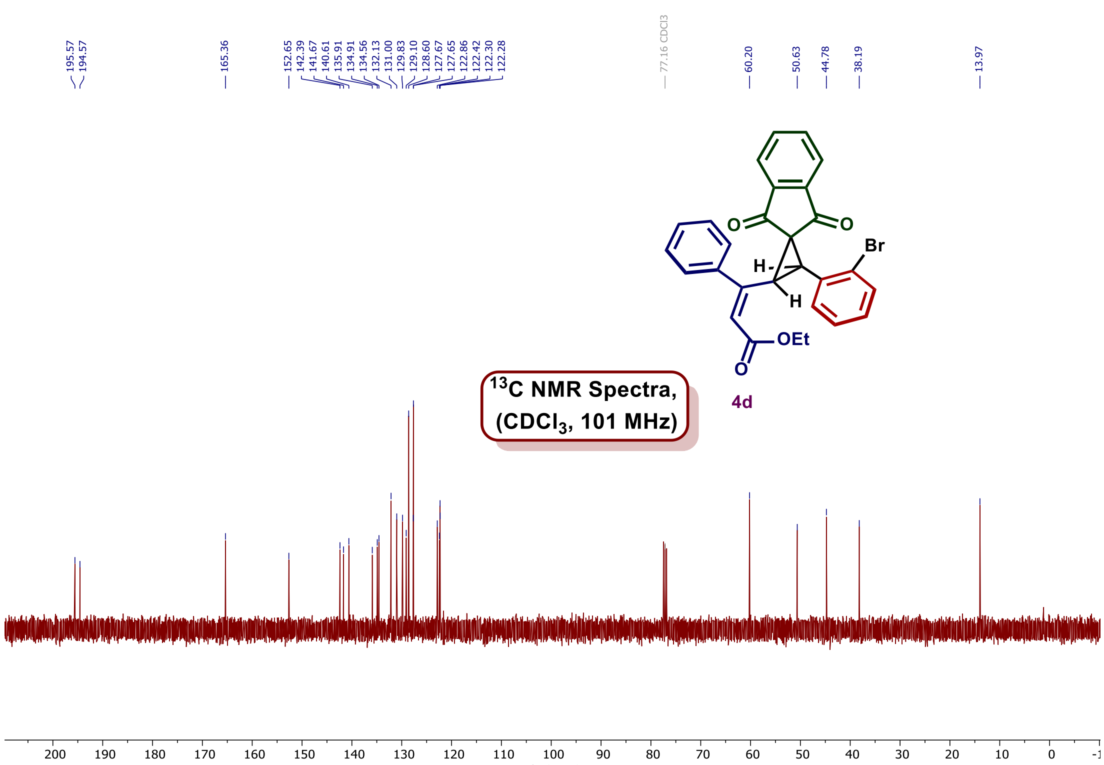
**ethyl (*E*)-3-(1',3'-dioxo-2-(m-tolyl)-1',3'-dihydrospiro[cyclopropane-1,2'-inden]-3-yl)-3-phenylacrylate (4c):**



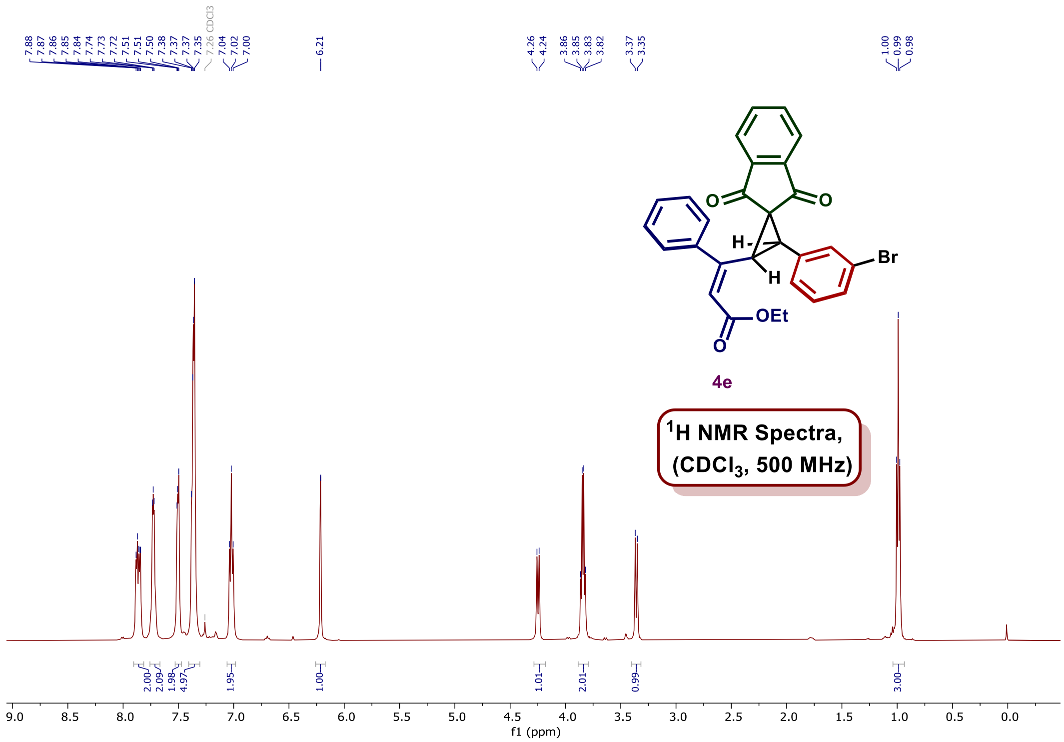


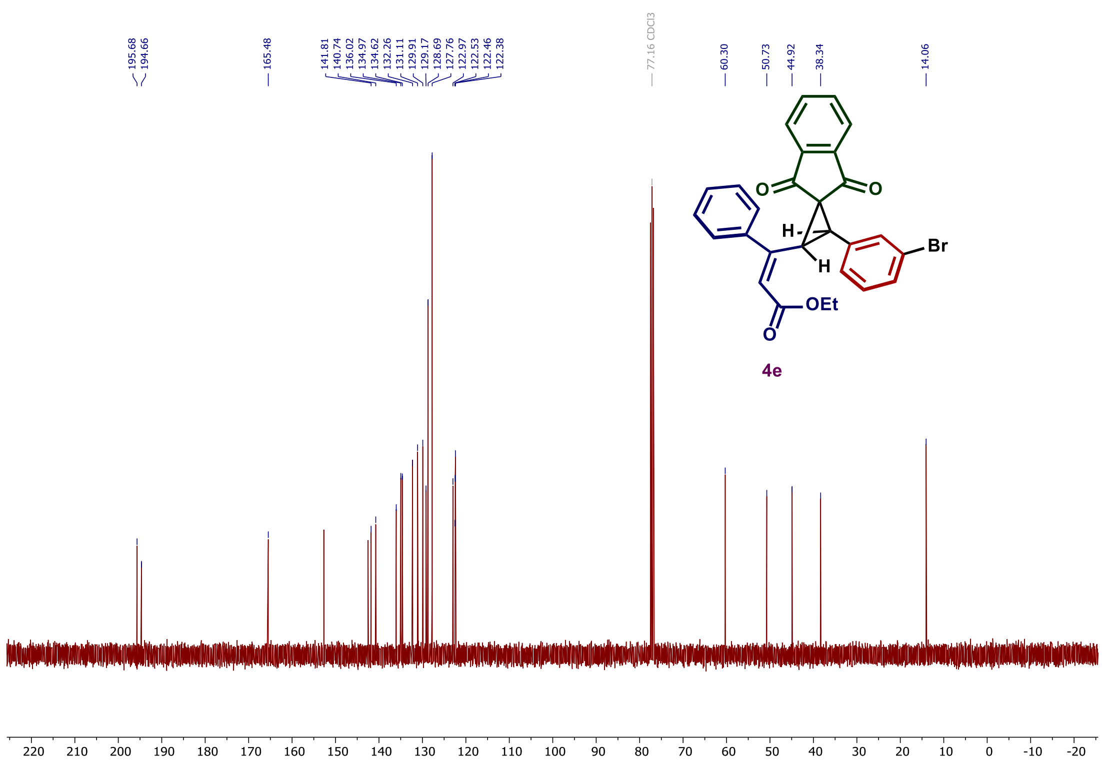
**ethyl (*E*)-3-(2-(2-bromophenyl)-1',3'-dioxo-1',3'-dihydrospiro[cyclopropane-1,2'-inden]-3-yl)-3-phenylacrylate (4d):**



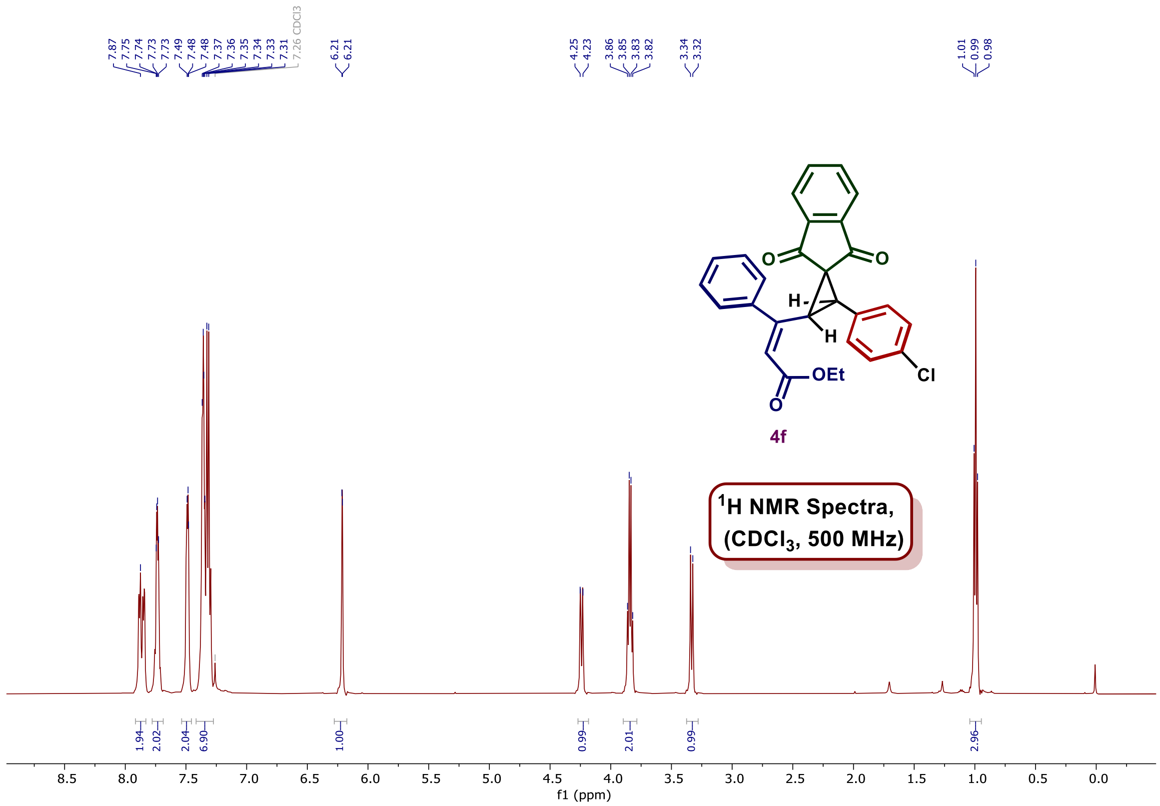



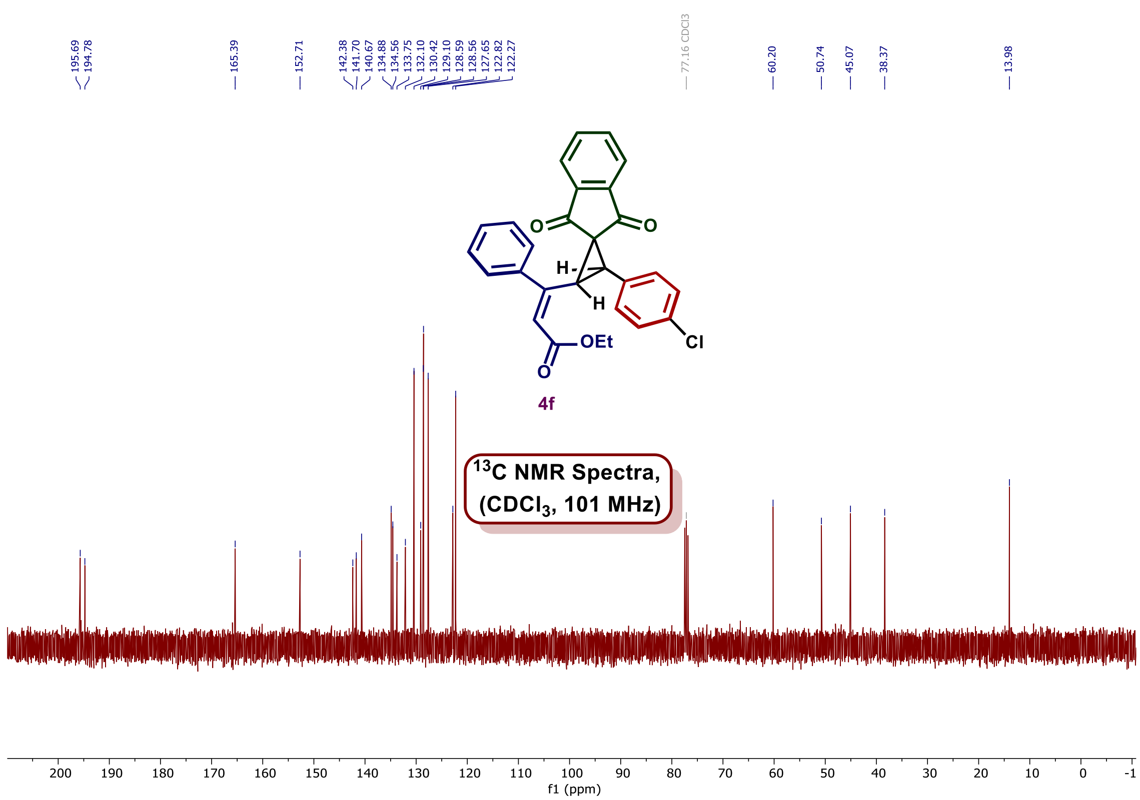
**ethyl (*E*)-3-(2-(3-bromophenyl)-1',3'-dioxo-1',3'-dihydrospiro[cyclopropane-1,2'-inden]-3-yl)-3-phenylacrylate (4e):**



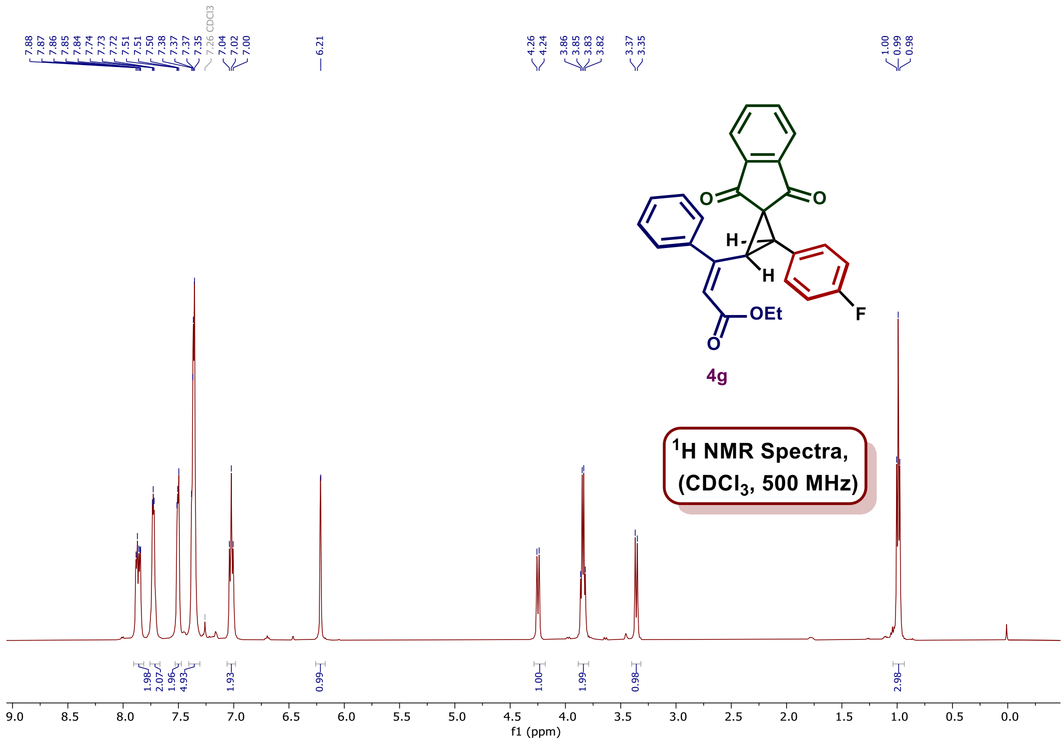



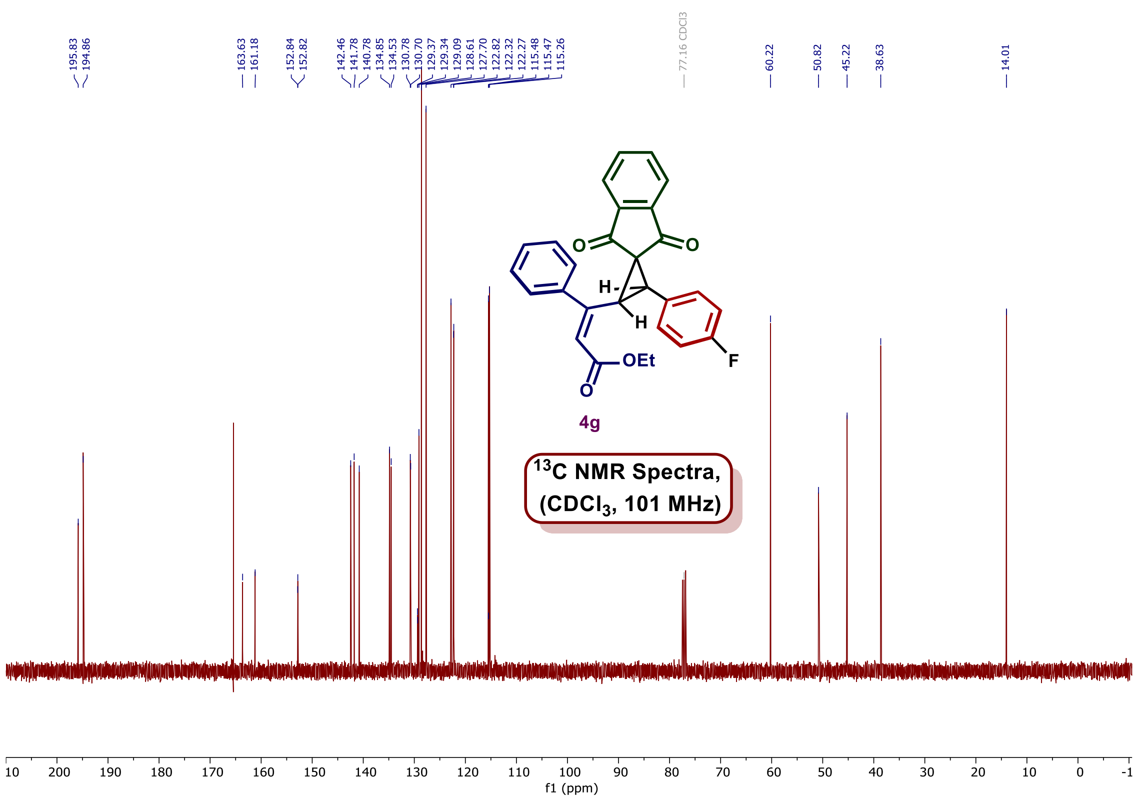
**ethyl (*E*)-3-(2-(4-chlorophenyl)-1',3'-dioxo-1',3'-dihydrospiro[cyclopropane-1,2'-inden]-3-yl)-3-phenylacrylate (4f):**

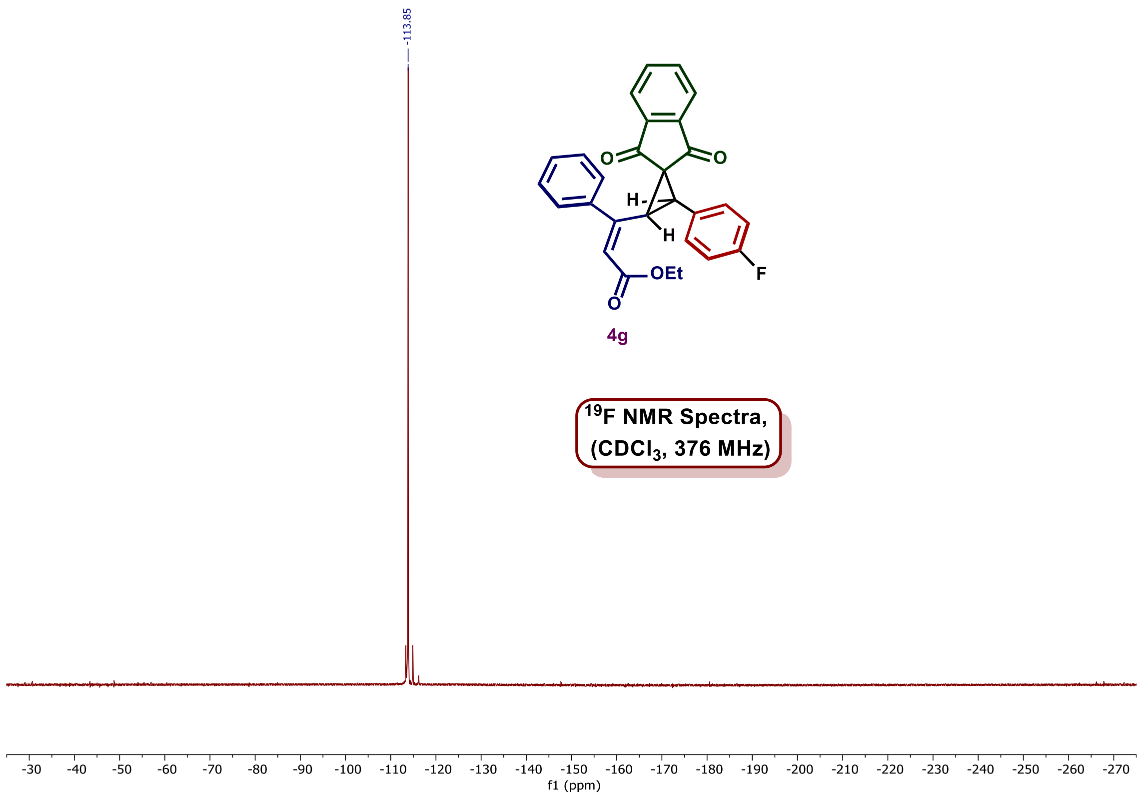


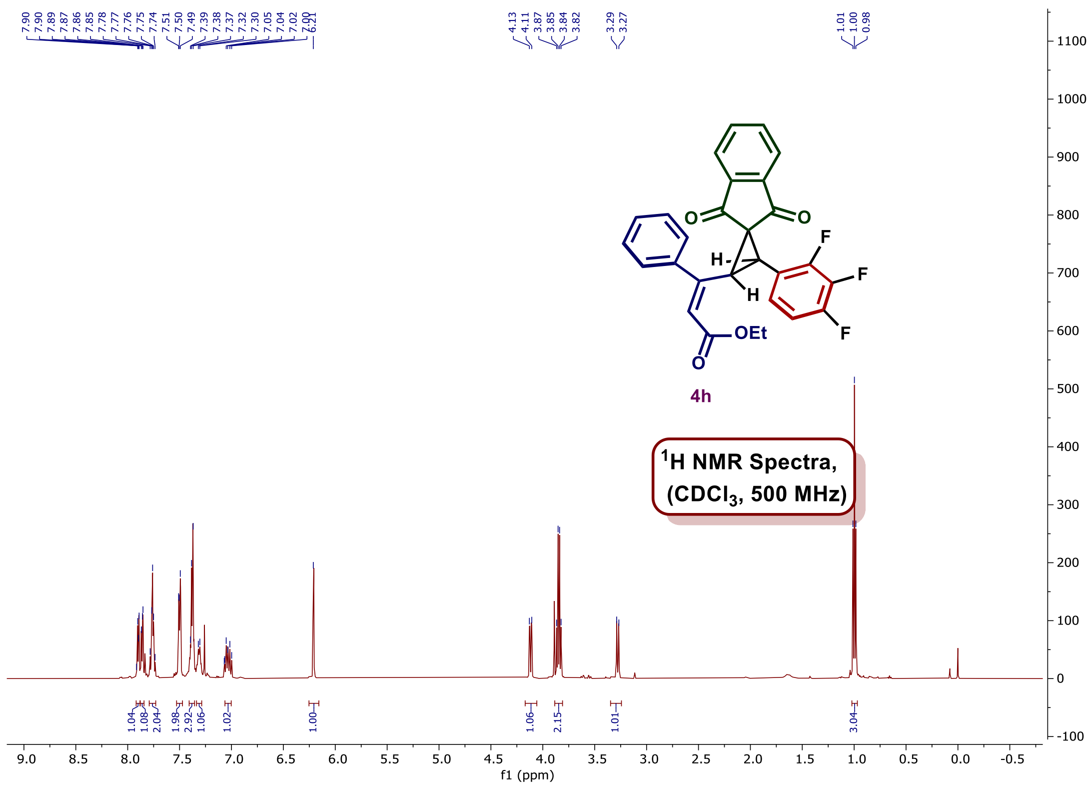
**ethyl (*E*)-3-(2-(4-fluorophenyl)-1',3'-dioxo-1',3'-dihydrospiro[cyclopropane-1,2'-inden]-3-yl)-3-phenlacrylate (4g):**

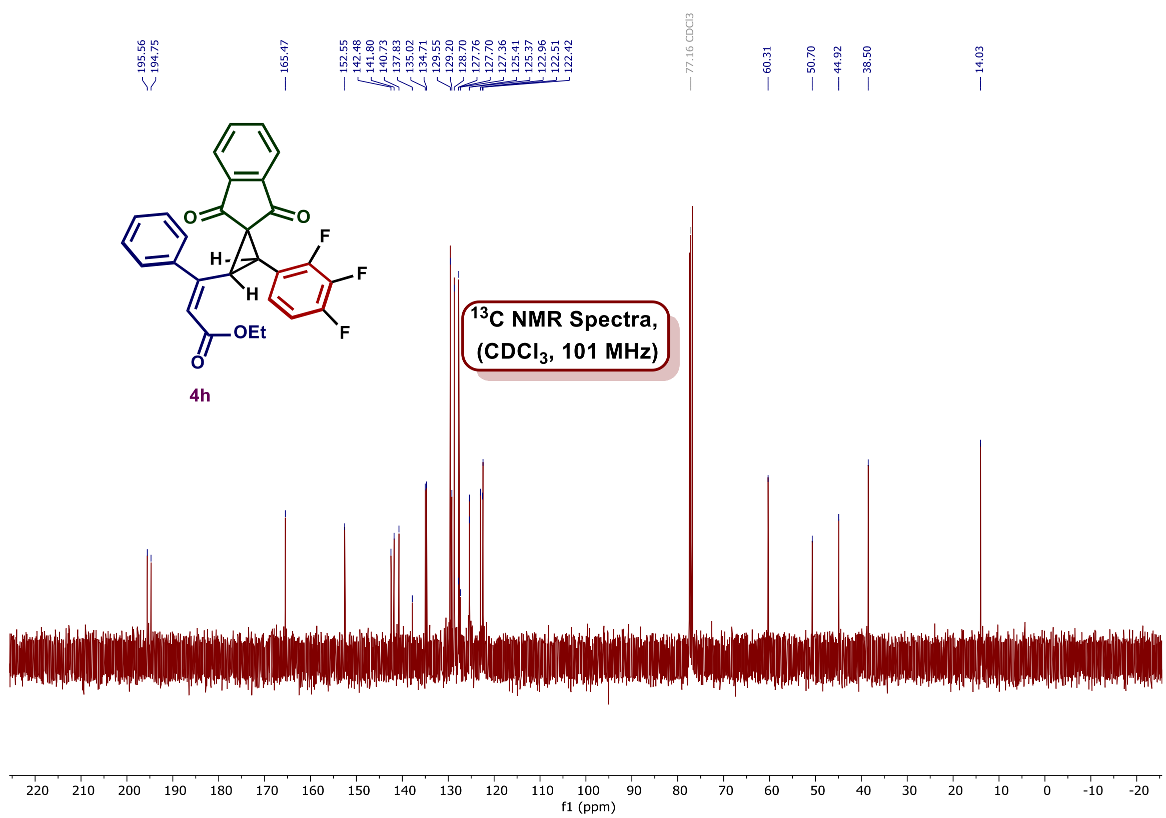


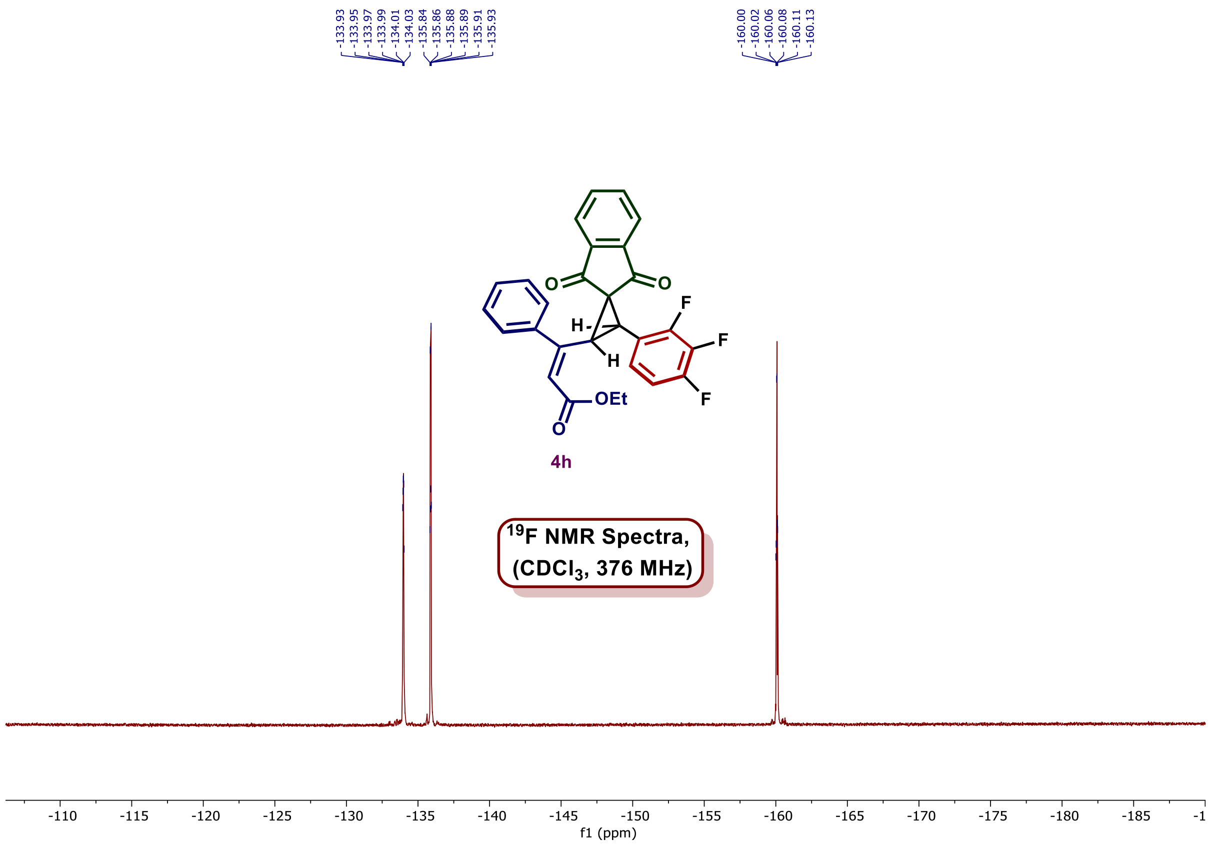




-113.85
O
O
H
H
OEt
O
F
4g
$^{19}$F NMR Spectra,
($CDCl_3$, 376 MHz)
-30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210 -220 -230 -240 -250 -260 -270
f1 (ppm)

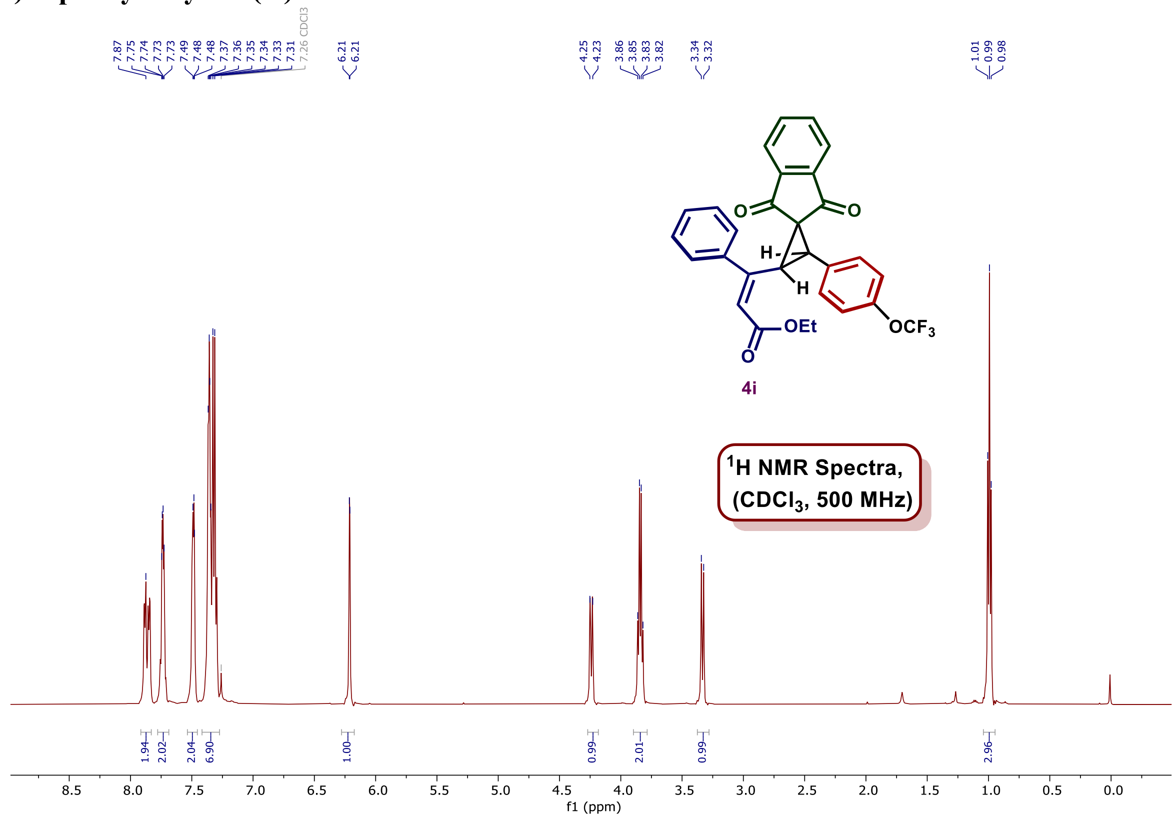
**ethyl (*E*)-3-(1',3'-dioxo-2-(2,3,4-trifluorophenyl)-1',3'-dihydrospiro[cyclopropane-1,2'-inden]-3-yl)-3-phenylacrylate (4h):**

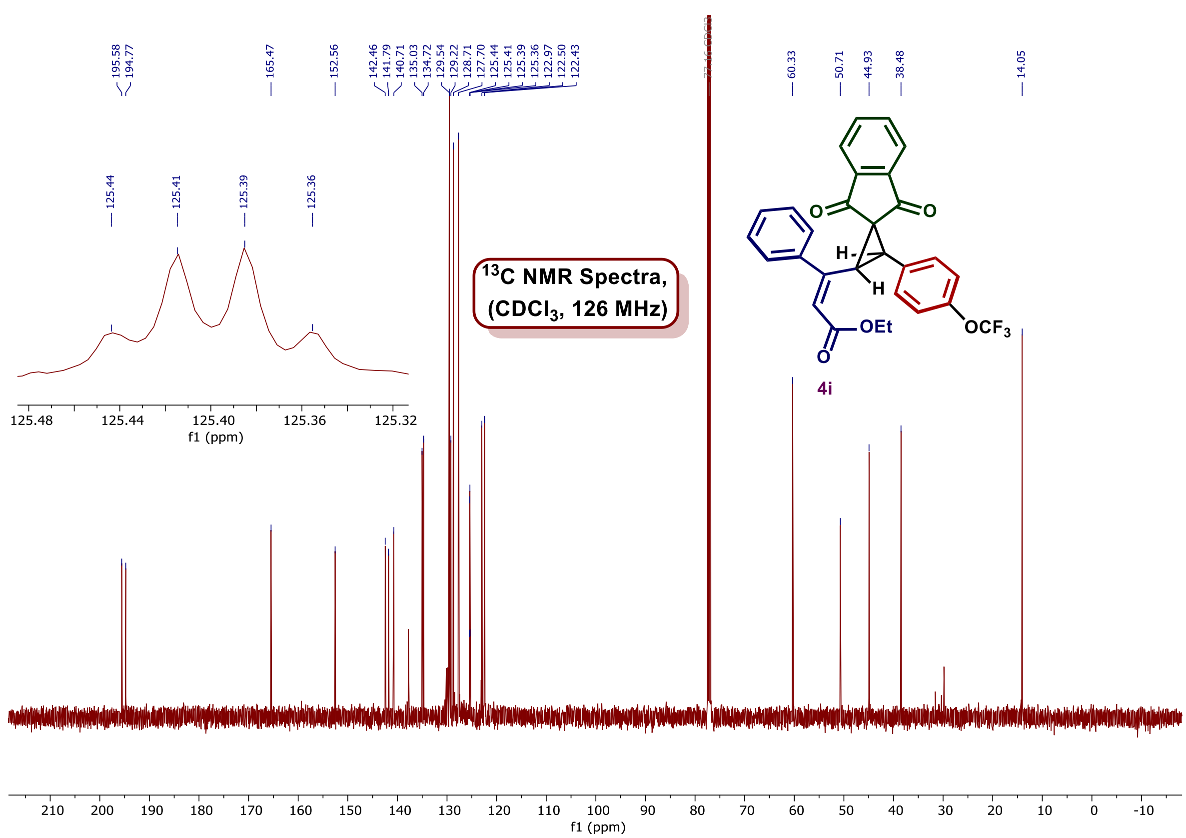


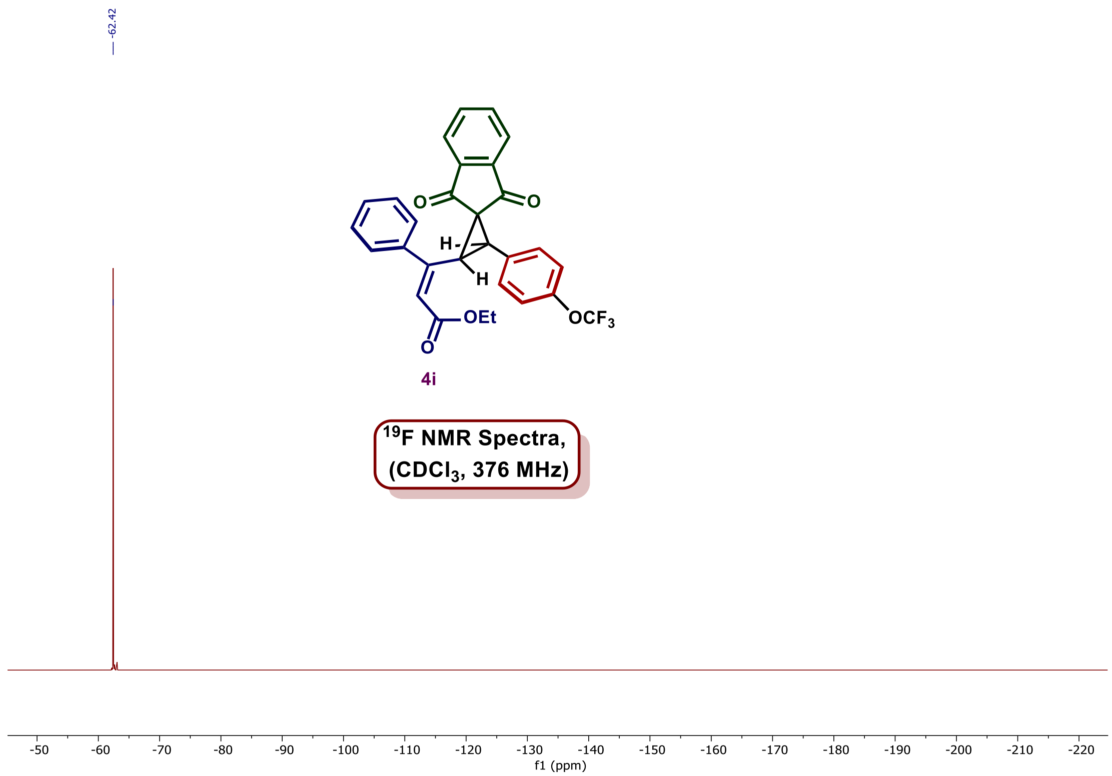




-133.93
-133.95
-133.97
-133.99
-134.01
-134.03
-135.84
-135.86
-135.88
-135.89
-135.91
-135.93
-160.00
-160.02
-160.06
-160.08
-160.11
-160.13
4h
$^{19}$F NMR Spectra,
(CDCl$_3$, 376 MHz)
f1 (ppm)

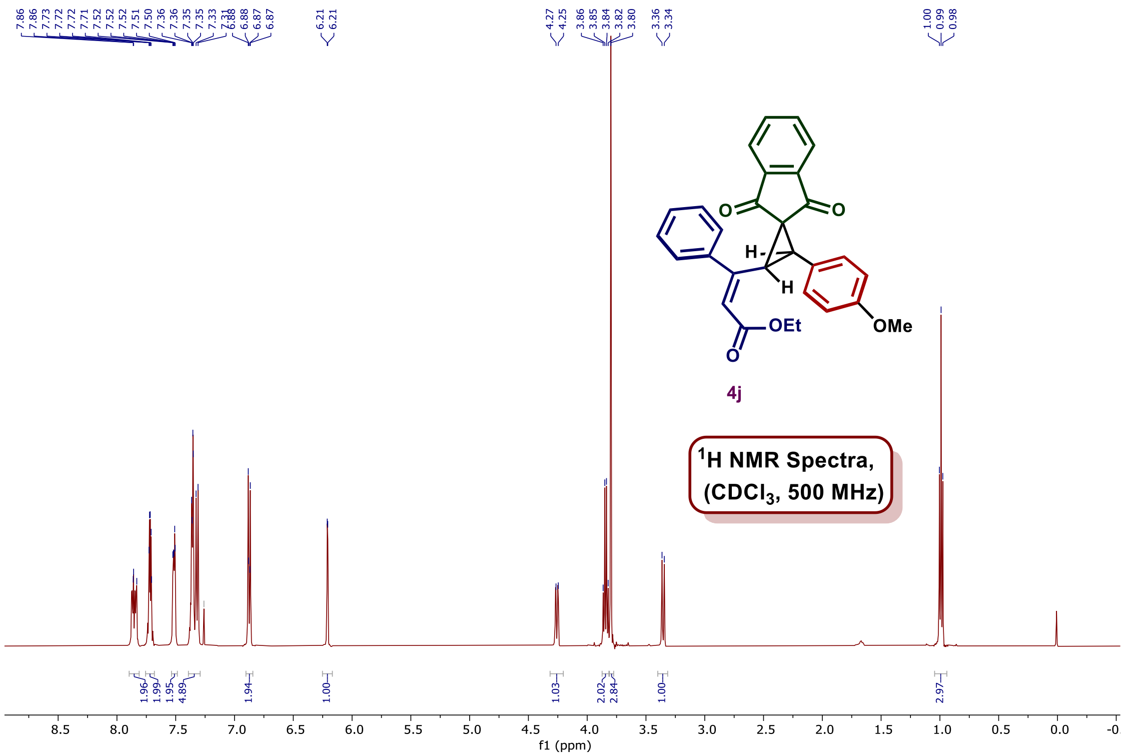
**ethyl (*E*)-3-(1',3'-dioxo-2-(4-(trifluoromethoxy)phenyl)-1',3'-dihydrospiro[cyclopropane-1,2'-inden]-3-yl)-3-phenylacrylate (4i):**

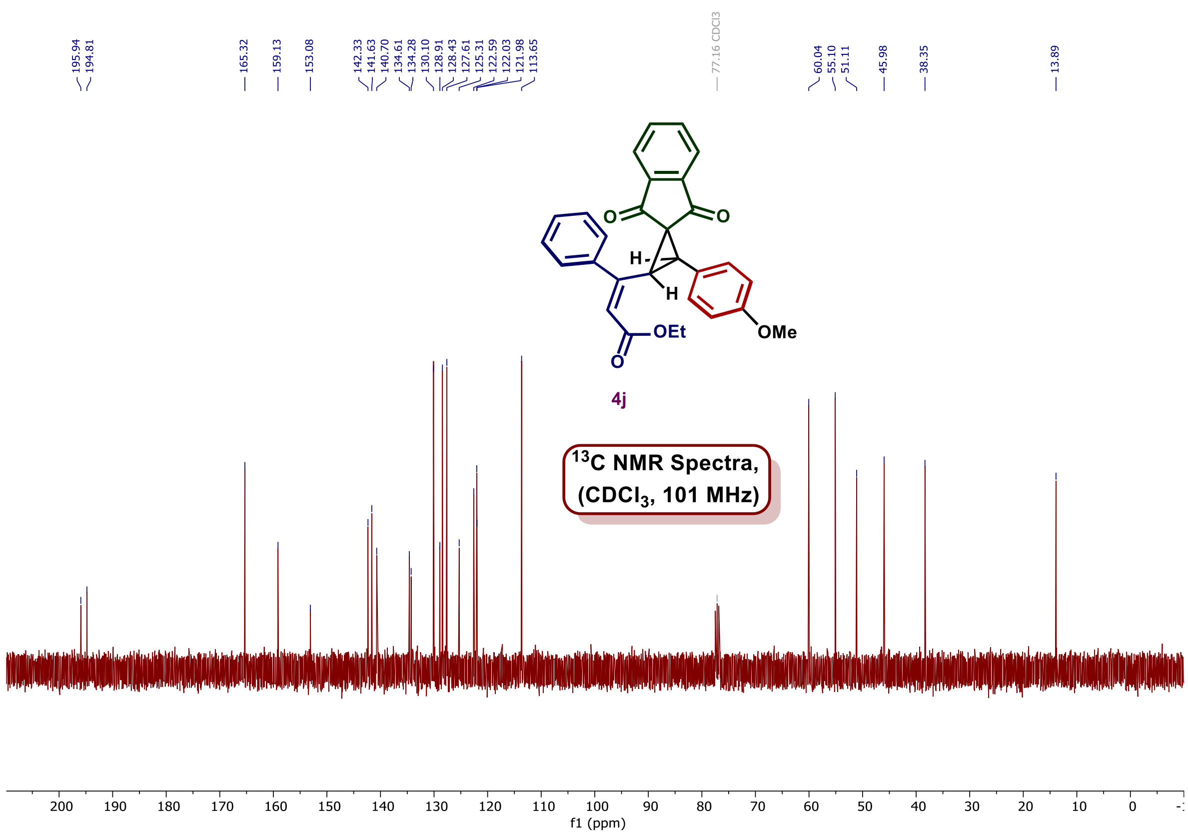


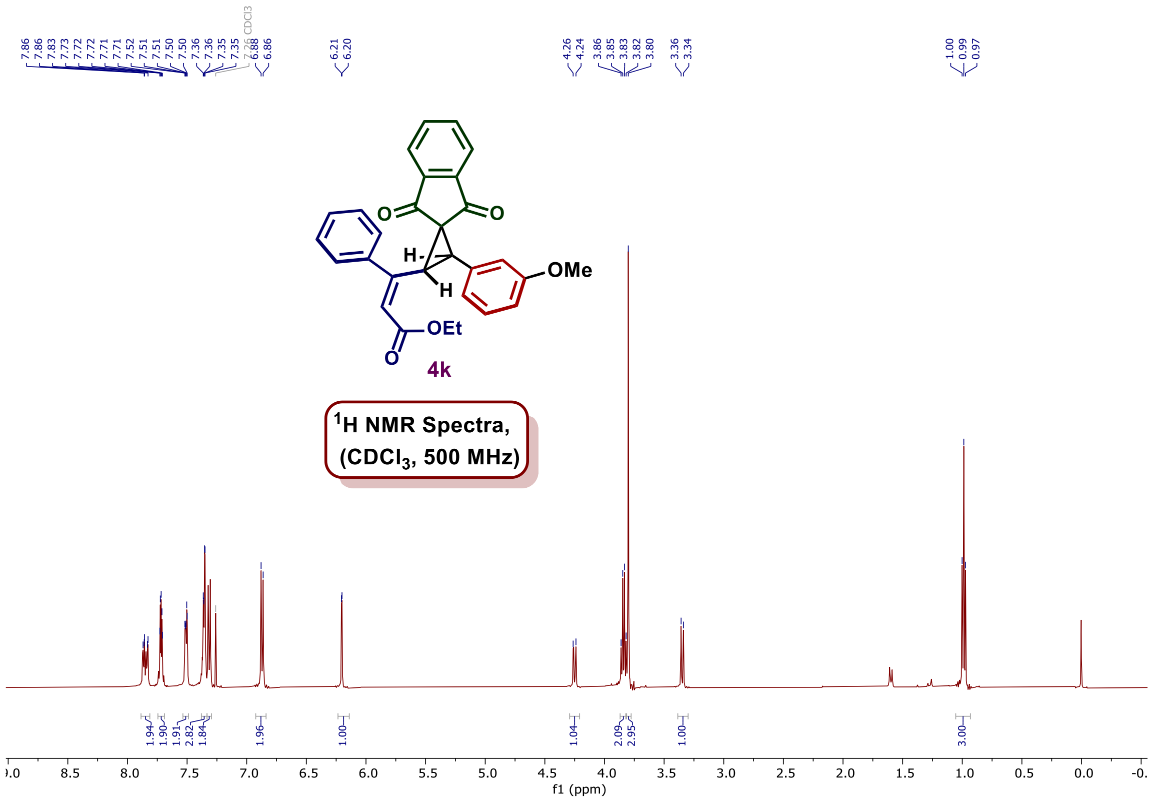

-62.42
O
O
H
H
OEt
O
$OCF_3$
4i
$^{19}F$ NMR Spectra,
($CDCl_3$, 376 MHz)
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-200
-210
-220
f1 (ppm)

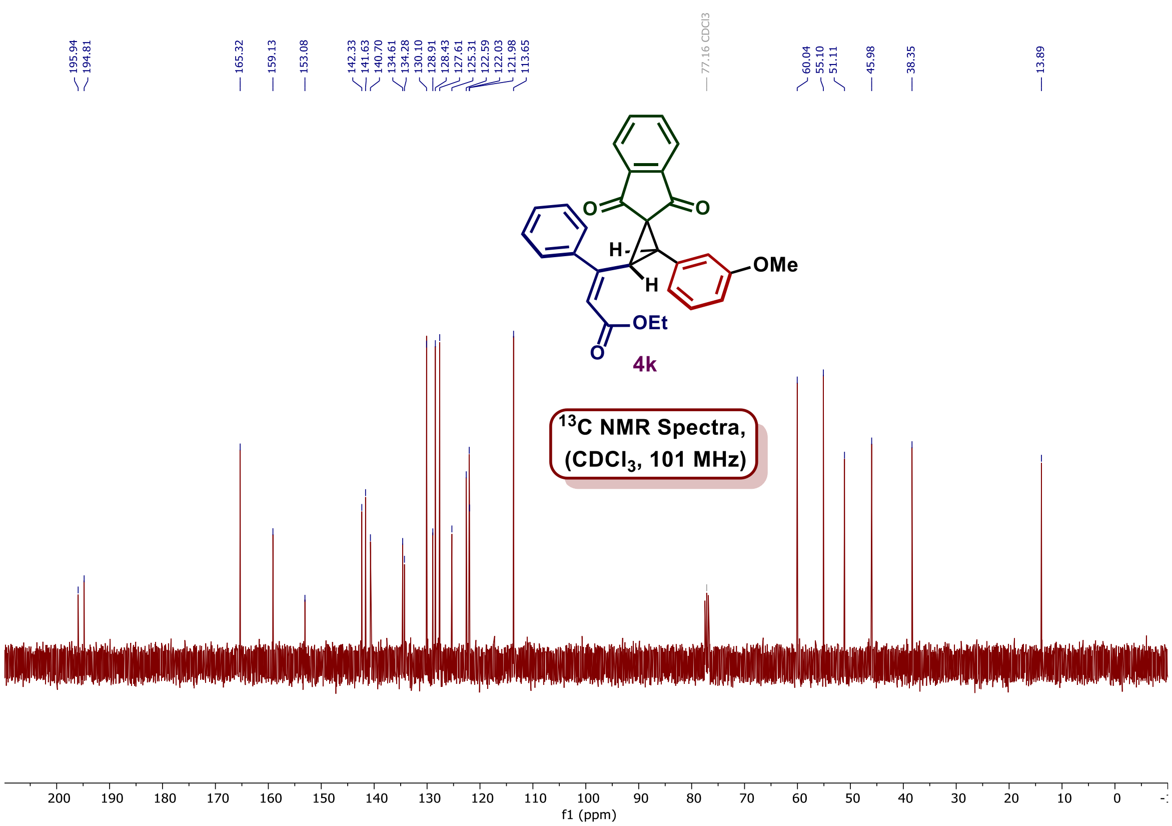
**ethyl (*E*)-3-(2-(4-methoxyphenyl)-1',3'-dioxo-1',3'-dihydrospiro[cyclopropane-1,2'-inden]-3-yl)-3-phenylacrylate (4j):**



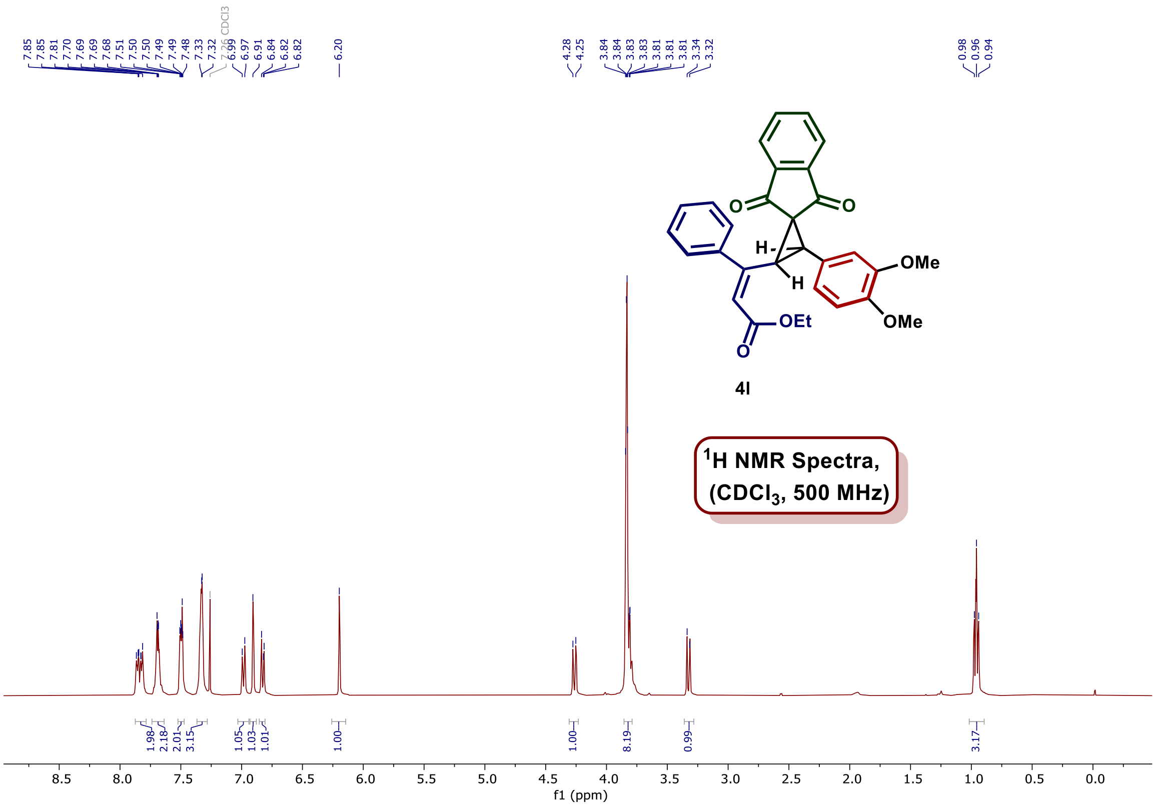



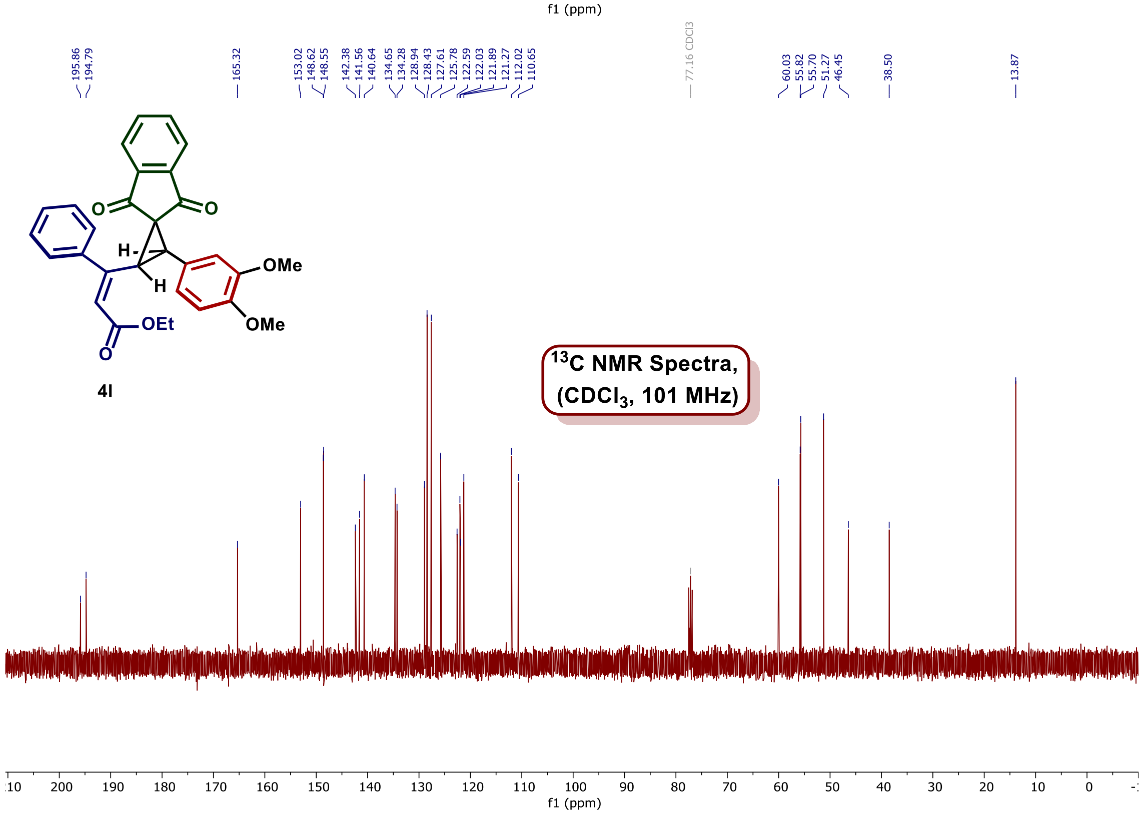
**ethyl (*E*)-3-(2-(3-methoxyphenyl)-1',3'-dioxo-1',3'-dihydrospiro[cyclopropane-1,2'-inden]-3-yl)-3-phenylacrylate (4k):**



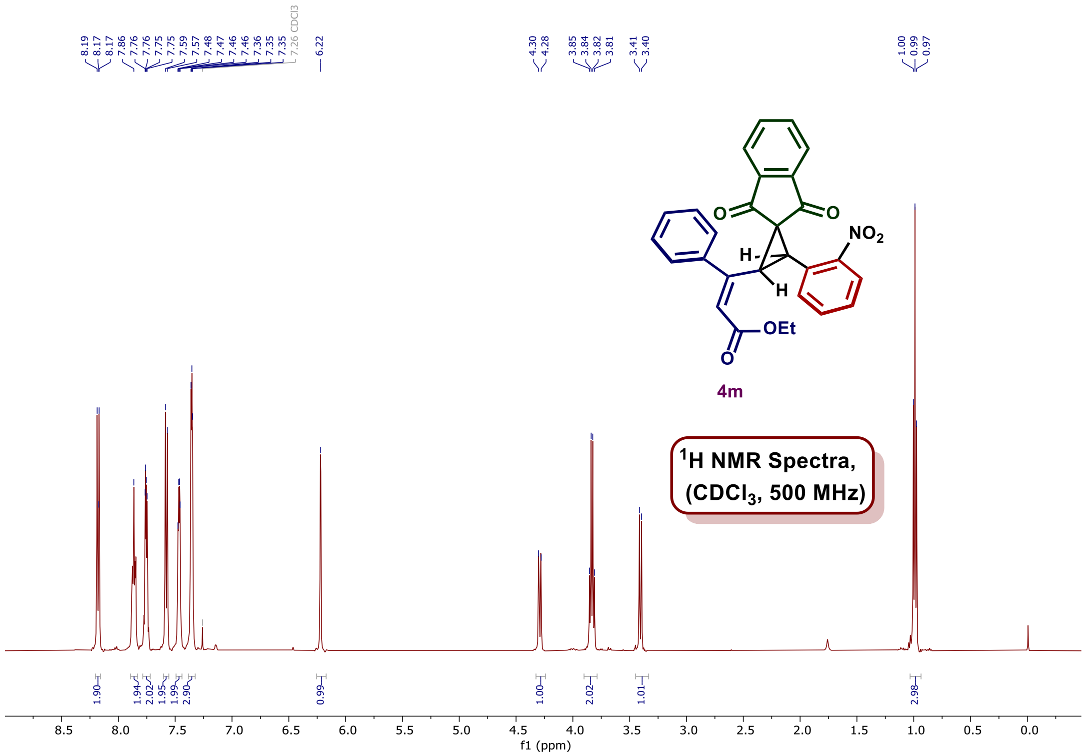



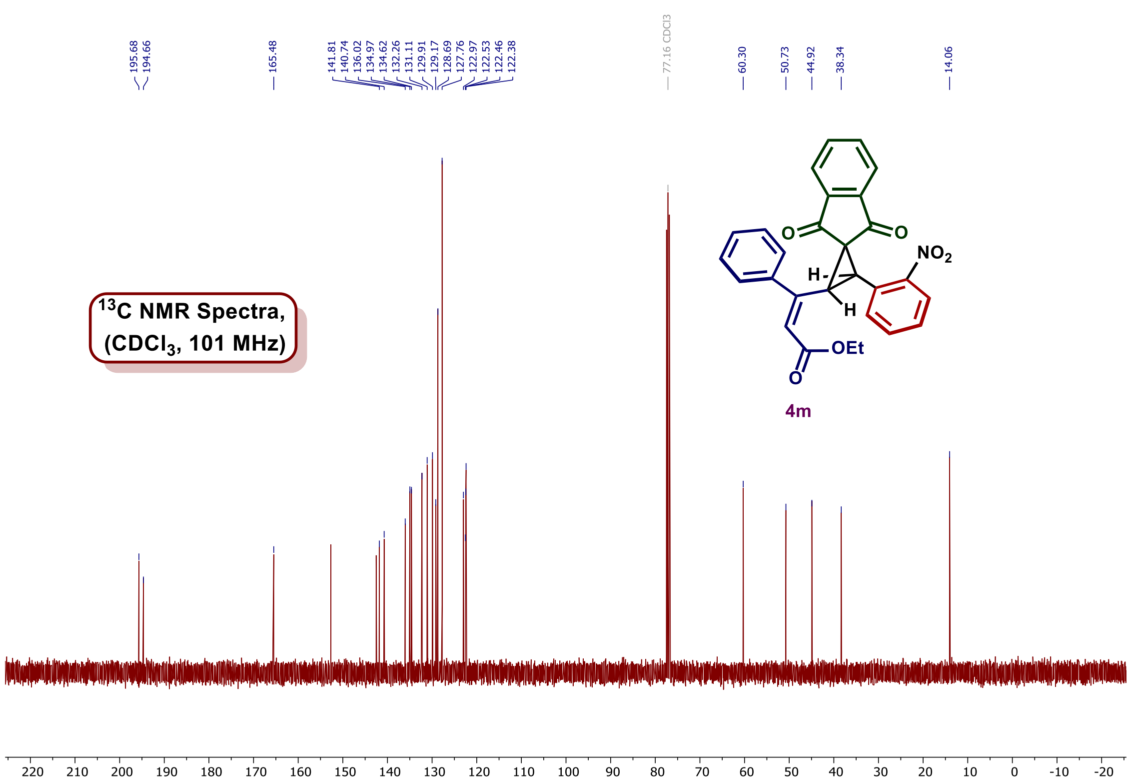
**ethyl (*E*)-3-(2-(3,4-dimethoxyphenyl)-1',3'-dioxo-1',3'-dihydrospiro[cyclopropane-1,2'-inden]-3-yl)-3-phenylacrylate (4l):**



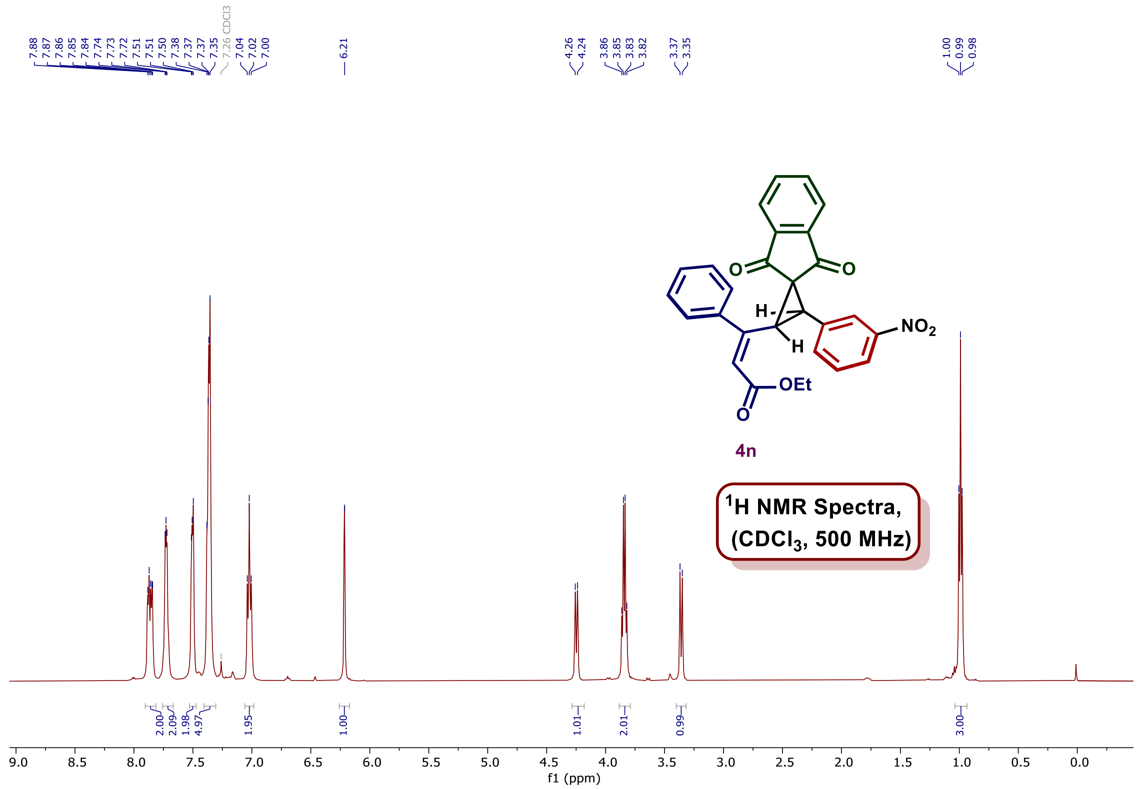



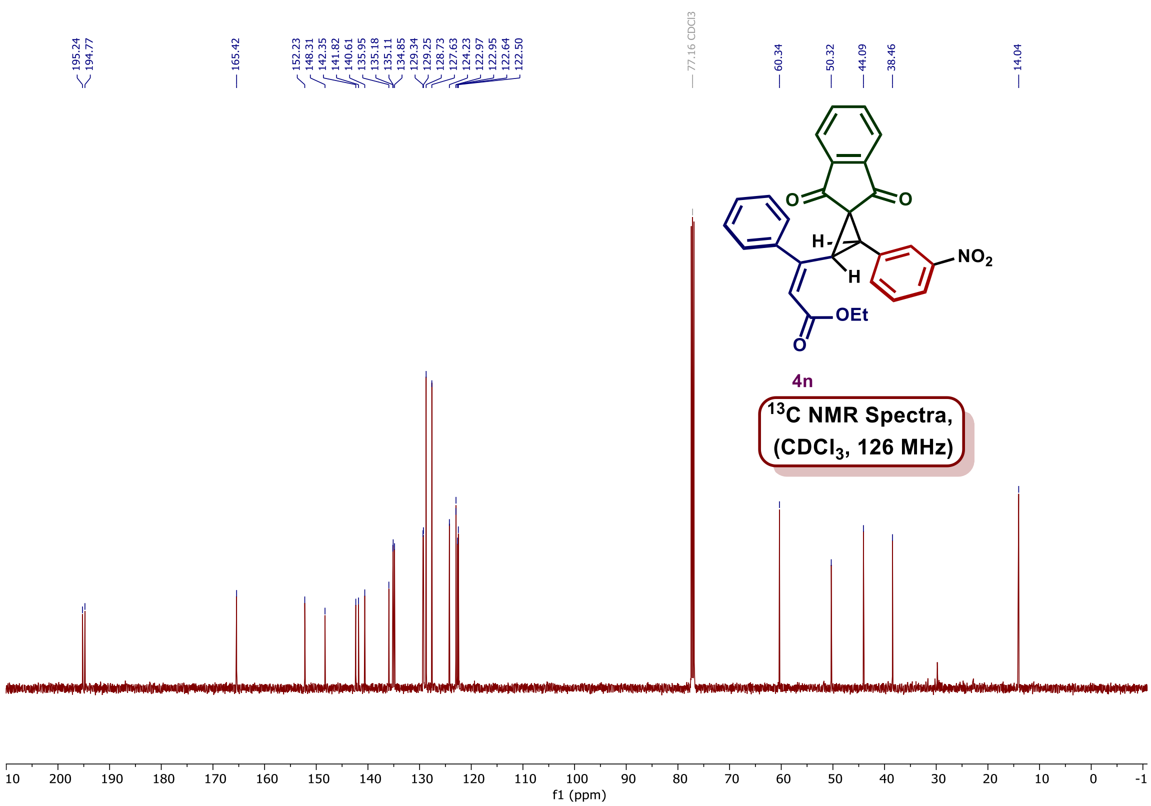
**ethyl (*E*)-3-(2-(2-nitrophenyl)-1',3'-dioxo-1',3'-dihydrospiro[cyclopropane-1,2'-inden]-3-yl)-3-phenylacrylate (4m):**



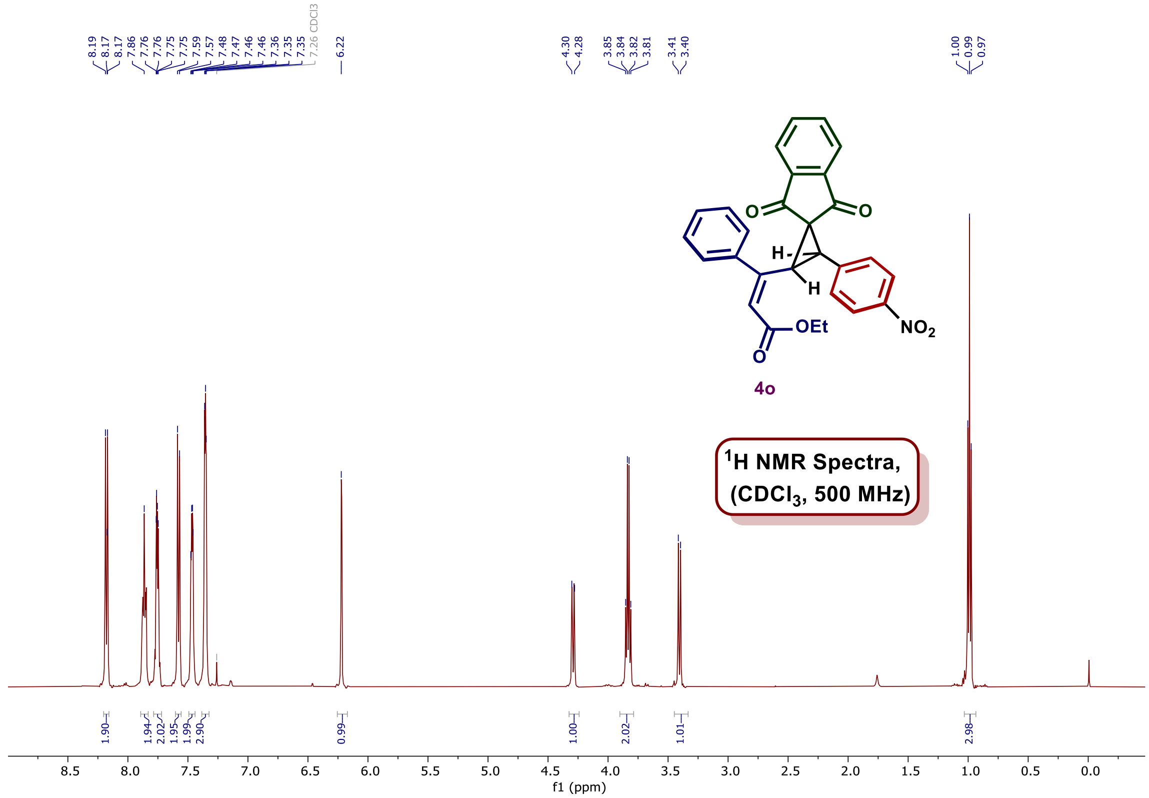



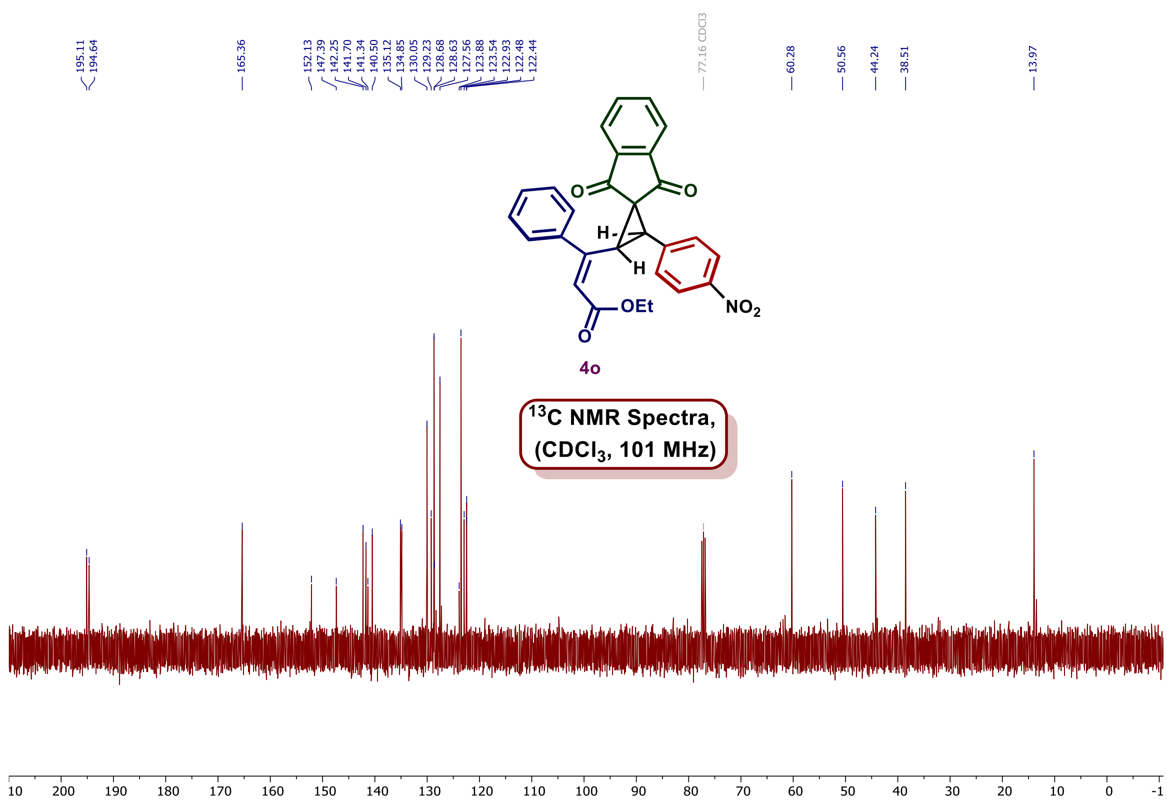
**ethyl (*E*)-3-(2-(3-nitrophenyl)-1',3'-dioxo-1',3'-dihydrospiro[cyclopropane-1,2'-inden]-3-yl)-3-phenylacrylate (4n):**



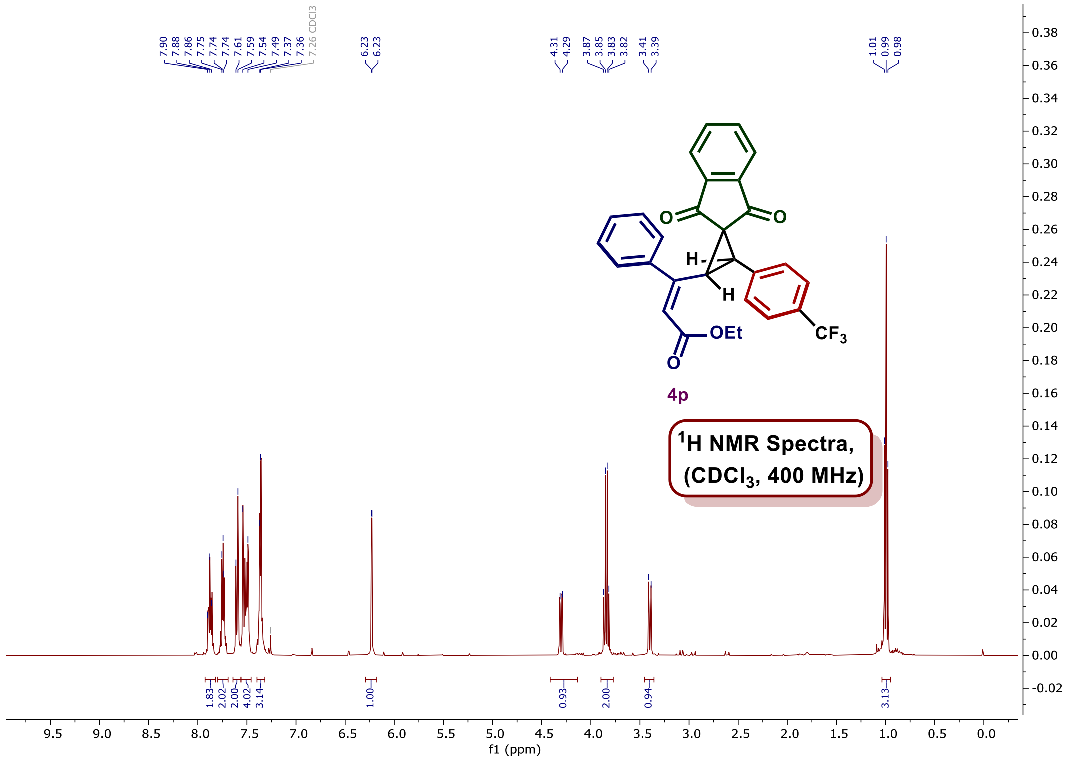



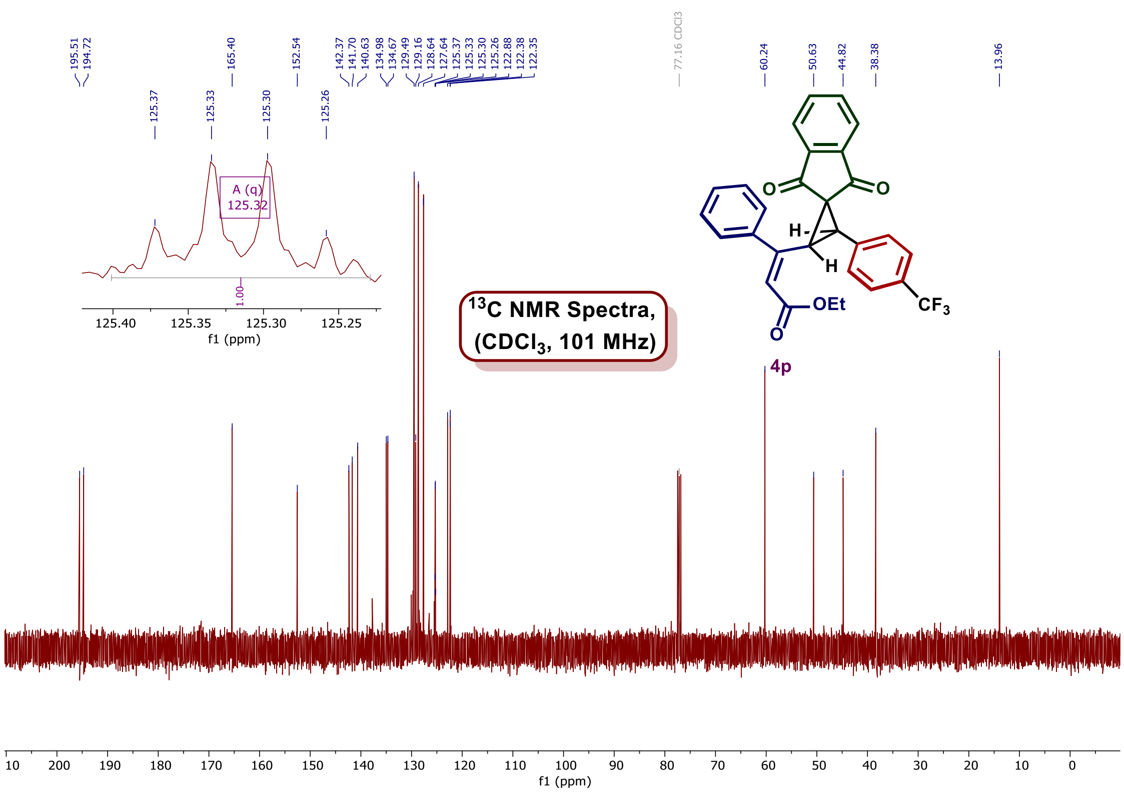
**ethyl (*E*)-3-(2-(4-nitrophenyl)-1',3'-dioxo-1',3'-dihydrospiro[cyclopropane-1,2'-inden]-3-yl)-3-phenylacrylate (4o):**

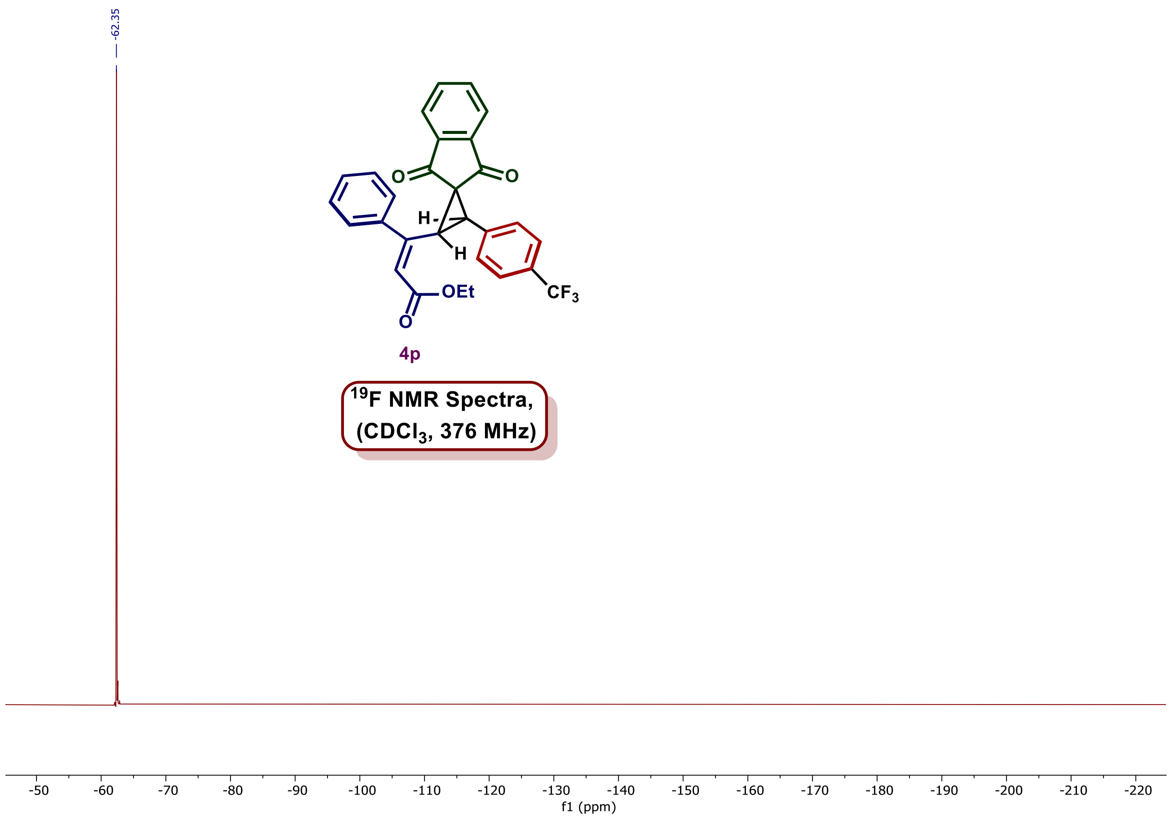


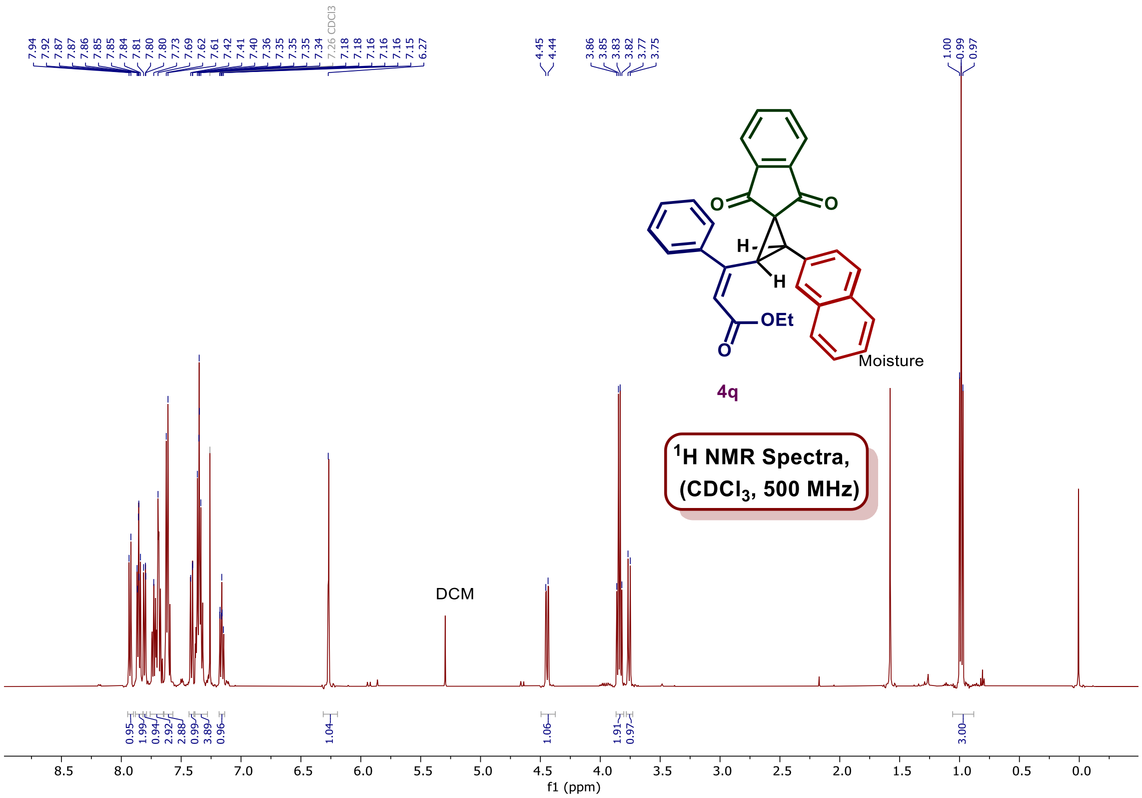
**ethyl (*E*)-3-(1',3'-dioxo-2-(4-(trifluoromethyl)phenyl)-1',3'-dihydrospiro[cyclopropane-1,2'-inden]-3-yl)-3-phenylacrylate (4p):**

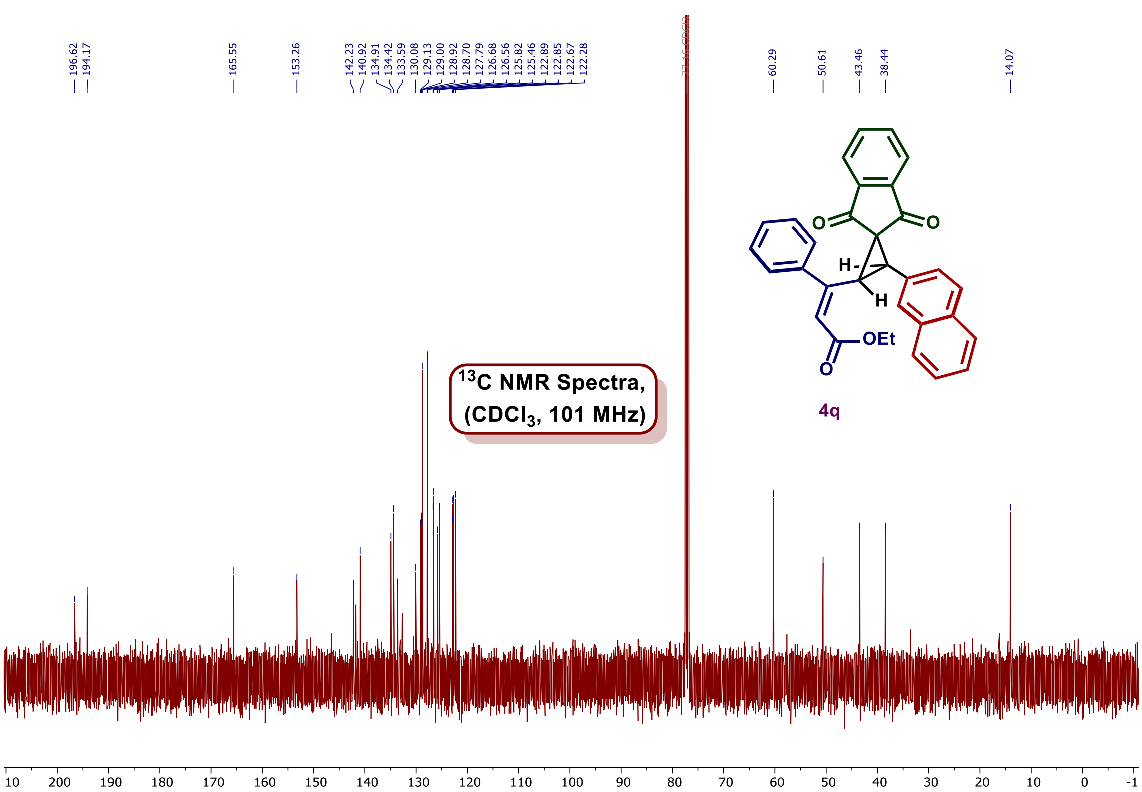


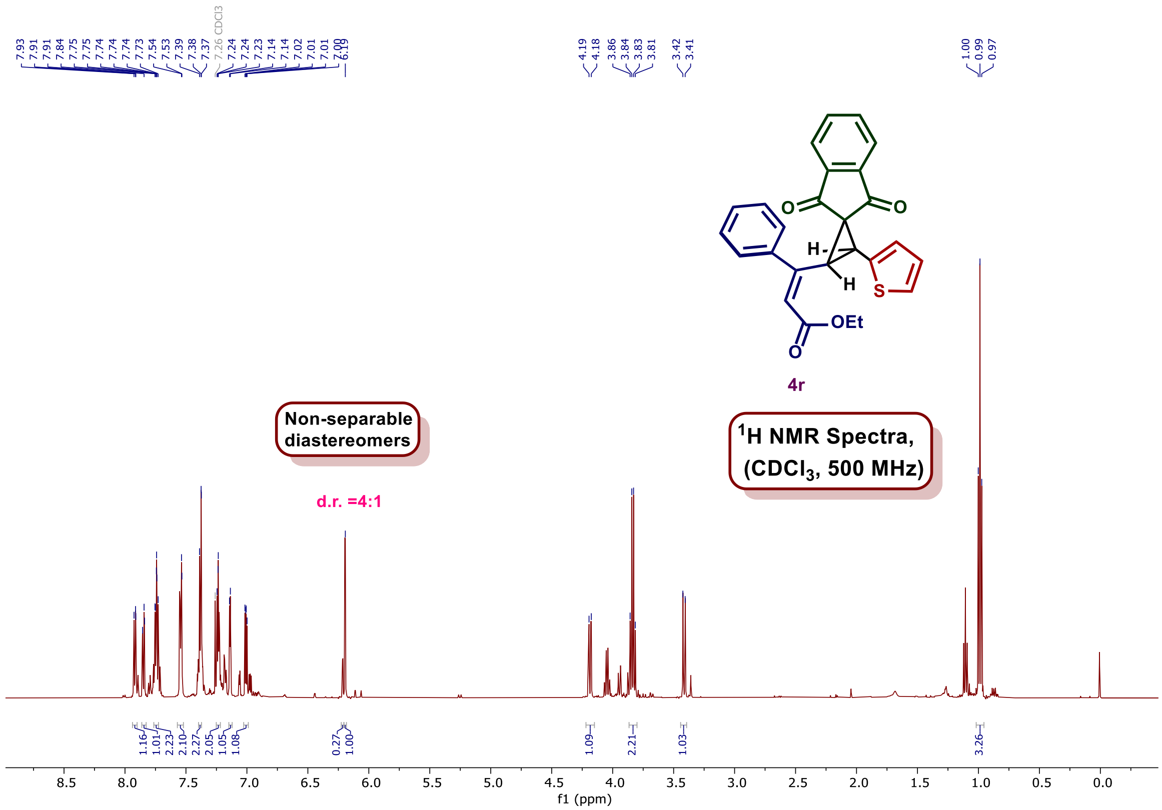

-62.35
O
O
H
H
OEt
O
CF3
4p
19F NMR Spectra,
(CDCl3, 376 MHz)
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-200
-210
-220
f1 (ppm)

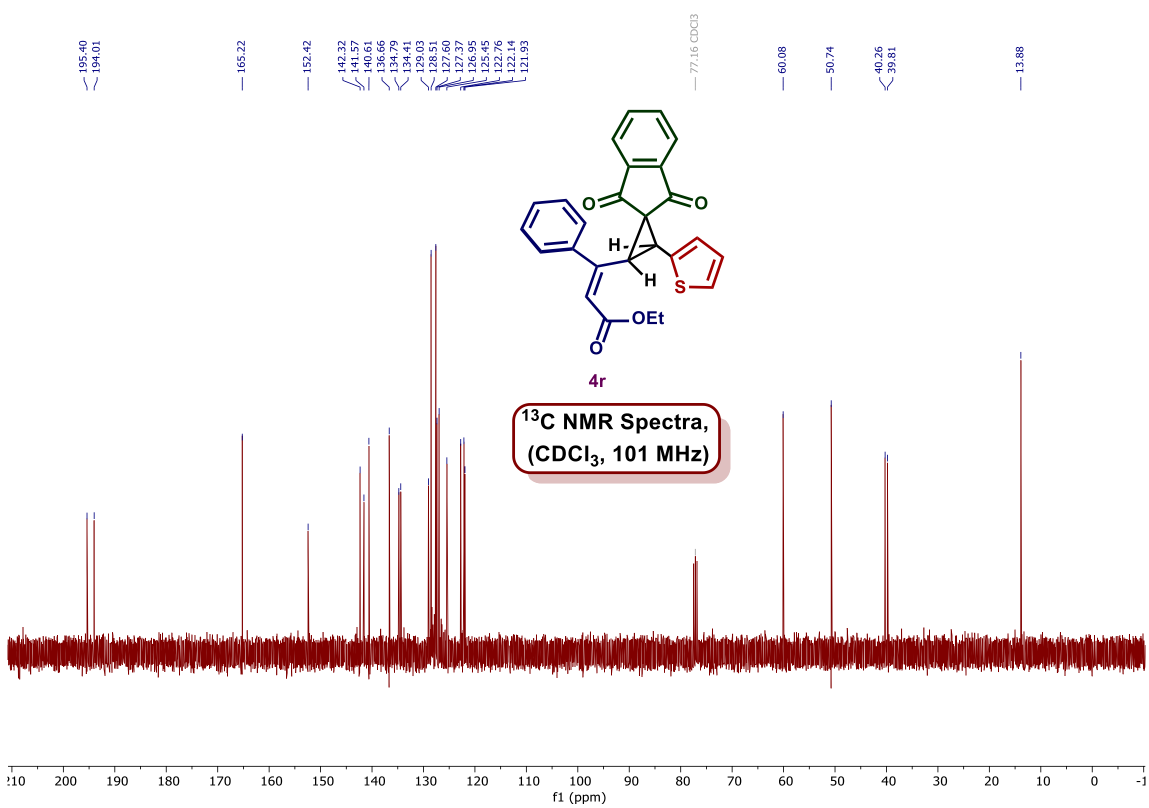
**ethyl (*E*)-3-(2-(naphthalen-2-yl)-1',3'-dioxo-1',3'-dihydrospiro[cyclopropane-1,2'-inden]-3-yl)-3-phenylacrylate (4q):**



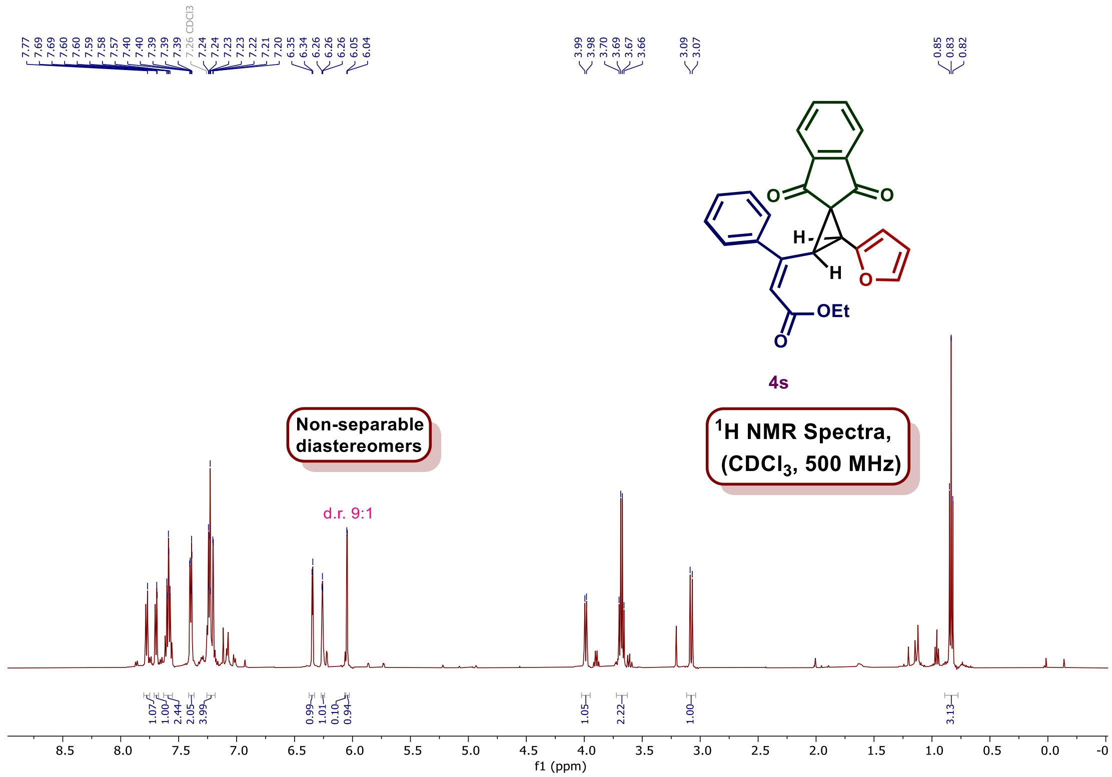



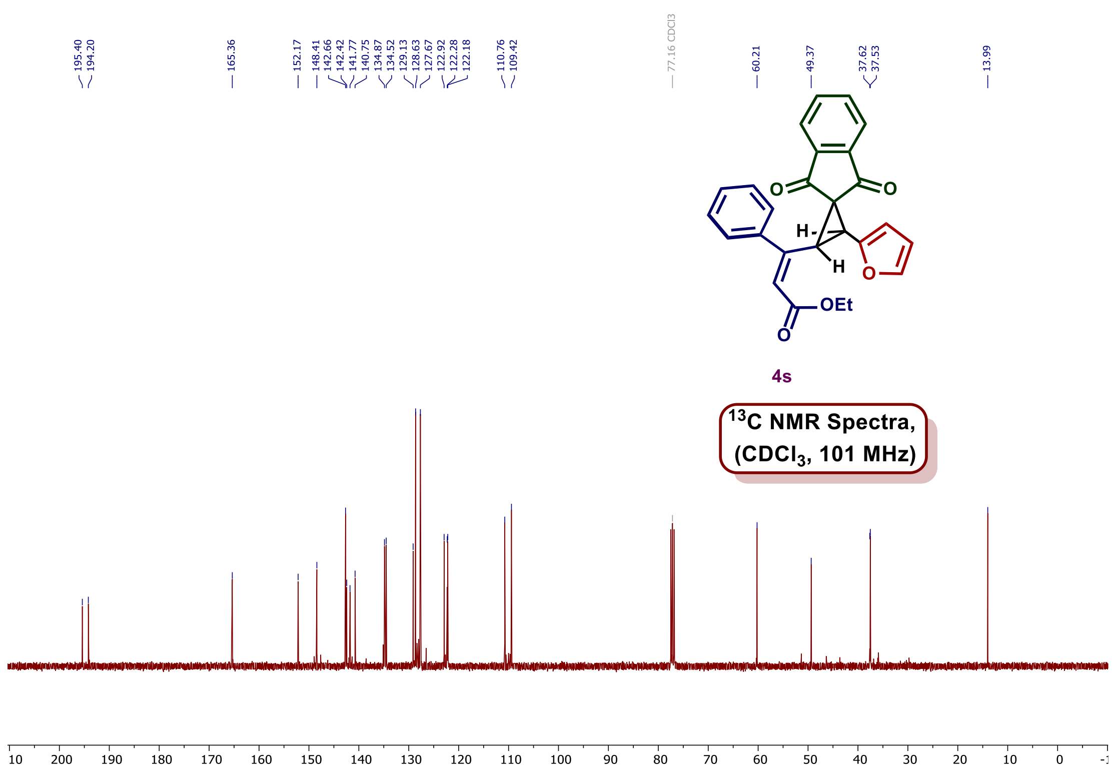
**ethyl (*E*)-3-(1',3'-dioxo-2-(thiophen-2-yl)-1',3'-dihydrospiro[cyclopropane-1,2'-inden]-3-yl)-3-phenylacrylate (4r):**



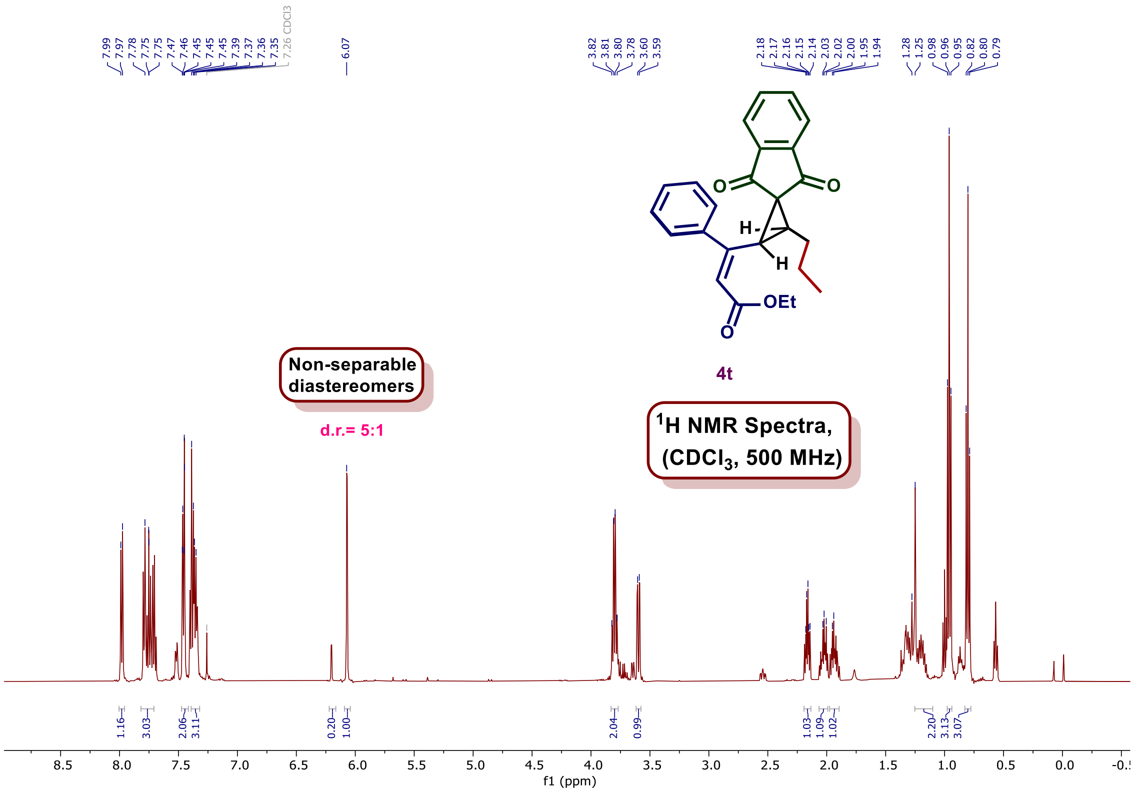



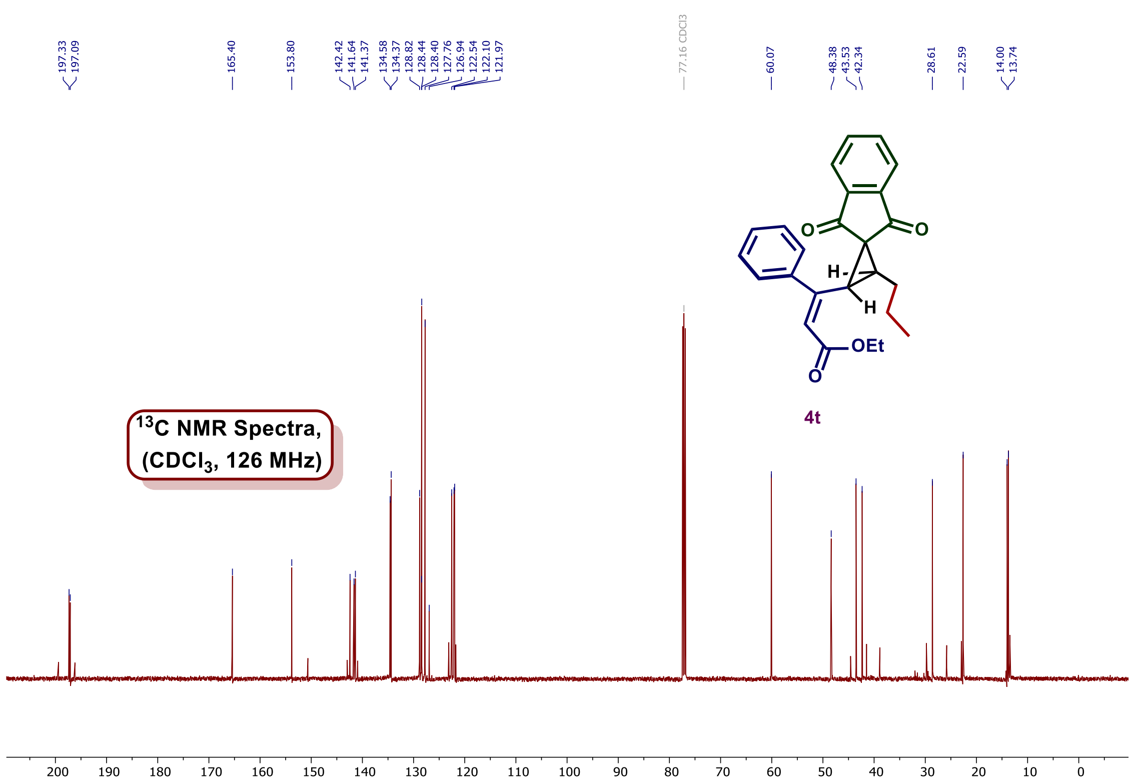
**ethyl (*E*)-3-(2-(furan-2-yl)-1',3'-dioxo-1',3'-dihydrospiro[cyclopropane-1,2'-inden]-3-yl)-3-phenylacrylate (4s):**



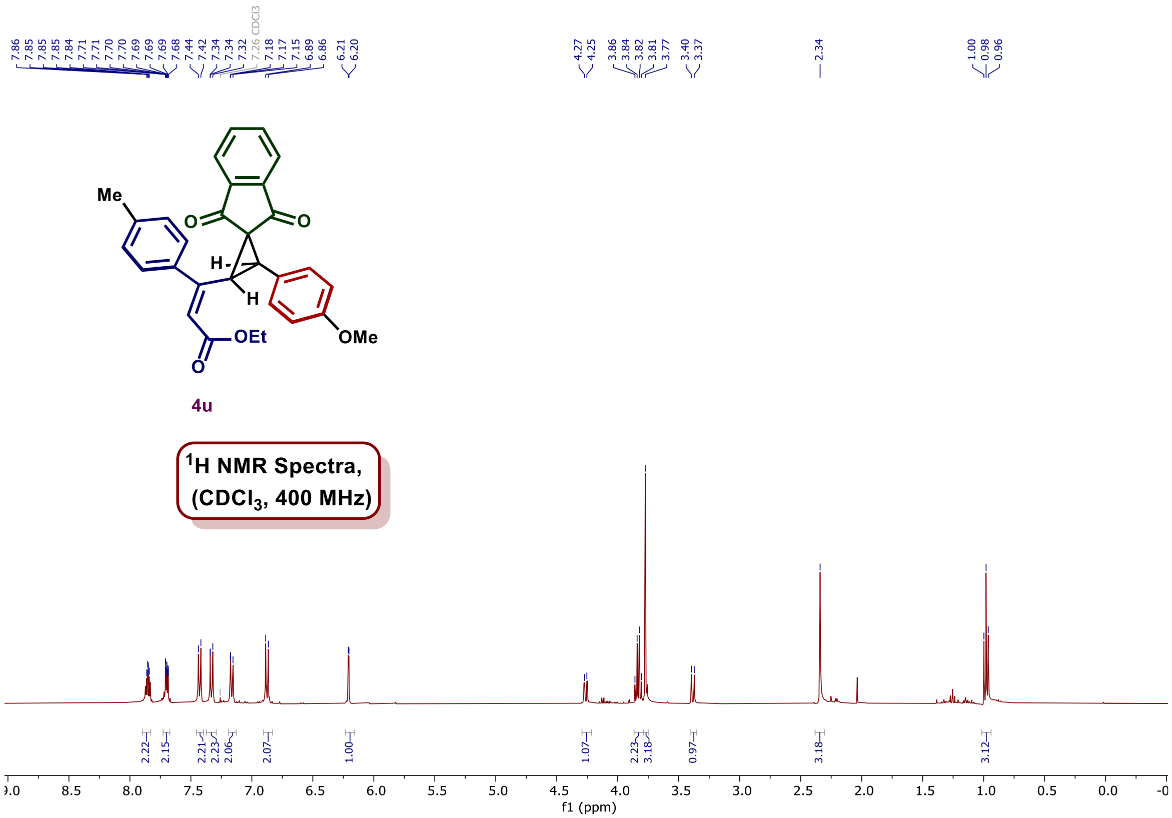



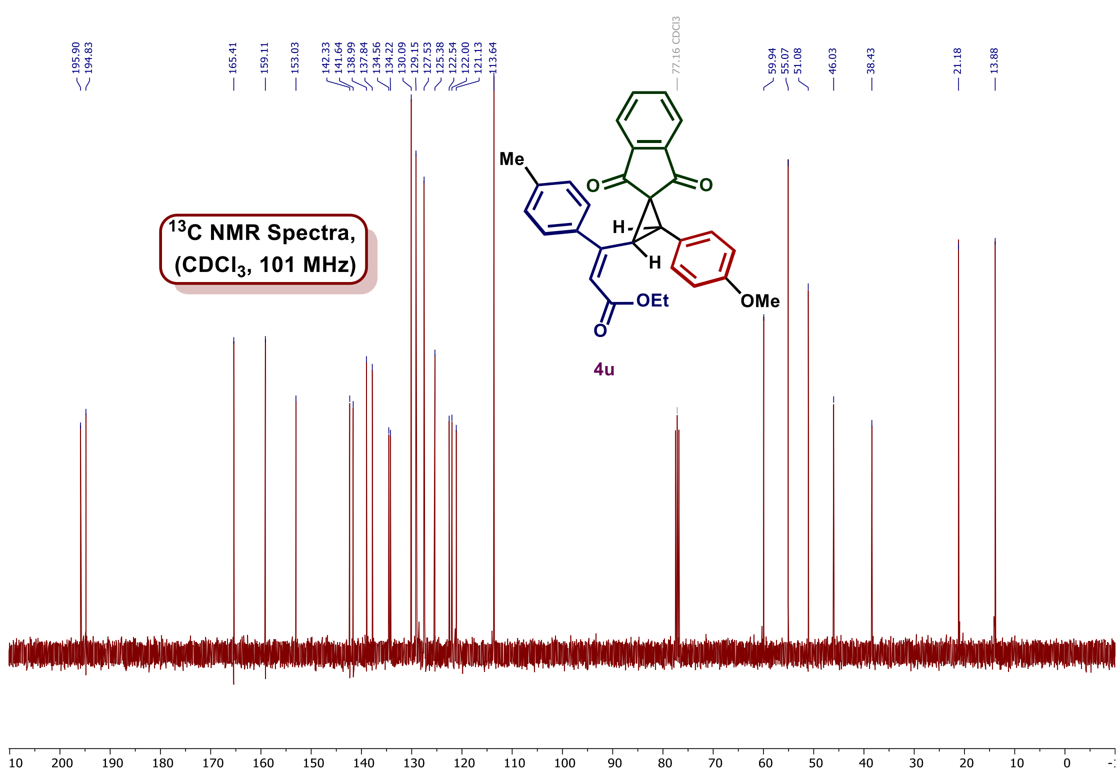
**ethyl (*E*)-3-(1',3'-dioxo-2-propyl-1',3'-dihydrospiro[cyclopropane-1,2'-inden]-3-yl)-3-phenylacrylate (4t):**



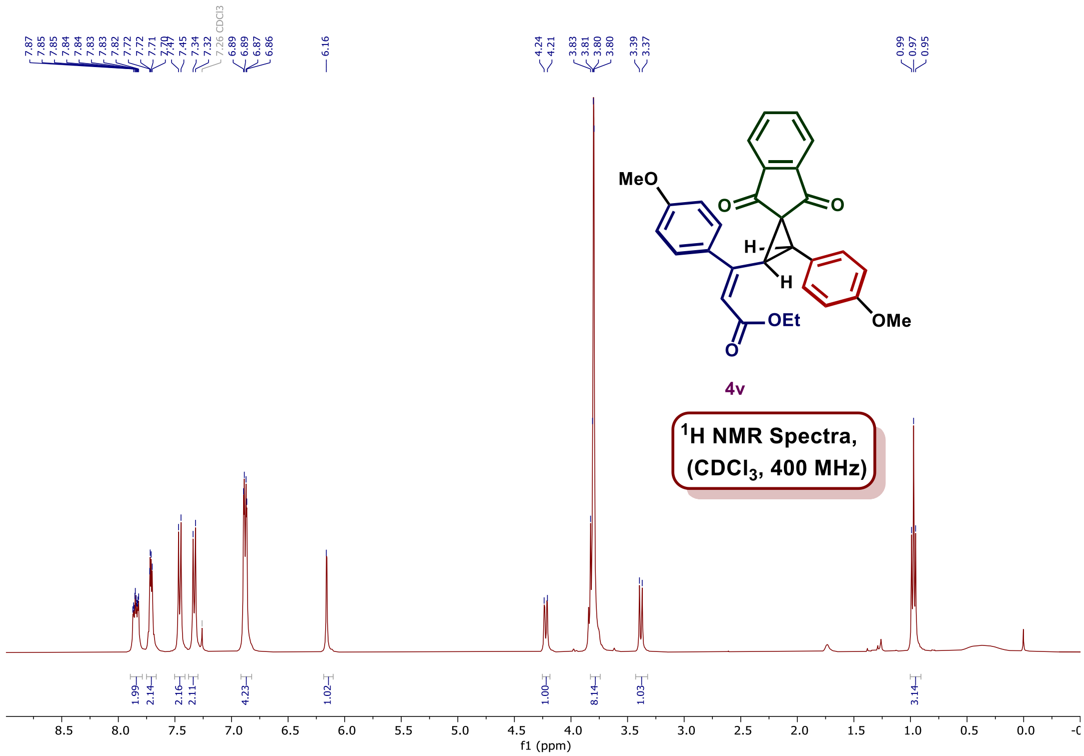



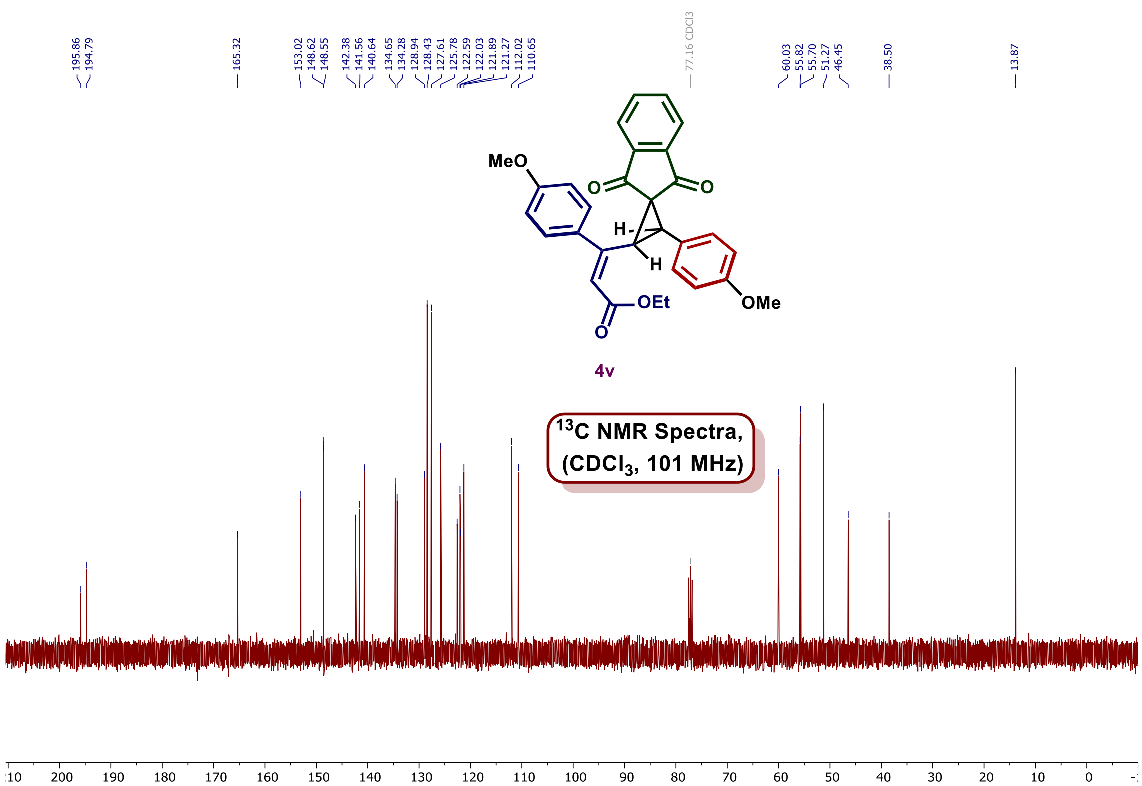
**ethyl (*E*)-3-(2-(4-methoxyphenyl)-1',3'-dioxo-1',3'-dihydrospiro[cyclopropane-1,2'-inden]-3-yl)-3-(p-tolyl)acrylate (4u):**



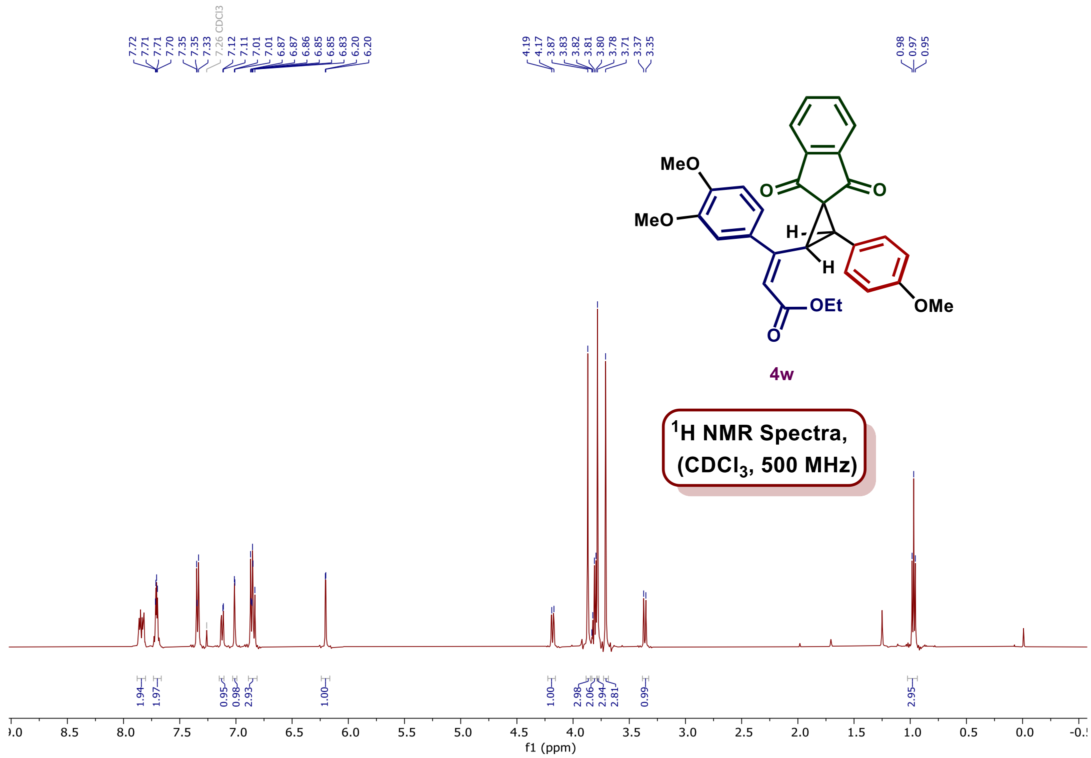



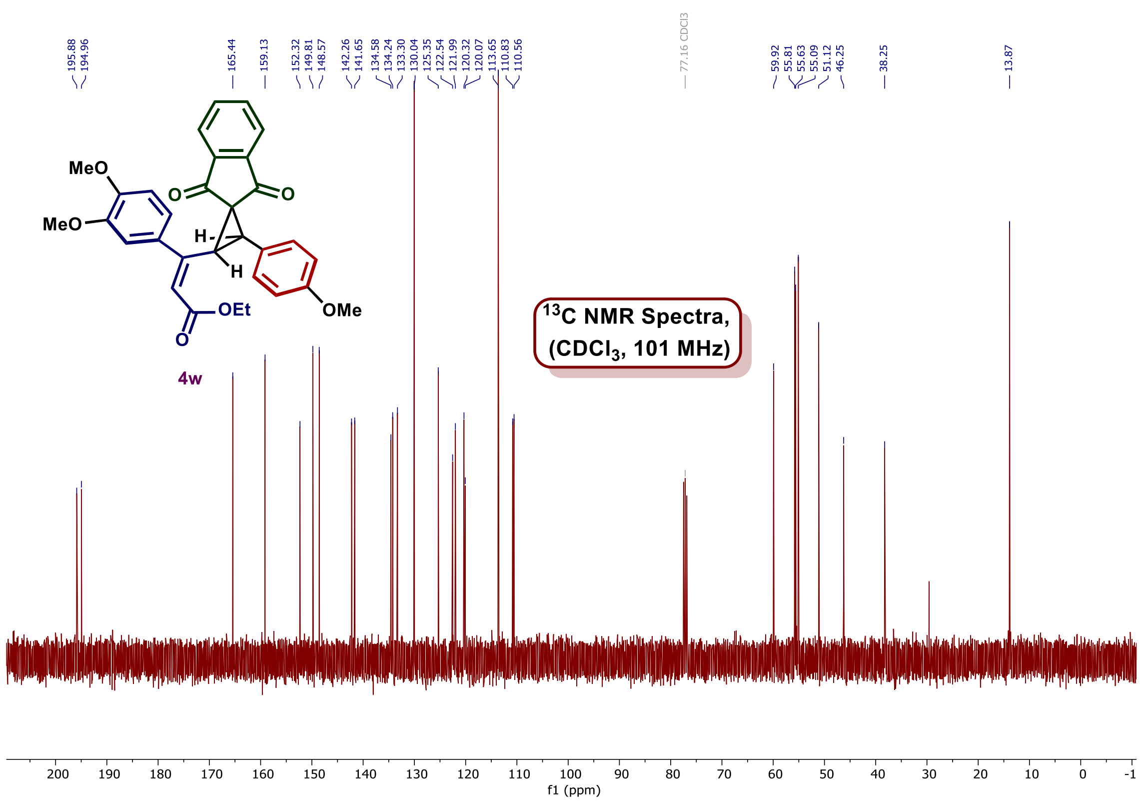
**ethyl (*E*)-3-(4-methoxyphenyl)-3-(2-(4-methoxyphenyl)-1',3'-dioxo-1',3'-dihydrospiro[cyclopropane-1,2'-inden]-3-yl) acrylate (4v):**



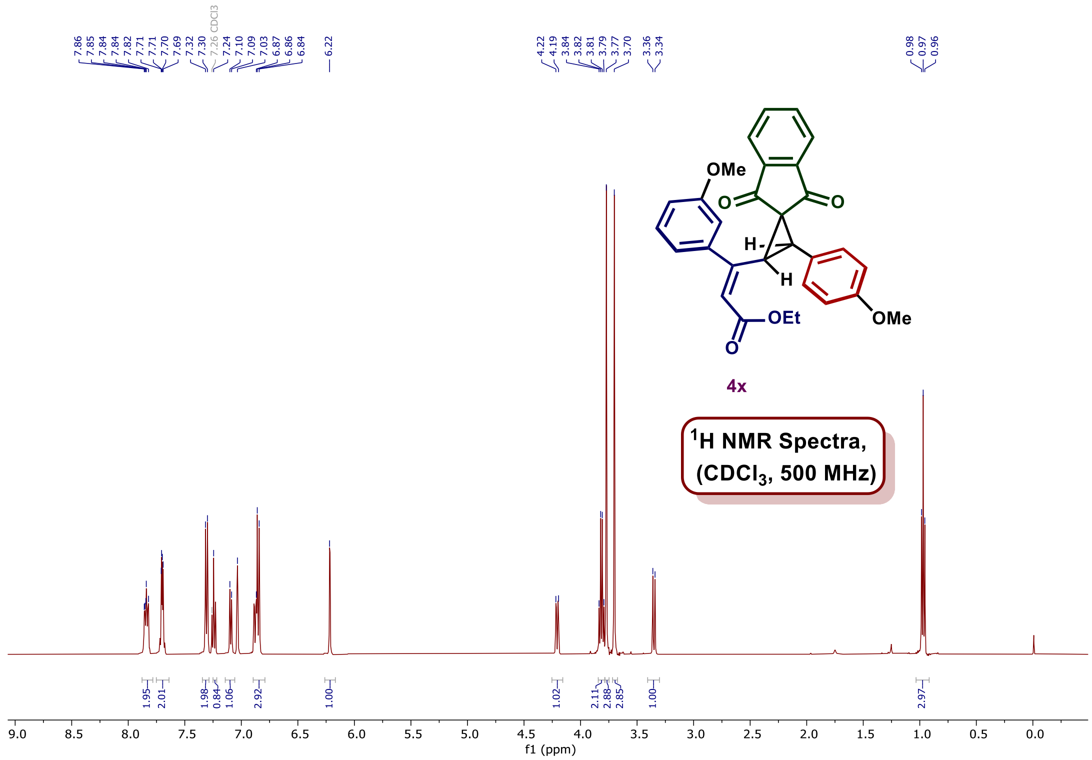



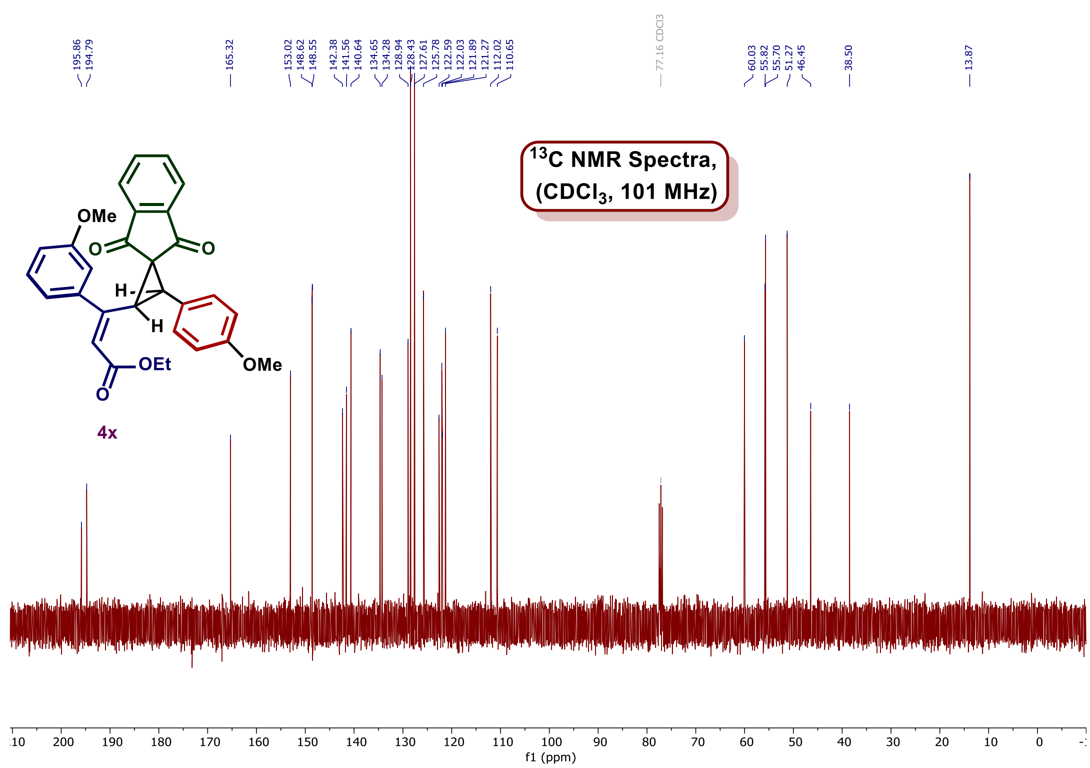
**ethyl (*E*)-3-(3,4-dimethoxyphenyl)-3-(2-(4-methoxyphenyl)-1',3'-dioxo-1',3'-dihydrospiro[cyclopropane-1,2'-inden]-3-yl)acrylate (4w):**



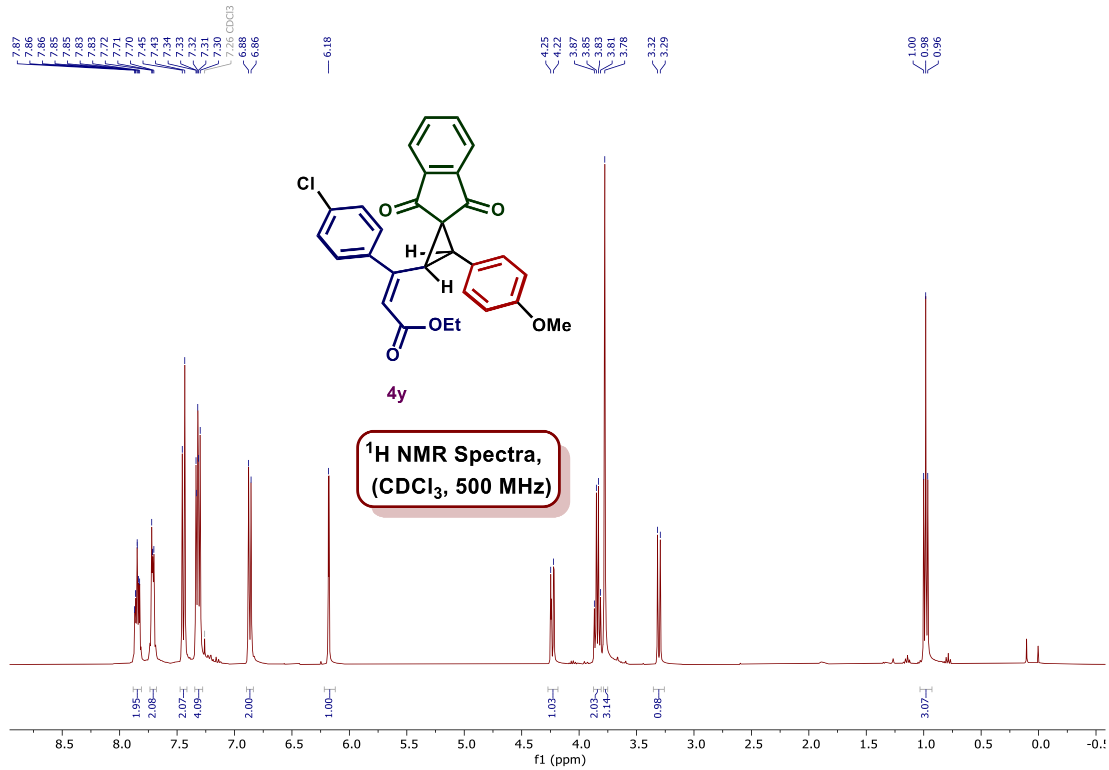



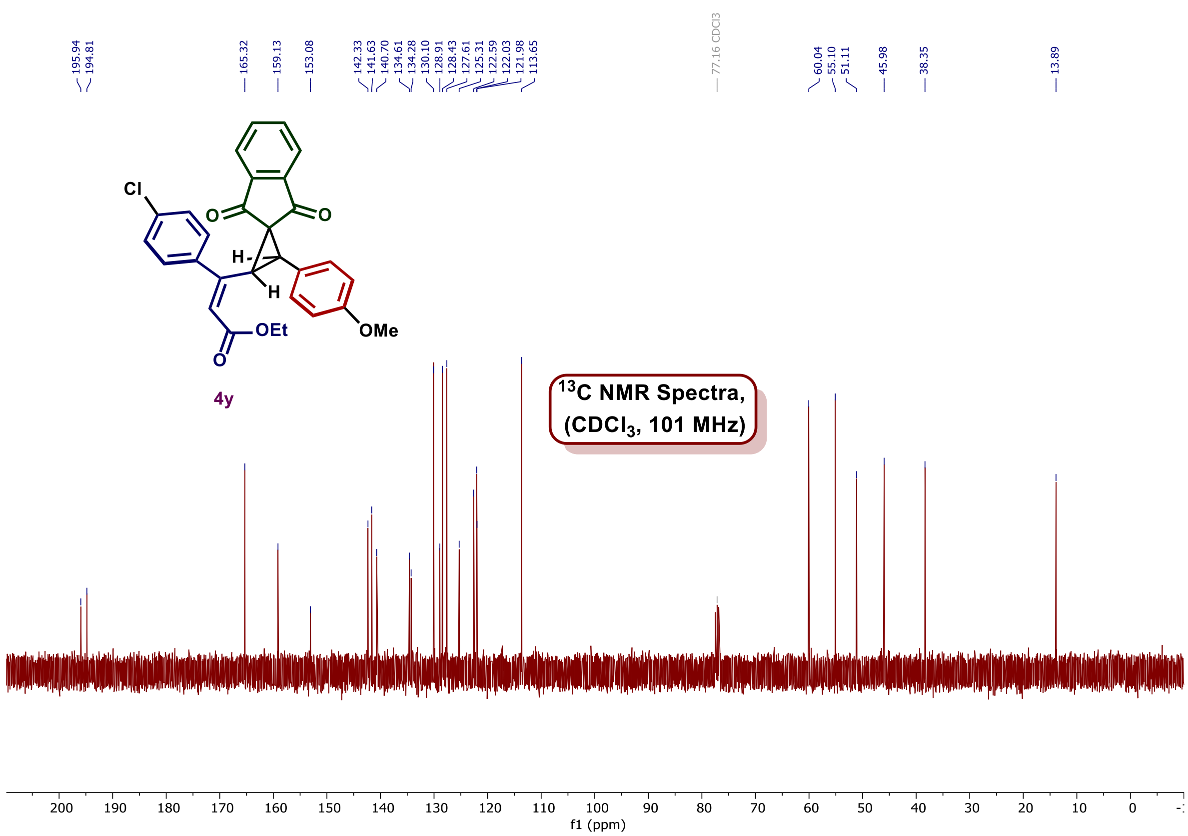
**ethyl (*E*)-3-(3-methoxyphenyl)-3-(2-(4-methoxyphenyl)-1',3'-dioxo-1',3'-dihydrospiro[cyclopropane-1,2'-inden]-3-yl)acrylate (4x):**



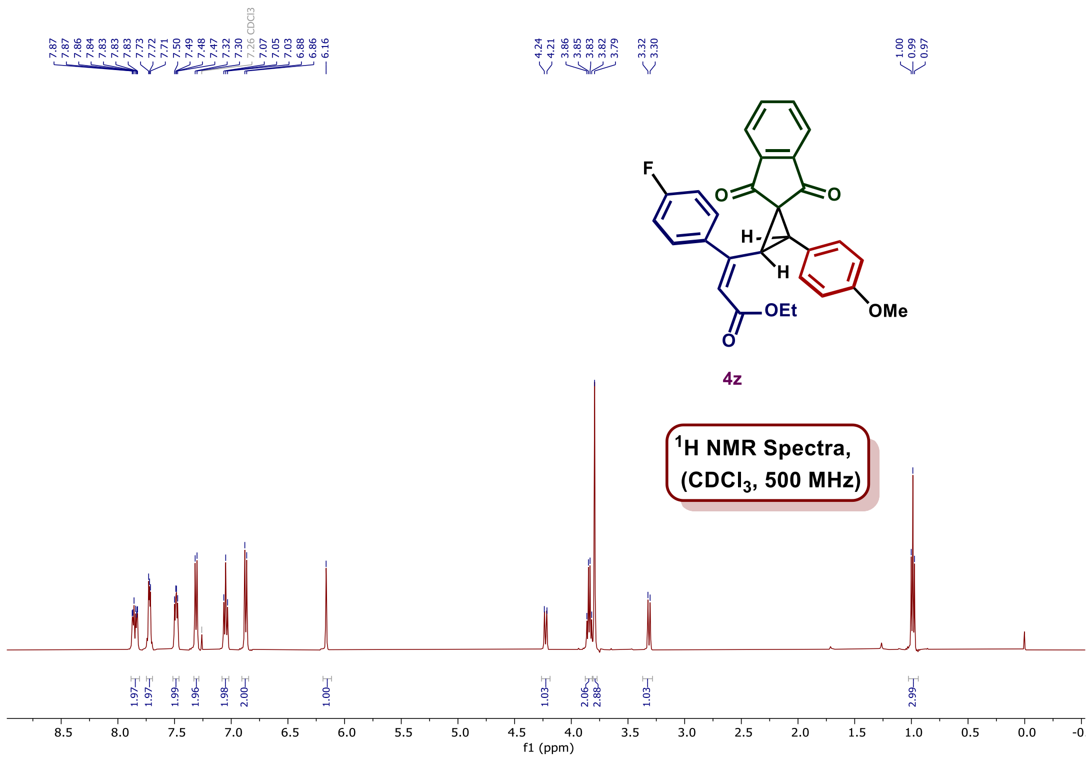



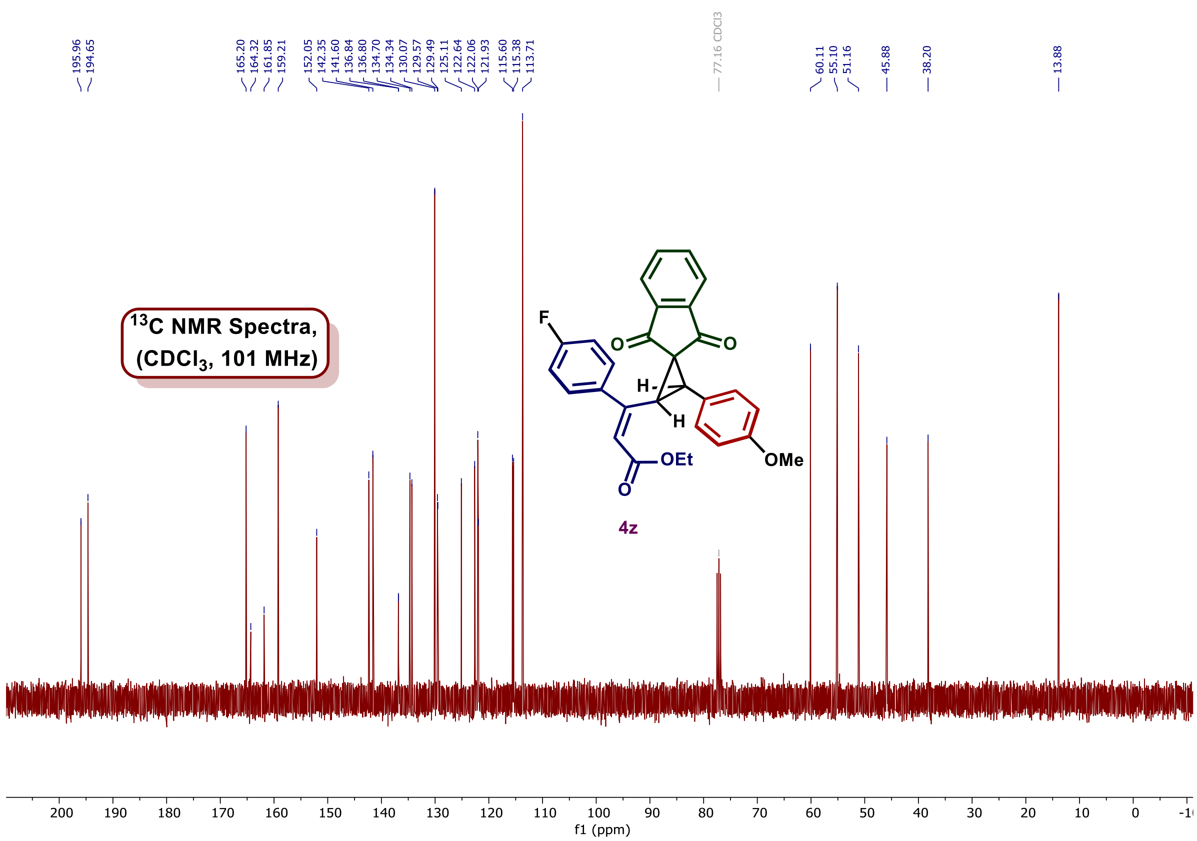
**ethyl (*E*)-3-(4-chlorophenyl)-3-(2-(4-methoxyphenyl)-1',3'-dioxo-1',3'-dihydrospiro[cyclopropane-1,2'-inden]-3-yl) acrylate (4y):**

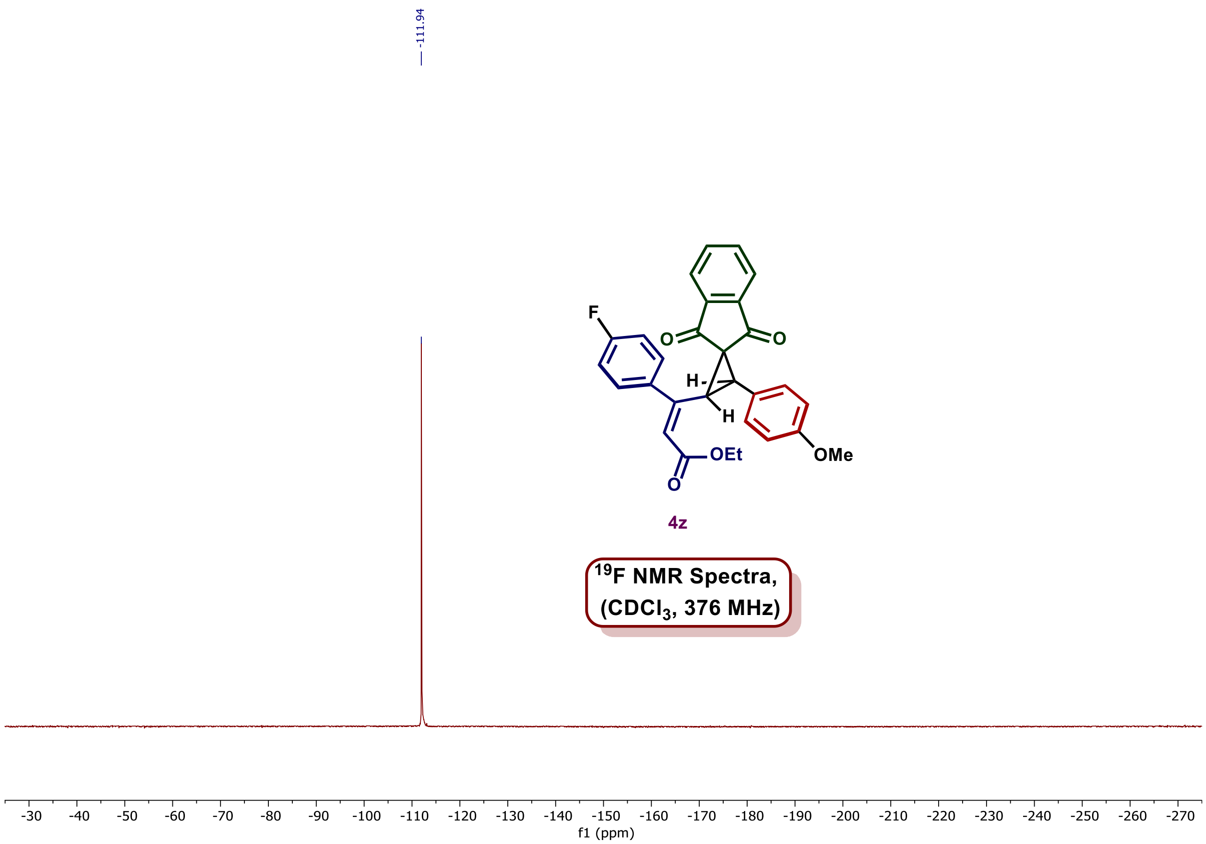


**ethyl (*E*)-3-(4-chlorophenyl)-3-(2-(4-methoxyphenyl)-1',3'-dioxo-1',3'-dihydrospiro[cyclopropane-1,2'-inden]-3-yl) acrylate (4z):**



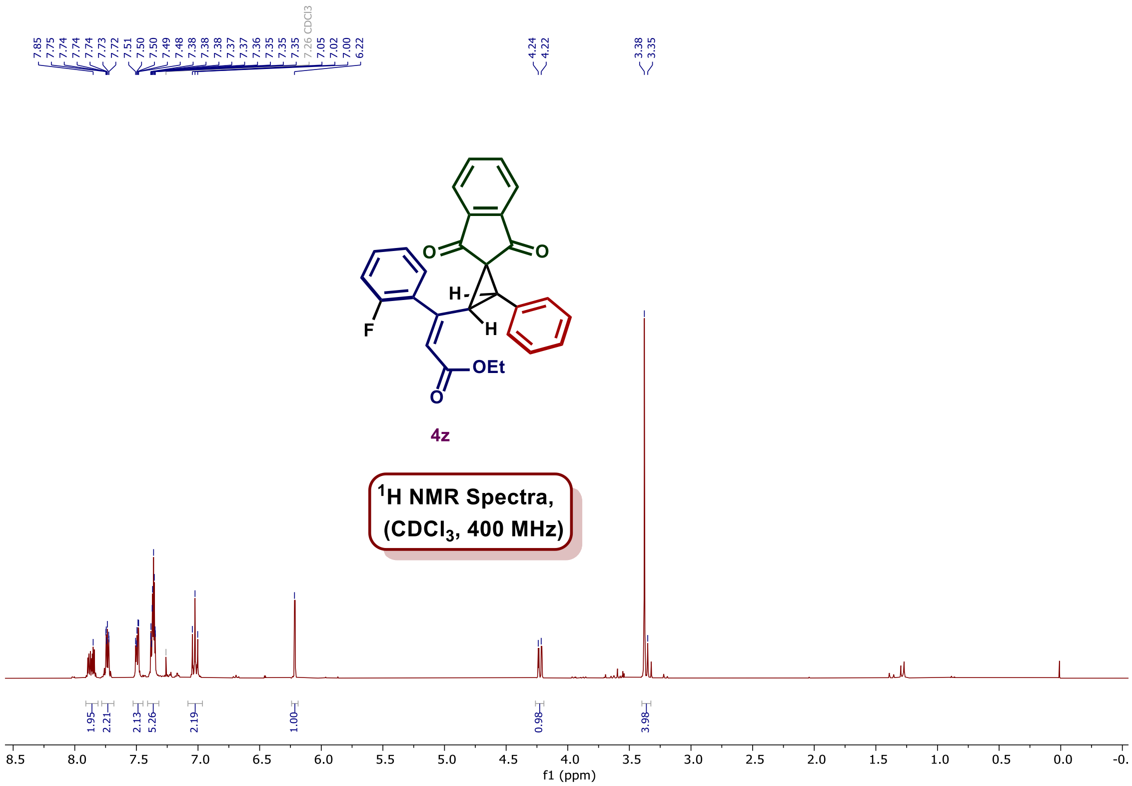



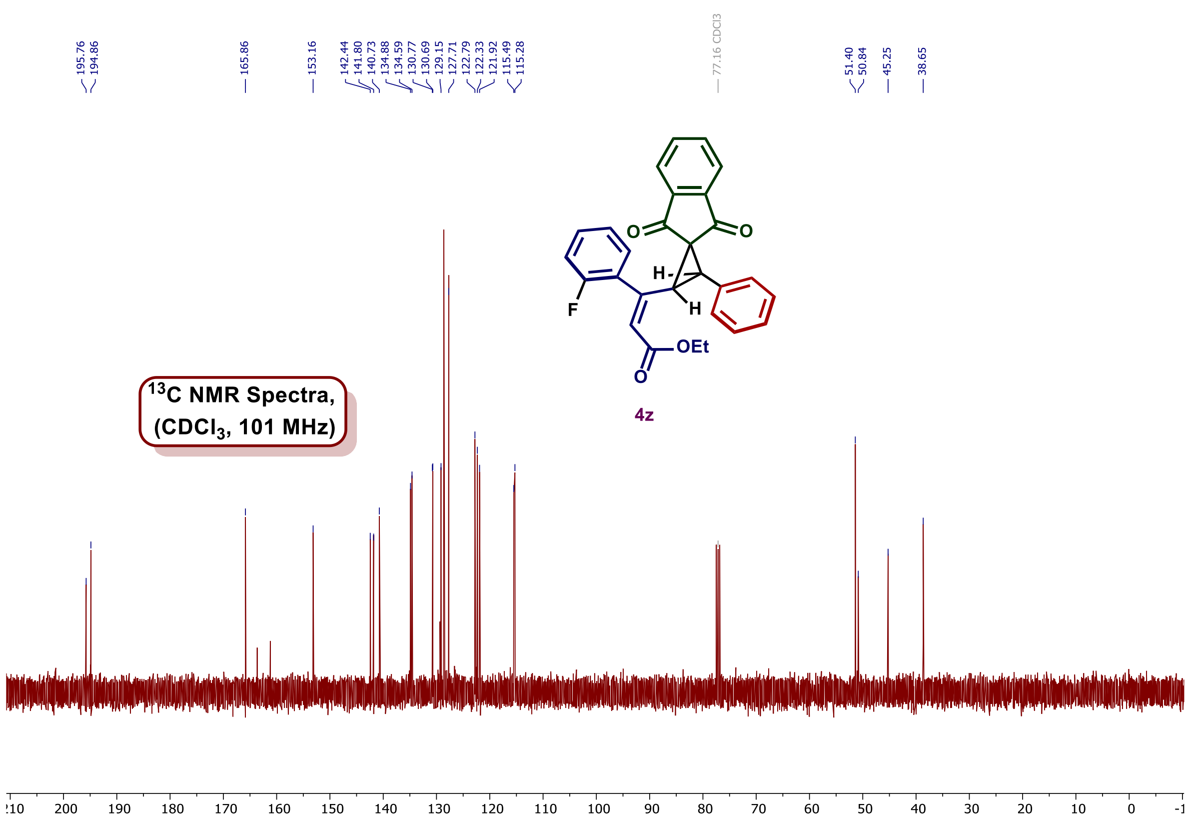


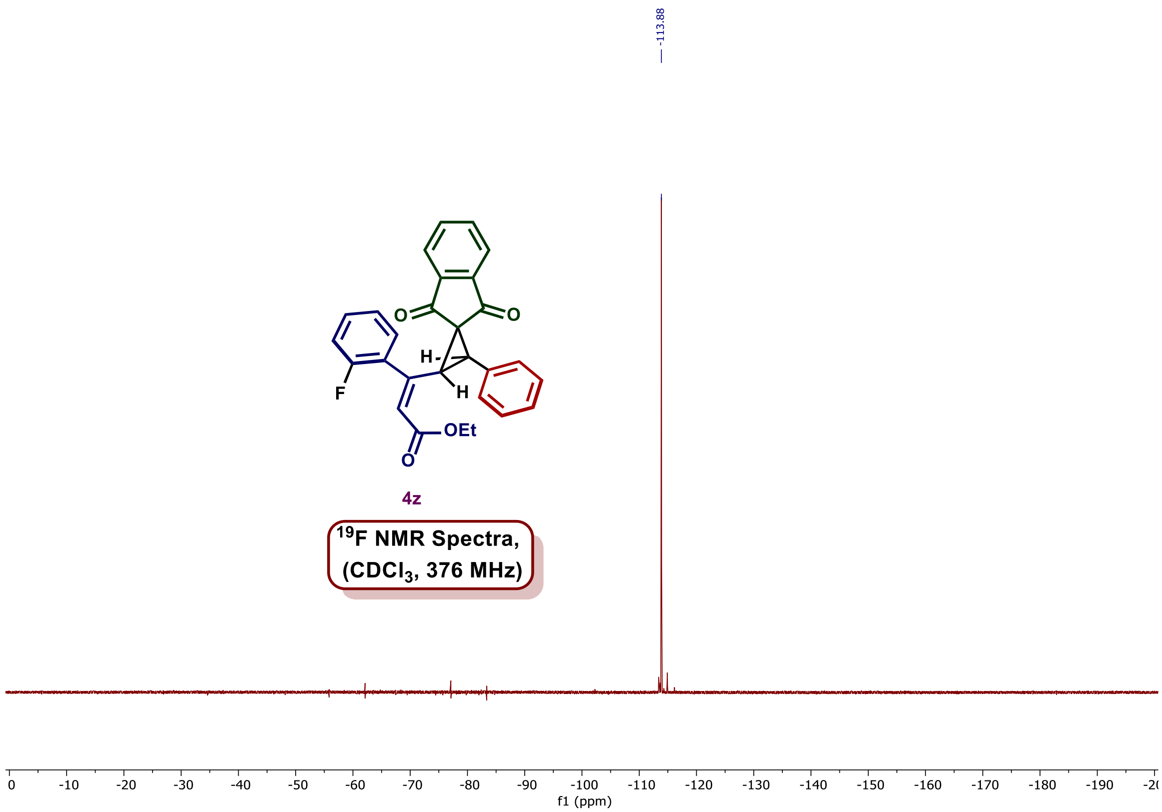

4z

$^{19}$F NMR Spectra,
($CDCl_3$, 376 MHz)

**Methyl (*E*)-3-(2-fluorophenyl)-3-(2-phenyl)-1',3'-dioxo-1',3'-dihydrospiro[cyclopropane-1,2'-inden]-3-yl) acrylate (4aa):**

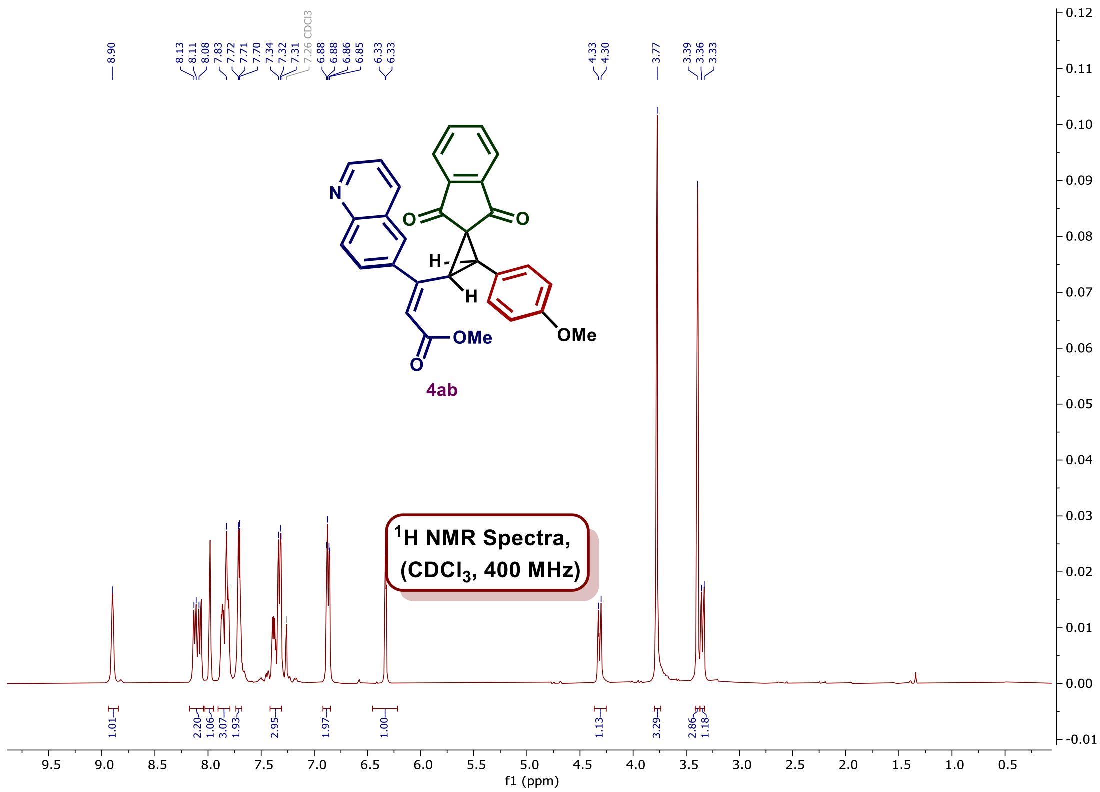


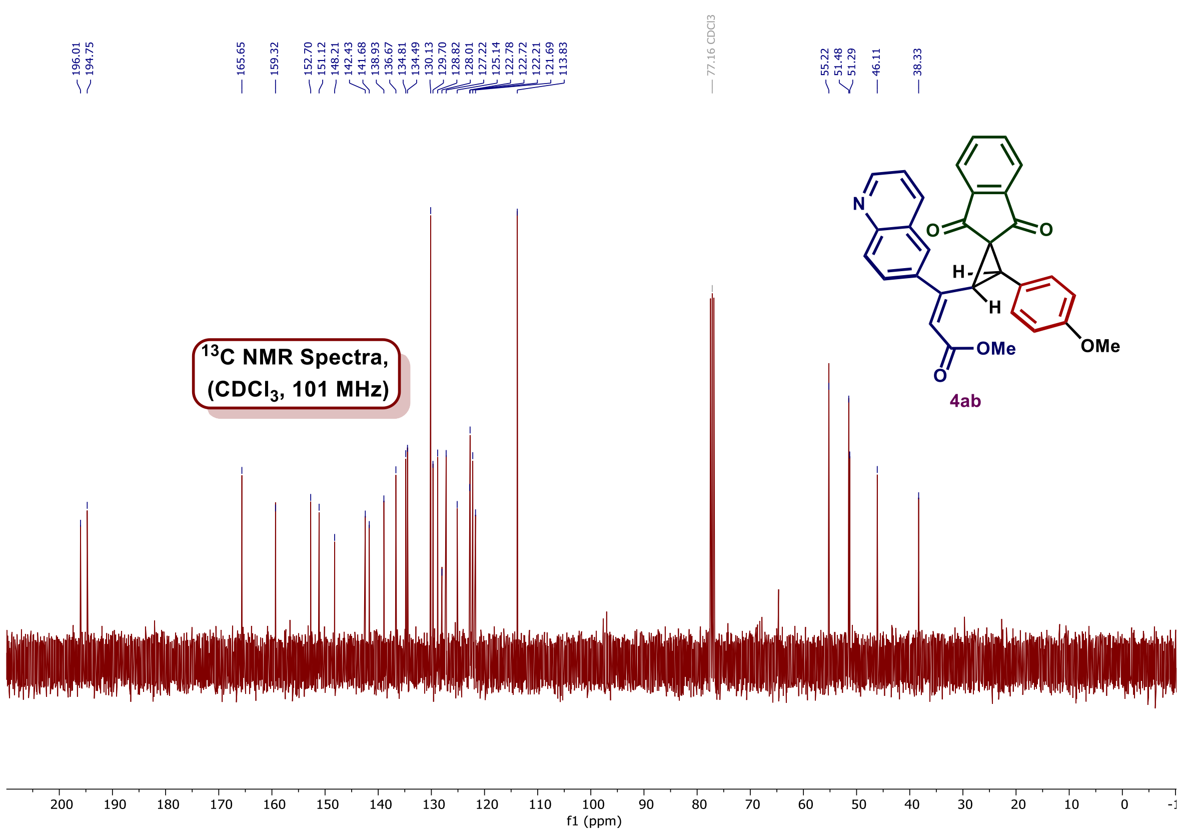





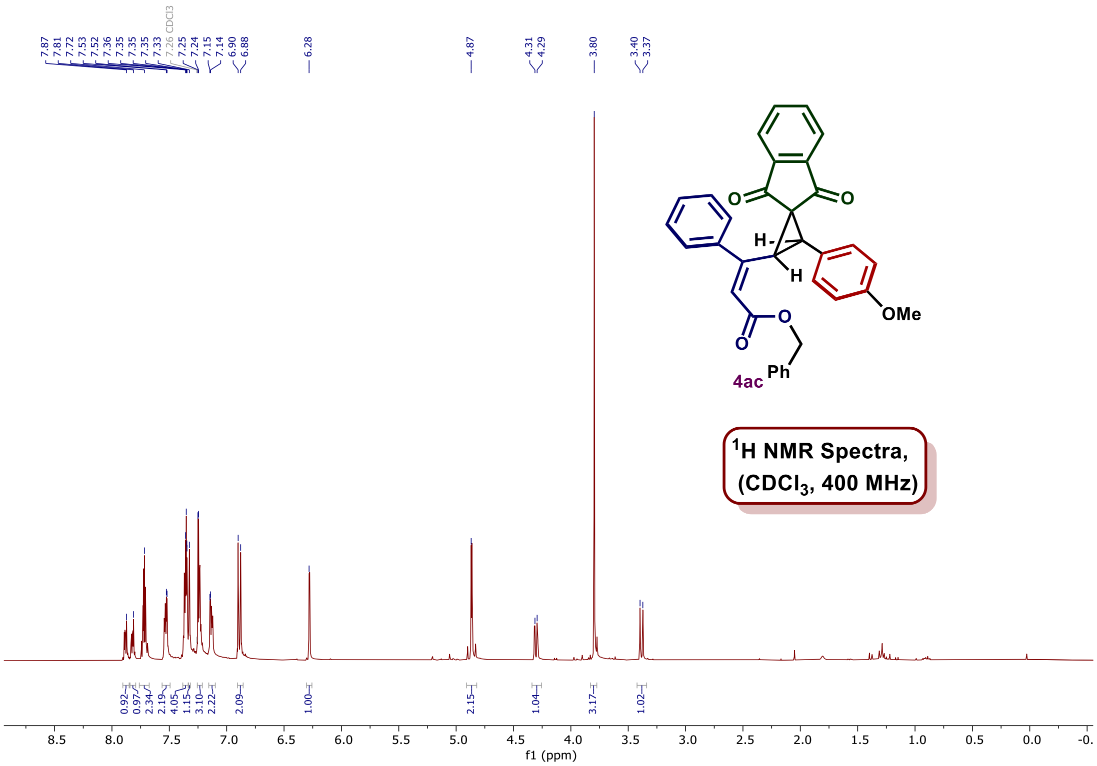
-113.88
O
O
H
H
F
OEt
O
4z
19F NMR Spectra,
(CDCl3, 376 MHz)
0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190
f1 (ppm)

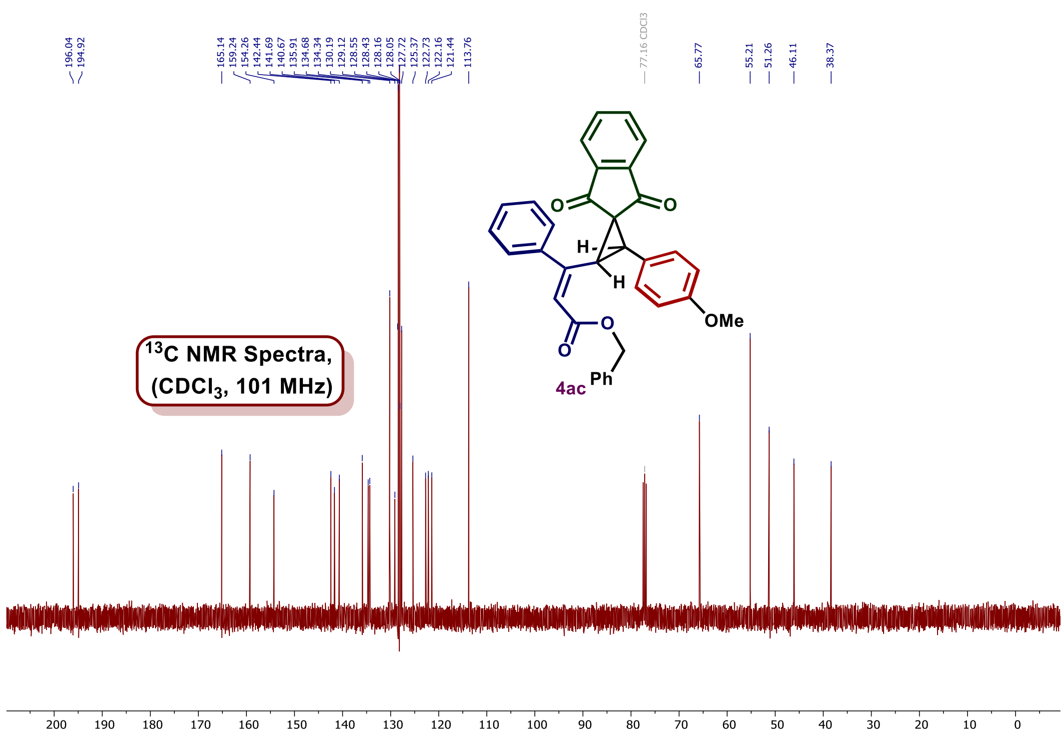
**methyl (*E*)-3-(2-(4-methoxyphenyl)-1',3'-dioxo-1',3'-dihydrospiro[cyclopropane-1,2'-inden]-3-yl)-3-(quinolin-6-yl)acrylate (4ab):**



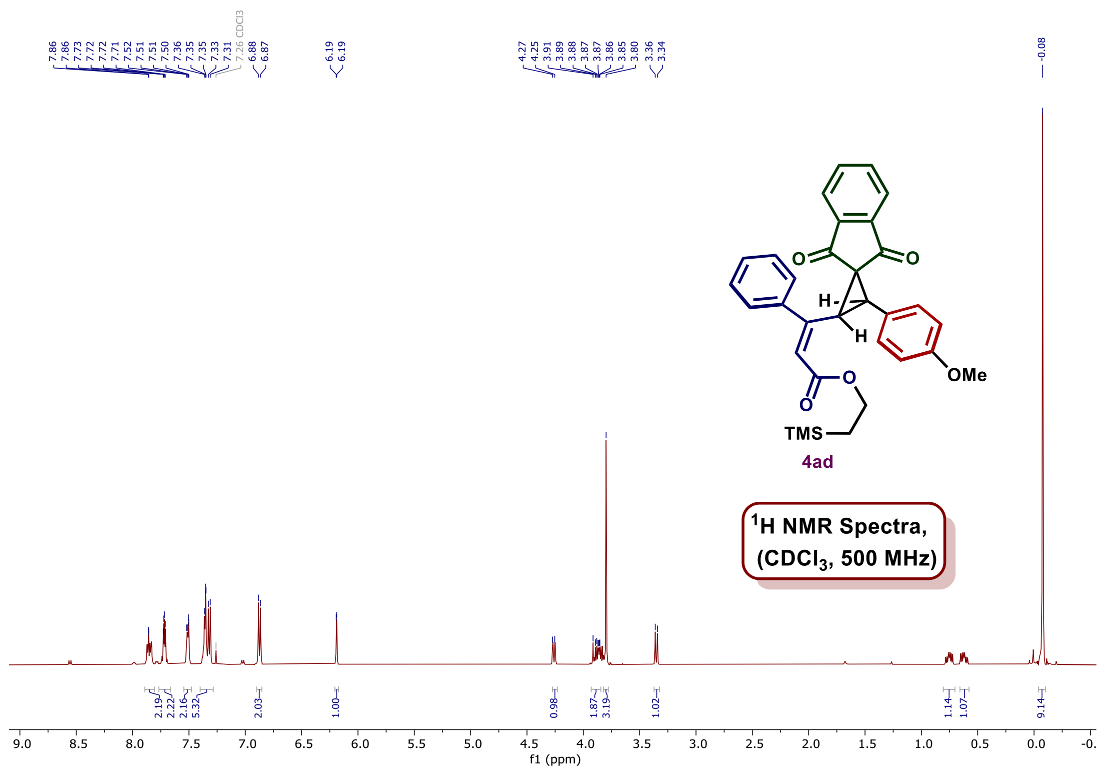


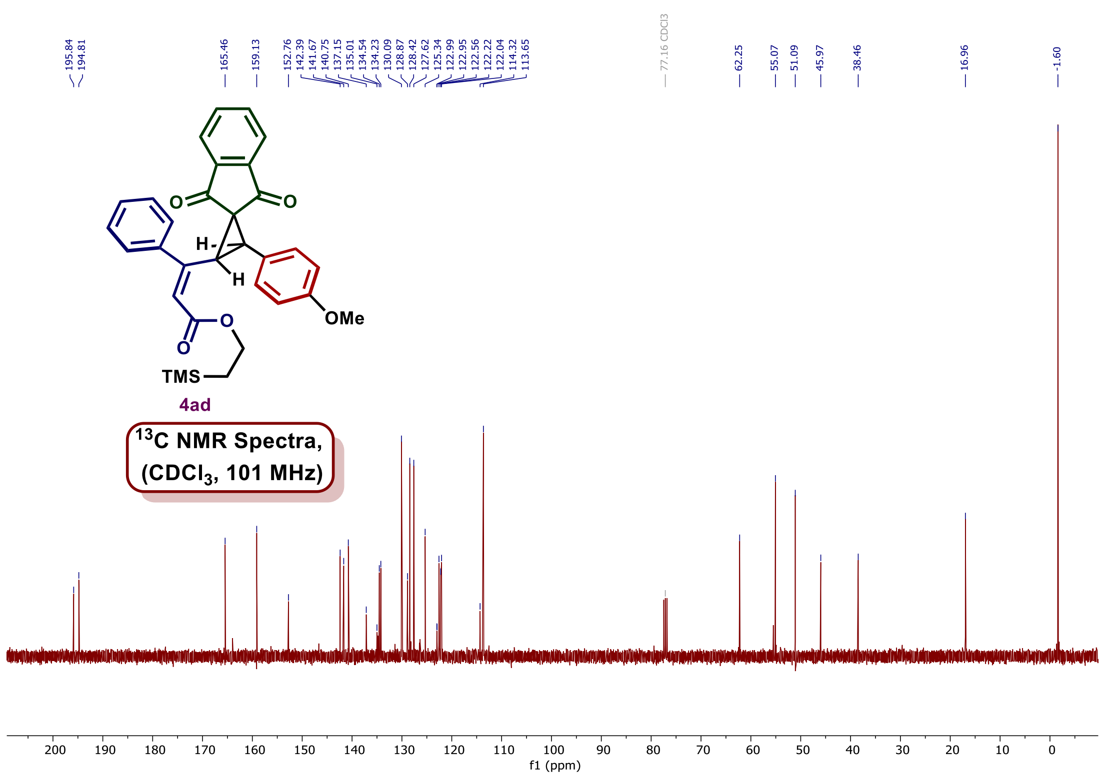
**benzyl (*E*)-3-(2-(4-methoxyphenyl)-1',3'-dioxo-1',3'-dihydrospiro[cyclopropane-1,2'-inden]-3-yl)-3-phenylacrylate (4ac):**



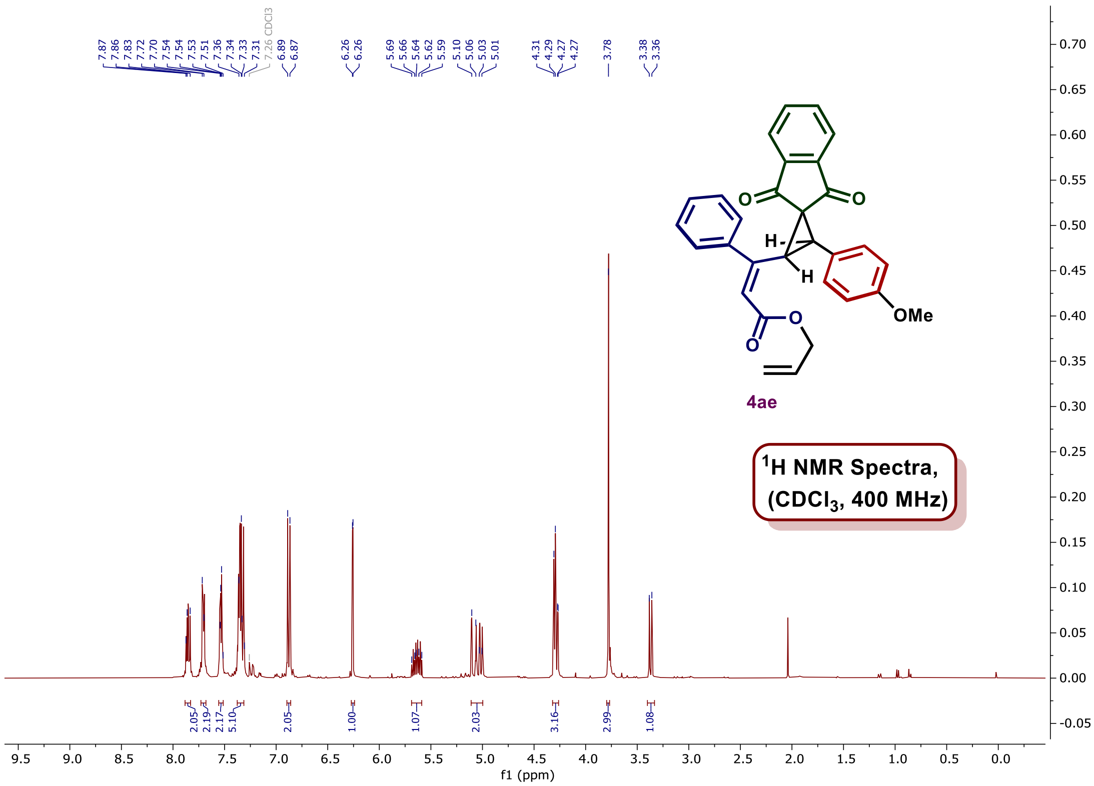



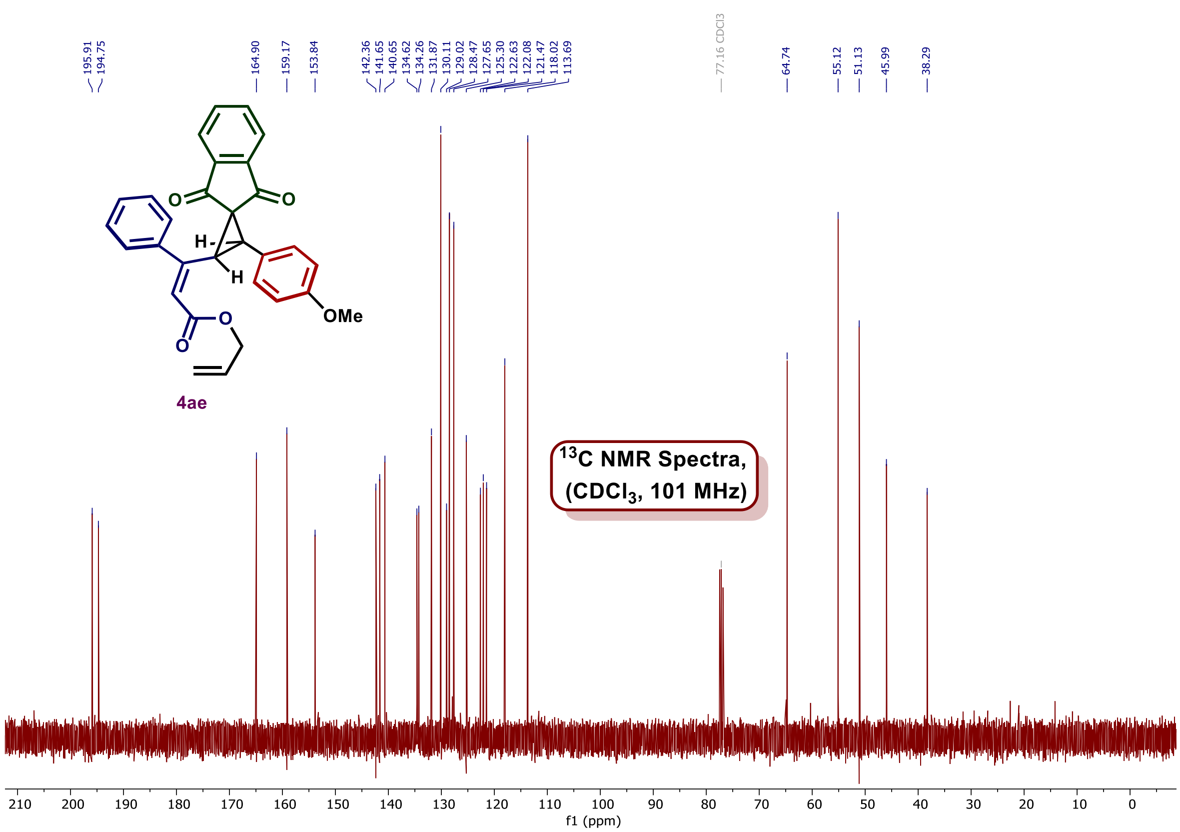
**2-(trimethylsilyl)ethyl (*E*)-3-(2-(4-methoxyphenyl)-1',3'-dioxo-1',3'-dihydrospiro[cyclopropane-1,2'-inden]-3-yl)-3-phenylacrylate (4ad):**



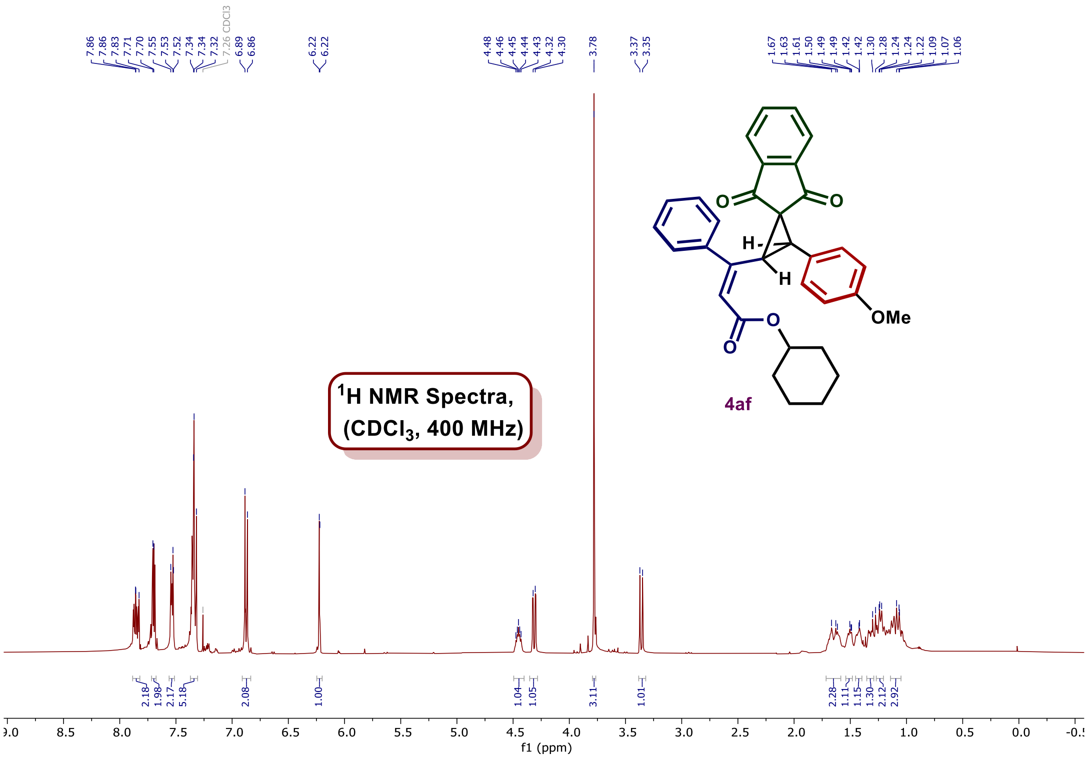



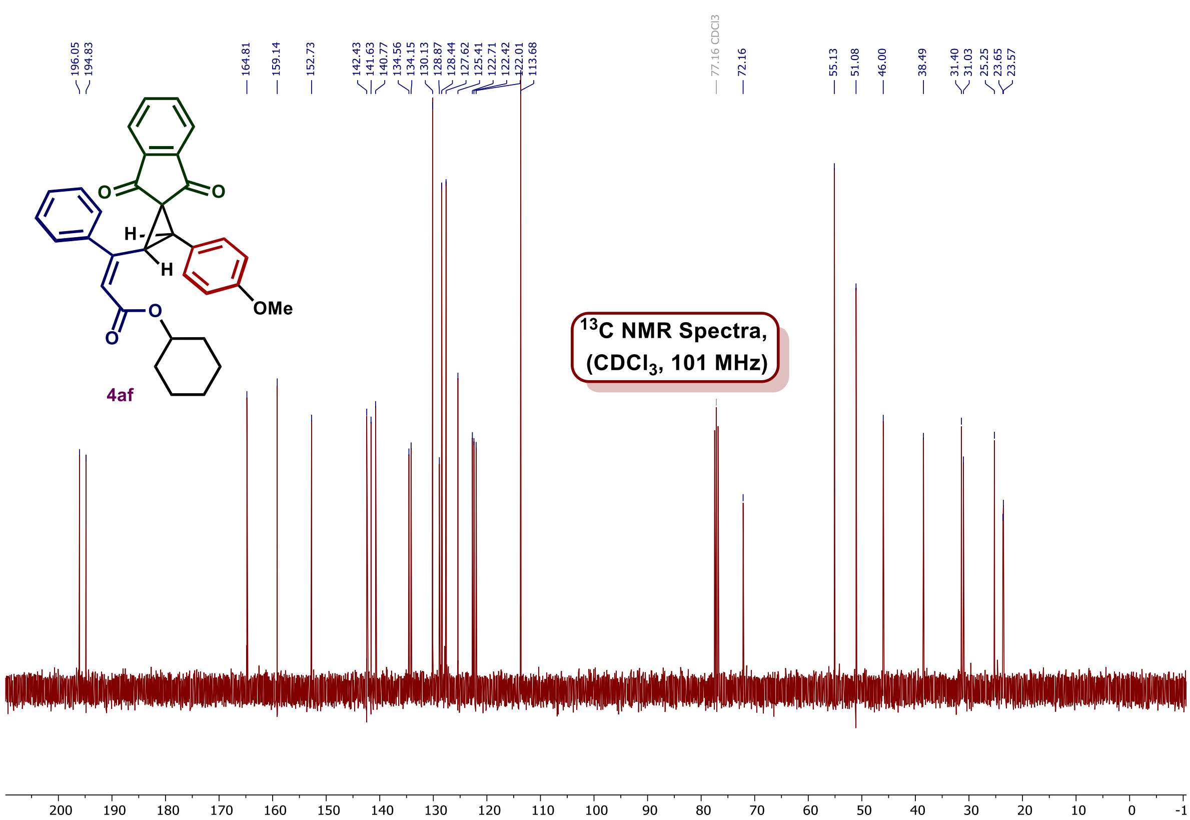
**allyl (*E*)-3-(2-(4-methoxyphenyl)-1',3'-dioxo-1',3'-dihydrospiro[cyclopropane-1,2'-inden]-3-yl)-3-phenylacrylate (4ae):**



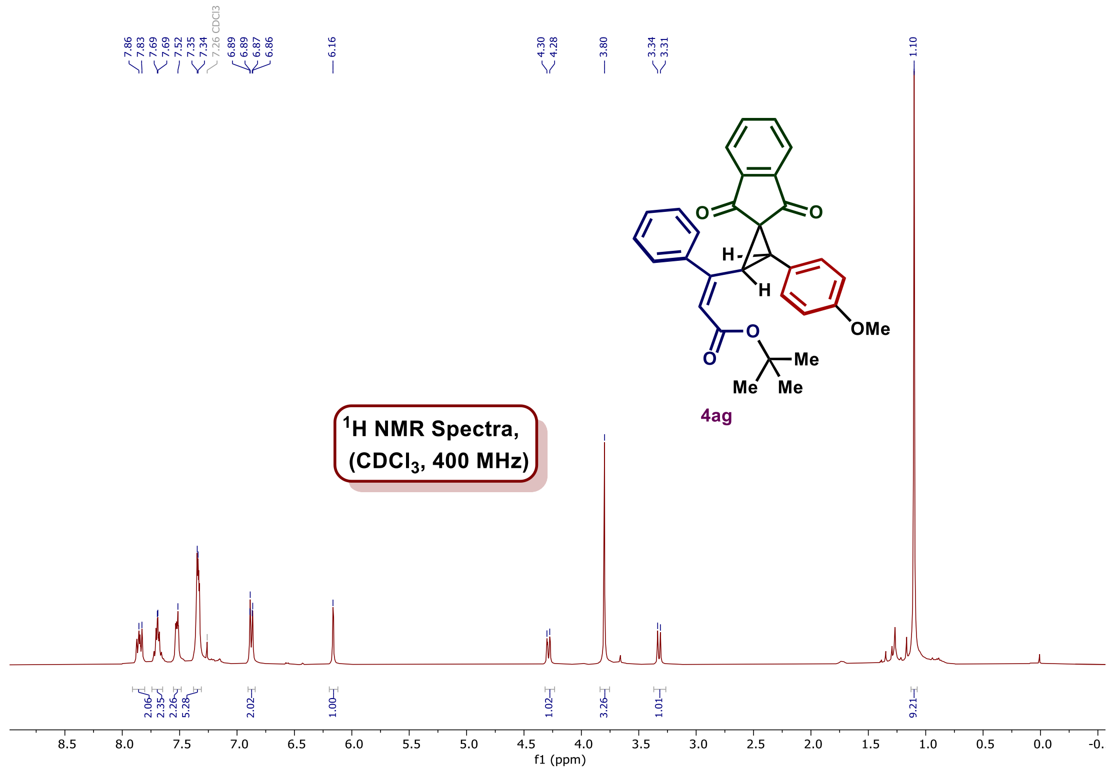



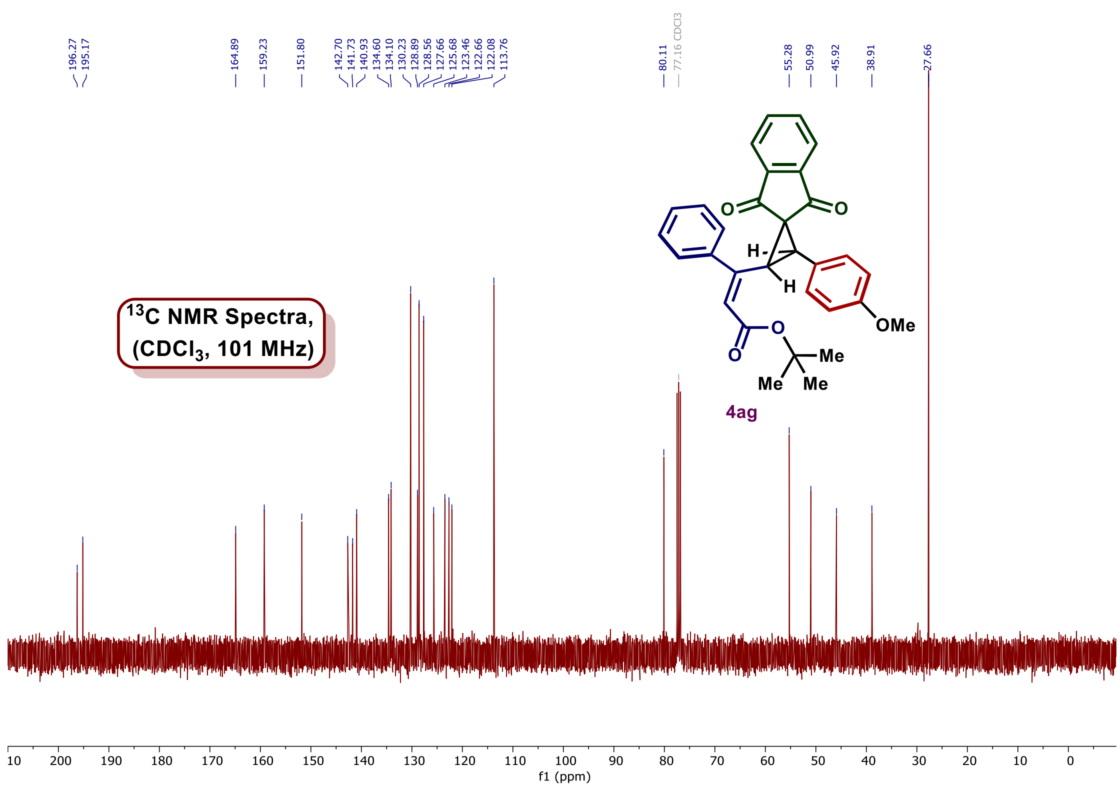
**cyclohexyl (*E*)-3-(2-(4-methoxyphenyl)-1',3'-dioxo-1',3'-dihydrospiro[cyclopropane-1,2'-inden]-3-yl)-3-phenylacrylate (4af):**



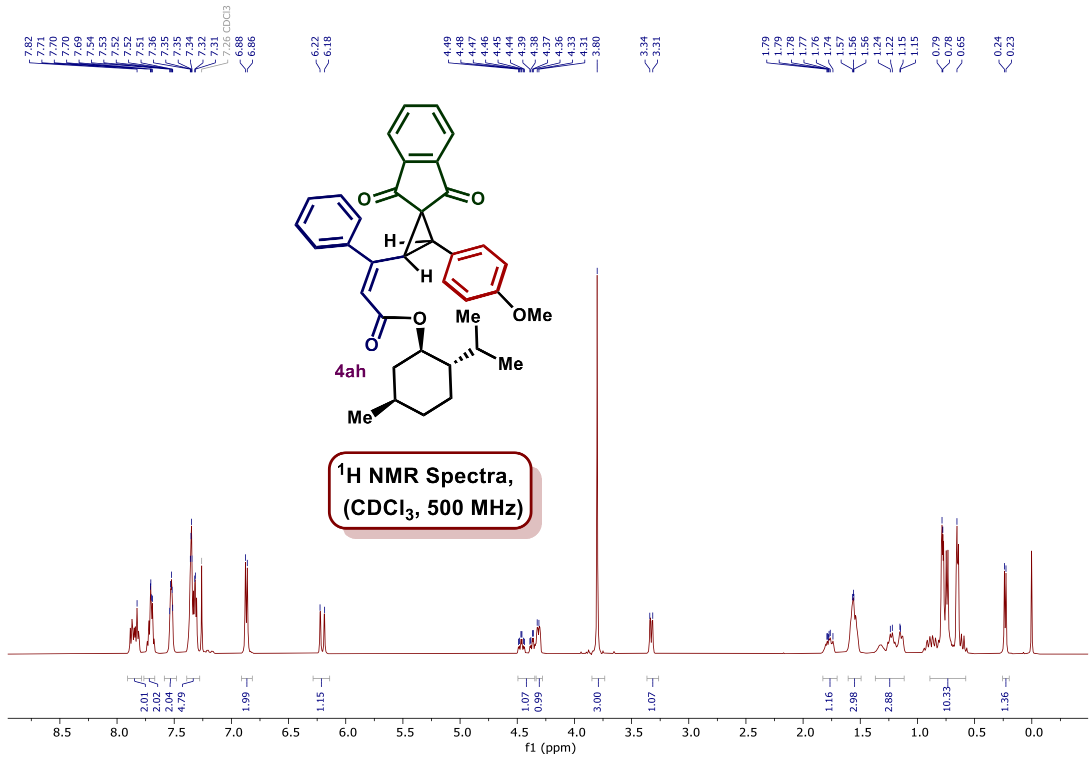



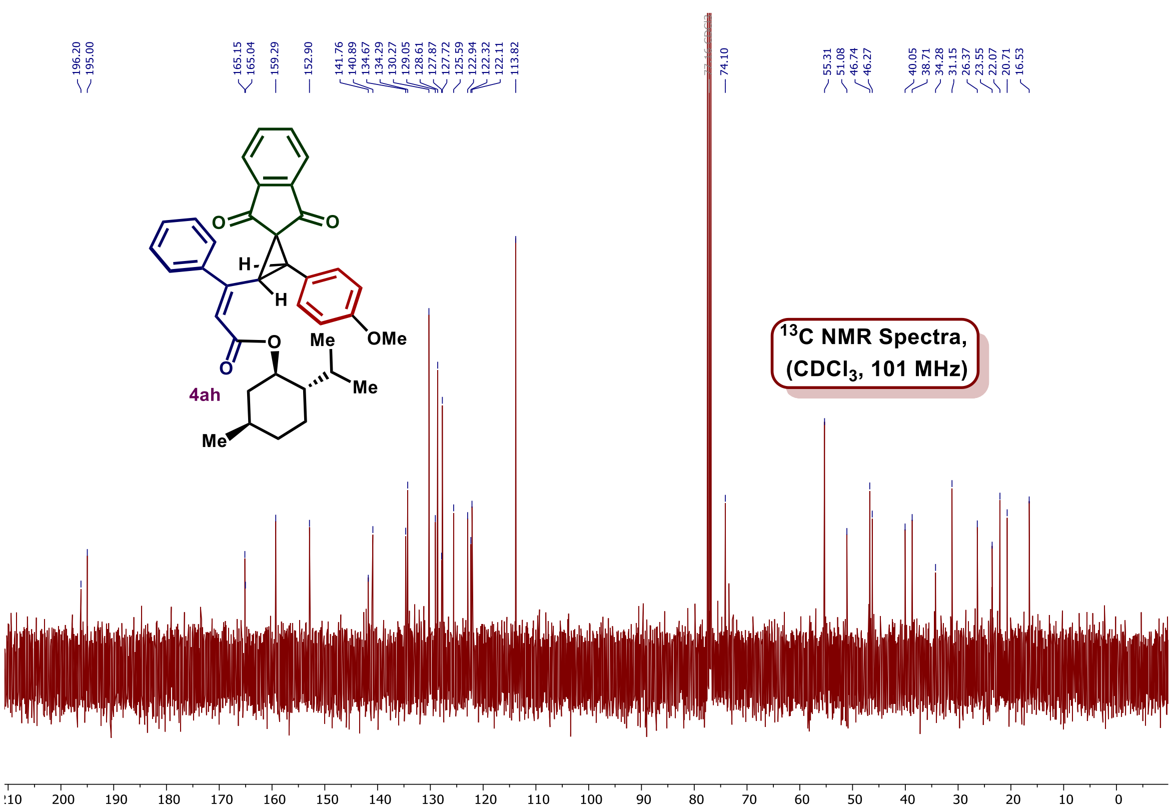
***tert*-butyl (*E*)-3-(2-(4-methoxyphenyl)-1',3'-dioxo-1',3'-dihydrospiro[cyclopropane-1,2'-inden]-3-yl)-3-phenylacrylate (4ag):**



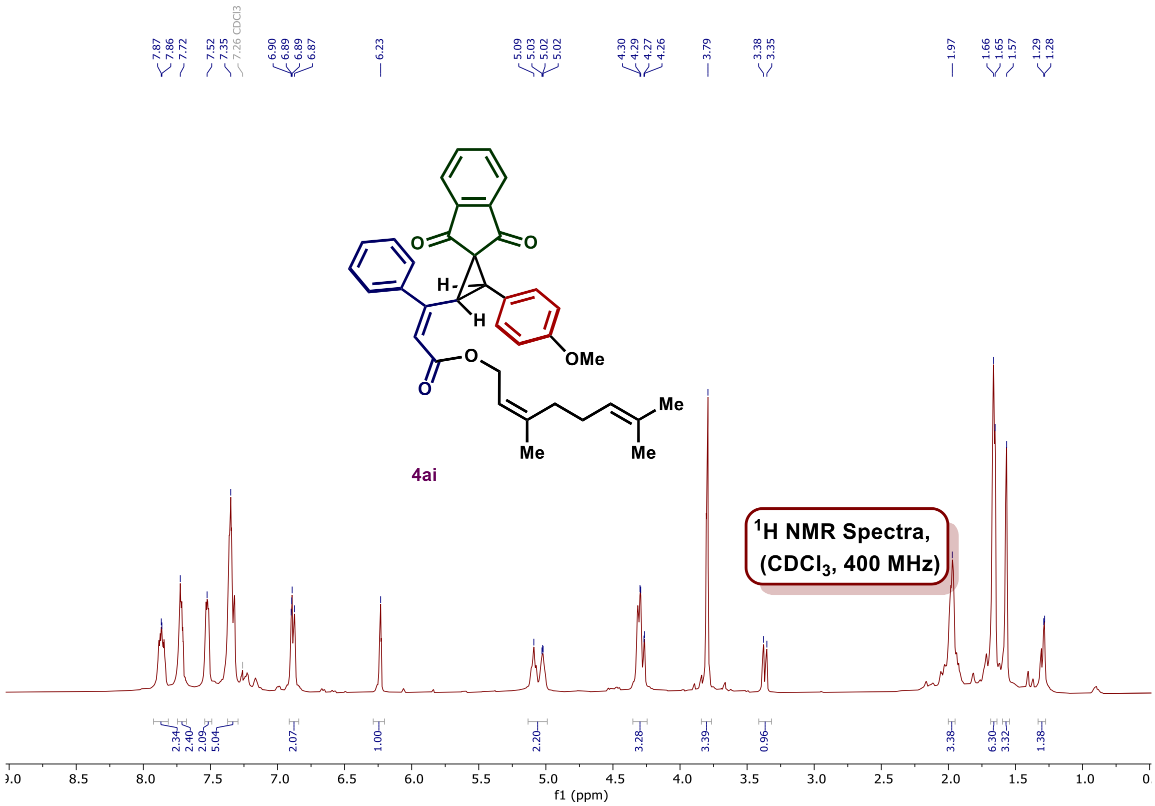



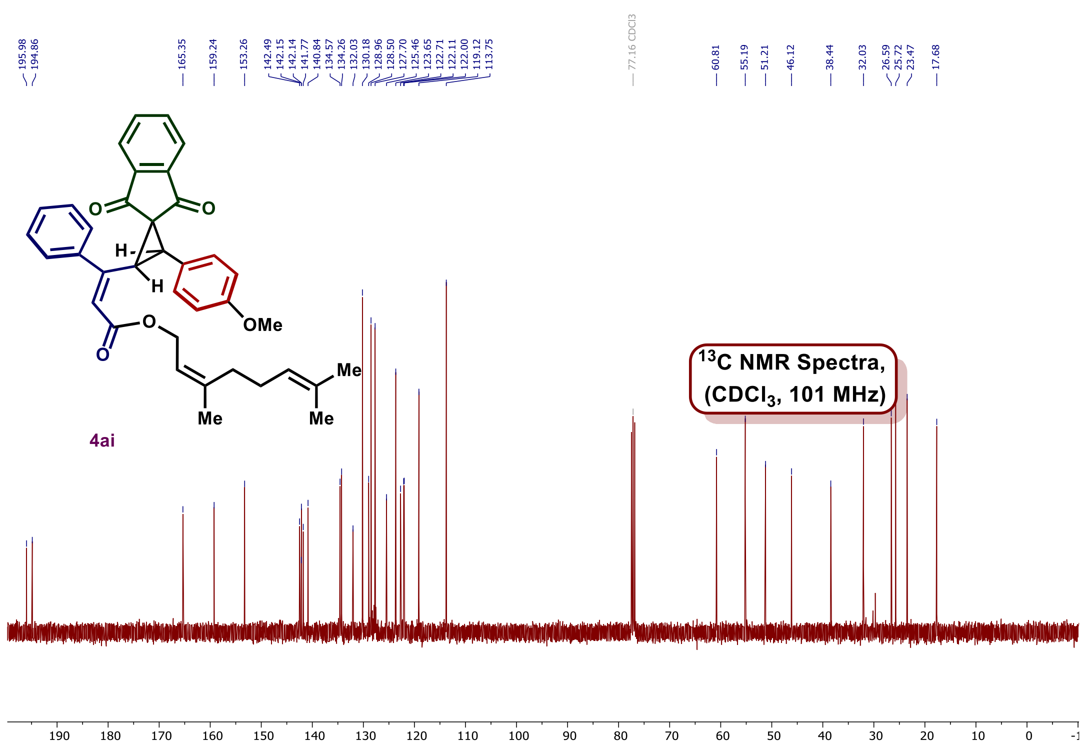
**(1*R*,2*S*,5*R*)-2-isopropyl-4-methylcyclohexyl (*E*)-3-(2-(4-methoxyphenyl)-1',3'-dioxo-1',3'-dihydrospiro[cyclopropane-1,2'-inden]-3-yl)-3-phenylacrylate (4ah):**



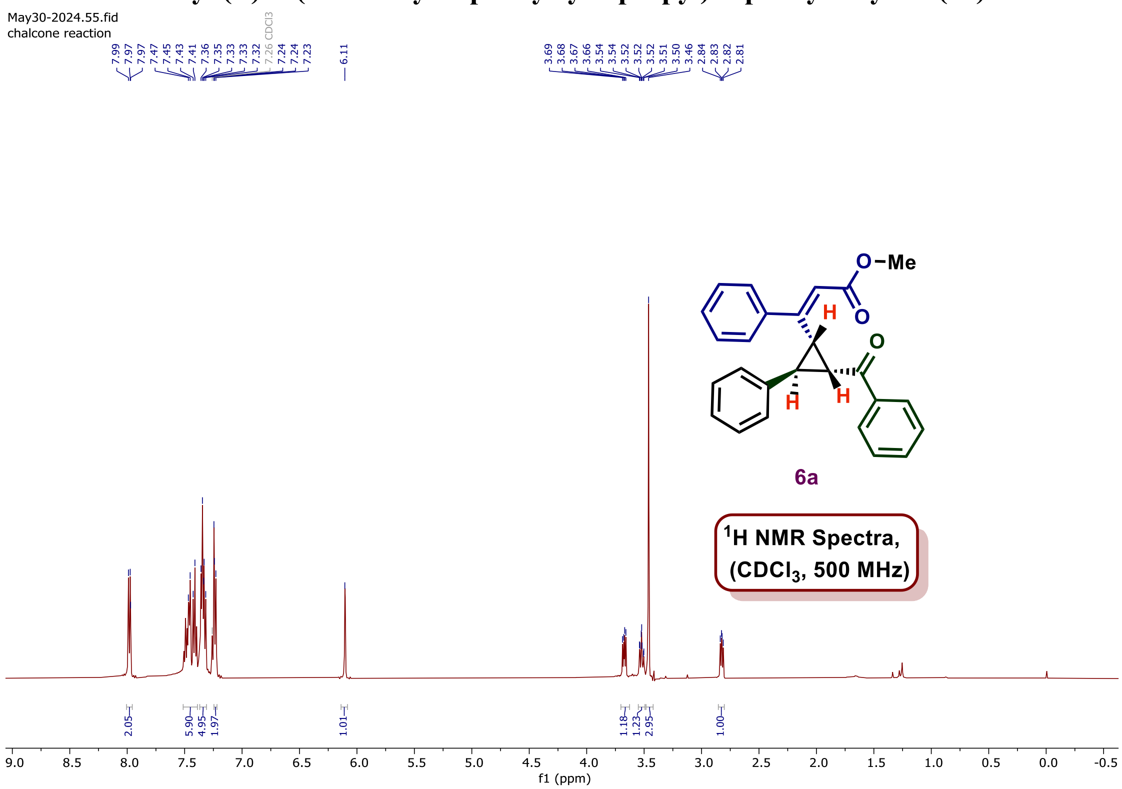



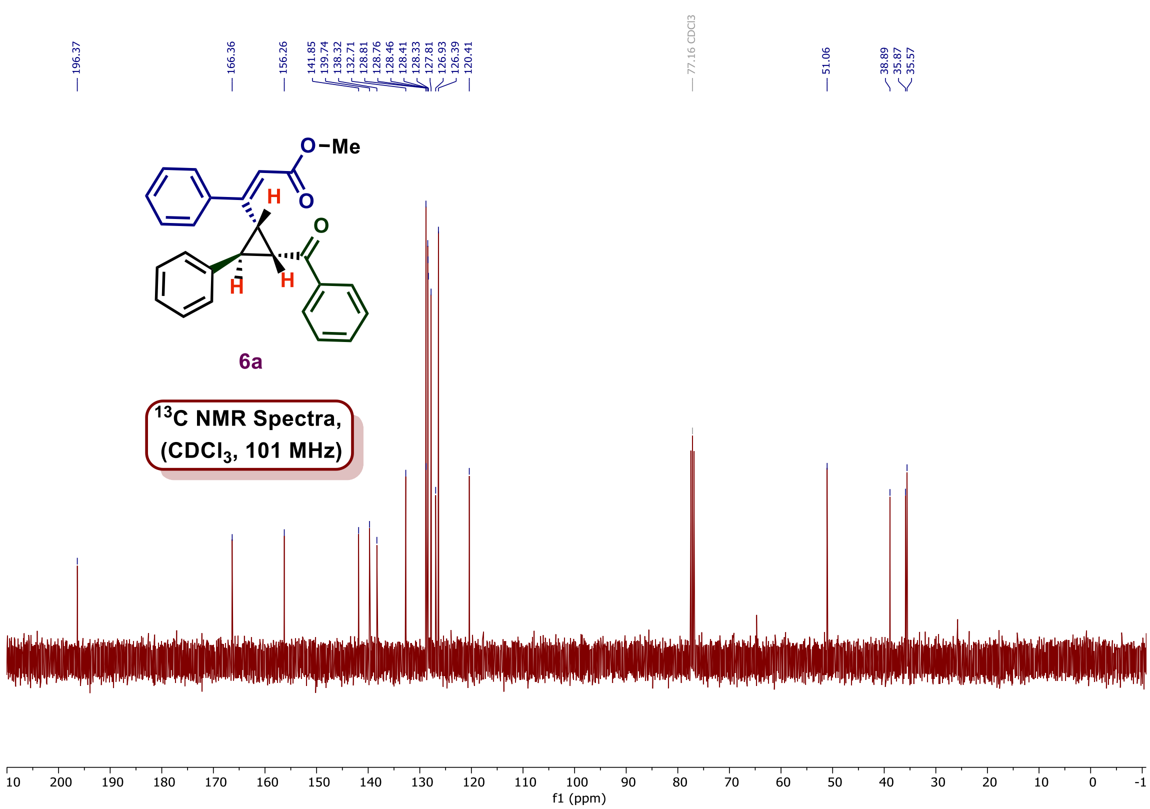
**(*Z*)-3,7-dimethylocta-2,6-dien-1-yl (*E*)-3-(2-(4-methoxyphenyl)-1',3'-dioxo-1',3'-dihydrospiro[cyclopropane-1,2'-inden]-3-yl)-3-phenylacrylate (4ai):**



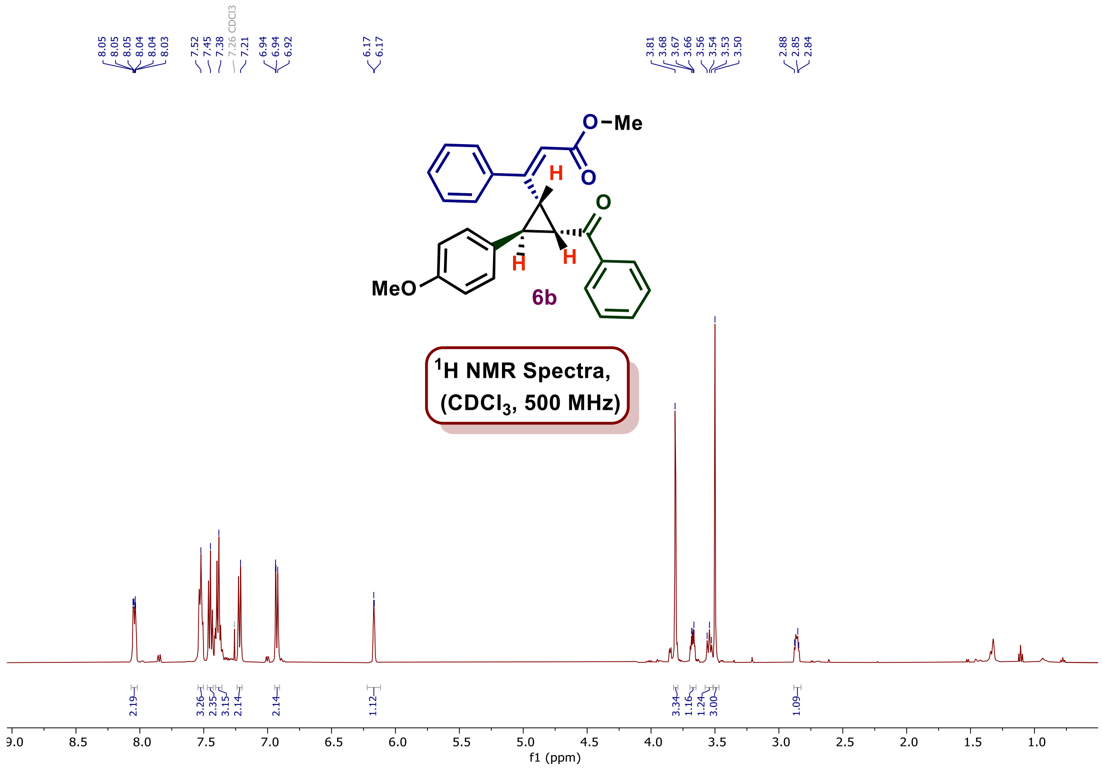



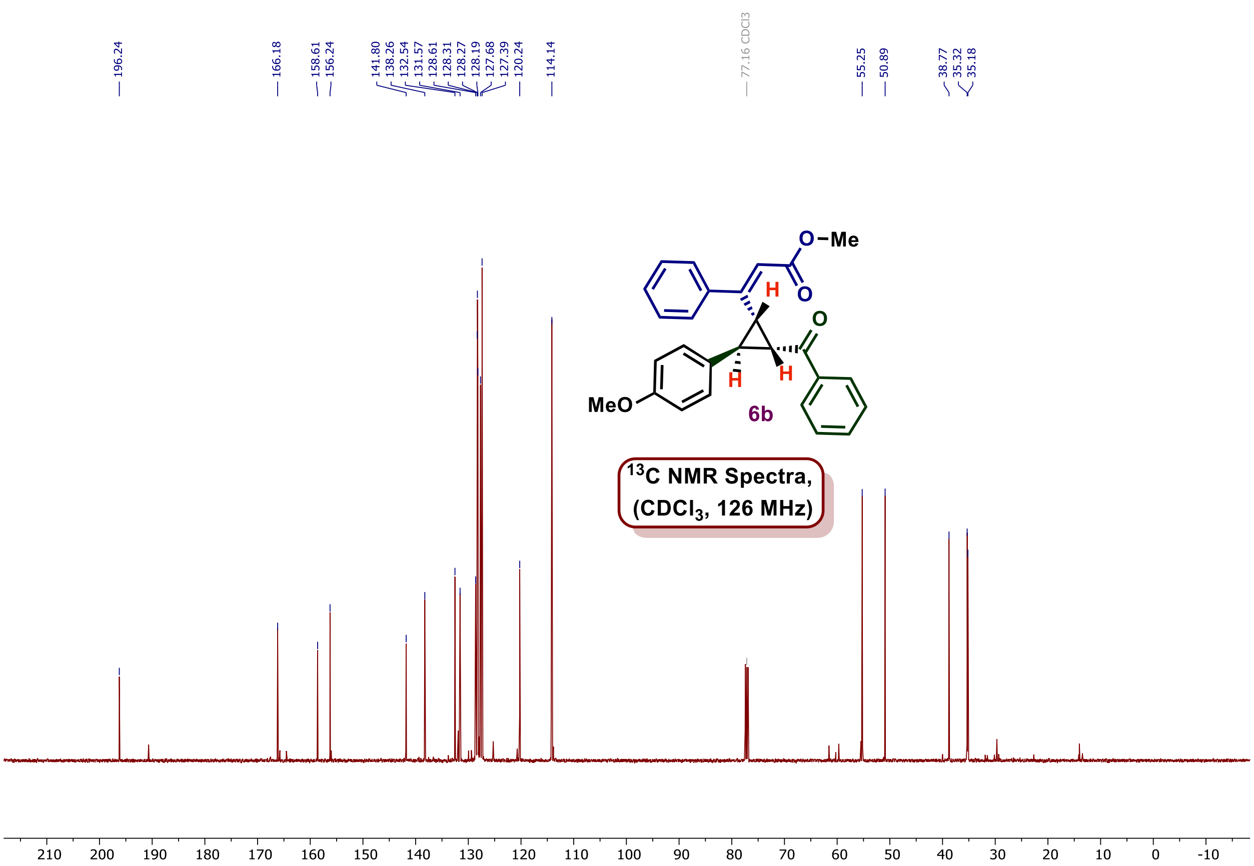
## methyl (*E*)-3-(-2-benzoyl-3-phenylcyclopropyl)-3-phenylacrylate (6a):



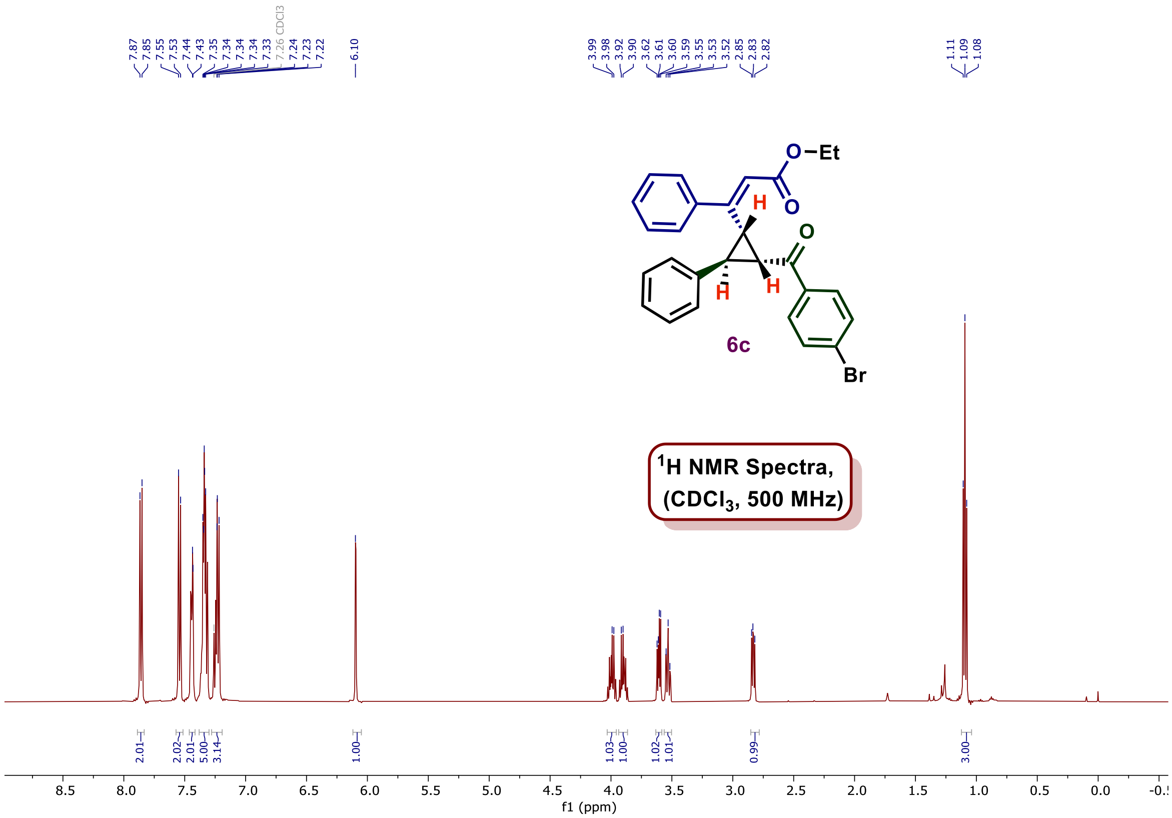



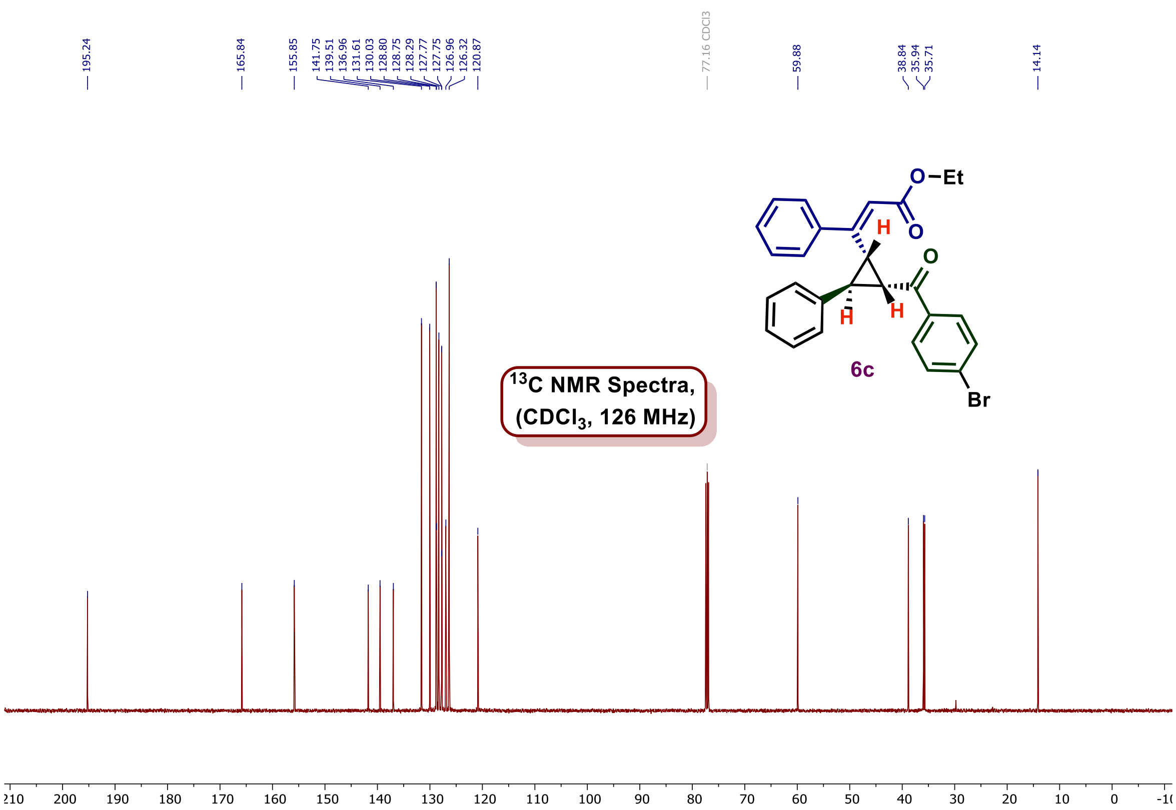
**methyl (*E*)-3-(-2-benzoyl-3-(4-methoxyphenyl)cyclopropyl)-3-phenylacrylate (6b):**



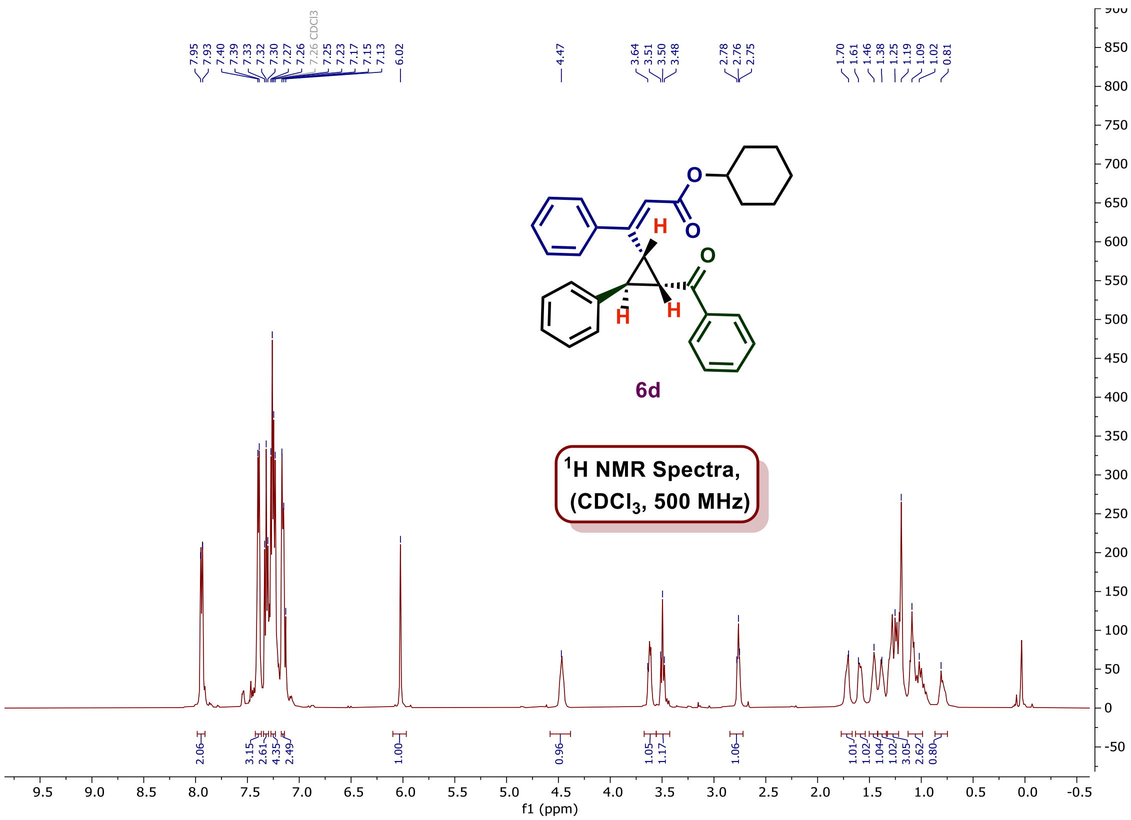



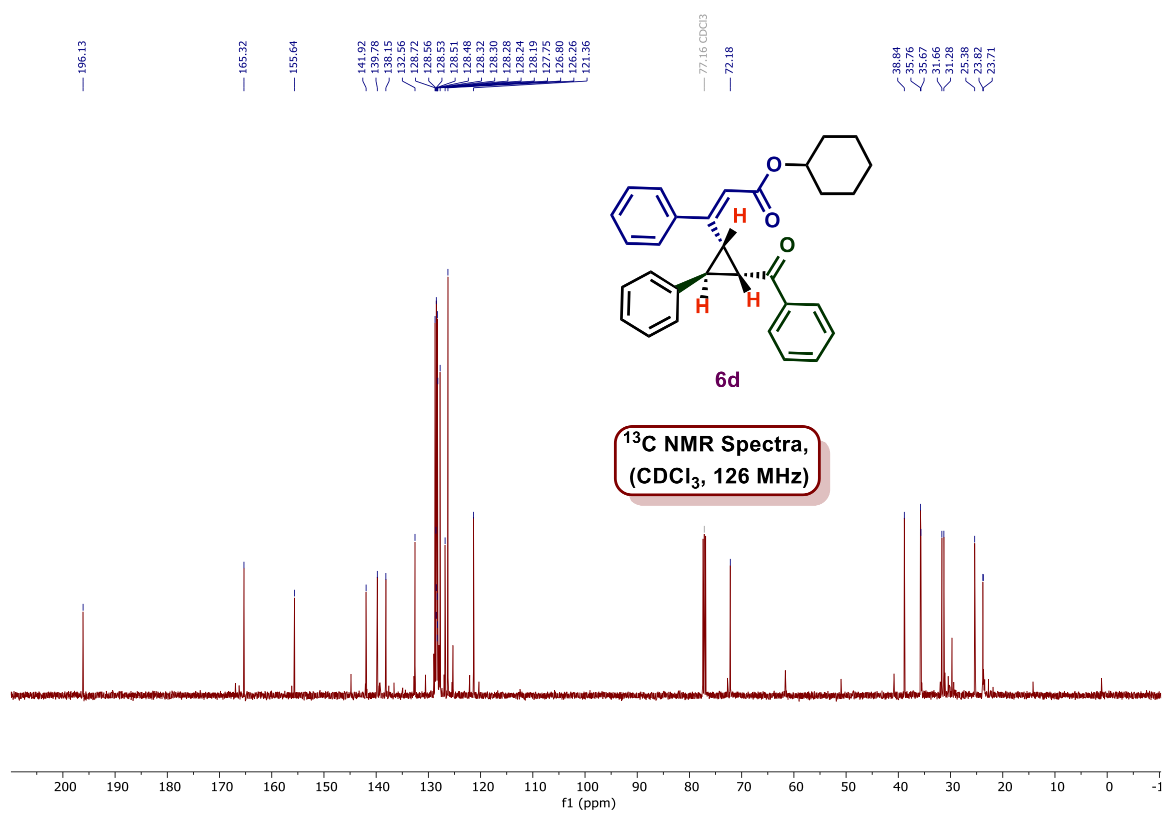
**ethyl (*E*)-3-(-2-(4-bromobenzoyl)-3-phenylcyclopropyl)-3-phenylacrylate (6c):**



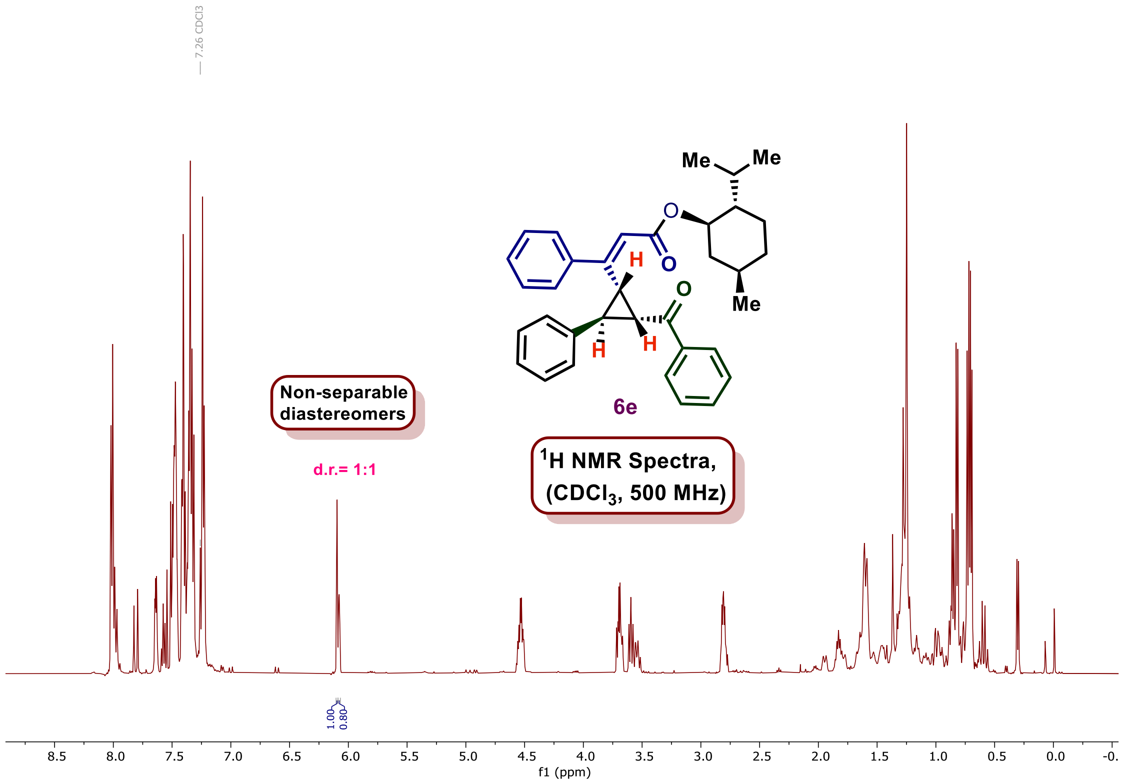



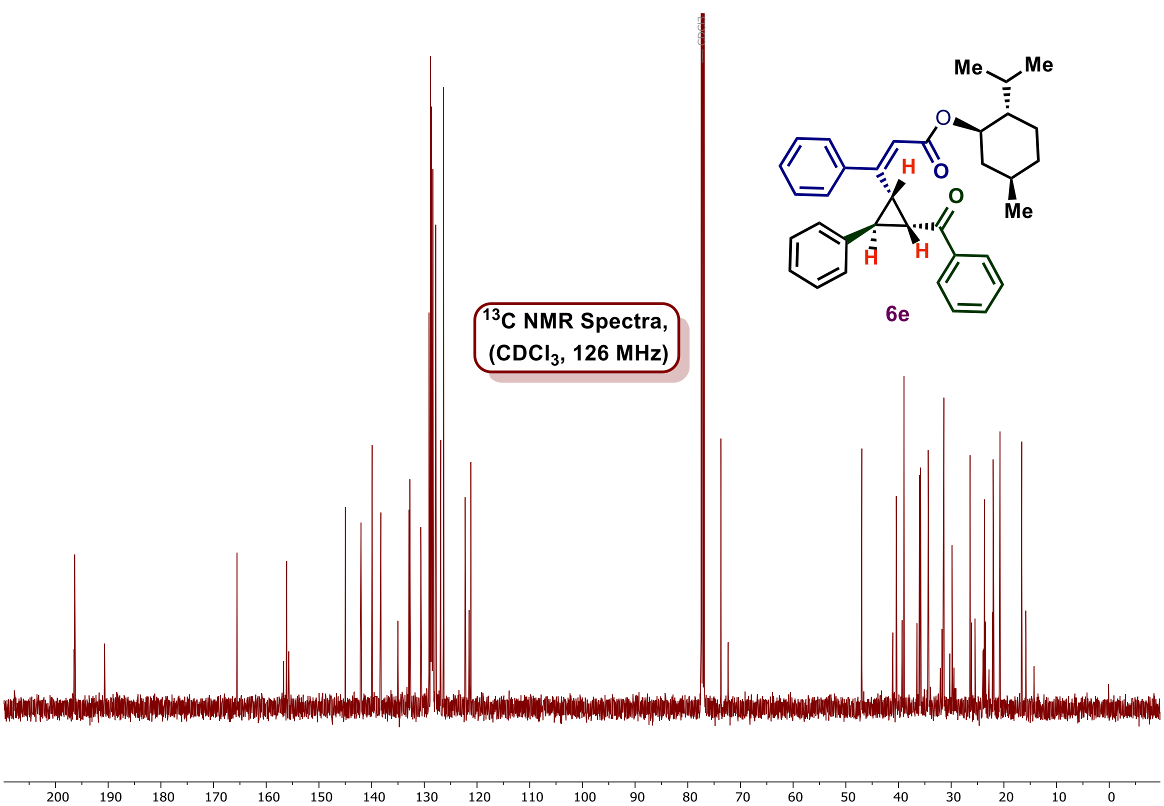
**cyclohexyl (*E*)-3-(-2-benzoyl-3-phenylcyclopropyl)-3-phenylacrylate (6d):**



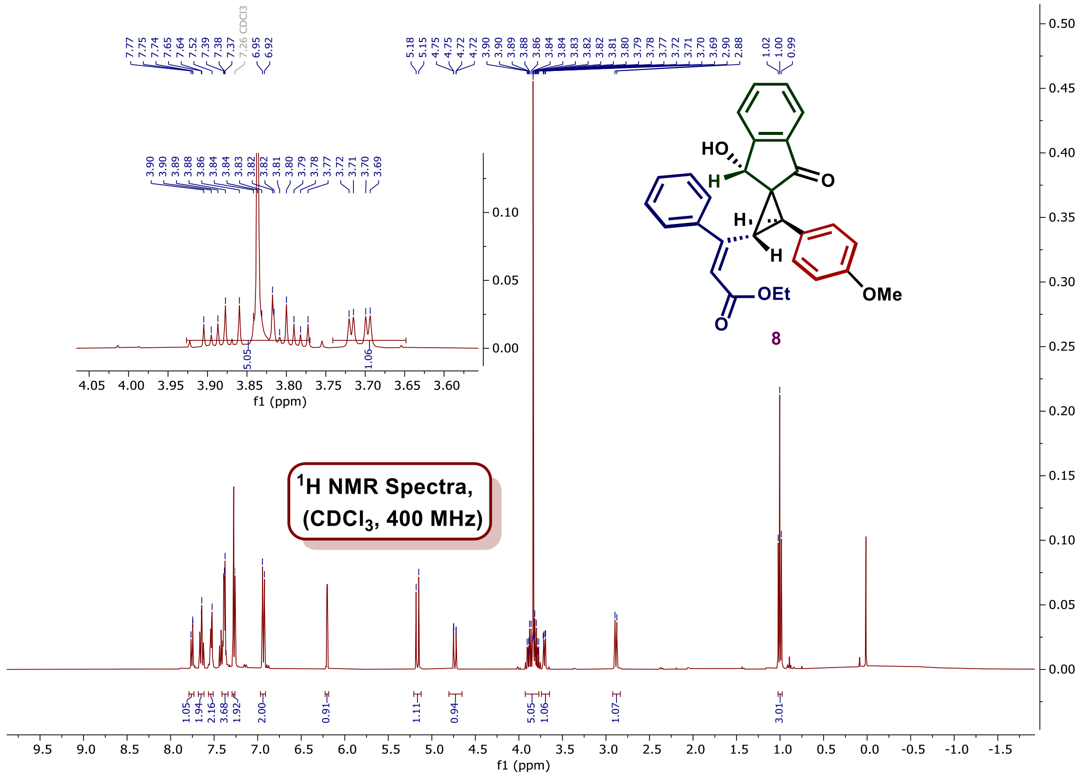



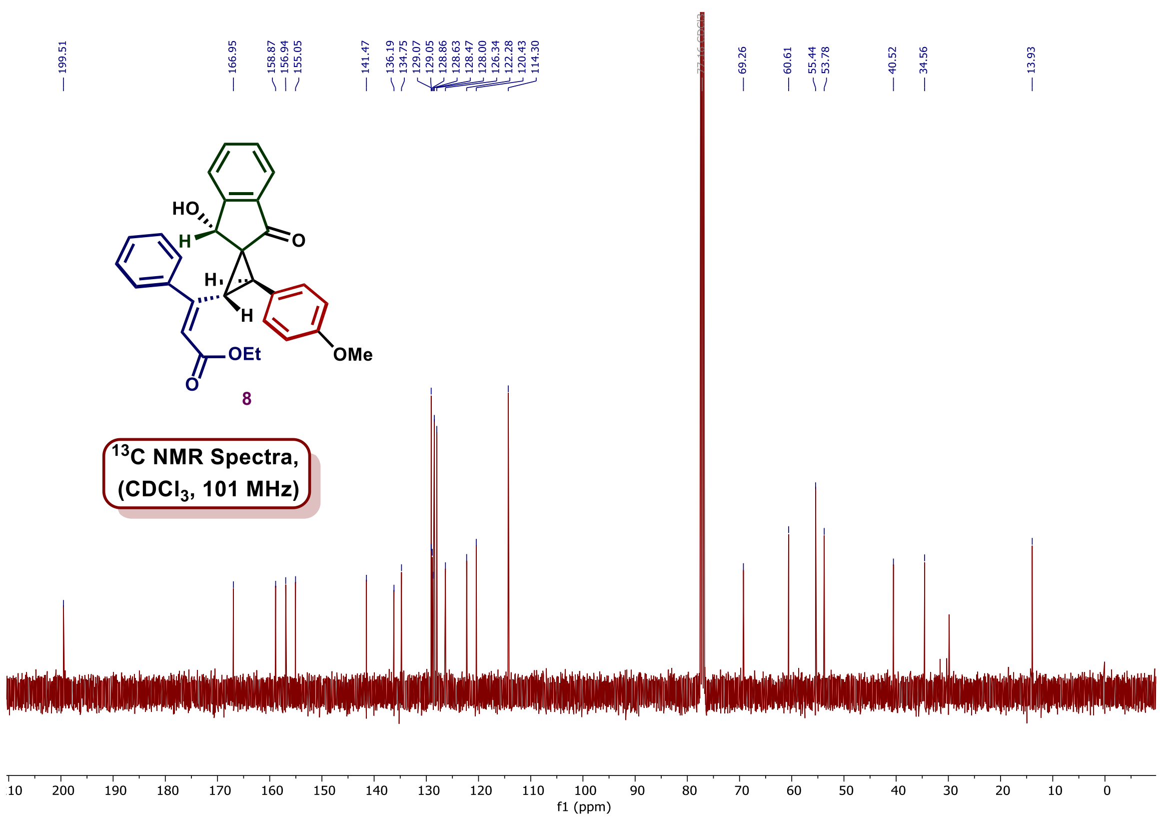
**(1*R*,2*S*,5*R*)-2-isopropyl-5-methylcyclohexyl (*E*)-3-(-2-benzoyl-3-phenylcyclopropyl)-3-phenylacrylate (6e):**



**ethyl (E)-3-(1'-hydroxy-2-(4-methoxyphenyl)-3'-oxo-1',3'-dihydrospiro[cyclopropane-1,2'-inden]-3-yl)-3-phenylacrylate (8)**



**methyl (E)-4-(dimethyl(oxo)-l6-sulfaneylidene)-5-oxo-5-phenylpent-2-enoate (1r):**