Supporting Information

Palladium-Catalyzed Enantioselective Rearrangement of Dienyl Cyclopropanes

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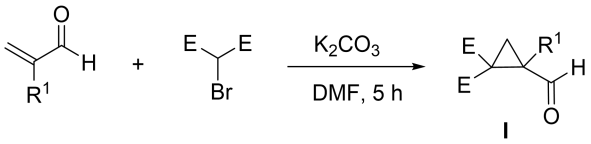
1. General Information

Unless stated otherwise, all reagents were purchased from commercial sources and used without further purification. Solvents were dried and distilled before use by standard procedures. Reactions were monitored by thin layer chromatography (TLC) using silica gel plates. Flash column chromatography was performed over silica gel (200-300 mesh). NMR spectra were recorded on a Bruker Avance operating at for ^{1}H NMR at 400 MHz, ^{13}C NMR at 100 MHz, ^{19}F NMR at 376 MHz and chemical shifts (δ) are reported in ppm relative to those of residual solvent signals: $CDCl_3$ (^{1}H NMR δ 7.26, ^{13}C NMR δ 77.00). All coupling constants (*J*) are reported in Hz. The following abbreviations were used to describe peak splitting patterns when appropriate: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, br = broad. HRMS were recorded on Waters Xevo G2-XS QT of mass spectrometer. The enantiomeric excesses of the products were determined by HPLC analysis on Shimadzu LC-20AT, using Chiralpak AD-H (4.6 mm Φ × 250 mmL), OJ-H (4.6 mm Φ × 250 mmL), AS-H (4.6 mm Φ × 250 mmL), and IC (4.6 mm Φ × 250 mmL) columns purchased from Daicel Chemical Industries.

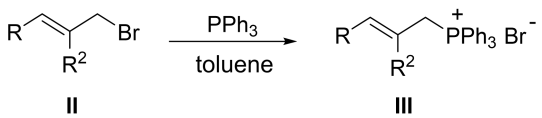
2. Synthesis of substrates 1, 4, 9 and 15

2.1 Procedure A:



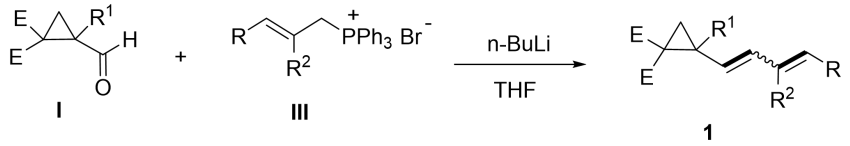
I

(1) To a solution of freshly distilled acrolein (1.2 equiv.) in DMF was added the bromomalonate (1.0 equiv.) followed by K_2CO_3 (2.0 equiv.). The heterogeneous mixture was allowed to stir vigorously until the reaction was completed by TLC analysis (ca. 5 hours). To the resultant mixture was added H_2O and extracted with ethyl acetate. After removal of solvent under reduced pressure, the resulting residue was purified by silica gel flash chromatography (PE/EA = 3:1) to obtain **I**.



II III

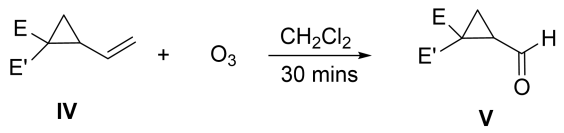
(2) **II** used in this study were prepared according to literature procedures.[1-2] To a solution of bromide **II** (5 mmol) in toluene was added triphenylphosphine (4.4 mmol) in one portion and the mixture was heated to 80 °C with vigorous stirring overnight before the reaction was placed in icewater. The desired product was collected on a filter and dried to give the titled compound **III** as a white solid.



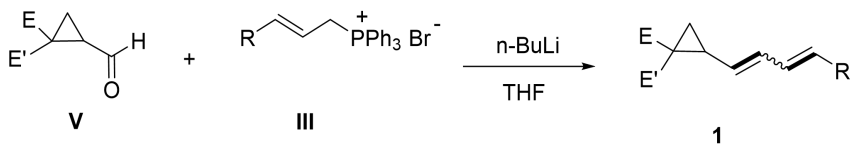
(3) To a suspension of **III** (5 mmol) in dry THF (22 mL) was added n-BuLi (5.8 mmol) dropwise at 0 °C. After stirring for 5 min at 0 °C, a solution of **I** (5.5 mmol, 1.1 equiv.) in THF (10 mL) was introduced. The solution was stirred for 25 minutes at 0 °C, the reaction mixture was added H_2O and extracted with ethyl acetate. After removal of solvent under reduced pressure, the resulting residue was purified by silica gel flash chromatography (PE/EA = 20:1-10:1) to obtain **1**.

The synthesis of substrates **3**, **9** and **15** refers to the method of substrate **1**.

2.2 Procedure B:

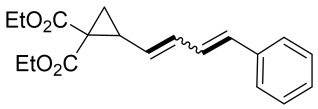


(1) Ozone was vigorously bubbled through a stirred solution of **IV** (7 mmol) at -78 °C in DCM (30 mL) until a blue/purple color persisted. Once the addition of ozone was ceased a steady stream of argon was bubbled through the cool solution for 10 minutes and subsequently treated with Me_2S (3 mL) in one portion, then warmed to room temperature with stirring for 12 hours. The reaction was concentrated in vacuo, diluted with Et_2O (100 mL) and washed with deionized water (50 mL). The aqueous layer was back extracted with Et_2O (2 x 50 mL) and combined organics were washed with brine (50 mL), dried with $MgSO_4$, filtered and concentrated in vacuo. The residue was chromatographed on silica gel eluting with PE:EA=3:1 to afford the desired product **V** as a clear oil.



(2) To a suspension of **III** (5 mmol) in dry THF (22 mL) was added n-BuLi (5.8 mmol) dropwise at 0 °C. After stirring for 5 min at 0 °C, a solution of **V** (5.5 mmol, 1.1 equiv.) in THF (10 mL) was introduced. The solution was stirred for 25 minutes at 0 °C, the reaction mixture was added H_2O and extracted with ethyl acetate. After removal of solvent under reduced pressure, the resulting residue was purified by silica gel flash chromatography (PE/EA = 10:1) to obtain **1**.

3. Characterization and NMR spectra of products 1, 4, 9 and 15

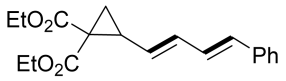


(*E*/*Z*)-diethyl 2-(4-phenylbuta-1,3-dien-1-yl)cyclopropane-1,1-dicarboxylate (1a) was synthesized by following Procedure A. The crude material was purified by normal-phase column chromatography using a gradient eluent of PE/EA (20:1-10:1) to provide **1a** as a yellow oil (943.1 mg, 60% yield).

^{1}H NMR(400 MHz, CDCl3) δ 7.38 – 7.27 (m, 2H), 7.24 – 7.10 (m, 3H), 6.67 – 6.39 (m, 2H), 6.39 – 6.18 (m, 1H), 5.42 – 4.84 (m, 1H), 4.21 – 4.00 (m, 4H), 2.96 – 2.52 (m, 1H), 1.69 – 1.53 (m, 2H), 1.22 – 1.15 (m, 6H).

^{13}C NMR (100 MHz, CDCl3) δ 169.7, 169.5, 167.5, 167.4, 137.1, 134.1, 134.1, 132.7, 132.0, 128.7, 128.6, 128.5, 128.0, 127.7, 127.5, 126.5, 126.3, 126.3, 123.8, 61.7, 61.6, 61.5, 36.5, 36.4, 31.1, 26.9, 21.9, 21.1, 14.2, 14.1, 14.1, 14.0.

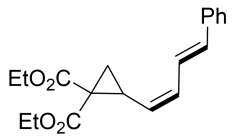
HRMS Exact mass calculated for $[C_{19}H_{22}O_4+Na]^+$ requires *m/z* = 337.1410, found *m/z* = 337.1413 (ESI+).



(*E*)-diethyl-2-((1E,3E)-4-phenylbuta-1,3-dien-1-yl)cyclopropane-1,1-dicarboxylate (E-1a) was purified from **1a** by normal-phase column chromatography using a gradient eluent of PE/EA (50:1-20:1) to provide ***E*-1a** as a yellow oil.

^{1}H NMR (400 MHz, CDCl3) δ 7.28 – 7.09 (m, 5H), 6.61 (dd, *J* = 15.6, 10.5 Hz, 1H), 6.47 – 6.27 (m, 2H), 5.32 (dd, *J* = 15.1, 8.9 Hz, 1H), 4.18 – 4.05 (m, 4H), 2.56 (td, *J* = 8.8, 7.4 Hz, 1H), 1.66 (dd, *J* = 7.5, 4.9 Hz, 1H), 1.53 (dd, *J* = 8.9, 4.9 Hz, 1H), 1.17 (dt, *J* = 8.6, 7.1 Hz, 6H).

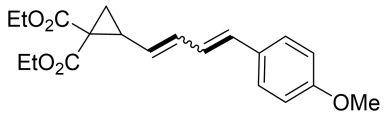
^{13}C NMR (100 MHz, $CDCl_3$) δ 169.5, 167.4, 137.1, 134.1, 132.0, 128.7, 128.3, 128.0, 127.5, 126.3, 61.6, 61.5, 36.4, 31.1, 21.1, 14.2, 14.0.



(*Z*)-diethyl-2-((1Z,3E)-4-phenylbuta-1,3-dien-1-yl)cyclopropane-1,1-dicarboxylate (*Z*-1a)

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40 – 7.31 (m, 2H), 7.26 – 7.03 (m, 4H), 6.51 (d, *J* = 15.5 Hz, 1H), 6.29 – 6.10 (m, 1H), 4.93 (t, *J* = 10.2 Hz, 1H), 4.23 – 4.07 (m, 4H), 2.90 (tdd, *J* = 9.6, 7.0, 1.1 Hz, 1H), 1.65 – 1.56 (m, 2H), 1.24 – 1.15 (m, 6H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 169.7, 167.6, 137.1, 134.1, 132.7, 128.6, 127.8, 126.5, 126.4, 123.8, 61.7, 61.5, 36.4, 26.9, 21.9, 14.1, 14.1.

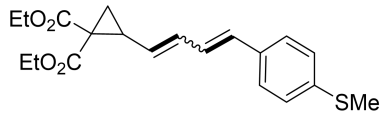


(*E*/*Z*)-diethyl-2-(4-(4-methoxyphenyl)buta-1,3-dien-1-yl)cyclopropane-1,1-dicarboxylate (1b) was synthesized by following Procedure A. The crude material was purified by normal-phase column chromatography using a gradient eluent of PE/EA (20:1-10:1) to provide **1b** as a yellow oil (895.4 mg, 52% yield).

^{1}H NMR (400 MHz, CDCl3) δ 7.43 – 7.27 (m, 2H), 7.06 – 6.81 (m, 2H), 6.69 – 6.16 (m, 3H), 5.39 – 4.92 (m, 1H), 4.51 – 4.04 (m, 4H), 3.81 (d, *J* = 6.0 Hz, 3H), 3.04 – 2.59 (m, 1H), 1.79 – 1.58 (m, 2H), 1.34 – 1.20 (m, 6H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 169.5, 169.5, 169.4, 167.6, 167.5, 167.4, 159.1, 159.1, 158.6, 134.3, 132.9, 132.9, 131.5, 130.0, 129.8, 129.4, 129.1, 127.7, 127.4, 127.3, 127.1, 126.0, 124.7, 122.2, 114.0, 113.9, 113.8, 113.6, 61.5, 61.5, 61.3, 55.1, 55.1, 36.5, 36.4, 36.1, 31.2, 31.2, 27.8, 22.4, 20.9, 14.1, 14.1, 14.0, 13.9.

HRMS Exact mass calculated for $[C_{20}H_{24}O_5+Na]^+$ requires *m/z* = 383.1829, found *m/z* = 383.1830 (ESI+).

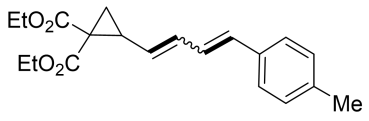


(*E*/*Z*)-diethyl-2-(4-(4-(methylthio)phenyl)buta-1,3-dien-1-yl)cyclopropane-1,1-dicarboxylate (1c) was synthesized by following Procedure A. The crude material was purified by normal-phase column chromatography using a gradient eluent of PE/EA (20:1-10:1) to provide **1c** as a yellow solid (1.05 g, 58% yield).

^{1}H NMR (400 MHz, CDCl3) δ 7.40 – 7.26 (m, 2H), 7.22 – 7.09 (m, 2H), 6.72 – 6.43 (m, 2H), 6.43 – 6.21 (m, 1H), 5.48 – 4.91 (m, 1H), 4.21 (dddd, *J* = 17.3, 10.9, 6.9, 3.7 Hz, 4H), 3.01 – 2.60 (m, 1H), 2.48 (d, *J* = 5.8 Hz, 3H), 1.74 – 1.61 (m, 2H), 1.26 (dt, *J* = 8.6, 7.1 Hz, 6H).

^{13}C NMR (100 MHz, CDCl3) δ 169.5, 167.5, 167.5, 138.1, 137.7, 134.1, 134.1, 134.0, 133.4, 132.7, 131.3, 128.5, 127.5, 126.9, 126.7, 126.7, 126.6, 126.5, 126.1, 123.2, 61.7, 61.6, 61.5, 36.5, 36.4, 31.2, 26.9, 21.9, 21.1, 15.7, 15.7, 15.7, 14.2, 14.1, 14.1, 14.0.

HRMS Exact mass calculated for $[C_{20}H_{24}O_4S+Na]^+$ requires *m/z* = 383.1288, found *m/z* = 383.1291 (ESI+).

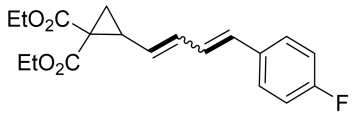


(*E*/*Z*)-diethyl 2-(4-(p-tolyl)buta-1,3-dien-1-yl)cyclopropane-1,1-dicarboxylate (1d) was synthesized by following Procedure A. The crude material was purified by normal-phase column chromatography using a gradient eluent of PE/EA (20:1-10:1) to provide **1d** as a yellow solid (853.9 mg, 52% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37 – 7.26 (m, 2H), 7.12 (t, *J* = 8.6 Hz, 2H), 6.77 – 6.53 (m, 1H), 6.53 – 6.20 (m, 2H), 5.44 – 4.90 (m, 1H), 4.49 – 3.94 (m, 4H), 3.05 – 2.59 (m, 1H), 2.34 (d, *J* = 6.6 Hz, 3H), 1.81 – 1.61 (m, 2H), 1.32 – 1.23 (m, 6H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 169.5, 167.4, 137.7, 137.4, 134.3, 134.2, 134.0, 132.8, 131.9, 129.3, 129.3, 128.0, 127.1, 126.4, 126.2, 125.7, 122.8, 61.7, 61.6, 61.4, 36.4, 36.4, 31.2, 26.9, 21.9, 21.2, 21.2, 21.1, 14.2, 14.1, 14.0, 14.0.

HRMS Exact mass calculated for $[C_{10}H_{24}O_4+Na]^+$ requires *m/z* = 351.1567, found *m/z* = 351.1563 (ESI+).



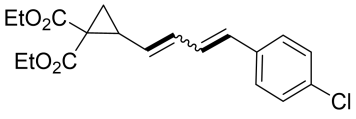
(*E*/*Z*)-diethyl-2-(4-(4-fluorophenyl)buta-1,3-dien-1-yl)cyclopropane-1,1-dicarboxylate (1e) was synthesized by following Procedure A. The crude material was purified by normal-phase column chromatography using a gradient eluent of PE/EA (20:1-10:1) to provide **1e** as a yellow solid (830.9 mg, 50% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.32 – 7.22 (m, 2H), 6.97 – 6.88 (m, 2H), 6.56 – 6.44 (m, 1H), 6.41 – 6.15 (m, 2H), 5.39 – 4.92 (m, 1H), 4.21 – 4.09 (m, 4H), 2.91 – 2.53 (m, 1H), 1.69 – 1.55 (m, 2H), 1.22 – 1.15 (m, 6H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 169.7, 169.5, 167.5, 167.4, 163.4, 161.0, 133.9, 133.3, 133.3, 132.8, 132.5, 130.7, 128.8, 128.7, 128.1, 128.0, 127.8, 127.8, 127.8, 127.7, 126.4, 123.6, 123.6, 115.6, 115.6, 115.4, 115.4, 61.7, 61.6, 61.5, 36.4, 31.1, 26.8, 21.9, 21.1, 14.2, 14.1, 14.0, 14.0.

^{19}F NMR (376 MHz, $CDCl_3$) δ -114.04 (d, *J* = 135.7 Hz).

HRMS Exact mass calculated for $[C_{19}H_{21}FO_4+Na]^+$ requires *m/z* = 355.1316, found *m/z* = 355.1320 (ESI+).



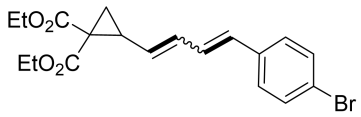
(*E*/*Z*)-diethyl-2-(4-(4-chlorophenyl)buta-1,3-dien-1-yl)cyclopropane-1,1-dicarboxylate (1f) was synthesized by following Procedure A. The crude material was purified

by normal-phase column chromatography using a gradient eluent of PE/EA (20:1-10:1) to provide **1f** as a yellow solid (959.3 mg, 55% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38 – 7.28 (m, 2H), 7.27 – 7.09 (m, 2H), 6.70 – 6.24 (m, 3H), 5.47 – 5.01 (m, 1H), 4.29 – 4.15 (m, 4H), 3.00 – 2.57 (m, 1H), 1.77 – 1.62 (m, 2H), 1.30 – 1.20 (m, 6H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 169.6, 169.4, 167.5, 167.4, 135.6, 135.6, 133.8, 133.3, 133.0, 132.6, 132.3, 130.6, 129.4, 128.7, 128.7, 128.6, 127.7, 127.4, 127.0, 124.3, 61.6, 61.5, 36.5, 31.0, 26.8, 21.9, 21.1, 14.2, 14.1, 14.1, 14.0.

HRMS Exact mass calculated for $[C_{19}H_{21}ClO_4+Na]^+$ requires *m/z* = 371.1021, found *m/z* = 371.1024 (ESI+).

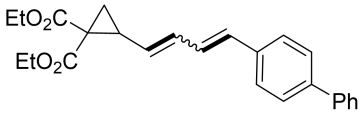


(*E*/*Z*)-diethyl-2-(4-(4-bromophenyl)buta-1,3-dien-1-yl)cyclopropane-1,1-dicarboxylate (1g) was synthesized by following Procedure A. The crude material was purified by normal-phase column chromatography using a gradient eluent of PE/EA (20:1-10:1) to provide **1g** as a yellow solid (983.2 mg, 50% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.45 – 7.35 (m, 2H), 7.28 – 7.20 (m, 2H), 6.76 – 6.21 (m, 3H), 5.49 – 4.99 (m, 1H), 4.29 – 4.15 (m, 4H), 3.00 – 2.57 (m, 1H), 1.76 – 1.62 (m, 2H), 1.30 – 1.23 (m, 6H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 169.5, 169.4, 167.5, 167.4, 137.1, 136.1, 134.1, 133.8, 132.7, 132.3, 132.0, 131.7, 131.7, 130.6, 129.6, 128.8, 128.7, 128.6, 128.6, 128.1, 128.0, 127.8, 127.5, 127.1, 126.5, 126.3, 124.5, 123.8, 121.2, 61.8, 61.7, 61.6, 61.5, 61.5, 36.5, 31.1, 31.0, 26.8, 21.9, 21.1, 14.2, 14.1, 14.1, 14.1.

HRMS Exact mass calculated for $[C_{19}H_{21}BrO_4+Na]^+$ requires *m/z* = 415.0515, found *m/z* = 415.0517 (ESI+).



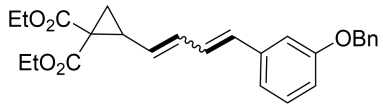
(*E*/*Z*)-diethyl-2-(4-([1,1'-biphenyl]-4-yl)buta-1,3-dien-1-yl)cyclopropane-1,1-dicarboxylate (1h) was synthesized by following Procedure A. The crude material was

purified by normal-phase column chromatography using a gradient eluent of PE/EA (20:1-10:1) to provide **1h** as a yellow solid (1.02 g, 52% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.57 – 7.29 (m, 9H), 6.97 – 5.97 (m, 3H), 5.53 – 4.70 (m, 1H), 4.13 (tddd, *J* = 17.9, 10.7, 6.2, 2.5 Hz, 4H), 2.96 – 2.48 (m, 1H), 1.73 – 1.48 (m, 2H), 1.22 – 1.14 (m, 6H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 169.5, 169.5, 167.5, 167.5, 140.6, 140.2, 140.2, 136.3, 136.2, 134.2, 134.1, 132.7, 132.4, 132.2, 131.5, 129.0, 128.9, 128.8, 128.8, 128.7, 128.2, 127.7, 127.3, 127.2, 127.1, 126.8, 126.8, 126.7, 61.7, 61.5, 61.5, 36.6, 36.5, 31.3, 31.2, 21.2, 21.1, 14.2, 14.1.

HRMS Exact mass calculated for $[C_{25}H_{26}O_4+H]^+$ requires *m/z* = 391.1904, found *m/z* = 391.1905 (ESI+).

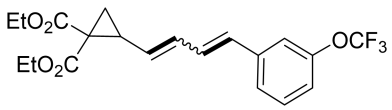


(*E*/*Z*)-diethyl-2-(4-(4-(benzyloxy)phenyl)buta-1,3-dien-1-yl)cyclopropane-1,1-dicarboxylate (1i) was synthesized by following Procedure A. The crude material was purified by normal-phase column chromatography using a gradient eluent of PE/EA (20:1-10:1) to provide **1i** as a yellow solid (1.11 g, 53% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.48 – 7.19 (m, 7H), 7.13 – 6.95 (m, 2H), 6.91 – 6.77 (m, 1H), 6.72 – 6.50 (m, 1H), 6.46 – 6.25 (m, 1H), 5.48 – 4.92 (m, 3H), 4.49 – 3.99 (m, 4H), 3.02 – 2.59 (m, 1H), 1.82 – 1.58 (m, 2H), 1.34 – 1.16 (m, 6H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 169.5, 167.6, 167.5, 159.0, 138.6, 136.9, 134.0, 133.9, 132.6, 131.8, 129.6, 129.6, 129.0, 128.6, 128.5, 128.0, 127.5, 127.5, 126.6, 124.2, 119.6, 119.3, 114.2, 114.0, 112.9, 112.6, 77.2, 70.0, 70.0, 61.7, 61.7, 61.5, 36.5, 36.4, 31.1, 26.9, 22.0, 21.1, 14.2, 14.2, 14.1.

HRMS Exact mass calculated for $[C_{26}H_{28}O_5+Na]^+$ requires *m/z* = 443.1829, found *m/z* = 443.1834 (ESI+).



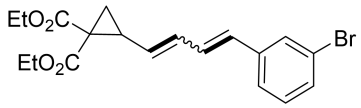
(*E*/*Z*)-diethyl-2-(4-(3-(trifluoromethoxy)phenyl)buta-1,3-dien-1-yl)cyclopropane-1,1-dicarboxylate (1j) was synthesized by following Procedure A. The crude material was purified by normal-phase column chromatography using a gradient eluent of PE/EA (20:1- 10:1 to provide **1j** as a yellow solid (1.08 g, 54% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.36 – 7.26 (m, 2H), 7.23 – 7.00 (m, 2H), 6.77 – 6.46 (m, 2H), 6.45 – 6.25 (m, 1H), 5.54 – 4.99 (m, 1H), 4.49 – 3.96 (m, 4H), 3.05 – 2.52 (m, 1H), 1.78 – 1.60 (m, 2H), 1.35 – 1.12 (m, 6H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 169.6, 169.4, 167.5, 167.4, 149.6, 149.6, 139.3, 139.3, 133.5, 132.4, 132.1, 130.3, 129.9, 129.8, 129.7, 127.8, 125.4, 124.8, 124.7, 121.7, 119.9, 119.6, 119.2, 118.8, 118.4, 61.8, 61.7, 61.5, 36.5, 36.5, 31.0, 26.7, 21.9, 21.1, 14.2, 14.1, 14.0.

^{19}F NMR (376 MHz, $CDCl_3$) δ -57.70 (d, J = 2.6 Hz).

HRMS Exact mass calculated for $[C_{20}H_{21}F_3O_5+Na]^+$ requires *m/z* = 421.1233, found *m/z* = 421.1237 (ESI+).

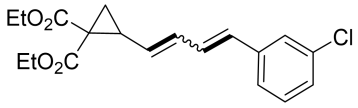


(*E*/*Z*)-diethyl-2-(4-(3-bromophenyl)buta-1,3-dien-1-yl)cyclopropane-1,1-dicarboxylate (1k) was synthesized by following Procedure A. The crude material was purified by normal-phase column chromatography using a gradient eluent of PE/EA (20:1-10:1) to provide **1k** as a white solid (1.02 g, 52% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.56 – 7.07 (m, 5H), 6.68 – 6.30 (m, 2H), 5.52 – 5.02 (m, 1H), 4.72 – 3.64 (m, 4H), 3.03 – 2.55 (m, 1H), 1.78 – 1.59 (m, 2H), 1.39 – 1.16 (m, 6H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 169.7, 169.5, 169.5, 167.6, 167.5, 143.2, 143.2, 137.1, 137.0, 134.4, 134.2, 134.1, 132.8, 132.7, 132.3, 132.2, 132.0, 128.8, 128.7, 128.6, 128.6, 128.6, 128.5, 128.5, 128.4, 128.1, 128.1, 128.0, 127.8, 127.8, 127.5, 126.6, 126.5, 126.4, 126.4, 126.3, 126.1, 125.8, 124.0, 123.8, 123.7, 123.5, 61.7, 61.6, 61.5, 36.5, 35.6, 33.6, 31.2, 31.1, 27.0, 26.9, 22.4, 22.4, 22.0, 21.1, 14.2, 14.1, 14.1, 14.6, 13.9.

HRMS Exact mass calculated for $[C_{19}H_{21}BrO_4+Na]^+$ requires *m/z* = 415.0515, found *m/z* = 415.0517 (ESI+).

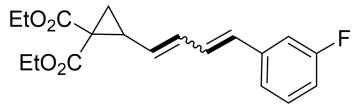


(*E*/*Z*)-diethyl-2-(4-(3-chlorophenyl)buta-1,3-dien-1-yl)cyclopropane-1,1-dicarboxylate (1l) was synthesized by following Procedure A. The crude material was purified by normal-phase column chromatography using a gradient eluent of PE/EA (20:1-10:1) to provide **1l** as a white solid (994.1 mg, 57% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40 – 7.30 (m, 1H), 7.26 – 7.10 (m, 3H), 6.82 – 6.09 (m, 3H), 5.50 – 5.02 (m, 1H), 4.32 – 4.10 (m, 4H), 3.01 – 2.60 (m, 1H), 1.76 – 1.62 (m, 2H), 1.35 – 1.21 (m, 6H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 169.6, 169.4, 167.5, 167.4, 139.0, 134.5, 134.5, 133.6, 132.5, 132.2, 130.4, 130.0, 129.8, 129.8, 129.4, 127.6, 127.5, 127.3, 126.3, 126.1, 125.1, 124.7, 124.5, 61.7, 61.5, 36.5, 31.0, 26.8, 21.9, 21.1, 14.2, 14.1, 14.1, 14.0.

HRMS Exact mass calculated for $[C_{19}H_{21}ClO_4+Na]^+$ requires *m/z* = 371.1021, found *m/z* = 371.1025 (ESI+).



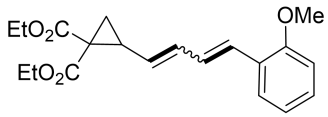
(*E*/*Z*)-diethyl-2-(4-(3-fluorophenyl)buta-1,3-dien-1-yl)cyclopropane-1,1-dicarboxylate (1m) was synthesized by following Procedure A. The crude material was purified by normal-phase column chromatography using a gradient eluent of PE/EA (20:1-10:1) to provide **1m** as a yellow solid (830.9 mg, 50% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.26 – 7.03 (m, 3H), 6.91 (qd, *J* = 9.7, 5.3 Hz, 1H), 6.77 – 6.53 (m, 1H), 6.52 – 6.08 (m, 2H), 5.54 – 5.01 (m, 1H), 4.30 – 4.07 (m, 4H), 3.06 – 2.48 (m, 1H), 1.78 – 1.62 (m, 2H), 1.34 – 1.18 (m, 6H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 169.6, 169.4, 167.5, 167.4, 164.3, 161.8, 139.5, 139.5, 139.4, 133.6, 132.8, 132.7, 132.2, 130.7, 130.6, 130.0, 130.0, 130.0, 129.9, 129.9, 129.3, 129.0, 128.2, 127.4, 125.0, 122.4, 122.4, 122.2, 122.2, 114.6, 114.4, 114.4, 114.1, 112.9, 112.7, 112.6, 112.4, 61.8, 61.7, 61.5, 36.5, 31.0, 26.8, 21.9. 21.1, 14.2, 14.1, 14.1, 14.03

^{19}F NMR (376 MHz, $CDCl_3$) δ -113.51 (d, *J* = 21.9 Hz).

HRMS Exact mass calculated for $[C_{19}H_{21}FO_4+Na]^+$ requires *m/z* = 355.1316, found *m/z* = 355.1320 (ESI+).

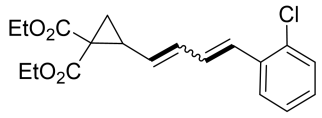


(*E*/*Z*)-diethyl-2-(4-(2-methoxyphenyl)buta-1,3-dien-1-yl)cyclopropane-1,1-dicarboxylate (1n) was synthesized by following Procedure A. The crude material was purified by normal-phase column chromatography using a gradient eluent of PE/EA (20:1-10:1) to provide **1n** as a white solid (981.6 mg, 57% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.54 – 7.41 (m, 1H), 7.22 – 7.17 (m, 1H), 7.05 – 6.61 (m, 4H), 6.53 – 6.30 (m, 1H), 5.55 – 4.85 (m, 1H), 4.28 – 4.15 (m, 4H), 3.84 (d, *J* = 4.4 Hz, 3H), 3.09 – 2.52 (m, 1H), 1.77 – 1.61 (m, 2H), 1.32 – 1.24 (m, 6H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 169.6, 169.4, 167.5, 167.4, 156.7, 156.6, 134.9, 133.4, 128.8, 128.7, 128.6, 128.6, 128.4, 127.9, 126.8, 126.6, 126.3, 126.0, 126.0, 125.5, 124.4, 120.6, 120.5, 110.8, 61.5, 61.5, 61.4, 61.3, 55.3, 36.4, 36.3, 31.1, 26.9, 21.8, 21.0, 14.1, 14.0, 14.0, 14.0.

HRMS Exact mass calculated for $[C_{20}H_{24}O_5+Na]^+$ requires *m/z* = 367.1516, found *m/z* = 367.1518 (ESI+).

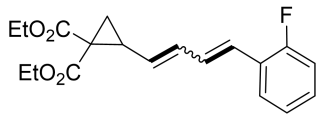


(*E*/*Z*)-diethyl-2-(4-(2-chlorophenyl)buta-1,3-dien-1-yl)cyclopropane-1,1-dicarboxylate (1o) was synthesized by following Procedure A. The crude material was purified by normal-phase column chromatography using a gradient eluent of PE/EA (20:1-10:1) to provide **1o** as a white solid (1.01 g, 58% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.41 – 7.15 (m, 4H), 6.75 – 6.40 (m, 2H), 6.43 – 6.16 (m, 1H), 5.51 – 4.97 (m, 1H), 4.36 – 4.07 (m, 4H), 3.03 – 2.53 (m, 1H), 1.80 – 1.60 (m, 2H), 1.26 (dp, *J* = 10.7, 3.7 Hz, 6H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 169.6, 169.4, 167.4, 139.0, 134.5, 133.6, 132.5, 132.2, 130.4, 130.0, 129.8, 129.8, 129.4, 127.6, 127.5, 127.3, 126.3, 126.1, 125.1, 124.7, 124.5, 61.7, 61.5, 36.5, 31.0, 26.8, 21.9, 21.1, 14.2, 14.0.

HRMS Exact mass calculated for $[C_{19}H_{21}ClO_4+Na]^+$ requires *m/z* = 371.1021, found *m/z* = 371.1025 (ESI+).



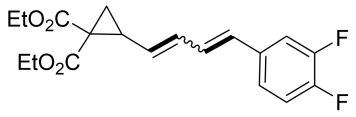
(*E*/*Z*)-diethyl-2-(4-(2-fluorophenyl)buta-1,3-dien-1-yl)cyclopropane-1,1-dicarboxylate (1p) was synthesized by following Procedure A. The crude material was purified by normal-phase column chromatography using a gradient eluent of PE/EA (20:1-10:1) to provide **1p** as a white solid (894.7 mg, 54% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.56 – 7.39 (m, 1H), 7.25 – 6.75 (m, 4H), 6.74 – 6.60 (m, 1H), 6.51 – 6.27 (m, 1H), 5.55 – 4.97 (m, 1H), 4.29 – 4.13 (m, 4H), 3.08 – 2.57 (m, 1H), 1.77 – 1.61 (m, 2H), 1.31 – 1.22 (m, 6H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 169.6, 169.4, 167.5, 167.4, 161.4, 158.9, 134.2, 132.8, 130.4, 130.3, 129.6, 128.9, 128.8, 128.6, 128.6, 127.2, 127.1, 127.0, 127.0, 126.9, 126.1, 126.1, 126.0, 125.9, 125.0, 124.9, 124.2, 124.1, 124.1, 124.1, 124.0, 124.0, 115.8, 115.6, 61.7, 61.6, 61.5, 36.4, 31.0, 26.8, 21.9, 21.1, 14.1, 14.1, 14.0.

^{19}F NMR (376 MHz, $CDCl_3$) δ -117.85 (d, *J* = 4.9 Hz).

HRMS Exact mass calculated for $[C_{19}H_{21}FO_4+H]^+$ requires *m/z* = 333.1497, found *m/z* = 333.1500 (ESI+).



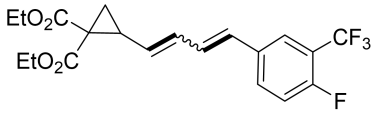
(*E*/*Z*)-diethyl-2-(4-(3,4-difluorophenyl)buta-1,3-dien-1-yl)cyclopropane-1,1-dicarboxylate (1q) was synthesized by following Procedure A. The crude material was purified by normal-phase column chromatography using a gradient eluent of PE/EA (20:1-10:1) to provide **1q** as a white solid (981.0 mg, 56% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.20 – 7.03 (m, 3H), 6.70 – 6.20 (m, 3H), 5.52 – 5.00 (m, 1H), 4.27 – 4.13 (m, 4H), 2.98 – 2.55 (m, 1H), 1.75 – 1.62 (m, 2H), 1.26 (qd, *J* = 7.2, 2.9 Hz, 6H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 169.6, 169.4, 167.4, 151.7, 134.5, 133.5, 132.0, 131.7, 129.9, 129.7, 129.1, 127.5, 124.8, 122.6, 122.5, 117.4, 117.2, 114.8, 114.7, 114.5, 114.3, 61.8, 61.7, 61.5, 36.5, 36.5, 31.0, 26.7, 21.9, 21.1, 14.2, 14.1, 14.1.

^{19}F NMR (376 MHz, $CDCl_3$) δ -137.84 (dd, *J* = 32.8, 21.1 Hz), -138.72 (dd, *J* = 143.7, 21.0 Hz).

HRMS Exact mass calculated for $[C_{19}H_{20}F_2O_4+Na]^+$ requires *m/z* = 373.1222, found *m/z* = 373.1225 (ESI+).



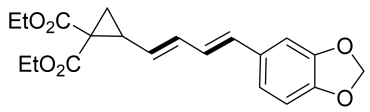
(*E*/*Z*)-diethyl-2-(4-(4-fluoro-3-(trifluoromethyl)phenyl)buta-1,3-dien-1-yl)cyclopropane-1,1-dicarboxylate (1r) was synthesized by following Procedure A. The crude material was purified by normal-phase column chromatography using a gradient eluent of PE/EA (20:1-10:1) to provide **1r** as a white solid (1.00 g, 50% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.65 – 7.45 (m, 2H), 7.17 – 7.09 (m, 1H), 6.82 – 6.17 (m, 3H), 5.54 – 4.98 (m, 1H), 4.32 – 4.12 (m, 4H), 3.05 – 2.58 (m, 1H), 1.77 – 1.62 (m, 2H), 1.31 – 1.23 (m, 6H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 169.6, 169.4, 167.4, 167.4, 160.1, 157.5, 133.7, 133.7, 133.3, 131.9, 131.3, 131.2, 131.2, 131.1, 130.5, 129.6, 129.6, 129.1, 127.9, 126.5, 125.3, 125.3, 124.6, 124.6, 123.8, 121.1, 118.8, 118.7, 118.5, 118.3, 117.3, 117.2, 117.1, 117.0, 61.8, 61.7, 61.6, 36.5, 36.5, 31.0, 26.7, 21.9, 21.1, 14.2, 14.1, 14.0.

^{19}F NMR (376 MHz, $CDCl_3$) δ -59.98 – -64.21 (m), -115.45 – -118.36 (m).

HRMS Exact mass calculated for $[C_{20}H_{20}F_4O_4+Na]^+$ requires *m/z* = 423.1190, found *m/z* = 423.1191 (ESI+).

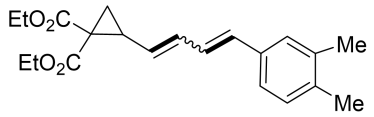


(*E*/*Z*)-diethyl-2-(4-(benzo[d][1,3]dioxol-5-yl)buta-1,3-dien-1-yl)cyclopropane-1,1-dicarboxylate (1s) was synthesized by following Procedure A. The crude material was purified by normal-phase column chromatography using a gradient eluent of PE/EA (20:1-10:1) to provide **1s** as a white solid (985.6 mg, 55% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 6.98 – 6.73 (m, 3H), 6.61 – 6.17 (m, 3H), 5.95 (d, *J* = 7.6 Hz, 2H), 5.39 – 4.95 (m, 1H), 4.30 – 4.15 (m, 4H), 3.00 – 2.60 (m, 1H), 1.76 – 1.62 (m, 2H), 1.30 – 1.21 (m, 6H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 169.7, 169.6, 167.5, 148.1, 148.0, 147.4, 147.2, 134.1, 133.7, 132.7, 131.7, 127.9, 126.5, 125.6, 122.3, 121.5, 121.3, 108.4, 105.6, 105.4, 101.1, 101.0, 61.7, 61.6, 61.5, 36.5, 36.4, 31.2, 26.9, 21.9, 21.1, 14.2, 14.1, 14.1, 14.1.

HRMS Exact mass calculated for $[C_{20}H_{22}O_6+Na]^+$ requires *m/z* = 381.1309, found *m/z* = 381.1310 (ESI+).

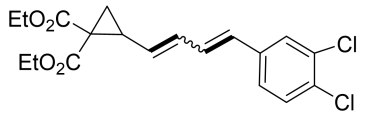


(*E*/*Z*)-diethyl-2-(4-(3,4-dimethylphenyl)buta-1,3-dien-1-yl)cyclopropane-1,1-dicarboxylate (1t) was synthesized by following Procedure A. The crude material was purified by normal-phase column chromatography using a gradient eluent of PE/EA (20:1-10:1) to provide **1t** as a white solid (907.5 mg, 53% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.23 – 7.04 (m, 3H), 6.89 – 6.11 (m, 3H), 5.48 – 4.85 (m, 1H), 4.55 – 3.69 (m, 4H), 3.07 – 2.55 (m, 1H), 2.25 (t, *J* = 3.3 Hz, 6H), 1.79 – 1.62 (m, 2H), 1.27 (ddd, *J* = 9.5, 7.6, 6.6 Hz, 6H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 169.6, 167.5, 136.7, 136.2, 134.8, 134.4, 134.3, 132.9, 132.1, 129.9, 129.9, 127.8, 127.7, 127.6, 127.0, 125.5, 124.1, 123.8, 122.7, 61.6, 61.5, 36.5, 31.2, 27.0, 22.0, 21.1, 19.7, 19.5, 14.2, 14.1.

HRMS Exact mass calculated for $[C_{21}H_{26}O_4+H]^+$ requires *m/z* = 343.1904, found *m/z* = 343.1907 (ESI+).

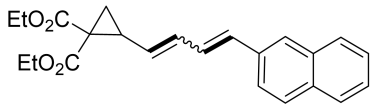


(*E*/*Z*)-diethyl-2-(4-(3,4-dichlorophenyl)buta-1,3-dien-1-yl)cyclopropane-1,1-dicarboxylate (1u) was synthesized by following Procedure A. The crude material was purified by normal-phase column chromatography using a gradient eluent of PE/EA (20:1-10:1) to provide **1u** as a white solid (996.5 mg, 52% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.49 – 7.32 (m, 2H), 7.23 – 7.12 (m, 1H), 6.71 – 6.22 (m, 3H), 5.49 – 5.02 (m, 1H), 4.28 – 4.12 (m, 4H), 3.00 – 2.60 (m, 1H), 1.76 – 1.62 (m, 2H), 1.26 (q, *J* = 7.2 Hz, 6H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 169.6, 169.4, 167.4, 167.4, 137.3, 137.2, 133.4, 132.7, 132.7, 131.9, 131.4, 131.2, 130.9, 130.5, 130.5, 130.4, 129.9, 129.2, 128.1, 128.0, 127.8, 125.6, 125.5, 125.4, 61.8, 61.7, 61.5, 36.5, 36.5, 31.0, 26.7, 21.9, 21.1, 14.2, 14.2, 14.1, 14.1, 14.0.

HRMS Exact mass calculated for $[C_{19}H_{20}Cl_2O_4+Na]^+$ requires *m/z* = 405.0631, found *m/z* = 405.0634 (ESI+).

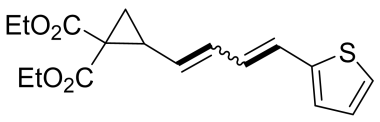


(*E*/*Z*)-diethyl-2-(4-(naphthalen-2-yl)buta-1,3-dien-1-yl)cyclopropane-1,1-dicarboxylate (1v) was synthesized by following Procedure A. The crude material was purified by normal-phase column chromatography using a gradient eluent of PE/EA (20:1-10:1) to provide **1v** as a white solid (984.0 mg, 54% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.83 – 7.39 (m, 7H), 6.94 – 6.59 (m, 2H), 6.57 – 6.28 (m, 1H), 5.58 – 5.02 (m, 1H), 4.41 – 4.16 (m, 4H), 3.13 – 2.61 (m, 1H), 1.80 – 1.64 (m, 2H), 1.33 – 1.24 (m, 6H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 169.8, 169.5, 167.6, 167.5, 134.6, 134.2, 133.6, 133.1, 132.9, 132.7, 132.1, 128.9, 128.5, 128.2, 128.2, 128.0, 127.9, 127.7, 127.6, 126.7, 126.5, 126.4, 126.3, 126.3, 125.9, 125.8, 124.1, 123.5, 123.3, 61.7, 61.5, 36.52, 31.2, 27.0, 22.0, 21.2, 14.2, 14.1.

HRMS Exact mass calculated for $[C_{23}H_{24}O_4+Na]^+$ requires *m/z* = 387.1567, found *m/z* = 387.1570 (ESI+).



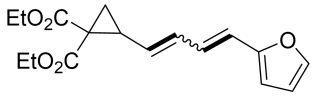
(*E*/*Z*)-diethyl-2-(4-(thiophen-2-yl)buta-1,3-dien-1-yl)cyclopropane-1,1-dicarboxylate (1w) was synthesized by following Procedure A. The crude material was purified

by normal-phase column chromatography using a gradient eluent of PE/EA (20:1-10:1) to provide **1w** as a white solid (849.1 mg, 53% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.19 – 6.94 (m, 3H), 6.77 – 6.16 (m, 3H), 5.44 – 4.94 (m, 1H), 4.27 – 4.12 (m, 4H), 3.00 – 2.54 (m, 1H), 1.80 – 1.62 (m, 2H), 1.30 – 1.23 (m, 6H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 169.5, 169.4, 167.5, 167.4, 142.5, 142.4, 133.5, 132.1, 128.5, 127.8, 127.5, 127.5, 127.2, 126.8, 126.2, 125.9, 124.8, 124.7, 124.3, 123.5, 61.6, 61.6, 61.4, 61.4, 36.4, 36.4, 31.1, 26.9, 21.9, 21.1, 14.1, 14.1, 14.0, 14.0, 13.9.

HRMS Exact mass calculated for $[C_{17}H_{20}O_4S+Na]^+$ requires *m/z* = 343.0975, found *m/z* = 343.0980 (ESI+).

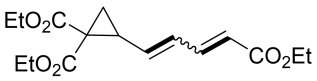


(*E*/*Z*)-diethyl 2-(4-(furan-2-yl)buta-1,3-dien-1-yl)cyclopropane-1,1-dicarboxylate (1x) was synthesized by following Procedure A. The crude material was purified by normal-phase column chromatography using a gradient eluent of PE/EA (20:1-10:1) to provide **1x** as a white solid (791.3 mg, 52% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.36 (dd, *J* = 15.2, 1.8 Hz, 1H), 7.10 – 6.58 (m, 1H), 6.40 – 6.37 (m, 1H), 6.36 – 6.08 (m, 3H), 5.41 – 4.96 (m, 1H), 4.26 – 4.15 (m, 4H), 3.00 – 2.62 (m, 1H), 1.74 – 1.60 (m, 2H), 1.26 (d, *J* = 7.5 Hz, 6H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 169.5, 167.4, 153.0, 142.4, 142.1, 133.7, 132.2, 128.9, 126.7, 126.6, 122.5, 121.4, 119.6, 111.6, 109.0, 108.5, 61.7, 61.5, 36.5, 31.2, 27.0, 21.1, 14.2, 14.1.

HRMS Exact mass calculated for $[C_{17}H_{20}O_5+Na]^+$ requires *m/z* = 327.1203, found *m/z* = 327.1203 (ESI+).

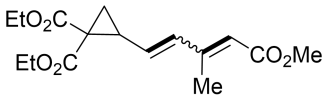


(*E*/*Z*)-diethyl-2-(5-ethoxy-5-oxopenta-1,3-dien-1-yl)cyclopropane-1,1-dicarboxylate (1y) was synthesized by following Procedure A. The crude material was purified by normal-phase column chromatography using a gradient eluent of PE/EA (20:1-10:1) to provide **1y** as a white solid (806.9 mg, 52% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.70 – 7.14 (m, 1H), 6.49 – 6.18 (m, 1H), 5.99 – 5.75 (m, 1H), 5.70 – 5.22 (m, 1H), 4.28 – 4.10 (m, 6H), 3.04 – 2.55 (m, 1H), 1.77 – 1.61 (m, 2H), 1.32 – 1.20 (m, 9H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 169.1, 169.0, 167.3, 167.1, 166.9, 166.8, 143.3, 138.5, 137.6, 134.7, 131.4, 129.7, 123.1, 120.9, 61.8, 61.8, 61.7, 61.6, 60.4, 60.3, 36.7, 30.6, 26.5, 21.9, 21.2, 14.2, 14.2, 14.1, 14.1, 13.9.

HRMS Exact mass calculated for $[C_{16}H_{22}O_6+Na]^+$ requires *m/z* = 333.1309, found *m/z* = 333.1314 (ESI+).

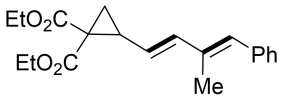


(*E*/*Z*)-diethyl-2-(5-ethoxy-3-methyl-5-oxopenta-1,3-dien-1-yl)cyclopropane-1,1-dicarboxylate (1z) was synthesized by following Procedure A. The crude material was purified by normal-phase column chromatography using a gradient eluent of PE/EA (20:1-10:1) to provide **1z** as a white solid (837.9 mg, 54% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.02 – 6.17 (m, 1H), 5.75 – 5.13 (m, 2H), 4.30 – 4.10 (m, 4H), 3.69 (d, *J* = 9.9 Hz, 3H), 2.88 – 2.61 (m, 1H), 2.17 (dd, *J* = 17.4, 1.3 Hz, 2H), 1.78 – 1.59 (m, 3H), 1.29 – 1.23 (m, 6H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 169.3, 169.2, 167.4, 167.3, 151.7, 151.3, 136.9, 135.8, 133.1, 131.6, 131.4, 130.8, 129.6, 129.6, 119.1, 118.9, 118.7, 116.7, 61.8, 61.7, 61.6, 61.6, 61.6, 51.1, 36.7, 36.66, 31.4, 30.8, 27.7, 24.8, 22.4, 21.3, 20.8, 14.2, 14.2, 14.2, 14.0, 14.0, 13.6.

HRMS Exact mass calculated for $[C_{16}H_{22}O_6+Na]^+$ requires *m/z* = 333.1309, found *m/z* = 333.1310 (ESI+).

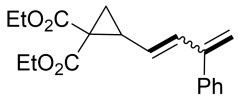


(*E*)-Diethyl-2-(3-methyl-4-phenylbuta-1,3-dien-1-yl)cyclopropane-1,1-dicarboxylate (1aa) was synthesized by following Procedure A. The crude material was purified by normal-phase column chromatography using a gradient eluent of PE/EA (20:1-10:1) to provide **1aa** as a white solid (853.9 mg, 52% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.36 – 7.26 (m, 4H), 7.24 – 7.18 (m, 1H), 6.59 – 6.39 (m, 2H), 5.41 – 5.29 (m, 1H), 4.32 – 4.10 (m, 4H), 2.69 (q, *J* = 8.6 Hz, 1H), 1.91 (d, *J* = 1.2 Hz, 3H), 1.77 (dd, *J* = 7.6, 4.9 Hz, 1H), 1.65 (dd, *J* = 8.9, 4.9 Hz, 1H), 1.27 (dt, *J* = 9.3, 7.1 Hz, 6H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 169.6, 167.6, 138.9, 137.6, 134.8, 131.1, 129.2, 128.1, 126.6, 123.9, 61.6, 61.4, 36.4, 31.4, 21.2, 14.2, 14.1, 13.7.

HRMS Exact mass calculated for $[C_{20}H_{24}O_4+Na]^+$ requires *m/z* = 351.1567, found *m/z* = 351.1570 (ESI+).

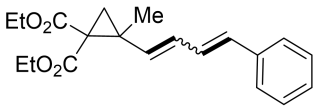


(*E*/*Z*)-diethyl 2-(3-phenylbuta-1,3-dien-1-yl)cyclopropane-1,1-dicarboxylate (1ab) was synthesized by following Procedure A. The crude material was purified by normal-phase column chromatography using a gradient eluent of PE/EA (20:1-10:1) to provide **1ab** as a white solid (880.3 mg, 56% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.34 – 7.09 (m, 5H), 6.53 – 6.20 (m, 1H), 5.53 – 5.01 (m, 3H), 4.26 – 3.85 (m, 4H), 2.67 – 2.46 (m, 1H), 1.59 – 1.50 (m, 2H), 1.23 – 1.15 (m, 3H), 1.14 – 1.05 (m, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 169.6, 169.2, 167.7, 167.3, 147.2, 144.1, 140.2, 139.9, 135.1, 133.2, 128.7, 128.3, 128.3, 128.1, 128.1, 127.7, 127.5, 126.7, 116.6, 116.4, 61.7, 61.5, 61.4, 36.2, 31.1, 28.4, 22.2, 20.9, 14.2, 14.0, 14.0.

HRMS Exact mass calculated for $[C_{19}H_{22}O_4+Na]^+$ requires *m/z* = 337.1410, found *m/z* = 337.1411 (ESI+).

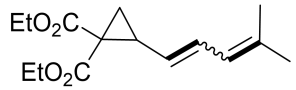


(*E*/*Z*)-diethyl-2-methyl-2-(4-phenylbuta-1,3-dien-1-yl)cyclopropane-1,1-dicarboxylate (1ac) was synthesized by following Procedure A. The crude material was purified by normal-phase column chromatography using a gradient eluent of PE/EA (20:1-10:1) to provide **3ac** as a yellow solid (919.5 mg, 56% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.54 – 7.27 (m, 5H), 6.79 – 6.49 (m, 1H), 6.40 – 6.14 (m, 1H), 5.90 – 5.60 (m, 1H), 4.41 – 3.99 (m, 4H), 1.86 – 1.72 (m, 1H), 1.72 – 1.49 (m, 2H), 1.45 – 1.37 (m, 3H), 1.36 – 1.08 (m, 6H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 168.3, 168.1, 137.4, 134.4, 133.5, 132.2, 131.8, 131.2, 130.9, 128.6, 128.6, 128.5, 127.6, 127.4, 126.6, 126.3, 124.7, 61.5, 61.4, 41.5, 40.8, 33.7, 31.5, 26.8, 26.3, 22.9, 18.6, 14.3, 14.1, 13.9.

HRMS Exact mass calculated for $[C_{20}H_{24}O_4+Na]^+$ requires *m/z* = 351.1567, found *m/z* = 351.1569 (ESI+).

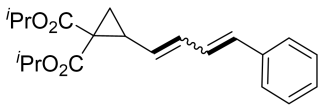


(*E*/*Z*)-diethyl 2-(5-methylhexa-1,3-dien-1-yl)cyclopropane-1,1-dicarboxylate (1ad) was synthesized by following Procedure A. The crude material was purified by normal-phase column chromatography using a gradient eluent of PE/EA (20:1-10:1) to provide **1ad** as a white solid (759.1 mg, 57% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 6.56 – 6.22 (m, 1H), 6.21 – 5.62 (m, 1H), 5.16 – 4.71 (m, 1H), 4.30 – 4.10 (m, 4H), 2.93 – 2.54 (m, 1H), 1.85 – 1.70 (m, 6H), 1.69 – 1.55 (m, 2H), 1.25 (dtd, *J* = 8.0, 7.2, 3.2 Hz, 6H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 169.7, 167.5, 137.5, 135.3, 130.6, 128.8, 124.8, 124.3, 122.8, 120.1, 61.6, 61.5, 61.3, 36.2, 36.1, 31.5, 26.8, 26.3, 25.9, 21.9, 21.1, 18.3, 18.1, 14.2, 14.1, 14.1, 14.0.

HRMS Exact mass calculated for $[C_{15}H_{22}O_4+Na]^+$ requires *m/z* = 289.1410, found *m/z* = 289.1411 (ESI+).

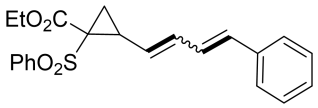


(*E*/*Z*)-diisopropyl 2-(4-phenylbuta-1,3-dien-1-yl)cyclopropane-1,1-dicarboxylate (1ae) was synthesized by following Procedure A. The crude material was purified by normal-phase column chromatography using a gradient eluent of PE/EA (20:1-10:1) to provide **1ae** as a white solid (856.1 mg, 50% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38 – 7.26 (m, 2H), 7.24 – 7.07 (m, 3H), 6.66 – 6.40 (m, 2H), 6.39 – 6.17 (m, 1H), 5.38 – 4.89 (m, 3H), 2.93 – 2.49 (m, 1H), 1.64 – 1.48 (m, 2H), 1.22 – 1.16 (m, 9H), 1.11 (d, *J* = 6.2 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 169.1, 167.1, 137.2, 137.1, 133.9, 133.8, 132.5, 131.8, 129.0, 128.6, 128.5, 128.1, 127.7, 127.5, 126.6, 126.5, 126.3, 124.0, 69.2, 69.2, 68.9, 68.9, 36.8, 30.6, 26.4, 21.9, 21.7, 21.7, 21.6, 21.6, 21.5, 20.8.

HRMS Exact mass calculated for $[C_{21}H_{26}O_4+Na]^+$ requires *m/z* = 365.1723, found *m/z* = 365.1725 (ESI+).

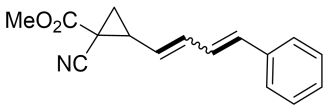


(*E*/*Z*)-ethyl-2-(4-phenylbuta-1,3-dien-1-yl)-1-(phenylsulfonyl)cyclopropane-1-carboxylate (1af) was synthesized by following Procedure B. The crude material was purified by normal-phase column chromatography using a gradient eluent of PE:EA=10:1 to provide **1af** as a white oil (1.09 g, 57% yield).

^{1}H NMR (600 MHz, $CDCl_3$) δ 8.01 – 7.95 (m, 2H), 7.65 – 7.58 (m, 1H), 7.57 – 7.50 (m, 2H), 7.39 – 7.29 (m, 4H), 7.23 – 7.13 (m, 1H), 6.71 – 6.59 (m, 1H), 6.56 – 6.31 (m, 2H), 5.58 – 5.20 (m, 1H), 4.15 – 4.05 (m, 2H), 3.37 – 2.94 (m, 1H), 2.41 – 2.33 (m, 1H), 2.05 – 2.03 (m, 1H), 1.14 – 1.11 (m, 3H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 164.6, 140.0, 136.8, 135.7, 135.2, 134.4, 133.6, 133.6, 133.0, 128.9, 128.8, 128.7, 128.6, 128.1, 127.8, 127.6, 126.7, 126.4, 126.1, 123.4, 123.1, 62.3, 62.3, 51.2, 32.3, 27.4, 21.0, 20.4, 13.8, 13.8.

HRMS Exact mass calculated for $[C_{22}H_{22}O_4S+Na]^+$ requires *m/z* = 405.1136, found *m/z* = 405.1135 (ESI+).

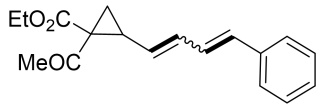


(*E*/*Z*)-methyl 1-cyano-2-(4-phenylbuta-1,3-dien-1-yl)cyclopropane-1-carboxylate (1ag) was synthesized by following Procedure B. The crude material was purified by normal-phase column chromatography using a gradient eluent of PE:EA=10:1 to provide **1ag** as a white oil (620.6 mg, 49% yield).

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.43 – 7.37 (m, 2H), 7.32 – 7.21 (m, 3H), 7.08 – 6.73 (m, 1H), 6.68 – 6.55 (m, 1H), 6.55 – 6.43 (m, 1H), 5.62 – 5.18 (m, 1H), 3.85 – 3.79 (m, 3H), 3.03 – 2.53 (m, 1H), 2.10 – 2.03 (m, 1H), 1.70 – 1.60 (m, 1H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 167.6, 136.7, 136.2, 135.9, 134.5, 133.8, 128.7, 128.6, 128.3, 127.9, 127.3, 126.7, 126.6, 126.5, 124.4, 122.8, 116.8, 60.3, 53.6, 34.4, 30.0, 25.4, 24.6, 21.5, 14.2.

HRMS Exact mass calculated for $[C_{16}H_{15}NO_2+Na]^+$ requires *m/z* = 276.1000, found *m/z* = 276.0998 (ESI+).

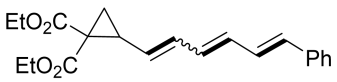


(*E*/*Z*)-ethyl 1-acetyl-2-(4-phenylbuta-1,3-dien-1-yl)cyclopropane-1-carboxylate (1ah) was synthesized by following Procedure A. The crude material was purified by normal-phase column chromatography using a gradient eluent of PE:EA=10:1 to provide **1ah** as a white oil (839.0 mg, 59% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.41 – 7.29 (m, 4H), 7.24 – 7.10 (m, 1H), 6.75 – 6.56 (m, 1H), 6.53 – 6.27 (m, 2H), 5.54 – 5.25 (m, 1H), 4.25 (p, *J* = 7.1 Hz, 2H), 3.08 – 2.65 (m, 1H), 2.44 (d, *J* = 16.3 Hz, 3H), 1.84 (dd, *J* = 7.7, 4.4 Hz, 1H), 1.68 (dd, *J* = 8.9, 4.4 Hz, 1H), 1.30 (t, *J* = 7.1 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 201.8, 168.8, 137.0, 134.5, 132.1, 128.6, 128.5, 128.0, 127.5, 126.3, 126.3, 61.5, 61.4, 43.8, 34.7, 34.7, 29.6, 23.8, 14.2, 14.2.

HRMS Exact mass calculated for $[C_{18}H_{20}O_3+Na]^+$ requires *m/z* = 307.1310, found *m/z* = 307.1312 (ESI+).

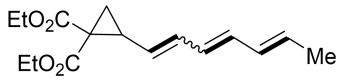


(*E*/*Z*)-diethyl-2-((5E)-6-phenylhexa-1,3,5-trien-1-yl)cyclopropane-1,1-dicarboxylate (4a) was synthesized by following Procedure A. The crude material was purified by normal-phase column chromatography using a gradient eluent of PE/EA (20:1-10:1) to provide **4a** as a white solid (936.2 mg, 55% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.42 – 7.29 (m, 4H), 7.24 – 7.18 (m, 1H), 6.91 – 6.75 (m, 1H), 6.62 – 6.19 (m, 4H), 5.41 – 4.95 (m, 1H), 4.27 – 4.14 (m, 4H), 2.96 – 2.61 (m, 1H), 1.74 – 1.62 (m, 2H), 1.27 (q, *J* = 7.3 Hz, 6H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 169.7, 169.5, 167.5, 167.4, 137.2, 137.2, 134.6, 134.0, 133.2, 132.7, 132.7, 132.6, 132.3, 128.9, 128.8, 128.6, 128.6, 128.6, 128.1, 127.6, 127.5, 126.4, 126.3, 61.7, 61.6, 61.5, 36.5, 36.4, 31.3, 26.9, 22.0, 21.2, 14.2, 14.1, 14.0.

HRMS Exact mass calculated for $[C_{21}H_{24}O_4+Na]^+$ requires *m/z* = 363.1567, found *m/z* = 363.1570 (ESI+).

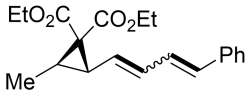


(*E*/*Z*)-diethyl 2-((5E)-hepta-1,3,5-trien-1-yl)cyclopropane-1,1-dicarboxylate (4b) was synthesized by following Procedure A . The crude material was purified by normal-phase column chromatography using a gradient eluent of PE/EA (20:1-10:1) to provide **4b** as a white solid (779.4 mg, 56% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 6.66 – 5.91 (m, 4H), 5.72 (ddq, *J* = 16.4, 13.8, 6.9 Hz, 1H), 5.33 – 4.79 (m, 1H), 4.29 – 4.10 (m, 4H), 2.91 – 2.52 (m, 1H), 1.77 (ddd, *J* = 8.4, 6.8, 1.5 Hz, 3H), 1.70 – 1.56 (m, 2H), 1.28 – 1.19 (m, 6H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 169.6, 167.5, 134.7, 134.2, 132.8, 132.7, 131.7, 131.5, 130.9, 130.3, 129.3, 127.1, 125.1, 124.9, 61.4, 36.4, 31.2, 26.9, 21.9, 21.0, 18.3, 18.3, 14.2, 14.1, 14.0.

HRMS Exact mass calculated for $[C_{16}H_{22}O_4+Na]^+$ requires *m/z* = 301.1410, found *m/z* = 301.1411 (ESI+).

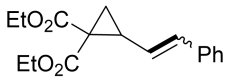


(*E*/*Z*)-diethyl-(2R,3R)-2-methyl-3-((1E,3E)-4-phenylbuta-1,3-dien-1-yl)cyclopropane-1,1-dicarboxylate (9) was synthesized by following Procedure B. The crude material was purified by normal-phase column chromatography using a gradient eluent of PE/EA (20:1-10:1) to provide **9** as a white solid (75.9 mg, 77% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.54 – 7.28 (m, 5H), 6.90 – 6.26 (m, 3H), 5.60 – 5.16 (m, 1H), 4.40 – 4.17 (m, 4H), 2.91 – 2.48 (m, 1H), 2.20 (dt, *J* = 7.6, 6.4 Hz, 1H), 1.39 – 1.18 (m, 9H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 168.0, 167.6, 137.2, 137.2, 133.6, 133.6, 132.2, 131.4, 129.0, 128.5, 128.5, 128.3, 127.6, 127.4, 126.5, 126.2, 124.1, 61.5, 61.4, 61.4, 61.4, 42.7, 42.6, 36.5, 32.2, 28.0, 27.5, 14.2, 14.2, 14.2, 14.1, 12.5, 12.3.

HRMS Exact mass calculated for $[C_{20}H_{21}O_4+Na]^+$ requires *m/z* = 351.1567, found *m/z* = 351.1570 (ESI+).

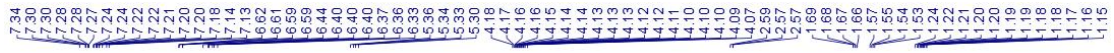


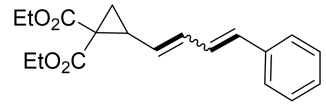
(*E*/*Z*)-diethyl 2-styrylcyclopropane-1,1-dicarboxylate (15) was synthesized by following Procedure A. The crude material was purified by normal-phase column chromatography using a gradient eluent of PE/EA (20:1-10:1) to provide **15** as a white solid (749.7 mg, 52% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.31 – 7.12 (m, 5H), 6.55 (dd, *J* = 15.8, 0.8 Hz, 1H), 5.88 – 5.00 (m, 1H), 4.24 – 3.99 (m, 4H), 2.93 – 2.60 (m, 1H), 1.75 – 1.56 (m, 2H), 1.20 (t, *J* = 7.2 Hz, 3H), 1.14 (t, *J* = 7.1 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 169.5, 167.5, 136.6, 136.5, 133.5, 133.3, 128.8, 128.5, 128.2, 1275.46, 127.1, 126.6, 126.0, 124.7, 61.6, 61.5, 36.5, 36.2, 31.1, 27.7, 22.4, 20.9, 14.2, 14.0.

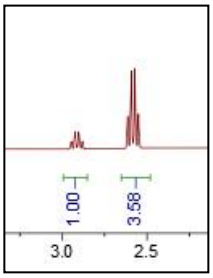
HRMS Exact mass calculated for $[C_{17}H_{20}O_4+Na]^+$ requires *m/z* = 311.1254, found *m/z* = 311.1252 (ESI+).



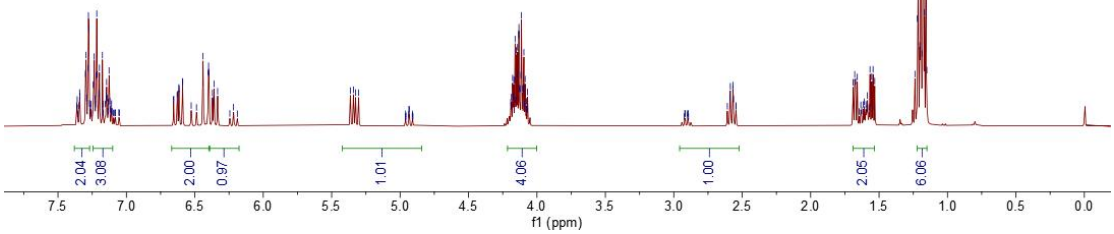


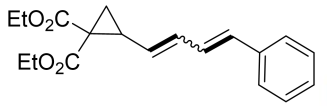
1a

^{1}H NMR, 400 MHz, $CDCl_3$



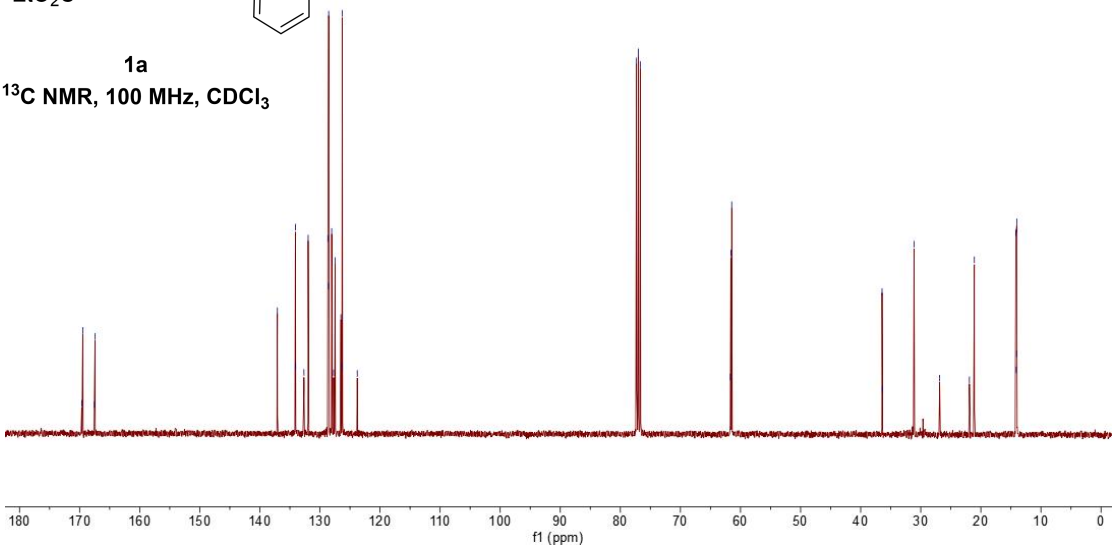
***Z*:*E* = 1:3.6**

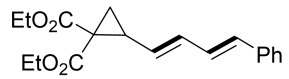




1a

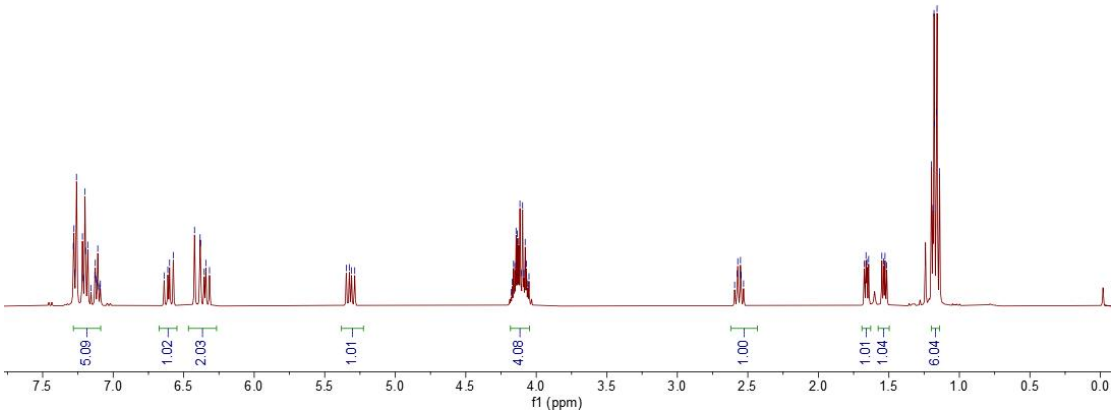
^{13}C NMR, 100 MHz, $CDCl_3$

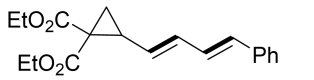




***E*-1a**

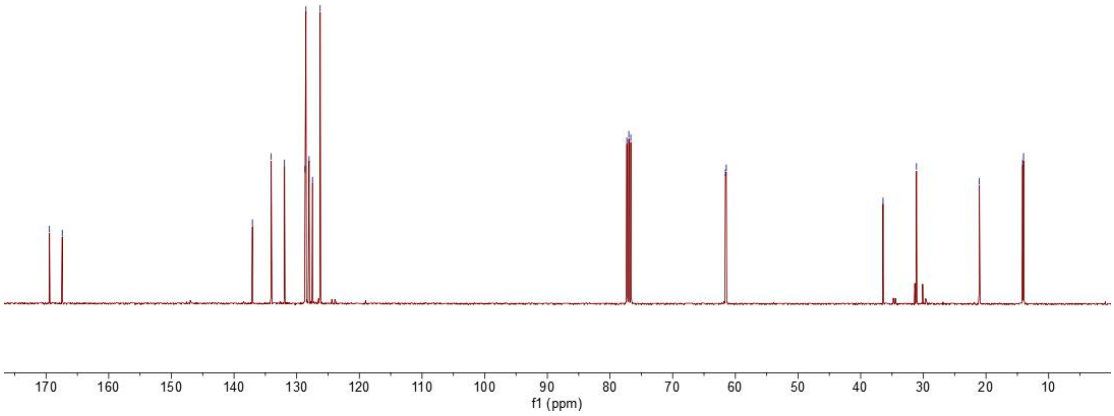
^{1}H NMR, 400MHz, $CDCl_3$

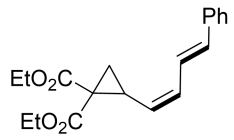




***E*-1a**

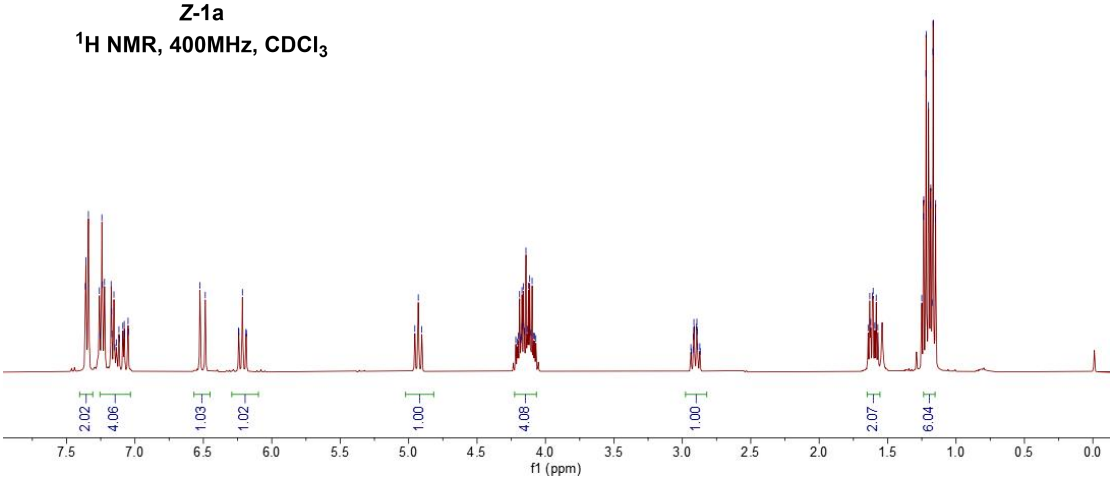
^{13}C NMR, 100MHz, $CDCl_3$

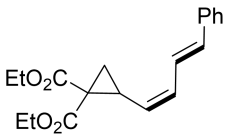




***Z*-1a**

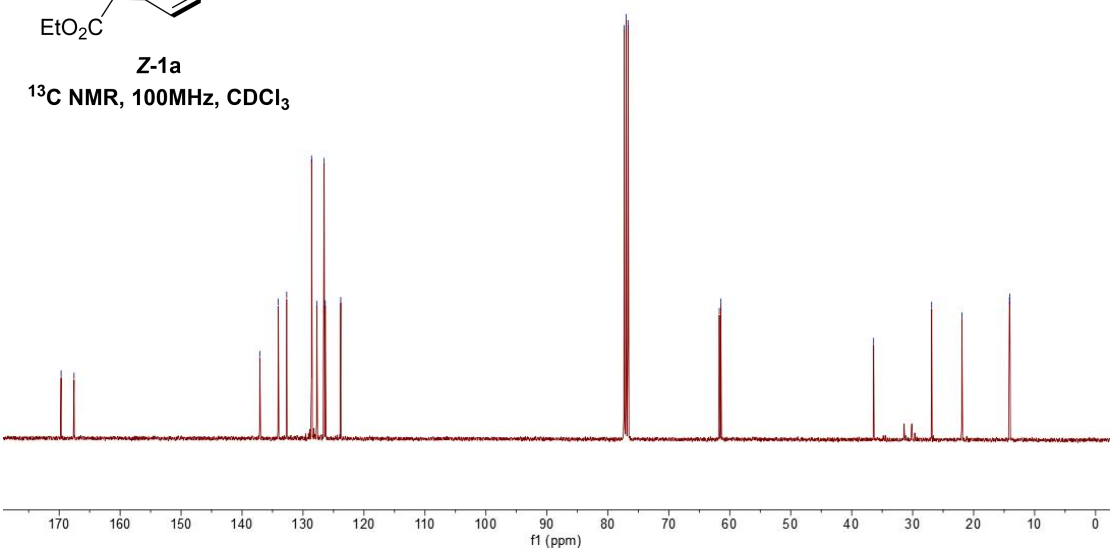
^{1}H NMR, 400MHz, $CDCl_3$

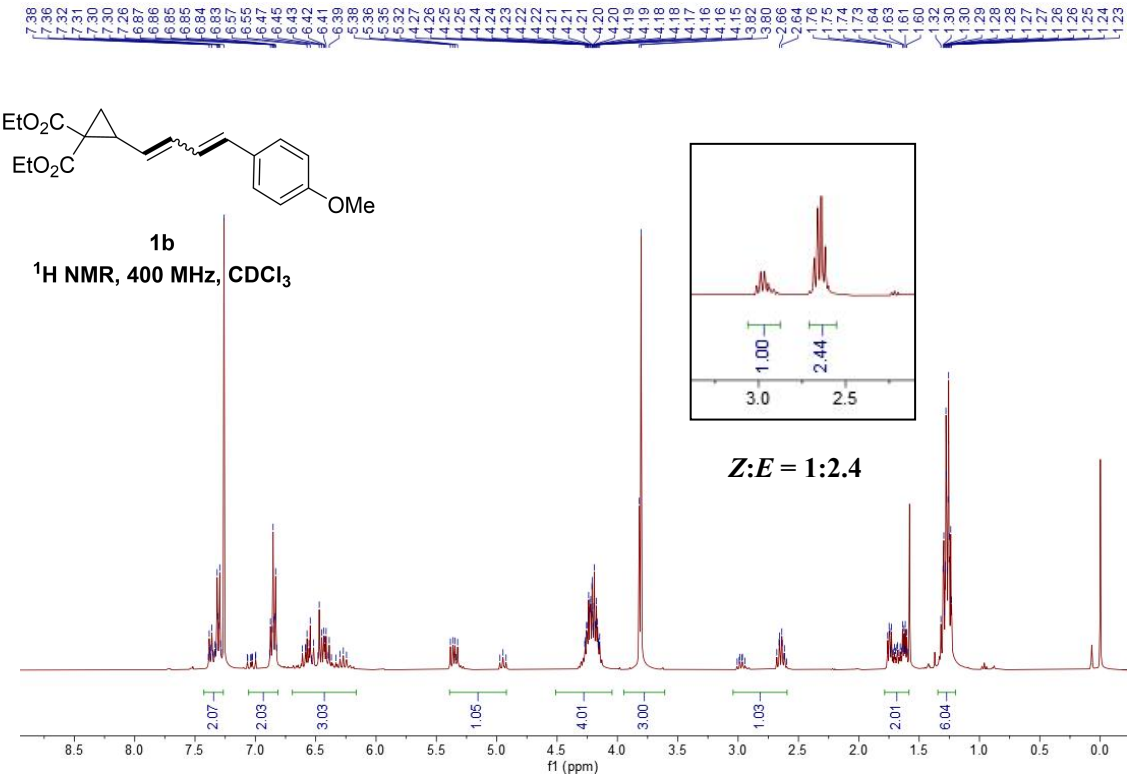


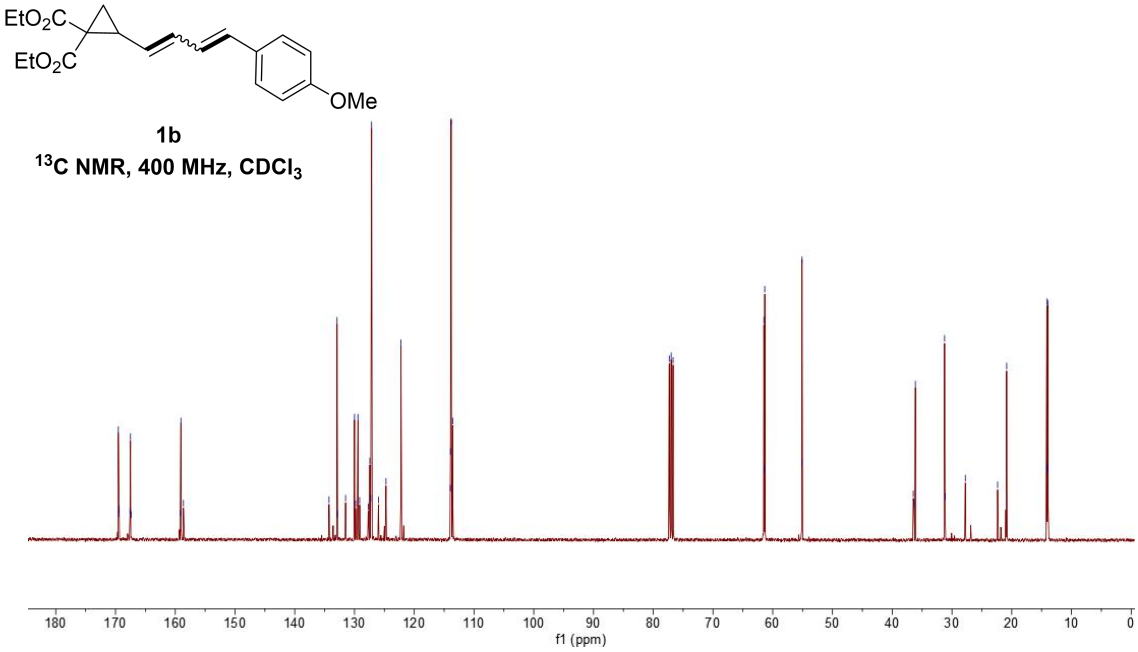


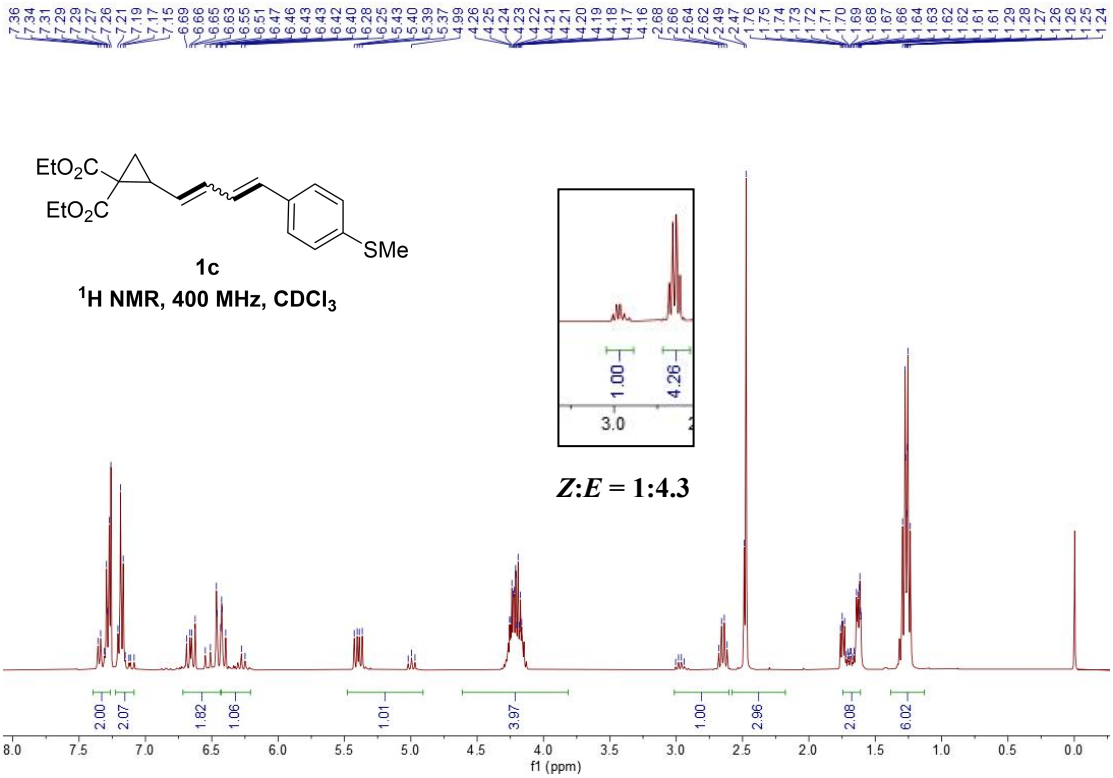
***Z*-1a**

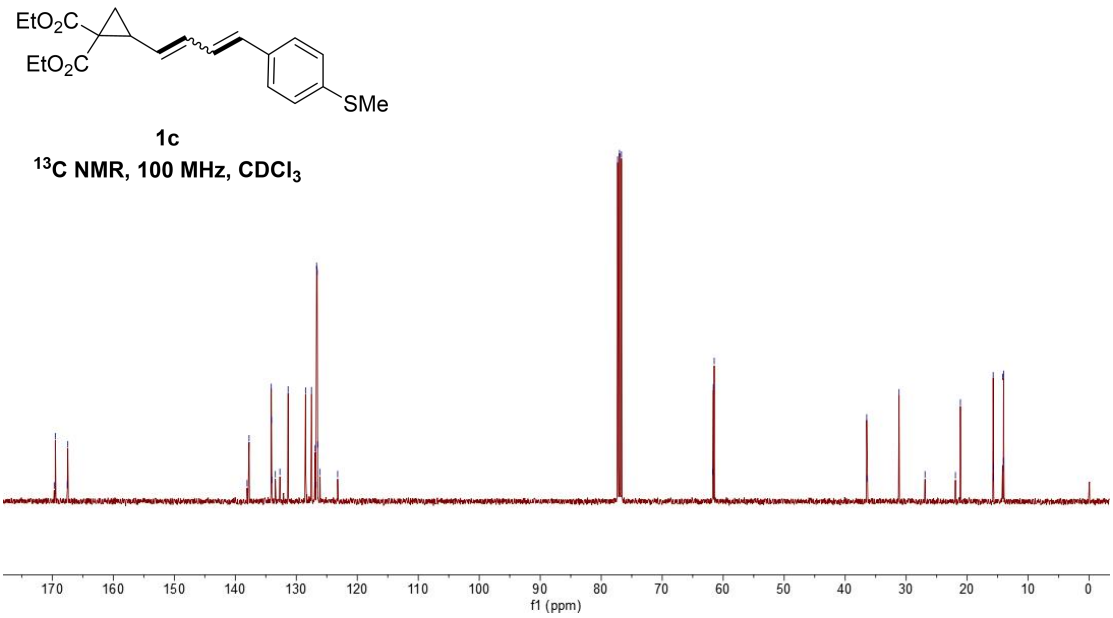
^{13}C NMR, 100MHz, $CDCl_3$

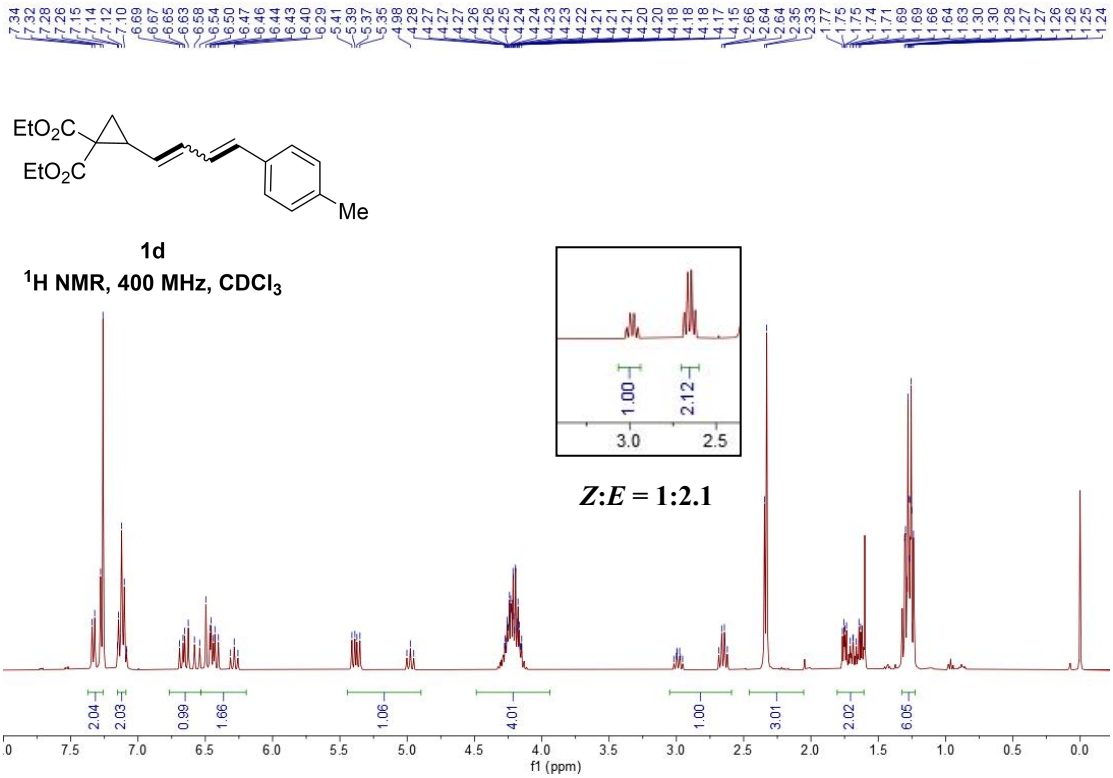


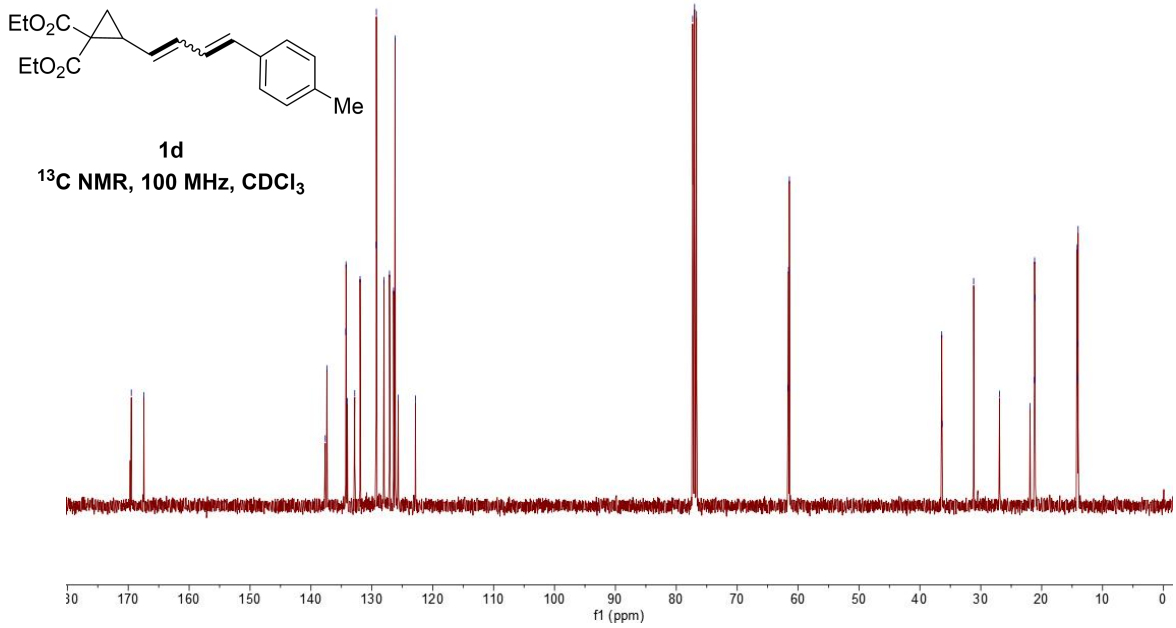

EtO2C
EtO2C
OMe
1b
1H NMR, 400 MHz, CDCl3
Z:E = 1:2.4
f1 (ppm)

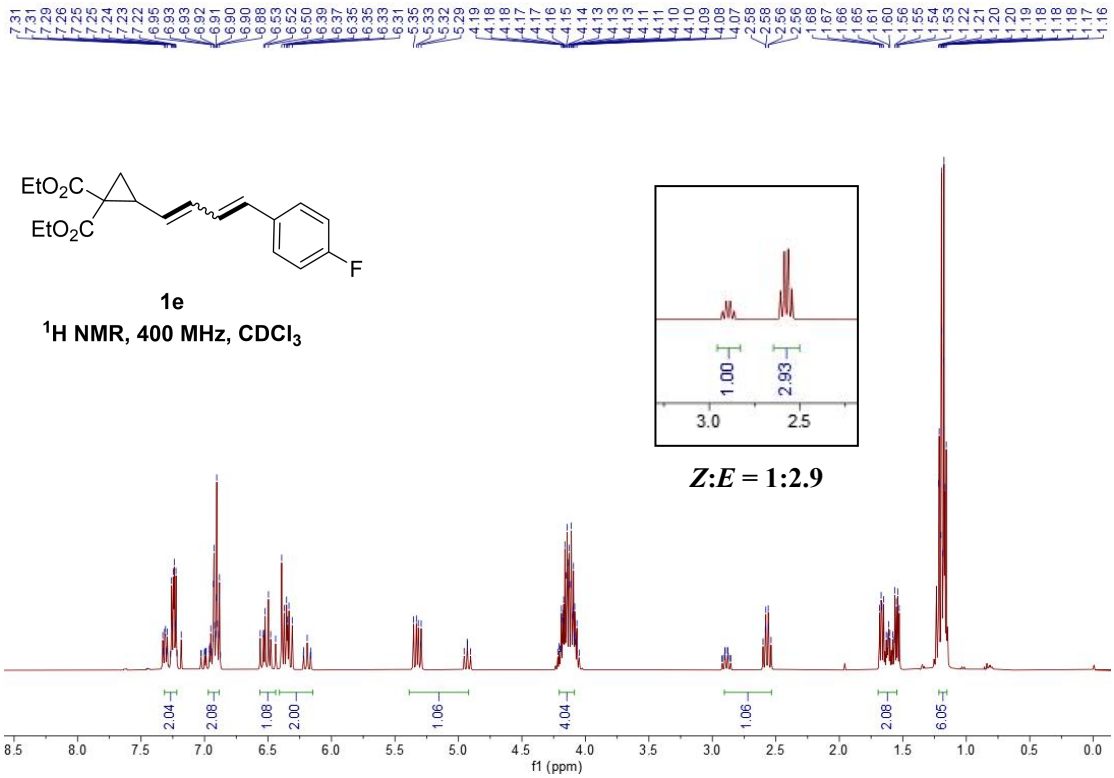

EtO2C
EtO2C
OMe
1b
13C NMR, 400 MHz, CDCl3
f1 (ppm)

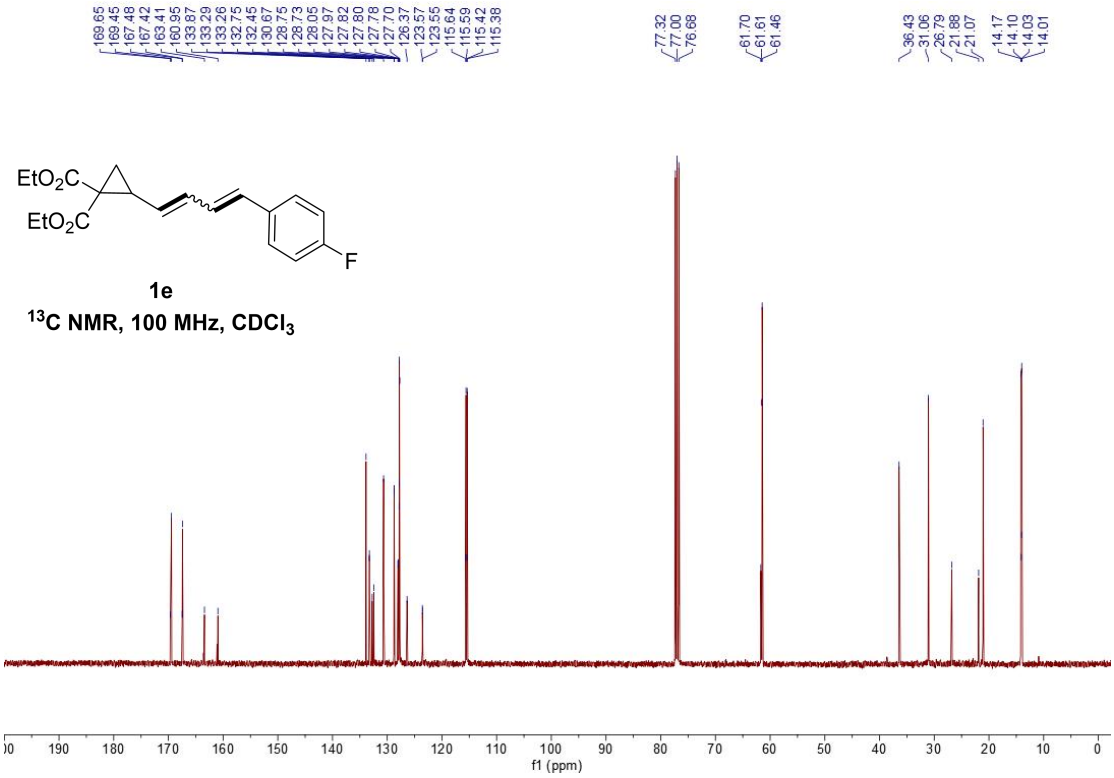

EtO2C
EtO2C
SMe
1c
1H NMR, 400 MHz, CDCl3
1.00
4.26
3.0
Z:E = 1:4.3
2.00
2.07
1.82
1.06
1.01
3.97
1.00
2.96
2.08
6.02
f1 (ppm)

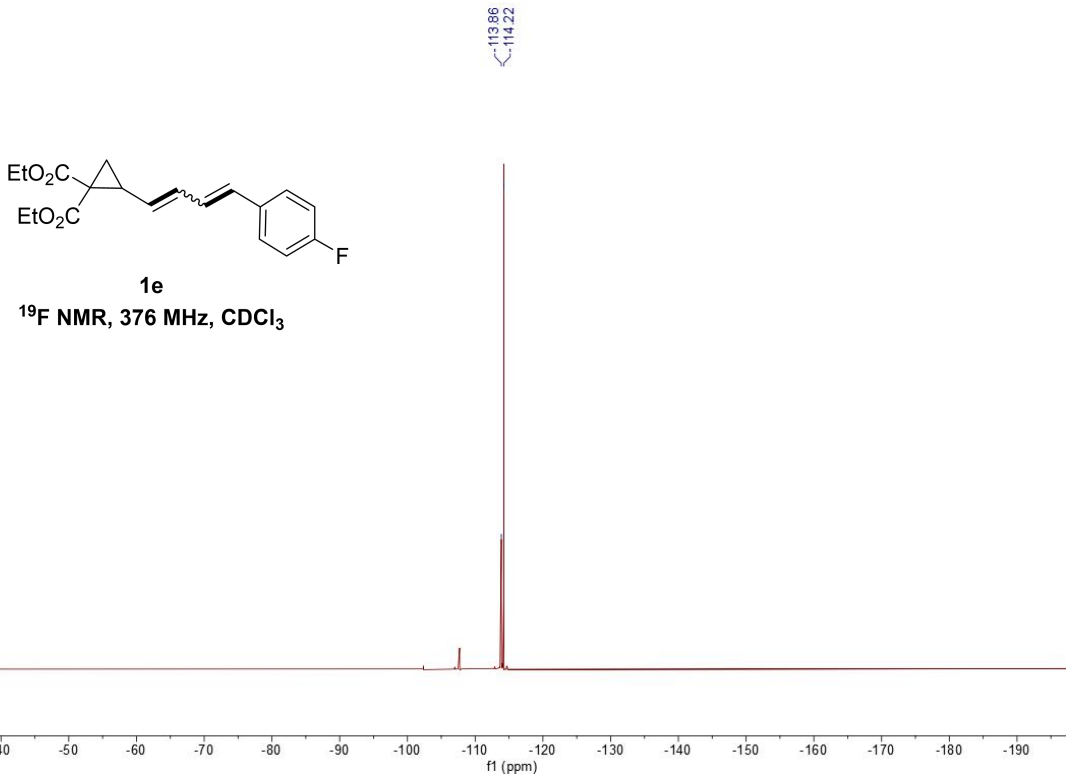

EtO2C
EtO2C
SMe
1c
13C NMR, 100 MHz, CDCl3
f1 (ppm)


EtO2C
EtO2C
Me
1d
1H NMR, 400 MHz, CDCl3
Z:E = 1:2.1
1.00
2.12
2.04
2.03
0.99
1.66
1.06
4.01
1.00
3.01
2.02
6.05
f1 (ppm)


EtO2C
EtO2C
Me
1d
13C NMR, 100 MHz, CDCl3
f1 (ppm)

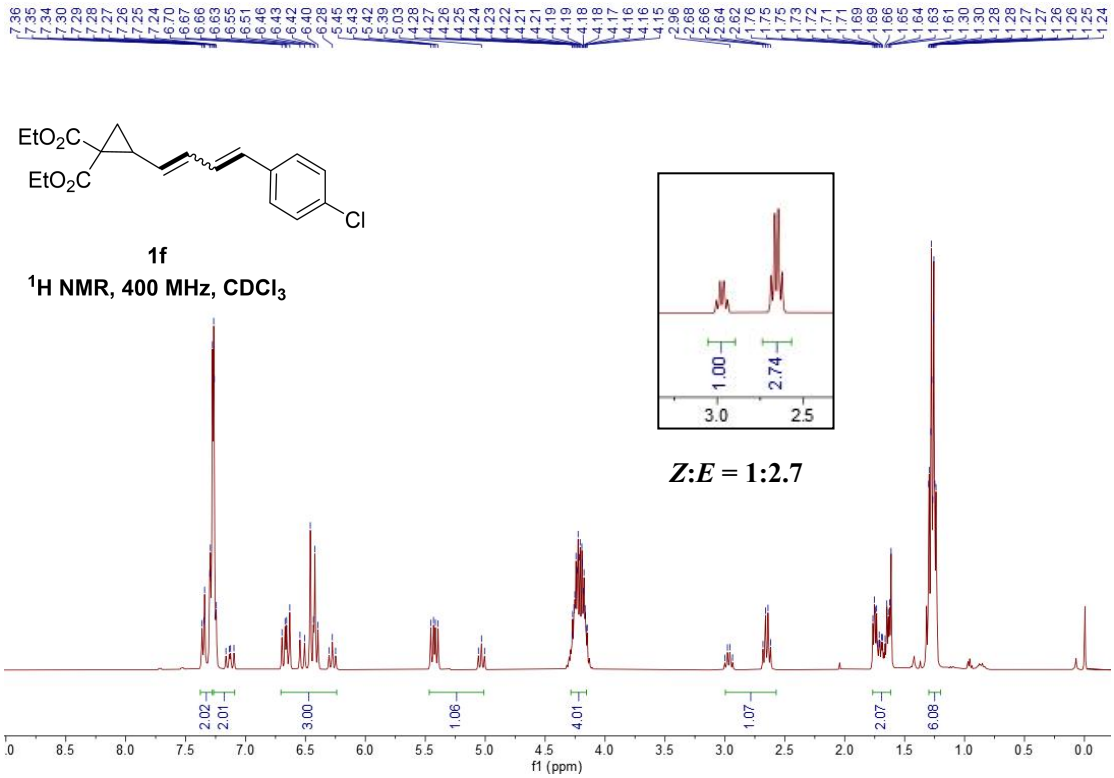

EtO2C
EtO2C
F
1e
1H NMR, 400 MHz, CDCl3
1.00
2.93
Z:E = 1:2.9
2.04
2.08
1.08
2.00
1.06
4.04
1.06
2.08
6.05
f1 (ppm)

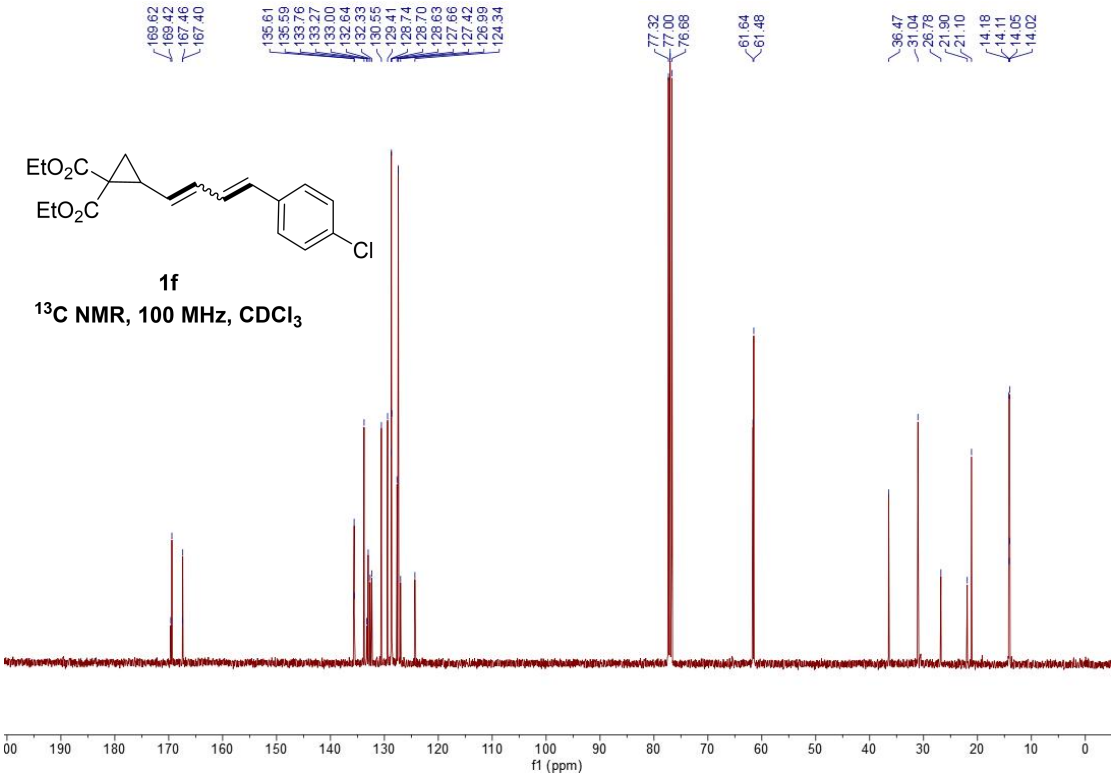

EtO2C
EtO2C
F
1e
13C NMR, 100 MHz, CDCl3
f1 (ppm)

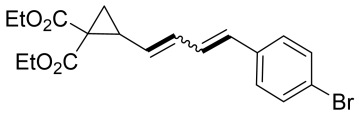


1e

^{19}F NMR, 376 MHz, $CDCl_3$

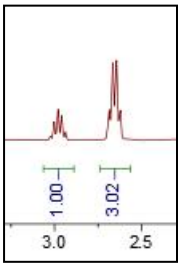

EtO2C
EtO2C
Cl
1f
1H NMR, 400 MHz, CDCl3
1.00
2.74
3.0
2.5
Z:E = 1:2.7
2.02
2.01
3.00
1.06
4.01
1.07
2.07
6.08
f1 (ppm)


EtO2C
EtO2C
Cl
1f
13C NMR, 100 MHz, CDCl3
f1 (ppm)

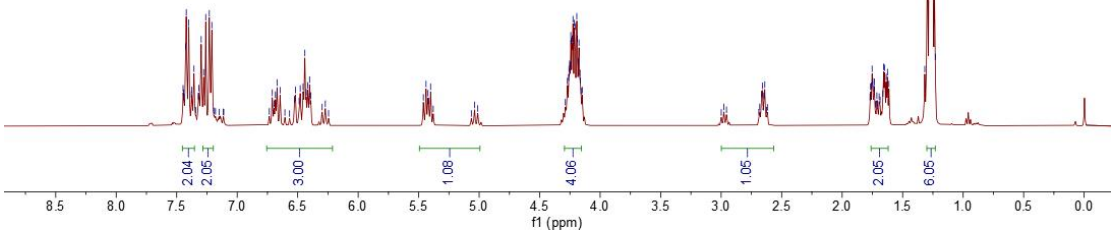


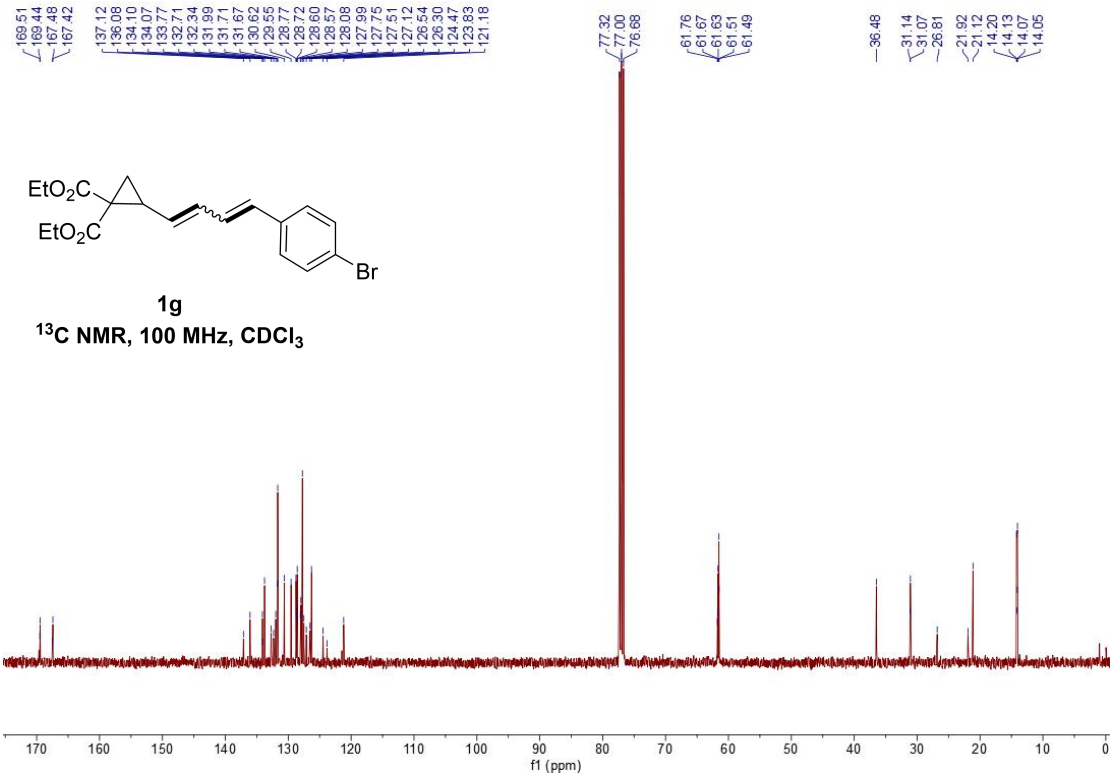
1g

^{1}H NMR, 400 MHz, $CDCl_3$



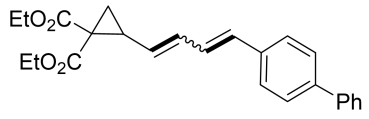
***Z*:*E* = 1:3.0**





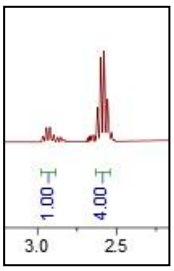
1g

^{13}C NMR, 100 MHz, $CDCl_3$

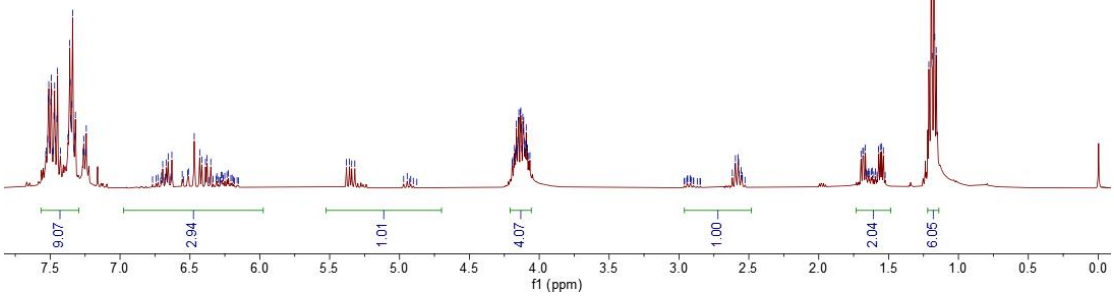


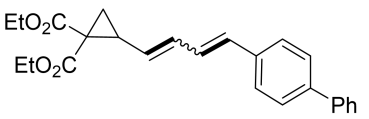
1h

^{1}H NMR, 400 MHz, $CDCl_3$



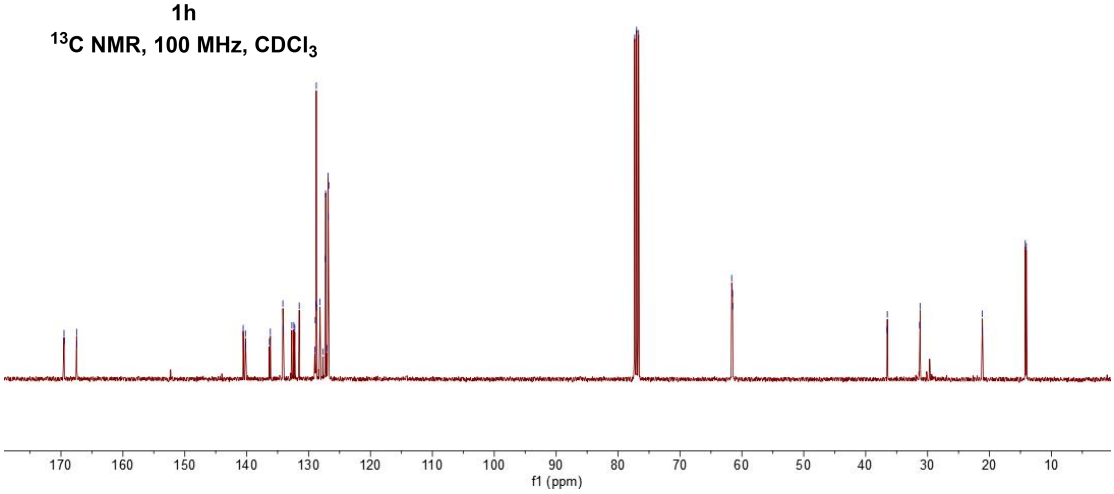
***Z*:*E* = 1:4.0**

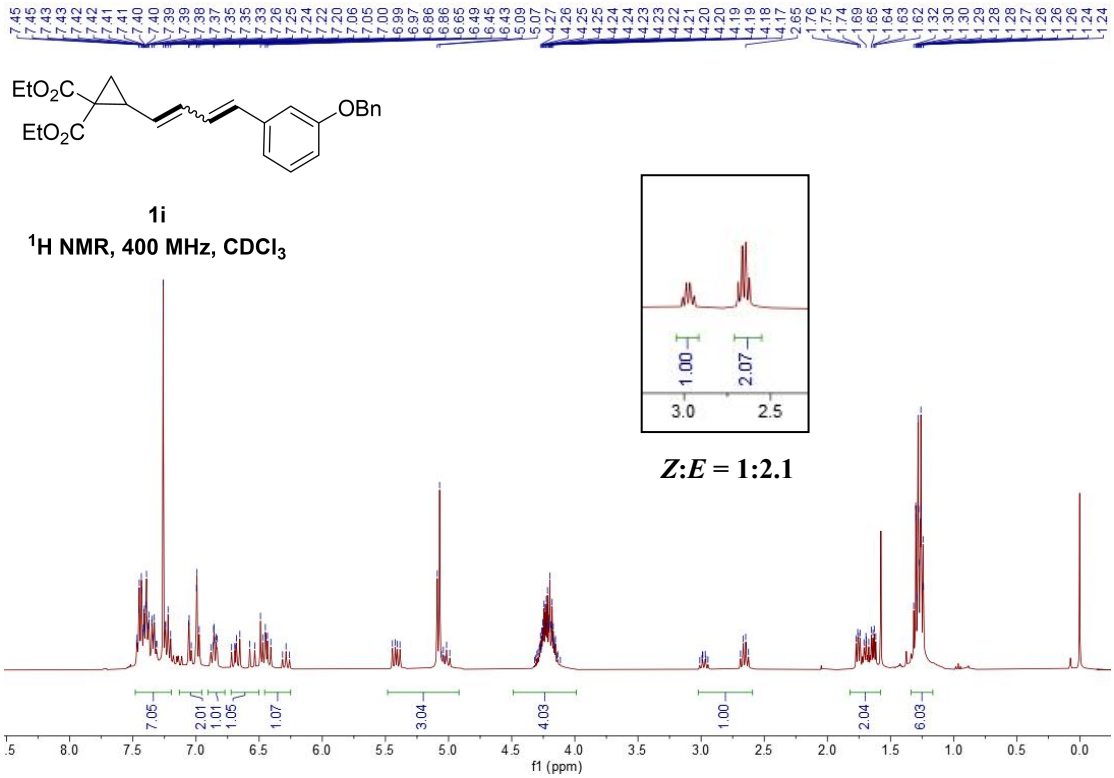


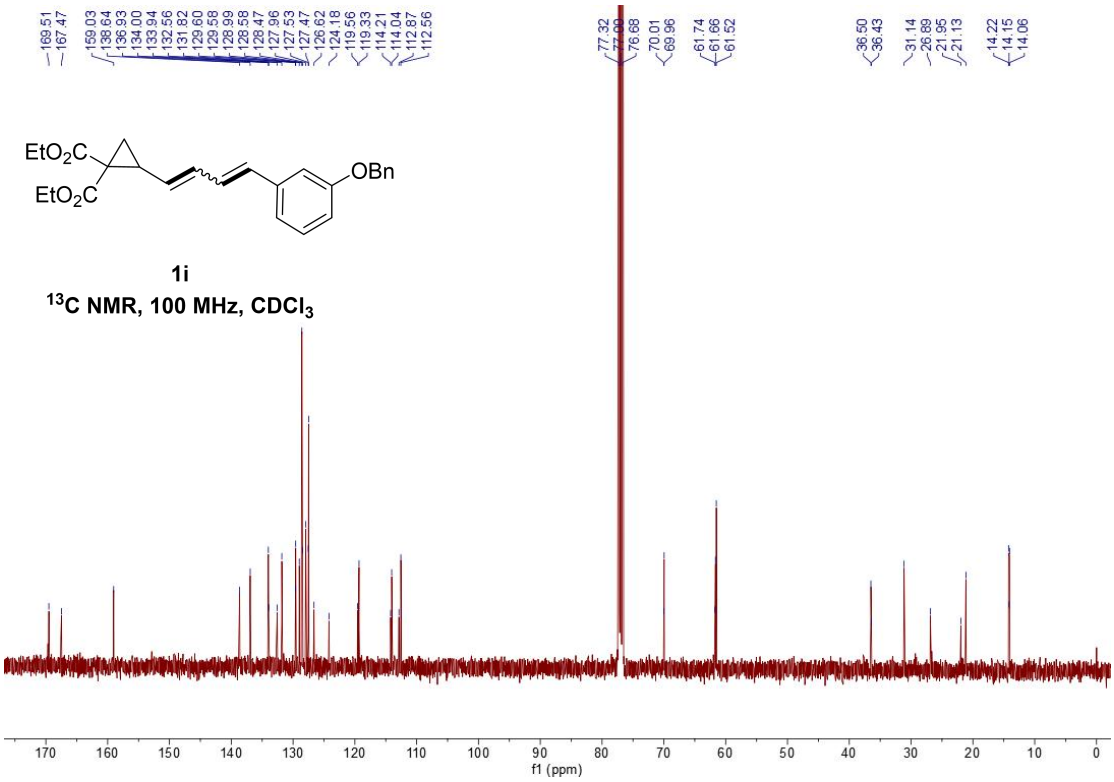


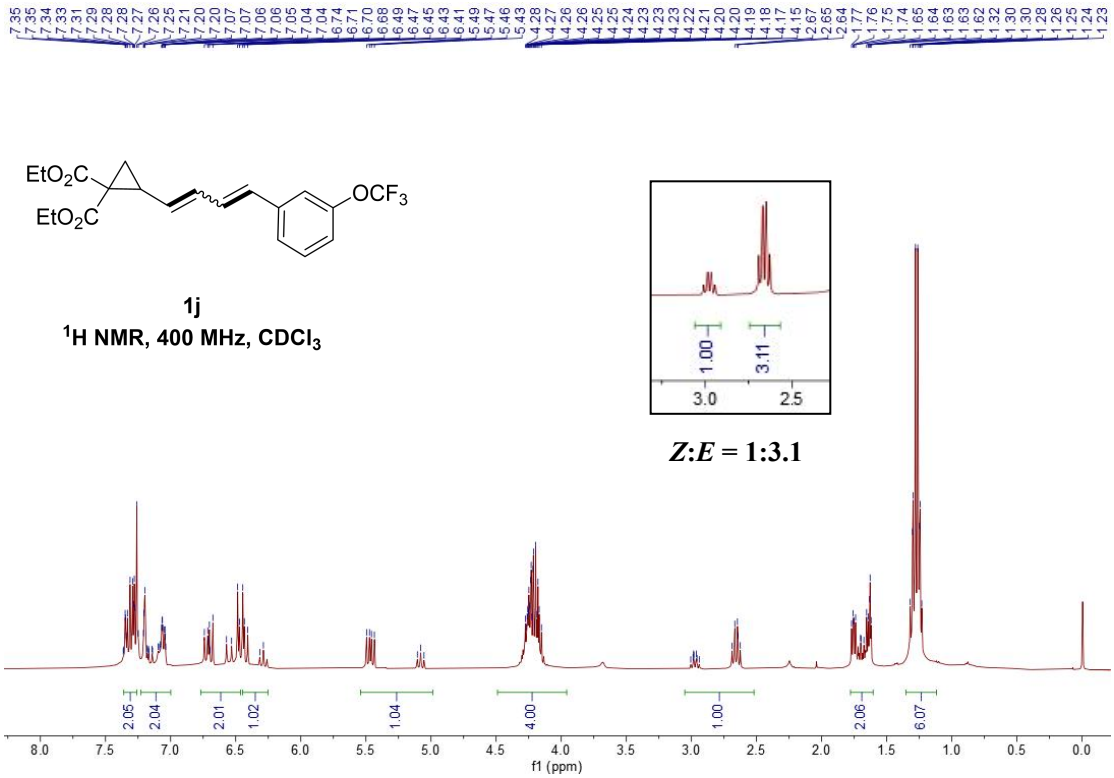
1h

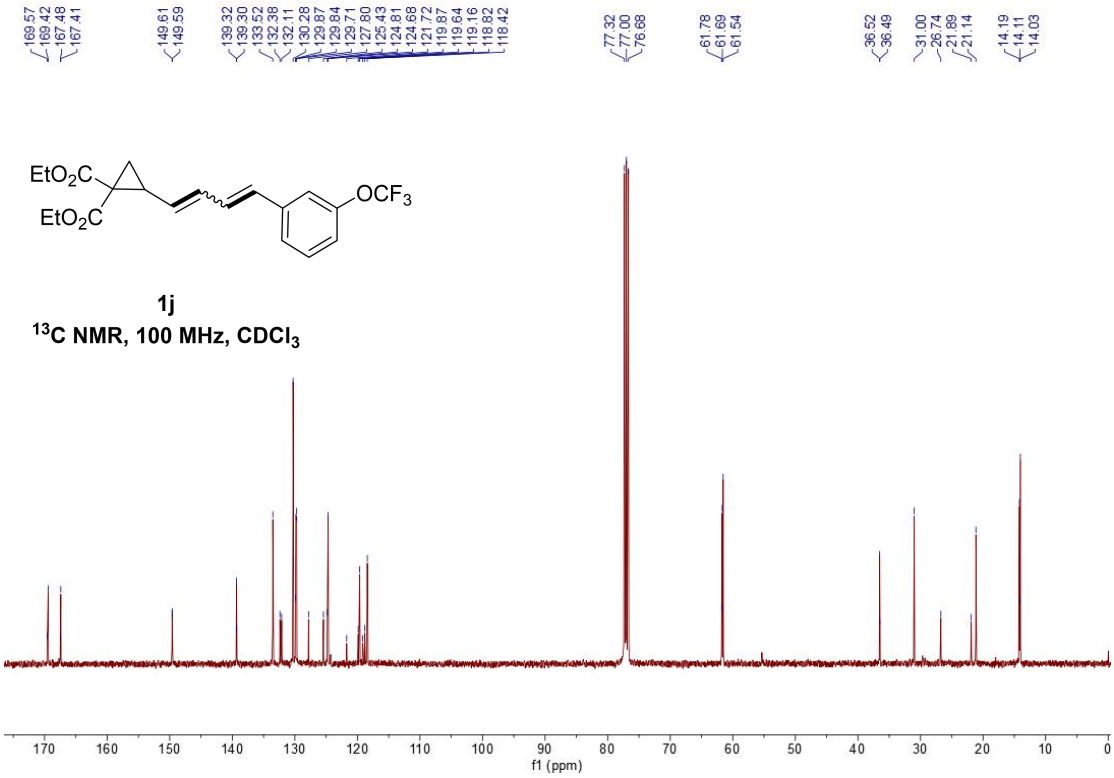
^{13}C NMR, 100 MHz, $CDCl_3$

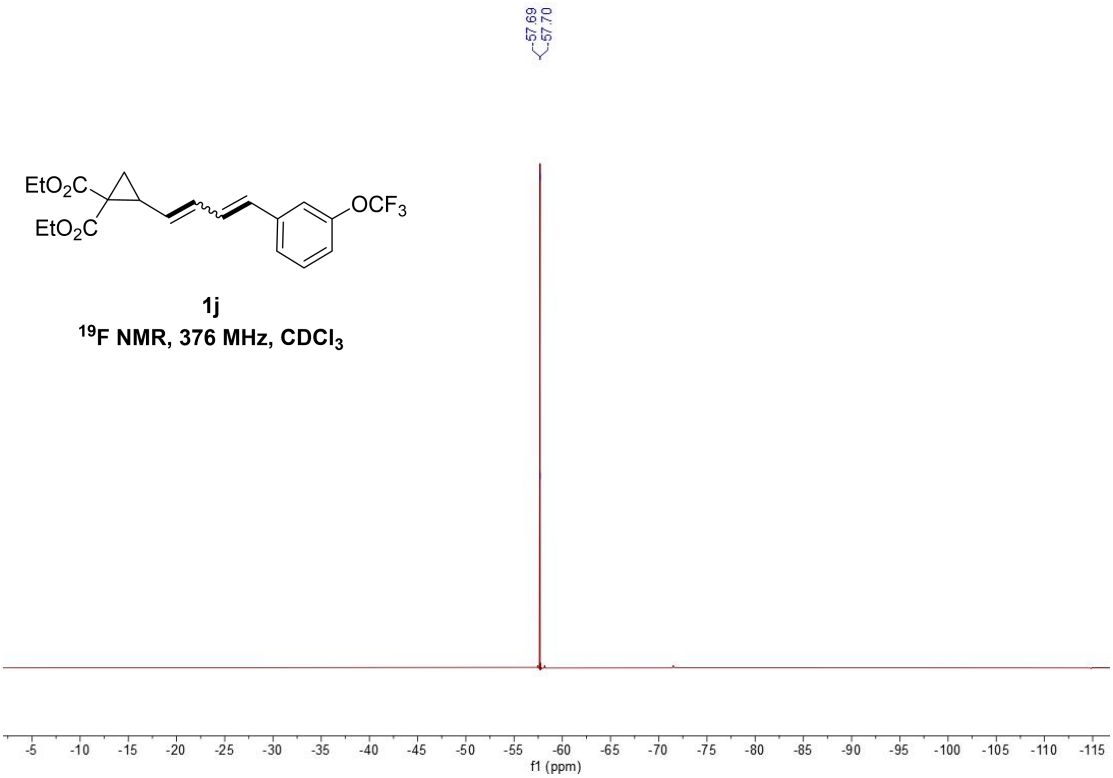



EtO2C
EtO2C
OBn
1i
1H NMR, 400 MHz, CDCl3
1.00
2.07
3.0
2.5
Z:E = 1:2.1
7.05
2.01
1.01
1.05
1.07
3.04
4.03
1.00
2.04
6.03
f1 (ppm)


EtO2C
EtO2C
OBn
1i
13C NMR, 100 MHz, CDCl3
f1 (ppm)

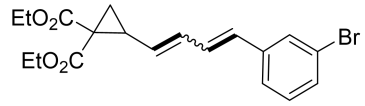

EtO2C
EtO2C
OCF3
1j
1H NMR, 400 MHz, CDCl3
1.00
3.11
Z:E = 1:3.1
f1 (ppm)


EtO2C
EtO2C
OCF3
1j
13C NMR, 100 MHz, CDCl3
f1 (ppm)



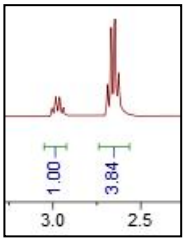
1j

^{19}F NMR, 376 MHz, $CDCl_3$

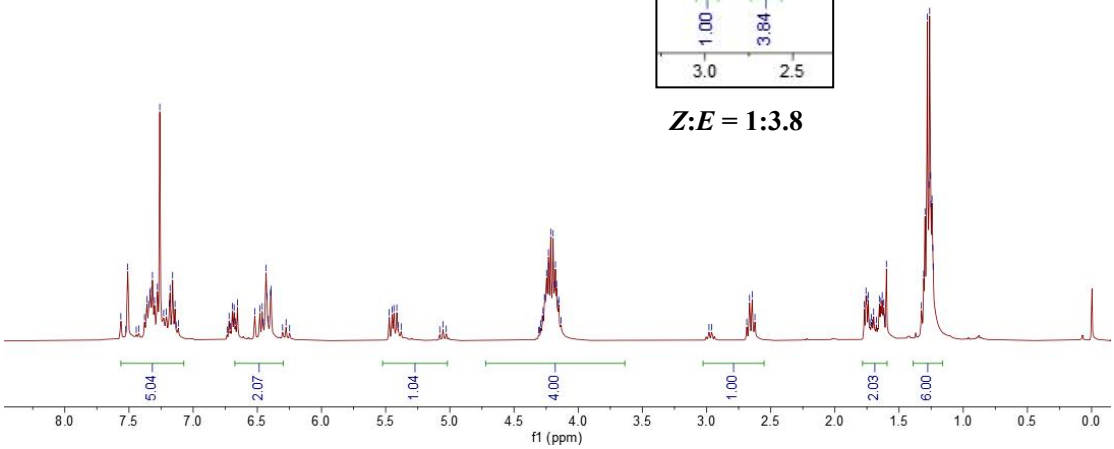


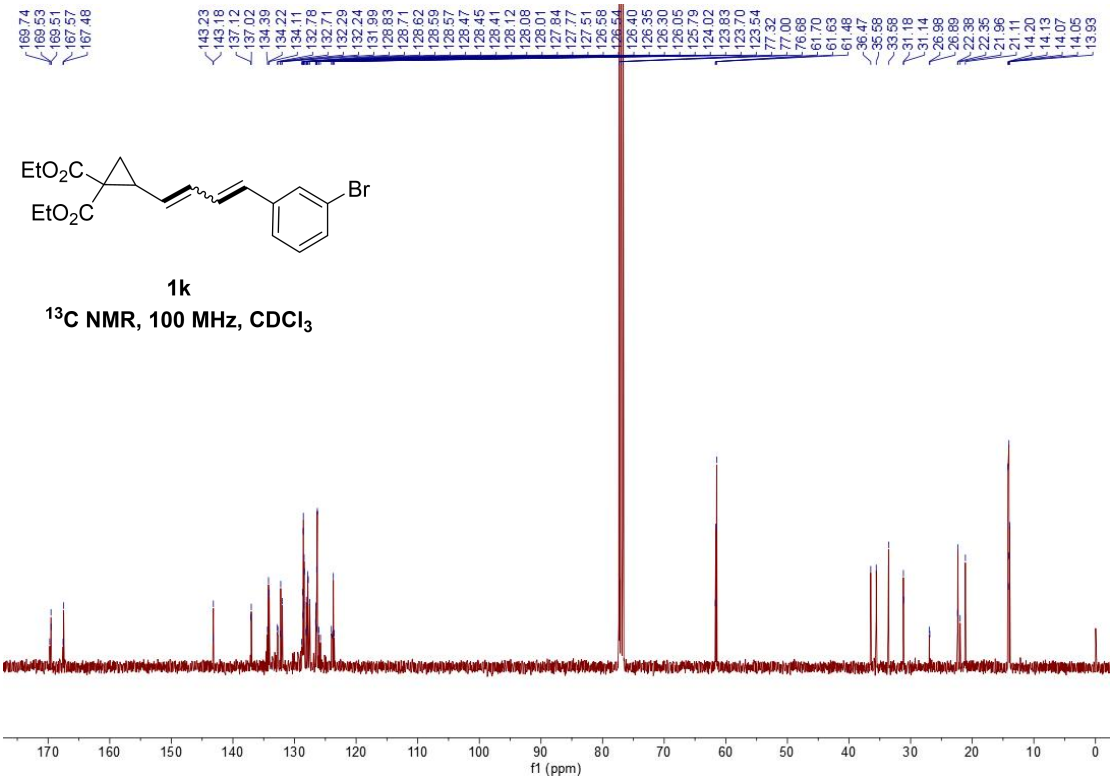
1k

^{1}H NMR, 400 MHz, CDCl$_3$



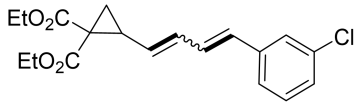
***Z*:*E* = 1:3.8**





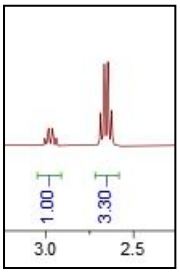
1k

^{13}C NMR, 100 MHz, CDCl$_3$

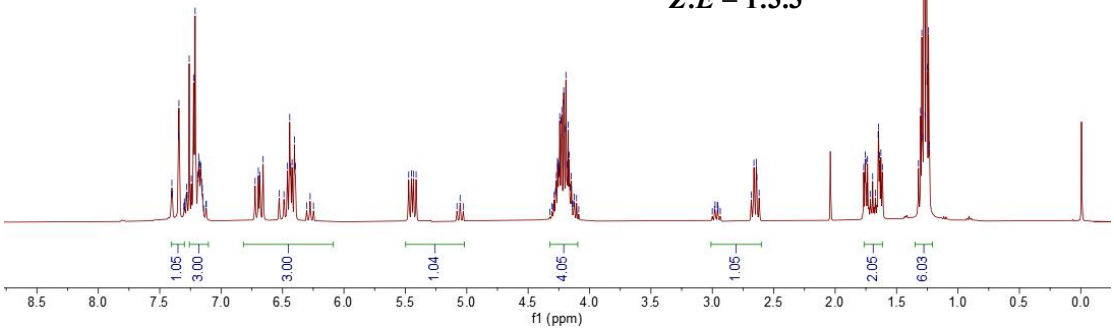


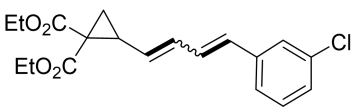
1l

^{1}H NMR, 400 MHz, $CDCl_3$



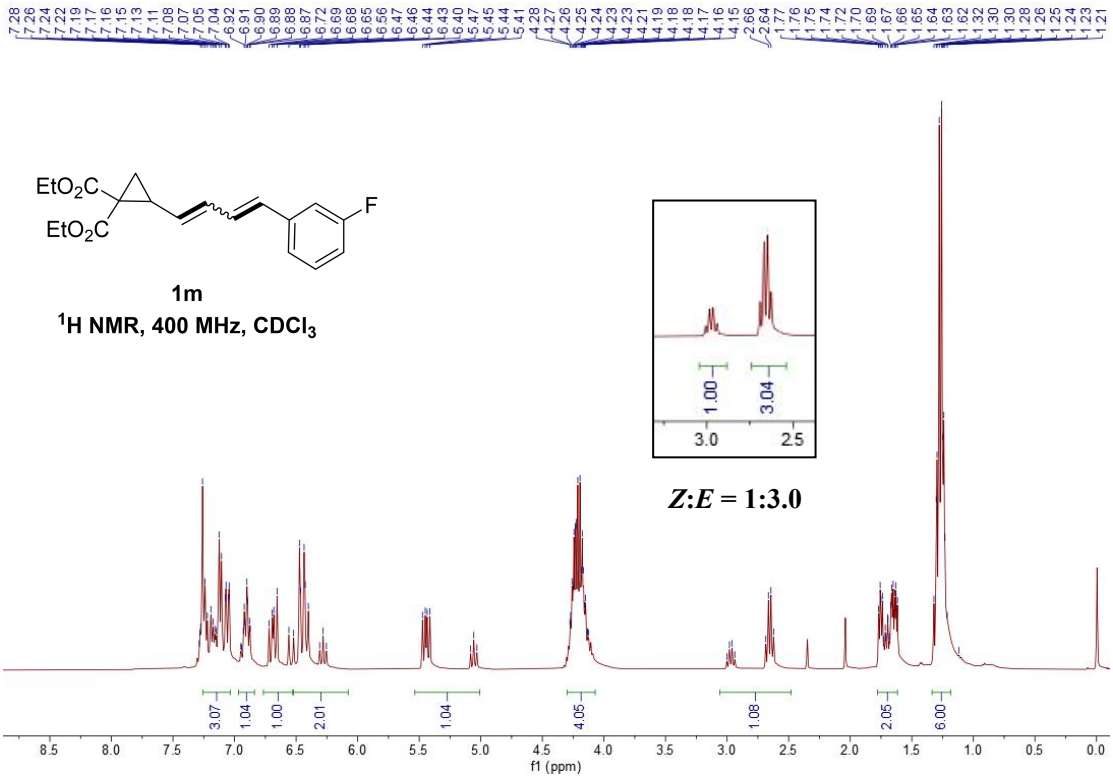
***Z*:*E* = 1:3.3**

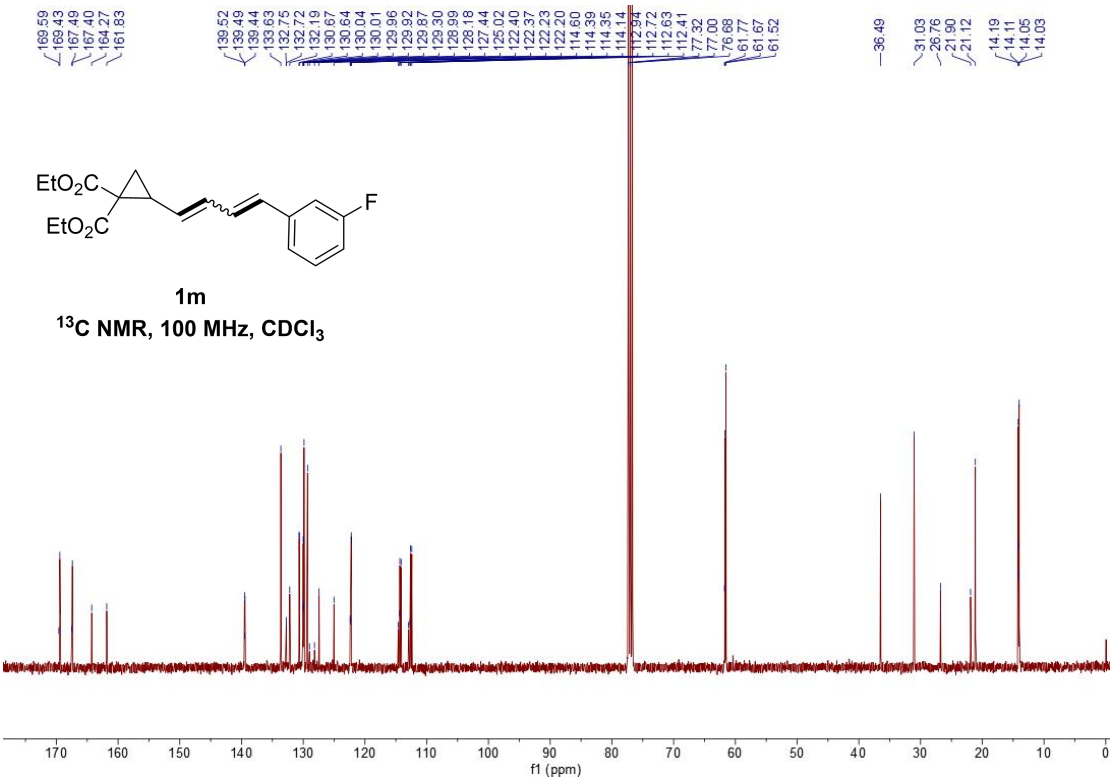


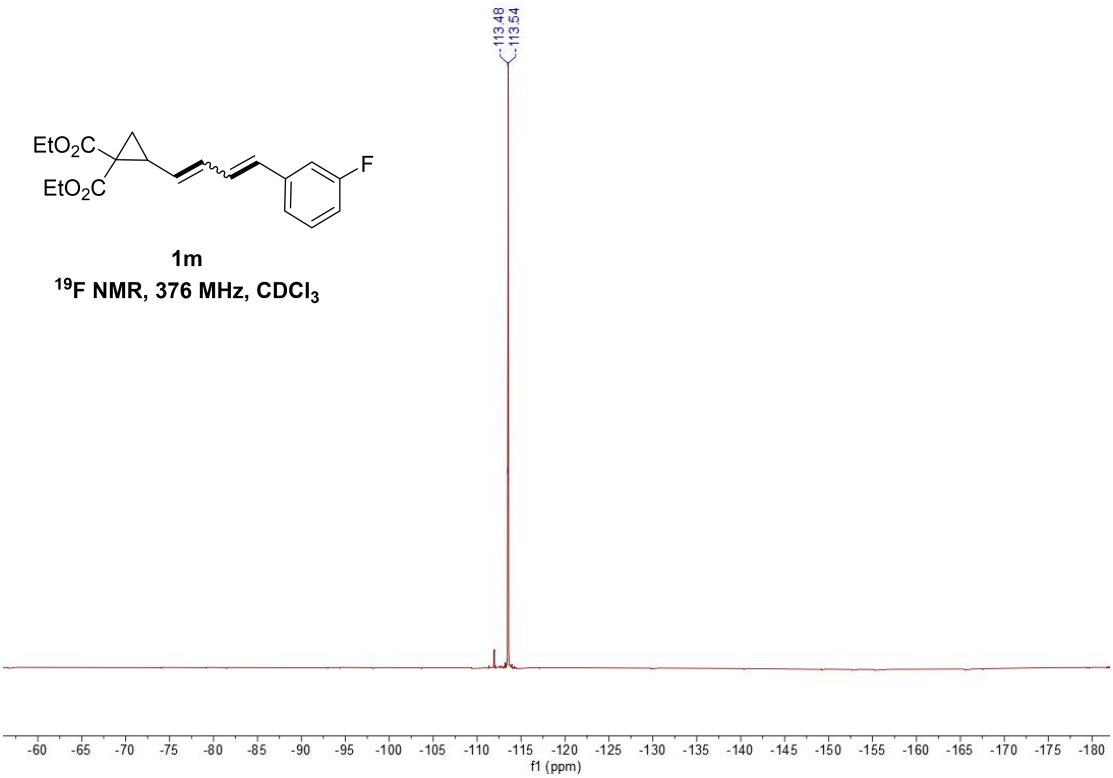


1l

^{13}C NMR, 100 MHz, $CDCl_3$

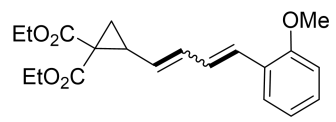

EtO2C
EtO2C
F
1m
1H NMR, 400 MHz, CDCl3
1.00
3.04
Z:E = 1:3.0
f1 (ppm)


EtO2C
EtO2C
F
1m
13C NMR, 100 MHz, CDCl3
f1 (ppm)



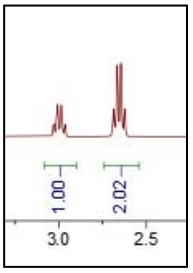
1m

^{19}F NMR, 376 MHz, $CDCl_3$

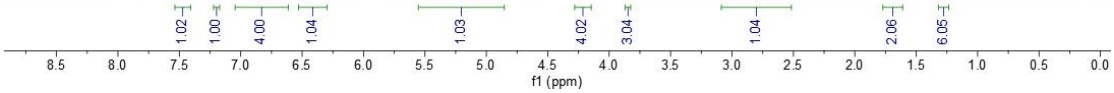


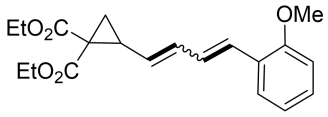
1n

^{1}H NMR, 400 MHz, $CDCl_3$



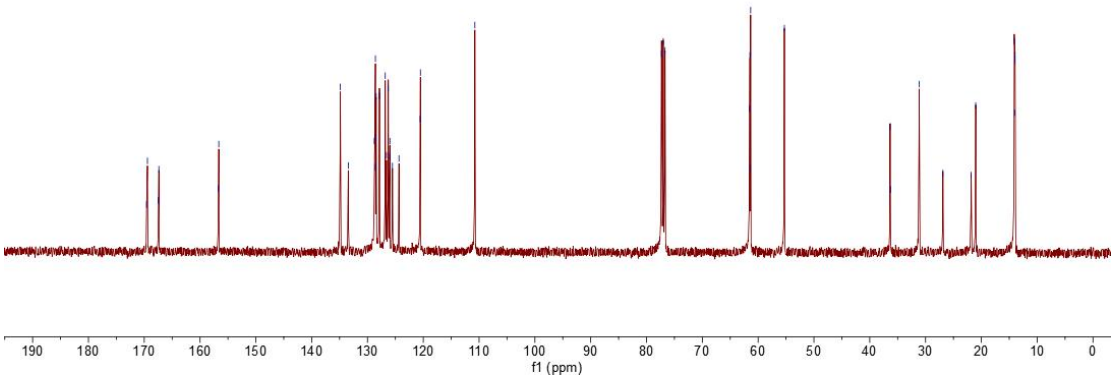
***Z*:*E* = 1:2.0**

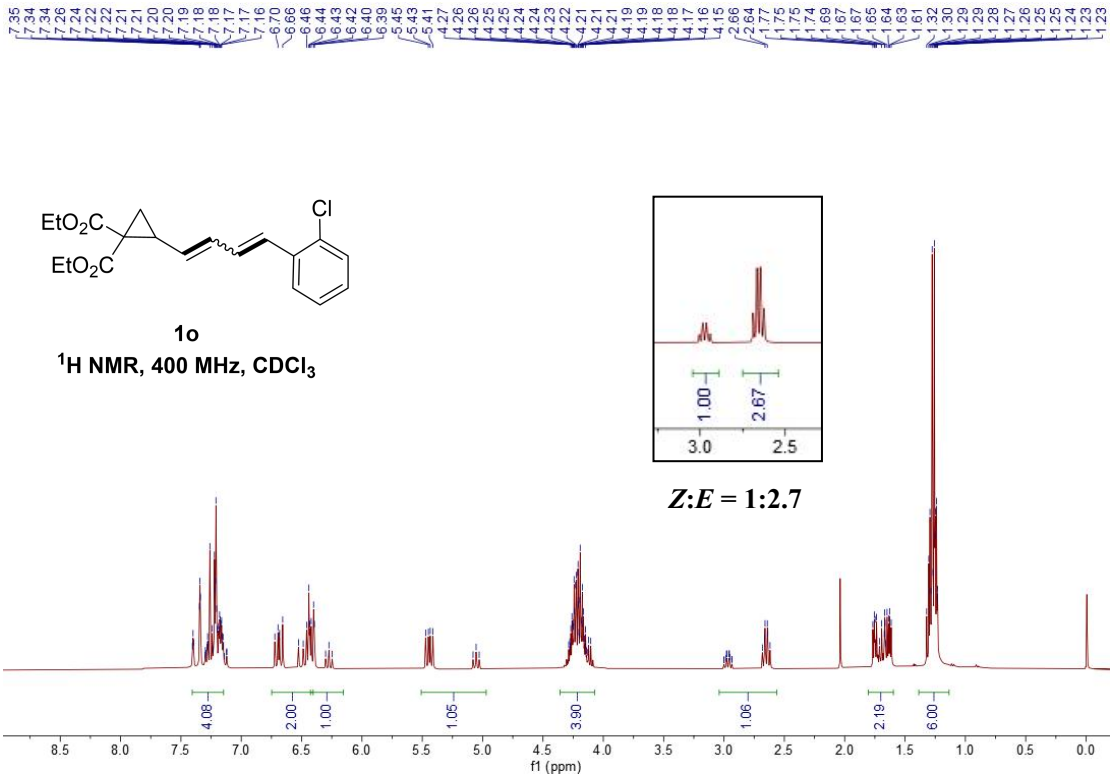


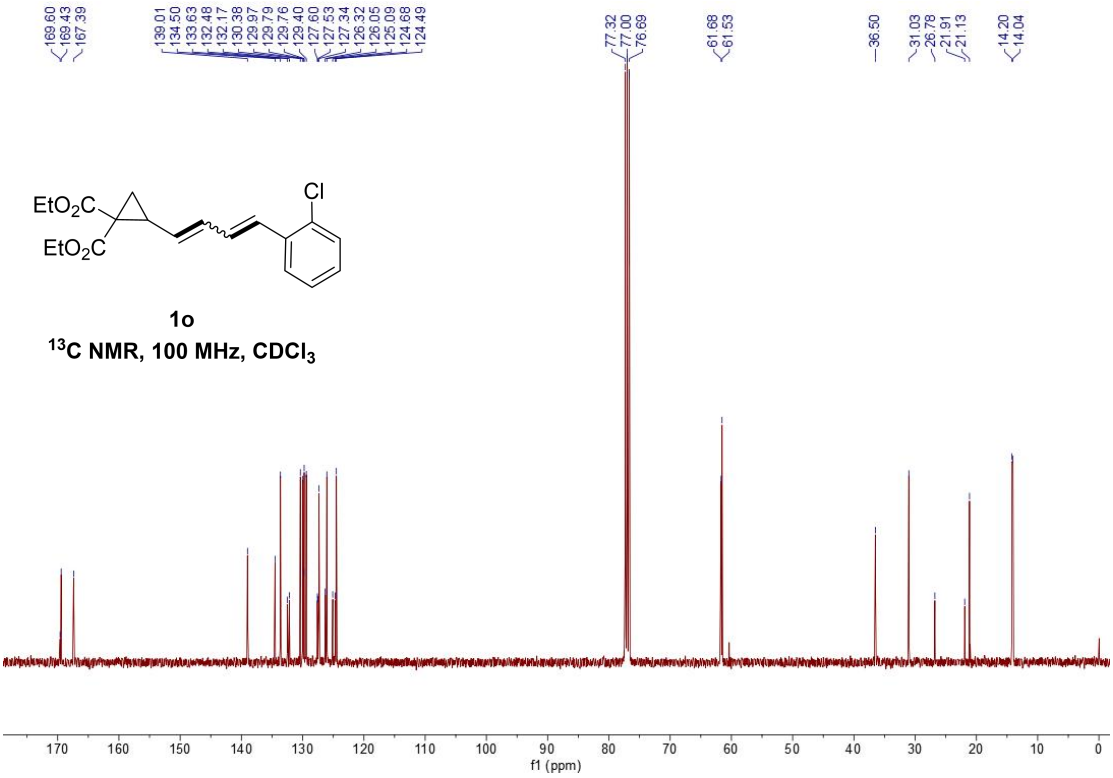


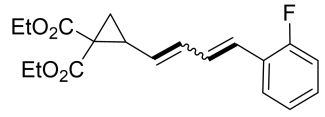
1n

^{13}C NMR, 100 MHz, $CDCl_3$



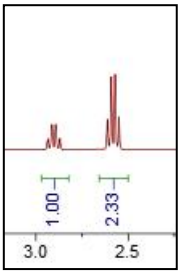

EtO2C
EtO2C
Cl
1o
1H NMR, 400 MHz, CDCl3
Z:E = 1:2.7
f1 (ppm)


EtO2C
EtO2C
Cl
1o
13C NMR, 100 MHz, CDCl3
f1 (ppm)

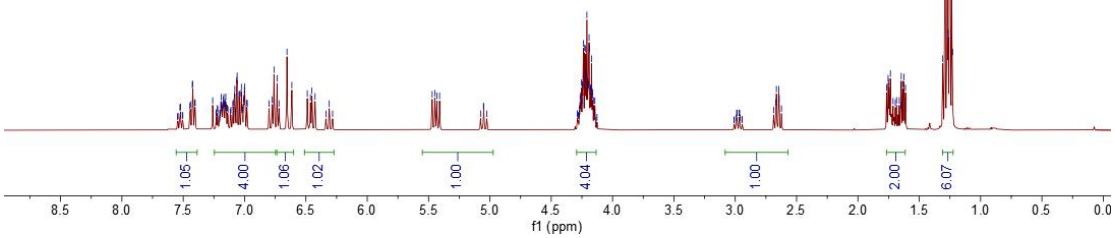


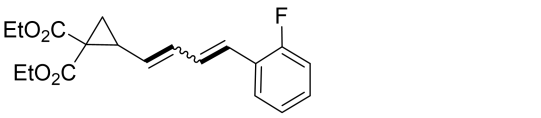
1p

^{1}H NMR, 400 MHz, $CDCl_3$



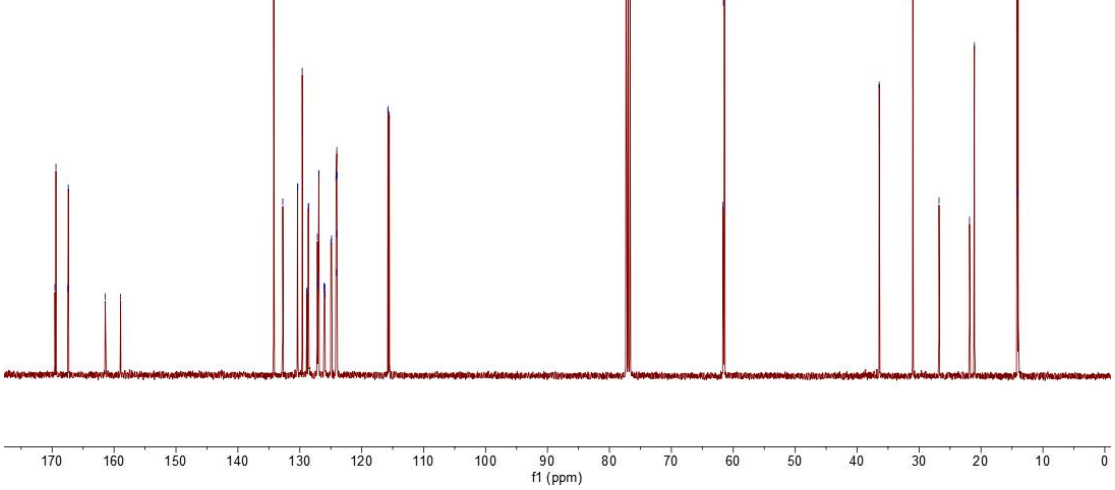
***Z*:*E* = 1:2.3**

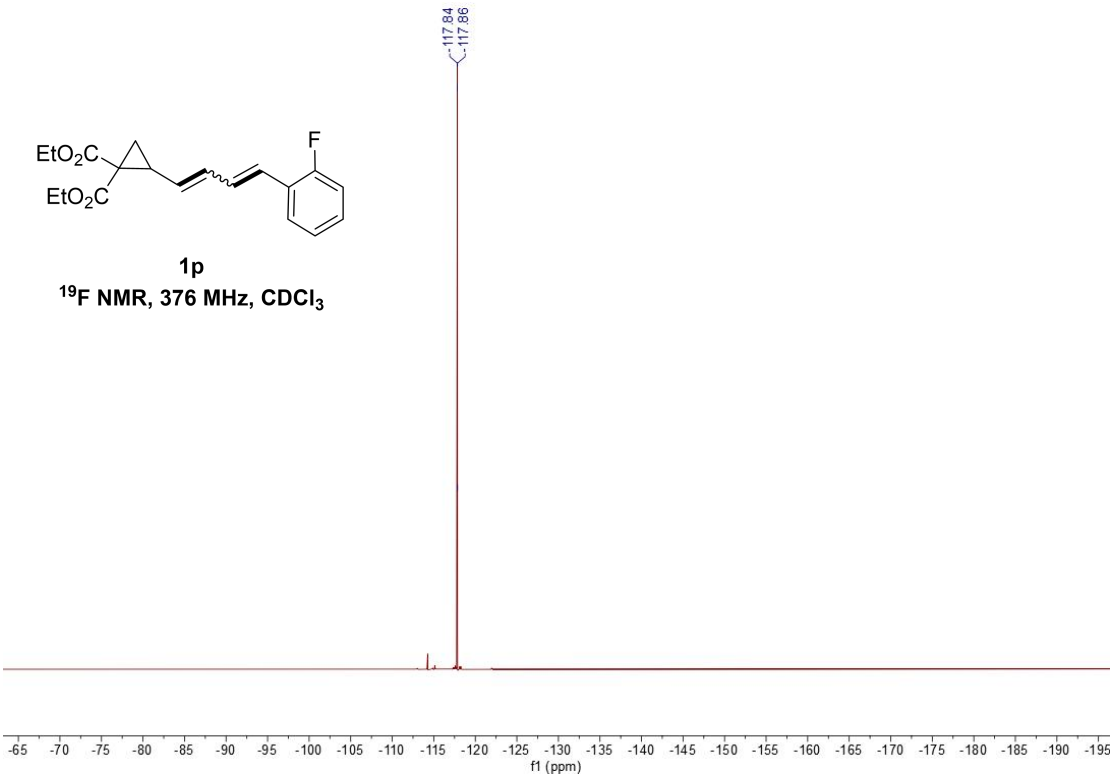




1p

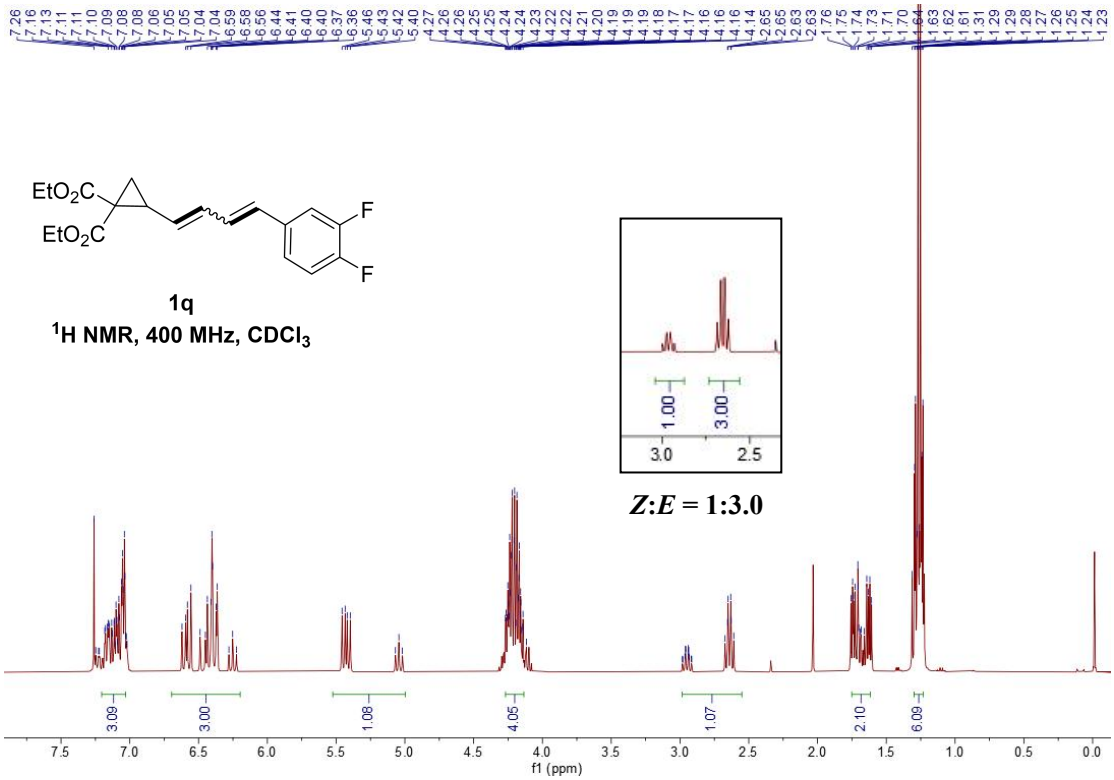
^{13}C NMR, 100 MHz, $CDCl_3$





1p

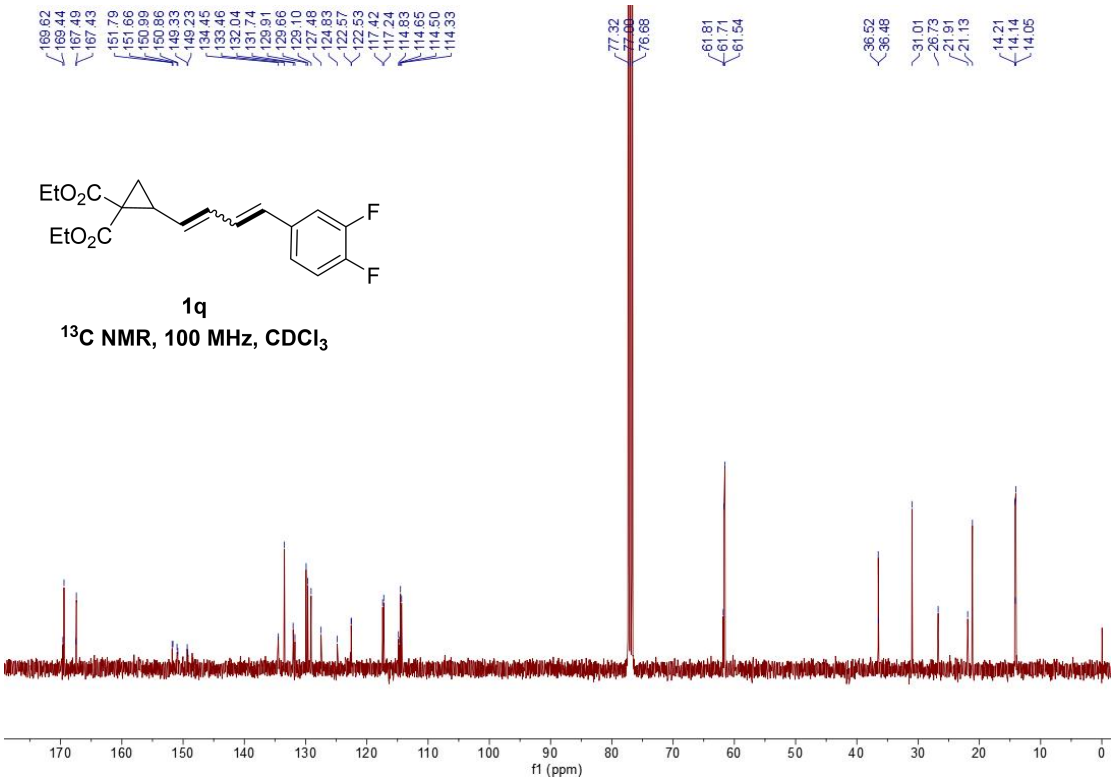
^{19}F NMR, 376 MHz, $CDCl_3$



1q

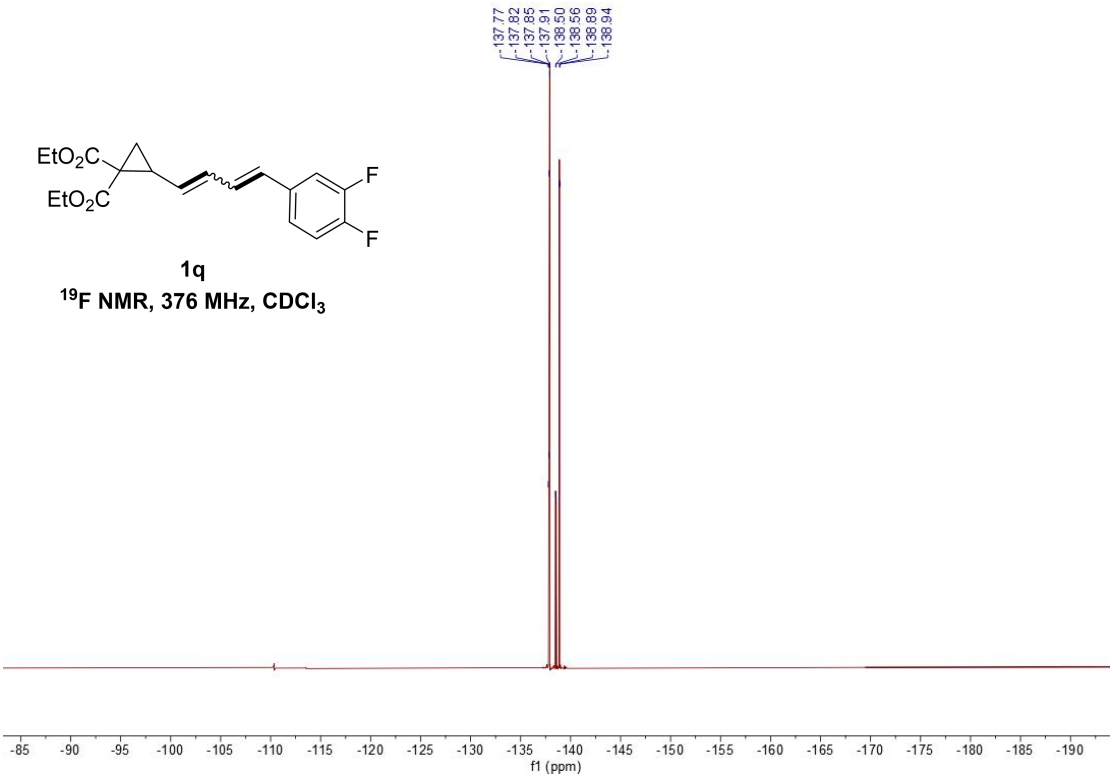
^{1}H NMR, 400 MHz, $CDCl_3$

***Z*:*E* = 1:3.0**



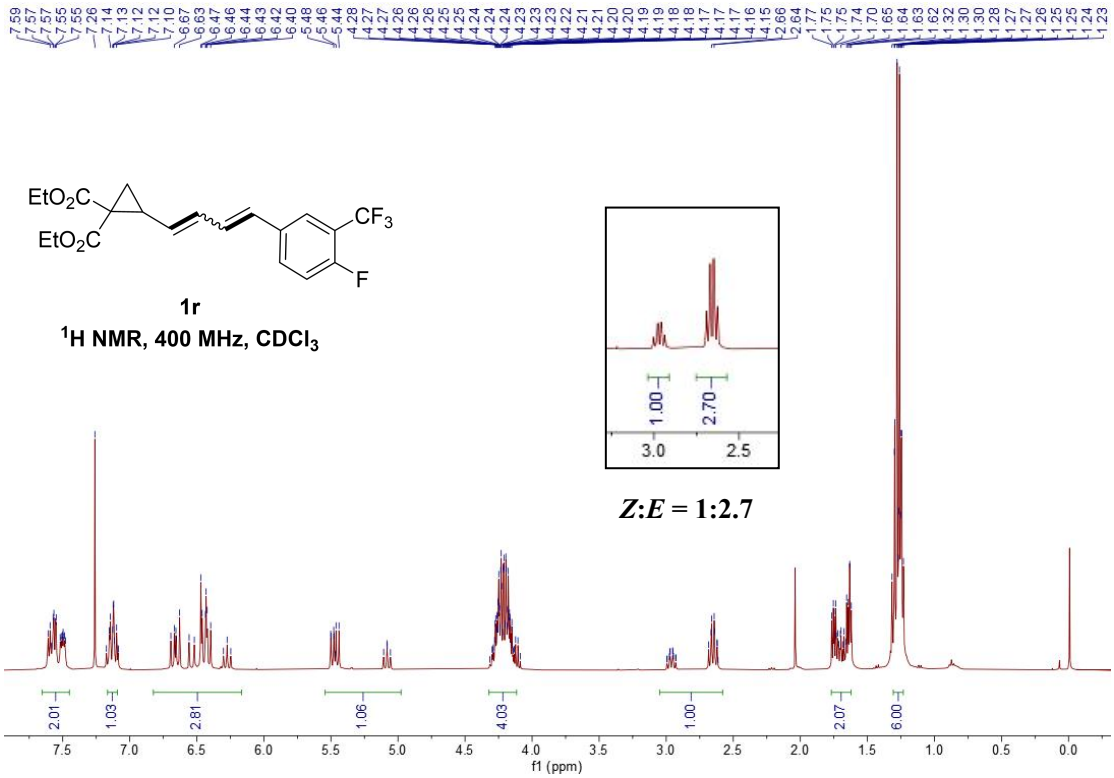
1q

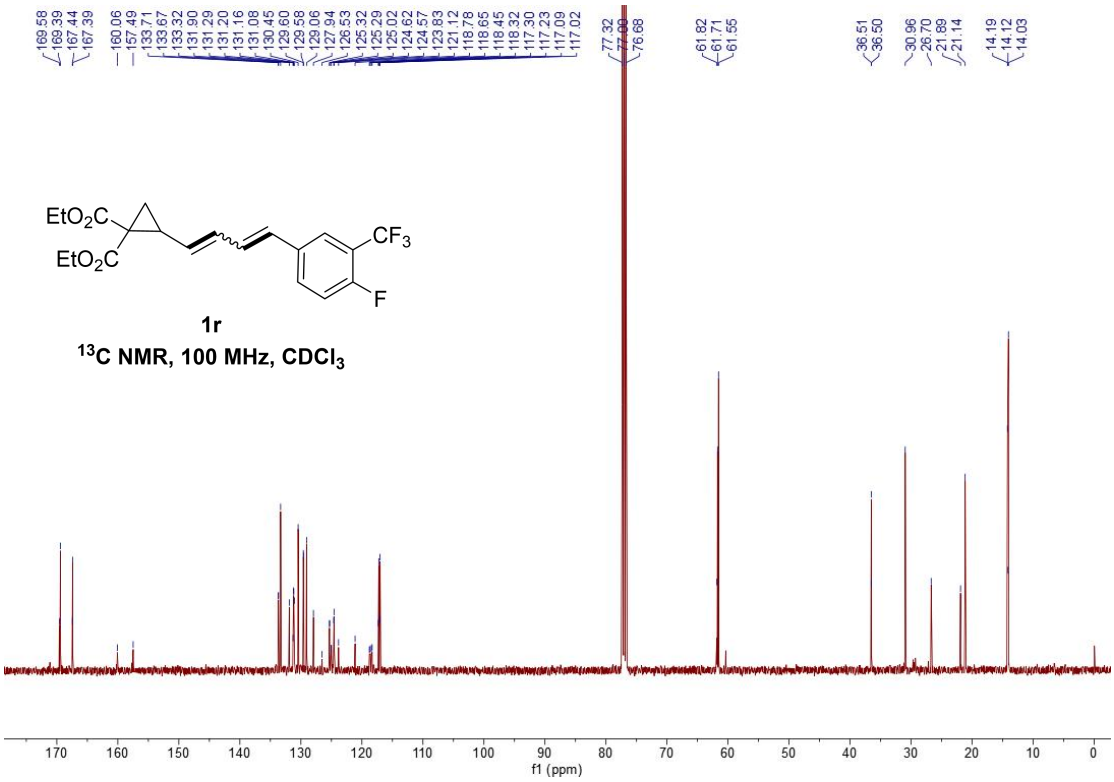
^{13}C NMR, 100 MHz, $CDCl_3$

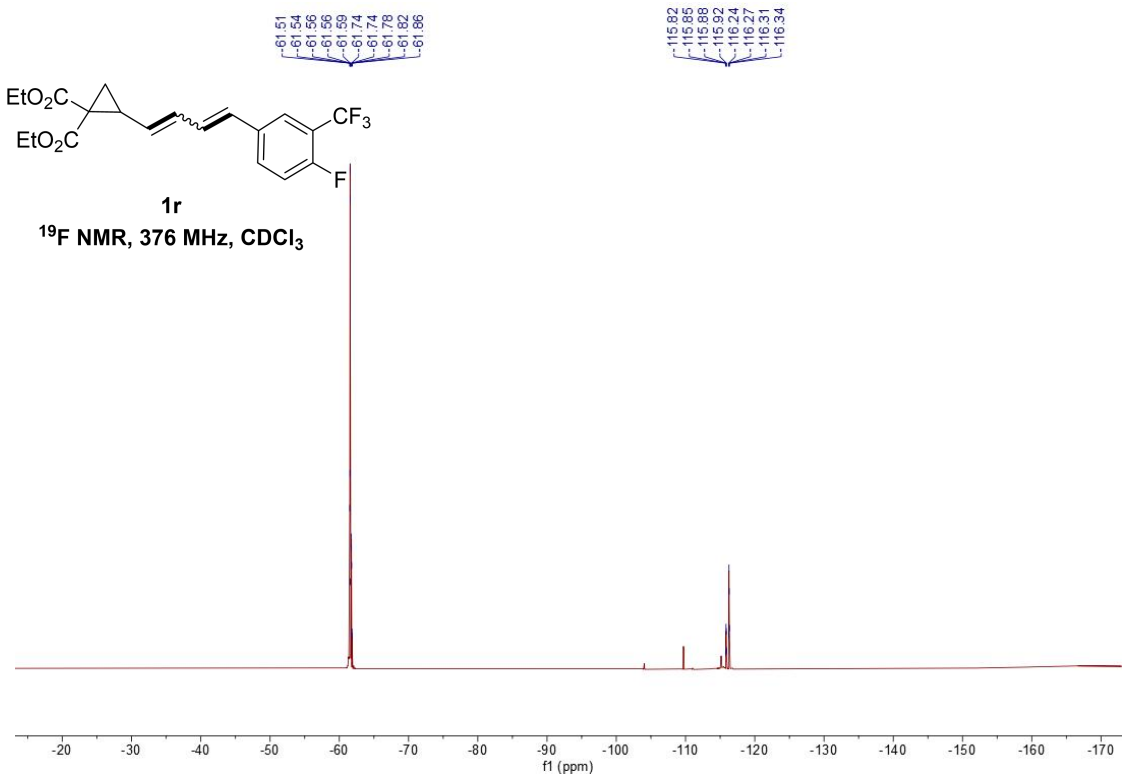


1q

^{19}F NMR, 376 MHz, $CDCl_3$

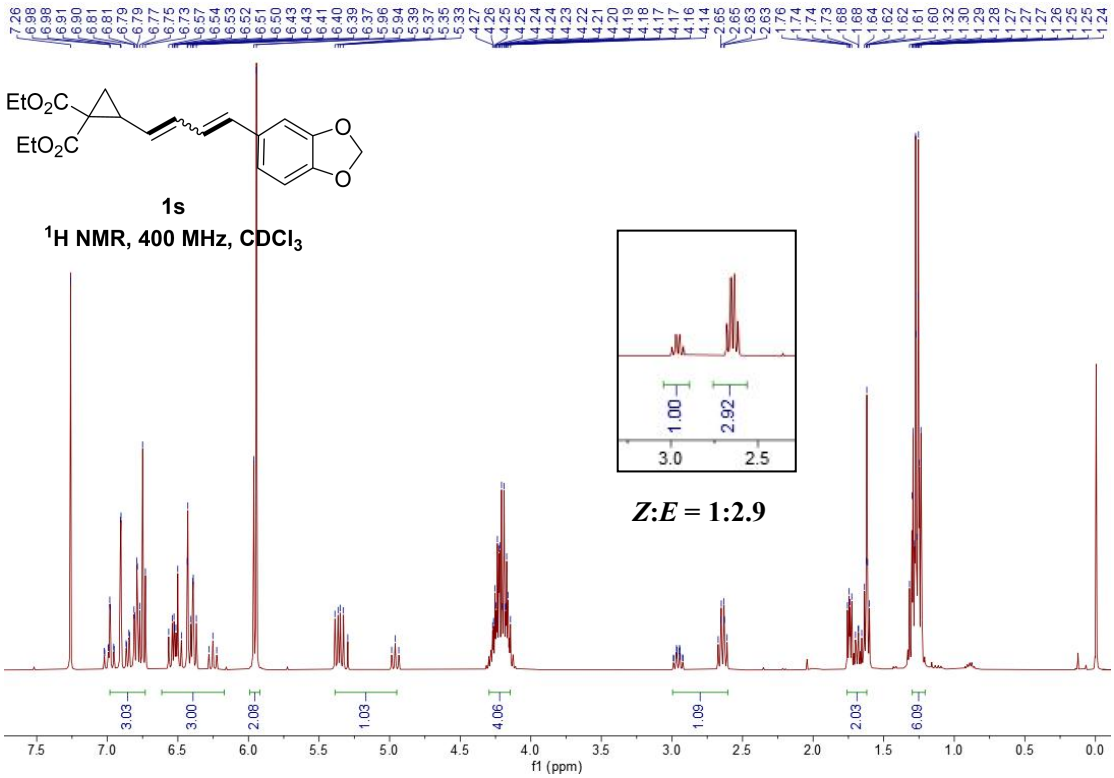

EtO2C
EtO2C
CF3
F
1r
1H NMR, 400 MHz, CDCl3
1.00
2.70
3.0
2.5
Z:E = 1:2.7
2.01
1.03
2.81
1.06
4.03
1.00
2.07
6.00
f1 (ppm)

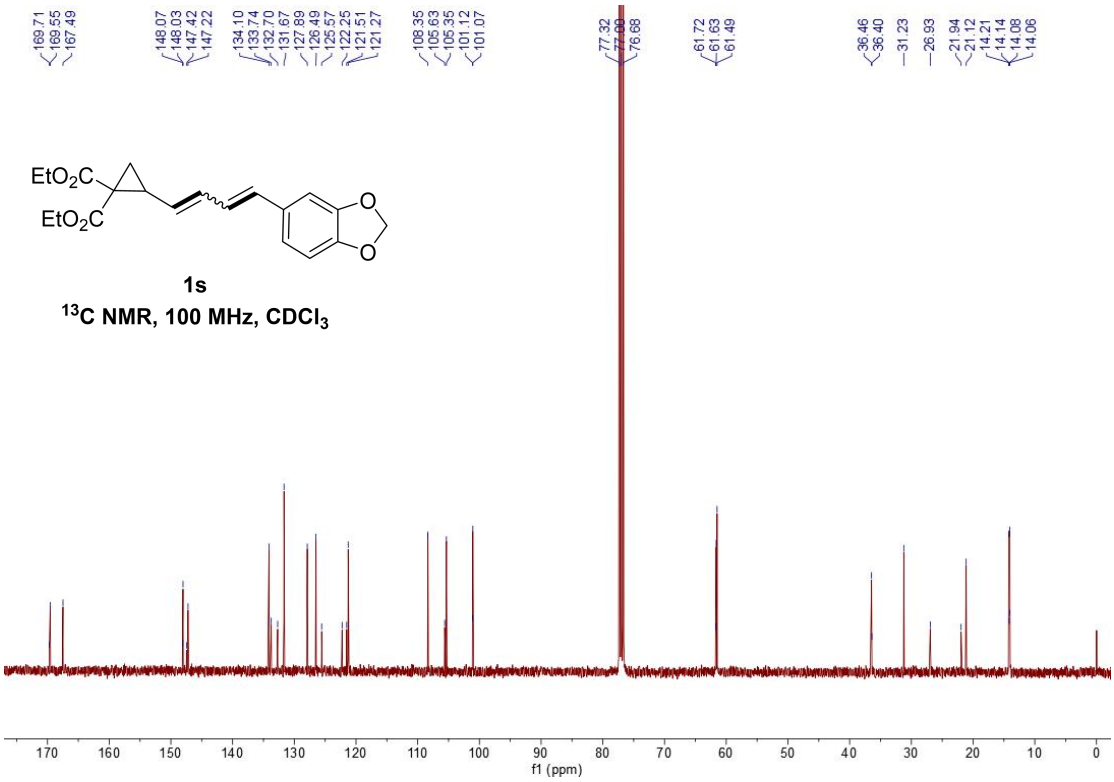

EtO2C
EtO2C
CF3
F
1r
13C NMR, 100 MHz, CDCl3
f1 (ppm)

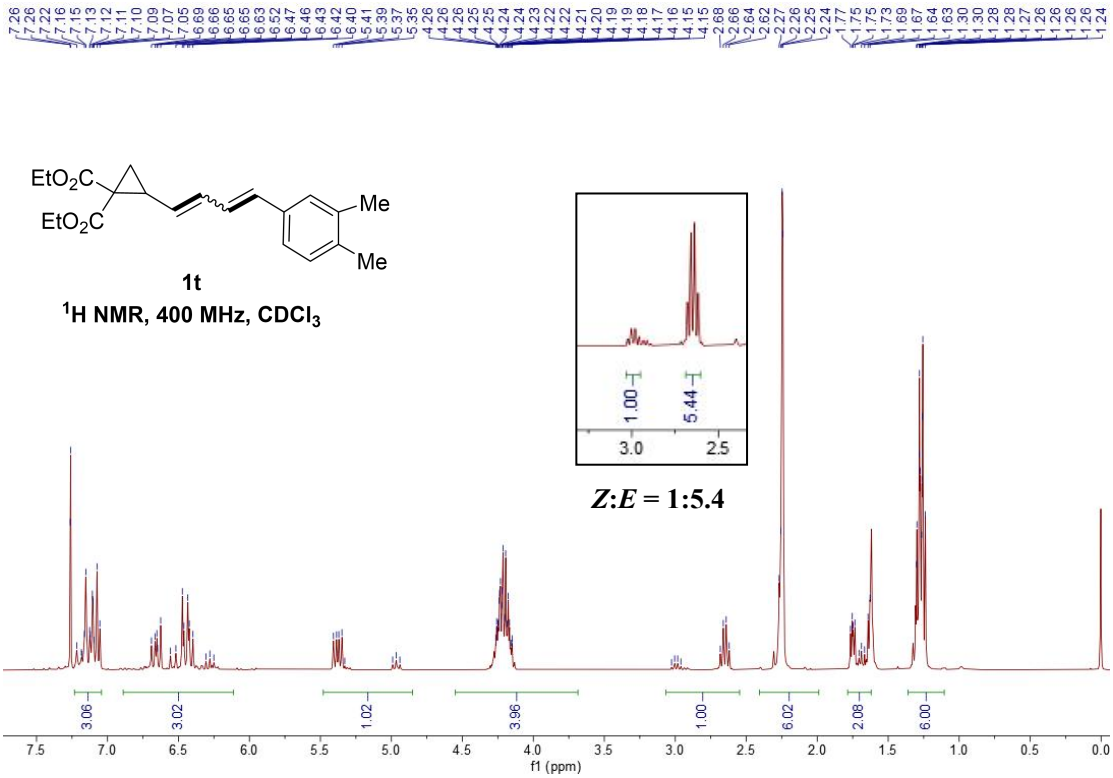


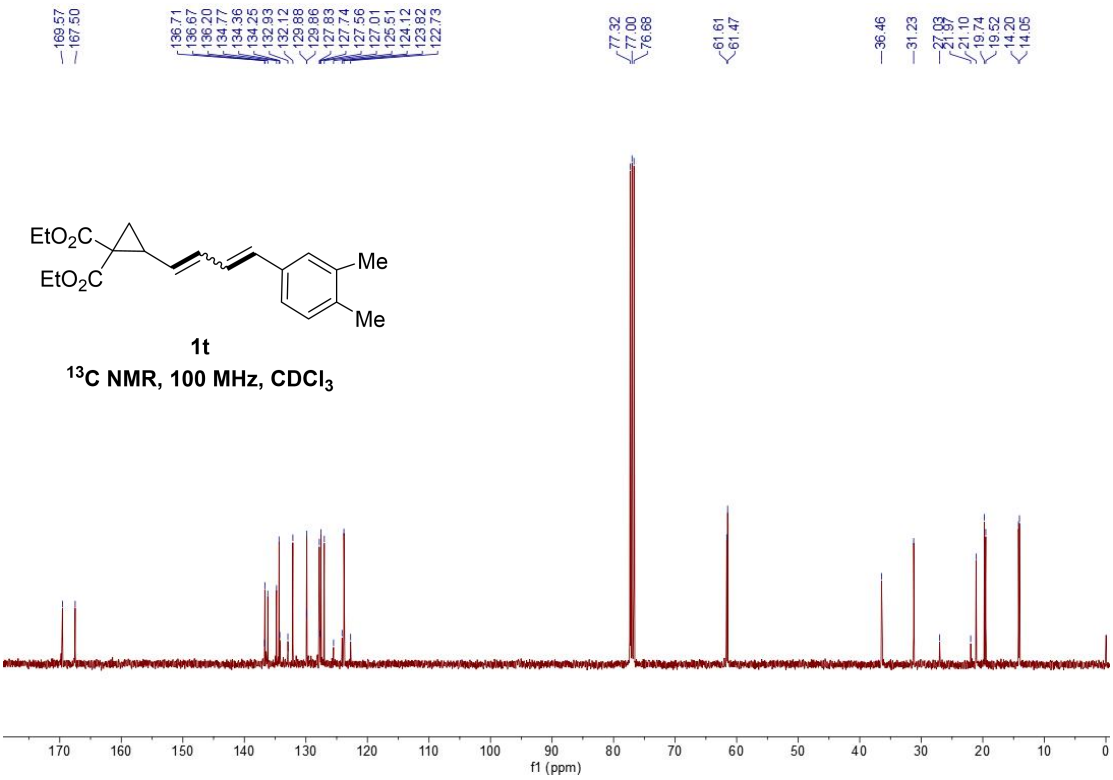
1r

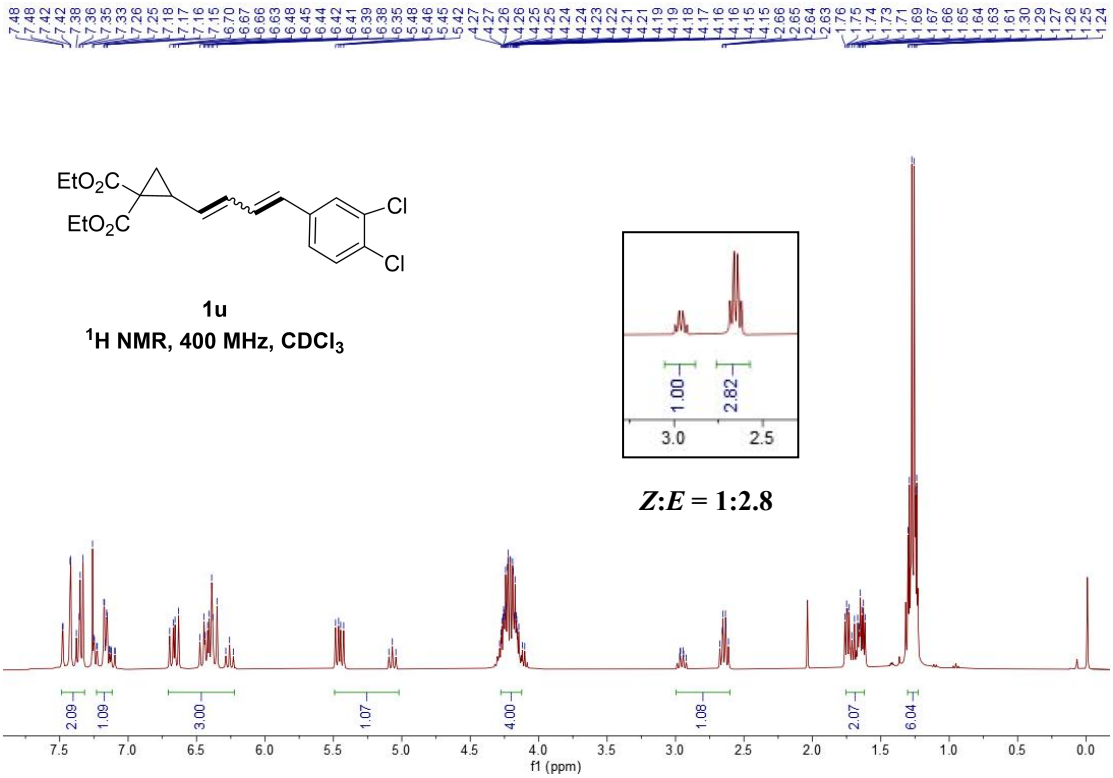
^{19}F NMR, 376 MHz, $CDCl_3$

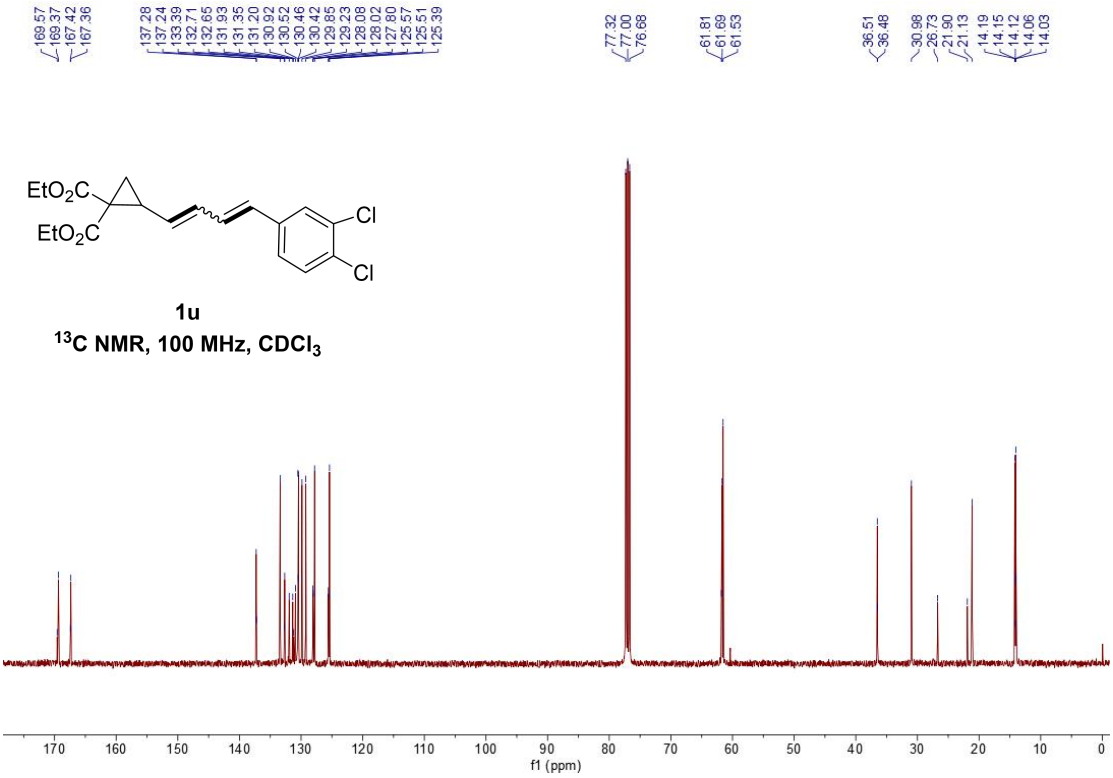

EtO2C
EtO2C
O
O
1s
1H NMR, 400 MHz, CDCl3
1.00
2.92
3.0
2.5
Z:E = 1:2.9
3.03
3.00
2.08
1.03
4.06
1.09
2.03
6.09
f1 (ppm)

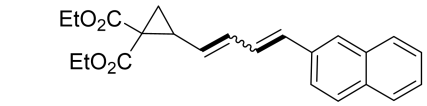

EtO2C
EtO2C
O
O
1s
13C NMR, 100 MHz, CDCl3
f1 (ppm)


EtO2C
EtO2C
Me
Me
1t
1H NMR, 400 MHz, CDCl3
1.00
5.44
3.0
2.5
Z:E = 1:5.4
3.06
3.02
1.02
3.96
1.00
6.02
2.08
6.00
f1 (ppm)


EtO2C
EtO2C
Me
Me
1t
13C NMR, 100 MHz, CDCl3
f1 (ppm)

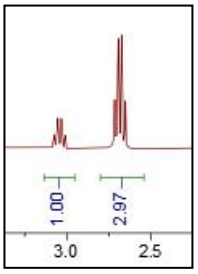

EtO2C
EtO2C
Cl
Cl
1u
1H NMR, 400 MHz, CDCl3
1.00
2.82
3.0
2.5
Z:E = 1:2.8
2.09
1.09
3.00
1.07
4.00
1.08
2.07
6.04
f1 (ppm)


EtO2C
EtO2C
Cl
Cl
1u
13C NMR, 100 MHz, CDCl3
f1 (ppm)

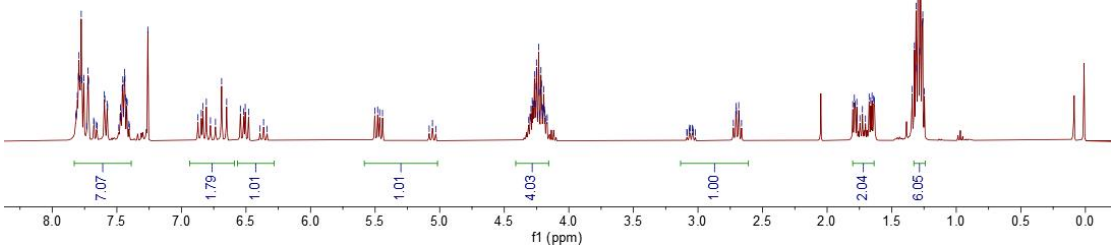


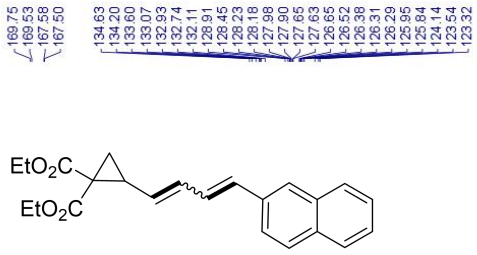
1v

^{1}H NMR, 400 MHz, $CDCl_3$



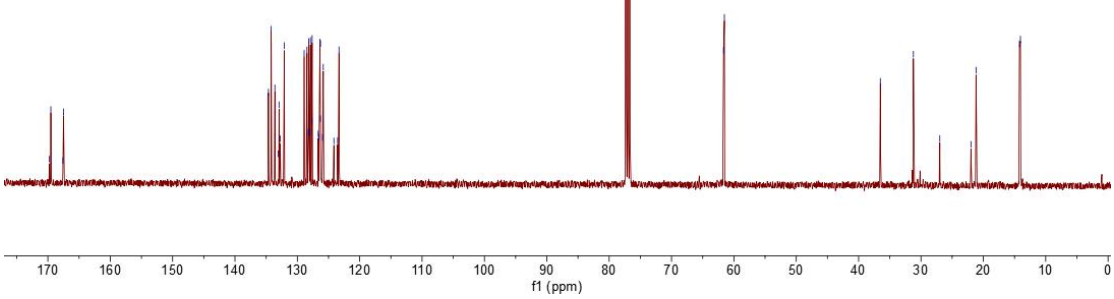
***Z*:*E* = 1:3.0**

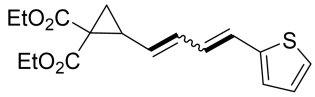




1v

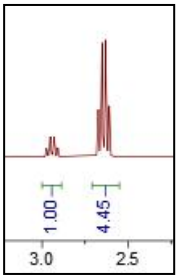
^{13}C NMR, 100 MHz, $CDCl_3$



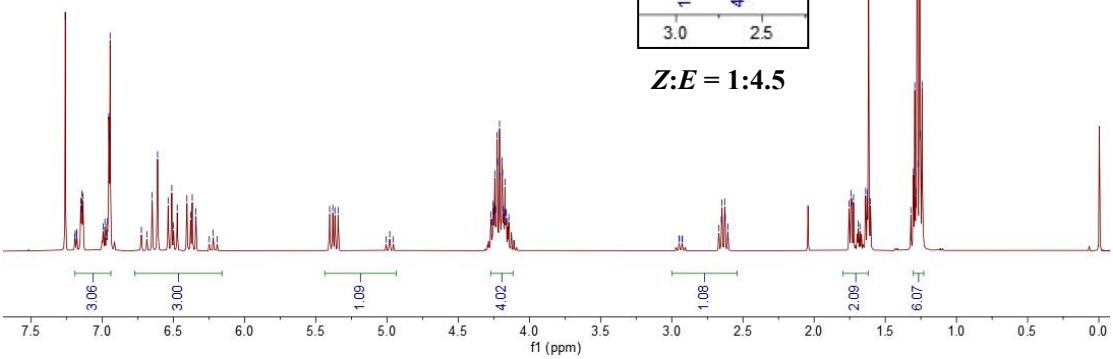


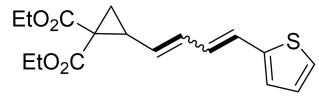
1w

^{1}H NMR, 400 MHz, $CDCl_3$



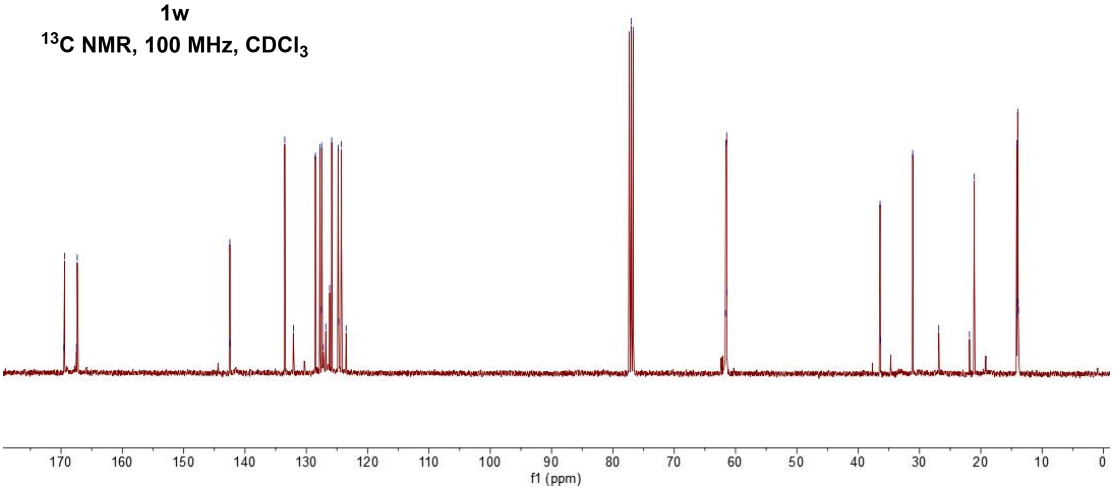
***Z*:*E* = 1:4.5**

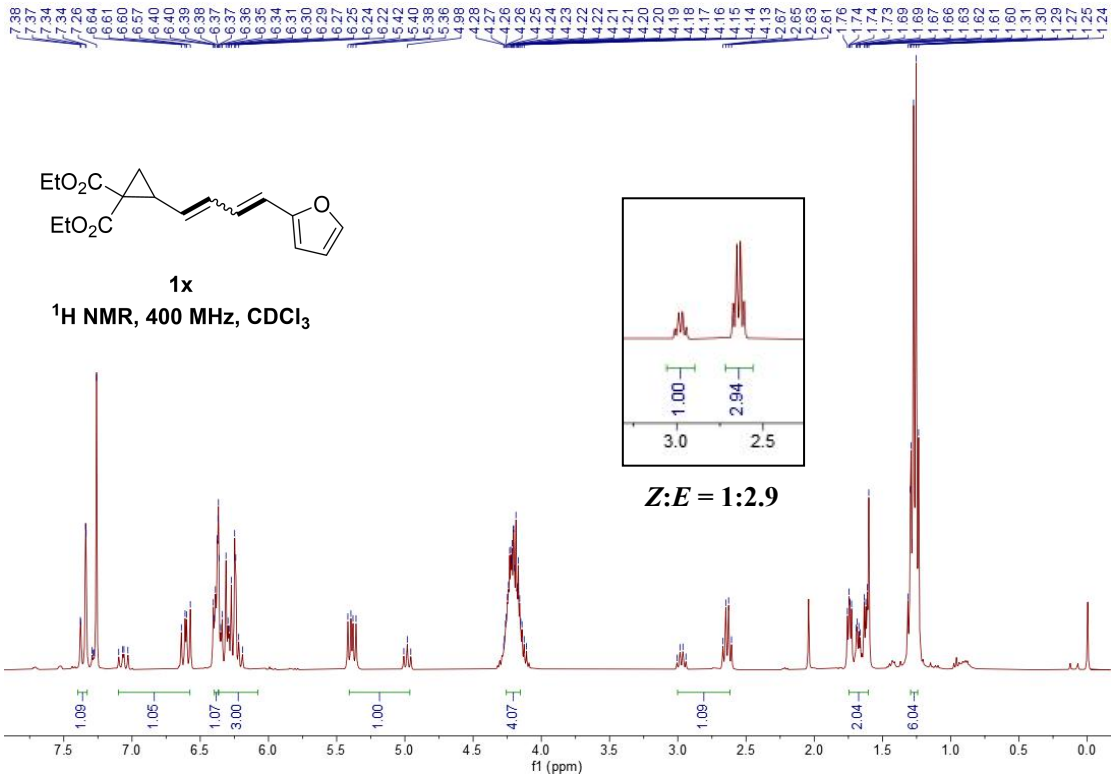


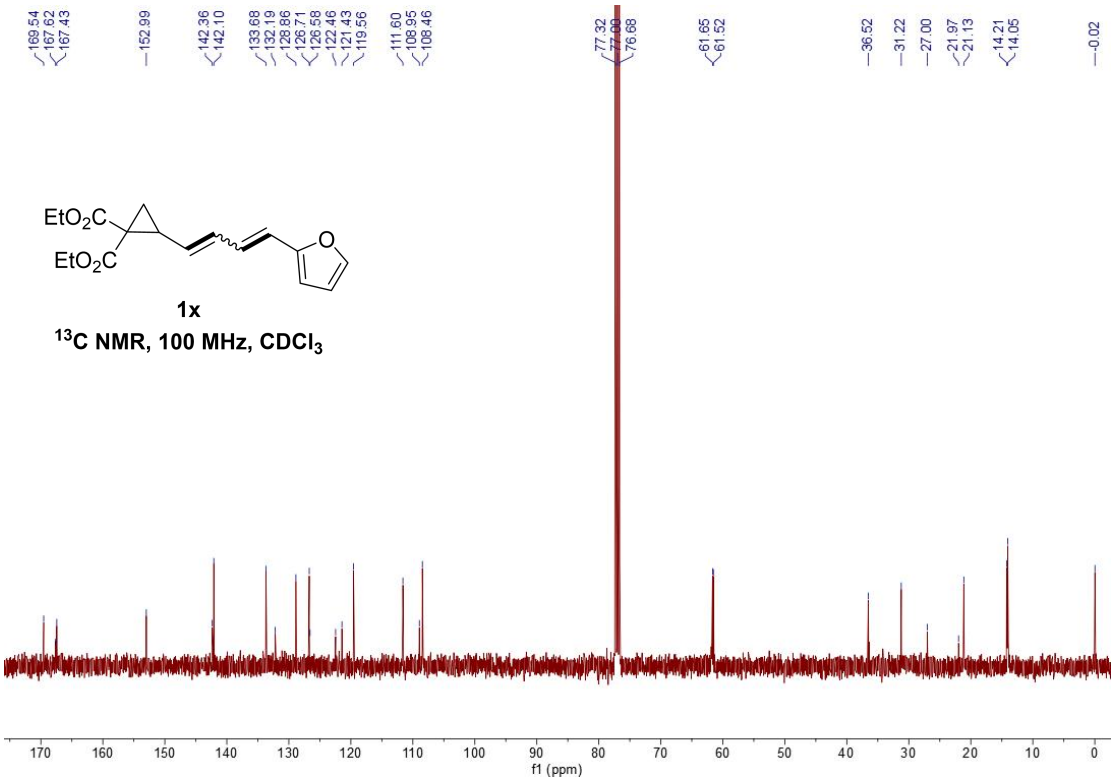


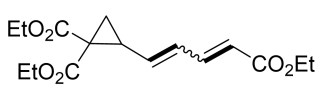
1w

^{13}C NMR, 100 MHz, $CDCl_3$



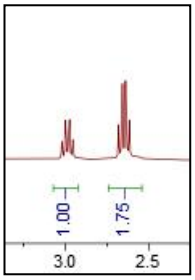

EtO2C
EtO2C
O
1x
1H NMR, 400 MHz, CDCl3
1.00
2.94
3.0
2.5
Z:E = 1:2.9
1.09
1.05
1.07
3.00
1.00
4.07
1.09
2.04
6.04
f1 (ppm)


EtO2C
EtO2C
O
1x
13C NMR, 100 MHz, CDCl3
f1 (ppm)

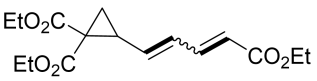


1y

^{1}H NMR, 400 MHz, $CDCl_3$

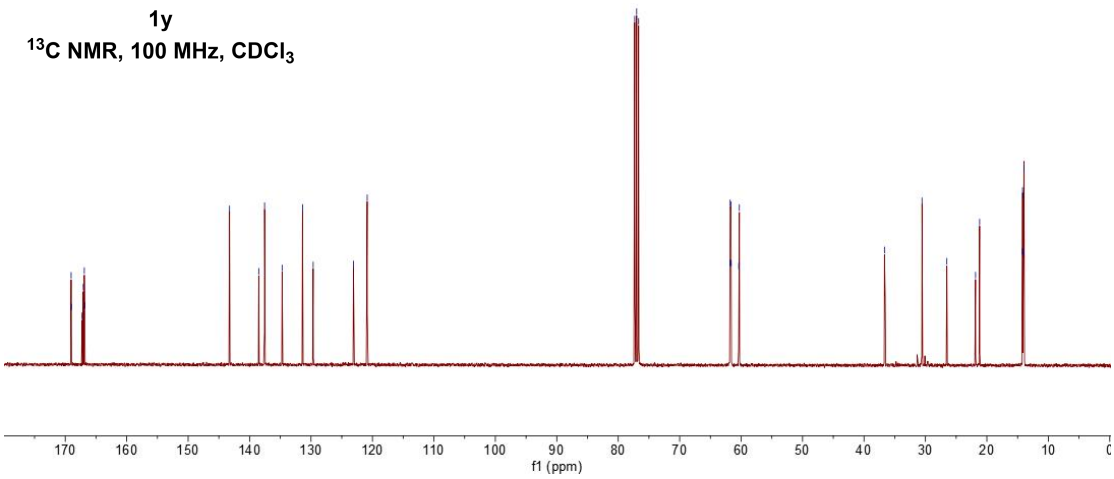


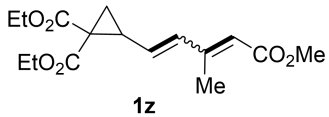
***Z*:*E* = 1:1.8**



1y

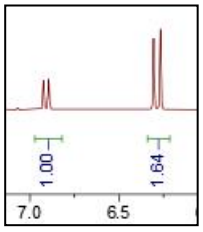
^{13}C NMR, 100 MHz, $CDCl_3$



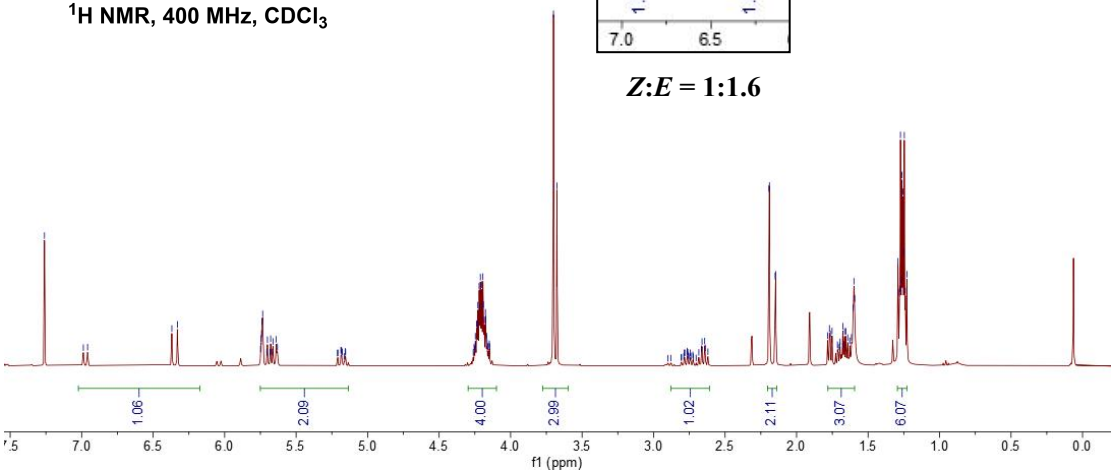


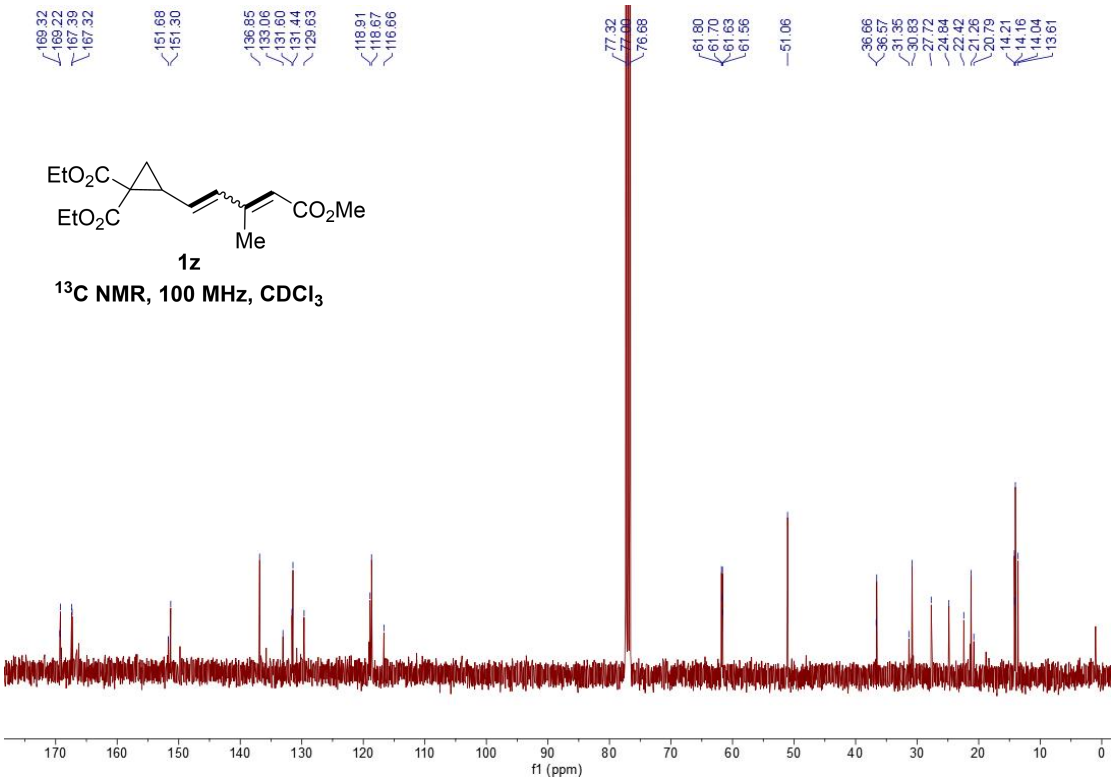
1z

^{1}H NMR, 400 MHz, $CDCl_3$



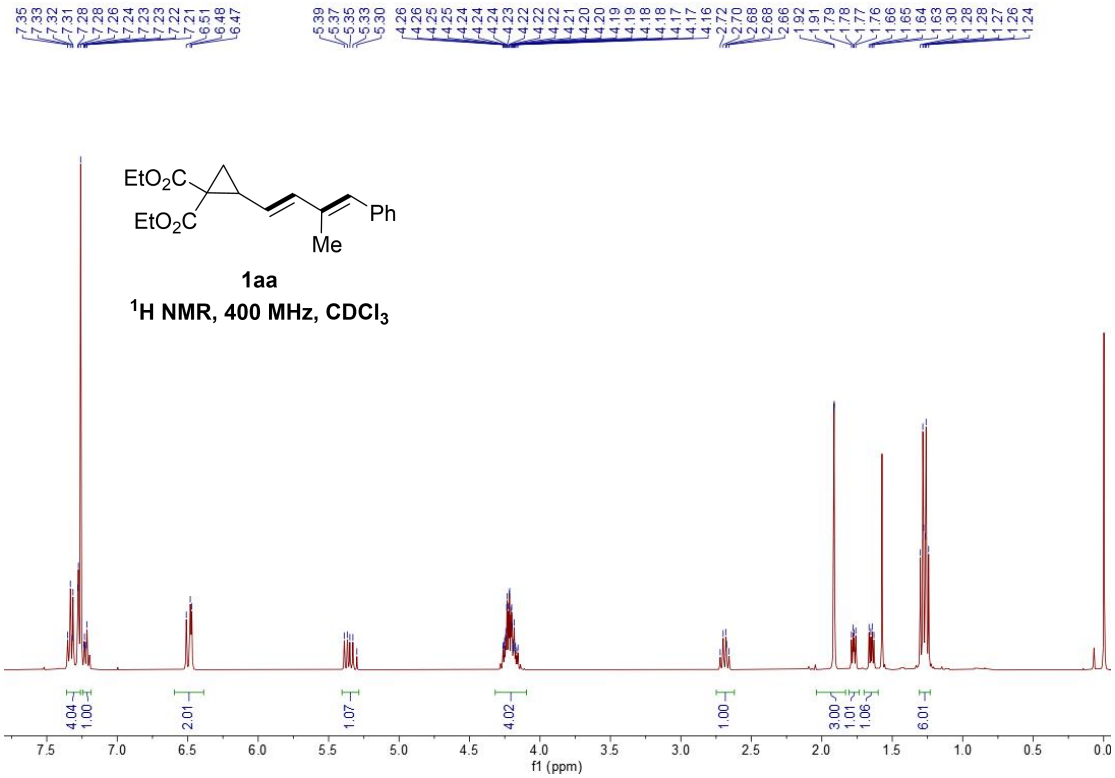
***Z*:*E* = 1:1.6**

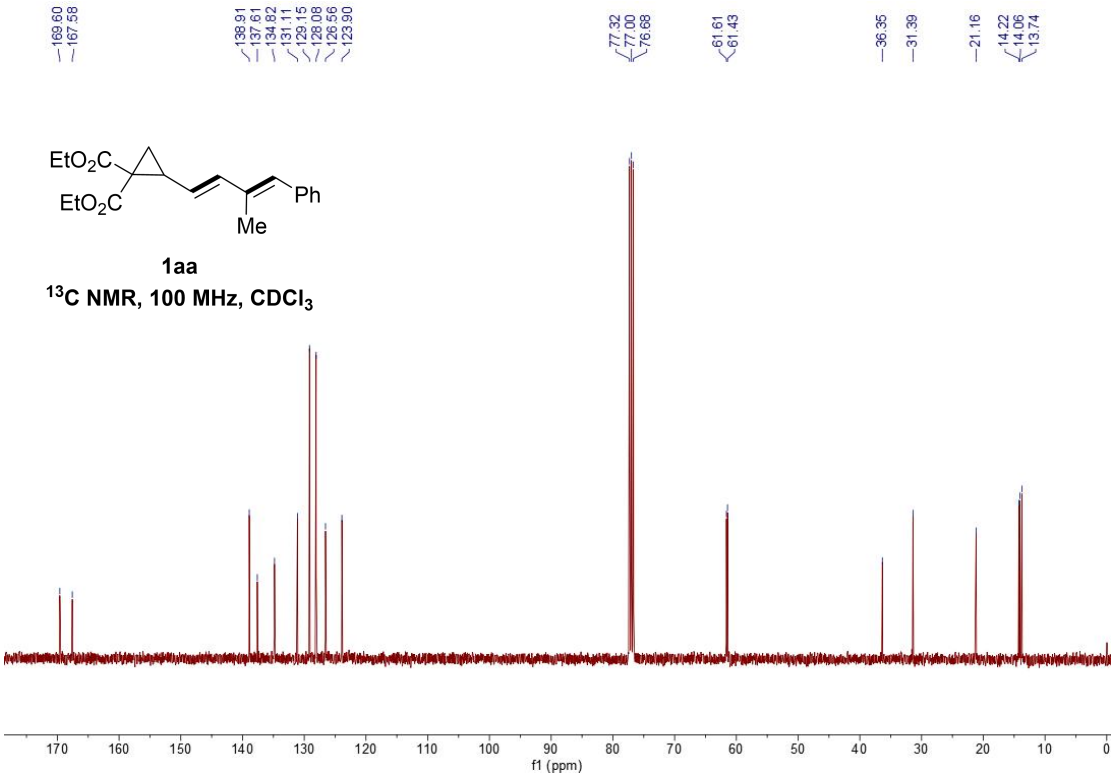


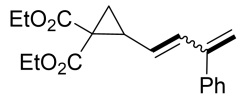


1z

^{13}C NMR, 100 MHz, $CDCl_3$

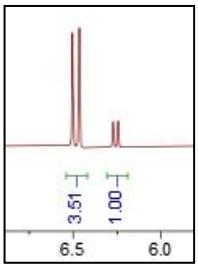

EtO2C
EtO2C
Ph
Me
1aa
1H NMR, 400 MHz, CDCl3
f1 (ppm)


EtO2C
EtO2C
Ph
Me
1aa
13C NMR, 100 MHz, CDCl3
f1 (ppm)

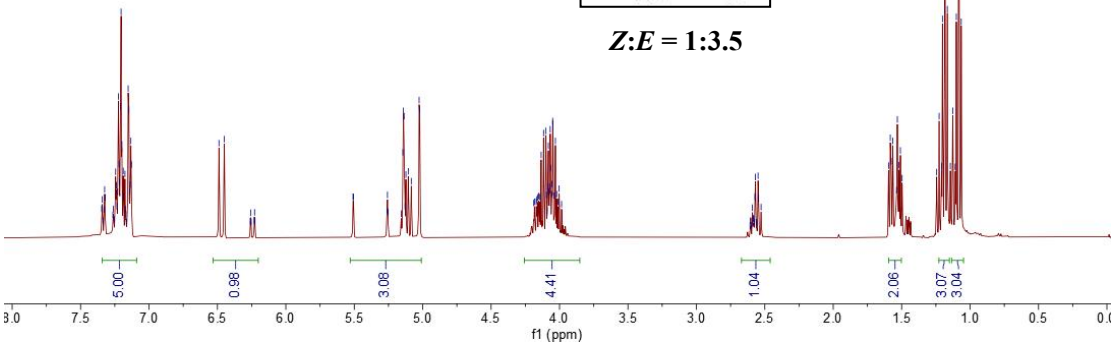


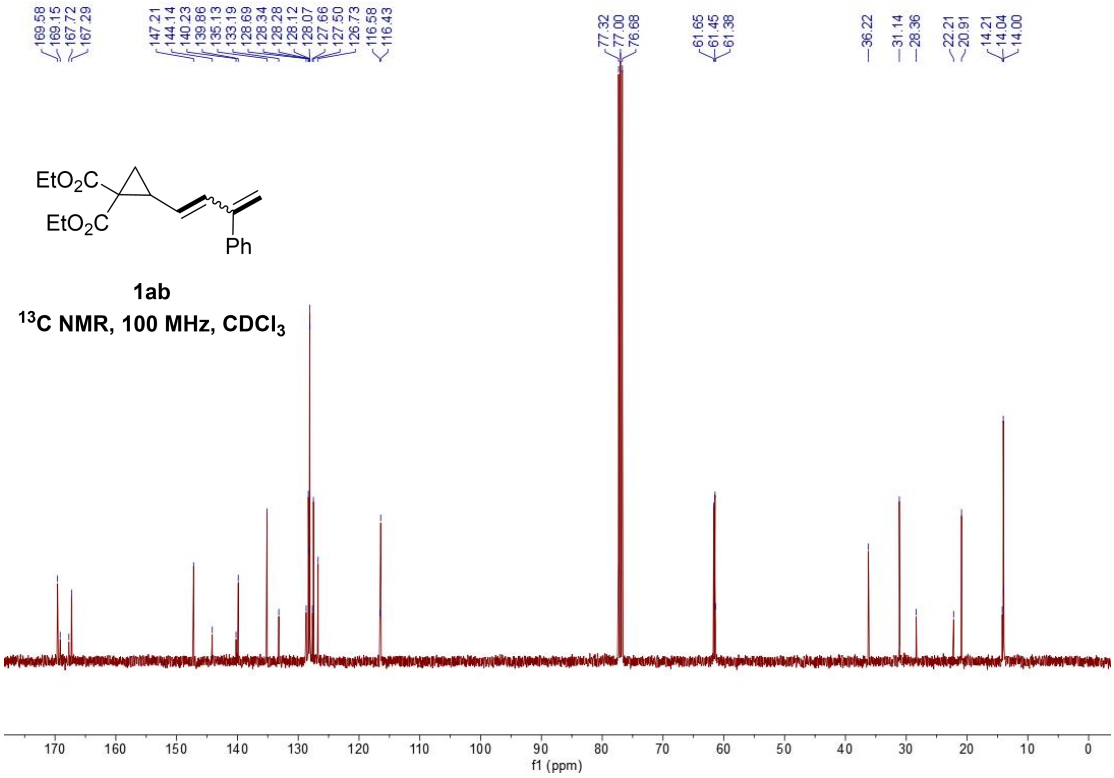
1ab

^{1}H NMR, 400 MHz, $CDCl_3$



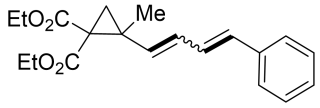
***Z*:*E* = 1:3.5**





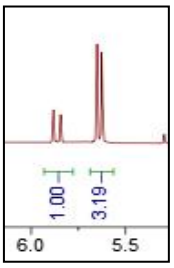
1ab

^{13}C NMR, 100 MHz, $CDCl_3$

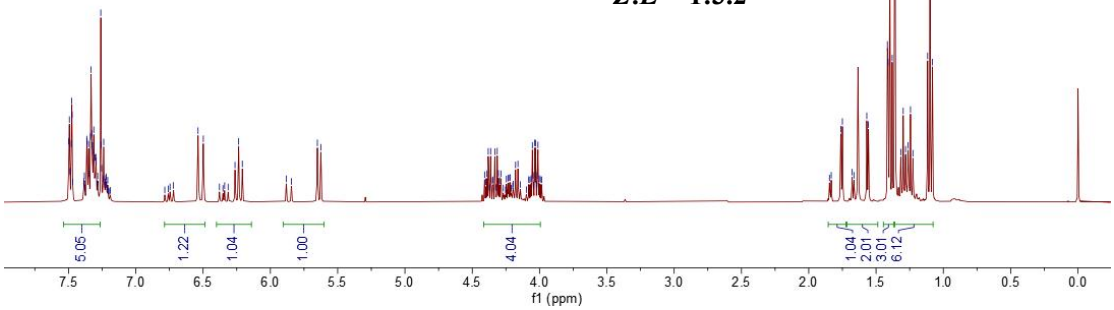


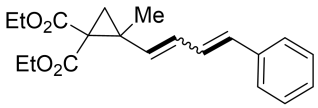
1ac

^{1}H NMR, 400 MHz, $CDCl_3$



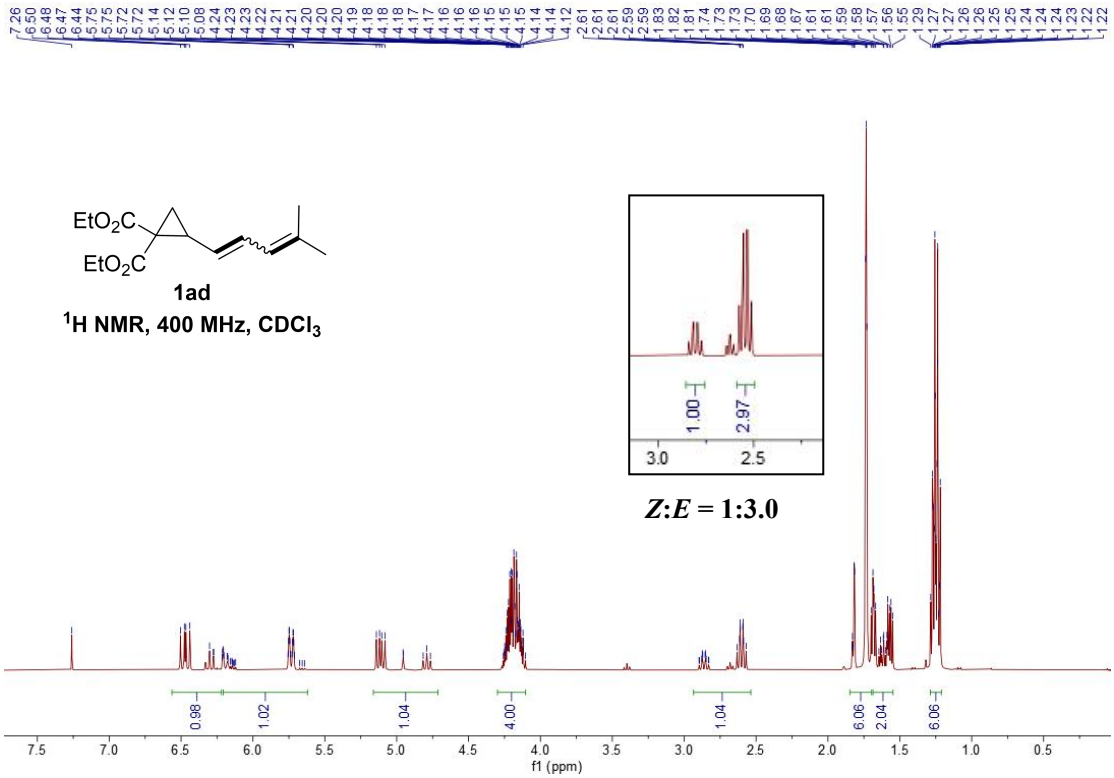
***Z*:*E* = 1:3.2**

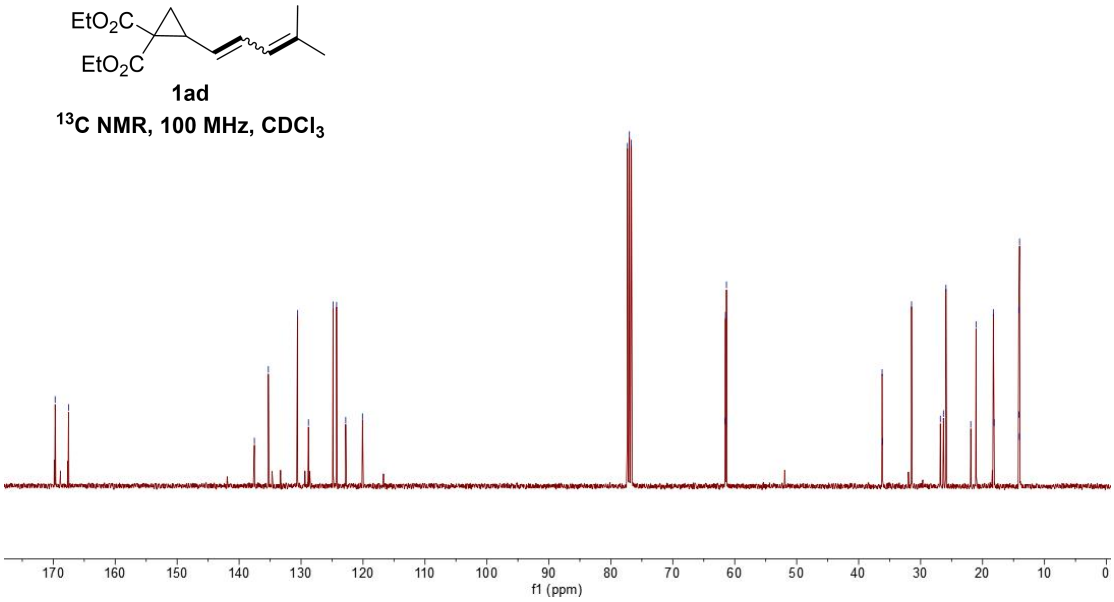


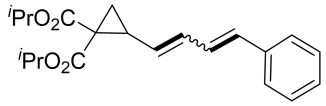


1ac

^{13}C NMR, 100 MHz, $CDCl_3$

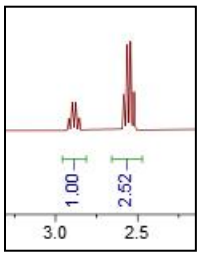

EtO2C
EtO2C
1ad
1H NMR, 400 MHz, CDCl3
1.00
2.97
Z:E = 1:3.0
0.98
1.02
1.04
4.00
1.04
6.06
2.04
6.06
f1 (ppm)


EtO2C
EtO2C
1ad
13C NMR, 100 MHz, CDCl3
f1 (ppm)

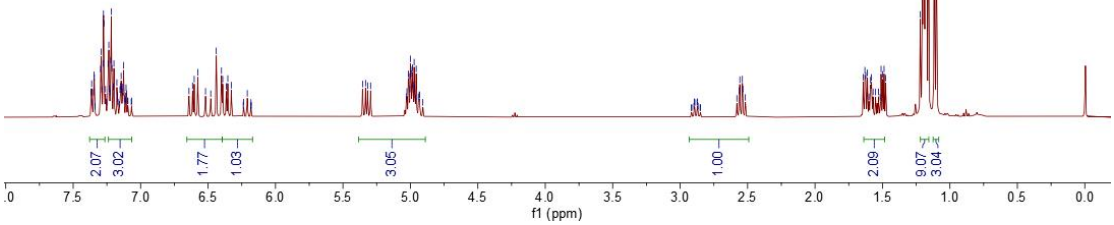


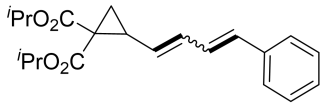
1ae

^{1}H NMR, 400 MHz, $CDCl_3$



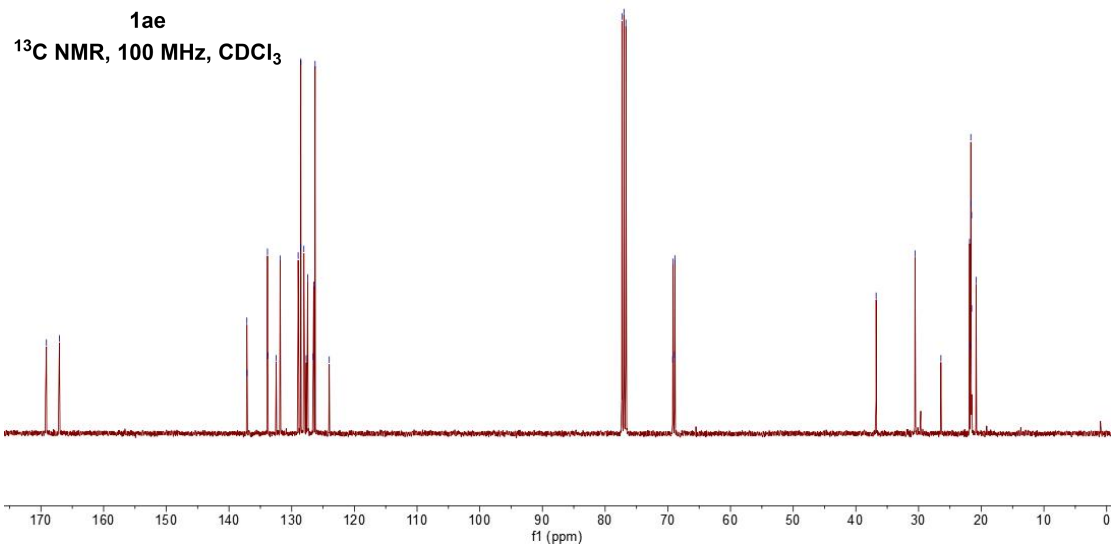
***Z*:*E* = 1:2.5**

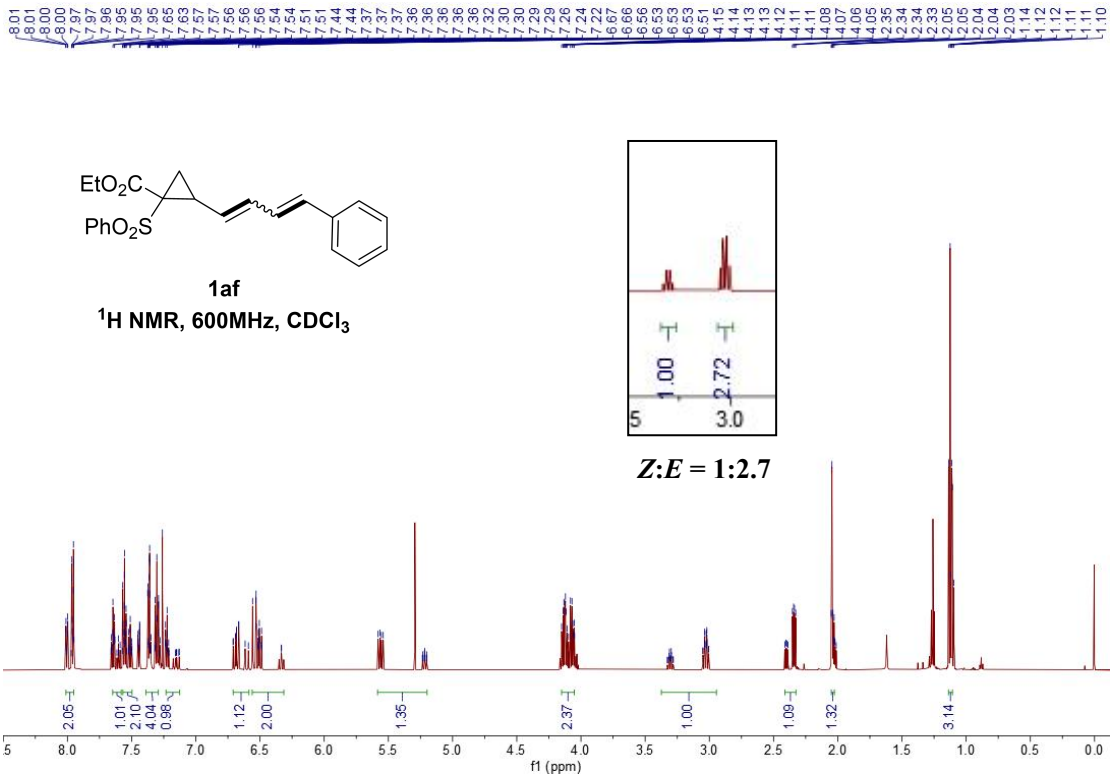


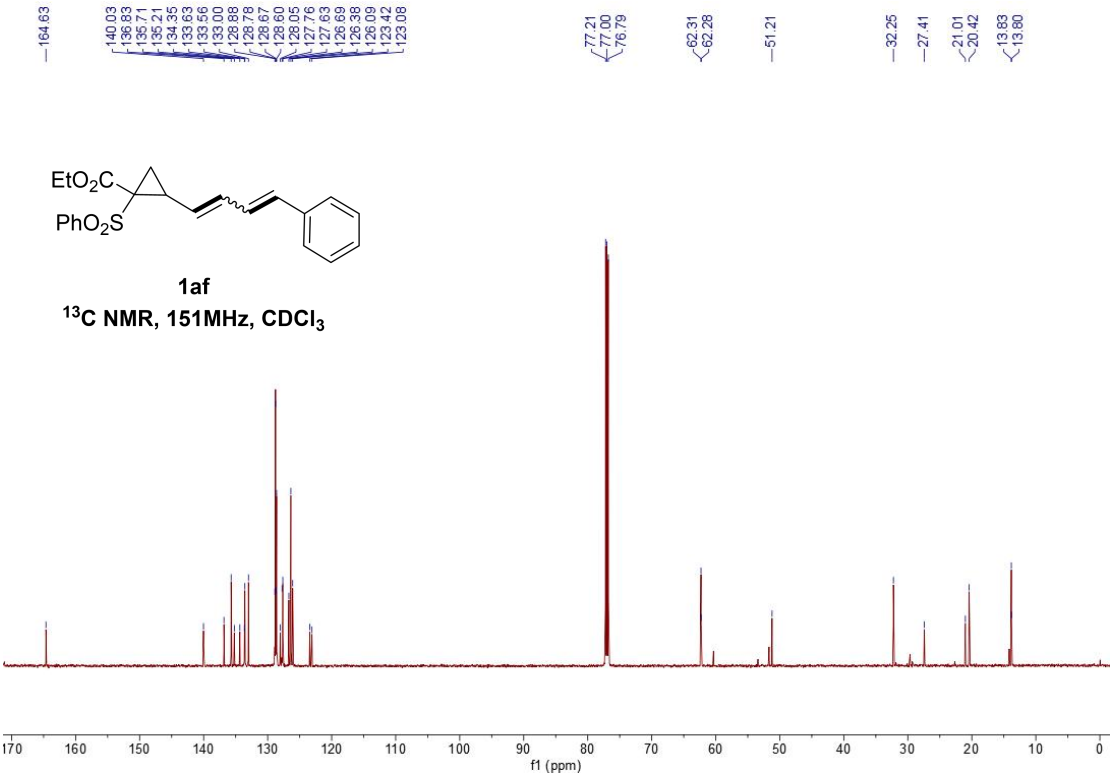


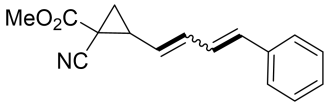
1ae

^{13}C NMR, 100 MHz, $CDCl_3$



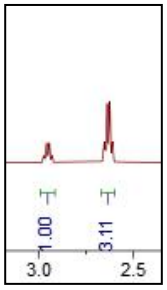

EtO2C
PhO2S
1af
1H NMR, 600MHz, CDCl3
Z:E = 1:2.7
f1 (ppm)


EtO2C
PhO2S
1af
13C NMR, 151MHz, CDCl3
f1 (ppm)

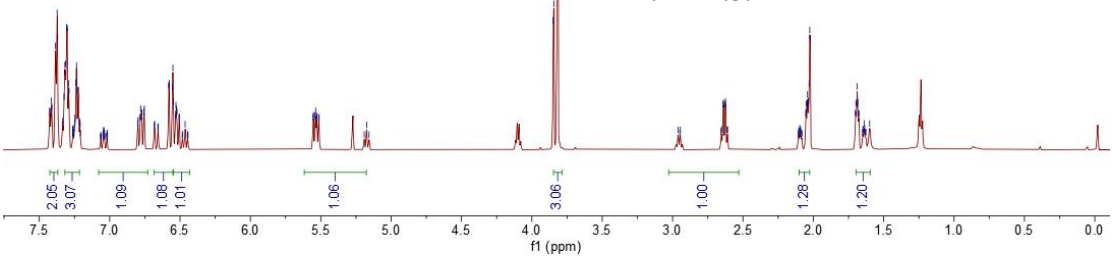


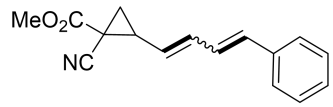
1ag

^{1}H NMR, 600MHz, $CDCl_3$



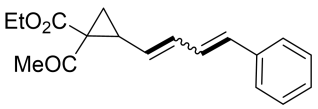
***Z*:*E* = 1:3.1**





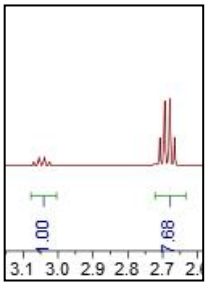
1ag

^{13}C NMR, 151MHz, $CDCl_3$

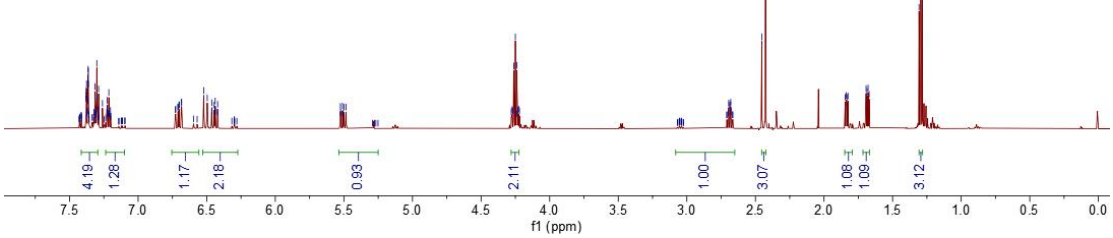


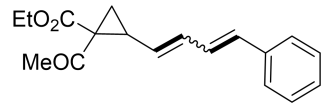
1ah

^{1}H NMR, 400MHz, $CDCl_3$



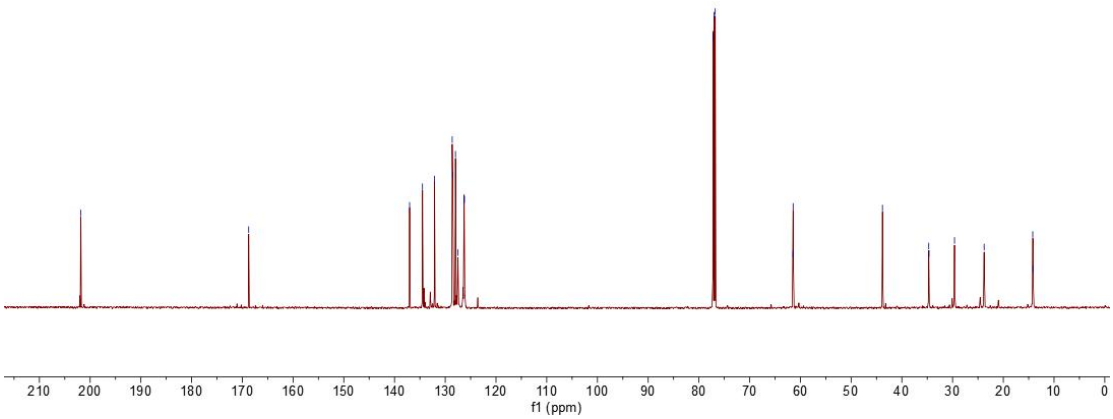
***Z*:*E* = 1:7.7**

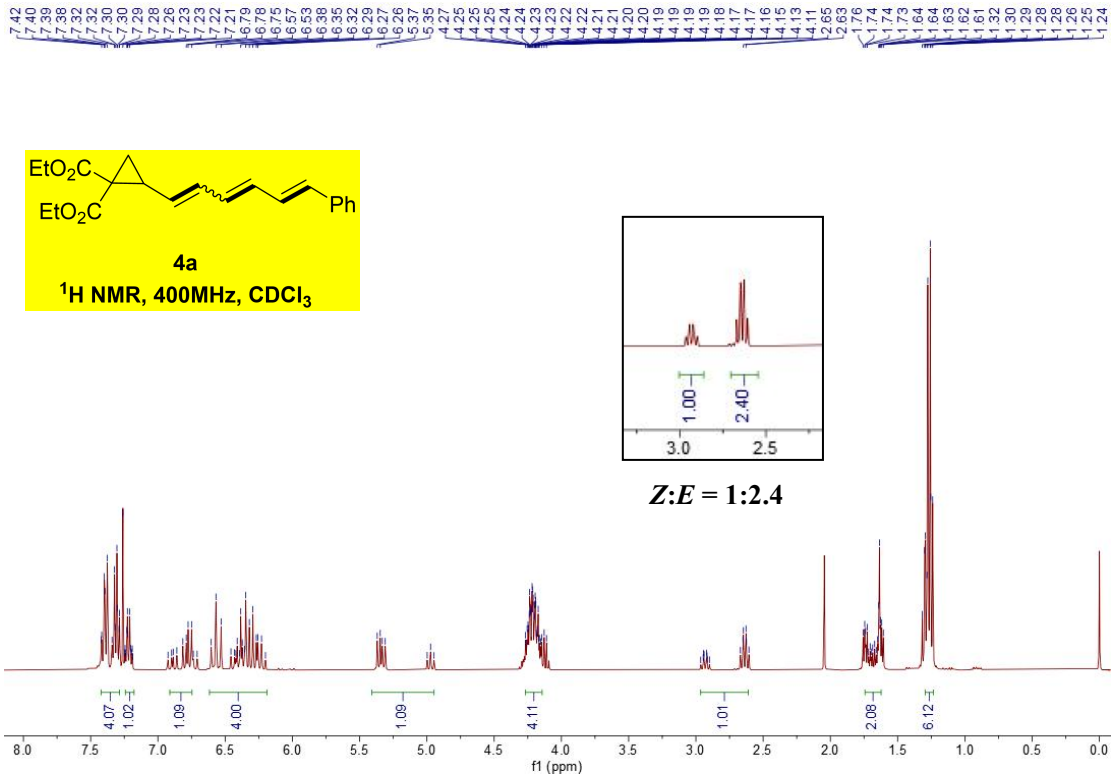


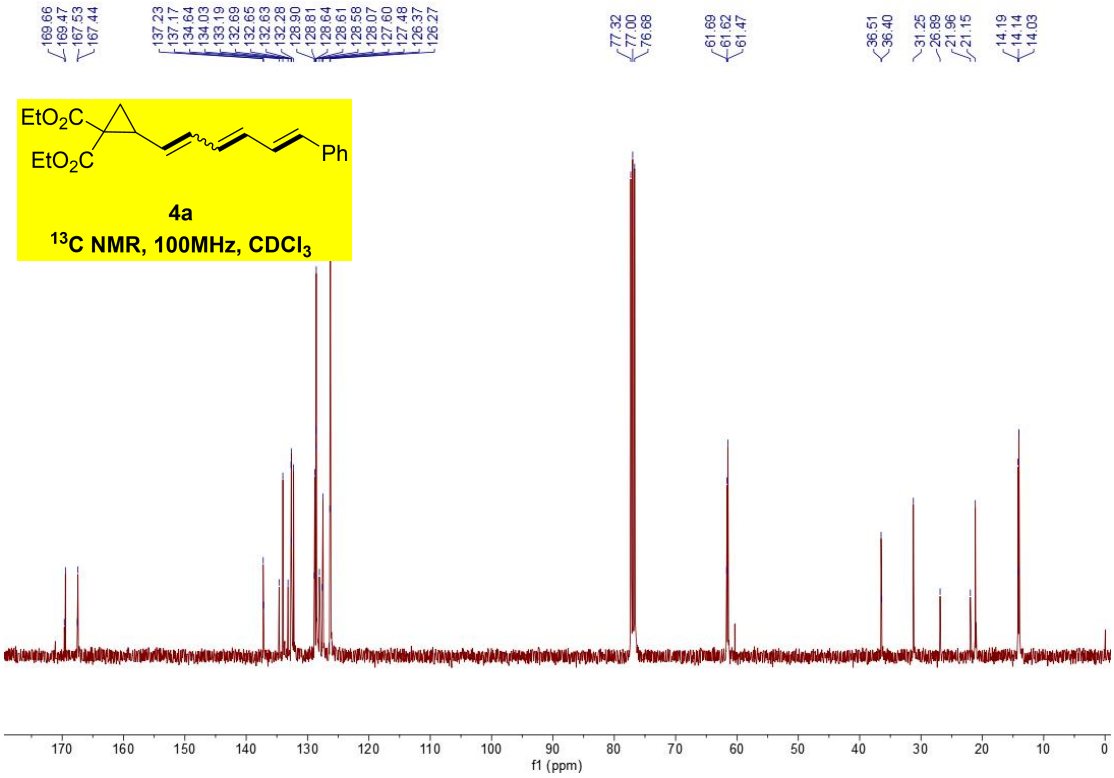


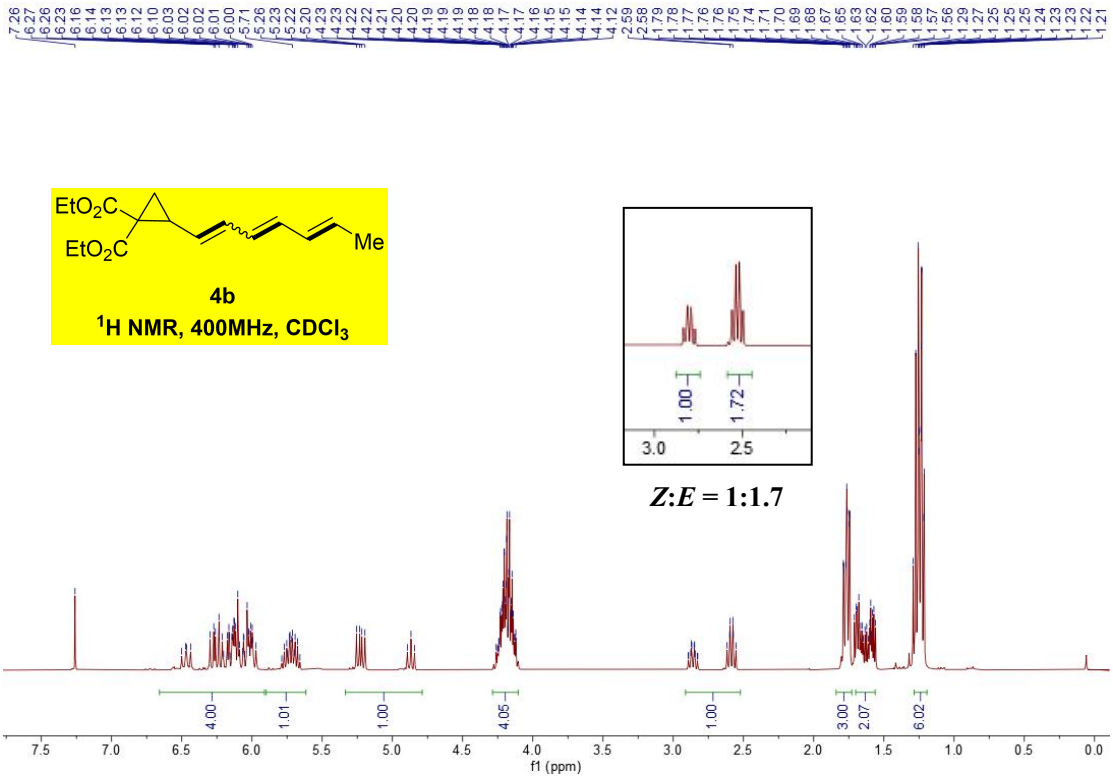
1ah

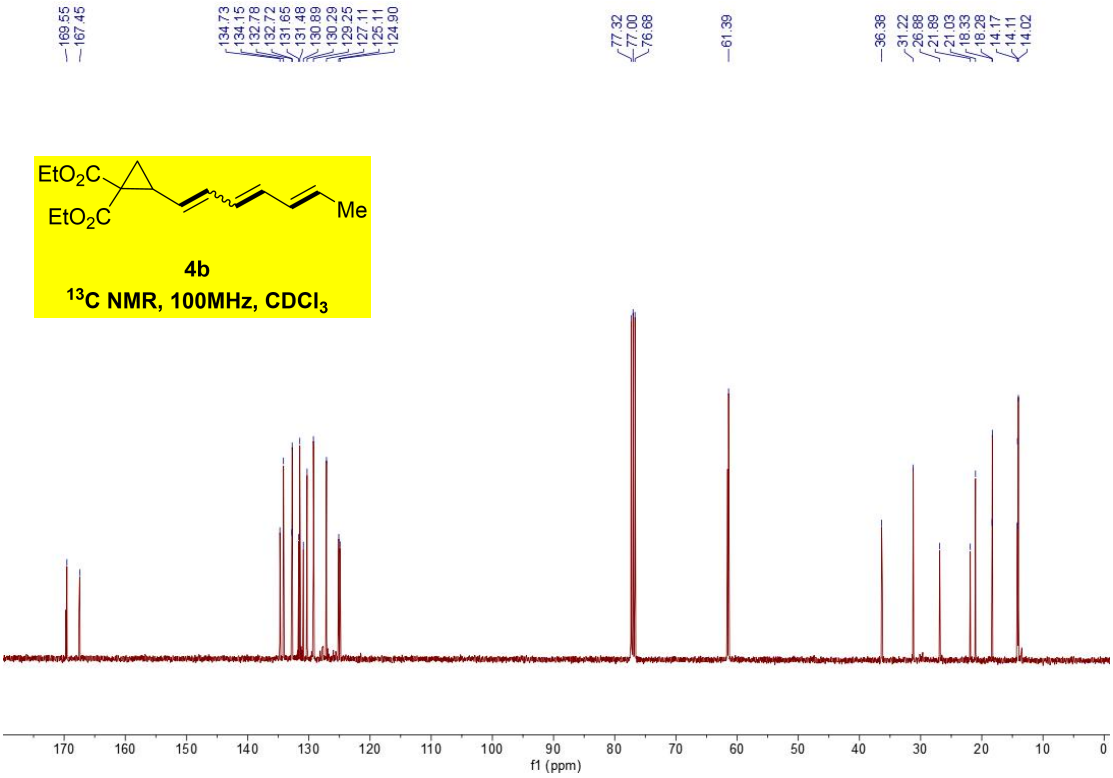
^{13}C NMR, 100MHz, $CDCl_3$

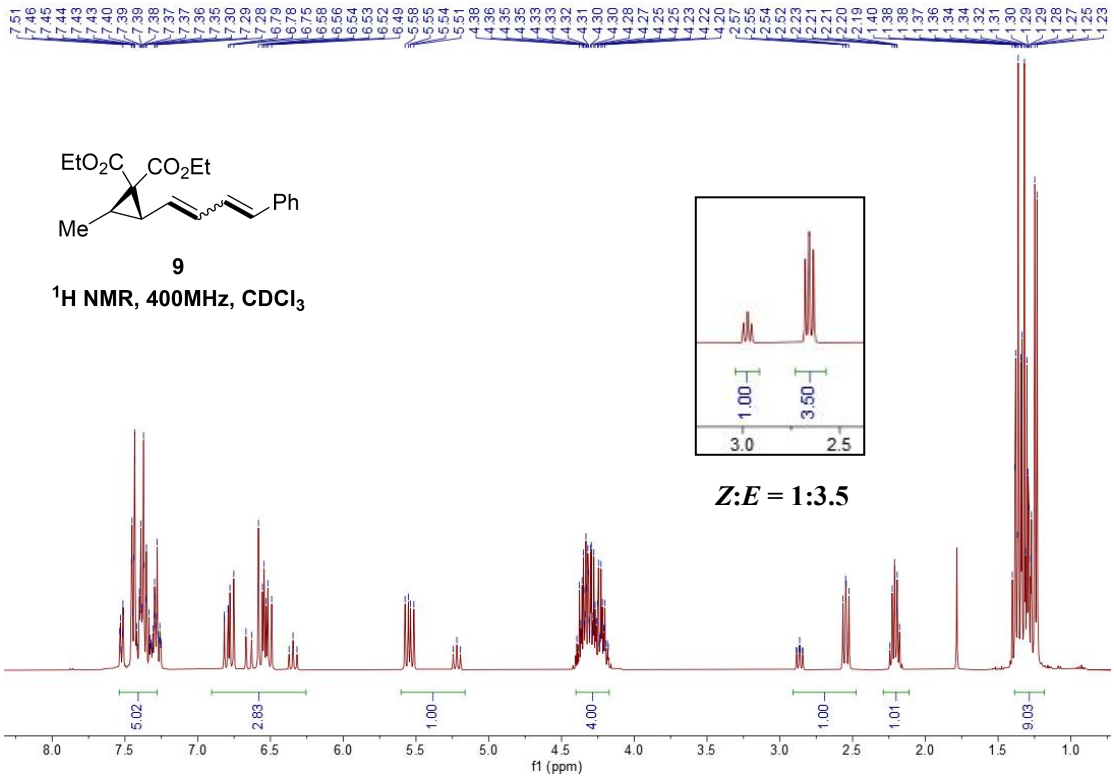


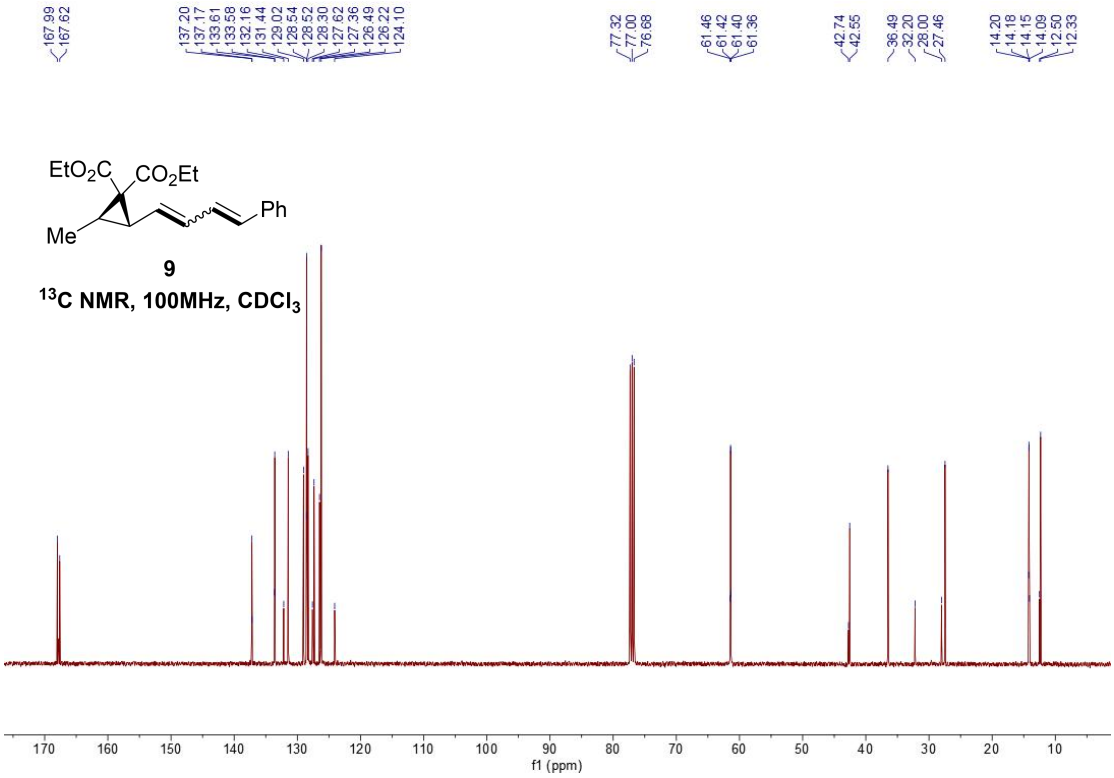

EtO2C
EtO2C
Ph
4a
1H NMR, 400MHz, CDCl3
1.00
2.40
Z:E = 1:2.4
f1 (ppm)

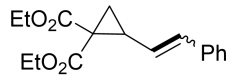

EtO2C
EtO2C
Ph
4a
13C NMR, 100MHz, CDCl3
f1 (ppm)


EtO2C
EtO2C
Me
4b
1H NMR, 400MHz, CDCl3
1.00
1.72
3.0
2.5
Z:E = 1:1.7
4.00
1.01
1.00
4.05
1.00
3.00
2.07
6.02
f1 (ppm)


EtO2C
EtO2C
Me
4b
13C NMR, 100MHz, CDCl3
f1 (ppm)

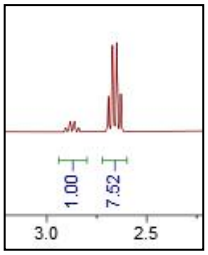

EtO2C
CO2Et
Me
Ph
9
1H NMR, 400MHz, CDCl3
1.00
3.50
Z:E = 1:3.5
5.02
2.83
1.00
4.00
1.00
1.01
9.03
f1 (ppm)


EtO2C
CO2Et
Me
Ph
9
13C NMR, 100MHz, CDCl3
f1 (ppm)

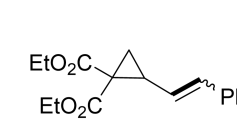


15

^{1}H NMR, 400MHz, $CDCl_3$



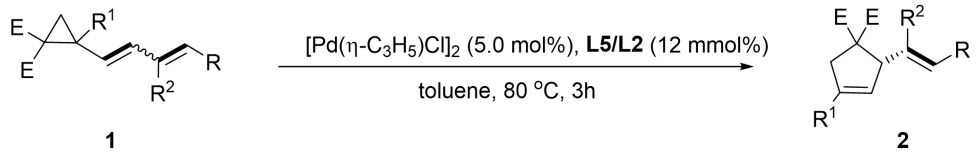
***Z*:*E* = 1:7.5**



15

^{13}C NMR, 100MHz, $CDCl_3$

4. Procedures for the dienyl cyclopropanes synthesis

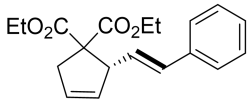


1 **2**

Procedure C:

Under anhydrous and oxygen-free conditions, to a dried tube equipped with a magnetic stir bar was added **1** (0.1 mmol), $[Pd(\eta\text{-}C_3H_5)Cl]_2$ (1.8 mg, 5.0 mol%), and **L2** (7.0 mg, 12 mol%) or **L5** (7.3 mg, 12 mol%), and toluene (1.0 mL), stirring the reaction mixture for 3 h at 80 ˚C. The solvent was removed in vacuo and the crude product was purified directly by column chromatography to afford the desired **2**.

5. Characterization and NMR spectra of products 2, 3, 5 and 10



Diethyl (S,E)-2-styrylcyclopent-3-ene-1,1-dicarboxylate (2a) was synthesized by following Procedure C from **1a**, after a flash column chromatography (PE: EA = 20:1) afforded the product **2a** as a white solid (29.9 mg, 95% yield).

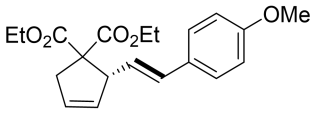
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.26 – 7.10 (m, 5H), 6.44 (d, *J* = 15.8 Hz, 1H), 5.93 (dd, *J* = 15.8, 9.0 Hz, 1H), 5.78 – 5.49 (m, 2H), 4.33 – 4.26 (m, 1H), 4.24 – 3.91 (m, 4H), 3.35 (dq, *J* = 17.4, 2.3 Hz, 1H), 2.73 (dt, *J* = 17.3, 2.2 Hz, 1H), 1.21 (t, *J* = 7.1 Hz, 3H), 1.04 (t, *J* = 7.1 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 171.9, 169.8, 137.0, 132.2, 131.4, 128.5, 128.4, 127.4, 127.3, 126.2, 64.0, 61.6, 61.4, 54.0, 39.9, 14.1, 14.0.

HRMS Exact mass calculated for $[C_{19}H_{22}O_4+Na]^+$ requires *m/z* = 337.1410, found *m/z* = 337.1411 (ESI+).

Optical: $[\alpha]^{25}_D$ = -278.3 ° (c = 0.35, CH_2Cl_2, 94 % e.e.)

HPLC (Chiralpak AD-H, 10% ^{i}PrOH/Hx eluent, 0.5 mL/min, 254 nm): major enantiomer t_R = 9.6 min, minor enantiomer t_R = 9.2 min.



Diethyl (S,E)-2-(4-methoxystyryl)cyclopent-3-ene-1,1-dicarboxylate (2b) was synthesized by following Procedure C from **1b**, after a flash column chromatography (PE: EA = 20:1) afforded the product **2b** as a yellow solid (32.0 mg, 93% yield).

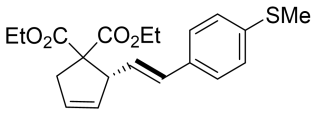
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.26 – 7.15 (m, 2H), 6.87 – 6.70 (m, 2H), 6.43 (d, *J* = 15.8 Hz, 1H), 5.82 (dd, *J* = 15.8, 9.1 Hz, 1H), 5.76 – 5.59 (m, 2H), 4.33 – 4.00 (m, 5H), 3.79 (s, 3H), 3.40 (dd, *J* = 17.4, 2.3 Hz, 1H), 2.82 – 2.63 (m, 1H), 1.25 (t, *J* = 7.1 Hz, 3H), 1.09 (t, *J* = 7.1 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 172.0, 169.9, 159.0, 131.7, 129.8, 128.2, 127.4, 125.0, 113.9, 64.0, 61.5, 61.3, 55.2, 54.0, 39.9, 14.1, 14.0.

HRMS Exact mass calculated for $[C_{20}H_{24}O_5+Na]^+$ requires *m/z* = 367.1516, found *m/z* = 357.1521 (ESI+).

Optical: $[\alpha]^{25}_D$ = -294.8 ° (c = 0.55, CH_2Cl_2, 92 % e.e.)

HPLC (Chiralpak OJ-H, 5% ^{i}PrOH/Hx eluent, 0.5 mL/min, 254 nm): major enantiomer t_R = 26.4 min, minor enantiomer t_R = 40.1 min.



Diethyl (S,E)-2-(4-(methylthio)styryl)cyclopent-3-ene-1,1-dicarboxylate (2c) was synthesized by following Procedure C from **1c**, after a flash column chromatography (PE: EA = 20:1) afforded the product **2c** as a yellow solid (32.1 mg, 89% yield).

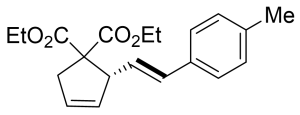
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.26 – 7.13 (m, 4H), 6.43 (d, *J* = 15.8 Hz, 1H), 5.93 (dd, *J* = 15.8, 9.0 Hz, 1H), 5.77 – 5.56 (m, 2H), 4.34 – 3.97 (m, 5H), 3.39 (dd, *J* = 17.5, 2.3 Hz, 1H), 2.77 (dt, *J* = 17.5, 2.1 Hz, 1H), 2.46 (s, 3H), 1.25 (t, *J* = 7.1 Hz, 3H), 1.09 (t, *J* = 7.1 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 171.8, 169.8, 137.5, 133.9, 131.6, 131.4, 128.4, 126.7, 126.6, 126.5, 63.9, 61.5, 61.3, 54.0, 39.9, 15.8, 14.1, 14.0.

HRMS Exact mass calculated for $[C_{20}H_{24}O_4S+Na]^+$ requires *m/z* = 383.1288, found *m/z* = 383.1289 (ESI+).

Optical: $[\alpha]^{25}_D$ = -420.8 ° (c = 0.30, CH_2Cl_2, 94 % e.e.)

HPLC (Chiralpak OJ-H, 5% ^{i}PrOH/Hx eluent, 0.5 mL/min, 254 nm): major enantiomer t_R = 28.3 min, minor enantiomer t_R = 36.4 min.



Diethyl (S,E)-2-(4-methylstyryl)cyclopent-3-ene-1,1-dicarboxylate (2d) was synthesized by following Procedure C from **1d**, after a flash column chromatography (PE: EA = 20:1) afforded the product **2d** as a white solid (27.9 mg, 85% yield).

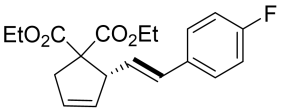
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.23 – 7.05 (m, 4H), 6.46 (d, *J* = 15.8 Hz, 1H), 5.92 (dd, *J* = 15.8, 9.1 Hz, 1H), 5.76 – 5.55 (m, 2H), 4.34 – 3.99 (m, 5H), 3.40 (dd, *J* = 17.4, 2.3 Hz, 1H), 2.82 – 2.65 (m, 1H), 2.31 (s, 3H), 1.26 (t, *J* = 7.1 Hz, 3H), 1.09 (t, *J* = 7.1 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 171.9, 169.9, 137.2, 134.2, 132.1, 131.6, 129.2, 128.2, 126.1, 63.9, 61.5, 61.3, 54.0, 40.0, 21.1, 14.1, 14.0.

HRMS Exact mass calculated for $[C_{20}H_{24}O_4+Na]^+$ requires *m/z* = 351.1567, found *m/z* = 351.1570 (ESI+).

Optical: $[\alpha]^{25}_D$ = -406.5 ° (c = 0.35, CH_2Cl_2, 93 % e.e.)

HPLC (Chiralpak OJ-H, 5% ^{i}PrOH/Hx eluent, 0.5 mL/min, 254 nm): major enantiomer t_R = 16.2 min, minor enantiomer t_R = 24.5 min.



Diethyl (S,E)-2-(4-fluorostyryl)cyclopent-3-ene-1,1-dicarboxylate (2e) was synthesized by following Procedure C from **1e**, after a flash column chromatography (PE: EA = 20:1) afforded the product **2e** as a white solid (29.3 mg, 88% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.27 (d, *J* = 7.8 Hz, 2H), 6.96 (t, *J* = 8.7 Hz, 2H), 6.45 (d, *J* = 15.8 Hz, 1H), 5.89 (dd, *J* = 15.8, 9.0 Hz, 1H), 5.78 – 5.57 (m, 2H), 4.34 – 3.99 (m, 5H), 3.39 (dd, *J* = 17.5, 2.3 Hz, 1H), 2.78 (dt, *J* = 17.4, 2.3 Hz, 1H), 1.26 (t, *J* = 7.2 Hz, 3H), 1.09 (t, *J* = 7.1 Hz, 3H).

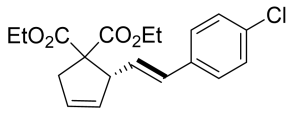
^{13}C NMR (100 MHz, $CDCl_3$) δ 171.8, 169.8, 162.2 (d, *J* = 246.5 Hz), 133.1 (d, *J* = 3.3 Hz), 131.3, 131.0, 128.5, 127.7 (d, *J* = 8.0 Hz), 127.1 (d, *J* = 2.2 Hz), 115.4 (d, *J* = 21.6 Hz), 63.9, 61.6, 61.3, 54.0, 39.9, 14.1, 14.0.

^{19}F NMR (376 MHz, $CDCl_3$) δ -114.72.

HRMS Exact mass calculated for $[C_{19}H_{21}FO_4+Na]^+$ requires *m/z* = 355.1316, found *m/z* = 355.1319 (ESI+).

Optical: $[\alpha]^{25}_D$ = -338.7 ° (c = 0.50, CH_2Cl_2, 94 % e.e.)

HPLC (Chiralpak AD-H, 5% ^{i}PrOH/Hx eluent, 0.5 mL/min, 254 nm): major enantiomer t_R = 13.2 min, minor enantiomer t_R = 11.6 min.



Diethyl (S,E)-2-(4-chlorostyryl)cyclopent-3-ene-1,1-dicarboxylate (2f) was synthesized by following Procedure C from **1f**, after a flash column chromatography (PE: EA = 10:1) afforded the product **2f** as a white solid (33.5 mg, 96% yield).

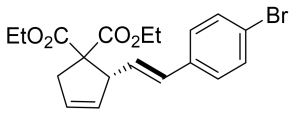
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.23 (s, 4H), 6.44 (d, *J* = 15.8 Hz, 1H), 5.96 (dd, *J* = 15.8, 9.0 Hz, 1H), 5.79 – 5.56 (m, 2H), 4.34 – 3.99 (m, 5H), 3.39 (dd, *J* = 17.5, 2.3 Hz, 1H), 2.78 (dt, *J* = 17.3, 2.3 Hz, 1H), 1.25 (t, *J* = 7.1 Hz, 3H), 1.08 (t, *J* = 7.1 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 171.7, 169.8, 135.5, 133.0, 131.1, 130.9, 128.7, 128.6, 128.1, 127.4, 63.9, 61.6, 61.3, 53.9, 39.9, 14.1, 14.0.

HRMS Exact mass calculated for $[C_{19}H_{21}ClO_4+Na]^+$ requires *m/z* = 371.1021, found *m/z* = 371.1025 (ESI+).

Optical: $[\alpha]^{25}_D$ = -317.5 ° (c = 0.40, CH_2Cl_2, 92 % e.e.)

HPLC (Chiralpak AD-H, 5% ^{i}PrOH/Hx eluent, 0.5 mL/min, 254 nm): major enantiomer t_R = 12.8 min, minor enantiomer t_R = 11.9 min.



Diethyl (S,E)-2-(4-bromostyryl)cyclopent-3-ene-1,1-dicarboxylate (2g) was synthesized by following Procedure C from **1g**, after a flash column chromatography (PE: EA = 20:1) afforded the product **2g** as a white solid (33.8 mg, 86% yield).

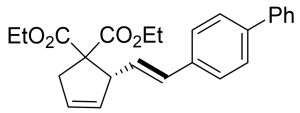
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.33 – 7.11 (m, 4H), 6.50 – 6.34 (m, 1H), 5.93 (dd, *J* = 15.8, 9.0 Hz, 1H), 5.78 – 5.47 (m, 2H), 4.28 – 3.93 (m, 5H), 3.34 (dt, *J* = 17.5, 2.6 Hz, 1H), 2.73 (dt, *J* = 17.5, 2.2 Hz, 1H), 1.21 (t, *J* = 7.1 Hz, 3H), 1.07 – 0.93 (m, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 171.8, 169.8, 131.6, 131.1, 131.0, 128.7, 128.5, 128.3, 127.7, 126.2, 63.9, 61.6, 61.4, 53.9, 40.0, 14.1, 14.0.

HRMS Exact mass calculated for $[C_{19}H_{21}BrO_4+Na]^+$ requires *m/z* = 415.0515, found *m/z* = 415.0516 (ESI+).

Optical: $[\alpha]^{25}_D$ = -341.7 ° (c = 0.44, CH_2Cl_2, 94 % e.e.)

HPLC (Chiralpak AD-H, 5% ^{i}PrOH/Hx eluent, 0.5 mL/min, 254 nm): major enantiomer t_R = 12.1 min, minor enantiomer t_R = 10.8 min.



Diethyl (S,E)-2-(2-([1,1'-biphenyl]-4-yl)vinyl)cyclopent-3-ene-1,1-dicarboxylate (2h) was synthesized by following Procedure C from **1h**, after a flash column chromatography (PE: EA = 20:1) afforded the product **2h** as a white solid (33.9 mg, 87% yield).

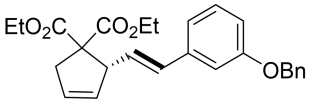
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.60 – 7.31 (m, 9H), 6.53 (d, *J* = 15.7 Hz, 1H), 6.03 (dd, *J* = 15.8, 9.0 Hz, 1H), 5.83 – 5.60 (m, 2H), 4.38 – 4.02 (m, 5H), 3.42 (dd, *J* = 17.5, 2.3 Hz, 1H), 2.79 (dt, *J* = 17.3, 2.2 Hz, 1H), 1.27 (s, 3H), 1.12 (t, *J* = 7.1 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 171.9, 169.9, 140.6, 140.1, 136.0, 131.8, 131.4, 128.8, 128.7, 128.5, 127.4, 127.2, 127.2, 126.9, 126.7, 61.6, 61.4, 54.0, 39.9, 14.2, 14.0.

HRMS Exact mass calculated for $[C_{25}H_{26}O_4+Na]^+$ requires *m/z* = 413.1723, found *m/z* = 413.1725 (ESI+).

Optical: $[\alpha]^{25}_D$ = -290.3 ° (c = 0.50, CH_2Cl_2, 93 % e.e.)

HPLC (Chiralpak AD-H, 5% ^{i}PrOH/Hx eluent, 0.5 mL/min, 254 nm): major enantiomer t_R = 15.0 min, minor enantiomer t_R = 15.5 min.



Diethyl (S,E)-2-(3-(benzyloxy)styryl)cyclopent-3-ene-1,1-dicarboxylate (2i) was synthesized by following Procedure C from **1i**, after a flash column chromatography (PE:EA = 20:1) afforded the product **2i** as a yellow oil (40.4 mg, 96% yield).

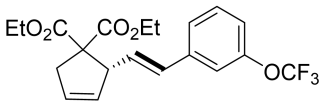
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.36 – 7.07 (m, 6H), 6.87 – 6.72 (m, 3H), 6.38 (d, *J* = 15.8 Hz, 1H), 5.90 (dd, *J* = 15.7, 9.0 Hz, 1H), 5.71 – 5.50 (m, 2H), 4.97 (s, 2H), 4.28 – 3.91 (m, 5H), 3.40 – 3.27 (m, 1H), 2.71 (dt, *J* = 17.5, 2.3 Hz, 1H), 1.18 (t, *J* = 7.1 Hz, 3H), 1.01 (t, *J* = 7.1 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 171.8, 169.8, 158.9, 138.5, 136.9, 132.1, 131.4, 129.5, 128.5, 128.5, 127.9, 127.7, 127.4, 119.2, 113.9, 112.5, 69.9, 63.9, 61.6, 61.4, 53.9, 39.9, 14.1, 14.0.

HRMS Exact mass calculated for $[C_{26}H_{28}O_5+Na]^+$ requires *m/z* = 443.1829, found *m/z* = 443.1829 (ESI+).

Optical: $[\alpha]^{25}_D$ = -269.2 ° (c = 0.35, CH_2Cl_2, 90 % e.e.)

HPLC (Chiralpak AD-H, 5% ^{i}PrOH/Hx eluent, 0.5 mL/min, 254 nm): major enantiomer t_R = 22.0 min, minor enantiomer t_R = 19.8 min.



Diethyl (S,E)-2-(3-(trifluoromethoxy)styryl)cyclopent-3-ene-1,1-dicarboxylate (2j) was synthesized by following Procedure C from **1j**, after a flash column chromatography (PE:EA = 20:1) afforded the product **2j** as a white solid (35.1 mg, 88% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.29 (t, *J* = 7.9 Hz, 1H), 7.26 – 6.99 (m, 3H), 6.47 (d, *J* = 15.8 Hz, 1H), 6.04 (dd, *J* = 15.8, 8.9 Hz, 1H), 5.90 – 5.36 (m, 2H), 4.39 – 3.88 (m, 5H), 3.51 – 3.23 (m, 1H), 2.87 – 2.73 (m, 1H), 1.26 (t, *J* = 7.1 Hz, 3H), 1.10 (t, *J* = 7.1 Hz, 3H).

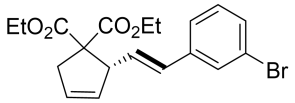
^{13}C NMR (100 MHz, $CDCl_3$) δ 171.7, 169.8, 149.5 (d, *J* = 1.8 Hz), 139.1, 130.9, 130.8, 129.8, 129.4, 128.9, 124.6, 120.4 (q, *J* = 257.0 Hz), 119.7, 118.5, 63.6, 61.6, 61.4, 53.8, 40.0, 14.0, 13.9.

^{19}F NMR (376 MHz, $CDCl_3$) δ -57.77.

HRMS Exact mass calculated for $[C_{20}H_{21}F_3O_5+Na]^+$ requires *m/z* = 421.1233, found *m/z* = 421.1234 (ESI+).

Optical: $[\alpha]^{25}_D$ = -90.2 ° (c = 0.35, CH_2Cl_2, 98 % e.e.)

HPLC (Chiralpak OJ-H, 2% ^{i}PrOH/Hx eluent, 0.5 mL/min, 254 nm): major enantiomer t_R = 12.3 min, minor enantiomer t_R = 13.9 min.



Diethyl (S,E)-2-(3-bromostyryl)cyclopent-3-ene-1,1-dicarboxylate (2k) was synthesized by following Procedure C from **1k**, after a flash column chromatography (PE: EA = 20:1) afforded the product **2k** as a white solid (37.8 mg, 96% yield).

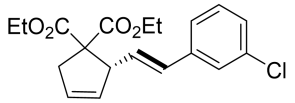
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.16 – 6.90 (m, 4H), 6.23 (d, *J* = 15.8 Hz, 1H), 5.81 (dd, *J* = 15.9, 8.7 Hz, 1H), 5.62 – 5.33 (m, 2H), 4.16 – 3.81 (m, 5H), 3.21 (dt, *J* = 17.5, 2.3 Hz, 1H), 2.60 (dt, *J* = 17.4, 2.4 Hz, 1H), 1.07 (t, *J* = 7.1 Hz, 3H), 0.92 (t, *J* = 7.1 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 171.7, 169.7, 139.1, 131.1, 130.7, 130.3, 130.0, 129.1, 128.8, 126.2, 124.9, 122.7, 63.9, 61.6, 61.4, 53.8, 39.9, 14.1, 14.0.

HRMS Exact mass calculated for $[C_{19}H_{21}BrO_4+Na]^+$ requires *m/z* = 415.0515, found *m/z* = 415.0517 (ESI+).

Optical: $[\alpha]^{25}_D$ = -280.0 ° (c = 0.50, CH_2Cl_2, 94 % e.e.)

HPLC (Chiralpak AD-H, 5% ^{i}PrOH/Hx eluent, 0.5 mL/min, 254 nm): major enantiomer t_R = 12.0 min, minor enantiomer t_R = 10.4 min.



Diethyl (S,E)-2-(3-chlorostyryl)cyclopent-3-ene-1,1-dicarboxylate (2l) was synthesized by following Procedure C from **1l**, after a flash column chromatography (PE: EA = 20:1) afforded the product **2l** as a white oil (31.0 mg, 89% yield).

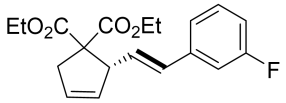
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.28 – 7.15 (m, 4H), 6.43 (d, *J* = 15.8 Hz, 1H), 6.00 (dd, *J* = 15.8, 9.0 Hz, 1H), 5.78 – 5.57 (m, 2H), 4.33 – 3.99 (m, 5H), 3.48 – 3.33 (m, 1H), 2.78 (dt, *J* = 17.4, 2.3 Hz, 1H), 1.26 (t, *J* = 7.1 Hz, 3H), 1.10 (t, *J* = 7.1 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 171.7, 169.8, 138.8, 134.4, 131.1, 130.8, 129.7, 129.0, 128.8, 127.4, 126.1, 124.4, 63.9, 61.6, 61.4, 53.8, 39.9, 14.1, 14.0.

HRMS Exact mass calculated for $[C_{19}H_{21}ClO_4+Na]^+$ requires *m/z* = 371.1021, found *m/z* = 371.1028 (ESI+).

Optical: $[\alpha]^{25}_D$ = -393.0 ° (c = 0.35, CH_2Cl_2, 94 % e.e.)

HPLC (Chiralpak AD-H, 5% ^{i}PrOH/Hx eluent, 0.5 mL/min, 254 nm): major enantiomer t_R = 11.9 min, minor enantiomer t_R = 10.6 min.



Diethyl (S,E)-2-(3-fluorostyryl)cyclopent-3-ene-1,1-dicarboxylate (2m) was synthesized by following Procedure C from **1m**, after a flash column chromatography (PE: EA = 20:1) afforded the product **2m** as a white oil (28.3 mg, 85% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.23 (td, *J* = 7.9, 5.9 Hz, 1H), 7.09 – 6.96 (m, 2H), 6.89 (td, *J* = 8.4, 2.5 Hz, 1H), 6.45 (d, *J* = 15.8 Hz, 1H), 6.00 (dd, *J* = 15.8, 9.0 Hz, 1H), 5.80 – 5.58 (m, 2H), 4.34 – 3.99 (m, 5H), 3.39 (dd, *J* = 17.5, 2.3 Hz, 1H), 2.79 (dd, *J* = 17.5, 2.4 Hz, 1H), 1.26 (t, *J* = 7.1 Hz, 3H), 1.10 (t, *J* = 7.1 Hz, 3H).

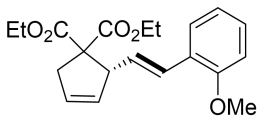
^{13}C NMR (100 MHz, $CDCl_3$) δ 171.7, 169.7, 163.0 (d, *J* = 245.1 Hz), 139.3 (d, *J* = 7.6 Hz), 131.1, 129.9 (d, *J* = 8.4 Hz), 128.8, 128.8, 122.1 (d, *J* = 2.9 Hz), 114.3, 114.1, 112.6 (d, *J* = 21.8 Hz), 63.9, 61.6, 61.4, 53.8, 39.9, 14.1, 14.0.

^{19}F NMR (376 MHz, $CDCl_3$) δ -113.63.

HRMS Exact mass calculated for $[C_{19}H_{21}FO_4+Na]^+$ requires *m/z* = 355.1316, found *m/z* = 355.1314 (ESI+).

Optical: $[\alpha]^{25}_D$ = -340.5 ° (c = 0.40, CH_2Cl_2, 94 % e.e.)

HPLC (Chiralpak AD-H, 5% ^{i}PrOH/Hx eluent, 0.5 mL/min, 254 nm): major enantiomer t_R = 12.0 min, minor enantiomer t_R = 10.8 min.



Diethyl (S,E)-2-(2-methoxystyryl)cyclopent-3-ene-1,1-dicarboxylate (2n) was synthesized by following Procedure C from **1n**, after a flash column chromatography (PE: EA = 20:1) afforded the product **2n** as a yellow solid (29.6 mg, 86% yield).

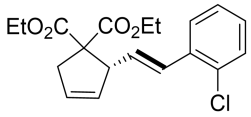
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.34 (dd, *J* = 7.7, 1.7 Hz, 1H), 7.18 (td, *J* = 7.8, 1.7 Hz, 1H), 6.96 – 6.73 (m, 3H), 5.94 (dd, *J* = 15.9, 9.2 Hz, 1H), 5.83 – 5.54 (m, 2H), 4.37 – 3.98 (m, 5H), 3.82 (s, 3H), 3.41 (dq, *J* = 17.5, 2.3 Hz, 1H), 2.77 (dt, *J* = 17.4, 2.3 Hz, 1H), 1.26 (t, *J* = 7.1 Hz, 3H), 1.12 (t, *J* = 7.1 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 171.9, 169.9, 156.5, 131.8, 128.4, 128.1, 127.7, 127.1, 126.6, 126.0, 120.5, 110.7, 64.0, 61.5, 61.3, 55.3, 54.4, 39.8, 14.0.

HRMS Exact mass calculated for $[C_{20}H_{24}O_5+Na]^+$ requires *m/z* = 367.1516, found *m/z* = 367.1520 (ESI+).

Optical: $[\alpha]^{25}_D$ = -382.9 ° (c = 0.25, CH_2Cl_2, 87 % e.e.)

HPLC (Chiralpak AD-H, 5% ^{i}PrOH/Hx eluent, 0.5 mL/min, 254 nm): major enantiomer t_R = 13.6 min, minor enantiomer t_R = 12.1 min.



Diethyl (S,E)-2-(2-chlorostyryl)cyclopent-3-ene-1,1-dicarboxylate (2o) was synthesized by following Procedure C from **1o**, after a flash column chromatography (PE: EA = 20:1) afforded the product **2o** as a white solid (26.9mg, 77% yield).

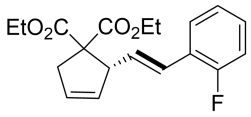
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.26 – 7.11 (m, 4H), 6.40 (d, *J* = 15.8 Hz, 1H), 5.98 (dd, *J* = 15.8, 9.0 Hz, 1H), 5.80 – 5.54 (m, 2H), 4.33 – 3.97 (m, 5H), 3.37 (dq, *J* = 17.5, 2.3 Hz, 1H), 2.76 (dt, *J* = 17.5, 2.3 Hz, 1H), 1.24 (t, *J* = 7.1 Hz, 3H), 1.08 (t, *J* = 7.1 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 171.7, 169.7, 138.8, 134.4, 131.1, 130.8, 129.7, 129.0, 128.8, 127.3, 126.1, 124.4, 63.9, 61.6, 61.4, 53.8, 39.9, 14.1, 14.0.

HRMS Exact mass calculated for $[C_{19}H_{21}ClO_4+Na]^+$ requires *m/z* = 371.1021, found *m/z* = 371.1025 (ESI+).

Optical: $[\alpha]^{25}_D$ = -97.1 ° (c = 0.45, CH_2Cl_2, 94 % e.e.)

HPLC (Chiralpak AD-H, 5% ^{i}PrOH/Hx eluent, 0.5 mL/min, 254 nm): major enantiomer t_R = 11.9 min, minor enantiomer t_R = 10.6 min.



Diethyl (S,E)-2-(2-fluorostyryl)cyclopent-3-ene-1,1-dicarboxylate (2p) was synthesized by following Procedure C from **1p**, after a flash column chromatography (PE: EA = 20:1) afforded the product **2p** as a white solid (26.9 mg, 81% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.36 (td, *J* = 7.7, 1.8 Hz, 1H), 7.16 (ddd, *J* = 7.4, 5.3, 1.9 Hz, 1H), 7.08 – 6.95 (m, 2H), 6.65 (d, *J* = 15.9 Hz, 1H), 6.05 (dd, *J* = 16.0, 9.0 Hz, 1H), 5.79 – 5.60 (m, 2H), 4.36 – 3.97 (m, 5H), 3.40 (dq, *J* = 17.4, 2.3 Hz, 1H), 2.84 – 2.73 (m, 1H), 1.26 (t, *J* = 7.1 Hz, 3H), 1.12 (t, *J* = 7.1 Hz, 3H).

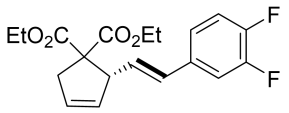
^{13}C NMR (100 MHz, $CDCl_3$) δ 171.8, 169.8, 160.1 (d, *J* = 249.1 Hz), 131.2, 130.0 (d, *J* = 4.6 Hz), 128.7, 128.6, 127.3 (d, *J* = 3.9 Hz), 124.8 (d, *J* = 3.8 Hz), 124.3, 124.0 (d, *J* = 3.6 Hz) , 115.6 , 64.0, 61.4, 61.4, 54.3, 39.8, 14.0, 13.9.

^{19}F NMR (376 MHz, $CDCl_3$) δ -118.30.

HRMS Exact mass calculated for $[C_{19}H_{21}FO_4+Na]^+$ requires *m/z* = 355.1316, found *m/z* = 355.1317 (ESI+).

Optical: $[\alpha]^{25}_D$ = -361.7 ° (c = 0.23, CH_2Cl_2, 90 % e.e.)

HPLC (Chiralpak AD-H, 5% ^{i}PrOH/Hx eluent, 0.5 mL/min, 254 nm): major enantiomer t_R = 11.8 min, minor enantiomer t_R = 10.7 min.



Diethyl (S,E)-2-(3,4-difluorostyryl)cyclopent-3-ene-1,1-dicarboxylate (2q) was synthesized by following Procedure C from **1q**, after a flash column chromatography (PE: EA = 20:1) afforded the product **2q** as a white oil (30.5 mg, 87% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.17 – 6.91 (m, 3H), 6.39 (d, *J* = 15.8 Hz, 1H), 5.91 (dd, *J* = 15.8, 8.9 Hz, 1H), 5.81 – 5.50 (m, 2H), 4.33 – 3.98 (m, 5H), 3.38 (dd, *J* = 17.5, 2.3 Hz, 1H), 2.88 – 2.69 (m, 1H), 1.25 (t, *J* = 7.1 Hz, 3H), 1.09 (t, *J* = 7.1 Hz, 3H).

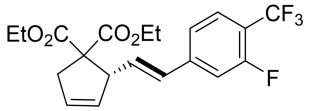
^{13}C NMR (100 MHz, $CDCl_3$) δ 171.7, 169.8, 150.4 (dd, *J* = 247.4, 10.9 Hz), 149.7 (dd, *J* = 248.4, 12.9 Hz), 134.2 (d, *J* = 5.7, 4.2 Hz), 131.0, 130.1, 128.9, 128.6 (d, *J* = 2.5 Hz), 122.4 (dd, *J* = 6.1, 3.5 Hz), 117.2 (d, *J* = 17.3 Hz), 114.5 (d, *J* = 17.5 Hz), 63.9, 61.7, 61.4, 53.7, 39.9, 14.1, 14.0.

^{19}F NMR (376 MHz, $CDCl_3$) δ -137.96 (d, *J* = 21.0 Hz), -139.27 (d, *J* = 21.2 Hz).

HRMS Exact mass calculated for $[C_{19}H_{20}F_2O_4+Na]^+$ requires *m/z* = 377.1222, found *m/z* = 377.1223 (ESI+).

Optical: $[\alpha]^{25}_D$ = -312.3 ° (c = 0.40, CH_2Cl_2, 94 % e.e.)

HPLC (Chiralpak AD-H, 5% ^{i}PrOH/Hx eluent, 0.5 mL/min, 254 nm): major enantiomer t_R = 13.0 min, minor enantiomer t_R = 11.5 min.



Diethyl

(S,E)-2-(3-fluoro-4-(trifluoromethyl)styryl)cyclopent-3-ene-1,1-dicarboxylate (2r) was synthesized by following Procedure C from **1r**, after a flash column chromatography (PE: EA = 20:1) afforded the product **2r** as a white oil (36.8 mg, 92% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.61 – 7.37 (m, 2H), 7.10 (t, *J* = 9.3 Hz, 1H), 6.46 (d, *J* = 15.9 Hz, 1H), 5.99 (dd, *J* = 15.8, 8.8 Hz, 1H), 5.82 – 5.51 (m, 2H), 4.35 – 3.83 (m, 5H), 3.38 (dd, *J* = 17.6, 2.3 Hz, 1H), 2.87 – 2.65 (m, 1H), 1.26 (t, *J* = 7.1 Hz, 3H), 1.10 (t, *J* = 7.1 Hz, 3H).

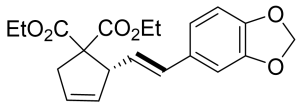
^{13}C NMR (100 MHz, $CDCl_3$) δ 171.7, 169.8, 158.8 (d, *J* = 257.8 Hz), 133.4 (d, *J* = 4.0 Hz), 131.1 (d, *J* = 8.2 Hz), 130.8, 129.7, 129.3 (d, *J* = 2.2 Hz), 129.1, 124.6 (d, *J* = 3.3 Hz), 122.5 (d, *J* = 272.2 Hz), 117.2, 117.0, 63.9, 61.7, 61.4, 53.7, 40.0, 14.1, 14.0.

^{19}F NMR (376 MHz, $CDCl_3$) δ -61.56 (d, *J* = 12.4 Hz), -116.43 (d, *J* = 12.7 Hz).

HRMS Exact mass calculated for $[C_{20}H_{20}F_4O_4+H]^+$ requires *m/z* = 401.1370, found *m/z* = 401.1375 (ESI+).

Optical: $[\alpha]^{25}_D$ = -207.0 ° (c = 0.40, CH_2Cl_2, 95 % e.e.)

HPLC (Chiralpak OJ-H, 5% ^{i}PrOH/Hx eluent, 0.5 mL/min, 254 nm): major enantiomer t_R = 12.3 min, minor enantiomer t_R = 14.3 min.



Diethyl

(S,E)-2-(2-(benzo[d][1,3]dioxol-5-yl)vinyl)cyclopent-3-ene-1,1-dicarboxylate (2s) was synthesized by following Procedure C from **1s**, after a flash column chromatography (PE: EA = 20:1) afforded the product **2s** as a yellow oil (30.1 mg, 84% yield).

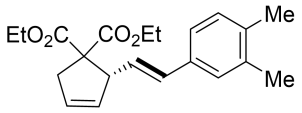
^{1}H NMR (400 MHz, $CDCl_3$) δ 6.84 (d, *J* = 1.5 Hz, 1H), 6.78 – 6.65 (m, 2H), 6.39 (d, *J* = 15.7 Hz, 1H), 5.93 (s, 2H), 5.87 – 5.53 (m, 3H), 4.34 – 3.99 (m, 5H), 3.39 (dd, *J* = 17.4, 2.3 Hz, 1H), 2.76 (ddd, *J* = 17.3, 2.5, 1.4 Hz, 1H), 1.25 (t, *J* = 7.1 Hz, 3H), 1.10 (t, *J* = 7.1 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 171.9, 169.8, 147.9, 147.0, 131.8, 131.5, 131.5, 128.3, 125.4, 120.8, 108.1, 105.5, 101.0, 63.9, 61.5, 61.3, 53.9, 39.9, 14.1, 14.0.

HRMS Exact mass calculated for $[C_{20}H_{22}O_6+Na]^+$ requires *m/z* = 381.1309, found *m/z* = 381.1313 (ESI+).

Optical: $[\alpha]^{25}_D$ = -320.7 ° (c = 0.50, CH_2Cl_2, 92 % e.e.)

HPLC (Chiralpak IC, 5% ^{i}PrOH/Hx eluent, 0.5 mL/min, 254 nm): major enantiomer t_R = 18.1 min, minor enantiomer t_R = 19.7 min.



Diethyl (S,E)-2-(3,4-dimethylstyryl)cyclopent-3-ene-1,1-dicarboxylate (2t) was synthesized by following Procedure C from **1t**, after a flash column chromatography (PE: EA = 20:1) afforded the product **2t** as a yellow solid (29.1 mg, 85% yield).

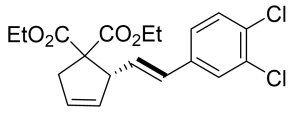
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.14 – 7.00 (m, 3H), 6.43 (d, *J* = 15.8 Hz, 1H), 5.90 (dd, *J* = 15.7, 9.1 Hz, 1H), 5.76 – 5.59 (m, 2H), 4.30 – 3.98 (m, 5H), 3.40 (dd, *J* = 17.4, 2.3 Hz, 1H), 2.80 – 2.68 (m, 1H), 2.22 (s, 6H), 1.26 (t, *J* = 7.1 Hz, 3H), 1.10 (t, *J* = 7.1 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 171.9, 169.9, 136.5, 135.9, 134.6, 132.2, 131.7, 129.7, 128.2, 127.4, 125.9, 123.7, 63.9, 61.5, 61.3, 54.1, 39.9, 19.7, 19.5, 14.1, 14.0.

HRMS Exact mass calculated for $[C_{21}H_{26}O_4+H]^+$ requires *m/z* = 343.1904, found *m/z* = 343.1906 (ESI+).

Optical: $[\alpha]^{25}_D$ = -341.0 ° (c = 0.51, CH_2Cl_2, 92 % e.e.)

HPLC (Chiralpak OJ-H, 5% ^{i}PrOH/Hx eluent, 0.5 mL/min, 254 nm): major enantiomer t_R = 16.3 min, minor enantiomer t_R = 25.0 min.



Diethyl (S,E)-2-(3,4-dichlorostyryl)cyclopent-3-ene-1,1-dicarboxylate (2u) was synthesized by following Procedure C from **1u**, after a flash column chromatography (PE: EA = 20:1) afforded the product **2u** as a white oil (34.5 mg, 90% yield).

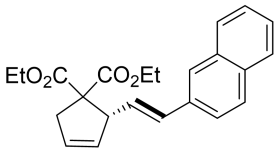
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.31 – 7.18 (m, 2H), 7.06 (dd, *J* = 8.3, 2.1 Hz, 1H), 6.33 (d, *J* = 15.8 Hz, 1H), 5.94 (dd, *J* = 15.8, 9.0 Hz, 1H), 5.77 – 5.47 (m, 2H), 4.29 – 3.87 (m, 5H), 3.41 – 3.26 (m, 1H), 2.73 (dt, *J* = 17.4, 2.4 Hz, 1H), 1.20 (t, *J* = 7.1 Hz, 3H), 1.04 (t, *J* = 7.1 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 171.6, 169.7, 137.1, 132.6, 131.0, 130.9, 130.4, 129.8, 129.6, 129.0, 127.9, 125.4, 63.9, 61.7, 61.4, 53.8, 40.0, 14.1, 14.0.

HRMS Exact mass calculated for $[C_{19}H_{20}Cl_2O_4+Na]^+$ requires *m/z* = 405.0631, found *m/z* = 405.0634 (ESI+).

Optical: $[\alpha]^{25}_D$ = -294.0° (c = 0.43, CH_2Cl_2, 92 % e.e.)

HPLC (Chiralpak AD-H, 5% ^{i}PrOH/Hx eluent, 0.5 mL/min, 254 nm): major enantiomer t_R = 13.7 min, minor enantiomer t_R = 11.8 min.



Diethyl (S,E)-2-(2-(naphthalen-2-yl)vinyl)cyclopent-3-ene-1,1-dicarboxylate (2v) was synthesized by following Procedure C from **1v**, after a flash column chromatography (PE: EA = 20:1) afforded the product **2v** as a yellow solid (30.6 mg, 84% yield).

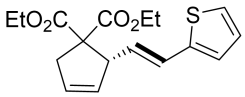
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.81 – 7.65 (m, 4H), 7.55 – 7.37 (m, 3H), 6.67 (d, *J* = 15.8 Hz, 1H), 6.13 (dd, *J* = 15.8, 9.0 Hz, 1H), 5.88 – 5.58 (m, 2H), 4.48 – 4.36 (m, 1H), 4.32 – 4.00 (m, 4H), 3.45 (dt, *J* = 17.5, 2.3 Hz, 1H), 2.81 (dt, *J* = 17.6, 2.3 Hz, 1H), 1.27 (d, *J* = 5.3 Hz, 3H), 1.08 (t, *J* = 7.1 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 171.9, 169.9, 134.4, 133.5, 132.9, 132.3, 131.4, 128.5, 128.1, 127.9, 127.7, 127.6, 126.2, 126.1, 125.7, 123.4, 64.0, 61.6, 61.4, 54.1, 40.0, 14.1, 14.0.

HRMS Exact mass calculated for $[C_{23}H_{24}O_4+Na]^+$ requires *m/z* = 387.1567, found *m/z* = 387.1567 (ESI+).

Optical: $[\alpha]^{25}_D$ = -359.4 ° (c = 0.35, CH_2Cl_2, 94 % e.e.)

HPLC (Chiralpak AD-H, 5% ^{i}PrOH/Hx eluent, 0.5 mL/min, 254 nm): major enantiomer t_R = 15.2 min, minor enantiomer t_R = 14.6 min.



Diethyl (S,E)-2-(2-(thiophen-2-yl)vinyl)cyclopent-3-ene-1,1-dicarboxylate (2w) was synthesized by following Procedure C from **1w**, after a flash column chromatography (PE: EA = 20:1) afforded the product **2w** as a white oil (28.2 mg, 88% yield).

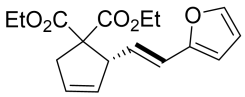
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.10 (dt, *J* = 5.2, 1.0 Hz, 1H), 6.94 – 6.83 (m, 2H), 6.60 (d, *J* = 15.6 Hz, 1H), 5.84 (dd, *J* = 15.6, 8.7 Hz, 1H), 5.76 – 5.57 (m, 2H), 4.32 – 4.04 (m, 5H), 3.38 (dd, *J* = 17.5, 2.3 Hz, 1H), 2.76 (dd, *J* = 17.5, 1.6 Hz, 1H), 1.26 (t, *J* = 7.1 Hz, 3H), 1.14 (t, *J* = 7.1 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 171.8, 169.8, 142.1, 131.1, 128.7, 127.2, 127.0, 125.4, 124.0, 63.9, 61.6, 61.5, 53.7, 40.0, 14.1, 14.0.

HRMS Exact mass calculated for $[C_{17}H_{20}O_4S+Na]^+$ requires *m/z* = 343.0975, found *m/z* = 343.0977 (ESI+).

Optical: $[\alpha]^{25}_D$ = -391.7 ° (c = 0.47, CH_2Cl_2, 95 % e.e.)

HPLC (Chiralpak AD-H, 5% ^{i}PrOH/Hx eluent, 0.5 mL/min, 254 nm): major enantiomer t_R = 13.9 min, minor enantiomer t_R = 13.1 min.



Diethyl (S,E)-2-(2-(furan-2-yl)vinyl)cyclopent-3-ene-1,1-dicarboxylate (2x) was synthesized by following Procedure C from **1x**, after a flash column chromatography (PE: EA = 20:1) afforded the product **2x** as a yellow oil (24.3 mg, 80% yield).

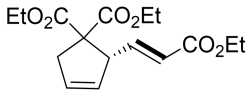
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.28 (d, *J* = 1.9 Hz, 1H), 6.42 – 6.25 (m, 2H), 6.16 (d, *J* = 3.3 Hz, 1H), 5.95 (dd, *J* = 15.8, 8.9 Hz, 1H), 5.81 – 5.49 (m, 2H), 4.31 – 4.05 (m, 5H), 3.37 (dq, *J* = 17.4, 2.4 Hz, 1H), 2.84 – 2.65 (m, 1H), 1.26 (d, *J* = 7.2 Hz, 3H), 1.13 (t, *J* = 7.1 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 171.8, 169.8, 152.6, 141.8, 131.2, 128.7, 126.0, 120.6, 111.1, 107.5, 64.0, 61.6, 61.4, 53.6, 39.9, 14.0, 13.9.

HRMS Exact mass calculated for $[C_{17}H_{20}O_5+Na]^+$ requires *m/z* = 327.1203, found *m/z* = 327.1205 (ESI+).

Optical: $[\alpha]^{25}_D$ = -59.4 ° (c = 0.35, CH_2Cl_2, 93 % e.e.)

HPLC (Chiralpak OJ-H, 5% ^{i}PrOH/Hx eluent, 0.5 mL/min, 254 nm): major enantiomer t_R = 17.5 min, minor enantiomer t_R = 24.6 min.



Diethyl (S,E)-2-(3-ethoxy-3-oxoprop-1-en-1-yl)cyclopent-3-ene-1,1-dicarboxylate (2y) was synthesized by following Procedure C from **1y**, after a flash column chromatography (PE: EA = 20:1) afforded the product **2y** as a white oil (27.3 mg, 88% yield).

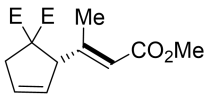
^{1}H NMR (400 MHz, $CDCl_3$) δ 6.75 (dd, *J* = 15.6, 8.4 Hz, 1H), 5.87 (dd, *J* = 15.6, 1.2 Hz, 1H), 5.84 – 5.73 (m, 1H), 5.57 – 5.47 (m, 1H), 4.31 – 4.10 (m, 7H), 3.32 (dd, *J* = 17.5, 2.2 Hz, 1H), 2.81 – 2.71 (m, 1H), 1.27 – 1.17 (m, 9H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 171.3, 169.3, 166.0, 145.3, 130.0, 129.5, 123.2, 63.6, 61.8, 61.6, 60.3, 52.6, 40.0, 14.2, 14.0, 13.9.

HRMS Exact mass calculated for $[C_{16}H_{22}O_6+Na]^+$ requires *m/z* = 333.1309, found *m/z* = 333.1310 (ESI+).

Optical: $[\alpha]^{25}_D$ = -258.3 ° (c = 0.35, CH_2Cl_2, 94 % e.e.)

HPLC (Chiralpak AD-H, 5% ^{i}PrOH/Hx eluent, 0.5 mL/min, 220 nm): major enantiomer t_R = 18.2 min, minor enantiomer t_R = 14.0 min.



E = CO_2Et

Diethyl (S,Z)-2-(4-methoxy-4-oxobut-2-en-2-yl)cyclopent-3-ene-1,1-dicarboxylate (2z) was synthesized by following Procedure C from **1z**, after a flash column

chromatography (PE: EA = 20:1) afforded the product **2z** as a white oil (29.8 mg, 96% yield).

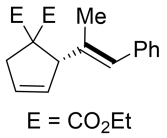
^{1}H NMR (400 MHz, $CDCl_3$) δ 5.87 – 5.44 (m, 3H), 4.33 – 3.99 (m, 5H), 3.66 (s, 3H), 3.39 (dd, *J* = 17.5, 2.4 Hz, 1H), 2.73 (dt, *J* = 17.6, 1.9 Hz, 1H), 2.12 (d, *J* = 1.4 Hz, 3H), 1.24 (t, *J* = 7.1 Hz, 3H), 1.17 (t, *J* = 7.2 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 171.7, 169.5, 166.8, 157.8, 130.7, 129.8, 118.5, 64.1, 61.8, 61.6, 59.9, 50.9, 41.2, 18.8, 14.0, 13.8.

HRMS Exact mass calculated for $[C_{17}H_{24}O_6+Na]^+$ requires *m/z* = 347.1465, found *m/z* = 347.1466 (ESI+).

Optical: $[\alpha]^{25}_D$ = -269.5 ° (c = 0.28, CH_2Cl_2, 93 % e.e.)

HPLC (Chiralpak AS-H, 2% ^{i}PrOH/Hx eluent, 0.5 mL/min, 214 nm): major enantiomer t_R = 12.4 min, minor enantiomer t_R = 13.2 min.



Diethyl (S,Z)-2-(1-phenylprop-1-en-2-yl)cyclopent-3-ene-1,1-dicarboxylate (2aa) was synthesized by following Procedure C from **1aa**, after a flash column chromatography (PE: EA = 20:1) afforded the product **2aa** as a yellow solid (30.5 mg, 93% yield).

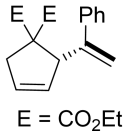
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.33 – 7.27 (m, 2H), 7.20 (dd, *J* = 7.9, 3.4 Hz, 3H), 6.37 (s, 1H), 5.84 – 5.57 (m, 2H), 4.41 (d, *J* = 3.0 Hz, 1H), 4.32 – 4.08 (m, 3H), 3.95 (ddd, *J* = 10.8, 7.2, 1.0 Hz, 1H), 3.44 (dd, *J* = 17.5, 2.4 Hz, 1H), 2.88 – 2.65 (m, 1H), 1.83 (t, *J* = 1.2 Hz, 3H), 1.29 – 1.24 (m, 3H), 1.16 – 1.02 (m, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 172.3, 170.1, 137.9, 136.9, 132.0, 128.9, 128.8, 128.5, 128.0, 126.2, 64.2, 61.5, 61.2, 60.0, 41.1, 17.3, 14.0, 13.9.

HRMS Exact mass calculated for $[C_{20}H_{24}O_4+Na]^+$ requires *m/z* = 351.1567, found *m/z* = 351.1570 (ESI+).

Optical: $[\alpha]^{25}_D$ = -314.9 ° (c = 0.40, CH_2Cl_2, 93 % e.e.)

HPLC (Chiralpak AD-H, 5% ^{i}PrOH/Hx eluent, 0.5 mL/min, 254 nm): major enantiomer t_R = 10.6 min, minor enantiomer t_R = 9.7 min.



Diethyl (S)-2-(1-phenylvinyl)cyclopent-3-ene-1,1-dicarboxylate (2ab) was synthesized by following Procedure C from **1ab**, after a flash column chromatography (PE: EA = 20:1) afforded the product **2ab** as a yellow oil (28.3 mg, 90% yield).

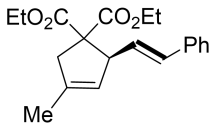
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.43 (dd, *J* = 7.4, 1.9 Hz, 2H), 7.26 – 7.14 (m, 3H), 5.82 – 5.55 (m, 2H), 5.42 (d, *J* = 0.9 Hz, 1H), 4.98 (s, 1H), 4.87 (q, *J* = 2.3 Hz, 1H), 4.22 – 4.02 (m, 2H), 3.82 (dq, *J* = 10.7, 7.1 Hz, 1H), 3.44 – 3.18 (m, 2H), 2.80 – 2.64 (m, 1H), 1.15 (t, *J* = 7.1 Hz, 3H), 0.74 (t, *J* = 7.2 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 172.2, 169.6, 146.4, 141.4, 132.9, 128.0, 127.9, 127.3, 126.5, 116.5, 64.2, 61.6, 60.9, 53.8, 40.4, 13.9, 13.3.

HRMS Exact mass calculated for $[C_{19}H_{22}O_4+Na]^+$ requires *m/z* = 337.1410, found *m/z* = 337.1412 (ESI+).

Optical: $[\alpha]^{25}_D$ = -134.0 ° (c = 0.40, CH_2Cl_2, 51 % e.e.)

HPLC (Chiralpak AD-H, 5% ^{i}PrOH/Hx eluent, 0.5 mL/min, 254 nm): major enantiomer t_R = 9.4 min, minor enantiomer t_R = 10.5 min.



Diethyl (R,E)-4-methyl-2-styrylcyclopent-3-ene-1,1-dicarboxylate (2ac) was synthesized by following Procedure C from **1ac**, after a flash column chromatography (PE: EA = 20:1) afforded the product **2ac** as a white oil (29.6 mg, 90% yield).

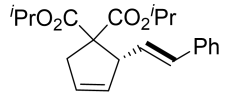
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.31 – 7.17 (m, 5H), 6.46 (d, *J* = 15.8 Hz, 1H), 5.99 (dd, *J* = 15.8, 8.9 Hz, 1H), 5.23 (q, *J* = 1.9 Hz, 1H), 4.38 – 4.11 (m, 3H), 4.11 – 3.93 (m, 2H), 3.35 (ddt, *J* = 16.3, 2.4, 1.3 Hz, 1H), 2.70 – 2.55 (m, 1H), 1.82 – 1.72 (m, 3H), 1.26 (t, *J* = 7.1 Hz, 3H), 1.08 (t, *J* = 7.1 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 172.0, 169.9, 138.3, 137.1, 131.7, 128.4, 128.1, 127., 126.2, 125.0, 64.4, 61.5, 61.3, 54.0, 43.7, 16.2, 14.1, 14.0.

HRMS Exact mass calculated for $[C_{20}H_{24}O_4+Na]^+$ requires *m/z* = 351.1567, found *m/z* = 351.1571 (ESI+).

Optical: $[\alpha]^{25}_D$ = -127.8 ° (c = 0.30, CH_2Cl_2, 86 % e.e.)

HPLC (Chiralpak OJ-H, 5% ^{i}PrOH/Hx eluent, 0.5 mL/min, 254 nm): major enantiomer t_R = 12.4 min, minor enantiomer t_R = 15.5 min.



Diisopropyl (S,E)-2-styrylcyclopent-3-ene-1,1-dicarboxylate (2ae) was synthesized by following Procedure C from **1ae**, after a flash column chromatography (PE: EA = 20:1) afforded the product **2ae** as a white oil (32.2 mg, 94% yield).

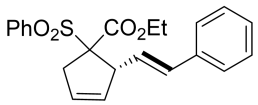
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.30 – 7.16 (m, 5H), 6.43 (d, *J* = 15.8 Hz, 1H), 5.91 (dd, *J* = 15.8, 9.2 Hz, 1H), 5.73 – 5.51 (m, 2H), 5.05 – 4.81 (m, 2H), 4.31 – 4.21 (m, 1H), 3.35 (dd, *J* = 17.5, 2.3 Hz, 1H), 2.72 – 2.61 (m, 1H), 1.19 (dd, *J* = 6.2, 1.0 Hz, 6H), 1.10 (d, *J* = 6.3 Hz, 3H), 0.95 (d, *J* = 6.3 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 171.4, 169.4, 137.0, 132.2, 131.6, 128., 128.3, 127.3, 127.3, 126.2, 68.9, 68.9, 63.7, 53.9, 40.1, 21.8, 21.6, 21.5.

HRMS Exact mass calculated for $[C_{21}H_{26}O_4+Na]^+$ requires *m/z* = 365.1723, found *m/z* = 365.1725 (ESI+).

Optical: $[\alpha]^{25}_D$ = -336.6 ° (c = 0.37, CH_2Cl_2, 90 % e.e.)

HPLC (Chiralpak OJ-H, 2% ^{i}PrOH/Hx eluent, 0.5 mL/min, 254 nm): major enantiomer t_R = 9.6 min, minor enantiomer t_R = 14.9 min.



Ethyl (2S)-1-(phenylsulfonyl)-2-((E)-styryl)cyclopent-3-ene-1-carboxylate (2af) was synthesized by following Procedure C from **1af**, after a flash column chromatography (PE: EA = 10:1) afforded the product **2af** as a white oil (33.3 mg, 87% yield, 12:1 dr).

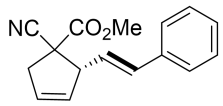
^{1}H NMR (600 MHz, $CDCl_3$) δ 8.01 – 7.85 (m, 2H), 7.79 – 7.64 (m, 1H), 7.62 – 7.50 (m, 2H), 7.42 – 7.19 (m, 5H), 6.43 – 6.32 (m, 1H), 5.90 (dd, *J* = 15.9, 8.2 Hz, 1H), 5.75 (dq, *J* = 6.3, 2.2 Hz, 1H), 5.57 (dq, *J* = 5.8, 2.2 Hz, 1H), 4.45 (ddt, *J* = 8.2, 2.1, 1.1 Hz, 1H), 4.15 – 3.88 (m, 2H), 3.46 – 3.21 (m, 2H), 1.06 (t, *J* = 7.1 Hz, 3H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 166.6, 137.3, 136.4, 134.0, 132.9, 130.6, 130.1, 129.3, 128.6, 128.5, 127.7, 126.2, 126.1, 82.1, 62.3, 53.8, 38.4, 13.9.

HRMS Exact mass calculated for $[C_{22}H_{22}O_4S+Na]^+$ requires *m/z* = 405.1136, found *m/z* = 405.1129 (ESI+).

Optical: $[\alpha]^{25}_D$ = -165.3 ° (c = 0.41, CH_2Cl_2, 96 % e.e., dr = 12:1)

HPLC (Chiralpak OD-H, 10% ^{i}PrOH/Hx eluent, 0.5 mL/min, 254 nm): major enantiomer t_R = 26.8 min, minor enantiomer t_R = 30.5 min.



Methyl (2S)-1-cyano-2-((E)-styryl)cyclopent-3-ene-1-carboxylate (2ag) was synthesized by following Procedure C from **1ag**, after a flash column chromatography (PE: EA = 10:1) afforded the product **2ag** as a white oil (22.8 mg, 90% yield, 4:1 dr).

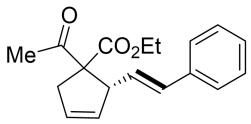
For the major isomer: **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.31 – 7.25 (m, 4H), 7.23 – 7.21 (m, 1H), 6.52 (dd, *J* = 15.8, 2.5 Hz, 1H), 5.96 – 5.78 (m, 2H), 5.64 (dq, *J* = 6.0, 2.2 Hz, 1H), 4.20 – 4.06 (m, 1H), 3.65 (d, *J* = 2.6 Hz, 3H), 3.37 (dt, *J* = 17.1, 2.3 Hz, 1H), 2.92 (dd, *J* = 17.1, 2.5 Hz, 1H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 167.1, 136.1, 134.2, 130.1, 129.1, 128.6, 128.1, 126.5, 124.5, 121.2, 59.6, 53.5, 51.2, 41.2.

HRMS Exact mass calculated for $[C_{16}H_{15}NO_2+Na]^+$ requires *m/z* = 276.1000, found *m/z* = 276.0997 (ESI+).

Optical: $[\alpha]^{25}_D$ = -287.5 ° (c = 0.44, CH_2Cl_2, 96 % e.e.)

HPLC (Chiralpak AD-H, 2% ^{i}PrOH/Hx eluent, 0.5 mL/min, 254 nm): major enantiomer t_R = 23.1 min, minor enantiomer t_R = 21.7 min.



Ethyl (2S)-1-acetyl-2-((E)-styryl)cyclopent-3-ene-1-carboxylate (2ah) was synthesized by following Procedure C from **1ah**, after a flash column chromatography (PE: EA = 10:1) afforded the product **2ah** as a white oil (4.8 mg, 17% yield, 6:1 dr).

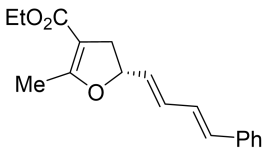
For the major isomer: **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.29 – 7.25 (m, 4H), 7.22 – 7.15 (m, 1H), 6.45 (d, *J* = 15.8 Hz, 1H), 5.95 (dd, *J* = 15.8, 9.1 Hz, 1H), 5.69 – 5.55 (m, 2H), 4.31 (ddt, *J* = 9.1, 1.7, 0.8 Hz, 1H), 4.09 – 3.99 (m, 2H), 3.40 (dq, *J* = 17.4, 2.3 Hz, 1H), 2.58 (dddd, *J* = 17.4, 2.7, 1.8, 0.9 Hz, 1H), 2.21 (s, 3H), 1.09 (t, *J* = 7.1 Hz, 3H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 202.0, 170.5, 137.0, 132.2, 132.1, 128.5 127.6, 127.4, 127.3, 126.2, 70.1, 61.5, 52.3, 38.6, 26.3, 14.1.

HRMS Exact mass calculated for $[C_{18}H_{20}O_3+Na]^+$ requires *m/z* = 307.1310, found *m/z* = 307.1313 (ESI+).

Optical: $[\alpha]^{25}_D$ = +40.2 ° (c = 0.38, CH_2Cl_2, 87 % e.e., dr = 6:1)

HPLC (Chiralpak AD-H, 10% ^{i}PrOH/Hx eluent, 0.5 mL/min, 254 nm): major enantiomer t_R = 10.2 min, minor enantiomer t_R = 9.5 min.



Ethyl-(R)-2-methyl-5-((1E,3E)-4-phenylbuta-1,3-dien-1-yl)-4,5-dihydrofuran-3-carboxylate (3) was synthesized by following Procedure C from **1ah**, after a flash column chromatography (PE: EA = 10:1) afforded the product **3** as a white oil (16.2 mg, 57% yield).

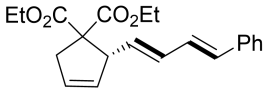
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.41 – 7.23 (m, 5H), 6.84 – 6.62 (m, 1H), 6.59 (dd, *J* = 15.6, 6.1 Hz, 1H), 6.41 (dd, *J* = 15.5, 10.3 Hz, 1H), 5.85 (dd, *J* = 14.9, 7.2 Hz, 1H), 5.29 – 4.91 (m, 1H), 4.24 – 4.05 (m, 2H), 3.21 – 2.97 (m, 1H), 2.70 (dd, *J* = 14.4, 7.9 Hz, 1H), 2.29 – 2.08 (m, 3H), 1.30 – 1.24 (m, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 167.49, 166.11, 136.82, 134.03, 132.61, 131.60, 128.62, 127.84, 127.55, 126.46, 101.76, 82.30, 59.49, 35.93, 14.44, 14.13.

HRMS Exact mass calculated for $[C_{18}H_{20}O_3+Na]^+$ requires *m/z* = 307.1310, found *m/z* = 307.1310 (ESI+).

Optical: $[\alpha]^{25}_D$ = +35.4 ° (c = 0.35, CH_2Cl_2, 29 % e.e.)

HPLC (Chiralpak AD-H, 10% ^{i}PrOH/Hx eluent, 0.5 mL/min, 254 nm): major enantiomer t_R = 16.6 min, minor enantiomer t_R = 14.7 min.



Diethyl-(S)-2-((1E,3E)-4-phenylbuta-1,3-dien-1-yl)cyclopent-3-ene-1,1-dicarboxylate (5a) was synthesized by following Procedure C from **4a**, after a flash column chromatography (PE: EA = 10:1) afforded the product **5a** as a white solid (26.9 mg, 79% yield).

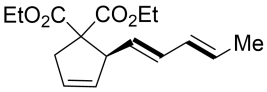
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39 – 7.27 (m, 4H), 7.24 – 7.18 (m, 1H), 6.69 (dd, *J* = 15.6, 10.4 Hz, 1H), 6.49 (d, *J* = 15.7 Hz, 1H), 6.30 (dd, *J* = 15.1, 10.4 Hz, 1H), 5.80 – 5.49 (m, 3H), 4.30 – 4.03 (m, 5H), 3.36 (dd, *J* = 17.5, 2.3 Hz, 1H), 2.76 (d, *J* = 17.4 Hz, 1H), 1.25 (d, *J* = 7.1 Hz, 3H), 1.18 (t, *J* = 7.1 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 171.9, 169.8, 137.2, 132.9, 132.0, 131.4, 131.4, 128.6, 128.4, 128.3, 127.5, 126.3, 64.0, 61.6, 61.4, 53.9, 39.8, 14.2, 14.0.

HRMS Exact mass calculated for $[C_{21}H_{24}O_4+Na]^+$ requires *m/z* = 363,1567, found *m/z* = 363.1572 (ESI+).

Optical: $[\alpha]^{25}_D$ = -330.6 ° (c = 0.40, CH_2Cl_2, 98 % e.e.)

HPLC (Chiralpak OJ-H, 3% ^{i}PrOH/Hx eluent, 0.5 mL/min, 254 nm): major enantiomer t_R = 44.0 min, minor enantiomer t_R = 51.4 min.



Diethyl (S)-2-((1E,3E)-penta-1,3-dien-1-yl)cyclopent-3-ene-1,1-dicarboxylate (5b) was synthesized by following Procedure C from **4b**, after a flash column chromatography (PE: EA = 10:1) afforded the product **5b** as a yellow oil (22.8 mg, 82% yield).

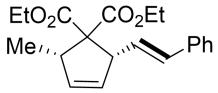
^{1}H NMR (400 MHz, $CDCl_3$) δ 6.08 (dd, *J* = 15.1, 10.4 Hz, 1H), 5.94 (ddd, *J* = 15.0, 10.4, 1.7 Hz, 1H), 5.70 – 5.47 (m, 3H), 5.29 (dd, *J* = 15.1, 9.0 Hz, 1H), 4.26 – 4.06 (m, 5H), 3.32 (dd, *J* = 17.4, 2.3 Hz, 1H), 2.76 – 2.63 (m, 1H), 1.71 (dd, *J* = 6.8, 1.6 Hz, 3H), 1.24 (t, *J* = 7.1 Hz, 3H), 1.18 (t, *J* = 7.1 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 171.9, 169.8, 132.9, 131.7, 131.0, 129.1, 127.9, 127.8, 63.9, 61.5, 61.2, 53.6, 39.7, 18.0, 14.1, 14.0.

HRMS Exact mass calculated for $[C_{16}H_{22}O_4+Na]^+$ requires *m/z* = 301.1410, found *m/z* = 301.1414 (ESI+).

Optical: $[\alpha]^{25}_D$ = +70.6 ° (c = 0.25, CH_2Cl_2, 86 % e.e.)

HPLC (Chiralpak IC, 2% ^{i}PrOH/Hx eluent, 0.5 mL/min, 254 nm): major enantiomer t_R = 15.2 min, minor enantiomer t_R = 13.0 min.



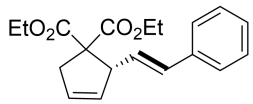
Diethyl (2R,5S)-2-methyl-5-((E)-styryl)cyclopent-3-ene-1,1-dicarboxylate (10) was synthesized by following Procedure C from **9**, after a flash column chromatography (PE: EA = 20:1) afforded the product **10** as a white oil (27.6 mg, 84% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.28 – 7.11 (m, 5H), 6.45 (d, *J* = 16.0 Hz, 1H), 6.27 (dd, *J* = 15.9, 7.7 Hz, 1H), 5.59 (s, 2H), 4.18 (p, *J* = 7.2 Hz, 2H), 4.08 – 3.88 (m, 3H), 3.32 (dd, *J* = 7.3, 2.3 Hz, 1H), 1.24 – 1.18 (m, 6H), 1.06 (t, *J* = 7.2 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 171.9, 168.4, 137.3, 134.7, 131.9, 129.7, 128.8, 128.5, 127.2, 126.2, 68.4, 61.3, 60.6, 54.9, 46.8, 16.0, 14.1, 14.1.

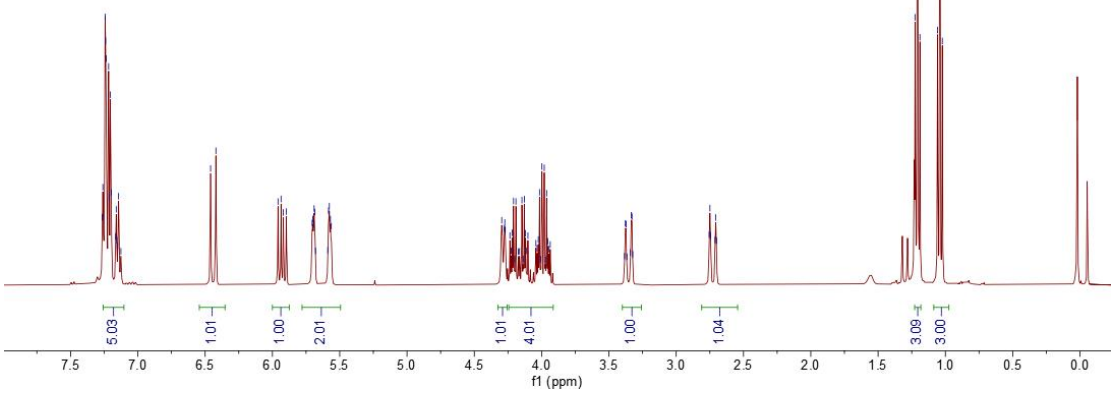
HRMS Exact mass calculated for $[C_{20}H_{24}O_4+Na]^+$ requires *m/z* = 351.1567, found *m/z* = 351.1570 (ESI+).

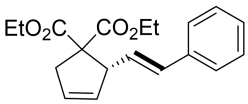
Optical: $[\alpha]^{25}_D$ = +96.76 ° (c = 0.25, CH_2Cl_2, ≥ 20:1dr.)



2a

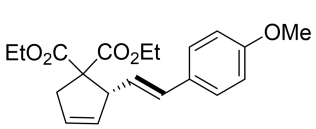
^{1}H NMR, 400 MHz, $CDCl_3$





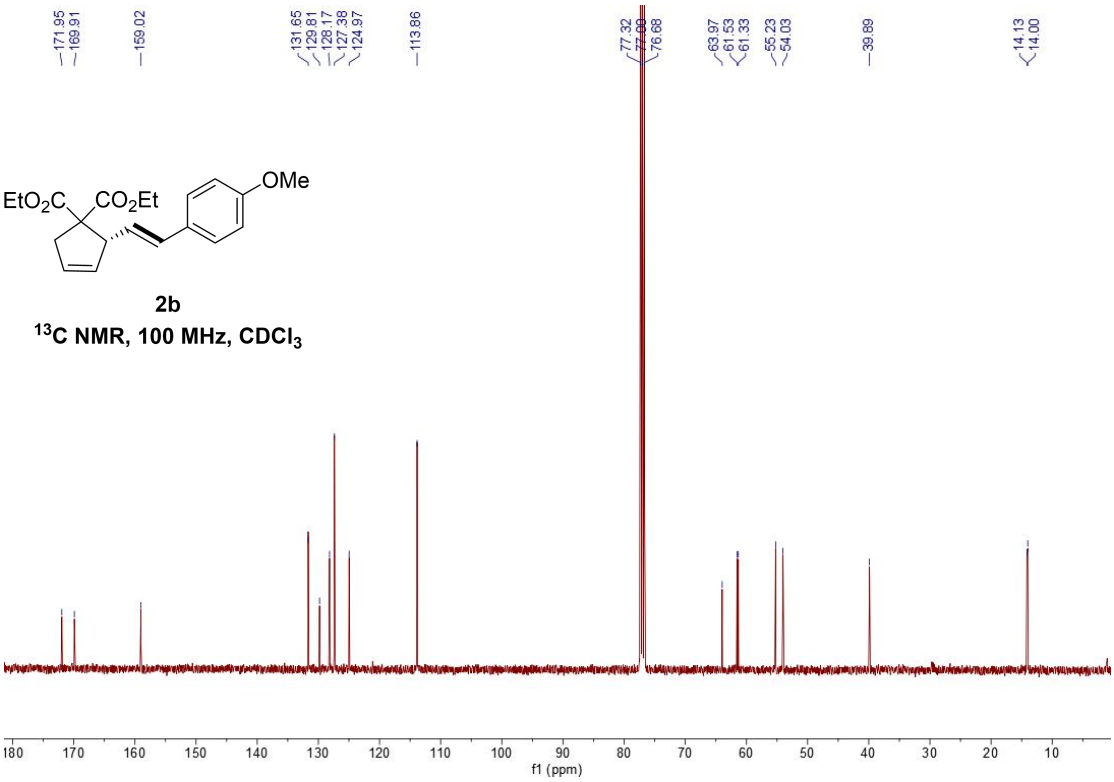
2a

^{13}C NMR, 100 MHz, $CDCl_3$



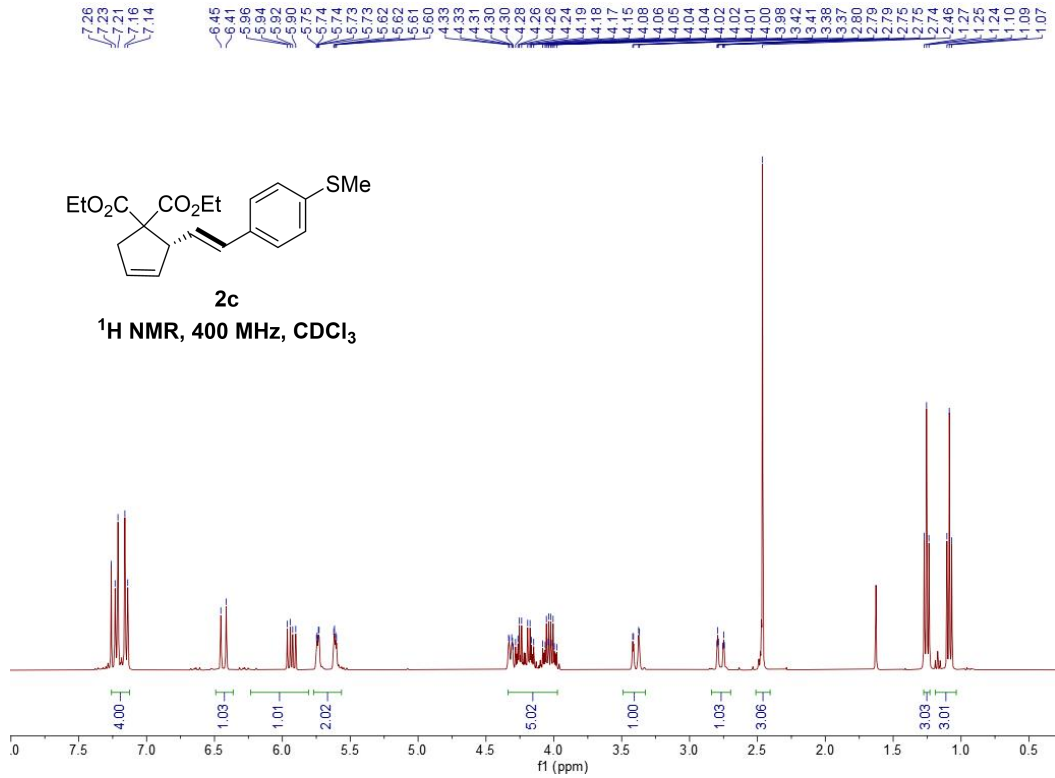
2b

^{1}H NMR, 400 MHz, $CDCl_3$



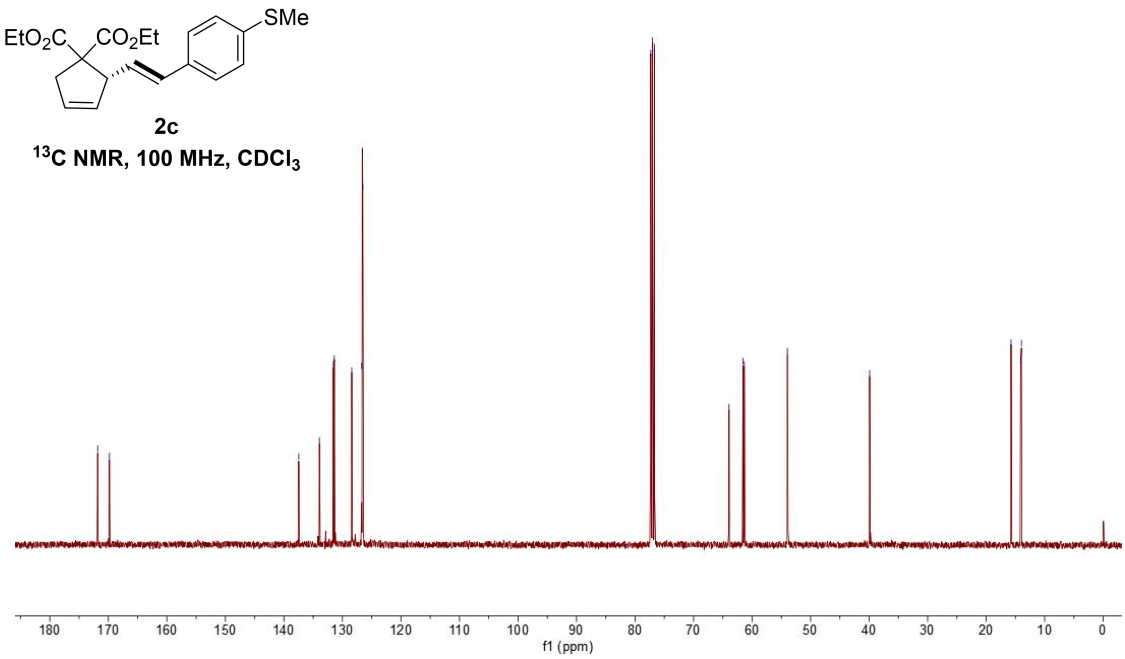
2b

^{13}C NMR, 100 MHz, $CDCl_3$



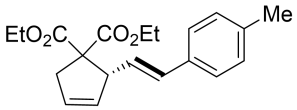
2c

^{1}H NMR, 400 MHz, $CDCl_3$



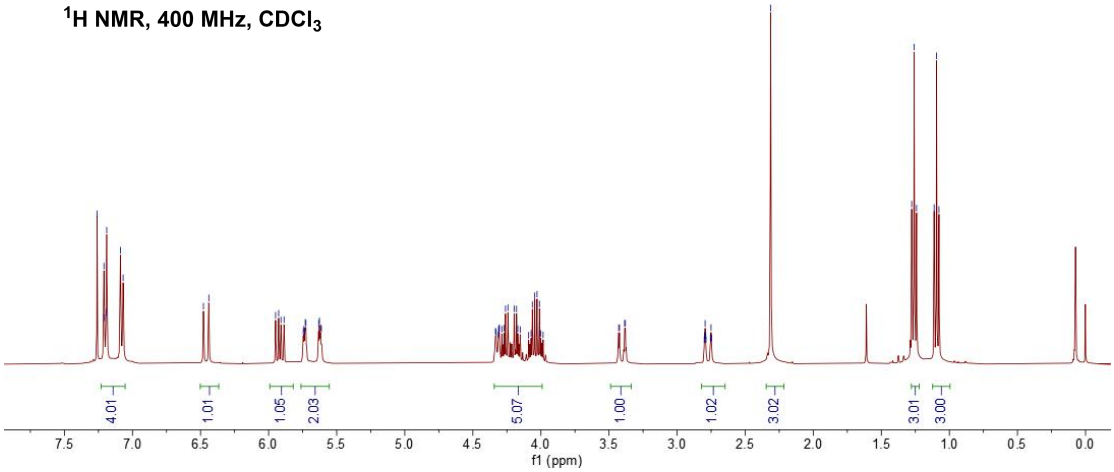
2c

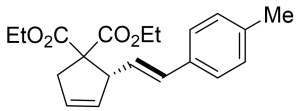
^{13}C NMR, 100 MHz, $CDCl_3$



2d

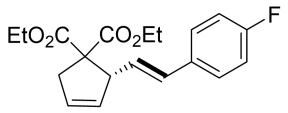
^{1}H NMR, 400 MHz, $CDCl_3$





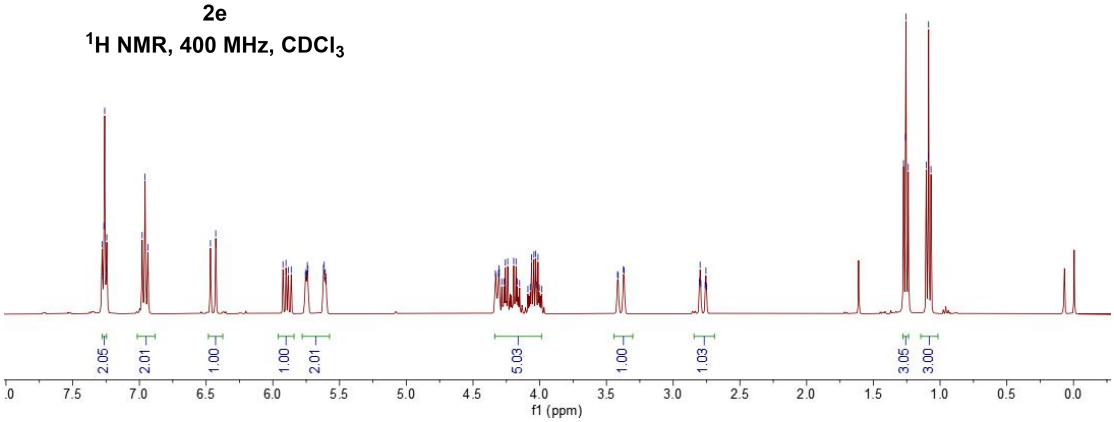
2d

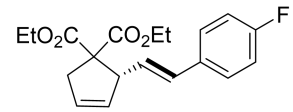
^{13}C NMR, 100 MHz, $CDCl_3$



2e

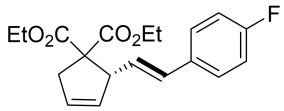
^{1}H NMR, 400 MHz, $CDCl_3$





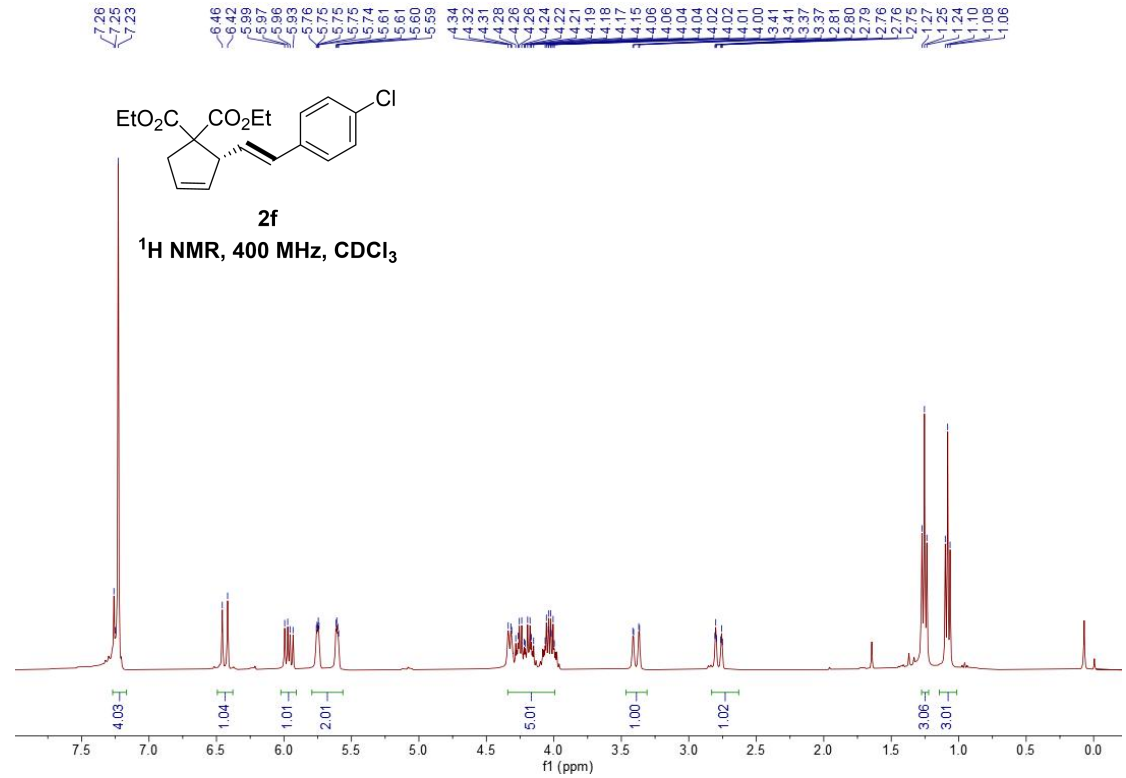
2e

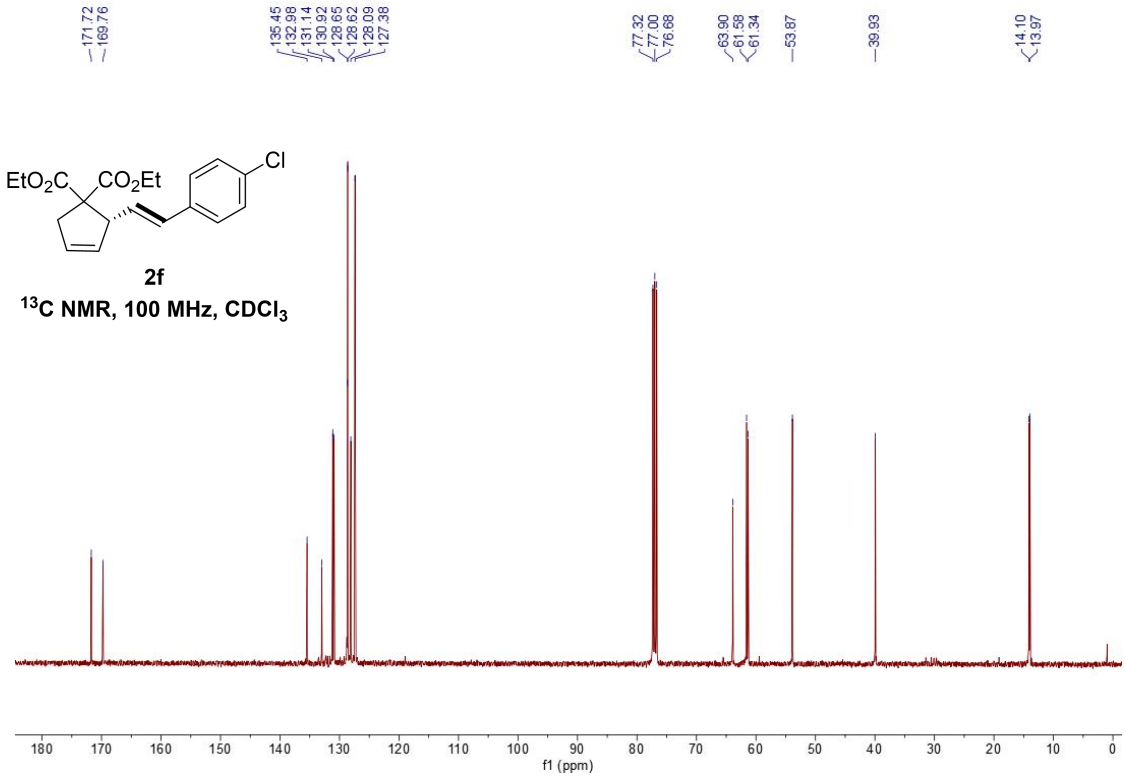
^{13}C NMR, 100 MHz, $CDCl_3$

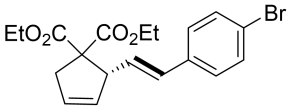


2e

^{19}F NMR, 376 MHz, $CDCl_3$

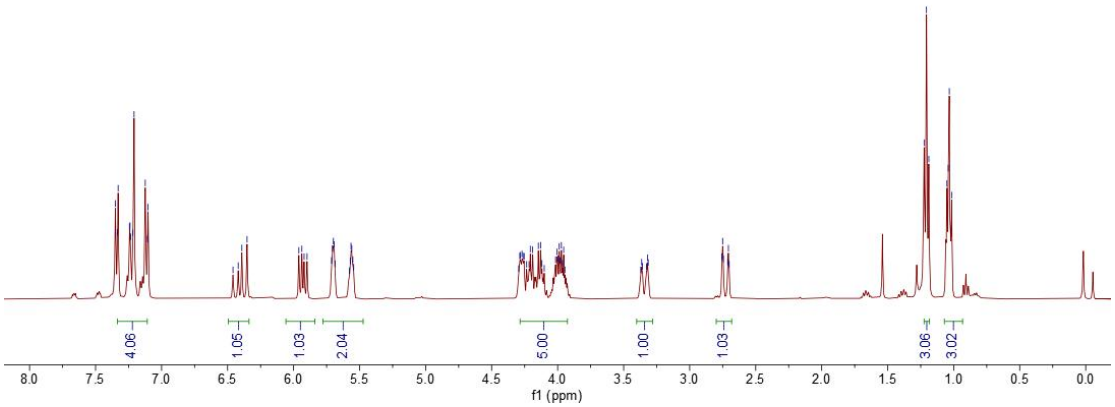

EtO2C
CO2Et
Cl
2f
1H NMR, 400 MHz, CDCl3
f1 (ppm)

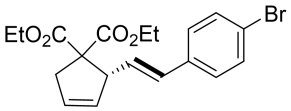

EtO2C
CO2Et
Cl
2f
13C NMR, 100 MHz, CDCl3
f1 (ppm)



2g

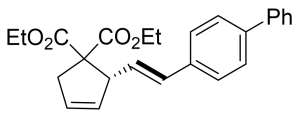
^{1}H NMR, 400 MHz, $CDCl_3$





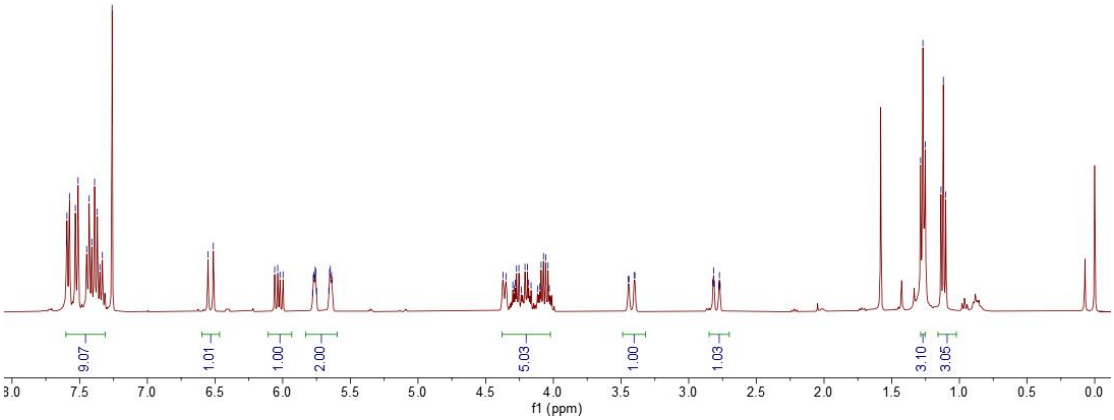
2g

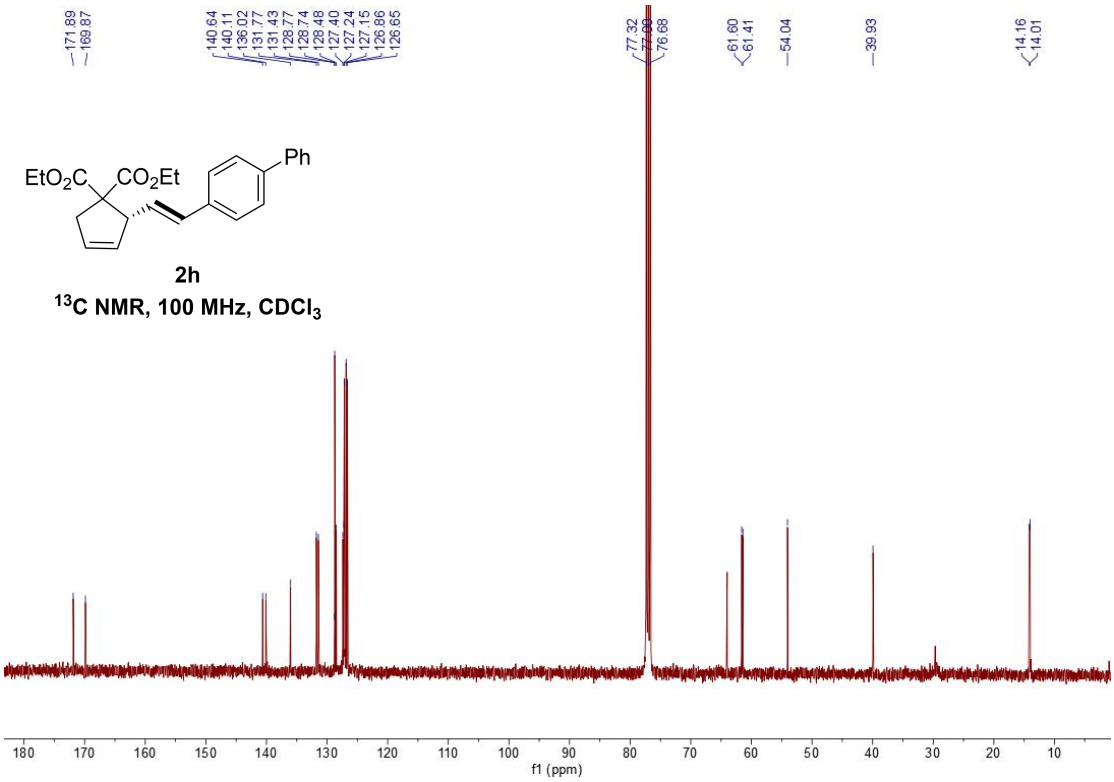
^{13}C NMR, 100 MHz, $CDCl_3$



2h

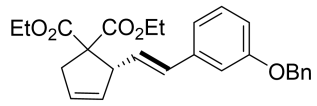
^{1}H NMR, 400 MHz, $CDCl_3$





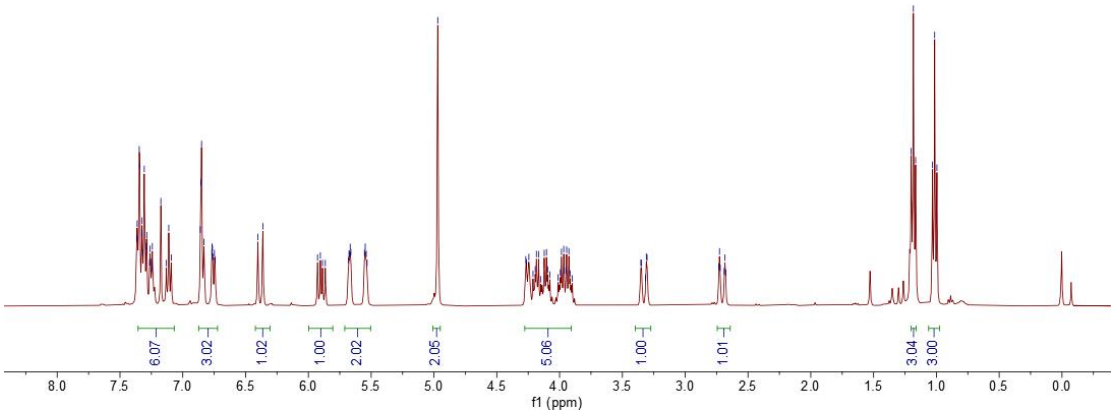
2h

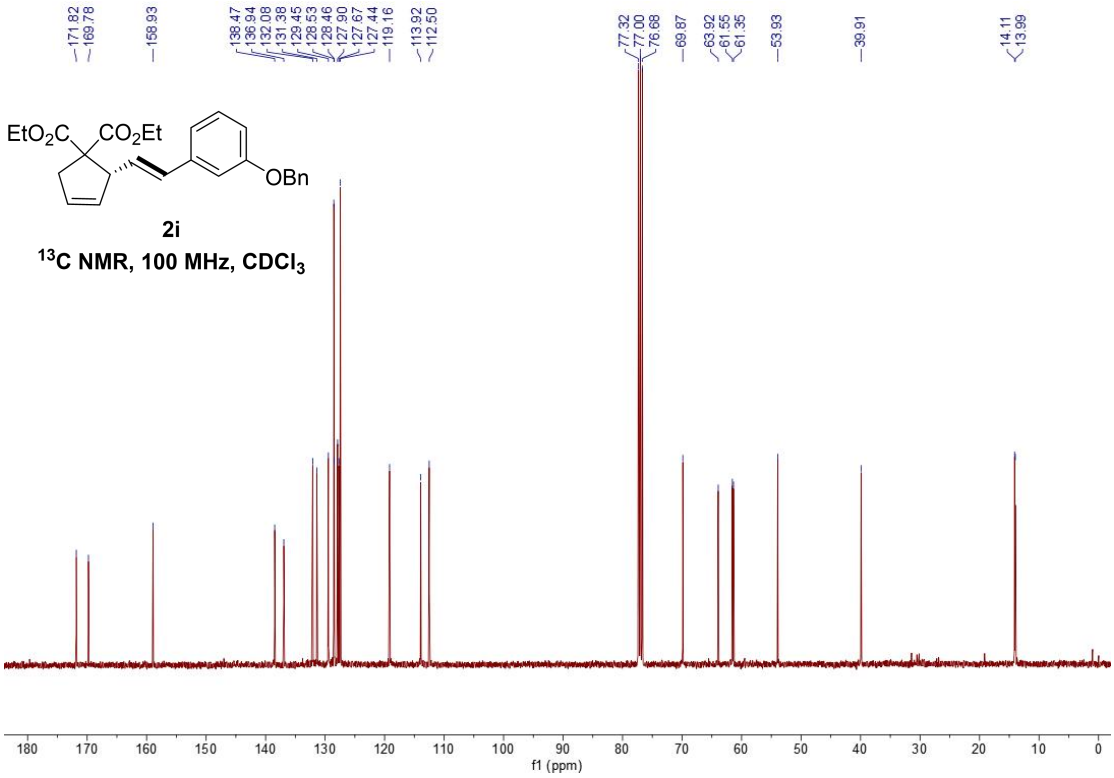
^{13}C NMR, 100 MHz, $CDCl_3$



2i

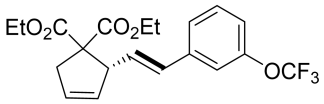
^{1}H NMR, 400 MHz, $CDCl_3$





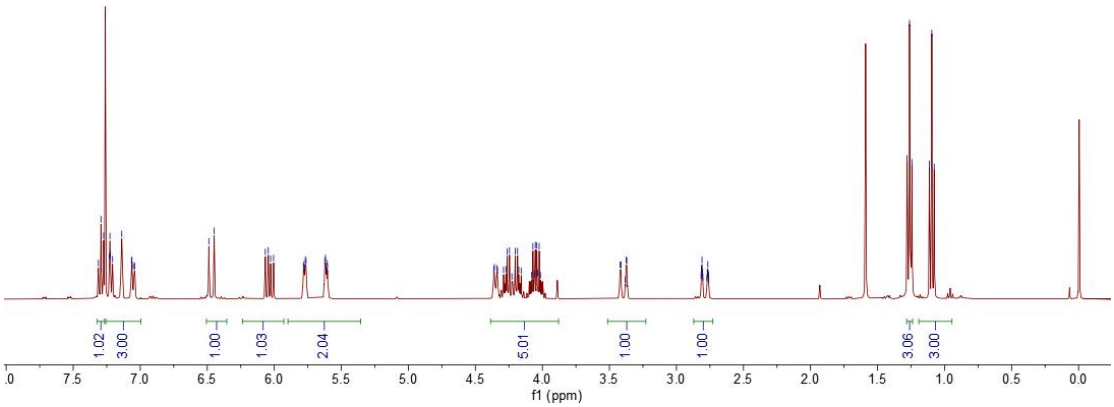
2i

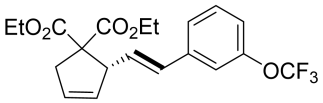
^{13}C NMR, 100 MHz, $CDCl_3$



2j

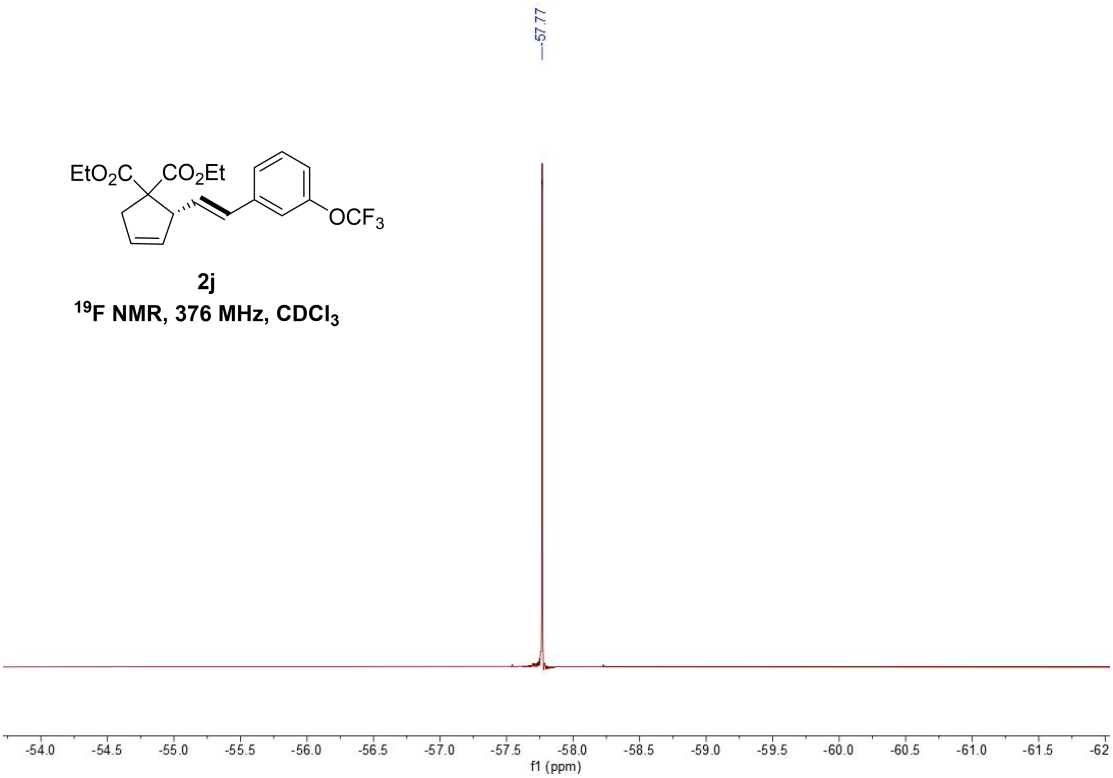
^{1}H NMR, 400 MHz, $CDCl_3$





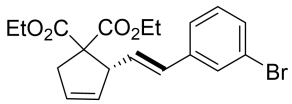
2j

^{13}C NMR, 100 MHz, $CDCl_3$



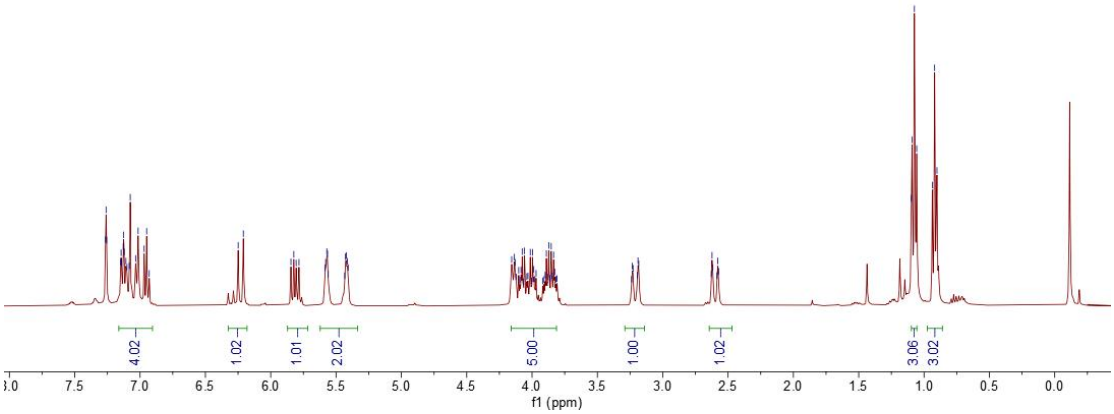
2j

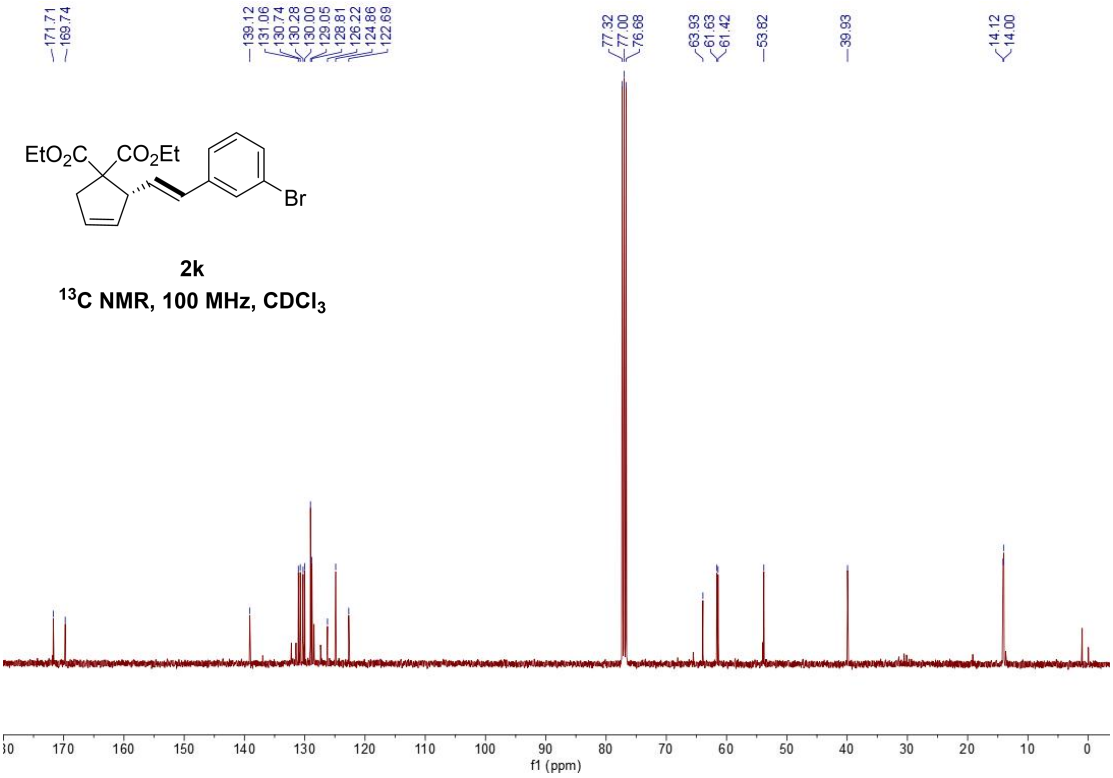
^{19}F NMR, 376 MHz, $CDCl_3$



2k

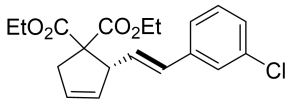
^{1}H NMR, 400 MHz, $CDCl_3$





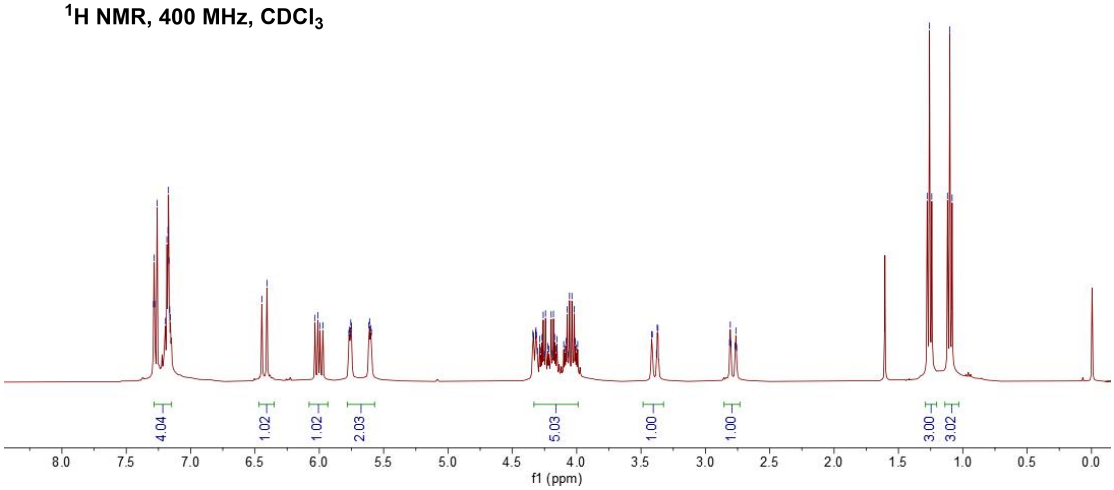
2k

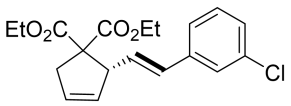
^{13}C NMR, 100 MHz, $CDCl_3$



2l

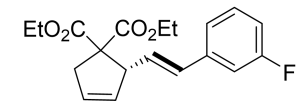
^{1}H NMR, 400 MHz, $CDCl_3$





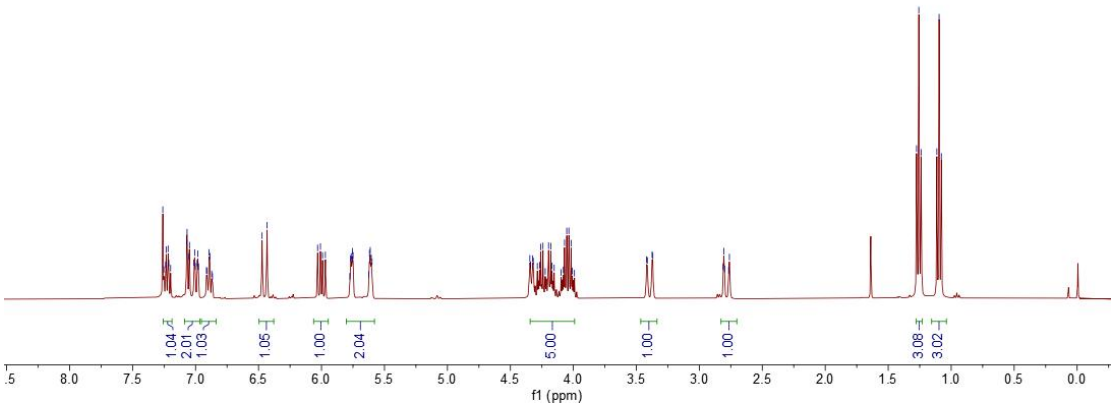
2l

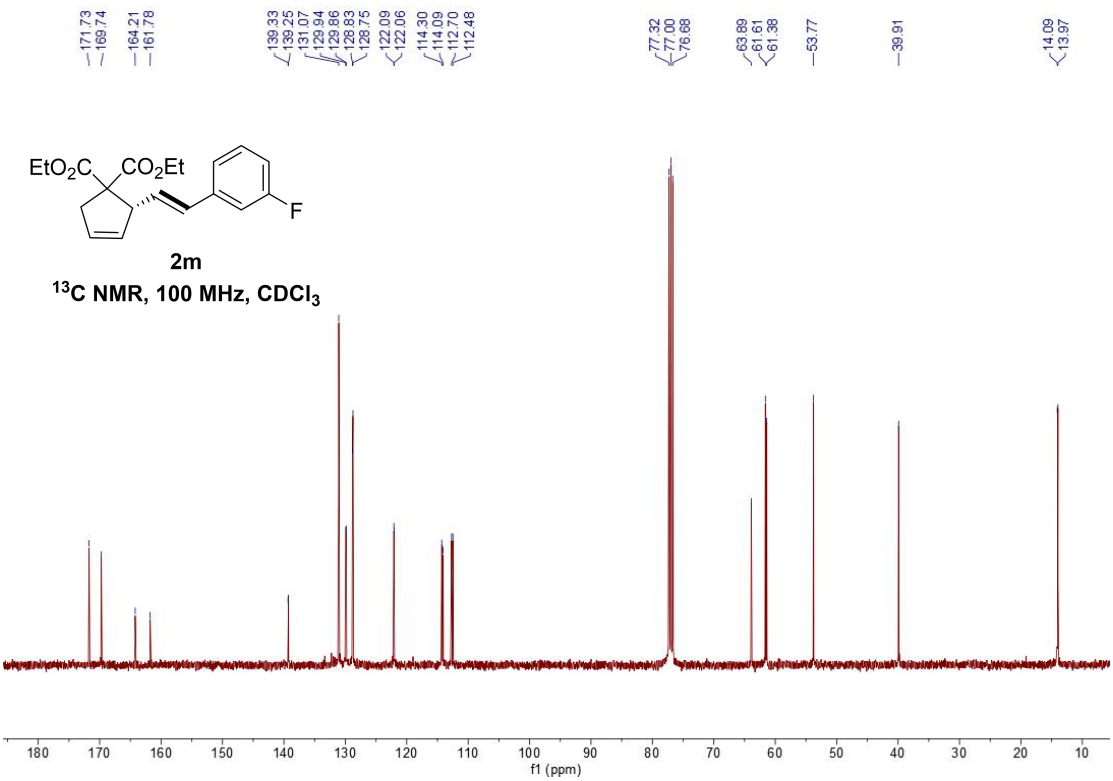
^{13}C NMR, 100 MHz, $CDCl_3$



2m

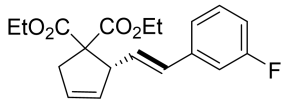
^{1}H NMR, 400 MHz, $CDCl_3$





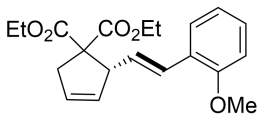
2m

^{13}C NMR, 100 MHz, $CDCl_3$



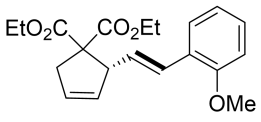
2m

^{19}F NMR, 376 MHz, $CDCl_3$



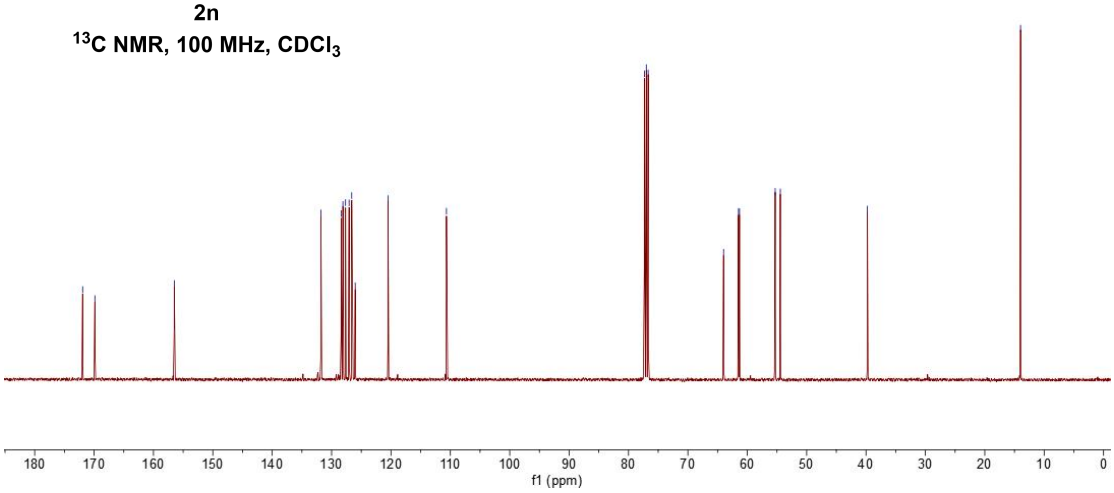
2n

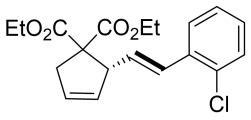
^{1}H NMR, 400 MHz, $CDCl_3$



2n

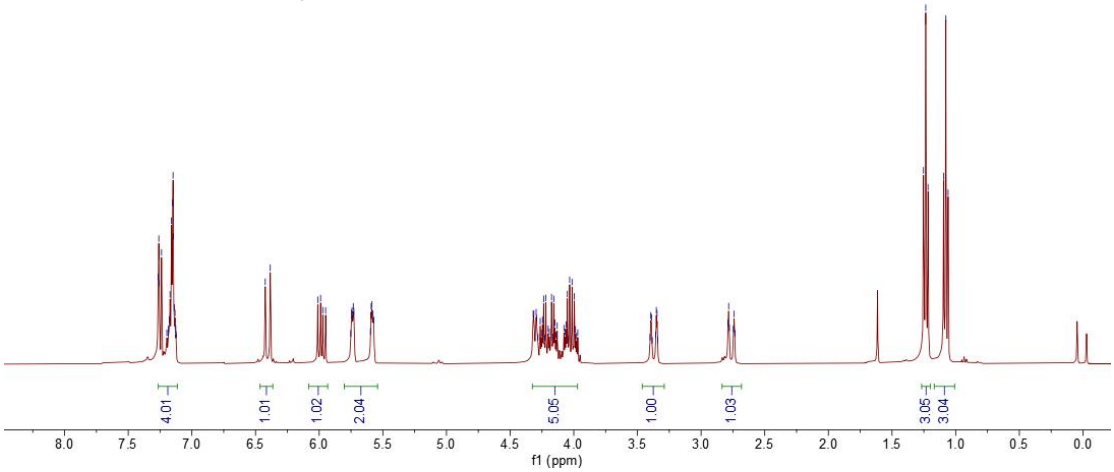
^{13}C NMR, 100 MHz, $CDCl_3$

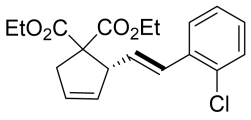




2o

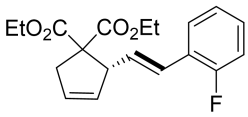
^{1}H NMR, 400 MHz, $CDCl_3$





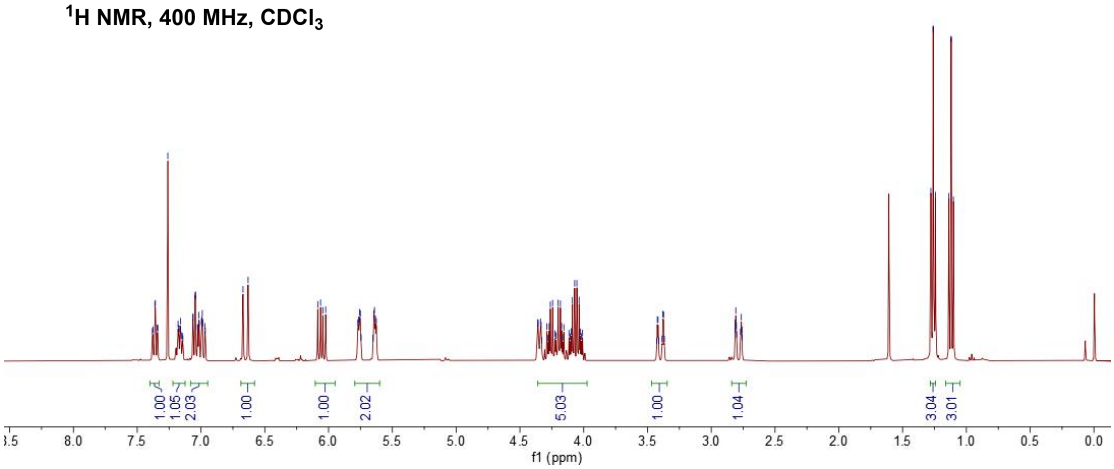
2o

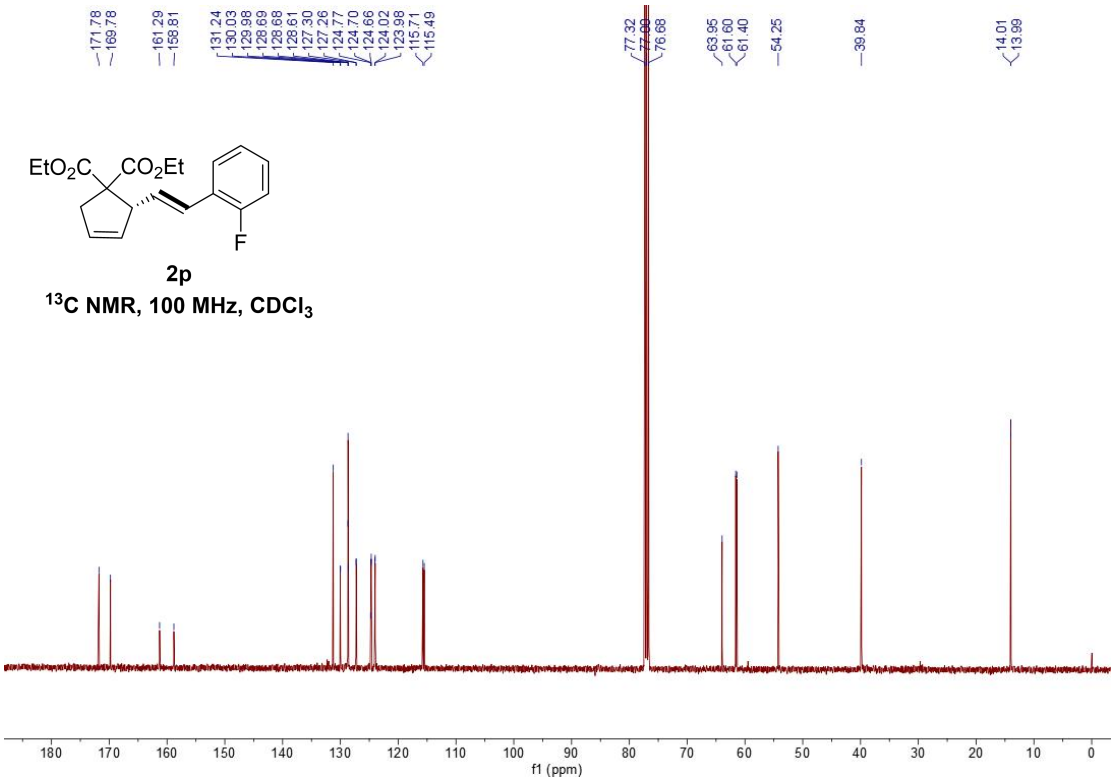
^{13}C NMR, 100 MHz, $CDCl_3$



2p

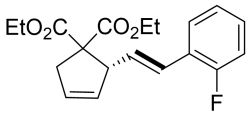
^{1}H NMR, 400 MHz, $CDCl_3$





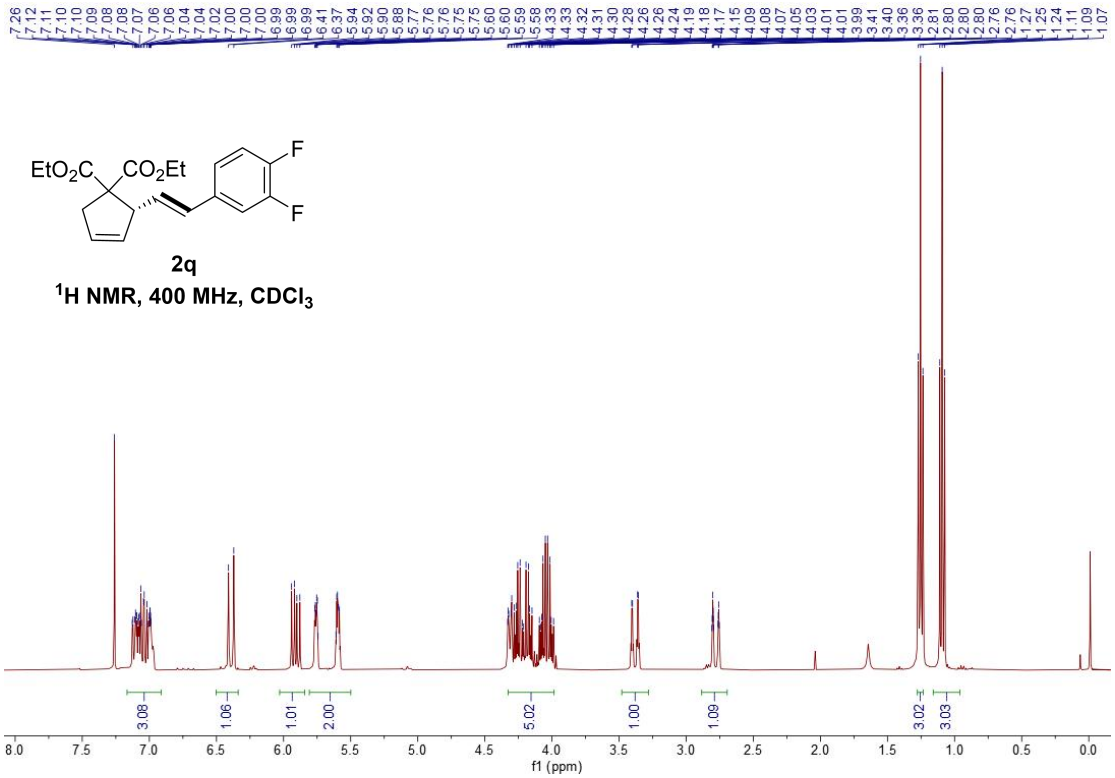
2p

^{13}C NMR, 100 MHz, $CDCl_3$



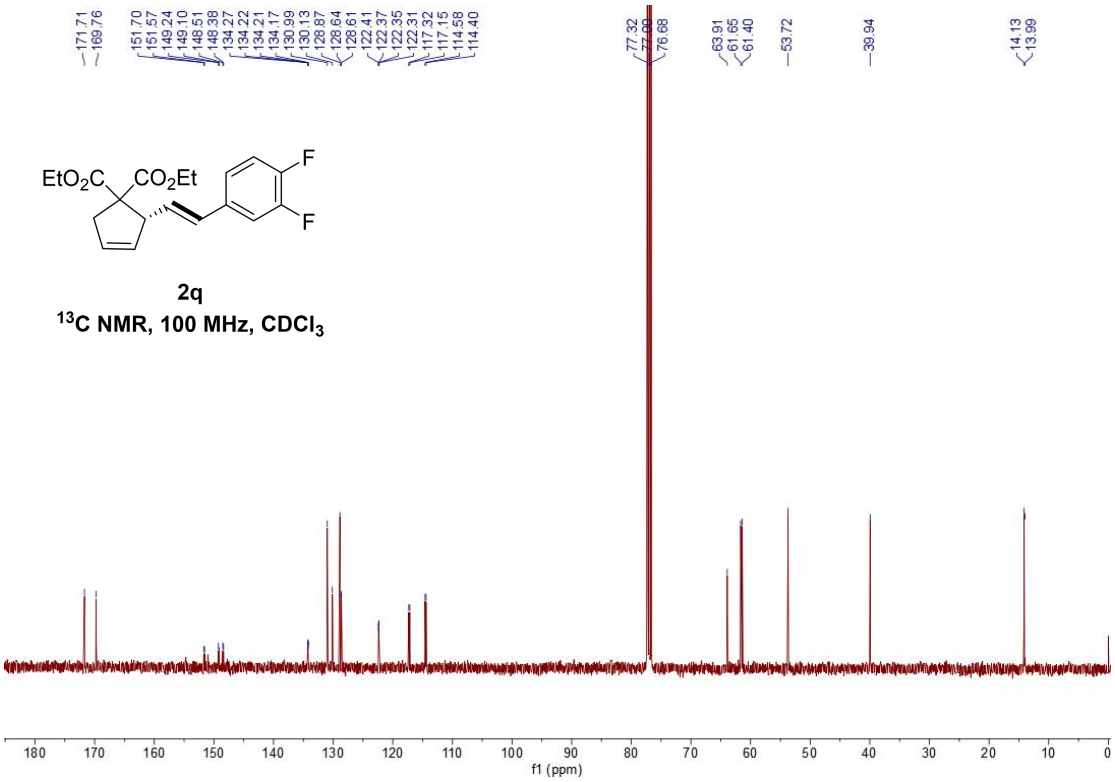
2p

^{19}F NMR, 376 MHz, $CDCl_3$



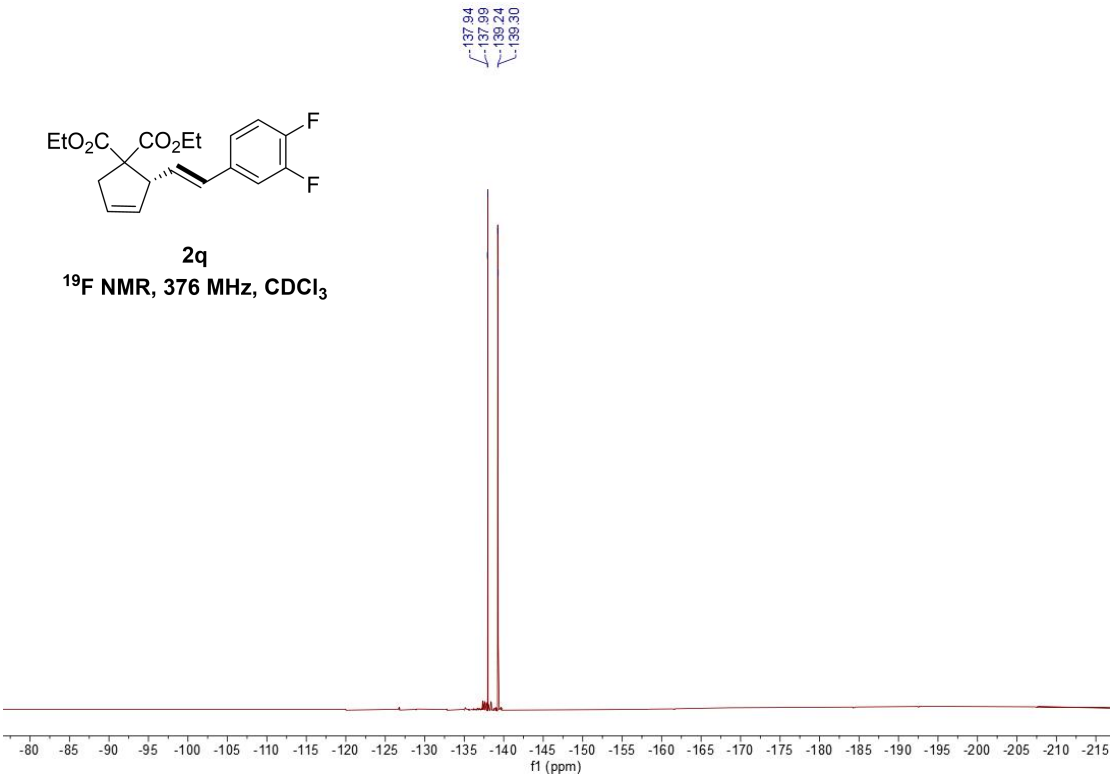
2q

^{1}H NMR, 400 MHz, $CDCl_3$



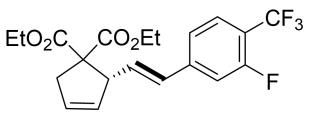
2q

^{13}C NMR, 100 MHz, $CDCl_3$



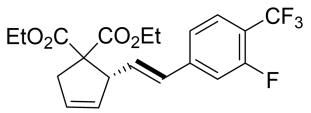
2q

^{19}F NMR, 376 MHz, $CDCl_3$



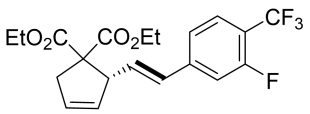
2r

^{1}H NMR, 400 MHz, $CDCl_3$



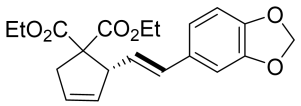
2r

^{13}C NMR, 100 MHz, $CDCl_3$



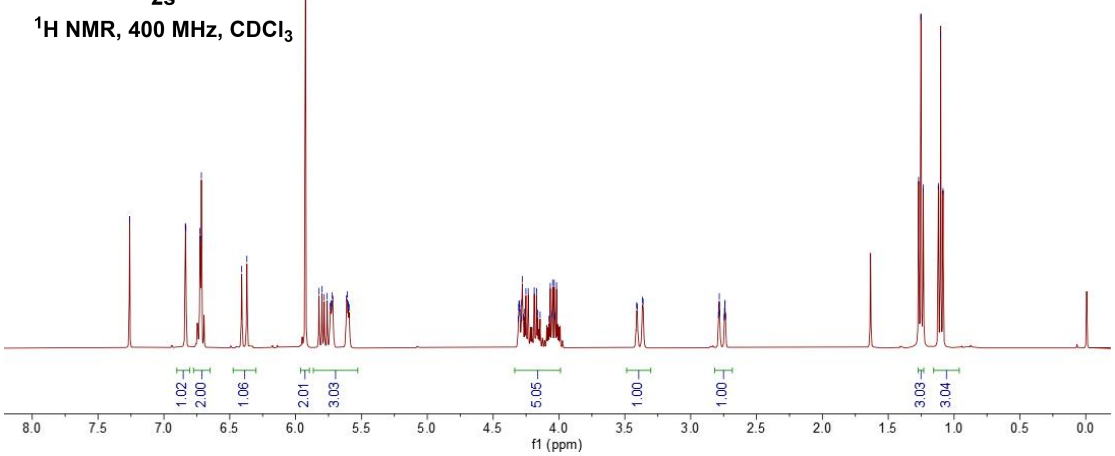
2r

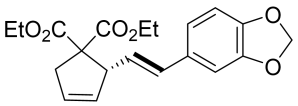
^{19}F NMR, 376 MHz, $CDCl_3$



2s

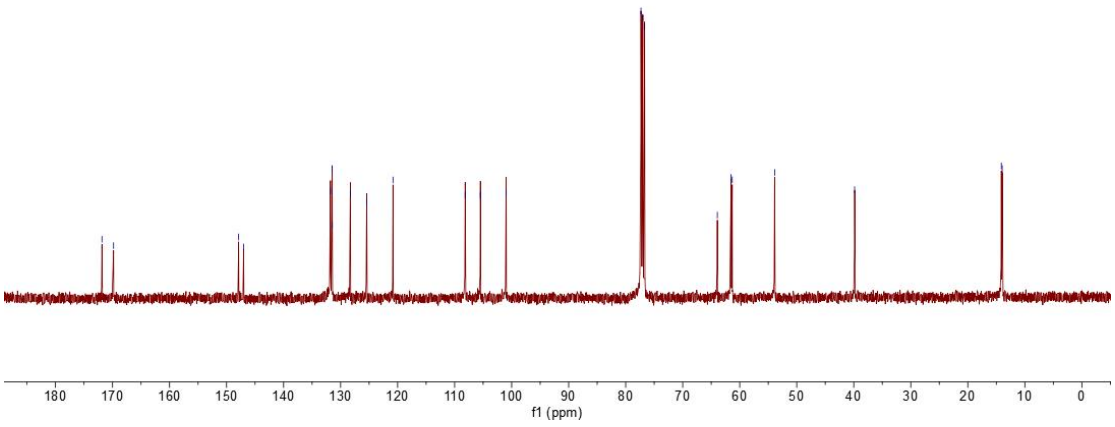
^{1}H NMR, 400 MHz, $CDCl_3$

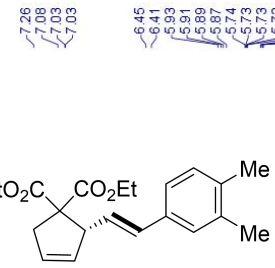




2s

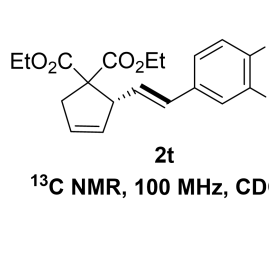
^{13}C NMR, 100 MHz, $CDCl_3$





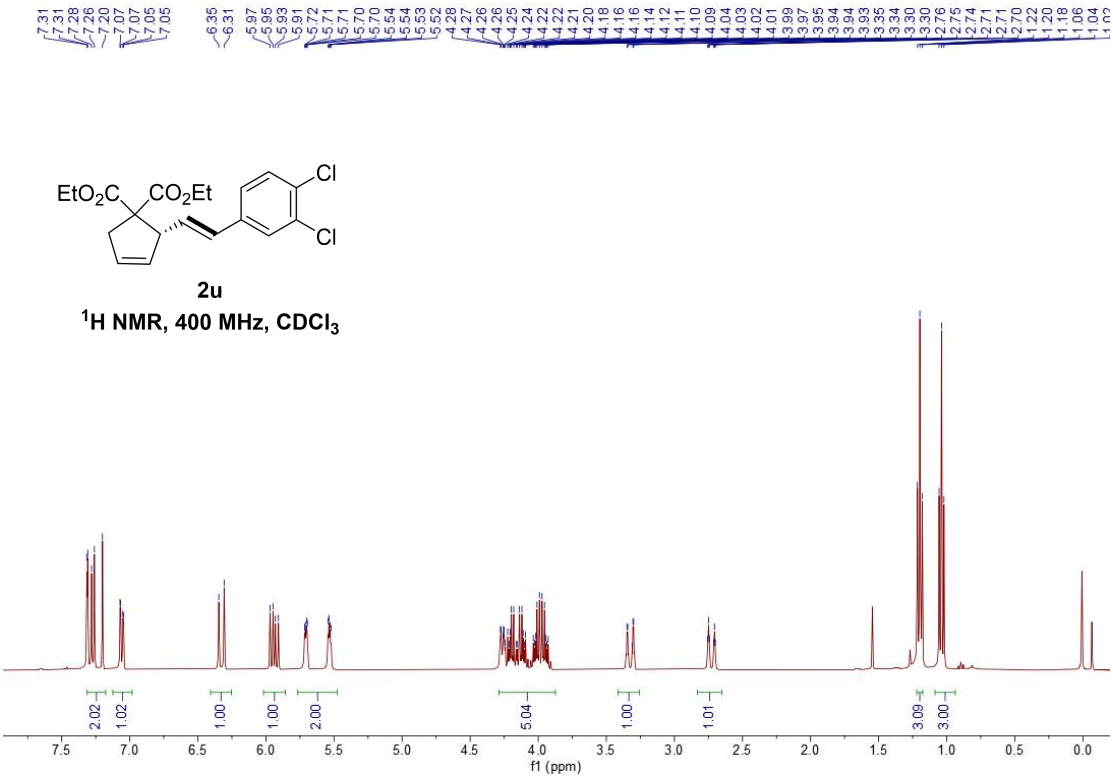
2t

^{1}H NMR, 400 MHz, $CDCl_3$



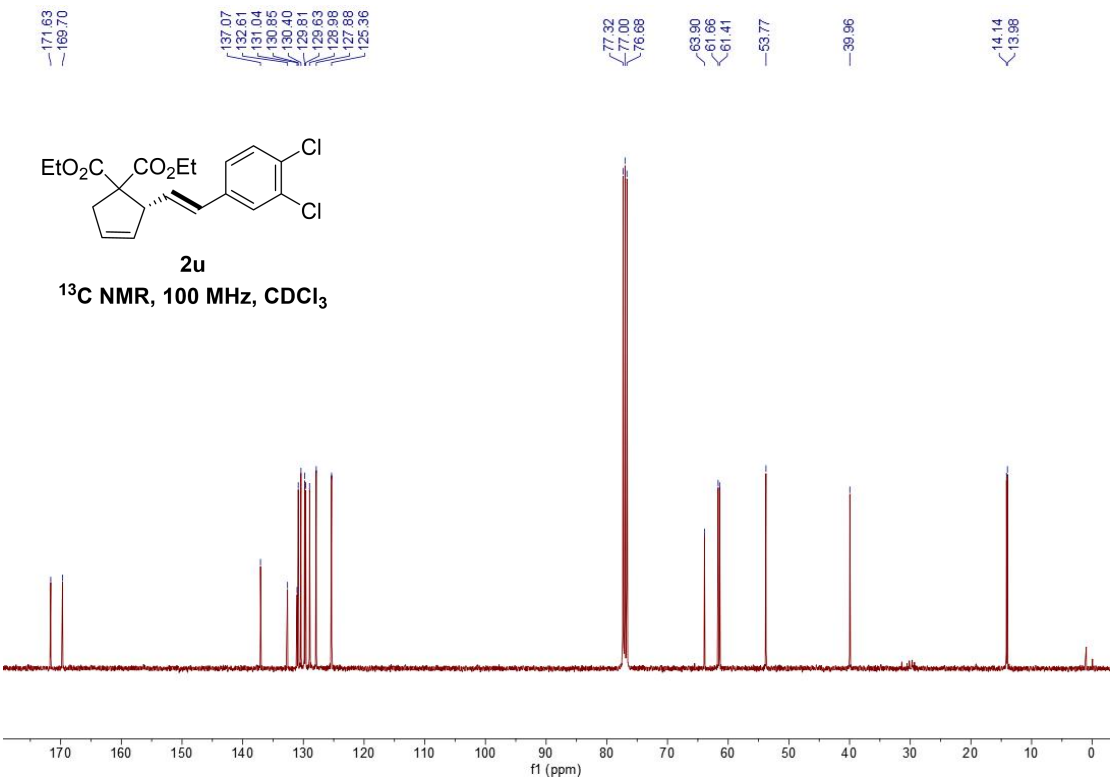
2t

^{13}C NMR, 100 MHz, $CDCl_3$



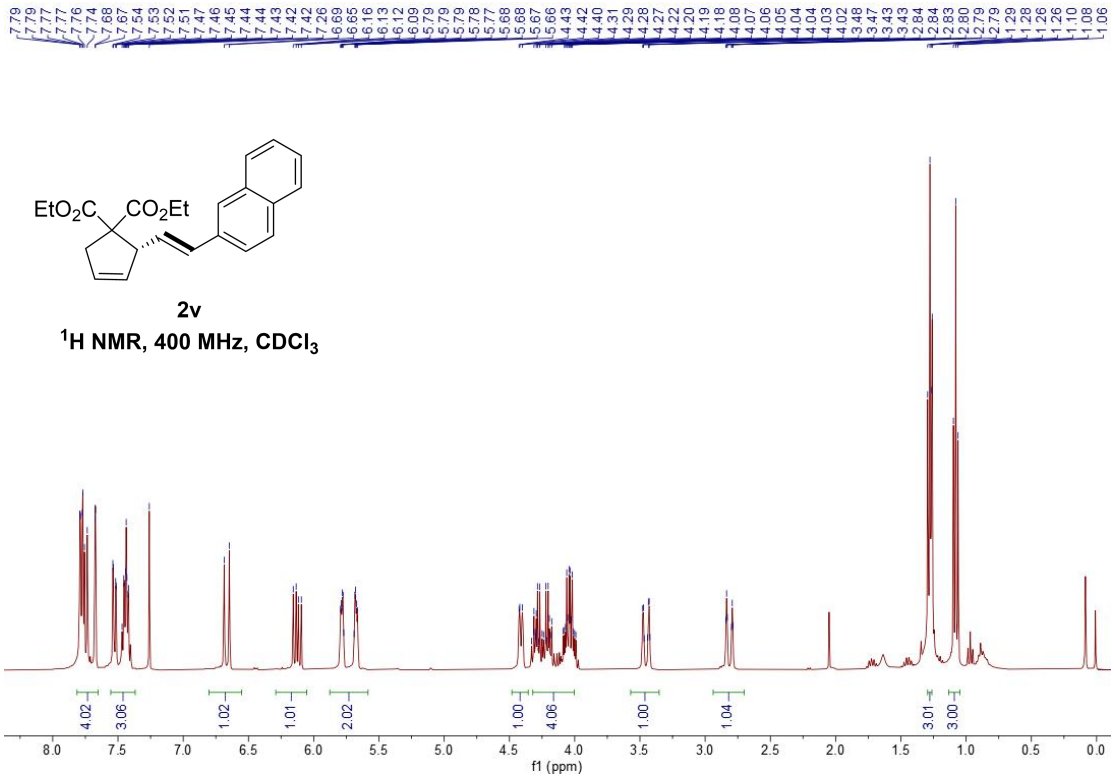
2u

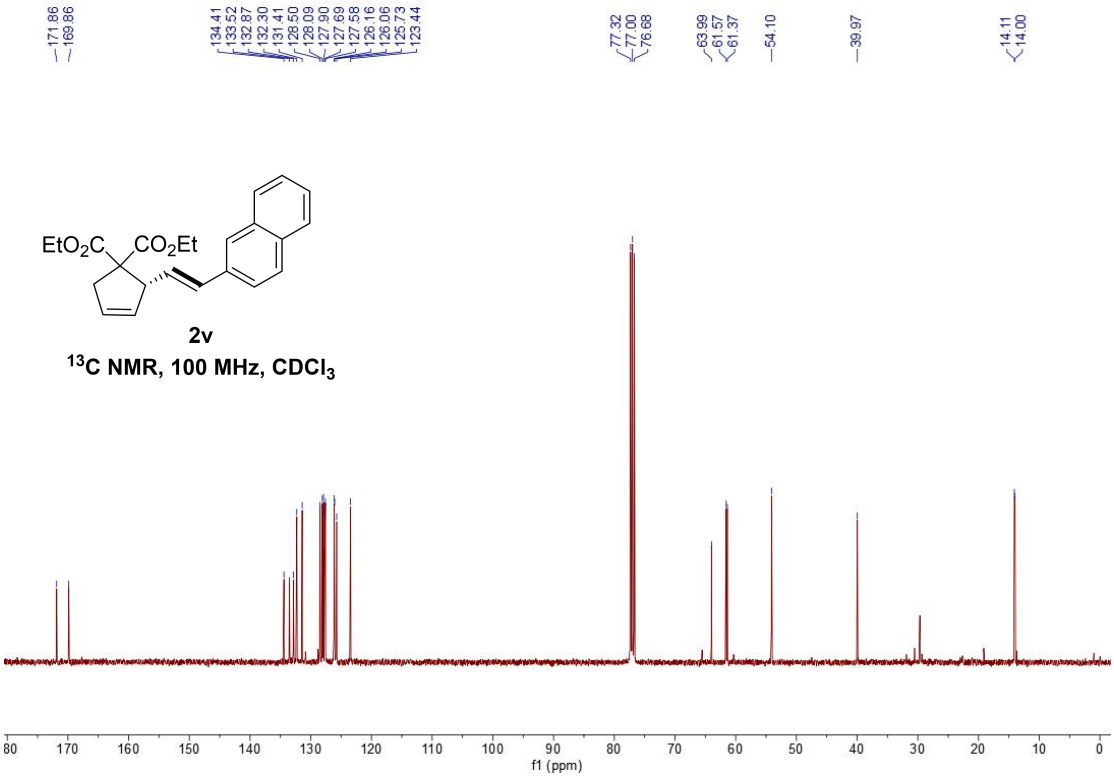
^{1}H NMR, 400 MHz, $CDCl_3$

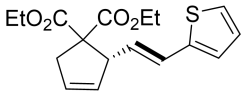


2u

^{13}C NMR, 100 MHz, $CDCl_3$

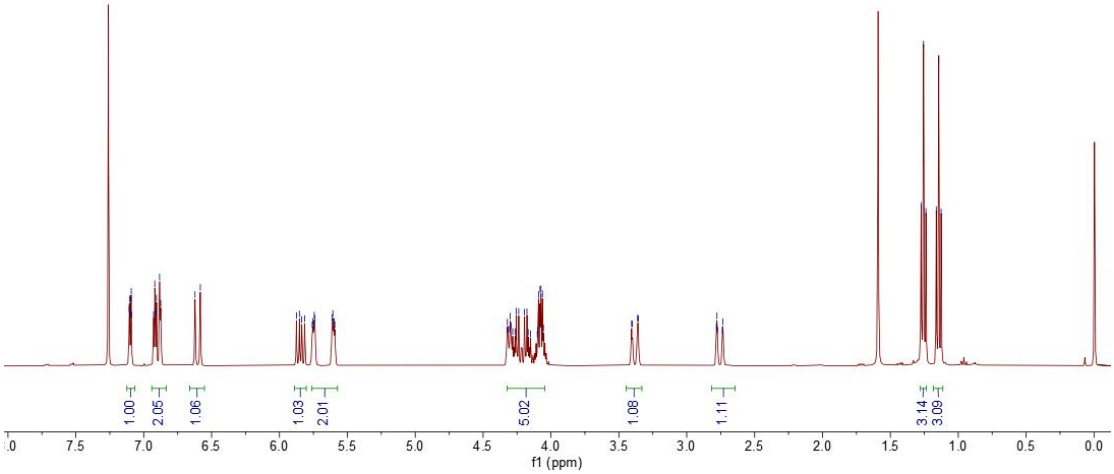

EtO2C
CO2Et
2v
1H NMR, 400 MHz, CDCl3
f1 (ppm)

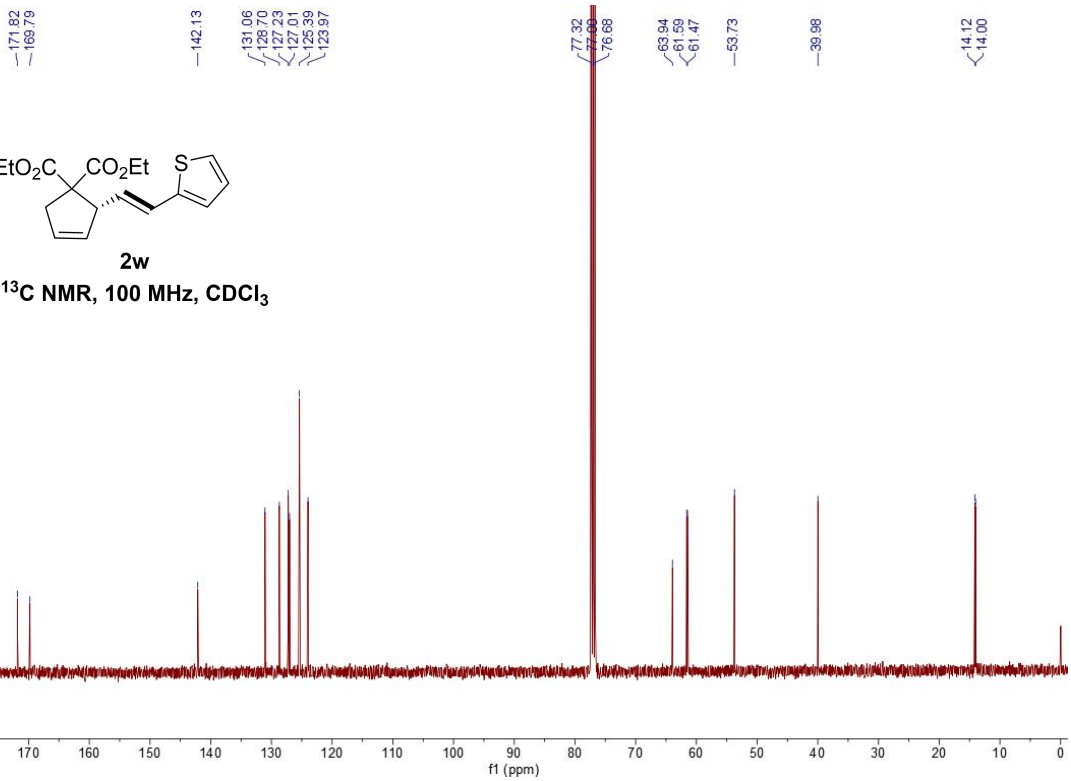

EtO2C
CO2Et
2v
13C NMR, 100 MHz, CDCl3
f1 (ppm)



2w

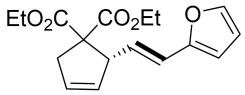
^{1}H NMR, 400 MHz, $CDCl_3$





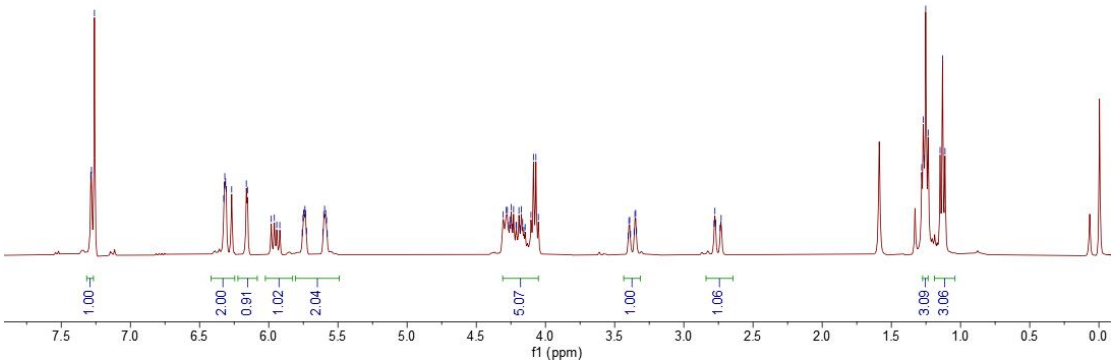
2w

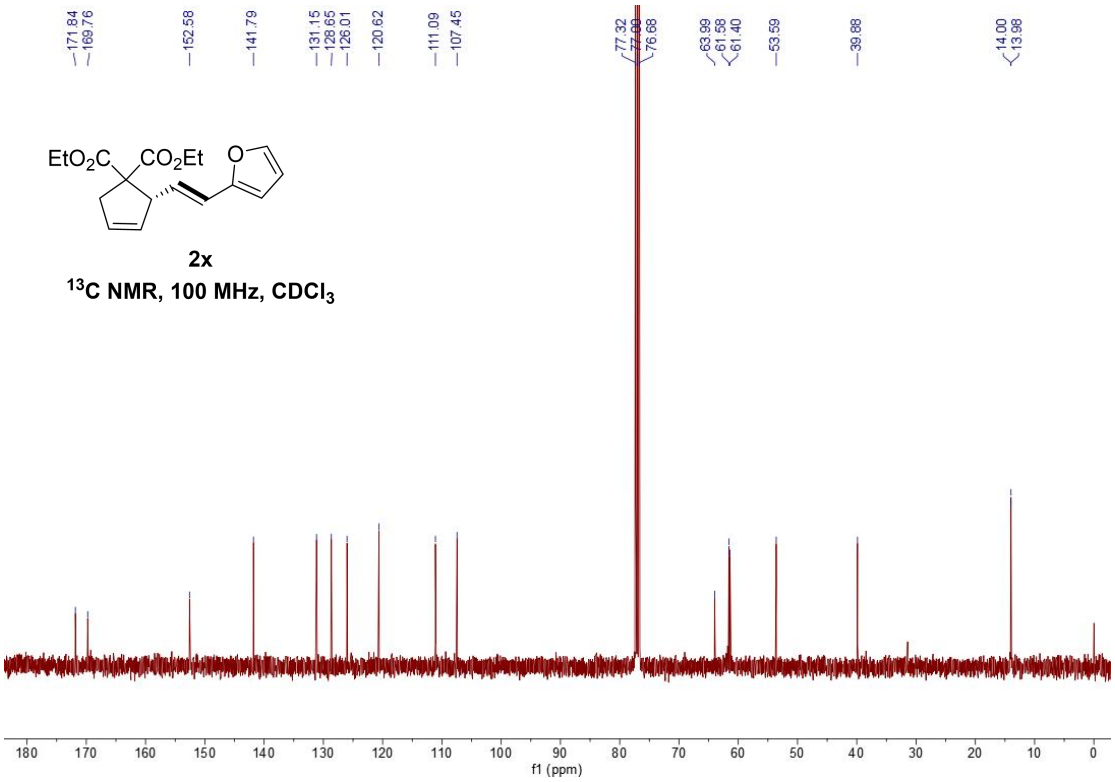
^{13}C NMR, 100 MHz, $CDCl_3$



2x

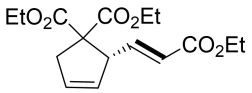
^{1}H NMR, 400 MHz, $CDCl_3$





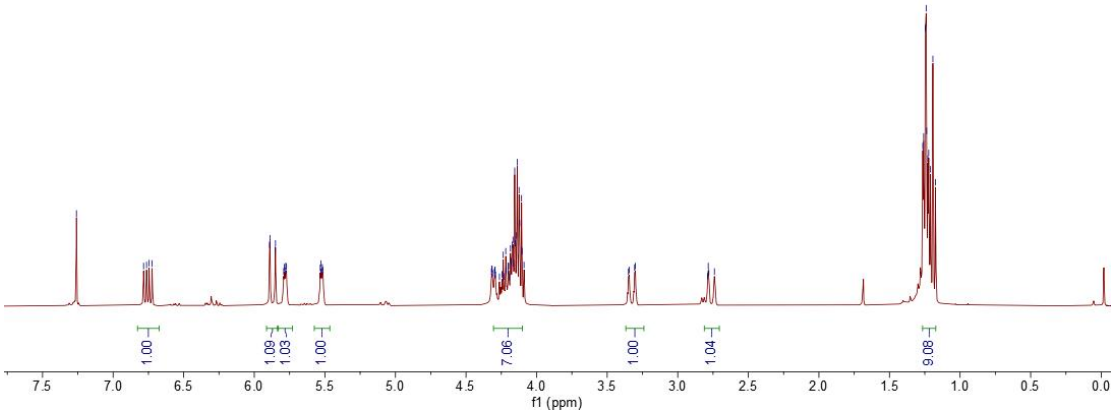
2x

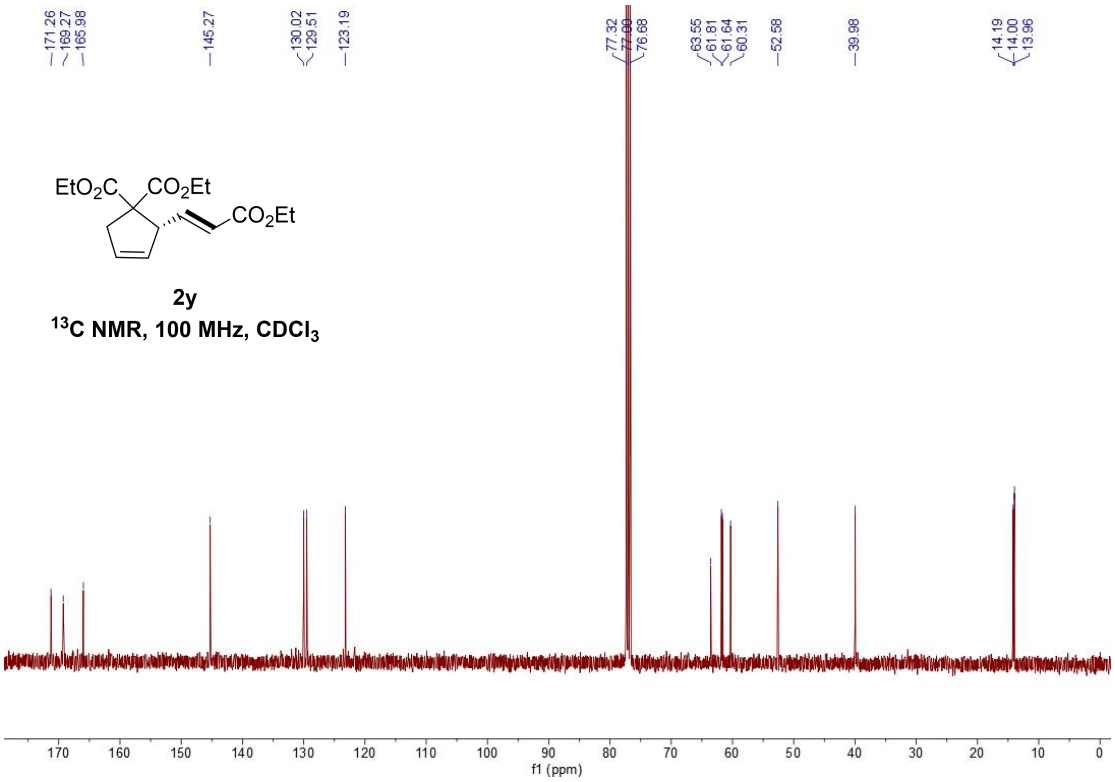
^{13}C NMR, 100 MHz, $CDCl_3$



2y

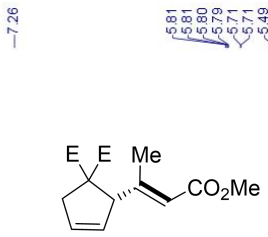
^{1}H NMR, 400 MHz, $CDCl_3$





2y

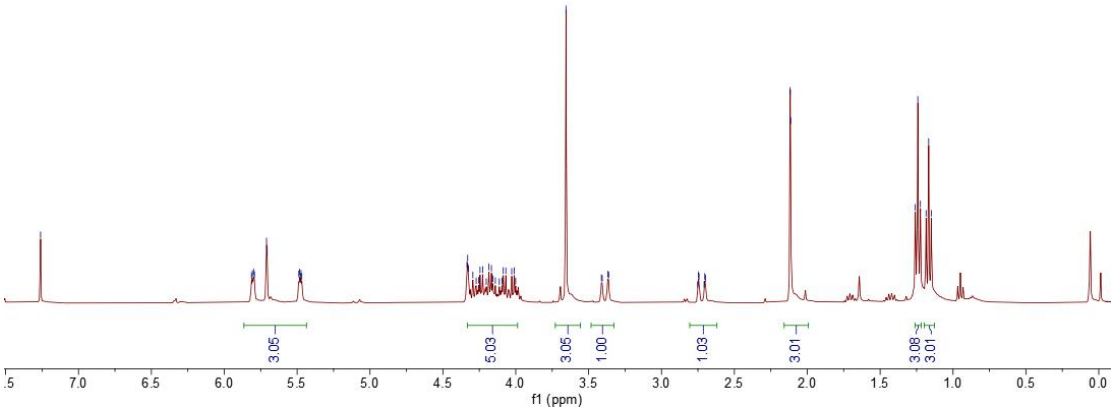
^{13}C NMR, 100 MHz, $CDCl_3$

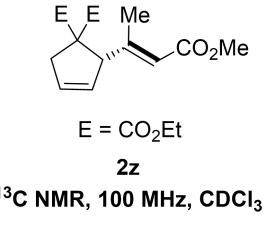


E = CO_2Et

2z

^{1}H NMR, 400 MHz, $CDCl_3$

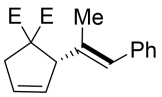




E = CO_2Et

2z

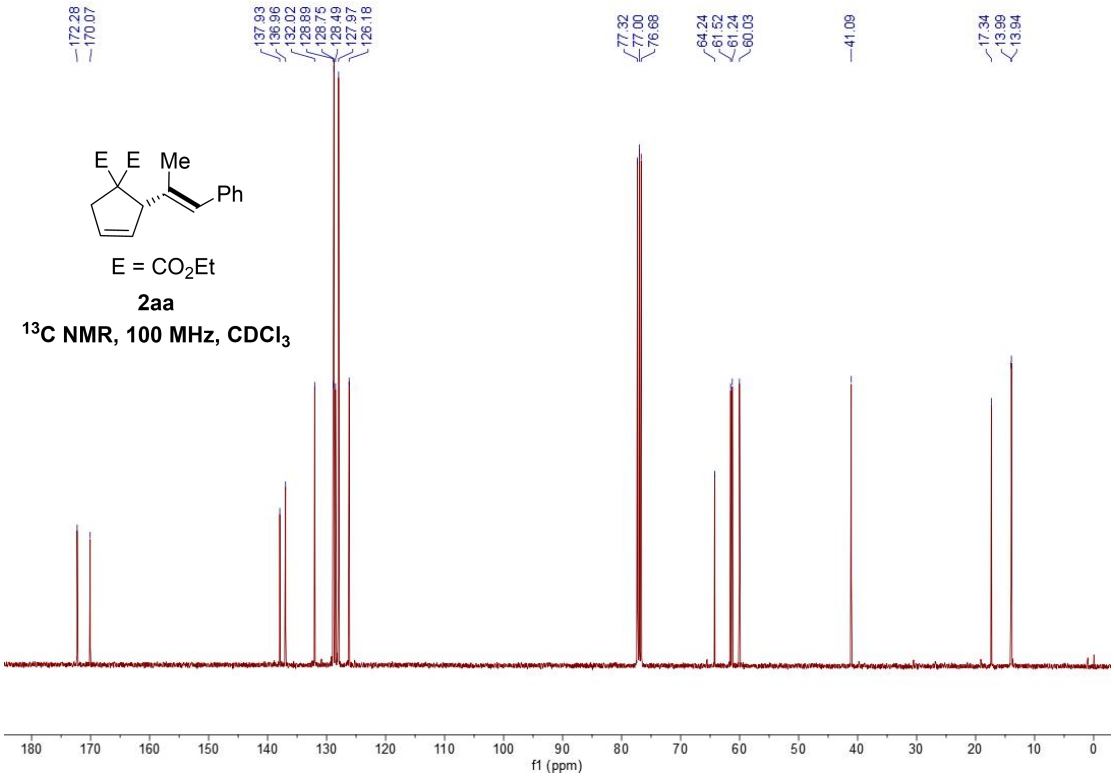
^{13}C NMR, 100 MHz, $CDCl_3$



E = CO_2Et

2aa

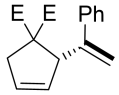
^{1}H NMR, 400 MHz, $CDCl_3$



E = CO_2Et

2aa

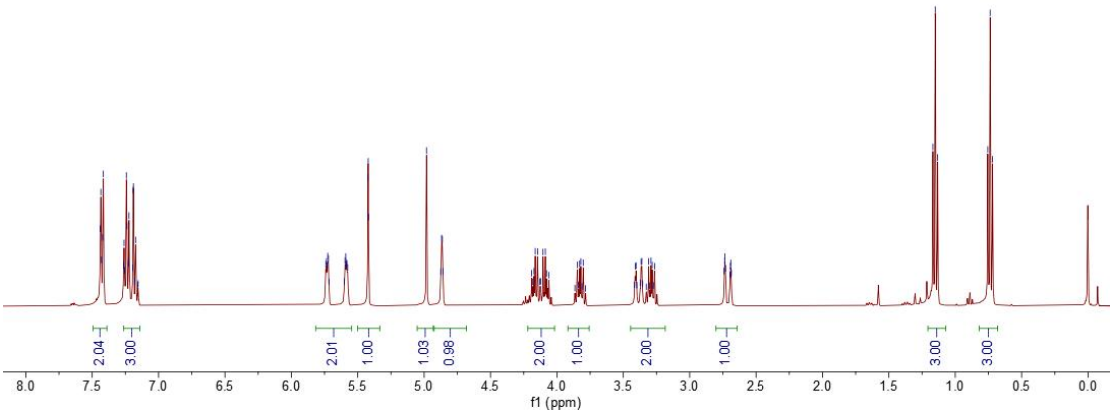
^{13}C NMR, 100 MHz, $CDCl_3$

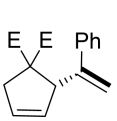


E = CO_2Et

2ab

^{1}H NMR, 400 MHz, $CDCl_3$

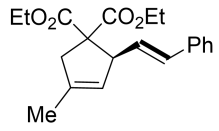




E = CO_2Et

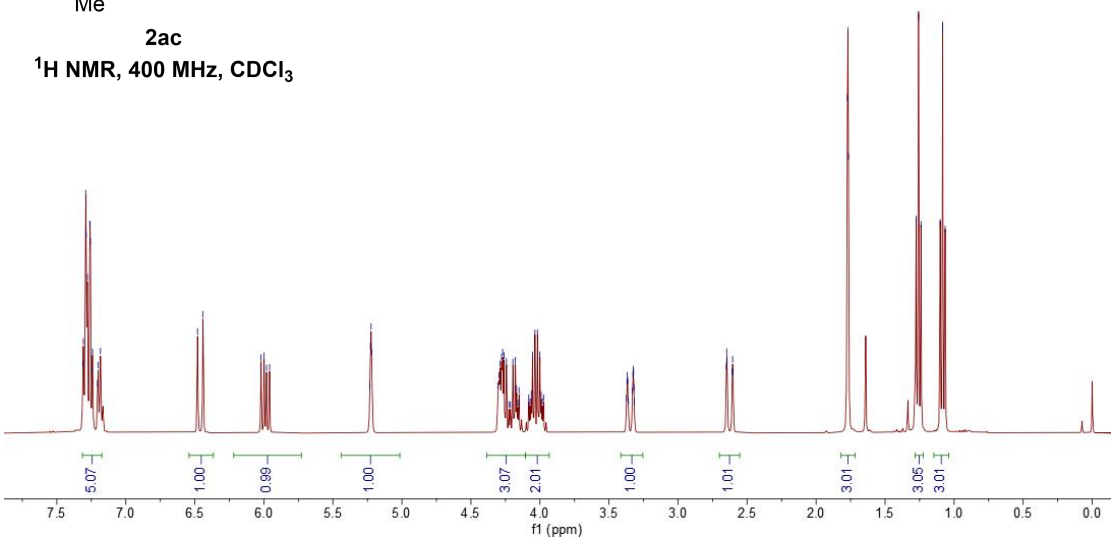
2ab

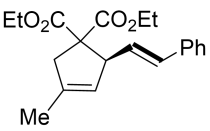
^{13}C NMR, 100 MHz, $CDCl_3$



2ac

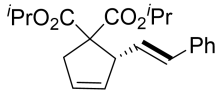
^{1}H NMR, 400 MHz, $CDCl_3$





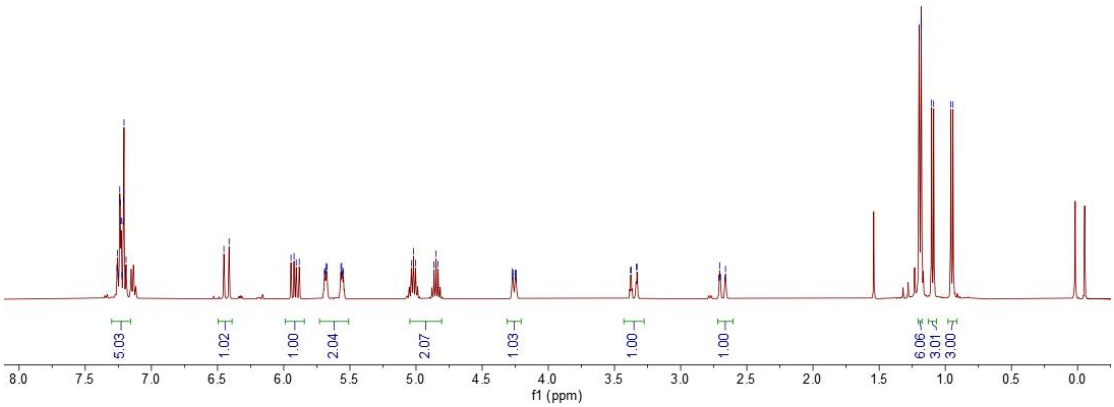
2ac

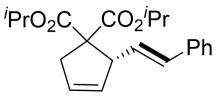
^{13}C NMR, 100 MHz, $CDCl_3$



2ae

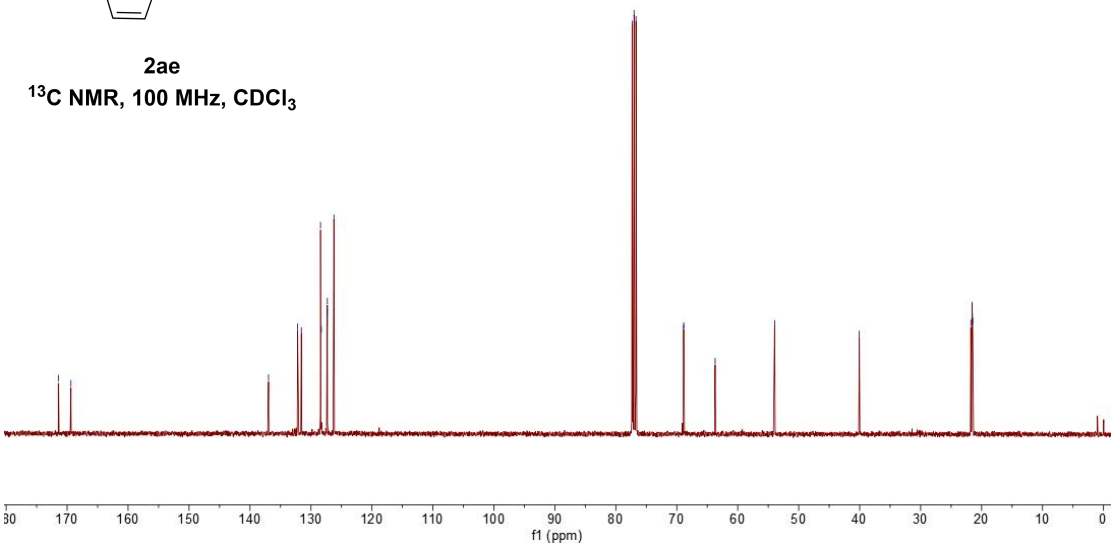
^{1}H NMR, 400 MHz, $CDCl_3$

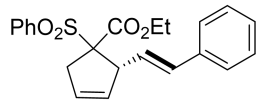




2ae

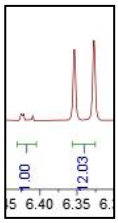
^{13}C NMR, 100 MHz, $CDCl_3$



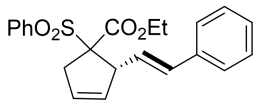


2af

^{1}H NMR, 600MHz, $CDCl_3$

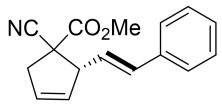


dr = 12:1



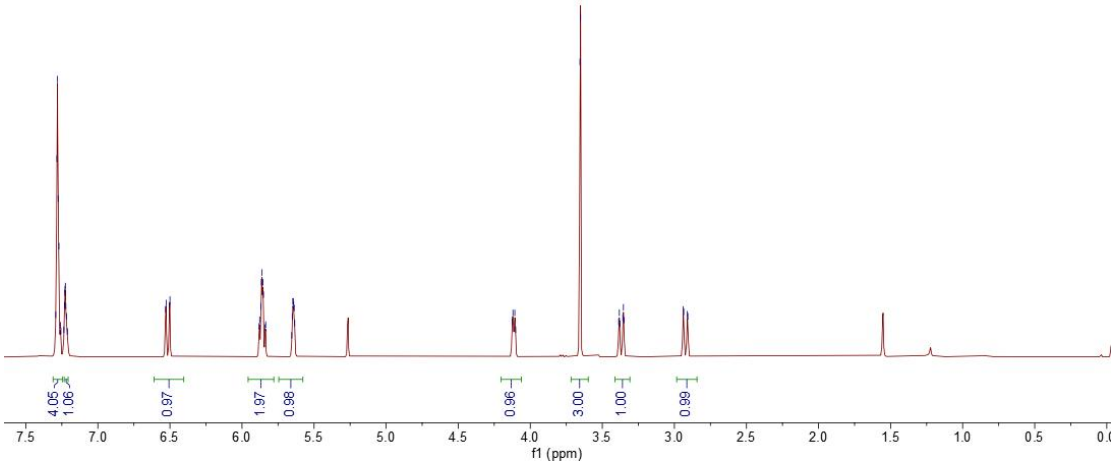
2af

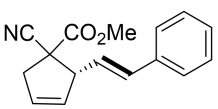
^{13}C NMR, 151MHz, $CDCl_3$



2ag

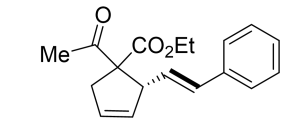
^{1}H NMR, 600MHz, $CDCl_3$





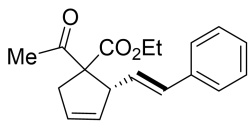
2ag

^{13}C NMR, 151MHz, $CDCl_3$



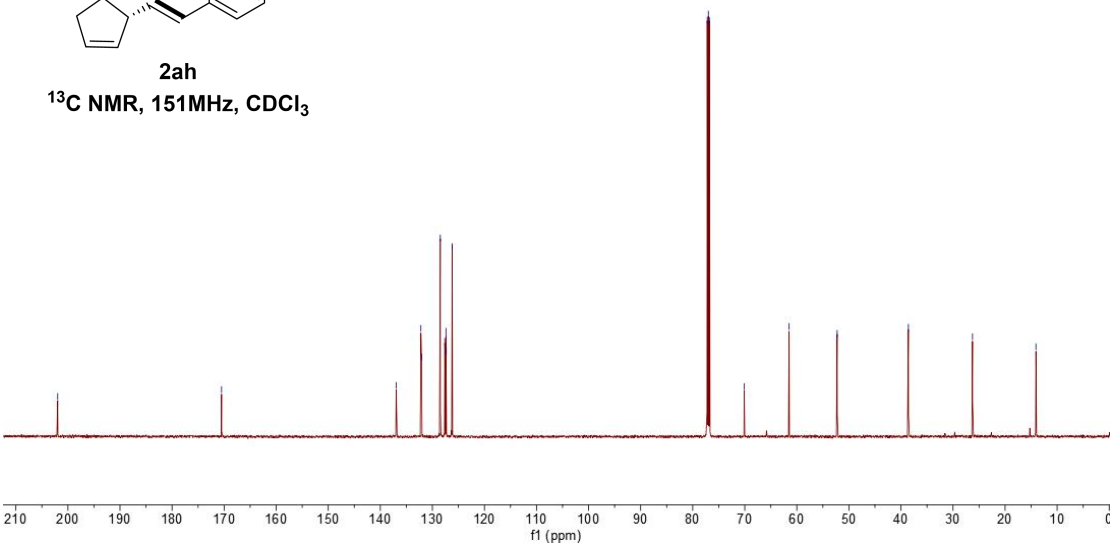
2ah

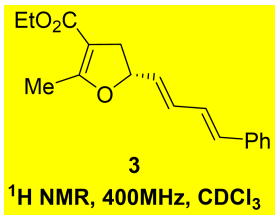
^{1}H NMR, 600MHz, $CDCl_3$



2ah

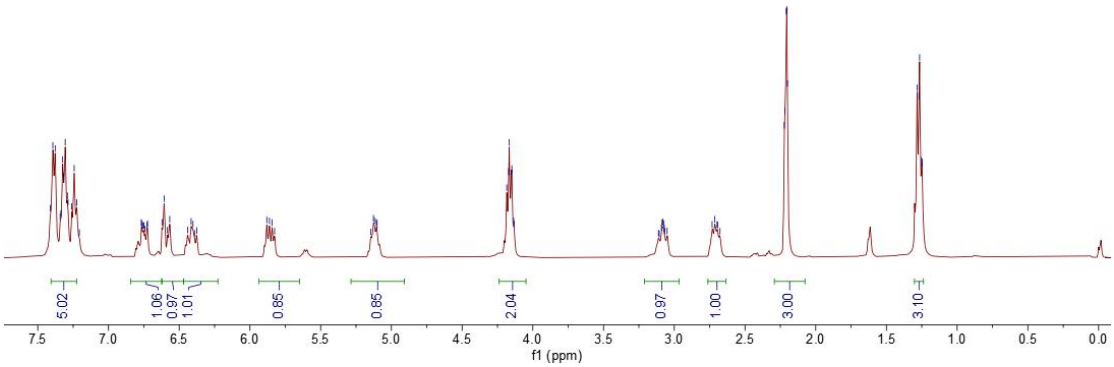
^{13}C NMR, 151MHz, $CDCl_3$

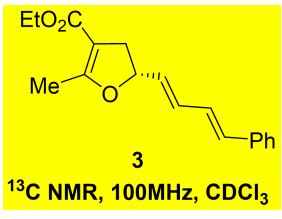




3

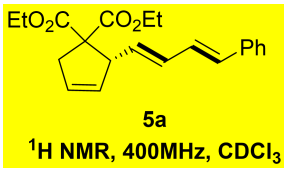
^{1}H NMR, 400MHz, $CDCl_3$





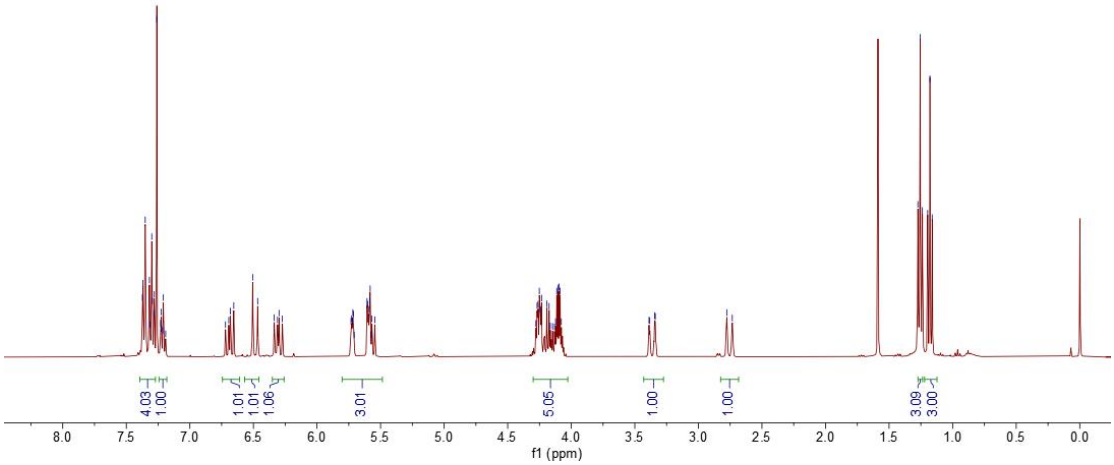
3

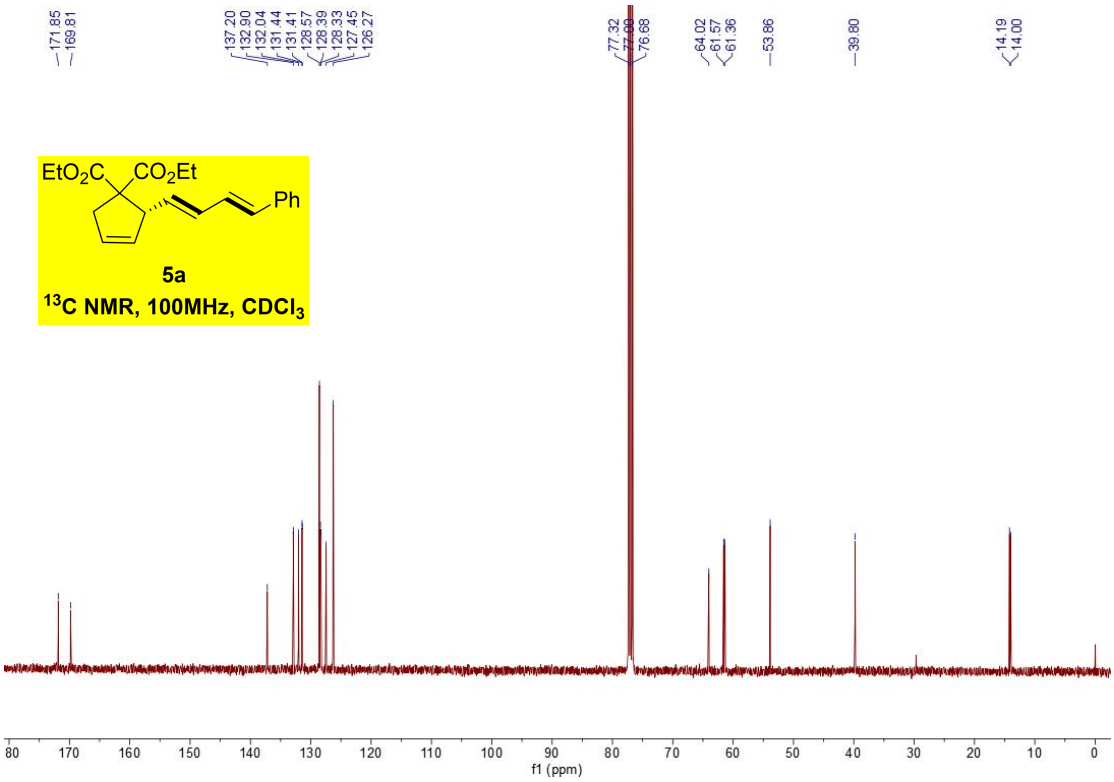
^{13}C NMR, 100MHz, $CDCl_3$



5a

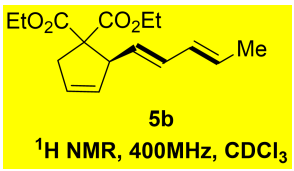
^{1}H NMR, 400MHz, $CDCl_3$





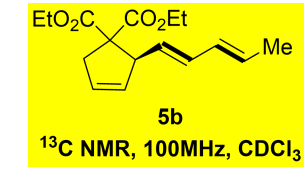
5a

^{13}C NMR, 100MHz, $CDCl_3$



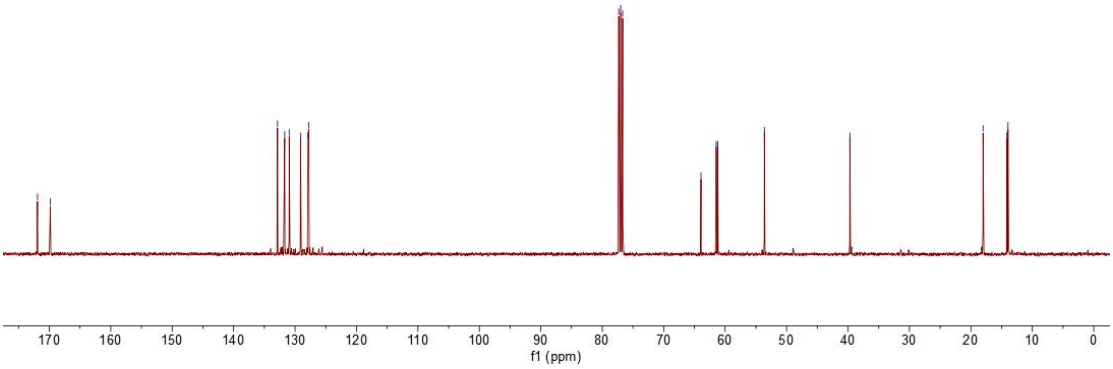
5b

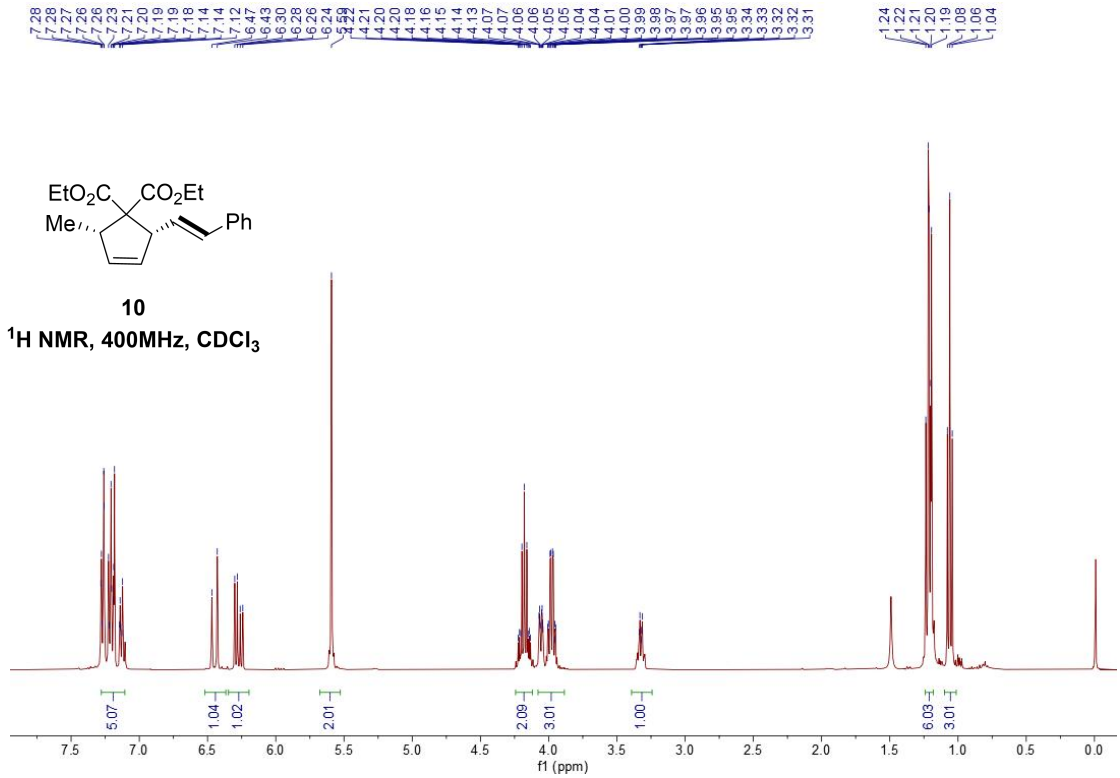
^{1}H NMR, 400MHz, $CDCl_3$

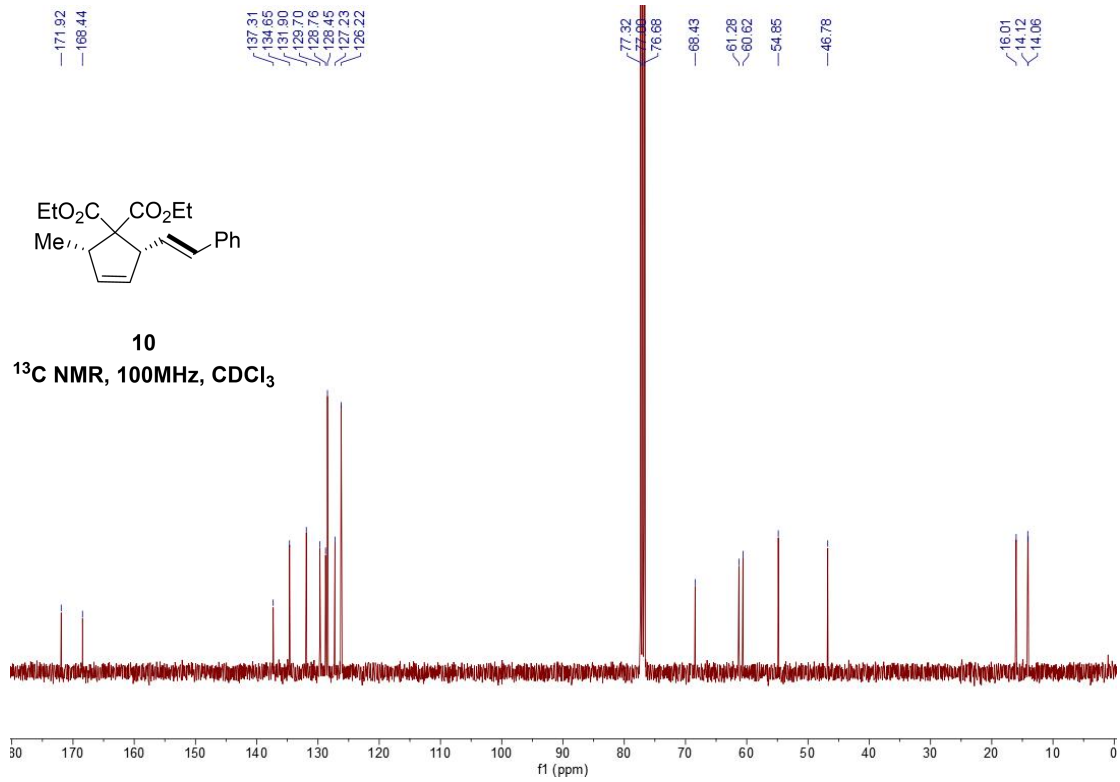


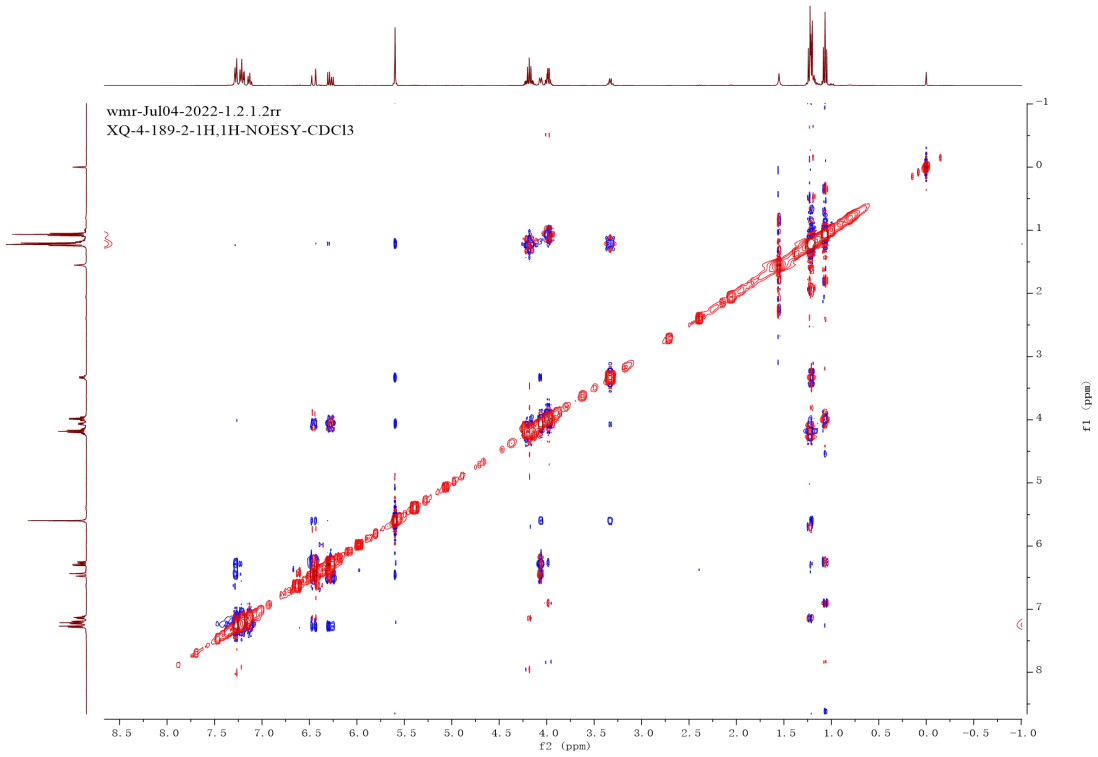
5b

^{13}C NMR, 100MHz, $CDCl_3$



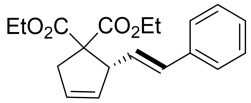

EtO2C
CO2Et
Me
Ph
10
1H NMR, 400MHz, CDCl3
f1 (ppm)


EtO2C
CO2Et
Me
Ph
10
13C NMR, 100MHz, CDCl3
f1 (ppm)

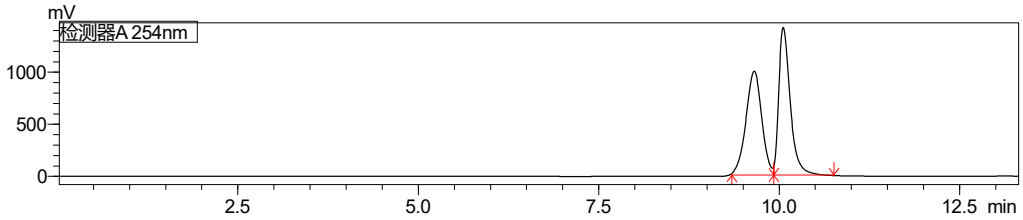

wmr-Jul04-2022-1.2.1.2rr
XQ-4-189-2-1H,1H-NOESY-CDCl3
f2 (ppm)
f1 (ppm)

6. HPLC analysis of 2, 3 and 5

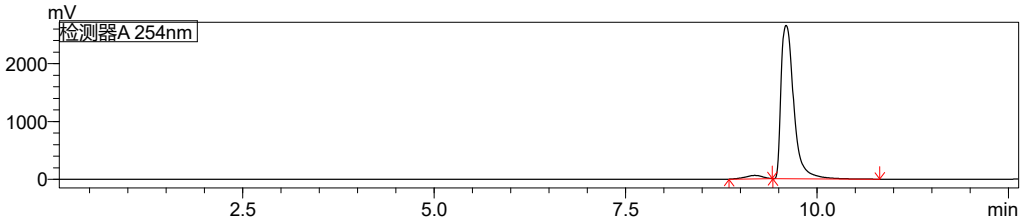
HPLC conditions: Chiralpak AD-H, 10% ^{i}PrOH/Hx eluent, 0.5 mL/min, 254 nm



2a

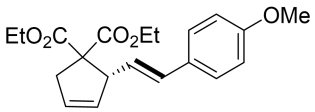


Peak#	Ret. Time	Height	Area%
1	9.653	996275	49.379
2	10.056	1417278	50.621

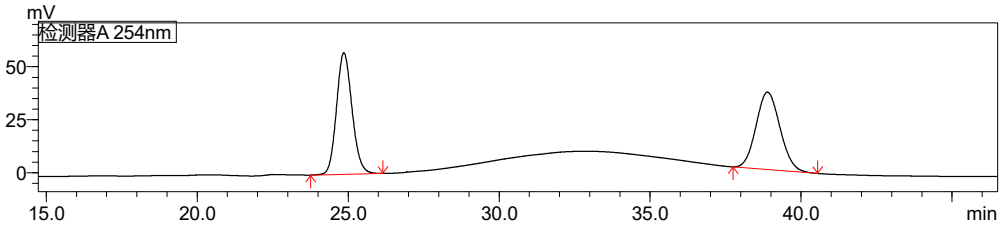


Peak#	Ret. Time	Height	Area%
1	9.188	59111	2.945
2	9.595	2652711	97.055

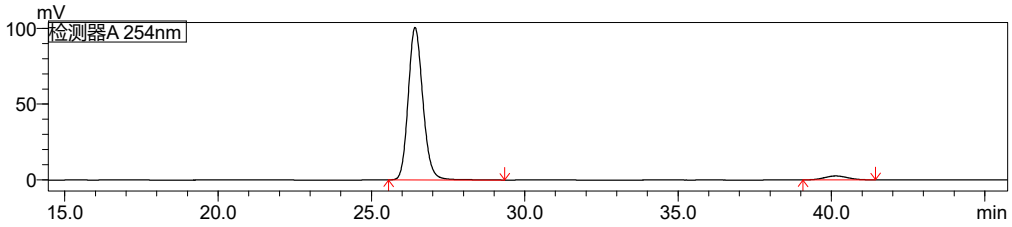
HPLC conditions: Chiralpak OJ-H, 5% ^{i}PrOH/Hx eluent, 0.5 mL/min, 254 nm



2b

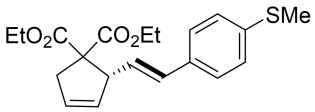


Peak#	Ret. Time	Height	Area%
1	24.856	57370	50.465
2	38.886	36532	49.535



Peak#	Ret. Time	Height	Area%
1	26.420	100756	96.051
2	40.140	2593	3.949

HPLC conditions: Chiralpak OJ-H, 10% ^{i}PrOH/Hx eluent, 0.5 mL/min, 254 nm



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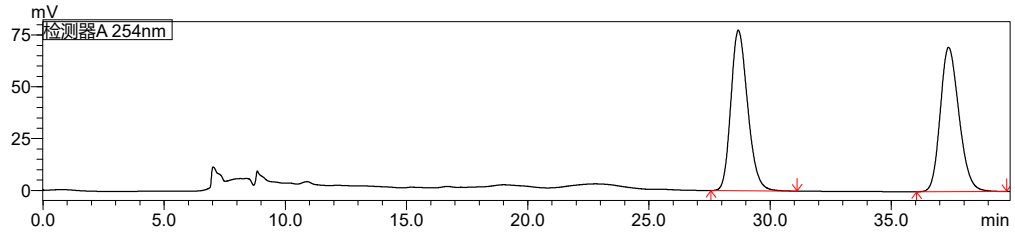
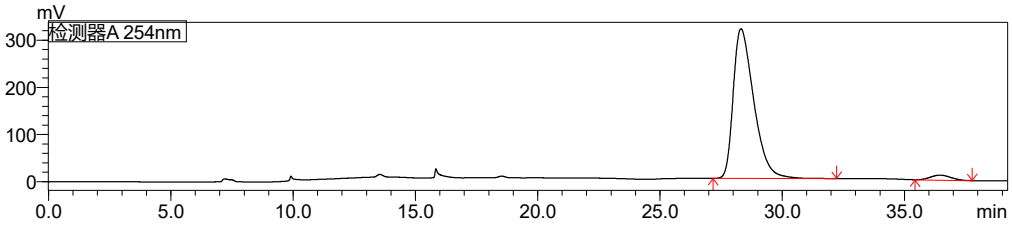
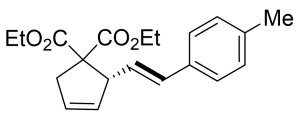


Peak#	Ret. Time	Height	Area%
1	28.684	77538	49.915
2	37.355	69618	50.085

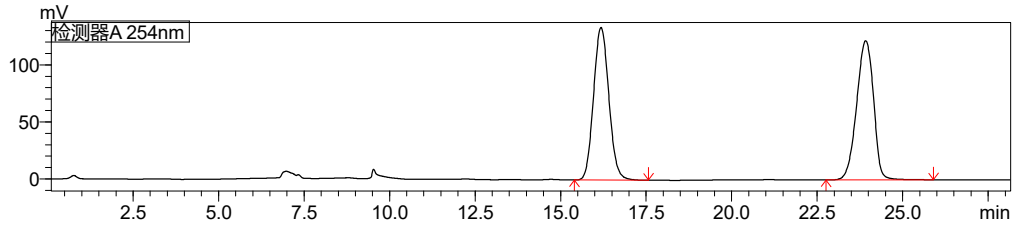


Peak#	Ret. Time	Height	Area%
1	28.318	317282	96.784
2	36.449	10623	3.216

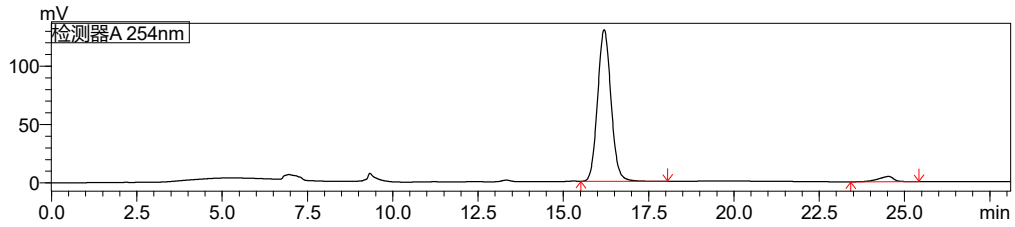
HPLC conditions: Chiralpak OJ-H, 5% ^{i}PrOH/Hx eluent, 0.5 mL/min, 254 nm



2d

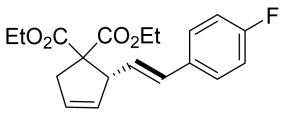


Peak#	Ret. Time	Height	Area%
1	16.183	133841	49.828
2	23.917	121997	50.172



Peak#	Ret. Time	Height	Area%
1	16.195	129927	96.666
2	24.528	4283	3.334

HPLC conditions: Chiralpak AD-H, 5% ^{i}PrOH/Hx eluent, 0.5 mL/min, 254 nm



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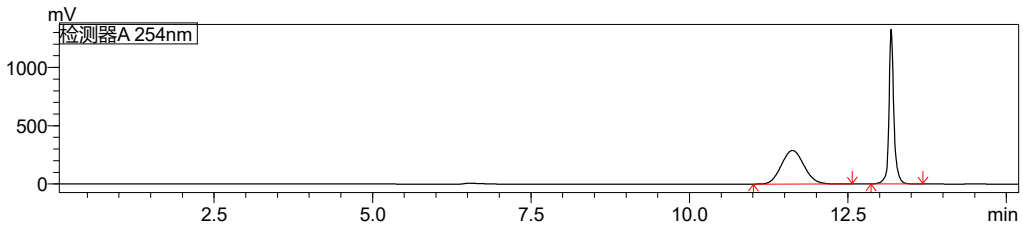
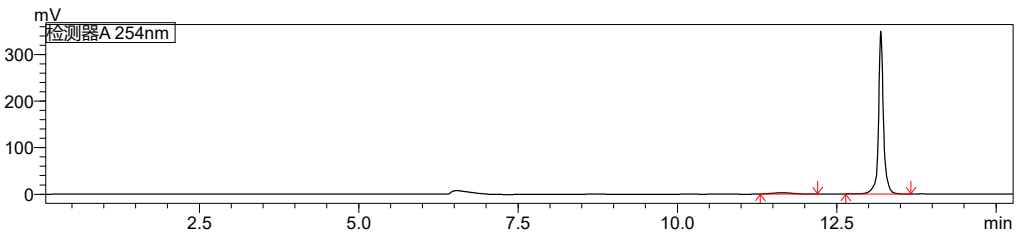


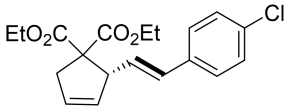
Peak#	Ret. Time	Height	Area%
1	11.625	288326	50.084
2	13.182	1326410	49.916



Peak#	Ret. Time	Height	Area%
1	11.648	2697	3.178

2	13.192	349425	96.822

HPLC conditions: Chiralpak AD-H, 5% ^{i}PrOH/Hx eluent, 0.5 mL/min, 254 nm



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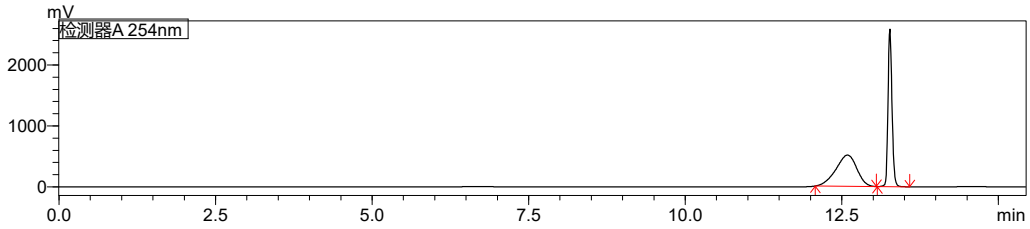
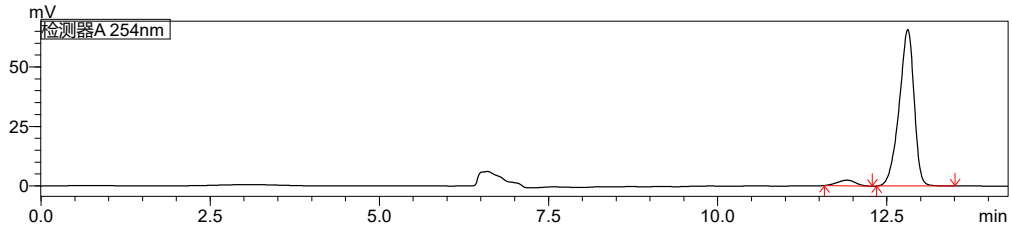
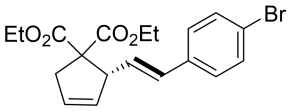


Peak#	Ret. Time	Height	Area%
1	12.591	512632	50.772
2	13.266	2584996	49.228

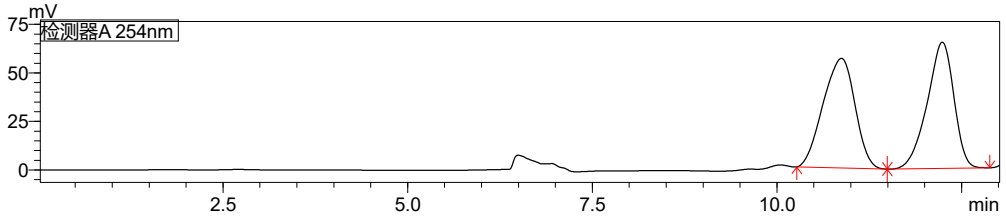


Peak#	Ret. Time	Height	Area%
1	11.910	2379	4.239
2	12.810	65792	95.761

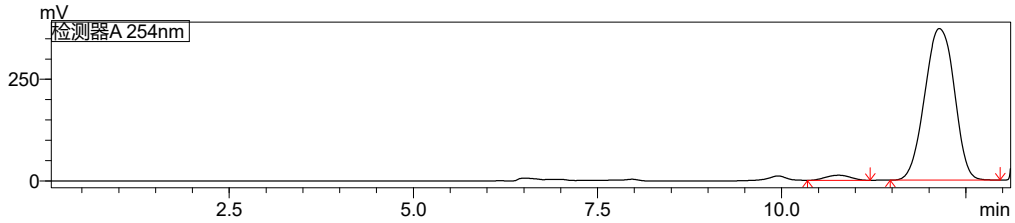
HPLC conditions: Chiralpak AD-H, 5% ^{i}PrOH/Hx eluent, 0.5 mL/min, 254 nm



2g

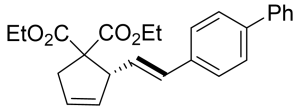


Peak#	Ret. Time	Height	Area%
1	10.873	56478	50.941
2	12.238	65057	49.059

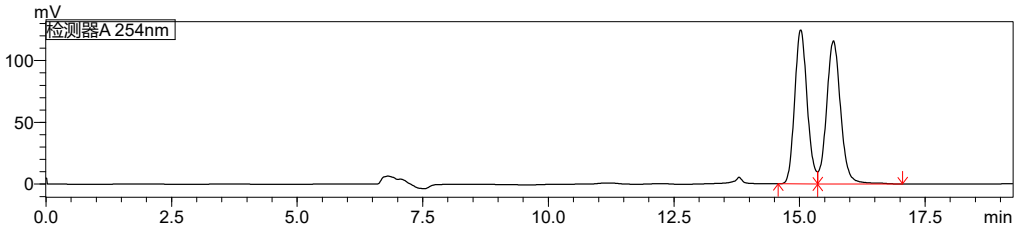


Peak#	Ret. Time	Height	Area%
1	10.772	12506	2.724
2	12.141	373080	97.276

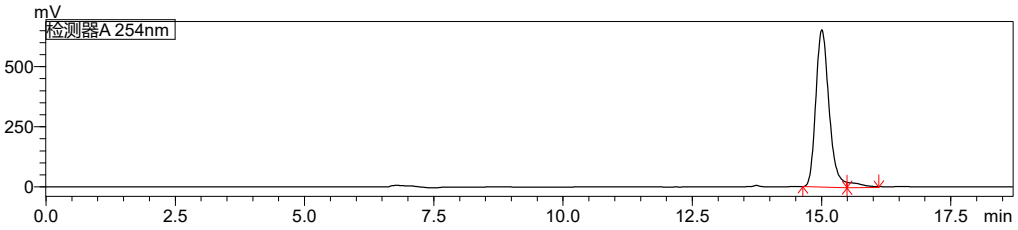
HPLC conditions: Chiralpak AD-H, 5% ^{i}PrOH/Hx eluent, 0.5 mL/min, 254 nm



2h

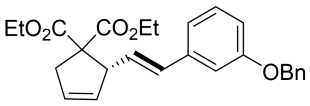


Peak#	Ret. Time	Height	Area%
1	15.023	124591	49.009
2	15.674	115787	50.991

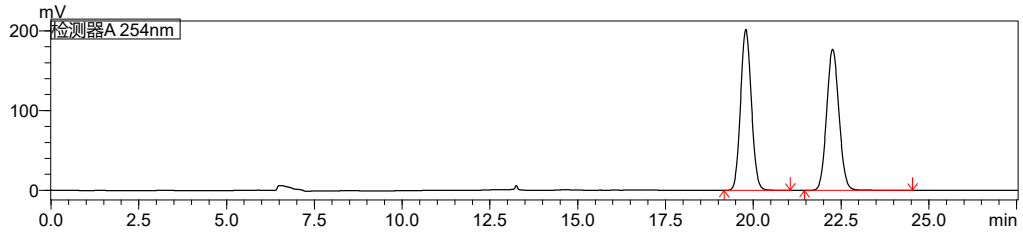


Peak#	Ret. Time	Height	Area%
1	15.005	654059	96.560
2	15.513	21372	3.440

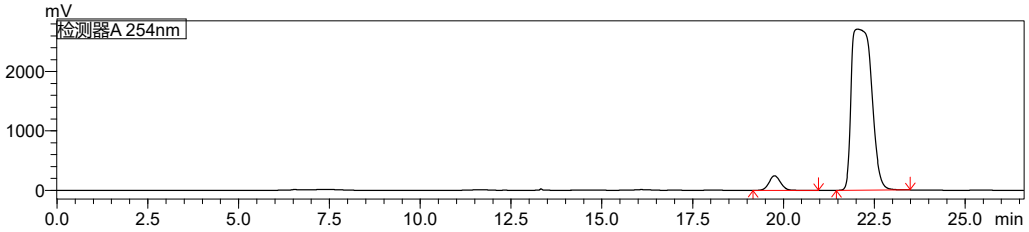
HPLC conditions: Chiralpak AD-H, 5% ^{i}PrOH/Hx eluent, 0.5 mL/min, 254 nm



2i

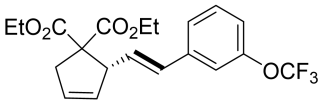


Peak#	Ret. Time	Height	Area%
1	19.787	202023	49.851
2	22.259	176985	50.149

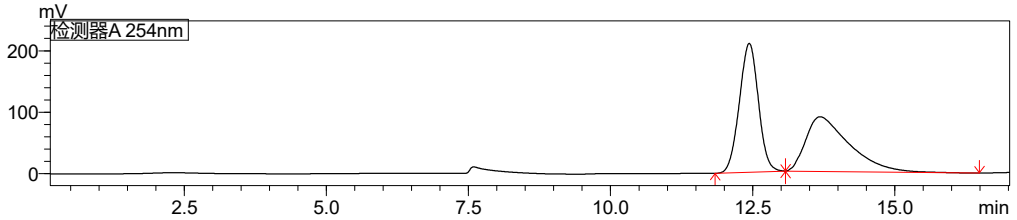


Peak#	Ret. Time	Height	Area%
1	19.756	245208	4.883
2	22.039	2709247	95.117

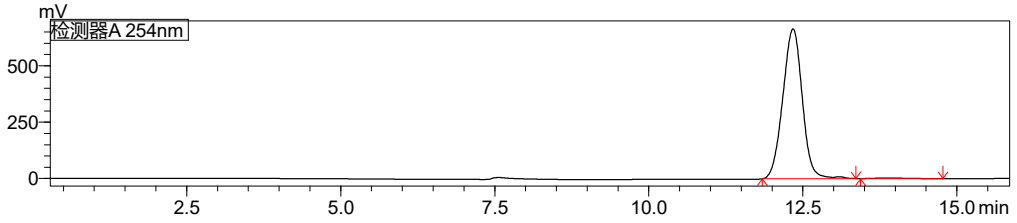
HPLC conditions: Chiralpak OJ-H, 2% ^{i}PrOH/Hx eluent, 0.5 mL/min, 254 nm



2j



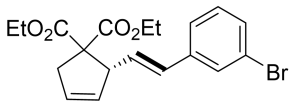
Peak#	Ret. Time	Height	Area%
1	12.439	209572	50.863
2	13.685	88898	49.137



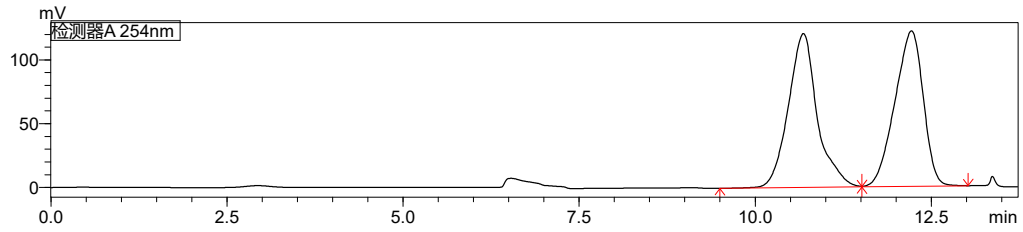
Peak#	Ret. Time	Height	Area%
1	12.341	665403	99.284

2	13.865	2685	0.716

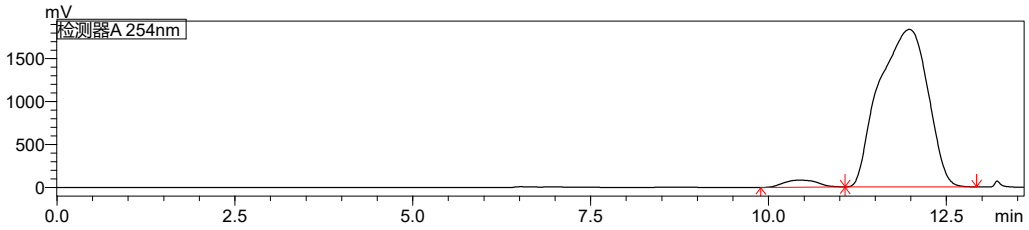
HPLC conditions: Chiralpak AD-H, 5% ^{i}PrOH/Hx eluent, 0.5 mL/min, 254 nm



2k

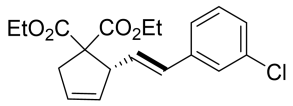


Peak#	Ret. Time	Height	Area%
1	10.684	120732	50.258
2	12.219	121956	49.742

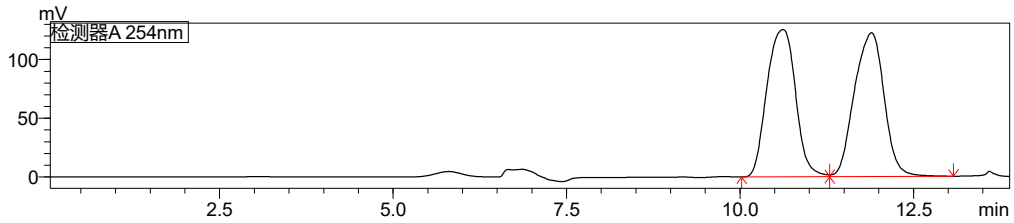


Peak#	Ret. Time	Height	Area%
1	10.433	82094	3.024
2	11.978	1834594	96.976

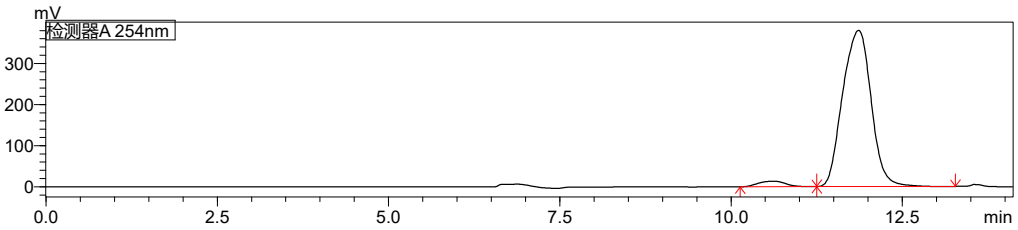
HPLC conditions: Chiralpak AD-H, 5% ^{i}PrOH/Hx eluent, 0.5 mL/min, 254 nm



2l

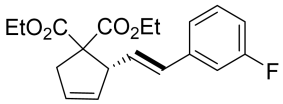


Peak#	Ret. Time	Height	Area%
1	10.617	125546	49.744
2	11.894	122410	50.256

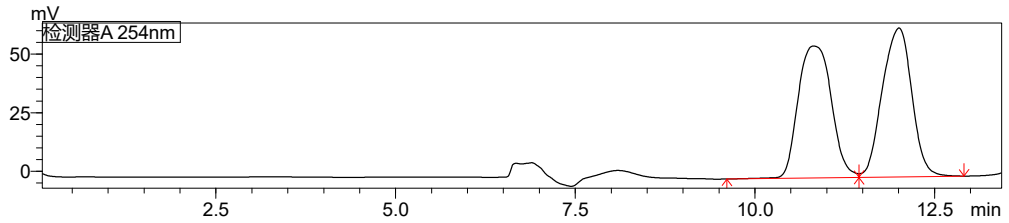


Peak#	Ret. Time	Height	Area%
1	10.617	13362	3.266
2	11.862	380089	96.734

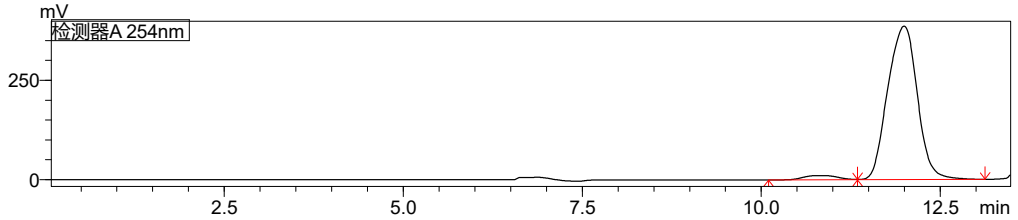
HPLC conditions: Chiralpak AD-H, 5% ^{i}PrOH/Hx eluent, 0.5 mL/min, 254 nm



2m

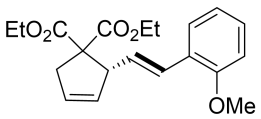


Peak#	Ret. Time	Height	Area%
1	10.817	56335	49.948
2	12.004	63649	50.052



Peak#	Ret. Time	Height	Area%
1	10.808	10602	3.002
2	11.996	386400	96.998

HPLC conditions: Chiralpak AD-H, 5% ^{i}PrOH/Hx eluent, 0.5 mL/min, 254 nm



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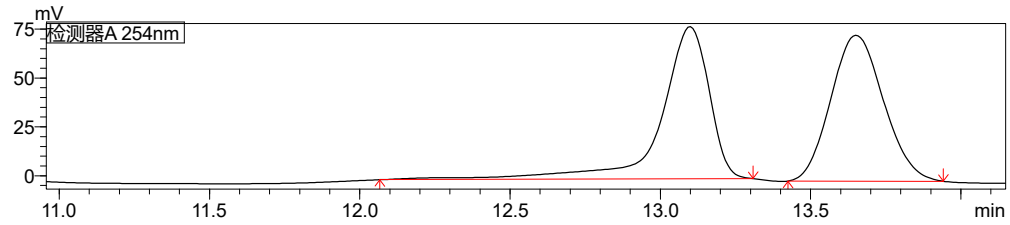
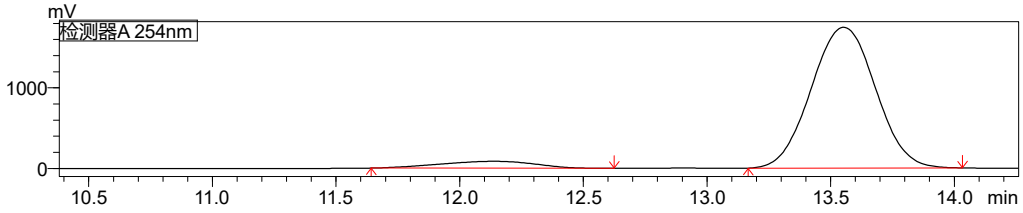
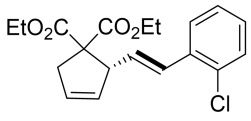


Peak#	Ret. Time	Height	Area%
1	13.098	79008	50.017
2	13.651	75219	49.983

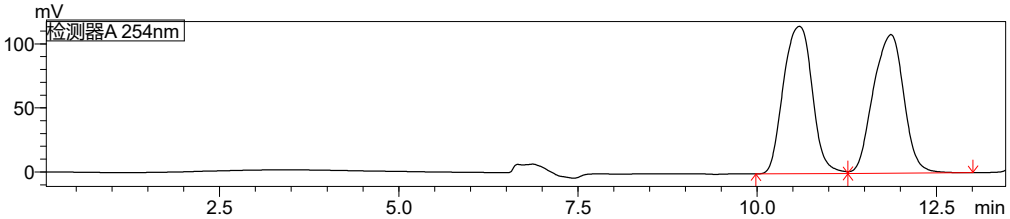


Peak#	Ret. Time	Height	Area%
1	12.137	83680	6.383
2	13.552	1751324	93.617

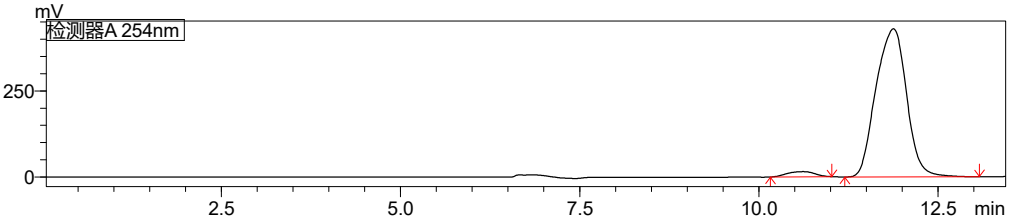
HPLC conditions: Chiralpak AD-H, 5% ^{i}PrOH/Hx eluent, 0.5 mL/min, 254 nm



2o



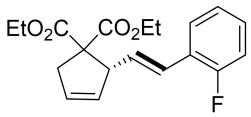
Peak#	Ret. Time	Height	Area%
1	10.590	115002	50.100
2	11.866	108229	49.900



Peak#	Ret. Time	Height	Area%
1	10.615	15154	3.104

2	11.877	430182	96.896

HPLC conditions: Chiralpak AD-H, 5% ^{i}PrOH/Hx eluent, 0.5 mL/min, 254 nm



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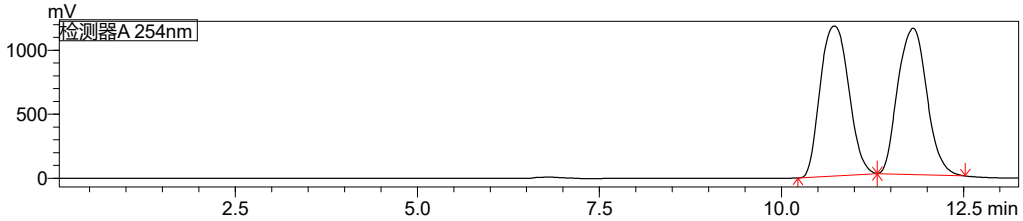
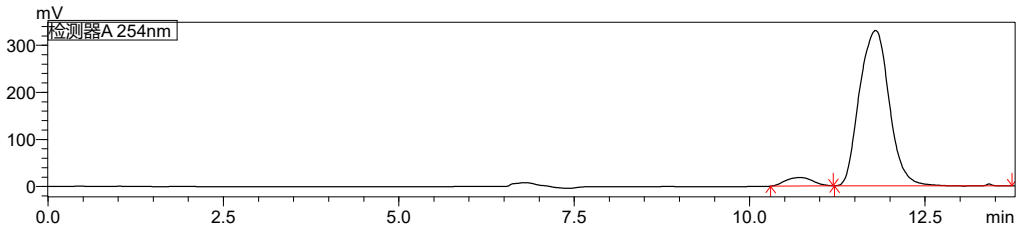
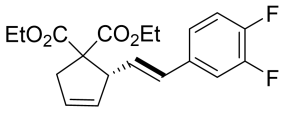


Peak#	Ret. Time	Height	Area%
1	10.725	1170128	50.196
2	11.809	1142409	49.804

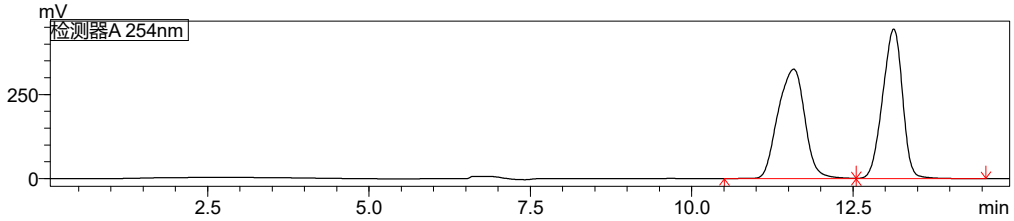


Peak#	Ret. Time	Height	Area%
1	10.715	17842	4.721
2	11.795	329903	95.279

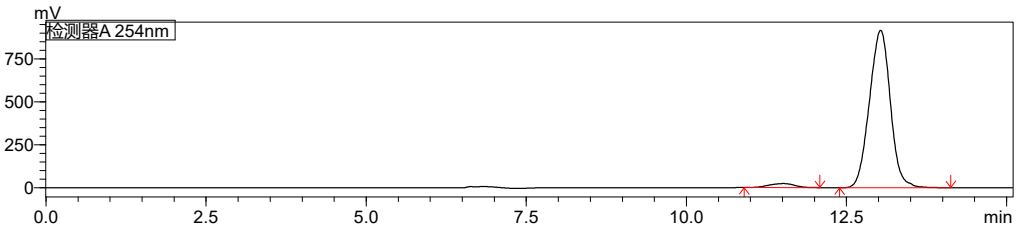
HPLC conditions: Chiralpak AD-H, 5% ^{i}PrOH/Hx eluent, 0.5 mL/min, 254 nm



2q

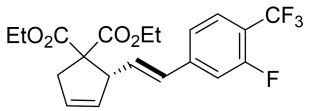


Peak#	Ret. Time	Height	Area%
1	11.581	326016	49.796
2	13.132	445115	50.204



Peak#	Ret. Time	Height	Area%
1	11.516	23159	2.973
2	13.032	917073	97.027

HPLC conditions: Chiralpak OJ-H, 5% ^{i}PrOH/Hx eluent, 0.5 mL/min, 254 nm



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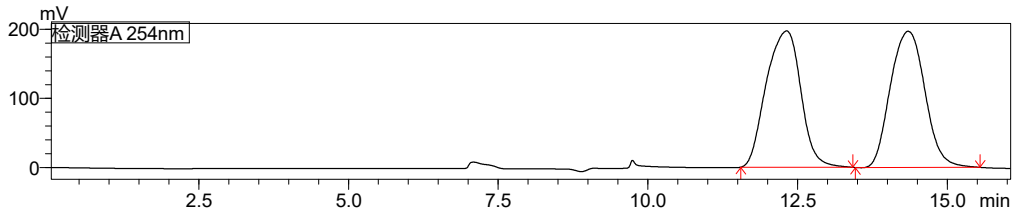
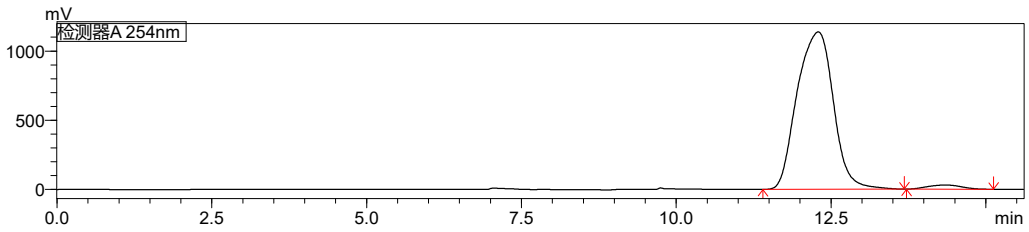
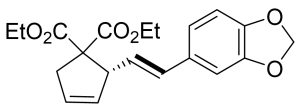


Peak#	Ret. Time	Height	Area%
1	12.316	198391	49.925
2	14.344	198168	50.075

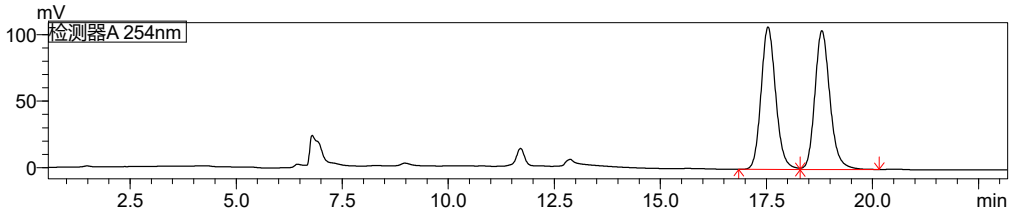


Peak#	Ret. Time	Height	Area%
1	12.291	1137409	97.581
2	14.349	29938	2.419

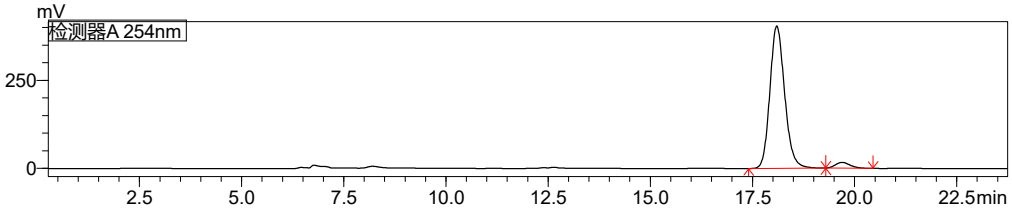
HPLC conditions: Chiralpak IC, 5% ^{i}PrOH/Hx eluent, 0.5 mL/min, 254 nm



2s

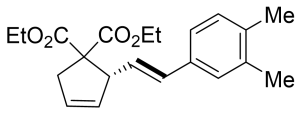


Peak#	Ret. Time	Height	Area%
1	17.537	106961	49.926
2	18.807	104260	50.074

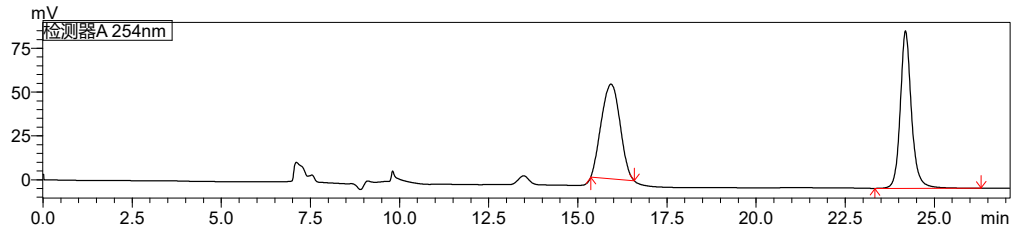


Peak#	Ret. Time	Height	Area%
1	18.094	404179	96.093
2	19.693	16430	3.907

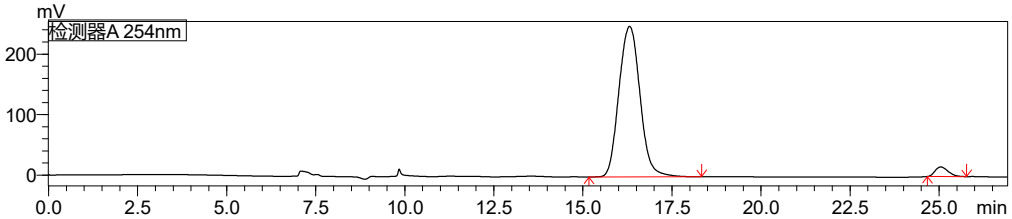
HPLC conditions: Chiralpak OJ-H, 5% ^{i}PrOH/Hx eluent, 0.5 mL/min, 254 nm



2t



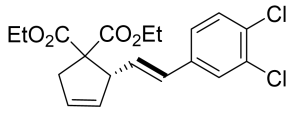
Peak#	Ret. Time	Height	Area%
1	15.928	54107	50.098
2	24.189	89958	49.902



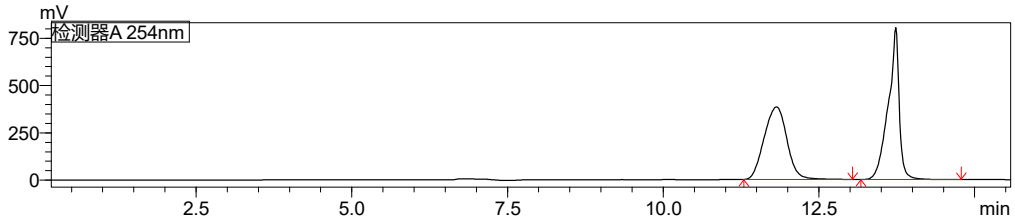
Peak#	Ret. Time	Height	Area%
1	16.306	248966	96.192

2	25.046	15928	3.808

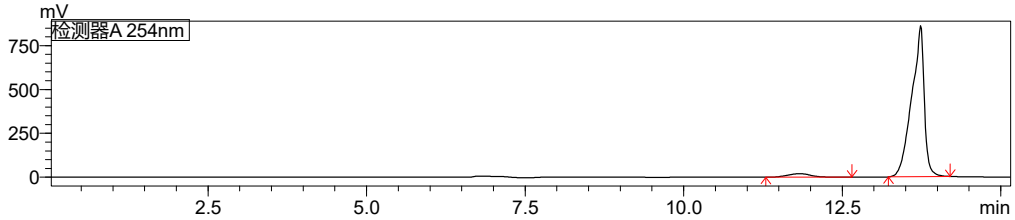
HPLC conditions: Chiralpak AD-H, 5% ^{i}PrOH/Hx eluent, 0.5 mL/min, 254 nm



2u

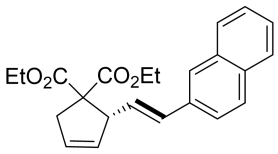


Peak#	Ret. Time	Height	Area%
1	11.816	384049	49.708
2	13.732	803606	50.292

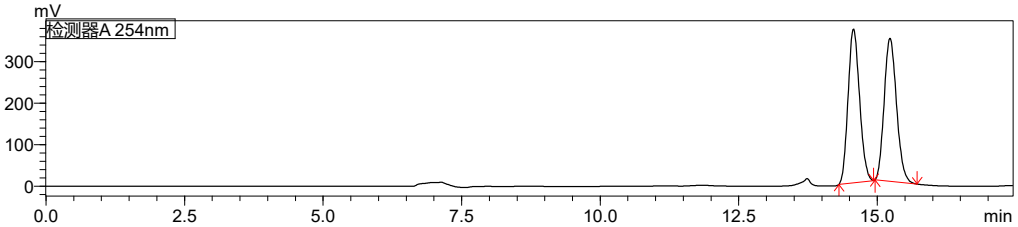


Peak#	Ret. Time	Height	Area%
1	11.831	19922	4.060
2	13.736	859285	95.940

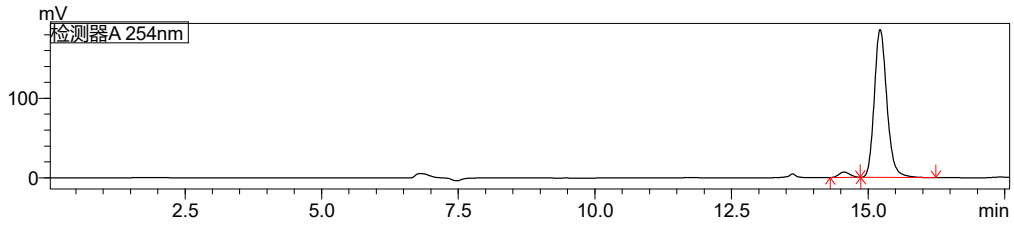
HPLC conditions: Chiralpak AD-H, 5% ^{i}PrOH/Hx eluent, 0.5 mL/min, 254 nm



2v

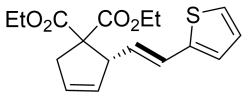


Peak#	Ret. Time	Height	Area%
1	14.570	370699	50.009
2	15.229	345007	49.991

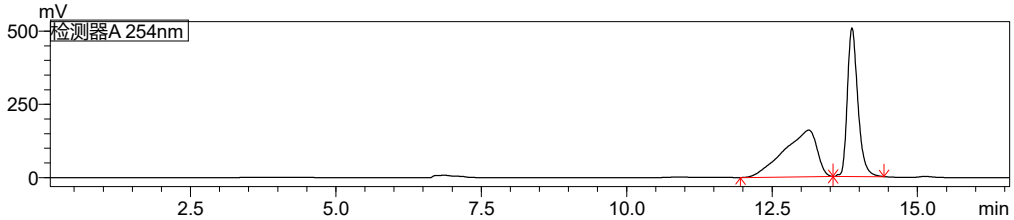


Peak#	Ret. Time	Height	Area%
1	14.558	6838	3.116
2	15.220	185907	96.884

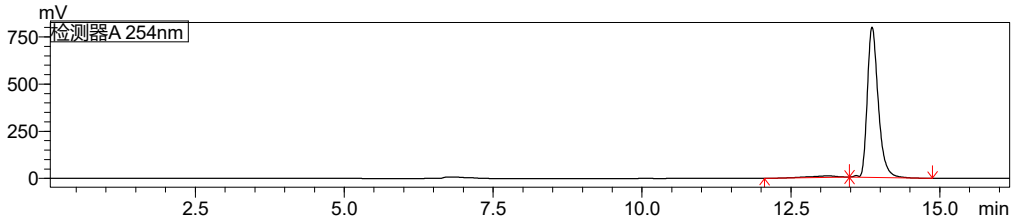
HPLC conditions: Chiralpak AD-H, 5% ^{i}PrOH/Hx eluent, 0.5 mL/min, 254 nm



2w

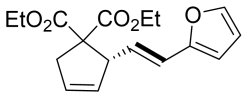


Peak#	Ret. Time	Height	Area%
1	13.130	159762	49.763
2	13.874	507639	50.237

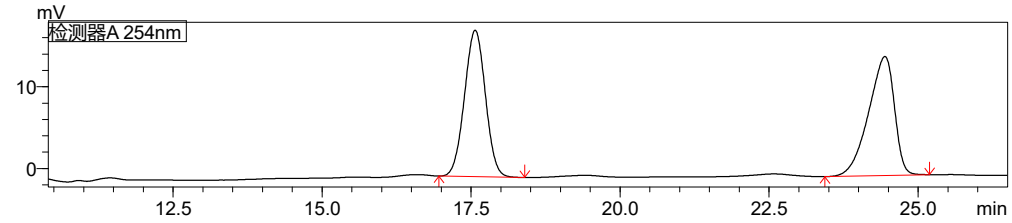


Peak#	Ret. Time	Height	Area%
1	13.122	7769	2.385
2	13.862	795644	97.615

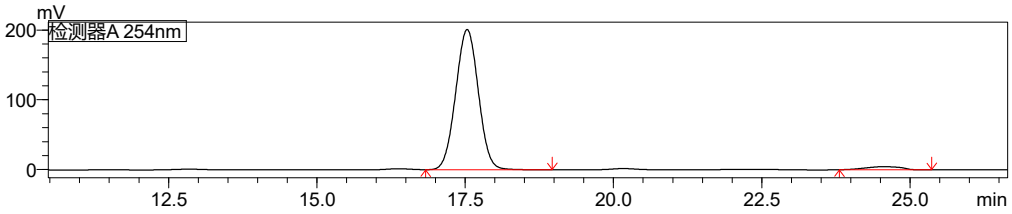
HPLC conditions: Chiralpak OJ-H, 5% ^{i}PrOH/Hx eluent, 0.5 mL/min, 254 nm



2x

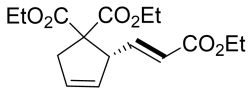


Peak#	Ret. Time	Height	Area%
1	17.567	17936	49.918
2	24.442	14575	50.082

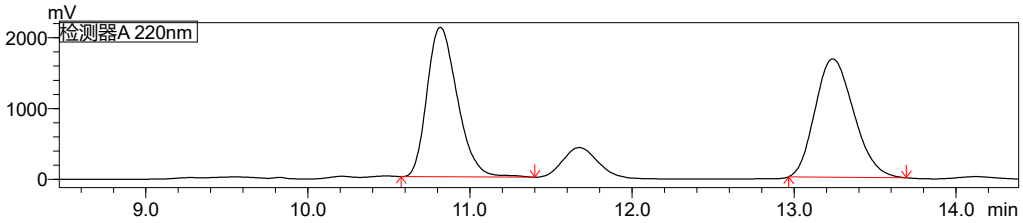


Peak#	Ret. Time	Height	Area%
1	17.532	200940	96.699
2	24.559	4402	3.301

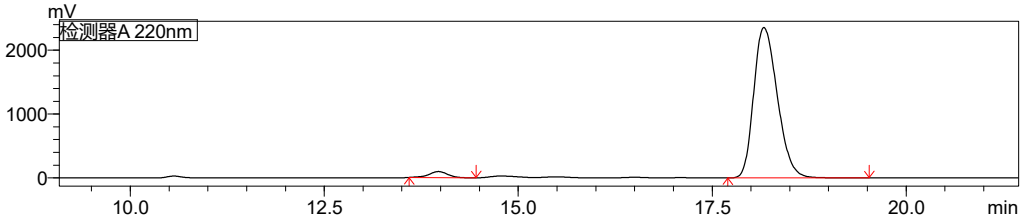
HPLC conditions: Chiralpak AD-H, 5% ^{i}PrOH/Hx eluent, 0.5 mL/min, 220 nm



2y



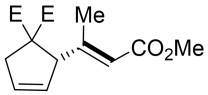
Peak#	Ret. Time	Height	Area%
1	10.816	2114825	49.807
2	13.238	1670348	50.193



Peak#	Ret. Time	Height	Area%
1	13.970	95109	3.083

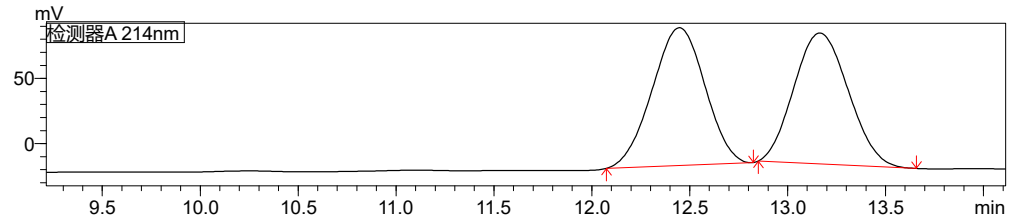
2	18.166	2356163	96.917

HPLC conditions: Chiralpak AS-H, 2% ^{i}PrOH/Hx eluent, 0.5 mL/min, 214 nm

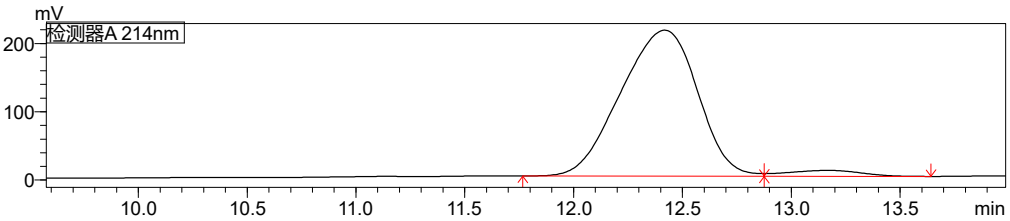


E = CO_2Et

2z

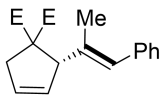


Peak#	Ret. Time	Height	Area%
1	12.447	105674	50.492
2	13.163	100475	49.508



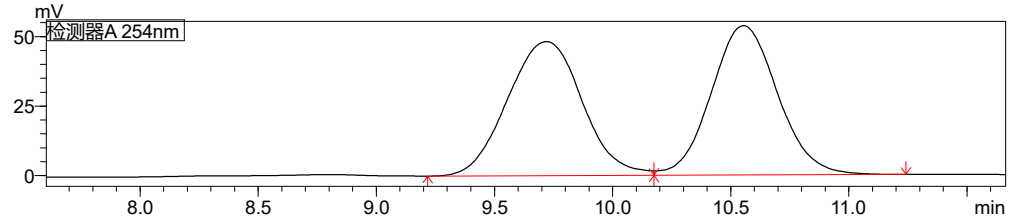
Peak#	Ret. Time	Height	Area%
1	12.418	213722	96.300
2	13.167	8652	3.700

HPLC conditions: Chiralpak AD-H, 5% ^{i}PrOH/Hx eluent, 0.5 mL/min, 254 nm



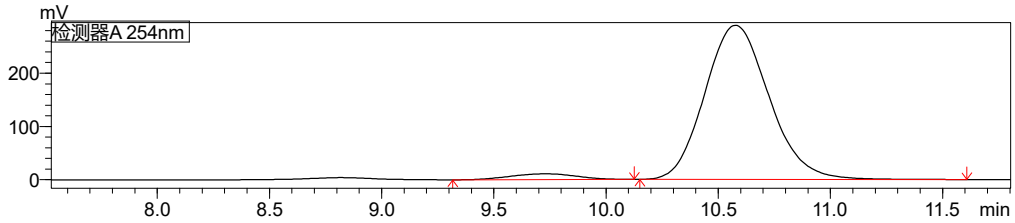
E = CO_2Et

2aa



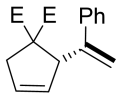
Peak#	Ret. Time	Height	Area%
1	9.720	48217	50.237

2	10.554	53734	49.763



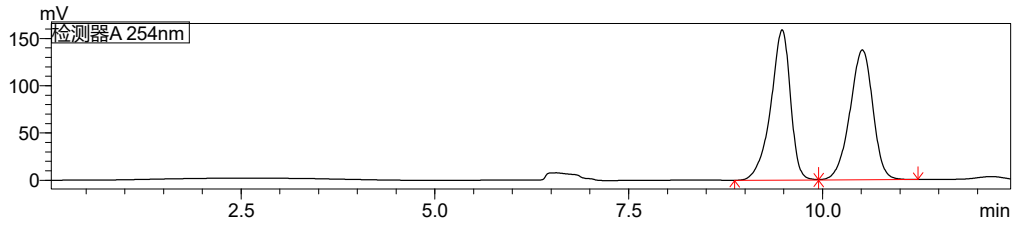
Peak#	Ret. Time	Height	Area%
1	9.730	10853	3.737
2	10.576	289365	96.263

HPLC conditions: Chiralpak AD-H, 5% ^{i}PrOH/Hx eluent, 0.5 mL/min, 254 nm

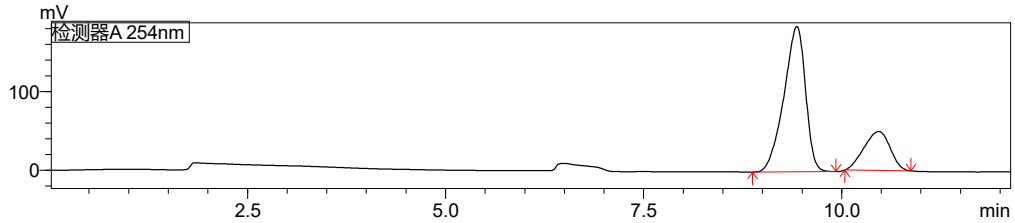


E = CO_2Et

2ab

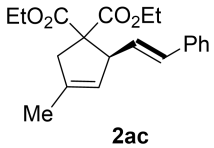


Peak#	Ret. Time	Height	Area%
1	9.479	159093	49.842
2	10.514	137574	50.158

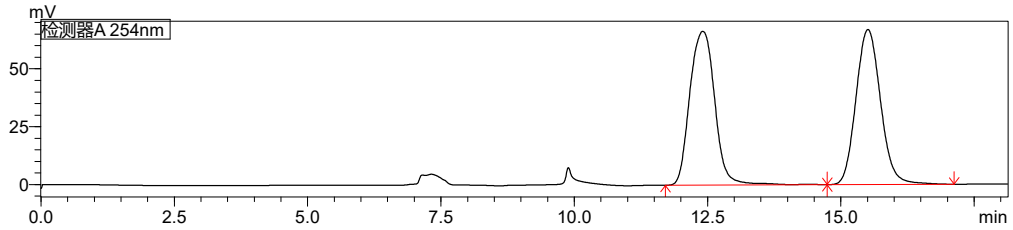


Peak#	Ret. Time	Height	Area%
1	9.433	184500	75.419
2	10.465	49520	24.581

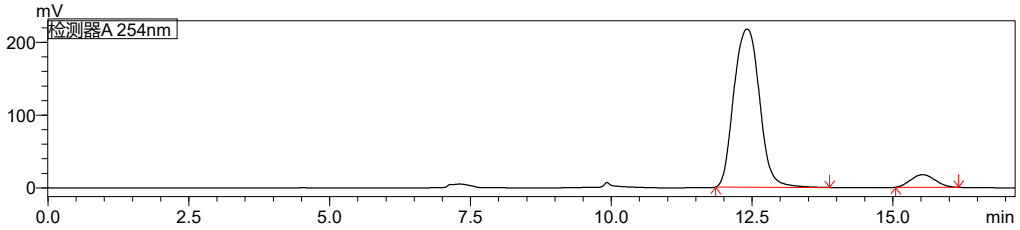
HPLC conditions: Chiralpak OJ-H, 5% ^{i}PrOH/Hx eluent, 0.5 mL/min, 254 nm



2ac

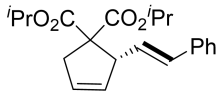


Peak#	Ret. Time	Height	Area%
1	12.409	66418	50.234
2	15.509	66988	49.766

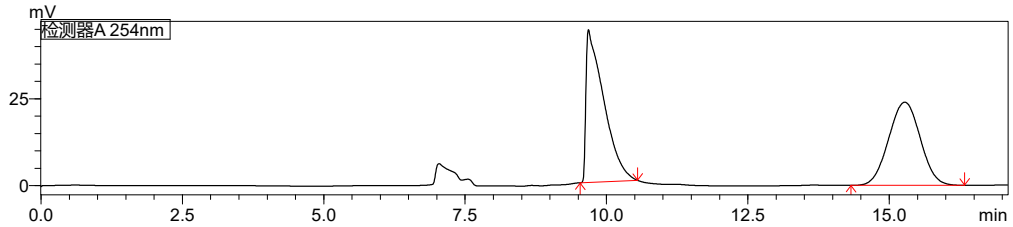


Peak#	Ret. Time	Height	Area%
1	12.409	217392	92.956
2	15.527	17360	7.044

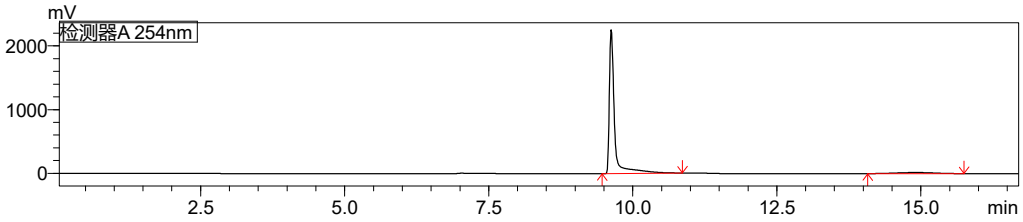
HPLC conditions: Chiralpak OJ-H, 5% ^{i}PrOH/Hx eluent, 0.5 mL/min, 254 nm



2ae

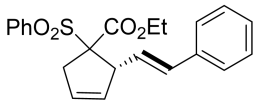


Peak#	Ret. Time	Height	Area%
1	9.681	44012	50.788
2	15.273	23963	49.212

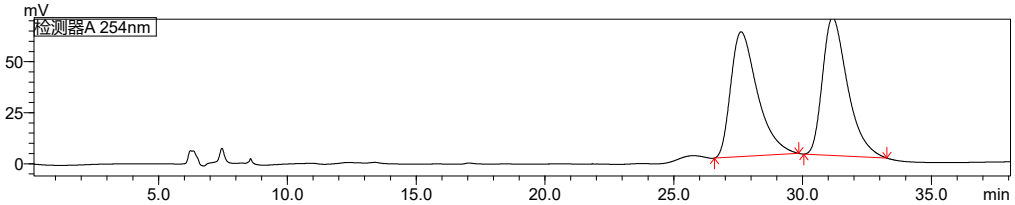


Peak#	Ret. Time	Height	Area%
1	9.626	2256407	95.094
2	14.911	16729	4.906

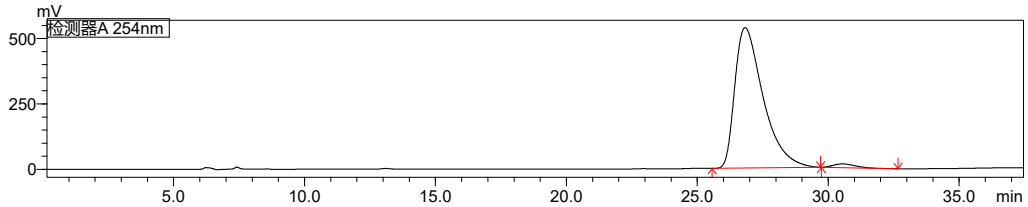
HPLC conditions: Chiralpak OD-H, 10% ^{i}PrOH/Hx eluent, 0.5 mL/min, 254 nm



2af

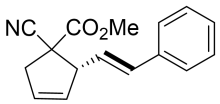


Peak#	Ret. Time	Height	Area%
1	27.614	61160	49.056
2	31.166	67600	50.944

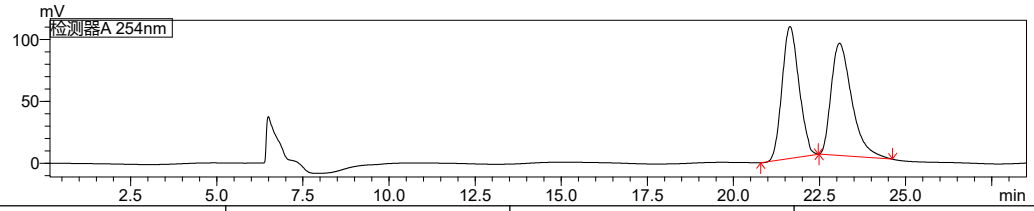


Peak#	Ret. Time	Height	Area%
1	26.824	536801	97.980
2	30.539	14347	2.020

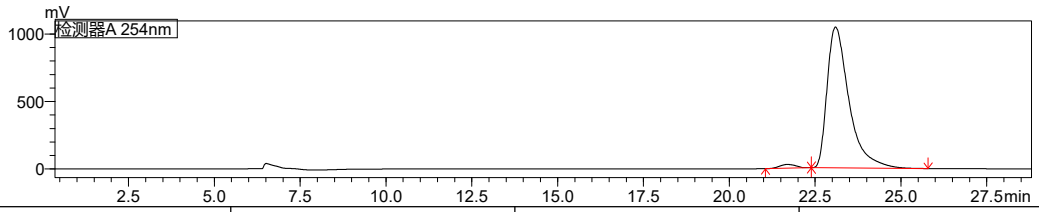
HPLC conditions: Chiralpak AD-H, 2% ^{i}PrOH/Hx eluent, 0.5 mL/min, 254 nm



2ag

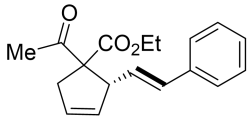


Peak#	Ret. Time	Height	Area%
1	21.640	106539	49.105
2	23.079	90697	50.895

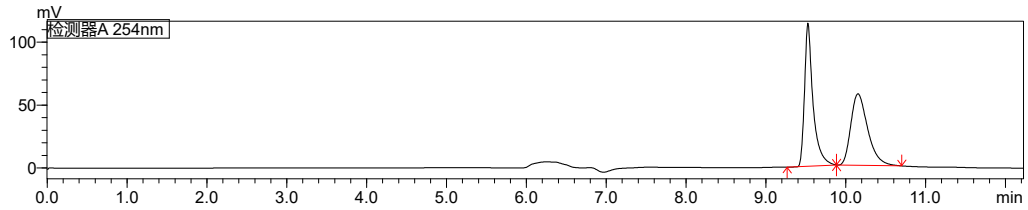


Peak#	Ret. Time	Height	Area%
1	21.695	28120	1.974
2	23.093	1045235	98.026

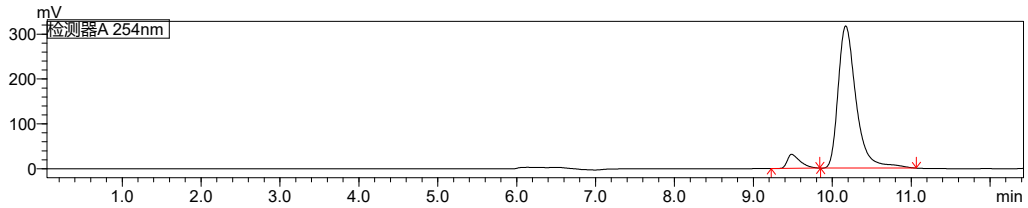
HPLC conditions: Chiralpak AD-H, 10% ^{i}PrOH/Hx eluent, 0.5 mL/min, 254 nm



2ah

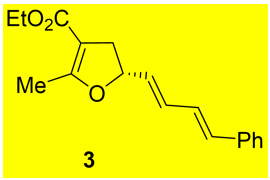


Peak#	Ret. Time	Height	Area%
1	9.525	113706	50.243
2	10.152	56874	49.757

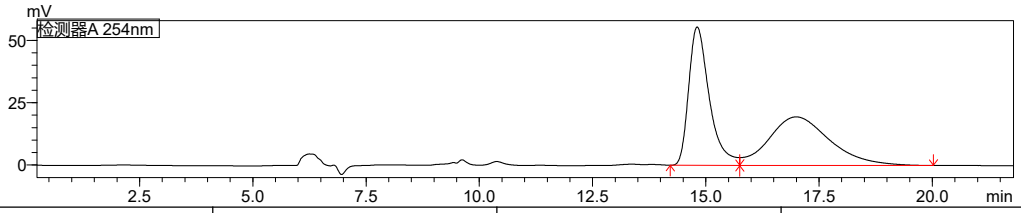


Peak#	Ret. Time	Height	Area%
1	9.485	31438	6.565
2	10.170	316984	93.435

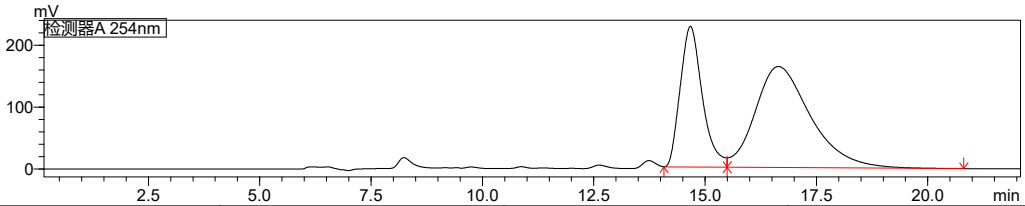
HPLC conditions: Chiralpak AD-H, 10% ^{i}PrOH/Hx eluent, 0.5 mL/min, 254 nm



3

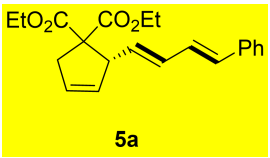


Peak#	Ret. Time	Height	Area%
1	14.808	55555	49.269
2	16.996	19475	50.731

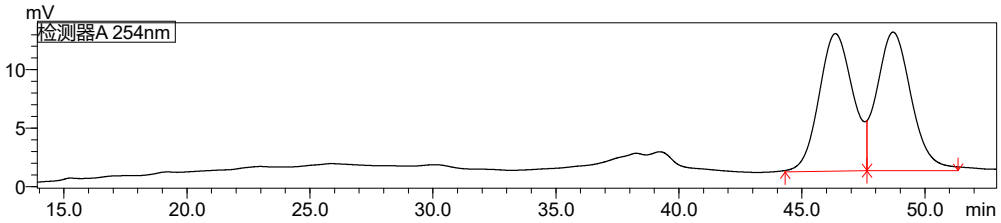


Peak#	Ret. Time	Height	Area%
1	14.669	227630	35.688
2	16.648	163491	64.312

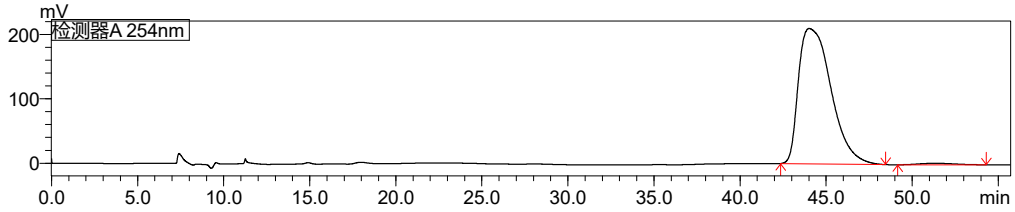
HPLC conditions: Chiralpak OJ-H, 3% ^{i}PrOH/Hx eluent, 0.5 mL/min, 254 nm



5a

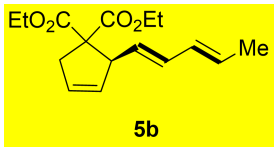


Peak#	Ret. Time	Height	Area%
1	46.359	11771	49.610
2	48.704	11849	50.390

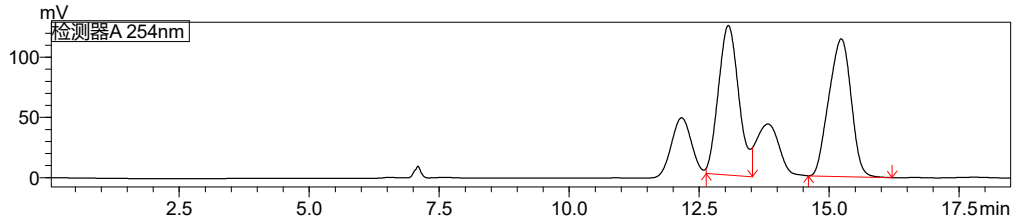


Peak#	Ret. Time	Height	Area%
1	44.004	210332	98.804
2	51.351	2332	1.196

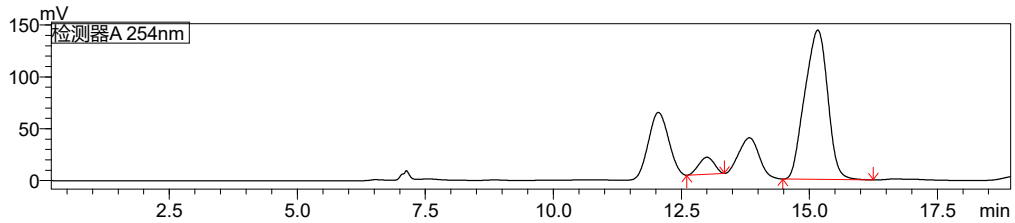
HPLC conditions: Chiralpak IC, 2% ^{i}PrOH/Hx eluent, 0.5 mL/min, 254 nm



5b

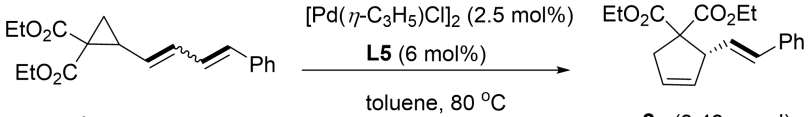


Peak#	Ret. Time	Height	Area%
1	13.059	124326	49.991
2	15.231	114353	50.009



Peak#	Ret. Time	Height	Area%
1	13.000	16526	7.256
2	15.164	144097	92.744

7. Gram scale reaction

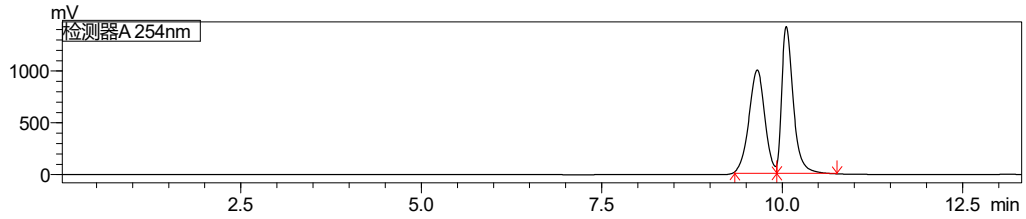


1a (4 mmol)

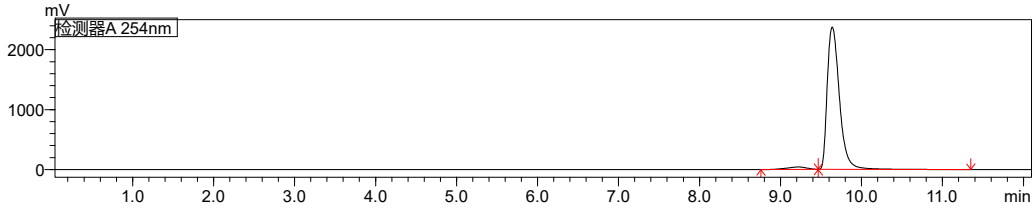
2a (3.48 mmol)
83%, 94% ee

Under anhydrous and oxygen-free conditions, to a dried tube equipped with a magnetic stir bar was added **1a** (4 mmol), $[Pd(\eta\text{-}C_3H_5)Cl]_2$ (36 mg, 2.5 mol%) and **L5** (140 mg, 6 mol%), and toluene (40 mL), stirring the reaction mixture for 3 h at 80 ˚C. The solvent was removed in vacuo and the crude product was purified directly by column chromatography to afford the desired **2a** (1.03 g, 83% yield, 94% ee).

HPLC conditions: Chiralpak AD-H, 10% ^{i}PrOH/Hx eluent, 0.5 mL/min, 254 nm

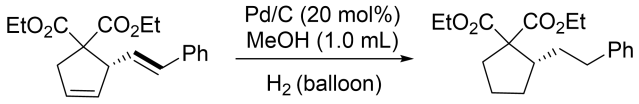


Peak#	Ret. Time	Height	Area%
1	9.653	996275	49.379
2	10.056	1417278	50.621



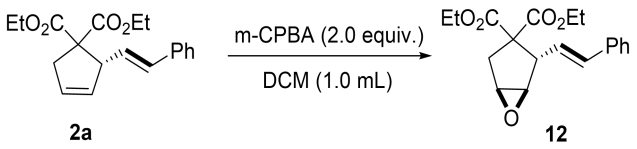
Peak#	Ret. Time	Height	Area%
1	9.220	39726	2.647
2	9.638	2373505	97.353

8. Synthetic transformations

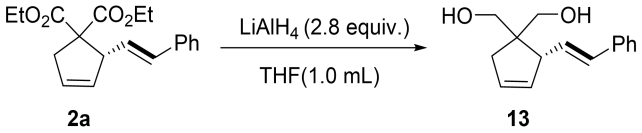


2a **11**

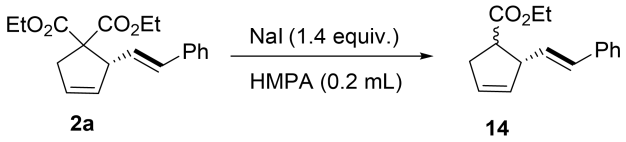
Under balloon pressure of H_2 conditions, to a dried tube equipped with a magnetic stir bar was added **2a** (31.3 mg, 0.1 mmol), Pd/C (2.1 mg, 20 mol%) and MeOH (1.0 mL), stirring the reaction mixture for 20 h at 25 ˚C. The residue was purified directly by column chromatography to afford the desired **11** as a yellow oil (28.7 mg, 90% yield).



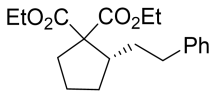
To a stirred solution of **2a** (31.4 mg, 0.1 mmol) in DCM (1.0 mL) was added m-CPBA (34.5 mg, 0.2 mmol) portionwise over 10 min at 0 ˚C. The resulting reaction mixture was allowed to warm to room temperature and stirred for 24 h. The precipitate was filtered and the filtrate was diluted with dichloromethane, washed with saturated aqueous $NaHCO_3$ solution and water. The organic layer was dried over Na_2SO_4 and the solvent was evaporated under reduced pressure. The residue was purified directly by column chromatography to afford the desired **12** as a white soild (13.2 mg, 40% yield).



To a suspension of $LiAlH_4$ (10.6 mg, 0.28 mmol) in dry THF (0.5 mL) was added a solution of **2a** (31.4 mg, 0.1 mmol) in dry THF (0.5 mL) dropwise at 0 ˚C. The resulting suspension was stirred overnight at 0˚C. The suspension was quenched with water, 15% sodium hydroxide, and water at the same temperature. The white gel suspension was filtered through a pad of Celite and concentrated in vacuo. The residue was purified directly by column chromatography to afford the desired **13** as a white oil (16.1 mg, 70% yield).



To a stirred solution of **2a** (31.4 mg, 0.1 mmol) in HMPA (0.2 mL) was added NaI (2.1 mg, 0.14 mmol), stirring the reaction mixture for 24 h at 110 ˚C. The residue was purified directly by column chromatography to afford the desired **14** as a yellow oil (19.3 mg, 80% yield).



Diethyl (S)-2-phenethylcyclopentane-1,1-dicarboxylate (11)

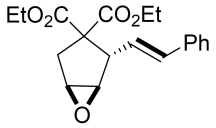
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.28 – 7.12 (m, 5H), 4.26 – 4.01 (m, 4H), 2.69 (ddd, *J* = 13.9, 10.5, 5.0 Hz, 1H), 2.60 – 2.46 (m, 2H), 2.38 (ddd, *J* = 13.8, 8.7, 7.3 Hz, 1H), 2.11 – 1.72 (m, 4H), 1.59 – 1.36 (m, 3H), 1.20 (td, *J* = 7.2, 4.9 Hz, 6H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 172.5, 171.6, 142.2, 128.3, 128.2, 125.7, 63.4, 61.0, 60.9, 45.9, 34.8, 34.5, 33.0, 30.8, 22.9, 14.1, 14.0.

HRMS Exact mass calculated for $[C_{19}H_{26}O_4+Na]^+$ requires *m/z* = 341.1723, found *m/z* = 341.1725 (ESI+).

Optical: $[\alpha]^{25}_D$ = +46.1 ° (c = 0.25, CH_2Cl_2, 93 % e.e.)

HPLC (Chiralpak IC-H, 2% ^{i}PrOH/Hx eluent, 0.5 mL/min, 220 nm): major enantiomer t_R = 14.7 min, minor enantiomer t_R = 13.6 min.



Diethyl (1R,2S,5S)-2-((E)-styryl)-6-oxabicyclo[3.1.0]hexane-3,3-dicarboxylate (12)

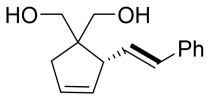
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.35 – 7.26 (m, 5H), 6.64 (d, *J* = 15.8 Hz, 1H), 5.79 (dd, *J* = 15.8, 10.2 Hz, 1H), 4.23 (dq, *J* = 7.1, 3.7 Hz, 2H), 4.11 – 3.99 (m, 3H), 3.60 – 3.40 (m, 2H), 2.89 (d, *J* = 15.0 Hz, 1H), 2.65 (dd, *J* = 15.0, 1.1 Hz, 1H), 1.27 (d, *J* = 7.1 Hz, 3H), 1.09 (t, *J* = 7.1 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 170.4, 168.43 136.4, 135.1, 128.6, 128.0, 126.4, 122.9, 61.9, 61.8, 60.5, 57.9, 55.2, 48.4, 33.7, 14.1, 14.0.

HRMS Exact mass calculated for $[C_{19}H_{22}O_5+Na]^+$ requires *m/z* = 353.1359, found *m/z* = 353.1360 (ESI+).

Optical: $[\alpha]^{25}_D$ = -200.4 ° (c = 0.32, CH_2Cl_2, 94 % e.e.)

HPLC (Chiralpak AD-H, 5% ^{i}PrOH/Hx eluent, 0.5 mL/min, 254 nm): major enantiomer t_R = 24.3 min, minor enantiomer t_R = 22.3 min.



(S,E)-(2-styrylcyclopent-3-ene-1,1-diyl)dimethanol (13)

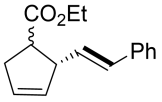
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.31 – 7.12 (m, 5H), 6.38 (d, *J* = 15.8 Hz, 1H), 6.12 (dd, *J* = 15.9, 8.8 Hz, 1H), 5.68 (dt, *J* = 6.1, 2.1 Hz, 1H), 5.54 (dt, *J* = 5.6, 2.2 Hz, 1H), 3.75 (d, *J* = 11.1 Hz, 1H), 3.67 – 3.52 (m, 3H), 3.28 (dt, *J* = 8.8, 2.2 Hz, 1H), 2.41 (s, 2H), 2.16 – 2.08 (m, 2H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 137.0, 132.3, 131.1, 129.7, 129.5, 128.6, 127.4, 126.2, 69.8, 67.5, 52.3, 51.2, 38.1.

HRMS Exact mass calculated for $[C_{15}H_{18}O_2+H]^+$ requires *m/z* = 231.1380, found *m/z* = 231.1382 (ESI+).

Optical: $[\alpha]^{25}_D$ = +183.6 ° (c = 0.45, CH_2Cl_2, 94 % e.e.)

HPLC (Chiralpak OD-H, 10% ^{i}PrOH/Hx eluent, 0.5 mL/min, 254 nm): major enantiomer t_R = 23.4 min, minor enantiomer t_R = 20.1 min.



Ethyl-2-((E)-styryl)cyclopent-3-ene-1-carboxylate (14)

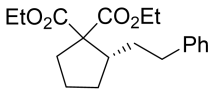
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.31 – 7.09 (m, 5H), 6.36 (t, *J* = 15.2 Hz, 1H), 6.19 – 5.89 (m, 1H), 5.83 – 5.49 (m, 2H), 4.18 – 3.89 (m, 2H), 3.80 – 3.53 (m, 1H), 3.40 – 2.38 (m, 3H), 1.21 – 1.05 (m, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 175.3, 173.4, 137.2, 132.2, 132.2, 131.6, 131.1, 130.60, 19.9, 129.7, 128.7, 128.6, 128.5, 128.4, 127.2, 126.6, 126.2, 126.2, 60.6, 60.3, 52.7, 51.4, 49.4, 47.5, 36.3, 33.9, 14.3.

HRMS Exact mass calculated for $[C_{16}H_{18}O_2+Na]^+$ requires *m/z* = 265.1199, found *m/z* = 265.1198 (ESI+).

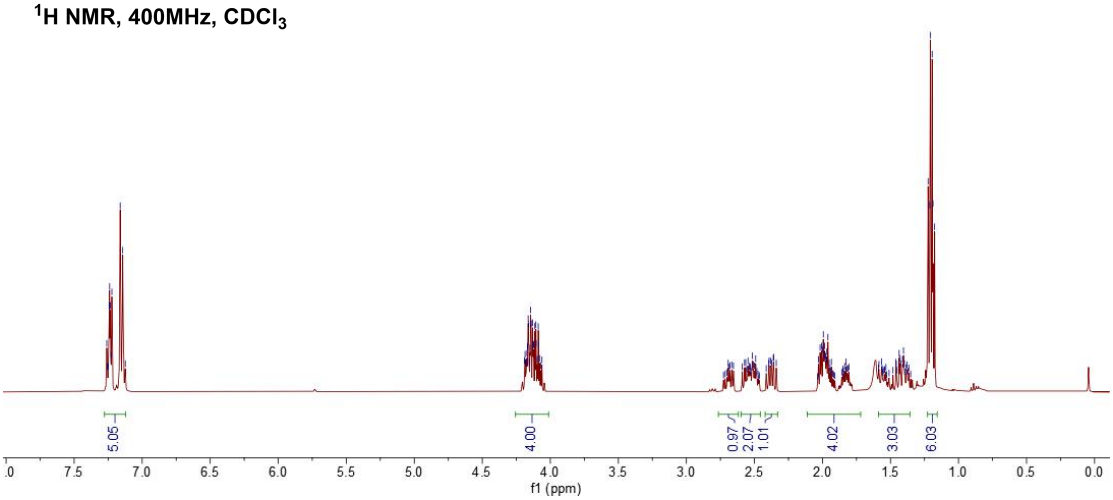
Optical: $[\alpha]^{25}_D$ = +117.4 ° (c = 0.40, CH_2Cl_2, 94 % e.e. dr = 3.4:1)

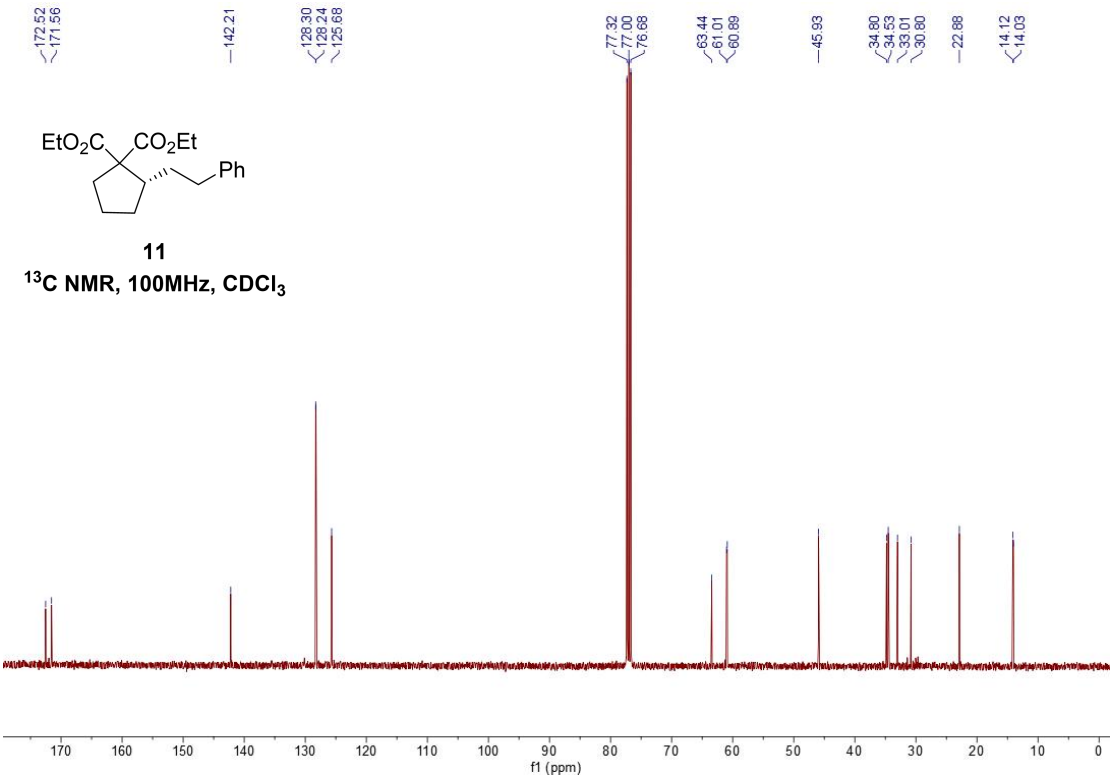
HPLC (Chiralpak OJ-H, 2% ^{i}PrOH/Hx eluent, 0.5 mL/min, 254 nm): major enantiomer t_R = 18.1 min, minor enantiomer t_R = 20.6 min.



11

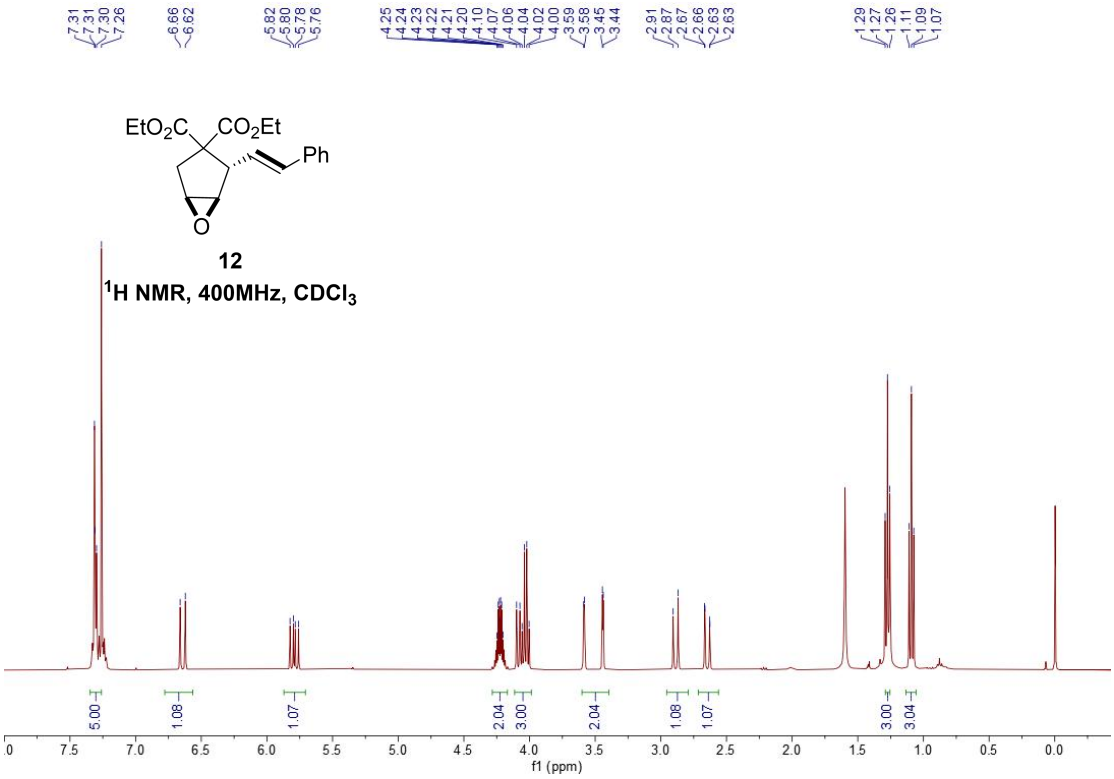
^{1}H NMR, 400MHz, $CDCl_3$

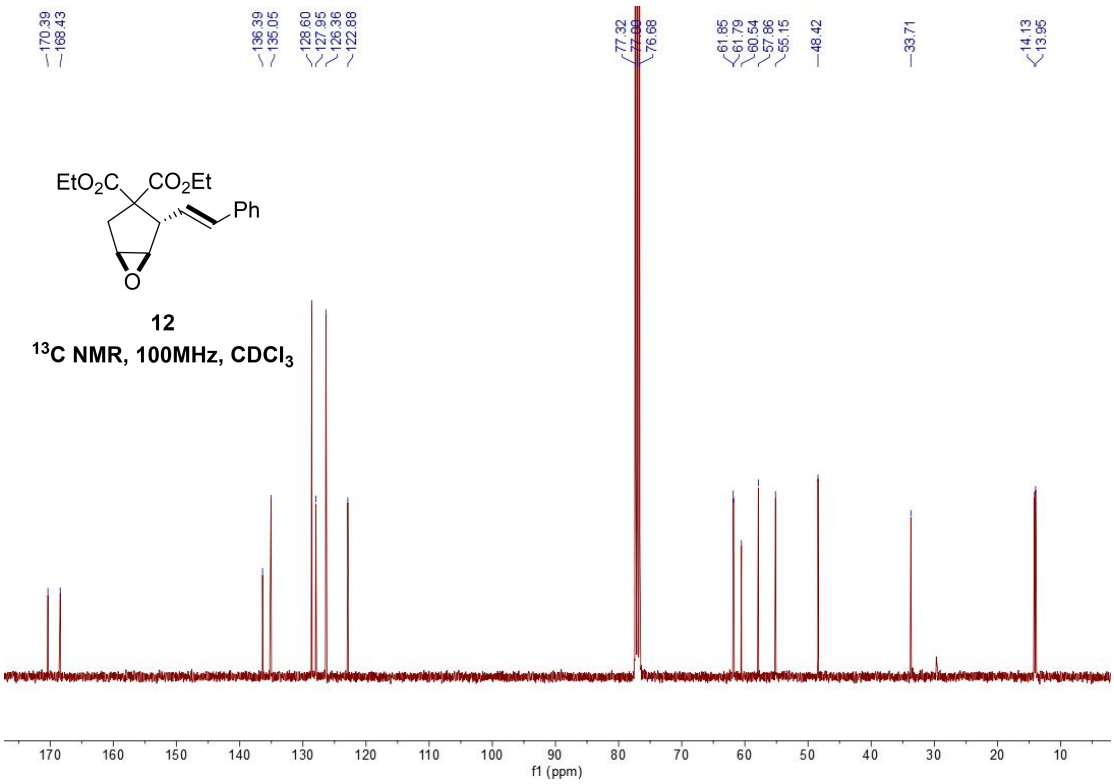




11

^{13}C NMR, 100MHz, $CDCl_3$


7.31
7.31
7.30
7.26
6.66
6.62
5.82
5.80
5.78
5.76
4.25
4.24
4.23
4.22
4.21
4.20
4.10
4.07
4.06
4.04
4.02
4.00
3.59
3.58
3.45
3.44
2.91
2.87
2.67
2.66
2.63
2.63
1.29
1.27
1.26
1.11
1.09
1.07
EtO2C
CO2Et
Ph
O
12
1H NMR, 400MHz, CDCl3
5.00
1.08
1.07
2.04
3.00
2.04
1.08
1.07
3.00
3.04
f1 (ppm)


170.39
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135.05
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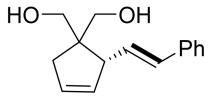
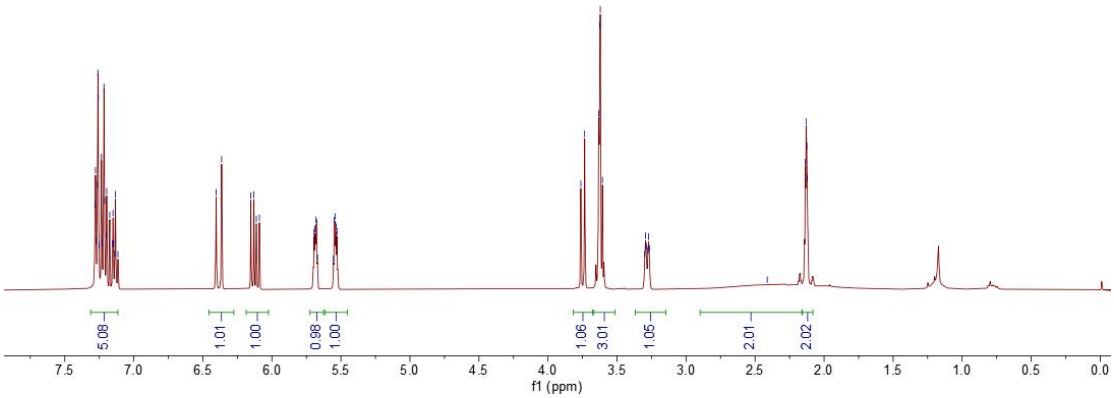
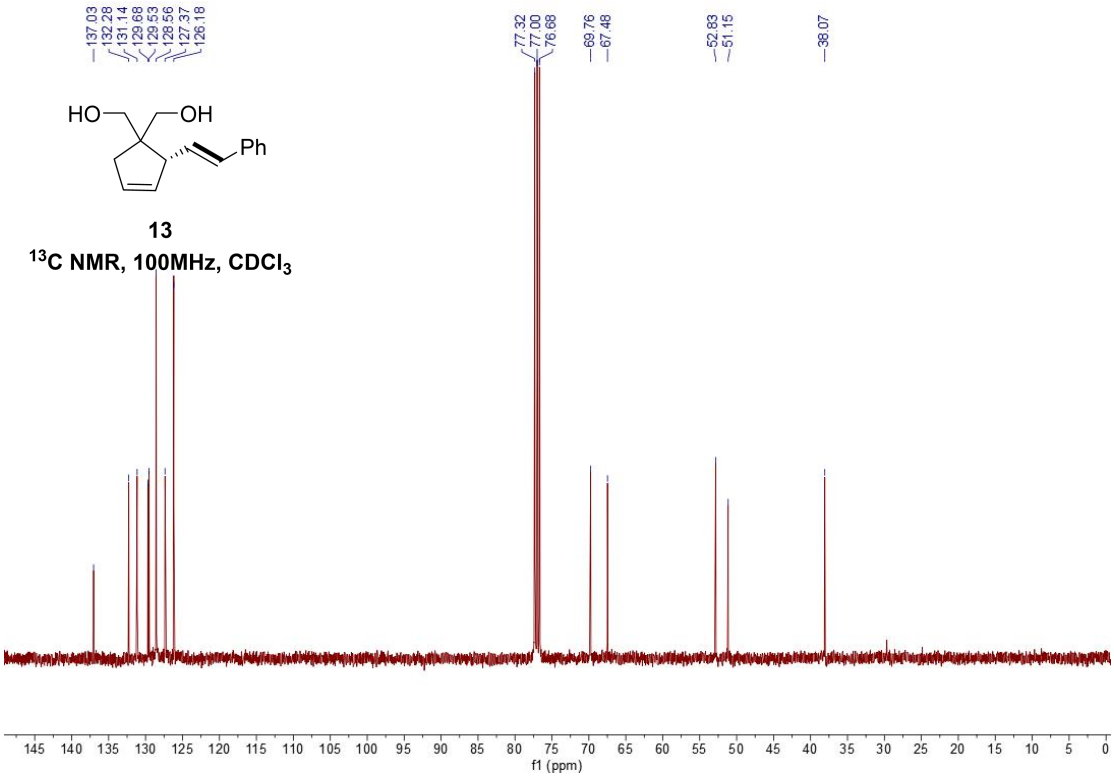
127.95
126.36
122.88
77.32
77.00
76.68
61.85
61.79
60.54
57.86
55.15
48.42
33.71
14.13
13.95
EtO2C
CO2Et
Ph
O
12
13C NMR, 100MHz, CDCl3
f1 (ppm)



13

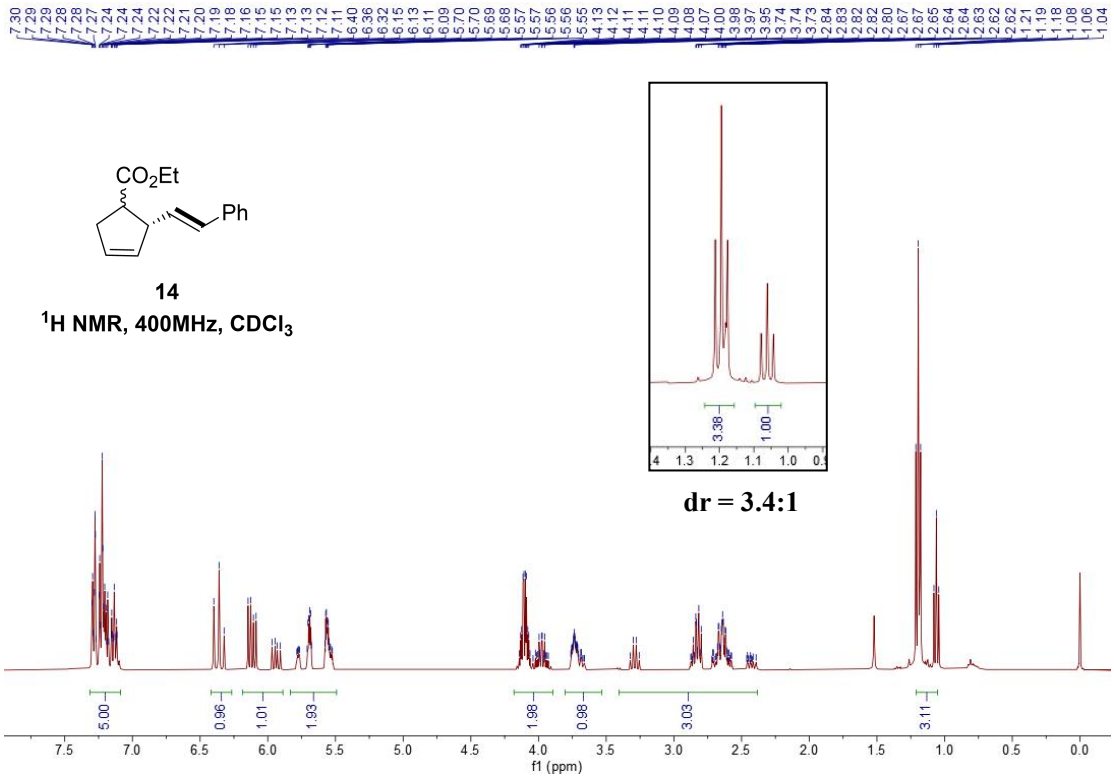
^{1}H NMR, 400MHz, $CDCl_3$





13

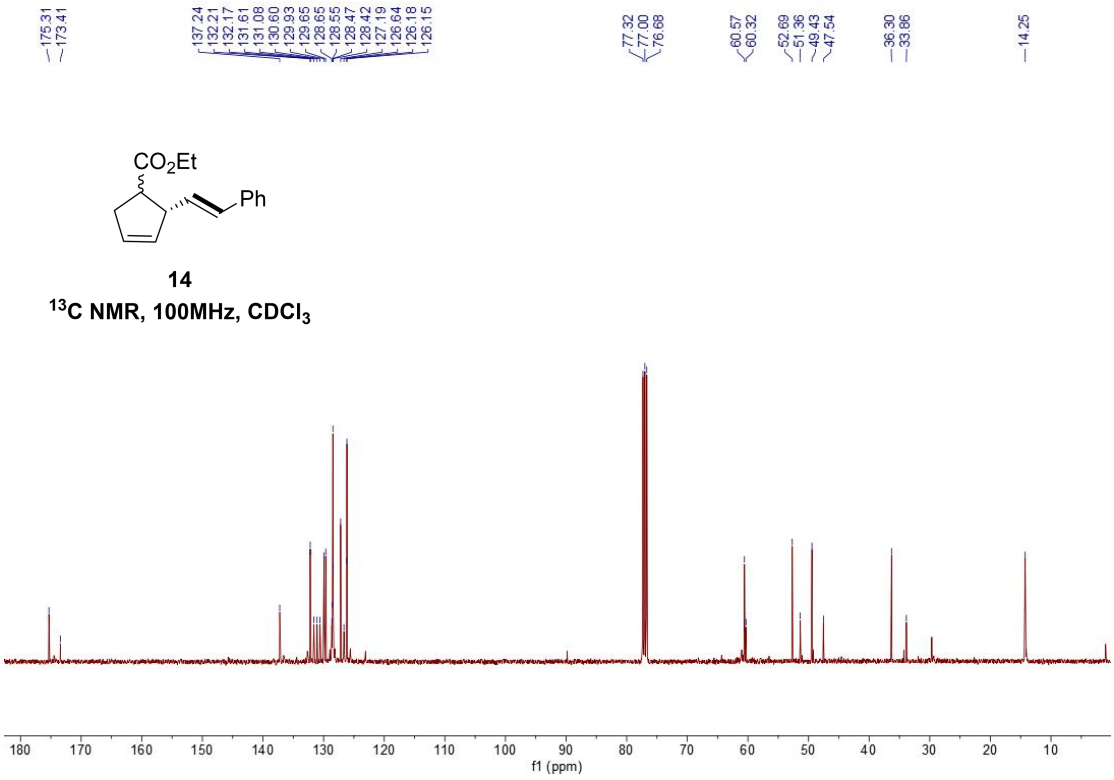
^{13}C NMR, 100MHz, $CDCl_3$



14

^{1}H NMR, 400MHz, $CDCl_3$

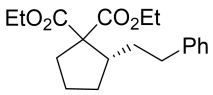
dr = 3.4:1



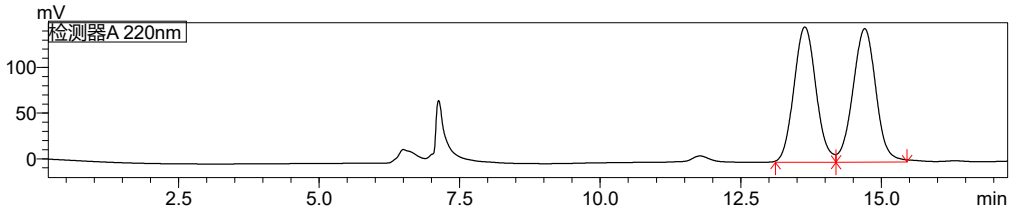
14

^{13}C NMR, 100MHz, $CDCl_3$

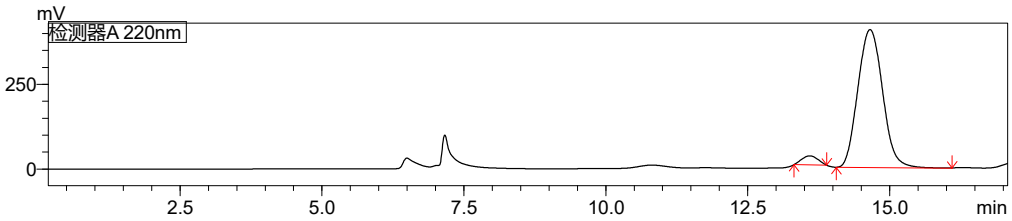
HPLC conditions: Chiralpak IC, 2% ^{i}PrOH/Hx eluent, 0.5 mL/min, 220 nm



11

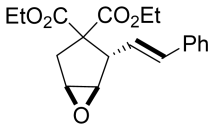


Peak#	Ret. Time	Height	Area%
1	13.639	149439	49.402
2	14.704	147287	50.598

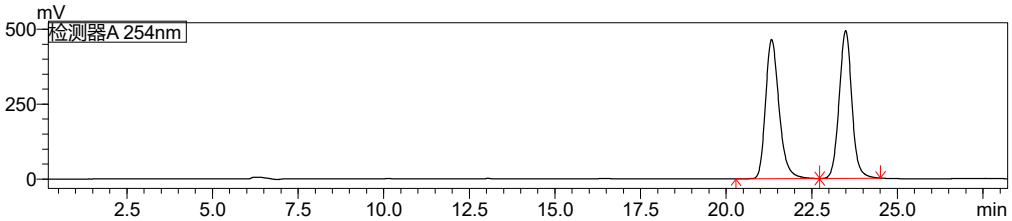


Peak#	Ret. Time	Height	Area%
1	13.592	25141	3.645
2	14.654	409380	96.355

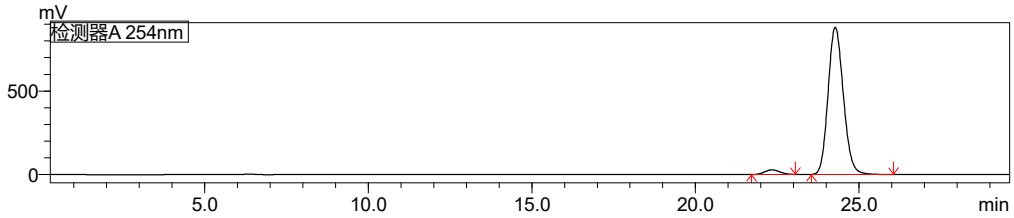
HPLC conditions: Chiralpak AD-H, 5% ^{i}PrOH/Hx eluent, 0.5 mL/min, 254 nm



12

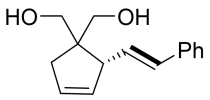


Peak#	Ret. Time	Height	Area%
1	21.326	465267	50.197
2	23.491	493599	49.803



Peak#	Ret. Time	Height	Area%
1	22.338	27693	3.014
2	24.271	881708	96.986

HPLC conditions: Chiralpak OD-H, 10% ^{i}PrOH/Hx eluent, 0.5 mL/min, 254 nm



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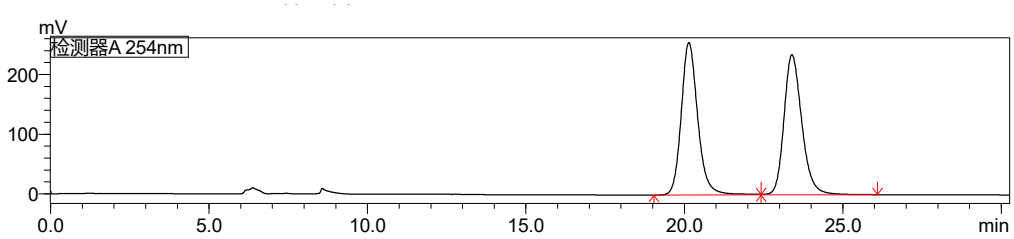
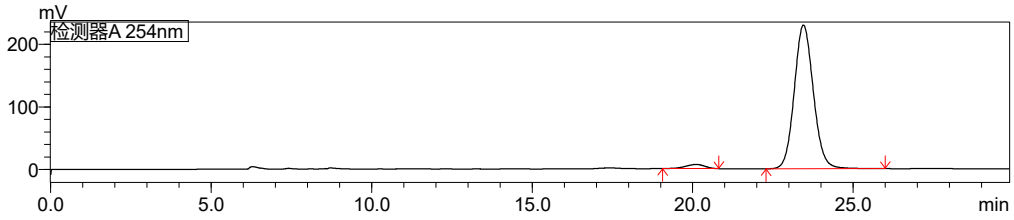
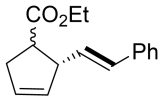


Peak#	Ret. Time	Height	Area%
1	20.140	255363	50.215
2	23.393	234669	49.785

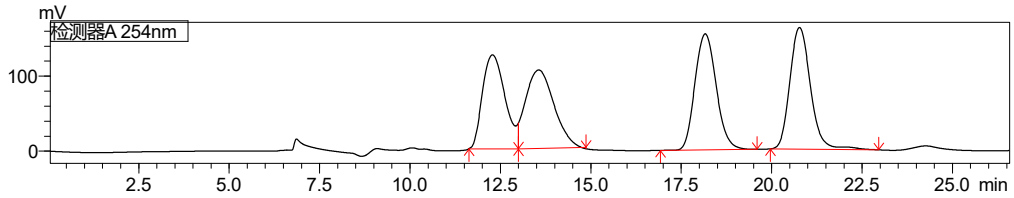


Peak#	Ret. Time	Height	Area%
1	20.108	6633	2.818
2	23.448	229854	97.182

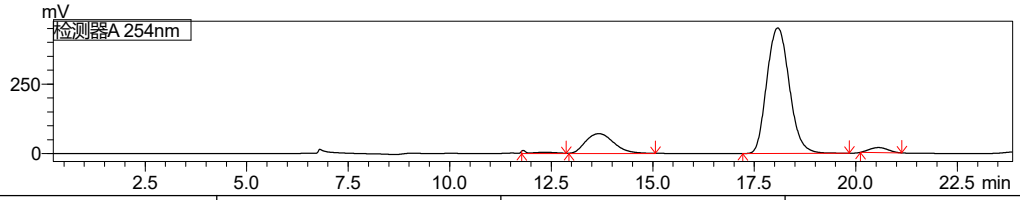
HPLC conditions: Chiralpak OJ-H, 2% ^{i}PrOH/Hx eluent, 0.5 mL/min, 254 nm



14



Peak#	Ret. Time	Height	Area%
1	12.278	126973	23.485
2	13.557	106660	23.848
3	18.163	154746	26.106
4	20.769	162131	26.561



Peak#	Ret. Time	Height	Area%
1	11.809	11080	1.098
2	13.671	71654	16.213
3	18.078	452106	80.068
4	20.559	17965	2.621

9. Crystallographic data for 2d.

Table 1 Crystal data and structure refinement for 2d.

Identification code	**2d**
Empirical formula	$C_{20}H_{24}O_4$
Formula weight	328.39
Temperature/K	150.00(10)
Crystal system	monoclinic
Space group	$P2_1$
a/Å	7.73185(8)
b/Å	5.91229(7)
c/Å	19.8978(2)
α/°	90
β/°	92.4788(10)
γ/°	90
Volume/Å^3	908.734(17)
Z	2
ρ_{calc}g/cm^3	1.200
μ/mm^{-1}	0.667

F(000)	352.0
Crystal size/mm^3	0.15 × 0.13 × 0.1
Radiation	Cu Kα (λ = 1.54184)
2Θ range for data collection/°	8.896 to 142.938
Index ranges	-9 ≤ h ≤ 9, -7 ≤ k ≤ 7, -23 ≤ l ≤ 24
Reflections collected	6616
Independent reflections	3229 [R_{int} = 0.0114, R_{sigma} = 0.0118]
Data/restraints/parameters	3229/1/221
Goodness-of-fit on F^2	1.077
Final R indexes [I>=2σ (I)]	R_1 = 0.0258, wR_2 = 0.0681
Final R indexes [all data]	R_1 = 0.0260, wR_2 = 0.0682
Largest diff. peak/hole / e Å^{-3}	0.16/-0.13
Flack/Hooft parameter	0.12(6)/0.19(3)

Crystal structure determination of [2d]

Crystal Data for $C_{20}H_{24}O_4$ (*M* =328.39 g/mol): monoclinic, space group $P2_1$ (no. 4), *a* = 7.73185(8) Å, *b* = 5.91229(7) Å, *c* = 19.8978(2) Å, *β* = 92.4788(10)°, *V* = 908.734(17) Å^3, *Z* = 2, *T* = 150.00(10) K, μ(Cu Kα) = 0.667 mm^{-1}, *Dcalc* = 1.200 g/cm^3, 6616 reflections measured (8.896° ≤ 2Θ ≤ 142.938°), 3229 unique (R_{int} = 0.0114, R_{sigma} = 0.0118) which were used in all calculations. The final R_1 was 0.0258 (I > 2σ(I)) and wR_2 was 0.0682 (all data).

Refinement model description

Table 2 Fractional Atomic Coordinates (×10^4) and Equivalent Isotropic Displacement Parameters (Å^2×10^3) for 2d. U_{eq} is defined as 1/3 of the trace of the orthogonalised U_{IJ} tensor.

Atom	*x*	*y*	*z*	U(eq)
O1	2619.2(15)	5655(2)	477.3(6)	32.6(3)
O2	4953.4(16)	3742(2)	876.5(6)	33.7(3)
O3	1250.1(14)	3423(2)	1724.7(6)	25.7(3)
O4	505.9(14)	6971(2)	1997.0(7)	32.8(3)
C1	3387.6(19)	6200(3)	1619.4(8)	21.7(3)
C2	3698(2)	8769(3)	1546.9(9)	26.5(4)
C3	5550(2)	9024(3)	1802.7(8)	27.0(4)
C4	6107(2)	7222(3)	2140.6(8)	26.9(4)
C5	4736.2(19)	5413(3)	2184.3(8)	23.7(3)
C6	4019(2)	5308(3)	2875.3(8)	25.5(3)
C7	4016(2)	3450(3)	3245.1(8)	27.9(4)
C8	3383(2)	3208(3)	3931.4(8)	28.9(4)
C9	3745(2)	1238(3)	4292.3(9)	36.8(4)

Table 2 Fractional Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Parameters ($Å^2 \times 10^3$) for 2d. U_{eq} is defined as 1/3 of the trace of the orthogonalised U_{IJ} tensor.

Atom	*x*	*y*	*z*	U(eq)
C10	3253(3)	987(4)	4949.4(10)	42.3(5)
C11	2368(2)	2687(4)	5265.8(9)	41.0(5)
C12	1962(3)	4628(4)	4902.0(9)	40.7(5)
C13	2466(2)	4895(3)	4245.7(9)	35.8(4)
C14	1886(3)	2462(5)	5992.0(11)	59.3(7)
C15	1538.8(19)	5632(3)	1800.3(7)	22.4(3)
C16	-443(2)	2587(3)	1905.1(9)	28.9(4)
C17	-530(2)	2273(4)	2649.8(10)	39.5(5)
C18	3776(2)	5013(3)	958.4(8)	23.4(3)
C19	2774(3)	4645(4)	-185.8(8)	38.5(4)
C20	1719(3)	2548(4)	-251.1(10)	47.9(5)

Table 3 Anisotropic Displacement Parameters ($Å^2 \times 10^3$) for 2d. The Anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U_{11}+2hka^*b^*U_{12}+\ldots]$.

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
O1	32.0(6)	42.1(7)	23.7(6)	-1.2(5)	-0.2(4)	2.2(5)
O2	34.0(6)	35.0(7)	32.7(6)	-5.4(5)	7.0(5)	8.9(5)
O3	21.9(5)	21.3(6)	34.4(6)	-3.0(5)	7.2(4)	-1.9(4)
O4	24.2(6)	25.0(7)	50.0(7)	-3.7(5)	10.4(5)	2.8(5)
C1	20.1(7)	19.8(8)	25.4(7)	-0.3(6)	3.3(6)	0.5(6)
C2	25.0(8)	19.8(8)	34.8(8)	1.5(7)	3.3(6)	0.6(6)
C3	25.0(8)	24.5(9)	32.0(8)	-6.5(6)	7.5(6)	-4.8(6)
C4	20.6(7)	32.4(9)	27.9(8)	-5.1(7)	3.5(6)	-0.6(7)
C5	21.7(7)	24.2(8)	25.4(7)	-1.0(6)	2.3(6)	3.6(6)
C6	24.5(7)	26.4(8)	25.7(8)	-1.7(6)	1.7(6)	2.6(6)
C7	26.5(8)	29.0(8)	28.3(8)	0.2(7)	0.3(6)	2.4(7)
C8	26.4(8)	32.1(9)	27.8(8)	3.9(7)	-2.0(6)	-2.3(7)
C9	39.5(10)	34.4(10)	36.0(9)	6.1(8)	-2.2(7)	0.1(8)
C10	44.6(11)	44.3(12)	37.4(10)	16.5(9)	-6.3(8)	-6.0(9)
C11	32.8(9)	60.9(13)	29.0(9)	8.9(9)	-1.1(7)	-11.5(9)
C12	36.3(10)	51.5(12)	35.0(9)	-1.3(9)	7.5(7)	0.1(9)
C13	35.3(9)	39.8(11)	32.6(9)	7.1(8)	4.9(7)	4.6(8)
C14	53.9(13)	93(2)	31.2(10)	12.6(12)	3.9(9)	-19.1(14)
C15	22.6(7)	21.5(8)	23.1(7)	-0.4(6)	1.9(6)	1.5(6)
C16	22.2(8)	27.0(8)	37.9(9)	-3.3(7)	4.3(6)	-5.4(7)
C17	35.8(10)	43.3(12)	40.1(10)	2.9(9)	8.0(8)	-9.3(9)

Table 3 Anisotropic Displacement Parameters ($Å^2×10^3$) for 2d. The Anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U_{11}+2hka^*b^*U_{12}+\ldots]$.

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
C18	23.7(7)	21.6(8)	25.3(7)	0.6(6)	5.0(6)	-3.5(6)
C19	41.0(10)	53.3(12)	21.2(8)	-1.7(8)	3.6(7)	-4.8(9)
C20	51.7(12)	55.2(13)	36.8(10)	-8.4(10)	1.9(9)	-11.2(11)

Table 4 Bond Lengths for 2d.

Atom	Atom	Length/Å	Atom	Atom	Length/Å
O1	C18	1.337(2)	C5	C6	1.506(2)
O1	C19	1.458(2)	C6	C7	1.323(3)
O2	C18	1.197(2)	C7	C8	1.477(2)
O3	C15	1.332(2)	C8	C9	1.391(3)
O3	C16	1.4586(19)	C8	C13	1.388(3)
O4	C15	1.2021(19)	C9	C10	1.386(3)
C1	C2	1.545(2)	C10	C11	1.383(3)
C1	C5	1.570(2)	C11	C12	1.386(3)
C1	C15	1.526(2)	C11	C14	1.514(3)
C1	C18	1.532(2)	C12	C13	1.388(2)
C2	C3	1.506(2)	C16	C17	1.498(2)
C3	C4	1.322(3)	C19	C20	1.486(3)
C4	C5	1.511(2)			

Table 5 Bond Angles for 2d.

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
C18	O1	C19	116.94(14)	C13	C8	C7	122.90(16)
C15	O3	C16	116.88(12)	C13	C8	C9	117.69(16)
C2	C1	C5	104.89(13)	C10	C9	C8	121.29(19)
C15	C1	C2	112.88(13)	C11	C10	C9	120.90(19)
C15	C1	C5	111.46(12)	C10	C11	C12	118.00(17)
C15	C1	C18	108.78(12)	C10	C11	C14	121.2(2)
C18	C1	C2	109.45(13)	C12	C11	C14	120.8(2)
C18	C1	C5	109.29(12)	C11	C12	C13	121.29(19)
C3	C2	C1	102.46(13)	C12	C13	C8	120.79(18)
C4	C3	C2	112.07(15)	O3	C15	C1	110.06(13)
C3	C4	C5	112.66(14)	O4	C15	O3	124.89(14)
C4	C5	C1	101.25(13)	O4	C15	C1	125.03(15)
C6	C5	C1	113.99(12)	O3	C16	C17	111.37(13)

Table 5 Bond Angles for 2d.

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
C6	C5	C4	111.63(13)	O1	C18	C1	109.57(13)
C7	C6	C5	123.51(15)	O2	C18	O1	124.76(14)
C6	C7	C8	127.12(17)	O2	C18	C1	125.64(14)
C9	C8	C7	119.40(17)	O1	C19	C20	110.77(15)

Table 6 Torsion Angles for 2d.

A	B	C	D	Angle/°	A	B	C	D	Angle/°
C1	C2	C3	C4	-15.51(18)	C9	C8	C13	C12	1.2(3)
C1	C5	C6	C7	121.89(17)	C9	C10	C11	C12	1.2(3)
C2	C1	C5	C4	-24.40(14)	C9	C10	C11	C14	-177.63(19)
C2	C1	C5	C6	95.60(15)	C10	C11	C12	C13	-1.7(3)
C2	C1	C15	O3	167.65(13)	C11	C12	C13	C8	0.5(3)
C2	C1	C15	O4	-13.9(2)	C13	C8	C9	C10	-1.8(3)
C2	C1	C18	O1	-66.36(16)	C14	C11	C12	C13	177.09(19)
C2	C1	C18	O2	112.08(18)	C15	O3	C16	C17	-80.28(19)
C2	C3	C4	C5	-0.56(19)	C15	C1	C2	C3	145.87(13)
C3	C4	C5	C1	16.04(17)	C15	C1	C5	C4	-146.86(13)
C3	C4	C5	C6	-105.62(16)	C15	C1	C5	C6	-26.86(18)
C4	C5	C6	C7	-124.14(17)	C15	C1	C18	O1	57.38(16)
C5	C1	C2	C3	24.33(15)	C15	C1	C18	O2	-124.18(17)
C5	C1	C15	O3	-74.60(16)	C16	O3	C15	O4	-0.9(2)
C5	C1	C15	O4	103.80(18)	C16	O3	C15	C1	177.52(12)
C5	C1	C18	O1	179.28(13)	C18	O1	C19	C20	90.87(19)
C5	C1	C18	O2	-2.3(2)	C18	C1	C2	C3	-92.83(15)
C5	C6	C7	C8	178.34(15)	C18	C1	C5	C4	92.87(14)
C6	C7	C8	C9	-168.95(17)	C18	C1	C5	C6	-147.13(13)
C6	C7	C8	C13	9.4(3)	C18	C1	C15	O3	45.97(17)
C7	C8	C9	C10	176.71(17)	C18	C1	C15	O4	-135.63(16)
C7	C8	C13	C12	-177.20(17)	C19	O1	C18	O2	2.8(2)
C8	C9	C10	C11	0.6(3)	C19	O1	C18	C1	-178.70(14)

Table 7 Hydrogen Atom Coordinates (Å×10^4) and Isotropic Displacement Parameters (Å^2×10^3) for 2d.

Atom	*x*	*y*	*z*	U(eq)
H2A	3552.13	9245.43	1081.41	32

Table 7 Hydrogen Atom Coordinates (Å×10^4) and Isotropic Displacement Parameters (Å^2×10^3) for 2d.

Atom	*x*	*y*	*z*	U(eq)
H2B	2919.63	9631.91	1817.72	32
H3	6221.53	10298.78	1731.21	32
H4	7222.31	7083.68	2330.82	32
H5	5218.79	3939.93	2066.79	28
H6	3554.39	6620.42	3051.4	31
H7	4460.43	2152.97	3052.07	34
H9	4330.3	65.39	4088.59	44
H10	3520.26	-343.28	5180.69	51
H12	1340.3	5774.38	5101.56	49
H13	2185.28	6219.54	4013.71	43
H14A	2853.84	2893.82	6282.32	89
H14B	1578.58	921.62	6081.36	89
H14C	919.25	3429.32	6072.73	89
H16A	-673.34	1154.98	1680.94	35
H16B	-1328.81	3652.47	1751.34	35
H17A	-1648.74	1697.09	2752.32	59
H17B	-342.66	3699.99	2871.53	59
H17C	347.24	1220.98	2803	59
H19A	3978.42	4289.35	-254.68	46
H19B	2388.54	5719.18	-528.86	46
H20A	1781.76	1960.89	-699.17	72
H20B	536.28	2887.66	-162.32	72
H20C	2157.35	1442.96	65.95	72

checkCIF/PLATON report

Structure factors have been supplied for datablock(s) 1-67-1

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No syntax errors found. CIF dictionary Interpreting this report

Datablock: 1-67-1

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

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                  alpha=90         beta=92.4788(10)      gamma=90
Temperature:      150 K

                  Calculated                  Reported
Volume            908.736(17)                 908.734(17)
Space group       P 21                        P 1 21 1
Hall group        P 2yb                       P 2yb
Moiety formula    C20 H24 O4                  C20 H24 O4
Sum formula       C20 H24 O4                  C20 H24 O4
Mr                328.39                      328.39
Dx,g cm-3         1.200                       1.200
Z                 2                           2
Mu (mm-1)         0.667                       0.667
F000              352.0                       352.0
F000'             353.08
h,k,lmax          9,7,24                      9,7,24
Nref              3546[ 1956]                 3229
Tmin,Tmax         0.905,0.935                 0.537,1.000
Tmin'             0.905

Correction method= # Reported T Limits: Tmin=0.537 Tmax=1.000
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Data completeness= 1.65/0.91        Theta(max)= 71.469

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S = 1.077                  Npar= 221
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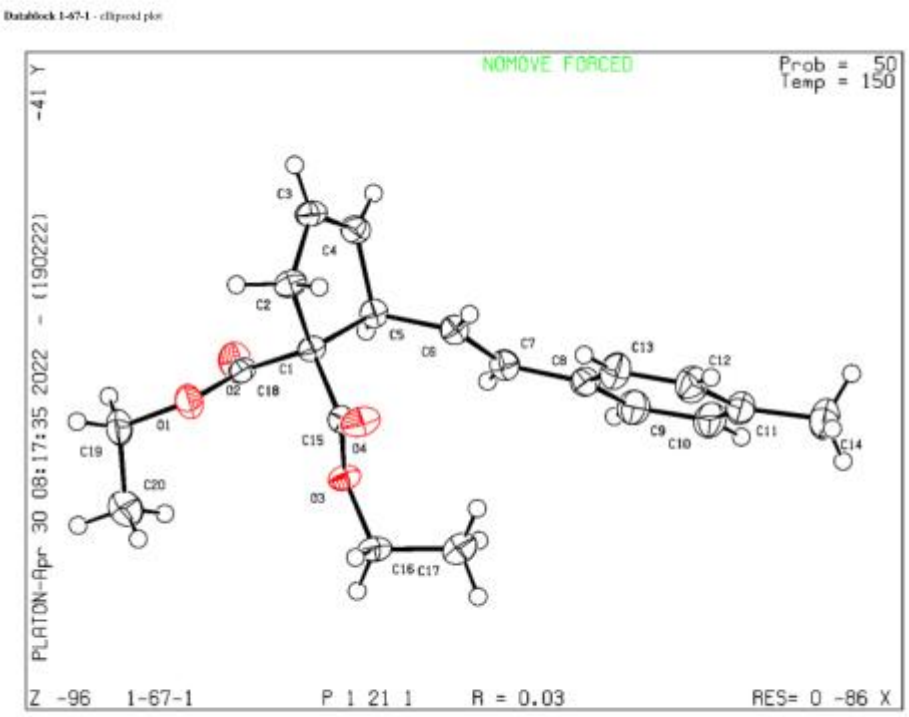

10. References

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2. S. Einaru, K. Shitamichi, T. Nagano, A. Matsumoto, K. Asano, and S. Matsubara, *Angew. Chem. Int. Ed.* 2018, **57**, 13863–13867.