Supplementary Information (SI) for Chemical Science.

Highly Stereoselective Synthesis of Polysubstituted Housanes and Spiro-Oxa-Housanes: Application and Mechanistic Insights

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1. General methods

1.1 Solvents, Reagents, Glassware and Reaction Setup

Unless otherwise specified, all reactions were conducted under an inert atmosphere of nitrogen or argon using hot air oven dried (120 ºC) glassware utilizing standard Schlenk-line technique. Air- and moisture-sensitive liquids and solutions were transferred via syringe into the reaction vessels through a rubber septum under inert atmosphere. Unless otherwise specified, all reagents were purchased at highest commercial quality and used as received. Non-anhydrous solvents were purchased at the highest commercial quality and used as received. Organic solvents used for carrying out reactions were dried using standard methods. All work up and purification were carried out with reagent grade solvents in air. Temperatures described 20 °C and below 20 °C were achieved using immersion cooler by Julabo and above 20 °C were achieved using heat-on block system from Radley's. The photoreactions were done by using KESSIL lamp (PR 160L-440 nm) by keeping distance of 5 cm from the reaction vessel. No filter was used in light-promoted reactions.

1.2 Analytical methods

Chromatography: Column chromatography was carried out using Sigma-Aldrich silica gel (60 Å, 230-400 mesh, 40-63 μm). Reactions were monitored by thin-layer chromatography (TLC), using aluminium-backed Merck Kieselgel 60 F254 fluorescent treated silica gel plates, which were visualized under UV light or by staining with aqueous basic $KMnO_4$, or phosphomolybdic acid solution in ethanol. **IR:** Infrared (FT-IR) spectra were recorded of neat sample on Bruker alfa FT-IR, ν_{max} in cm^{-1} and the bands are characterized as strong (s), medium (m), and weak (w). **Melting Point**: Melting points were measured in open glass capillary on a Buchi M-560 melting point apparatus. **NMR:** NMR spectra were recorded on Bruker Ultrashield spectrometer at 400 MHz (for ^{1}H-NMR), 101 MHz (for ^{13}C-NMR), 376 MHz (for ^{19}F-NMR). Chemical shifts are reported in ppm from tetramethylsilane with the solvent resonance as internal standard ($CDCl_3$: δ 7.26 ppm for ^{1}H-NMR and δ 77.00 ppm for ^{13}C-NMR). For ^{1}H-NMR, data are reported as follows: chemical shift, multiplicity (s = singlet, brs = broad singlet, d = doublet, dd = doublet of doublets, ddd = doublet of doublet of doublets, t = triplet, q = quartet, dt = doublet of triplets, m = multiplet etc.), coupling constants (Hz) and integration. **NMR yields:** Following work up or/and solvent evaporation, dibromomethane (relative to limiting starting material) was added to the crude residue. The resultant mixture was dissolved in $CDCl_3$, and a 0.5 mL sample of the resultant solution taken for ^{1}H-NMR analysis. Yields were calculated based on the integrals of known product resonances relative to dibromomethane (2H, at 4.94 ppm in $CDCl_3$). **MS**: High Resolution Mass Spectrometry (HRMS) was performed on Waters e2695 XEVO G2-XS Q-TOF instrument.

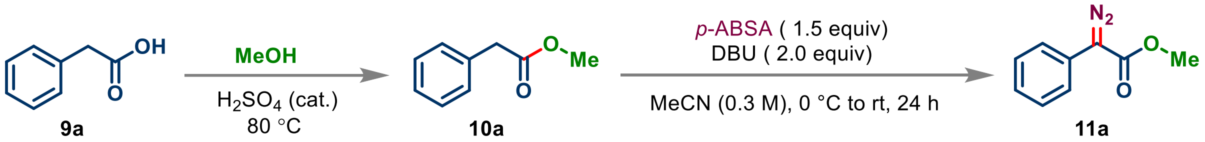
Important Safety Note

Handling of diazo compounds should only be done in a well-ventilated fume cupboard using an additional blast shield. No incidents occurred handling of diazo compounds during the preparation of this manuscript, yet the reader should be aware of carcinogenicity and explosiveness of the herein described diazo compounds. Any reactions described in this manuscript should not be performed without strict risk assessment and proper safety precautions.

2. Procedures for starting materials synthesis:

2.1 Procedures for the synthesis of diazo compounds:

Methyl 2-diazo-2-phenylacetate (11a)



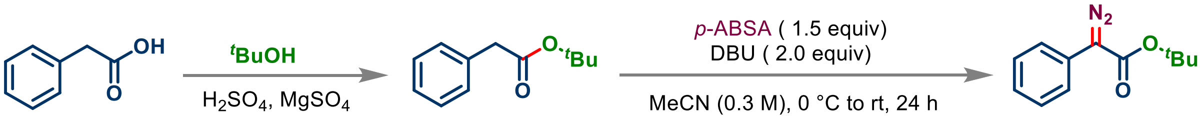
Step-1: Following a slightly modified procedure,[1] a 100 mL round bottom flask was charged with phenylacetic acid **(9a)** (5.44 g, 40.0 mmol, 1.00 equiv) in methanol (40 mL). Then, 4-6 drops of concentrated H_2SO_4 were added to the resulting mixture at room temperature and allowed to stir overnight at 80 °C. After concentrating the reaction mixture, the residue was diluted with water (40 mL) and the reaction mixture was extracted with ethyl acetate (3×60 mL). The combined organic layers were washed with saturated $NaHCO_3$ (30 mL) followed by 20 mL brine, dried over Na_2SO_4, and then the solvent was removed via rotary evaporation to yield compound **10a** as a colorless oil (5.20 g, 34.6 mmol, 86%). This product was used in the next step without further purification.

Step-2: Following a slightly modified procedure,[1] a 100 mL two-neck round bottom flask charged with methyl 2-phenylacetate **(10a)** (1.50 g, 10.0 mmol, 1.00 equiv), *p*-ABSA (3.6 g, 15 mmol, 1.5 equiv) and MeCN (30 mL, 0.3 M) under argon atmosphere. The reaction mixture was cooled to 0 °C in an ice bath. To this ice-cold solution, DBU (3.0 mL, 20 mmol, 2.0 equiv) was added dropwise while stirring, and the reaction mixture was allowed to stir at room temperature for 24 h. The reaction mixture was quenched with water (30 mL), and the organic phase was extracted with diethyl ether (2×50 mL). The combined organic layers were dried over Na_2SO_4 and then concentrated via rotary evaporation. The crude product was purified by flash column chromatography (silica, 1:20 v/v Et_2O:Hexane) to afford the title product **11a** as a red liquid (1.4 g, 7.9 mmol, 79%).

- **TLC (Et_2O:Hexane, 1:9 v/v):** $R_f = 0.6$, UV, $KMnO_4$.
- **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.52 – 7.45 (m, 2H, Ar*H*), 7.43 – 7.34 (m, 2H, Ar*H*), 7.23 – 7.15 (m, 1H, Ar*H*), 3.87 (s, 3H, CO_2CH_3).
- **^{13}C NMR (101 MHz, $CDCl_3$):** δ 165.6, 128.9, 125.8, 125.4, 124.0, 51.9. One carbon was not resolved at 101 MHz.

  The characterization data matched the reported values.[1]

tert-Butyl 2-diazo-2-phenylacetate (11b)



9a **10b** **11b**

Step-1: Following a slightly modified procedure,[2] a 250 mL round bottom flask was charged with phenylacetic acid **(9a)** (5.44 g, 40.0 mmol, 1.00 equiv) and 160 mL of HPLC grade CH_2Cl_2. Then, 24 g of $MgSO_4$ and 5 mL of concentrated H_2SO_4 were added to the resulting mixture at room temperature. To this solution, *tert*-butanol (19.0 mL, 200 mmol, 5.00 equiv) was added dropwise while stirring, and the reaction mixture was allowed to stir at room temperature for 20 h. After completion of the reaction, the reaction mixture was quenched with saturated $NaHCO_3$ (100 mL). The product was extracted with CH_2Cl_2 (2 × 50 mL), washed with 100 mL brine, and then, dried over Na_2SO_4. The volatiles were evaporated, and the residue was purified by silica gel column chromatography (1:50 v/v Et_2O:Hexane) to give *tert*-butyl 2-phenylacetate **10b** as a colorless oil (3.50 g, 18.2 mmol, 45%).

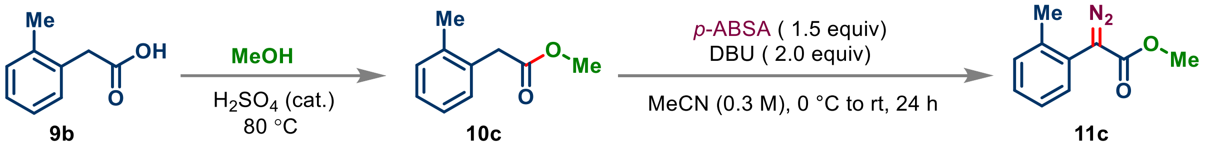
- **TLC (Et_2O:Hexane, 1:9 v/v):** $R_f = 0.7$, UV, $KMnO_4$.
- **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.45 – 7.12 (m, 5H, Ar*H*), 3.56 (s, 2H, $ArCH_2CO_2{}^tBu_3$), 1.49 (s, 9H, $CO_2{}^tBu$).
- **^{13}C NMR (101 MHz, $CDCl_3$):** δ 170.7, 134.5, 129.0, 128.3, 126.7, 80.5, 42.5, 27.9.

  The characterization data matched the reported values.[2]

Step-2: Following a slightly modified procedure,[1] a 100 mL two-neck round bottom flask charged with *tert*-butyl 2-phenylacetate **(10b)** (1.92 g, 10.0 mmol, 1.00 equiv), *p*-ABSA (3.6 g, 15 mmol, 1.5 equiv) and MeCN (30 mL, 0.3 M) under argon atmosphere. The reaction mixture was cooled to 0 °C in an ice bath. To this ice-cold solution, DBU (3.0 mL, 20 mmol, 2.0 equiv) was added dropwise while stirring, and the reaction mixture was allowed to stir at room temperature for 24 h. The reaction mixture was quenched with water (30 mL), and the organic phase was extracted with diethyl ether (2×50 mL). The combined organic layers were dried over Na_2SO_4 and then concentrated via rotary evaporation. The crude product was purified by flash column chromatography (silica, 1:20 v/v Et_2O:Hexane) to afford the title product **11b** as a yellow liquid (1.1 g, 5.0 mmol, 50%).

- **TLC (Et_2O:Hexane, 1:9 v/v):** $R_f = 0.6$, UV, $KMnO_4$.
- **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.51 – 7.45 (m, 2H, Ar*H*), 7.38 (t, *J* = 7.8 Hz, 2H, Ar*H*), 7.19 – 7.14 (m, 1H, Ar*H*), 1.57 (s, 9H, $CO_2{}^t\!Bu_3$).
- **^{13}C NMR (101 MHz, $CDCl_3$):** δ 164.5, 128.8, 126.0, 125.4, 123.9, 81.9, 63.6, 28.3. The characterization data matched the reported values.[2]

Methyl 2-diazo-2-(*o*-tolyl)acetate (11c)



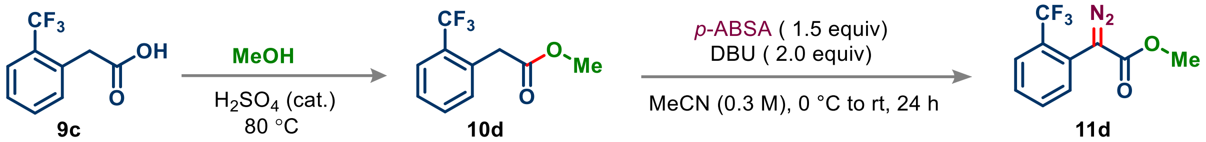
Step-1: Following a slightly modified procedure,[1] a 100 mL round bottom flask was charged with 2-(*o*-tolyl)acetic acid **(9b)** (6.0 g, 40 mmol, 1.0 equiv) in methanol (40 mL). Then, 4-6 drops of concentrated H_2SO_4 were added to the resulting mixture at room temperature and allowed to stir overnight at 80 °C. After concentrating the reaction mixture, the residue was diluted with water (40 mL) and the reaction mixture was extracted with ethyl acetate (3×60 mL). The combined organic layers were washed with saturated $NaHCO_3$ (30 mL) followed by 20 mL brine, dried over Na_2SO_4 and then the solvent was removed via rotary evaporation to yield compound **10c** as a colorless oil (5.50 g, 33.5 mmol, 82%). This product was used in the next step without further purification.

Step-2: Following a slightly modified procedure,[1] a 100 mL two-neck round bottom flask charged with methyl 2-(*o*-tolyl)acetate **(10c)** (1.64 g, 10.0 mmol, 1.00 equiv), *p*-ABSA (3.60 g, 15.0 mmol, 1.5 equiv) and MeCN (30 mL, 0.3 M) under argon atmosphere. The reaction mixture was cooled to 0 °C in an ice bath. To this ice-cold solution, DBU (3.0 mL, 20.0 mmol, 2.0 equiv) was added dropwise while stirring, and the reaction mixture was allowed to stir at room temperature for 24 h. The reaction mixture was quenched with water (30 mL, and the organic layer was extracted with diethyl ether (2×50 mL). The combined organic layers were dried over Na_2SO_4 and then concentrated via rotary evaporation. The crude product was purified by flash column chromatography (silica, 1:20 v/v Et_2O:Hexane) to afford the title product **11c** as an orange oil (1.4 g, 7.3 mmol, 73%).

- **TLC (Et_2O:Hexane, 1:9 v/v):** R_f = 0.50, UV, $KMnO_4$.
- **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.40–7.37 (m, 1H, Ar*H*), 7.30–7.23 (m, 3H, Ar*H*), 3.83 (s, 3H, CO_2CH_3), 2.32 (s, 3H, ArCH_3)
- **^{13}C NMR (101 MHz, $CDCl_3$):** δ 166.7, 137.9, 131.1, 130.9, 129.1, 126.6, 124.3, 52.3, 20.1. One carbon was not resolved at 101 MHz.

The characterization data matched the reported values.[3]

Methyl 2-diazo-2-(2-(trifluoromethyl)phenyl)acetate (11d)



Step-1: Following a slightly modified procedure,[1] a 100 mL round bottom flask was charged with 2-(2-(trifluoromethyl)phenyl)acetic acid **(9c)** (8.16 g, 40.0 mmol, 1.00 equiv) in methanol (40 mL). Then, 4-6 drops of concentrated H_2SO_4 were added to the resulting mixture at room temperature and allowed to stir overnight at 80 °C. After concentrating the reaction mixture, the residue was diluted with water (40 mL) and the reaction mixture was extracted with ethyl acetate (3×60 mL). The combined organic layers were washed with saturated $NaHCO_3$ (30 mL) followed by 20 mL brine, dried over Na_2SO_4 and then the solvent was removed via rotary evaporation to yield compound **10d** as a colorless oil (8.00 g, 36.7 mmol, 91%). This product was used in the next step without further purification.

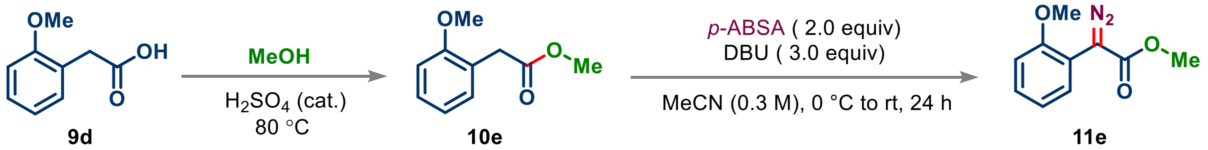
Step-2: Following a slightly modified procedure,[1] a 100 mL two-neck round bottom flask charged with methyl 2-(2-(trifluoromethyl)phenyl)acetate **(10d)** (2.18 g, 10.0 mmol, 1.00 equiv), *p*-ABSA (3.60 g, 15.0 mmol, 1.50 equiv) and MeCN (30 mL, 0.3 M) under argon atmosphere. The reaction mixture was cooled to 0 °C in an ice bath. To this ice-cold solution, DBU (3.00 mL, 20.0 mmol, 2.00 equiv) was added dropwise while stirring, and the reaction mixture was allowed to stir at room temperature for 24 h. The reaction mixture was quenched with water (30 mL), and the organic phase was extracted with diethyl ether (2×50 mL). The organic layers were dried over Na_2SO_4 and then concentrated via rotary evaporation. The crude product was purified by flash column chromatography (silica, 1:20 v/v Et_2O:Hexane) to afford the title product **11d** as a yellow liquid (1.9 g, 7.8 mmol, 77%).

- **TLC (Et_2O:Hexane, 1:9 v/v):** R_f = 0.50, UV, $KMnO_4$.

- **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.74 (d, J = 7.9 Hz, 1H, ArH), 7.65 – 7.46 (m, 3H, ArH), 3.81 (s, 3H, CO_2CH_3).
- **^{13}C NMR (101 MHz, $CDCl_3$):** δ 166.2, 134.4, 132.2, 129.9 (q, J = 30.1 Hz), 129.4, 126.8 (q, J = 5.3 Hz), 123.7 (q, J = 274.72 Hz), 123.4 (d, J = 2.0 Hz), 52.3. One carbon was not resolved at 101 MHz.
- **^{19}F NMR (377 MHz, $CDCl_3$):** δ -61.66.

The characterization data matched the reported values.[1]

Methyl 2-diazo-2-(2-methoxyphenyl)acetate (11e)



Step-1: Following a slightly modified procedure,[1] a 100 mL round bottom flask was charged with 2-(2-methoxyphenyl)acetic acid **(9d)** (6.64 g, 40.0 mmol, 1.0 equiv) in methanol (40 mL). Then, 4-6 drops of concentrated H_2SO_4 were added to the resulting mixture at room temperature and allowed to stir overnight at 80 °C. After concentrating the reaction mixture, the residue was diluted with water (40 mL) and the reaction mixture was extracted with ethyl acetate (3×60 mL). The combined organic layers were washed with saturated $NaHCO_3$ (30 mL) followed by 20 mL brine, dried over Na_2SO_4 and then the solvent was removed via rotary evaporation to yield compound **10e** as a colorless oil (6.30 g, 34.4 mmol, 87%). This product was used in the next step without further purification.

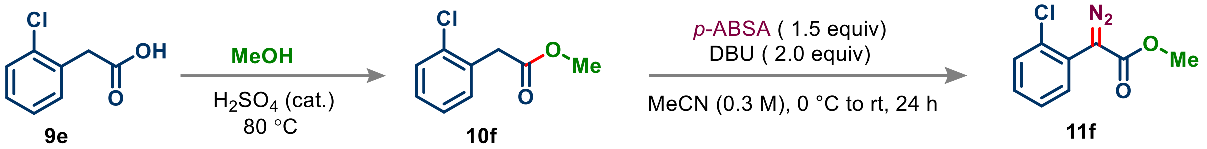
Step-2: Following a slightly modified procedure,[1] a 100 mL two-neck round bottom flask charged with methyl 2-(2-methoxyphenyl)acetate **(10e)** (1.80 g, 10.0 mmol, 1.00 equiv), *p*-ABSA (4.80 g, 20.0 mmol, 2.00 equiv) and MeCN (30 mL, 0.3 M) under argon atmosphere. The reaction mixture was cooled to 0 °C in an ice bath. To this ice-cold solution, DBU (4.50 mL, 30.0 mmol, 3.0 equiv) was added dropwise while stirring, and the reaction mixture was allowed to stir at room temperature for 24 h. The reaction mixture was quenched with water (30 mL), and the organic layer was extracted with diethyl ether (2×50 mL). The combined organic layers were dried over Na_2SO_4 and then concentrated via rotary evaporation. The crude product was purified by flash column chromatography (silica, 1:20 v/v Et_2O:Hexane) to afford the title product **11e** as an orange solid (1.6 g, 7.7 mmol, 77%).

- **TLC (Et_2O:Hexane, 1:9 v/v):** R_f = 0.40, UV, $KMnO_4$.

- **^{1}H NMR (400 MHz, CDCl$_3$):** δ 7.54 (dd, *J* = 7.8, 1.7 Hz, 1H, Ar*H*), 7.27–7.22 (m, 1H, Ar*H*), 7.01 (td, *J* = 7.6, 1.2 Hz, 1H, Ar*H*), 6.88 (dd, *J* = 8.3, 1.2 Hz, 1H, Ar*H*), 3.84 (s, 3H, ArO*CH*$_3$), 3.82 (s, 3H, CO$_2$*CH*$_3$).
- **^{13}C NMR (101 MHz, CDCl$_3$):** δ 166.8, 155.6, 130.3, 128.8, 121.3, 113.8, 111.0, 55.7, 52.1 One carbon was not resolved at 101 MHz.

The characterization data matched the reported values.[4]

Methyl 2-(2-chlorophenyl)-2-diazoacetate (11f)



Step-1: Following a slightly modified procedure,[1] a 100 mL round bottom flask was charged with 2-(2-chlorophenyl)acetic acid **(9e)** (6.8 g, 40 mmol, 1.0 equiv) in methanol (40 mL). Then, 4-6 drops of concentrated H_2SO_4 were added to the resulting mixture at room temperature and allowed to stir overnight at 80 °C. After concentrating the reaction mixture, the residue was diluted with water (40 mL) and the reaction mixture was extracted with ethyl acetate (3×60 mL). The combined organic layers were washed with saturated $NaHCO_3$ (30 mL) followed by 20 mL brine, dried over Na_2SO_4 and then the solvent was removed via rotary evaporation to yield compound **10f** as a colorless oil (6.30 g, 34.2 mmol, 86%). This product was used in the next step without further purification.

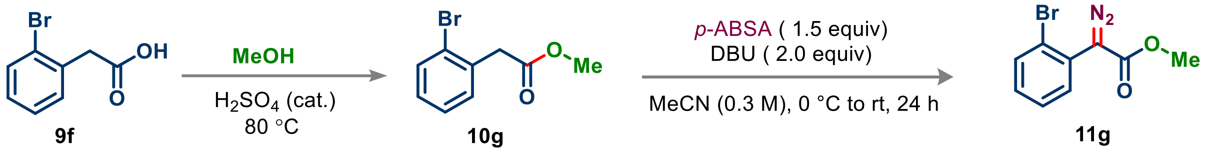
Step-2: Following a slightly modified procedure,[1] a 100 mL two-neck round bottom flask charged with methyl methyl 2-(2-chlorophenyl)acetate **(10f)** (1.84 g, 10.0 mmol, 1.00 equiv), *p*-ABSA (3.60 g, 15.0 mmol, 1.5 equiv) and MeCN (30 mL, 0.3 M) under argon atmosphere. The reaction mixture was cooled to 0 °C in an ice bath. To this ice-cold solution, DBU (3.00 mL, 20.0 mmol, 2.0 equiv) was added dropwise while stirring, and the reaction mixture was allowed to stir at room temperature for 24 h. The reaction mixture was quenched with water (30 mL), and the organic layer was extracted with diethyl ether (2×50 mL). The combined organic layers were dried over Na_2SO_4 and then concentrated via rotary evaporation. The crude product was purified by flash column chromatography (silica, 1:20 v/v Et_2O:Hexane) to afford the title product **11f** as a yellow liquid (1.65 g, 7.80 mmol, 78%).

- **TLC (Et_2O:Hexane, 1:9 v/v):** R_f = 0.40, UV, $KMnO_4$
- **^{1}H NMR (400 MHz, CDCl$_3$):** δ 7.53 (dd, *J* = 7.7, 1.9 Hz, 1H, Ar*H*), 7.39 (dd, *J* = 7.9, 1.6 Hz, 1H, Ar*H*), 7.26 (m, 2H, Ar*H*), 3.81 (s, 3H, CO$_2$C*H*$_3$).

- **^{13}C NMR (101 MHz, $CDCl_3$):** δ 165.6, 133.5, 132.1, 129.8, 129.4, 127.0, 123.7, 61.6, 52.0.

The characterization data matched the reported values.[3]

Methyl 2-(2-bromophenyl)-2-diazoacetate (11g)



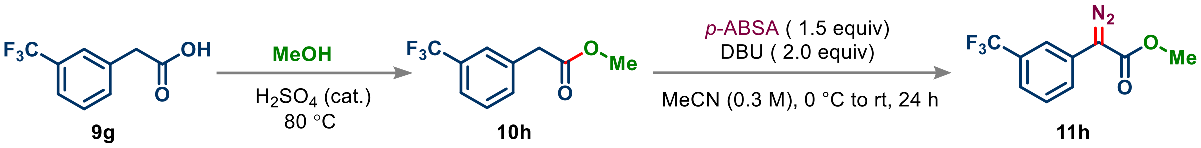
Step-1: Following a slightly modified procedure,[1] a 100 mL round bottom flask was charged with 2-(2-bromophenyl)acetic acid **(9f)** (8.52 g, 40.0 mmol, 1.00 equiv) in methanol (40 mL). Then, 4-6 drops of concentrated H_2SO_4 were added to the resulting mixture at room temperature and was allowed to stir overnight at 80 °C. After concentrating the reaction mixture, the residue was diluted with water (40 mL) and the reaction mixture was extracted with ethyl acetate (3×60 mL). The combined organic layers were washed with saturated $NaHCO_3$ (30 mL) followed by 20 mL brine, dried over Na_2SO_4 and then the solvent was removed via rotary evaporation to yield compound **10g** as a colorless oil (8.00 g, 34.9 mmol, 88%). This product was used in the next step without further purification.

Step-2: Following a slightly modified procedure,[1] a 100 mL two-neck round bottom flask charged with methyl 2-(2-bromophenyl)acetate **(10g)** (2.29 g, 10.0 mmol, 1.00 equiv), *p*-ABSA (3.60 g, 15.0 mmol, 1.50 equiv) and MeCN (30 mL, 0.3 M) under argon atmosphere. The reaction mixture was cooled to 0 °C in an ice bath. To this ice-cold solution, DBU (3.0 mL, 20.0 mmol, 2.0 equiv) was added dropwise while stirring, and the reaction mixture was allowed to stir at room temperature for 24 h. The reaction mixture was quenched with water (30 mL), and the organic layer was extracted with diethyl ether (2×50 mL), dried over Na_2SO_4 and then concentrated via rotary evaporation. The crude product was purified by flash column chromatography (silica, 1:20 v/v Et_2O:Hexane) to afford the title product **11g** as a yellow liquid (2.0 g, 7.9 mmol, 79%).

- **TLC (Et_2O:Hexane, 1:9 v/v):** R_f = 0.40, UV, $KMnO_4$
- **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.62 (d, J = 8.0 Hz, 1H, Ar*H*), 7.51 (dd, J = 7.9, 1.7 Hz, 1H, Ar*H*), 7.41 – 7.33 (m, 1H, Ar*H*), 7.25 – 7.11 (m, 1H, Ar*H*), 3.84 (s, 3H, CO_2CH_3).
- **^{13}C NMR (101 MHz, $CDCl_3$):** δ 166.0, 133.3, 133.0, 130.1, 127.7, 125.7, 124.5, 52.3. One carbon was not resolved at 101 MHz.

The characterization data matched the reported values.[1]

Methyl 2-diazo-2-(3-(trifluoromethyl)phenyl)acetate (11h)



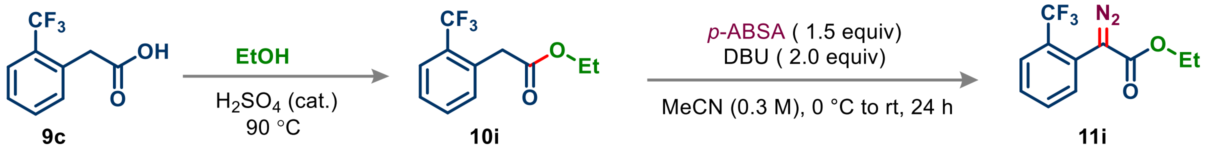
Step-1: Following a slightly modified procedure,[1] a 100 mL round bottom flask was charged with 2-(3-(trifluoromethyl)phenyl)acetic acid **(9g)** (8.16 g, 40.0 mmol, 1.00 equiv) in methanol (40 mL). Then, 4-6 drops of concentrated H_2SO_4 were added to the resulting mixture at room temperature and allowed to stir overnight at 80 °C. After concentrating the reaction mixture, the residue was diluted with water (40 mL) and the reaction mixture was extracted with ethyl acetate (3×60 mL). The combined organic phases were washed with saturated $NaHCO_3$ (30 mL) followed by 20 mL brine, dried over Na_2SO_4 and then the solvent was removed via rotary evaporation to yield compound **10h** as a colorless oil (7.60 g, 34.8 mmol, 88%). This product was used in the next step without further purification.

Step-2: Following a slightly modified procedure,[1] a 100 mL two-neck round bottom flask charged with methyl 2-(3-(trifluoromethyl)phenyl)acetate **(10h)** (2.18 g, 10.0 mmol, 1.00 equiv), *p*-ABSA (3.6 g, 15 mmol, 1.5 equiv) and MeCN (30 mL, 0.3 M) under argon atmosphere. The reaction mixture was cooled to 0 °C in an ice bath. To this ice-cold solution, DBU (3.0 mL, 20 mmol, 2.0 equiv) was added dropwise while stirring, and the reaction mixture was allowed to stir at room temperature for 24 h. The reaction mixture was quenched with water (30 mL), and the organic phase was extracted with diethyl ether (2×50 mL). The combined organic layers were dried over Na_2SO_4 and then concentrated via rotary evaporation. The crude product was purified by flash column chromatography (silica, 1:20 v/v Et_2O:Hexane) to afford the title product **11h** as a yellow solid (1.5 g, 6.1 mmol, 61%).

- **TLC (Et_2O:Hexane, 1:9 v/v):** $R_f = 0.55$, UV, $KMnO_4$.
- **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.79 (s, 1H, Ar*H*), 7.64 (d, *J* = 7.9 Hz, 1H, Ar*H*), 7.50 (t, *J* = 7.9 Hz, 1H, Ar*H*), 7.43 (d, *J* = 7.8 Hz, 1H, Ar*H*), 3.89 (s, 3H, CO_2CH_3).
- **^{13}C NMR (101 MHz, $CDCl_3$):** δ 165.1, 131.6 (q, *J* =30.7 Hz), 129.5, 127.2, 126.8, 124.1 (q, *J* = 272.6 Hz), 122.5 (q, *J* = 4.0 Hz), 120.6 (q, *J* = 4.0 Hz), 52.3. One carbon was not resolved at 101 MHz.
- **^{19}F NMR (377 MHz, $CDCl_3$):** δ -63.34.

The characterization data matched the reported values.[5]

Ethyl 2-diazo-2-(2-(trifluoromethyl)phenyl)acetate (11i)



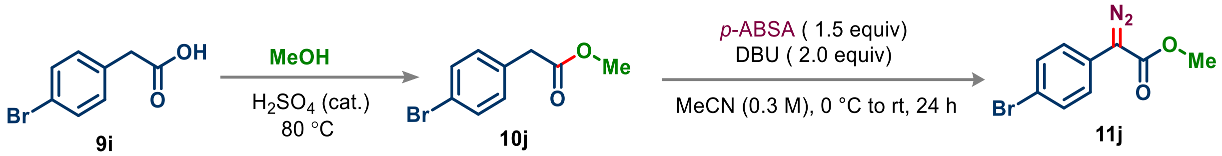
Step-1: Following a slightly modified procedure,[1] a 100 mL round bottom flask was charged with 2-(2-(trifluoromethyl)phenyl)acetic acid **(9c)** (4.08 g, 20.0 mmol, 1.00 equiv) in methanol (20 mL). Then, 2-3 drops of concentrated H_2SO_4 were added to the resulting mixture at room temperature and allowed to stir overnight at 90 °C. After concentrating the reaction mixture, the residue was diluted with water (20 mL) and the reaction mixture was extracted with ethyl acetate (3×30 mL). The combined organic layers were washed with saturated $NaHCO_3$ (15 mL) followed by 10 mL brine, dried over Na_2SO_4 and then the solvent was removed via rotary evaporation to yield compound **10i** as a colorless oil (3.20 g, 13.8 mmol, 69%). This product was used in the next step without further purification.

Step-2: Following a slightly modified procedure,[1] a 100 mL two-neck round bottom flask charged with methyl ethyl 2-(2-(trifluoromethyl)phenyl)acetate **(10i)** (2.32 g, 10.0 mmol, 1.00 equiv), *p*-ABSA (3.6 g, 15 mmol, 1.5 equiv) and MeCN (30 mL, 0.3 M) under argon atmosphere. The reaction mixture was cooled to 0 °C in an ice bath. To this ice-cold solution, DBU (3.0 mL, 20 mmol, 2.0 equiv) was added dropwise while stirring, and the reaction mixture was allowed to stir at room temperature for 24 h. The reaction mixture was quenched with water (30 mL), and the organic phase was extracted with diethyl ether (2×50 mL), dried over Na_2SO_4 and then concentrated via rotary evaporation. The crude product was purified by flash column chromatography (silica, 1:20 v/v Et_2O:Hexane) to afford the title product **11i** as a yellow liquid (2.10 g, 8.13 mmol, 81%).

- **TLC (Et_2O:Hexane, 1:9 v/v):** $R_f = 0.51$, UV, $KMnO_4$.
- **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.72 (d, J = 7.9 Hz, 1H, Ar*H*), 7.58 (d, J = 4.4 Hz, 2H, Ar*H*), 7.51 – 7.42 (m, 1H, Ar*H*), 4.27 (q, J = 7.1 Hz, 2H, $CO_2CH_2CH_3$), 1.27 (t, J = 7.2 Hz, 3H, $CO_2CH_2CH_3$).
- **^{13}C NMR (101 MHz, $CDCl_3$):** δ 165.7, 134.3, 132.1, 129.8 (q, J = 30.2 Hz), 129.2, 126.7 (q, J = 5.3 Hz), 122.4 (q, J = 274.72 Hz), 61.3, 58.4, 14.2. One carbon was not resolved at 101 MHz.
- **^{19}F NMR (377 MHz, $CDCl_3$):** δ -61.7.

The characterization data matched the reported values.[6]

Methyl 2-(4-bromophenyl)-2-diazoacetate (11j)



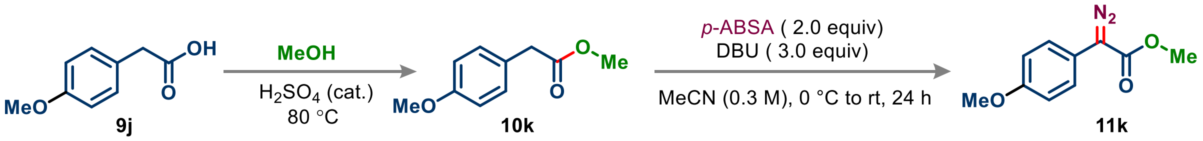
Step-1: Following a slightly modified procedure,[1] a 100 mL round bottom flask was charged with 2-(4-bromophenyl)acetic acid **(9i)** (8.52 g, 40.0 mmol, 1.00 equiv) in methanol (40 mL). Then, 4-6 drops of concentrated H_2SO_4 were added to the resulting mixture at room temperature and allowed to stir overnight at 80 °C. After concentrating the reaction mixture, the residue was diluted with water (40 mL) and the reaction mixture was extracted with ethyl acetate (3×60 mL). The combined organic layers were washed with saturated $NaHCO_3$ (30 mL) followed by 20 mL brine, dried over Na_2SO_4 and then the solvent was removed via rotary evaporation to yield compound **10j** as a colorless oil (7.90 g, 34.5 mmol, 86%). This product was used in the next step without further purification.

Step-2: Following a slightly modified procedure,[1] a 100 mL two-neck round bottom flask charged with methyl 2-(4-bromophenyl)acetate **(10j)** (2.29 g, 10.0 mmol, 1.00 equiv), *p*-ABSA (3.6 g, 15mmol, 1.5 equiv) and MeCN (30 mL, 0.3 M) under argon atmosphere. The reaction mixture was cooled to 0 °C in an ice bath. To this ice-cold solution, DBU (3.0 mL, 20 mmol, 2.0 equiv) was added dropwise while stirring, and the reaction mixture was allowed to stir at room temperature for 24 h. The reaction mixture was quenched with water (30 mL), and the organic layer was extracted with diethyl ether (2×50 mL). The combined organic layers were dried over Na_2SO_4 and then concentrated via rotary evaporation. The crude product was purified by flash column chromatography (silica, 1:20 v/v Et_2O:Hexane) to afford the title product **11j** as a yellow liquid (2.2 g, 8.6 mmol, 86%).

- **TLC (Et_2O:Hexane, 1:9 v/v):** $R_f = 0.50$, UV, $KMnO_4$.
- **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.50 (dd, $J = 8.6$, 1.6 Hz, 2H, Ar*H*), 7.36 (dd, $J = 8.7$, 1.6 Hz, 2H, Ar*H*), 3.87 (s, 3H, CO_2CH_3).
- **^{13}C NMR (101 MHz, $CDCl_3$):** δ 165.2, 132.0, 125.3, 124.7, 119.3, 52.1. One carbon was not resolved at 101 MHz.

The characterization data matched the reported values.[1]

Methyl 2-diazo-2-(4-methoxyphenyl)acetate (11k)



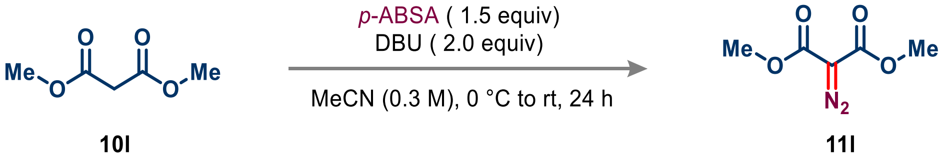
Step-1: Following a slightly modified procedure,[1] a 100 mL round bottom flask was charged with 2-(4-methoxyphenyl)acetic acid **(9j)** (6.64 g, 40.0 mmol, 1.0 equiv) in methanol (40 mL). Then, 4-6 drops of concentrated H_2SO_4 were added to the resulting mixture at room temperature and allowed to stir overnight at 80 °C. After concentrating the reaction mixture, the residue was diluted with water (40 mL) and the reaction mixture was extracted with ethyl acetate (3×60 mL). The combined organic layers were washed with saturated $NaHCO_3$ (30 mL) followed by 20 mL brine, dried over Na_2SO_4 and then the solvent was removed via rotary evaporation to yield compound **10k** as a colorless oil (6.35 g, 34.5 mmol, 88%). This product was used in the next step without further purification.

Step-2: Following a slightly modified procedure,[1] a 100 mL two-neck round bottom flask charged with methyl 2-(2-methoxyphenyl)acetate **(10k)** (1.8 g, 10 mmol, 1.0 equiv), *p*-ABSA (4.8 g, 20 mmol, 2.0 equiv) and MeCN (30 mL, 0.3 M) under argon atmosphere. The reaction mixture was cooled to 0 °C in an ice bath. To this ice-cold solution, DBU (4.5 mL, 30 mmol, 3.0 equiv) was added dropwise while stirring, and the reaction mixture was allowed to stir at room temperature for 24 h. The reaction mixture was quenched with water (30 mL), and the organic phase was extracted with diethyl ether (2×50 mL). The combined organic layers were dried over Na_2SO_4 and then concentrated via rotary evaporation. The crude product was purified by flash column chromatography (silica, 1:20 v/v Et_2O:Hexane) to afford the title product **11k** as a red liquid (1.45 g, 7.00 mmol, 70%).

- **TLC (Et_2O:Hexane, 1:9 v/v):** R_f = 0.30, UV, $KMnO_4$.
- **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.42 – 7.33 (m, 2H, Ar*H*), 6.98 – 6.90 (m, 2H, Ar*H*), 3.85 (s, *J* = 1.4 Hz, 3H, ArOCH_3), 3.80 (s, *J* = 1.6 Hz, 3H, CO_2CH_3).
- **^{13}C NMR (101 MHz, $CDCl_3$):** δ 166.2, 158.0, 125.9, 116.8, 114.6, 55.3, 51.9. One carbon was not resolved at 101 MHz.

  The characterization data matched the reported values.[1]

Dimethyl 2-diazomalonate (11l)

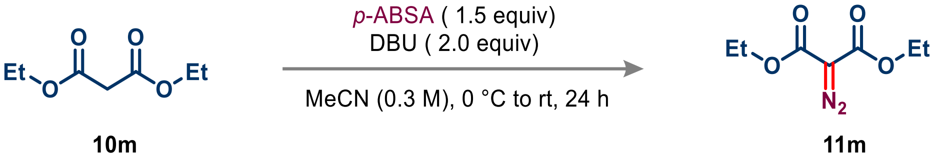


Following a slightly modified procedure,[1] a 100 mL two-neck round bottom flask charged with dimethyl malonate (**10l**) (2.2 mL, 19 mmol, 1.0 equiv), *p*-ABSA (6.8 g, 28.5 mmol, 1.50 equiv) and MeCN (57 mL, 0.3 M) under argon atmosphere. The reaction mixture was cooled to 0 °C in an ice bath. To this ice-cold solution, DBU (5.68 mL, 38.0 mmol, 2.00 equiv) was added dropwise while stirring, and the reaction mixture was allowed to stir at room temperature for 24 h. The reaction mixture was quenched with water (60 mL), and the organic layer was extracted with diethyl ether (2×100 mL). The combined organic layers were dried over Na_2SO_4 and then concentrated via rotary evaporation. The crude product was purified by flash column chromatography (silica, 1:10-3:7 v/v Et_2O:Hexane) to afford the title product **11l** as a pale-yellow liquid (1.6 g, 8.6 mmol, 53%, solid at -20 °C).

- **TLC (Et_2O:Hexane, 4:6 v/v):** $R_f = 0.25$, UV, $KMnO_4$.
- **^{1}H NMR (400 MHz, $CDCl_3$):** δ 3.85 (s, 6H, CO_2CH_3).
- **^{13}C NMR (101 MHz, $CDCl_3$):** δ 161.2, 52.4. One carbon was not resolved at 101 MHz.

  The characterization data matched the reported values.[1]

Diethyl 2-diazomalonate (11m)



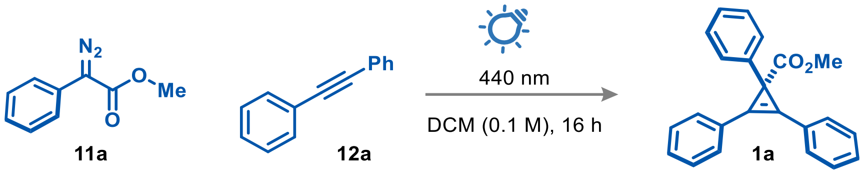
Following a slightly modified procedure,[1] a 100 mL two-neck round bottom flask charged with diethyl malonate (**10m**) (1.5 mL, 10.0 mmol, 1.0 equiv), *p*-ABSA (3.6 g, 15.0 mmol, 1.50 equiv) and MeCN (30 mL, 0.3 M) under argon atmosphere. The reaction mixture was cooled to 0 °C in an ice bath. To this ice-cold solution, DBU (3.1 mL, 20.0 mmol, 2.00 equiv) was added dropwise while stirring, and the reaction mixture was allowed to stir at room temperature for 24 h. The reaction mixture was quenched with water (30 mL), and the organic layer was extracted with diethyl ether (2×500 mL). The combined organic layers were dried over Na_2SO_4 and then concentrated via rotary evaporation. The crude product was purified by flash column chromatography (silica, 1:10-3:7 v/v Et_2O:Hexane) to afford the title product **11m** as a pale-yellow liquid (1.1 g, 6.0 mmol, 60%).

- **TLC (Et_2O:Hexane, 1:1 v/v):** R_f = 0.50, UV.
- **^{1}H NMR (400 MHz, $CDCl_3$):** δ 4.36 – 4.22 (m, 4H, $CO_2\mathit{CH_2}CH_3$), 1.39 – 1.26 (m, 6H, $CO_2CH_2\mathit{CH_3}$).
- **^{13}C NMR (101 MHz, $CDCl_3$):** δ 161.0, 61.6, 14.3. One carbon was not resolved at 101 MHz.

  The characterization data matched the reported values.[1]

2.2 Procedures for the synthesis of Cyclopropenes:

Methyl-1,2,3-triphenylcycloprop-2-ene-1-carboxylate (1a)

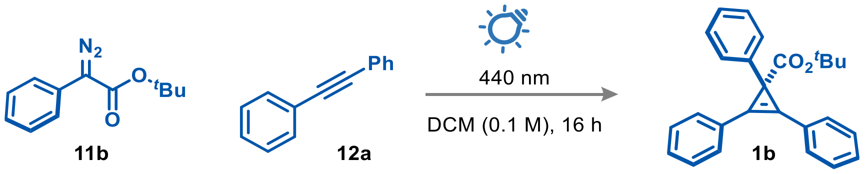


Following a slightly modified procedure,[7] in a 100 mL sealed tube, the diazo compound **11a** (880 mg, 5.00 mmol, 1.00 equiv) and diphenyl acetylene **(12a)** (6.23 g, 35.0 mmol, 7.0 equiv) were dissolved in 50 mL dry DCM under argon. The solution was stirred at room temperature with the irradiation of 440 nm blue LEDs (Kessil lamp). After 16 h, the solvent was evaporated under vacuum and the residue was purified by flash chromatography using 3% Et_2O/hexane as eluent to afford the title compound **1a** (1.10 g, 3.37 mmol, 67%) as colorless solid.

- **TLC (Et_2O/Hexane, 2:8 v/v):** $R_f = 0.50$, UV, $KMnO_4$.
- **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.76 (d, *J* = 8.1 Hz, 4H, Ar*H*), 7.52 – 7.45 (m, 6H, Ar*H*), 7.44 – 7.37 (m, 2H, Ar*H*), 7.31 – 7.26 (m, 2H, Ar*H*), 7.23 – 7.17 (m, 1H, Ar*H*), 3.72 (s, 3H, CO_2CH_3).
- **^{13}C NMR (101 MHz, $CDCl_3$):** δ 174.4, 140.0, 129.9, 129.4, 129.0, 128.14, 128.06 126.5, 126.4, 111.3, 52.1, 35.4.

  The characterization data matched the reported values.[7]

tert-Butyl 1,2,3-triphenylcycloprop-2-ene-1-carboxylate (1b)

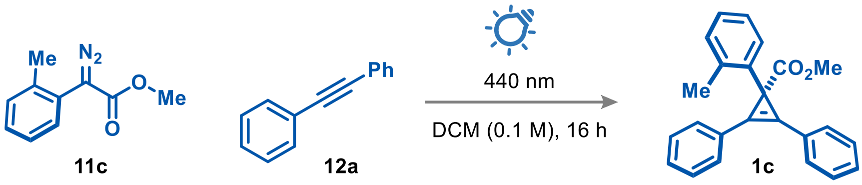


Following a slightly modified procedure,[7] in a 100 mL sealed tube, the diazo compound **11b** (654 mg, 3.00 mmol, 1.00 equiv) and diphenyl acetylene **(12a)** (3.74 g, 21.0 mmol, 7.00 equiv) were dissolved in 30 mL dry DCM under argon. The solution was stirred at room temperature with the irradiation of 440 nm blue LEDs (Kessil lamp). After 16 h, the solvent was evaporated under vacuum and the residue was purified by flash chromatography using 2% Et_2O/hexane as eluent to afford the title compound **1a** (200 mg, 0.54 mmol, 18%) as colorless sticky solid. (*See Spectra*)

- **TLC (Et_2O/Hexane, 1:9 v/v):** $R_f = 0.50$, UV, $KMnO_4$.

- **^{1}H NMR (400 MHz, CDCl$_3$):** δ 7.79 – 7.74 (m, 4H, Ar*H*), 7.50 – 7.44 (m, 6H, Ar*H*), 7.41 – 7.36 (m, 2H, Ar*H*), 7.29 – 7.23 (m, 2H, Ar*H*), 7.21 – 7.14 (m, 1H, Ar*H*), 1.42 (s, 9H, CO$_2$^{t}*Bu*).
- **^{13}C NMR (101 MHz, CDCl$_3$):** δ 173.1, 140.7, 129.8, 129.1, 128.9, 128.0, 127.9, 127.0, 126.1, 111.8, 80.5, 36.7, 28.1.
- **IR (Neat, cm^{-1}):** υ 2949 (m), 2918 (w), 2858 (m), 1725 (s), 1488 (m), 1448 (m), 1263 (s), 756 (m), 698 (m).
- **HRMS (ESI):** Calcd. for $C_{26}H_{24}O_2Na^+$ $[M+Na]^+$ 391.1674; found: 391.1676

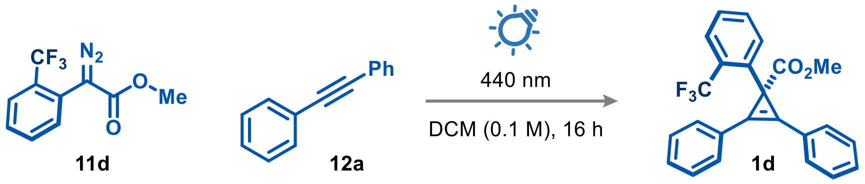
Methyl-2,3-diphenyl-1-(*o*-tolyl)cycloprop-2-ene-1-carboxylate (1c)



Following a slightly modified procedure,[7] in a 100 mL sealed tube, the diazo compound **11c** (570 mg, 3.00 mmol, 1.00 equiv) and diphenyl acetylene **(12a)** (3.74 g, 21.0 mmol, 7.00 equiv) were dissolved in 30 mL dry DCM under argon. The solution was stirred at room temperature with the irradiation of 440 nm blue LEDs (Kessil lamp). After 16 h, the solvent was evaporated under vacuum and the residue was purified by flash chromatography using 3% Et$_2$O/hexane as eluent to afford the tittled compound **1c** (600 mg, 1.76 mmol, 59%) as sticky solid. (*See Spectra*)

- **TLC (Et$_2$O/Hexane, 2:8 v/v):** R$_f$ = 0.40, UV, KMnO$_4$.
- **^{1}H NMR (400 MHz, CDCl$_3$):** δ 7.82 – 7.77 (m, 4H, Ar*H*), 7.49 (t, *J* = 7.5 Hz, 4H, Ar*H*), 7.43 – 7.38 (m, 2H, Ar*H*), 7.24 – 7.13 (m, 3H, Ar*H*), 7.04 (td, *J* = 7.4, 1.7 Hz, 1H, Ar*H*), 3.76 (s, 3H, CO$_2$C*H*$_3$), 2.57 (s, 3H, ArC*H*$_3$).
- **^{13}C NMR (101 MHz, CDCl$_3$):** δ 174.9, 139.5, 137.2, 130.4, 129.6, 129.3, 128.9, 128.2, 127.3, 127.1, 125.9, 113.8, 52.3, 36.2, 20.6.
- **IR (Neat, cm^{-1}):** υ 2953 (s), 2922 (s), 2854 (m), 1721 (s), 1490 (m), 1452 (m), 1263 (s), 758 (s), 689 (m).
- **HRMS (ESI):** Calcd. for $C_{24}H_{20}O_2Na^+$ $[M+Na]^+$ 363.1361; found: 363.1366

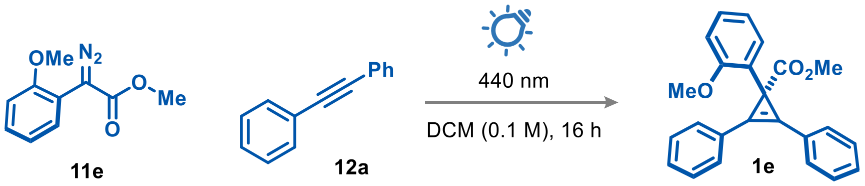
Methyl-2,3-diphenyl-1-(2-(trifluoromethyl)phenyl)cycloprop-2-ene-1-carboxylate (1d)



Following a slightly modified procedure,[7] in a 100 mL sealed tube, the diazo compound **11d** (1.22 g, 5.00 mmol, 1.00 equiv) and diphenyl acetylene **(12a)** (6.23 g, 35.0 mmol, 7.00 equiv) were dissolved in 50 mL dry DCM under argon. The solution was stirred at room temperature with the irradiation of 440 nm blue LEDs (Kessil lamp). After 16 h, the solvent was evaporated under vacuum and the residue was purified by flash chromatography using 3% Et$_2$O/hexane as eluent to afford the title compound **1d** (1.10 g, 2.80 mmol, 56%) as brown solid. (*See Spectra*)

- **Melting point:** 126 - 128 °C.
- **TLC (Et$_2$O/Hexane, 2:8 v/v):** R$_f$ = 0.40, UV, KMnO$_4$.
- **^{1}H NMR (400 MHz, CDCl$_3$):** δ 7.82 – 7.77 (m, 4H, Ar*H*), 7.66 (dd, *J* = 5.6, 3.7 Hz, 1H, Ar*H*), 7.53 – 7.47 (m, 4H, Ar*H*), 7.46 – 7.41 (m, 3H, Ar*H*), 7.39 – 7.34 (m, 2H, Ar*H*), 3.74 (s, 3H, CO$_2$C*H*$_3$).
- **^{13}C NMR (101 MHz, CDCl$_3$):** δ 174, 138.8, 131.8, 130.2, 129.55, 129.54 (q, *J* = 30.3 Hz), 129.5, 129.0, 127.4, 127.3 (q, *J* = 5.0 Hz), 126.9, 125.1 (q, 123.7, *J* = 275.7 Hz), 113.5, 52.1, 36.7.
- **^{19}F NMR (377 MHz, CDCl$_3$)** δ -56.65.
- **IR (Neat, cm^{-1}):** υ 2954 (w), 2922 (w), 2856 (w), 1727 (s), 1491 (m), 1453 (m), 1264 (m), 759 (s), 691 (w).
- **HRMS (ESI):** Calcd. for $C_{24}H_{17}F_3O_2Na^+$ [M+Na]$^+$ 417.1078; found: 417.1078.

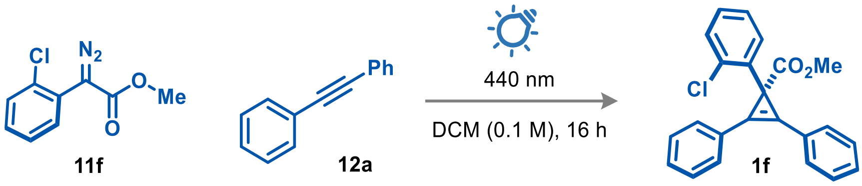
Methyl-1-(2-methoxyphenyl)-2,3-diphenylcycloprop-2-ene-1-carboxylate (1e)



Following a slightly modified procedure,[7] in a 100 mL sealed tube, the diazo compound **11e** (1.03 g , 5.00 mmol, 1.00 equiv) and diphenyl acetylene **(12a)** (6.23 g, 35.0 mmol, 7.00 equiv) were dissolved in 50 mL dry DCM under argon. The solution was stirred at room temperature with the irradiation of 440 nm blue LEDs (Kessil lamp). After 16 h, the solvent was evaporated under vacuum and the residue was purified by flash chromatography using 3% Et_2O/hexane as eluent to afford the title compound **1e** (800 mg, 2.24 mmol, 45%) as sticky solid. (*See Spectra*)

- **TLC (Et_2O/Hexane, 2:8 v/v):** R_f = 0.50, UV, $KMnO_4$.
- **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.88 (d, *J* = 7.5 Hz, 4H, Ar*H*), 7.50 (t, *J* = 7.7 Hz, 4H, Ar*H*), 7.41 (t, *J* = 7.5 Hz, 2H, Ar*H*), 7.26 – 7.19 (m, 2H, Ar*H*), 6.94 (d, *J* = 8.1 Hz, 1H, Ar*H*), 6.82 (t, *J* = 7.5 Hz, 1H, Ar*H*), 3.98 (s, 3H, ArOCH_3), 3.73 (s, 3H, CO_2CH_3).
- **^{13}C NMR (101 MHz, $CDCl_3$):** δ 174.9, 158.4, 130.1, 130.0, 129.2, 128.8, 128.6, 128.2, 127.2, 120.6, 113, 110.7, 55.4, 52 3, 33.0.
- **IR (Neat, cm^{-1}):** υ 2953 (w), 2922 (m), 2852 (w), 1723 (s), 1490 (m), 1455 (m), 1260 (m), 754 (s), 690 (m).
- **HRMS (ESI):** Calcd. for $C_{24}H_{20}O_3H^+$ $[M+H]^+$ 357.1491; found: 357.1494.

Methyl-1-(2-chlorophenyl)-2,3-diphenylcycloprop-2-ene-1-carboxylate (1f)

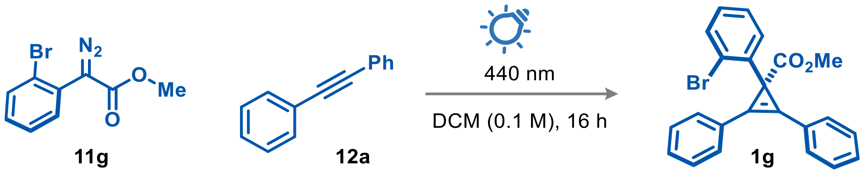


Following a slightly modified procedure,[7] in a 100 mL sealed tube, the diazo compound **11f** (630 mg , 3.00 mmol, 1.00 equiv) and diphenyl acetylene **(12a)** (3.74 g, 21.0 mmol, 7.00 equiv) were dissolved in 30 mL dry DCM under argon. The solution was stirred at room temperature with the irradiation of 440 nm blue LEDs (Kessil lamp). After 16 h, the solvent was evaporated under vacuum and the residue was purified by flash chromatography using 3% Et_2O/hexane as eluent to afford the title compound **1f** (550 mg, 1.53 mmol, 51%) as sticky solid. (*See Spectra*)

- **TLC (Et_2O/Hexane, 2:8 v/v):** R_f = 0.50, UV, $KMnO_4$.
- **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.89 (d, *J* = 7.0 Hz, 4H, Ar*H*), 7.50 (t, *J* = 7.6 Hz, 4H, Ar*H*), 7.45-7.37 (m, 3H, Ar*H*), 7.29 – 7.25 (m, 1H, Ar*H*), 7.21 – 7.14 (m, 1H, Ar*H*), 7.12 – 7.06 (m, 1H, Ar*H*), 3.77 (s, 3H, CO_2CH_3).
- **^{13}C NMR (101 MHz, $CDCl_3$):** δ 174.0, 139.2, 134.8, 129.9, 129.61, 129.55 129.5, 129.0, 128.4, 126.9, 126.6, 112.9, 52.4, 35.8.
- **IR (Neat, cm^{-1}):** υ 3061 (w), 2922 (m), 2854 (w), 1724 (s), 1439 (m), 1287 (w), 1217 (s), 752 (s), 689 (m).

- **HRMS (ESI):** Calcd. for $C_{23}H_{17}ClO_2Na^+$ $[M+Na]^+$ 383.0815; found: 383.0813.

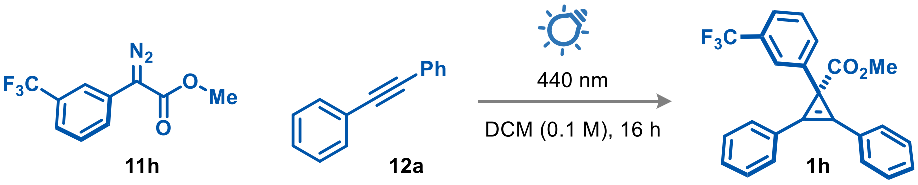
Methyl-1-(2-bromophenyl)-2,3-diphenylcycloprop-2-ene-1-carboxylate (1g)



Following a slightly modified procedure,[7] in a 100 mL sealed tube, the diazo compound **11g** (510 mg , 2.00 mmol, 1.00 equiv) and diphenyl acetylene (12a) (2.50 g, 14.0 mmol, 7.00 equiv) were dissolved in 20 mL dry DCM under argon. The solution was stirred at room temperature with the irradiation of 440 nm blue LEDs (Kessil lamp). After 16 h, the solvent was evaporated under vacuum and the residue was purified by flash chromatography using 3% Et_2O/hexane as eluent to afford the title compound **1g** (450 mg, 1.11 mmol, 56%) as brown sticky solid. (*See Spectra*)

- **TLC (Et_2O/Hexane, 2:8 v/v):** $R_f = 0.40$, UV, $KMnO_4$.
- **^1H NMR (400 MHz, $CDCl_3$):** δ 7.92 (d, $J = 7.7$ Hz, 4H), 7.58 (d, $J = 7.8$ Hz, 1H), 7.52 – 7.46 (m, 4H, Ar*H*)), 7.45-7.39 (m, 2H, Ar*H*)), 7.27-7.24 (m, 1H, Ar*H*)), 7.17 – 7.06 (m, 2H, Ar*H*)), 3.78 (s, 3H, CO_2CH_3).
- **^{13}C NMR (101 MHz, $CDCl_3$):** δ 173.8, 141.1, 133.03, 129.97, 129.8, 129.6, 129.0, 128.5, 127.5, 126.7, 125.0, 113.1, 52.4, 37.9.
- **IR (Neat, cm^{-1}):** υ 3060 (w), 2921 (s), 2854 (m), 1727 (s), 1458 (m), 1286 (w), 1216 (m), 1057 (m), 689 (m).
- **HRMS (ESI):** calcd. for $C_{23}H_{17}BrO_2H^+$ $[M+Na]^+$ 405.0490; found: 405.0492.

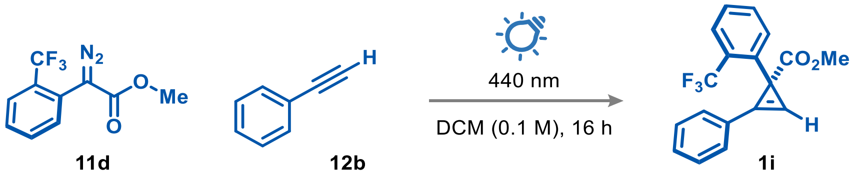
Methyl-2,3-diphenyl-1-(3-(trifluoromethyl)phenyl)cycloprop-2-ene-1-carboxylate (1h)



Following a slightly modified procedure,[6] in a 100 mL sealed tube, the diazo compound **11h** (611 mg, 2.50 mmol, 1.00 equiv) and diphenyl acetylene **(12a)** (3.11 g, 17.5 mmol, 7.00 equiv) were dissolved in 25 mL dry DCM under argon. The solution was stirred at room temperature with the irradiation of 440 nm blue LEDs (Kessil lamp). After 16 h, the solvent was evaporated under vacuum and the residue was purified by flash chromatography using 3-5% Et_2O/hexane as eluent to afford the title compound **1h** (500 mg, 1.27 mmol, 50%) as colorless sticky solid. (*See Spectra*)

- **TLC (Et_2O/Hexane, 2:8 v/v):** R_f = 0.40, UV, $KMnO_4$.
- **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.87 (s, 1H, Ar*H*), 7.77 (d, *J* = 7.6 Hz, 4H, Ar*H*), 7.67 (d, *J* = 8.1 Hz, 1H, Ar*H*), 7.56 – 7.36 (m, 8H, Ar*H*), 3.74 (s, 3H, CO_2CH_3).
- **^{13}C NMR (101 MHz, $CDCl_3$):** δ 173.8, 141.1, 131.4, 130.5, 130.2, 129.8, 129.7, 129.1, 128.5, 126.0, 124.9 (q, *J* = 4.0 Hz), 123.2 (q, *J* = 4.0 Hz), 110.5, 52.2, 34.9.
- **^{19}F NMR (377 MHz, $CDCl_3$)** δ -62.39.
- **IR (Neat, cm^{-1}):** υ 3064 (w), 2952 (w), 2345 (m), 1728 (s), 1443 (w), 1314 (s), 1214 (m), 1120 (s), 758 (s).
- **HRMS (ESI):** Calcd. for $C_{24}H_{17}F_3O_2Na^+$ $[M+Na]^+$ 417.1078; found: 417.1080.

Methyl-2-phenyl-1-(2-(trifluoromethyl)phenyl)cycloprop-2-ene-1-carboxylate (1i)

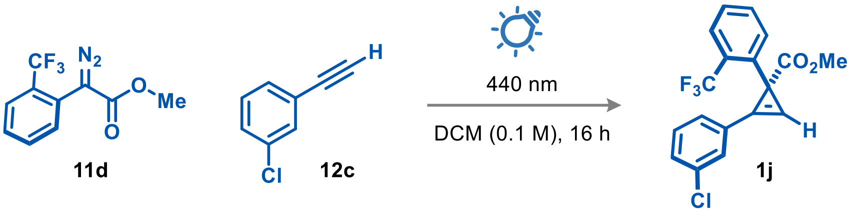


Following a slightly modified procedure,[7] in a 100 mL sealed tube, the diazo compound **11d** (732 mg. 3.00 mmol, 1.00 equiv) and ethynylbenzene **(12b)** (3.06 g, 30.0 mmol, 10.0 equiv) were dissolved in 30 mL dry DCM under argon. The solution was stirred at an ambient temperature with the irradiation of 440 nm blue LEDs (Kessil lamp). After 16 h, the solvent was evaporated under vacuum and the residue was purified by flash chromatography using 3% Et_2O/hexane as eluent to afford the title compound **1i** (610 mg, 1.92 mmol, 63%) as brown solid. (*See Spectra*)

- **Melting point:** 99-101 °C.
- **TLC (Et_2O/Hexane, 2:8 v/v):** R_f = 0.40, UV, $KMnO_4$.
- **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.71 – 7.62 (m, 3H, Ar*H*), 7.55 – 7.33 (m, 6H, Ar*H*), 7.30 (s, 1H, C=C*H*), 3.69 (s, 3H, CO_2CH_3).
- **^{13}C NMR (101 MHz, $CDCl_3$):** δ 174.9, 140.4 (q, *J* = 1.8 Hz), 132.0, 131.1, 130.1, 129.6, 129.1 (q, *J* = 30.3 Hz), 129.0, 127.4, 126.6 (q, *J* = 5 Hz), 125.8, 124.7 (q, *J* = 274.7 Hz), 117.6, 103.7 (q, *J* = 3.6 Hz), 52.4, 32.7.
- **^{19}F NMR (377 MHz, $CDCl_3$)** δ -59.53.

- **IR (Neat, cm^{-1}):** υ 2923 (s), 2855 (m), 2361 (w), 1748 (s), 1461 (w), 1295 (w), 755 (w), 656 (w).
- **HRMS (ESI):** Calcd. for $C_{18}H_{13}F_3O_2Na^+$ $[M+Na]^+$ 341.0765; found: 341.0765.

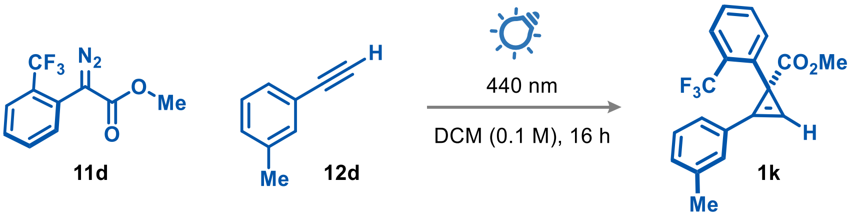
Methyl-2-(3-chlorophenyl)-1-(2-(trifluoromethyl)phenyl)cycloprop-2-ene-1-carboxylatecarboxylate (1j)



Following a slightly modified procedure,[7] in a 100 mL sealed tube, the diazo compound **11d** (732 mg. 3.00 mmol, 1.00 equiv) and 1-chloro-3-ethynylbenzene **(12c)** (4.1 g, 30 mmol, 10 equiv) were dissolved in 30 mL dry DCM under argon. The solution was stirred at room temperature with the irradiation of 440 nm blue LEDs (Kessil lamp). After 16 h, the solvent was evaporated under vacuum and the residue was purified by flash chromatography using 3% Et_2O/hexane as eluent to afford the title compound **1j** (550 mg, 1.56 mmol, 52%) as brown liquid. (*See Spectra*)

- **TLC (Et_2O/Hexane, 2:8 v/v):** $R_f = 0.40$, UV, $KMnO_4$.
- **^1H NMR (400 MHz, $CDCl_3$):** δ 7.66 - 7.63 (m, 2H, Ar*H*), 7.58 – 7.53 (m, 1H, Ar*H*), 7.48 – 7.35 (m, 6H, Ar*H*), 3.69 (s, 3H, CO_2CH_3).
- **^{13}C NMR (101 MHz, $CDCl_3$):** δ 174.5, 139.9, 135.0, 132.1, 131.0, 130.3, 130.2, 129.3, 129.1 (q, J = 30.3 Hz), 127.62, 127.58, 126.7 (q, J = 5 Hz), 124.6 (q, J = 274.7 Hz), 116.9, 105.5, 52.5, 33.1. One carbon was not resolved at 101 MHz.
- **^{19}F NMR (377 MHz, $CDCl_3$)** δ -59.48.
- **IR (Neat, cm^{-1}):** υ 3061 (w), 3022 (w), 2949 (w), 1720 (s), 1443 (w), 1215 (s), 756 (m), 690 (m).
- **HRMS (ESI):** Calcd. for $C_{18}H_{12}F_3O_2Na^+$ $[M+Na]^+$ 375.0376; found: 375.0373

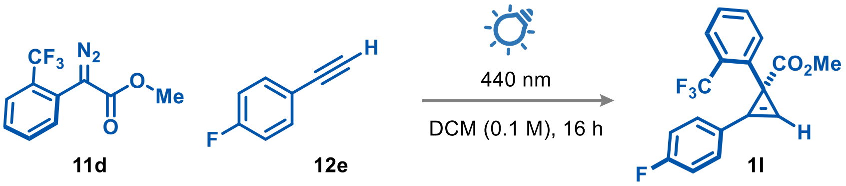
Methyl-2-(m-tolyl)-1-(2-(trifluoromethyl)phenyl)cycloprop-2-ene-1-carboxylate (1k)



Following a slightly modified procedure,[7] in a 100 mL sealed tube, the diazo compound **11d** (732 mg. 3.0 mmol, 1.0 equiv) and 1-ethynyl-3-methylbenzene **(12d)** (3.3 g, 30 mmol, 10 equiv) were dissolved in 30 mL dry DCM under argon. The solution was stirred at room temperature with the irradiation of 440 nm blue LEDs (Kessil lamp). After 16 h, the solvent was evaporated under vacuum and the residue was purified by flash chromatography using 4% Et_2O/hexane as eluent to afford the title compound **1k** (470 mg, 1.41 mmol, 47%) as brown liquid. (*See Spectra*)

- **TLC (Et_2O/Hexane, 2:8 v/v):** R_f = 0.45, UV, $KMnO_4$.
- **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.67 (d, *J* = 6.4 Hz, 1H, Ar*H*), 7.60 - 7.47 (m, 3H, Ar*H*), 7.47-7.34 (m, 3H, Ar*H*), 7.33 – 7.24 (m, 2H, Ar*H*), 3.72 (s, 3H, CO_2CH_3), 2.45 (s, 3H, ArCH_3).
- **^{13}C NMR (101 MHz, $CDCl_3$):** δ 175.0, 140.5, 138.8, 132.0, 131.1, 131.0, 130.1, 129.1 (q, *J* = 30.3 Hz), 128.9, 127.4, 126.7, 126.6 (q, *J* = 5 Hz), 125.7, 124.7 (q, *J* = 274.7 Hz), 117.6, 103.5 (q, *J* = 4 Hz), 52.4, 32.6, 21.3.
- **^{19}F NMR (377 MHz, $CDCl_3$)** δ -59.54.
- **IR (Neat, cm^{-1}):** υ 2922 (s), 2854 (w), 1726 (s), 1443 (w), 1313 (s), 1211 (m), 1119 (s), 768 (m).
- **HRMS (ESI):** calcd. for $C_{19}H_{15}F_3O_2Na^+$ $[M+Na]^+$ 355.0922; found: 355.0922.

Methyl-2-(4-fluorophenyl)-1-(2-(trifluoromethyl)phenyl)cycloprop-2-ene-1-carboxylate (1l)

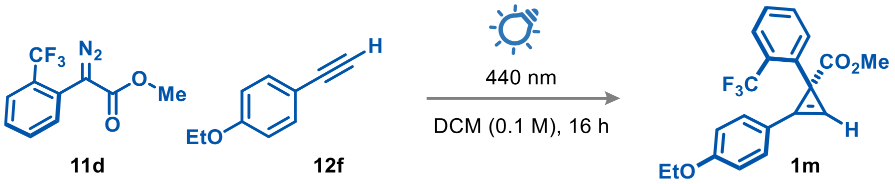


Following a slightly modified procedure,[7] in a 100 mL sealed tube, the diazo compound **11d** (488 mg. 2.00 mmol, 1.00 equiv) and 1-ethynyl-4-fluorobenzene **(12e)** (2.4 g, 20 mmol, 10 equiv) were dissolved in 20 mL dry DCM under argon. The solution was stirred at room temperature with the irradiation of 440 nm blue LEDs (Kessil lamp). After 16 h, the solvent was evaporated under vacuum and the residue was purified by flash chromatography using 3-5% Et_2O/hexane as eluent to afford the title compound **1l** (390 mg, 1.16 mmol, 58%) as brown liquid. (*See Spectra*)

- **TLC (Et_2O/Hexane, 2:8 v/v):** R_f = 0.50, UV, $KMnO_4$.

- **^{1}H NMR (400 MHz, CDCl$_3$):** δ 7.69 - 7.62 (m, 3H, Ar*H*), 7.51 – 7.34 (m, 3H, Ar*H*), 7.28 (s, 1H, C=C*H*), 7.21 – 7.14 (m, 2H, Ar*H*), 3.69 (s, 3H, CO$_2$C*H*$_3$).
- **^{13}C NMR (101 MHz, CDCl$_3$):** δ 174.8, 164.8, 162.3, 140.2, 132.0, 131.6, 131.5, 130.9, 129.1 (q, *J* = 30.3 Hz), 127.5, 126.7 (q, *J* = 5.0 Hz), 124.7 (q, *J* = 274.7 Hz), 122.1 (d, *J* = 3.3 Hz), 116.8, 116.3 (d, *J* = 22.2 Hz), 103.3, 52.4, 32.8.
- **^{19}F NMR (377 MHz, CDCl$_3$)** δ -59.46, -108.89.
- **IR (Neat, cm^{-1}):** υ 2951 (w), 2920 (m), 2859 (w), 1720 (s), 1444 (m), 1263 (m), 1214 (s), 1123 (w), 755 (s).
- **HRMS (ESI):** Calcd. for $C_{18}H_{12}F_4O_2H^+$ $[M+H]^+$ 337.0852; found: 337.0850.

Methyl-2-(4-ethoxyphenyl)-1-(2-(trifluoromethyl)phenyl)cycloprop-2-ene-1-carboxylate (1m)

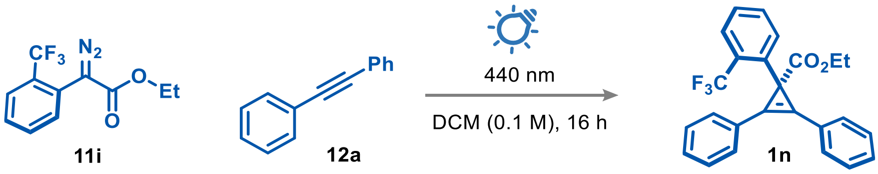


Following a slightly modified procedure,[7] in a 100 mL sealed tube, the diazo compound **11d** (488 mg. 2.00 mmol, 1.00 equiv) and 1-ethoxy-4-ethynylbenzene **(12f)** (2.93 g, 20.0 mmol, 10.0 equiv) were dissolved in 20 mL dry DCM under argon. The solution was stirred at room temperature with the irradiation of 440 nm blue LEDs (Kessil lamp). After 16 h, the solvent was evaporated under vacuum and the residue was purified by flash chromatography using 4-7% Et$_2$O/hexane as eluent to afford the title compound **1m** (370 mg, 1.00 mmol, 50%) as brown liquid. (*See Spectra*)

- **TLC (Et2O/Hexane, 2:8 v/v):** R$_f$ = 0.30, UV, KMnO$_4$.
- **^{1}H NMR (400 MHz, CDCl$_3$):** δ 7.66 – 7.58 (m, 3H, Ar*H*), 7.55 – 7.51 (m, 1H, Ar*H*), 7.43 – 7.32 (m, 2H, Ar*H*), 7.13 (s, 1H, C=C*H*), 6.98 (d, *J* = 8.8 Hz, 2H, Ar*H*), 4.09 (q, *J* = 7.0 Hz, 2H, ArOC*H*$_2$CH$_3$), 3.68 (s, 3H, CO$_2$C*H*$_3$), 1.45 (t, *J* = 7.0 Hz, 3H, ArOCH$_2$C*H*$_3$).
- **^{13}C NMR (101 MHz, CDCl$_3$):** δ 175.1, 160.4, 140.8, 132.0, 131.2, 131.0, 129.1 (q, *J* = 30.3 Hz), 127.3, 126.6 (q, *J* = 5 Hz), 124.7 (q, *J* = 274.7 Hz), 118.1, 117.3, 115.0, 100.8, 63.6, 52.3, 32.5, 14.7.
- **^{19}F NMR (377 MHz, CDCl$_3$)** δ -59.51.

- **IR (Neat, cm^{-1}):** υ 2983 (w), 2946 (w), 1724 (s), 1604 (s), 1441 (s), 1245 (s), 1210 (s), 1115 (m), 768 (m).
- **HRMS (ESI):** Calcd. for $C_{20}H_{17}F_3O_3H$ $[M+H]^+$ 363.1208; found: 363.1209.

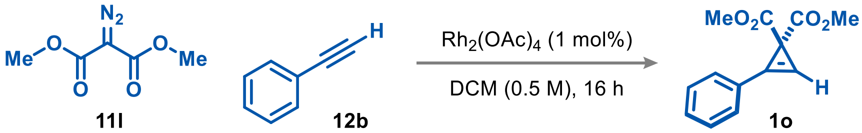
Ethyl-2,3-diphenyl-1-(2-(trifluoromethyl)phenyl)cycloprop-2-ene-1-carboxylate (1n)



Following a slightly modified procedure,[7] in a 100 mL sealed tube, the diazo compound **11i** (774 mg, 3.00 mmol, 1.00 equiv) and diphenyl acetylene **(12a)** (3.74 g, 21.0 mmol, 7.00 equiv) were dissolved in 30 mL dry DCM under argon. The solution was stirred at room temperature with the irradiation of 440 nm blue LEDs (Kessil lamp). After 16 h, the solvent was evaporated under vacuum and the residue was purified by flash chromatography using 4% Et_2O/hexane as eluent to afford the title compound **1n** (700 g, 1.71 mmol, 57%) as colorless sticky solid. (*See Spectra*)

- **TLC (Et_2O/Hexane, 2:8 v/v):** R_f = 0.35, UV, $KMnO_4$.
- **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.79 (d, *J* = 7.6 Hz, 4H, Ar*H*), 7.64 (dd, *J* = 5.7, 3.6 Hz, 1H, Ar*H*), 7.50 (t, *J* = 7.5 Hz, 4H, Ar*H*), 7.42 (dd, *J* = 8.8, 6.2 Hz, 3H, Ar*H*), 7.38 – 7.33 (m, 2H, Ar*H*), 4.22 (q, *J* = 7.1 Hz, 2H, $CO_2CH_2CH_3$), 1.21 (t, *J* = 7.1 Hz, 3H, $CO_2CH_2CH_3$).
- **^{13}C NMR (101 MHz, $CDCl_3$):** δ 173.4, 138.8, 131.8, 130.3, 129.53 (q, *J* = 31.3 Hz), 129.47, 128.9, 127.3, 127.2 (q, *J* = 5 Hz), 127.0, 125.1 (q, *J* = 274.7 Hz), 113.6, 61.0, 36.9, 14.1.
- **^{19}F NMR (377 MHz, $CDCl_3$)** δ -56.40.
- **IR (Neat, cm^{-1}):** υ 2922 (m), 2855 (w), 1723 (s), 1447 (w), 1314 (s), 1252 (m), 1210 (m), 1119 (s), 759 (s), 689 (m).
- **HRMS (ESI):** Calcd. for $C_{25}H_{19}F_3O_2Na^+$ $[M+Na]^+$ 431.1235; found: 431.1235.

Dimethyl 2-phenylcycloprop-2-ene-1,1-dicarboxylate (1o)

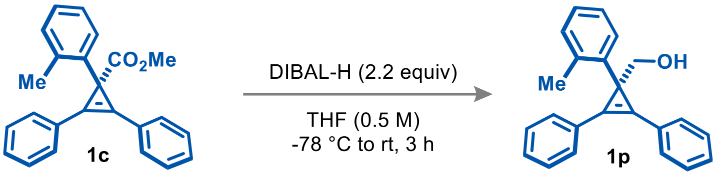


Following a slightly modified procedure,[8] dimethyl 2-diazomalonate (**11l**) (506 mg, 3.20 mmol, 1.00 equiv.) was dissolved in DCM (0.5 M) and the resulting solution was added via syringe pump to a suspension of $Rh_2(OAc)_4$ (0.01 equiv) and phenyl acetylene **(12b)** (980 mg, 9.6 mmol, 3.0 equiv) in DCM (0.8 M) at room temperature over 10 h. After the addition was complete, the reaction mixture was allowed to stir for another 10 h. The reaction mixture was then filtered through a small pad of silica eluting with CH_2Cl_2, and the filtrate was concentrated under reduced pressure. After 20 h, the solvent was evaporated under vacuum and the residue was purified by flash chromatography using 10-20% Et_2O/hexane as eluent to afford the title compound **1o** (435 mg, 1.87 mmol, 58%) as pale yellow solid.

- **TLC (Et_2O/Hexane, 3:7 v/v):** R_f = 0.40, UV, $KMnO_4$.
- **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.65 – 7.58 (m, 2H, Ar*H*), 7.46 – 7.39 (m, 3H, Ar*H*), 6.89 (s, 1H, C=*CH*), 3.72 (s, 6H, CO_2*CH_3*).
- **^{13}C NMR (101 MHz, $CDCl_3$):** δ 171.0, 130.5, 130.2, 128.8, 123.8, 112.1, 95.1, 52.3, 32.7.

  The characterization data matched the reported value.[8]

2,3-Diphenyl-1-(*o*-tolyl)cycloprop-2-en-1-yl)methanol (1p)

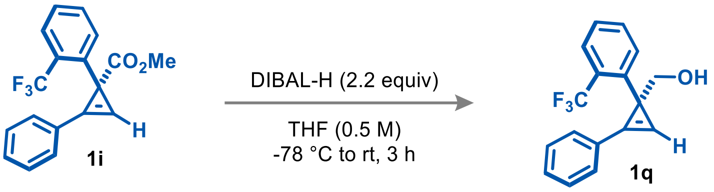


Following a slightly modified procedure,[9] a stirred solution of ester **1c** (340 mg, 1.00 mmol, 1.00 equiv) in THF (2 mL) was cooled to –78 °C. To this, DIBAL-H (2.2 mL, 2.2 mmol, 2.2 equiv) was added dropwise, and the mixture was allowed to stir for 2 h at –78 °C, and then the cold bath was removed, and the mixture was allowed to stir while it was warmed to rt over 1 h. Next, the mixture was quenched with saturated aqueous $NaHCO_3$ (1 mL) and stirred for 30 min. Then 5 mL 1M HCl was added to remove the alumina gel. Then, the reaction mixture was extracted with diethyl ether (3 × 10 mL). The combined organic layers were dried with Na_2SO_4 and then concentrated. The residue was purified by chromatography using 7-10% Et_2O/hexane to give the title compound **1p** (180 mg, 0.57 mmol, 57%) as a colorless oil. (*See Spectra*)

- **TLC (Et_2O/Hexane, 3:7 v/v):** R_f = 0.30, UV, $KMnO_4$.
- **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.89 – 7.75 (m, 3H, Ar*H*), 7.49 (td, *J* = 7.4, 3.2 Hz, 4H, Ar*H*), 7.43 – 7.33 (m, 3H, Ar*H*), 7.28 – 7.24 (m, 1H, Ar*H*), 7.18 – 7.04 (m, 3H, Ar*H*), 4.30 (s, 2H, C*CH_2*OH), 2.58 (s, 3H, Ar*CH_3*).

- **^{13}C NMR (101 MHz, CDCl$_3$):** δ 142.6, 136.5, 130.9, 129.8, 129.7, 129.2, 128.8, 128.7, 126.8, 126.0, 120.6, 67.3, 37.0, 21.6.
- **IR (Neat, cm^{-1}):** υ 3323 (w), 2922 (s), 2854 (m), 1457 (w), 1377 (w), 1298 (w), 1184 (w), 1034 (w), 756 (w), 699 (m).
- **Mass:** Calcd. for $C_{23}H_{18}ONa^+$ $[M+Na]^+$ 335.1412; found: 335.1417.

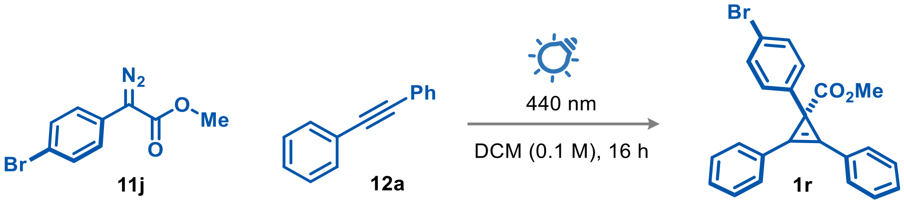
2-Phenyl-1-(2-(trifluoromethyl)phenyl)cycloprop-2-en-1-yl)methanol (1q)



Following a slightly modified procedure,[9] a stirred solution of ester **1i** (954 mg, 3.00 mmol, 1.00 equiv) in THF (6 mL) was cooled to –78 °C. To this, DIBAL-H (6.6 mL, 6.6 mmol, 2.2 equiv) was added dropwise, and the mixture was allowed to stir for 2 h at –78 °C, and the mixture was allowed to stir while it was warmed to rt over 1 h. Next, the mixture was quenched with saturated aqueous $NaHCO_3$ (3 mL) and stirred for 30 min. Then 15 mL 1M HCl was added to remove the alumina gel. Then, the reaction mixture was extracted with diethy ether (3 × 20 mL). The combined organic layers were dried with Na_2SO_4 and then concentrated. The residue was purified by chromatography using 7-10% Et_2O/hexane to give the title compound **1q** (600 mg, 2.00 mmol, 66%) as a brown liquid. (*See Spectra*)

- **TLC (Et_2O/Hexane, 3:7 v/v):** R_f = 0.25, UV, $KMnO_4$.
- **^{1}H NMR (400 MHz, CDCl$_3$):** δ 7.80 (d, *J* = 7.6 Hz, 2H, Ar*H*), 7.72 (d, *J* = 7.7 Hz, 1H, Ar*H*), 7.66 (d, *J* = 7.9 Hz, 1H, Ar*H*), 7.52-7.38 (m, 5H, Ar*H*), 7.34 (t, *J* = 7.7 Hz, 1H, Ar*H*), 4.27 (d, *J* = 11.4 Hz, 1H, CCH_2OH), 3.82 (d, *J* = 11.4 Hz, 1H, CCH_2OH), 1.66 – 1.58 (m, 1H, CCH_2*OH*).
- **^{13}C NMR (101 MHz, CDCl$_3$):** δ 143.5, 132.5, 132.0, 129.4, 129.3, 128.8, 128.7 (q, *J* = 20.2 Hz), 128.1, 126.9, 126.8, 126.7 (q, *J* = 4 Hz), 124.7 (q, *J* = 102.8 Hz), 109.0, 68.8, 33.7.
- **^{19}F NMR (377 MHz, CDCl$_3$):** δ -59.14.
- **IR (Neat, cm^{-1}):** υ 3409 (w), 2923 (w), 2853 (w), 1447 (w), 1313 (s), 1268 (w), 1117 (s), 1037 (m), 765 (m), 655 (m).
- **Mass:** Calcd. for $C_{17}H_{13}F_3ONa^+$ $[M+Na]^+$ 313.0816; found: 313.0812.

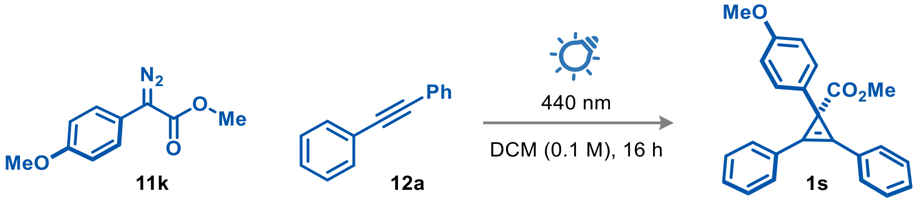
Methyl-1-(4-bromophenyl)-2,3-diphenylcycloprop-2-ene-1-carboxylate (1r)



Following a slightly modified procedure,[7] in a 100 mL sealed tube, the diazo compound **11j** (510 mg, 2.00 mmol, 1.00 equiv) and diphenyl acetylene **(12a)** (2.5 g, 14 mmol, 7.0 equiv) were dissolved in 20 mL dry DCM under argon. The solution was stirred at room temperature with the irradiation of 440 nm blue LEDs (Kessil lamp). After 16 h, the solvent was evaporated under vacuum and the residue was purified by flash chromatography using 3-5% Et_2O/hexane as eluent to afford the title compound **1r** (500 mg, 1.24 mmol, 62%) as colorless sticky solid. (*See Spectra*)

- **TLC (Et_2O/Hexane, 2:8 v/v):** $R_f = 0.50$, UV, $KMnO_4$.
- **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.76 – 7.72 (m, 4H, Ar*H*), 7.53 – 7.47 (m, 4H, Ar*H*), 7.46 – 7.38 (m, 6H, Ar*H*), 3.72 (s, 3H, CO_2CH_3).
- **^{13}C NMR (101 MHz, $CDCl_3$):** δ 174.0, 139.1, 131.1, 129.9, 129.8, 129.6, 129.1, 126.1, 120.2, 110.7, 52.2, 34.7.
- **IR (Neat, cm^{-1}):** υ 2922 (m), 2854 (w), 1728 (s), 1444 (w), 1314 (s), 1252 (m), 1213 (m), 1120 (s), 760 (s), 689 (w).
- **HRMS (ESI):** calcd. for $C_{23}H_{17}BrO_2H^+$ $[M+H]^+$ 405.0490; found: 405.0493.

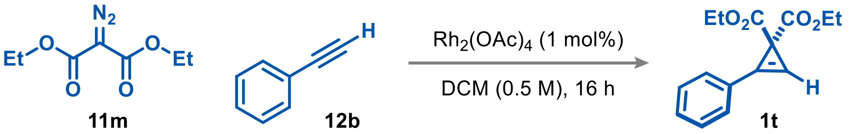
Methyl 1-(4-methoxyphenyl)-2,3-diphenylcycloprop-2-ene-1-carboxylate (1s)



Following a slightly modified procedure,[7] in a 100 mL sealed tube, the diazo compound **11k** (412 mg, 2.00 mmol, 1.00 equiv) and diphenyl acetylene **(12a)** (2.5 g, 14 mmol, 7.0 equiv) were dissolved in 20 mL dry DCM under argon. The solution was stirred at room temperature with the irradiation of 440 nm blue LEDs (Kessil lamp). After 16 h, the solvent was evaporated under vacuum and the residue was purified by flash chromatography using 5-10% Et_2O/hexane as eluent to afford the title compound **1s** (420 mg, 1.17 mmol, 59%) as colorless sticky solid. (*See Spectra*)

- **TLC (Et_2O/Hexane, 2:8 v/v):** $R_f = 0.30$, UV, $KMnO_4$.
- **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.83 – 7.78 (m, 4H, Ar*H*), 7.56 – 7.38 (m, 8H, Ar*H*), 6.87 (d, *J* = 8.7 Hz, 2H, Ar*H*), 3.78 (s, 3H, ArOCH_3), 3.75 (s, 3H, CO_2CH_3).
- **^{13}C NMR (101 MHz, $CDCl_3$):** δ 174.8, 158.3, 132.3, 130.0, 129.5, 129.4, 129.1, 126.7, 113.6, 111.7, 55.3, 52.2, 34.8.
- **IR (Neat, cm^{-1}):** υ 2923 (m), 2855 (w), 1728 (s), 1445 (w), 1315 (s), 1250 (m), 1213 (m), 1120 (s), 759 (s), 689 (w).
- **HRMS (ESI):** Calcd. for $C_{24}H_{20}O_3H^+$ $[M+H]^+$ 357.1491; found: 357.1495.

Dimethyl 2-phenylcycloprop-2-ene-1,1-dicarboxylate (1t)

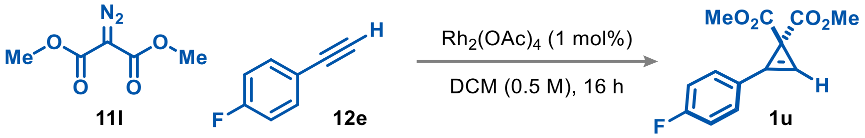


Following a slightly modified procedure,[8] diethyl 2-diazomalonate (**11m**) (931 mg, 5.00 mmol, 1.00 equiv.) was dissolved in DCM (0.5 M) and the resulting solution was added via syringe pump to a suspension of $Rh_2(OAc)_4$ (0.01 equiv) and phenyl acetylene **(12b)** (1.6 ml, 15.0 mmol, 3.00 equiv) in DCM (0.8 M) at room temperature over 10 h. After the addition was complete, the reaction mixture was allowed to stir for another 10 h. The reaction mixture was then filtered through a small pad of silica eluting with CH_2Cl_2, and the filtrate was concentrated under reduced pressure. After 20 h, the solvent was evaporated under vacuum and the residue was purified by flash chromatography using 10-20% Et_2O/hexane as eluent to afford the title compound **1t** (650 mg, 2.50 mmol, 50%) as pale-yellow liquid.

- **TLC (Et_2O/Hexane, 1:1 v/v):** R_f = 0.50, UV, $KMnO_4$.
- **^1H NMR (400 MHz, $CDCl_3$):** δ 7.67 – 7.57 (m, 2H, Ar*H*), 7.46 – 7.34 (m, 3H, Ar*H*), 6.89 (s, 1H, C=*CH*), 4.18 (td, *J* = 7.0, 1.3 Hz, 4H, $CO_2CH_2CH_3$), 1.31 – 1.12 (m, 6H, $CO_2CH_2CH_3$).
- **^{13}C NMR (101 MHz, $CDCl_3$):** δ 170.8, 130.4, 130.3, 128.8, 124.1, 112.5, 95.4, 61.1, 33.2, 14.11.

  The characterization data matched the reported value.[8]

Dimethyl 2-phenylcycloprop-2-ene-1,1-dicarboxylate (1u)



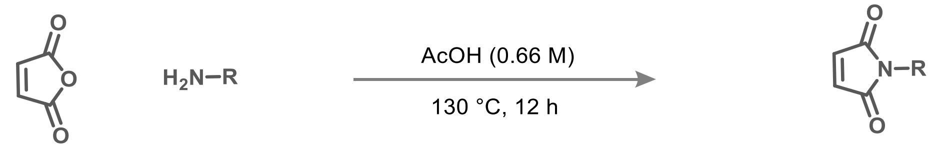
Following a slightly modified procedure,[8] dimethyl 2-diazomalonate (**11l**) (506 mg, 3.20 mmol, 1.00 equiv.) was dissolved in DCM (0.5 M) and the resulting solution was added via syringe pump to a suspension of $Rh_2(OAc)_4$ (0.01 equiv) and 1-ethynyl-4-fluorobenzene **(12e)** (1.15 g, 9.60 mmol, 3.00 equiv) in DCM (0.8 M) at room temperature over 10 h. After the addition was complete, the reaction mixture was allowed to stir for another 10 h. The reaction mixture was then filtered through a small pad of silica eluting with CH_2Cl_2, and the filtrate was concentrated under reduced pressure. After 20 h, the solvent was evaporated under vacuum and the residue was purified by flash chromatography using 15-20% Et_2O/hexane as eluent to afford the title compound **1u** (385 mg, 1.54 mmol, 48%) as pale yellow solid.

- **TLC (Et_2O/Hexane, 3:7 v/v):** R_f = 0.40, UV, $KMnO_4$.
- **^1H NMR (400 MHz, $CDCl_3$):** δ 7.62 (dd, *J* = 8.7, 5.4 Hz, 2H, Ar*H*), 7.14 (t, *J* = 8.7 Hz, 2H, Ar*H*), 6.86 (s, 1H, C=*CH*), 3.74 (s, 6H, CO_2CH_3).
- **^{13}C NMR (101 MHz, $CDCl_3$):** δ 171.0, 165.2, 162.7, 132.4 (d, *J* = 8.8 Hz), 120.3 (d, *J* = 3.4 Hz), 116.3 (d, *J* = 22.2 Hz), 111.3, 94.8 (d, *J* = 2.7 Hz), 52.5, 32.9.
- **^{19}F NMR (377 MHz, $CDCl_3$)** δ -108.03.

  The characterization data matched the reported value.[8]

2.3 Procedures for the synthesis of Maleimides:

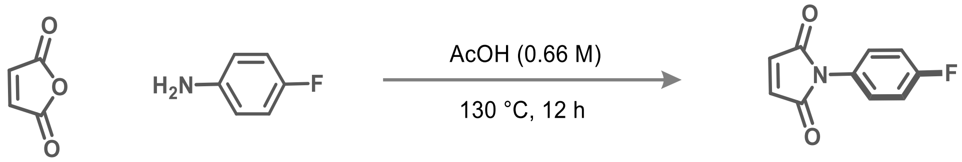
General Procedure:



13 **14** **2**

Following a slightly modified procedure,[10] in a 100 mL round bottom flask, maleic anhydride **13** (2.0 equiv) and primary amine **14** (1.0 equiv) were stirred in acetic acid (1.5 mL per mmol of amine) until maleic anhydride dissolved completely. The reaction mixture was refluxed for 12 h at 130 °C. After completion of the reaction, the reaction mixture was then allowed to cool down to room temperature and the whole reaction mixture was transferred to a 500 mL beaker. A saturated $NaHCO_3$ aqueous solution was added to the beaker containing the reaction mixture until the effervescence stops. The aqueous mixture was extracted with ethyl acetate (3x20 mL per 5 mmol of amine). The combined organic layers were washed with 1 M HCl (2x50 mL per 5 mmol of amine) and brine solution (30 mL per 5 mmol of amine), respectively. The solvent was removed under vacuum and the residue was purified by flash chromatography using EtOAc/hexane as eluent to afford the title compound **2** (Compounds **2i**, **2l**, **2n** were purchased at highest commercial quality and used as received).

1-(4-Fluorophenyl)-1*H*-pyrrole-2,5-dione (2b)



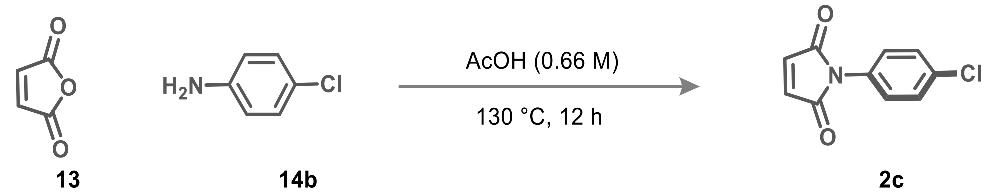
13 **14a** **2b**

Following general procedure,[10] in a 100 mL round bottom flask, maleic anhydride **(13)** (3.96 g, 20.0 mmol, 2.00 equiv) and 4-fluoroaniline **(14a)** (1.1 g, 10 mmol, 1.0 equiv) were stirred in acetic acid (15 mL) until maleic anhydride dissolved completely. The reaction mixture was refluxed for 12 h at 130 °C. After completion of the reaction, the reaction mixture was then allowed to cool down to room temperature and the whole reaction mixture was transferred to a 500 mL beaker. A saturated $NaHCO_3$ aqueous solution was added to the beaker containing the reaction mixture until the effervescence stops. The aqueous mixture was extracted with ethyl acetate (3x40 mL). The combined organic layers were washed with 1 M HCl (2x100 mL) and brine solution (60 mL), respectively. The solvent was removed under vacuum and the residue was purified by flash chromatography using 20-30% EtOAc/hexane as eluent to afford the title compound **2b** (800 mg, 4.20 mmol, 42%) as yellow solid.

- **TLC (EtOAc/Hexane, 3:7 v/v):** R_f = 0.50, UV, $KMnO_4$.
- **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.31 (dd, *J* = 8.8, 4.9 Hz, 2H, Ar*H*)), 7.15 (t, *J* = 8.5 Hz, 2H, Ar*H*)), 6.84 (s, 2H, C=C*H*).
- **^{13}C NMR (101 MHz, $CDCl_3$):** δ 169.4, 160.5, 134.0, 127.6, 127.0, 116.0.
- **^{19}F NMR (377 MHz, $CDCl_3$):** δ -113.12.

  The characterization data matched the reported value.[10]

1-(4-Chlorophenyl)-1*H*-pyrrole-2,5-dione (2c)

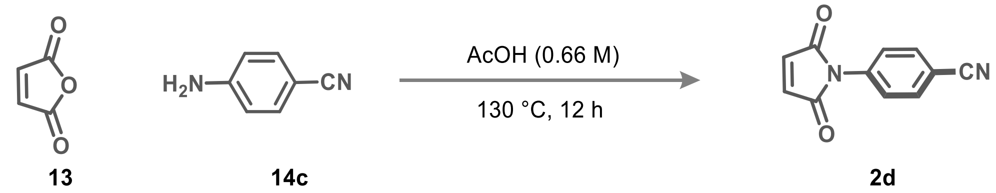


Following general procedure,[10] in a 100 mL round bottom flask, maleic anhydride **(13)** (3.96 g, 20.0 mmol, 2.00 equiv) and 4-chloroaniline **(14b)** (1.27 g, 10.0 mmol, 1.00 equiv) were stirred in acetic acid (15 mL) until maleic anhydride dissolved completely. The reaction mixture was refluxed for 12 h at 130 °C. After completion of the reaction, the reaction mixture was then allowed to cool down to room temperature and the whole reaction mixture was transferred to a 500 mL beaker. A saturated $NaHCO_3$ aqueous solution was added to the beaker containing the reaction mixture until the effervescence stops. The aqueous mixture was extracted with ethyl acetate (3x40 mL). The combined organic layers were washed with 1 M HCl (2x100 mL) and brine solution (60 mL), respectively. The excess solvent was removed under under vacuum and the residue was purified by flash chromatography using 15-30% EtOAc/hexane as eluent to afford the tittled compound **2c** (700 mg, 3.3 mmol, 33%) as yellow solid.

- **TLC (EtOAc/Hexane, 3:7 v/v):** R_f = 0.45, UV, $KMnO_4$.
- **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.43 (d, *J* = 8.6 Hz, 2H, Ar*H*), 7.31 (d, *J* = 8.5 Hz, 2H, Ar*H*), 6.85 (s, 2H, C=C*H*).
- **^{13}C NMR (101 MHz, $CDCl_3$):** δ 169.1, 134.2, 133.6, 129.7, 129.3, 127.1.

  The characterization data matched the reported value.[10]

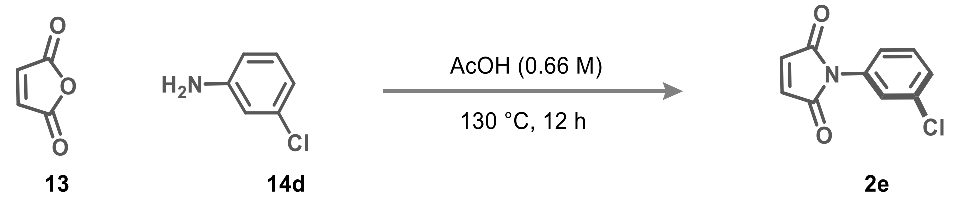
4-(2,5-Dioxo-2,5-dihydro-1*H*-pyrrol-1-yl)benzonitrile (2d)



Following general procedure,[10] in a 100 mL round bottom flask, maleic anhydride **(13)** (3.96 g, 20.0 mmol, 2.00 equiv) and 4-aminobenzonitrile **(14c)** (1.18 g, 10.0 mmol, 1.00 equiv) were stirred in acetic acid (15 mL) until maleic anhydride dissolved completely. The reaction mixture was refluxed for 12 h at 130 °C. After completion of the reaction, the reaction mixture was then allowed to cool down to room temperature and the whole reaction mixture was transferred to a 500 mL beaker. A saturated $NaHCO_3$ aqueous solution was added to the beaker containing the reaction mixture until the effervescence stops. The aqueous mixture was extracted with ethyl acetate (3x40 mL). The combined organic layers were washed with 1 M HCl (2x100 mL) and brine solution (60 mL) respectively. The solvent was removed under vacuum and the residue was purified by flash chromatography using 15-30% EtOAc/hexane as eluent to afford the title compound **2d** (650 mg, 3.30 mmol, 33%) as colorless solid.

- **TLC (EtOAc/Hexane, 3:7 v/v):** $R_f = 0.50$, UV, $KMnO_4$.
- **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.75 (d, *J* = 8.5 Hz, 2H, Ar*H*), 7.59 (d, *J* = 8.4 Hz, 2H, Ar*H*), 6.90 (s, 2H, C=C*H*).
- **^{13}C NMR (101 MHz, $CDCl_3$):** δ 168.5, 135.3, 134.5, 132.9, 125.6, 118.1, 111.0. The characterization data matched the reported value.[11]

1-(3-Chlorophenyl)-1*H*-pyrrole-2,5-dione (2e)



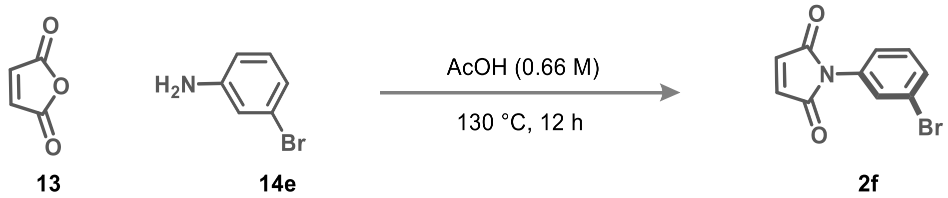
Following general procedure,[10] in a 100 mL round bottom flask, maleic anhydride **(13)** (3.96 g, 20.0 mmol, 2.00 equiv) and 3-chloroaniline **(14d)** (1.27 g, 10 mmol, 1.00 equiv) were stirred in acetic acid (15 mL) until maleic anhydride dissolved completely. The reaction mixture was refluxed for 12 h at 130 °C. After completion of the reaction, the reaction mixture was then allowed to cool down to room temperature and the whole reaction mixture was transferred to a

500 mL beaker. A saturated $NaHCO_3$ aqueous solution was added to the beaker containing the reaction mixture until the effervescence stops. The aqueous mixture was extracted with ethyl acetate (3x40 mL). The combined organic layers were washed with 1 M HCl (2x100 mL) and brine solution (60 mL), respectively. The solvent was removed under vacuum and the residue was purified by flash chromatography using 20-30% EtOAc/hexane as eluent to afford the title compound **2e** (1.1 g, 5.3 mmol, 53%) as colorless solid.

- **TLC (EtOAc/Hexane, 3:7 v/v):** R_f = 0.40, UV, $KMnO_4$.
- **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.40-7.28 (3H, m, Ar*H*), 7.27-7.22 (1H, m, Ar*H*), 6.82 (2H, s, C=C*H*).
- **^{13}C NMR (101 MHz, $CDCl_3$):** δ 168.9, 134.4, 134.1, 132.2, 129.9, 127.8, 125.9, 123.8.

The characterization data matched the reported value.[11]

1-(3-Bromophenyl)-1*H*-pyrrole-2,5-dione (2f)



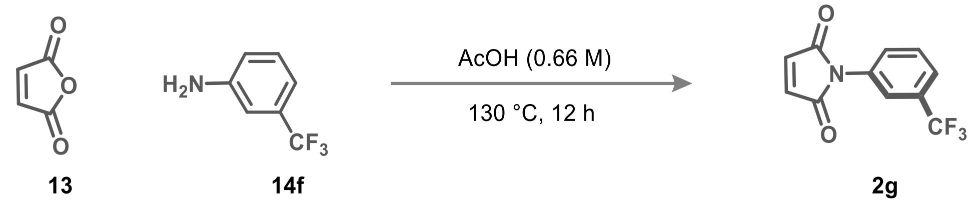
Following general procedure,[10] in a 100 mL round bottom flask, maleic anhydride **(13)** (3.96 g, 20.0 mmol, 2.00 equiv) and 3-bromoaniline **(14e)** (1.27 g, 10.0 mmol, 1.00 equiv) were stirred in acetic acid (15 mL) until maleic anhydride dissolved completely. The reaction mixture was refluxed for 12 h at 130 °C. After completion of the reaction, the reaction mixture was then allowed to cool down to room temperature and the whole reaction mixture was transferred to a 500 mL beaker. A saturated $NaHCO_3$ aqueous solution was added to the beaker containing the reaction mixture until the effervescence stops. The aqueous mixture was extracted with ethyl acetate (3x40 mL). The combined organic layers were washed with 1 M HCl (2x100 mL) and brine solution (60 mL), respectively. The excess solvent was removed under vacuum and the residue was purified by flash chromatography using 15-20% EtOAc/hexane as eluent to afford the title compound **2f** (750 mg, 3.00 mmol, 30%) as yellow solid.

- **TLC (EtOAc/Hexane, 3:7 v/v):** R_f = 0.30, UV, $KMnO_4$.

- **^{1}H NMR (400 MHz, CDCl$_3$):** δ 7.53 (s, 1H, Ar*H*), 7.49 – 7.46 (m, 1H, Ar*H*), 7.34 – 7.28 (m, 2H, Ar*H*), 6.83 (s, 2H, C=C*H*).
- **^{13}C NMR (101 MHz, CDCl$_3$):** δ 168.9, 134.1, 132.3, 130.8, 130.2, 128.7, 124.3, 122.2.

The characterization data matched the reported value.[12]

1-(3-(Trifluoromethyl)phenyl)-1*H*-pyrrole-2,5-dione (2g)

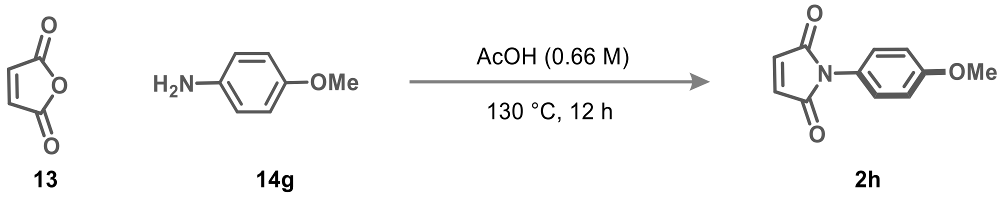


Following general procedure,[10] in a 100 mL round bottom flask, maleic anhydride **(13)** (3.96 g, 20.0 mmol, 2.00 equiv) and 3-(trifluoromethyl)aniline **(14f)** (1.61 g, 10 mmol, 1.00 equiv) were stirred in acetic acid (15 mL) until maleic anhydride dissolved completely. The reaction mixture was refluxed for 12 h at 130 °C. After completion of the reaction, the reaction mixture was then allowed to cool down to room temperature and the whole reaction mixture was transferred to a 500 mL beaker. A saturated $NaHCO_3$ aqueous solution was added to the beaker containing the reaction mixture until the effervescence stops. The aqueous mixture was extracted with ethyl acetate (3x40 mL). The combined organic layers were washed with 1 M HCl (2x100 mL) and brine solution (60 mL), respectively. The solvent was removed under vacuum and the residue was purified by flash chromatography using 15-25% EtOAc/hexane as eluent to afford the title compound **2g** (950 mg, 3.9 0mmol, 39%) as colorless semi-solid.

- **TLC (EtOAc/Hexane, 3:7 v/v):** R_f = 0.50, UV, $KMnO_4$.
- **^{1}H NMR (400 MHz, CDCl$_3$):** δ 7.66 (s, 1H, Ar*H*), 7.62 – 7.54 (m, 3H, Ar*H*), 6.84 (s, 2H, C=C*H*).
- **^{13}C NMR (101 MHz, CDCl$_3$):** δ 168.9, 134.2, 131.8, 131.4 (q, *J* = 32.3 Hz), 129.6, 128.9, 124.3 (q, *J* = 4.0 Hz), 123.5 (q, *J* = 273.7 Hz), 122.6 (q, *J* = 4.0 Hz).
- **^{19}F NMR (377 MHz, CDCl$_3$):** δ -62.63.

  The characterization data matched the reported value.[13]

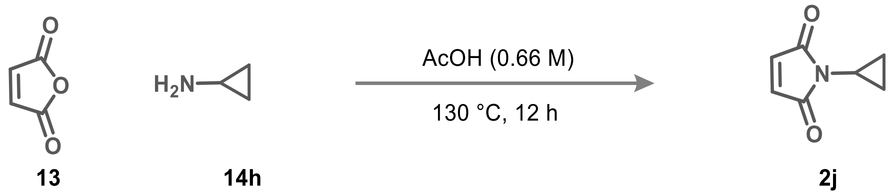
1-(4-Methoxyphenyl)-1H-pyrrole-2,5-dione (2h)



Following general procedure,[10] in a 100 mL round bottom flask, maleic anhydride **(13)** (3.96 g, 20.0 mmol, 2.00 equiv) and 4-methoxyaniline **(14g)** (1.23 g, 10.0 mmol, 1.00 equiv) were stirred in acetic acid (15 mL) until maleic anhydride dissolved completely. The reaction mixture was refluxed for 12 h at 130 °C. After completion of the reaction, the reaction mixture was then allowed to cool down to room temperature and the whole reaction mixture was transferred to a 500 mL beaker. A saturated $NaHCO_3$ aqueous solution was added to the beaker containing the reaction mixture until the effervescence stops. The aqueous mixture was extracted with ethyl acetate (3x40 mL). The combined organic layers were washed with 1 M HCl (2x100 mL) and brine solution (60 mL), respectively. The solvent was removed under vacuum and the residue was purified by flash chromatography using 15-20% EtOAc/hexane as eluent to afford the title compound **2h** (850 mg, 4.20 mmol, 42%) as yellow solid.

- **TLC (EtOAc/Hexane, 3:7 v/v):** R_f = 0.50, UV, $KMnO_4$.
- **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.21 (d, *J* = 9.0 Hz, 2H, Ar*H*), 6.97 (d, *J* = 8.9 Hz, 2H, Ar*H*), 6.80 (s, 2H, C=C*H*), 3.81 (s, 3H, ArOCH_3).
- **^{13}C NMR (101 MHz, $CDCl_3$):** δ 169.8, 159.0, 134.0, 127.5, 123.6, 114.4, 55.4. The characterization data matched the reported value.[10]

1-Cyclopropyl-1*H*-pyrrole-2,5-dione (2j)

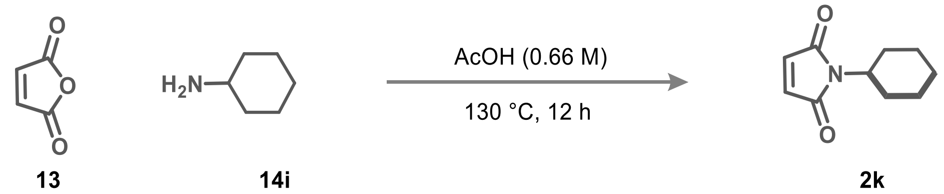


Following general procedure,[10] in a 100 mL round bottom flask, maleic anhydride **(13)** (3.96 g, 20.0 mmol, 2.00 equiv) and cyclopropylamine **(14h)** (570 mg, 10.0 mmol, 1.00 equiv) were stirred in acetic acid (15 mL) until maleic anhydride dissolved completely. The reaction mixture was refluxed for 12 h at 130 °C. After completion of the reaction, the reaction mixture was then allowed to cool down to room temperature and the whole reaction mixture was transferred to a 500 mL beaker. A saturated $NaHCO_3$ aqueous solution was added to the beaker containing the reaction mixture until the effervescence stops. The aqueous mixture was extracted with ethyl acetate (3x40 mL). The combined organic layers were further washed with 1 M HCl (2x100 mL) and brine solution (60 mL), respectively. The solvent was removed under vacuum and the residue was purified by flash chromatography using 10-20% EtOAc/hexane as eluent to afford the title compound **2j** (550 mg, 3.60 mmol, 36%) as colorless solid.

- **TLC (EtOAc/Hexane, 3:7 v/v):** $R_f = 0.60$, UV, $KMnO_4$.
- **^{1}H NMR (400 MHz, $CDCl_3$):** δ 6.54 (s, 2H, C=C*H*), 2.38 (tt, *J* = 7.3, 3.8 Hz, 1H), 0.88 – 0.54 (m, 4H).
- **^{13}C NMR (101 MHz, $CDCl_3$):** δ 170.9, 133.6, 19.9, 4.5.

The characterization data matched the reported value.[14]

1-Cyclohexyl-1*H*-pyrrole-2,5-dione (2k)



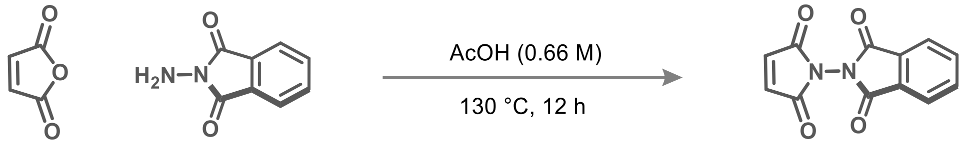
Following general procedure,[10] in a 100 mL round bottom flask, maleic anhydride **(13)** (3.96 g, 20.0 mmol, 2.00 equiv) and cyclohexylamine **(14i)** (990 mg, 10.0 mmol, 1.00 equiv) were stirred in acetic acid (15 mL) until maleic anhydride dissolved completely. The reaction mixture was refluxed for 12 h at 130 °C. After completion of the reaction, the reaction mixture was then allowed to cool down to room temperature and the whole reaction mixture was transferred to a 500 mL beaker. A saturated $NaHCO_3$ aqueous solution was added to the beaker containing the reaction mixture until the effervescence stops. The aqueous mixture was extracted with ethyl acetate (3x40 mL). The combined organic layers were washed with 1 M HCl (2x100 mL) and brine solution (60 mL), respectively. The solvent was removed under vacuum and the residue was purified by flash chromatography using 10-25% EtOAc/hexane as eluent to afford the title compound **2k** (750 mg, 4.20 mmol, 42%) as yellow solid.

- **TLC (EtOAc/Hexane, 3:7 v/v):** $R_f = 0.60$, UV, $KMnO_4$.

- **^{1}H NMR (400 MHz, CDCl$_3$):** δ 6.59 (s, 2H, C=C*H*), 3.86 (tt, *J* = 12.5, 4.0 Hz, 1H), 2.00 (qd, *J* = 12.5, 3.5 Hz, 2H), 1.81 – 1.75 (m, 2H), 1.63 – 1.58 (m, 3H), 1.32 – 1.13 (m, 3H).
- **^{13}C NMR (101 MHz, CDCl$_3$):** δ 170.8, 133.8, 50.6, 29.8, 25.8, 24.9.

  The characterization data matched the reported value.[10]

2-(2,5-Dioxo-2,5-dihydro-1*H*-pyrrol-1-yl)isoindoline-1,3-dione (2m)

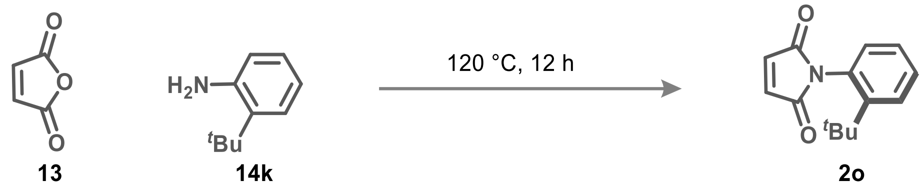


13 **14j** **2m**

Following general procedure,[10] in a 100 mL round bottom flask, maleic anhydride **(13)** (1.98 g, 10.0 mmol, 2.00 equiv) and 2-aminoisoindoline-1,3-dione **(14j)** (0.81 g, 5.0 mmol, 1.0 equiv) were stirred in acetic acid (7.5 mL) until maleic anhydride dissolved completely. The reaction mixture was refluxed for 12 h at 130 °C. After completion of the reaction, the reaction mixture was then allowed to cool down to room temperature and the whole reaction mixture was transferred to a 250 mL beaker. A saturated $NaHCO_3$ aqueous solution was added to the beaker containing the reaction mixture until the effervescence stops. The aqueous mixture was extracted with ethyl acetate (3x20 mL). The combined organic layers were washed with 1 M HCl (2x50 mL) and brine solution (30 mL), respectively. The solvent was removed under vacuum and the residue was purified by flash chromatography using 25-30% EtOAc/hexane as eluent to afford the title compound **2m** (250 mg, 1.03 mmol, 20%) as colorless sticky solid. (*See Spectra*)

- **TLC (EtOAc/Hexane, 4:6 v/v):** R_f = 0.30, UV, $KMnO_4$.
- **^{1}H NMR (400 MHz, CDCl$_3$):** δ 7.98-7.92 (m, 2H, Ar*H*), 7.86-7.81 (m, 2H, Ar*H*), 6.96 (s, 2H, C=C*H*).
- **^{13}C NMR (101 MHz, CDCl$_3$):** δ 165.2, 163.3, 135.1, 133.9, 129.8, 124.4.
- **IR (Neat, cm^{-1}):** υ 2923 (w), 2854 (w), 1742 (s), 1464 (w), 1296 (m), 1152 (w), 1082 (w), 793 (w), 679 (w).
- **HRMS (ESI):** calcd. for $C_{12}H_6N_2O_4H^+$ $[M+H]^+$ 243.0406; found: 243.0413.

2-(2,5-Dioxo-2,5-dihydro-1H-pyrrol-1-yl)isoindoline-1,3-dione (2o)



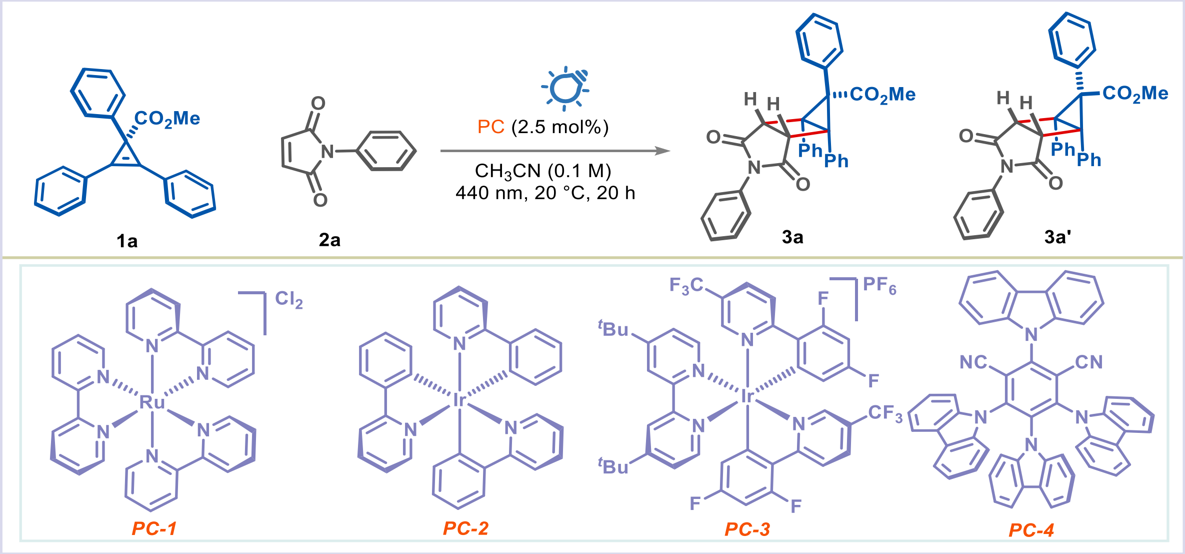
Following slightly modified procedure,[15] 2-*tert*-butylaniline **(14k)** (1.50 g, 10.0 mmol. 1.00 equiv) and maleic anhydride **(13)** (2.85 g, 29.0 mmol, 2.90 equiv) were mixed in a 50 mL sealed round-bottomed flask and heated to 120 °C for 16 h. After cooling to room temperature, the solid was taken up in EtOAc (100 mL) and the whole reaction mixture was transferred to a 500 mL beaker. A saturated $NaHCO_3$ aqueous solution was added to the beaker containing the reaction mixture until the effervescence stops. The aqueous mixture was extracted with ethyl acetate (3x40 mL). The combined organic layers were washed with M HCl (2x100 mL) and brine solution (60 mL), respectively. The solvent was removed under vacuum and the residue was purified by flash chromatography using 15-30% EtOAc/hexane as eluent to afford the title compound **2o** (1.3 g, 5.6 mmol, 56%) as a colorless solid.

- **TLC (EtOAc/Hexane, 4:6 v/v):** R_f = 0.30, UV, $KMnO_4$.
- **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.59 (d, *J* = 8.1 Hz, 1H, Ar*H*), 7.40 (t, *J* = 7.7 Hz, 1H, Ar*H*), 7.28 (t, *J* = 7.6 Hz, 1H, Ar*H*), 6.90 (d, *J* = 7.7 Hz, 1H, Ar*H*), 6.87 (s, 2H, C=C*H*), 1.29 (s, 9H).
- **^{13}C NMR (101 MHz, $CDCl_3$):** δ 170.7, 149.4, 134.8, 131.2, 129.7, 129.1, 128.5, 127.1, 35.3, 31.4.

  The characterization data matched the reported value.[15]

3. Optimization of Housane Synthesis:

3.1 Screening of Photocatalysts

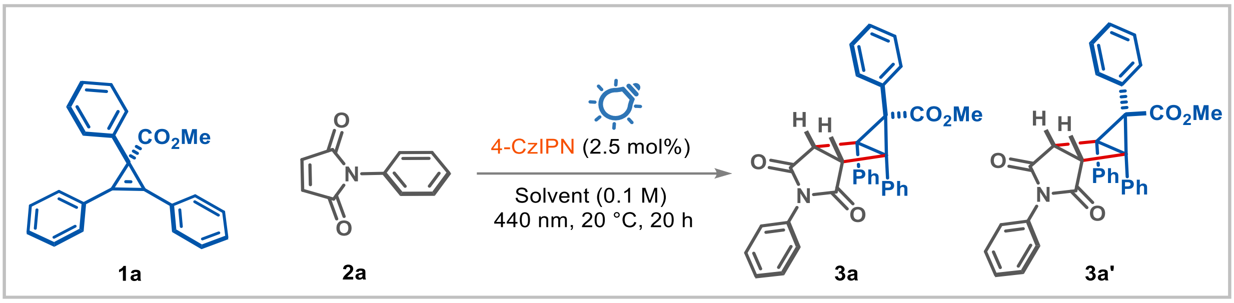


A flame-dried 5 mL Schlenk tube was charged with cyclopropene **1a** (32.6 mg, 0.100 mmol, 1.00 equiv), maleimide **2a** (34.6 mg, 0.200 mmol, 2.00 equiv), PC (2.5 mol%) and anhydrous CH_3CN (1.0 mL). The solution was irradiated using a 440 nm Kessil lamp for 20 h at 20 °C. Next, the reaction mixture was concentrated under reduced pressure and the crude product was submitted to ^{1}H-NMR. The yield and *dr* ratio of the crude product was calculated by ^{1}H-NMR using CH_2Br_2 (7.0 µl, 0.10 mmol) as an internal standard.

Entry	Photocatalyst (PC)	$E_{1/2}$ ($M^*/M^{-\cdot}$) (V)	$E_{1/2}$ ($M^{+\cdot}/M^*$) (V)	E_T (Kcal/mol)	Yield (3a+3a') (%)
1	$[Ru(bpy)_3]Cl_2$	+0.77	-0.81	46.5	0
2	*fac*-$[Ir(ppy)_3]$	+0.31	-1.73	58.1	25
3	$[Ir[dF(CF_3)ppy]_2(dtbbpy)]PF_6$	+1.21	-0.89	61.8	82
4	4-CzIPN	+1.35	-1.04	62	92
5	TXO*	+1.18	-1.11	65.3	82

* Using 405 nm.

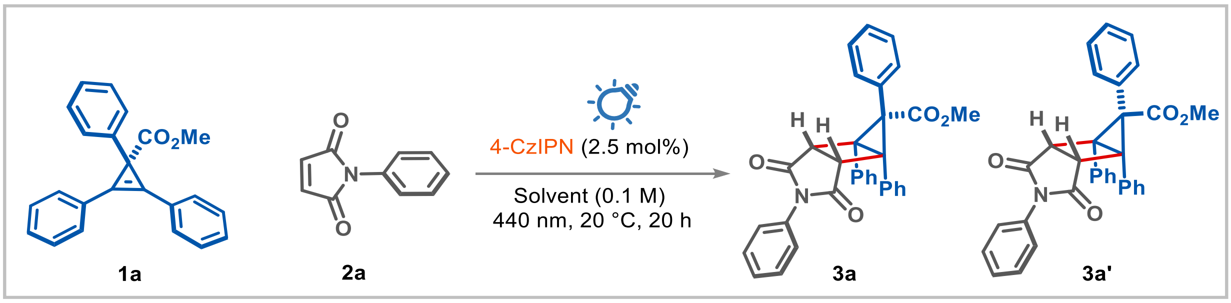
3.2 Screening of Solvents



A flame-dried 5 mL Schlenk tube was charged with cyclopropene **1a** (32.6 mg, 0.100 mmol, 1.00 equiv), maleimide **2a** (34.6 mg, 0.200 mmol, 2.00 equiv), 4-CzIPN (2.0 mg, 2.5 mol%) and anhydrous solvent (1.0 mL). The solution was irradiated using a 440 nm Kessil lamp for 20 h at 20 °C. Next, the reaction mixture was concentrated under reduced pressure and the crude product was submitted to ^{1}H-NMR. The yield and *dr* ratio of the crude product was calculated by ^{1}H NMR using CH_2Br_2 (7.0 µl, 0.10 mmol) as an internal standard.

Entry	**Solvent**	**Yield (%)**	***dr***
1	Acetonitrile	92	3:1
2	DCE	85	3:1
3	EtOAc	85	3:1
4	$PhCF_3$	70	3:1
5	DCM	95	3:1

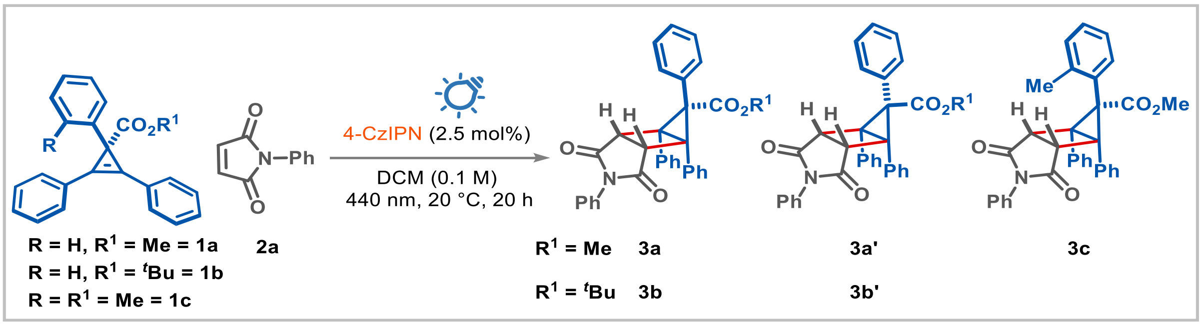
3.3 Screening of maleimide equivalency



A flame-dried 5 mL Schlenk tube was charged with cyclopropene **1a** (32.6 mg, 0.100 mmol, 1.00 equiv), maleimide **2a** (xx equiv), 4-CzIPN (2.0 mg, 2.5 mol%) and anhydrous DCM (1.0 mL). The solution was irradiated using a 440 nm Kessil lamp for 20 h at 20 °C. Next, the reaction mixture was concentrated under reduced pressure and the crude product was submitted to ^{1}H-NMR. The yield and *dr* ratio of the crude product was calculated by ^{1}H NMR using CH_2Br_2 (7.0 µl, 0.10 mmol) as an internal standard.

Entry	Equivalency of 2a	Yield (%)	*dr*
1	1.5	70	3:1
2	2.0	95	3:1

3.4 Steric effect

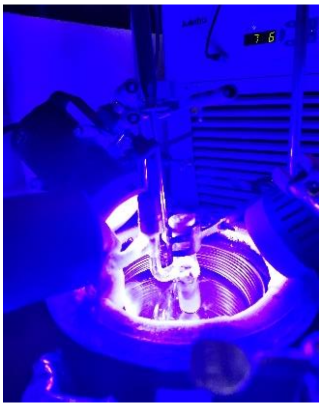


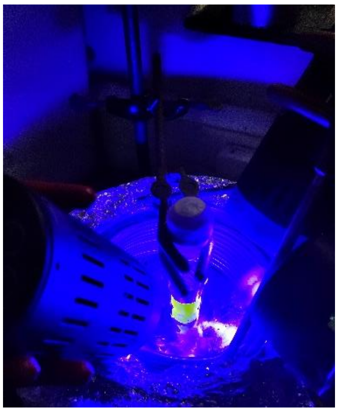
A flame-dried 5 mL Schlenk tube was charged with cyclopropene **1** (xx mg, 0.100 mmol, 1.00 equiv), maleimide **2a** (34.6 mg, 0.200 mmol, 2.00 equiv), 4-CzIPN (2.0 mg, 2.5 mol%) and anhydrous DCM (1.0 mL). The solution was irradiated using a 440 nm Kessil lamp for 20 h at 20 °C. Next, the reaction mixture was concentrated under reduced pressure and the crude product was submitted to ^{1}H-NMR. The yield and *dr* ratio of the crude product was calculated by ^{1}H NMR using CH_2Br_2 (7.0 µl, 0.10 mmol) as an internal standard.

Entry	Cyclopropene (xx)	Yield (%)	*dr*
1	**1a**	95	3:1
2	**1b**	96	3:1
3	**1c**	94	>20:1

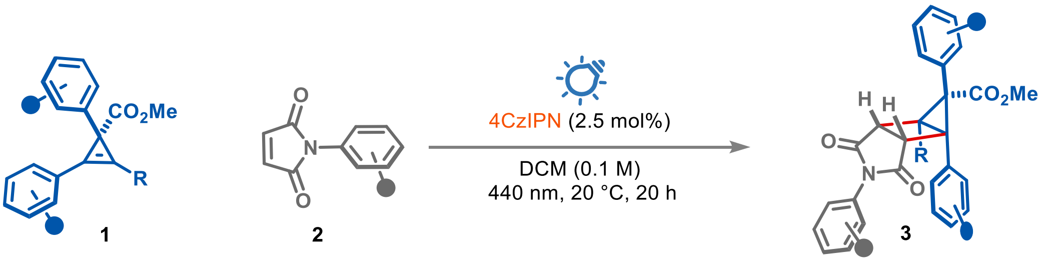
4.0. Scope of Diastereoselective Synthesis of Housane:

Photo reaction set-up:

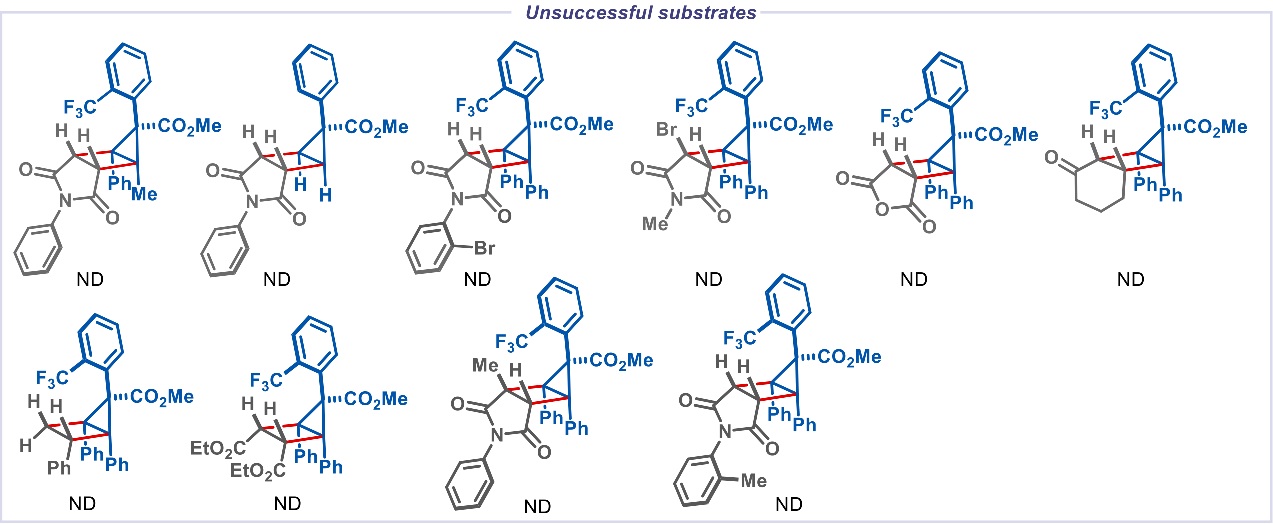




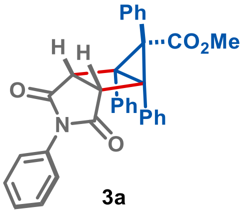
General Procedure-1:



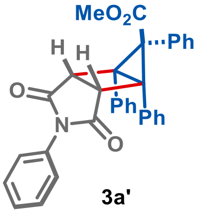
A flame-dried 25 mL Schlenk tube was charged with cyclopropene **1** (0.30 mmol, 1.0 equiv), maleimide **2** (0.60 mmol, 2.0 equiv), 4CzIPN (6.0 mg, 2.5 mol%) and anhydrous DCM (3.0 mL). The solution was irradiated using a 440 nm Kessil lamp for 20 h at 20 °C. Next, the reaction mixture was concentrated under reduced pressure, and the crude product was purified by column chromatography using Et_2O:hexane mixture as a mobile phase to afford compound **3**.



Methyl-6,8-dioxo-2,3,4,7-tetraphenyl-7-azatricyclo[3.3.0.02,4]octane-3-carboxylate (3a/3a')



3a



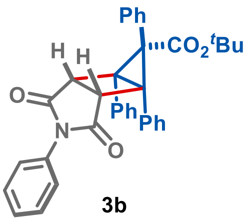
3a'

Following the general procedure-1, using cyclopropene **1a** (98 mg, 0.30 mmol, 1.0 equiv), maleimide **2a** (104 mg, 0.600 mmol, 2.00 equiv), and 4CzIPN (6.0 mg, 7.5 µmol, 0.025 equiv) in anhydrous DCM (3 mL, 0.1 M). The crude product was purified by column chromatography using 20-40% Et_2O:hexane mixture as a mobile phase to afford the pure product **3a+3a'** as a light yellow semi-solid (123 mg, 0.240 mmol, 82%, *dr* 3:1). (*See Spectra*)

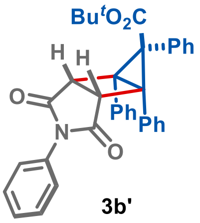
- **TLC (Et_2O:Hexane, 1:1 v/v):** $R_f = 0.30$, UV, $KMnO_4$.
- **^{1}H NMR (400 MHz, $CDCl_3$) for 3a:** δ 7.75 (d, *J* = 7.8 Hz, 2H, Ar*H*), 7.60 – 7.53 (m, 6H, Ar*H*), 7.50 – 7.31 (m, 10H, Ar*H*), 7.26 (d, *J* = 3.6 Hz, 2H, Ar*H*), 3.23 (s, 2H, *CH*), 3.14 (s, 3H, CO_2CH_3).
- **^{13}C NMR (101 MHz, $CDCl_3$) for 3a:** δ 173.7, 168.1, 132.8, 132.4, 131.6, 131.4, 129.6, 129.2, 129.0, 128.6, 128.4, 128.2, 128.1, 126.0, 53.3, 52.0, 51.6, 47.4.
- **IR (Neat, cm^{-1}) for 3a:** υ 2922 (m), 2854 (w), 1717 (s), 1378 (w), 1257 (w), 1198 (m), 757 (m), 697 (w).
- **HRMS (ESI) for 3a:** Calcd. for $C_{33}H_{25}NO_4H^+$ $[M+H]^+$ 500.1862; found: 500.1862.

- **^{1}H NMR (400 MHz, $CDCl_3$) for 3a':** δ 7.42 (t, *J* = 7.6 Hz, 2H, Ar*H*), 7.32 (dt, *J* = 6.5, 3.3 Hz, 5H, Ar*H*), 7.28 – 7.22 (m, 8H, Ar*H*), 7.03 – 6.97 (m, 1H, Ar*H*), 6.90 (t, *J* = 7.6 Hz, 2H, Ar*H*), 6.77 (d, *J* = 7.7 Hz, 2H, Ar*H*), 3.92 (s, 3H, CO_2CH_3), 3.81 (s, 2H, *CH*).
- **^{13}C NMR (101 MHz, $CDCl_3$) for 3a':** δ 173.9, 169.4, 132.4, 132.1, 131.7, 130.5, 130.3, 129.1, 128.5, 128.1, 127.9, 127.4, 127.2, 126.0, 53.8, 52.8, 49.4, 47.6.
- **IR (Neat, cm^{-1}) for 3a':** υ 2952 (m), 2856 (w), 1714 (s), 1376 (m), 1248 (m), 1200 (m), 748 (m), 700 (w).
- **HRMS (ESI) for 3a':** Calcd. for $C_{33}H_{25}NO_4H^+$ $[M+H]^+$ 500.1862; found: 500.1860.

tert-Butyl-6,8-dioxo-2,3,4,7-tetraphenyl-7-azatricyclo[3.3.0.02,4]octane-3-carboxylate (3b/3b’)



3b

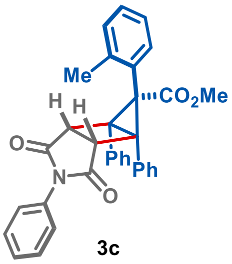


3b'

Following the general procedure-1, using cyclopropene **1b** (110 mg, 0.30 mmol, 1.0 equiv), maleimide **2a** (104 mg, 0.600 mmol, 2.00 equiv), and 4CzIPN (6.0 mg, 7.5 µmol, 0.025 equiv) in anhydrous DCM (3 mL, 0.1 M). The crude product was purified by column chromatography using 15-20% Et_2O:hexane mixture as a mobile phase to afford the pure product **3b+3b’** as a light yellow semi-solid (122 mg, 0.220 mmol, 75%, *dr* 3:1). (*See Spectra*)

- **TLC (Et_2O:Hexane, 4:6 v/v):** $R_f = 0.40$, UV, $KMnO_4$.
- **^1H NMR (400 MHz, $CDCl_3$) for both diastereomers:** δ 7.81 – 7.76 (m, 1.5H, Ar*H*), 7.64 – 7.56 (m, 4.5H, Ar*H*), 7.52 – 7.45 (m, 2.2H, Ar*H*), 7.42 (td, *J* = 8.8, 7.9, 2.1 Hz, 4H, Ar*H*), 7.38 – 7.31 (m, 4.5H, Ar*H*), 7.29 – 7.23 (m, 2H, Ar*H*), 7.02 – 6.97 (m, 0.3H, Ar*H*), 6.91 (dd, *J* = 8.5, 6.9 Hz, 0.5H, Ar*H*), 6.84 – 6.80 (m, 0.5H, Ar*H*), 3.90 (s, 0.5H, *CH*), 3.20 (s, 1.5H, *CH*), 1.60 (s, 2.25H, $CO_2{}^tBu$), 0.64 (s, 6.75H, $CO_2{}^tBu$).
- **^{13}C NMR (101 MHz, $CDCl_3$) for both diastereomers:** δ 174.0, 173.8, 168.1, 167.2, 133.7, 133.0, 132.9, 132.5, 131.8, 131.4, 130.3, 130.2, 130.0, 129.2, 129.0, 128.9, 128.5, 128.4, 128.3, 128.2, 128.0, 127.9, 127.7, 127.2, 126.8, 126.0, 125.9, 82.7, 81.9, 54.5, 53.3, 52.3, 49.5, 48.2, 47.5, 28.0, 26.7. One carbon was not resolved at 101 MHz.
- **IR (Neat, cm^{-1}) for 3a:** υ 2935 (w), 2855 (w), 1720 (s), 1378 (m), 1254 (w), 1165 (m), 848 (w), 758 (w).
- **HRMS (ESI) for 3a:** Calcd. for $C_{36}H_{31}NO_4H^+$ $[M+H]^+$ 542.2331 found: 542.2333.

Methyl-6,8-dioxo-2,4,7-triphenyl-3-(o-tolyl)-7-azatricyclo[3.3.0.02,4]octane-3-carboxylate (3c)

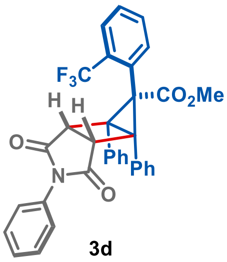


3c

Following the general procedure-1, using cyclopropene **1c** (102 mg, 0.300 mmol, 1.00 equiv), maleimide **2a** (104 mg, 0.600 mmol, 2.00 equiv), and 4CzIPN (6.0 mg, 7.5 µmol, 0.025 equiv) in anhydrous DCM (3 mL, 0.1 M). The crude product was purified by column chromatography using 25-40% Et_2O:hexane mixture as a mobile phase to afford the pure product **3c** as a paleyellow semi-solid (130 mg, 0.250 mmol, 84%, *dr* > 20:1). (*See Spectra*)

- **TLC (Et_2O:Hexane, 1:1 v/v):** R_f = 0.30, UV, $KMnO_4$.
- **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.78 – 7.74 (m, 1H, Ar*H*), 7.67 – 7.56 (m, 4H, Ar*H*), 7.40 (ddt, *J* = 23.3, 10.9, 7.7 Hz, 12H, Ar*H*), 7.21 (dt, *J* = 8.1, 2.3 Hz, 2H, Ar*H*), 3.39 – 3.34 (m, 1H, *CH*), 3.28 (s, 3H, CO_2CH_3), 3.12 – 3.07 (m, 1H, *CH*), 2.70 (s, 3H, ArCH_3).
- **^{13}C NMR (101 MHz, $CDCl_3$):** δ 173.7, 173.6, 167.6, 139.0, 132.5, 132.38, 132.37, 131.5, 130.21, 130.18, 129.0, 128.5, 128.4, 128.1, 128.0, 127.6, 127.4, 126.2, 125.9, 53.4, 52.0, 50.3, 48.8, 47.9, 45.3, 20.6. Two carbons were not resolved at 101 MHz.
- **IR (Neat, cm^{-1}):** υ 2922 (m), 2855 (w), 1719 (s), 1375 (m), 1260 (m), 1200 (m), 753 (m), 700 (w).
- **HRMS (ESI):** Calcd. for $C_{34}H_{27}NO_4Na^+$ $[M+Na]^+$ 536.1838; found: 536.1840.

Methyl-6,8-dioxo-2,4,7-triphenyl-3-(2-(trifluoromethyl)phenyl)-7-azatricyclo[3.3.0.02,4]octane-3-carboxylate (3d)



3d

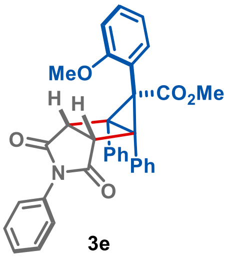
Following the general procedure-1, using cyclopropene **1d** (118 mg, 0.300 mmol, 1.00 equiv), maleimide **2a** (104 mg, 0.600 mmol, 2.00 equiv), and 4CzIPN (6.0 mg, 7.5 µmol, 0.025 equiv) in anhydrous DCM (3 mL, 0.1 M). The crude product was purified by column chromatography using 25-40% Et_2O:hexane mixture as a mobile phase to afford the pure product **3d** as a pale yellow semi-solid (140 mg, 0.247 mmol, 82%, *dr* > 20:1). (*See Spectra*)

- **TLC (Et_2O:Hexane, 1:1 v/v):** R_f = 0.30, UV, $KMnO_4$.
- **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.91 (t, *J* = 9.0 Hz, 2H, Ar*H*), 7.75 (t, *J* = 7.6 Hz, 1H, Ar*H*), 7.67 (d, *J* = 7.4 Hz, 2H, Ar*H*), 7.61 (t, *J* = 7.7 Hz, 1H, Ar*H*), 7.50 (d, *J* = 7.2 Hz,

2H, Ar*H*), 7.45 – 7.30 (m, 9H, Ar*H*), 7.15 (d, *J* = 7.7 Hz, 2H, Ar*H*), 3.39 (d, *J* = 3.9 Hz, 1H, *CH*), 3.28 (s, 3H, CO_2CH_3), 3.18 (d, *J* = 3.9 Hz, 1H, *CH*).

- **^{13}C NMR (101 MHz, $CDCl_3$):** δ 173.6, 172.9, 167.2, 135.2, 132.0, 131.9, 131.6, 131.5, 130.9, 130.5, 130.2, 129.1, 128.9, 128.5, 128.4, 128.2, 127.8, 127.6 (q, *J* = 5 Hz), 127.1, 126.0, 124.2 (q, *J* = 274.7 Hz), 116.0, 53.4, 53.0, 52.2, 48.5, 48.0, 45.5.
- **^{19}F NMR (377 MHz, $CDCl_3$):** δ -58.29.
- **IR (Neat, cm^{-1}):** υ 3059 (w), 2952 (w), 1714 (s), 1599 (w), 1444 (m), 1255 (m), 1171 (s), 1114 (s), 1034 (m), 733 (m), 697 (s).
- **HRMS (ESI):** Calcd. for $C_{34}H_{24}F_3NO_4Na^+$ $[M+Na]^+$ 590.1555; found: 590.1559.

Methyl-3-(2-methoxyphenyl)-6,8-dioxo-2,4,7-triphenyl-7-azatricyclo[3.3.0.02,4]octane-3-carboxylate (3e)

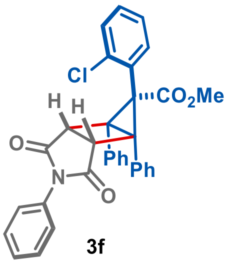


Following the general procedure-1, using cyclopropene **1e** (107 mg, 0.300 mmol, 1.00 equiv), maleimide **2a** (104 mg, 0.600 mmol, 2.00 equiv), and 4CzIPN (6.0 mg, 7.5 µmol, 0.025 equiv) in anhydrous DCM (3 mL, 0.1 M). The crude product was purified by column chromatography using 20-40% Et_2O:hexane mixture as a mobile phase to afford the pure product **3e** as a paleyellow semi-solid (137 mg, 0.245 mmol, 86%, *dr* > 20:1). (*See Spectra*)

- **TLC (Et_2O:Hexane, 1:1 v/v):** R_f = 0.35, UV, $KMnO_4$.
- **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.79 – 7.67 (m, 3H, Ar*H*), 7.60 – 7.53 (m, 2H, Ar*H*), 7.50 - 7.46 (m, 3H, Ar*H*), 7.45 – 7.32 (m, 8H, Ar*H*), 7.31 – 7.26 (m, 1H, Ar*H*), 7.20 (td, *J* = 7.3, 2.4 Hz, 1H, Ar*H*), 7.14 (dd, *J* = 8.5, 2.6 Hz, 1H, Ar*H*), 4.04 (s, 3H, ArOCH_3), 3.37 (t, *J* = 2.9 Hz, 1H, *CH*), 3.20 (s, 3H, CO_2CH_3), 3.03 (t, *J* = 3.0 Hz, 1H, *CH*).
- **^{13}C NMR (101 MHz, $CDCl_3$):** δ 174.1, 173.8, 168.0, 158.6, 133.3, 133.1, 132.9, 131.8, 130.1, 130.0, 129.9, 129.1, 128.4, 128.0, 127.8, 127.7, 127.5, 126.0, 121.0, 120.8, 111.3, 55.3, 52.6, 51.8, 50.1, 49.8, 48.1, 46.8.
- **IR (Neat, cm^{-1}):** υ 2925 (w), 2849 (w), 1717 (s), 1494 (m), 1455 (w), 1374 (m), 1242 (m), 1197 (w), 756 (m), 700 (m).

- **HRMS (ESI):** Calcd. for $C_{34}H_{27}NO_5H^+$ $[M+H]^+$ 530.1967; found: 530.1969.

Methyl-3-(2-chlorophenyl)-6,8-dioxo-2,4,7-triphenyl-7 azatricyclo[3.3.0.02,4]octane-3-carboxylate (3f)

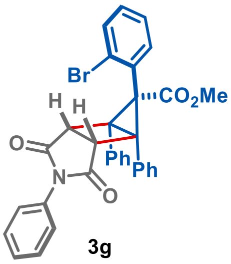


3f

Following the general procedure-1, using cyclopropene **1f** (108 mg, 0.300 mmol, 1.00 equiv), maleimide **2a** (104 mg, 0.600 mmol, 2.00 equiv), and 4CzIPN (6.0 mg, 7.5 µmol, 0.025 equiv) in anhydrous DCM (3 mL, 0.1 M). The crude product was purified by column chromatography using 20-40% Et_2O:hexane mixture as a mobile phase to afford the pure product **3f** as a pale yellow semi-solid (119 mg, 0.222 mmol, 74%, *dr* 10:1). (*See Spectra*)

- **TLC (Et_2O:Hexane, 1:1 v/v):** $R_f = 0.35$, UV, $KMnO_4$.
- **^1H NMR (400 MHz, $CDCl_3$):** δ 7.80 (dd, *J* = 7.5, 1.8 Hz, 1H, Ar*H*), 7.74 (d, *J* = 7.4 Hz, 2H, Ar*H*), 7.64 – 7.57 (m, 1H, Ar*H*), 7.52 (d, *J* = 7.3 Hz, 2H, Ar*H*), 7.40 (m, 11H, Ar*H*), 7.20 (d, *J* = 7.8 Hz, 2H, Ar*H*), 3.31 (m, 1H, *CH*), 3.29 (s, 3H, CO_2CH_3), 3.20 (d, *J* = 3.7 Hz, 1H, *CH*).
- **^{13}C NMR (101 MHz, $CDCl_3$):** δ 173.6, 173.2, 166.9, 136.0, 133.9, 132.2, 131.74, 131.67, 131.4, 130.9, 130.7, 130.1, 129.9, 129.1, 128.5, 128.2, 128.1, 127.8, 127.3, 127.2, 126.0, 52.8, 52.4, 52.1, 49.5, 48.1, 45.8.
- **IR (Neat, cm^{-1}):** υ 2922 (m), 2855 (w), 1718 (s), 1442 (m), 1375 (w), 1243 (m), 1199 (m), 754 (m), 698 (m).
- **HRMS (ESI):** Calcd. for $C_{33}H_{24}ClNO_4H^+$ $[M+H]^+$ 534.1472; found: 534.1470.

Methyl-3-(2-bromophenyl)-6,8-dioxo-2,4,7-triphenyl-7-azatricyclo[3.3.0.02,4]octane-3-carboxylate (3g)

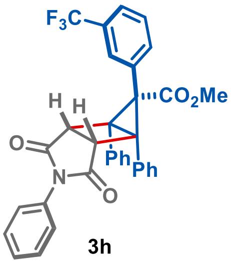


3g

Following the general procedure-1, using cyclopropene **1g** (121 mg, 0.300 mmol, 1.00 equiv), maleimide **2a** (104 mg, 0.600 mmol, 2.00 equiv), and 4CzIPN (6.0 mg, 7.5 µmol, 0.025 equiv) in anhydrous DCM (3 mL, 0.1 M). The crude product was purified by column chromatography using 25-40% Et_2O:hexane mixture as a mobile phase to afford the pure product **3g** as a pale yellow semi-solid (118 mg, 0.204 mmol, 68%, *dr* 8:1). (*See Spectra*)

- **TLC (Et_2O:Hexane, 1:1 v/v):** R_f = 0.30, UV, $KMnO_4$.
- **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.79 (t, *J* = 7.1 Hz, 4H, Ar*H*), 7.50 (d, *J* = 7.6 Hz, 3H, Ar*H*), 7.45 – 7.30 (m, 10H, Ar*H*), 7.17 (d, *J* = 7.6 Hz, 2H, Ar*H*), 3.32 (s, 3H, CO_2CH_3), 3.31-3.29 (m, 1H, *CH*), 3.23 (d, *J* = 3.8 Hz, 1H, *CH*).
- **^{13}C NMR (101 MHz, $CDCl_3$):** δ 173.5, 173.2, 166.8, 134.2, 134.0, 133.3, 132.0, 131.6, 131.5, 131.3, 130.2, 129.9, 129.1, 128.5, 128.3, 128.1, 127.8, 127.6, 127.0, 126.1, 126.0, 54.5, 52.4, 52.2, 49.3, 48.2, 45.7.
- **IR (Neat, cm^{-1}):** υ 3057 (w), 2951 (w), 1714 (s), 1597 (w), 1435 (m), 1240 (m), 1198 (s), 1071 (s), 1023 (w), 755 (m), 699 (w).
- **HRMS (ESI):** Calcd. for $C_{33}H_{24}BrNO_4Na$ $[M+Na]^+$ 600.0786; found: 600.0784.

Methyl-6,8-dioxo-2,4,7-triphenyl-3-(3-(trifluoromethyl)phenyl)-7-azatricyclo[3.3.0.02,4]octane-3-carboxylate (3h)



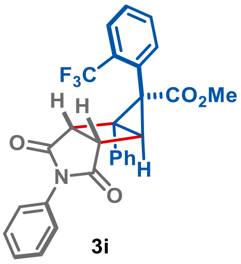
3h

Following the general procedure-1, using cyclopropene **1h** (118 mg, 0.300 mmol, 1.00 equiv), maleimide **2a** (104 mg, 0.600 mmol, 2.00 equiv), and 4CzIPN (6.0 mg, 7.5 µmol, 0.025 equiv) in anhydrous DCM (3 mL, 0.1 M). The crude product was purified by column chromatography using 25-25% Et_2O:hexane mixture as a mobile phase to afford the pure product **3h** as a pale yellow semi-solid (44.0 mg, 0.078 mmol, 25%, *dr* 5:1). (*See Spectra*)

- **TLC (Et_2O:Hexane, 1:1 v/v):** R_f = 0.35, UV, $KMnO_4$.
- **^{1}H NMR (400 MHz, $CDCl_3$):** For major diastereomer δ 7.97-7.93 (m, 2H, Ar*H*), 7.80 – 7.69 (m, 2H, Ar*H*), 7.58 – 7.53 (m, 4H, Ar*H*), 7.50 – 7.34 (m, 9H, Ar*H*), 7.28-7.25 (m, 2H, Ar*H*), 3.20-3.13 (m, 2H, *CH*), 3.16 (s, 3H, CO_2CH_3).

- **^{13}C NMR (101 MHz, CDCl$_3$):** For major diastereomer δ 173.2, 167.4, 134.9, 133.8, 132.3, 131.6 (q, *J* = 22.2 Hz), 131.6, 129.7, 129.6, 129.2, 128.7, 128.31, 128.28, 127.8 (d, *J* = 3.8 Hz), 126.0, 125.4 (d, *J* = 3.8 Hz), 123.8 (q, *J* = 181.8 Hz), 53.1, 52.1, 51.7, 47.3.
- **^{19}F NMR (377 MHz, CDCl$_3$):** δ -62.32.
- **IR (Neat, cm^{-1}):** υ 2915 (w), 2855 (w), 1720 (s), 1441 (w), 1375 (m), 1237 (m), 1170 (m), 1027 (w), 754 (m), 699 (m).
- **HRMS (ESI):** Calcd. for $C_{34}H_{24}F_3NO_4Na^+$ [M+Na]$^+$ 590.1555; found: 590.1558.

Methyl-6,8-dioxo-2,7-diphenyl-3-(2-(trifluoromethyl)phenyl)-7-azatricyclo[3.3.0.02,4]octane-3-carboxylate (3i)

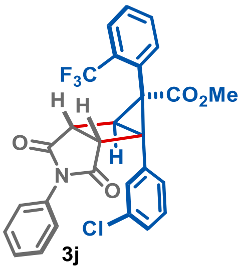


3i

Following the general procedure-1, using cyclopropene **1i** (95.5 mg, 0.300 mmol, 1.00 equiv), maleimide **2a** (104 mg, 0.600 mmol, 2.00 equiv), and 4CzIPN (6.0 mg, 7.5 µmol, 0.025 equiv) in anhydrous DCM (3 mL, 0.1 M). The crude product was purified by column chromatography using 20-30% Et_2O:Hexane mixture as a mobile phase to afford the pure product **3i** as a pale yellow semi-solid (105 mg, 0.216 mmol, 72%, *dr* > 20:1). (*See Spectra*)

- **TLC (Et_2O:Hexane, 1:1 v/v):** R_f = 0.35, $KMnO_4$.
- **^{1}H NMR (400 MHz, CDCl$_3$):** δ 7.93 (d, *J* = 7.7 Hz, 1H, Ar*H*), 7.84 (d, *J* = 7.9 Hz, 1H, Ar*H*), 7.75 (t, *J* = 7.5 Hz, 1H, Ar*H*), 7.58 (t, *J* = 7.7 Hz, 1H, Ar*H*), 7.40 (m, 8H, Ar*H*), 7.21 – 7.16 (m, 2H, Ar*H*), 3.76 (d, *J* = 1.9 Hz, 1H, *CH*), 3.30 (dd, *J* = 3.5, 1.9 Hz, 1H, *CH*), 3.26 (s, 3H, CO_2CH_3), 2.73 (d, *J* = 3.5 Hz, 1H, *CH*) .
- **^{13}C NMR (101 MHz, CDCl$_3$):** δ 175.1, 173.6, 168.3, 135.0, 132.1, 131.7, 131.5, 130.5 (q, *J* = 31.3 Hz), 130.3, 129.4, 129.1, 128.9, 128.7, 128.6, 128.5, 127.3 (q, *J* = 5 Hz), 126.1, 124.0 (q, *J* = 274.7 Hz), 52.4, 48.4, 47.8, 46.2, 40.3 (q, *J* = 2.2 Hz), 36.4.
- **^{19}F NMR (377 MHz, CDCl$_3$):** δ -59.74.
- **IR (Neat, cm^{-1}):** υ 2922 (m), 2855 (w), 1715 (s), 1496 (w), 1445 (m), 1243 (m), 1174 (s), 1117 (m), 1032 (w), 756 (w), 699 (m).
- **HRMS (ESI):** Calcd. for $C_{28}H_{20}F_3NO_4Na^+$ [M+Na]$^+$ 514.1242; found: 514.1245.

Methyl-2-(3-chlorophenyl)-6,8-dioxo-7-phenyl-3-(2-(trifluoromethyl)phenyl)-7-azatricyclo[3.3.0.02,4]octane-3-carboxylate (3j)

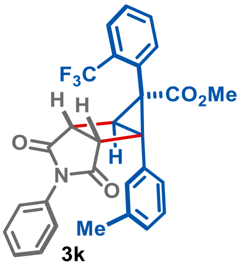


3j

Following the general procedure-1, using cyclopropene **1j** (106 mg, 0.300 mmol, 1.00 equiv), maleimide **2a** (104 mg, 0.600 mmol, 2.00 equiv), and 4CzIPN (6.0 mg, 7.5 µmol, 0.025 equiv) in anhydrous DCM (3 mL, 0.1 M). The crude product was purified by column chromatography using 25-35% Et_2O:Hexane mixture as a mobile phase to afford the pure product **3j** as a pale yellow semi-solid (85.0 mg, 0.162 mmol, 53%, *dr* > 20:1). (*See Spectra*)

- **TLC (Et_2O:Hexane, 3:2 v/v):** $R_f = 0.30$, $KMnO_4$.
- **^1H NMR (400 MHz, $CDCl_3$):** δ 7.87-7.81 (m, 2H, Ar*H*), 7.79 – 7.73 (m, 1H, Ar*H*), 7.64 – 7.56 (m, 1H, Ar*H*), 7.48-7.42 (m, 3H, Ar*H*), 7.42 – 7.36 (m, 1H, Ar*H*), 7.33 (s, 3H, Ar*H*), 7.18 (dd, *J* = 8.4, 1.3 Hz, 2H, Ar*H*), 3.74 (d, *J* = 1.9 Hz, 1H, *CH*), 3.32 (s, 3H, CO_2CH_3), 3.28 (dd, *J* = 3.6, 1.9 Hz, 1H, *CH*), 2.73 (d, *J* = 3.6 Hz, 1H, *CH*).
- **^{13}C NMR (101 MHz, $CDCl_3$):** δ 174.8, 173.4, 168.1, 134.8, 134.4, 133.9, 132.2, 131.4, 130.7, 130.4, 129.9, 129.8, 129.6, 129.1, 128.9, 128.8, 127.6, 127.5 (q, *J* = 5 Hz), 126.1, 124.0 (q, *J* = 274.7 Hz), 52.6, 48.5, 47.7, 45.5, 40.3, 36.6.
- **^{19}F NMR (377 MHz, $CDCl_3$):** δ -59.77.
- **IR (Neat, cm^{-1}):** υ 2922 (s), 2856 (m), 2346 (m), 1718 (s), 1256 (m), 1195 (m), 754 (s).
- **HRMS (ESI):** Calcd. for $C_{28}H_{19}ClF_3NO_4H^+$ $[M+H]^+$ 526.1033; found: 526.1035.

Methyl-6,8-dioxo-7-phenyl-2-(m-tolyl)-3-(2-(trifluoromethyl)phenyl)-7-azatricyclo[3.3.0.02,4]octane-3-carboxylate (3k)

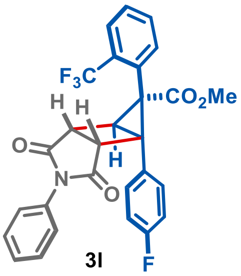


3k

Following the general procedure-1, using cyclopropene **1k** (100 mg, 0.300 mmol, 1.00 equiv), maleimide **2a** (104 mg, 0.600 mmol, 2.00 equiv), and 4CzIPN (6.0 mg, 7.5 µmol, 0.025 equiv) in anhydrous DCM (3 mL, 0.1 M). The crude product was purified by column chromatography using 25-30% Et_2O:Hexane mixture as a mobile phase to afford the pure product **3k** as a pale yellow semi-solid (100 mg, 0.198 mmol, 66%, *dr* > 20:1). (*See Spectra*)

- **TLC (Et_2O:Hexane, 3:2 v/v):** R_f = 0.30, $KMnO_4$.
- **^1H NMR (400 MHz, $CDCl_3$):** δ 7.92 (d, *J* = 7.6 Hz, 1H, Ar*H*), 7.84 (d, *J* = 7.9 Hz, 1H, Ar*H*), 7.76 (t, *J* = 7.6 Hz, 1H, Ar*H*), 7.58 (t, *J* = 7.7 Hz, 1H, Ar*H*), 7.45 (dd, *J* = 8.3, 6.7 Hz, 2H, Ar*H*), 7.38 (t, *J* = 7.4 Hz, 1H, Ar*H*), 7.32 – 7.18 (m, 5H, Ar*H*), 7.15 (d, *J* = 7.4 Hz, 1H, Ar*H*), 3.72 (d, *J* = 1.8 Hz, 1H, *CH*), 3.28 (s, 3H, CO_2CH_3), 3.27 - 3.24 (m, 1H, *CH*), 2.72 (d, *J* = 3.5 Hz, 1H, *CH*), 2.37 (s, 3H, ArCH_3).
- **^{13}C NMR (101 MHz, $CDCl_3$):** δ 175.1, 173.7, 168.4, 138.1, 135.0, 132.1, 131.7, 131.6, 130.7, 130.4, 130.1, 129.5, 129.2, 128.7, 128.4, 128.1, 127.4 (q, *J* = 5 Hz), 126.4, 126.1, 124.0 (q, *J* = 274.7 Hz), 52.4, 48.3, 47.9, 46.3, 40.3, 36.3, 21.3.
- **^{19}F NMR (377 MHz, $CDCl_3$):** δ -59.77.
- **IR (Neat, cm^{-1}):** υ 2923 (m), 2855 (w), 1719 (s), 1378 (w), 1312 (w), 1266 (w), 1176 (m), 1126 (m), 713 (w).
- **HRMS (ESI):** Calcd. for $C_{29}H_{22}F_3NO_4H^+$ $[M+H]^+$ 506.1579; found: 506.1576.

Methyl-2-(4-fluorophenyl)-6,8-dioxo-7-phenyl-3-(2-(trifluoromethyl)phenyl)-7-azatricyclo[3.3.0.02,4]octane-3-carboxylate (3l)



3l

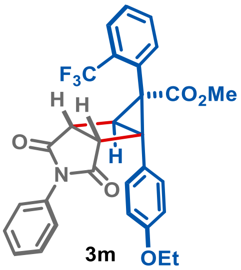
Following the general procedure-1, using cyclopropene **1l** (101 mg, 0.300 mmol, 1.00 equiv), maleimide **2a** (104 mg, 0.600 mmol, 2.00 equiv), and 4CzIPN (6.0 mg, 7.5 µmol, 0.025 equiv) in anhydrous DCM (3 mL, 0.1 M). The crude product was purified by column chromatography using 25-40% Et_2O:Hexane mixture as a mobile phase to afford the pure product **3l** as a pale yellow semi-solid (109 mg, 0.214 mmol, 71%, *dr* > 20:1). (*See Spectra*)

- **TLC (Et_2O:Hexane, 1:1 v/v):** R_f = 0.30, UV, $KMnO_4$.
- **^1H NMR (400 MHz, $CDCl_3$):** δ 7.85 (dd, *J* = 10.2, 7.8 Hz, 2H, Ar*H*), 7.75 (t, *J* = 7.6 Hz, 1H, Ar*H*), 7.59 (t, *J* = 7.7 Hz, 1H, Ar*H*), 7.47 – 7.35 (m, 5H, Ar*H*), 7.16 (d, *J* = 7.4

Hz, 2H, Ar*H*), 7.08 (t, *J* = 8.5 Hz, 2H, Ar*H*), 3.74 (d, *J* = 1.9 Hz, 1H, *CH*), 3.29 (s, 3H, CO_2CH_3), 3.28 - 3.25 (m, 1H, *CH*), 2.72 (d, *J* = 3.6 Hz, 1H, *CH*).

- **^{13}C NMR (101 MHz, $CDCl_3$):** δ 174.9, 173.6, 168.2, 163.9, 161.4, 134.8, 132.2, 131.5, 131.3 (d, *J* = 8.5 Hz), 130.6 (q, *J* = 31.3 Hz), 130.1, 129.2, 129.0 (d, *J* = 27.8 Hz), 127.7 (d, *J* = 3.3 Hz), 127.5 (q, *J* = 5 Hz), 126.1, 124.0 (q, *J* = 274.7 Hz), 115.6 (d, *J* = 21.8 Hz), 52.5, 48.5, 47.7, 45.4, 40.2, 36.6.
- **^{19}F NMR (377 MHz, $CDCl_3$):** δ -59.80, -112.23.
- **IR (Neat, cm^{-1}):** υ 2922 (w), 2855 (w), 1717 (s), 1379 (m), 1265 (m), 1175 (m), 1036 (w), 767 (w), 716 (w).
- **HRMS (ESI):** Calcd. for $C_{28}H_{19}F_4NO_4H^+$ $[M+H]^+$ 510.1328; found: 510.1328.

Methyl-2-(4-ethoxyphenyl)-6,8-dioxo-7-phenyl-3-(2-(trifluoromethyl)phenyl)-7-azatricyclo[3.3.0.02,4]octane-3-carboxylate (3m)



3m

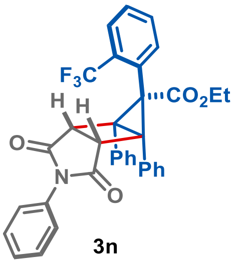
Following the general procedure-1, using cyclopropene **1m** (108 mg, 0.300 mmol, 1.00 equiv), maleimide **2a** (104 mg, 0.600 mmol, 2.00 equiv), and 4CzIPN (6.0 mg, 7.5 µmol, 0.025 equiv) in anhydrous DCM (3 mL, 0.1 M). The crude product was purified by column chromatography using 25-40% Et_2O:Hexane mixture as a mobile phase to afford the pure product **3m** as a pale yellow semi-solid (106 mg, 0.200 mmol, 66%, *dr* > 20:1). (*See Spectra*)

- **TLC (Et_2O:Hexane, 2:3 v/v):** R_f = 0.2, UV, $KMnO_4$.
- **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.90 (d, *J* = 7.6 Hz, 1H, Ar*H*), 7.85 – 7.80 (m, 1H, Ar*H*), 7.76 – 7.74 (m, 1H, Ar*H*), 7.57 (t, *J* = 7.7 Hz, 1H, Ar*H*), 7.44 (t, *J* = 7.5 Hz, 2H, Ar*H*), 7.39 – 7.31 (m, 3H, Ar*H*), 7.19 (d, *J* = 7.2 Hz, 2H, Ar*H*), 6.89 (d, *J* = 9.0 Hz, 2H, Ar*H*), 4.02 (q, *J* = 7.0 Hz, 2H, $ArOCH_2CH_3$)), 3.71 (d, *J* = 1.9 Hz, 1H, *CH*), 3.28 (s, 3H, CO_2CH_3), 3.25 (m, 1H, *CH*), 2.70 (d, *J* = 3.6 Hz, 1H, *CH*), 1.41 (t, *J* = 7.0 Hz, 3H, $ArOCH_2CH_3$).
- **^{13}C NMR (101 MHz, $CDCl_3$):** δ 174.8, 174.0, 167.1, 135.1, 131.9, 131.8, 131.5, 131.4, 130.8, 130.2 (q, *J* = 30.3 Hz), 130.0, 128.8, 128.3, 128.1, 127.7, 127.5 (q, *J* = 5.0 Hz),

126.9, 124.2 (q, J = 274.7 Hz), 53.1, 53.0, 52.2, 48.5, 47.9, 45.7, 25.0. One carbon was not resolved at 101 MHz.

- **^{19}F NMR (377 MHz, $CDCl_3$):** δ -59.78.
- **IR (Neat, cm^{-1}):** υ 2923 (m), 2855 (w), 1718 (s), 1378 (m), 1252 (m), 1174 (m), 1041 (w), 768 (w), 716 (w).
- **HRMS (ESI):** Calcd. for $C_{30}H_{24}F_3NO_5Na^+$ $[M+Na]^+$ 558.1504; found: 558.1509.

Ethyl-6,8-dioxo-2,4,7-triphenyl-3-(2-(trifluoromethyl)phenyl)-7-azatricyclo[3.3.0.02,4]octane-3-carboxylate (3n)



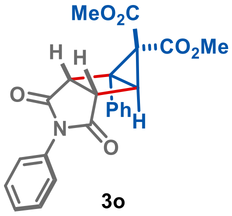
3n

Following the general procedure-1, using cyclopropene **1n** (123 mg, 0.300 mmol, 1.00 equiv), maleimide **2a** (104 mg, 0.600 mmol, 2.00 equiv), and 4CzIPN (6.0 mg, 7.5 μmol, 0.025 equiv) in anhydrous DCM (3 mL, 0.1 M). The crude product was purified by column chromatography using 25-40% Et_2O:hexane mixture as a mobile phase to afford the pure product **3n** as a pale yellow solid (144 mg, 0.247 mmol, 82%, *dr* > 20:1). (*See Spectra*)

- **Melting point:** 221-223 °C.
- **TLC (Et_2O:Hexane, 1:1 v/v):** R_f = 0.40, UV, $KMnO_4$.
- **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.92 (dd, J = 14.4, 7.8 Hz, 2H, ArH), 7.75 (t, J = 7.7 Hz, 1H, ArH), 7.69 (d, J = 7.5 Hz, 2H, ArH), 7.61 (t, J = 7.7 Hz, 1H, ArH), 7.53 (d, J = 7.3 Hz, 2H, ArH), 7.38 (qd, J = 12.7, 10.8, 6.8 Hz, 9H, ArH), 7.17 (d, J = 7.8 Hz, 2H, ArH), 3.80 - 3.64 (m, 2H, $CO_2CH_2CH_3$), 3.40 (d, J = 3.9 Hz, 1H, CH), 3.19 (d, J = 3.8 Hz, 1H, CH), 0.71 (t, J = 7.1 Hz, 3H, $CO_2CH_2CH_3$).
- **^{13}C NMR (101 MHz, $CDCl_3$):** δ 173.6, 172.9, 166.8, 135.1, 132.0, 131.9, 131.6, 131.5, 130.9, 130.3 (q, J = 30.3 Hz), 130.2, 129.1, 128.8, 128.5, 128.3, 128.1, 127.7, 127.5 (q, J = 5 Hz), 127.0, 125.9, 124.2 (q, J = 274.7 Hz), 61.2, 53.3, 53.1, 48.3, 48.1, 45.6, 13.2. One carbon was not resolved at 101 MHz.
- **^{19}F NMR (377 MHz, $CDCl_3$):** δ -58.11.
- **IR (Neat, cm^{-1}):** υ 2922 (m), 2855 (w), 1715 (s), 1447 (m), 1274 (m), 1242 (m), 1173 (s), 1032 (w), 758 (w), 699 (m).

- **HRMS (ESI):** Calcd. for $C_{35}H_{26}F_3NO_4Na^+$ [M+Na]$^+$ 604.1712; found: 604.1713.

Dimethyl-6,8-dioxo-2,7-diphenyl-7-azatricyclo[3.3.0.02,4]octane-3,3-dicarboxylatecarboxylate (3o)

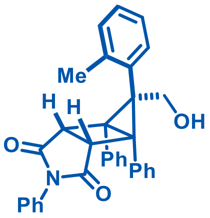


3o

Following the general procedure-1, using cyclopropene **1o** (70 mg, 0.30 mmol, 1.0 equiv), maleimide **2a** (104 mg, 0.600 mmol, 2.00 equiv), and 4CzIPN (6.0 mg, 7.5 µmol, 0.025 equiv) in anhydrous DCM (3 mL, 0.1 M). The crude product was purified by column chromatography using 25-40% Et_2O:hexane mixture as a mobile phase to afford the pure product **3o** as a pale yellow semi-solid (55.0 mg, 0.136 mmol, 45%). (*See Spectra*)

- **TLC (Et_2O:Hexane, 1:1 v/v):** $R_f = 0.2$, UV, $KMnO_4$.
- **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.48 – 7.43 (m, 2H, Ar*H*), 7.41 – 7.36 (m, 1H, Ar*H*), 7.33 (bs, 5H, Ar*H*), 7.22 (d, *J* = 7.8 Hz, 2H, Ar*H*), 3.93 (s, 3H, CO_2CH_3), 3.71 – 3.65 (m, 1H, *CH*), 3.45 (s, 3H, CO_2CH_3), 3.39 (d, *J* = 1.8 Hz, 1H, *CH*), 3.22 (d, *J* = 3.1 Hz, 1H, *CH*).
- **^{13}C NMR (101 MHz, $CDCl_3$):** δ 174.7, 172.9, 165.5, 165.4, 131.4, 130.7, 129.2, 129.1, 128.8, 128.4, 53.1, 52.8, 48.9, 47.9, 46.5, 40.7, 34.7. Two carbons were not resolved at 101 MHz.
- **IR (Neat, cm^{-1}):** υ 2920 (s), 2853 (m), 1718 (s), 1457 (m), 1381 (m), 1274 (m), 1197 (m), 699 (w).
- **HRMS (ESI):** Calcd. for $C_{23}H_{19}NO_6Na$ [M+Na]$^+$ 428.1110; found: 428.1108.

3-(Hydroxymethyl)-2,4,7-triphenyl-3-(o-tolyl)-7-azatricyclo[3.3.0.02,4]octane-6,8-dione (3p)

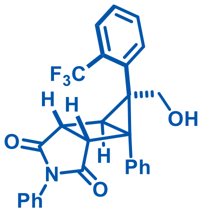


3p

Following the general procedure-1, using cyclopropene **1p** (94 mg, 0.30 mmol, 1.0 equiv), maleimide **2a** (104 mg, 0.600 mmol, 2.00 equiv), and 4CzIPN (6.0 mg, 7.5 µmol, 0.025 equiv) in anhydrous DCM (3 mL, 0.1 M). The crude product was purified by column chromatography using 25-50% Et_2O:hexane mixture as a mobile phase to afford the pure product **3p** as a pale yellow solid (88 mg, 0.18 mmol, 60%, *dr* > 20:1). (*See Spectra*)

- **Melting point:** 201-203 °C.
- **TLC (Et_2O:Hexane, 1:1 v/v):** $R_f = 0.25$, UV, $KMnO_4$.
- **^1H NMR (400 MHz, $CDCl_3$):** δ 7.59 (d, *J* = 7.2 Hz, 1H, Ar*H*), 7.45 (dd, *J* = 17.6, 7.4 Hz, 4H, Ar*H*), 7.37 – 7.22 (m, 11H, Ar*H*), 7.19 (s, 1H, Ar*H*), 7.11 (d, *J* = 7.8 Hz, 2H, Ar*H*), 3.69 – 3.57 (m, 2H, CCH_2OH), 3.20 (d, *J* = 3.9 Hz, 1H, *CH*)), 3.01 (d, *J* = 3.8 Hz, 1H, *CH*)), 2.58 (s, 3H, ArCH_3).
- **^{13}C NMR (101 MHz, $CDCl_3$):** δ 174.6, 174.3, 138.5, 133.2, 133.0, 132.6, 132.5, 131.8, 131.7, 130.4, 129.9, 129.1, 128.5, 128.4, 128.2, 128.2, 127.7, 126.5, 126.0, 64.4, 49.9, 47.4, 46.9, 46.3, 45.9, 20.4. One carbon was not resolved at 101 MHz.
- **IR (Neat, cm^{-1}):** υ 2923 (m), 2855 (w), 2344 (m), 1375 (m), 1263 (m), 1199 (m), 753 (s), 702 (m).
- **HRMS (ESI):** Calcd. for $C_{33}H_{27}NO_3Na^+$ $[M+Na]^+$ 508.1889; found: 508.1888.

3-(hydroxymethyl)-2,7-diphenyl-3-(2-(trifluoromethyl)phenyl)-7-azatricyclo[3.3.0.02,4]octane-6,8-dione (3q)



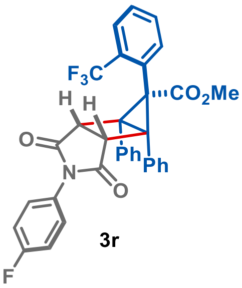
3q

Following the general procedure-1, using cyclopropene **1q** (87 mg, 0.30 mmol, 1.0 equiv), maleimide **2a** (104 mg, 0.600 mmol, 2.00 equiv), and 4CzIPN (6.0 mg, 7.5 µmol, 0.025 equiv) in anhydrous DCM (3 mL, 0.1 M). The crude product was purified by column chromatography using 25-50% Et_2O:hexane mixture as a mobile phase to afford the pure product **3q** as a pale yellow semi-solid (63 mg, 0.13 mmol, 45%, *dr* > 20:1). (*See Spectra*)

- **Melting point:** 177-177 °C.
- **TLC (Et_2O:Hexane, 1:1 v/v):** $R_f = 0.25$, UV, $KMnO_4$.
- **^1H NMR (400 MHz, $CDCl_3$):** δ 7.85 (dd, *J* = 10.5, 7.9 Hz, 2H, Ar*H*), 7.71 (t, *J* = 7.6 Hz, 1H, Ar*H*), 7.55 (t, *J* = 7.8 Hz, 2H, Ar*H*), 7.45 (t, *J* = 7.2 Hz, 2H, Ar*H*), 7.42-7.31 (m, 5H, Ar*H*), 7.07 (d, *J* = 7.6 Hz, 2H, Ar*H*), 4.02 (d, *J* = 12.3 Hz, 1H, CCH_2OH), 3.30 (d, *J* = 12.4 Hz, 1H, CCH_2OH), 3.12 (s, 1H, *CH*), 3.00 (s, 1H, *CH*), 2.86 (d, *J* = 3.5 Hz, 1H, *CH*).

- **^{13}C NMR (101 MHz, CDCl$_3$):** δ 175.9, 174.3, 135.3, 133.0, 132.7, 131.9, 131.6, 130.4 (q, J = 30.3 Hz), 129.1, 129.0, 128.99, 128.53, 128.51, 128.1 (q, J = 5 Hz), 126.2, 125.3, 124.4 (q, J = 274.7 Hz), 65.2 (q, J = 3.1 Hz), 47.5, 46.3, 43.2, 40.7 (q, J = 2.6 Hz), 32.2 (q, J = 3.3 Hz).
- **^{19}F NMR (377 MHz, CDCl3):** δ -57.51.
- **IR (Neat, cm^{-1}):** υ 2921 (s), 2853 (m), 1713 (s), 1496 (w), 1379 (m), 1266 (w), 1176 (m), 1043 (w), 769 (w), 698 (w).
- **HRMS (ESI):** Calcd. for $C_{27}H_{20}F_3NO_3H^+$ $[M+H]^+$ 464.1474; found: 464.1471.

Methyl-7-(4-fluorophenyl)-6,8-dioxo-2,4-diphenyl-3-(2-(trifluoromethyl) phenyl)-7-azatricyclo[3.3.0.02,4]octane-3-carboxylate (3r)



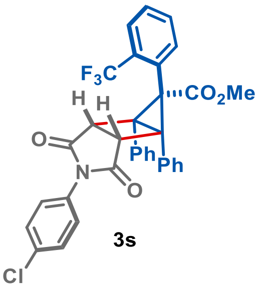
3r

Following the general procedure-1, using cyclopropene **1d** (118 mg, 0.300 mmol, 1.00 equiv), maleimide **2b** (115 mg, 0.600 mmol, 2.00 equiv), and 4CzIPN (6.0 mg, 7.5 µmol, 0.025 equiv) in anhydrous DCM (3 mL, 0.1 M). The crude product was purified by column chromatography using 25-45% Et$_2$O:hexane mixture as a mobile phase to afford the pure product **3r** as a pale yellow semi-solid (124 mg, 0.212 mmol, 70%, *dr* > 20:1). (*See Spectra*)

- **TLC (Et$_2$O:Hexane, 1:1 v/v):** R$_f$ = 0.30, UV, KMnO$_4$.
- **^{1}H NMR (400 MHz, CDCl$_3$):** δ 7.91 (t, J = 7.5 Hz, 2H, Ar*H*), 7.75 (t, J = 7.6 Hz, 1H, Ar*H*), 7.68-7.58 (m, 3H, Ar*H*), 7.48 (d, J = 6.2 Hz, 2H, Ar*H*), 7.43-7.29 (m, 6H, Ar*H*), 7.16 – 7.06 (m, 4H, Ar*H*), 3.39 (d, J = 3.8 Hz, 1H, *CH*), 3.28 (s, 3H, CO$_2$*CH$_3$*), 3.17 (d, J = 3.8 Hz, 1H, *CH*).
- **^{13}C NMR (101 MHz, CDCl$_3$):** δ 173.6, 172.8, 167.2, 163.3, 160.8, 135.1, 132.0, 131.7 (d, J = 16.5 Hz), 131.3, 130.8, 130.3 (q, J = 30.3 Hz), 130.1, 128.9, 128.4, 128.2, 127.9 (d, J = 3.2 Hz), 127.7, 127.6 (q, J = 5 Hz), 127.5 (d, J = 3.5 Hz), 127.1, 124.2 (q, J = 274.7 Hz), 116.1 (d, J = 23.0 Hz), 53.3, 53.0, 52.3, 48.4, 48.0, 45.4.
- **^{19}F NMR (377 MHz, CDCl$_3$):** δ -58.28, -112.06.
- **IR (Neat, cm^{-1}):** υ 2922 (m), 2855 (w), 1717 (s), 1375 (m), 1243 (m), 1197 (m), 756 (w), 698 (w).

- **HRMS (ESI):** Calcd. for $C_{34}H_{23}F_4NO_4Na^+$ $[M+Na]^+$ 608.1461; found: 608.1465.

Methyl-7-(4-chlorophenyl)-6,8-dioxo-2,4-diphenyl-3-(2-(trifluoromethyl)phenyl)-7-azatricyclo[3.3.0.02,4]octane-3-carboxylate (3s)

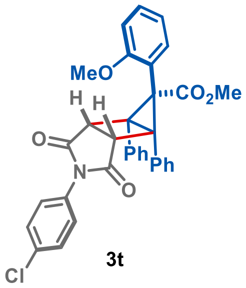


3s

Following the general procedure-1, using cyclopropene **1d** (118 mg, 0.300 mmol, 1.00 equiv), maleimide **2c** (124 mg, 0.600 mmol, 2.00 equiv), and 4CzIPN (6.0 mg, 7.5 µmol, 0.025 equiv) in anhydrous DCM (3 mL, 0.1 M). The crude product was purified by column chromatography using 20-45% Et_2O:hexane mixture as a mobile phase to afford the pure product **3s** as a pale yellow semi-solid (125 mg, 0.208 mmol, 69%, *dr* > 20:1). (*See Spectra*)

- **TLC (Et_2O:Hexane, 1:1 v/v):** $R_f = 0.35$, UV, $KMnO_4$.
- **^1H NMR (400 MHz, $CDCl_3$):** δ 7.90 (t, $J = 6.8$ Hz, 2H, Ar*H*)), 7.75 (t, $J = 7.6$ Hz, 1H, Ar*H*)), 7.66 – 7.58 (m, 3H, Ar*H*)), 7.49 – 7.45 (m, 2H, Ar*H*)), 7.43 – 7.29 (m, 8H, Ar*H*)), 7.10 (d, $J = 8.5$ Hz, 2H, Ar*H*)), 3.38 (d, $J = 3.9$ Hz, 1H, C*H*), 3.28 (s, 3H, CO_2CH_3), 3.17 (d, $J = 3.8$ Hz, 1H, C*H*).
- **^{13}C NMR (101 MHz, $CDCl_3$):** δ 173.4, 172.6, 167.2, 135.1, 134.3, 132.0, 131.7, 131.5, 131.3, 130.8, 130.3 (q, $J = 30.3$ Hz), 130.1, 130.0, 129.3, 128.9, 128.5, 128.2, 127.9, 127.6 (q, $J = 5.0$ Hz), 127.1, 127.0, 124.2 (q, $J = 274.7$ Hz), 53.3, 53.0, 52.3, 48.3, 48.0, 45.5.
- **^{19}F NMR (377 MHz, $CDCl_3$):** δ -58.28.
- **IR (Neat, cm^{-1}):** υ 2919 (w), 2854 (w), 1722 (s), 1442 (m), 1376 (m), 1261 (m), 1175 (m), 1043 (w), 753 (s), 647 (m).
- **HRMS (ESI):** Calcd. for $C_{34}H_{23}ClF_3NO_4Na^+$ $[M+Na]^+$ 624.1165; found: 624.1163.

Methyl-7-(4-chlorophenyl)-3-(2-methoxyphenyl)-6,8-dioxo-2,4-diphenyl-7-azatricyclo[3.3.0.02,4]octane-3-carboxylate (3t)

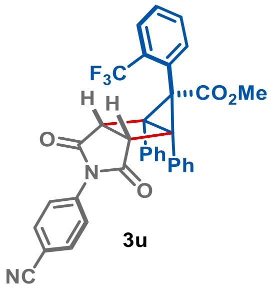


3t

Following the general procedure-1, using cyclopropene **1e** (107 mg, 0.300 mmol, 1.00 equiv), maleimide **2c** (124 mg, 0.600 mmol, 2.00 equiv), and 4CzIPN (6.0 mg, 7.5 µmol, 0.025 equiv) in anhydrous DCM (3 mL, 0.1 M). The crude product was purified by column chromatography using 25-40% Et_2O:hexane mixture as a mobile phase to afford the pure product **3t** as a pale yellow semi-solid (136 mg, 0.241 mmol, 80%, *dr* > 20:1). (*See Spectra*)

- **TLC (Et_2O:Hexane, 1:1 v/v):** $R_f = 0.25$, UV, $KMnO_4$.
- **^1H NMR (400 MHz, $CDCl_3$):** δ 7.70 – 7.63 (m, 3H, Ar*H*), 7.54 – 7.44 (m, 3H, Ar*H*), 7.43 – 7.29 (m, 8H, Ar*H*), 7.24 – 7.19 (m, 2H, Ar*H*), 7.16 (td, *J* = 7.5, 1.1 Hz, 1H, Ar*H*), 7.13 – 7.08 (m, 1H, Ar*H*), 4.01 (s, 3H, ArOCH_3), 3.33 (d, *J* = 3.8 Hz, 1H, *CH*), 3.16 (s, 3H, CO_2CH_3), 2.99 (d, *J* = 3.7 Hz, 1H, *CH*).
- **^{13}C NMR (101 MHz, $CDCl_3$):** δ 173.9, 173.6, 168.0, 158.6, 134.2, 133.2, 133.1, 132.8, 130.2, 130.1, 129.8, 129.3, 128.1, 127.9, 127.8, 127.6, 127.2, 120.90, 120.86, 120.8, 111.3, 55.3, 52.5, 51.8, 50.0, 49.8, 48.0, 46.8.
- **IR (Neat, cm^{-1}):** υ 2922 (m), 2853 (w), 1717 (s), 1374 (m), 1267 (w), 1196 (m), 1090 (w), 1021 (m), 756 (m), 696 (m).
- **HRMS (ESI):** Calcd. for $C_{34}H_{26}ClNO_5H$ $[M+H]^+$ 564.1578; found: 564.1580.

Methyl-7-(4-cyanophenyl)-6,8-dioxo-2,4-diphenyl-3-(2-(trifluoromethyl)phenyl)-7-azatricyclo[3.3.0.02,4]octane-3-carboxylate (3u)

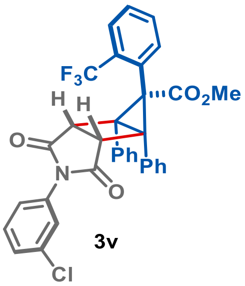


3u

Following the general procedure-1, using cyclopropene **1d** (118 mg, 0.300 mmol, 1.00 equiv), maleimide **2d** (119 mg, 0.600 mmol, 2.00 equiv), and 4CzIPN (6.0 mg, 7.5 µmol, 0.025 equiv) in anhydrous DCM (3 mL, 0.1 M). The crude product was purified by column chromatography using 25-50% Et_2O:hexane mixture as a mobile phase to afford the pure product **3u** as a pale yellow semi-solid (134 mg, 0.226 mmol, 75%, *dr* > 20:1). (*See Spectra*)

- **TLC (Et_2O:Hexane, 3:2 v/v):** R_f = 0.30, UV, $KMnO_4$.
- **^1H NMR (400 MHz, $CDCl_3$):** δ 7.93 - 7.88 (m, 2H, Ar*H*), 7.79 – 7.74 (m, 1H, Ar*H*), 7.70 – 7.59 (m, 5H, Ar*H*), 7.48 – 7.30 (m, 10H, Ar*H*), 3.42 (d, *J* = 3.9 Hz, 1H, *CH*), 3.28 (s, 3H, CO_2CH_3), 3.20 (d, *J* = 3.9 Hz, 1H, *CH*).
- **^{13}C NMR (101 MHz, $CDCl_3$):** δ 172.9, 172.2, 167.0, 135.4, 135.0, 132.9, 132.1, 131.5, 131.4, 131.1, 130.7, 130.2 (q, *J* = 31.3 Hz), 130.0, 129.0, 128.5, 128.2, 127.9, 127.5 (q, *J* = 5.0 Hz), 127.1, 126.3, 124.2 (q, *J* = 274.7 Hz), 117.9, 112.0, 53.2, 52.9, 52.3, 48.1, 47.9, 45.5.
- **^{19}F NMR (377 MHz, $CDCl_3$):** δ -58.27.
- **IR (Neat, cm^{-1}):** υ 2922 (m), 2855 (w), 1723 (s), 1371 (m), 1316 (m), 1256 (w), 1173 (m), 756 (w), 698 (w).
- **HRMS (ESI):** Calcd. for $C_{35}H_{23}F_3N_2O_4Na^+$ $[M+Na]^+$ 615.1508; found: 615.1506.

Methyl-7-(3-chlorophenyl)-6,8-dioxo-2,4-diphenyl-3-(2-(trifluoromethyl)phenyl)-7-azatricyclo[3.3.0.02,4]octane-3-carboxylate (3v)



3v

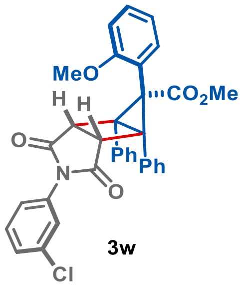
Following the general procedure-1, using cyclopropene **1d** (118 mg, 0.300 mmol, 1.00 equiv), maleimide **2e** (124 mg, 0.600 mmol, 2.00 equiv), and 4CzIPN (6.0 mg, 7.5 µmol, 0.025 equiv) in anhydrous DCM (3 mL, 0.1 M). The crude product was purified by column chromatography using 20-30% Et_2O:hexane mixture as a mobile phase to afford the pure product **3v** as a pale yellow semi-solid (141 mg, 0.235 mmol, 78%, *dr* > 20:1). (*See Spectra*)

- **TLC (Et_2O:Hexane, 1:1 v/v):** R_f = 0.50, UV, $KMnO_4$.
- **^1H NMR (400 MHz, $CDCl_3$):** δ 7.95 – 7.88 (m, 2H, Ar*H*), 7.77 - 7.72 (m, 1H, Ar*H*), 7.70 – 7.66 (m, 2H, Ar*H*), 7.62 (t, *J* = 7.7 Hz, 1H, Ar*H*), 7.52 – 7.47 (m, 2H, Ar*H*), 7.46

– 7.31 (m, 8H, Ar*H*), 7.22-7.20 (m, 1H, Ar*H*), 7.09-7.03 (m, 1H, Ar*H*), 3.41 (d, *J* = 3.9 Hz, 1H, *CH*), 3.29 (s, 3H, CO_2CH_3), 3.19 (d, *J* = 3.9 Hz, 1H, *CH*).

- **^{13}C NMR (101 MHz, $CDCl_3$):** δ 173.2, 172.5, 167.1, 135.1, 134.5, 132.5, 132.0, 131.6, 131.5, 131.2, 130.8, 130.2 (q, *J* = 30.3 Hz), 130.0, 128.9, 128.7, 128.4, 128.2, 127.9, 127.5 (q, *J* = 5.0 Hz), 127.1, 126.1, 124.2 (q, *J* = 274.7 Hz), 124.0, 53.3, 52.9, 52.3, 48.3, 47.9, 45.4. One carbon was not resolved at 101 MHz.
- **^{19}F NMR (377 MHz, $CDCl_3$):** δ -58.24.
- **IR (Neat, cm^{-1}):** υ 2919 (w), 2856 (w), 1723 (s), 1482 (w), 1371 (w), 1261 (w), 1174 (m), 1039 (w), 756 (w), 701 (m).
- **HRMS (ESI):** Calcd. for $C_{34}H_{23}ClF_3NO_4Na^+$ $[M+Na]^+$ 624.1165; found: 624.1163.

Methyl-7-(3-chlorophenyl)-3-(2-methoxyphenyl)-6,8-dioxo-2,4-diphenyl-7-azatricyclo[3.3.0.02,4]octane-3-carboxylate (3w)



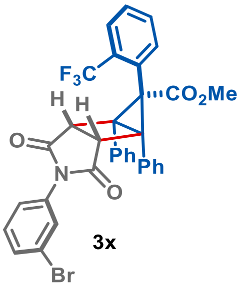
3w

Following the general procedure-1, using cyclopropene **1e** (107 mg, 0.300 mmol, 1.00 equiv), maleimide **2e** (124 mg, 0.600 mmol, 2.00 equiv), and 4CzIPN (6.0 mg, 7.5 µmol, 0.025 equiv) in anhydrous DCM (3 mL, 0.1 M). The crude product was purified by column chromatography using 25-40% Et_2O:hexane mixture as a mobile phase to afford the pure product **3w** as a pale yellow semi-solid (125 mg, 0.222 mmol, 74%, *dr* > 20:1). (*See Spectra*)

- **TLC (Et_2O:Hexane, 1:1 v/v):** $R_f = 0.25$, UV, $KMnO_4$.
- **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.69 – 7.65 (m, 3H, Ar*H*), 7.53 – 7.50 (m, 2H, Ar*H*), 7.47 (ddd, *J* = 8.2, 7.4, 1.7 Hz, 1H, Ar*H*), 7.40 - 7.36 (m, 5H, Ar*H*), 7.36 – 7.31 (m, 3H, Ar*H*), 7.29 (t, *J* = 1.9 Hz, 1H, Ar*H*), 7.19 – 7.15 (m, 2H, Ar*H*), 7.11 (dd, *J* = 8.4, 1.1 Hz, 1H, Ar*H*), 4.02 (s, 3H, ArO*CH*$_3$), 3.33 (d, *J* = 3.8 Hz, 1H, *CH*), 3.16 (s, 3H, CO_2CH_3), 2.99 (d, *J* = 3.8 Hz, 1H, *CH*).
- **^{13}C NMR (101 MHz, $CDCl_3$):** δ 173.7, 173.5, 168.0, 158.6, 134.6, 133.2, 133.1, 132.9, 130.1, 130.1, 130.0, 129.8, 128.6, 128.1, 128.0, 127.9, 127.8, 127.6, 126.3, 124.1, 120.93, 120.90, 111.3, 55.3, 52.5, 51.8, 50.0, 49.8, 48.0, 46.8.

- **IR (Neat, cm^{-1}):** υ 2923 (m), 2853 (w), 1719 (s), 1370 (w), 1267 (w), 1196 (m), 1025 (m), 759 (w), 700 (m).
- **HRMS (ESI):** Calcd. for $C_{34}H_{26}ClNO_5H^+$ $[M+H]^+$ 564.1578; found: 564.1574.

Methyl-7-(3-bromophenyl)-6,8-dioxo-2,4-diphenyl-3-(2-(trifluoromethyl)phenyl)-7-azatricyclo[3.3.0.02,4]octane-3-carboxylate (3x)

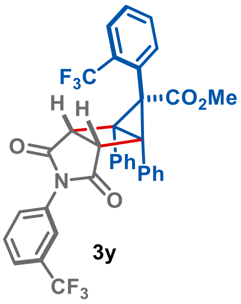


3x

Following the general procedure-1, using cyclopropene **1d** (118 mg, 0.300 mmol, 1.00 equiv), maleimide **2f** (151 mg, 0.600 mmol, 2.00 equiv), and 4CzIPN (6.0 mg, 7.5 µmol, 0.025 equiv) in anhydrous DCM (3 mL, 0.1 M). The crude product was purified by column chromatography using 20-30% Et_2O:hexane mixture as a mobile phase to afford the pure product **3x** as a pale yellow semi-solid (144 mg, 0.223 mmol, 74%, *dr* > 20:1). (*See Spectra*)

- **TLC (Et_2O:Hexane, 2:3 v/v):** $R_f = 0.35$, UV, $KMnO_4$.
- **^1H NMR (400 MHz, $CDCl_3$):** δ 7.96 – 7.86 (m, 2H, Ar*H*), 7.78-7.72 (m, 1H, Ar*H*), 7.67 (d, *J* = 6.5 Hz, 2H, Ar*H*), 7.62 (t, *J* = 7.7 Hz, 1H, Ar*H*), 7.51-7.47 (m, 3H, Ar*H*), 7.46 – 7.34 (m, 7H, Ar*H*), 7.31 – 7.25 (m, 1H, Ar*H*), 7.13-7.09 (m, 1H, Ar*H*), 3.40 (d, *J* = 3.9 Hz, 1H, *CH*), 3.28 (s, 3H, CO_2CH_3), 3.19 (d, *J* = 3.9 Hz, 1H, *CH*).
- **^{13}C NMR (101 MHz, $CDCl_3$):** δ 173.2, 172.5, 167.1, 135.1, 132.7, 132.0, 131.7, 131.6, 131.5, 131.2, 130.8, 130.3, 130.2 (q, *J* = 31.3 Hz), 130.1, 128.9, 128.4, 128.2, 127.9, 127.7, 127.5 (q, *J* = 5.0 Hz), 127.1, 124.5, 124.2 (q, *J* = 274.7 Hz), 122.3, 53.3, 53.0, 52.3, 48.2, 47.9, 45.4.
- **^{19}F NMR (377 MHz, $CDCl_3$):** δ -58.28.
- **IR (Neat, cm^{-1}):** υ 2922 (m), 2855 (w), 1721 (s), 1477 (w), 1442 (w), 1256 (w), 1172 (m), 767 (w), 700 (m).
- **HRMS (ESI):** Calcd. for $C_{34}H_{23}BrF_3NO_4Na^+$ $[M+Na]^+$ 668.0660; found: 668.0662.

Methyl-6,8-dioxo-2,4-diphenyl-3-(2-(trifluoromethyl)phenyl)-7-(3-(trifluoromethyl)phenyl)-7-azatricyclo[3.3.0.02,4]octane-3-carboxylate (3y)

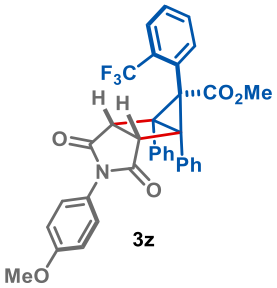


3y

Following the general procedure-1, using cyclopropene **1d** (118 mg, 0.300 mmol, 1.00 equiv), maleimide **2g** (145 mg, 0.600 mmol, 2.00 equiv), and 4CzIPN (6.0 mg, 7.5 µmol, 0.025 equiv) in anhydrous DCM (3 mL, 0.1 M). The crude product was purified by column chromatography using 20-35% Et_2O:hexane mixture as a mobile phase to afford the pure product **3y** as a pale yellow semi-solid (140 mg, 0.220 mmol, 73%, *dr* > 20:1). (*See Spectra*)

- **TLC (Et_2O:Hexane, 2:3 v/v):** R_f = 0.40, UV, $KMnO_4$.
- **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.91 (t, *J* = 7.5 Hz, 2H, Ar*H*), 7.77 (t, *J* = 7.6 Hz, 1H, Ar*H*), 7.66 (d, *J* = 6.5 Hz, 2H, Ar*H*), 7.61 (d, *J* = 11.0 Hz, 2H, Ar*H*), 7.54 (t, *J* = 7.9 Hz, 1H, Ar*H*), 7.48 (bs, 3H, Ar*H*), 7.44 – 7.32 (m, 7H, Ar*H*), 3.42 (d, *J* = 3.9 Hz, 1H, *CH*), 3.28 (s, 3H, CO_2CH_3), 3.20 (d, *J* = 3.9 Hz, 1H, *CH*).
- **^{13}C NMR (101 MHz, $CDCl_3$):** δ 173.2, 172.5, 167.1, 135.1, 132.1, 131.6 (q, *J* = 33.3 Hz), 131.5, 131.3, 130.8, 130.3 (q, *J* = 30.3 Hz), 130.1, 129.7, 129.1, 129.0, 128.5, 128.2, 128.0, 127.8, 127.6 (q, *J* = 5.0 Hz), 127.4, 127.2, 125.2, 124.2 (q, *J* = 274.7 Hz), 123.3 (q, *J* = 273.7 Hz), 122.9 (q, *J* = 3.8 Hz), 53.3, 53.1, 52.3, 48.2, 47.9, 45.5.
- **^{19}F NMR (377 MHz, $CDCl_3$):** δ -58.33, -62.75.
- **IR (Neat, cm^{-1}):** υ 2921 (m), 2856 (w), 1718 (s), 1374 (w), 1252 (m), 1197 (m), 1175 (m), 754 (s), 699 (w).
- **HRMS (ESI):** Calcd. for $C_{35}H_{23}F_6NO_4H^+$ $[M+H]^+$ 636.1610; found: 636.1608.

Methyl-7-(4-methoxyphenyl)-6,8-dioxo-2,4-diphenyl-3-(2-(trifluoromethyl)phenyl)-7-azatricyclo[3.3.0.02,4]octane-3-carboxylate (3z)

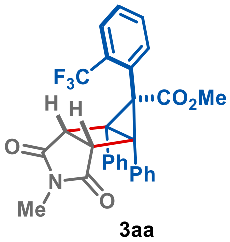


3z

Following the general procedure-1, using cyclopropene **1d** (118 mg, 0.300 mmol, 1.00 equiv), maleimide **2h** (122 mg, 0.600 mmol, 2.00 equiv), and 4CzIPN (6.0 mg, 7.5 μmol, 0.025 equiv) in anhydrous DCM (3 mL, 0.1 M). The crude product was purified by column chromatography using 20-40% Et_2O:hexane mixture as a mobile phase to afford the pure product **3z** as a pale yellow semi-solid (76.0 mg, 0.127 mmol, 42%, *dr* > 20:1). (*See Spectra*)

- **TLC (Et_2O:Hexane, 1:1 v/v):** R_f = 0.35, UV, $KMnO_4$.
- **^1H NMR (400 MHz, $CDCl_3$):** δ 7.90 (t, *J* = 8.6 Hz, 2H, Ar*H*), 7.74 (t, *J* = 7.5 Hz, 1H, Ar*H*), 7.68 – 7.57 (m, 3H, Ar*H*), 7.50 - 7.45 (m, 2H, Ar*H*), 7.43 – 7.29 (m, 6H, Ar*H*), 7.05 (d, *J* = 9.0 Hz, 2H, Ar*H*), 6.92 (d, *J* = 9.0 Hz, 2H, Ar*H*), 3.78 (s, 3H, ArOCH_3), 3.36 (d, *J* = 3.9 Hz, 1H, *CH*), 3.27 (s, 3H, CO_2CH_3), 3.15 (d, *J* = 3.9 Hz, 1H, *CH*).
- **^{13}C NMR (101 MHz, $CDCl_3$):** δ 173.9, 173.1, 167.3, 159.4, 135.2, 132.0, 131.8, 131.7, 131.4, 130.9, 130.3 (q, *J* = 30.3 Hz), 130.2, 128.9, 128.4, 128.2, 127.8, 127.5 (q, *J* = 5.0 Hz), 127.2, 127.0, 124.2 (q, *J* = 274.7 Hz), 114.4, 55.4, 53.4, 52.9, 52.3, 48.5, 48.0, 45.4, 45.4.
- **^{19}F NMR (377 MHz, $CDCl_3$):** δ -58.28.
- **IR (Neat, cm^{-1}):** υ 2923 (m), 2855 (w), 2348 (m), 1718 (s), 1375 (m), 1254 (m), 1197 (m), 1033 (w), 753 (s), 698 (w).
- **HRMS (ESI):** Calcd. for $C_{35}H_{26}F_3NO_5Na$ $[M+Na]^+$ 620.1661; found: 620.1664.

Methyl-7-methyl-6,8-dioxo-2,4-diphenyl-3-(2-(trifluoromethyl)phenyl)-7-azatricyclo[3.3.0.02,4]octane-3-carboxylate (3aa)

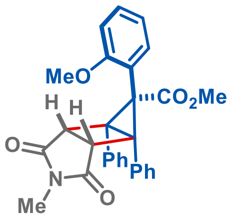


3aa

Following the general procedure-1, using cyclopropene **1d** (118 mg, 0.300 mmol, 1.00 equiv), maleimide **2i** (67 mg, 0.60 mmol, 2.0 equiv), and 4CzIPN (6.0 mg, 7.5 μmol, 0.025 equiv) in anhydrous DCM (3 mL, 0.1 M). The crude product was purified by column chromatography using 30-40% Et_2O:hexane mixture as a mobile phase to afford the pure product **3aa** as a pale yellow semi-solid (104 mg, 0.206 mmol, 68%, *dr* > 20:1). (*See Spectra*)

- **TLC (Et_2O:Hexane, 1:1 v/v):** R_f = 0.30, UV, $KMnO_4$.
- **^1H NMR (400 MHz, $CDCl_3$):** δ 7.87 (d, *J* = 8.3 Hz, 2H, Ar*H*), 7.76 – 7.70 (m, 1H, Ar*H*), 7.62 – 7.52 (m, 3H, Ar*H*), 7.39 (bs, 5H, Ar*H*), 7.35 – 7.28 (m, 3H, Ar*H*), 3.25 (s, 3H, CO_2CH_3), 3.21 (d, *J* = 3.8 Hz, 1H, *CH*), 3.04 (d, *J* = 3.9 Hz, 1H, *CH*), 2.93 (s, 3H, $-NCH_3$).
- **^{13}C NMR (101 MHz, $CDCl_3$):** δ 174.8, 174.0, 167.1, 135.1, 131.9, 131.8, 131.5, 131.4, 130.8, 130.6 (q, *J* = 30.3 Hz), 130.0, 128.8, 128.3, 128.1, 127.7, 127.5 (q, *J* = 5.0 Hz), 126.9, 124.2 (q, *J* = 274.7 Hz), 53.1, 53.0, 52.2, 48.5, 47.9, 45.7, 25.0.
- **^{19}F NMR (377 MHz, $CDCl_3$):** δ -58.32.
- **IR (Neat, cm^{-1}):** υ 2918 (w), 2535 (w), 1708 (s), 1493 (w), 1436 (m), 1317 (m), 1231 (m), 1178 (m), 760 (w), 702 (m).
- **HRMS (ESI):** Calcd. for $C_{29}H_{22}F_3NO_4Na^+$ $[M+Na]^+$ 528.1399; found: 528.1400.

Methyl-3-(2-methoxyphenyl)-7-methyl-6,8-dioxo-2,4-diphenyl-7-azatricyclo[3.3.0.02,4]octane-3-carboxylate (3ab)



3ab

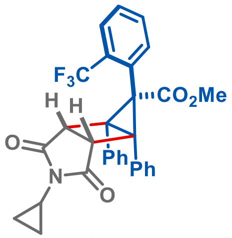
Following the general procedure-1, using cyclopropene **1e** (107 mg, 0.300 mmol, 1.00 equiv), maleimide **2i** (67 mg, 0.60 mmol, 2.0 equiv), and 4CzIPN (6.0 mg, 7.5 μmol, 0.025 equiv) in anhydrous DCM (3 mL, 0.1 M). The crude product was purified by column chromatography using 20-30% Et_2O:hexane mixture as a mobile phase to afford the pure product **3ab** as a pale yellow semi-solid (111 mg, 0.238 mmol, 78%, *dr* > 20:1). (*See Spectra*)

- **TLC (Et_2O:Hexane, 1:1 v/v):** R_f = 0.45, UV, $KMnO_4$.
- **^1H NMR (400 MHz, $CDCl_3$):** δ 7.63 (d, *J* = 1.7 Hz, 1H, Ar*H*), 7.57 (d, *J* = 7.2 Hz, 2H, Ar*H*), 7.47 – 7.40 (m, 3H, Ar*H*), 7.39 – 7.20 (m, 6H, Ar*H*), 7.14 (td, *J* = 7.4, 1.1 Hz,

1H, Ar*H*), 7.09 (dd, *J* = 8.4, 1.0 Hz, 1H, Ar*H*), 3.99 (s, 3H, ArO*CH*$_3$), 3.17 (d, *J* = 3.8 Hz, 1H, *CH*), 3.14 (s, 3H, CO$_2$*CH*$_3$), 3.00 (s, 3H, -N*CH*$_3$), 2.84 (d, *J* = 3.7 Hz, 1H, *CH*).

- **^{13}C NMR (101 MHz, CDCl$_3$):** δ 175.2, 175.0, 168.0, 158.5, 133.3, 133.1, 133.0, 130.0, 129.9, 129.7, 127.9, 127.8, 127.6, 127.5, 121.0, 120.8, 111.2, 55.3, 52.4, 51.7, 50.0, 49.8, 48.1, 46.9, 24.9.
- **IR (Neat, cm^{-1}):** υ 2923 (m), 2854 (w), 1707 (s), 1457 (w), 1380 (m), 1239 (m), 1187 (w), 1023 (w), 759 (w), 699 (w).
- **HRMS (ESI):** Calcd. for $C_{29}H_{25}NO_5Na^+$ [M+Na]$^+$ 490.1630; found: 490.1633.

Methyl-7-cyclopropyl-6,8-dioxo-2,4-diphenyl-3-(2-(trifluoromethyl)phenyl)-7-azatricyclo[3.3.0.02,4]octane-3-carboxylate (3ac)

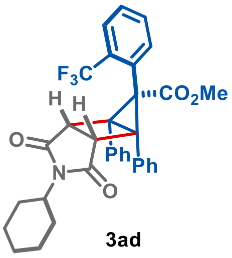


3ac

Following the general procedure-1, using cyclopropene **1d** (118 mg, 0.300 mmol, 1.00 equiv), maleimide **2j** (82 mg, 0.60 mmol, 2.0 equiv), and 4CzIPN (6.0 mg, 7.5 µmol, 0.025 equiv) in anhydrous DCM (3 mL, 0.1 M). The crude product was purified by column chromatography using 25-40% Et$_2$O:hexane mixture as a mobile phase to afford the pure product **3ac** as a pale yellow semi-solid (128 mg, 0.241 mmol, 84%, *dr* > 20:1). (*See Spectra*)

- **TLC (Et$_2$O:Hexane, 1:1 v/v):** R$_f$ = 0.30, UV, KMnO$_4$.
- **^{1}H NMR (400 MHz, CDCl$_3$):** δ 7.88 – 7.83 (m, 2H, Ar*H*), 7.74 - 7.68 (m, 1H, Ar*H*), 7.62 – 7.51 (m, 3H, Ar*H*), 7.43 – 7.28 (m, 8H, Ar*H*), 3.24 (s, 3H, CO$_2$*CH*$_3$), 3.14 (d, *J* = 3.9 Hz, 1H, *CH*), 2.95 (d, *J* = 3.9 Hz, 1H, *CH*), 2.53 (tt, *J* = 6.9, 4.3 Hz, 1H, -NC*H*), 0.94-0.81 (m, 3H, -NCH*CH*$_2$), 0.69 – 0.59 (m, 1H, -NCH*CH*$_2$).
- **^{13}C NMR (101 MHz, CDCl$_3$):** δ 175.0, 174.3, 167.2, 135.1, 132.0, 131.9, 131.7, 131.4, 130.7, 130.3 (q, *J* = 30.3 Hz), 130.0, 128.8, 128.3, 128.1, 127.6, 127.5 (q, *J* = 5.0 Hz), 126.9, 124.2 (q, *J* = 182.8 Hz), 53.2, 53.0, 52.1, 48.3, 47.5, 45.0, 22.3, 4.9, 4.8.
- **^{19}F NMR (377 MHz, CDCl$_3$):** δ -58.32.
- **IR (Neat, cm^{-1}):** υ 2923 (w), 2855 (w), 1714 (s), 1397 (w), 1316 (m), 1232 (m), 1178 (m), 1038 (w), 759 (w), 700 (w).
- **HRMS (ESI):** Calcd. for $C_{31}H_{24}F_3NO_4Na^+$ [M+Na]$^+$ 554.1555; found: 554.1558.

Methyl-7-cyclohexyl-6,8-dioxo-2,4-diphenyl-3-(2-(trifluoromethyl)phenyl)-7-azatricyclo[3.3.0.02,4]octane-3-carboxylate (3ad)

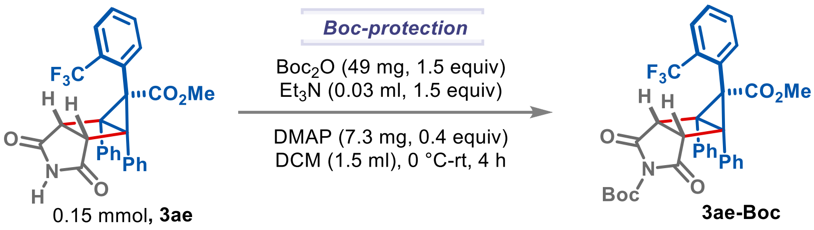


3ad

Following the general procedure-1, using cyclopropene **1d** (118 mg, 0.300 mmol, 1.00 equiv), maleimide **2k** (108 mg, 0.600 mmol, 2.00 equiv), and 4CzIPN (6.0 mg, 7.5 µmol, 0.025 equiv) in anhydrous DCM (3 mL, 0.1 M). The crude product was purified by column chromatography using 20-30% Et_2O:hexane mixture as a mobile phase to afford the pure product **3ad** as a pale yellow semi-solid (121 mg, 0.211 mmol, 70%, *dr* > 20:1). (*See Spectra*)

- **TLC (Et_2O:Hexane, 2:3 v/v):** R_f = 0.30, UV, $KMnO_4$.
- **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.87 (d, *J* = 4.7 Hz, 2H, Ar*H*), 7.71 (t, *J* = 7.6 Hz, 1H, Ar*H*), 7.58 (t, *J* = 7.9 Hz, 3H, Ar*H*), 7.48 – 7.39 (m, 5H, Ar*H*), 7.32 (d, *J* = 7.2 Hz, 3H, Ar*H*), 3.95 – 3.82 (m, 1H, -N*CH*), 3.25 (s, 3H, CO_2CH_3), 3.13 (d, *J* = 3.9 Hz, 1H, *CH*), 2.96 (d, *J* = 3.9 Hz, 1H, *CH*), 2.04 (dqd, *J* = 51.6, 12.5, 3.5 Hz, 2H, -NCHCH_2), 1.77 (t, *J* = 11.1 Hz, 2H, -NCHCH_2), 1.64 – 1.42 (m, 3H, -NCH$CH_2CH_2CH_2$), 1.33 – 1.08 (m, 3H, -NCH$CH_2CH_2CH_2$).
- **^{13}C NMR (101 MHz, $CDCl_3$):** δ 174.7, 173.9, 167.3, 135.1, 132.0, 131.9, 131.7, 131.5, 130.8, 130.3 (q, *J* = 31.3 Hz), 130.2, 128.7, 128.3, 128.0, 127.6, 127.4 (q, *J* = 5.0 Hz), 126.7, 124.2 (q, *J* = 274.7 Hz), 53.3, 52.9, 52.1, 51.6, 48.6, 47.6, 45.0, 28.5, 28.2, 25.6, 24.7. One carbon was not resolved at 101 MHz.
- **^{19}F NMR (377 MHz, $CDCl_3$):** δ -58.29.
- **IR (Neat, cm^{-1}):** υ 2922 (m), 2854 (w), 1706 (s), 1449 (w), 1368 (w), 1237 (m), 1180 (m), 1043 (w), 754 (s), 700 (m).
- **HRMS (ESI):** Calcd. for $C_{34}H_{30}F_3NO_4Na$ $[M+Na]^+$ 596.2025; found: 596.2025.

Methyl-6,8-dioxo-2,4-diphenyl-3-(2-(trifluoromethyl)phenyl)-7-azatricyclo[3.3.0.02,4]octane-3-carboxylate (3ae)



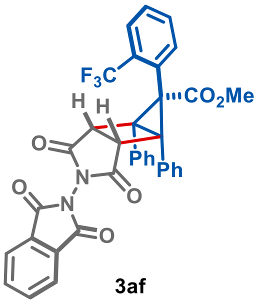
0.15 mmol, **3ae**

3ae-Boc

Following the general procedure-1, using cyclopropene **1d** (118 mg, 0.300 mmol, 1.00, equiv), maleimide **2l** (58 mg, 0.60 mmol, 2.0 equiv), and 4CzIPN (6.0 mg, 7.5 µmol, 0.025 equiv) in anhydrous DCM (3 mL, 0.1 M). The crude product was not able to purify by column chromatography. The yield is calculated by using dibromomethane as an internal standard (68%, *dr* > 20:1). However, NMR of the subsequent Boc protected product **3ae-Boc** was given. (*See Spectra*)

- **TLC (Et_2O:Hexane, 1:1 v/v):** $R_f = 0.30$, UV, $KMnO_4$.
- **^1H NMR (400 MHz, $CDCl_3$):** δ 7.88 – 7.83 (m, 2H, Ar*H*), 7.75 – 7.71 (m, 1H, Ar*H*), 7.60 (dd, *J* = 8.3, 6.7 Hz, 3H, Ar*H*), 7.48 – 7.46 (m, 2H, Ar*H*), 7.38 (dddt, *J* = 8.9, 7.2, 5.6, 1.5 Hz, 3H, Ar*H*), 7.35 – 7.28 (m, 3H, Ar*H*), 3.24 (s, 3H, CO_2CH_3), 3.21 (d, *J* = 3.8 Hz, 1H, *CH*), 3.02 (d, *J* = 3.9 Hz, 1H, *CH*), 1.51 (s, 9H, $-NCO_2C(CH_3)_3$).
- **^{13}C NMR (101 MHz, $CDCl_3$):** δ 170.7, 169.6, 167.1, 146.0, 135.2, 132.0, 131.5, 131.3, 131.2, 130.8, 130.3 (q, *J* = 20.2 Hz), 130.2, 129.0, 128.4, 128.2, 127.8, 127.5 (q, *J* = 5.0 Hz), 127.1, 124.2 (q, *J* = 183.8 Hz), 86.5, 53.1, 52.4, 52.2, 48.3, 48.2, 46.1, 27.6.
- **^{19}F NMR (377 MHz, $CDCl_3$):** δ -58.34.
- **IR (Neat, cm^{-1}):** υ 2923 (w), 2855 (w), 1723 (s), 1585 (w), 1478 (w), 1314 (m), 1316 (m), 1174 (m), 1073 (m), 1038 (w), 766 (w), 700 (w).
- **HRMS (ESI):** Calcd. for $C_{28}H_{20}F_3NO_4H^+$ $[M+H]^+$ 492.1423; found: 492.1424 for **3ae** Calcd. for $C_{33}H_{28}F_3NO_6Na^+$ $[M+Na]^+$ 614.1766; found: 614.1764 for **3ae-Boc.**

Methyl-7-(1,3-dioxoisoindolin-2-yl)-6,8-dioxo-2,4-diphenyl-3-(2-(trifluoromethyl)phenyl)-7-azatricyclo[3.3.0.02,4]octane-3-carboxylate (3af)

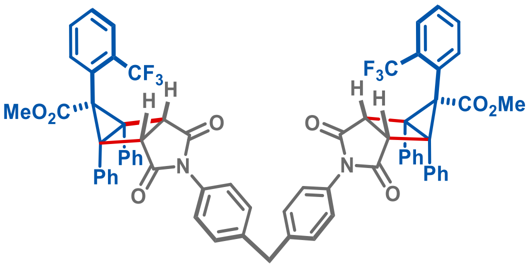


3af

Following the general procedure-1, using cyclopropene **1d** (118 mg, 0.300 mmol, 1.00 equiv), maleimide **2m** (145 mg, 0.600 mmol, 2.00 equiv), and 4CzIPN (6.0 mg, 7.5 µmol, 0.025 equiv) in anhydrous DCM (3 mL, 0.1 M). The crude product was purified by column chromatography using 25-40% Et_2O:hexane mixture as a mobile phase to afford the pure product **3af** as a pale yellow semi-solid (121 mg, 0.211 mmol, 85%, *dr* > 20:1). (*See Spectra*)

- **TLC (Et_2O:Hexane, 3:2 v/v):** R_f = 0.30, UV, $KMnO_4$.
- **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.91 (d, *J* = 7.6 Hz, 3H, Ar*H*), 7.86 (d, *J* = 6.5 Hz, 1H, Ar*H*), 7.81-7.70 (m, 7H, Ar*H*), 7.64 (t, *J* = 7.7 Hz, 1H, Ar*H*), 7.46 – 7.27 (m, 6H, Ar*H*), 3.43 (d, *J* = 3.8 Hz, 1H, *CH*), 3.28 (s, 3H, CO_2CH_3), 3.27 - 3.25 (m, 1H, *CH*).
- **^{13}C NMR (101 MHz, $CDCl_3$):** δ 170.0, 168.9, 167.3, 162.8, 162.4, 135.2, 135.1, 135.0, 132.2, 131.4, 131.1, 131.0, 130.9, 130.5, 130.4 (q, *J* = 30.3 Hz), 129.8, 129.7, 129.1, 128.6, 128.4, 127.9, 127.7 (q, *J* = 5 Hz), 127.0, 124.4, 124.3, 124.2 (q, *J* = 274.7 Hz), 53.6, 52.3, 51.9, 49.0, 46.8, 44.3.
- **^{19}F NMR (377 MHz, $CDCl_3$):** δ -58.29.
- **IR (Neat, cm^{-1}):** υ 2919 (w), 2853 (w), 1749 (s), 1598 (w), 1441 (w), 1268 (m), 1177 (m), 1044 (w), 753 (s), 669 (m).
- **HRMS (ESI):** Calcd. for $C_{36}H_{23}F_3N_2O_6Na^+$ $[M+Na]^+$ 659.1406; found: 659.1407

Methyl-7-(4-(4-((1R,3R,4R,5S)-3-(methoxycarbonyl)-6,8-dioxo-2,4-diphenyl-3-(2-(trifluoromethyl)phenyl)-7-azatricyclo[3.3.0.02,4]octan-7-yl)benzyl)phenyl)-6,8-dioxo-2,4-diphenyl-3-(2-(trifluoromethyl)phenyl)-7-azatricyclo[3.3.0.02,4]octane-3-carboxylate (3ag)

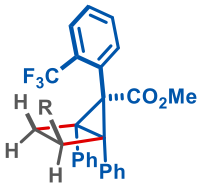


3ag

Following the general procedure-1, using cyclopropene **1d** (118 mg, 0.300 mmol, 1.00 equiv), maleimide **2n** (107.4 mg, 0.300 mmol, 2.00 equiv), and 4CzIPN (6.0 mg, 7.5 µmol, 0.025 equiv) in anhydrous DCM (3 mL, 0.1 M). The crude product was not able to purify by column chromatography. The yield is calculated by using dibromomethane as an internal standard (91%, *dr* > 20:1). (*See Spectra*)

- **TLC (EtOAc: Hexane, 4:6 v/v):** R_f = 0.40, UV, $KMnO_4$.
- **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.83 – 7.75 (m, 4H, Ar*H*), 7.65 – 7.61 (m, 2H, Ar*H*), 7.55 (dd, *J* = 7.4, 3.7 Hz, 4H, Ar*H*), 7.52 – 7.47 (m, 2H, Ar*H*), 7.40 – 7.36 (m, 4H, Ar*H*), 7.30 – 7.22 (m, 10H, Ar*H*), 7.21 – 7.19 (m, 2H, Ar*H*), 7.12 (d, *J* = 8.4 Hz, 2H, Ar*H*), 7.09 – 7.06 (m, 2H, Ar*H*), 6.98 – 6.93 (m, 4H, Ar*H*), 3.89 (s, 2H, ArCH_2Ar), 3.26 (t, *J* = 4.2 Hz, 2H, *CH*), 3.16 (s, 6H, CO_2CH_3), 3.04 (dd, *J* = 4.7, 3.9 Hz, 2H, *CH*).
- **^{13}C NMR (101 MHz, $CDCl_3$):** δ 173.6, 172.9, 167.2, 141.0, 140.8, 140.1, 135.2, 132.0, 131.8, 131.6, 130.8, 130.3 (q, *J* = 20.2 Hz), 130.2, 129.7, 128.9, 128.3, 128.2, 127.8, 127.5 (q, *J* = 3.3 Hz), 127.0, 126.0, 124.2 (q, *J* = 182.8 Hz), 53.4, 53.0, 52.2, 48.4, 48.0, 45.5, 41.0.
- **^{19}F NMR (377 MHz, $CDCl_3$):** δ -58.26.
- **IR (Neat, cm^{-1}):** υ 2922 (s), 2854 (w), 1718 (s), 1459 (w), 1377 (w), 1316 (w), 1175 (m), 699 (w).
- **HRMS (ESI):** Calcd. for $C_{69}H_{48}F_6N_2O_8H^+$ $[M+H]^+$ 1147.3393; found: 1147.3392.

2-ethyl 5-methyl-1,4-diphenyl-5-(2-(trifluoromethyl)phenyl)bicyclo[2.1.0]pentane-2,5-dicarboxylate (3ah)

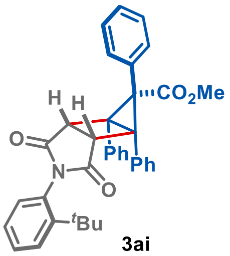


3ah, R = CO$_2$Et

Following the general procedure-1, using cyclopropene **1d** (118 mg, 0.300 mmol, 1.00 equiv), ethyl acrylate (300 mg, 3.00 mmol, 10.0 equiv), and [Ir{dF(CF$_3$)ppy}$_2$(dtbpy)]PF$_6$ (8.4 mg, 7.5 μmol, 0.025 equiv) in anhydrous DCM (3 mL, 0.1 M). The crude product was purified by column chromatography using 7% Et$_2$O:hexane mixture as a mobile phase to afford the pure product **3ah** as a coluorless semi-solid (37 mg, 0.075 mmol, 25%, *dr* > 20:1). (*See Spectra*)

- **TLC (Et$_2$O:Hexane, 3:7 v/v):** R$_f$ = 0.35, UV, KMnO$_4$.
- **^{1}H NMR (400 MHz, CDCl$_3$):** δ 7.90 – 7.83 (m, 1H, Ar*H*), 7.79 (dd, *J* = 7.6, 1.6 Hz, 1H, Ar*H*), 7.61 – 7.48 (m, 6H, Ar*H*), 7.42 – 7.28 (m, 5H, Ar*H*), 7.27 – 7.21 (m, 1H, Ar*H*), 3.92 – 3.84 (m, 1H, CO$_2$*CH$_2$*CH$_3$), 3.69 (ddd, *J* = 12.0, 10.6, 6.4 Hz, 2H, CO$_2$*CH$_2$*CH$_3$, *CH*), 3.25 (s, 3H, CO$_2$*CH$_3$*), 2.65 (dd, *J* = 12.7, 10.3 Hz, 1H, *CH*), 2.29 (dd, *J* = 12.8, 5.7 Hz, 1H, *CH*), 1.04 (t, *J* = 7.1 Hz, 3H, CO$_2$CH$_2$*CH$_3$*).
- **^{13}C NMR (101 MHz, CDCl$_3$):** δ 171.8, 169.2, 137.3, 136.8, 135.7, 133.1, 130.9, 130.5 (d, *J* = 1.9 Hz), 129.81, 129.8 (q, *J* = 31.3 Hz), 128.2, 128.1, 127.2, 127.1, 126.5, 124.3 (q, *J* = 274.7 Hz), 60.1, 51.9, 49.4, 48.8, 44.9, 43.4, 30.9, 13.6.
- **^{19}F NMR (377 MHz, CDCl$_3$):** δ -58.5.
- **IR (Neat, cm^{-1}):** υ 2933 (w), 2524 (w), 1745 (s), 1592 (m), 1440 (w), 1258 (m), 1190 (w), 1045 (w), 798 (s).
- **HRMS (ESI):** Calcd. for C$_{32}$H$_{25}$F$_3$O$_2$Na$^+$ [M+Na]$^+$ 521.1704; found: 521.1711

Methyl-7-(2-(*tert*-butyl)phenyl)-6,8-dioxo-2,3,4-triphenyl-7-azatricyclo[3.3.0.02,4]octane-3-carboxylate (3ai)

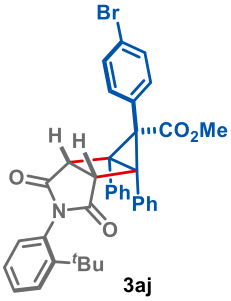


3ai

Following the general procedure-1, using cyclopropene **1a** (98 mg, 0.30 mmol, 1.0 equiv), maleimide **2o** (137 mg, 0.600 mmol, 2.00 equiv), and 4CzIPN (6.0 mg, 7.5 µmol, 0.025 equiv) in anhydrous DCM (3 mL, 0.1 M). The crude product was purified by column chromatography using 15-25% Et_2O:hexane mixture as a mobile phase to afford the pure product **3ai** as a pale yellow semi-solid (109 mg, 0.196 mmol, 65%, *dr* 7:1). (*See Spectra*)

- **TLC (Et_2O:Hexane, 1:1 v/v):** R_f = 0.45, UV, $KMnO_4$.
- **^{1}H NMR (400 MHz, $CDCl_3$):** For both diastereomers δ 7.84 – 7.76 (m, 2H, Ar*H*), 7.68 – 7.61 (m, 6H, Ar*H*), 7.60 – 7.52 (m, 2H, Ar*H*), 7.49 – 7.29 (m, 8H, Ar*H*), 7.04 – 6.97 (m, 1H, Ar*H*), 3.95 (s, 0.14H, CO_2CH_3), 3.90 (s, 0.05H, *CH*), 3.27 (d, *J* = 1.8 Hz, 1.95H, *CH*), 3.18 (s, 2.84H, CO_2CH_3), 1.33 (s, 0.6H, $ArC(CH_3)_3$), 1.22 (s, 8.4H, $ArC(CH_3)_3$).
- **^{13}C NMR (101 MHz, $CDCl_3$):** For both diastereomers δ 174.9, 174.8, 169.3, 167.9, 148.1, 148.0, 132.7, 132.3, 132.1, 131.3, 130.6, 130.1, 129.84, 129.76, 129.7, 129.6, 129.1, 129.0, 128.4, 128.0, 127.9, 127.8, 127.5, 127.4, 127.2, 53.9, 53.5, 52.7, 51.9, 51.5, 49.1, 47.6, 47.3, 35.8, 35.7, 31.6, 31.5. Twenty-one carbons were not resolved at 101 MHz.
- **IR (Neat, cm^{-1}):** υ 2922 (w), 2857 (w), 1718 (s), 1490 (w), 1443 (m), 1238 (m), 1198 (m), 1075 (w), 756 (w), 700 (m).
- **HRMS (ESI):** Calcd. for $C_{37}H_{33}NO_4H^+$ $[M+H]^+$ 556.2488; found: 556.2488.

Methyl-3-(4-bromophenyl)-7-(2-(*tert*-butyl)phenyl)-6,8-dioxo-2,4-diphenyl-7-azatricyclo[3.3.0.02,4]octane-3-carboxylate (3aj)

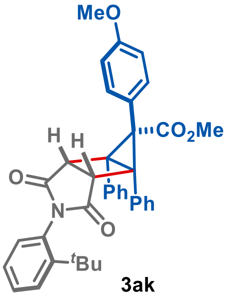


3aj

Following the general procedure-1, using cyclopropene **1r** (122 mg, 0.300 mmol, 1.00 equiv), maleimide **2o** (137 mg, 0.600 mmol, 2.00 equiv), and 4CzIPN (6.0 mg, 7.5 µmol, 0.025 equiv) in anhydrous DCM (3 mL, 0.1 M). The crude product was not able to purify by column chromatography (the compound got decomposed while purifying). The yield is calculated by using dibromomethane as an internal standard (48%, *dr* 7:1). (*See Spectra*)

- **TLC (Et_2O:Hexane, 1:1 v/v):** R_f = 0.40, UV, $KMnO_4$.
- **^1H NMR (400 MHz, $CDCl_3$):** δ 7.77 – 7.72 (m, 6H, Ar*H*), 7.65 – 7.61 (m, 4H, Ar*H*), 7.51 (t, *J* = 7.8 Hz, 5H, Ar*H*), 7.38 – 7.26 (m, 3H, Ar*H*), 3.93 (s, 0.4H, CO_2CH_3), 3.85 (s, 0.24H, *CH*), 3.19 (s, 1.85H, *CH*), 3.17 (s, 2.6H, CO_2CH_3), 1.20 (s, 9H, $ArC(CH_3)_3$).
- **IR (Neat, cm^{-1}):** υ 2955 (w), 2922 (m), 2858 (w), 1718 (s), 1491 (w), 1443 (w), 1374 (m), 1238 (m), 1198 (m), 756 (w), 700 (m).
- **HRMS (ESI):** Calcd. for $C_{37}H_{32}BrNO_4H$ $[M+H]^+$ 634.1593; found: 634.1592.

Methyl-7-(2-(*tert*-butyl)phenyl)-3-(4-methoxyphenyl)-6,8-dioxo-2,4-diphenyl-7-azatricyclo[3.3.0.02,4]octane-3-carboxylate (3ak)



3ak

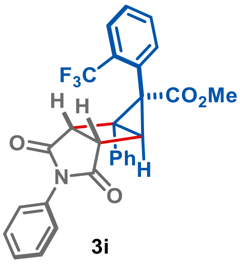
Following the general procedure-1, using cyclopropene **1s** (107 mg, 0.300 mmol, 1.00 equiv), maleimide **2o** (137 mg, 0.600 mmol, 2.00 equiv), and 4CzIPN (6.0 mg, 7.5 µmol, 0.025 equiv) in anhydrous DCM (3 mL, 0.1 M). The crude product was purified by column chromatography using 20-35% Et_2O:hexane mixture as a mobile phase to afford the pure product **3ak** as a pale yellow semi-solid (50.0 mg, 0.085 mmol, 28%, *dr* 7:1). (*See Spectra*)

- **TLC (Et_2O:Hexane, 1:1 v/v):** R_f = 0.4, UV, $KMnO_4$.
- **^1H NMR (400 MHz, $CDCl_3$):** For both diastereomers δ 7.65 (d, *J* = 8.6 Hz, 2H, Ar*H*), 7.59 (d, *J* = 7.2 Hz, 4H, Ar*H*), 7.54 (dd, *J* = 7.8, 1.9 Hz, 1H, Ar*H*), 7.46 – 7.32 (m, 8H, Ar*H*), 7.11 (d, *J* = 8.6 Hz, 2H, Ar*H*), 6.97 – 6.93 (m, 1H, Ar*H*), 3.92 (s, 2.8H, *CH*, $ArOCH_3$), 3.73 (s, 0.3H, CO_2CH_3), 3.51 (s, 0.3H, $ArOCH_3$), 3.21 (s, 1.9H, *CH*), 3.15 (s, 2.7H, CO_2CH_3), 1.40 (s, 1H, $ArC(CH_3)_3$), 1.18 (s, 8H, $ArC(CH_3)_3$).
- **^{13}C NMR (101 MHz, $CDCl_3$):** For both diastereomers δ 174.9, 168.3, 169.6, 159.5, 159.0, 147.6, 148.2, 143.5, 142.4, 137.8, 135.2, 134.3, 132.9, 132.5, 131.4, 132.1, 130.4, 130.0, 129.9, 129.7, 129.2, 128.7, 128.6, 128.3, 128.1, 127.9, 127.6, 127.5,

127.2, 126.3, 124.3, 117.7, 114.5, 113.2, 56.5, 55.3, 55.2, 53.0, 52.0, 51.9, 51.6, 50.3, 48.4, 47.4, 35.8, 35.7, 31.7, 31.6. Twelve carbons were not resolved at 101 MHz.

- **IR (Neat, cm^{-1}):** υ 2922 (s), 2855 (w), 1718 (s), 1374 (m), 1246 (m), 1198 (m), 1045 (w), 754 (m).
- **HRMS (ESI):** Calcd. for $C_{38}H_{35}NO_5Na^+$ $[M+Na]^+$ 608.2413; found: 608.2417.

Scale up:

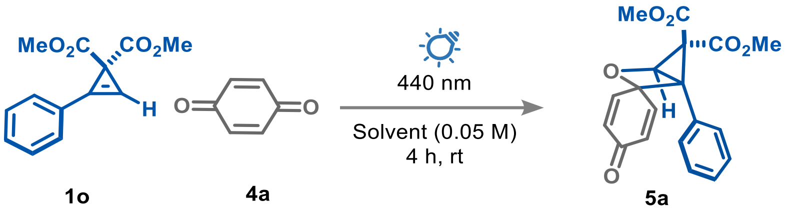


3i

Following the general procedure-1, using cyclopropene **1i** (636 mg, 2.00 mmol, 1.00 equiv), maleimide **2a** (692 mg, 4.00 mmol, 2.00 equiv), and 4CzIPN (40 mg, 0.05 mmol, 0.025 equiv) in anhydrous DCM (20 mL, 0.1 M). The crude product was purified by column chromatography using 20-30% Et_2O:Hexane mixture as a mobile phase to afford the pure product **3i** as a pale yellow semi-solid (770 mg, 1.56 mmol, 78%, *dr* > 20:1). (*See Spectra*)

5. Optimization of Spiro-Oxa-Housane Synthesis:

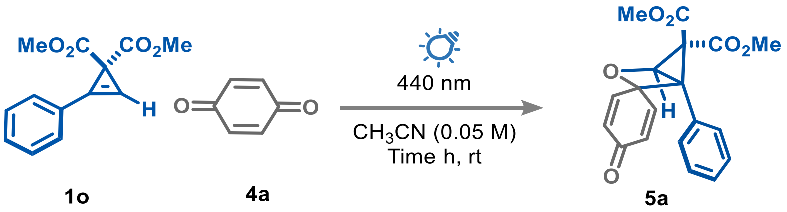
5.1 Screening of Solvents



A flame-dried 5 mL Schlenk tube was charged with cyclopropene **1o** (23.4 mg, 0.100 mmol, 1.00 equiv), benzoquinone **4a** (22 mg, 0.20 mmol, 2.0 equiv) and anhydrous solvent (2.0 mL). The solution was irradiated using a 440 nm Kessil lamp for 4 h at rt. Next, the reaction mixture was concentrated under reduced pressure and the crude product was submitted to ^{1}H-NMR. The yield of the crude product was calculated by ^{1}H NMR using CH_2Br_2 (7.0 µl, 0.10 mmol) as an internal standard.

Entry	**Solvent**	**Yield (%)**
1	Acetone	18
2	DCM	25
5	Acetonitile	30

5.2 Screening of Reaction Time



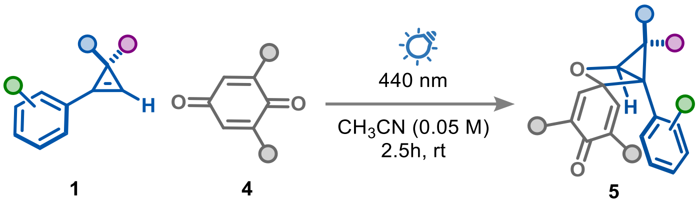
A flame-dried 5 mL Schlenk tube was charged with cyclopropene **1o** (23.4 mg, 0.100 mmol, 1.00 equiv), benzoquinone **4a** (22 mg, 0.20 mmol, 2.0 equiv) and anhydrous CH_3CN (1.0 mL). The solution was irradiated using a 440 nm Kessil lamp for xx h at rt. Next, the reaction mixture was concentrated under reduced pressure and the crude product was submitted to ^{1}H-NMR. The yield of the crude product was calculated by ^{1}H NMR using CH_2Br_2 (7.0 µl, 0.10 mmol) as an internal standard.

Entry	**Time**	**Yield (%)**

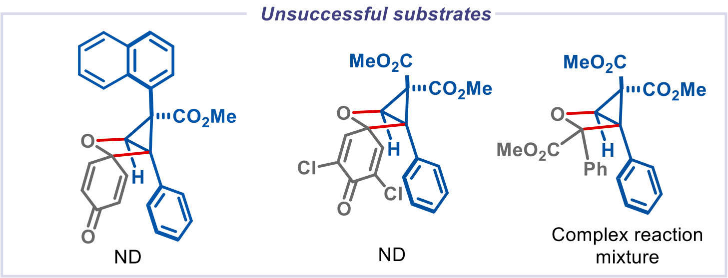
1	4	30
5	2.5	64

5.3 Scope of Spiro-Oxa- Housane:

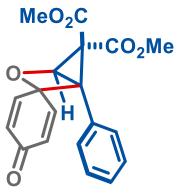
General Procedure-2:



A flame-dried 25 mL Schlenk tube was charged with cyclopropene **1** (0.30 mmol, 1.0 equiv), benzoquinone **4** (0.60 mmol, 2.0 equiv) and anhydrous CH_3CN (6.0 mL). The solution was irradiated using a 440 nm Kessil lamp for 2.5 h at rt. Next, the reaction mixture was concentrated under reduced pressure, and the crude product was purified by column chromatography using Et_2O:hexane mixture as a mobile phase to afford compound **5**.



Dimethyl-4'-oxo-1-phenyl-3-oxaspiro[bicyclo[2.1.0]pentane-2,1'-cyclohexane]-2',5'-diene-5,5-dicarboxylate (5a)



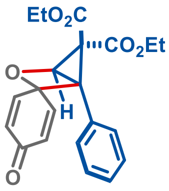
5a

Following the general procedure-2, using cyclopropene **1o** (70 mg, 0.30 mmol, 1.0 equiv), benzoquinone **4a** (65 mg, 0.60 mmol, 2.0 equiv), and in anhydrous CH_3CN (6.0 mL). The crude product was purified by column chromatography using 15-25% Et_2O:hexane mixture as a mobile phase to afford the pure product **5a** as a colorless semi-solid (53 mg, 0.156 mmol, 52%). (*See Spectra*)

- **TLC (Et_2O:Hexane, 1:1 v/v):** R_f = 0.25, UV, $KMnO_4$.

- **^{1}H NMR (400 MHz, CDCl$_3$):** δ 7.26 (m, 5H, Ar*H*), 7.10 (ddd, *J* = 10.5, 8.2, 3.1 Hz, 2H, C=C*CH*), 6.21 – 6.16 (m, 1H, C=C*CH*), 6.10 – 6.04 (m, 1H, C=C*CH*), 5.50 (s, 1H, O*CH*), 3.97 (s, 3H, CO_2CH_3), 3.40 (s, 3H, CO_2CH_3).
- **^{13}C NMR (101 MHz, CDCl$_3$):** δ 184.5, 166.3, 165.0, 147.8, 140.9, 131.0, 130.6, 129.7, 129.6, 128.9, 128.4, 82.0, 69.9, 53.3, 52.7, 46.9, 45.5.
- **IR (Neat, cm^{-1}):** υ 2935 (w), 2525 (w), 2170 (s), 1710 (s), 1516 (m), 1246 (m), 1164 (m), 1084 (w), 841 (m).
- **HRMS (ESI):** Calcd. for $C_{19}H_{16}O_6H^+$ [M+H]$^+$ 341.1025; found: 341.1029.

Diethyl-4'-oxo-1-phenyl-3-oxaspiro[bicyclo[2.1.0]pentane-2,1'-cyclohexane]-2',5'-diene-5,5-dicarboxylate (5b)

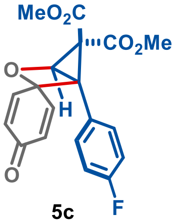


5b

Following the general procedure-2, using cyclopropene **1t** (83 mg, 0.30 mmol, 1.0 equiv), benzoquinone **4a** (65 mg, 0.60 mmol, 2.0 equiv), and in anhydrous CH_3CN (6.0 mL). The crude product was purified by column chromatography using 20-25% Et_2O:hexane mixture as a mobile phase to afford the pure product **5b** as a colorless semi-solid (71.0 mg, 0.193 mmol, 64%). (*See Spectra*)

- **TLC (Et_2O:Hexane, 1:1 v/v):** R_f = 0.4, UV, $KMnO_4$.
- **^{1}H NMR (400 MHz, CDCl$_3$):** δ 7.31 – 7.23 (m, 5H, Ar*H*), 7.21 (dd, *J* = 10.5, 3.1 Hz, 1H, C=C*CH*), 7.12 (dd, *J* = 10.2, 3.1 Hz, 1H, , C=C*CH*), 6.17 (dd, *J* = 10.5, 2.1 Hz, 1H, , C=C*CH*), 6.08 (dd, *J* = 10.1, 2.0 Hz, 1H, , C=C*CH*), 5.50 (s, 1H, O*CH*), 4.44 (tq, *J* = 7.1, 3.7 Hz, 2H, $CO_2CH_2CH_3$), 3.85 (qd, *J* = 7.1, 1.4 Hz, 2H, $CO_2CH_2CH_3$), 1.41 (t, *J* = 7.1 Hz, 3H, $CO_2CH_2CH_3$), 0.88 (t, *J* = 7.1 Hz, 3H, $CO_2CH_2CH_3$).
- **^{13}C NMR (101 MHz, CDCl$_3$):** δ 184.5, 165.9, 164.7, 148.0, 141.3, 130.8, 130.6, 129.8, 129.7, 128.8, 128.3, 82.0, 69.8, 62.3, 61.9, 46.5, 45.7, 14.0, 13.5.
- **IR (Neat, cm^{-1}):** υ 2939 (w), 2538 (w), 2170 (s), 1708 (s), 1520 (m), 1250 (m), 1180 (m), 767 (m).
- **HRMS (ESI):** Calcd. for $C_{21}H_{20}O_6H^+$ [M+H]$^+$ 369.1338; found: 369.1342.

Dimethyl-1-(4-fluorophenyl)-4'-oxo-3-oxaspiro[bicyclo[2.1.0]pentane-2,1'-cyclohexane]-2',5'-diene-5,5-dicarboxylate (5c)

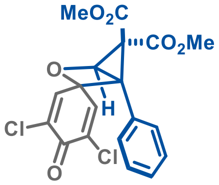


5c

Following the general procedure-2, using cyclopropene **1u** (75 mg, 0.30 mmol, 1.0 equiv), benzoquinone **4a** (65 mg, 0.60 mmol, 2.0 equiv), and in anhydrous CH_3CN (6.0 mL). The crude product was purified by column chromatography using 15-25% Et_2O:hexane mixture as a mobile phase to afford the pure product **5c** as a colorless semi-solid (63.0 mg, 0.176 mmol, 58%). (*See Spectra*)

- **TLC (Et_2O:Hexane, 1:1 v/v):** R_f = 0.30, UV, $KMnO_4$.
- **^1H NMR (400 MHz, $CDCl_3$):** δ 7.26 – 7.20 (m, 2H, Ar*H*), 7.12 – 7.01 (m, 2H, C=C*CH*), 6.95 (t, *J* = 8.6 Hz, 2H, Ar*H*), 6.18 (d, *J* = 10.4 Hz, 1H, C=C*CH*), 6.09 (d, *J* = 10.1 Hz, 1H, C=C*CH*), 5.47 (s, 1H, O*CH*), 3.96 (s, 3H, CO_2CH_3), 3.44 (s, 3H, CO_2CH_3).
- **^{13}C NMR (101 MHz, $CDCl_3$):** δ 184.3, 166.2, 164.9, 163.9, 161.5, 147.7, 140.8, 131.5 (d, *J* = 8.6 Hz), 130.9 (d, *J* = 32.1 Hz), 125.5 (d, *J* = 3.3 Hz), 115.5 (d, *J* = 21.9 Hz), 81.9, 69.9, 53.3, 52.8, 46.0, 45.3.
- **^{19}F NMR (377 MHz, $CDCl_3$):** δ -111.55.
- **IR (Neat, cm^{-1}):** υ 2938 (w), 2520 (w), 2168 (s), 1715 (s), 1498 (m), 1250 (m), 1158 (m), 1090 (w), 798 (m).
- **HRMS (ESI):** Calcd. for $C_{19}H_{15}FO_6H^+$ $[M+H]^+$ 359.0931; found: 359.0930.

Dimethyl-3',5'-dichloro-4'-oxo-1-phenyl-3-oxaspiro[bicyclo[2.1.0]pentane-2,1'-cyclohexane]-2',5'-diene-5,5-dicarboxylate (5d)

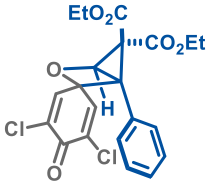


5d

Following the general procedure-2, using cyclopropene **1o** (70 mg, 0.30 mmol, 1.0 equiv), benzoquinone **4b** (106 mg, 0.600 mmol, 2.00 equiv), and in anhydrous CH_3CN (6.0 mL). The crude product was purified by column chromatography using 10-20% Et_2O:hexane mixture as a mobile phase to afford the pure product **5d** as a colorless semi-solid (82 mg, 0.20 mmol, 67%). (*See Spectra*)

- **TLC (Et_2O:Hexane, 1:1 v/v):** R_f = 0.50, UV, $KMnO_4$.
- **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.43 (d, *J* = 2.8 Hz, 1H, C=C*CH*), 7.35 – 7.27 (m, 6H, Ar*H*, C=C*CH*), 5.51 (s, 1H, O*CH*), 4.00 (s, 3H, CO_2CH_3), 3.41 (s, 3H, CO_2CH_3).
- **^{13}C NMR (101 MHz, $CDCl_3$):** δ 171.8, 165.8, 164.6, 144.1, 137.6, 134.2, 133.3, 129.6, 129.4, 129.0, 128.7, 83.2, 69.8, 53.5, 52.9, 46.5, 45.8.
- **IR (Neat, cm^{-1}):** υ 2934 (w), 2526 (w), 2171 (s), 1716 (s), 1519 (m), 1244 (m), 1171 (m), 1087 (w), 805 (w).
- **HRMS (ESI):** Calcd. for $C_{19}H_{14}Cl_2O_6H^+$ $[M+H]^+$ 409.0246; found: 409.0244.

Diethyl-3',5'-dichloro-4'-oxo-1-phenyl-3-oxaspiro[bicyclo[2.1.0]pentane-2,1'-cyclohexane]-2',5'-diene-5,5-dicarboxylate (5e)

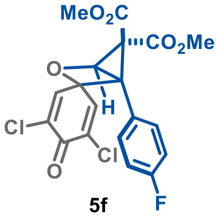


5e

Following the general procedure-2, using cyclopropene **1t** (83 mg, 0.30 mmol, 1.0 equiv), benzoquinone **4b** (106 mg, 0.600 mmol, 2.00 equiv), and in anhydrous CH_3CN (6.0 mL). The crude product was purified by column chromatography using 10-15% Et_2O:hexane mixture as a mobile phase to afford the pure product **5e** as a colourless semi-solid (65 mg, 0.15 mmol, 50%). (*See Spectra*)

- **TLC (Et_2O:Hexane, 1:1 v/v):** R_f = 0.50, UV, $KMnO_4$.
- **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.51 (bs, 1H, C=C*CH*), 7.34-7.27 (m, 6H, Ar*H*, C=C*CH*), 5.51 (s, 1H, O*CH*), 4.55 – 4.39 (m, 2H, $CO_2CH_2CH_3$), 3.86 (q, *J* = 7.0 Hz, 2H, $CO_2CH_2CH_3$), 1.43 (t, *J* = 7.1 Hz, 3H, $CO_2CH_2CH_3$), 0.88 (t, *J* = 7.1 Hz, 3H, $CO_2CH_2CH_3$).
- **^{13}C NMR (101 MHz, $CDCl_3$):** δ 171.9, 165.3, 164.2, 144.3, 137.9, 134.0, 133.2, 129.7, 129.3, 129.0, 128.7, 83.2, 69.8, 62.7, 62.1, 46.2, 46.0, 14.0, 13.5.
- **IR (Neat, cm^{-1}):** υ 2938 (w), 2524 (w), 2170 (s), 1712 (s), 1520 (m), 1242 (m), 1178 (m), 1084 (w), 799 (w).
- **HRMS (ESI):** Calcd. for $C_{21}H_{18}Cl_2O_6H^+$ $[M+H]^+$ 437.0559; found: 437.0555.

Dimethyl-3',5'-dichloro-1-(4-fluorophenyl)-4'-oxo-3-oxaspiro[bicyclo[2.1.0]pentane-2,1'-cyclohexane]-2',5'-diene-5,5-dicarboxylate (5f)

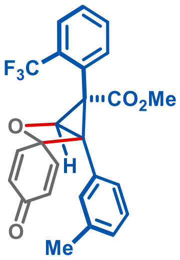


5f

Following the general procedure-2, using cyclopropene **1u** (75 mg, 0.30 mmol, 1.0 equiv), benzoquinone **4b** (106 mg, 0.600 mmol, 2.00 equiv), and in anhydrous CH_3CN (6.0 mL). The crude product was purified by column chromatography using 10-15% Et_2O:hexane mixture as a mobile phase to afford the pure product **5f** as a colourless semi-solid (57 mg, 0.134 mmol, 44%). (*See Spectra*)

- **TLC (Et_2O:Hexane, 1:1 v/v):** $R_f = 0.50$, UV, $KMnO_4$.
- **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.39 (d, *J* = 2.9 Hz, 1H, C=C*CH*), 7.29 – 7.26 (m, 3H, Ar*H*), 7.01 (t, *J* = 8.6 Hz, 2H, Ar*H* , C=C*CH*), 5.49 (s, 1H, O*CH*), 4.00 (s, 3H, CO_2CH_3), 3.45 (s, 3H, CO_2CH_3).
- **^{13}C NMR (101 MHz, $CDCl_3$):** δ 171.8, 165.7, 164.5, 164.2, 161.8, 143.9, 137.4, 133.9 (d, *J* = 87.6 Hz), 131.6 (d, *J* = 8.5 Hz), 124.8 (d, *J* = 3.6 Hz), 116.0 (d, *J* = 22.0 Hz), 83.1, 69.9, 53.6, 53.0, 45.8, 45.7.
- **^{19}F NMR (377 MHz, $CDCl_3$):** δ -110.48.
- **IR (Neat, cm^{-1}):** υ 2938 (w), 2525 (w), 2172 (s), 1710 (s), 1518 (m), 1248 (m), 1168 (m), 1077 (w), 810 (w).
- **HRMS (ESI):** Calcd. for $C_{19}H_{13}Cl_2FO_6H^+$ $[M+H]^+$ 427.0151; found: 427.0151.

Methyl-4'-oxo-1-(m-tolyl)-5-(2-(trifluoromethyl)phenyl)-3-oxaspiro[bicyclo[2.1.0]pentane-2,1'-cyclohexane]-2',5'-diene-5-carboxylate (5g)

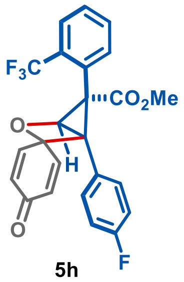


5g

Following the general procedure-2, using cyclopropene **1k** (100 mg, 0.300 mmol, 1.00 equiv), benzoquinone **4a** (65 mg, 0.60 mmol, 2.0 equiv), and in anhydrous CH_3CN (6.0 mL). The crude product was purified by column chromatography using 10-15% Et_2O:hexane mixture as a mobile phase to afford the pure product **5g** as a colourless semi-solid (66 mg, 0.15 mmol, 50%, *dr* > 20:1). (*See Spectra*)

- **TLC (Et_2O:Hexane, 1:1 v/v):** R_f = 0.50, UV, $KMnO_4$.
- **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.98 (d, *J* = 7.7 Hz, 1H, Ar*H*), 7.82 (d, *J* = 7.8 Hz, 1H, Ar*H*), 7.74 (t, *J* = 7.6 Hz, 1H, Ar*H*), 7.61 (t, *J* = 7.6 Hz, 1H, Ar*H*), 7.20 (t, *J* = 7.8 Hz, 1H, Ar*H*), 7.11 (d, *J* = 7.4 Hz, 3H), 7.06 (dd, *J* = 10.2, 3.0 Hz, 1H, C=C*CH*), 6.06 (dd, *J* = 10.5, 3.0 Hz, 1H, C=C*CH*), 5.99 (dd, *J* = 10.2, 2.0 Hz, 1H, C=C*CH*), 5.91 (dd, *J* = 10.5, 2.1 Hz, 1H, C=C*CH*), 5.79 (s, 1H, O*CH*), 3.26 (s, 3H, CO_2CH_3), 2.34 (s, 3H, ArCH_3).
- **^{13}C NMR (101 MHz, $CDCl_3$):** δ 184.7, 167.6, 149.3, 138.1, 136.7, 131.8 (d, *J* = 1.8 Hz), 131.3, 130.7, 130.4, 130.0, 129.9, 129.7, 129.4, 129.1, 129.0, 128.3, 127.0 (q, *J* = 5.5 Hz), 126.7, 124.0 (q, *J* = 274.7 Hz), 81.3, 70.8 (d, *J* = 2.5 Hz), 52.2, 46.8, 45.0, 21.4.
- **^{19}F NMR (377 MHz, $CDCl_3$):** δ -59.75.
- **IR (Neat, cm^{-1}):** υ 2936 (w), 2520 (w), 2170 (s), 1715 (s), 1520 (m), 1250 (m), 1171 (m), 1087 (w), 810 (w).
- **HRMS (ESI):** Calcd. for $C_{25}H_{19}F_3O_4H^+$ $[M+H]^+$ 441.1314; found: 441.1313.

Methyl-1-(4-fluorophenyl)-4'-oxo-5-(2-(trifluoromethyl)phenyl)-3-oxaspiro[bicyclo[2.1.0]pentane-2,1'-cyclohexane]-2',5'-diene-5-carboxylate (5h)



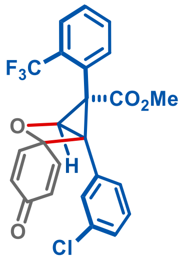
5h

Following the general procedure-2, using cyclopropene **1l** (101 mg, 0.300 mmol, 1.00 equiv), benzoquinone **4a** (65 mg, 0.60 mmol, 2.0 equiv), and in anhydrous CH_3CN (6.0 mL). The crude product was purified by column chromatography using 10-15% Et_2O:hexane mixture as a mobile phase to afford the pure product **5h** as a colourless solid (51.0 mg, 0.115 mmol, 38%, *dr* > 20:1). (*See Spectra*)

- **Melting point:** 195-198 °C.
- **TLC (Et_2O:Hexane, 1:1 v/v):** R_f = 0.45, UV, $KMnO_4$.

- **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.92 (d, *J* = 7.6 Hz, 1H, Ar*H*), 7.82 (dd, *J* = 7.9, 1.4 Hz, 1H, Ar*H*), 7.77 – 7.70 (m, 1H, Ar*H*), 7.64 – 7.58 (m, 1H, Ar*H*), 7.34 – 7.27 (m, 2H, Ar*H*), 7.06 – 6.98 (m, 3H, Ar*H*, C=C*CH*), 6.07 – 5.97 (m, 2H, C=C*CH*), 5.92 (dd, *J* = 10.5, 2.0 Hz, 1H, C=C*CH*), 5.78 (s, 1H, O*CH*), 3.28 (s, 3H, CO_2CH_3).
- **^{13}C NMR (101 MHz, $CDCl_3$):** δ 184.5, 167.6, 163.8, 161.3, 149.1, 142.2, 136.6, 131.4 (d, *J* = 8.4 Hz), 131.3, 130.6 (q, *J* = 31.3 Hz), 130.1, 129.8, 129.3, 127.1 (q, *J* = 5.4 Hz), 126.8 (d, *J* = 3.5 Hz), 123.9 (q, *J* = 274.7 Hz), 115.6 (d, *J* = 21.8 Hz), 81.2, 71.0, 52.4, 46.2, 45.0.
- **^{19}F NMR (377 MHz, $CDCl_3$):** δ -59.78, -111.95.
- **IR (Neat, cm^{-1}):** υ 2928 (w), 2530 (w), 2169 (s), 1712 (s), 1518 (m), 1252 (m), 1168 (m), 1077 (w), 805 (w).
- **HRMS (ESI):** Calcd. for $C_{24}H_{16}F_4O_4H^+$ $[M+H]^+$ 445.1063; found: 445.1058.

Methyl-1-(3-chlorophenyl)-4'-oxo-5-(2-(trifluoromethyl)phenyl)-3-oxaspiro[bicyclo[2.1.0]pentane-2,1'-cyclohexane]-2',5'-diene-5-carboxylate (5i)



5i

Following the general procedure-2, using cyclopropene **1j** (106 mg, 0.300 mmol, 1.00 equiv), benzoquinone **4a** (65 mg, 0.60 mmol, 2.0 equiv), and in anhydrous CH_3CN (6.0 mL). The crude product was not able to purify by column chromatography (the compound got decomposed while purifying). The yield is calculated by using dibromomethane as an internal standard (30%, *dr* > 20:1). (*See Spectra*)

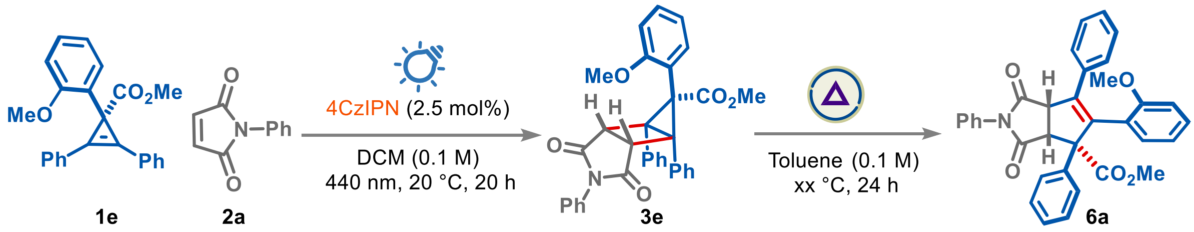
- **TLC (Et_2O:Hexane, 1:1 v/v):** R_f = 0.50, UV, $KMnO_4$.
- **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.90 (d, *J* = 7.7 Hz, 1H, Ar*H*), 7.82 (d, *J* = 8.1 Hz, 1H, Ar*H*), 7.74 (t, *J* = 7.5 Hz, 1H, Ar*H*), 7.62 (t, *J* = 7.8 Hz, 2H, Ar*H*), 7.29 (d, *J* = 1.7 Hz, 2H, Ar*H*), 7.22 – 7.19 (m, 1H, Ar*H*), 7.03 (dd, *J* = 10.2, 2.9 Hz, 1H, C=C*CH*), 6.03 (dd, *J* = 9.7, 2.3 Hz, 2H, C=C*CH*), 5.93 (dd, *J* = 10.5, 2.0 Hz, 1H, C=C*CH*), 5.78 (s, 1H, O*CH*), 3.31 (s, 3H, CO_2CH_3).
- **^{19}F NMR (377 MHz, $CDCl_3$):** δ -59.77.
- **HRMS (ESI):** Calcd. for $C_{24}H_{16}ClF_3O_4H^+$ $[M+H]^+$ 461.0767; found: 461.0762.

6. Application of Housanes: Stereospecific Synthesis of Bicyclic imide derivatives

6.1 Screening of Temperature:

Step-1: Following the general procedure-1, using cyclopropene **1e** (36 mg, 0.10 mmol, 1.0 equiv), maleimide **2a** (35 mg, 0.20 mmol, 2.0 equiv), and 4CzIPN (2.0 mg, 2.5 mol%) in anhydrous DCM (1 mL, 0.1 M). The solution was irradiated using a 440 nm Kessil lamp for 20 h at 20 °C. Then, the solvent was removed via rotary evaporation and the crude product was used in the next step without further purification

Step-2: A flame-dried 25 mL sealed round bottom flask was charged with crude housane **3e** and anhydrous toluene (1.0 mL). The solution was refluxed at different temperatures for 24 h. Next, the reaction mixture was concentrated under reduced pressure and the crude product was submitted to ^{1}H-NMR analysis. The yield and *dr* of the crude product was calculated by ^{1}H-NMR using CH_2Br_2 (7.0 µl, 0.10 mmol) as an internal standard.

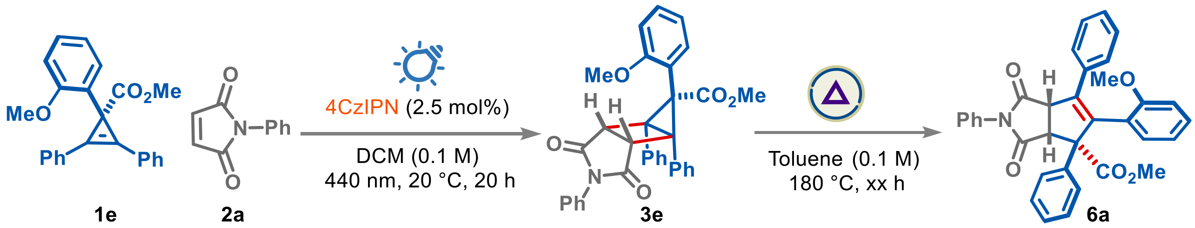


Entry	Temperature (°C)	Yield (%)	*dr*
1	150	20	>20:1
2	165	34	>20:1
2	180	54	>20:1

6.2 Screening of reaction time

Step-1: Following the general procedure-1, using cyclopropene **1e** (36 mg, 0.10 mmol, 1.0 equiv), malemide **2a** (35 mg, 0.20 mmol, 2.0 equiv), and 4CzIPN (2.0 mg, 2.5 mol%) in anhydrous DCM (1 mL, 0.1 M). The solution was irradiated using a 440 nm Kessil lamp for 20 h at 20 °C. Then, the solvent was removed via rotary evaporation and the crude product was used in the next step without further purification

Step-2: A flame-dried 25 mL sealed round bottom flask was charged with housane **3e** and anhydrous toluene (1.0 mL). The solution was refluxed at 180 °C for different times. Next, the reaction mixture was concentrated under reduced pressure and the crude product was submitted to ^{1}H-NMR analysis. The yield and *dr* of the crude product was calculated by ^{1}H-NMR using CH_2Br_2 (7.0 µl, 0.10 mmol) as an internal standard.

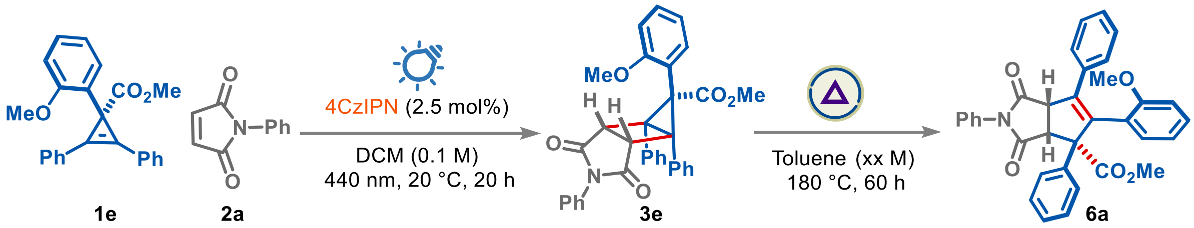


Entry	Reaction time (h)	Yield (%)	*dr*
1	24	54	>20:1
2	48	62	>20:1
2	60	70	>20:1

6.3 Screening of Concentration:

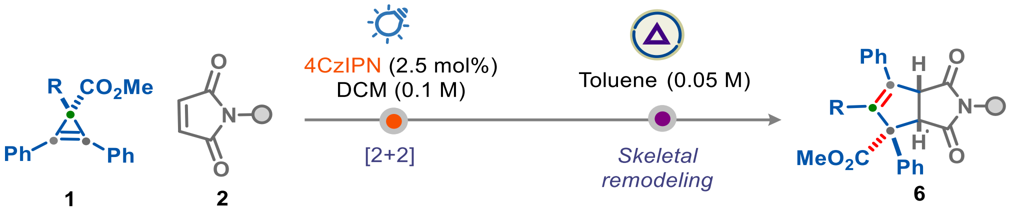
Step-1: Following the general procedure-1, using cyclopropene **1e** (36 mg, 0.10 mmol, 1.0 equiv), maleimide **2a** (35 mg, 0.20 mmol, 2.0 equiv), and 4CzIPN (2.0 mg, 2.5 mol%) in anhydrous DCM (1 mL, 0.1 M). The solution was irradiated using a 440 nm Kessil lamp for 20 h at 20 °C. Then the solvent was removed via rotary evaporation and the crude product was used in the next step without further purification

Step-2: A flame-dried 25 mL sealed round bottom flask was charged with housane **3e** and anhydrous toluene. The solution was refluxed at 180 °C for 60 h. Next, the reaction mixture was concentrated under reduced pressure and the crude product was submitted to ^{1}H-NMR analysis. The yield and *dr* of the crude product was calculated by ^{1}H-NMR using CH_2Br_2 (7.0 µl, 0.10 mmol) as an internal standard.



Entry	Concentration (M)	Yield (%)	*dr*
1	0.1	70	>20:1
2	0.05	85	>20:1

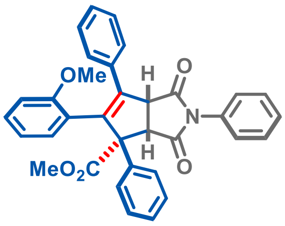
6.4 General Procedure-3: Synthesis of bicyclic imide derivatives



Step-1: Following the general procedure-1, using cyclopropene **1** (0.30 mmol, 1.0 equiv), maleimide **2** (0.60 mmol, 2.0 equiv), and 4CzIPN (6.0 mg, 7.5 μmol, 0.025 equiv) in anhydrous DCM (3 mL, 0.1 M). Then, the solvent was removed via rotary evaporation and the crude product was used in the next step without further purification

Step-2: A flame-dried 25 mL sealed round bottom flask was charged with housane **3** and anhydrous toluene (6.0 mL). The solution was refluxed at 180 °C for 60 h. Next, the reaction mixture was concentrated under reduced pressure, and the crude product was purified by column chromatography using Et_2O:hexane mixture as a mobile phase to afford the title compound **6**.

Methyl-5-(2-methoxyphenyl)-1,3-dioxo-2,4,6-triphenyl-1,2,3,3a,4,6a-hexahydrocyclopenta[c]pyrrole-4-carboxylate (6a)



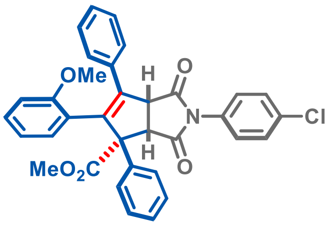
6a

Step-1: Following the general procedure-1, using cyclopropene **1e** (107 mg, 0.300 mmol, 1.00 equiv), maleimide **2a** (104 mg, 0.600 mmol, 2.00 equiv), and 4CzIPN (6.0 mg, 7.5 μmol, 0.025 equiv) in anhydrous DCM (3 mL, 0.1 M). Then, the solvent was removed via rotary evaporation and the crude product was used in the next step without further purification.

Step-2: A flame-dried 25 mL sealed round bottom flask was charged with housane **3e** and anhydrous toluene (6.0 mL). The solution was refluxed at 180 °C for 60 h. Next, the reaction mixture was concentrated under reduced pressure, and the crude product was purified by column chromatography using 30-40% Et_2O:hexane mixture as a mobile phase to afford the title compound **6a** (135 mg, 0.250 mmol, 85%, *dr* > 20:1) as colorless semi-solid. (*See Spectra*)

- **TLC (Et_2O:Hexane, 1:1 v/v):** $R_f = 0.45$, UV, $KMnO_4$
- **^1H NMR (400 MHz, $CDCl_3$):** δ 7.47 – 7.42 (m, 4H, Ar*H*), 7.38 – 7.34 (m, 3H, Ar*H*), 7.26 – 7.14 (m, 9H, Ar*H*), 7.05 (dd, *J* = 7.7, 1.7 Hz, 1H, Ar*H*), 6.83 (td, *J* = 7.5, 1.1 Hz, 1H, Ar*H*), 6.61 (dd, *J* = 8.3, 1.1 Hz, 1H, Ar*H*), 4.77 (d, *J* = 9.0 Hz, 1H, *CH*), 4.09 (d, *J* = 9.0 Hz, 1H, *CH*), 3.77 (s, 3H, CO_2CH_3), 3.18 (s, 3H, ArOCH_3).
- **^{13}C NMR (101 MHz, $CDCl_3$):** δ 175.6, 173.9, 172.7, 156.5, 141.8, 140.2, 137.0, 135.2, 132.1, 129.8, 129.5, 128.9, 128.4, 128.3, 128.1, 128.0, 127.7, 127.5, 127.0, 126.4, 124.4, 120.3, 111.4, 71.6, 55.4, 54.7, 54.3, 52.7.
- **IR (Neat, cm^{-1}):** υ 2922 (m), 2854 (w), 1742 (s), 1494 (m), 1378 (m), 1247 (m), 1187 (m), 1058 (w), 738 (m), 696 (m).
- **HRMS (ESI):** Calcd. for $C_{34}H_{27}NO_5H^+$ $[M+H]^+$ 530.1967; found: 530.1965.

Methyl-2-(4-chlorophenyl)-5-(2-methoxyphenyl)-1,3-dioxo-4,6-diphenyl-1,2,3,3a,4,6a-hexahydrocyclopenta[c]pyrrole-4-carboxylate (6b)



6b

Step-1: Following the general procedure-1, using cyclopropene **1e** (107 mg, 0.300 mmol, 1.00 equiv), maleimide **2c** (124 mg, 0.600 mmol, 2.00 equiv), and 4CzIPN (6.0 mg, 7.5 μmol, 0.025 equiv) in anhydrous DCM (3 mL, 0.1 M). Then the solvent was removed via rotary evaporation and the crude product was used in the next step without further purification.

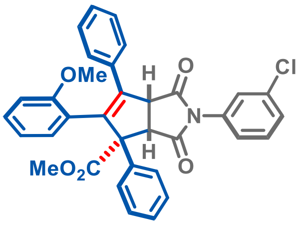
Step-2: A flame-dried 25 mL sealed round bottom flask was charged with housane **3t** and anhydrous toluene (6.0 mL). The solution was refluxed at 180 °C for 60 h. Next, the reaction mixture was concentrated under reduced pressure, and the crude product was purified by column chromatography using 35-40% Et_2O:hexane mixture as a mobile phase to afford the title compound **6b** (142 mg, 0.250 mmol, 84%, *dr* > 20:1) as colorless semi-solid. (*See Spectra*)

- **TLC (Et_2O:Hexane, 1:1 v/v):** $R_f = 0.50$, UV, $KMnO_4$
- **^1H NMR (400 MHz, $CDCl_3$):** δ 7.44 (dd, *J* = 13.9, 8.0 Hz, 4H, Ar*H*), 7.35 (d, *J* = 8.4 Hz, 2H, Ar*H*), 7.29 – 7.14 (m, 9H, Ar*H*), 7.04 – 7.01 (m, 1H, Ar*H*), 6.83 (t, *J* = 7.5 Hz,

1H, Ar*H*), 6.63 (d, *J* = 8.3 Hz, 1H, Ar*H*), 4.77 (d, *J* = 9.0 Hz, 1H, *CH*), 4.08 (d, *J* = 9.0 Hz, 1H, *CH*), 3.77 (s, 3H, CO_2CH_3), 3.20 (s, 3H, $ArOCH_3$).

- **^{13}C NMR (101 MHz, $CDCl_3$):** δ 175.5, 173.7, 172.8, 156.4, 141.8, 140.2, 136.9, 135.1, 134.1, 130.6, 129.7, 129.5, 129.1, 128.2, 128.05, 128.02, 127.8, 127.7, 127.6, 127.0, 124.2, 120.4, 111.4, 71.8, 55.5, 54.7, 54.3, 52.8.
- **IR (Neat, cm^{-1}):** υ 2923 (m), 2854 (w), 1742 (s), 1492 (m), 1379 (m), 1248 (m), 1187 (m), 1091 (w), 754 (m), 698 (w).
- **HRMS (ESI):** Calcd. for $C_{34}H_{26}ClNO_5Na^+$ $[M+Na]^+$ 586.1397; found: 586.1398.

Methyl-2-(3-chlorophenyl)-5-(2-methoxyphenyl)-1,3-dioxo-4,6-diphenyl-1,2,3,3a,4,6a-hexahydrocyclopenta[c]pyrrole-4-carboxylate (6c)



6c

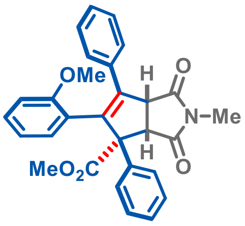
Step-1: Following the general procedure-1, using cyclopropene **1e** (107 mg, 0.300 mmol, 1.00 equiv), maleimide **2e** (124 mg, 0.600 mmol, 2.00 equiv), and 4CzIPN (6.0 mg, 7.5 μmol, 0.025 equiv) in anhydrous DCM (3 mL, 0.1 M). Then, the solvent was removed via rotary evaporation and the crude productwas used in the next step without further purification.

Step-2: A flame-dried 25 mL sealed round bottom flask was charged with housane **3w** and anhydrous toluene (6.0 mL). The solution was refluxed at 180 °C for 60 h. Next, the reaction mixture was concentrated under reduced pressure, and the crude product was purified by column chromatography using 35-40% Et_2O:hexane mixture as a mobile phase to afford the title compound **6c** (136 mg, 0.240 mmol, 80%, *dr* > 20:1) as colorless solid. (*See Spectra*)

- **Melting Point:** 218-220 °C.
- **TLC (Et_2O:Hexane, 1:1 v/v):** $R_f = 0.50$, UV, $KMnO_4$
- **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.46 – 7.42 (m, 3H, Ar*H*), 7.39 – 7.32 (m, 2H, Ar*H*), 7.30 (dt, *J* = 7.7, 1.6 Hz, 1H, Ar*H*), 7.26 – 7.23 (m, 2H, Ar*H*), 7.21 – 7.15 (m, 7H, Ar*H*), 7.02 (dd, *J* = 7.7, 1.7 Hz, 1H, Ar*H*), 6.82 (td, *J* = 7.5, 1.1 Hz, 1H, Ar*H*), 6.62 (dd, *J* = 8.4, 1.1 Hz, 1H, Ar*H*), 4.76 (d, *J* = 9.1 Hz, 1H, *CH*), 4.07 (d, *J* = 9.0 Hz, 1H, *CH*), 3.77 (s, 3H, CO_2CH_3), 3.19 (s, 3H, $ArOCH_3$).

- **^{13}C NMR (101 MHz, CDCl$_3$):** δ 175.3, 173.6, 172.8, 156.4, 141.8, 140.1, 136.9, 135.0, 134.5, 133.1, 129.9, 129.7, 129.5, 128.6, 128.2, 128.07, 128.05, 127.8, 127.6, 127.1, 126.7, 124.6, 124.2, 120.4, 111.4, 71.9, 55.5, 54.8, 54.3, 52.9.
- **IR (Neat, cm^{-1}):** υ 2920 (s), 2853 (m), 1740 (m), 1702 (s), 1457 (m), 1378 (w), 1268 (w), 1247 (m), 757 (w).
- **HRMS (ESI):** Calcd. for $C_{34}H_{26}ClNO_5H^+$ $[M+H]^+$ 564.1578; found: 564.1580.

Methyl-5-(2-methoxyphenyl)-2-methyl-1,3-dioxo-4,6-diphenyl-1,2,3,3a,4,6a-hexahydrocyclopenta[c]pyrrole-4-carboxylate (6d)



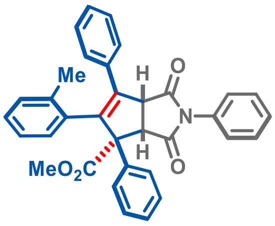
6d

Step-1: Following the general procedure-1, using cyclopropene **1e** (107 mg, 0.300 mmol, 1.00 equiv), maleimide **2k** (67 mg, 0.60 mmol, 2.0 equiv), and 4CzIPN (6.0 mg, 7.5 µmol, 0.025 equiv) in anhydrous DCM (3 mL, 0.1 M). Then, the solvent was removed via rotary evaporation and the crude product was used in the next step without further purification.

Step-2: A flame-dried 25 mL sealed round bottom flask was charged with housane **3ab** and anhydrous toluene (6.0 mL). The solution was refluxed at 180 °C for 60 h. Next, the reaction mixture was concentrated under reduced pressure, and the crude product was purified by column chromatography using 35-50% Et_2O:hexane mixture as a mobile phase to afford the title compound **6d** (121 mg, 0.260 mmol, 86%, *dr* > 20:1) as colorless semi-solid. (*See Spectra*)

- **TLC (Et_2O:Hexane, 1:1 v/v):** $R_f = 0.25$, UV, $KMnO_4$
- **^{1}H NMR (400 MHz, CDCl$_3$):** δ 7.39 (d, *J* = 6.9 Hz, 2H, Ar*H*), 7.27 – 7.13 (m, 9H, Ar*H*), 7.06 – 7.02 (m, 1H, Ar*H*), 6.82 (t, *J* = 7.6 Hz, 1H, Ar*H*), 6.58 (d, *J* = 8.3 Hz, 1H, Ar*H*), 4.65 (d, *J* = 8.7 Hz, 1H, *CH*), 3.97 (d, *J* = 8.7 Hz, 1H, *CH*), 3.77 (s, 3H, CO_2CH_3), 3.12 (s, 3H, ArOCH_3), 3.02 (s, 3H, -NCH_3).
- **^{13}C NMR (101 MHz, CDCl$_3$):** δ 176.7, 175.1, 172.4, 156.3, 141.6, 139.9, 136.6, 135.1, 129.7, 129.4, 128.1, 128.0, 127.8, 127.7, 127.5, 126.9, 124.2, 120.3, 111.2, 70.9, 55.2, 54.6, 54.3, 52.5, 24.9.
- **IR (Neat, cm^{-1}):** υ 2921 (s), 2853 (m), 1740 (m), 1702 (s), 1492 (w), 1378 (m), 1247 (m), 1190 (w), 1026 (w), 760 (w), 701 (w).
- **HRMS (ESI):** Calcd. for $C_{29}H_{25}NO_5Na^+$ $[M+Na]^+$ 490.1630; found: 490.1628.

Methyl-1,3-dioxo-2,4,6-triphenyl-5-(o-tolyl)-1,2,3,3a,4,6a-hexahydrocyclopenta[c]pyrrole-4-carboxylate (6e)



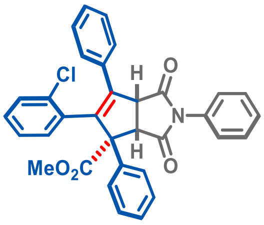
6e

Step-1: Following the general procedure-1, using cyclopropene **1c** (102 mg, 0.300 mmol, 1.00 equiv), maleimide **2a** (104 mg, 0.600 mmol, 2.00 equiv), and 4CzIPN (6.0 mg, 7.5 µmol, 0.025 equiv) in anhydrous DCM (3 mL, 0.1 M). Then, the solvent was removed via rotary evaporation and the crude product was used in the next step without further purification.

Step-2: A flame-dried 25 mL sealed round bottom flask was charged with housane **3c** and anhydrous toluene (6.0 mL). The solution was refluxed at 180 °C for 60 h. Next, the reaction mixture was concentrated under reduced pressure, and the crude product was purified by column chromatography using 25-40% Et_2O:hexane mixture as a mobile phase to afford the title compound **6e** (131 mg, 0.25 mmol, 85%, *dr* > 20:1) as colorless semi-solid. (*See Spectra*)

- **TLC (Et_2O:Hexane, 1:1 v/v):** R_f = 0.35, UV, $KMnO_4$
- **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.56 (d, *J* = 7.8 Hz, 1H, Ar*H*), 7.45 (t, *J* = 7.6 Hz, 2H, Ar*H*), 7.40 – 7.33 (m, 3H, Ar*H*), 7.24 – 7.07 (m, 12H, Ar*H*), 6.81 (d, *J* = 7.6 Hz, 1H, Ar*H*), 4.95 (d, *J* = 8.5 Hz, 1H, *CH*), 4.56 (d, *J* = 8.5 Hz, 1H, *CH*), 3.82 (s, 3H, CO_2CH_3), 0.95 (s, 3H, ArCH_3).
- **^{13}C NMR (101 MHz, $CDCl_3$):** δ 175.5, 173.7, 172.4, 141.7, 138.9, 137.7, 137.3, 134.1, 133.7, 131.8, 130.3, 129.8, 129.2, 129.0, 128.6, 128.2, 128.0, 127.9, 127.7, 127.5, 127.4, 126.4, 125.6, 72.0, 53.7, 52.7, 51.7, 18.4.
- **IR (Neat, cm^{-1}):** υ 2919 (s), 2853 (m), 1715 (s), 1496 (w), 1378 (m), 1241 (w), 1192 (m), 1069 (w), 741 (w), 697 (w).
- **HRMS (ESI):** Calcd. for $C_{34}H_{27}NO_4Na^+$ $[M+Na]^+$ 536.1838; found: 536.1842.

Methyl-5-(2-chlorophenyl)-1,3-dioxo-2,4,6-triphenyl-1,2,3,3a,4,6a-hexahydrocyclopenta[c]pyrrole-4-carboxylate (6f)



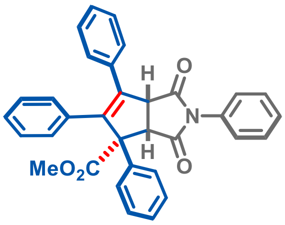
6f

Step-1: Following the general procedure-1, using cyclopropene **1f** (108 mg, 0.300 mmol, 1.00 equiv), maleimide **2a** (104 mg, 0.600 mmol, 2.00 equiv), and 4CzIPN (6.0 mg, 7.5 µmol, 0.025 equiv) in anhydrous DCM (3 mL, 0.1 M). Then, the solvent was removed via rotary evaporation and the crude product was used in the next step without further purification.

Step-2: A flame-dried 25 mL sealed round bottom flask was charged with housane **3f** and anhydrous toluene (6.0 mL). The solution was refluxed at 180 °C for 60 h. Next, the reaction mixture was concentrated under reduced pressure, and the crude product was purified by column chromatography using 30-45% Et_2O:hexane mixture as a mobile phase to afford the title compound **6f** (128 mg, 0.240 mmol, 80%, *dr* 10:1) as colorless semi-solid. (*See Spectra*)

- **TLC (Et_2O:Hexane, 1:1 v/v):** $R_f = 0.40$, UV, $KMnO_4$
- **^1H NMR (400 MHz, $CDCl_3$):** δ 7.46 (t, *J* = 7.6 Hz, 2H, Ar*H*), 7.41 – 7.32 (m, 4H, Ar*H*), 7.31 – 7.05 (m, 13H, Ar*H*), 4.88 (bs, 1H, *CH*), 4.42 (bs, 1H, *CH*), 3.80 (s, 3H, CO_2CH_3)).
- **^{13}C NMR (101 MHz, $CDCl_3$):** δ 175.4, 173.6, 140.7, 138.5, 135.2, 134.0, 133.8, 132.0, 131.6, 130.1, 129.4, 129.2, 128.8, 128.7, 128.4, 127.7, 126.6, 71.9, 54.2, 52.9. Seven carbons were not resolved at 101 MHz.
- **IR (Neat, cm^{-1}):** υ 2922 (m), 2854 (w), 1710 (s), 1495 (w), 1378 (m), 1241 (w), 1188 (m), 1066 (w), 735 (s), 694 (m).
- **HRMS (ESI):** Calcd. for $C_{33}H_{24}ClNO_4H$ $[M+H]^+$ 534.1472; found: 534.1470.

Methyl-1,3-dioxo-2,4,5,6-tetraphenyl-1,2,3,3a,4,6a-hexahydrocyclopenta[c]pyrrole-4-carboxylate (6g)



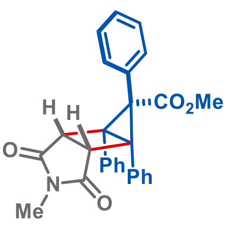
6g

Following the general procedure-3 (second step), a flame-dried 25 mL sealed round bottom flask was charged with housane **3a** (74.9 mg, 0.150 mmol, 1.00 equiv) in anhydrous toluene (3.0 mL, 0.05 M). The solution was refluxed at 180 °C for 60 h. Next, the reaction mixture was concentrated under reduced pressure, and the crude product was purified by column chromatography using 20-25% Et_2O:hexane mixture as a mobile phase to afford the title compound **6g** (62 mg, 0.12 mmol, 82%, *dr* > 20:1) as colorless semi-solid. (*See Spectra*)

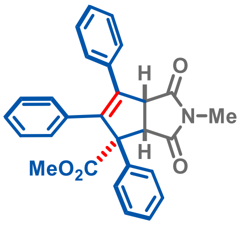
- **TLC (Et_2O:Hexane, 4:6 v/v):** $R_f = 0.40$, UV, $KMnO_4$

- **^{1}H NMR (400 MHz, CDCl$_3$):** δ 7.52 – 7.44 (m, 4H, Ar*H*), 7.41 – 7.30 (m, 8H, Ar*H*), 7.29-7.22 (m, 3H, Ar*H*), 7.12 (dt, *J* = 15.6, 7.3 Hz, 3H, Ar*H*), 7.01 – 6.96 (m, 2H, Ar*H*), 4.66 (d, *J* = 8.8 Hz, 1H, *CH*), 4.01 (d, *J* = 8.8 Hz, 1H, *CH*), 3.72 (s, 3H, CO$_2$*CH$_3$*).
- **^{13}C NMR (101 MHz, CDCl$_3$):** δ 175.2, 173.9, 172.1, 142.2, 141.9, 138.7, 134.8, 134.6, 131.9, 129.9, 129.7, 129.5, 129.0, 128.5, 128.3, 128.2, 128.1, 128.0, 127.8, 127.2, 126.4, 70.7, 55.6, 55.0, 52.8.
- **IR (Neat, cm^{-1}):** υ 2921 (m), 2853 (w), 1742 (w), 1712 (s), 1495 (w), 1378 (m), 1240 (w), 1189 (m), 1069 (w), 765 (w), 698 (m).
- **HRMS (ESI):** Calcd. for $C_{33}H_{25}NO_4H^+$ $[M+H]^+$ 500.1862; found: 500.1862.

Methyl-2-methyl-1,3-dioxo-4,5,6-triphenyl-1,2,3,3a,4,6a-hexahydrocyclopenta[c]pyrrole-4-carboxylate (6h)



3al



6h

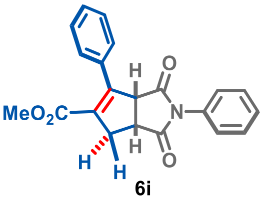
Step-1: Following the general procedure-1, using cyclopropene **1a** (98 mg, 0.30 mmol, 1.0 equiv), maleimide **2i** (67 mg, 0.60 mmol, 2.0 equiv), and 4CzIPN (6.0 mg, 7.5 µmol, 0.025 equiv) in anhydrous DCM (3 mL, 0.1 M). The crude product was purified by column chromatography using 25-40% Et$_2$O:hexane mixture as a mobile phase to afford the pure product **3al** as a pale yellow semi-solid (79 mg, 0.18 mmol, 60% (major diastereomer), *dr* 3:1). We couldn't isolate the minor diastereomer. (*See Spectra*)

- **TLC (Et$_2$O:Hexane, 1:1 v/v):** R_f = 0.40, UV, KMnO$_4$.
- **^{1}H NMR (400 MHz, CDCl$_3$):** For major diastereomer δ 7.70 (d, *J* = 7.7 Hz, 2H, Ar*H*), 7.58 – 7.52 (m, 2H, Ar*H*), 7.48 – 7.30 (m, 11H, Ar*H*), 3.11 (s, 3H, CO$_2$*CH$_3$*), 3.07 (s, 2H, *CH*), 3.00 (s, 3H, -N*CH$_3$*).
- **^{13}C NMR (101 MHz, CDCl$_3$):** For major diastereomer δ 174.8, 168.0, 132.8, 132.5, 131.3, 129.5, 128.9, 128.3, 128.0, 127.9, 53.4, 51.9, 51.4, 47.4, 25.0.
- **IR (Neat, cm^{-1}):** υ 2922 (m), 2856 (w), 1717 (s), 1456 (w), 1378 (m), 1239 (m), 1187 (w), 1040 (w), 759 (m), 700 (w).
- **HRMS (ESI):** Calcd. for $C_{28}H_{23}NO_4H$ [M+H]+ 438.1705; found: 438.1708

Step-2: A flame-dried 25 mL sealed round bottom flask was charged with housane **3al** (65.5 mg, 0.150 mmol, 1.00 equiv) in anhydrous toluene (3.0 mL, 0.05 M). The solution was refluxed at 180 °C for 60 h. Next, the reaction mixture was concentrated under reduced pressure, and the crude product was purified by column chromatography using 35% Et_2O:hexane mixture as a mobile phase to afford the title compound **6h** (49.5 mg, 0.110 mmol, 75%, *dr* > 20:1) as colorless semi-solid. (*See Spectra*)

- **TLC (Et_2O:Hexane, 1:1 v/v):** R_f = 0.30, UV, $KMnO_4$
- **^1H NMR (400 MHz, $CDCl_3$):** δ 7.43 (d, *J* = 7.0 Hz, 2H, Ar*H*), 7.36 – 7.21 (m, 8H, Ar*H*), 7.16 – 7.04 (m, 3H, Ar*H*), 6.91 (d, *J* = 7.1 Hz, 2H, Ar*H*), 4.53 (d, *J* = 8.4 Hz, 1H, *CH*), 3.88 (d, *J* = 8.4 Hz, 1H, *CH*), 3.70 (s, 3H, CO_2CH_3), 3.03 (s, 3H, -NCH_3).
- **^{13}C NMR (101 MHz, $CDCl_3$):** δ 176.2, 175.0, 171.9, 142.0, 141.8, 138.4, 134.8, 134.6, 129.9, 129.4, 128.22, 128.17, 128.1, 128.04, 128.03, 127.7, 127.2, 70.0, 55.4, 55.0, 52.6, 25.0.
- **IR (Neat, cm^{-1}):** υ 2922 (m), 2854 (w), 1778 (w), 1709 (s), 1493 (m), 1377 (m), 1246 (m), 1185 (m), 1058 (w), 737 (m), 696 (m).
- **HRMS (ESI):** Calcd. for $C_{28}H_{23}NO_4H^+$ $[M+H]^+$ 438.1705; found: 438.1710.

Methyl-1,3-dioxo-2,6-diphenyl-1,2,3,3a,4,6a-hexahydrocyclopenta[c]pyrrole-5-carboxylate (6i)



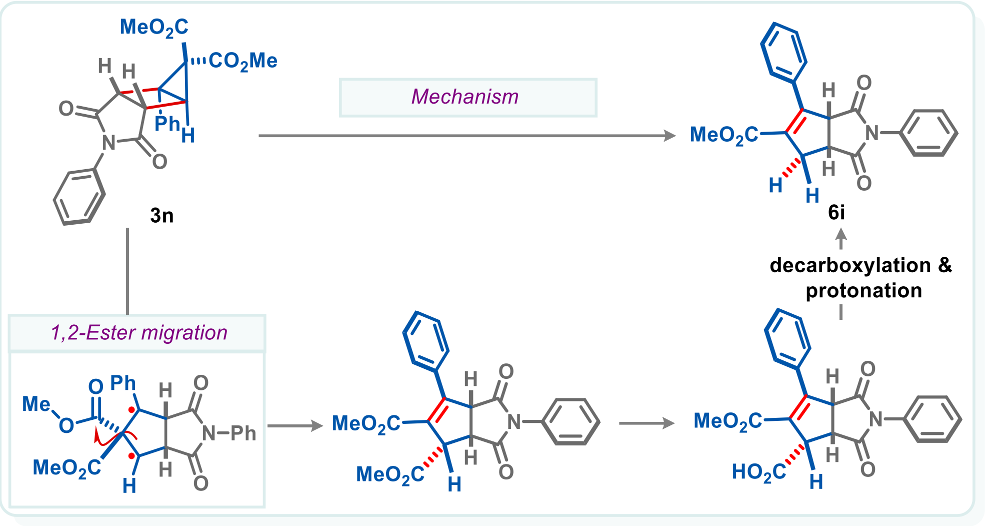
6i

Step-1: Following the general procedure-1, using cyclopropene **1o** (70 mg, 0.30 mmol, 1.0 equiv), maleimide **2a** (104 mg, 0.600 mmol, 2.00 equiv), and 4CzIPN (6.0 mg, 7.5 μmol, 0.025 equiv) in anhydrous DCM (3 mL, 0.1 M). Then, the solvent was removed via rotary evaporation and the product was used in the next step without further purification.

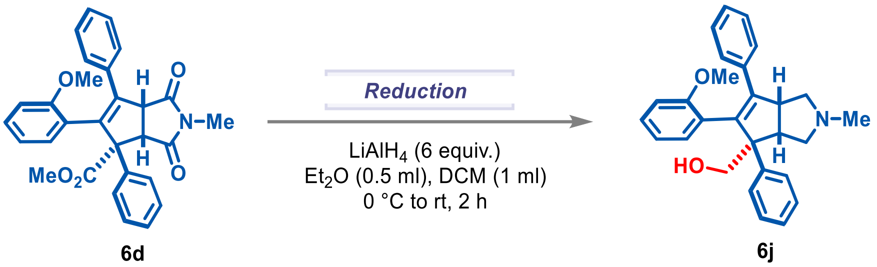
Step-2: A flame-dried 25 mL sealed round bottom flask was charged with housane **3o** and anhydrous toluene (6.0 mL). The solution was refluxed at 180 °C for 60 h. Next, the reaction mixture was concentrated under reduced pressure, and the crude product was purified by column chromatography using 25-40% Et_2O:hexane mixture as a mobile phase to afford the title compound **6i** (38 mg, 0.11 mmol, 36%) as colorless sticky solid. (*See Spectra*)

- **TLC (Et_2O:Hexane, 1:1 v/v):** R_f = 0.30, UV, $KMnO_4$
- **^1H NMR (400 MHz, $CDCl_3$):** δ 7.53 (dd, *J* = 8.4, 1.3 Hz, 2H, Ar*H*), 7.39 – 7.25 (m, 7H, Ar*H*), 7.21 – 7.19 (m, 1H, Ar*H*), 4.14 (d, *J* = 3.5 Hz, 1H, *CH*), 3.95 (d, *J* = 3.6 Hz, 1H, *CH*), 3.67 (s, 3H, CO_2CH_3), 3.59 – 3.50 (m, 2H, *CH*).

- **^{13}C NMR (101 MHz, CDCl$_3$):** δ 173.8, 173.5, 169.2, 144.0, 134.1, 131.9 (d, *J* = 6.0 Hz), 129.2, 129.0, 128.9, 128.5, 126.8, 126.6, 116.1, 52.4, 46.0, 45.4, 34.4.
- **IR (Neat, cm^{-1}):** υ 2922 (m), 2854 (w), 1713 (s), 1454 (w), 1378 (m), 1243 (w), 1191 (m), 1065 (w), 742 (w), 697 (w).
- **HRMS (ESI):** Calcd. for $C_{21}H_{17}NO_4H^+$ $[M+H]^+$ 348.1236; found: 348.1237.



5-(2-methoxyphenyl)-2-methyl-4,6-diphenyl-1,2,3,3a,4,6a-hexahydro-3,5-cyclopenta[c]pyrrol-4-yl)methanol (6j)



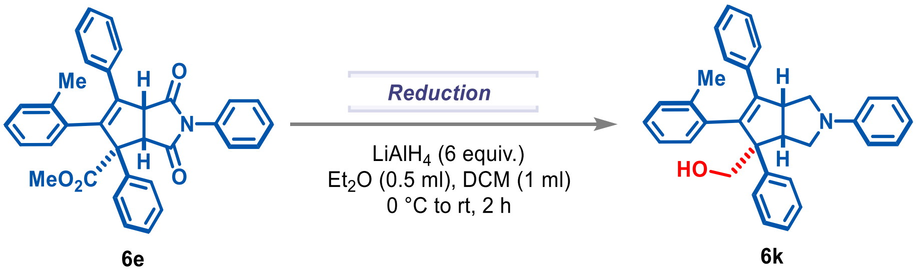
Following a slightly modified procedure, a 10 mL Schlenk tube was charged with $LiAlH_4$ (23 mg, 0.60 mmol, 6.0 equiv) in Et_2O (0.5 mL, 0.2 M). Then, the solution of cyclopentene ester **6d** (47 mg, 0.10 mmol, 1.0 equiv) in CH_2Cl_2 (1.0 mL, 0.1 M) was added at 0 °C under nitrogen. The mixture was stirred at room temperature for 2 h, and H_2O (3 mL) was carefully added at 0 °C. The organic phase was extracted with EtOAc (2×5 mL), dried over Na_2SO_4 and then concentrated via rotary evaporation. The crude product was purified by flash column chromatography (7:3 v/v EtOAc: Hexane and then 100 mL 19:1 v/v EtOAc: Et_3N) to afford the title product **6j** as a colorless liquid (25 mg, 0.06 mmol, 60%). (*See Spectra*)

- **TLC (EtOAc: Hexane, 8:2 v/v):** R_f = 0.10, UV, $KMnO_4$
- **^{1}H NMR (400 MHz, CDCl$_3$):** δ 7.28 (dd, *J* = 8.5, 1.3 Hz, 2H, Ar*H*), 7.16 (t, *J* = 7.7 Hz, 2H, Ar*H*), 7.13 – 7.05 (m, 8H, Ar*H*), 6.90 – 6.84 (m, 1H, Ar*H*), 6.53 (d, *J* = 8.3 Hz,

1H, Ar*H*), 4.43 (d, *J* = 11.8 Hz, 1H, *CH*), 4.18 (d, *J* = 11.8 Hz, 1H, *CH*), 4.13 (td, *J* = 9.1, 2.1 Hz, 1H, *CH*), 3.49-3.35 (m, 2H, *CH*), 3.22 (s, 4H, *CH*, ArO*CH₃*), 2.94 – 2.90 (m, 1H, *CH*), 2.37 (s, 4H, *CH*, -N*CH₃*).

- **^{13}C NMR (101 MHz, CDCl$_3$):** δ 156.4, 147.4, 143.4, 137.9, 137.5, 131.1, 128.1, 128.0, 127.6, 127.5, 126.5, 126.4, 126.2, 125.8, 120.2, 110.9, 65.4, 64.3, 60.3, 58.6, 54.7, 53.7, 52.2, 40.8.
- **IR (Neat, cm^{-1}):** υ 3057 (w), 2922 (s), 2852 (m), 2794 (w), 1684 (w), 1491 (m), 1249 (m), 1149 (w), 1029 (w), 756 (m), 700 (w).
- **HRMS (ESI):** Calcd. for $C_{28}H_{29}NO_2H^+$ $[M+H]^+$ 412.2277; found: 412.2277.

5-(2-methoxyphenyl)-2-methyl-4,6-diphenyl-1,2,3,3a,4,6a-hexahydro-3,5-cyclopenta[c]pyrrol-4-yl)methanol (6k)



6e

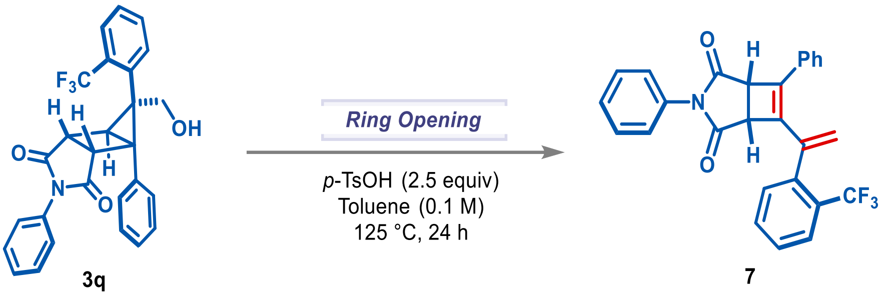
6k

Following a slightly modified procedure, a 10 mL Schlenk tube was charged with $LiAlH_4$ (23 mg, 0.60 mmol, 6.0 equiv) in Et_2O (0.5 mL, 0.2 M). Then, the solution of cyclopentene ester **6e** (52 mg, 0.10 mmol, 1.0 equiv) in CH_2Cl_2 (1.0 mL, 0.1 M) was added at 0 °C under nitrogen. The mixture was stirred at room temperature for 2 h, and H_2O (3 mL) was carefully added at 0 °C. The organic phase was extracted with EtOAc (2×5 mL), dried over Na_2SO_4 and then concentrated via rotary evaporation. The crude product was purified by flash column chromatography (2:8 v/v Et_2O:Hexane) to afford the title product **6k** as a colorless sticky solid (30.0 mg, 0.065 mmol, 65%). (*See Spectra*)

- **TLC (Et_2O:Hexane, 1:1 v/v):** R_f = 0.30, UV, $KMnO_4$
- **^{1}H NMR (400 MHz, CDCl$_3$):** δ 7.47 – 7.37 (m, 2H, Ar*H*), 7.2-7.20 (m, 5H, Ar*H*), 7.18 – 7.13 (m, 2H, Ar*H*), 7.12 – 7.08 (m, 3H, Ar*H*), 6.97 (dd, *J* = 6.7, 3.1 Hz, 2H, Ar*H*), 6.90 (d, *J* = 7.6 Hz, 1H, Ar*H*), 6.86 – 6.77 (m, 4H, Ar*H*), 4.45 (td, *J* = 8.2, 2.9 Hz, 1H, *CH*), 4.32 (s, 2H, *CH*), 3.88 (td, *J* = 10.2, 8.6, 6.0 Hz, 2H, *CH*), 3.74 (dt, *J* = 8.5, 4.5 Hz, 1H, *CH*), 3.60 (t, *J* = 9.4 Hz, 1H, *CH*), 3.31 (dd, *J* = 9.7, 2.7 Hz, 1H, *CH*), 2.83 (bs, 1H, CH₂*OH*), 1.14 (s, 3H, Ar*CH₃*).

- **^{13}C NMR (101 MHz, CDCl$_3$):** δ 148.2, 143.4, 141.3, 140.6, 137.0, 136.3, 135.4, 130.4, 130.0, 129.1, 128.5, 128.2, 128.0, 127.9, 127.6, 127.2, 127.0, 126.6, 126.3, 125.3, 118.2, 114.4, 65.7, 63.6, 53.4, 51.0, 50.0, 48.7, 19.0.
- **IR (Neat, cm^{-1}):** υ 2922 (s), 2855 (m), 2347 (w), 1858 (w), 1459 (w), 1264 (w), 753 (w), 648 (w).
- **HRMS (ESI):** Calcd. for $C_{33}H_{31}NOH^+$ $[M+H]^+$ 458.2484; found: 458.2482.

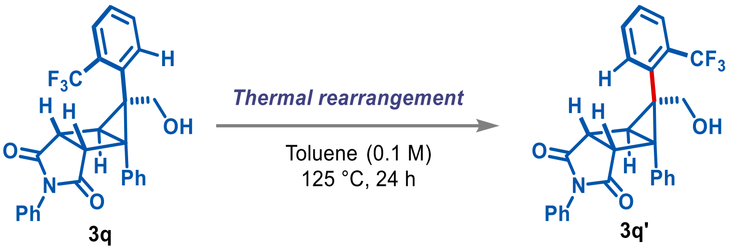
3,6-Diphenyl-7-(1-(2-(trifluoromethyl)phenyl)vinyl)-3-azabicyclo[3.2.0]hept-6-ene-2,4-dione (7)



A flame-dried 25 mL Schlenk tube was charged with housane **3q** (47 mg, 0.10 mmol, 1.0 equiv) and *p*-TsOH (43 mg, 0.25 mmol, 2.5 equiv) in anhydrous toluene (1.0 mL, 0.1 M). The solution was refluxed at 125 °C for 24 hours. Next, the reaction mixture was concentrated under reduced pressure, and the crude product was purified by column chromatography using 15-25% Et_2O:hexane mixture as a mobile phase to afford the title compound **7** (30 mg, 0.067 mmol, 67%) as colorless sticky solid. (*See Spectra*)

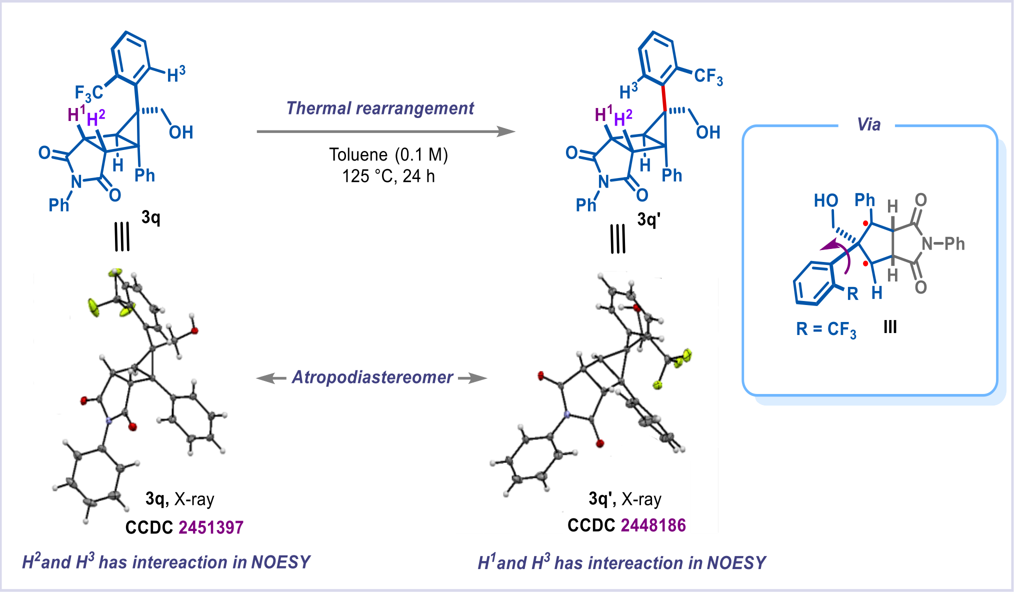
- **TLC (Et_2O:Hexane, 1:1 v/v):** $R_f = 0.45$, UV, $KMnO_4$
- **^{1}H NMR (400 MHz, CDCl$_3$):** δ 7.64 (d, *J* = 7.6 Hz, 1H, Ar*H*), 7.52 – 7.27 (m, 8H, Ar*H*), 7.11 (t, *J* = 7.3 Hz, 1H, Ar*H*), 7.02 (t, *J* = 7.6 Hz, 2H, Ar*H*), 6.91 (d, *J* = 7.7 Hz, 2H, Ar*H*), 6.19 (s, 1H, C=C*H*), 5.51 (s, 1H, C=C*H*), 4.18 (d, *J* = 6.9 Hz, 2H, C*H*).
- **^{13}C NMR (101 MHz, CDCl$_3$):** δ 174.0, 173.3, 140.1, 139.8, 138.7, 138.1 (q, *J* = 2.0 Hz), 132.0, 131.94, 131.87, 131.5, 129.0, 128.8, 128.5 (d, *J* = 2.3 Hz), 128.1, 128.0, 127.9, 127.6, 126.64, 126.57 (q, *J* = 5.0 Hz), 124.0 (q, *J* = 275.7 Hz), 123.4, 44.52, 44.49.
- **^{19}F NMR (377 MHz, CDCl$_3$):** δ -58.05.
- **IR (Neat, cm^{-1}):** υ 2923 (m), 2854 (w), 1714 (s), 1496 (w), 1379 (m), 1267 (w), 1172 (m), 1064 (w), 765 (w), 695 (w).
- **HRMS (ESI):** Calcd. for $C_{27}H_{18}F_3NO_2Na$ $[M+Na]^+$ 468.1187; found: 468.1185.

3-(hydroxymethyl)-2,7-diphenyl-3-(2-(trifluoromethyl)phenyl)-7-azatricyclo[3.3.0.02,4]octane-6,8-dione (3q’)



A flame-dried 25 mL Schlenk tube was charged with housane **3q** (47 mg, 0.10 mmol, 1.0 equiv) in anhydrous toluene (1.0 mL, 0.1 M). The solution was refluxed at 125 °C for 24 h. Next, the reaction mixture was concentrated under reduced pressure, and the crude product was purified by column chromatography using 25-40% Et_2O:hexane mixture as a mobile phase to afford the titled compound **3q’** (15 mg, 0.032 mmol, 32%) as colorless solid. (*See Spectra*)

- **Melting Point:** 187-189 °C.
- **TLC (Et_2O:Hexane, 6:4 v/v):** R_f = 0.20, UV, $KMnO_4$
- **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.86 (d, *J* = 7.7 Hz, 1H, Ar*H*), 7.71 – 7.67 (m, 2H, Ar*H*), 7.57 – 7.52 (m, 1H, Ar*H*), 7.45 (d, *J* = 7.1 Hz, 2H, Ar*H*), 7.41 – 7.29 (m, 6H, Ar*H*), 6.98 – 6.95 (m, 2H, Ar*H*), 3.91 (d, *J* = 12.2 Hz, 1H, *CH*), 3.23 (d, *J* = 12.2 Hz, 1H, *CH*), 3.13 (dd, *J* = 3.6, 1.7 Hz, 1H, *CH*), 2.99 (d, *J* = 1.7 Hz, 1H, *CH*), 2.81 (d, *J* = 3.6 Hz, 1H, *CH*).
- **^{13}C NMR (101 MHz, $CDCl_3$):** δ 176.6, 173.8, 136.0, 132.8, 132.4, 132.0, 131.6, 130.0 (q, *J* = 30.3 Hz), 129.5, 129.1, 128.6, 128.5, 128.4, 128.2, 127.7 (q, *J* = 5.0 Hz), 126.3, 124.4 (q, *J* = 274.7 Hz), 65.6 (q, *J* = 3.2 Hz), 48.5, 45.9, 45.7, 41.0, 29.0.
- **^{19}F NMR (377 MHz, $CDCl_3$):** δ -58.05.
- **IR (Neat, cm^{-1}):** υ 2922 (s), 2855 (m), 2782 (w), 1459 (w), 1375 (w), 1142 (w), 753 (w), 697 (w).
- **HRMS (ESI):** Calcd. for $C_{27}H_{20}F_3NO_3H^+$ $[M+H]^+$ 464.1474; found: 464.1476



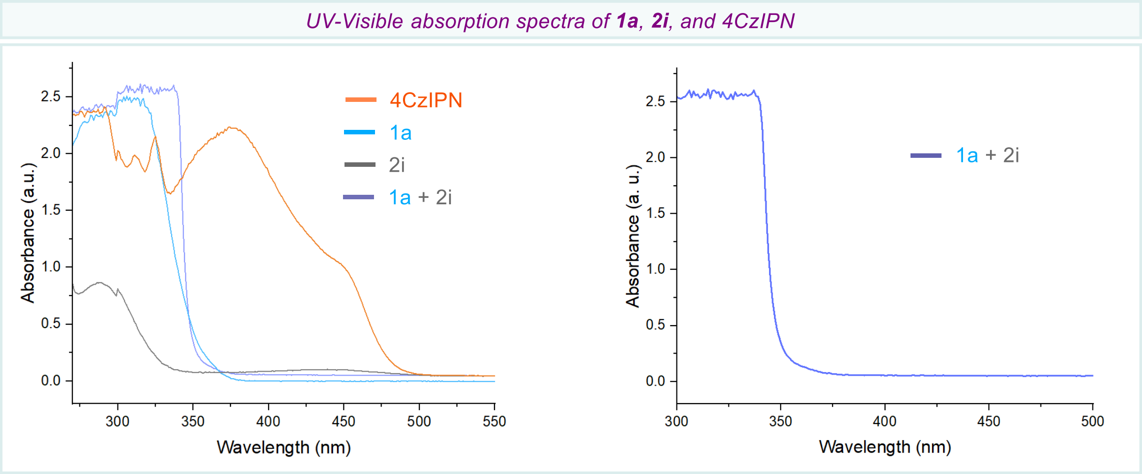
H^{2}and H^3 has intereaction in NOESY

H^{1}and H^3 has intereaction in NOESY

7.0 Mechanistic investigations:

7.1 UV-Visible spectroscopy:

UV/vis absorption spectra were recorded on a Duetta spectrophotometer from HORIBA Scientific. The samples were measured in Starna® fluorescence quartz cuvettes.



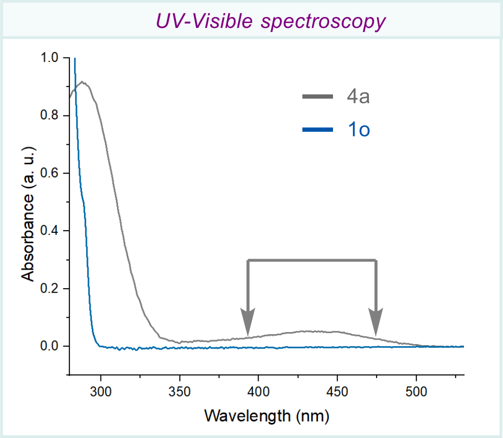


Figure 1: UV-Vis absorbance spectra of compounds **1a**, **2i** in DCM (0.001 M) and 4CzIPN in DCM (0.0001M) and compounds **1o**, **4a** in CH_3CN (0.001 M).

7.2 Stern-Volmer Analysis:

Quenching studies were carried out on a Duetta spectrophotometer from HORIBA Scientific using Starna® fluorescence quartz cuvettes. luminescence quenching studies were carried out using a ($1{\cdot}10^{-}4$ M) solution of photocatalyst and variable concentrations of substrate in dry DCM at room temperature under an argon atmosphere. The samples were prepared in 0.5 mL quartz cuvettes inside an argon filled glove-box, and sealed with parafilm. The solutions were irradiated at 365 nm and the luminescence was measured at maximum emission wavelength of each photocatalyst. (I_0 = emission intensity of the photocatalyst in isolation at the specified wavelength; I = observed intensity as a function of the quencher concentration.

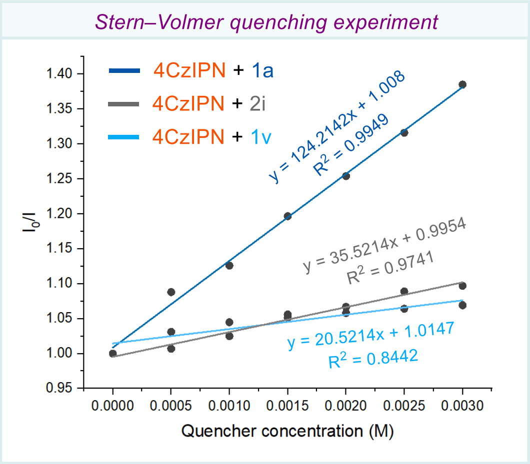


Figure 2: Luminescence quenching of the excited state of 4CzIPN using **1a**, **1v** and **2i** in DCM.

7.3 Cyclic Voltammetry:

Redox potential measurements for 1a

Cyclic voltammogram (CV) was collected at room temperature using a CHI 400 A potentiostat. A 2 mm glassy carbon disc electrode, an Ag/AgCl (2 M LiCl in ethanol) electrode, and a platinum sheet electrode were used as the working, reference, and counter electrodes, respectively and were all supplied by Metrohm. The electrolyte solution contained 0.1 M tetrabutylammonium hexafluorophosphate ($TBAPF_6$) and 2 mM of the given substrate in MeCN. Before each measurement, the solution was purged with N_2 gas to avoid the interference of atmospheric oxygen. The scan rate was set at 0.1 V/s (E_{step} = 0.002 V) and 10 scans were taken for each compound in the potential window of 0.0 V to +1.6 V.

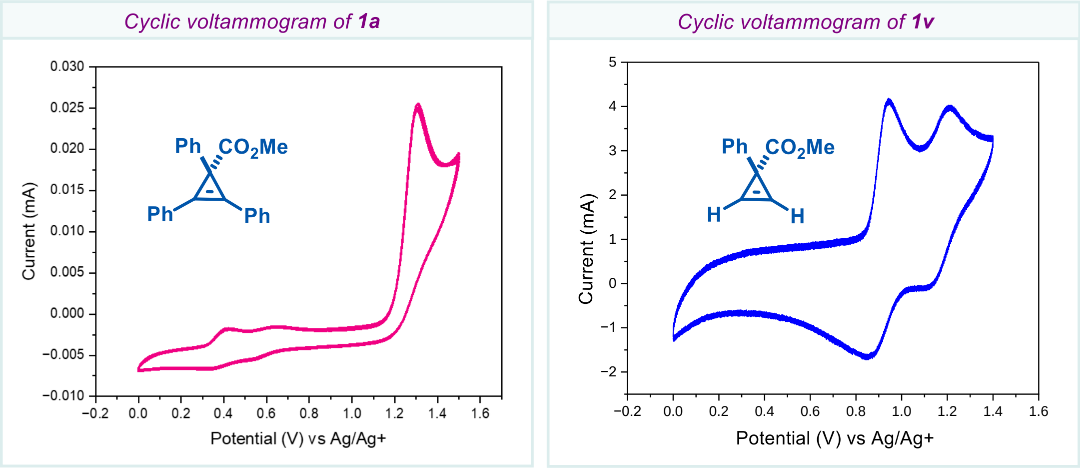
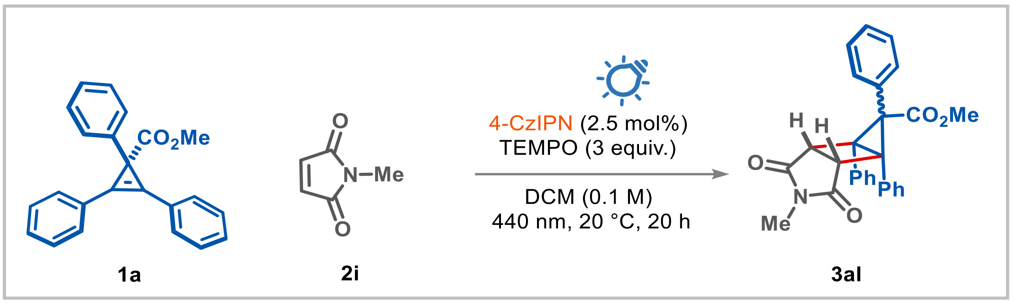


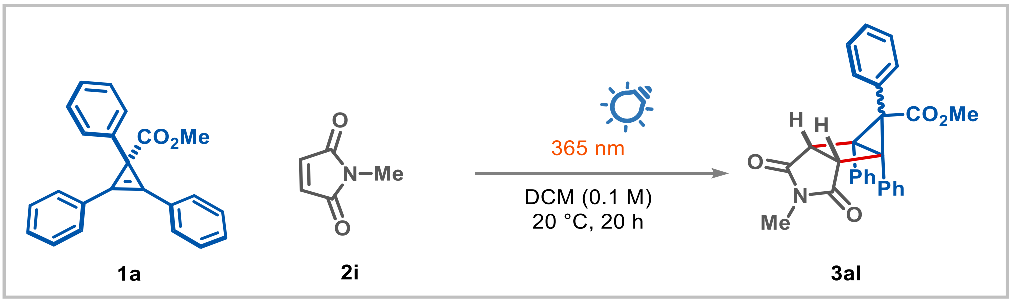
Figure 3: Cyclic voltammetry of **1a** and **1v** in 0.1 M $TBAPF_6$ (MeCN) using a 2 mm glassy carbon disk working electrode, Pt sheet counter electrode and an Ag/AgCl (2 M LiCl in ethanol) reference electrode. Set at 0.1 V/s scan rate.

7.4 Radical Trapping Experiment:



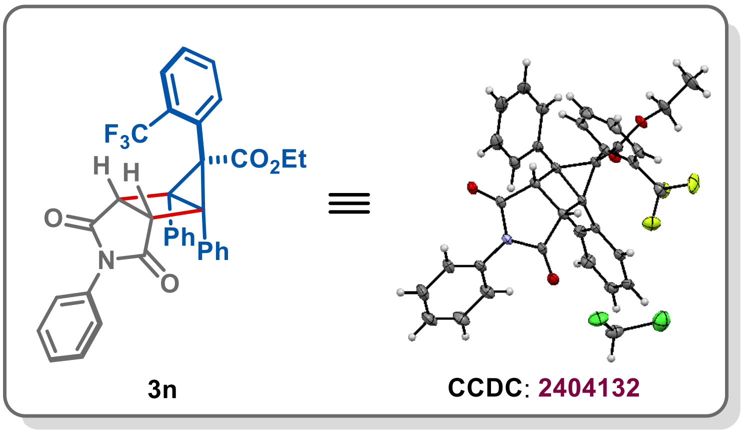
A flame-dried 5 mL Schlenk tube was charged with cyclopropene **1a** (33 mg, 0.10 mmol, 1.0 equiv), maleimide **2i** (22 mg, 0.20 mmol, 2.0 equiv), TEMPO (47 mg, 0.30 mmol, 3.0 equiv), 4-CzIPN (2.0 mg, 2.5 mol%) and anhydrous DCM (1.0 mL). The solution was irradiated using a 440 nm Kessil lamp for 20 h at 20 °C. Next, the reaction mixture was concentrated under reduced pressure and the crude product was submitted to ^{1}H-NMR. When the radical trapping agent 2,2,6,6-tetramethylpiperidin-1-yloxyl (TEMPO) was added to the standard reaction, product formation was entirely suppressed. The yield and *dr* ratio of the crude product was calculated by ^{1}H-NMR using CH_2Br_2 (7.0 µl, 0.10 mmol) as an internal standard. (*See Spectra*)

7.5 Reaction at 365 nm:



A flame-dried 5 mL vial was charged with cyclopropene **1a** (37 mg, 0.10 mmol, 1.0 equiv), maleimide **2i** (22 mg, 0.20 mmol, 2.0 equiv) and anhydrous DCM (1.0 mL). The solution was irradiated using a 365 nm lamp (using Photo-Cube by Thales Nano) for 20 h at 20 °C. Next, the reaction mixture was concentrated under reduced pressure and the crude product was submitted to ^{1}H-NMR. The yield and *dr* ratio of the crude product was calculated by ^{1}H NMR using CH_2Br_2 (7.0 µl, 0.10 mmol) as an internal standard. (*See Spectra*)

8.0 Crystal Structures:



3n

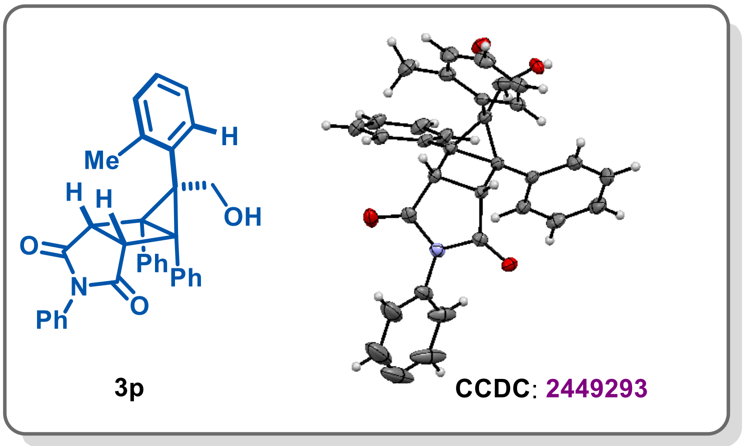
CCDC: **2404132**

Suitable crystals of compound **3n** were obtained by slowly evaporating a mixture of petroleum ether and dichloromethane solution at ambient temperature. Good quality single crystals were selected under an optical microscope equipped with a polarizer. A single crystal was affixed to a MiTeGen advanced lithographic cryo-loop using NVH oil. A high-resolution data set of crystal **3m** was collected in a Bruker D8 Quest diffractometer, equipped with a Photon II area detector with monochromated MoK$_{\alpha}$ radiation (λ= 0.71073 Å) at 120 K temperature. The X ray generator was operated at 45 kV and 30 mA. A preliminary set of cell constants and an orientation matrix were calculated from a set of fast scans (180 frames). Data was collected with ω scan width of 0.5° at different settings of φ and 2θ with a frame time of 20 secs keeping the sample to detector distance fixed at 45 mm, and 3-axis goniometer with fixed Kappa/Chi axis (54.736°). The X-ray data collection was monitored by the APEX4 software (Bruker). All the data were corrected for Lorentzian, polarization, and absorption effects using SAINT and SADABS programs (Bruker). The structure was solved using the APEX4 (Bruker) program suite using direct methods with the SHELXS - 97 (Sheldrick, 2008) structure refinement program. Using Least Squares minimization, the model was refined with a version of SHELXL - 2019/1 (Sheldrick, 2019). An ORTEP view of the structure was shown with the 50% probability displacement ellipsoids and the packing diagram was made using Mercury software 2022.3.0.

Table 1: Crystal Data of compound **3n**

CCDC number	**2404132**
Identification code	**3n**
Empirical formula	$C_{35}H_{26}F_3NO_4$
Formula weight	581.5912
Temperature	120(2) K
Wavelength	Monoclinic
Space group	C/c
Unit cell dimensions	a = 23.2091(7) Å, b = 10.1744(3) Å, c = 14.2246(5) Å, α = 90°, β = 113.837(1), γ = 90°
Volume	3072.45(17) Å^3
Z	4
Density (calc)(mg/m^3)	1.441
Absorption coefficient (mm^{-1})	0.272
F(000)	1376.0
Crystal size (mm^3)	0.498 x 0.244 x 0.132
Theta range for data collection	2.93 to 30.52°.
Index ranges	-33<=h<=33, -14<=k<=14, -20<=l<=20
Reflections collected	43797
Completeness to theta = 25.242°	99.6 %
Absorption correction	Semi-empirical from equivalents
Refinement method	Full-matrix least-squares on F2
Data / restraints / parameters	8756 / 2 / 416
Goodness-of-fit on F^2	1.067

Final R indices [I>2sigma(I)]	R1 = 0.0550, wR2 = 0.1462
R indices (all data)	R1 = 0.0609, wR2 = 0.1503
Extinction coefficient	NA



3p

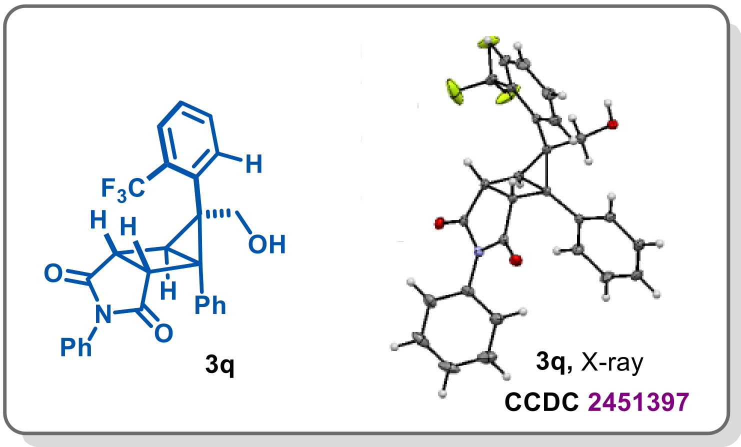
CCDC: 2449293

Suitable crystals of compound **3p** were obtained by slowly evaporating a mixture of petroleum ether and dichloromethane solution at ambient temperature. Good quality single crystals were selected under an optical microscope equipped with a polarizer. A single crystal was affixed to a MiTeGen advanced lithographic cryo-loop using NVH oil. A high-resolution data set of crystal **3p** was collected in a Bruker D8 Quest diffractometer, equipped with a Photon II area detector with monochromated MoK$_\alpha$ radiation (λ= 0.71073 Å) at 120 K temperature. The X ray generator was operated at 45 kV and 30 mA. A preliminary set of cell constants and an orientation matrix were calculated from a set of fast scans (180 frames). Data was collected with ω scan width of 0.5° at different settings of φ and 2θ with a frame time of 20 secs keeping the sample to detector distance fixed at 45 mm, and 3-axis goniometer with fixed Kappa/Chi axis (54.736°). The X-ray data collection was monitored by the APEX4 software (Bruker). All the data were corrected for Lorentzian, polarization, and absorption effects using SAINT and SADABS programs (Bruker). The structure was solved using the APEX4 (Bruker) program suite using direct methods with the SHELXS - 97 (Sheldrick, 2008) structure refinement program. Using Least Squares minimization, the model was refined with a version of SHELXL - 2019/1 (Sheldrick, 2019). An ORTEP view of the structure was shown with the 50% probability displacement ellipsoids and the packing diagram was made using Mercury software 2022.3.0.

Table 3: Crystal Data of compound **3p**

CCDC number	**2449293**
Identification code	**3p**
Empirical formula	$C_{33}H_{27}NO_3$
Formula weight	485.19
Temperature	120(2) K
Wavelength	Trigonal
Space group	R -3 :H
Unit cell dimensions	a = 35.3662(15) Å, b = 35.3662(15) Å, c = 9.9973(7) Å, α = 90.0, β = 90.0, γ = 120.0
Volume	10829.0(12) Å^3
Z	16
Density (calc)(mg/m^3)	1.336
Absorption coefficient (mm^{-1})	0.085
F(000)	4580
Crystal size (mm^3)	0.498 x 0.244 x 0.132
Theta range for data collection	2.692 to 27.265°.
Index ranges	-45<=h<=45, -45<=k<=45, -12<=l<=12
Reflections collected	91396
Completeness to theta = 25.242°	99.68 %
Absorption correction	Semi-empirical from equivalents
Refinement method	Full-matrix least-squares on F2
Data / restraints / parameters	5391 / 0 / 351
Goodness-of-fit on F^2	0.993
Final R indices [I>2sigma(I)]	R1 = 0.0627, wR2 = 0.1518

R indices (all data)	R1 = 0.0766, wR2 = 0.1615
Extinction coefficient	NA

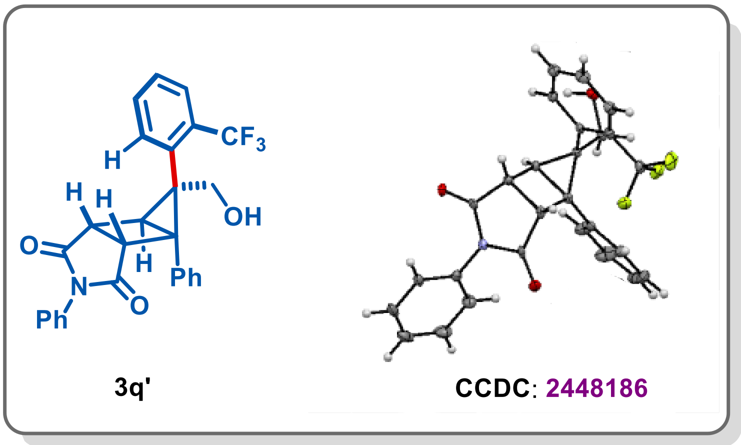


Suitable crystals of compound **3q** were obtained by slowly evaporating a mixture of petroleum ether and ethyl acetate solution at ambient temperature. Good quality single crystals were selected under an optical microscope equipped with a polarizer. A single crystal was affixed to a MiTeGen advanced lithographic cryo-loop using NVH oil. A high-resolution data set of crystal **3q** was collected in a Bruker D8 Quest diffractometer, equipped with a Photon II area detector with monochromated MoK$_\alpha$ radiation (λ= 0.71073 Å) at 120 K temperature. The X ray generator was operated at 45 kV and 30 mA. A preliminary set of cell constants and an orientation matrix were calculated from a set of fast scans (180 frames). Data was collected with ω scan width of 0.5° at different settings of φ and 2θ with a frame time of 20 secs keeping the sample to detector distance fixed at 45 mm, and 3-axis goniometer with fixed Kappa/Chi axis (54.736°). The X-ray data collection was monitored by the APEX4 software (Bruker). All the data were corrected for Lorentzian, polarization, and absorption effects using SAINT and SADABS programs (Bruker). The structure was solved using the APEX4 (Bruker) program suite using direct methods with the SHELXS - 97 (Sheldrick, 2008) structure refinement program. Using Least Squares minimization, the model was refined with a version of SHELXL - 2019/1 (Sheldrick, 2019). An ORTEP view of the structure was shown with the 50% probability displacement ellipsoids and the packing diagram was made using Mercury software 2022.3.0.

Table 3: Crystal Data of compound **3q**

CCDC number	**2451397**
Identification code	**3q**
Empirical formula	$C_{27}H_{20}F_3NO_3$
Formula weight	463.14
Temperature	120(2) K
Wavelength	Triclinic
Space group	P -1
Unit cell dimensions	a = 11.3001(7) Å, b = 13.4126(8) Å, c = 16.3714(9) Å, α = 76.397(2), β = 75.850(2), γ = 67.123(2)
Volume	2189.3(2) Å^3
Z	2
Density (calc)(mg/m^3)	1.406
Absorption coefficient (mm^{-1})	0.109
F(000)	960.0
Crystal size (mm^3)	0.498 x 0.244 x 0.132
Theta range for data collection	2.7657 to 31.567°.
Index ranges	-16<=h<=16, -19<=k<=19, -24<=l<=24
Reflections collected	91255
Completeness to theta = 25.242°	99.8 %
Absorption correction	Semi-empirical from equivalents
Refinement method	Full-matrix least-squares on F2
Data / restraints / parameters	14303 / 0 / 619
Goodness-of-fit on F^2	1.174

Final R indices [I>2sigma(I)]	R1 = 0.0829, wR2 = 0.1774
R indices (all data)	R1 = 0.1004, wR2 = 0.1858
Extinction coefficient	NA



3q'

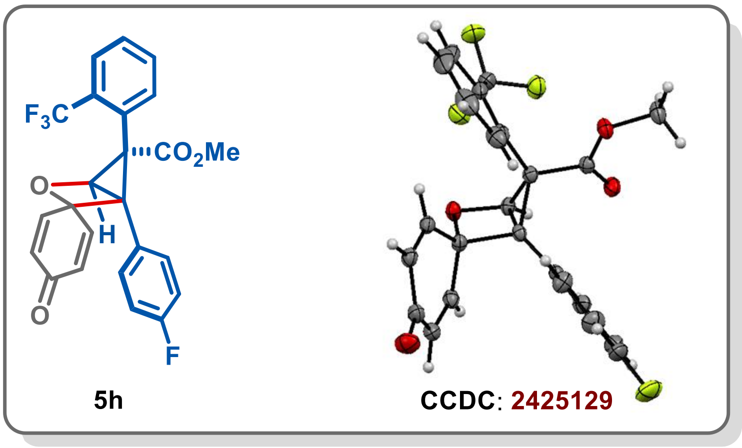
CCDC: **2448186**

Suitable crystals of compound **3q’** were obtained by slowly evaporating a mixture of petroleum ether and dichloromethane solution at ambient temperature. Good quality single crystals were selected under an optical microscope equipped with a polarizer. A single crystal was affixed to a MiTeGen advanced lithographic cryo-loop using NVH oil. A high-resolution data set of crystal **3q’** was collected in a Bruker D8 Quest diffractometer, equipped with a Photon II area detector with monochromated MoK$_\alpha$ radiation (λ= 0.71073 Å) at 120 K temperature. The X ray generator was operated at 45 kV and 30 mA. A preliminary set of cell constants and an orientation matrix were calculated from a set of fast scans (180 frames). Data was collected with ω scan width of 0.5° at different settings of φ and 2θ with a frame time of 20 secs keeping the sample to detector distance fixed at 45 mm, and 3-axis goniometer with fixed Kappa/Chi axis (54.736°). The X-ray data collection was monitored by the APEX2 software (Bruker). All the data were corrected for Lorentzian, polarization, and absorption effects using SAINT and SADABS programs (Bruker). The structure was solved using the APEX2 (Bruker) program suite using direct methods with the SHELXS - 97 (Sheldrick, 2008) structure refinement program. Using Least Squares minimization, the model was refined with a version of SHELXL - 2019/1 (Sheldrick, 2019). An ORTEP view of the structure was shown with the 50% probability displacement ellipsoids and the packing diagram was made using Mercury software 2022.3.0.

Table 3: Crystal Data of compound **3q’**

CCDC number	**2448186**
Identification code	**3q'**
Empirical formula	$C_{27}H_{20}F_3NO_3$
Formula weight	463.13
Temperature	120(2) K
Wavelength	Monoclinic
Space group	P 21
Unit cell dimensions	a = 11.8938(8) Å, b = 7.7392(5) Å, c = 25.6881(18) Å, α = 90.0, β = 97.182(2), γ = 90.0
Volume	2346.0(3) $Å^3$
Z	4
Density (calc)(mg/m^3)	1.432
Absorption coefficient (mm^{-1})	0.218
F(000)	1044
Crystal size (mm^3)	0.498 x 0.244 x 0.132
Theta range for data collection	2.751 to 30.530°.
Index ranges	-17<=h<=17, -11<=k<=11, -36<=l<=36
Reflections collected	67605
Completeness to theta = 25.242°	99.6 %
Absorption correction	Semi-empirical from equivalents
Refinement method	Full-matrix least-squares on F2
Data / restraints / parameters	13963 / 1 / 648
Goodness-of-fit on F^2	0.745
Final R indices [I>2sigma(I)]	R1 = 0.0572, wR2 = 0.1638

R indices (all data)	R1 = 0.0667, wR2 = 0.1756
Extinction coefficient	NA



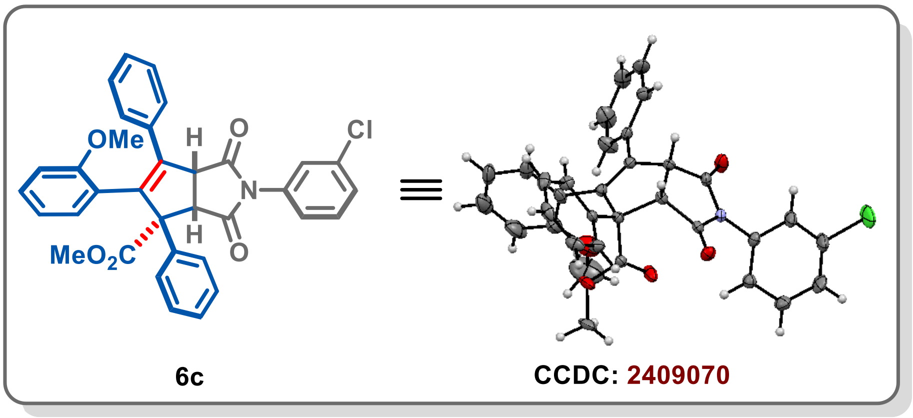
Suitable crystals of compound **5h** were obtained by slowly evaporating a mixture of petroleum ether and diethylether solution at ambient temperature. Good quality single crystals were selected under an optical microscope equipped with a polarizer. A single crystal was affixed to a MiTeGen advanced lithographic cryo-loop using NVH oil. A high-resolution data set of crystal **5h** was collected in a Bruker D8 Quest diffractometer, equipped with a Photon II area detector with monochromated MoK$_\alpha$ radiation (λ= 0.71073 Å) at 120 K temperature. The X ray generator was operated at 45 kV and 30 mA. A preliminary set of cell constants and an orientation matrix were calculated from a set of fast scans (180 frames). Data was collected with ω scan width of 0.5° at different settings of φ and 2θ with a frame time of 20 secs keeping the sample to detector distance fixed at 45 mm, and 3-axis goniometer with fixed Kappa/Chi axis (54.736°). The X-ray data collection was monitored by the APEX4 software (Bruker). All the data were corrected for Lorentzian, polarization, and absorption effects using SAINT and SADABS programs (Bruker). The structure was solved using the APEX4 (Bruker) program suite using direct methods with the SHELXS - 97 (Sheldrick, 2008) structure refinement program. Using Least Squares minimization, the model was refined with a version of SHELXL - 2019/1 (Sheldrick, 2019). An ORTEP view of the structure was shown with the 50% probability displacement ellipsoids and the packing diagram was made using Mercury software 2022.3.0.

Table 3: Crystal Data of compound **5h**

CCDC number	**2425129**

Identification code	**5h**
Empirical formula	$C_{24}H_{16}F_4O_4$
Formula weight	444.37
Temperature	120(2) K
Wavelength	Triclinic
Space group	P -1
Unit cell dimensions	a = 8.5086(7) Å, b = 10.3951(9) Å, c = 11.770(1) Å, α = 94.161(3), β = 106.191(3), γ = 91.831(3)
Volume	995.62(15) $Å^3$
Z	2
Density (calc)(mg/m^3)	1.482
Absorption coefficient (mm^{-1})	0.125
F(000)	456.0
Crystal size (mm^3)	0.498 x 0.244 x 0.132
Theta range for data collection	2.50 to 27.657 °.
Index ranges	-11<=h<=11, -13<=k<=13, -15<=l<=15
Reflections collected	35748
Completeness to theta = 25.242°	99.7 %
Absorption correction	Semi-empirical from equivalents
Refinement method	Full-matrix least-squares on F2
Data / restraints / parameters	4545 / 0 / 290
Goodness-of-fit on F^2	1.038
Final R indices [I>2sigma(I)]	R1 = 0.0402, wR2 = 0.1053
R indices (all data)	R1 = 0.0437, wR2 = 0.1079

Extinction coefficient	NA



6c

CCDC: 2409070

Suitable crystals of compound **6c** were obtained by slowly evaporating a mixture of petroleum ether and dichloromethane solution at ambient temperature. Good quality single crystals were selected under an optical microscope equipped with a polarizer. A single crystal was affixed to a MiTeGen advanced lithographic cryo-loop using NVH oil. A high-resolution data set of crystal **6c** was collected in a Bruker D8 Quest diffractometer, equipped with a Photon II area detector with monochromated MoK$_\alpha$ radiation (λ= 0.71073 Å) at 120 K temperature. The X ray generator was operated at 45 kV and 30 mA. A preliminary set of cell constants and an orientation matrix were calculated from a set of fast scans (180 frames). Data was collected with ω scan width of 0.5° at different settings of φ and 2θ with a frame time of 20 secs keeping the sample to detector distance fixed at 45 mm, and 3-axis goniometer with fixed Kappa/Chi axis (54.736°). The X-ray data collection was monitored by the APEX4 software (Bruker). All the data were corrected for Lorentzian, polarization, and absorption effects using SAINT and SADABS programs (Bruker). The structure was solved using the APEX3 (Bruker) program suite using direct methods with the SHELXT 2019/2 (Sheldrick, 2018) structure refinement program. Using Least Squares minimization, the model was refined with a version of SHELXL - 2019/2 (Sheldrick, 2019). An ORTEP view of the structure was shown with the 50% probability displacement ellipsoids and the packing diagram was made using Mercury software 2022.3.0.**Table 2**: Crystal Data of compound **6c**

CCDC number	**2409070**
Identification code	**6c**
Empirical formula	$C_{34}H_{26}$ClNO5

Formula weight	564.01
Temperature	120(2) K
Wavelength	Monoclinic
Space group	P 21/n
Unit cell dimensions	a = 12.0072(7) Å, b = 11.2445(9) Å, c = 20.5394(16) Å α = 90°, β = 91.189(3)°, γ = 90°
Volume	2772.5(3) Å^3
Z	4
Density (calc)(mg/m^3)	1.351
Absorption coefficient (mm^{-1})	0.182
F(000)	1148.0
Crystal size (mm^3)	0.498 x 0.244 x 0.132
Theta range for data collection	3.2 to 27.7°
Index ranges	-15<=h<=15, -14<=k<=14, -26<=l<=26
Reflections collected	17518
Completeness to theta = 25.242°	97.5 %
Absorption correction	Semi-empirical from equivalents
Refinement method	Full-matrix least-squares on F2
Data / restraints / parameters	6282 / 0 / 438
Goodness-of-fit on F^2	1.093
Final R indices [I>2sigma(I)]	R1 = 0.1115, wR2 = 0.2520
R indices (all data)	R1 = 0.1466, wR2 = 0.2710
Extinction coefficient	NA

9.0 DFT Analysis:

All calculations were carried out with the DFT method using the Gaussian16 program.[16] The structures were optimized with solvent effects of dichloromethane by using the SMD model[17] at the (U)M06/6-31+G(d,p) level of theory.[18] Harmonic analyses were performed at the same level of theory to verify all the stationary points as minima or first-order saddle points, and to obtain the thermodynamic contributions to enthalpy and free energy at 298 K and 1 atm pressure. The connection of every TS to its respective reactant and product was verified by intrinsic reaction coordinate (IRC) analysis.[19] To obtain more accurate values, single point calculations were performed at SMD(Dichloromethane)/(U)M06/6-311+G(d,p) (for 2+2 cycloaddition) and SMD(Toluene)/(U)M06/6-311+g(d,p)//(U)M06/6-31+g(d,p) (for 1,2-ester migration) level. The Gibbs Free Energy corrections obtained at 298 K and 1 atm were added to the calculated single-point energies. The optimized structures were generated using CYLview software.[20]

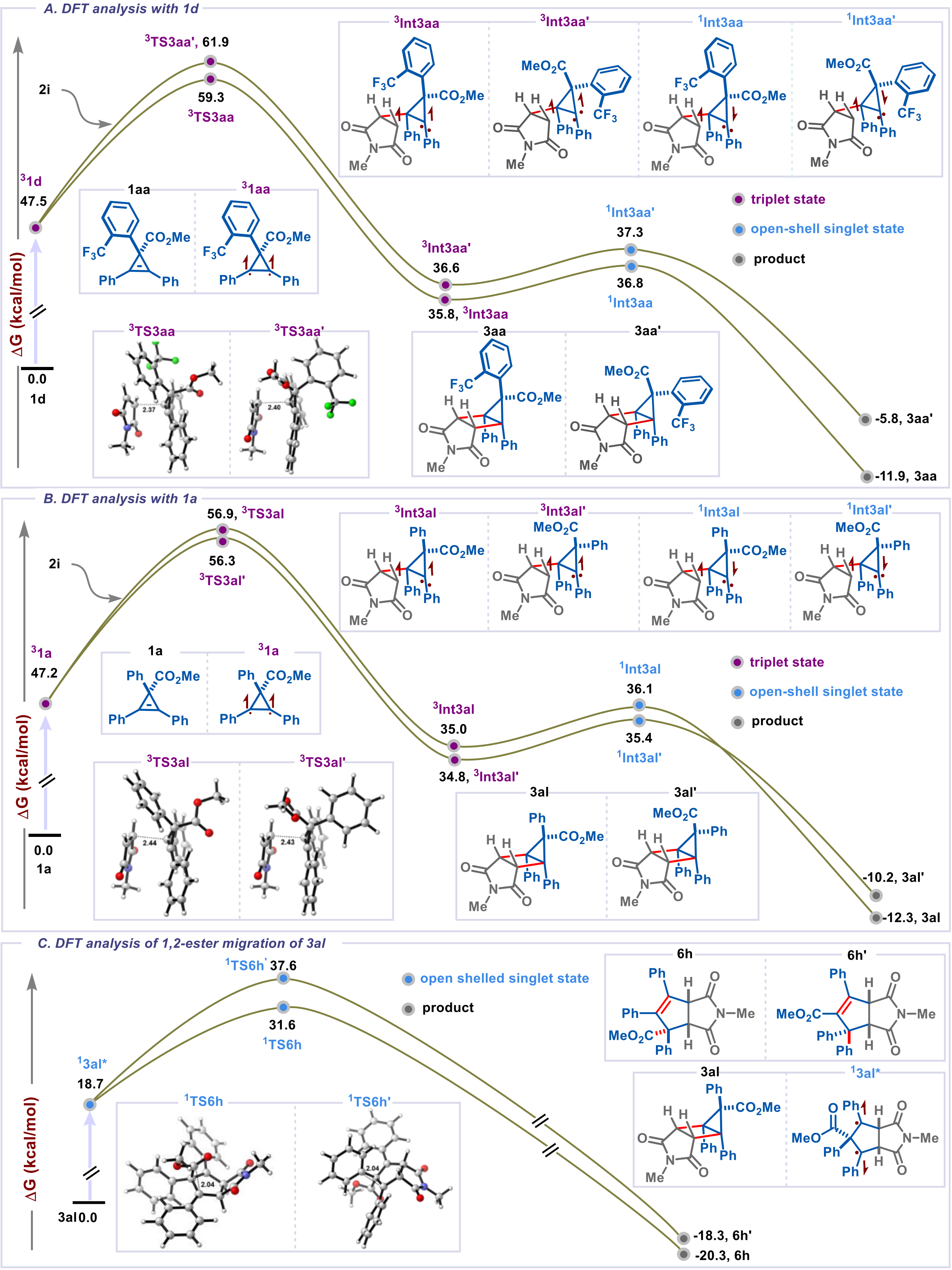
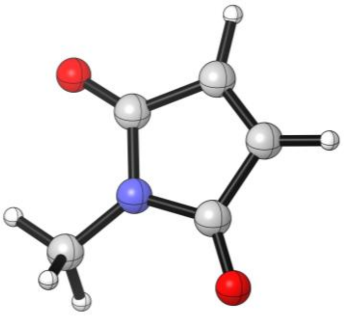


Figure 4: (A and B) The free energy profile for [2+2] cycloaddition of maleimide **2i** and cyclopropene **1d** and **1a.** (C) The free energy profile for 1,2-ester migration of **3al**. (Note: Distances in Å).

New Coordinates

2i



Number of imaginary frequencies: 0

Electronic energy: HF=-398.5259765

Zero-point correction= 0.096044 (Hartree/Particle)

Thermal correction to Energy= 0.103214

Thermal correction to Enthalpy= 0.104158

Thermal correction to Gibbs Free Energy= 0.064324

Sum of electronic and zero-point Energies= -398.429932

Sum of electronic and thermal Energies= -398.422763

Sum of electronic and thermal Enthalpies= -398.421819

Sum of electronic and thermal Free Energies= -398.461653

Cartesian Coordinates

C	1.149745	-0.182845	-0.000045
C	0.695625	-1.609601	0.000037
C	-0.637519	-1.633292	0.000029
C	-1.139204	-0.222608	-0.000041
N	-0.009820	0.590259	-0.000304
O	2.282798	0.239865	0.000059
O	-2.284302	0.167425	0.000056
C	-0.045965	2.034960	0.000095
H	1.401581	-2.431175	0.000095
H	-1.313145	-2.479952	0.000085
H	0.986302	2.392208	0.000435
H	-0.564790	2.404816	-0.889281
H	-0.565270	2.404280	0.889415

^{3}2i

Number of imaginary frequencies: 0

Electronic energy: HF=-398.4294274

Zero-point correction= 0.091323 (Hartree/Particle)

Thermal correction to Energy= 0.099218

Thermal correction to Enthalpy= 0.100162

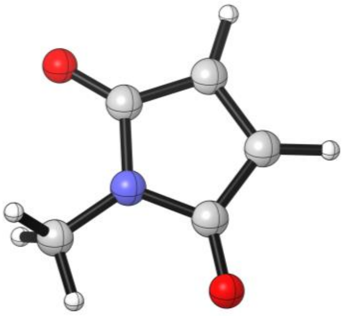
Thermal correction to Gibbs Free Energy= 0.058023

Sum of electronic and zero-point Energies= -398.338105

Sum of electronic and thermal Energies= -398.330209

Sum of electronic and thermal Enthalpies= -398.329265

Sum of electronic and thermal Free Energies= -398.371405



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Cartesian Coordinates

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C	1.200621	-0.200960	0.000108
C	0.780292	-1.577533	0.000008
C	-0.711990	-1.608387	-0.000021
C	-1.183904	-0.249515	0.000064
N	-0.008906	0.541757	0.000027
O	2.314856	0.295410	0.000017
O	-2.314220	0.211314	-0.000066
C	-0.055199	1.976952	-0.000054
H	1.455480	-2.423607	-0.000060
H	-1.351494	-2.481697	-0.000161
H	0.970164	2.352181	-0.000307
H	-0.598119	2.331778	-0.883902
H	-0.597693	2.331910	0.884005

1a

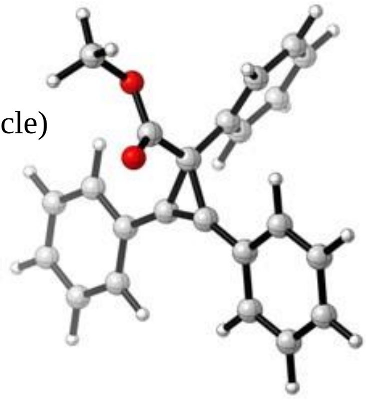
Number of imaginary frequencies: 0

Electronic energy: HF=-1036.9971713

Zero-point correction= 0.341944 (Hartree/Particle)

Thermal correction to Energy= 0.363387

Thermal correction to Enthalpy= 0.364331



Thermal correction to Gibbs Free Energy= 0.288799

Sum of electronic and zero-point Energies= -1036.655227

Sum of electronic and thermal Energies= -1036.633784

Sum of electronic and thermal Enthalpies= -1036.632840

Sum of electronic and thermal Free Energies= -1036.708372

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Cartesian Coordinates

……

H	-0.684520	2.546478	-3.790323
H	-5.234282	-0.185501	-0.073308
C	-0.198970	2.617512	-2.819518
C	-4.383947	-0.851656	-0.197354
C	-0.408106	1.621497	-1.869693
H	-5.597419	-2.569985	-0.661942
H	-2.920640	0.680083	0.230589
H	0.790950	4.478498	-3.269647
C	0.625830	3.699976	-2.528557
C	-3.094109	-0.364708	-0.025477
C	-4.587542	-2.189808	-0.528068
H	-1.514602	1.722382	3.927701
H	-1.476054	3.426708	3.363105
C	-0.935923	2.479624	3.389984
C	0.197815	1.690780	-0.613757
O	-0.750258	2.096103	2.028967
C	-3.495199	-3.042911	-0.686479
C	-1.991630	-1.216114	-0.183583
C	-0.081937	0.943525	1.840390
C	1.241492	3.776412	-1.281211
C	0.029055	0.582129	0.384733
O	0.327878	0.259916	2.752000
C	-2.204467	-2.561988	-0.515810
C	-0.664754	-0.699446	0.009178
C	1.028814	2.780242	-0.334951
H	0.029050	2.603396	3.891068

H	-3.653593	-4.087841	-0.942378
H	1.893475	4.614562	-1.045030
C	0.632424	-0.766704	0.098092
H	-1.347419	-3.222564	-0.632757
H	-1.048763	0.773141	-2.108382
C	1.915271	-1.403938	0.015100
C	2.036406	-2.734012	-0.412398
C	3.066366	-0.686661	0.364436
C	3.286421	-3.332469	-0.485142
C	4.428010	-2.611770	-0.134324
C	4.315330	-1.289313	0.290141
H	1.140672	-3.288649	-0.685927
H	3.374507	-4.364448	-0.816280
H	2.962305	0.343601	0.699902
H	5.204673	-0.727740	0.565417
H	5.406333	-3.082934	-0.191978
H	1.514467	2.851461	0.638044

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^{3}**1a**

Number of imaginary frequencies: 0

Electronic energy: HF=-1036.9164485

Zero-point correction= 0.337691 (Hartree/Particle)

Thermal correction to Energy= 0.359799

Thermal correction to Enthalpy= 0.360743

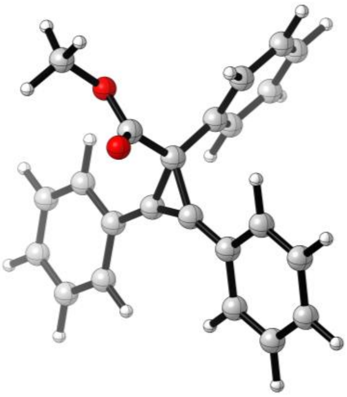
Thermal correction to Gibbs Free Energy= 0.282002

Sum of electronic and zero-point Energies= -1036.578758

Sum of electronic and thermal Energies= -1036.556650

Sum of electronic and thermal Enthalpies= -1036.555705

Sum of electronic and thermal Free Energies= -1036.634446



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Cartesian Coordinates

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H	-0.236656	2.681149	-3.772195

H	-5.231780	-0.105216	-0.465809
C	0.177469	2.689003	-2.766561
C	-4.376963	-0.777750	-0.479127
C	-0.168653	1.680279	-1.871385
H	-5.573099	-2.530295	-0.915172
H	-2.952817	0.778901	-0.048739
H	1.309869	4.495783	-3.074162
C	1.043117	3.706107	-2.375853
C	-3.114675	-0.279889	-0.246947
C	-4.572451	-2.146541	-0.733357
H	-1.969621	1.544824	3.752917
H	-2.329552	3.139934	3.010793
C	-1.570342	2.371310	3.157652
C	0.353621	1.676616	-0.577958
O	-1.213652	1.919202	1.850972
C	-3.470656	-3.017007	-0.748731
C	-1.975931	-1.150916	-0.264381
C	-0.261990	0.973896	1.809009
C	1.565787	3.708665	-1.083906
C	0.028106	0.568537	0.383896
O	0.268501	0.505800	2.788310
C	-2.197503	-2.542986	-0.519474
C	-0.708770	-0.646541	-0.065462
C	1.225966	2.697962	-0.192221
H	-0.697901	2.787521	3.670211
H	-3.624340	-4.076777	-0.939648
H	2.242433	4.500330	-0.770317
C	0.673655	-0.758076	0.177820
H	-1.341863	-3.215347	-0.522270
H	-0.850954	0.887047	-2.174099
C	1.889152	-1.400975	0.115017
C	2.003288	-2.743238	-0.370322
C	3.081819	-0.740471	0.551758
C	3.229645	-3.369934	-0.410899

C	4.387523	-2.703278	0.020065
C	4.296645	-1.385270	0.500006
H	1.104227	-3.253684	-0.710325
H	3.301789	-4.389610	-0.782750
H	2.999575	0.274313	0.936247
H	5.194035	-0.872331	0.838361
H	5.350982	-3.205442	-0.015917
H	1.639712	2.701872	0.816775

^{3}TS3al

Number of imaginary frequencies: 1 (-196.3563 cm-1)

Electronic energy: HF=-1435.4557252

Zero-point correction= 0.435290 (Hartree/Particle)

Thermal correction to Energy= 0.465102

Thermal correction to Enthalpy= 0.466047

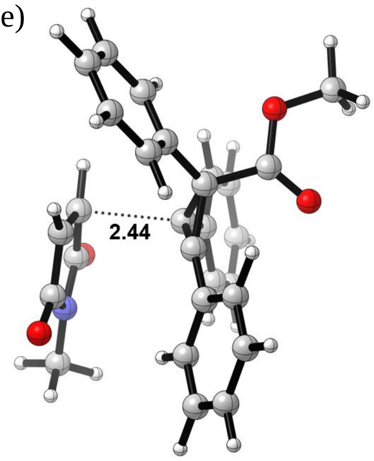
Thermal correction to Gibbs Free Energy= 0.370899

Sum of electronic and zero-point Energies= -1435.020435

Sum of electronic and thermal Energies= -1434.990623

Sum of electronic and thermal Enthalpies= -1434.989679

Sum of electronic and thermal Free Energies= -1435.084826



Cartesian Coordinates

H	0.075684	-4.229125	3.479238
C	0.636749	-3.501129	2.898275
H	2.559292	-4.322858	3.440643
H	-3.156243	-3.746724	-1.798842
C	2.035956	-3.549950	2.883388
H	-1.121749	-2.464578	2.220044
C	-0.035417	-2.526789	2.187218
C	-3.070771	-2.663468	-1.757881
H	-1.792519	-2.687616	-0.024229
C	-2.313368	-2.067294	-0.752292

H	-4.286083	-2.337777	-3.506169
C	-3.702513	-1.874416	-2.714331
C	2.760376	-2.603130	2.150745
C	0.682729	-1.559841	1.432416
H	3.846493	-2.645882	2.132528
C	2.102513	-1.620860	1.437569
C	-2.183550	-0.680174	-0.691125
O	-1.644083	0.581326	2.694926
C	-3.582213	-0.486903	-2.654884
C	0.004616	-0.591095	0.691579
O	2.566745	-2.443558	-1.782842
C	-1.345441	-0.050758	0.388819
C	-2.078136	0.551519	1.567373
C	-2.831715	0.105738	-1.645362
H	-4.180100	1.037758	3.066713
H	-4.073791	0.135631	-3.398924
C	2.044318	-1.354197	-1.926738
H	2.659904	-0.896282	0.846226
O	-3.250966	1.087086	1.204449
C	-3.971338	1.737958	2.252983
C	0.649182	-1.020427	-2.258627
H	-0.104968	-1.777605	-2.439188
H	4.530890	-0.973236	-1.324988
C	-0.049039	0.683153	0.093956
H	-2.740902	1.189857	-1.596108
H	4.318441	0.707341	-0.734505
C	4.131296	0.016246	-1.564047
N	2.713862	-0.125734	-1.788271
H	2.262160	1.357344	1.271385
H	-3.389769	2.577161	2.647280
C	0.513712	0.340357	-2.252370
H	-4.899428	2.090420	1.802413
C	1.656362	2.217626	0.991947
C	1.858073	0.939482	-2.064756

C	0.396473	2.001512	0.398608
H	4.633905	0.407349	-2.455489
C	2.106929	3.505916	1.228177
O	2.195211	2.106033	-2.124951
H	-0.333122	0.936182	-2.572659
H	3.078276	3.663702	1.690012
C	-0.395237	3.116639	0.052816
H	-1.367036	2.950409	-0.411104
C	1.318104	4.600034	0.871918
C	0.064339	4.400330	0.286487
H	1.678547	5.610152	1.049939
H	-0.548090	5.254960	0.009863

^{3}TS3al’

Number of imaginary frequencies: 1 (-184.2529 cm-1)

Electronic energy: HF=-1435.4584269

Zero-point correction= 0.435812 (Hartree/Particle)

Thermal correction to Energy= 0.465447

Thermal correction to Enthalpy= 0.466391

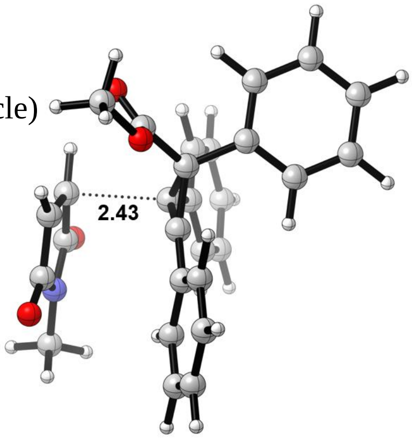
Thermal correction to Gibbs Free Energy= 0.371351

Sum of electronic and zero-point Energies= -1435.022615

Sum of electronic and thermal Energies= -1434.992980

Sum of electronic and thermal Enthalpies= -1434.992036

Sum of electronic and thermal Free Energies= -1435.087076



Cartesian Coordinates

H	-1.068274	-4.750671	-2.115695
C	-1.321308	-3.695789	-2.040098
H	-3.026916	-3.856829	-3.356673
H	5.773548	-0.403571	0.706999
C	-2.424534	-3.192730	-2.741997
H	0.299279	-3.241601	-0.690892

C	-0.555000	-2.862807	-1.249326
C	4.889659	-0.510571	0.082457
H	3.533554	-0.340546	1.744129
C	3.627709	-0.482415	0.668551
H	6.008127	-0.688369	-1.750842
C	5.021492	-0.668471	-1.294412
C	-2.755480	-1.836439	-2.645174
C	-0.876212	-1.481176	-1.141053
H	-3.618490	-1.448719	-3.181184
C	-1.999546	-0.988449	-1.860564
C	2.481117	-0.621250	-0.118595
O	1.281591	-0.536148	2.913706
C	3.881782	-0.798933	-2.083262
C	-0.101031	-0.640639	-0.344006
O	-3.847636	-1.131400	0.897969
C	1.107946	-0.558687	0.504345
C	1.078574	-1.152380	1.892775
C	2.619460	-0.778050	-1.499846
H	1.867438	-3.019803	3.583957
H	3.973410	-0.921818	-3.159854
C	-3.066997	-0.238705	1.172082
H	-2.261468	0.064366	-1.766388
O	0.864107	-2.471663	1.844945
C	0.892583	-3.147897	3.104666
C	-1.884522	-0.266308	2.046520
H	-1.600147	-1.155771	2.596427
H	-3.785035	2.159490	-0.989901
C	0.251605	0.630700	0.155709
H	1.731599	-0.883304	-2.121847
H	-4.895698	2.201598	0.394455
C	-4.203902	1.566024	-0.169733
N	-3.143141	1.070410	0.671308
H	-0.846123	1.868274	-1.961211
H	0.116232	-2.753905	3.768038

C	-1.276634	0.959808	2.009957
H	0.706937	-4.198674	2.883192
C	-0.122815	2.483224	-1.427185
C	-2.131899	1.869219	1.206441
C	0.551829	1.937177	-0.317025
H	-4.747035	0.703346	-0.566273
C	0.138162	3.781701	-1.833190
O	-2.017721	3.064366	1.014196
H	-0.458243	1.322237	2.621485
H	-0.384552	4.197591	-2.690803
C	1.492287	2.729742	0.374074
H	2.002840	2.302369	1.236753
C	1.064339	4.558456	-1.136311
C	1.740984	4.027615	-0.033379
H	1.259424	5.580874	-1.450520
H	2.460977	4.637509	0.506421

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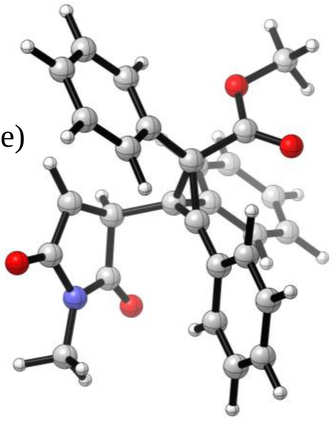
^{3}Int3al



Number of imaginary frequencies: 0

Electronic energy: HF=-1435.5000772

Zero-point correction= 0.438987 (Hartree/Particle)

Thermal correction to Energy= 0.468075

Thermal correction to Enthalpy= 0.469020

Thermal correction to Gibbs Free Energy= 0.376813

Sum of electronic and zero-point Energies= -1435.061090

Sum of electronic and thermal Energies= -1435.032002

Sum of electronic and thermal Enthalpies= -1435.031058

Sum of electronic and thermal Free Energies= -1435.123264

……

Cartesian Coordinates

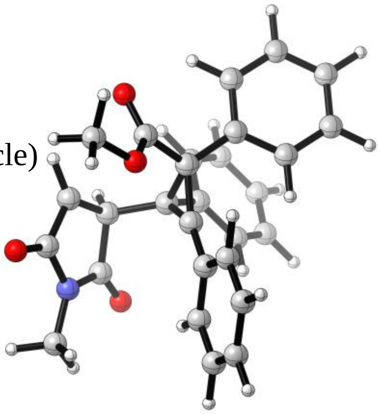
……

H	-4.133937	-1.666697	-2.889979
O	-0.531956	-2.289730	-2.388449

C	-3.408217	-1.946186	-2.120389
C	-1.020088	-1.203671	-2.160859
H	-2.936175	-2.898035	-2.374799
H	-3.931956	-2.031507	-1.162179
N	-2.371349	-0.943984	-2.032269
H	0.441959	0.303511	-2.693849
C	-0.267721	0.102530	-1.879599
H	2.585598	0.603966	-2.172249
C	-2.650301	0.424595	-1.846289
H	0.308589	5.339351	-0.834839
O	-3.774302	0.881223	-1.744949
H	4.744861	-0.537450	-2.542999
C	-0.185859	4.509780	-0.334339
C	-1.367392	1.100308	-1.833899
C	2.790460	-0.342724	-1.670799
H	-1.280815	2.173928	-1.949499
C	4.011852	-0.975112	-1.869009
H	-2.030831	5.585197	-0.034409
C	-1.498669	4.648978	0.115511
C	0.493593	3.309742	-0.155879
H	1.511773	3.195003	-0.520809
C	0.540830	-0.155178	-0.575229
C	1.834471	-0.888166	-0.807819
C	-2.126087	3.582546	0.752121
C	-0.134865	2.229190	0.473561
C	4.296504	-2.164641	-1.199909
C	-0.193090	-0.344130	0.668361
C	-1.445825	2.381908	0.934191
C	0.553968	0.902342	0.603601
H	-3.153207	3.675964	1.095421
H	-1.148495	-2.764162	-0.011949
H	5.250225	-2.663489	-1.355389
C	2.132154	-2.072815	-0.135849
C	3.355895	-2.707963	-0.331009

C	-1.401916	-2.457622	1.002831
C	-0.938238	-1.203991	1.484211
H	-1.949913	1.539387	1.405611
O	2.783396	1.675826	0.805971
C	1.854618	0.898674	1.379381
H	1.404094	-2.495257	0.553851
C	-2.156794	-3.284164	1.816551
H	-2.503852	-4.241724	1.434481
C	-1.252349	-0.837032	2.818911
H	3.571217	-3.632773	0.198651
H	-0.866821	0.104429	3.206401
H	4.714125	2.274500	0.811731
C	4.087917	1.588889	1.383411
O	2.048739	0.247775	2.377941
C	-2.469495	-2.900044	3.124261
C	-2.007467	-1.675573	3.618421
H	4.462489	0.563109	1.294891
H	4.064706	1.874688	2.438641
H	-3.062753	-3.554785	3.757871
H	-2.235798	-1.382824	4.640581

^{3}Int3al’



Number of imaginary frequencies: 0

Electronic energy: HF=-1435.5011173

Zero-point correction= 0.439014 (Hartree/Particle)

Thermal correction to Energy= 0.468043

Thermal correction to Enthalpy= 0.468987

Thermal correction to Gibbs Free Energy= 0.377133

Sum of electronic and zero-point Energies= -1435.062104

Sum of electronic and thermal Energies= -1435.033074

Sum of electronic and thermal Enthalpies= -1435.032130

Sum of electronic and thermal Free Energies= -1435.123984

……

Cartesian Coordinates

……

H	3.390253	-0.475168	4.814205
H	3.204111	1.656477	3.547833
C	2.748212	-0.415739	3.938815
C	2.644315	0.781516	3.224438
H	-2.683460	3.727983	1.816795
C	2.020104	-1.536384	3.524457
H	-4.058148	-0.967203	2.851670
H	2.097415	-2.468425	4.079627
C	1.829136	0.867876	2.108639
C	-2.585803	3.145637	0.903596
H	1.744593	1.805879	1.560789
H	-0.763610	2.185062	1.539559
C	-3.773579	-1.167445	1.821315
H	-5.761933	-1.724860	1.206235
C	-1.504630	2.282463	0.747750
H	-4.386393	3.930880	0.021266
C	-4.726580	-1.592608	0.900954
C	1.203451	-1.468764	2.410739
C	-3.538571	3.261508	-0.103772
C	1.088695	-0.262408	1.670398
H	-1.710897	-0.657665	2.152247
C	-2.449777	-0.997511	1.428116
C	-4.344516	-1.848307	-0.413512
H	0.641912	-2.339311	2.076858
C	-1.364996	1.532510	-0.417731
C	-2.061003	-1.239080	0.108137
H	3.994500	2.775681	-0.154073
C	-3.404255	2.515544	-1.273457
C	0.247491	-0.204715	0.551752
H	4.581995	1.123192	0.215767
H	-5.081702	-2.181727	-1.140468
C	-3.023212	-1.671613	-0.810412

C	4.222972	1.792916	-0.572867
O	3.946747	-0.649661	-2.073782
C	-0.246076	0.546525	-0.592092
C	-2.321063	1.658917	-1.428188
C	-0.638720	-0.971146	-0.312105
C	2.975906	0.057119	-1.872322
N	3.010546	1.265332	-1.156022
H	-4.149839	2.594427	-2.061154
C	1.600516	-0.118022	-2.301882
C	1.776607	1.891056	-1.096460
H	-2.731368	-1.863779	-1.839697
H	4.999724	1.879949	-1.338396
O	1.562216	2.966790	-0.582201
C	0.745693	0.947136	-1.722780
H	-2.229050	1.053055	-2.331084
C	-0.057666	-2.036882	-1.207351
O	1.036325	-2.590893	-0.672069
H	1.306743	-0.842390	-3.052299
H	0.174445	1.483762	-2.493638
O	-0.518230	-2.364812	-2.279644
C	1.692505	-3.580110	-1.470732
H	2.518728	-3.949171	-0.863613
H	1.000180	-4.387024	-1.725896
H	2.080576	-3.128287	-2.389457

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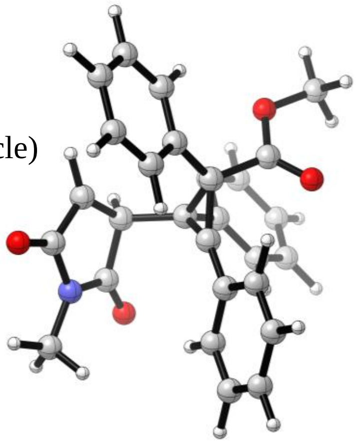
^{1}Int3al



Number of imaginary frequencies: 0

Electronic energy: HF=-1435.4687375

Zero-point correction= 0.438587 (Hartree/Particle)

Thermal correction to Energy= 0.467823

Thermal correction to Enthalpy= 0.468767

Thermal correction to Gibbs Free Energy= 0.377168

Sum of electronic and zero-point Energies= -1435.030150

Sum of electronic and thermal Energies= -1435.000915

Sum of electronic and thermal Enthalpies= -1434.999971

Sum of electronic and thermal Free Energies= -1435.091569

Cartesian Coordinates

H	-1.905232	-1.830273	4.635449
H	-2.497815	-4.058338	3.704525
C	-1.673535	-2.064870	3.599139
C	-2.003736	-3.320107	3.077579
H	-0.763303	-0.151502	3.215037
C	-1.044565	-1.121084	2.807921
O	2.090676	0.319743	2.343956
C	-1.687652	-3.625740	1.750222
H	3.906515	2.157272	2.458296
C	-0.727611	-1.409843	1.454591
H	-1.932612	-4.605553	1.346065
C	3.935888	1.935870	1.387866
C	1.794695	0.997847	1.389444
C	-1.057605	-2.693589	0.943753
H	4.422742	0.966573	1.233283
H	-2.110188	1.112073	1.378541
H	1.691990	-2.410333	0.342394
H	3.960208	-3.275980	-0.135715
C	-0.108624	-0.439663	0.655757
O	2.615792	1.904312	0.840705
C	-1.710378	2.055396	1.008754
C	0.480943	0.890845	0.644307
H	4.465649	2.719828	0.845789
C	3.634219	-2.342208	-0.587325
C	2.354661	-1.860305	-0.322691
H	-3.586526	3.084204	1.199224
C	-2.543515	3.165764	0.904358
C	-0.374070	2.123915	0.601865

H	-0.803966	-2.936510	-0.087770
C	0.556308	-0.099520	-0.589939
C	1.915910	-0.667752	-0.895774
C	4.489802	-1.635351	-1.425953
C	-2.045869	4.365393	0.406754
C	0.121347	3.338149	0.110781
H	5.487318	-2.014575	-1.635176
C	-0.709638	4.448678	0.015713
H	-2.695962	5.232455	0.319361
C	2.786574	0.042365	-1.729230
C	4.063532	-0.436208	-1.995569
H	1.157521	3.400482	-0.212153
H	-3.361011	-2.641929	-1.259317
C	-0.303650	0.140130	-1.875015
C	-1.425505	1.108141	-1.834655
C	-2.693492	0.405371	-1.874589
C	-1.020632	-1.184468	-2.150777
H	-0.314632	5.383764	-0.375202
N	-2.376830	-0.961576	-2.039085
O	-3.827728	0.841175	-1.807621
O	-0.507686	-2.261642	-2.370009
C	-3.367396	-2.007215	-2.152759
H	2.467959	0.996255	-2.151752
H	4.729118	0.128615	-2.644481
H	-1.362439	2.185864	-1.927938
H	-4.345191	-1.530949	-2.254707
H	0.391717	0.359120	-2.696750
H	-3.150915	-2.627873	-3.026818

^{1}Int3al'

Number of imaginary frequencies: 0

Electronic energy: HF=-1435.4787621

Zero-point correction= 0.438459 (Hartree/Particle)

Thermal correction to Energy= 0.467651

Thermal correction to Enthalpy= 0.468595

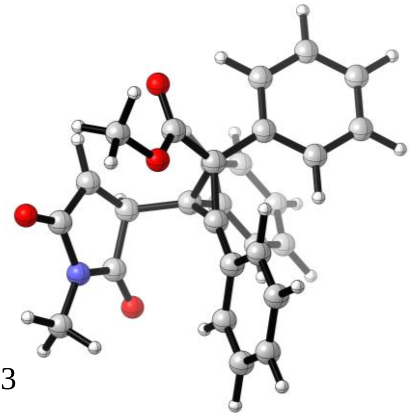
Thermal correction to Gibbs Free Energy= 0.377039

Sum of electronic and zero-point Energies= -1435.040303

Sum of electronic and thermal Energies= -1435.011112

Sum of electronic and thermal Enthalpies= -1435.010167

Sum of electronic and thermal Free Energies= -1435.101723



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Cartesian Coordinates

……

H	2.949464	2.169304	4.685410
H	2.814623	3.439617	2.552765
C	2.393446	1.763665	3.843680
C	2.317547	2.476335	2.643744
H	-2.891394	4.056664	-0.284896
C	1.749177	0.527475	3.958286
H	-4.183070	0.273016	2.857421
H	1.805312	-0.029640	4.890641
C	1.609389	1.971441	1.565755
C	-2.733548	3.108557	-0.793547
H	1.555201	2.530116	0.632844
H	-0.918276	2.667595	0.283617
C	-3.826332	-0.367532	2.054176
H	-5.747862	-1.276062	1.700079
C	-1.622420	2.331581	-0.475607
H	-4.510368	3.276581	-1.998264
C	-4.701319	-1.234445	1.407304
C	1.041469	0.006507	2.890583
C	-3.639387	2.672631	-1.755142
C	0.952865	0.716637	1.664585
H	-1.813107	0.373797	2.181101
C	-2.488251	-0.315332	1.676072
C	-4.226270	-2.048893	0.382530
H	0.545109	-0.958925	2.970845

C	-1.405613	1.116756	-1.121521
C	-2.005176	-1.121929	0.642176
H	4.265226	1.504493	-0.219256
C	-3.428421	1.457736	-2.405511
C	0.211104	0.173612	0.604161
H	5.106815	0.336509	-1.283668
H	-4.901905	-2.730107	-0.129919
C	-2.890481	-1.993542	-0.000621
C	4.318207	1.090470	-1.232335
O	3.854553	-1.729848	-1.791573
C	-0.238588	0.239295	-0.768534
C	-2.315314	0.687808	-2.091473
C	-0.572907	-0.984130	0.196946
C	2.936074	-0.931369	-1.827364
N	3.069249	0.448370	-1.572808
H	-4.137411	1.106284	-3.151420
C	1.533831	-1.149367	-2.134241
C	1.882772	1.134998	-1.735995
H	-2.526206	-2.628934	-0.803027
H	4.524455	1.903509	-1.934507
O	1.757793	2.338522	-1.658108
C	0.777953	0.106018	-1.963431
H	-2.161364	-0.274972	-2.581480
C	0.141992	-2.295618	-0.036875
O	1.338005	-2.318956	0.567384
H	1.154943	-2.086779	-2.525320
H	0.212930	0.366590	-2.868830
O	-0.300754	-3.227055	-0.671758
C	2.104715	-3.515465	0.384453
H	3.007051	-3.379344	0.980382
H	1.535620	-4.385261	0.723596
H	2.373619	-3.637334	-0.669536

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Number of imaginary frequencies: 0

Electronic energy: HF=-1435.5812458

Zero-point correction= 0.443120 (Hartree/Particle)

Thermal correction to Energy= 0.471579

Thermal correction to Enthalpy= 0.472523

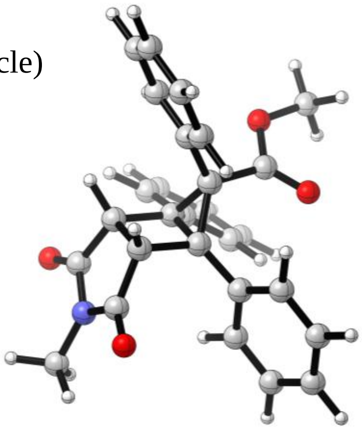
Thermal correction to Gibbs Free Energy= 0.381966

Sum of electronic and zero-point Energies= -1435.138125

Sum of electronic and thermal Energies= -1435.109667

Sum of electronic and thermal Enthalpies= -1435.108723

Sum of electronic and thermal Free Energies= -1435.199280



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Cartesian Coordinates

……

H	-4.987837	-0.618039	-2.167074
H	-0.484788	4.916376	-1.848104
C	-4.279732	-1.115537	-1.508491
C	-0.157094	4.228514	-1.072288
C	-3.180138	-0.417102	-1.021519
H	0.521928	5.787321	0.252930
H	-0.726651	2.485757	-2.192738
H	-5.335375	-2.994014	-1.532342
C	-0.300121	2.859167	-1.263454
C	-4.475804	-2.448140	-1.150865
C	0.408281	4.716214	0.103367
H	-3.127545	1.492501	3.370674
C	-2.828292	2.113701	2.521699
H	-3.665836	2.716786	2.170675
C	-2.261063	-1.044834	-0.177772
O	-2.441379	1.301141	1.413594
C	0.120885	1.953579	-0.283202

C	0.836145	3.822761	1.081240
C	-1.446273	0.437463	1.653001
C	-3.569120	-3.078517	-0.303262
O	-0.937138	0.287259	2.737824
C	-1.087654	-0.294047	0.379924
C	0.697744	2.450549	0.891337
C	-0.123150	0.508064	-0.503129
C	-2.467181	-2.378320	0.180231
H	1.287658	4.191799	1.999431
H	-1.993612	2.756109	2.821750
H	-3.717761	-4.117358	-0.018462
C	0.336042	-0.764255	0.229173
H	1.034256	1.765070	1.666643
H	-1.752082	-2.869410	0.840761
C	1.846505	-1.730974	-1.581166
C	1.184440	0.216836	-2.671597
N	2.217736	-0.672321	-2.408660
O	2.558931	-2.663672	-1.292060
O	1.270002	1.152311	-3.436064
C	3.529686	-0.543127	-3.005065
H	3.460687	-0.609901	-4.094984
H	4.151773	-1.353441	-2.618855
H	3.963000	0.426617	-2.743021
C	0.426658	-1.490353	-1.133353
C	-0.020296	-0.204059	-1.858981
H	-0.163888	-2.407356	-1.232625
H	-0.918728	-0.219595	-2.486586
C	1.338212	-1.007948	1.297771
C	1.093092	-1.951483	2.296764
C	2.587375	-0.385281	1.247367
C	3.568314	-0.689075	2.187031
C	2.071992	-2.260842	3.232410
C	3.312303	-1.628135	3.181167
H	2.792168	0.347582	0.466313

H	0.117039	-2.430759	2.350141
H	1.865254	-2.994075	4.008280
H	4.534887	-0.193125	2.138560
H	4.077773	-1.868091	3.915325
H	-3.030348	0.630282	-1.282462

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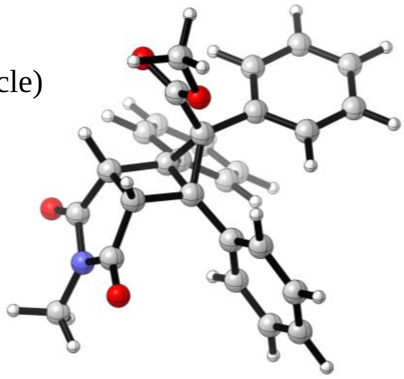


Number of imaginary frequencies: 0

Electronic energy: HF=-1435.5804366

Zero-point correction= 0.443624 (Hartree/Particle)

Thermal correction to Energy= 0.471889

Thermal correction to Enthalpy= 0.472833

Thermal correction to Gibbs Free Energy= 0.383614

Sum of electronic and zero-point Energies= -1435.136813

Sum of electronic and thermal Energies= -1435.108548

Sum of electronic and thermal Enthalpies= -1435.107604

Sum of electronic and thermal Free Energies= -1435.196823

Cartesian Coordinates

H	5.10419	0.98255	0.22084
H	1.26437	5.16843	-0.01906
C	4.34445	0.24701	-0.03206
C	1.20013	4.18286	-0.47390
C	3.08350	0.33252	0.54358
H	2.20389	4.77194	-2.28799
H	0.17296	3.33100	1.20962
H	5.61060	-0.83611	-1.40004
C	0.58733	3.14555	0.22087
C	4.62757	-0.77229	-0.93926
C	1.72441	3.96137	-1.74424
H	2.01455	-2.29630	4.20859
C	1.02950	-2.60209	3.84469

H	0.96016	-3.68865	3.79216
C	2.08584	-0.59520	0.21933
O	0.82406	-2.13128	2.51045
C	0.48995	1.86833	-0.34190
C	1.62870	2.69497	-2.31497
C	0.89471	-0.80091	2.35017
C	3.64952	-1.71234	-1.24730
O	1.08262	-0.02307	3.25740
C	0.75150	-0.43551	0.89568
C	1.01770	1.65628	-1.62057
C	-0.08096	0.77966	0.48632
C	2.38662	-1.63169	-0.66401
H	2.03757	2.50873	-3.30539
H	0.26314	-2.20022	4.51456
H	3.86678	-2.51795	-1.94483
C	-0.56176	-0.65405	0.19185
H	0.97646	0.66656	-2.07072
H	1.63280	-2.37337	-0.91182
C	-3.04512	-0.36324	0.64313
C	-2.34837	1.82630	1.01309
N	-3.31966	0.98967	0.47417
O	-3.78940	-1.26665	0.33806
O	-2.44840	3.03171	1.06218
C	-4.54507	1.49378	-0.10766
H	-5.12265	2.04399	0.64132
H	-5.11934	0.63805	-0.46874
H	-4.31243	2.17176	-0.93362
C	-1.67081	-0.48075	1.25476
C	-1.20602	0.97019	1.51465
H	-1.68063	-1.21906	2.06535
H	-0.90121	1.27676	2.52077
C	-0.83557	-1.43568	-1.03877
C	-0.81758	-2.83255	-0.96531
C	-1.25178	-0.82334	-2.22112

C	-1.17304	-3.60176	-2.06570
C	-1.60371	-1.59435	-3.32723
C	-1.56034	-2.98254	-3.25356
H	-0.52366	-3.30845	-0.02914
H	-1.15517	-4.68688	-1.99659
H	-1.83907	-3.58360	-4.11575
H	-1.30808	0.26326	-2.27238
H	-1.92057	-1.10602	-4.24576
H	2.85406	1.13712	1.24144

1d

Number of imaginary frequencies: 0

Electronic energy: HF= -1373.9510688

Zero-point correction= 0.347522 (Hartree/Particle)

Thermal correction to Energy= 0.372231

Thermal correction to Enthalpy= 0.373175

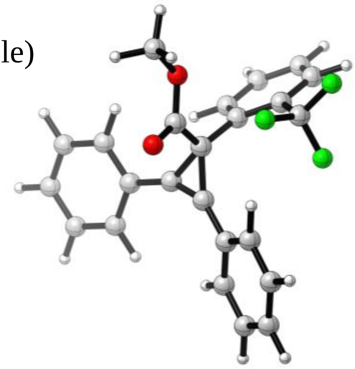
Thermal correction to Gibbs Free Energy= 0.291393

Sum of electronic and zero-point Energies= -1373.603547

Sum of electronic and thermal Energies= -1373.578838

Sum of electronic and thermal Enthalpies= -1373.577894

Sum of electronic and thermal Free Energies= -1373.659675



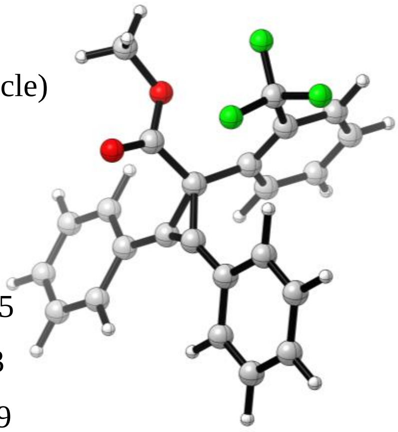
Cartesian Coordinates

H	0.34078	-3.42821	-3.20919
H	5.01515	-2.54531	0.57954
C	-0.31836	-2.87810	-2.54186
C	4.65939	-1.57041	0.25517
C	0.22208	-2.02042	-1.59178
H	6.63117	-0.81969	-0.17952
H	2.58336	-2.04522	0.60123
H	-2.13551	-3.69689	-3.36870
C	-1.69635	-3.02961	-2.63192

C	3.29776	-1.29368	0.26602
C	5.56611	-0.60135	-0.16875
H	0.43650	-2.20638	3.88319
H	-0.66620	-3.48684	3.27215
C	-0.45980	-2.41620	3.29204
C	-0.57620	-1.29175	-0.70607
O	-0.27179	-2.02677	1.93273
C	5.10660	0.65055	-0.57702
C	2.82775	-0.03851	-0.14494
C	-0.00238	-0.72341	1.74470
C	-2.51446	-2.31031	-1.77139
C	0.11100	-0.38111	0.28539
O	0.17894	0.05976	2.64823
C	3.74775	0.93327	-0.56460
C	1.42006	0.25553	-0.09595
C	-1.97008	-1.45262	-0.81386
H	-1.30532	-1.87176	3.72545
H	5.81331	1.40966	-0.90355
H	-3.59364	-2.41107	-1.84231
C	0.39981	1.06203	-0.05030
H	3.38386	1.91138	-0.87299
H	1.30228	-1.90564	-1.53429
C	-2.95252	-0.64411	-0.01399
F	-4.14441	-1.25356	0.09024
F	-3.18490	0.54797	-0.59612
F	-2.55485	-0.38153	1.24407
C	-0.17023	2.38193	-0.13478
C	0.44850	3.35494	-0.93330
C	-1.31736	2.71903	0.59347
C	-0.07304	4.63966	-1.00266
C	-1.21283	4.96934	-0.27082
C	-1.82983	4.00814	0.52723
H	1.33090	3.08523	-1.51118
H	0.40811	5.38640	-1.62981

H	-1.78765	1.96699	1.22097
H	-2.71675	4.26438	1.10138
H	-1.62051	5.97605	-0.32399

^{3}1d



Number of imaginary frequencies: 0

Electronic energy: HF= -1373.8712684

Zero-point correction= 0.343853 (Hartree/Particle)

Thermal correction to Energy= 0.368795

Thermal correction to Enthalpy= 0.369739

Thermal correction to Gibbs Free Energy= 0.286692

Sum of electronic and zero-point Energies= -1373.527415

Sum of electronic and thermal Energies= -1373.502473

Sum of electronic and thermal Enthalpies= -1373.501529

Sum of electronic and thermal Free Energies= -1373.584577

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Cartesian Coordinates

……

H	0.52783	-0.87434	4.35339
H	-4.75781	-2.88365	0.82432
C	0.98697	-0.89532	3.36809
C	-4.51056	-1.85234	0.58315
C	0.21389	-0.63652	2.24446
H	-6.57867	-1.22431	0.47180
H	-2.38716	-2.19365	0.63193
H	2.95510	-1.40180	4.09635
C	2.33854	-1.18858	3.22741
C	-3.19008	-1.47373	0.47442
C	-5.53946	-0.91789	0.38367
H	-0.70568	-3.56687	-2.57388
H	0.67214	-4.32989	-1.70486
C	0.28241	-3.40611	-2.13336
C	0.75348	-0.65244	0.95288

O	0.20592	-2.47686	-1.05157
C	-5.22246	0.41030	0.06328
C	-2.84598	-0.12302	0.15696
C	-0.22988	-1.25089	-1.38097
C	2.89684	-1.20470	1.95762
C	-0.17151	-0.33046	-0.18960
O	-0.64724	-0.94876	-2.47115
C	-3.90749	0.80995	-0.05255
C	-1.52054	0.27018	0.09764
C	2.12591	-0.93090	0.82578
H	0.96185	-3.02644	-2.90353
H	-6.02071	1.12983	-0.10415
H	3.95331	-1.43025	1.83267
C	-0.51235	1.11434	-0.40586
H	-3.65657	1.83491	-0.31861
H	-0.84642	-0.41704	2.35650
C	2.87865	-1.01439	-0.47320
F	3.18477	-2.28590	-0.78979
F	4.05054	-0.35521	-0.39480
F	2.23038	-0.49751	-1.52823
C	0.05204	2.37948	-0.34397
C	-0.75656	3.50110	0.01647
C	1.42298	2.61679	-0.66351
C	-0.22327	4.77307	0.04436
C	1.12474	4.98494	-0.27563
C	1.93724	3.89496	-0.62524
H	-1.79967	3.32829	0.27533
H	-0.85230	5.61582	0.32203
H	2.04920	1.77642	-0.95112
H	2.98344	4.05936	-0.87247
H	1.53991	5.98936	-0.25244

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^{3}TS3aa

Number of imaginary frequencies: 1 (-294.2836 cm-1)

Electronic energy: HF=-1772.4104837

Zero-point correction= 0.441159 (Hartree/Particle)

Thermal correction to Energy= 0.474063

Thermal correction to Enthalpy= 0.475007

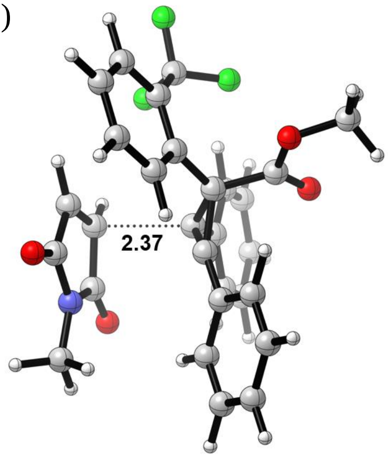
Thermal correction to Gibbs Free Energy= 0.374350

Sum of electronic and zero-point Energies= -1771.969325

Sum of electronic and thermal Energies= -1771.936420

Sum of electronic and thermal Enthalpies= -1771.935476

Sum of electronic and thermal Free Energies= -1772.036133



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Cartesian Coordinates

……

H	0.744005	-4.622585	0.165803
C	1.290848	-3.690926	0.049163
H	1.838171	5.001044	-0.925865
H	3.034508	-4.607375	-0.825999
C	0.921907	4.439968	-0.759666
H	-0.305951	-2.515079	0.855855
C	2.560658	-3.681799	-0.510780
H	-0.349480	6.180195	-0.871222
C	0.698849	-2.495485	0.440082
C	-0.308312	5.103277	-0.725858
O	-2.552351	1.180624	-2.414736
H	1.937674	2.559830	-0.584094
C	0.980972	3.071166	-0.572001
H	0.255225	0.925161	-2.720354
C	-1.481037	4.383780	-0.499457
C	-1.850471	0.187715	-2.357942
C	-0.197331	2.327290	-0.346630
C	-0.360735	0.088419	-2.413081
C	3.223048	-2.471094	-0.679165
C	1.337716	-1.267470	0.273076
C	-1.430620	3.011931	-0.314613

H	-2.438746	4.896823	-0.467371
C	-0.167973	0.903884	-0.191954
H	2.952446	-0.571803	4.389320
O	1.862447	-0.256696	2.718664
C	2.626513	-1.271874	-0.291256
H	3.104397	1.082328	3.707775
H	4.213724	-2.453879	-1.123329
H	-3.920072	-1.933326	-1.121582
C	0.621645	-0.017107	0.733109
C	2.417595	0.259536	3.929465
N	-2.316873	-1.112281	-2.199500
C	1.151307	0.625031	1.999410
H	-2.344045	2.453313	-0.138069
C	-3.704032	-1.497748	-2.104099
C	-0.035824	-1.242415	-2.427810
H	-4.312468	-0.601459	-2.251110
H	0.935949	-1.702909	-2.560504
C	-0.866369	0.010772	0.654325
C	-1.258881	-2.033345	-2.229478
O	0.920105	1.753469	2.358596
H	1.626791	0.624952	4.591070
C	3.360252	-0.002287	-0.601818
H	-3.942757	-2.237276	-2.874800
F	4.646331	-0.210295	-0.910034
F	3.351735	0.881930	0.413640
F	2.812645	0.632636	-1.661180
H	-3.401826	0.617947	0.004480
O	-1.398064	-3.238437	-2.127385
C	-2.009401	-0.340102	1.370738
C	-3.307050	0.040585	0.923683
C	-1.908834	-1.117490	2.559928
H	-0.920616	-1.401887	2.919919
C	-4.430039	-0.339530	1.632787
H	-5.414423	-0.043376	1.277304

C	-3.043099	-1.487155	3.255333
C	-4.310982	-1.104316	2.799491
H	-2.949738	-2.075098	4.165285
H	-5.200067	-1.398960	3.351166

^{3}TS3aa'

Number of imaginary frequencies: 1 (-241.2317 cm-1)

Electronic energy: HF=-1772.4049385

Zero-point correction= 0.441206 (Hartree/Particle)

Thermal correction to Energy= 0.473990

Thermal correction to Enthalpy= 0.474934

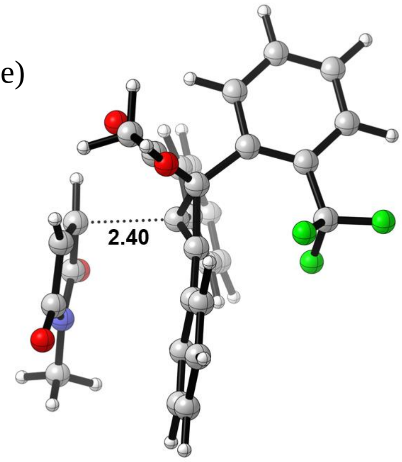
Thermal correction to Gibbs Free Energy= 0.375195

Sum of electronic and zero-point Energies= -1771.963732

Sum of electronic and thermal Energies= -1771.930948

Sum of electronic and thermal Enthalpies= -1771.930004

Sum of electronic and thermal Free Energies= -1772.029744



Cartesian Coordinates

F	-3.293216	-1.984669	-2.522077
H	-4.941325	-0.831390	-1.530124
C	-2.391469	-1.496113	-1.655500
F	-1.540419	-0.753297	-2.383421
H	2.091342	-4.682743	-0.956218
F	-1.709528	-2.550247	-1.184107
C	-4.411146	-0.472123	-0.654207
C	2.092406	-3.614025	-1.157334
C	-3.040295	-0.715297	-0.544848
H	3.790558	-3.715969	-2.490176
H	0.406336	-3.226561	0.120668
H	-6.170738	0.382749	0.231722
C	1.147481	-2.807646	-0.553647
C	-5.104255	0.204867	0.339178

C	3.050194	-3.071929	-2.022762
H	0.642421	-2.514753	3.928309
C	-0.308457	-2.829641	3.488154
H	-0.304068	-3.903317	3.301604
C	-2.332001	-0.257759	0.581510
O	-0.494947	-2.212518	2.210480
C	1.143280	-1.407210	-0.790436
C	3.056361	-1.697176	-2.274215
C	-0.559329	-0.878962	2.215598
C	-4.420349	0.639816	1.466852
O	-0.468253	-0.200900	3.213624
C	-0.833278	-0.352594	0.821120
C	2.125853	-0.874515	-1.669871
C	0.203120	-0.541031	-0.218483
C	-3.055982	0.410285	1.576940
H	3.802196	-1.268049	-2.939913
H	-1.123656	-2.557749	4.164466
H	-4.943101	1.165130	2.262277
C	-0.022332	0.784620	0.230745
H	2.136725	0.198328	-1.854502
H	-2.525129	0.764671	2.458162
C	2.544796	2.059161	0.764599
C	3.520228	-0.007248	1.065050
N	3.557315	1.197496	0.347441
O	2.387136	3.192390	0.355101
O	4.300768	-0.927857	0.921375
C	4.538293	1.529757	-0.654403
H	5.147520	0.638929	-0.829573
H	5.177420	2.353855	-0.319818
H	4.045248	1.833977	-1.585427
C	1.747151	1.302324	1.769584
C	2.378449	0.109021	1.987291
H	0.993301	1.776104	2.386733
H	2.145743	-0.662712	2.711223

C	-0.393138	2.046797	-0.320127
C	-1.099253	2.987409	0.458821
C	0.015171	2.410599	-1.619030
C	-1.383162	4.243084	-0.046257
C	-0.279026	3.667838	-2.121189
C	-0.973485	4.588983	-1.337348
H	-1.396968	2.717255	1.470843
H	-1.918760	4.964969	0.565231
H	-1.192997	5.579225	-1.728930
H	0.554425	1.685578	-2.226142
H	0.038172	3.937239	-3.125413

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^{3}Int3aa

Number of imaginary frequencies: 0

Electronic energy: HF=-1772.4514859

Zero-point correction= 0.444469 (Hartree/Particle)

Thermal correction to Energy= 0.476930

Thermal correction to Enthalpy= 0.477874

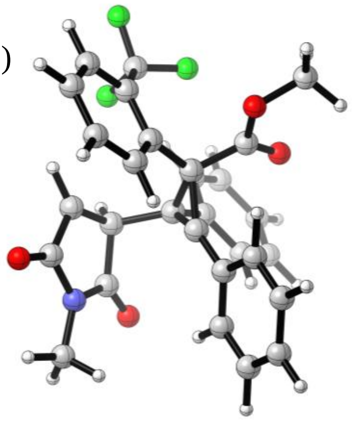
Thermal correction to Gibbs Free Energy= 0.378788

Sum of electronic and zero-point Energies= -1772.007017

Sum of electronic and thermal Energies= -1771.974556

Sum of electronic and thermal Enthalpies= -1771.973612

Sum of electronic and thermal Free Energies= -1772.072698



Cartesian Coordinates

F	2.839128	-0.336909	-1.780346
H	4.488343	2.255139	-0.378003
C	3.349076	-0.128441	-0.542320
F	4.674637	-0.018694	-0.695250
H	1.211702	-4.655237	-2.329171
F	3.134929	-1.259553	0.145048
C	3.476509	2.277714	0.015712

C	0.416631	-4.136869	-1.798083
C	2.738901	1.096697	0.076313
H	-0.805741	-5.897255	-1.573593
H	1.427977	-2.241949	-1.858323
H	3.510580	4.396370	0.378349
C	0.534334	-2.775882	-1.539469
C	2.926216	3.482531	0.440611
C	-0.711566	-4.832689	-1.372217
H	1.437676	-1.921483	4.147403
C	2.266598	-1.459901	3.602854
H	2.873628	-0.847148	4.269911
C	1.418147	1.107528	0.563834
O	1.777083	-0.573298	2.596282
C	-0.468458	-2.096563	-0.845887
C	-1.717637	-4.158053	-0.687098
C	0.991541	-1.150689	1.668366
C	1.627466	3.505025	0.931247
O	0.641878	-2.302512	1.721594
C	0.553417	-0.122024	0.648515
C	-1.595746	-2.798260	-0.425921
C	-0.316524	-0.620478	-0.582547
C	0.893794	2.326418	0.998475
H	-2.603026	-4.692668	-0.351199
H	2.873868	-2.248101	3.146324
H	1.175492	4.439759	1.252037
C	-0.908832	0.008051	0.578900
H	-2.380016	-2.282516	0.122957
H	-0.129780	2.352048	1.367363
C	-0.904094	2.551203	-1.993597
C	-1.819962	0.427933	-2.236124
N	-2.072182	1.785636	-2.178661
O	-0.877061	3.767480	-1.948642
O	-2.660770	-0.418744	-2.447717
C	-3.386837	2.357705	-2.358513

H	-3.872547	1.898054	-3.223723
H	-3.265654	3.432275	-2.513242
H	-4.008497	2.184839	-1.472785
C	0.186744	1.599532	-1.898764
C	-0.336608	0.209176	-1.909981
H	1.220487	1.906954	-2.002752
H	0.130985	-0.401788	-2.693841
C	-2.028039	0.233693	1.392760
C	-1.856572	0.637862	2.742599
C	-3.350480	0.091042	0.894511
C	-4.436272	0.348299	1.712973
C	-2.953793	0.887080	3.547738
C	-4.249048	0.748079	3.040018
H	-3.497914	-0.223791	-0.138396
H	-0.845781	0.736762	3.137890
H	-2.805765	1.189260	4.581855
H	-5.443395	0.233494	1.318740
H	-5.108061	0.946228	3.676186

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^{3}Int3aa'

Number of imaginary frequencies: 0

Electronic energy: HF=-1772.4508255

Zero-point correction= 0.444528 (Hartree/Particle)

Thermal correction to Energy= 0.476915

Thermal correction to Enthalpy= 0.477860

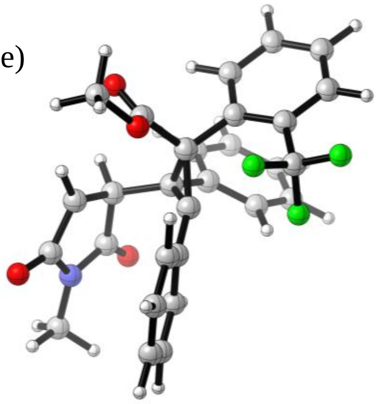
Thermal correction to Gibbs Free Energy= 0.379315

Sum of electronic and zero-point Energies= -1772.006298

Sum of electronic and thermal Energies= -1771.973910

Sum of electronic and thermal Enthalpies= -1771.972966

Sum of electronic and thermal Free Energies= -1772.071511



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Cartesian Coordinates

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F	-3.220606	-2.848679	-1.762459
H	-4.834145	-1.332872	-1.189021
C	-2.288434	-2.060627	-1.202183
F	-1.581888	-1.538095	-2.220321
H	2.832323	-4.134705	-1.252016
F	-1.465484	-2.871400	-0.519537
C	-4.268680	-0.773696	-0.450042
C	2.641158	-3.077205	-1.418347
C	-2.899627	-1.011822	-0.315653
H	4.312721	-2.832767	-2.761432
H	0.932541	-3.031790	-0.109297
H	-5.977029	0.334027	0.231992
C	1.573970	-2.468269	-0.779136
C	-4.912414	0.154966	0.356331
C	3.475733	-2.346193	-2.266995
H	1.098782	-2.480183	3.812297
C	0.231085	-2.926611	3.316041
H	0.431477	-3.967966	3.065020
C	-2.148737	-0.291285	0.627341
O	-0.026582	-2.268003	2.072009
C	1.325120	-1.087956	-0.962515
C	3.230158	-0.987216	-2.478002
C	-0.335816	-0.971806	2.158206
C	-4.188581	0.834331	1.329253
O	-0.394770	-0.360825	3.202881
C	-0.646028	-0.368767	0.809371
C	2.172631	-0.363314	-1.838905
C	0.281623	-0.387152	-0.315118
C	-2.826365	0.604760	1.459668
H	3.869434	-0.415889	-3.147731
H	-0.636856	-2.846934	3.976243
H	-4.679210	1.552948	1.980900
C	0.156212	0.911066	0.348758
H	1.970751	0.694740	-2.011676

H	-2.254784	1.142545	2.212707
C	2.354368	2.165398	0.303705
C	3.598021	0.389799	1.146460
N	3.586796	1.540503	0.340819
O	2.117488	3.163593	-0.339509
O	4.564025	-0.330912	1.314242
C	4.714435	1.982470	-0.444737
H	5.509364	1.241896	-0.329366
H	5.062103	2.962640	-0.103911
H	4.423814	2.064905	-1.497713
C	1.382676	1.360188	1.182860
C	2.263957	0.280084	1.706227
H	1.030864	2.005234	2.004749
H	2.038195	-0.437189	2.485598
C	-0.661389	2.018290	-0.245006
C	-1.011948	3.139804	0.510234
C	-1.156227	1.903907	-1.544795
C	-1.848686	4.116535	-0.014950
C	-2.002299	2.876102	-2.070721
C	-2.353330	3.984766	-1.306945
H	-0.634976	3.254932	1.525717
H	-2.108598	4.984121	0.587160
H	-3.010926	4.747178	-1.717717
H	-0.885952	1.033930	-2.142970
H	-2.382461	2.767157	-3.083823

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^{1}Int3aa

Number of imaginary frequencies: 0

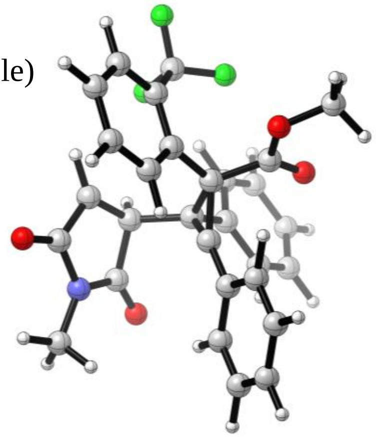
Electronic energy: HF=-1772.4522366

Zero-point correction= 0.444578 (Hartree/Particle)

Thermal correction to Energy= 0.476894

Thermal correction to Enthalpy= 0.477839

Thermal correction to Gibbs Free Energy= 0.380848



Sum of electronic and zero-point Energies= -1772.007659

Sum of electronic and thermal Energies= -1771.975342

Sum of electronic and thermal Enthalpies= -1771.974398

Sum of electronic and thermal Free Energies= -1772.071389

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Cartesian Coordinates

....

F	-2.857699	0.378945	-1.708729
H	-4.519912	-2.164292	-0.191528
C	-3.344136	0.192843	-0.457135
F	-4.673393	0.094818	-0.581742
H	-1.158869	4.649305	-2.387014
F	-3.104999	1.331976	0.208634
C	-3.493733	-2.196947	0.162186
C	-0.354990	4.121696	-1.878801
C	-2.733656	-1.029913	0.166708
H	0.922028	5.852838	-1.749771
H	-1.416860	2.253829	-1.849495
H	-3.550848	-4.306960	0.571811
C	-0.496818	2.770945	-1.582680
C	-2.947978	-3.403316	0.590572
C	0.808740	4.796199	-1.518758
H	-1.289084	2.056878	4.126719
C	-2.137276	1.595863	3.612130
H	-2.738093	1.008642	4.307177
C	-1.394424	-1.054720	0.604569
O	-1.684514	0.678373	2.616184
C	0.516905	2.080918	-0.915930
C	1.825406	4.110487	-0.861068
C	-0.912842	1.221358	1.656860
C	-1.631094	-3.440721	1.026264
O	-0.543838	2.368465	1.673291
C	-0.512271	0.165063	0.651193
C	1.679169	2.760788	-0.560993

C	0.337128	0.617208	-0.605299
C	-0.873967	-2.274285	1.040227
H	2.738389	4.628315	-0.576657
H	-2.742765	2.382811	3.151042
H	-1.182366	-4.377713	1.344948
C	0.946382	0.014855	0.552653
H	2.472813	2.236489	-0.034212
H	0.161929	-2.310287	1.372243
C	0.664570	-2.618344	-1.996553
C	1.753818	-0.579875	-2.234728
N	1.898545	-1.950176	-2.139593
O	0.540670	-3.828755	-1.958324
O	2.659641	0.195576	-2.452261
C	3.169680	-2.624133	-2.270356
H	3.691867	-2.263685	-3.161300
H	2.972053	-3.695371	-2.352088
H	3.797570	-2.431382	-1.393029
C	-0.345756	-1.579191	-1.934562
C	0.290097	-0.243766	-1.932590
H	-1.399947	-1.797681	-2.054324
H	-0.125965	0.410074	-2.709757
C	2.075903	-0.222303	1.350734
C	1.915233	-0.587607	2.712738
C	3.393198	-0.128755	0.828479
C	4.484518	-0.393870	1.637551
C	3.018046	-0.843616	3.508217
C	4.308204	-0.752090	2.977650
H	3.532740	0.149704	-0.215719
H	0.908560	-0.651751	3.125234
H	2.878203	-1.114781	4.552023
H	5.487791	-0.317775	1.224619
H	5.171762	-0.955523	3.605982

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^{1}Int3aa'

Number of imaginary frequencies: 0

Electronic energy: HF=-1772.4505179

Zero-point correction= 0.444433 (Hartree/Particle)

Thermal correction to Energy= 0.476853

Thermal correction to Enthalpy= 0.477797

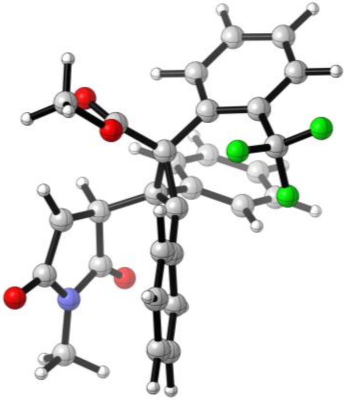
Thermal correction to Gibbs Free Energy= 0.380127

Sum of electronic and zero-point Energies= -1772.006085

Sum of electronic and thermal Energies= -1771.973665

Sum of electronic and thermal Enthalpies= -1771.972721

Sum of electronic and thermal Free Energies= -1772.070391



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Cartesian Coordinates

....

F	-3.221339	-2.826776	-1.800212
H	-4.829382	-1.342927	-1.171884
C	-2.285574	-2.047600	-1.232967
F	-1.604257	-1.487357	-2.248329
H	2.865859	-4.136386	-1.210919
F	-1.442341	-2.872903	-0.594834
C	-4.263453	-0.801673	-0.420155
C	2.663858	-3.082883	-1.389310
C	-2.891320	-1.032996	-0.302686
H	4.339637	-2.833803	-2.725532
H	0.947395	-3.042105	-0.090024
H	-5.977171	0.270355	0.303734
C	1.586724	-2.478589	-0.761817
C	-4.910292	0.097221	0.416471
C	3.494443	-2.351442	-2.240990
H	1.216976	-2.362320	3.865400
C	0.372760	-2.860144	3.377732
H	0.624167	-3.895158	3.147383
C	-2.139558	-0.334560	0.657437
O	0.083959	-2.239751	2.120933

C	1.323625	-1.104153	-0.962048
C	3.234693	-0.998082	-2.468672
C	-0.290010	-0.959294	2.180552
C	-4.185341	0.754858	1.402978
O	-0.373346	-0.331973	3.214065
C	-0.633590	-0.392364	0.822730
C	2.166849	-0.379430	-1.841156
C	0.277534	-0.406782	-0.315061
C	-2.820513	0.533094	1.517437
H	3.871095	-0.426963	-3.141249
H	-0.498648	-2.809489	4.036235
H	-4.676753	1.451495	2.077530
C	0.143886	0.895684	0.335589
H	1.954171	0.674482	-2.025725
H	-2.248680	1.055488	2.280853
C	2.320895	2.185170	0.244192
C	3.609496	0.465571	1.133400
N	3.568512	1.592431	0.295472
O	2.056667	3.156438	-0.428825
O	4.592832	-0.227290	1.317158
C	4.682192	2.037305	-0.508100
H	5.489825	1.311690	-0.386136
H	5.017854	3.028896	-0.188812
H	4.380839	2.095981	-1.559590
C	1.372314	1.382836	1.151334
C	2.280952	0.341963	1.703514
H	1.010463	2.042396	1.956886
H	2.075025	-0.355126	2.506187
C	-0.699611	1.987353	-0.250459
C	-1.080304	3.090926	0.516736
C	-1.185518	1.876968	-1.553680
C	-1.937011	4.054377	-0.000647
C	-2.051813	2.835542	-2.071745
C	-2.432251	3.926439	-1.296609

H	-0.713603	3.201087	1.536634
H	-2.220957	4.907651	0.610992
H	-3.105759	4.678010	-1.701527
H	-0.891250	1.021609	-2.161018
H	-2.424514	2.730168	-3.087995

3aa

Number of imaginary frequencies: 0

Electronic energy: HF=-1772.5337582

Zero-point correction= 0.449051 (Hartree/Particle)

Thermal correction to Energy= 0.480587

Thermal correction to Enthalpy= 0.481531

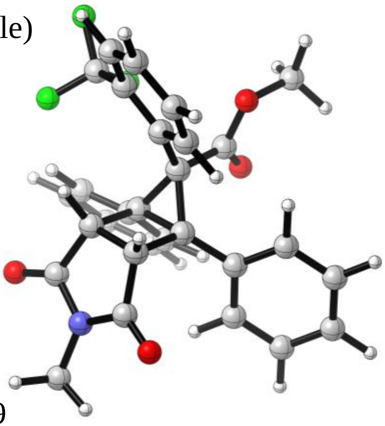
Thermal correction to Gibbs Free Energy= 0.385549

Sum of electronic and zero-point Energies= -1772.084708

Sum of electronic and thermal Energies= -1772.053171

Sum of electronic and thermal Enthalpies= -1772.052227

Sum of electronic and thermal Free Energies= -1772.148209



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Cartesian Coordinates

……

F	-2.818177	2.123772	-0.583950
H	-5.006417	-0.036485	-1.542022
C	-3.248170	1.036250	0.092794
F	-4.545552	1.250495	0.356523
H	-0.154570	4.848732	1.877041
F	-2.611582	1.030671	1.269826
C	-4.092932	-0.623985	-1.524584
C	0.345867	3.884441	1.920090
C	-3.037640	-0.219988	-0.705037
H	1.636228	4.437219	3.555227
H	-0.780084	3.086715	0.279912
H	-4.824002	-2.074092	-2.931095
C	-0.013786	2.884833	1.024268

C	-3.993306	-1.770916	-2.299714
C	1.350242	3.654882	2.855822
H	-1.112968	-3.062560	3.339834
C	-1.985112	-2.454585	3.078181
H	-2.885567	-3.068061	3.040084
C	-1.839742	-0.952533	-0.669648
O	-1.831793	-1.907563	1.767700
C	0.614194	1.634761	1.054702
C	1.990233	2.419401	2.886218
C	-0.762691	-1.109521	1.611986
C	-2.829041	-2.528550	-2.246270
O	0.013140	-0.868482	2.503911
C	-0.649541	-0.619848	0.192612
C	1.626258	1.416256	1.994109
C	0.235303	0.632241	0.020304
C	-1.775673	-2.117467	-1.440350
H	2.775895	2.228056	3.613501
H	-2.093756	-1.655076	3.816477
H	-2.738092	-3.441005	-2.830305
C	0.770384	-0.750726	-0.361866
H	2.112950	0.447830	2.049111
H	-0.869013	-2.719308	-1.397670
C	2.116876	-0.048058	-2.406259
C	1.202149	2.028487	-1.890389
N	2.321556	1.324860	-2.325698
O	2.909912	-0.842500	-2.857379
O	1.122291	3.234562	-1.880308
C	3.530174	1.985254	-2.770401
H	3.323956	2.608418	-3.645958
H	4.258318	1.212590	-3.026446
H	3.915811	2.624937	-1.971485
C	0.744642	-0.348146	-1.848983
C	0.153531	1.022466	-1.471747
H	0.208552	-1.009160	-2.537769

H	-0.830732	1.317365	-1.849265
C	1.800991	-1.662149	0.202051
C	1.479681	-2.978953	0.541150
C	3.127658	-1.242367	0.329283
C	4.106275	-2.113662	0.793972
C	2.456280	-3.853524	1.005508
C	3.773143	-3.421712	1.134485
H	3.397408	-0.219690	0.066393
H	0.448620	-3.322781	0.451693
H	2.187144	-4.873822	1.268337
H	5.133018	-1.768942	0.889050
H	4.538318	-4.102971	1.498560

3aa’

Number of imaginary frequencies: 0

Electronic energy: HF=-1772.5286169

Zero-point correction= 0.449156 (Hartree/Particle)

Thermal correction to Energy= 0.480369

Thermal correction to Enthalpy= 0.481313

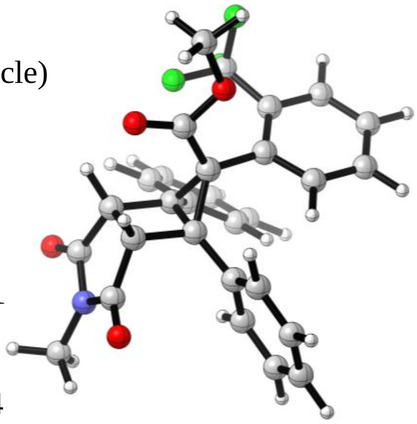
Thermal correction to Gibbs Free Energy= 0.387019

Sum of electronic and zero-point Energies= -1772.079461

Sum of electronic and thermal Energies= -1772.048248

Sum of electronic and thermal Enthalpies= -1772.047304

Sum of electronic and thermal Free Energies= -1772.141597



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Cartesian Coordinates

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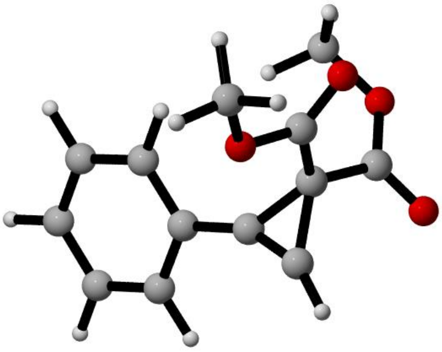
F	4.320637	0.112923	1.128243
H	4.512857	-0.605271	-1.470508
C	3.255608	0.553530	0.424938
F	3.707844	1.540437	-0.363429
H	1.474374	4.534841	-1.614837
F	2.430267	1.117902	1.318822

C	3.543168	-1.080422	-1.341643
C	1.156751	3.508725	-1.782162
C	2.666370	-0.574634	-0.382684
H	1.693222	3.504591	-3.869259
H	0.538973	3.240130	0.253655
H	3.890317	-2.550938	-2.871132
C	0.631732	2.774595	-0.724544
C	3.199431	-2.175561	-2.121071
C	1.278200	2.932780	-3.042693
H	2.824390	-0.860932	3.955506
C	2.410596	-1.812826	3.607550
H	3.201784	-2.553654	3.491389
C	1.396096	-1.154064	-0.194901
O	1.839158	-1.651098	2.308241
C	0.212144	1.452048	-0.905991
C	0.861224	1.618886	-3.238312
C	0.844006	-0.754983	2.225259
C	1.974907	-2.793023	-1.906048
O	0.393945	-0.196762	3.200409
C	0.402146	-0.582736	0.791493
C	0.329727	0.886821	-2.182468
C	-0.300984	0.709650	0.277096
C	1.098164	-2.289005	-0.951619
H	0.949472	1.155644	-4.218379
H	1.657436	-2.158100	4.321340
H	1.692269	-3.672568	-2.479333
C	-1.094628	-0.574794	0.455902
H	0.022832	-0.141688	-2.356472
H	0.148254	-2.789625	-0.805785
C	-3.290925	0.402109	1.232657
C	-2.109241	2.385379	0.939460
N	-3.322121	1.721465	0.791994
O	-4.250321	-0.333257	1.283909
O	-1.961024	3.568516	0.729072

C	-4.524482	2.389445	0.342323
H	-4.814102	3.171353	1.051099
H	-5.315323	1.639870	0.270376
H	-4.347590	2.852577	-0.632348
C	-1.868670	0.080902	1.623849
C	-1.076741	1.386922	1.419752
H	-1.841974	-0.425001	2.591869
H	-0.490634	1.796508	2.246327
C	-1.844539	-1.495837	-0.436963
C	-2.135930	-2.783173	0.026751
C	-2.404842	-1.065085	-1.638777
C	-2.936382	-3.638804	-0.717718
C	-3.206101	-1.924255	-2.388853
C	-3.467958	-3.212205	-1.934483
H	-1.726324	-3.107500	0.984331
H	-3.154772	-4.637069	-0.346146
H	-4.096824	-3.879795	-2.518439
H	-2.225325	-0.047683	-1.982753
H	-3.634345	-1.578807	-3.326828

1o

Number of imaginary frequencies : 0 Electronic energy : HF=-802.9688699
Zero-point correction= 0.222984 (Hartree/Particle)
Thermal correction to Energy= 0.239395
Thermal correction to Enthalpy= 0.240339
Thermal correction to Gibbs Free Energy= 0.177186
Sum of electronic and zero-point Energies= -802.745886
Sum of electronic and thermal Energies= -802.729475
Sum of electronic and thermal Enthalpies= -802.728531
Sum of electronic and thermal Free Energies= -802.791684



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Cartesian Coordinates

C	-0.470900	-0.276845	-1.950060
C	0.358123	-0.159798	-0.969285
C	-1.092397	-0.331430	-0.583184
H	-0.748489	-0.333482	-2.989505
C	1.678703	-0.009952	-0.403551
C	1.855512	0.570619	0.857141
C	2.798628	-0.427180	-1.134046
C	3.133235	0.730754	1.380152
H	0.985493	0.919222	1.411271
C	4.072941	-0.271104	-0.605076
H	2.654333	-0.882686	-2.111372
C	4.242500	0.306679	0.652340
H	3.264387	1.188469	2.357477
H	4.938300	-0.603735	-1.172887
H	5.241236	0.426849	1.064848
C	-1.917020	0.822898	-0.115438
C	-1.590316	-1.718182	-0.194465
C	-1.322101	-1.208677	2.160251
H	-0.379967	-0.692153	1.940993
H	-2.113281	-0.484166	2.371534
H	-1.169489	-1.857021	3.024897
C	-2.169433	3.149927	-0.138162
H	-3.160545	3.097069	-0.598105
H	-2.288329	3.220136	0.947119
H	-1.616180	4.008833	-0.518715
O	-1.394889	2.002390	-0.485987
O	-2.951942	0.716654	0.506321
O	-1.703827	-2.067311	1.094311
O	-1.833382	-2.535931	-1.048051

^{3}**1o**

Number of imaginary frequencies : 0 Electronic energy : HF

Zero-point correction= 0.220912 (Hartree/Particl

Thermal correction to Energy= 0.237256

Thermal correction to Enthalpy= 0.238201

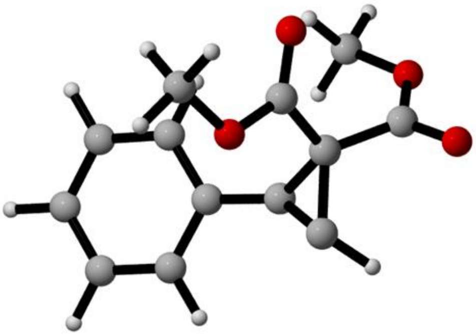
Thermal correction to Gibbs Free Energy= 0.175314

Sum of electronic and zero-point Energies= -802.656654

Sum of electronic and thermal Energies= -802.640310

Sum of electronic and thermal Enthalpies= -802.639366

Sum of electronic and thermal Free Energies= -802.702252



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Cartesian Coordinates

……

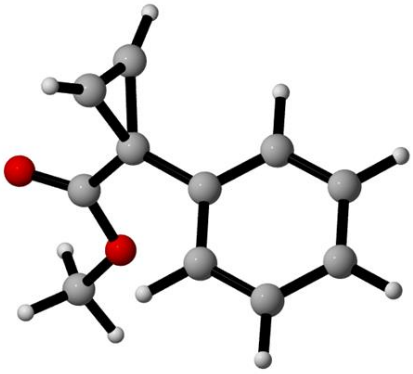
C	-0.688049	-0.300894	-1.968478
C	0.085877	-0.750501	-0.841042
C	-1.231283	-0.090711	-0.590066
H	-1.241013	-0.886511	-2.700613
C	1.398677	-0.596331	-0.370728
C	1.704515	-0.351627	0.995340
C	2.477151	-0.723235	-1.287249
C	3.017316	-0.243931	1.411551
H	0.892810	-0.235091	1.711369
C	3.786579	-0.621480	-0.854067
H	2.247130	-0.903268	-2.335351
C	4.067674	-0.383763	0.494972
H	3.236072	-0.047817	2.458619
H	4.600770	-0.721678	-1.567900
H	5.098117	-0.304586	0.832133
C	-1.174242	1.238016	0.105622
C	-2.526927	-0.861546	-0.321251
C	-1.591300	-1.649820	1.768177
H	-0.679333	-2.089991	1.349790
H	-1.396150	-0.653067	2.177182
H	-1.975342	-2.296607	2.558197
C	-0.153527	3.337499	0.153032

H	-1.103391	3.860365	0.293541
H	0.312285	3.168104	1.129113
H	0.510662	3.911325	-0.492891
O	-0.361419	2.091329	-0.515806
O	-1.767143	1.478421	1.133885
O	-2.626153	-1.595135	0.789811
O	-3.437457	-0.826020	-1.106398

1v

Number of imaginary frequencies : 0 Electronic energy : HF=-575.1983676

Zero-point correction= 0.179452 (Hartree/Particle)



Thermal correction to Energy= 0.191362

Thermal correction to Enthalpy= 0.192306

Thermal correction to Gibbs Free Energy= 0.140250

Sum of electronic and zero-point Energies= -575.018915

Sum of electronic and thermal Energies= -575.007006

Sum of electronic and thermal Enthalpies= -575.006061

Sum of electronic and thermal Free Energies= -575.058117

……

Cartesian Coordinates

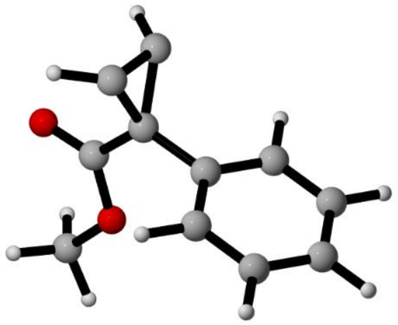
……

C	-0.858268	2.165113	0.898144
C	-0.876689	2.294268	-0.381024
C	-0.627696	0.895852	0.119892
H	-0.934368	2.549745	1.902757
H	-0.999711	2.878008	-1.280496
C	0.749847	0.301706	0.058116
C	1.695504	0.794555	-0.840500
C	1.130229	-0.715948	0.937590
C	2.989072	0.280203	-0.871759
H	1.415188	1.595978	-1.523509
C	2.421167	-1.231173	0.912978

H	0.403174	-1.110174	1.646259
C	3.355756	-0.735520	0.005607
H	3.711303	0.674728	-1.583020
H	2.700752	-2.021438	1.606230
H	4.365800	-1.138111	-0.014081
C	-1.815358	-0.024238	0.036841
O	-1.496639	-1.242848	-0.425495
O	-2.946321	0.301149	0.324200
C	-2.589045	-2.149310	-0.564822
H	-3.079891	-2.312291	0.399368
H	-3.326386	-1.756494	-1.271369
H	-2.159302	-3.079399	-0.938160

^{3}**1v**

Number of imaginary frequencies : 0 Electronic energy : HF=-575.0957887
Zero-point correction= 0.177585 (Hartree/Particle)
Thermal correction to Energy= 0.189711
Thermal correction to Enthalpy= 0.190655
Thermal correction to Gibbs Free Energy= 0.136372
Sum of electronic and zero-point Energies= -574.918204
Sum of electronic and thermal Energies= -574.906078
Sum of electronic and thermal Enthalpies= -574.905134
Sum of electronic and thermal Free Energies= -574.959417



Cartesian Coordinates

C	-0.809571	2.108052	0.904316
C	-0.829084	2.236252	-0.559942
C	-0.651749	0.884931	0.051158
H	-1.631275	2.279490	1.598131
H	-1.683566	2.518962	-1.173378
C	0.754967	0.356826	0.023952

C	1.489956	0.359694	-1.162687
C	1.337360	-0.138867	1.193117
C	2.786169	-0.146139	-1.184834
H	1.035281	0.758716	-2.067762
C	2.630202	-0.647526	1.170695
H	0.762777	-0.127119	2.118140
C	3.356807	-0.650993	-0.019281
H	3.352606	-0.144219	-2.113115
H	3.075994	-1.037104	2.082861
H	4.370514	-1.044463	-0.036238
C	-1.815097	-0.042544	-0.021825
O	-1.446399	-1.326064	-0.124618
O	-2.971237	0.325753	0.009588
C	-2.518142	-2.266112	-0.199799
H	-3.140711	-2.210761	0.698062
H	-3.143135	-2.065871	-1.075019
H	-2.048303	-3.246597	-0.280661

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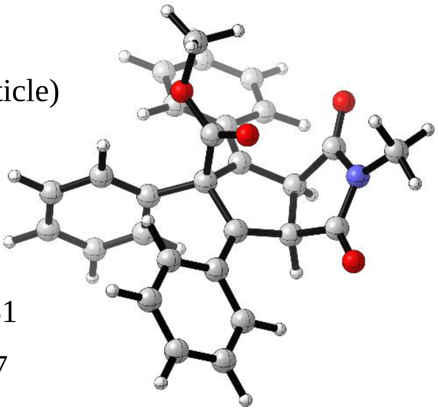
^{1}3al*



Number of imaginary frequencies: 0

Electronic energy: HF= -1435.5508441

Zero-point correction= 0.441513 (Hartree/Particle)

Thermal correction to Energy= 0.469967

Thermal correction to Enthalpy= 0.470911

Thermal correction to Gibbs Free Energy= 0.381283

Sum of electronic and zero-point Energies= -1435.109331

Sum of electronic and thermal Energies= -1435.080877

Sum of electronic and thermal Enthalpies= -1435.079933

Sum of electronic and thermal Free Energies= -1435.169561

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Cartesian Coordinates

....

H	-0.23516	-4.04539	-2.66533
H	-5.44551	1.40727	-1.82304
C	-0.19981	-3.71100	-1.63123
C	-4.78890	0.69563	-1.32794
C	-0.14553	-2.35243	-1.34806
H	-6.37681	-0.68662	-0.84291
H	-3.06849	1.90689	-1.64690
H	-0.25375	-5.70425	-0.80895
C	-3.43508	0.96826	-1.24199
C	-0.20975	-4.63959	-0.59290
C	-5.31295	-0.47297	-0.77397
H	-0.60488	0.30089	4.20717
C	-1.46103	0.27531	3.52748
H	-2.28216	-0.29613	3.96044
C	-0.10645	-1.89011	-0.02991
O	-1.11921	-0.39700	2.31017
C	-2.53363	0.07645	-0.59878
C	-4.45394	-1.35909	-0.12102
C	-0.13544	0.16658	1.60336
C	-0.15829	-4.19149	0.72260
O	0.51626	1.10796	2.00014
C	-0.02617	-0.37662	0.16603
C	-3.09839	-1.09677	-0.02887
C	-1.14269	0.38094	-0.56258
C	-0.10599	-2.82761	1.00258
H	-4.84847	-2.27003	0.32353
H	-1.77900	1.29935	3.30784
H	-0.15989	-4.90555	1.54307
C	1.23900	0.18648	-0.47779
H	-2.46313	-1.80532	0.49053
H	-0.08225	-2.50108	2.03907
C	1.57262	2.66403	-0.74009

C	-0.68834	2.84585	-0.25938
N	0.56833	3.40056	-0.12453
O	2.73396	2.99444	-0.79010
O	-1.69396	3.27759	0.25766
C	0.82665	4.53829	0.73265
H	0.10708	5.33189	0.51751
H	1.84510	4.88081	0.53987
H	0.72744	4.23764	1.78131
C	0.93474	1.39976	-1.31496
C	-0.56884	1.62024	-1.17328
H	1.26597	1.28489	-2.35824
H	-1.04942	1.87632	-2.12758
C	2.55473	-0.33541	-0.31633
C	3.60892	0.08367	-1.16676
C	2.87691	-1.27979	0.69001
C	4.16055	-1.77994	0.82332
C	4.88850	-0.42759	-1.03177
C	5.17644	-1.36553	-0.03966
H	2.11241	-1.60901	1.38674
H	3.41912	0.83244	-1.93017
H	5.67291	-0.08642	-1.70324
H	4.37520	-2.49730	1.61214
H	6.18297	-1.76297	0.06590
H	-0.14100	-1.62952	-2.16453

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^{1}TS6h

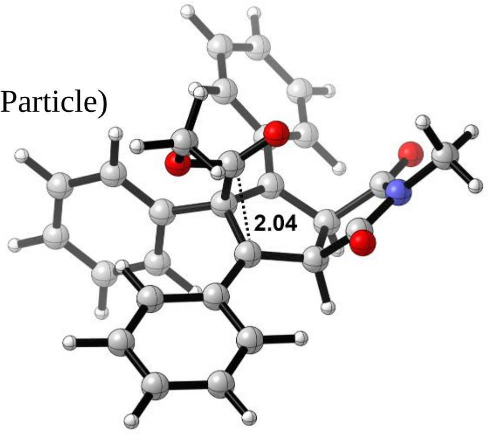
Number of imaginary frequencies: 1 (-299.6635 cm^{-1})

Electronic energy: HF=-1435.5082177

Zero-point correction= 0.440182 (Hartree/Particle)

Thermal correction to Energy= 0.468053

Thermal correction to Enthalpy= 0.468997



Thermal correction to Gibbs Free Energy= 0.381979

Sum of electronic and zero-point Energies= -1435.068036

Sum of electronic and thermal Energies= -1435.040165

Sum of electronic and thermal Enthalpies= -1435.039221

Sum of electronic and thermal Free Energies= -1435.126239

……

Cartesian Coordinates

……

H	-0.65134	-4.06832	-2.79701
H	-5.40833	1.85042	-1.27842
C	-0.49121	-3.74657	-1.77077
C	-4.77347	1.03178	-0.94705
C	-0.35179	-2.39530	-1.48570
H	-6.41803	-0.32376	-0.59204
H	-2.99693	2.19231	-1.15131
H	-0.54557	-5.74371	-0.95759
C	-3.40210	1.21685	-0.89729
C	-0.42995	-4.68452	-0.74106
C	-5.34083	-0.18104	-0.55754
H	-0.99138	0.50302	3.93917
C	-1.74831	0.19808	3.21143
H	-2.45885	-0.49904	3.65719
C	-0.14761	-1.95521	-0.17365
O	-1.15169	-0.50452	2.11718
C	-2.52683	0.18442	-0.47100
C	-4.50425	-1.20568	-0.11544
C	-0.29096	0.22857	1.39553
C	-0.21994	-4.25521	0.56436
O	0.27885	1.22015	1.81333
C	0.00396	-0.45900	-0.00049
C	-3.12965	-1.03719	-0.07291
C	-1.11513	0.42543	-0.46048

C	-0.07571	-2.89799	0.84903
H	-4.92867	-2.15782	0.19566
H	-2.27018	1.08573	2.83324
H	-0.17181	-4.97825	1.37533
C	1.27240	0.06608	-0.51609
H	-2.51522	-1.86096	0.27297
H	0.05662	-2.57991	1.87935
C	1.74703	2.55184	-0.80448
C	-0.47715	2.91231	-0.25368
N	0.82000	3.39161	-0.21805
O	2.93056	2.78044	-0.90014
O	-1.42547	3.46176	0.25647
C	1.17959	4.56295	0.55192
H	2.23332	4.77938	0.36626
H	1.01797	4.36082	1.61637
H	0.55612	5.40899	0.25219
C	1.00651	1.31246	-1.32185
C	-0.48254	1.63463	-1.09707
H	1.30532	1.17647	-2.37499
H	-1.00922	1.88690	-2.02847
C	2.56449	-0.43014	-0.21221
C	2.80404	-1.26162	0.91129
C	3.67437	-0.11289	-1.03702
C	4.92591	-0.64310	-0.78238
C	4.06290	-1.77655	1.16383
C	5.13069	-1.48130	0.31513
H	3.53875	0.55031	-1.88587
H	1.99785	-1.46082	1.61059
H	4.22085	-2.40011	2.04055
H	5.75538	-0.39460	-1.43983
H	6.11916	-1.88565	0.51826
H	-0.42061	-1.65769	-2.28605

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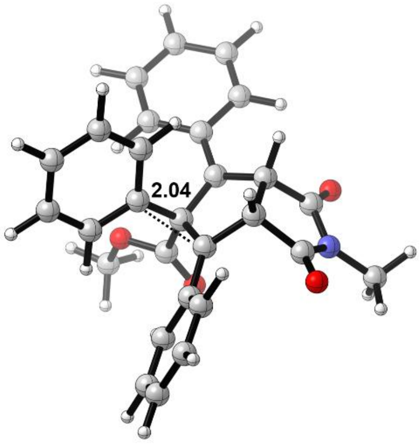
^{1}TS6h'



Number of imaginary frequencies: 1 (-300.4478 cm^{-1})

Electronic energy: HF=-1435.5014036

Zero-point correction= 0.440200 (Hartree/Particle)

Thermal correction to Energy= 0.468409

Thermal correction to Enthalpy= 0.469353

Thermal correction to Gibbs Free Energy= 0.380152

Sum of electronic and zero-point Energies= -1435.061203

Sum of electronic and thermal Energies= -1435.032995

Sum of electronic and thermal Enthalpies= -1435.032051

Sum of electronic and thermal Free Energies= -1435.121252

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Cartesian Coordinates

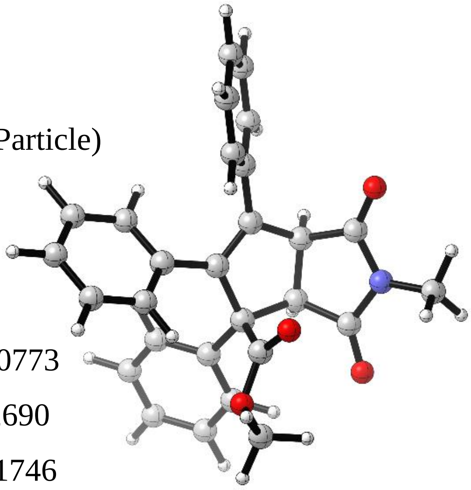
……

H	-1.15066	-4.74661	-0.47658
H	-5.42595	-0.56394	-1.55532
C	-0.65497	-3.86522	-0.87674
C	-4.69621	-0.61872	-0.75133
C	-0.62754	-2.70568	-0.12130
H	-6.08329	-1.45675	0.67383
H	-3.13504	0.20560	-1.95398
H	-0.09615	-4.81828	-2.73292
C	-3.40090	-0.18435	-0.97574
C	-0.06407	-3.90721	-2.14119
C	-5.06419	-1.12198	0.49651
H	1.72836	-0.82423	3.99991
C	1.14811	-1.67458	3.63151
H	1.69882	-2.60525	3.76788
C	0.02199	-1.55089	-0.60262
O	0.93256	-1.55345	2.22243
C	-2.42137	-0.24956	0.03962

C	-4.11794	-1.18080	1.51655
C	0.28924	-0.44975	1.83689
C	0.59182	-2.77734	-2.62062
O	-0.15424	0.37881	2.60068
C	0.20549	-0.29331	0.33413
C	-2.81530	-0.75397	1.29693
C	-1.06964	0.14063	-0.27590
C	0.66935	-1.62342	-1.85127
H	-4.39890	-1.55061	2.49999
H	0.19140	-1.71114	4.16114
H	1.08610	-2.80107	-3.58895
C	1.29869	0.56939	-0.12889
H	-2.11350	-0.76426	2.12469
H	1.25593	-0.78273	-2.21331
C	0.53872	2.97869	-0.15916
C	-1.58541	2.47824	-0.94617
N	-0.80087	3.33305	-0.18746
O	1.41062	3.63149	0.36535
O	-2.72587	2.69789	-1.28171
C	-1.28213	4.58456	0.36041
H	-2.36326	4.62215	0.21397
H	-0.80650	5.42985	-0.14631
H	-1.03760	4.63097	1.42477
C	0.69716	1.67427	-0.94337
C	-0.74732	1.24233	-1.27404
H	1.29641	1.91197	-1.83552
H	-0.94003	0.95679	-2.31882
C	2.68369	0.26559	-0.12616
C	3.19094	-1.02504	0.18424
C	3.62705	1.25770	-0.50855
C	4.97967	0.97674	-0.56575
C	4.55098	-1.29000	0.12179

C	5.45717	-0.29891	-0.25141
H	3.28007	2.27061	-0.70269
H	2.50750	-1.82112	0.46323
H	4.90771	-2.29052	0.35765
H	5.67642	1.76360	-0.84654
H	6.52172	-0.51465	-0.29712
H	-1.11656	-2.69409	0.84886

6h



Number of imaginary frequencies: 0

Electronic energy: HF=-1435.6153413

Zero-point correction= 0.444569 (Hartree/Particle)

Thermal correction to Energy= 0.472651

Thermal correction to Enthalpy= 0.473595

Thermal correction to Gibbs Free Energy= 0.384555

Sum of electronic and zero-point Energies= -1435.170773

Sum of electronic and thermal Energies= -1435.142690

Sum of electronic and thermal Enthalpies= -1435.141746

Sum of electronic and thermal Free Energies= -1435.230787

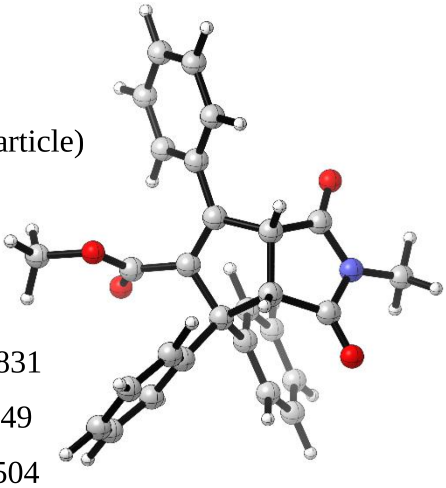
Cartesian Coordinates

H	-0.43612	-3.91455	2.98777
H	-2.93551	-3.47395	-2.57576
C	0.06564	-3.59478	2.07750
C	-3.09697	-2.48793	-2.14609
C	-0.15923	-2.31187	1.58648
H	-5.13106	-2.33807	-2.83657
H	-1.10938	-2.38590	-1.35542
H	1.09399	-5.46672	1.79362
C	-2.05900	-1.86718	-1.44984
C	0.92260	-4.46371	1.41046

C	-4.32303	-1.85335	-2.29358
H	-2.27046	0.07118	3.75768
C	-2.99049	0.47600	3.03892
H	-3.98467	0.06569	3.21560
C	0.47580	-1.86680	0.42094
O	-2.64044	0.08631	1.70846
C	-2.23549	-0.60459	-0.88634
C	-4.50517	-0.58345	-1.74664
C	-1.45286	0.51236	1.28957
C	1.55244	-4.03948	0.24198
O	-0.67760	1.12901	1.98863
C	0.25670	-0.51533	-0.13697
C	-3.47210	0.03356	-1.05533
C	-1.12198	0.15262	-0.17261
C	1.32927	-2.75915	-0.24607
H	-5.45664	-0.06925	-1.86223
H	-3.00055	1.56739	3.11607
H	2.21692	-4.71131	-0.29628
C	1.23191	0.28937	-0.60659
H	-3.62106	1.02970	-0.63783
H	1.81410	-2.43983	-1.16698
C	1.12847	2.82728	-0.42417
C	-1.17722	2.75239	-0.17982
N	-0.01816	3.46659	0.04460
O	2.25439	3.23826	-0.27875
O	-2.28211	3.09075	0.19276
C	0.00935	4.65174	0.87449
H	-0.69035	5.39538	0.48444
H	1.02813	5.04412	0.86502
H	-0.28203	4.39107	1.89766
C	0.68229	1.57307	-1.16495
C	-0.82390	1.49265	-0.94424

H	0.96725	1.70889	-2.21919
H	-1.39589	1.49122	-1.87745
C	2.68628	0.06168	-0.54917
C	3.29702	-0.26932	0.66519
C	3.48259	0.21076	-1.68871
C	4.85583	0.00137	-1.62412
C	4.67042	-0.46876	0.73183
C	5.45305	-0.34076	-0.41360
H	3.02248	0.48405	-2.63757
H	2.68152	-0.35854	1.55916
H	5.13307	-0.71944	1.68350
H	5.46221	0.11261	-2.51998
H	6.52791	-0.49708	-0.36071
H	-0.83390	-1.65775	2.13329

6h'



Number of imaginary frequencies: 0

Electronic energy: HF=-1435.6086937

Zero-point correction= 0.443863 (Hartree/Particle)

Thermal correction to Energy= 0.472245

Thermal correction to Enthalpy= 0.473189

Thermal correction to Gibbs Free Energy= 0.382741

Sum of electronic and zero-point Energies= -1435.164831

Sum of electronic and thermal Energies= -1435.136449

Sum of electronic and thermal Enthalpies= -1435.135504

Sum of electronic and thermal Free Energies= -1435.225952

……

Cartesian Coordinates

……

H	-3.49574	-4.03001	0.71385
H	-4.78374	1.69168	1.56905
C	-2.92888	-3.50121	-0.04898

C	-3.71303	1.52602	1.66200
C	-2.40467	-2.24449	0.23867
H	-3.52037	2.68163	3.47297
H	-3.61524	0.34656	-0.12713
H	-3.14386	-5.05666	-1.52729
C	-3.05379	0.75924	0.70885
C	-2.72990	-4.07730	-1.29959
C	-3.00513	2.08408	2.72444
H	2.19079	-3.69055	1.97663
C	1.54746	-3.93195	1.12387
H	2.04162	-4.64179	0.46049
C	-1.67355	-1.52971	-0.71726
O	1.30837	-2.76444	0.33724
C	-1.67503	0.53231	0.79526
C	-1.63440	1.87061	2.81898
C	0.68335	-1.76712	0.97416
C	-1.98656	-3.38880	-2.25265
O	0.31523	-1.82757	2.12691
C	0.46714	-0.60812	0.06866
C	-0.97623	1.10138	1.86180
C	-0.95826	-0.23002	-0.32669
C	-1.45784	-2.13590	-1.95851
H	-1.06804	2.29706	3.64345
H	0.60133	-4.34059	1.49240
H	-1.80634	-3.82982	-3.23026
C	1.42038	0.17109	-0.46729
H	0.09544	0.94024	1.96103
H	-0.84498	-1.64898	-2.71392
C	0.71328	2.59275	-0.84200
C	-1.44365	2.04546	-1.51302
N	-0.59662	3.02547	-1.00724
O	1.61326	3.24957	-0.37284

O	-2.58451	2.24491	-1.86333
C	-1.06851	4.34090	-0.63129
H	-1.52496	4.83669	-1.49252
H	-0.21124	4.91399	-0.27203
H	-1.81816	4.24974	0.16231
C	0.78630	1.17298	-1.39315
C	-0.67445	0.74398	-1.54134
H	1.30814	1.23336	-2.35936
H	-0.88669	0.24780	-2.49090
C	2.86235	0.13689	-0.19967
C	3.78490	0.50441	-1.18648
C	3.34852	-0.24847	1.05778
C	4.71434	-0.29736	1.30666
C	5.15111	0.45112	-0.93902
C	5.62133	0.04639	0.30731
H	2.64974	-0.48113	1.86049
H	3.43443	0.83056	-2.16350
H	5.85142	0.73423	-1.72110
H	5.07140	-0.59017	2.29114
H	6.69019	0.01317	0.50381
H	-2.55700	-1.82011	1.22809

Single point energy calculations at SMD(Dichloromethane)/UM06/6-311+G(d,p)

Species	Single Point Energy ΔE (a.u.)
2i	-398.6227537
^{3}2i	-398.5288155
1a	-1037.215116
^{3}1a	-1037.1330291
^{3}TS3al	-1435.7649938

^{3}TS3al’	-1435.7663178
^{3}Int3al	-1435.8058293
^{3}Int3al’	-1435.8053741
^{1}Int3al	-1435.8050794
^{1}Int3al’	-1435.8053859
3al	-1435.8863857
3al’	-1435.8845932
1d	-1374.2459826
^{3}1d	-1374.1656031
^{3}TS3aa	-1772.792852
^{3}TS3aa’	-1772.7896325
^{3}Int3aa	-1772.8348218
^{3}Int3aa’	-1772.8340364
^{1}Int3aa	-1772.835189
^{1}Int3aa’	-1772.8336867
3aa	-1772.9175311
3aa’	-1772.9093138
1o	-803.1525181
^{3}1o	-803.0575995
1v	-575.3277278
^{3}1v	-575.2203514

Single point energy calculations at SMD(Toluene)/(U)M06/6-311+G(d,p)

Species	Single Point Energy ΔE (a.u.)

3al	-1435.8778977
^{1}3al*	-1435.8473502
^{1}TS6h	-1435.8275633
^{1}TS6h’	-1435.8162343
6h	-1435.9128188
6h’	-1435.9078284

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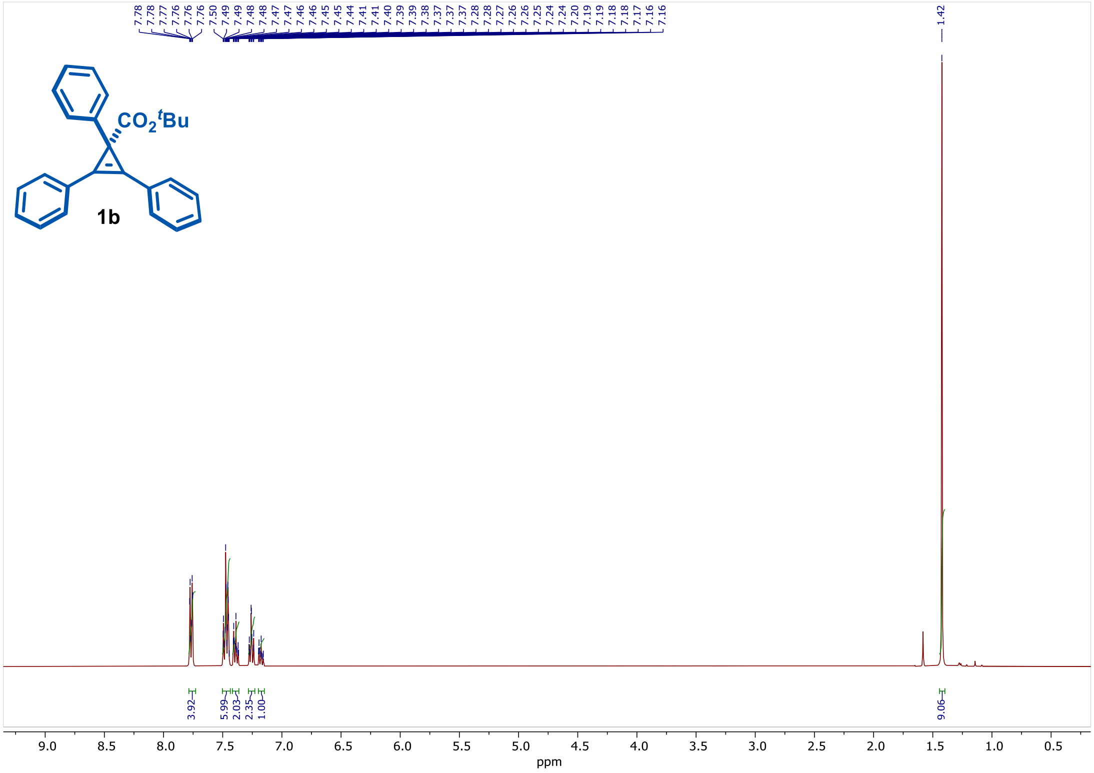
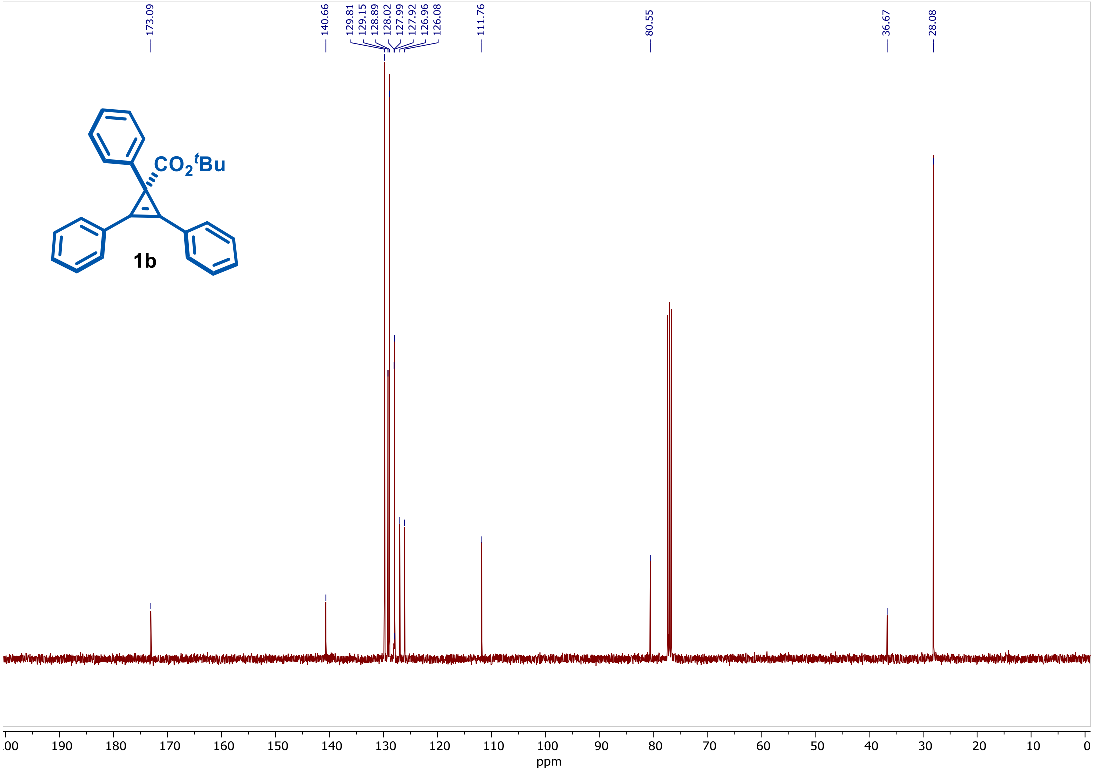
11. Spectra for new compounds:

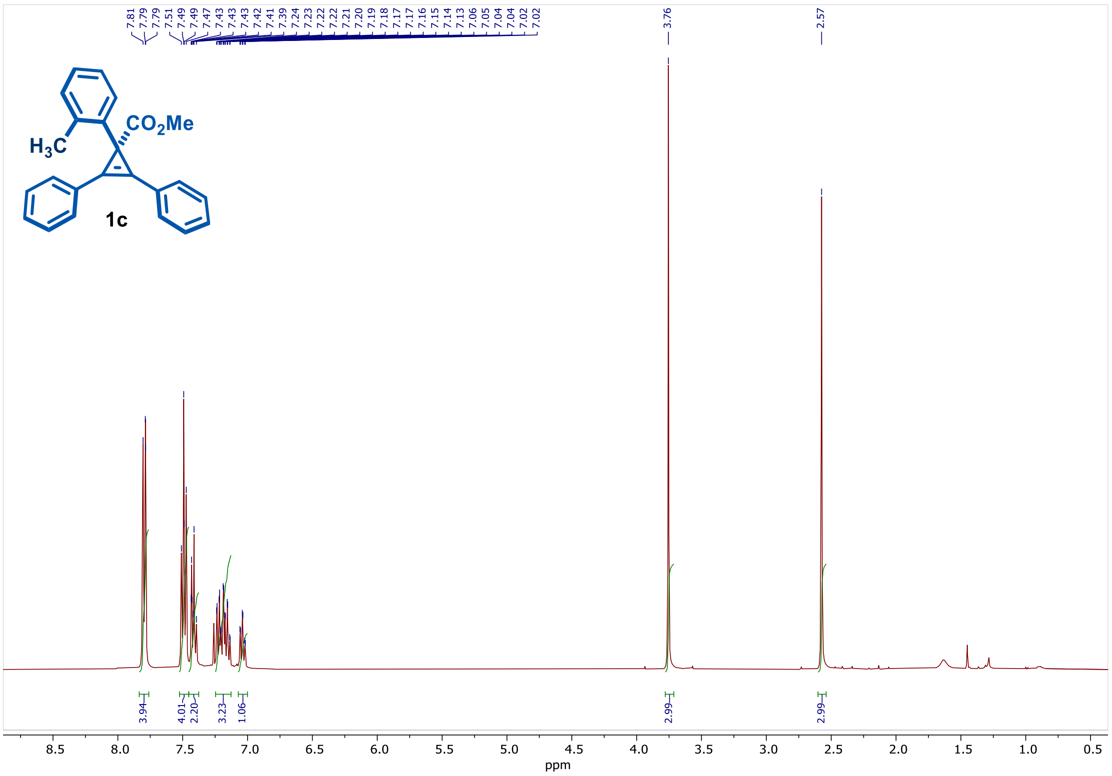
^{1}H-NMR (400 MHz, CDCl$_3$) of compound 1b (see procedure)



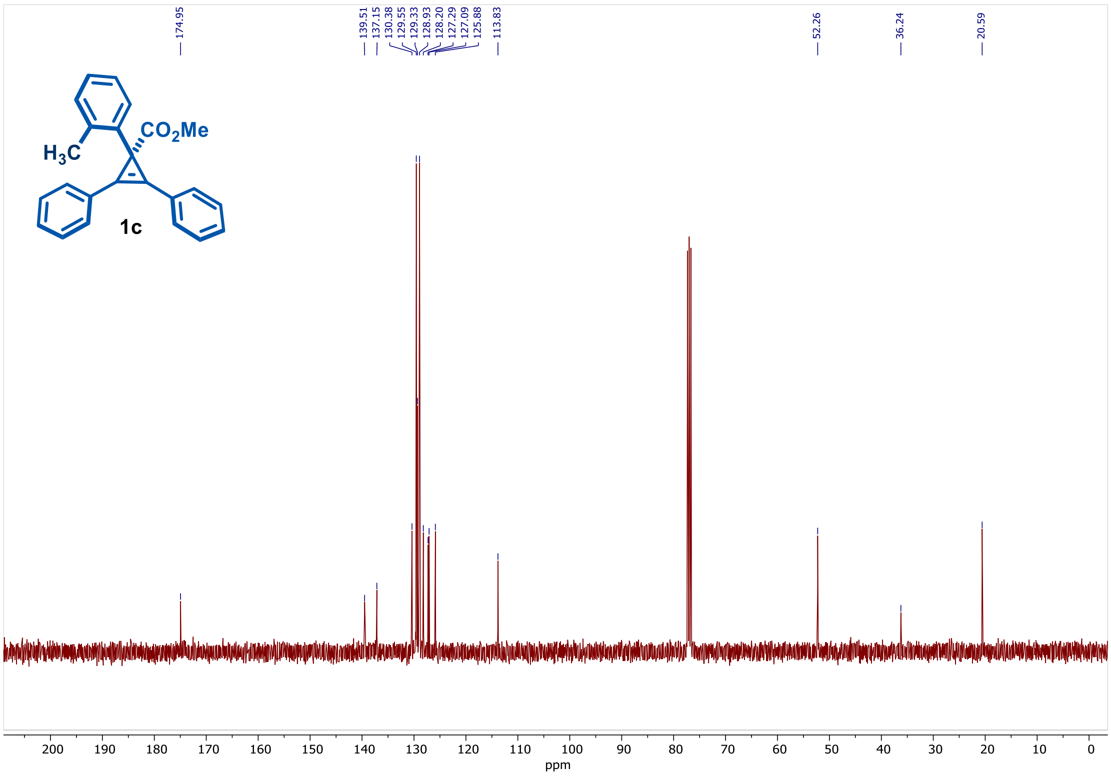
^{13}C-NMR (101 MHz, CDCl$_3$) of compound 1b



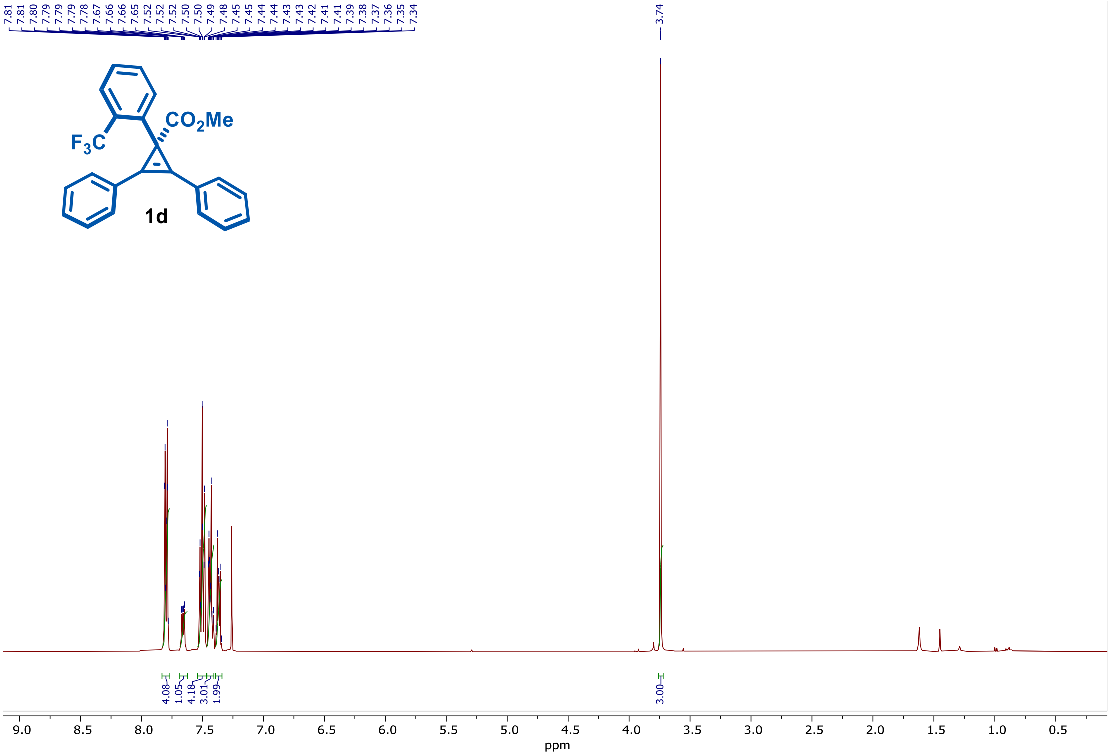
^{1}H-NMR (400 MHz, CDCl$_3$) of compound 1c (see procedure)



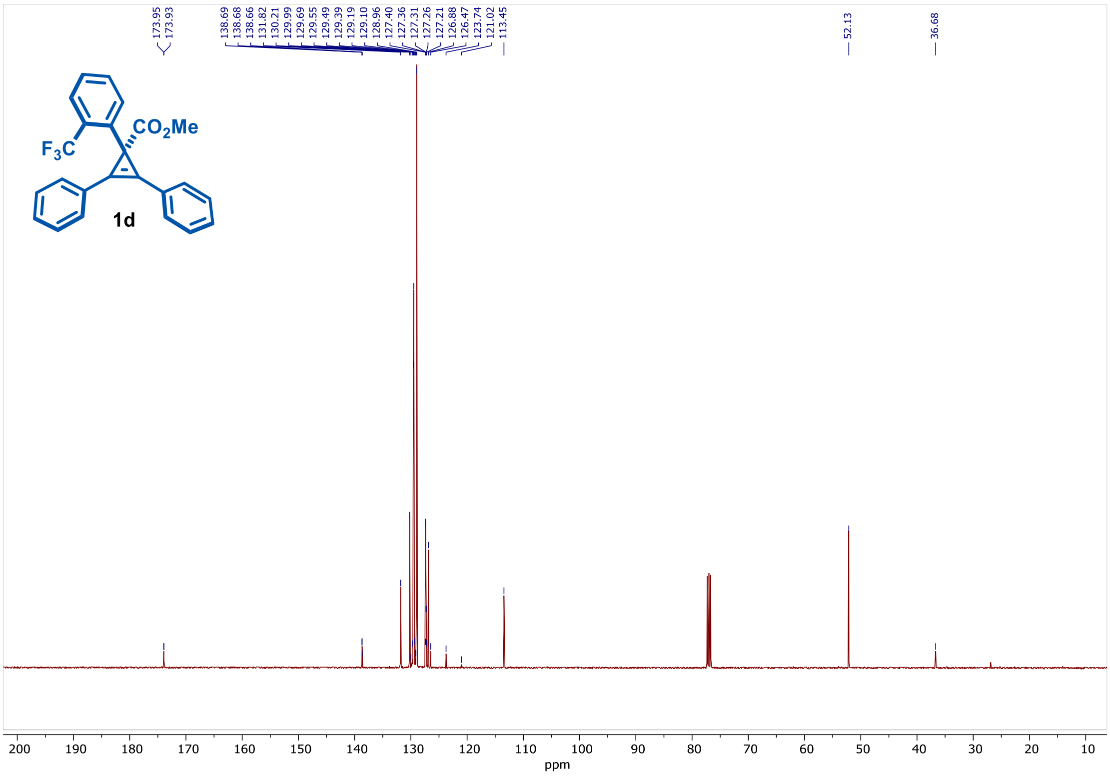
^{13}C-NMR (101 MHz, CDCl$_3$) of compound 1c



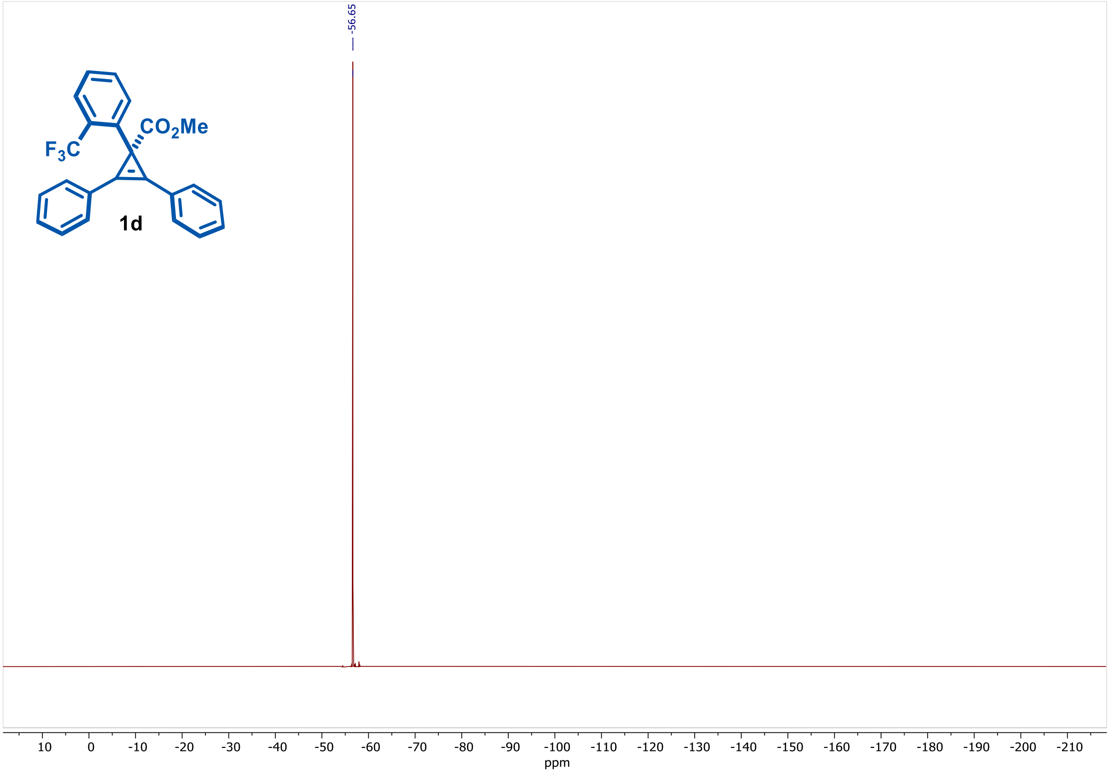
^{1}H-NMR (400 MHz, $CDCl_3$) of compound 1d (see procedure)



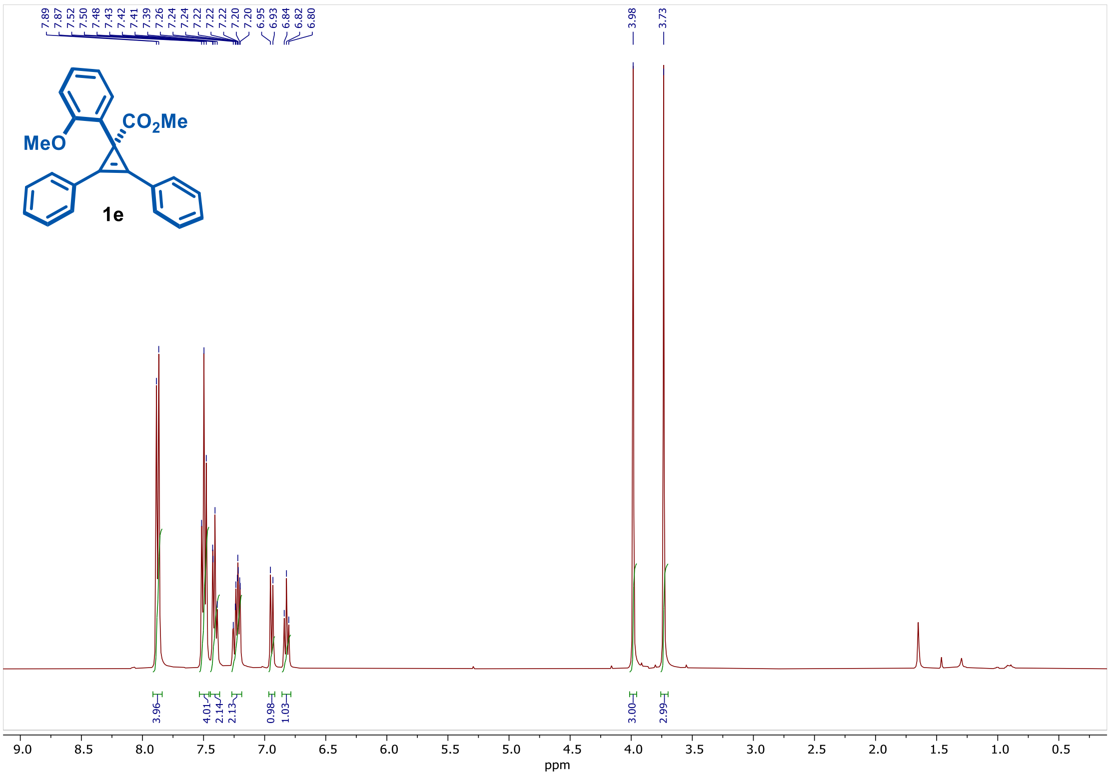
^{13}C-NMR (101 MHz, $CDCl_3$) of compound 1d



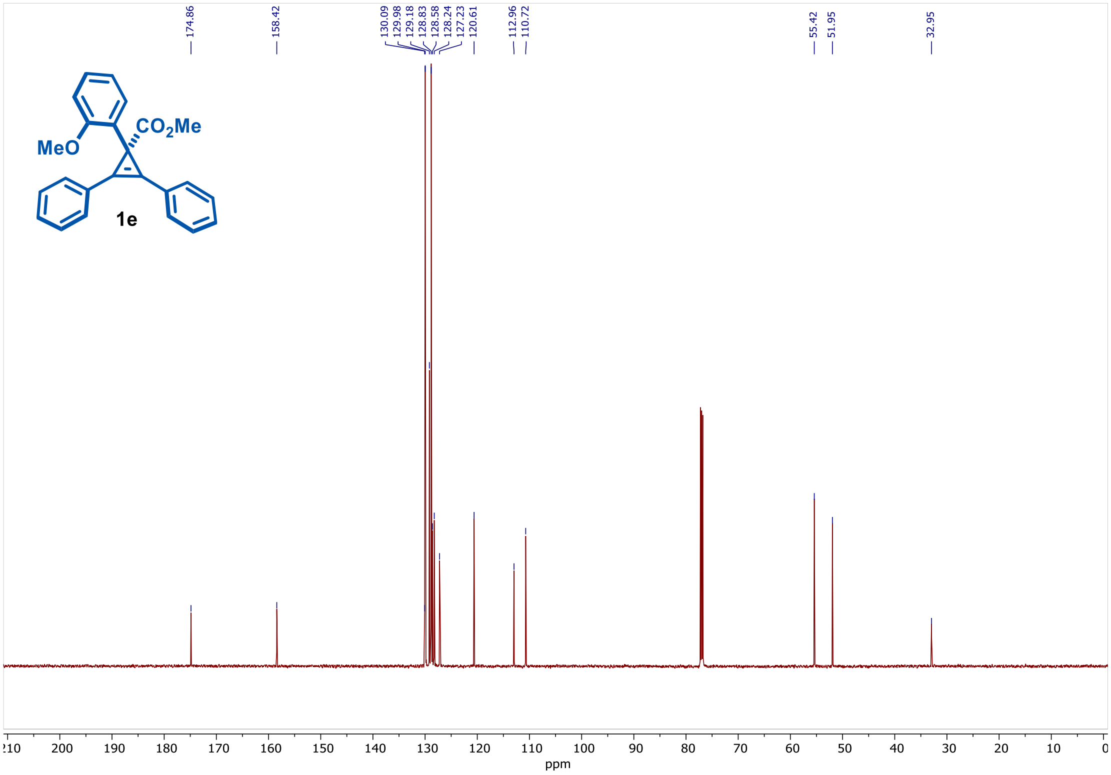
^{19}F-NMR (377 MHz, $CDCl_3$) of compound 1d



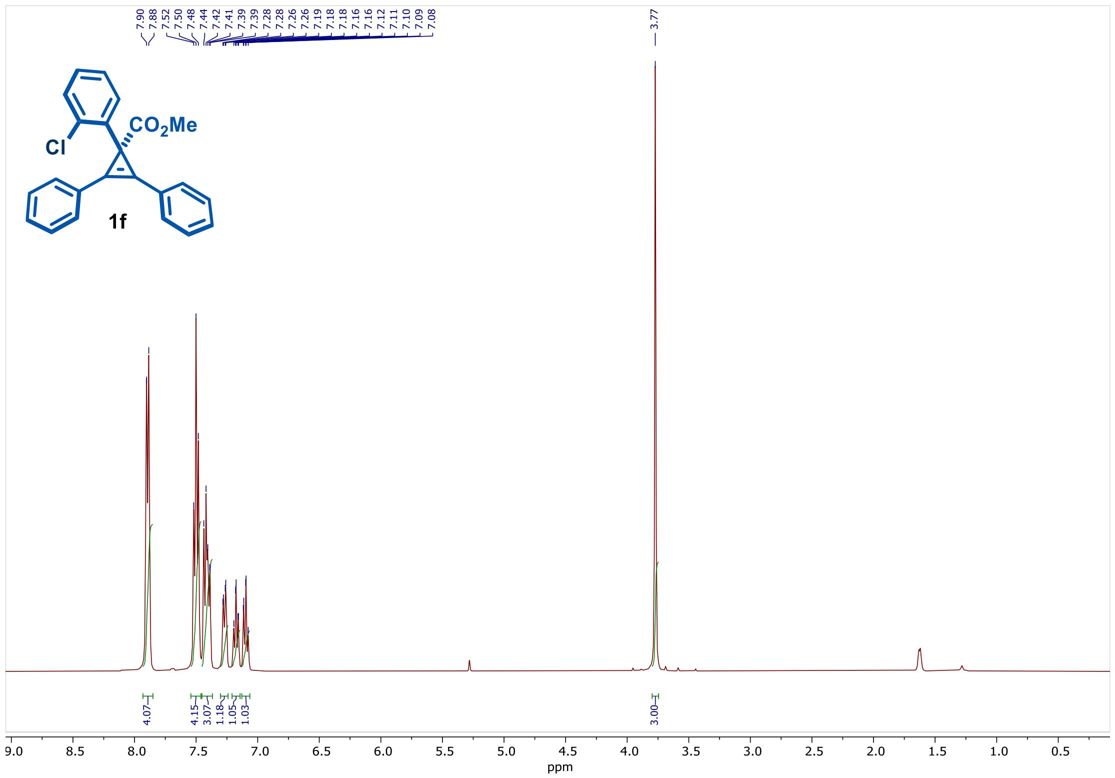
^{1}H-NMR (400 MHz, $CDCl_3$) of compound 1e (see procedure)



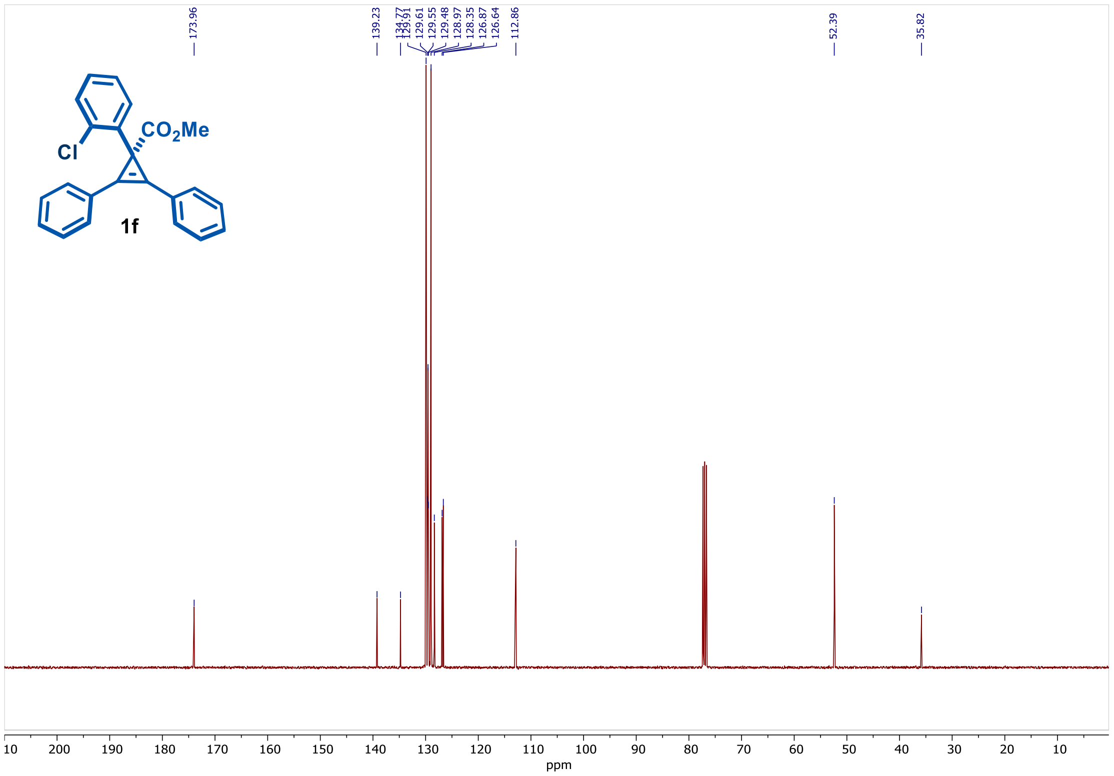
^{13}C-NMR (101 MHz, $CDCl_3$) of compound 1e



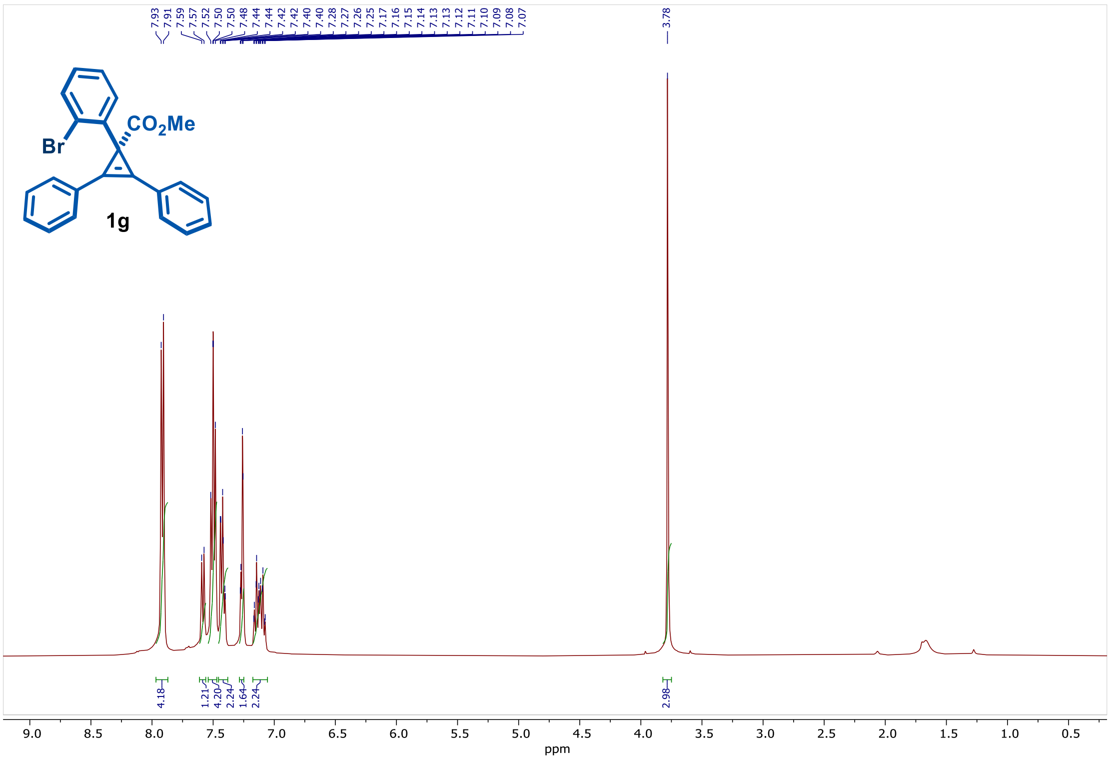
^{1}H-NMR (400 MHz, CDCl$_3$) of compound 1f (see procedure)



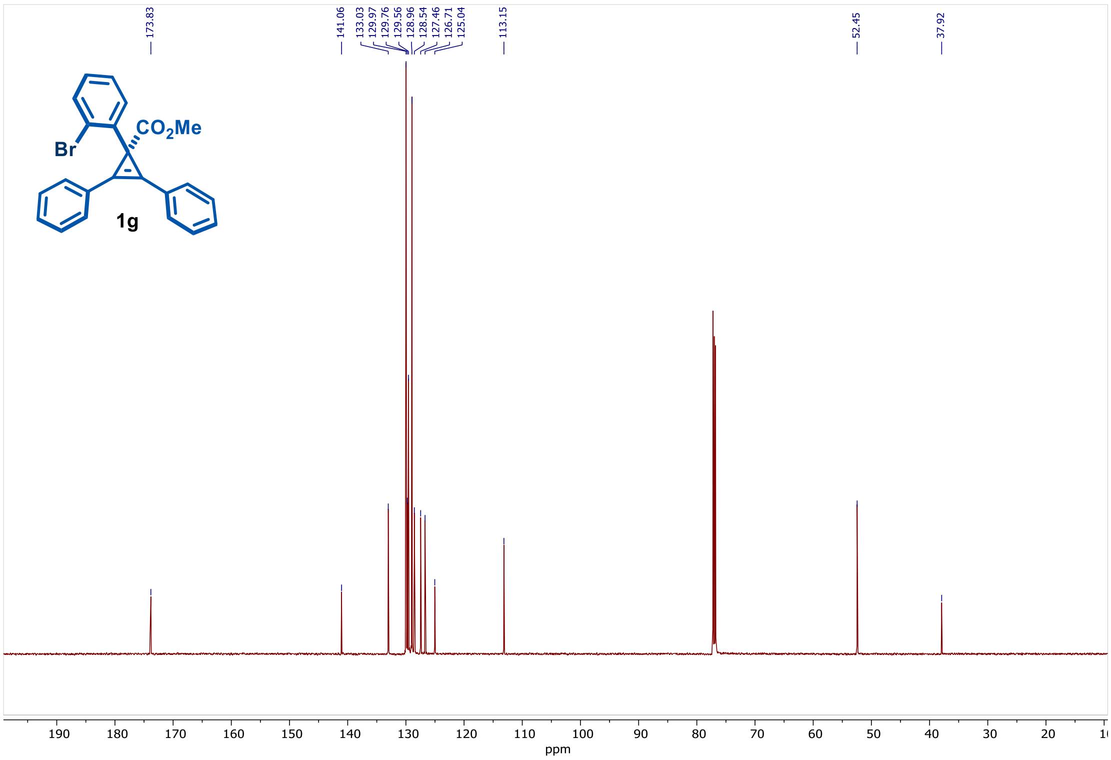
^{13}C-NMR (101 MHz, CDCl$_3$) of compound 1f



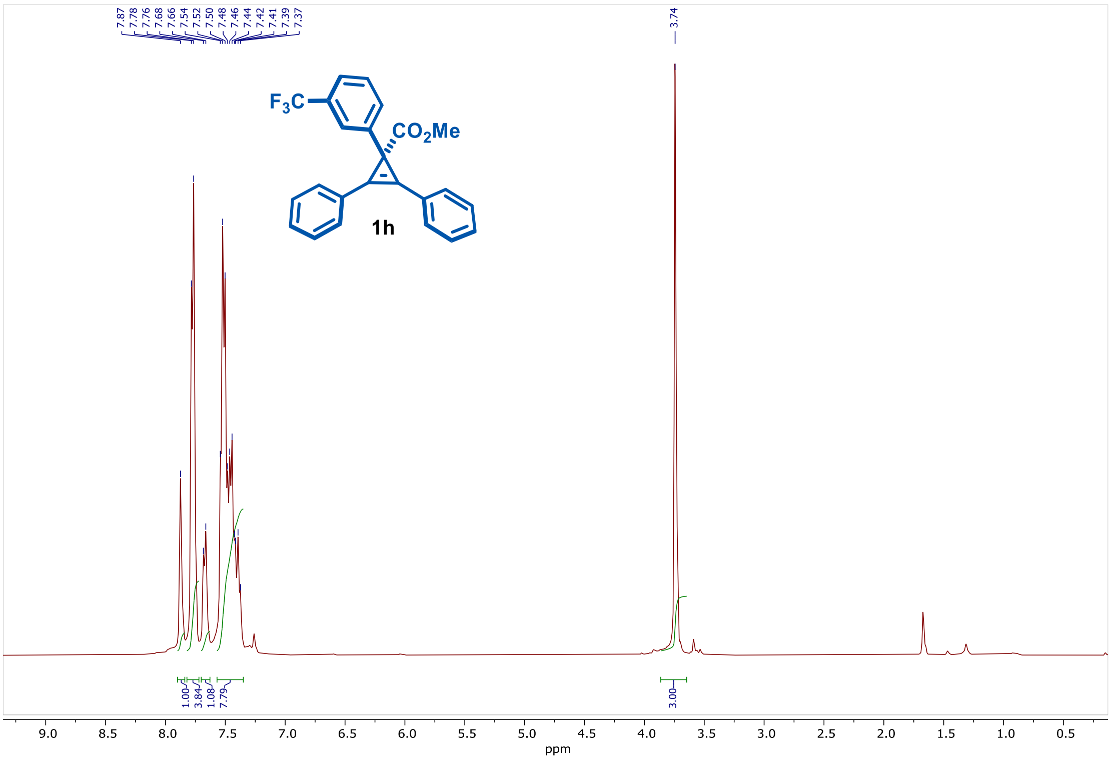
^{1}H-NMR (400 MHz, CDCl$_3$) of compound 1g (see procedure)



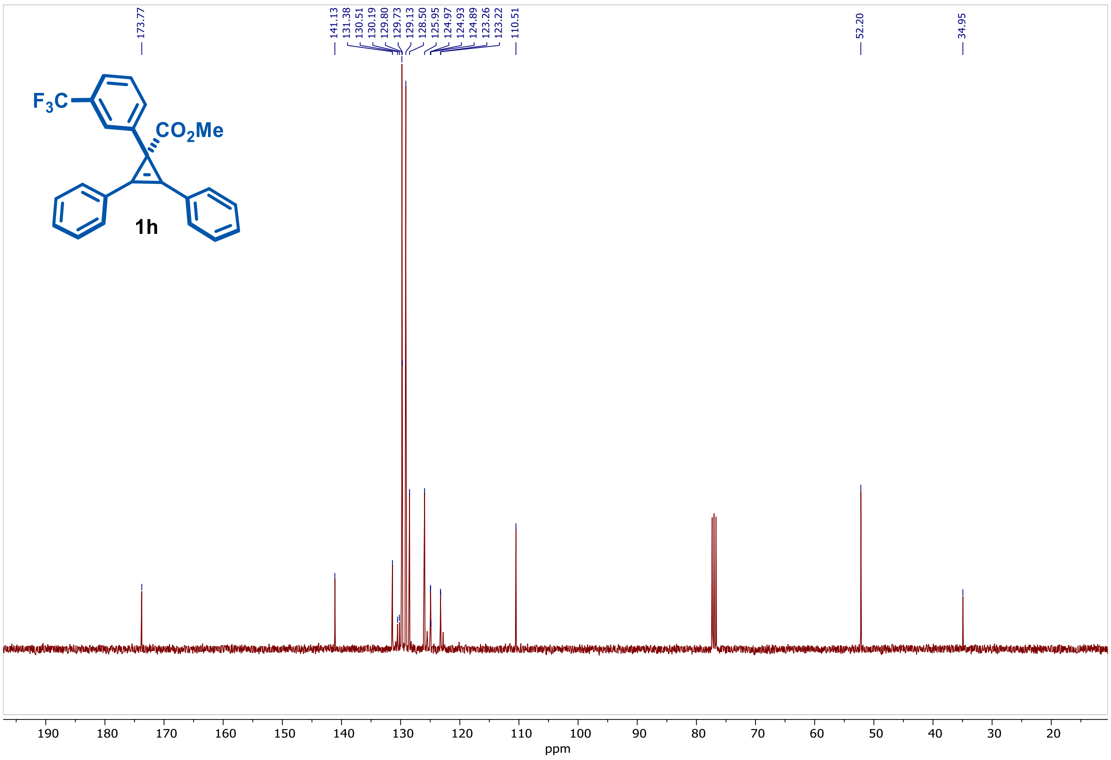
^{13}C-NMR (101 MHz, CDCl$_3$) of compound 1g



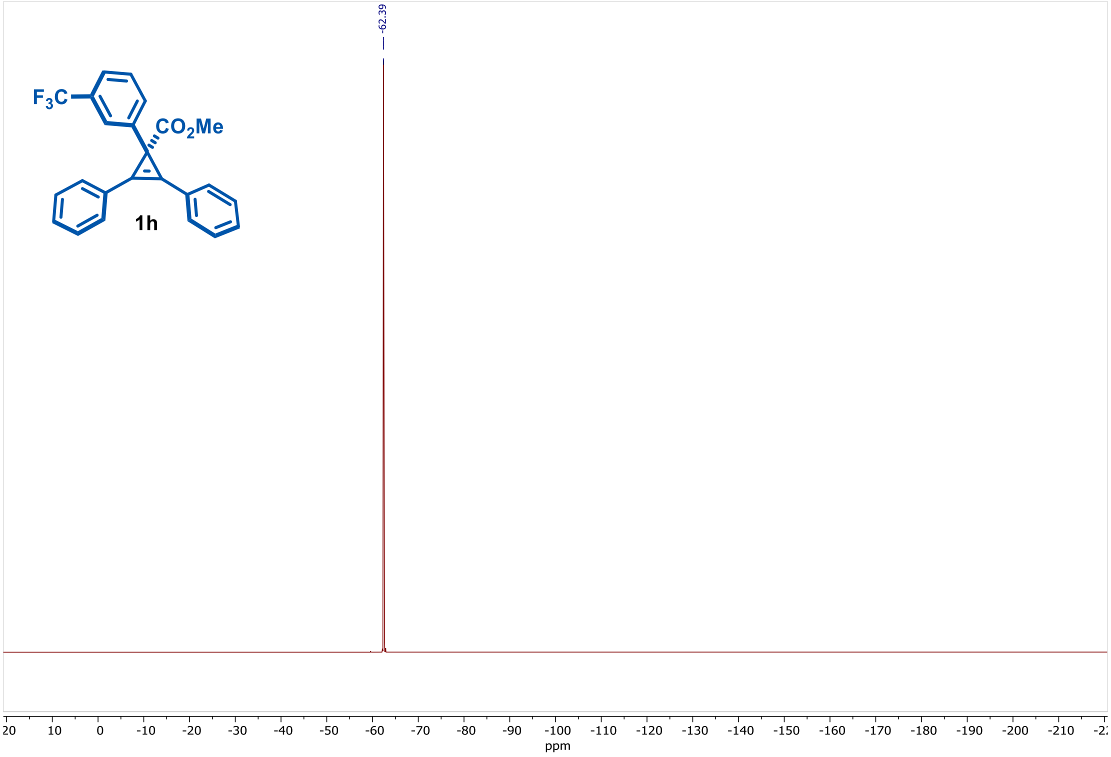
^{1}H-NMR (400 MHz, CDCl$_3$) of compound 1h (see procedure)



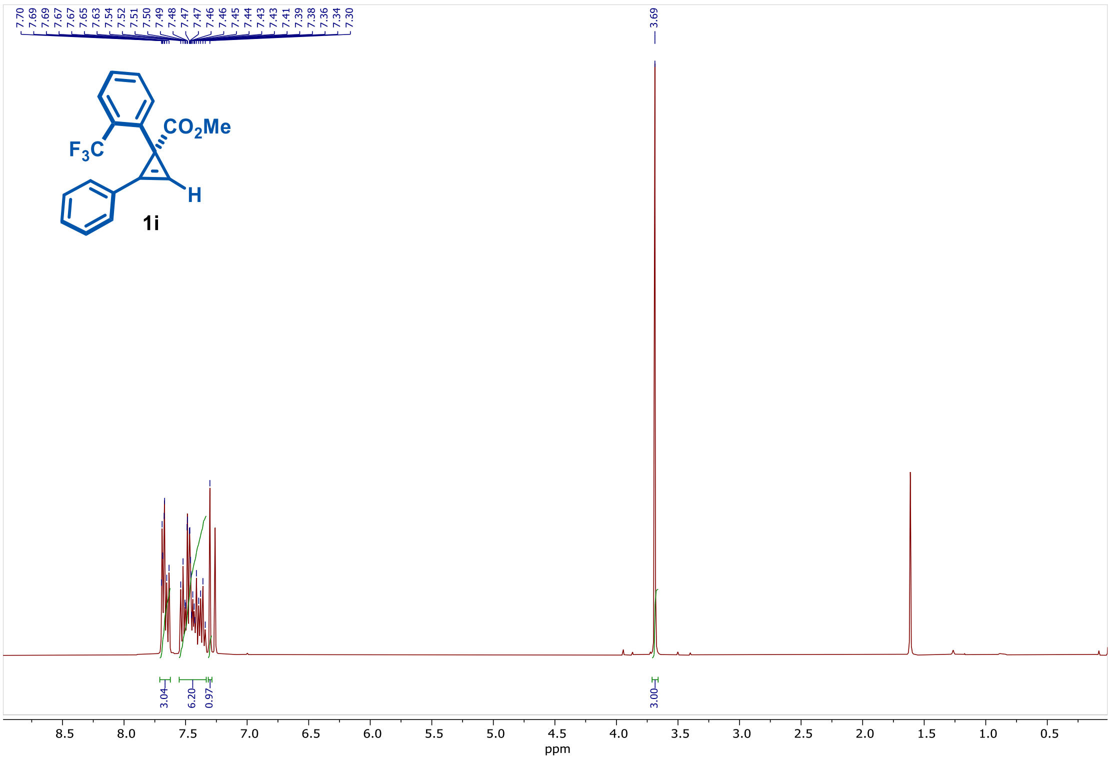
^{13}C-NMR (101 MHz, CDCl$_3$) of compound 1h



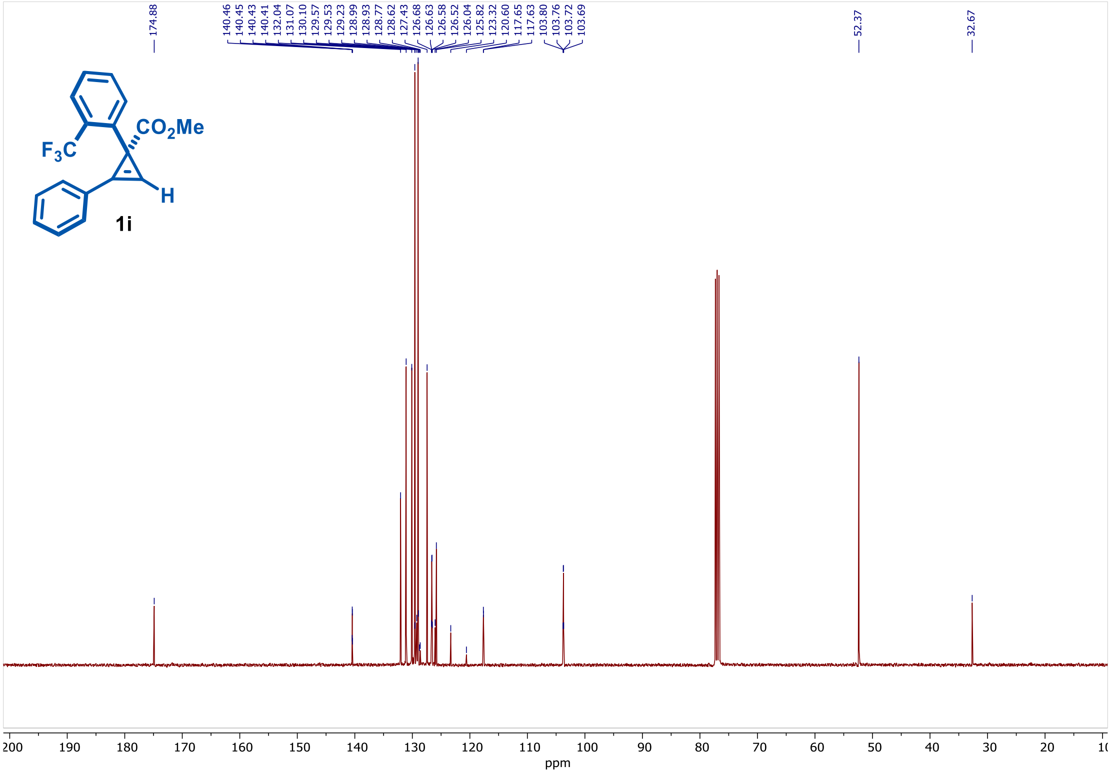
^{19}F-NMR (377 MHz, $CDCl_3$) of compound 1h



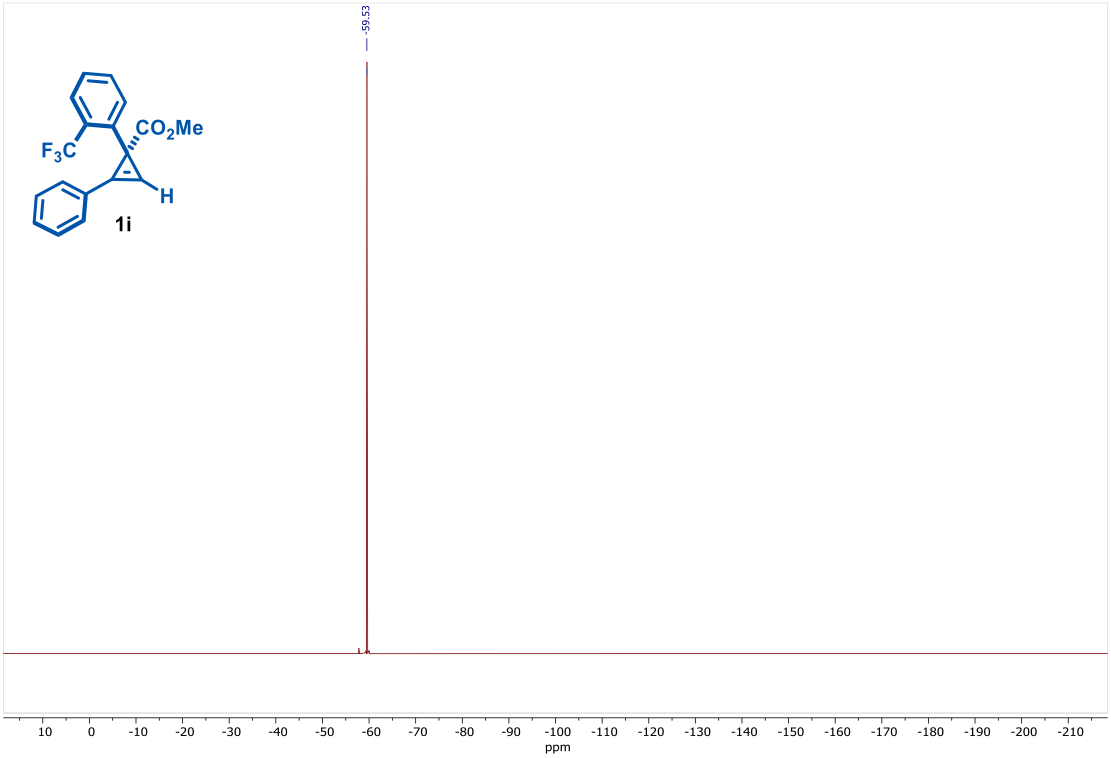
^{1}H-NMR (400 MHz, CDCl$_3$) of compound 1i (see procedure)



^{13}C-NMR (101 MHz, CDCl$_3$) of compound 1i



^{19}F-NMR (377 MHz, $CDCl_3$) of compound 1i



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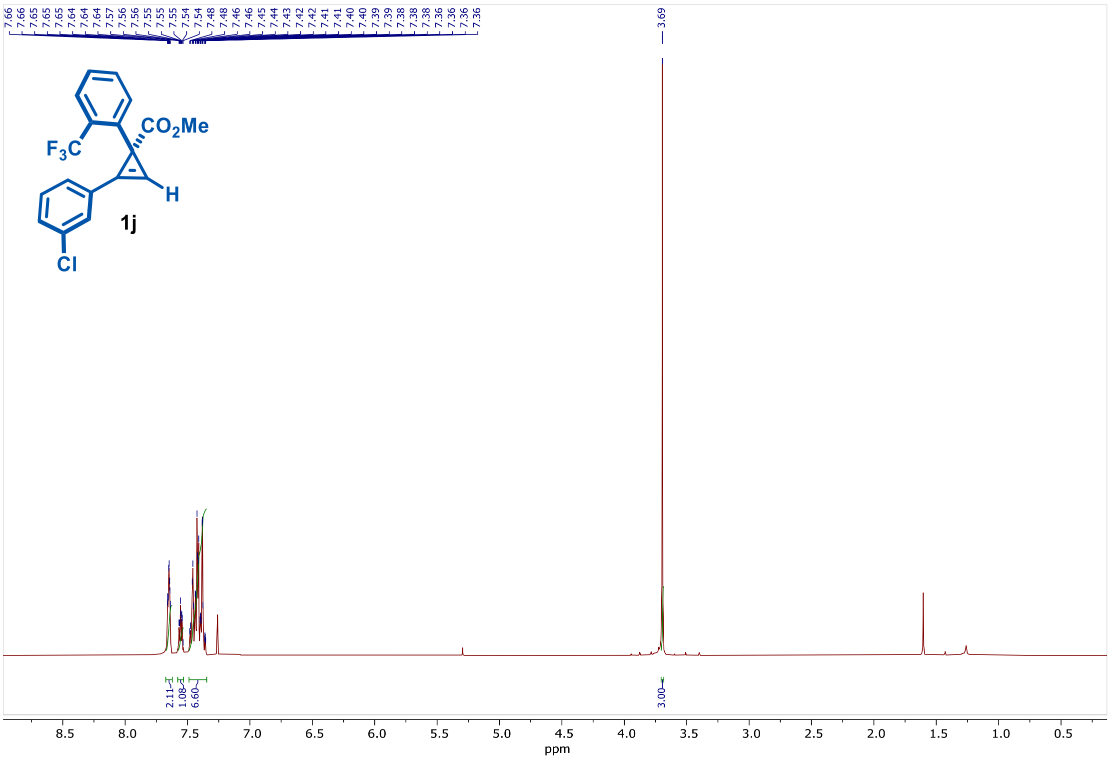

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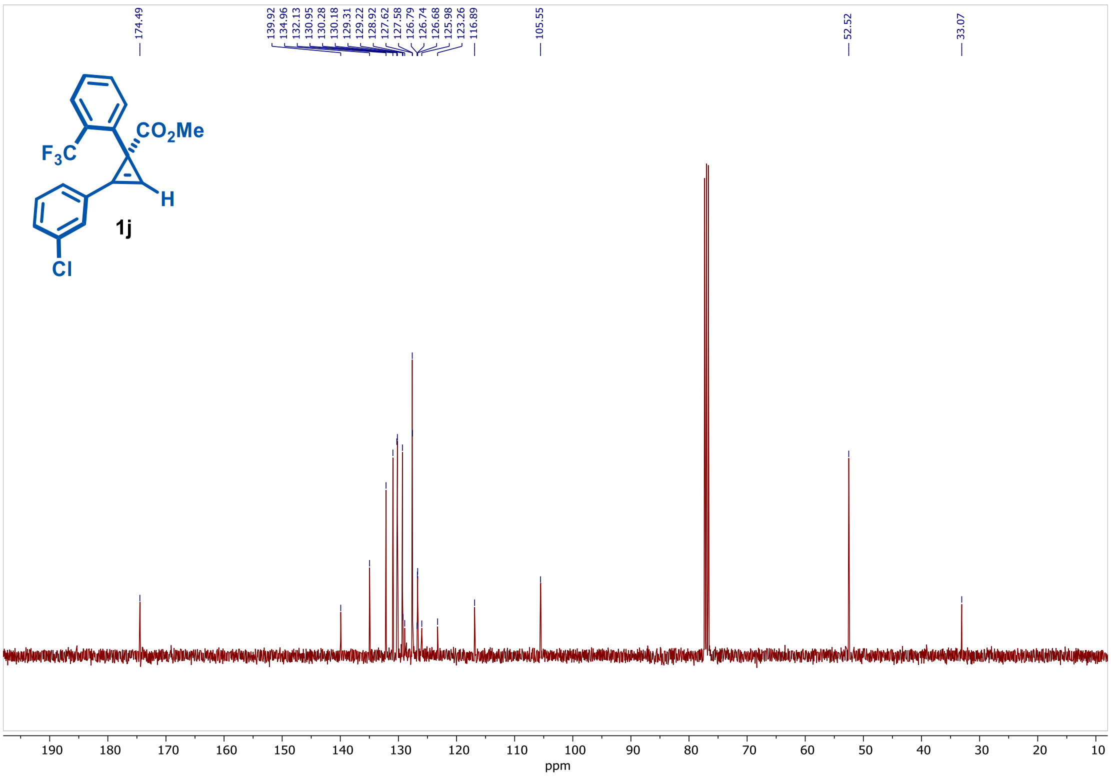

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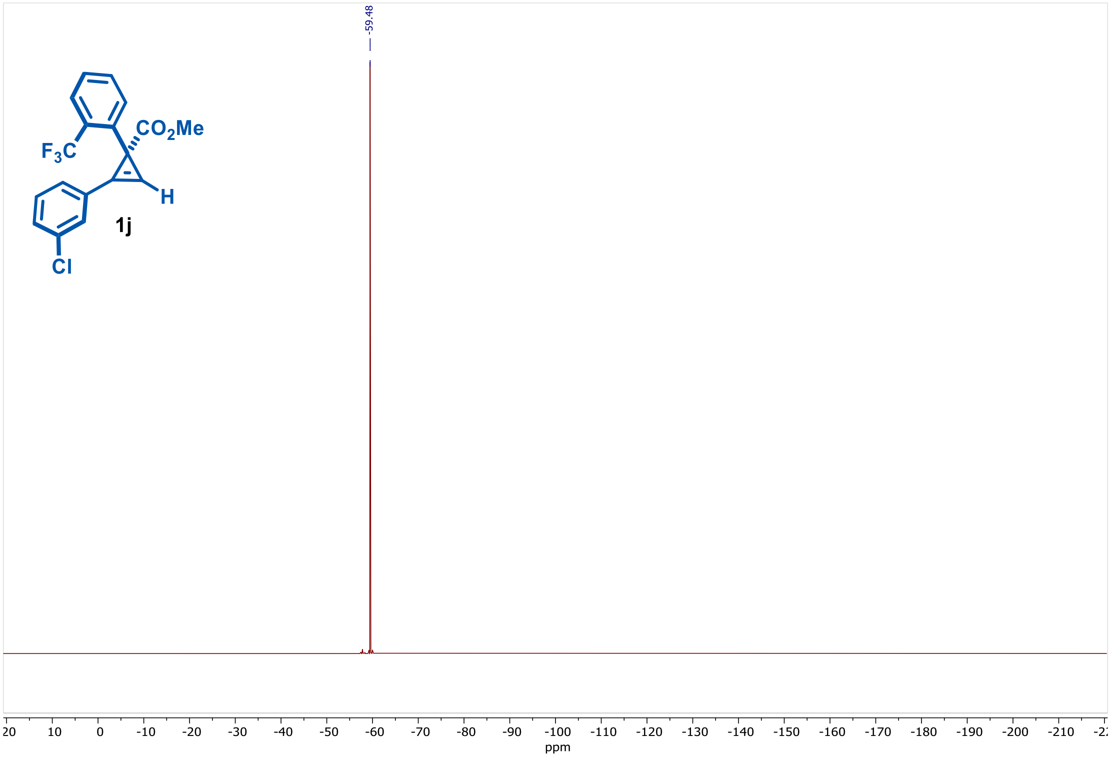
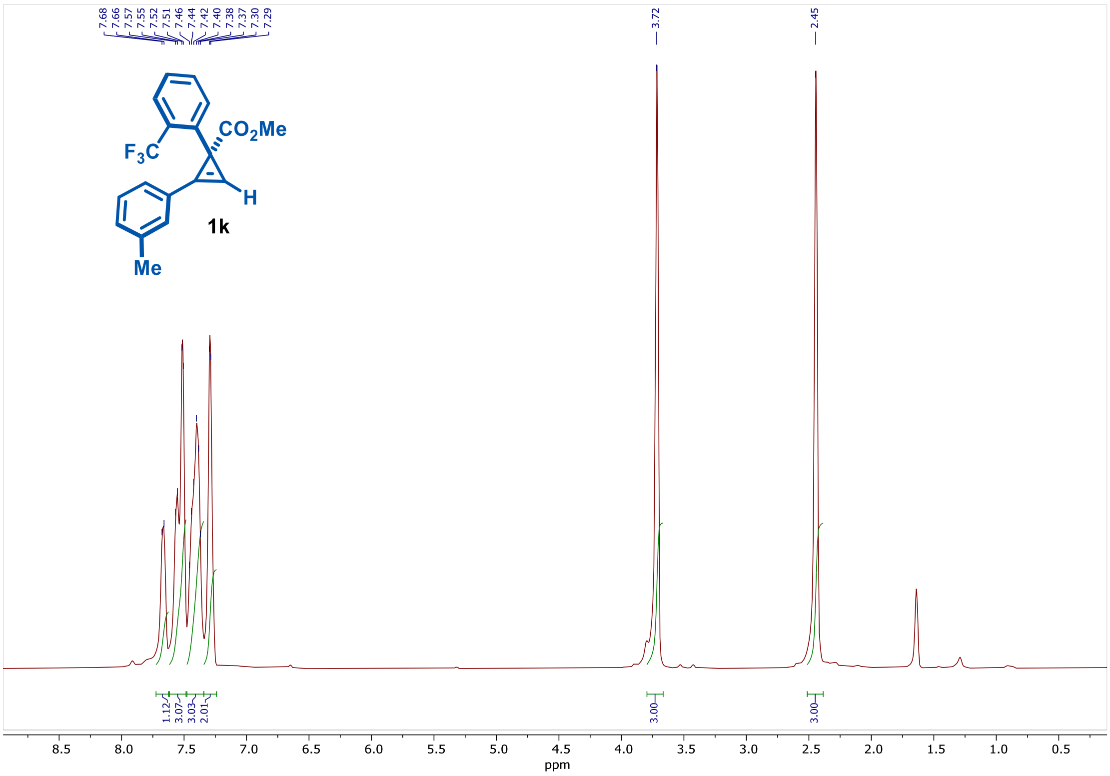
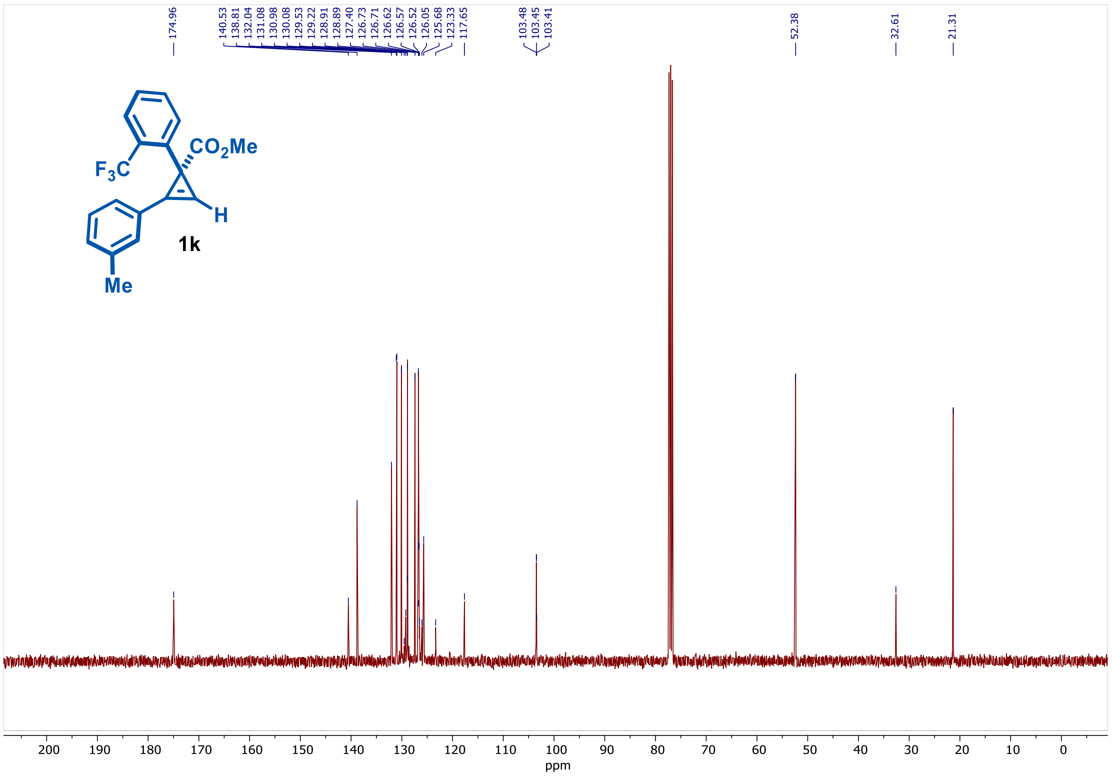


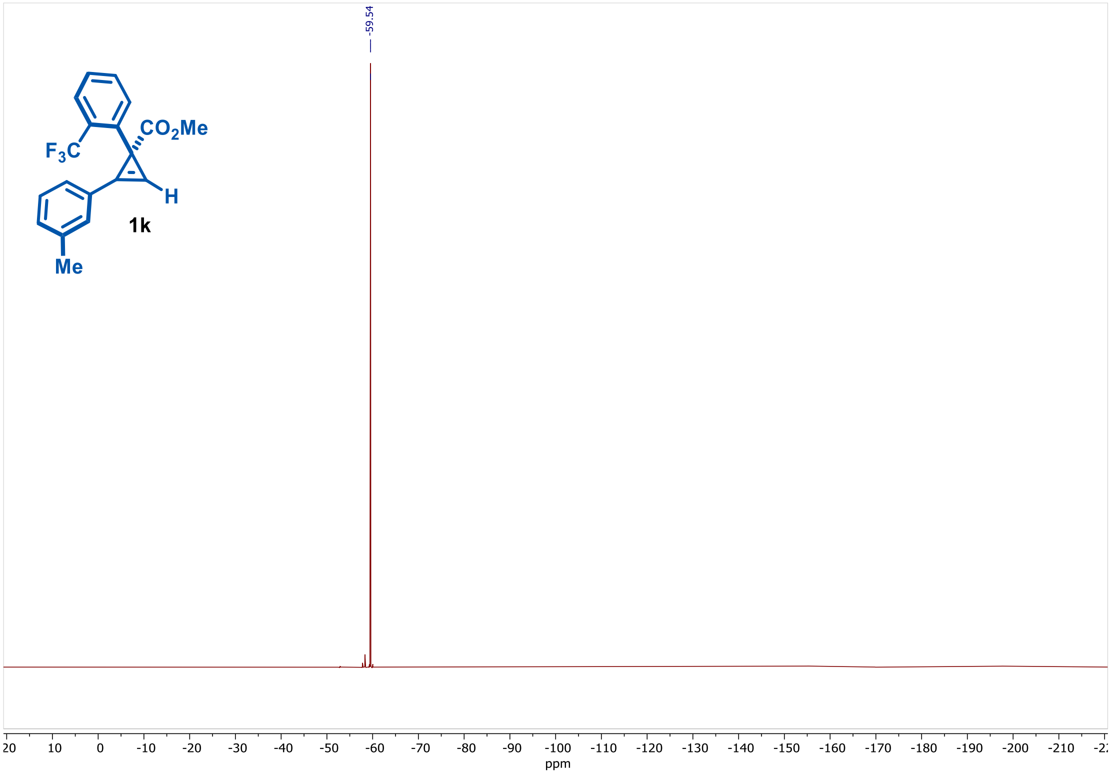
^{1}H-NMR (400 MHz, CDCl$_3$) of compound 1k (see procedure)



^{13}C-NMR (101 MHz, CDCl$_3$) of compound 1k



^{19}F-NMR (377 MHz, $CDCl_3$) of compound 1k



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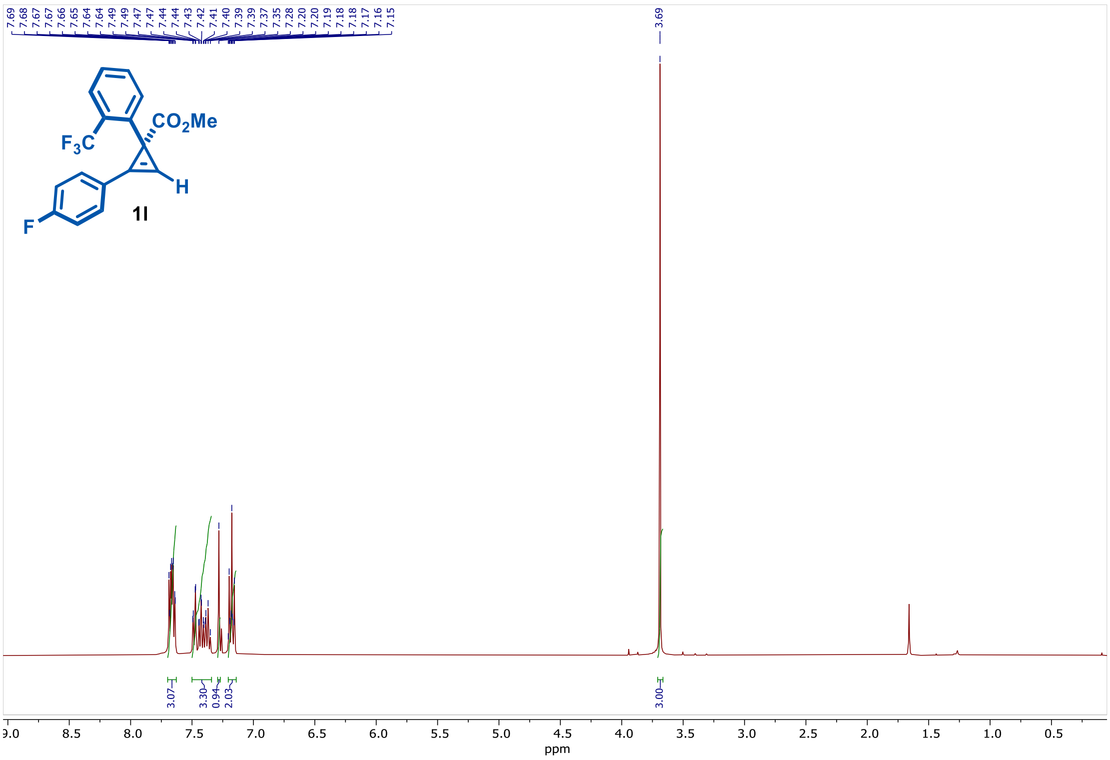
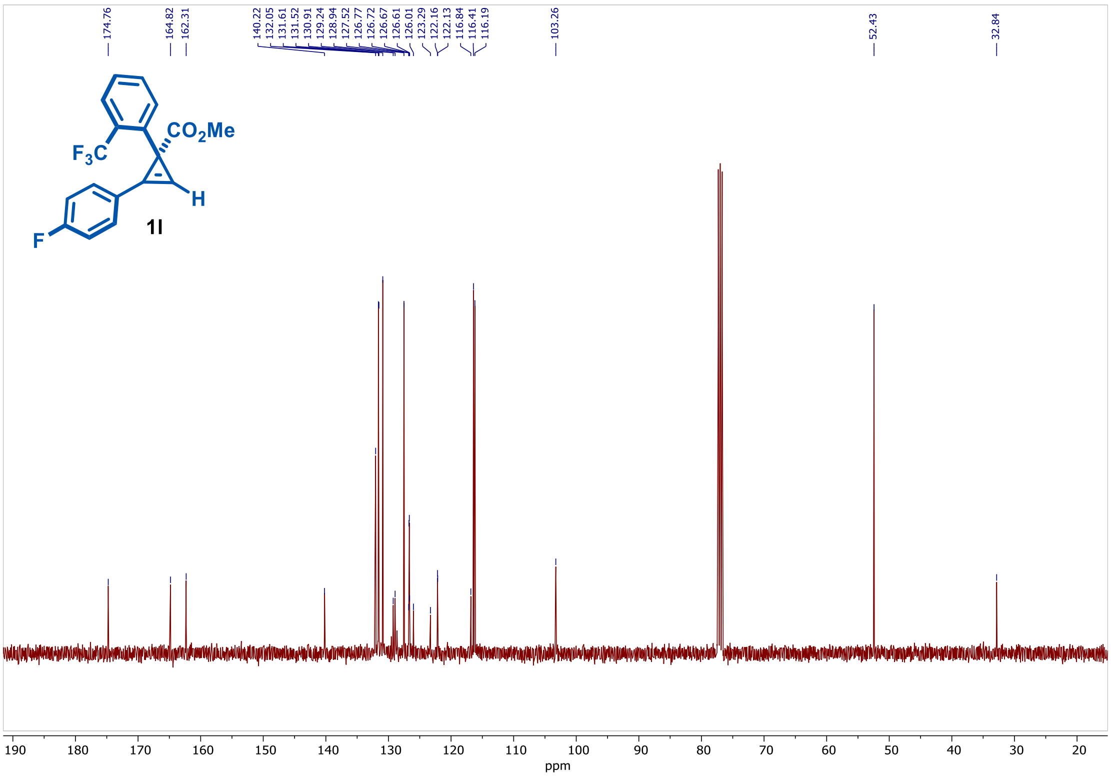
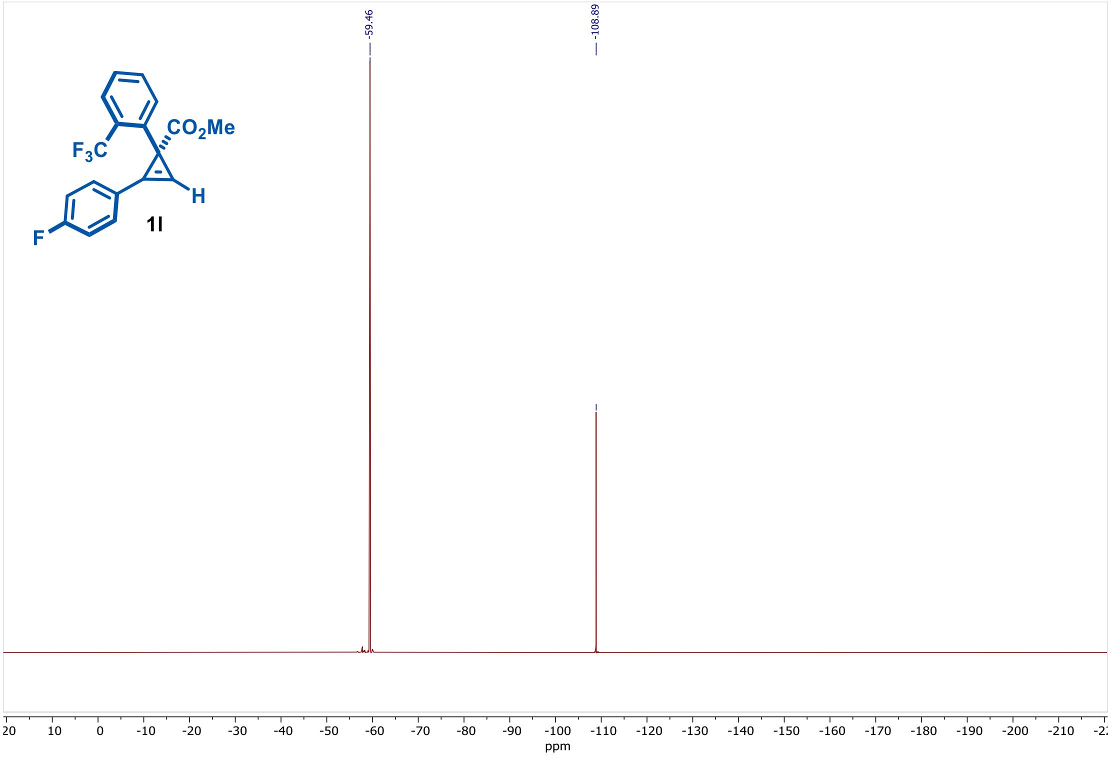


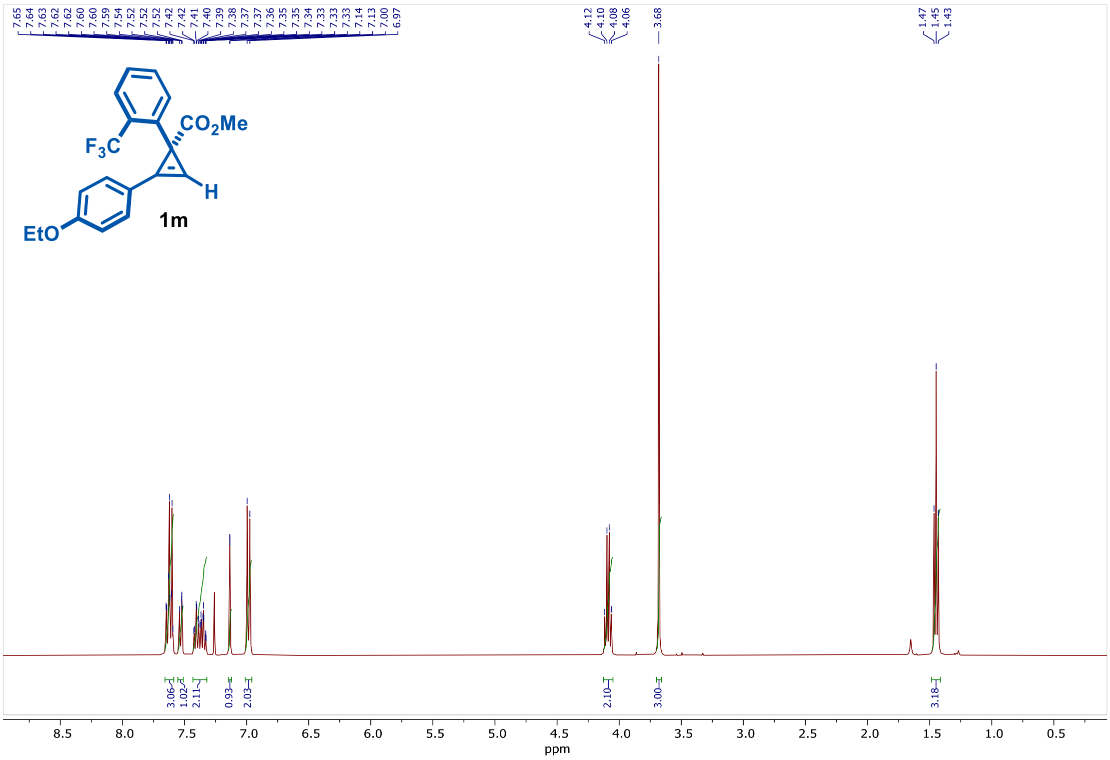
^{13}C-NMR (101 MHz, CDCl$_3$) of compound 1l



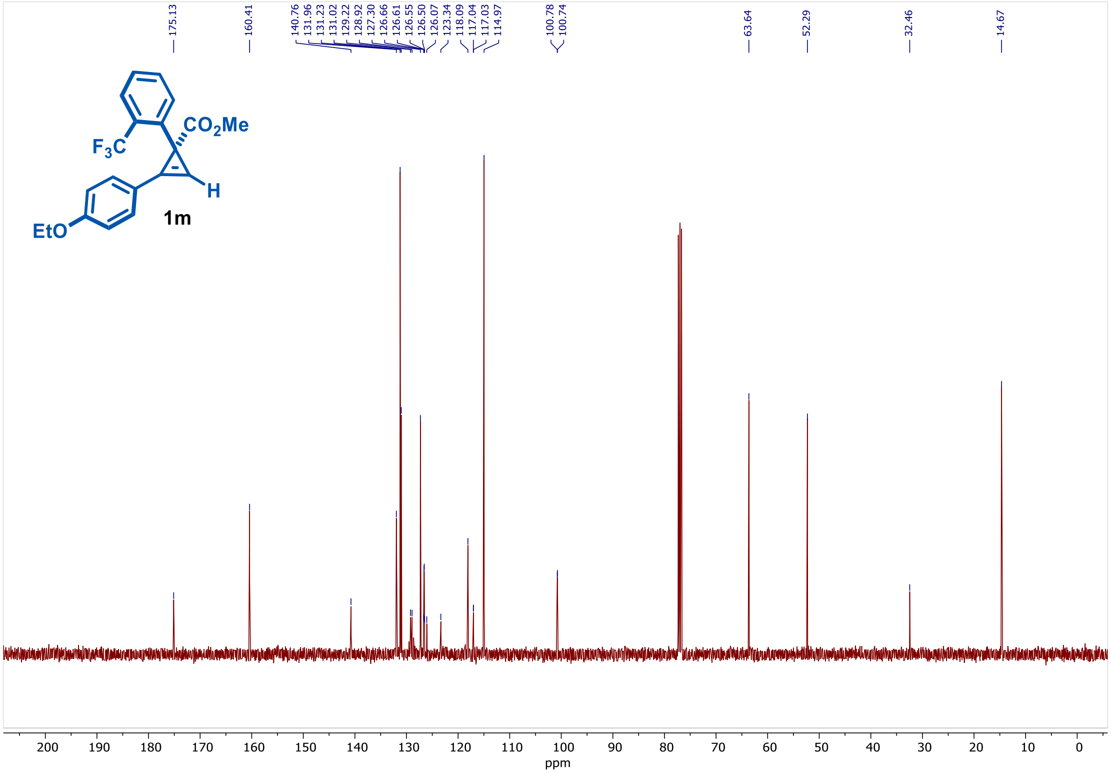
^{19}F-NMR (377 MHz, CDCl$_3$) of compound 1l



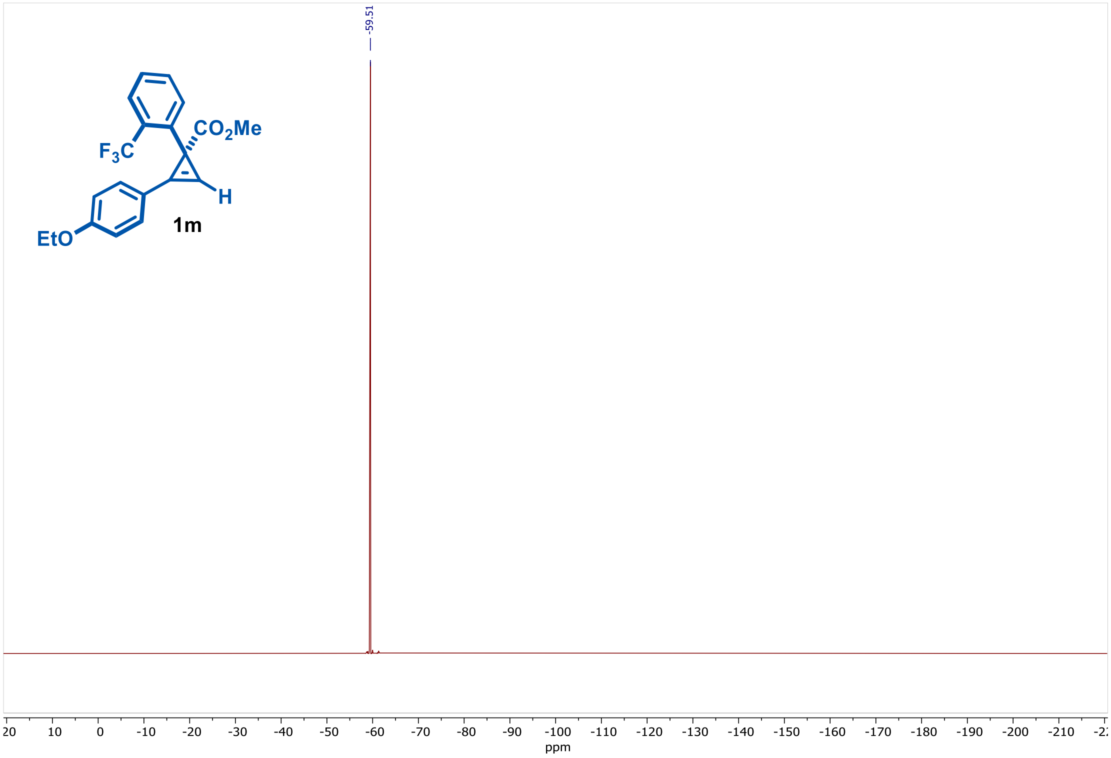
^{1}H-NMR (400 MHz, CDCl$_3$) of compound 1m (see procedure)



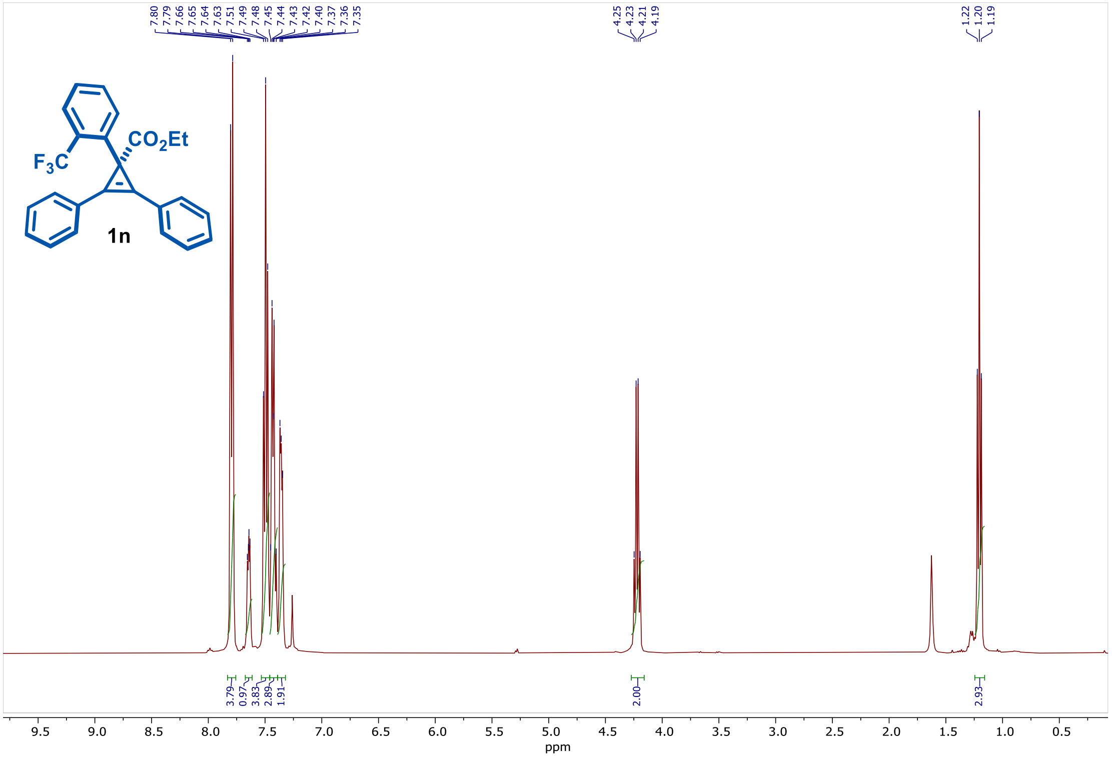
^{13}C-NMR (101 MHz, CDCl$_3$) of compound 1m



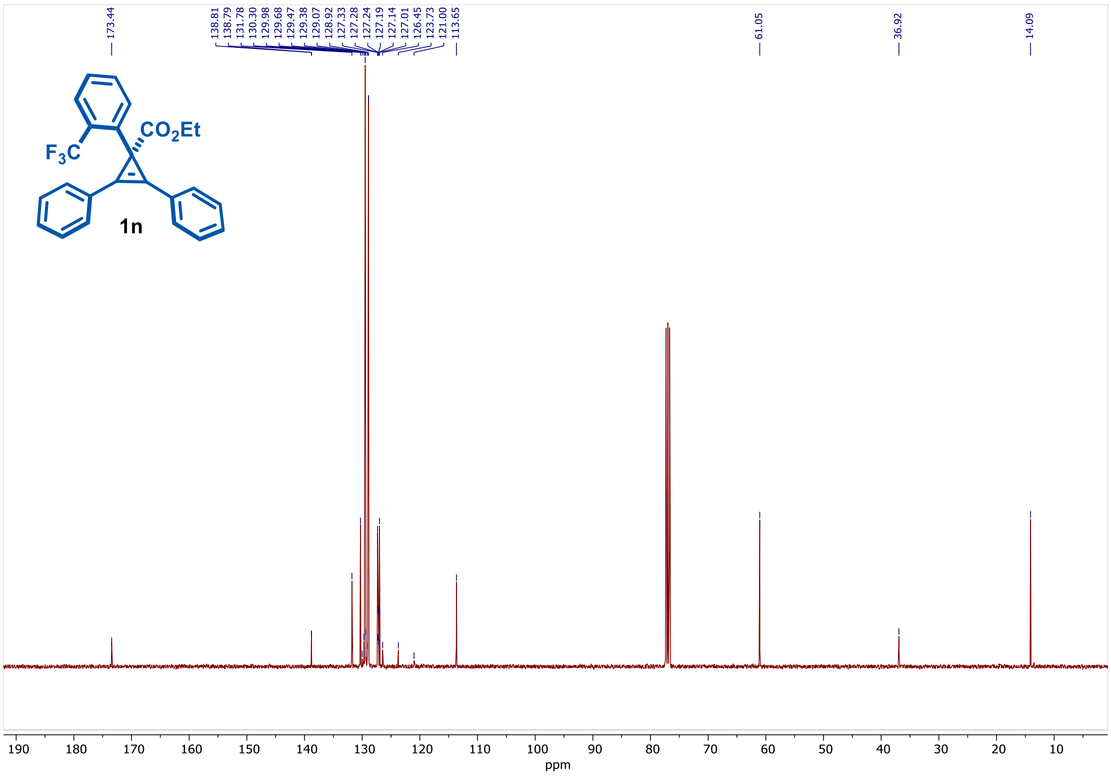
^{19}F-NMR (377 MHz, $CDCl_3$) of compound 1m



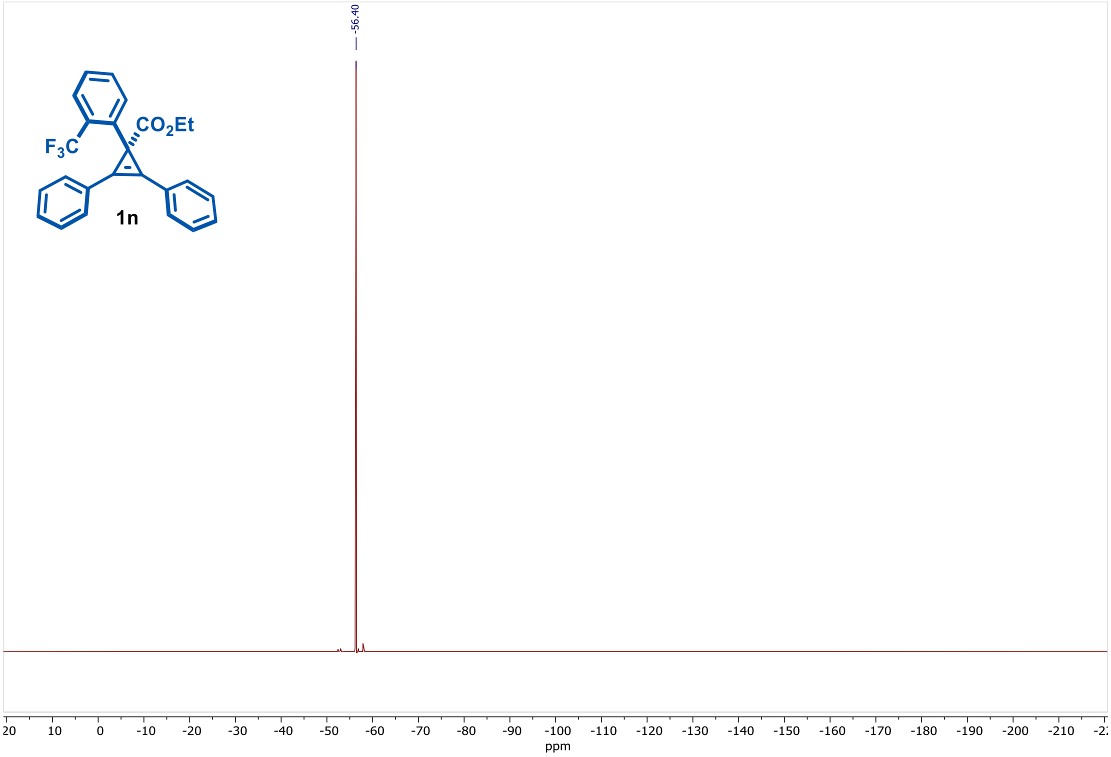
^{1}H-NMR (400 MHz, CDCl$_3$) of compound 1n (see procedure)



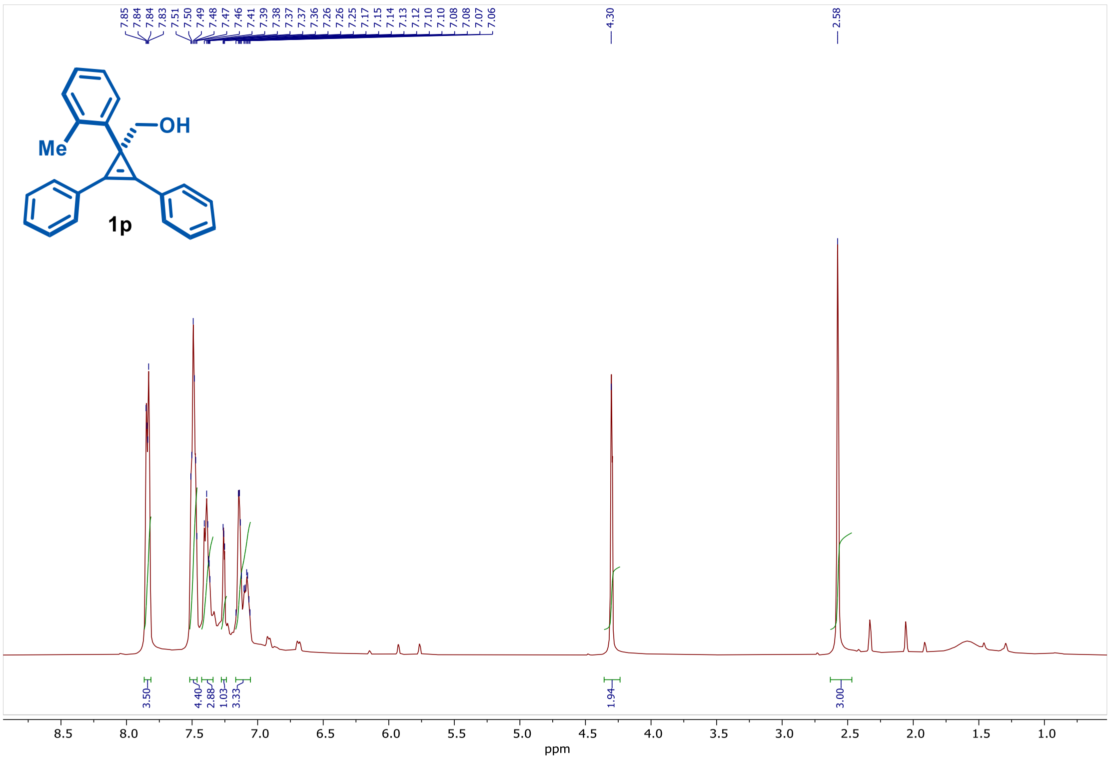
^{13}C-NMR (101 MHz, CDCl$_3$) of compound 1n



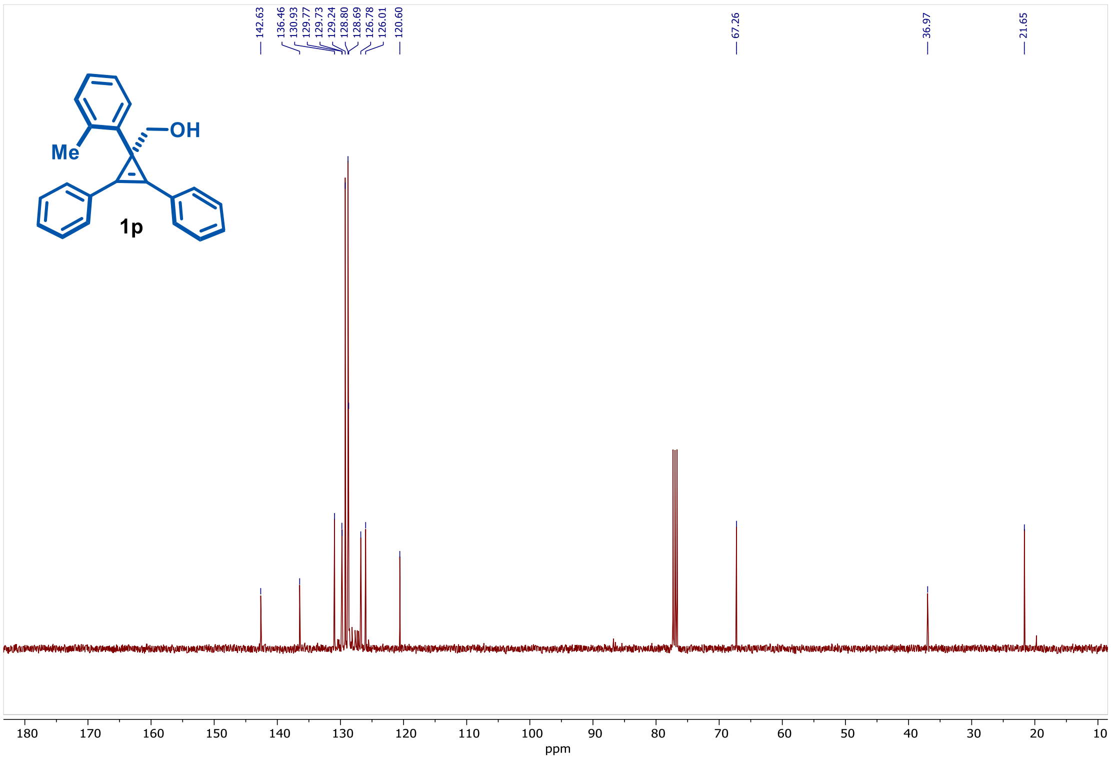
^{19}F-NMR (377 MHz, $CDCl_3$) of compound 1n



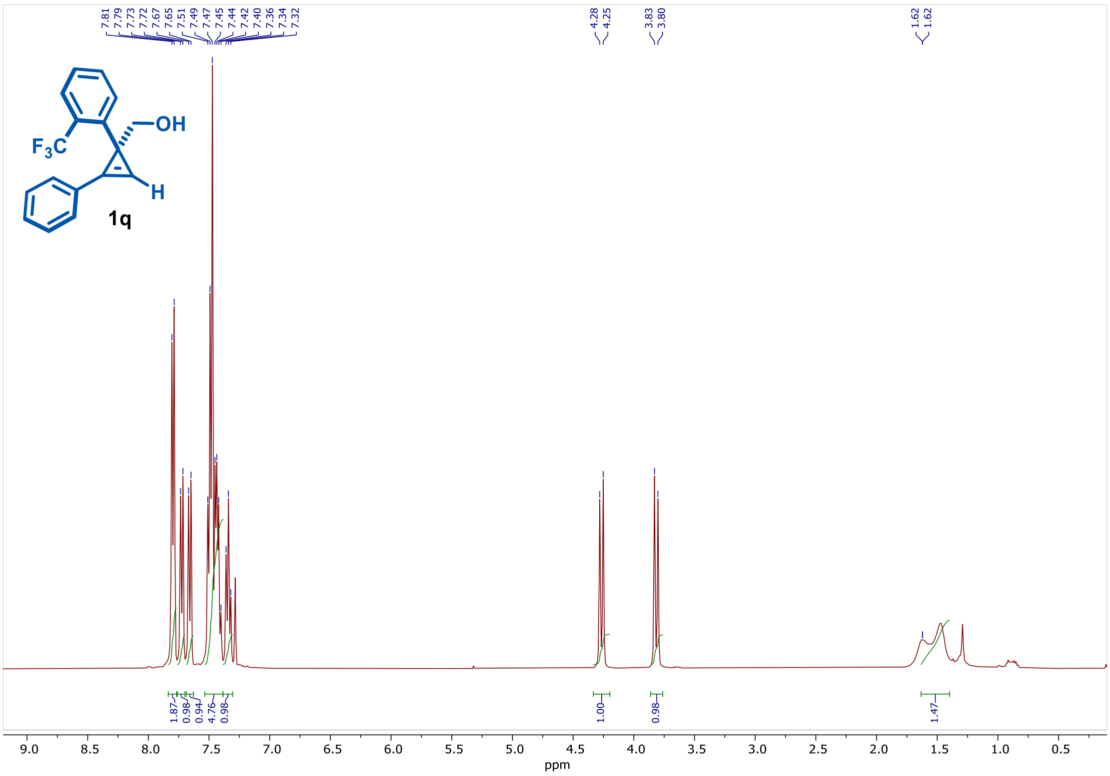
^{1}H-NMR (400 MHz, CDCl$_3$) of compound 1p (see procedure)



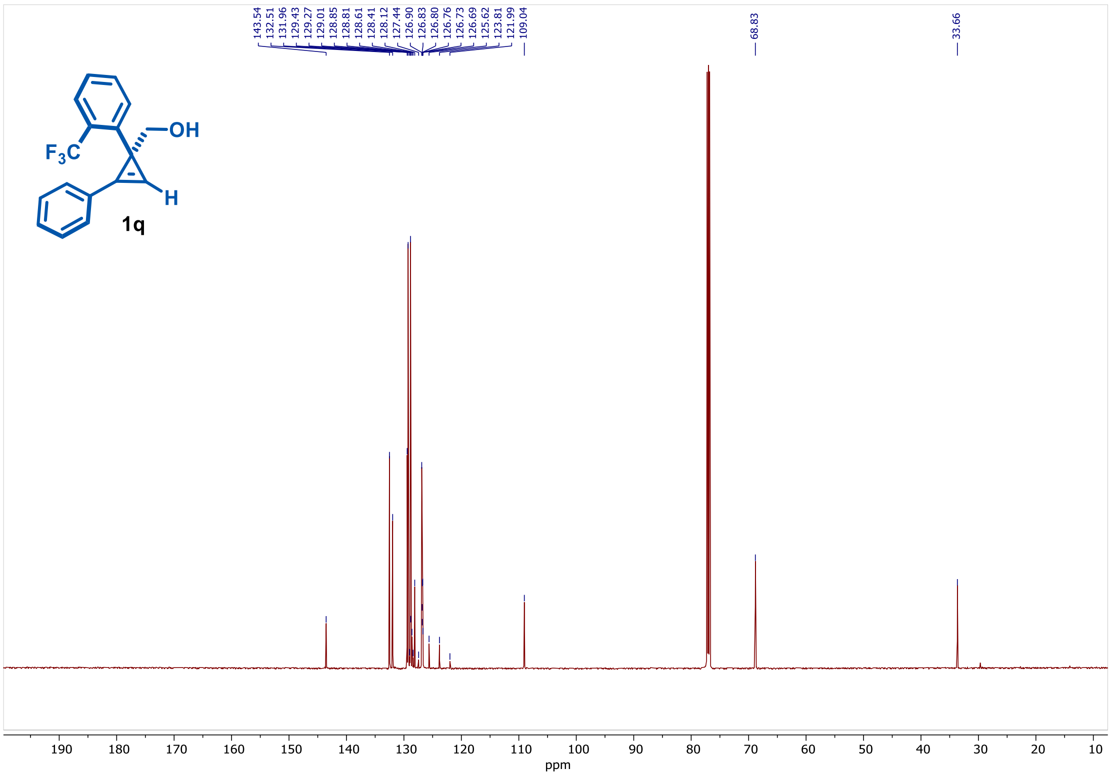
^{13}C-NMR (101 MHz, CDCl$_3$) of compound 1p



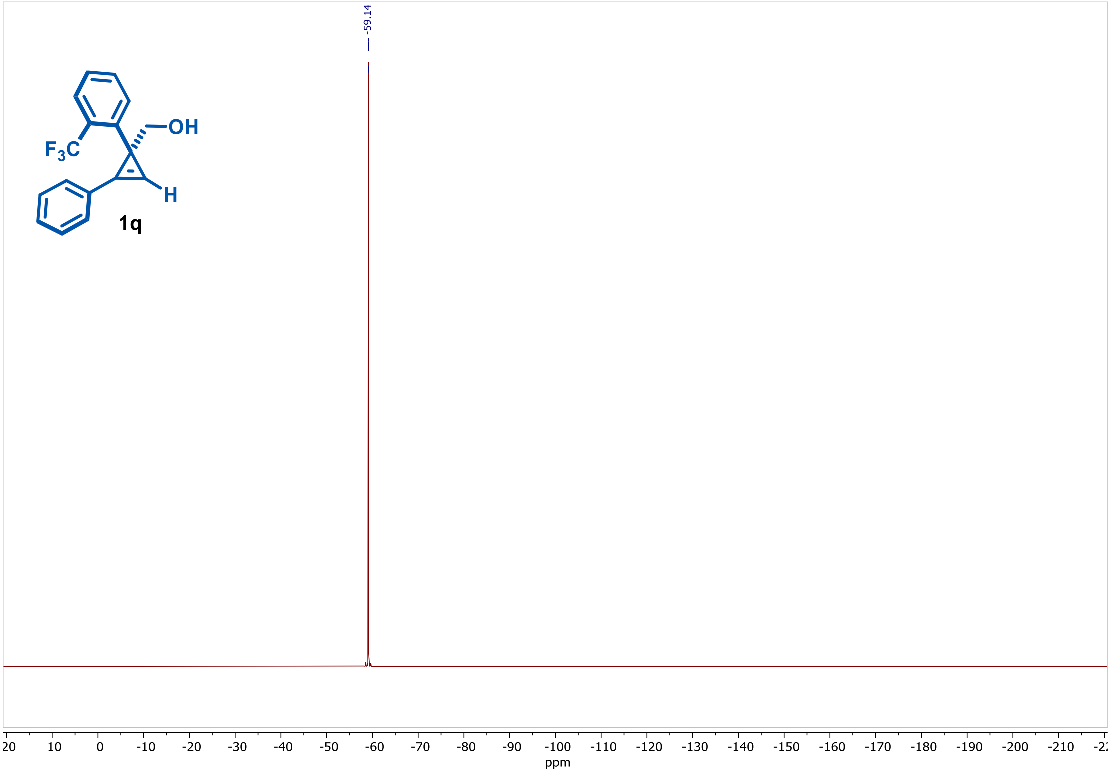
^{1}H-NMR (400 MHz, $CDCl_3$) of compound 1q (see procedure)



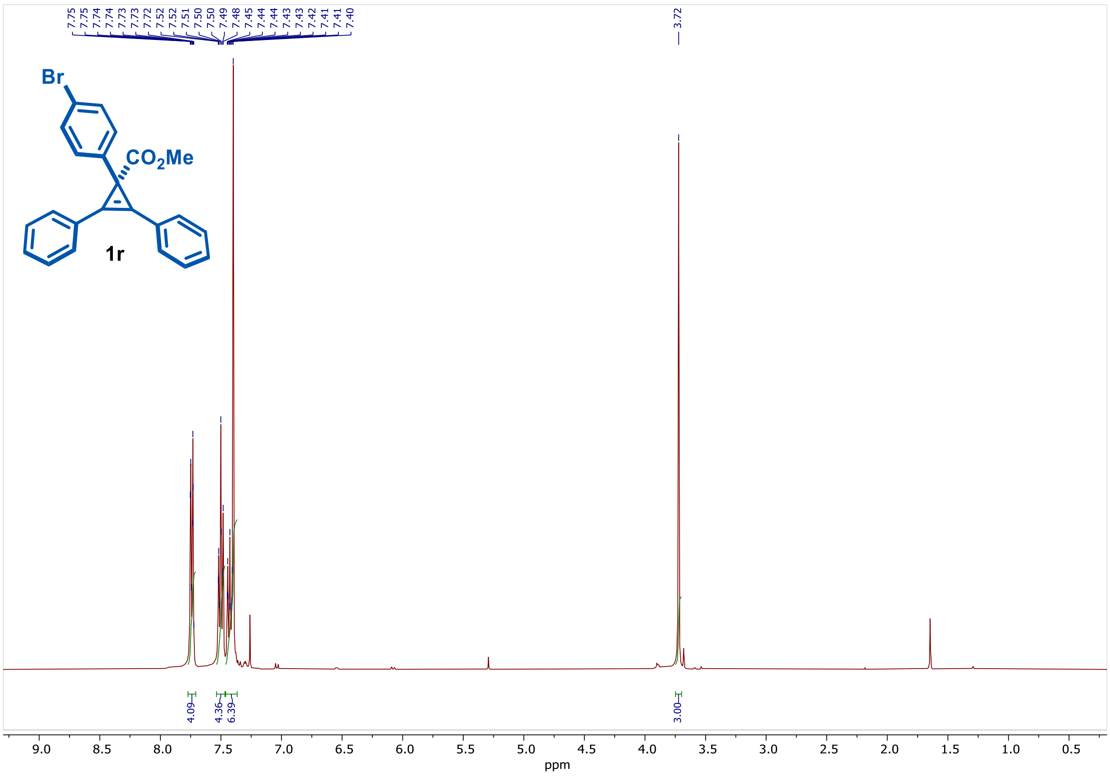
^{13}C-NMR (101 MHz, $CDCl_3$) of compound 1q



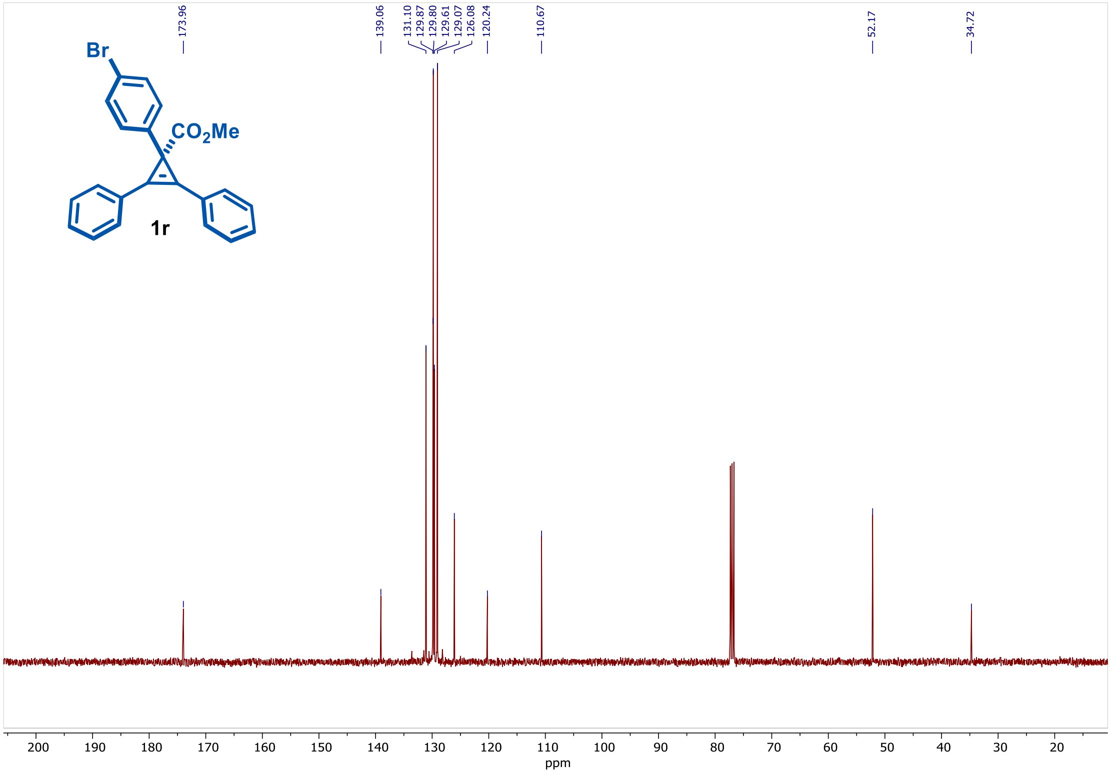
^{19}F-NMR (377 MHz, $CDCl_3$) of compound 1q



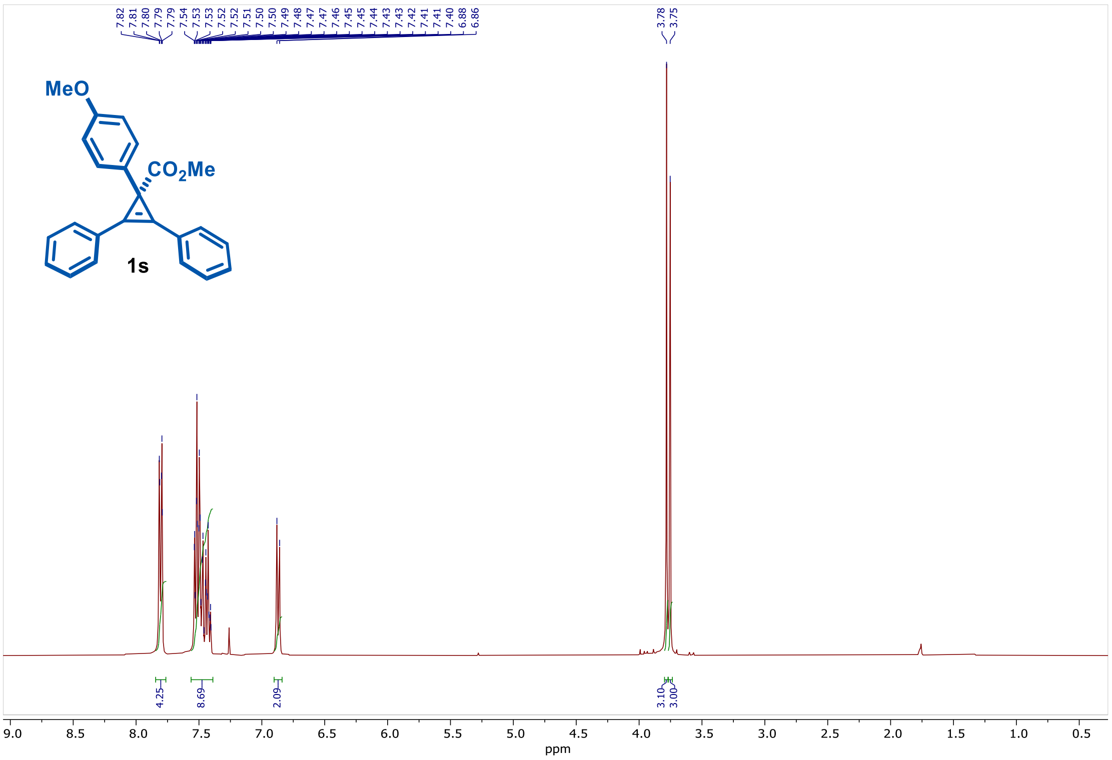
^{1}H-NMR (400 MHz, CDCl$_3$) of compound 1r (see procedure)



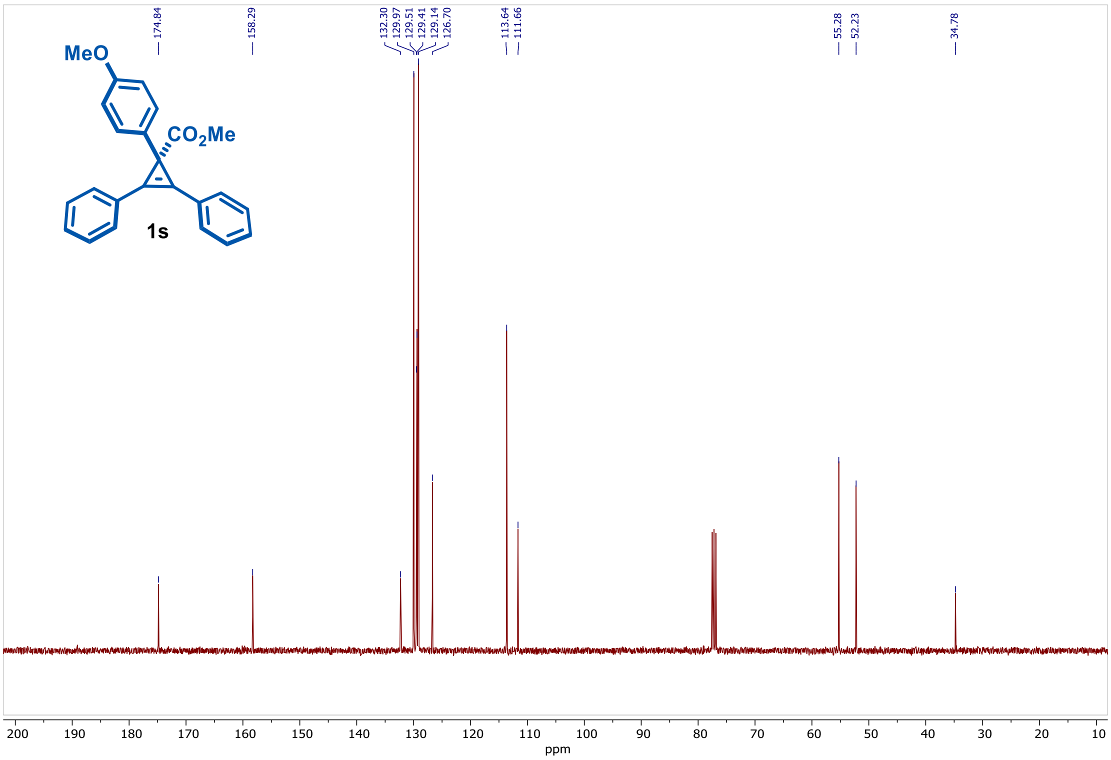
^{13}C-NMR (101 MHz, CDCl$_3$) of compound 1r



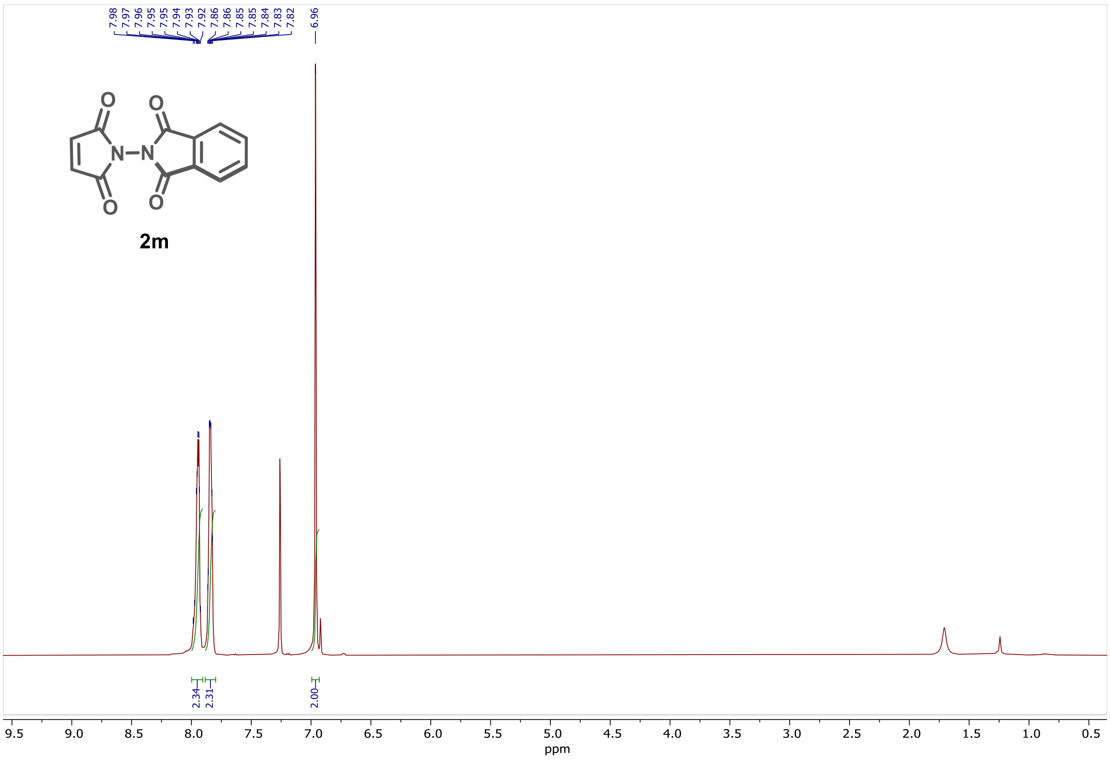
^{1}H-NMR (400 MHz, $CDCl_3$) of compound 1s (see procedure)



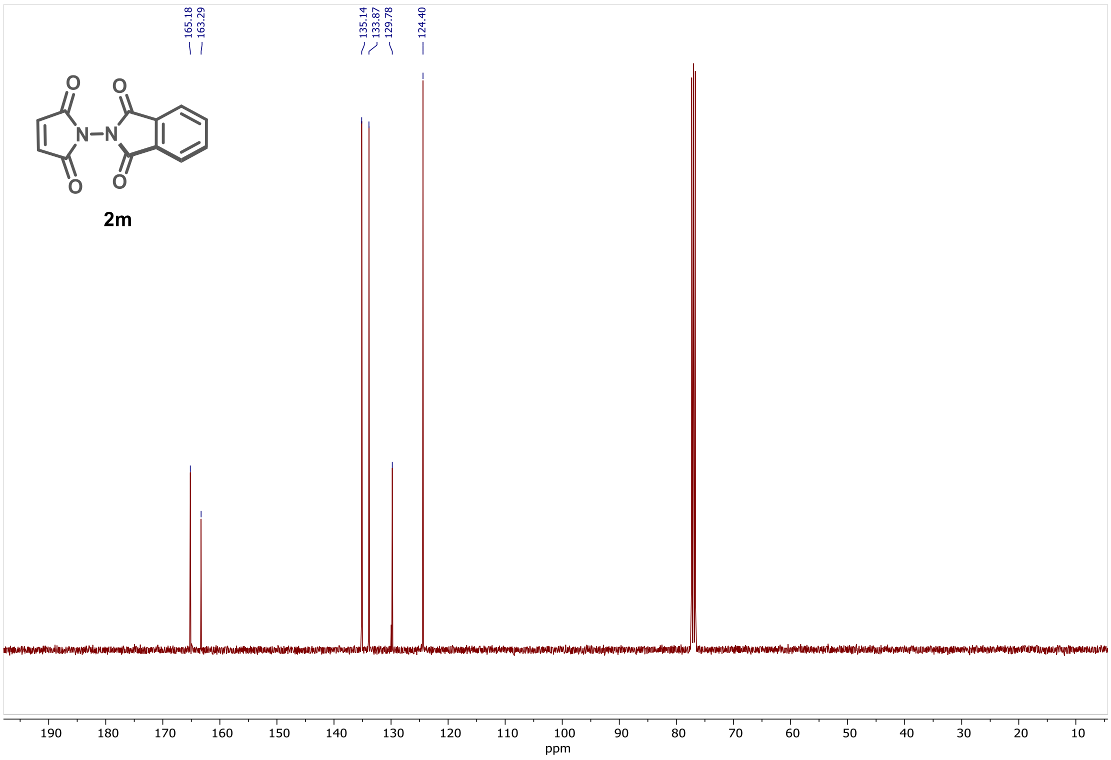
^{13}C-NMR (101 MHz, $CDCl_3$) of compound 1s



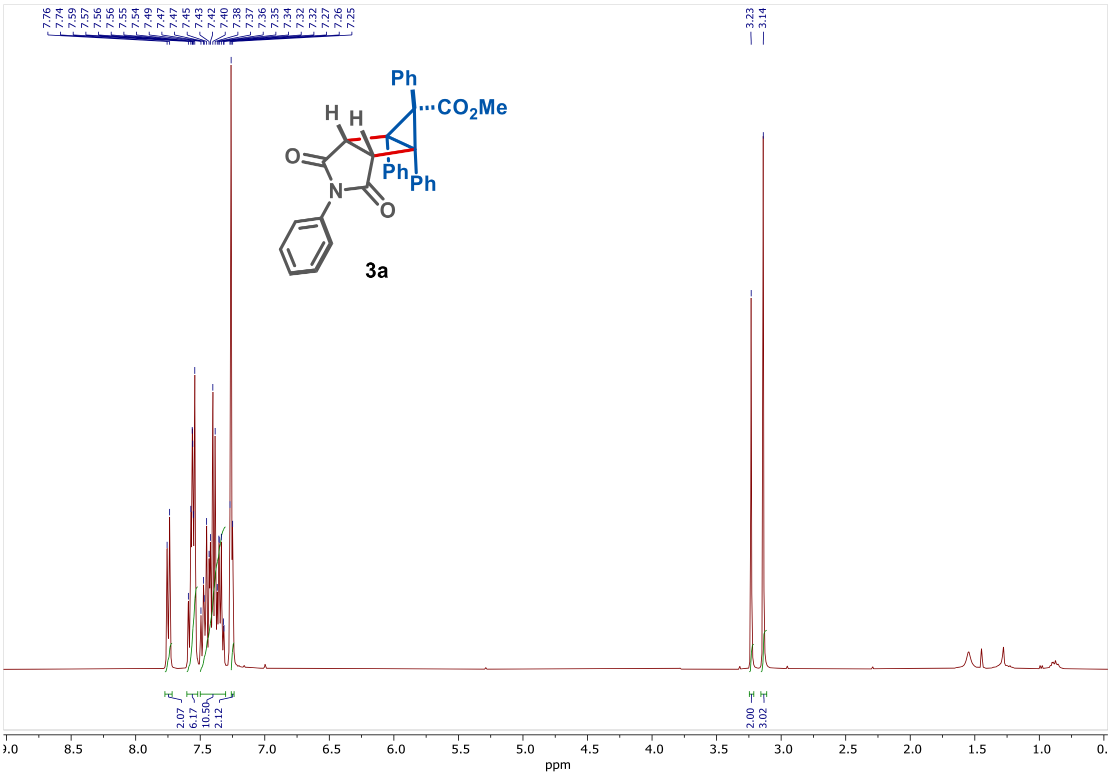
^{1}H-NMR (400 MHz, CDCl$_3$) of compound 2m (see procedure)



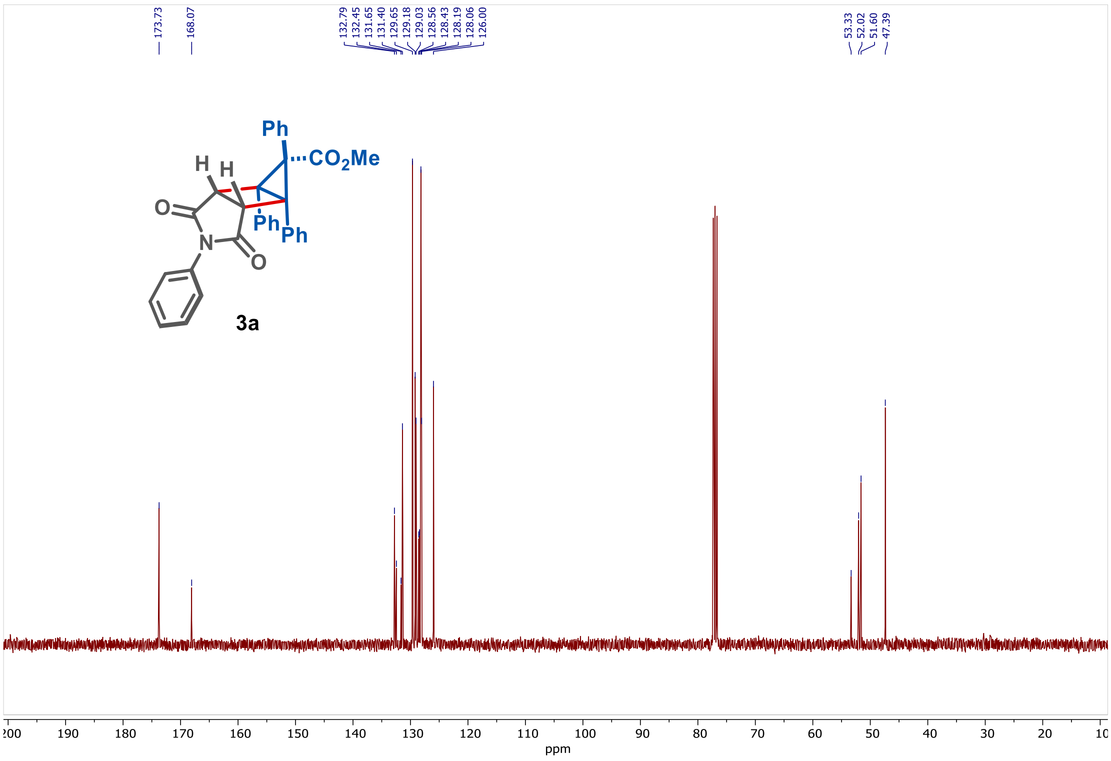
^{13}C-NMR (101 MHz, CDCl$_3$) of compound 2m



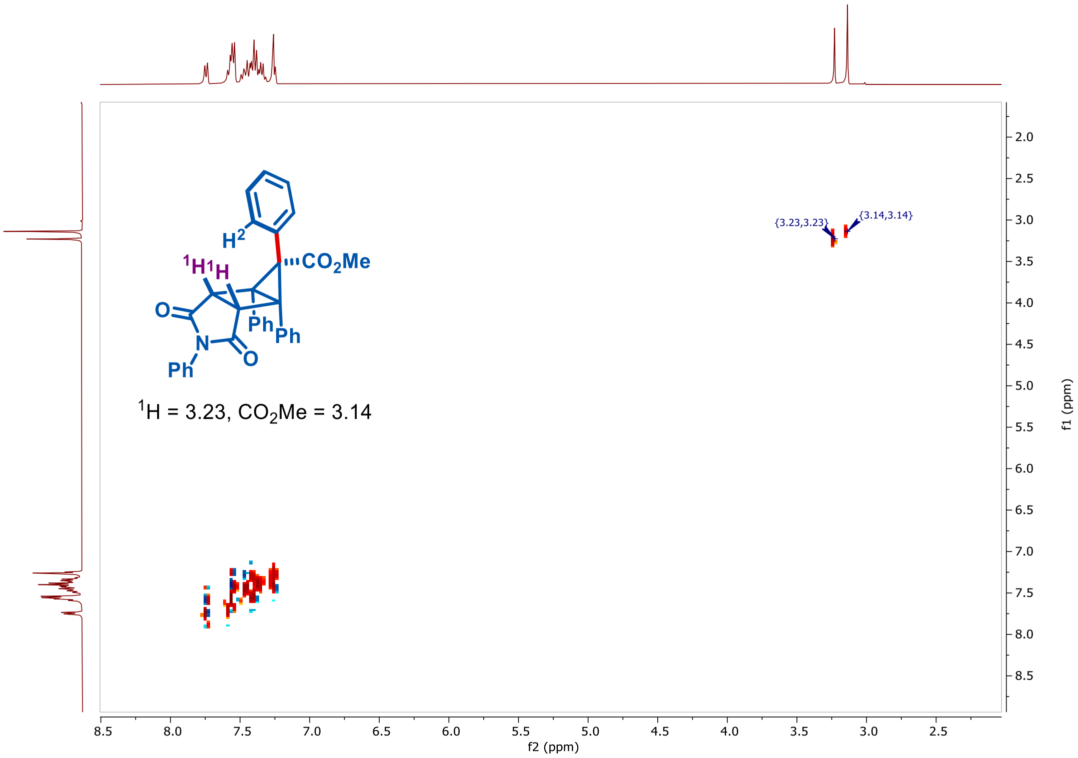
^{1}H-NMR (400 MHz, CDCl$_3$) of compound 3a (see procedure)



^{13}C-NMR (101 MHz, CDCl$_3$) of compound 3a



COSY of compound 3a



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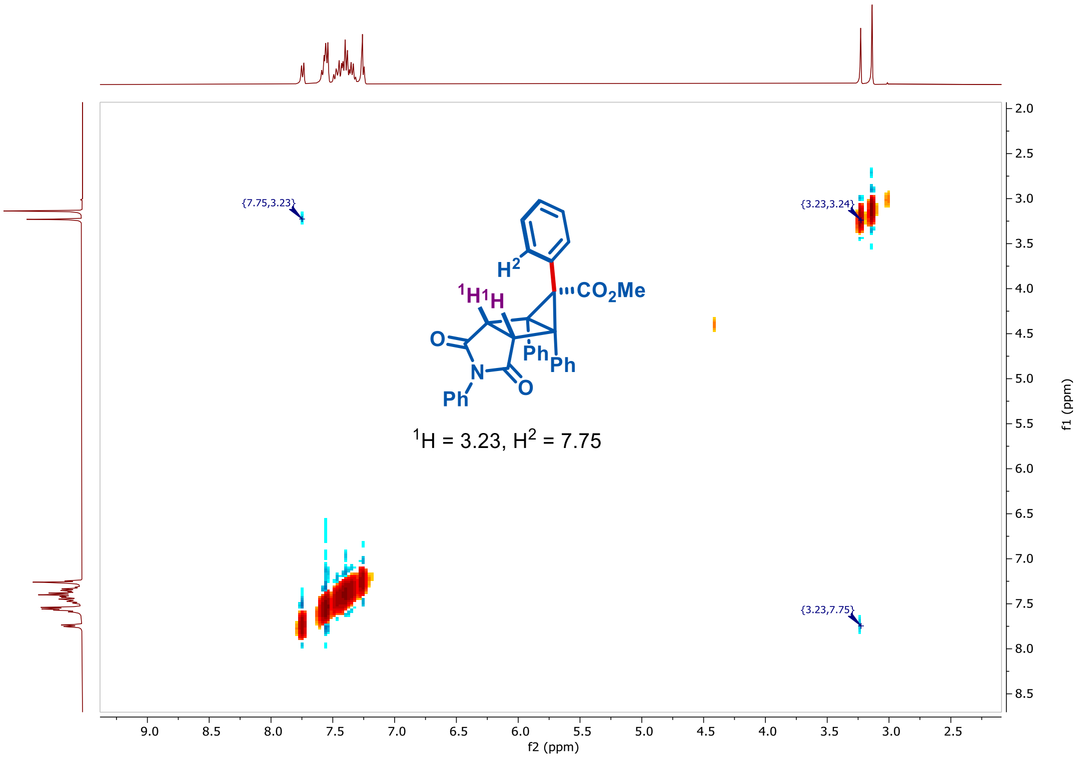
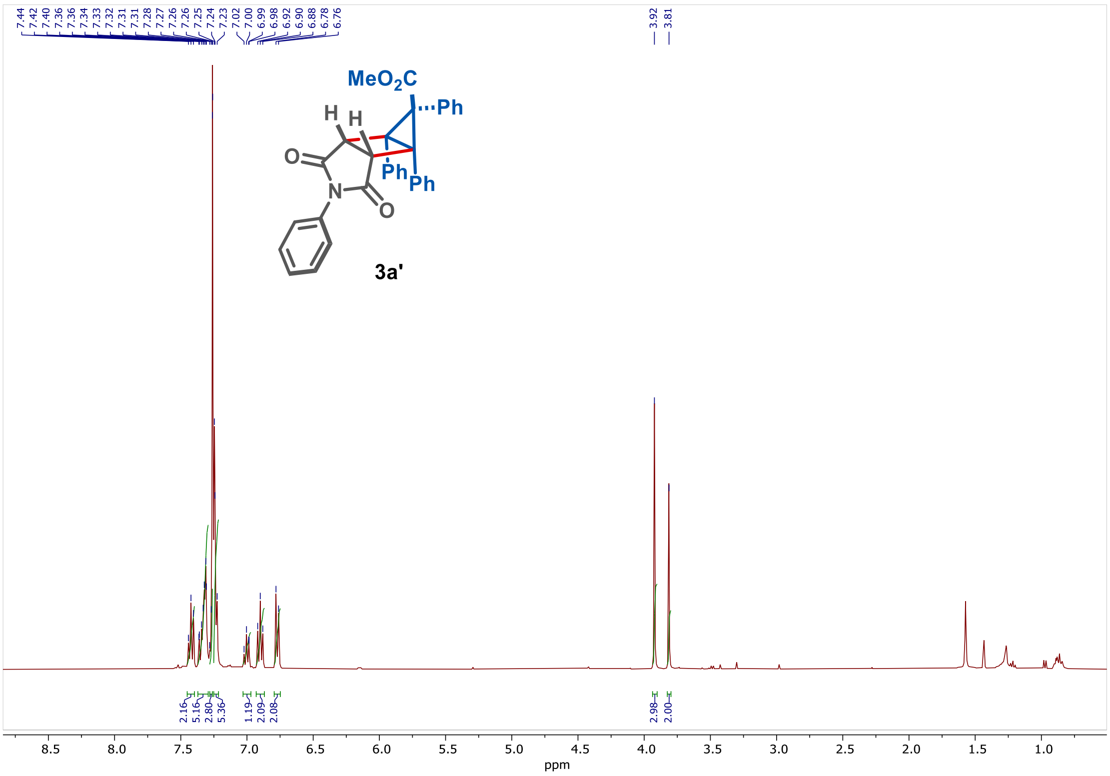
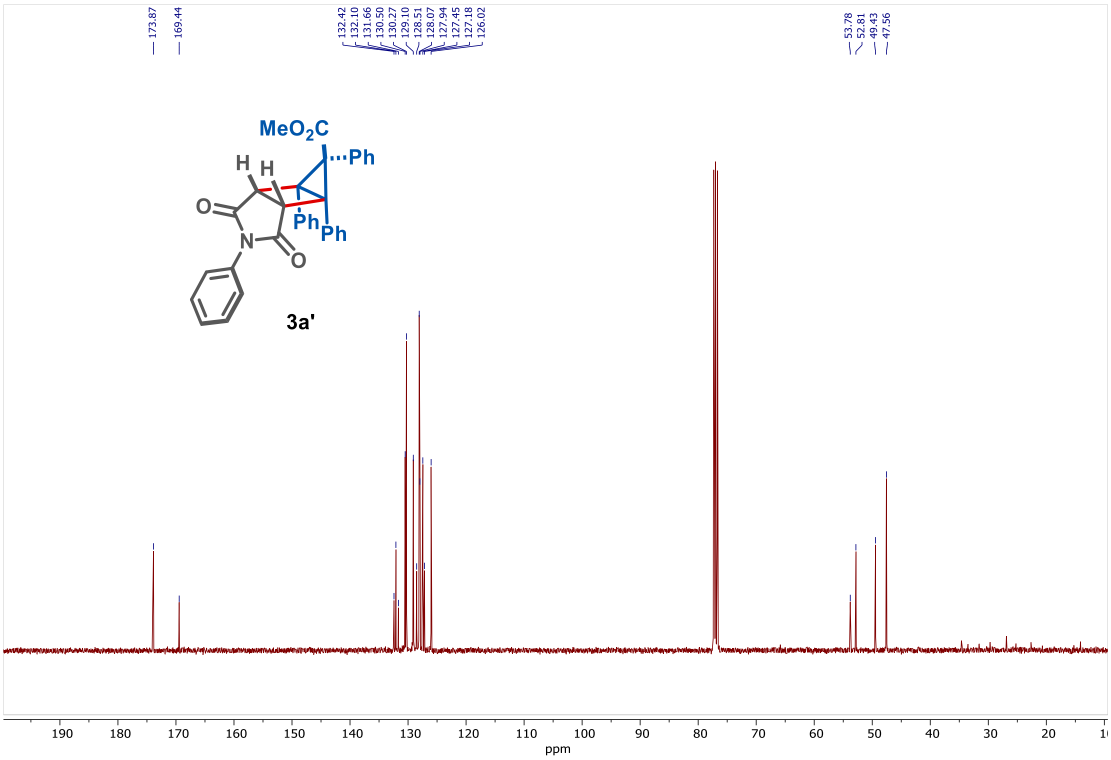


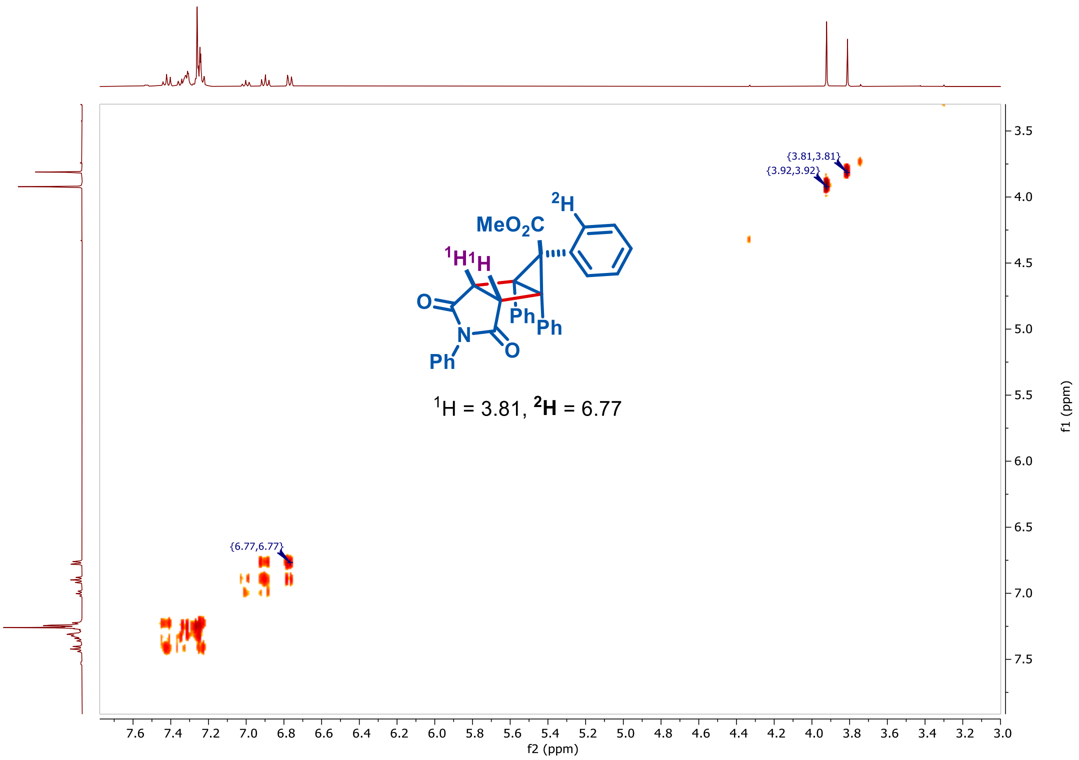
^{1}H-NMR (400 MHz, CDCl$_3$) of compound 3a’ (see procedure)



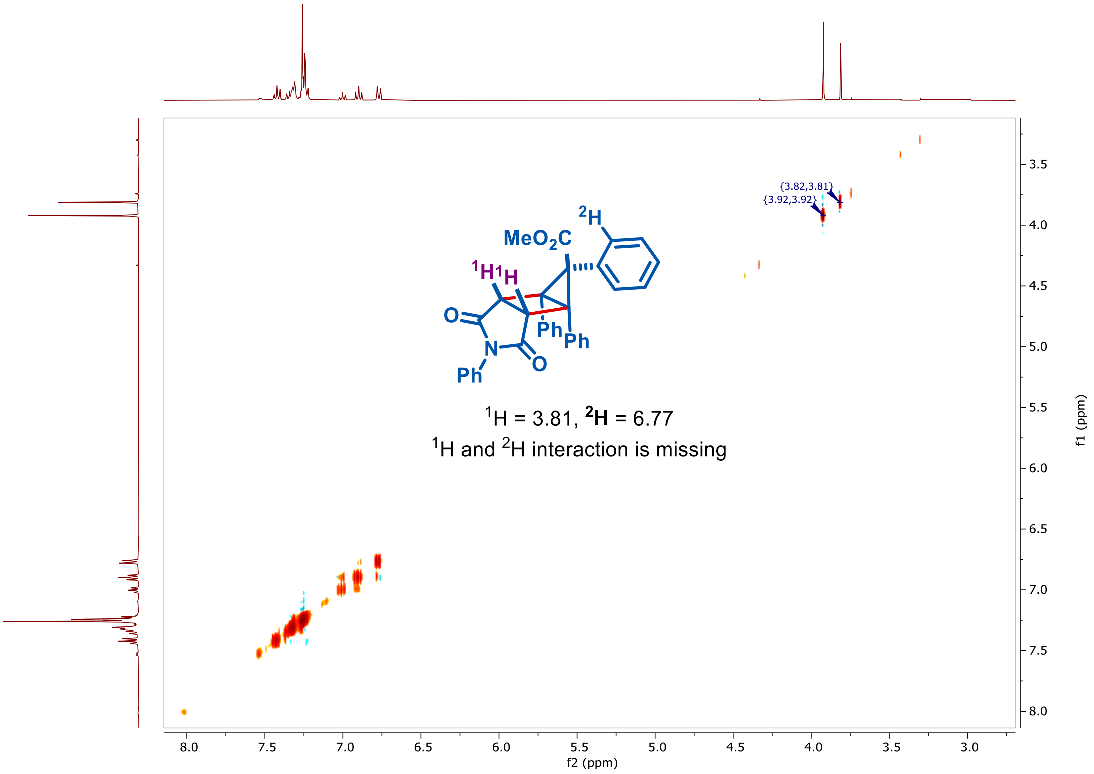
^{13}C-NMR (101 MHz, CDCl$_3$) of compound 3a’



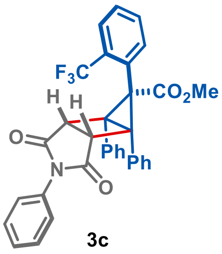
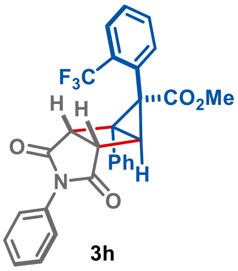
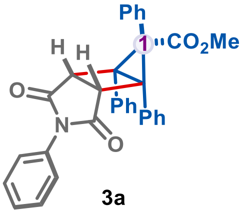
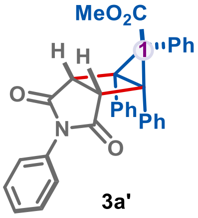
COSY of compound 3a’



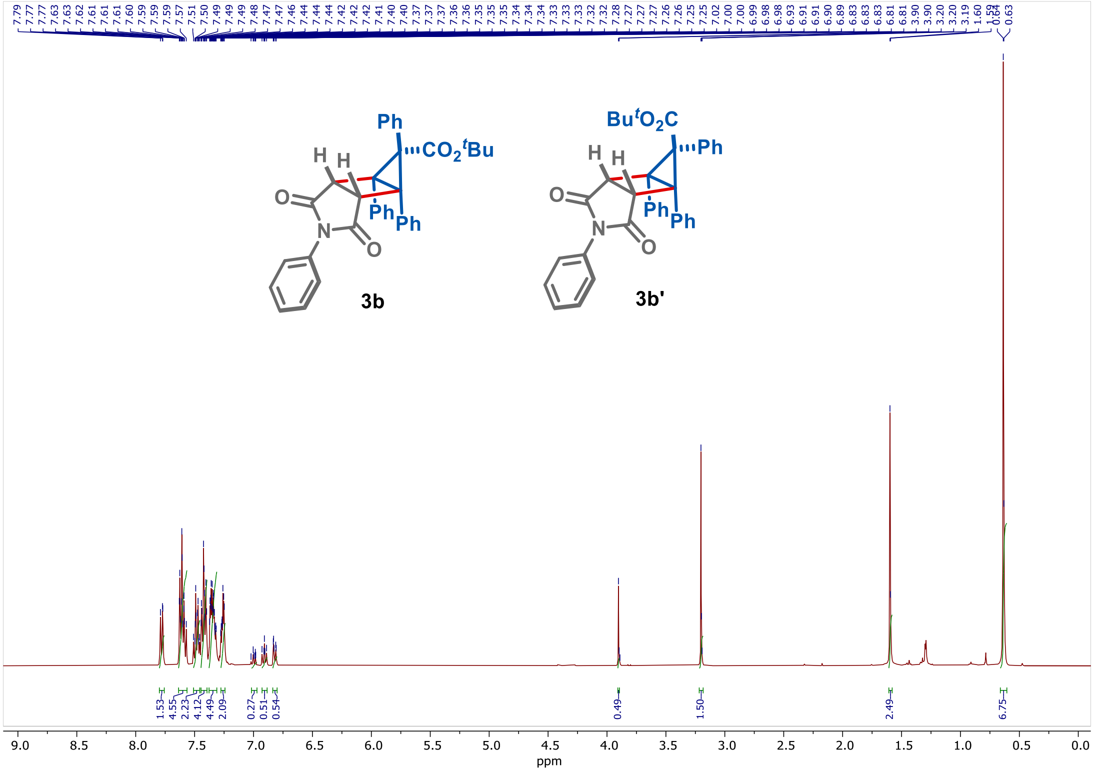
NOESY of compound 3a’



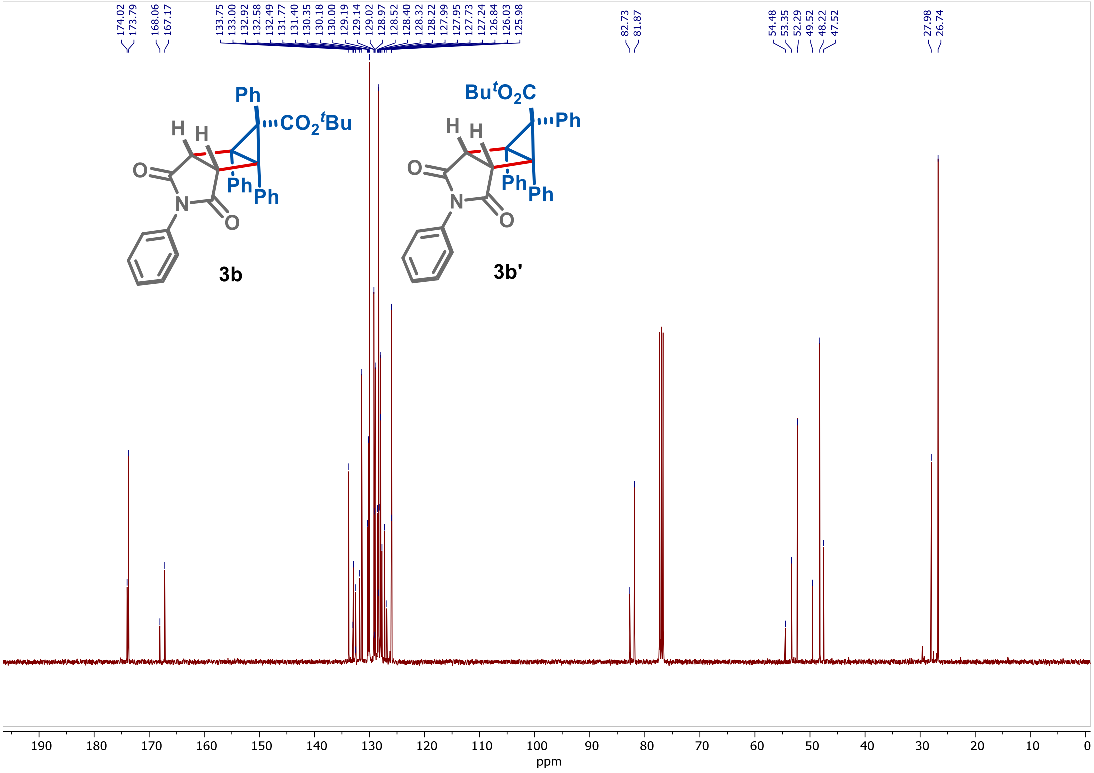
We have compared the NMR data of **3c** and **3h** with **3a** (all are major diastereomers) and assigned the stereochemistry.

Housanes	^{1}H-NMR
 **3c**	• 3.39 (d, *J* = 3.9 Hz, 1H, ***CH***), 3.18 (d, *J* = 3.9 Hz, 1H, ***CH***), 3.28 (s, 3H, CO$_2$***CH$_3$***).
 **3h**	• 3.30 (dd, *J* = 3.5 Hz, 1H, ***CH***), 3.26 (s, 3H, CO$_2$***CH$_3$***), 2.73 (d, *J* = 3.5 Hz, 1H, ***CH***).
 **3a**  **3a'**	• Major: 3.23 (s, 2H, ***CH***), 3.14 (s, 3H, CO$_2$***CH$_3$***). • Minor: 3.92 (s, 3H, CO$_2$***CH$_3$***), 3.81 (s, 2H, ***CH***).

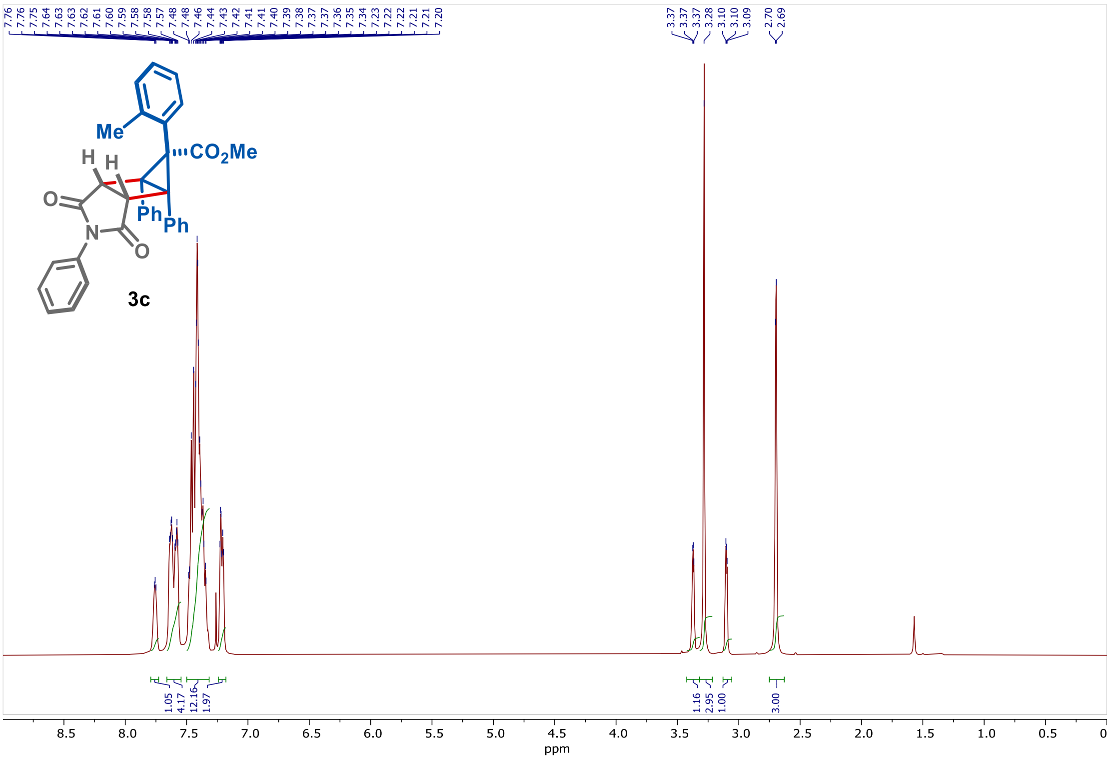
^{1}H-NMR (400 MHz, CDCl$_3$) of compound 3b/3b’ (see procedure)



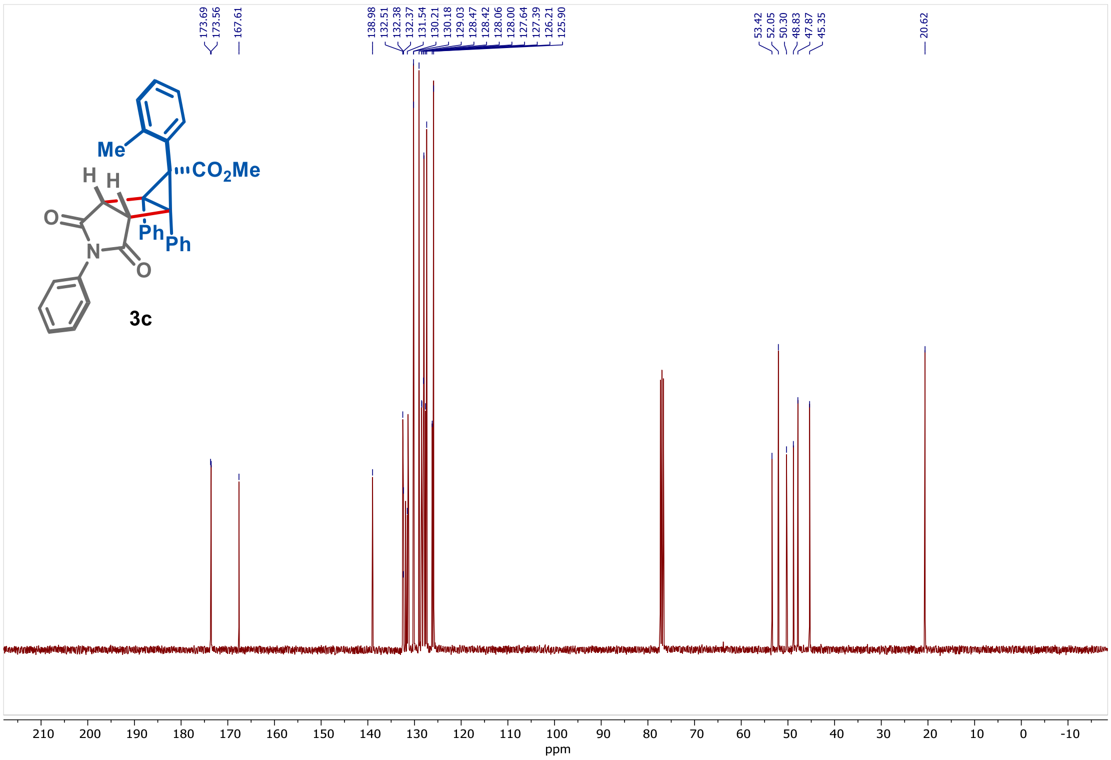
^{13}C-NMR (101 MHz, CDCl$_3$) of compound 3b/3b’



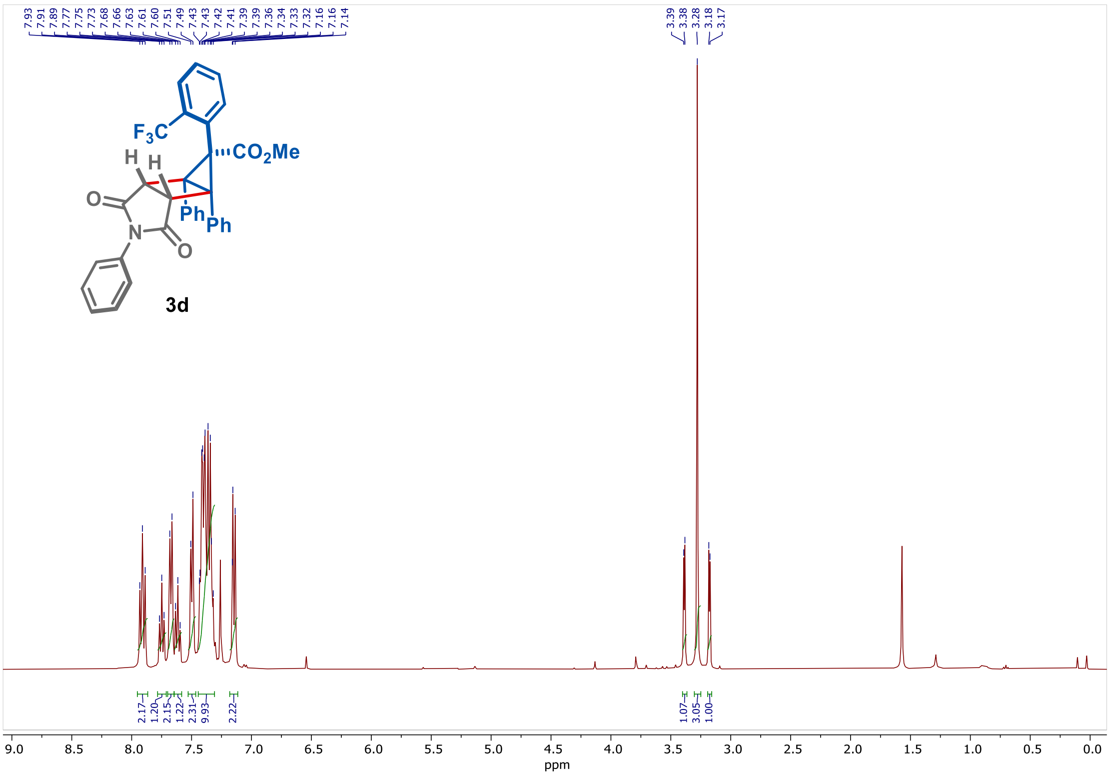
^{1}H-NMR (400 MHz, CDCl$_3$) of compound 3c (see procedure)



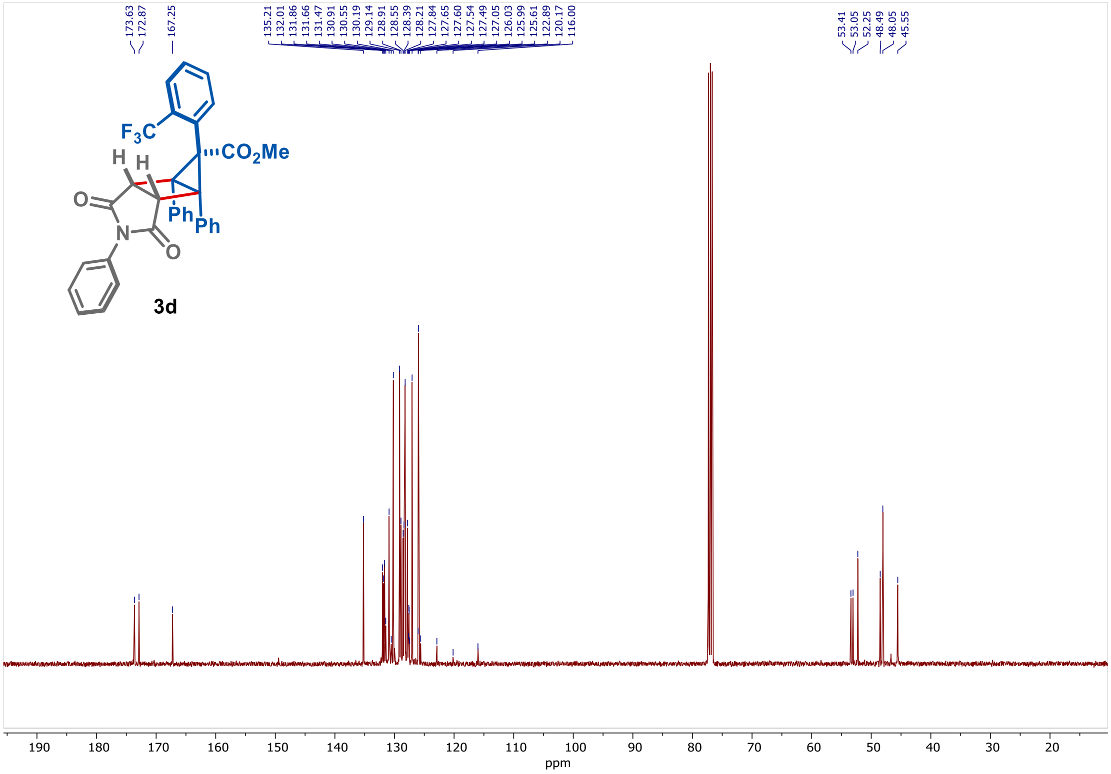
^{13}C-NMR (101 MHz, CDCl$_3$) of compound 3c



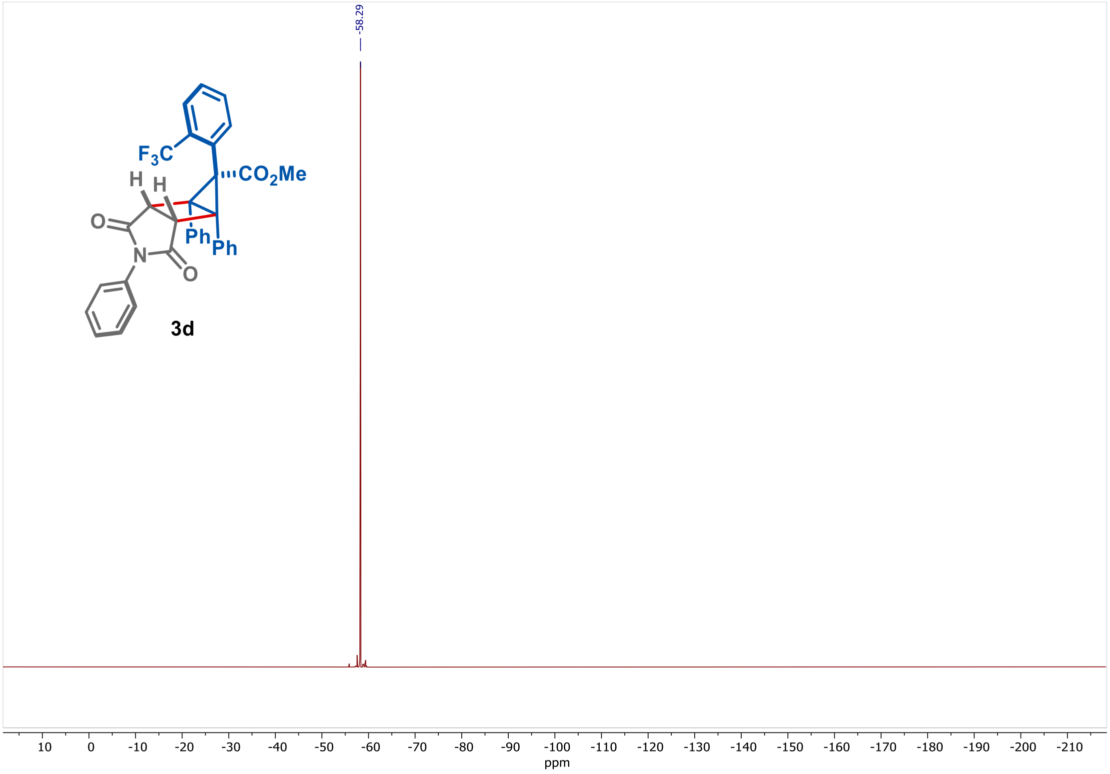
^{1}H-NMR (400 MHz, CDCl$_3$) of compound 3d (see procedure)



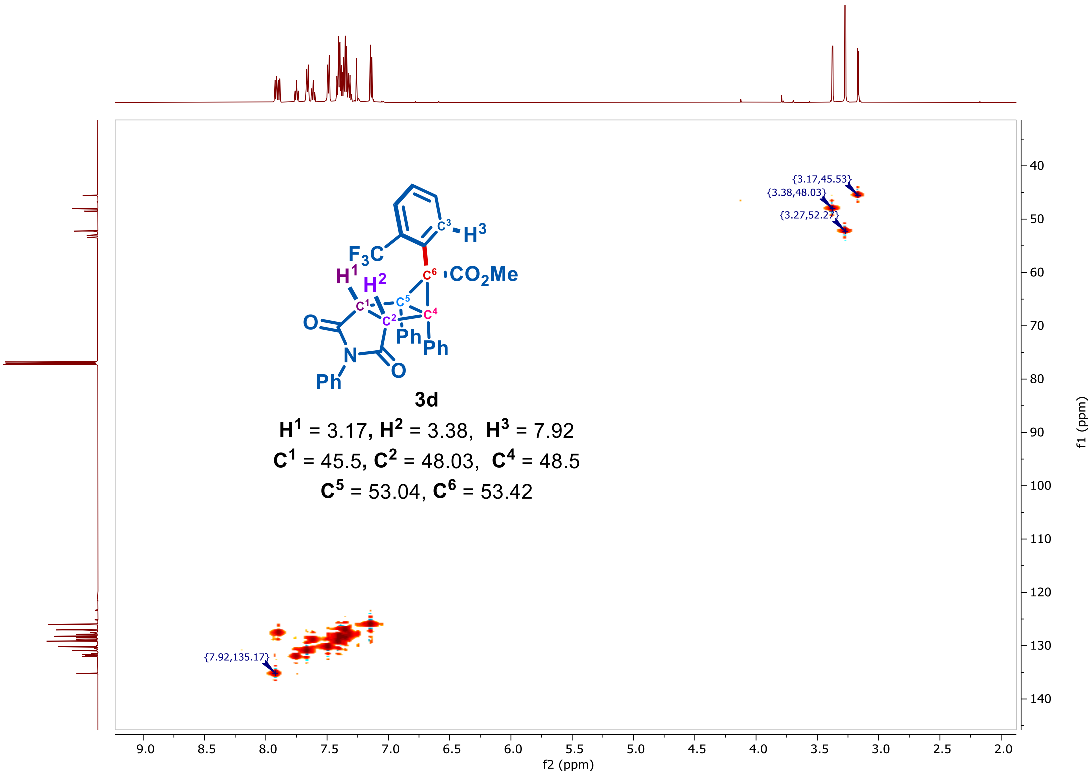
^{13}C-NMR (101 MHz, CDCl$_3$) of compound 3d



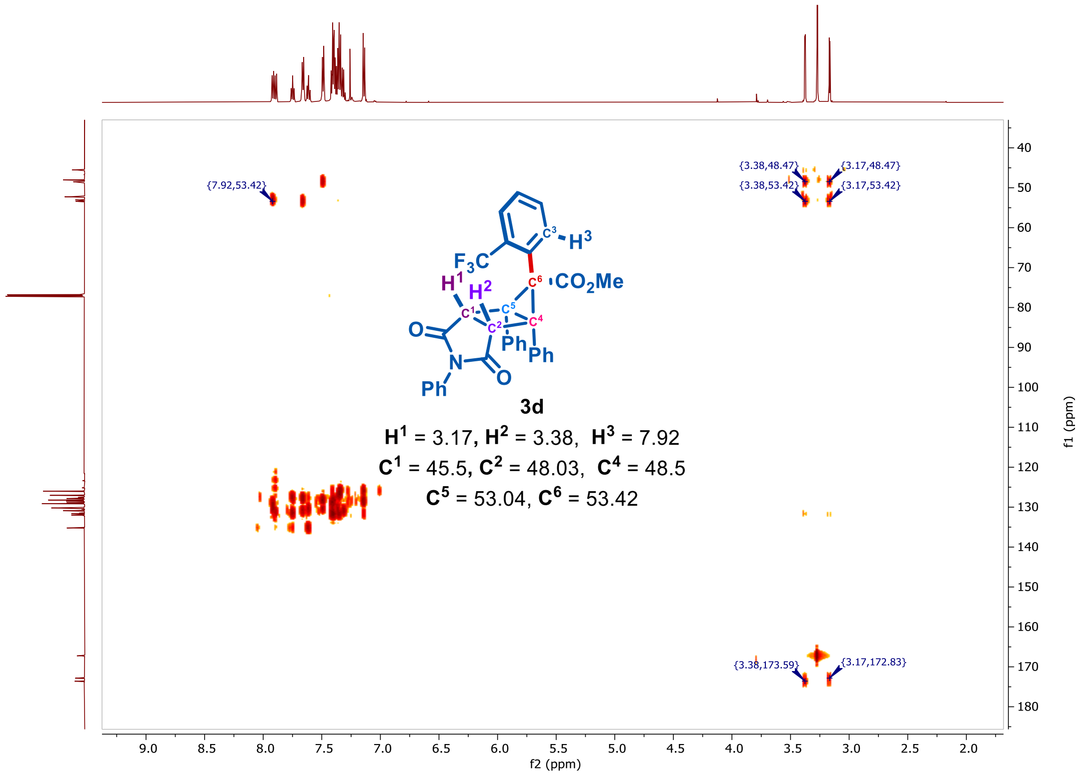
^{19}F-NMR (377 MHz, $CDCl_3$) of compound 3d



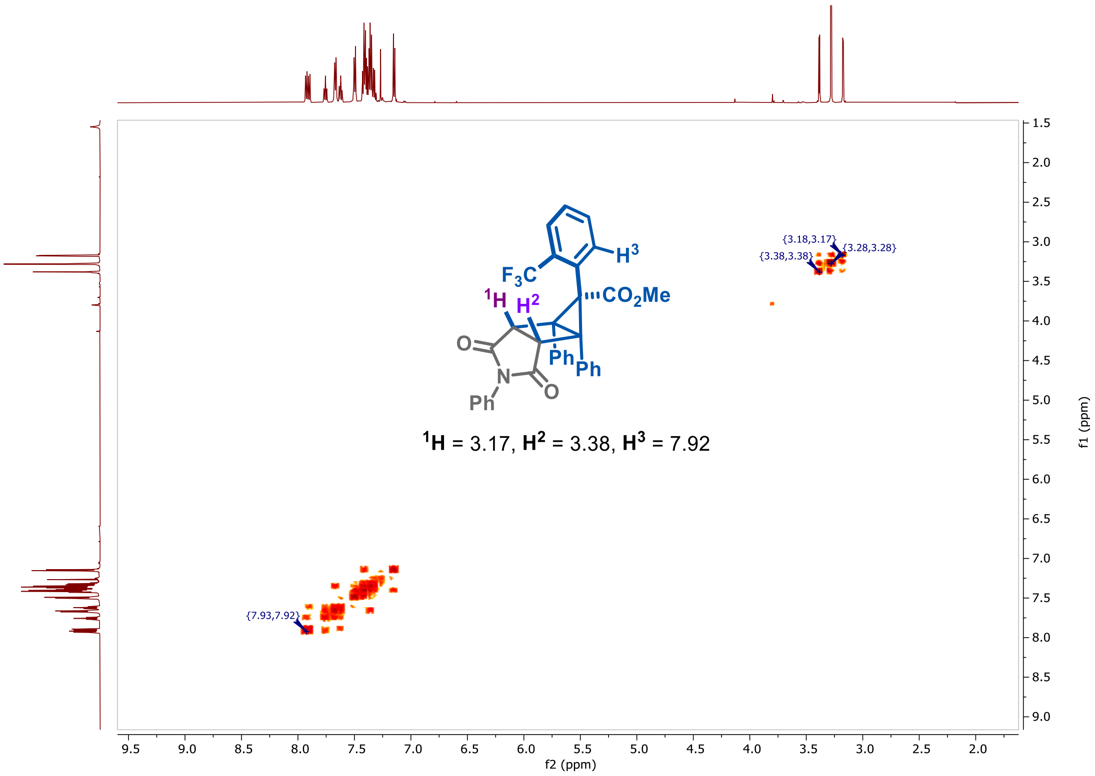
HSQC of compound 3d



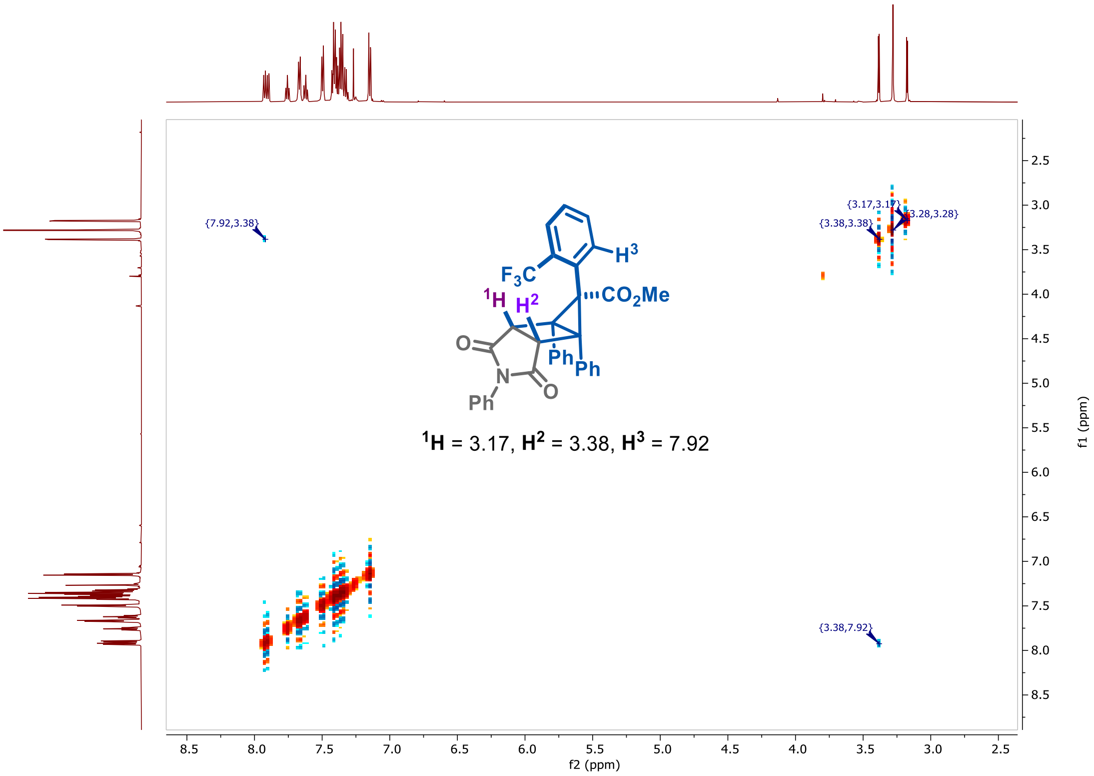
HMBC of compound 3d



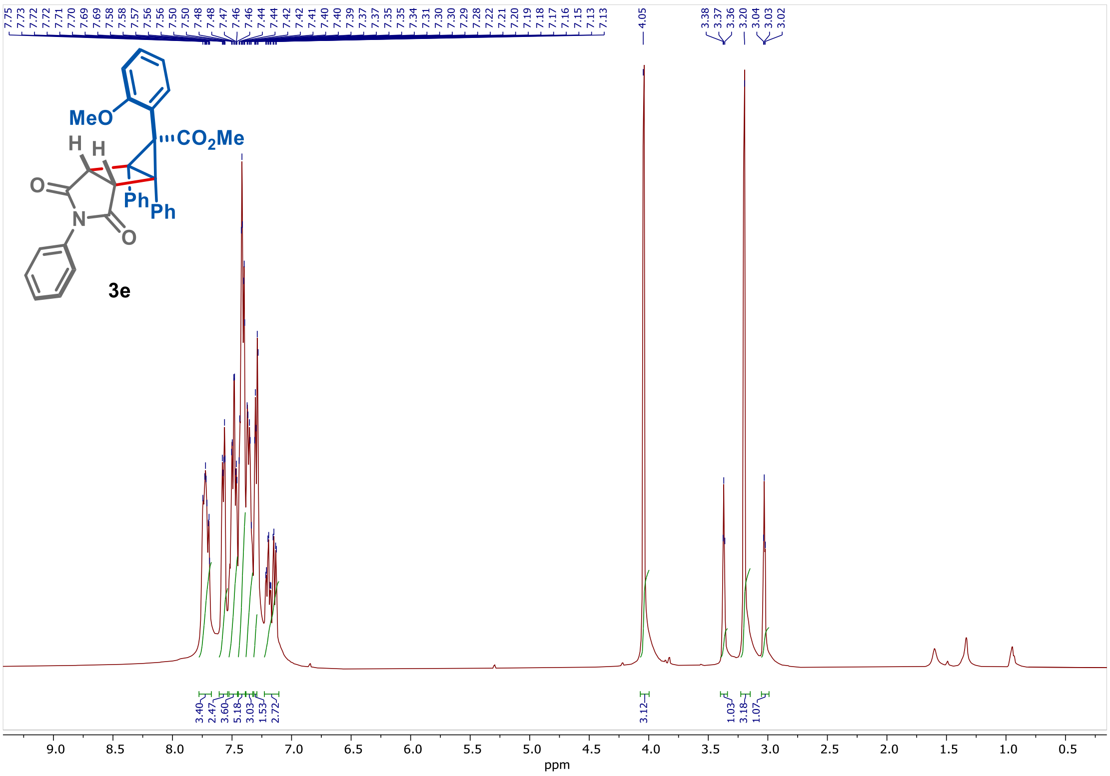
COSY of compound 3d



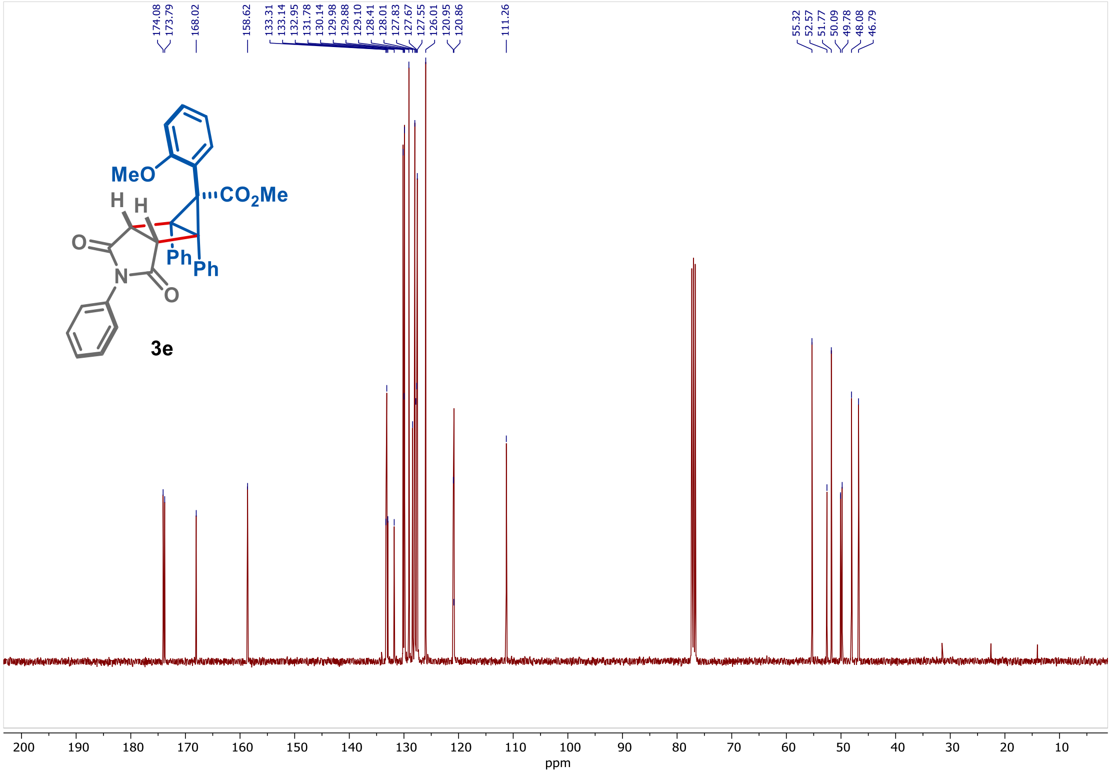
NOESY of compound 3d



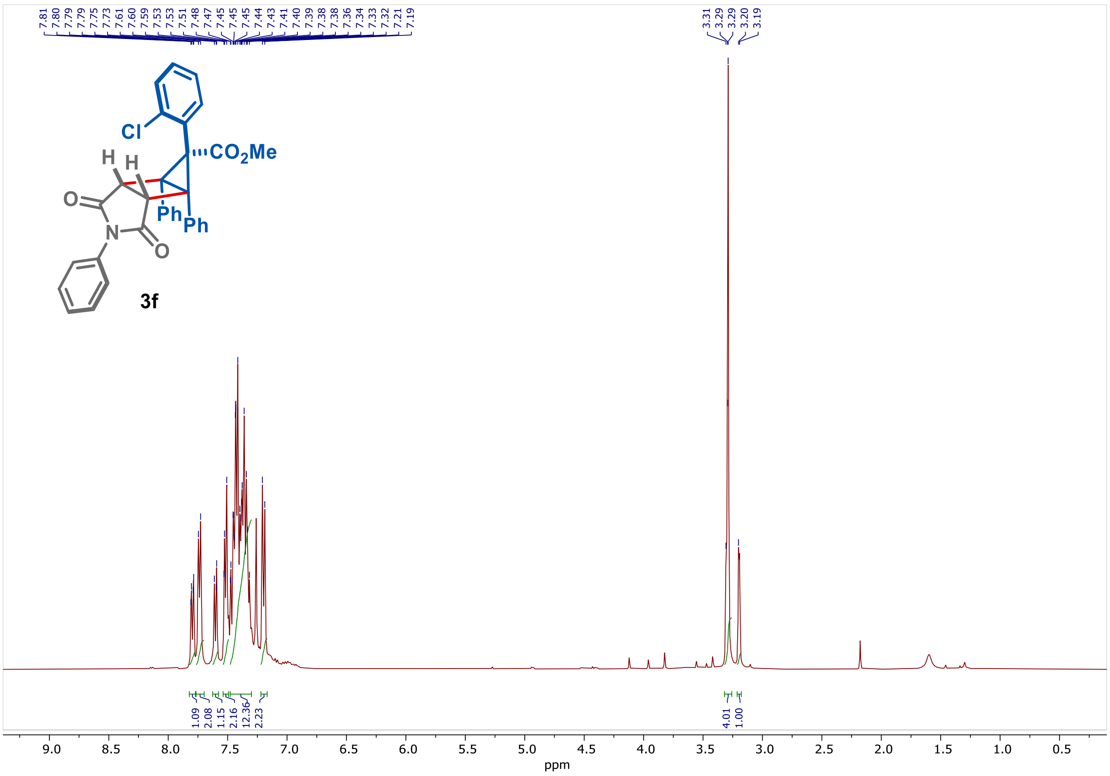
^{1}H-NMR (400 MHz, $CDCl_3$) of compound 3e (see procedure)



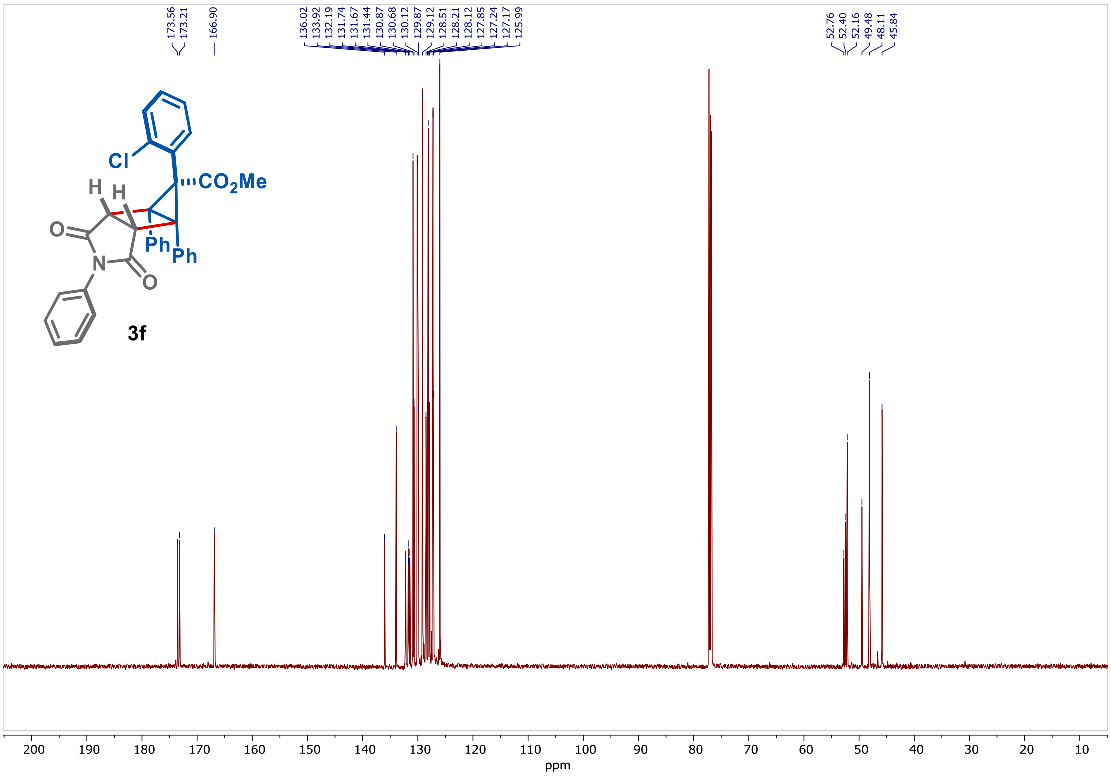
^{13}C-NMR (101 MHz, $CDCl_3$) of compound 3e



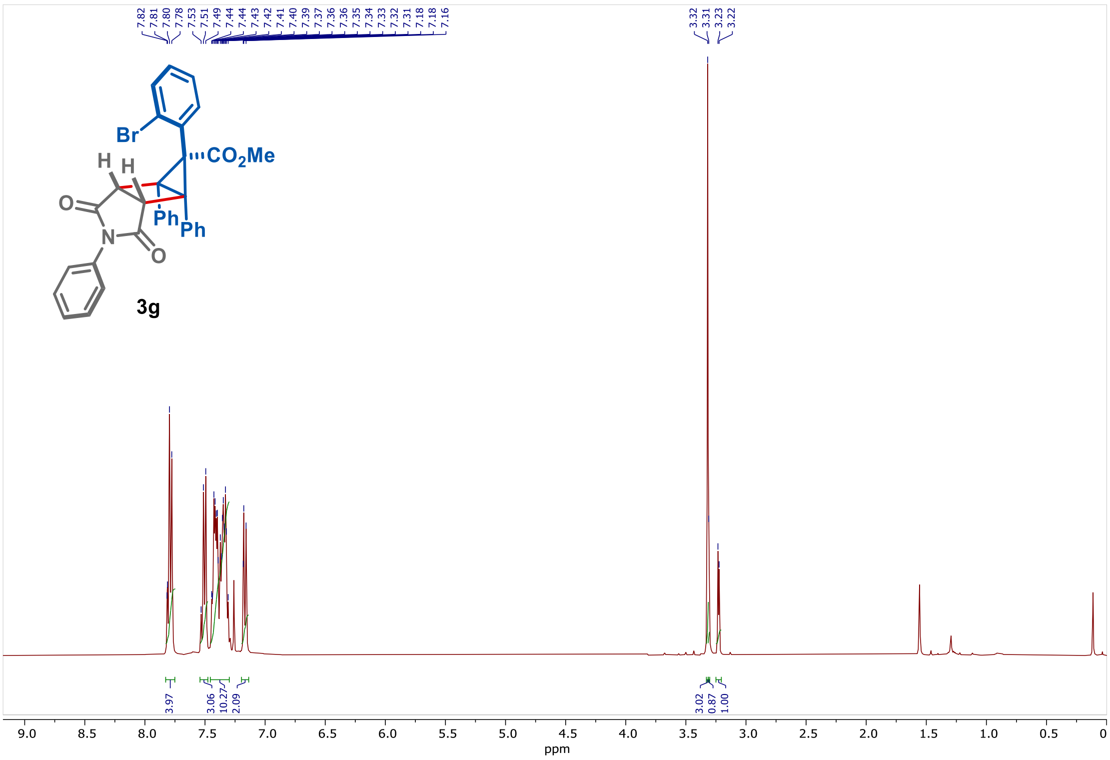
^{1}H-NMR (400 MHz, $CDCl_3$) of compound 3f (see procedure)



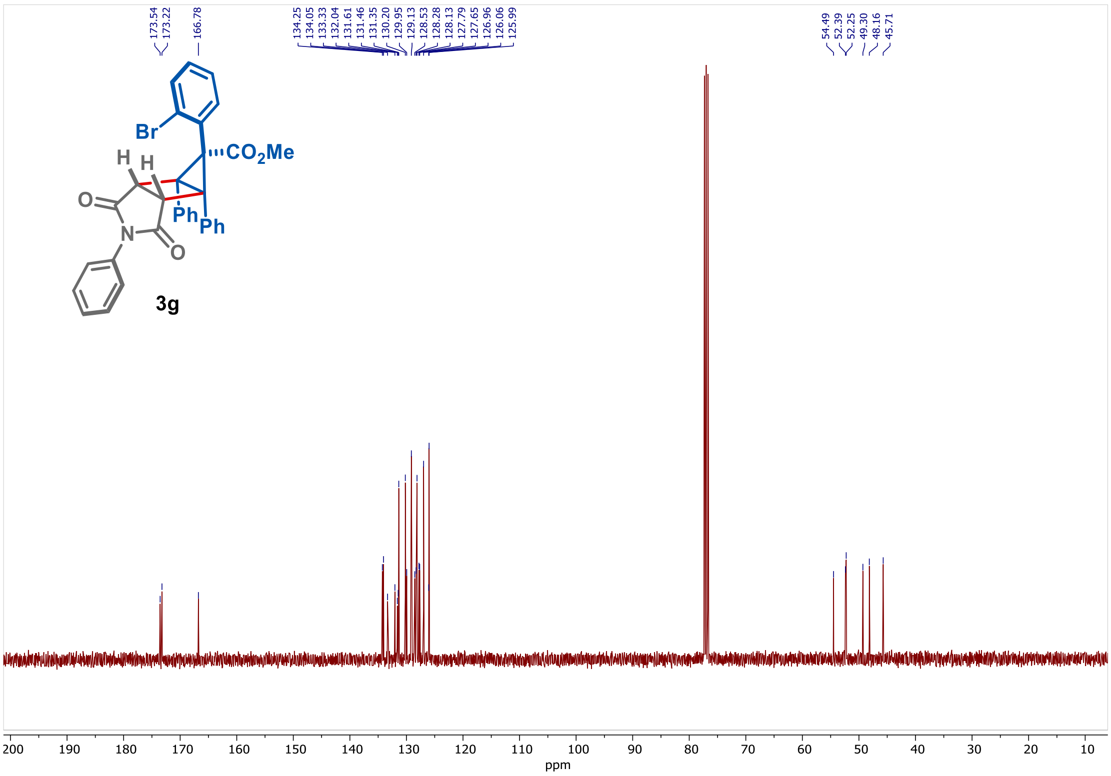
^{13}C-NMR (101 MHz, $CDCl_3$) of compound 3f



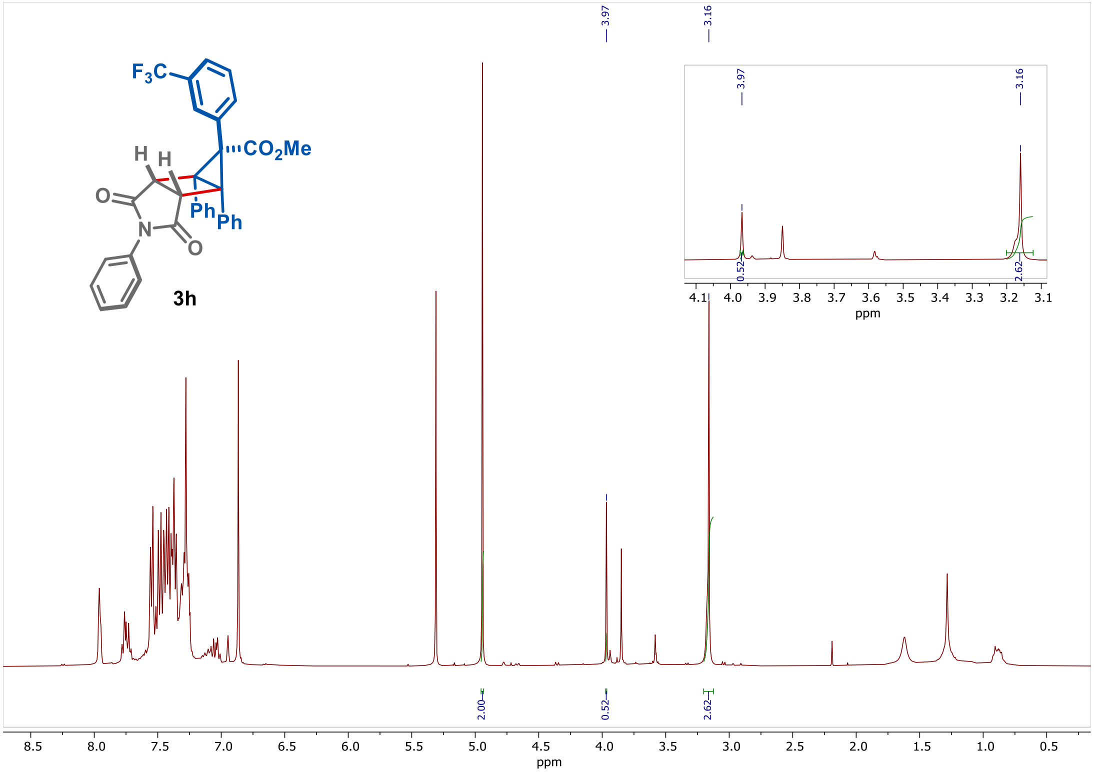
^{1}H-NMR (400 MHz, CDCl$_3$) of compound 3g (see procedure)



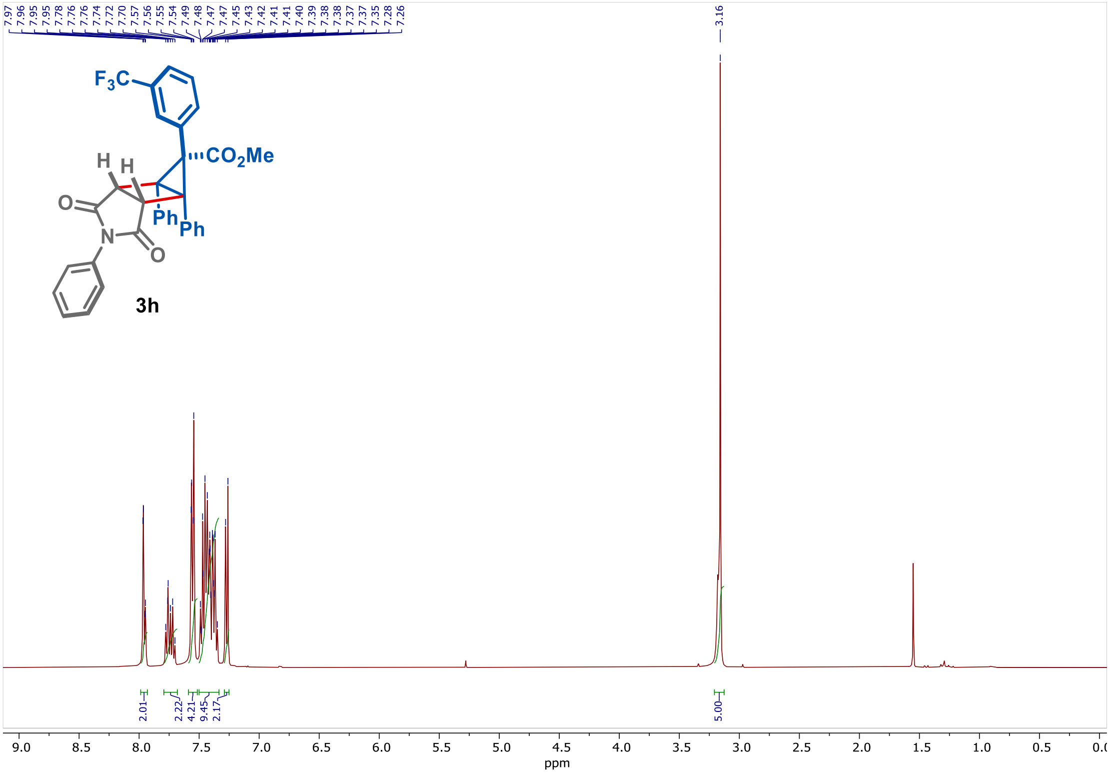
^{13}C-NMR (101 MHz, CDCl$_3$) of compound 3g



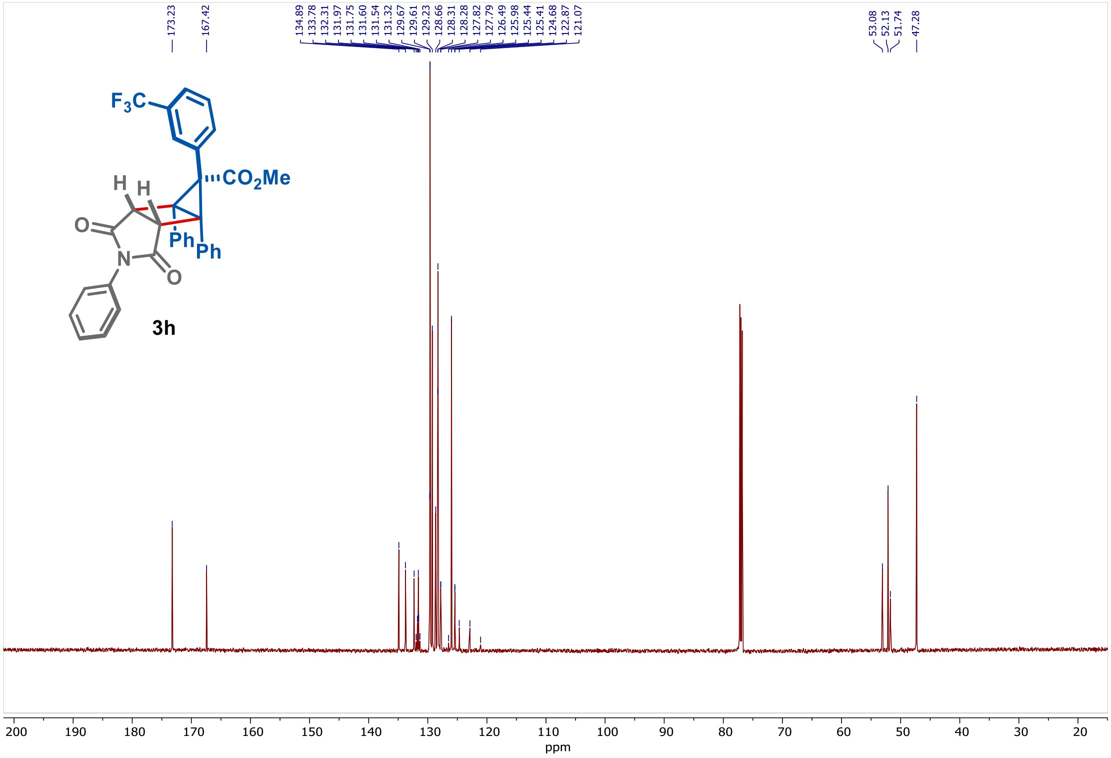
^{1}H-NMR (400 MHz, CDCl$_3$) of crude compound 3h (see procedure)



^{1}H-NMR (400 MHz, CDCl$_3$) of compound 3h (see procedure)

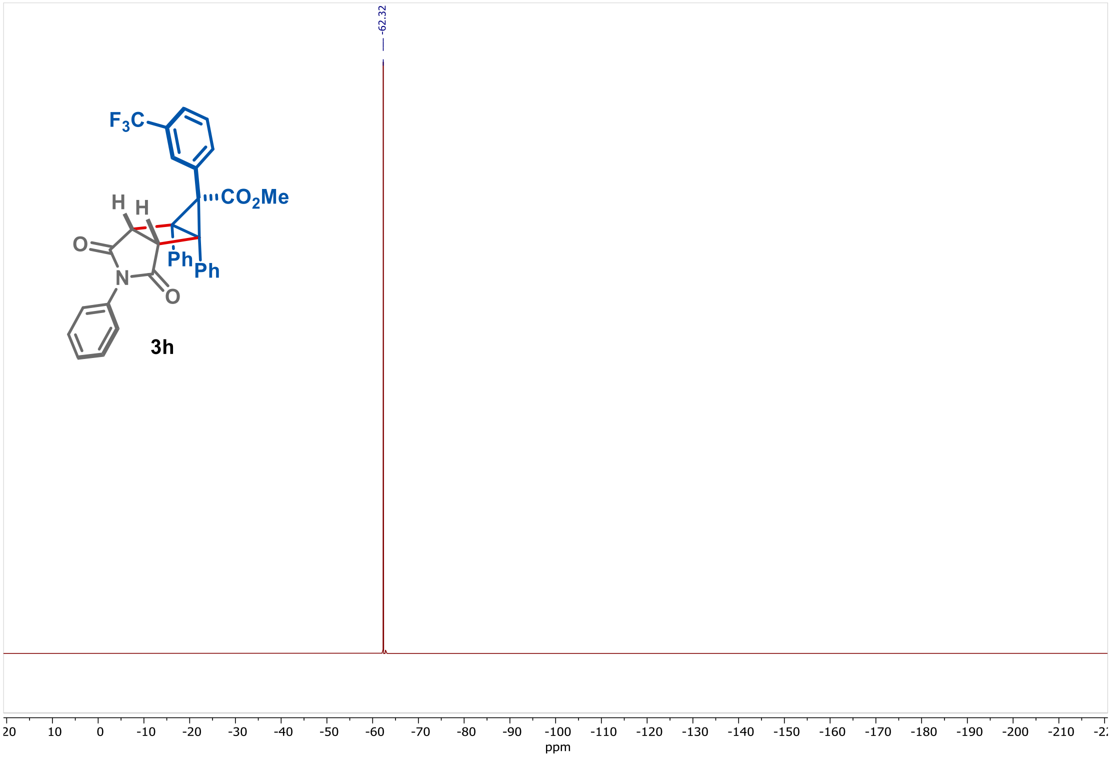


^{13}C-NMR (101 MHz, CDCl$_3$) of compound 3h



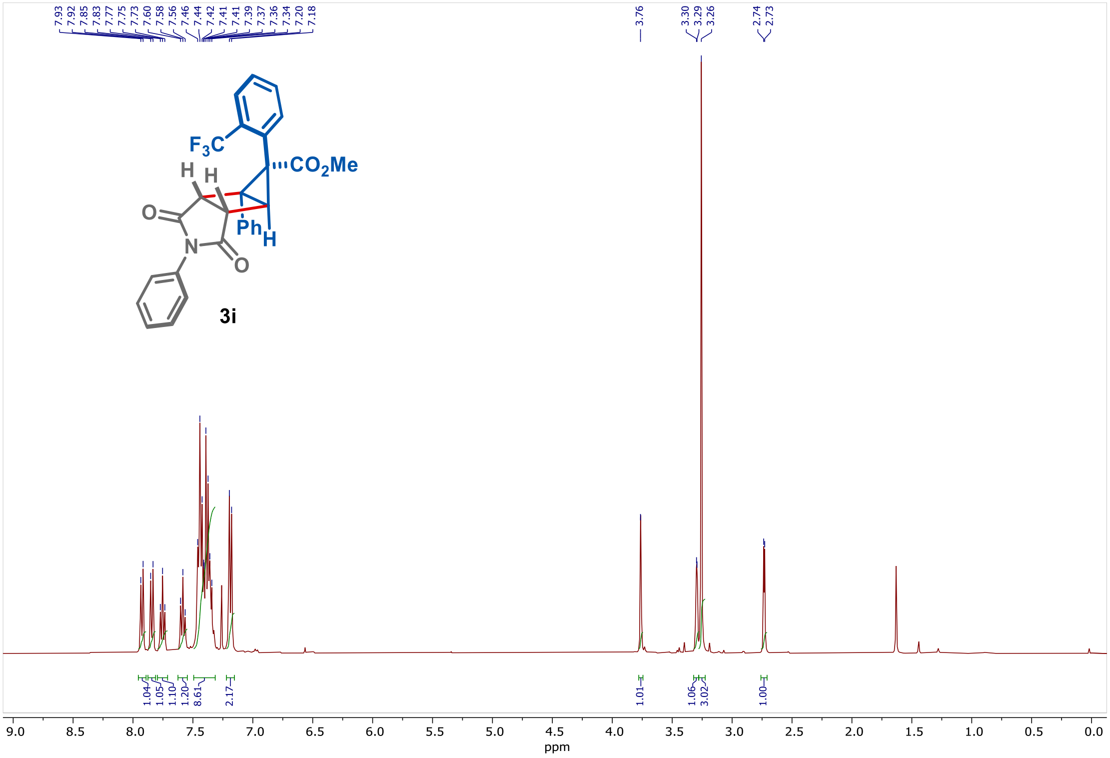
3h

^{19}F-NMR (377 MHz, CDCl$_3$) of compound 3h

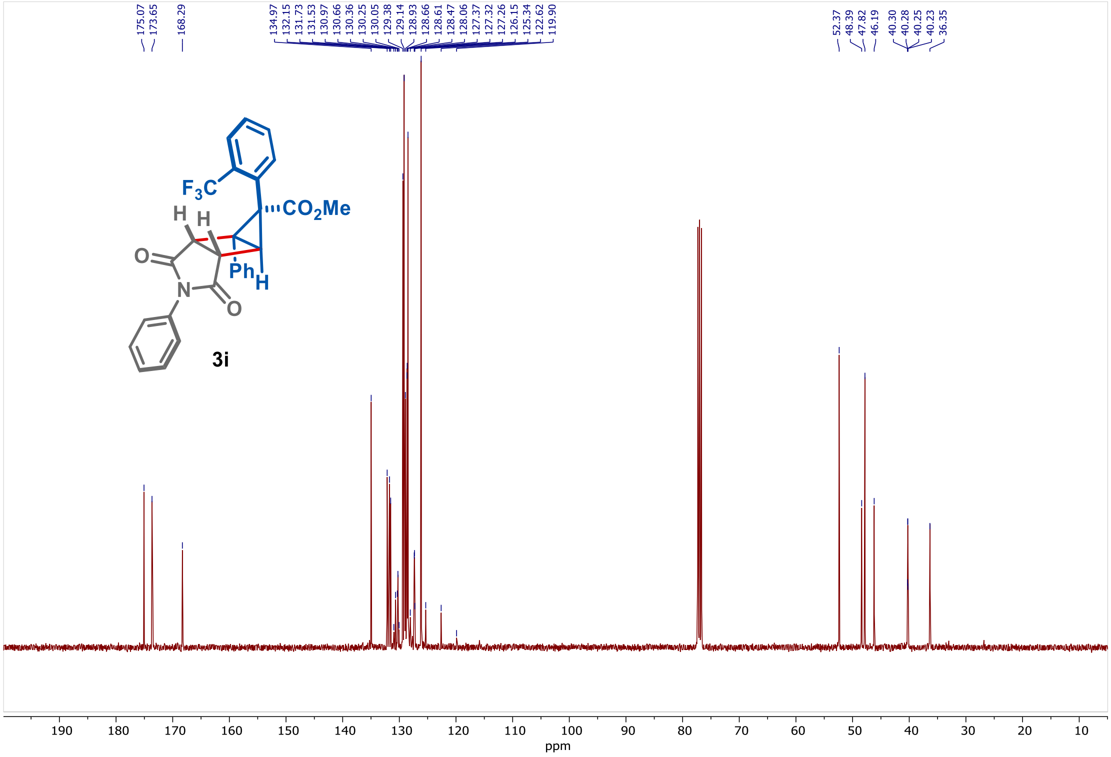


3h

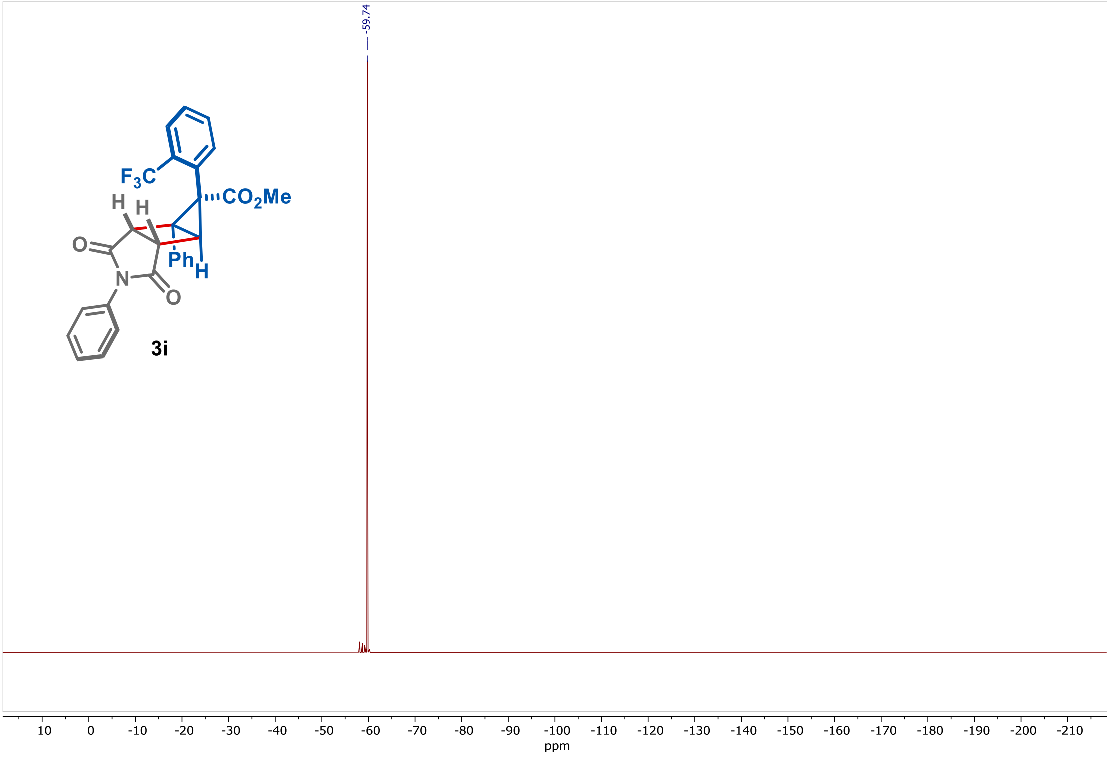
^{1}H-NMR (400 MHz, $CDCl_3$) of compound 3i (see procedure)



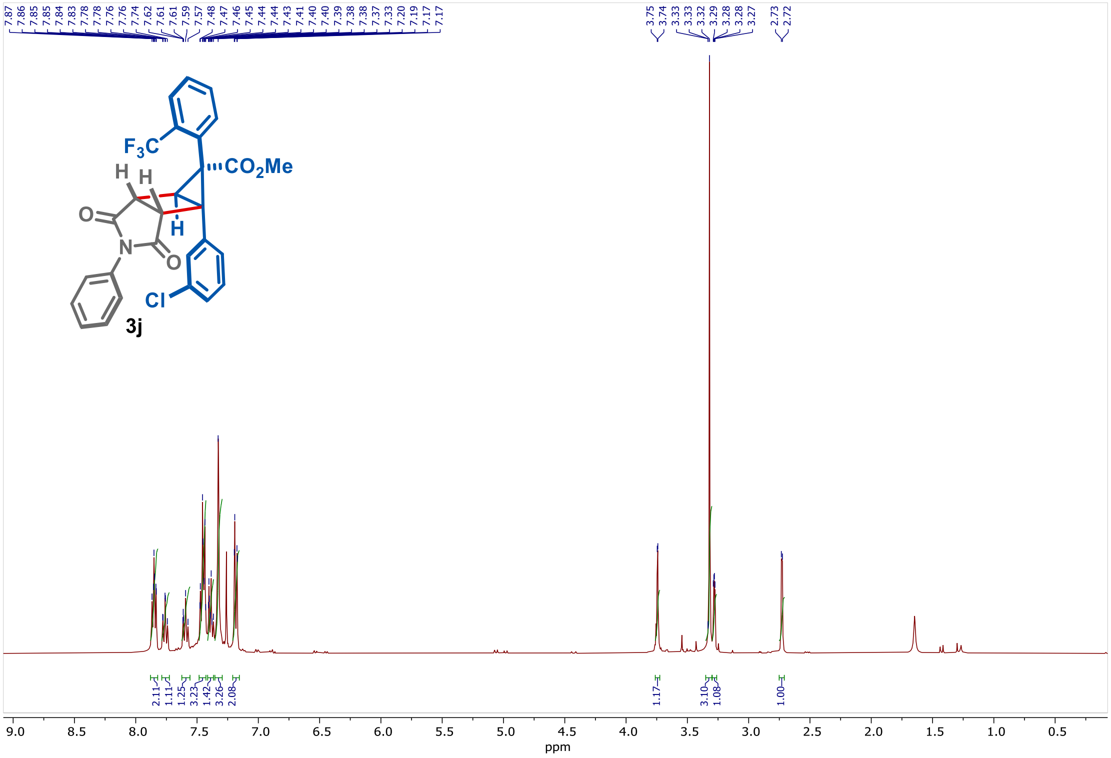
^{13}C-NMR (101 MHz, $CDCl_3$) of compound 3i



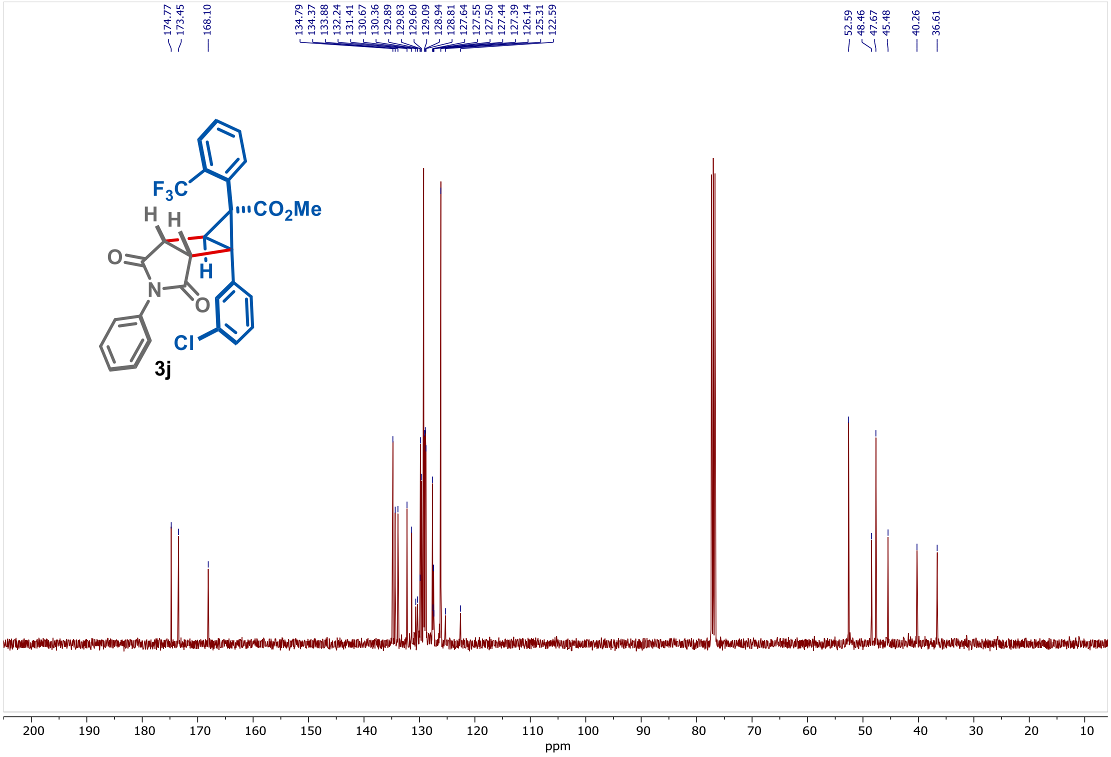
^{19}F-NMR (377 MHz, CDCl$_3$) of compound 3i



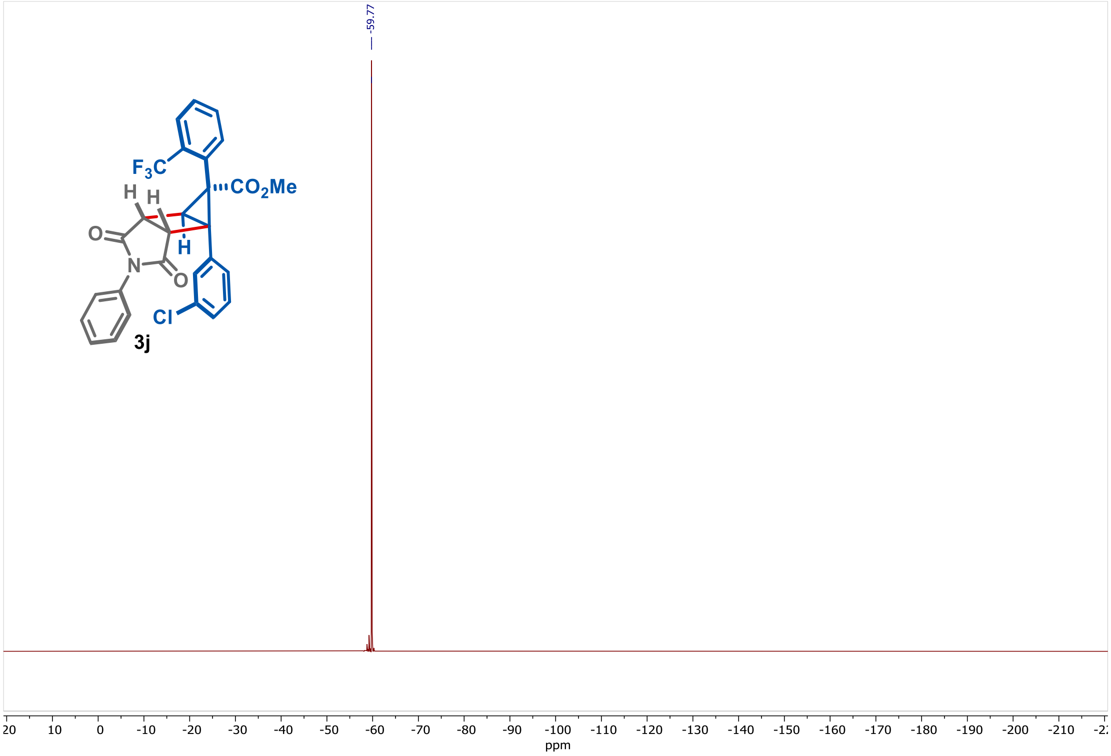
^{1}H-NMR (400 MHz, CDCl$_3$) of compound 3j (see procedure)



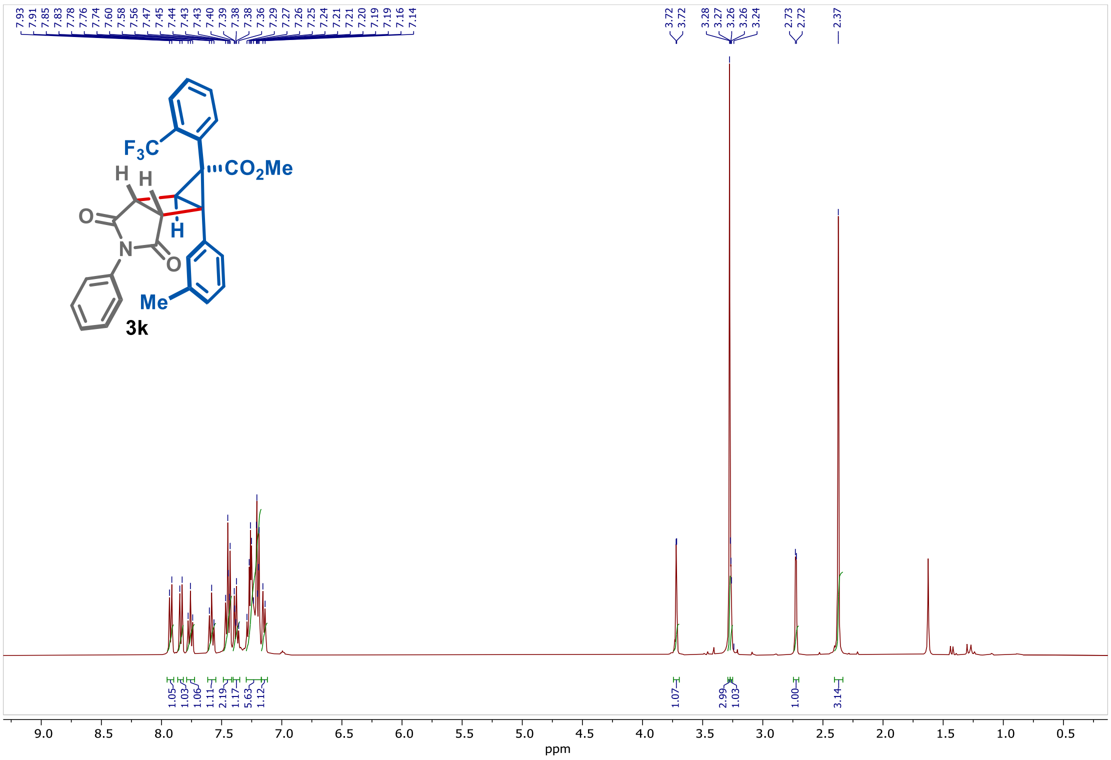
^{13}C-NMR (101 MHz, CDCl$_3$) of compound 3j



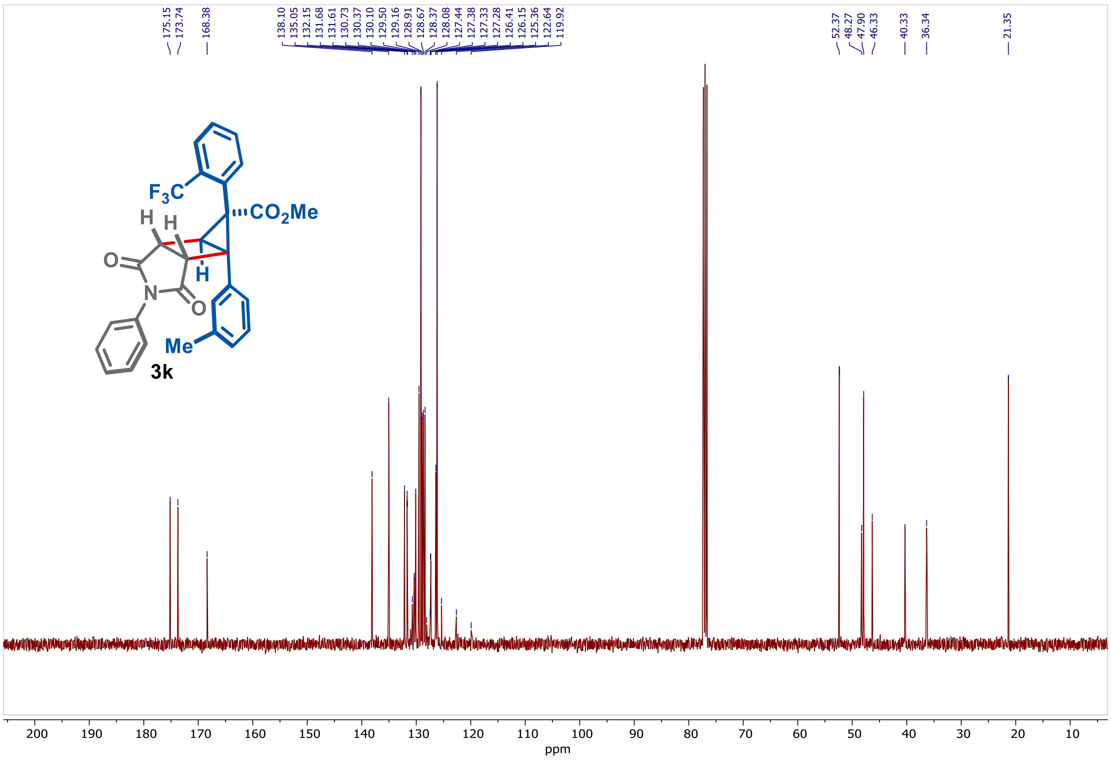
^{19}F-NMR (377 MHz, $CDCl_3$) of compound 3j



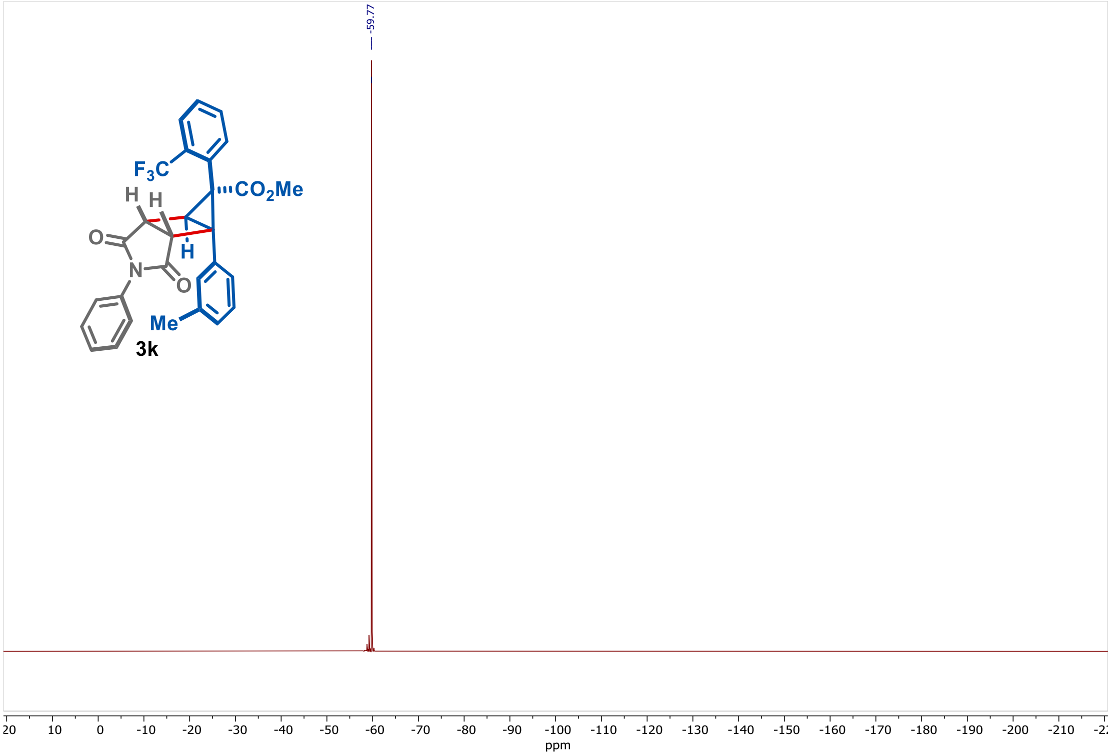
^{1}H-NMR (400 MHz, $CDCl_3$) of compound 3k (see procedure)



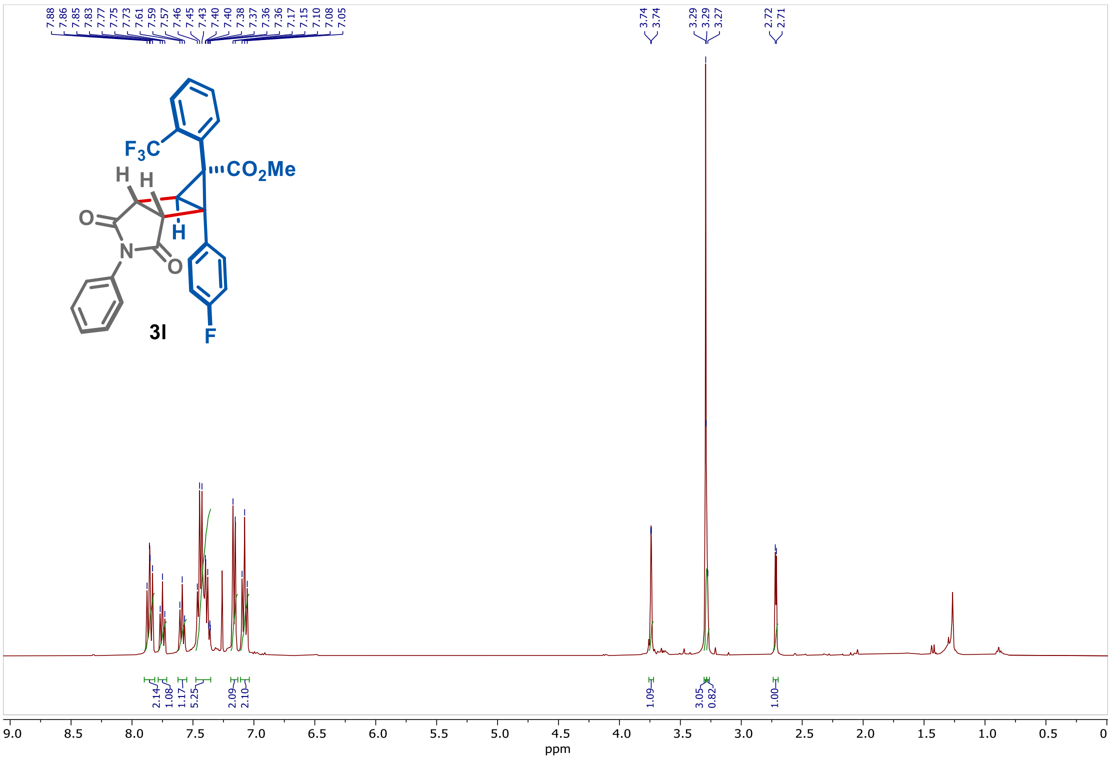
^{13}C-NMR (101 MHz, $CDCl_3$) of compound 3k



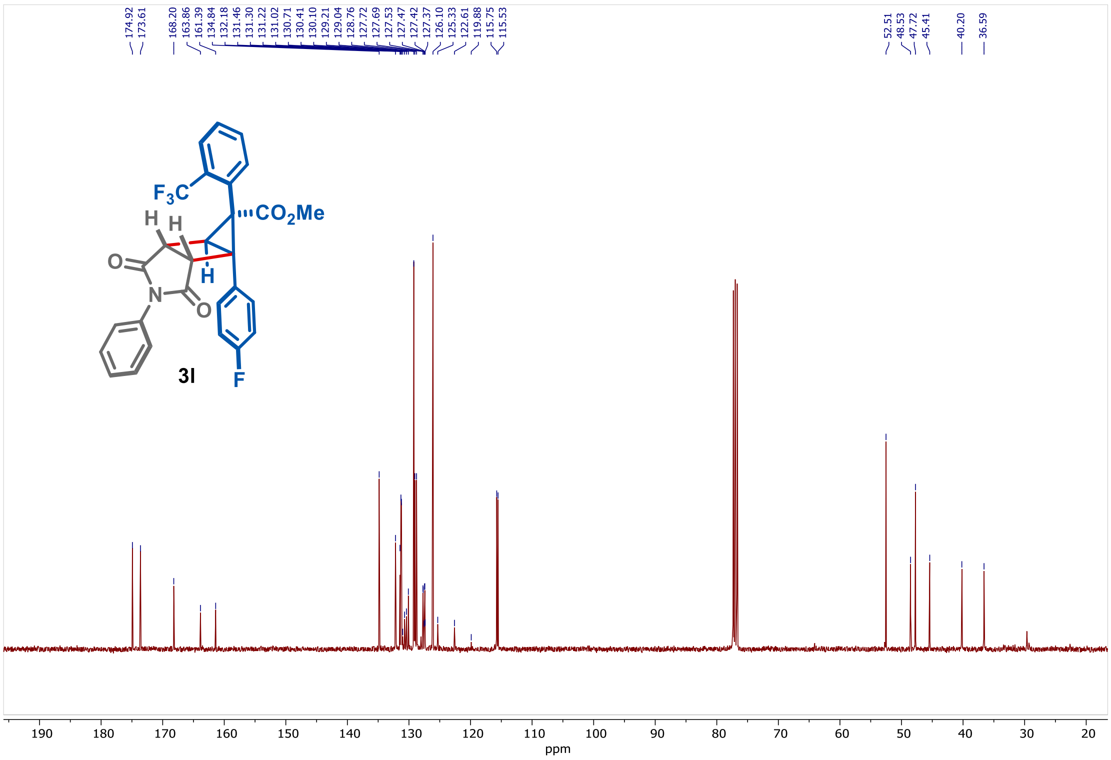
^{19}F-NMR (377 MHz, CDCl$_3$) of compound 3k



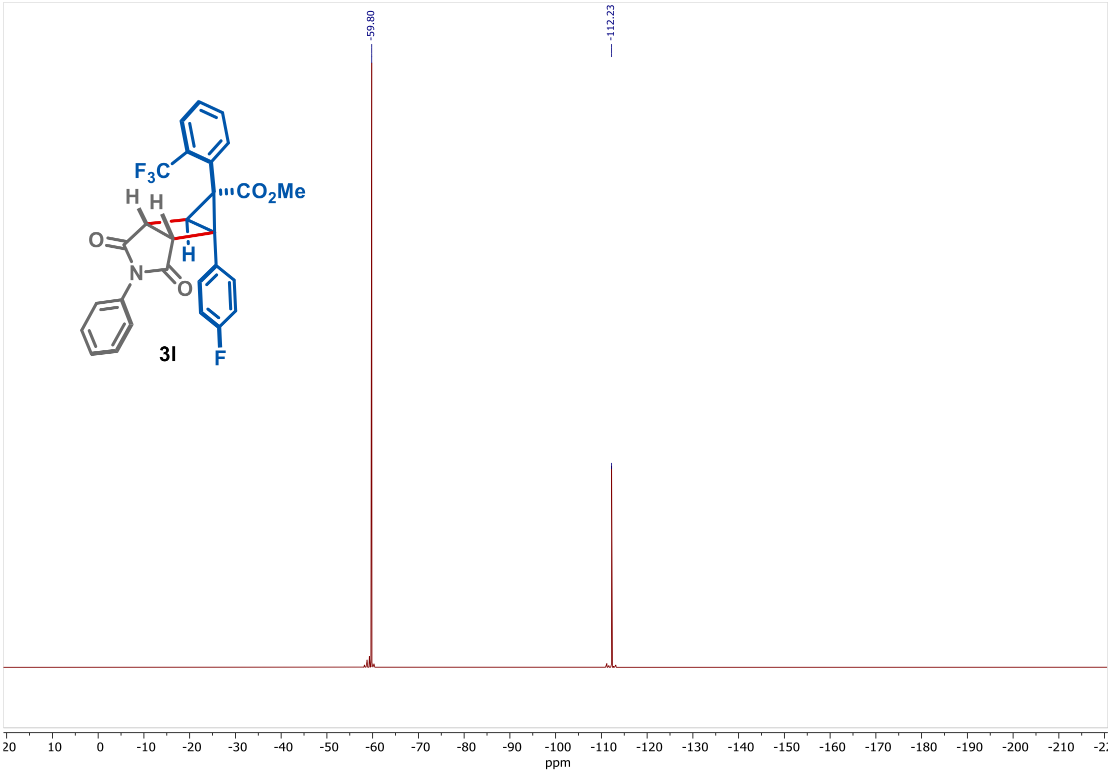
^{1}H-NMR (400 MHz, CDCl$_3$) of compound 3l (see procedure)



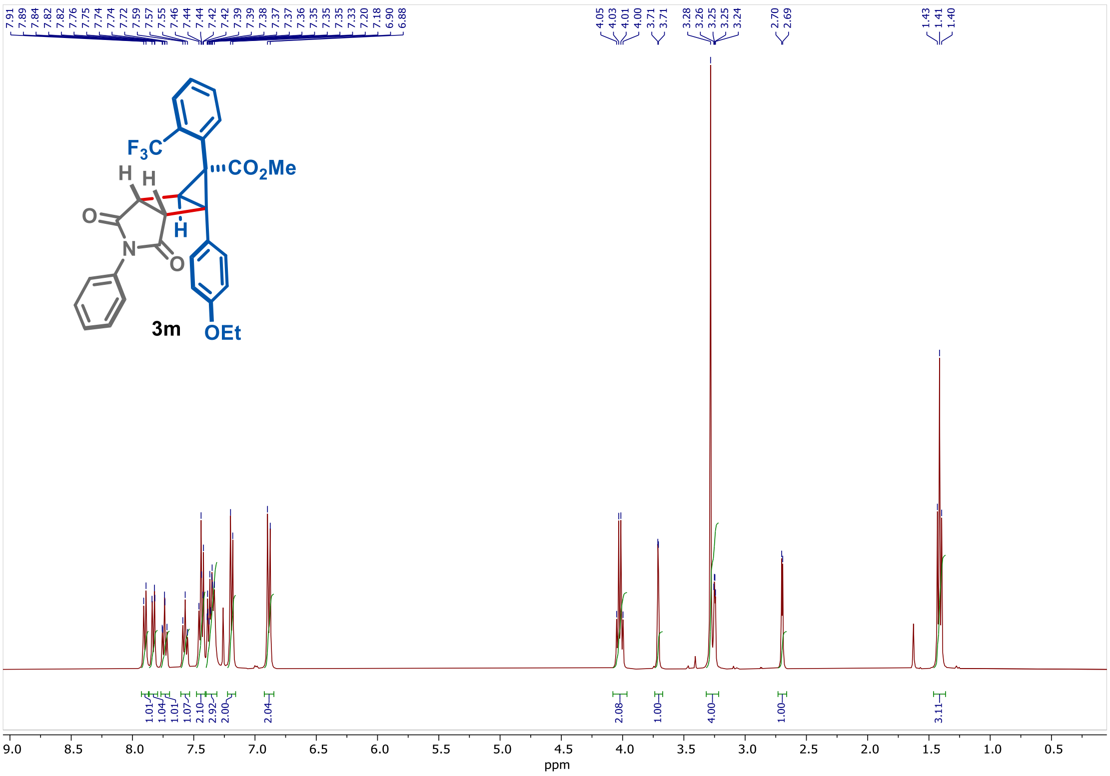
^{13}C-NMR (101 MHz, CDCl$_3$) of compound 3l



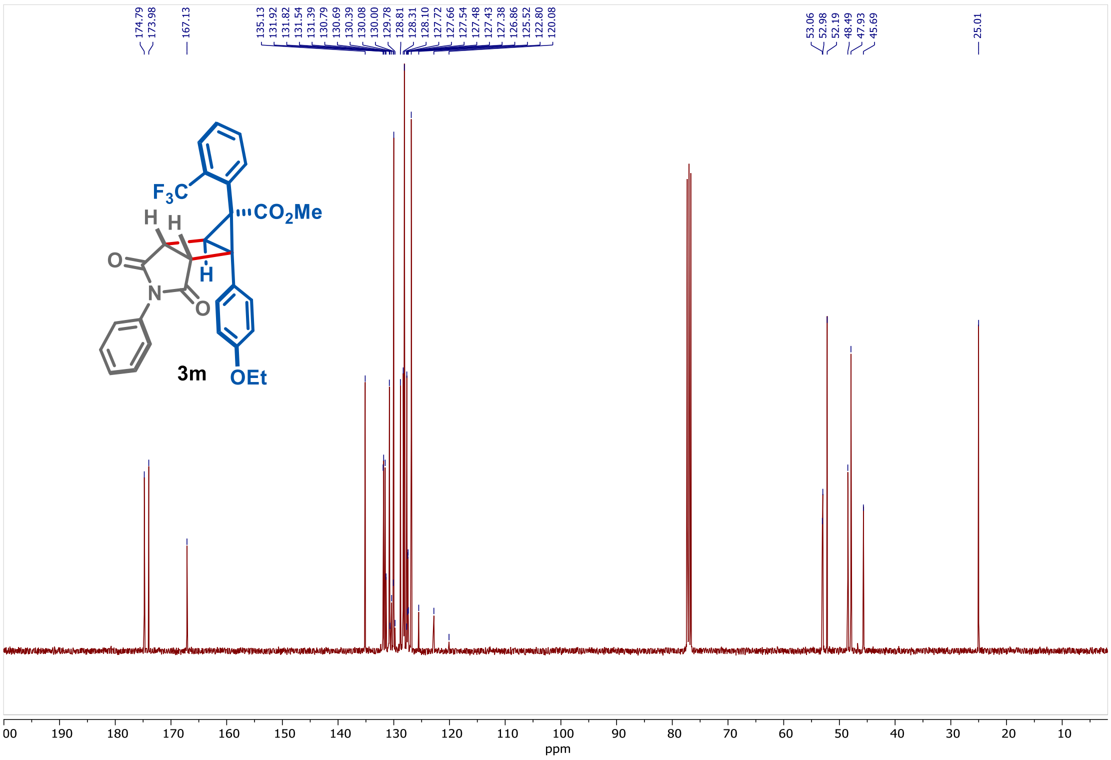
^{19}F-NMR (377 MHz, $CDCl_3$) of compound 3l



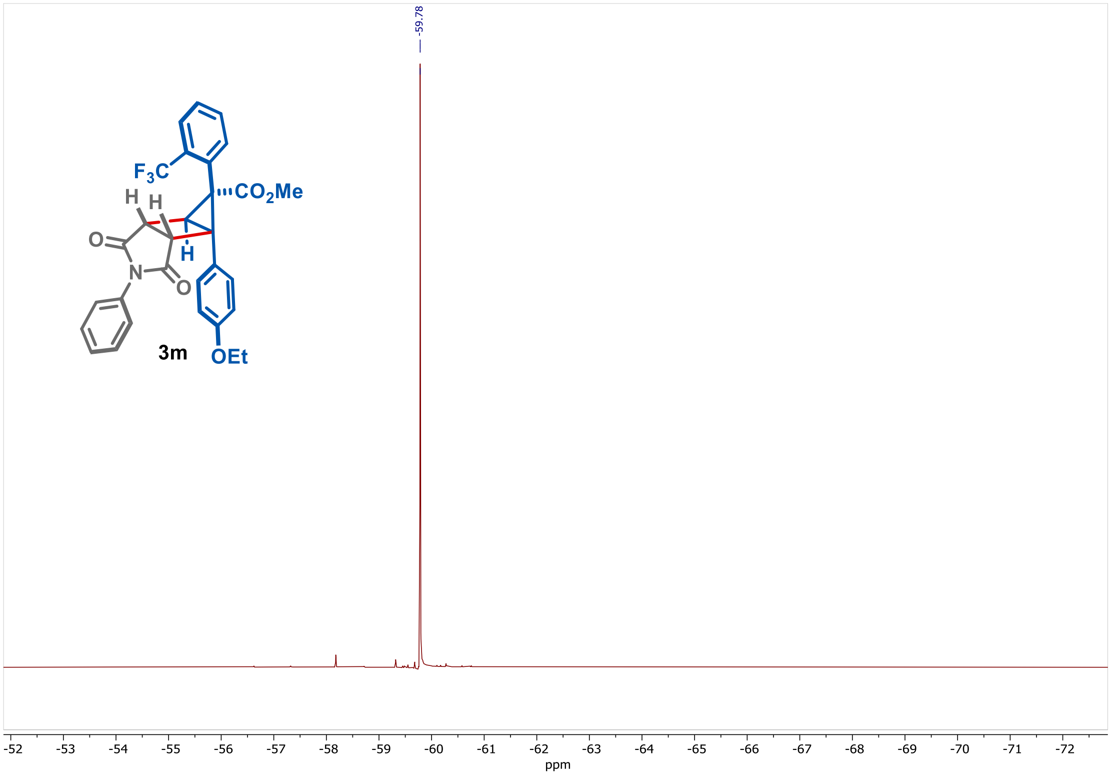
^{1}H-NMR (400 MHz, CDCl$_3$) of compound 3m (see procedure)



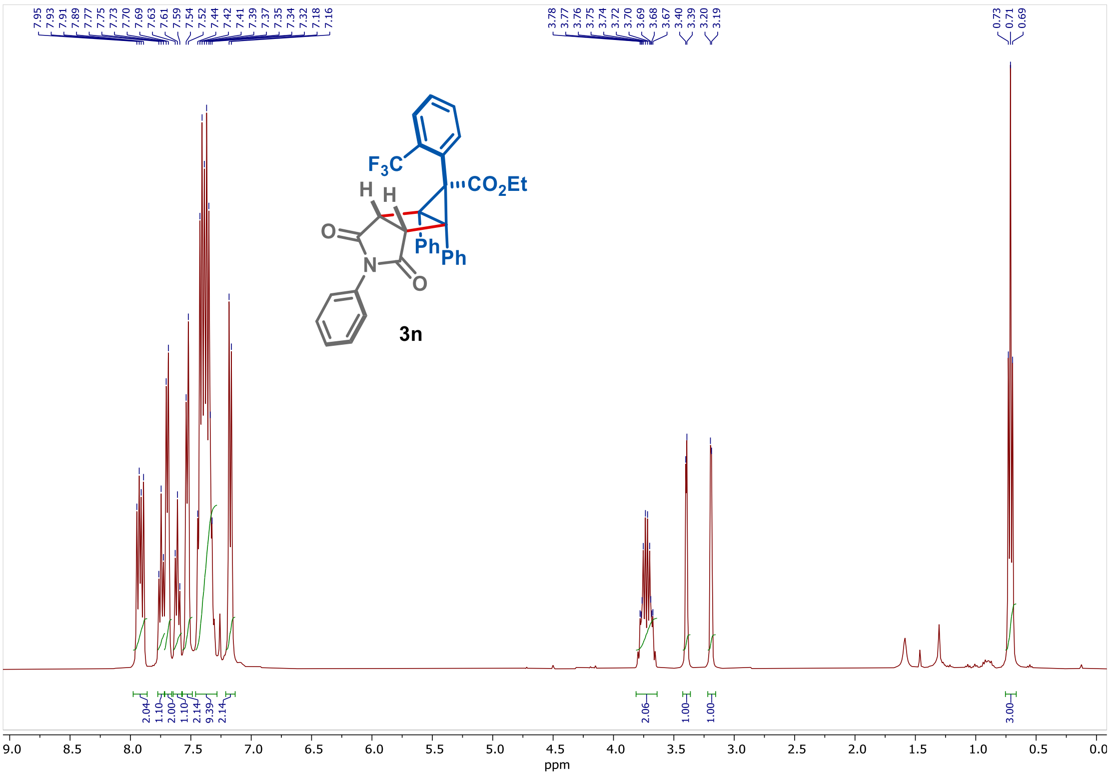
^{13}C-NMR (101 MHz, CDCl$_3$) of compound 3m



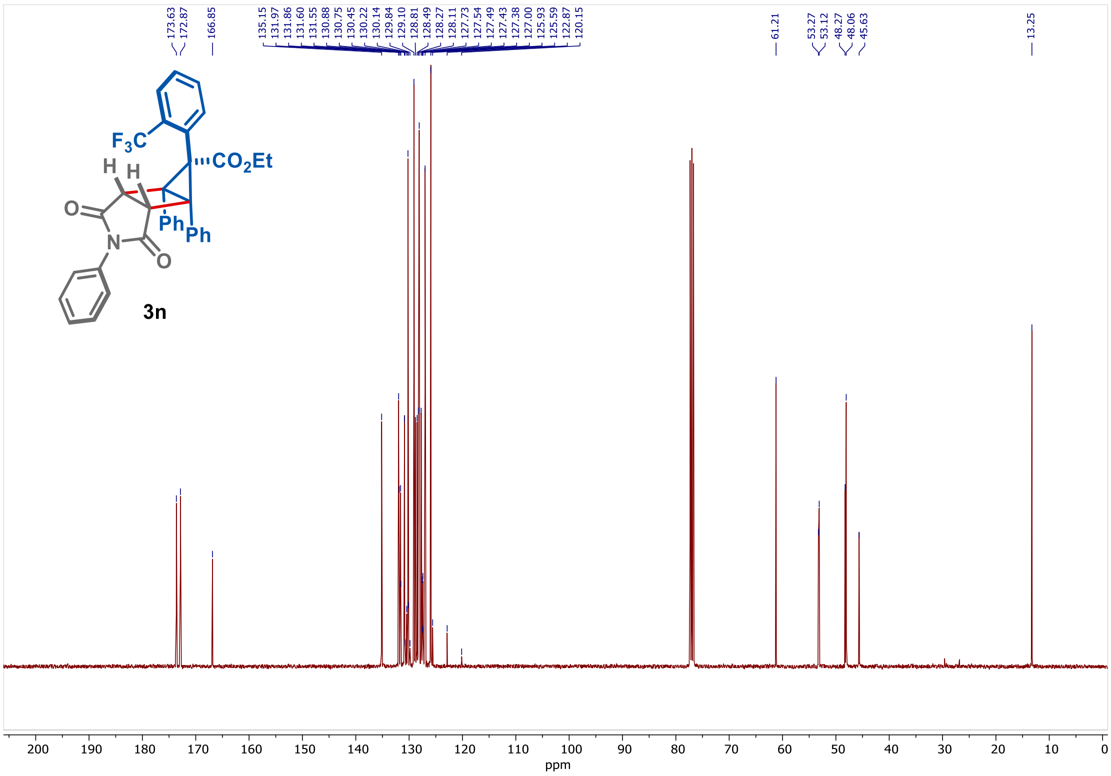
^{19}F-NMR (377 MHz, $CDCl_3$) of compound 3m



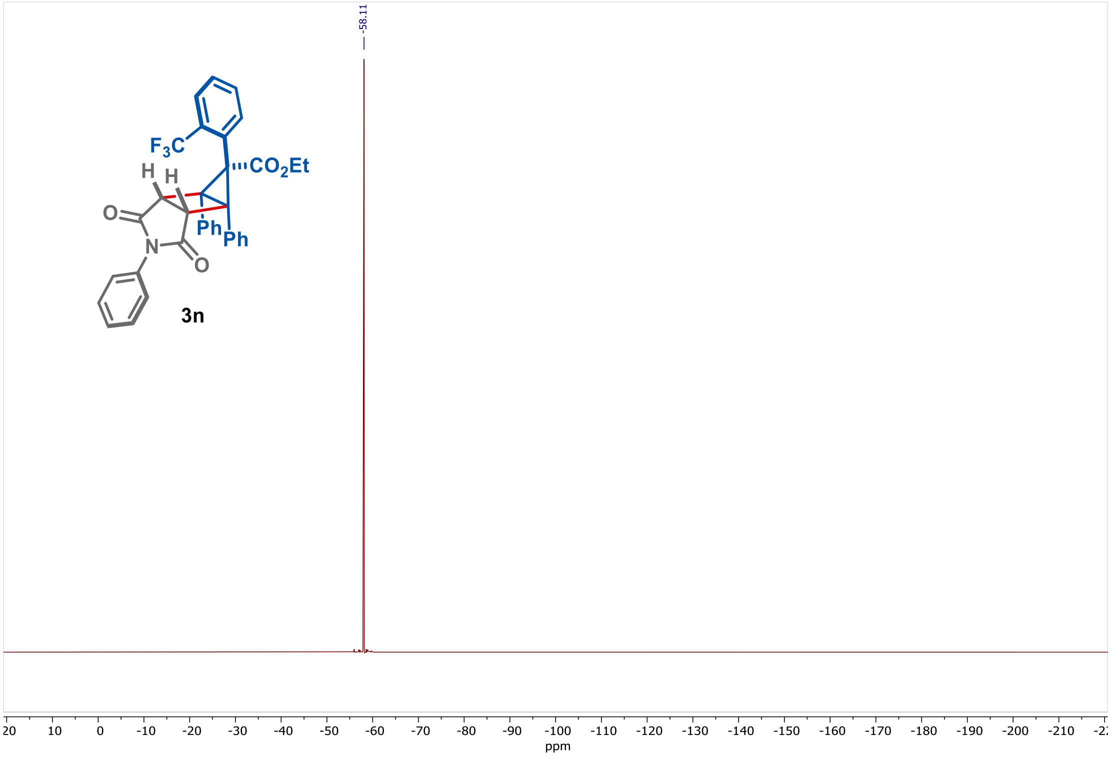
^{1}H-NMR (400 MHz, $CDCl_3$) of compound 3n (see procedure)



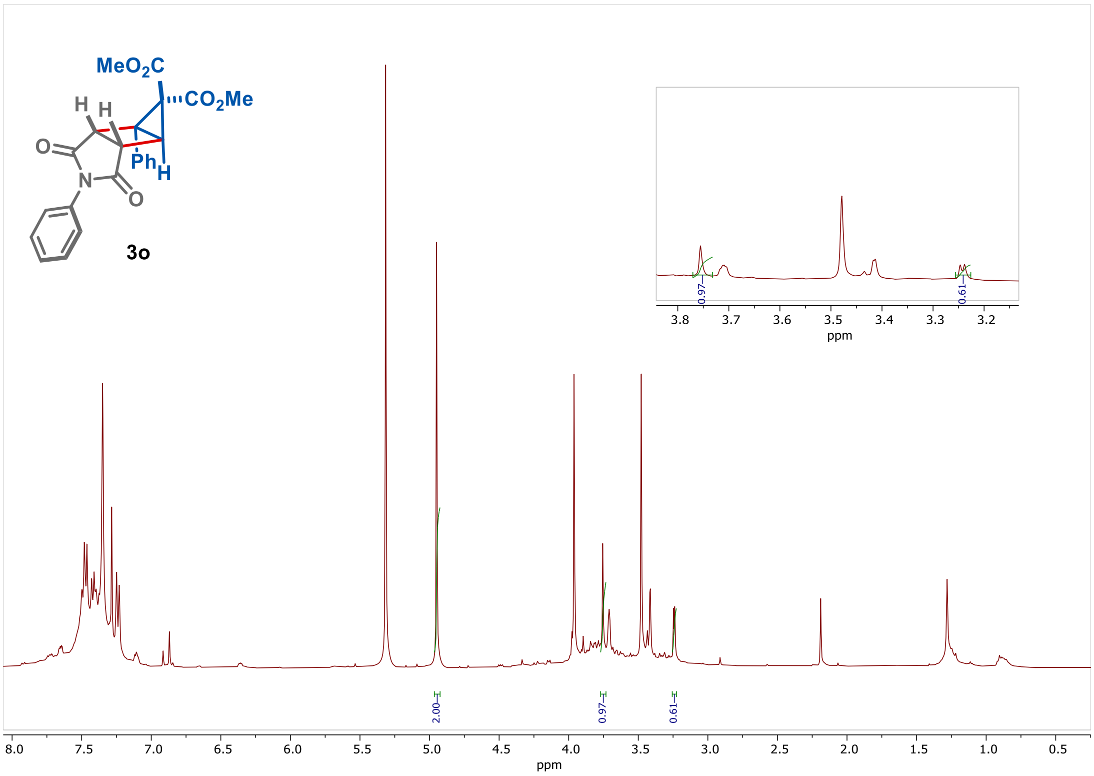
^{13}C-NMR (101 MHz, $CDCl_3$) of compound 3n



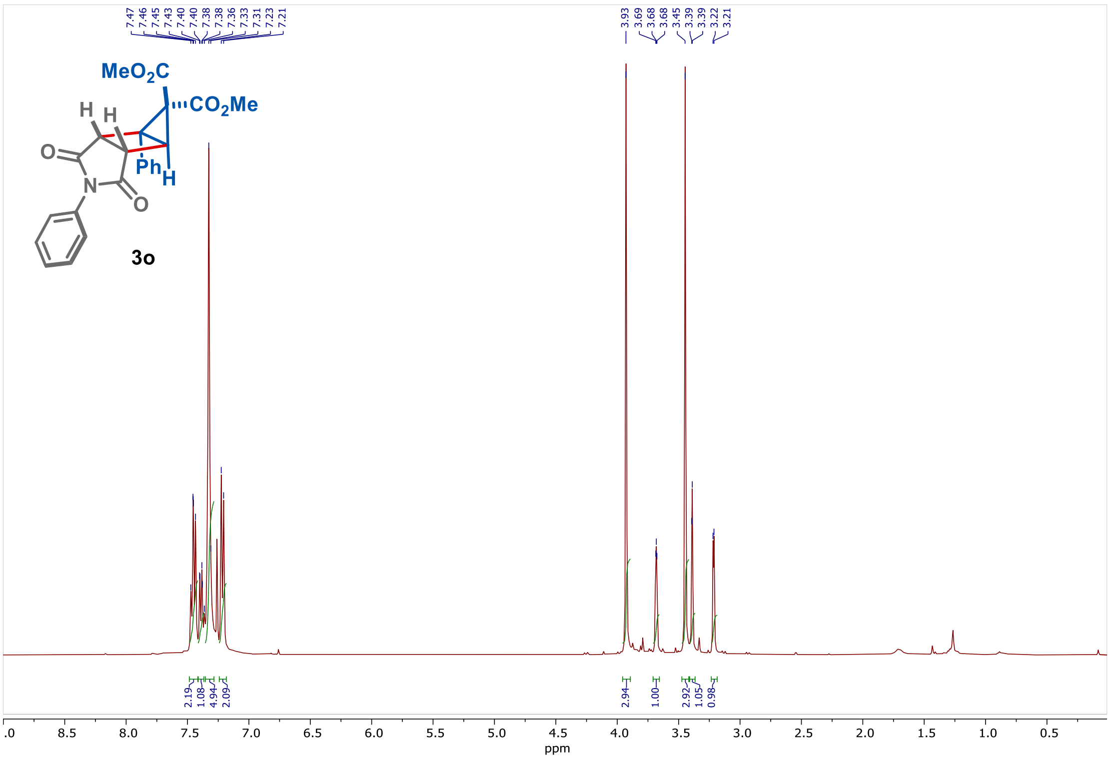
^{19}F-NMR (377 MHz, CDCl$_3$) of compound 3n



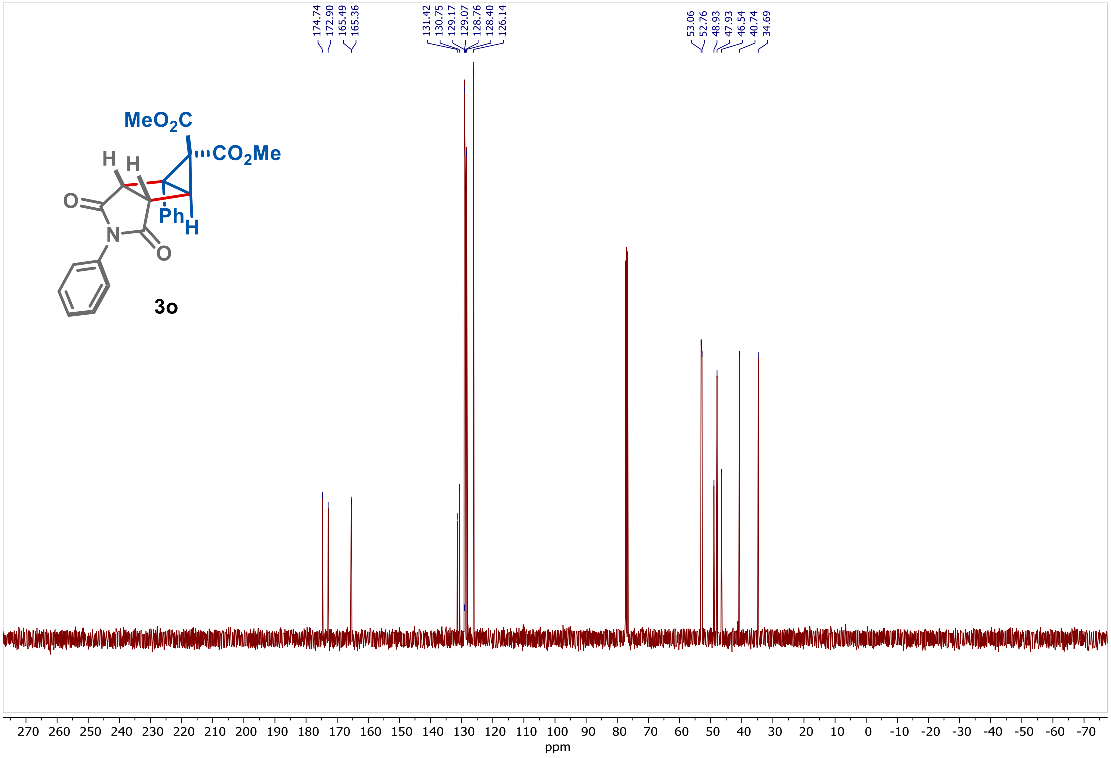
^{1}H-NMR (400 MHz, CDCl$_3$) of compound 3o (Crude) (see procedure)



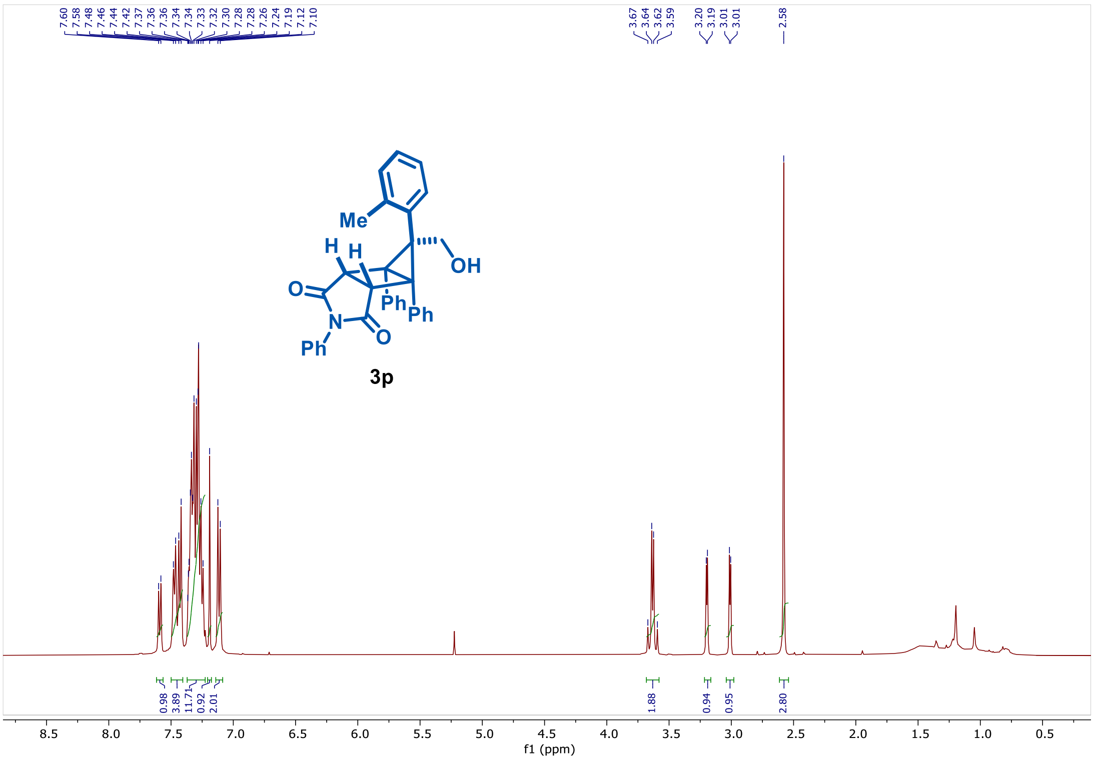
^{1}H-NMR (400 MHz, CDCl$_3$) of compound 3o (see procedure)



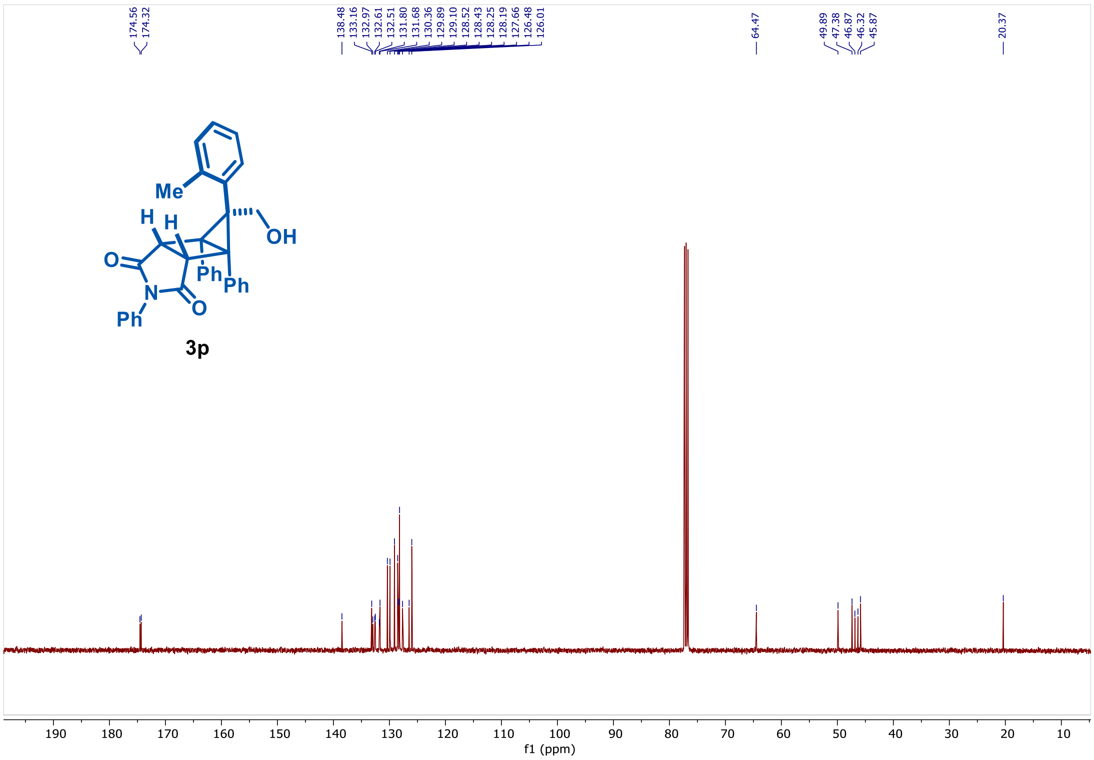
^{13}C-NMR (101 MHz, CDCl$_3$) of compound 3o



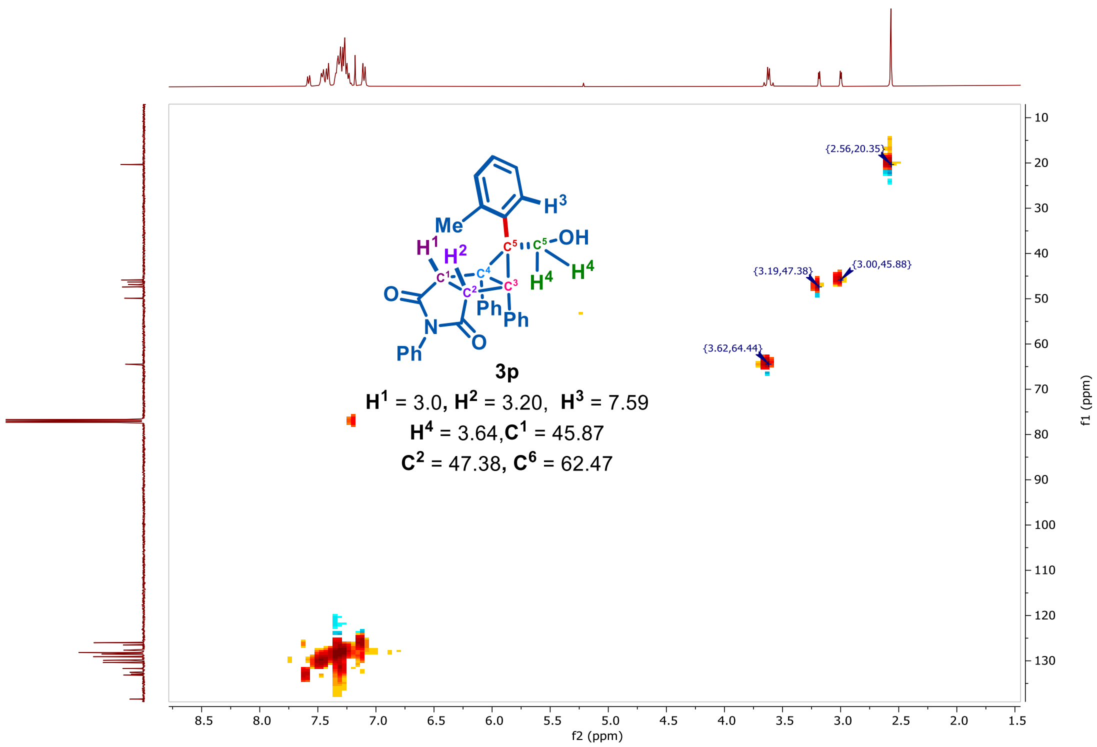
^{1}H-NMR (400 MHz, $CDCl_3$) of compound 3p (see procedure)



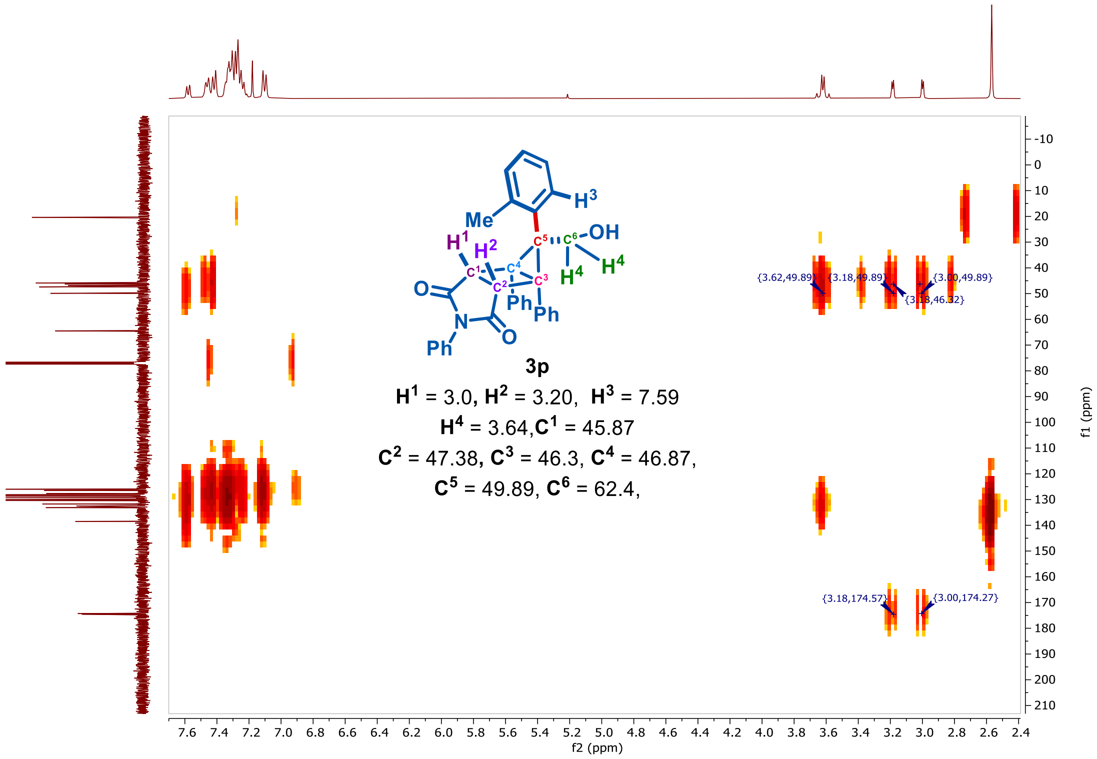
^{13}C-NMR (101 MHz, $CDCl_3$) of compound 3p



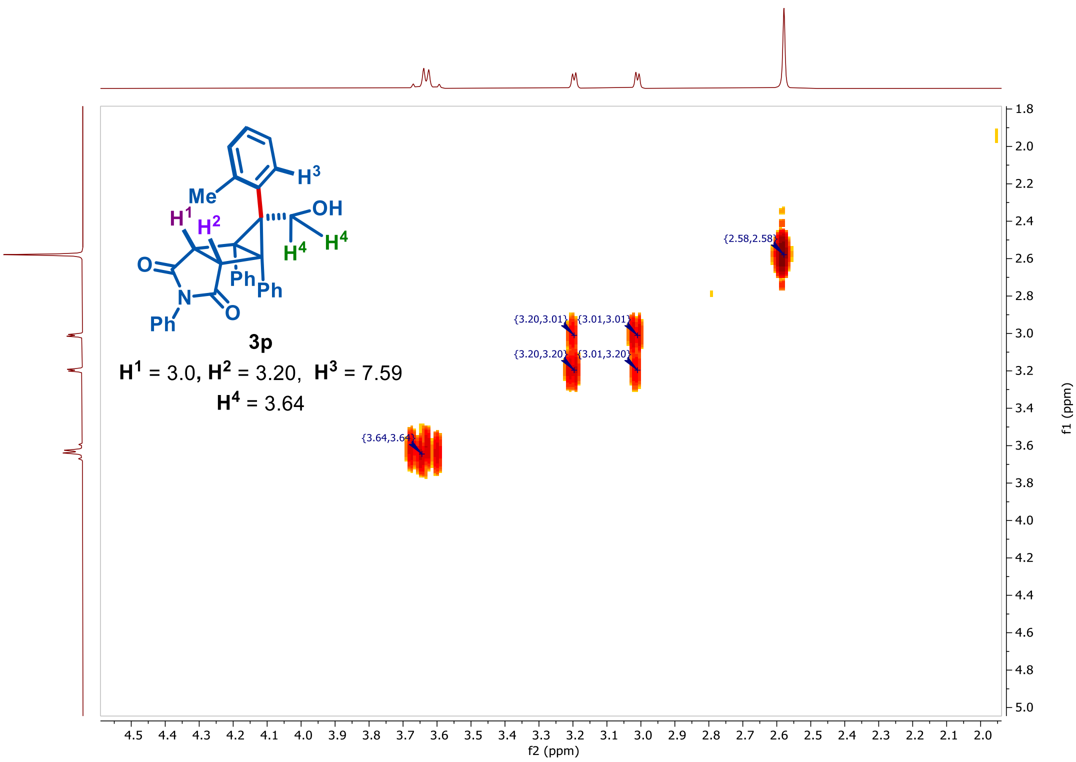
HSQC of compound 3p



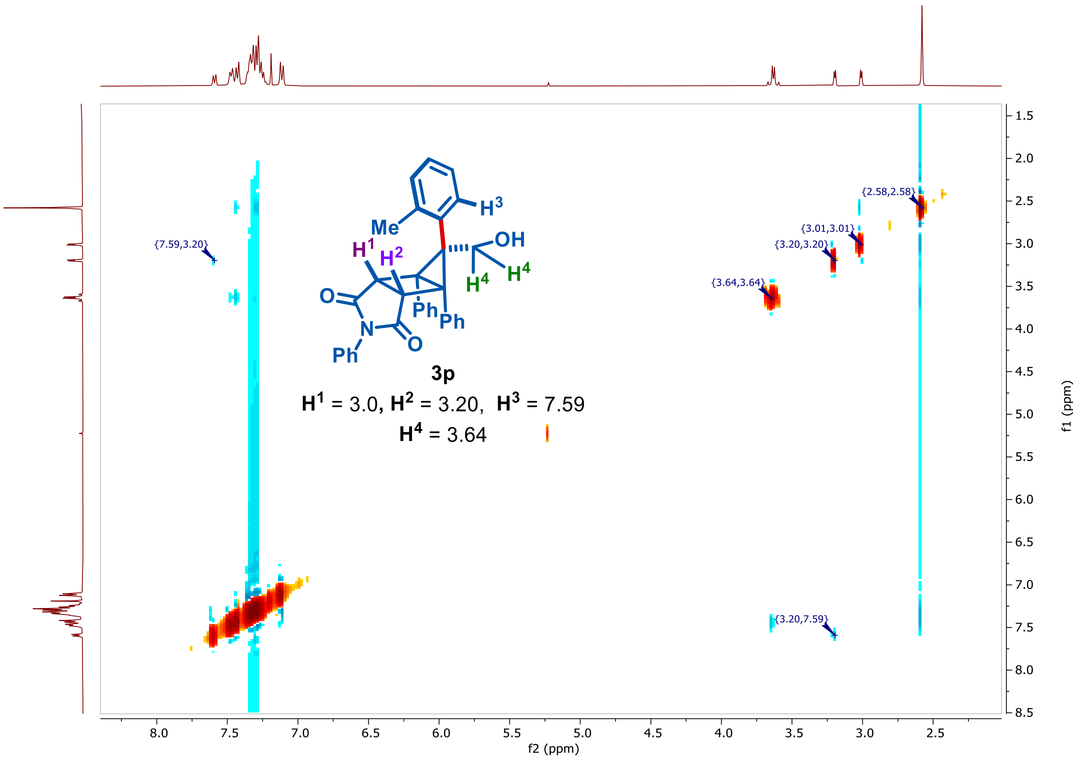
HMBC of compound 3p



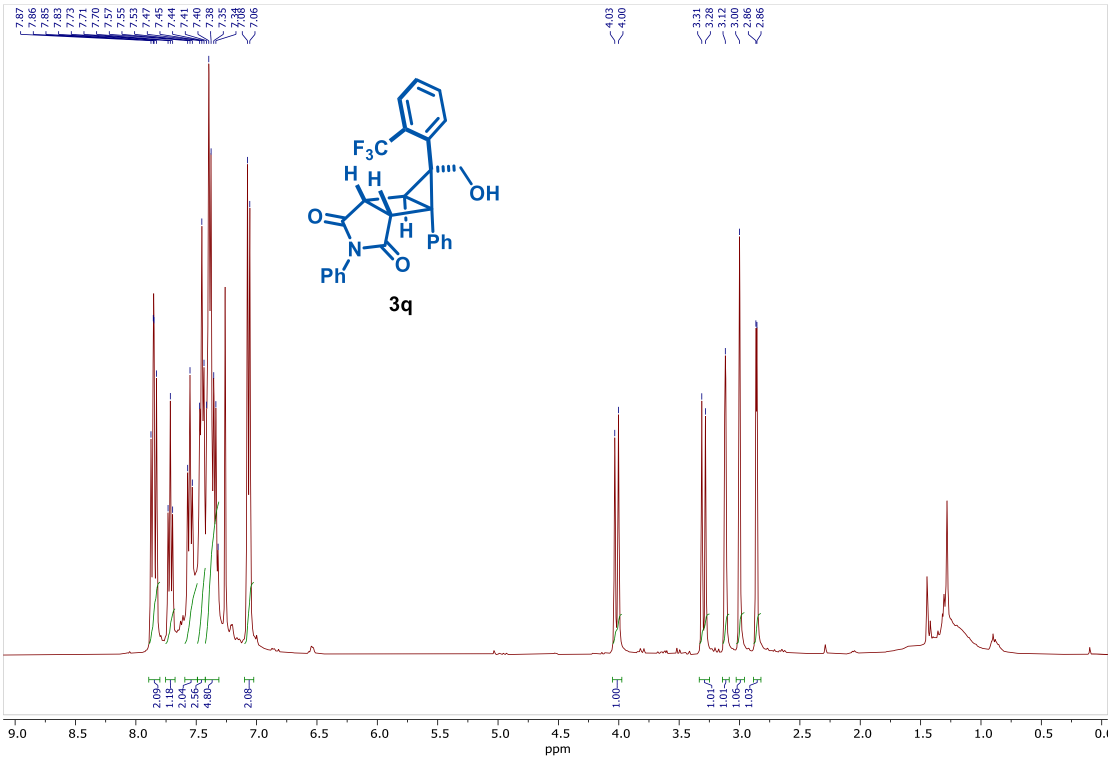
COSY of compound 3p



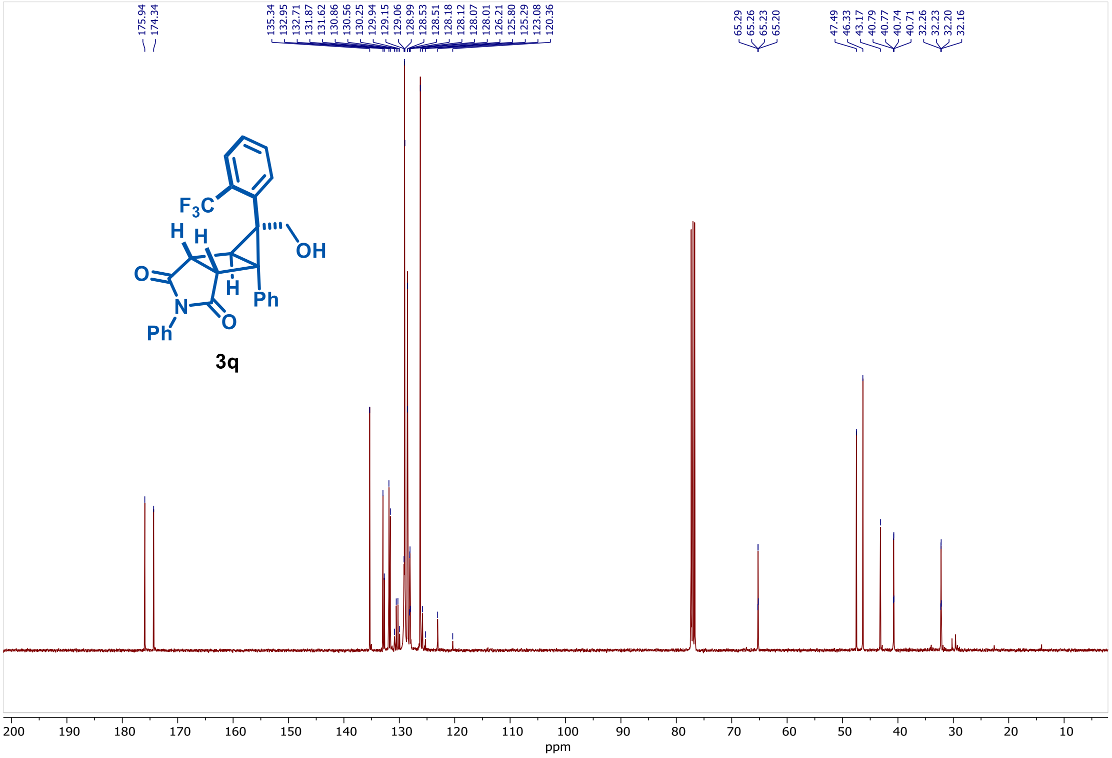
NOESY of compound 3p



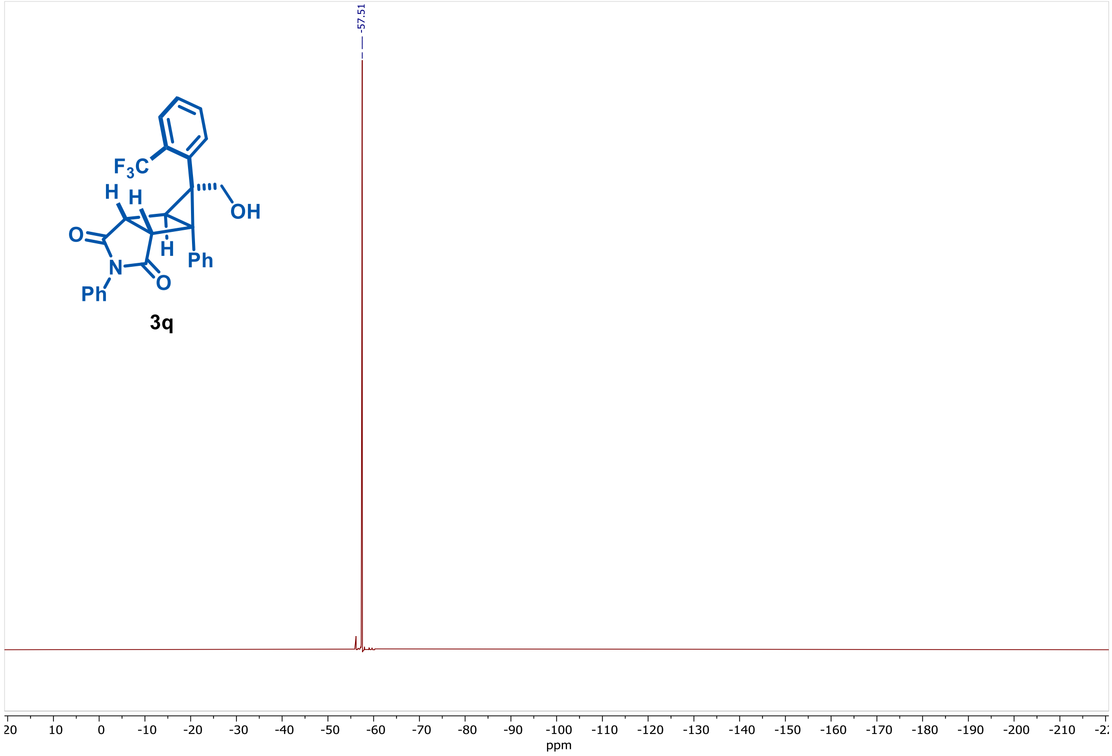
^{1}H-NMR (400 MHz, $CDCl_3$) of compound 3q (see procedure)



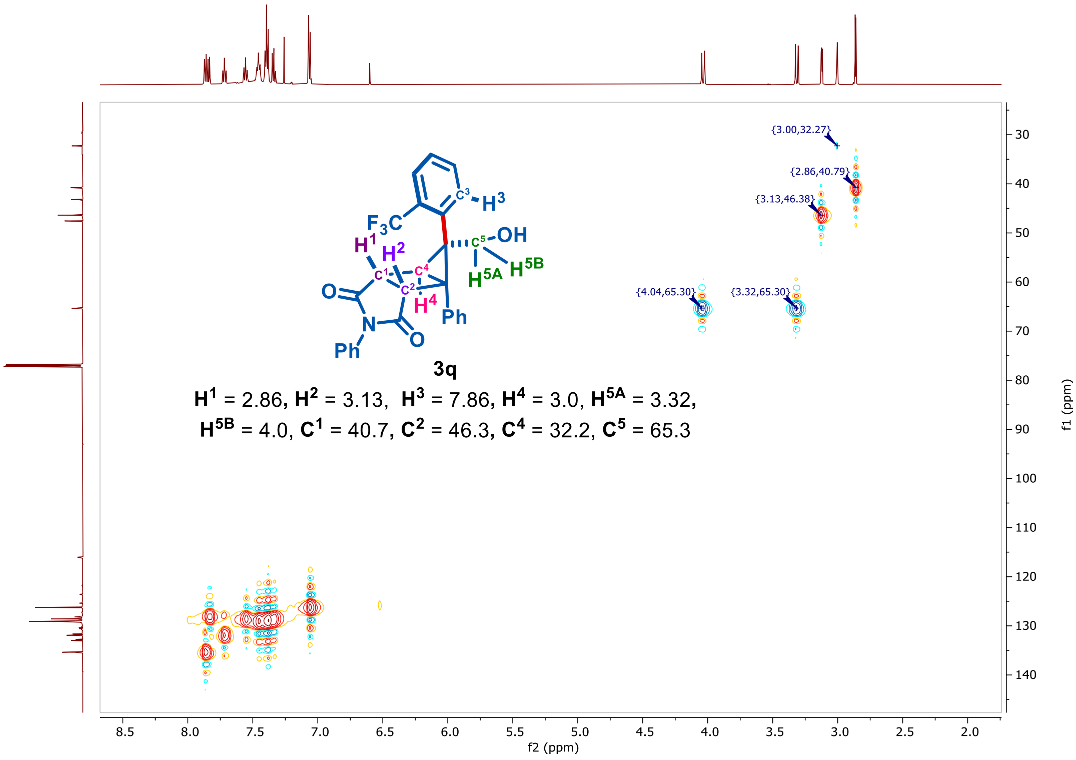
^{13}C-NMR (101 MHz, $CDCl_3$) of compound 3q



^{19}F-NMR (377 MHz, CDCl$_3$) of compound 3q

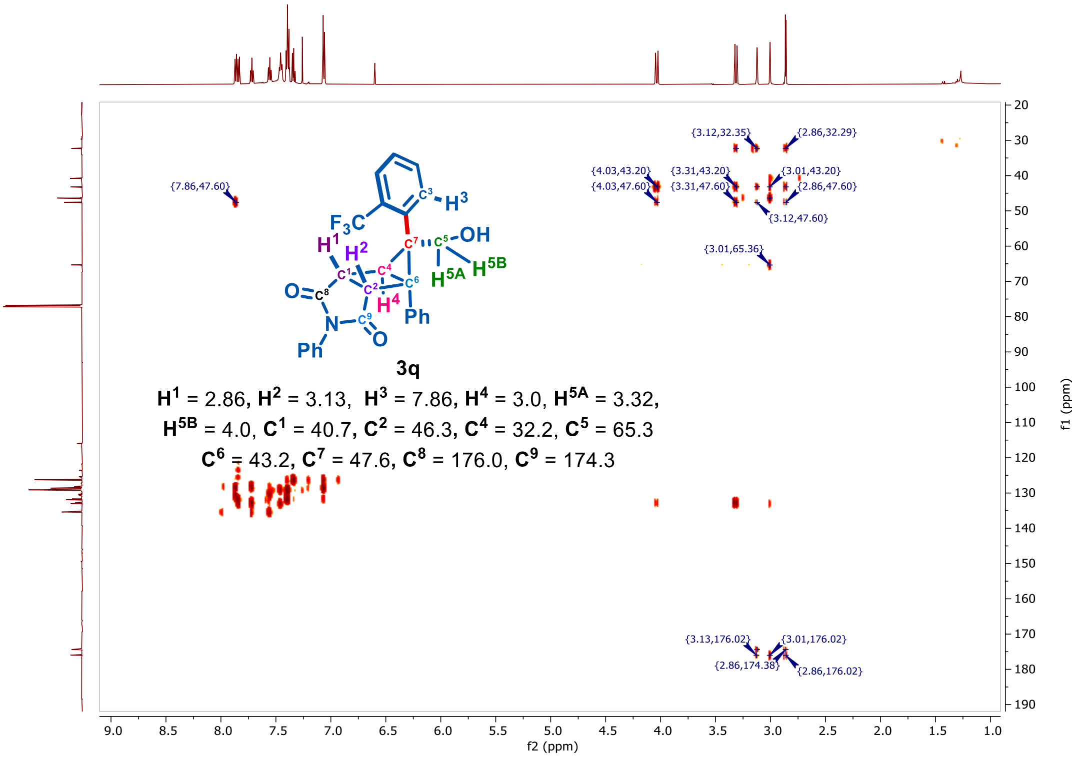


HSQC of compound 3q

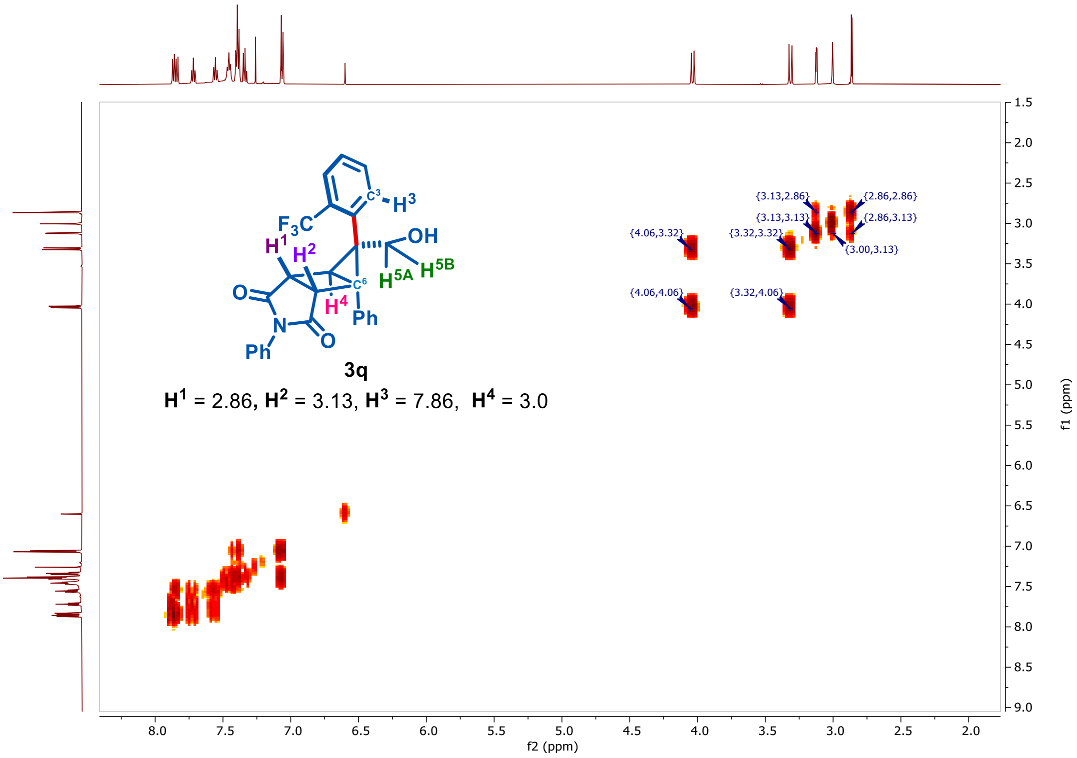


H^1 = 2.86, H^2 = 3.13, H^3 = 7.86, H^4 = 3.0, H^{5A} = 3.32, H^{5B} = 4.0, C^1 = 40.7, C^2 = 46.3, C^4 = 32.2, C^5 = 65.3

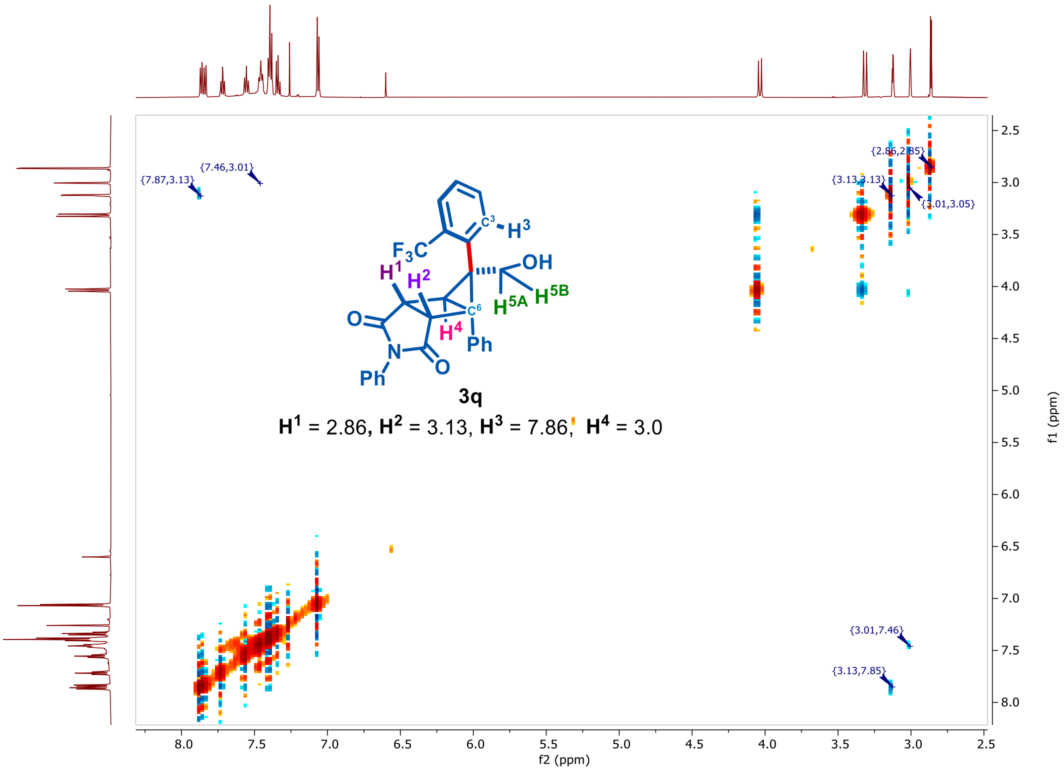
HMBC of compound 3q



COSY of compound 3q



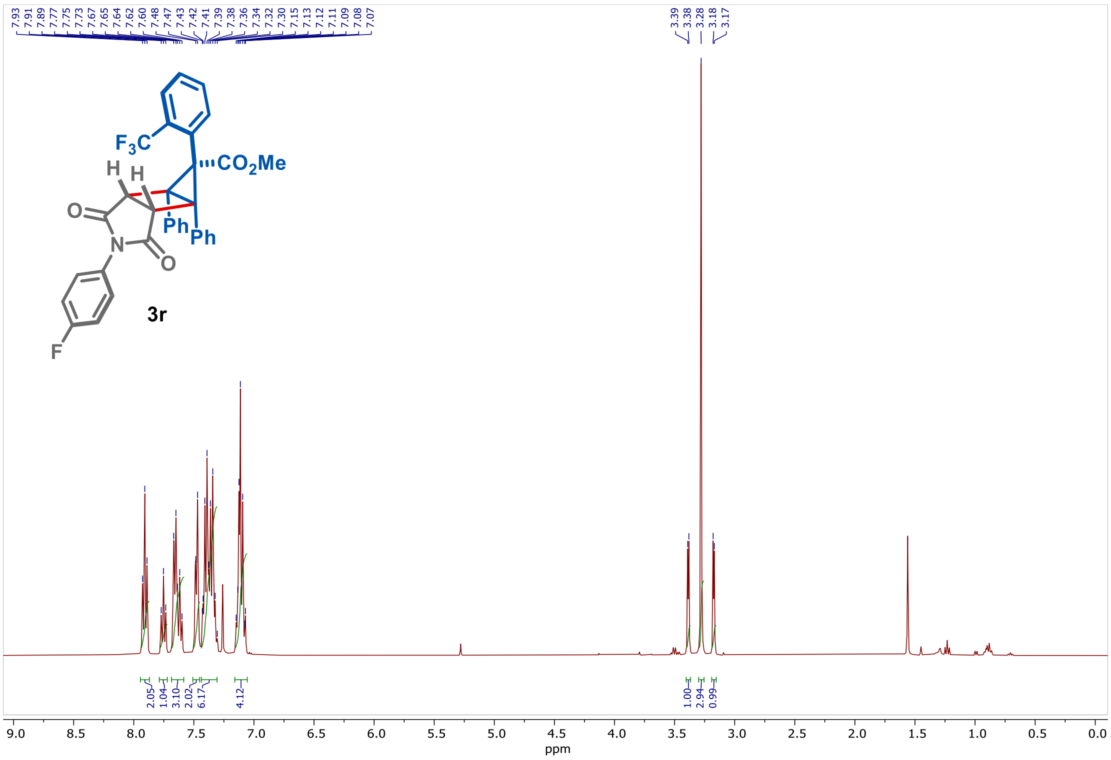
NOESY of compound 3q



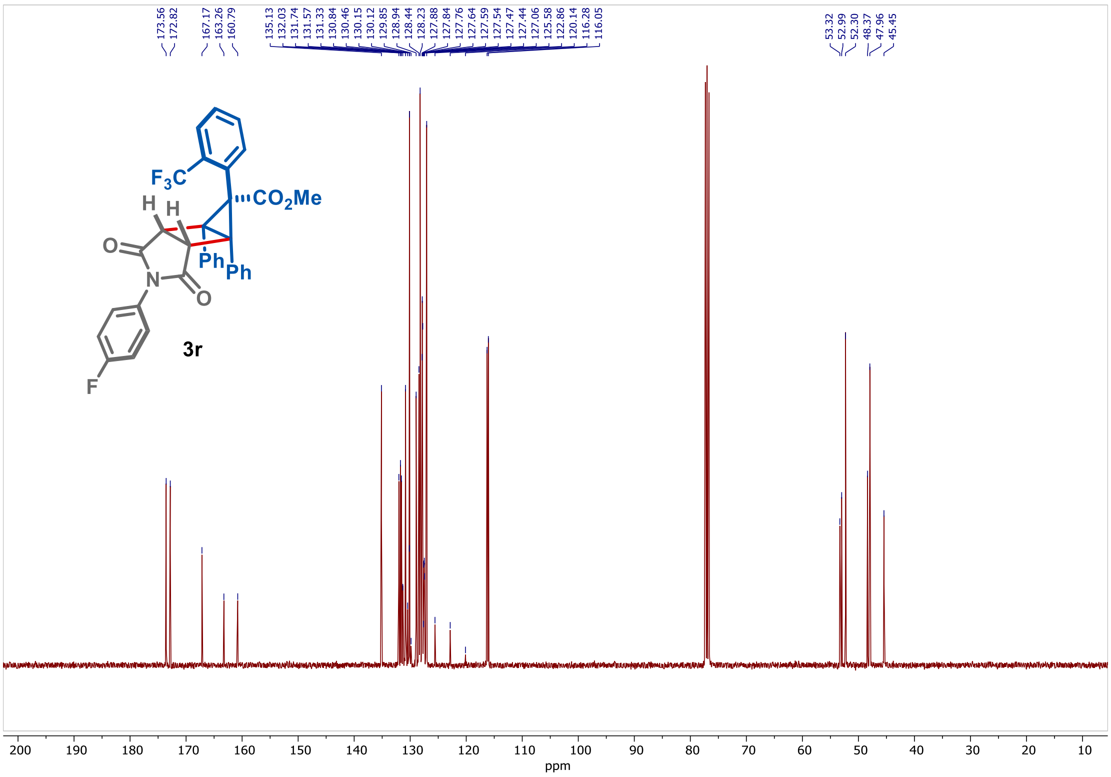
3q

H^{1} = 2.86, **H**^{2} = 3.13, **H**^{3} = 7.86, **H**^{4} = 3.0

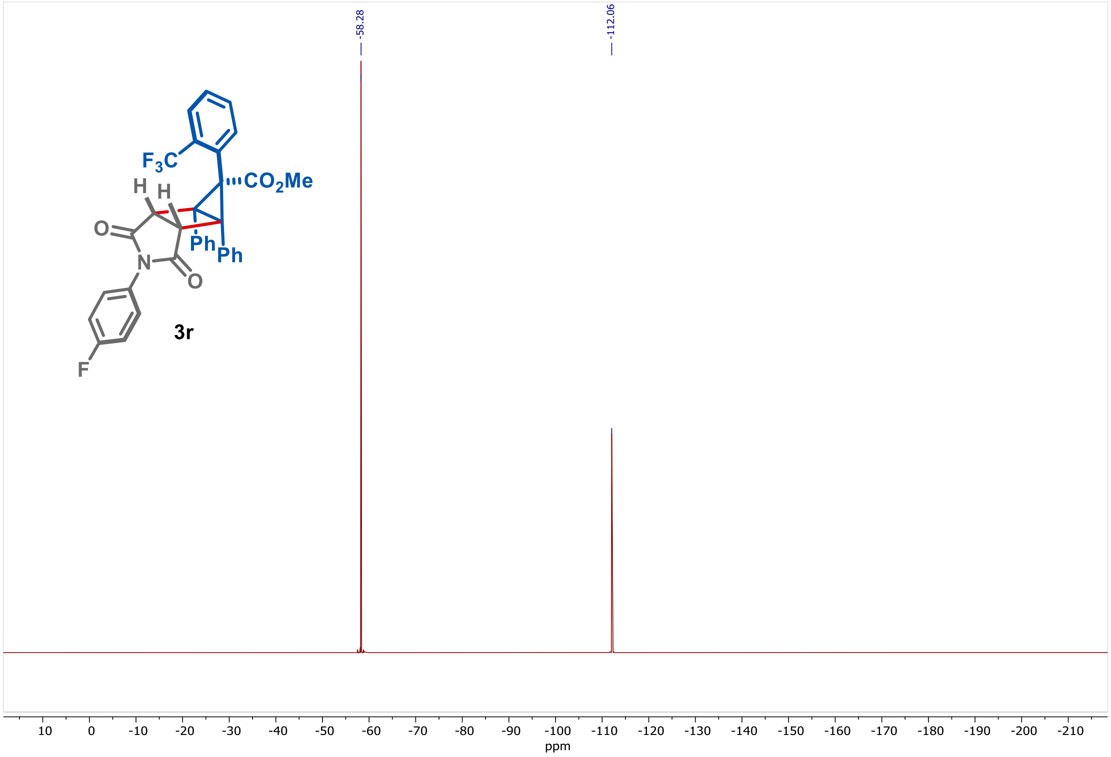
^{1}H-NMR (400 MHz, $CDCl_3$) of compound 3r (see procedure)



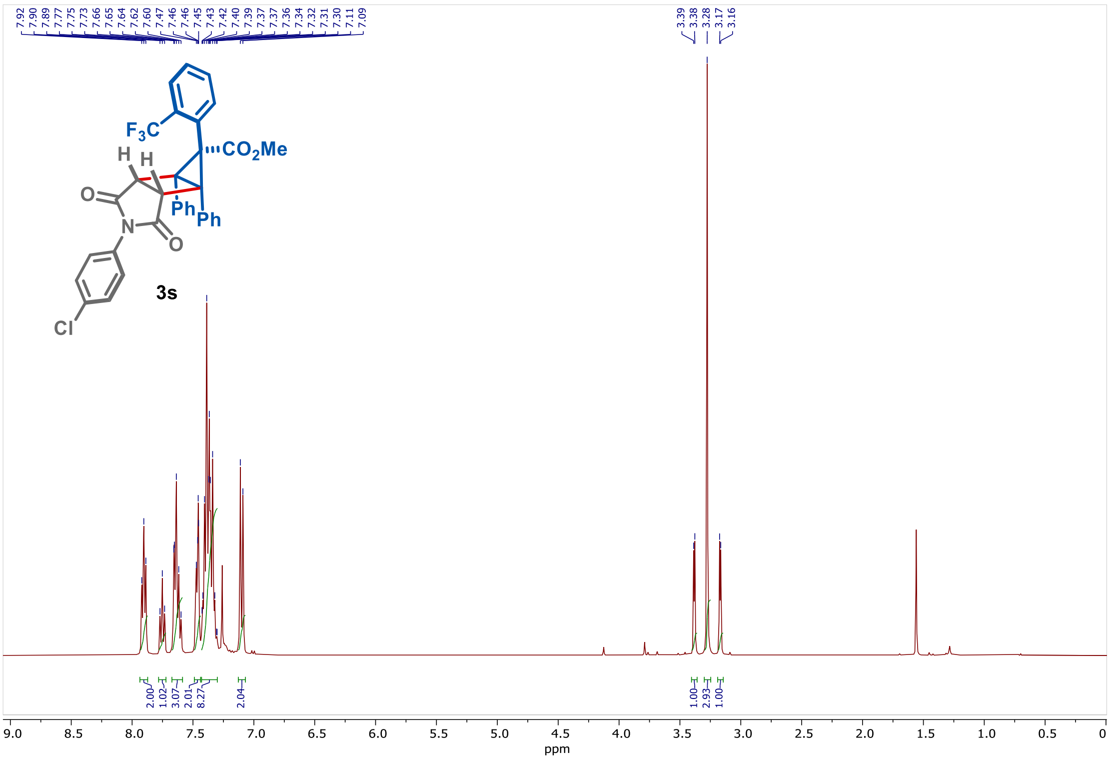
^{13}C-NMR (101 MHz, $CDCl_3$) of compound 3r



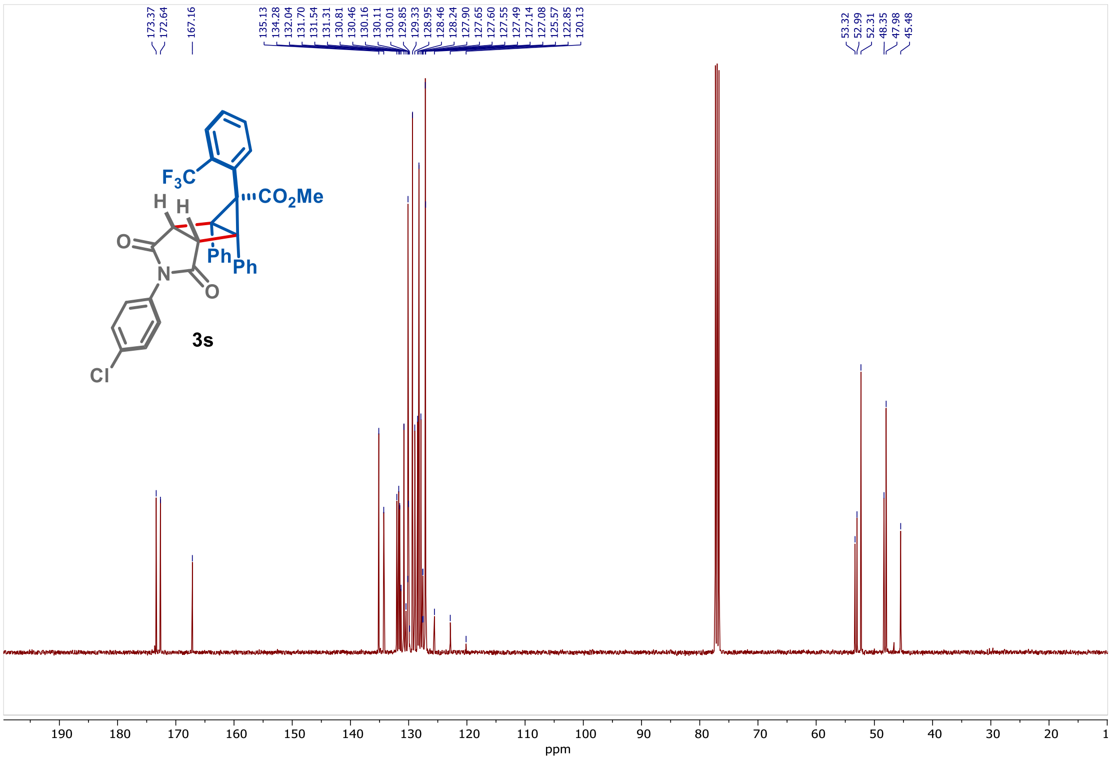
^{19}F-NMR (377 MHz, $CDCl_3$) of compound 3r



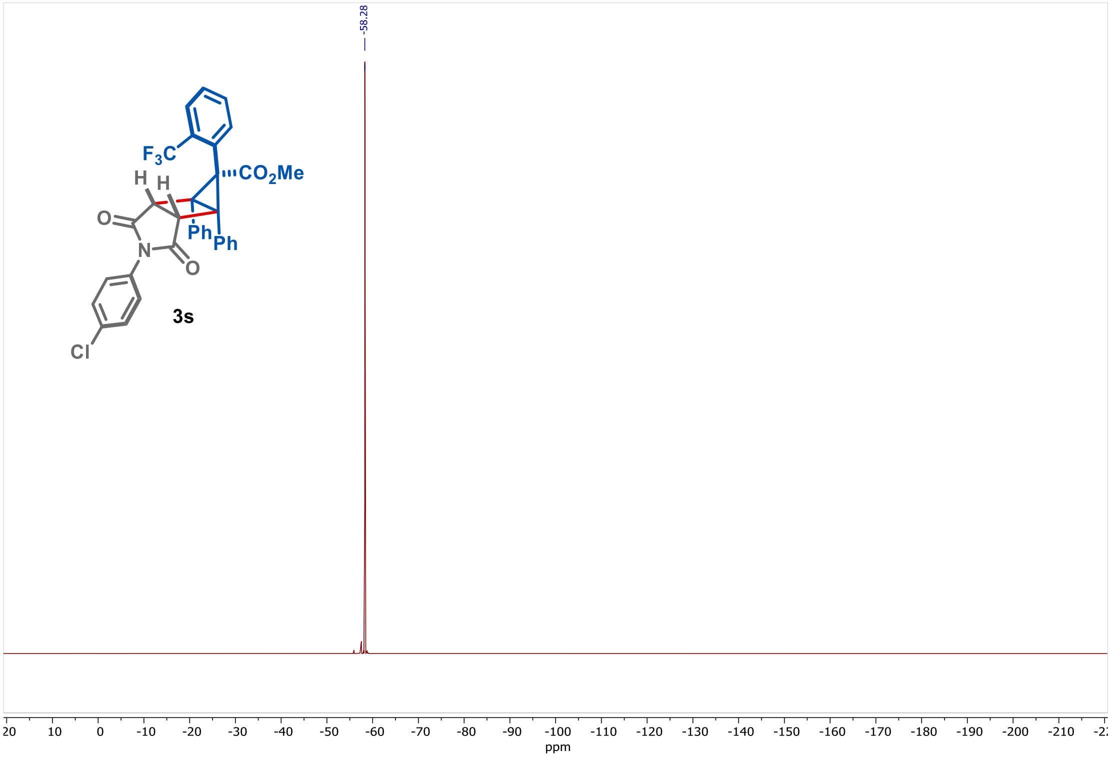
^{1}H-NMR (400 MHz, CDCl$_3$) of compound 3s (see procedure)



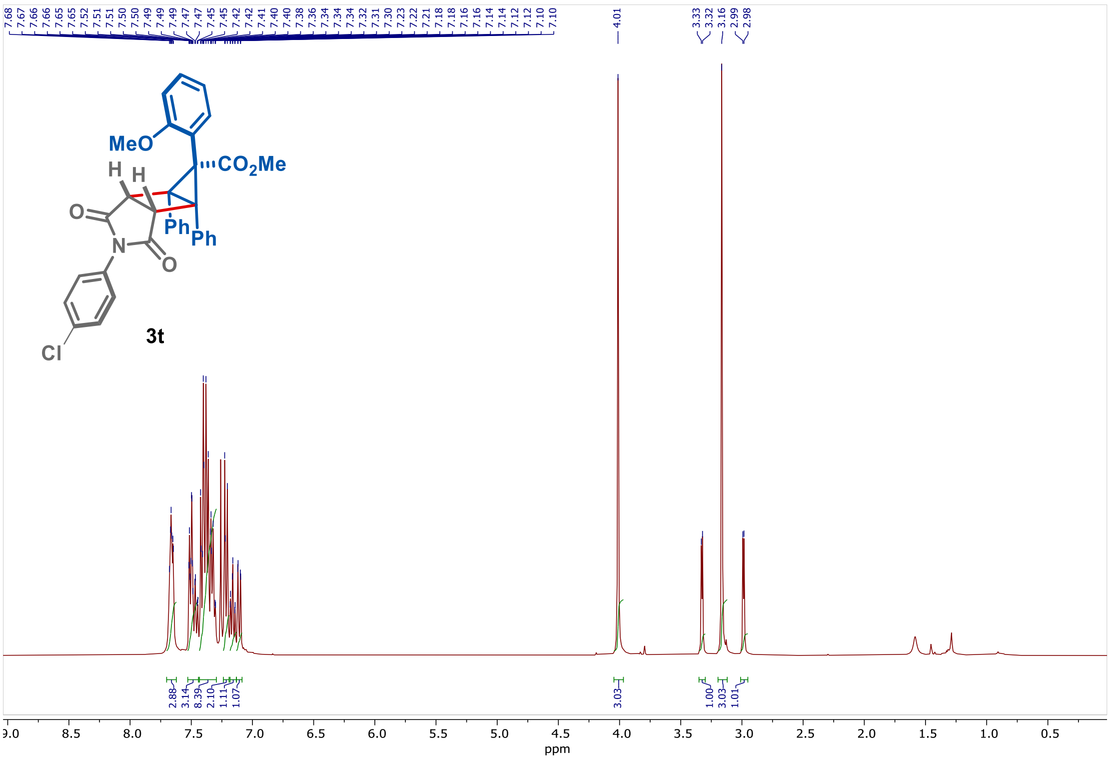
^{13}C-NMR (101 MHz, CDCl$_3$) of compound 3s



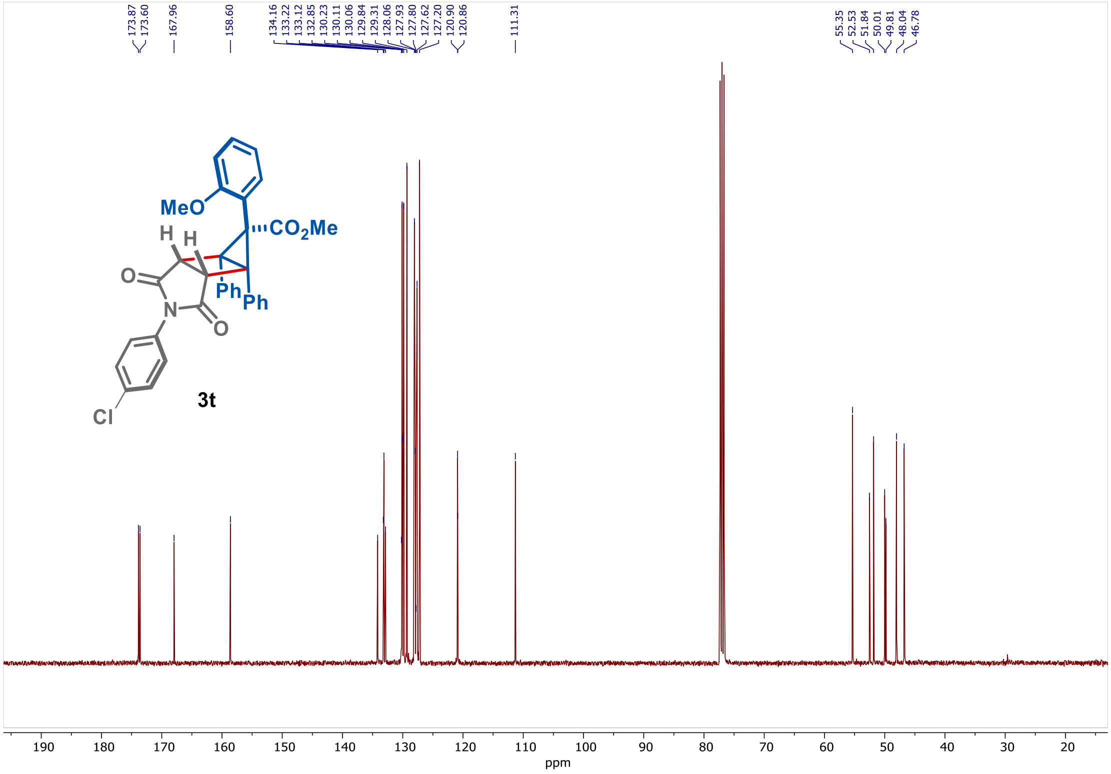
^{19}F-NMR (377 MHz, $CDCl_3$) of compound 3s



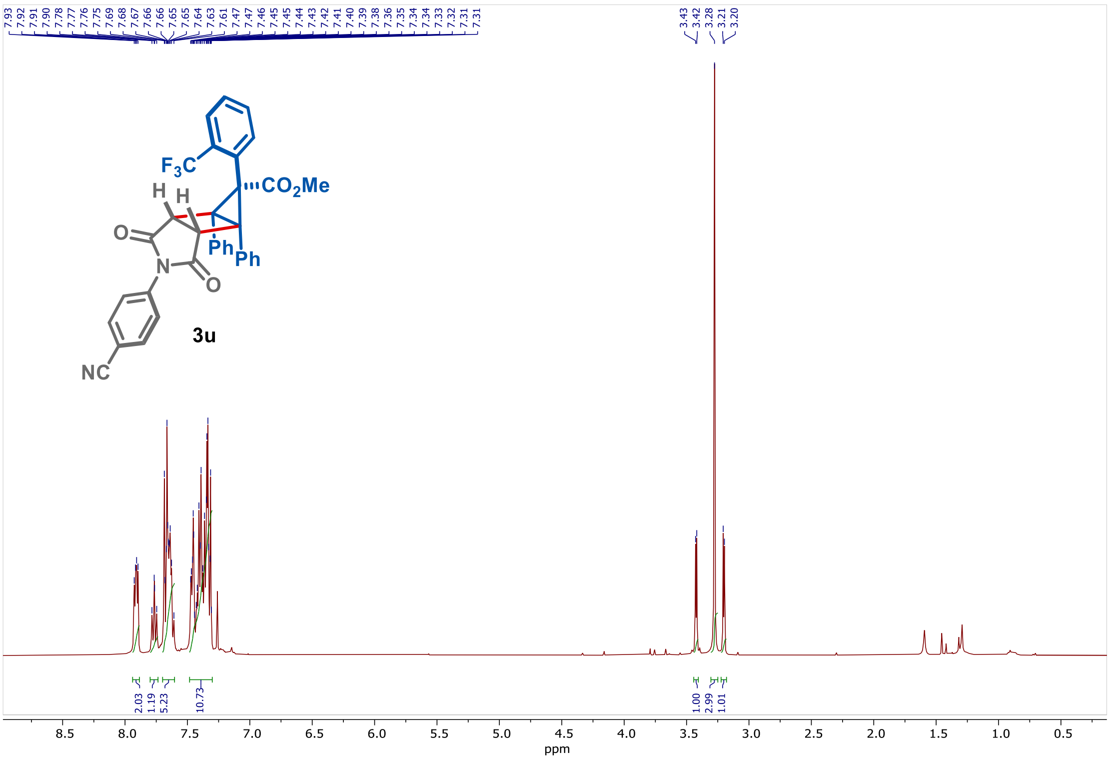
^{1}H-NMR (400 MHz, CDCl$_3$) of compound 3t (see procedure)



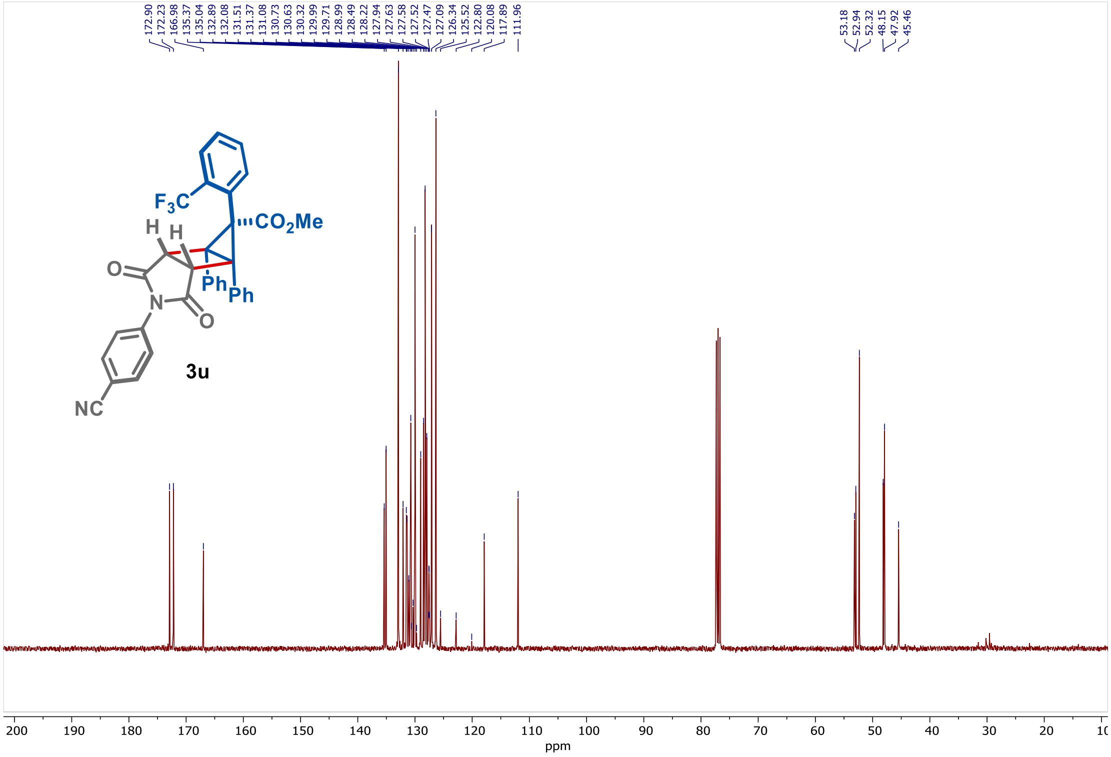
^{13}C-NMR (101 MHz, CDCl$_3$) of compound 3t



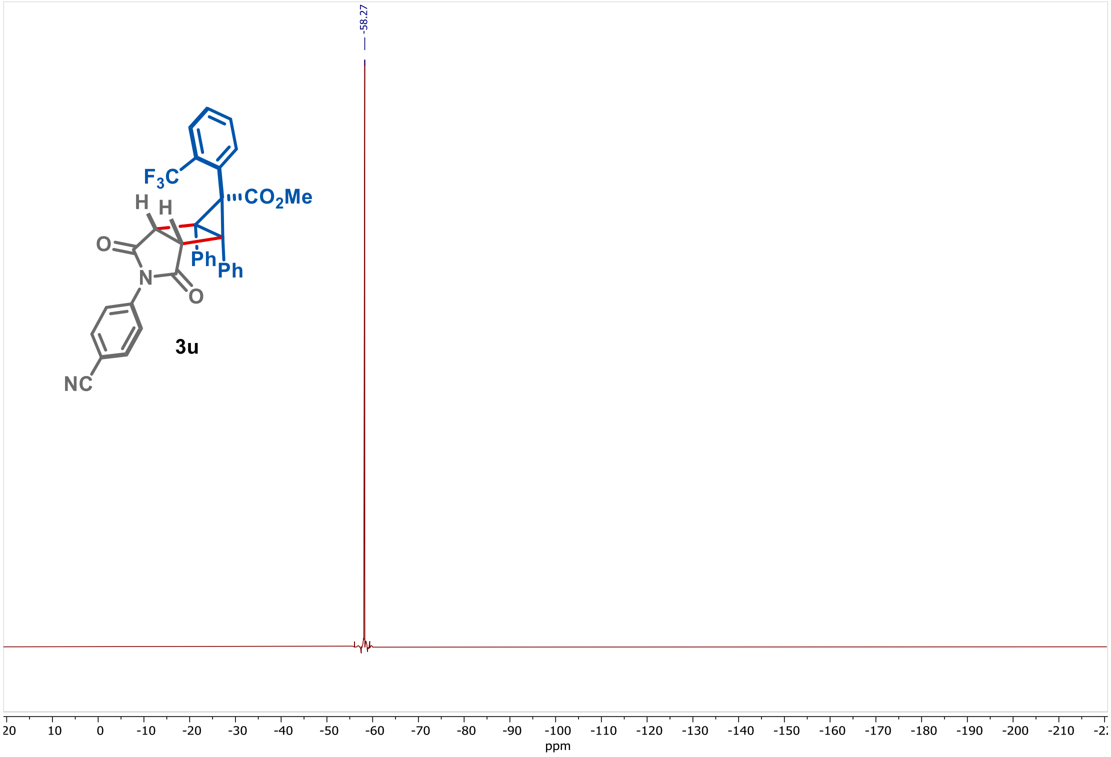
^{1}H-NMR (400MHz, $CDCl_3$) of compound 3u (see procedure)



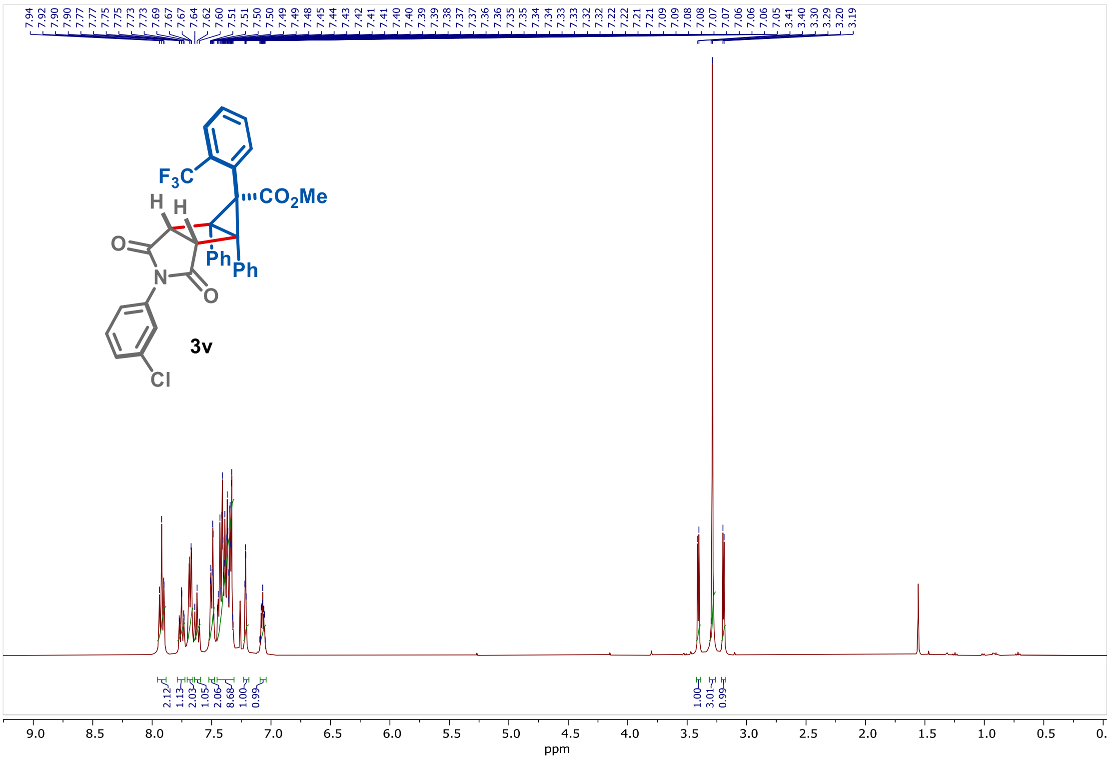
^{13}C-NMR (101 MHz, $CDCl_3$) of compound 3u



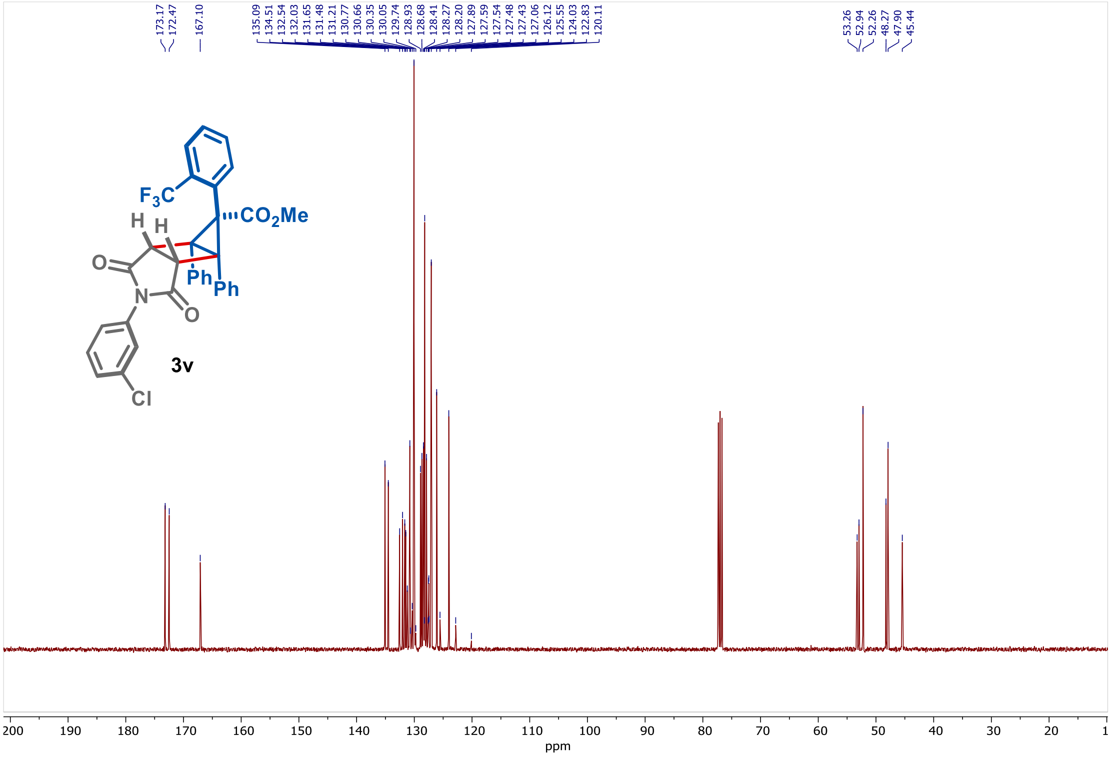
^{19}F-NMR (377 MHz, CDCl$_3$) of compound 3u



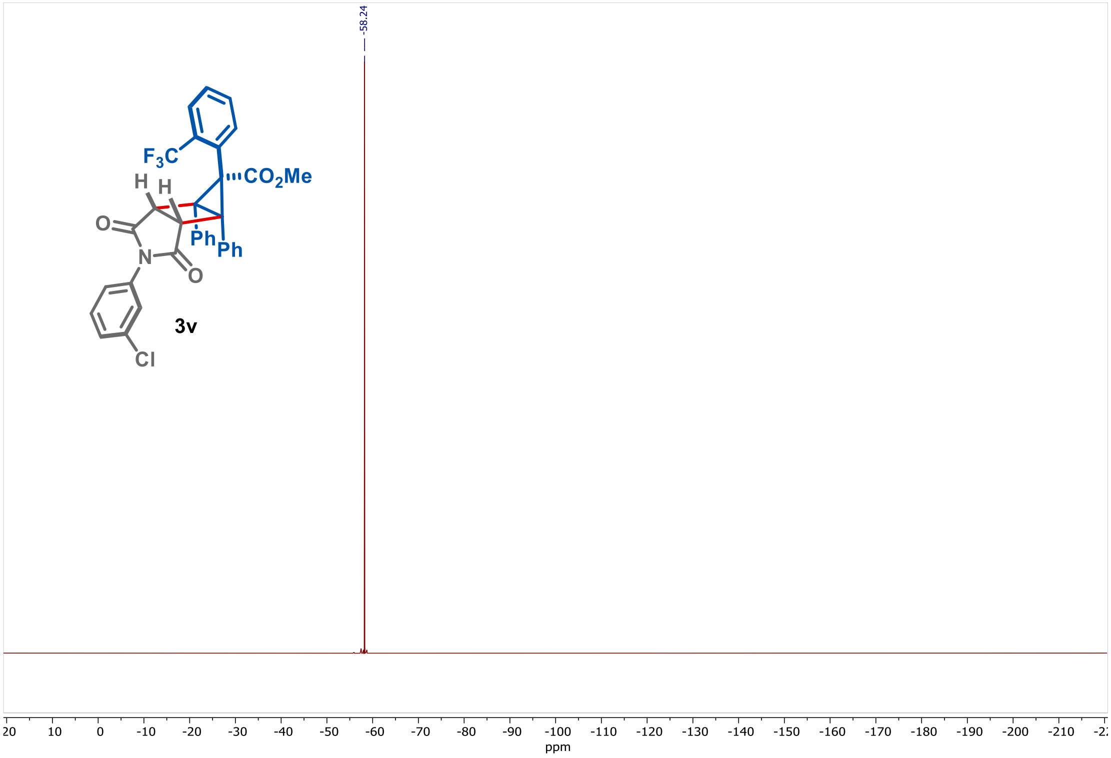
^{1}H-NMR (400 MHz, CDCl$_3$) of compound 3v (see procedure)



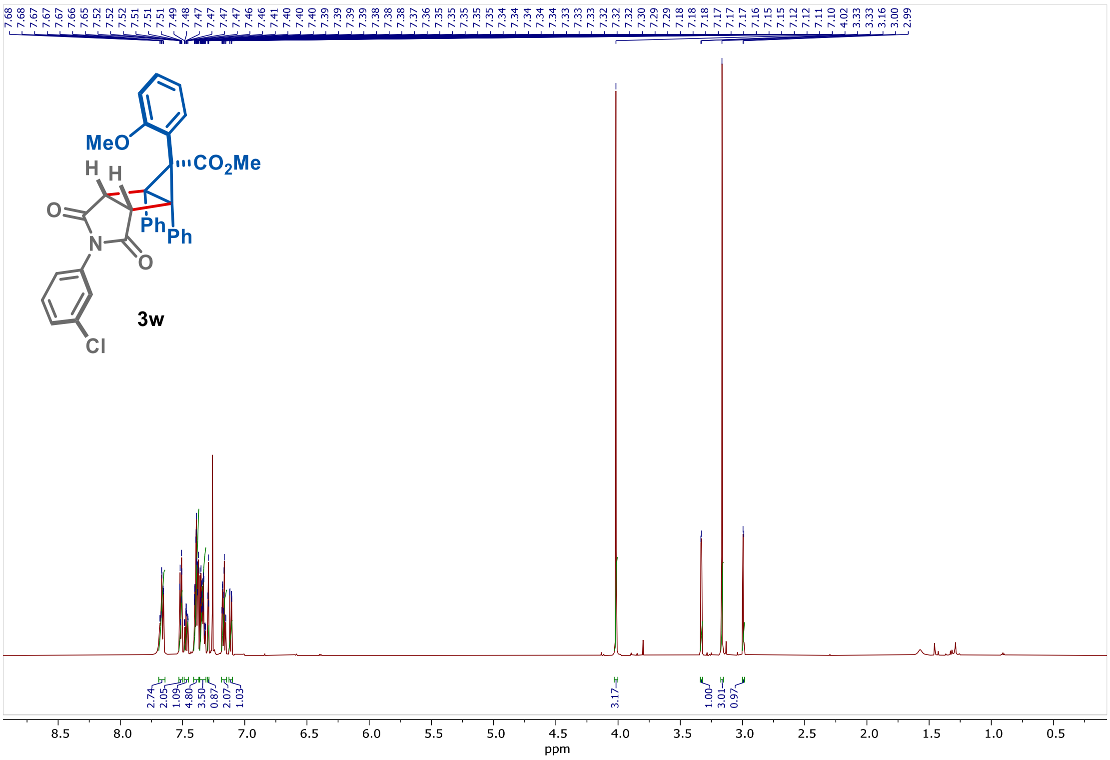
^{13}C-NMR (101 MHz, CDCl$_3$) of compound 3v



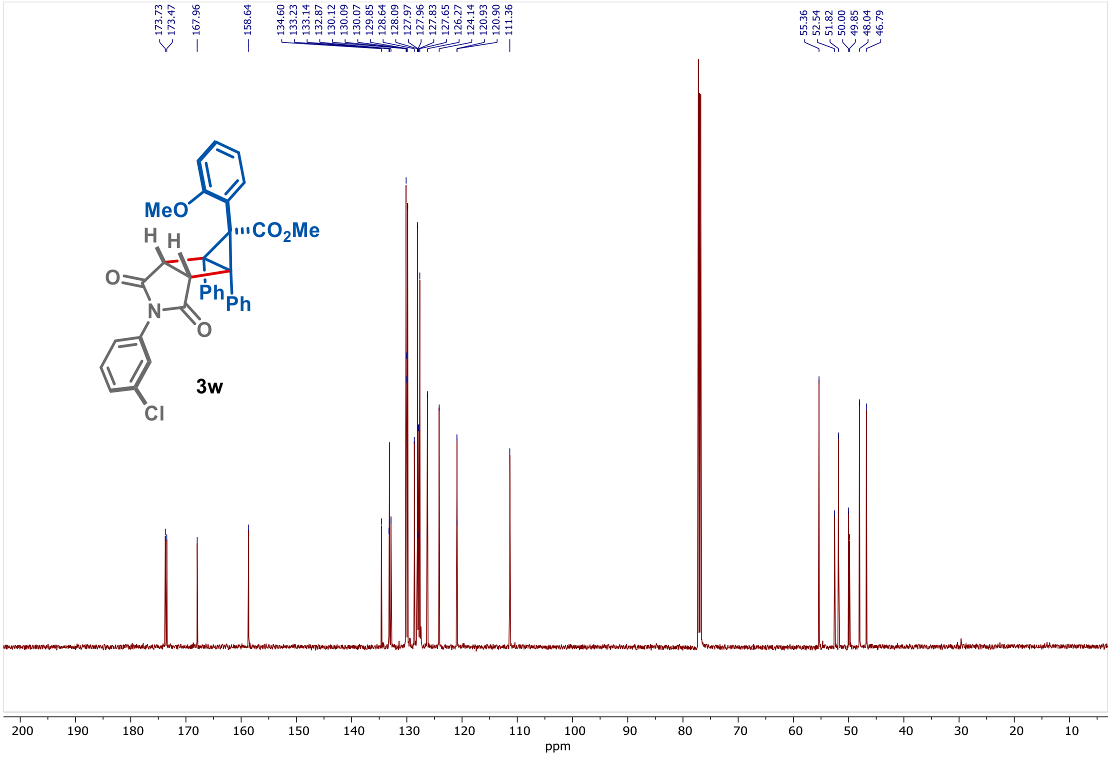
^{19}F-NMR (377 MHz, $CDCl_3$) of compound 3v



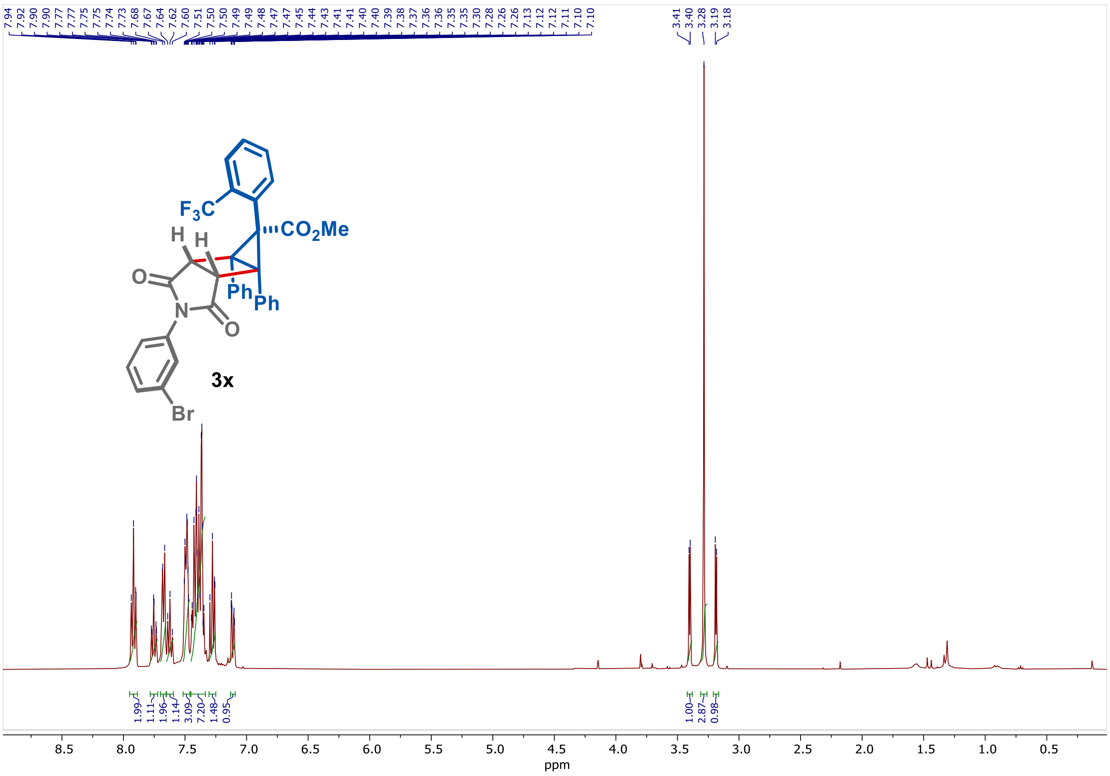
^{1}H-NMR (400 MHz, CDCl$_3$) of compound 3w (see procedure)



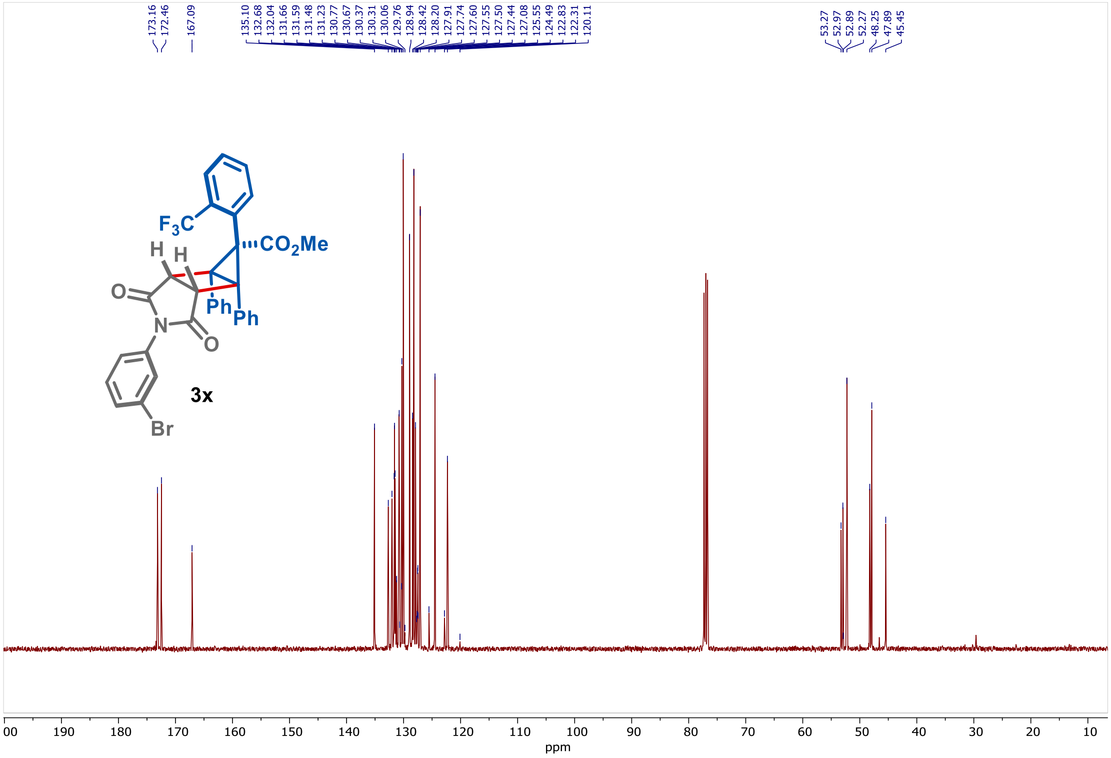
^{13}C-NMR (101 MHz, CDCl$_3$) of compound 3w



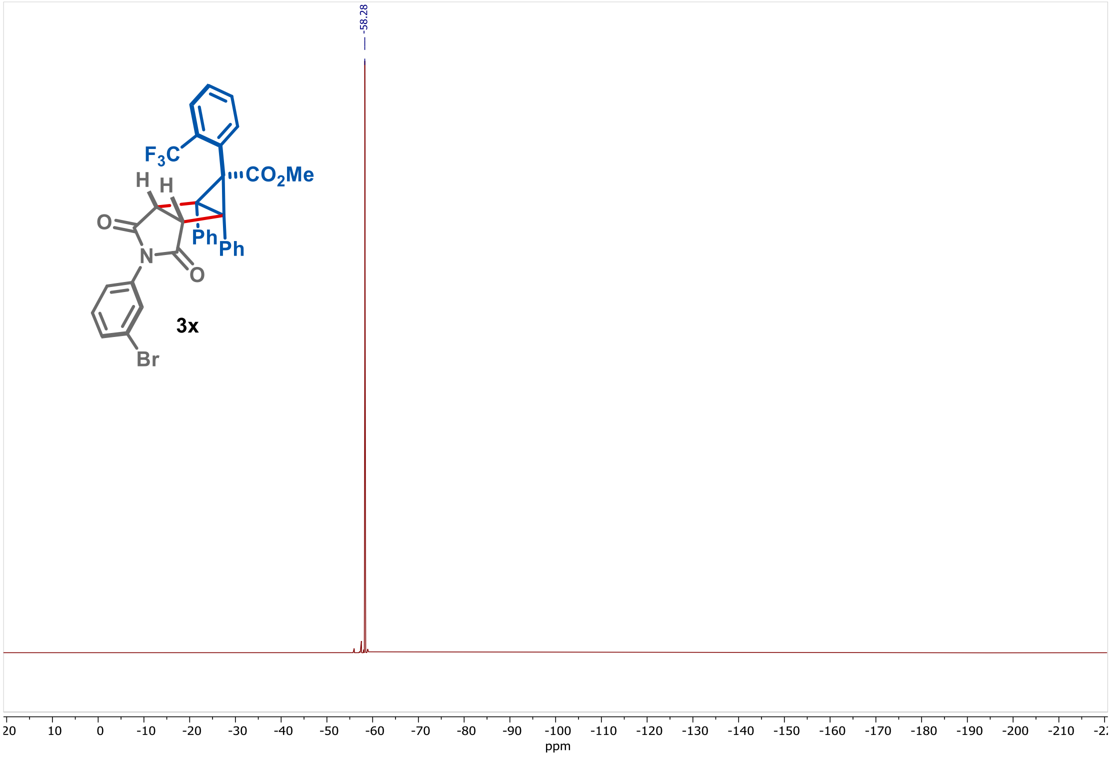
^{1}H-NMR (400 MHz, CDCl$_3$) of compound 3x (see procedure)



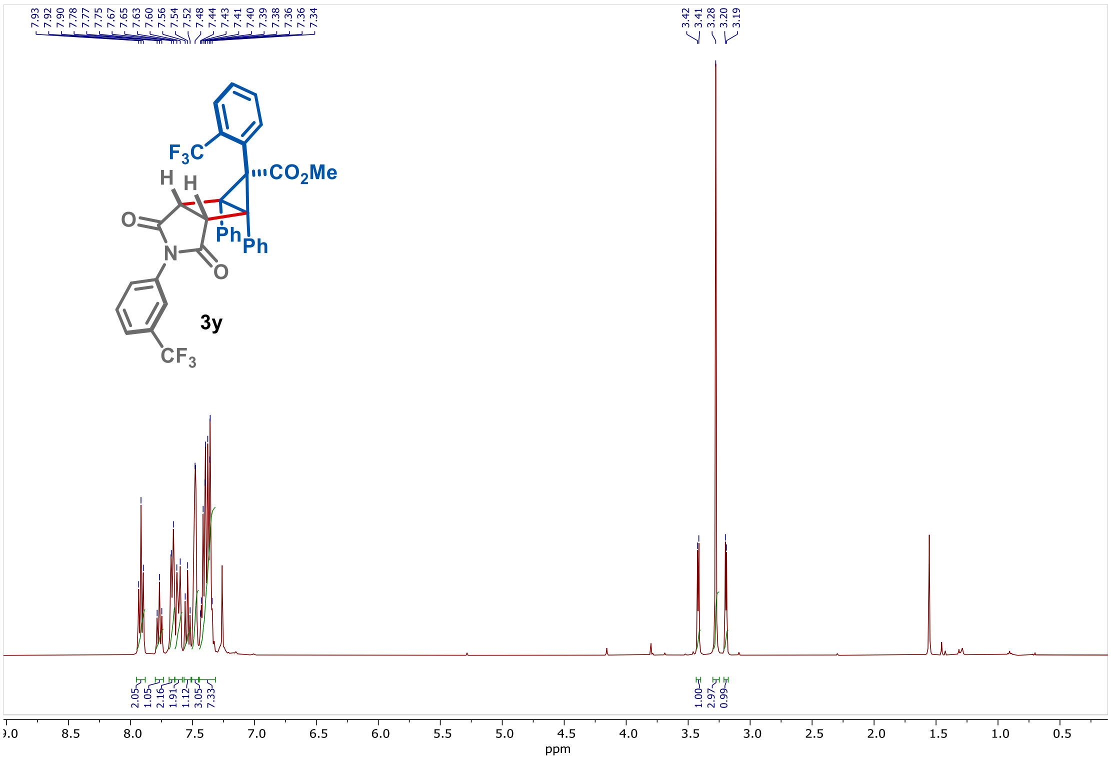
^{13}C-NMR (101 MHz, CDCl$_3$) of compound 3x



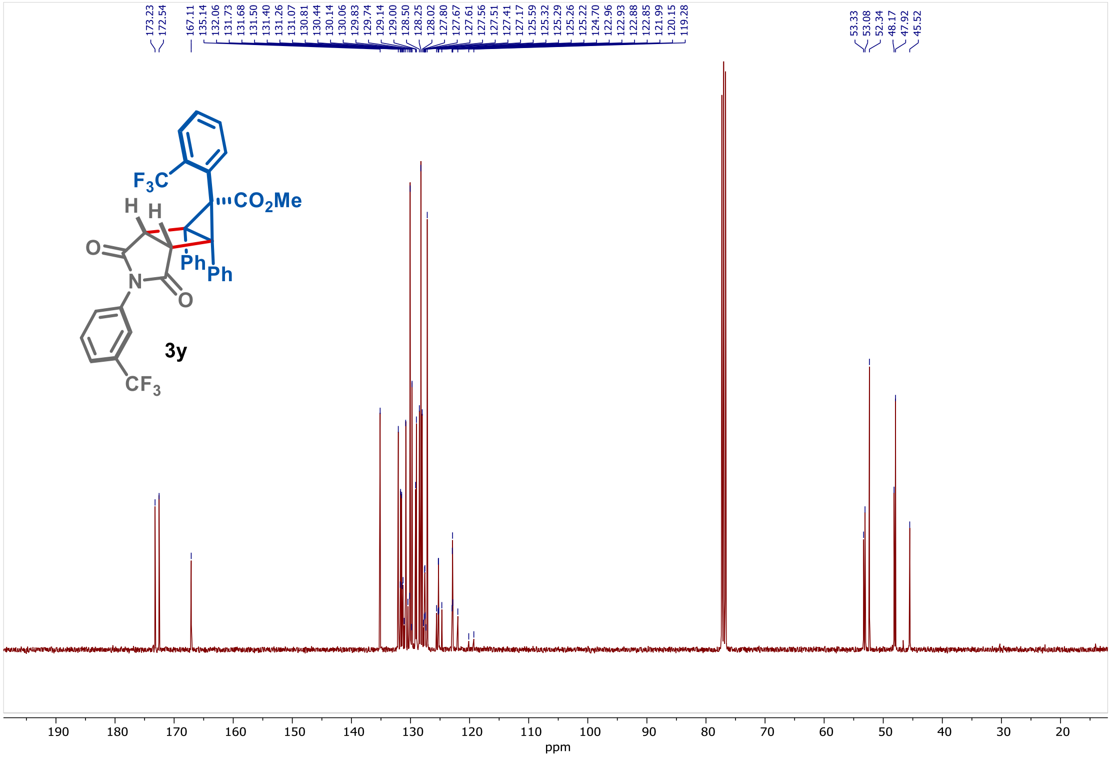
^{19}F-NMR (377 MHz, $CDCl_3$) of compound 3x



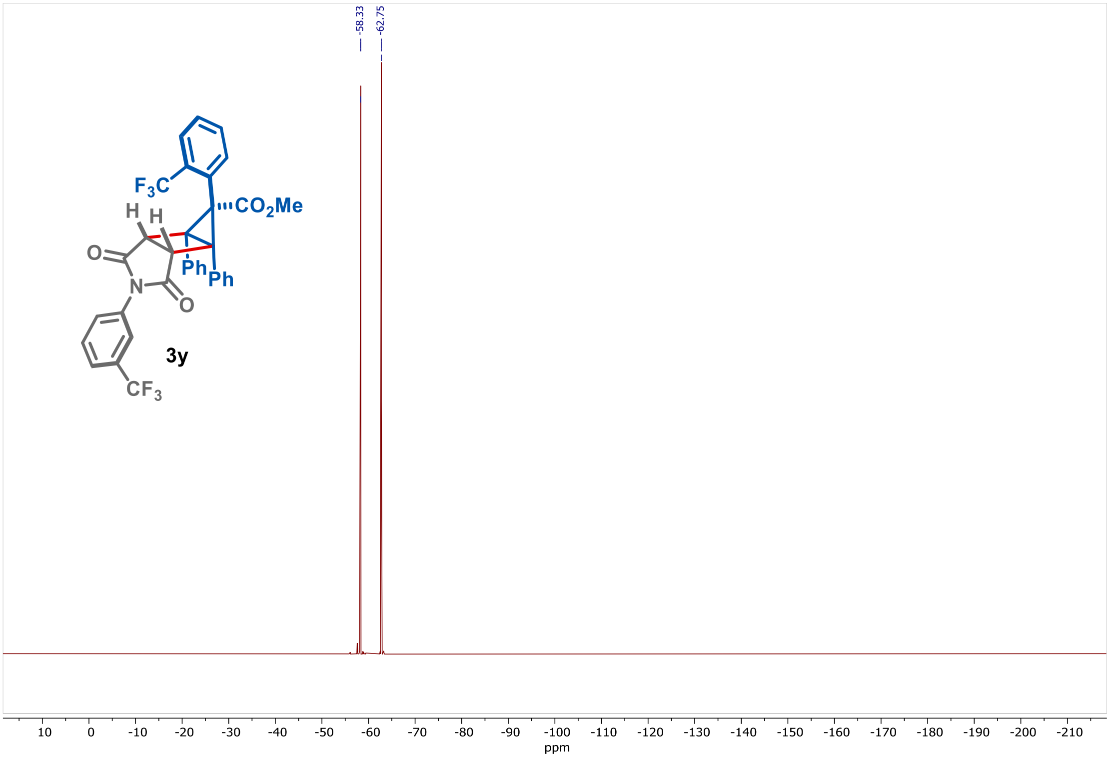
^{1}H-NMR (400 MHz, CDCl$_3$) of compound 3y (see procedure)



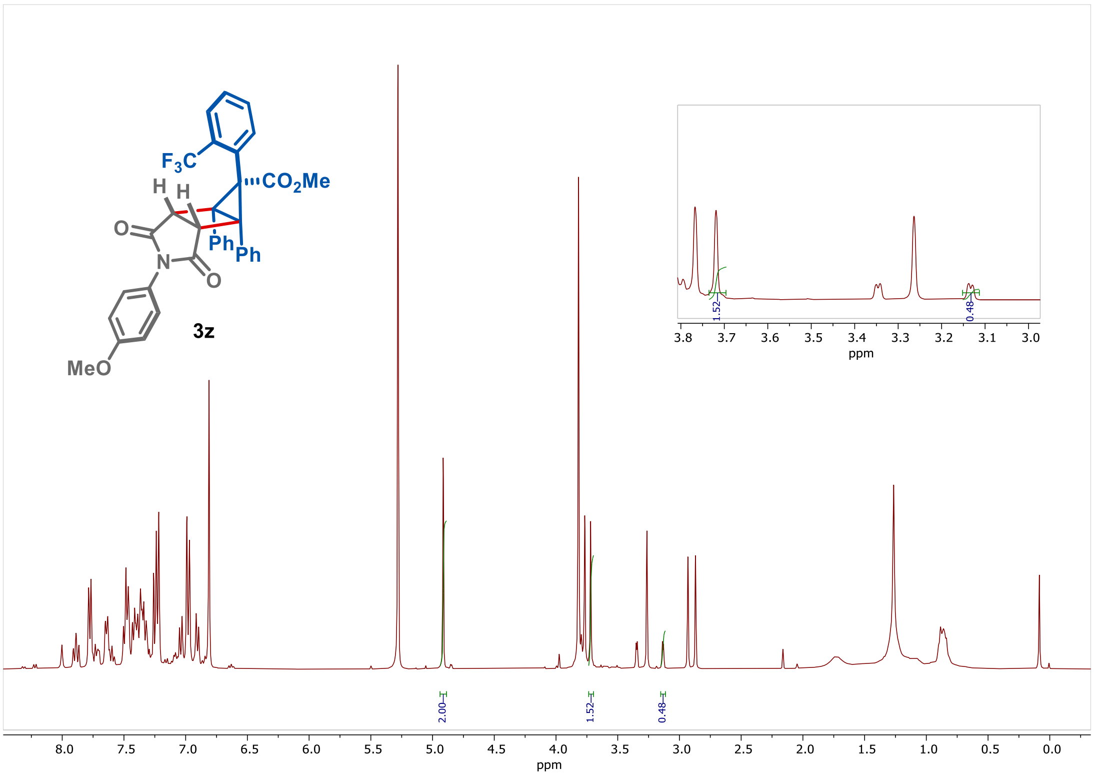
^{13}C-NMR (101 MHz, CDCl$_3$) of compound 3y



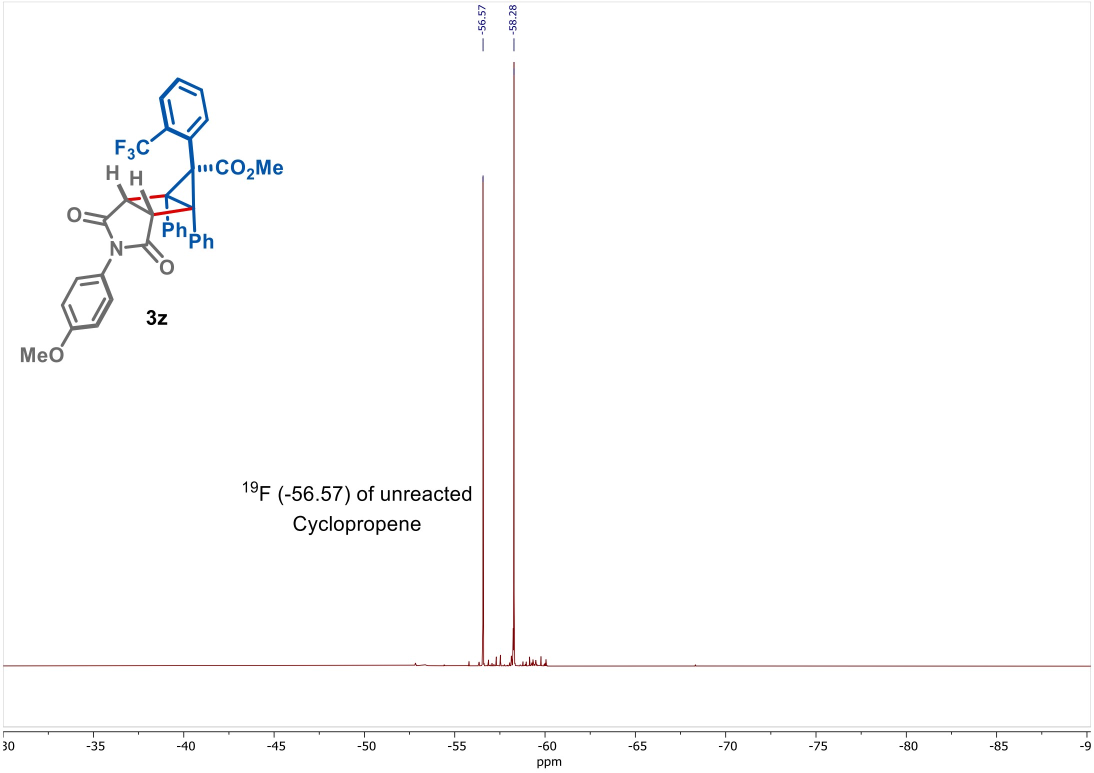
^{19}F-NMR (377 MHz, $CDCl_3$) of compound 3y



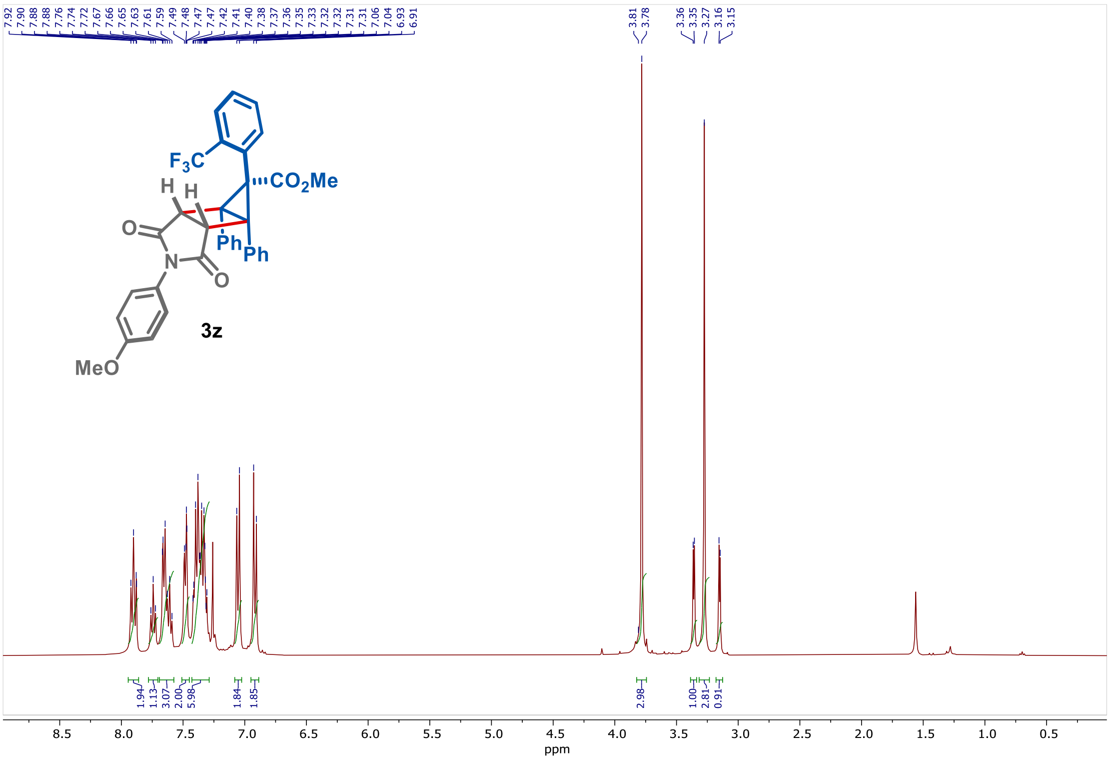
^{1}H-NMR (400 MHz, CDCl$_3$) of compound 3z (Crude) (see procedure)



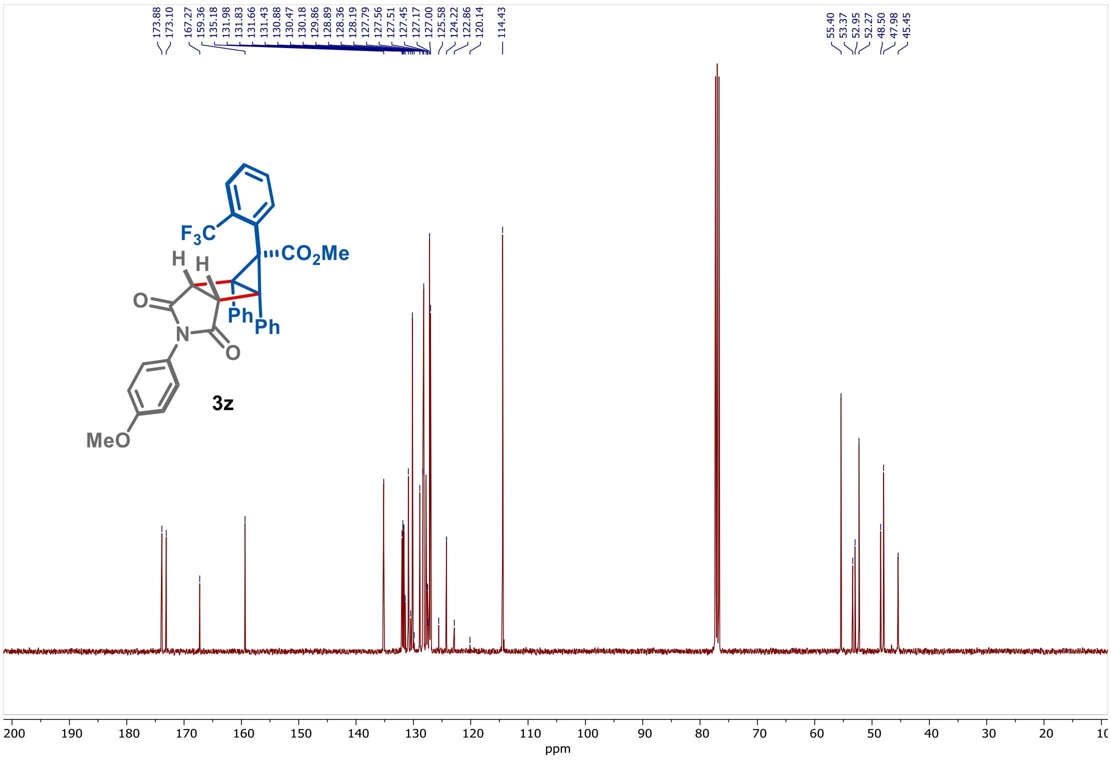
^{19}F-NMR (377 MHz, CDCl$_3$) of compound 3z (Crude)



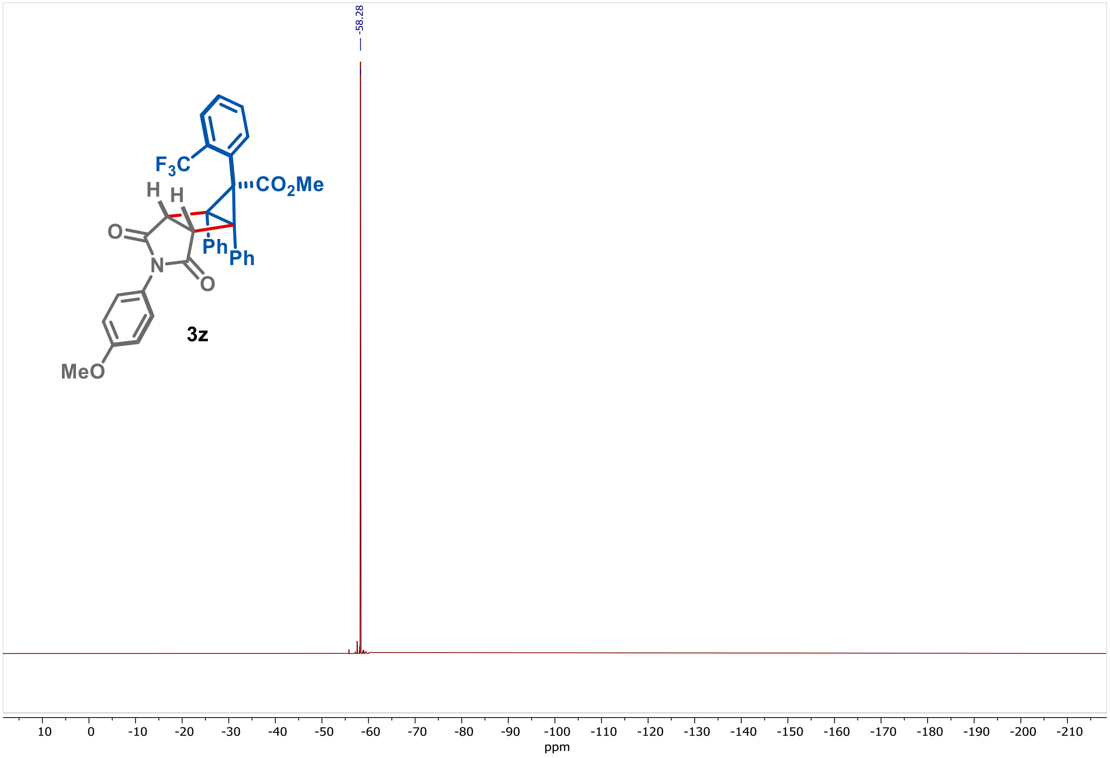
^{1}H-NMR (400 MHz, CDCl$_3$) of compound 3z (see procedure)



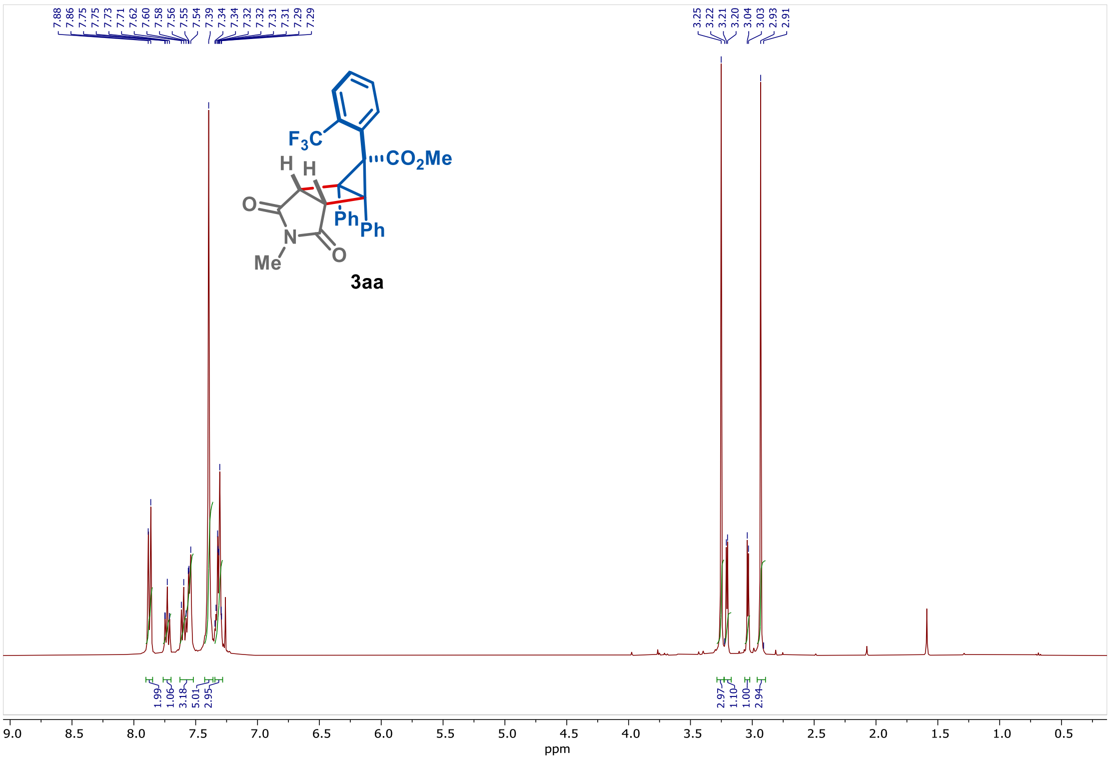
^{13}C-NMR (101 MHz, CDCl$_3$) of compound 3z



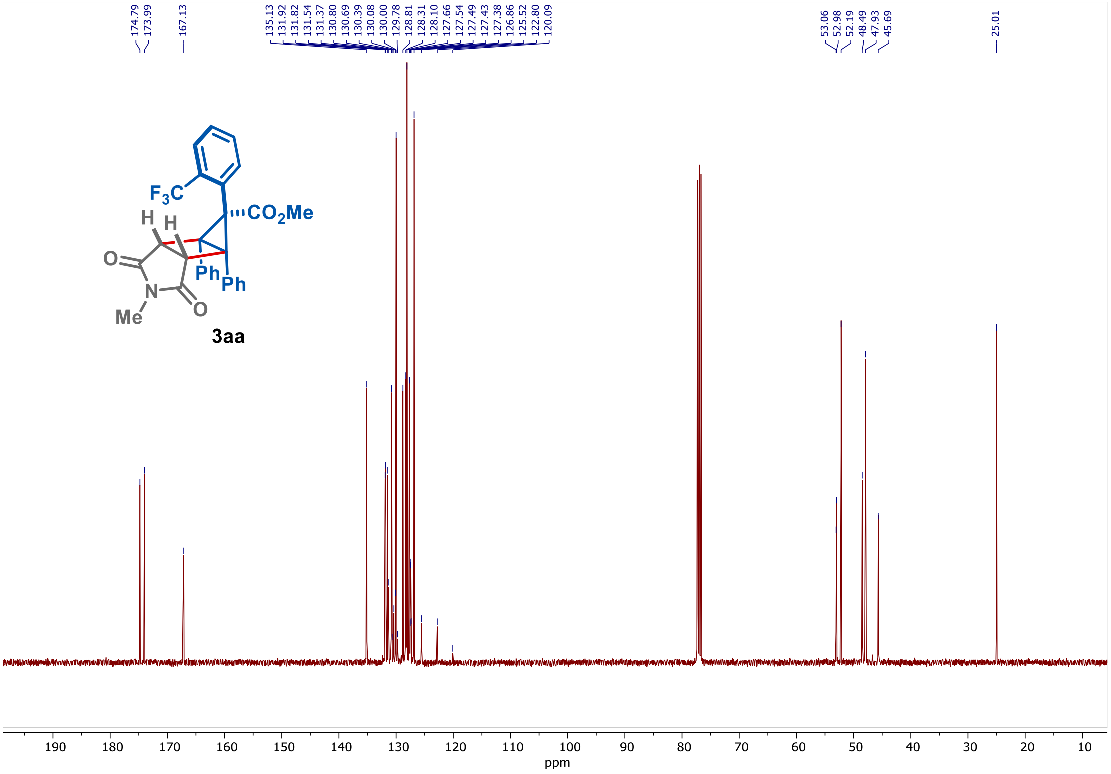
^{19}F-NMR (377 MHz, $CDCl_3$) of compound 3z



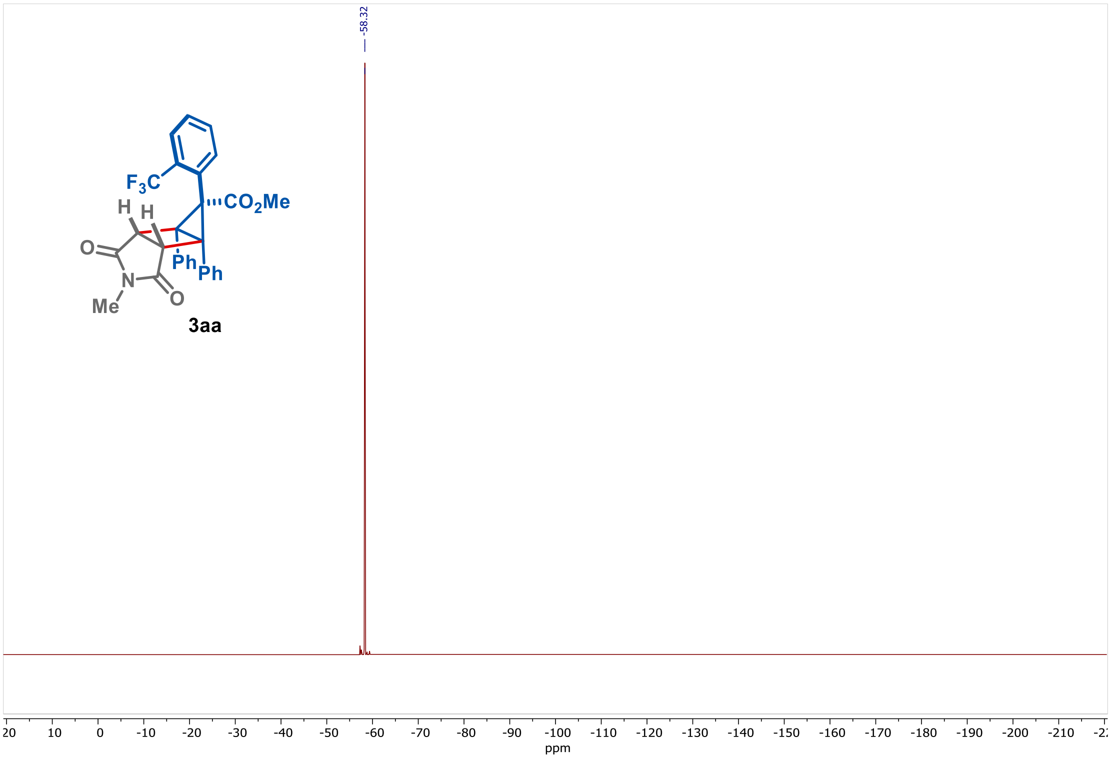
^{1}H-NMR (400 MHz, CDCl$_3$) of compound 3aa (see procedure)



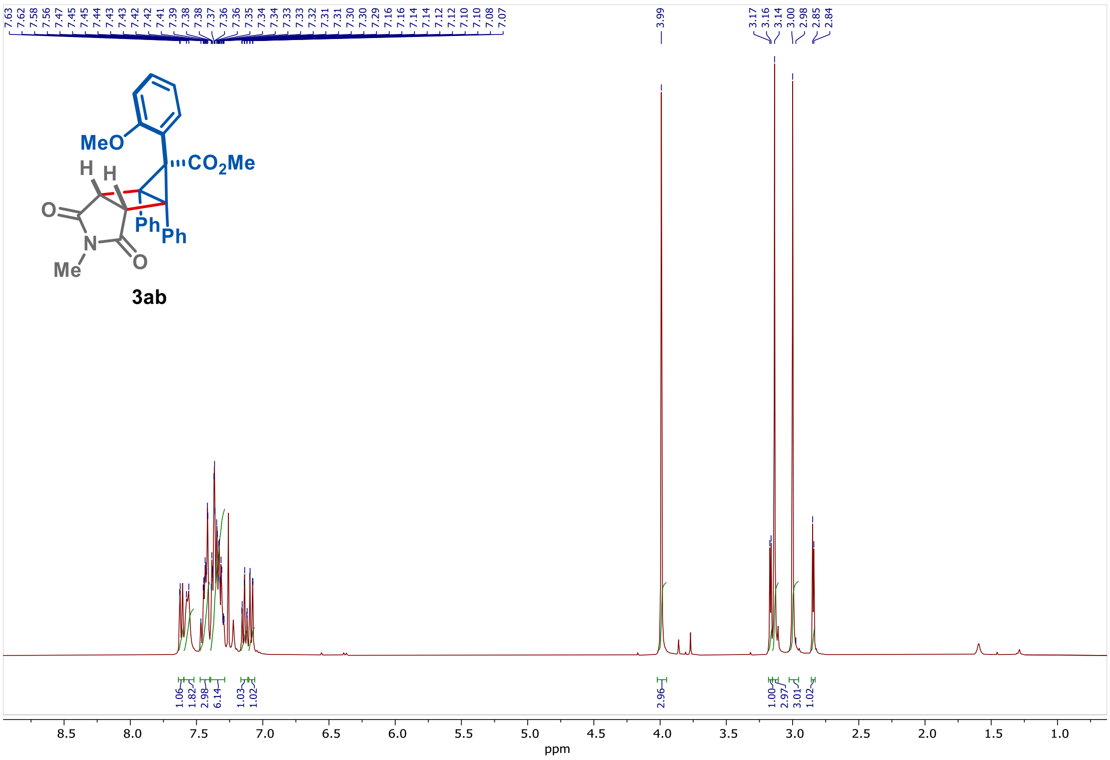
^{13}C-NMR (101 MHz, CDCl$_3$) of compound 3aa



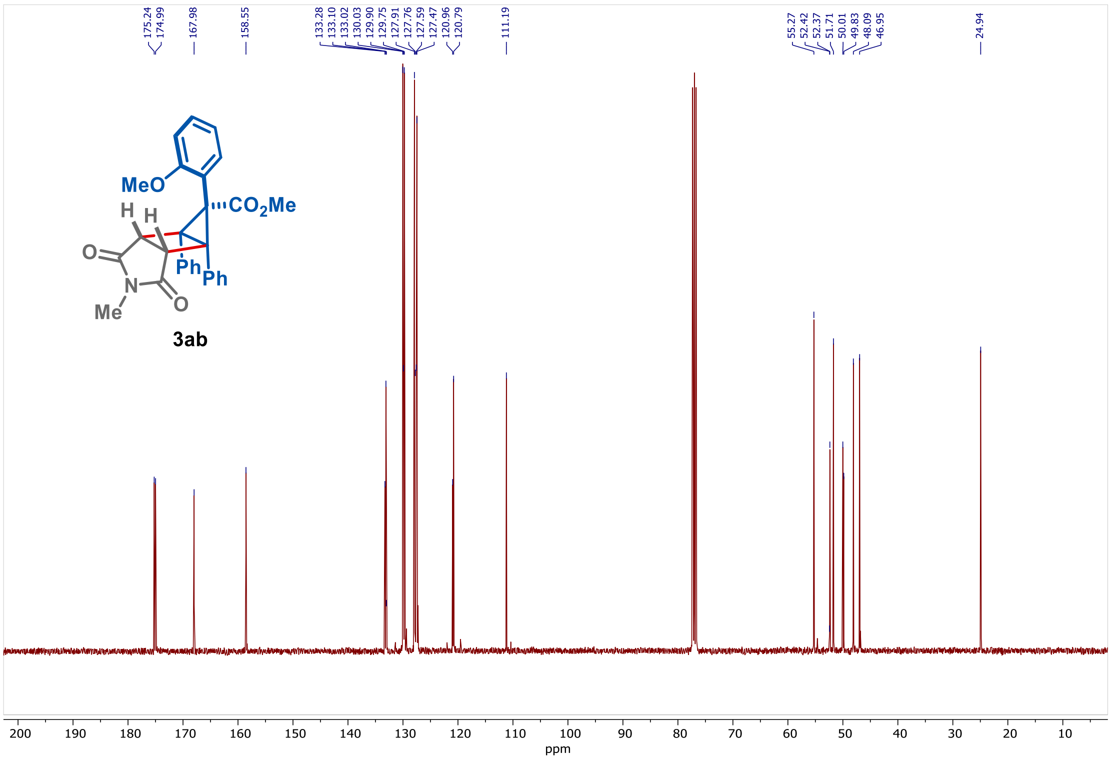
^{19}F-NMR (377 MHz, $CDCl_3$) of compound 3aa



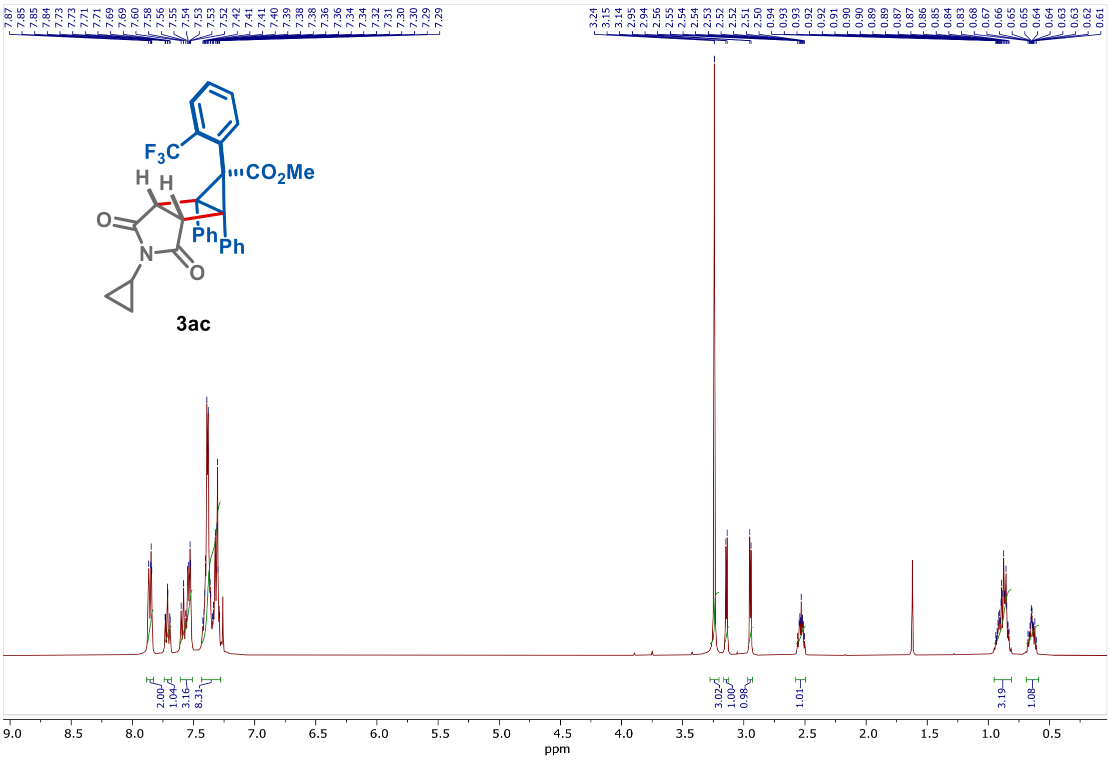
^{1}H-NMR (400 MHz, CDCl$_3$) of compound 3ab (see procedure)



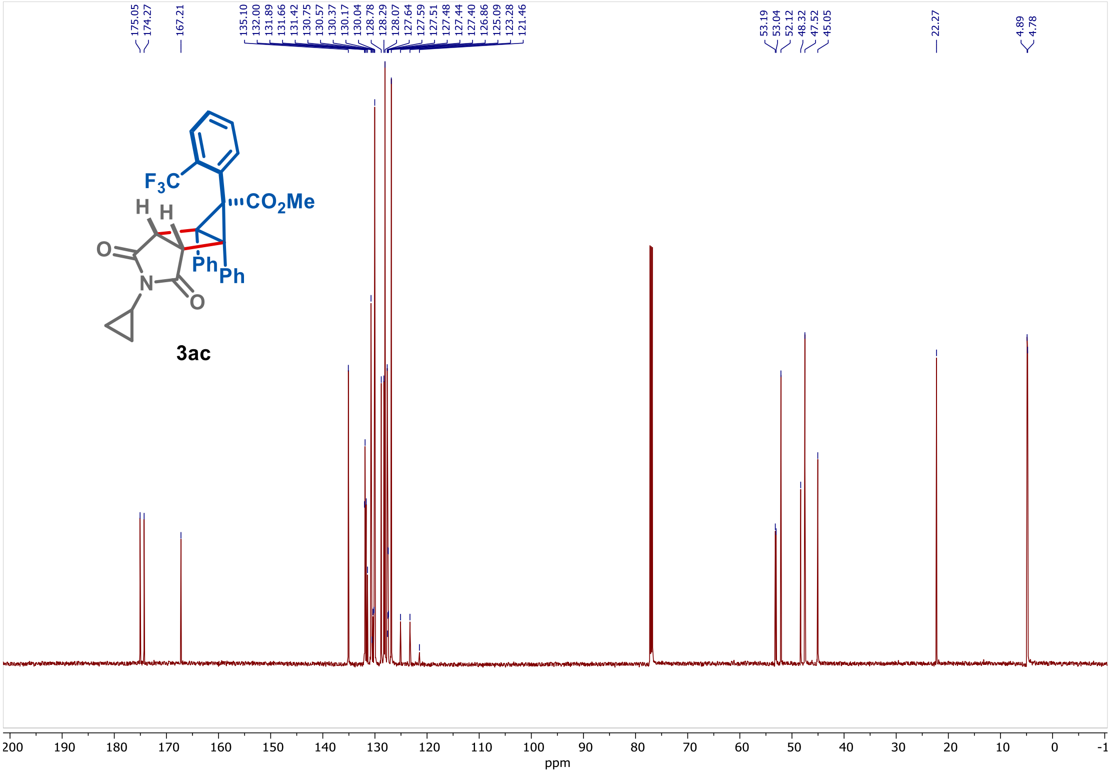
^{13}C-NMR (101 MHz, CDCl$_3$) of compound 3ab



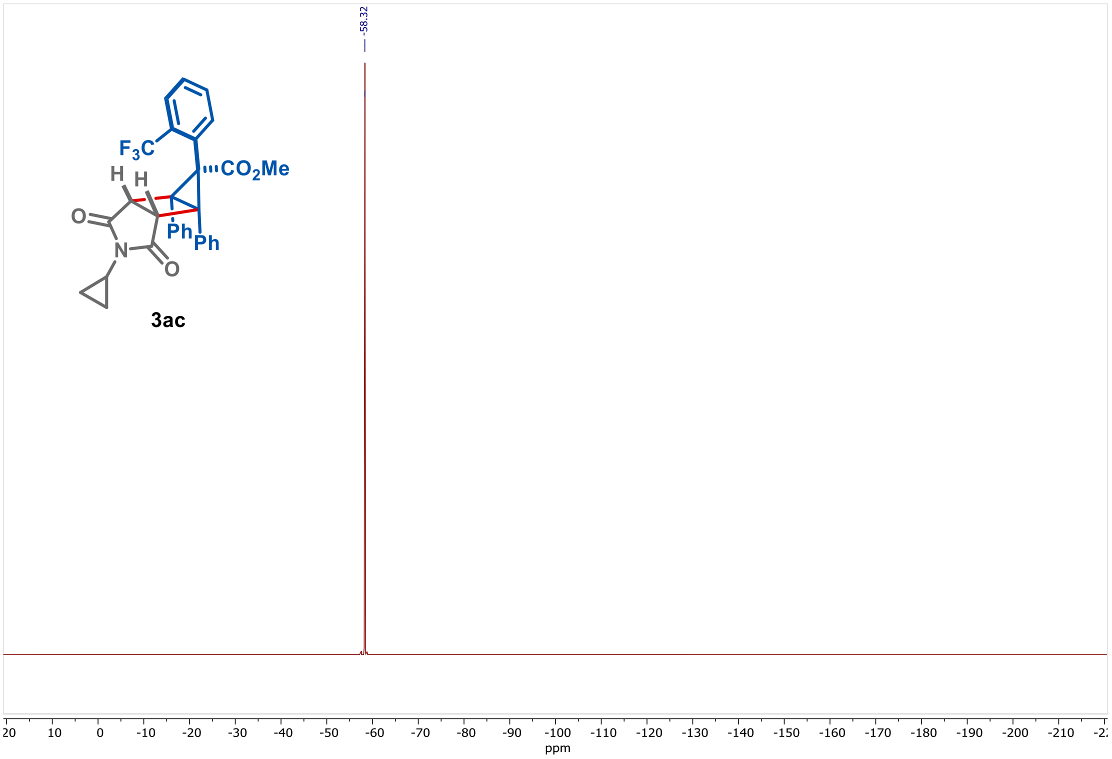
^{1}H-NMR (400 MHz, CDCl$_3$) of compound 3ac (see procedure)



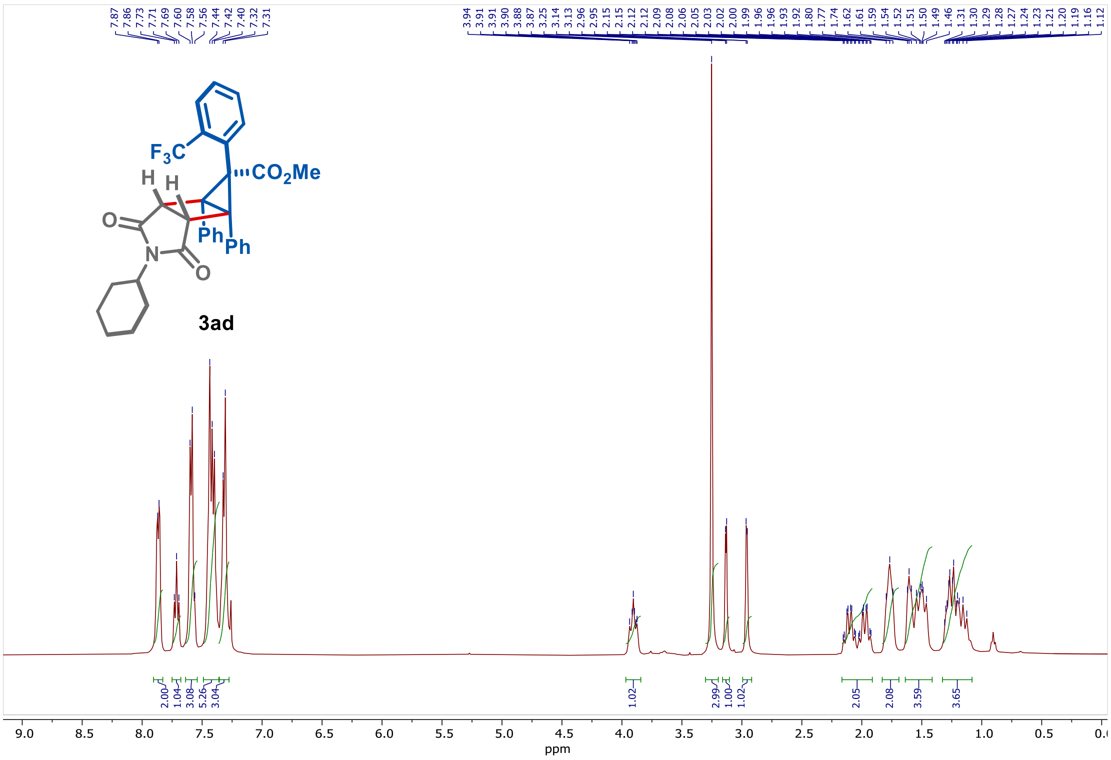
^{13}C-NMR (101 MHz, CDCl$_3$) of compound 3ac



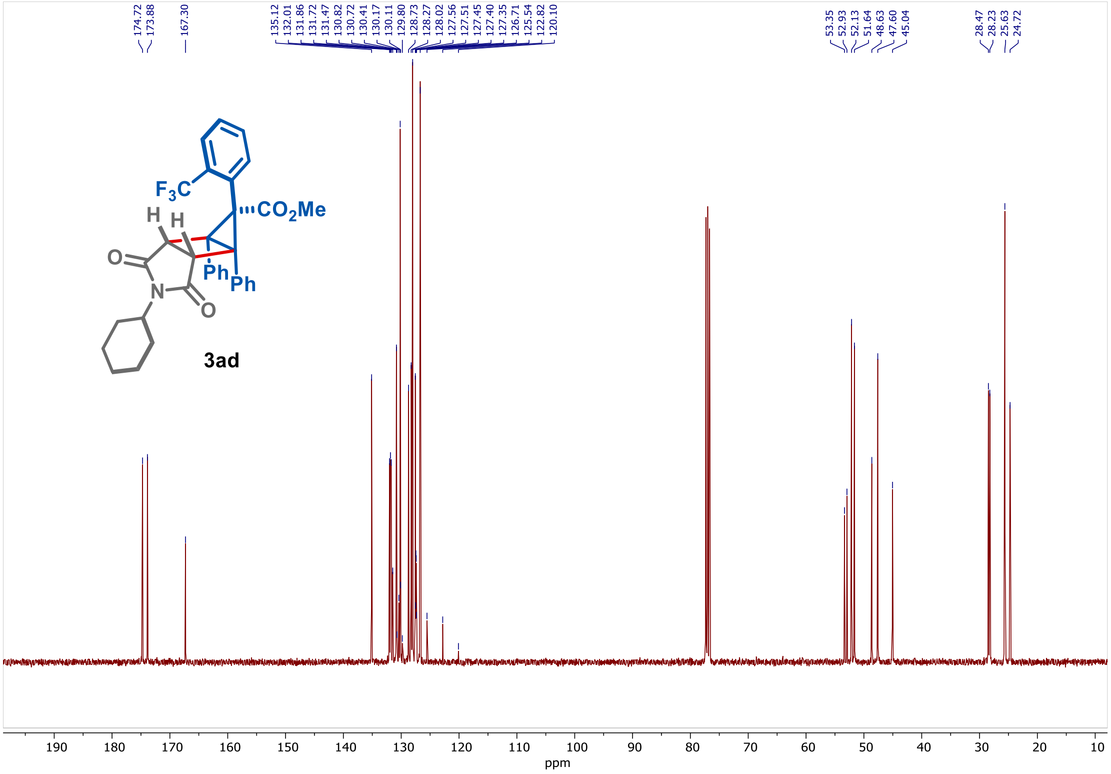
^{19}F-NMR (377 MHz, CDCl$_3$) of compound 3ac



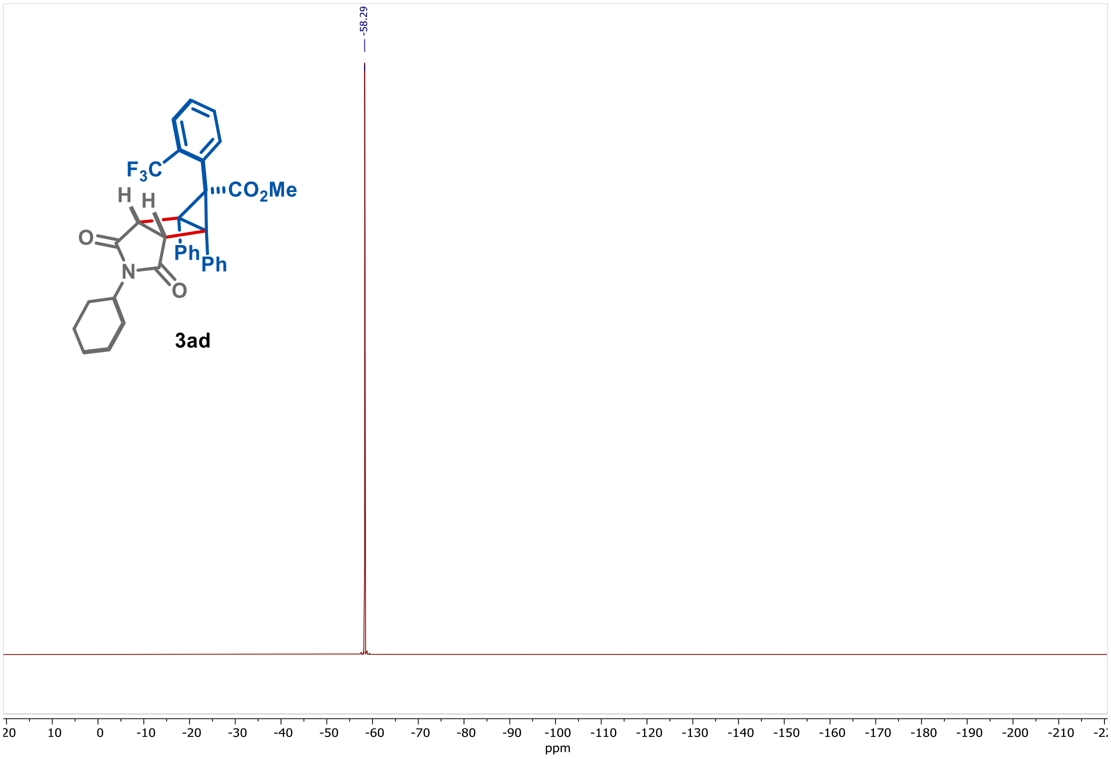
^{1}H-NMR (400 MHz, CDCl$_3$) of compound 3ad (see procedure)



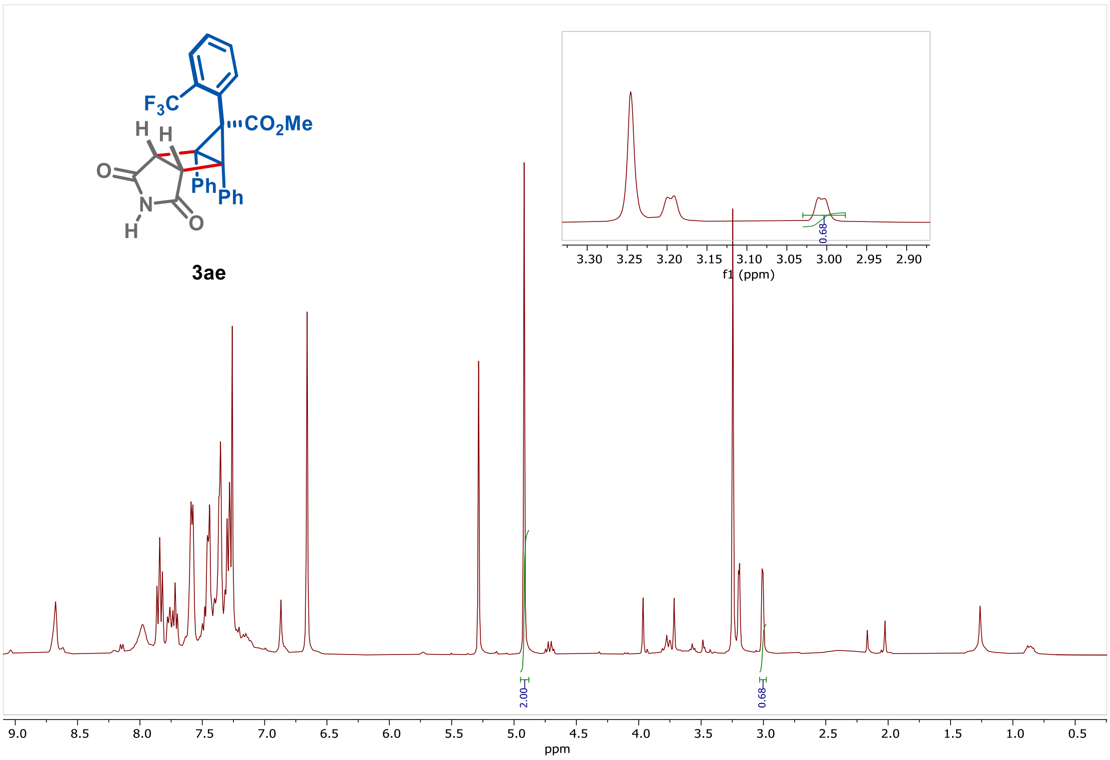
^{13}C-NMR (101 MHz, CDCl$_3$) of compound 3ad



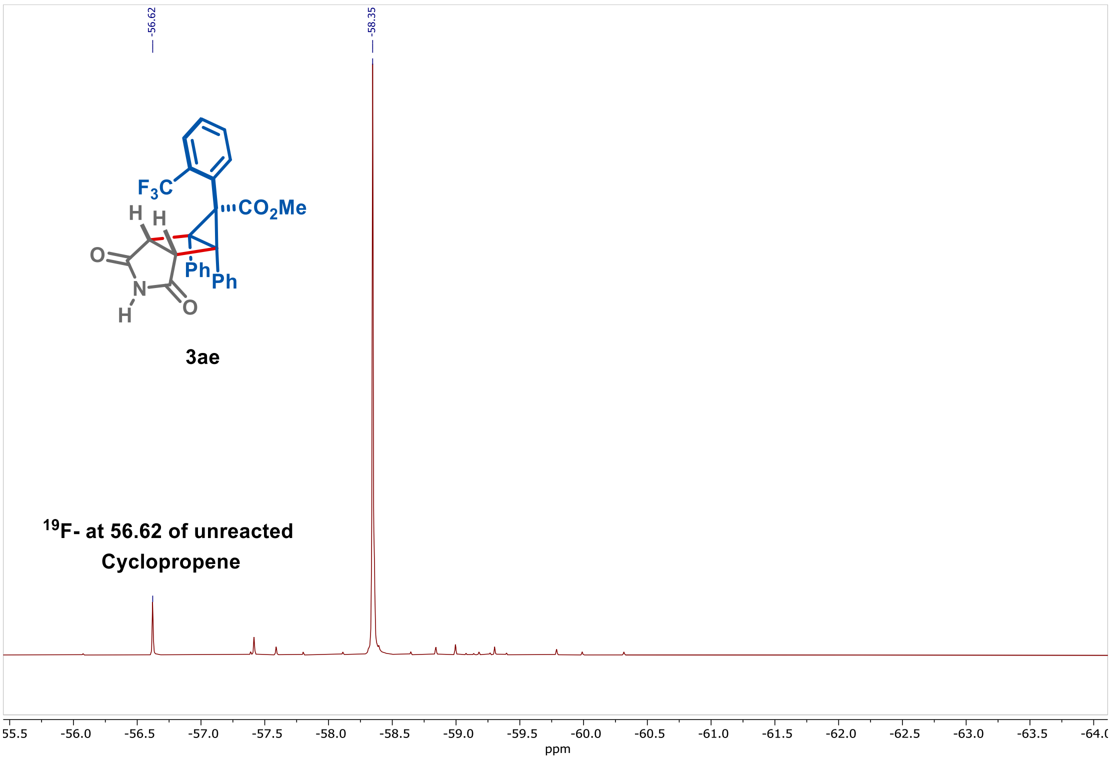
^{19}F-NMR (377 MHz, $CDCl_3$) of compound 3ad



^{1}H-NMR (400 MHz, $CDCl_3$) of compound 3ae (Crude) (see procedure)

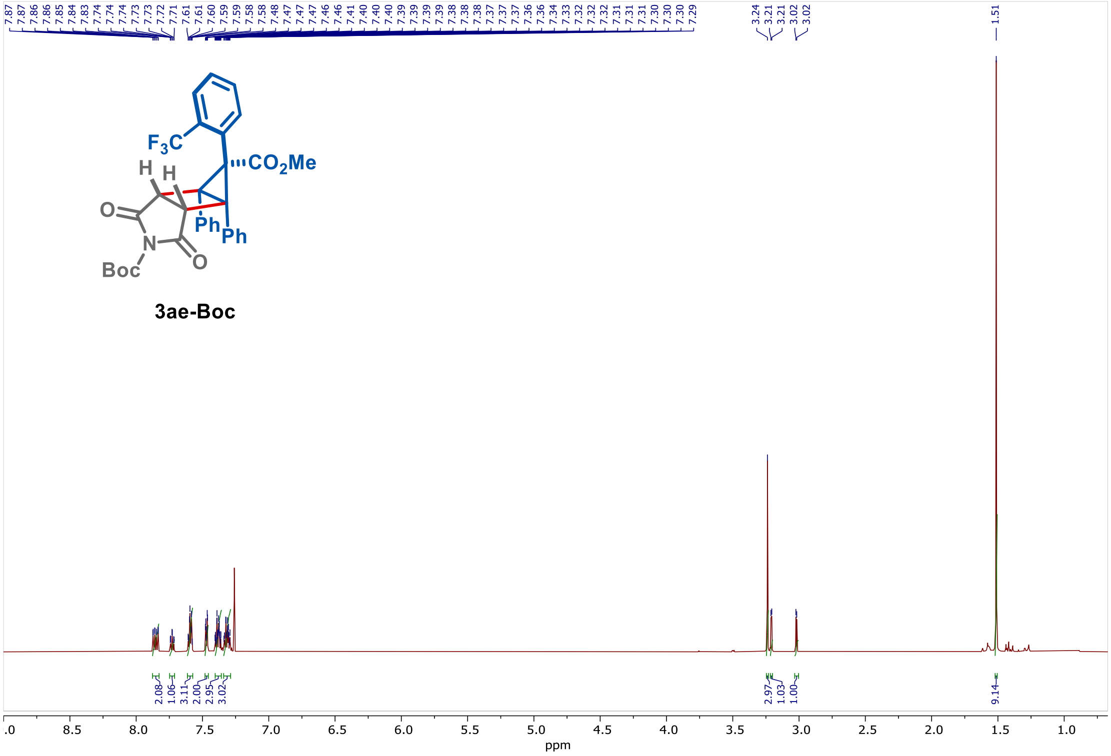


^{19}F-NMR (377 MHz, $CDCl_3$) of compound 3ae

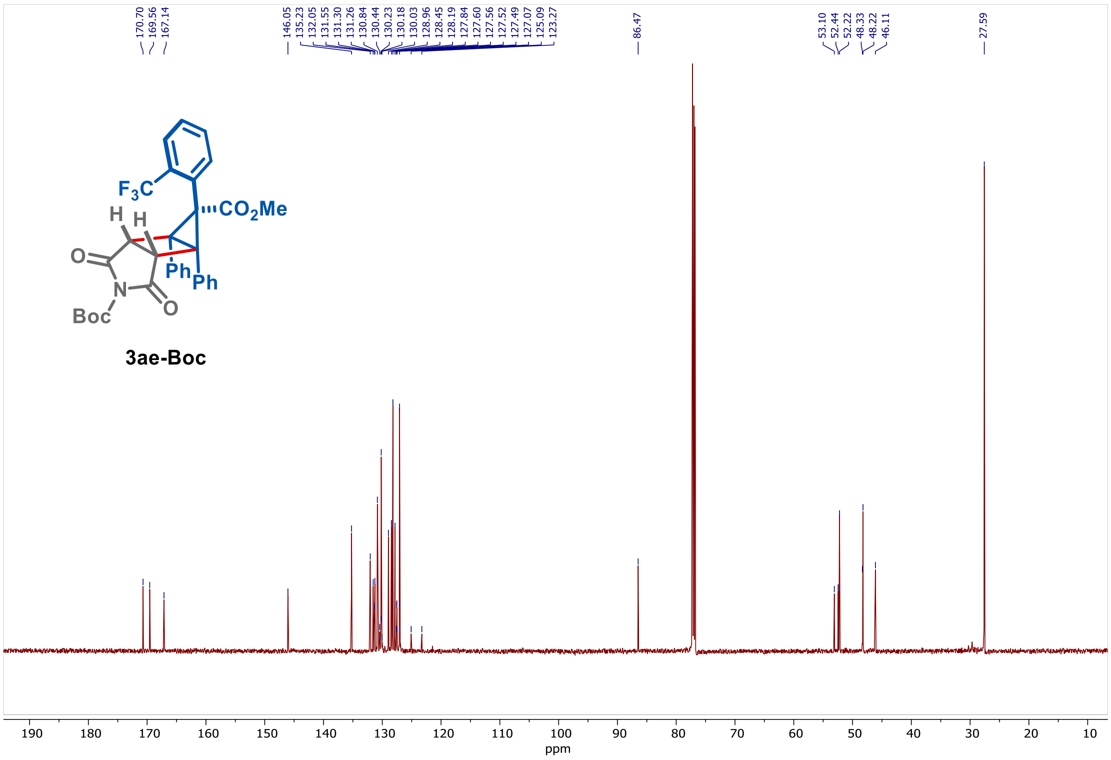


^{19}F- at 56.62 of unreacted Cyclopropene

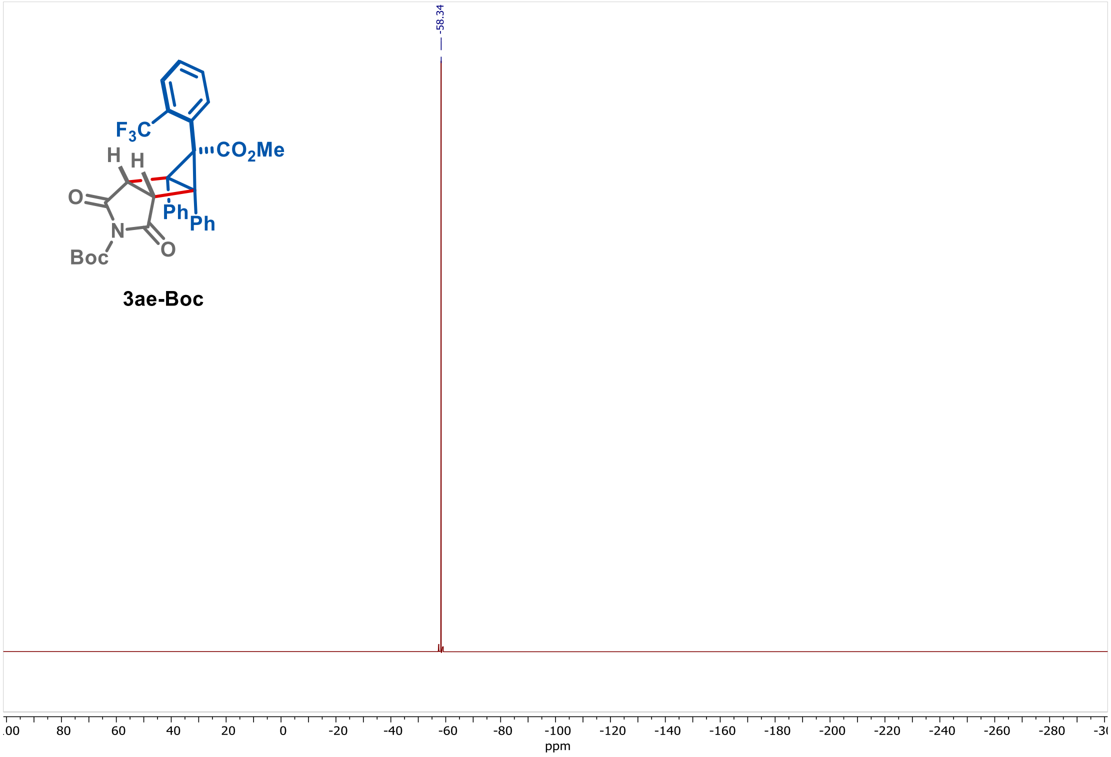
^{1}H-NMR (400 MHz, $CDCl_3$) of compound 3ae-Boc (see procedure)



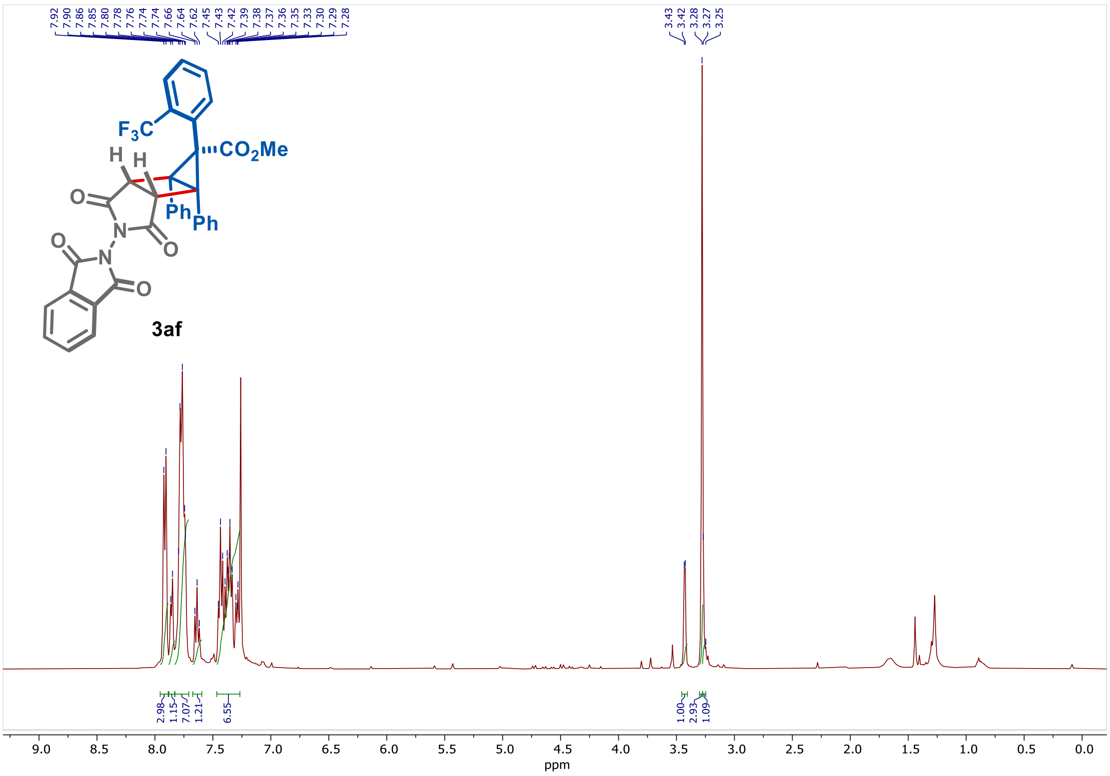
^{13}C-NMR (101 MHz, $CDCl_3$) of compound 3ae-Boc



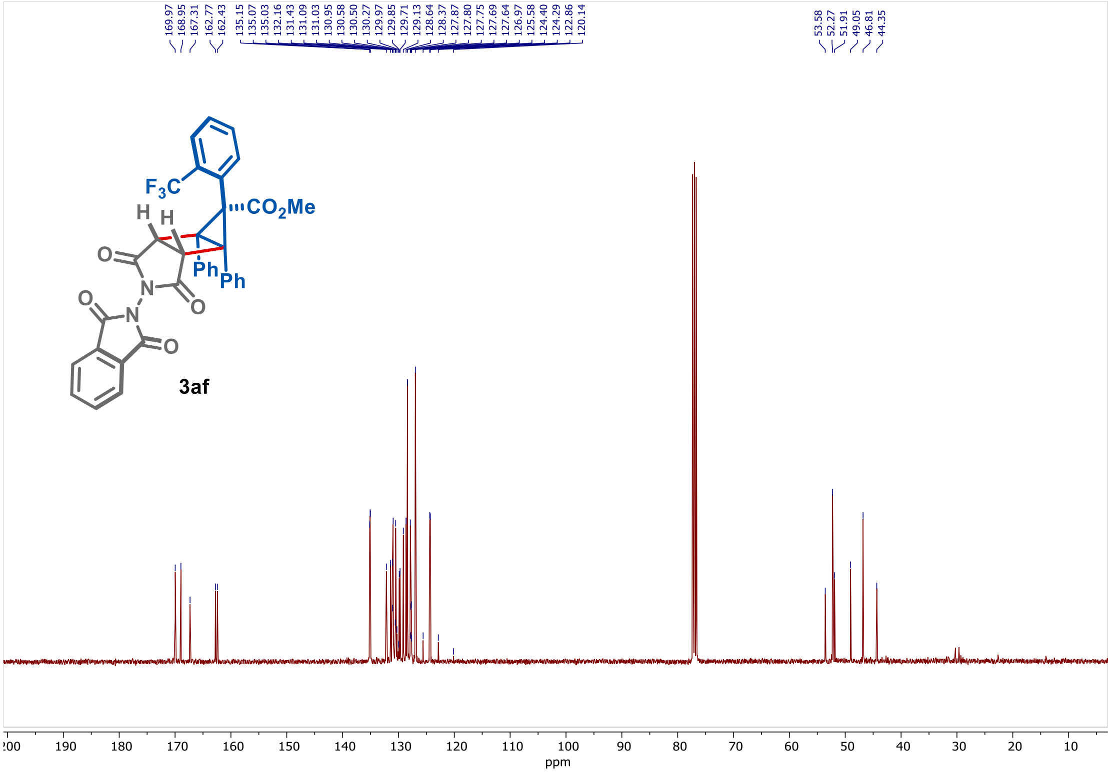
^{19}F-NMR (377 MHz, CDCl$_3$) of compound 3ae-Boc



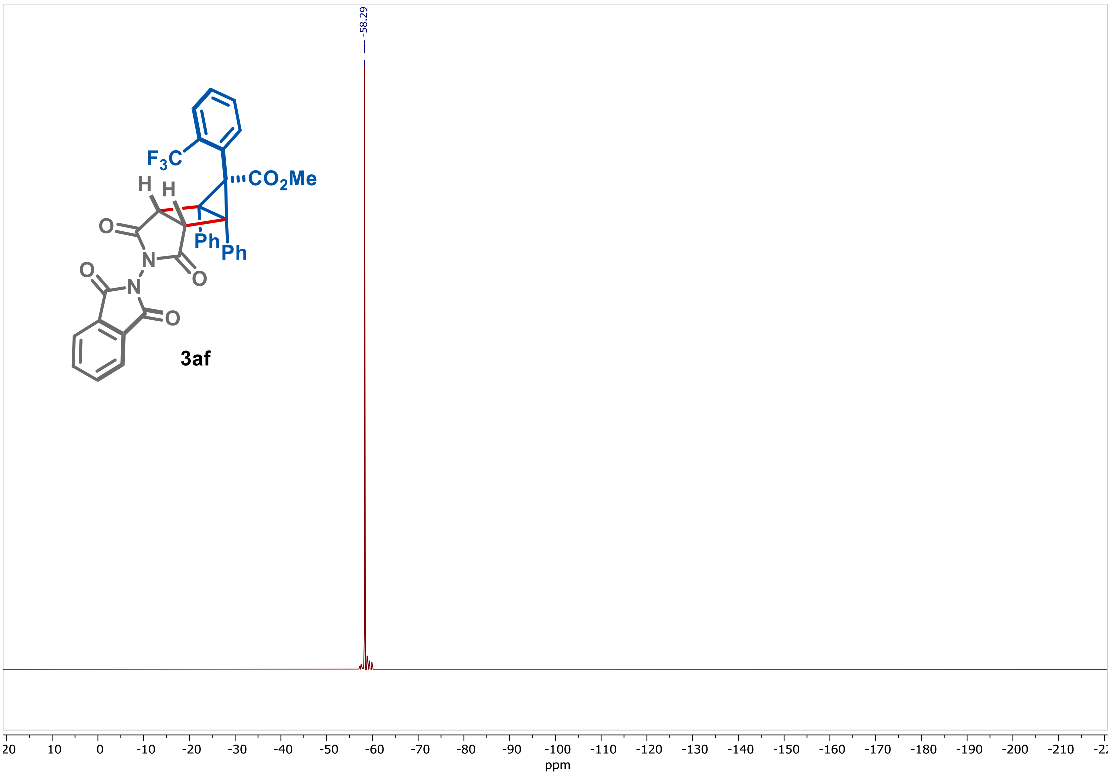
^{1}H-NMR (400 MHz, CDCl$_3$) of compound 3af (see procedure)



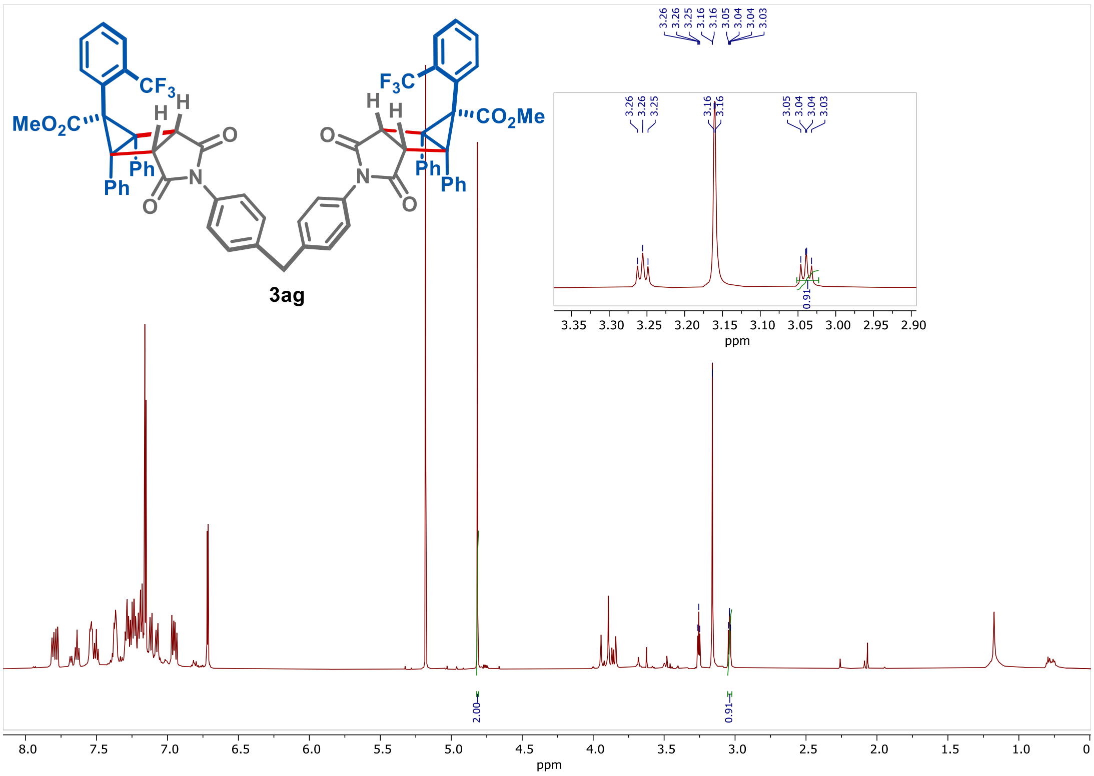
^{13}C-NMR (101 MHz, CDCl$_3$) of compound 3af



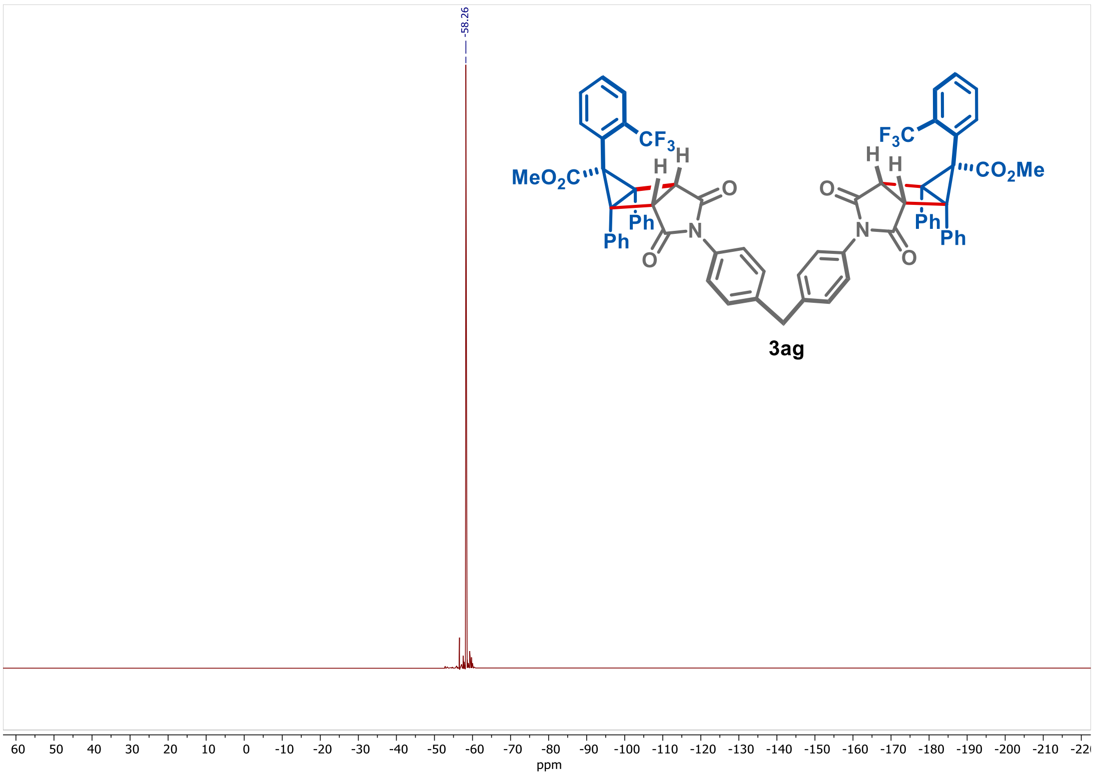
^{19}F-NMR (377 MHz, $CDCl_3$) of compound 3af



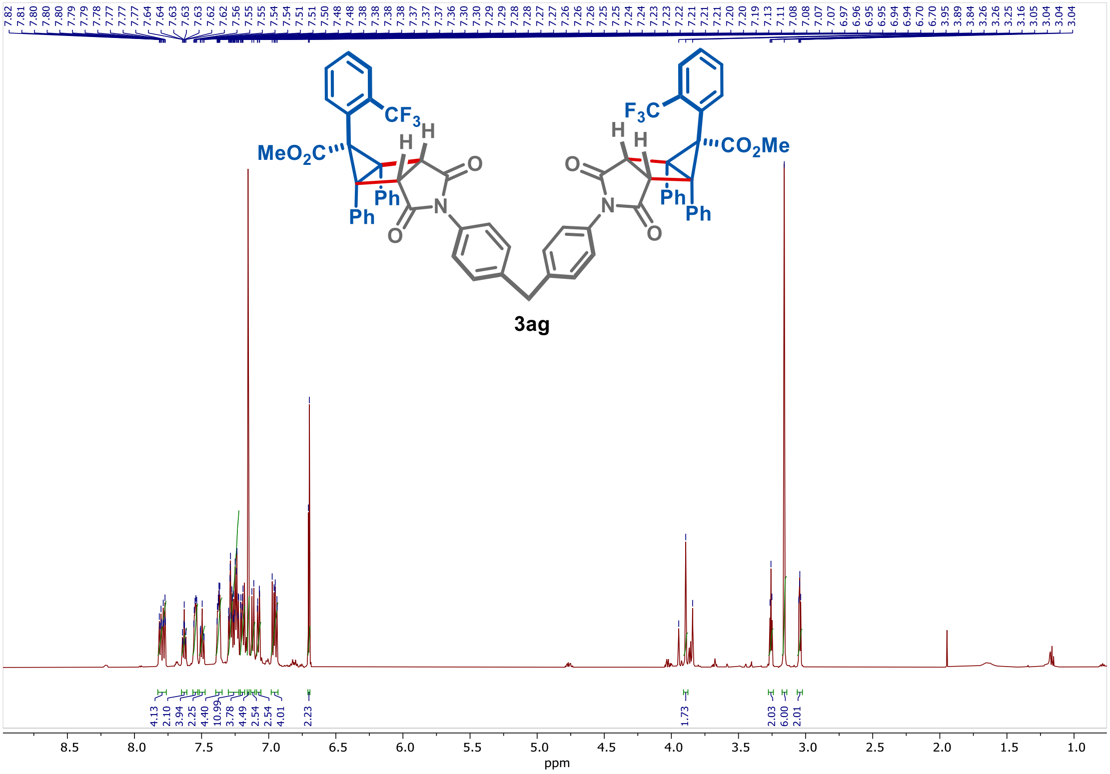
^{1}H-NMR (400 MHz, CDCl$_3$) of compound 3ag (Crude) (see procedure)



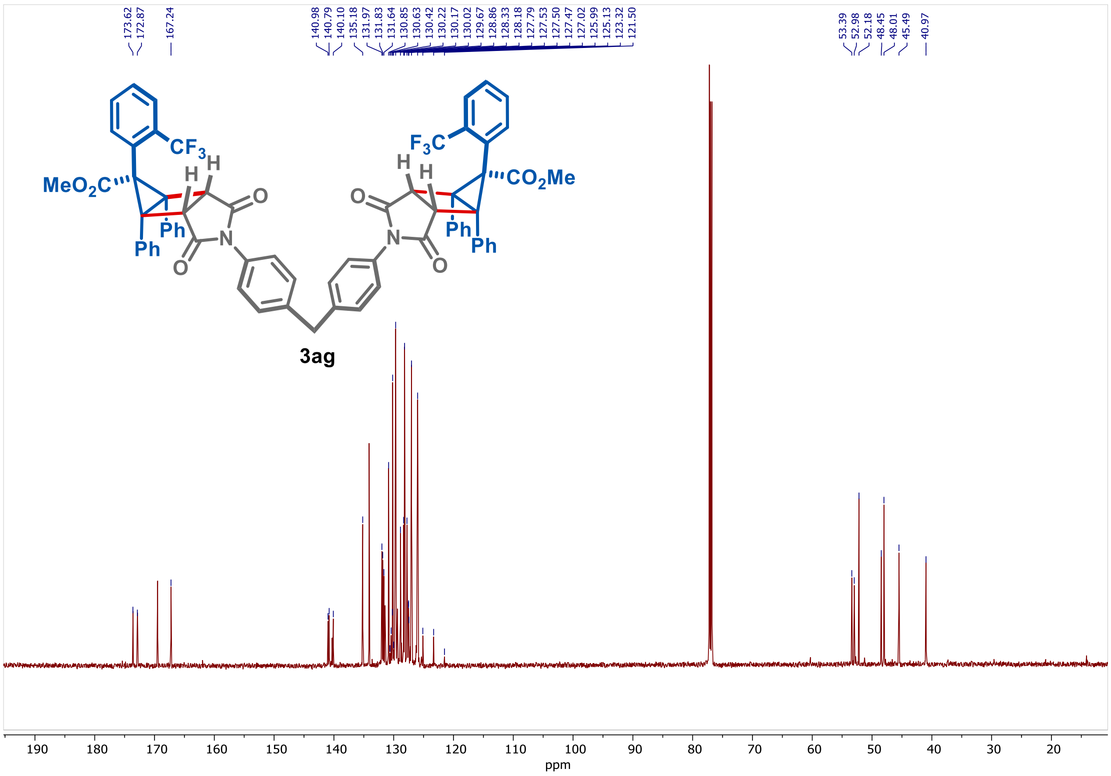
^{19}F-NMR (377 MHz, CDCl$_3$) of compound 3ag (crude)



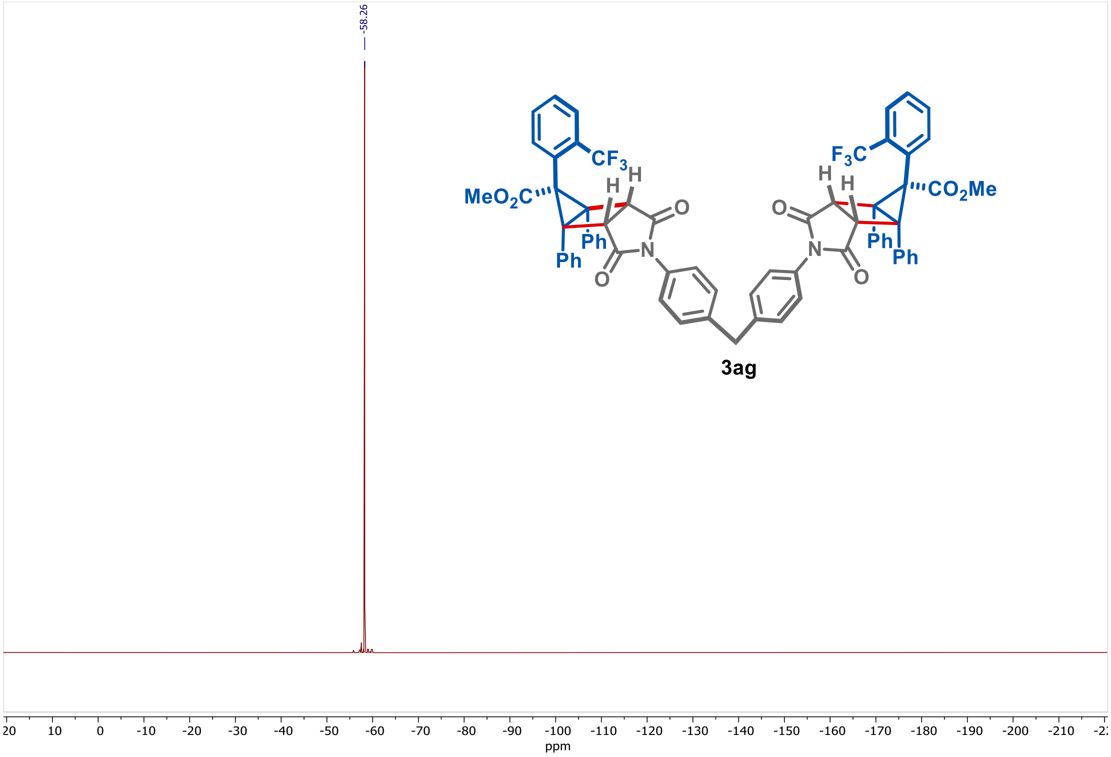
^{1}H-NMR (400 MHz, CDCl$_3$) of impure compound 3ag (see procedure)



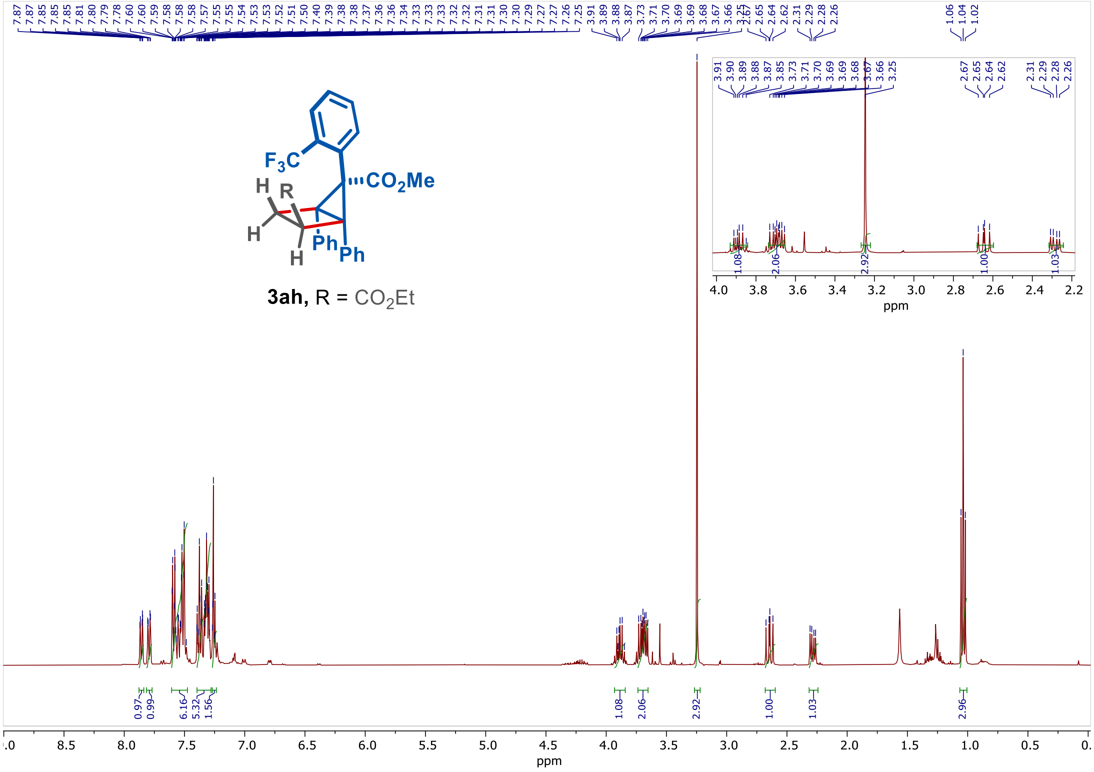
^{13}C-NMR (101 MHz, CDCl$_3$) of impure compound 3ag



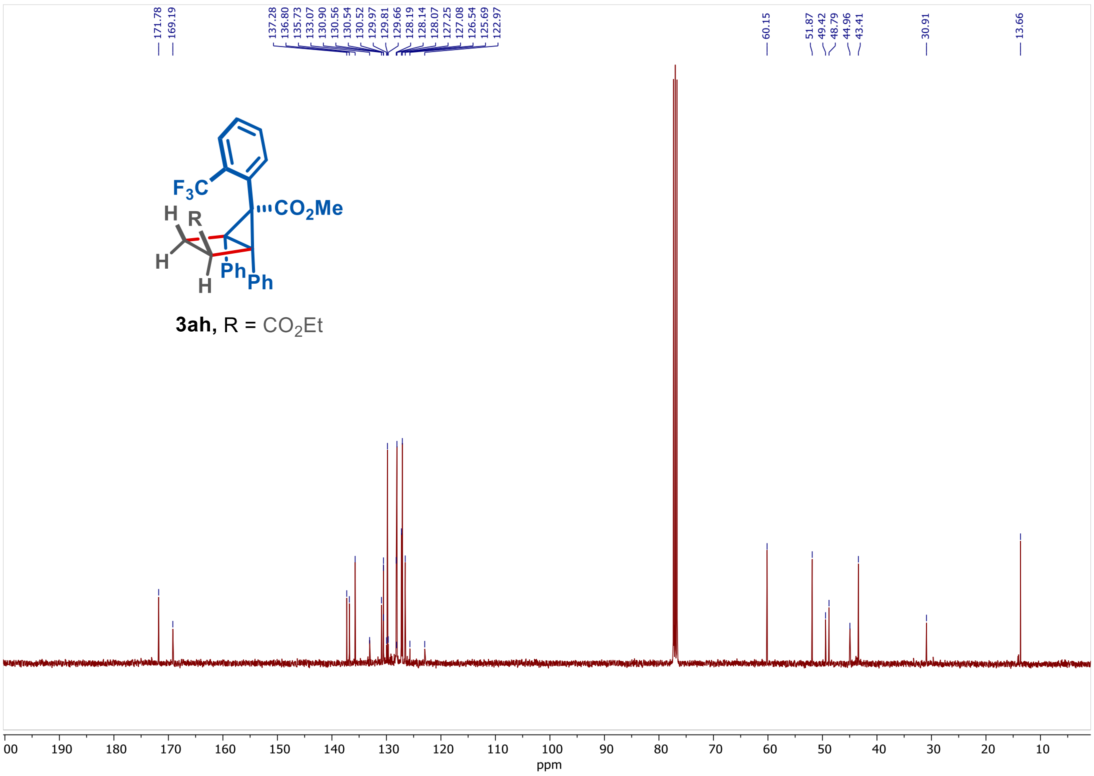
^{19}F-NMR (377 MHz, $CDCl_3$) of impure compound 3ag



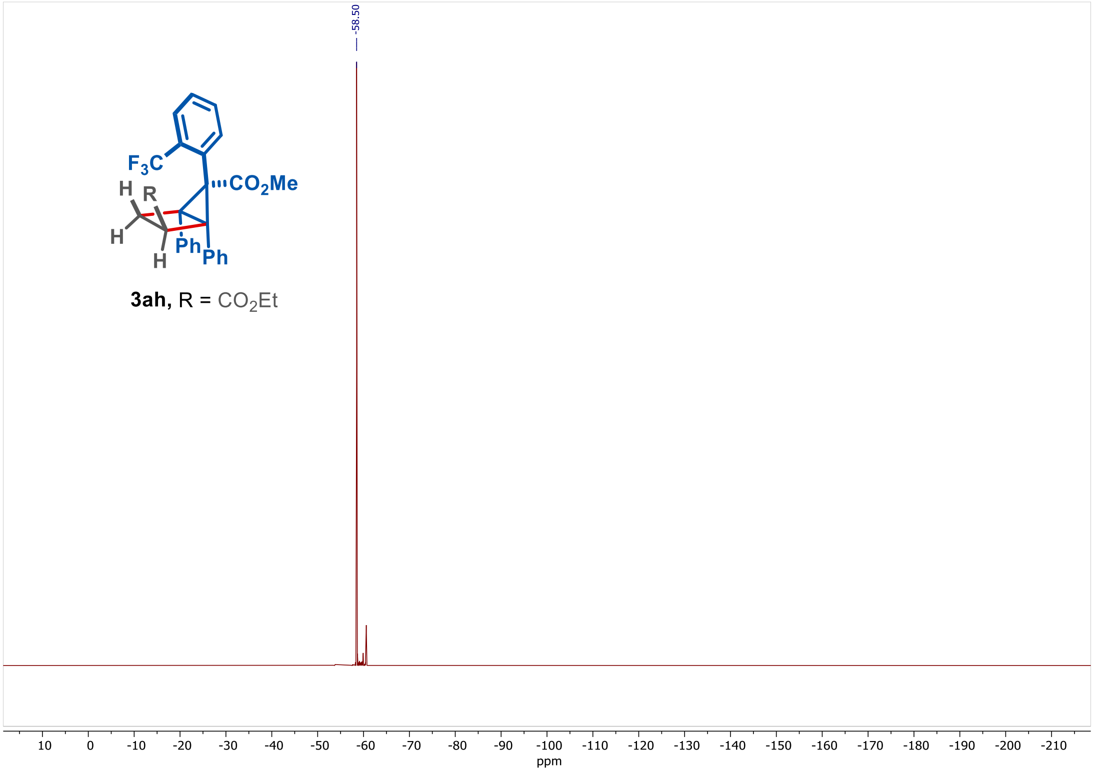
^{1}H-NMR (400 MHz, CDCl$_3$) of compound 3ah (see procedure)



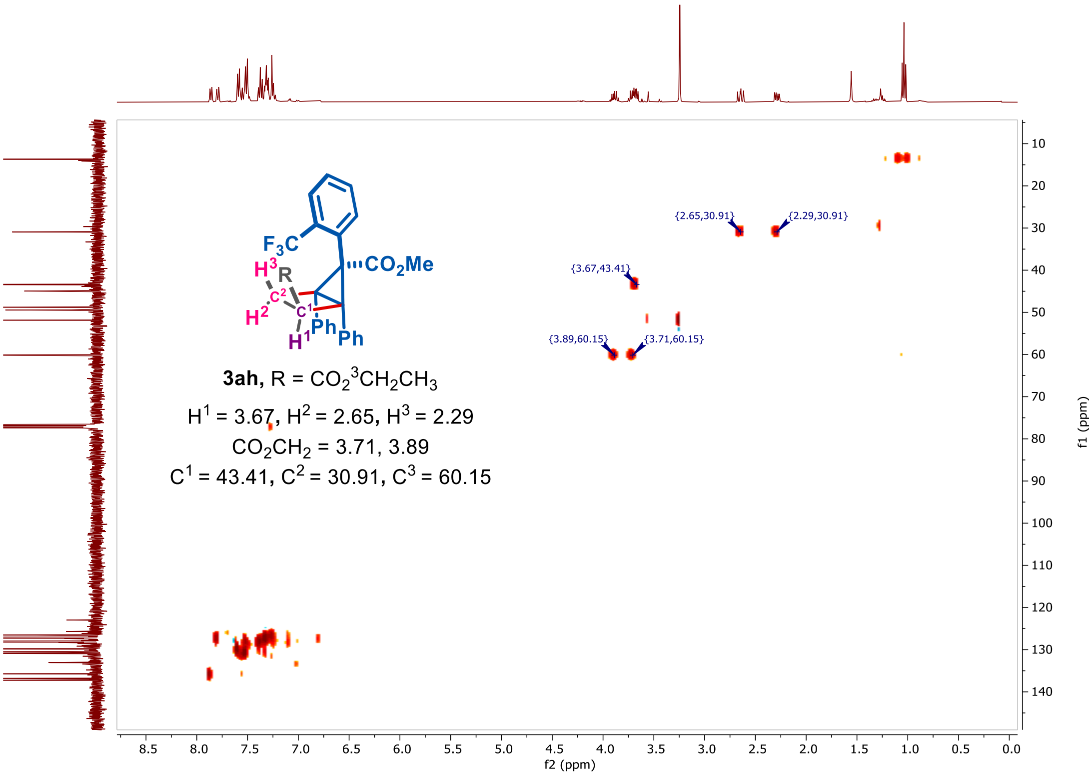
^{13}C-NMR (101 MHz, CDCl$_3$) of compound 3ah



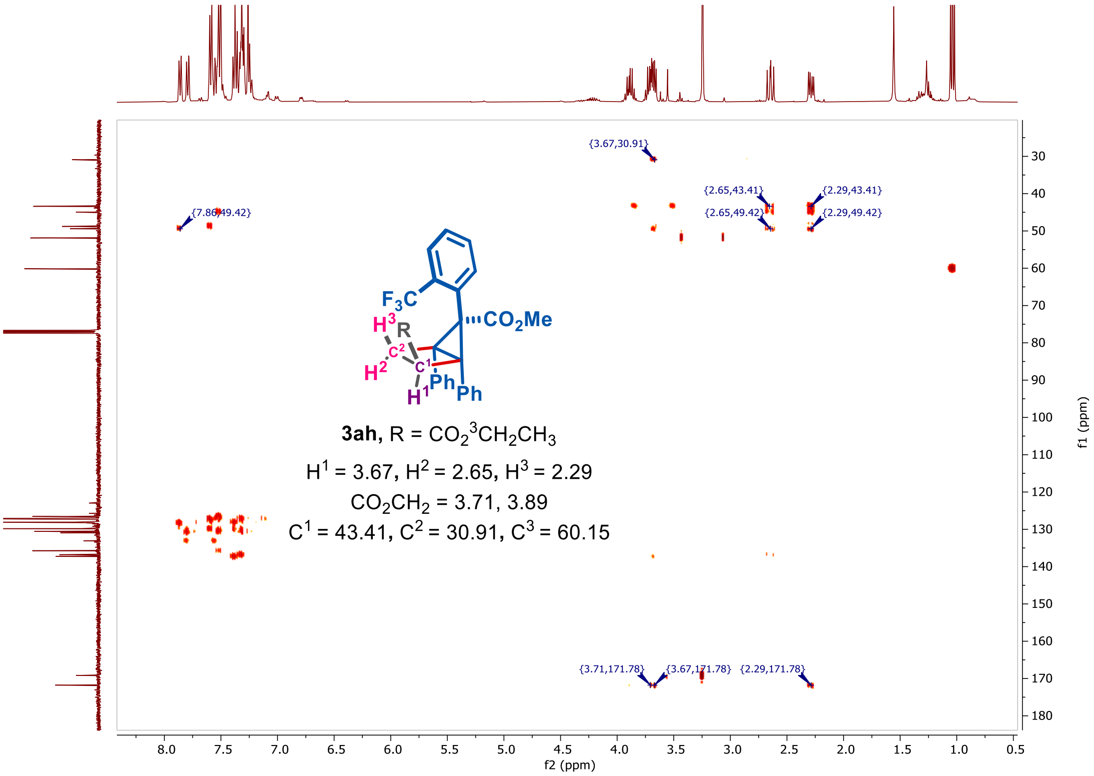
^{19}F-NMR (377 MHz, $CDCl_3$) of compound 3ah



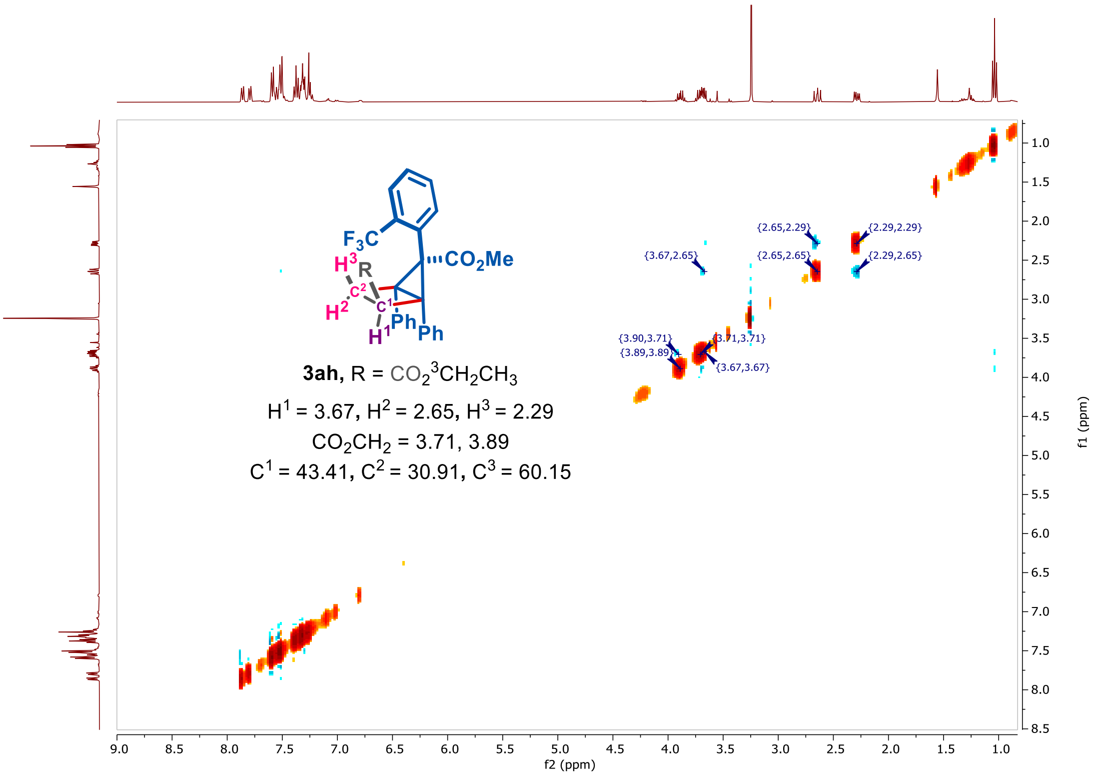
HSQC of compound 3ah



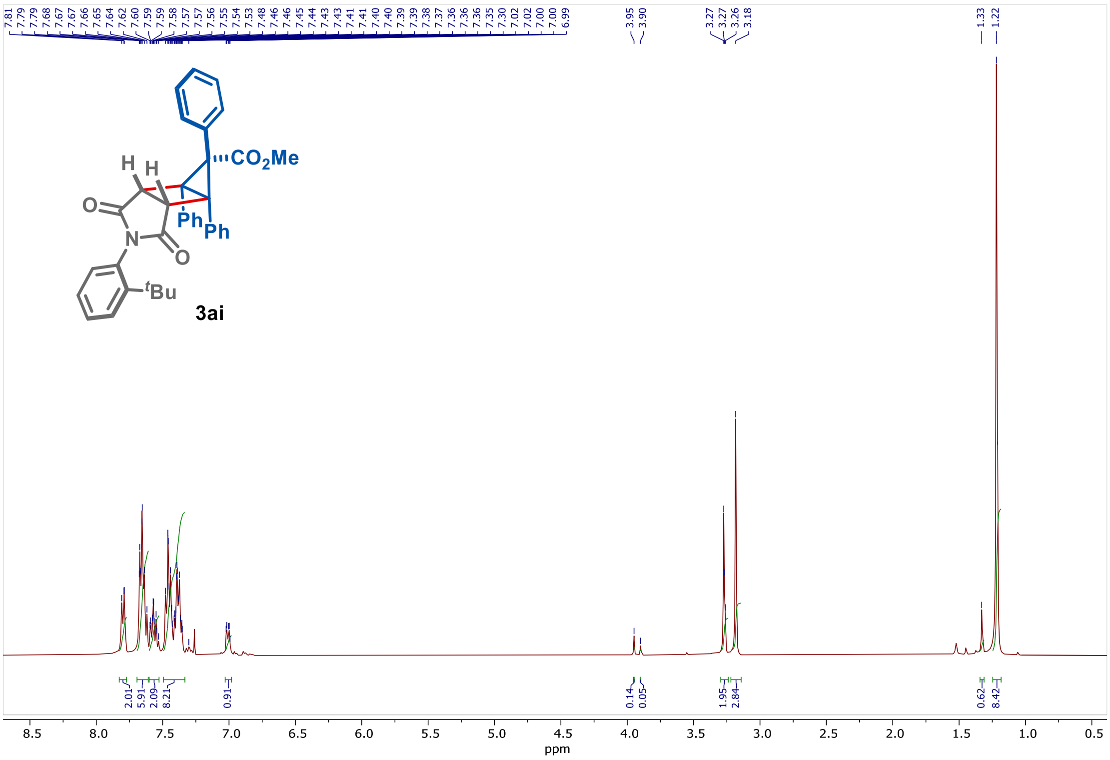
HMBC of compound 3ah



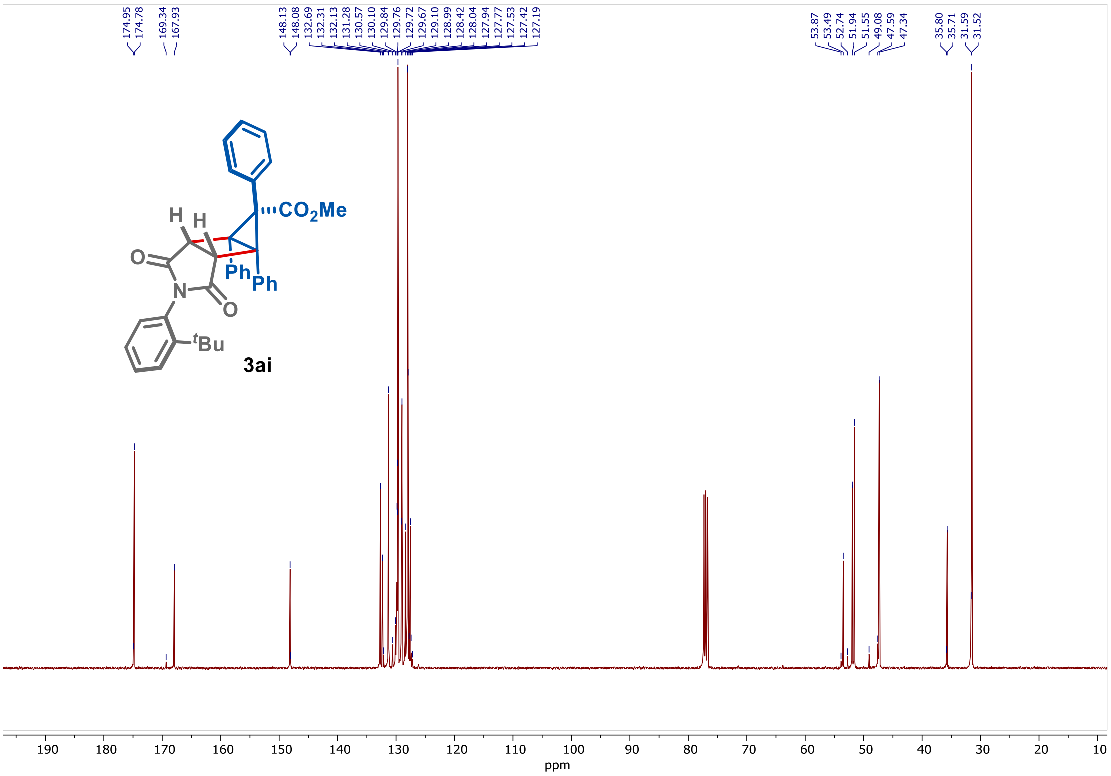
NOESY of compound 3ah



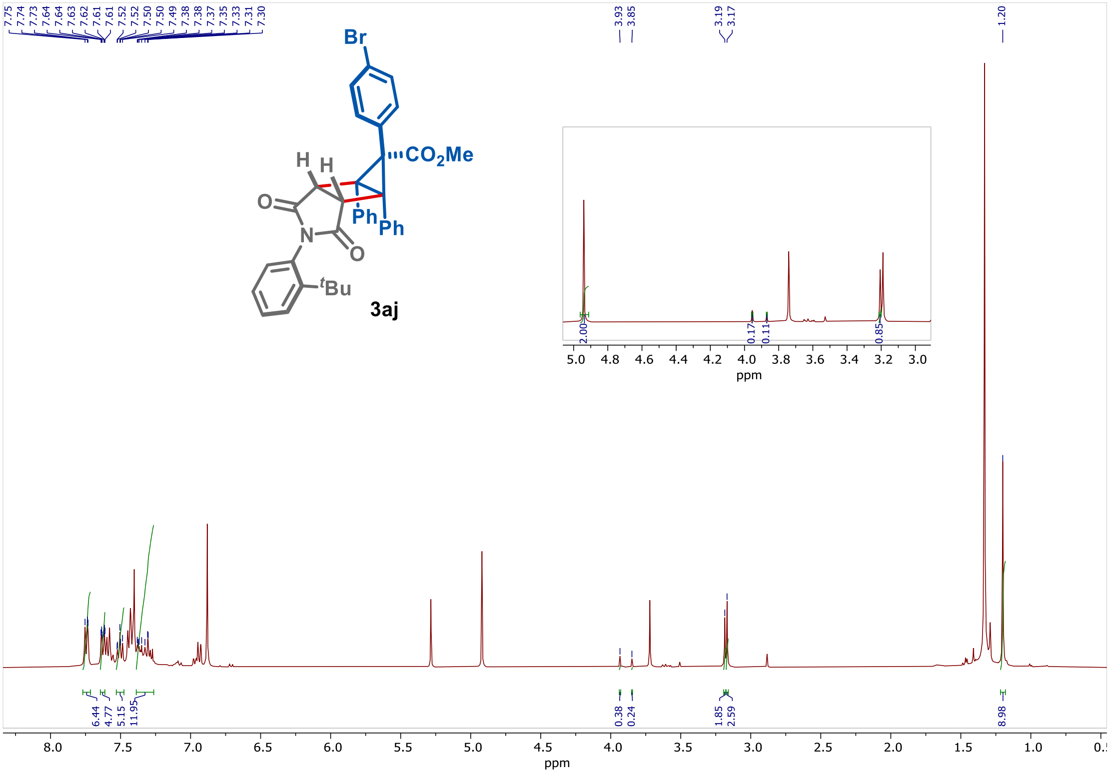
^{1}H-NMR (400 MHz, CDCl$_3$) of compound 3ai (see procedure)



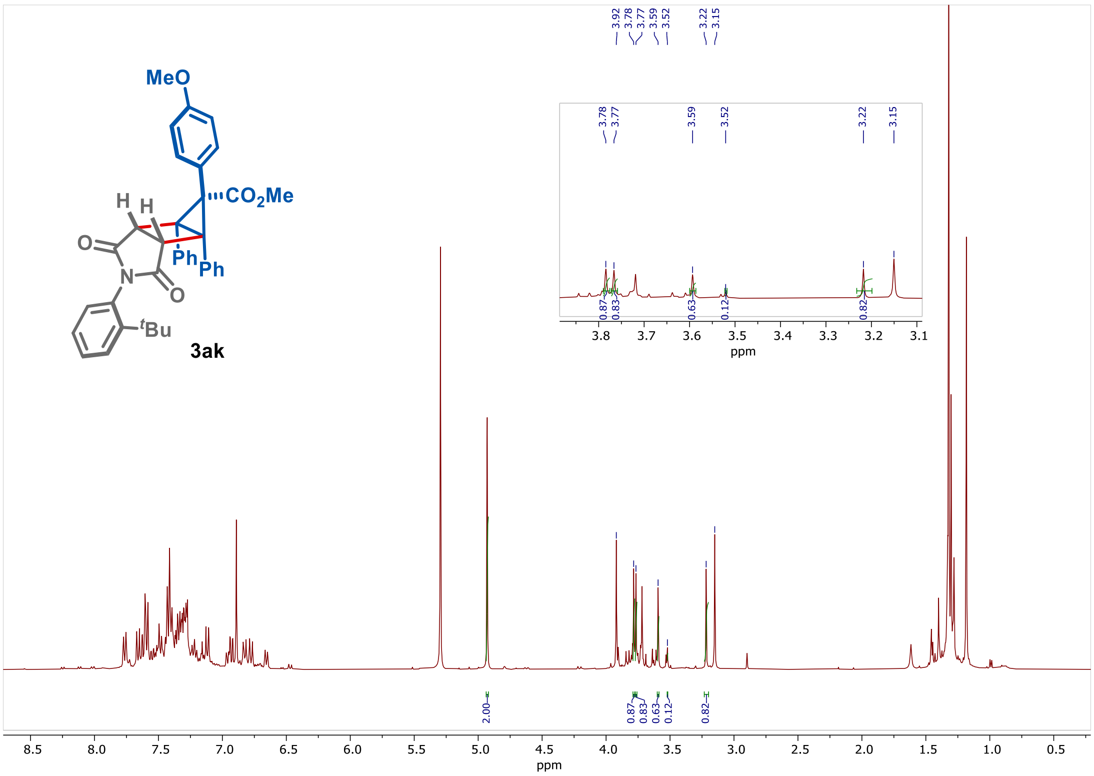
^{13}C-NMR (101 MHz, CDCl$_3$) of compound 3ai



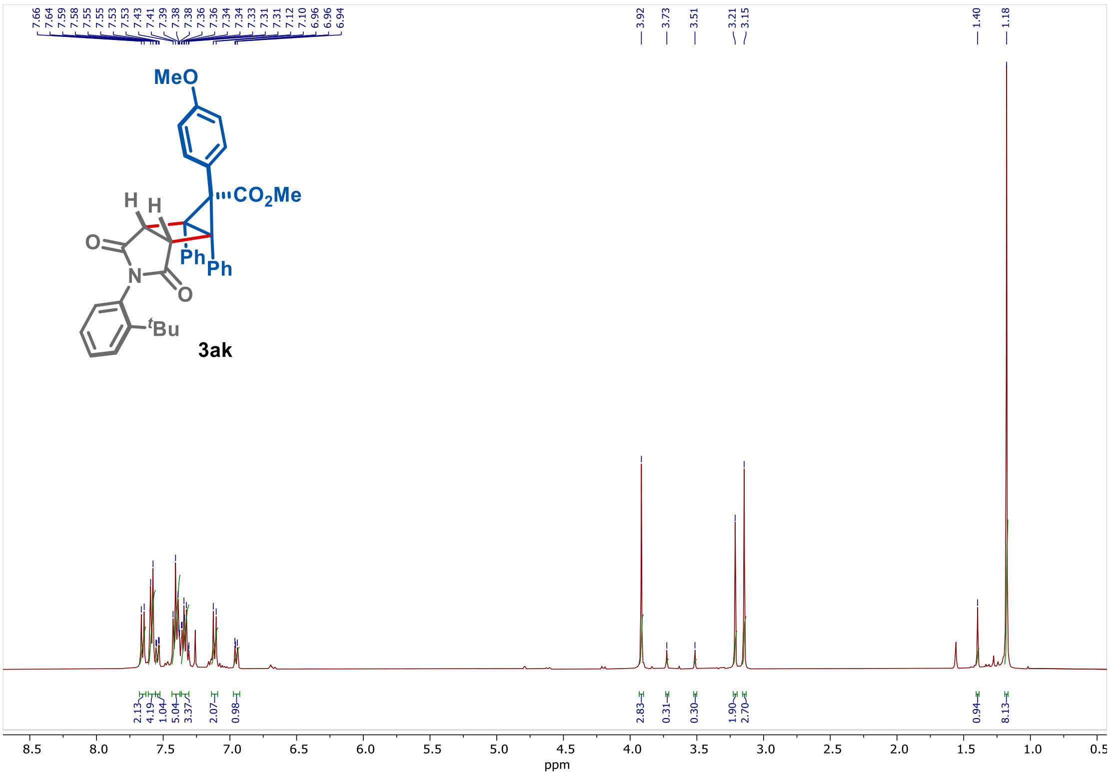
^{1}H-NMR (400 MHz, CDCl$_3$) of compound 3aj crude (see procedure)



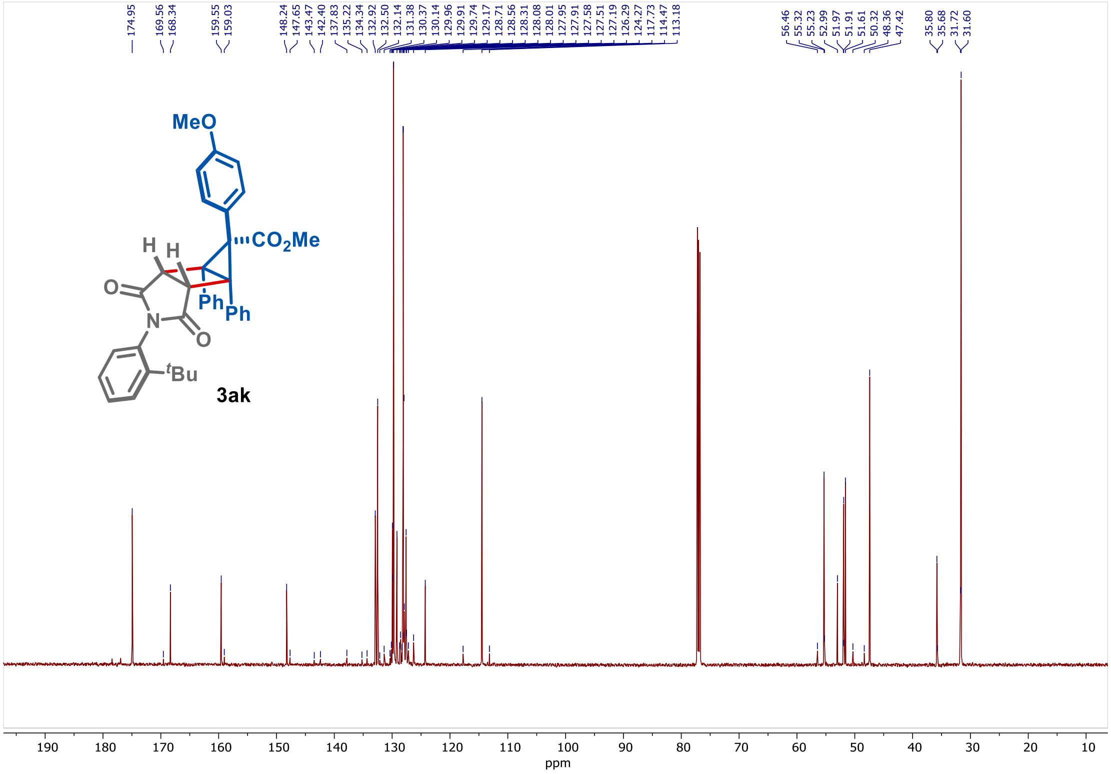
^{1}H-NMR (400 MHz, CDCl$_3$) of compound 3ak (crude) (see procedure)



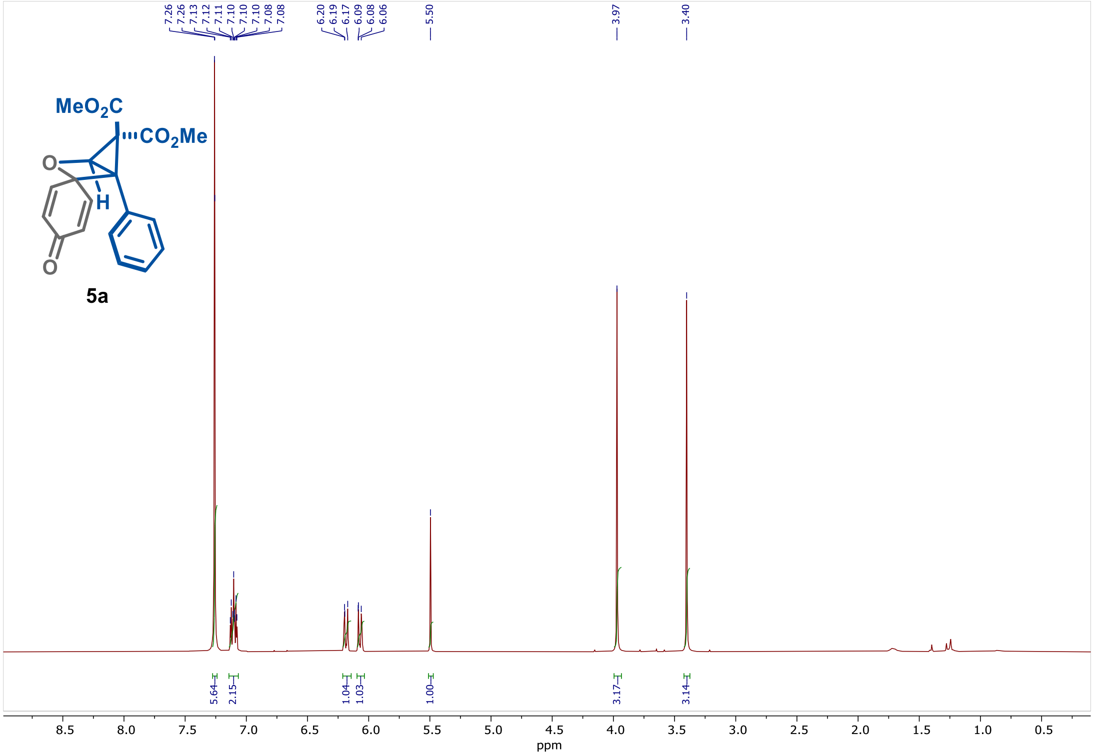
^{1}H-NMR (400 MHz, CDCl$_3$) of compound 3ak (see procedure)



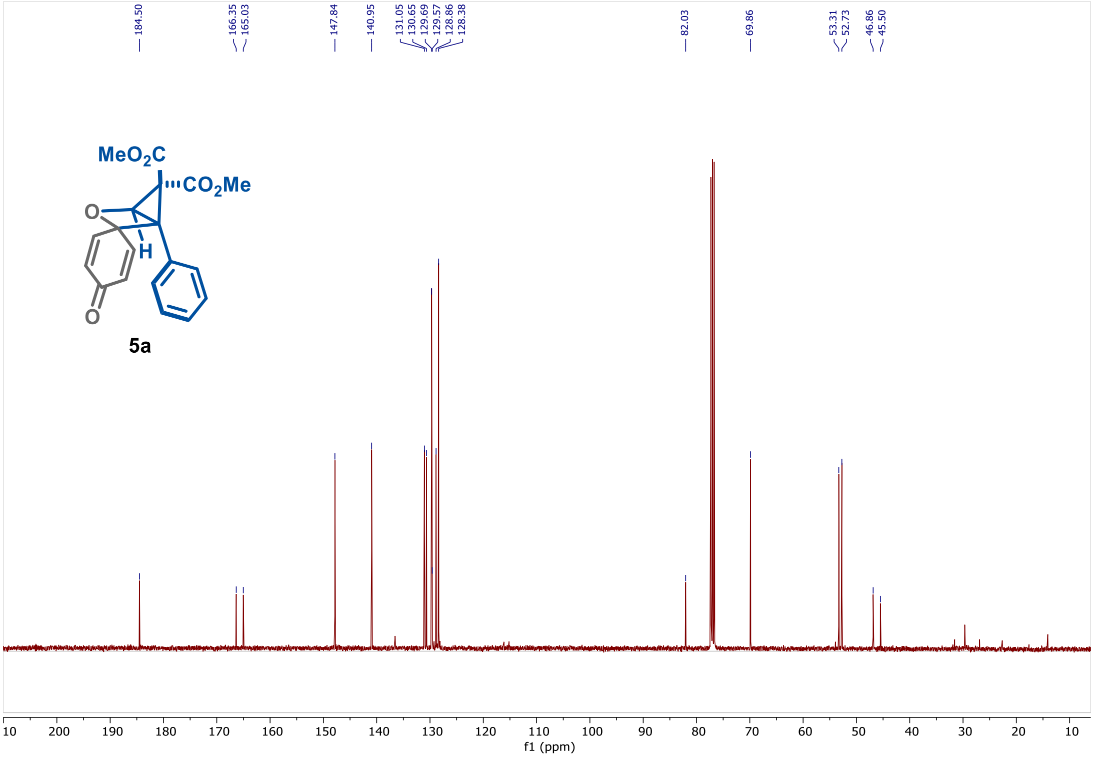
^{13}C-NMR (101 MHz, CDCl$_3$) of compound 3ak



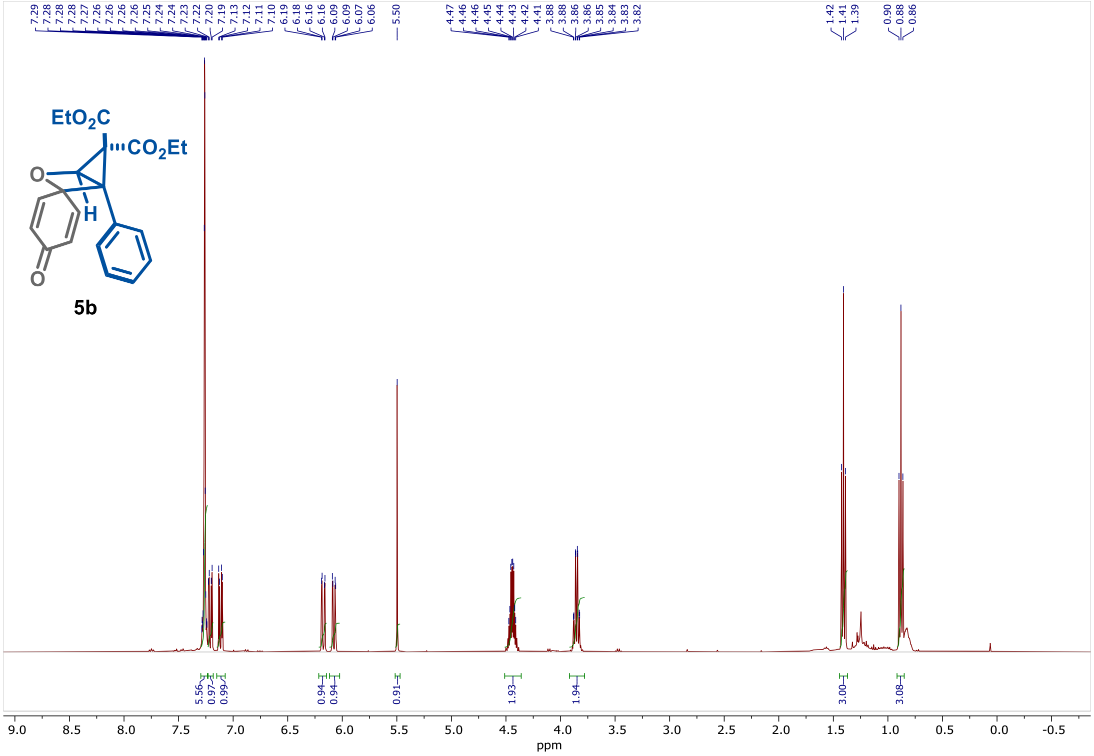
^{1}H-NMR (400 MHz, CDCl$_3$) of compound 5a (see procedure)



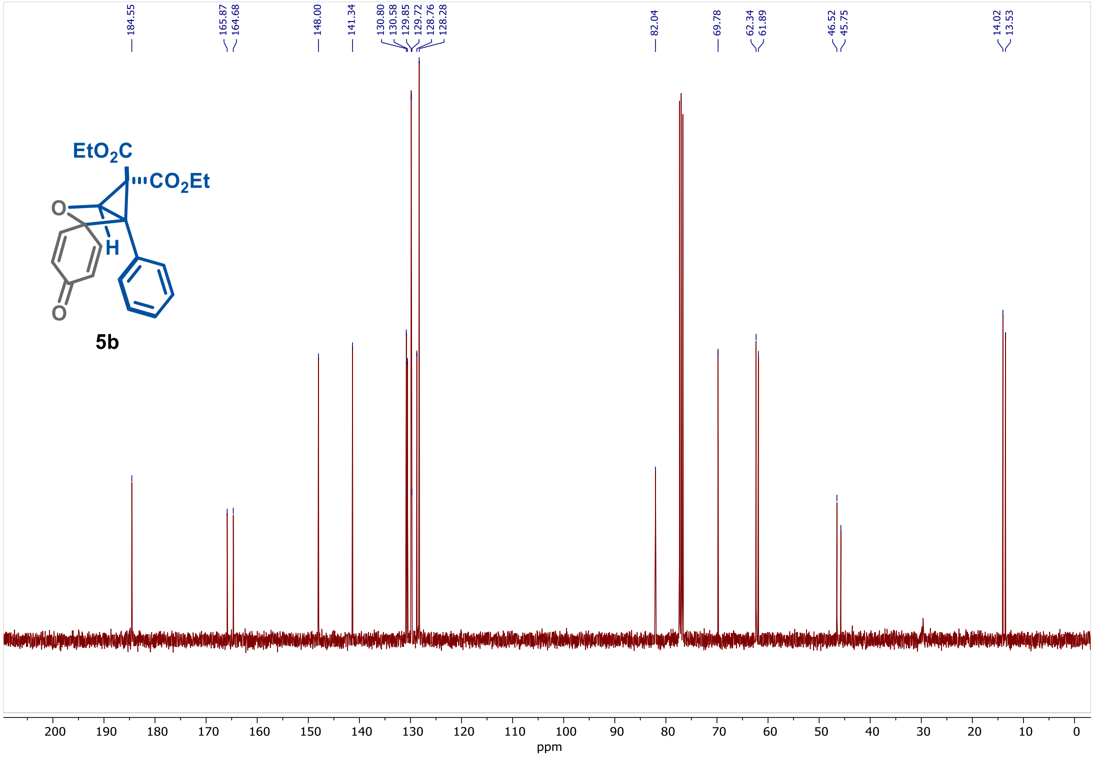
^{13}C-NMR (101 MHz, CDCl$_3$) of compound 5a



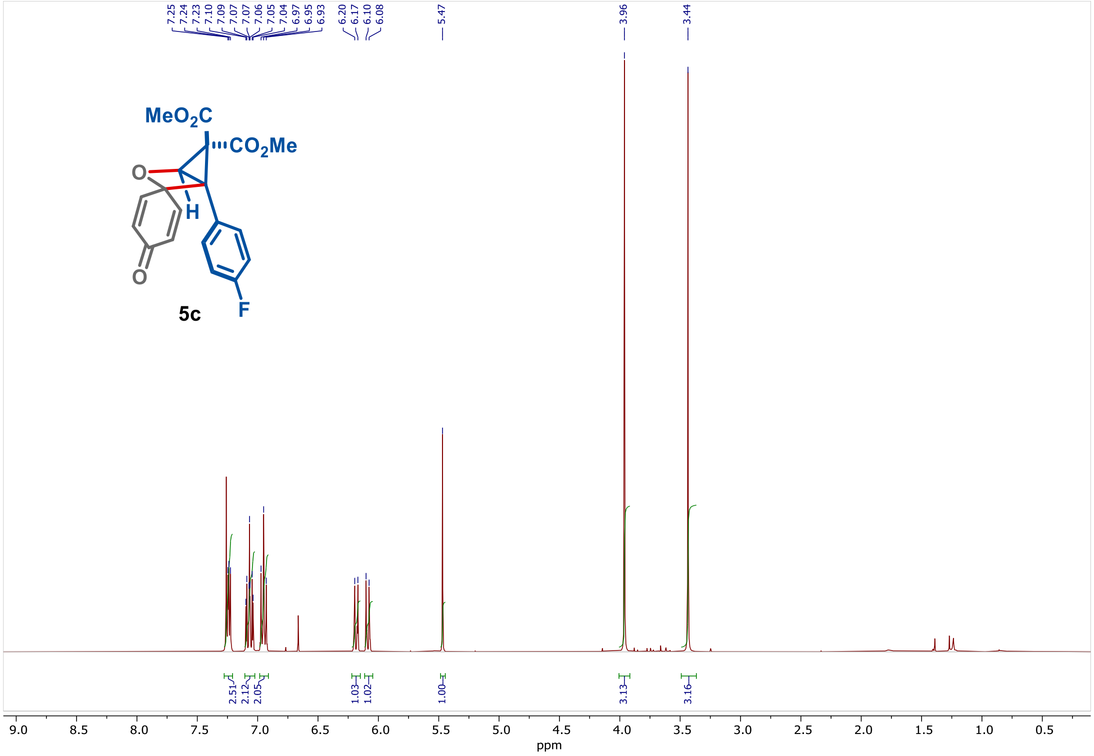
^{1}H-NMR (400 MHz, CDCl$_3$) of compound 5b (see procedure)



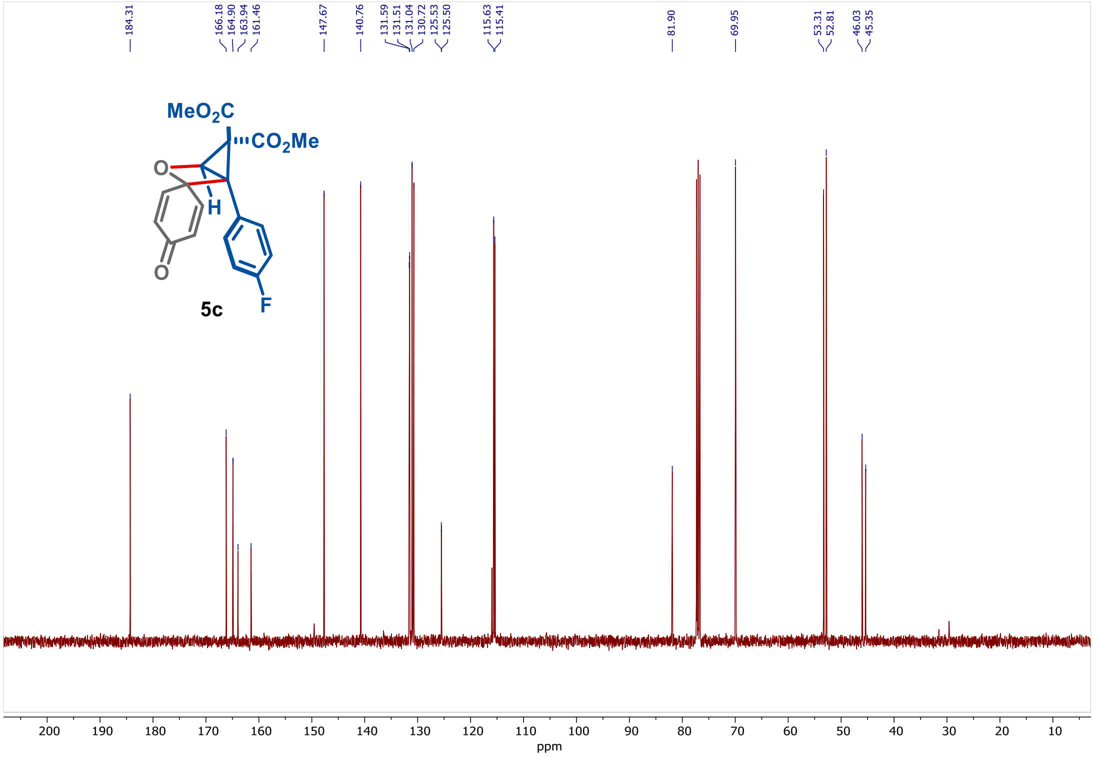
^{13}C-NMR (101 MHz, CDCl$_3$) of compound 5b



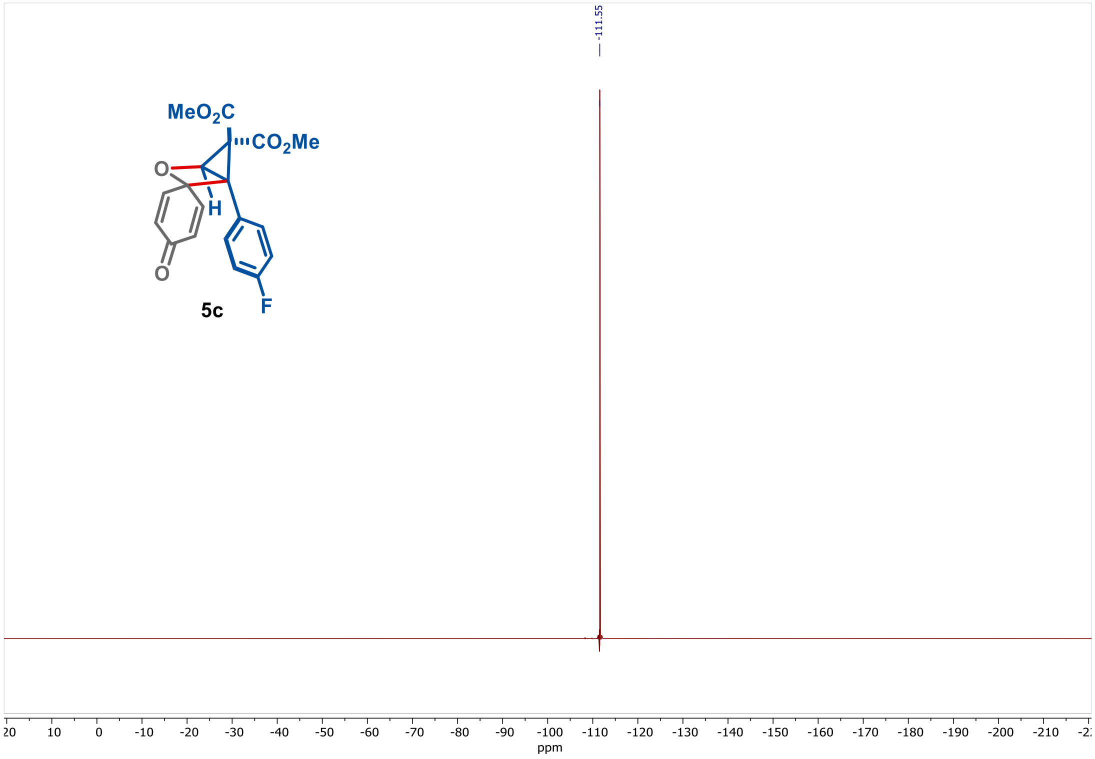
^{1}H-NMR (400 MHz, CDCl$_3$) of compound 5c (see procedure)



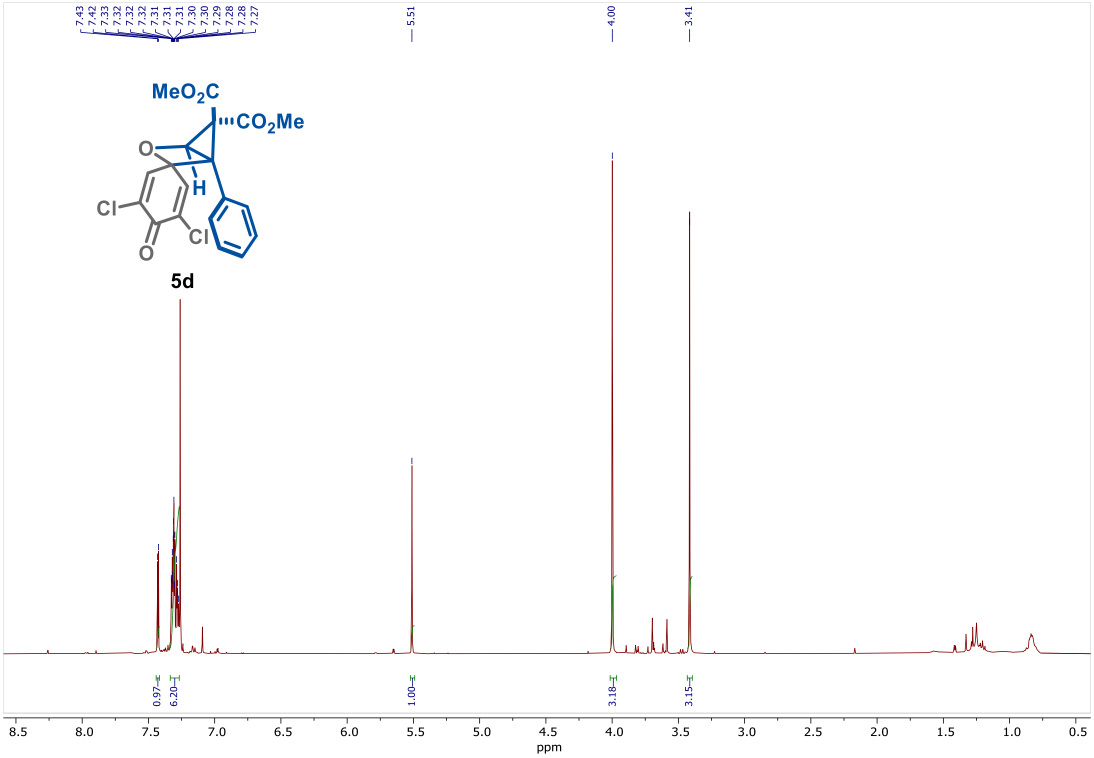
^{13}C-NMR (101 MHz, CDCl$_3$) of compound 5c



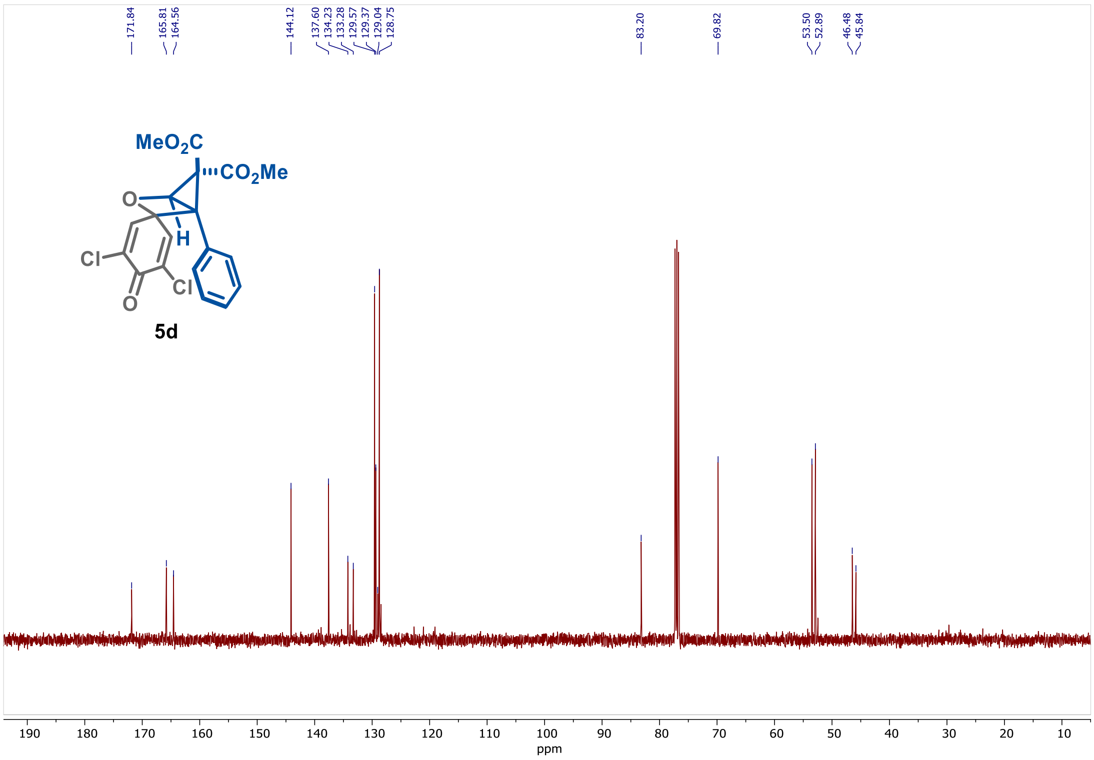
^{19}F-NMR (377 MHz, $CDCl_3$) of compound 5c



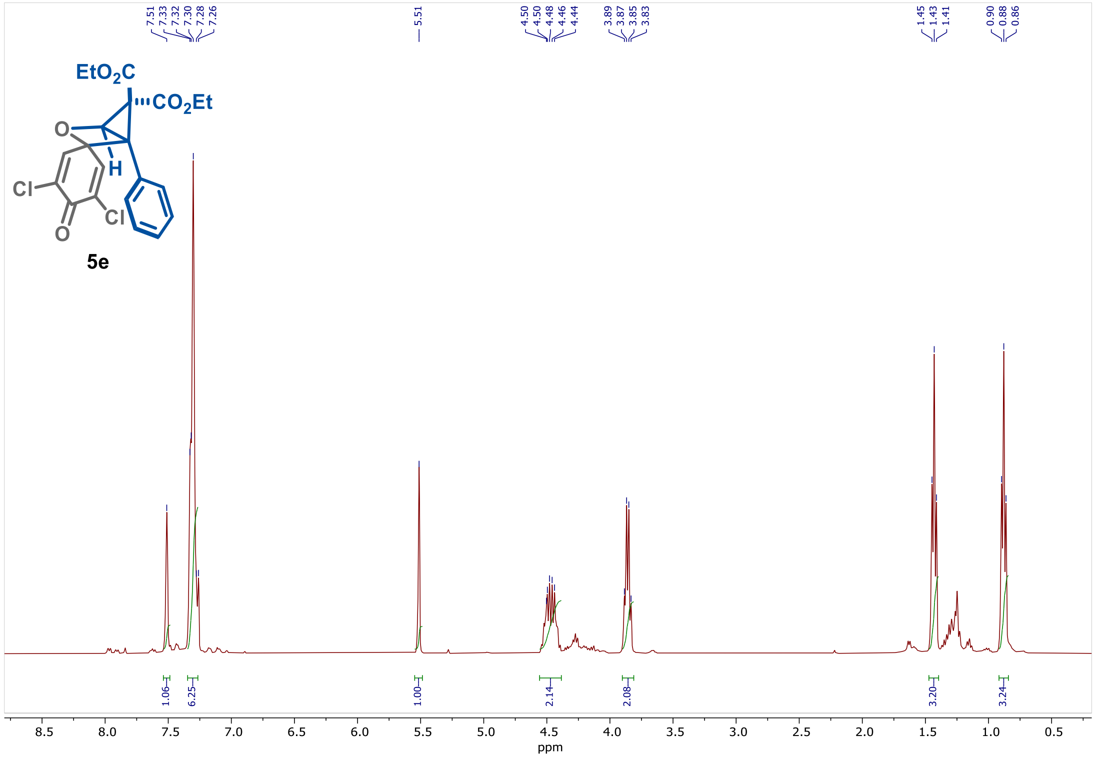
^{1}H-NMR (400 MHz, $CDCl_3$) of compound 5d (see procedure)



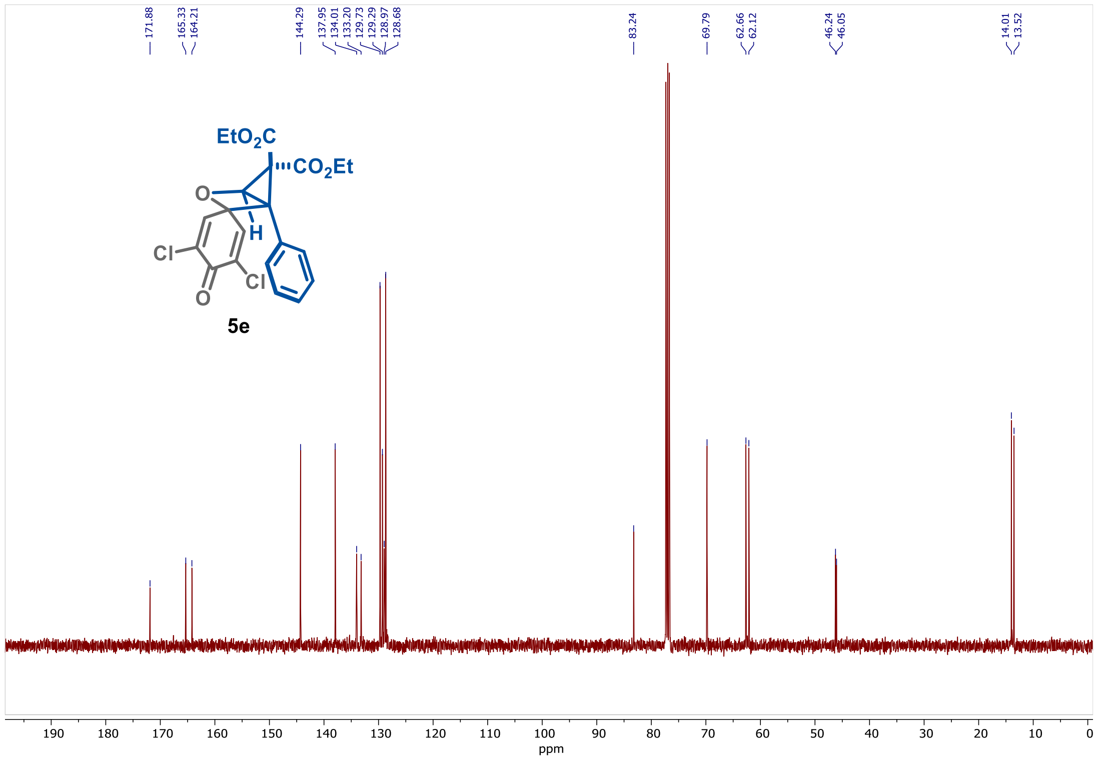
^{13}C-NMR (101 MHz, $CDCl_3$) of compound 5d



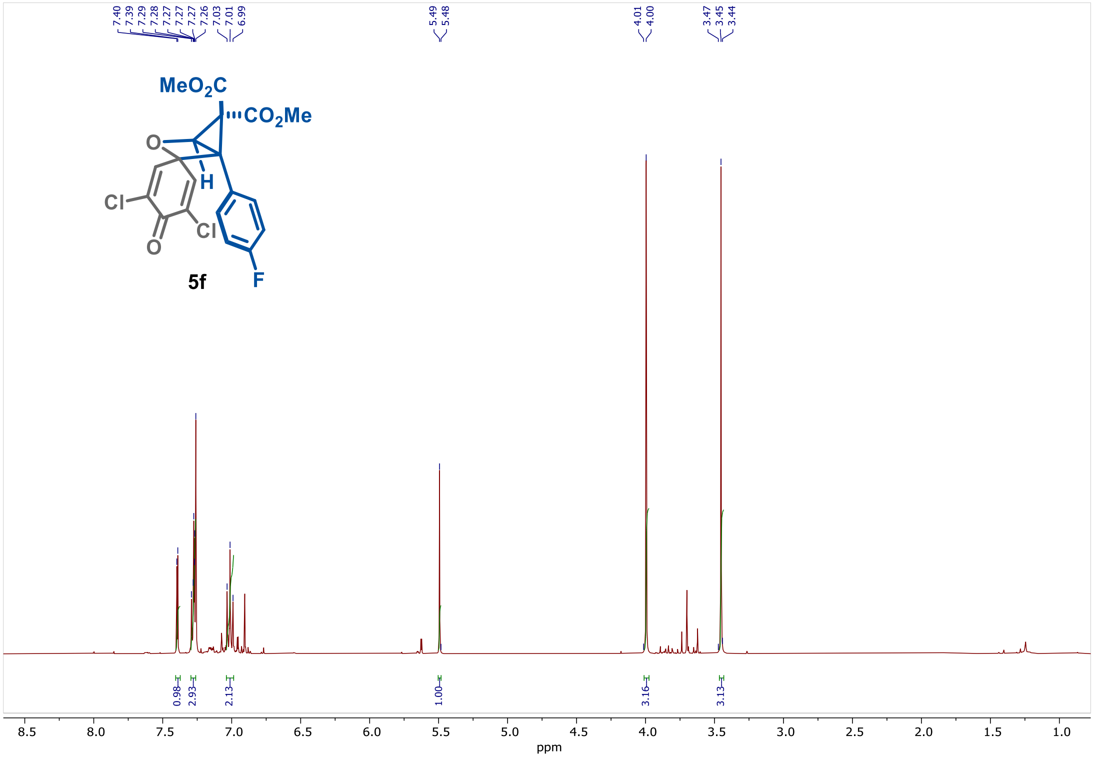
^{1}H-NMR (400 MHz, CDCl$_3$) of compound 5e (see procedure)



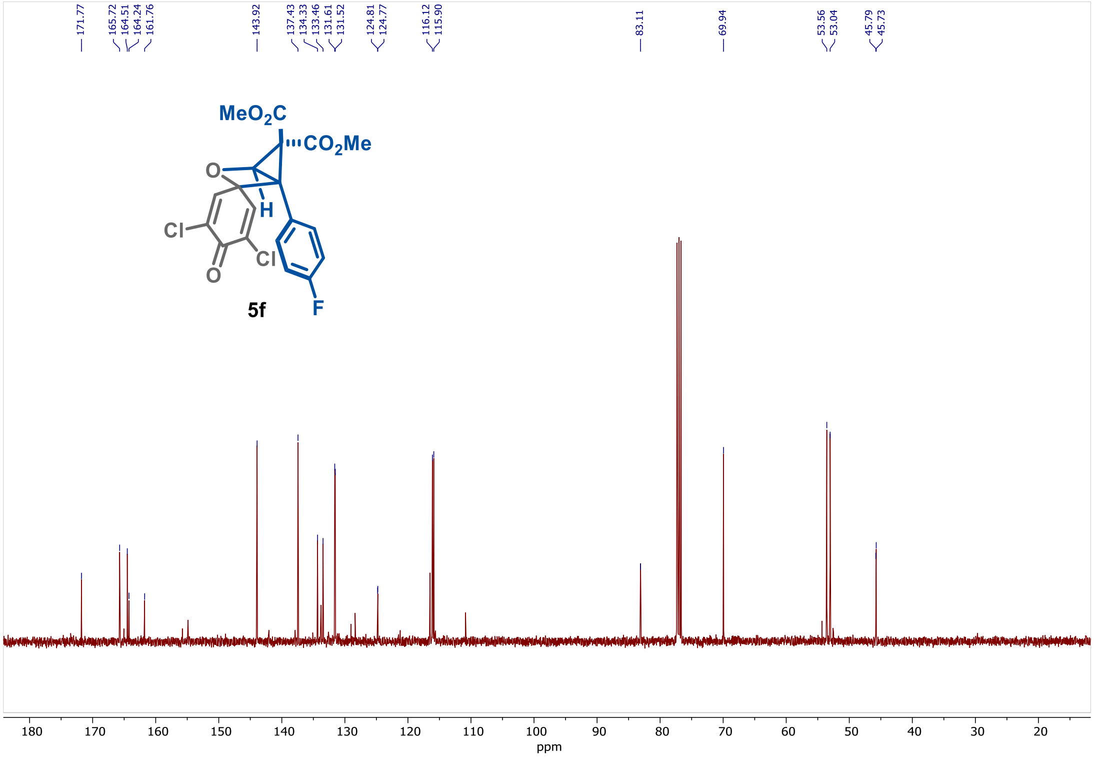
^{13}C-NMR (101 MHz, CDCl$_3$) of compound 5e



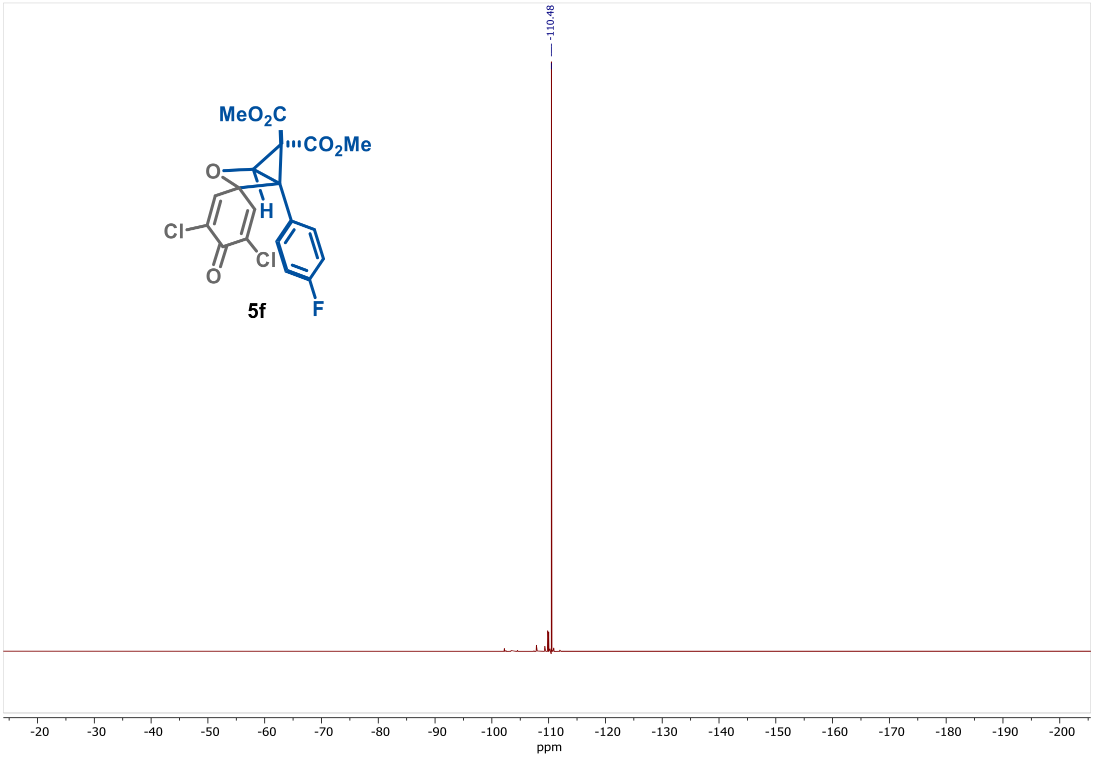
^{1}H-NMR (400 MHz, CDCl$_3$) of compound 5f (see procedure)



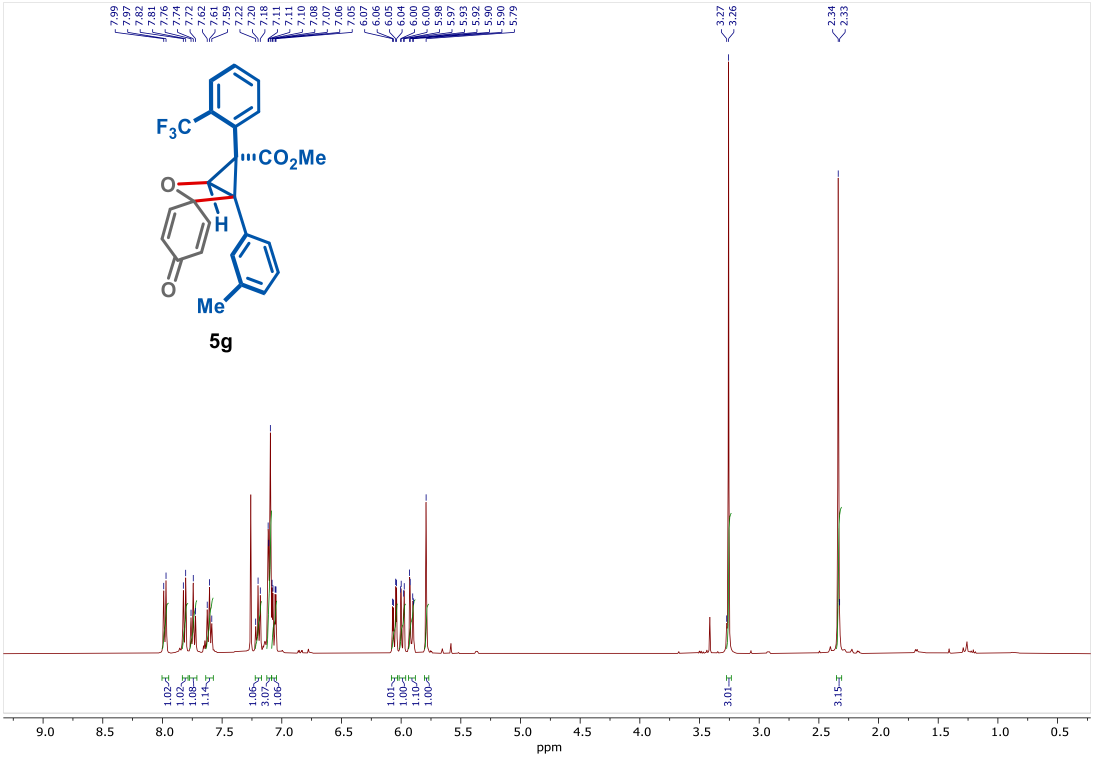
^{13}C-NMR (101 MHz, CDCl$_3$) of compound 5f



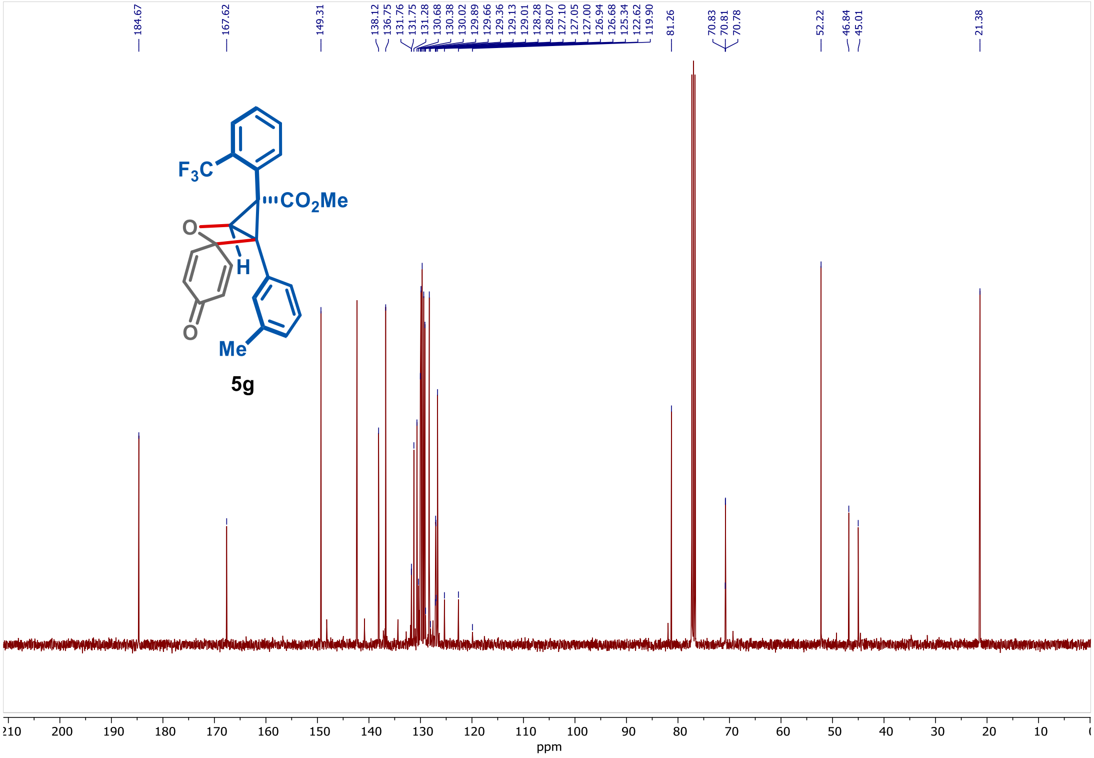
^{19}F-NMR (377 MHz, CDCl$_3$) of compound 5f



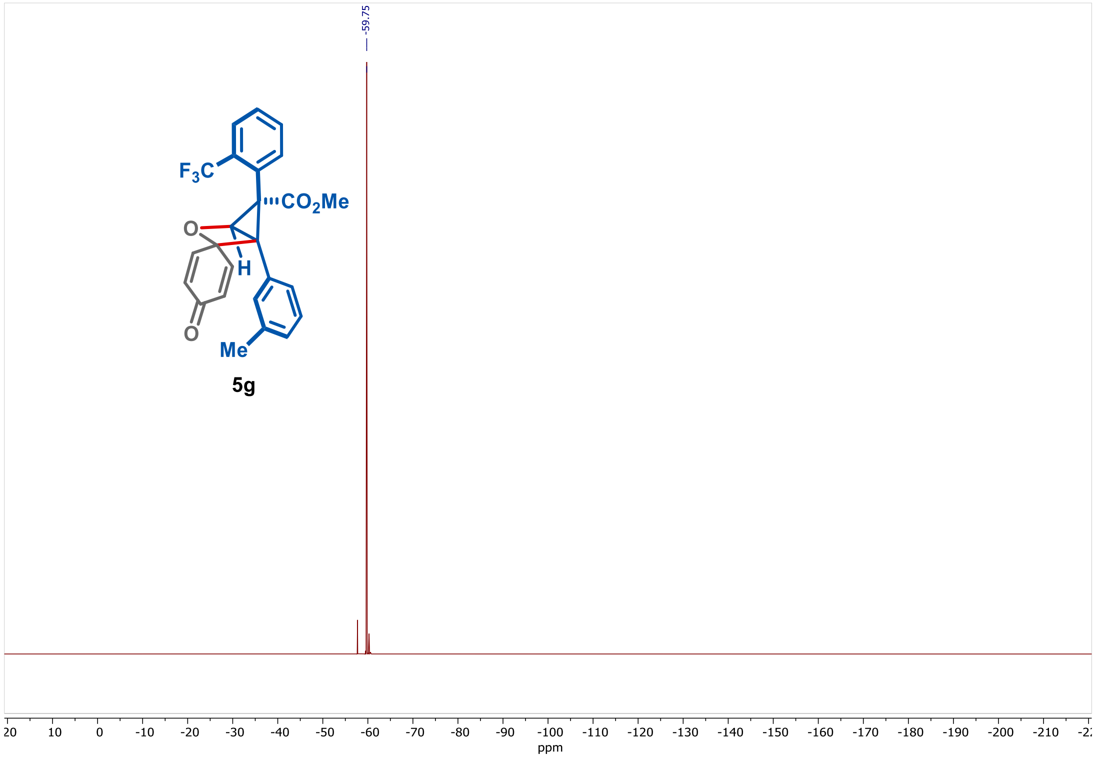
^{1}H-NMR (400 MHz, CDCl$_3$) of compound 5g (see procedure)



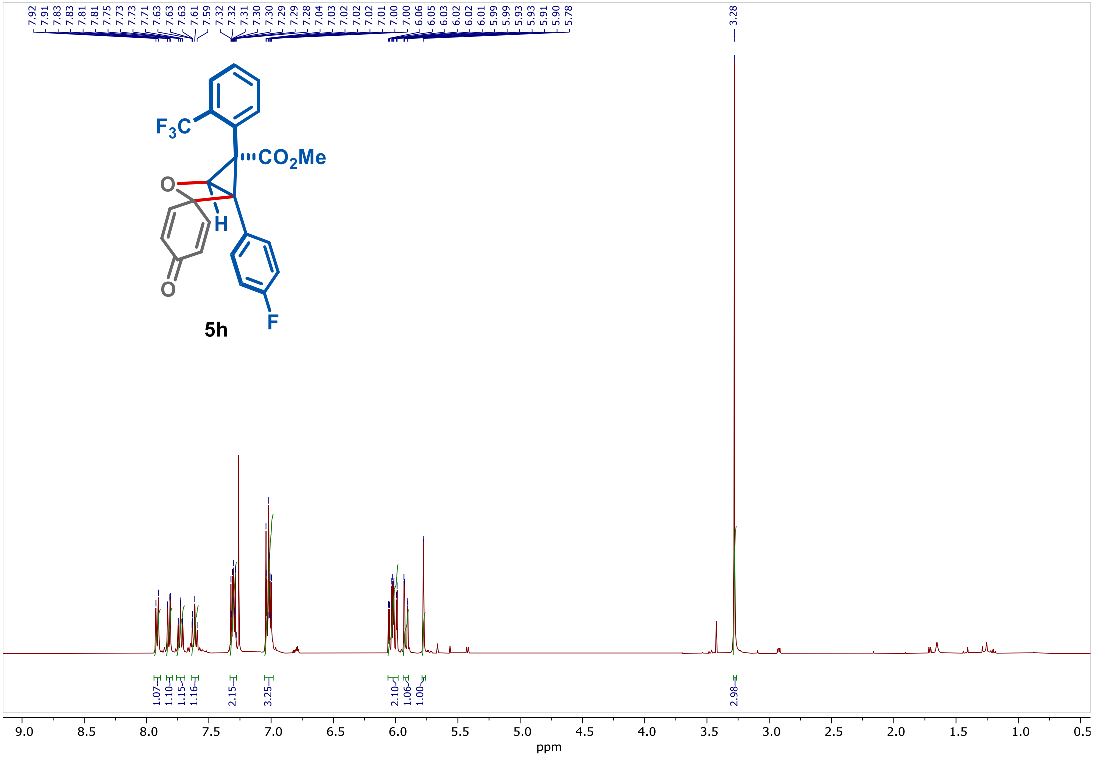
^{13}C-NMR (101 MHz, CDCl$_3$) of compound 5g



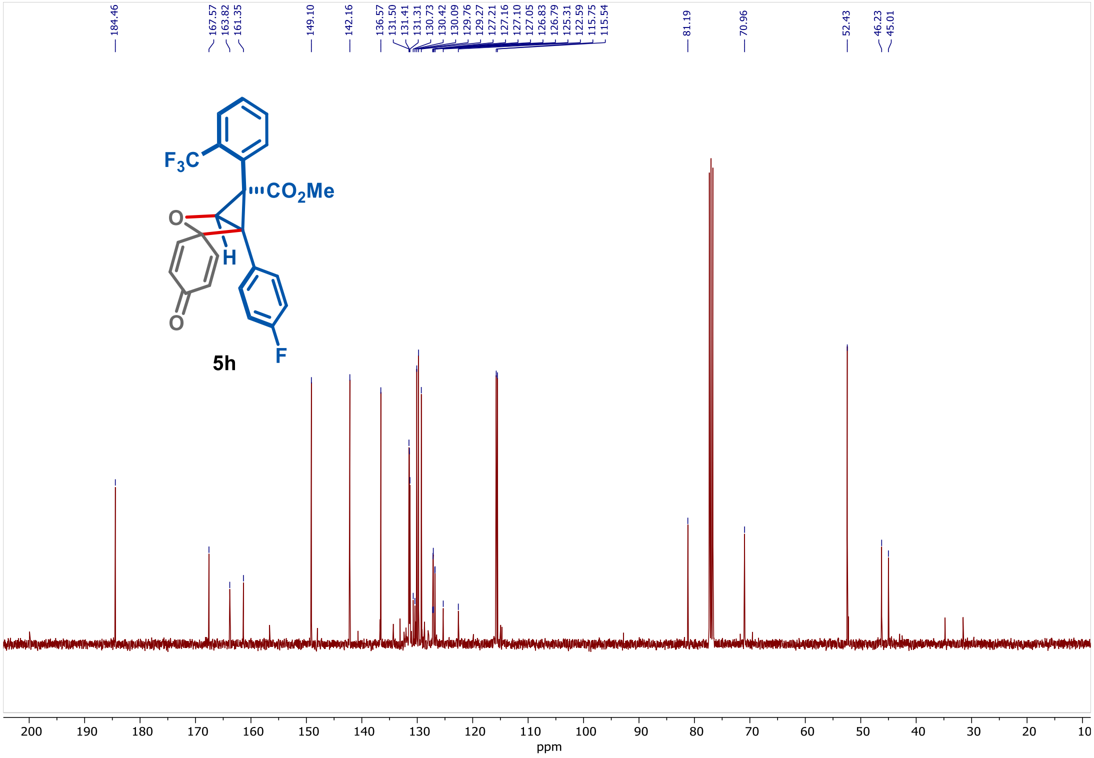
^{19}F-NMR (377 MHz, $CDCl_3$) of compound 5g



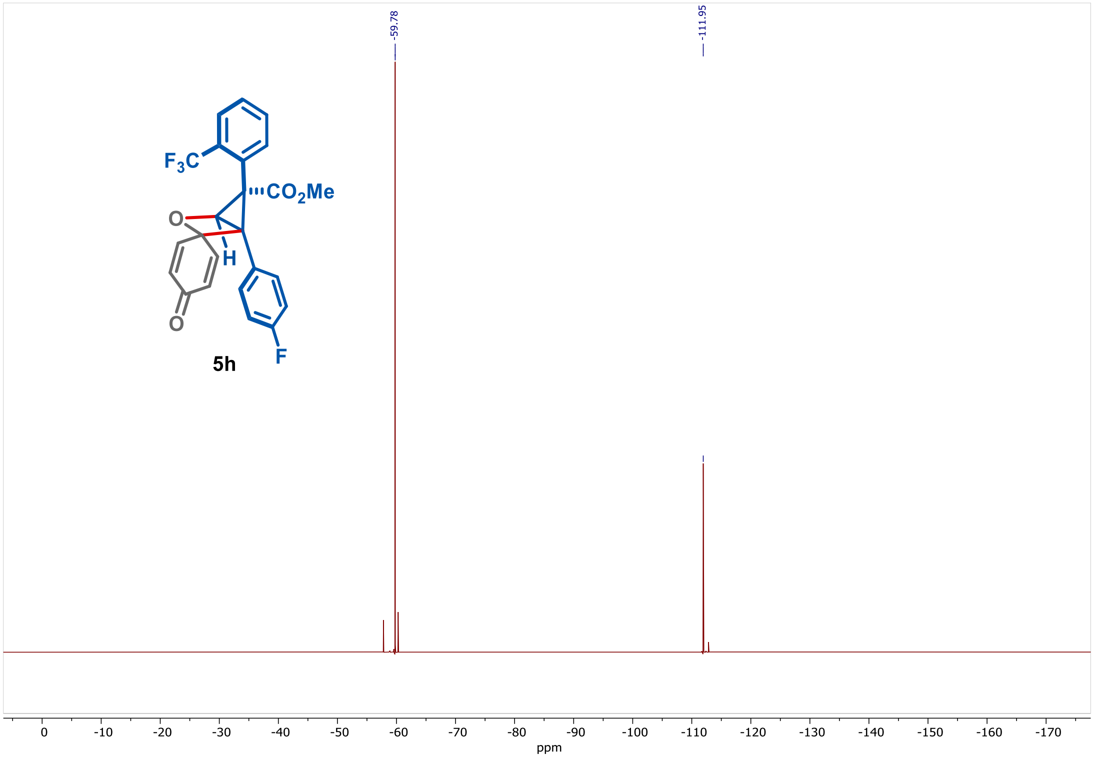
^{1}H-NMR (400 MHz, CDCl$_3$) of compound 5h (see procedure)



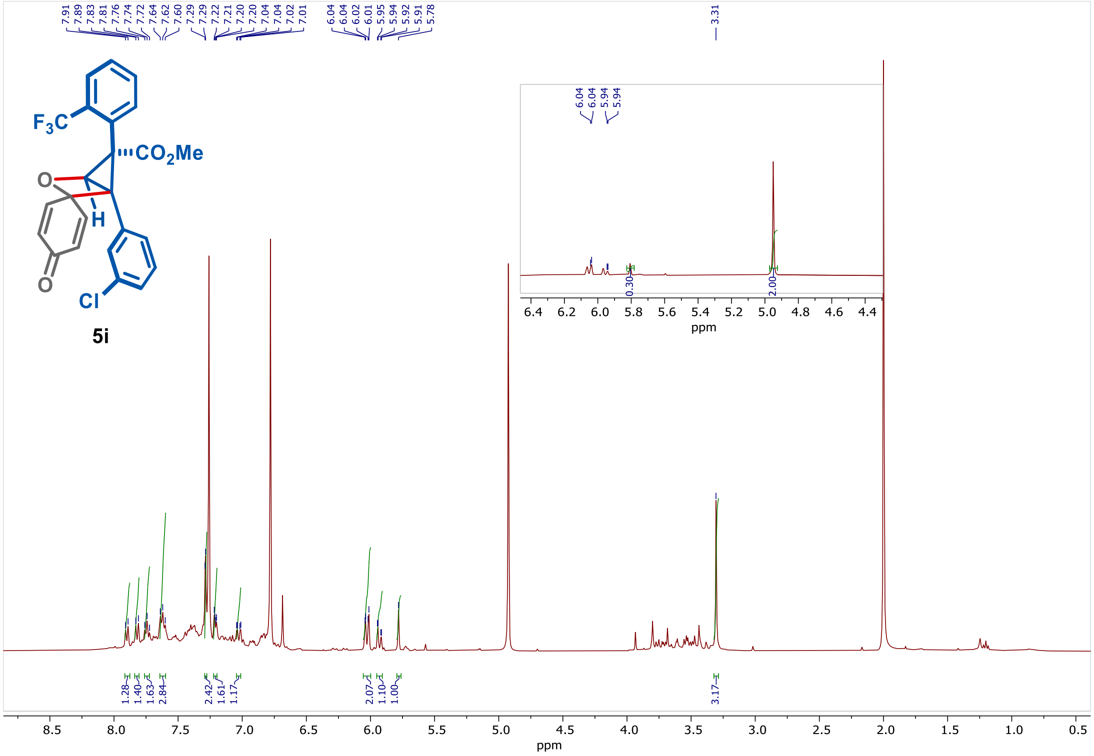
^{13}C-NMR (101 MHz, CDCl$_3$) of compound 5h



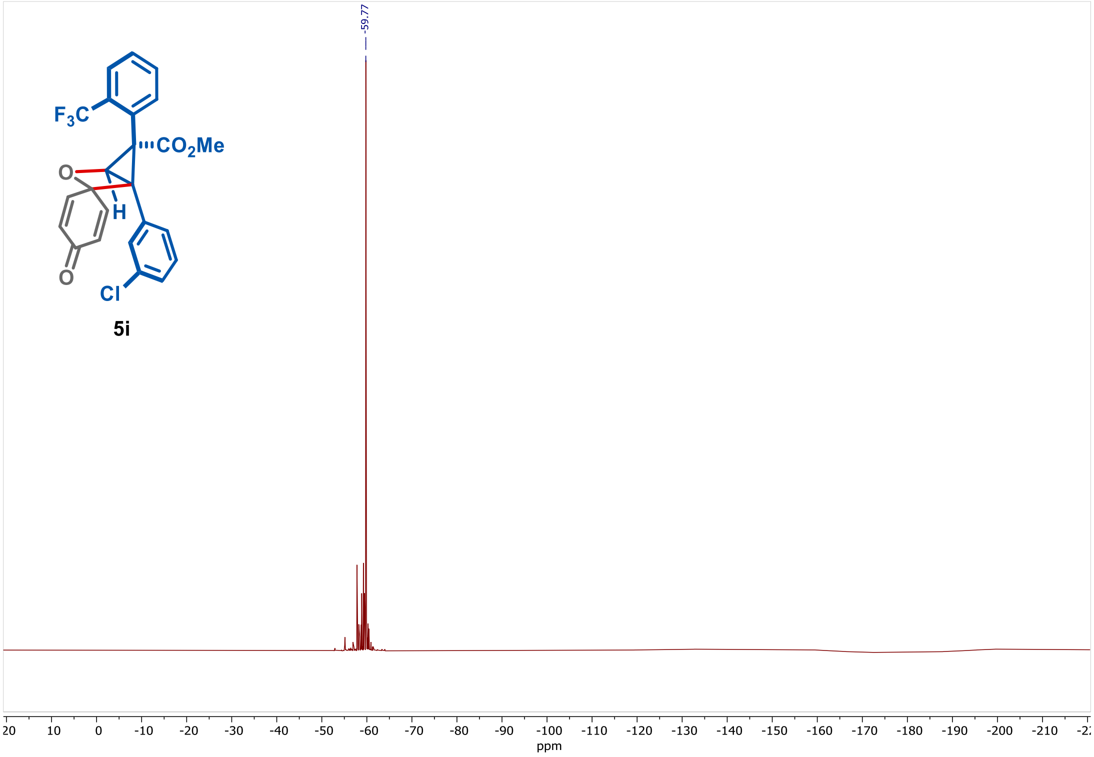
^{19}F-NMR (377 MHz, $CDCl_3$) of compound 5h



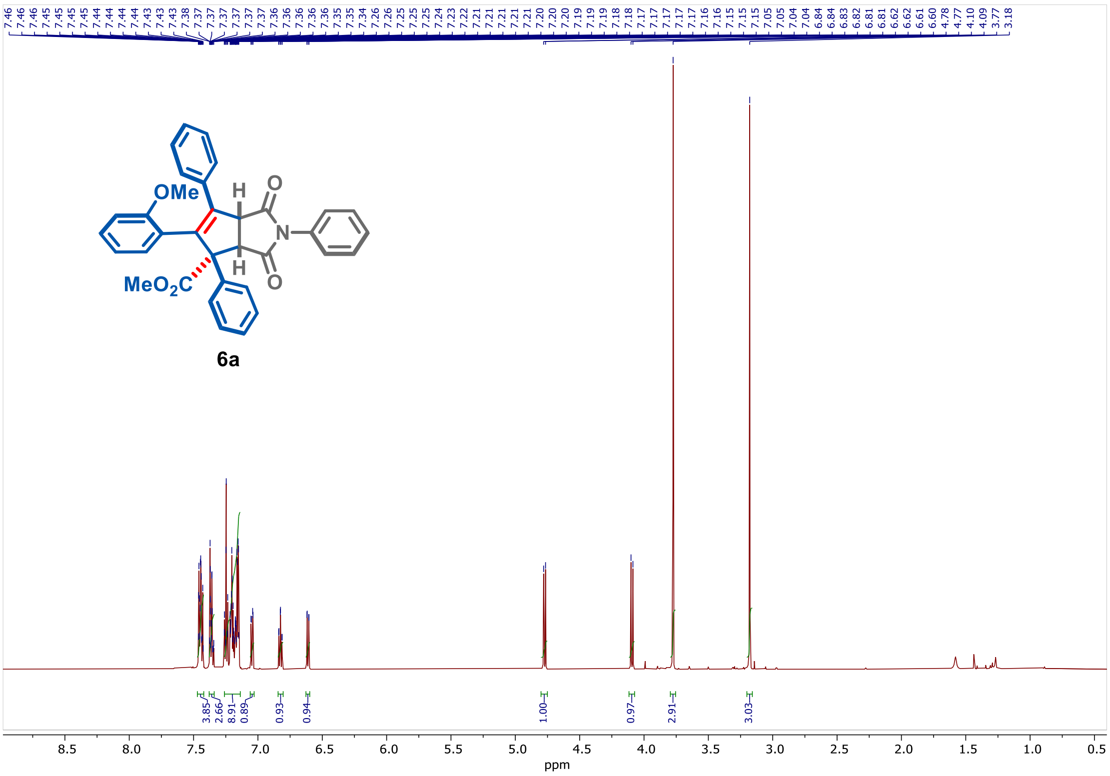
^{1}H-NMR (400 MHz, $CDCl_3$) of compound 5i (see procedure)



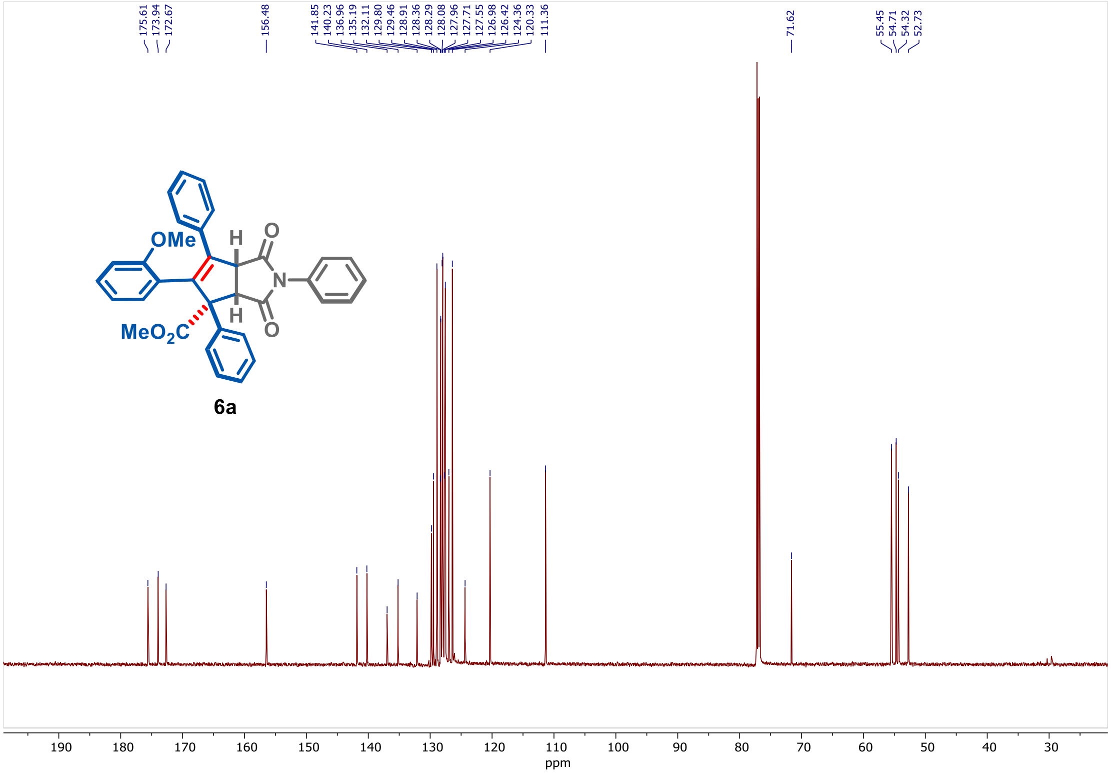
^{19}F-NMR (377 MHz, $CDCl_3$) of compound 5i



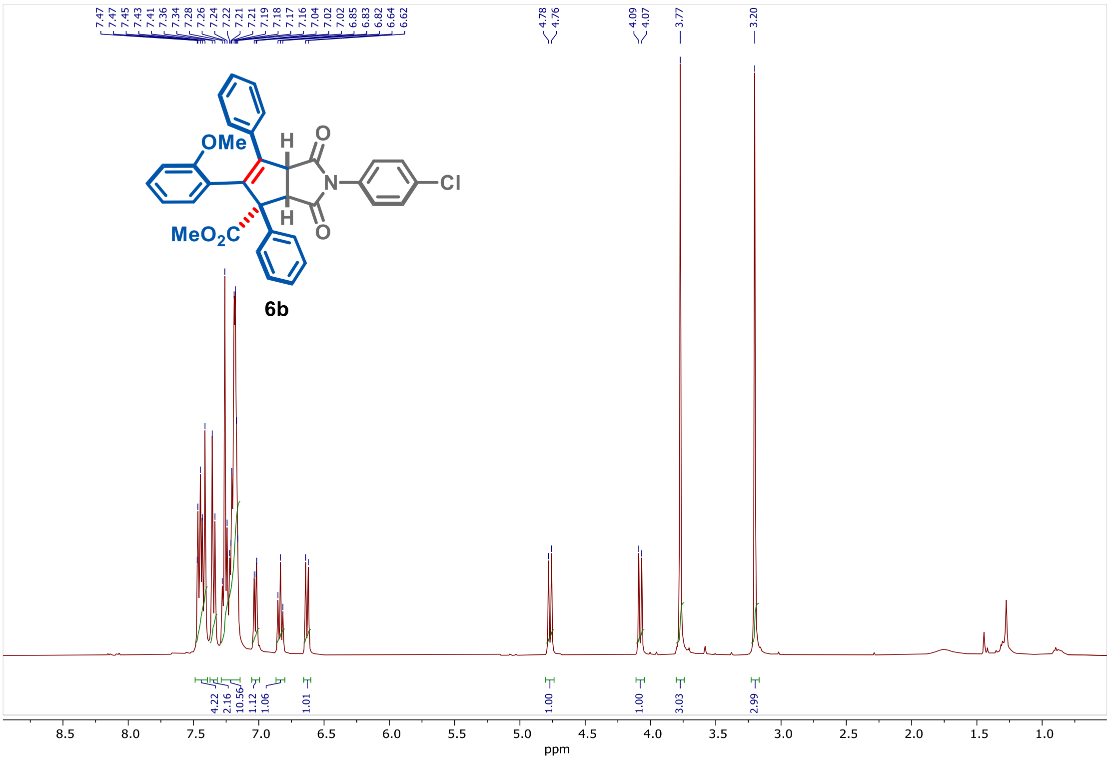
^{1}H-NMR (400 MHz, $CDCl_3$) of compound 6a (see procedure)



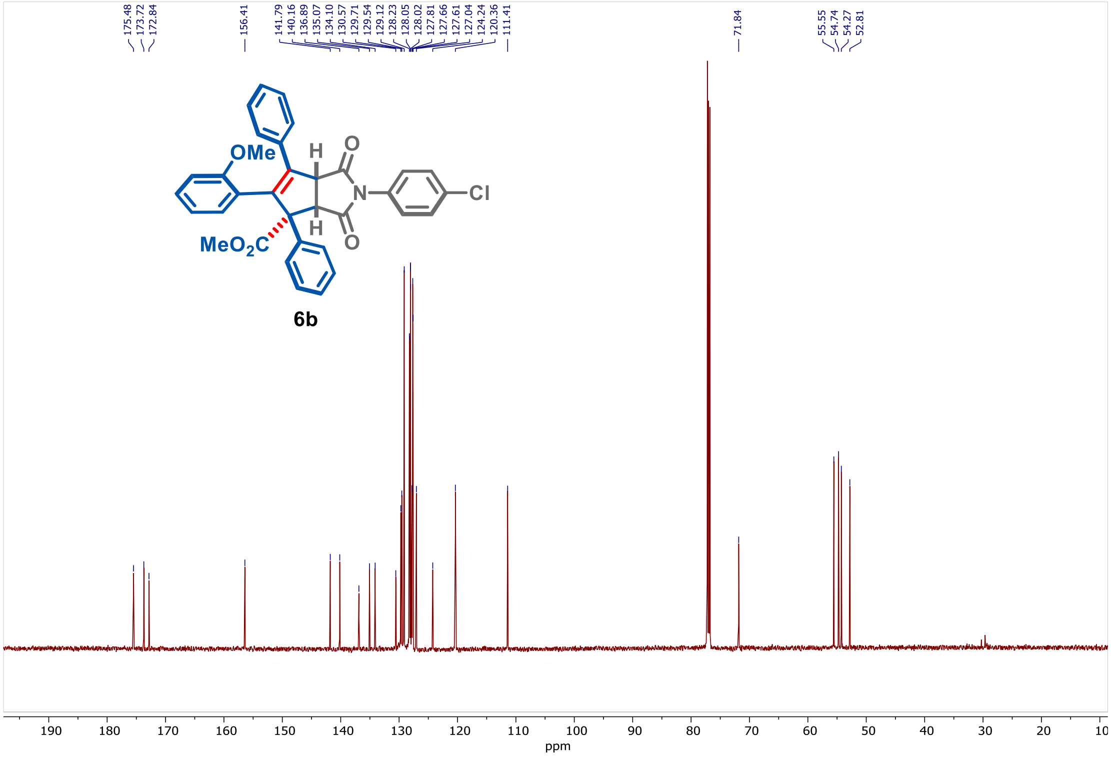
^{13}C-NMR (101 MHz, $CDCl_3$) of compound 6a



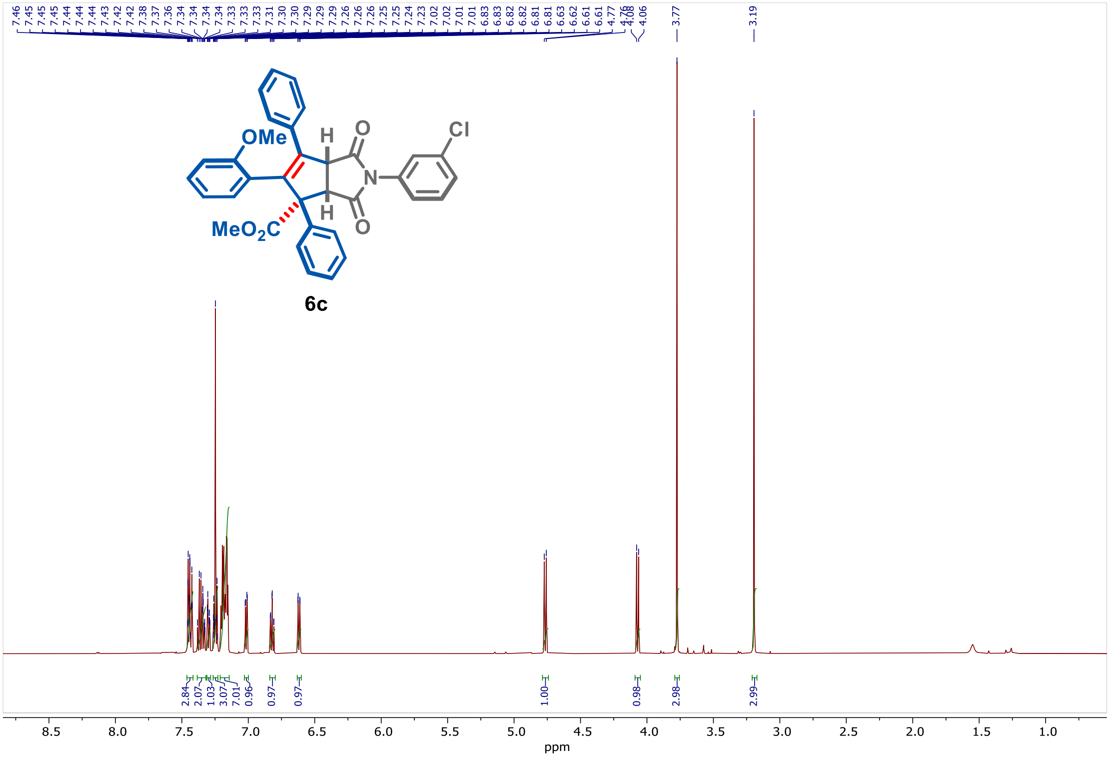
^{1}H-NMR (400 MHz, $CDCl_3$) of compound 6b (see procedure)



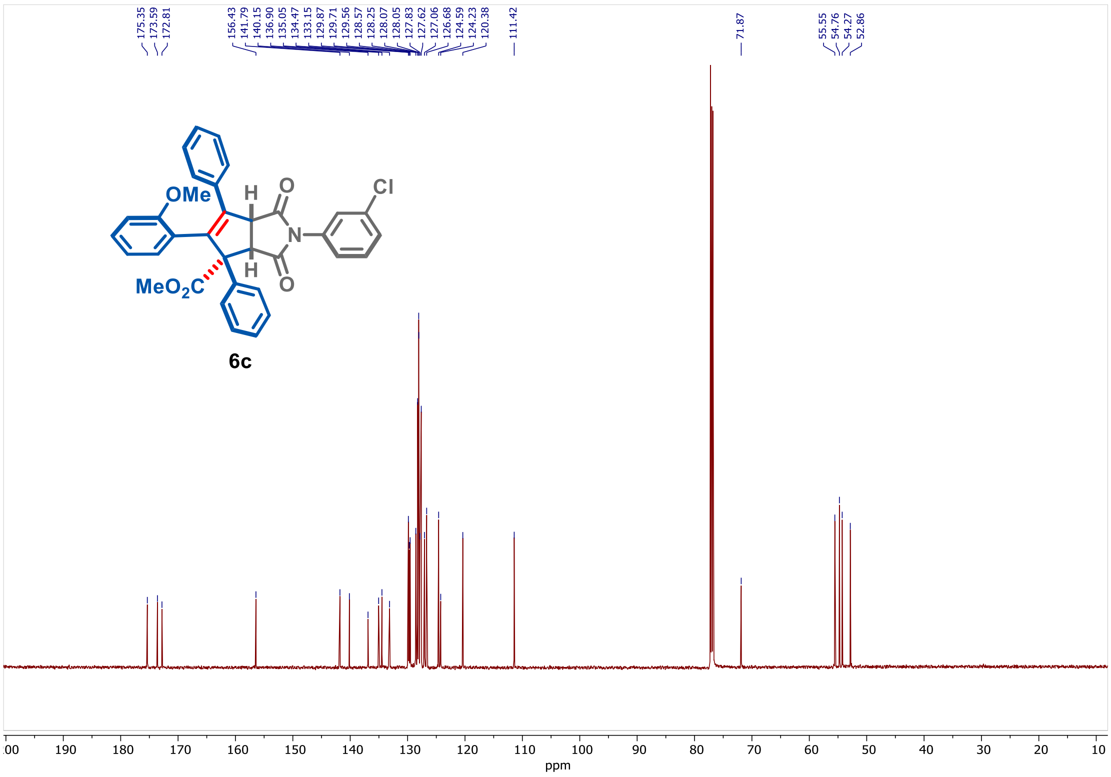
^{13}C-NMR (101 MHz, $CDCl_3$) of compound 6b



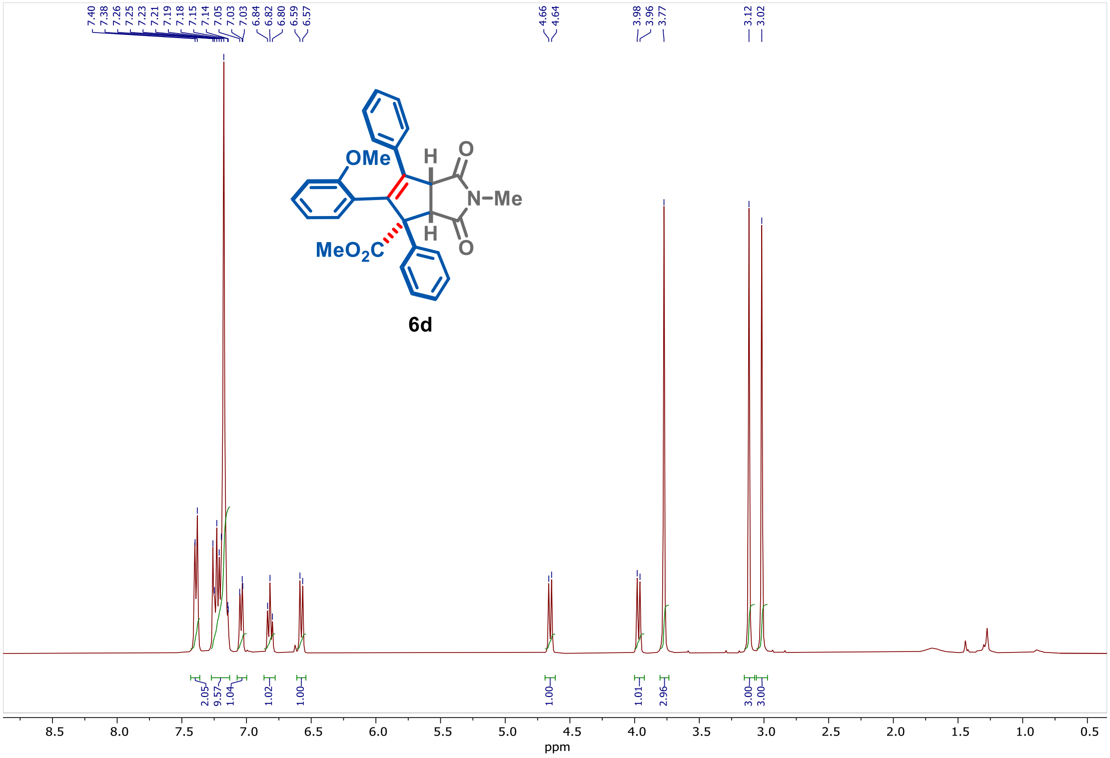
^{1}H-NMR (400 MHz, CDCl$_3$) of compound 6c (see procedure)



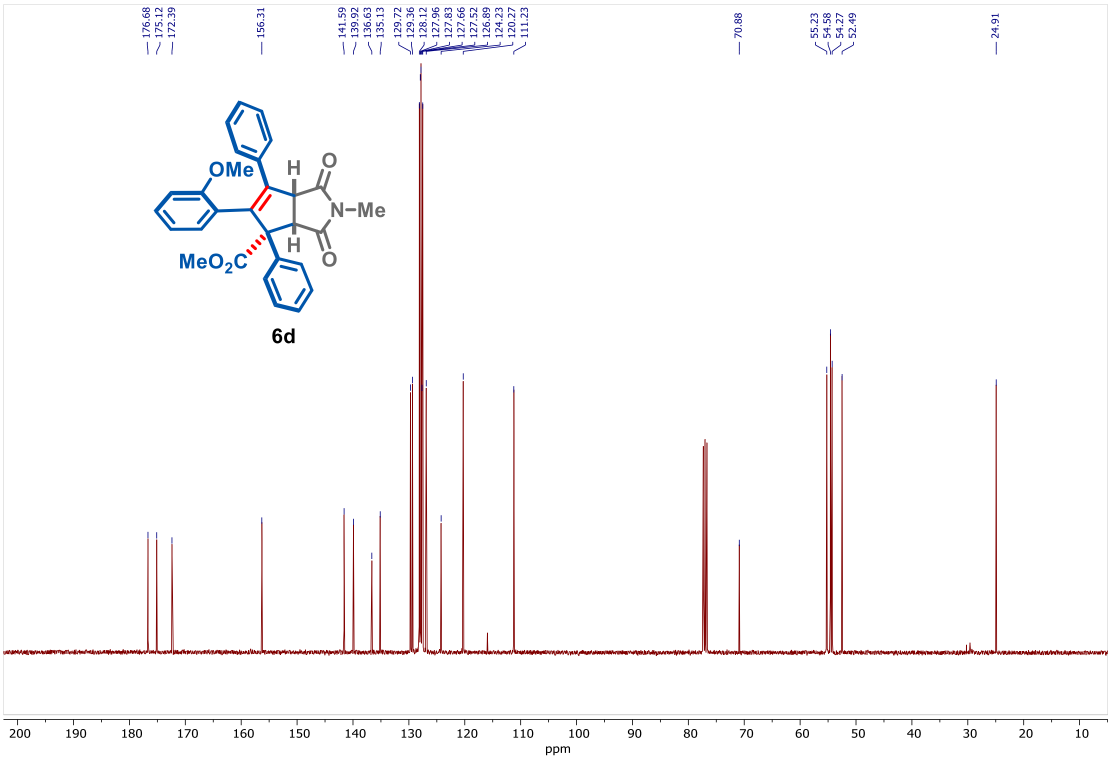
^{13}C-NMR (101 MHz, CDCl$_3$) of compound 6c



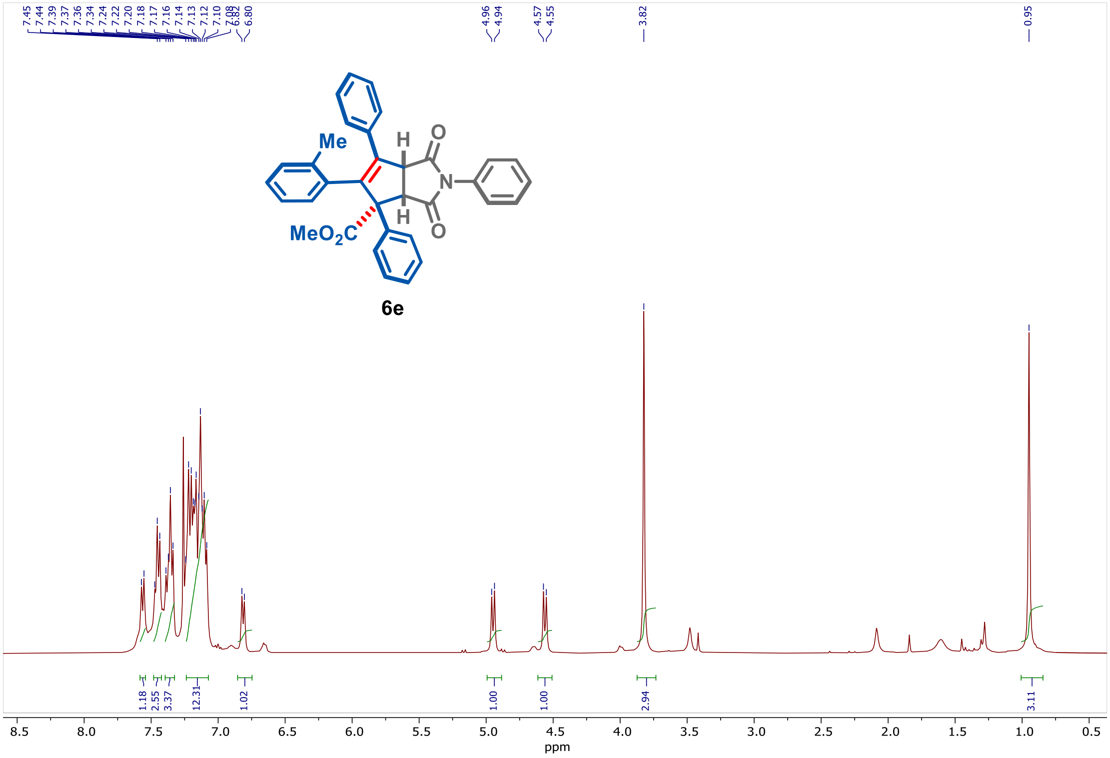
^{1}H-NMR (400 MHz, CDCl$_3$) of compound 6d (see procedure)



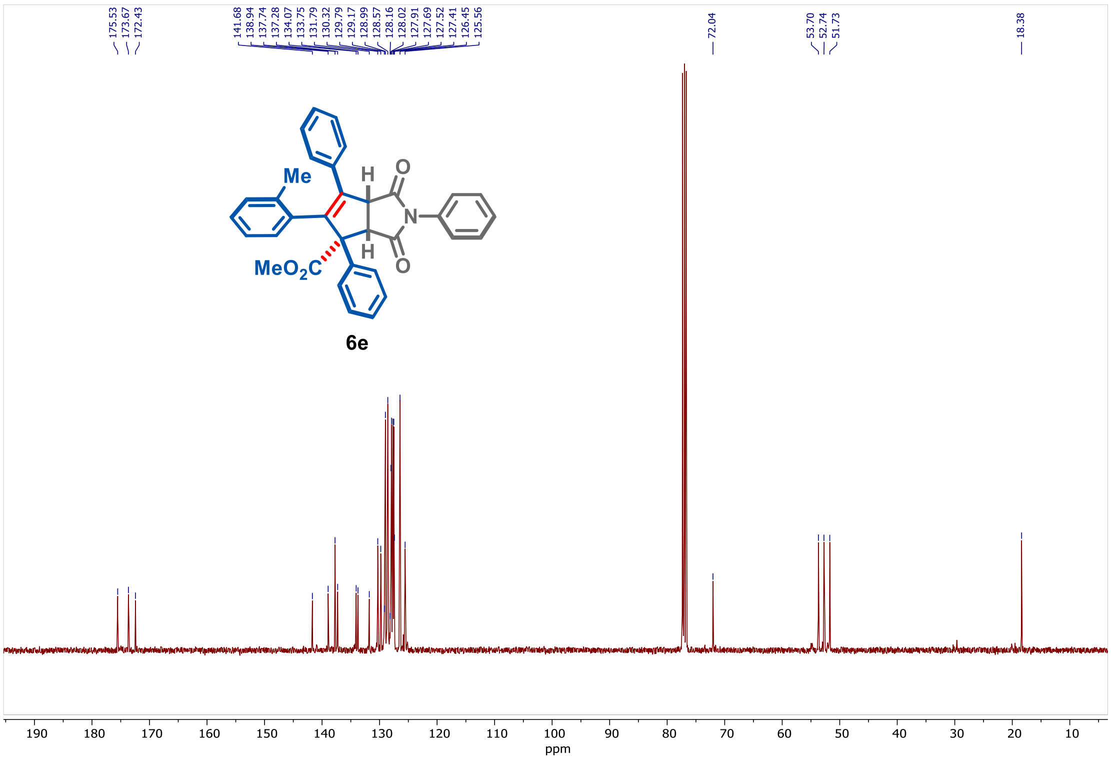
^{13}C-NMR (101 MHz, CDCl$_3$) of compound 6d



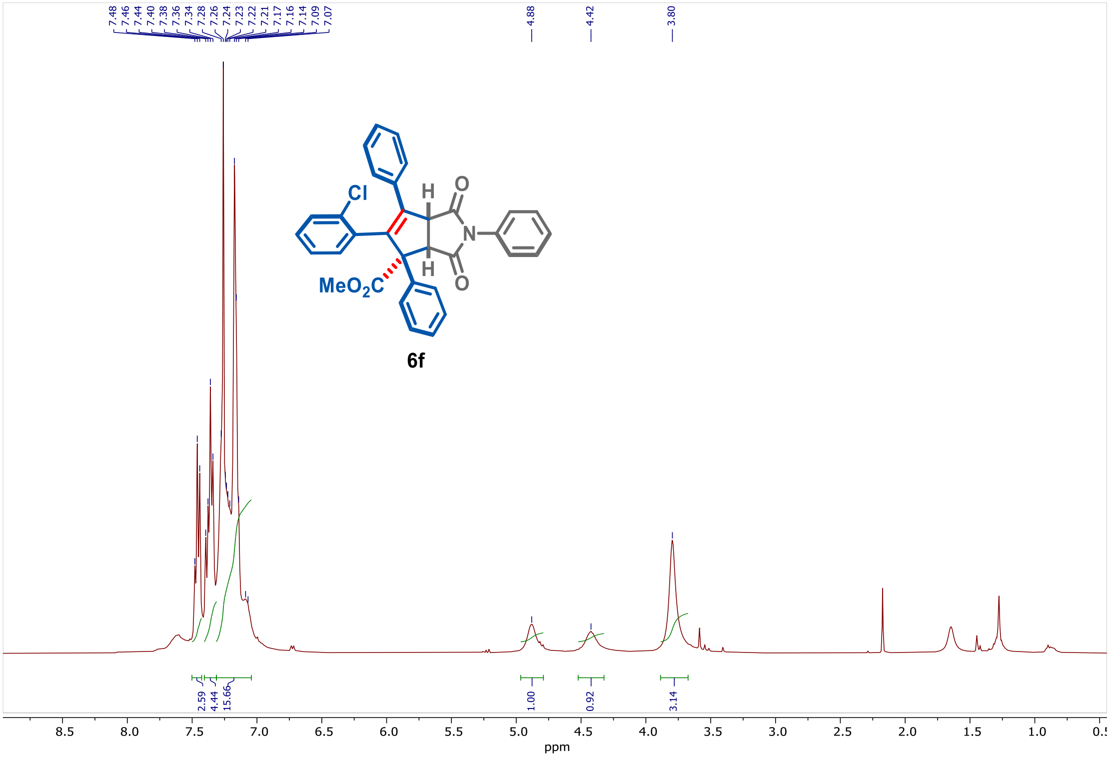
^{1}H-NMR (400 MHz, $CDCl_3$) of compound 6e (see procedure)



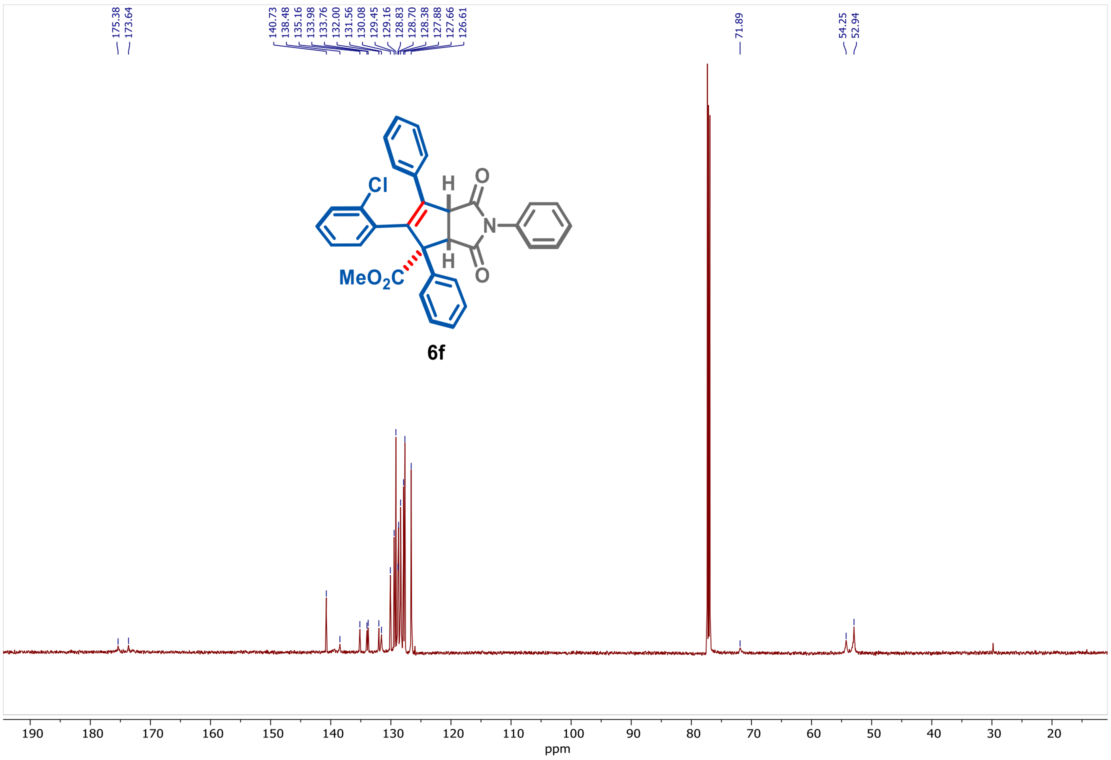
^{13}C-NMR (101 MHz, $CDCl_3$) of compound 6e



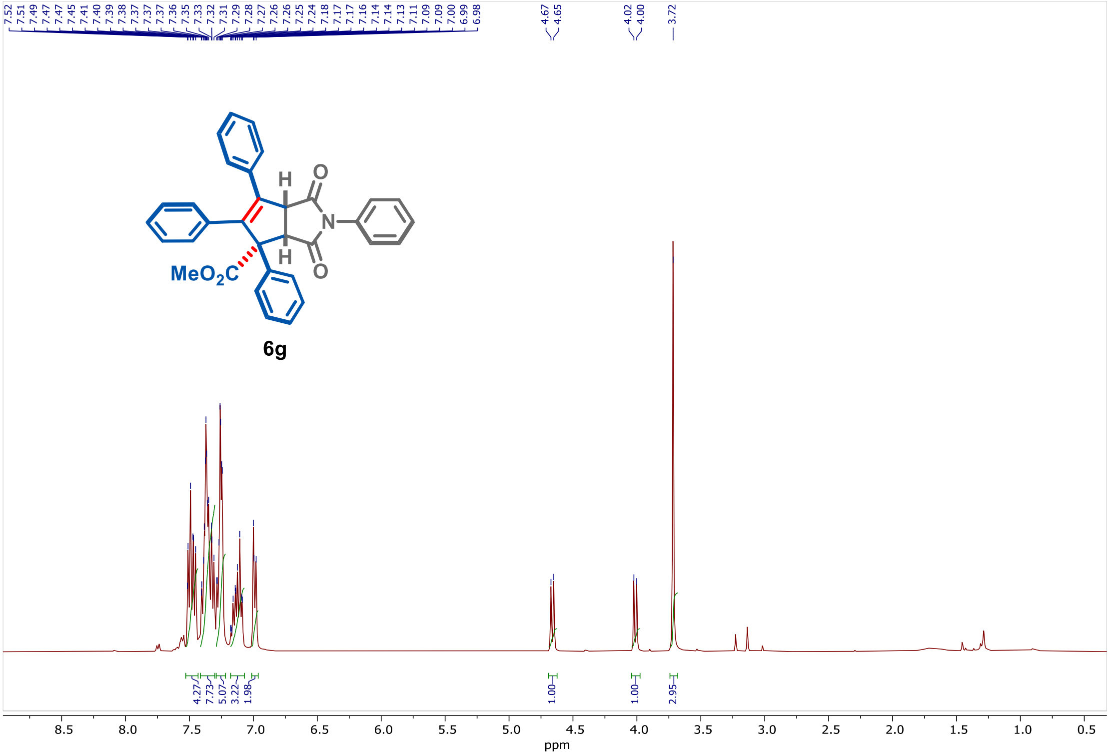
^{1}H-NMR (400 MHz, $CDCl_3$) of compound 6f (see procedure)



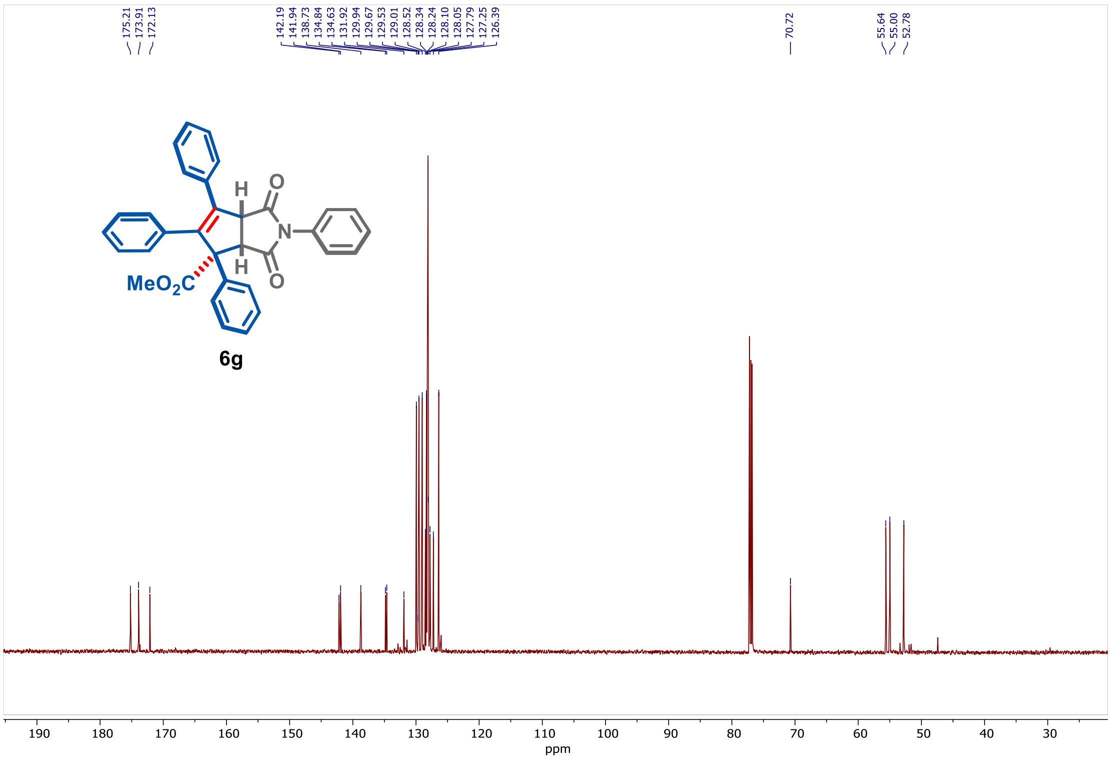
^{13}C-NMR (101 MHz, $CDCl_3$) of compound 6f



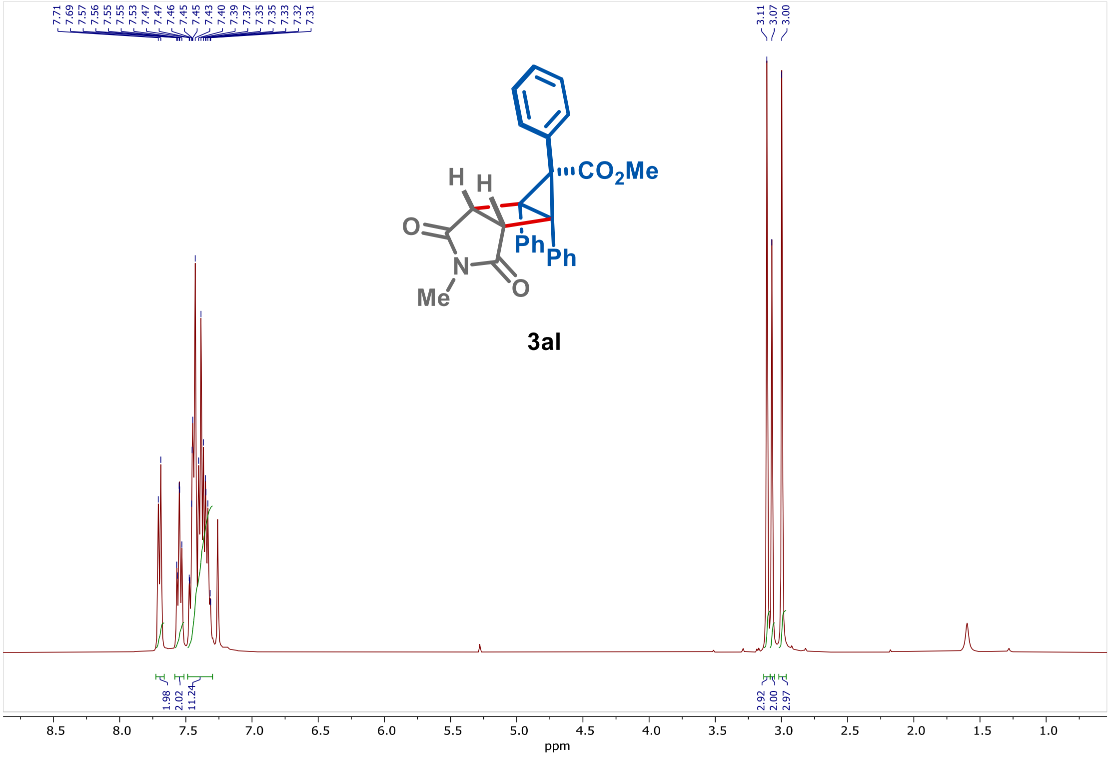
^{1}H-NMR (400 MHz, CDCl$_3$) of compound 6g (see procedure)



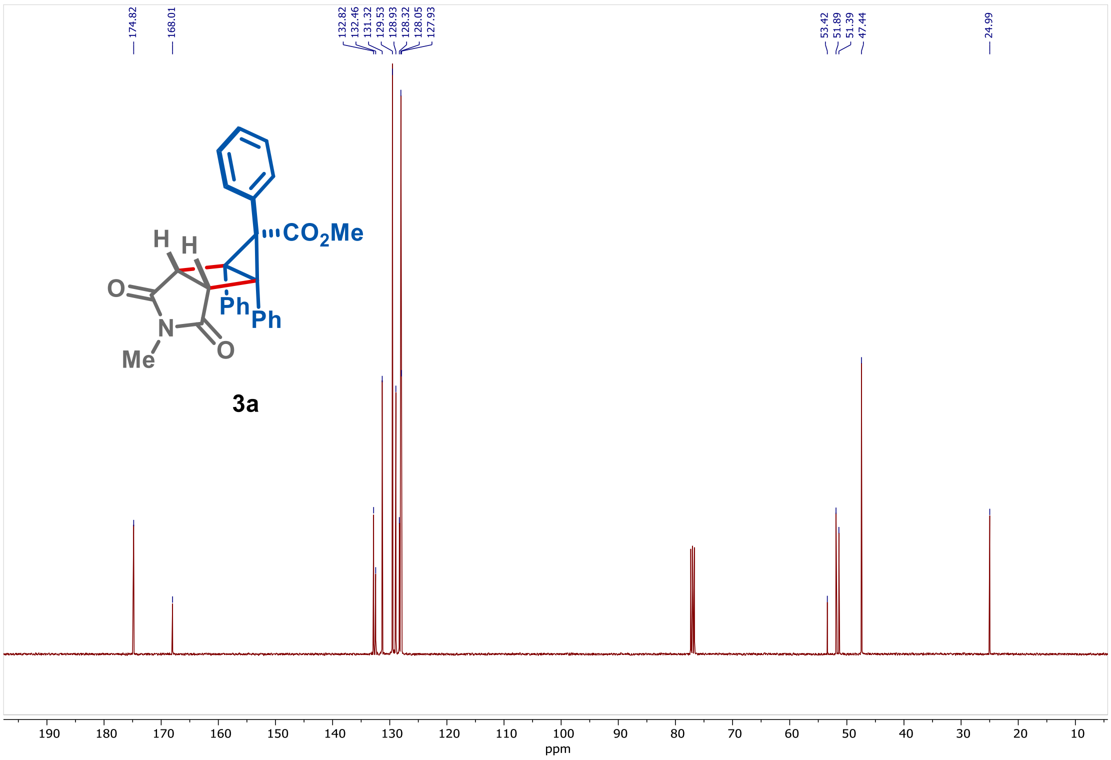
^{13}C-NMR (101 MHz, CDCl$_3$) of compound 6g



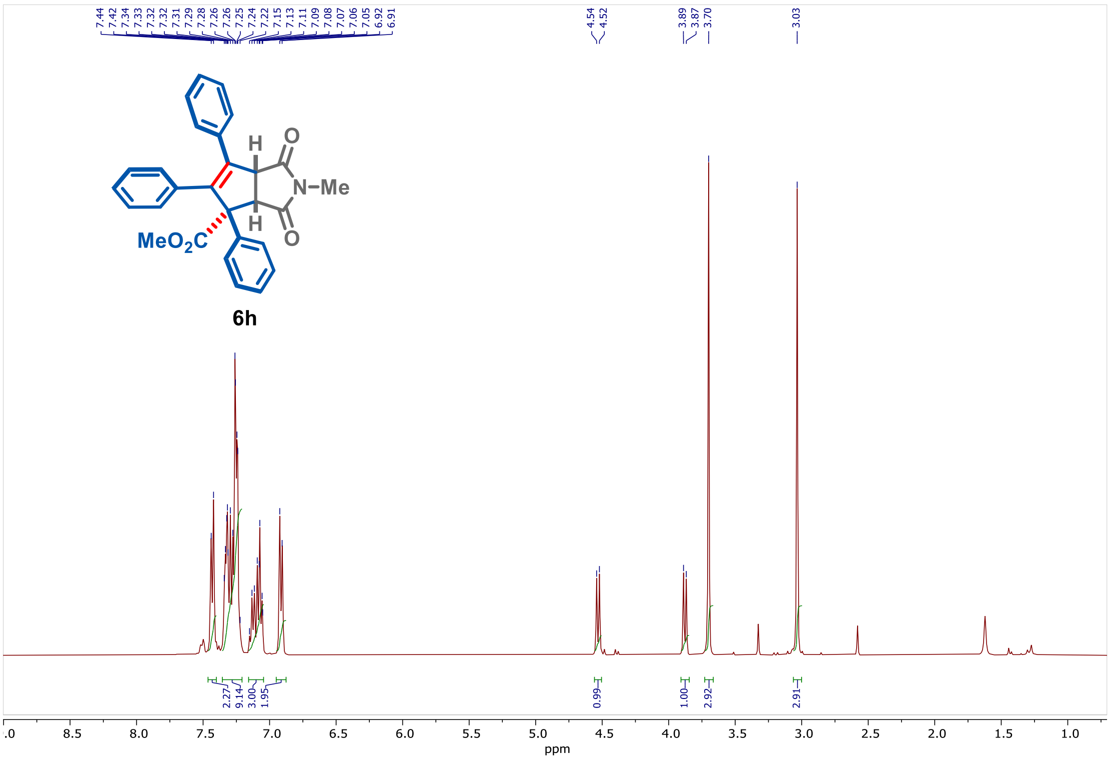
^{1}H-NMR (400 MHz, $CDCl_3$) of compound 3al (see procedure) (major diastereomer)



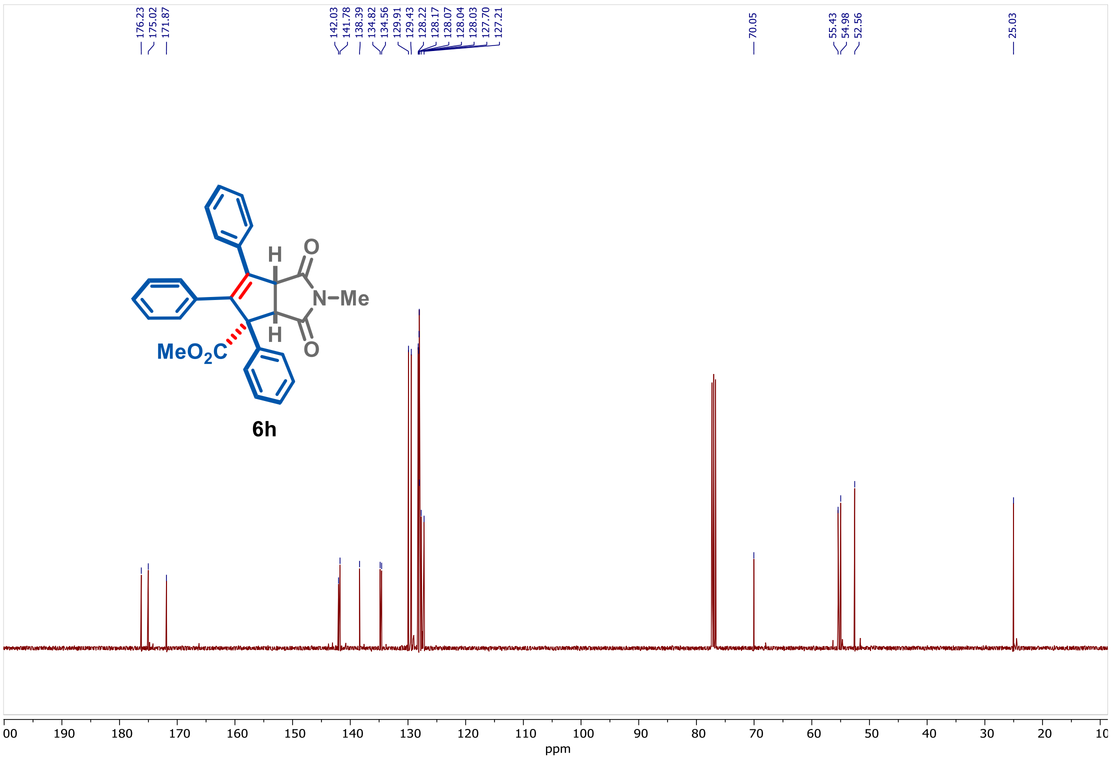
^{13}C-NMR (101 MHz, $CDCl_3$) of compound 3al (major diastereomer)



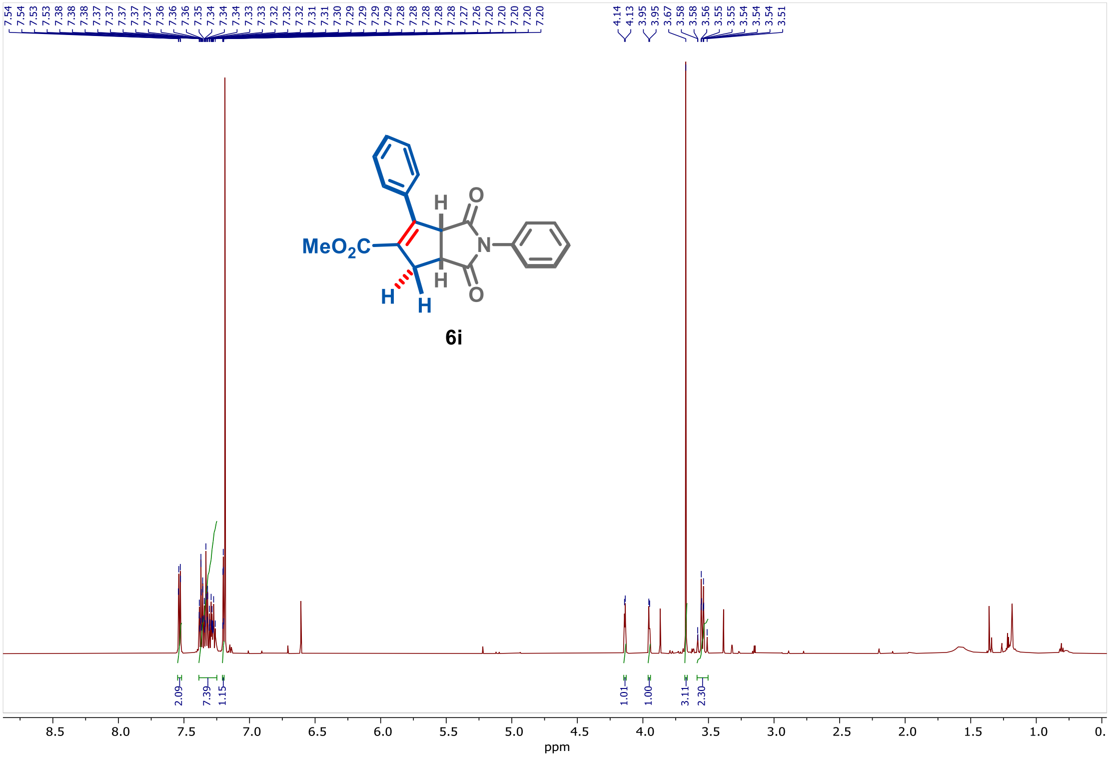
^{1}H-NMR (400 MHz, CDCl$_3$) of compound 6h (see procedure)



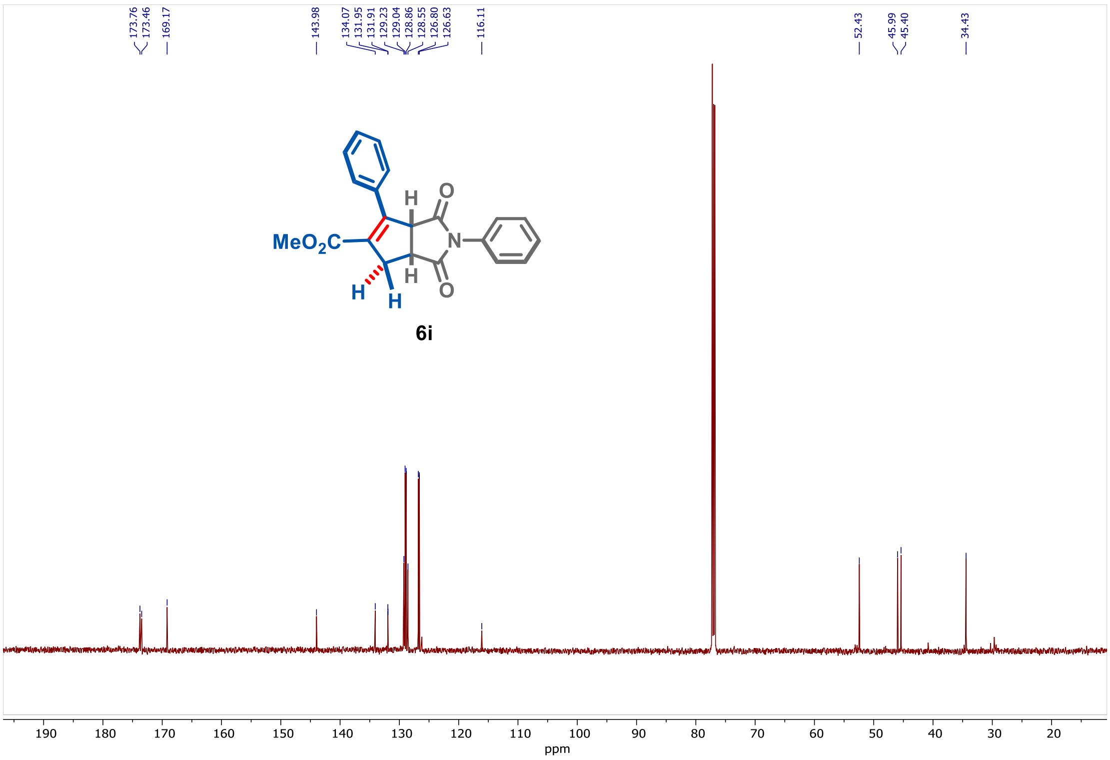
^{13}C-NMR (101 MHz, CDCl$_3$) of compound 6h



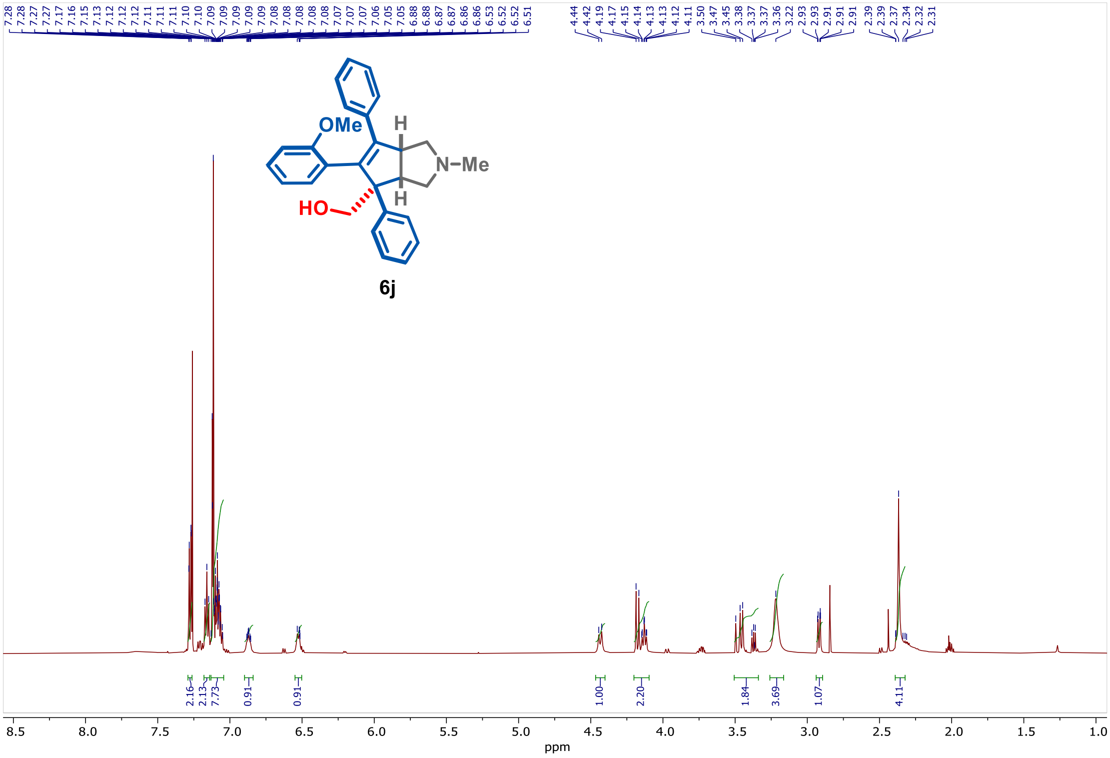
^{1}H-NMR (400 MHz, CDCl$_3$) of compound 6i (see procedure)



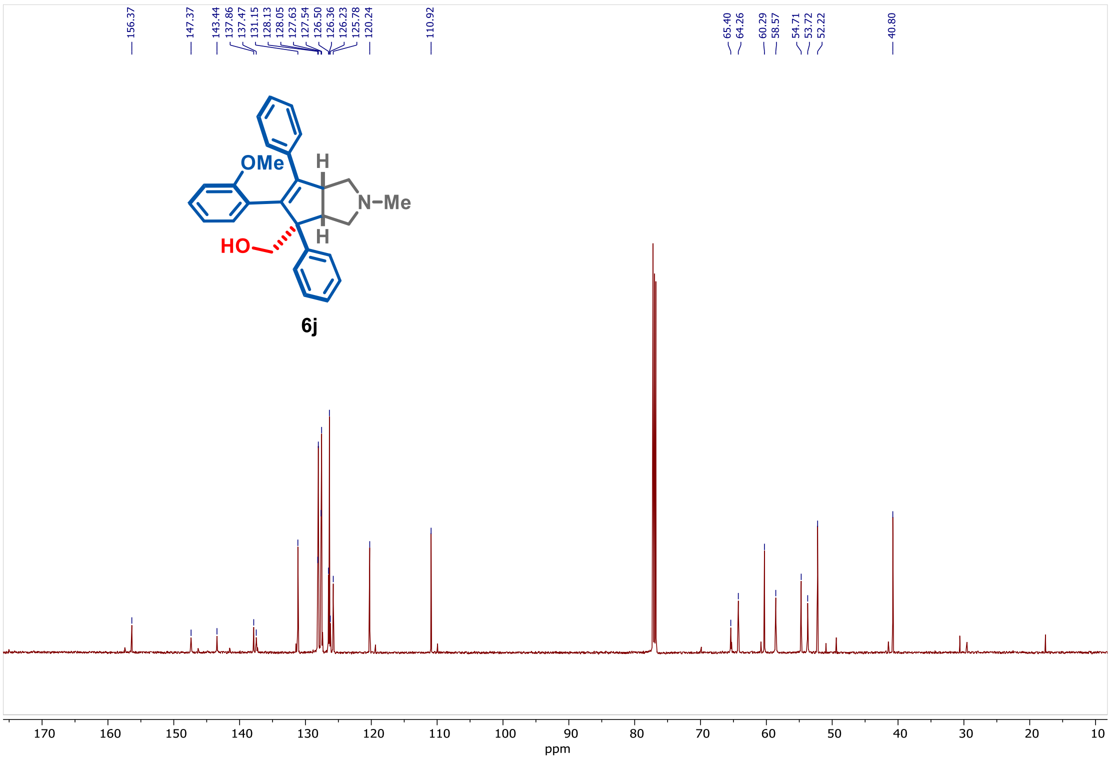
^{13}C-NMR (101 MHz, CDCl$_3$) of compound 6i



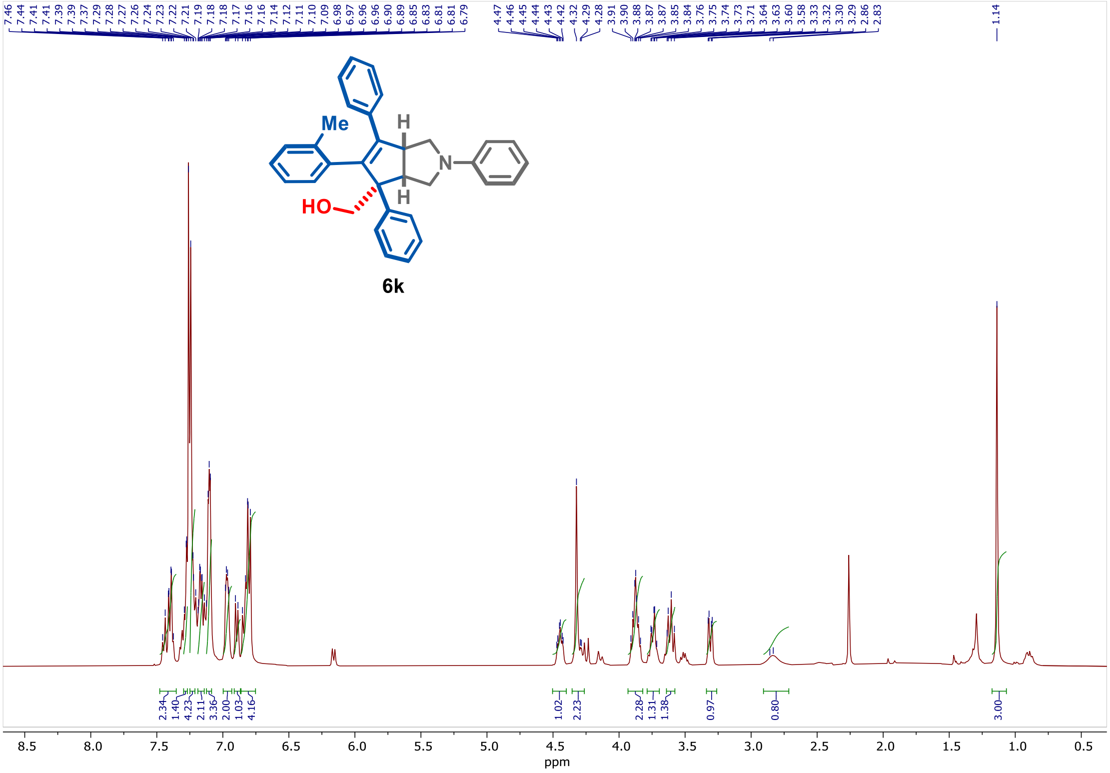
^{1}H-NMR (400 MHz, $CDCl_3$) of compound 6j (see procedure)



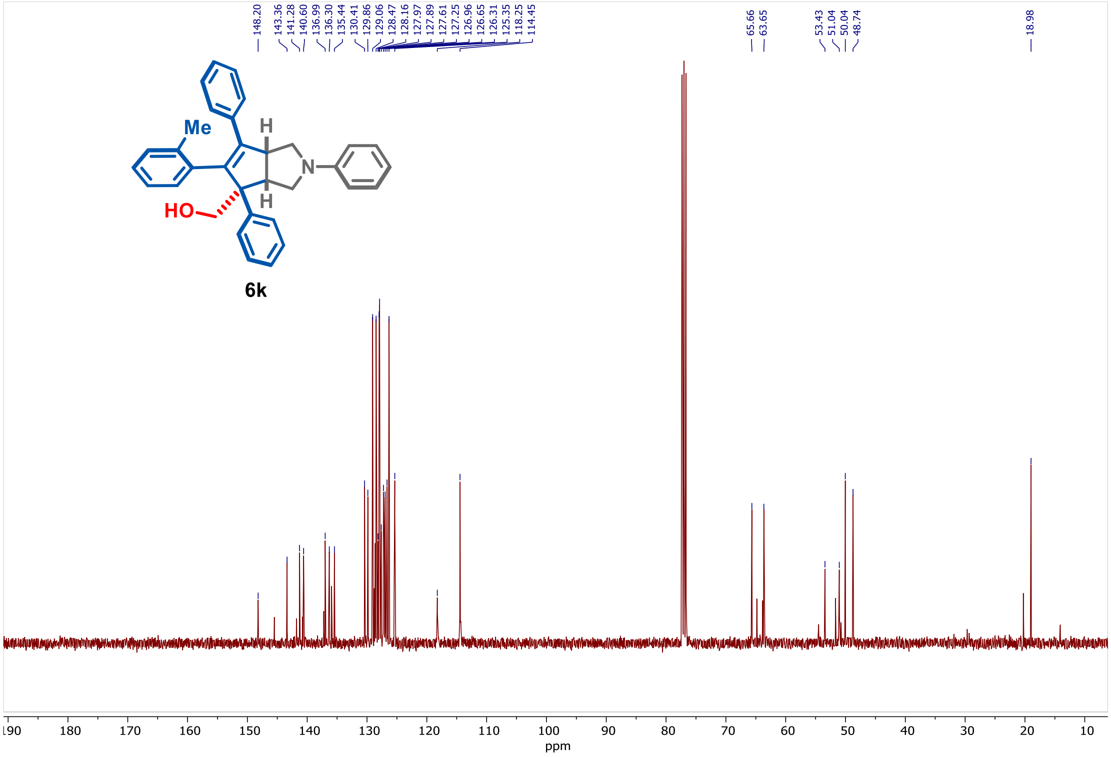
^{13}C-NMR (101 MHz, $CDCl_3$) of compound 6j



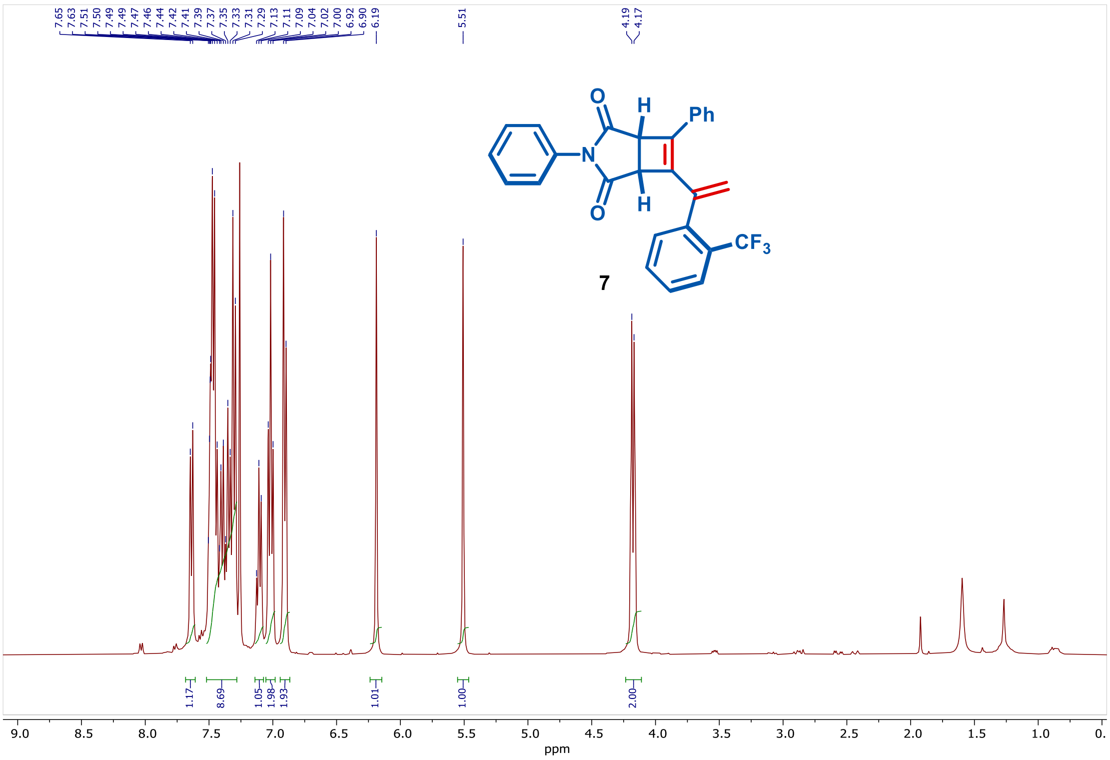
^{1}H-NMR (400 MHz, CDCl$_3$) of compound 6k (see procedure)



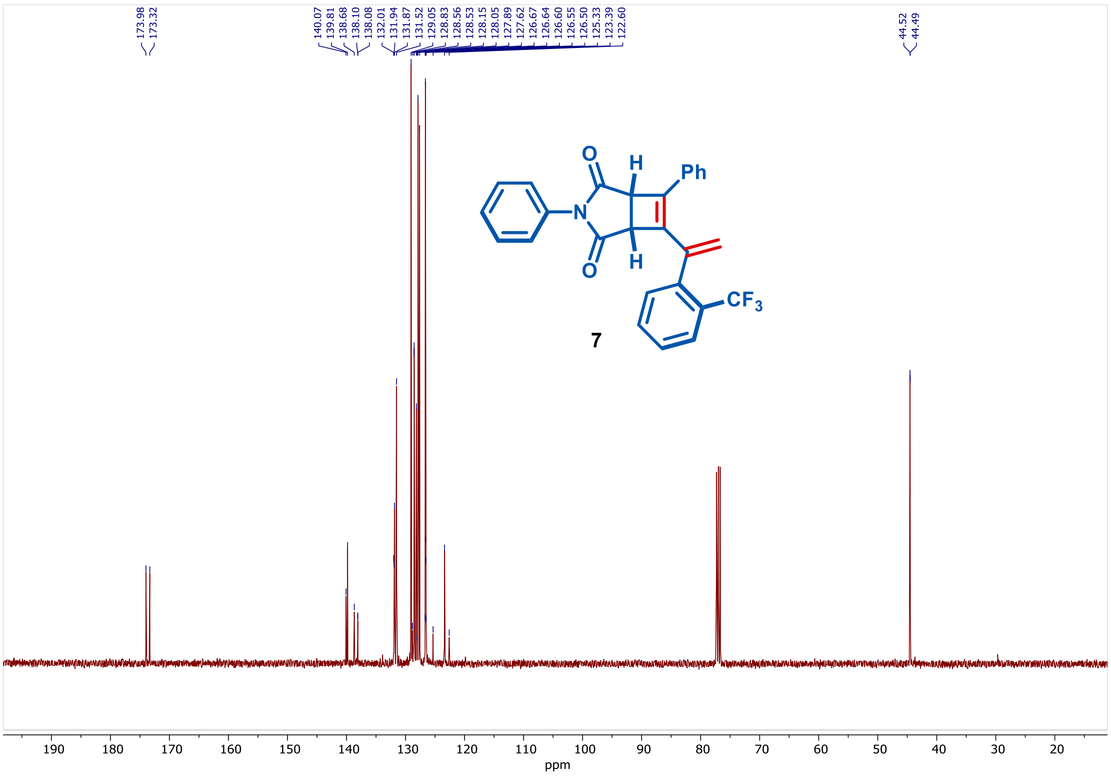
^{13}C-NMR (101 MHz, CDCl$_3$) of compound 6k



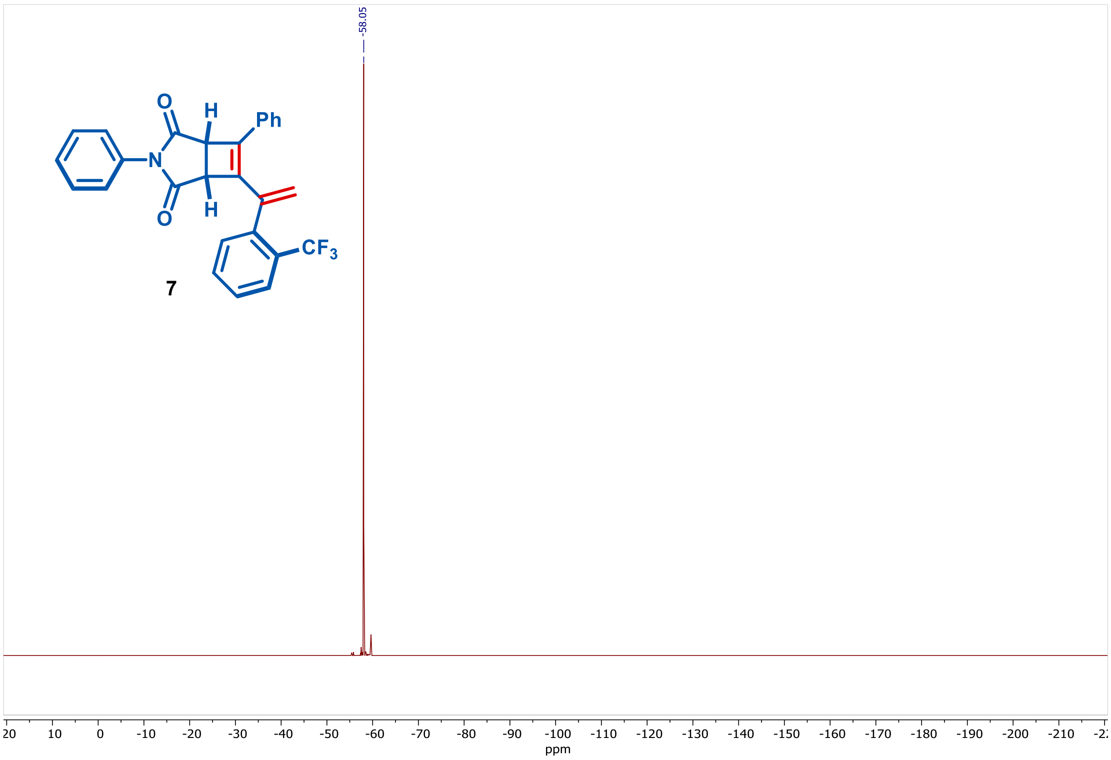
^{1}H-NMR (400 MHz, CDCl$_3$) of compound 7 (see procedure)



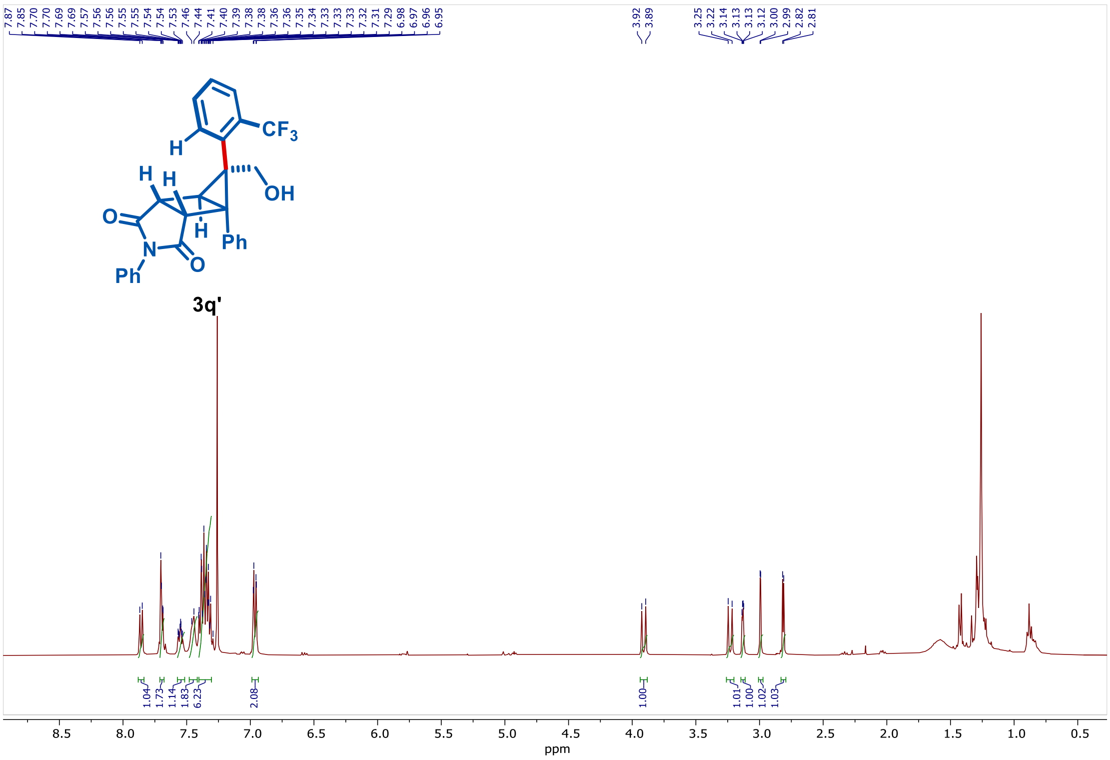
^{13}C-NMR (101 MHz, CDCl$_3$) of compound 7



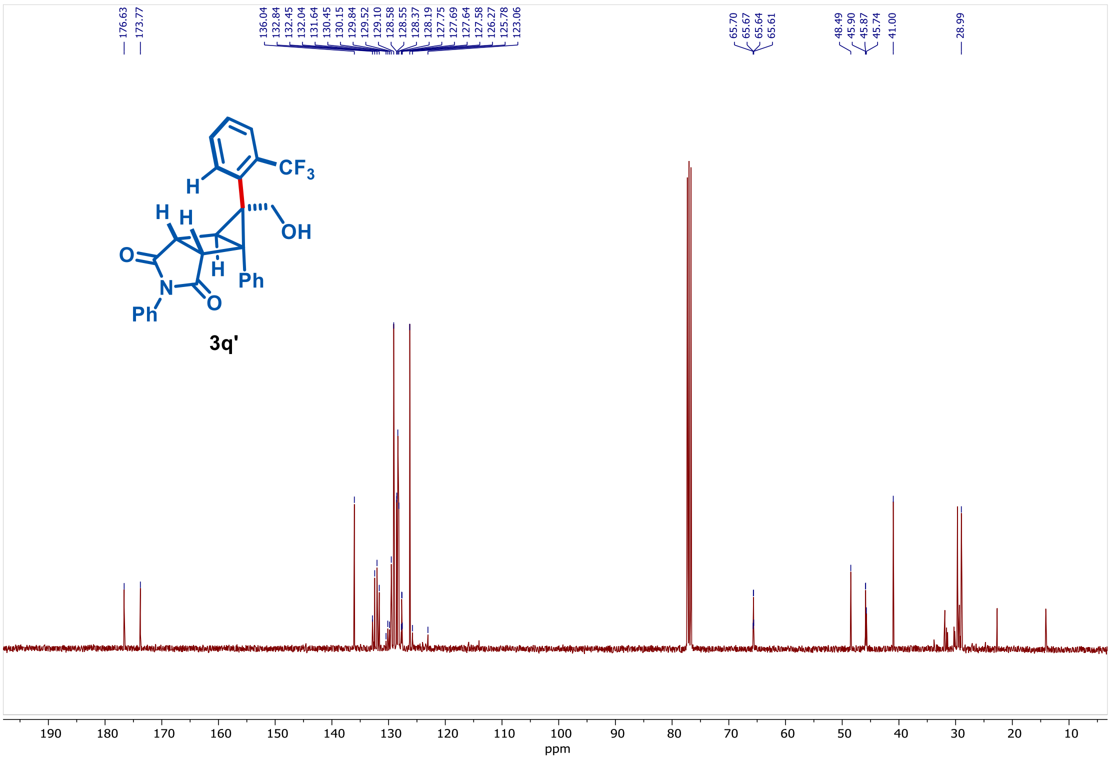
^{19}F-NMR (377 MHz, $CDCl_3$) of compound 7



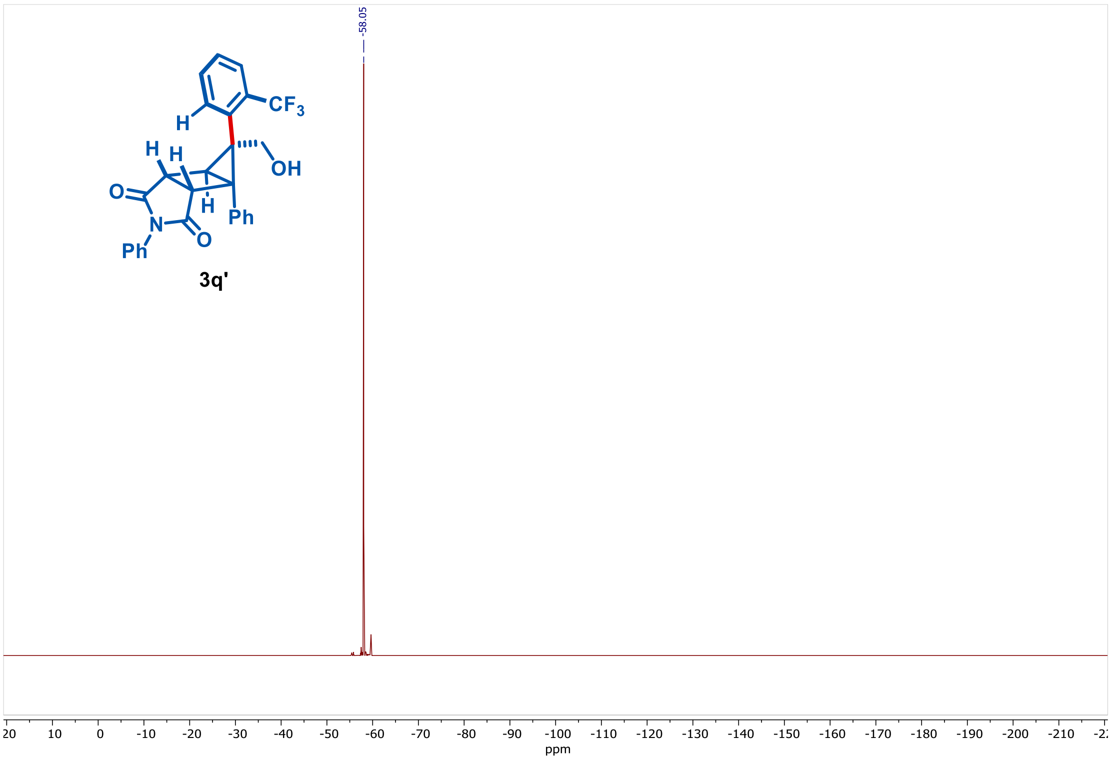
^{1}H-NMR (400 MHz, CDCl$_3$) of compound 3q’ (see procedure)



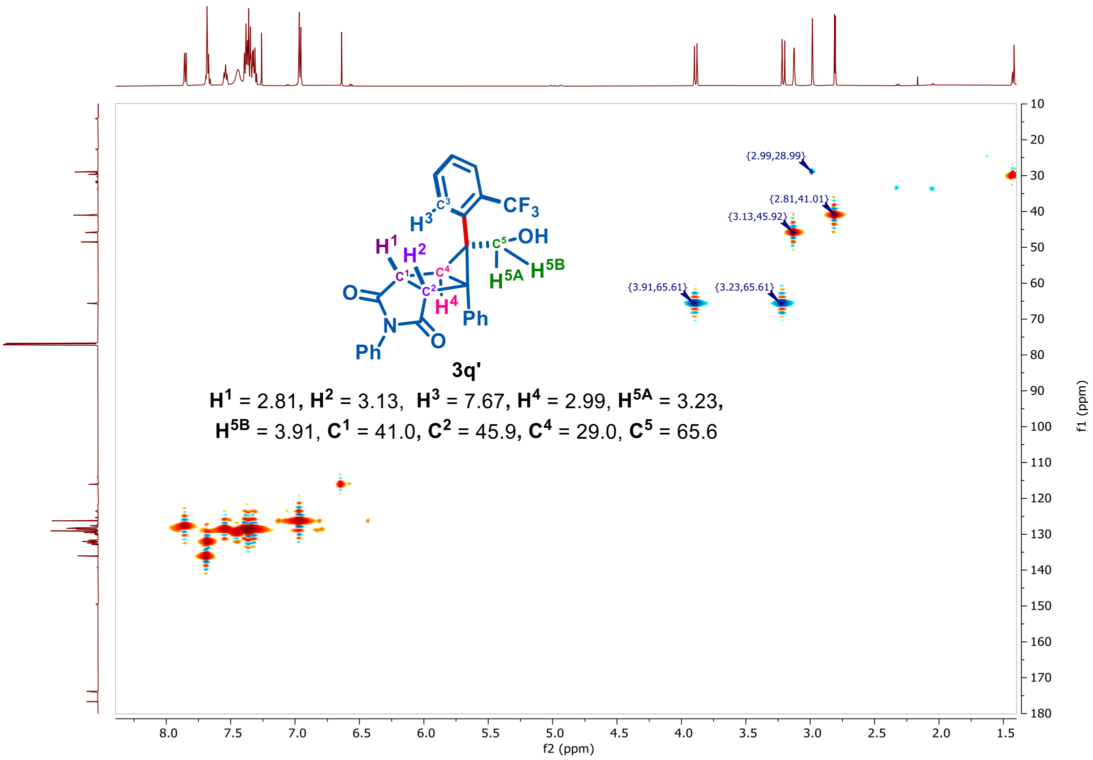
^{13}C-NMR (101 MHz, CDCl$_3$) of compound 3q’



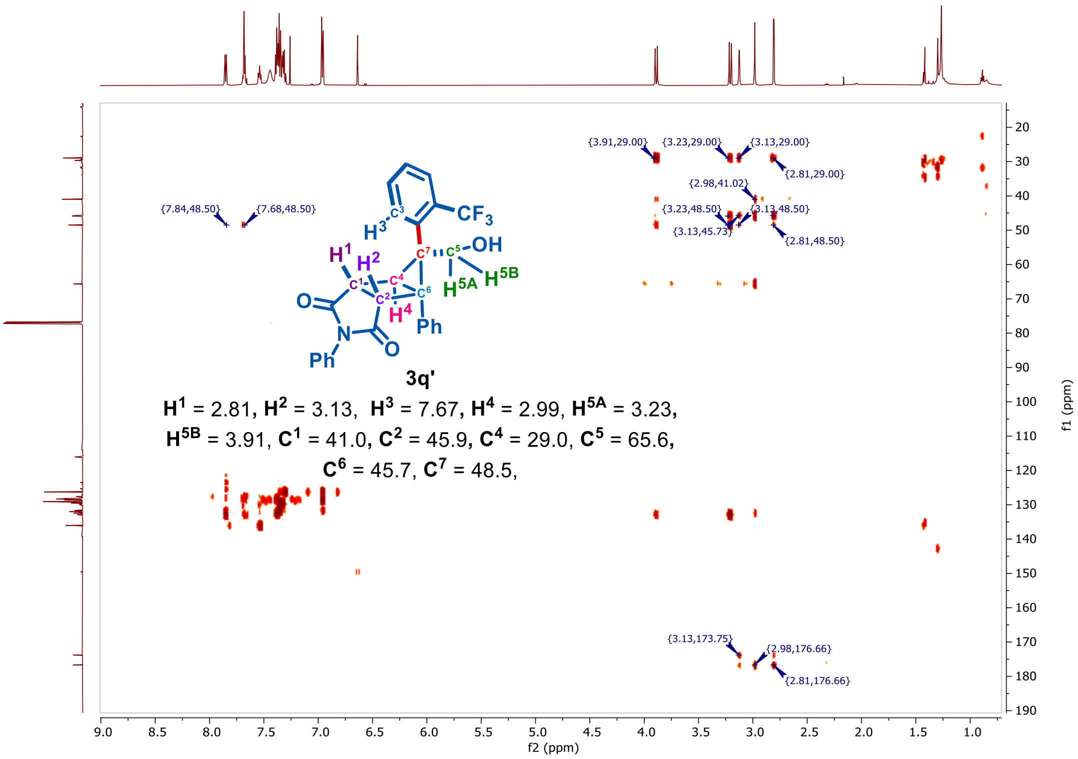
^{19}F-NMR (377 MHz, CDCl$_3$) of compound 3q’



HSQC of compound 3q’

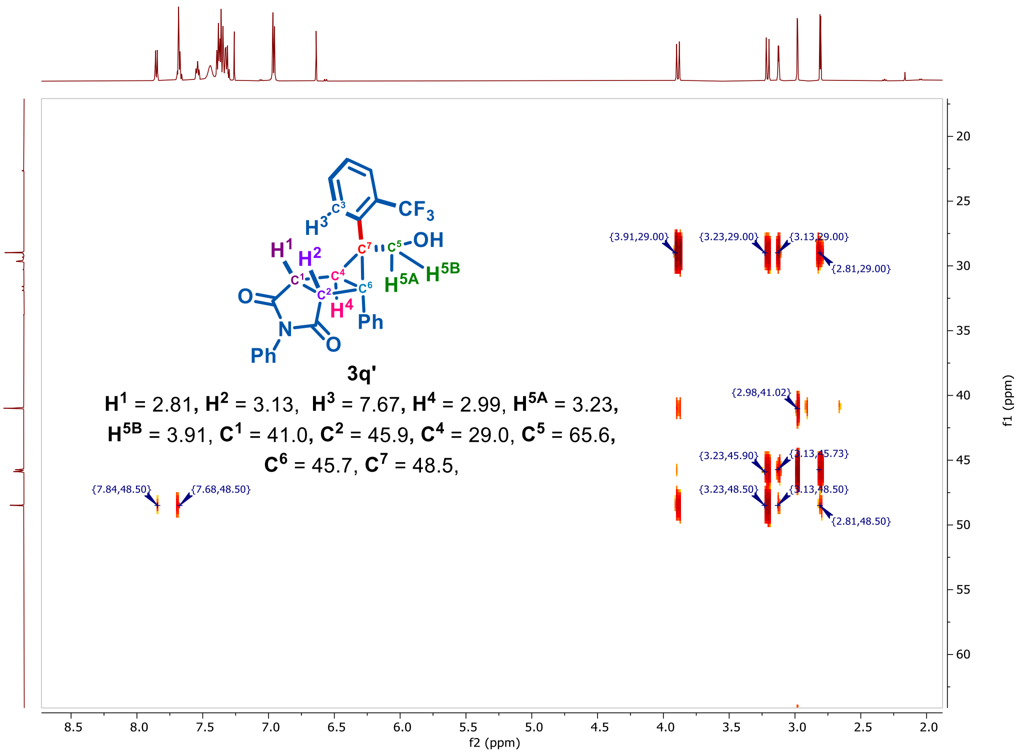


HMBC of compound 3q’



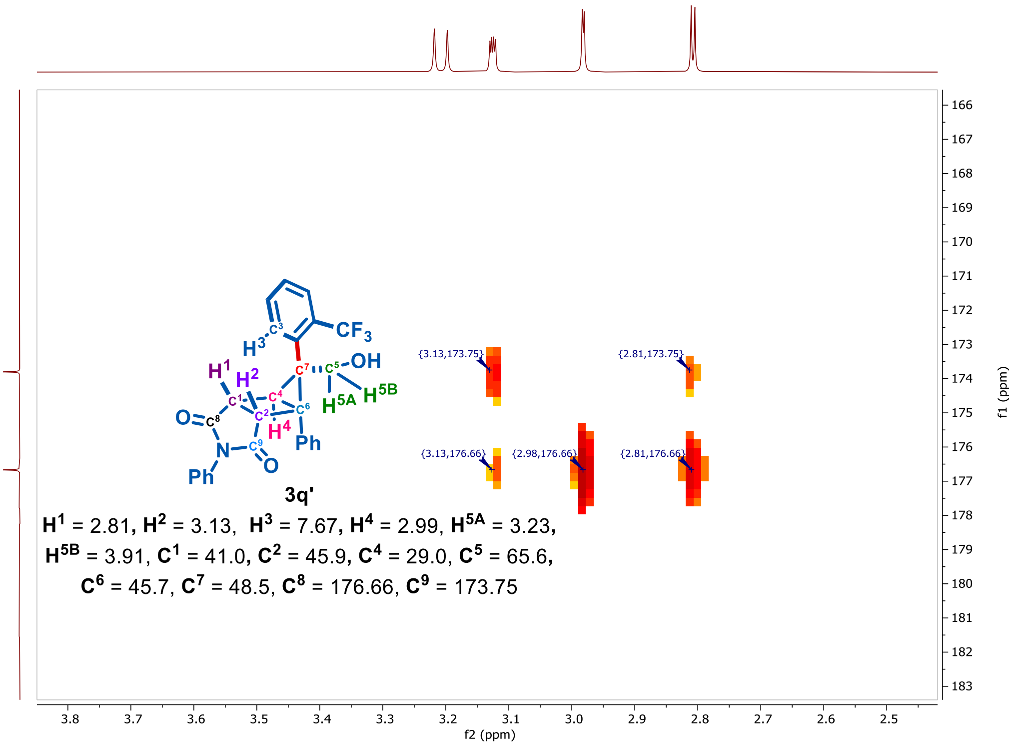
H^1 = 2.81, H^2 = 3.13, H^3 = 7.67, H^4 = 2.99, H^{5A} = 3.23,
H^{5B} = 3.91, C^1 = 41.0, C^2 = 45.9, C^4 = 29.0, C^5 = 65.6,
C^6 = 45.7, C^7 = 48.5,

HMBC of compound 3q’

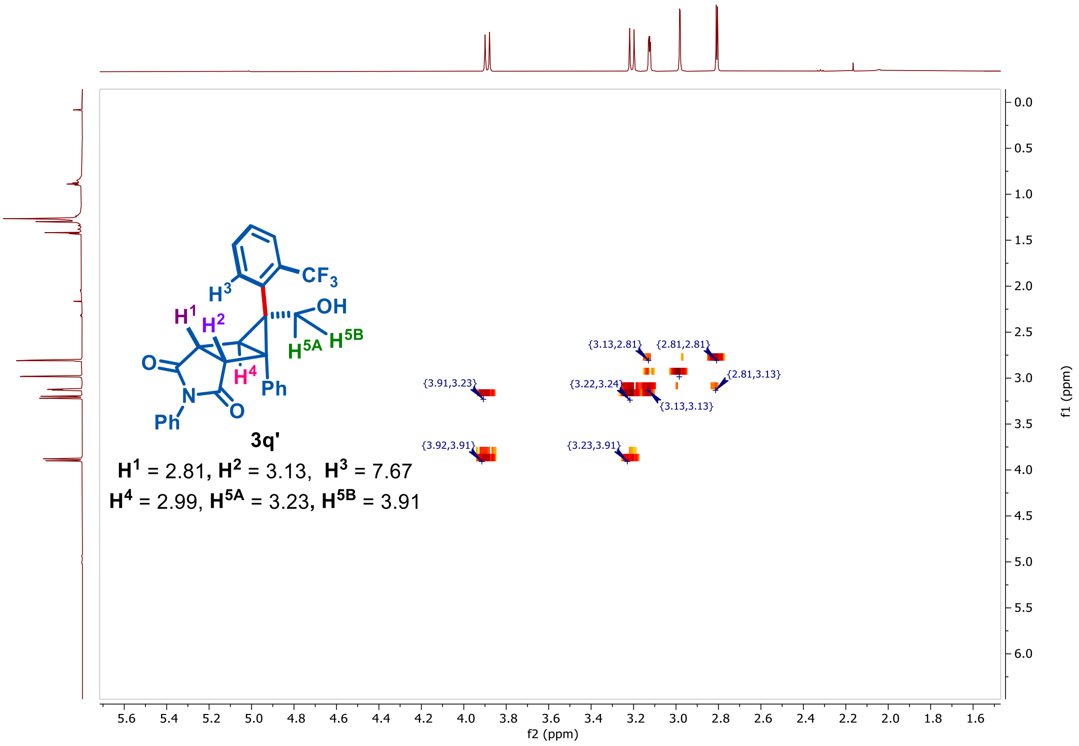


H^1 = 2.81, H^2 = 3.13, H^3 = 7.67, H^4 = 2.99, H^{5A} = 3.23,
H^{5B} = 3.91, C^1 = 41.0, C^2 = 45.9, C^4 = 29.0, C^5 = 65.6,
C^6 = 45.7, C^7 = 48.5,

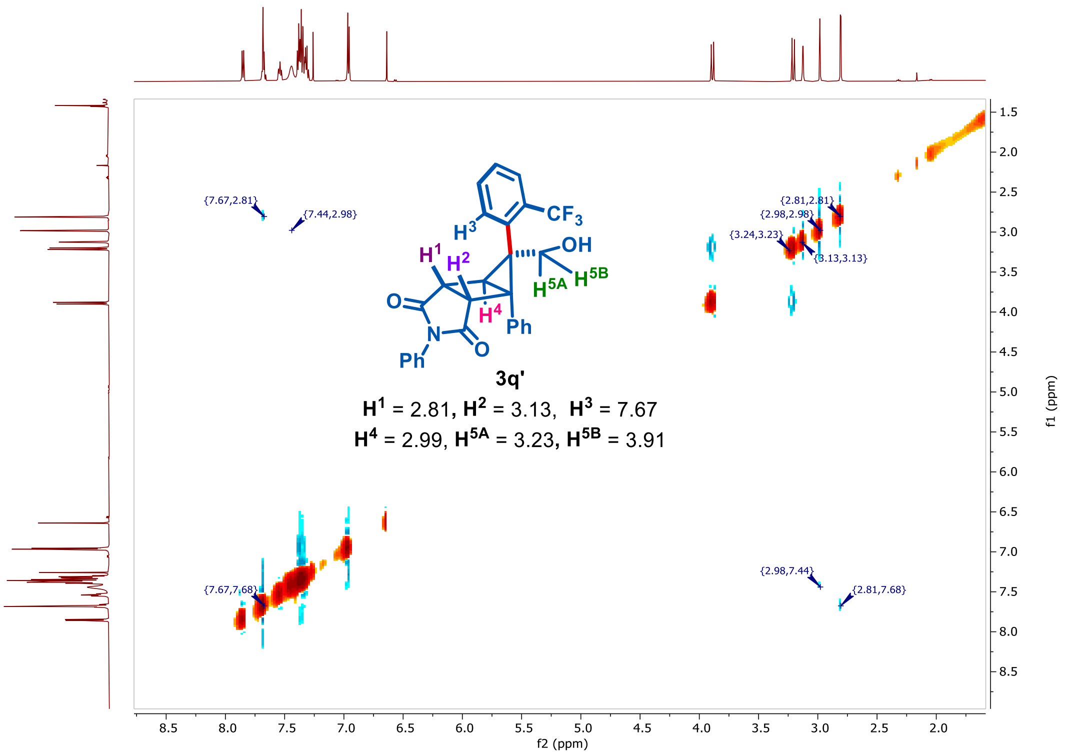
HMBC of compound 3q’



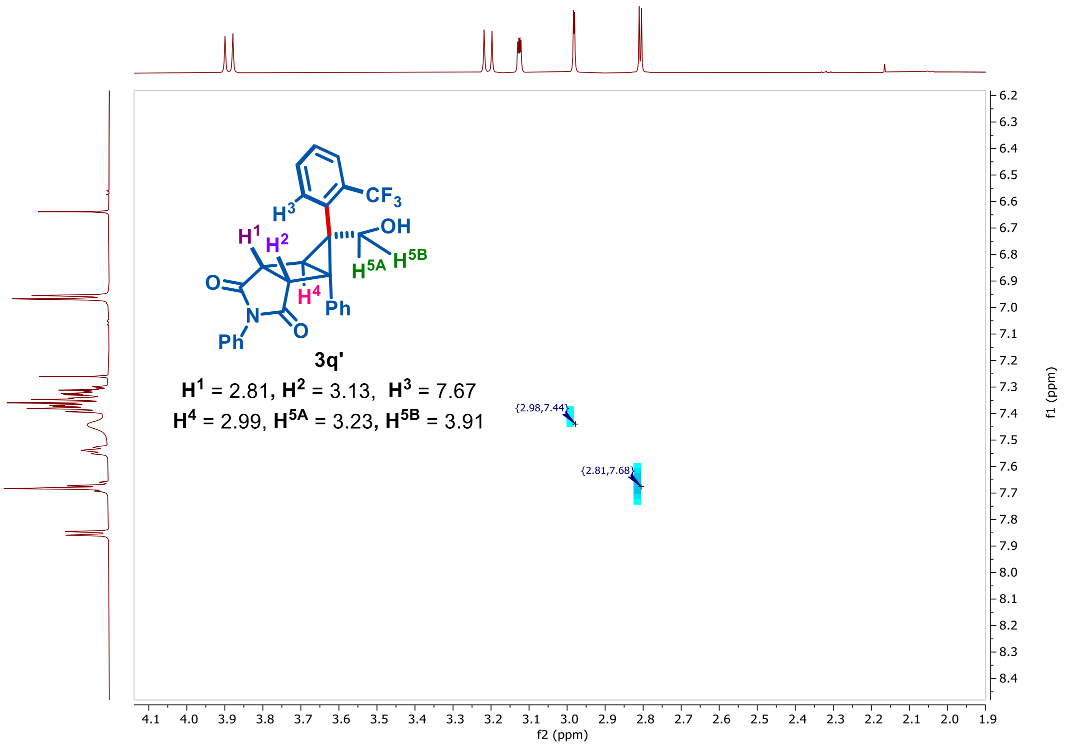
COSY of compound 3q’



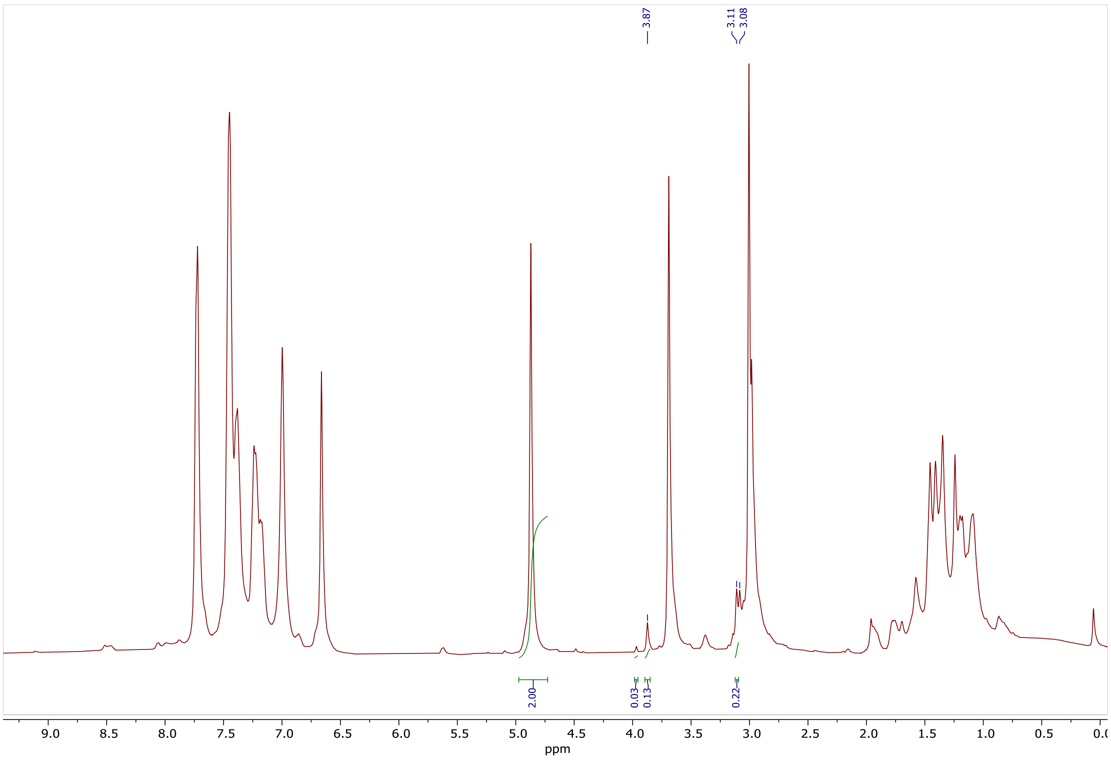
NOESY of compound 3q’



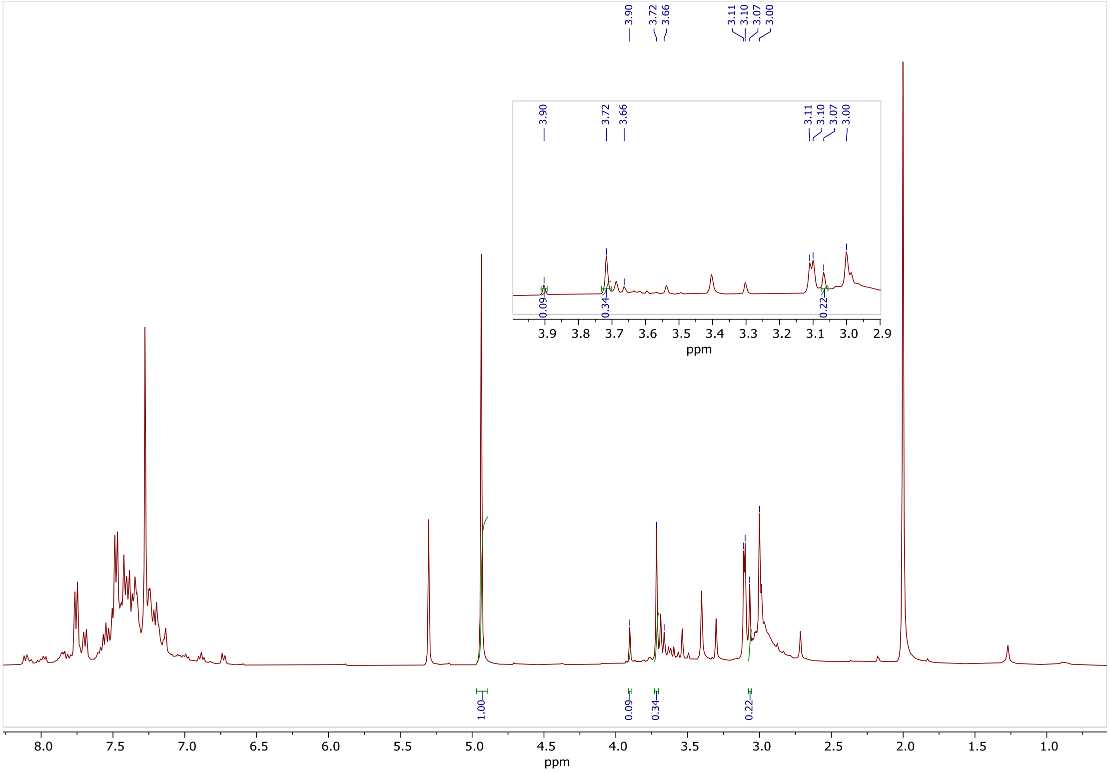
NOESY of compound 3q’



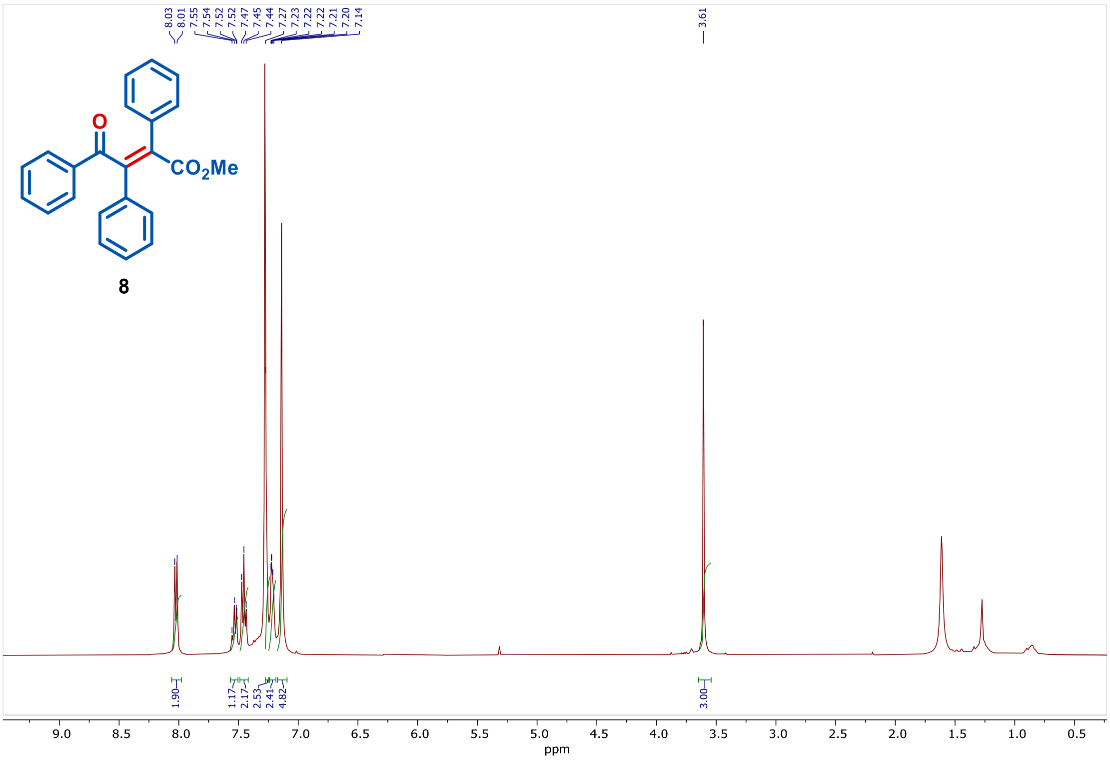
^{1}H-NMR (400 MHz, $CDCl_3$) of TEMPO reaction (see procedure)



^{1}H-NMR (400 MHz, $CDCl_3$) of UV-365 reaction (see procedure)



^{1}H-NMR (400 MHz, $CDCl_3$) of compound 8



^{13}C-NMR (101 MHz, $CDCl_3$) of compound 8