Supporting Information

Radical Cation Cyclopropanations via Chromium Photooxidative Catalysis

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Materials and Methods

Cr(III) catalysts were synthesized as described by Shores and Damrauer.[1] $Ru(bpz)_3(PF_6)_2$ and $Ru(bpy)_3Cl_2$ were purchased from Sigma-Aldrich. $Ru(bpy)_3(PF_6)_2$ and methyl viologen bis(hexafluorophosphate) were prepared according to the procedures by Yoon and coworkers.[2] All solvents, excluding nitromethane and 1,2-dichloroethane, were purified by passing through activated alumina columns. All reagents were used as received unless otherwise noted. Commercially available chemicals were purchased from Alfa Aesar (Ward Hill, MA), Sigma-Aldrich (St. Louis, MO), Oakwood Products (West Columbia, SC), Strem (Newburport, MA), and TCI America (Portland, OR). Qualitative TLC analysis was performed on 250 mm thick, 60 Å, glass backed, F254 silica (Silicycle, Quebec City, Canada). Visualization was accomplished with UV light and exposure to *p*-anisaldehyde or $KMnO_4$ stain solutions followed by heating. Flash chromatography was performed using Silicycle silica gel (230-400 mesh). Reactions under near-UV irradiation (NUV) were performed in a Luzchem photoreactor (LZC-ORG) equipped with 10 lamps of wavelengths 419, 350, and 300 nm. Irradiation with visible light was performed in a closed box using a 23 W compact fluorescent light bulb (EcoSmart 23 W bright white CFL spiral light bulb, 1600 lumens). The temperature of this closed box when operating was measured at approximately 35-40 °C. Cycloadditions using all modes of irradiation were performed using borosilicate vials. ^{1}H NMR spectra were acquired on a Varian Mercury Plus 400 MHz NMR and are reported relative to $SiMe_4$ (δ 0.00). ^{13}C NMR spectra were acquired on a Varian Mercury Plus NMR (at 100 MHz) or a Varian Unity Inova NMR (at 125 MHz) and are reported relative to $SiMe_4$ (δ 0.0). IR spectra were obtained on a Nicolet 380 FT-IR. High-resolution mass spectrometry data was acquired by the University of Georgia Proteomics and Mass Spectrometry Core Facility on a Bruker Esquire 3000 Plus Ion Trap Spectrophotometer.

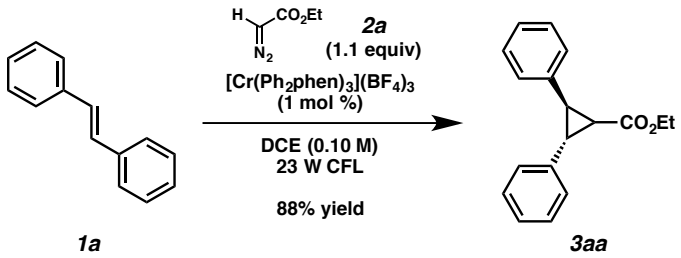
Safety/Hazards

Diazo compounds are generally toxic, irritants, and are documented to have numerous physical and health hazards. Care should be taken when handling and synthesizing diazo compounds, and the proper personal protective equipment should be utilized.

Cyclopropanations - Reaction Scope

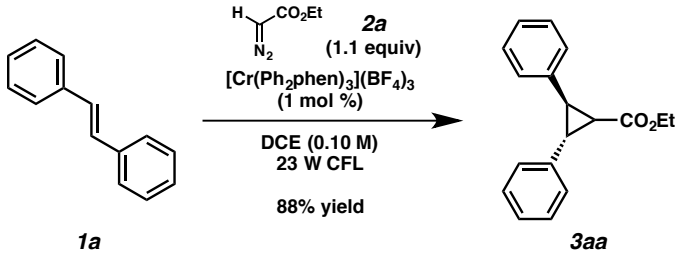
General Procedure for the photocatalyzed cyclopropanation: A solution of (*E*)-alkene (1 equiv), diazo species (1.1-2.2 equiv), and $[Cr(Ph_2phen)_3](BF_4)_3$ (1-2 mol %) in DCE (0.10 M) was prepared in a flame-dried borosilicate vial open to air. The vial was then capped and placed on a stir plate in a closed box lined with aluminum foil and equipped with a 23 W compact fluorescent light bulb. The reaction mixture was irradiated with stirring until consumption of the alkene was complete, as determined by TLC. Once finished, the reaction mixture was concentrated via rotary evaporation and purified by flash column chromatography to afford the desired product.

Alkene Scope

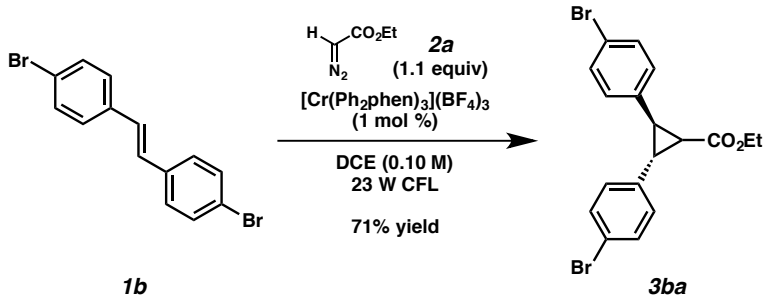


Cyclopropane 3aa. Prepared according to the *General Procedure* using 18.0 mg *trans*-stilbene (0.0999 mmol), 14.7 mg ethyl diazoacetate (85% wt. solution in CH_2Cl_2, 0.110 mmol), 1.3 mg $[Cr(Ph_2phen)_3](BF_4)_3$ (0.999 μmol), and 1.0 mL DCE. The reaction mixture was irradiated for 14 h. The crude product was purified by flash chromatography (100% hexanes → 19:1 hexanes/acetone eluent) to afford cyclopropane **3aa**[3] (23.5 mg, 88% yield) as a colorless oil.
TLC: R_f = 0.32 in 19:1 hexanes/acetone, visualized by UV.
^{1}H NMR (400 MHz; $CDCl_3$): δ 7.36-7.21 (comp. m, 10H), 3.95 (dq, *J* = 7.2, 1.8 Hz, 2H), 3.22 (dd, *J* = 7.0, 5.2 Hz, 1H), 2.94 (dd, *J* = 9.4, 7.0 Hz, 1H), 2.42 (dd, *J* = 9.4, 5.2 Hz, 1H), 1.04 (t, *J* = 7.2 Hz, 3H).
^{13}C NMR (100 MHz; $CDCl_3$): δ 170.1, 139.8, 136.3, 129.3, 128.8, 128.2, 127.1, 126.8, 60.6, 34.6, 31.4, 29.4, 14.2.
IR (ATR, neat): 3050, 3997, 1729, 1948, 1177, 752, 696 cm^{-1}.
HRMS (ESI+): *m/z* calc'd for $(M+H)^+$ $[C_{18}H_{18}O_2 + H]^+$: 267.1380 found 267.1381.

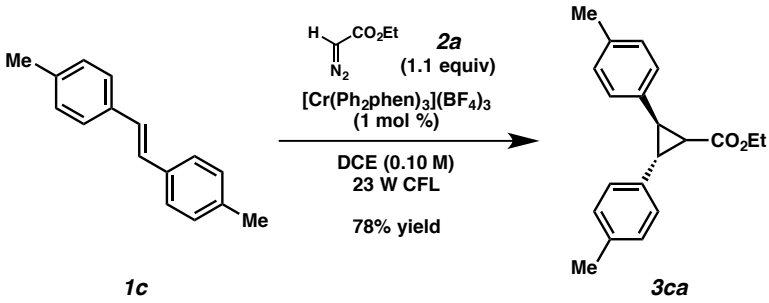
(Gram Scale Experiment)



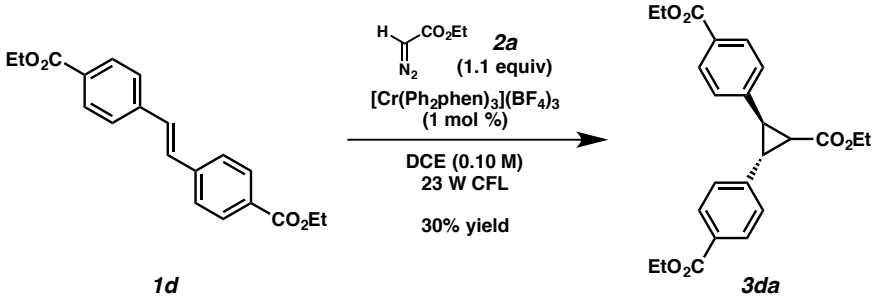
Inside a flame-dried round bottom flask open to air, a solution containing 1.00 g *trans*-stilbene (5.55 mmol), 820 mg ethyl diazoacetate (85% solution in CH_2Cl_2, 6.11 mmol), and 72.7 mg $[Cr(Ph_2phen)_3](BF_4)_3$ (0.0555 mmol) in 56 mL DCE was prepared. The flask was then fitted with a rubber septa and needle outlet open to air and placed in a closed box, lined with aluminum foil, and equipped with a 23 W compact fluorescent light bulb. The reaction mixture was irradiated with stirring until consumption of the alkene was complete (43 h), as determined by TLC. The reaction was concentrated via rotary evaporation, and the crude product was purified by flash chromatography (100% hexanes → 19:1 hexanes/acetone eluent) to afford *trans*-cyclopropane **3aa** (1.30 g, 88% yield) as a colorless oil.



Cyclopropane 3ba. Prepared according to the *General Procedure* using 34.0 mg *trans*-4,4'-dibromostilbene (0.101 mmol), 15.0 mg ethyl diazoacetate (85% wt. solution in CH_2Cl_2, 0.111 mmol), 1.3 mg $[Cr(Ph_2phen)_3](BF_4)_3$ (1.01 μmol), and 1.0 mL DCE. The reaction mixture was irradiated for 14 h. The crude product was purified by flash chromatography (100% hexanes → 9:1 hexanes/Et_2O eluent) to afford cyclopropane **3ba** (30.3 mg, 71% yield) as a white solid.
TLC: R_f = 0.34 in 9:1 hexanes/Et_2O, visualized by UV.
^{1}H NMR (400 MHz; $CDCl_3$): δ 7.45 (d, *J* = 8.4 Hz, 2H), 7.43 (d, *J* = 8.4 Hz, 2H) 7.20 (d, *J* = 8.4 Hz, 2H), 7.10 (d, *J* = 8.4 Hz, 2H), 3.98 (dq, *J* = 7.2, 2.4 Hz, 2H), 3.12 (dd, *J* = 7.0, 5.2 Hz, 1H), 2.81 (dd, *J* = 9.6, 7.0 Hz, 1H), 2.38 (dd, *J* = 9.6, 5.2 Hz, 1H), 1.09 (t, *J* = 7.2 Hz, 3H).
^{13}C NMR (100 MHz; $CDCl_3$): δ 169.6, 138.3, 134.9, 131.9, 131.4, 130.9, 128.5, 121.1, 120.7, 60.9, 33.8, 31.3, 28.9, 14.3.
IR (ATR, neat): 1724, 1490, 1178, 1073, 1010, 817 cm^{-1}.
HRMS (ESI+): *m/z* calc'd for $(M+H)^+$ $[C_{18}H_{16}Br_2O_2 + H]^+$: 424.9569, found 424.9572.

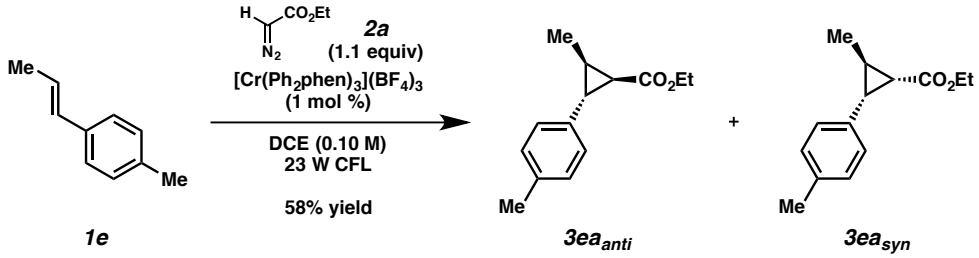


Cyclopropane 3ca. Prepared according to the *General Procedure* using 21.1 mg 4,4'-dimethyl-*trans*-stilbene (0.101 mmol), 15.0 mg ethyl diazoacetate (85% wt. solution in CH_2Cl_2, 0.111 mmol), 1.3 mg $[Cr(Ph_2phen)_3](BF_4)_3$ (1.01 μmol), and 1.0 mL DCE. The reaction mixture was irradiated for 24 h. The crude product was purified by flash chromatography (100% hexanes → 9:1 hexanes/Et_2O eluent) to afford cyclopropane **3ca** (23.3 mg, 78% yield) as a colorless oil.
TLC: R_f = 0.37 in 9:1 hexanes/Et_2O, visualized by UV.
Spectroscopic data were in accordance with the published values.[3]

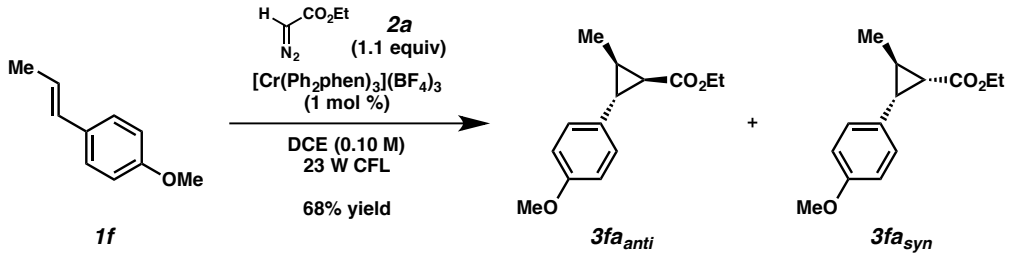


Cyclopropane 3da. Prepared according to the *General Procedure* using 32.0 mg *E*-alkene **1d** (0.0986 mmol), 14.6 mg ethyl diazoacetate (85% wt. solution in CH_2Cl_2, 0.109 mmol), 1.3 mg $[Cr(Ph_2phen)_3](BF_4)_3$ (0.986 μmol), and 1.0 mL DCE. The

reaction mixture was irradiated for 72 h. The crude product was purified by flash chromatography (3:2 hexanes/Et_2O as eluent) to afford cyclopropane **3da** (12.0 mg, 30% yield) as a colorless oil.
TLC: R_f = 0.33 in 3:2 hexanes/Et_2O, visualized by UV.
^{1}H NMR (400 MHz; $CDCl_3$): δ 8.01 (d, *J* = 8.4 Hz, 2H), 7.99 (d, *J* = 8.4 Hz, 2H), 7.41 (d, *J* = 8.0 Hz, 2H), 7.30 (d, *J* = 8.0 Hz, 2H), 4.40-4.34 (comp. m, 4H), 3.96 (q, *J* = 7.0 Hz, 1H), 3.28 (dd, *J* = 7.0, 5.2 Hz, 1H), 2.98 (dd, *J* = 9.8, 7.0 Hz, 1H), 2.52 (dd, *J* = 9.8, 5.2 Hz, 1H), 1.40 (t, *J* = 7.2 Hz, 3H), 1.39 (t, *J* = 7.2 Hz, 3H), 1.06 (t, *J* = 7.0 Hz, 3H).
^{13}C NMR (100 MHz; $CDCl_3$): δ 169.4, 166.5, 166.4, 144.5, 141.0, 130.1, 129.6, 129.4, 129.3, 129.2, 126.6, 61.13, 61.06, 61.0, 34.7, 32.0, 29.5, 14.5, 14.3.
IR (ATR, neat): 2984, 1717, 1275, 1180, 1104, 1020 cm^{-1}.
HRMS (ESI+): *m/z* calc'd for $(M+H)^+$ $[C_{24}H_{26}O_6 + H]^+$: 411.1802, found 411.1804.

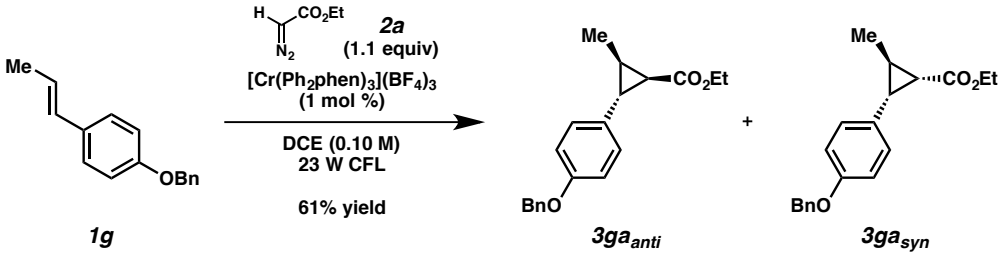


Cyclopropane 3ea. Prepared according to the *General Procedure* using 13.5 mg *E*-alkene **1e** (0.102 mmol), 15.1 mg ethyl diazoacetate (85% wt. solution in CH_2Cl_2, 0.112 mmol), 1.3 mg $[Cr(Ph_2phen)_3](BF_4)_3$ (1.02 μmol), and 1.0 mL DCE. The reaction mixture was irradiated for 24 h. Diastereomeric ratio (1:1.1 anti/syn) was determined by ^{1}H NMR analysis of the crude mixture. The crude product was purified by flash chromatography (100% hexanes → 19:1 hexanes/EtOAc eluent) to afford *trans*-cyclopropane **3ea** (13.0 mg, 58% yield) as a colorless oil.
TLC: R_f = 0.36 in 9:1 hexanes/Et_2O, visualized by UV. Stained purple by *p*-anisaldehyde.
^{1}H NMR (400 MHz; $CDCl_3$): Major (syn): δ 7.12 (d, *J* = 8.2 Hz, 2H), 7.05 (d, *J* = 8.2 Hz, 2H), 4.16 (dq, *J* = 7.2, 4.4 Hz, 2H), 2.34-2.33 (m, 1H), 2.29 (s, 3H), 2.04 (app. quintet, *J* = 6.0 Hz, 1H), 1.78 (dd, *J* = 9.2, 5.2 Hz, 1H), 1.26 (d, *J* = 6.0 Hz, 3H), 1.02 (t, *J* = 7.2 Hz, 3H).
Minor (anti): δ 6.97 (d, *J* = 7.8 Hz, 2H), 7.08 (d, *J* = 7.8 Hz, 2H), 3.89 (dq, *J* = 7.2, 2.8 Hz, 2H), 2.37 (dd, *J* = 6.4, 5.2 Hz, 1H), 2.31 (s, 3H), 1.97 (dd, *J* = 9.2, 5.2 Hz, 1H), 1.67-1.62 (comp. m, 1H), 1.34 (d, *J* = 6.0 Hz, 3H), 1.28 (t, *J* = 7.2 Hz, 3H).
^{13}C NMR (125 MHz; $CDCl_3$): δ 171.9, 171.2, 137.7, 136.1, 133.7, 129.4, 129.2, 129.1, 128.7, 126.1, 60.6, 60.2, 34.1, 32.2, 30.1, 29.4, 25.6, 21.2, 21.1, 19.9, 17.9, 14.5, 14.2, 12.2.
IR (ATR, neat): 2981, 1731, 1439, 1375, 1181, 1163, 1047 cm^{-1}.
HRMS (ESI+): *m/z* calc'd for $(M + Na)^+$ $[C_{14}H_{18}O_2 + Na]^+$: 241.1199, found 241.1200.

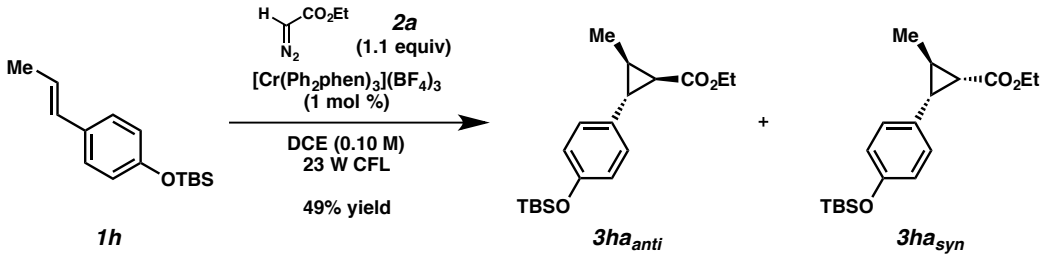


Cyclopropane 3fa. Prepared according to the *General Procedure* using 14.7 mg *trans*-anethole (0.0992 mmol), 14.6 mg ethyl diazoacetate (85% wt. solution in CH_2Cl_2, 0.109 mmol), 1.3 mg $[Cr(Ph_2phen)_3](BF_4)_3$ (0.992 μmol), and 1.0 mL DCE. The reaction mixture was irradiated for 25 h. Diastereomeric ratio (1.1:1 anti/syn) was determined by ^{1}H NMR analysis of the crude mixture. The crude product was purified by flash chromatography (100% hexanes → 9:1 hexanes/EtOAc eluent) to afford cyclopropane **3fa** (15.8 mg, 68% yield) as a colorless oil.
TLC: R_f = 0.45 in 9:1 hexanes/EtOAc, visualized by UV.
^{1}H NMR (400 MHz; $CDCl_3$): Major (anti): δ 7.01 (d, *J* = 8.8 Hz, 2H), 6.82 (d, *J* = 8.8 Hz, 2H), 4.17 (dq, *J* = 7.2, 1.6 Hz, 2H), 3.78 (s, 3H), 2.36 (dd, *J* = 6.2, 5.2 Hz, 1H), 1.93 (dd, *J* = 9.0, 5.2 Hz, 1H), 1.65-1.59 (comp. m, 1H), 1.34 (d, *J* = 6.4 Hz,

3H), 1.28 (t, *J* = 7.2 Hz, 3H).
Minor (syn): δ 7.16 (d, *J* = 8.8 Hz, 2H), 6.79 (d, *J* = 8.8 Hz, 2H), 3.89 (dq, *J* = 7.2, 1.2 Hz, 2H), 3.77 (s, 3H), 2.29 (dd, *J* = 8.8, 7.2 Hz, 1H), 2.02 (app. sextet, *J* = 6.0 Hz, 1H), 1.77 (dd, *J* = 8.8, 5.2 Hz, 1H), 1.26 (d, *J* = 6.0 Hz, 3H), 1.03 (t, *J* = 7.2 Hz, 3H).
^{13}C NMR (100 MHz; $CDCl_3$): δ 171.9, 171.1, 158.32, 158.27, 132.7, 130.2, 128.8, 127.3, 114.0, 113.4, 60.5, 60.2, 55.4, 55.3, 33.7, 31.9, 30.1, 29.2, 25.3, 20.0, 17.9, 14.5, 14.3, 12.1.
IR (ATR, neat): 2959, 1722, 1518, 1246, 1163, 1035, 829 cm^{-1}.
HRMS (ESI+): *m/z* calc'd for $(M + Na)^+$ $[C_{14}H_{18}O_3 + Na]^+$: 257.1154, found 257.1149.

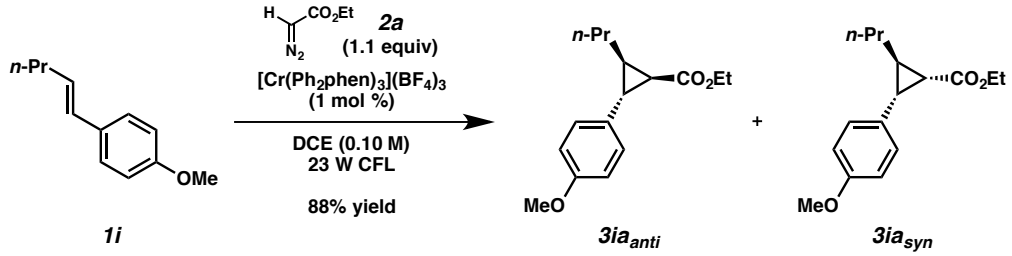


Cyclopropane 3ga. Prepared with a slight modification to the *General Procedure* using 22.5 mg *E*-alkene **1g** (0.100 mmol), 14.8 mg ethyl diazoacetate (85% wt. solution in CH_2Cl_2, 0.110 mmol), 1.3 mg $[Cr(Ph_2phen)_3](BF_4)_3$ (1.00 μmol), and 1.0 mL DCE. The reaction mixture was irradiated for 42 h *with a needle outlet open to air*. Diastereomeric ratio (~1:1 anti/syn) was determined by ^{1}H NMR analysis of the crude mixture. The crude product was purified by flash chromatography (100% hexanes → 9:1 hexanes/EtOAc eluent) to afford cyclopropane **3ga** (19.1 mg, 61% yield) as a white solid.
TLC: R_f = 0.44 in 9:1 hexanes/EtOAc, visualized by UV.
^{1}H NMR (400 MHz; $CDCl_3$): Anti: δ 7.43-7.30 (comp. m, 5H), 7.01 (d, *J* = 8.4 Hz, 2H), 6.89 (d, *J* = 8.4 Hz, 2H), 5.04 (s, 2H), 4.17 (qd, *J* = 7.0, 2.0 Hz, 2H), 2.37 (dd, *J* = 6.4, 5.0 Hz, 1H), 1.94 (dd, *J* = 9.2, 5.0 Hz, 1H), 1.65-1.59 (comp. m, 1H), 1.34 (d, *J* = 6.0 Hz, 3H), 1.29 (t, *J* = 7.0 Hz, 3H).
Syn: δ 7.43-7.30 (comp. m, 5H), 7.16 (d, *J* = 8.4 Hz, 2H), 6.87 (d, *J* = 8.4 Hz, 2H), 5.03 (s, 3H), 3.89 (qd, *J* = 7.2, 1.2 Hz, 2H), 2.30 (dd, *J* = 9.2, 7.0 Hz, 1H), 2.03 (app. sextet, *J* = 6.0 Hz, 1H), 1.78 (dd, *J* = 9.2, 5.2 Hz, 1H), 1.26 (d, *J* = 6.0 Hz, 3H), 1.02 (t, *J* = 7.2 Hz, 3H).
^{13}C NMR (100 MHz; $CDCl_3$): δ 171.9, 171.1, 157.6, 157.5, 137.3, 137.2, 133.0, 130.2, 129.2, 128.70, 128.67, 128.1, 128.0, 127.6, 127.5, 127.3, 115.0, 114.4, 70.2, 70.1, 60.5, 60.2, 33.8, 31.9, 30.1, 29.3, 25.3, 20.0, 17.9, 14.5, 14.3, 12.1.
IR (ATR, neat): 2980, 1721, 1514, 1454, 1371, 1242, 1175, 1026 cm^{-1}.
HRMS (ESI+): *m/z* calc'd for $(M+H)^+$ $[C_{20}H_{22}O_3 + H]^+$: 311.1647, found 311.1643.



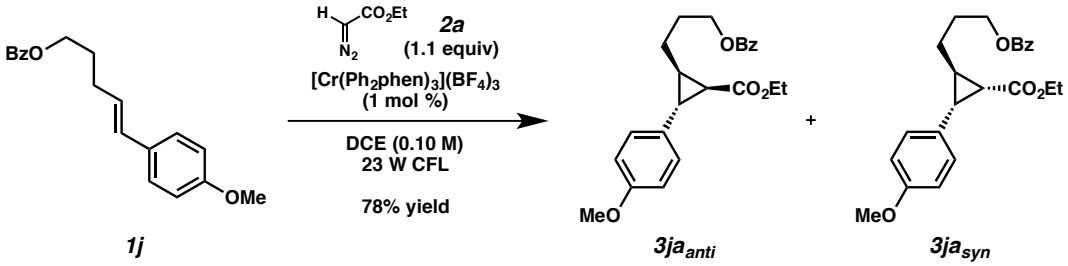
Cyclopropane 3ha. Prepared according to the *General Procedure* using 26.4 mg *E*-alkene **1h** (0.106 mmol), 15.7 mg ethyl diazoacetate (85% wt. solution in CH_2Cl_2, 0.117 mmol), 1.4 mg $[Cr(Ph_2phen)_3](BF_4)_3$ (1.06 μmol), and 1.1 mL DCE. The reaction mixture was irradiated for 25 h. Diastereomeric ratio (1.2:1 anti/syn) was determined by ^{1}H NMR analysis of the crude mixture. The crude product was purified by flash chromatography (100% hexanes → 9:1 hexanes/Et_2O eluent) to afford cyclopropane **3ha** (17.4 mg, 49% yield) as a colorless oil.
TLC: R_f = 0.40 in 9:1 hexanes/Et_2O, visualized by UV.
^{1}H NMR (400 MHz; $CDCl_3$): Major (anti): δ 6.93 (d, *J* = 7.8 Hz, 2H), 6.74 (d, *J* = 7.8 Hz, 2H), 4.16 (qd, *J* = 7.2, 1.6 Hz, 2H), 2.34 (dd, *J* = 6.2, 5.1 Hz, 1H), 1.93 (dd, *J* = 9.2, 5.1 Hz, 1H), 1.64-1.59 (comp. m, 1H), 1.33 (d, *J* = 6.0 Hz, 3H), 0.98 (t, *J* = 7.2 Hz, 3H), 0.98 (s, 9H), 0.17 (s, 6H).

Minor (syn): δ 7.09 (d, *J* = 8.4 Hz, 2H), 6.72 (d, *J* = 8.4 Hz, 2H), 3.86 (qd, *J* = 7.2, 3.0 Hz, 2H), 2.27 (dd, *J* = 9.2, 7.0 Hz, 1H), 2.02 (app. sextet, *J* = 6.0 Hz, 1H), 1.76 (dd, *J* = 9.2, 5.2 Hz, 1H), 1.28 (t, *J* = 7.2 Hz, 3H), 1.24 (d, *J* = 6.0 Hz, 3H), 0.96 (s, 9H), 0.16 (s, 6H).
^{13}C NMR (100 MHz; $CDCl_3$): δ 171.9, 171.0, 154.4, 154.2, 133.3, 130.1, 129.5, 127.1, 120.2, 119.6, 60.5, 60.1, 33.8, 32.0, 30.4, 29.4, 25.8, 25.7, 25.4, 19.7, 18.4, 17.9, 14.5, 14.3, 12.2, -4.3.
IR (ATR, neat): 2957, 2856, 1724, 1512, 1254, 1175, 914, 837, 781 cm^{-1}.
HRMS (ESI+): *m/z* calc'd for $(M + H)^+$ $[C_{19}H_{30}O_3Si + H]^+$: 335.2037, found 335.2033.



1i *3ia$_{anti}$* *3ia$_{syn}$*

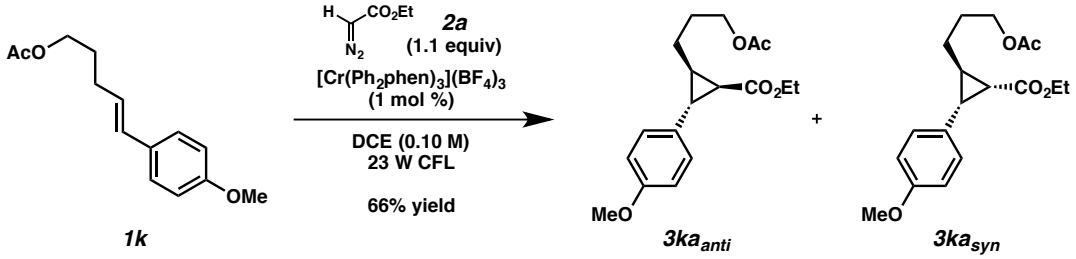
Cyclopropane 3ia. Prepared according to the *General Procedure* using 18.4 mg *E*-alkene **1i** (0.104 mmol), 15.4 mg ethyl diazoacetate (85% wt. solution in CH_2Cl_2, 0.115 mmol), 1.4 mg $[Cr(Ph_2phen)_3](BF_4)_3$ (1.04 μmol), and 1.0 mL DCE. The reaction mixture was irradiated for 14 h. Diastereomeric ratio (1.2:1 anti/syn) was determined by ^{1}H NMR analysis of the crude mixture. The crude product was purified by flash chromatography (100% hexanes → 9:1 hexanes/EtOAc eluent) to afford cyclopropane **3ia** (24.0 mg, 88% yield) as a colorless oil.
TLC: R_f = 0.45 in 9:1 hexanes/EtOAc, visualized by UV.
^{1}H NMR (400 MHz; $CDCl_3$): Major (anti): δ 7.02 (d, *J* = 8.6 Hz, 2H), 6.81 (d, *J* = 8.6 Hz, 2H), 4.16 (q, *J* = 7.2 Hz, 2H), 3.78 (s, 3H), 2.41 (dd, *J* = 6.4, 5.1 Hz, 1H), 1.94 (dd, *J* = 9.0, 5.1 Hz, 1H), 1.74-1.34 (comp. m, 5H), 1.28 (t, *J* = 7.2 Hz, 3H), 0.93 (t, *J* = 7.2 Hz, 3H).
Minor (syn): δ 7.16 (d, *J* = 8.2 Hz, 2H), 6.80 (d, *J* = 8.2 Hz, 2H), 3.90 (qd, *J* = 7.2, 1.2 Hz, 2H), 3.77 (s, 3H), 2.31 (dd, *J* = 9.2, 7.0 Hz, 1H), 2.01-1.98 (comp. m, 1H), 1.79 (dd, *J* = 9.2, 4.8 Hz, 1H), 1.74-1.34 (comp. m, 4H), 1.03 (t, *J* = 7.2 Hz, 3H), 0.98 (t, *J* = 7.2 Hz, 3H).
^{13}C NMR (100 MHz; $CDCl_3$): δ 172.1, 171.2, 158.34, 158.27, 132.8, 130.3, 129.0, 127.4, 114.0, 113.4, 60.5, 60.2, 55.4, 55.3, 35.1, 32.7, 31.1, 31.0, 29.0, 28.9, 28.6, 25.6, 22.8, 22.3, 14.5, 14.3, 14.03, 13.96.
IR (ATR, neat): 2959, 1721, 1516, 1246, 1175, 1036, 843 cm^{-1}.
HRMS (ESI+): *m/z* calc'd for $(M+H)^+$ $[C_{16}H_{22}O_3 + H]^+$: 263.1642, found 262.1638.



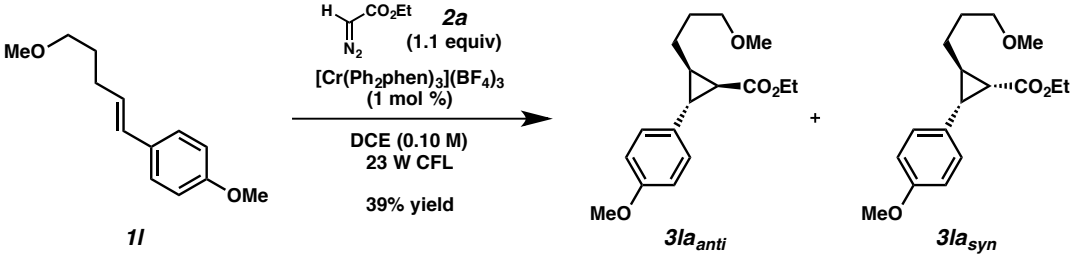
1j *3ja$_{anti}$* *3ja$_{syn}$*

Cyclopropane 3ja. Prepared according to the *General Procedure* using 24.0 mg *E*-alkene **1j** (0.0810 mmol), 12.0 mg ethyl diazoacetate (85% wt. solution in CH_2Cl_2, 0.0891 mmol), 1.1 mg $[Cr(Ph_2phen)_3](BF_4)_3$ (0.810 μmol), and 0.8 mL DCE. The reaction mixture was irradiated for 9 h. Diastereomeric ratio (1.2:1 anti/syn) was determined by ^{1}H NMR analysis of the crude mixture. The crude product was purified by flash chromatography (100% hexanes → 4:1 hexanes/EtOAc eluent) to afford cyclopropane **3ja** (24.1 mg, 78% yield) as a colorless oil.
TLC: R_f = 0.47 in 4:1 hexanes/EtOAc, visualized by UV.
^{1}H NMR (400 MHz; $CDCl_3$): Major (anti): δ 8.05 (d, *J* = 7.2 Hz, 2H), 7.58-7.54 (m, 1H), 7.47-7.42 (m, 2H), 7.02 (d, *J* = 8.8 Hz, 2H), 6.81 (d, *J* = 8.8 Hz, 2H), 4.39 (t, *J* = 6.4 Hz, 2H), 4.15 (q, *J* = 7.2 Hz, 2H), 3.78 (s, 3H), 2.45 (dd, *J* = 6.4, 5.6 Hz, 1H), 2.10-1.52 (comp. m, 6H), 1.27 (t, *J* = 7.2 Hz, 3H).
Minor (syn): δ 8.05 (d, *J* = 7.2 Hz, 2H), 7.58-7.54 (m, 1H), 7.47-7.42 (m, 2H), 7.16 (d, *J* = 8.2 Hz, 2H), 6.79 (d, *J* = 8.2 Hz,

2H), 4.35 (t, *J* = 5.8 Hz, 2H), 3.90 (qd, *J* = 7.2, 0.8 Hz, 2H), 3.77 (s, 3H), 2.36 (dd, *J* = 9.2, 7.0 Hz, 1H), 2.10-1.52 (comp. m, 6H), 1.02 (t, *J* = 7.2 Hz, 3H).
^{13}C NMR (100 MHz; $CDCl_3$): δ 171.9, 170.9, 166.7, 158.45, 158.38, 133.1, 133.0, 132.3, 130.7, 130.5, 130.4, 130.2, 129.7, 128.50, 128.46, 127.4, 114.1, 113.5, 97.5, 64.63, 64.58, 60.7, 60.3, 55.5, 55.3, 32.6, 31.1, 30.6, 29.6, 29.0, 28.7, 28.53, 28.46, 25.1, 23.6, 14.5, 14.3, 11.4.
IR (ATR, neat): 2935, 1717, 1515, 1452, 1272, 1247, 1175, 1111, 1026, 830, 711 cm^{-1}.
HRMS (ESI+): *m/z* calc'd for $(M+H)^+$ $[C_{23}H_{26}O_5 + H]^+$: 383.1853, found 383.1847.

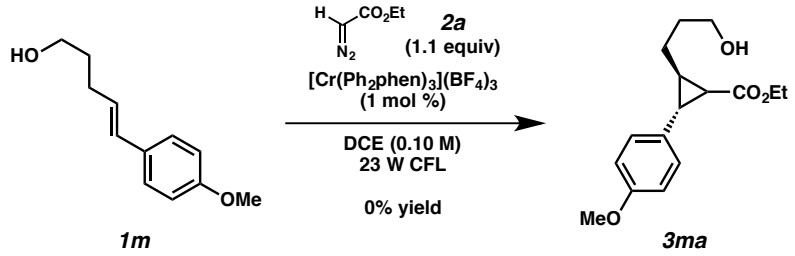


Cyclopropane 3ka. Prepared according to the *General Procedure* using 41.5 mg *E*-alkene **1k** (0.177 mmol), 26.1 mg ethyl diazoacetate (85% wt. solution in CH_2Cl_2, 0.195 mmol), 2.3 mg $[Cr(Ph_2phen)_3](BF_4)_3$ (1.77 μmol), and 1.8 mL DCE. The reaction mixture was irradiated for 48 h. Diastereomeric ratio (1.2:1 anti/syn) was determined by ^{1}H NMR analysis of the crude mixture. The crude product was purified by flash chromatography (1:1 hexanes/Et_2O eluent) to afford cyclopropane **3ka** (37.6 mg, 66% yield) as a colorless oil.
TLC: R_f = 0.43 in 1:1 hexanes/Et_2O, visualized by UV.
^{1}H NMR (400 MHz; $CDCl_3$): Major (anti): δ 7.01 (d, *J* = 8.6 Hz, 2H), 6.82 (d, *J* = 8.6 Hz, 2H), 4.16 (qd, *J* = 7.2, 0.8 Hz, 2H), 4.13 (t, *J* = 6.4 Hz, 2H), 3.78 (s, 3H), 2.42 (dd, *J* = 6.6, 5.0 Hz, 1H), 2.03 (s, 3H), 1.97 (dd, *J* = 9.0, 5.0 Hz, 1H), 1.86-1.80 (comp. m, 3H), 1.63-1.55 (comp. m, 2H), 1.28 (t, *J* = 7.2 Hz, 3H).
Minor (syn): δ 7.15 (d, *J* = 8.4 Hz, 2H), 6.79 (d, *J* = 8.4 Hz, 2H), 4.09 (t, *J* = 6.0 Hz, 2H), 3.90 (qd, *J* = 7.2, 0.8 Hz, 2H), 3.77 (s, 3H), 2.33 (dd, *J* = 9.0, 7.0 Hz, 1H), 2.05 (s, 3H), 2.02-1.97 (comp. m, 1H), 1.80-1.71 (comp. m, 3H), 1.50-1.43 (comp. m, 2H), 1.02 (t, *J* = 7.2 Hz, 3H).
^{13}C NMR (100 MHz; $CDCl_3$): δ 171.8, 171.2, 170.8, 158.42, 158.36, 132.3, 130.2, 128.5, 127.4, 114.0, 113.5, 64.13, 64.11, 60.6, 60.3, 55.4, 55.3, 32.6, 31.1, 30.5, 29.5, 28.9, 28.6, 28.5, 28.2, 25.1, 23.4, 21.1, 14.4, 14.2.
IR (ATR, neat): 2963, 1729, 1517, 1454, 1368, 1244, 1174, 1033, 830 cm^{-1}.
HRMS (ESI+): *m/z* calc'd for $(M+H)^+$ $[C_{18}H_{24}O_5 + H]^+$: 321.1697, found 321.1693.



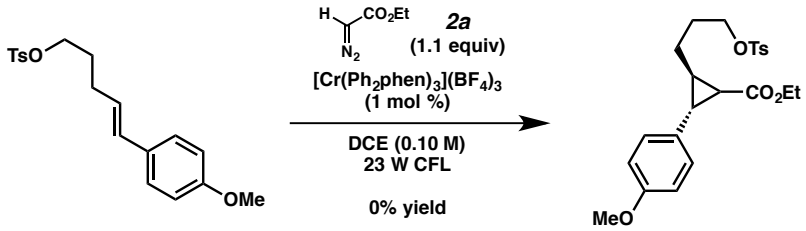
Cyclopropane 3la. Prepared according to the *General Procedure* using 21.2 mg *E*-alkene **1l** (0.103 mmol), 15.2 mg ethyl diazoacetate (85% wt. solution in CH_2Cl_2, 0.113 mmol), 1.3 mg $[Cr(Ph_2phen)_3](BF_4)_3$ (1.03 μmol), and 1.0 mL DCE. The reaction mixture was irradiated for 42 h. Diastereomeric ratio (1.1:1 anti/syn) was determined by ^{1}H NMR analysis of the crude mixture. The crude product was purified by flash chromatography (100% hexanes → 7:1:1:1 hexanes/EtOAc/Et_2O/CH_2Cl_2 eluent) to afford cyclopropane **3la** (11.7 mg, 39% yield) as a pale yellow oil.
TLC: R_f = 0.51 in 7:1:1:1 hexanes/EtOAc/Et_2O/CH_2Cl_2, visualized by UV.
^{1}H NMR (400 MHz; $CDCl_3$): Major (anti): δ 7.02 (d, *J* = 8.4 Hz, 2H), 6.81 (d, *J* = 8.4 Hz, 2H), 4.16 (q, *J* = 7.2 Hz, 2H), 3.78 (s, 3H), 3.44 (t, *J* = 6.2 Hz, 2H), 3.33 (s, 3H), 2.41 (dd, *J* = 6.2, 5.2 Hz, 1H), 1.95 (dd, *J* = 9.2, 5.2 Hz, 1H), 1.83-1.57 (comp. m, 5H), 1.28 (t, *J* = 7.2 Hz, 3H).
Minor (syn): δ 7.15 (d, *J* = 8.4 Hz, 2H), 6.80 (d, *J* = 8.4 Hz, 2H), 3.90 (qd, *J* = 7.2, 1.2 Hz, 2H), 3.77 (s, 3H), 3.39 (t, *J*= 6.0

Hz, 2H), 3.32 (s, 3H), 2.33 (dd, *J* = 9.2, 7.2 Hz, 1H), 2.00-1.94 (comp. m, 1H), 1.83-1.57 (comp. m, 4H), 1.52-1.43 (comp. m, 1H), 1.03 (t, *J* = 7.2 Hz, 3H).
^{13}C NMR (100 MHz; $CDCl_3$): δ 172.0, 171.1, 158.4, 143.5, 132.6, 130.3, 128.8, 127.4, 114.0, 113.5, 72.5, 72.2, 60.6, 60.3, 58.74, 58.68, 55.5, 55.3, 32.7, 31.2, 30.9, 29.59, 29.57, 29.2, 28.9, 28.6, 25.4, 23.6, 14.5, 14.3.
IR (ATR, neat): 2934, 1724, 1516, 1449, 1377, 1248, 1175, 1117, 1036 cm^{-1}.
HRMS (ESI+): *m/z* calc'd for $(M+H)^+$ $[C_{17}H_{24}O_4 + H]^+$: 293.1747, found 293.1746.



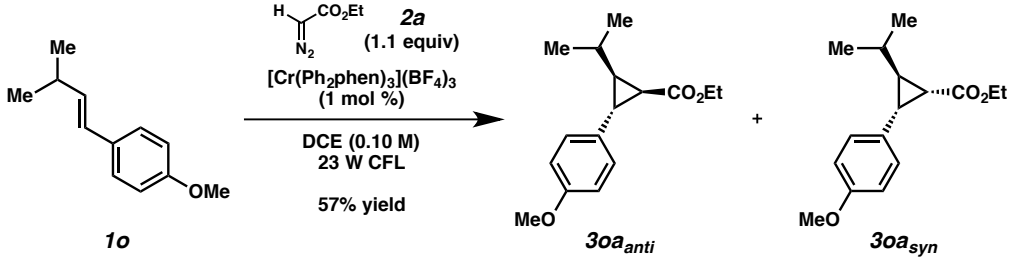
1m *3ma*

Cyclopropane 3ma. Reaction performed according to the *General Procedure* using 19.2 mg of *E*-alkene **1m** (0.0999 mmol), 14.7 mg ethyl diazoacetate (85% wt. solution in CH_2Cl_2, 0.113 mmol), 1.3 mg $[Cr(Ph_2phen)_3](BF_4)_3$ (0.999 μmol), and 1.0 mL DCE. The reaction mixture was irradiated for 40 h. Cyclopropane **3ma** was not observed.



1n *3na*

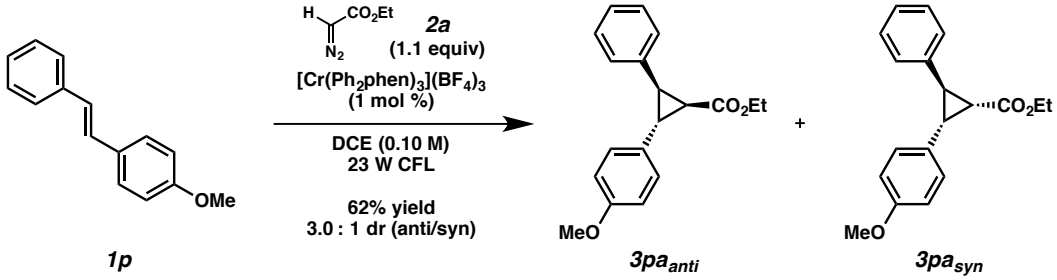
Cyclopropane 3na. Reaction performed according to the *General Procedure* using 35.6 mg of *E*-alkene **1n** (0.103 mmol), 15.2 mg ethyl diazoacetate (85% wt. solution in CH_2Cl_2, 0.113 mmol), 1.3 mg $[Cr(Ph_2phen)_3](BF_4)_3$ (1.03 μmol), and 1.0 mL DCE. The reaction mixture was irradiated for 43 h. Cyclopropane **3na** was not observed. Instead, a product resulting from a tosyloxy transfer to ethyl diazoacetate[4] was observed.



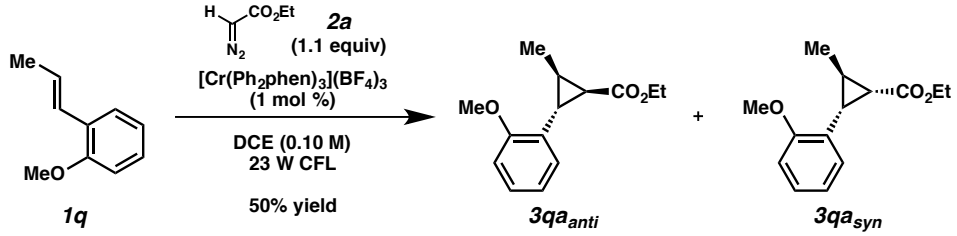
1o *3oa$_{anti}$* *3oa$_{syn}$*

Cyclopropane 3oa. Prepared according to the *General Procedure* using 18.8 mg *E*-alkene **1o** (0.107 mmol), 15.8 mg ethyl diazoacetate (85% wt. solution in CH_2Cl_2, 0.118 mmol), 1.4 mg $[Cr(Ph_2phen)_3](BF_4)_3$ (0.999 μmol), and 1.1 mL DCE. The reaction mixture was irradiated for 17 h. Diastereomeric ratio (1:1.1 anti/syn) was determined by ^{1}H NMR analysis of the crude mixture. The crude product was purified by flash chromatography (100% hexanes → 9:1 hexanes/Et_2O eluent) to afford *trans*-cyclopropane **3oa** (15.9 mg, 57% yield) as a colorless oil.
TLC: R_f = 0.29 in 9:1 hexanes/Et_2O, visualized by UV. Stained blue by *p*-anisaldehyde.
^{1}H NMR (400 MHz; $CDCl_3$): Major (syn): δ 7.03 (d, *J* = 8.4 Hz, 2H), 6.81 (d, *J* = 8.4 Hz, 2H), 4.17 (qd, *J* = 5.4, 7.0 Hz, 2H), 3.77 (s, 3H), 2.36 (app. t, *J* = 8.0 Hz, 1H), 1.88-1.80 (comp. m, 3H), 1.28 (t, *J* = 7.0 Hz, 3H), 1.09 (d, *J* = 6.4 Hz, 6H).
Minor (anti): δ 7.15 (d, *J* = 8.6 Hz, 2H), 6.80 (d, *J* = 8.6 Hz, 2H), 3.90 (q, *J* = 7.2 Hz, 2H), 3.78 (s, 3H), 2.46 (dd, *J* = 6.4,

5.1 Hz, 1H), 1.95 (dd, *J* = 9.4, 5.1 Hz, 1H), 1.34-1.20 (comp. m, 2H), 1.06 (d, *J* = 6.8 Hz, 3H), 1.02 (t, *J* = 7.2 Hz, 3H), 0.92 (d, *J* = 6.8 Hz, 3H).
^{13}C NMR (125 MHz; $CDCl_3$): δ 172.2, 171.3, 158.4, 158.3, 132.8, 130.3, 129.1, 127.6, 114.0, 113.5, 60.6, 60.2, 55.5, 55.3, 39.3, 33.7, 32.2, 31.8, 30.9, 28.7, 28.0, 26.8, 22.7, 22.3, 21.9, 21.7, 14.5, 14.3.
IR (ATR, neat): 2959, 1731, 1518, 1247, 1178, 1159, 1038 cm^{-1}.
HRMS (ESI+): *m/z* calc'd for $(M + Na)^+$ $[C_{16}H_{22}O_3 + Na]^+$: 285.1461, found 285.1461.

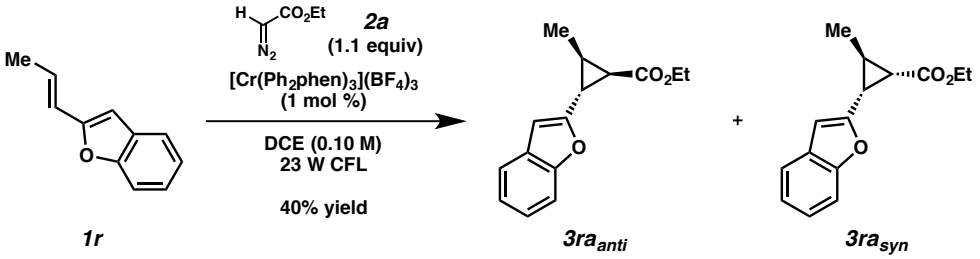


Cyclopropane 3pa. Prepared according to the *General Procedure* using 20.8 mg *E*-alkene **1p** (0.0989 mmol), 14.6 mg ethyl diazoacetate (85% wt. solution in CH_2Cl_2, 0.109 mmol), 1.3 mg $[Cr(Ph_2phen)_3](BF_4)_3$ (0.989 μmol), and 1.0 mL DCE. The reaction mixture was irradiated for 72 h. Diastereomeric ratio (3.0:1 anti/syn) was determined by ^{1}H NMR analysis of the crude mixture. The crude product was purified by flash chromatography (100% hexanes → 9:1 hexanes/EtOAc eluent) to afford cyclopropane **3pa** (18.2 mg, 62% yield) as a colorless oil.
TLC: R_f = 0.21 in 9:1 hexanes/Et_2O, visualized by UV.
^{1}H NMR (400 MHz; $CDCl_3$): Major (anti): δ 7.38-6.83 (comp. m, 9H), 4.00-3.90 (comp. m, 2H), 3.80 (s, 3H), 3.18 (dd, *J* = 7.2, 5.2 Hz, 1H), 2.88 (dd, *J* = 7.2, 5.2 Hz, 1H), 2.39-2.32 (comp. m, 1H), 1.10-1.02 (comp. m, 3H).
Minor (syn): δ 7.38-6.83 (comp. m, 9H), 4.00-3.90 (comp. m. 2H), 3.79 (s, 3H), 3.19 (dd, *J* = 7.2, 5.2 Hz, 1H), 2.88 (dd, *J* = 7.2, 5.2 Hz, 1H), 2.39-2.32 (comp. m, 1H), 1.10-1.02 (comp. m, 3H).
^{13}C NMR (100 MHz; $CDCl_3$): δ 170.3, 158.6, 143.5, 136.4, 132.7, 131.7, 130.3, 129.3, 128.7, 128.3, 128.2, 128.0, 127.0, 126.7, 114.6, 114.2, 113.7, 113.6, 60.60, 60.56, 55.5, 55.3, 34.3, 34.0, 31.4, 31.2, 29.6, 28.8, 14.3, 14.2.
IR (ATR, neat): 2980, 1724, 1516, 1248, 1177, 1036, 827, 696 cm^{-1}.
HRMS (ESI+): *m/z* calc'd for $(M+H)^+$ $[C_{19}H_{20}O_3 + H]^+$: 297.1485, found 297.1482.

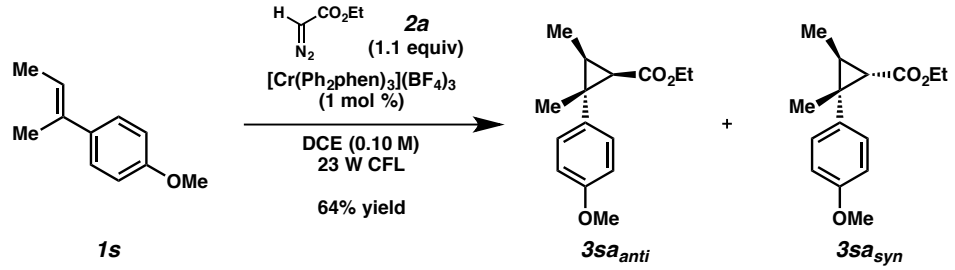


Cyclopropane 3qa. Prepared according to the *General Procedure* using 16.5 mg *E*-alkene **1q** (0.111 mmol), 16.4 mg ethyl diazoacetate (85% wt. solution in CH_2Cl_2, 0.122 mmol), 1.5 mg $[Cr(Ph_2phen)_3](BF_4)_3$ (1.11 μmol), and 1.10 mL DCE. The reaction mixture was irradiated for 27 h. Diastereomeric ratio (1:1.2 anti/syn) was determined by ^{1}H NMR analysis of the crude mixture. The crude product was purified by flash chromatography (100% hexanes → 3:1 hexanes/Et_2O eluent) to afford cyclopropane **3qa** (18.2 mg, 50% yield) as a colorless oil.
TLC: R_f = 0.55 in 3:1 hexanes/Et_2O, visualized by UV.
^{1}H NMR (400 MHz; $CDCl_3$): Major (syn): δ 7.21-7.17 (comp. m, 2H), 6.88 (app. td, *J* = 7.6, 2.4 Hz, 1H), 6.80 (d, *J* = 7.6 Hz, 1H), 3.88 (q, *J* = 7.2 Hz, 2H), 3.80 (s, 3H), 2.29 (dd, *J* = 9.2, 7.2 Hz, 1H), 2.00-1.92 (comp. m, 1H), 1.84 (dd, *J* = 9.2, 5.2 Hz, 1H), 1.28 (d, *J* = 6.0 Hz, 3H), 1.00 (t, *J* = 7.2 Hz, 3H).
Minor (anti): δ 7.17 (ddd, *J* = 8.4, 6.8, 2.6 Hz, 1H), 6.90-6.83 (comp. m, 3H), 4.18 (m, 2H), 3.83 (s, 3H), 2.63 (dd, *J* = 6.8, 5.2 Hz, 1H), 1.97 (dd, *J* = 9.2, 5.2 Hz, 1H), 1.67-1.61 (comp. m, 1H), 1.36 (d, *J* = 6.0 Hz, 2H), 1.29 (t, *J* = 7.2 Hz, 3H).
^{13}C NMR (100 MHz; $CDCl_3$): δ 172.3, 171.6, 158.7, 130.3, 129.0, 127.9, 127.4, 126.0, 125.5, 120.5, 120.1, 110.5, 109.9, 60.4, 59.9, 55.6, 55.4, 31.7, 29.9, 29.3, 27.9, 27.4, 24.5, 20.2, 18.0, 14.6, 14.3, 12.3.

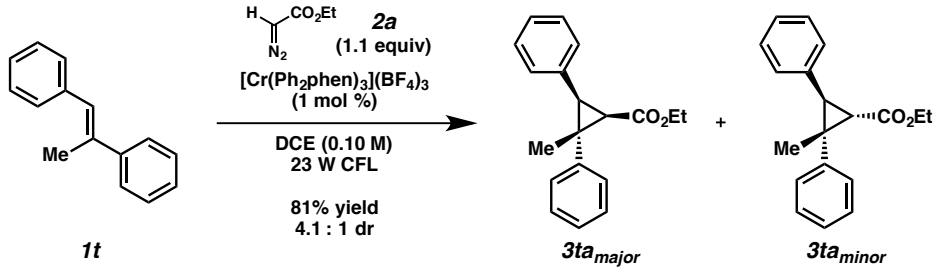
IR (ATR, neat): 2978, 1724, 1497, 1248, 1180, 1163, 1030, 750 cm^{-1}.
HRMS (ESI+): *m/z* calc'd for $(M+H)^+$ $[C_{14}H_{18}O_3 + H]^+$: 235.1329, found 235.1330.



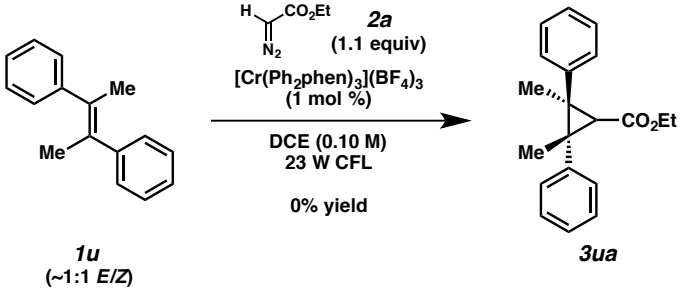
Cyclopropane 3ra. Prepared according to the *General Procedure* using 17.3 mg alkene **1r** (0.109 mmol, 9:1 *E/Z* mixture), 16.1 mg ethyl diazoacetate (85% wt. solution in CH_2Cl_2, 0.120 mmol), 1.4 mg $[Cr(Ph_2phen)_3](BF_4)_3$ (1.09 μmol), and 1.1 mL DCE. Diastereomeric ratio (1:1.1 anti/syn) was determined by ^{1}H NMR analysis of the crude mixture. The reaction mixture was irradiated for 36 h. The crude product was purified by flash chromatography (100% hexanes → 9:1 hexanes/Et_2O eluent) to afford *trans*-cyclopropane **3ra** (10.7 mg, 40% yield) as a colorless oil.
TLC: R_f = 0.47 in 9:1 hexanes/EtOAc, visualized by UV. Stained pink by *p*-anisaldehyde.
^{1}H NMR (400 MHz; $CDCl_3$): Major (syn): δ 7.48-7.44 (m, 1H), 7.39-7.34 (m, 1H) 7.21-7.15 (m, 2H), 6.50 (s, 1H), 4.18 (dq, *J* = 7.2, 5.2 Hz, 2H), 2.34 (dd, *J* = 8.6, 6.6 Hz, 1H), 2.12 (app. quintet, *J* = 6.0 Hz, 1H), 1.92-1.89 (m, 1H), 1.31 (d, *J* = 6.4 Hz, 3H), 1.03 (t, *J* = 7.2 Hz, 3H).
Minor (anti): δ 7.48-7.44 (m, 1H), 7.39-7.34 (m, 2H), 7.21-7.15 (m, 2H), 6.44 (s, 1H), 3.95 (dq, *J* = 7.2, 3.6 Hz, 2H), 2.53 (dd, *J* = 6.2, 5.0 Hz, 1H), 2.28 (dd, *J* = 9.6, 5.0 Hz, 1H), 1.96-1.92 (m, 1H), 1.36 (d, *J* = 6.4 Hz, 3H), 1.29 (t, *J* = 7.2 Hz, 3H).
^{13}C NMR (125 MHz; $CDCl_3$): δ 171.1, 170.3, 156.8, 154.7, 154.5, 154.4, 128.9, 123.6, 123.5, 122.8, 122.6, 120.7, 120.3, 111.0, 110.83, 110.81, 104.3, 102.0, 60.9, 60.6, 29.9, 27.8, 26.5, 25.7, 23.6, 20.6, 17.5, 14.5, 14.2, 11.7.
IR (ATR, neat): 2961, 1728, 1454, 1257, 1184, 750 cm^{-1}.
HRMS (ESI+): *m/z* calc'd for $(M + Na)^+$ $[C_{15}H_{16}O_3 + Na]^+$: 267.0992, found 267.0993.



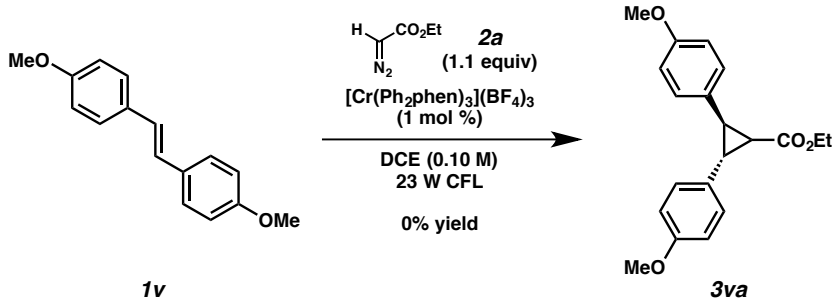
Cyclopropane 3sa. Prepared according to the *General Procedure* using 16.2 mg (*E*)-alkene **1s** (0.0999 mmol), 14.7 mg ethyl diazoacetate (85% wt. solution in CH_2Cl_2, 0.110 mmol), 1.3 mg $[Cr(Ph_2phen)_3](BF_4)_3$ (0.999 μmol), and 1.0 mL DCE. The reaction mixture was irradiated for 14 h. Diastereomeric ratio (1:1.2 anti/syn) was determined by ^{1}H NMR analysis of the crude mixture. The crude product was purified by flash chromatography (100% hexanes → 9:1 hexanes/EtOAc eluent) to afford *trans*-cyclopropane **3sa** (15.9 mg, 64% yield) as a colorless oil.
TLC: R_f = 0.41 in 9:1 hexanes/EtOAc, visualized by UV.
^{1}H NMR (400 MHz; $CDCl_3$): Major (syn): δ 7.14 (d, *J* = 8.6 Hz, 2H), 6.80 (d, *J* = 8.6 Hz, 2H), 3.91-3.84 (m, 2H), 3.77 (s, 3H), 2.05 (app. quintet, *J* = 6.3 Hz, 1H), 1.49 (d, *J* = 5.6 Hz, 1H), 1.41 (s, 3H), 1.28 (d, *J* = 6.3 Hz, 3H), 1.02 (t, *J* = 7.0 Hz, 3H).
Minor (anti): δ 7.20 (d, *J* = 8.8 Hz, 2H), 6.83 (d, *J* = 8.8 Hz, 2H), 4.18-4.12 (dq, *J* = 7.2, 1.2 Hz, 2H), 3.79 (s, 3H), 1.87 (d, *J* = 8.8 Hz, 1H), 1.71-1.63 (comp. m, 1H), 1.48 (s, 3H), 1.38 (d, *J* = 6.8 Hz, 3H), 1.29 (t, *J* = 7.2 Hz, 3H).
^{13}C NMR (100 MHz; $CDCl_3$): δ 171.82, 171.77, 158.2, 158.1, 140.5, 136.2, 129.8, 128.6, 113.9, 113.7, 60.2, 60.0, 55.4, 55.3, 36.1, 35.5, 33.2, 29.0, 26.4, 24.7, 23.0, 15.7, 14.6, 14.3, 12.8, 8.4.
IR (ATR, neat): 2976, 1724, 1516, 1244, 1171, 1036, 831 cm^{-1}.
HRMS (ESI+): *m/z* calc'd for $(M + H)^+$ $[C_{15}H_{20}O_3 + H]^+$: 249.1485, found 249.1488.



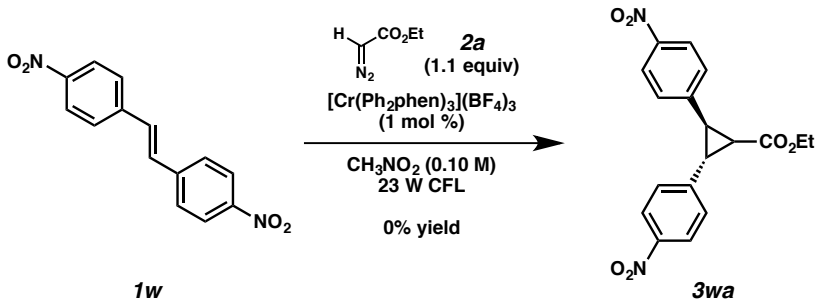
Cyclopropane 3ta. Prepared according to the *General Procedure* using 19.5 mg *E*-alkene **1t** (0.100 mmol), 14.8 mg ethyl diazoacetate (85% wt. solution in CH_2Cl_2, 0.110 mmol), 1.3 mg $[Cr(Ph_2phen)_3](BF_4)_3$ (1.00 μmol), and 1.0 mL DCE. The reaction mixture was irradiated for 14 h. Diastereomeric ratio (4.1:1 major/minor) was determined by ^{1}H NMR analysis of the crude mixture. The crude product was purified by flash chromatography (100% petroleum ether → 9:1 petroleum ether/EtOAc eluent) to afford cyclopropane **3ta** (22.9 mg, 81% yield) as a colorless oil.
TLC: R_f = 0.47 in 9:1 hexanes/Et_2O, visualized by UV.
^{1}H NMR (400 MHz; $CDCl_3$): Major: δ 7.43-7.17 (m, 10H), 4.19-4.10 (m, 2H), 2.97 (d, *J* = 9.6 Hz, 1H), 2.37 (d, *J* = 9.6 Hz, 1H), 1.54 (s, 3H), 1.26 (t, *J* = 7.2 Hz, 3H).
Minor: δ 7.43-7.17 (m, 10H), 3.98-3.88 (m, 2H), 3.40 (d, *J* = 5.8 Hz, 1H), 2.33 (d, *J* = 5.8 Hz, 1H), 1.20 (s, 3H), 1.01 (t, *J* = 7.2 Hz, 3H).
^{13}C NMR (100 MHz; $CDCl_3$): δ 170.6, 147.6, 136.8, 135.1, 130.5, 129.2, 128.8, 128.5, 128.2, 127.8, 126.8, 60.5, 60.3, 38.3, 35.6, 35.1, 35.0, 33.0, 30.4, 24.0, 18.4, 14.5, 14.2.
IR (ATR, neat): 2980, 1732, 1445, 1152, 1053, 764, 698 cm^{-1}.
HRMS (ESI+): *m/z* calc'd for $(M + H)^+$ $[C_{19}H_{20}O_2 + H]^+$: 281.1536, found 281.1537.



Cyclopropane 3ua. Reaction performed according to the *General Procedure* using 21.5 mg of alkene **1u** (0.103 mmol), 15.2 mg ethyl diazoacetate (85% wt. solution in CH_2Cl_2, 0.114 mmol), 1.3 mg $[Cr(Ph_2phen)_3](BF_4)_3$ (1.03 μmol), and 1.0 mL DCE. The reaction mixture was irradiated for 72 h. Cyclopropane **3ua** was not observed.



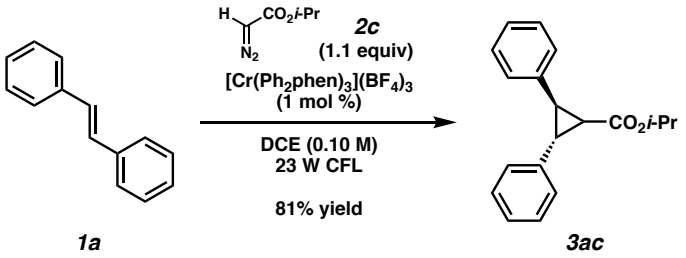
Cyclopropane 3va. Reaction performed according to the *General Procedure* using 24.0 mg of *E*-alkene **1v** (0.0999 mmol), 14.7 mg ethyl diazoacetate (85% wt. solution in CH_2Cl_2, 0.113 mmol), 1.3 mg $[Cr(Ph_2phen)_3](BF_4)_3$ (0.999 μmol), and 1.0 mL DCE. The reaction mixture was irradiated for 53 h. Cyclopropane **3va** was not observed.



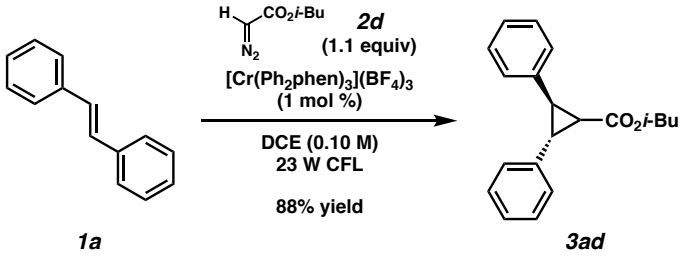
1w *3wa*

Cyclopropane 3wa. Reaction performed according to the *General Procedure* using 27.0 mg of *E*-alkene **1w** (0.0999 mmol), 14.7 mg ethyl diazoacetate (85% wt. solution in CH_2Cl_2, 0.113 mmol), 1.3 mg $[Cr(Ph_2phen)_3](BF_4)_3$ (0.999 μmol), and 1.0 mL CH_3NO_2. The reaction mixture was irradiated for 24 h. Cyclopropane **3wa** was not observed.

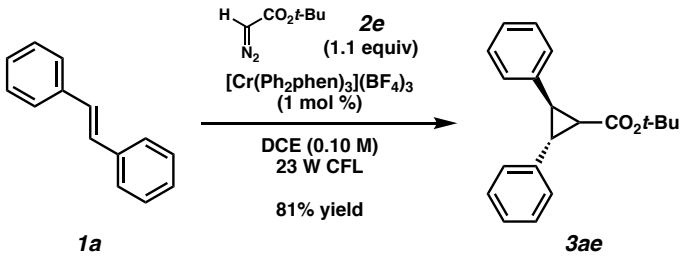
Diazo Scope



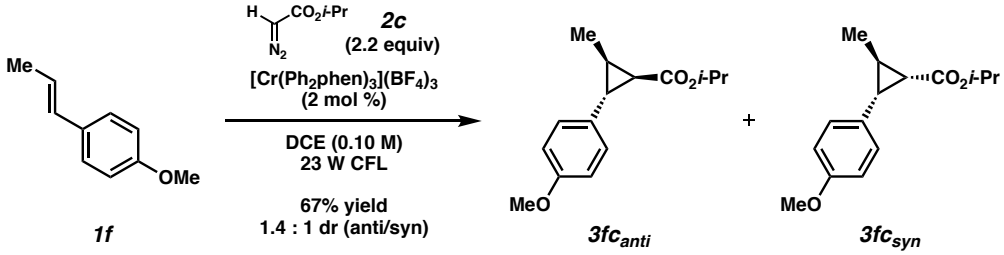
Cyclopropane 3ac. Prepared according to the *General Procedure* using 18.1 mg *trans*-stilbene (0.100 mmol), 14.8 mg diazoacetate **2c** (0.110 mmol), 1.3 mg $[Cr(Ph_2phen)_3](BF_4)_3$ (1.00 μmol), and 1.0 mL DCE. The reaction mixture was irradiated for 24 h. The crude product was purified by flash chromatography (100% hexanes → 9:1 hexanes/acetone eluent) to afford cyclopropane **3ac** (22.7 mg, 81% yield) as a colorless oil.
TLC: R_f = 0.52 in 9:1 hexanes/acetone, visualized by UV.
^{1}H NMR (400 MHz; $CDCl_3$): δ 7.35-7.21 (m, 10H), 4.84-4.75 (app. septet, *J* = 6.2 Hz, 1H), 3.21 (dd, *J* = 6.8, 5.2 Hz, 1H), 2.92 (dd, *J* = 9.6, 6.8 Hz, 1H), 2.40 (dd, *J* = 9.6, 5.2 Hz, 1H), 1.04 (d, *J* = 6.4 Hz, 3H), 0.97 (d, *J* = 6.0 Hz, 3H).
^{13}C NMR (100 MHz; $CDCl_3$): δ 169.6, 139.8, 136.3, 129.3, 128.7, 128.2, 127.0, 126.8, 68.0, 34.5, 31.6, 29.0, 22.0, 21.6.
IR (ATR, neat): 2978, 1721, 1179, 1105, 750, 696 cm^{-1}.
HRMS (ESI+): *m/z* calc'd for $(M + H)^+$ $[C_{19}H_{20}O_2 + H]^+$: 281.1536, found 281.1536.



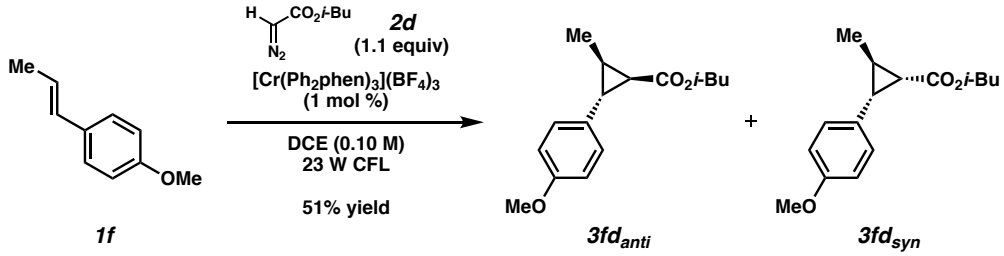
Cyclopropane 3ad. Prepared according to the *General Procedure* using 18.1 mg *trans*-stilbene (0.100 mmol), 15.7 mg diazoacetate **2d** (0.110 mmol), 1.3 mg $[Cr(Ph_2phen)_3](BF_4)_3$ (1.00 μmol), and 1.0 mL DCE. The reaction mixture was irradiated for 60 h. The crude product was purified by flash chromatography (100% hexanes → 19:1 hexanes/acetone eluent) to afford cyclopropane **3ad** (25.9 mg, 88% yield) as a colorless oil.
TLC: R_f = 0.28 in hexanes/Et_2O, visualized by UV.
^{1}H NMR (400 MHz; $CDCl_3$): δ 7.40-7.23 (m, 10H), 3.74-3.62 (m, 2H), 3.21 (dd, *J* = 7.0, 5.2 Hz, 1H), 2.94 (dd, *J* = 9.6, 7.0 Hz, 1H), 2.44 (dd, *J* = 9.6, 5.2 Hz, 1H), 1.71 (app. septet, *J* = 6.6 Hz, 1H), 0.79 (d, *J* = 6.4 Hz, 6H).
^{13}C NMR (100 MHz; $CDCl_3$): δ 170.2, 139.8, 136.3, 129.3, 128.8, 128.3, 127.1, 126.82, 126.77, 70.9, 34.6, 31.5, 29.4, 27.7, 19.12, 19.10.
IR (ATR, neat): 2961, 1728, 1171, 752, 696 cm^{-1}.
HRMS (ESI+): *m/z* calc'd for $(M + H)^+$ $[C_{20}H_{22}O_2 + H]^+$: 295.1693, found 295.1693.



Cyclopropane 3ae. Prepared according to the *General Procedure* using 17.7 mg *trans*-stilbene (0.0982 mmol), 15.4 mg diazoacetate **2e** 0.108 mmol), 1.3 mg $[Cr(Ph_2phen)_3](BF_4)_3$ (0.982 μmol), and 1.0 mL DCE. The reaction mixture was irradiated for 48 h. The crude product was purified by flash chromatography (100% hexanes → 19:1 hexanes/acetone eluent) to afford *trans*-cyclopropane **3ae** (20.2 mg, 70% yield) as a colorless oil.
TLC: R_f = 0.32 in 19:1 hexanes/acetone, visualized by UV.
^{1}H NMR (400 MHz; $CDCl_3$): δ 7.37-7.23 (m, 10H), 3.15 (dd, *J* = 6.8, 5.2 Hz, 1H), 2.88 (dd, *J* = 9.6, 6.8 Hz, 1H), 2.35 (dd, *J* = 9.6, 5.2 Hz, 1H), 1.21 (s, 9H).
^{13}C NMR (100 MHz; $CDCl_3$): δ 169.2, 140.1, 136.5, 129.5, 128.7, 128.1, 126.9, 126.8, 126.7, 80.7, 34.4, 32.4, 28.8, 28.0.
IR (ATR, neat): 2976, 1724, 1497, 1366, 1144, 741, 696 cm^{-1}.
HRMS (ESI+): *m/z* calc'd for $(M + H)^+$ $[C_{20}H_{22}O_2 + H]^+$: 295.1693, found 295.1693.

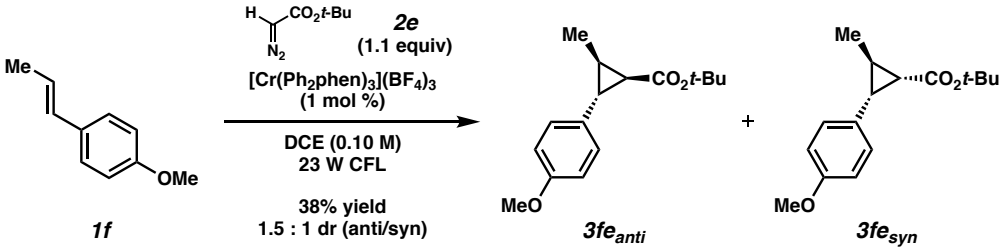


Cyclopropane 3fc. Prepared with a modification to the *General Procedure* using 15.4 mg *trans*-anethole (0.104 mmol), 14.6 mg diazoacetate **2c** (0.114 mmol), 1.4 mg $[Cr(Ph_2phen)_3](BF_4)_3$ (1.04 μmol), and 1.0 mL DCE. The reaction mixture was irradiated for 36 h. Then, an additional 1.3 mg (1.04 μmol) of catalyst and 14.6 mg (0.114 mmol) of diazoacetate were added to the mixture, and the reaction mixture was irradiated for another 33 h. Diastereomeric ratio (1.4:1 anti/syn) was determined by ^{1}H NMR analysis of the crude mixture. The crude product was purified by flash chromatography (100% hexanes → 9:1 hexanes/EtOAc eluent) to afford cyclopropane **3fc** (17.3 mg, 67% yield) as a colorless oil.
TLC: R_f = 0.41 in 9:1 hexanes/EtOAc, visualized by UV.
^{1}H NMR (400 MHz; $CDCl_3$): Major (anti): δ 7.01 (d, *J* = 8.6 Hz, 2H), 6.81 (d, *J* = 8.6 Hz, 2H), 5.04 (app. septet, *J* = 6.4 Hz, 1H), 3.78 (s, 3H), 2.35 (dd, *J* = 6.2, 5.0 Hz, 1H), 1.91 (dd, *J* = 9.2, 5.0 Hz, 1H), 1.62-1.58 (comp. m, 1H), 1.33 (d, *J* = 6.4 Hz, 3H), 1.25 (d, *J* = 6.4 Hz, 6H).
Minor (syn): δ 7.15 (d, *J* = 8.6 Hz, 2H), 6.79 (d, *J* = 8.6 Hz, 2H), 4.74 (app. septet, *J* = 6.1 Hz, 1H), 3.77 (s, 3H), 2.28 (dd, *J* = 9.2, 6.8 Hz, 1H), 2.01 (app. sextet, *J* = 6.2 Hz, 1H), 1.74 (dd, *J* = 9.2, 5.2 Hz, 1H), 1.25 (d, *J* = 6.2 Hz, 3H), 1.00 (d, *J* = 6.1 Hz, 3H), 0.97 (d, *J* = 6.1 Hz, 3H).
^{13}C NMR (100 MHz; $CDCl_3$): δ 171.4, 158.2, 136.6, 132.9, 130.3, 129.5, 129.0, 127.7, 127.2, 114.0, 113.4, 67.9, 67.4, 55.5, 55.3, 33.6, 31.6, 30.3, 29.6, 25.3, 22.2, 22.1, 21.6, 19.6, 17.9, 12.1.
IR (ATR, neat): 2980, 1721, 1516, 1248, 1175, 1146, 1109, 1038 cm^{-1}.
HRMS (ESI+): *m/z* calc'd for $(M + H)^+$ $[C_{15}H_{20}O_3 + H]^+$: 249.1485, found 249.1486.

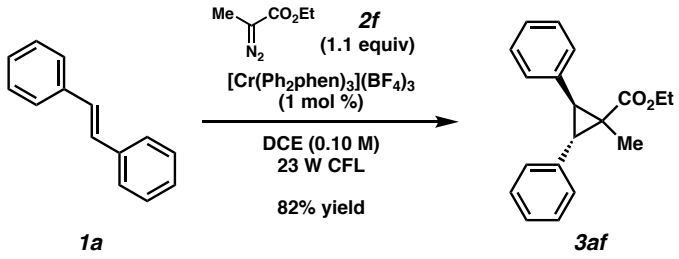


Cyclopropane 3fd. Prepared according to the *General Procedure* using 15.5 mg *trans*-anethole (0.105 mmol), 16.4 mg diazoacetate **2d** (0.115 mmol), 1.4 mg $[Cr(Ph_2phen)_3](BF_4)_3$ (1.05 μmol), and 1.1 mL DCE. The reaction mixture was irradiated for 60 h. Diastereomeric ratio (1.1:1 anti/syn) was determined by ^{1}H NMR analysis of the crude mixture. The crude product was purified by flash chromatography (100% hexanes → 9:1 hexanes/EtOAc eluent) to afford *trans*-cyclopropane **3fd** (14.0 mg, 51% yield) as a colorless oil.
TLC: R_f = 0.33 in 9:1 hexanes/Et_2O, visualized by UV.

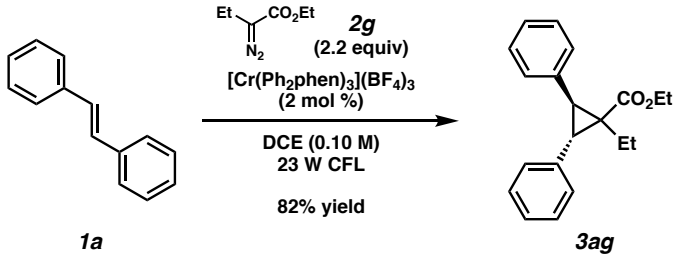
^{1}H NMR (400 MHz; $CDCl_3$): Major (anti): δ 7.01 (d, *J* = 8.6 Hz, 2H), 6.82 (d, *J* = 8.6 Hz, 2H), 3.94-3.87 (m, 2H), 3.78 (s, 3H), 2.37 (dd, *J* = 6.0, 5.2 Hz, 1H), 1.98-1.91 (comp. m, 2H), 1.64-1.60 (comp. m, 1H), 1.34 (d, *J* = 6.4 Hz, 3H), 0.95 (d, *J* = 6.8 Hz, 6H).
Minor (syn): δ 7.15 (d, *J*= 8.8 Hz, 2H), 6.79 (d, *J* = 8.8 Hz, 2H), 3.77 (m, 3H), 3.68-3.56 (m, 2H), 2.29 (dd, *J* = 9.2, 7.0 Hz, 1H), 2.03-1.99 (m, 1H), 1.79 (dd, *J* = 9.2, 5.2 Hz, 1H), 1.72-1.65 (m, 1H), 1.26 (d, *J* = 6.0 Hz, 3H), 0.77 (d, *J* = 6.4 Hz, 6H).
^{13}C NMR (100 MHz; $CDCl_3$): δ 172.0, 171.3, 158.4, 158.3, 132.8, 130.2, 128.9, 127.3, 114.0, 113.5, 70.8, 70.5, 55.5, 55.3, 33.7, 31.9, 30.1, 29.3, 27.9, 27.7, 25.3, 20.0, 19.3, 19.1, 17.9, 12.2.
IR (ATR, neat): 2959, 1724, 1516, 1285, 1248, 1171, 1038 cm^{-1}.
HRMS (ESI+): *m/z* calc'd for $(M + H)^+$ $[C_{16}H_{22}O_3 + H]^+$: 263.1642, found 263.1638.



Cyclopropane 3fe. Prepared according to the *General Procedure* using 14.8 mg *trans*-anethole (0.0999 mmol), 15.6 mg diazoacetate **2e** (0.110 mmol) 1.3 mg $[Cr(Ph_2phen)_3](BF_4)_3$ (0.999 μmol), and 1.0 mL DCE. The reaction mixture was irradiated for 69 h. Diastereomeric ratio (1.5:1 anti/syn) was determined by ^{1}H NMR analysis of the crude mixture. The crude product was purified by flash chromatography (100% hexanes → 9:1 hexanes/EtOAc eluent) to afford cyclopropane **3fe** (10.0 mg, 38% yield) as a colorless oil.
TLC: R_f = 0.52 in 9:1 hexanes/EtOAc, visualized by UV.
^{1}H NMR (400 MHz; $CDCl_3$): Major (anti): δ 7.00 (d, *J* = 8.6 Hz, 2H), 6.81 (d, *J* = 8.6 Hz, 2H), 3.78 (s, 3H), 2.29 (dd, *J* = 6.0, 5.3 Hz, 1H), 1.87 (dd, *J* = 9.4, 5.3 Hz, 1H), 1.56-1.50 (comp. m, 1H), 1.47 (s, 9H), 1.31 (d, *J* = 6.4 Hz, 3H).
Minor (syn): δ 7.15 (d, *J* = 8.2 Hz, 2H), 6.79 (d, *J* = 8.2 Hz, 2H), 3.77 (s, 3H), 2.24 (dd, *J* = 9.2, 6.8 Hz, 1H), 1.94 (app. sextet, *J* = 6.0 Hz, 1H), 1.68 (dd, *J* = 9.2, 5.0 Hz, 1H), 1.23 (d, *J* = 6.0 Hz, 3H), 1.18 (s, 9H).
^{13}C NMR (100 MHz; $CDCl_3$): δ 171.1, 158.3, 158.2, 133.1, 130.4, 129.3, 127.2, 114.0, 113.4, 80.6, 80.0, 55.5, 55.4, 33.3, 31.2, 31.1, 30.4, 28.4, 28.0, 25.2, 19.2, 17.8, 12.1.
IR (ATR, neat): 2976, 1717, 1516, 1366, 1248, 1152, 1038 cm^{-1}.
HRMS (ESI+): *m/z* calc'd for $(M + Na)^+$ $[C_{16}H_{22}O_3 + Na]^+$: 285.1461, found 285.1463.



Cyclopropane 3af. Prepared with a slight modification to the *General Procedure* using 17.9 mg *trans*-stilbene (0.0993 mmol), 14.0 mg diazoacetate **2f** (0.109 mmol), 1.3 mg $[Cr(Ph_2phen)_3](BF_4)_3$ (0.993 μmol), and 1.0 mL DCE. The reaction mixture was irradiated for 48 h. The crude product was purified by flash chromatography (100% hexanes → 19:1 hexanes/EtOAc as eluent) to afford cyclopropane **3af** (22.8 mg, 82% yield) as a colorless oil.
TLC: R_f = 0.37 in 19:1 hexanes/EtOAc, visualized by UV.
^{1}H NMR (400 MHz; $CDCl_3$): δ 7.36-7.22 (m, 10H), 3.87-3.84 (m, 2H), 3.60 (d, *J* = 7.4 Hz, 1H), 2.78 (d, *J* = 7.4 Hz, 1H), 1.21 (s, 3H), 0.88 (t, *J* = 7.2 Hz, 3H).
^{13}C NMR (100 MHz; $CDCl_3$): δ 172.3, 137.3, 137.2, 129.4, 129.2, 128.5, 128.1, 127.0, 126.8, 60.6, 37.7, 33.9, 33.7, 16.5, 14.0.
IR (ATR, neat): 2981, 1717, 1498, 1447, 1260, 1243, 1145, 1029, 749, 697 cm^{-1}.
HRMS (ESI+): *m/z* calc'd for $(M+H)^+$ $[C_{19}H_{20}O_2 + H]^+$: 281.1536, found 281.1522**.**



Cyclopropane 3ag. Prepared with a modification to the *General Procedure* using 17.8 mg *trans*-stilbene (0.0988 mmol), 15.5 mg diazoacetate **2g** (0.109 mmol), 1.3 mg $[Cr(Ph_2phen)_3](BF_4)_3$ (0.988 μmol), and 1.0 mL DCE. The reaction mixture was irradiated for 48 h, at which point an additional 1.3 mg (0.988 μmol) of catalyst and 15.5 mg (0.109 mmol) of diazoacetate were added, and the reaction mixture was irradiated for another 24 h. The crude product was purified by flash chromatography (100% hexanes → 9:1 hexanes/Et_2O eluent) to afford cyclopropane **3ag** (23.8 mg, 82% yield) as a colorless oil.

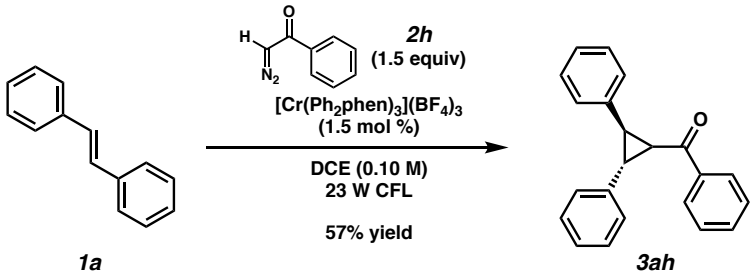
TLC: R_f = 0.52 in 9:1 hexanes/Et_2O, visualized by UV.

^{1}H NMR (400 MHz; $CDCl_3$): δ 7.34-7.21 (m, 10H), 3.91-3.83 (m, 2H), 3.64 (d, *J* = 7.6 Hz, 1H), 2.84 (d, *J* = 7.6 Hz, 1H), 1.66 (dq, *J* = 14.4, 7.3 Hz, 1H), 1.43 (dq, *J* = 14.4, 7.1 Hz, 1H), 0.94-0.88 (m, 6H).

^{13}C NMR (100 MHz; $CDCl_3$): δ 171.6, 137.3, 137.0, 129.4, 129.1, 128.4, 128.1, 126.9, 126.7, 60.4, 40.3, 35.6, 34.4, 23.5, 14.0, 12.0.

IR (ATR, neat): 2976, 1721, 1497 1246, 1148, 745, 696 cm^{-1}.

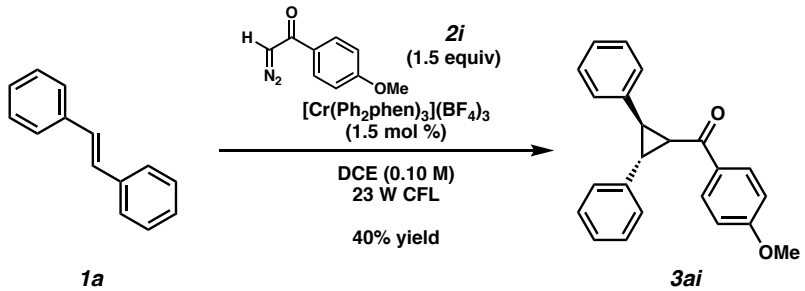
HRMS (ESI+): *m/z* calc'd for $(M + H)^+$ $[C_{20}H_{22}O_2 + H]^+$: 295.1693, found 295.1694.



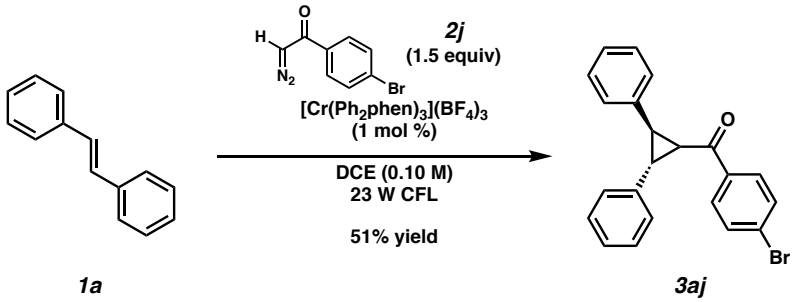
Cyclopropane 3ah. Prepared according to the *General Procedure* using 18.0 mg *trans*-stilbene (0.0999 mmol), 16.0 mg diazoketone **2h** (0.150 mmol), 2.0 mg $[Cr(Ph_2phen)_3](BF_4)_3$ (1.50 μmol), and 1.0 mL DCE. The reaction mixture was irradiated for 48 h. The crude product was purified by flash chromatography (100% hexanes → 9:1 hexanes/Et_2O eluent) to afford *trans*-cyclopropane **3ah** (16.9 mg, 57% yield) as a white solid.

TLC: R_f = 0.36 in 9:1 hexanes/Et_2O, visualized by UV.

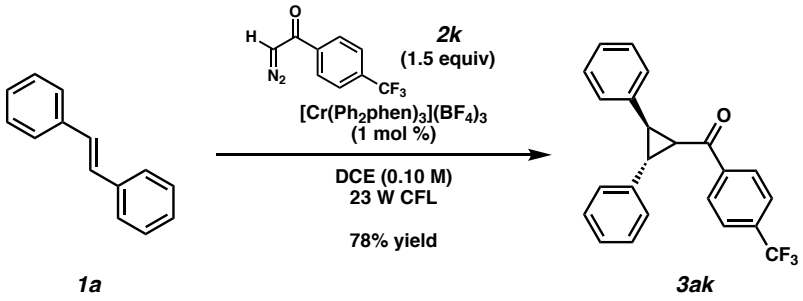
All spectroscopic data were in accordance with the published values.[5]



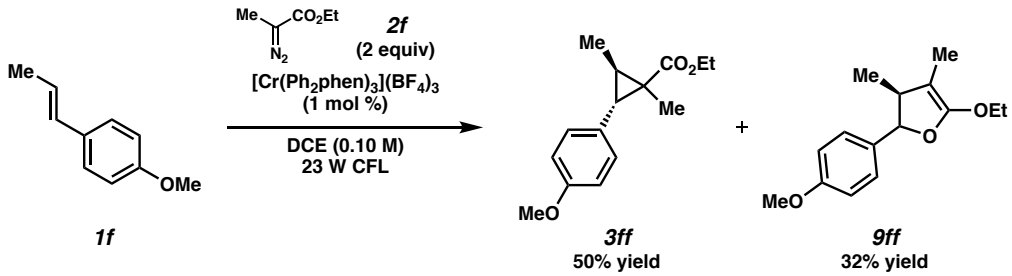
Cyclopropane 3ai. Prepared according to the *General Procedure* using 18.0 mg *trans*-stilbene (0.0999 mmol), 26.4 mg diazoketone **2i** (0.150 mmol), 1.3 mg $[Cr(Ph_2phen)_3](BF_4)_3$ (0.999 μmol), and 1.0 mL DCE. The reaction mixture was irradiated for 48 h. The crude product was purified by flash chromatography (100% hexanes → 4:1 hexanes/Et_2O eluent) to afford *trans*-cyclopropane **3ai** (13.2 mg, 40% yield) as a white solid.
TLC: R_f = 0.26 in 4:1 hexanes/Et_2O, visualized by UV.
All spectroscopic data were in accordance with the published values.[5]



Cyclopropane 3aj. Prepared according to the *General Procedure* using 18.0 mg *trans*-stilbene (0.0999 mmol), 33.8 mg diazoketone **2j** (0.150 mmol), 1.3 mg $[Cr(Ph_2phen)_3](BF_4)_3$ (0.999 μmol), and 1.0 mL DCE. The reaction mixture was irradiated for 48 h. The crude product was purified by flash chromatography (100% hexanes → 9:1 hexanes/Et_2O eluent) to afford *trans*-cyclopropane **3aj** (19.1 mg, 51% yield) as a pale yellow solid.
TLC: R_f = 0.41 in 9:1 hexanes/Et_2O, visualized by UV.
All spectroscopic data were in accordance with the published values.[5]

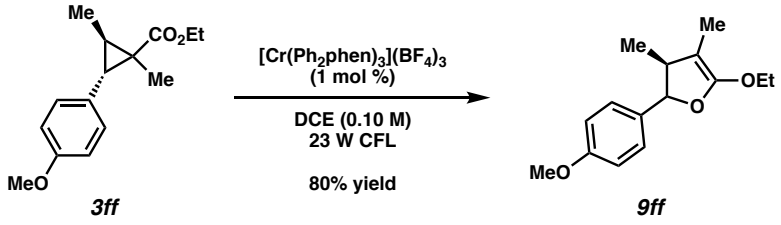


Cyclopropane 3ak. Prepared according to the *General Procedure* using 18.1 mg *trans*-stilbene (0.100 mmol), 32.0 mg diazoketone **2k** (0.110 mmol), 1.3 mg $[Cr(Ph_2phen)_3](BF_4)_3$ (1.00 μmol), and 1.0 mL DCE. The reaction mixture was irradiated for 13 h. The crude product was purified by flash chromatography (100% hexanes → 19:1 hexanes/EtOAc eluent) to afford *trans*-cyclopropane **3ak** (28.6 mg, 78% yield) as a colorless oil that solidified upon standing.
TLC: R_f = 0.35 in 19:1 hexanes/EtOAc, visualized by UV.
^{1}H NMR (400 MHz; $CDCl_3$): δ 8.04 (d, *J* = 8.3 Hz, 2H), 7.70 (d, *J* = 8.3 Hz, 2H), 7.38-7.19 (comp. m, 10H), 3.66 (app. t, *J* = 6.2 Hz, 1H), 3.35 (app. d, *J* = 6.0 Hz, 2H).
^{13}C NMR (125 MHz; $CDCl_3$): δ 194.3, 141.1, 139.6, 135.2, 129.2, 128.8, 128.5, 128.4 127.3, 127.1, 127.0, 126.6, 125.8 (q, $J_{C\text{-}F}$ = 15 Hz), 125.7, 38.4, 36.9, 30.4.
IR (ATR, neat): 3054, 1577, 1324, 1170, 1128, 1067, 1016, 756, 696 cm^{-1}.
HRMS (ESI+): *m/z* calc'd for $(M+H)^+$ $[C_{23}H_{17}F_3O + H]^+$: 367.1304, found 367.1306**.**



Cyclopropane 3ff. Prepared according to the *General Procedure* using 14.7 mg *trans*-anethole (0.0992 mmol), 14.0 mg diazoacetate **2f** (0.109 mmol), 1.3 mg $[Cr(Ph_2phen)_3](BF_4)_3$ (0.992 μmol), and 1.0 mL DCE. The reaction mixture was irradiated for 48 h. Diastereomeric ratio (**3ff**: 1.1:1 anti/syn; **9ff**: 1.5:1 major/minor) was determined by ^{1}H NMR analysis of the crude mixture. The crude products were purified by flash chromatography (100% hexanes → 9:1 hexanes/Et_2O → 9:1 hexanes/EtOAc eluent) to afford 12.3 mg of cyclopropane **3ff** (50% yield) and 7.8 mg of dihydrofuran **9ff** (32% yield).
TLC: R_f = 0.43 in 9:1 hexanes/EtOAc, visualized by UV and stained purple with *p*-anisaldehyde.
^{1}H NMR (400 MHz; $CDCl_3$): Major (anti): δ 7.09 (d, *J* = 8.6 Hz, 2H), 6.82 (d, *J* = 8.6 Hz, 2H), 4.19 (q, *J* = 7.2 Hz, 2H), 3.79 (s, 3H), 2.72 (d, *J* = 7.2 Hz, 1H), 2.21 (app. q, *J* = 6.4 Hz, 1H), 1.31 (d, *J* = 6.4 Hz, 3H), 1.29 (t, *J* = 7.2 Hz, 3H), 0.97 (s, 3H).
Minor (syn): δ 7.11 (d, *J* = 8.6 Hz, 2H), 6.77 (d, *J* = 8.6 Hz, 2H), 3.81-3.77 (comp m., 2H), 3.77 (s, 3H), 1.92 (d, *J* = 7.2 Hz, 1H), 1.46-1.40 (m, 1H), 1.43 (s, 3H), 1.26 (d, *J* = 6.4 Hz, 3H), 0.89 (t, *J* = 7.0 Hz, 3H).
^{13}C NMR (100 MHz; $CDCl_3$): δ 174.0, 173.1, 158.3, 158.2, 130.2, 130.0, 129.8, 113.6, 113.3, 60.6, 60.2, 55.4, 40.7, 36.4, 31.7, 30.6, 28.3, 23.3, 16.2, 15.3, 14.5, 14.1, 13.4, 12.7.
IR (ATR, neat): 2975, 1719, 1515, 1474, 1247, 1174, 1158, 1033 cm^{-1}.
HRMS (ESI+): *m/z* calc'd for $(M+Na)^+$ $[C_{15}H_{20}O_3 + Na]^+$: 271.1305, found 271.1305.

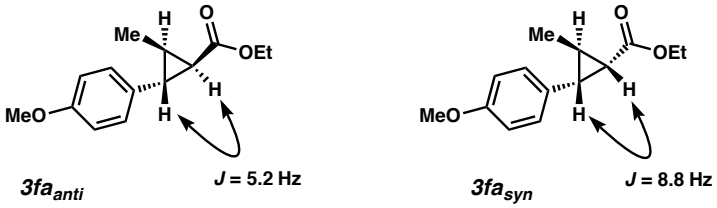
Dihydrofuran 9ff.
TLC: R_f = 0.31 in 17:3 hexanes/EtOAc, visualized by UV and stained gray with *p*-anisaldehyde.
^{1}H NMR (400 MHz; $CDCl_3$): Major: δ 7.31 (d, *J* = 8.6 Hz, 2H), 6.90 (d, *J* = 8.6 Hz, 2H), 4.89 (d, *J* = 9.6 Hz, 1H), 4.35-4.25 (comp. m, 2H), 3.81 (s, 3H), 2.69 (dq, *J* = 9.6, 7.0 Hz, 1H), 1.65 (s, 3H), 1.36 (t, *J* = 7.2 Hz, 3H), 1.03 (d, *J* = 7.0 Hz, 3H).
Minor: δ 7.29 (d, *J* = 8.6 Hz, 2H), 6.89 (d, *J* = 8.6 Hz, 2H), 4.68 (d, *J* = 8.4 Hz, 1H), 4.35-4.25 (comp. m, 2H), 3.80 (s, 3H), 3.25 (qd, *J* = 8.4 Hz, 7.2 Hz, 1H), 1.46 (s, 3H), 1.34 (t, *J* = 6.4 Hz, 3H), 1.12 (d, *J* = 7.2 Hz, 3H).
^{13}C NMR (125 MHz; $CDCl_3$): δ 173.8, 171.3, 160.4, 160.3, 129.2, 128.8, 127.0, 126.7, 114.4, 114.3, 90.9, 88.6, 88.4, 87.9, 61.9, 61.7, 61.1, 55.4, 54.6, 21.8, 17.4, 14.5, 14.4, 12.5, 11.5.
IR (ATR, neat): 2981, 1733, 1612, 1516, 1462, 1251, 1177, 1109, 1030, 829 cm^{-1}.
HRMS (ESI+): *m/z* calc'd for $(M+H)^+$ $[C_{15}H_{20}O_3 + H]^+$: 249.1485, found 249.1485.



Cyclopropane to Dihydrofuran Rearrangement. A solution of cyclopropane **3ff** (7.7 mg (0.0310 mmol) and $[Cr(Ph_2phen)_3](BF_4)_3$ (0.4 mg) in DCE (0.5 mL) was prepared in a flame-dried borosilicate vial open to air. The vial was then capped and placed in a closed box, lined with aluminum foil, and equipped with a 23 W compact fluorescent light bulb. The reaction mixture was irradiated for 45 h. The reaction mixture was concentrated via rotary evaporation and purified by flash column chromatography (100% hexanes → 17:3 hexanes/EtOAc eluent) to afford 6.1 mg of dihydrofuran **9ff** (80% yield).

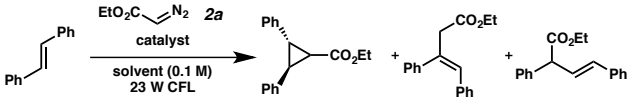
Diastereomer Assignments

For the cyclopropane products where diastereomers were formed, their stereochemistry was assigned by analysis of NMR data. Specifically, coupling constants for two of the cyclopropyl protons could be identified and evaluated, and their relative values gave a strong indication of relative positioning. An anti relationship of the two protons would have a smaller coupling constant than the corresponding syn relationship. An example using compound **3fa** is depicted below.



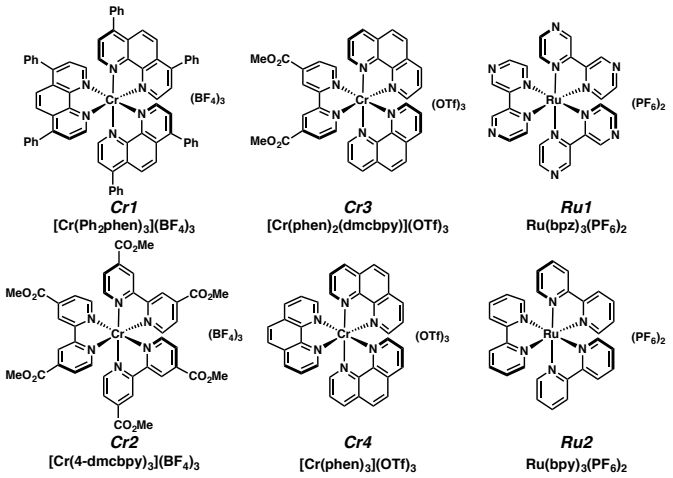
Optimization Studies

Table 1 ***(Reproduced).*** Optimization of Cr-catalyzed cyclopropanation.



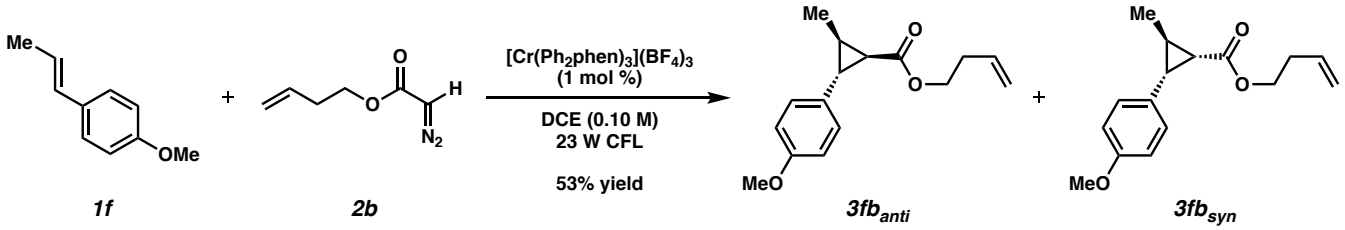
entry	catalyst (mol %)	solvent	equiv *2a*	time (h)	NMR yield[a] *3aa*	*4aa*	*5aa*
1[b]	***Cr1*** (1)	CH_3NO_2	5	24	60	8	7
2	***Cr1*** (1)	CH_3NO_2	5	24	61	10	8
3	***Cr1*** (1)	CH_3NO_2	1.1	40	60	8	11
4	***Cr2*** (1)	CH_3NO_2	1.1	40	5	1	1
5	***Cr3*** (1)	CH_3NO_2	1.1	40	40	8	7
6	***Cr4*** (1)	CH_3NO_2	1.1	40	50	9	8
7	***Ru1*** (1)	CH_3NO_2	1.1	24	3	0	0
8	***Ru1*** (1)	CH_3NO_2	5	14	9	4	5
9	***Ru2*** (5) ***+ MV*** (15)[c]	CH_3NO_2	5	21	12	2	2
10	***Ru2*** (5)	CH_3NO_2	5	21	0	0	0
11	***Cr1*** (1)	$CHCl_3$	1.1	24	18	1	2
12	***Cr1*** (1)	acetone	1.1	24	57	5	8
13	***Cr1*** (1)	CH_2Cl_2	1.1	24	73	2	7
14	***Cr1*** (1)	CH_3CN	1.1	24	67	8	10
15	***Cr1*** (1)	DCE	1.1	24	73	0	5
16	none	DCE	1.1	14	0	0	0
17	$CrCl_3$ (10)	DCE	1.1	49	0	0	0
18[d]	***Cr1*** (1)	DCE	1.1	49	0	0	0

[a] Determined using veratraldehyde as a standard. [c] Near UV light (bulbs at 300, 350, and 419 nm) used instead of 23 W CFL. [c] MV: methyl viologen^{2+}·$(PF_6)_2$. [d] Reaction performed in dark (foil wrapped).

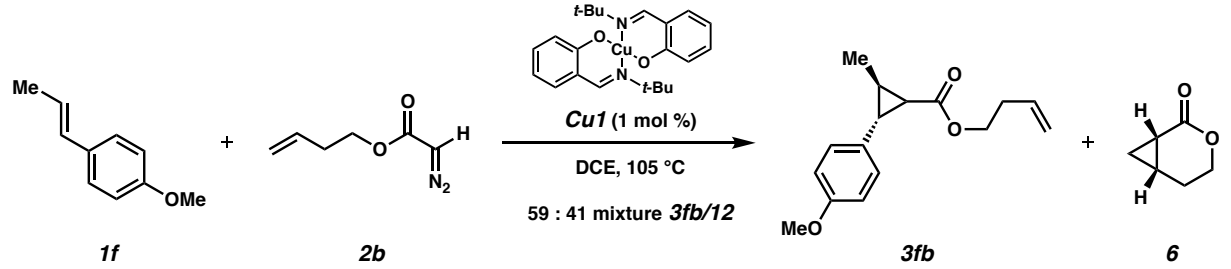


General Procedure for Optimization Experiments: A flame-dried 1-dram borosilicate vial open to air was charged with *trans*-stilbene (18.0 mg, 0.0999 mmol), ethyl diazoacetate (1.1 or 5.0 equiv), catalyst, and 1.0 mL solvent (0.1 M). The vial was then capped. The solution was irradiated with the indicated light source, stirring for the indicated time and then concentrated via rotary evaporation. The resulting crude product was analyzed by ^{1}H NMR, using veratraldehyde as a standard. Compounds **4aa** and **5aa** were identified by comparison to compounds reported in the literature.[6]

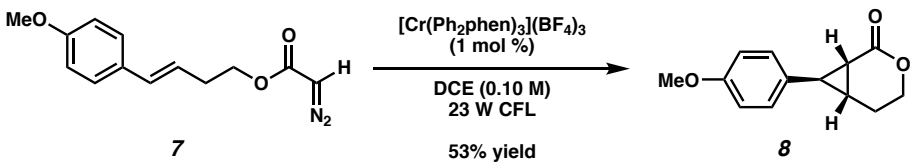
Chemoselectivity Experiments



Cyclopropane 3fb. Prepared according to the *General Procedure* using 14.8 mg *trans*-anethole (0.0999 mmol), 15.4 mg diazoacetate **2b** (0.110 mmol), 1.3 mg $[Cr(Ph_2phen)_3](BF_4)_3$ (0.999 μmol), and 1.0 mL DCE. The reaction mixture was irradiated for 72 h. Diastereomeric ratio (1.1:1 anti/syn) was determined by ^{1}H NMR analysis of the crude mixture. The crude product was purified by flash chromatography (100% hexanes → 9:1 hexanes/EtOAc eluent) to afford *trans*-cyclopropane **3fb** (13.9 mg, 53% yield) as a colorless oil.
TLC: R_f = 0.29 in 9:1 hexanes/Et_2O, visualized by UV. Stained blue by *p*-anisaldehyde.
^{1}H NMR (400 MHz; $CDCl_3$): Major (anti): δ 7.01 (d, *J* = 8.6 Hz, 2H), 6.82 (d, *J* = 8.6 Hz, 2H), 5.81 (ddt, *J* = 17.0, 10.3, 6.8 Hz, 1H), 5.15-4.98 (comp. m, 2H), 4.17 (dt, *J* = 6.8, 1.5 Hz, 2H), 3.78 (s, 3H), 2.41 (app. q, *J* = 6.8 Hz, 2H), 2.36 (dd, *J* = 6.6, 5.0 Hz, 1H), 1.93 (dd, *J* = 9.2, 5.0 Hz, 1H), 1.67-1.58 (comp. m, 1H), 1.33 (d, *J* = 6.4 Hz, 3H).
Minor (syn): δ 7.15 (d, *J* = 8.4 Hz, 2H), 6.79 (d, *J* = 8.4 Hz, 2H), 5.63 (ddt, *J* = 17.0, 10.5, 6.6 Hz, 1H), 5.15-4.98 (comp. m, 2H), 3.95-3.84 (comp. m, 2H), 3.77 (s, 3H), 2.30 (dd, *J* = 9.2, 7.0 Hz, 1H), 2.15 (app. qd, *J* = 6.8, 1.2 Hz, 2H), 2.01 (app. sextet, *J* = 6.0 Hz, 1H), 1.78 (dd, *J* = 9.2, 5.2 Hz, 1H), 1.26 (d, *J* = 6.0 Hz, 3H).
^{13}C NMR (100 MHz; $CDCl_3$): δ 171.9, 171.1, 158.4, 158.3, 134.31, 134.27, 132.7, 130.2, 128.8, 127.3, 117.3, 117.0, 114.0, 113.5, 63.7, 63.4, 55.5, 55.3, 33.9, 33.4, 33.1, 32.0, 30.0, 29.2, 25.4, 20.1, 17.9, 12.2.
IR (ATR, neat): 2960, 1724, 1517, 1248, 1168, 1037, 917, 829 cm^{-1}.
HRMS (ESI+): *m/z* calc'd for $(M + H)^+$ $[C_{16}H_{20}O_3 + H]^+$: 261.1485, found 261.1472.



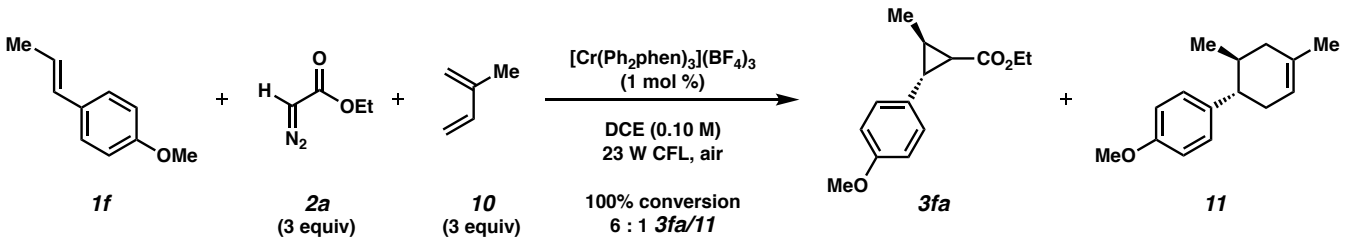
Cu-Catalyzed Experiment. To a flame-dried round bottom flask was added *trans*-anethole (**1f**, 0.150 mL, 1.01 mmol), copper catalyst **Cu1**[7] (4.2 mg, 0.0101 mmol), and 3.0 mL of DCE. The flask was fitted with a reflux condenser and placed in an oil bath that was subsequently heated to 105 °C. To this reaction mixture, a solution of diazo **2b** (1.10 mL, 1.0 M solution in CH_2Cl_2, 1.10 mmol) in 2.0 mL of DCE, was added *via* syringe pump at a rate of 500 μL/h. After ~6 h, the reaction mixture was allowed to cool to room temperature. The reaction mixture was concentrated via rotary evaporation and the crude reaction mixture was analyzed by ^{1}H NMR. Through ^{1}H NMR analysis, it was determined that a 59:41 ratio was obtained of **3fb:12**, with <20% consumption of either **1f** or **2b**. The presence of compound **12** was confirmed by comparison to literature data.[8] Unreacted *trans*-anethole was observed, as were diazo dimerization products (assigned by comparison to dimethyl fumarate and maleate).

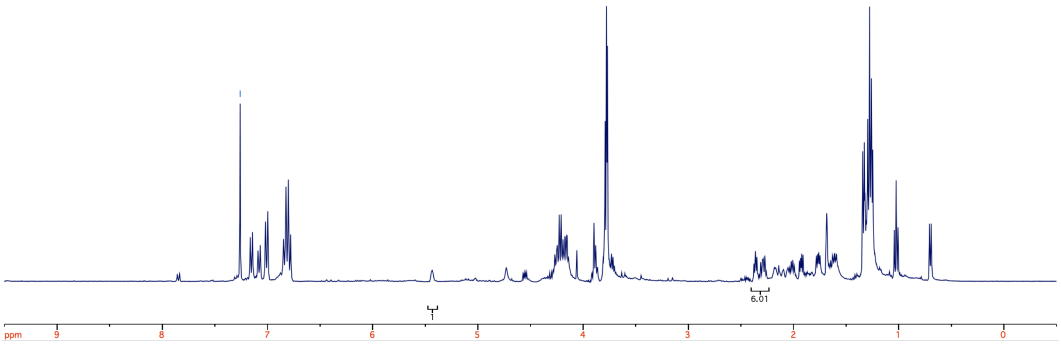


Cyclopropane 8. Prepared using 25.7 mg diazo ester **7** (0.104 mmol), 1.3 mg $[Cr(Ph_2phen)_3](BF_4)_3$ (1.04 μmol), and 1.0 mL DCE. The reaction mixture was irradiated for 48 h. The crude product was purified by flash chromatography (3:1 → 1:1 hexanes/EtOAc eluent) to afford cyclopropane **8** (12.1 mg, 53% yield) as a colorless oil. The stereochemical assignment of cyclopropane **8** was determined by analogy to a similar lactone compound.[8]
TLC: R_f = 0.40 in 1:1 hexanes/EtOAc, visualized by UV and stained blue with *p*-anisaldehyde.
^{1}H NMR (400 MHz; $CDCl_3$): δ 7.04 (d, *J* = 8.6 Hz, 2H), 6.84 (d, *J* = 8.6 Hz, 2H), 4.34 (dd, *J* = 12.3, 6.2 Hz, 1H), 4.25 (app. td, *J* = 12.3, 4.1 Hz, 1H), 3.79 (s, 3H), 2.90 (app. t, *J* = 4.1 Hz, 1H), 2.25 (app. td, *J* = 13.0, 6.2 Hz, 1H), 2.14-2.10 (comp. m, 3H).
^{13}C NMR (100 MHz; $CDCl_3$): δ 169.9, 158.8, 130.1, 127.6, 114.3, 64.7, 55.5, 26.5, 24.6, 23.5, 20.6.
IR (ATR, neat): 2934, 1721, 1516, 1248, 1082, 1034, 806 cm^{-1}.
HRMS (ESI+): *m/z* calc'd for $(M + H)^+$ $[C_{13}H_{14}O_3 + H]^+$: 219.1016, found 219.1016.

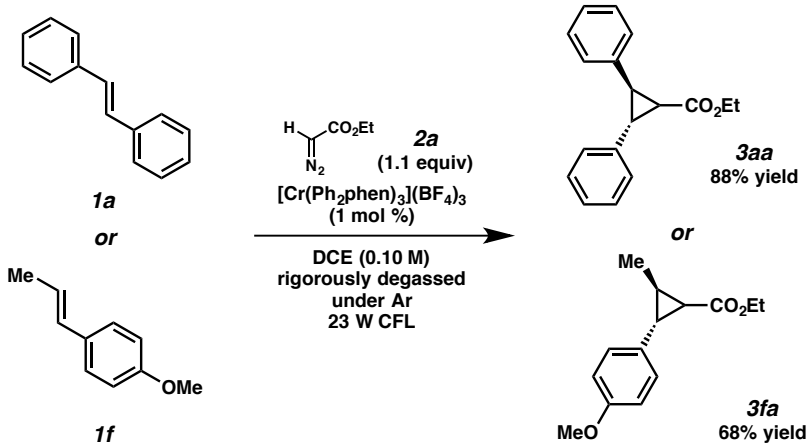
Nucleophile Competition Experiment

A solution containing 14.8 mg *trans*-anethole (0.0999 mmol, 1 equiv), 37.3 µL ethyl diazoacetate (85% wt. solution in CH_2Cl_2, 0.300 mmol, 3 equiv), 30.0 µL isoprene (0.300 mmol, 3 equiv), and 1.3 mg $[Cr(Ph_2phen)_3](BF_4)_3$ (0.999 µmol, 1 mol %) in 1.0 mL DCE was prepared in a flame-dried borosilicate vial open to air. The vial was then capped and placed in a closed box, lined with aluminum foil, and equipped with a 23 W compact fluorescent light bulb. The mixture was irradiated for 48 h at which point it was concentrated *via* rotary evaporation. The crude product was analyzed by ^{1}H NMR to determine the ratio of product distribution.





Oxygen-Free Experiments



Cyclopropane 3aa. A solution containing 18.0 mg *trans*-stilbene (0.0999 mmol), 14.7 mg ethyl diazoacetate (0.110 mmmol, 85% wt. solution in CH_2Cl_2, 1.1 equiv), and 1.3 mg $[Cr(Ph_2phen)_3](BF_4)_3$ (0.999 μmol, 1 mol %) in 1.0 mL of deoxygenated DCE was prepared in a flame-dried schlenk flask under argon. The reaction mixture was degassed by freeze-pump-thaw method (3x) and kept under argon. The flask was placed above a stir plate, surrounded with aluminum foil, and irradiated with a 23 W compact fluorescent light bulb. The mixture was irradiated for 60 h at which point it was concentrated *via* rotary evaporation. The crude product was purified by flash column chromatography (100% hexanes → 19:1 hexanes/acetone eluent) to afford cyclopropane **3aa** (23.5 mg, 88% yield) as a colorless oil.

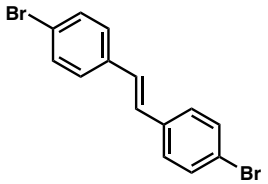
Cyclopropane 3fa. A solution containing 14.7 mg *trans*-anethole (0.0992 mmol), 14.6 mg ethyl diazoacetate (0.110 mmol, 85% wt. solution in CH_2Cl_2, 1.1 equiv), and 1.3 mg $[Cr(Ph_2phen)_3](BF_4)_3$ (0.992 μmol, 1 mol %) in 1.00 mL of deoxygenated DCE was prepared in a flame-dried schlenk flask under argon. The reaction mixture was degassed by freeze-pump-thaw method (3x) and kept under argon. The flask was placed above a stir plate, surrounded with aluminum foil, and irradiated with a 23 W compact fluorescent light bulb. The mixture was irradiated for 60 h at which point it was concentrated *via* rotary evaporation. The crude product was purified by flash column chromatography (100% hexanes → 9:1 hexanes/EtOAc eluent) to afford cyclopropane **3fa** (15.8mg, 68% yield) as a colorless oil.

Substrate Synthesis

General Notes: All reactions were performed in flame-dried glassware under argon. Aldehydes were used directly from commercial sources with no further purification. Alkyltriphenylphosphonium halides for Wittig reactions were dried under vacuum at 105 ˚C overnight prior to use. Alkenes were prepared from the reported procedures in the literature and the pure *E* isomer was subjected to the *General Procedure.* Where relevant, all spectroscopic data were consistent with the published values.

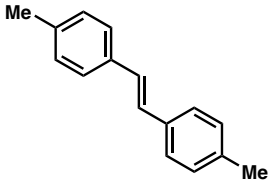
Alkene Substrates

General Procedure for alkene geometry enrichment: When mixtures of *E* and *Z* isomers could be improved to greatly favor the *E* isomer, the protocol as previously described by Yoon[9] was followed. The mixture of isomers was dissolved in benzene (0.25 M), AIBN (0.15 equiv), and PhSH (0.5 equiv) were added, and the reaction was heated at reflux for 1 h. Upon cooling to room temperature, the mixture was washed sequentially with 1 M aq. NaOH and brine, dried over $MgSO_4$, and concentrated using rotary evaporation. The residue was purified by flash column chromatography to afford the desired product as a single *E* isomer.



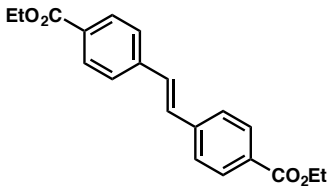
1b

Stilbene 1b. Stilbene **1b** was synthesized according to the procedure described by Winter.[10]



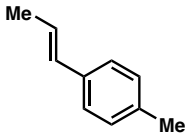
1c

Stilbene 1c. Stilbene **1c** was synthesized according to the procedure described by Batey.[11]



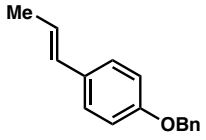
1d

Stilbene 1d. Stilbene **1d** was synthesized in two steps from the corresponding dicarboxylic acid via reported procedures.[12]



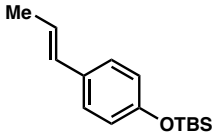
1e

Alkene 1e. Alkene **1e** was prepared according to the procedure described by Nicewicz and coworkers.[13] To improve the isomeric ratio, the *E/Z* mixture was dissolved in benzene (0.25 M), AIBN (0.10 equiv) and PhSH (0.10 equiv) were added, and the reaction was heated at reflux overnight. The mixture was cooled to room temperature, diluted with Et_2O, and washed sequentially with sat. aq. $NaHCO_3$, then brine. The organic layer was dried over $MgSO_4$, filtered, concentrated via rotary evaporation, and purified by flash column chromatography to afford alkene **1e** as a single *E* isomer.



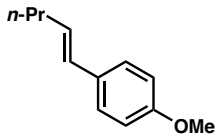
1g

Alkene 1g. Alkene **1g** was prepared according to our reported procedure,[14] and the alkene geometry was enriched according to the above General Procedure.



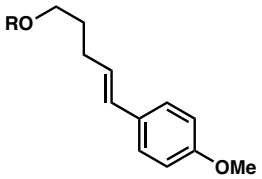
1h

Alkene 1h. Alkene **1h** was prepared according to the procedure described by Yoon.[15]



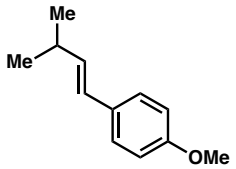
1i

Alkene 1i. Alkene **1i** was prepared according to our reported procedure,[14] and the alkene geometry was enriched according to the above General Procedure.



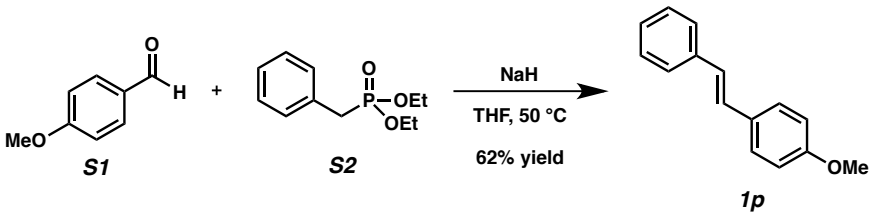
1j **(R = Bz)**
1k **(R = Ac)**
1l **(R = Me)**
1m **(R = H)**
1n **(R = Ts)**

Alkenes 1j-1n. Alkenes **1j-1n** were prepared according to our reported procedures,[14] and the alkene geometry was enriched according to the above General Procedure.

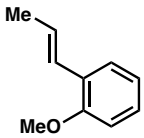


1o

Alkene 1o. Alkene **1o** was prepared according to the procedure described by Yoon, and the alkene geometry was enriched according to the above General Procedure.[9a]

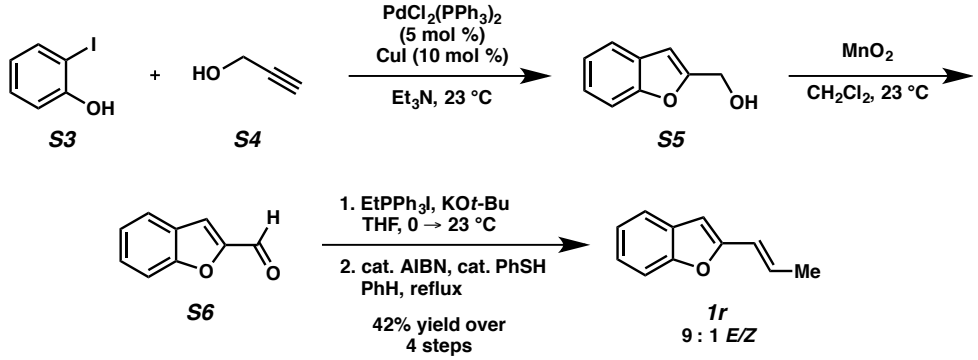


Stilbene 1p. Under an argon atmosphere, NaH (792 mg, 60% dispersion in mineral oil, 19.8 mmol, 3.0 equiv) was added to a solution of *p*-anisaldehyde (0.80 mL, 6.60 mmol, 1.0 equiv) and diethyl benzylphosphonate (1.40 mL, 6.60 mmol, 1.0 equiv) in THF (22.0 mL, 0.3 M) at room temperature. The resulting mixture was stirred at 50 ˚C for 30 min. The reaction mixture was cooled to room temperature and H_2O (25 mL) was added, which caused a white solid to precipitate. The reaction mixture was filtered, and the white precipitate was washed with water. The crude product was recrystallized from hot EtOH, filtered, washed with cold EtOH, and dried in vacuo to yield alkene **1p** (857 mg, 62% yield) as fine white crystals.
TLC: R_f = 0.63 in 9:1 hexanes/EtOAc, visualized by UV.
All spectroscopic data were in accordance with the published values.[16]



1q

Alkene 1q. Alkene **1q** was prepared according to our reported procedure,[14] and the alkene geometry was enriched according to the above General Procedure.



Alkene 1r. Alkene **1r** was synthesized in 4 steps from 2-iodophenol. A solution of 2-iodophenol (500 mg, 2.27 mmol) and propargyl alcohol (0.144 mL, 2.50 mmol) in triethylamine (5.0 mL, 0.454 M) at 23 ˚C was degassed with argon via bubbling for 15 min. CuI (43.0 mg, 0.227 mmol) was added followed by $PdCl_2(PPh_3)_2$ (80.0 mg, 0.114 mmol), and the mixture was

stirred at 23 ˚C overnight. Upon completion, the mixture was filtered through a SiO_2 plug, washing with EtOAc (25 mL). The filtrate was concentrated under reduced pressure and carried directly to the next transformation without further purification. The crude carbinol (**S5**) was dissolved in 13.6 mL CH_2Cl_2 (0.484 M), and 1.90 g (10 equiv) of MnO_2 was added to the mixture. After stirring overnight, the mixture was filtered through a celite plug using CH_2Cl_2 as the eluent (25 mL). The filtrate was concentrated under reduced pressure to give crude aldehyde **S6**, which was carried directly to the next transformation without further purification. In a dry round bottom flask, 1.11 g of $EtPPh_3I$ (2.66 mmol, 1.4 equiv) and KO*t*-Bu (2.47 mmol, 1.3 equiv) were added. The reaction flask was placed in an ice-water bath, and THF (5 mL, 0.4 M) was added to the mixture. The solution was stirred at 0 ˚C for 0.5 h, at which point a solution of aldehyde **S6** in 1.0 mL THF was added dropwise via syringe. The mixture was allowed to warm to room temperature and stirred overnight. Once complete, the mixture was quenched with sat. aq. NH_4Cl (10 mL) and H_2O (5 mL), and it was extracted with Et_2O (3 x 25 mL). The combined organic layers were washed with brine (40 mL) and dried over $MgSO_4$. The $MgSO_4$ was filtered, and the solvent was removed via rotary evaporation to give an amorphous residue that was purified by silica gel chromatography (100% hexanes → 19:1 hexanes/Et_2O) to afford alkene **1r** (253 mg, 4:1 *E/Z* mixture, 70% yield over 3 steps) as a colorless oil. To further enrich the *E* geometry, 250 mg (1.58 mmol) of alkene **1r** was dissolved in 6.4 mL of benzene (0.25 M). To the solution was added 26.0 mg AIBN (0.158 mmol) and 0.02 mL PhSH (0.158 mmol), and the mixture was heated to reflux and stirred overnight. After cooling to room temperature, the mixture was diluted with Et_2O (15 mL), transferred to a separatory funnel and washed with sat. aq. $NaHCO_3$ (10 mL). The organic layer was dried over $MgSO_4$, filtered, and concentrated via rotary evaporation to afford a cloudy oil that was purified by flash column chromatography (100% hexanes → 19:1 hexanes/Et_2O) to afford alkene **1r** (152 mg, 60% yield, ~9:1 trans/cis) as a colorless oil.

TLC: R_f = 0.79 in 9:1 hexanes/Et_2O, visualized by UV, stained yellow by $KMnO_4$.

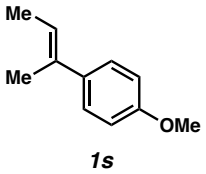
(Note: NMR spectroscopic data reported is for the E isomer only.)

^{1}H NMR (400 MHz; $CDCl_3$): δ 7.49 (d, *J* = 7.6 Hz, 1H), 7.41 (d, *J* = 7.6 Hz, 1H), 7.23-7.15 (m, 2H), 6.49 (dd, *J* = 15.6, 6.8 Hz, 1H), 6.45 (br s, 1H), 6.34 (dd, *J* = 15.6, 1.6 Hz, 1H), 1.94 (dd, *J* = 6.8, 1.2 Hz, 3H).

^{13}C NMR (125 MHz; $CDCl_3$): δ 155.3, 154.7, 129.2, 128.7, 124.0, 122.8, 120.7, 120.1, 110.9, 102.6, 18.7.

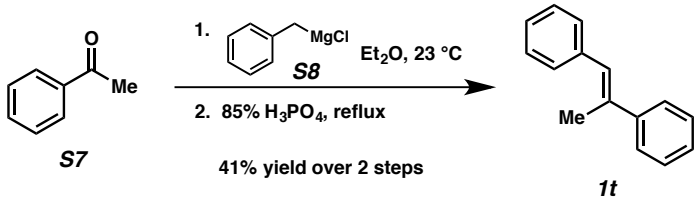
IR (ATR, neat): 2932, 1652, 1453, 1254, 959, 748 cm^{-1}.

HRMS (ESI+): *m/z* calc'd for $(M^{\bullet})^+$ $[C_{11}H_{10}O^{\bullet}]^+$: 158.0726, found 158.0726.



1s

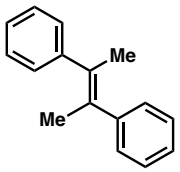
Alkene 1s. Alkene **1s** was prepared according to the procedure described by Castle.[17]



S7 ***1t***

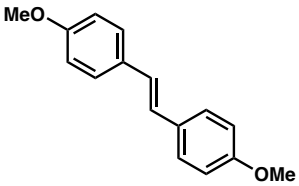
Stilbene 1t. A suspension of magnesium turnings (560 mg, 23.0 mmol, 2.3 equiv) in dry Et_2O (11.1 mL) was prepared in a flame-dried round bottom flask fitted with a reflux condenser. A solution of benzyl chloride (2.30 mL, 20.0 mmol, 2.0 equiv) in dry Et_2O (11.1 mL) was added dropwise at room temperature, and bubbling indicated the formation of benzyl magnesium chloride. Once bubbling ceased, the mixture was set to a gentle reflux at 35 ˚C for approximately 15 min, and then cooled to room temperature. To this freshly prepared Grignard solution was added acetophenone (1.17 mL, 10.0 mmol, 1.0 equiv) dropwise at ambient temperature. The reaction mixture was stirred at room temperature until determined complete by TLC (~1 h). The reaction mixture was quenched with sat. aq. NH_4Cl (25 mL) and extracted with Et_2O (3 x 25 mL). The combined organic phases were washed with brine (60 mL), dried over $MgSO_4$, filtered, and concentrated by rotary evaporation. The crude product was then refluxed in 85% phosphoric acid (17.0 mL, 0.6 M) for 12 h. After cooling to room temperature, the reaction mixture was poured into H_2O (25 mL) and extracted with Et_2O (3 x 25 mL). The combined organic phases were then washed with H_2O (60 mL), then brine (60 mL), dried over $MgSO_4$, filtered, and concentrated by rotary

evaporation. The crude product was recrystallized from hot EtOH. The crystals were collected by filtration, washed with cold EtOH, and dried in vacuo to provide alkene **1t** (800 mg, 41% yield over two steps) as white crystals.
TLC: R_f = 0.77 in 9:1 hexanes/Et_2O, visualized by UV.
All spectroscopic data were consistent with previously reported values.[18]



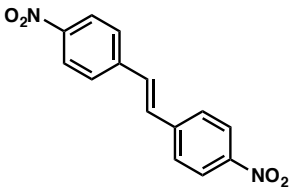
1u
(~1:1 *E/Z*)

Alkene 1u. Alkene **1u** was prepared according to the procedure described by Konwar and Dutta.[19]



1v

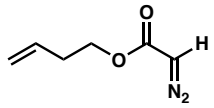
Stilbene 1v. Stilbene **1v** was synthesized according to the procedure described by Kam.[20]



1w

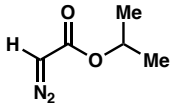
Stilbene 1w. Stilbene **1w** was synthesized according to the procedure described by Bendig.[21]

Diazo Substrates



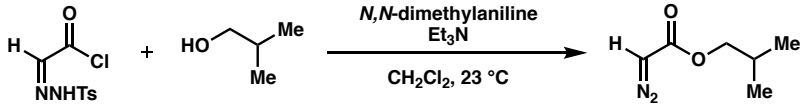
2b

Diazoester 2b. Diazoester **2b** was synthesized according to the procedure described by Moody.[22]



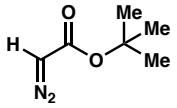
2c

Diazoacetate 2c. Diazoacetate **2c** was synthesized according to the procedure described by Hodgson.[23]



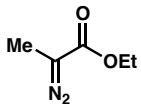
S9 *S10* *2d*

Diazoacetate 2d. To synthesize diazoacetate **2d**, a modified procedure by Corey and Myers[24] was followed. At room temperature, *N,N*-dimethylaniline (0.600 mL, 4.60 mmol, 1.2 equiv) was added dropwise to a solution of dry dichloromethane (6.30 mL) containing glyoxalyl chloride tosylhydrazone (1.00 g, 3.80 mmol) and 2-methyl-1-propanol (0.530 mL, 5.70 mmol, 1.5 equiv). The resulting mixture was stirred at room temperature for 1 h. Triethylamine (2.70 mL, 19.0 mmol, 5.0 equiv) was added, and the resulting mixture was stirred for 30 min, before being poured into water (10 mL). The resulting mixture was extracted with Et_2O (3 x 10 mL). The combined organic extracts were washed once with brine (40 mL) and dried over $MgSO_4$. The $MgSO_4$ was filtered, and the solvent removed via rotary evaporation to give a yellow oil, which was purified by silica gel flash chromatography (9:1 hexanes/Et_2O eluent) to give diazoacetate **2d** (280 mg, 52% yield) as a yellow oil.
TLC: R_f = 0.52 in 9:1 hexanes/EtOAc, visualized by UV.
All spectroscopic data were in accordance with the published values.[25]



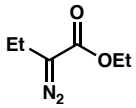
2e

Diazoacetate 2e. Diazoacetate **2e** was synthesized according to the procedure described by Johnson.[26]



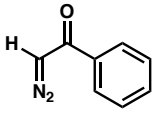
2f

Diazopropionate 2f. Diazopropionate **2f** was synthesized according to the procedure described by Wang and Lin.[27]



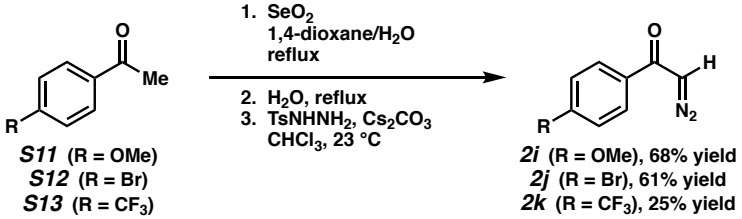
2g

Diazobutyrate 2g. Diazobutyrate **2g** was synthesized according to the procedure described by Wulff.[28]

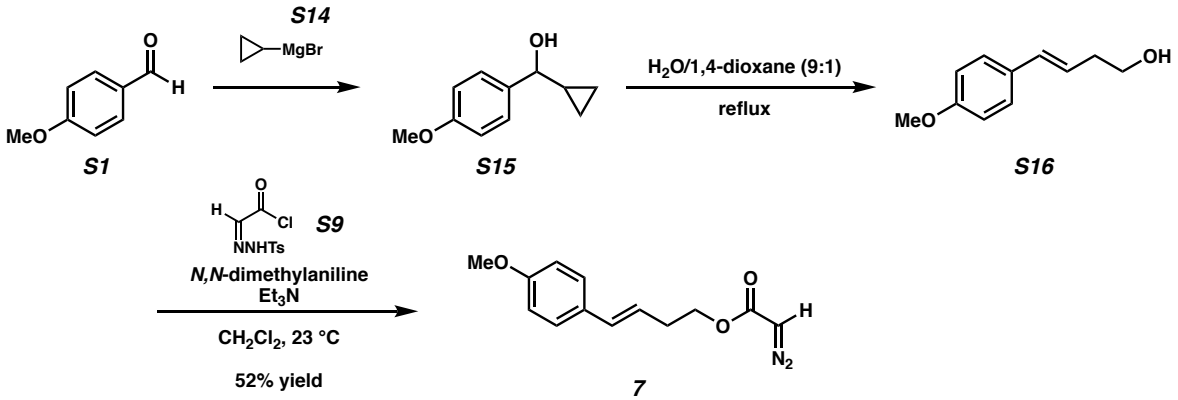


2h

Diazoketone 2h. Diazoketone **2h** was synthesized according to the procedure described by Wu.[29]



Diazoketones 2i-2k. Diazoketones **2i-2k** were synthesized from their respective, commercially available, para-substituted acetophenone precursors. Employing a reported α-oxidation procedure,[30] to a round bottom flask containing 333 mg of SeO_2 (3.00 mmol, 1 equiv), 1.5 mL of 1,4-dioxane (1.98 M) and 0.1 mL of H_2O (41.6 M) was added *p*-substituted acetophenone (3.00 mmol, 1 equiv). The mixture was refluxed overnight and after cooling to room temperature, the solvent was removed via rotary evaporation. 7.2 mL of H_2O (0.416 M) was added to the crude residue, and the mixture was refluxed for another 5 h. The mixture was allowed to cool to room temperature then placed in an ice-water bath to give an off-white precipitate that was filtered and dried in vacuo. Employing a reported diazotization procedure,[29] approximately 1 mmol of the crude solid was dissolved in 2.0 mL of $CHCl_3$ (0.5 M) along with 186 mg of $TsNHNH_2$ (0.999 mmol, 1 equiv) and 977 mg of Cs_2CO_3 (3.00 mmol, 3 equiv). The mixture was stirred for 5 min at room temperature. 50 mL of H_2O was added, and the mixture was extracted with EtOAc (3 x 40 mL). The combined organic layers were washed with brine (50 mL) and dried over $MgSO_4$. The $MgSO_4$ was filtered, and the solvent was removed via rotary evaporation to give a yellow amorphous residue that was purified by silica gel flash chromatography to give pure diazoketone (R = OCH_3 (68%), Br (61%), CF_3 (25%) yields over three steps). All spectroscopic data were in accordance with the published values (–OCH_3,[30] –Br,[30] and –CF_3[31]).



Diazoacetate 7. To synthesize diazoacetate **13**, the procedure of McCormick procedure was followed to synthesize carbinol **S15**,[32] which was rearranged to homoallylic alcohol **S16** using the conditions reported by Qu.[33] A modification of the Corey and Myers protocol[24] for the synthesis of diazoacetates was then followed to furnish diazoacetate **13**. At room temperature, *N,N*-dimethylaniline (0.150 mL, 1.20 mmol, 1.2 equiv) was added dropwise to a solution of dry dichloromethane (1.60 mL) containing glyoxalyl chloride tosylhydrazone (287 mg, 1.10 mmol, 1.1 equiv) and alcohol **S16** (178 mg, 1.00 mmol). The resulting mixture was stirred at room temperature for 1 h. Triethylamine (0.700 mL, 5.00 mmol, 5.0 equiv) was added, and the resulting mixture was stirred for 30 min, before being poured into water (5.0 mL). The resulting mixture was extracted with Et_2O (3 x 5 mL). The combined organic extracts were washed once with brine (15 mL) and dried over $MgSO_4$. The $MgSO_4$ was filtered and the solvent removed via rotary evaporation to give a yellow oil, which was purified by silica gel flash chromatography (9:1 hexanes/EtOAc eluent) to give diazoacetate **7** (118 mg, 48% yield) as a yellow oil that solidified upon cooling.

TLC: R_f = 0.28 in 9:1 hexanes/EtOAc, visualized by UV.

^{1}H NMR (400 MHz; $CDCl_3$): δ 7.28 (d, *J* = 8.8 Hz, 2H), 6.85 (d, *J* = 8.8 Hz, 2H), 6.41 (d, *J* = 16.0 Hz, 1H), 6.01 (dt, *J* = 16.0, 7.2 Hz, 1H), 4.75 (br. s, 1H), 4.26 (t, *J* = 6.6 Hz, 2H), 3.80 (s, 3H), 2.54 (app. qd, *J* = 6.8, 1.2 Hz, 2H).

^{13}C NMR (100 MHz; $CDCl_3$): δ 159.1, 132.1, 130.2, 127.4, 125.4, 123.2, 114.1, 64.4, 55.4, 46.4, 32.7.

IR (ATR, neat): 2109, 1692, 1608, 1511, 1395, 1359, 1246, 1175, 1033 cm^{-1}.

HRMS (ESI+): *m/z* calc'd for $(M + Na)^+$ $[C_{13}H_{14}N_2O_3 + Na]^+$: 269.0897, found 269.0898.

References

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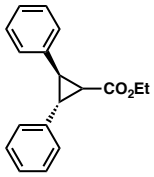
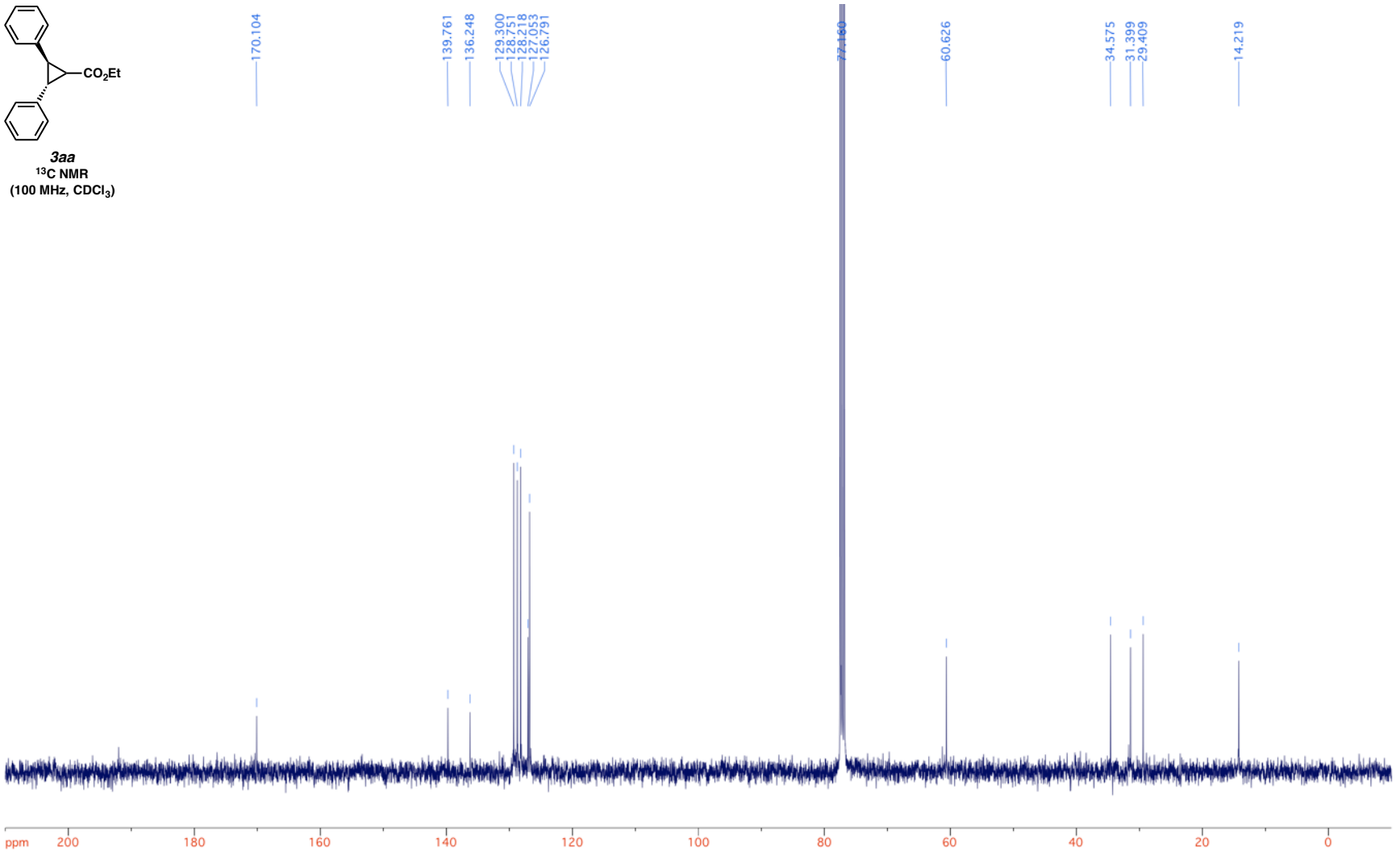
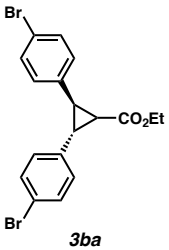
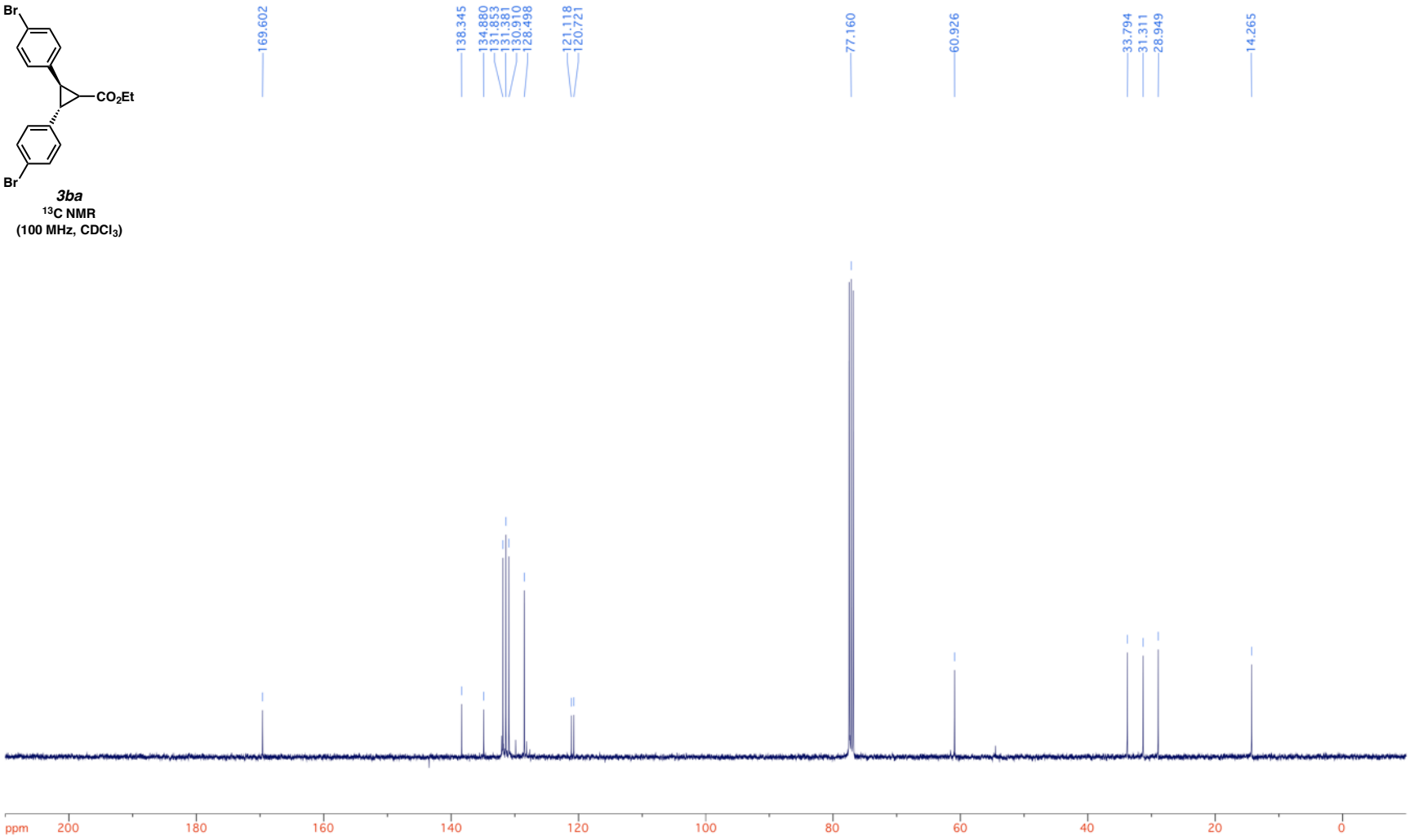


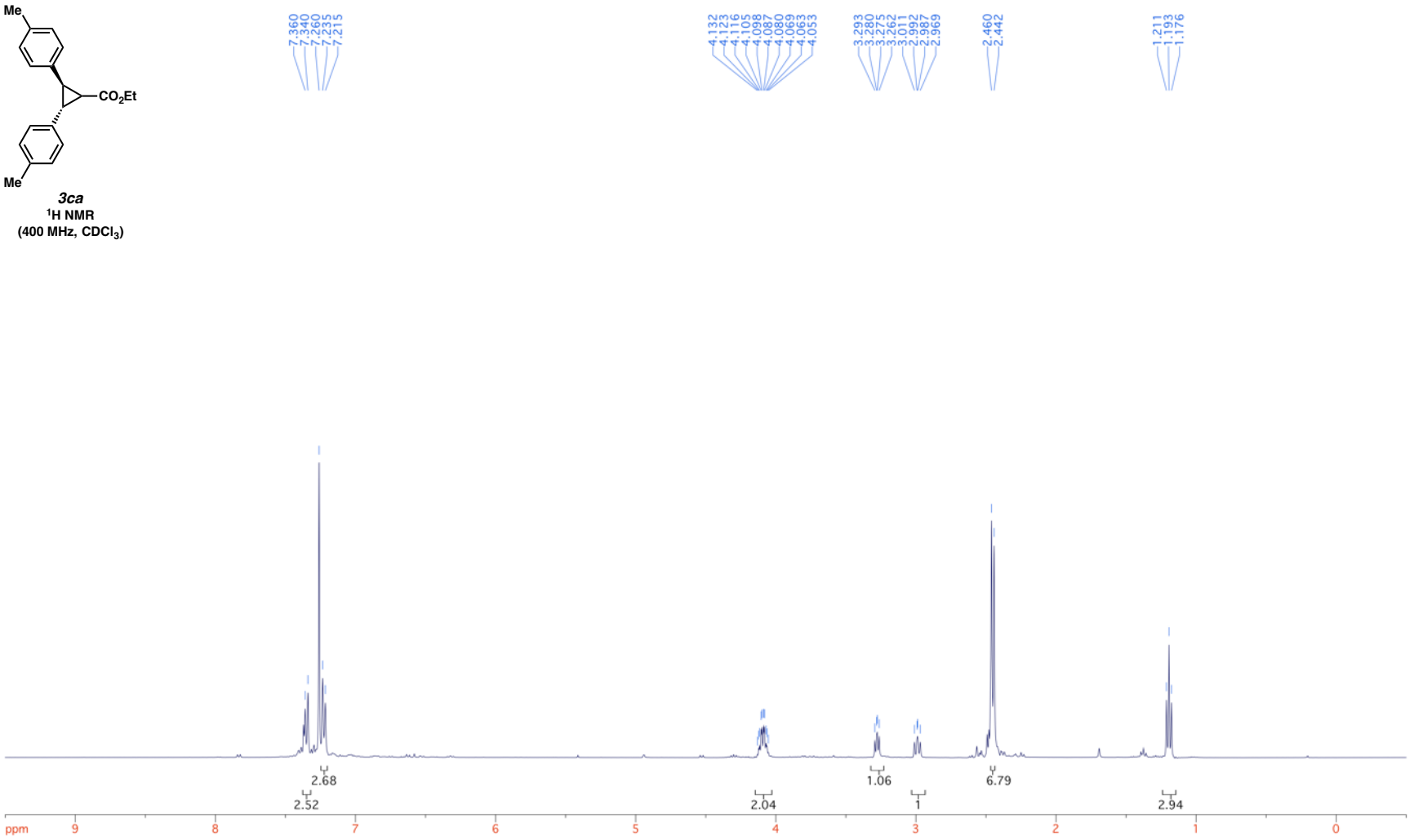
3aa
^{1}H NMR
(400 MHz, $CDCl_3$)


CO2Et
3aa
13C NMR
(100 MHz, CDCl3)
170.104
139.761
136.248
129.300
128.751
128.218
127.053
126.791
77.160
60.626
34.575
31.399
29.409
14.219
ppm
200
180
160
140
120
100
80
60
40
20
0

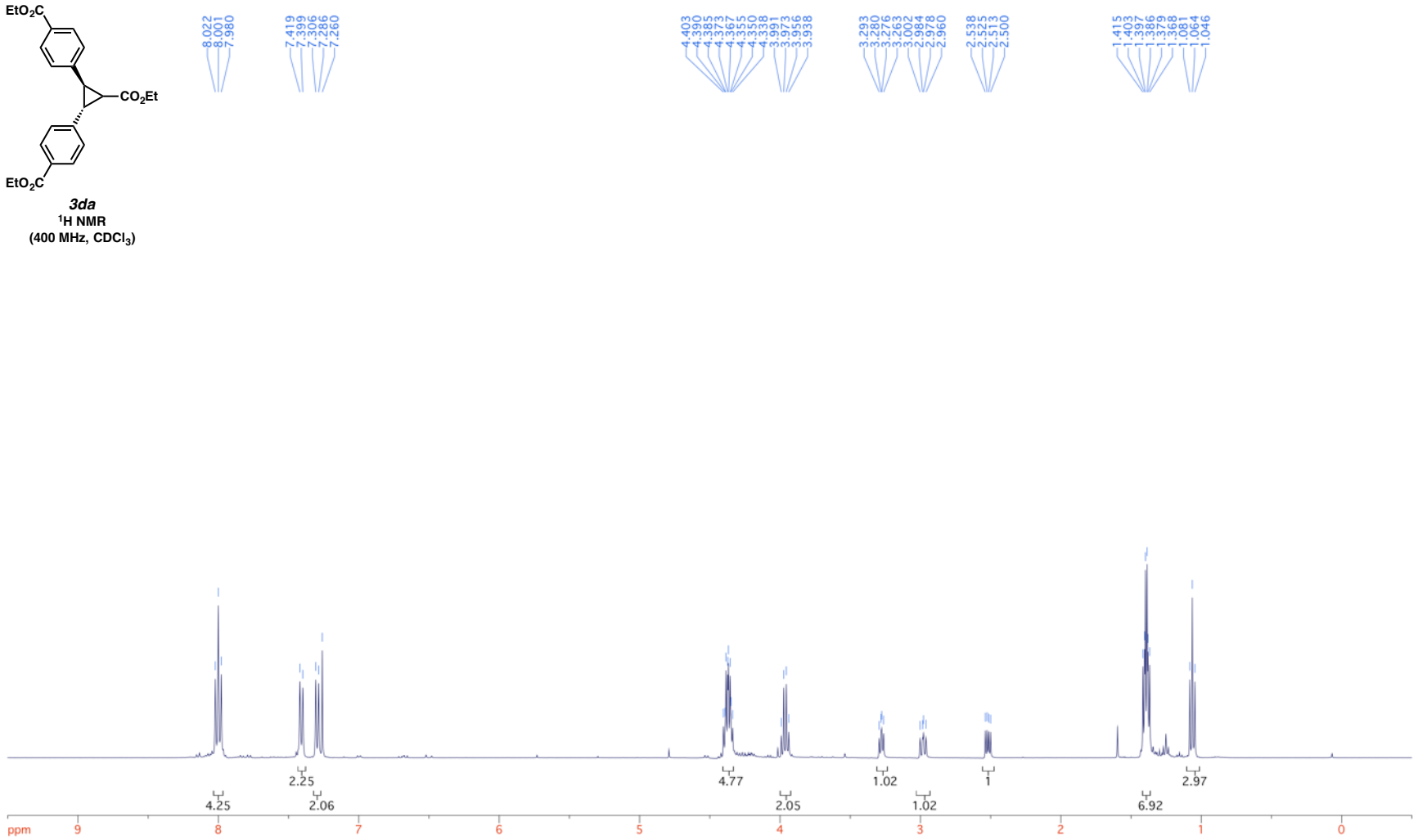


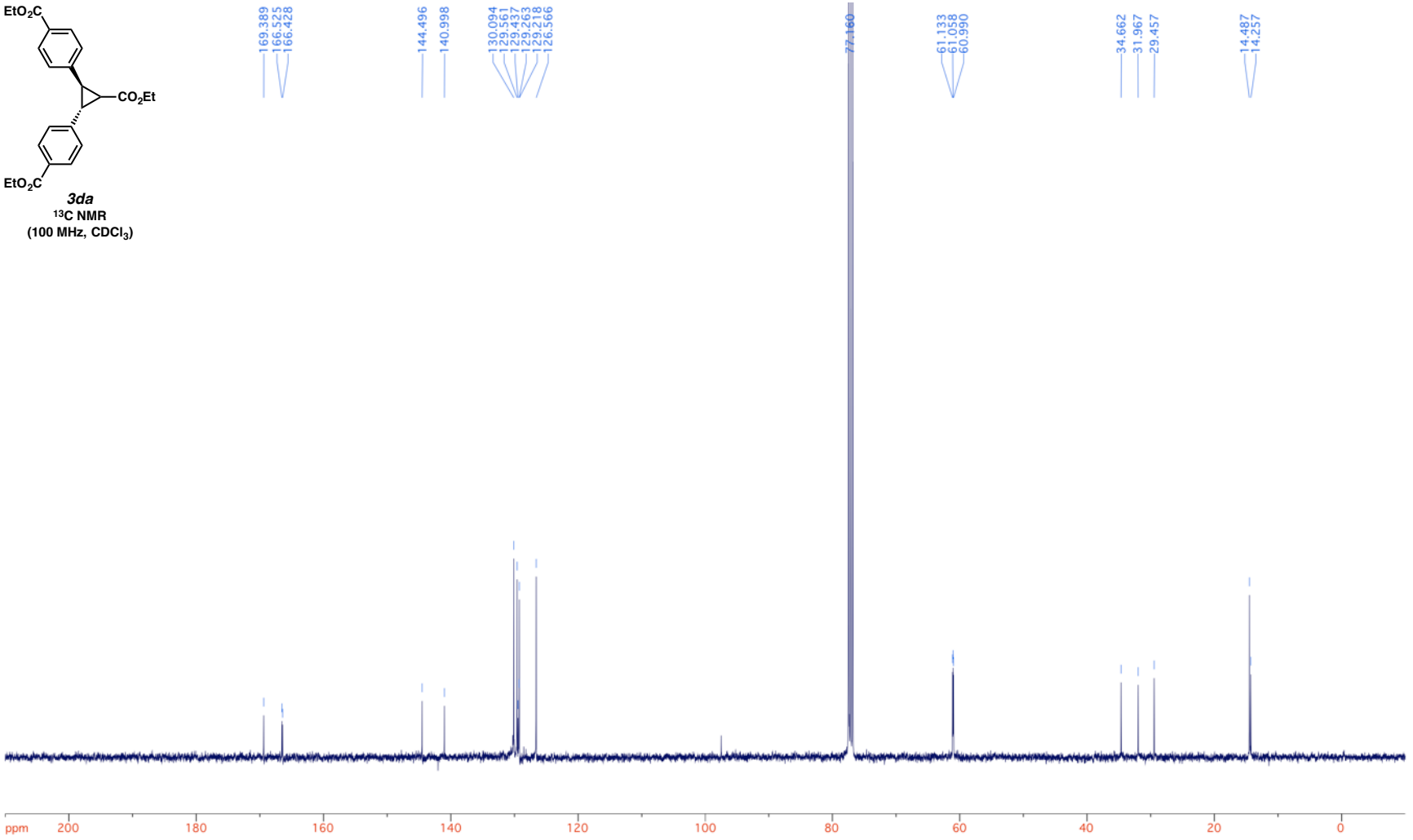
3ba
^{1}H NMR
(400 MHz, $CDCl_3$)

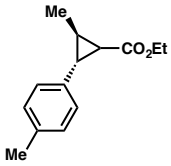

Br
CO2Et
Br
3ba
13C NMR
(100 MHz, CDCl3)
169.602
138.345
134.880
131.853
131.381
130.910
128.498
121.118
120.721
77.160
60.926
33.794
31.311
28.949
14.265
ppm
200
180
160
140
120
100
80
60
40
20
0



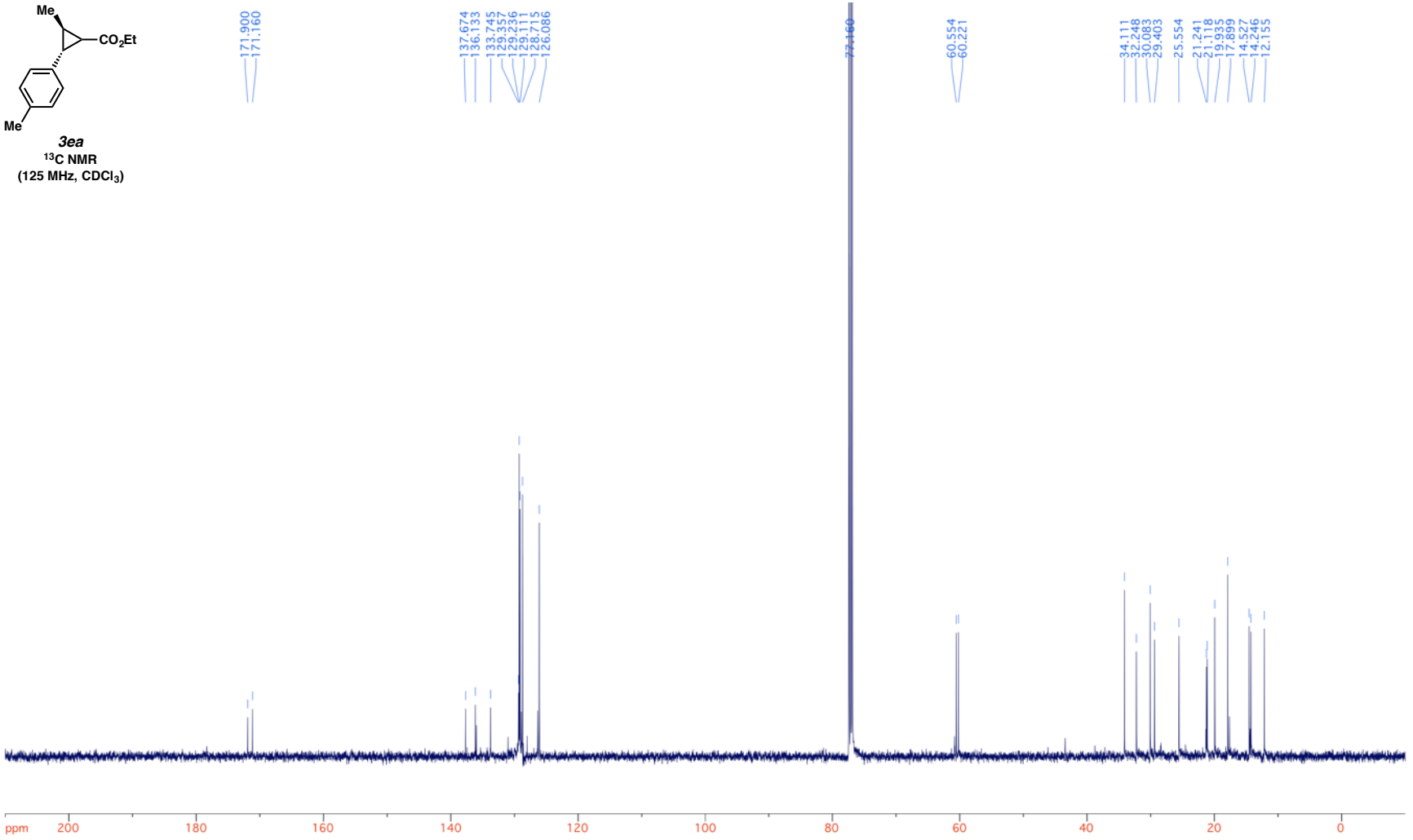
3ca
^{1}H NMR
(400 MHz, $CDCl_3$)


EtO2C
CO2Et
EtO2C
3da
1H NMR
(400 MHz, CDCl3)
8.022
8.001
7.980
7.419
7.399
7.306
7.286
7.260
4.403
4.390
4.385
4.373
4.367
4.355
4.338
4.331
3.973
3.956
3.938
3.293
3.280
3.276
3.263
3.002
2.984
2.978
2.960
2.538
2.525
2.513
2.500
1.415
1.403
1.397
1.386
1.379
1.368
1.081
1.064
1.046
2.25
4.25
2.06
4.77
2.05
1.02
1.02
1
2.97
6.92
ppm
9
8
7
6
5
4
3
2
1
0

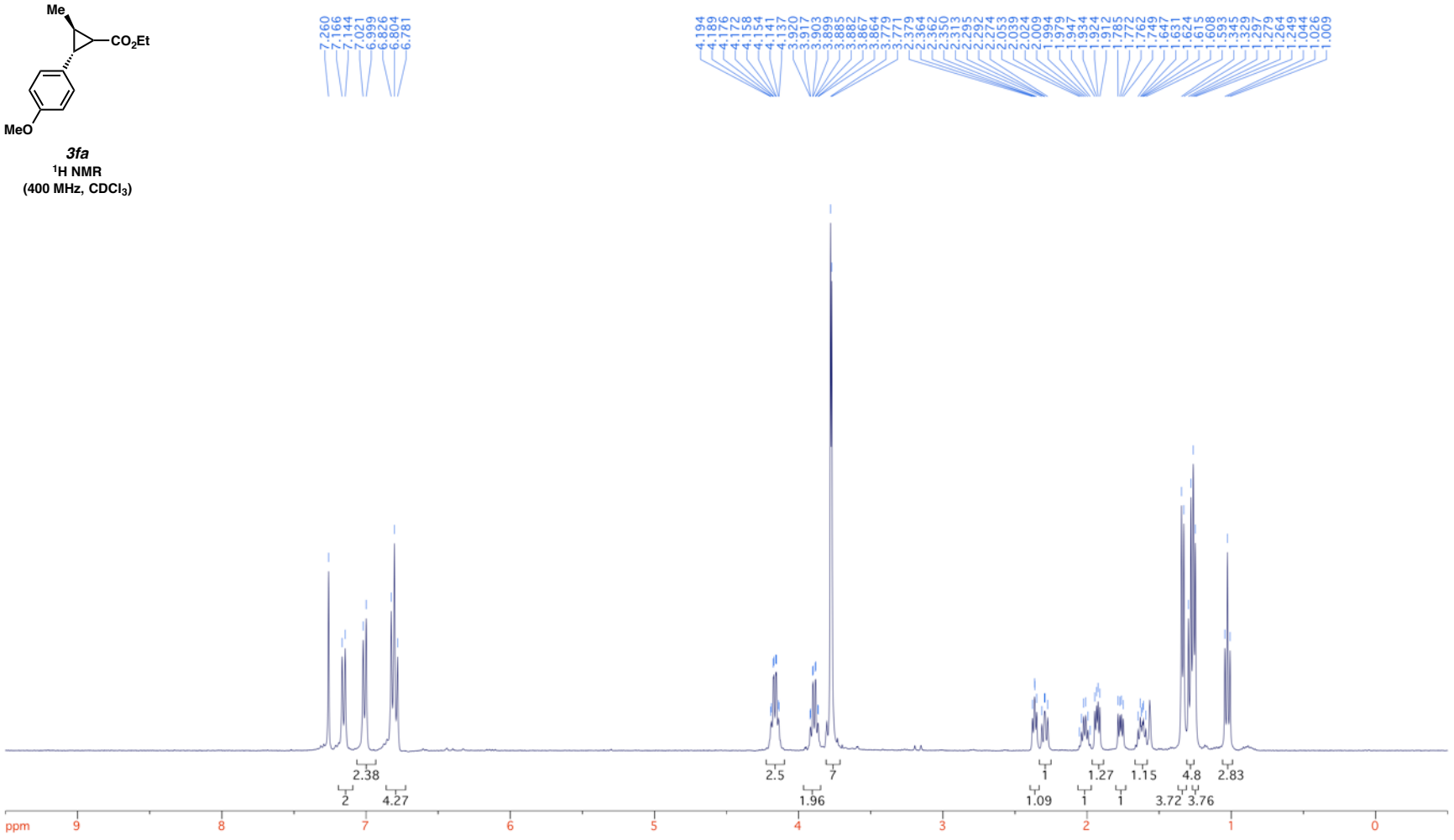

EtO2C
CO2Et
EtO2C
3da
13C NMR
(100 MHz, CDCl3)
169.389
166.525
166.428
144.496
140.998
130.094
129.561
129.437
129.263
129.218
126.566
77.160
61.133
61.058
60.990
34.662
31.967
29.457
14.487
14.257
ppm
200
180
160
140
120
100
80
60
40
20
0



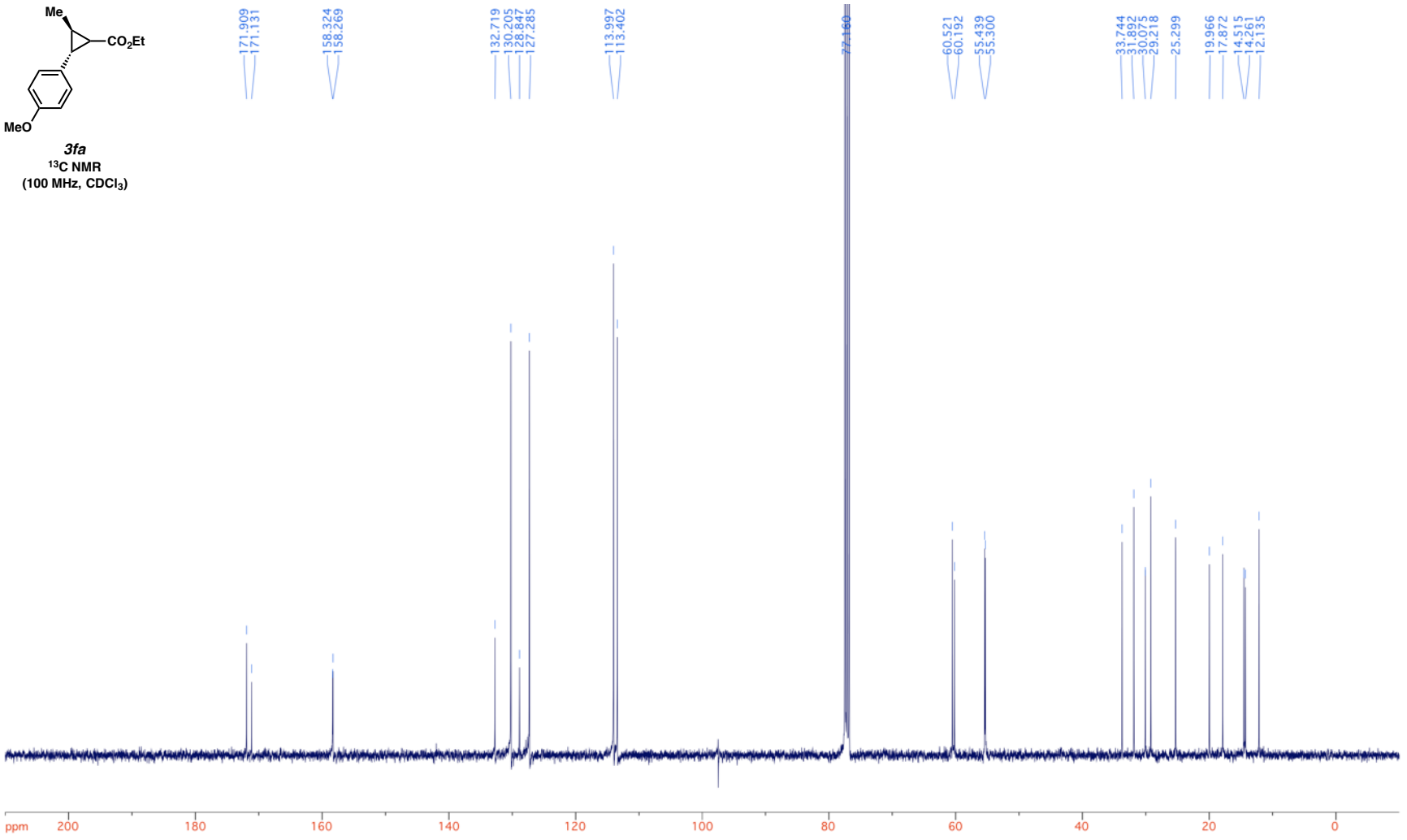
3ea
^{1}H NMR
(400 MHz, $CDCl_3$)

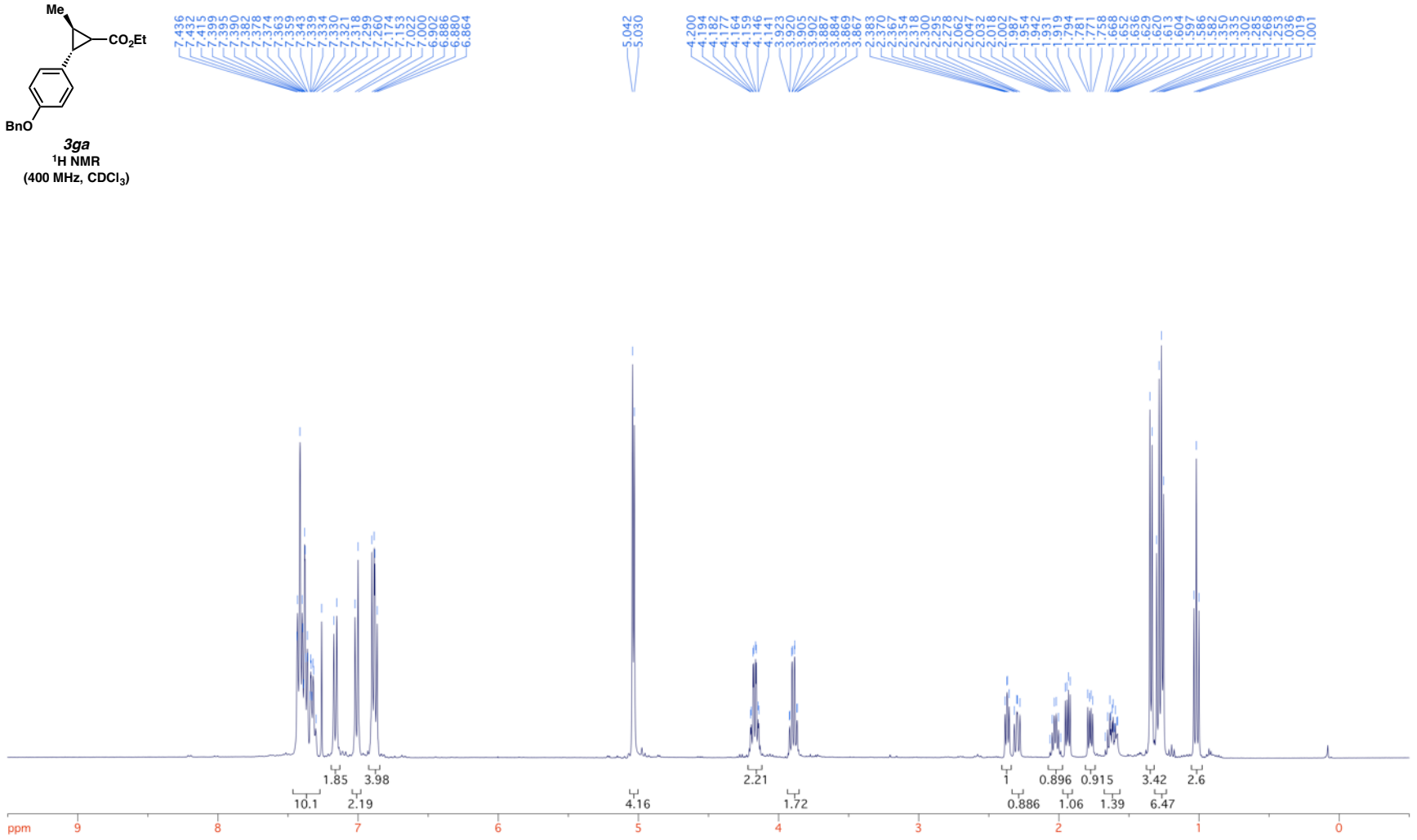


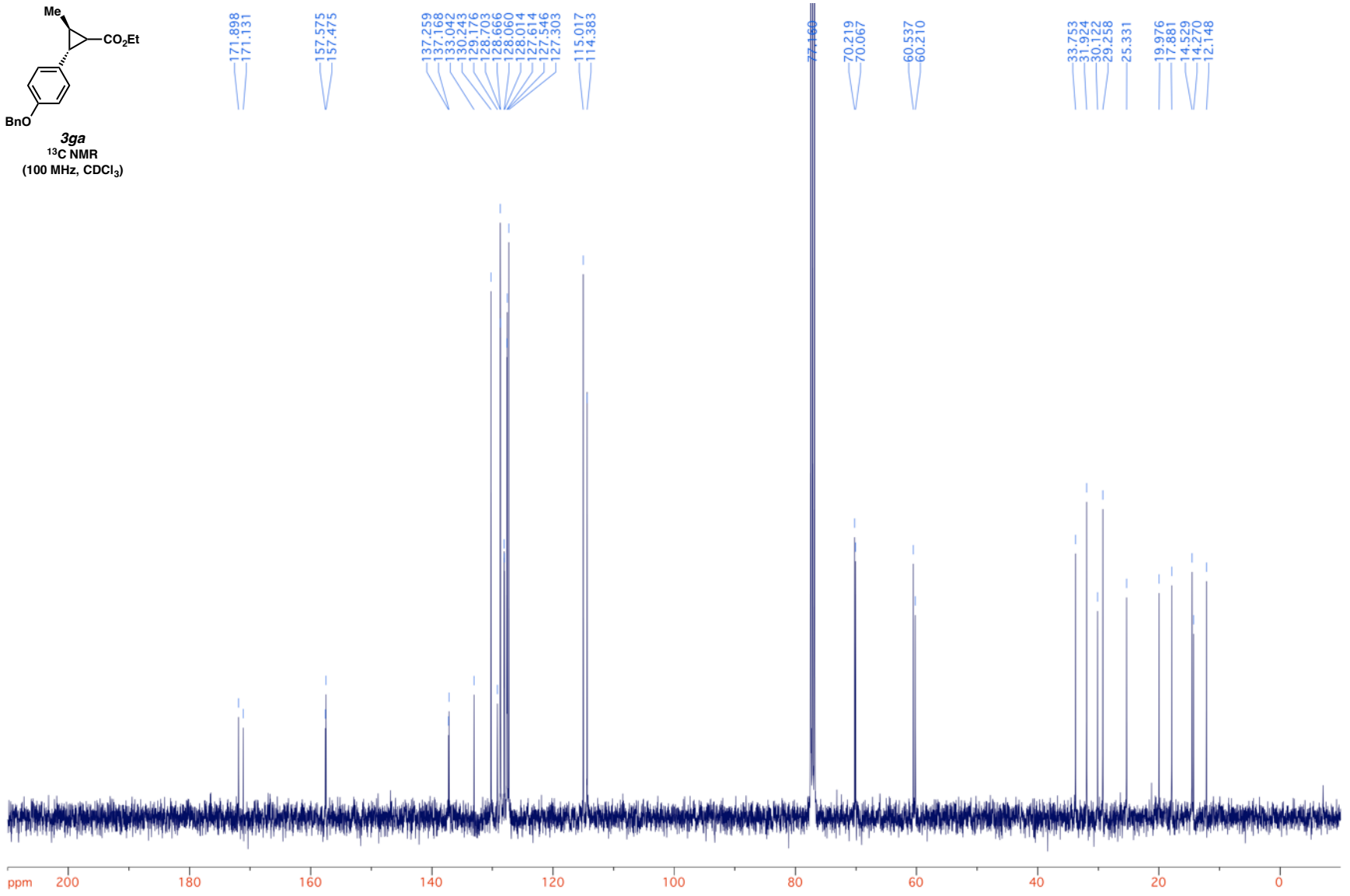
3ea
^{13}C NMR
(125 MHz, $CDCl_3$)

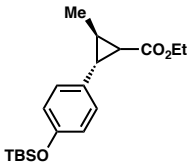


3fa
^{1}H NMR
(400 MHz, $CDCl_3$)

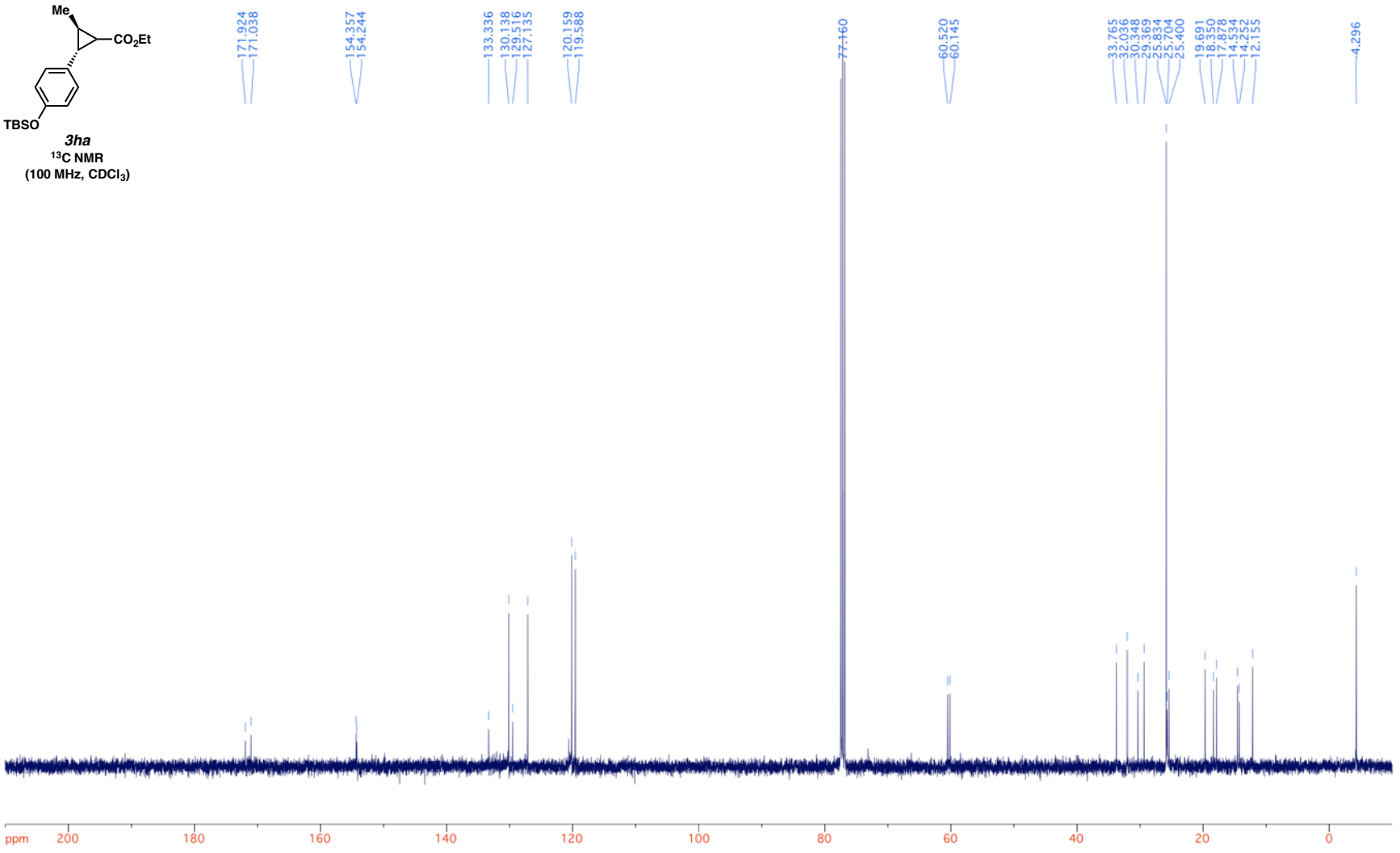

Me
CO2Et
MeO
3fa
13C NMR
(100 MHz, CDCl3)
171.909
171.131
158.324
158.269
132.719
130.205
128.847
127.285
113.997
113.402
77.160
60.521
60.192
55.439
55.300
33.744
31.892
30.075
29.218
25.299
19.966
17.872
14.515
14.261
12.135
ppm
200
180
160
140
120
100
80
60
40
20
0

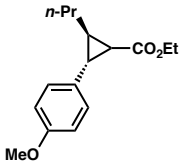

Me
CO2Et
BnO
3ga
1H NMR
(400 MHz, CDCl3)
7.436
7.432
7.415
7.409
7.395
7.390
7.382
7.378
7.374
7.363
7.359
7.343
7.339
7.334
7.330
7.321
7.318
7.299
7.260
7.174
7.153
7.022
7.000
6.902
6.886
6.880
6.864
5.042
5.030
4.200
4.194
4.182
4.177
4.164
4.159
4.146
4.141
3.923
3.920
3.905
3.902
3.887
3.884
3.869
3.867
2.383
2.370
2.367
2.354
2.318
2.300
2.295
2.278
2.062
2.047
2.032
2.018
2.002
1.987
1.944
1.942
1.931
1.919
1.794
1.781
1.771
1.758
1.668
1.652
1.636
1.629
1.620
1.613
1.604
1.597
1.586
1.582
1.350
1.335
1.302
1.285
1.268
1.233
1.036
1.019
1.001
1.85
3.98
2.21
1
0.896
0.915
3.42
2.6
10.1
2.19
4.16
1.72
0.886
1.06
1.39
6.47
ppm
9
8
7
6
5
4
3
2
1
0


Me
CO2Et
BnO
3ga
13C NMR
(100 MHz, CDCl3)
171.898
171.131
157.575
157.475
137.259
137.168
133.042
130.243
129.176
128.703
128.666
128.060
128.014
127.614
127.546
127.303
115.017
114.383
77.160
70.219
70.067
60.537
60.210
33.753
31.924
30.122
29.258
25.331
19.976
17.881
14.529
14.270
12.148
ppm
200
180
160
140
120
100
80
60
40
20
0

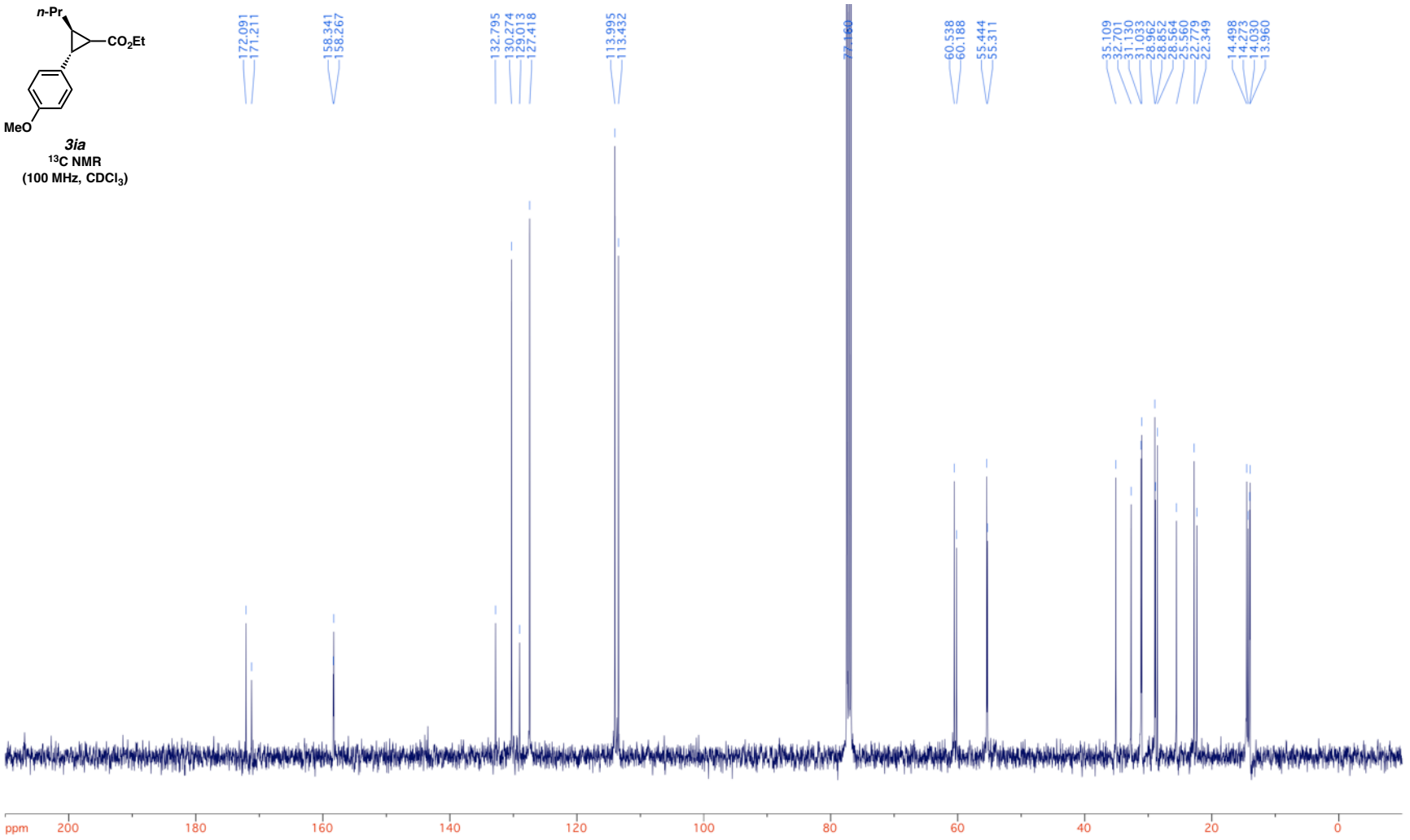


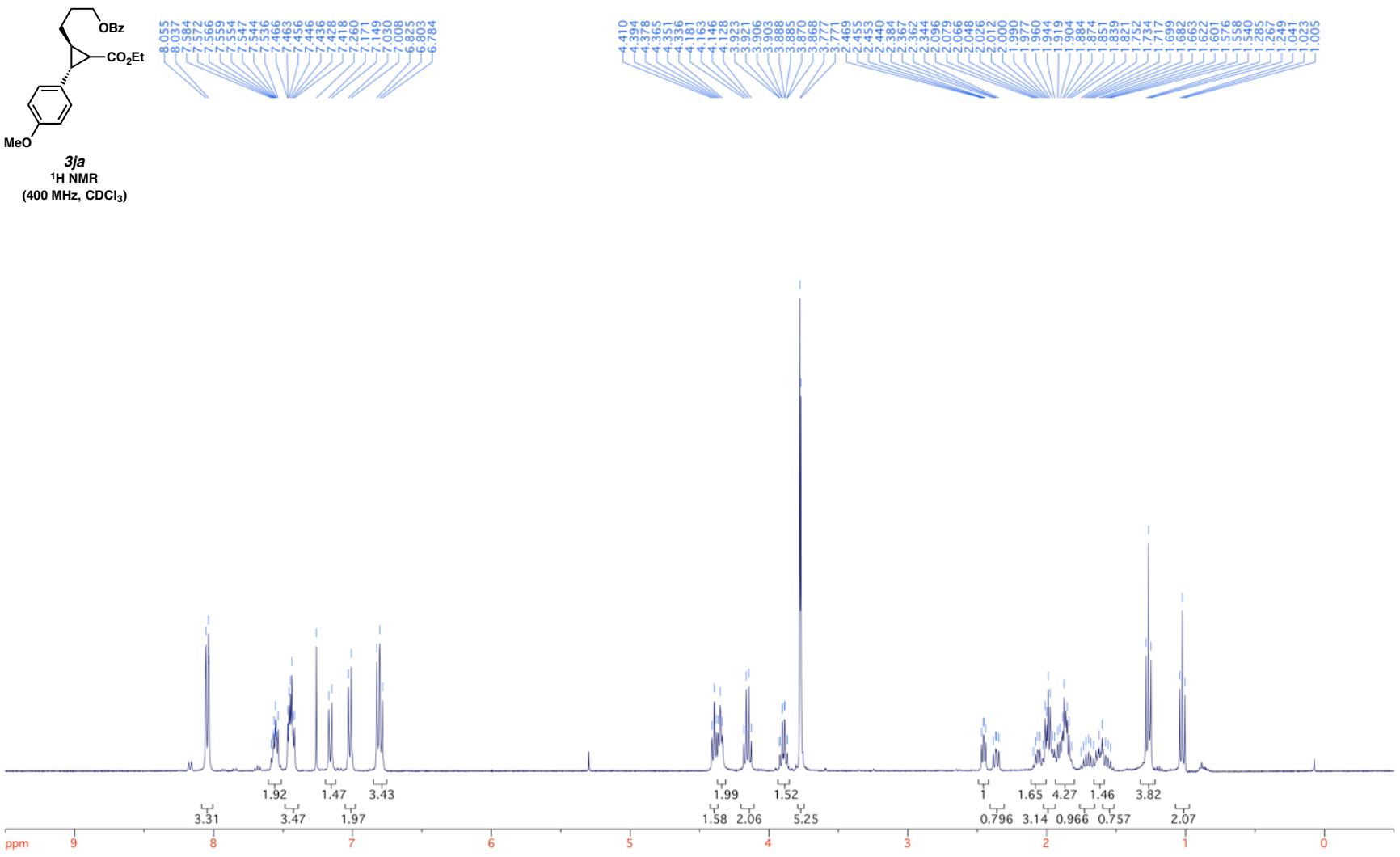
3ha
^{1}H NMR
(400 MHz, $CDCl_3$)

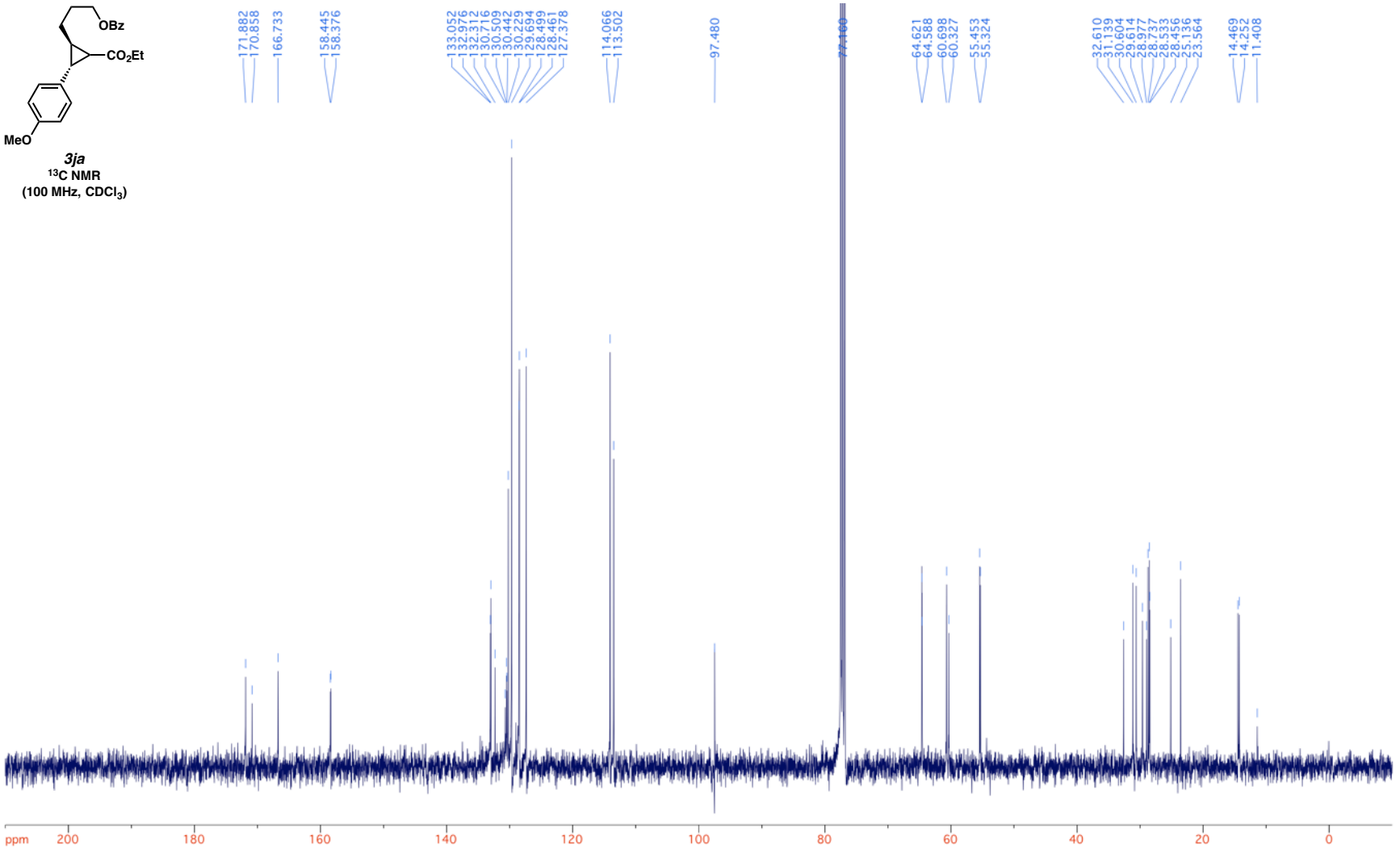

Me
CO2Et
TBSO
3ha
13C NMR
(100 MHz, CDCl3)
171.924
171.038
154.357
154.244
133.336
130.138
129.516
127.135
120.159
119.588
77.160
60.520
60.145
33.765
32.036
30.348
29.869
25.704
25.400
19.691
18.350
17.878
14.534
14.252
12.155
-4.296
ppm
200
180
160
140
120
100
80
60
40
20
0

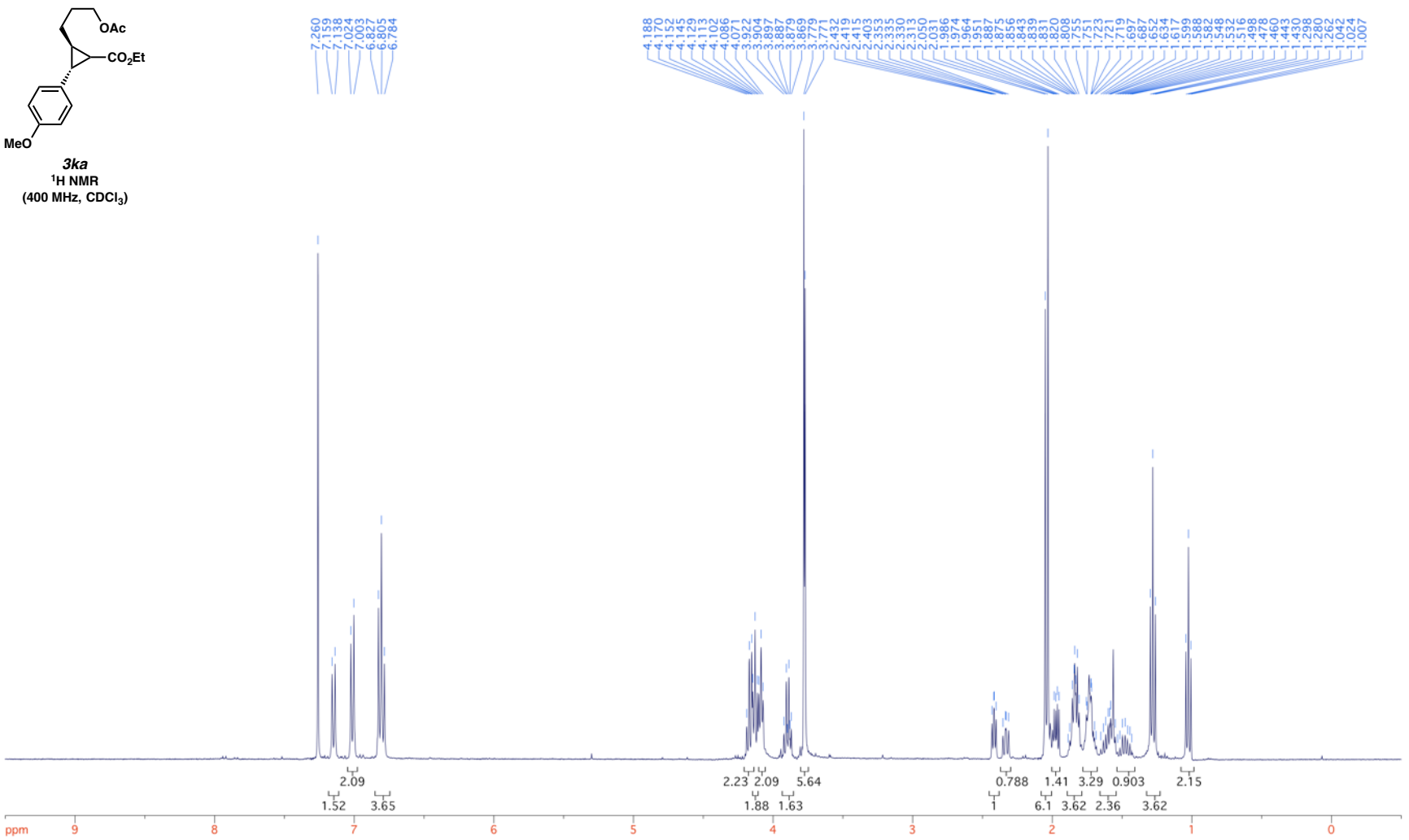


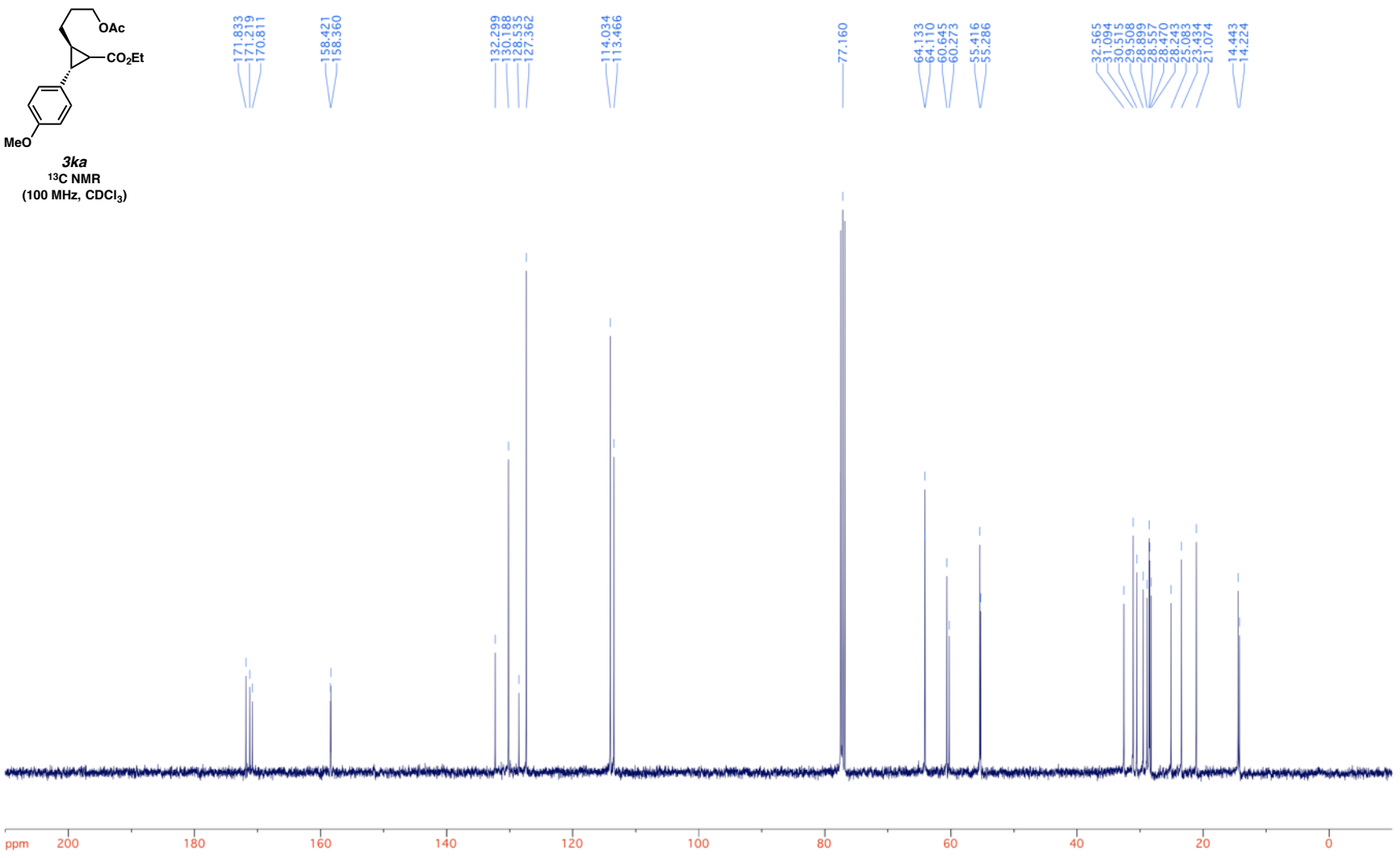
3ia
^{1}H NMR
(400 MHz, $CDCl_3$)


n-Pr
CO2Et
MeO
3ia
13C NMR
(100 MHz, CDCl3)
172.091
171.211
158.341
158.267
132.795
130.274
129.013
127.418
113.995
113.432
77.160
60.538
60.188
55.444
55.311
35.109
32.701
31.130
31.033
28.962
28.852
28.564
25.560
22.779
22.349
14.498
14.273
14.030
13.960
ppm
200
180
160
140
120
100
80
60
40
20
0

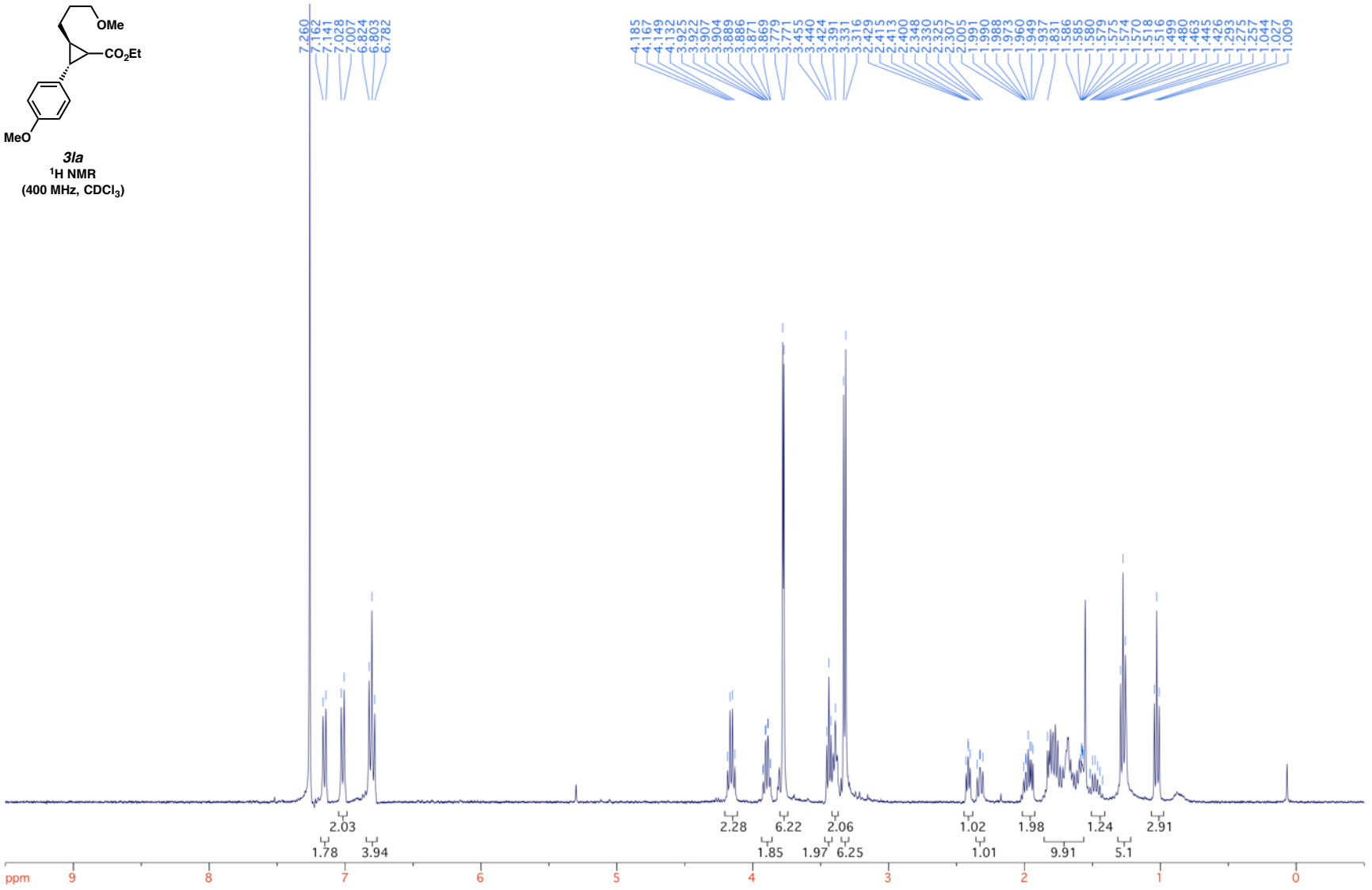

OBz
CO2Et
MeO
3ja
1H NMR
(400 MHz, CDCl3)
8.055
8.037
7.594
7.572
7.566
7.559
7.554
7.547
7.544
7.536
7.466
7.463
7.446
7.436
7.428
7.418
7.260
7.171
7.149
7.030
7.008
6.825
6.803
6.784
4.410
4.394
4.378
4.365
4.351
4.336
4.181
4.163
4.146
4.128
3.923
3.921
3.906
3.903
3.888
3.885
3.870
3.868
3.777
3.771
2.469
2.455
2.453
2.440
2.384
2.367
2.362
2.344
2.096
2.079
2.066
2.048
2.026
2.012
2.000
1.990
1.977
1.960
1.944
1.919
1.904
1.894
1.874
1.851
1.839
1.821
1.732
1.717
1.699
1.682
1.663
1.622
1.601
1.576
1.558
1.540
1.285
1.267
1.249
1.041
1.023
1.005
1.92
1.47
3.43
3.31
3.47
1.97
1.99
1.52
1.58
2.06
5.25
1
1.65
4.27
1.46
3.82
0.796
3.14
0.966
0.757
2.07
ppm
9
8
7
6
5
4
3
2
1
0

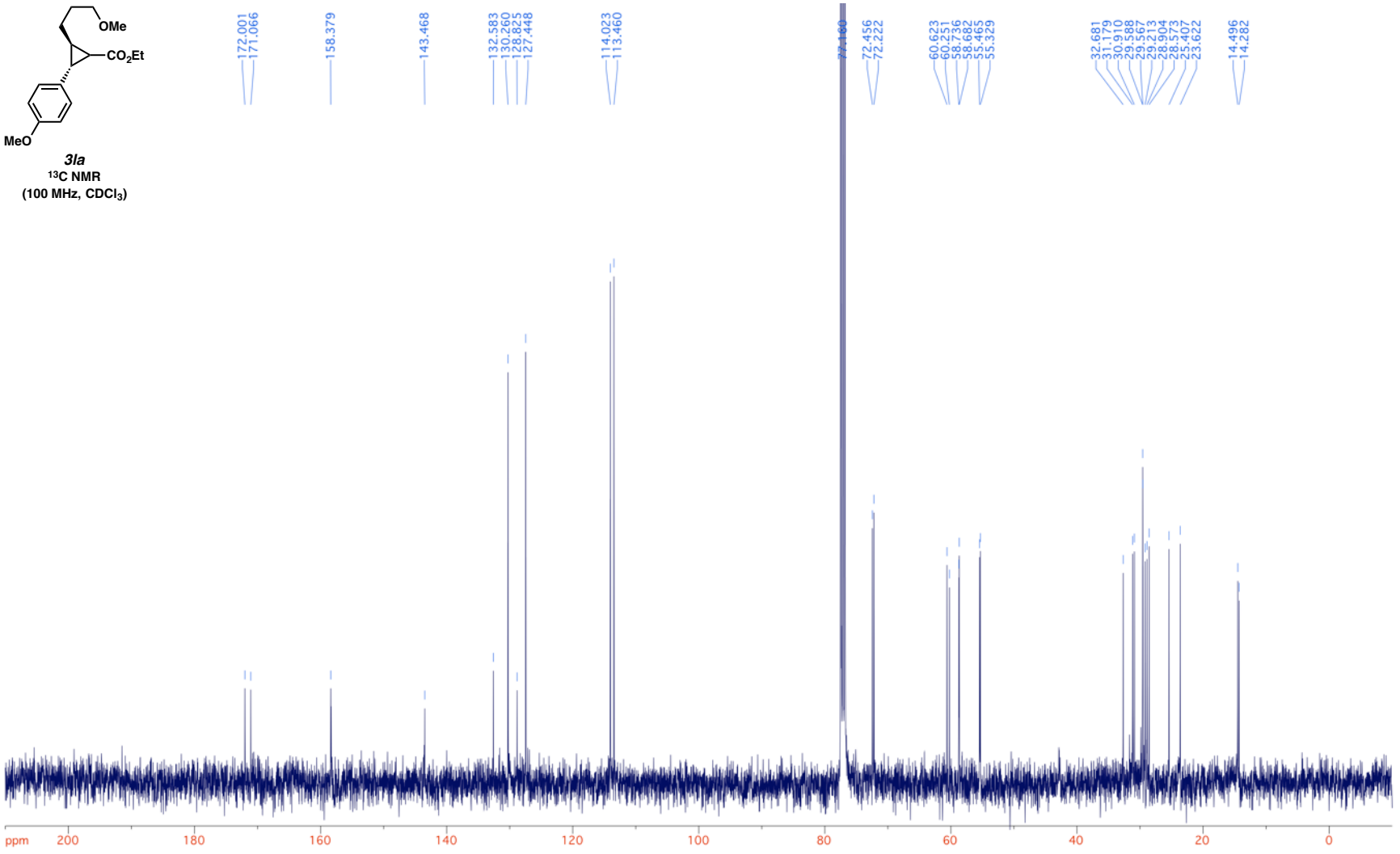

OBz
CO2Et
MeO
3ja
13C NMR
(100 MHz, CDCl3)
171.882
170.858
166.733
158.445
158.376
133.052
132.976
132.312
130.716
130.509
130.442
130.229
129.694
128.499
128.461
127.378
114.066
113.502
97.480
77.160
64.621
64.588
60.698
60.327
55.453
55.324
32.610
31.139
30.604
29.614
28.977
28.737
28.533
28.456
25.136
23.564
14.469
14.252
11.408
ppm
200
180
160
140
120
100
80
60
40
20
0

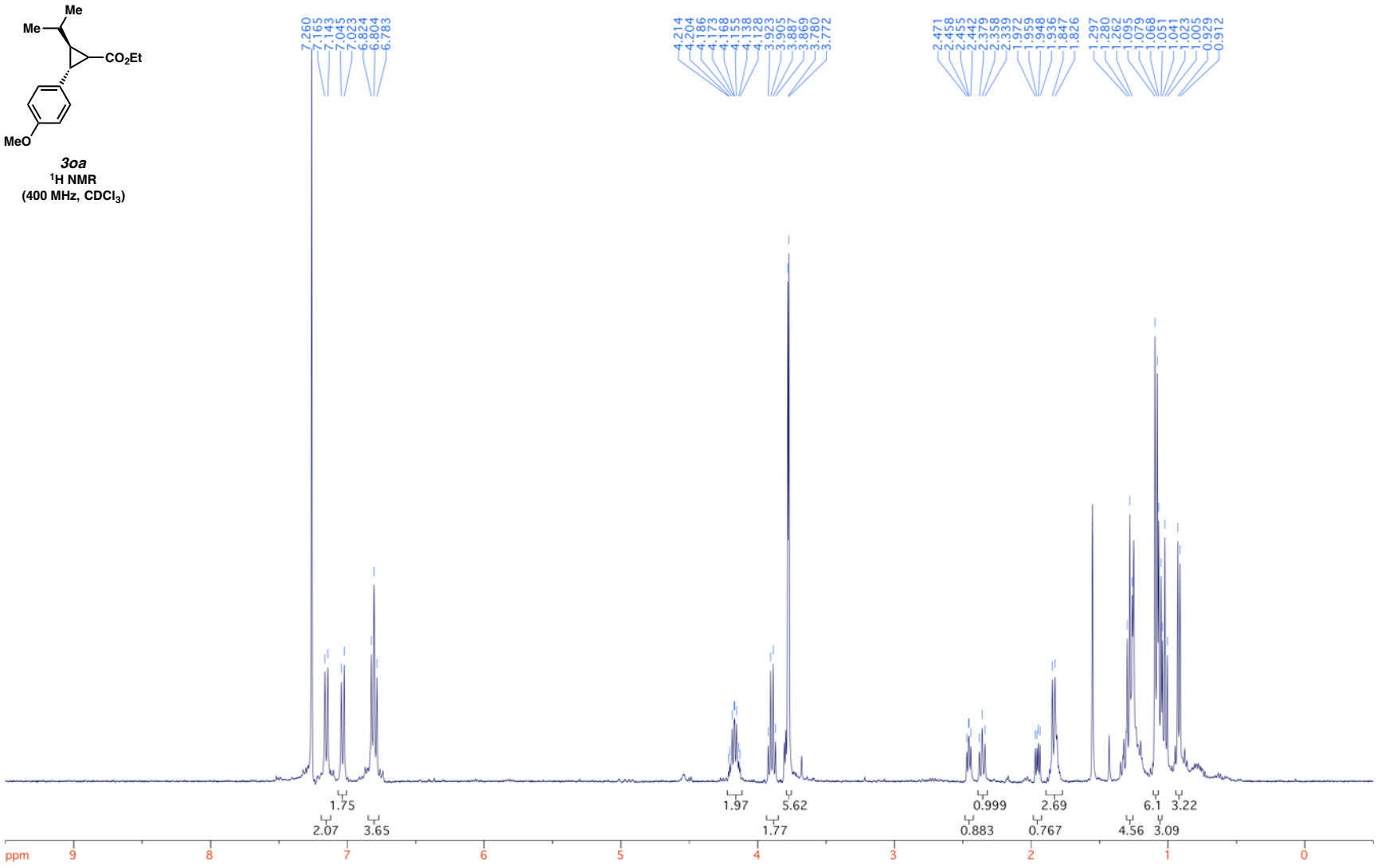

OAc
CO2Et
MeO
3ka
1H NMR
(400 MHz, CDCl3)
7.260
7.159
7.138
7.024
7.003
6.827
6.805
6.784
4.188
4.170
4.152
4.145
4.129
4.113
4.102
4.086
4.071
3.922
3.904
3.897
3.887
3.869
3.859
3.771
2.432
2.419
2.415
2.403
2.353
2.335
2.330
2.313
2.050
2.031
1.986
1.974
1.964
1.951
1.887
1.875
1.856
1.843
1.839
1.831
1.820
1.808
1.755
1.751
1.723
1.711
1.699
1.687
1.652
1.634
1.617
1.599
1.588
1.582
1.548
1.532
1.516
1.498
1.478
1.460
1.443
1.430
1.298
1.280
1.262
1.042
1.024
1.007
2.09
1.52
3.65
2.23
2.09
1.88
5.64
1.63
0.788
1
1.41
6.1
3.29
3.62
0.903
2.36
2.15
3.62
ppm
9
8
7
6
5
4
3
2
1
0

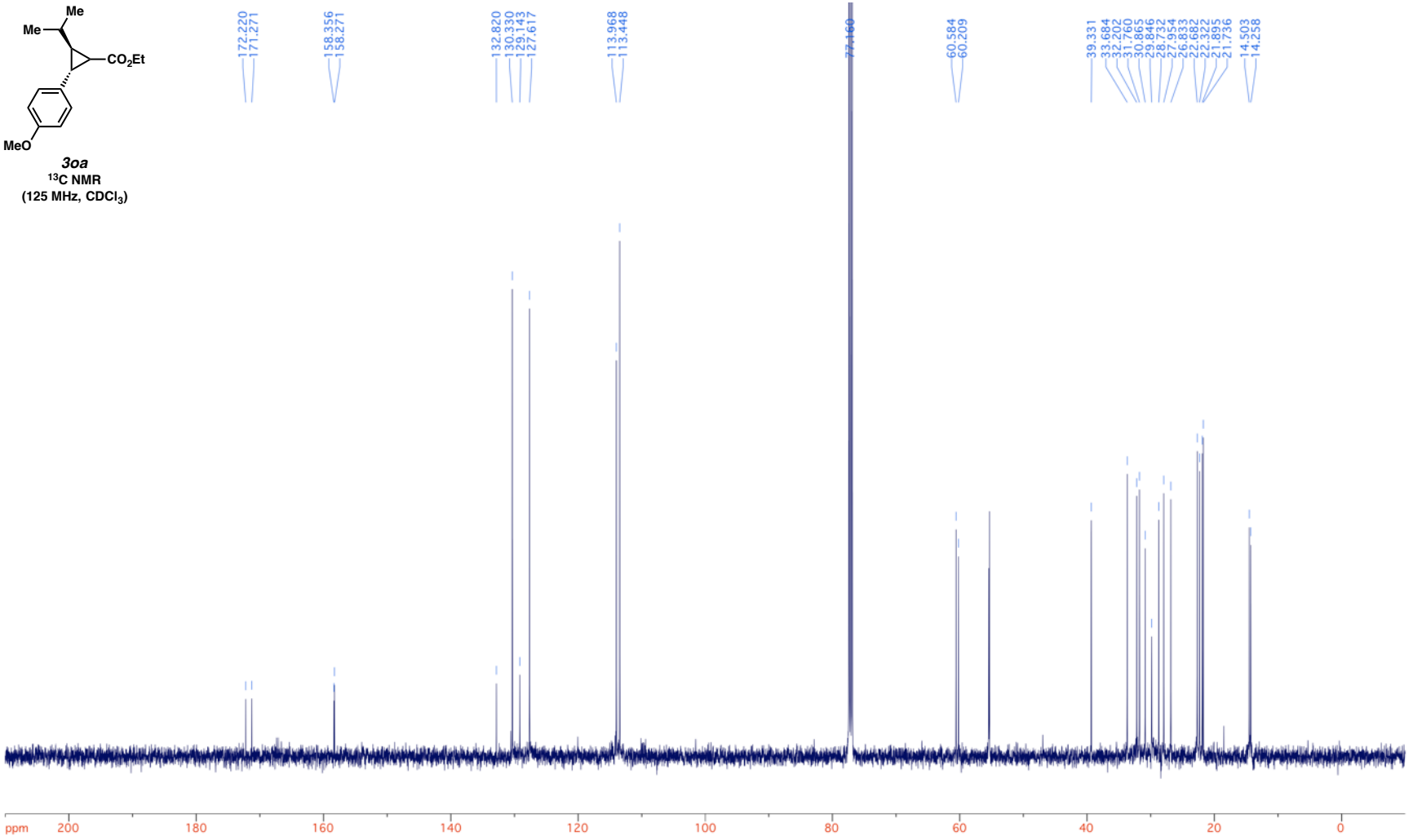


3ka
^{13}C NMR
(100 MHz, $CDCl_3$)

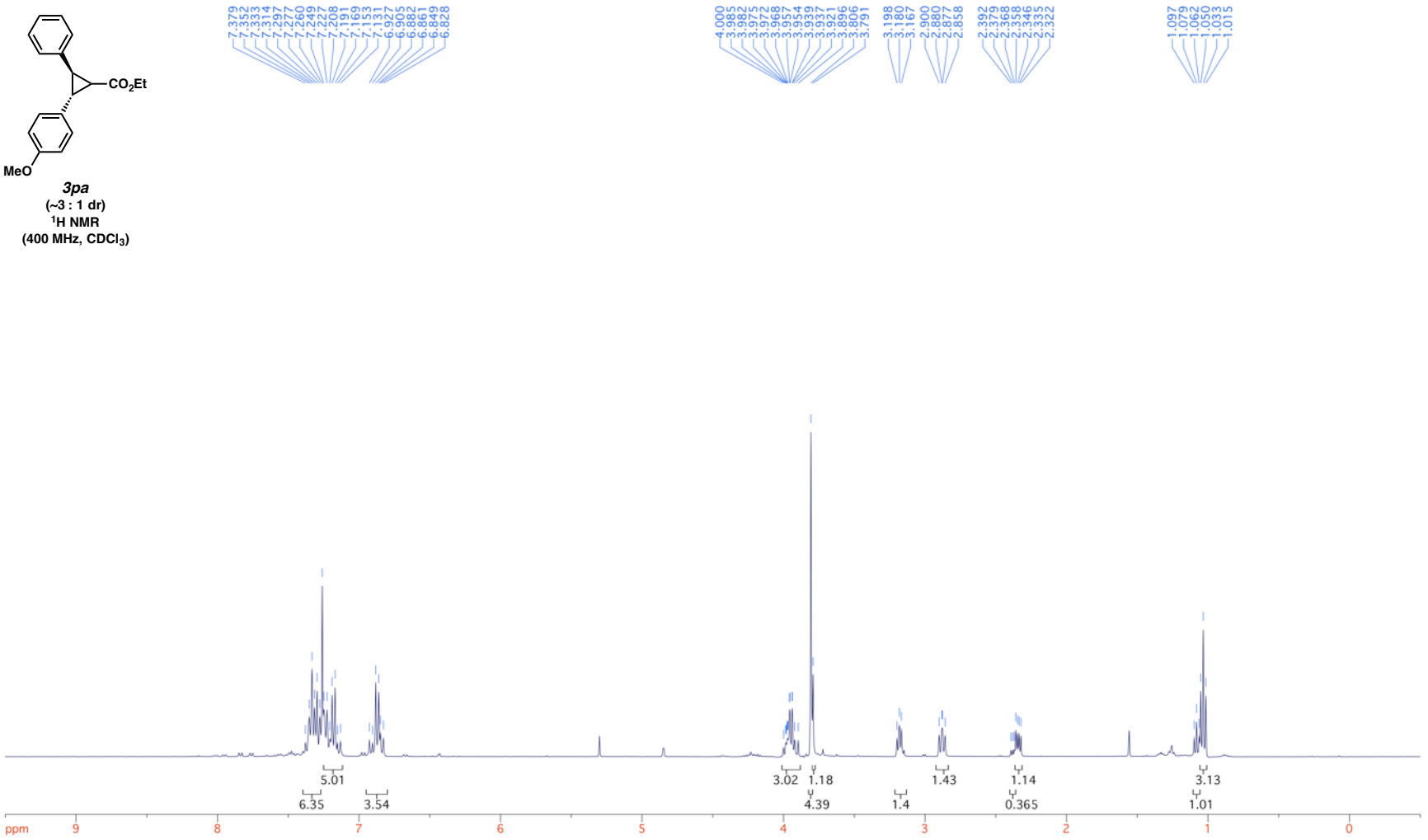

OMe
CO2Et
MeO
3la
1H NMR
(400 MHz, CDCl3)
7.260
7.162
7.141
7.028
7.007
6.824
6.803
6.782
4.185
4.167
4.149
4.132
3.925
3.922
3.907
3.904
3.889
3.886
3.871
3.869
3.779
3.771
3.455
3.440
3.424
3.391
3.331
3.316
2.429
2.415
2.413
2.400
2.348
2.330
2.325
2.307
2.005
1.991
1.990
1.988
1.973
1.960
1.949
1.937
1.831
1.586
1.585
1.580
1.579
1.575
1.574
1.570
1.518
1.516
1.499
1.480
1.463
1.445
1.426
1.293
1.275
1.257
1.044
1.027
1.009
2.03
1.78
3.94
2.28
1.85
6.22
1.97
2.06
6.25
1.02
1.01
1.98
9.91
1.24
5.1
2.91
ppm
9
8
7
6
5
4
3
2
1
0


OMe
CO2Et
MeO
3la
13C NMR
(100 MHz, CDCl3)
172.001
171.066
158.379
143.468
132.583
130.260
128.825
127.448
114.023
113.460
77.160
72.456
72.222
60.623
60.251
58.736
58.682
55.465
55.329
32.681
31.179
30.910
29.588
29.567
29.213
28.904
28.573
25.407
23.622
14.496
14.282
ppm
200
180
160
140
120
100
80
60
40
20
0

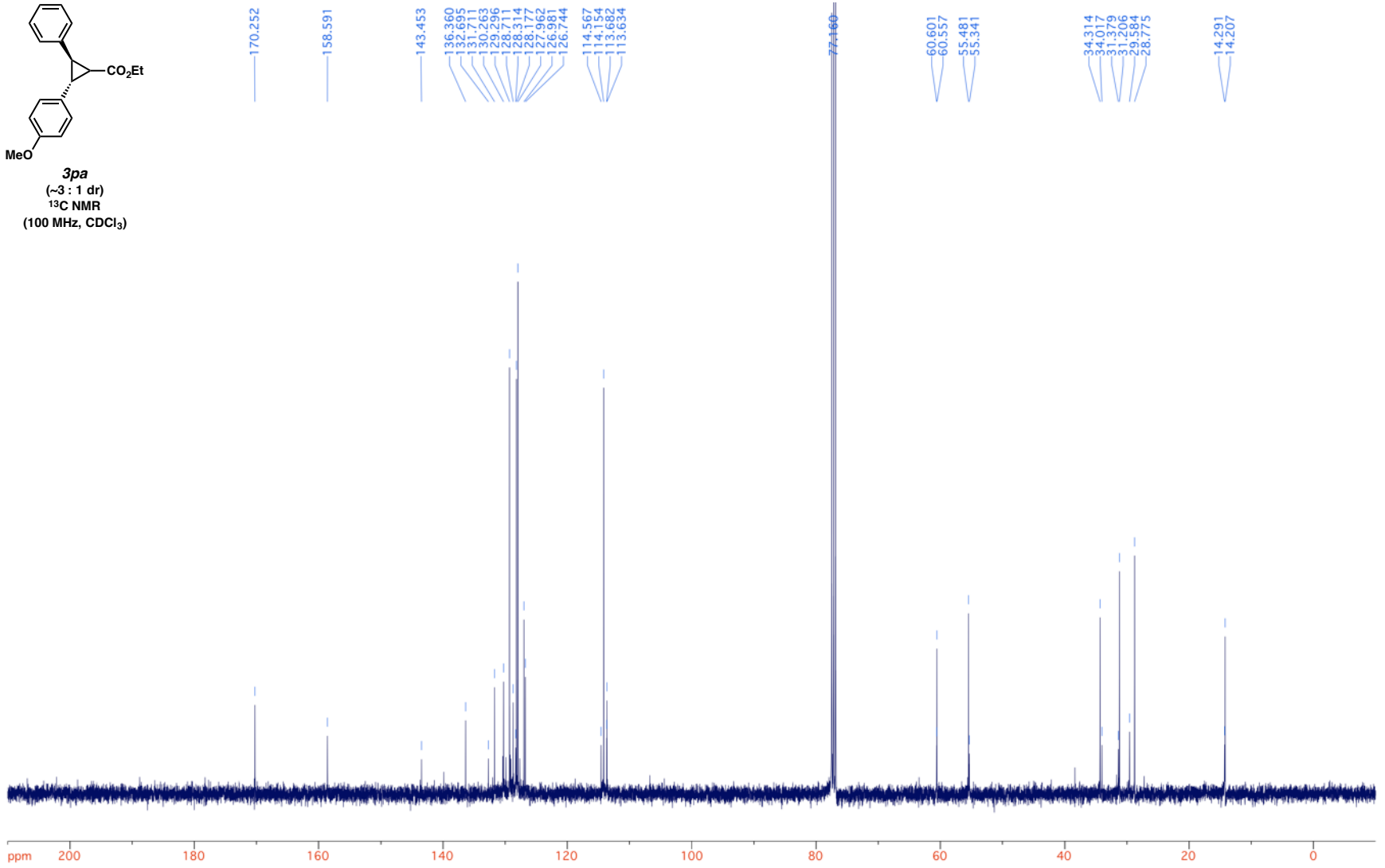

Me
Me
CO2Et
MeO
3oa
1H NMR
(400 MHz, CDCl3)
7.260
7.165
7.143
7.045
7.023
6.824
6.804
6.783
4.214
4.204
4.186
4.173
4.168
4.155
4.138
4.128
3.923
3.905
3.887
3.869
3.780
3.772
2.471
2.458
2.455
2.442
2.379
2.358
2.339
1.972
1.959
1.948
1.936
1.847
1.826
1.297
1.280
1.262
1.095
1.079
1.068
1.051
1.041
1.023
1.005
0.929
0.912
1.75
2.07
3.65
1.97
1.77
5.62
0.999
0.883
2.69
0.767
6.1
4.56
3.22
3.09
ppm
9
8
7
6
5
4
3
2
1
0

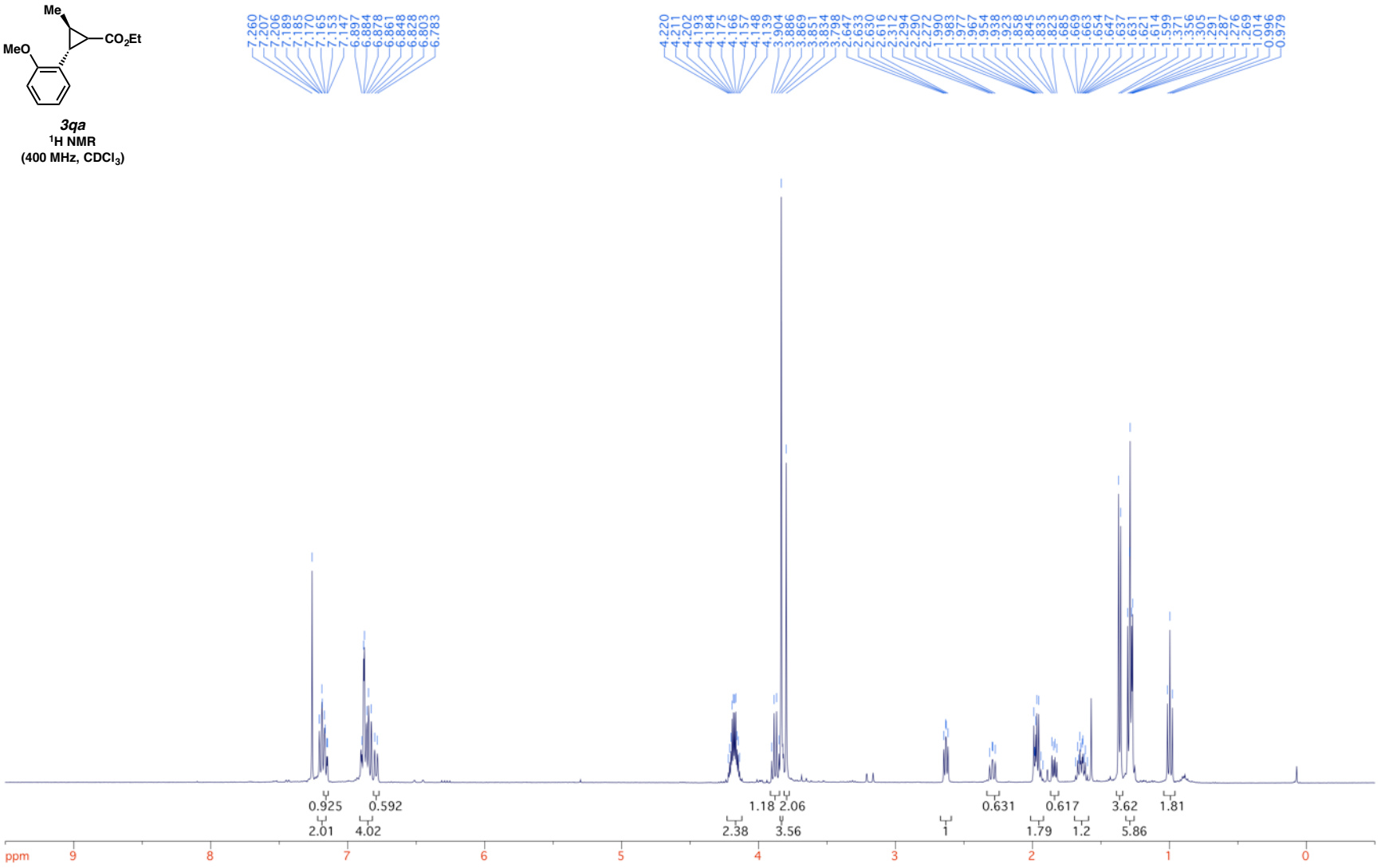


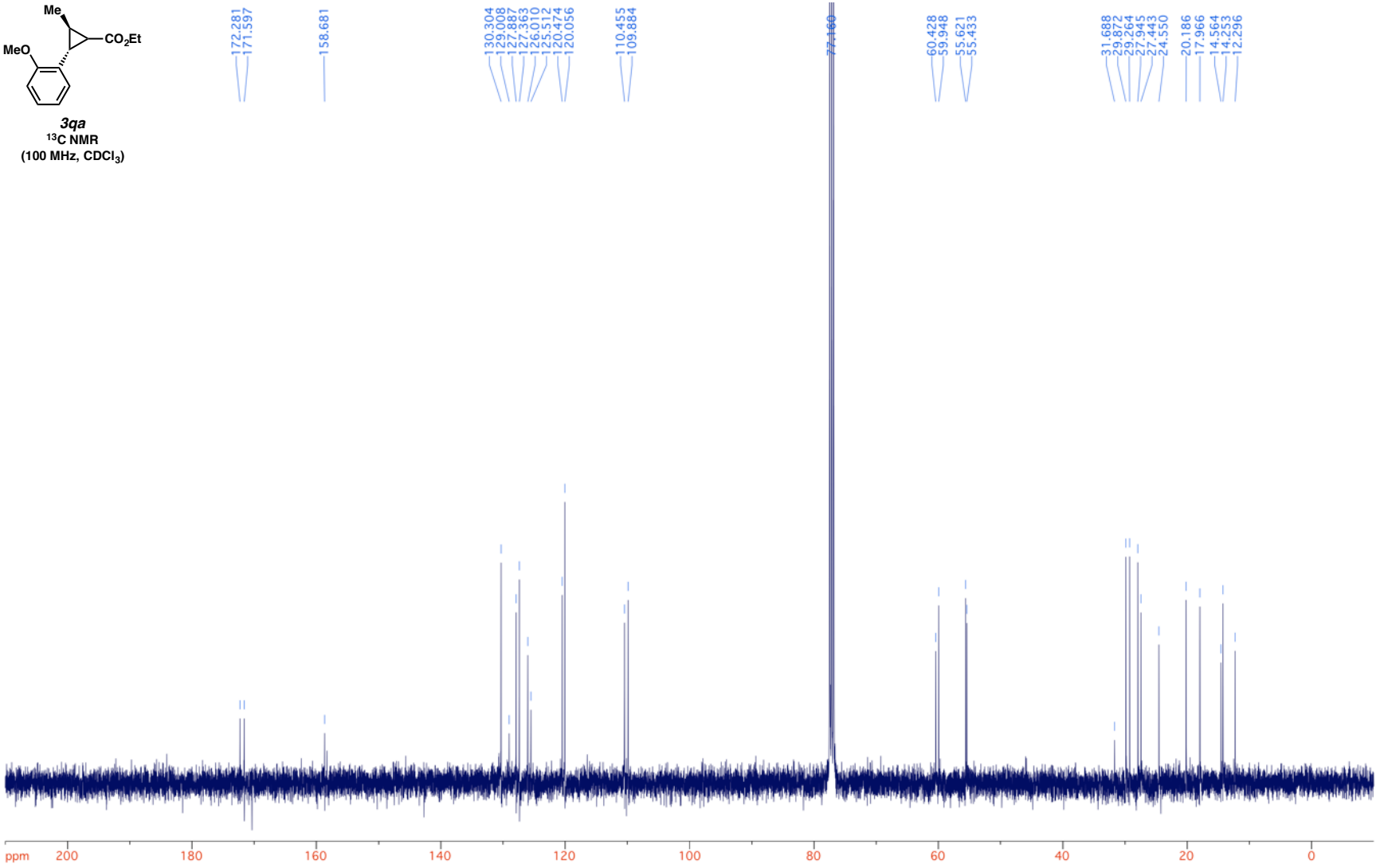
3oa
^{13}C NMR
(125 MHz, $CDCl_3$)

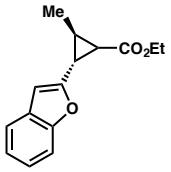


3pa
(~3 : 1 dr)
^{1}H NMR
(400 MHz, $CDCl_3$)

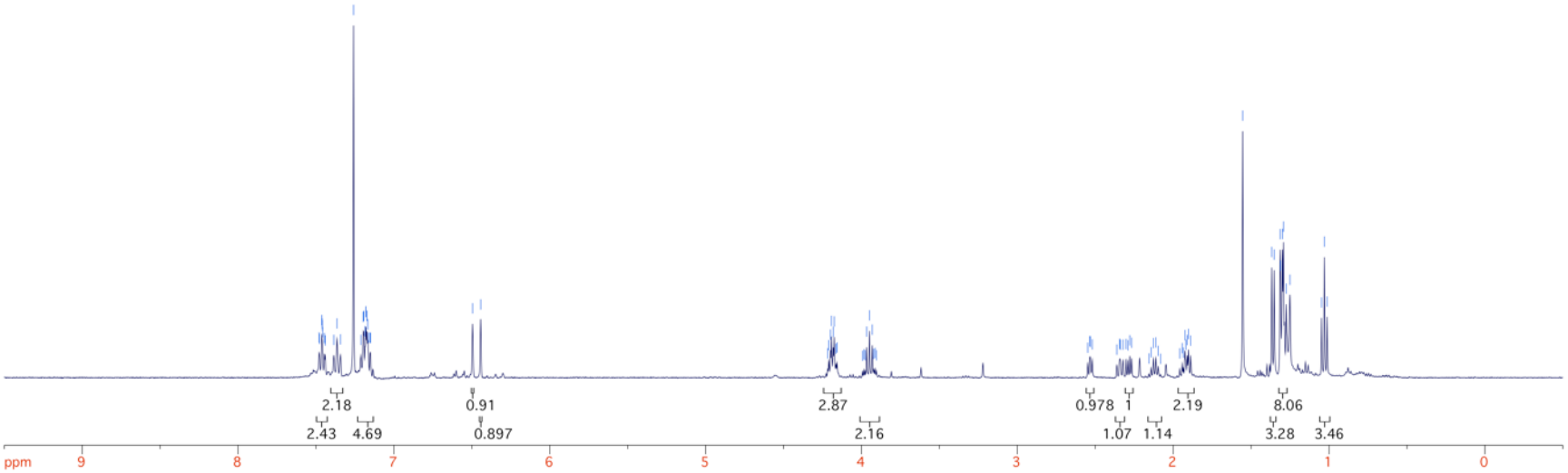

CO2Et
MeO
3pa
(~3 : 1 dr)
13C NMR
(100 MHz, CDCl3)
170.252
158.591
143.453
136.360
132.695
131.711
130.263
129.296
128.711
128.314
128.177
127.962
126.981
126.744
114.567
114.154
113.682
113.634
77.160
60.601
60.557
55.481
55.341
34.314
34.017
31.379
31.206
29.594
28.775
14.291
14.207
ppm
200
180
160
140
120
100
80
60
40
20
0

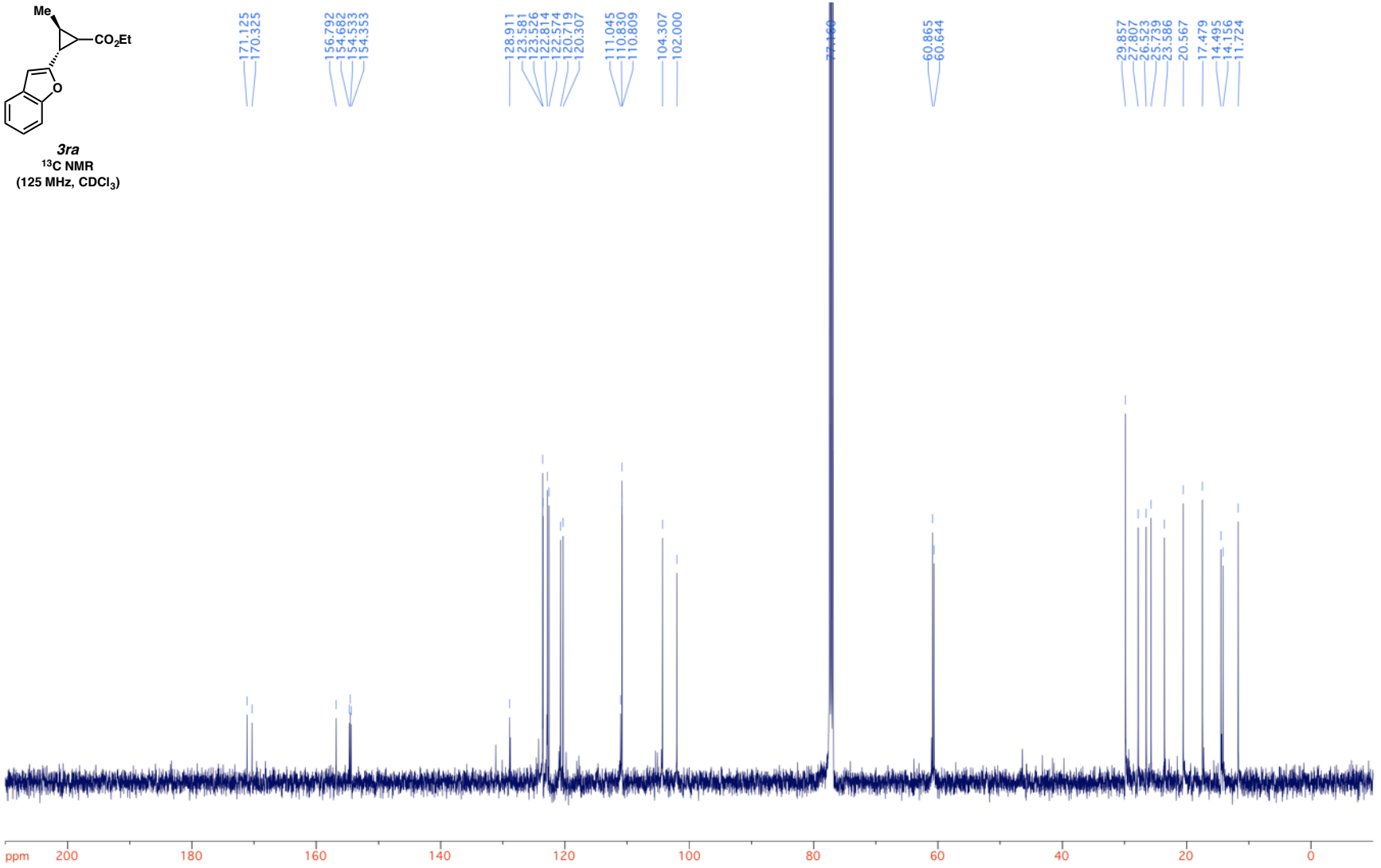

Me
CO2Et
MeO
3qa
1H NMR
(400 MHz, CDCl3)
7.260
7.207
7.206
7.189
7.185
7.170
7.165
7.153
7.147
6.897
6.884
6.878
6.861
6.848
6.828
6.803
6.783
4.220
4.211
4.202
4.193
4.184
4.175
4.166
4.157
4.148
4.139
3.904
3.886
3.869
3.851
3.834
3.798
2.647
2.633
2.630
2.616
2.312
2.294
2.290
2.272
1.990
1.983
1.977
1.967
1.954
1.938
1.923
1.858
1.845
1.835
1.823
1.685
1.669
1.663
1.654
1.647
1.637
1.631
1.621
1.614
1.599
1.371
1.356
1.305
1.291
1.287
1.276
1.269
1.014
0.996
0.979
0.925
0.592
1.18
2.06
0.631
0.617
3.62
1.81
2.01
4.02
2.38
3.56
1
1.79
1.2
5.86
ppm
9
8
7
6
5
4
3
2
1
0


Me
CO2Et
MeO
3qa
13C NMR
(100 MHz, CDCl3)
172.281
171.597
158.681
130.304
129.008
127.887
127.363
126.010
125.512
120.474
120.056
110.455
109.884
77.160
60.428
59.948
55.621
55.433
31.688
29.872
29.264
27.945
27.443
24.550
20.186
17.966
14.564
14.253
12.296
ppm
200
180
160
140
120
100
80
60
40
20
0

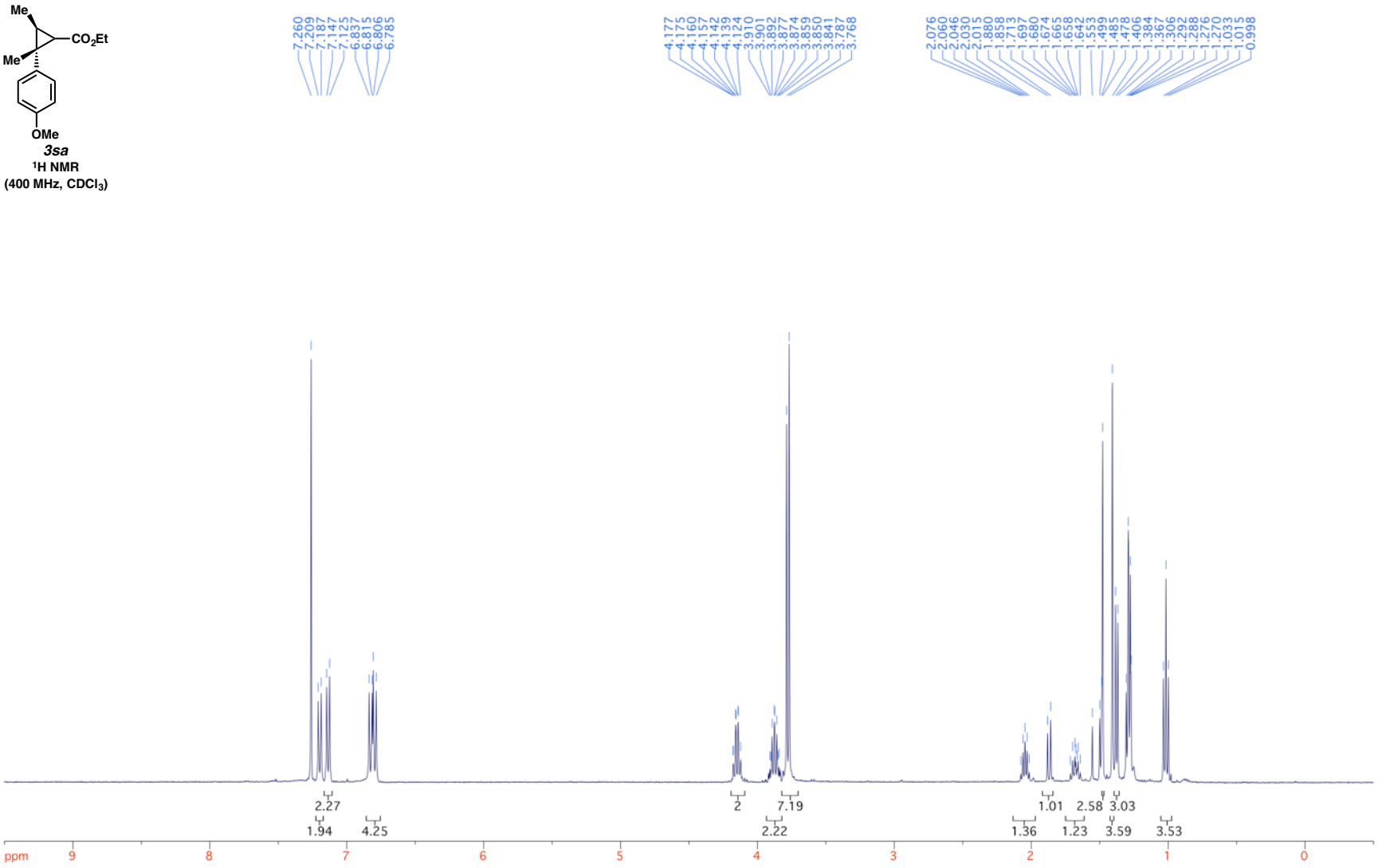


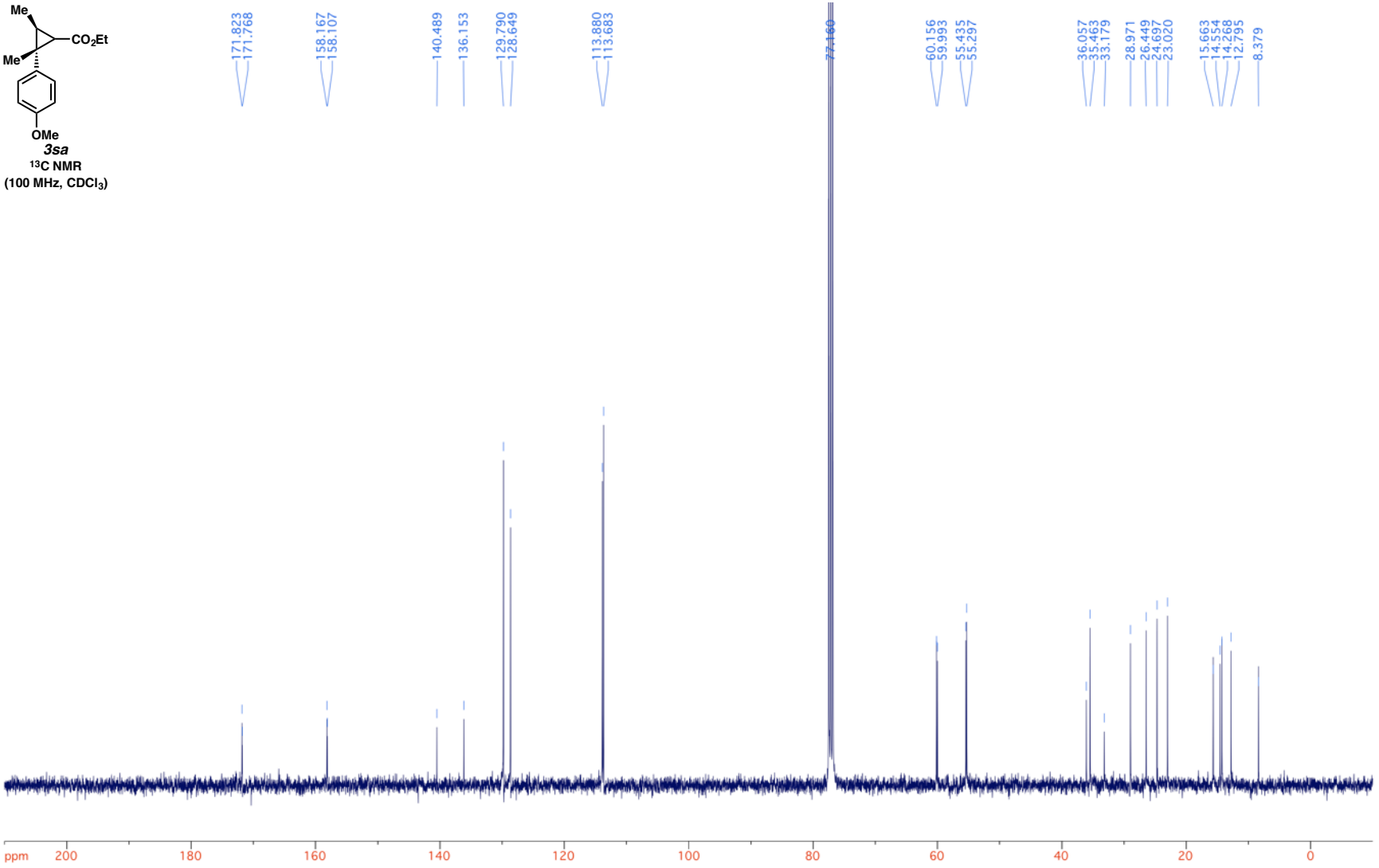
3ra
^{1}H NMR
(400 MHz, $CDCl_3$)

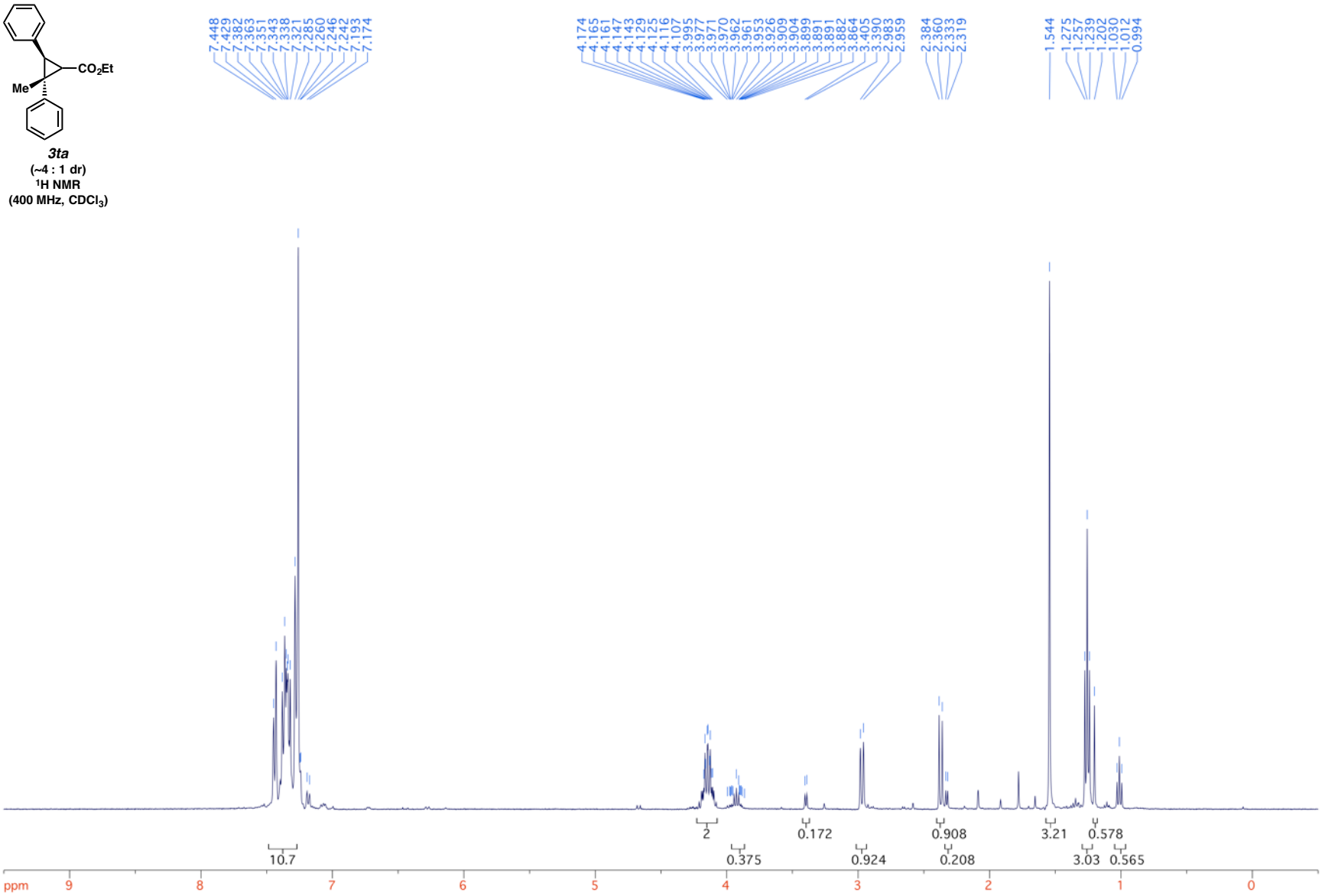




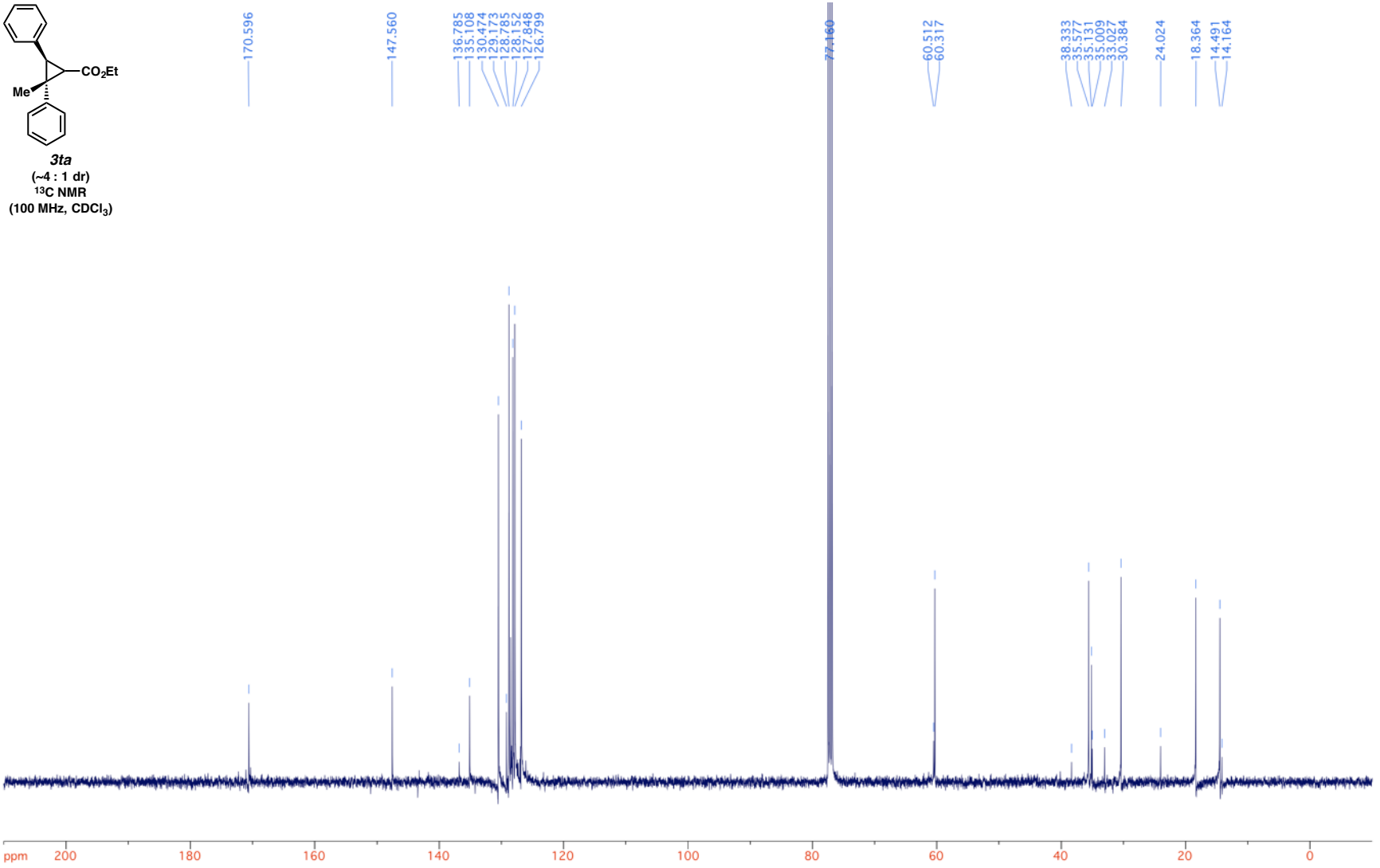
3ra
^{13}C NMR
(125 MHz, $CDCl_3$)

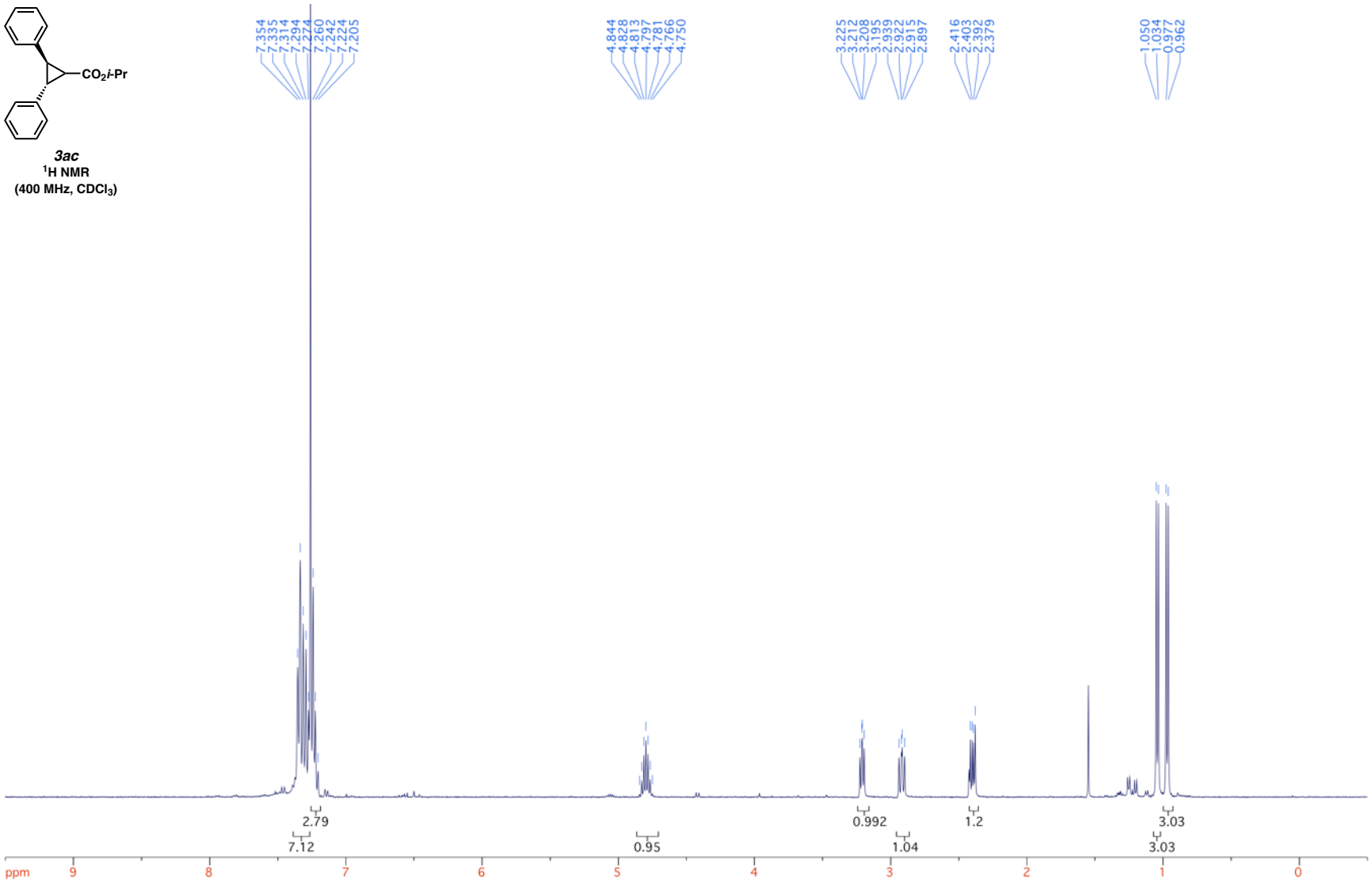

Me
CO2Et
Me
OMe
3sa
1H NMR
(400 MHz, CDCl3)
7.260
7.209
7.187
7.147
7.125
6.837
6.815
6.806
6.785
4.177
4.175
4.160
4.157
4.142
4.139
4.124
3.910
3.901
3.892
3.877
3.874
3.859
3.850
3.841
3.787
3.768
2.076
2.060
2.046
2.030
2.015
1.880
1.858
1.713
1.697
1.680
1.674
1.665
1.658
1.642
1.553
1.499
1.485
1.478
1.406
1.384
1.367
1.306
1.292
1.288
1.276
1.270
1.033
1.015
0.998
2.27
1.94
4.25
2
7.19
2.22
1.01
1.36
2.58
1.23
3.03
3.59
3.53
ppm
9
8
7
6
5
4
3
2
1
0

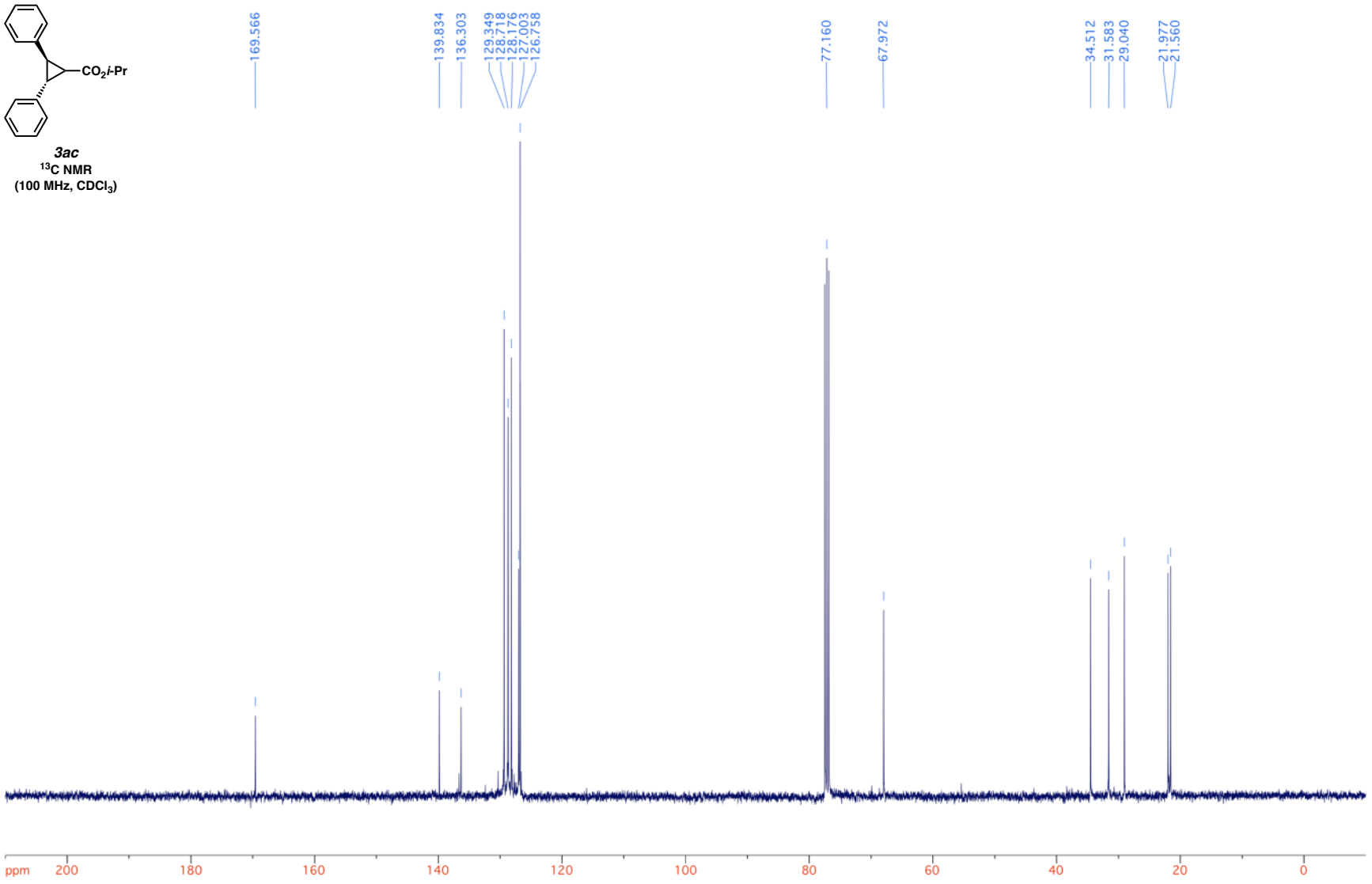

Me
CO2Et
Me
OMe
3sa
13C NMR
(100 MHz, CDCl3)
171.823
171.768
158.167
158.107
140.489
136.153
129.790
128.649
113.880
113.683
77.160
60.156
59.993
55.435
55.297
36.057
35.463
33.179
28.971
26.449
24.697
23.020
15.663
14.554
14.268
12.795
8.379
ppm
200
180
160
140
120
100
80
60
40
20
0

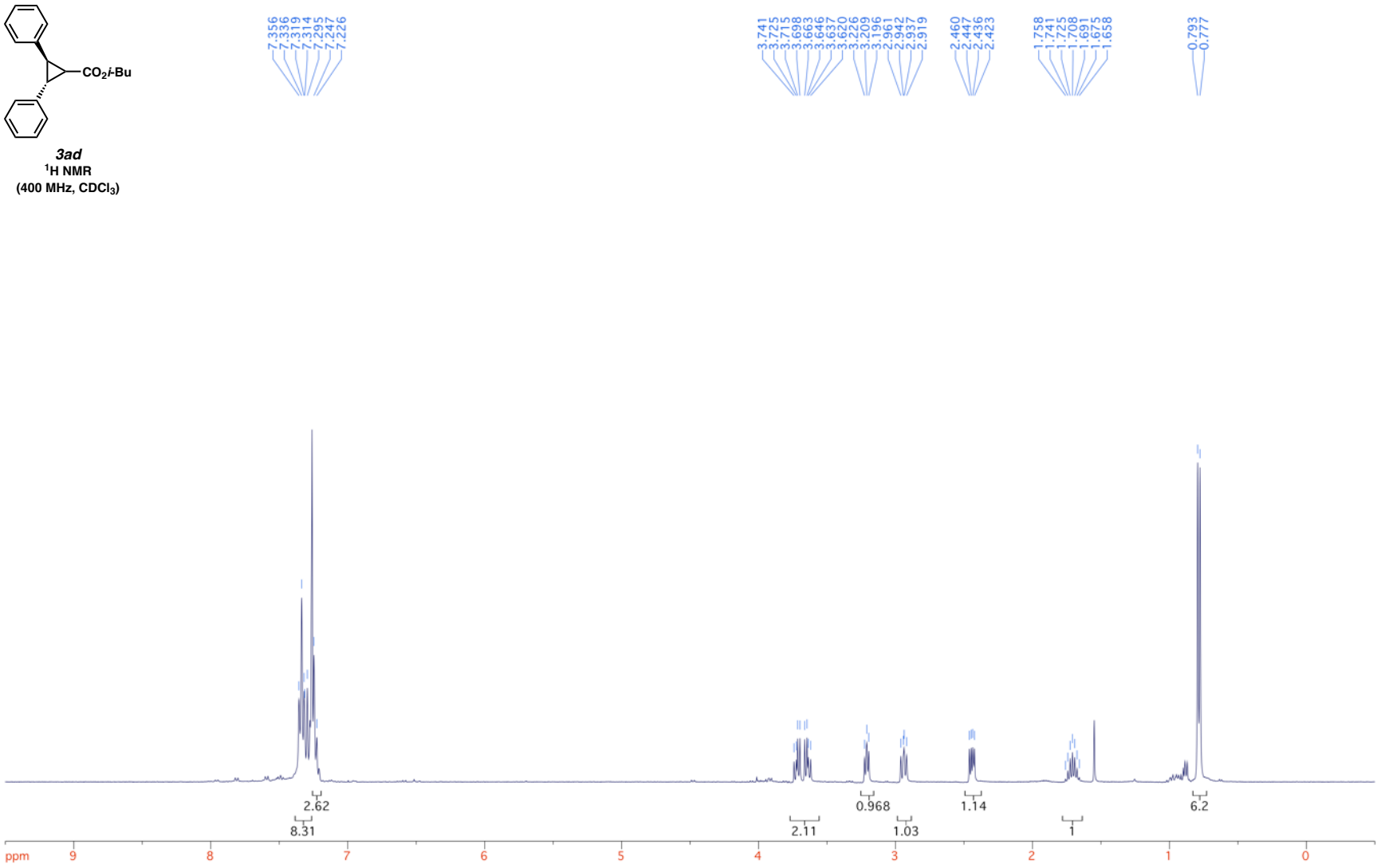


3ta
(~4 : 1 dr)
^{1}H NMR
(400 MHz, $CDCl_3$)

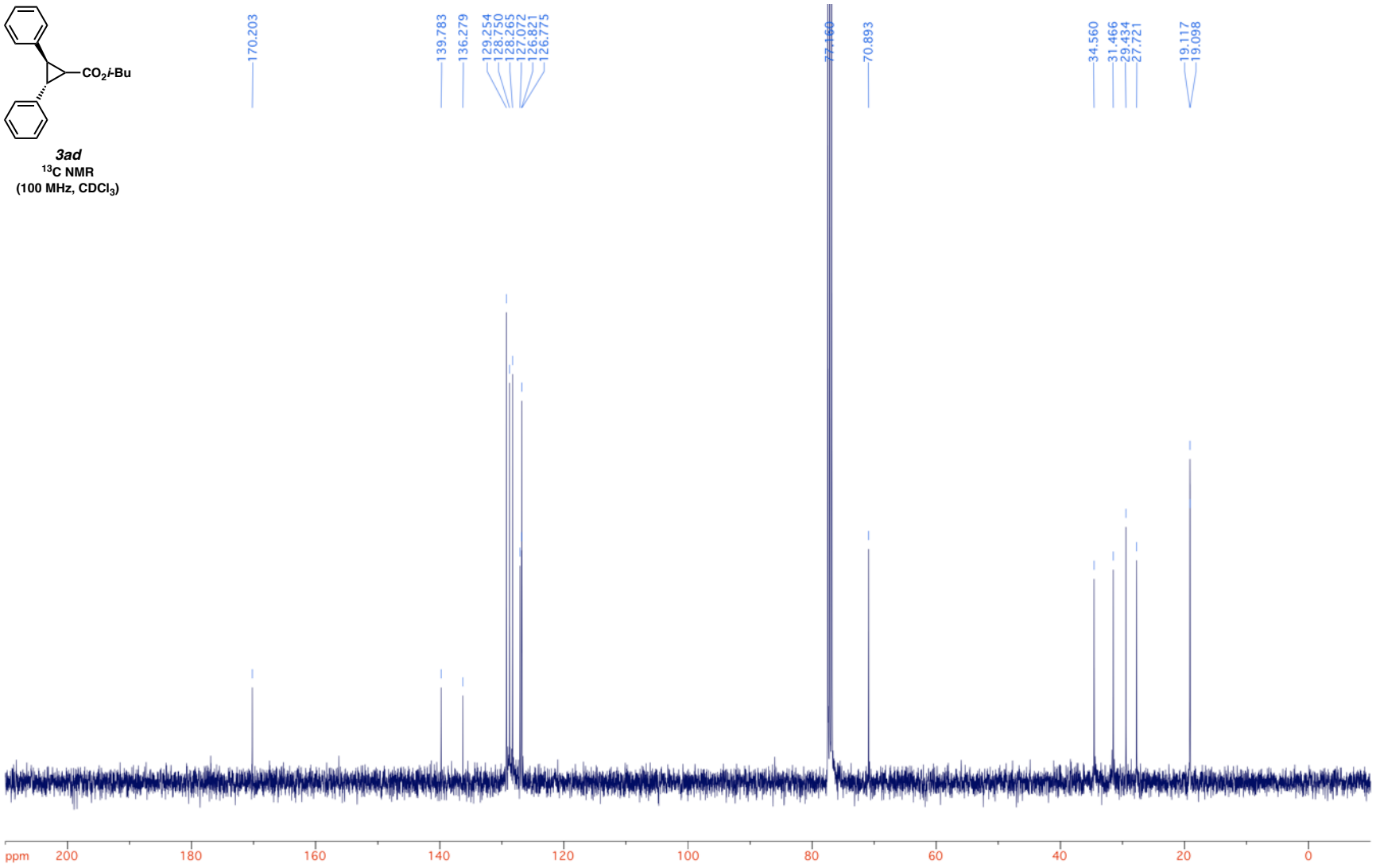

CO2Et
Me
3ta
(~4 : 1 dr)
13C NMR
(100 MHz, CDCl3)
170.596
147.560
136.785
135.108
130.474
129.173
128.785
128.552
127.848
126.799
77.160
60.512
60.317
38.333
35.577
35.131
35.009
33.027
30.384
24.024
18.364
14.491
14.164
ppm
200
180
160
140
120
100
80
60
40
20
0

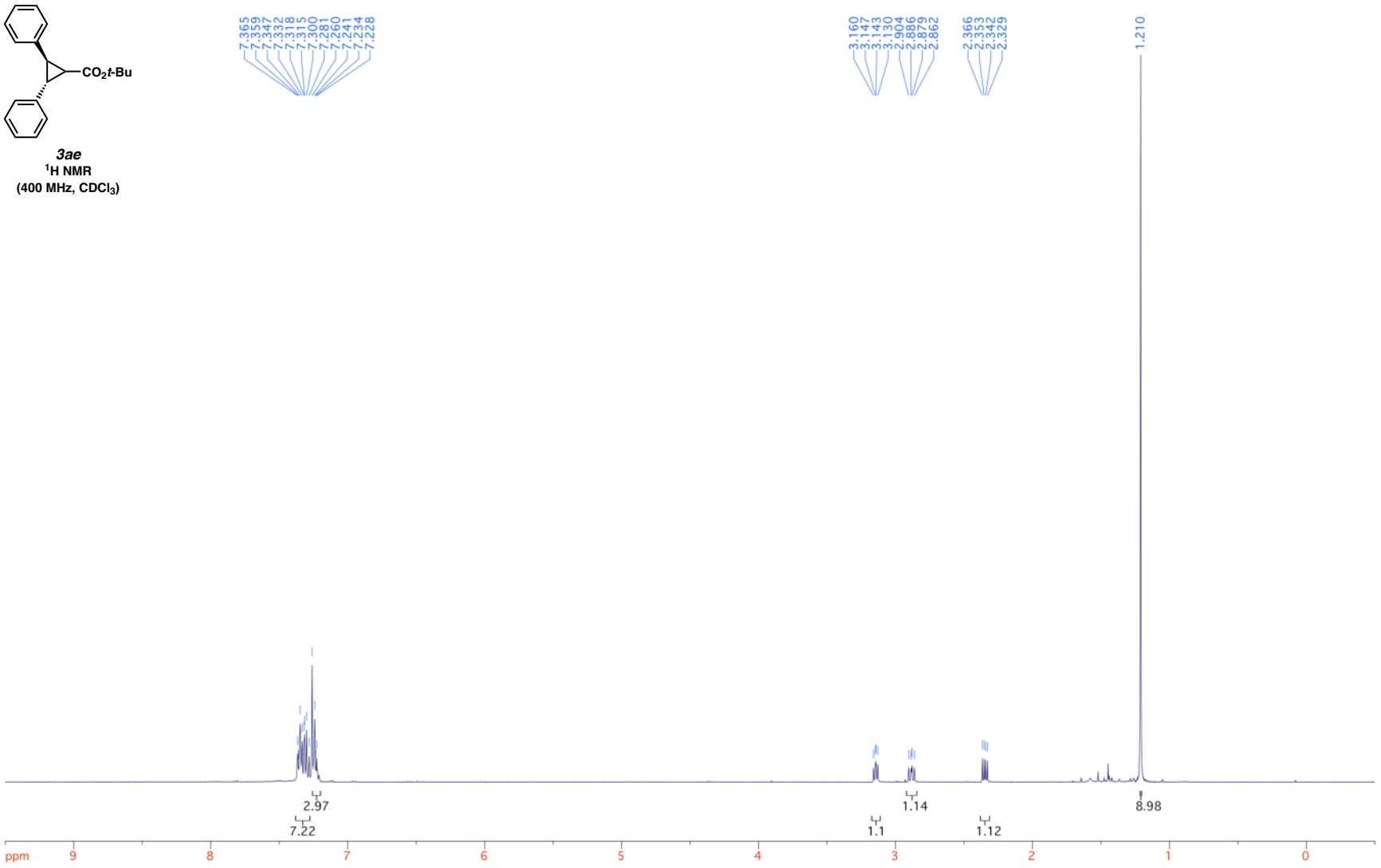

CO2i-Pr
3ac
1H NMR
(400 MHz, CDCl3)
7.354
7.335
7.314
7.294
7.274
7.260
7.242
7.224
7.205
4.844
4.828
4.813
4.797
4.781
4.766
4.750
3.225
3.212
3.208
3.195
2.939
2.922
2.915
2.897
2.416
2.403
2.392
2.379
1.050
1.034
0.977
0.962
2.79
7.12
0.95
0.992
1.04
1.2
3.03
3.03
ppm
9
8
7
6
5
4
3
2
1
0


CO2i-Pr
3ac
13C NMR
(100 MHz, CDCl3)
169.566
139.834
136.303
129.349
128.718
128.176
127.003
126.758
77.160
67.972
34.512
31.583
29.040
21.977
21.560
ppm
200
180
160
140
120
100
80
60
40
20
0

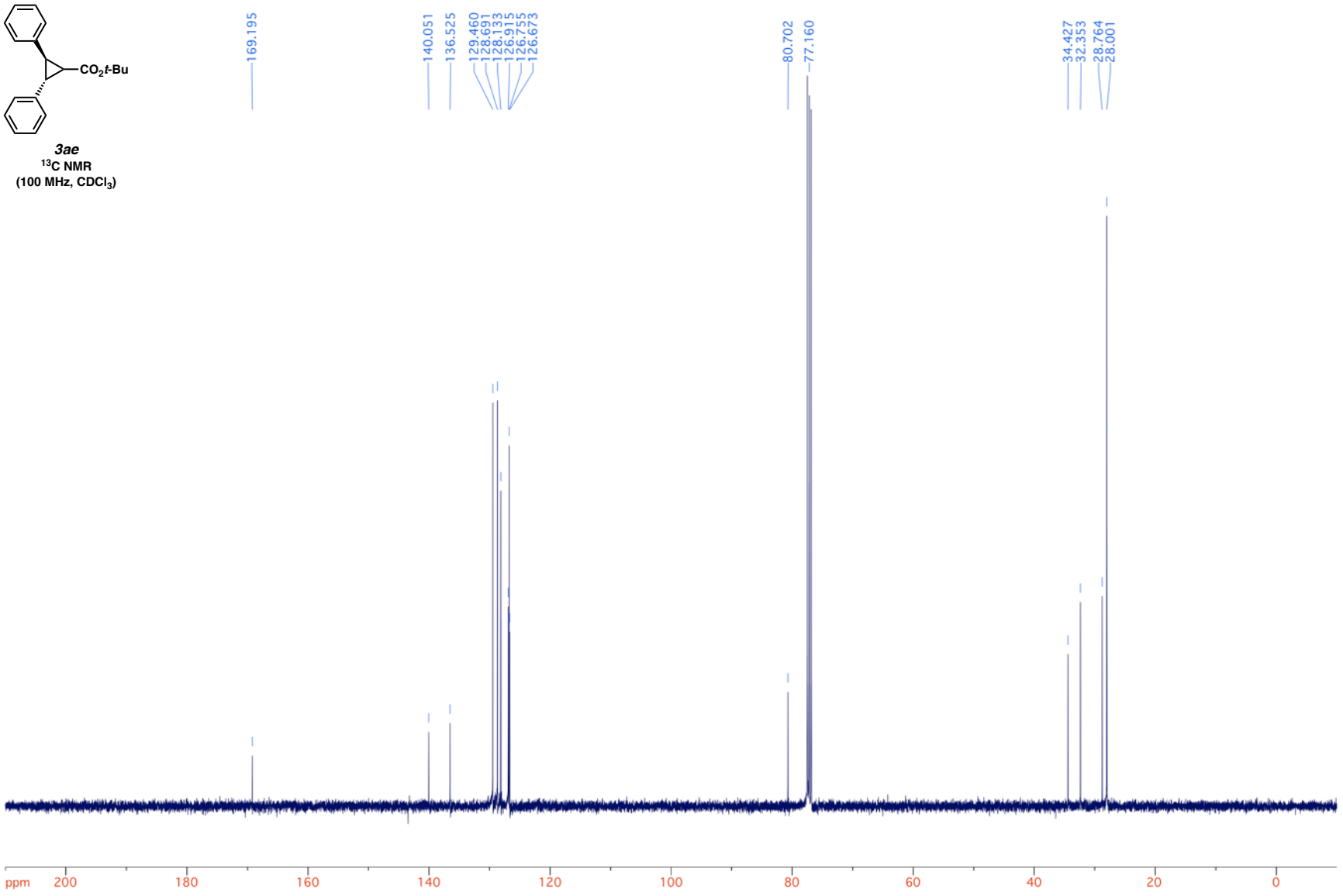


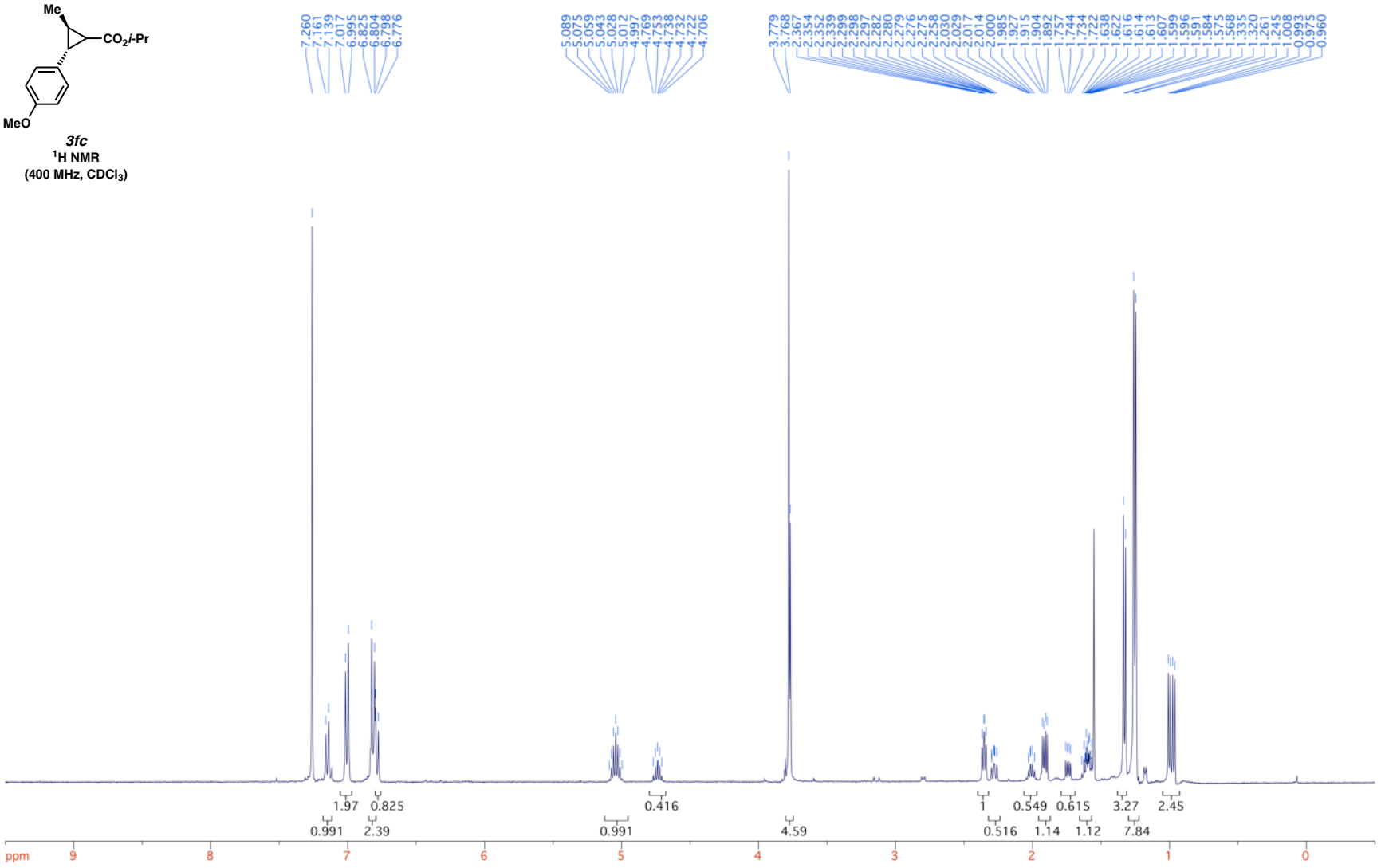
3ad
^{1}H NMR
(400 MHz, $CDCl_3$)

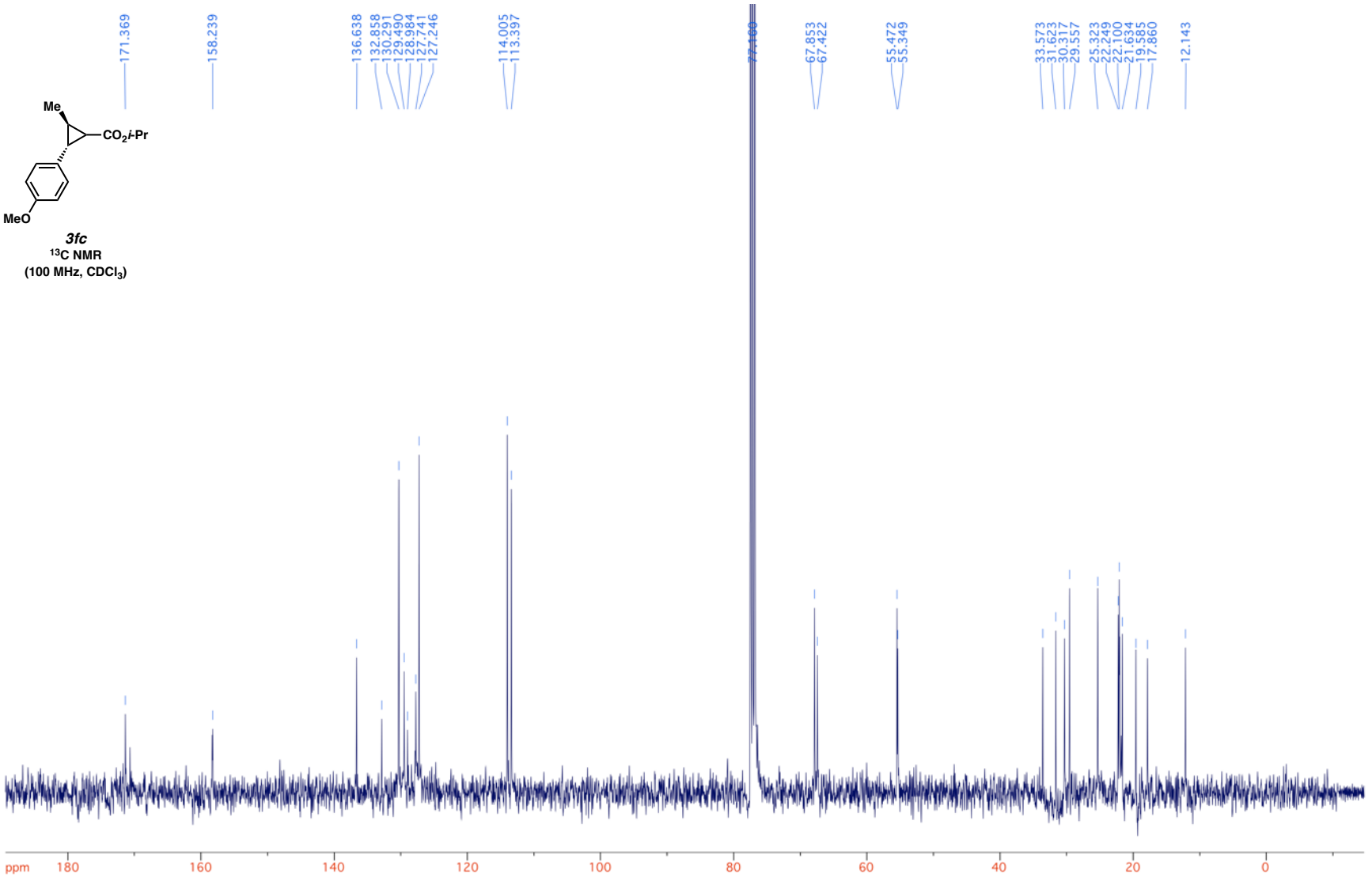

CO2i-Bu
3ad
13C NMR
(100 MHz, CDCl3)
170.203
139.783
136.279
129.254
128.750
128.265
127.072
126.821
126.775
77.160
70.893
34.560
31.466
29.434
27.721
19.117
19.098
ppm
200
180
160
140
120
100
80
60
40
20
0



3ae
^{1}H NMR
(400 MHz, $CDCl_3$)


CO2t-Bu
3ae
13C NMR
(100 MHz, CDCl3)
169.195
140.051
136.525
129.460
128.691
128.133
126.915
126.755
126.673
80.702
77.160
34.427
32.353
28.764
28.001
ppm
200
180
160
140
120
100
80
60
40
20
0


Me
CO2i-Pr
MeO
3fc
1H NMR
(400 MHz, CDCl3)
7.260
7.161
7.159
7.017
6.995
6.825
6.804
6.798
6.776
5.089
5.075
5.059
5.043
5.028
5.012
4.997
4.769
4.753
4.738
4.732
4.722
4.706
3.779
3.768
3.367
2.354
2.352
2.339
2.299
2.298
2.297
2.282
2.280
2.279
2.276
2.275
2.258
2.030
2.029
2.017
2.014
2.000
1.985
1.927
1.915
1.904
1.892
1.757
1.744
1.734
1.722
1.638
1.622
1.616
1.614
1.613
1.607
1.599
1.596
1.591
1.584
1.575
1.568
1.335
1.320
1.261
1.245
1.008
0.993
0.975
0.960
1.97
0.825
0.991
2.39
0.416
0.991
4.59
1
0.549
0.615
3.27
2.45
0.516
1.14
1.12
7.84
ppm
9
8
7
6
5
4
3
2
1
0


171.369
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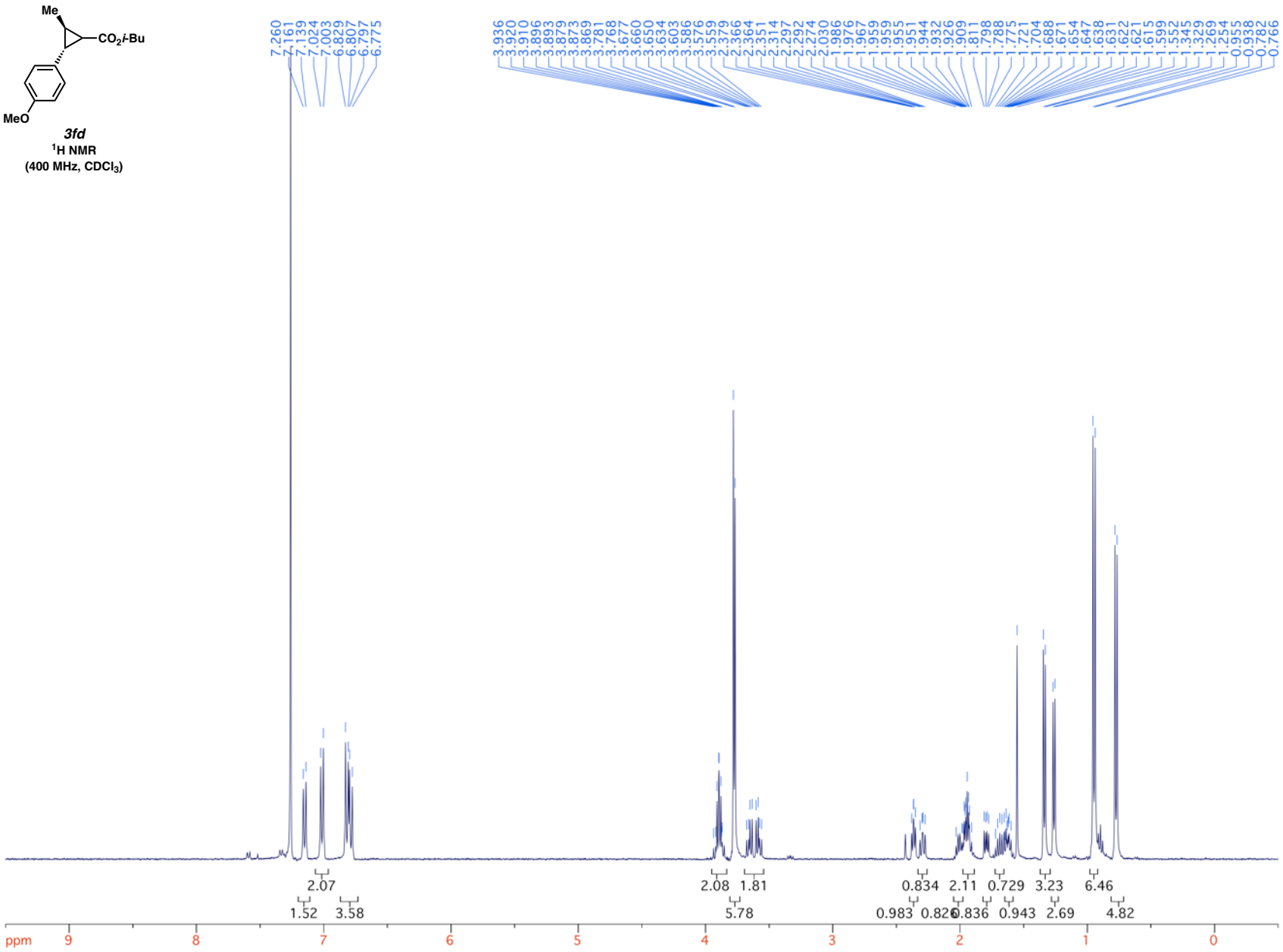
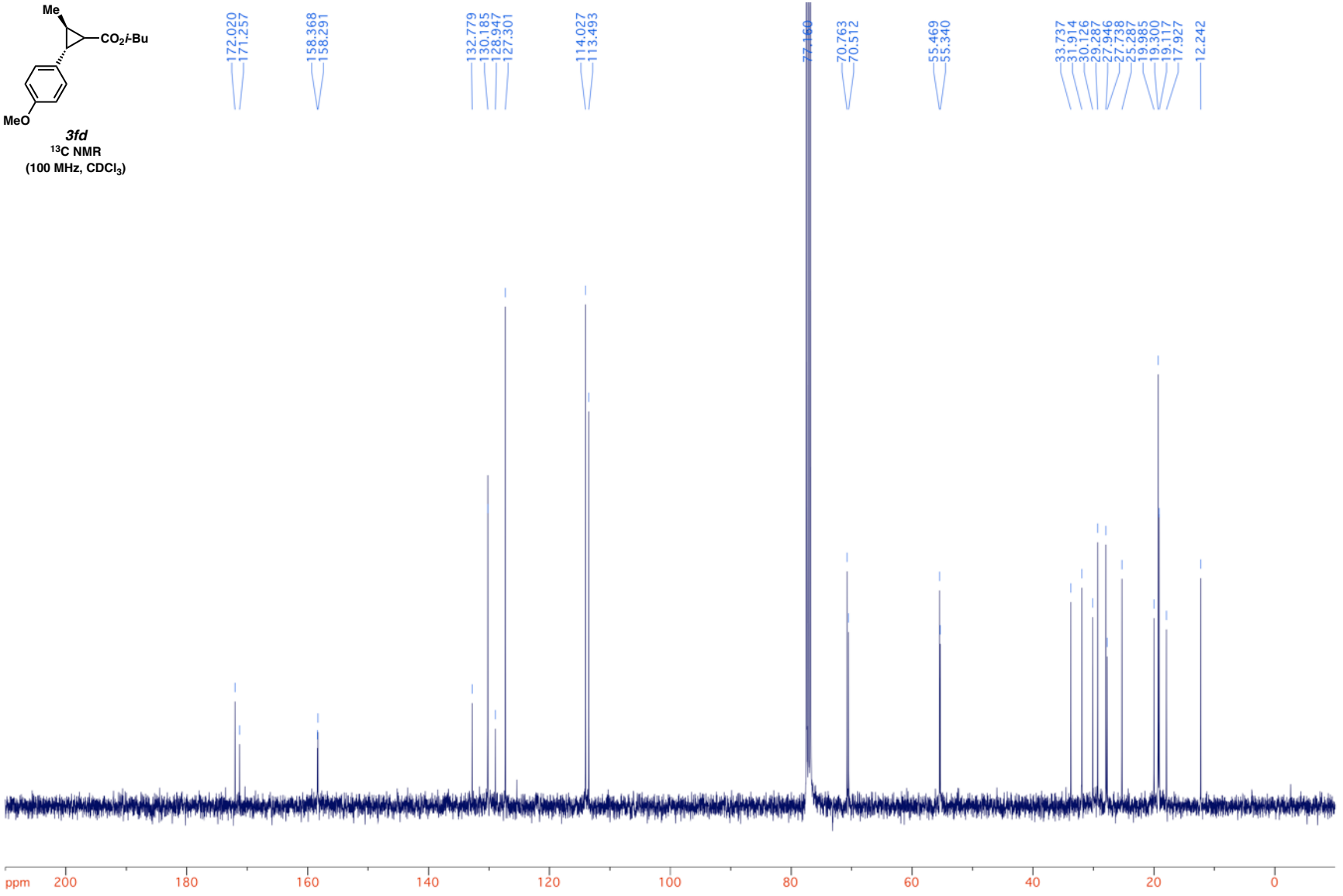
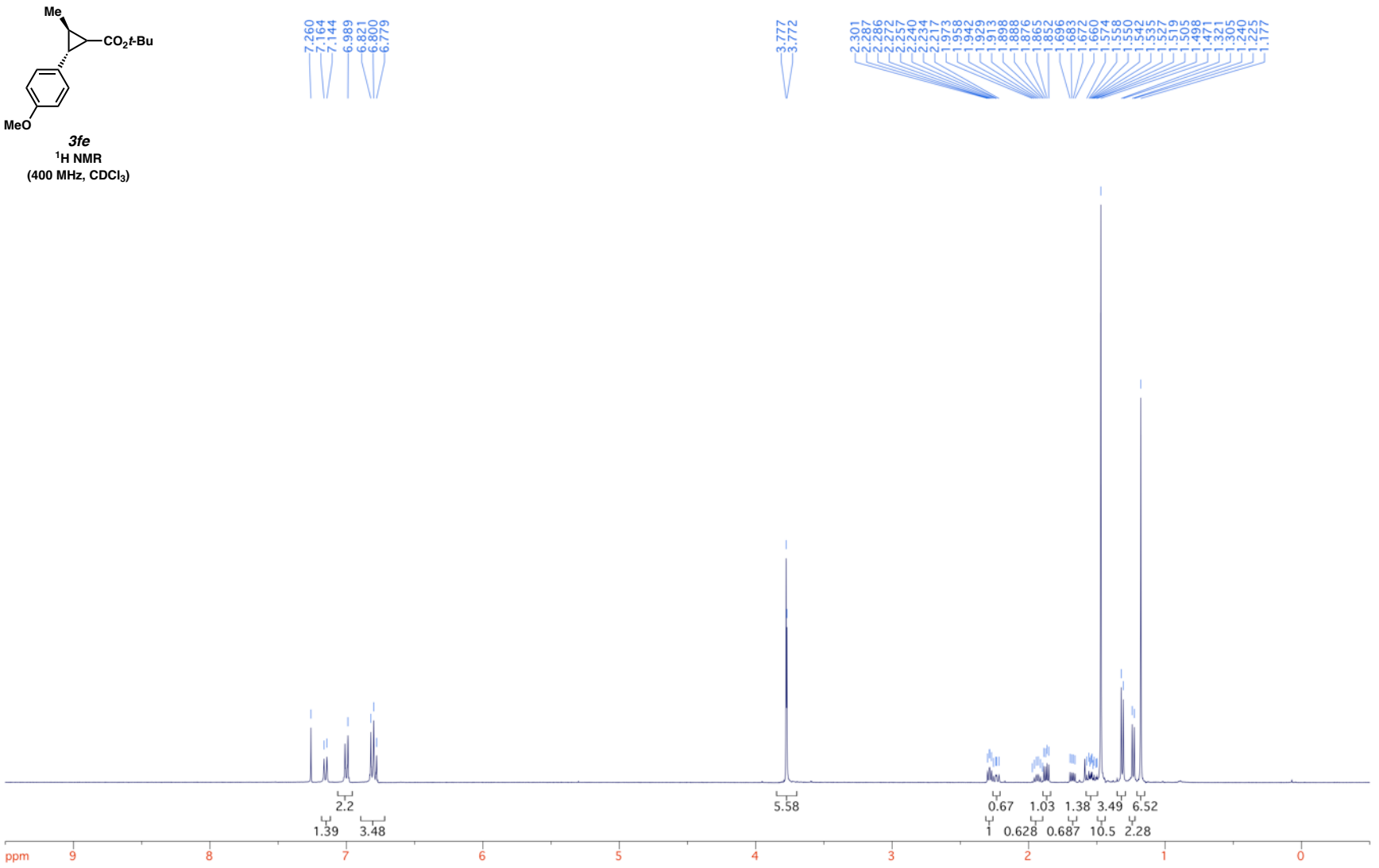
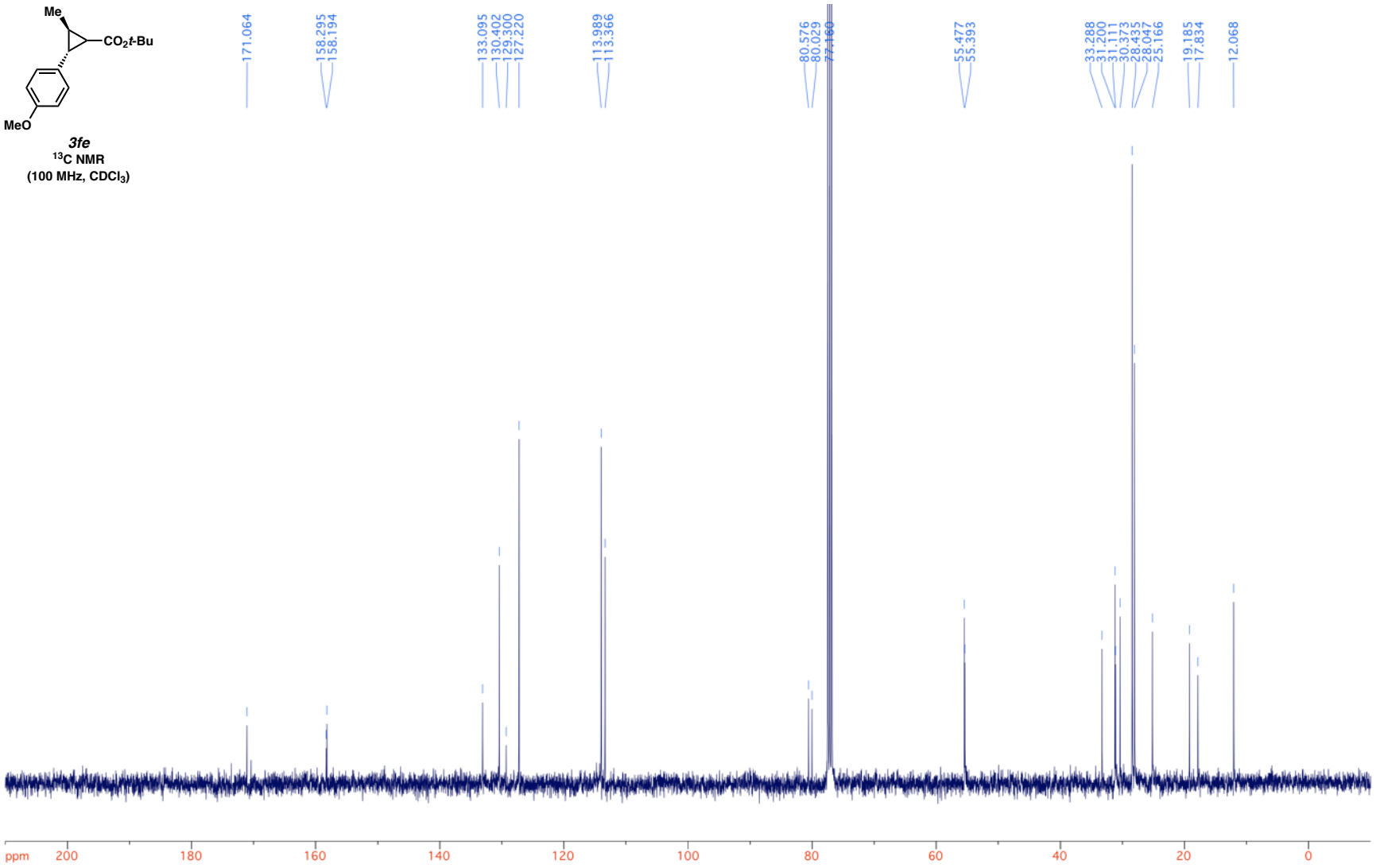
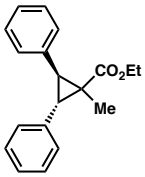
136.638
132.858
130.291
129.490
128.984
127.741
127.246
114.005
113.397
77.160
67.853
67.422
55.472
55.349
33.573
31.623
30.317
29.557
25.323
22.249
22.100
21.634
19.585
17.860
12.143
Me
CO2i-Pr
MeO
3fc
13C NMR
(100 MHz, CDCl3)
ppm
180
160
140
120
100
80
60
40
20
0


Me
CO2i-Bu
MeO
3fd
1H NMR
(400 MHz, CDCl3)
7.260
7.161
7.139
7.024
7.003
6.829
6.807
6.797
6.775
3.936
3.920
3.910
3.896
3.893
3.879
3.873
3.869
3.781
3.768
3.677
3.660
3.650
3.634
3.603
3.586
3.576
3.559
3.379
2.366
2.364
2.351
2.314
2.297
2.292
2.274
2.030
1.986
1.976
1.967
1.959
1.959
1.955
1.951
1.944
1.932
1.926
1.909
1.811
1.798
1.788
1.775
1.721
1.704
1.688
1.671
1.654
1.647
1.638
1.631
1.622
1.621
1.615
1.599
1.552
1.345
1.329
1.269
1.254
0.955
0.938
0.782
0.766
2.07
1.52
3.58
2.08
1.81
5.78
0.834
2.11
0.729
3.23
6.46
0.983
0.826
0.836
0.943
2.69
4.82
ppm
9
8
7
6
5
4
3
2
1
0

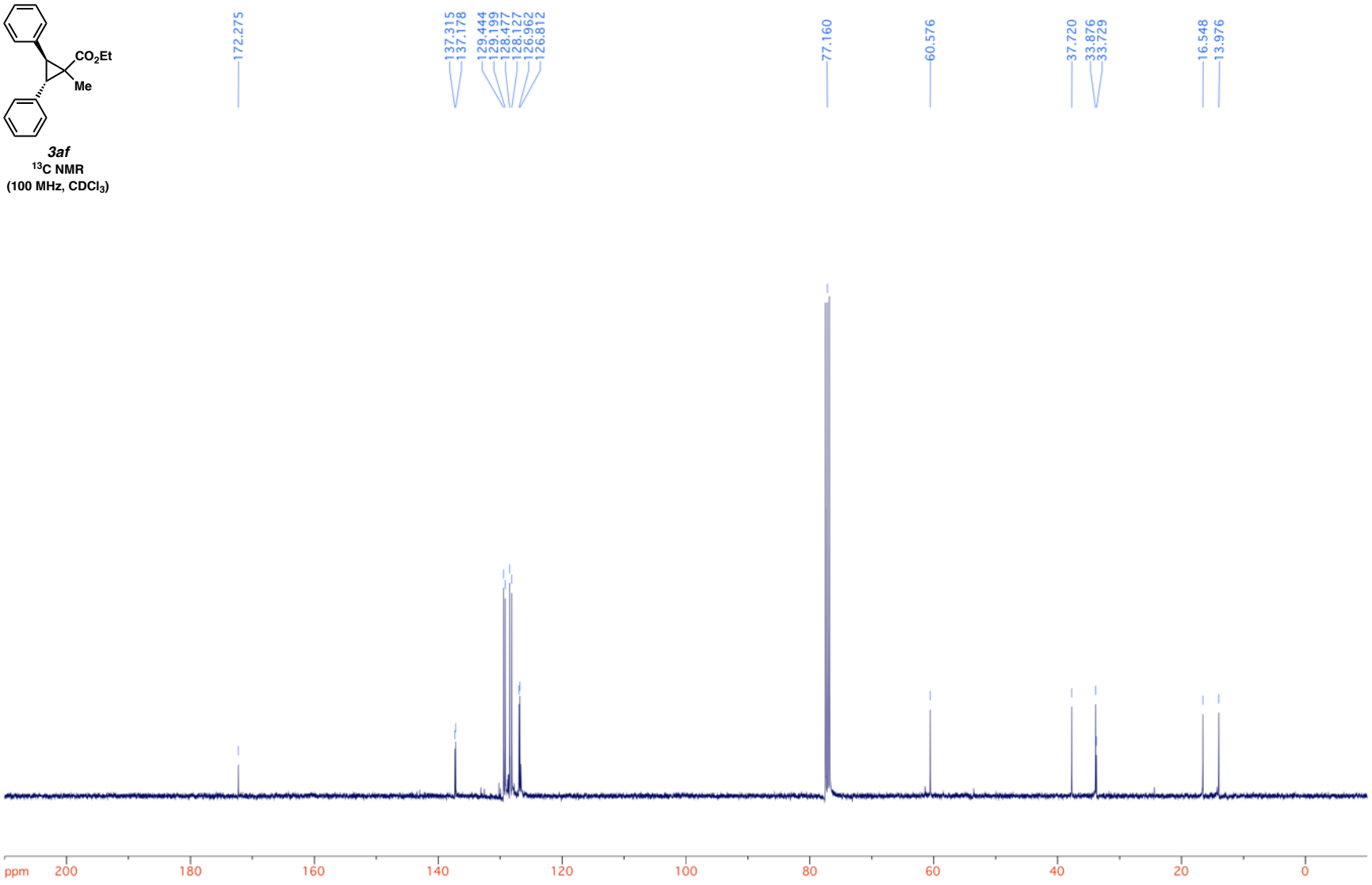

Me
CO2i-Bu
MeO
3fd
13C NMR
(100 MHz, CDCl3)
172.020
171.257
158.368
158.291
132.779
130.185
128.947
127.301
114.027
113.493
77.160
70.763
70.512
55.469
55.340
33.737
31.914
30.126
29.287
27.946
27.738
25.287
19.985
19.300
19.117
17.927
12.242
ppm
200
180
160
140
120
100
80
60
40
20
0


Me
CO2t-Bu
MeO
3fe
1H NMR
(400 MHz, CDCl3)
7.260
7.164
7.144
6.989
6.821
6.800
6.779
3.777
3.772
2.301
2.287
2.286
2.272
2.257
2.240
2.234
2.217
1.973
1.958
1.942
1.929
1.913
1.898
1.888
1.876
1.865
1.852
1.696
1.683
1.672
1.660
1.574
1.558
1.550
1.542
1.535
1.527
1.519
1.505
1.498
1.471
1.321
1.305
1.240
1.225
1.177
2.2
1.39
3.48
5.58
0.67
1.03
1.38
3.49
6.52
1
0.628
0.687
10.5
2.28
ppm
9
8
7
6
5
4
3
2
1
0

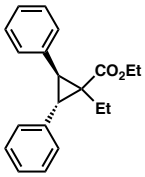

Me
CO2t-Bu
MeO
3fe
13C NMR
(100 MHz, CDCl3)
171.064
158.295
158.194
133.095
130.402
129.300
127.220
113.989
113.366
80.576
80.029
77.160
55.477
55.393
33.288
31.200
31.111
30.373
28.435
28.047
25.166
19.185
17.834
12.068
ppm
200
180
160
140
120
100
80
60
40
20
0



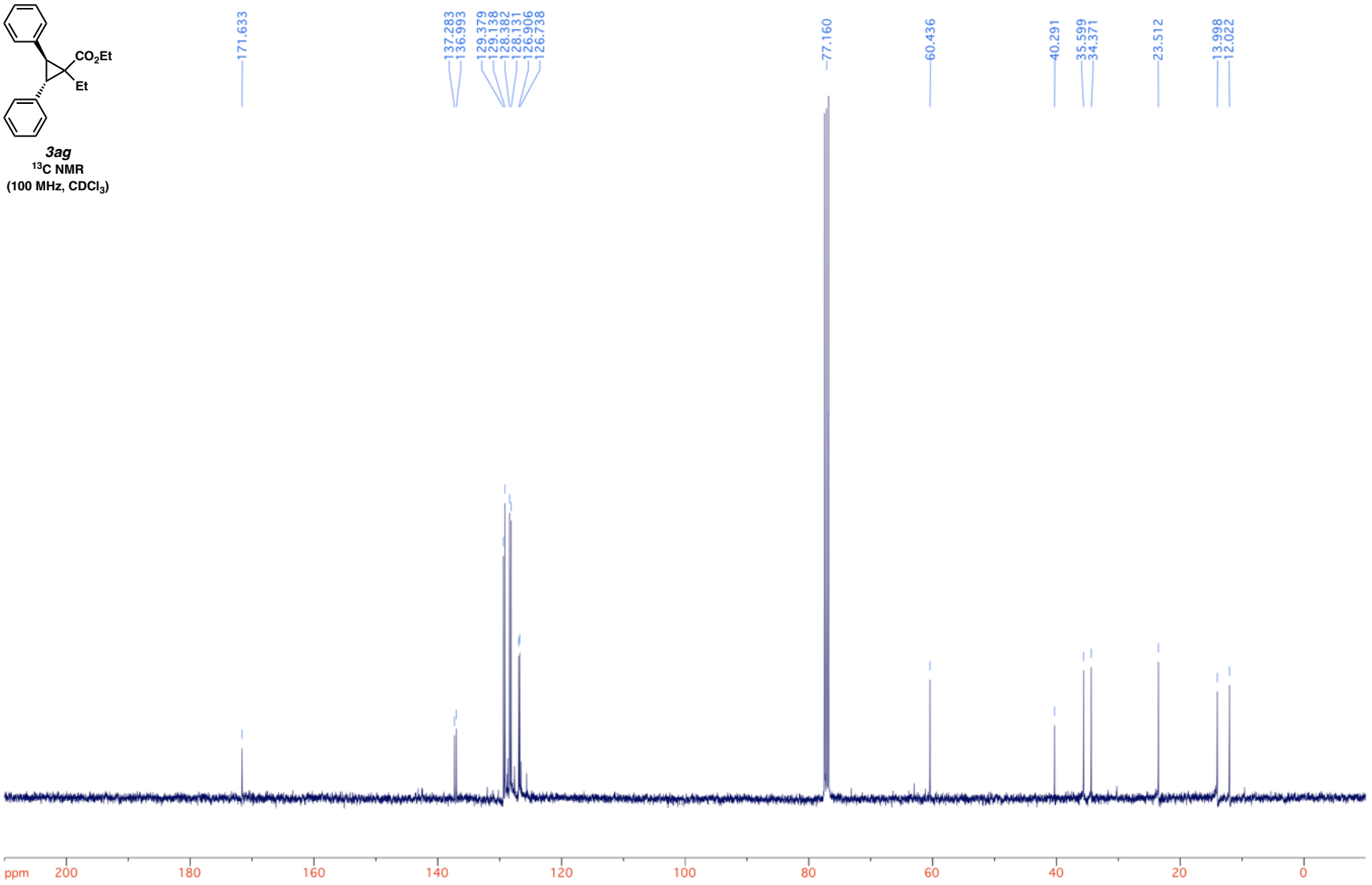
3af
^{1}H NMR
(400 MHz, $CDCl_3$)



3af
^{13}C NMR
(100 MHz, $CDCl_3$)

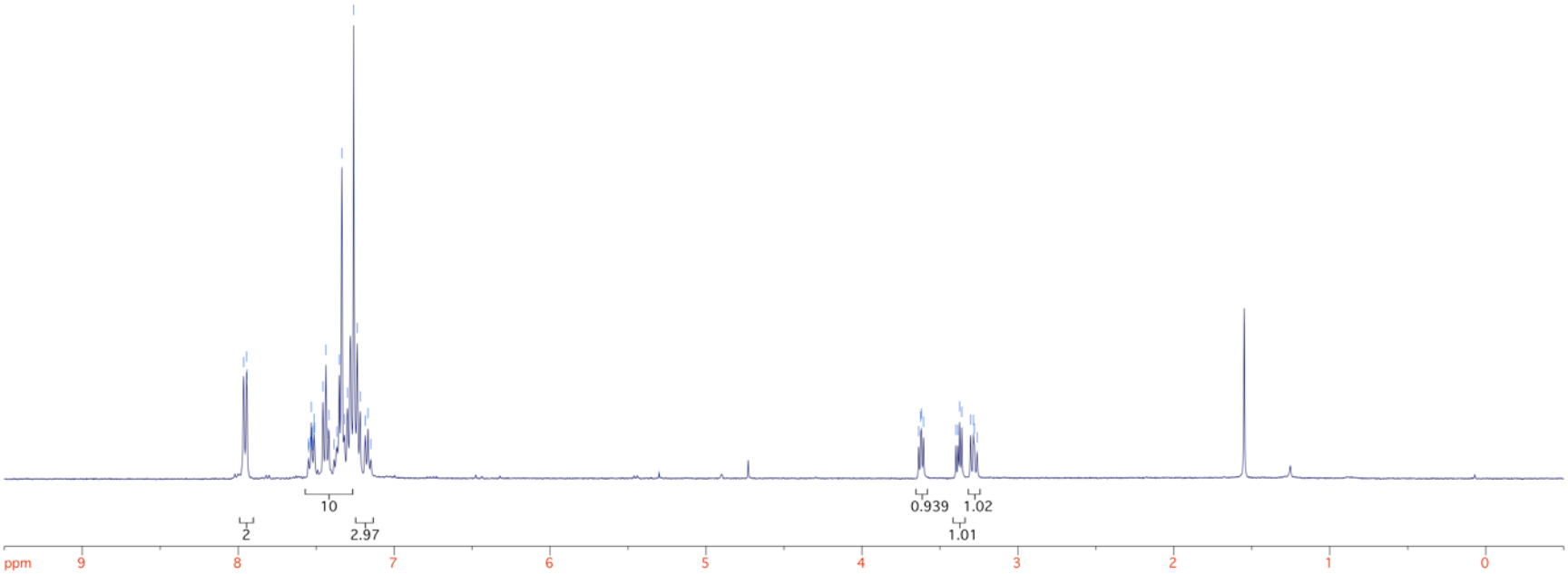


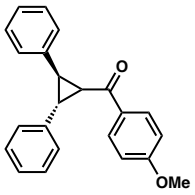
3ag
^{1}H NMR
(400 MHz, $CDCl_3$)



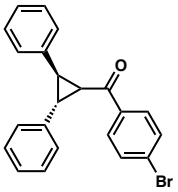
3ag
^{13}C NMR
(100 MHz, $CDCl_3$)

3ah
^{1}H NMR
(400 MHz, $CDCl_3$)

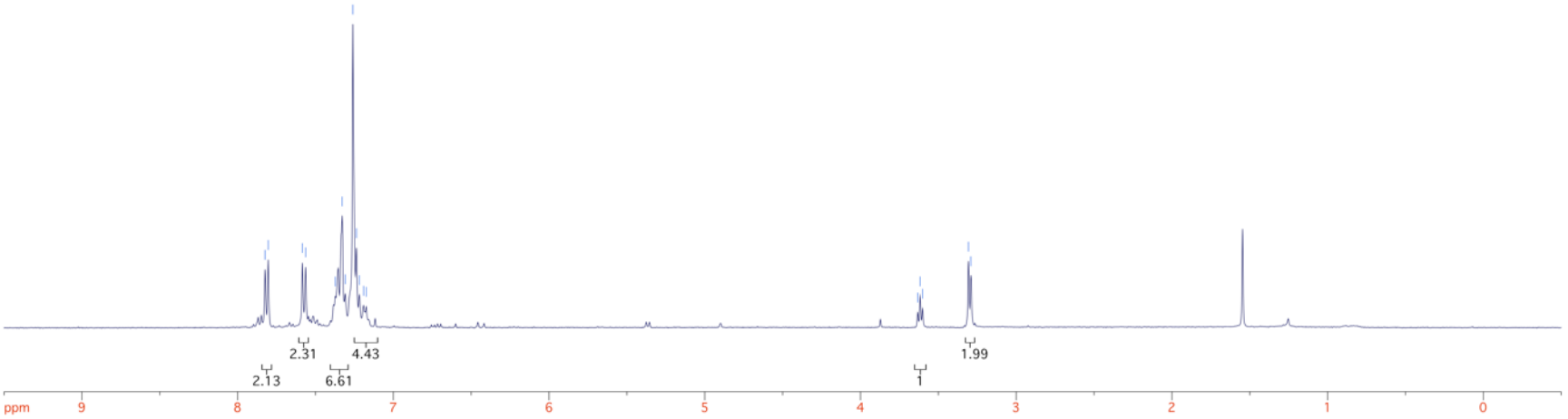


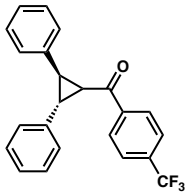


3ai
^{1}H NMR
(400 MHz, $CDCl_3$)

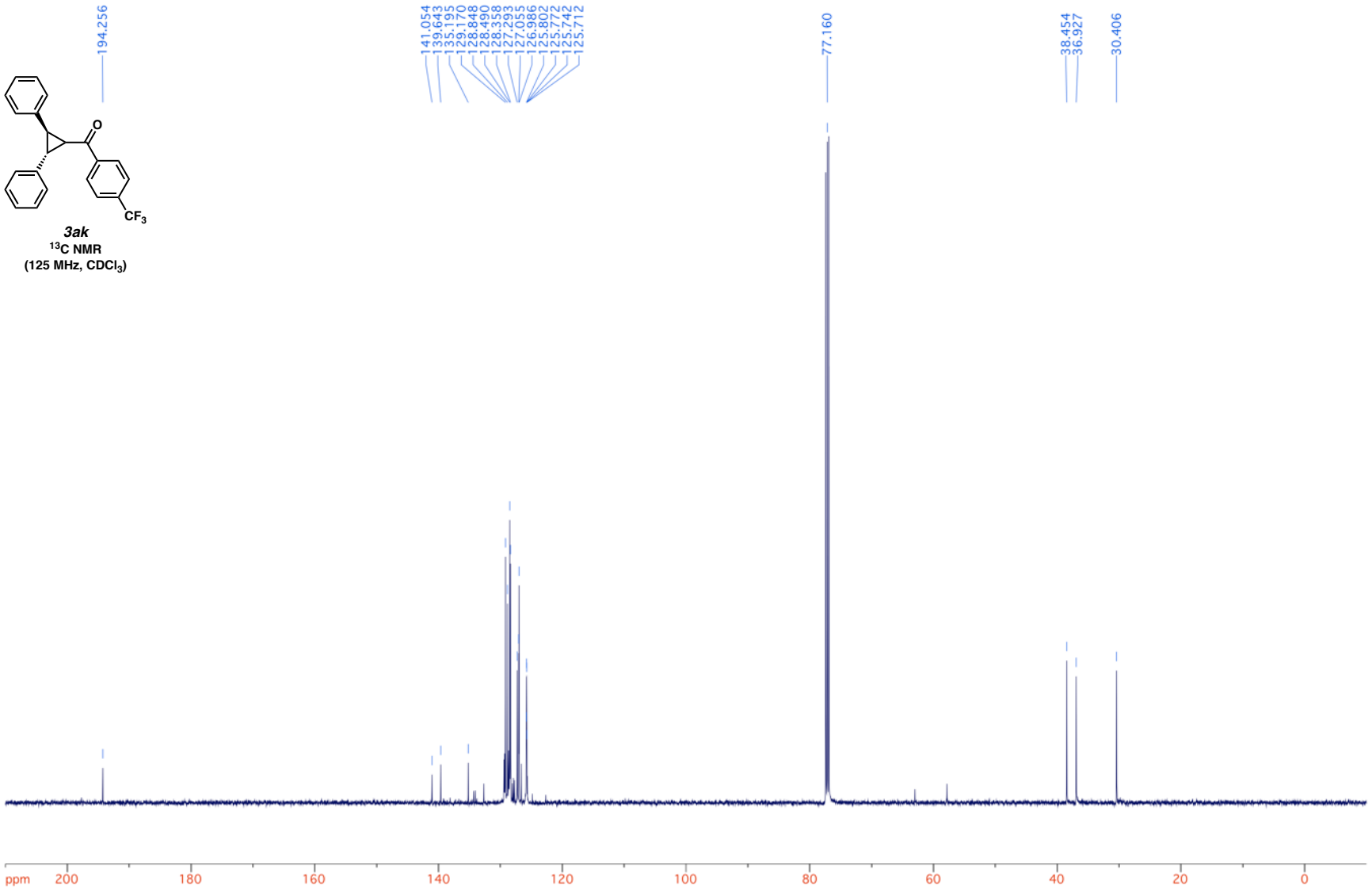


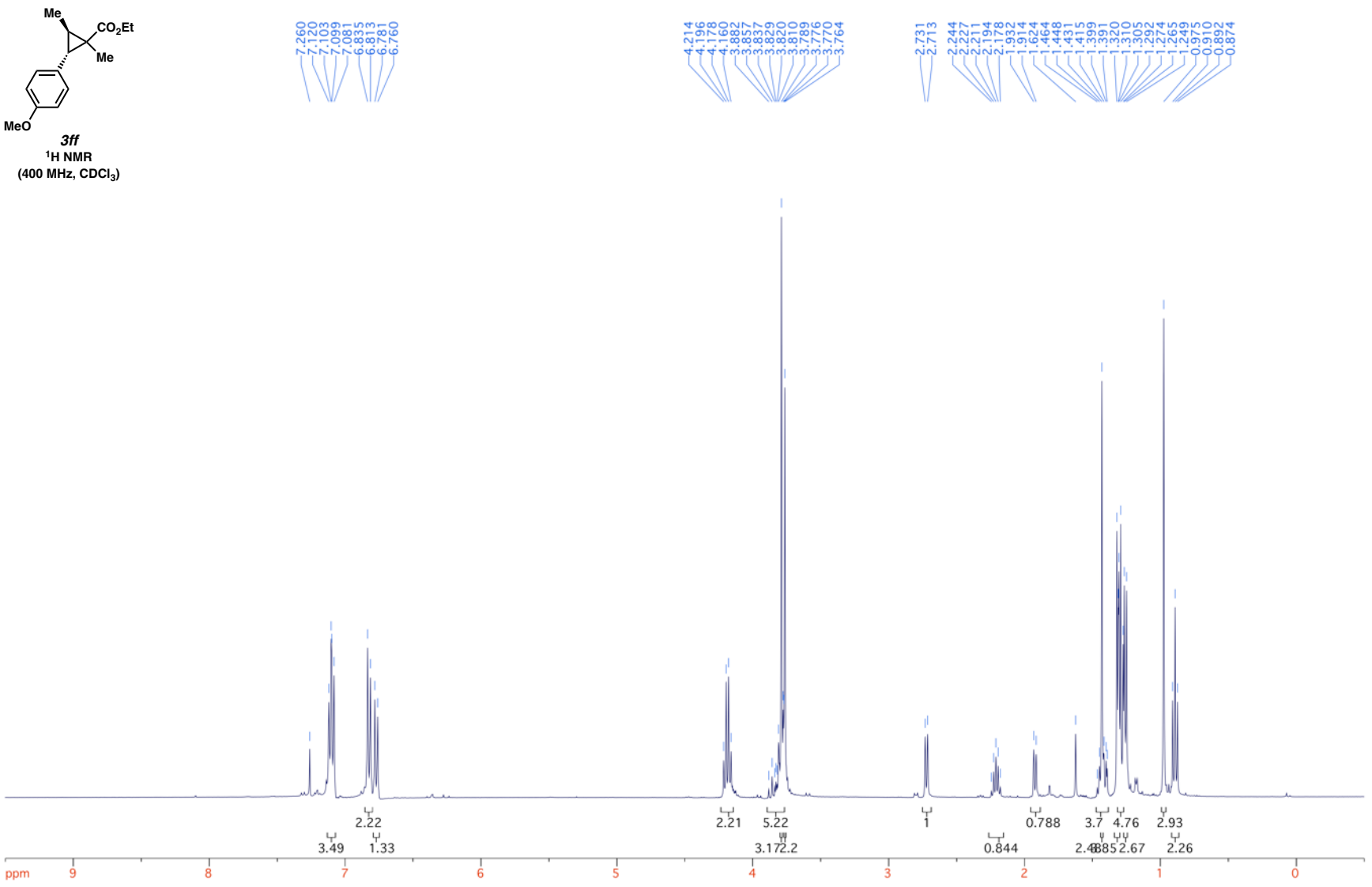
3aj
^{1}H NMR
(400 MHz, $CDCl_3$)



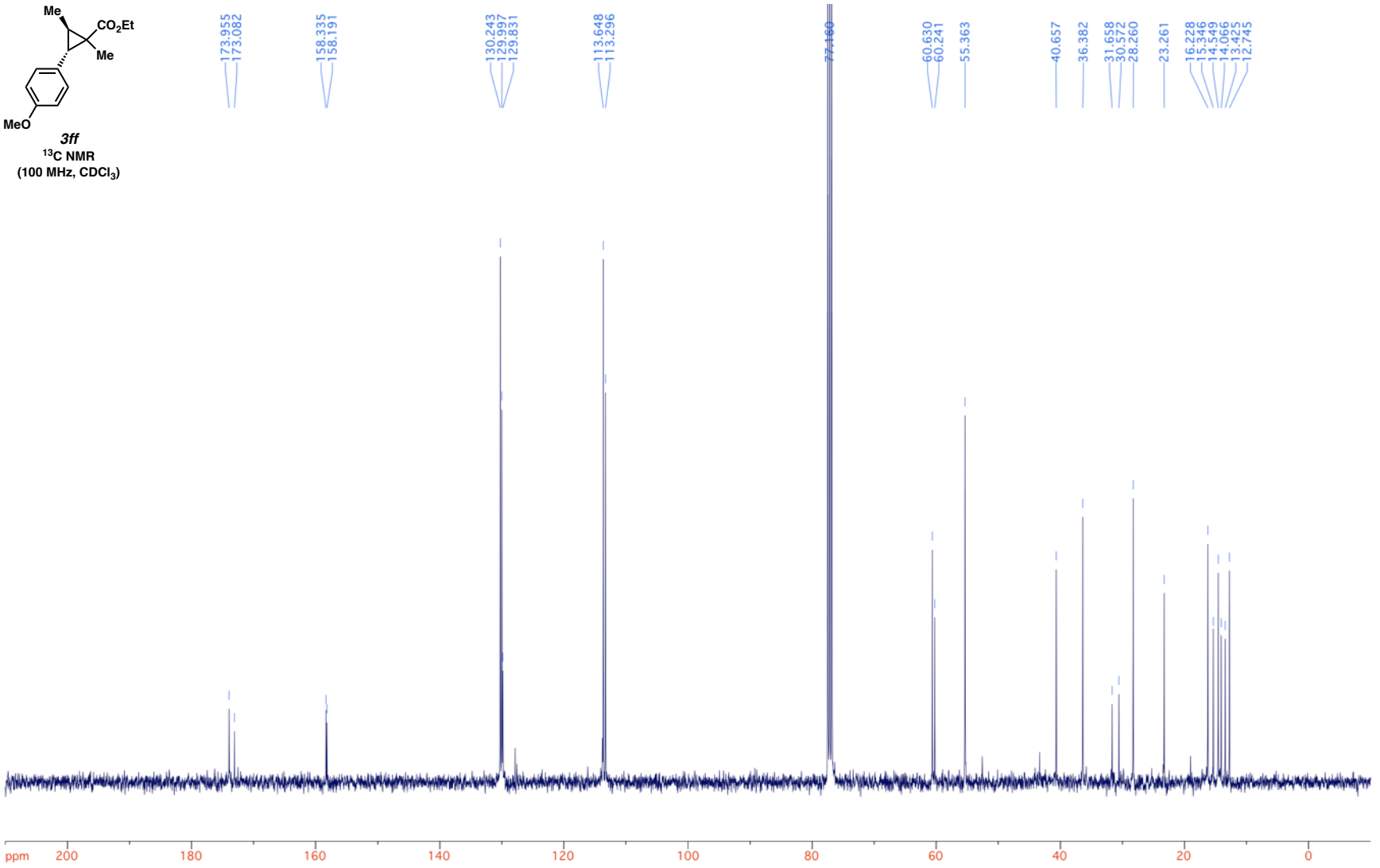


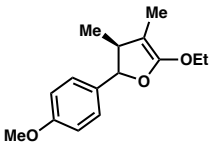
3ak
^{1}H NMR
(400 MHz, $CDCl_3$)


194.256
141.054
139.643
135.195
129.170
128.848
128.490
128.358
127.293
127.055
126.986
125.802
125.772
125.742
125.712
77.160
38.454
36.927
30.406
O
CF3
3ak
13C NMR
(125 MHz, CDCl3)
ppm
200
180
160
140
120
100
80
60
40
20
0

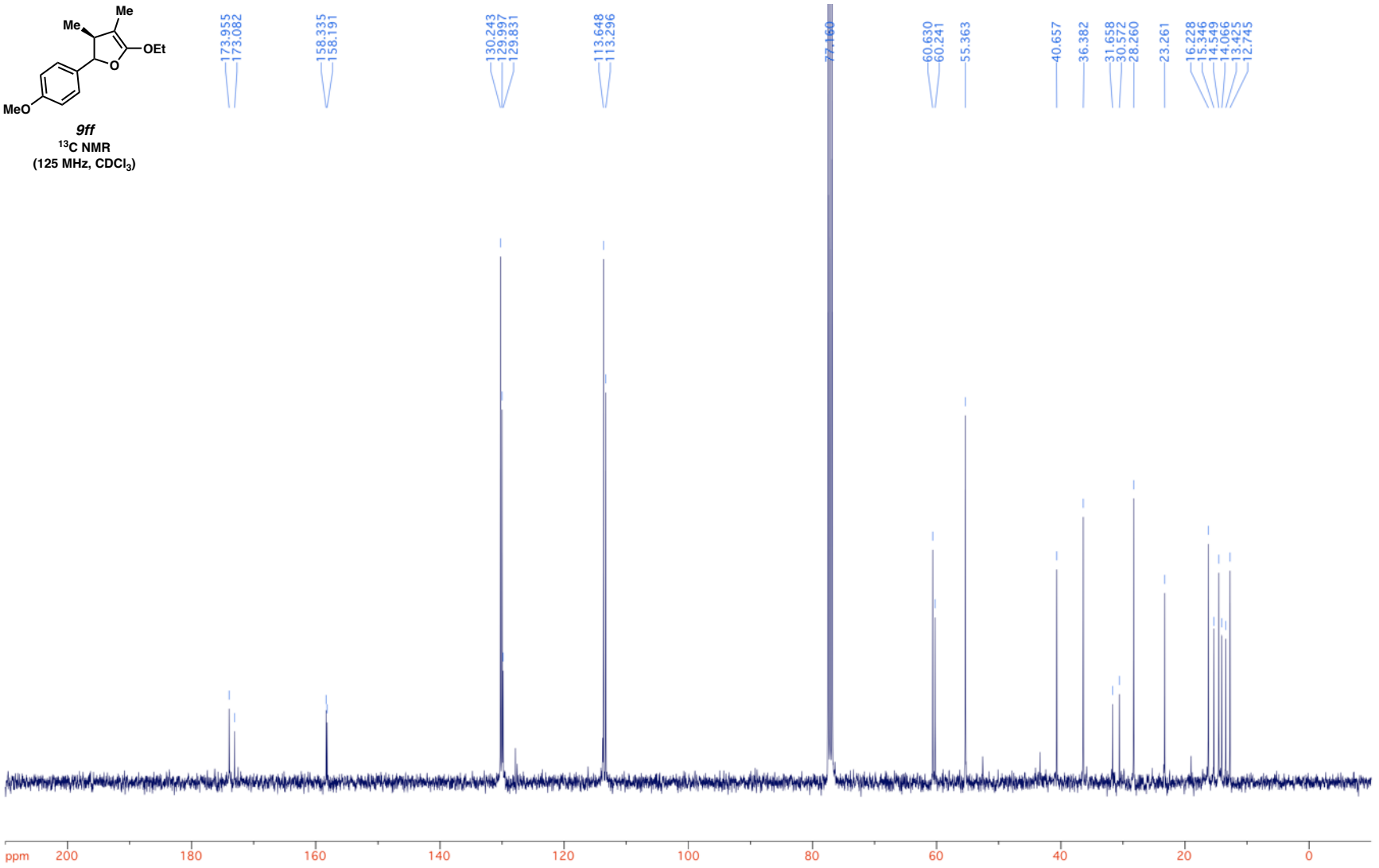


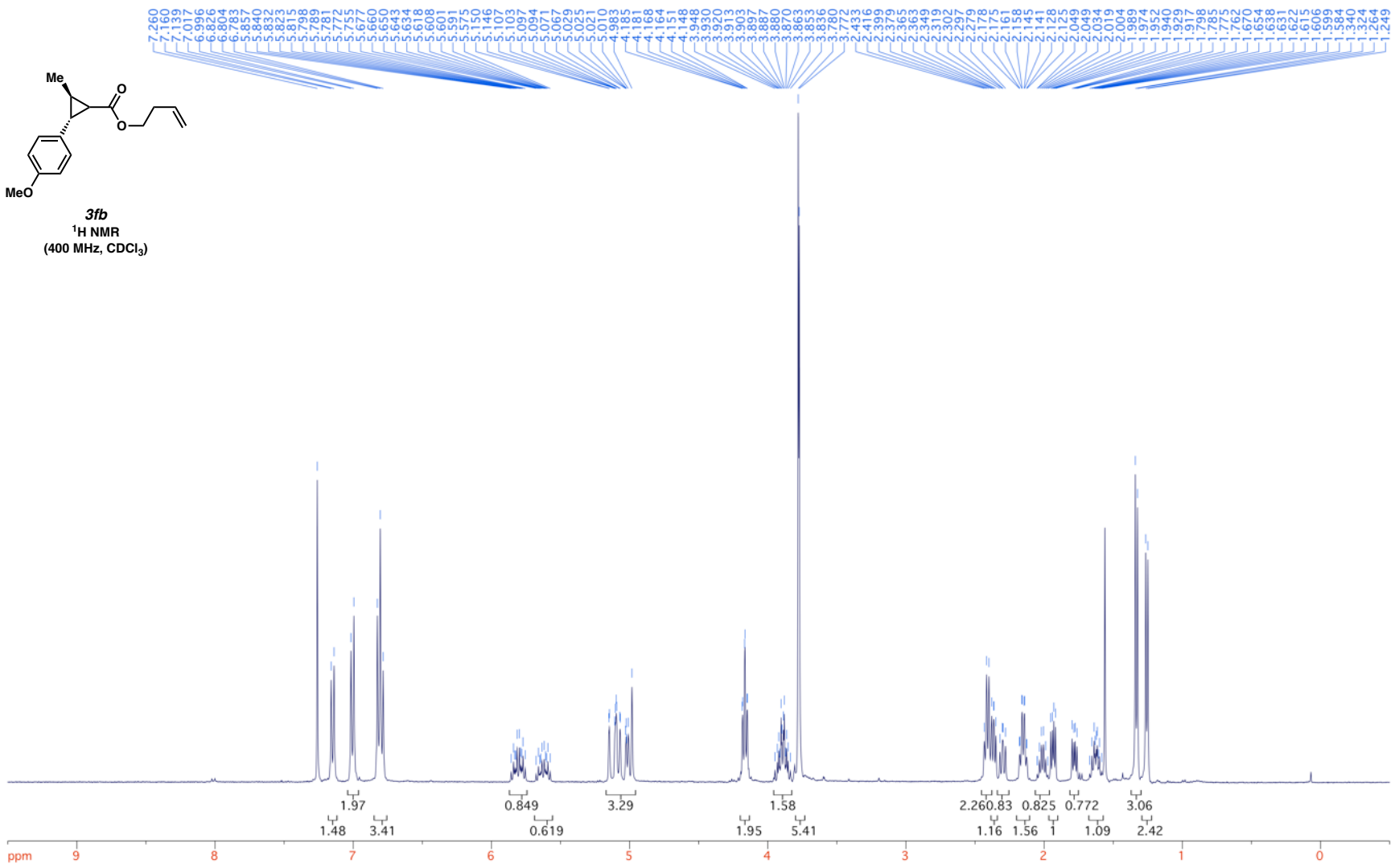
3ff
^{1}H NMR
(400 MHz, $CDCl_3$)

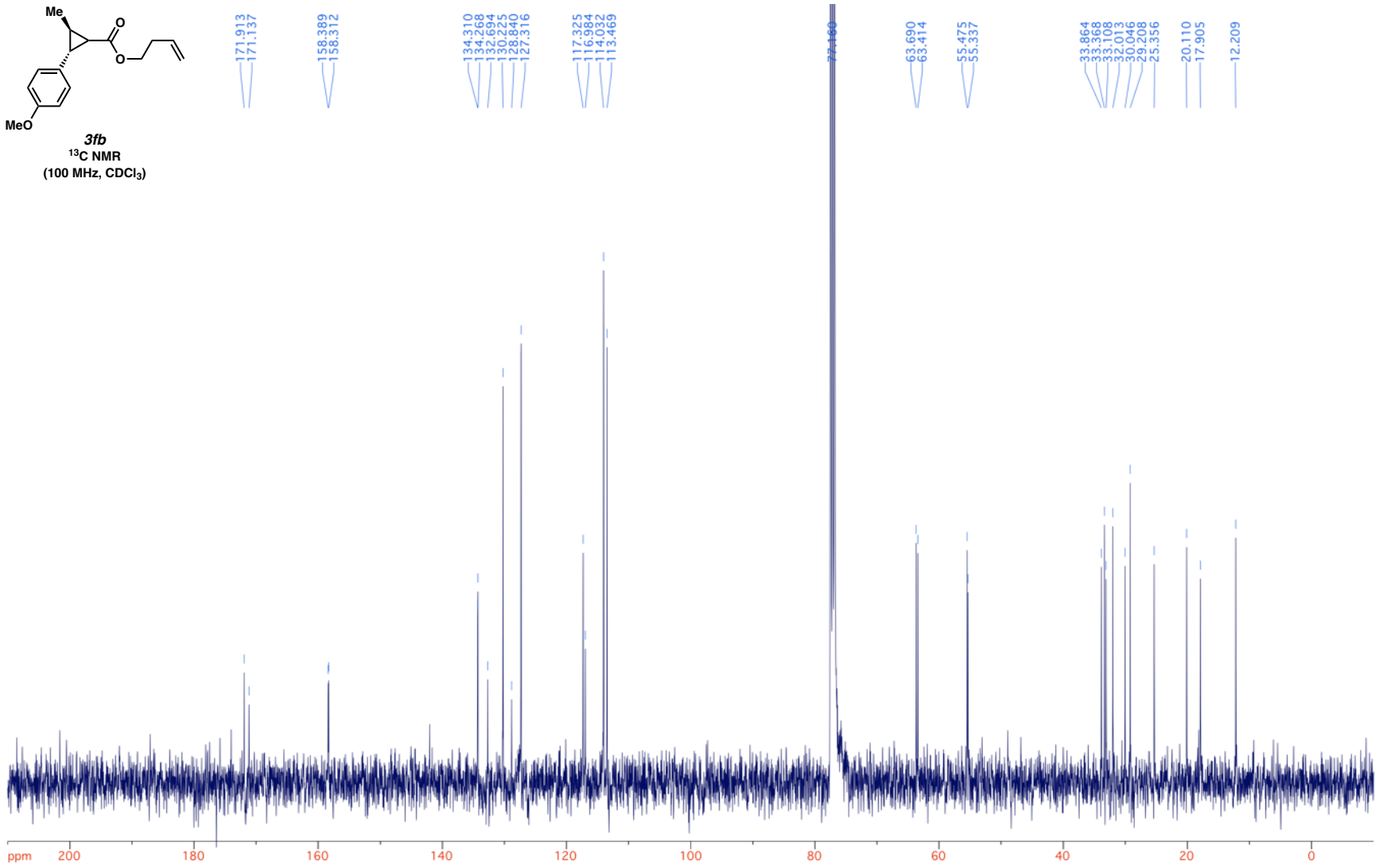

Me
CO2Et
Me
MeO
3ff
13C NMR
(100 MHz, CDCl3)
173.955
173.082
158.335
158.191
130.243
129.997
129.831
113.648
113.296
77.160
60.630
60.241
55.363
40.657
36.382
31.658
30.572
28.260
23.261
16.228
15.346
14.549
14.066
13.425
12.745
ppm
200
180
160
140
120
100
80
60
40
20
0



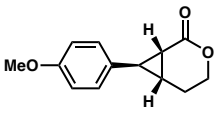
9ff
^{1}H NMR
(400 MHz, $CDCl_3$)


Me
Me
OEt
O
MeO
9ff
13C NMR
(125 MHz, CDCl3)
173.955
173.082
158.335
158.191
130.243
129.997
129.831
113.648
113.296
77.160
60.630
60.241
55.363
40.657
36.382
31.658
30.572
28.260
23.261
16.228
15.346
14.549
14.066
13.425
12.745
ppm
200
180
160
140
120
100
80
60
40
20
0

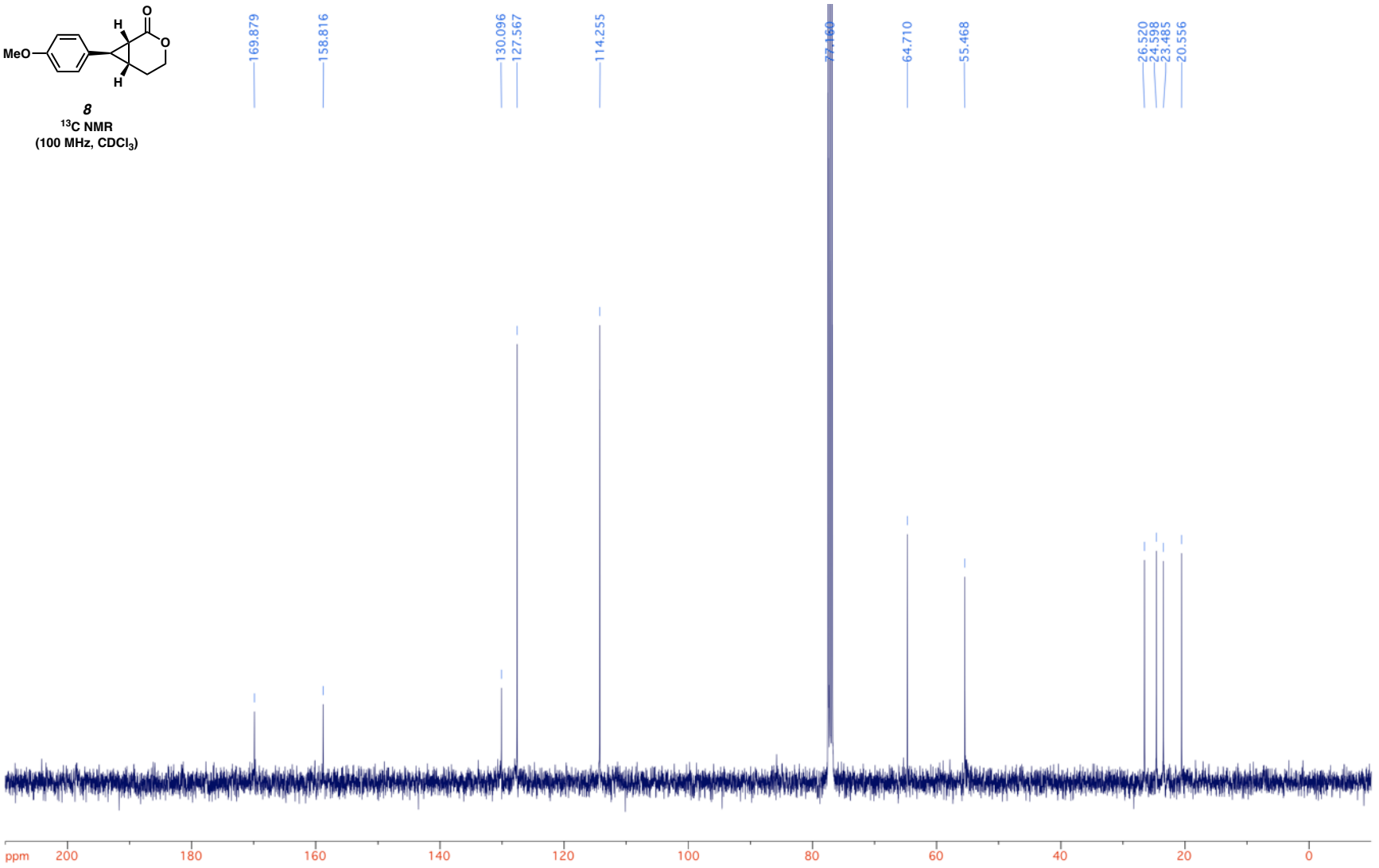

Me
O
O
MeO
3fb
1H NMR
(400 MHz, CDCl3)
1.97
1.48
3.41
0.849
0.619
3.29
1.58
1.95
5.41
2.26
0.83
1.16
0.825
1.56
1
0.772
1.09
3.06
2.42
ppm
9
8
7
6
5
4
3
2
1
0



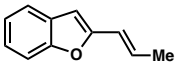
3fb
^{13}C NMR
(100 MHz, $CDCl_3$)



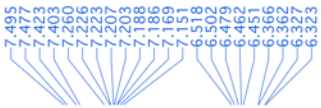
8
^{1}H NMR
(400 MHz, $CDCl_3$)

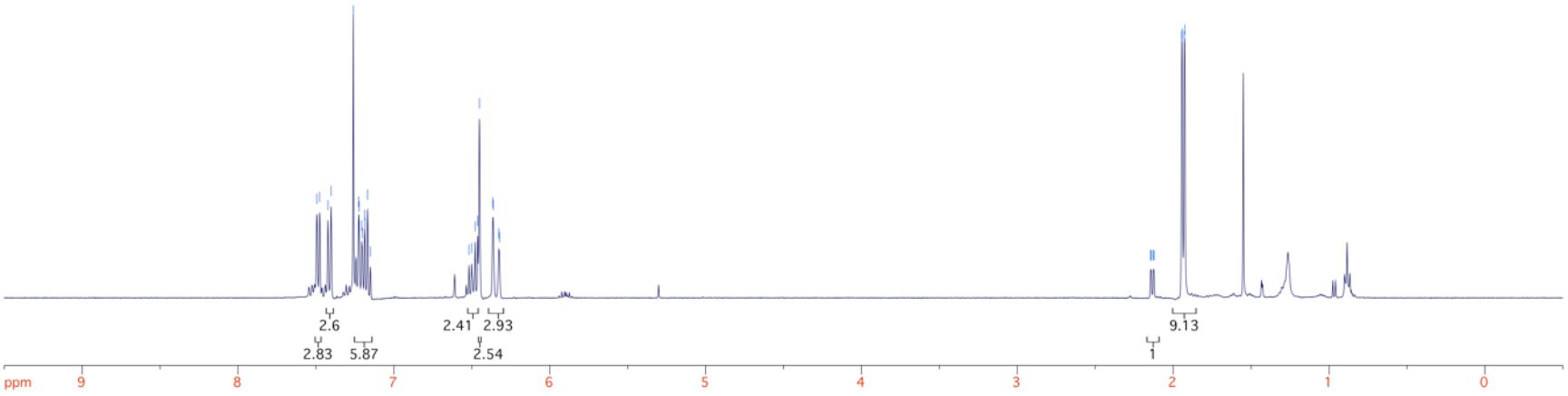


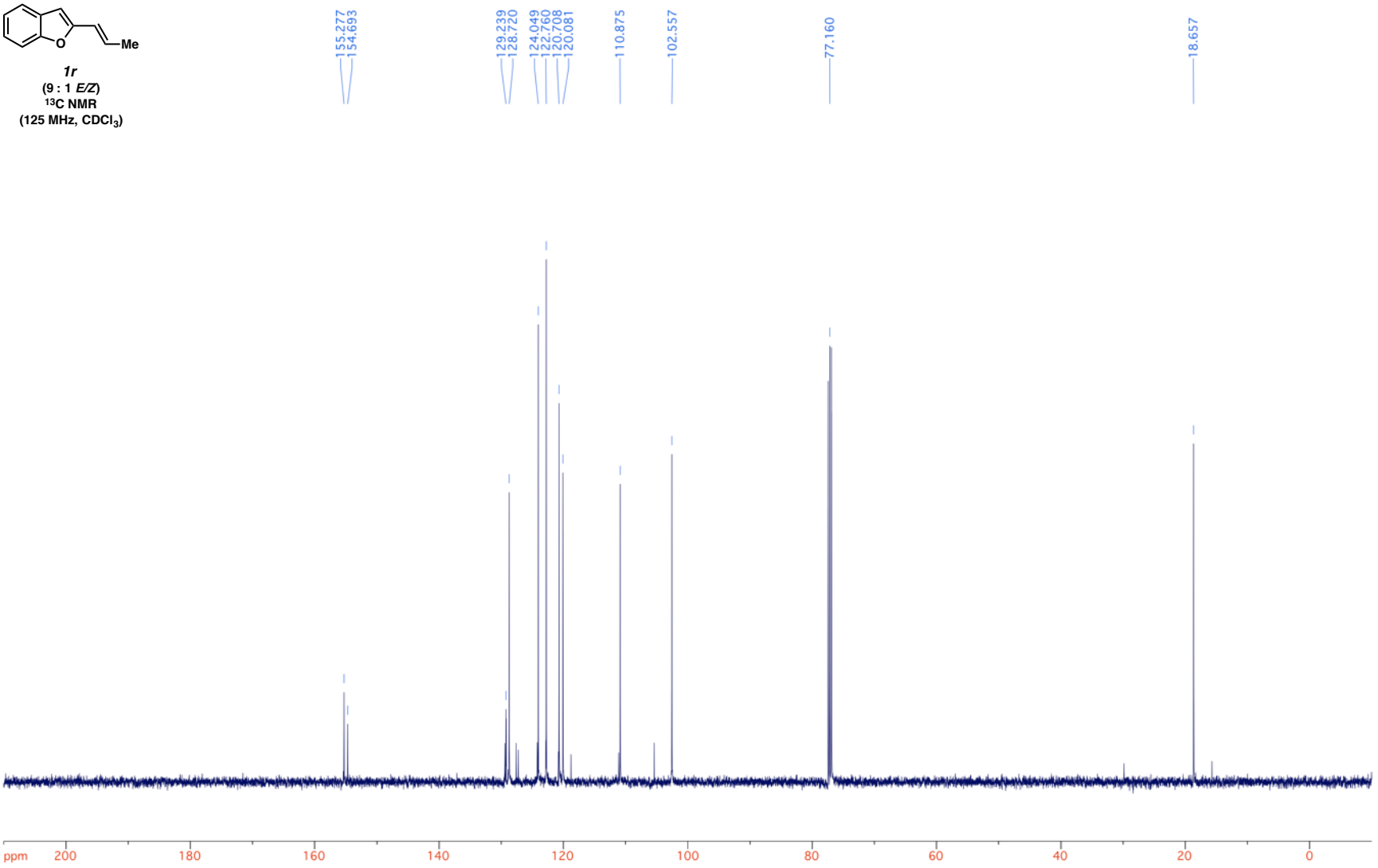
8
^{13}C NMR
(100 MHz, $CDCl_3$)



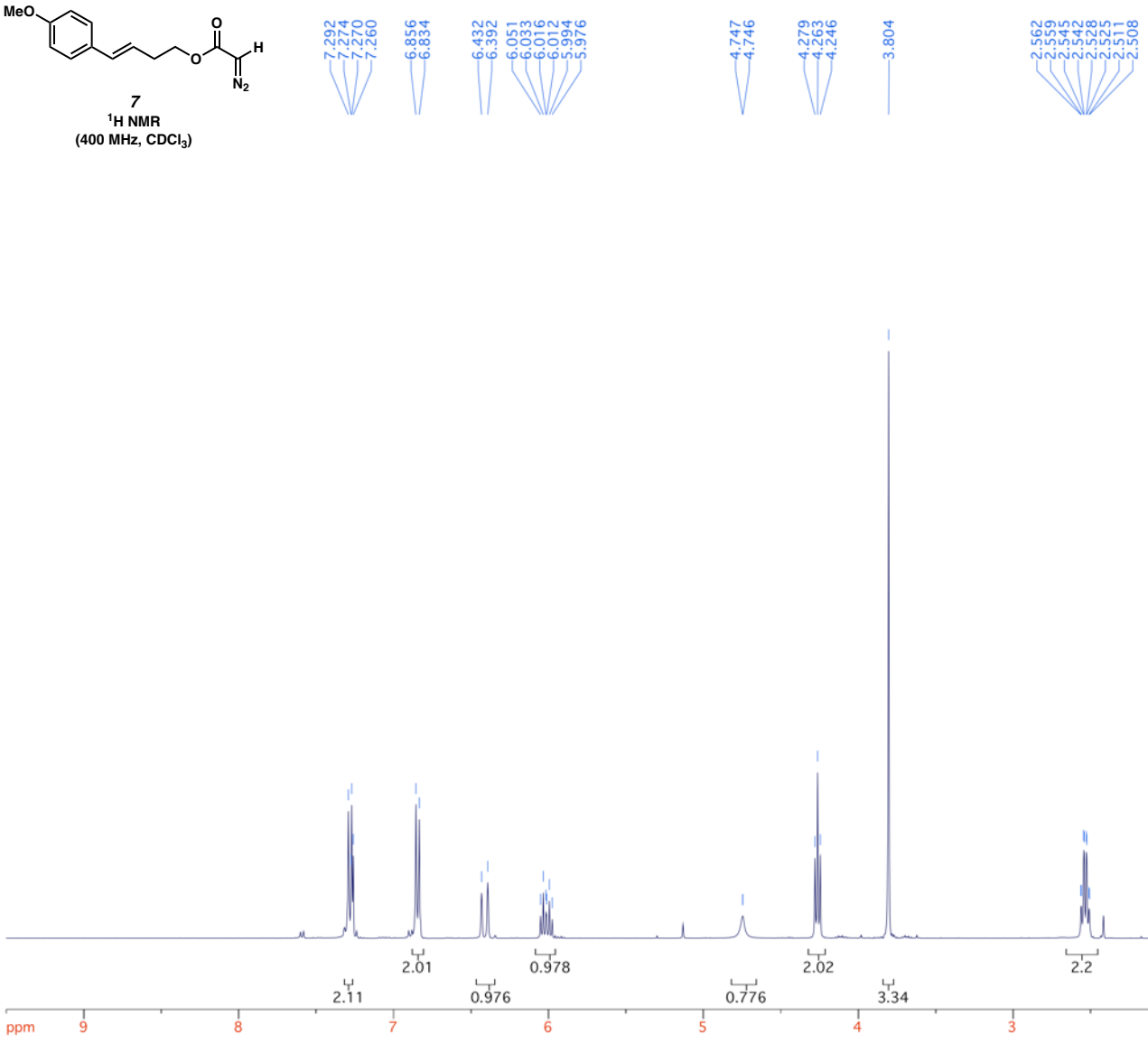
1r
(9 : 1 *E/Z*)
^{1}H NMR
(400 MHz, $CDCl_3$)

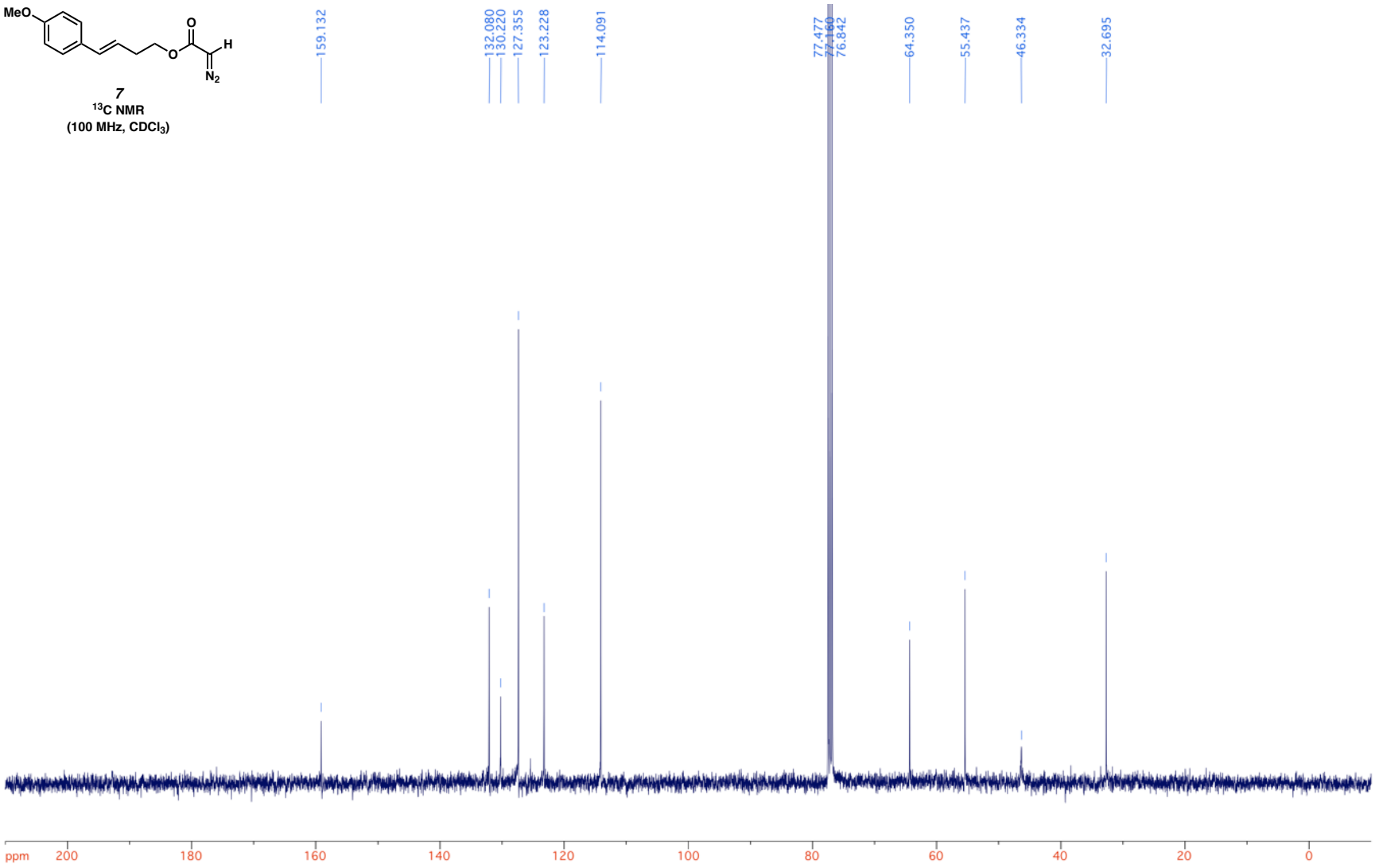






1r
(9 : 1 *E/Z*)
^{13}C NMR
(125 MHz, $CDCl_3$)


MeO
O
O
H
N2
7
1H NMR
(400 MHz, CDCl3)
7.292
7.274
7.270
7.260
6.856
6.834
6.432
6.392
6.051
6.033
6.016
6.012
5.994
5.976
4.747
4.746
4.279
4.263
4.246
3.804
2.562
2.559
2.545
2.542
2.528
2.525
2.511
2.508
2.11
2.01
0.976
0.978
0.776
2.02
3.34
2.2
ppm
9
8
7
6
5
4
3
2
1
0


MeO
O
O
H
N2
7
13C NMR
(100 MHz, CDCl3)
159.132
132.080
130.220
127.355
123.228
114.091
77.477
77.160
76.842
64.350
55.437
46.334
32.695
ppm
200
180
160
140
120
100
80
60
40
20
0