Supplementary Information (SI) for Chemical Science.

SUPPLEMENTARY INFORMATION

Pulsed Electrolysis Enables Unexpected Lactonization of Bicyclobutane Carboxylic Acids

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1. General Information

^{1}H NMR and ^{13}C NMR were recorded on Bruker DRX-400 (400 MHz for ^{1}H and 100 MHz for ^{13}C NMR), Bruker Avance III 500 (500 MHz for for ^{1}H and 125 MHz for ^{13}C NMR), Bruker Avance III 600 (600 MHz for for ^{1}H and 150 MHz for ^{13}C NMR), Bruker Avance III 700 (700 MHz for for ^{1}H and 175 MHz for ^{13}C NMR) spectrometers at ambient temperature; the chemical shifts (δ) were measured in ppm with respect to the solvent (DMSO-d_6, ^{1}H: δ = 2.50 ppm, ^{13}C: δ = 39.52 ppm; CD_3CN, ^{1}H: δ = 1.94 ppm, ^{13}C: δ = 118.26 (Me-CN) ppm; $CDCl_3$, ^{1}H: δ = 7.26 ppm, ^{13}C: δ = 77.16 ppm; D_2O ^{1}H: δ = 4.79 ppm). Coupling constants (*J*) are given in Hertz. Splitting patterns of an apparent multiplets associated with an averaged coupling constants were designated as s (singlet), d (doublet), t (triplet), q (quartet), dd (doublet of doublets), dt (doublet of triplets), m (multiplet), app (apparent), and br (broadened). Dibromomethane was used as an internal standard for quantitative NMR studies. Raw NMR data were processed with MestReNova® software.

Cyclic voltammetry (CV) was performed on BioLogic Potentiostat SP-50, raw data were processed with EC-Lab® Express software. The same equipment and software were used to perform pulsed electrolysis. For reactions at constant direct current mode, Matsusada R4K36-0.1-L (230V) was used as a power supply.

Potentials of electrodes were externally measured with multimeter Handskit® DT-925A.

Single-crystal X-ray diffraction data were collected on a Bruker D8 Venture diffractometer. Data collection/reduction were performed with APEX2, and structure solution/refinement with SHELX within Olex2 software.

High resolution mass spectra were recorded on Bruker micro Time-of-Flight (TOF)-MS equipped with an ESI source.

Melting points were measured on Buchi Melting Point M-560.

To determine the purity of compounds **S1**, **1**, **2**, and **3**, Agilent 7890 gas chromatograph equipped with 5975C EI-MSD Triple-Axis Detector and HP5MS column was used.

All commercially available compounds were used as provided without further purification. Solvents for chromatography were HPLC grade. Anhydrous and degassed THF and MeCN were purchased from Sigma-Aldrich in Sure/Seal™ bottles, kept inside a glove box, and used as received.

Basic alumina for the column chromatography (60-325 mesh, Brockmann activity I) was purchased from Fisher Scientific.

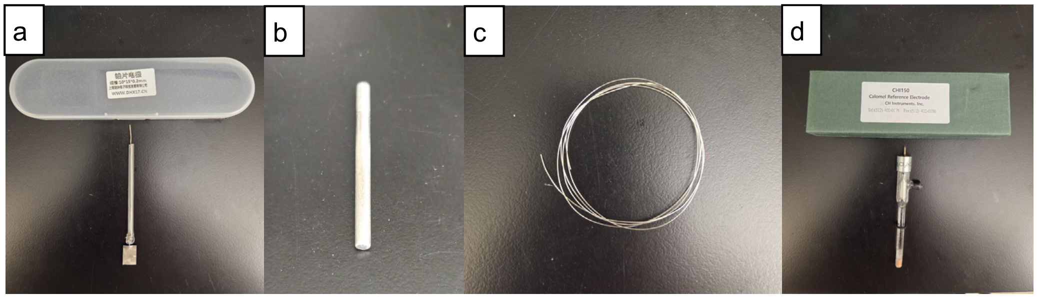


Figure S1. Electrodes used for this study: (a) platinum plate (H×W×D 10×15×0.2 mm, immersed area 200 mm^2), used as an anode and a cathode; (b) stainless steel rod (Ø 4 mm, L 50 mm, immersed area 150 mm^2), use as a cathode; (c) platinum wire (Ø 0.3 mm, L 60 mm, immersed area 19 mm^2), used as an anode; (d) saturated calomel electrode (KCl_{sat}), used as a reference electrode.

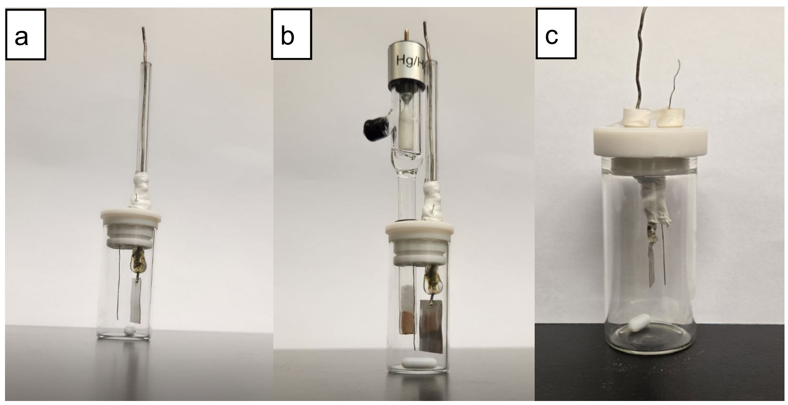


Figure S2. Cells used in this study: (a) two-electrode cell used during optimization studies (Ø 19 mm, L 38 mm; spin bar Ø 3 mm, L 10 mm; distance from the spin bar to electrodes = 2 mm; distance between electrodes = 5 mm); (b) three-electrode cell used during optimization studies, for analytical purposes and for performing preparative experiments at 0.2 and 0.5 mmol scales (Ø 19 mm, L 38 mm; spin bar Ø 3 mm, L 10 mm; distance from the spin bar to electrodes = 2 mm; distance between cathode and anode = 5 mm, distance between reference electrode and anode as working electrode = 3 mm); (c) two-electrode cell used for 1.0 mmol scale reactions (Ø 27 mm, L 60 mm; spin bar Ø 3 mm, L 10 mm; distance from the spin bar to electrodes = 15 mm; distance between cathode and anode = 5 mm).

Cleaning and Preparation of Platinum Electrodes

Before every experiment, platinum electrodes were soaked in Piranha solution (H_2SO_4 conc./H_2O_2 30%, 3:1) for 15 minutes followed by sonication for 15 minutes. ***WARNING! Extreme care should be taken when working with Piranha solution! Highly corrosive! Strong oxidizer! Causes severe burns! Risk of fire or explosion on contact with organic materials! All surfaces that come into contact with Piranha solution must be dry and free of visible organic residues. Wear appropriate PPE at all times. Refer to your institution's SOP before use.*** After, the electrodes were washed with deionized water, soaked in acetonitrile for 60 minutes, rinsed with acetone, thoroughly wiped and dried under vacuum for 15 minutes.

2. SYNTHESIS OF STARTING MATERIALS

In order to access key starting materials – bicyclo[1.1.0]butane-1-carboxylic acids **1** – a set of bicyclo[1.1.0]butane-1-carboxylic acid methyl esters **S1** were synthesized following published protocols (**S1a,c,e-g,k,n,p,q,s**;[1] **S1b,i,l,t;**[2] **S1d,h,j**;[3] **S1m**;[4] **S1o**;[5] **S1r**[6]) All obtained esters **S1** are known compounds; physicochemical data of the samples matched the previously reported values.

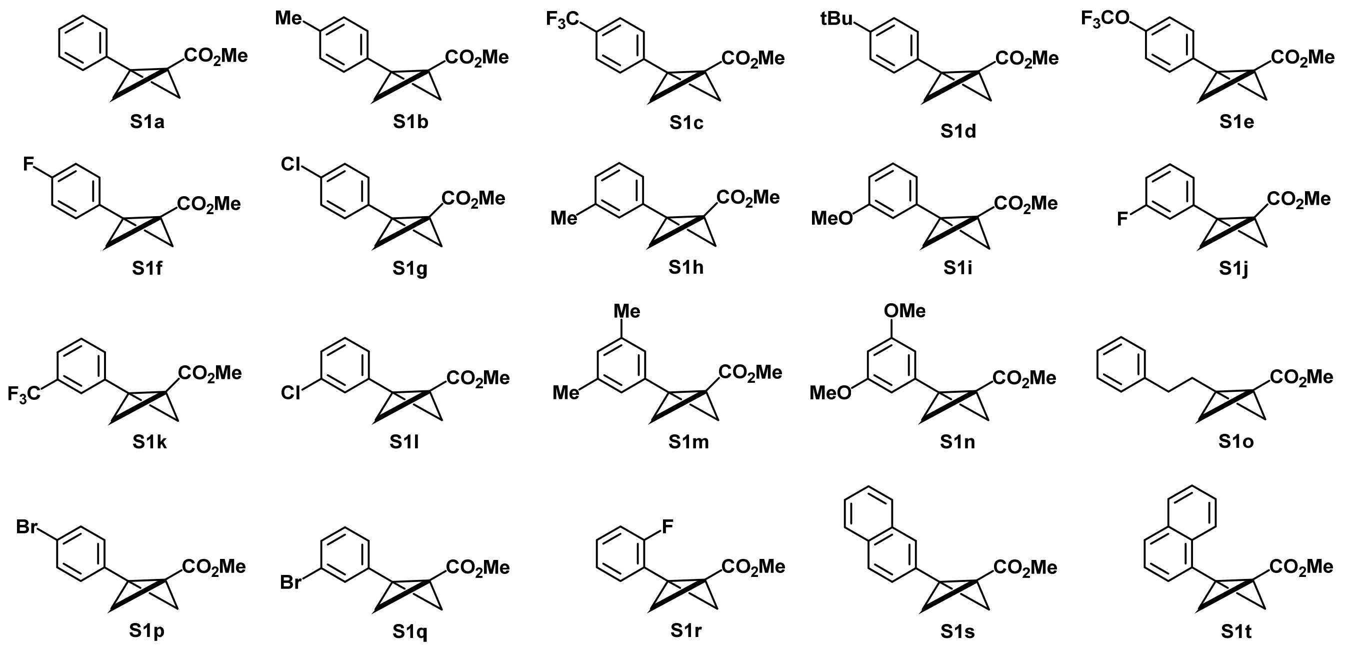
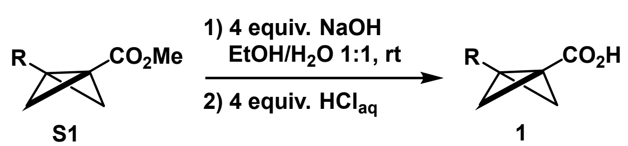


Figure S3. List of BCB esters used as precursors for key starting materials **1**

General protocol for the synthesis of acids **1**

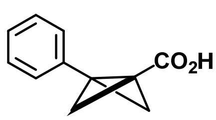


Ester **S1** (4 mmol) was dissolved in EtOH (5 mL) at ambient temperature followed by addition of water (5 mL). To the formed suspension, NaOH (16 mmol, 640 mg, 4 equiv.) was added in one portion, and the reaction mixture was stirred at ambient temperature until full conversion of ester **S1**, which can be monitored by TLC (from 4 to 20 h). Upon full conversion of ester **S1**, the reaction mixture was diluted with water (100 mL), which resulted in the formation of a clear solution. *If the* *solution was cloudy, it was washed with ethyl acetate (20 mL), and the organic phase was discarded. It is important that the reaction mixture after dilution remain clear, as any water-insoluble material may complicate the subsequent isolation of acid **1**.* The diluted reaction mixture was carefully acidified by portionwise addition of 0.5 M HCl (32 mL, 1 equiv. relative to the NaOH added) with vigorous stirring. Acid **1**, which was formed as a white solid upon acidification, was collected by filtration, washed with water (100 mL), air-dried, and then dried under vacuum at ambient temperature. Analysis by GC-MS and NMR confirmed that acids **1** were of high purity, so no further purification was performed.

Note 1. Nearly all acids **1** are moderately stable and could be stored in air at ambient temperature for at least two weeks without noticeable degradation.

Note 2. Acid **1o** was quickly decomposing; therefore is was stored as a sodium salt obtained following the general protocol while using 1 equiv. NaOH (instead of 4 equiv.); the salt was obtained by concentrating the reaction mixture to dryness and was converted to acid **1o** immediately before use.

Note 3. Acids **1** are hygroscopic; therefore they should be further dried before use if exposed to air.



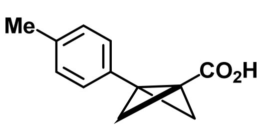
3-phenylbicyclo[1.1.0]butane-1-carboxylic acid (1a)[7]

White solid, 495 mg (71%); m.p. = 143 – 144 °C.

^{1}H NMR (500 MHz, DMSO-d$_6$): δ = 11.84 (br s, 1H), 7.37 – 7.31 (m. 4H), 7.26 – 7.23 (m, 1H), 2.87 (s, 2H), 1.55 (s, 2H) ppm.

^{13}C {^{1}H} NMR (125 MHz, DMSO-d$_6$): δ = 170.2, 133.9, 128.4 (2C), 126.7, 125.9 (2C), 35.3 (2C), 31.7, 23.2 ppm.

HRMS (ESI-TOF) *m/z* calcd for $C_{11}H_{11}O_2$ $[M+H]^+$ 175.0768, found 175.0754.



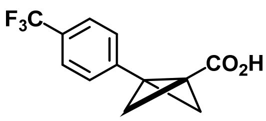
3-(*p*-tolyl)bicyclo[1.1.0]butane-1-carboxylic acid (1b)

White solid, 400 mg (53%); m.p. = 106 – 108 °C.

^{1}H NMR (400 MHz, DMSO-d$_6$): δ = 11.80 (br s, 1H), 7.24 (app d AA'BB', ^3J = 7.9 Hz, 2H), 7.13 (app d AA'BB', ^3J = 7.9 Hz, 2H), 2.84 (s, 2H), 2.27 (s, 3H), 1.52 (s, 2H) ppm.

^{13}C {^{1}H} NMR (100 MHz, DMSO-d$_6$): δ = 170.3, 136.1, 130.7, 129.1 (2C), 125.9 (2C), 35.3 (2C), 31.9, 22.9, 20.7 ppm.

HRMS (ESI-TOF) *m/z* calcd for $C_{12}H_{13}O_2$ $[M+H]^+$ 189.0910, found 189.0916.



3-(4-(trifluoromethyl)phenyl)bicyclo[1.1.0]butane-1-carboxylic acid (1c)

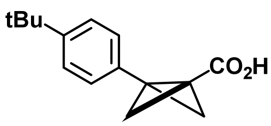
White solid, 726 mg (75%); m.p. = 153 – 155 °C.

^{1}H NMR (400 MHz, DMSO-d$_6$): δ = 12.03 (br s, 1H), 7.68 (app d AA'BB', ^3J = 8.2 Hz, 2H), 7.56 (app d AA'BB', ^3J = 8.2 Hz, 2H), 2.97 (s, 2H), 1.65 (s, 2H) ppm.

^{13}C {^{1}H} NMR (100 MHz, DMSO-d$_6$): δ = 169.8, 139.5, 127.1 (q, $^2J_{CF}$ = 32 Hz), 126.6 (2C), 125.3 (q, $^3J_{CF}$ = 4 Hz, 2C), 124.4 (q, $^1J_{CF}$ = 271 Hz), 35.8 (2C), 30.6, 24.8 ppm.

^{19}F {H} NMR (375 MHz, DMSO-d$_6$): δ = -60.83 ppm.

HRMS (ESI-TOF) *m/z* calcd for $C_{12}H_9F_3NaO_2$ [M+Na]$^+$ 265.0447, found 265.0442.



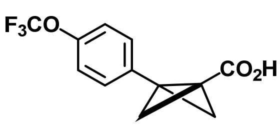
3-(4-(tert-butyl)phenyl)bicyclo[1.1.0]butane-1-carboxylic acid (1d)

White solid, 718 mg (78%); m.p. = 122 – 124 °C.

^{1}H NMR (400 MHz, DMSO-d$_6$): δ = 11.83 (br s, 1H), 7.35 (app d AA'BB', ^3J = 8.4 Hz, 2H), 7.27 (app d AA'BB', ^3J = 8.4 Hz, 2H), 2.84 (s, 2H), 1.53 (s, 2H), 1.26 (s, 9H) ppm.

^{13}C {^{1}H} NMR (100 MHz, DMSO-d$_6$): δ = 170.5, 149.2, 130.7, 125.8 (2C), 125.3 (2C), 35.3 (2C), 34.3, 31.9, 31.1 (3C), 22.8 ppm.

HRMS (ESI-TOF) *m/z* calcd for $C_{15}H_{19}O_2$ [M+H]$^+$ 231.1380, found 231.1366.



3-(4-(trifluoromethoxy)phenyl)bicyclo[1.1.0]butane-1-carboxylic acid (1e)

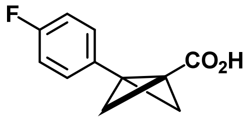
White solid, 877 mg (85%); m.p. = 142 – 144 °C.

^{1}H NMR (400 MHz, DMSO-d$_6$): δ = 12.00 (br s, 1H), 7.47 (app d AA'BB', ^3J = 8.5 Hz, 2H), 7.32 (app d AA'BB', ^3J = 8.5 Hz, 2H), 2.90 (s, 2H), 1.60 (s, 2H) ppm.

^{13}C {^{1}H} NMR (100 MHz, DMSO-d$_6$): δ = 170.1, 147.2, 133.8, 127.8 (2C), 121.1 (2C), 120.1 (q, $^1J_{CF}$ = 254 Hz), 35.7 (2C), 30.7, 23.6 ppm.

^{19}F {H} NMR (375 MHz, DMSO-d$_6$): δ = -56.86 ppm.

HRMS (ESI-TOF) *m/z* calcd for $C_{12}H_{10}F_3O_3$ [M+H]$^+$ 259.0557, found 259.0559.



3-(4-fluorophenyl)bicyclo[1.1.0]butane-1-carboxylic acid (1f)

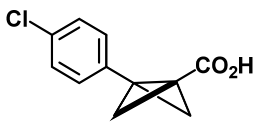
White solid, 629 mg (82%); m.p. = 141 – 143 °C.

^{1}H NMR (400 MHz, DMSO-d_6): δ = 11.9 (br s), 7.41 – 7.37 (m, 2H), 7.19 – 7.14 (m, 2H), 2.86 (s, 2H), 1.55 (s, 2H) ppm.

^{13}C {^{1}H} NMR (100 MHz, DMSO-d_6): δ = 170.3, 161.4 (d, $^1J_{CF}$ = 243 Hz), 130.2 (d, $^4J_{CF}$ = 3 Hz), 127.9 (d, $^3J_{CF}$ = 8 Hz, 2C), 115.4 (d, $^2J_{CF}$ = 22 Hz, 2C), 35.6 (2C), 31.2, 22.9 ppm.

^{19}F {H} NMR (375 MHz, DMSO-d_6): δ = -115.77 ppm.

HRMS (ESI-TOF) *m/z* calcd for $C_{11}H_{10}FO_2$ $[M+H]^+$ 193.0659, found 193.0649.



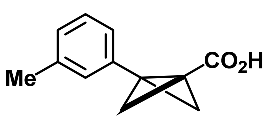
3-(4-chlorophenyl)bicyclo[1.1.0]butane-1-carboxylic acid (1g)

White solid, 656 mg (79%); m.p. = 133 – 133 °C.

^{1}H NMR (500 MHz, DMSO-d_6): δ = 11.96 (br s, 1H), 7.40 – 7.36 (m, 4H), 2.88 (s, 2H), 1.58 (s, 2H) ppm.

^{13}C {^{1}H} NMR (125 MHz, DMSO-d_6): δ = 170.1, 133.3, 131.4, 128.4 (2C), 127.7 2C), 35.6 (2C), 31.0, 23.7 ppm.

HRMS (ESI-TOF) *m/z* calcd for $C_{11}H_9{}^{35}ClNaO_2$ $[M+Na]^+$ 231.0183, found 231.0185.



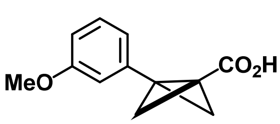
3-(m-tolyl)bicyclo[1.1.0]butane-1-carboxylic acid (1h)

White solid, 616 mg (82%); m.p. = 129 – 131 °C.

^{1}H NMR (500 MHz, DMSO-d_6): δ = 11.83 (br s, 1H), 7.23 – 7.13 (m, 3H), 7.07 – 7.05 (m, 1H), 2.85 (s, 2H), 2.29 (s, 3H), 1.53 (s, 2H) ppm.

^{13}C {^{1}H} NMR (125 MHz, DMSO-d_6): δ = 170.3, 137.6, 133.8, 128.3, 127.5, 126.5, 123.1, 35.3 (2C), 31.8, 23.1, 21.0 ppm.

HRMS (ESI-TOF) *m/z* calcd for $C_{12}H_{13}O_2$ $[M+H]^+$ 189.0910, found 189.0951.



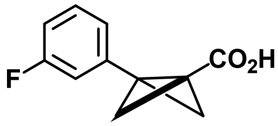
3-(3-methoxyphenyl)bicyclo[1.1.0]butane-1-carboxylic acid (1i)

White solid, 669 mg (82%); m.p. = 114 – 116 °C.

^{1}H NMR (400 MHz, DMSO-d_6): δ = 11.89 (br s, 1H), 7.24 (t, ^3J = 7.9 Hz, 1H), 6.93 – 6.81 (m, 3H), 3.74 (s, 3H), 2.86 (s, 2H), 1.53 (s, 2H) ppm.

^{13}C {^{1}H} NMR (100 MHz, DMSO-d_6): δ = 170.3, 159.4, 135.6, 129.6, 118.4, 122.2, 111.7, 55.1, 35.5 (2C), 31.7, 23.3 ppm.

HRMS (ESI-TOF) *m/z* calcd for $C_{12}H_{13}O_3$ $[M+H]^+$ 205.0859, found 205.0850.



3-(3-fluorophenyl)bicyclo[1.1.0]butane-1-carboxylic acid (1j)

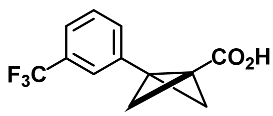
White solid, 598 mg (78%); m.p. = 162 – 164 °C.

^{1}H NMR (500 MHz, DMSO-d_6): δ = 11.97 (br s, 1H), 7.39 – 7.34 (m, 1H), 7.21 – 7.18 (m, 2H), 7.09 – 7.04 (m, 1H), 2.91 (s, 2H), 1.58 (, 2H) ppm.

^{13}C {^{1}H} NMR (125 MHz, DMSO-d_6): δ = 170.0, 162.3 (d, $^{1}J_{CF}$ = 243 Hz), 137.3 (d, $^{3}J_{CF}$ = 8 Hz), 130.4 (d, $^{3}J_{CF}$ = 9 Hz), 122.2 (d, $^{4}J_{CF}$ = 2 Hz), 113.5 (d, $^{3}J_{CF}$ = 21 Hz), 112.7 (d, $^{2}J_{CF}$ = 23 Hz), 35.7 (2C), 31.0 (d, $^{4}J_{CF}$ = 2 Hz), 24.0 ppm.

^{19}F {H} NMR (470 MHz, DMSO-d_6): δ = -113.42 ppm.

HRMS (ESI-TOF) *m/z* calcd for $C_{11}H_9FNaO_2$ $[M+Na]^+$ 215.0479, found 215.0471.



3-(3-(trifluoromethyl)phenyl)bicyclo[1.1.0]butane-1-carboxylic acid (1k)

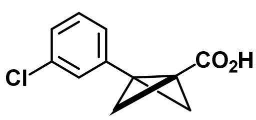
White solid, 774 mg (80%); m.p. = 127 – 128 °C.

^{1}H NMR (500 MHz, DMSO-d_6): δ = 12.02 (br s, 1H), 7.67 – 7.65 (m, 2H), 7.61 – 7.55 (m, 2H), 2.98 (s, 2H), 1.63 (s, 2H) ppm.

^{13}C {^{1}H} NMR (125 MHz, DMSO-d_6): δ = 170.0, 136.1, 130.0, 129.6, 129.4 (q, $^{2}J_{CF}$ = 33 Hz), 124.2 (q, $^{1}J_{CF}$ = 273 Hz), 123.3 (q, $^{3}J_{CF}$ = 4 Hz), 122.2 (q, $^{3}J_{CF}$ = 4 Hz), 35.8 (2C), 30.7, 24.2 ppm.

^{19}F {H} NMR (470 MHz, DMSO-d_6): δ = -61.14 ppm.

HRMS (ESI-TOF) *m/z* calcd for $C_{12}H_{10}F_3O_2$ $[M+Na]^+$ 243.0627, found 243.0619.



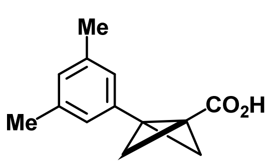
3-(3-chlorophenyl)bicyclo[1.1.0]butane-1-carboxylic acid (1l)

White solid, 649 (78%); m.p. = 154 – 156 °C.

^{1}H NMR (400 MHz, DMSO-d_6): δ = 12.00 (br s, 1H), 7.41 – 7.29 (m, 4H), 2.92 (s, 2H), 1.58 (s, 2H) ppm.

^{13}C {^{1}H} NMR (100 MHz, DMSO-d_6): δ = 170.0, 137.0, 133.3, 130.3, 126.7, 125.5, 124.8, 35.7 (2C), 30.8, 24.0 ppm.

HRMS (ESI-TOF) *m/z* calcd for $C_{11}H_9{}^{35}ClNaO_2$ $[M+Na]^+$ 231.0183, found 231.0180.



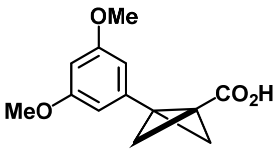
3-(3,5-dimethylphenyl)bicyclo[1.1.0]butane-1-carboxylic acid (1m)

White solid, 574 mg (71%); m.p. = 114 – 116 °C.

^{1}H NMR (400 MHz, DMSO-d_6): δ = 11.83 (br s, 1H), 6.96 (s, 2H), 6.84 (s, 1H), 2.83 (s, 2H), 2.24 (s, 6H), 1.50 (s, 2H) ppm.

^{13}C {^{1}H} NMR (100 MHz, DMSO-d_6): δ = 170.4, 137.4 (2C), 133.7, 128.5, 123.7 (2C), 35.2 (2C), 31.9, 23.1, 20.9 (2C) ppm.

HRMS (ESI-TOF) *m/z* calcd for $C_{13}H_{15}O_2$ $[M+H]^+$ 203.1067, found 203.1074.



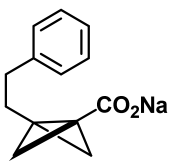
3-(3,5-dimethoxyphenyl)bicyclo[1.1.0]butane-1-carboxylic acid (1n)

White solid, 711 mg (76%); m.p. = 119 – 121 °C.

^{1}H NMR (400 MHz, DMSO-d$_6$): δ = 11.88 (br s, 1H), 6.47 (s, 2H), 6.39 (s, 1H), 3.73 (s, 6H), 2.83 (s, 2H), 1.51 (s, 2H) ppm.

^{13}C {^{1}H} NMR (100 MHz, DMSO-d$_6$): δ = 170.2, 160.5 (2C), 136.4, 104.2 (2C), 98.7, 55.2 (2C), 35.6 (2C), 31.7, 23.2 ppm.

HRMS (ESI-TOF) *m/z* calcd for $C_{13}H_{15}O_4$ $[M+H]^+$ 235.0965, found 235.0954.



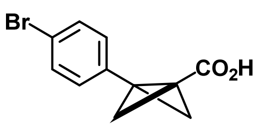
sodium 3-phenethylbicyclo[1.1.0]butane-1-carboxylate (1o)

Waxy solid, 887 mg (99%); m.p. was not clearly determined – visual phase transition starts at ≈230 °C.

^{1}H NMR (600 MHz, D$_2$O, water suppression, presaturation at 4.8 ppm): δ = 7.23 – 7.20 (m, 2H), 7.17 – 7.16 (m, 2H), 7.13 – 7.11 (m, 1H), 2.70 (t, ^3J = 7.8 Hz, 2H), 2.01 (t, ^3J = 7.8 Hz, 2H), 1.91 (s, 2H), 0.93 (s, 2H) ppm.

^{13}C {^{1}H} NMR (100 MHz, D$_2$O): δ = 180.9, 142.1, 128.7 (2C), 128.5 (2C), 126.0, 36.6 (2C), 34.0, 29.0, 27.5, 14.7 ppm.

HRMS (ESI-TOF) *m/z* calcd for $C_{13}H_{13}Na_2O_2$ $[M+Na]^+$ 247.0705, found 247.0719.



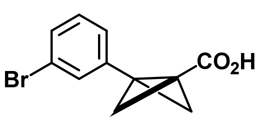
3-(4-bromophenyl)bicyclo[1.1.0]butane-1-carboxylic acid (1p)

White solid, 796 mg (79%); m.p. = 141 – 143 °C.

^{1}H NMR (400 MHz, DMSO-d$_6$): δ = 11.96 (br s, 1H), 7.51 (app d AA'BB', ^3J = 8.0 Hz, 2H), 7.31 (app d AA'BB', ^3J = 8.0 Hz, 2H), 2.88 (s, 2H), 1.57 (2, 2H) ppm.

^{13}C {^{1}H} NMR (100 MHz, DMSO-d$_6$): δ = 170.0, 133.8, 131.3 (2C), 128.0 (2C), 119.8, 35.6 (2C), 31.0, 23.7 ppm.

HRMS (ESI-TOF) *m/z* calcd for $C_{11}H_{10}{}^{79}BrO_2$ $[M+H]^+$ 252.9859, found 252.9863.



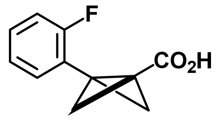
3-(3-bromophenyl)bicyclo[1.1.0]butane-1-carboxylic acid (1q)

White solid, 826 mg (82%); m.p. = 129 – 131 °C.

^{1}H NMR (500 MHz, DMSO-d$_6$): δ = 12.00 (br s, 1H), 7.54 (s, 1H), 7.44 (d, ^3J = 7.9 Hz, 1H), 7.36 (d, ^3J = 7.4 Hz, 1H), 7.26 (t, ^3J = 7.3 Hz, 1H), 2.91 (s, 2H), 1.57 (s, 2H) ppm.

^{13}C {^{1}H} NMR (125 MHz, DMSO-d$_6$): δ = 170.0, 137.2, 130.5, 129.5, 128.3, 125.1, 121.9, 35.7 (2C), 30.7, 24.0 ppm.

HRMS (ESI-TOF) *m/z* calcd for $C_{11}H_{10}{}^{79}BrO_2$ $[M+H]^+$ 252.9859, found 252.9855.



3-(2-fluorophenyl)bicyclo[1.1.0]butane-1-carboxylic acid (1r)

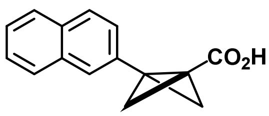
White solid, 553 mg (72%), m.p. = 128 – 130 °C.

^{1}H NMR (400 MHz, DMSO-d_6): δ = 12.14 (br s, 1H), 7.39 – 7.35 (m, 1H), 7.31 – 7.26 (m, 1H), 7.20 – 7.14 (m, 2H), 2.82 (s, 2H), 1.60 (s, 2H) ppm.

^{13}C {^{1}H} NMR (100 MHz, DMSO-d_6): δ = 170.4, 161.2 (d, $^{1}J_{CF}$ = 247 Hz), 129.3 (d, J_{CF} = 3 Hz), 128.7 (d, J_{CF} = 8 Hz), 124.6 (d, J_{CF} = 3 Hz), 121.3 (d, $^{2}J_{CF}$ = 12 Hz), 115.9 (d, $^{2}J_{CF}$ = 22 Hz), 37.2 (2C), 26.7, 21.7 ppm.

^{19}F {H} NMR (375 MHz, DMSO-d_6): δ = -116.30 ppm.

HRMS (ESI-TOF) *m/z* calcd for $C_{11}H_{10}FO_2$ [M+H]$^+$ 193.0659, found 193.0658.



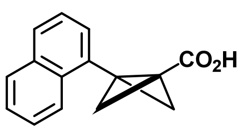
3-(naphthalen-2-yl)bicyclo[1.1.0]butane-1-carboxylic acid (1s)

White solid, 573 mg (64%); m.p. = 122 – 124 °C.

^{1}H NMR (400 MHz, DMSO-d_6): δ = 11.87 (br s, 1H), 7.93 – 7.86 (m, 4H), 7.53 – 7.45 (m, 3H), 3.03 (s, 2H), 1.65 (s, 2H) ppm.

^{13}C {^{1}H} NMR (100 MHz, DMSO-d_6): δ = 170.3, 133.0, 131.9, 131.7, .128.0, 127.6, 127.3, 126.5, 125.7, 125.0, 123.7, 35.6 (2C), 32.2, 23.7 ppm.

HRMS (ESI-TOF) *m/z* calcd for $C_{15}H_{12}NaO_2$ [M+Na]$^+$ 247.0730, found 247.0726.



3-(naphthalen-1-yl)bicyclo[1.1.0]butane-1-carboxylic acid (1t)

White solid, 528 mg (59%); m.p. = 123 – 125 °C.

^{1}H NMR (500 MHz, DMSO-d_6): δ = 12.35 (br s, 1H), 8.34 (app d, ^{3}J = 7.2 Hz, 1H), 7.96 (app d, ^{3}J = 7.2 Hz, 1H), 7.86 (app d, ^{3}J = 7.2 Hz, 1H), 7.59 – 7.56 (m, 2 H), 7.46 (app t, ^{3}J = 7.7 Hz, 1H), 7.35 (app d, ^{3}J = 7.2 Hz, 1H), 2.64 (s, 2H), 1.83 (s, 2H) ppm.

^{13}C {^{1}H} NMR (125 MHz, DMSO-d_6): δ = 171.2, 133.58, 133.53, 130.9, 128.6, 127.5, 126.4, 126.1, 125.4, 124.5, 122.3, 39.1 (2C), 28.1, 20.8 ppm.

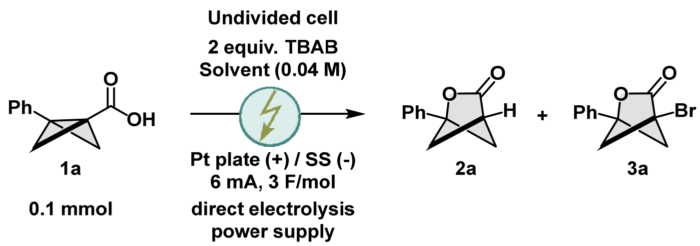
HRMS (ESI-TOF) *m/z* calcd for $C_{15}H_{12}NaO_2$ [M+Na]$^+$ 247.0730, found 247.0727.

3 SELECTED RESULTS OF OPTIMIZATION STUDIES

General Comments

During optimization, we encountered poor reproducibility for direct electrolysis using a power supply. Reproducibility issues affected both the yield of **2a** and the **2a**/**3a** ratio. Tables S1–S5 summarize the direct-electrolysis data, reporting the highest yields observed across consecutive runs. The dispersion was too high to provide a statistically meaningful range of yields. By contrast, pulsed electrolysis afforded consistent results for both the yield of **2a** and the **2a**/**3a** ratio (Table S6). The largest deviation was ±10%.

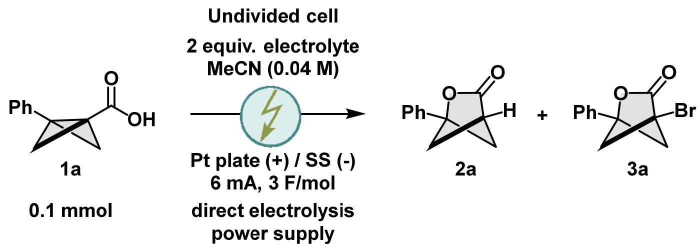
Table S1. Screening of solvents.



Entry[1]	Solvent	NMR Yield of 2a, %[2]	NMR Yield of 3a, %[3]
1	MeCN	55	–
2	DMA	trace	–
3	AcOH	trace	–
4	EtOH	trace	–
5	$PhCF_3$	40	–
6	DCM	trace	–
7	DCE	trace	–
8	THF	trace	–

[1] 0.1 mmol scale, ambient temperature, spin rate 600 rpm, SS = stainless steel
[2] CH_2Br_2 was used as an internal standard
[3] Yield of **3a** was not quantified at this stage

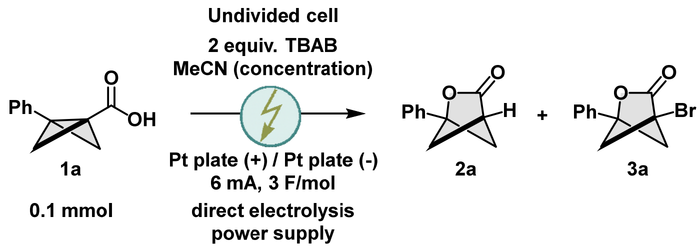
Table S2. Screening of electrolytes.



Entry[1]	Electrolyte	Time, h[2]	NMR Yield of 2a, %[3]	NMR Yield of 3a, %[3]
1	TBAB	3.5	55	10
2	TBACl	3.5	Not detected[4]	-
3	TBAI	3.5	40	-
4	Pr_4NBr	3.5	50	10
5	TBA PF_6	1	Not detected[4]	-
6	Li PF_6	3	Not detected[4]	-
7	LiBr	2	Not detected[4]	Not detected[4]
8	Bu_4PBr	3.5	Not detected[4]	Not detected[4]

[1] 0.1 mmol scale, ambient temperature, spin rate 600 rpm, SS stands for stainless steel
[2] Full conversion
[3] CH_2Br_2 was used as an internal standard
[4] Decomposition of the reaction mixture

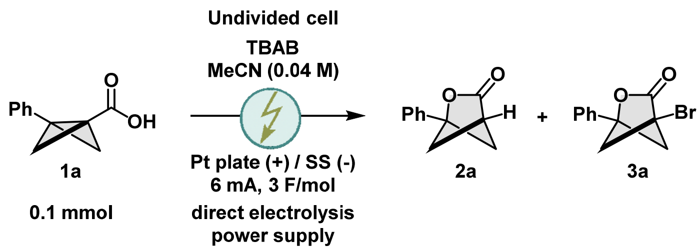
Table S3. Different concentrations of **1a**.



Entry[1]	Concentration	NMR Yield of 2a, %[2]	NMR Yield of 3a, %[2]
1	0.04	55	15
2	0.04[3]	0	0
3	0.01	15	20
4	0.007	10	30

[1] 0.1 mmol scale, ambient temperature, spin rate 600 rpm
[2] CH_2Br_2 was used as an internal standard
[3] No stirring

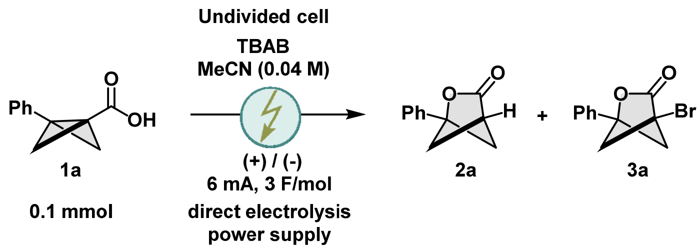
Table S4. 1a-to-electrolyte ratios.



Entry[1]	1a/TBAB Ratio	NMR Yield of 2a, %[2]	NMR Yield of 3a, %[2]
1	1:2	55	15
2	1:3	50	15
3	1:4	35	25
4	1:1	50	15
5	1:0.75	25	10
6	1:0.5	15	15
7	1/0	0[3]	0
8	1:2[4]	15	n.d.
9	1:2[5]	15	20
10	1:2[6]	20	n.d.

[1] 0.1 mmol scale, ambient temperature, spin rate 600 rpm, SS = stainless steel
[2] CH_2Br_2 was used as an internal standard
[3] Conversion of **1a** = 10%
[4] Concentration of **1a** = 0.02 M
[5] Concentration of **1a** = 0.08 M
[6] Thermostated at 60° C

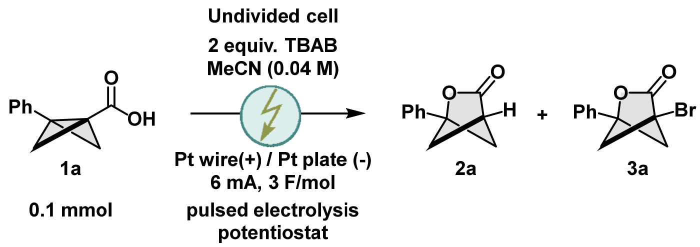
Table S5. Different Current Densities.



Entry[1]	Anode	Cathode	NMR Yield of 2a, %[2]	NMR Yield of 3a, %[2]
1	Pt plate[3]	Pt plate[3]	55	15
2	Pt plate[3]	SS rod[4]	55	15
3	Pt wire[5]	Pt plate[3]	75 (72)[6]	10
4	Pt wire[5]	SS rod[4]	75 (71)	10
5	Pt plate[3]	Pt wire[5]	0	15

[1] 0.1 mmol scale, ambient temperature, spin rate 600 rpm
[2] CH_2Br_2 was used as an internal standard
[3] j =3.0 mA/cm^2
[4] j =4.3 mA/cm^2
[5] j =31.6 mA/cm^2
[6] Isolated yield

Table S6. Screening Parameters for Pulsed Electrolysis.



Entry[1]	Program (pulse, s / resting time, s)	NMR Yield of 2a, %[2]	NMR Yield of 3a, %[2]
1	10/10	70	5
2	10/20	65	5
3	10/30	65	5
4	20/0.5	35	20
5	20/20	65	5
6	20/30	80 (78)[3]	5
7	20/30[4] 2 F/mol	65	5
8	20/30[5] 4 F/mol	80	5
9	20/30[6]	50	40
10	5/20	35	20
11	2/3	70	10

[1] 0.1 mmol scale, ambient temperature, spin rate 600 rpm
[2] CH_2Br_2 was used as an internal standard
[3] Isolated yield, 0.2 mmol scale, concentration of **1a** = 0.08 M
[4] Total charge = 2 F/mol
[5] Total charge = 4 F/mol
[6] Total charge = 1.5 F/mol

Synthetic procedure designed for optimization studies (Table S5, Entry 1)

Reaction vial (Figure S2, a) was charged with acid **1a** (17.5 mg, 0.1 mmol), TBAB (64 mg, 0.2 mmol, 2 equiv.), MeCN (2.5 mL) and a spin bar inside a glove box (argon). Platinum plates were mounted (Figure S1, a) and spin rate was set to 600 rpm. Direct current of 6 mA was passed through the media for 80 min (3 F/mol) using a power supply. Upon completion, reaction vial was removed from the glove box, the reaction mixture was transferred into a round-bottom flask, concentrated to dryness, further dried under vacuum. The residue was dissolved in $CDCl_3$ (around 0.5 mL), dibromomethatne (7 μL, 1 equiv.) was added, the mixture was transferred to the NMR tube and analyzed by ^{1}H NMR.

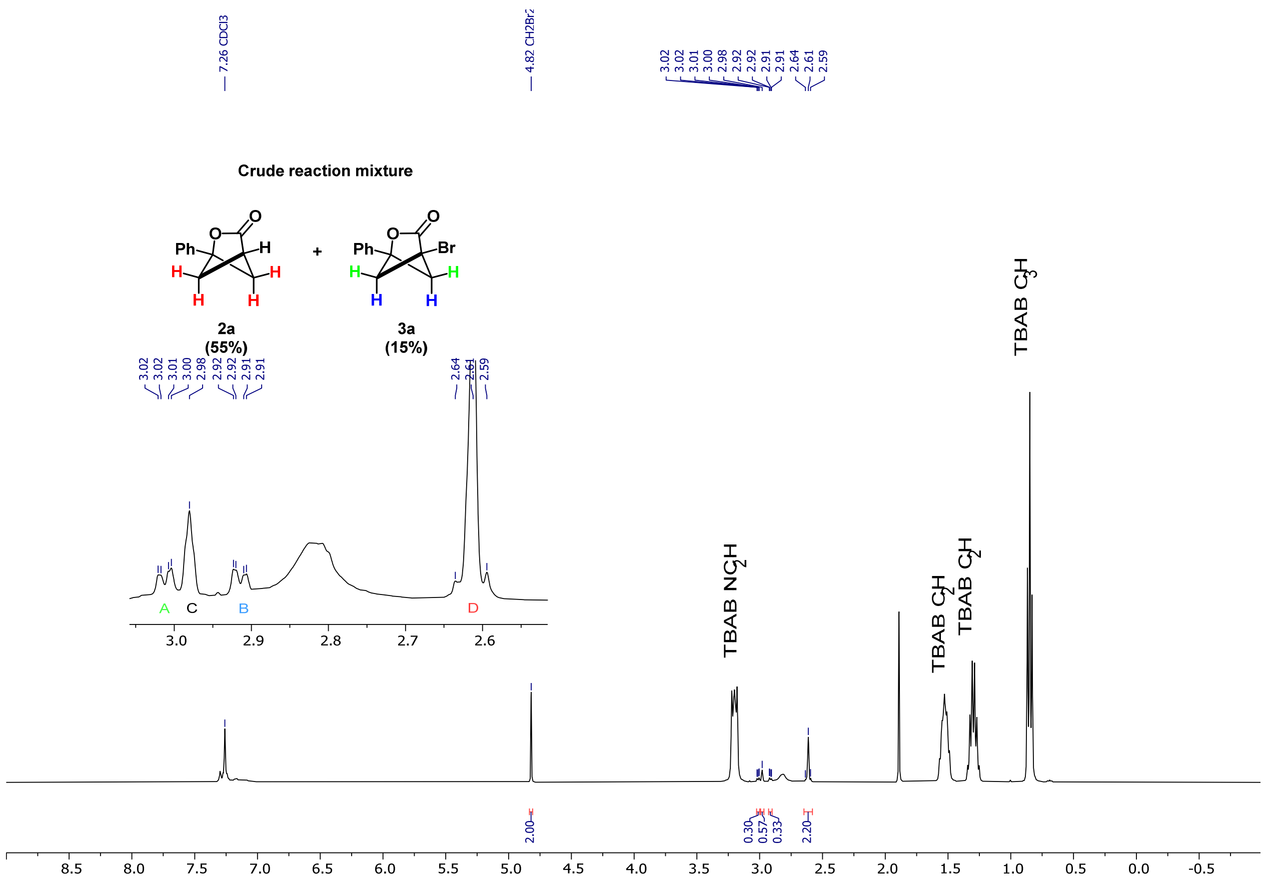


Figure S4. ^{1}H NMR of crude reaction mixture with CH_2Br_2 as an internal standard (Table 5, Entry 1), 400 MHz, $CDCl_3$.

Synthetic procedure for the analytical scale experiment under optimized conditions (Table S6, Entry 6)

Reaction vial (Figure S2, a) was charged with acid **1a** (17.5 mg, 0.1 mmol), TBAB (64 mg, 0.2 mmol, 2 equiv.), MeCN (2.5 mL) and a spin bar inside a glove box (argon). Platinum wire (anode, Figure 1, c) and platinum plate (cathode, Figure S1, a) were mounted, and spin rate was set to 600 rpm. Pulsed electrolysis was performed using a potentiostat and a suitable software for programming. The following sequence was performed: 20 s pulse of direct current, 6 mA, followed by 30 s resting period, 240 cycles (200 min, 3 F/mol). Upon completion, reaction vial was removed from the glove box, the reaction mixture was transferred into a round-bottom flask, concentrated to dryness, further dried under vacuum. The residue was dissolved in $CDCl_3$ (around 0.5 mL), dibromomethatne (7 μL, 1 equiv.) was added, the mixture was transferred to the NMR tube and analyzed by ^{1}H NMR.

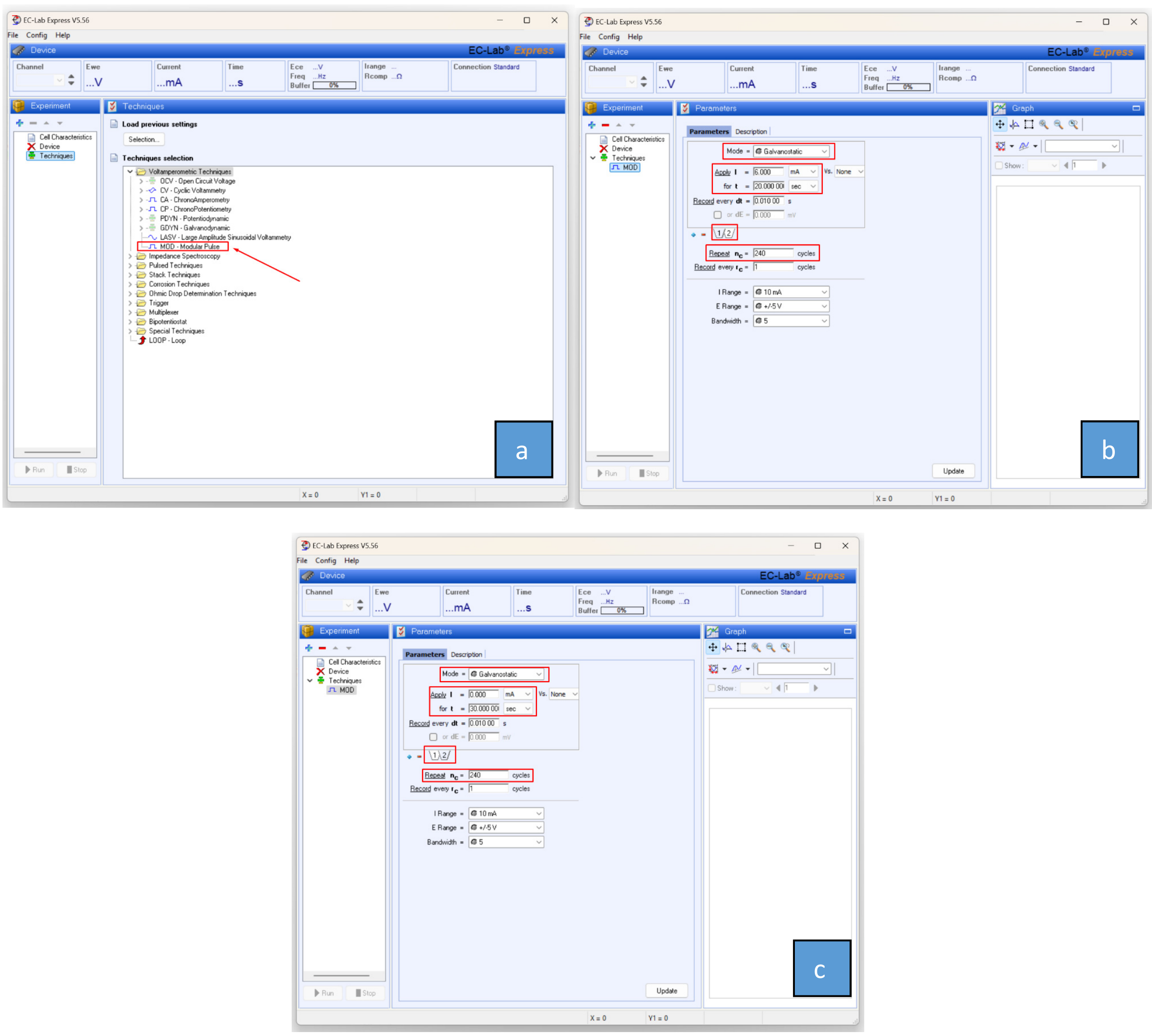
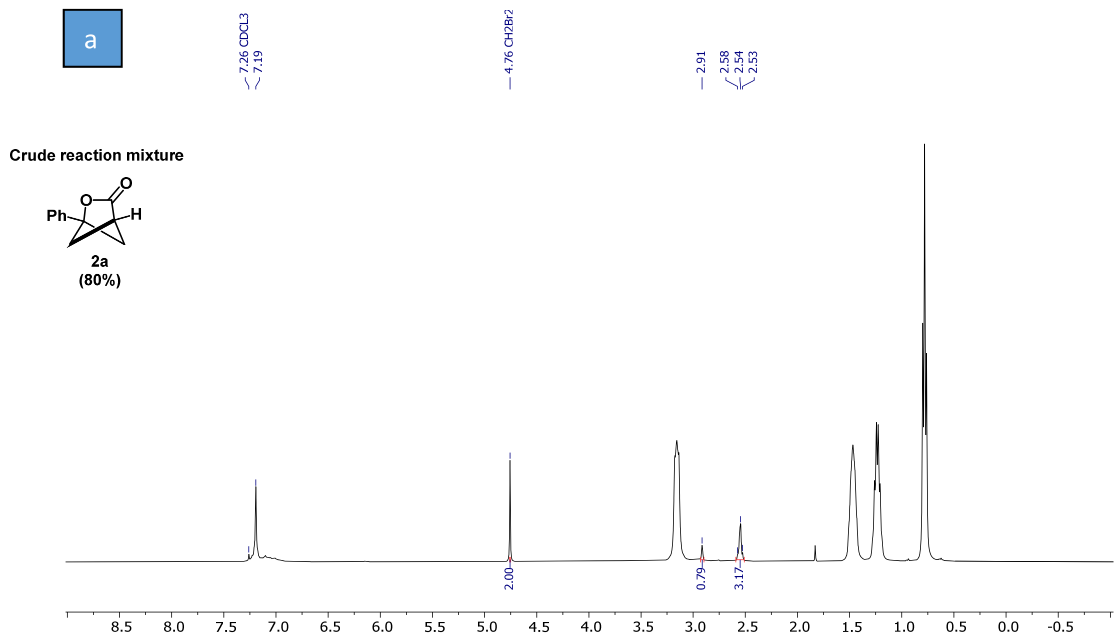


Figure S5. Instructions for programming the pulse sequence using EC-Lab® Express software: (a) create Modular Pulse experiment; (b) set the parameters for electrolysis step; (c) set the parameters for the resting period.



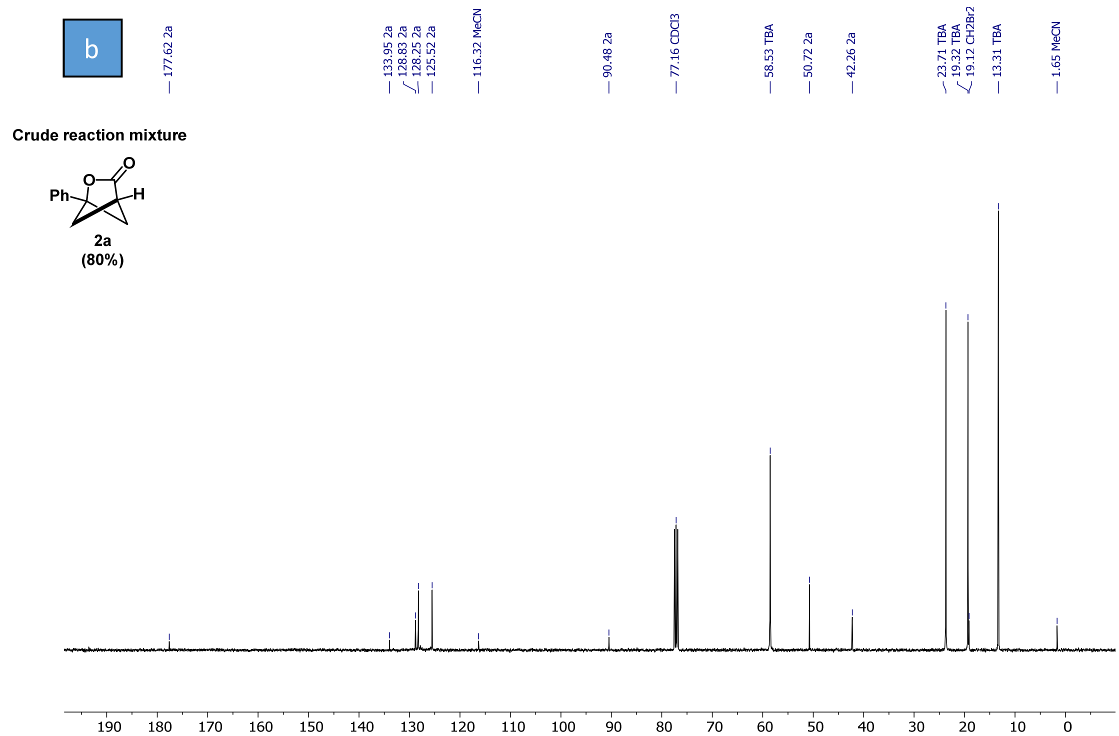
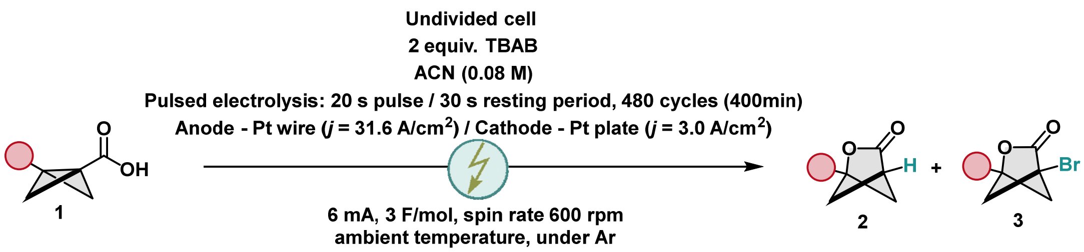


Figure S6. ^1H (a) and ^{13}C (b) NMR spectra of crude reaction mixture with CH_2Br_2 as an internal standard (Table 6, Entry 6), 400 and 100 MHz respectively, $CDCl_3$.

4. SYNTHESIS OF PRODUCTS 2 AND 3

General protocol for the synthesis of products 2 and 3



Reaction vial (Figure S2, a) was charged with acid **1** (0.1 mmol), TBAB (64 mg, 0.2 mmol, 2 equiv.), MeCN (2.5 mL) and a spin bar inside a glove box (argon). Platinum wire (anode, Figure 1, c) and platinum plate (cathode, Figure S1, a) were mounted, and spin rate was set to 600 rpm. Pulsed electrolysis was performed using a potentiostat and a suitable software for programming. The following sequence was performed: 20 s pulse of direct current, 6 mA, followed by 30 s resting period, 480 cycles (400 min, 3 F/mol, see Figure S5 for instructions). Upon completion, the reaction vial was removed from the glove box, the reaction mixture was transferred into a round-bottom flask and dry-loaded onto Celite (about 700 mg). Compounds **2** and **3** were purified by column chromatography (basic aluminum oxide, n-hexane/ethyl acetate gradient from 20:1 to 10:1).

Note 1. Compounds **2** and **3** are sensitive to acids. Basic alumina proved to be the sorbent of choice for column chromatography; however, purification should be performed as quickly as possible to minimize degradation. For purification, short columns constructed from 10-mL plastic syringes, packed from the bottom with a cotton plug followed by ca. 4 mL of basic alumina, were used.

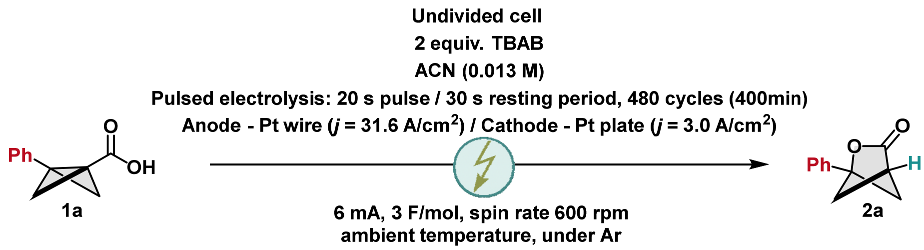
Note 2. Different brands of basic alumina showed varying performance. In our experience, basic alumina from Fisher Scientific (60-325 mesh, Brockmann activity I) gave the most consistent results.

Note 3. Compounds **2** and **3** are barely detectable on TLC: they are weakly UV-active and give only very faint spots after staining with common reagents such as acidic $KMnO_4$, *p*-anisaldehyde, iodine fumes, or cerium-ammonium molybdate. At the same time, compounds **2** and **3** can be detected by GC-MS, which can be used to study the eluate.

Note 4. Generally, compounds **3** are less polar and elute first with an eluent of n-hexane/ethyl acetate from 20:1 to 15:1.

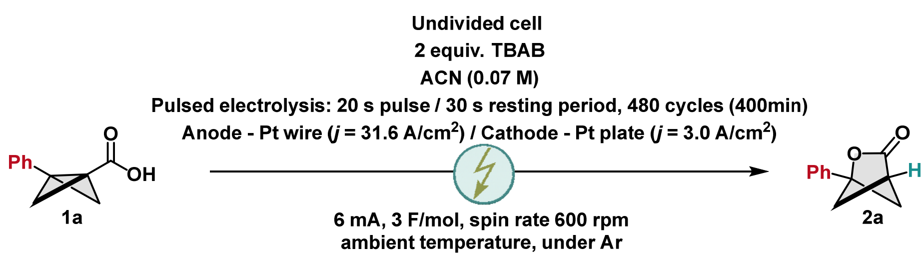
Note 5. Compounds **2** and **3** are moderately stable in $CDCl_3$. When a clean sample of a compound was dissolved in $CDCl_3$ and analyzed by NMR within 60 min, early signs of degradation were already detectable.

*Synthesis of product **2a** at 0.5 mmol scale*

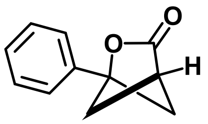


Reaction vial (Figure S2, a) was charged with acid **1a** (88 mg, 0.5 mmol), TBAB (322 mg, 1 mmol, 2 equiv.), MeCN (4 mL) and a spin bar inside a glove box (argon). Platinum wire (anode, Figure 1, c) and platinum plate (cathode, Figure S1, a) were mounted, and spin rate was set to 600 rpm. Pulsed electrolysis was performed using a potentiostat and a suitable software for programming. The following sequence was performed: 20 s pulse of direct current, 6 mA, followed by 30 s resting period, 1200 cycles (1000 min, 3 F/mol, see Figure S5 for instructions). Upon completion, the reaction vial was removed from the glove box, the reaction mixture was transferred into a round-bottom flask and dry-loaded onto Celite (about 700 mg). Compound **2a** was purified by column chromatography (basic aluminum oxide, n-hexane/ethyl acetate gradient from 15:1 to 10:1).

*Synthesis of product **2a** at 1.0 mmol scale*



Reaction vial (Figure S2, c) was charged with acid **1a** (174 mg, 1.0 mmol), TBAB (644 mg, 2 mmol, 2 equiv.), MeCN (15 mL) and a spin bar inside a glove box (argon). Platinum wire (anode, Figure 1, c) and platinum plate (cathode, Figure S1, a) were mounted, and spin rate was set to 600 rpm. Pulsed electrolysis was performed using a potentiostat and a suitable software for programming. The following sequence was performed: 20 s pulse of direct current, 6 mA, followed by 30 s resting period, 2400 cycles (2000 min, 3 F/mol, see Figure S5 for instructions). Upon completion,the reaction vial was removed from the glove box, the reaction mixture was transferred into a round-bottom flask and dry-loaded onto Celite (about 1 g). Compound **2a** was purified by column chromatography (basic aluminum oxide, n-hexane/ethyl acetate gradient from 15:1 to 10:1).



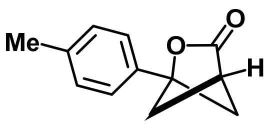
1-phenyl-2-oxabicyclo[2.1.1]hexan-3-one (2a)

Colorless oil, 27 mg (78%) – 0.2 mmol scale; 57 mg (65%) – 0.5 mmol scale; 117 mg (67%) – 1.0 mmol scale; compound **1a** could be crystallized from n-hexane/ethyl acetate (transparent needles) or n-hexane/THF/ (transparent plates), m.p. = 59 – 61 °C (n-hexane/ethyl acetate).

^{1}H NMR (500 MHz, CD_3CN): δ = 7.45 – 7.41 (m, 5H), 3.05 (t, ^{3}J = 2.5 Hz, 1H), 2.77 – 2.71 (m, 4H) ppm.

^{13}C {^{1}H} NMR (125 MHz, CD_3CN): δ = 178.9, 135.9, 130.0, 129.5 (2C), 126.9 (2C), 91.5, 51.5 (2C), 43.4 ppm.

HRMS (ESI-TOF) *m/z* calcd for $C_{11}H_{10}NaO_2$ $[M+Na]^+$ 197.0573, found 197,0573.



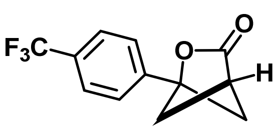
1-(p-tolyl)-2-oxabicyclo[2.1.1]hexan-3-one (2b)

Colorless oil, 28 mg (76%).

^{1}H NMR (400 MHz, CD_3CN): δ = 7.32 (app d AA’BB’, ^{3}J = 7.9 Hz, 2H), 7.25 (app d AA’BB’, ^{3}J = 7.9 Hz, 2H), 3.04 – 3.02 (m, 1H), 2.74 – 2.69 (m, 4H), 2.35 (s, 3H) ppm.

^{13}C {^{1}H} NMR (125 MHz, CD_3CN): δ = 179.0, 140.2, 133.1, 130.1 (2C), 127.0 (2C), 91.6, 51.5 (2C), 43.5, 21.2 ppm.

HRMS (ESI-TOF) *m/z* calcd for $C_{12}H_{13}O_2$ $[M+H]^+$ 189.0910, found 189.0915.



1-(4-(trifluoromethyl)phenyl)-2-oxabicyclo[2.1.1]hexan-3-one (2c)

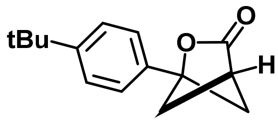
Colorless oil, 34 mg (71%).

^{1}H NMR (500 MHz, CD_3CN): δ = 7.76 (app d AA’BB’, ^{3}J = 8.4 Hz, 2H), 7.63 (app d AA’BB’, ^{3}J = 8.4 Hz, 2H), 3.09 (t, ^{3}J = 2.7 Hz, 1H), 2.86 – 2.81 (m, 2H), 2.76 – 2.71 (m. 2H) ppm.

^{13}C {^{1}H} NMR (125 MHz, CD_3CN): δ = 178. 3, 140.3, 131.3 (q, $^{2}J_{CF}$ = 32 Hz), 127.8 (2C), 126.6 (q, $^{3}J_{CF}$ = 4 Hz, 2C), 125.2 (q, $^{1}J_{CF}$ = 272 Hz), 90.5, 51.8 (2C), 43.6 ppm.

^{19}F {^{1}H} NMR (470 MHz, CD_3CN): δ = -63.3 ppm.

HRMS (ESI-TOF) *m/z* calcd for $C_{12}H_9F_3NaO_2$ $[M+Na]^+$ 265.0447, found 265.0455.



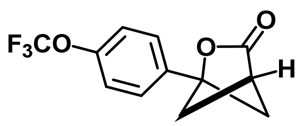
1-(4-(tert-butyl)phenyl)-2-oxabicyclo[2.1.1]hexan-3-one (2d)

Colorless oil, 38 mg (82%).

^{1}H NMR (500 MHz, CD_3CN): δ = 7.49 (app d AA'BB', ^3J = 7.9 Hz, 2H), 7.36 (app d AA'BB', ^3J = 7.9 Hz, 2H), 3.03 (t, ^3J = 2.6 Hz, 1H), 2.57 – 2.70 (m, 4H), 1.31 (s, 9H) ppm.

^{13}C {^{1}H} NMR (125 MHz, CD_3CN): δ = 179.0, 153.3, 133.2, 126.8 (2C), 126.5 (2C), 91.5, 51.5 (2C), 43.5, 35.3, 31.4 (3C) ppm.

HRMS (ESI-TOF) *m/z* calcd for $C_{15}H_{18}NaO_2$ [M+Na]$^+$ 253.1199, found 253.1209.



1-(4-(trifluoromethoxy)phenyl)-2-oxabicyclo[2.1.1]hexan-3-one (2e)

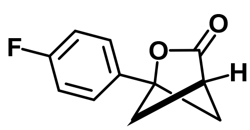
Colorless oil, 38 mg (74%).

^{1}H NMR (500 MHz, CD_3CN): δ = 7.55 – 7.53 (m, 2H), 7.37 – 7.35 (m, 2H), 3.06 (t, J^3 = 2.7 Hz, 1H), 2.82 – 2.79 (m, 2H), 2.77 – 2.70 (m, 2H) ppm.

^{13}C {^{1}H} NMR (125 MHz, CD_3CN): δ = 178.5, 150.3, 135.3, 129.1 (2C), 122.2 (2C), 121.5 (q, J^1_{CF} = 256 Hz), 90.6, 51.7 (2C), 43.5 ppm.

^{19}F {^{1}H} NMR (470 MHz, CD_3CN): δ = -58.6 ppm.

HRMS (ESI-TOF) *m/z* calcd for $C_{12}H_9F_3NaO_3$ [M+Na]$^+$ 281.0396, found 281.0406.



1-(4-fluorophenyl)-2-oxabicyclo[2.1.1]hexan-3-one (2f)

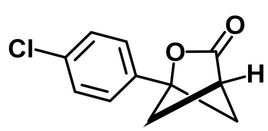
Colorless oil, 28 mg (73%).

^{1}H NMR (500 MHz, CD_3CN): δ = 7.49 – 7.45 (m, 2H), 7.20 – 7.16 (m, 2H), 3.05 (t, J^3 = 2.7 Hz, 1H), 2.77 – 2.71 (m, 4H) ppm.

^{13}C {^{1}H} NMR (125 MHz, CD_3CN): δ = 178.7, 163.9 (d, $^1J_{CF}$ = 246 Hz), 132.2 (d, $^4J_{CF}$ = 3 Hz), 129.3 (d, $^3J_{CF}$ = 9 Hz, 2C), 116.4 (d, $^2J_{CF}$ = 22 Hz, 2C), 90.9, 51.5 (2C), 43.5 ppm.

^{19}F {^{1}H} NMR (375 MHz, CD_3CN): δ = -114.1 ppm.

HRMS (ESI-TOF) *m/z* calcd for $C_{11}H_9FNaO_2$ [M+Na]$^+$ 215.0479, found 215.0487.



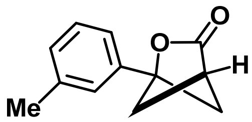
1-(4-chlorophenyl)-2-oxabicyclo[2.1.1]hexan-3-one (2g)

Colorless oil, 29 mg (69%).

^{1}H NMR (500 MHz, CD_3CN): δ = 7.47 – 7.41 (m, 4H), 3.05 (t, ^3J = 2.7 Hz, 1H), 2.80 – 2.73 (m, 2H), 2.71 – 2.68 (m, 2H) ppm.

^{13}C {^{1}H} NMR (125 MHz, CD_3CN): δ = 178.6, 135.4, 134.9, 129.7 (2C), 128.8 (2C), 90.7, 51.6 (2C), 43.5 ppm.

HRMS (ESI-TOF) *m/z* calcd for $C_{11}H_9{}^{35}ClNaO_2$ [M+Na]$^+$ 231.0183, found 231.0190.



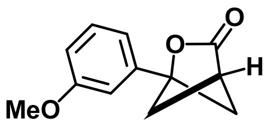
1-(m-tolyl)-2-oxabicyclo[2.1.1]hexan-3-one (2h)

Colorless oil, 28 mg (76%).

^{1}H NMR (500 MHz, CD_3CN): δ = 7.34 – 7.22 (m, 4H), 3.04-3.02 (m, 1H), 2.75 – 2.70 (m, 4H), 2.36 (s, 3H) ppm.

^{13}C {^{1}H} NMR (125 MHz, CD_3CN): δ = 178.9, 139.5, 136.0, 130.7, 129.5, 127.6, 124.0, 91.6, 51.5 (2C), 43.5, 21.3 ppm.

HRMS (ESI-TOF) *m/z* calcd for $C_{12}H_{12}NaO_2$ $[M+Na]^+$ 211.0730, found 211.0737.



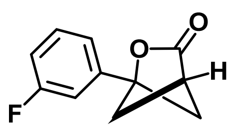
1-(3-methoxyphenyl)-2-oxabicyclo[2.1.1]hexan-3-one (2i)

Colorless oil, 30 mg (73%).

^{1}H NMR (500 MHz, CD_3CN): δ = 7.35 (t, ^3J = 7.6 Hz, 1H), 7.02 – 6.96 (m, 3H), 3.81 (s, 3H), 3.05 – 3.04 (m, 1H), 2.77 – 2.70 (m, 4H) ppm.

^{13}C {^{1}H} NMR (125 MHz, CD_3CN): δ = 178.8, 160.8, 137.5, 130.8, 119.1. 115.6. 112.5, 91.3, 56.0, 51.6 (2C), 43.5 ppm.

HRMS (ESI-TOF) *m/z* calcd for $C_{12}H_{12}NaO_3$ $[M+Na]^+$ 227.0679, found 227.0683.



1-(3-fluorophenyl)-2-oxabicyclo[2.1.1]hexan-3-one (2j)

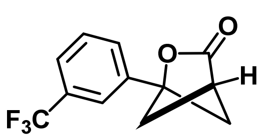
Colorless oil, 27 mg, (71%).

^{1}H NMR (500 MHz, CD_3CN): δ = 7.47 – 7.46 (m, 1H), 7.28 – 7.26 (m, 1H), 7.22 – 7.14 (m, 2H), 3.06 (t, ^3J = 2.7 Hz, 1H), 2.82 – 2.76 (m, 2H), 2.73 – 2.69 (m, 2H) ppm.

^{13}C {^{1}H} NMR (125 MHz, CD_3CN): δ = 178.4, 163.6 (d, $^1J_{CF}$ = 245 Hz), 138.6 (d, $^3J_{CF}$ = 8 Hz), 131.6 (d, $^3J_{CF}$ = 8 Hz), 123.0 (d, $^4J_{CF}$ = 3 Hz), 116.8 (d, $^2J_{CF}$ = 21 Hz), 114.1 (d, $^2J_{CF}$ = 23 Hz), 90.6, 51.7 (2C), 43.5 ppm.

^{19}F {^{1}H} NMR (470 MHz, CD_3CN): δ = -114.2 ppm.

HRMS (ESI-TOF) *m/z* calcd for $C_{11}H_{10}FO_2$ $[M+H]^+$ 193.0659, found 193.0661.



1-(3-(trifluoromethyl)phenyl)-2-oxabicyclo[2.1.1]hexan-3-one (2k)

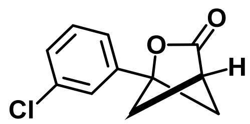
Colorless oil, 35 mg (73%).

^{1}H NMR (600 MHz, CD_3CN): δ = 7.76 – 7.71 (m, 3H), 7.66 – 7.63 (m, 1H), 3.09 (t, ^3J = 2.7 Hz, 1H), 2.86 – 2.82 (m, 2H), 2.77 – 2.73 (m, 2H) ppm.

^{13}C {^{1}H} NMR (150 MHz, CD_3CN): δ = 178.3, 137.2, 131.2 (q, $^2J_{CF}$ = 33 Hz), 131.0, 130.7, 126.8 (q, $^3J_{CF}$ = 4 Hz), 125.2 (q, $^1J_{CF}$ = 272 Hz), 123.9 (q, $^3J_{CF}$ = 4 Hz), 90.5, 51.7 (2C), 43.5 ppm.

^{19}F {^{1}H} NMR (470 MHz, CD_3CN): δ = -63.2 ppm.

HRMS (ESI-TOF) *m/z* calcd for $C_{12}H_9F_3NaO_2$ $[M+Na]^+$ 265.0447, found 265.0458.



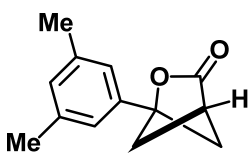
1-(3-chlorophenyl)-2-oxabicyclo[2.1.1]hexan-3-one (2l)

Colorless oil, 19 mg (45%).

^{1}H NMR (500 MHz, CD_3CN): δ = 7.48 – 7.47 (m, 1H), 7.44 – 7.43 (m, 2H), 7.40 – 7.37 (m, 1H), 3.06 (t, ^3J = 2.7 Hz, 1H), 2.81 – 2.76 (m, 2H), 2.73 – 2.69 (m, 2H) ppm.

^{13}C {^{1}H} NMR (125 MHz, CD_3CN): δ = 178.4, 138.2, 135.0, 131.3, 130.0, 127.1, 125.6, 90.5, 51.7 (2C), 43.5 ppm.

HRMS (ESI-TOF) *m/z* calcd for $C_{11}H_{10}{}^{79}ClO_2$ [M+H]$^+$ 209.0364, found 209.0370.



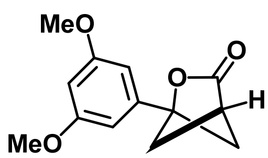
1-(3,5-dimethylphenyl)-2-oxabicyclo[2.1.1]hexan-3-one (2m)

Colorless oil, 30 mg (75%).

^{1}H NMR (400 MHz, CD_3CN): δ = 7.06 (s, 3H), 3.03 – 3.02 (m, 1H), 2.73 – 2.68 (m, 4H), 2.32 (s, 6H) ppm.

^{13}C {^{1}H} NMR (100 MHz, CD_3CN): δ = 179.0, 139.4, 135.9, 131.5, 124.7 (3C), 91.6, 51.5 (2C), 43.5, 21.2 (2C) ppm.

HRMS (ESI-TOF) *m/z* calcd for $C_{13}H_{14}NaO_2$ [M+Na]$^+$ 225.0886, found 225.0889.



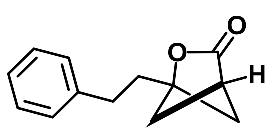
1-(3,5-dimethoxyphenyl)-2-oxabicyclo[2.1.1]hexan-3-one (2n)

Colorless oil, 32 mg (68%).

^{1}H NMR (600 MHz, CD_3CN): δ = 6.57 (d, ^4J = 2.3 Hz, 2H), 6.51 (t, ^4J = 2.3 Hz, 1H), 3.79 (s, 6H), 3.03 (t, ^3J = 2.7 Hz, 1H), 2.77 – 2.73 (m, 2H), 2.71 – 2.67 (m, 2H) ppm.

^{13}C {^{1}H} NMR (150 MHz, CD_3CN): δ = 178.8, 162.1 (2C), 138.3, 105.0 (2C), 101.6, 91.3, 56.1 (2C), 51.6 (2C), 43.4 ppm.

HRMS (ESI-TOF) *m/z* calcd for $C_{13}H_{14}NaO_4$ [M+Na]$^+$ 257.0784, found 257.0788.



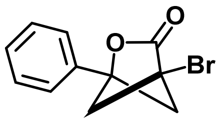
1-phenethyl-2-oxabicyclo[2.1.1]hexan-3-one (2o)

Colorless oil, 29 mg (71%).

^{1}H NMR (500 MHz, CD_3CN): δ = 7.33 – 7.21 (m, 5H), 2.90 – 2.89 (m, 1H), 2.77 – 2.74 (m, 2H), 2.38 – 2.35 (m, 2H), 2.32 – 2.88 (m, 2H), 2.16 – 2.13 (m, ^3J = 7.9 Hz, 2H) ppm.

^{13}C {^{1}H} NMR (125 MHz, CD_3CN): δ = 179.6, 142.4, 129.37 (2C), 129.25 (2C), 127.0, 92.5, 50.1, 43.7, 33.7, 31.0 ppm.

HRMS (ESI-TOF) *m/z* calcd for $C_{13}H_{14}NaO_2$ [M+Na]$^+$ 225.0886, found 225.0888.



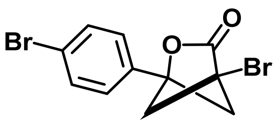
4-bromo-1-phenyl-2-oxabicyclo[2.1.1]hexan-3-one (3a)

White solid; the yield of **3a** did not exceed 5% under standard reaction conditions, the data were acquired using a combined sample of compound **3a**; compound **3a** can be crystallized from n-hexane/ethyl acetate (transparent colorless prisms); m.p. = 79 – 81 °C (n-hexane/ethyl acetate).

^{1}H NMR (500 MHz, CD_3CN): δ = 7.48 – 7.43 (m, 5H), 3.23 – 3.19 (m, 2H), 3.15 – 3.10 (m, 2H) ppm.

^{13}C {^{1}H} NMR (125 MHz, CD_3CN): δ = 173.2, 134.2, 130.7, 129.8 (2C), 127.1 (2C), 88.9, 58.9 (2C), 50.4 ppm.

HRMS (ESI-TOF) *m/z* calcd for $C_{11}H_9O_2$ $[M\text{-}Br]^+$ 173.0597, found 173.0595.



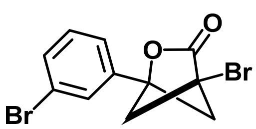
4-bromo-1-(4-bromophenyl)-2-oxabicyclo[2.1.1]hexan-3-one (3b)

Colorless oil, 44 mg (68%).

^{1}H NMR (400 MHz, CD_3CN): δ = 7.63 (app d AA'BB', ^3J = 7.8 Hz, 2H), 7.35 (app d AA'BB', ^3J = 7.8 Hz, 2H), 3.22 – 3.09 (m, 4H) ppm.

^{13}C {^{1}H} NMR (125 MHz, CD_3CN): δ = 172.9, 133.5,132.9 (2C), 129.1 (2C), 124.3, 88.2, 59.0, 50.2 ppm.

HRMS (ESI-TOF) *m/z* calcd for $C_{11}H_8{}^{79}BrO_2$ $[M\text{-}Br]^+$ 250.9702, found 250.9705.



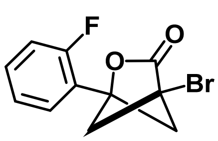
4-bromo-1-(3-bromophenyl)-2-oxabicyclo[2.1.1]hexan-3-one (3c)

Colorless oil, 47 mg (71%).

^{1}H NMR (400 MHz, CD_3CN): δ = 7.63 – 7.61 (m, 2H), 7.46 – 7.37 (m, 2H), 3.22 – 3.11 (m, 4H) ppm.

^{13}C {^{1}H} NMR (100 MHz, CD_3CN): δ = 172.8, 136.6, 133.6, 131.8, 130.2, 126.1, 123.2, 87.8, 59.1 (2C), 50.1 ppm.

HRMS (ESI-TOF) *m/z* calcd for $C_{11}H_8{}^{79}BrO_2$ $[M\text{-}Br]^+$ 250.9702, found 250.9707.



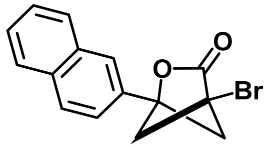
4-bromo-1-(2-fluorophenyl)-2-oxabicyclo[2.1.1]hexan-3-one (3d)

Colorless oil, 39 mg (72%).

^{1}H NMR (400 MHz, CD_3CN): δ = 7.52 – 7.49 (m, 1H), 7.42 – 7.39 (m, 1H), 7.30 – 7.19 (m, 2H), 3.36 – 3.30 (m, 2H), 3.20 – 3.14 (m, 2H) ppm.

^{13}C {^{1}H} NMR (100 MHz, CD_3CN): δ = 172.9, 162.1 (d, $^1J_{CF}$ = 250 Hz), 133.5 (d, $^3J_{CF}$ = 9 Hz), 130.3 (d, J_{CF} = 3 Hz), 125.7 (d, J_{CF} = 4 Hz), 121.0 (d, $^2J_{CF}$ = 13 Hz), 117.1 (d, $^2J_{CF}$ = 21 Hz), 85.6, 58.8 (2C), 50.4 ppm.

HRMS (ESI-TOF) *m/z* calcd for $C_{11}H_8FO_2$ $[M\text{-}Br]^+$ 194.0503, found 191.0501.



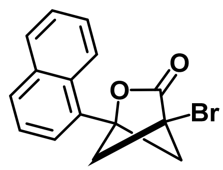
4-bromo-1-(naphthalen-2-yl)-2-oxabicyclo[2.1.1]hexan-3-one (3e)

Colorless oil, 33 mg (54%).

^{1}**H NMR** (400 MHz, CD_3CN): δ = 7.99 – 7.93 (m, 4H), 7.60 – 7.53 (m, 3H), 3.32 – 3.18 (m, 4H) ppm.

^{13}**C {^{1}H} NMR** (100 MHz, CD_3CN): δ = 173.2, 134.6 133.8, 131.6, 129.7, 129.2, 128.8, 128.2, 127.9, 126.9, 124.2, 89.0, 59.0 (2C), 50.4 ppm.

HRMS (ESI-TOF) *m/z* calcd for $C_{15}H_{11}O_2$ $[M\text{-}Br]^+$ 223.0754, found 223.0754.



4-bromo-1-(naphthalen-1-yl)-2-oxabicyclo[2.1.1]hexan-3-one (3f)

Colorless oil, 34 mg (56%).

^{1}**H NMR** (400 MHz, CD_3CN): δ = 8.17 – 8.15 (m, 1H), 8.03 – 7.97 (m, 2H), 7.62 – 7.47 (m, 4H), 3.63 – 3.58 (m, 2H), 3.25 – 3.19 (m, 2H) ppm.

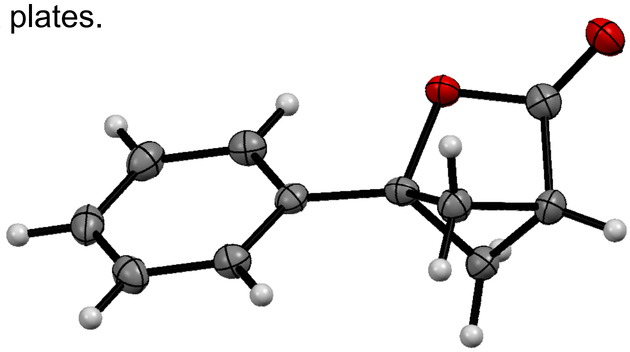
^{13}**C {^{1}H} NMR** (100 MHz, CD_3CN): δ = 173.3, 134.9, 132.1, 131.8, 129.85, 129.69, 127.94, 127.88, 127.5, 126.1, 125.9, 89.6, 59.0 (2C), 50.0 ppm.

HRMS (ESI-TOF) *m/z* calcd for $C_{15}H_{11}O_2$ $[M\text{-}Br]^+$ 223.0754, found 223.0752.

5. SINGLE CRYSTAL X-RAY DIFFRACTION DATA

*Crystallographic data for compound **2a***

Crystals suitable for single crystal X-Ray diffraction studies were obtained via crystallization from the solution of compound **2a** in THF/n-hexane at -25 °C (freezer). About 50 mg of compound **2a** was dissolved in a minimal amount of THF, and the mixture was diluted with 10 mL of n-hexane in a glass vial (Ø 20 mm, L 70 mm) and placed into a freezer for 7 days. Compound **2a** was obtained in a form of colourless transparent plates.

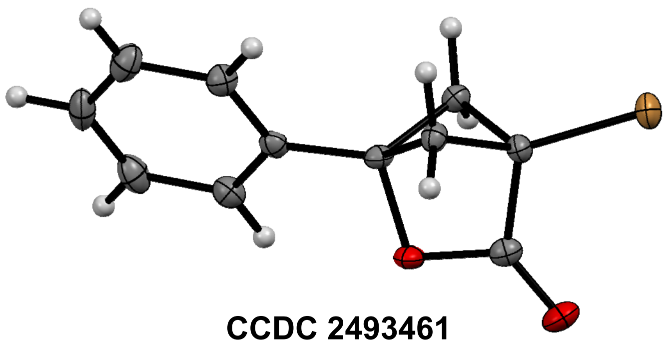


CCDC 2493459

Empirical formula	$C_{11}H_{10}O_2$
Formula weight	174.19
Temperature	120 K
Wavelength	1.54178 Å (CuKα)
Crystal system	Monoclinic
Space group	$P2_1/c$
Unit cell dimensions	a = 7.5720 Å, b = 5.5244 Å, c = 20.5726 Å α = 90°, β = 93.618°, γ = 90°
Volume	858.85(5) Å^3
Z	4
Absorption coefficient (μ)	0.747 mm^{-1}
F(000)	368
Theta range for data collection	5.86 to 68.23°
Independent reflections	1563
Completeness to θ = 25.242°	0.993
Refinement method	Full-matrix least-squares on F^2 (SHELX-type refinement)
Goodness-of-fit on F^2 (S)	1.032
Final R indices [I > 2σ(I)]	R_1 = 0.0328, wR_2 = 0.0818
R indices (all data)	R_1 (all) = 0.0328, wR_2 (all) = 0.0818

*Crystallographic data for compound **3a***

Crystals suitable for single crystal X-Ray diffraction studies were obtained via slow evaporation of the solution of compound **3a** in ethyl acetate/n-hexane at ambient temperature on air. About 50 mg of compound **3a** was dissolved in a minimal amount of ethyl acetate and diluted with 10 mL of n-hexane in a glass vial (Ø 20 mm, L 70 mm) and left at ambient conditions for evaporation. Compound **3a** was obtained in a form of colourless transparent prisms.

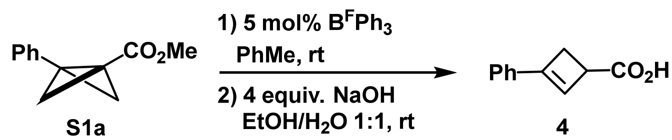


CCDC 2493461

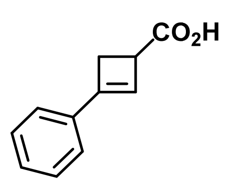
Empirical formula	$C_{11}H_9BrO_2$
Formula weight	253.09
Temperature	120 K
Wavelength	1.54178 Å (CuKα)
Crystal system	Triclinic
Space group	P1
Unit cell dimensions	a = 6.3703 Å, b = 9.0082 Å, c = 9.2840 Å α = 69.206°, β = 80.672°, γ = 88.246°
Volume	491.26 Å³
Z	2
Absorption coefficient (μ)	5.456 mm⁻¹
F(000)	252
Theta range for data collection	5.16 to 68.02°
Independent reflections	1781
Completeness to θ = 25.242°	0.989
Refinement method	Full-matrix least-squares on F² (SHELX-type refinement)
Goodness-of-fit on F² (S)	1.114
Final R indices [I > 2σ(I)]	R_1 = 0.0193, wR_2 = 0.0457
R indices (all data)	R_1 (all) = 0.0193, wR_2 (all) = 0.0457

6. MECHANISTIC STUDIES

*Synthesis of cyclobutene **4** and its assessment as a potential intermediate in the formation of compounds **2** and **3**.*



For the first step, an analytical procedure reported by Fend *et al.* was adopted.[8] Round-bottom flask (25 mL) was charged with ester **S1a** (94 mg, 0.5 mmol), toluene (4 mL) and a spin bar inside a glove box (argon). Tris(pentafluorophenyl)borane (13 mg, 5 mol%) was added to the resulted mixture at room temperature, and the contents of the flask were stirred for 16 h. Upon completion, the flask was removed from the glove box, quenched with 4 drops of water and concentrated to dryness. The residue was redissolved in EtOH (2 mL). Water (2 mL) followed by NaOH (80 mg, 2 mmol, 4 equiv.) were added, and the reaction mixture was stirred for 4h until full consumption of the intermediate ester (TLC control). The reaction mixture was poured into water and neutralized by slow addition of 0.5 M HCl (2 mL) upon vigorous stirring. Resulting suspension was extracted with DCM (2 ×15 mL), combined organic phase was washed with water and brine, dried over anhydrous sodium sulfate, filtered, concentrated and dried under vacuum. The dried residue was cyclobutane **4** in a form of a white solid of high purity.



3-phenylcyclobut-2-ene-1-carboxylic acid (4)

White solid, 69 mg (79%); m.p. = 114 – 116 °C.

^{1}H NMR (400 MHz, CD_3CN): δ = 7.42 – 7.30 (m, 5H), 6.32 (d, ^3J = 1.2 Hz, 1H), 3.62 (dt, ^3J = 4.9, 1.4 Hz, 1H), 3.07 (dd, ^2J = 13.1 Hz, ^3J = 4.9 Hz, 1H), 2.93 (dd, ^2J = 13.1 Hz, ^3J = 2.0 Hz, 1H) ppm. Resonance for carboxylic H has not been detected.

^{13}C {^{1}H} NMR (100 MHz, CD_3CN): δ = 174.9, 149.1, 134.8, 129.5 (2C), 129.3, 126.1, 125.5 (2C), 41.9, 33.2 ppm.

HRMS (ESI-TOF) *m/z* calcd for $C_{11}H_{11}O_2$ $[M+H]^+$ 175.0754, found 175.0745.

Cyclobutane **4** (0.1 mmol) was subjected to standard electrochemical conditions. After 3 F/mol of charge had passed, the reaction mixture was concentrated, redissolved in MeCN-d_3 and analyzed by ^{1}H NMR. Neither **2a** nor **3a** was detected in the reaction mixture.

*<u>Electrolysis of **1a** in a divided cell.</u>*

Figure S7. Divided cell used for the experiment (compartment description: Ø 15 mm, L = 45 mm; spin bar Ø 3 mm, L = 10 mm; distance from the spin bar to electrodes = 3 mm; nafion was used as semipermeable membrane).

Inside a glove box, a compartment equipped with platinum wire anode was charged with acid **1a** (17.5 mg, 0.1 mmol), TBAB (64 mg, 0.2 mmol, 2 equiv.) and acetonitrile (3.5 mL); a compartment equipped with platinum plate cathode was charged with TBAB (64 mg) and acetonitrile (3.5 mL). Spin rate was set to 600 rpm. Pulsed electrolysis was performed using a potentiostat and a suitable software for programming. The following sequence was performed: 20 s pulse of direct current, 6 mA, followed by 30 s resting period, 240 cycles (200 min, 3 F/mol, see Figure S5 for instructions). Upon completion, the reaction vial was removed from the glove box, the contents of the anode compartment was concentrated, redissolved in MeCN-d_3 and analyzed by ^{1}H NMR. Neither **2a** nor **3a** was detected in the reaction mixture.

__Hydrogen detection experiment__

Hydrogen detection test was performed under the best conditions found for direct electrolysis with a power supply as a source (Table S5, Entry 3). A three-neck round-bottom flask was charged with acid **1a** (35 mg, 0.2 mmol), TBAB (128 mg, 0.4 mmol, 2 equiv.), acetonitrile (7 mL) and a spin bar. Platinum wire (anode, Figure 1, c) and a platinum plate (cathode, Figure S1, a) were mounted through the rubber septum placed in the central neck so that the distance between electrodes was 5 mm and the distance from the electrodes to the spin bar was 5 mm. The spin rate was set to 600 rpm. A two-neck adapter was attached to the side neck of the flask. One neck of the adapter was connected to the argon inlet, and the other was used to vent the gas from the flask to the detector. Argon flow was set to 5 mL/min. The reaction mixture was bubbled with argon for 30 min after which the power supply was switched on with the current set to 6 mA. The reaction was constantly under positive argon pressure. The evolved gas was analyzed by an online gas chromatograph Shimadzu GC-8A equipped with a TCD detector in a periodical manner (10 min/cycle). After 60 min, the formation of hydrogen was detected.

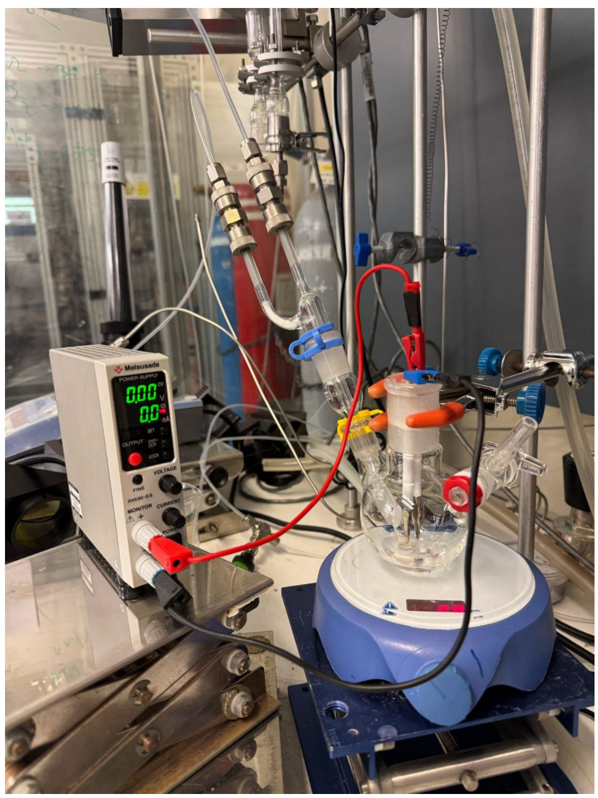


Figure S8. Setup for the hydrogen detection experiment.

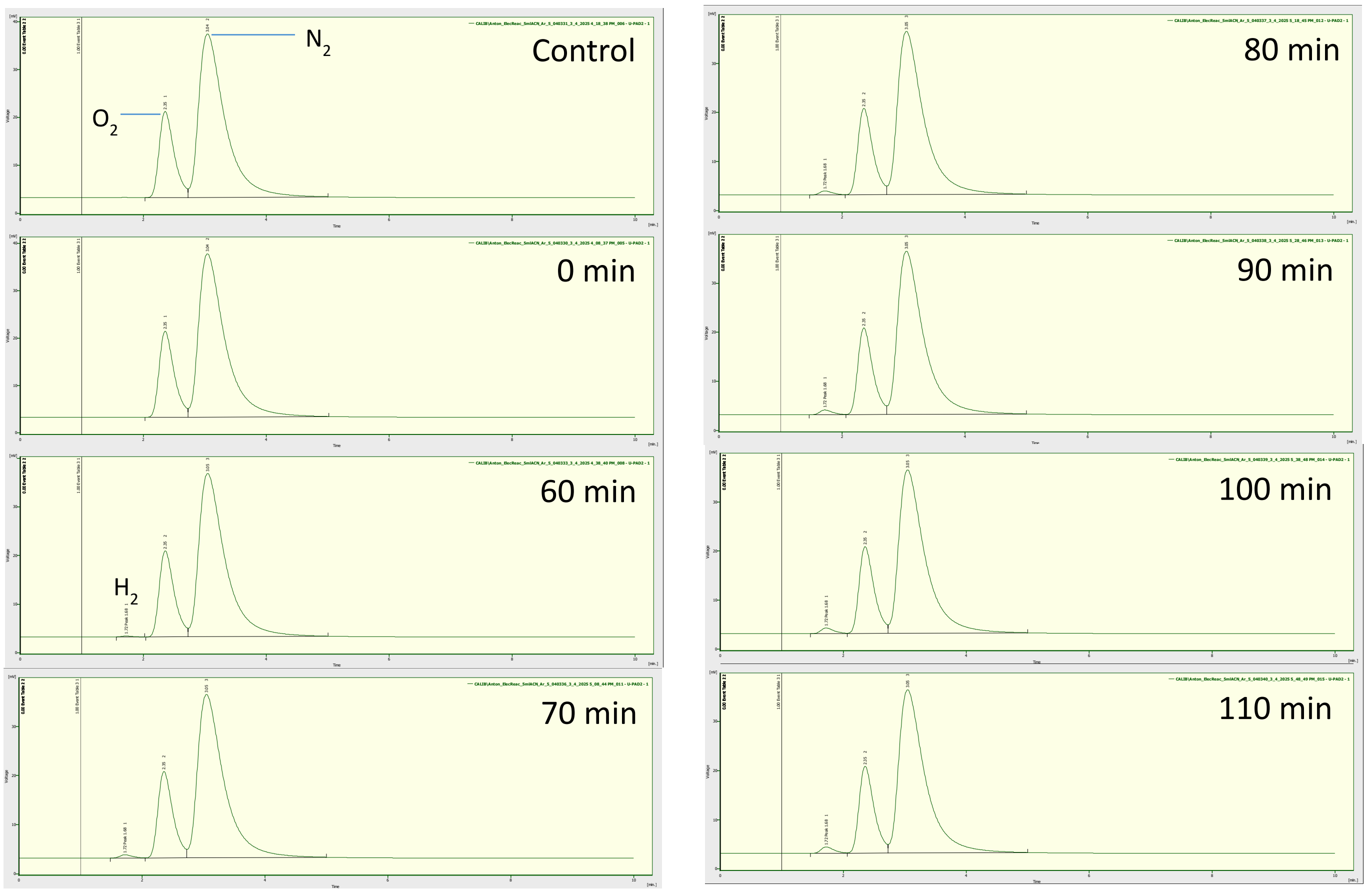


Figure S9. Results of the hydrogen detection test.

Deuterium abstraction experiment

Reaction vial (Figure S2, a) was charged with acid **1a** (17.5 mg, 0.1 mmol), TBAB (32 mg, 0.2 mmol, 2 equiv.), MeCN-d_3 (2.5 mL) and a spin bar inside a glove box (argon). Platinum wire (anode, Figure 1, c) and platinum plate (cathode, Figure S1, a) were mounted, and spin rate was set to 600 rpm. Pulsed electrolysis was performed using a potentiostat and a suitable software for programming. The following sequence was performed: 20 s pulse of direct current, 6 mA, followed by 30 s resting period, 240 cycles (200 min, 3 F/mol). Upon completion, reaction vial was removed from the glove box, the reaction mixture was transferred into a round-bottom flask and dry-loaded onto Celite (about 350 mg). Celite deposit was put on top of the layer of basic alumina (4 mL of alumina in a 10-mL plastic syringe protected with a cotton pad on the bottom). Quick column chromatography with a single fraction (n-hexane/ethyl acetate 13:1, 30 mL) afforded clean the amount of D-enriched **2a** suitable for analysis.

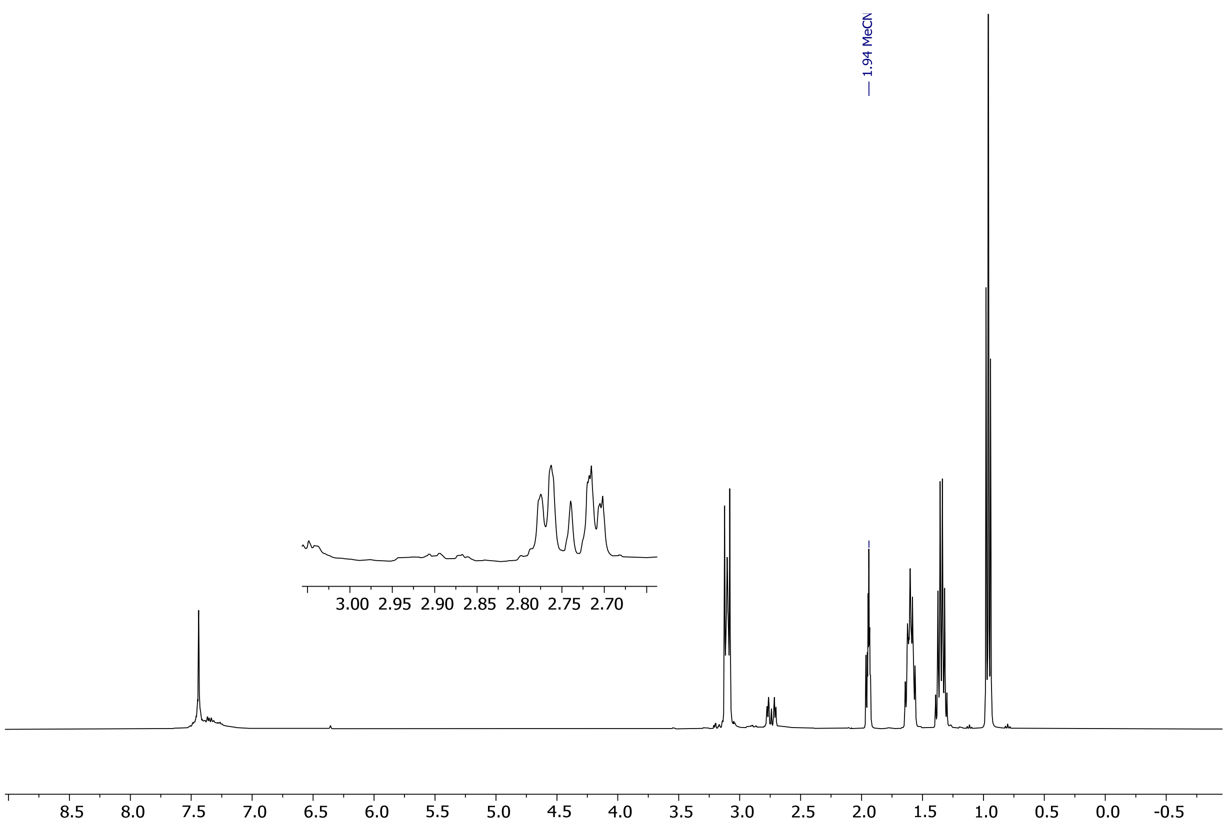


Figure S10. ^{1}H NMR spectrum of the crude reaction mixture obtained with 1 equiv. TBAB, 400 MHz, MeCN-d_3

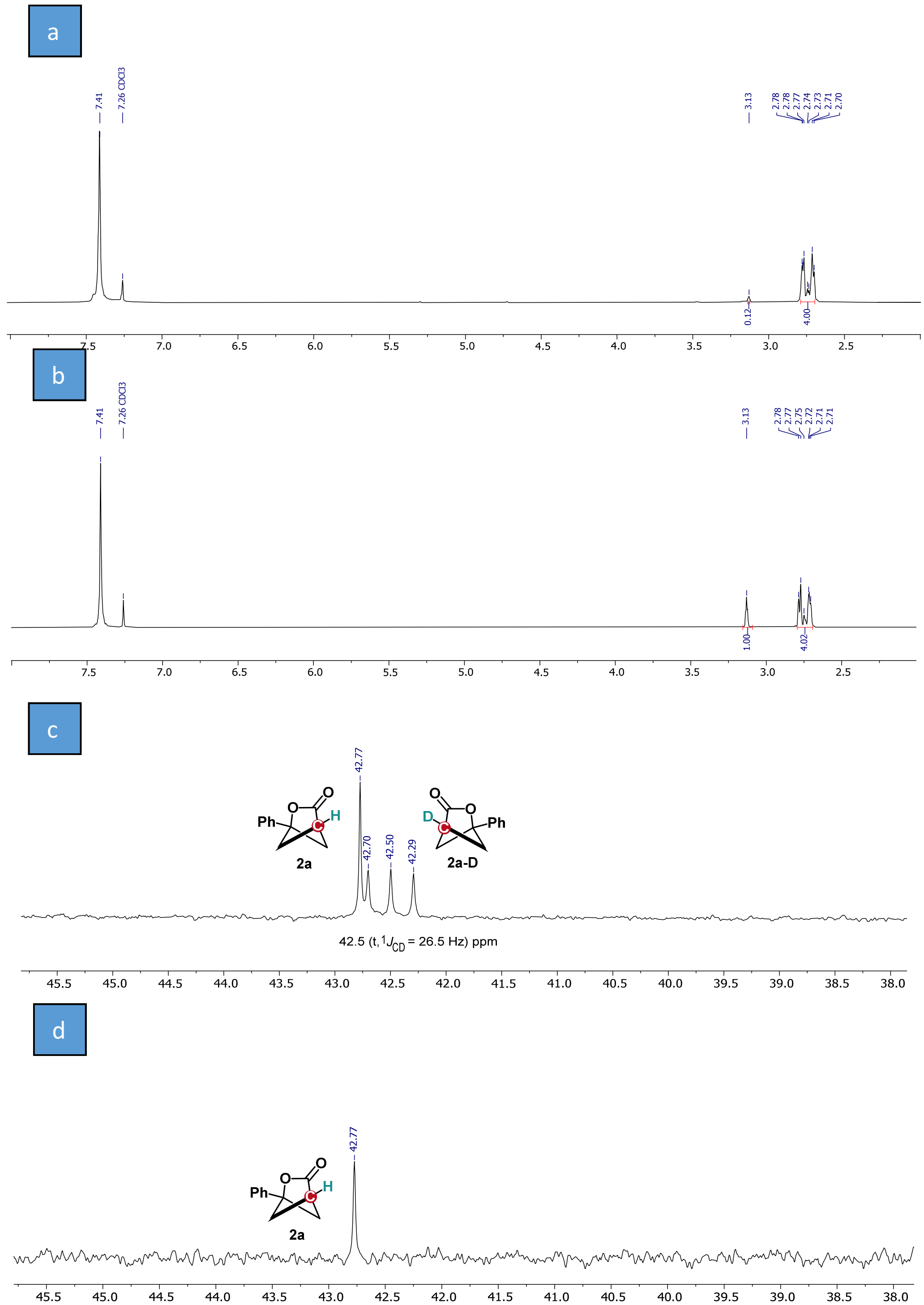


Figure S11. Comparison of NMR data for pure **2a** and D-enriched **2a**: (a) ^{1}H NMR of partially deuterated purified **2a** obtained with 1 equiv. TBAB, 400 MHz, $CDCl_3$; (b) ^{1}H NMR of pure **2a**, 400 MHz, $CDCl_3$; (c) fragment of ^{13}C NMR of partially deuterated purified **2a** obtained with 1 equiv. TBAB, 125 MHz, $CDCl_3$; (d) fragment of ^{13}C NMR of non-deuterated **2a**, 100 MHz, $CDCl_3$.

Cyclic voltammetry data

All measurements were performed under anhydrous conditions in argon-filled glovebox. The cell for the analysis was equipped with a glass vial (working volume is 10 mL) and Teflon cap, equipped with O-ring for tight sealing. Glassy carbon was used as a working electrode (circle, d = 3 mm), platinum wire as a counter electrode, and saturated calomel electrode (SCE) as a reference electrode. All measurements were conducted in 0.1 M solutions of nBu_4NPF_6 in MeCN at a scan rate of 100 mV/s.

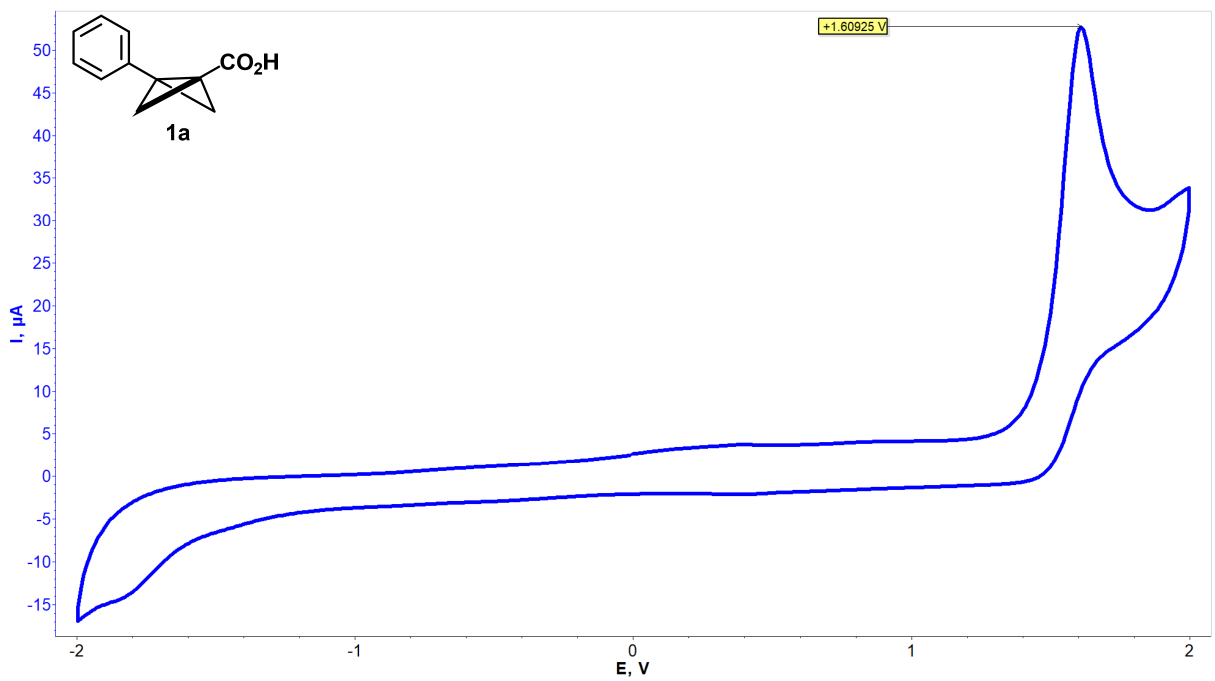


Figure S12. CV trace of compound **1a**.

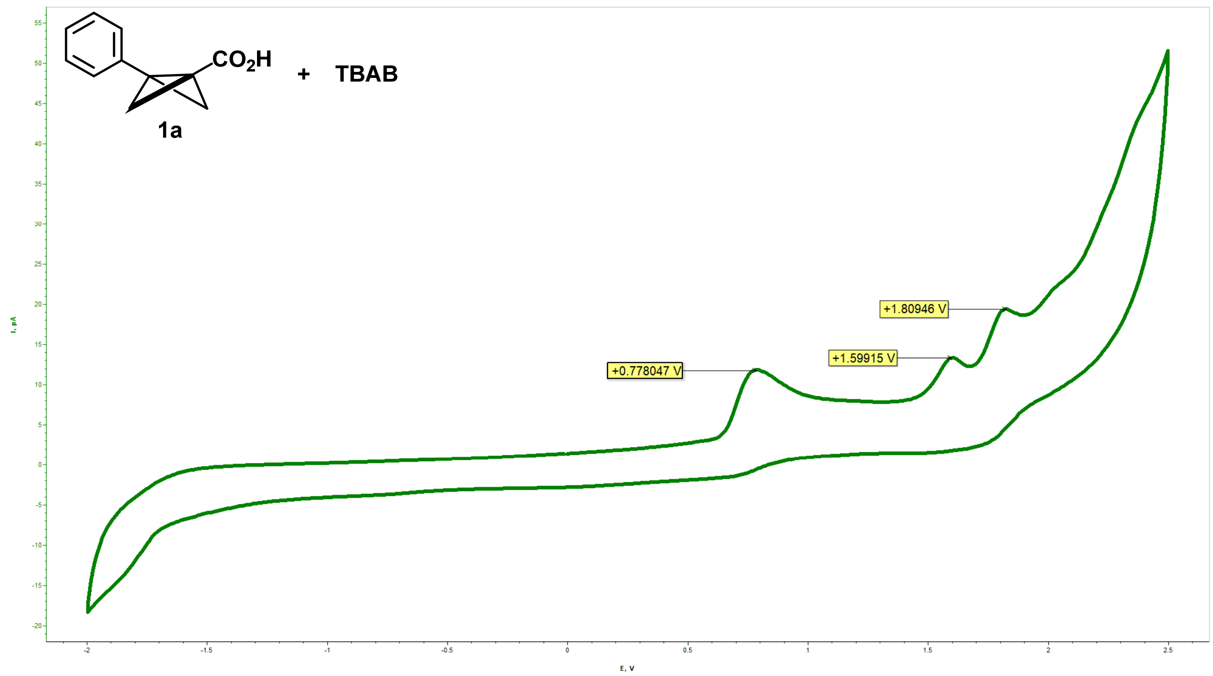


Figure S13. CV trace of compound **1a** in the presence of TBAB.

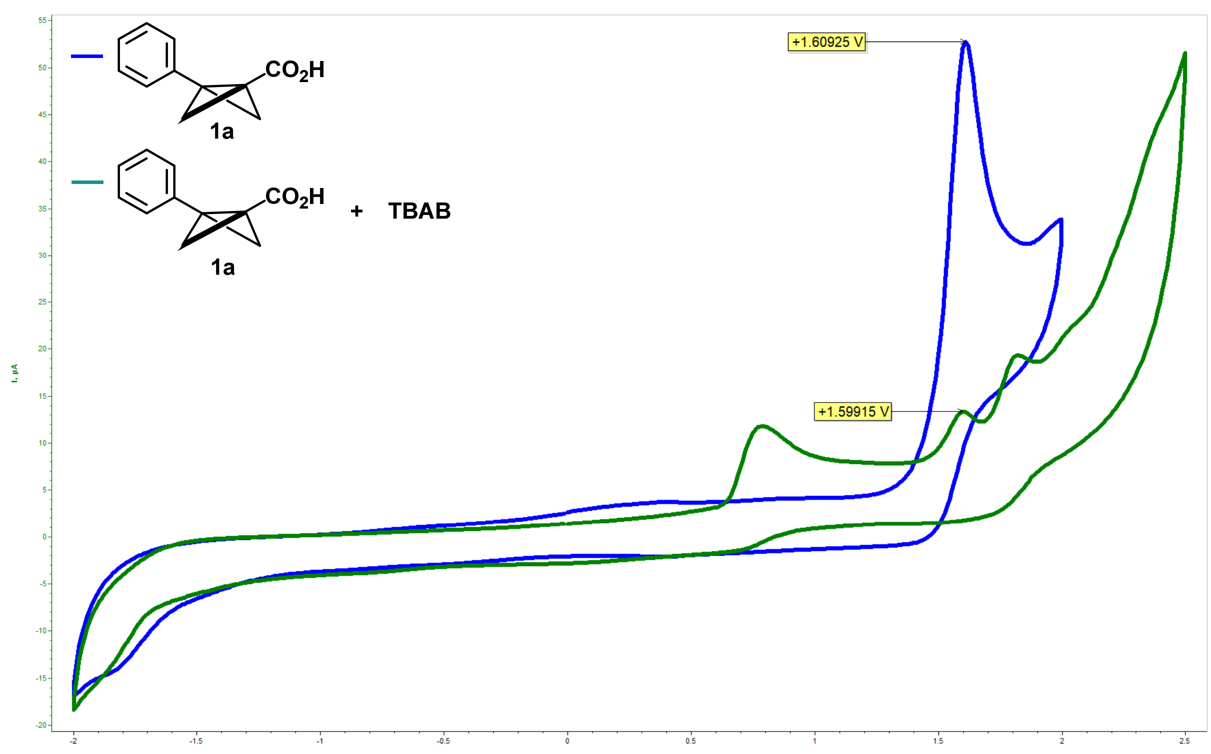


Figure S14. Superimposed CV traces.

Monitoring of changes in electrodes potential

Electrolysis was performed at 0.1 mmol scale with respect to **1a** under standard reaction conditions with SCE as a reference electrode in a three-electrode cell (Figure S2, b). The potential of anode (platinum wire, working electrode) was measured constantly against SCE. The potential of a counter electrode (platinum plate, cathode) was periodically measured with a multimeter (Figure S16). The potential of anode was measured at the beginning of the experiment and then every 16 min (a step of ca. 0.25 F/mol) up to 2 F/mol, then at 2.5 F/mol and at 3F/mol.

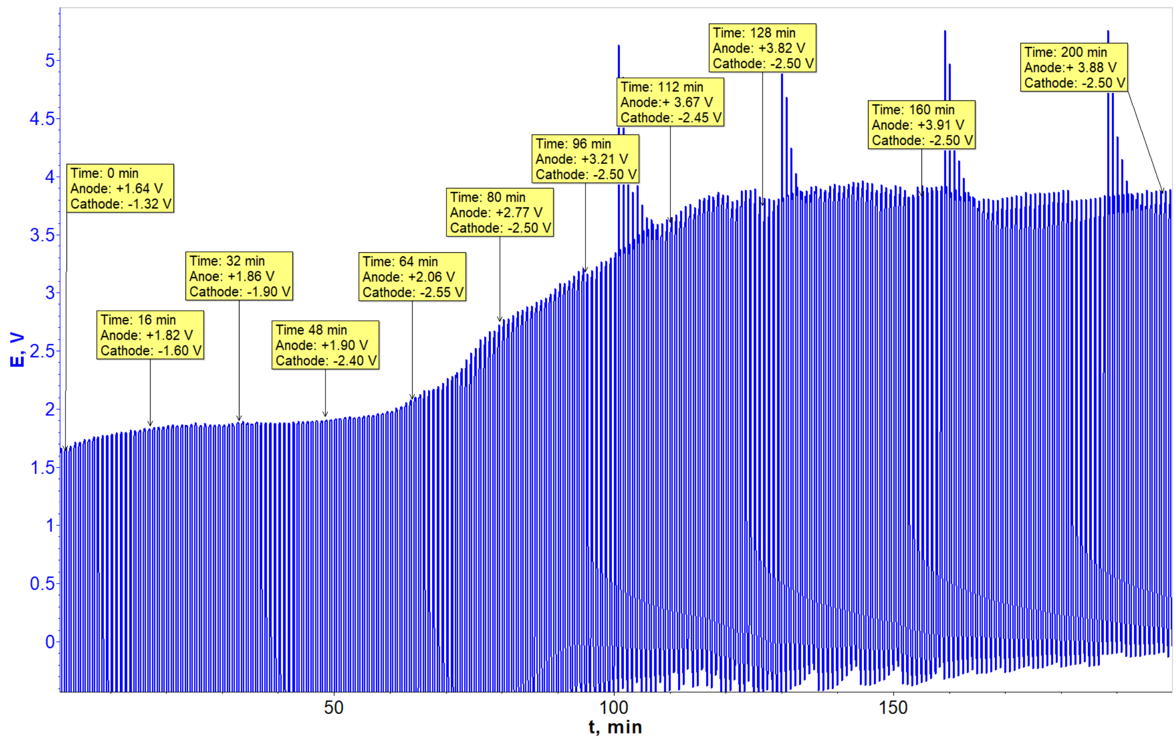
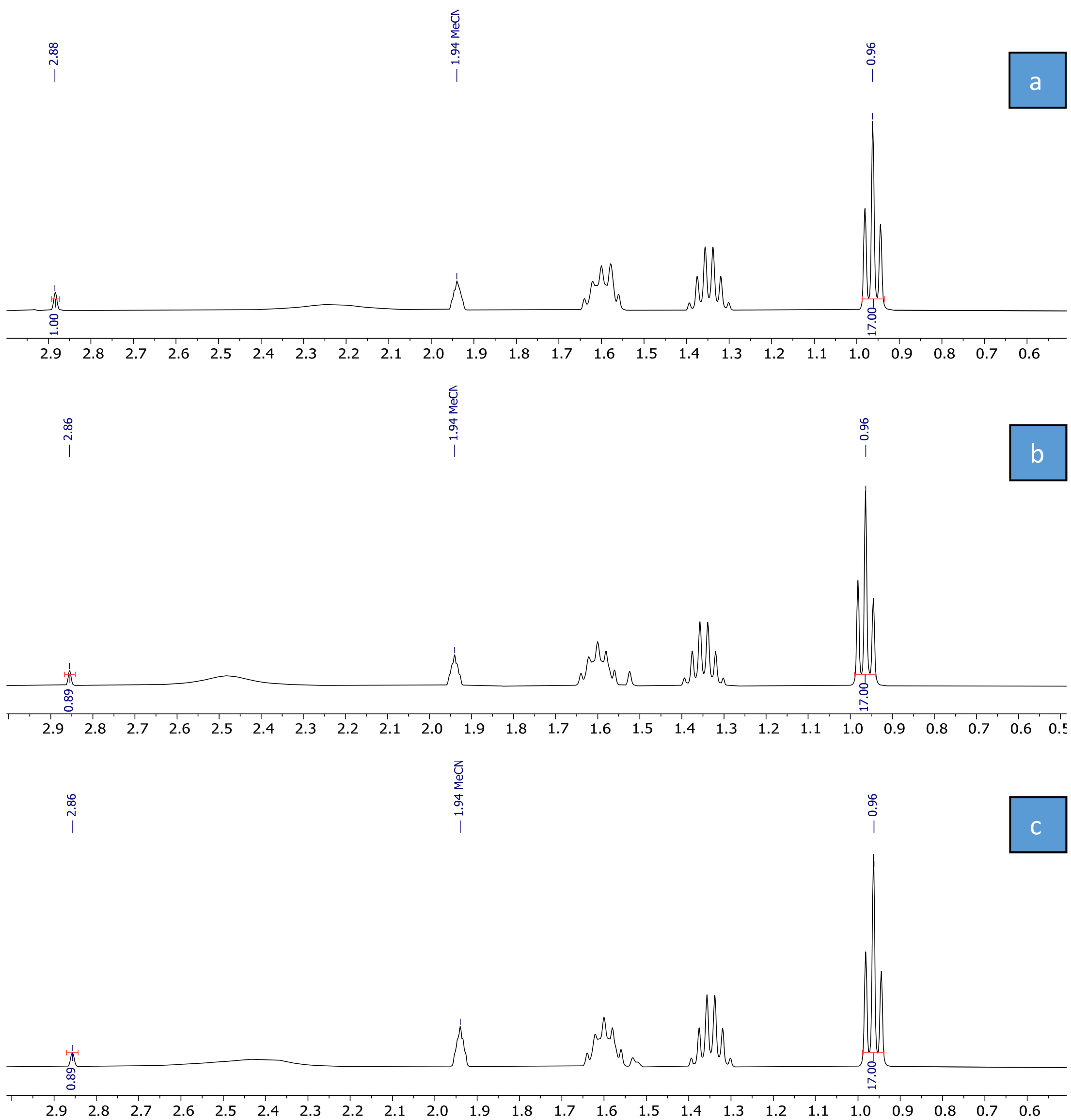


Figure S15. Chronopotentiometry performed during electrolysis of **1a** under standard conditions.

Figure S16. Multimeter used in the study.

Electricity on/off experiment

Experiment was performed at 0.2 mmol scale with respect to **1a** under standard reaction conditions with 2 equiv. TBAB in 3.5 mL of MeCN-d_3. Before running the electrolysis, 100 µL aliquot was transferred to NMR tube, diluted with 400 µL of MeCN-d_3 and analyzed by ^{1}H NMR to assess the initial integral ratio between the resonance of two equivalent protons in CH_2 groups of **1a** at 2.88 ppm (singlet) and the resonance of terminal methyl groups of TBAB at 0.96 ppm (triplet, ^3J = 7.3 Hz, 12H×2). The ratio was determined to be 1:17 (0% conversion), which was used for further calculations of **1a** conversion. During pulsed electrolysis, the process was interrupted every 33 min (ca. 0.25 F/mol) for another 33 min until 0.75 F/mol charge passed. The aliquot (100 µL) was taken at the beginning and at the end of every 33 min resting period. The aliquots were diluted with 400 µL MeCN-d_3 and analyzed by ^{1}H NMR. The integral ratios of resonances of the same protons used for initial calibration were used to determine the conversion of **1a**.



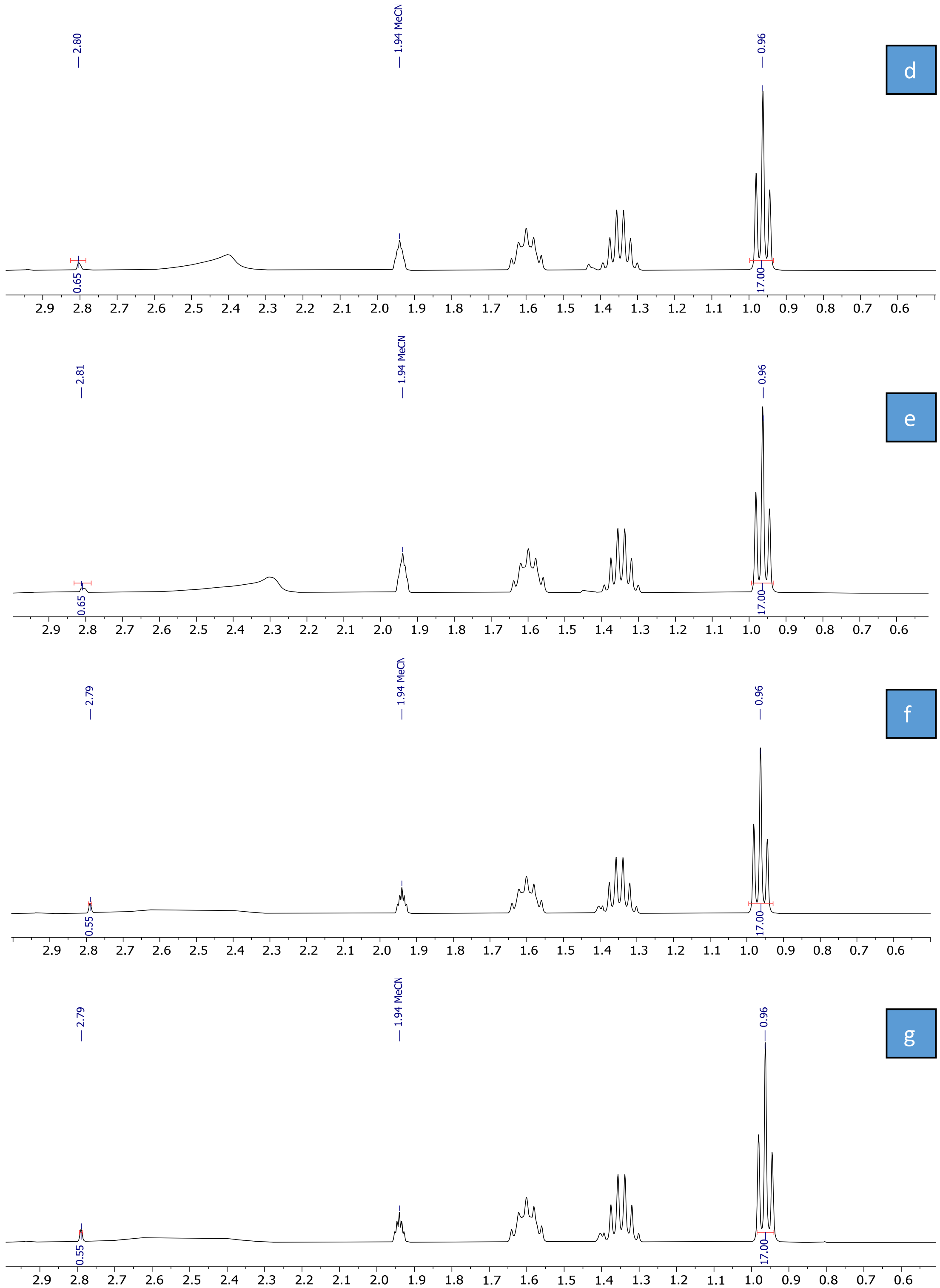


Figure S17. Progress reaction monitoring: (a) 0 min; (b) after 33 min of electrolysis; (c) after 33 min of electrolysis + 33 min resting period; (d) after 66 min of electrolysis; (e) after 66 min of electrolysis + 33 min resting period; (f) after 99 min of electrolysis; (g) after 99 min of electrolysis + 33 min resting period; ^{1}H NMR, 400 MHz, CD_3CN.

Control experiments with styrenes

Experiments were performed at 0.1 mmol scale with respect to styrene **S2** and **S4** under standard reaction conditions with 2 equiv. TBAB in 2.5 mL of MeCN. Upon completion, the reaction mixtures were analyzed by GC-MS. In case of reaction with **S2**, the obtained GC-MS data was compared with data obtained for the authentic samples of possible brominated products.

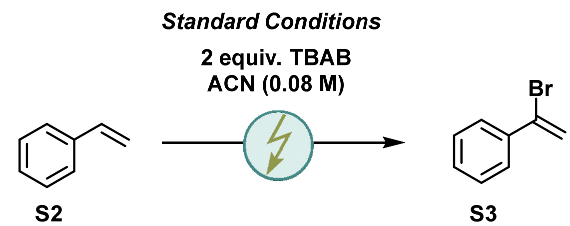
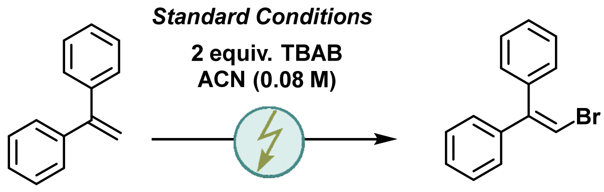


Figure S18. GC-MS data for the control experiment of styrene **S2**.



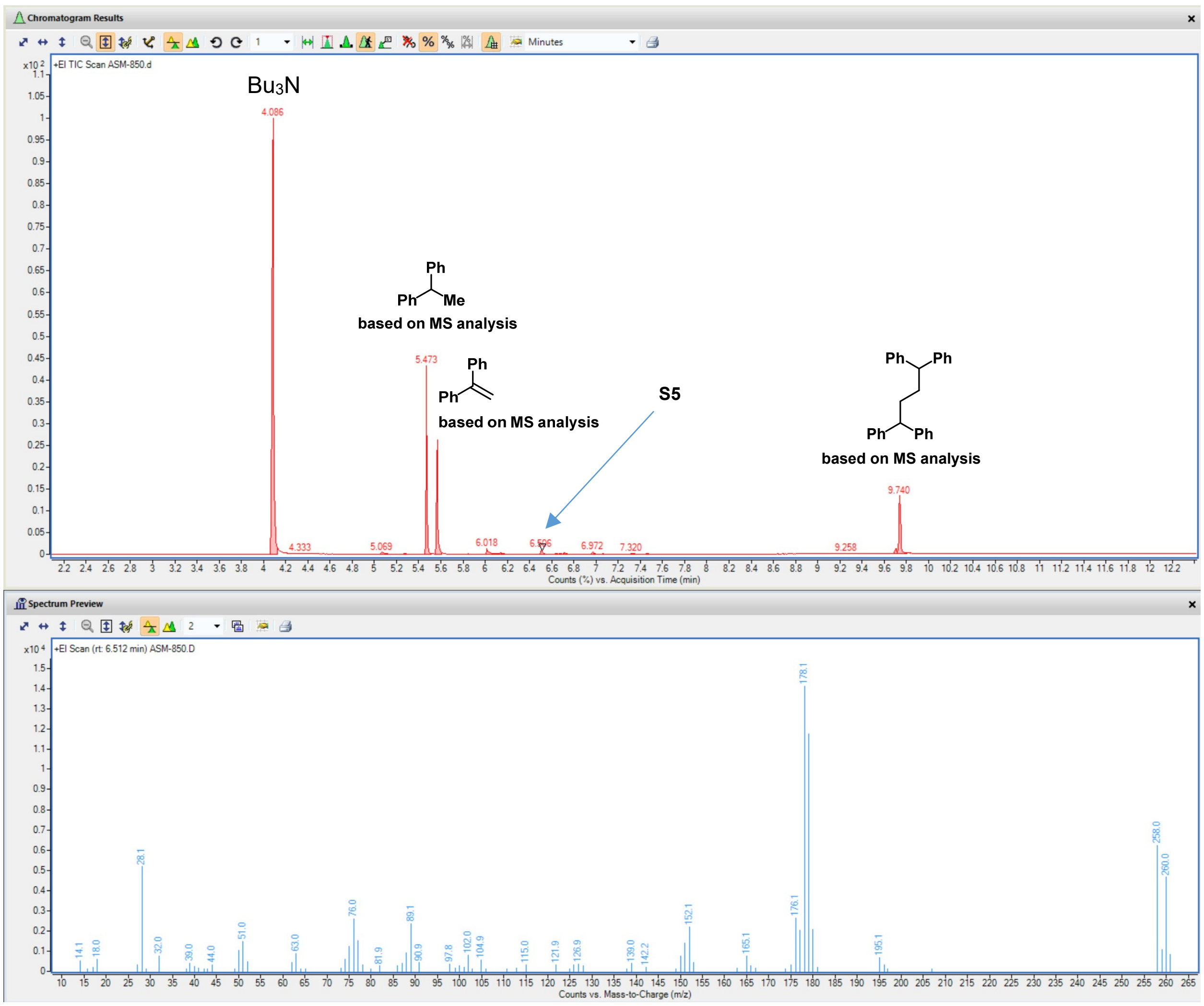


Figure S19. GC-MS data for the control experiment of styrene **S4**.

7. COMPUTATIONAL STUDIES

Computation details

All computations employed density functional theory (DFT) implemented in the Gaussian 16 (C.02 version) suite of programs.[9] Geometry optimizations were carried out with the Long-range corrected hybrid density functional with dispersion correction (wB97xD).[10] Ahlrichs' split valence plus polarization basis set (def2-SVP) was used for geometric optimization for all atoms.[11] The frequency analyses were executed on the optimized geometries at the same level of theory to confirm the nature of stationary points on the potential energy surface either as minima or the transition states characterized by first-order saddle points and to obtain the thermochemical energy values. The minima were identified by having a full set of real frequencies, whereas the transition states possess only one imaginary frequency. The transition states search was conducted through a potential energy surface (PES) scan of the relevant bonds and subsequent optimizations were performed by utilizing the default Berny algorithm, implemented in the Gaussian 16 code. Intrinsic reaction coordinate (IRC) calculations were enforced to ensure that the transition state connects the corresponding real minima.[12] Single-point calculations were performed on the optimized geometries with the higher basis set (def2-TZVPP) basis set on all atoms to improve the accuracy of the energies obtained.[11] All calculations, geometry optimization and single point, were performed in acetonitrile solvent (ε = 35.688) and evaluated by a self-consistent reaction field (SCRF) approach using the SMD continuum solvation model.[13] Tight wave function convergence criteria and "ultrafine" (99,950) grid were used in numerical integration during all theoretical calculations. Unless specified otherwise, free energy values, ΔG, are used throughout the text. The ΔG value is obtained by augmenting the in solvent electronic energy, ΔE, calculated at the ωB97XD(SMD, acetonitrile)/def2-TZVPP level, with the corresponding free energy corrections calculated at the wB97XD(SMD, acetonitrile)/def2-SVP level in gas phase.

Redox potential Calculations

The following equation (S1) has been used to calculate the standard redox potential ($\mathrm{E}_{1/2}^{\mathrm{red}}$)

$$\mathrm{E}_{1/2}^{\mathrm{red}} = -\frac{\Delta G_{\mathrm{red}}}{nF} - \mathrm{E}_{\mathrm{ref}} \qquad \text{(S1)}$$

where ΔG_{red} is the free energy change of reduction process, n represents the number of electron transferred, F is the Faraday constant (23.06 kcal volt^{-1} g^{-1}) and $\mathrm{E}_{\mathrm{ref}}$ is the standard potential of the reference electrode. The value of $\mathrm{E}_{\mathrm{ref}}$ is 4.4 V for standard calomel electrode (SCE) and 5.6 V Pt(111) electrode respectively at 298.15 K in acetonitrile solvent.

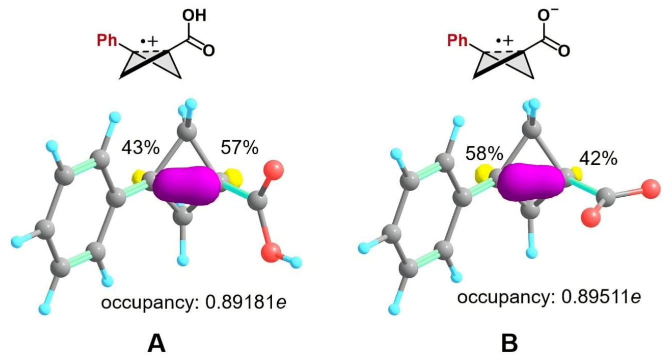


Figure S20. Localized molecular orbital, electron occupancy, and contribution of carbon atoms (in %) in bridging bond of intermediate **A** and **B**.

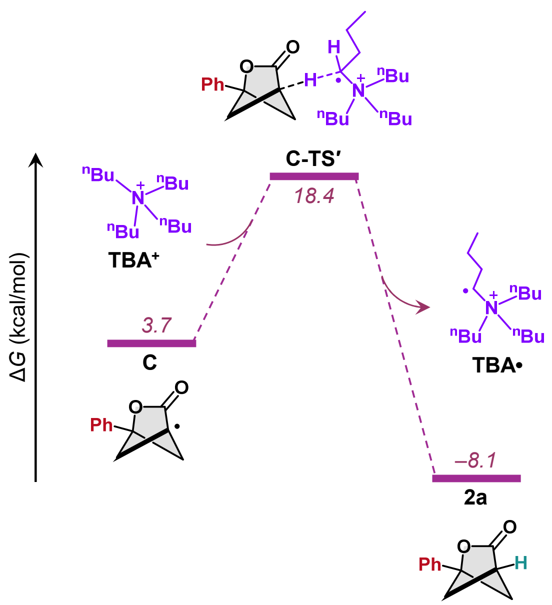


Figure S21. Energetics of HAT from TBAB to intermediate C. The reported energy values were calculated at ωB97xD(SMD, acetonitrile)/def2-TZVPP//ωB97xD(SMD, acetonitrile)/def2-SVP level of theory.

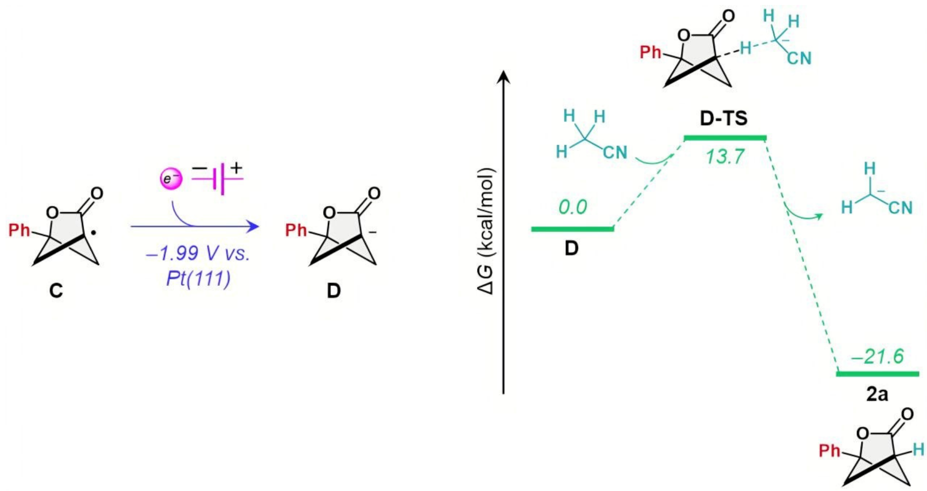


Figure S22. Energetics of reduction of C and followed by hydride transfer from MeCN. The reported energy values were calculated at ωB97xD(SMD, acetonitrile)/def2-TZVPP//ωB97xD(SMD, acetonitrile)/def2-SVP level of theory.

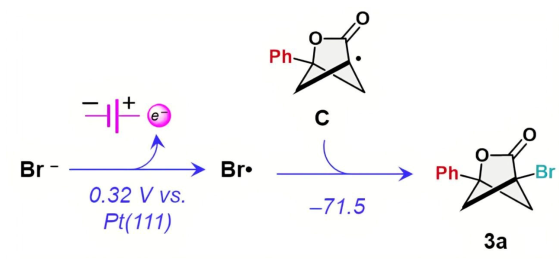


Figure S23. Energetics of bromo lactone **3a** formation. The reported energy values were calculated at ωB97xD(SMD, acetonitrile)/def2-TZVPP//ωB97xD(SMD, acetonitrile)/def2-SVP level of theory.

Cartesian coordinates (Å) of reactants, product, intermediates and transition states at ωB97xD(SMD, acetonitrile)/def2-SVP level of theory. E represents the electronic energy in Hartree at ωB97xD(SMD, acetonitrile)/def2-TZVPP level of theory.

1a

23

E: -575.639643158

C	1.315267	0.526010	-0.076705
C	1.080956	1.877070	0.585900
C	1.852904	0.801337	1.289689
C	1.739839	1.788136	-0.754836
H	2.810566	2.021431	-0.813163
H	1.147610	2.118746	-1.613120
H	2.933113	0.951133	1.412960
H	1.358648	0.306065	2.130375
C	0.297586	-0.459135	-0.489991
C	-0.315769	-0.373568	-1.749416
C	-0.089269	-1.490957	0.378704
C	-1.303819	-1.283958	-2.119785
H	-0.014443	0.407722	-2.450290
C	-1.077255	-2.400165	0.004736
H	0.391399	-1.588987	1.354437
C	-1.691221	-2.299061	-1.244124
H	-1.771449	-1.200843	-3.103795
H	-1.365532	-3.197231	0.694264
H	-2.463364	-3.014011	-1.537608
C	-0.269708	2.381728	0.847409
O	-0.926555	3.019129	0.056598
O	-0.722262	2.033447	2.055637
H	-1.635555	2.357669	2.133498

A

23

E: -575.423855977

C	1.242941	0.452455	-0.124970
C	1.076302	1.950593	0.625496
C	1.737972	0.781737	1.255578
C	1.582406	1.773601	-0.755714
H	2.665567	1.938174	-0.863602
H	0.978940	2.149032	-1.586825
H	2.834158	0.864179	1.315489
H	1.271641	0.312424	2.126023
C	0.265818	-0.504567	-0.519227
C	-0.291843	-0.461026	-1.824462
C	-0.125212	-1.536196	0.374868
C	-1.219073	-1.411379	-2.210217
H	0.015346	0.321189	-2.520403
C	-1.053596	-2.479634	-0.024683
H	0.309772	-1.583542	1.374366
C	-1.601412	-2.417803	-1.313076
H	-1.650909	-1.379175	-3.211742
H	-1.358295	-3.271733	0.661126
H	-2.334047	-3.166064	-1.623482
C	-0.224481	2.585447	0.980639
O	-0.848170	3.259080	0.202878
O	-0.571427	2.332729	2.231842
H	-1.420713	2.772187	2.421470

B

22

E: -574.967520048

C	1.223481	0.442989	-0.098286
C	1.039024	1.935485	0.687201
C	1.690919	0.749137	1.296507
C	1.571764	1.780078	-0.689511
H	2.657329	1.940683	-0.794407
H	0.981172	2.171980	-1.523774
H	2.787939	0.809701	1.385804
H	1.201405	0.265529	2.147756
C	0.255381	-0.522409	-0.538992
C	-0.277833	-0.457312	-1.845189
C	-0.145650	-1.572489	0.316103
C	-1.196516	-1.405778	-2.272530
H	0.034308	0.341896	-2.520050
C	-1.064854	-2.516234	-0.120439
H	0.269033	-1.640876	1.323551
C	-1.593600	-2.434428	-1.412458
H	-1.607482	-1.347483	-3.282405
H	-1.373604	-3.323398	0.546873
H	-2.316736	-3.179061	-1.752765
C	-0.217807	2.640892	1.128524
O	-1.311001	2.111377	0.927368
O	0.095725	3.719243	1.661024

B-TS

22

E: -574.937045312

C	1.828204	0.232871	-0.270339
C	1.014243	1.742966	0.563237
C	1.918304	0.646125	1.154094

C	1.726907	1.619137	-0.795388
H	2.699254	2.135388	-0.783776
H	1.182394	1.791050	-1.730858
H	2.914032	1.042893	1.405621
H	1.540889	-0.034488	1.925748
C	1.906651	-1.058010	-0.922037
C	1.858135	-1.141421	-2.323460
C	2.087509	-2.221831	-0.156442
C	1.986059	-2.376404	-2.948797
H	1.720540	-0.235875	-2.918043
C	2.215110	-3.453644	-0.788327
H	2.128803	-2.156756	0.932847
C	2.162576	-3.531095	-2.182266
H	1.948936	-2.442224	-4.038053
H	2.356934	-4.358760	-0.194306
H	2.263316	-4.500338	-2.676205
C	-0.426129	1.276264	0.471191
O	-1.402135	1.887872	0.870749
O	-0.366672	0.135946	-0.102838

C

22

E: -574.967756111

C	1.300362	0.181502	-0.258699
C	1.171701	1.949284	0.552351
C	2.116921	0.796067	0.913329
C	1.298506	1.572868	-0.933529
H	2.271741	1.832980	-1.368129
H	0.466950	1.801211	-1.613253
H	3.163537	0.973919	0.636455

H	2.021842	0.316928	1.896854
C	1.662248	-1.103620	-0.932645
C	2.150734	-1.114398	-2.241169
C	1.530120	-2.309271	-0.232330
C	2.504587	-2.321064	-2.846970
H	2.255166	-0.177363	-2.793182
C	1.879655	-3.512442	-0.840467
H	1.147986	-2.303668	0.791224
C	2.368816	-3.520292	-2.148971
H	2.884481	-2.322131	-3.871171
H	1.771521	-4.450182	-0.290476
H	2.643828	-4.464737	-2.624497
C	-0.165491	1.339757	0.892362
O	-1.130145	1.720493	1.486349
O	-0.051208	0.113821	0.318917

C-TS

28

E: -707.724675436

C	-1.735397	2.245428	4.817352
C	-0.552886	3.028518	3.447776
C	-0.933148	3.573036	4.839216
C	-0.557404	1.605813	4.050082
H	0.312806	1.410951	4.689134
H	-0.784305	0.754394	3.394176
H	-0.104504	3.547330	5.557742
H	-1.506824	4.507624	4.903341
C	-2.414470	1.658175	6.011403
C	-3.544239	2.290289	6.545951
C	-1.919677	0.500815	6.617057

C	-4.171778	1.764863	7.672792
H	-3.934134	3.194977	6.073384
C	-2.547618	-0.021780	7.748794
H	-1.039648	0.001985	6.204247
C	-3.673571	0.608090	8.277196
H	-5.054234	2.260801	8.083745
H	-2.155371	-0.927825	8.216304
H	-4.165995	0.197738	9.161974
C	-1.905112	3.042997	2.776956
O	-2.284243	3.406094	1.702315
O	-2.698859	2.503655	3.733029
H	0.493237	3.547311	2.631624
C	1.371455	4.015659	1.851879
H	1.119772	5.077801	1.743248
H	1.250693	3.454968	0.916865
C	2.649990	3.805988	2.467237
N	3.661020	3.615144	3.001812

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23

E: -575.657806268

C	1.315791	0.166058	-0.237667
C	1.197717	1.908222	0.768637
C	1.432598	0.451146	1.270191
C	2.044949	1.506521	-0.474710
H	3.118408	1.448922	-0.254740
H	1.856508	2.017201	-1.430504
H	2.447827	0.306685	1.660280
H	0.681288	-0.009123	1.928287
C	1.656653	-1.116847	-0.920536

C	1.226291	-1.348991	-2.233127
C	2.440078	-2.078122	-0.275560
C	1.575323	-2.527964	-2.888188
H	0.610417	-0.602845	-2.740098
C	2.791761	-3.257189	-0.934258
H	2.778336	-1.907931	0.749338
C	2.360277	-3.484530	-2.240637
H	1.233030	-2.701920	-3.911112
H	3.402958	-4.003029	-0.420686
H	2.633423	-4.408707	-2.755524
C	-0.179098	1.725086	0.168778
O	-1.178290	2.384423	0.210599
O	-0.075795	0.552584	-0.499176
H	1.366500	2.804933	1.371460

D

22

E: -575.098795951

C	1.297062	0.166406	-0.228913
C	1.193772	1.987571	0.813940
C	1.389720	0.462306	1.269783
C	2.039842	1.493910	-0.449368
H	3.118569	1.422015	-0.236990
H	1.885753	1.979896	-1.430131
H	2.390207	0.283930	1.693679
H	0.625385	-0.014649	1.909843
C	1.638369	-1.122970	-0.916581
C	1.193205	-1.372824	-2.222419
C	2.454861	-2.070536	-0.290061
C	1.558381	-2.543075	-2.885114

H	0.548936	-0.641501	-2.715777
C	2.822367	-3.243206	-0.953066
H	2.805798	-1.891583	0.729547
C	2.375959	-3.482800	-2.252443
H	1.201760	-2.725352	-3.902156
H	3.458423	-3.975009	-0.448713
H	2.661332	-4.400979	-2.771778
C	-0.146567	1.755168	0.162108
O	-1.179772	2.379907	0.138157
O	-0.069502	0.553038	-0.521194

D-TS

28

E: -707.857510715

C	-1.956969	2.489169	4.685572
C	-0.947584	3.369537	3.102889
C	-0.955398	3.654444	4.663504
C	-1.121692	1.860085	3.560555
H	-0.173728	1.425053	3.910368
H	-1.646721	1.151960	2.897256
H	0.009183	3.408165	5.132248
H	-1.324790	4.625817	5.033684
C	-2.425717	1.779425	5.919681
C	-3.768901	1.772877	6.311356
C	-1.484755	1.109212	6.713529
C	-4.163200	1.108327	7.474417
H	-4.507139	2.291802	5.698159
C	-1.878496	0.446460	7.874106
H	-0.431968	1.107484	6.417760
C	-3.221288	0.443636	8.258886

H	-5.216010	1.110839	7.767886
H	-1.133192	-0.072156	8.482222
H	-3.531050	-0.076726	9.168459
C	-2.413549	3.641284	2.882291
O	-3.030912	4.223505	2.027955
O	-3.069324	3.051467	3.939718
H	0.461368	3.638803	2.466157
C	1.743437	3.708139	2.176666
H	2.040872	4.768022	2.162414
H	1.901486	3.259469	1.183833
C	2.463007	2.990561	3.180514
N	2.958586	2.384177	4.044545

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53

E: -686.093910053

N	0.218292	-0.689590	-0.063298
C	0.606041	0.230920	1.073460
H	0.065706	-0.131192	1.956253
H	1.676981	0.070450	1.253411
C	0.761294	-2.071922	0.223522
H	0.601922	-2.662148	-0.688252
H	1.843702	-1.953789	0.354313
C	0.792045	-0.209886	-1.377358
H	0.512517	-0.962408	-2.124429
H	0.259268	0.716714	-1.627397
C	0.319947	1.710488	0.873630
H	0.859422	2.101733	-0.002714
H	-0.752868	1.882399	0.696485
C	2.295069	0.014270	-1.416544

H	2.607156	0.739517	-0.649311
H	2.834088	-0.923769	-1.213060
C	0.176494	-2.788571	1.429680
H	0.352570	-2.210351	2.349841
H	-0.912993	-2.909682	1.326692
C	0.752417	2.498841	2.110105
H	0.216024	2.113854	2.993935
H	1.824767	2.319144	2.297639
C	0.500487	3.994241	1.967764
H	0.818782	4.539424	2.869253
H	1.053187	4.411524	1.110722
H	-0.569349	4.204582	1.808699
C	0.814706	-4.169650	1.580106
H	0.645062	-4.749424	0.656825
H	1.907913	-4.057106	1.677100
C	0.269796	-4.939177	2.776248
H	0.743774	-5.928678	2.862729
H	0.453891	-4.395900	3.717020
H	-0.817489	-5.094651	2.688282
C	2.710045	0.539477	-2.791047
H	2.385218	-0.174353	-3.567053
H	2.173948	1.481906	-2.995316
C	4.211603	0.769525	-2.901475
H	4.483873	1.150161	-3.897581
H	4.558247	1.503024	-2.155869
H	4.771202	-0.164913	-2.735008
C	-1.290106	-0.707003	-0.173005
H	-1.670838	-0.892993	0.839297
H	-1.586959	0.310150	-0.455889
C	-1.885432	-1.704179	-1.153180

H	-1.526792	-1.508955	-2.175479
H	-1.589537	-2.733285	-0.896875
C	-3.411337	-1.610387	-1.133890
H	-3.772705	-1.797693	-0.108360
H	-3.716499	-0.580362	-1.385118
C	-4.070192	-2.590173	-2.096122
H	-3.807520	-3.630824	-1.846791
H	-5.166893	-2.504349	-2.062866
H	-3.750570	-2.405256	-3.134249

C-TS′

75

E: -1261.05511882

C	-1.558312	2.685775	5.131532
C	-0.288863	3.217232	3.704570
C	-0.041909	2.426494	5.013634
C	-1.652278	2.498855	3.595372
H	-1.562655	1.446850	3.296382
H	-2.478339	3.004729	3.076795
H	0.200477	1.372428	4.830798
H	0.607097	2.867936	5.782678
C	-2.478451	2.037804	6.113462
C	-3.791846	2.505022	6.248241
C	-2.053285	0.945828	6.874293
C	-4.666653	1.886153	7.138008
H	-4.126249	3.360363	5.656646
C	-2.932936	0.324400	7.762026
H	-1.029408	0.577275	6.776167
C	-4.239169	0.793352	7.895765
H	-5.688906	2.257615	7.240894

H	-2.592735	-0.528134	8.354342
H	-4.926751	0.308318	8.592633
C	-0.736499	4.536557	4.282238
O	-0.458657	5.675675	4.035446
O	-1.603285	4.153415	5.248369
N	2.689559	3.083923	1.831286
C	3.097375	3.267490	3.276365
H	2.389453	2.682370	3.872242
H	4.080503	2.791548	3.382395
C	2.719930	1.608508	1.501923
H	2.492049	1.530537	0.431728
H	3.757830	1.284719	1.643614
C	3.646345	3.806510	0.895229
H	3.348847	3.511457	-0.119272
H	3.434815	4.877375	1.005510
C	3.123256	4.698425	3.781992
H	3.809787	5.317031	3.182371
H	2.122787	5.151145	3.705158
C	5.128797	3.545587	1.104452
H	5.450291	3.913955	2.091126
H	5.351887	2.468069	1.070532
C	1.788637	0.723104	2.313837
H	2.116806	0.676616	3.363117
H	0.764184	1.124699	2.315870
C	3.563711	4.729987	5.245249
H	2.903307	4.071934	5.835769
H	4.578559	4.305938	5.331132
C	3.538564	6.135634	5.831065
H	3.863311	6.135614	6.882591
H	4.206128	6.811969	5.273369

H	2.523320	6.562161	5.792542
C	1.758063	-0.693194	1.741621
H	1.410101	-0.653971	0.695410
H	2.783622	-1.098797	1.711433
C	0.859470	-1.621604	2.548260
H	0.845266	-2.635623	2.120853
H	1.204204	-1.701921	3.591758
H	-0.178395	-1.251557	2.567926
C	5.943530	4.256497	0.023154
H	5.633147	3.886399	-0.968644
H	5.706299	5.333877	0.038851
C	7.443716	4.059428	0.198649
H	8.008068	4.577113	-0.591722
H	7.786696	4.453253	1.168842
H	7.712484	2.991591	0.158438
C	1.327130	3.672418	1.616631
H	0.601692	3.371111	2.637945
H	1.415465	4.760554	1.709314
C	0.557032	3.264884	0.385311
H	1.187386	3.359303	-0.516198
H	0.252435	2.207569	0.445562
C	-0.684590	4.142224	0.220844
H	-1.277704	4.115359	1.150294
H	-0.368886	5.190721	0.089893
C	-1.553440	3.712233	-0.953095
H	-1.918856	2.681159	-0.821232
H	-2.430803	4.367972	-1.058962
H	-0.990719	3.748439	-1.899746

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E: -685.420392471

N	2.704559	3.127583	1.864303
C	3.102852	3.331691	3.308990
H	2.281587	2.920546	3.909032
H	3.987636	2.708387	3.487388
C	2.583732	1.633051	1.586264
H	2.564428	1.528194	0.493280
H	3.507435	1.172599	1.958219
C	3.731841	3.723918	0.920103
H	3.387294	3.482479	-0.092982
H	3.665666	4.812502	1.044911
C	3.360984	4.777498	3.694646
H	4.260647	5.158919	3.186585
H	2.517441	5.410939	3.373403
C	5.160605	3.244065	1.107517
H	5.522461	3.476329	2.121163
H	5.223758	2.152082	0.981863
C	1.367117	0.964639	2.201731
H	1.344512	1.121640	3.291604
H	0.444001	1.405524	1.792266
C	3.548859	4.908003	5.205290
H	2.640476	4.546765	5.716563
H	4.368996	4.243925	5.527608
C	3.847351	6.337881	5.636938
H	3.974752	6.406265	6.727950
H	4.771348	6.711495	5.167188
H	3.029311	7.018556	5.351229
C	1.379071	-0.535696	1.910733
H	1.427629	-0.693929	0.819914

H	2.298953	-0.979280	2.328035
C	0.160193	-1.251099	2.478767
H	0.192758	-2.328977	2.258988
H	0.103288	-1.133296	3.572819
H	-0.772478	-0.849423	2.051187
C	6.079595	3.918855	0.088793
H	5.722351	3.693053	-0.930255
H	6.007871	5.013535	0.205689
C	7.531646	3.481891	0.232644
H	8.172785	3.980661	-0.509884
H	7.923851	3.726395	1.232879
H	7.636496	2.394373	0.089979
C	1.411593	3.783174	1.637778
H	0.789998	3.853616	2.531746
C	0.853974	3.952024	0.274602
H	1.414543	4.729654	-0.278381
H	0.988493	3.024566	-0.315685
C	-0.628340	4.324163	0.313464
H	-1.183553	3.531688	0.842483
H	-0.753054	5.242605	0.910964
C	-1.215901	4.527625	-1.076194
H	-1.126767	3.612826	-1.683962
H	-2.282849	4.791294	-1.021638
H	-0.696711	5.337238	-1.613825

3a

52

E: -685.420392471

N	2.704559	3.127583	1.864303
C	3.102852	3.331691	3.308990

H	2.281587	2.920546	3.909032
H	3.987636	2.708387	3.487388
C	2.583732	1.633051	1.586264
H	2.564428	1.528194	0.493280
H	3.507435	1.172599	1.958219
C	3.731841	3.723918	0.920103
H	3.387294	3.482479	-0.092982
H	3.665666	4.812502	1.044911
C	3.360984	4.777498	3.694646
H	4.260647	5.158919	3.186585
H	2.517441	5.410939	3.373403
C	5.160605	3.244065	1.107517
H	5.522461	3.476329	2.121163
H	5.223758	2.152082	0.981863
C	1.367117	0.964639	2.201731
H	1.344512	1.121640	3.291604
H	0.444001	1.405524	1.792266
C	3.548859	4.908003	5.205290
H	2.640476	4.546765	5.716563
H	4.368996	4.243925	5.527608
C	3.847351	6.337881	5.636938
H	3.974752	6.406265	6.727950
H	4.771348	6.711495	5.167188
H	3.029311	7.018556	5.351229
C	1.379071	-0.535696	1.910733
H	1.427629	-0.693929	0.819914
H	2.298953	-0.979280	2.328035
C	0.160193	-1.251099	2.478767
H	0.192758	-2.328977	2.258988
H	0.103288	-1.133296	3.572819

H	-0.772478	-0.849423	2.051187
C	6.079595	3.918855	0.088793
H	5.722351	3.693053	-0.930255
H	6.007871	5.013535	0.205689
C	7.531646	3.481891	0.232644
H	8.172785	3.980661	-0.509884
H	7.923851	3.726395	1.232879
H	7.636496	2.394373	0.089979
C	1.411593	3.783174	1.637778
H	0.789998	3.853616	2.531746
C	0.853974	3.952024	0.274602
H	1.414543	4.729654	-0.278381
H	0.988493	3.024566	-0.315685
C	-0.628340	4.324163	0.313464
H	-1.183553	3.531688	0.842483
H	-0.753054	5.242605	0.910964
C	-1.215901	4.527625	-1.076194
H	-1.126767	3.612826	-1.683962
H	-2.282849	4.791294	-1.021638
H	-0.696711	5.337238	-1.613825

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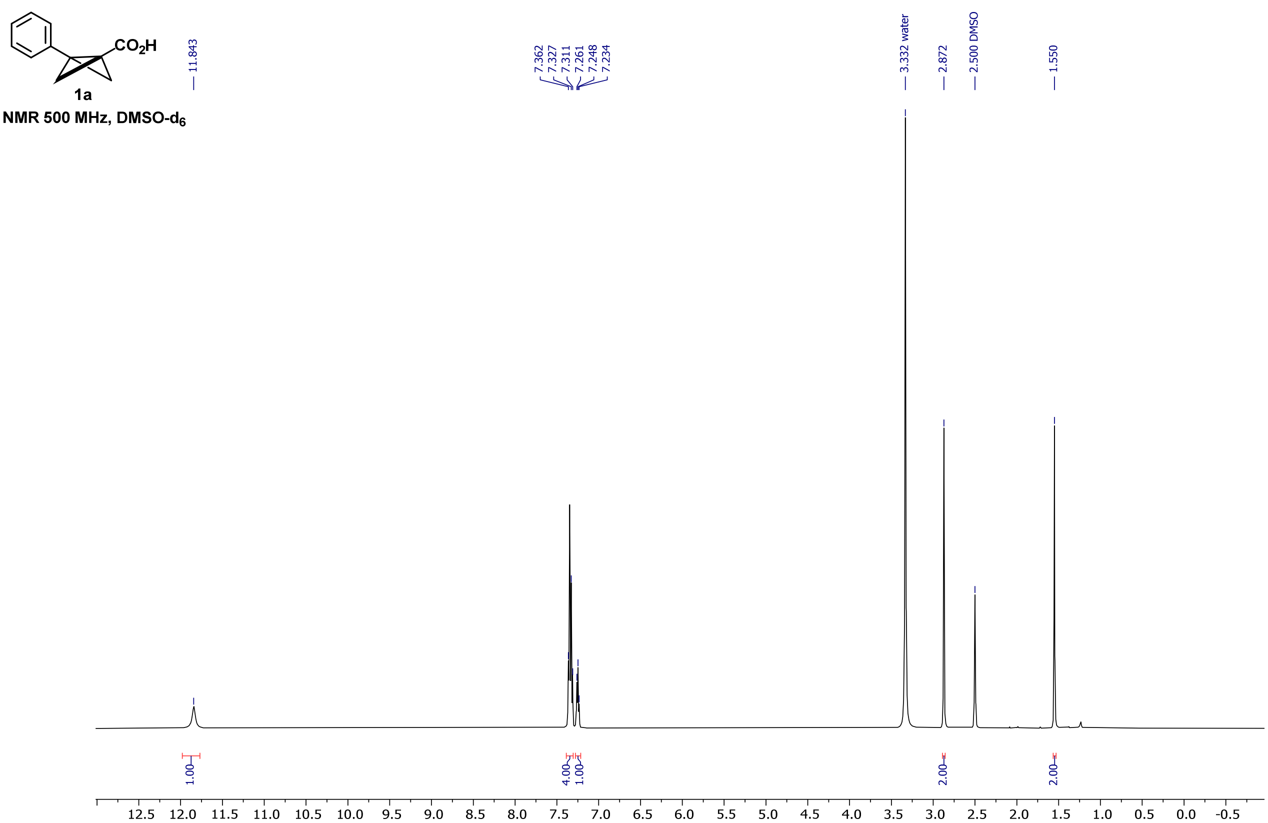
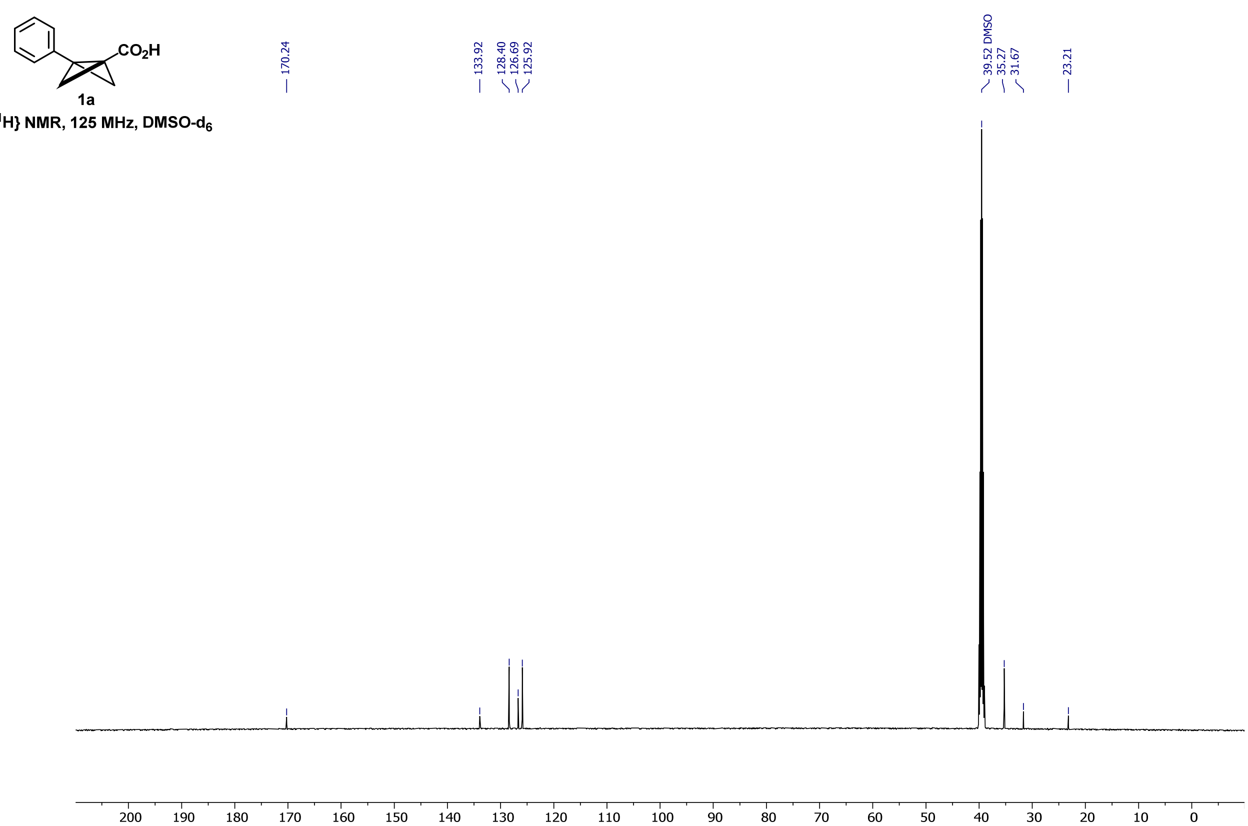
9. COPIES OF NMR SPECTRA FOR ALL NEW COMPOUNDS



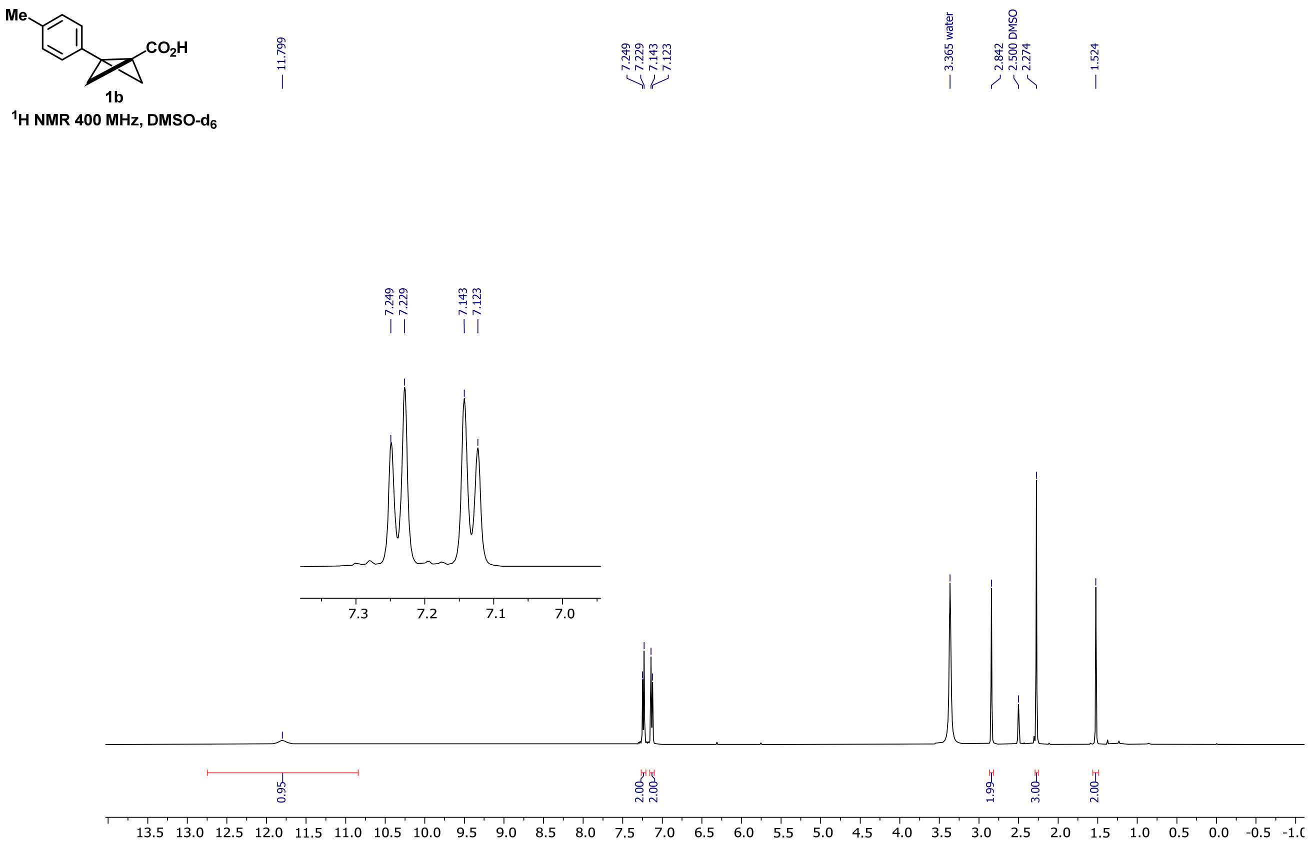
1a

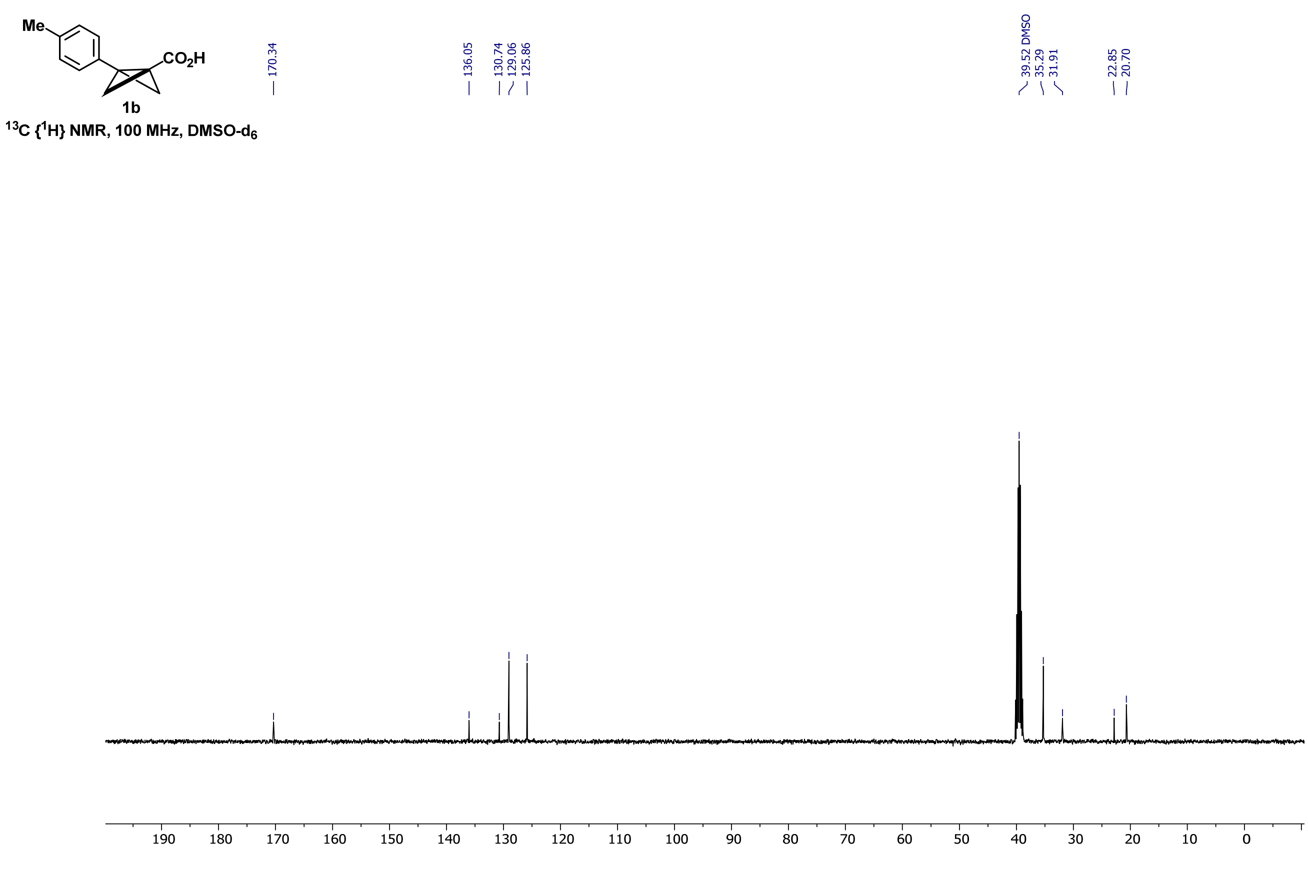
^{1}H NMR 500 MHz, DMSO-d$_6$

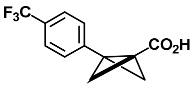


1a

^{13}C {^{1}H} NMR, 125 MHz, DMSO-d$_6$

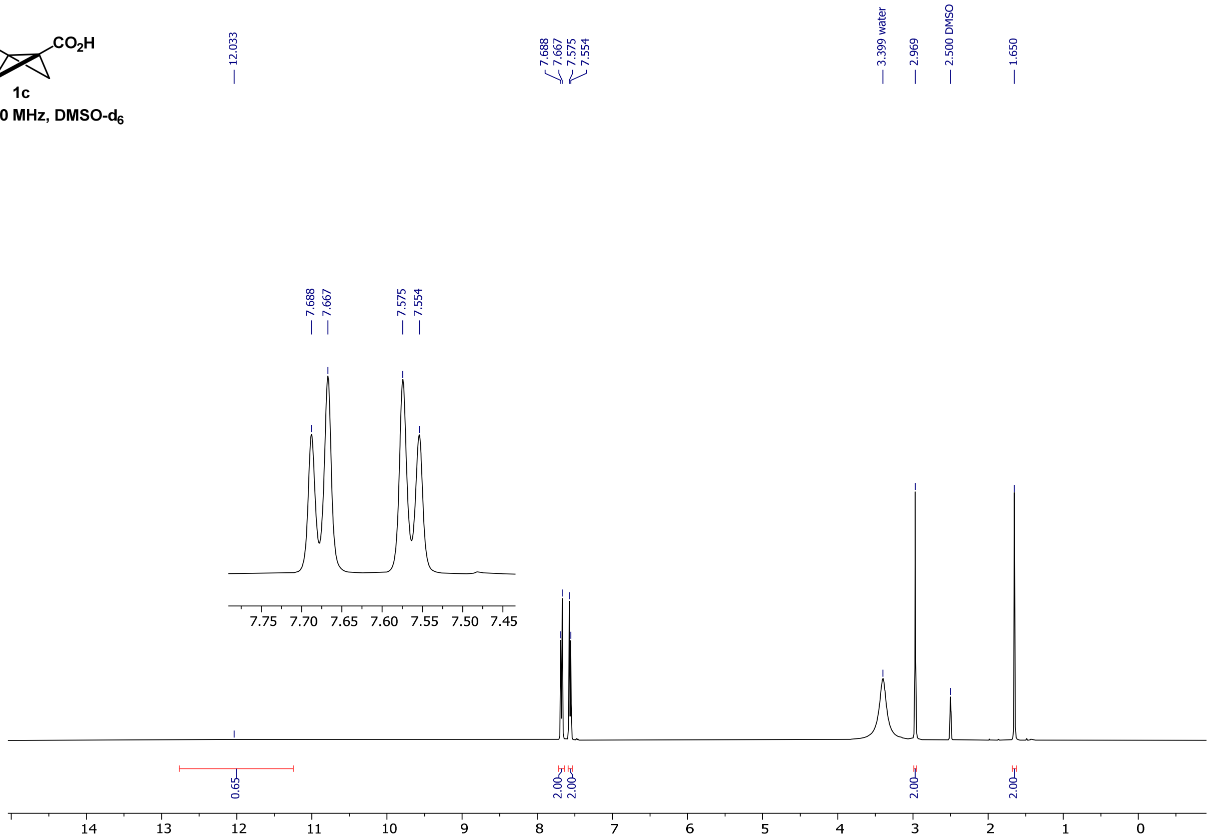

Me
CO_2H
1b
^1H NMR 400 MHz, DMSO-d$_6$
11.799
7.249
7.229
7.143
7.123
3.365 water
2.842
2.500 DMSO
2.274
1.524
0.95
2.00
2.00
1.99
3.00
2.00

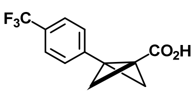

Me
CO_2H
1b
^{13}C {^1H} NMR, 100 MHz, DMSO-d$_6$
170.34
136.05
130.74
129.06
125.86
39.52 DMSO
35.29
31.91
22.85
20.70



1c

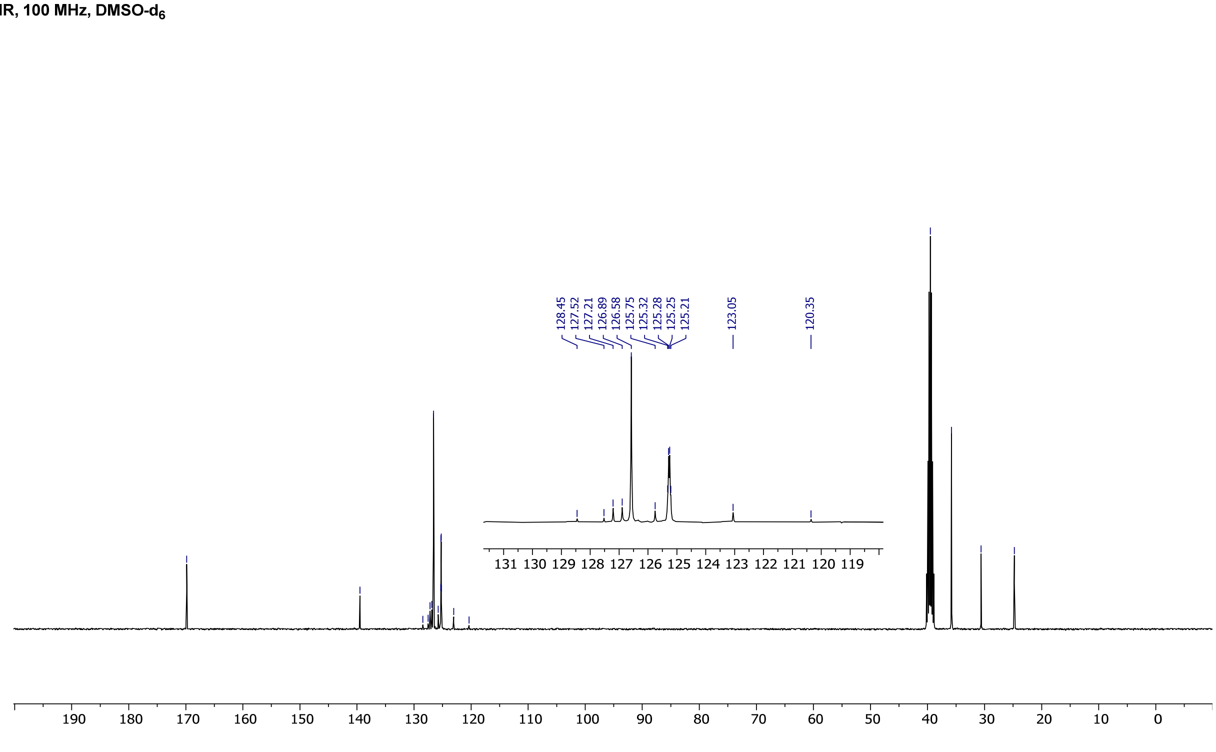
^1H NMR 400 MHz, DMSO-d_6

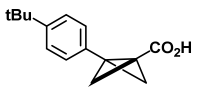




1c

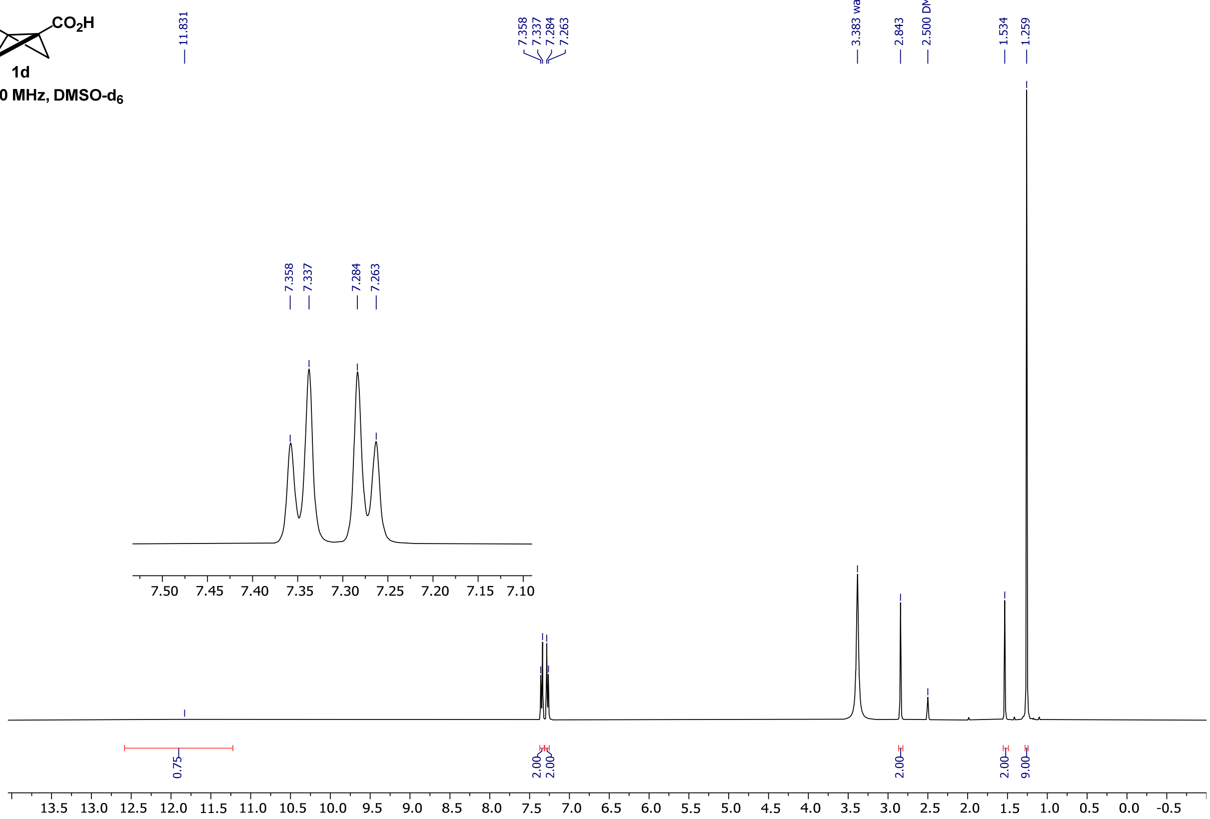
^{13}C {^1H} NMR, 100 MHz, DMSO-d_6

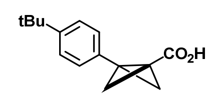




1d

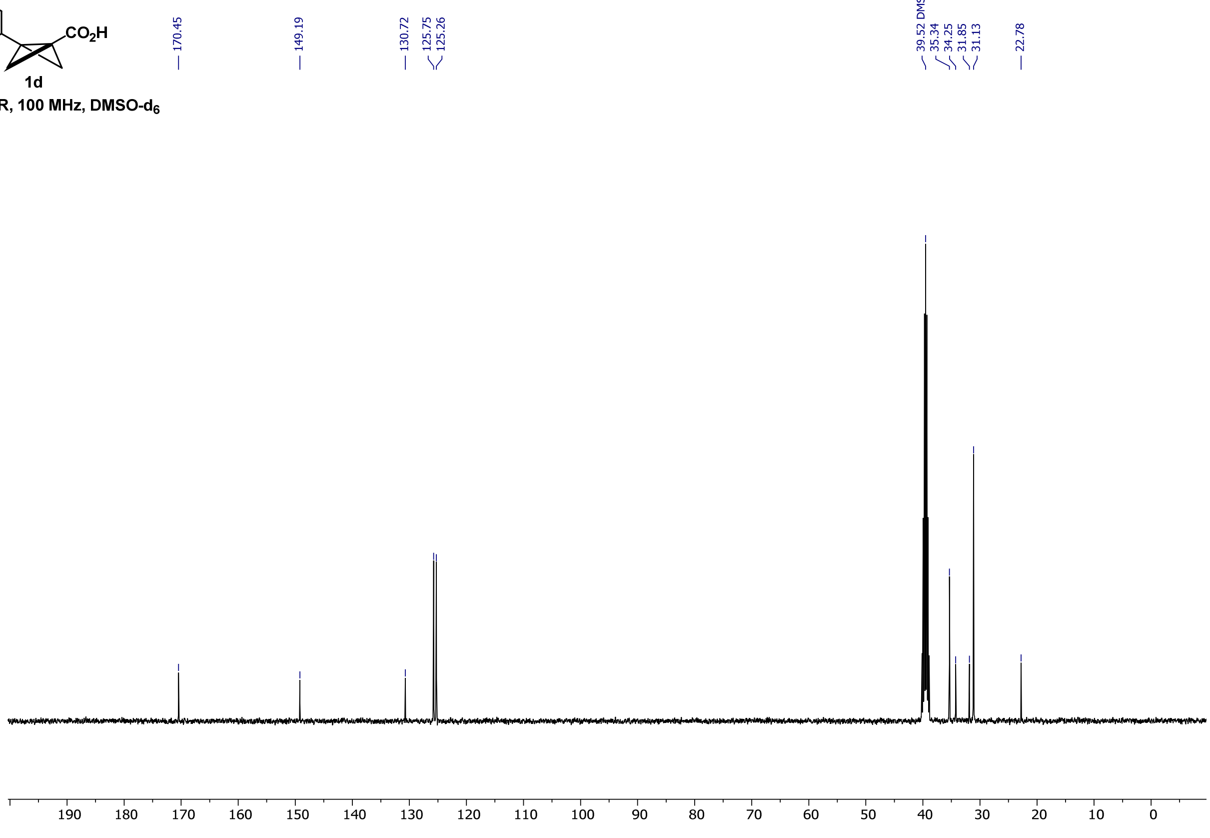
^{1}H NMR 400 MHz, DMSO-d$_6$

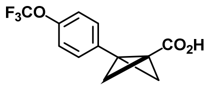




1d

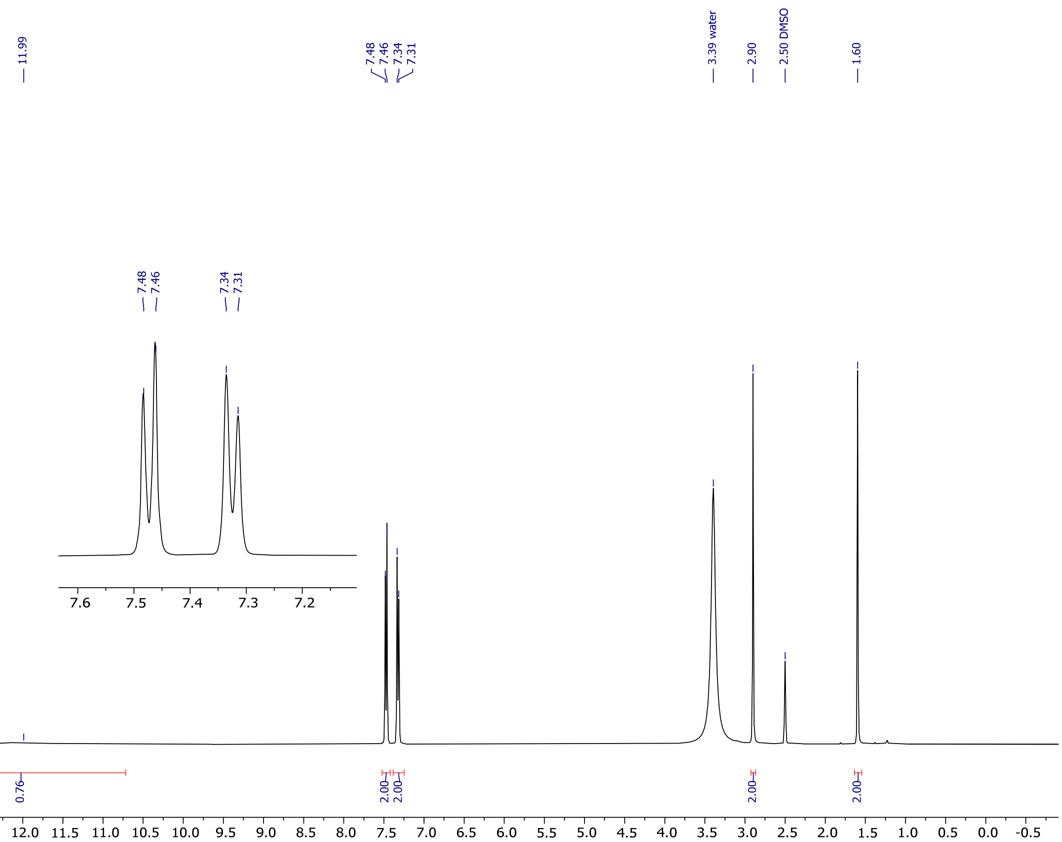
^{13}C {^{1}H} NMR, 100 MHz, DMSO-d$_6$

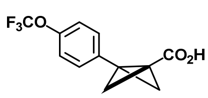




1e

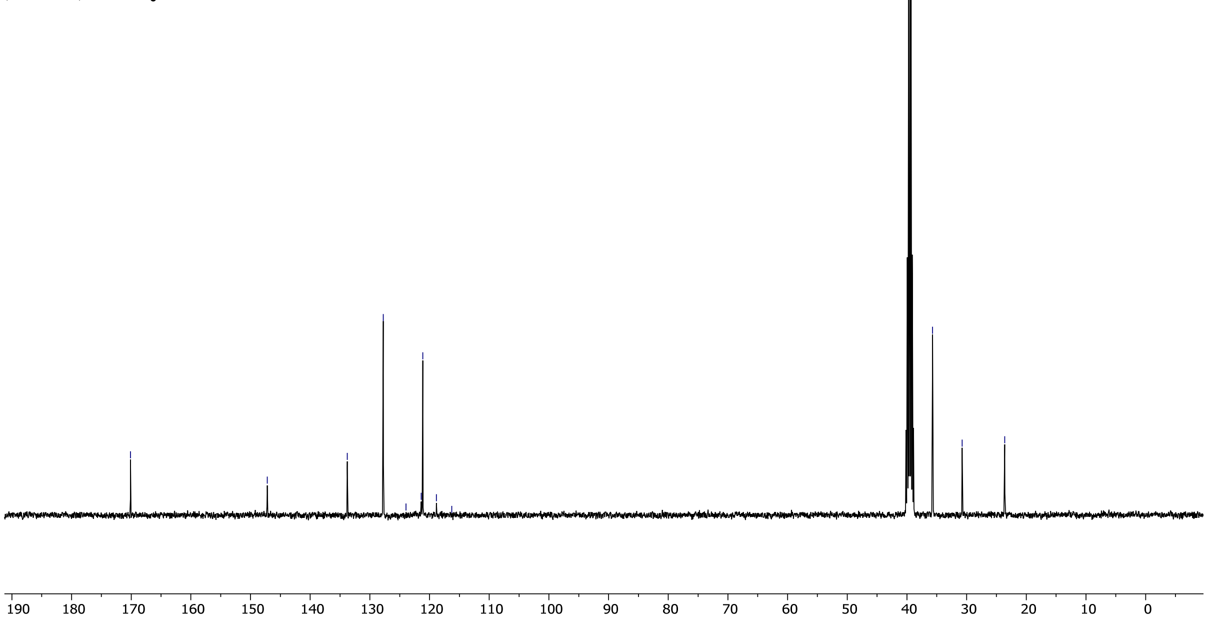
^{1}H NMR 400 MHz, DMSO-d_6

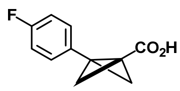




1e

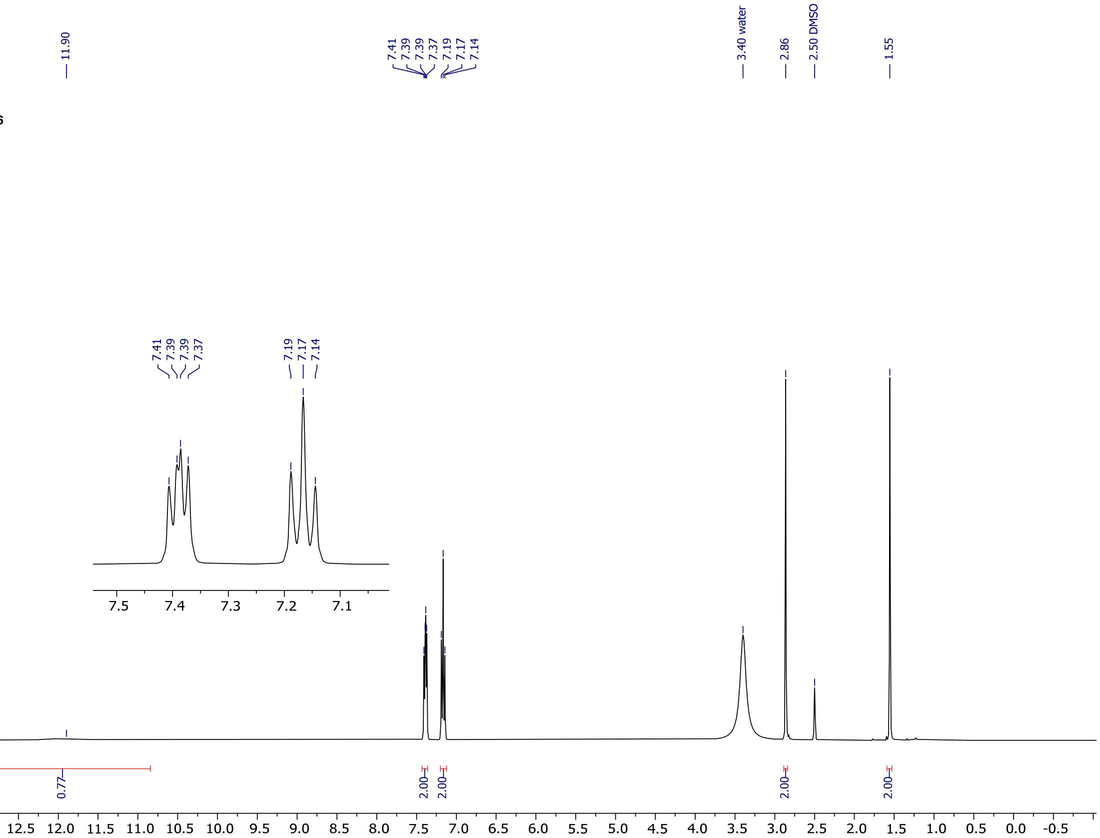
^{13}C {^{1}H} NMR, 100 MHz, DMSO-d_6

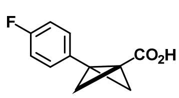




1f

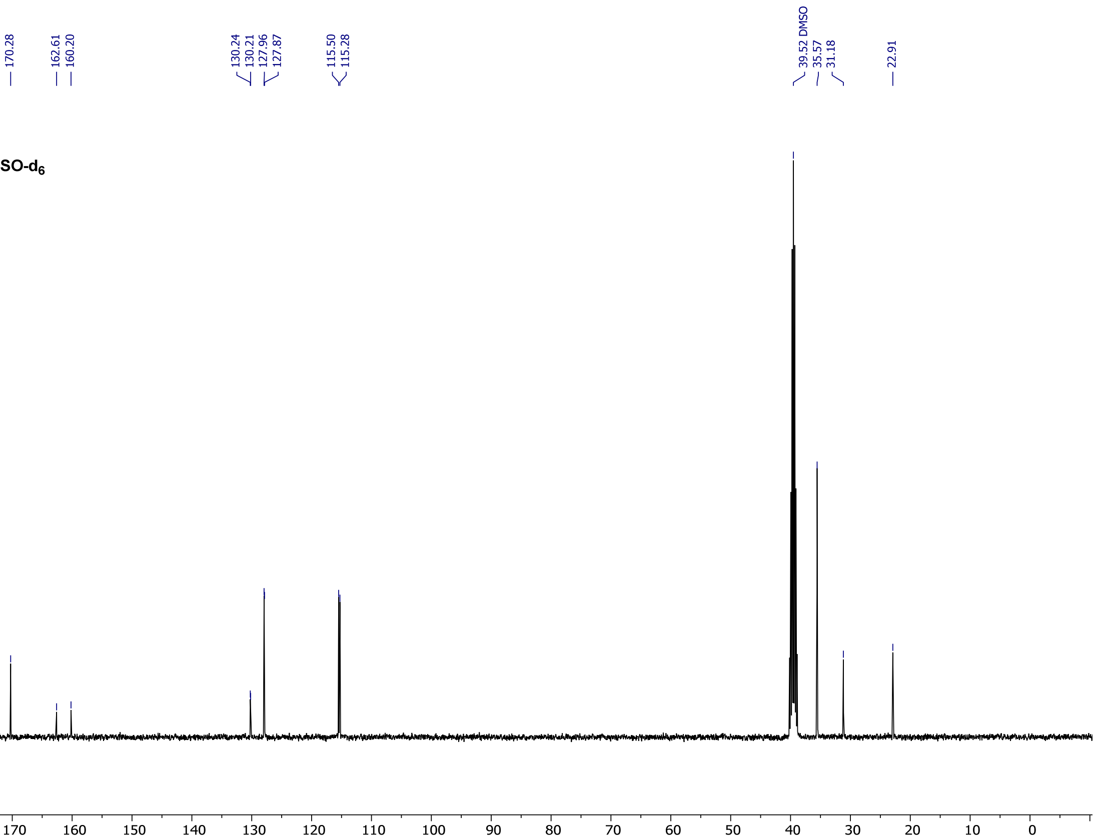
^{1}H NMR 400 MHz, DMSO-d_6

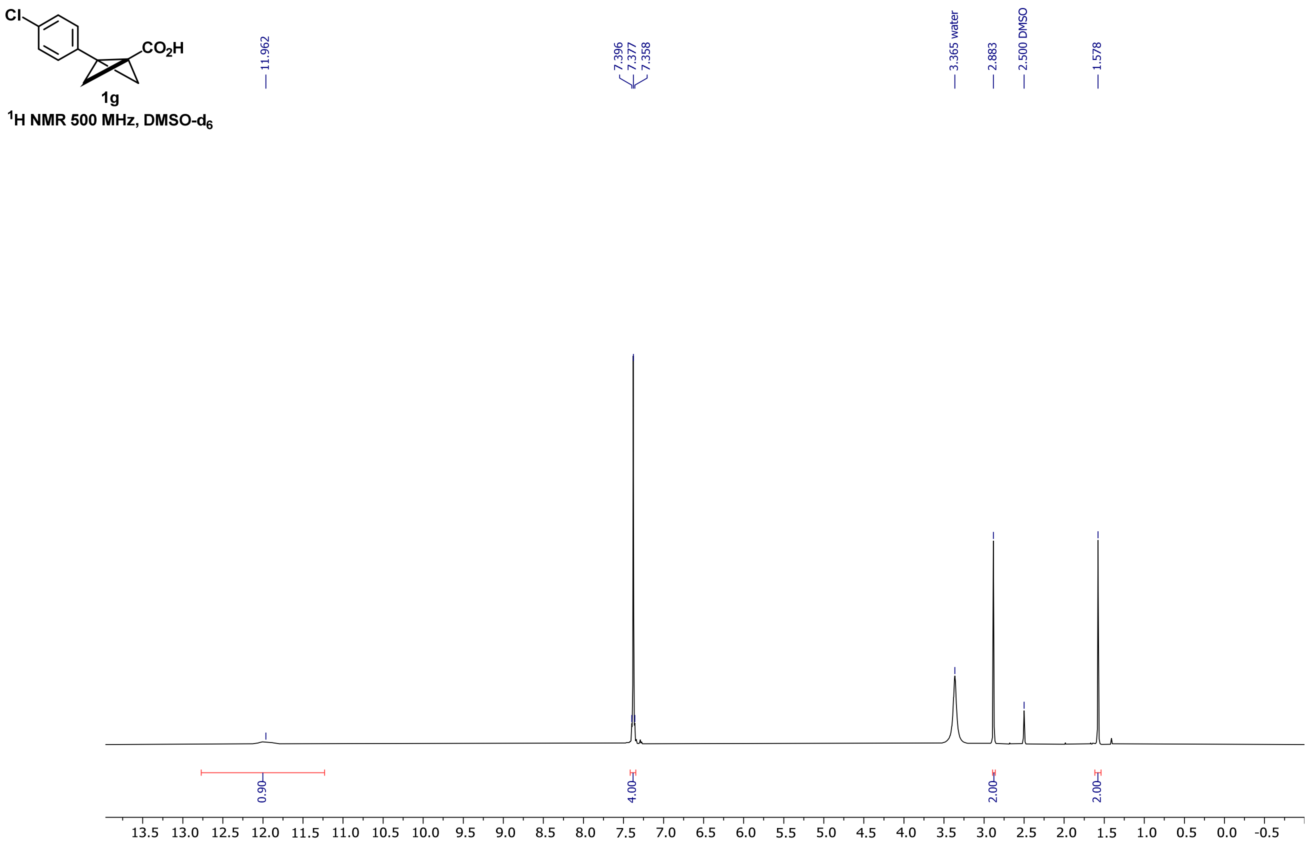


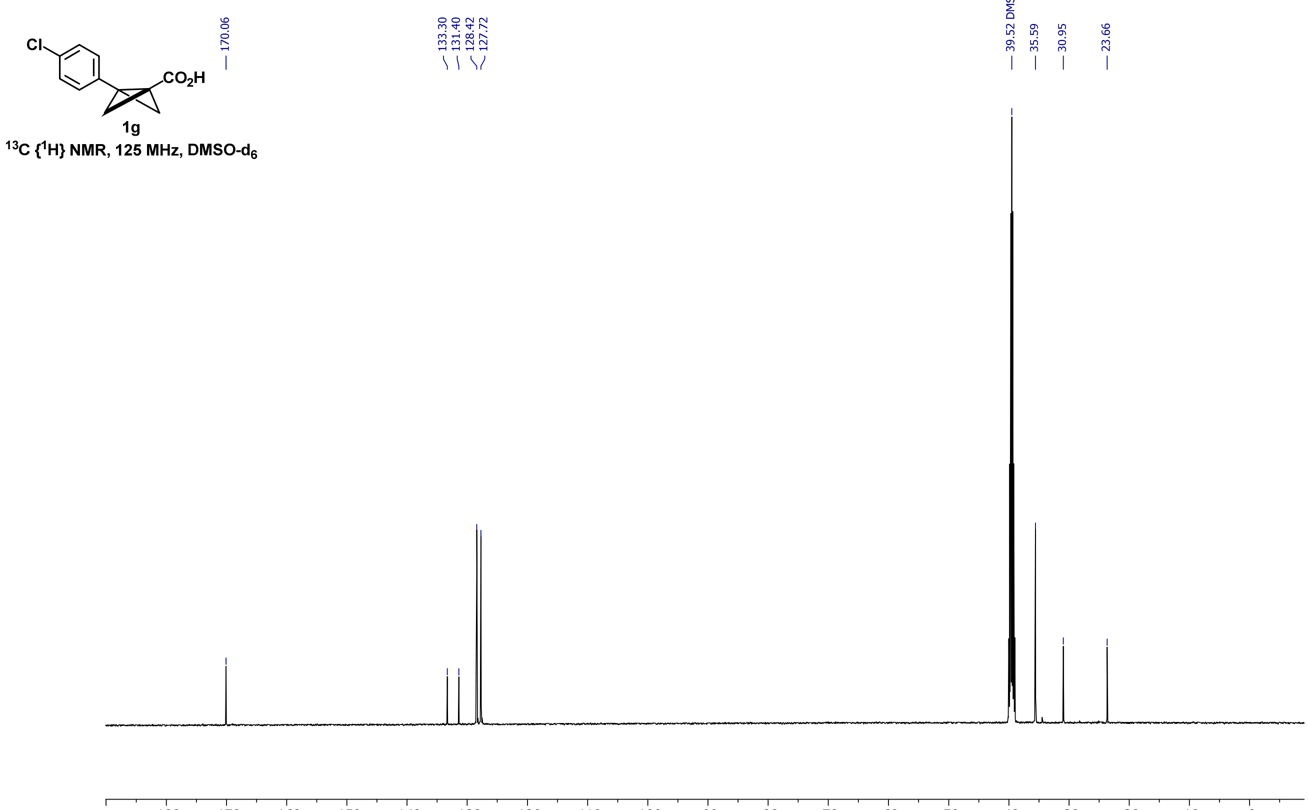


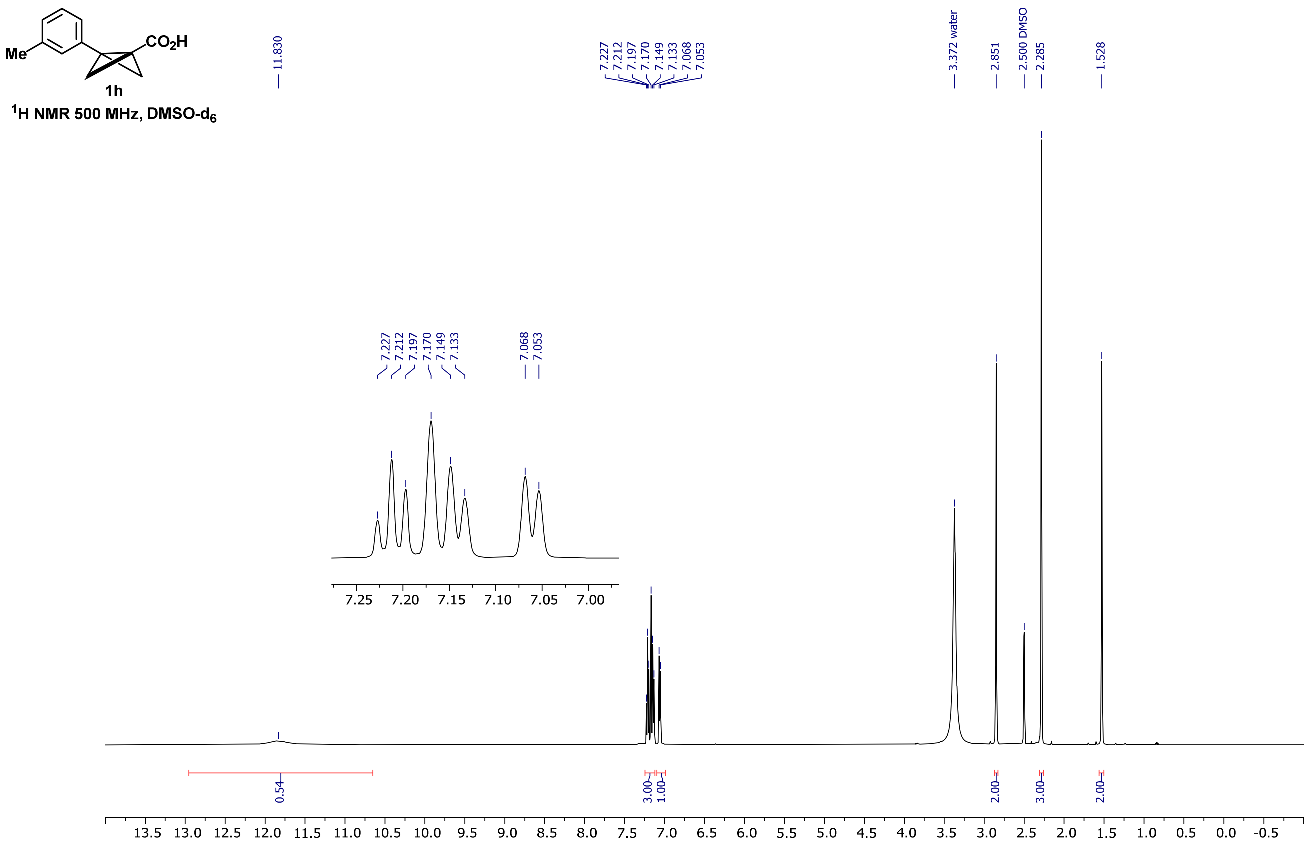
1f

^{13}C {^{1}H} NMR, 100 MHz, DMSO-d_6



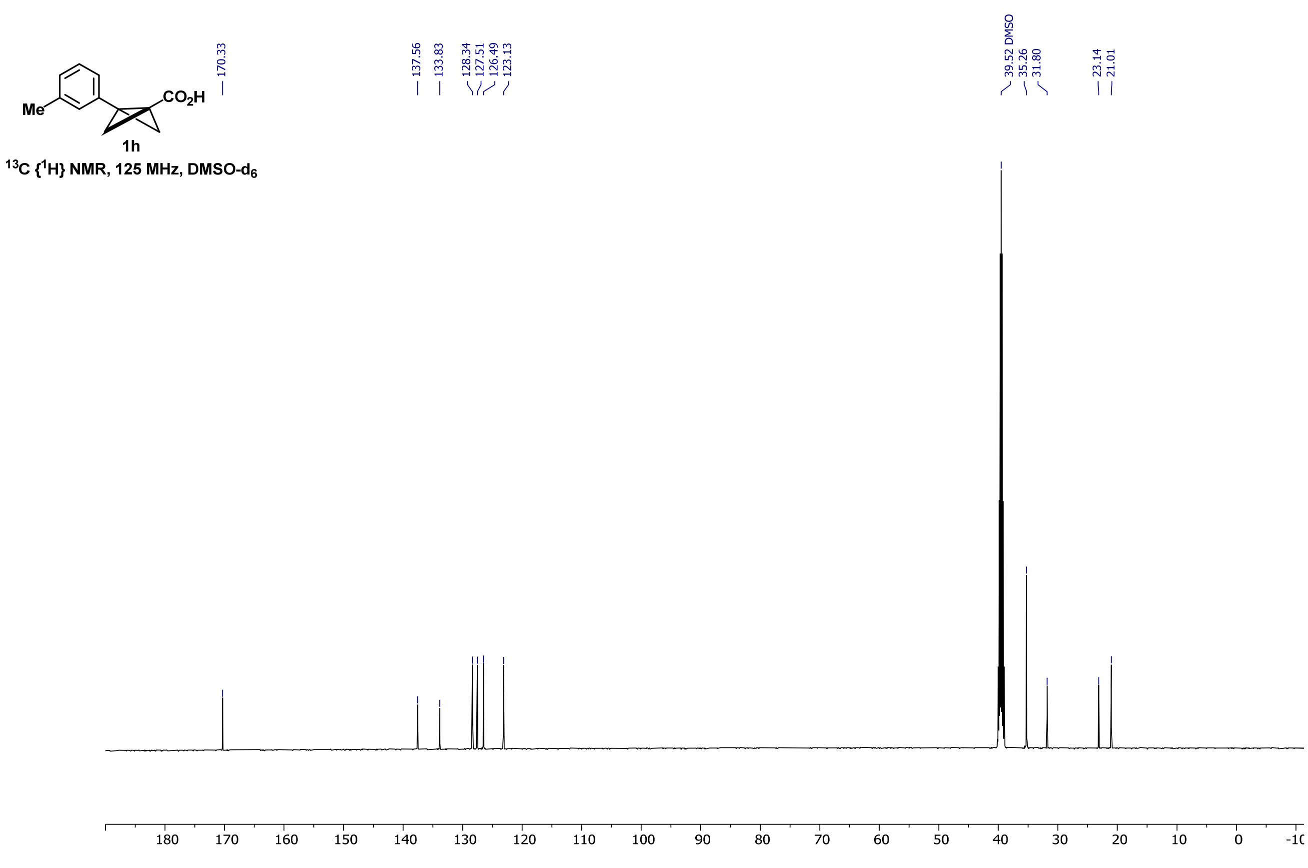

Cl
CO2H
1g
1H NMR 500 MHz, DMSO-d6
11.962
7.396
7.377
7.358
3.365 water
2.883
2.500 DMSO
1.578
0.90
4.00
2.00
2.00
13.5 13.0 12.5 12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5


Cl
CO2H
1g
13C {1H} NMR, 125 MHz, DMSO-d6
170.06
133.30
131.40
128.42
127.72
39.52 DMSO
35.59
30.95
23.66
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0



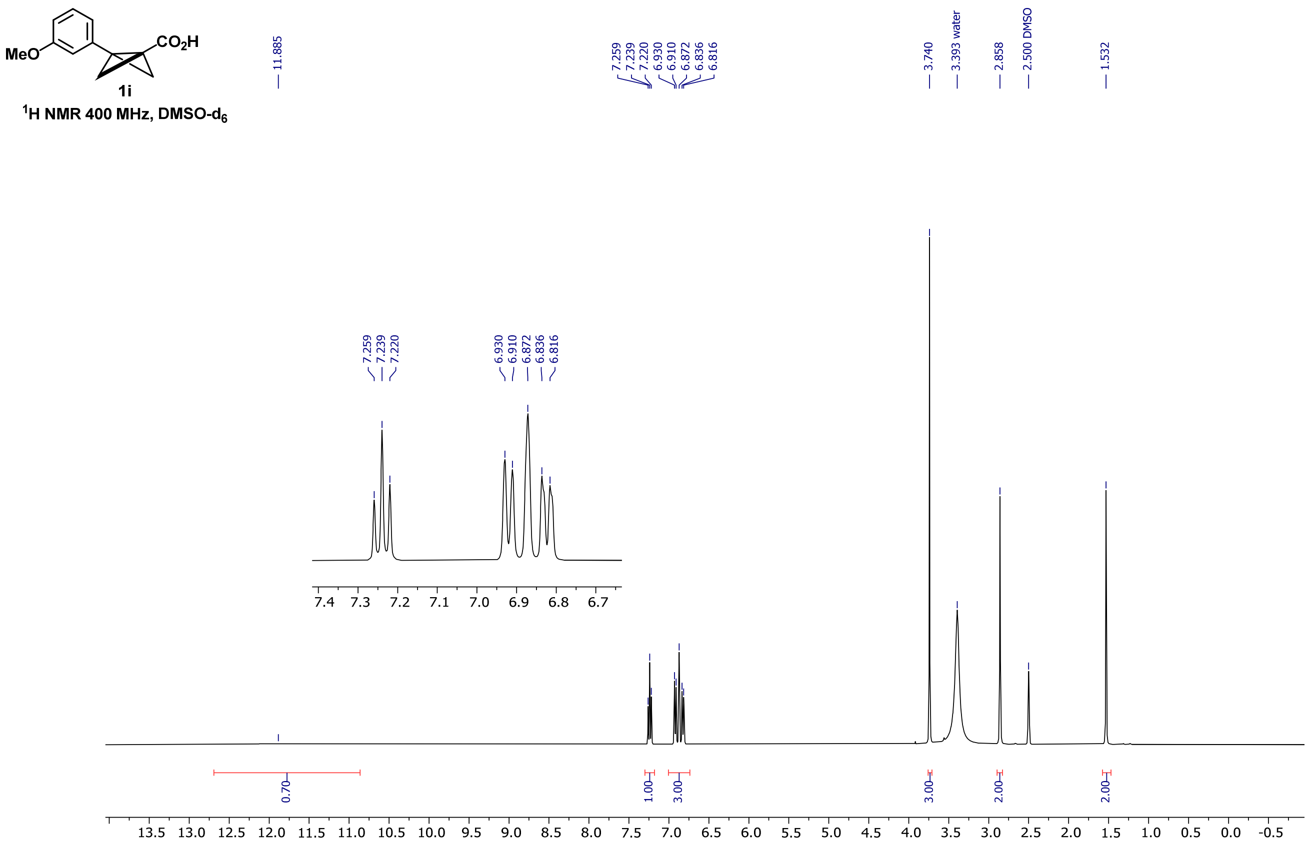
1h

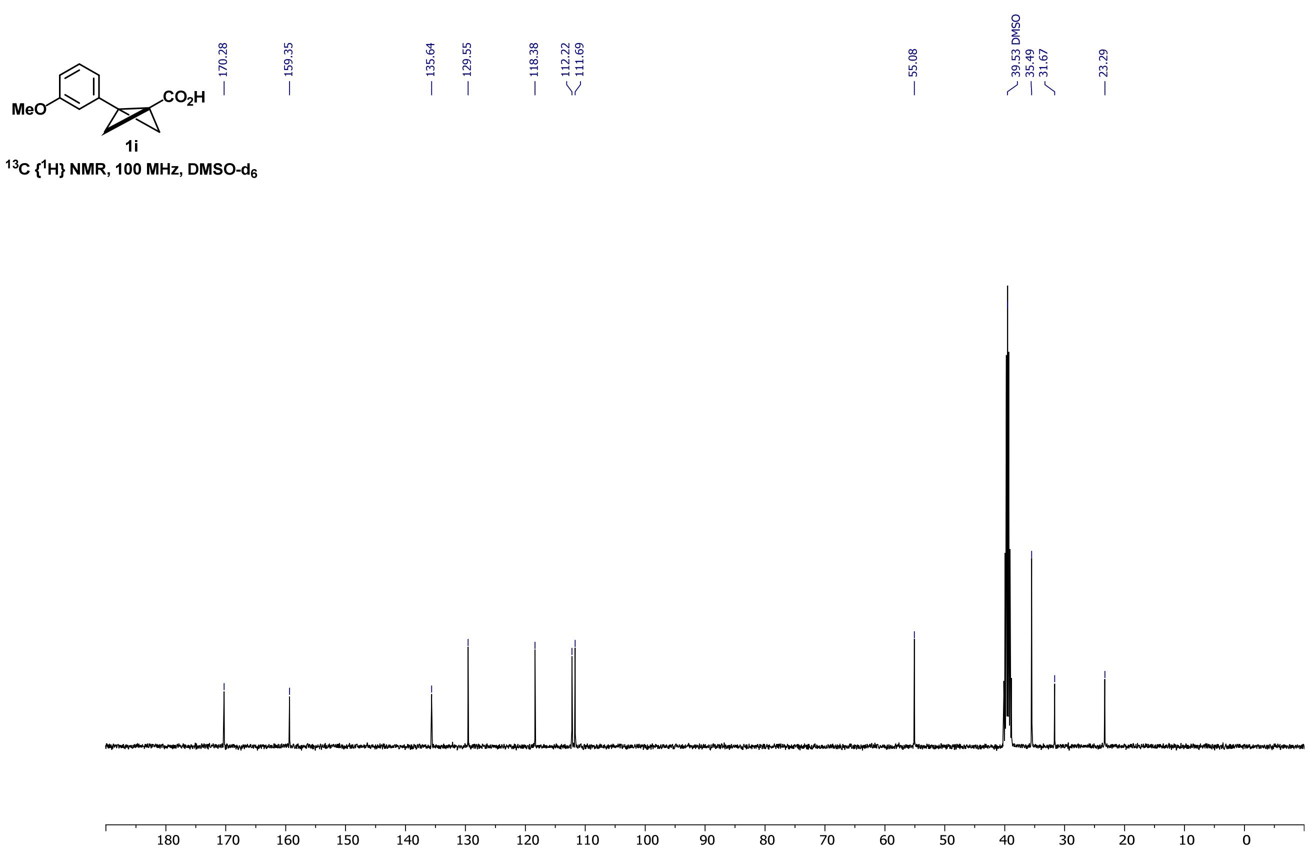
^{1}H NMR 500 MHz, DMSO-d$_6$

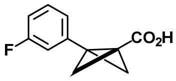


1h

^{13}C {^{1}H} NMR, 125 MHz, DMSO-d$_6$

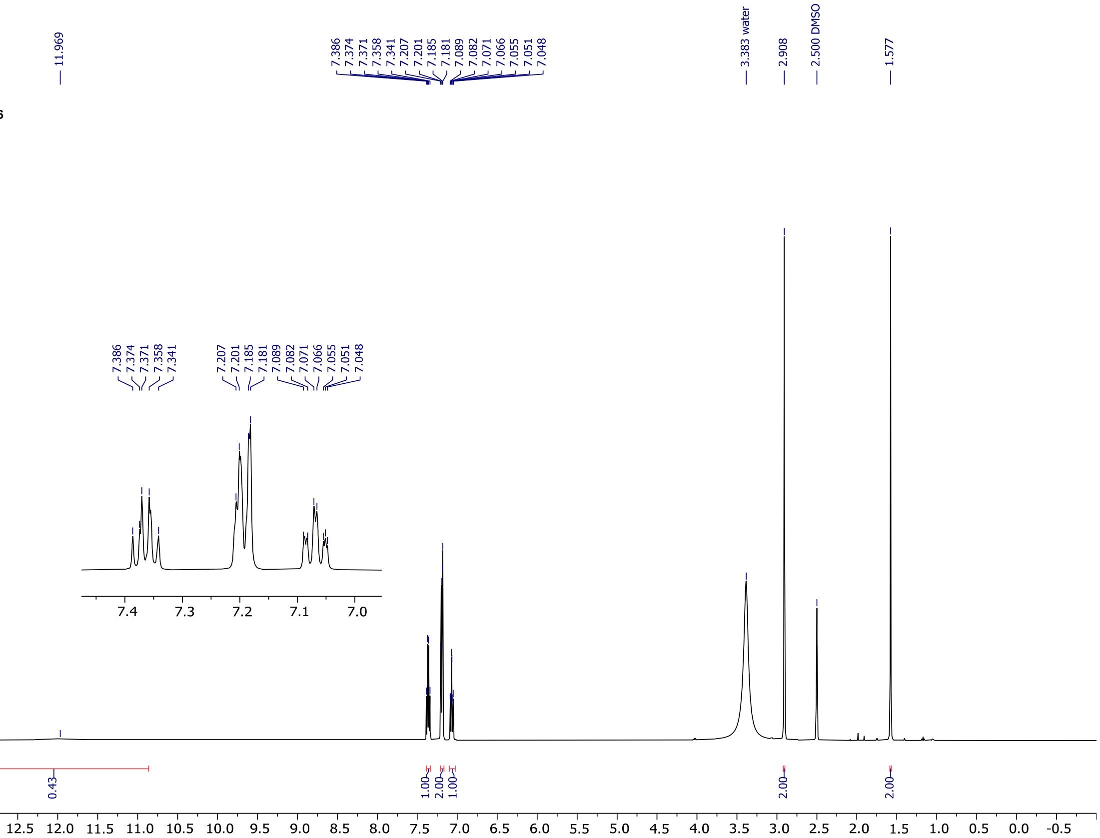

MeO
CO_2H
1i
^{1}H NMR 400 MHz, DMSO-d_6
11.885
7.259
7.239
7.220
6.930
6.910
6.872
6.836
6.816
3.740
3.393 water
2.858
2.500 DMSO
1.532
0.70
1.00
3.00
3.00
2.00
2.00

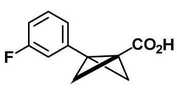

MeO
CO_2H
1i
^{13}C {^{1}H} NMR, 100 MHz, DMSO-d_6
170.28
159.35
135.64
129.55
118.38
112.22
111.69
55.08
39.53 DMSO
35.49
31.67
23.29



1j

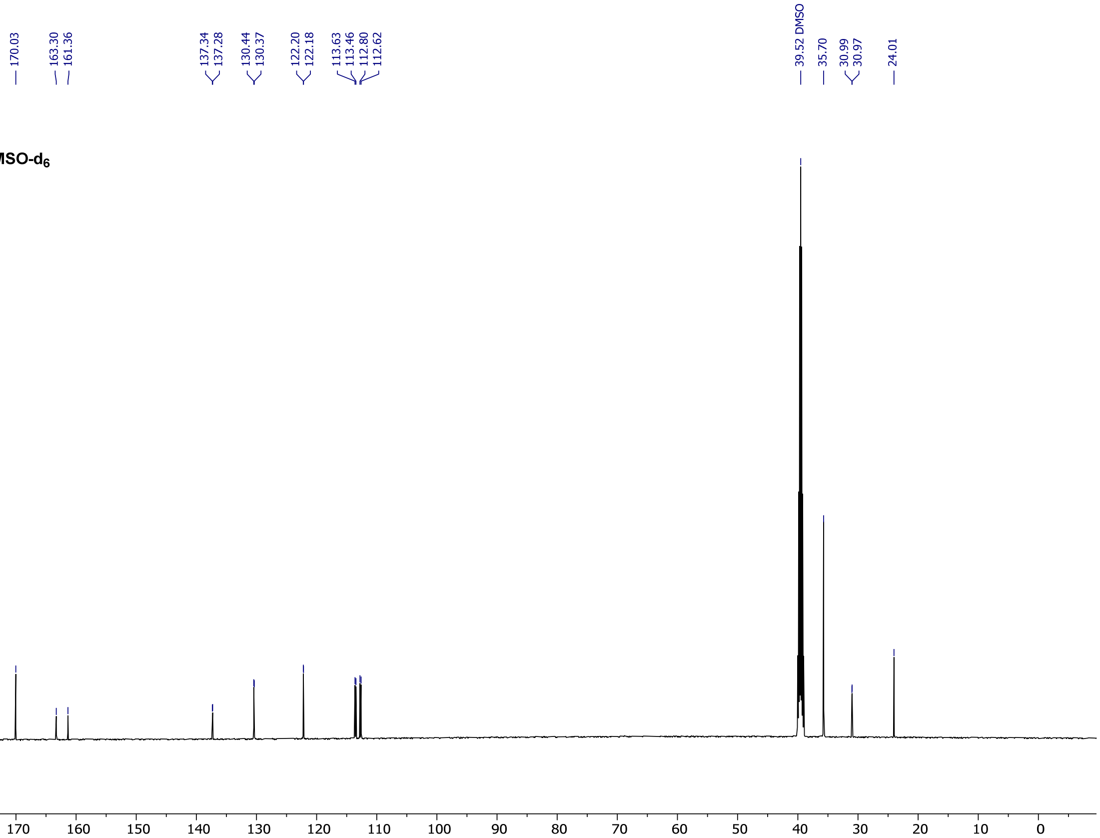
^{1}H NMR 500 MHz, DMSO-d_6

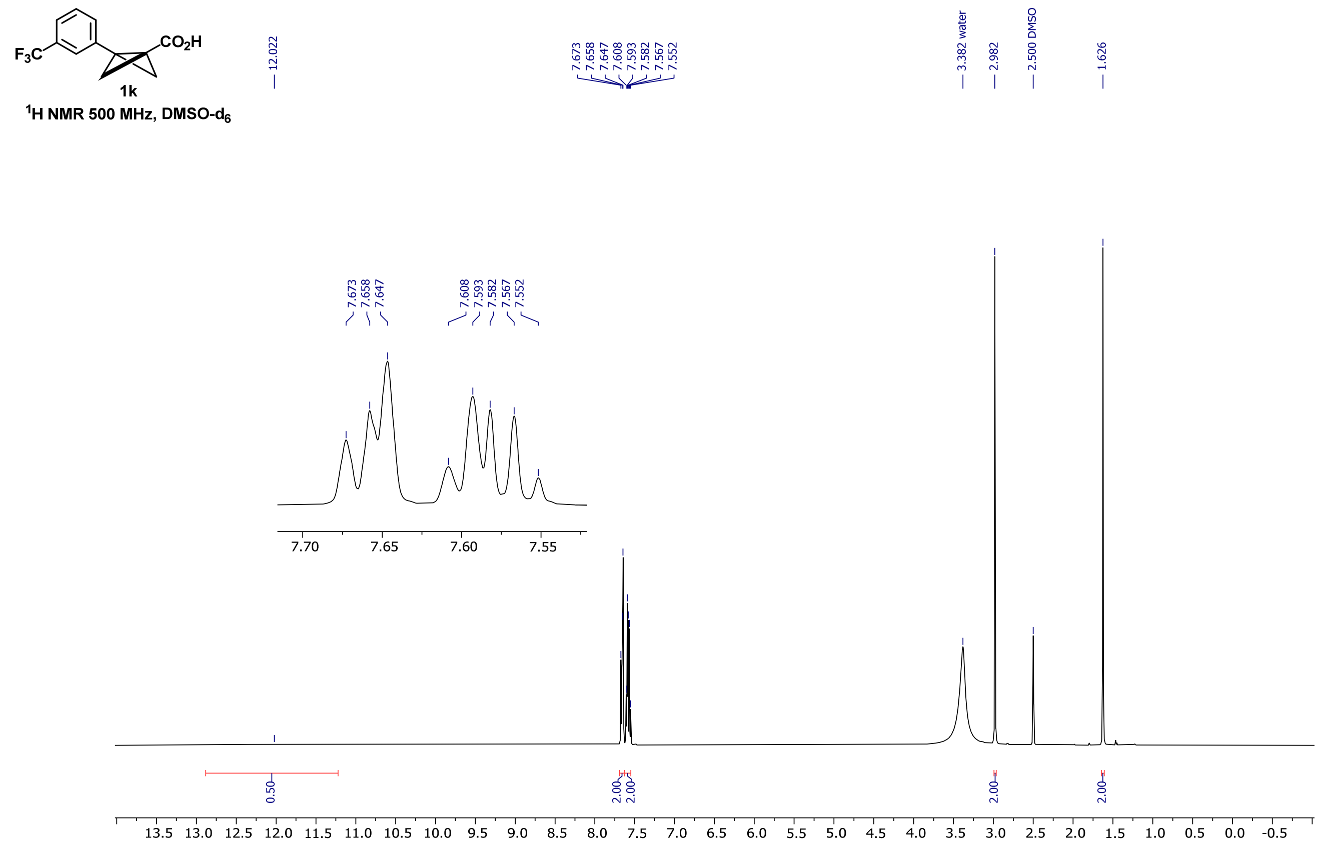


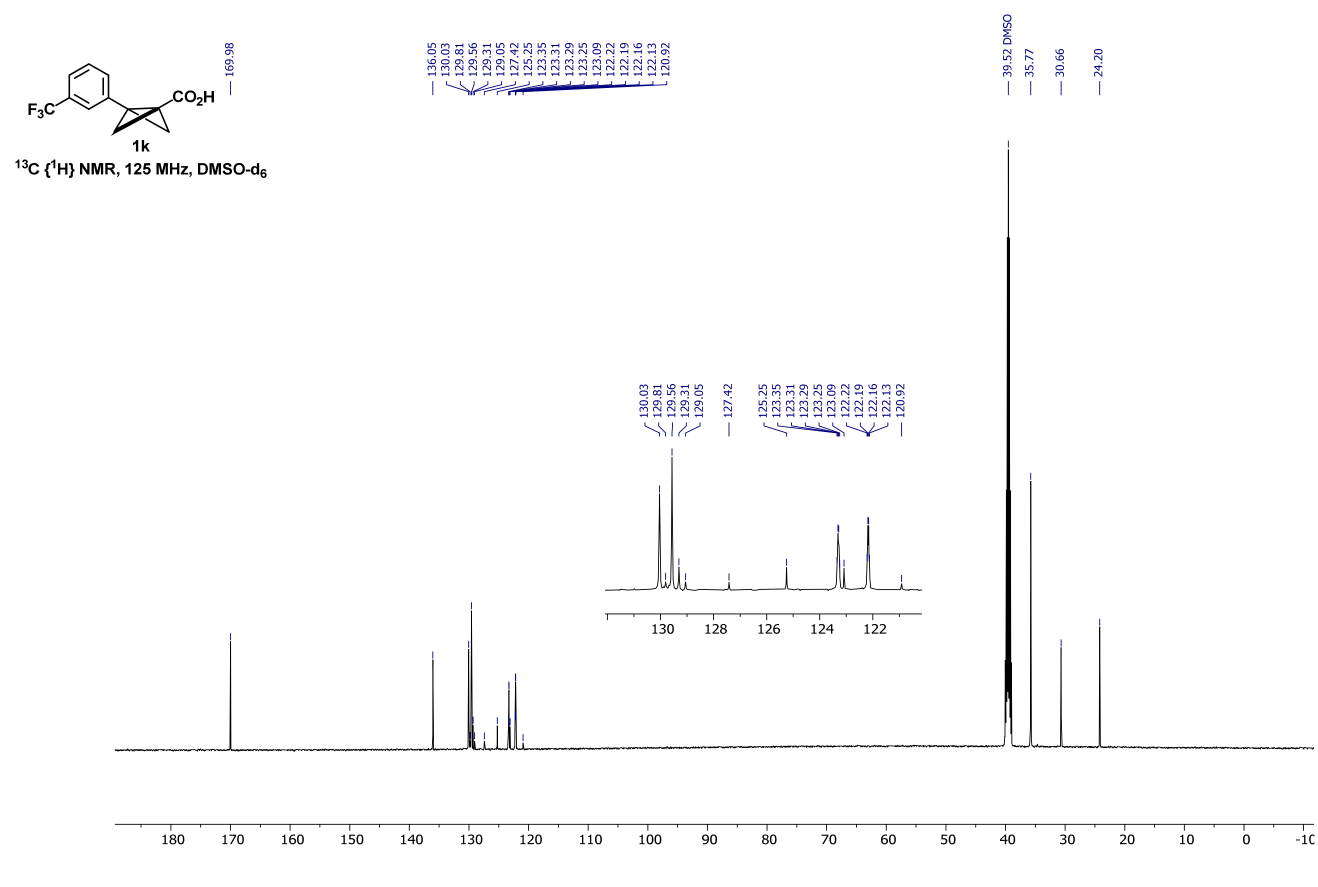


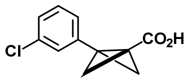
1j

^{13}C {^{1}H} NMR, 125 MHz, DMSO-d_6



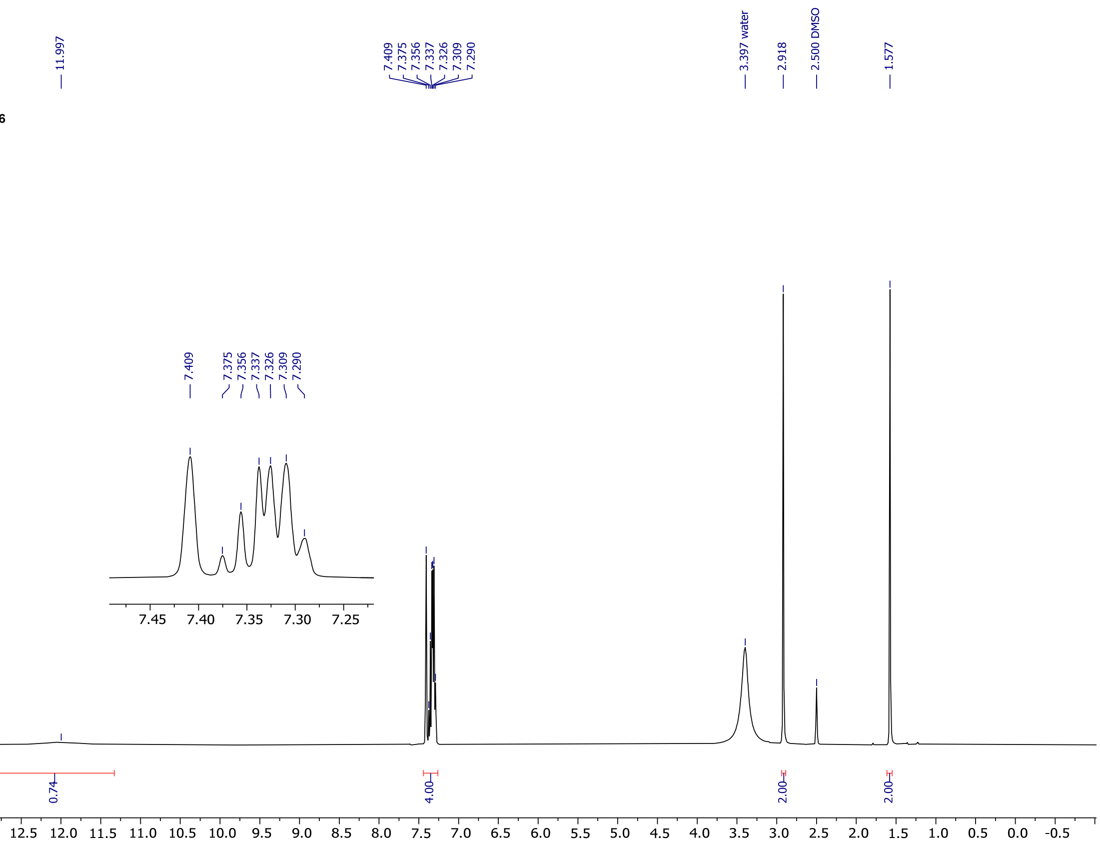

F3C
CO2H
1k
1H NMR 500 MHz, DMSO-d6
12.022
7.673
7.658
7.647
7.608
7.593
7.582
7.567
7.552
3.382 water
2.982
2.500 DMSO
1.626
0.50
2.00
2.00
2.00
2.00

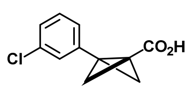

F3C
CO2H
1k
13C {1H} NMR, 125 MHz, DMSO-d6
169.98
136.05
130.03
129.81
129.56
129.31
129.05
127.42
125.25
123.35
123.31
123.29
123.25
123.09
122.22
122.19
122.16
122.13
120.92
39.52 DMSO
35.77
30.66
24.20



1l

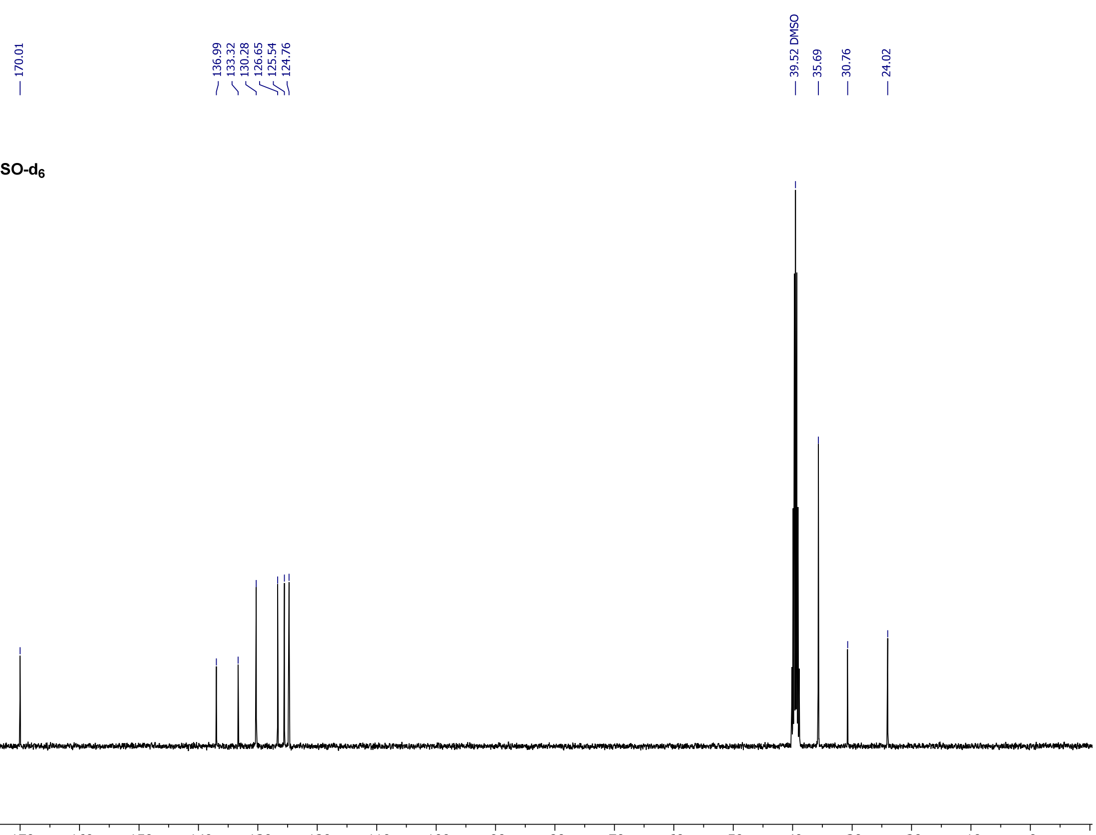
^{1}H NMR 400 MHz, DMSO-d_6

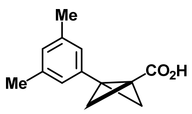




1l

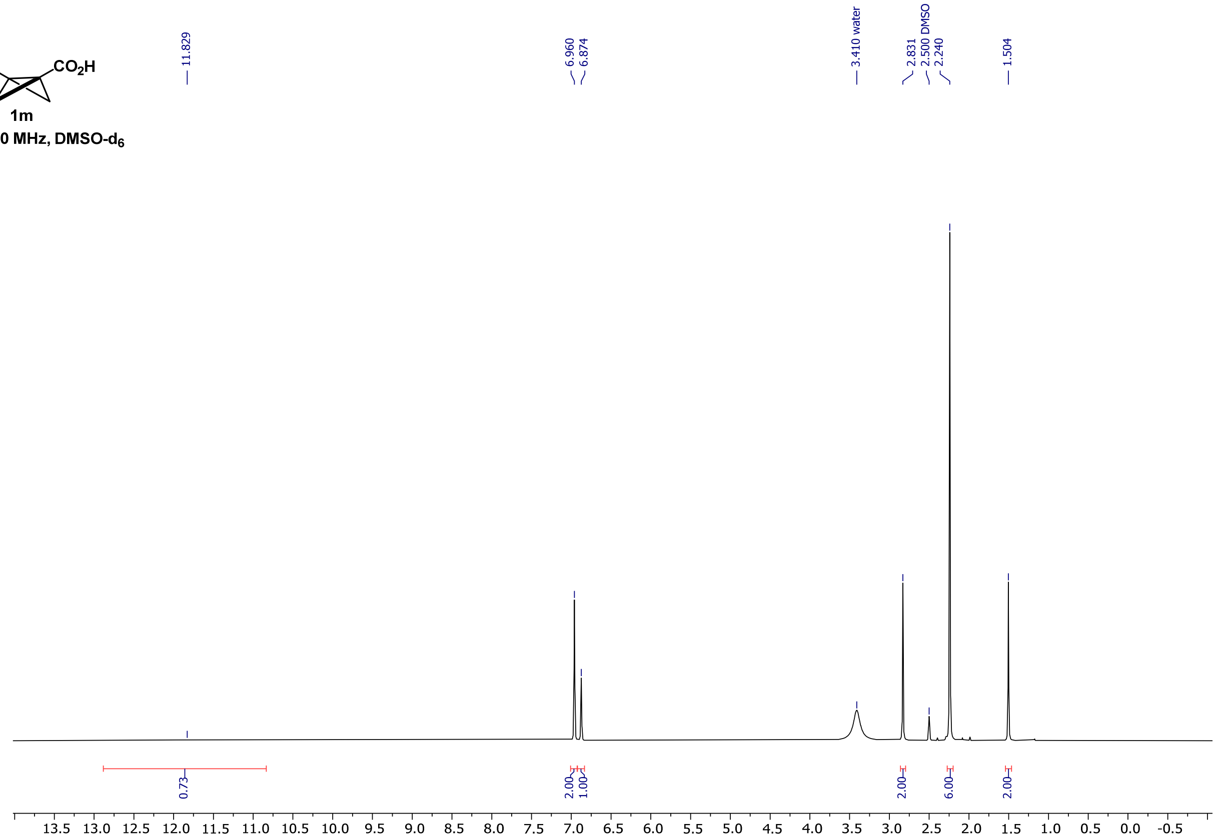
^{13}C {^{1}H} NMR, 100 MHz, DMSO-d_6

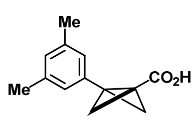




1m

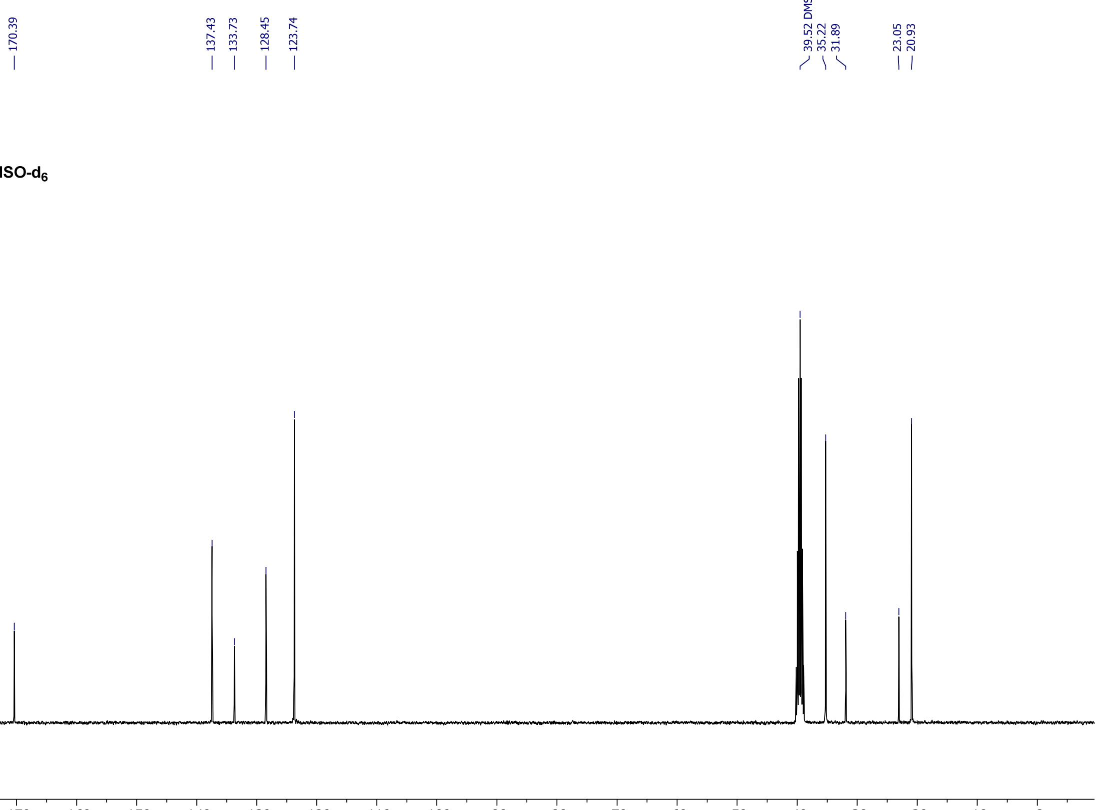
[1]H NMR 400 MHz, DMSO-d$_6$

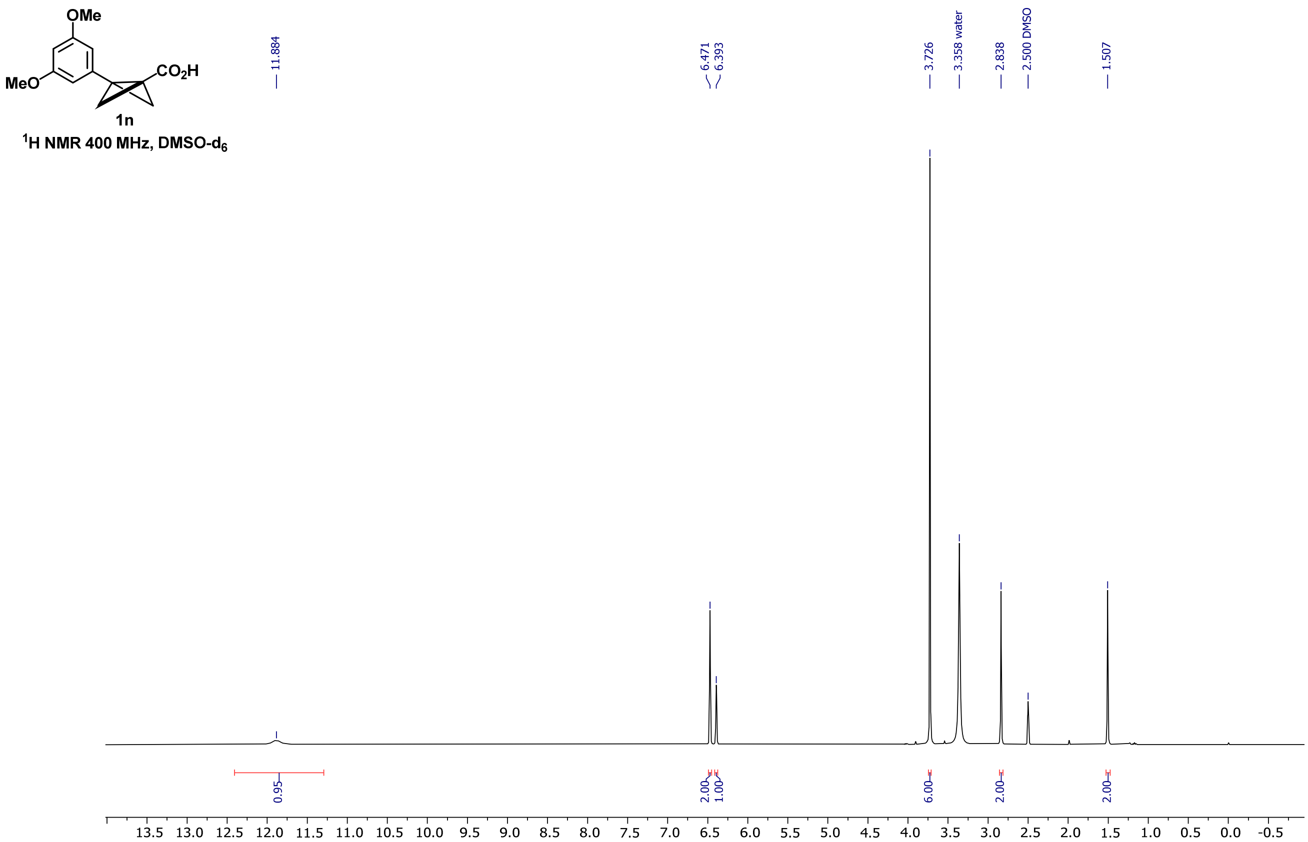




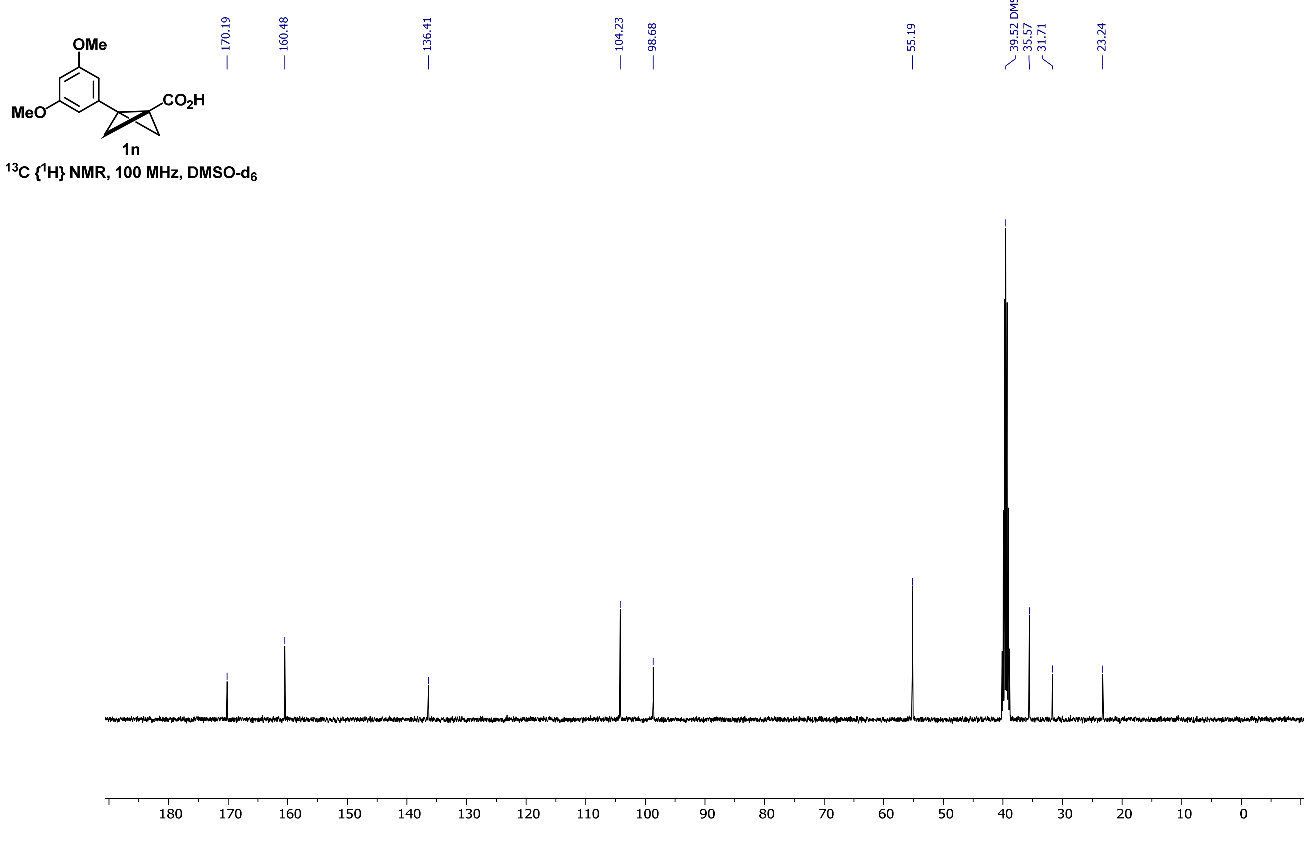
1m

[13]C {[1]H} NMR, 100 MHz, DMSO-d$_6$

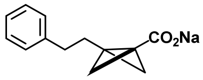




OMe
MeO
CO_2H
1n
^{1}H NMR 400 MHz, DMSO-d_6
11.884
6.471
6.393
3.726
3.358 water
2.838
2.500 DMSO
1.507
0.95
2.00
1.00
6.00
2.00
2.00
13.5 13.0 12.5 12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5



OMe
MeO
CO_2H
1n
^{13}C {^{1}H} NMR, 100 MHz, DMSO-d_6
170.19
160.48
136.41
104.23
98.68
55.19
39.52 DMSO
35.57
31.71
23.24
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0

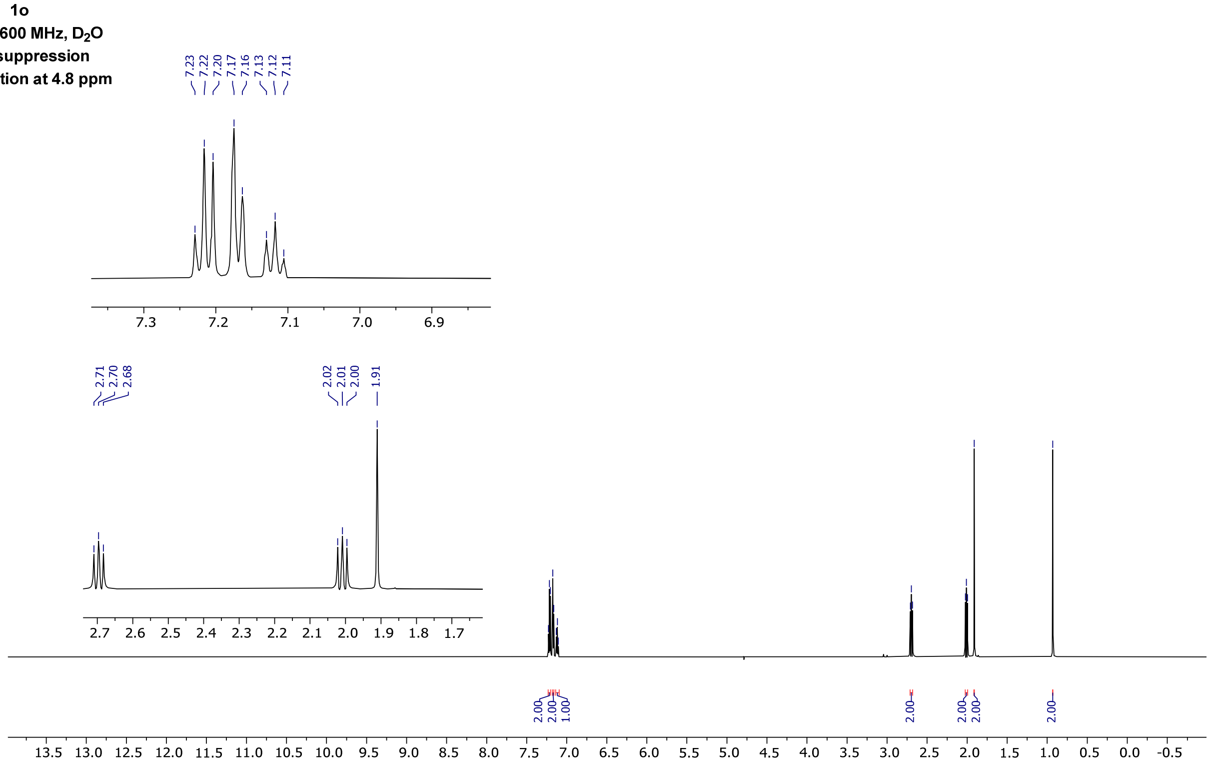


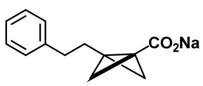
1o

^1H NMR 600 MHz, D_2O

water suppression

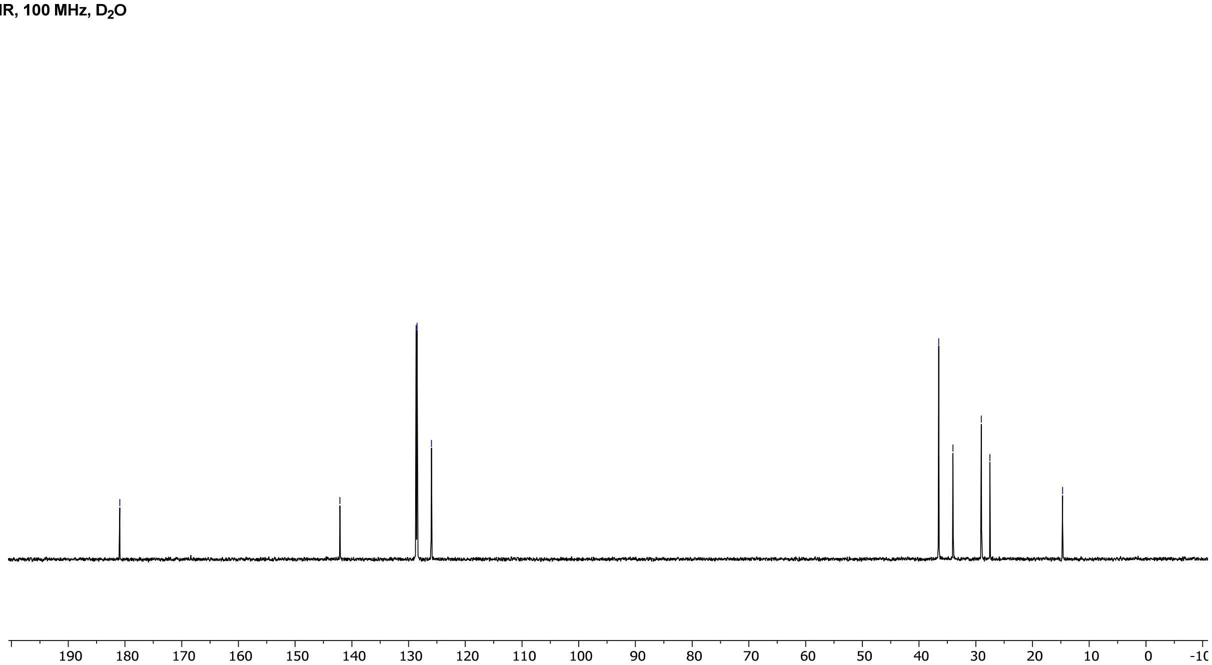
presaturation at 4.8 ppm

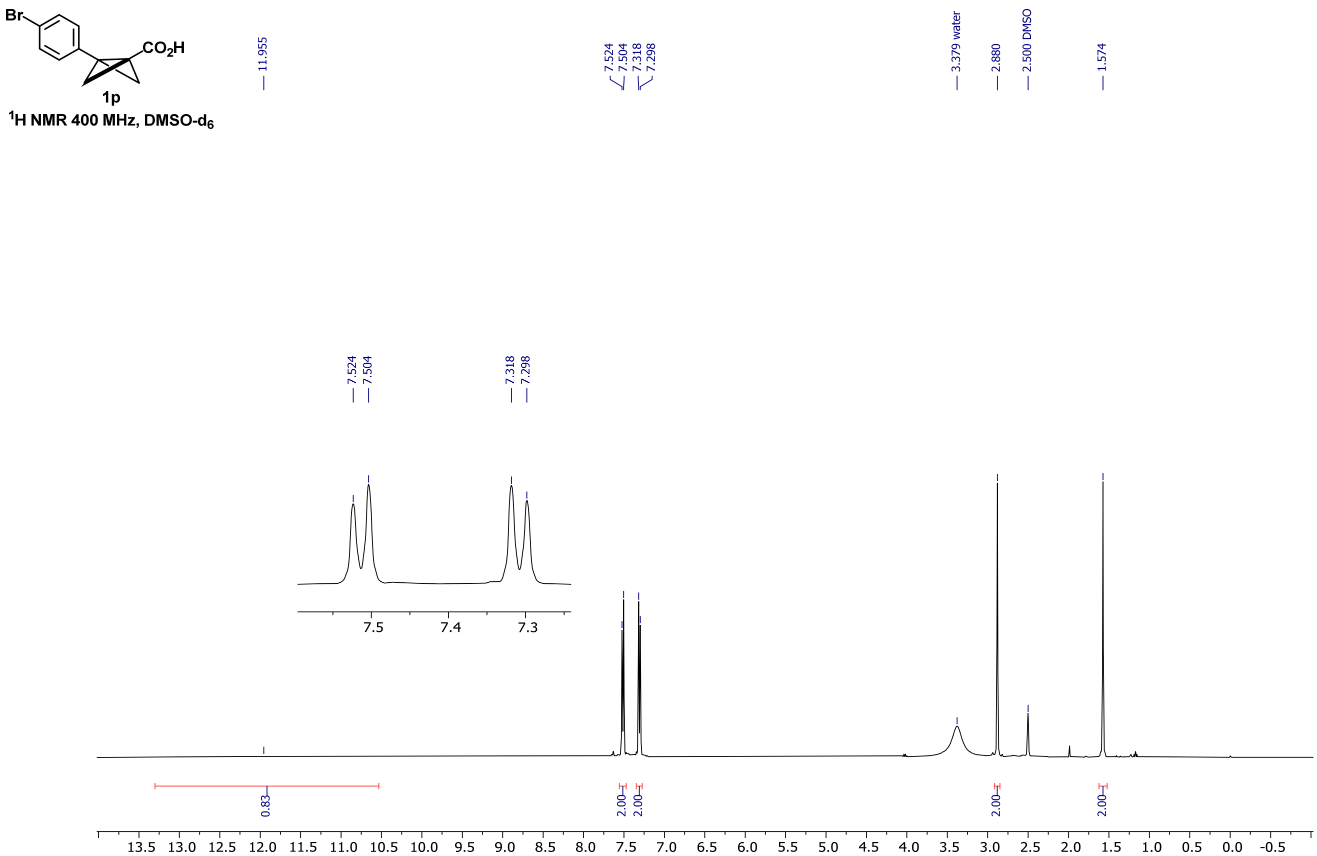


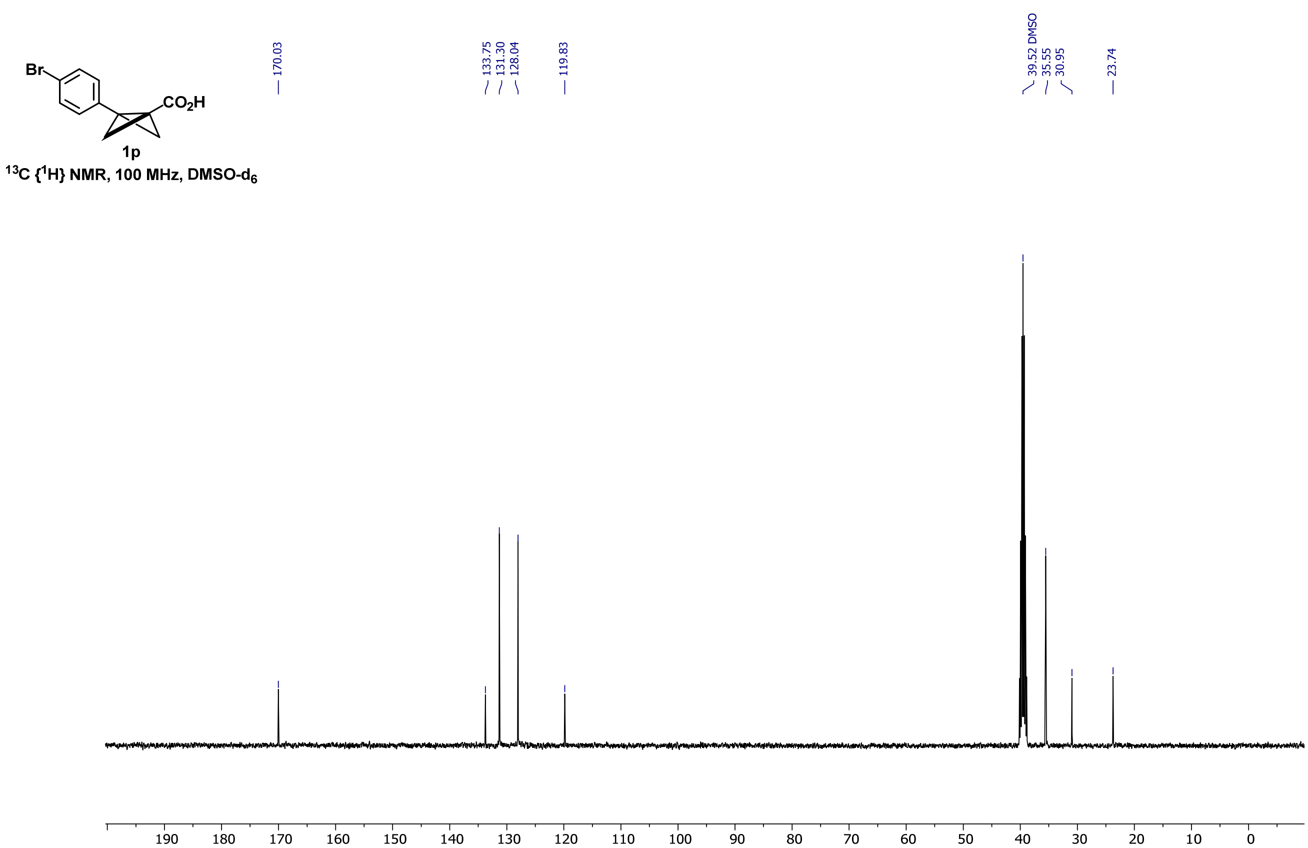


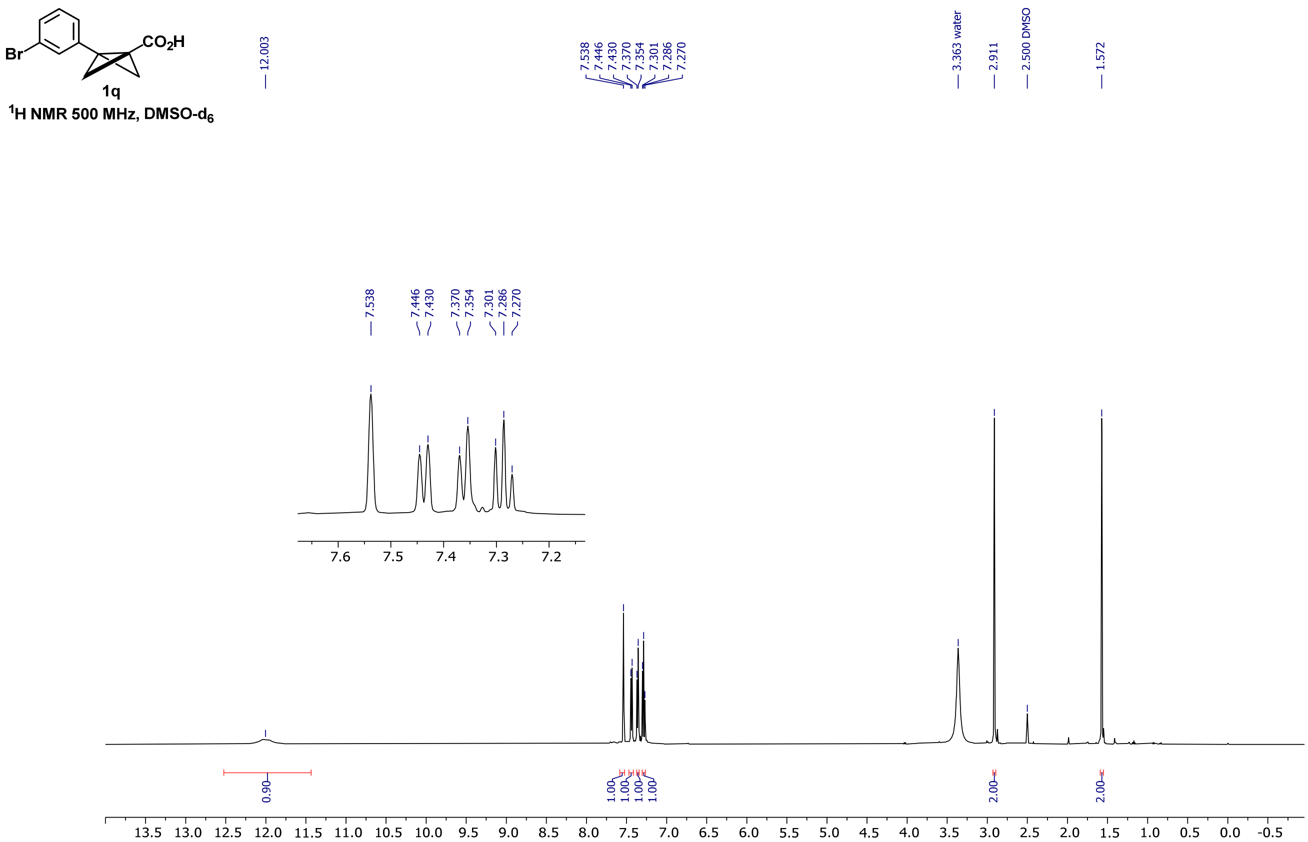
1o

^{13}C {^1H} NMR, 100 MHz, D_2O

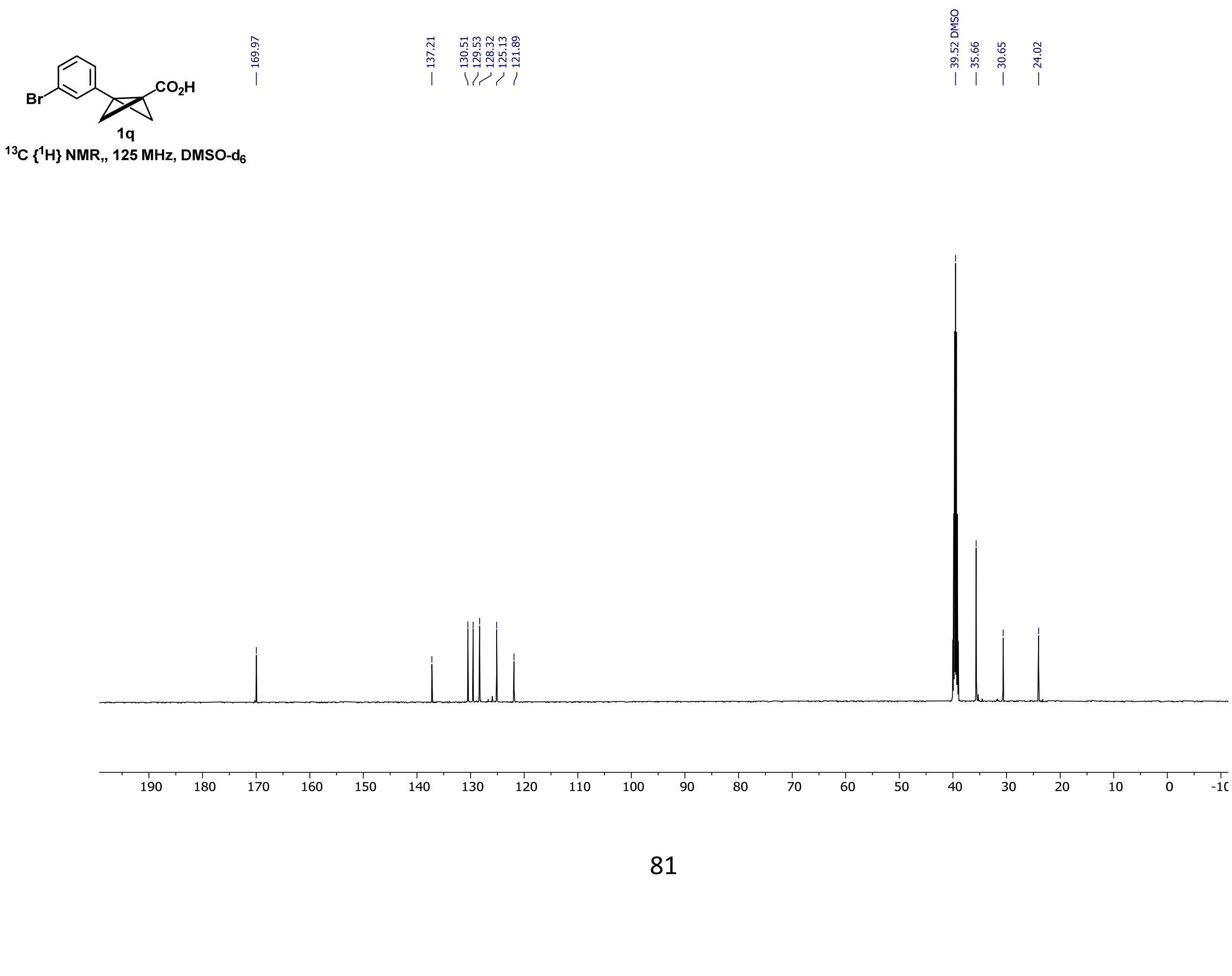



Br
CO2H
1p
1H NMR 400 MHz, DMSO-d6
11.955
7.524
7.504
7.318
7.298
3.379 water
2.880
2.500 DMSO
1.574
0.83
2.00
2.00
2.00
2.00

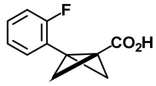

Br
CO2H
1p
13C {1H} NMR, 100 MHz, DMSO-d6
170.03
133.75
131.30
128.04
119.83
39.52 DMSO
35.55
30.95
23.74



Br
CO_2H
1q
^{1}H NMR 500 MHz, DMSO-d$_6$
12.003
7.538 7.446 7.430 7.370 7.354 7.301 7.286 7.270
3.363 water
2.911
2.500 DMSO
1.572
0.90
1.00 1.00 1.00 1.00
2.00
2.00

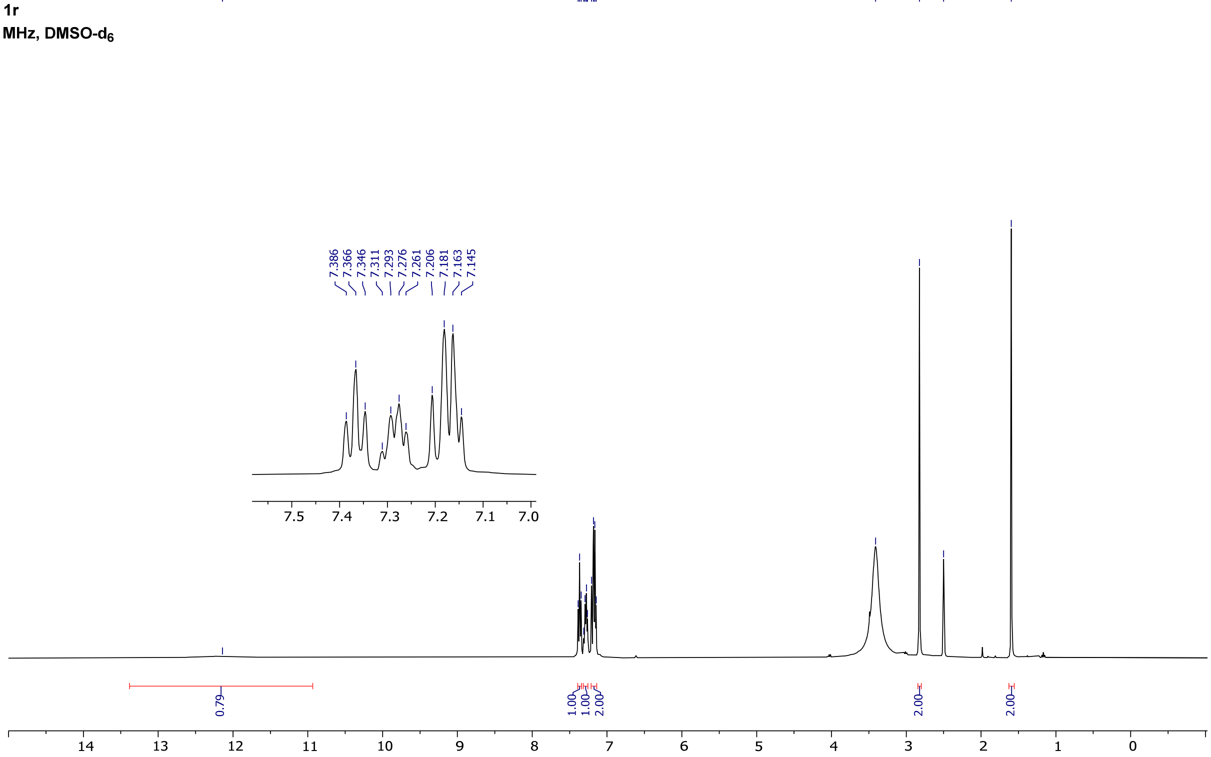


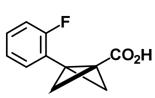
Br
CO_2H
1q
^{13}C {^{1}H} NMR,, 125 MHz, DMSO-d$_6$
169.97
137.21
130.51 129.53 128.32 125.13 121.89
39.52 DMSO
35.66
30.65
24.02



1r

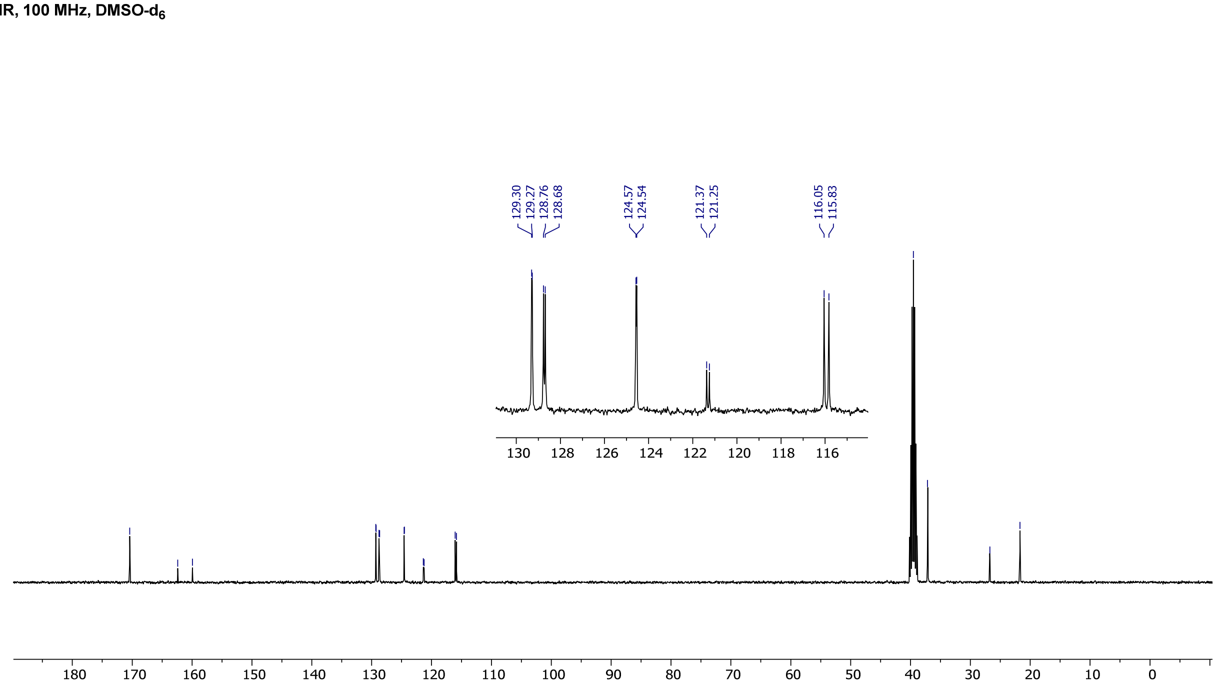
[1]H NMR 400 MHz, DMSO-d6

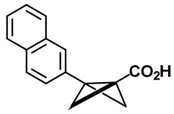




1r

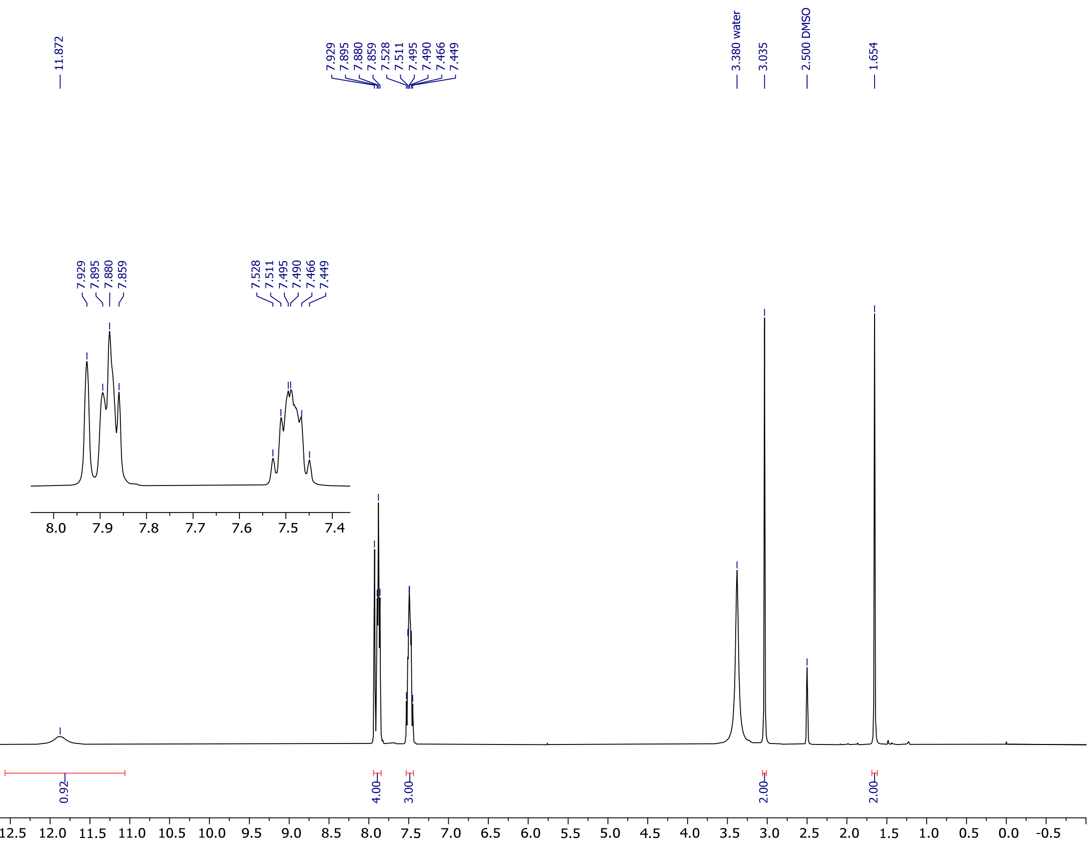
[13]C {[1]H} NMR, 100 MHz, DMSO-d6

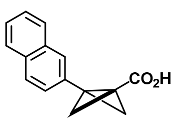




1s

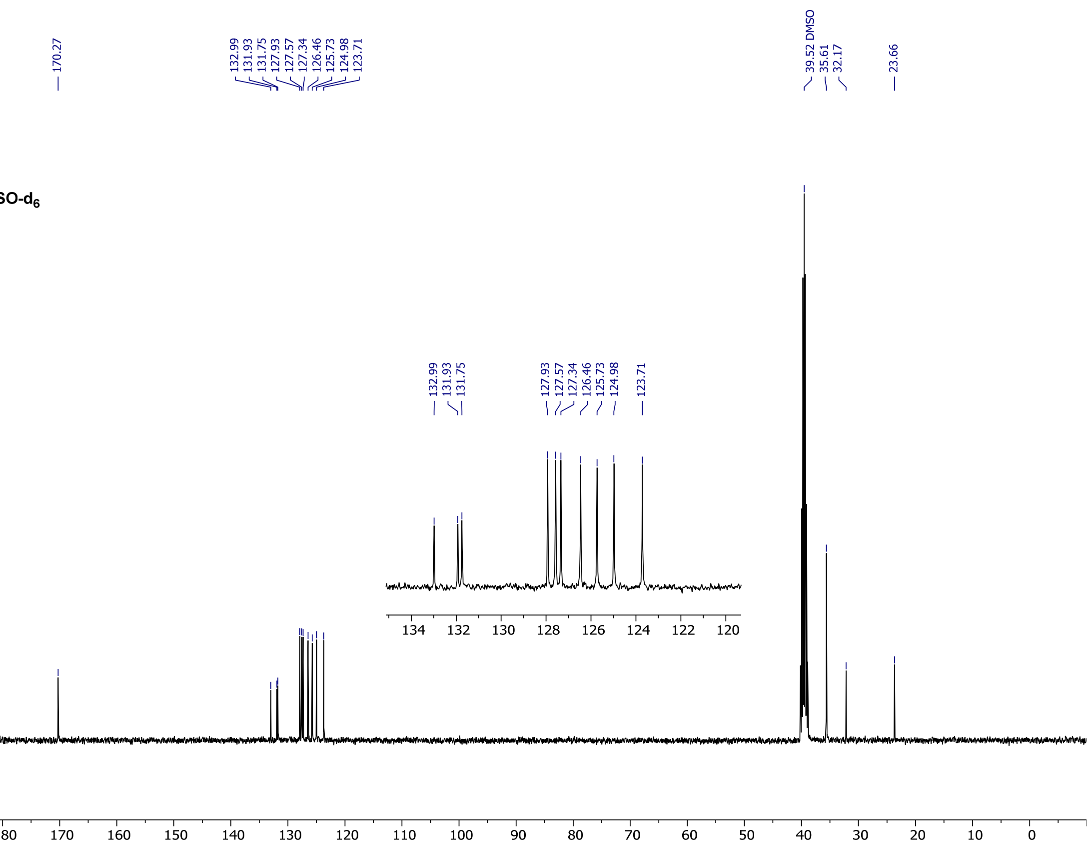
^{1}H NMR 400 MHz, DMSO-d$_6$

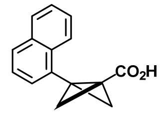




1s

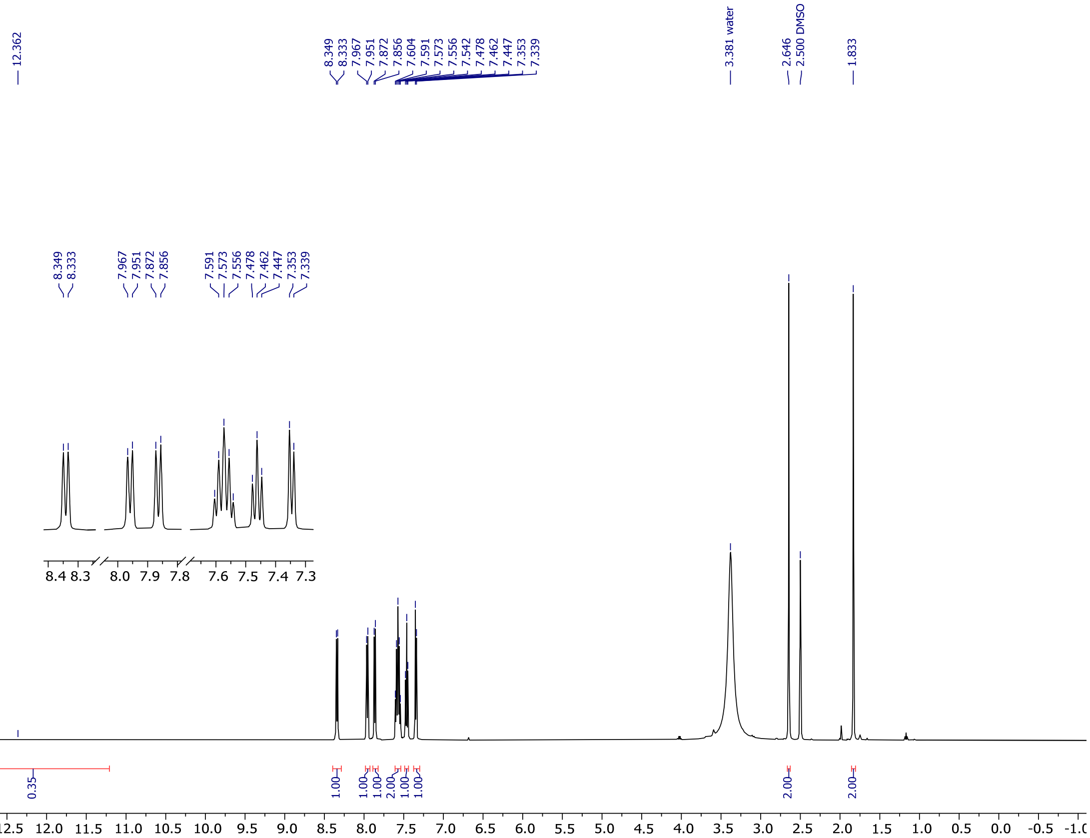
^{13}C {^{1}H} NMR, 100 MHz, DMSO-d$_6$

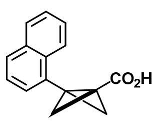




1t

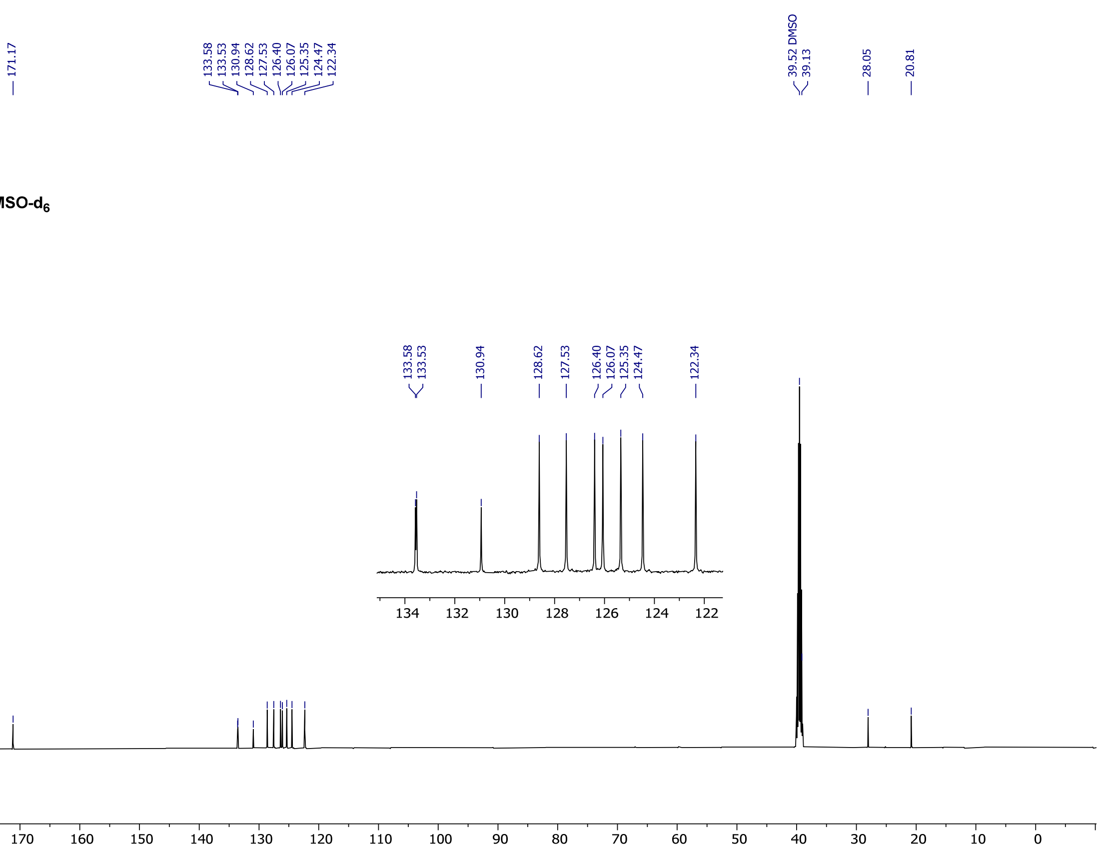
^{1}H NMR 500 MHz, DMSO-d$_6$

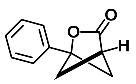




1t

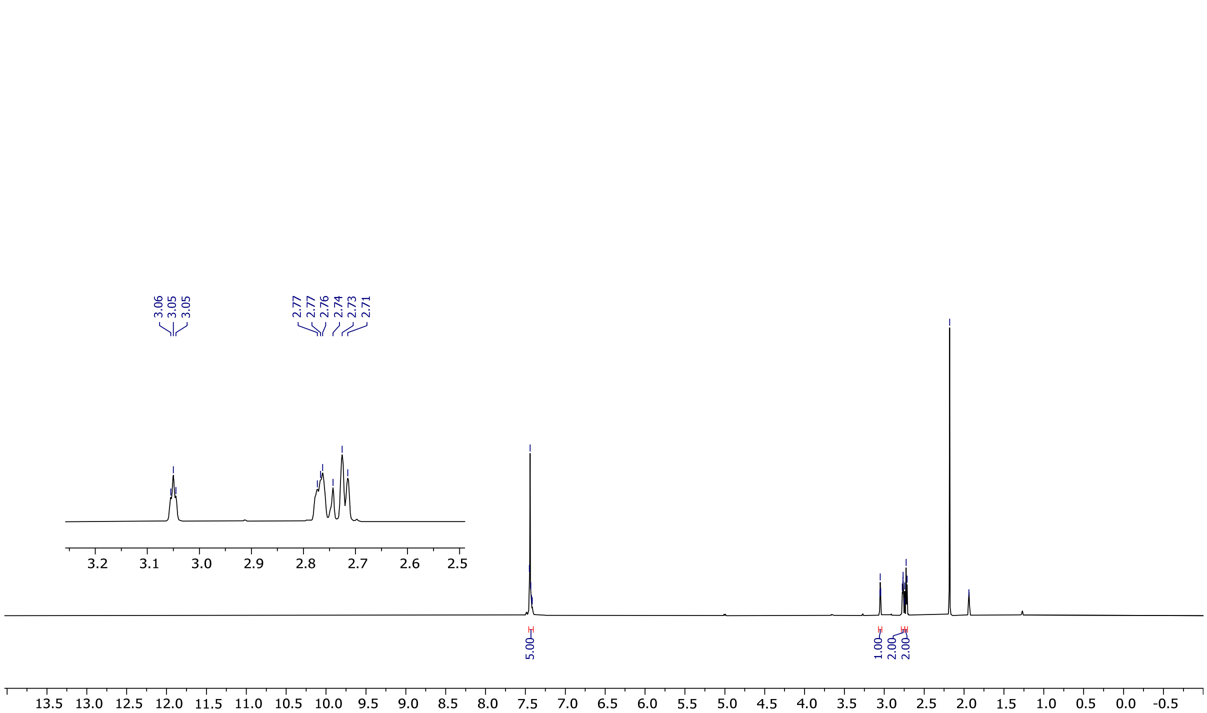
^{13}C {^{1}H} NMR, 125 MHz, DMSO-d$_6$

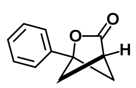




2a

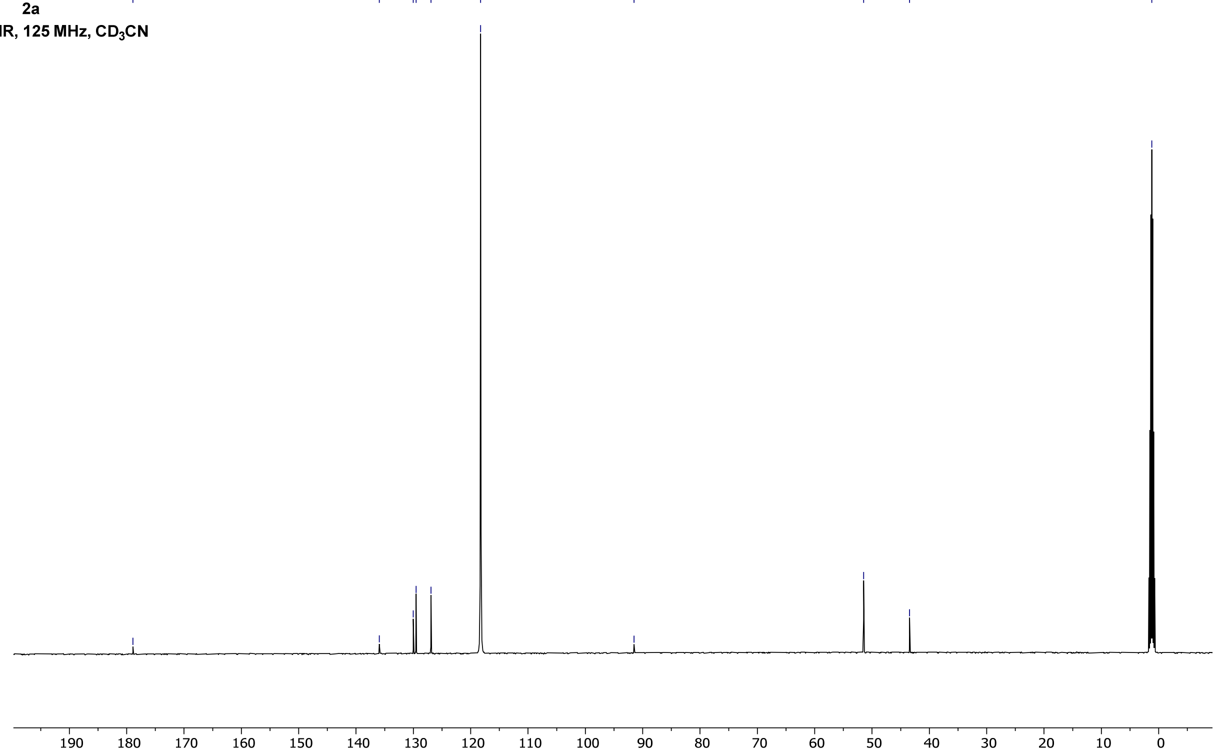
^{1}H NMR, 500 MHz, CD_3CN

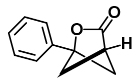




2a

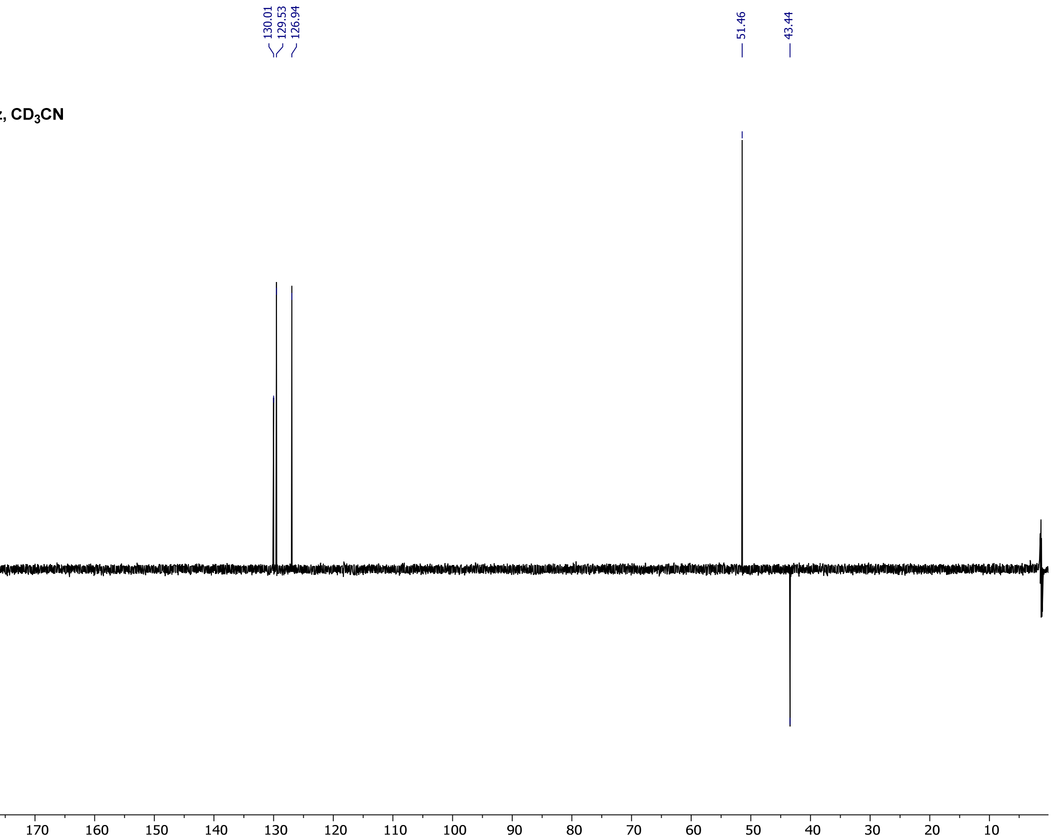
^{13}C {^{1}H} NMR, 125 MHz, CD_3CN

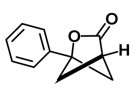




2a

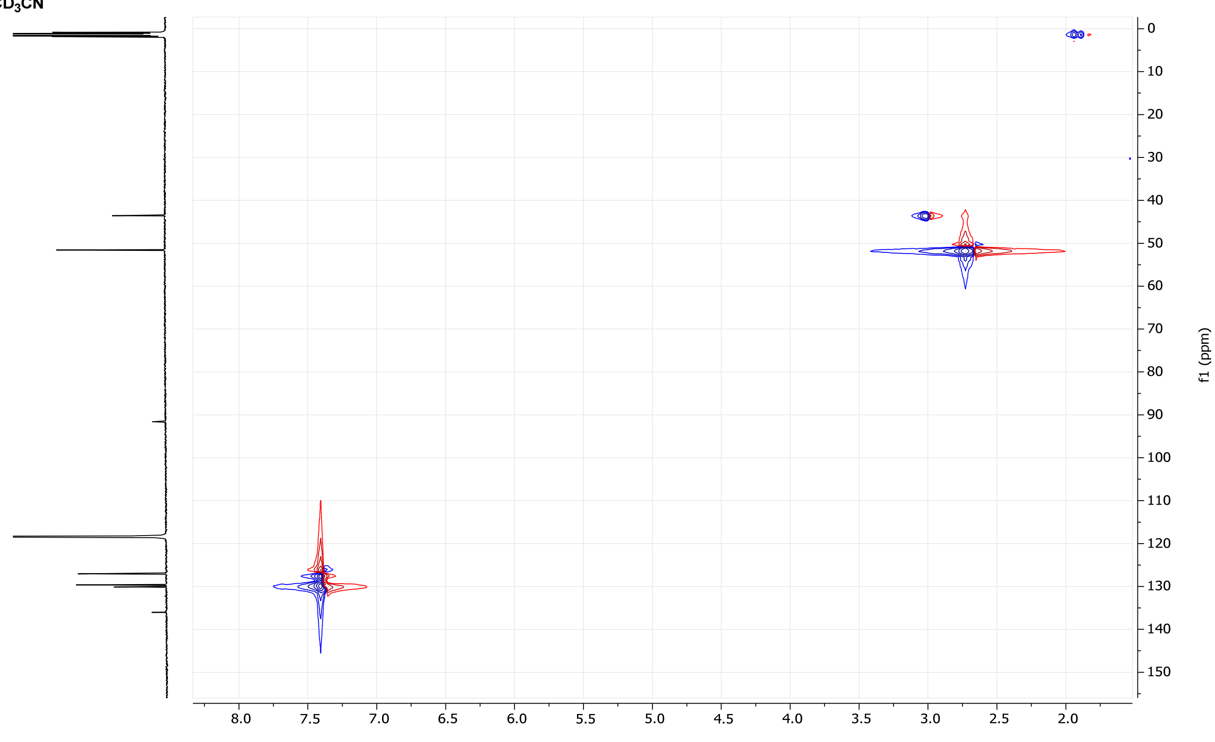
^{13}C {^{1}H} DEPT-135 NMR, 200 MHz, CD_3CN

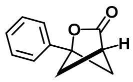




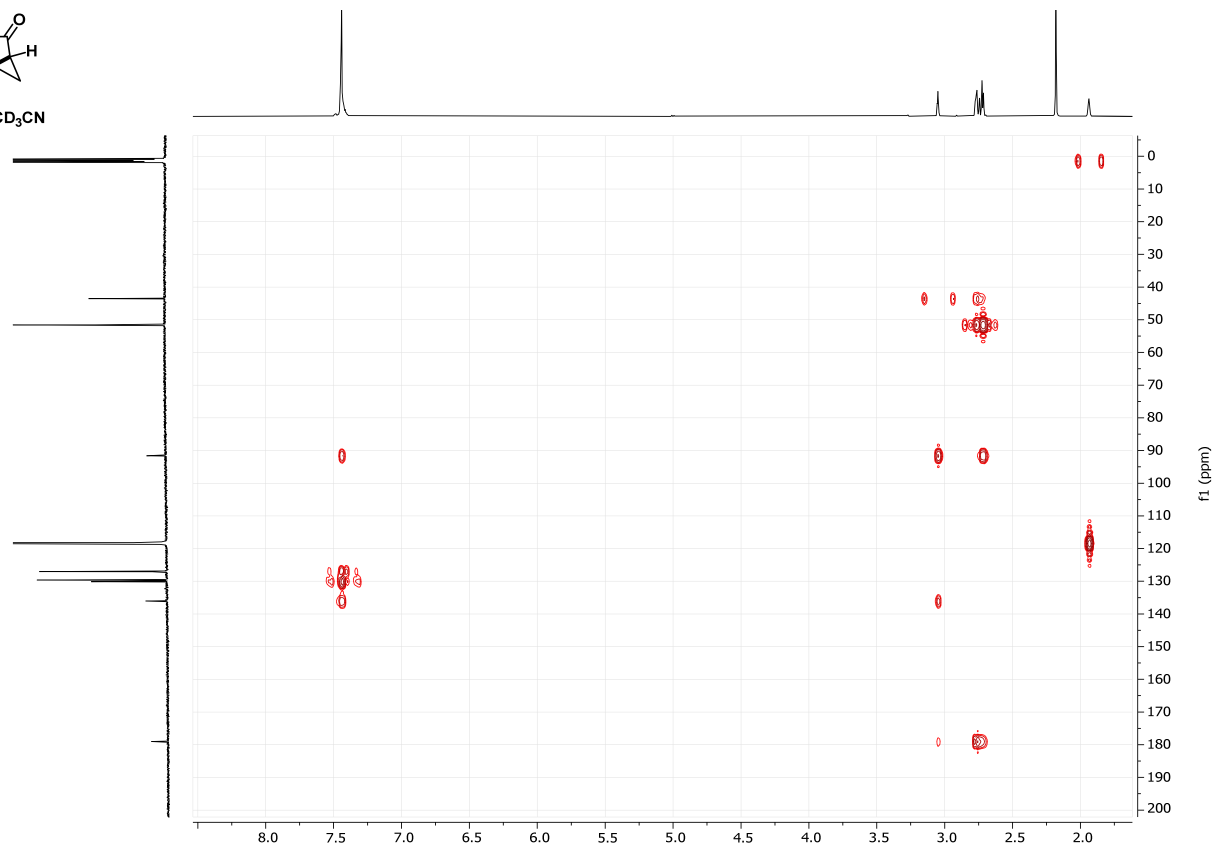
2a

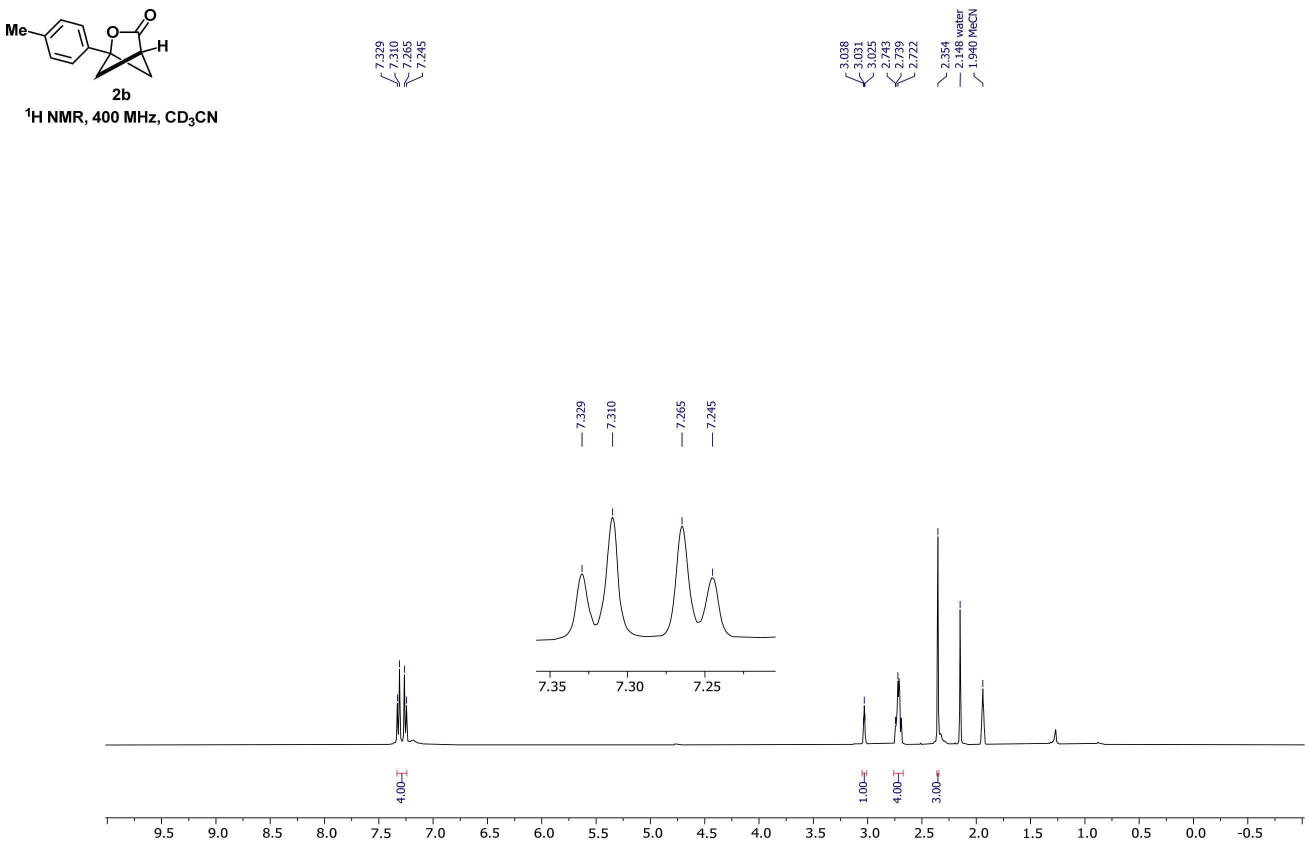
HSQC, CD_3CN

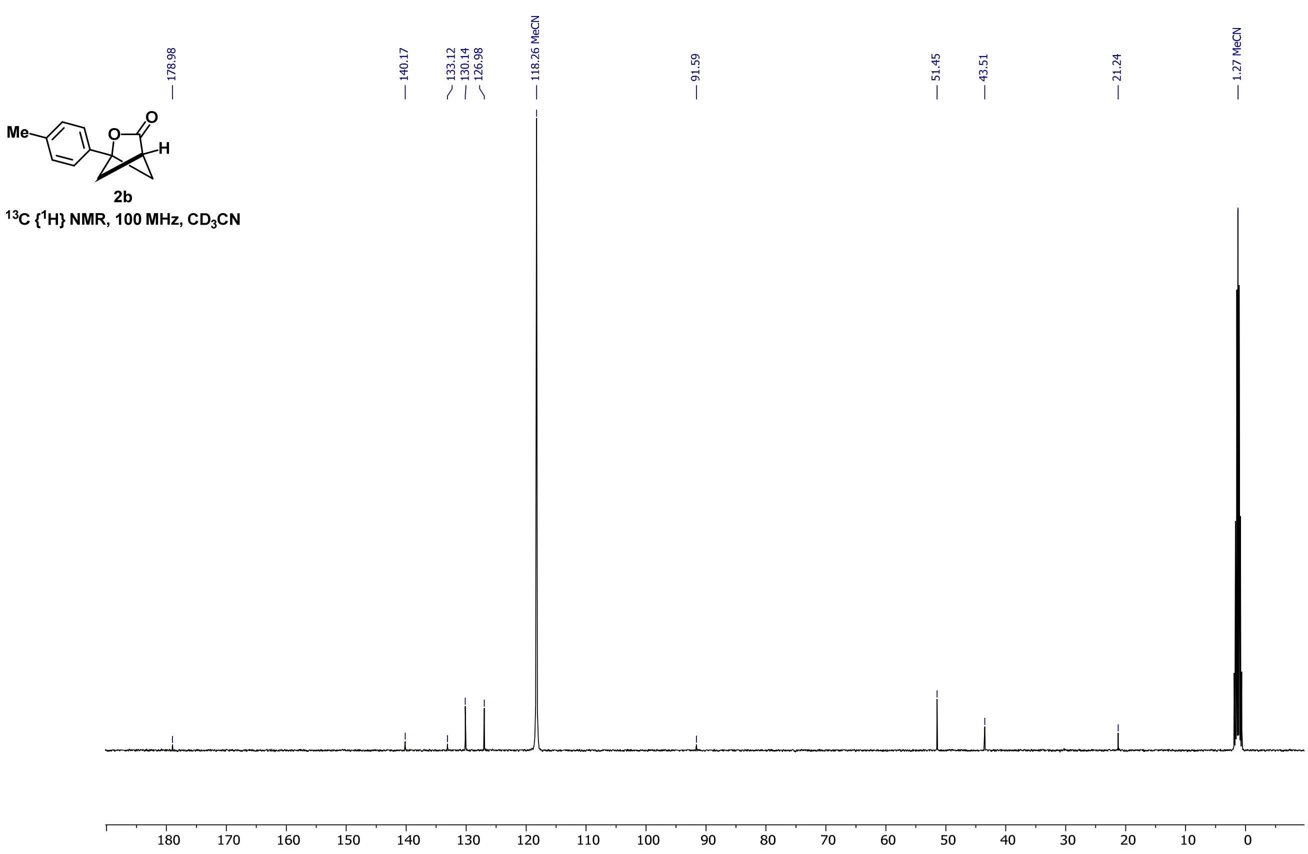


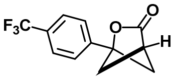


2a
HMBC, CD_3CN



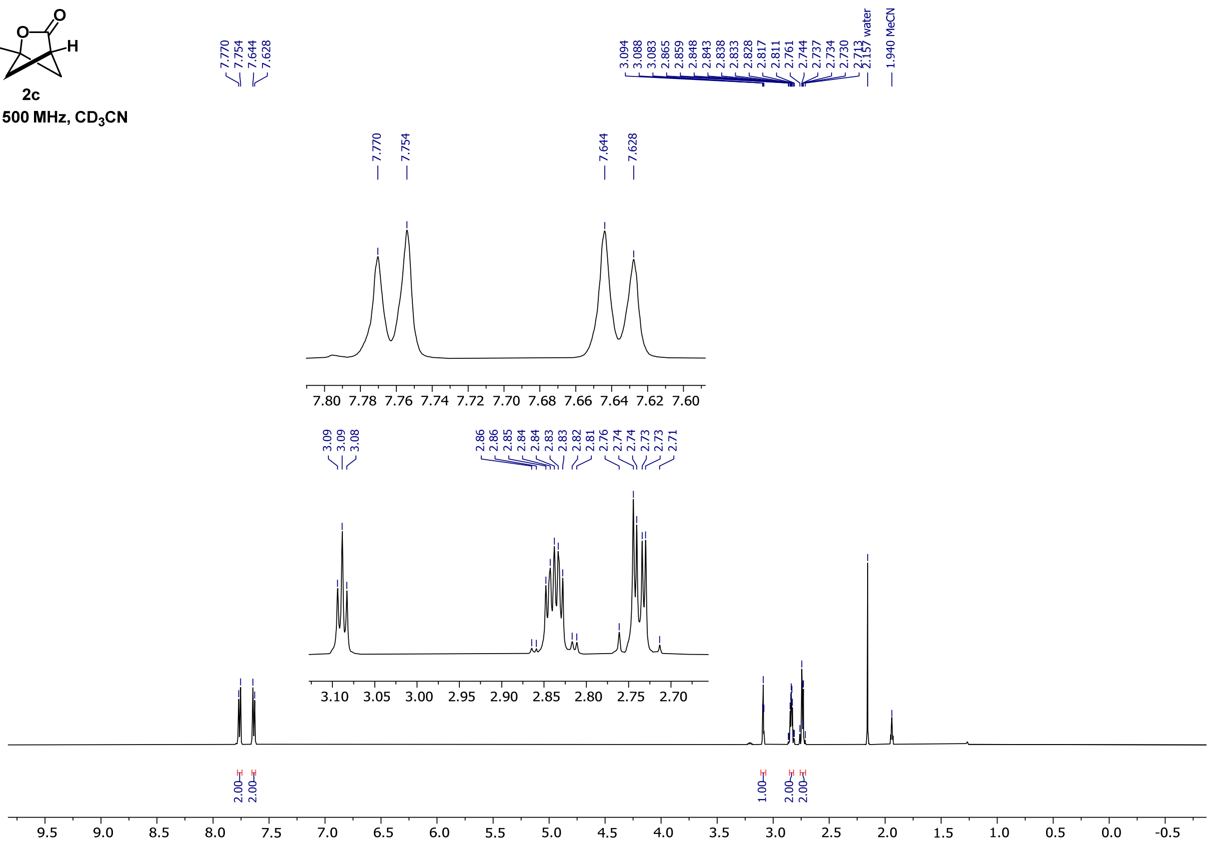

Me
O
O
H
2b
^{1}H NMR, 400 MHz, CD_3CN
7.329
7.310
7.265
7.245
3.038
3.031
3.025
2.743
2.739
2.722
2.354
2.148 water
1.940 MeCN
7.35
7.30
7.25
4.00
1.00
4.00
3.00
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5

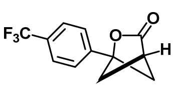

Me
O
O
H
2b
^{13}C {^{1}H} NMR, 100 MHz, CD_3CN
178.98
140.17
133.12
130.14
126.98
118.26 MeCN
91.59
51.45
43.51
21.24
1.27 MeCN
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0



2c

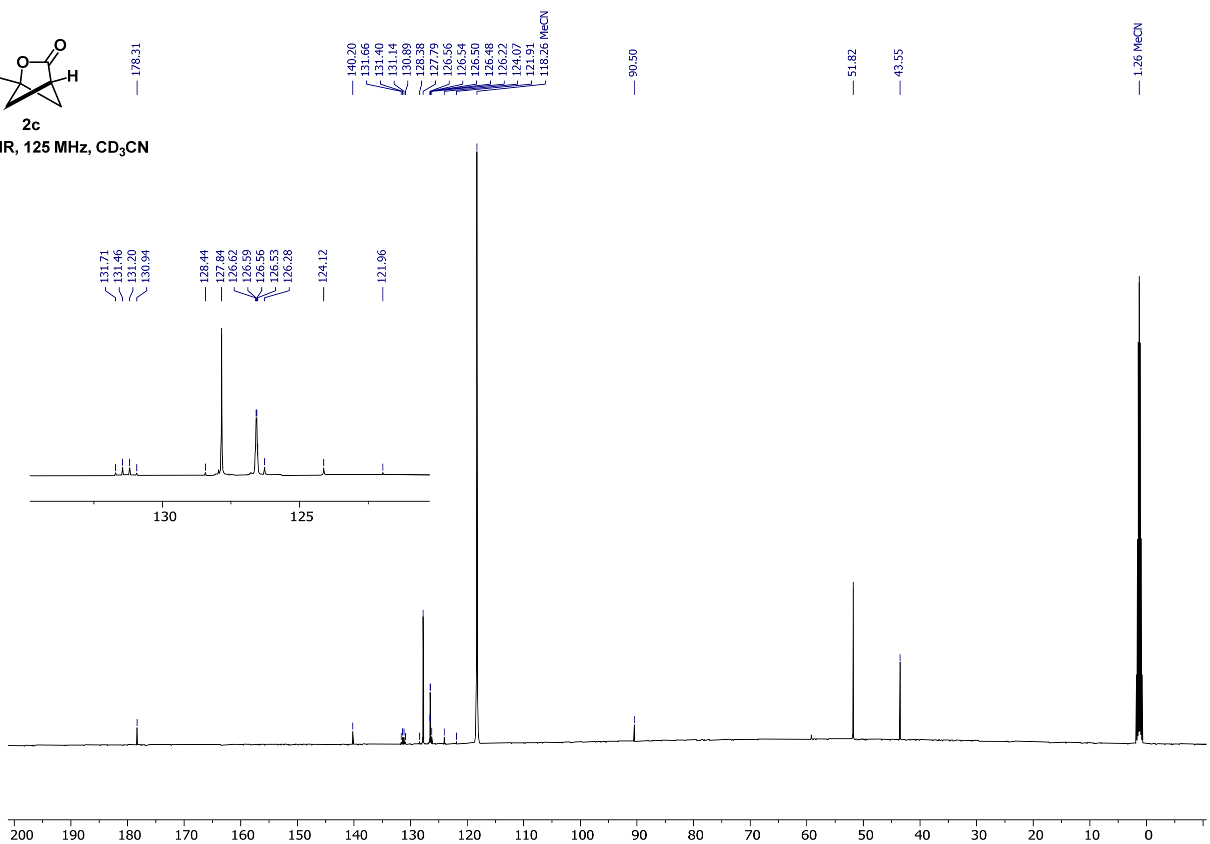
^{1}H NMR, 500 MHz, CD_3CN

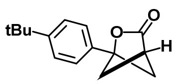




2c

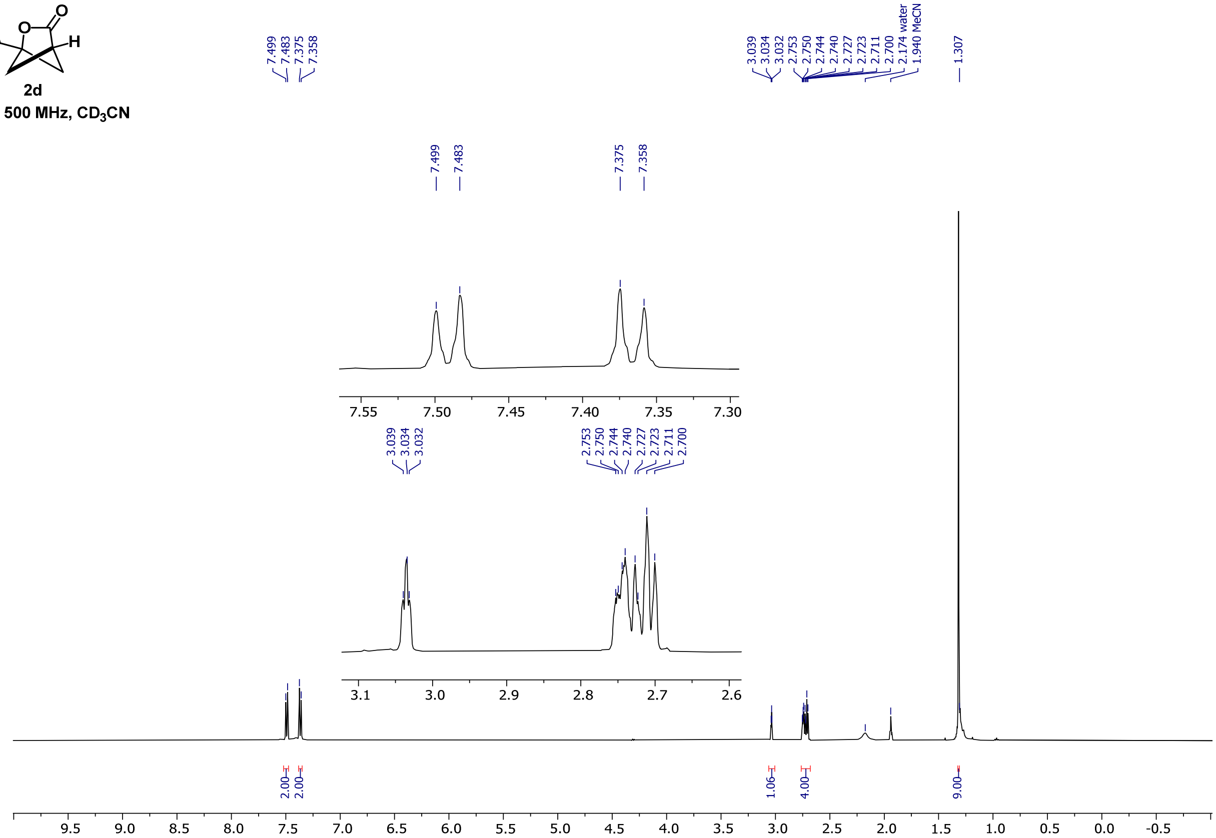
^{13}C {^{1}H} NMR, 125 MHz, CD_3CN

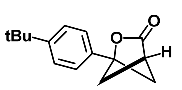




2d

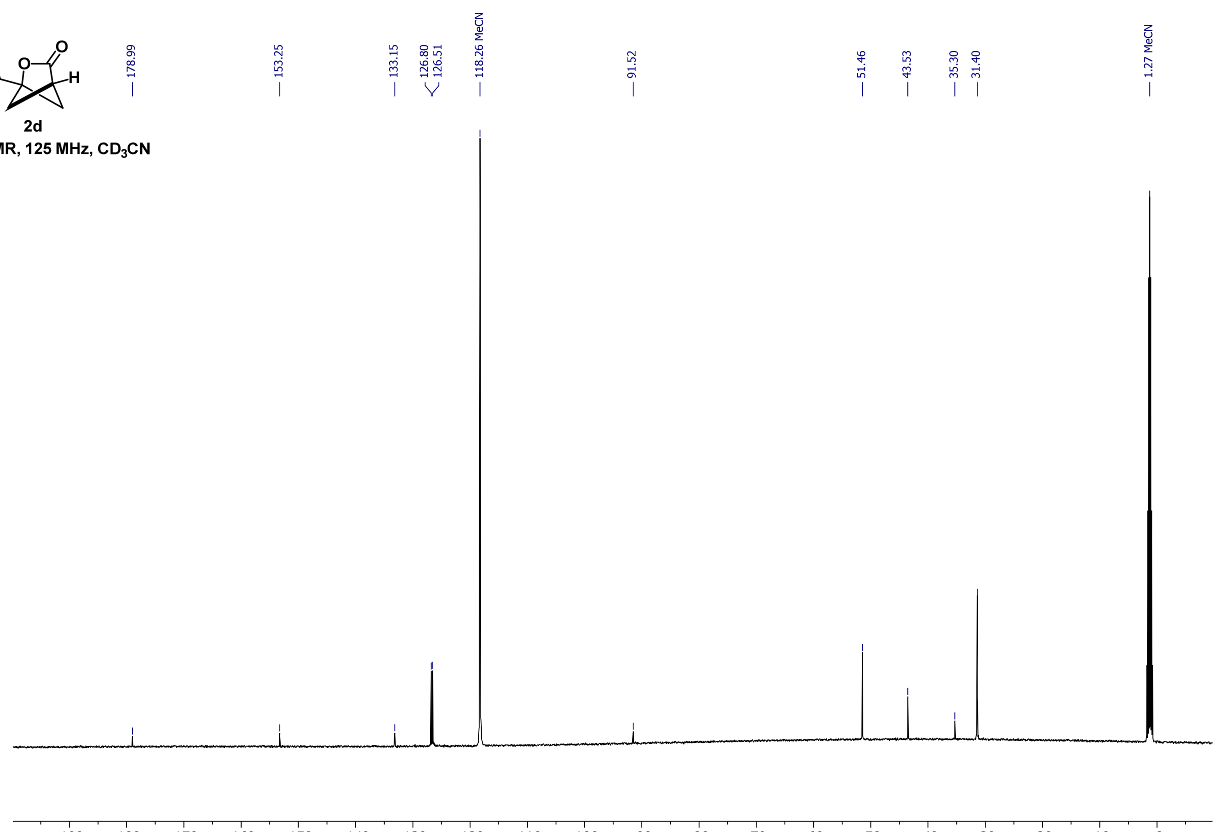
^{1}H NMR, 500 MHz, CD_3CN

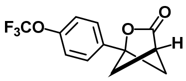




2d

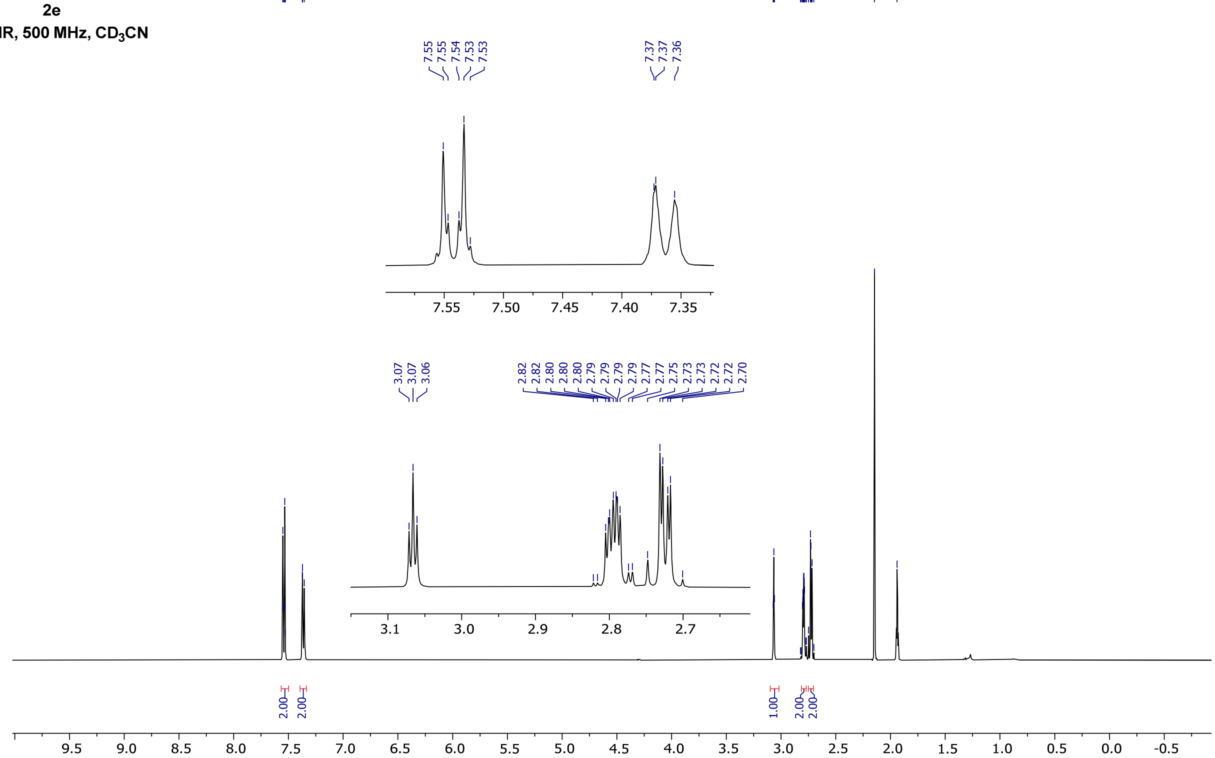
^{13}C {^{1}H} NMR, 125 MHz, CD_3CN

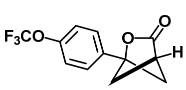




2e

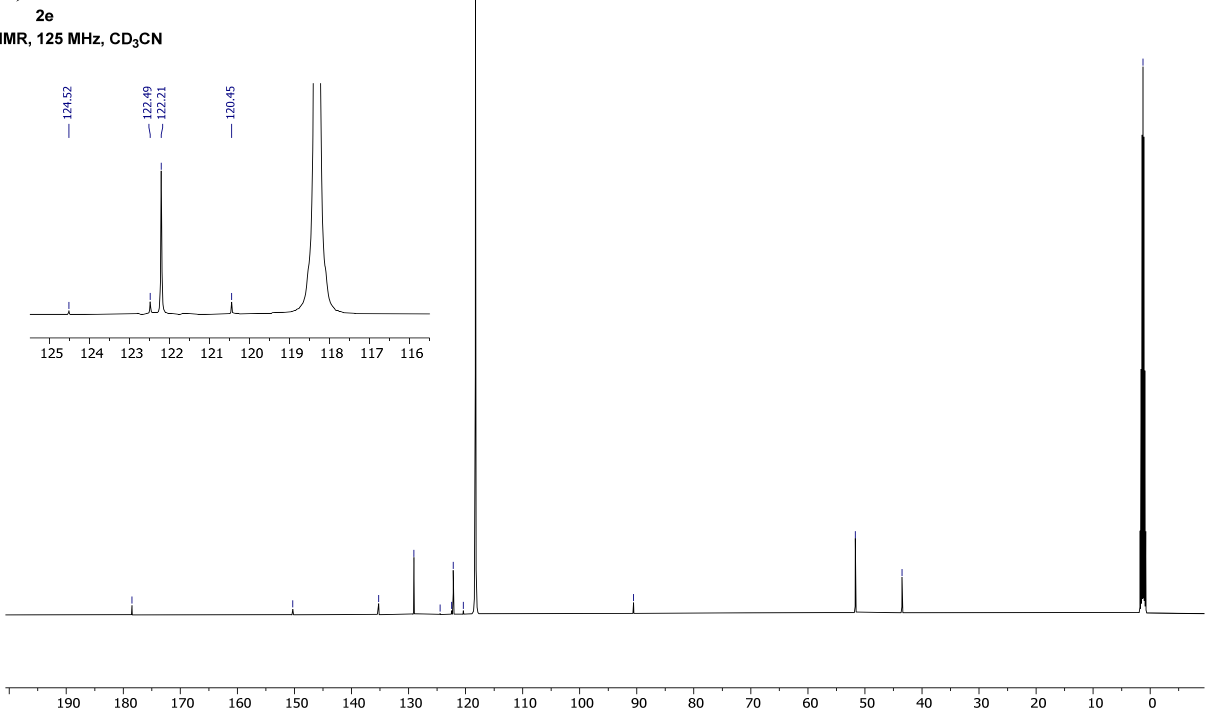
^{1}H NMR, 500 MHz, CD$_3$CN

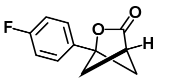




2e

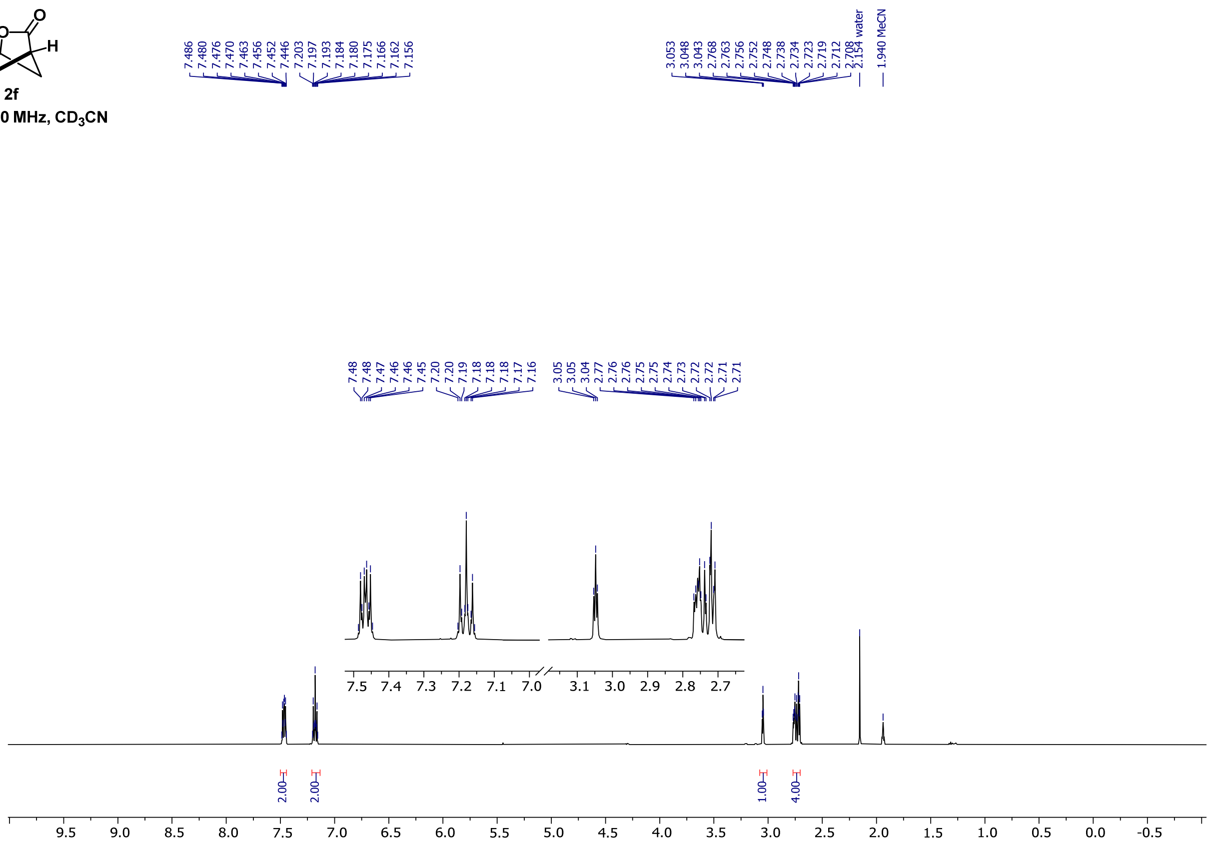
^{13}C {^{1}H} NMR, 125 MHz, CD$_3$CN

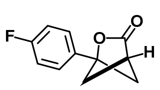




2f

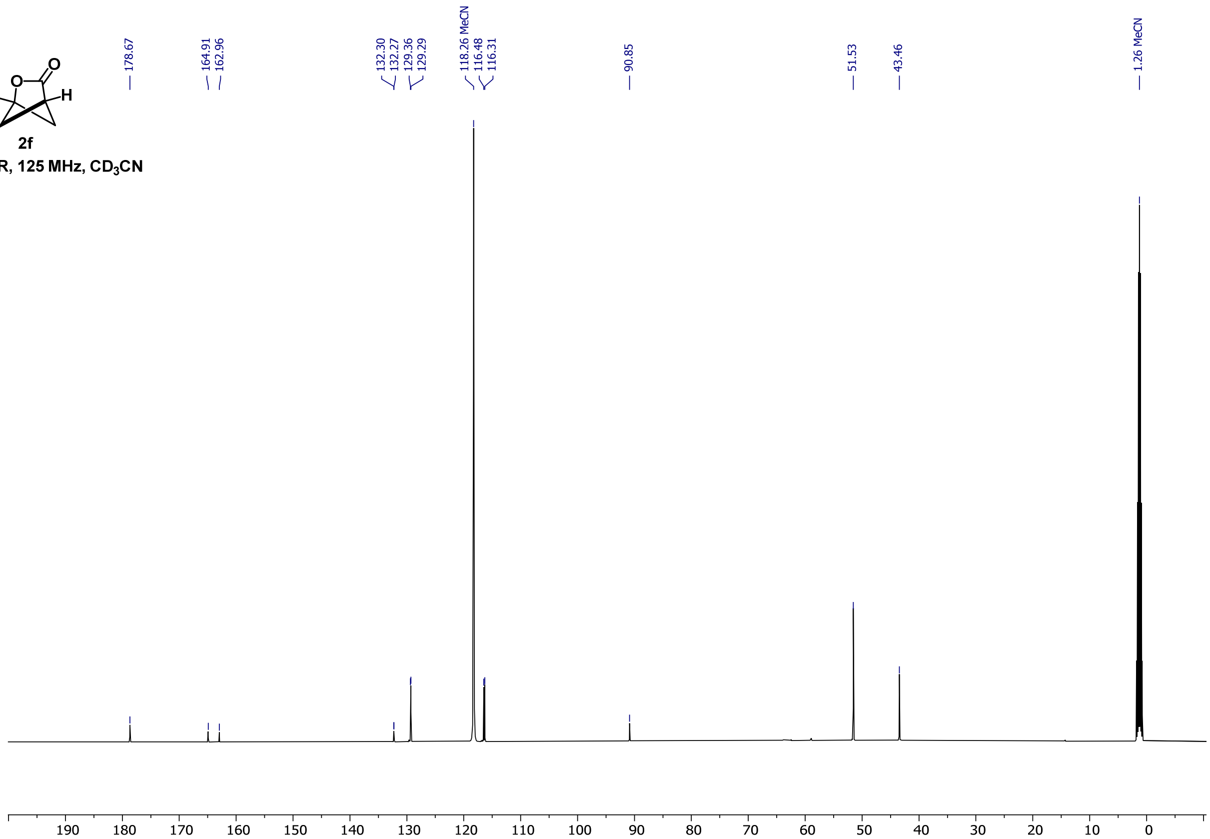
^{1}H NMR, 500 MHz, CD$_3$CN

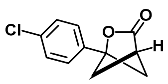




2f

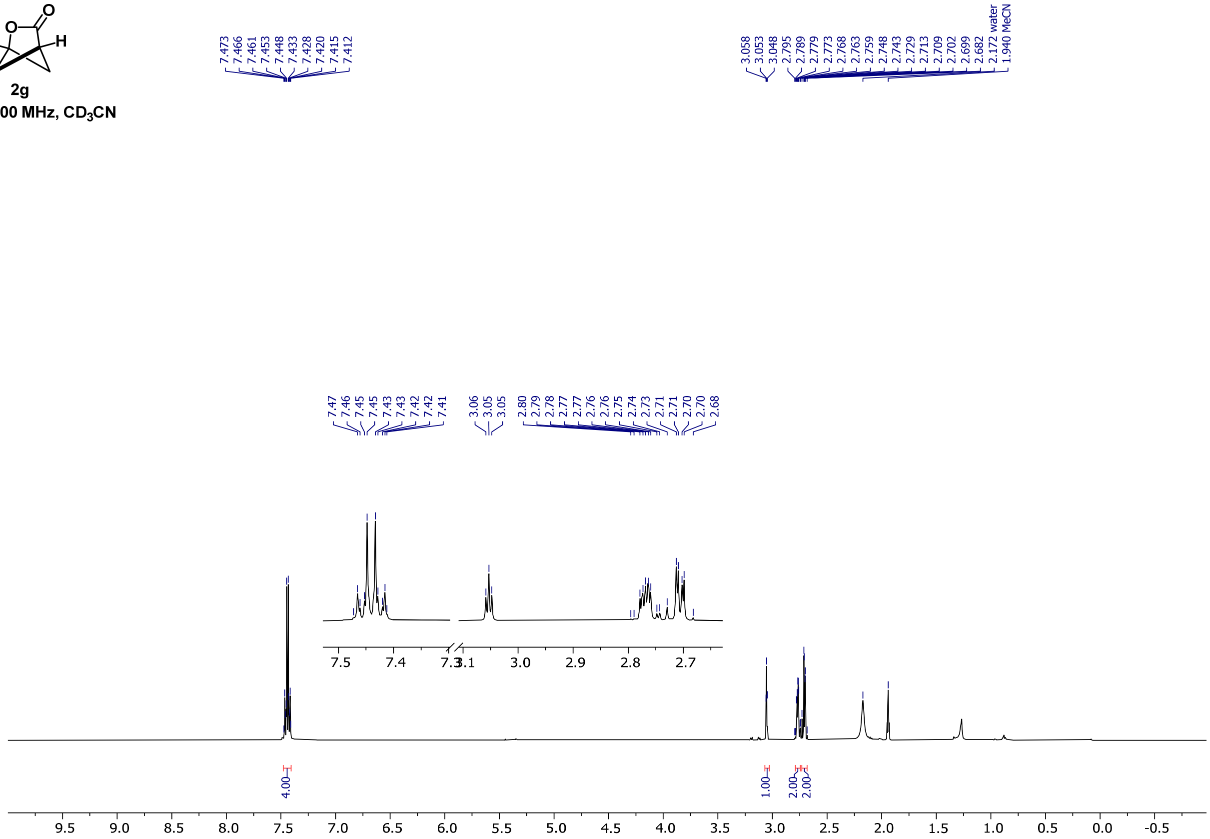
^{13}C {^{1}H} NMR, 125 MHz, CD$_3$CN

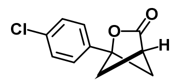




2g

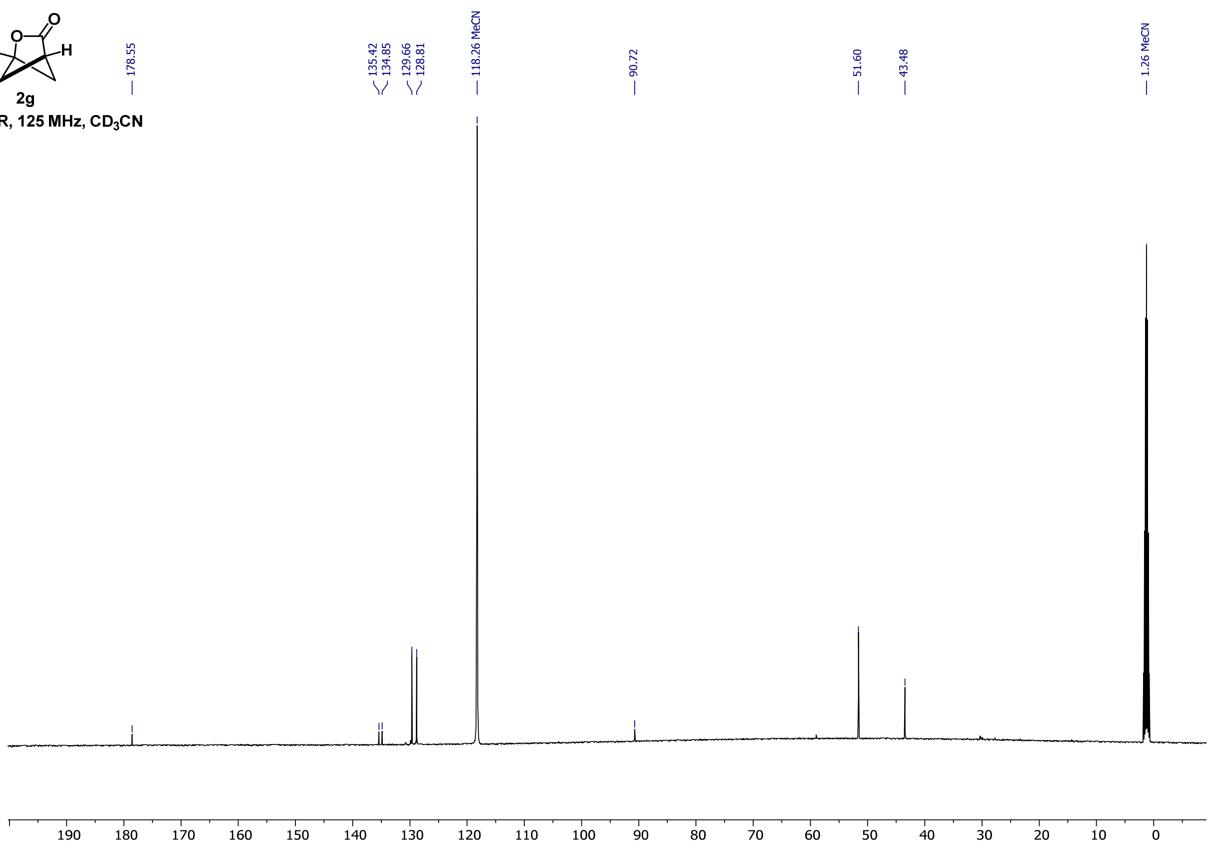
^{1}H NMR, 500 MHz, CD_3CN

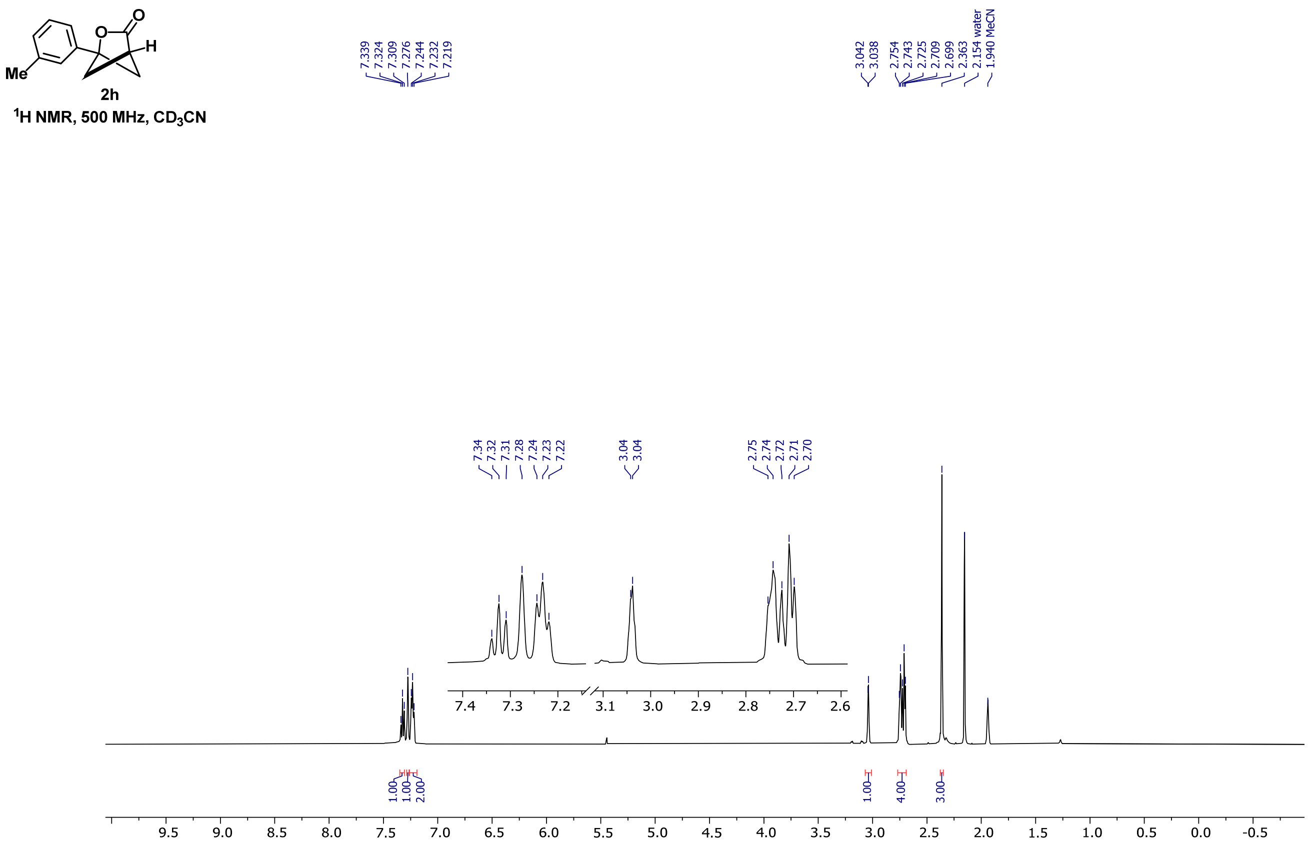




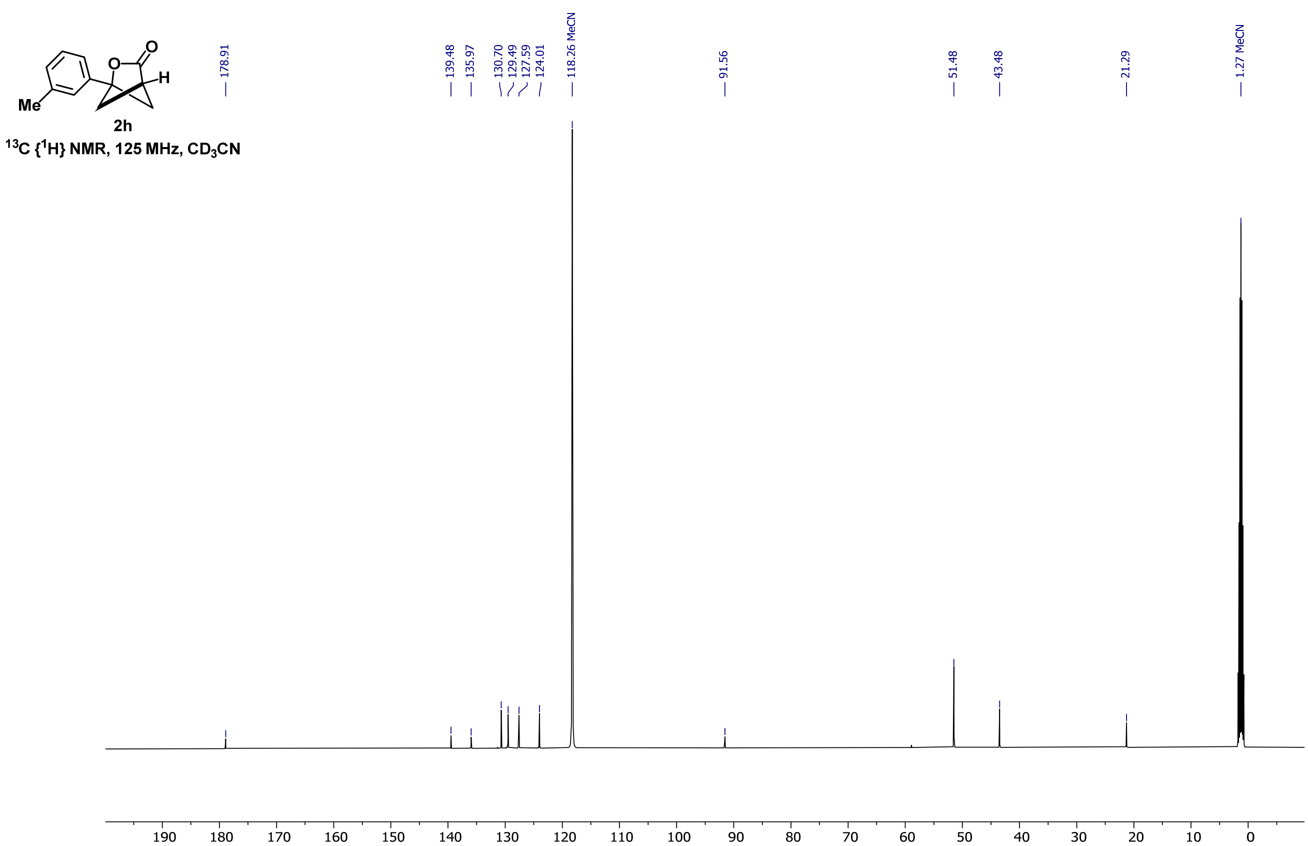
2g

$^{13}C\ \{^1H\}$ NMR, 125 MHz, CD_3CN

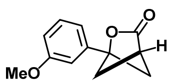




Me
O
O
H
2h
1H NMR, 500 MHz, CD3CN
7.339
7.324
7.309
7.276
7.244
7.232
7.219
3.042
3.038
2.754
2.743
2.725
2.709
2.699
2.363
2.154 water
1.940 MeCN
1.00
1.00
2.00
1.00
4.00
3.00

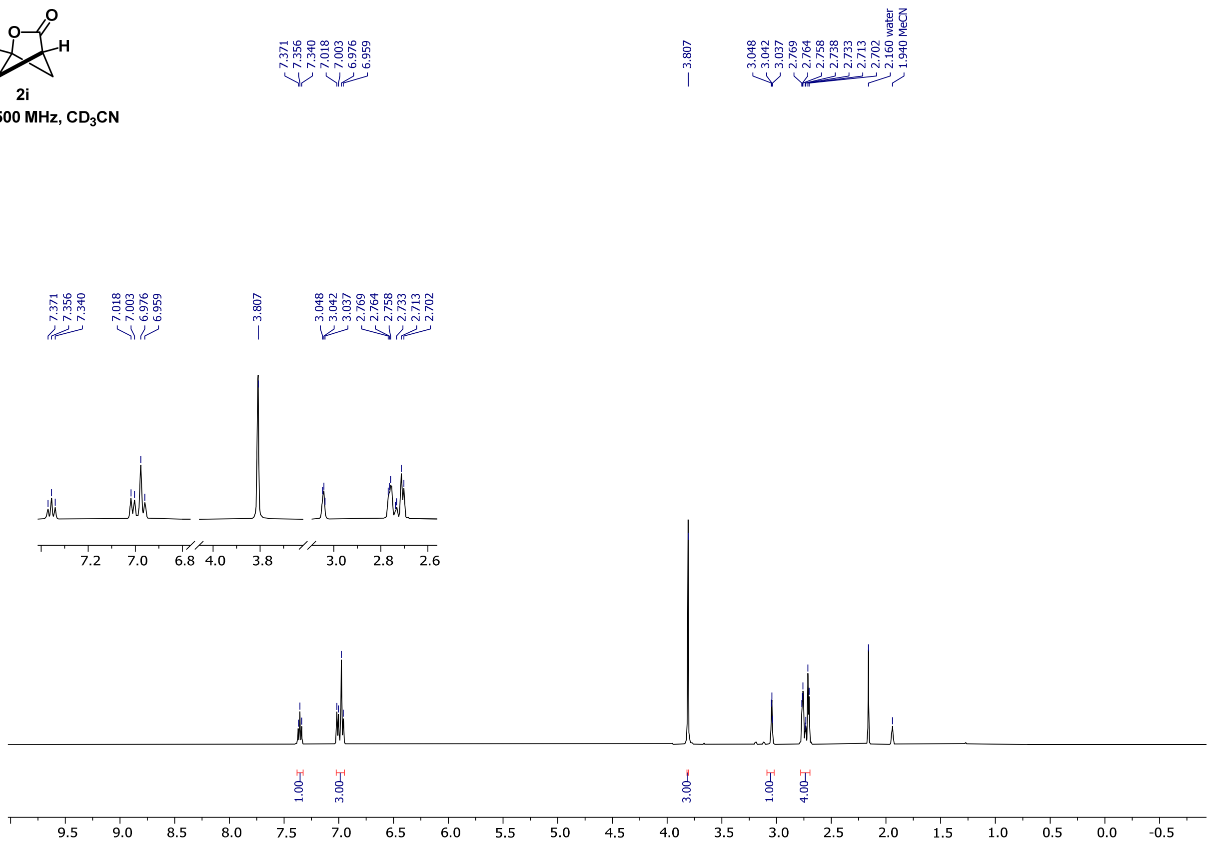


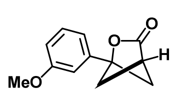
Me
O
O
H
2h
13C {1H} NMR, 125 MHz, CD3CN
178.91
139.48
135.97
130.70
129.49
127.59
124.01
118.26 MeCN
91.56
51.48
43.48
21.29
1.27 MeCN



2i

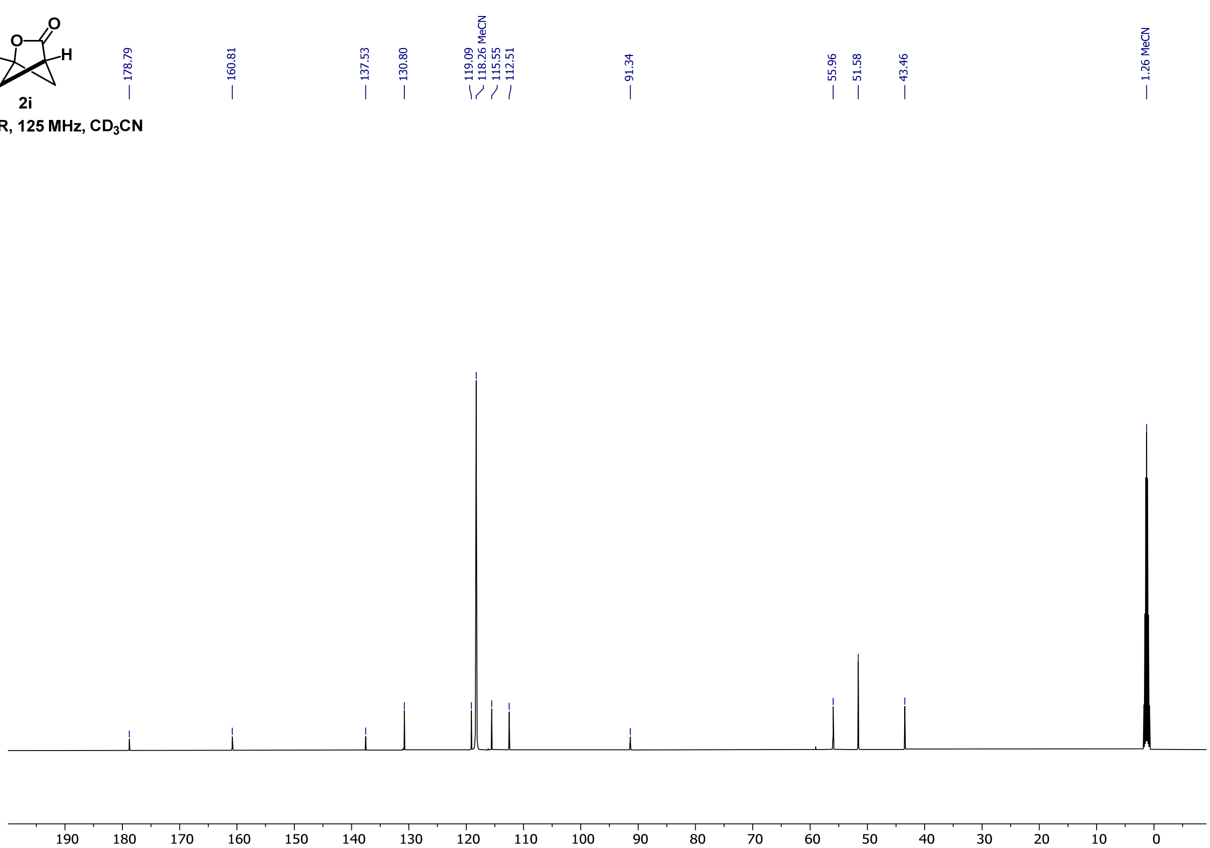
^{1}H NMR, 500 MHz, CD_3CN

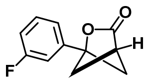




2i

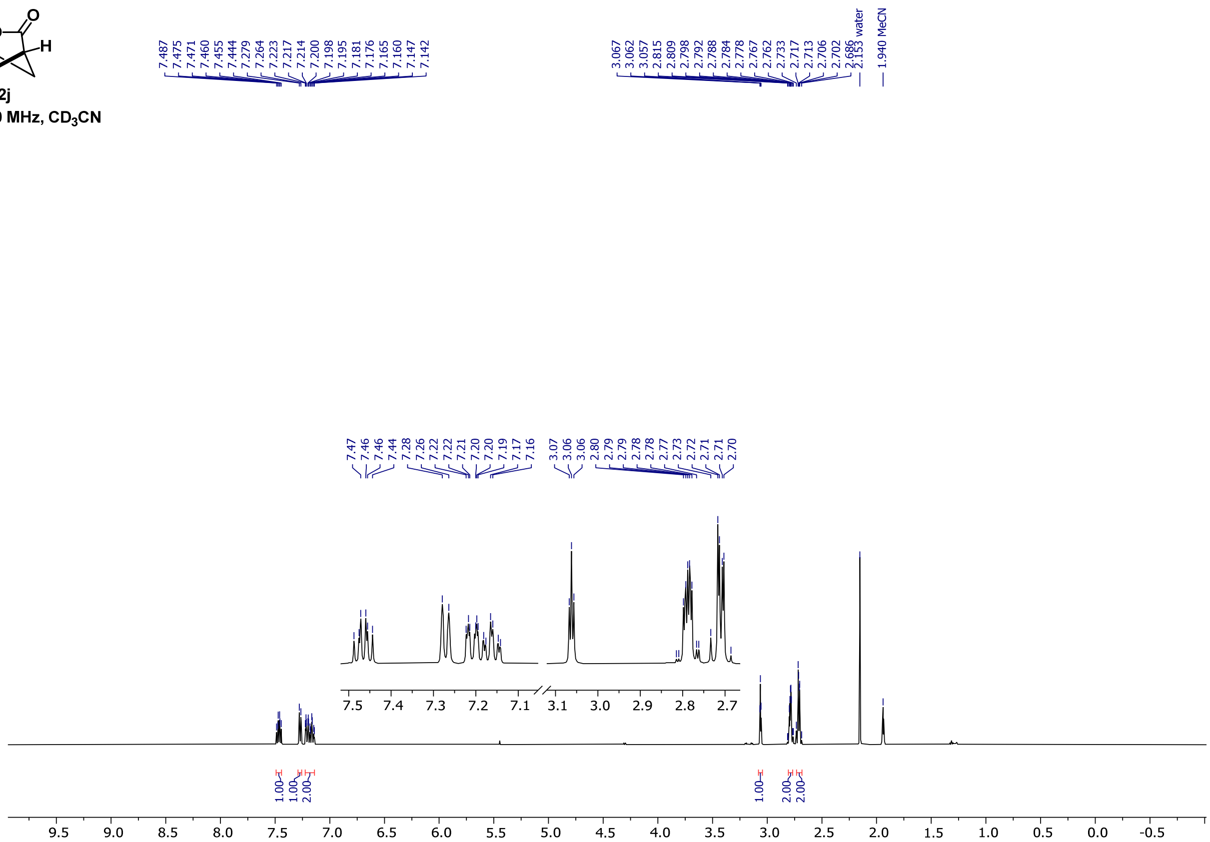
^{13}C {^{1}H} NMR, 125 MHz, CD_3CN

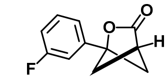




2j

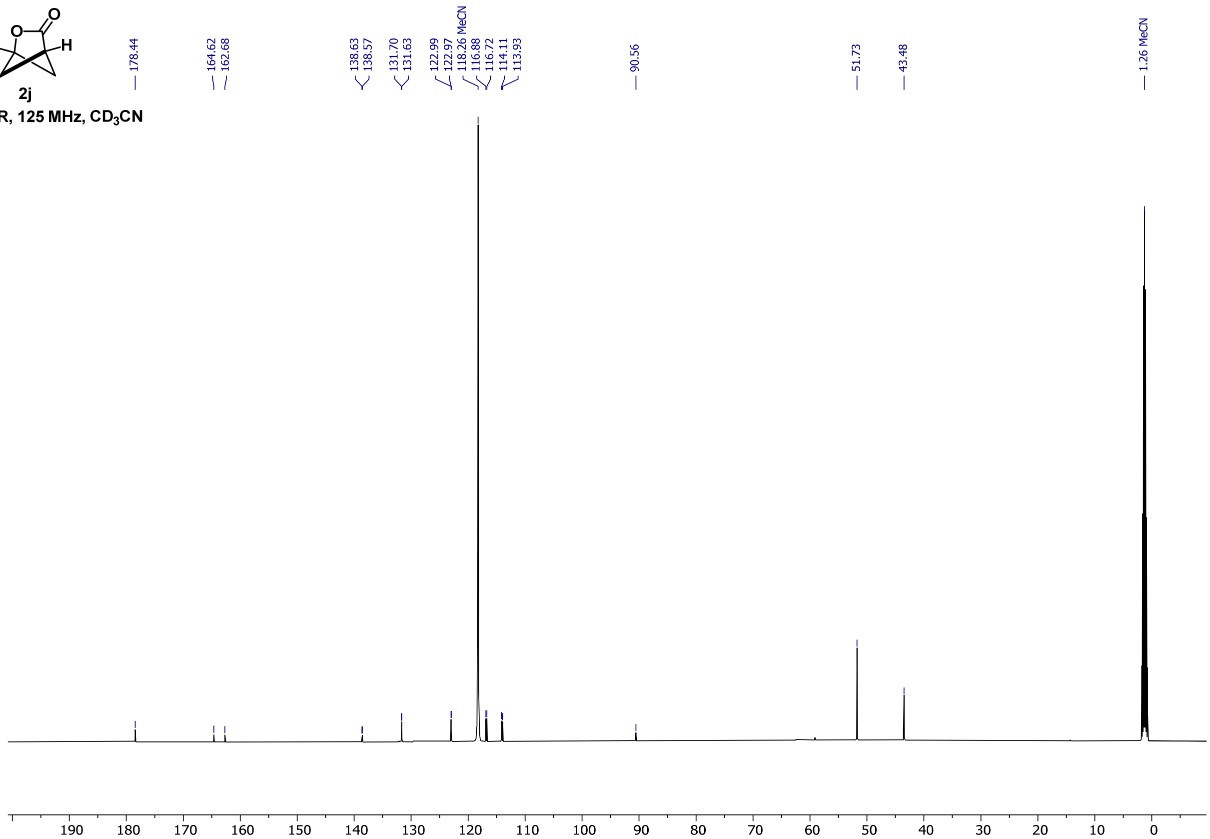
^{1}H NMR, 500 MHz, CD_3CN

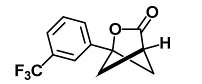




2j

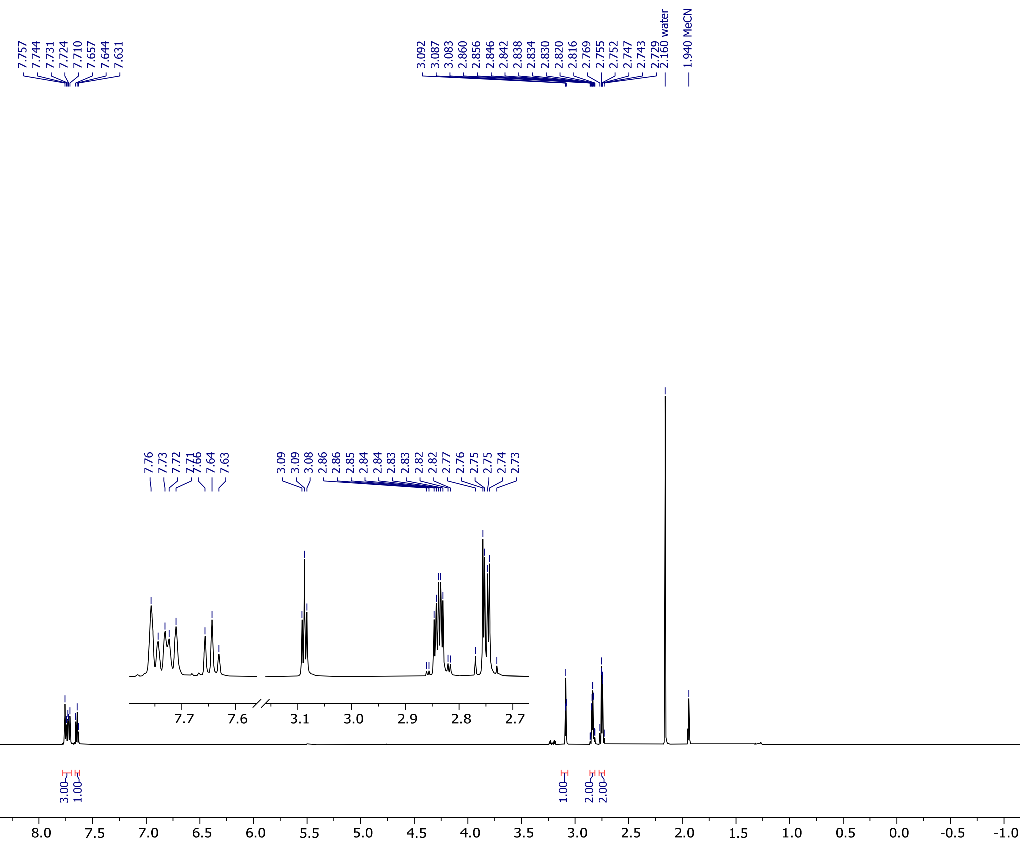
^{13}C {^{1}H} NMR, 125 MHz, CD_3CN

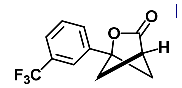




2k

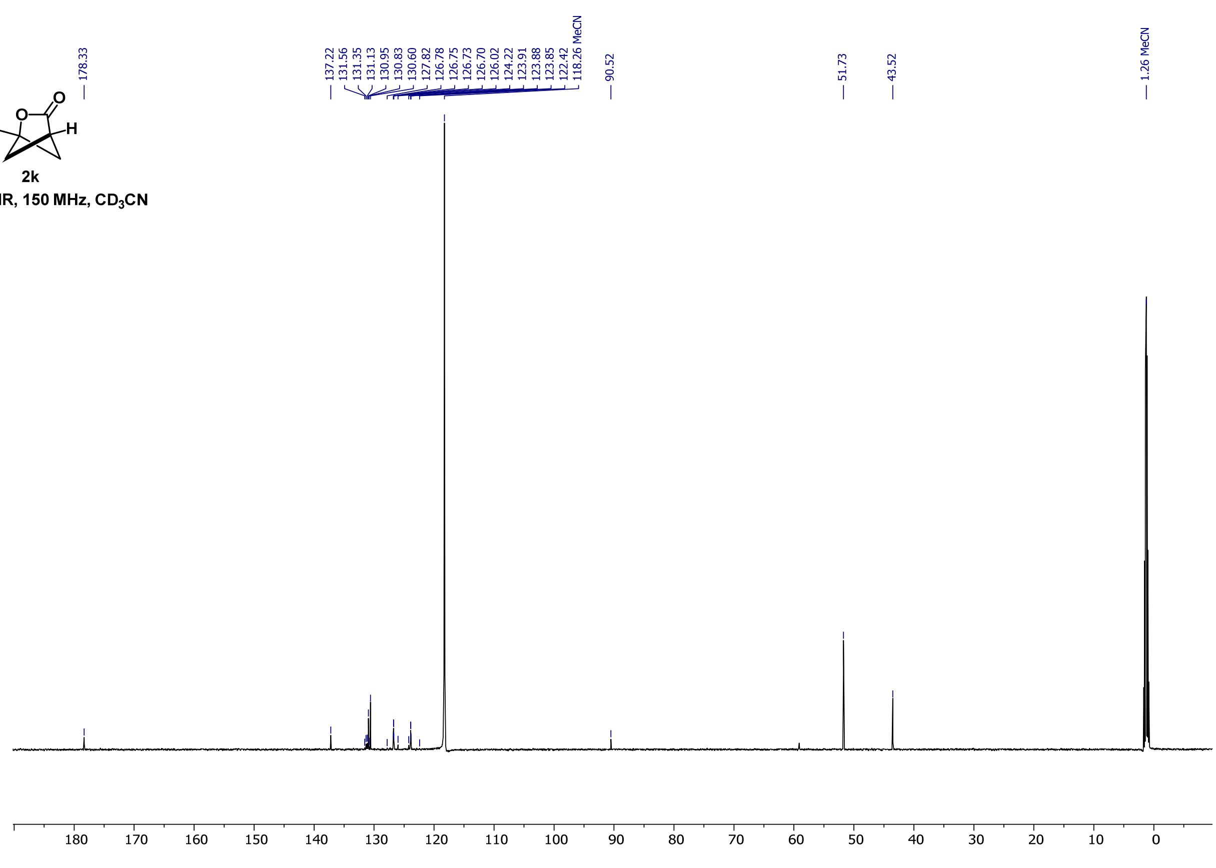
^{1}H NMR, 600 MHz, CD_3CN

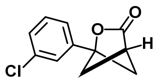




2k

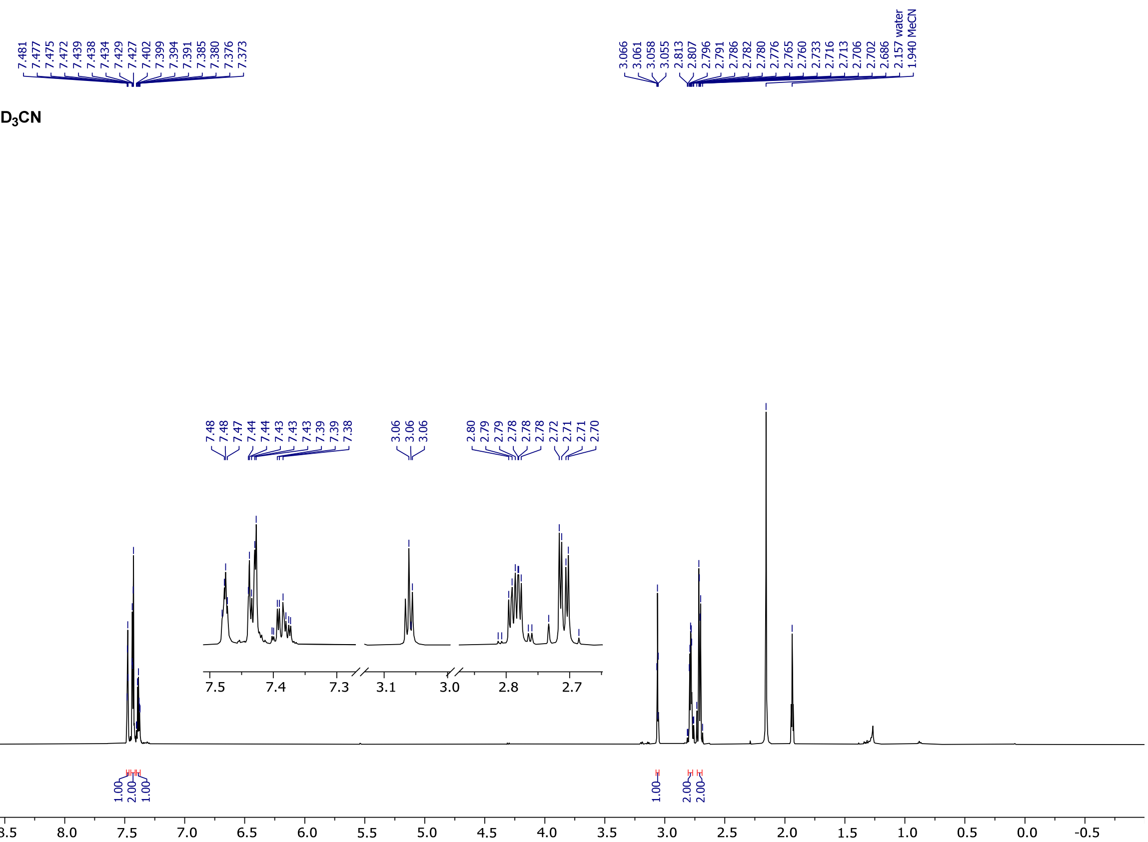
^{13}C {^{1}H} NMR, 150 MHz, CD_3CN

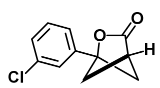




2l

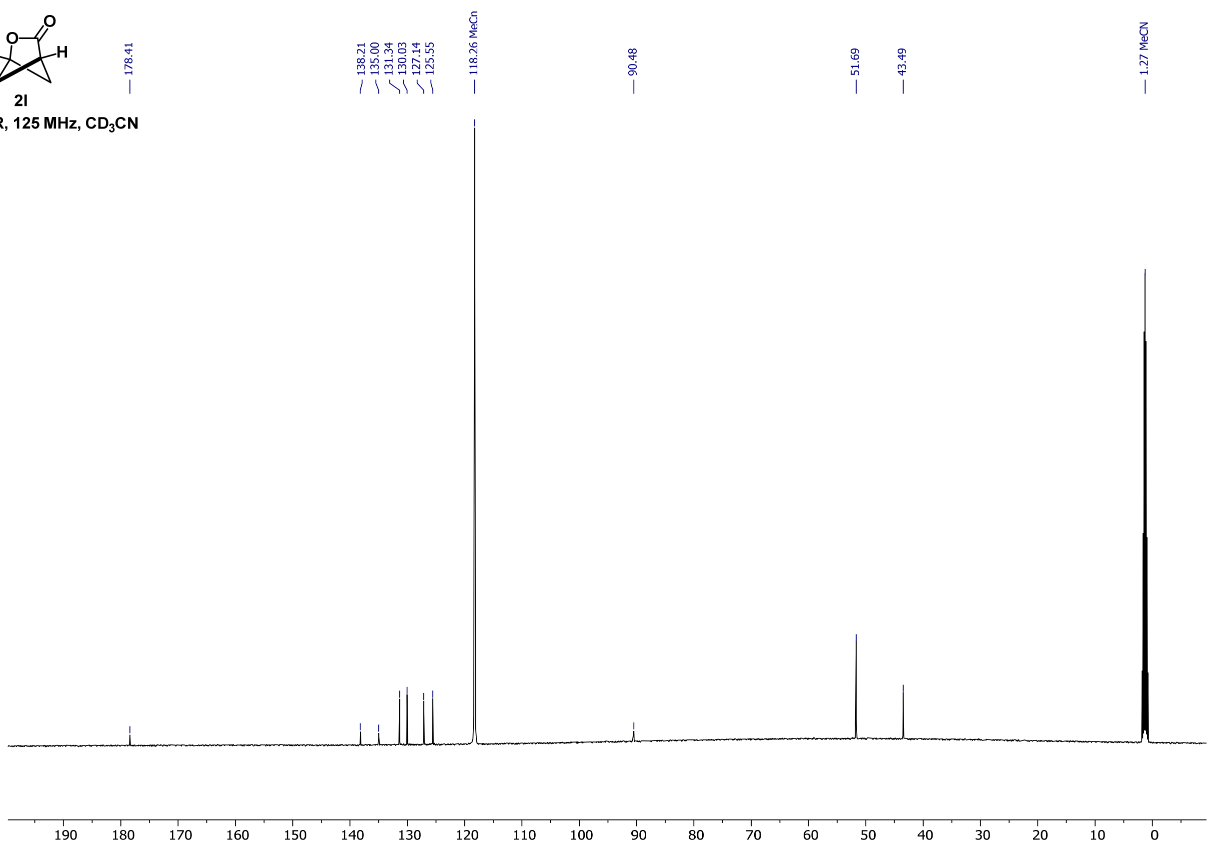
[1]H NMR, 500 MHz, CD_3CN

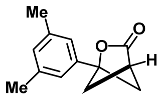




2l

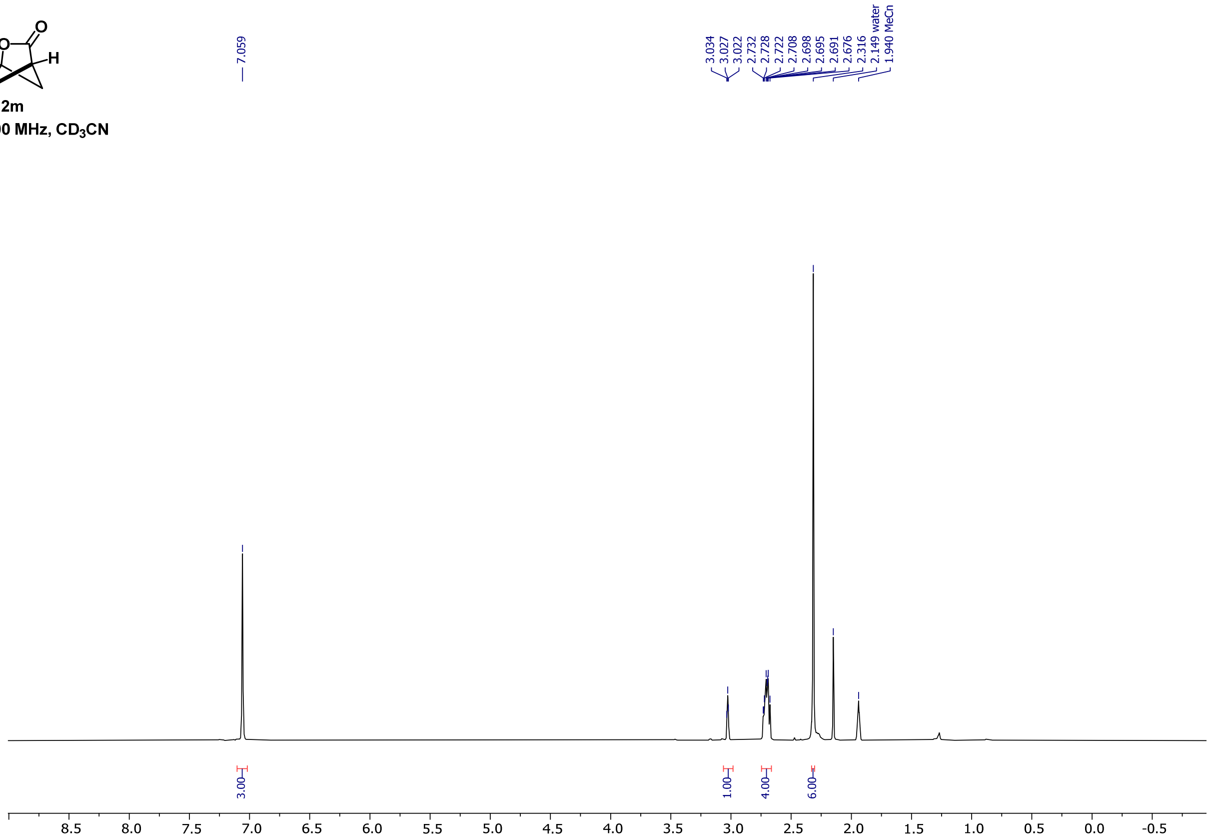
[13]C {[1]H} NMR, 125 MHz, CD_3CN

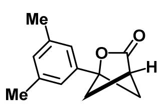




2m

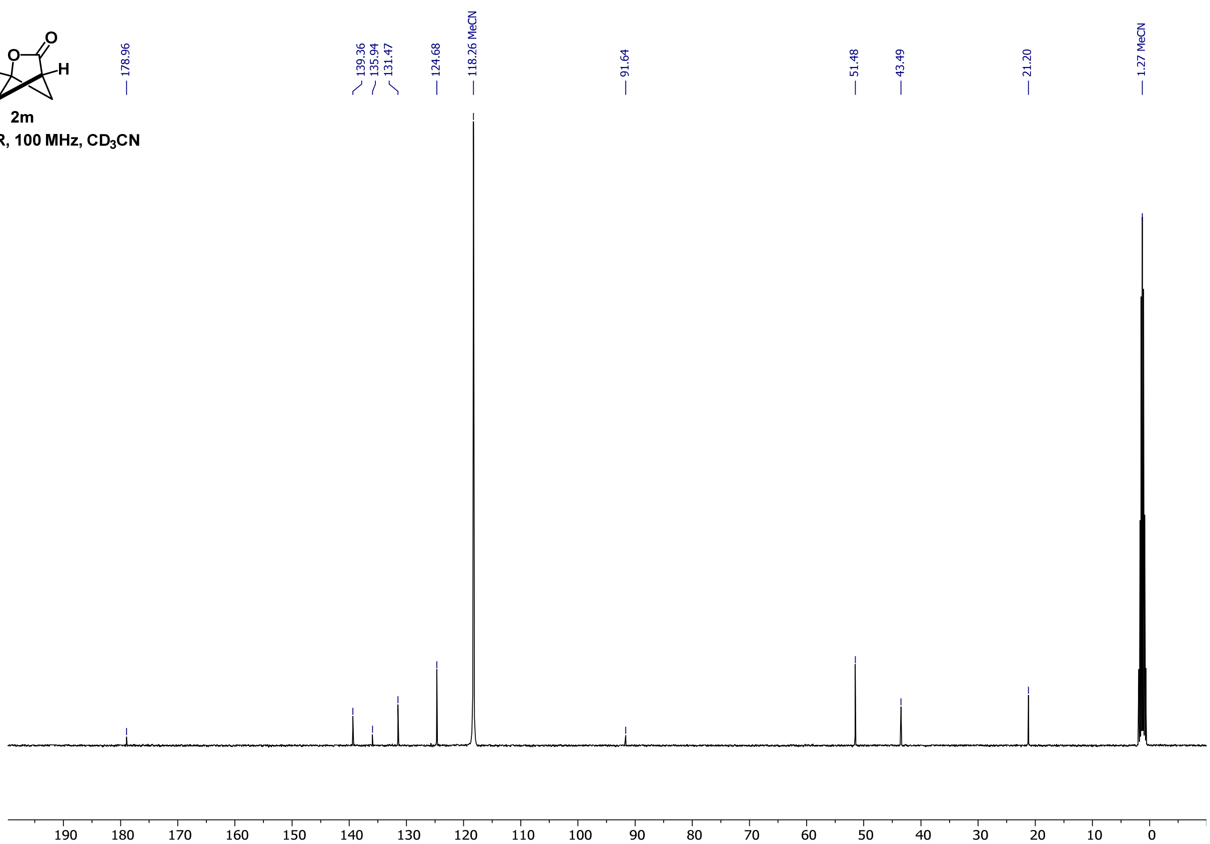
^{1}H NMR, 400 MHz, CD_3CN

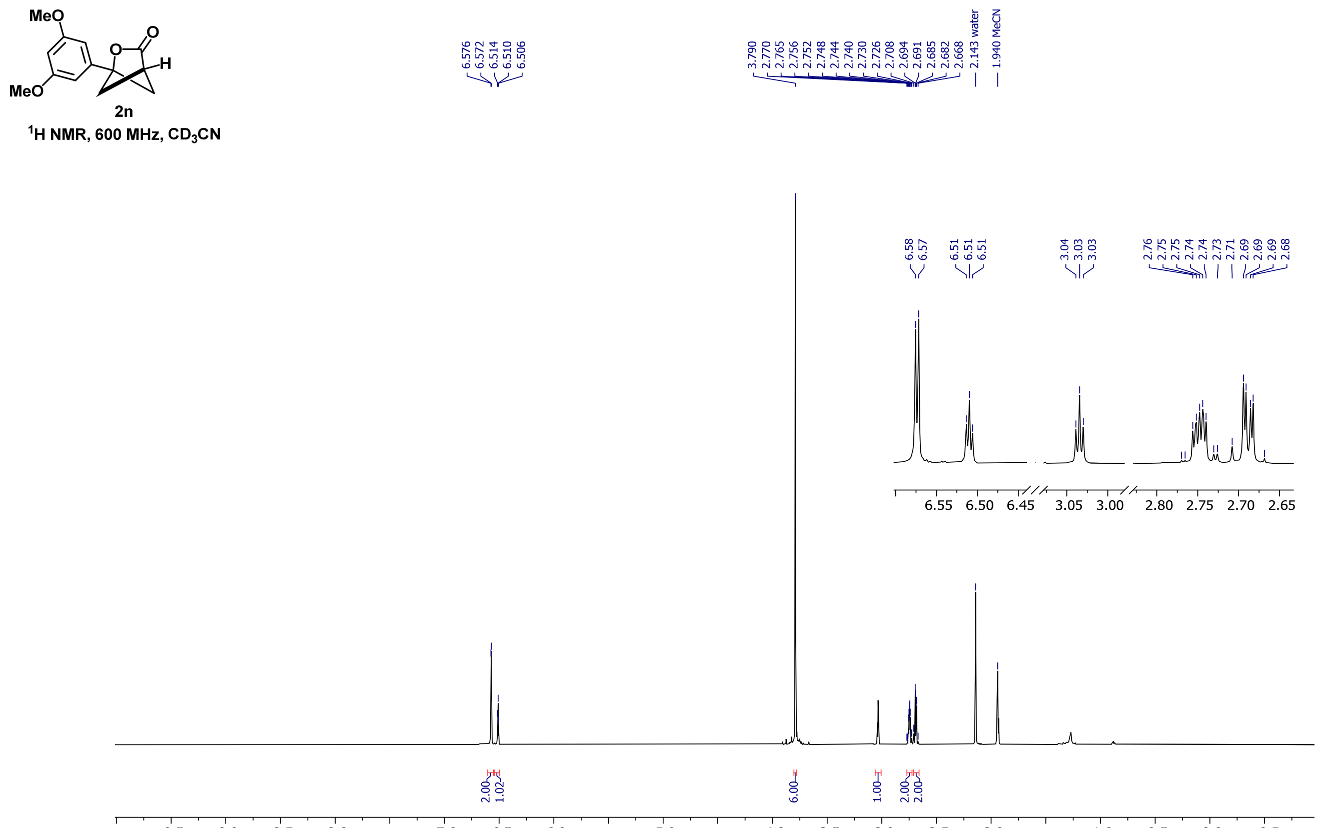


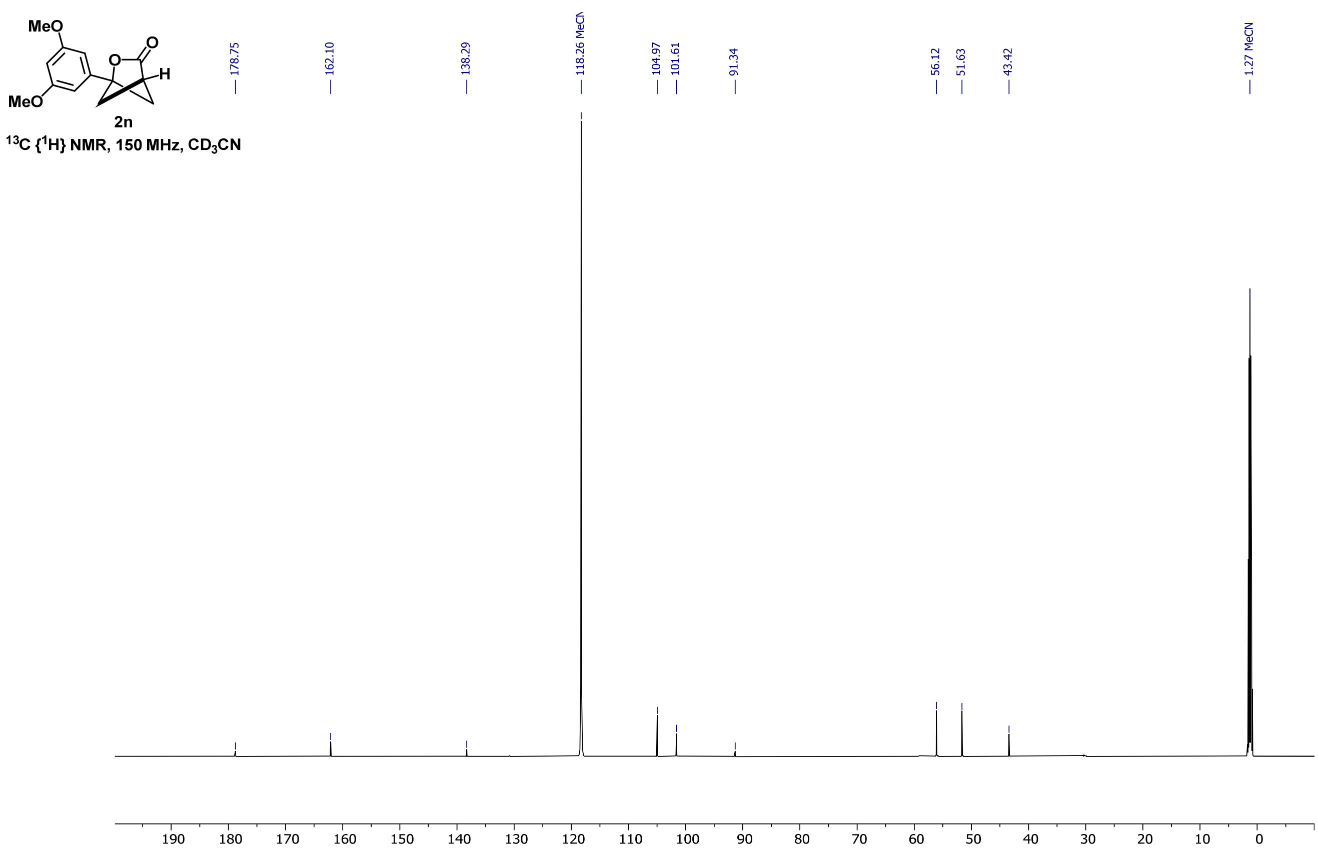


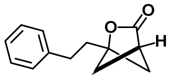
2m

$^{13}C\{^{1}H\}$ NMR, 100 MHz, CD_3CN



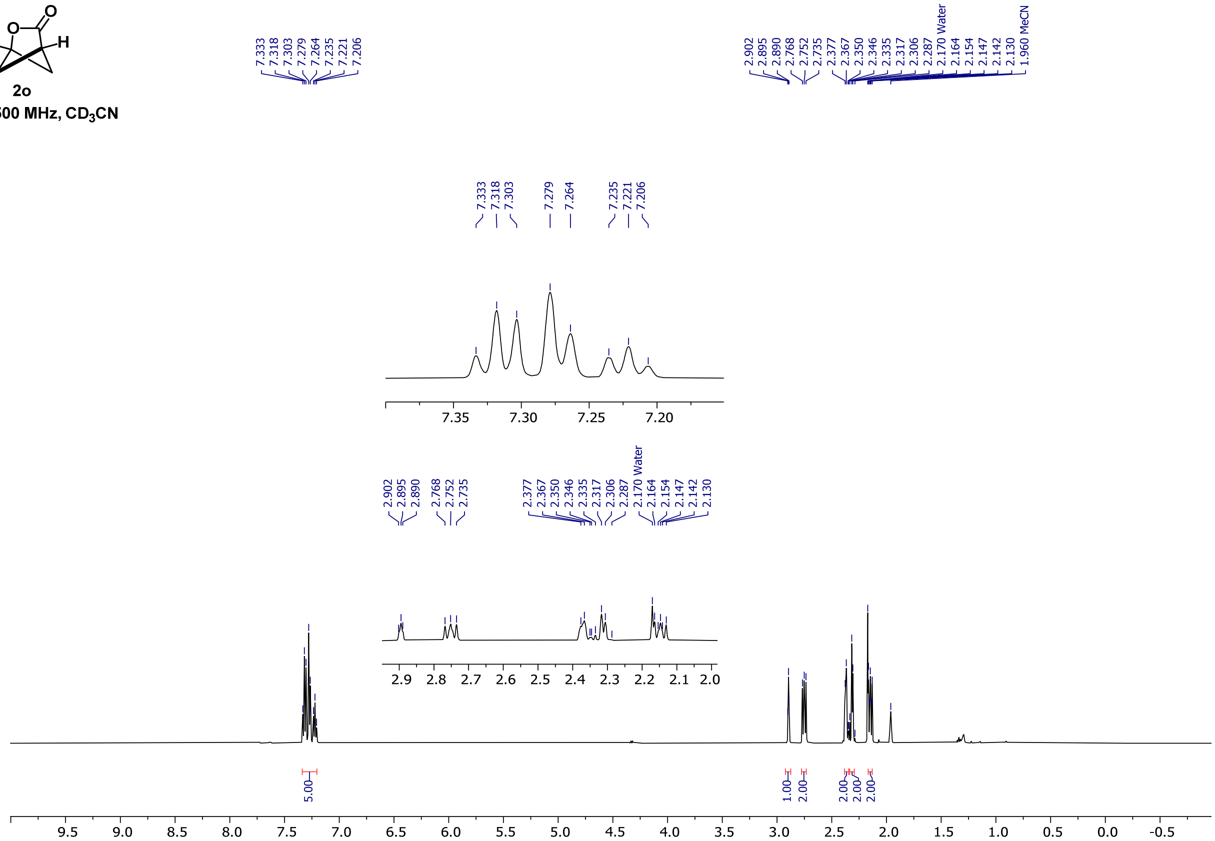

MeO
MeO
O
O
H
2n
1H NMR, 600 MHz, CD3CN
6.576 6.572 6.514 6.510 6.506
3.790 2.770 2.765 2.756 2.752 2.748 2.744 2.740 2.730 2.726 2.708 2.694 2.691 2.685 2.682 2.668
2.143 water
1.940 MeCN
6.58 6.57 6.51 6.51 6.51
3.04 3.03 3.03
2.76 2.75 2.75 2.74 2.74 2.73 2.71 2.69 2.69 2.69 2.68
2.00 1.02 6.00 1.00 2.00 2.00
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5

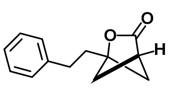

MeO
MeO
O
O
H
2n
13C {1H} NMR, 150 MHz, CD3CN
178.75 162.10 138.29 118.26 MeCN 104.97 101.61 91.34 56.12 51.63 43.42 1.27 MeCN
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0



2o

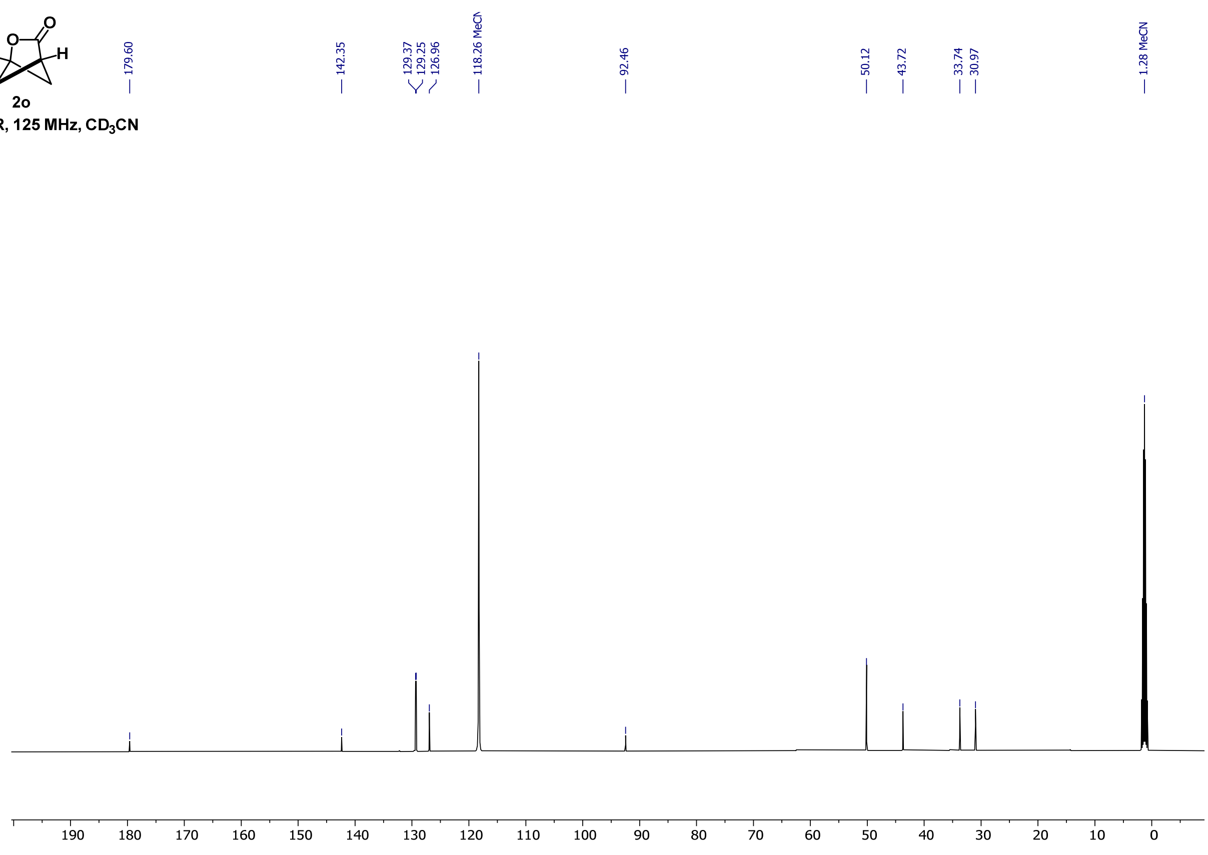
^{1}H NMR, 500 MHz, CD_3CN

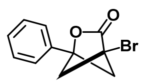




2o

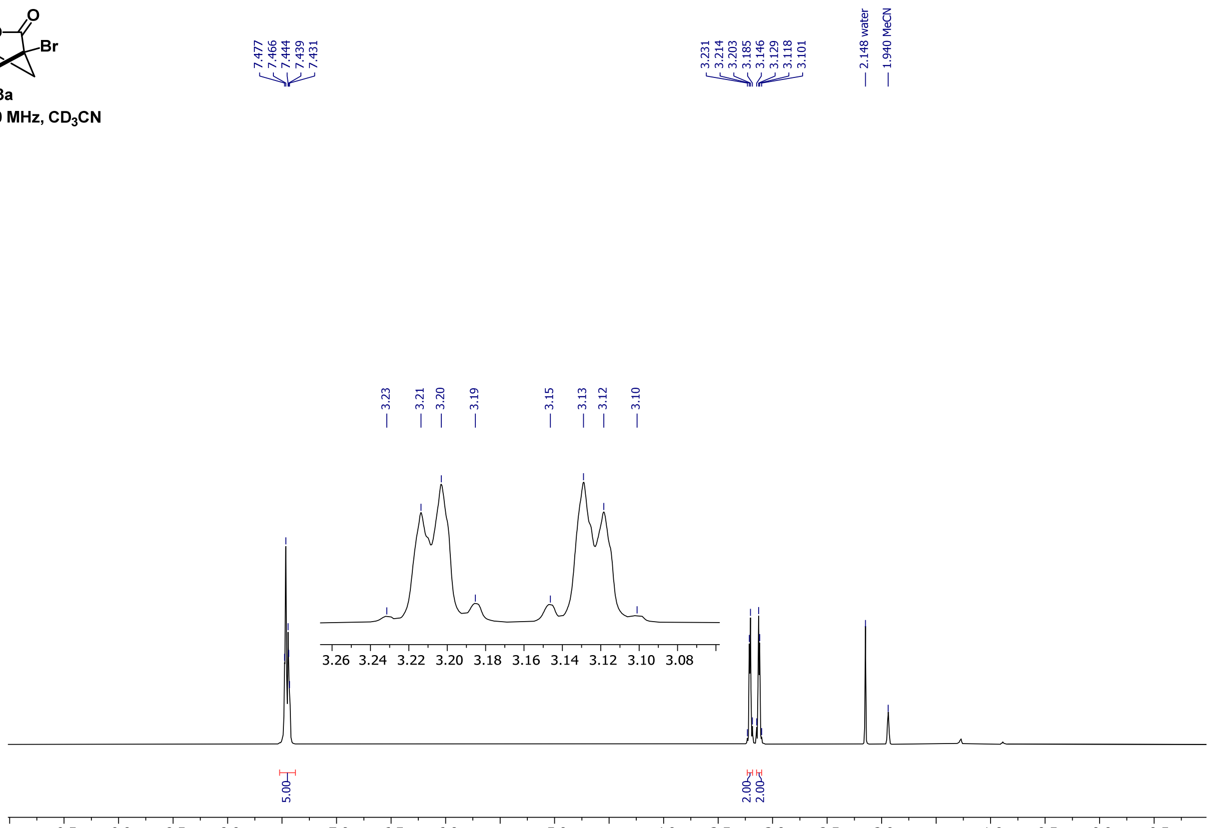
^{13}C {^{1}H} NMR, 125 MHz, CD_3CN

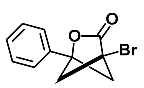




3a

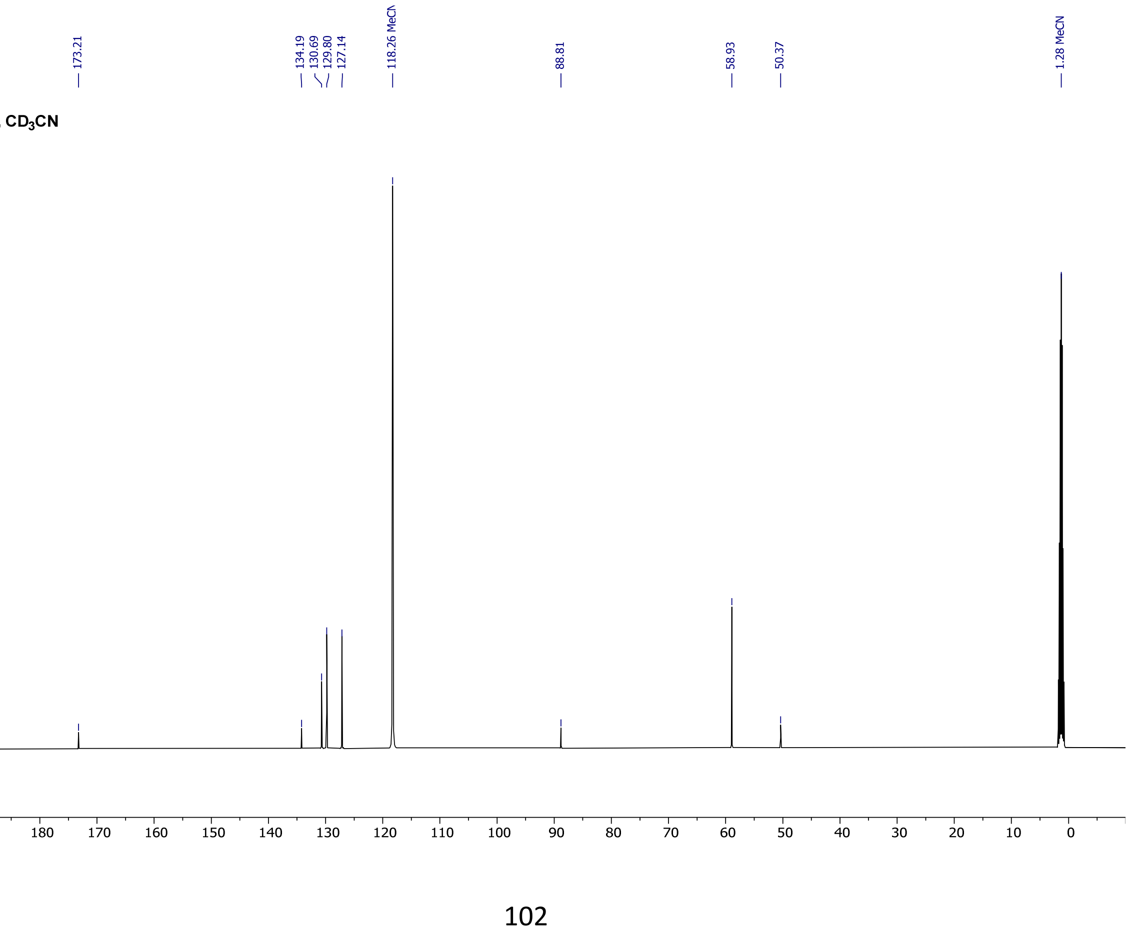
^{1}H NMR, 500 MHz, CD_3CN

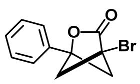




3a

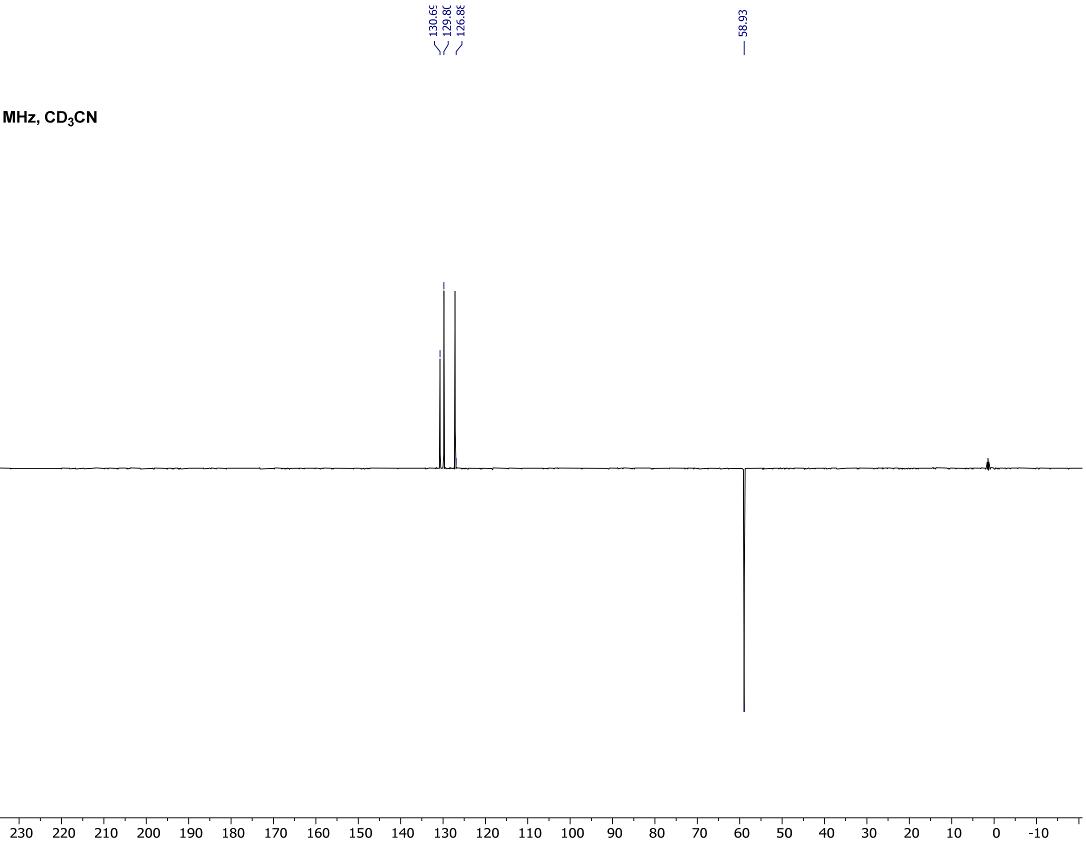
^{13}C {^{1}H} NMR, 125 MHz, CD_3CN

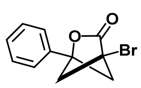




3a

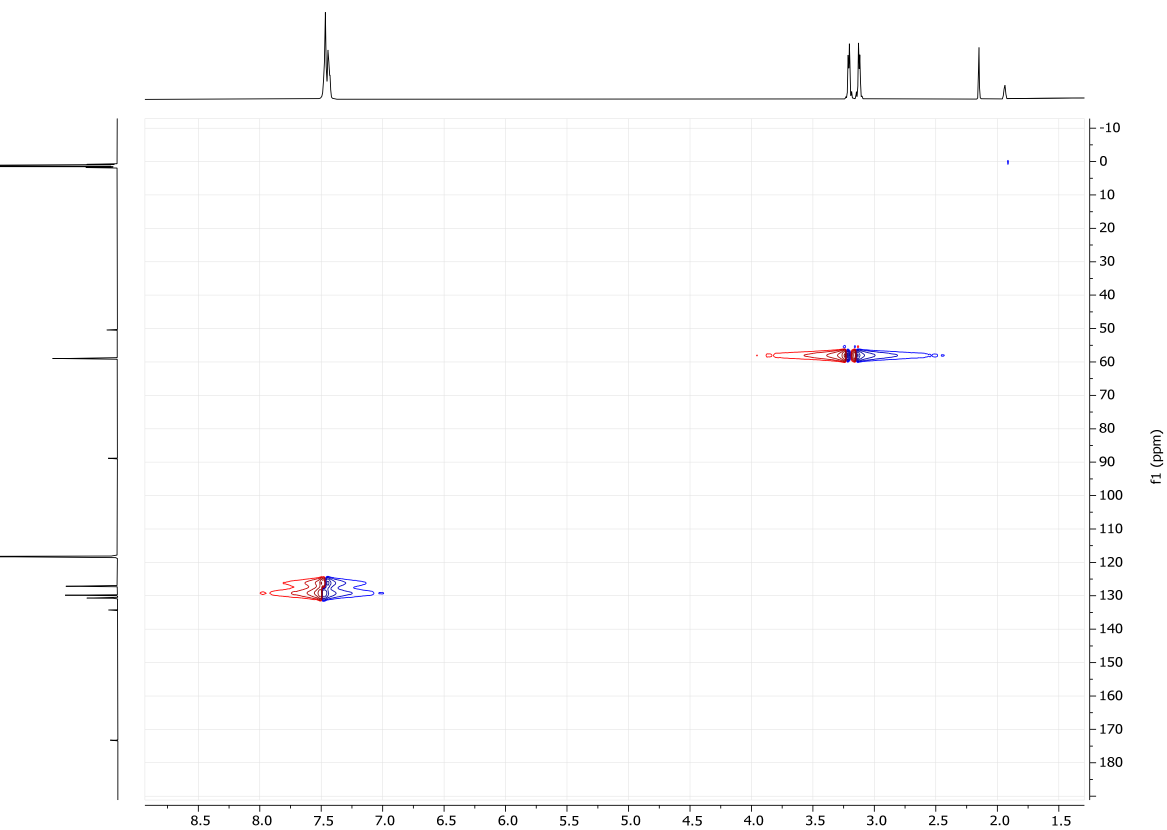
$^{13}C\ \{^{1}H\}$ DEPT-135 NMR, 125 MHz, CD_3CN

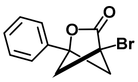




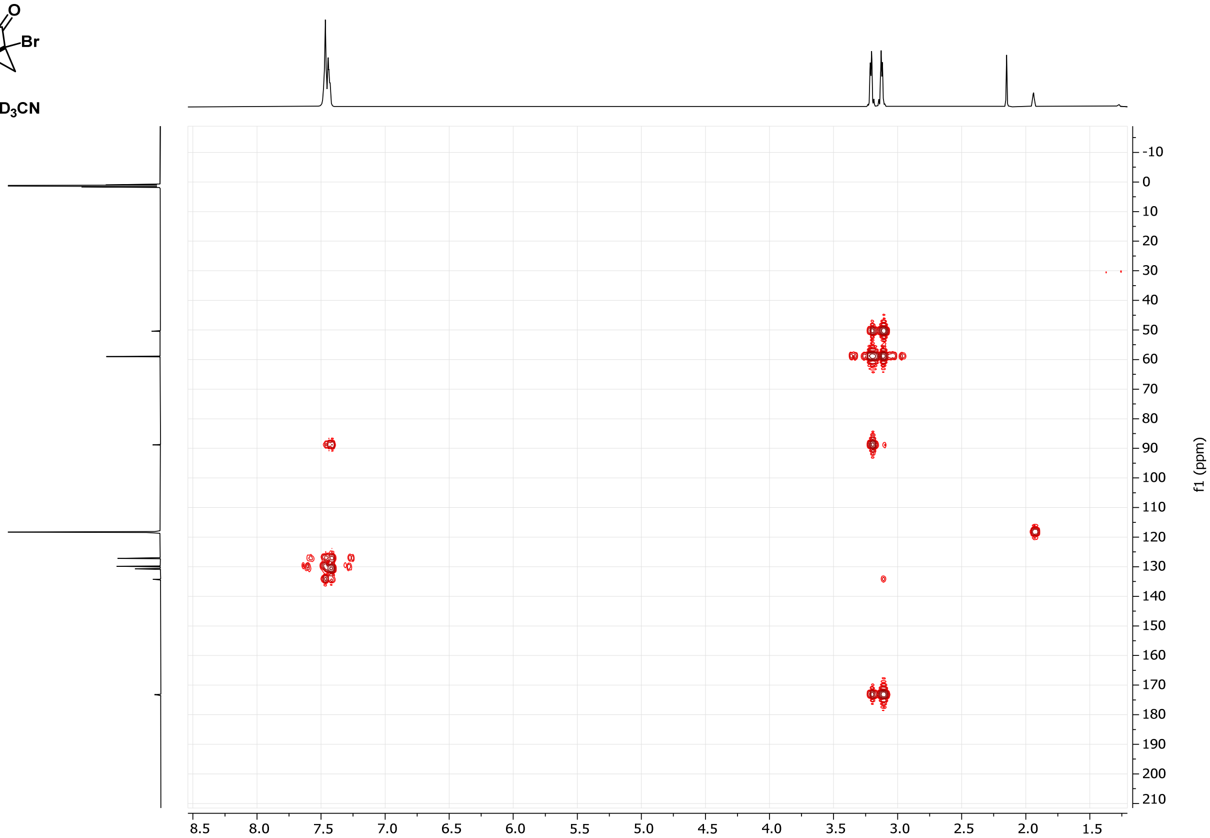
3a

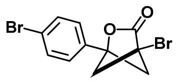
HSQC, CD_3CN





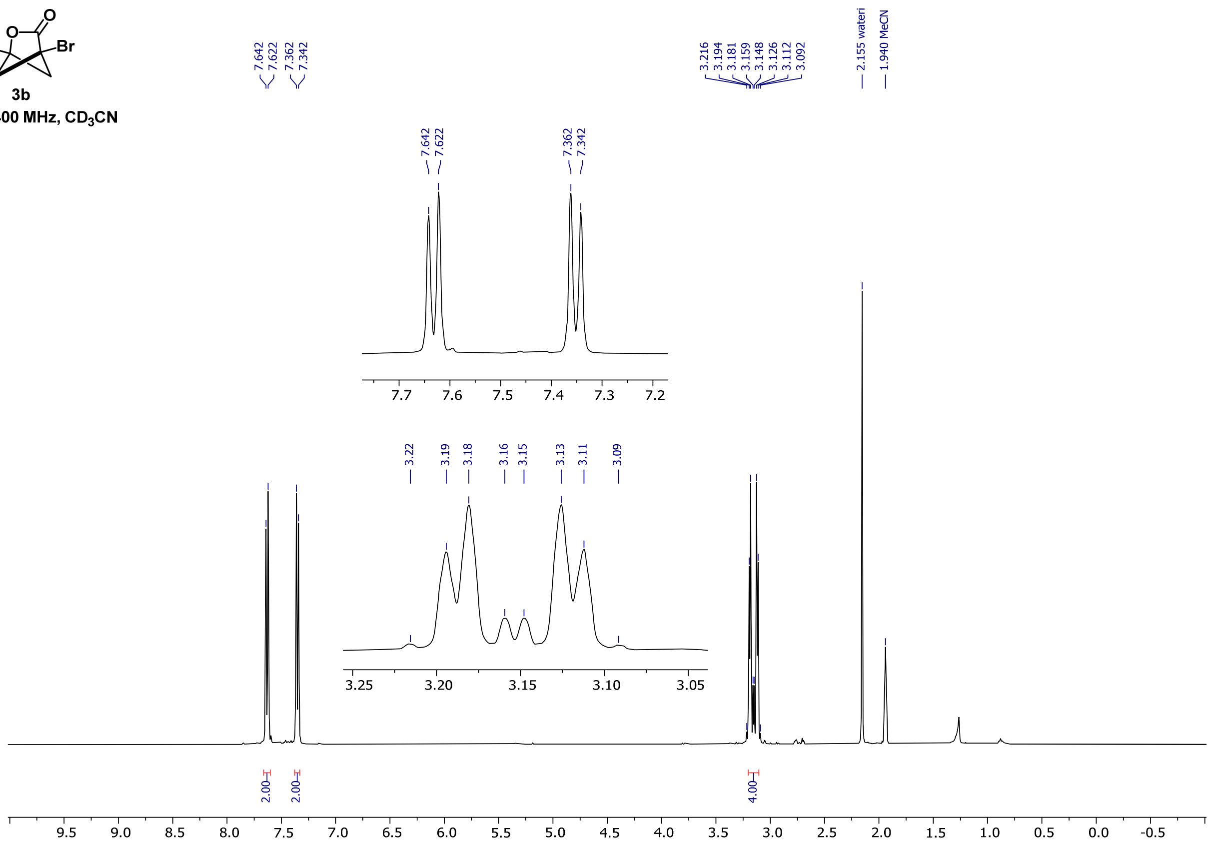
3a
HMBC, CD_3CN

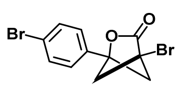




3b

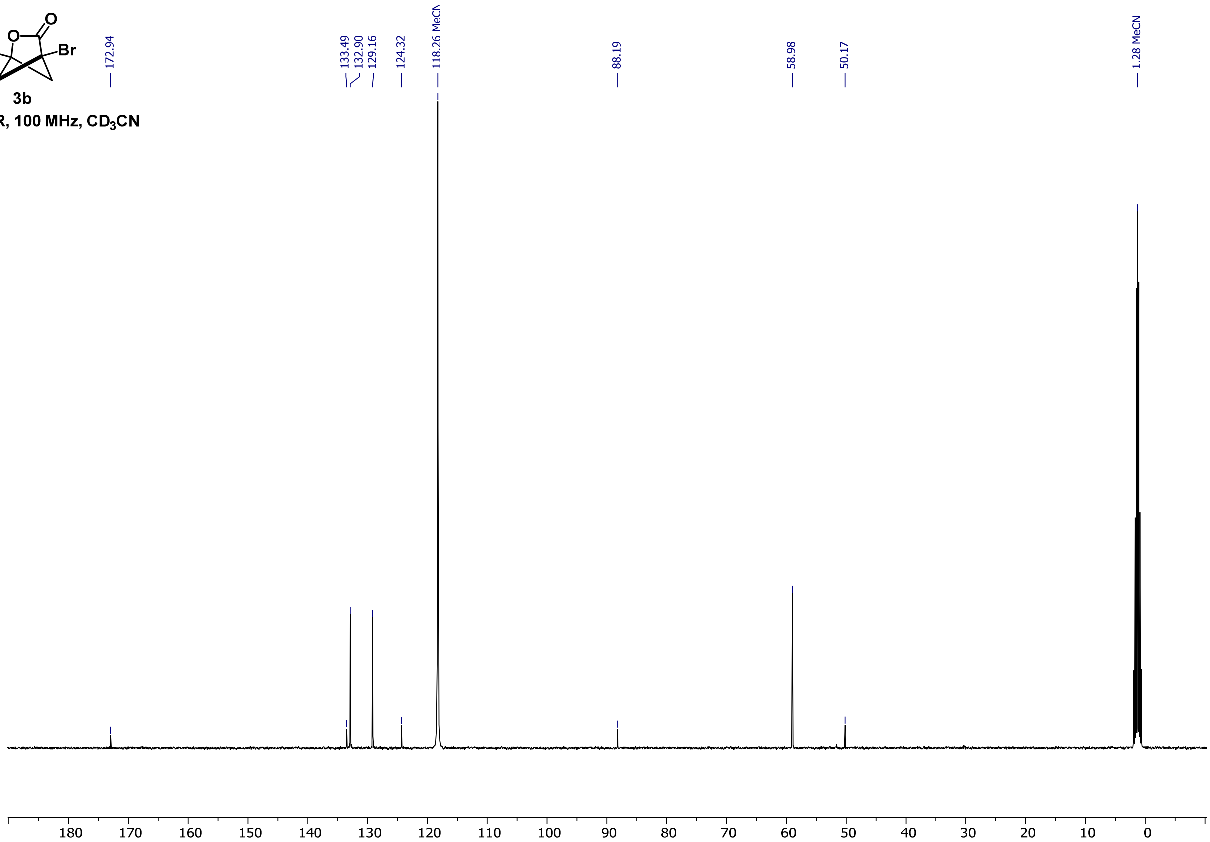
^{1}H NMR, 400 MHz, CD_3CN

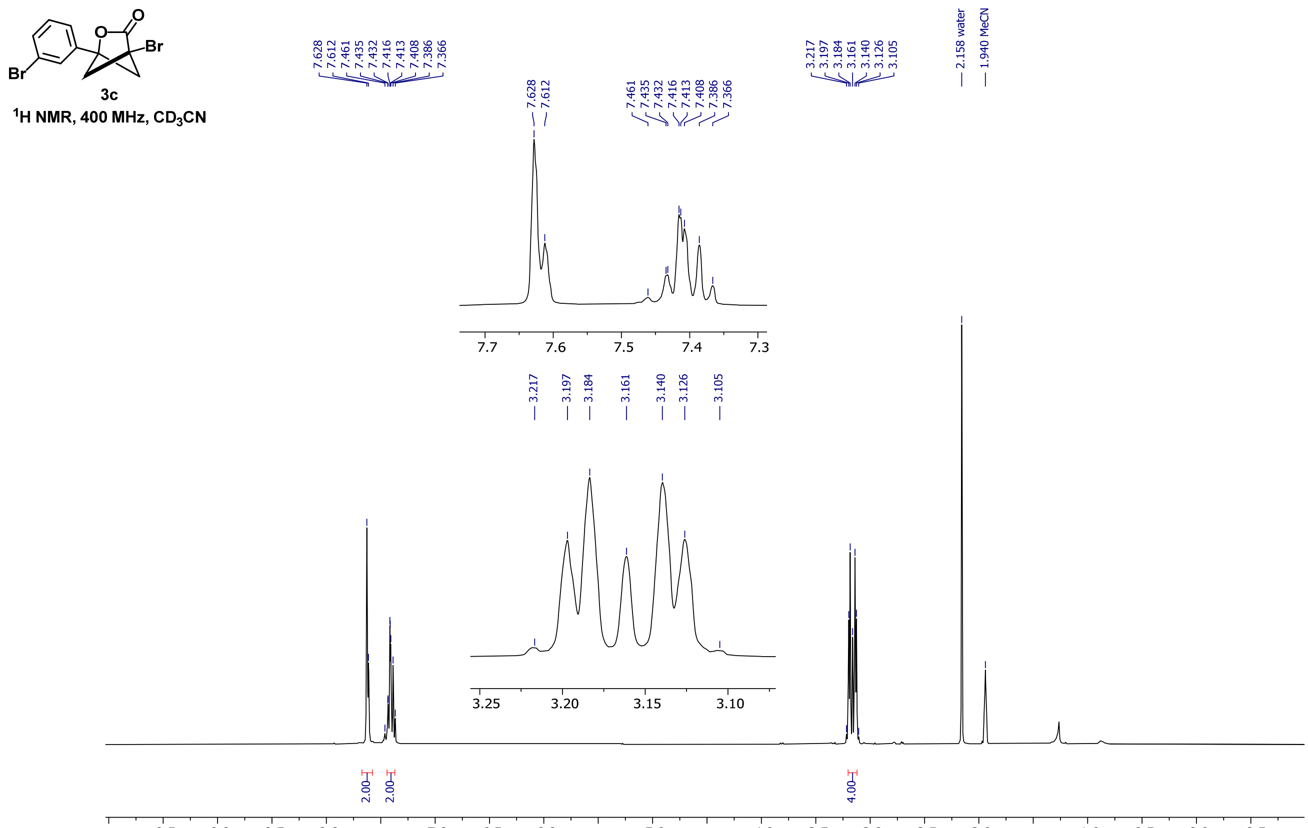


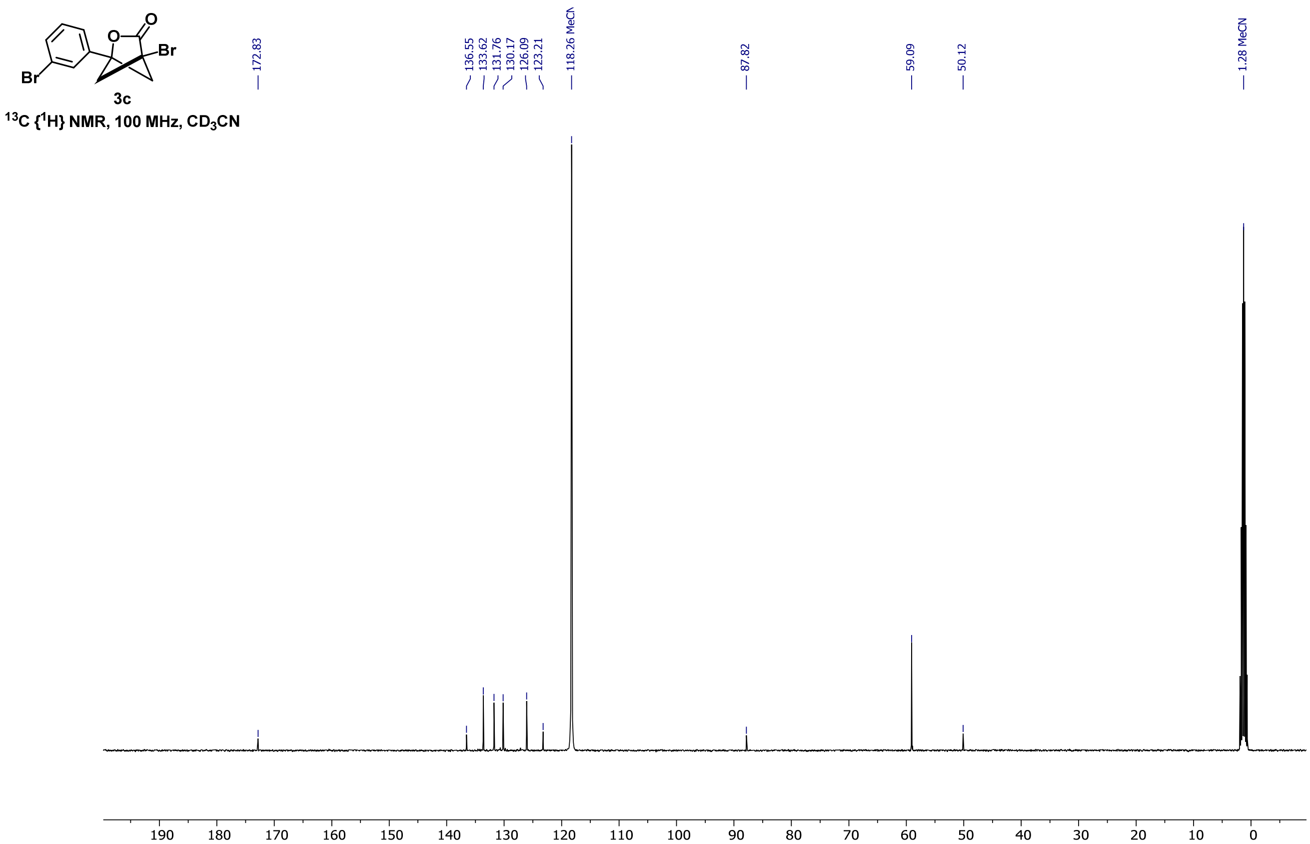


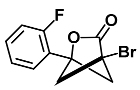
3b

$^{13}C\{^1H\}$ NMR, 100 MHz, CD_3CN



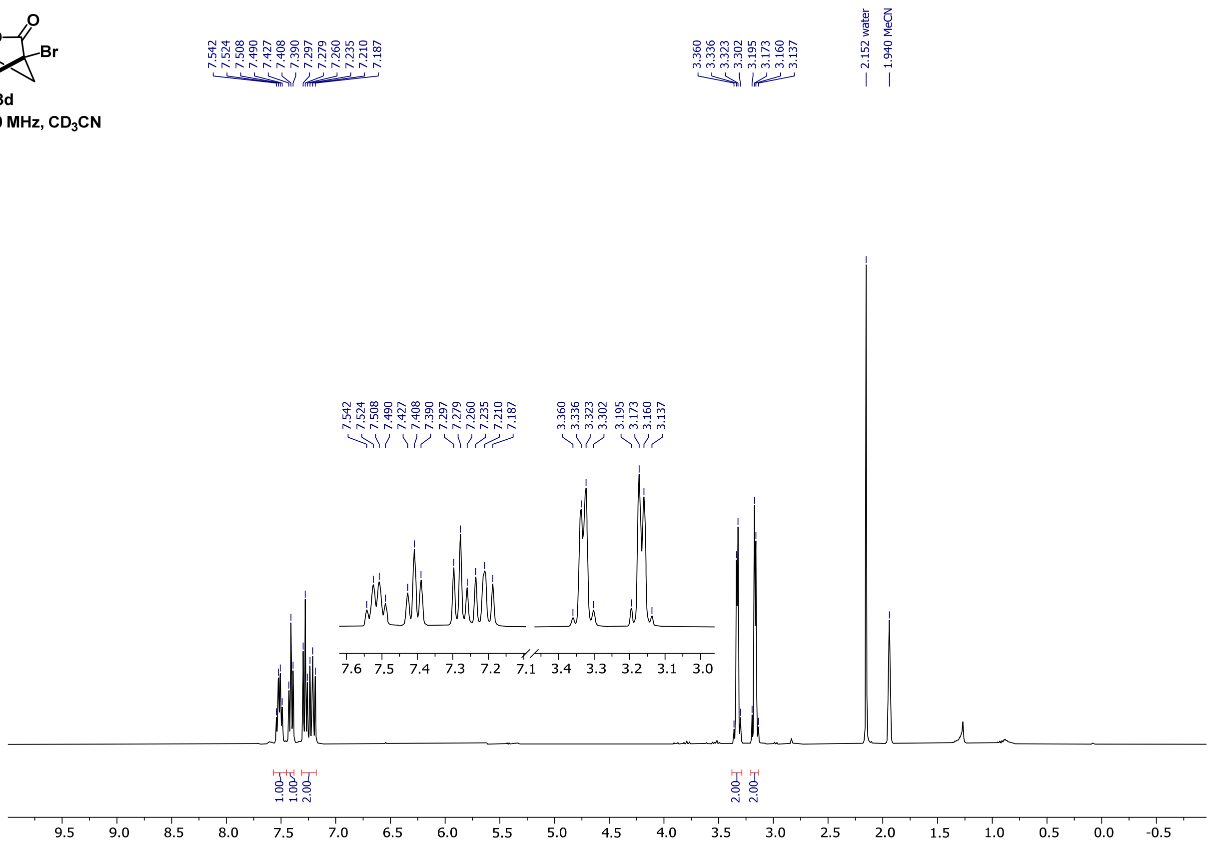

Br
O
O
Br
3c
^{1}H NMR, 400 MHz, CD_3CN
7.628 7.612 7.461 7.435 7.432 7.416 7.413 7.408 7.386 7.366
3.217 3.197 3.184 3.161 3.140 3.126 3.105
2.158 water
1.940 MeCN
2.00 2.00 4.00
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5

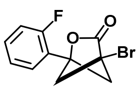

Br
O
O
Br
3c
^{13}C {^{1}H} NMR, 100 MHz, CD_3CN
172.83
136.55 133.62 131.76 130.17 126.09 123.21
118.26 MeCN
87.82
59.09
50.12
1.28 MeCN
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0



3d

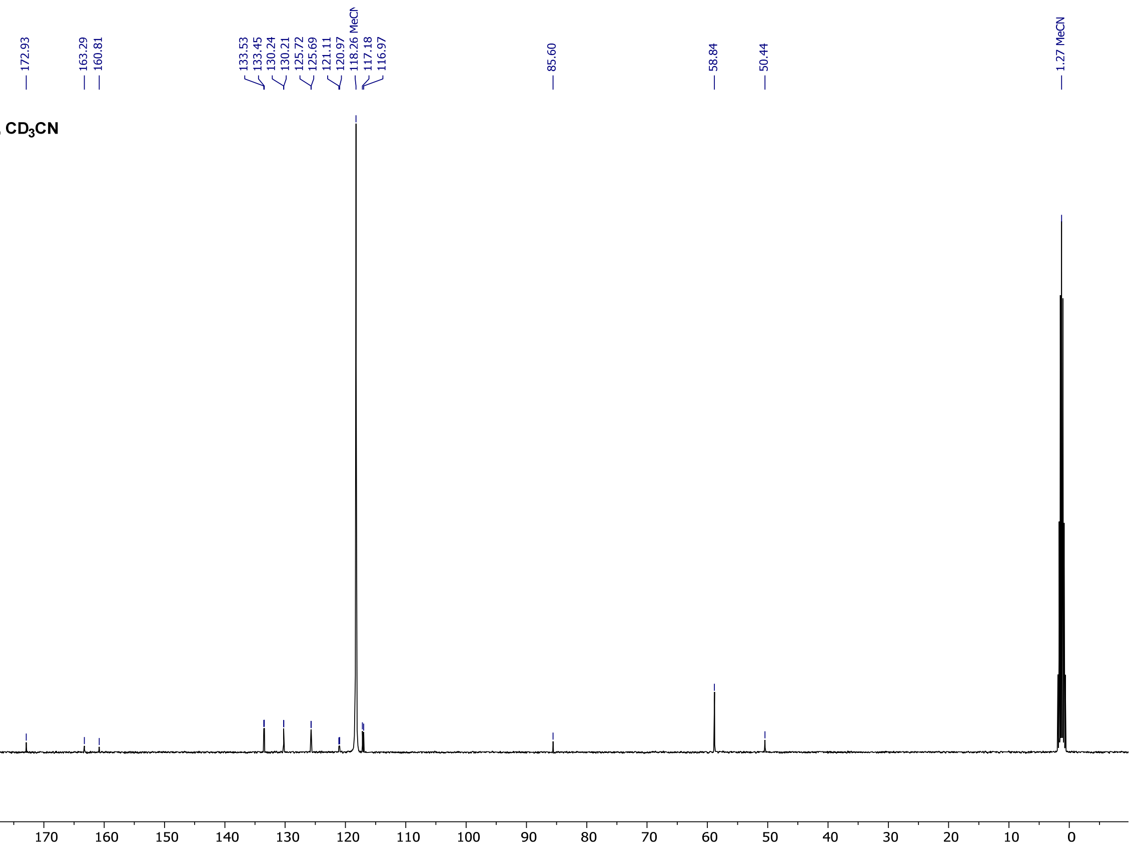
^{1}H NMR, 400 MHz, CD_3CN

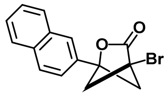




3d

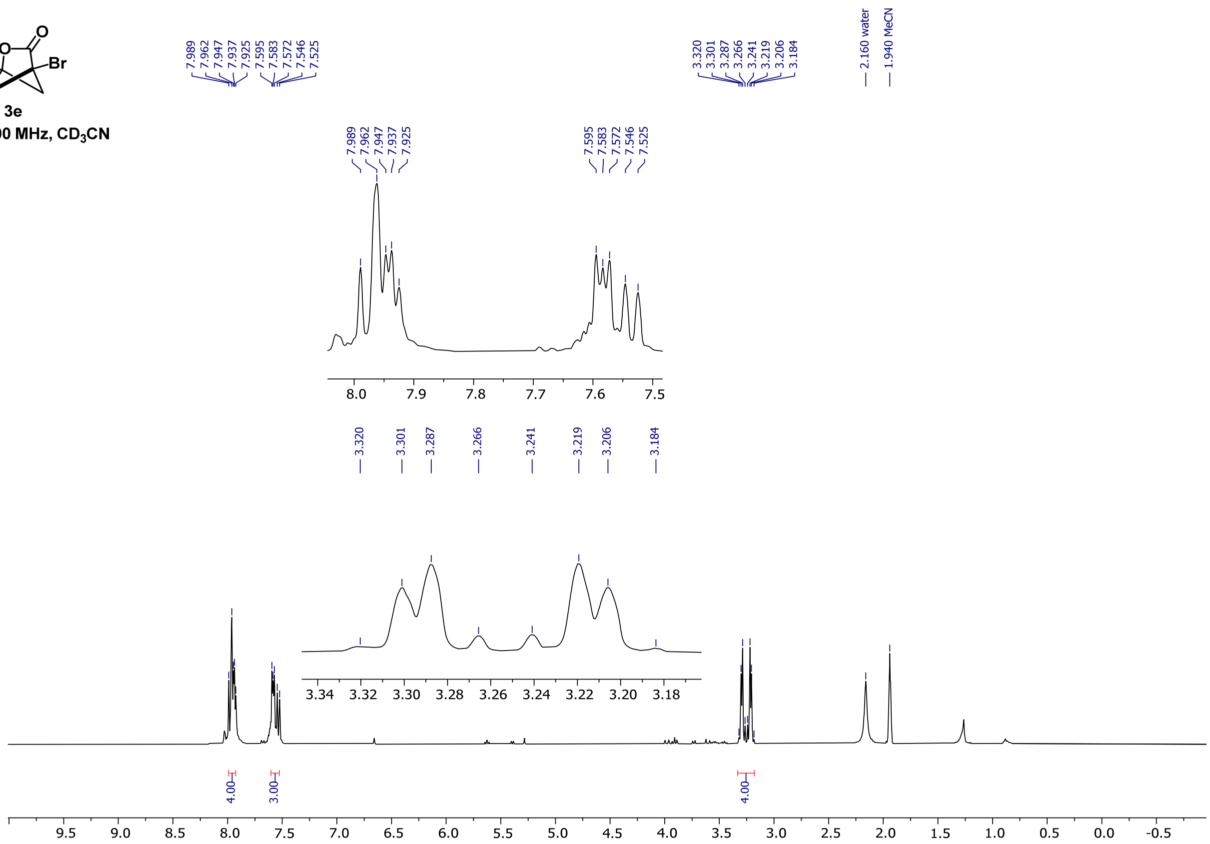
^{13}C {^{1}H} NMR, 100 MHz, CD_3CN

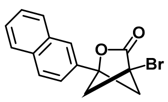




3e

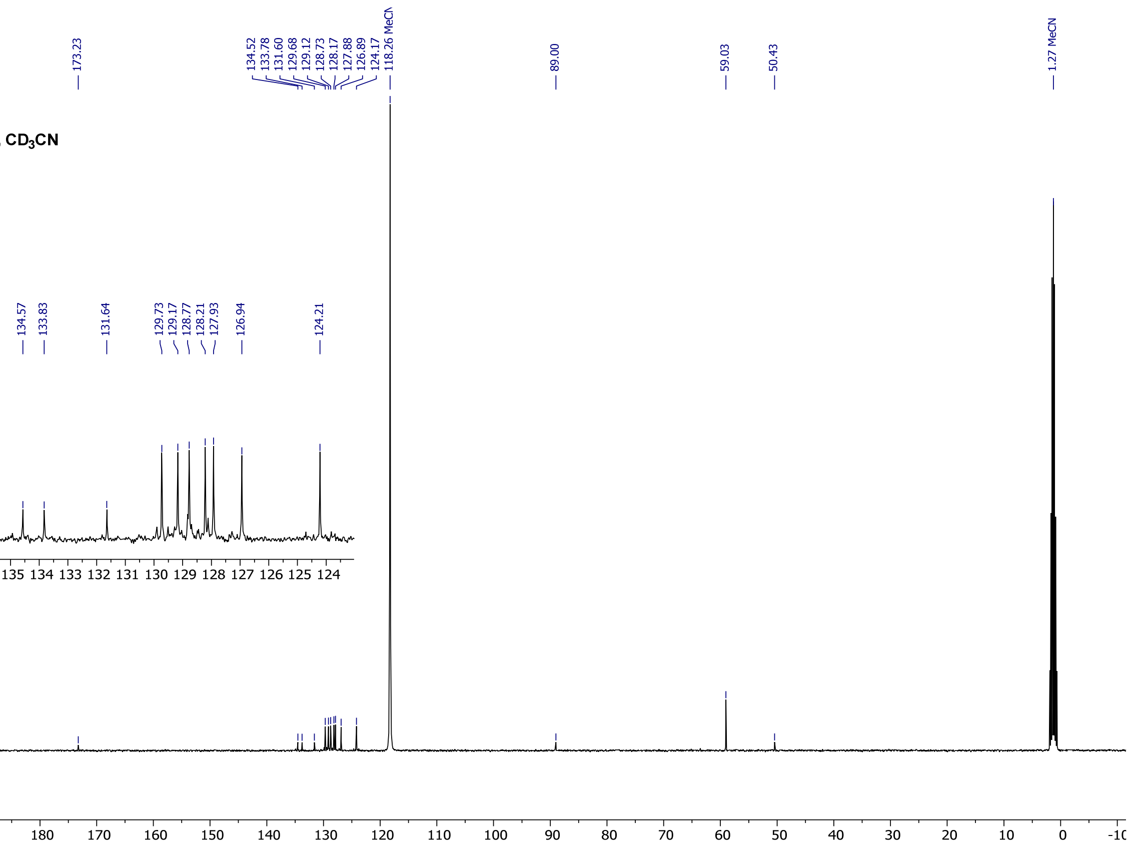
^{1}H NMR, 400 MHz, CD_3CN

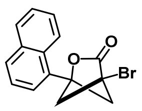




3e

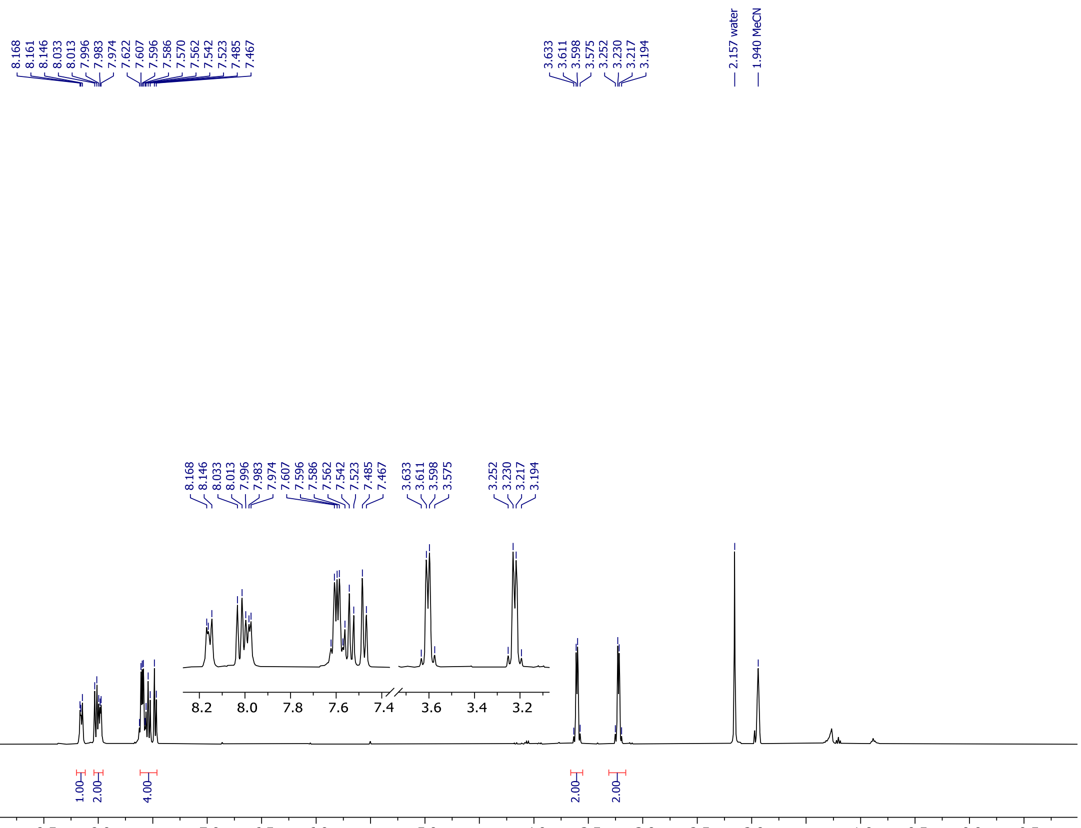
$^{13}C\{^{1}H\}$ NMR, 100 MHz, CD_3CN

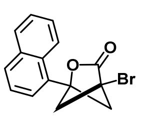




3f

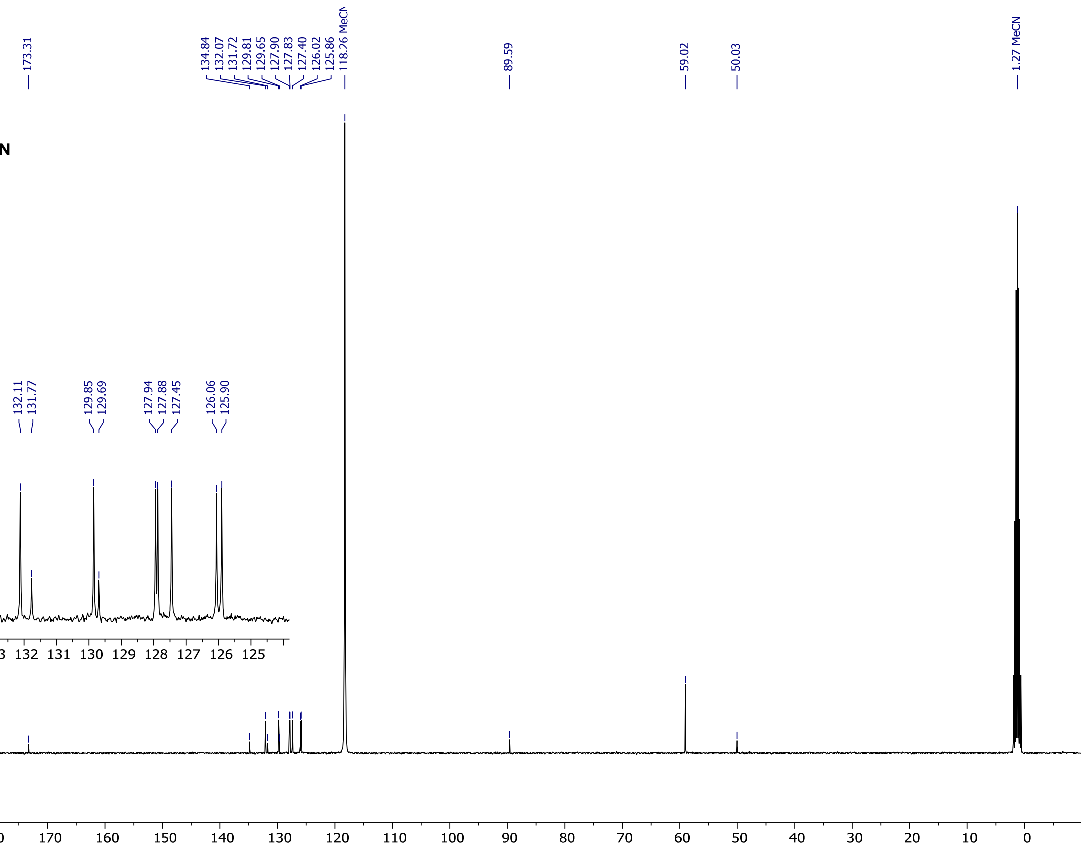
^{1}H NMR, 400 MHz, CD_3CN

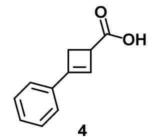




3f

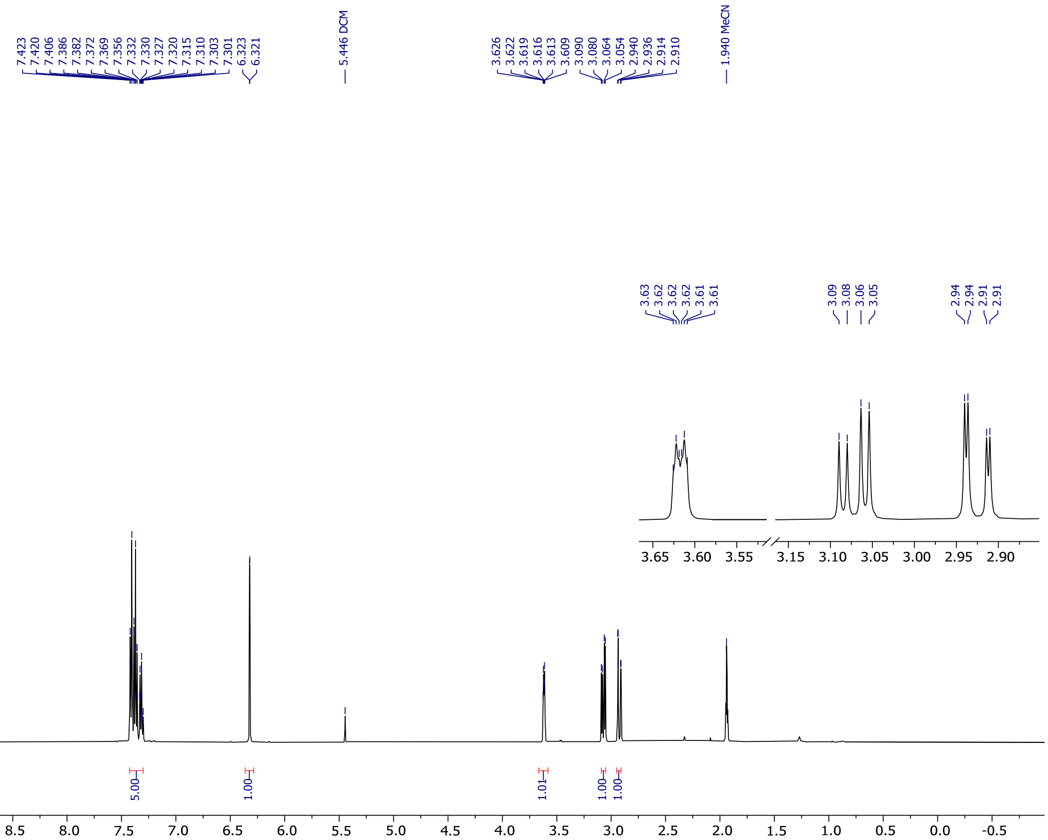
^{13}C {^{1}H} NMR, 100 MHz, CD_3CN

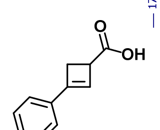




4

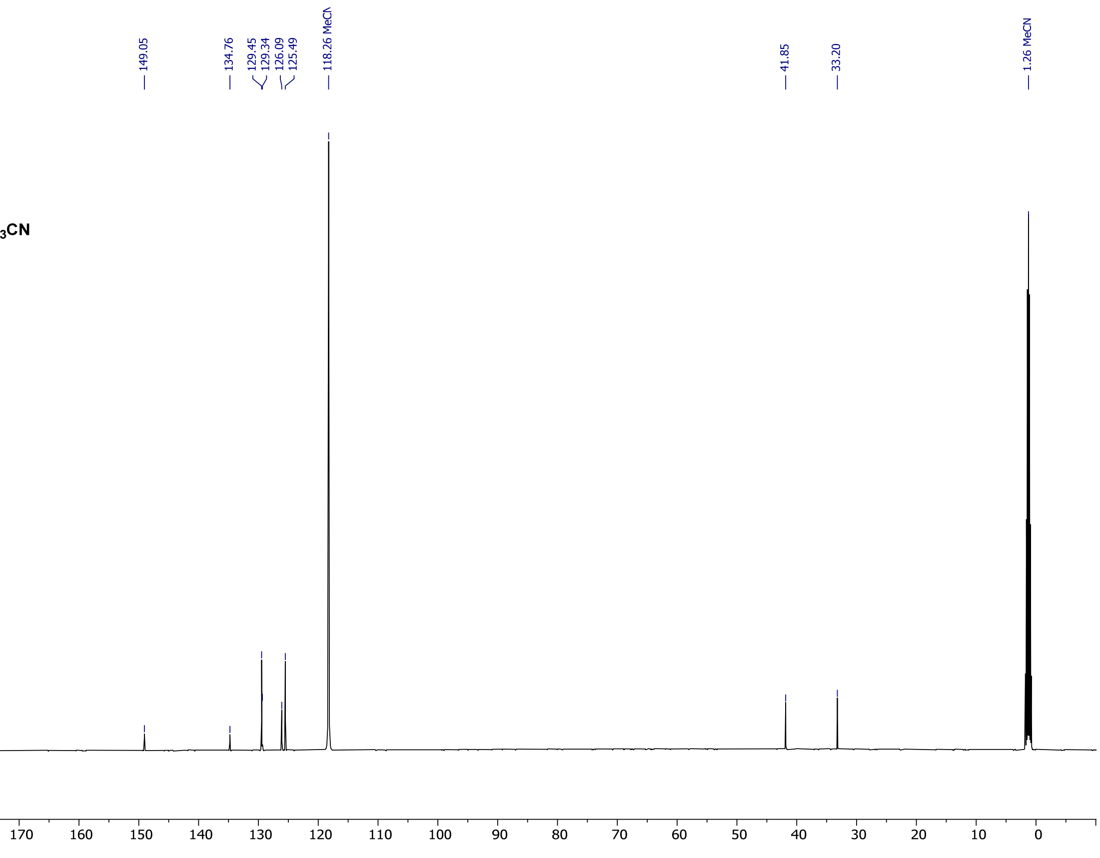
^{1}H NMR, 500 MHz, CD_3CN

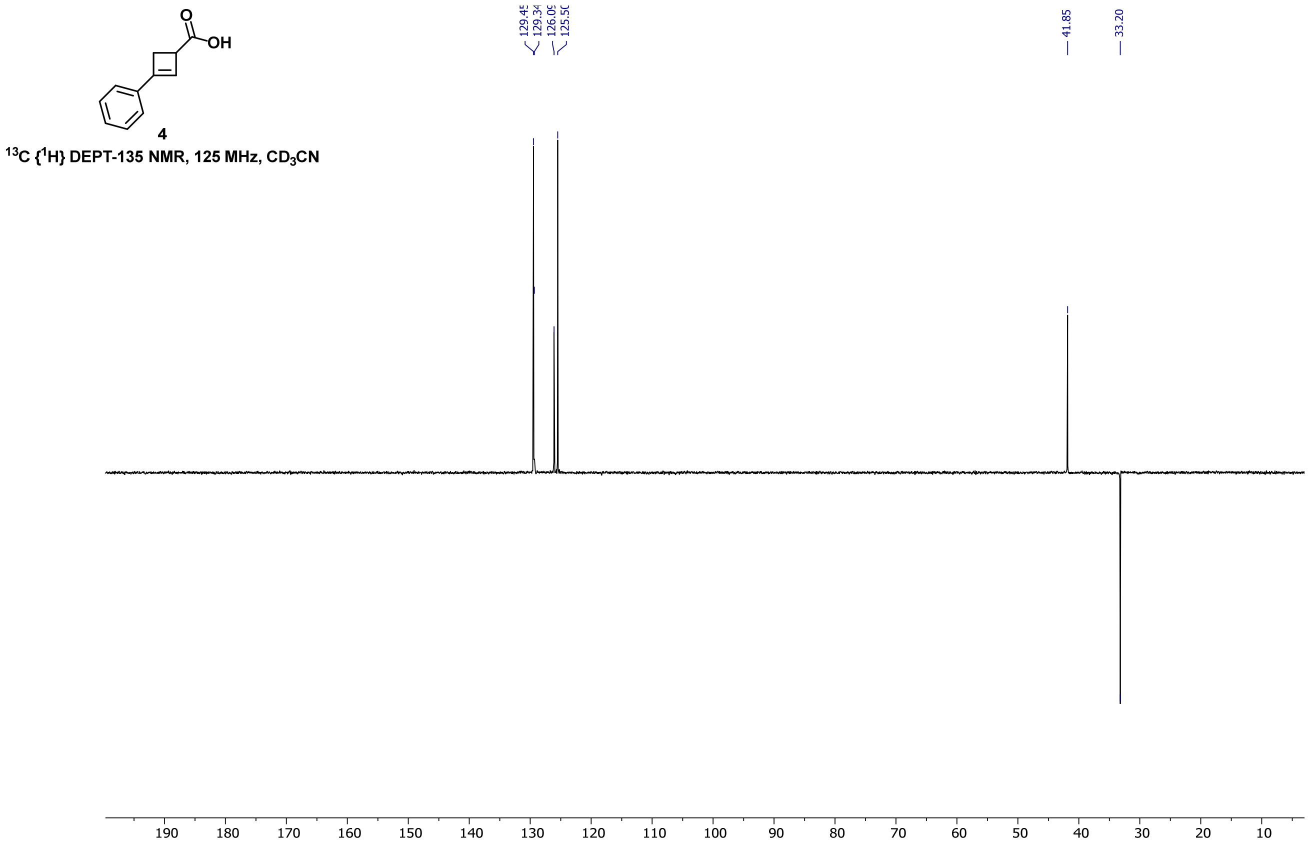


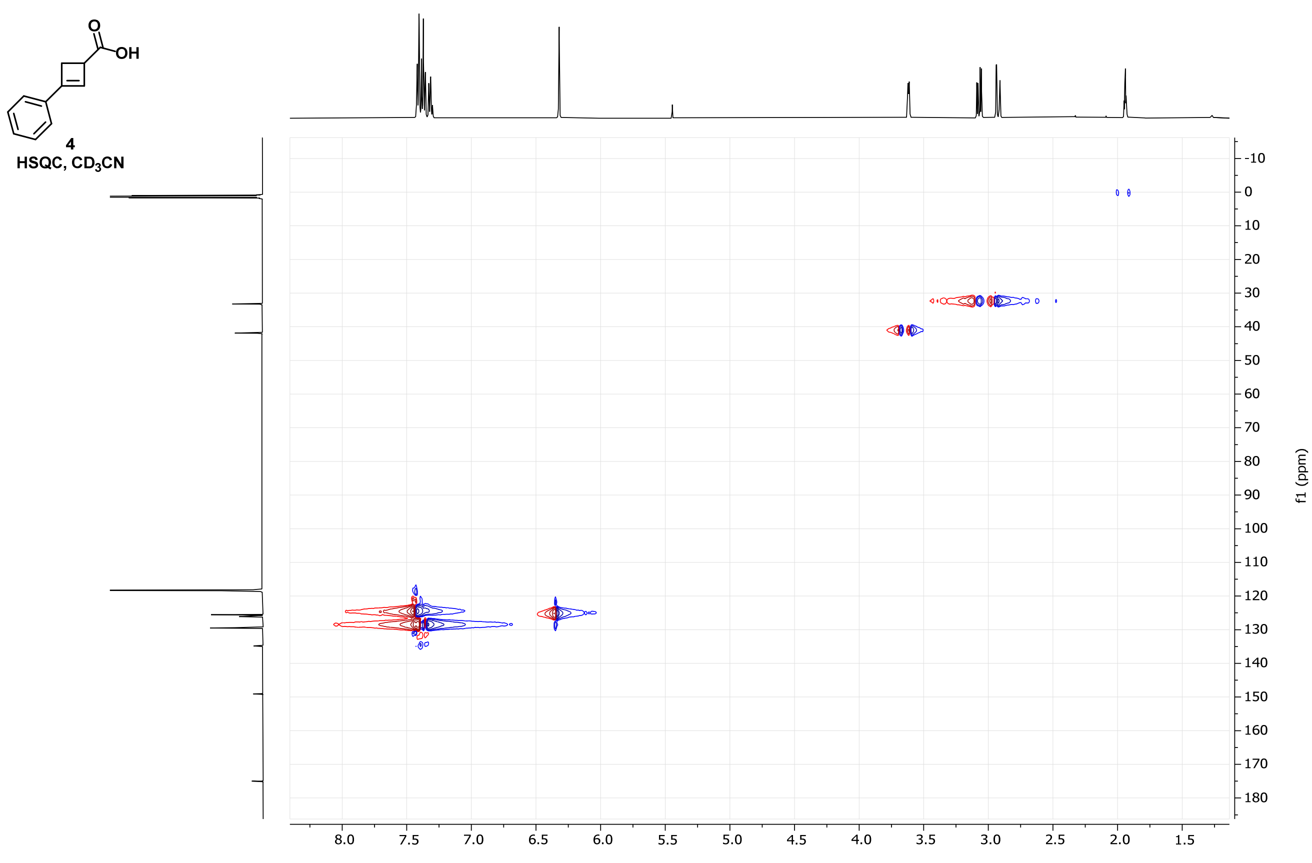


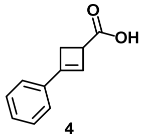
4

^{13}C {^{1}H} NMR, 125 MHz, CD_3CN




4
^{13}C {^{1}H} DEPT-135 NMR, 125 MHz, CD$_3$CN
129.45
129.34
126.09
125.50
41.85
33.20


4
HSQC, CD$_3$CN
f1 (ppm)



4
HMBC, CD_3CN