Supporting Information

Organocatalytic Enantioselective oxa-Piancatelli Rearrangement

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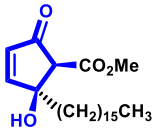
I. General information:

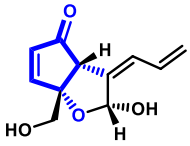
Infrared (FT-IR) spectra were recorded on a FTIR spectrometer (JASCO FT/IR-4100), ν_{max} in cm^{-1} and the bands are characterized as broad (br), strong (s), medium (m), and weak (w). NMR spectra were recorded on Brucker Avance III HD (400 MHz), a Varian MERCURYplus 400 (400 MHz) or a Varian MERCURYplus 300 (300 MHz). Chemical shifts are reported in ppm from tetramethylsilane with the solvent resonance as internal standard [$CDCl_3$: δ 7.26, CD_2Cl_2: δ 5.32, CD_3OD: δ 3.31 for ^{1}H-NMR and $CDCl_3$: δ 77.16, CD_2Cl_2: δ 53.84, CD_3OD: δ 49.00 for ^{13}C-NMR]. For ^{1}H-NMR, data are reported as follows: chemical shift, multiplicity (s = singlet, d = doublet, dd = double doublet, ddd = doublet of doublet of doublets, t = triplet, q = quartet, br = broad, m = multiplet), coupling constants (Hz) and integration. High resolution mass spectrometry ESI-HRMS was performed on a Brucker ESI-TOF microTOF, and EI-HRMS was performed on MAT 8230 Finnigan (Thermo Scientific) instrument. Optical rotations were measured using a Polarotronic polarimeter (Schmidt & Haensch). Melting points are uncorrected and were determined on a Büchi melting point apparatus. Enantiomeric ratios were determined by Jasco MD-4015 using stationary phase chiral columns (25 cm × 0.46 cm) in comparison with authentic racemic compounds.

THF, CH_2Cl_2, and toluene for reactions were purified and dried by a Solvent Purification System MB SPS-800 (Braun). The solvents for column chromatography and TLC were distilled from indicated drying agents: hexane (KOH), ethyl acetate (KOH), *tert*-butyl methyl ether (KOH), dichloromethane (CaH_2). Thin-layer chromatography was performed using ALUGRAM® Xtra SIL G/UV_{254} pre-coated plates (0.20 mm). Spots were visualized by UV (λ = 254 nm) and were treated with a vanillin solution in methanol (technical grade). Flash column chromatography was performed by using Merck silica gel 60 230-400 mesh (0.040-0.063 mm). All reactions that required heating were heated using an oil bath. NMR yields were determined by using 1,3,5-trimethoxybenzene as an internal standard. Unless otherwise noted, all reported yields of the chiral phosphoric acid catalyzed oxa-Piancatelli Rearrangements are isolated yields.

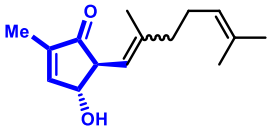
II. Representative examples of natural products containing γ-hydroxy cyclopentenone core structures:



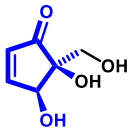
utenone A



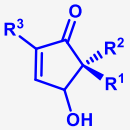
didemnenone A



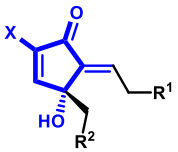
E-litseaverticillol A
Z-litseaverticillol B



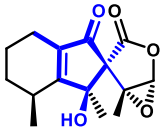
pentenomycin



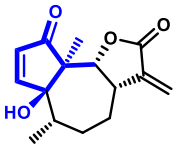
γ-hydroxycyclopentenone



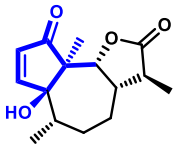
X = I, Br, Cl
punaglandins



ligulolide A
sesquiterpene



parthenin



hymenolin

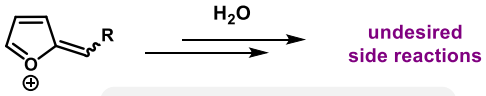
III. Challenges associated with the asymmetric oxa-Piancatelli rearrangement:

A) Poor nucleophilicity of H_2O compare to aryl amines:

H_2O <<< $ArNH_2$

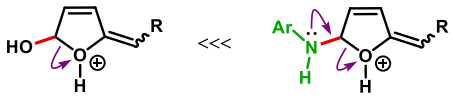
poor nucleophilicity of H_2O

B) Intrinsic instability of furanoxonium ion leds to the undesired side reactions in the presence of poor nucleophile such as H_2O:



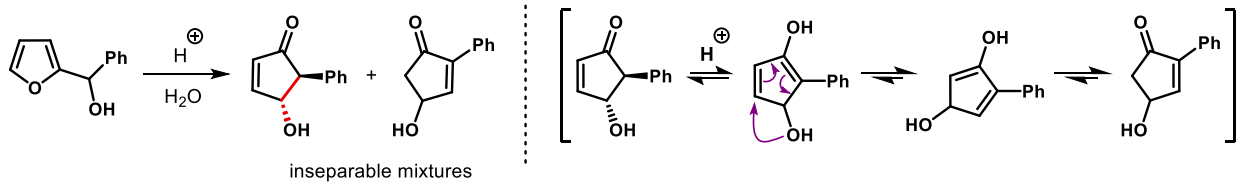
intrinsic instability of furanoxonium ion

C) Inefficient ring-opening step compare to aza-Piancatelli rearrangment:



inefficient ring-opening step

D) Isomerization of product under acidic conditions:

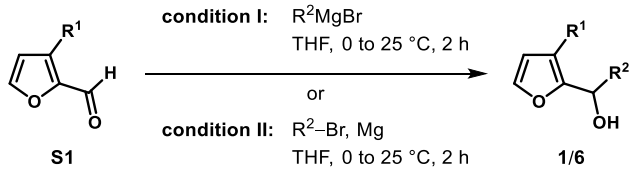


inseparable mixtures

IV. Procedure for the synthesis of 2-furyl carbinols:

3-Substituted furan-2-carbaldehydes (**S1**) were prepared according to the literature procedure.[1]

General procedure A: Preparation of secondary 2-furyl carbinols

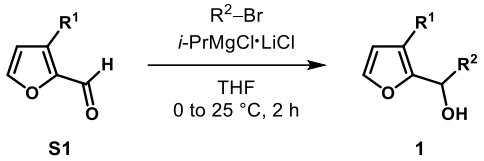


Condition I: In an oven and vacuum-dried round-bottom flask, **S1** (1.5 equiv.) was taken, degassed, purged with nitrogen, and dissolved in dry THF (5.0 mL/mmol of **S1**). Then, the solution was cooled to 0 °C and commercially available Grignard reagent R^2MgBr (1.1 equiv.) was added dropwise. The resulting solution was first stirred at 0 °C for 1 h, then warmed to 25 °C and stirred for another 1 h. The reaction was quenched with pH 6.0 buffer (10 mL) and the organic layer was separated from the aqueous layer. The aqueous layer was extracted with EtOAc (3 × 10.0 mL). Combined organic layer was washed with brine (10.0 mL), dried over anh. Na_2SO_4 and concentrated under reduced pressure to obtain crude product. The crude product was purified by silica-gel column chromatography (7-10% EtOAc in hexane) to obtain **1**.

Condition II: In an oven and vacuum-dried two-necked round-bottom flask, equipped with reflux condenser, magnesium turnings (2.6 equiv.) were taken and heated to 150 °C for 30 min under vacuum. The flask was cooled to 25 °C, purged with nitrogen and one crystal of iodine was added along with dry THF (1.7 mL/mmol of **S1**). To this mixture, corresponding aryl/alkyl bromide (R^2–Br, 2.5 equiv.) was added and the resulting solution was refluxed at 70 °C for 1 h. The reaction mixture was cooled to 0 °C and diluted with dry THF (1.7 mL/mmol of **S**). Next, a solution of **S1** (1.0 equiv.) in dry THF (1.7 mL/mmol of **S1**) was added, and the resulting solution was first stirred at 0 °C for 1 h, then warmed to 25 °C and stirred for another 1 h. The reaction was quenched with pH 6.0 buffer (10 mL) and the organic layer was separated from the aqueous layer. The aqueous layer was extracted with EtOAc (3 × 10.0 mL). Combined organic layer was washed with brine (10.0 mL), dried over anh. Na_2SO_4 and concentrated under reduced pressure to obtain crude product. The crude product was purified by silica-gel column chromatography (6-10% EtOAc in hexane) to obtain **1**/**6**.

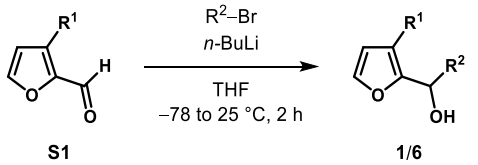
[1] A. Hiscox, K. Ribeiro, R. A. Batey, *Org. Lett.* **2018**, *20*, 6668.

General procedure B: Preparation of secondary 2-furyl carbinols



In an oven and vacuum-dried round-bottom flask, aryl/heteroaryl bromide (R^2–Br, 2.5 equiv.) was taken, degassed, purged with nitrogen, and dissolved in dry THF (2.5 mL/mmol of **S1**). To this solution, *i*-PrMgCl·LiCl (1.3 M in THF, 2.6 equiv.) was added and the resulting solution was stirred at 25 °C for 1 h. Then, the reaction mixture was cooled to 0 °C and a solution of **S1** (1.0 equiv.) in dry THF (2.5 mL/mmol of **S1**) was added dropwise. The resulting solution was first stirred at 0 °C for 1 h, then warmed to 25 °C and stirred for another 1 h. The reaction was quenched with pH 6.0 buffer (10 mL) and the organic layer was separated from the aqueous layer. The aqueous layer was extracted with EtOAc (3 × 10.0 mL). Combined organic layer was washed with brine (10.0 mL), dried over anh. Na_2SO_4 and concentrated under reduced pressure to obtain crude product. The crude product was purified by silica-gel column chromatography (6-10% EtOAc in hexane) to obtain **1**.

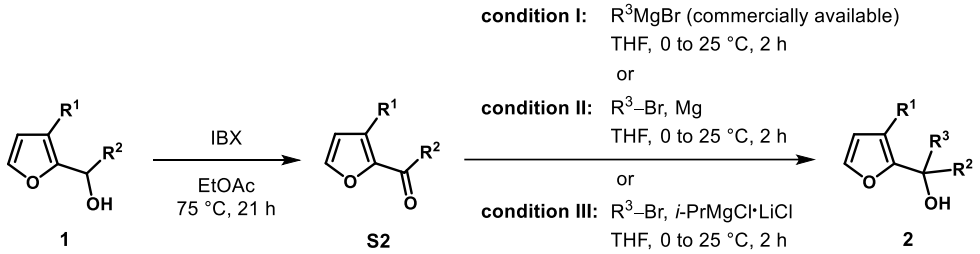
General procedure C: Preparation of secondary 2-furyl carbinols



In an oven and vacuum-dried round-bottom flask, aryl bromide (R^2–Br, 2.0 equiv.) was taken under nitrogen atmosphere, dissolved in dry THF (2.5 mL/mmol of **S1**) and cooled to −78 °C. To this solution, *n*-BuLi (2.5 M in hexane, 2.4 equiv.) was added and the resulting solution was stirred at −78 °C for 2 h. Next, a solution of **S1** (1.0 equiv.) in dry THF (2.5 mL/mmol of **S1**) was added at −78 °C. The resulting solution was warmed to 0 °C, stirred at for 1 h, then warmed to 25 °C and stirred for another 1 h. The reaction was quenched with sat. NH_4Cl solution (10 mL) and the organic layer was separated from the aqueous layer. The aqueous layer was extracted with EtOAc (3 × 10.0 mL). Combined organic layer was washed with brine (10.0 mL), dried over anh. Na_2SO_4 and concentrated under reduced pressure to obtain crude product. The crude product was purified by silica-gel column chromatography (7-10% EtOAc in hexane) to obtain **1**/**6**.

General procedure D: Preparation of tertiary 2-furyl carbinols

Selected secondary 2-furyl carbinols (**1**) were oxidized to the corresponding ketones (**S2**), which were then converted to the tertiary 2-furyl carbinols (**2**) by using the following scheme:



In an oven and vacuum-dried round-bottom flask, equipped with reflux condenser, secondary 2-furyl carbinol **1** (1.0 equiv.) was taken and dissolved in EtOAc (10.0 mL/mmol of **1**). To this solution, 2-iodoxybenzoic acid (IBX) (2.0 equiv.) was added and the resulting solution was stirred at 70 °C for 21 h. Solid was removed by filtering through a cotton plug and washed with EtOAc. The filtrate was concentrated under reduced pressure and the residue was passed through a small bed of silica-gel to obtain **S2**. The ketone **S2** was subjected to the next step without further purification.

Condition I: In an oven and vacuum-dried round-bottom flask, **S2** was taken, degassed, purged with nitrogen, and dissolved in dry THF (10.0 mL/mmol of **1**). Then, the solution was cooled to 0 °C and commercially available Grignard reagent R^3MgBr (1.5 equiv.) was added dropwise. The resulting solution was first stirred at 0 °C for 1 h, then warmed to 25 °C and stirred for another 1 h. The reaction was quenched with pH 6.0 buffer (10 mL) and the organic layer was separated from the aqueous layer. The aqueous layer was extracted with EtOAc (3 × 10.0 mL). Combined organic layer was washed with brine (10.0 mL), dried over anh. Na_2SO_4 and concentrated under reduced pressure to obtain crude product. The crude product was purified by silica-gel column chromatography (5-10% EtOAc in hexane) to obtain **2**.

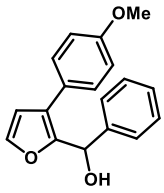
Condition II: In an oven and vacuum-dried two-necked round-bottom flask, equipped with reflux condenser, magnesium turnings (2.6 equiv.) were taken and heated to 150 °C for 30 min under vacuum. The flask was cooled to 25 °C, purged with nitrogen and one crystal of iodine was added along with dry THF (3.4 mL/mmol of **1**). To this mixture, corresponding aryl bromide (R^3–Br, 2.5 equiv.) was added and the resulting solution was refluxed at 70 °C for 1 h. The reaction mixture was cooled to 0 °C and diluted with dry THF (3.4 mL/mmol of **1**). Next, a solution of **S2** in dry THF (3.4 mL/mmol of **1**) was added, and the resulting solution was first stirred at 0 °C for 1 h, then warmed to 25 °C and stirred for another 1 h. The reaction was quenched with pH 6.0 buffer (10 mL) and the organic layer was separated from the aqueous layer. The aqueous layer was extracted with EtOAc (3 × 10.0 mL). Combined organic layer was washed with brine (10.0 mL), dried over anh. Na_2SO_4 and concentrated under reduced pressure to obtain crude product. The

crude product was purified by silica-gel column chromatography (7-10% EtOAc in hexane) to obtain **2**.

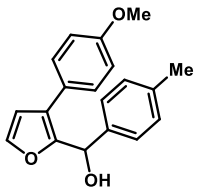
Condition III: In an oven and vacuum-dried round-bottom flask, aryl bromide (R^3–Br, 2.5 equiv.) was taken, degassed, purged with nitrogen, and dissolved in dry THF (5.0 mL/mmol of **1**). To this solution, *i*-PrMgCl·LiCl (1.3 M in THF, 2.6 equiv.) was added and the resulting solution was stirred at 25 °C for 1 h. Then, the reaction mixture was cooled to 0 °C and a solution of **S2** in dry THF (5.0 mL/mmol of **1**) was added dropwise. The resulting solution was first stirred at 0 °C for 1 h, then warmed to 25 °C and stirred for another 1 h. The reaction was quenched with pH 6.0 buffer (10 mL) and the organic layer was separated from the aqueous layer. The aqueous layer was extracted with EtOAc (3 × 10.0 mL). Combined organic layer was washed with brine (10.0 mL), dried over anh. Na_2SO_4 and concentrated under reduced pressure to obtain crude product. The crude product was purified by silica-gel column chromatography (7-10% EtOAc in hexane) to obtain **2**.

[*Note*: These secondary and tertiary 2-furyl carbinols (**1**/**6** and **2**) are sensitive to temperature, pH, and rotary evaporation at 25 °C is necessary.]

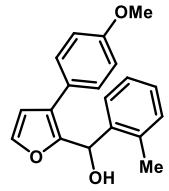
Compound 1a: Prepared according to General Procedure A, Condition I; Starting from 3-(4-methoxyphenyl)furan-2-carbaldehyde (1.30 g, 6.280 mmol, 1.0 equiv.); Purified by silica-gel flash column chromatography (10% EtOAc in hexane); Yellow thick oil (1.68 g, 5.993 mmol, 95% yield); **FT-IR (Thin film):** 3421 (br), 1519 (s), 1452 (w), 1247 (s), 1182 (m), 1032 (m), 833 (s), 763 (w); **^{1}H-NMR (400 MHz, CD_2Cl_2):** δ 7.44-7.34 (m, 7H), 7.32-7.27 (m, 1H), 6.96 (d, *J* = 8.7 Hz, 2H), 6.55 (d, *J* = 1.9 Hz, 1H), 5.95 (d, *J* = 5.7 Hz, 1H), 3.83 (s, 3H), 2.53 (d, *J* = 5.7 Hz, 1H); **^{13}C-NMR (100 MHz, CD_2Cl_2):** δ 159.5, 149.9, 142.5, 141.9, 129.7, 128.8, 128.1, 126.8, 125.7, 124.2, 114.5, 112.1, 68.4, 55.7; **HRMS (ESI+):** Calcd. for $C_{18}H_{16}O_3$ ($[M+Na]^+$): 303.0992, Found: 303.0993.



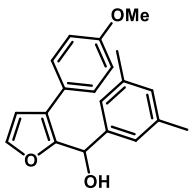
Compound 1b: Prepared according to General Procedure A, Condition II; Starting from 3-(4-methoxyphenyl)furan-2-carbaldehyde (600.0 mg, 2.970 mmol, 1.0 equiv.); Purified by silica-gel flash column chromatography (7% EtOAc in hexane); Yellow thick oil (700.0 mg, 2.378 mmol, 80% yield); **FT-IR (Thin film):** 3434 (br), 2921 (w), 1604 (m), 1518 (s), 1248 (s), 1179 (s), 1032 (s), 894 (w); **^{1}H-NMR (400 MHz, CD_2Cl_2):** δ 7.41 (d, *J* = 1.9 Hz, 1H), 7.38 (d, *J* = 8.7 Hz, 2H), 7.31 (d, *J* = 8.0 Hz, 2H), 7.18 (d, *J* = 7.7 Hz, 2H), 6.96 (d, *J* = 8.7 Hz, 2H), 6.54 (d, *J* = 1.9 Hz, 1H), 5.91 (d, *J* = 5.1 Hz, 1H), 3.83 (s, 3H), 2.48 (d, *J* = 5.6 Hz, 1H), 2.34 (s, 3H); **^{13}C-NMR (100 MHz, CD_2Cl_2):** δ 159.4, 150.1, 142.4, 138.9, 138.0, 129.7, 129.5, 126.8, 125.8, 123.9, 114.5, 112.0, 68.3, 55.7, 21.2; **HRMS (ESI+):** Calcd. for $C_{19}H_{18}O_3$ ($[M+Na]^+$): 317.1148, Found: 317.1151.



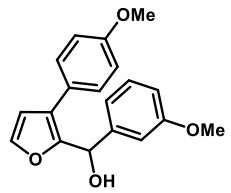
Compound 1c: Prepared according to General Procedure A, Condition II; Starting from 3-(4-methoxyphenyl)furan-2-carbaldehyde (600.0 mg, 2.970 mmol, 1.0 equiv.); Purified by silica-gel flash column chromatography (5% EtOAc in hexane); Colorless oil (843.0 mg, 2.860 mmol, 96% yield); **FT-IR (Thin film):** 3409 (br), 2934 (w), 1604 (m), 1518 (s), 1462 (m), 1248 (s), 1179 (m), 1032 (m), 835 (m), 744 (s); **^{1}H-NMR (400 MHz, CD_2Cl_2):** δ 7.65 (dd, *J* = 7.7, 1.5 Hz, 1H), 7.41-7.38 (m, 3H), 7.25 (td, *J* = 7.5, 1.6 Hz, 1H), 7.19 (td, *J* = 7.4, 1.6 Hz, 1H), 7.12 – 7.09 (m, 1H), 6.96 (d, *J* = 8.7 Hz, 2H), 6.54 (d, *J* = 1.9 Hz, 1H), 6.02 (d, *J* = 5.2 Hz, 1H), 3.83 (s, 3H), 2.43 (d, *J* = 5.3 Hz, 1H), 2.00 (s, 3H); **^{13}C-NMR (75 MHz, CD_2Cl_2):** δ 159.5, 149.3, 142.4, 139.8, 135.7, 130.7, 129.6, 128.0, 126.3, 126.3, 125.8, 124.2, 114.5, 111.9, 66.2, 55.7, 19.0; **HRMS (ESI+):** Calcd. for $C_{19}H_{18}O_3$ ([M+Na]+): 317.1148, Found: 317.1141.



Compound 1d: Prepared according to General Procedure A, Condition II; Starting from 3-(4-methoxyphenyl)furan-2-carbaldehyde (300.0 mg, 1.480 mmol, 1.0 equiv.); Purified by silica-gel flash column chromatography (6% EtOAc in hexane); Yellow oil (439.0 mg, 1.420 mmol, 96% yield); **FT-IR (Thin film):** 3213 (br), 3039 (w), 2915 (s), 1606 (s), 1516 (s), 1250 (s), 1180 (s), 1036 (s), 834 (s), 754 (s); **^{1}H-NMR (400 MHz, CD_2Cl_2):** δ 7.42 (d, *J* = 1.9 Hz, 1H), 7.39 (d, *J* = 8.8 Hz, 2H), 7.04-7.03 (m, 2H), 6.98-6.94 (m, 3H), 6.54 (d, *J* = 1.9 Hz, 1H), 5.87 (d, *J* = 5.5 Hz, 1H), 3.83 (s, 3H), 2.48 (d, *J* = 5.6 Hz, 1H), 2.31 (s, 6H); **^{13}C-NMR (100 MHz, CD_2Cl_2):** 159.4, 150.1, 142.4, 141.7, 138.5, 129.8, 129.7, 125.8, 124.5, 123.9, 114.5, 112.0, 68.4, 55.7, 21.5; **HRMS (ESI+):** Calcd. for $C_{20}H_{20}O_3$ ([M+Na]+): 331.1305, Found: 331.1296.



Compound 1e: Prepared according to General Procedure A, Condition II; Starting from 3-(4-methoxyphenyl)furan-2-carbaldehyde (600.0 mg, 2.970 mmol, 1.0 equiv.); Purified by silica-gel flash column chromatography (7% EtOAc in hexane); Yellow thick oil (887.0 mg, 2.858 mmol, 96% yield); **FT-IR (Thin film):** 3444 (br), 2835 (w), 1602 (m), 1518 (s), 1249 (s), 1033 (s), 962 (m), 835 (m); **^{1}H-NMR (400 MHz, CD_2Cl_2):** δ 7.42 (d, *J* = 1.9 Hz, 1H), 7.39 (d, *J* = 8.7 Hz, 2H), 7.26 (t, *J* = 7.9 Hz, 1H), 7.01-7.00 (m, 1H), 6.98-6.94 (m, 1H), 6.96 (d, *J* = 8.7 Hz, 2H), 6.83 (dd, *J* = 8.3, 2.7 Hz, 1H), 6.54 (d, *J* = 1.9 Hz, 1H), 5.92 (d, *J* = 5.7 Hz, 1H), 3.83 (s, 3H), 3.79 (s, 3H), 2.53 (d, *J* = 5.7 Hz, 1H); **^{13}C-NMR (100 MHz, CD_2Cl_2):** δ 160.2, 159.5, 149.8, 143.5, 142.4, 129.8, 129.7, 125.7, 124.2, 119.0, 114.5, 113.4, 112.5, 112.1, 68.3, 55.7, 55.6; **HRMS (ESI+):** Calcd. for $C_{19}H_{18}O_4$ ($[M+Na]^+$): 333.1097, Found: 333.1100.

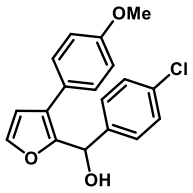


Compound 1f: Prepared according to General Procedure A, Condition II; Starting from 3-(4-methoxyphenyl)furan-2-carbaldehyde (600.0 mg, 2.970 mmol, 1.0 equiv.); Purified by silica-gel flash column chromatography (5% EtOAc in hexane); Orange solid (814.0 mg, 2.490 mmol, 84% yield); **m.p.** 80-82 °C; **FT-IR (Thin film):** 3412 (br), 3366 (s), 3002 (w), 1610 (m), 1519 (s), 1248 (s), 1180 (s), 1036 (m), 836 (s), 775 (m); **^{1}H-NMR (400 MHz, CD_2Cl_2):** δ 7.42 (d, *J* = 1.9 Hz, 1H), 7.37 (d, *J* = 8.8 Hz, 2H), 7.34 (d, *J* = 8.4 Hz, 2H), 7.24 (d, *J* = 8.4 Hz, 2H), 6.95 (d, *J* = 8.7 Hz, 2H), 6.54 (d, *J* = 1.9 Hz, 1H), 5.91 (d, *J* = 5.5 Hz, 1H), 3.82 (s, 3H), 2.50 (d, *J* = 5.7 Hz, 1H), 2.47 (s, 3H); **^{13}C-NMR (100 MHz, CD_2Cl_2):** 159.5, 149.7, 142.5, 138.6, 138.5, 129.7, 127.4, 126.7, 125.7, 124.1, 114.5, 112.1, 68.1, 15.9; **HRMS (ESI+):** Calcd. for $C_{19}H_{18}O_3S$ ([M+Na]+): 349.0869, Found: 349.0864.

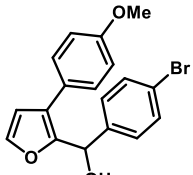
Compound 1g: Prepared according to General Procedure A, Condition II; Starting from 3-(4-methoxyphenyl)furan-2-carbaldehyde (600.0 mg, 2.970 mmol, 1.0 equiv.); Purified by silica-gel flash column chromatography (5% EtOAc in hexane); Pale-yellow solid (910.0 mg, 2.550 mmol, 86% yield); **m.p.** 100-102 °C; **FT-IR (Thin film):** 3398 (br), 3031 (w), 2934 (w), 1615 (m), 1521 (s), 1248 (s), 1183 (s), 989 (s), 833 (s), 699 (s); **^{1}H-NMR (400 MHz, CD_2Cl_2):** δ 7.61 (d, *J* = 8.4 Hz, 4H), 7.50 (d, *J* = 8.3 Hz, 2H), 7.46-7.40 (m, 5H), 7.37-7.33 (m, 1H), 6.97 (d, *J* = 8.7 Hz, 2H), 6.56 (d, *J* = 1.9 Hz, 1H), 6.00 (d, *J* = 5.6 Hz, 1H), 3.83 (s, 3H), 2.55 (d, *J* = 5.7 Hz, 1H); **^{13}C-NMR (100 MHz, CD_2Cl_2):** 159.5, 149.8, 142.5, 141.1, 140.9, 129.8, 129.2, 127.8, 127.5, 127.4, 127.3, 125.7, 124.2, 114.6, 112.1, 68.2, 55.7; **HRMS (ESI+):** Calcd. for $C_{24}H_{20}O_3$ ([M+Na]+): 379.1305, Found: 379.1302.

Compound 1h: Prepared according to General Procedure B; Starting from 3-(4-methoxyphenyl)furan-2-carbaldehyde (600.0 mg, 2.970 mmol, 1.0 equiv.); Purified by silica-gel flash column chromatography (7% EtOAc in hexane); Yellow thick oil (649.0 mg, 2.176 mmol, 73% yield); **FT-IR (Thin film):** 3435 (br), 1591 (m), 1518 (s), 1487 (w), 1465 (s), 1247 (s), 1179 (m), 834 (m); **^{1}H-NMR (300 MHz, CD_2Cl_2):** δ 7.42 (d, *J* = 1.9 Hz, 1H), 7.38 (d, *J* = 8.9 Hz, 2H), 7.34-7.29 (m, 1H), 7.20-7.15 (m, 2H), 7.03-6.98 (m, 1H), 6.96 (d, *J* = 8.9 Hz, 2H), 6.55 (d, *J* = 1.8 Hz, 1H), 5.95 (d, *J* = 5.2 Hz, 1H), 3.83 (s, 3H), 2.58 (d, *J* = 5.6 Hz, 1H); **^{13}C-NMR (75 MHz, CD_2Cl_2):** δ 163.3 (d, *J* = 245.0 Hz), 159.6, 149.2, 144.5 (d, *J* = 6.9 Hz), 142.7, 130.3 (d, *J* = 8.1 Hz), 129.7, 125.5, 124.6, 122.5 (d, *J* = 2.6 Hz), 114.8 (d, *J* = 21.3 Hz), 114.6, 113.8 (d, *J* = 22.7 Hz), 112.2, 67.8 (d, *J* = 2.0 Hz), 55.7; **HRMS (ESI+):** Calcd. for $C_{18}H_{15}FO_3$ ([M+Na]$^{+}$): 321.0897, Found: 321.0895.

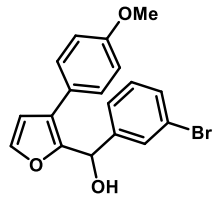
Compound 1i: Prepared according to General Procedure A, Condition I; Starting from 3-(4-methoxyphenyl)furan-2-carbaldehyde (702.0 mg, 3.470 mmol, 1.0 equiv.); Purified by silica-gel flash column chromatography (6% EtOAc in hexane); Yellow thick oil (814.0 mg, 2.586 mmol, 75% yield); **FT-IR (Thin film):** 3408 (br), 1518 (s), 1491 (m), 1249 (s), 1179 (s), 1091 (m), 960 (m), 833 (s); **^{1}H-NMR (400 MHz, CD_2Cl_2):** δ 7.41 (d, *J* = 1.9 Hz, 1H), 7.38-7.32 (m, 6H), 6.95 (d, *J* = 8.9 Hz, 2H), 6.54 (d, *J* = 1.8 Hz, 1H), 5.93 (d, *J* = 2.8 Hz, 1H), 3.83 (s, 3H); **^{13}C-NMR (100 MHz, CD_2Cl_2):** δ 159.5, 149.4, 142.6, 140.4, 133.7, 129.7, 128.8, 128.4, 125.5, 124.5, 114.6, 112.1, 67.8, 55.7; **HRMS (ESI+):** Calcd. for $C_{18}H_{15}ClO_3$ ([M+Na]$^+$): 337.0602, Found: 337.0596.



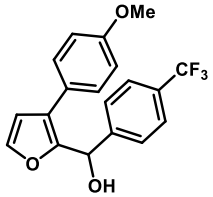
Compound 1j: Prepared according to General Procedure B; Starting from 3-(4-methoxyphenyl)furan-2-carbaldehyde (400.0 mg, 1.976 mmol, 1.0 equiv.); Purified by silica-gel flash column chromatography (7% EtOAc in hexane); Yellow thick oil (649.0 mg, 1.807mmol, 91% yield); **FT-IR (Thin film):** 3407 (br), 1518 (s), 1486 (m), 1249 (s), 1179 (m), 1146 (m), 1070 (w), 834 (s); **^{1}H-NMR (400 MHz, CD_2Cl_2):** δ 7.48 (d, *J* = 8.5 Hz, 2H), 7.41 (d, *J* = 1.9 Hz, 1H), 7.36 (d, *J* = 8.8 Hz, 2H), 7.32-7.28 (m, 2H), 6.95 (d, *J* = 8.7 Hz, 2H), 6.54 (d, *J* = 1.9 Hz, 1H), 5.91 (d, *J* = 5.3 Hz, 1H), 3.83 (s, 3H), 2.54 (d, *J* = 5.5 Hz, 1H); **^{13}C-NMR (100 MHz, CD_2Cl_2):** δ 159.5, 149.3, 142.6, 140.9, 131.8, 129.7, 128.7, 125.5, 124.5, 121.8, 114.6, 112.2, 67.9, 55.7; **HRMS (ESI+):** Calcd. for $C_{18}H_{15}BrO_3$ ([M+Na]$^+$): 381.0097, Found: 381.0090.



Compound 1k: Prepared according to General Procedure B; Starting from 3-(4-methoxyphenyl)furan-2-carbaldehyde (600.0 mg, 2.970 mmol, 1.0 equiv.); Purified by silica-gel flash column chromatography (5% EtOAc in hexane); Orange oil (924.0 mg, 2.570 mmol, 86% yield); **FT-IR (Thin film):** 3417 (br), 2836 (m), 1597 (s), 1571 (s), 1518 (s), 1298 (m), 1247 (s), 1179 (s), 1032 (s), 961 (s), 896 (m), 834 (s), 755 (s), 604 (s); **^{1}H-NMR (400 MHz, CD_2Cl_2):** δ 7.61-7.60 (m, 1H), 7.44-7.41 (m, 2H), 7.37 (d, *J* = 8.8 Hz, 2H), 7.33 (dt, *J* = 7.7, 1.8 Hz, 1H), 7.23 (t, *J* = 7.8 Hz, 1H), 6.96 (d, *J* = 8.8 Hz, 2H), 6.55 (d, *J* = 1.9 Hz, 1H), 5.92 (d, *J* = 5.6 Hz, 1H), 3.83 (s, 3H), 2.53 (d, *J* = 5.6 Hz, 1H); **^{13}C-NMR (75 MHz, CD_2Cl_2):** δ 159.6, 149.1, 144.1, 142.7, 131.1, 130.4, 129.9, 129.7, 125.6, 125.5, 124.7, 122.8, 114.6, 112.2, 67.8, 55.7; **HRMS (ESI+):** Calcd. for $C_{18}H_{15}BrO_3$ ([M+Na]+): 381.0097, Found: 381.0090.

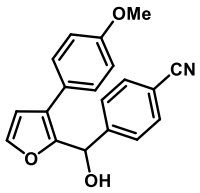


Compound 1l: Prepared according to General Procedure A, Condition II; Starting from 3-(4-methoxyphenyl)furan-2-carbaldehyde (600.0 mg, 2.970 mmol, 1.0 equiv.); Purified by silica-gel flash column chromatography (5% EtOAc in hexane); Yellow oil (995.0 mg, 2.860 mmol, 96% yield); **FT-IR (Thin film):** 3388 (br), 3154 (w), 2839 (w), 1619 (m), 1519 (s), 1326 (s), 1249 (s), 1178 (s), 1122 (s), 1067 (s), 834 (s); **^{1}H-NMR (400 MHz, CD_2Cl_2):** δ 7.62 (d, *J* = 8.1 Hz, 2H),

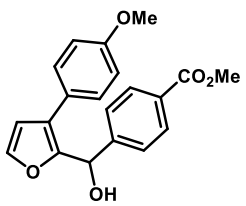


7.55 (d, *J* = 8.9 Hz, 2H), 7.41 (d, *J* = 1.9 Hz, 1H), 7.38 (d, *J* = 8.8 Hz, 2H), 6.96 (d, *J* = 8.7 Hz, 2H), 6.55 (d, *J* = 1.9 Hz, 1H), 6.01 (d, *J* = 5.3 Hz, 1H), 3.83 (s, 3H), 2.66 (d, *J* = 5.5 Hz, 1H); **^{13}C-NMR (100 MHz, CD_2Cl_2):** 159.6, 149.0, 145.8, 142.8, 129.9 (q, *J* = 32.3 Hz), 129.8, 127.2, 125.7 (q, *J* = 3.8 Hz), 125.2 (q, *J* = 54.7 Hz), 124.7 (q, *J* = 272.0 Hz), 115.7 (q, *J* = 118.0 Hz), 114.6, 112.2, 67.9, 55.7; **HRMS (ESI+):** Calcd. for $C_{19}H_{15}F_3O_3$ ([M+H]+): 349.1046, Found: 349.1048.

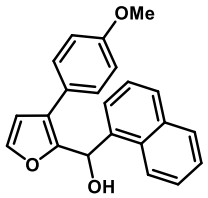
Compound 1m: Prepared according to General Procedure B; Starting from 3-(4-methoxyphenyl)furan-2-carbaldehyde (600.0 mg, 2.970 mmol, 1.0 equiv.); Purified by silica-gel flash column chromatography (14% EtOAc in hexane); Yellow thick oil (742.0 mg, 2.430 mmol, 82% yield); **FT-IR (Thin film):** 3397 (br), 2240 (s), 1516 (s), 1245 (s), 1027 (m), 962 (m), 832 (m), 771 (m); **^{1}H-NMR (400 MHz, $CDCl_3$):** δ 7.62 (d, *J* = 8.5 Hz, 2H), 7.51 (d, *J* = 8.0 Hz, 2H), 7.38 (d, *J* = 1.9 Hz, 1H), 7.35 (d, *J* = 8.7 Hz, 2H), 6.95 (d, *J* = 8.7 Hz, 2H), 6.52 (d, *J* = 1.9 Hz, 1H), 5.98 (s, 1H), 3.84 (s, 3H), 2.58 (br s, 1H); **^{13}C-NMR (100 MHz, $CDCl_3$):** δ 159.3, 148.2, 146.4, 142.7, 132.4, 129.5, 127.3, 125.0, 118.9, 114.5, 112.1, 111.6, 67.7, 55.5; **HRMS (ESI+):** Calcd. for $C_{19}H_{15}NO_3$ ($[M+Na]^+$): 328.0944, Found: 328.0943.



Compound 1n: Prepared according to General Procedure B; Starting from 3-(4-methoxyphenyl)furan-2-carbaldehyde (600.0 mg, 2.970 mmol, 1.0 equiv.); Purified by silica-gel flash column chromatography (12% EtOAc in hexane); Pale-yellow thick oil (848.0 mg, 2.510 mmol, 85% yield); **FT-IR (Thin film):** 3447 (br), 3006 (w), 2952 (w), 1720 (s), 1610 (m), 1519 (s), 1284 (s), 1115 (m), 835 (m), 734 (m); **^{1}H-NMR (300 MHz, CD_2Cl_2):** δ 7.99 (d, *J* = 8.6 Hz, 2H), 7.50-7.47 (m, 2H), 7.41-7.36 (m, 3H), 6.96 (d, *J* = 8.8 Hz, 2H), 6.55 (d, *J* = 1.9 Hz, 1H), 6.00 (d, *J* = 5.2 Hz, 1H), 3.88 (s, 3H), 3.82 (s, 3H), 2.67 (d, *J* = 5.5 Hz, 1H); **^{13}C-NMR (75 MHz, CD_2Cl_2):** 167.1, 159.6, 149.2, 146.7, 142.7, 130.0, 129.9, 129.7, 126.8, 125.5, 124.7, 114.6, 112.2, 68.1, 55.7, 52.4; **HRMS (ESI+):** Calcd. for $C_{20}H_{18}O_5$ ([M+Na]+): 361.1046, Found: 361.1048.

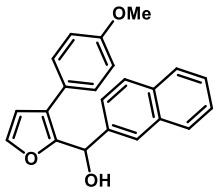


Compound 1o: Prepared according to General Procedure A, Condition II; Starting from 3-(4-methoxyphenyl)furan-2-carbaldehyde (600.0 mg, 2.970 mmol, 1.0 equiv.); Purified by silica-gel flash column chromatography (5% EtOAc in hexane); Blueish solid (885.0 mg, 2.680 mmol, 90% yield); **m.p.** 102-104 °C; **FT-IR (Thin film):** 3437 (br), 3051 (w), 1600 (w), 1518 (s), 1248 (s), 1033 (m), 834 (m), 785 (s); **^{1}H-NMR (300 MHz, CD_2Cl_2):** δ 7.88-7.81 (m, 2H), 7.77-7.74 (m, 1H), 7.73-7.69 (m, 1H), 7.54-7.49 (m, 1H), 7.47-7.42 (m, 3H), 7.38-7.32 (m, 2H), 6.97 (d, *J* = 8.8 Hz, 2H), 6.60-6.57 (m, 2H), 3.83 (s, 3H), 2.65 (d, *J* = 5.6 Hz, 1H); **^{13}C-NMR (75 MHz, CD_2Cl_2):** δ 159.5, 149.7, 142.5, 137.2, 134.2, 130.9, 129.7, 129.1, 128.9, 126.6, 126.0, 125.7, 125.7, 124.3,

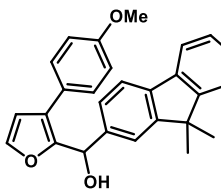


124.1, 123.7, 114.6, 112.0, 66.3, 55.7; **HRMS (ESI+):** Calcd. for $C_{22}H_{18}O_3$ ([M+Na]+): 353.1148, Found: 353.1152.

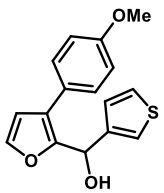
Compound 1p: Prepared according to General Procedure A, Condition II; Starting from 3-(4-methoxyphenyl)furan-2-carbaldehyde (600.0 mg, 2.970 mmol, 1.0 equiv.); Purified by silica-gel flash column chromatography (7% EtOAc in hexane); Yellow thick oil (835.0 mg, 2.527 mmol, 85% yield); **FT-IR (Thin film):** 3434 (br), 1518 (s), 1248 (s), 1179 (m), 1145 (w), 1031 (s), 834 (s), 760 (s); **^{1}H-NMR (300 MHz, CD_2Cl_2):** δ 7.91-7.90 (m, 1H), 7.88-7.82 (m, 3H), 7.53-48 (m, 3H), 7.46-7.41 (m, 3H), 6.97 (d, *J* = 8.8 Hz, 2H), 6.57 (d, *J* = 1.9 Hz, 1H), 6.12 (d, *J* = 4.7 Hz, 1H), 3.83 (s, 3H), 2.65 (d, *J* = 5.2 Hz, 1H); **^{13}C-NMR (75 MHz, CD_2Cl_2):** δ 159.5, 149.8, 142.6, 139.3, 133.7, 133.3, 129.8, 128.5, 128.4, 128.0, 126.6, 126.5, 125.7, 125.3, 125.1, 124.4, 114.6, 112.1, 68.6, 55.7; **HRMS (ESI+):** Calcd. for $C_{22}H_{18}O_3$ ([M+Na]$^+$): 353.1148, Found: 353.1150.



Compound 1q: Prepared according to General Procedure B; Starting from 3-(4-methoxyphenyl)furan-2-carbaldehyde (500.0 mg, 2.470 mmol, 1.0 equiv.); Purified by silica-gel flash column chromatography (5% EtOAc in hexane); Orange solid (648.0 mg, 1.630 mmol, 66% yield); **m.p.** 46-48 °C; **FT-IR (Thin film):** 3434 (br), 2959 (m), 1615 (m), 1519 (m), 1448 (m), 1247 (m), 1034 (m), 832 (m), 739 (s); **^{1}H-NMR (400 MHz, CD_2Cl_2):** δ 7.74-7.72 (m, 1H), 7.70 (d, *J* = 7.9 Hz, 1H), 7.58 (m, 1H), 7.47-7.45 (m, 2H), 7.44-7.40 (m, 2H), 7.37-7.32 (m, 3H), 6.97 (d, *J* = 8.8 Hz, 2H), 6.57 (d, *J* = 1.8 Hz, 1H), 6.03 (d, *J* = 5.4 Hz, 1H), 3.83 (s, 3H), 2.59 (d, *J* = 5.6 Hz, 1H), 1.48 (d, *J* = 4.7 Hz, 6H); **^{13}C-NMR (100 MHz, CD_2Cl_2):** 159.5, 154.4, 150.0, 142.4, 141.1, 139.2, 139.2, 129.8, 127.7, 127.4, 125.9, 125.8, 124.1, 123.0, 121.3, 120.4, 120.2, 114.5, 112.2, 68.7, 55.7, 47.3, 27.3, 27.3; **HRMS (ESI+):** Calcd. for $C_{27}H_{24}O_3$ ([M+Na]+): 419.1618, Found: 419.1617.



Compound 1r: Prepared according to General Procedure B; Starting from 3-(4-methoxyphenyl)furan-2-carbaldehyde (600.0 mg, 2.970 mmol, 1.0 equiv.); Purified by silica-gel flash column chromatography (8% EtOAc in hexane); Yellow thick oil (359.0 mg, 1.254 mmol, 42% yield); **FT-IR (Thin film):** 3444 (br), 2931 (w), 1604 (m), 1517 (s), 1249 (s), 1179 (m), 1032 (m), 834 (s); **^{1}H-NMR (400 MHz, CD_2Cl_2):** δ 7.44 (d, *J* = 1.8 Hz, 1H), 7.36 (d, *J* = 8.8 Hz, 2H), 7.34-7.31 (m, 1H), 7.28-7.27 (m, 1H), 7.11 (dd, *J* = 5.0, 1.4 Hz, 1H), 6.95 (d, *J* = 8.8 Hz, 2H), 6.55 (d, *J* = 1.9 Hz, 1H), 5.98 (s, 1H), 3.82 (s, 3H), 2.54 (br s, 1H); **^{13}C-NMR (75 MHz, CD_2Cl_2):** δ 159.4, 149.6, 143.2, 142.4, 129.7, 127.0, 126.5, 125.7, 123.8, 122.4, 114.5, 112.0, 65.2, 55.7; **HRMS (ESI+):** Calcd. for $C_{16}H_{14}O_3S$ ([M+Na]$^+$): 309.0556, Found: 309.0562. [*Note*: This compound is very unstable, sensitive to silica-gel, temperature, and rotary evaporation at 20 °C is necessary.]

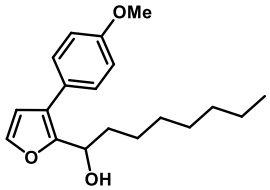


Compound 1s: Prepared according to General Procedure C (thiophene was used instead of 2-bromothiophene to generate corresponding 2-thienyllithium); Starting from 3-(4-methoxyphenyl)furan-2-carbaldehyde (500.0 mg, 2.470 mmol, 1.0 equiv.); Purified by silica-gel flash column chromatography (4% EtOAc in hexane); Orange oil (589.0 mg, 2.060 mmol, 83% yield); **FT-IR (Thin film):** 3434 (br), 3109 (w), 2836 (w), 1604 (m), 1518 (s), 1249 (s), 1179 (m), 1031 (m), 958 (m), 835 (m), 704 (m); **^{1}H-NMR (400 MHz, CD_2Cl_2):** δ 7.48 (d, *J* = 1.8 Hz, 1H), 7.35 (d, *J* = 8.8 Hz, 2H), 7.32 (dd, *J* = 4.9, 1.4 Hz, 1H), 6.99-6.94 (m, 4H), 6.56 (d, *J* = 1.9 Hz, 1H), 6.14 (dd, *J* = 6.3, 1.0 Hz, 1H), 3.82 (s, 3H), 2.73 (d, *J* = 6.3 Hz, 1H); **^{13}C-NMR (100 MHz, CD_2Cl_2):** 159.5, 148.9, 145.6, 142.6, 129.7, 127.1, 126.0, 125.5, 125.5, 123.9, 114.6, 112.1, 65.0, 55.7; **HRMS (ESI+):** Calcd. for $C_{16}H_{14}O_3S$ ([M+Na]+): 309.0556, Found: 309.0554.

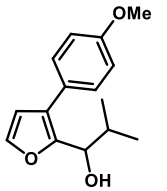
Compound 1t: Prepared according to General Procedure A, Condition II; Starting from 3-(4-methoxyphenyl)furan-2-carbaldehyde (600.0 mg, 2.970 mmol, 1.0 equiv.); Purified by silica-gel flash column chromatography (11% EtOAc in hexane); Yellow thick oil (814.0 mg, 2.510 mmol, 85% yield); **FT-IR (Thin film):** 3444 (br), 2902 (m), 1604 (m), 1234 (m), 1442 (m), 1180 (s), 1034 (s), 835 (s), 769 (m); **^{1}H-NMR (300 MHz, CD_2Cl_2):** δ 7.42 (d, *J* = 1.9 Hz, 1H), 7.35 (d, *J* = 8.8 Hz, 2H), 6.96-6.93 (m, 3H), 6.85 (ddd, *J* = 8.0, 1.7, 0.7 Hz, 1H), 6.77 (d, *J* = 8.0 Hz, 1H), 6.53 (d, *J* = 1.9 Hz, 1H), 5.95 (s, 2H), 5.85 (d, *J* = 5.4 Hz, 1H), 3.82 (s, 3H), 2.46 (d, *J* = 5.5 Hz, 1H); **^{13}C-NMR (75 MHz, CD_2Cl_2):** 159.5, 149.8, 148.3, 147.6, 142.4, 135.9, 129.7, 125.7, 123.9, 120.2, 114.5, 112.1, 108.3, 107.6, 101.7, 68.3, 55.7; **HRMS (ESI+):** Calcd. for $C_{19}H_{16}O_5$ ([M+Na]+): 347.0890, Found: 347.0881.

Compound 1u: Prepared according to General Procedure A, Condition I; Starting from 3-(4-methoxyphenyl)furan-2-carbaldehyde (600.0 mg, 2.970 mmol, 1.0 equiv.); Purified by silica-gel flash column chromatography (10% EtOAc in hexane); White thick oil (608.0 mg, 2.618 mmol, 88% yield); **FT-IR (Thin film):** 3303 (br), 2967 (m), 1614 (m), 1519 (s), 1275 (m), 1250 (s), 885 (s), 731 (m); **^{1}H-NMR (400 MHz, CD_2Cl_2):** δ 7.41 (d, *J* = 1.8 Hz, 1H), 7.36 (d, *J* = 8.7 Hz, 2H), 6.94 (d, *J* = 8.7 Hz, 2H), 6.51 (d, *J* = 1.8 Hz, 1H), 4.70-4.65 (m, 1H), 3.82 (s, 3H), 1.99-1.93 (m, 2H), 1.92-1.88 (m, 1H), 0.89 (t, *J* = 7.4 Hz, 3H); **^{13}C-NMR (100 MHz, CD_2Cl_2):** δ 159.3, 151.1, 141.8, 129.7, 126.1, 123.6, 114.4, 111.9, 68.0, 55.7, 29.1, 10.4; **HRMS (ESI+):** Calcd. for $C_{14}H_{16}O_3$ ([M+Na]$^+$): 255.0992, Found: 255.0998.

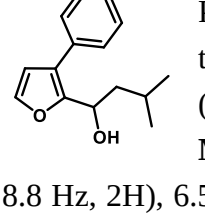
Compound 1v: Prepared according to General Procedure A, Condition II; Starting from 3-(4-methoxyphenyl)furan-2-carbaldehyde (300.0 mg, 1.483 mmol, 1.0 equiv.); Purified by silica-gel flash column chromatography (10% EtOAc in hexane); White thick oil (241.0 mg, 0.797 mmol, 54% yield); **FT-IR (Thin film):** 3443 (br), 2927 (s), 1519 (s), 1465 (w), 1248 (s), 1037 (m), 890 (m), 834 (s); **^{1}H-NMR (300 MHz, CD_2Cl_2):** δ 7.41 (d, *J* = 1.9 Hz, 1H), 7.35 (d, *J* = 8.8 Hz, 2H), 6.94 (d, *J* = 8.8 Hz, 2H), 6.50 (d, *J* = 1.9 Hz, 1H), 4.78-4.72 (m, 1H), 3.82 (s, 3H), 1.95-1.87 (m, 3H), 1.37-1.26 (m, 6H), 1.24-1.17 (m, 3H), 0.89-0.84 (m, 3H); **^{13}C-NMR (75 MHz, CD_2Cl_2):** δ 159.3, 151.3, 141.7, 129.7, 126.1, 123.4, 114.4, 111.9, 66.6, 55.7, 36.1, 32.2, 29.7, 29.6, 26.2, 23.0, 14.3; **HRMS (ESI+):** Calcd. for $C_{19}H_{26}O_3$ ($[M+Na]^+$): 325.1774 , Found: 325.1768.



Compound 1w: Prepared according to General Procedure A, Condition I; Starting from 3-(4-methoxyphenyl)furan-2-carbaldehyde (300.0 mg, 1.483 mmol, 1.0 equiv.); Purified by silica-gel flash column chromatography (7% EtOAc in hexane); White thick oil (215.0 mg, 0.873 mmol, 59% yield); **FT-IR (Thin film):** 3419 (br), 2959 (m), 1518 (s), 1247 (s), 1179 (m), 1032 (m), 834 (m), 751 (w); **^{1}H-NMR (400 MHz, CD_2Cl_2):** δ 7.41 (d, *J* = 1.8 Hz, 1H), 7.35 (d, *J* = 8.9 Hz, 2H), 6.94 (d, *J* = 8.9 Hz, 2H), 6.49 (d, *J* = 1.8 Hz, 1H), 4.36 (dd, *J* = 8.9, 5.6 Hz, 1H), 3.82 (s, 3H), 2.26-2.17 (m, 1H), 1.94 (d, *J* = 6.0 Hz, 1H), 1.07 (d, *J* = 6.7 Hz, 3H), 0.74 (d, *J* = 6.8 Hz, 3H); **^{13}C-NMR (100 MHz, CD_2Cl_2):** δ 159.3, 151.0, 141.7, 129.8, 126.1, 124.0, 114.4, 112.0, 72.3, 55.7, 33.9, 19.4, 19.2; **HRMS (ESI+):** Calcd. for $C_{15}H_{18}O_3$ ($[M+Na]^+$): 269.1148, Found: 269.1141.



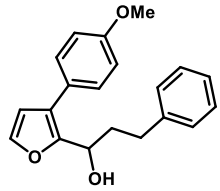
Compound 1x: Prepared according to General Procedure A, Condition II; Starting from 3-(4-methoxyphenyl)furan-2-carbaldehyde (300.0 mg, 1.483 mmol, 1.0 equiv.); Purified by silica-gel flash column chromatography (7% EtOAc in hexane); White thick oil (233.0 mg, 0.895 mmol, 60% yield); **FT-IR (Thin film):** 3389 (br), 2956 (m), 1604 (w), 1519 (s), 1466 (m), 1248 (s), 1179 (m), 834 (m); **^{1}H-NMR (300 MHz, CD_2Cl_2):** δ 7.41 (d, *J* = 1.9 Hz, 1H), 7.36 (d, *J* = 8.8 Hz, 2H), 6.95 (d, *J* = 8.8 Hz, 2H), 6.50 (d, *J* = 1.9 Hz, 1H), 4.86-4.81 (m, 1H), 3.82 (s, 3H), 1.92-1.82 (m, 2H), 1.78-1.69 (m, 1H), 1.67-1.58 (m, 1H), 0.87 (d, *J* = 6.6 Hz, 3H), 0.85 (d, *J* = 6.6 Hz, 3H); **^{13}C-NMR (75 MHz, CD_2Cl_2):** δ 159.3, 151.4, 141.7, 129.7, 126.1, 123.2, 114.5, 112.0, 64.9, 55.7, 44.9, 25.3, 23.1, 22.3; **HRMS (ESI+):** Calcd. for $C_{16}H_{20}O_3$ ($[M+Na]^+$): 283.1305, Found: 283.1304.



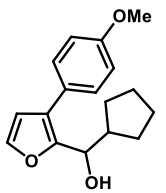
Compound 1y: Prepared according to General Procedure A, Condition II; Starting from 3-(4-methoxyphenyl)furan-2-carbaldehyde (300.0 mg, 1.483 mmol, 1.0 equiv.); Purified by silica-gel flash column chromatography (8% EtOAc in hexane); White thick oil (345.0 mg, 1.336 mmol, 90% yield); **FT-IR (Thin film):** 3397 (br), 2934 (m), 1603 (w), 1519 (s), 1293 (m), 1248 (s), 957 (w), 834 (s); **^{1}H-**

NMR (300 MHz, CD_2Cl_2): δ 7.42 (d, *J* = 1.9 Hz, 1H), 7.35 (d, *J* = 8.9 Hz, 2H), 6.94 (d, *J* = 8.9 Hz, 2H), 6.51 (d, *J* = 1.9 Hz, 1H), 5.85-5.73 (m, 1H), 5.01-4.91 (m, 2H), 4.81-4.75 (m, 1H), 3.82 (s, 3H), 2.12-2.00 (m, 4H), 1.97-1.95 (m, 1 H); **^{13}C-NMR (75 MHz, CD_2Cl_2):** δ 159.3, 150.9, 141.9, 138.4, 129.7, 126.0, 123.5, 115.2, 114.5, 112.0, 66.1, 55.7, 35.2, 30.4; **HRMS (ESI+):** Calcd. for $C_{16}H_{18}O_3$ ($[M+Na]^+$): 281.1148, Found: 281.1139.

Compound 1z: Prepared according to General Procedure A, Condition II; Starting from 3-(4-methoxyphenyl)furan-2-carbaldehyde (300.0 mg, 1.483 mmol, 1.0 equiv.); Purified by silica-gel flash column chromatography (8% EtOAc in hexane); White thick oil (369.0 mg, 1.197 mmol, 81% yield); **FT-IR (Thin film):** 3397 (br), 2951 (w), 1604 (m), 1519 (s), 1291 (m), 1248 (s), 955 (m), 834 (s); **^{1}H-NMR (400 MHz, CD_2Cl_2):** δ 7.43 (d, *J* = 1.9 Hz, 1H), 7.28 (d, *J* = 8.7 Hz, 2H), 7.26-7.21 (m, 2H), 7.19-7.12 (m, 3H), 6.91 (d, *J* = 8.7 Hz, 2H), 6.52 (d, *J* = 1.9 Hz, 1H), 4.77 (q, *J* = 6.5 Hz, 1H), 3.82 (s, 3H), 2.71-2.56 (m, 2H), 2.31-2.15 (m, 2H), 1.99 (d, *J* = 5.4 Hz, 1H); **^{13}C-NMR (100 MHz, CD_2Cl_2):** δ 159.3, 150.9, 142.0, 142.0, 129.7, 128.8, 128.7, 126.2, 125.9, 123.5, 114.5, 111.9, 65.8, 55.7, 37.7, 32.4; **HRMS (ESI+):** Calcd. for $C_{20}H_{20}O_3$ ($[M+Na]^+$): 331.1305, Found: 331.1307.



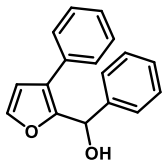
Compound 1aa: Prepared according to General Procedure A, Condition II; Starting from 3-(4-methoxyphenyl)furan-2-carbaldehyde (300.0 mg, 1.483 mmol, 1.0 equiv.); Purified by silica-gel flash column chromatography (7% EtOAc in hexane); Colorless oil (128.0 mg, 0.470 mmol, 32% yield); **FT-IR (Thin film):** 3436 (br), 2953 (m), 1604 (w), 1518 (s), 1248 (s), 1179 (m), 957 (m), 834 (m); **^{1}H-NMR (400 MHz, CD_2Cl_2):** δ 7.40 (d, *J* = 1.9 Hz, 1H), 7.37 (d, *J* = 8.7 Hz, 2H), 6.94 (d, *J* = 8.8 Hz, 2H), 6.49 (d, *J* = 1.8 Hz, 1H), 4.46 (d, *J* = 9.5 Hz, 1H), 3.82 (s, 3H), 2.58-2.48 (m, 1H), 1.97 (br s, 1H), 1.94-1.89 (m, 1H), 1.63-1.56 (m, 2H), 1.53-1.44 (m, 4H), 1.02-0.95 (m, 1H); **^{13}C-NMR (100 MHz, CD_2Cl_2):** δ 159.3, 151.4, 141.7, 129.8, 126.2, 123.6, 114.4, 111.9, 70.9, 55.7, 45.3, 30.4, 29.4, 26.0, 25.8; **HRMS (ESI+):** Calcd. for $C_{17}H_{20}O_3$ ($[M+Na]^+$): 295.1305, Found: 295.1309.



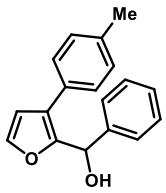
Compound 1ab: Prepared according to General Procedure A, Condition II; Starting from 3-(4-methoxyphenyl)furan-2-carbaldehyde (300.0 mg, 1.483 mmol, 1.0 equiv.); Purified by silica-gel flash column chromatography (7% EtOAc in hexane); Colorless oil (256.0 mg, 0.894 mmol, 60% yield); **FT-IR (Thin film):** 3435 (br), 2926 (s), 1518 (s), 1247 (s), 1178 (m), 1034 (m), 891 (m), 756 (m); **^{1}H-NMR (400 MHz, CD_2Cl_2):** δ 7.41 (d, *J* = 1.8 Hz, 1H), 7.34 (d, *J* = 8.8 Hz, 2H), 6.94 (d, *J* = 8.7 Hz, 2H63), 6.48 (d, *J* = 1.9 Hz, 1H), 4.4 0 (dd, *J* = 9.1, 5.9 Hz, 1H), 3.82 (s, 3H), 2.15-2.09 (m, 1H), 1.96-1.87 (m, 2H), 1.80-1.74 (m, 1H), 1.67-1.60 (m, 2H), 1.30-1.23 (m, 2H), 1.20-1.08 (m, 3H), 1.06-0.97 (m, 1H), 0.78-0.78 (m, 1H); **^{13}C-NMR (100 MHz, CD_2Cl_2):** δ 159.3, 150.9, 141.7, 129.8,

126.2, 124.1, 114.4, 111.9, 71.2, 55.7, 43.2, 30.2, 29.7, 26.8, 26.4, 26.3; **HRMS (ESI+):** Calcd. for $C_{18}H_{22}O_3$ ([M+Na]$^+$): 309.1461, Found: 309.1454.

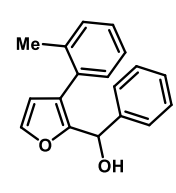
Compound 1ac: Prepared according to General Procedure A, Condition I; Starting from 3-phenylfuran-2-carbaldehyde (238.0 mg, 1.380 mmol, 1.0 equiv.); Purified by silica-gel flash column chromatography (7% EtOAc in hexane); Yellow solid (209.0 mg, 0.835 mmol, 61% yield); **m.p.** 75-77 °C; **FT-IR (Thin film):** 3541 (s), 1509 (m), 1492 (m), 1450 (m), 1249 (w), 1143 (s), 962 (m), 837 (m); **^{1}H-NMR (400 MHz, $CDCl_3$):** δ 7.46-7.41 (m, 6H), 7.40-7.36 (m, 3H), 7.35-7.29 (m, 2H), 6.56 (d, *J* = 1.9 Hz, 1H), 5.99 (d, *J* = 5.8 Hz, 1H), 2.43 (d, *J* = 6.0 Hz, 1H); **^{13}C-NMR (100 MHz, $CDCl_3$):** δ 149.9, 142.4, 141.3, 133.2, 128.9, 128.6, 128.4, 128.0, 127.4, 126.7, 124.4, 111.8, 68.3; **HRMS (ESI+):** Calcd. for $C_{17}H_{14}O_2$ ([M+Na]$^+$): 273.0886, Found: 273.0886.



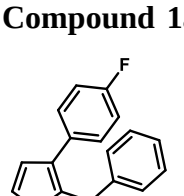
Compound 1ad: Prepared according to General Procedure A, Condition I; Starting from 3-(p-tolyl)furan-2-carbaldehyde (528.0 mg, 2.836 mmol, 1.0 equiv.); Purified by silica-gel flash column chromatography (7% EtOAc in hexane); Yellow thick oil (643.0 mg, 2.433 mmol, 86% yield); **FT-IR (Thin film):** 3409 (br), 1519 (s), 1450 (m), 1185 (w), 1146 (s), 960 (s), 821 (m), 788 (w); **^{1}H-NMR (300 MHz, CD_2Cl_2):** δ 7.44-7.40 (m, 3H), 7.39-7.34 (m, 4H), 7.32-7.28 (m, 1H), 7.27-7.23 (m, 2H), 6.57 (d, *J* = 1.9 Hz, 1H), 5.97 (d, *J* = 5.5 Hz, 1H), 2.50 (d, *J* = 5.7 Hz, 1H), 2.39 (s, 3H); **^{13}C-NMR (75 MHz, CD_2Cl_2):** δ 150.1, 142.5, 141.9, 137.6, 130.4, 129.8, 128.8, 128.5, 128.1, 126.8, 124.5, 112.0, 68.4, 21.3; **HRMS (ESI+):** Calcd. for $C_{18}H_{16}O_2$ ([M+Na]$^+$): 287.1043, Found: 287.1049.



Compound 1ae: Prepared according to General Procedure A, Condition I; Starting from 3-(2-methylphenyl)furan-2-carbaldehyde (600.0 mg, 3.220 mmol, 1.0 equiv.); Purified by silica-gel flash column chromatography (5% EtOAc in hexane); Yellow solid (840.0 mg, 3.180 mmol, 99% yield); **m.p.** 60-62 °C; **FT-IR (Thin film):** 3333 (br), 3321 (s), 3029 (m), 2922 (w), 1604 (m), 1493 (s), 1319 (m), 1237 (s), 1013 (s), 752 (s); **^{1}H-NMR (400 MHz, CD_2Cl_2):** δ 7.45 (d, *J* = 1.9 Hz, 1H), 7.38-7.31 (m, 4H), 7.30-7.25 (m, 3H), 7.24-7.21 (m, 2H), 6.44 (d, *J* = 1.8 Hz, 1H), 5.66 (d, *J* = 5.5 Hz, 1H), 2.42 (d, *J* = 5.5 Hz, 1H), 2.26 (s, 3H); **^{13}C-NMR (100 MHz, CD_2Cl_2):** 151.0, 142.2, 141.9, 137.5, 132.9, 130.8, 130.6, 128.7, 128.2, 128.0, 126.7, 126.1, 123.6, 113.2, 68.3, 20.6; **HRMS (ESI+):** Calcd. for $C_{18}H_{16}O_2$ ([M+Na]+): 287.1043, Found: 287.1034.



Compound 1af: Prepared according to General Procedure A, Condition I; Starting from 3-(4-fluorophenyl)furan-2-carbaldehyde (647.0 mg, 3.402 mmol, 1.0 equiv.); Purified by silica-gel flash column chromatography (7% EtOAc in hexane); Off-white solid (872.0 mg, 3.250 mmol, 96% yield); **m.p.** 60-62 °C; **FT-IR (Thin film):** 3290 (br), 1602 (m), 1517 (s), 1492 (m), 1336 (w), 1222 (s), 962 (s), 835 (s), 720 (m); **^{1}H-NMR (400 MHz, CD_2Cl_2):** δ 7.46-7.40 (m, 5H), 7.38-7.34 (m, 2H), 7.32-7.28 (m,



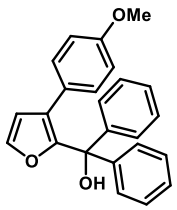
1H), 7.15-7.09 (m, 2H), 6.55 (d, *J* = 1.8 Hz, 1H), 5.93 (d, *J* = 5.6 Hz, 1H), 2.53 (d, *J* = 5.7 Hz, 1H); **^{13}C-NMR (100 MHz, CD_2Cl_2):** δ 162.6 (d, *J* = 245.8 Hz), 150.4, 142.6, 141.6, 130.4 (d, *J* = 8.0 Hz), 129.6 (d, *J* = 3.3 Hz), 128.8, 128.2, 126.8, 123.6, 115.9 (d, *J* = 21.6 Hz), 112.1, 68.4; **HRMS (ESI+):** Calcd. for $C_{17}H_{13}FO_2$ ([M+Na]$^+$): 291.0792, Found: 291.0794.

Compound 1ag: Prepared according to General Procedure A, Condition I; Starting from 3-(2-fluorophenyl)furan-2-carbaldehyde (160.0 mg, 0.840 mmol, 1.0 equiv.); Purified by silica-gel flash column chromatography (5% EtOAc in hexane); Yellow oil (218.0 mg, 0.810 mmol, 96% yield); **FT-IR (Thin film):** 3398 (br), 3031 (w), 2924 (w), 1514 (m), 1492 (m), 1454 (m), 1145 (m), 1012 (m), 965 (m), 756 (s), 699 (m); **^{1}H-NMR (400 MHz, CD_2Cl_2):** δ 7.48 (d, *J* = 1.9 Hz, 1H), 7.42-7.39 (m, 3H), 7.38-7.33 (m, 3H), 7.31-7.28 (m, 1H), 7.24-7.15 (m, 2H), 6.57 (t, *J* = 1.8 Hz, 1H), 5.86 (d, *J* = 5.0 Hz, 1H), 2.55 (d, *J* = 5.3 Hz, 1H); **^{13}C-NMR (100 MHz, CD_2Cl_2):** 160.3 (d, *J* = 246.1 Hz), 159.0, 151.7, 142.7, 141.4, 131.7 (d, *J* = 3.3 Hz), 129.8 (d, *J* = 8.1 Hz), 128.7, 128.1, 126.8, 124.8 (d, *J* = 3.7 Hz), 118.1, 116.2 (d, *J* = 22.4 Hz), 112.8 (d, *J* = 2.3 Hz), 68.4 (d, *J* = 2.4 Hz); **HRMS (ESI+):** Calcd. for $C_{17}H_{13}FO_2$ ([M+Na]+): 291.0792, Found: 291.0790. [*Note*: This compound is very unstable, sensitive to silica-gel, temperature, and rotary evaporation at 20 °C is necessary.]

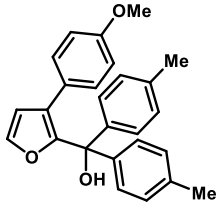
Compound 1ah: Prepared according to General Procedure A, Condition I; Starting from 3-(1-naphtalen-1-yl)furan-2-carbaldehyde (600.0 mg, 2.700 mmol, 1.0 equiv.); Purified by silica-gel flash column chromatography (5% EtOAc in hexane); Brown oil (608.0 mg, 2.020 mmol, 75% yield); **FT-IR (Thin film):** 3365 (br), 3045 (w), 1508 (m), 1451 (m), 1145 (m), 1014 (m), 938 (m), 779 (s), 698 (m); **^{1}H-NMR (300 MHz, CD_2Cl_2):** δ 7.95-7.88 (m, 3H), 7.56-7.44 (m, 5H), 7.38-7.25 (m, 5H), 6.60 (d, *J* = 1.8 Hz, 1H), 5.69 (d, *J* = 5.4 Hz, 1H), 2.43 (d, *J* = 5.5 Hz, 1H); **^{13}C-NMR (75 MHz, CD_2Cl_2):** 151.9, 142.5, 141.7, 134.2, 132.8, 131.0, 128.7, 128.5, 128.2, 128.0, 126.8, 126.7, 126.4, 126.2, 125.8, 122.4, 114.0, 68.3; **HRMS (ESI+):** Calcd. for $C_{21}H_{16}O_2$ ([M+Na]+): 323.1043, Found: 323.1045.

Compound 1ai: Prepared according to General Procedure A, Condition I; Starting from 3-(thiophen-3-yl)furan-2-carbaldehyde (600.0 mg, 3.370 mmol, 1.0 equiv.); Purified by silica-gel flash column chromatography (5% EtOAc in hexane); Red oil (775.0 mg, 3.020 mmol, 90% yield); **FT-IR (Thin film):** 3377 (br), 3105 (w), 2920 (w), 1493 (m), 1450 (m), 1166 (m), 1186 (m), 1144 (s), 1016 (s), 898 (s), 855 (s), 786 (s), 751 (s), 701 (s) 651 (m); **^{1}H-NMR (400 MHz, CD_2Cl_2):** δ 7.44-7.41 (m, 4H), 7.39-7.37 (m, 2H), 7.34 (dd, *J* = 3.0, 1.3 Hz, 1H), 7.33-7.30 (m, 1H), 7.26 (dd, *J* = 5.0, 1.3 Hz, 1H), 6.58 (d, *J* = 1.9 Hz, 1H), 6.04 (br s, 1H), 2.56 (br s, 1H); **^{13}C-NMR (100 MHz, CD_2Cl_2):** 150.4, 142.5, 141.6, 133.6, 128.8, 128.2, 128.0, 126.8, 126.5, 122.2, 119.4, 111.9, 68.6; **HRMS (ESI+):** Calcd. for $C_{15}H_{12}O_2S$ ([M+Na]+): 279.0450, Found: 279.0455.

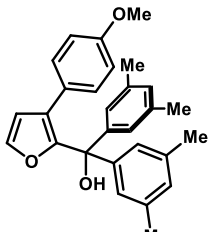
Compound 2a: Prepared according to General Procedure D, Condition I; Starting from **1a** (900.0 mg, 3.210 mmol, 1.0 equiv.); Purified by silica-gel flash column chromatography (7% EtOAc in hexane); Yellow thick oil (961.0 mg, 2.696 mmol, 84% yield, over two steps); **FT-IR (Thin film):** 3442 (br), 1519 (s), 1447 (m), 1245 (s), 1179 (m), 1028 (s), 974 (w), 754 (s); **^{1}H-NMR (400 MHz, $CDCl_3$):** δ 7.38 (d, *J* = 1.9 Hz, 1H), 7.29-7.28 (m, 2H), 7.27-7.26 (m, 6H), 7.26-7.25 (m, 2H), 7.02 (d, *J* = 8.6 Hz, 2H), 6.70 (d, *J* = 8.8 Hz, 2H), 6.43 (d, *J* = 1.8 Hz, 1H), 3.76 (s, 3H), 3.07 (br s, 1H); **^{13}C-NMR (100 MHz, $CDCl_3$):** δ 158.7, 151.7, 145.4, 140.8, 130.3, 128.0, 127.7, 126.3, 123.3, 114.1, 113.7, 79.7, 55.4; **HRMS (ESI+):** Calcd. for $C_{24}H_{20}O_3$ ([M+Na]$^+$): 379.1305, Found: 379.1301.



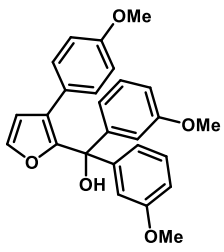
Compound 2b: Prepared according to General Procedure D, Condition II; Starting from **1b** (400.0 mg, 1.359 mmol, 1.0 equiv.); Purified by silica-gel flash column chromatography (7% EtOAc in hexane); Yellow thick oil (144.0 mg, 0.375 mmol, 28% yield, over two steps); **FT-IR (Thin film):** 3476 (br), 2921 (w), 1518 (s), 1246 (s), 1178 (m), 1034 (m), 877 (w), 786 (m); **^{1}H-NMR (400 MHz, CD_2Cl_2):** δ 7.38 (d, *J* = 1.8 Hz, 1H), 7.12-7.08 (m, 7H), 7.06-7.02 (m, 3H), 6.70 (d, *J* = 8.7 Hz, 2H), 6.45 (d, *J* = 1.8 Hz, 1H), 3.75 (s, 3H), 2.98 (s, 1H), 2.32 (s, 6H); **^{13}C-NMR (100 MHz, CD_2Cl_2):** δ 159.0, 152.4, 143.1, 140.9, 137.6, 130.6, 128.9, 127.7, 126.7, 123.4, 114.4, 113.8, 79.6, 55.6, 21.1; **HRMS (ESI+):** Calcd. for $C_{26}H_{24}O_3$ ([M+Na]$^+$): 407.1618, Found: 407.1616.



Compound 2c: Prepared according to General Procedure D, Condition II; Starting from **1d** (400.0 mg, 1.300 mmol, 1.0 equiv.); Purified by silica-gel flash column chromatography (5% EtOAc in hexane); Colorless oil (383.0 mg, 0.930 mmol, 72% yield, over two steps); **FT-IR (Thin film):** 3481 (br), 3007 (w), 2917 (m), 1599 (m), 1519 (s), 1246 (s), 1178 (m), 1037 (s), 833 (m), 758 (s); **^{1}H-NMR (400 MHz, CD_2Cl_2):** δ 7.40 (d, *J* = 1.8 Hz, 1H), 7.01 (d, *J* = 8.8 Hz, 2H), 6.88-6.85 (m, 6H), 6.70 (d, *J* = 8.8 Hz, 2H), 6.44 (d, *J* = 1.8 Hz, 1H), 3.75 (s, 3H), 2.97 (s, 1H), 2.23 (s, 12H); **^{13}C-NMR (100 MHz, CD_2Cl_2):** 158.9, 152.4, 145.7, 140.8, 137.7, 130.5, 129.4, 126.9, 125.6, 123.6, 114.4, 113.6, 79.6, 55.6, 21.6; **HRMS (ESI+):** Calcd. for $C_{28}H_{28}O_3$ ([M+Na]+): 435.1931, Found: 435.1927.

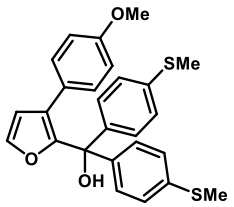


Compound 2d: Prepared according to General Procedure D, Condition II; Starting from **1e** (326.0 mg, 1.050 mmol, 1.0 equiv.); Purified by silica-gel flash column chromatography (10% EtOAc in hexane); Colorless thick oil (155.0 mg, 0.372 mmol, 35% yield, over two steps); **FT-IR (Thin film):** 3474 (br), 2835 (w), 1599 (s), 1247 (w), 1036 (s), 833 (m), 777 (s); **^{1}H-NMR (400 MHz, CD_2Cl_2):** δ 7.40 (d, *J* = 1.8 Hz, 1H), 7.19-7.15 (m, 2H), 7.03 (d, *J* = 8.7 Hz, 2H), 6.84-6.82 (m, 4H), 6.79-6.76 (m, 2H), 6.70 (d, *J* = 8.7 Hz, 2H), 6.45 (d, *J* = 1.8 Hz,



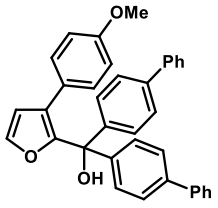
1H), 3.75 (s, 3H), 3.71 (s, 6H), 3.09 (s, 1H); **^{13}C-NMR (100 MHz, CD_2Cl_2):** δ 159.8, 159.0, 151.8, 147.1, 141.0, 130.5, 129.2, 126.5, 123.8, 120.2, 114.4, 113.9, 113.8, 113.1, 79.6, 55.6, 55.5; **HRMS (ESI+):** Calcd. for $C_{26}H_{24}O_5$ ($[M+Na]^+$): 439.1516, Found: 439.1521.

Compound 2e: Prepared according to General Procedure D, Condition II; Starting from **1f** (450.0



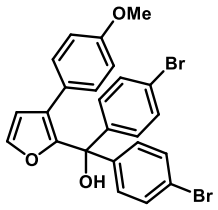
mg, 1.380 mmol, 1.0 equiv.); Purified by silica-gel flash column chromatography (6% EtOAc in hexane); Yellow oil (351.0 mg, 0.780 mmol, 57% yield, over two steps); **FT-IR (Thin film):** 3458 (br), 3004 (w), 2921 (m), 2834 (w), 1596 (m), 1519 (s), 1493 (s), 1246 (s), 1093 (m), 1034 (m), 813 (s), 756 (s); **^{1}H-NMR (300 MHz, CD_2Cl_2):** δ 7.40 (d, *J* = 1.8 Hz, 1H), 7.16-7.13 (m, 4H), 7.12-7.09 (m, 4H), 6.98 (d, *J* = 8.7 Hz, 2H), 6.68 (d, *J* = 8.7 Hz, 2H), 6.44 (d, *J* = 1.8 Hz, 1H), 3.75 (s, 3H), 3.09 (s, 1H), 2.45 (s, 6H); **^{13}C-NMR (75 MHz, CD_2Cl_2):** 159.0, 151.7, 142.3, 141.1, 138.4, 130.5, 128.3, 126.4, 126.0, 124.0, 114.5, 113.8, 79.2, 55.6, 15.8; **HRMS (ESI+):** Calcd. for $C_{26}H_{24}O_3S_2$ ([M+Na]+): 471.1059, Found: 471.1065.

Compound 2f: Prepared according to General Procedure D, Condition II; Starting from **1g** (600.0



mg, 1.680 mmol, 1.0 equiv.); Purified by silica-gel flash column chromatography (5% EtOAc in hexane); Pale-yellow solid (598.0 mg, 1.180 mmol, 70% yield, over two steps); **m.p.** 141-143 °C; **FT-IR (Thin film):** 3420 (br), 3030 (w), 1616 (m), 1518 (s), 1486 (s), 1246 (s), 1178 (m), 1034 (m), 832 (s), 768 (s), 755 (s), 699 (s); **^{1}H-NMR (400 MHz, CD_2Cl_2):** δ 7.61-7.58 (m, 4H), 7.52-7.49 (m, 4H), 7.47-7.43 (m, 5H), 7.39-7.33 (m, 6H), 7.04 (d, *J* = 8.7 Hz, 2H), 6.67 (d, *J* = 8.7 Hz, 2H), 6.49 (d, *J* = 1.8 Hz, 1H), 3.66 (s, 3H), 3.23 (s, 1H); **^{13}C-NMR (100 MHz, CD_2Cl_2):** 159.0, 151.8, 144.6, 141.2, 141.1, 140.7, 130.6, 129.2, 128.3, 127.8, 127.4, 126.9, 126.5, 124.2, 114.6, 113.7, 79.4, 55.5; **HRMS (ESI+):** Calcd. for $C_{36}H_{28}O_3$ ([M+Na]+): 531.1931, Found: 531.1924.

Compound 2g: Prepared according to General Procedure D, Condition III; Starting from **1j** (500.0



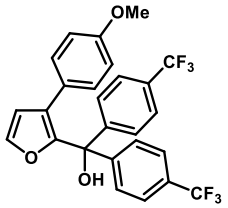
mg, 1.392 mmol, 1.0 equiv.); Purified by silica-gel flash column chromatography (10% EtOAc in hexane); White solid (291.0 mg, 0.566 mmol, 41% yield, over two steps); **m.p.** 55-57 °C; **FT-IR (Thin film):** 3457 (br), 2929 (w), 1518 (s), 1396 (s), 1247 (s), 974 (m), 754 (m); **^{1}H-NMR (400 MHz, CD_2Cl_2):** δ 7.41 (d, *J* = 1.8 Hz, 1H), 7.36 (d, *J* = 8.7 Hz, 4H), 7.11 (d, *J* = 8.6 Hz, 4H), 6.94 (d, *J* = 8.7 Hz, 2H), 6.69 (d, *J* = 8.7 Hz, 2H), 6.45 (d, *J* = 1.8 Hz, 1H), 3.76 (s, 3H), 3.19 (s, 1H); **^{13}C-NMR (100 MHz, CD_2Cl_2):** δ 159.2, 150.7, 144.3, 141.4, 131.4, 130.5, 129.7, 125.9, 124.5, 122.1, 114.6, 113.9, 78.9, 55.7; **HRMS (ESI+):** Calcd. for $C_{24}H_{18}Br_2O_3$ ($[M+Na]^+$): 534.9515, Found: 534.9496.

Compound 2h: Prepared according to General Procedure D, Condition III; Starting from **1k** (400.0 mg, 1.110 mmol, 1.0 equiv.); Purified by silica-gel flash column chromatography (5% EtOAc in hexane); Yellow oil (241 mg, 0.47 mmol, 42% yield, over two steps); **FT-IR (Thin film):** 3465 (br), 2929 (w), 1568 (m), 1519 (s), 1247 (s), 1178 (m), 1034 (m), 787 (m), 756 (s); **^{1}H-NMR (300 MHz, CD_2Cl_2):** δ 7.42 (t, *J* = 1.8 Hz, 3H), 7.39 (t, *J* = 1.9 Hz, 1H), 7.36 (t, *J* = 1.8 Hz, 1H), 7.20-7.15 (m, 3H), 7.12 (d, *J* = 7.8 Hz, 1H), 6.98 (d, *J* = 8.7 Hz, 2H), 6.71 (d, *J* = 8.7 Hz, 2H), 6.46 (d, *J* = 1.8 Hz, 1H), 3.76 (s, 3H), 3.21 (s, 1H); **^{13}C-NMR (75 MHz, CD_2Cl_2):** 159.2, 150.4, 147.3, 141.6, 131.2, 130.8, 130.5, 129.9, 126.6, 125.9, 124.7, 122.6, 114.6, 113.9, 78.7, 55.6; **HRMS (ESI+):** Calcd. for $C_{24}H_{18}Br_2O_3$ ([M+Na]+): 534.9515, Found: 534.9515.

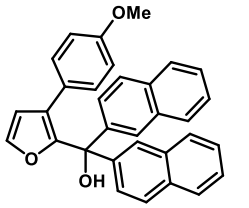
Compound 2i: Prepared according to General Procedure D, Condition I; Starting from **1i** (400.0 mg, 1.270 mmol, 1.0 equiv.); Purified by silica-gel flash column chromatography (5% EtOAc in hexane); Yellow thick oil (253.0 mg, 0.595 mmol, 47% yield, over two steps); **FT-IR (Thin film):** 3464 (br), 2835 (w), 1614 (w), 1519 (s), 1490 (s), 1401 (m), 1247 (s), 879 (m), 728 (m); **^{1}H-NMR (400 MHz, CD_2Cl_2):** δ 7.38 (d, *J* = 1.8 Hz, 1H), 7.22-7.19 (m, 4H), 7.17-7.14 (m, 4H), 6.93 (d, *J* = 8.8 Hz, 2H), 6.70 (d, *J* = 8.8 Hz, 2H), 6.42 (d, *J* = 1.8 Hz, 1H), 3.77 (s, 3H), 3.13 (s, 1H); **^{13}C-NMR (100 MHz, CD_2Cl_2):** δ 158.9, 150.7, 143.4, 141.1, 133.8, 130.2, 129.0, 128.2, 125.7, 124.0, 114.3, 113.8, 78.7, 55.5; **HRMS (ESI+):** Calcd. for $C_{24}H_{18}Cl_2O_3$ ($[M+Na]^+$): 447.0525, Found: 447.0516.

Compound 2j: Prepared according to General Procedure D, Condition III; Starting from **1h** (400.0 mg, 1.341 mmol, 1.0 equiv.); Purified by silica-gel flash column chromatography (7% EtOAc in hexane); Yellow thick oil (143.0 mg, 0.364 mmol, 27% yield, over two steps); **FT-IR (Thin film):** 3465 (br), 1612 (m), 1590 (s), 1519 (s), 1442 (m), 1246 (s), 1179 (w), 1034 (m), 834 (s); **^{1}H-NMR (400 MHz, CD_2Cl_2):** δ 7.42 (d, *J* = 1.8 Hz, 1H), 7.26-7.21 (m, 2H), 7.06-6.99 (m, 6H), 6.97-6.92 (m, 2H), 6.71 (d, *J* = 8.7 Hz, 2H), 6.47 (d, *J* = 1.9 Hz, 1H), 3.75 (s, 3H), 3.21 (s, 1H); **^{13}C-NMR (100 MHz, CD_2Cl_2):** δ 163.0 (d, *J* = 244.9 Hz), 159.2, 150.7, 147.8 (d, *J* = 6.8 Hz), 141.5, 130.5, 129.9 (d, *J* = 8.3 Hz), 126.0, 124.4, 123.5 (d, *J* = 2.9 Hz), 115.0 (d, *J* = 2.6 Hz), 114.8, 114.6, 113.9, 78.9, 55.6; **HRMS (ESI+):** Calcd. for $C_{24}H_{18}F_2O_3$ ($[M+Na]^+$): 415.1116, Found: 415.1122.

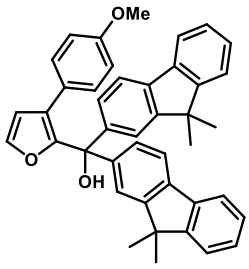
Compound 2k: Prepared according to General Procedure D, Condition II; Starting from **1l** (600.0 mg, 1.720 mmol, 1.0 equiv.); Purified by silica-gel flash column chromatography (8% EtOAc in hexane); Red solid (520.0 mg, 1.060 mmol, 62% yield, over two steps); **m.p.** 94-96 °C; **FT-IR (Thin film):** 3456 (br), 2997 (w), 2844 (w), 1617 (m), 1517 (s), 1417 (s), 1322 (s), 1166 (s), 1111 (s), 1068 (s), 1017 (s), 835 (s), 759 (s), 608 (s); **^{1}H-NMR (400 MHz, CD_2Cl_2):** δ 7.50 (d, *J* = 8.2 Hz, 4H), 7.44 (d, *J* = 1.8 Hz, 1H), 7.40 (d, *J* = 8.0 Hz, 4H), 6.91 (d, *J* = 8.7 Hz, 2H), 6.64 (d, *J* = 8.7 Hz, 2H), 6.47 (d, *J* = 1.8 Hz, 1H), 3.72 (s, 3H), 3.36 (s, 1H); **^{13}C-NMR (100 MHz, CD_2Cl_2):** 159.2, 150.1, 148.7, 141.7, 130.5, 129.9 (q, *J* = 32.3 Hz), 128.3, 125.7, 125.3 (q, *J* = 3.8 Hz), 125.2, 124.6 (q, *J* = 272 Hz), 114.7, 113.8, 78.9, 55.5; **HRMS (ESI+):** Calcd. for $C_{26}H_{18}F_6O_3$ ([M+Na]+): 515.1052, Found: 515.1060.



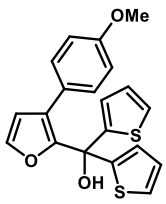
Compound 2l: Prepared according to General Procedure D, Condition II; Starting from **1o** (500.0 mg, 1.513 mmol, 1.0 equiv.); Purified by silica-gel flash column chromatography (6% EtOAc in hexane); White solid (251.0 mg, 0.550 mmol, 36% yield, over two steps); **m.p.** 56-58 °C; **FT-IR (Thin film):** 3454 (br), 1519 (m), 1385 (w), 1247 (m), 1034 (w), 811 (m), 748 (w); **^{1}H-NMR (400 MHz, CD_2Cl_2):** δ 7.83-7.81 (m, 2H), 7.76-7.73 (m, 4H), 7.70-7.69 (m, 2H), 7.51-7.44 (m, 7H), 7.03 (d, *J* = 8.7 Hz, 2H), 6.53 (d, *J* = 8.8 Hz, 2H), 6.52 (d, *J* = 1.9 Hz, 1H), 3.60 (s, 3H), 3.37 (s, 1H); **^{13}C-NMR (100 MHz, CD_2Cl_2):** δ 159.0, 151.8, 143.0, 141.3, 133.2, 130.5, 128.8, 128.0, 127.8, 126.7, 126.6, 126.4, 126.3, 126.3, 124.2, 114.5, 113.7, 80.1, 55.5; **HRMS (ESI+):** Calcd. for $C_{32}H_{24}O_3$ ([M+Na]$^+$): 479.1618, Found: 479.1602.



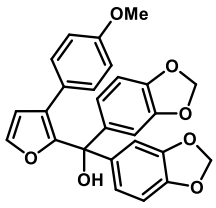
Compound 2m: Prepared according to General Procedure D, Condition III; Starting from **1q** (400.0 mg, 1.010 mmol, 1.0 equiv.); Purified by silica-gel flash column chromatography (5% EtOAc in hexane); Yellow solid (507.0 mg, 0.860 mmol, 85% yield, over two steps); **m.p.** 67-69 °C; **FT-IR (Thin film):** 3426 (br), 3061 (w), 2959 (m), 1604 (m), 1518 (s), 1448 (m), 1295 (m), 1247 (s), 1178 (m), 1032 (m), 962 (m), 834 (s), 759 (s), 739 (s); **^{1}H-NMR (400 MHz, CD_2Cl_2):** δ 7.72-7.69 (m, 2H), 7.59 (d, *J* = 8.0 Hz, 2H), 7.46 (d, *J* = 1.8 Hz, 1H), 7.44-7.41 (m, 4H), 7.34-7.30 (m, 4H), 7.21 (dd, *J* = 8.0, 1.8 Hz, 2H), 7.03 (d, *J* = 8.7 Hz, 2H), 6.58 (d, *J* = 8.8 Hz, 2H), 6.50 (d, *J* = 1.8 Hz, 1H), 3.57 (s, 3H), 3.25 (s, 1H), 1.40 (s, 6H), 1.39 (s, 6H); **^{13}C-NMR (75 MHz, CD_2Cl_2):** 158.9, 154.5, 153.8, 152.3, 145.0, 141.0, 139.2, 139.0, 130.6, 127.7, 127.4, 127.2, 126.5, 124.0, 123.0, 122.3, 120.4, 119.5, 114.6, 113.7, 80.3, 55.5, 47.2, 27.3, 27.2; **HRMS (ESI+):** Calcd. for $C_{42}H_{36}O_3$ ([M+Na]+): 611.2557, Found: 611.2555.



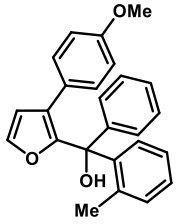
Compound 2n: Followed General Procedure D to obtain the corresponding ketone (**S2**), then followed General Procedure C (thiophene was used instead of 2-bromothiophene to generate corresponding 2-thienyllithium); Starting from **1s** (400.0 mg, 1.400 mmol, 1.0 equiv.); Purified by silica-gel flash column chromatography (5% EtOAc in hexane); Brown solid (195.0 mg, 0.530 mmol, 38% yield, over two steps); **m.p.** 103-105 °C; **FT-IR (Thin film):** 3509 (br), 3114 (w), 2966 (w), 2839 (w), 1611 (m), 1516 (s), 1296 (m), 1237 (s), 1183 (s), 1029 (m), 996 (s), 833 (s), 713 (s); **^{1}H-NMR (400 MHz, CD_2Cl_2):** δ 7.42 (d, *J* = 1.8 Hz, 1H), 7.28 (dd, *J* = 5.0, 1.3 Hz, 2H), 7.15 (d, *J* = 8.7 Hz, 2H), 6.90 (dd, *J* = 5.0, 3.6 Hz, 2H), 6.87 (dd, *J* = 3.6, 1.3 Hz, 2H), 6.77 (d, *J* = 8.7 Hz, 2H), 6.45 (d, *J* = 1.8 Hz, 1H), 3.77 (s, 3H), 3.49 (s, 1H); **^{13}C-NMR (100 MHz, CD_2Cl_2):** 159.2, 150.4, 149.9, 141.2, 130.6, 126.8, 126.8, 126.2, 126.1, 123.2, 114.7, 113.9, 75.9, 55.6; **HRMS (ESI+):** Calcd. for $C_{20}H_{16}O_3S_2$ ([M+Na]+): 391.0433, Found: 391.0434.



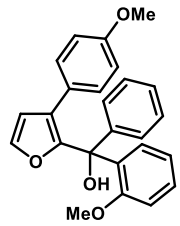
Compound 2o: Prepared according to General Procedure D, Condition II; Starting from **1t** (500.0 mg, 1.540 mmol, 1.0 equiv.); Purified by silica-gel flash column chromatography (12% EtOAc in hexane); Light-blue solid (438.0 mg, 0.990 mmol, 64% yield, over two steps); **m.p.** 52-54 °C; **FT-IR (Thin film):** 3445 (br), 2896 (w), 1614 (m), 1519 (s), 1485 (s), 1438 (m), 1244 (s), 1178 (m), 1038 (s), 934 (m), 805 (m); **^{1}H-NMR (400 MHz, CD_2Cl_2):** δ 7.39 (d, *J* = 1.8 Hz, 1H), 7.00 (d, *J* = 8.8 Hz, 2H), 6.73-6.72 (m, 1H), 6.71-6.67 (m, 7H), 6.43 (d, *J* = 1.8 Hz, 1H), 5.91-5.90 (m, 4H), 3.76 (s, 3H), 3.06 (s, 1H); **^{13}C-NMR (100 MHz, CD_2Cl_2):** 159.0, 152.0, 147.8, 147.4, 141.0, 139.7, 130.5, 126.6, 123.8, 121.3, 114.5, 113.7, 108.9, 107.6, 101.7, 79.4, 55.6; **HRMS (ESI+):** Calcd. for $C_{26}H_{20}O_7$ ([M+Na]+): 467.1101, Found: 467.1109.



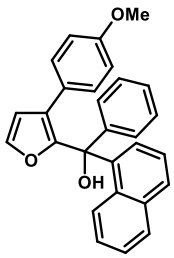
Compound 2p: Prepared according to General Procedure D, Condition I; Starting from **1c** (270.0 mg, 0.920 mmol, 1.0 equiv.); Purified by silica-gel flash column chromatography (5% EtOAc in hexane); White solid (199.0 mg, 0.540 mmol, 59% yield, over two steps); **m.p.** 132-134 °C; **FT-IR (Thin film):** 3419 (br), 2999 (w), 2919 (w), 2837 (w), 1600 (m), 1572 (m), 1519 (s), 1248 (s), 1147 (s), 1038 (s), 840 (s), 748 (s), 709 (s), 617 (m), 558 (m); **^{1}H-NMR (300 MHz, CD_2Cl_2):** δ 7.40 (d, *J* = 1.8 Hz, 1H), 7.31-7.29 (m, 5H), 7.18 (td, *J* = 7.3, 1.4 Hz, 1H), 7.13-7.09 (m, 1H), 7.07-7.01 (m, 3H), 6.74-6.69 (m, 3H), 6.47 (d, *J* = 1.8 Hz, 1H), 3.75 (s, 3H), 3.08 (s, 1H), 2.06 (s, 3H); **^{13}C-NMR (75 MHz, CD_2Cl_2):** 159.2, 152.3, 145.4, 143.5, 140.8, 138.7, 132.6, 130.4, 129.1, 128.4, 128.3, 127.8, 127.8, 126.5, 125.4, 123.1, 114.5, 114.0, 80.9, 55.6, 21.1; **HRMS (ESI+):** Calcd. for $C_{25}H_{22}O_3$ ([M+Na]+): 393.1461, Found: 393.1466.



Compound 2q: Prepared according to General Procedure D, Condition II; Starting from **1a** (230.0 mg, 0.820 mmol, 1.0 equiv.); Purified by silica-gel flash column chromatography (6% EtOAc in hexane); White solid (227.0 mg, 0.590 mmol, 72% yield, over two steps); **m.p.** 119-121 °C; **FT-IR (Thin film):** 3520 (br), 3065 (w), 2942 (m), 2841 (m), 1599 (s), 1520 (s), 1488 (s), 1241 (s), 1188 (s), 1024 (s), 876 (s), 829 (s), 755 (s), 702 (s), 672 (m); **^{1}H-NMR (400 MHz, CD_2Cl_2):** δ 7.34-7.30 (m, 6H), 7.26 (ddd, *J* = 8.2, 7.4, 1.7 Hz, 1H), 7.11 (d, *J* = 8.9 Hz, 2H), 6.88 (dd, *J* = 8.3, 1.1 Hz, 1H), 6.81 (td, *J* = 7.6, 1.2 Hz, 1H), 6.68 (d, *J* = 8.8 Hz, 2H), 6.56 (dd, *J* = 7.7, 1.7 Hz, 1H), 6.51 (d, *J* = 1.8 Hz, 1H), 4.92 (s, 1H), 3.74 (s, 3H), 3.66 (s, 3H); **^{13}C-NMR (100 MHz, CD_2Cl_2):** 158.6, 157.7, 151.9, 145.2, 140.6, 134.2, 130.6, 129.7, 129.6, 128.2, 127.8, 127.7, 126.9, 123.1, 120.9, 114.1, 113.2, 112.1, 79.7, 56.1, 55.5; **HRMS (ESI+):** Calcd. for $C_{25}H_{22}O_4$ ([M+Na]+): 409.1410, Found: 409.1405.

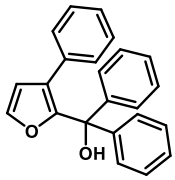


Compound 2r: Prepared according to General Procedure D, Condition II; Starting from **1a** (214 mg, 0.763 mmol, 1.0 equiv.); Purified by silica-gel flash column chromatography (4% EtOAc in hexane); White solid (215.0 mg, 0.540 mmol, 71% yield, over two steps); **m.p.** 51-53 °C; **FT-IR (Thin film):** 3456 (br), 3060 (w), 2957 (m), 1599 (m), 1519 (s), 1446 (s), 1247 (s), 1034 (s), 833 (s), 759 (s), 700 (s), 633 (m); **^{1}H-NMR (300 MHz, CD_2Cl_2):** δ 7.38 (td, *J* = 3.8, 1.6 Hz, 2H), 7.32 (dd, *J* = 7.2, 1.4 Hz, 1H), 7.27-7.25 (m, 5H), 7.08-7.02 (m, 3H), 6.74 (d, *J* = 8.8 Hz, 2H), 6.67 (dd, *J* = 7.9, 1.4 Hz, 1H), 6.47 (d, *J* = 1.8 Hz, 1H), 3.75 (s, 3H), 3.24 (hept, *J* = 6.8 Hz, 1H), 3.16 (s, 1H), 1.01 (d, *J* = 6.8 Hz, 3H), 0.83 (d, *J* = 6.8 Hz, 3H); **^{13}C-NMR (75 MHz, CD_2Cl_2):** 159.2, 152.8, 150.0, 145.8, 142.7, 140.8, 130.4, 128.8, 128.8, 128.3, 128.1, 127.8, 127.7, 126.6, 125.1, 122.8, 114.6, 114.1, 81.1, 55.6, 30.0, 24.7, 23.8; **HRMS (ESI+):** Calcd. for $C_{27}H_{26}O_3$ ([M+Na]+): 421.1774, Found: 421.1782.

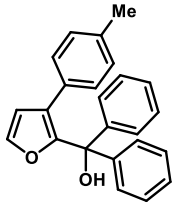


Compound 2s: Prepared according to General Procedure D, Condition II; Starting from **1a** (214 mg, 0.763 mmol, 1.0 equiv.); Purified by silica-gel flash column chromatography (4% EtOAc in hexane); White solid (146.0 mg, 0.360 mmol, 47% yield, over two steps); **m.p.** 65-67 °C; **FT-IR (Thin film):** 3435 (br), 1619 (m), 1519 (m), 1247 (m), 1033 (m), 802 (m), 778 (m), 701 (m); **^{1}H-NMR (400 MHz, CD_2Cl_2):** δ 8.11-8.08 (m, 1H), 7.82-7.78 (m, 2H), 7.40-7.35 (m, 3H), 7.35-7.28 (m, 5H), 7.27-7.23 (m, 1H), 7.00 (d, *J* = 8.8 Hz, 2H), 6.89 (dd, *J* = 7.3, 1.2 Hz, 1H), 6.66 (d, *J* = 8.8 Hz, 2H), 6.48 (d, *J* = 1.8 Hz, 1H), 3.72 (s, 3H), 3.39 (s, 1H); **^{13}C-NMR (100 MHz, CD_2Cl_2):** 159.1, 152.4, 145.6, 141.0, 135.2, 131.9, 130.3, 129.9, 128.9, 128.3, 127.9, 127.9, 127.7, 126.4, 125.7, 125.7, 124.7, 123.3, 114.6, 113.9, 81.3, 55.6; **HRMS (ESI+):** Calcd. for $C_{28}H_{22}O_3$ ([M+Na]+): 429.1461, Found: 429.1463.

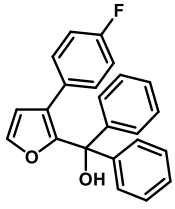
Compound 2t: Prepared according to General Procedure D, Condition I; Starting from **1ac** (444.0 mg, 1.775 mmol, 1.0 equiv.); Purified by silica-gel flash column chromatography (6% EtOAc in hexane); Colorless oil (414.0 mg, 1.268 mmol, 71% yield, over two steps); **FT-IR (Thin film):** 3443 (w), 1491 (w), 1447 (m), 1144 (m), 1025 (m), 1279 (s), 868 (w), 752 (s); **^{1}H-NMR (400 MHz, CD_2Cl_2):** δ 7.43 (d, *J* = 1.8 Hz, 1H), 7.28-7.27 (m, 2H), 7.27-7.26 (m, 6H), 7.25-7.23 (m, 2H), 7.18-7.11 (m, 5H), 6.50 (d, *J* = 1.8 Hz, 1H), 3.06 (s, 1H); **^{13}C-NMR (100 MHz, CD_2Cl_2):** δ 152.2, 145.7, 141.2, 134.4, 129.5, 128.3, 128.2, 127.9, 127.8, 127.2, 124.3, 114.4, 79.8; **HRMS (ESI+):** Calcd. for $C_{23}H_{18}O_2$ ([M+Na]$^+$): 349.1199, Found: 349.1201.



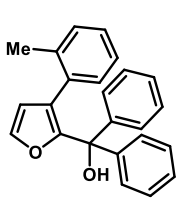
Compound 2u: Prepared according to General Procedure D, Condition I; Starting from **1ad** (400.0 mg, 1.513 mmol, 1.0 equiv.); Purified by silica-gel flash column chromatography (7% EtOAc in hexane); White solid (219.0 mg, 0.643 mmol, 43% yield, over two steps); **m.p.** 108-110 °C; **FT-IR (Thin film):** 3417 (br), 2519 (m), 1447 (s), 1343 (w), 1146 (m), 1028 (m), 867 (m), 824 (s); **^{1}H-NMR (400 MHz, CD_2Cl_2):** δ 7.40 (d, *J* = 1.8 Hz, 1H), 7.30-7.27 (m, 5H), 7.27-7.23 (m, 5H), 7.04-6.99 (m, 4H), 6.48 (d, *J* = 1.9 Hz, 1H), 3.05 (s, 1H), 2.29 (s, 3H); **^{13}C-NMR (100 MHz, CD_2Cl_2):** δ 152.2, 145.9, 141.1, 137.1, 131.3, 129.3, 129.1, 128.2, 127.9, 127.8, 123.9, 114.4, 79.9, 21.2; **HRMS (ESI+):** Calcd. for $C_{24}H_{20}O_2$ ([M+Na]$^+$): 363.1356, Found: 363.1360.



Compound 2v: Prepared according to General Procedure D, Condition I; Starting from **1af** (500.0 mg, 1.864 mmol, 1.0 equiv.); Purified by silica-gel flash column chromatography (3% EtOAc in hexane); Yellow thick oil (344.0 mg, 0.999 mmol, 54% yield, over two steps); **FT-IR (Thin film):** 3465 (br), 2924 (w), 1519 (s), 1491 (s), 1446 (s), 1337 (s), 1162 (s), 812 (m), 723 (w); **^{1}H-NMR (400 MHz, CD_2Cl_2):** δ 7.43 (d, *J* = 1.8 Hz, 1H), 7.26-7.25 (m, 4H), 7.25-7.22 (m, 6H), 7.07-7.03 (m, 2H), 6.85-6.79 (m, 2H), 6.46 (d, *J* = 1.8 Hz, 1H), 3.05 (s, 1H); **^{13}C-NMR (100 MHz, CD_2Cl_2):** δ 162.1 (d, *J* = 245.2 Hz), 152.2, 145.4, 141.3, 131.2 (d, *J* = 8.1 Hz), 130.4 (d, *J* = 3.5 Hz), 128.3, 128.0, 127.8, 123.6, 114.9 (d, *J* = 21.5 Hz), 114.4, 79.6; **HRMS (ESI+):** Calcd. for $C_{23}H_{17}FO_2$ ([M+Na]$^+$): 367.1105, Found: 367.1091.



Compound 2w: Prepared according to General Procedure D, Condition I; Starting from **1ae** (500.0 mg, 1.890 mmol, 1.0 equiv.); Purified by silica-gel flash column chromatography (2% EtOAc in hexane); Colorless oil (533.0 mg, 1.570 mmol, 83% yield, over two steps); **FT-IR (Thin film):** 3560 (br), 3025 (w), 2921 (w), 1491 (m), 1448 (m), 1338 (m), 1145 (m), 868 (m), 762 (s), 699 (s); **^{1}H-NMR (400 MHz, CD_2Cl_2):** δ 7.46 (d, *J* = 1.8 Hz, 1H), 7.24-7.23 (m, 2H), 7.23-7.22 (m, 8H), 7.10-7.09 (m, 2H), 6.98-6.93 (m, 1H), 6.92-6.89 (m, 1H), 6.34 (d, *J* = 1.8 Hz, 1H), 2.84 (s, 1H), 2.13 (s, 3H); **^{13}C-NMR (100 MHz, CD_2Cl_2):** 152.0, 145.6, 141.2, 137.3, 133.9, 130.6, 130.1, 128.1, 127.9, 127.9,



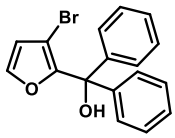
127.8, 125.6, 123.0, 114.5, 79.7, 2 0.6; **HRMS (ESI+):** Calcd. for $C_{24}H_{20}O_3$ ([M+Na]+): 363.1356, Found: 363.1352.

Compound 2x: Prepared according to General Procedure D, Condition I; Starting from **1ag** (150.0 mg, 0.560 mmol, 1.0 equiv.); Purified by silica-gel flash column chromatography (5% EtOAc in hexane); Yellow oil (144.0 mg, 0.420 mmol, 75% yield, over two steps); **FT-IR (Thin film):** 3464 (br), 3060 (m), 3029 (w), 1599 (m), 1514 (m), 1490 (s), 1448 (s), 1337 (m), 1215 (m), 1145 (m), 1032 (m), 814 (m), 754 (s), 700 (s); **^{1}H-NMR (400 MHz, CD_2Cl_2):** δ 7.49 (d, *J* = 1.8 Hz, 1H), 7.34-7.32 (m, 1H), 7.28-7.26 (m, 4H), 7.21-7.18 (m, 5H), 7.13-7.09 (m, 1H), 6.98 (td, *J* = 7.6, 1.9 Hz, 1H), 6.91-6.87 (m, 1H), 6.86-6.83 (m, 1H), 6.44 (dd, *J* = 1.9, 0.9 Hz, 1H), 3.08 (d, *J* = 2.0 Hz, 1H); **^{13}C-NMR (100 MHz, CD_2Cl_2):** 159.9 (d, *J* = 244.7 Hz), 153.2, 145.0, 141.5, 132.1 (d, *J* = 3.0 Hz), 129.3 (d, *J* = 8.1 Hz), 128.4, 128.1, 127.9, 127.8, 127.5, 123.9 (d, *J* = 3.6 Hz), 115.4 (d, *J* = 22.5 Hz), 114.5 (d, *J* = 1.4 Hz), 79.4; **HRMS (ESI+):** Calcd. for $C_{23}H_{17}FO_3$ ([M+Na]+): 367.1105, Found: 367.1099. [*Note*: This compound is very unstable, sensitive to silica-gel, temperature, and rotary evaporation at 20 °C is necessary.]

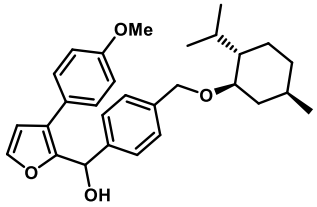
Compound 2y: Prepared according to General Procedure D, Condition I; Starting from **1ai** (400.0 mg, 1.560 mmol, 1.0 equiv.); Purified by silica-gel flash column chromatography (5% EtOAc in hexane); Pale-yellow solid (427.0 mg, 1.280 mmol, 82% yield, over two steps); **m.p.** 78-80 °C; **FT-IR (Thin film):** 3377 (br), 3105 (w), 3028 (w), 1493 (m), 1450 (m), 1186 (m), 1144 (s), 1016 (s), 898 (s), 855 (s), 786 (s), 751 (s), 701 (s), 651 (m); **^{1}H-NMR (300 MHz, CD_2Cl_2):** δ 7.39 (d, *J* = 1.9 Hz, 1H), 7.31-7.28 (m, 10H), 7.18 (dd, *J* = 4.9, 3.0 Hz, 1H), 6.95 (dd, *J* = 3.0, 1.3 Hz, 1H), 6.92 (dd, *J* = 4.9, 1.3 Hz, 1H), 6.55 (d, *J* = 1.8 Hz, 1H), 3.23 (s, 1H); **^{13}C-NMR (75 MHz, CD_2Cl_2):** 152.6, 145.6, 141.2, 134.1, 129.0, 128.3, 128.0, 127.7, 125.5, 123.2, 119.0, 114.0, 79.6; **HRMS (ESI+):** Calcd. for $C_{21}H_{16}O_2S$ ([M+Na]+): 355.0763, Found: 355.0761.

Compound 2z: Prepared according to General Procedure D, Condition I; Starting from [2,3'-bifuran]-2'-yl(phenyl)methanol (130.0 mg, 0.540 mmol, 1.0 equiv.); Purified by silica-gel flash column chromatography (8% EtOAc in hexane); Pink solid (136.0 mg, 0.430 mmol, 80% yield, over two steps); **m.p.** 115-117 °C; **FT-IR (Thin film):** 3445 (br), 3145 (w), 3026 (w), 1492 (m), 1447 (m), 1216 (m), 1018 (m), 857 (m), 753 (s), 701 (s), 636 (m); **^{1}H-NMR (400 MHz, CD_2Cl_2):** δ 7.33 (d, *J* = 1.9 Hz, 1H), 7.32-7.28 (m, 10H), 7.27 (dd, *J* = 1.9, 0.7 Hz, 1H), 6.69 (d, *J* = 1.9 Hz, 1H), 6.35 (dd, *J* = 3.4, 1.9 Hz, 1H), 6.28 (dd, *J* = 3.4, 0.8 Hz, 1H), 4.38 (s, 1H); **^{13}C-NMR (100 MHz, CD_2Cl_2):** 153.7, 148.0, 145.5, 142.1, 141.5, 128.2, 127.9, 127.7, 114.0, 111.8, 111.4, 108.0, 79.1; **HRMS (ESI+):** Calcd. for $C_{21}H_{16}O_3$ ([M+Na]+): 339.0992, Found: 339.0989.

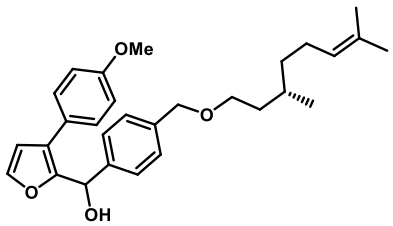
Compound 2aa: Prepared according to General Procedure D, Condition I; Starting from (3-bromofuran-2-yl)(phenyl)methanol (400.0 mg, 1.590 mmol, 1.0 equiv.); Purified by silica-gel flash column chromatography (5% EtOAc in hexane); Off-white solid (423.0 mg, 1.285 mmol, 81% yield, over two steps); **m.p.** 55-57 °C; **FT-IR (Thin film):** 3435 (br), 1492 (w), 1492 (m), 1447 (s), 1184 (m), 1141 (m), 987 (s), 755 (s); **^{1}H-NMR (400 MHz, CD_2Cl_2):** δ 7.36 (d, *J* = 2.0 Hz, 1H), 7.35-7.32 (m, 6H), 7.31-7.27 (m, 4H), 6.50 (d, *J* = 2.0 Hz, 1H), 3.40 (s, 1H); **^{13}C-NMR (100 MHz, CD_2Cl_2):** δ 153.3, 144.3, 142.3, 128.4, 128.3, 127.9, 115.9, 9 8.0, 79.2; **HRMS (ESI+):** Calcd. for $C_{17}H_{13}BrO_2$ ([M+Na]$^+$): 350.9991, Found: 350.9989.



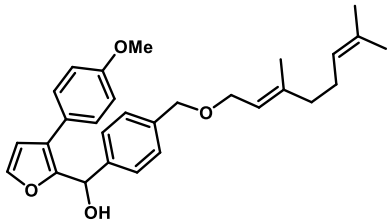
Compound 6a: Prepared according to General Procedure A, Condition II; Starting from 3-(4-methoxyphenyl)furan-2-carbaldehyde (300.0 mg, 1.483 mmol, 1.0 equiv.); Purified by silica-gel flash column chromatography (7% EtOAc in hexane); Yellow thick oil (542.0 mg, 1.208 mmol, 82% yield); **FT-IR (Thin film):** 3406 (br), 2953 (s), 1518 (s), 1248 (s), 1179 (s), 960 (m), 833 (s), 756 (m); **^{1}H-NMR (400 MHz, CD_2Cl_2):** δ 7.41 (d, *J* = 1.9 Hz, 1H), 7.39-7.37 (m, 4H), 7.34-7.32 (m, 2H), 6.96 (d, *J* = 8.7 Hz, 2H), 6.54 (d, *J* = 1.8 Hz, 1H), 5.94 (d, *J* = 5.7 Hz, 1H), 4.64 (d, *J* = 11.5 Hz, 1H), 4.37 (d, *J* = 11.5 Hz, 1H), 3.83 (s, 3H), 3.18 (td, *J* = 10.5, 4.1 Hz, 1H), 2.52 (d, *J* = 5.7 Hz, 1H), 2.30-2.18 (m, 2H), 1.74-1.66 (m, 1H), 1.65-1.61 (m, 2H), 1.42-1.33 (m, 1H), 1.30-1.25 (m, 1H), 1.05-0.98 (m, 1H), 0.94 (d, *J* = 6.5 Hz, 3H), 0.90 (d, *J* = 7.1 Hz, 3H), 0.88-0.85 (m, 1H), 0.73 (dd, *J* = 7.0, 1.6 Hz, 3H); **^{13}C-NMR (100 MHz, CD_2Cl_2):** δ 159.5, 149.9, 142.4, 140.9, 139.5, 129.7, 128.2, 126.7, 125.8, 124.1, 114.5, 112.0, 79.3, 70.3, 68.3, 55.7, 48.9, 40.8, 35.0, 32.0, 26.1, 23.8, 22.6, 21.2, 16.4; **HRMS (ESI+):** Calcd. for $C_{29}H_{36}O_4$ ([M+Na]$^+$): 471.2506, Found: 471.2506.



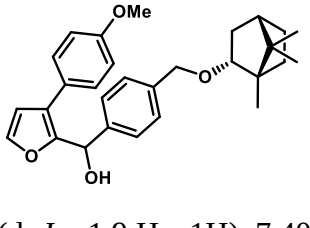
Compound 6b: Prepared according to General Procedure A, Condition II; Starting from 3-(4-methoxyphenyl)furan-2-carbaldehyde (202.0 mg, 1.000 mmol, 1.0 equiv.); Purified by silica-gel flash column chromatography (7% EtOAc in hexane); Yellow thick oil (318.0 mg, 0.709 mmol, 71% yield); **FT-IR (Thin film):** 3409 (br), 2924 (s), 1604 (w), 1518 (s), 1248 (s), 1178 (s), 1034 (m), 894 (w), 833 (s); **^{1}H-NMR (400 MHz, CD_2Cl_2):** δ 7.41 (d, *J* = 1.9 Hz, 1H), 7.40-7.36 (m, 4H), 7.33-7.31 (m, 2H), 6.96 (d, *J* = 8.7 Hz, 2H), 6.54 (d, *J* = 1.8 Hz, 1H), 5.94 (d, *J* = 5.6 Hz, 1H), 5.13-5.09 (m, 1H), 4.47 (s, 2H), 3.83 (s, 3H), 3.54-3.46 (m, 2H), 2.53 (d, *J* = 5.7 Hz, 1H), 2.06-1.91 (m, 2H), 1.68 (s, 3H), 1.66-1.63 (m, 1H), 1.60 (s, 3H), 1.60-1.57 (m, 1H), 1.45-1.30 (m, 2H), 1.21-1.12 (m, 1H), 0.89 (d, *J* = 6.6 Hz, 3H); **^{13}C-NMR (100 MHz, CD_2Cl_2):** δ 159.5, 149.9, 142.4, 141.0, 139.0, 131.4, 129.7, 128.0, 126.8, 125.8, 125.2, 124.1, 114.5, 112.1, 72.8, 69.2, 68.3, 55.7, 37.6, 37.1, 30.0, 25.9, 25.8, 19.7, 17.7; **HRMS (ESI+):** Calcd. for $C_{29}H_{36}O_4$ ([M+Na]$^+$): 471.2506, Found: 471.2504.



Compound 6c: Prepared according to General Procedure A, Condition II; Starting from 3-(4-methoxyphenyl)furan-2-carbaldehyde (202.0 mg, 1.000 mmol, 1.0 equiv.); Purified by silica-gel flash column chromatography (9% EtOAc in hexane); Yellow thick oil (366.0 mg, 0.820 mmol, 82% yield); **FT-IR (Thin film):** 3408 (br), 2916 (m), 1518 (s), 1292 (w), 1248 (s), 1179 (m), 894 (w), 834 (m), 727 (w); **^{1}H-NMR (400 MHz, CD_2Cl_2):** δ 7.41 (d, *J* = 1.9 Hz, 1H), 7.40-7.36 (m, 4H), 7.33-7.31 (m, 2H), 6.95 (d, *J* = 8.7 Hz, 2H), 6.54 (d, *J* = 1.9 Hz, 1H), 5.94 (d, *J* = 5.6 Hz, 1H), 5.39-5.35 (m, 1H), 5.14-5.10 (m, 1H), 4.46 (s, 2H), 4.02 (d, *J* = 6.6 Hz, 2H), 3.83 (s, 3H), 2.53 (d, *J* = 5.7 Hz, 1H), 2.15-2.09 (m, 2H), 2.07-2.03 (m, 2H), 1.68 (s, 3H), 1.65 (s, 3H), 1.61 (s, 3H); **^{13}C-NMR (100 MHz, CD_2Cl_2):** δ 159.5, 149.9, 142.4, 141.0, 140.5, 138.9, 132.0, 129.7, 128.2, 126.8, 125.8, 124.4, 124.1, 121.4, 114.5, 112.1, 71.8, 68.3, 67.1, 55.7, 40.0, 26.8, 25.8, 17.8, 16.6; **HRMS (ESI+):** Calcd. for $C_{29}H_{34}O_4$ ($[M+Na]^+$): 469.2349, Found: 469.2354.



Compound 6d: Prepared according to General Procedure A, Condition II; Starting from 3-(4-methoxyphenyl)furan-2-carbaldehyde (202.0 mg, 1.000 mmol, 1.0 equiv.); Purified by silica-gel flash column chromatography (7% EtOAc in petroleum eth er); Yellow thick oil (369.0 mg, 0.826 mmol, 83% yield); **FT-IR (Thin film):** 3435 (br), 2951 (s), 1518 (s), 1248 (s), 1178 (m), 1119 (s), 833 (m), 758 (s); **^{1}H-NMR (300 MHz, CD_2Cl_2):** δ 7.42 (d, *J* = 1.9 Hz, 1H), 7.40-7.32 (m, 6H), 6.96 (d, *J* = 8.7 Hz, 2H), 6.54 (d, *J* = 1.9 Hz, 1H), 5.94 (s, 1H), 4.55 (d, *J* = 12.0 Hz, 1H), 4.42 (d, *J* = 12.0 Hz, 1H), 3.83 (s, 3H), 3.75-3.70 (m, 1H), 2.50 (s, 1H) , 2.21-2.11 (m, 1H), 2.09- 2.00 (m, 1H), 1.79-1.73 (m, 1H), 1.67-1.64 (m, 1H), 1.30-1.27 (m, 1H), 1.24-1.19 (m, 1H), 1.10 (dd, *J* = 13.0, 3.4 Hz, 1H), 0.91 (s, 3H), 0.86 (d, *J* = 3.4 Hz, 6H); **^{13}C-NMR (75 MHz, CD_2Cl_2):** δ 159.5, 149.9, 142.4, 140.8, 139.7, 129.7, 127.8, 126.7, 125.8, 124.1, 114.5, 112.0, 85.0, 71.7, 68.3, 55.7, 49.7, 48.2, 45.6, 36.5, 28.6, 27.2, 19.9, 19.0, 14.2; **HRMS (ESI+):** Calcd. for $C_{29}H_{34}O_4$ ($[M+Na]^+$): 469.2349, Found: 469.2346.



Compound 6e: Prepared according to General Procedure A, Condition II; Starting from 3-(4-methoxyphenyl)furan-2-carbaldehyde (148.0 mg, 0.732 mmol, 1.0 equiv.); Purified by silica-gel flash column chromatography (7% EtOAc in petroleum eth er); Yellow thick oil (168.0 mg, 0.376 mmol, 51% yield); **FT-IR (Thin film):** 3426 (br), 2952 (s), 1518 (s), 1463 (m), 1248 (s), 1178 (m), 1034 (s), 833 (s), 727 (w); **^{1}H-NMR (400 MHz, CD_2Cl_2):** δ 7.42 (d, *J* = 1.8 Hz, 1H), 7.40-7.34 (m, 6H), 6.96 (d, *J* = 8.8 Hz, 2H), 6.54 (d, *J* = 1.9 Hz, 1H), 5.95 (s, 1H), 4.58 (d, *J* = 11.9 Hz, 1H), 4.43 (d, *J* = 11.7 Hz, 1H), 3.83 (s, 3H), 3.05 (d, *J* = 1.9 Hz, 1H), 2.52 (br s, 1H), 1.81-1.67 (m, 2H), 1.65-1.64 (m, 1H), 1.50-1.46 (m, 1H), 1.45-1.36 (m, 1H), 1.11 (s, 3H), 1.10-1.07 (m, 1H), 1.05 (s, 3H), 1.03-0.99 (m, 1H), 0.98 (s, 3H); **^{13}C-NMR (100 MHz, CD_2Cl_2):** δ 159.5, 149.9, 142.4, 140.9, 139.6, 129.7, 127.9, 126.7, 125.8, 124.1, 114.5,

112.1, 93.1, 73.7, 68.3, 55.7, 49.6, 49.3, 41.7, 39.9, 31.8, 26.5, 26.4, 20.9, 20.3; **HRMS (ESI+):** Calcd. for $C_{29}H_{34}O_4$ ($[M+Na]^+$): 469.2349, Found: 469.2346.

Compound 6f: Prepared according to General Procedure C; Starting from 3-(4-methoxyphenyl)furan-2-carbaldehyde (101.0 mg, 0.500 mmol, 1.0 equiv.); Purified by silica-gel flash column chromatography (7% EtOAc in hexane); Yellow thick oil (210.0 mg, 0.380 mmol, 76% yield); **FT-IR (Thin film):** 3443 (br), 2932 (m), 1519 (s), 1383 (m), 1251 (s), 1176 (m), 1069 (s), 960 (w); **^{1}H-NMR (400 MHz, CD_2Cl_2):** δ 7.42 (d, *J* = 1.9 Hz, 1H), 7.41-7.36 (m, 4H), 7.35-7.33 (m, 2H), 6.96 (d, *J* = 8.7 Hz, 2H), 6.54 (d, *J* = 1.9 Hz, 1H), 5.94 (d, *J* = 5.5 Hz, 1H), 5.49 (d, *J* = 5.0 Hz, 1H), 4.60-4.58 (m, 1H), 4.57-4.50 (m, 2H), 4.30 (dd, *J* = 5.0, 2.4 Hz, 1H), 4.23 (dd, *J* = 7.9, 1.9 Hz, 1H), 4.00-3.96 (m, 1H), 3.83 (s, 3H), 3.64 (dd, *J* = 10.1, 5.4 Hz, 1H), 3.58 (dd, *J* = 10.1, 7.0 Hz, 1H), 2.55 (d, *J* = 5.7 Hz, 1H), 1.51 (s, 3H), 1.41 (s, 3H), 1.32 (s, 6H); **^{13}C-NMR (100 MHz, CD_2Cl_2):** δ 159.5, 149.9, 142.5, 141.2, 138.5, 129.7, 128.2, 126.9, 125.8, 124.1, 114.6, 112.0, 109.5, 108.9, 96.8, 73.3, 71.7, 71.2, 71.1, 69.7, 68.3, 67.4, 55.7, 26.3, 26.2, 25.1, 24.6; **HRMS (ESI+):** Calcd. for $C_{31}H_{36}O_9$ ($[M+Na]^+$): 575.2252, Found: 575.2255.

Compound 6g: Prepared according to General Procedure C; Starting from 3-(4-methoxyphenyl)furan-2-carbaldehyde (101.0 mg, 0.500 mmol, 1.0 equiv.); Purified by silica-gel flash column chromatography (12% EtOAc in petroleum eth er); Yellow thick oil (183.0 mg, 0.316 mmol, 63% yield); **FT-IR (Thin film):** 3444 (br), 2926 (m), 1609 (m), 1518 (s), 1250 (s), 1035 (m), 960 (m), 834 (s); **^{1}H-NMR (400 MHz, CD_2Cl_2):** δ 7.42 (d, *J* = 1.9 Hz, 1H), 7.41-7.37 (m, 4H), 7.35-7.33 (m, 2H), 7.18 (d, *J* = 8.5 Hz, 1H), 6.96 (d, *J* = 8.8 Hz, 2H), 6.68-6.65 (m, 1H), 6.61-6.60 (m, 1H), 6.55 (d, *J* = 1.9 Hz, 1H), 5.95 (d, *J* = 5.5 Hz, 1H), 4.54 (s, 2H), 3.83 (s, 3H), 3.74 (s, 3H), 3.54-3.49 (m, 1H), 2.89-2.78 (m, 2H), 2.51 (d, *J* = 5.7 Hz, 1H), 2.32-2.26 (m, 1H), 2.21-2.14 (m, 1H), 2.12-2.02 (m, 2H), 1.90-1.85 (m, 1H), 1.74-1.66 (m, 1H), 1.63-1.57 (m, 1H), 1.54-1.47 (m, 1H), 1.45-1.33 (m, 4H), 1.26-1.20 (m, 1H), 0.85 (s, 3H); **^{13}C-NMR (100 MHz, CD_2Cl_2):** δ 159.5, 157.9, 149.9, 142.4, 140.9, 139.5, 138.5, 133.2, 129.7, 127.8, 126.7, 126.6, 125.8, 124.1, 114.5, 114.0, 112.1, 111.7, 89.1, 71.7, 68.3, 55.7, 55.5, 50.6, 44.4, 43.8, 39.1, 38.4, 30.2, 28.4, 27.7, 26.9, 23.5, 12.0; **HRMS (ESI+):** Calcd. for $C_{38}H_{42}O_5$ ($[M+Na]^+$): 601.2924, Found: 601.2931.

Compound 6h: Prepared according to General Procedure C; Starting from 3-(4-methoxyphenyl)furan-2-carbaldehyde (101.0 mg, 0.500 mmol, 1.0 equiv.); Purified by silica-gel flash column chromatography (12% EtOAc in petroleum eth er); Yellow thick oil (170.0 mg, 0.250 mmol, 50% yield); **FT-IR (Thin film):** 3420 (br), 2933 (s), 1519 (s), 1465 (m), 1248 (m), 1180 (w), 960 (w), 894 (s); **^{1}H-NMR (300 MHz, CD_2Cl_2):** δ 7.41 (d, *J* = 1.9 Hz, 1H), 7.39-7.36 (m, 4H), 7.33-7.31 (m, 2H), 6.95 (d, *J* = 8.9 Hz, 2H), 6.54 (d, *J* = 1.9 Hz, 1H), 5.94 (s, 1H), 5.36-5.34 (m, 1H), 4.53 (s, 2H), 3.83 (s, 3H), 3.30-3.20 (m, 1H), 2.44-2.37 (m, 1H), 2.28-2.19 (m, 1H), 2.12 (s, 1H), 2.05-1.78 (m, 6H), 1.63-1.57 (m, 2H), 1.55-1.44 (m, 7H), 1.42-1.30 (m, 5H), 1.21-1.07 (m, 7H), 1.02 (s, 3H), 0.93 (d, *J* = 6.5 Hz, 3H), 0.87 (dd, *J* = 6.6, 1.2 Hz, 6H), 0.69 (s, 3H); **^{13}C-NMR (75 MHz, CD_2Cl_2):** δ 159.5, 149.9, 142.4, 141.4, 140.9, 139.4, 129.7, 128.0, 126.8, 125.7, 124.1, 121.9, 114.5, 112.0, 79.1, 69.8, 68.3, 57.2, 56.6, 55.7, 50.7, 42.7, 40.3, 39.9, 39.6, 37.7, 37.3, 36.6, 36.2, 32.4, 32.3, 28.9, 28.6, 28.4, 24.8, 24.2, 23.0, 22.7, 21.5, 19.6, 18.9, 12.0; **HRMS (ESI+):** Calcd. for $C_{46}H_{62}O_4$ ($[M+Na]^+$): 701.4540, Found: 701.4542.

Compound 2′ was known and prepared by following representative literature procedures.[2]

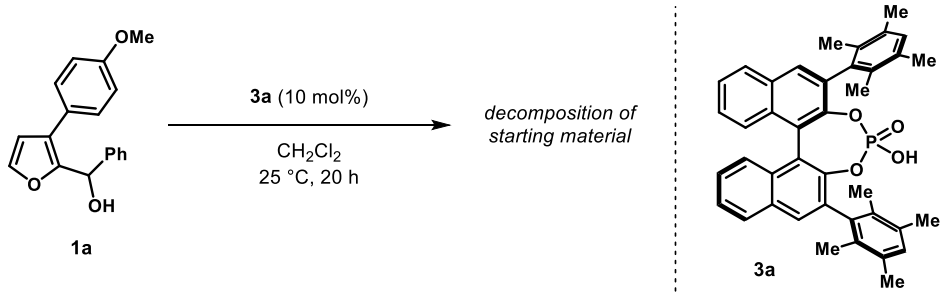
Compound 1a′: Prepared according to General Procedure A, Condition I; Starting from 4-(4-methoxyphenyl)furan-2-carbaldehyde (600.0 mg, 2.970 mmol, 1.0 equiv.); Purified by silica-gel flash column chromatography (10% EtOAc in hexane); Yellow solid (739.0 mg, 2.636 mmol, 89% yield); **m.p.** 87-89 °C; **FT-IR (Thin film):** 3444 (br), 1556 (m), 1505 (s), 1181 (m), 1024 (s), 928 (m), 701 (s); **^{1}H-NMR (400 MHz, CD_2Cl_2):** δ 7.63 (d, *J* = 1.0 Hz, 1H), 7.49-7.45 (m, 2H), 7.42-7.34 (m, 5H), 6.89 (d, *J* = 8.8 Hz, 2H), 6.44 (t, *J* = 0.9 Hz, 1H), 5.83 (d, *J* = 3.7 Hz, 1H), 3.80 (s, 3H), 2.55 (d, *J* = 4.2 Hz, 1H); **^{13}C-NMR (100 MHz, CD_2Cl_2):** δ 159.3, 157.6, 141.4, 137.8, 128.9, 128.5, 127.2, 127.1, 127.0, 125.1, 114.6, 106.8, 70.5, 55.7; **HRMS (ESI+):** Calcd. for $C_{18}H_{16}O_3$ ($[M+H]^+$): 281.1172, Found: 281.1175.

[2] H. W. Gschwend, H. R. Rodriguez, *Org. React.* **1979**, *26*, 1.

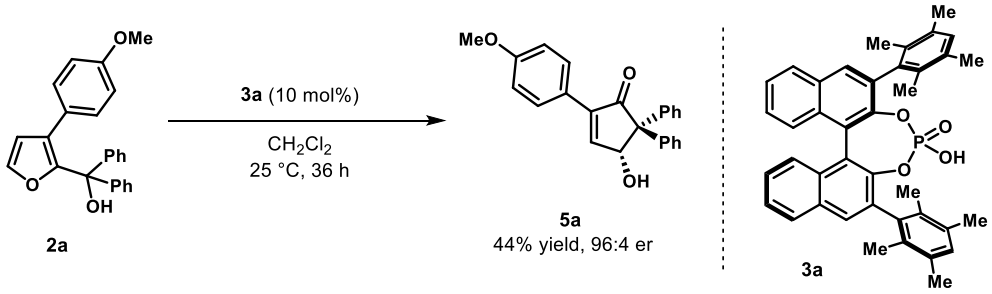
V. Catalyst and reaction conditions optimization for the enantioselective oxa-Piancatelli rearrangement:

Scheme S1: Preliminary studies

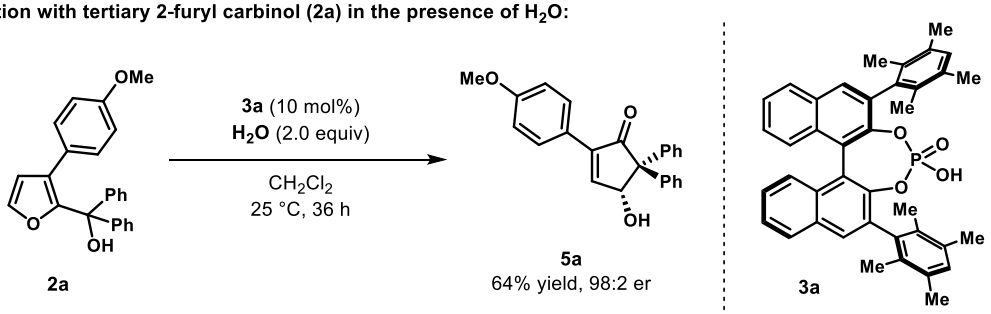
- **Reaction with secondary 2-furyl carbinol (1a):**



- **Reaction with tertiary 2-furyl carbinol (2a):**



- **Reaction with tertiary 2-furyl carbinol (2a) in the presence of H_2O:**



- **Reaction with secondary 2-furyl carbinol (1a) in the presence of H_2O:**

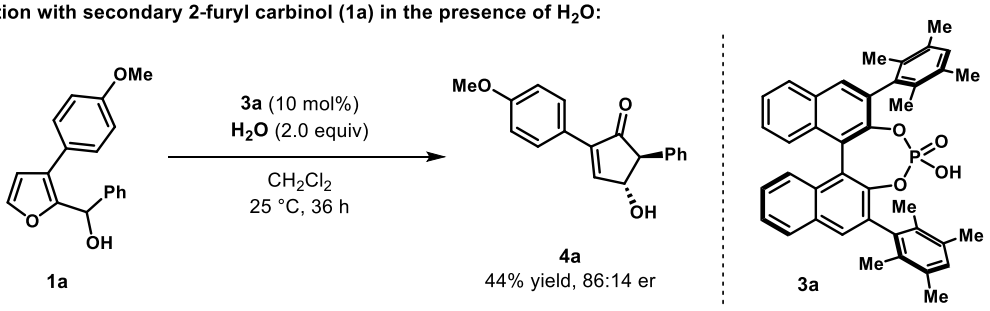
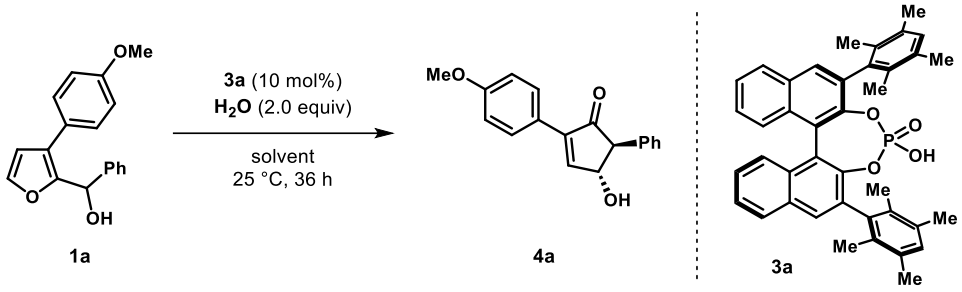


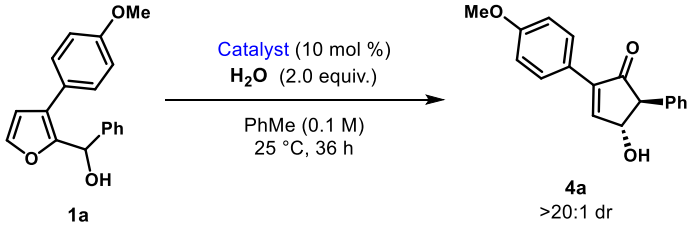
Table S1: Optimization of solvent[a]



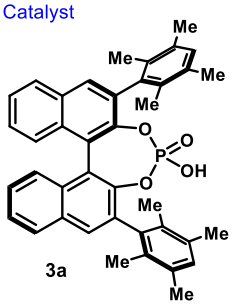
entry	solvent	yield (%)[b]	er[c]
1	CH_2Cl_2	44	86:14
2	CH_3CN	7	n.d.
3	Cyclohexane	18	89:11
4	THF	<5	n.d.
5	PhMe	(50)	89:11
6[d]	PhMe	56	89:11
7	PhMe/CH_2Cl_2 (1.5:1)	57	89.5:10.5
8	Acetone	<5	n.d.

[a]Reaction conditions: 0.05 mmol of **1a** 0.2 mmol of H_2O, and catalyst **3a** (2 mol %) in 0.5 mL solvent. [b]Yields were determined by ^{1}H-NMR spectroscopy with 1,3,5-trimethoxybenzene as internal standard. Isolated yields are given in the parentheses. [c]The enantiomeric ratio (er) was determined by HPLC analysis on a chiral stationary phase; n.d. = not determined. [d]10.0 equiv H_2O was used as an additive.

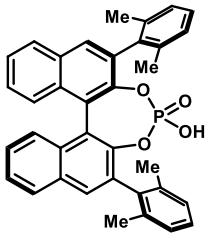
Table S2: Catalyst screening[a]



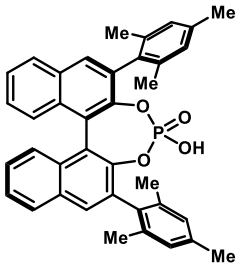
Catalyst



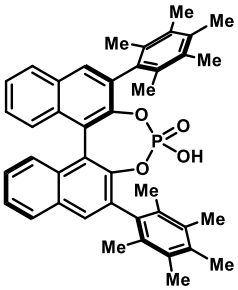
Yield = 50%
er = 89:11



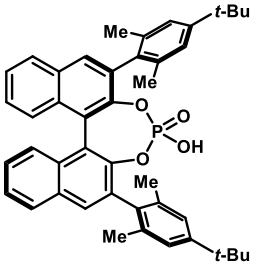
Yield = 86%
er = 92.5:7.5



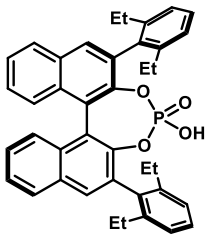
Yield = 78%
er = 93:7



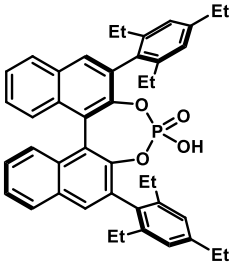
Yield = 42%
er = 86.5:13.5



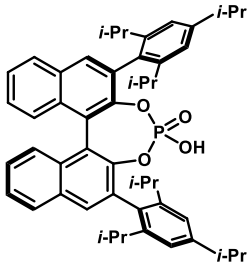
Yield = 55%
er = 90:10



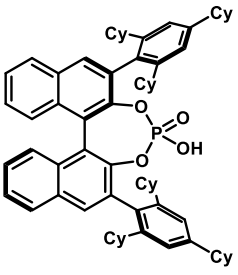
Yield = 81%
er = 95:5



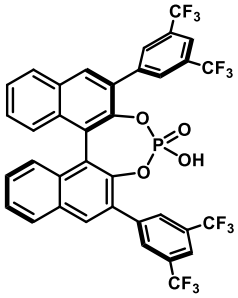
Yield = 72%
er = 94:6



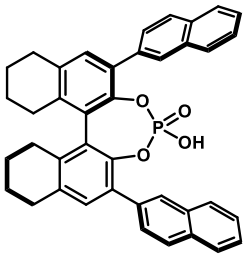
Yield = 72%
er = 94:6



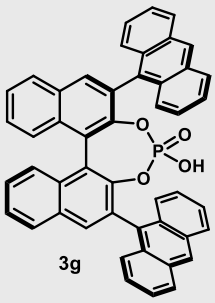
Yield = 25%
er = 91:9



Yield = 48%
er = 89.5:10.5



Yield = 82%
er = 96.5:3.5



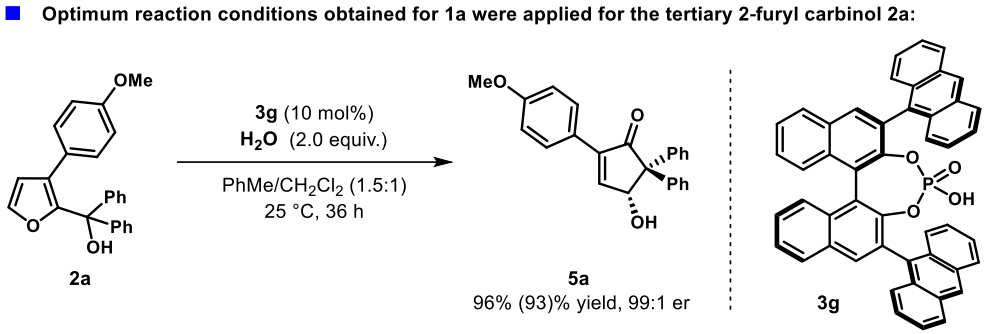
Yield = (83%)
er = 97:3

PhMe/CH_2Cl_2 (1.5:1) as solvent

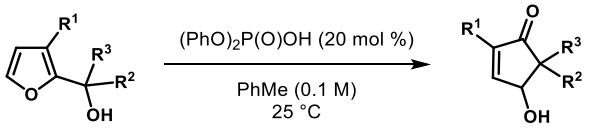
Yield = 96% (96%)
er = 98:2

[a]Reaction conditions: 0.05 mmol of **1a**, 0.2 mmol of H_2O, and catalyst **3** (10 mol %) in 0.5 mL PhMe. The diastereomeric ratio (dr) was determined by ^{1}H NMR and was >20:1 in all cases. [b]Yields were determined by ^{1}H-NMR spectroscopy with 1,3,5-trimethoxybenzene as internal standard. Isolated yields are given in the parentheses. [c]The enantiomeric ratio (er) was determined by HPLC analysis on a chiral stationary phase.

Scheme S2: Optimization of reaction conditions for the tertiary 2-furyl carbinol (**2a**)

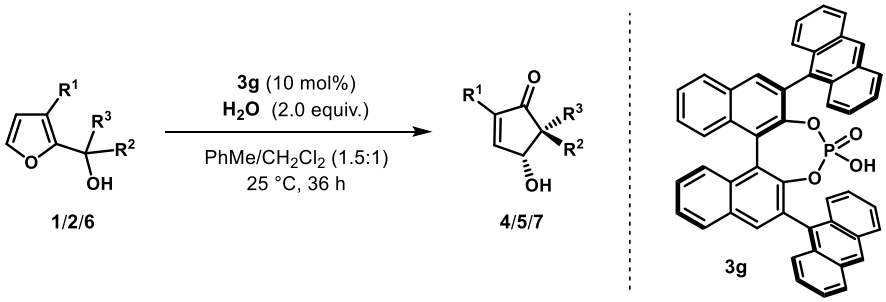


VI. General procedure for the preparation of racemic products (*rac*-4/5):



In a glass-vial, 2-furyl carbinols **1**/**2** (0.05 mmol, 1.0 equiv) and H_2O (1.8 µL, 0.10 mmol, 2.0 equiv) were taken in 0.5 mL of toluene. To this solution, diphenyl hydrogen phosphate (2.5 mg, 0.01 mmol, 20 mol%) was added and the resulting suspension was stirred at 25 °C until TLC reveals the complete consumption of **1**/**2**. The crude mixture was purified by preparative TLC (ALUGRAM® Xtra SIL G/UV_{254} pre-coated plates of 0.20 mm thickness) to obtain the racemic product (*rac*-**4**/**5**) samples for HPLC analysis.

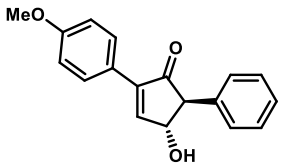
VII. Typical procedure for the catalytic enantioselective oxa-Piancatelli rearrangement:



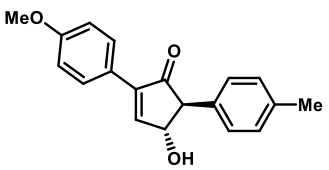
In a screw-cap vial, 2-furyl carbinols **1**/**2**/**6** (0.10 mmol, 1.0 equiv) and H_2O (3.6 µL, 0.20 mmol, 2.0 equiv) were taken with 0.5 mL of toluene/CH_2Cl_2 (1.5:1) and stirred for 5 min. To this solution, catalyst **3g** (7.0 mg, 0.01 mmol, 10 mol%) was added along with 0.5 mL of toluene/CH_2Cl_2 (1.5:1) and the resulting mixture was stirred at 25 °C until TLC (20% EtOAc in hexane) revealed complete consumption of **1**/**2**/**6** (36 h). The reaction mixture was concentrated

under reduced pressure to obtain a reddish-brown oil. This residue was purified by preparative TLC (20-30% EtOAc in hexane) to obtain **4**/**5**/**7**. The enantiomeric excess was determined by HPLC on a chiral stationary phase. The diastereomeric ratio was determined via ^{1}H-NMR of the crude reaction mixture. Unless otherwise noted, the diastereomeric ratio was >20:1 in all cases.

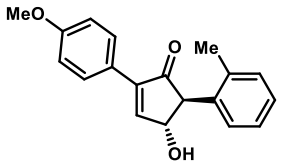
Compound 4a: Purified by preparative TLC (20% EtOAc in hexane); Yellow thick oil (27.0 mg, 0.096mmol, 96% yield); **FT-IR (Thin film):** 3436 (br), 1707 (s), 1604 (m), 1510 (s), 1258 (s), 1180 (m), 1030 (w), 831 (m); **^{1}H-NMR (400 MHz, CDCl$_3$):** δ 7.75 (d, *J* = 8.9 Hz, 1H), 7.58 (d, *J* = 2.5y Hz, 1H), 7.36-7.33 (m, 2H), 7.31-7.29 (m, 1H), 7.17-7.14 (m, 1H), 6.93 (d, *J* = 8.9 Hz, 1H), 4.94 (t, *J* = 2.7 Hz, 1H), 3.83 (s, 3H), 3.59 (d, *J* = 2.8 Hz, 1H), 2.60 (br s, 1H); **^{13}C-NMR (100 MHz, CDCl$_3$):** δ 203.7, 160.5, 152.8, 142.9, 137.3, 129.1, 129.0, 128.5, 127.5, 123.0, 114.1, 76.7, 63.8, 55.4; **HRMS (ESI+):** Calcd. for $C_{18}H_{16}O_3$ ([M+Na]$^+$): 303.0992, Found: 303.0990; **Optical rotation:** $[\alpha]_D^{24}$ +28.0 (*c* 1.0, $CHCl_3$) for an enantiomerically enriched sample with 98:2 er. The enantiomeric ratio was determined by HPLC analysis using Daicel Chiralpak IB column (90:10 *n*-Hexane/*i*-PrOH, 1.0 mL/min, 245 nm, τ_{major} = 29.6 min, τ_{minor} = 35.2 min). The absolute stereochemistry of the product **4a** was assigned in analogy with **4j**.



Compound 4b: Purified by preparative TLC (20% EtOAc in hexane); Yellow thick oil (24.0 mg, 0.082 mmol, 82% yield); **FT-IR (Thin film):** 3425 (br), 1709 (s), 1606 (m), 1510 (s), 1258 (s), 1258 (s), 1180 (m), 1032 (m), 833 (m); **^{1}H-NMR (400 MHz, CDCl$_3$):** δ 7.76 (d, *J* = 8.9 Hz, 2H), 7.58 (d, *J* = 2.5 Hz, 1H), 7.16 (d, *J* = 7.8 Hz, 2H), 7.05 (d, *J* = 8.1 Hz, 2H), 6.93 (d, *J* = 8.8 Hz, 2H), 4.93 (t, *J* = 2.7 Hz, 1H), 3.83 (s, 3H), 3.56 (d, *J* = 2.9 Hz, 1H), 2.54 (br s, 1H), 2.34 (s, 3H); **^{13}C-NMR (100 MHz, CDCl$_3$):** δ 203.8, 160.5, 152.7, 142.8, 137.2, 134.2, 129.7, 129.1, 128.4, 123.1, 114.1, 76.7, 63.5, 55.4, 21.2; **HRMS (ESI+):** Calcd. for $C_{19}H_{18}O_3$ ([M+Na]$^+$): 317.1148, Found: 317.1145; **Optical rotation:** $[\alpha]_D^{24}$ +24.0 (*c* 1.0, $CHCl_3$) for an enantiomerically enriched sample with 97.5:2.5 er. The enantiomeric ratio was determined by HPLC analysis using Daicel Chiralpak IB column (90:10 *n*-Hexane/*i*-PrOH, 1.0 mL/min, 230 nm, τ_{major} = 33.7 min, τ_{minor} = 39.7 min). The absolute stereochemistry of the product **4b** was assigned in analogy with **4j**.

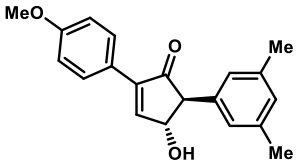


Compound 4c: Purified by preparative TLC (20% EtOAc in hexane); Yellow thick oil (28.0 mg, 0.095 mmol, 95% yield); **FT-IR (Thin film):** 3435 (br), 2838 (w), 1708 (s), 1605 (m), 1510 (s), 1258 (s), 1180 (s), 1110 (m), 1032 (m), 833 (m), 753 (m); **^{1}H-NMR (300 MHz, CDCl$_3$):** δ 7.78 (d, *J* = 8.9 Hz, 2H), 7.61 (d, *J* = 2.5 Hz, 1H), 7.23-7.13 (m, 3H), 6.94 (d, *J* = 8.8 Hz, 2H), 4.98 (t, *J* = 2.6 Hz, 1H), 3.88 (d, *J* = 2.8 Hz, 1H), 3.84 (s, 3H), 2.35 (s, 3H), 2.22 (br s, 1H); **^{13}C-NMR (75 MHz, CDCl$_3$):** δ 204.0, 160.6, 152.5, 143.1, 137.2, 136.1, 131.0, 129.2, 128.4, 127.6, 126.6, 123.1, 114.2, 76.7, 61.4, 55.5, 20.3; **HRMS (ESI+):** Calcd. for $C_{19}H_{18}O_3$

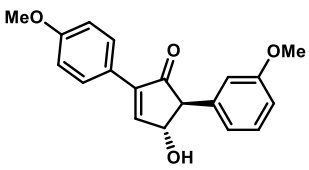


([M+H]+): 295.1329, Found: 295.1333; **Optical rotation:** $[\alpha]_D^{24}$ +22.0 (*c* 1.0, $CHCl_3$) for an enantiomerically enriched sample with 97:3 er. The enantiomeric ratio was determined by HPLC analysis using Daicel Chiralpak IC column (90:10 *n*-Hexane/*i*-PrOH, 1.0 mL/min, 232 nm, τ_{minor} = 24.6 min, τ_{major} = 32.9 min). The absolute stereochemistry of the product **4c** was assigned in analogy with **4j**.

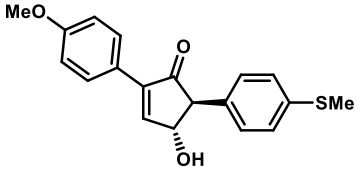
Compound 4d: Purified by preparative TLC (20% EtOAc in hexane); Yellow thick oil (27.0 mg, 0.088 mmol, 88% yield); **FT-IR (Thin film):** 3415 (br), 3012 (w), 2917 (m), 2840 (m), 1766 (m), 1710 (s), 1605 (s), 1510 (s), 1442 (m), 1306 (m), 1257 (s), 1180 (s), 1112 (s), 1032 (s), 837 (s), 754 (s), 693 (m); **^{1}H-NMR (400 MHz, $CDCl_3$):** δ 7.78 (d, *J* = 8.8 Hz, 2H), 7.61 (d, *J* = 2.5 Hz, 1H), 6.95-6.93 (m, 3H), 6.78 (s, 2H), 4.97 (t, *J* = 2.7 Hz, 1H), 3.84 (s, 3H), 3.54 (d, *J* = 2.8 Hz, 1H), 2.30 (s, 6H); **^{13}C-NMR (75 MHz, $CDCl_3$):** δ 203.8, 160.6, 152.6, 143.0, 138.6, 137.2, 129.3, 129.2, 126.3, 123.1, 114.1, 76.9, 63.9, 55.5, 21.4; **HRMS (ESI+):** Calcd. for $C_{20}H_{20}O_3$ ([M+H]+): 309.1485, Found: 309.1490; **Optical rotation:** $[\alpha]_D^{24}$ +16.0 (*c* 1.0, $CHCl_3$) for an enantiomerically enriched sample with 97:3 er. The enantiomeric ratio was determined by HPLC analysis using Daicel Chiralpak IB column (90:10 *n*-Hexane/*i*-PrOH, 1.0 mL/min, 240 nm, τ_{major} = 22.0 min, τ_{minor} = 39.6 min). The absolute stereochemistry of the product **4d** was assigned in analogy with **4j**.



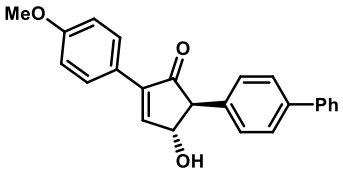
Compound 4e: Purified by preparative TLC (20% EtOAc in hexane); Brown thick oil (27.0 mg, 0.087 mmol, 87% yield); **FT-IR (Thin film):** 3437 (br), 2837 (w), 1709 (s), 1604 (s), 1510 (s), 1258 (s), 1035 (s), 924 (w); **^{1}H-NMR (400 MHz, $CDCl_3$):** δ 7.76 (d, *J* = 8.8 Hz, 2H), 7.60 (d, *J* = 2.5 Hz, 1H), 7.29-7.25 (m, 1H), 6.93 (d, *J* = 8.8 Hz, 2H), 6.85-6.82 (m, 1H), 6.75 (d, *J* = 7.6 Hz, 1H), 6.72-6.71 (m, 1H), 4.97 (t, *J* = 2.7 Hz, 1H), 3.83 (s, 3H), 3.79 (s, 3H), 3.59 (d, *J* = 2.8 Hz, 1H); **^{13}C-NMR (100 MHz, $CDCl_3$):** δ 203.4, 160.5, 160.1, 152.8, 142.9, 138.8, 130.1, 129.1, 123.0, 120.8, 114.4, 114.1, 112.9, 76.6, 63.8, 55.4, 55.4; **HRMS (ESI+):** Calcd. For $C_{19}H_{18}O_4$ ($[M+Na]^+$): 333.1097, Found: 333.1087; **Optical rotation:** $[\alpha]_D^{24}$ +24.0 (*c* 1.0, $CHCl_3$) for an enantiomerically enriched sample with 97:3 er. The enantiomeric ratio was determined by HPLC analysis using Daicel Chiralpak IC column (80:20 *n*-Hexane/*i*-PrOH, 1.0 mL/min, 230 nm, τ_{minor} = 25.7 min, τ_{major} = 31.8 min). The absolute stereochemistry of the product **4e** was assigned in analogy with **4j**.



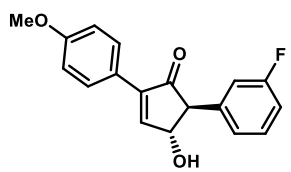
Compound 4f: Purified by preparative TLC (20% EtOAc in hexane); Yellow thick oil (21.0 mg, 0.064 mmol, 64% yield); **FT-IR (Thin film):** 3435 (br), 2918 (w), 1707 (s), 1605 (m), 1510 (s), 1257 (s), 1180 (m), 1030 (m), 831 (m), 804 (m); **^{1}H-NMR (400 MHz, $CDCl_3$):** δ 7.77 (d, *J* = 8.8 Hz, 2H), 7.61 (d, *J* = 2.5 Hz, 1H), 7.26 (d, *J* = 8.2 Hz, 2H), 7.11 (d, *J* = 8.3 Hz, 2H), 6.93 (d, *J* = 8.7 Hz, 2H), 4.97 (t, *J* = 2.8 Hz, 1H), 3.84 (s, 3H), 3.60 (d, *J* = 2.9 Hz, 1H), 2.48 (s, 3H), 2.31 (br s, 1H); **^{13}C-NMR (75 MHz, $CDCl_3$):** δ 203.3, 160.6, 152.5, 143.0, 137.8, 134.1, 129.1, 129.0, 127.4, 123.0, 114.2, 76.7, 63.4, 55.5, 16.1; **HRMS (ESI+):** Calcd. for $C_{19}H_{18}O_3S$ ([M+H]+): 327.1049, Found: 327.1054; **Optical rotation:** $[\alpha]_D^{24}$ +30.0 (*c* 1.0, $CHCl_3$) for an enantiomerically enriched sample with 98.5:1.5 er. The enantiomeric ratio was determined by HPLC analysis using Daicel Chiralpak IA column (70:30 *n*-Hexane/*i*-PrOH, 1.0 mL/min, 254 nm, τ_{major} = 13.8 min, τ_{minor} = 26.4 min). The absolute stereochemistry of the product **4f** was assigned in analogy with **4j**.



Compound 4g: Purified by preparative TLC (20% EtOAc in hexane); Yellow thick oil (30.0 mg, 0.084 mmol, 84% yield); **FT-IR (Thin film):** 3452 (br), 1710 (s), 1606 (m), 1510 (s), 1490 (m), 1257 (s), 1180 (s), 1023 (m), 830 (s), 763 (s); **^{1}H-NMR (400 MHz, $CDCl_3$):** δ 7.79 (d, *J* = 8.9 Hz, 2H), 7.64 (d, *J* = 2.5 Hz, 1H), 7.60-7.57 (m, 4H), 7.46-7.42 (m, 2H), 7.37-7.33 (m, 1H), 7.28-7.26 (m, 2H), 6.95 (d, *J* = 8.9 Hz, 2H), 5.05 (t, *J* = 2.7 Hz, 1H), 3.84 (s, 3H), 3.70 (d, *J* = 2.9 Hz, 1H); **^{13}C-NMR (100 MHz, $CDCl_3$):** δ 203.4, 160.6, 152.5, 143.0, 140.9, 140.6, 136.3, 129.2, 129.0, 128.9, 127.8, 127.5, 127.3, 123.0, 114.2, 76.8, 63.6, 55.5; **HRMS (ESI+):** Calcd. for $C_{24}H_{20}O_3$ ([M+Na]+): 379.1305, Found: 379.1307; **Optical rotation:** $[\alpha]_D^{23}$ +32.0 (*c* 1.0, $CHCl_3$) for an enantiomerically enriched sample with 97:3 er. The enantiomeric ratio was determined by HPLC analysis using Daicel Chiralpak IB column (80:20 *n*-Hexane/*i*-PrOH, 1.0 mL/min, 248 nm, τ_{major} = 22.3 min, τ_{minor} = 31.1 min). The absolute stereochemistry of the product **4g** was assigned in analogy with **4j**.

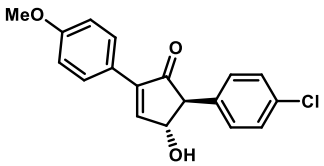


Compound 4h: Purified by preparative TLC (20% EtOAc in hexane); Yellow thick oil (25.0 mg, 0.084 mmol, 84% yield); **FT-IR (Thin film):** 3438 (br), 1710 (s), 1606 (s), 1511 (s), 1257 (s), 1181 (m), 1032 (m), 927 (w); **^{1}H-NMR (300 MHz, $CDCl_3$):** δ 7.74 (d, *J* = 8.8 Hz, 1H), 7.58 (d, *J* = 2.5 Hz, 1H), 7.35-7.27 (m, 1H), 7.02-6.96 (m, 1H), 6.93 (d, *J* = 8.9 Hz, 2H), 6.90-6.86 (m, 1H), 4.93 (t, *J* = 2.7 Hz, 1H), 3.83 (s, 3H), 3.61 (d, *J* = 2.9 Hz, 1H), 2.50 (br s, 1H); **^{13}C-NMR (75 MHz, $CDCl_3$):** δ 202.9, 163.1 (d, *J* = 246.6 Hz), 160.6, 152.7, 142.9, 139.5 (d, *J* = 7.5 Hz), 130.5 (d, *J* = 8.3 Hz), 129.1, 124.3 (d, *J* = 3.0 Hz), 122.8, 115.5 (d, *J* = 21.7 Hz), 114.5 (d, *J* = 21.0 Hz), 114.2, 76.4, 63.3 (d, *J* = 1.8 Hz), 55.4; **HRMS (ESI+):** Calcd. for $C_{18}H_{15}FO_3$ ($[M+Na]^+$): 321.0897, Found: 321.0893; **Optical rotation:** $[\alpha]_D^{24}$ +42.0 (*c* 1.0, $CHCl_3$) for an enantiomerically enriched sample with 99:1 er. The enantiomeric ratio was determined by HPLC analysis using Daicel

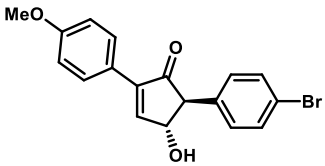


Chiralpak IB column (90:10 *n*-Hexane/*i*-PrOH, 1.0 mL/min, 245 nm, τ_{major} = 27.7 min, τ_{minor} = 37.1 min). The absolute stereochemistry of the product **4h** was assigned in analogy with **4j**.

Compound 4i: Purified by preparative TLC (20% EtOAc in hexane); Yellow solid (27.0 mg, 0.086 mmol, 86% yield); **m.p.** 103-105 °C; **FT-IR (Thin film):** 3437 (br), 1709 (s), 1605 (s), 1510 (s), 1258 (s), 1180 (m), 1015 (m), 831 (m); **^{1}H-NMR (300 MHz, $CDCl_3$):** δ 7.73 (d, *J* = 8.8 Hz, 2H), 7.57 (d, *J* = 2.5 Hz, 1H), 7.31 (d, *J* = 8.4 Hz, 2H), 7.09 (d, *J* = 8.4 Hz, 2H), 6.92 (d, *J* = 8.9 Hz, 2H), 4.89 (t, *J* = 2.7 Hz, 1H), 3.83 (s, 3H), 3.58 (d, *J* = 2.9 Hz, 1H), 2.64 (br s, 1H); **^{13}C-NMR (75 MHz, $CDCl_3$):** δ 203.2, 160.6, 152.7, 142.8, 135.7, 133.5, 129.9, 129.2, 129.1, 122.8, 114.2, 76.5, 63.1, 55.5; **HRMS (ESI+):** Calcd. for $C_{18}H_{15}ClO_3$ ($[M+Na]^+$): 337.0602, Found: 337.0595; **Optical rotation:** $[\alpha]_D^{24}$ +36.0 (*c* 1.0, $CHCl_3$) for an enantiomerically enriched sample with 97:3 er. The enantiomeric ratio was determined by HPLC analysis using Daicel Chiralpak IB column (90:10 *n*-Hexane/*i*-PrOH, 1.0 mL/min, 245 nm, τ_{major} = 33.5 min, τ_{minor} = 44.2 min). The absolute stereochemistry of the product **4i** was assigned in analogy with **4j**.



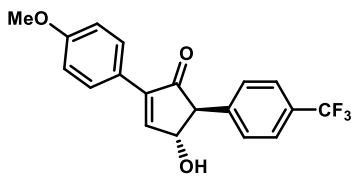
Compound 4j: Purified by preparative TLC (20% EtOAc in hexane); Pale-yellow solid (33.0 mg, 0.092 mmol, 92% yield); **m.p.** 130-132 °C; **FT-IR (Thin film):** 3435 (br), 1709 (s), 1605 (m), 1510 (s), 1257 (s), 1180 (m), 1111 (m), 831 (m); **^{1}H-NMR (300 MHz, $CDCl_3$):** δ 7.74 (d, *J* = 8.9 Hz, 2H), 7.59 (d, *J* = 2.5 Hz, 1H), 7.48 (d, *J* = 8.4 Hz, 2H), 7.05 (d, *J* = 8.4 Hz, 2H), 6.93 (d, *J* = 8.9 Hz, 2H), 4.92 (t, *J* = 2.7 Hz, 1H), 3.83 (s, 3H), 3.59 (d, *J* = 2.9 Hz, 1H), 2.46 (br s, 1H); **^{13}C-NMR (75 MHz, $CDCl_3$):** δ 202.93, 160.7, 152.6, 142.9, 136.2, 132.1, 130.2, 129.1, 122.8, 121.6, 114.2, 76.5, 63.2, 55.5; **HRMS (ESI+):** Calcd. for $C_{18}H_{15}BrO_3$ ($[M+H]^+$): 359.0277, Found: 359.0282; **Optical rotation:** $[\alpha]_D^{24}$ +34.0 (*c* 1.0, $CHCl_3$) for an enantiomerically enriched sample with 98:2 er. The enantiomeric ratio was determined by HPLC analysis using Daicel Chiralpak IB column (90:10 *n*-Hexane/*i*-PrOH, 1.0 mL/min, 230 nm, τ_{major} = 34.8 min, τ_{minor} = 45.9 min). The relative and absolute stereochemistry of the product **4j** was determined by single crystal X-Ray diffraction analysis.



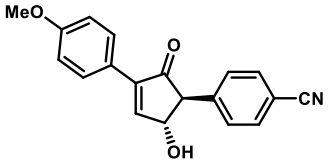
Compound 4k: Purified by preparative TLC (20% EtOAc in hexane); Yellow solid (30.0 mg, 0.084 mmol, 84% yield); **m.p.** 128-130 °C; **FT-IR (Thin film):** 3457 (br), 1708 (s), 1605 (m), 1510 (s), 1257 (s), 1180 (m), 1031 (m), 833 (m), 687 (m); **^{1}H-NMR (400 MHz, $CDCl_3$):** δ 7.77 (d, *J* = 8.8 Hz, 2H), 7.62 (d, *J* = 2.5 Hz, 1H), 7.44 (ddd, *J* = 7.9, 2.0, 1.1 Hz, 1H), 7.35 (t, *J* = 1.8 Hz, 1H), 7.24 (t, *J* = 7.9 Hz, 1H), 7.13 (dt, *J* = 7.7, 1.5 Hz, 1H), 6.94 (d, *J* = 8.9 Hz, 2H), 4.98 (t, *J* = 2.7 Hz, 1H), 3.84 (s, 3H), 3.62 (d, *J* = 2.9 Hz, 1H); **^{13}C-NMR (100 MHz, $CDCl_3$):** δ 202.6, 160.7, 152.4, 143.0, 139.5, 131.6, 130.7, 130.6, 129.2, 127.3, 123.1, 122.8, 114.2, 76.5, 63.3, 55.5; **HRMS (ESI+):** Calcd. for $C_{18}H_{15}BrO_3$ ([M+Na]+): 381.0097, Found:

381.0097; **Optical rotation:** $[\alpha]_D^{24}$ +40.0 (*c* 1.0, $CHCl_3$) for an enantiomerically enriched sample with 98:2 er. The enantiomeric ratio was determined by HPLC analysis using Daicel Chiralpak IA column (90:10 *n*-Hexane/*i*-PrOH, 1.0 mL/min, 240 nm, τ_{major} = 30.3 min, τ_{minor} = 41.1 min). The absolute stereochemistry of the product **4k** was assigned in analogy with **4j**.

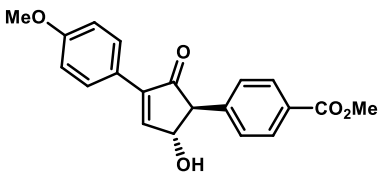
Compound 4l: Purified by preparative TLC (20% EtOAc in hexane); Yellow thick oil (31.0 mg, 0.089 mmol, 89% yield); **FT-IR (Thin film):** 3442 (br), 1694 (s), 1604 (m), 1511 (s), 1329 (s), 1261 (m), 1125 (m), 1066 (m), 832 (m), 806 (m); **^{1}H-NMR (400 MHz, $CDCl_3$):** δ 7.77-7.74 (m, 2H), 7.62-7.60 (m, 3H), 7.30 (d, *J* = 8.5 Hz, 2H), 6.94 (d, *J* = 8.9 Hz, 2H), 4.99-4.97 (m, 1H), 3.84 (s, 3H), 3.71-3.70 (m, 1H); **^{13}C-NMR (100 MHz, $CDCl_3$):** δ 202.6, 160.7, 152.6, 143.0, 141.2 (d, *J* = 1.5 Hz), 129.9 (q, *J* = 32.6 Hz), 129.2, 129.0, 126.0 (q, *J* = 3.8 Hz), 124.2 (q, *J* = 272.1 Hz), 122.7, 114.2, 76.4, 63.5, 55.5; **HRMS (ESI+):** Calcd. for $C_{19}H_{15}F_3O_3$ ([M+Na]+): 371.0866, Found: 371.0866; **Optical rotation:** $[\alpha]_D^{23}$ +30.0 (*c* 1.0, $CHCl_3$) for an enantiomerically enriched sample with 97:3 er. The enantiomeric ratio was determined by HPLC analysis using Daicel Chiralpak IB column (90:10 *n*-Hexane/*i*-PrOH, 1.0 mL/min, 240 nm, τ_{major} = 27.9 min, τ_{minor} = 33.7 min). The absolute stereochemistry of the product **4l** was assigned in analogy with **4j**.



Compound 4m: Purified by preparative TLC (20% EtOAc in hexane); Yellow thick oil (25.0 mg, 0.082 mmol, 82% yield); **FT-IR (Thin film):** 3452 (br), 1710 (s), 1606 (s), 1510 (s), 1257 (s), 1180 (m), 1031 (m), 832 (m); **^{1}H-NMR (400 MHz, $CDCl_3$):** δ 7.73 (d, *J* = 8.9 Hz, 2H), 7.62 (d, *J* = 2.5 Hz, 1H), 7.60 (d, *J* = 8.3 Hz, 2H), 7.30 (d, *J* = 8.3 Hz, 2H), 6.93 (d, *J* = 8.9 Hz, 2H), 4.98 (t, *J* = 2.8 Hz, 1H), 3.83 (s, 3H), 3.71 (d, *J* = 3.0 Hz, 1H); **^{13}C-NMR (100 MHz, $CDCl_3$):** δ 202.2, 160.7, 152.8, 142.8, 132.7, 129.4, 129.1, 122.6, 118.8, 114.2, 111.3, 76.0, 63.6, 55.5; **HRMS (ESI+):** Calcd. for $C_{19}H_{15}NO_3$ ($[M+H]^+$): 306.1125, Found: 306.1114; **Optical rotation:** $[\alpha]_D^{24}$ +46.0 (*c* 1.0, $CHCl_3$) for an enantiomerically enriched sample with 96.5:3.5 er. The enantiomeric ratio was determined by HPLC analysis using Daicel Chiralpak IB column (80:20 *n*-Hexane/*i*-PrOH, 1.0 mL/min, 245 nm, τ_{minor} = 28.2 min, τ_{major} = 31.5 min). The absolute stereochemistry of the product **4m** was assigned in analogy with **4j**.

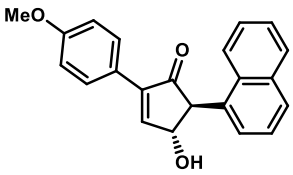


Compound 4n: Purified by preparative TLC (20% EtOAc in hexane); Yellow solid (33.0 mg, 0.098 mmol, 98% yield); **m.p.** 179-181 °C; **FT-IR (Thin film):** 3477 (br), 2917 (w), 1699 (s), 1605 (m), 1511 (s), 1385 (m), 1287 (m), 1181 (m), 1107 (m), 1020 (m), 761 (m); **^{1}H-NMR (400 MHz, CD_2Cl_2):** δ 8.02 (d, *J* = 8.3 Hz, 2H), 7.76 (d, *J* = 8.9 Hz, 2H), 7.66 (d, *J* = 2.5 Hz, 1H), 7.29 (d, *J* = 8.3 Hz, 2H), 6.95 (d, *J* = 8.9 Hz, 2H), 5.03-5.02 (m, 1H), 3.89 (s, 3H), 3.83 (s, 3H), 3.71 (d, *J* = 3.0 Hz, 1H), 2.44 (br s, 1H); **^{13}C-NMR (100 MHz, CD_2Cl_2):** δ

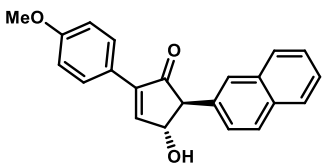


202.9, 167.0, 161.0, 153.4, 143.0, 130.3, 129.8, 129.4, 129.0, 123.3, 114.3, 76.6, 64.0, 55.7 52.4; **HRMS (ESI+):** Calcd. for $C_{20}H_{18}O_5$ ([M+H]+): 339.1227, Found: 339.1217; **Optical rotation:** $[\alpha]_D^{24}$ +30.0 (*c* 0.33, $CHCl_3$) for an enantiomerically enriched sample with 97:3 er. The enantiomeric ratio was determined by HPLC analysis using Daicel Chiralpak IB column (85:15 *n*-Hexane/*i*-PrOH, 1.0 mL/min, 244 nm, τ_{major} = 32.9 min, τ_{minor} = 39.0 min). The absolute stereochemistry of the product **4n** was assigned in analogy with **4j**.

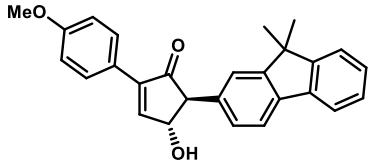
Compound 4o: Purified by preparative TLC (20% EtOAc in hexane); Yellow thick oil (32.0 mg, 0.097 mmol, 97% yield); **FT-IR (Thin film):** 3437 (br), 3049 (w), 2923 (w), 1708 (s), 1605 (m), 1510 (s), 1258 (s), 1180 (m), 1119 (m), 1032 (m), 837 (m), 797 (m), 779 (m); **^{1}H-NMR (400 MHz, $CDCl_3$):** δ 7.90-7.88 (m, 1H), 7.86 (d, *J* = 8.9 Hz, 2H), 7.82 (d, *J* = 8.4 Hz, 1H), 7.81-7.75 (m, 1H), 7.67 (d, *J* = 2.5 Hz, 1H), 7.52-7.47 (m, 2H), 7.46-7.42 (m, 1H), 7.28 (d, *J* = 1.2 Hz, 1H), 6.97 (d, *J* = 8.9 Hz, 2H), 5.14 (t, *J* = 2.7 Hz, 1H), 4.27 (d, *J* = 2.8 Hz, 1H), 3.86 (s, 3H); **^{13}C-NMR (75 MHz, $CDCl_3$):** δ 204.0, 160.7, 152.1, 143.2, 134.4, 134.0, 132.1, 129.3, 129.2, 128.4, 127.3, 126.7, 126.0, 125.7, 123.7, 123.1, 114.2, 76.6, 55.5; **HRMS (ESI+):** Calcd. for $C_{22}H_{18}O_3$ ([M+Na]+): 353.1148, Found: 353.1137; **Optical rotation:** $[\alpha]_D^{23}$ +62.0 (*c* 1.0, $CHCl_3$) for an enantiomerically enriched sample with 96:4 er. The enantiomeric ratio was determined by HPLC analysis using Daicel Chiralpak IB column (80:20 *n*-Hexane/*i*-PrOH, 0.5 mL/min, 240 nm, τ_{minor} = 54.4 min, τ_{major} = 59.8 min). The absolute stereochemistry of the product **4o** was assigned in analogy with **4j**.



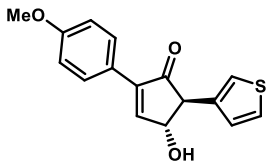
Compound 4p: Purified by preparative TLC (20% EtOAc in hexane); Yellow thick oil (22.0 mg, 0.067 mmol, 67% yield); **FT-IR (Thin film):** 3490 (br), 1705 (s), 1605 (m), 1509 (s), 1257 (m), 1181 (m), 1108 (m), 815 (m); **^{1}H-NMR (400 MHz, $CDCl_3$):** δ 7.82-7.76 (m, 5H), 7.66 (s, 1H), 7.59 (d, *J* = 2.5 Hz, 1H), 7.50-7.46 (m, 2H), 7.19 (d, *J* = 10.3 Hz, 1H), 6.94 (d, *J* = 8.9 Hz, 2H), 5.00 (t, *J* = 2.7 Hz, 1H), 3.83 (s, 3H), 3.74 (d, *J* = 2.9 Hz, 1H); **^{13}C-NMR (100 MHz, $CDCl_3$):** δ 203.7, 160.6, 152.8, 142.9, 134.7, 133.6, 132.8, 129.2, 128.9, 127.9, 127.8, 127.8, 126.5, 126.1, 126.0, 123.0, 114.2, 76.6, 64.0, 55.5; **HRMS (ESI+):** Calcd. For $C_{22}H_{18}O_3$ ($[M+H]^+$): 331.1329, Found: 331.1320; **Optical rotation:** $[\alpha]_D^{24}$ +16.0 (*c* 1.0, $CHCl_3$) for an enantiomerically enriched sample with 96:4 er. The enantiomeric ratio was determined by HPLC analysis using Daicel Chiralpak IB column (80:20 *n*-Hexane/*i*-PrOH, 1.0 mL/min, 230 nm, τ_{major} = 20.9 min, τ_{minor} = 26.2 min). The absolute stereochemistry of the product **4p** was assigned in analogy with **4j**.



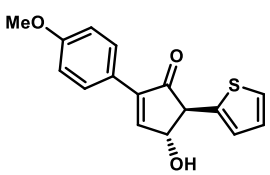
Compound 4q: Purified by preparative TLC (20% EtOAc in hexane); Yellow thick oil (31.0 mg, 0.078 mmol, 78% yield); **FT-IR (Thin film):** 3444 (br), 3009 (w), 2960 (m), 1710 (s), 1606 (m), 1510 (s), 1449 (m), 1305 (m), 1257 (s), 1180 (s), 1032 (m), 832 (m), 759 (s), 740 (s); **^{1}H-NMR (400 MHz, $CDCl_3$):** δ 7.70 (d, *J* = 8.8 Hz, 2H), 7.62-7.58 (m, 2H), 7.54 (d, *J* = 2.5 Hz, 1H), 7.34-7.32 (m, 1H), 7.26-7.20 (m, 2H), 7.15 (d, *J* = 1.6 Hz, 1H), 7.03 (dd, *J* = 7.8, 1.6 Hz, 1H), 6.85 (d, *J* = 8.8 Hz, 2H), 4.94 (t, *J* = 2.7 Hz, 1H), 3.74 (s, 3H), 3.62 (d, *J* = 2.8 Hz, 1H), 2.08 (br s, 1H), 1.38 (d, *J* = 2.5 Hz, 6H); **^{13}C-NMR (75 MHz, $CDCl_3$):** δ 203.6, 160.6, 154.4, 153.8, 152.5, 143.0, 138.9, 138.7, 136.3, 129.2, 127.4, 127.3, 127.1, 123.1, 123.0, 122.7, 120.5, 120.1, 114.2, 77.0, 64.3, 55.5, 47.1, 27.3; **HRMS (ESI+):** Calcd. for $C_{27}H_{24}O_3$ ([M+H]+): 397.1798, Found: 397.1796; **Optical rotation:** $[\alpha]_D^{23}$ +30.0 (*c* 1.0, $CHCl_3$) for an enantiomerically enriched sample with 97:3 er. The enantiomeric ratio was determined by HPLC analysis using Daicel Chiralpak IB column (80:20 *n*-Hexane/*i*-PrOH, 1.0 mL/min, 272 nm, τ_{major} = 13.5 min, τ_{minor} = 19.5 min). The absolute stereochemistry of the product **4q** was assigned in analogy with **4j**.



Compound 4r: Purified by preparative TLC (20% EtOAc in hexane); Yellow thick oil (16.0 mg, 0.056 mmol, 56% yield); **FT-IR (Thin film):** 3439 (br), 1709 (s), 1606 (m), 1510 (s), 1258 (s), 1180 (s), 1112 (m), 1032 (m); **^{1}H-NMR (400 MHz, $CDCl_3$):** δ 7.75 (d, *J* = 8.9 Hz, 2H), 7.57 (d, *J* = 2.5 Hz, 1H), 7.35 (dd, *J* = 5.0, 2.9 Hz, 1H), 7.23-7.22 (m, 1H), 7.02 (dd, *J* = 5.0, 1.3 Hz, 1H), 6.93 (d, *J* = 8.9 Hz, 2H), 5.00 (t, *J* = 2.8 Hz, 1H), 3.83 (s, 3H), 3.77 (d, *J* = 3.0 Hz, 1H), 2.26 (br s, 1H); **^{13}C-NMR (100 MHz, $CDCl_3$):** δ 202.6, 160.6, 152.1, 142.7, 136.6, 129.1, 127.1, 126.5, 123.0, 122.6, 114.2, 75.9, 58.9, 55.5; **HRMS (ESI+):** Calcd. For $C_{16}H_{14}O_3S$ ($[M+Na]^+$): 309.0556, Found: 309.0554; **Optical rotation:** $[\alpha]_D^{24}$ +28.0 (*c* 1.0, $CHCl_3$) for an enantiomerically enriched sample with 98:2 er. The enantiomeric ratio was determined by HPLC analysis using Daicel Chiralpak IB column (90:10 *n*-Hexane/*i*-PrOH, 1.0 mL/min, 245 nm, τ_{major} = 34.6 min, τ_{minor} = 39.7 min). The absolute stereochemistry of the product **4r** was assigned in analogy with **4j**.

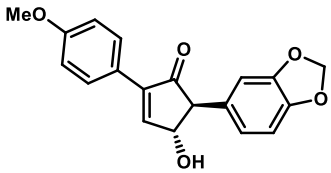


Compound 4s: Purified by preparative TLC (20% EtOAc in hexane); Red thick oil (16.0 mg, 0.056 mmol, 56% yield); **FT-IR (Thin film):** 3449 (br), 2923 (m), 1711 (s), 1604 (m), 1510 (s), 1257 (s), 1180 (m), 1031 (m), 832 (m), 702 (m); **^{1}H-NMR (400 MHz, $CDCl_3$):** δ 7.76 (d, *J* = 8.9 Hz, 2H), 7.58 (d, *J* = 2.5 Hz, 1H), 7.27 (dd, *J* = 4.8, 1.6 Hz, 1H), 7.05-7.02 (m, 2H), 6.94 (d, *J* = 8.9 Hz, 2H), 5.09 (t, *J* = 2.8 Hz, 1H), 3.94 (d, *J* = 3.1 Hz, 1H), 3.84 (s, 3H), 1.90 (br s, 1H); **^{13}C-NMR (75 MHz, $CDCl_3$):** δ 201.2, 160.6, 151.7, 142.3, 138.1, 129.1, 127.3, 126.1, 125.0, 122.9, 114.2, 76.74, 58.7, 55.5; **HRMS (ESI+):** Calcd. for $C_{16}H_{14}O_3S$ ([M+Na]+): 309.0556, Found: 309.0560; **Optical rotation:** $[\alpha]_D^{24}$ +2.0 (*c* 1.0, $CHCl_3$) for an enantiomerically

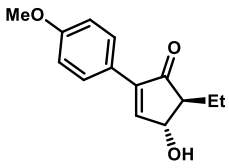


enriched sample with 97:3 er. The enantiomeric ratio was determined by HPLC analysis using Daicel Chiralpak IA column (80:20 *n*-Hexane/*i*-PrOH, 1.0 mL/min, 245 nm, τ_{major} = 19.1 min, τ_{minor} = 26.1 min). The absolute stereochemistry of the product **4s** was assigned in analogy with **4j**.

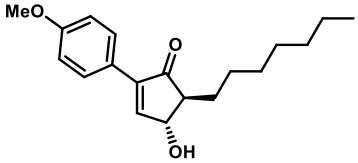
Compound 4t: Purified by preparative TLC (20% EtOAc in hexane); Yellow thick oil (23.0 mg, 0.071 mmol, 71% yield); **FT-IR (Thin film):** 3437 (br), 2900 (w), 1709 (s), 1605 (m), 1509 (s), 1443 (m), 1248 (s), 1180 (m), 1037 (s), 803 (m); **^{1}H-NMR (300 MHz, $CDCl_3$):** δ 7.76 (d, *J* = 8.9 Hz, 2H), 7.59 (d, *J* = 2.5 Hz, 1H), 6.93 (d, *J* = 8.9 Hz, 2H), 6.80 (d, *J* = 7.9 Hz, 1H), 6.68-6.62 (m, 2H), 5.94 (q, *J* = 1.2 Hz, 2H), 4.93 (t, *J* = 2.7 Hz, 1H), 3.83 (s, 3H), 3.55 (d, *J* = 2.9 Hz, 1H), 2.17 (br s, 1H); **^{13}C-NMR (100 MHz, $CDCl_3$):** δ 203.4, 160.6, 152.4, 148.3, 147.1, 142.9, 130.9, 129.1, 123.0, 122.0, 114.2, 108.8, 108.7, 101.3, 76.8, 63.6, 55.5; **HRMS (ESI+):** Calcd. for $C_{19}H_{16}O_5$ ([M+Na]+): 347.0890, Found: 347.0885; **Optical rotation:** $[\alpha]_D^{24}$ +24.0 (*c* 1.0, $CHCl_3$) for an enantiomerically enriched sample with 97.5:2.5 er. The enantiomeric ratio was determined by HPLC analysis using Daicel Chiralpak IB column (80:20 *n*-Hexane/*i*-PrOH, 1.0 mL/min, 284 nm, τ_{major} = 22.4 min, τ_{minor} = 26.5 min). The absolute stereochemistry of the product **4t** was assigned in analogy with **4j**.



Compound 4u: Purified by preparative TLC (20% EtOAc in hexane); White thick oil (15.0 mg, 0.065 mmol, 65% yield); **FT-IR (Thin film):** 3436 (br), 1686 (s), 1604 (s), 1512 (s), 1465 (m), 1258 (s), 1095 (s), 836 (s); **^{1}H-NMR (400 MHz, $CDCl_3$):** δ 7.70 (d, *J* = 8.8 Hz, 2H), 7.48 (d, *J* = 2.6 Hz, 1H), 6.91 (d, *J* = 8.8 Hz, 2H), 4.69 (t, *J* = 2.5 Hz, 1H), 3.82 (s, 3H), 2.39-2.35 (m, 1H), 2.06 (br s, 1H), 2.02-1.92 (m, 1H), 1.67-1.55 (m, 1H), 1.07 (t, *J* = 7.4 Hz, 3H); **^{13}C-NMR (75 MHz, $CDCl_3$):** δ 206.1, 160.4, 152.9, 142.9, 129.0, 123.2, 114.1, 74.1, 58.4, 55.4, 22.0, 11.7; **HRMS (ESI+):** Calcd. For $C_{14}H_{16}O_3$ ([M+Na]$^+$): 255.0992, Found: 255.0994; **Optical rotation:** $[\alpha]_D^{24}$ +64.0 (*c* 1.0, $CHCl_3$) for an enantiomerically enriched sample with 97:3 er. The enantiomeric ratio was determined by HPLC analysis using Daicel Chiralpak IB column (90:10 *n*-Hexane/*i*-PrOH, 1.0 mL/min, 245 nm, τ_{major} = 14.5 min, τ_{minor} = 18.0 min). The absolute stereochemistry of the product **4u** was assigned in analogy with **4j**.

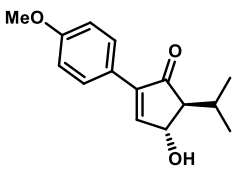


Compound 4v: Purified by preparative TLC (20% EtOAc in hexane); Off-white thick oil (20.0 mg, 0.066 mmol, 66% yield); **FT-IR (Thin film):** 3464 (br), 2926 (s), 1685 (s), 1603 (m), 1512 (s), 1256 (s), 1034 (s), 837 (s); **^{1}H-NMR (400 MHz, $CDCl_3$):** δ 7.70 (d, *J* = 8.8 Hz, 2H), 7.47 (d, *J* = 2.5 Hz, 1H), 6.90 (d, *J* = 8.9 Hz, 2H), 4.68 (t, *J* = 2.5 Hz, 1H), 3.82 (s, 3H), 2.42-2.38 (m, 1H), 2.10 (br s, 1H), 1.95-1.90 (m, 1H), 1.56-1.46 (m, 2H), 1.36-1.25 (m, 9H), 0.90-0.86 (m, 3H); **^{13}C-NMR (100 MHz, $CDCl_3$):** δ 206.2, 160.4, 152.9, 142.8, 129.0, 123.3, 114.1, 74.6, 57.2, 55.4, 31.9, 29.8, 29.3, 29.2, 27.5, 22.8, 14.2;

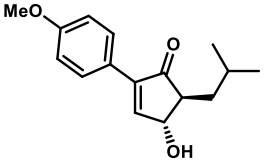


HRMS (ESI+): Calcd. For $C_{19}H_{26}O_3$ ([M+H]$^+$): 303.1955, Found: 303.1948; **Optical rotation:** $[\alpha]_D^{24}$ +62.0 (*c* 1.0, $CHCl_3$) for an enantiomerically enriched sample with 99:1 er. The enantiomeric ratio was determined by HPLC analysis using Daicel Chiralpak IB column (90:10 *n*-Hexane/*i*-PrOH, 1.0 mL/min, 245 nm, τ_{major} = 11.7 min, τ_{minor} = 14.8 min). The absolute stereochemistry of the product **4v** was assigned in analogy with **4j**.

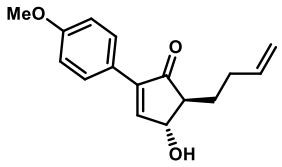
Compound 4w: Purified by preparative TLC (20% EtOAc in hexane); White thick oil (17.0 mg, 0.069 mmol, 69% yield); **FT-IR (Thin film):** 3481 (br), 2959 (m), 1685 (s), 1511 (s), 1258 (s), 1186 (m), 1031 (m), 833 (m); **^{1}H-NMR (400 MHz, $CDCl_3$):** 7.70 (d, *J* = 8.8 Hz, 2H), 7.49 (d, *J* = 2.6 Hz, 1H), 6.91 (d, *J* = 8.8 Hz, 2H), 4.81 (t, *J* = 2.4 Hz, 1H), 3.82 (s, 3H), 2.42-2.39 (m, 1H), 2.37-2.34 (m, 1H), 1.99 (br s, 1H), 1.15 (d, *J* = 6.7 Hz, 3H), 0.89 (d, *J* = 6.6 Hz, 3H); **^{13}C-NMR (100 MHz, $CDCl_3$):** δ 205.9, 160.4, 153.3, 143.4, 129.0, 123.3, 114.1, 70.7, 62.6, 55.4, 27.7, 20.9, 18.5; **HRMS (ESI+):** Calcd. For $C_{15}H_{18}O_3$ ([M+Na]$^+$): 269.1148, Found: 269.1149; **Optical rotation:** $[\alpha]_D^{24}$ +60.0 (*c* 1.0, $CHCl_3$) for an enantiomerically enriched sample with 99:1 er. The enantiomeric ratio was determined by HPLC analysis using Daicel Chiralpak IB column (90:10 *n*-Hexane/*i*-PrOH, 1.0 mL/min, 240 nm, τ_{major} = 11.9 min, τ_{minor} = 16.8 min). The absolute stereochemistry of the product **4w** was assigned in analogy with **4j**.



Compound 4x: Purified by preparative TLC (20% EtOAc in hexane); White thick oil (20.0 mg, 0.077 mmol, 77% yield); **FT-IR (Thin film):** 3465 (br), 2957 (m), 1603 (m), 1510 (s), 1254 (s), 1183 (m), 1254 (s), 840 (s); **^{1}H-NMR (400 MHz, $CDCl_3$):** δ 7.68 (d, *J* = 8.8 Hz, 2H), 7.46 (d, *J* = 2.6 Hz, 1H), 6.90 (d, *J* = 8.8 Hz, 2H), 4.64 (t, *J* = 2.5 Hz, 1H), 3.81 (s, 3H), 2.50-2.45 (m, 1H), 2.11 (br s, 1H), 1.97-1.89 (m, 1H), 1.81-1.74 (m, 1H), 1.40-1.33 (m, 1H), 1.01-0.98 (m, 6H); **^{13}C-NMR (100 MHz, $CDCl_3$):** δ 206.6, 160.4, 152.8, 142.6, 129.0, 123.3, 114.1, 75.3, 55.4, 55.4, 38.8, 26.6, 23.6, 22.0; **HRMS (ESI+):** Calcd. For $C_{16}H_{20}O_3$ ([M+Na]$^+$): 283.1305, Found: 283.1305; **Optical rotation:** $[\alpha]_D^{24}$ +66.0 (*c* 1.0, $CHCl_3$) for an enantiomerically enriched sample with 97.5:2.5 er. The enantiomeric ratio was determined by HPLC analysis using Daicel Chiralpak IB column (90:10 *n*-Hexane/*i*-PrOH, 1.0 mL/min, 290 nm, τ_{major} = 13.1 min, τ_{minor} = 17.6 min). The absolute stereochemistry of the product **4x** was assigned in analogy with **4j**.

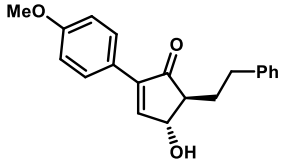


Compound 4y: Purified by preparative TLC (20% EtOAc in hexane); Off-white thick oil (20.0 mg, 0.077 mmol, 77% yield); **FT-IR (Thin film):** 3470 (br), 1685 (s), 1602 (m), 1510 (s), 1293 (s), 1254 (s), 1181 (s), 1100 (s); **^{1}H-NMR (400 MHz, $CDCl_3$):** δ 7.69 (d, *J* = 8.8 Hz, 2H), 7.47 (d, *J* = 2.6 Hz, 1H), 6.91 (d, *J* = 8.9 Hz, 2H), 5.89 (ddt, *J* = 16.9, 10.2, 6.6 Hz, 1H), 5.11 (dq, *J* = 17.1, 1.7 Hz, 1H), 5.05-5.02 (m, 1H), 4.67 (t, *J* = 2.6 Hz, 1H), 3.82 (s, 3H), 2.42 (ddd , *J* = 9.5, 4.6, 2.6 Hz, 1H), 2.34-2.28 (m, 1H), 2.13 (br s, 1H), 2.10-2.04 (m, 1H), 1.66-1.56 (m, 1H); **^{13}C-**

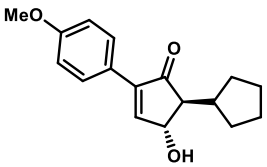


NMR (100 MHz, $CDCl_3$): δ 205.8, 160.4, 152.8, 142.8, 138.5, 129.0, 123.2, 115.7, 114.1, 74.6, 56.7, 55.4, 31.9, 28.4; **HRMS (ESI+):** Calcd. For $C_{16}H_{18}O_3$ ($[M+H]^+$): 259.1329, Found: 259.1334; **Optical rotation:** $[\alpha]_D^{24}$ +64.0 (*c* 1.0, $CHCl_3$) for an enantiomerically enriched sample with 98:2 er. The enantiomeric ratio was determined by HPLC analysis using Daicel Chiralpak IB column (90:10 *n*-Hexane/*i*-PrOH, 1.0 mL/min, 245 nm, τ_{major} = 14.0 min, τ_{minor} = 17.8 min). The absolute stereochemistry of the product **4y** was assigned in analogy with **4j**.

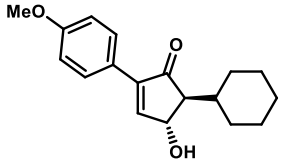
Compound 4z: Purified by preparative TLC (20% EtOAc in hexane); Off-white thick oil (21.0 mg, 0.068 mmol, 68% yield); **FT-IR (Thin film):** 3436 (br), 1716 (s), 1603 (m), 1510 (s), 1258 (s), 1181 (m), 875 (w), 754 (m); **^{1}H-NMR (400 MHz, $CDCl_3$):** δ 7.74 (d, *J* = 8.8 Hz, 2H), 7.49 (d, *J* = 2.6 Hz, 1H), 7.38-7.30 (m, 4H), 7.28-7.24 (m, 1H), 6.95 (d, *J* = 8.9 Hz, 2H), 4.69 (t, *J* = 2.5 H z, 1H), 3.86 (s, 3H), 2.98-2.86 (m, 2H), 2.49-2.45 (m, 1H), 2.40-2.31 (m, 1H), 1.99 (br s, 1H), 1.94-1.85 (m, 1H); **^{13}C-NMR (100 MHz, $CDCl_3$):** δ 205.7, 160.4, 152.8, 142.8, 141.6, 129.0, 128.7, 126.3, 123.2, 114.1, 74.9, 56.7, 55.4, 33.7, 30.8; **HRMS (ESI+):** Calcd. For $C_{20}H_{20}O_3$ ($[M+Na]^+$): 331.1305, Found: 331.1301; **Optical rotation:** $[\alpha]_D^{24}$ +30 .0 (*c* 1.0, $CHCl_3$) for an enantiomerically enriched sample with 98:2 er. The enantiomeric ratio was determined by HPLC analysis using Daicel Chiralpak IB column (90:10 *n*-Hexane/*i*-PrOH, 1.0 mL/min, 245 nm, τ_{major} = 23.1 min, τ_{minor} = 29.4 min). The absolute stereochemistry of the product **4z** was assigned in analogy with **4j**.



Compound 4aa: Purified by preparative TLC (20% EtOAc in hexane); Yellow thick oil (16.0 mg, 0.059 mmol, 59% yield); **FT-IR (Thin film):** 3481 (br), 2945 (s), 1684 (s), 1604 (s), 1511 (s), 1292 (s), 1256 (s), 838 (s); **^{1}H-NMR (400 MHz, $CDCl_3$):** δ 7.70 (d, *J* = 8.9 Hz, 2H), 7.48 (d, *J* = 2.6 Hz, 1H), 6.91 (d, *J* = 8.8 Hz, 2H), 4.74 (t, *J* = 2.5 Hz, 1H), 3.82 (s, 3H), 2.49 (dd, *J* = 6.5, 2.4 Hz, 1H), 2.37-2.26 (m, 1H), 2.03-1.97 (m, 1H), 1.92 (br s, 1H), 1.79-1.48 (m, 7H); **^{13}C-NMR (100 MHz, $CDCl_3$):** δ 206.0, 160.4, 152.8, 143.2, 129.1, 123.3, 114.1, 72.6, 60.4, 55.4, 39.7, 30.8, 29.3, 25.5, 25.3; **HRMS (ESI+):** Calcd. For $C_{17}H_{20}O_3$ ($[M+H]^+$): 273.1485, Found: 273.1484; **Optical rotation:** $[\alpha]_D^{24}$ +52.0 (*c* 1.0, $CHCl_3$) for an enantiomerically enriched sample with 99:1 er. The enantiomeric ratio was determined by HPLC analysis using Daicel Chiralpak IB column (90:10 *n*-Hexane/*i*-PrOH, 1.0 mL/min, 245 nm, τ_{major} = 13.9 min, τ_{minor} = 19.1 min). The absolute stereochemistry of the product **4aa** was assigned in analogy with **4j**.

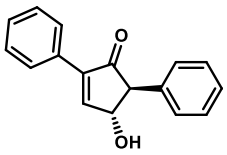


Compound 4ab: Purified by preparative TLC (20% EtOAc in hexane); Yellow thick oil (19.0 mg, 0.066 mmol, 66% yield); **FT-IR (Thin film):** 3434 (br), 2925 (s), 1704 (s), 1606 (s), 1510 (s), 1255 (s), 1034 (s), 835 (m); **^{1}H-NMR (400 MHz, $CDCl_3$):** δ 7.69 (d, *J* = 8.8 Hz, 2H), 7.48 (d, *J* = 2.6 Hz, 1H), 6.90 (d, *J* = 8.8 Hz, 2H), 4.83 (t, *J* = 2.6 Hz, 1H), 3.82 (s, 3H), 2.37 (dd, *J* = 4.4, 2.4

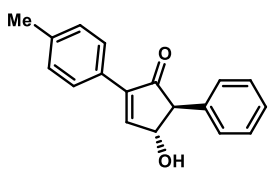


Hz, 1H), 2.06-2.00 (m, 1H), 2.03 (br s, 1H), 1.84-1.76 (m, 2H), 1.73-1.67 (m, 2H), 1.52-1.47 (m, 1H), 1.37-1.25 (m, 3H), 1.19-1.05 (m, 2H); **^{13}C-NMR (100 MHz, $CDCl_3$):** δ 206.1, 160.4, 153.3, 143.4, 129.0, 123.3, 114.1, 71.2, 62.4, 55.4, 37.9, 31.4, 28.9, 26.7, 26.4, 26.3; **HRMS (ESI+):** Calcd. For $C_{18}H_{22}O_3$ ($[M+Na]^+$): 309.1461, Found: 309.1471; **Optical rotation:** $[\alpha]_D^{24}$ +54.0 (*c* 1.0, $CHCl_3$) for an enantiomerically enriched sample with 98:2 er. The enantiomeric ratio was determined by HPLC analysis using Daicel Chiralpak IB column (90:10 *n*-Hexane/*i*-PrOH, 1.0 mL/min, 245 nm, τ_{major} = 13.2 min, τ_{minor} = 19.3 min). The absolute stereochemistry of the product **4ab** was assigned in analogy with **4j**.

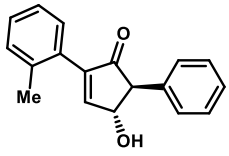
Compound 4ac: Purified by preparative TLC (20% EtOAc in hexane); Yellow thick oil (21.0 mg, 0.084 mmol, 84% yield); **FT-IR (Thin film):** 3460 (br), 1698 (s), 1492 (m), 1448 (m), 1297 (s), 1111 (m), 1062 (s), 898 (w); **^{1}H-NMR (400 MHz, $CDCl_3$):** δ 7.78-7.76 (m, 2H), 7.69 (d, *J* = 2.4 Hz, 1H), 7.44-7.40 (m, 3H), 7.36-7.34 (m, 2H), 7.32-7.28 (m, 1H), 7.19-7.16 (m, 2H), 4.98 (t, *J* = 2.7 Hz, 1H), 3.64 (d, *J* = 2.9 Hz, 1H), 2.40 (br s, 1H); **^{13}C-NMR (100 MHz, $CDCl_3$):** δ 203.2, 154.7, 143.7, 137.2, 130.5, 129.4, 129.1, 128.7, 128.5, 127.8, 127.6, 76.7, 63.8; **HRMS (ESI+):** Calcd. For $C_{17}H_{14}O_2$ ($[M+H]^+$): 251.1067, Found: 251.1068; **Optical rotation:** $[\alpha]_D^{24}$ +8.0 (*c* 1.0, $CHCl_3$) for an enantiomerically enriched sample with 97:3 er. The enantiomeric ratio was determined by HPLC analysis using Daicel Chiralpak IB column (90:10 *n*-Hexane/*i*-PrOH, 1.0 mL/min, 254 nm, τ_{major} = 22.2 min, τ_{minor} = 33.8 min). The absolute stereochemistry of the product **4ac** was assigned in analogy with **4j**.



Compound 4ad: Purified by preparative TLC (20% EtOAc in hexane); Brown thick oil (24.0 mg, 0.091 mmol, 91% yield); **FT-IR (Thin film):** 3419 (br), 1709 (s), 1510 (m), 1303 (m), 1112 (m), 1038 (m), 932 (m), 817 (s); **^{1}H-NMR (400 MHz, $CDCl_3$):** δ 7.68 (d, *J* = 8.2 Hz, 2H), 7.64 (d, *J* = 2.5 Hz, 1H), 7.37-7.28 (m, 3H), 7.22 (d, *J* = 7.9 Hz, 2H), 7.18-7.16 (m, 2H), 4.96 (t, *J* = 2.7 Hz, 1H), 3.61 (d, *J* = 2.9 Hz, 1H), 2.43 (br s, 1H), 2.38 (s, 3H); **^{13}C-NMR (100 MHz, $CDCl_3$):** δ 203.4, 153.9, 143.5, 139.5, 137.2, 129.4, 129.0, 128.5, 127.6, 127.5, 76.7, 63.8, 21.5; **HRMS (ESI+):** Calcd. For $C_{18}H_{16}O_2$ ($[M+Na]^+$): 287.1043, Found: 287.1047; **Optical rotation:** $[\alpha]_D^{24}$ +18.0 (*c* 1.0, $CHCl_3$) for an enantiomerically enriched sample with 97:3 er. The enantiomeric ratio was determined by HPLC analysis using Daicel Chiralpak IB column (80:20 *n*-Hexane/*i*-PrOH, 1.0 mL/min, 275 nm, τ_{major} = 10.0 min, τ_{minor} = 12.3 min). The absolute stereochemistry of the product **4ad** was assigned in analogy with **4j**.

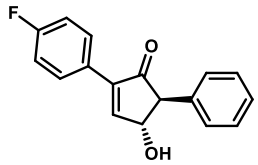


Compound 4ae: Purified by preparative TLC (20% EtOAc in hexane); Yellow thick oil (23.0 mg, 0.087 mmol, 87% yield); **FT-IR (Thin film):** 3421 (br), 3027 (w), 2924 (w), 1704 (s), 1496 (m), 1454 (m), 1313 (m), 1131 (m), 1038 (m), 749 (s), 699 (s); **^{1}H-NMR (400 MHz, $CDCl_3$):** δ 7.48-7.46 (m, 1H), 7.39-7.35 (m, 2H), 7.32-

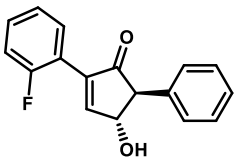


7.30 (m, 1H), 7.29-7.27 (m, 1H), 7.26-7.23 (m, 1H), 7.23-7.21 (m, 2H), 7.20-7.18 (m, 2H), 5.01 (dt, *J* = 3.5, 2.3 Hz, 1H), 3.63 (d, *J* = 2.7 Hz, 1H), 2.29 (br s, 1H), 2.28 (s, 3H); **^{13}C-NMR (100 MHz, CDCl$_3$):** δ 203.0, 157.7, 157.6, 146.7, 146.7, 137.2, 136.6, 130.8, 130.6, 129.6, 129.1, 129.0, 128.5, 127.6, 125.9, 77.3, 62.7, 20.5; **HRMS (ESI+):** Calcd. for $C_{18}H_{17}O_2$ ([M+H]+): 265.1223, Found: 265.1225; **Optical rotation:** $[\alpha]_D^{23}$ –12.0 (*c* 1.0, $CHCl_3$) for an enantiomerically enriched sample with 96:4 er. The enantiomeric ratio was determined by HPLC analysis using Daicel Chiralpak IB column (90:10 *n*-Hexane/*i*-PrOH, 1.0 mL/min, 230 nm, τ_{major} = 19.8 min, τ_{minor}= 28.0 min). The absolute stereochemistry of the product **4ae** was assigned in analogy with **4j**.

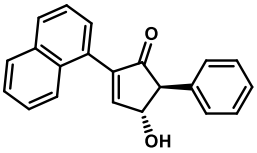
Compound 4af: Purified by preparative TLC (20% EtOAc in hexane); Brown thick oil (24.0 mg, 0.089 mmol, 89% yield); **FT-IR (Thin film):** 3424 (br), 1709 (s), 1601 (s), 1508 (s), 1229 (s), 1161 (s), 932 (w), 834 (s); **^{1}H-NMR (400 MHz, CDCl$_3$):** δ 7.55-7.49 (m, 2H), 7.39 (d, *J* = 2.5 Hz, 1H), 7.12-7.08 (m, 2H), 7.07-7.00 (m, 1H), 6.92-6.89 (m, 2H), 6.87-6.81 (m, 2H), 4.72 (t, *J* = 2.7 Hz, 1H), 3.37 (d, *J* = 2.9 Hz, 1H), 2.18 (br s, 1H); **^{13}C-NMR (100 MHz, CDCl$_3$):** δ 203.2, 163.4 (d, *J* = 249.5 Hz), 154.4, 142.5, 137.0, 129.7 (d, *J* = 8.3 Hz), 129.1, 128.5, 127.7, 126.6 (d, *J* = 3.5 Hz), 115.8 (d, *J* = 21.6 Hz), 76.6, 63.8; **HRMS (ESI+):** Calcd. For $C_{17}H_{13}FO_2$ ($[M+H]^+$): 269.0972, Found: 269.0966; **Optical rotation:** $[\alpha]_D^{24}$ +4.0 (*c* 1.0, $CHCl_3$) for an enantiomerically enriched sample with 97:3 er. The enantiomeric ratio was determined by HPLC analysis using Daicel Chiralpak IB column (90:10 *n*-Hexane/*i*-PrOH, 1.0 mL/min, 230 nm, τ_{minor} = 19.3 min, τ_{major} = 21.4 min). The absolute stereochemistry of the product **4af** was assigned in analogy with **4j**.



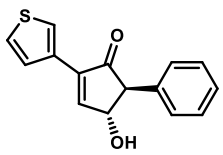
Compound 4ag: Purified by preparative TLC (20% EtOAc in hexane); Yellow thick oil (20.0 mg, 0.075 mmol, 75% yield); **FT-IR (Thin film):** 3422 (br), 3030 (w), 1712 (s), 1492 (s), 1452 (m), 1316 (m), 1124 (m), 936 (w), 753 (s), 699 (s); **^{1}H-NMR (400 MHz, CDCl$_3$):** δ 7.92-7.88 (m, 2H), 7.38-7.33 (m, 3H), 7.33-7.28 (m, 1H), 7.21-7.17 (m, 3H), 7.15-7.12 (m, 1H), 5.06-5.03 (m, 1H), 3.63-3.62 (m, 1H), 2.28 (br s, 1H); **^{13}C-NMR (100 MHz, CDCl$_3$):** δ 203.0, 160.8 (d, *J* = 250.9 Hz), 158.7 (d, *J* = 8.6 Hz), 138.0, 137.0, 130.7 (d, *J* = 8.7 Hz), 130.5 (d, *J* = 2.9 Hz), 129.1, 128.6, 127.7, 124.3 (d, *J* = 3.6 Hz), 118.6 (d, *J* = 12.7 Hz), 116.0 (d, *J* = 22.3 Hz), 77.1, 62.9; **HRMS (ESI+):** Calcd. for $C_{17}H_{13}FO_2$ ([M+Na]+): 291.0792, Found: 291.0804; **Optical rotation:** $[\alpha]_D^{23}$ –8.0 (*c* 1.0, $CHCl_3$) for an enantiomerically enriched sample with 97:3 er. The enantiomeric ratio was determined by HPLC analysis using Daicel Chiralpak IA column (95:5 *n*-Hexane/*i*-PrOH, 1.0 mL/min, 254 nm, τ_{major} = 40.4 min, τ_{minor} = 51.2 min). The absolute stereochemistry of the product **4ag** was assigned in analogy with **4j**.



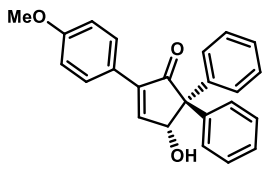
Compound 4ah: Purified by preparative TLC (20% EtOAc in hexane); Yellow thick oil (25.0 mg, 0.083 mmol, 83% yield); **FT-IR (Thin film):** 3431 (br), 3060 (w), 1710 (s), 1497 (w), 1307 (w), 1139 (m), 803 (m), 780 (s), 748 (m), 698 (m); **^{1}H-NMR (300 MHz, $CDCl_3$):** δ 7.90-7.80 (m, 3H), 7.68 (d, *J* = 2.3 Hz, 1H), 7.53-7.49 (m, 2H), 7.48-7.45 (m, 2H), 7.43-7.37 (m, 2H), 7.35-7.30 (m, 1H), 7.27 (d, *J* = 1.7 Hz, 1H), 7.26-7.25 (m, 1H), 5.14 (t, *J* = 2.6 Hz, 1H), 3.77 (d, *J* = 2.8 Hz, 1H), 2.30 (br s, 1H); **^{13}C-NMR (75 MHz, $CDCl_3$):** δ 203.2, 158.8, 145.2, 137.2, 133.8, 131.4, 129.4, 129.2, 128.7, 128.6, 128.5, 127.7, 127.5, 126.6, 126.2, 125.3, 125.0, 77.3, 62.9; **HRMS (ESI+):** Calcd. for $C_{21}H_{16}O_2$ ([M+H]+): 301.1223, Found: 301.1232; **Optical rotation:** $[\alpha]_D^{23}$ −20.0 (*c* 1.0, $CHCl_3$) for an enantiomerically enriched sample with 94:6 er. The enantiomeric ratio was determined by HPLC analysis using Daicel Chiralpak IB column (80:20 *n*-Hexane/*i*-PrOH, 1.0 mL/min, 230 nm, τ_{major} = 19.1 min, τ_{minor} = 47.0 min). The absolute stereochemistry of the product **4ah** was assigned in analogy with **4j**.



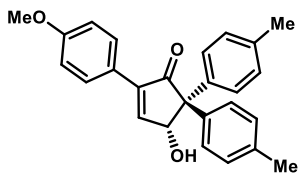
Compound 4ai: Purified by preparative TLC (20% EtOAc in hexane); Yellow thick oil (22.0 mg, 0.086 mmol, 86% yield); **FT-IR (Thin film):** 3420 (br), 3028 (w), 2918 (w), 1704 (s), 1497 (m), 1109 (m), 1034 (m), 795 (s), 744 (m), 699 (s); **^{1}H-NMR (400 MHz, $CDCl_3$):** δ 8.18 (dd, *J* = 3.0, 1.3 Hz, 1H), 7.61 (d, *J* = 2.5 Hz, 1H), 7.43 (dd, *J* = 5.1, 1.3 Hz, 1H), 7.38-7.34 (m, 3H), 7.32-7.28 (m, 1H), 7.18-7.16 (m, 2H), 5.02 (t, *J* = 2.7 Hz, 1H), 3.61 (d, *J* = 2.8 Hz, 1H), 2.23 (br s, 1H); **^{13}C-NMR (100 MHz, $CDCl_3$):** δ 203.2, 152.2, 138.7, 137.1, 131.0, 129.1, 128.5, 127.6, 126.2, 126.1, 126.0, 77.0, 63.5; **HRMS (ESI+):** Calcd. for $C_{15}H_{12}O_2S$ ([M+H]+): 257.0631, Found: 257.0635; **Optical rotation:** $[\alpha]_D^{23}$ +12.0 (*c* 1.0, $CHCl_3$) for an enantiomerically enriched sample with 94:6 er. The enantiomeric ratio was determined by HPLC analysis using Daicel Chiralpak IB column (90:10 *n*-Hexane/*i*-PrOH, 1.0 mL/min, 250 nm, τ_{major} = 21.5 min, τ_{minor} = 28.6 min). The absolute stereochemistry of the product **4ai** was assigned in analogy with **4j**.



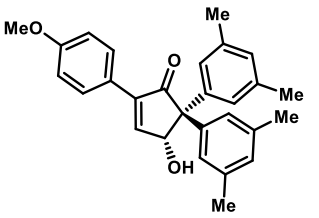
Compound 5a: Purified by preparative TLC (20% EtOAc in hexane); Yellow thick oil (33.0 mg, 0.093mmol, 93% yield); **FT-IR (Thin film):** 3465 (br), 1710 (s), 1606 (s), 1510 (s), 1444 (m), 1258 (s), 1180 (s), 835 (s); **^{1}H-NMR (400 MHz, $CDCl_3$):** δ 7.79 (d, *J* = 8.9 Hz, 2H), 7.73 (d, *J* = 2.8 Hz, 1H), 7.50-7.47 (m, 2H), 7.37-7.28 (m, 6H), 7.17-7.15 (m, 2H), 6.94 (d, *J* = 8.9 Hz, 2H), 5.55 (s, 1H), 3.84 (s, 3H); **^{13}C-NMR (100 MHz, $CDCl_3$):** δ 203.9, 160.7, 152.7, 142.9, 140.8, 140.3, 129.9, 129.2, 128.7, 128.7, 128.6, 127.6, 127.4, 123.1, 114.2, 76.3, 67.2, 55.5; **HRMS (ESI+):** Calcd. For $C_{24}H_{20}O_3$ ($[M+H]^+$): 357.1485, Found: 357.1477; **Optical rotation:** $[\alpha]_D^{24}$ −344.0 (*c* 1.0, $CHCl_3$) for an enantiomerically enriched sample with 99:1 er. The enantiomeric ratio was determined by HPLC analysis using Daicel Chiralpak IE column (90:10 *n*-Hexane/*i*-PrOH, 1.0 mL/min, 245 nm, τ_{major}= 35.6 min, τ_{minor} = 49.0 min). The absolute stereochemistry of the product **5a** was assigned in analogy with **4j**.



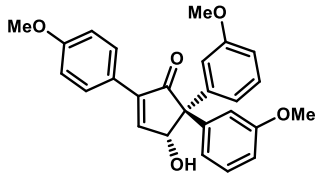
Compound 5b: Purified by preparative TLC (20% EtOAc in hexane); Yellow thick oil (37.0 mg, 0.096 mmol, 96% yield); **FT-IR (Thin film):** 3466 (br), 1709 (s), 1606 (m), 1510 (s), 1257 (s), 1180 (m), 1033 (m), 835 (m); **^{1}H-NMR (400 MHz, $CDCl_3$):** δ 7.79 (d, *J* = 8.8 Hz, 2H), 7.71 (d, *J* = 2.8 Hz, 1H), 7.37 (d, *J* = 8.3 Hz, 2H), 7.16-7.11 (m, 4H), 7.03 (d, *J* = 8.3 Hz, 2H), 6.93 (d, *J* = 8.9 Hz, 2H), 5.51 (d, *J* = 2.8 Hz, 1H), 3.83 (s, 3H), 2.33 (d, *J* = 6.4 Hz, 6H); **^{13}C-NMR (75 MHz, $CDCl_3$):** δ 204.3, 160.6, 152.7, 142.7, 137.9, 137.4, 137.3, 137.0, 129.8, 129.4, 129.2, 129.2, 128.5, 123.2, 114.1, 76.2, 66.6, 55.5, 21.1, 21.1; **HRMS (ESI+):** Calcd. For $C_{26}H_{24}O_3$ ([M+H]$^+$): 385.1798, Found: 385.1803; **Optical rotation:** $[\alpha]_D^{24}$ –294.0 (*c* 1.0, $CHCl_3$) for an enantiomerically enriched sample with 98.5:1.5 er. The enantiomeric ratio was determined by HPLC analysis using Daicel Chiralpak IB column (95:5 *n*-Hexane/*i*-PrOH, 1.0 mL/min, 245 nm, τ_{major}= 31.0 min, τ_{minor} = 35.2 min). The absolute stereochemistry of the product **5b** was assigned in analogy with **4j**.



Compound 5c: Purified by preparative TLC (20% EtOAc in hexane); Yellow thick oil (37.0 mg, 0.090 mmol, 90% yield); **FT-IR (Thin film):** 3476 (br), 3006 (w), 2915 (w), 1708 (s), 1604 (s), 1511 (s), 1257 (s), 1180 (m), 1119 (m), 1034 (m), 835 (m), 755 (s); **^{1}H-NMR (400 MHz, $CDCl_3$):** δ 7.80-7.78 (m, 2H), 7.73 (d, *J* = 2.8 Hz, 1H), 7.09 (s, 2H), 6.96-6.95 (m, 1H), 6.94-6.92 (m, 3H), 6.75 (s, 2H), 5.49 (d, *J* = 2.8 Hz, 1H), 3.84 (s, 3H), 2.30 (s, 6H), 2.26 (s, 6H), 1.64 (br s, 1H); **^{13}C-NMR (100 MHz, $CDCl_3$):** δ 204.3, 160.6, 152.9, 142.8, 140.7, 140.1, 138.3, 137.9, 129.4, 129.2, 129.1, 127.5, 126.4, 123.4, 114.1, 76.4, 66.9, 55.5, 21.7; **HRMS (ESI+):** Calcd. for $C_{28}H_{28}O_3$ ([M+Na]+): 435.1931, Found: 435.1932; **Optical rotation:** $[\alpha]_D^{24}$ –244.0 (*c* 1.0, $CHCl_3$) for an enantiomerically enriched sample with 98:2 er. The enantiomeric ratio was determined by HPLC analysis using Daicel Chiralpak IB column (95:5 *n*-Hexane/*i*-PrOH, 1.0 mL/min, 248 nm, τ_{major} = 14.3 min, τ_{minor} = 17.1 min). The absolute stereochemistry of the product **5c** was assigned in analogy with **4j**.

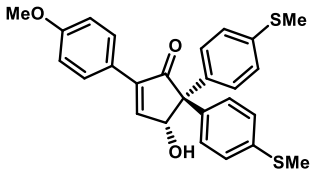


Compound 5d: Purified by preparative TLC (20% EtOAc in hexane); Colorless oil (36.0 mg, 0.086 mmol, 86% yield); **FT-IR (Thin film):** 3475 (br), 1708 (s), 1604 (s), 1580 (s), 1511 (s), 1488 (m), 1292 (m), 1256 (s); **^{1}H-NMR (400 MHz, $CDCl_3$):** δ 7.81 (d, *J* = 8.9 Hz, 2H), 7.76 (d, *J* = 2.8 Hz, 1H), 7.32-7.25 (m, 2H), 7.15-7.11 (m, 2H), 6.97 (d, *J* = 8.9 Hz, 2H), 6.88-6.84 (m, 2H), 6.78-6.76 (m, 2H), 5.54 (d, *J* = 2.8 Hz, 1H), 3.87 (s, 3H), 3.80 (s, 3H), 3.76 (s, 3H); **^{13}C-NMR (75 MHz, $CDCl_3$):** δ 203.5, 160.6, 159.8, 159.7, 152.8, 142.9, 142.1, 141.6, 129.7, 129.4, 129.2, 123.1, 121.9, 121.0, 116.3, 114.9, 114.1, 112.7, 112.6, 76.5, 66.8, 55.4, 55.4, 55.3; **HRMS (ESI+):** Calcd. For $C_{26}H_{24}O_5$ ([M+Na]$^+$): 439.1516, Found: 439.1521; **Optical rotation:** $[\alpha]_D^{24}$ –266.0 (*c* 1.0, $CHCl_3$) for an enantiomerically enriched sample

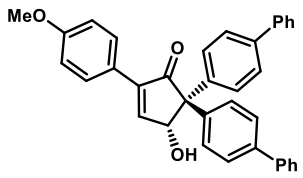


with 98:2 er. The enantiomeric ratio was determined by HPLC analysis using Daicel Chiralpak IB column (90:10 *n*-Hexane/*i*-PrOH, 1.0 mL/min, 245 nm, τ_{minor} = 32.3 min, τ_{major} = 37.5 min). The absolute stereochemistry of the product **5d** was assigned in analogy with **4j**.

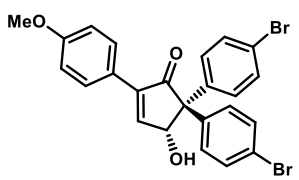
Compound 5e: Purified by preparative TLC (20% EtOAc in hexane); Red thick oil (37.0 mg, 0.083 mmol, 83% yield); **FT-IR (Thin film):** 3453 (br), 2919 (w), 1710 (s), 1605 (m), 1510 (s), 1494 /s), 1256 (s), 1179 (m), 1095 (m), 834 (m), 812 (m); **^{1}H-NMR (400 MHz, $CDCl_3$):** δ 7.76 (d, *J* = 8.9 Hz, 2H), 7.71 (d, *J* = 2.8 Hz, 1H), 7.38 (d, *J* = 8.6 Hz, 2H), 7.21 (d, *J* = 8.6 Hz, 2H), 7.17 (d, *J* = 8.5 Hz, 2H), 7.05 (d, *J* = 8.6 Hz, 2H), 6.93 (d, *J* = 8.9 Hz, 2H), 5.47 (d, *J* = 2.8 Hz, 1H), 3.83 (s, 3H), 2.46 (s, 3H), 2.45 (s, 3H), 1.74 (br s, 1H); **^{13}C-NMR (100 MHz, $CDCl_3$):** δ 203.7, 160.7, 152.5, 142.8, 138.2, 137.9, 137.4, 136.8, 130.4, 129.2, 129.0, 126.5, 126.4, 123.0, 114.2, 76.1, 66.4, 55.5, 15.8, 15.6; **HRMS (ESI+):** Calcd. for $C_{26}H_{24}O_3S_2$ ([M+Na]+): 471.1059, Found: 471.1063; **Optical rotation:** $[\alpha]_D^{24}$ −268.0 (*c* 1.0, $CHCl_3$) for an enantiomerically enriched sample with 98.5:1.5 er. The enantiomeric ratio was determined by HPLC analysis using Daicel Chiralpak IB column (85:15 *n*-Hexane/*i*-PrOH, 1.0 mL/min, 260 nm, τ_{minor} = 26.6 min, τ_{major} = 31.8 min). The absolute stereochemistry of the product **5e** was assigned in analogy with **4j**.



Compound 5f: Purified by preparative TLC (20% EtOAc in hexane); Orange thick oil (49.0 mg, 0.096 mmol, 96% yield); **FT-IR (Thin film):** 3446 (br), 3029 (w), 2837 (w), 1712 (s), 1605 (s), 1510 (s), 1487 (s), 1258 (s), 1180 (s), 1113 (m), 944 (m), 832 (s), 752 (s), 698 (s); **^{1}H-NMR (400 MHz, $CDCl_3$):** δ 7.83 (d, *J* = 8.8 Hz, 2H), 7.78 (d, *J* = 2.8 Hz, 1H), 7.62-7.59 (m, 6H), 7.59-7.57 (m, 2H), 7.57-7.56 (m, 2H), 7.46-7.42 (m, 4H), 7.37-7.33 (m, 2H), 7.28 (d, *J* = 8.5 Hz, 2H), 6.96 (d, *J* = 8.9 Hz, 2H), 5.63 (d, *J* = 2.8 Hz, 1H), 3.85 (s, 3H); **^{13}C-NMR (100 MHz, $CDCl_3$):** δ 203.9, 160.7, 152.7, 142.9, 140.6, 140.5, 140.3, 139.8, 139.2, 130.4, 129.2, 129.1, 129.0, 128.9, 127.6, 127.6, 127.4, 127.3, 127.2, 123.1, 114.2, 76.4, 66.9, 55.5; **HRMS (ESI+):** Calcd. for $C_{36}H_{28}O_3$ ([M+H]+): 509.2111, Found: 509.2104; **Optical rotation:** $[\alpha]_D^{23}$ −244.0 (*c* 1.0, $CHCl_3$) for an enantiomerically enriched sample with 99:1 er. The enantiomeric ratio was determined by HPLC analysis using Daicel Chiralpak IB column (80:20 *n*-Hexane/*i*-PrOH, 1.0 mL/min, 256 nm, τ_{major} = 38.1 min, τ_{minor} = 48.3 min). The absolute stereochemistry of the product **5f** was assigned in analogy with **4j**.

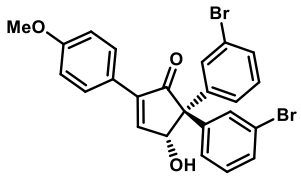


Compound 5g: Purified by preparative TLC (20% EtOAc in hexane); Colorless oil (50.0 mg, 0.097 mmol, 97% yield); **FT-IR (Thin film):** 3465 (br), 1710 (s), 1606 (m), 1510 (s), 1257 (m), 1179 (m), 1010 (m), 831 (m); **^{1}H-NMR (400 MHz, $CDCl_3$):** δ 7.75 (d, *J* = 8.9 Hz, 2H), 7.70 (d, *J* = 2.8 Hz, 1H), 7.48-.42 (m, 4H), 7.30 (d, *J* = 8.7 Hz, 2H), 7.00 (d, *J* = 8.6 Hz, 2H), 6.93 (d, *J*

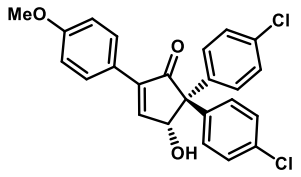


= 8.9 Hz, 2H), 5.46 (d, *J* = 2.8 Hz, 1H), 3.83 (s, 3H); **^{13}C-NMR (75 MHz, $CDCl_3$):** δ 203.1, 160.8, 152.2, 142.8, 139.5, 138.9, 131.8, 131.8, 131.7, 130.2, 129.2, 122.6, 122.0, 121.9, 114.2, 76.0, 66.4, 55.5; **HRMS (ESI+):** Calcd. For $C_{24}H_{18}Br_2O_3$ ($[M+Na]^+$): 534.9515, Found: 534.9517; **Optical rotation:** $[\alpha]_D^{24}$ −248.0 (*c* 1.0, $CHCl_3$) for an enantiomerically enriched sample with 99:1 er. The enantiomeric ratio was determined by HPLC analysis using Daicel Chiralpak IB column (90:10 *n*-Hexane/*i*-PrOH, 1.0 mL/min, 245 nm, τ_{minor} = 21.3 min, τ_{major} = 26.2 min). The absolute stereochemistry of the product **5g** was assigned in analogy with **4j**.

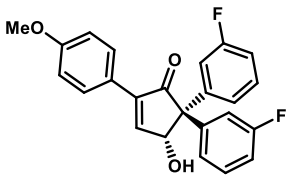
Compound 5h: Purified by preparative TLC (20% EtOAc in hexane); Yellow thick oil (51.0 mg, 0.099 mmol, 99% yield); **FT-IR (Thin film):** 3465 (br), 3009 (w), 2837 (w), 1709 (s), 1606 (m), 1561 (m), 1510 (s), 1473 (m), 1257 (s), 1180 (m), 1117 (m), 834 (m), 758 (m); **^{1}H-NMR (400 MHz, $CDCl_3$):** δ 7.76 (d, *J* = 8.9 Hz, 2H), 7.73 (d, *J* = 2.8 Hz, 1H), 7.60 (t, *J* = 1.9 Hz, 1H), 7.45-7.42 (m, 2H), 7.38-7.35 (m, 1H), 7.30 (t, *J* = 1.9 Hz, 1H), 7.21 (dt, *J* = 9.3, 8.0 Hz, 2H), 7.09-7.06 (m, 1H), 6.94 (d, *J* = 8.9 Hz, 2H), 5.47 (d, *J* = 2.8 Hz, 1H), 3.84 (s, 3H), 1.65 (br s, 1H); **^{13}C-NMR (75 MHz, $CDCl_3$):** δ 202.7, 160.9, 152.3, 142.8, 142.6, 142.0, 132.9, 131.3, 131.0, 130.9, 130.2, 130.2, 129.2, 128.6, 127.4, 122.9, 122.9, 122.6, 114.2, 76.1, 66.5, 55.5; **HRMS (ESI+):** Calcd. for $C_{24}H_{18}Br_2O_3$ ([M+Na]+): 534.9515, Found: 534.9517; **Optical rotation:** $[\alpha]_D^{23}$ −196.0 (*c* 1.0, $CHCl_3$) for an enantiomerically enriched sample with 99:1 er. The enantiomeric ratio was determined by HPLC analysis using Daicel Chiralpak IA column (90:10 *n*-Hexane/*i*-PrOH, 1.0 mL/min, 240 nm, τ_{minor} = 24.6 min, τ_{major} = 50.3 min). The absolute stereochemistry of the product **5h** was assigned in analogy with **4j**.



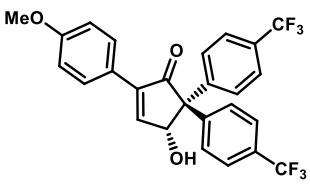
Compound 5i: Purified by preparative TLC (20% EtOAc in hexane); Yellow thick oil (40.0 mg, 0.094 mmol, 94% yield); **FT-IR (Thin film):** 3466 (br), 1710 (s), 1606 (m), 1510 (s), 1494 (s), 1257 (s), 1013 (m), 817 (s); **^{1}H-NMR (300 MHz, $CDCl_3$):** δ 7.75 (d, *J* = 8.8 Hz, 2H), 7.71 (d, *J* = 2.8 Hz, 1H), 7.39-7.27 (m, 6H), 7.07 (d, *J* = 8.6 Hz, 2H), 6.94 (d, *J* = 8.7 Hz, 2H), 5.47 (d, *J* = 2.8 Hz, 1H), 3.83 (s, 3H); **^{13}C-NMR (75 MHz, $CDCl_3$):** δ 203.2, 160.8, 152.3, 142.8, 139.0, 138.5, 133.8, 133.7, 131.3, 129.9, 129.2, 128.8, 122.7, 114.2, 76.1, 66.3, 55.5; **HRMS (ESI+):** Calcd. For $C_{24}H_{18}Cl_2O_3$ ($[M+Na]^+$): 447.0525, Found: 447.0521; **Optical rotation:** $[\alpha]_D^{24}$ −280.0 (*c* 1.0, $CHCl_3$) for an enantiomerically enriched sample with 99:1 er. The enantiomeric ratio was determined by HPLC analysis using Daicel Chiralpak IB column (90:10 *n*-Hexane/*i*-PrOH, 1.0 mL/min, 245 nm, τ_{minor} = 19.6 min, τ_{major} = 24.7 min). The absolute stereochemistry of the product **5i** was assigned in analogy with **4j**.



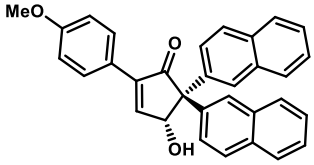
Compound 5j: Purified by preparative TLC (20% EtOAc in hexane); Yellow thick oil (38.0 mg, 0.097 mmol, 97% yield); **FT-IR (Thin film):** 3466 (br), 1709 (s), 1608 (s), 1586 (s), 1511 (s), 1257 (s), 1032 (m), 827 (s); **^{1}H-NMR (400 MHz, $CDCl_3$):** δ 7.80 (d, *J* = 8.8 Hz, 2H), 7.76 (d, *J* = 2.8 Hz, 1H), 7.39-7.24 (m, 4H), 7.06-6.93 (m, 5H), 6.92-6.90 (m, 1H), 5.52 (d, *J* = 2.8 Hz, 1H), 3.87 (s, 3H); **^{13}C-NMR (100 MHz, $CDCl_3$):** 202.8, 162.9 (d, *J* = 246.2 Hz), 162.8 (d, *J* = 247.0 Hz), 160.8, 152.4, 142.9, 142.8 (d, *J* = 7.3 Hz), 142.2 (d, *J* = 7.0 Hz), 130.2 (d, *J* = 7.7 Hz), 130.1 (d, *J* = 7.9 Hz), 129.2, 125.4 (d, *J* = 3.0 Hz), 124.2 (d, *J* = 2.9 Hz), 122.7, 117.3 (d, *J* = 22.9 Hz), 115.9 (d, *J* = 23.1 Hz), 114.9 (d, *J* = 11.2 Hz), 114.7 (d, *J* = 11.3 Hz), 114.2, 76.4, 66.5, 55.5; **HRMS (ESI+):** Calcd. For $C_{24}H_{18}F_2O_3$ ($[M+H]^+$): 393.1297, Found: 393.1298; **Optical rotation:** $[\alpha]_D^{24}$ –280.0 (*c* 1.0, $CHCl_3$) for an enantiomerically enriched sample with 99:1 er. The enantiomeric ratio was determined by HPLC analysis using Daicel Chiralpak IB column (90:10 *n*-Hexane/*i*-PrOH, 1.0 mL/min, 230 nm, τ_{minor} = 17.5 min, τ_{major} = 19.2 min). The absolute stereochemistry of the product **5j** was assigned in analogy with **4j**.



Compound 5k: Purified by preparative TLC (20% EtOAc in hexane); Yellow thick oil (49.0 mg, 0.099 mmol, 99% yield); **FT-IR (Thin film):** 3467 (br), 2842 (w), 1713 (s), 1607 (m), 1512 (s), 1328 (s), 1259 (s), 1169 (s), 1121 (s), 1071 (s), 1018 (s), 831 (s), 760 (m); **^{1}H-NMR (400 MHz, $CDCl_3$):** δ 7.77 (dd, *J* = 5.9, 3.0 Hz, 3H), 7.63-7.60 (m, 3H), 7.58-7.55 (m, 3H), 7.28 (d, *J* = 8.2 Hz, 2H), 6.95 (d, *J* = 8.9 Hz, 2H), 5.57 (d, *J* = 2.8 Hz, 1H), 3.84 (s, 3H), 1.66 (br s, 1H); **^{13}C-NMR (100 MHz, $CDCl_3$):** δ 202.6, 161.0, 152.1, 144.3, 143.7, 142.9, 130.5, 130.0 (q, *J* = 32.8 Hz), 129.9 (q, *J* = 32.8 Hz), 129.2, 129.0, 125.7 (q, *J* = 3.9 Hz), 125.6 (q, *J* = 3.8 Hz), 124.1 (q, *J* = 272.0 Hz), 124.0 (q, *J* = 271.9 Hz), 122.4, 114.3, 76.2, 67.1, 55.5; **HRMS (ESI+):** Calcd. for $C_{26}H_{18}F_6O_3$ ([M+H]+): 493.1233, Found: 493.1226; **Optical rotation:** $[\alpha]_D^{24}$ −212.0 (*c* 1.0, $CHCl_3$) for an enantiomerically enriched sample with 98.5:1.5 er. The enantiomeric ratio was determined by HPLC analysis using Daicel Chiralpak IB column (90:10 *n*-Hexane/*i*-PrOH, 1.0 mL/min, 236 nm, τ_{minor} = 14.4 min, τ_{major} = 18.0 min). The absolute stereochemistry of the product **5k** was assigned in analogy with **4j**.

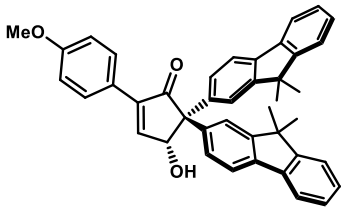


Compound 5l: Purified by preparative TLC (20% EtOAc in hexane); Off-white thick oil (43.0 mg, 0.094 mmol, 94% yield); **FT-IR (Thin film):** 3452 (br), 1708 (s), 1604 (s), 1510 (s), 1258 (s), 1180 (m), 1107 (m), 809 (s); **^{1}H-NMR (400 MHz, $CDCl_3$):** δ 7.99 (d, *J* = 1.9 Hz, 1H), 7.84-7.80 (m, 7H), 7.79-7.73 (m, 3H), 7.56 (dd, *J* = 8.7, 2.0 Hz, 1H), 7.51-7.44 (m, 4H), 7.26-7.24 (m, 1H), 6.96 (d, *J* = 8.8 Hz, 2H), 5.76 (d, *J* = 2.8 Hz, 1H), 3.84 (s, 3H); **^{13}C-NMR (100 MHz, $CDCl_3$):** δ 203.8, 160.7, 152.5, 142.8, 138.2, 137.4, 133.2, 133.2, 132.6, 132.5, 129.3, 129.2, 128.4, 128.4, 128.3, 128.3, 127.8, 127.6, 127.6, 127.3, 126.9, 126.6,

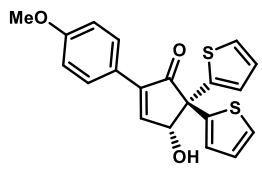


126.5, 126.4, 126.4, 123.1, 114.2, 76.3, 67.4, 55.5; **HRMS (ESI+):** Calcd. For $C_{32}H_{24}O_3$ ($[M+Na]^+$): 479.1618, Found: 479.1623; **Optical rotation:** $[\alpha]_D^{24}$ –332.0 (*c* 1.0, $CHCl_3$) for an enantiomerically enriched sample with 99:1 er. The enantiomeric ratio was determined by HPLC analysis using Daicel Chiralpak IF column (75:25 *n*-Hexane/*i*-PrOH, 1.0 mL/min, 230 nm, τ_{major} = 29.3 min, τ_{minor} = 39.3 min). The absolute stereochemistry of the product **5l** was assigned in analogy with **4j**.

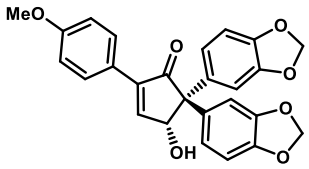
Compound 5m: Purified by preparative TLC (20% EtOAc in hexane); Reddish-brown solid (48.0 mg, 0.082 mmol, 82% yield); **m.p.** 165-167 °C; **FT-IR (Thin film):** 3465 (br), 3011 (w), 2959 (m), 1708 (s), 1606 (m), 1510 (s), 1448 (m), 1257 (m), 1180 (m), 836 (m), 758 (s), 740 (s); **^{1}H-NMR (400 MHz, $CDCl_3$):** δ 7.83-7.80 (m, 3H), 7.74-7.70 (m, 3H), 7.67 (d, *J* = 7.9 Hz, 1H), 7.59 (d, *J* = 1.8 Hz, 1H), 7.50 (dd, *J* = 8.1, 1.8 Hz, 1H), 7.43-7.39 (m, 2H), 7.34-7.31 (m, 4H), 7.23 (d, *J* = 1.7 Hz, 1H), 7.18 (dd, *J* = 8.0, 1.8 Hz, 1H), 6.97 (d, *J* = 8.8 Hz, 2H), 5.64 (d, *J* = 2.8 Hz, 1H), 3.85 (s, 3H), 1.69 (br s, 1H), 1.48 (s, 3H), 1.42 (d, *J* = 3.2 Hz, 6H), 1.35 (s, 3H); **^{13}C-NMR (100 MHz, $CDCl_3$):** δ 204.0, 160.7, 154.1, 154.0, 154.0, 152.9, 143.3, 140.0, 139.4, 138.8, 138.8, 138.6, 138.5, 129.3, 128.6, 127.7, 127.5, 127.3, 127.2, 127.1, 124.6, 123.4, 123.3, 122.8, 120.3, 120.3, 120.1, 119.9, 114.2, 76.8, 67.8, 55.5, 47.1, 47.1, 27.2, 27.2, 27.1; **HRMS (ESI+):** Calcd. for $C_{42}H_{36}O_3$ ([M+H]+): 589.2737, Found: 589.2740; **Optical rotation:** $[\alpha]_D^{24}$ −206.0 (*c* 1.0, $CHCl_3$) for an enantiomerically enriched sample with 98:2 er. The enantiomeric ratio was determined by HPLC analysis using Daicel Chiralpak IC column (90:10 *n*-Hexane/EtOAc, 0.5 mL/min, 276 nm, τ_{major} = 21.2 min, τ_{minor} = 24.4 min). The absolute stereochemistry of the product **5m** was assigned in analogy with **4j**.



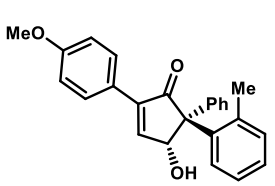
Compound 5n: Purified by preparative TLC (20% EtOAc in hexane); Blue thick oil (26.0 mg, 0.071 mmol, 71% yield); **FT-IR (Thin film):** 3465 (br), 2930 (w), 1714 (s), 1605 (m), 1510 (s), 1257 (s), 1180 (m), 1030 (m), 831 (m), 813 (m), 703 (s); **^{1}H-NMR (400 MHz, $CDCl_3$):** δ 7.78 (d, *J* = 8.9 Hz, 2H), 7.65 (d, *J* = 2.5 Hz, 1H), 7.36-7.33 (m, 2H), 7.24 (dd, *J* = 5.2, 1.2 Hz, 1H), 7.06 (dd, *J* = 5.2, 3.6 Hz, 1H), 6.98-6.94 (m, 3H), 6.78 (dd, *J* = 3.6, 1.2 Hz, 1H), 5.46 (d, *J* = 2.5 Hz, 1H), 3.85 (s, 3H), 1.98 (br s, 1H); **^{13}C-NMR (100 MHz, $CDCl_3$):** δ 199.9, 160.9, 152.5, 143.0, 142.6, 142.5, 129.2, 127.7, 127.3, 126.8, 126.6, 126.4, 126.0, 122.7, 114.3, 78.6, 62.6, 55.5; **HRMS (ESI+):** Calcd. for $C_{20}H_{16}O_3S_2$ ([M+H]+): 369.0614, Found: 369.0608; **Optical rotation:** $[\alpha]_D^{24}$ −16.0 (*c* 0.25, $CHCl_3$) for an enantiomerically enriched sample with 98:2 er. The enantiomeric ratio was determined by HPLC analysis using Daicel Chiralpak IA column (80:20 *n*-Hexane/*i*-PrOH, 1.0 mL/min, 290 nm, τ_{minor} = 22.7 min, τ_{major} = 48.9 min). The absolute stereochemistry of the product **5n** was assigned in analogy with **4j**.



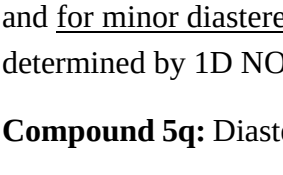
Compound 5o: Purified by preparative TLC (20% EtOAc in hexane); Brown thick oil (37.0 mg, 0.083 mmol, 83% yield); **FT-IR (Thin film):** 3477 (br), 2898 (w), 1706 (m), 1605 (m), 1504 (s), 1487 (s), 1241 (s), 1038 (s), 932 (m), 807 (m), 756 (m); **^{1}H-NMR (400 MHz, $CDCl_3$):** δ 7.77 (d, *J* = 8.9 Hz, 2H), 7.69 (d, *J* = 2.7 Hz, 1H), 7.00 (d, *J* = 2.0 Hz, 1H), 6.97-6.92 (m, 3H), 6.76 (dd, *J* = 9.4, 8.4 Hz, 2H), 6.64-6.61 (m, 2H), 5.95-5.94 (m, 4H), 5.41 (d, *J* = 2.7 Hz, 1H), 3.83 (s, 3H), 1.66 (br s, 1H); **^{13}C-NMR (100 MHz, $CDCl_3$):** δ 203.7, 160.7, 152.5, 148.0, 148.0, 147.1, 146.9, 142.7, 134.6, 134.0, 129.2, 123.1, 121.5, 114.2, 110.6, 109.7, 108.3, 108.0, 101.4, 101.3, 76.5, 66.3, 55.5; **HRMS (ESI+):** Calcd. for $C_{26}H_{20}O_7$ ([M+H]+): 445.1282, Found: 445.1284; **Optical rotation:** $[\alpha]_D^{24}$ −232.0 (*c* 0.25, $CHCl_3$) for an enantiomerically enriched sample with 99:1 er. The enantiomeric ratio was determined by HPLC analysis using Daicel Chiralpak IB column (80:20 *n*-Hexane/*i*-PrOH, 1.0 mL/min, 240 nm, τ_{minor} = 27.1 min, τ_{major} = 33.4 min). The absolute stereochemistry of the product **5o** was assigned in analogy with **4j**.



Compound 5p: Diastereoselectivity (dr) = 10:1 was determined by ^{1}H NMR analysis of the crude reaction mixture. Purified by preparative TLC (20% EtOAc in hexane); Yellow thick oil (33.0 mg, 0.089 mmol, 89% yield); **FT-IR (Thin film):** 3477 (br), 3013 (w), 2838 (w), 1708 (s), 1605 (s), 1511 (s), 1257 (s), 1180 (s), 1033 (m), 835 (s), 757 (s), 702 (m); **^{1}H-NMR (300 MHz, $CDCl_3$):** <u>major diastereomer</u> δ 7.77 (d, *J* = 8.9 Hz, 2H), 7.69 (d, *J* = 2.8 Hz, 1H), 7.39-7.36 (m, 1H), 7.34-7.28 (m, 3H), 7.24-7.22 (m, 2H), 7.20-7.16 (m, 3H), 6.93 (d, *J* = 8.9 Hz, 2H), 5.34 (d, *J* = 2.8 Hz, 1H), 3.83 (s, 3H), 2.11 (s, 3H), 1.85 (br s, 1H); **^{13}C-NMR (75 MHz, $CDCl_3$):** <u>major diastereomer</u> δ 204.1, 160.6, 151.5, 142.9, 139.3, 139.0, 138.6, 133.1, 129.5, 129.2, 128.7, 128.3, 127.6, 127.3, 126.0, 123.3, 114.1, 77.7, 68.0, 55.4, 22.6; **HRMS (ESI+):** Calcd. for $C_{25}H_{22}O_3$ ([M+H]+): 371.1642, Found: 371.1639; **Optical rotation:** $[\alpha]_D^{24}$ −110.0 (*c* 1.0, $CHCl_3$) for an enantiomerically enriched sample with 97:3 er for each of the diastereomers. The enantiomeric ratio was determined by HPLC analysis using Daicel Chiralpak IA column (80:20 *n*-Hexane/*i*-PrOH, 1.0 mL/min, 245 nm, <u>for major diastereomer</u> τ_{minor} = 9.8 min, τ_{major} = 17.4 min and <u>for minor diastereomer</u> τ_{minor} = 15.9 min, τ_{major} = 17.4 min). The relative stereochemistry was determined by 1D NOE.

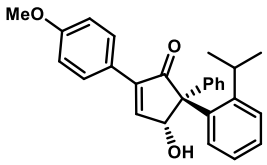


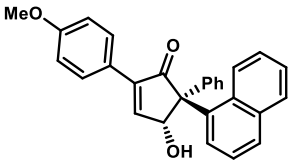
Compound 5q: Diastereoselectivity (dr) = 1.6:1 was determined by ^{1}H NMR analysis of the crude reaction mixture. Purified (both diastereomers are separable) by preparative TLC (20% EtOAc in hexane); Yellow thick oil (37.0 mg, 0.096 mmol, 96% combined yield). **<u>Major diastereomer:</u>** Obtained as yellow thick oil (23.0 mg, 0.060 mmol, 60% yield); **FT-IR (Thin film):** 3482 (br), 3007 (w), 2838 (m), 1707 (s), 1605 (s), 1510 (s), 1489 (s), 1463 (m), 1306 (m), 1243 (s),1179 (s), 1028 (s), 835 (s), 755 (s), 703 (m); **^{1}H-NMR (300 MHz, $CDCl_3$):** δ 7.82



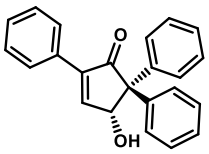
(d, *J* = 8.3 Hz, 2H), 7.79 (dd, *J* = 2.6, 0.7 Hz, 1H), 7.68 (dd, *J* = 7.9, 1.3 Hz, 1H), 7.43-7.37 (m, 1H), 7.30-7.24 (m, 3H), 7.18-7.15 (m, 2H), 7.09-7.03 (m, 2H), 6.98 (d, *J* = 8.3 Hz, 2H), 5.27 (d, *J* = 2.5 Hz, 1H), 3.87 (s, 3H), 3.76 (s, 3H), 2.97 (br s, 1H); **^{13}C-NMR (100 MHz, $CDCl_3$):** δ 203.7, 160.5, 158.1, 153.4, 142.9, 137.6, 129.6, 129.5, 129.4, 129.1, 128.8, 127.9, 126.9, 123.5, 121.5, 114.1, 112.3, 79.7, 65.9, 56.0, 55.5; **HRMS (ESI+):** Calcd. for $C_{25}H_{22}O_4$ ([M+Na]+): 409.1410, Found: 409.1401; **Optical rotation:** $[\alpha]_D^{24}$ +222.0 (*c* 1.0, $CHCl_3$) for an enantiomerically enriched sample with 98:2 er. The enantiomeric ratio was determined by HPLC analysis using Daicel Chiralpak IC column (95:5 *n*-Hexane/*i*-PrOH, 1.0 mL/min, 245 nm, τ_{minor} = 34.5 min, τ_{major} = 38.4 min). The relative stereochemistry was determined by 1D NOE. **Minor diastereomer:** Obtained as yellow thick oil (14.0 mg, 0.036 mmol, 36% yield); **FT-IR (Thin film):** 3510 (br), 3006 (w), 2934 (w), 2837 (w), 1712 (s), 1605 (s), 1511 (s), 1490 (s), 1462 (m), 1305 (m), 1246 (s), 1179 (s), 1028 (m), 835 (s), 754 (s), 701 (m); **^{1}H-NMR (300 MHz, $CDCl_3$):** δ 7.78 (d, *J* = 8.8 Hz, 2H), 7.65 (d, *J* = 3.1 Hz, 1H), 7.37-7.27 (m, 6H), 7.08-7.05 (m, 1H), 6.97 (d, *J* = 7.8 Hz, 2H), 6.93 (d, *J* = 8.8 Hz, 2H), 5.57 (d, *J* = 3.1 Hz, 1H), 3.83 (s, 3H), 3.62 (s, 3H); **^{13}C-NMR (75 MHz, $CDCl_3$):** δ 205.2, 160.4, 157.3, 151.1, 141.6, 140.6, 131.7, 130.1, 129.1, 129.0, 128.5, 128.1, 127.2, 123.8, 122.0, 114.1, 112.9, 77.7, 65.1, 56.1, 55.5; **HRMS (ESI+):** Calcd. for $C_{25}H_{22}O_4$ ([M+Na]+): 409.1410, Found: 409.1394; **Optical rotation:** $[\alpha]_D^{24}$ −180.0 (*c* 1.0, $CHCl_3$) for an enantiomerically enriched sample with >99.5:0.5 er. The enantiomeric ratio was determined by HPLC analysis using Daicel Chiralpak IC column (95:5 *n*-Hexane/*i*-PrOH, 1.0 mL/min, 245 nm, τ_{major} = 37.1 min, τ_{minor} = 42.0 min).

Compound 5r: Diastereoselectivity (dr) > 20:1 was determined by ^{1}H NMR analysis of the crude reaction mixture. Purified by preparative TLC (20% EtOAc in hexane); Yellow solid (35.0 mg, 0.088 mmol, 88% yield); **m.p.** 173-175 °C; **FT-IR (Thin film):** 3465 (br), 2918 (w), 1712 (m), 1686 (s), 1511 (s), 1385 (s), 1257 (s), 1180 (m), 1033 (m), 831 (m), 761 (m), 596 (s); **^{1}H-NMR (400 MHz, $CDCl_3$):** δ 7.79 (d, *J* = 8.9 Hz, 2H), 7.68 (d, *J* = 2.8 Hz, 1H), 7.44 (dd, *J* = 7.8, 1.6 Hz, 1H), 7.39-7.35 (m, 2H), 7.33-7.31 (m, 2H), 7.29-7.26 (m, 1H), 7.23-7.16 (m, 3H), 6.96 (d, *J* = 8.9 Hz, 2H), 5.39 (d, *J* = 2.8 Hz, 1H), 3.86 (s, 3H), 3.01 (hept, *J* = 6.7 Hz, 1H), 2.01 (br s, 1H), 1.15 (d, *J* = 6.7 Hz, 3H), 0.90 (d, *J* = 6.8 Hz, 3H); **^{13}C-NMR (100 MHz, $CDCl_3$):** δ 203.7, 160.6, 151.0, 149.9, 142.9, 140.2, 137.8, 129.4, 129.1, 128.7, 128.5, 128.0, 128.0, 127.2, 125.7, 123.3, 114.1, 77.9, 68.1, 55.5, 30.3, 24.2, 24.0; **HRMS (ESI+):** Calcd. for $C_{27}H_{26}O_3$ ([M+H]+): 399.1955, Found: 399.1952; **Optical rotation:** $[\alpha]_D^{24}$ −48.0 (*c* 1.0, $CHCl_3$) for an enantiomerically enriched sample with 95:5 er. The enantiomeric ratio was determined by HPLC analysis using Daicel Chiralpak IB column (95:5 *n*-Hexane/*i*-PrOH, 1.0 mL/min, 245 nm, τ_{major} = 18.9 min, τ_{minor} = 23.9 min). The relative stereochemistry was determined by 1D NOE.

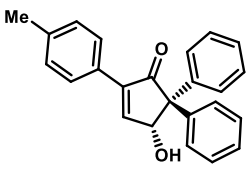


Compound 5s: Diastereoselectivity (dr) = 11.4:1 was determined by ^{1}H NMR analysis of the crude reaction mixture. Purified by preparative TLC (20% EtOAc in hexane); Blue thick oil (37.0 mg, 0.091 mmol, 91% yield); **FT-IR (Thin film):** 3476 (br), 2925 (w), 1705 (s), 1605 (m), 1510 (s), 1258 (s), 1180 (m), 836 (m), 778 (m), 754 (m), 701 (m); **^{1}H-NMR (300 MHz, $CDCl_3$):** 

major diastereomer δ 7.94-7.90 (m, 1H), 7.89-7.86 (m, 1H), 7.85-7.78 (m, 3H), 7.69 (d, *J* = 2.7 Hz, 1H), 7.66 (dd, *J* = 7.4, 1.2 Hz, 1H), 7.45-7.40 (m, 2H), 7.32-7.27 (m, 1H), 7.26-7.22 (m, 3H), 7.18-7.13 (m, 2H), 6.94 (d, *J* = 8.9 Hz, 2H), 5.41 (d, *J* = 2.8 Hz, 1H), 3.84 (s, 3H); **^{13}C-NMR (75 MHz, $CDCl_3$):** major diastereomer δ 204.3, 160.7, 152.6, 142.8, 139.3, 136.8, 135.3, 132.6, 129.7, 129.3, 129.2, 128.9, 128.6, 127.6, 127.2, 126.6, 125.7, 125.6, 125.3, 123.2, 114.2, 78.9, 67.7, 55.5; **HRMS (ESI+):** Calcd. for $C_{28}H_{22}O_3$ ([M+H]+): 407.1642, Found: 407.1636; **Optical rotation:** $[\alpha]_D^{24}$ −40.0 (*c* 0.25, $CHCl_3$) for an enantiomerically enriched sample with 98.5:1.5 er. The enantiomeric ratio was determined by HPLC analysis using Daicel Chiralpak IA column (80:20 *n*-Hexane/*i*-PrOH, 1.0 mL/min, 230 nm, for major diastereomer τ_{minor} = 12.2 min, τ_{major} = 18.0 min). The absolute stereochemistry of the product **5s** was assigned in analogy with **5p**.

Compound 5t: Purified by preparative TLC (20% EtOAc in hexane); Off-white thick oil (29.0 mg, 0.089 mmol, 89% yield); **FT-IR (Thin film):** 3485 (br), 1704 (s), 1494 (s), 1447 (m), 1119 (m), 1067 (s), 830 (w), 759 (s); **^{1}H-NMR (400 MHz, $CDCl_3$):** 

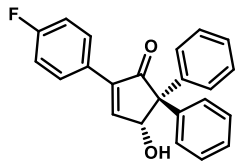
δ 7.83 (d, *J* = 2.7 Hz, 1H), 7.81-7.78 (m, 2H), 7.51-7.48 (m , 2H), 7.45-7.40 (m, 3H), 7.38-7.29 (m, 6H), 7.18-7.15 (m, 2H), 5.58 (d, *J* = 2.7 Hz, 1H); **^{13}C-NMR (100 MHz, $CDCl_3$):** δ 203.6, 154.7, 143.6, 140.7, 140.2, 130.6, 129.9, 129.5, 128.8, 128.7, 128.7, 128.6, 127.8, 127.7, 127.5, 76.3, 67.2; **HRMS (ESI+):** Calcd. For $C_{23}H_{18}O_2$ ($[M+H]^+$): 327.1380, Found: 327.1381; **Optical rotation:** $[\alpha]_D^{24}$ –390.0 (*c* 1.0, $CHCl_3$) for an enantiomerically enriched sample with 98:2 er. The enantiomeric ratio was determined by HPLC analysis using Daicel Chiralpak IB column (90:10 *n*-Hexane/*i*-PrOH, 1.0 mL/min, 230 nm, τ_{major} = 12.3 min, τ_{minor} = 14.7 min). The absolute stereochemistry of the product **5t** was assigned in analogy with **4j**.

Compound 5u: Purified by preparative TLC (20% EtOAc in hexane); White thick oil (33.0 mg, 0.097 mmol, 97% yield); **FT-IR (Thin film):** 3446 (br), 1711 (s), 1495 (m), 1444 (w), 1303 (w), 1116 (m), 822 (s), 756 (s); **^{1}H-NMR (400 MHz, $CDCl_3$):** 

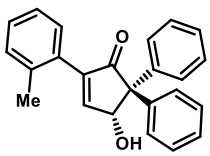
δ 7.78 (d, *J* = 2.7 Hz, 1H), 7.71 (d, *J* = 8.2 Hz, 2H), 7.51-7.48 (m, 2H), 7.38-7.29 (m, 6H), 7.23 (d, *J* = 7.9 Hz, 2H), 7.17-7.14 (m, 2H), 5.57 (d, *J* = 2.7 Hz, 1H), 2.39 (s, 3H); **^{13}C-NMR (100 MHz, $CDCl_3$):** δ 203.7, 153.8, 143.4, 140.8, 140.3, 139.6, 129.9, 129.4, 128.7, 128.7, 128.6, 127.7, 127.7, 127.6, 127.4, 76.3, 67.2, 21.5; **HRMS (ESI+):** Calcd. For $C_{24}H_{20}O_2$ ($[M+H]^+$): 341.1536, Found: 341.1533; **Optical rotation:**

$[\alpha]_D^{24}$ –326.0 (*c* 1.0, $CHCl_3$) for an enantiomerically enriched sample with 99:1 er. The enantiomeric ratio was determined by HPLC analysis using Daicel Chiralpak IE column (95:5 *n*-Hexane/*i*-PrOH, 1.0 mL/min, 230 nm, τ_{major} = 36.9 min, τ_{minor} = 50.9 min). The absolute stereochemistry of the product **5u** was assigned in analogy with **4j**.

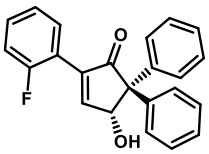
Compound 5v: Purified by preparative TLC (20% EtOAc in hexane); White thick oil (30.0 mg, 0.087 mmol, 87% yield); **FT-IR (Thin film):** 3648 (br), 1712 (s), 1601 (w), 1507 (s), 1224 (s), 1068 (s), 975 (w), 839 (s); **^{1}H-NMR (300 MHz, $CDCl_3$):** δ 7.84-7.77 (m, 3H), 7.50-7.46 (m, 2H), 7.39-7.27 (m, 6H), 7.17-7.07 (m, 4H), 5.56 (d, *J* = 2.7 Hz, 1H); **^{13}C-NMR (75 MHz, $CDCl_3$):** δ 203.6, 163.5 (d, *J* = 249.7 Hz), 154.3 (d, *J* = 1.5 Hz), 142.4, 140.6, 140.1, 129.9, 129.7 (d, *J* = 8.2 Hz), 128.8, 128.6, 128.6, 127.6 (d, *J* = 12.4 Hz), 126.7, 126.7, 115.8 (d, *J* = 21.6 Hz), 76.2, 67.1; **HRMS (ESI+):** Calcd. For $C_{23}H_{17}FO_2$ ($[M+Na]^+$): 367.1105, Found: 367.1100; **Optical rotation:** $[\alpha]_D^{24}$ –344.0 (*c* 1.0, $CHCl_3$) for an enantiomerically enriched sample with 99:1 er. The enantiomeric ratio was determined by HPLC analysis using Daicel Chiralpak IE column (90:10 *n*-Hexane/*i*-PrOH, 1.0 mL/min, 245 nm, τ_{major} = 12.5 min, τ_{minor} = 15.9 min). The absolute stereochemistry of the product **5v** was assigned in analogy with **4j**.



Compound 5w: Purified by preparative TLC (20% EtOAc in hexane); Yellow thick oil (15.0 mg, 0.044 mmol, 44% yield); **FT-IR (Thin film):** 3453 (br), 3059 (w), 2922 (w), 1712 (s), 1495 (m), 1445 (m), 1131 (m), 755 (s), 700 (s); **^{1}H-NMR (300 MHz, $CDCl_3$):** δ 7.66 (d, *J* = 2.7 Hz, 1H), 7.49-7.46 (m, 2H), 7.41-7.38 (m, 1H), 7.36-7.35 (m, 2H), 7.34-7.32 (m, 2H), 7.31-7.27 (m, 2H), 7.24-7.21 (m, 5H), 5.58 (d, *J* = 2.7 Hz, 1H), 2.14 (s, 3H), 1.68 (br s, 1H); **^{13}C-NMR (75 MHz, $CDCl_3$):** δ 203.2, 157.0, 146.5, 140.8, 139.8, 136.7, 130.6, 130.0, 129.6, 129.0, 128.8, 128.6, 127.7, 127.5, 125.9, 76.9, 66.4, 20.2; **HRMS (ESI+):** Calcd. for $C_{24}H_{20}O_2$ ([M+H]+): 341.1536, Found: 341.1528; **Optical rotation:** $[\alpha]_D^{23}$ –210.0 (*c* 1.0, $CHCl_3$) for an enantiomerically enriched sample with 97.5:2.5 er. The enantiomeric ratio was determined by HPLC analysis using Daicel Chiralpak IB column (95:5 *n*-Hexane/*i*-PrOH, 1.0 mL/min, 230 nm, τ_{major} = 21.4 min, τ_{minor} = 40.2 min). The absolute stereochemistry of the product **5w** was assigned in analogy with **4j**.

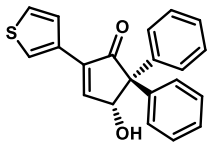


Compound 5x: Purified by preparative TLC (20% EtOAc in hexane); Yellow thick oil (28.0 mg, 0.081 mmol, 81% yield); **FT-IR (Thin film):** 3647 (br), 3060 (w), 2924 (w), 1715 (s), 1492 (s), 1446 (m), 1316 (m), 1240 (m), 1125 (m), 1092 (m), 843 (m), 757 (s), 700 (s); **^{1}H-NMR (400 MHz, $CDCl_3$):** δ 8.01 (t, *J* = 2.4 Hz, 1H), 7.88 (td, *J* = 7.6, 1.8 Hz, 1H), 7.53-7.50 (m, 2H), 7.39-7.28 (m, 7H), 7.22-7.13 (m, 4H), 5.62 (d, *J* = 2.4 Hz, 1H), 1.69 (br s, 1H); **^{13}C-NMR (100 MHz, $CDCl_3$):** δ 203.3, 160.8 Hz (d, *J* = 250.8 Hz), 158.8 (d, *J* = 8.1 Hz), 140.6, 140.0, 138.1 (d, *J* = 2.0 Hz), 130.8 (d, *J* = 8.7 Hz), 130.5 (d, *J* = 2.9 Hz), 129.9, 128.8, 128.7, 128.6, 127.7, 127.5, 124.3 (d, *J* = 3.6 Hz), 118.7 (d, *J* =

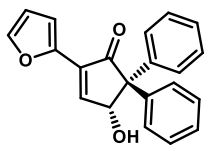


12.7 Hz), 116.0 (d, J = 22.2 Hz), 76.8, 66.3; **HRMS (ESI+):** Calcd. for $C_{23}H_{17}FO_2$ ([M+H]+): 345.1285, Found: 345.1278; **Optical rotation:** $[\alpha]_D^{23}$ −336.0 (*c* 1.0, $CHCl_3$) for an enantiomerically enriched sample with 99:1 er. The enantiomeric ratio was determined by HPLC analysis using Daicel Chiralpak IH column (90:10 *n*-Hexane/*i*-PrOH, 1.0 mL/min, 230 nm, τ_{major} = 14.3 min, τ_{minor} = 17.8 min). The absolute stereochemistry of the product **5x** was assigned in analogy with **4j**.

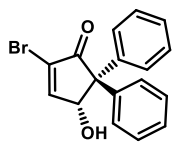
Compound 5y: Purified by preparative TLC (20% EtOAc in hexane); Yellow solid (31.0 mg, 0.093 mmol, 93% yield); **m.p.** 167-169 °C; **FT-IR (Thin film):** 3481 (br), 3118 (m), 1704 (s), 1496 (m), 1303 (m), 1193 (m), 1070 (s), 805 (s), 762 (s), 700 (s); **^{1}H-NMR (400 MHz, $CDCl_3$):** δ 8.23 (dd, J = 3.0, 1.2 Hz, 1H), 7.74 (d, J = 2.8 Hz, 1H), 7.49-7.46 (m, 2H), 7.45 (dd, J = 5.2, 1.3 Hz, 1H), 7.38-7.32 (m, 4H), 7.31-7.26 (m, 3H), 7.15-7.13 (m, 2H), 5.58 (d, J = 2.8 Hz, 1H), 1.67 (br s, 1H); **^{13}C-NMR (75 MHz, $CDCl_3$):** δ 203.8, 152.3, 140.7, 140.2, 138.5, 131.0, 129.9, 128.8, 128.6, 127.7, 127.5, 126.3, 126.1, 126.0, 76.6, 66.9; **HRMS (ESI+):** Calcd. for $C_{21}H_{16}O_2S$ ([M+H]+): 333.0944, Found: 333.0944; **Optical rotation:** $[\alpha]_D^{24}$ −332.0 (*c* 1.0, $CHCl_3$) for an enantiomerically enriched sample with 97.5:2.5 er. The enantiomeric ratio was determined by HPLC analysis using Daicel Chiralpak IA column (90:10 *n*-Hexane/*i*-PrOH, 1.0 mL/min, 230 nm, τ_{minor} = 25.7 min, τ_{major} = 50.0 min). The absolute stereochemistry of the product **5y** was assigned in analogy with **4j**.



Compound 5z: Purified by preparative TLC (20% EtOAc in hexane); Yellow thick oil (26.0 mg, 0.082 mmol, 82% yield); **FT-IR (Thin film):** 3446 (br), 3022 (w), 2925 (w), 1714 /s), 1496 (m), 1445 (m), 1325 (m), 1123 (m), 1013 (m), 754 (s), 699 (s); **^{1}H-NMR (400 MHz, $CDCl_3$):** δ 7.77 (d, J = 2.8 Hz, 1H), 7.50 (d, J = 1.8 Hz, 1H), 7.48-7.44 (m, 2H), 7.37-7.28 (m, 6H), 7.20 (d, J = 3.4 Hz, 1H), 7.14-7.12 (m, 2H), 6.49 (dd, J = 3.4, 1.8 Hz, 1H), 5.59 (d, J = 2.9 Hz, 1H), 1.57 (br s, 1H); **^{13}C-NMR (100 MHz, $CDCl_3$):** δ 201.8, 149.5, 145.8, 143.7, 140.5, 140.0, 134.5, 129.9, 128.8, 128.6, 128.6, 127.7, 127.5, 112.3, 111.9, 76.9, 66.9; **HRMS (ESI+):** Calcd. for $C_{21}H_{16}O_3$ ([M+Na]+): 339.0992, Found: 339.0989; **Optical rotation:** $[\alpha]_D^{24}$ −330.0 (*c* 1.0, $CHCl_3$) for an enantiomerically enriched sample with 96.5:3.5 er. The enantiomeric ratio was determined by HPLC analysis using Daicel Chiralpak IA column (90:10 *n*-Hexane/*i*-PrOH, 1.0 mL/min, 240 nm, τ_{minor} = 14.3 min, τ_{major} = 23.4 min). The absolute stereochemistry of the product **5z** was assigned in analogy with **4j**.



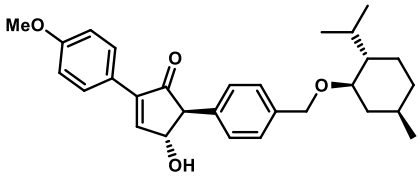
Compound 5aa: Purified by preparative TLC (20% EtOAc in hexane); Yellow thick oil (29.0 mg, 0.088 mmol, 88% yield); **FT-IR (Thin film):** 3446 (br), 1725 (s), 1597 (m), 1496 (m), 1445 (m), 1259 (m), 1061 (m), 679 (m); **^{1}H-NMR (400 MHz, $CDCl_3$):** δ 7.84 (d, J = 2.8 Hz, 1H), 7.45-7.42 (m, 2H), 7.38-7.28 (m, 6H), 7.07-7.04 (m, 2H), 5.49 (d, J = 2.7 Hz, 1H); **^{13}C-NMR (100 MHz, $CDCl_3$):** δ 198.4, 159.1, 139.6, 139.0, 129.7, 128.9, 128.8, 128.5, 128.2, 128.0, 127.9, 77.5, 65.0; **HRMS (ESI+):** Calcd. For



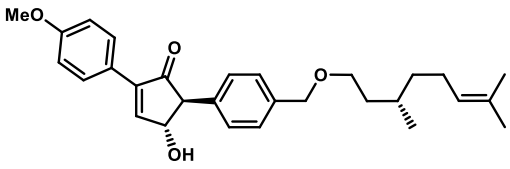
$C_{17}H_{13}BrO_2$ ([M+Na]$^+$): 350.9991, Found: 350.9997; **Optical rotation:** $[\alpha]_D^{24}$ –290.0 (*c* 1.0, $CHCl_3$) for an enantiomerically enriched sample with 94:6 er. The enantiomeric ratio was determined by HPLC analysis using Daicel Chiralpak IF column (95:5 *n*-Hexane/*i*-PrOH, 1.0 mL/min, 245 nm, τ_{major} = 15.9 min, τ_{minor} = 23.8 min). The absolute stereochemistry of the product **5aa** was assigned in analogy with **4j**.

[Note: The dehalogenation of **5aa** under Pd-catalysis (*Tetrahedron Lett*. **2017**, *58*, 2830-2834) failed due to the harsh reaction conditions leading to dehydration and complex product formation.]

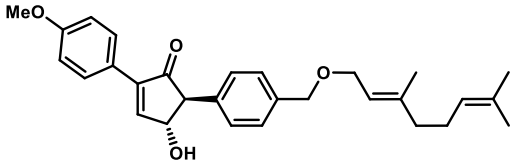
Compound 7a: Diastereoselectivity (dr) > 20:1 was determined by ^{1}H NMR analysis of the crude reaction mixture. Purified by preparative TLC (20% EtOAc in hexane); Yellow thick oil (36.0 mg, 0.080 mmol, 80% yield); **FT-IR (Thin film):** 3407 (br), 2954 (s), 1712 (s), 1606 (m), 1510 (s), 1258 (s), 1180 (s), 924 (w); **^{1}H-NMR (400 MHz, $CDCl_3$):** δ 7.75 (d, *J* = 8.9 Hz, 2H), 7.57 (d, *J* = 2.5 Hz, 1H), 7.32 (d, *J* = 8.0 Hz, 2H), 7.11 (d, *J* = 8.1 Hz, 2H), 6.93 (d, *J* = 8.9 Hz, 2H), 4.87 (t, *J* = 2.7 Hz, 1H), 4.63 (d, *J* = 11.4 Hz, 1H), 4.38 (d, *J* = 11.4 Hz, 1H), 3.83 (s, 3H), 3.50 (d, *J* = 2.8 Hz, 1H), 3.19 (td, *J* = 10.6, 4.1 Hz, 1H), 2.83 (br s, 1H), 2.32-2.24 (m, 1H), 2.20-2.16 (m, 1H), 1.68-1.61 (m, 2H), 1.40-1.35 (m, 1H), 1.32-1.26 (m, 1H), 1.03-0.96 (m, 1H), 0.94 (d, *J* = 6.5 Hz, 3H), 0.92-0.90 (m, 1H), 0.89 (d, *J* = 7.0 Hz, 3H), 0.85-0.81 (m, 1H), 0.73 (d, *J* = 6.9 Hz, 3H); **^{13}C-NMR (100 MHz, $CDCl_3$):** δ 203.7, 160.5, 152.9, 142.8, 138.3, 136.6, 129.1, 128.5, 123.1, 114.1, 79.2, 76.7, 70.3, 63.6, 55.4, 48.4, 40.5, 34.7, 31.7, 25.7, 23.4, 22.5, 21.2, 16.2; **HRMS (ESI+):** Calcd. For $C_{29}H_{36}O_4$ ([M+Na]$^+$): 471.2506, Found: 471.2509; **Optical rotation:** $[\alpha]_D^{24}$ –24.0 (*c* 1.0, $CHCl_3$). The absolute stereochemistry of the product **7a** was assigned in analogy with **4j**.



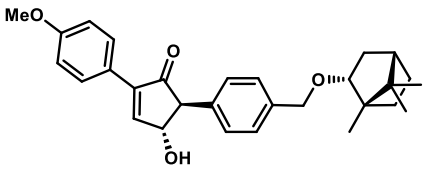
Compound 7b: Diastereoselectivity (dr) > 20:1 was determined by ^{1}H NMR analysis of the crude reaction mixture. Purified by preparative TLC (20% EtOAc in hexane); Yellow oil (39.0 mg, 0.087 mmol, 87% yield); **FT-IR (Thin film):** 3410 (br), 2852 (m), 1712 (s), 1606 (m), 1510 (s), 1258 (s), 1180 (m), 929 (w), 831 (m); **^{1}H-NMR (400 MHz, $CDCl_3$):** δ 7.76 (d, *J* = 8.9 Hz, 2H), 7.58 (d, *J* = 2.5 Hz, 1H), 7.32 (d, *J* = 8.1 Hz, 2H), 7.13 (d, *J* = 8.1 Hz, 2H), 6.93 (d, *J* = 8.9 Hz, 2H), 5.12-5.09 (m, 1H), 4.91 (t, *J* = 2.7 Hz, 1H), 4.48 (s, 2H), 3.83 (s, 3H), 3.55 (d, *J* = 2.9 Hz, 1H), 3.53-3.48 (m, 2H), 2.04-1.93 (m, 2H), 1.68 (s, 3H), 1.67-1.63 (m, 1H), 1.60 (s, 3H), 1.58-1.54 (m, 1H), 1.47-1.40 (m, 1H), 1.37-1.30 (m, 1H), 1.21-1.12 (m, 1H), 0.89 (d, *J* = 6.6 Hz, 3H); **^{13}C-NMR (100 MHz, $CDCl_3$):** δ 203.6, 160.5, 152.8, 142.9, 138.0, 136.6, 131.3, 129.1, 128.6, 128.3, 124.9, 123.1, 114.1, 76.7, 72.7, 69.1, 63.6, 55.4, 37.4, 36.8, 29.7, 25.9, 25.6, 19.7, 17.8; **HRMS (ESI+):** Calcd. For $C_{29}H_{36}O_4$ ([M+Na]$^+$): 471.2506, Found: 471.2507; **Optical rotation:** $[\alpha]_D^{24}$ +22.0 (*c* 1.0, $CHCl_3$). The absolute stereochemistry of the product **7b** was assigned in analogy with **4j**.



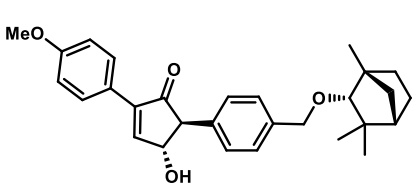
Compound 7c: Purified by preparative TLC (20% EtOAc in hexane); Yellow oil (36.0 mg, 0.081 mmol, 81% yield); **FT-IR (Thin film):** 3410 (br), 1712 (s), 1606 (m), 1511 (s), 1306 (m), 1258 (s), 928 (w), 831 (m); **^{1}H-NMR (400 MHz, $CDCl_3$):** δ 7.75 (d, *J* = 8.9 Hz, 2H), 7.57 (d, *J* = 2.5 Hz, 1H), 7.32 (d, *J* = 8.1 Hz, 2H), 7.12 (d, *J* = 8.1 Hz, 2H), 6.93 (d, *J* = 9.0 Hz, 2H), 5.41-5.37 (m, 1H), 5.12-5.08 (m, 1H), 4.87 (t, *J* = 2.7 Hz, 1H), 4.48 (s, 2H), 4.04 (d, *J* = 6.8 Hz, 2H), 3.83 (s, 3H), 3.51 (d, *J* = 2.9 Hz, 1H), 2.14-2.13 (m, 1H), 2.09-2.03 (m, 1H), 1.68 (s, 3H), 1.65 (s, 3H), 1.61 (s, 3H); **^{13}C-NMR (75 MHz, $CDCl_3$):** δ 203.7, 160.5, 152.9, 142.8, 140.7, 137.8, 136.7, 131.8, 129.1, 128.6, 128.5, 124.1, 123.1, 120.8, 114.1, 76.7, 71.7, 66.8, 63.6, 55.4, 39.7, 26.5, 25.8, 17.8, 16.7; **HRMS (ESI+):** Calcd. For $C_{29}H_{34}O_4$ ($[M+Na]^+$): 469.2349, Found: 469.2338; **Optical rotation:** $[\alpha]_D^{24}$ +26.0 (*c* 1.0, $CHCl_3$) for an enantiomerically enriched sample with 95:5 er. The enantiomeric ratio was determined by HPLC analysis using Daicel Chiralpak IB column (90:10 *n*-Hexane/*i*-PrOH, 1.0 mL/min, 245 nm, τ_{major} = 30.1 min, τ_{minor} = 35.8 min). The absolute stereochemistry of the product **7c** was assigned in analogy with **4j**.



Compound 7d: Diastereoselectivity (dr) > 20:1 was determined by ^{1}H NMR analysis of the crude reaction mixture. Purified by preparative TLC (20% EtOAc in hexane); Yellow thick oil (43.0 mg, 0.096 mmol, 96% yield); **FT-IR (Thin film):** 3433 (br), 2951 (s), 1712 (s), 1606 (m), 1510 (s), 1258 (s), 1118 (m), 831 (m); **^{1}H-NMR (400 MHz, $CDCl_3$):** δ 7.75 (d, *J* = 8.9 Hz, 2H), 7.57 (d, *J* = 2.5 Hz, 1H), 7.32 (d, *J* = 8.1 Hz, 2H), 7.11 (d, *J* = 8.1 Hz, 2H), 6.93 (d, *J* = 8.9 Hz, 2H), 4.90 (t, *J* = 2.7 Hz, 1H), 4.55 (d, *J* = 12.2 Hz, 1H), 4.43 (d, *J* = 12.2 Hz, 1H), 3.83 (s, 3H), 3.71 (ddd, *J* = 9.4, 3.3, 1.8 Hz, 1H), 3.54 (d, *J* = 2.8 Hz, 1H), 2.74 (br s, 1H), 2.17-2.05 (m, 2H), 1.76-1.69 (m, 1H), 1.65 (t, *J* = 4.6 Hz, 1H), 1.29-1.21 (m, 2H), 1.10 (dd, *J* = 13.0, 3.3 Hz, 1H), 0.91 (s, 3H), 0.86 (s, 3H), 0.84 (s, 3H); **^{13}C-NMR (100 MHz, $CDCl_3$):** δ 203.8, 160.5, 152.9, 142.8, 138.8, 136.2, 129.1, 128.4, 127.9, 123.1, 114.1, 84.7, 76.7, 71.4, 63.6, 55.4, 49.5, 48.0, 45.2, 36.3, 28.4, 26.9, 19.9, 19.0, 14.2; **HRMS (ESI+):** Calcd. For $C_{29}H_{34}O_4$ ($[M+H]^+$): 447.2530, Found: 447.2533; **Optical rotation:** $[\alpha]_D^{24}$ −12.0 (*c* 1.0, $CHCl_3$). The absolute stereochemistry of the product **7d** was assigned in analogy with **4j**.

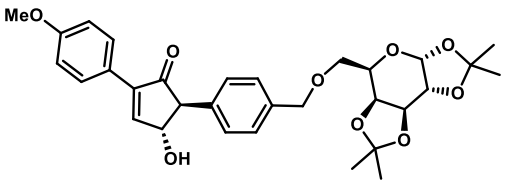


Compound 7e: Diastereoselectivity (dr) > 20:1 was determined by ^{1}H NMR analysis of the crude reaction mixture. Purified by preparative TLC (20% EtOAc in hexane); Yellow thick oil (41.0 mg, 0.092 mmol, 92% yield); **FT-IR (Thin film):** 3434 (br), 2954 (m), 1712 (s), 1606 (m), 1510 (s), 1258 (s), 1180 (m), 831 (m); **^{1}H-NMR (400 MHz, $CDCl_3$):** δ 7.76 (d, *J* = 8.9 Hz, 2H), 7.58 (d, *J* = 2.5 Hz, 1H), 7.34 (d, *J* = 8.2 Hz, 2H), 7.12 (d, *J* = 8.1 Hz, 2H), 6.93 (d, *J* = 8.9 Hz, 2H), 4.92 (t, *J* = 2.7 Hz,

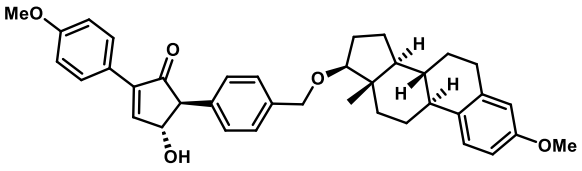


1H), 4.59 (d, *J* = 12.0 Hz, 1H), 4.42 (d, *J* = 12.1 Hz, 1H), 3.83 (s, 3H), 3.58 (d, *J* = 2.8 Hz, 1H), 3.03 (d, *J* = 1.8 Hz, 1H), 1.84-1.77 (m, 1H), 1.73-1.68 (m, 1H), 1.65-1.64 (m, 1H), 1.47-1.36 (m, 2H), 1.10 (s, 3H), 1.10-1.06 (m, 1H), 1.04 (s, 3H), 1.03-1.00 (m, 1H), 0.98 (s, 3H); **^{13}C-NMR (100 MHz, $CDCl_3$):** δ 203.7, 160.5, 152.8, 142.8, 138.8, 136.2, 129.1, 128.3, 128.0, 123.1, 114.1, 92.8, 76.7, 73.2, 63.6, 55.4, 49.4, 48.9, 41.6, 39.7, 31.9, 26.3, 26.2, 20.9, 20.3; **HRMS (ESI+):** Calcd. For $C_{29}H_{34}O_4$ ($[M+H]^+$): 447.2530, Found: 447.2535; **Optical rotation:** $[\alpha]_D^{24}$ +42.0 (*c* 1.0, $CHCl_3$). The absolute stereochemistry of the product **7e** was assigned in analogy with **4j**.

Compound 7f: Diastereoselectivity (dr) > 20:1 was determined by ^{1}H NMR analysis of the crude reaction mixture. Purified by preparative TLC (30% EtOAc in hexane); Yellow thick oil (50.0 mg, 0.091 mmol, 91% yield); **FT-IR (Thin film):** 3457 (br), 1712 (s), 1606 (s), 1511 (s), 1257 (s), 1069 (s), 920 (w), 757 (m); **^{1}H-NMR (400 MHz, $CDCl_3$):** δ 7.75 (d, *J* = 8.9 Hz, 2H), 7.60 (d, *J* = 2.5 Hz, 1H), 7.32 (d, *J* = 8.0 Hz, 2H), 7.11 (d, *J* = 8.2 Hz, 2H), 6.92 (d, *J* = 8.9 Hz, 2H), 5.54 (d, *J* = 5.0 Hz, 1H), 4.88 (t, *J* = 2.7 Hz, 1H), 4.61-4.58 (m, 2H), 4.52 (d, *J* = 12.1 Hz, 1H), 4.31 (dd, *J* = 5.0, 2.4 Hz, 1H), 4.25 (dd, *J* = 7.9, 1.9 Hz, 1H), 4.03-3.99 (m, 1H), 3.83 (s, 3H), 3.71-3.62 (m, 2H), 3.54 (d, *J* = 2.9 Hz, 1H), 1.53 (s, 3H), 1.44 (s, 3H), 1.33 (d, *J* = 3.0 Hz, 6H); **^{13}C-NMR (100 MHz, $CDCl_3$):** δ 203.7, 160.5, 153.0, 142.7, 137.5, 136.8, 129.1, 128.6, 128.5, 123.1, 114.1, 109.4, 108.7, 96.5, 76.6, 73.1, 71.3, 70.8, 70.7, 69.2, 67.1, 63.6, 55.4, 26.2, 26.1, 25.1, 24.6; **HRMS (ESI+):** Calcd. For $C_{31}H_{36}O_9$ ($[M+Na]^+$): 575.2252, Found: 575.2256; **Optical rotation:** $[\alpha]_D^{24}$ –30.0 (*c* 1.0, $CHCl_3$). The absolute stereochemistry of the product **7f** was assigned in analogy with **4j**.



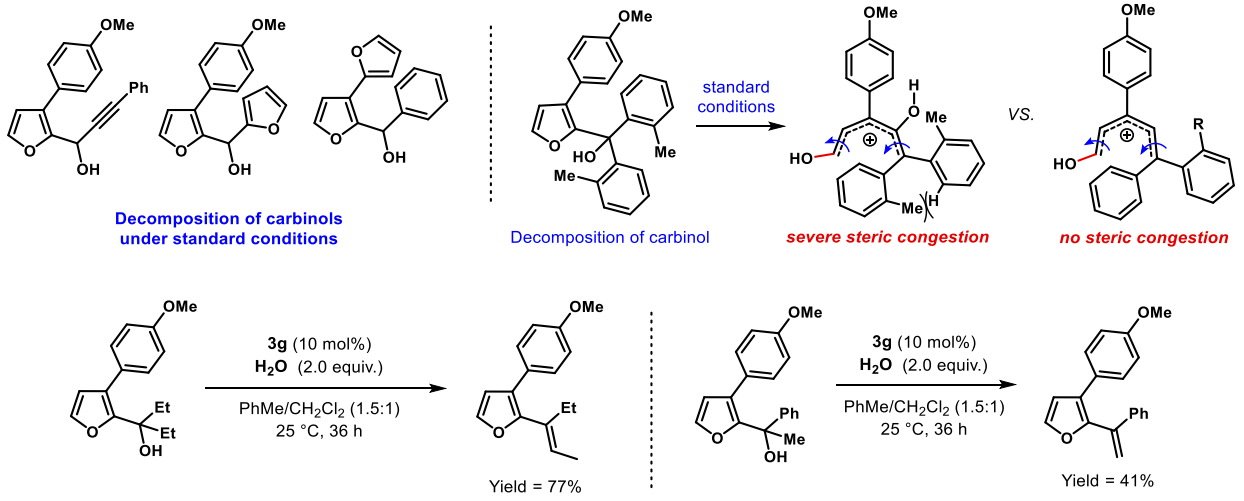
Compound 7g: Diastereoselectivity (dr) > 20:1 was determined by ^{1}H NMR analysis of the crude reaction mixture. Purified by preparative TLC (20% EtOAc in hexane); Yellow thick oil (51.0 mg, 0.088 mmol, 88% yield); **FT-IR (Thin film):** 3436 (br), 2931 (m), 1711 (s), 1607 (m), 1510 (s), 1256 (s), 1036 (s), 831 (m); **^{1}H-NMR (400 MHz, $CDCl_3$):** δ 7.77 (d, *J* = 8.9 Hz, 2H), 7.59 (d, *J* = 2.5 Hz, 1H), 7.34 (d, *J* = 8.1 Hz, 2H), 7.21 (d, *J* = 8.7 Hz, 1H), 7.14 (d, *J* = 8.1 Hz, 2H), 6.94 (d, *J* = 8.9 Hz, 2H), 6.72 (dd, *J* = 8.6, 2.8 Hz, 1H), 6.63 (d, *J* = 2.8 Hz, 1H), 4.92 (t, *J* = 2.7 Hz, 1H), 4.56 (s, 2H), 3.84 (s, 3H), 3.78 (s, 3H), 3.56 (d, *J* = 2.8 Hz, 1H), 3.51 (t, *J* = 8.3 Hz, 1H), 2.88-2.83 (m, 2H), 2.31-2.27 (m, 1H), 2.21-2.15 (m, 1H), 2.11-2.00 (m, 2H), 1.90-1.85 (m, 1H), 1.72-1.58 (m, 2H), 1.53-1.47 (m, 1H), 1.43-1.29 (m, 4H), 1.23-1.16 (m, 1H), 0.87 (s, 3H); **^{13}C-NMR (100 MHz, $CDCl_3$):** δ 203.7, 160.5, 157.5, 152.8, 142.8, 138.6, 138.1, 136.4, 132.9, 129.1, 128.5, 128.0, 126.5, 123.1, 114.1, 113.9, 111.6, 88.5, 76.7, 71.5, 63.6, 55.4, 55.3, 50.4, 44.1, 43.6, 38.8, 38.1, 30.0, 28.1, 27.4, 26.6, 23.3, 12.0; **HRMS**



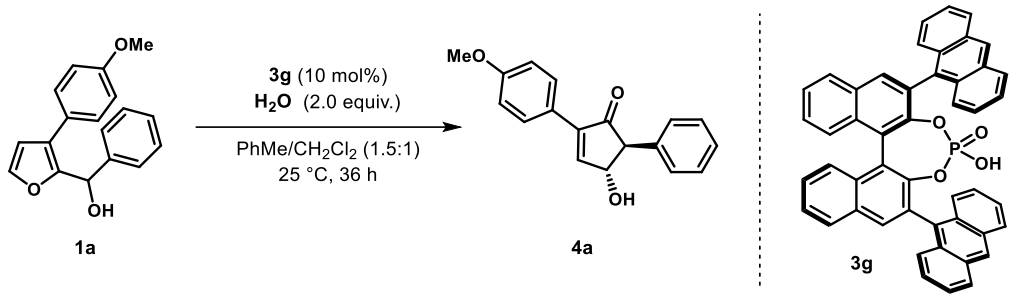
(ESI+): Calcd. For $C_{38}H_{42}O_5$ ([M+H]$^+$): 579.3105, Found: 579.3102; **Optical rotation:** $[\alpha]_D^{24}$ +40.0 (*c* 1.0, $CHCl_3$) The absolute stereochemistry of the product **7g** was assigned in analogy with **4j**.

Compound 7h: Diastereoselectivity (dr) > 20:1 was determined by ^{1}H NMR analysis of the crude reaction mixture. Purified by preparative TLC (30% EtOAc in hexane); Yellow thick oil (55.0 mg, 0.081 mmol, 81% yield); **FT-IR (Thin film):** 3465 (br), 2952 (s), 1710 (s), 1511 (s), 1258 (s), 1180 (m), 1024 (m), 834 (w); **^{1}H-NMR (400 MHz, $CDCl_3$):** δ 7.76 (d, *J* = 8.9 Hz, 2H), 7.57 (d, *J* = 2.5 Hz, 1H), 7.32 (d, *J* = 8.1 Hz, 2H), 7.11 (d, *J* = 8.1 Hz, 2H), 6.93 (d, *J* = 8.9 Hz, 2H), 5.35 (d, *J* = 5.5 Hz, 1H), 4.87 (t, *J* = 2.8 Hz, 1H), 4.54 (s, 2H), 3.83 (s, 3H), 3.51 (d, *J* = 2.9 Hz, 1H), 3.32-3.24 (m, 1H), 2.73 (br s, 1H), 2.44-2.39 (m, 1H), 2.31-2.24 (m, 1H), 2.03-1.93 (m, 3H), 1.88-1.79 (m, 2H), 1.61-1.43 (m, 8H), 1.41-1.20 (m, 5H), 1.20-1.05 (m, 7H), 1.04-0.99 (m, 1H), 1.01 (s, 3H), 0.92 (d, *J* = 6.5 Hz, 3H), 0.87 (d, *J* = 8.4 Hz, 6H), 0.68 (s, 3H); **^{13}C-NMR (100 MHz, $CDCl_3$):** δ 203.7, 160.5, 152.9, 142.8, 141.0, 138.3, 136.6, 129.1, 128.6, 128.3, 123.1, 121.8, 114.1, 78.8, 76.7, 69.7, 63.6, 56.9, 56.3, 55.4, 50.3, 42.5, 39.9, 39.7, 39.3, 37.4, 37.0, 36.3, 35.9, 32.1, 32.0, 28.6, 28.4, 28.2, 24.4, 24.0, 23.0, 22.7, 21.2, 19.5, 18.9, 12.0; **HRMS (ESI+):** Calcd. For $C_{46}H_{62}O_4$ ([M+Na]$^+$): 701.4540, Found: 701.4543; **Optical rotation:** $[\alpha]_D^{24}$ +2.0 (*c* 1.0, $CHCl_3$). The absolute stereochemistry of the product **7h** was assigned in analogy with **4j**.

VIII. Unsuccessful substrates for enantioselective oxa-Piancatelli rearrangement:

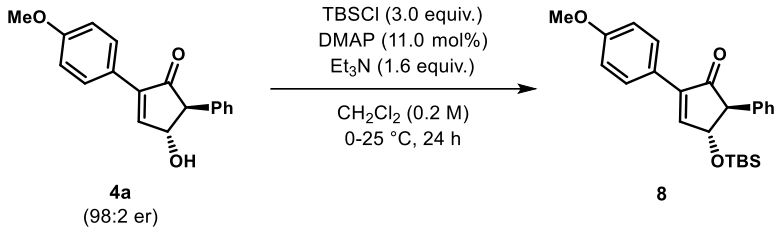


IX. Large scale synthesis of 4a:



In an oven and vacuum-dried 100 mL reaction tube, 2-furyl carbinol **1a** (561.0 mg, 2.00 mmol, 1.0 equiv) and H_2O (72.0 µL, 4.00 mmol, 2.0 equiv) were taken with 10.0 mL of toluene/CH_2Cl_2 (1.5:1) and stirred for 5 min. To this solution, catalyst **3g** (140.0 mg, 0.20 mmol, 10 mol%) was added along with 10.0 mL of toluene/CH_2Cl_2 (1.5:1) and the resulting mixture was stirred at 25 °C until TLC (20% EtOAc in hexane) revealed complete consumption of **1a** (36 h). The reaction mixture was concentrated under reduced pressure to obtain a reddish-brown oil. This residue was purified by silica-gel flash column chromatography (13% EtOAc in hexane) to obtain **4a** as yellow thick oil (527.0 mg, 1.88 mmol, 94% yield) with 98:2 er.

X. Procedure for the γ-hydroxy protection of 4a:

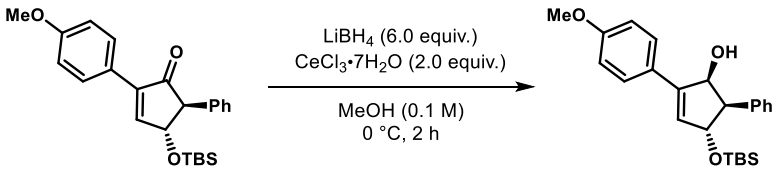


In an oven dried 10 mL round-bottom flask, **4a** (204.0 mg, 0.73 mmol, 1.0 equiv), TBSCl (330.0 mg, 2.19 mmol, 3.0 equiv), and DMAP (9.8 mg, 0.08 mmol, 0.11 equiv) were taken, degassed, purged with nitrogen, and dissolved in 3.5 mL dry CH_2Cl_2. Then, the reaction mixture was cooled to 0 °C and Et_3N (0.16 mL, 1.17 mmol, 1.6 equiv) was added dropwise. The reaction mixture was then slowly warmed to 25 °C and stirred for 24 h under nitrogen. The reaction was quenched with H_2O (10 mL) and the organic layer was separated from the aqueous layer. The aqueous layer was extracted with EtOAc (3 × 10.0 mL). Combined organic layer was washed with brine (10.0 mL), dried over anh. Na_2SO_4 and concentrated under reduced pressure to obtain crude product. The crude product was purified by silica-gel column chromatography (2% EtOAc in hexane) to obtain **8** as a colorless oil, essentially as a single diastereomer (254.0 mg, 0.644 mmol, 88% yield); **FT-IR (Thin film):** 2954 (m), 1715 (s), 1606 (m), 1510 (s), 1258 (s), 1180 (m), 906 (w), 779 (m); **^{1}H-NMR (300 MHz, $CDCl_3$):** δ 7.77 (d, *J* = 8.9 Hz, 2H), 7.52 (d, *J* = 2.5 Hz, 1H), 7.38-7.27 (m, 3H), 7.16-7.13 (m, 2H), 6.93 (d, *J* = 9.0 Hz, 2H), 4.93 (t, *J* = 2.6 Hz, 1H), 3.83 (s,

3H), 3.62 (d, *J* = 2.8 Hz, 1H), 0.89 (s, 9H), -0.01 (s, 3H), -0.05 (s, 3H); **^{13}C-NMR (75 MHz, $CDCl_3$):** δ 203.8, 160.4, 153.8, 142.3, 137.7, 129.1, 128.9, 128.7, 127.4, 123.3, 114.1, 76.7, 64.6, 55.4, 25.9, 18.2, -4.5, -4.7; **HRMS (ESI+):** Calcd. For $C_{24}H_{30}O_3Si$ ($[M+H]^+$): 395.2037, Found: 395.2037; **Optical rotation:** $[\alpha]_D^{24}$ –6.0 (*c* 1.0, $CHCl_3$) for an enantiomerically enriched sample with 97.5:2.5 er. The enantiomeric ratio was determined by HPLC analysis using Daicel Chiralpak IE column (95:5 *n*-Hexane/*i*-PrOH, 1.0 mL/min, 245 nm, τ_{minor} = 18.4 min, τ_{major} = 19.5 min). The absolute stereochemistry of the product **8** was assigned in analogy with **4j**.

[*Note*: This compound is sensitive to silica-gel and rapid chromatographic purification is necessary.]

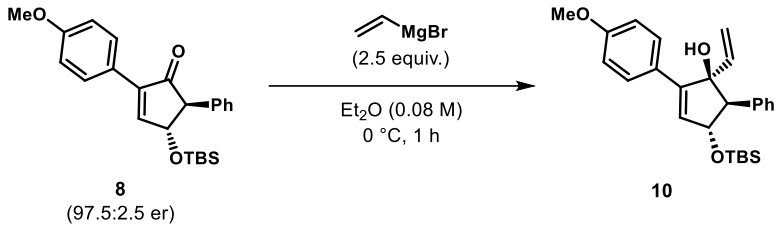
XI. Procedure for selective reduction of the carbonyl group of 8:



8 (97.5:2.5 er) → **9**

In an oven dried 10 mL 2-necked round-bottom flask, **8** (30.0 mg, 0.075 mmol, 1.0 equiv.) and $CeCl_3 \cdot 7H_2O$ (56.0 mg, 0.15 mmol, 2.0 equiv.) were taken in 0.75 mL of dry methanol under nitrogen and the resulting solution was cooled to 0 °C. To this solution, $LiBH_4$ (10.0 mg, 0.45 mmol, 6.0 equiv.) was added portionwise and the resulting mixture was stirred at 0 °C. After 2 h, the reaction mixture was quenched with 2 mL of sat. NH_4Cl solution and diluted with 5 mL EtOAc. The organic layer was separated from the aqueous layer and the aqueous layer was extracted with EtOAc (3 × 5.0 mL). The combined organic layer was washed with brine (5.0 mL), dried over anh. Na_2SO_4 and concentrated under reduced pressure. The crude product was purified by preparative TLC (10% EtOAc in hexane) to obtain **9** as a yellow oil, essentially as a single diastereomer (19.0 mg, 0.048 mmol, 64% yield); **FT-IR (Thin film):** 3472 (br), 2929 (m), 1603 (s), 1512 (s), 1255 (s), 1179 (s), 1033 (m), 835 (s); **^{1}H-NMR (400 MHz, $CDCl_3$):** δ 7.55 (d, *J* = 9.0 Hz, 2H), 7.41-7.35 (m, 4H), 7.32-7.29 (m, 1H), 6.89 (d, *J* = 8.9 Hz, 2H), 6.25 (d, *J* = 1.8 Hz, 1H), 5.34 (dt, *J* = 6.3, 1.7 Hz, 1H), 5.15 (d, *J* = 5.4 Hz, 1H), 3.82 (s, 3H), 3.36 (t, *J* = 6.2 Hz, 1H), 0.81 (s, 9H), -0.06 (s, 3H), -0.16 (s, 3H); **^{13}C-NMR (100 MHz, $CDCl_3$):** δ 159.7, 143.5, 137.6, 131.4, 129.9, 128.6, 127.9, 127.3, 127.2, 114.1, 81.5, 76.8, 61.0, 55.4, 25.9, 18.2, -4.6, -4.6; **HRMS (EI):** Calcd. for $C_{24}H_{32}O_3Si$ (M^+): 396.2115, Found: 396.2128; **Optical rotation:** $[\alpha]_D^{24}$ –76.0 (*c* 1.0, $CHCl_3$) for an enantiomerically enriched sample with 97.5:2.5 er. The enantiomeric ratio was determined by HPLC analysis using Daicel Chiralpak IA column (95:5 *n*-Hexane/*i*-PrOH, 1.0 mL/min, 260 nm, τ_{major} = 25.5 min, τ_{minor} = 38.2 min). The relative stereochemistry was determined by 1D NOE experiment.

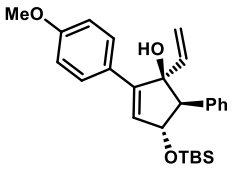
XII. Procedure for vinyl Grignard addition on the carbonyl group of 8:



8 (97.5:2.5 er) **10**

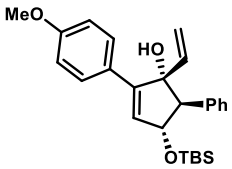
In an oven dried 10 mL 2-necked round-bottom flask, **8** (30.0 mg, 0.075 mmol, 1.0 equiv.) was taken in 1.0 mL of dry Et_2O under nitrogen and the resulting solution was cooled to 0 °C. To this solution, vinyl magnesium bromide (1 M in THF) (0.2 mL, 0.19 mmol, 2.5 equiv.) was added dropwise and the resulting mixture was stirred at 0 °C. After 2 h, the reaction mixture was quenched with 2 mL H_2O and diluted with 5 mL EtOAc. The organic layer was separated from the aqueous layer and the aqueous layer was extracted with EtOAc (3 × 5.0 mL). The combined organic layer was washed with brine (5.0 mL), dried over anh. Na_2SO_4 and concentrated under reduced pressure. The crude product (with 1.2:1 dr, as obtained from ^{1}H-NMR) was purified by preparative TLC (10% EtOAc in hexane) to obtain **10** (both diastereomers are separable) as a yellow thick oil (20.0 mg, 0.047 mmol, 63% combined yield).

Compound 10 (major diastereomer)**:** Purified by preparative TLC (10% EtOAc in hexane);



Yellow thick oil (12.0 mg, 0.028 mmol, 38% yield); **FT-IR (Thin film):** 3491 (br), 2855 (s), 1606 (s), 1513 (s), 1473 (s), 1253 (s), 1034 (s), 884 (m); **^{1}H-NMR (400 MHz, CD_2Cl_2):** δ 7.53 (d, *J* = 8.8 Hz, 2H), 7.39-7.35 (m, 2H), 7.33-7.29 (m, 3H), 6.83 (d, *J* = 8.9 Hz, 2H), 6.21 (d, *J* = 1.9 Hz, 1H), 6.04 (dd, *J* = 17.3, 10.8 Hz, 1H), 5.29 (dd, *J* = 6.1, 1.9 Hz, 1H), 5.10 (dd, *J* = 10.8, 1.2 Hz, 1H), 5.05 (dd, *J* = 17.3, 1.2 Hz, 1H), 3.79 (s, 3H), 3.27 (d, *J* = 6.1 Hz, 1H), 1.70 (s, 1H), 0.81 (s, 9H), -0.03 (s, 3H), -0.18 (s, 3H); **^{13}C-NMR (100 MHz, CD_2Cl_2):** δ 159.8, 145.6, 143.6, 136.6, 133.2, 130.6, 129.2, 128.7, 127.8, 127.6, 113.8, 113.7, 85.3, 80.0, 66.5, 55.6, 25.9, 18.3, -4.6; **HRMS (ESI+):** Calcd. For $C_{26}H_{34}O_3Si$ ($[M+Na]^+$): 445.2169, Found: 445.2180; **Optical rotation:** $[\alpha]_D^{24}$ –24.0 (*c* 1.0, $CHCl_3$) for an enantiomerically enriched sample with 97:3 er. The enantiomeric ratio was determined by HPLC analysis using Daicel Chiralpak IB column (95:5 *n*-Hexane/*i*-PrOH, 1.0 mL/min, 264 nm, τ_{minor} = 5.8 min, τ_{major} = 7.2 min). The relative stereochemistry was determined by 1D NOE experiment.

Compound 10 (minor diastereomer)**:** Purified by preparative TLC (10% EtOAc in hexane);

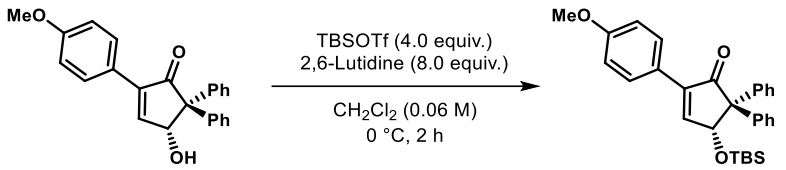


Yellow thick oil (8.0 mg, 0.029 mmol, 25% yield); **FT-IR (Thin film):** 3445 (br), 2955 (m), 1606 (m), 1512 (s), 1255 (s), 1180 (m), 992 (s), 837 (s); **^{1}H-NMR (400 MHz, CD_2Cl_2):** δ 7.59 (d, *J* = 8.9 Hz, 2H), 7.33-7.23 (m, 5H), 6.84 (d, *J* = 8.9 Hz, 2H), 6.21 (d, *J* = 1.9 Hz, 1H), 5.57 (dd, *J* = 17.3, 10.7 Hz, 1H), 5.10 (dd, *J* = 17.4, 1.5 Hz, 1H), 5.03-4.98 (m, 2H), 3.79 (s, 3H), 3.37 (d,

J = 7.0 Hz, 1H), 2.30 (s, 1H), 0.81 (s, 9H), 0.02 (s, 3H), -0.15 (s, 3H); **^{13}C-NMR (75 MHz, $CDCl_3$):** δ 159.9, 146.0, 140.8, 137.6, 130.5, 130.2, 129.1, 128.2, 127.2, 126.9, 114.6, 113.9, 86.6, 76.9, 70.4, 55.6, 25.9, 18.3, -4.5, -4.6; **HRMS (EI):** Calcd. for $C_{26}H_{34}O_3Si$ (M^+): 422.2272, Found: 422.2283; **Optical rotation:** $[\alpha]_D^{24}$ –108.0 (*c* 1.0, $CHCl_3$) for an enantiomerically enriched sample with 97.5:2.5 er. The enantiomeric ratio was determined by HPLC analysis using Daicel Chiralpak IA column (90:10 *n*-Hexane/*i*-PrOH, 1.0 mL/min, 265 nm, τ_{minor} = 12.0 min, τ_{major} = 14.1 min).

[*Note*: This compound **10** is sensitive to temperature, pH, and rotary evaporation at 25 °C is necessary.]

XIII. Procedure for the γ-hydroxy protection of 5a:

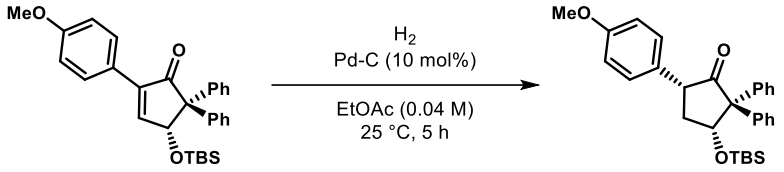


5a (99:1 er) → **11**

In an oven dried 10 mL round-bottom flask, **5a** (120.0 mg, 0.34 mmol, 1.0 equiv) was taken, degassed, purged with nitrogen, and dissolved in 6.0 mL dry CH_2Cl_2. Then, the solution was cooled to 0 °C and 2,6-lutidine (0.32 mL, 2.70 mmol, 8.0 equiv) was added dropwise. The resulting solution was stirred for 5 min and TBSOTf (0.30 mL, 1.34 mmol, 4.0 equiv) was added and stirred for 2 h at 0 °C under nitrogen. The reaction was quenched with 5 mL of sat. $NaHCO_3$ solution and the organic layer was separated from the aqueous layer. The aqueous layer was extracted with CH_2Cl_2 (3 × 5.0 mL). The combined organic layer was washed with brine (5.0 mL), dried over anh. Na_2SO_4 and concentrated under reduced pressure to obtain crude product. The crude product was purified by silica-gel column chromatography (2% EtOAc in hexane) to obtain **11** as a colorless oil (156.0 mg, 0.331 mmol, 97% yield); **FT-IR (Thin film):** 2855 (m), 1715 (s), 1606 (m), 1510 (s), 1258 (s), 1121 (s), 1034 (m), 834 (s); **^{1}H-NMR (400 MHz, $CDCl_3$):** δ 7.72 (d, *J* = 8.9 Hz, 2H), 7.61 (d, *J* = 2.7 Hz, 1H), 7.41-7.38 (m, 2H), 7.35-7.30 (m, 2H), 7.29-7.27 (m, 1H), 7.25-7.15 (m, 5H), 6.91 (d, *J* = 8.9 Hz, 2H), 5.40 (d, *J* = 2.7 Hz, 1H), 3.82 (s, 3H), 0.73 (s, 9H), 0.08 (s, 3H), -0.15 (s, 3H); **^{13}C-NMR (100 MHz, $CDCl_3$):** δ 204.2, 160.5, 152.8, 141.8, 141.6, 140.6, 130.9, 129.1, 128.9, 128.4, 127.5, 127.2, 126.5, 123.6, 114.1, 77.9, 68.4, 55.5, 25.7, 18.0, -4.1, -4.9; **HRMS (ESI+):** Calcd. For $C_{30}H_{34}O_3Si$ ($[M+H]^+$): 471.2350, Found: 471.2354; **Optical rotation:** $[\alpha]_D^{24}$ –140.0 (*c* 1.0, $CHCl_3$) for an enantiomerically enriched sample with 99:1 er. The enantiomeric ratio was determined by HPLC analysis using Daicel Chiralpak IE column (95:5 *n*-Hexane/*i*-PrOH, 1.0 mL/min, 254 nm, τ_{minor} = 12.8 min, τ_{major} = 13.6 min). The absolute stereochemistry of the product **11** was assigned in analogy with **4j**.

[*Note*: This compound is sensitive to silica-gel and rapid chromatographic purification is necessary.]

XIV. Procedure for selective reduction of the conjugated double bond of 11:

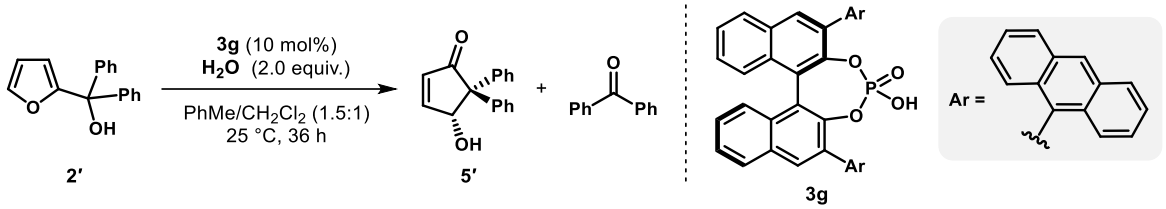


11 (99:1 er) **12**

In an oven dried 10 mL 2-necked round-bottom flask, **11** (35 mg, 0.075 mmol, 1.0 equiv.) and 10% Pd-C (8 mg, 0.008 mmol, 0.1 equiv.) was taken in 2.0 mL of dry EtOAc. The resulting mixture was degassed and stirred under H_2 balloon pressure for 5 h at 25 °C. The reaction mixture was filtered over Celite® and washed with EtOAc. The filtrate was concentrated under reduced pressure to obtain crude. The crude product was purified by preparative TLC (5% EtOAc in hexane) to obtain **12** as a colorless oil, essentially as a single diastereomer (27.0 mg, 0.057 mmol, 76% yield); **FT-IR (Thin film):** 2954 (m), 1742 (s), 1513 (s), 1252 (s), 1079 (m), 1034 (m), 835 (s), 777 (s); **^{1}H-NMR (400 MHz, $CDCl_3$):** δ 7.36-7.27 (m, 7H), 7.24-7.20 (m, 3H), 7.08 (d, *J* = 8.8 Hz, 2H), 6.82 (d, *J* = 8.9 Hz, 2H), 4.90 (dd, *J* = 6.8, 5.3 Hz, 1H), 3.78 (s, 3H), 3.58-3.53 (m, 1H), 2.82 (ddd, *J* = 13.2, 10.0, 5.3 Hz, 1H), 2.39 (ddd, *J* = 13.2, 8.6, 6.7 Hz, 1H), 0.82 (s, 9H), -0.10 (s, 3H), -0.27 (s, 3H); **^{13}C-NMR (100 MHz, $CDCl_3$):** δ 214.4, 158.7, 141.5, 138.7, 131.6, 130.9, 129.8, 128.8, 128.5, 127.6, 127.3, 126.9, 114.1, 68.1, 55.4, 52.1, 37.0, 25.9, 18.2, -4.8, -5.4; **HRMS (ESI+):** Calcd. For $C_{30}H_{36}O_3Si$ ($[M+Na]^+$): 495.2326, Found: 495.2327; **Optical rotation:** $[\alpha]_D^{24}$ –50.0 (*c* 1.0, $CHCl_3$) for an enantiomerically enriched sample with 99:1 er. The enantiomeric ratio was determined by HPLC analysis using Daicel Chiralpak IE column (90:10 *n*-Hexane/*i*-PrOH, 1.0 mL/min, 230 nm, τ_{major} = 9.7 min, τ_{minor} = 15.0 min). The relative stereochemistry was determined by 1D NOE experiment.

XV. Control experiments:

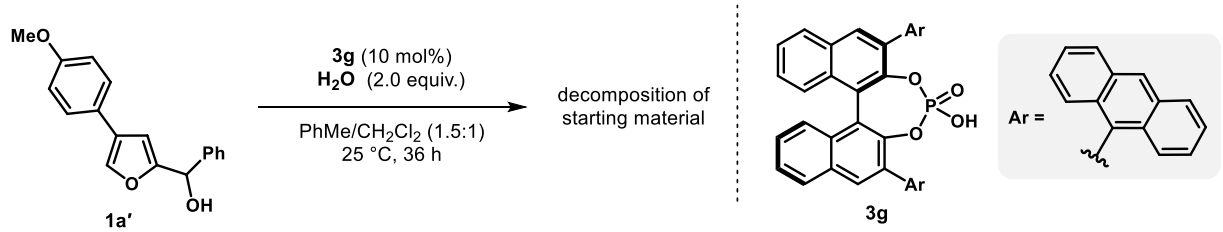
A) Reaction with tertiary 2-furyl carbinol 2′:



In a screw-cap vial, 2-furyl carbinol **2′** (25.0 mg, 0.10 mmol, 1.0 equiv) and H_2O (3.6 µL, 0.20 mmol, 2.0 equiv) were taken with 0.5 mL of toluene/CH_2Cl_2 (1.5:1) and stirred for 5 min. To this solution, catalyst **3g** (7.0 mg, 0.01 mmol, 10 mol%) was added along with 0.5 mL of toluene/CH_2Cl_2 (1.5:1) and the resulting mixture was stirred at 25 °C until TLC (20% EtOAc in hexane) revealed complete consumption of **2′** (36 h). The reaction mixture was concentrated under reduced pressure to obtain a reddish-brown oil. This residue was purified by preparative TLC (20% EtOAc in hexane) to obtain **5′** as a yellow oil (4.0 mg, 0.016 mmol, 16% yield) and benzophenone as colorless oil (2.0 mg, 0.011 mmol, 11% yield). The spectroscopic data is in agreement with the literature.[3]

Compound 5′: ^{1}H-NMR (400 MHz, $CDCl_3$): δ 8.01 (dd, *J* = 5.9, 2.4 Hz, 1H), 7.71-7.68 (m, 2H), 7.63-7.52 (m, 6H), 7.39-7.36 (m, 2H), 6.69 (dd, *J* = 5.9, 1.3 Hz, 1H), 5.81 (dd, *J* = 2.5, 1.3 Hz, 1H), 1.86 (br s, 1H).

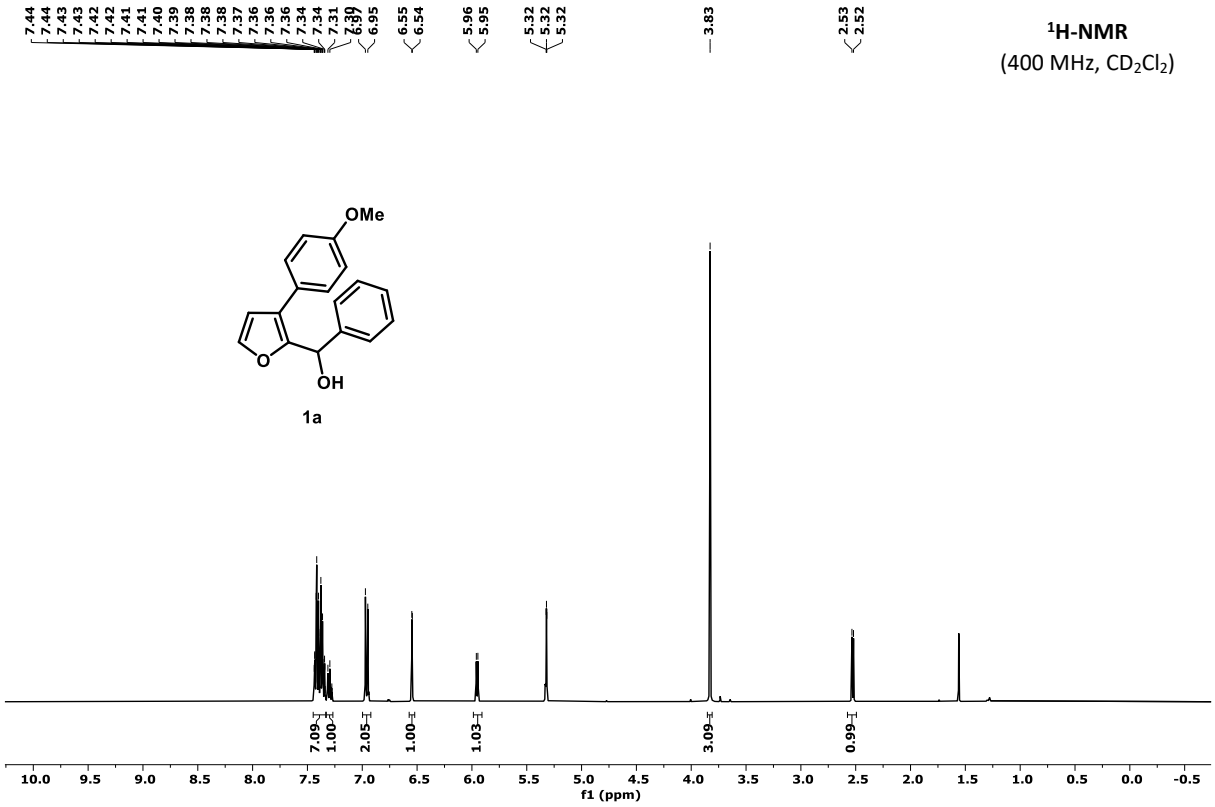
B) Reaction with secondary 2-furyl carbinol 1a′:



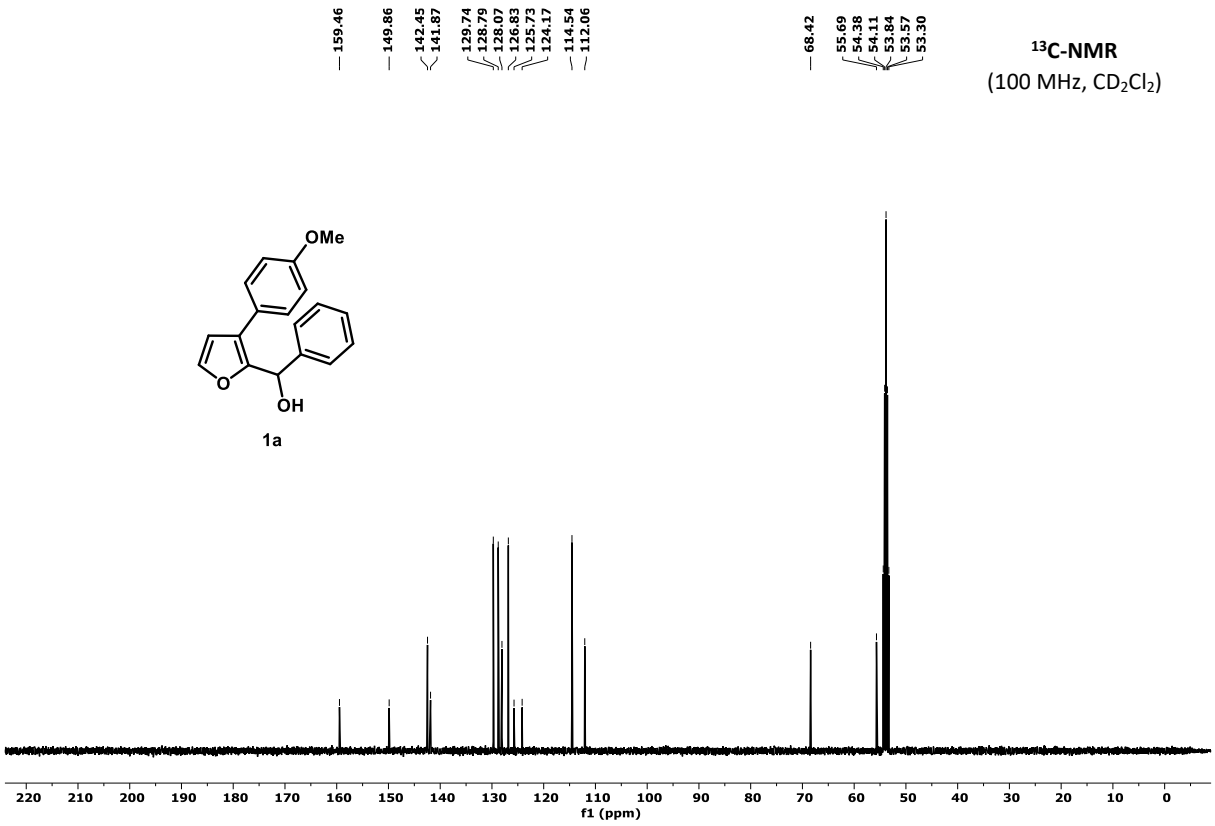
In a screw-cap vial, 2-furyl carbinol **1a′** (28.0 mg, 0.10 mmol, 1.0 equiv) and H_2O (3.6 µL, 0.20 mmol, 2.0 equiv) were taken with 0.5 mL of toluene/CH_2Cl_2 (1.5:1) and stirred for 5 min. To this solution, catalyst **3g** (7.0 mg, 0.01 mmol, 10 mol%) was added along with 0.5 mL of toluene/CH_2Cl_2 (1.5:1) and the resulting mixture was stirred at 25 °C for 36 h. After 36 h, the reaction only leads to the decomposition of alcohol **1a′** as observed by TLC (20% EtOAc in hexane).

[3] D. Fisher, L. I. Palmer, J. E. Cook, J. E. Davis, J. Read de Alaniz, *Tetrahedron* **2014**, *70*, 4105.

XVI. NMR-Spectra and HPLC-Chromatograms

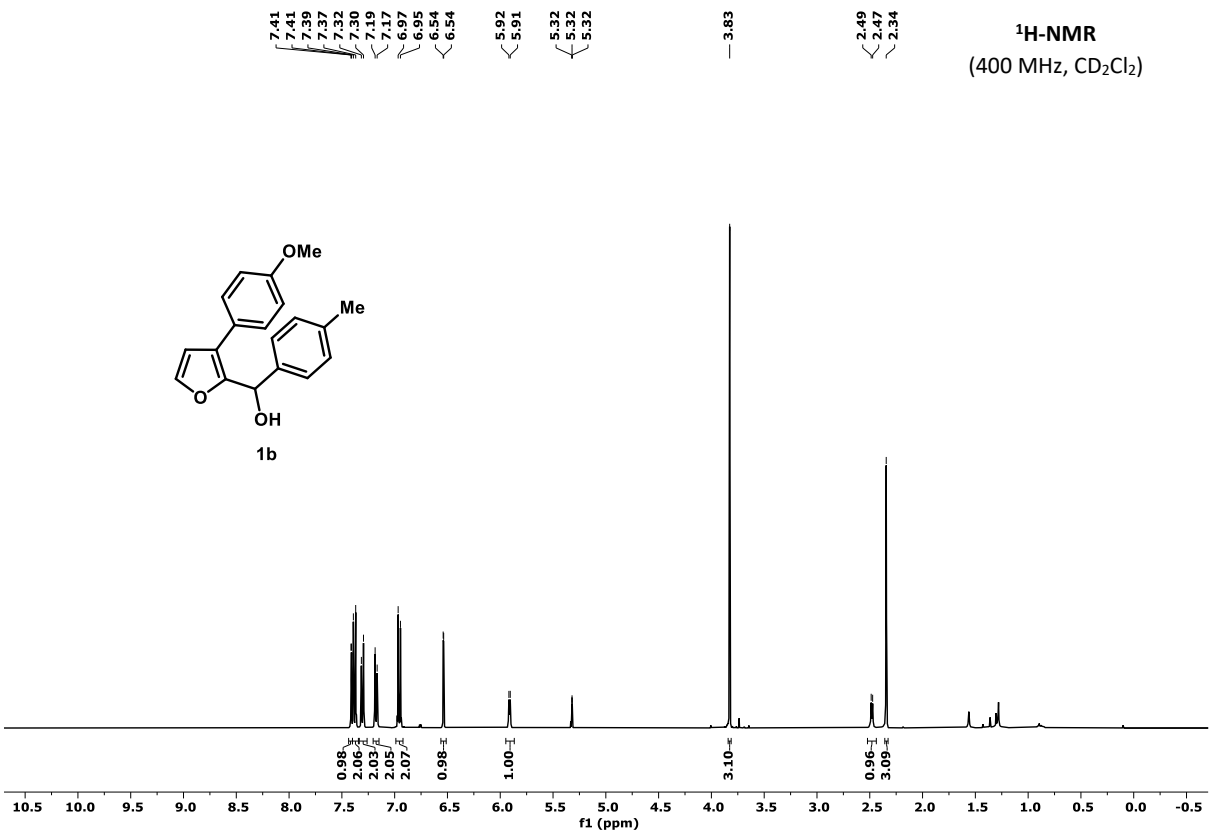


^{1}H-NMR
(400 MHz, CD_2Cl_2)

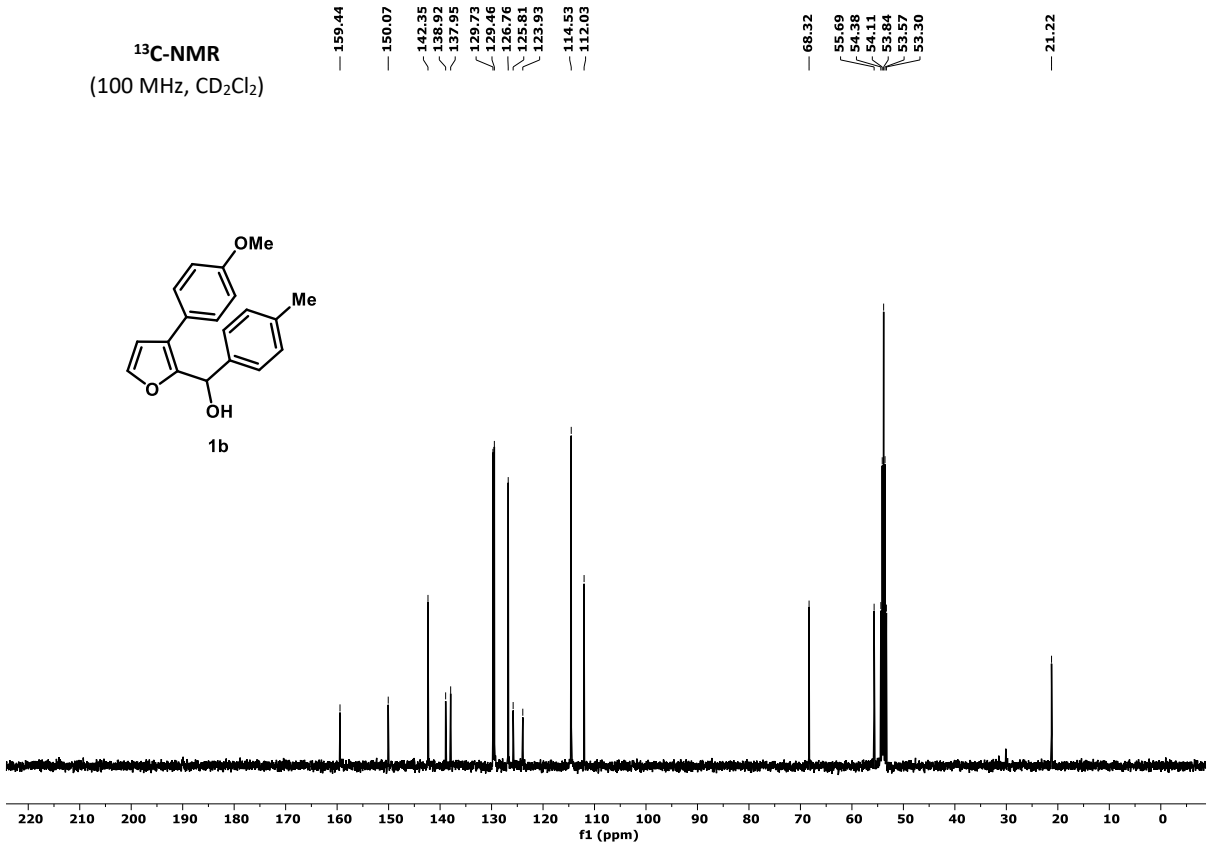


^{13}C-NMR
(100 MHz, CD_2Cl_2)

^{1}H-NMR
(400 MHz, CD_2Cl_2)



^{13}C-NMR
(100 MHz, CD_2Cl_2)



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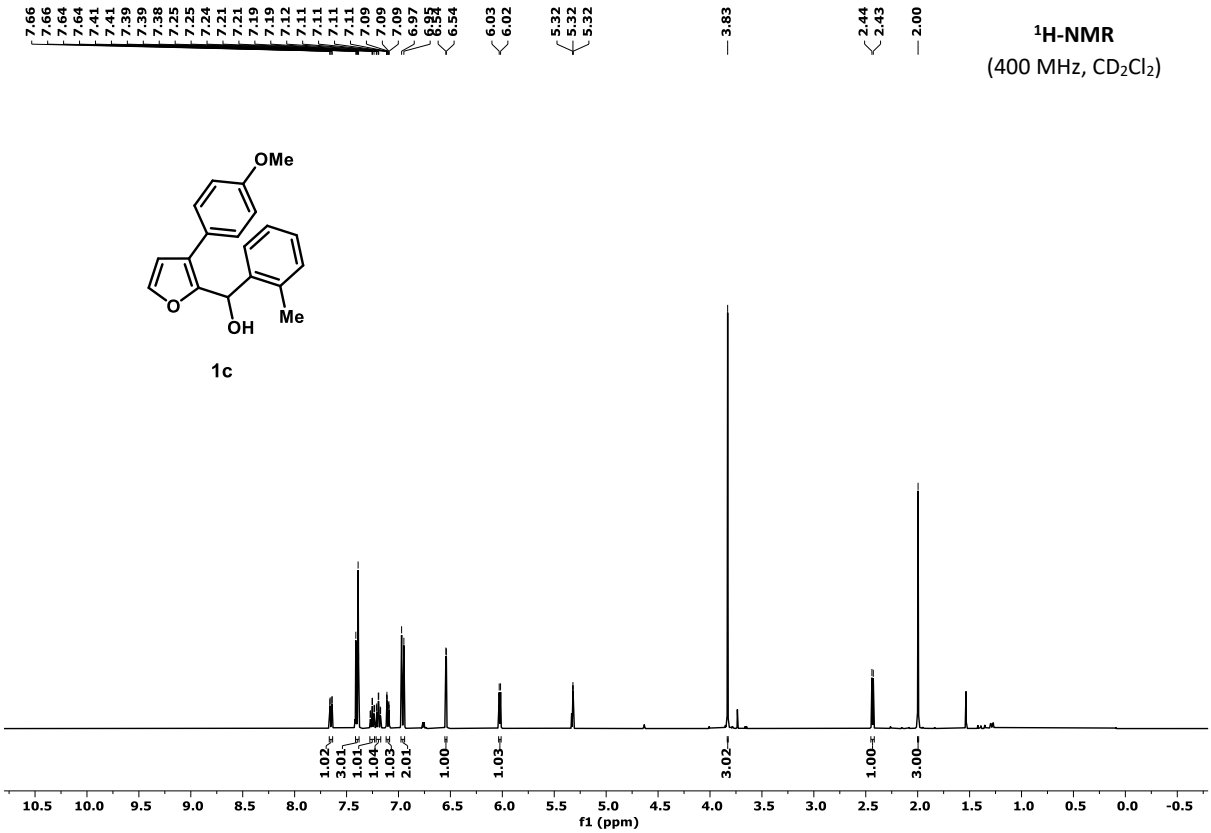
(400 MHz, CD_2Cl_2)



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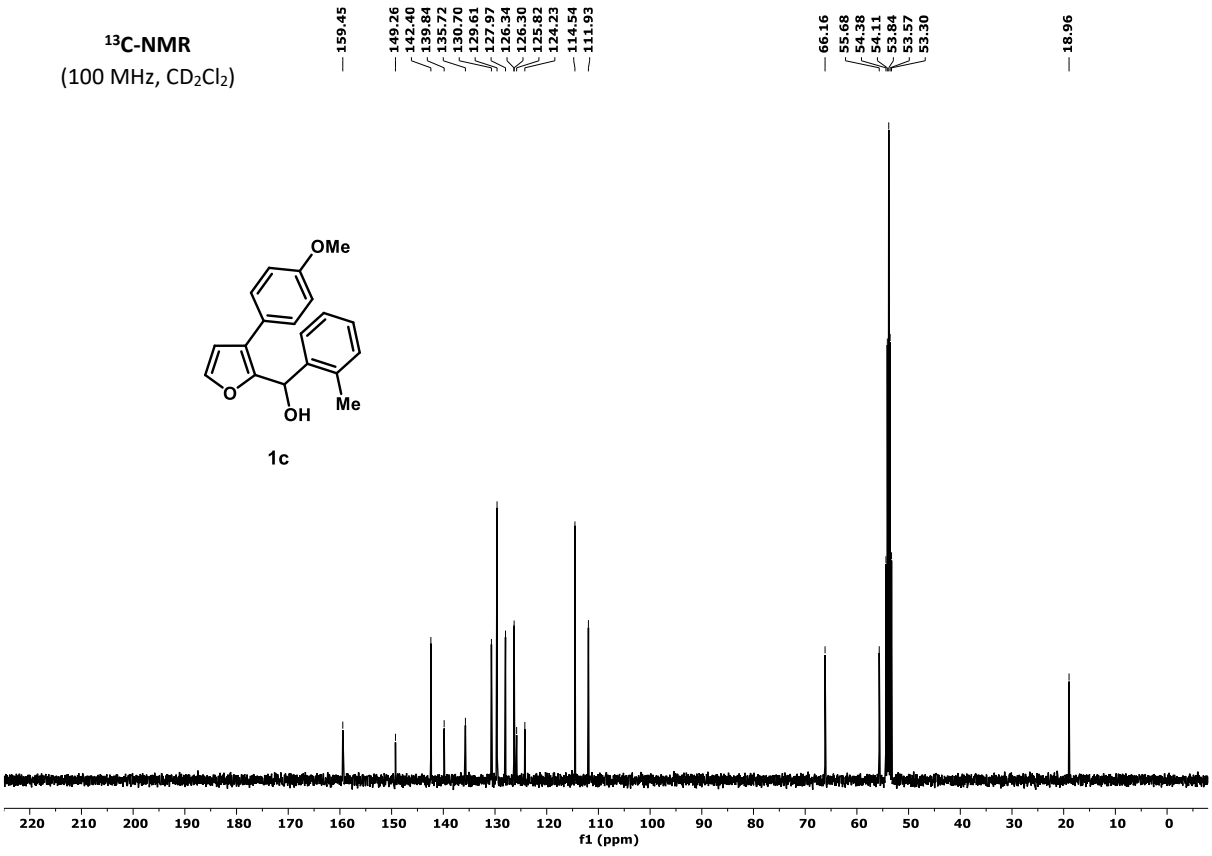
(100 MHz, CD_2Cl_2)



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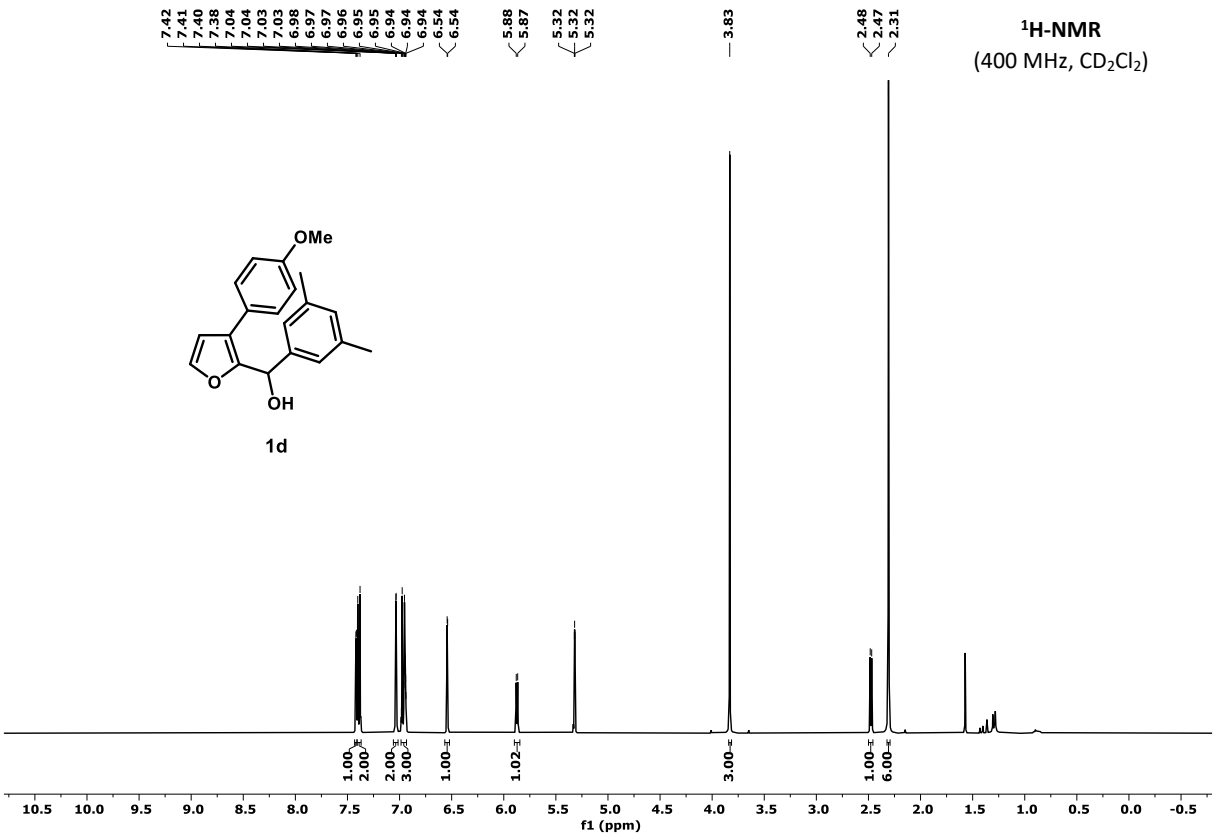
(400 MHz, CD_2Cl_2)



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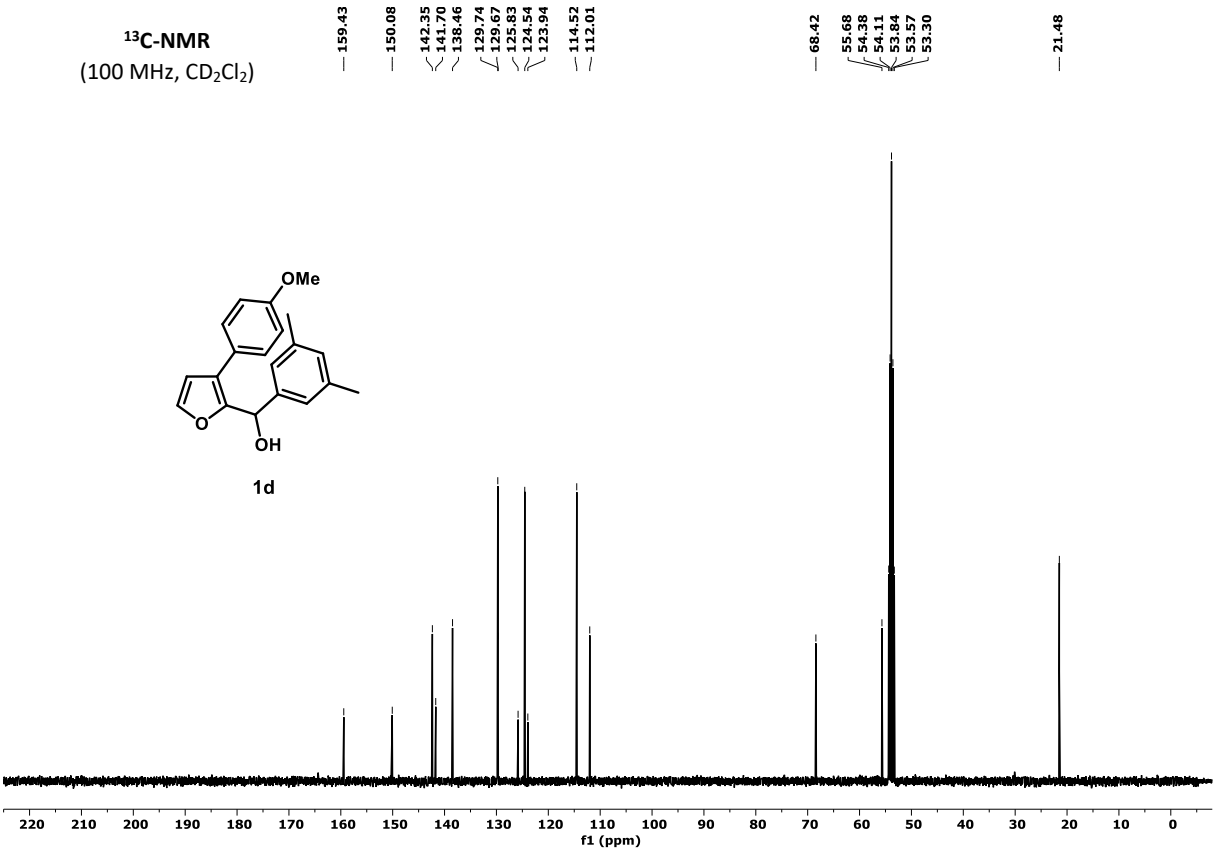
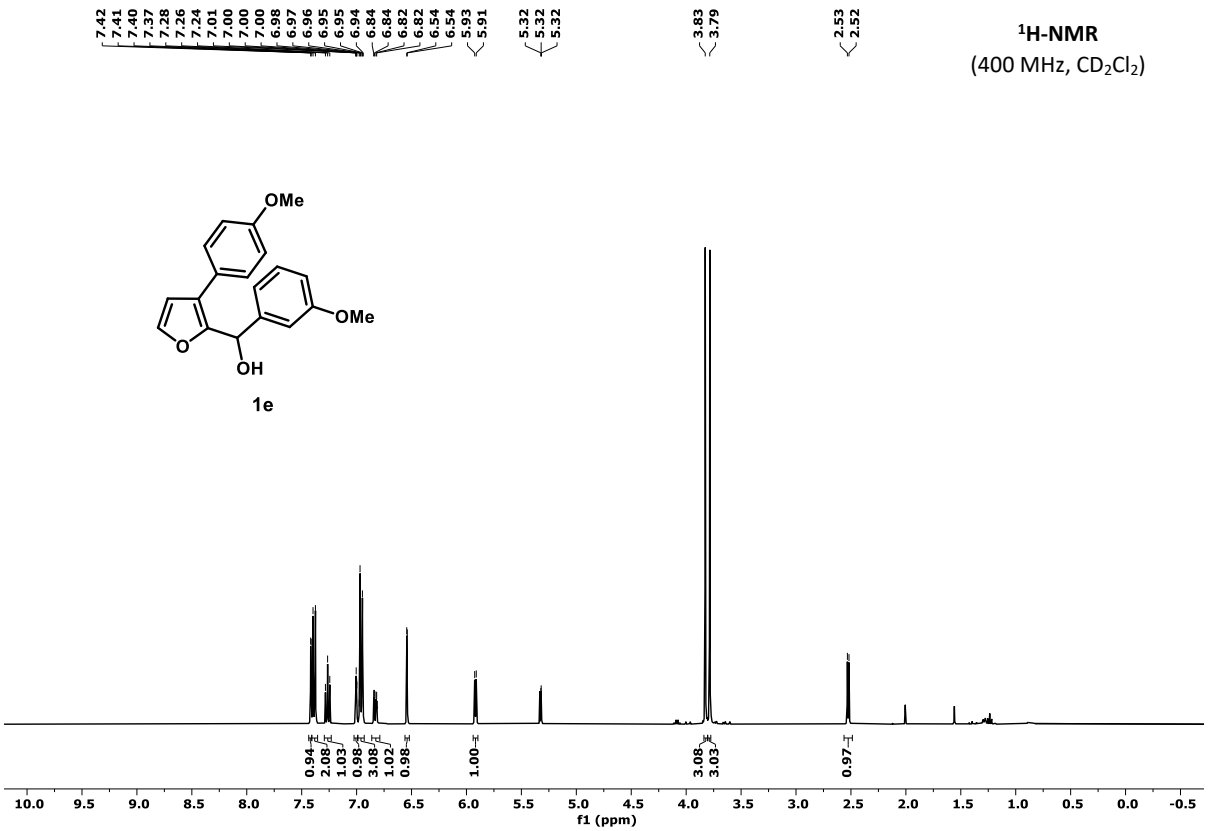
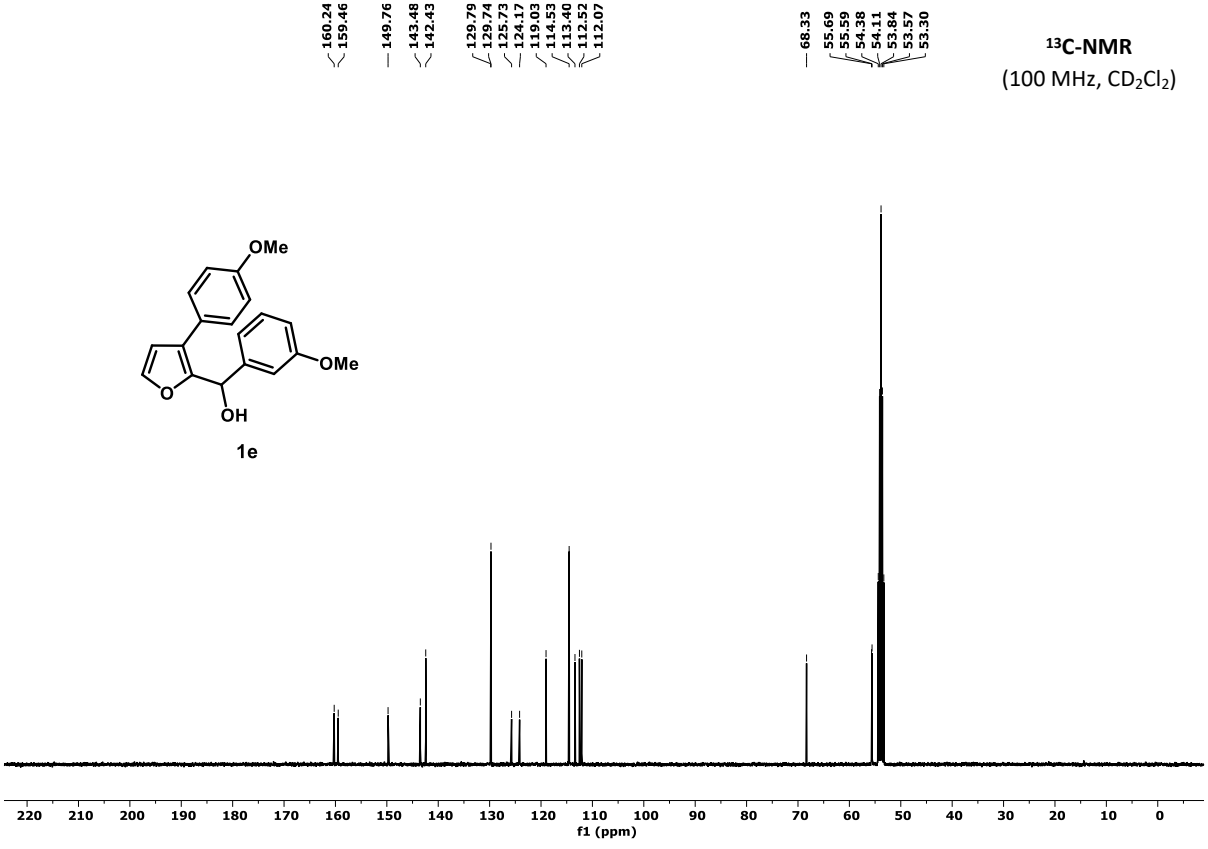
(100 MHz, CD_2Cl_2)



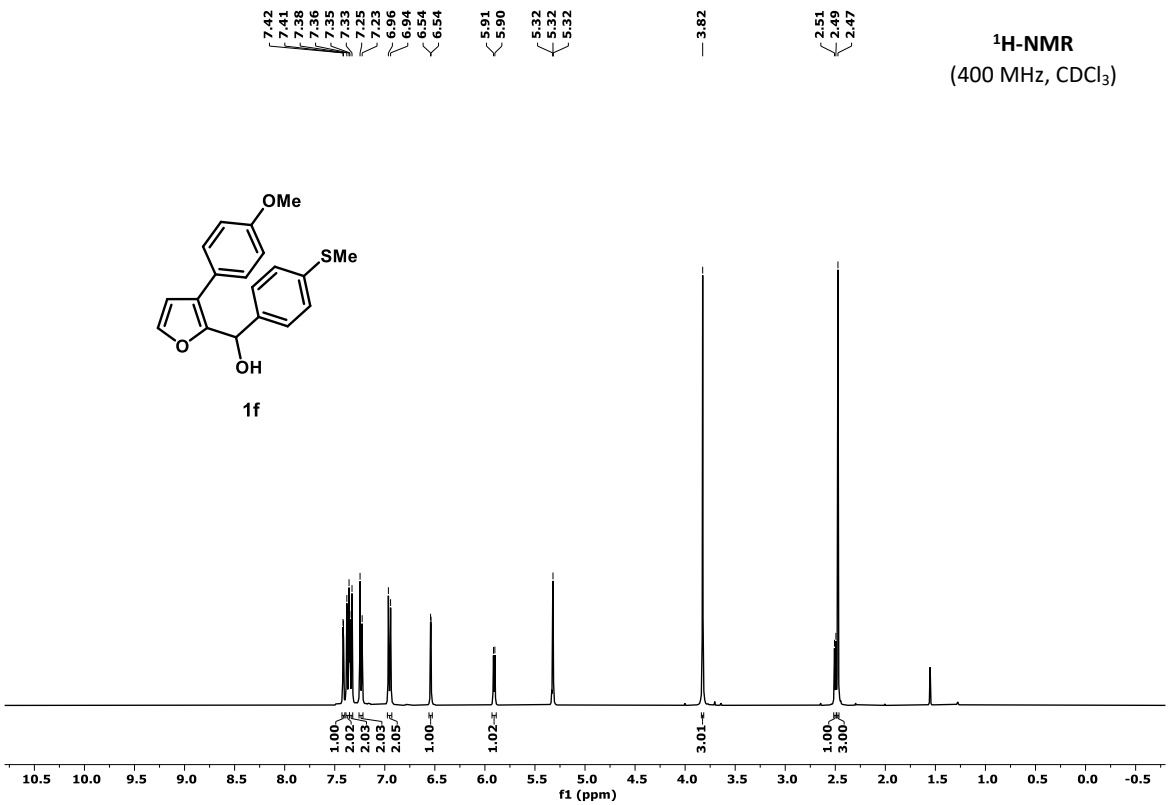
^{1}H-NMR
(400 MHz, CD_2Cl_2)



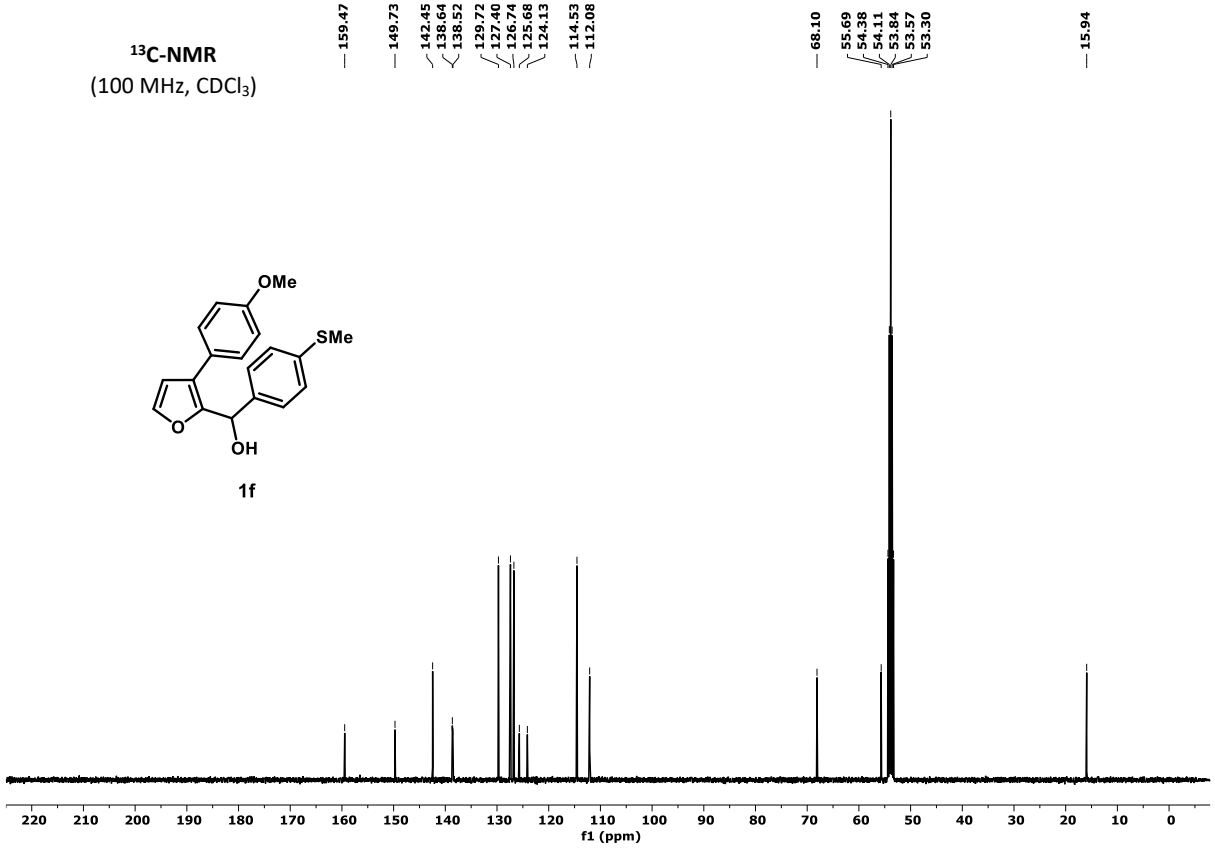
^{13}C-NMR
(100 MHz, CD_2Cl_2)



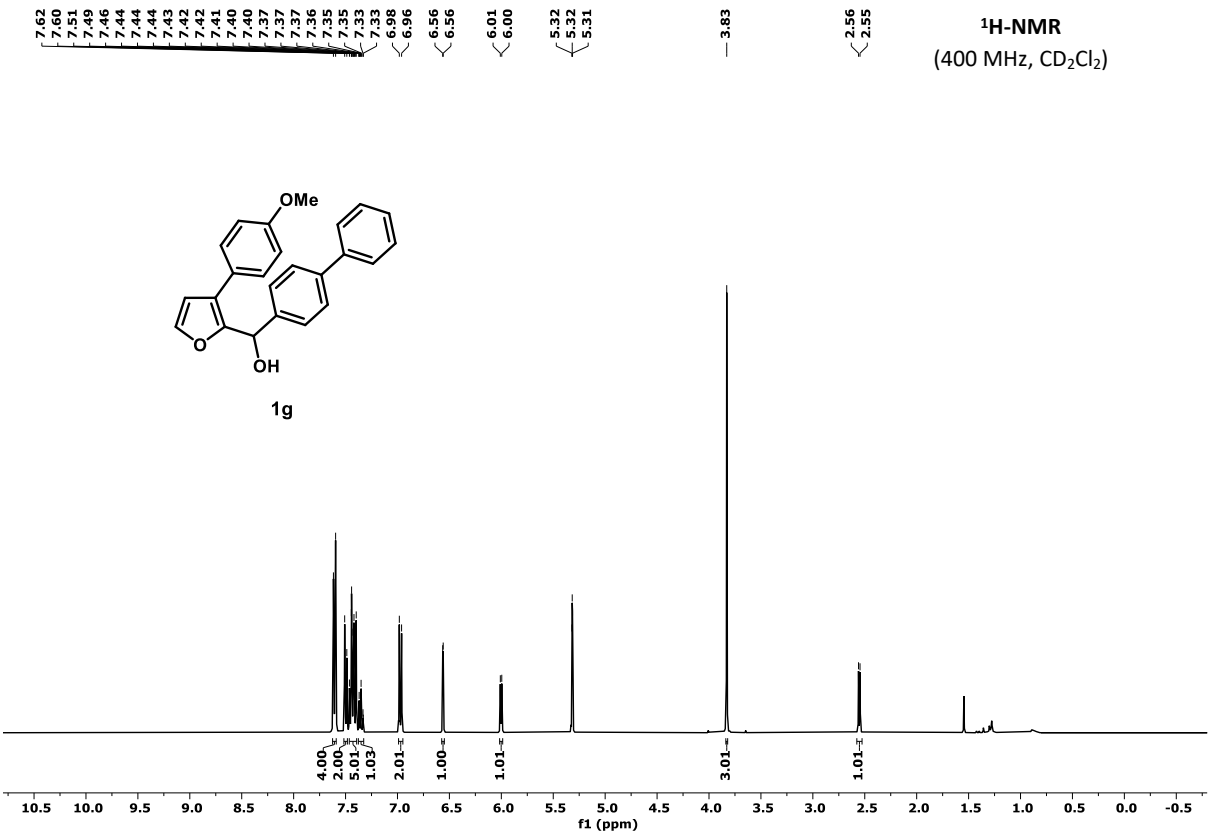
^{1}H-NMR
(400 MHz, $CDCl_3$)



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



^{1}H-NMR
(400 MHz, CD_2Cl_2)



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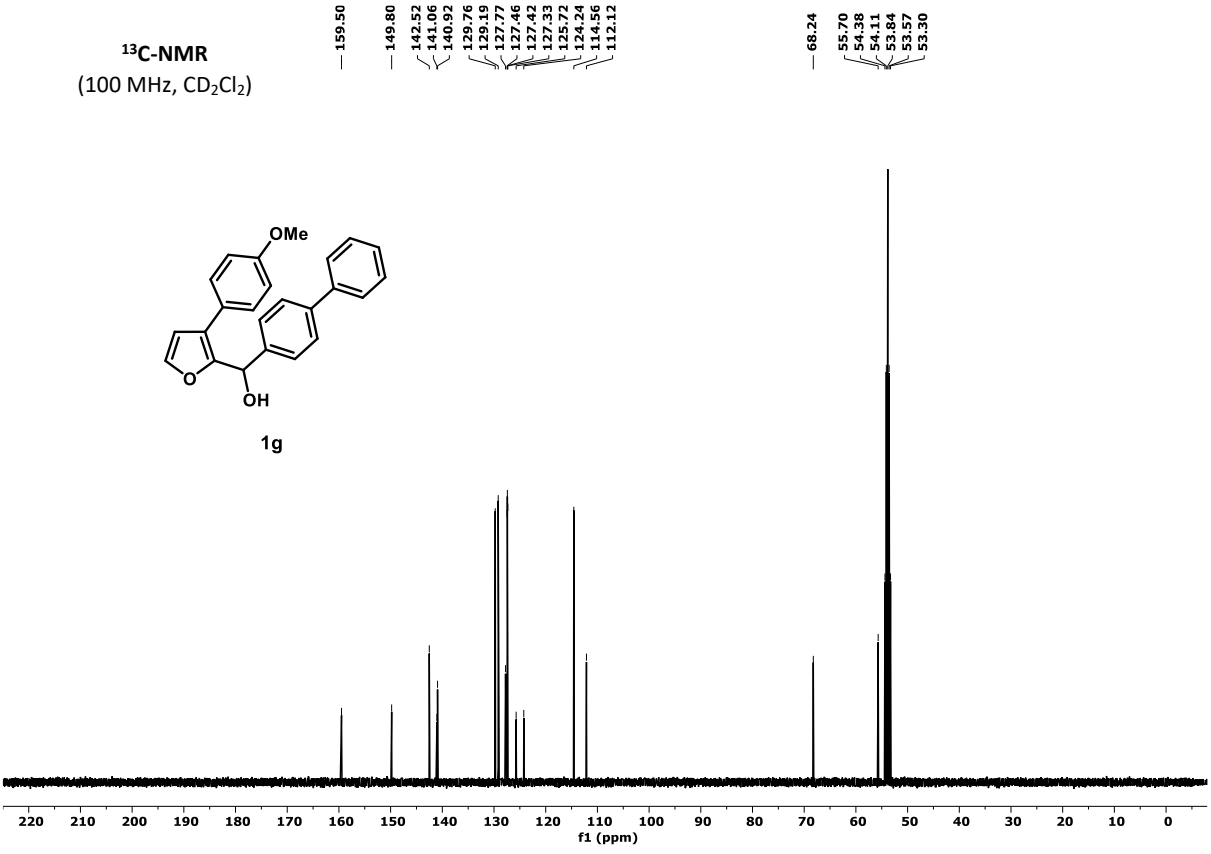
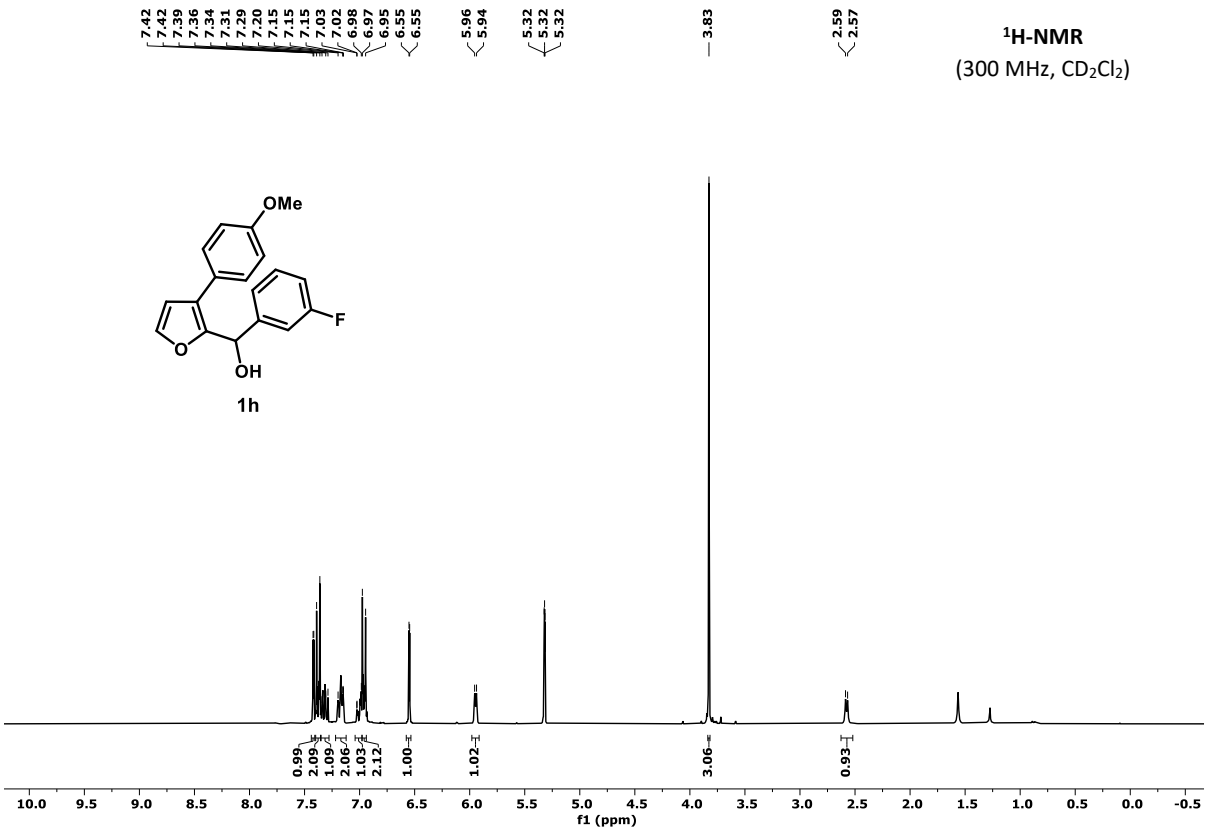
(100 MHz, CD_2Cl_2)





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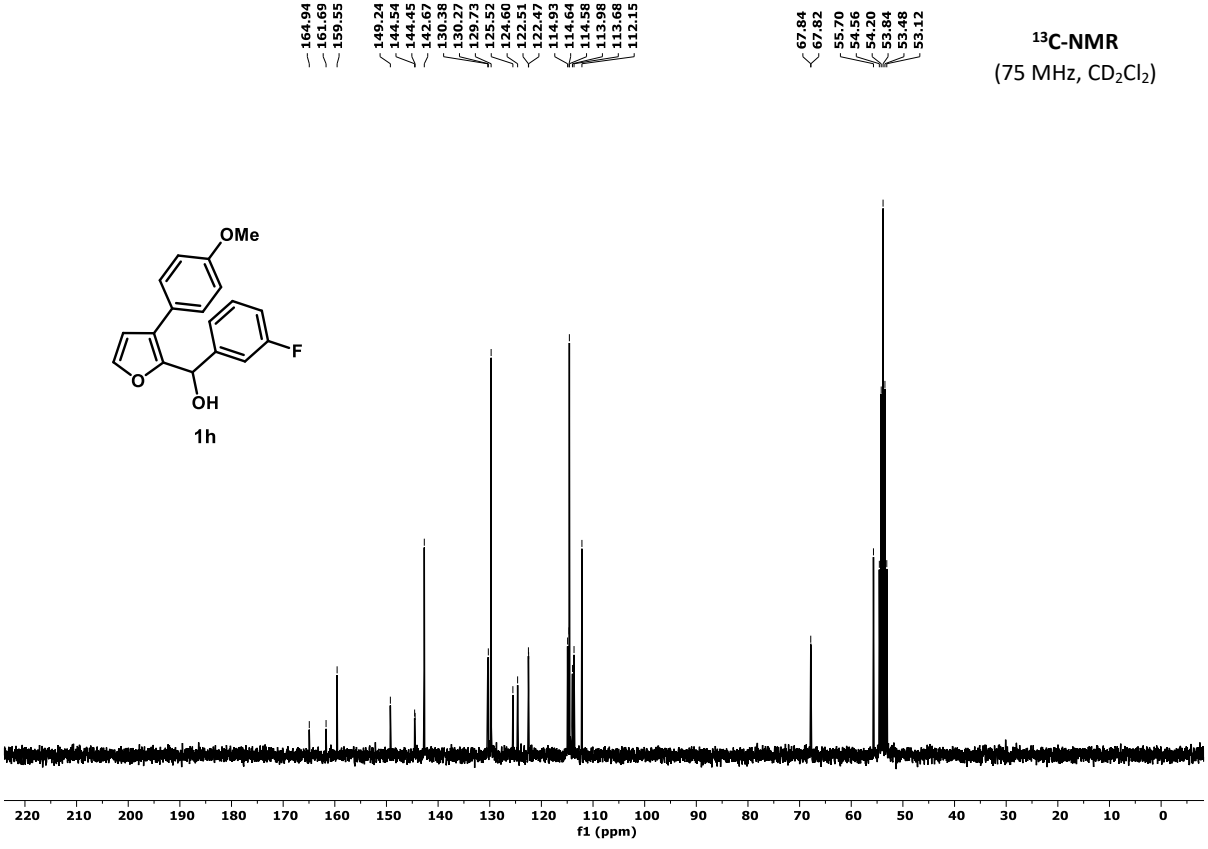
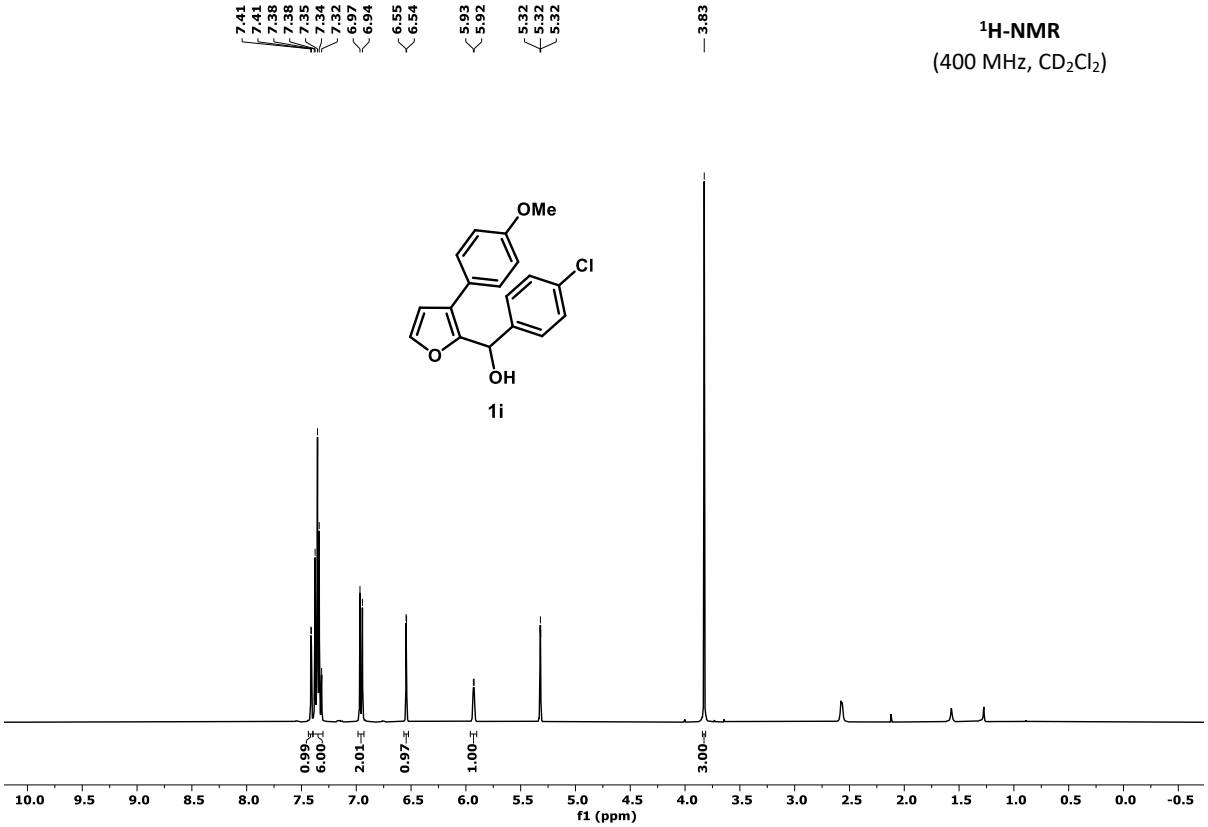
(300 MHz, CD_2Cl_2)

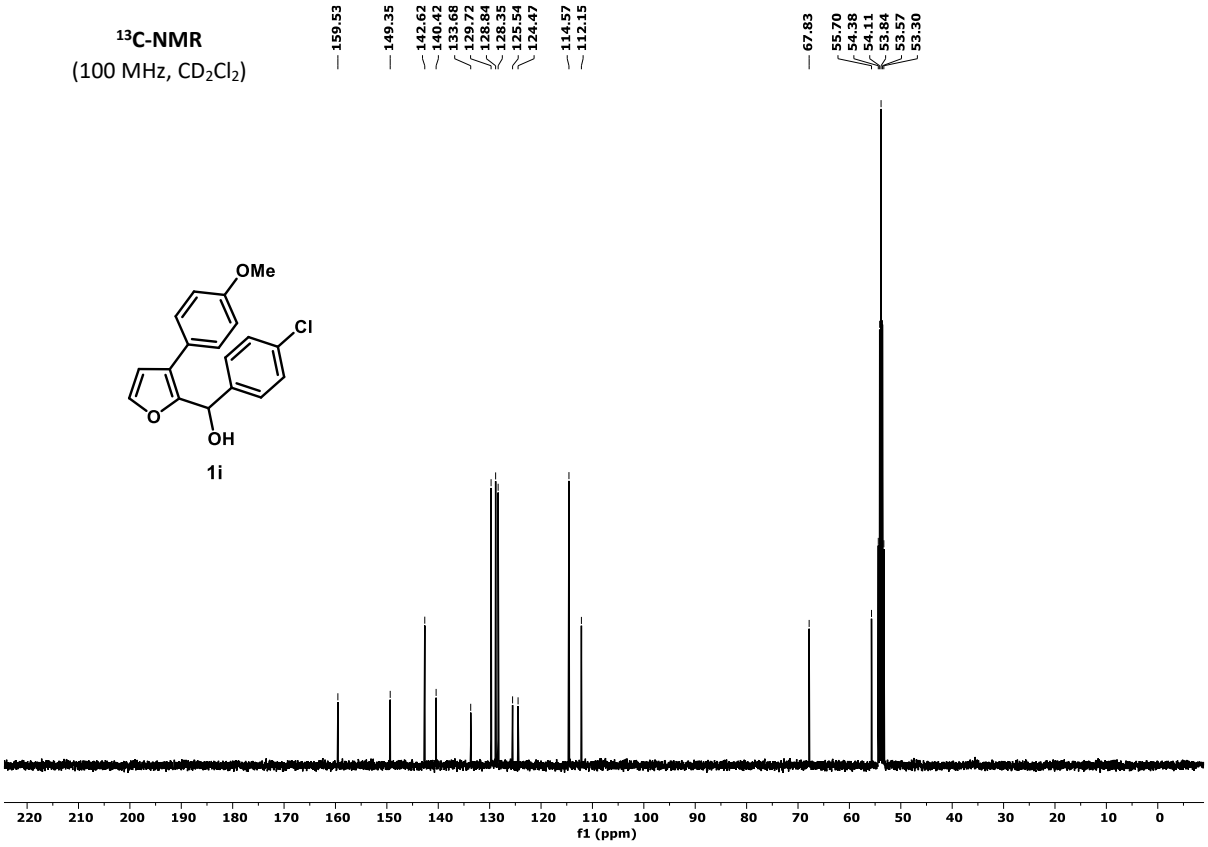


^{13}C-NMR
(75 MHz, CD_2Cl_2)

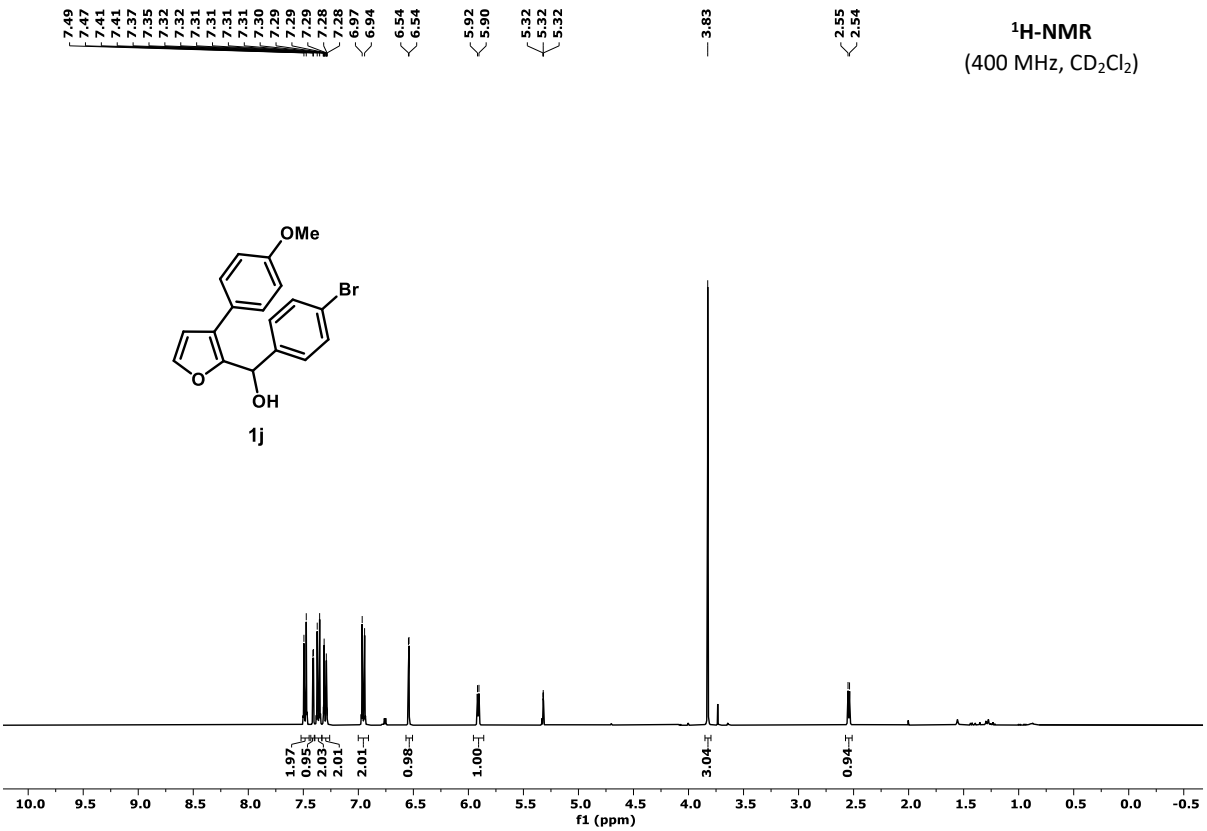
^{1}H-NMR
(400 MHz, CD_2Cl_2)



^{13}C-NMR
(100 MHz, CD_2Cl_2)



^{1}H-NMR
(400 MHz, CD_2Cl_2)



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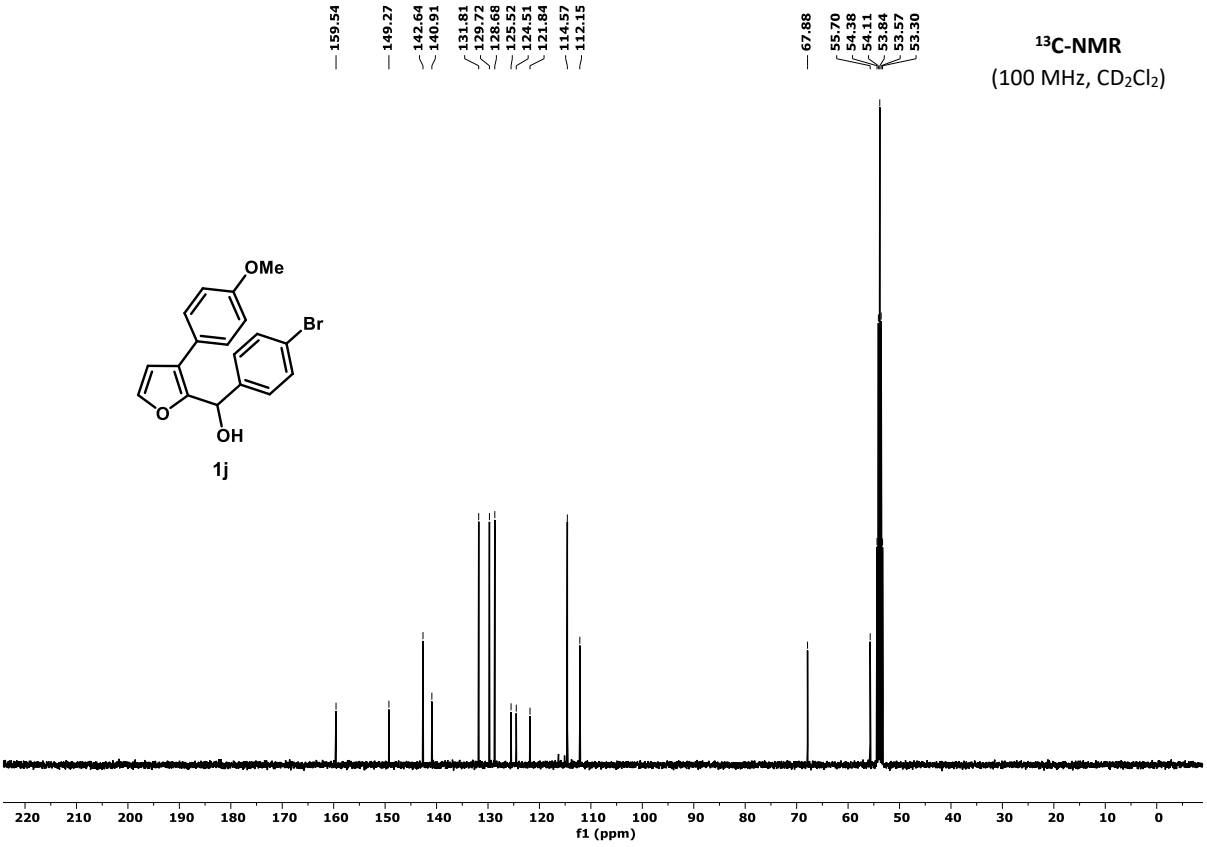
(100 MHz, CD_2Cl_2)



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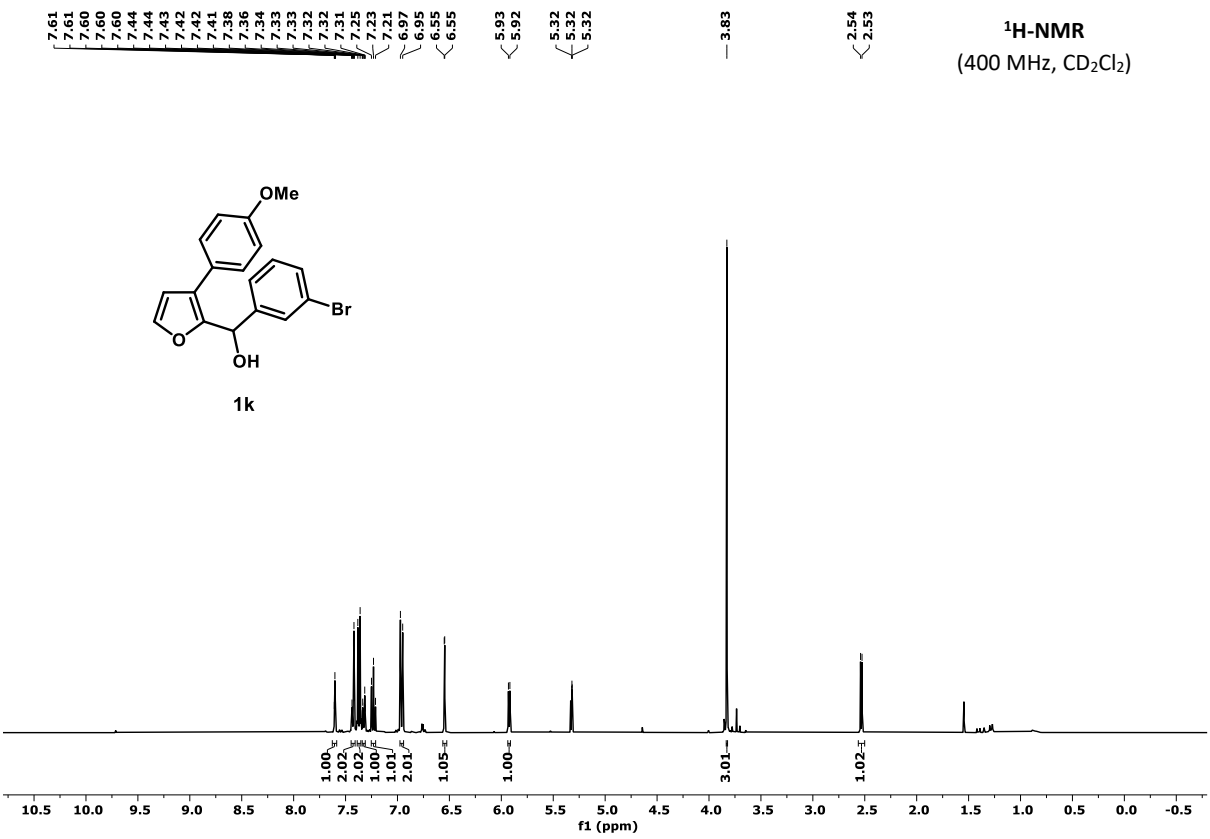
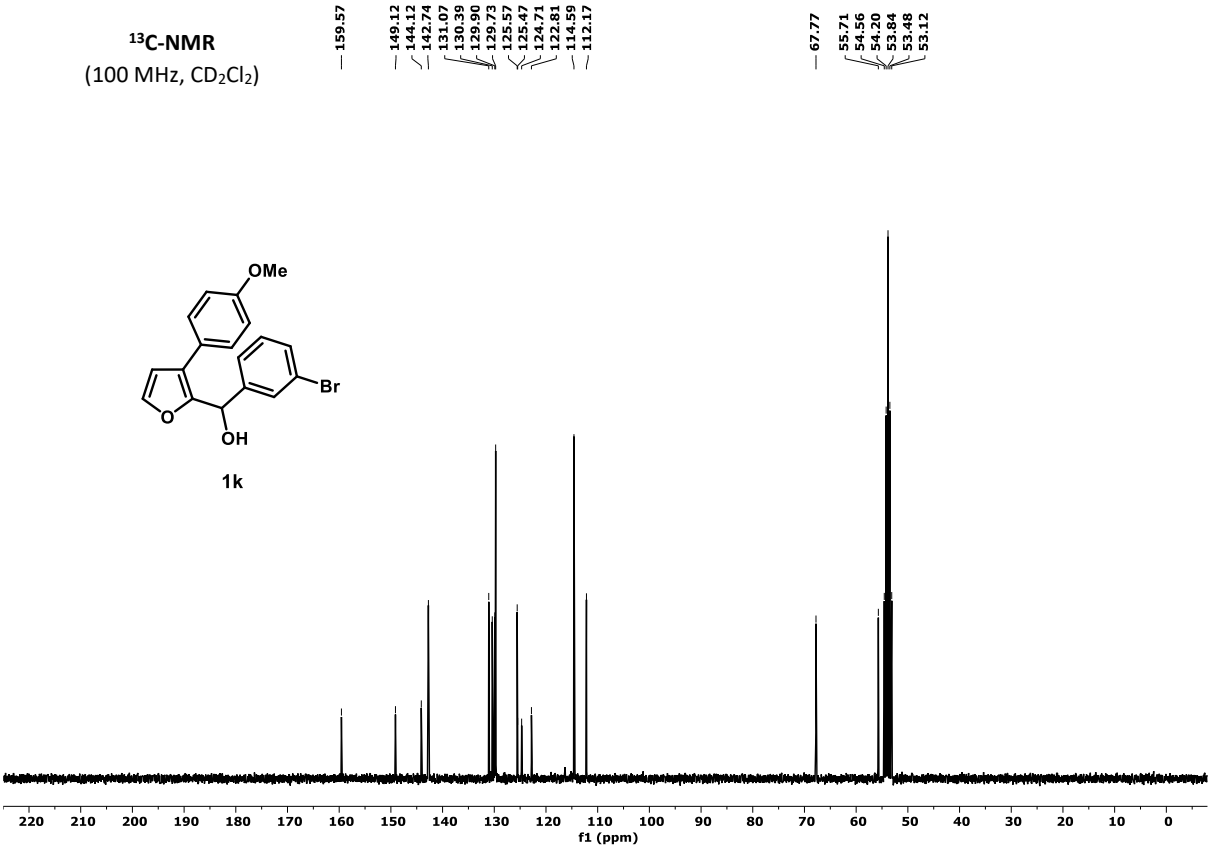
(400 MHz, CD_2Cl_2)



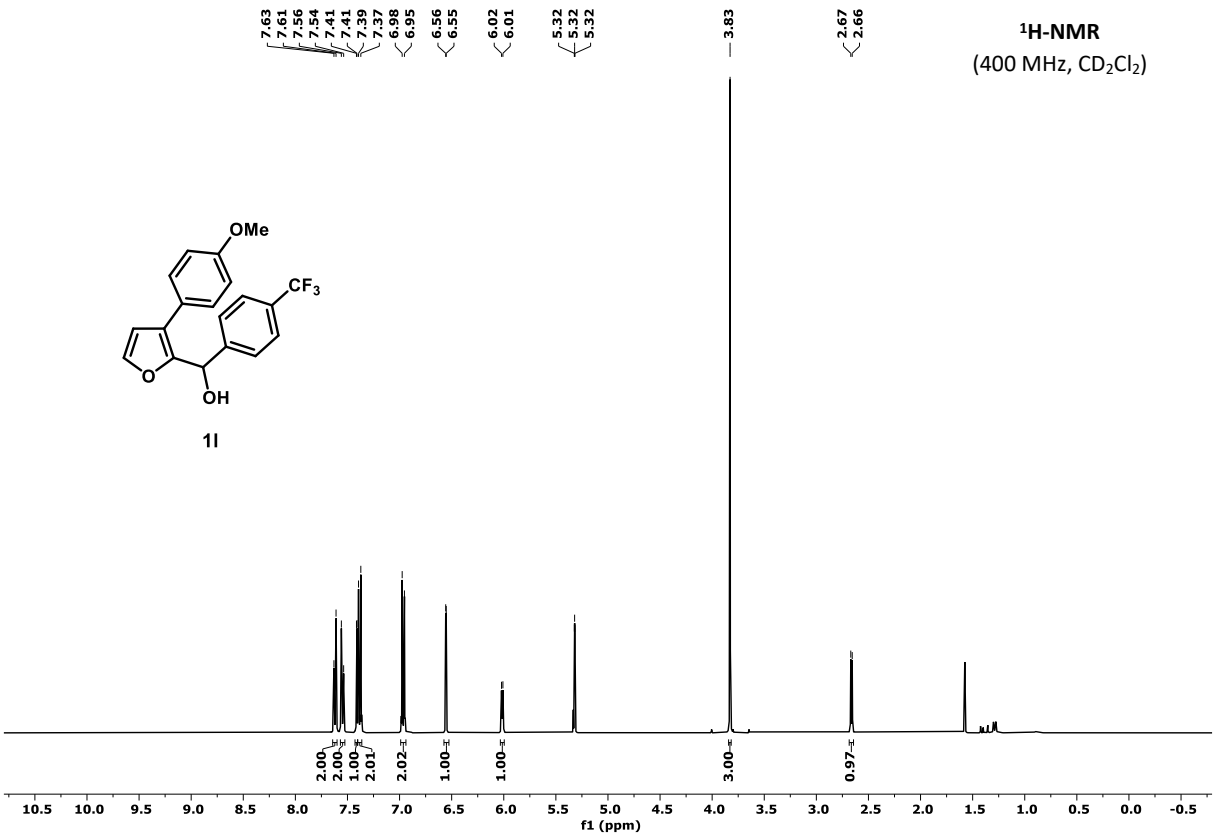
1k

^{13}C-NMR
(100 MHz, CD_2Cl_2)



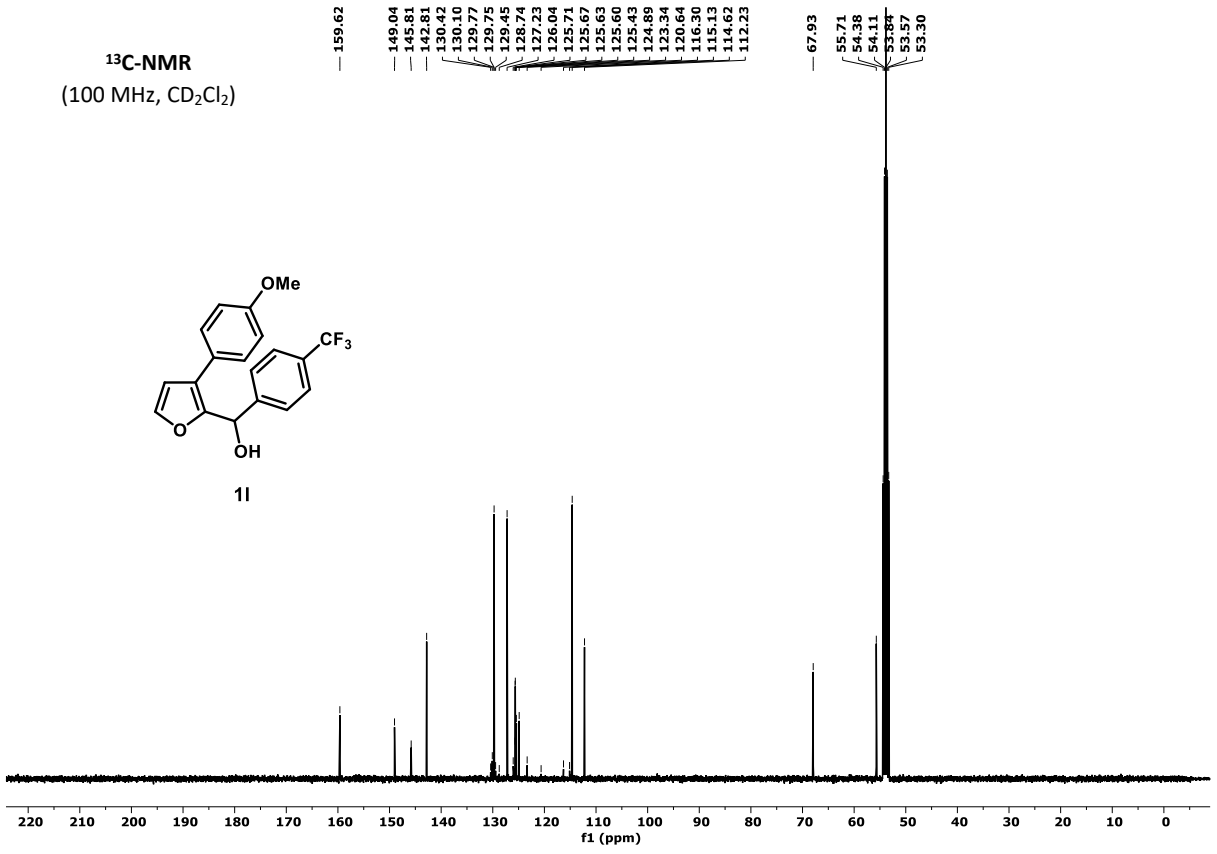
1k

^{1}H-NMR
(400 MHz, CD_2Cl_2)



1l

^{13}C-NMR
(100 MHz, CD_2Cl_2)



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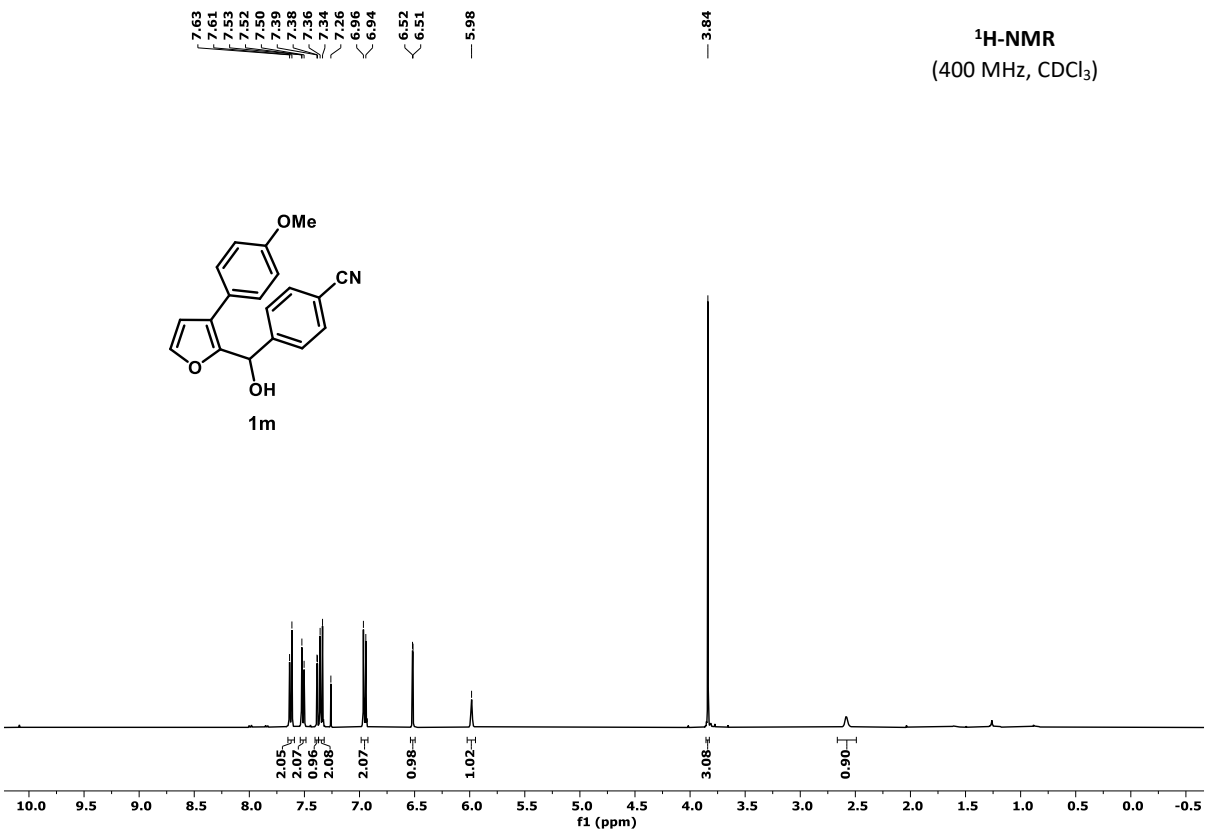
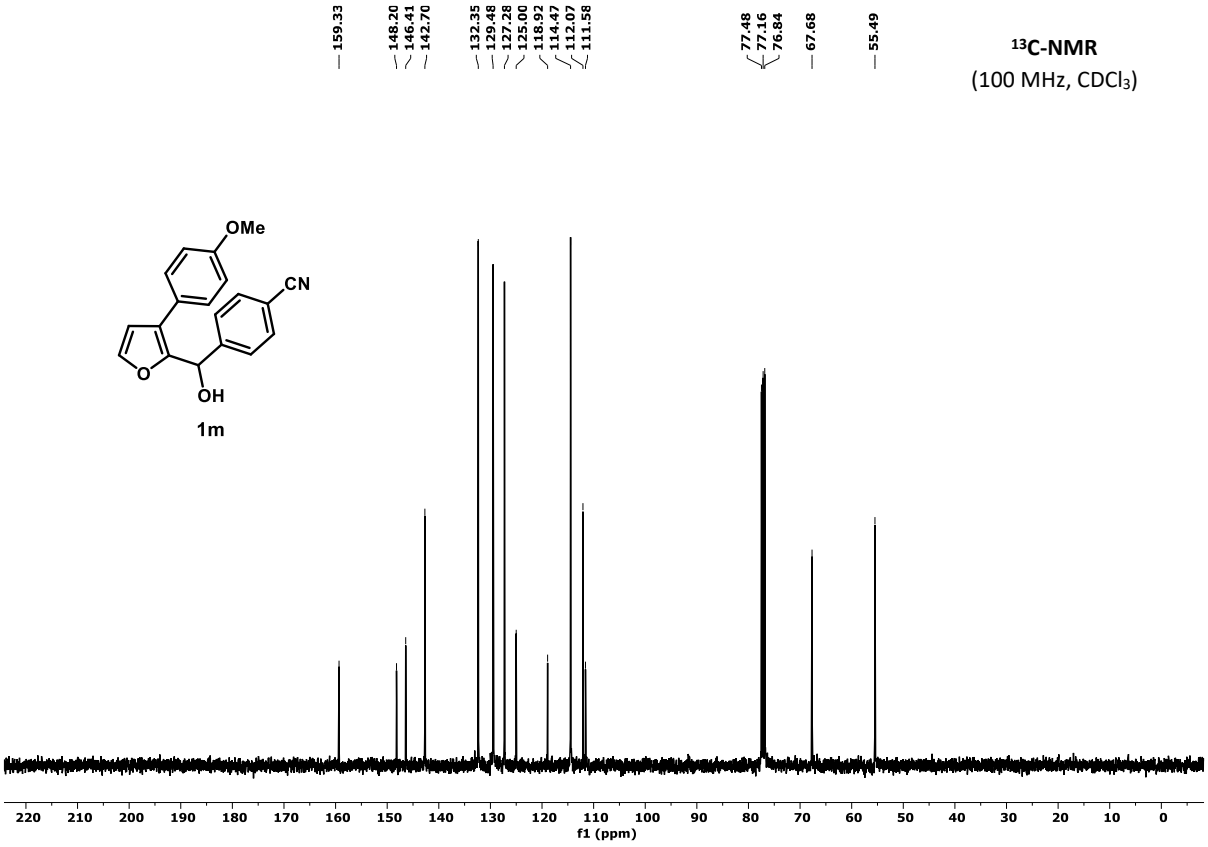
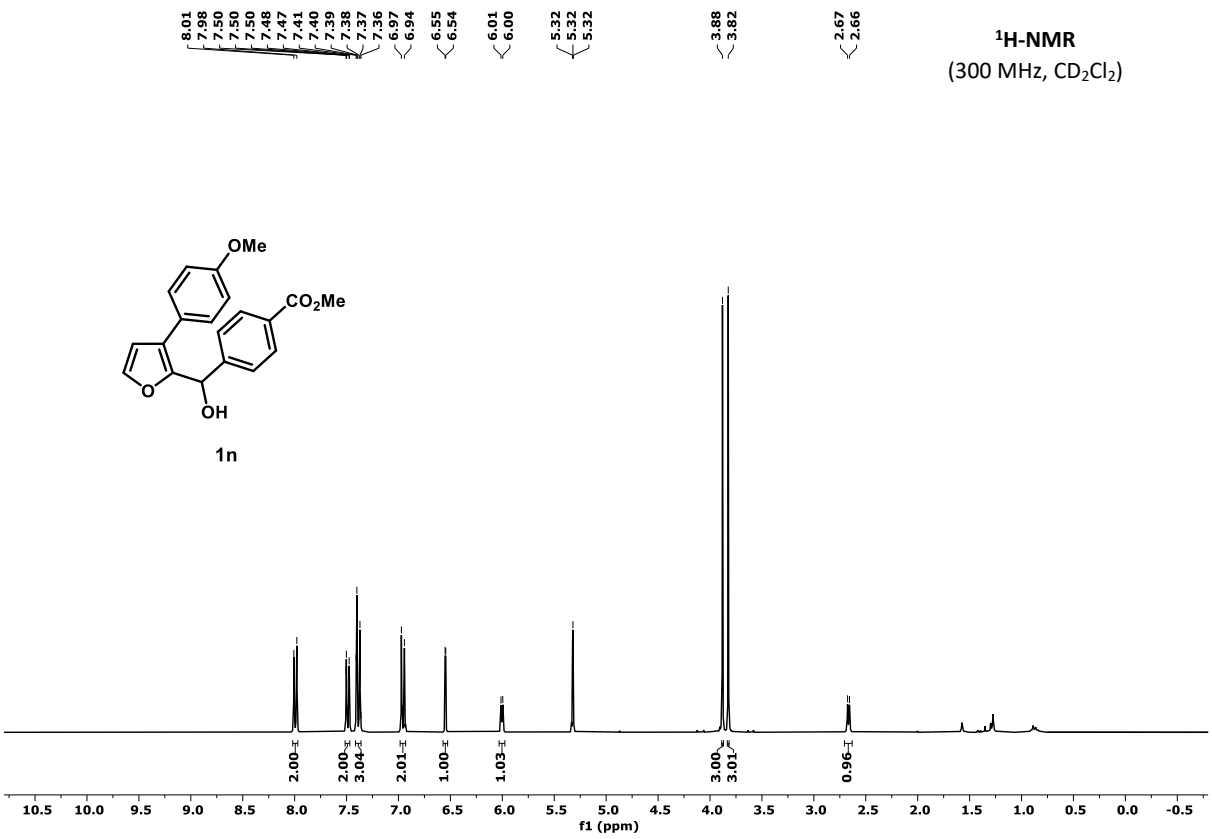


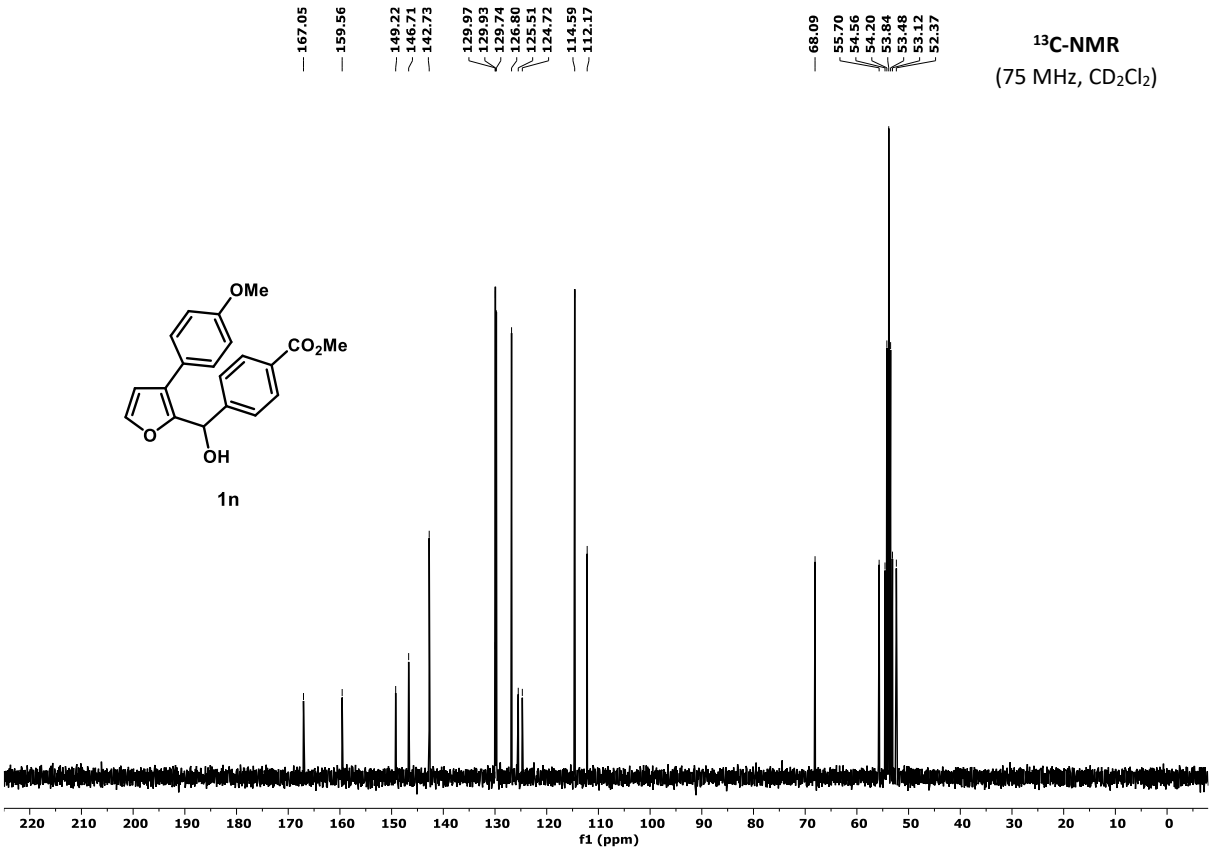
^{1}H-NMR
(400 MHz, $CDCl_3$)



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

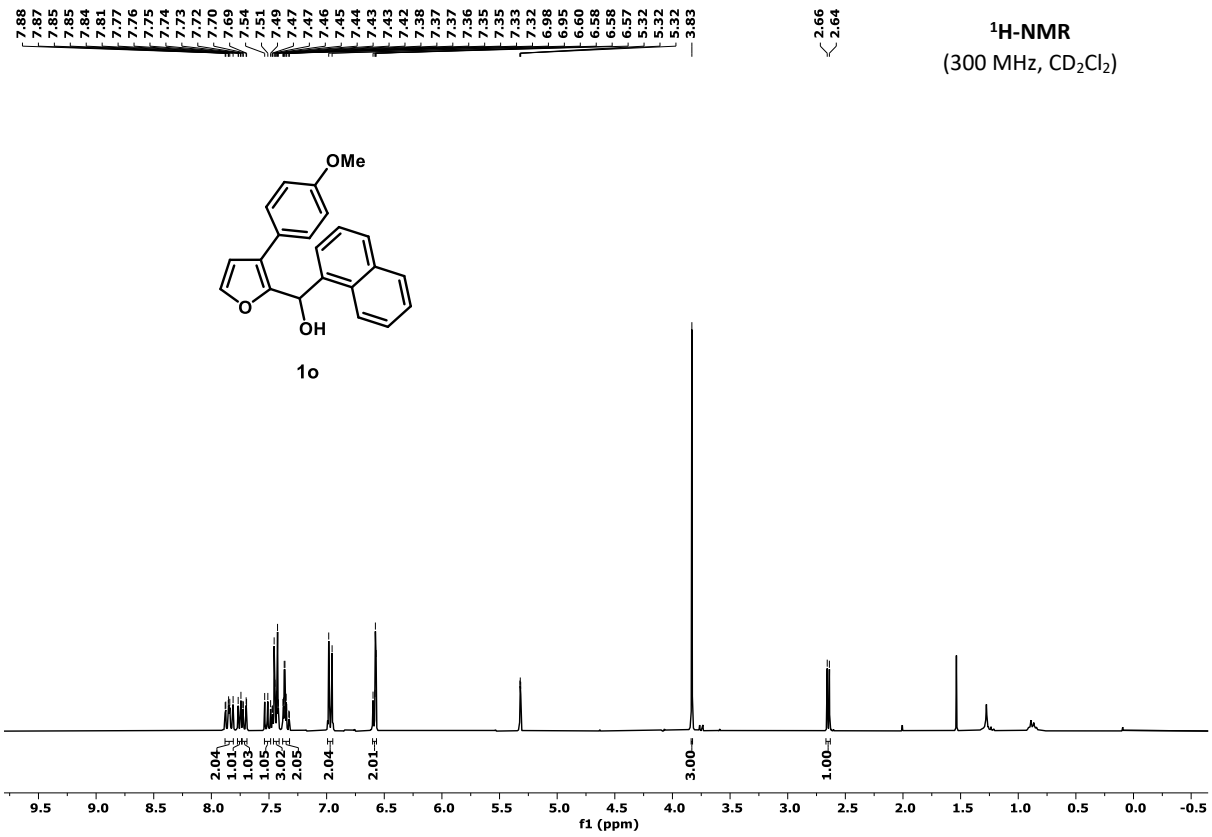


^{1}H-NMR
(300 MHz, CD_2Cl_2)

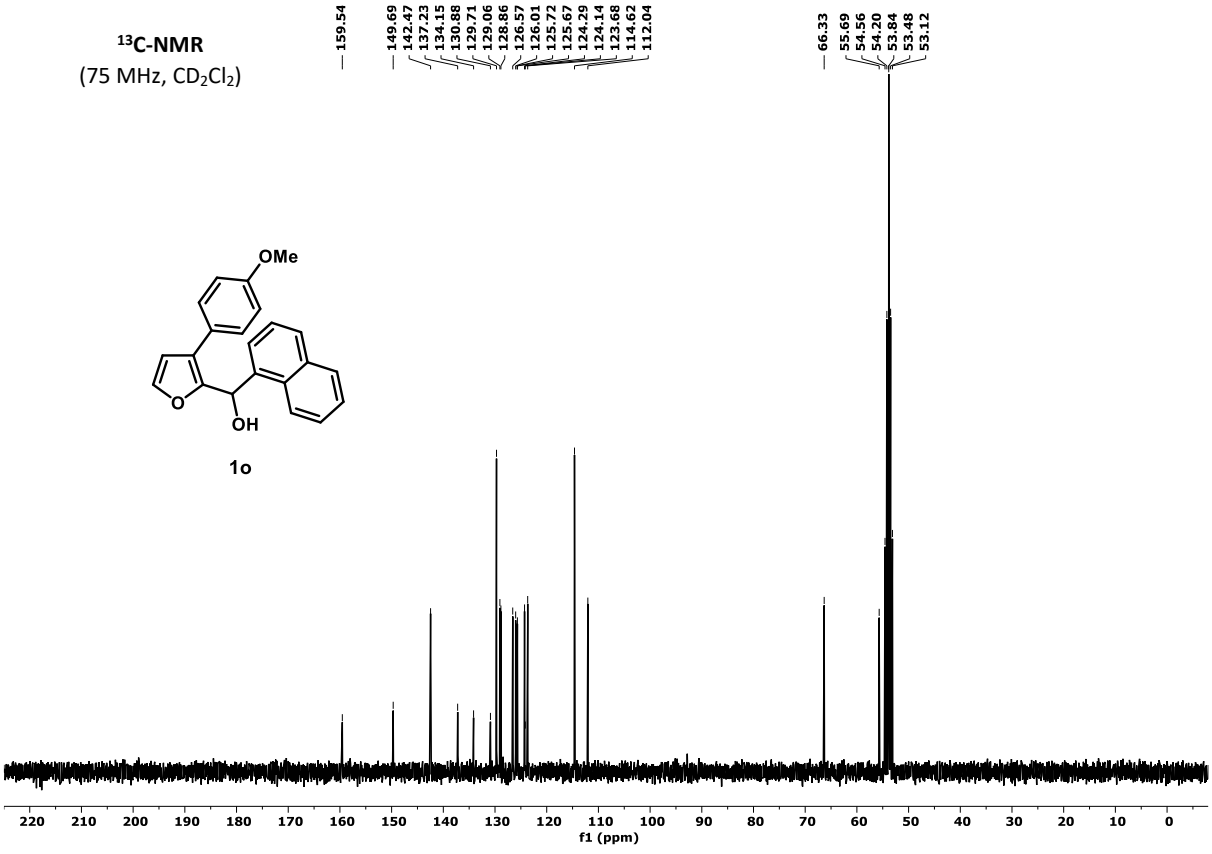


^{13}C-NMR
(75 MHz, CD_2Cl_2)

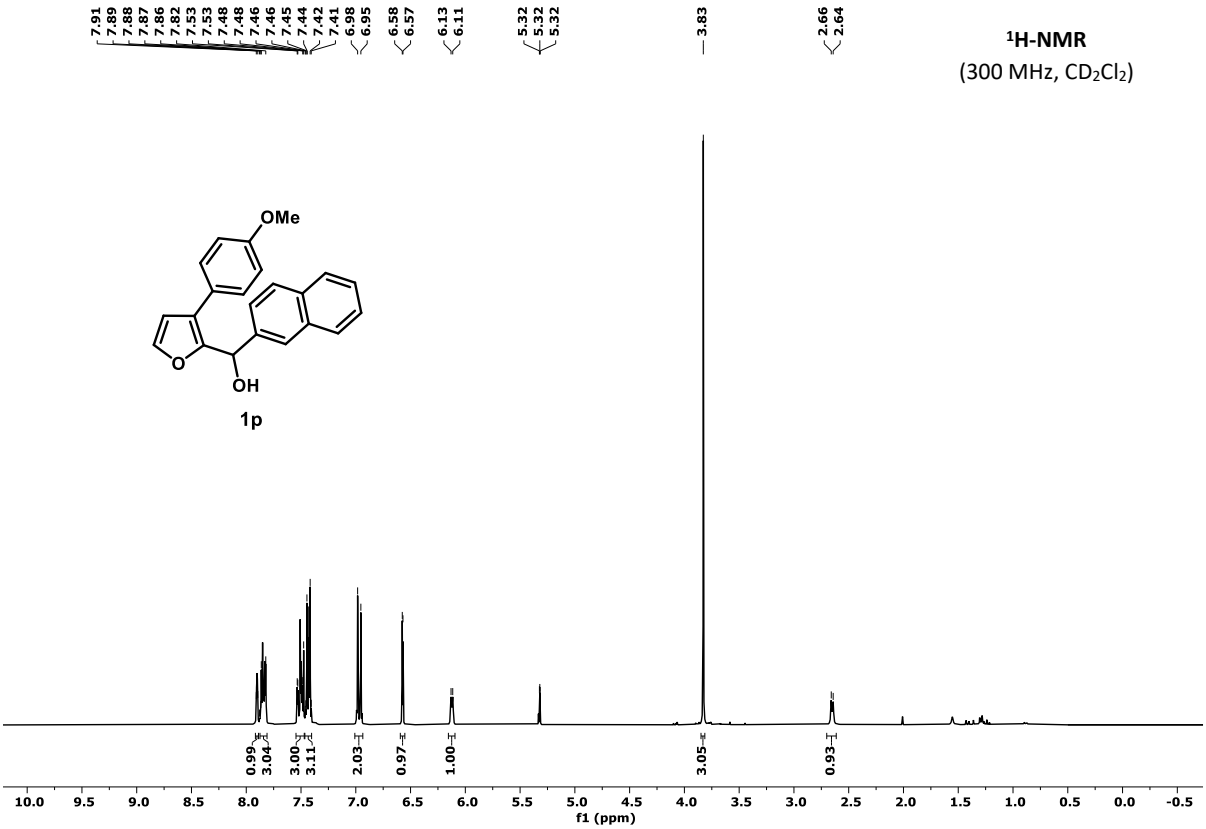
^{1}H-NMR
(300 MHz, CD_2Cl_2)



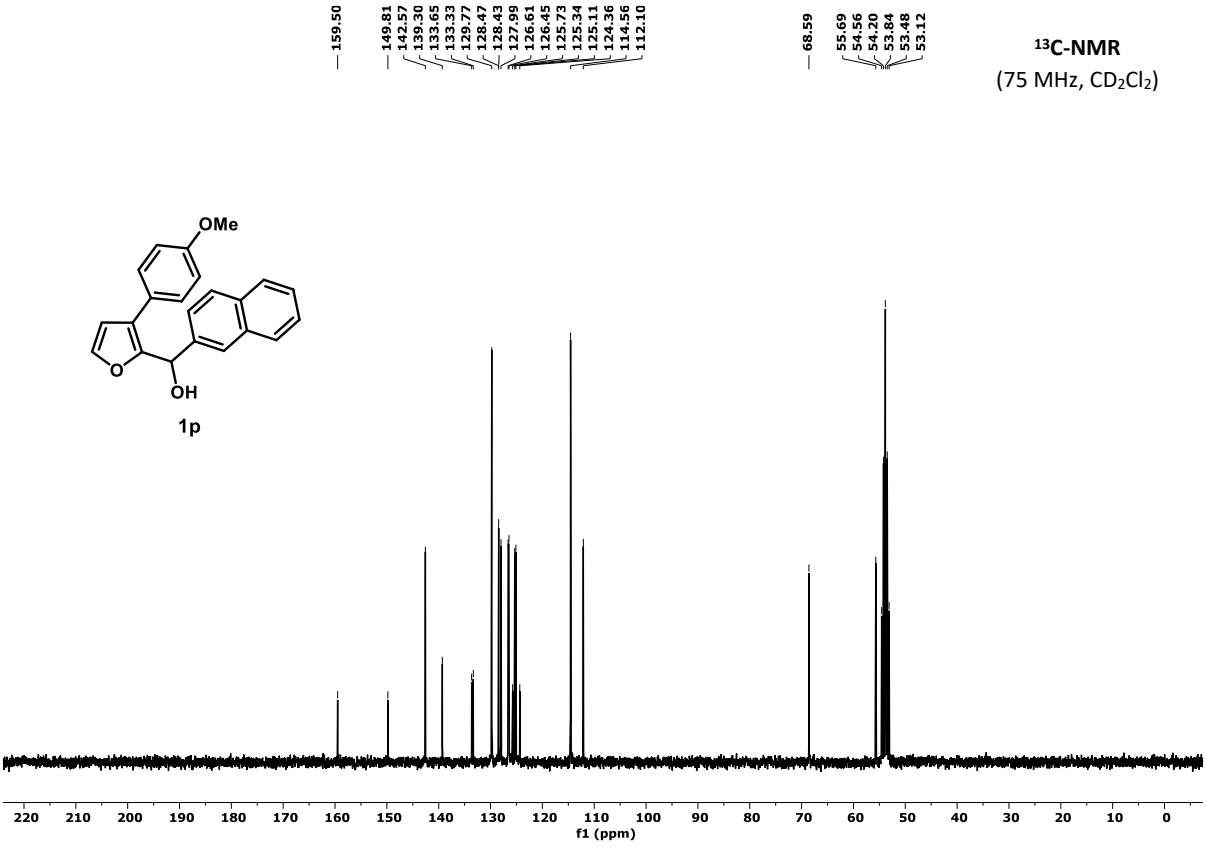
^{13}C-NMR
(75 MHz, CD_2Cl_2)

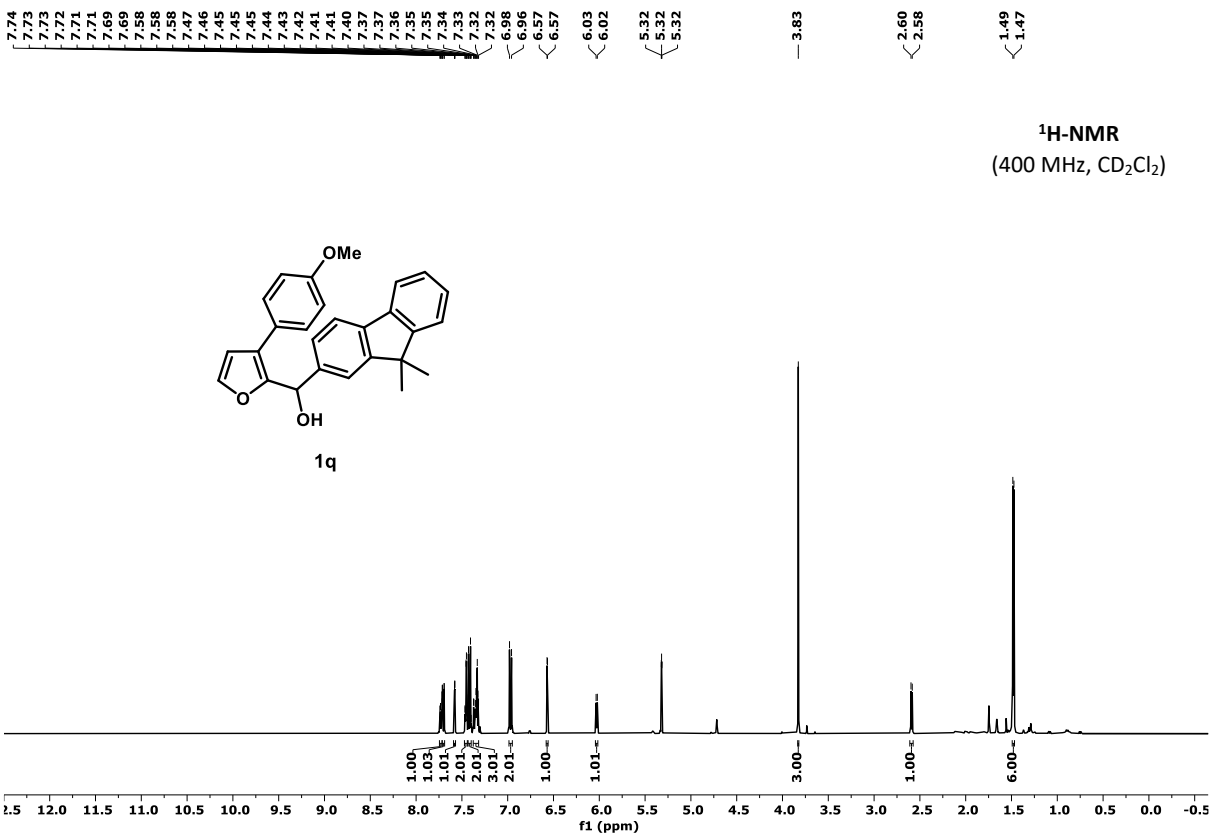


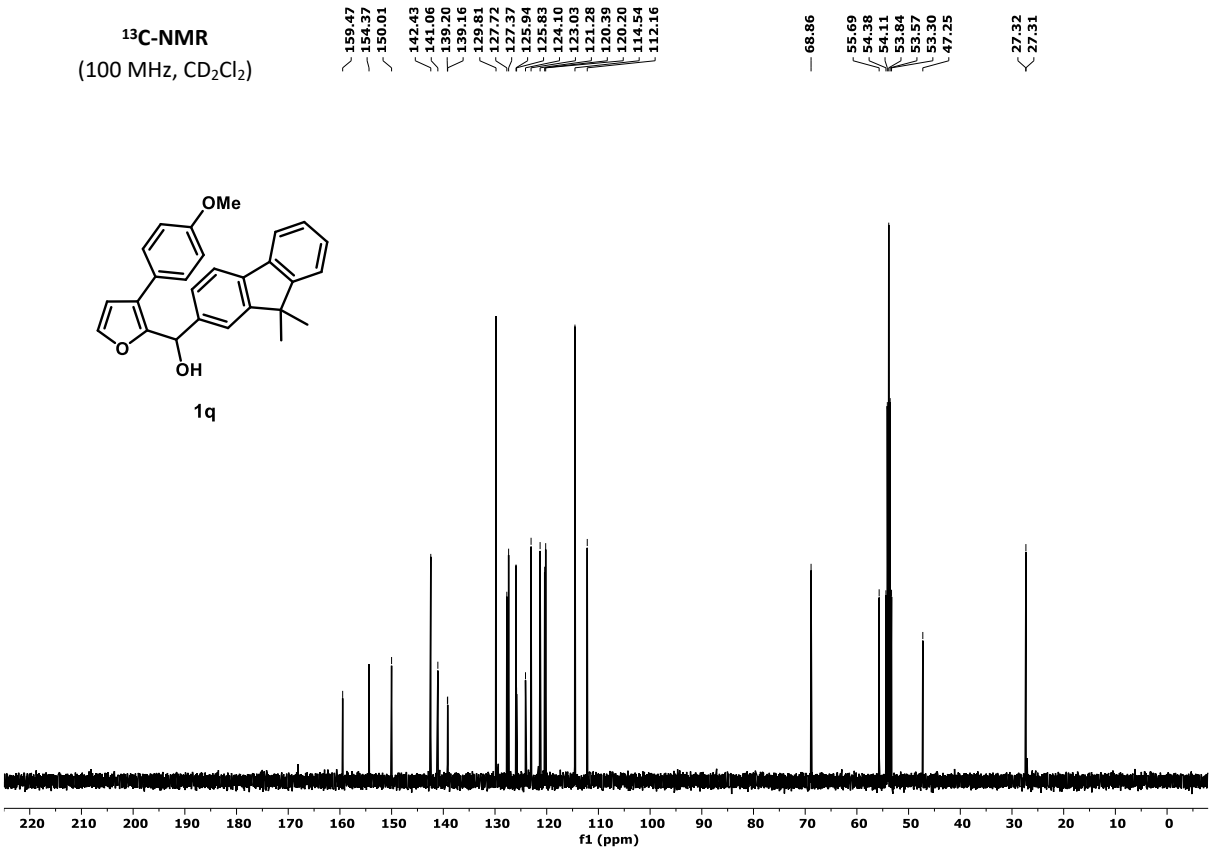
^{1}H-NMR
(300 MHz, CD_2Cl_2)



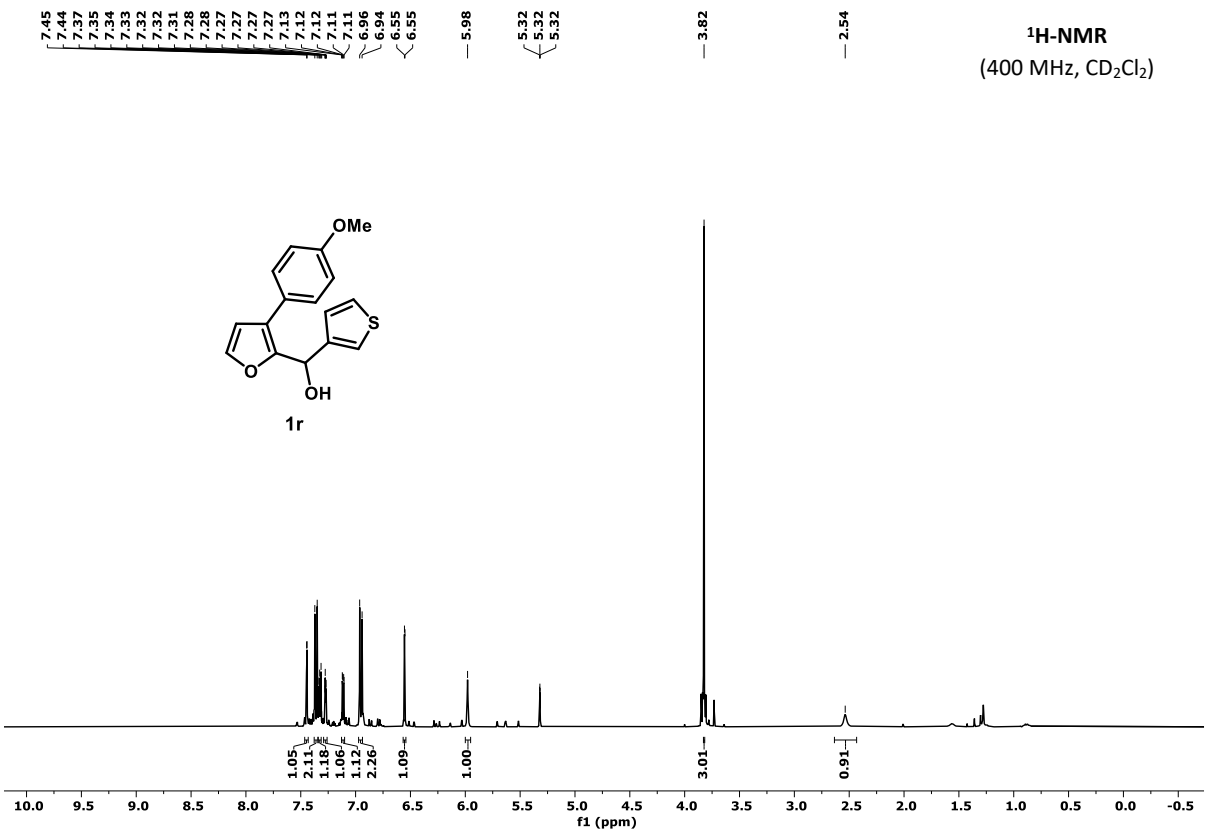
^{13}C-NMR
(75 MHz, CD_2Cl_2)



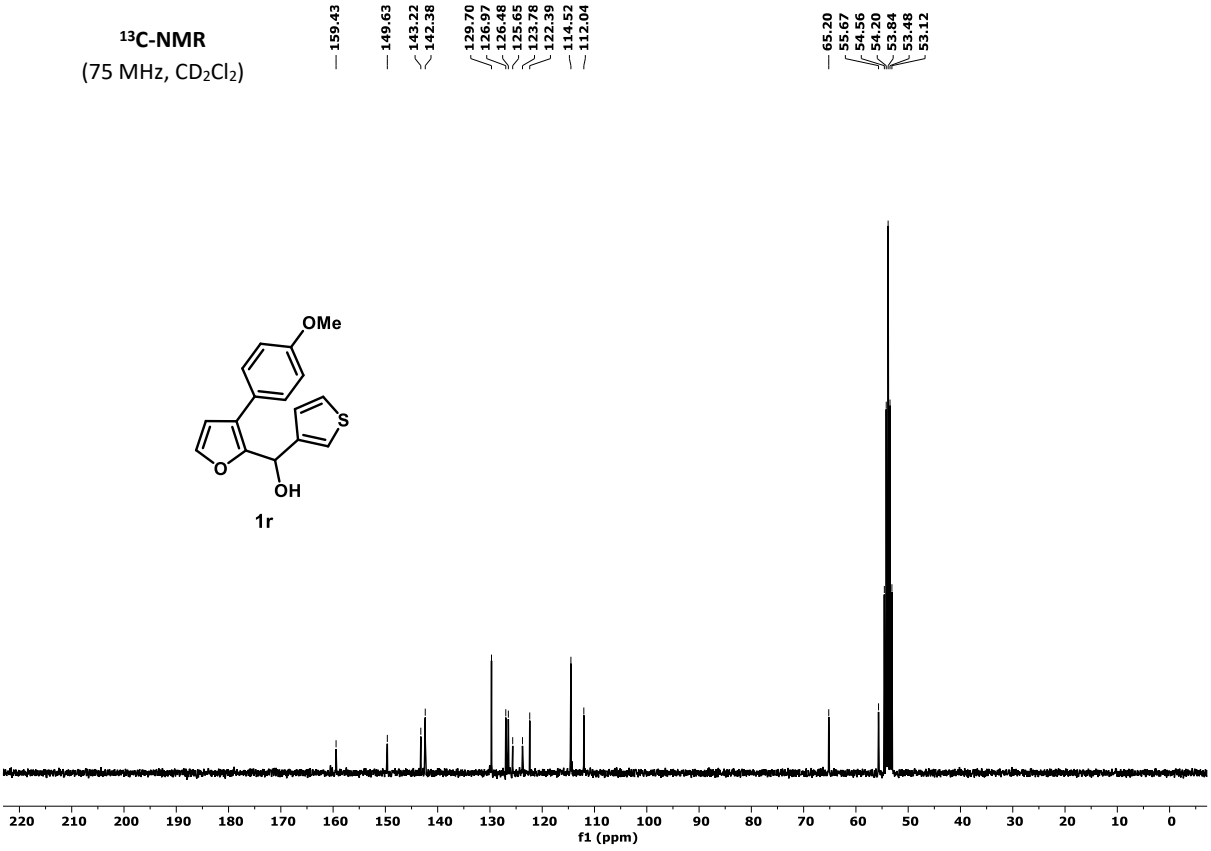

7.74 7.73 7.73 7.72 7.71 7.71 7.69 7.69 7.58 7.58 7.58 7.47 7.46 7.45 7.45 7.44 7.43 7.42 7.41 7.41 7.40 7.37 7.37 7.36 7.35 7.35 7.34 7.33 7.32 7.32 6.98 6.96 6.57 6.57 6.03 6.02 5.32 5.32 5.32 3.83 2.60 2.58 1.49 1.47
1H-NMR
(400 MHz, CD2Cl2)
OMe
O
OH
1q
1.00 1.03 1.01 2.01 2.01 3.01 2.01 1.00 1.01 3.00 1.00 6.00
f1 (ppm)


13C-NMR
(100 MHz, CD2Cl2)
159.47 154.37 150.01 142.43 141.06 139.20 139.16 129.81 127.72 127.37 125.94 125.83 124.10 123.03 121.28 120.39 120.20 114.54 112.16 68.86 55.69 54.38 54.11 53.84 53.57 53.30 47.25 27.32 27.31
OMe
O
OH
1q
f1 (ppm)

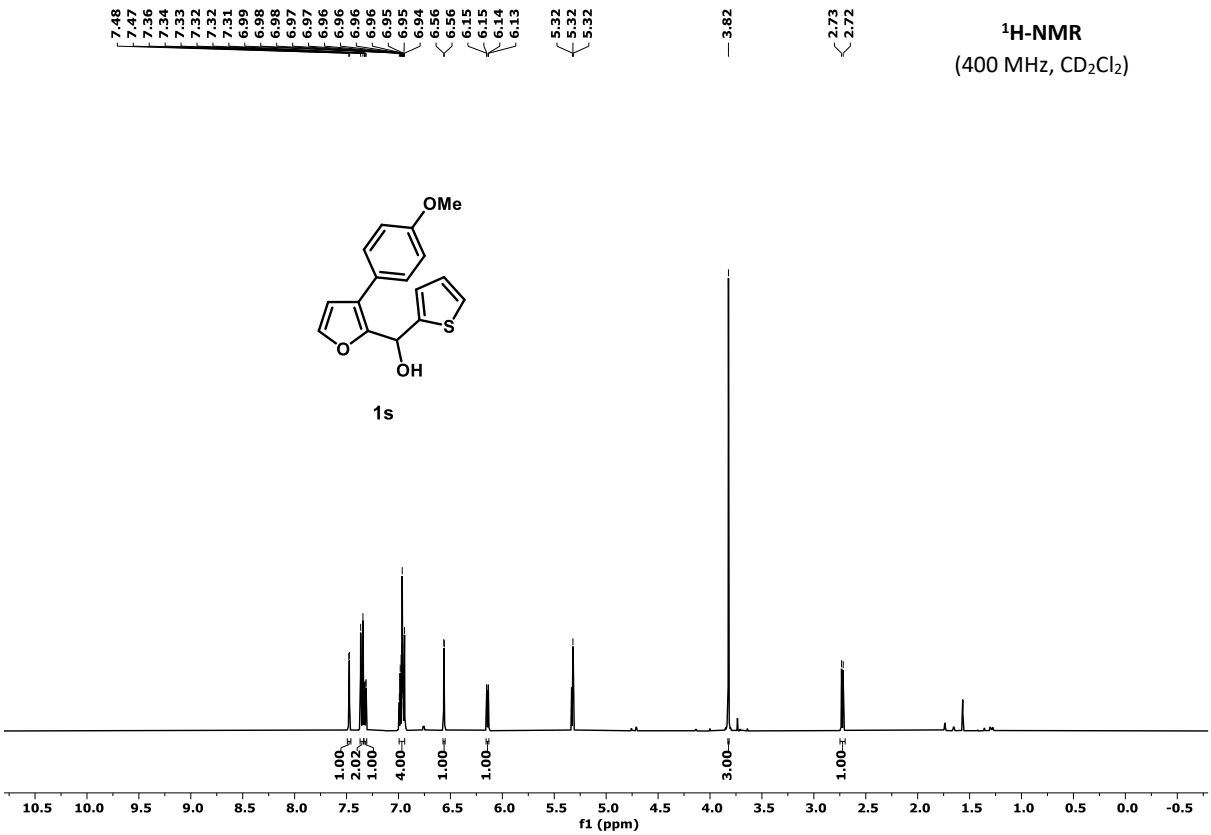
^{1}H-NMR
(400 MHz, CD_2Cl_2)



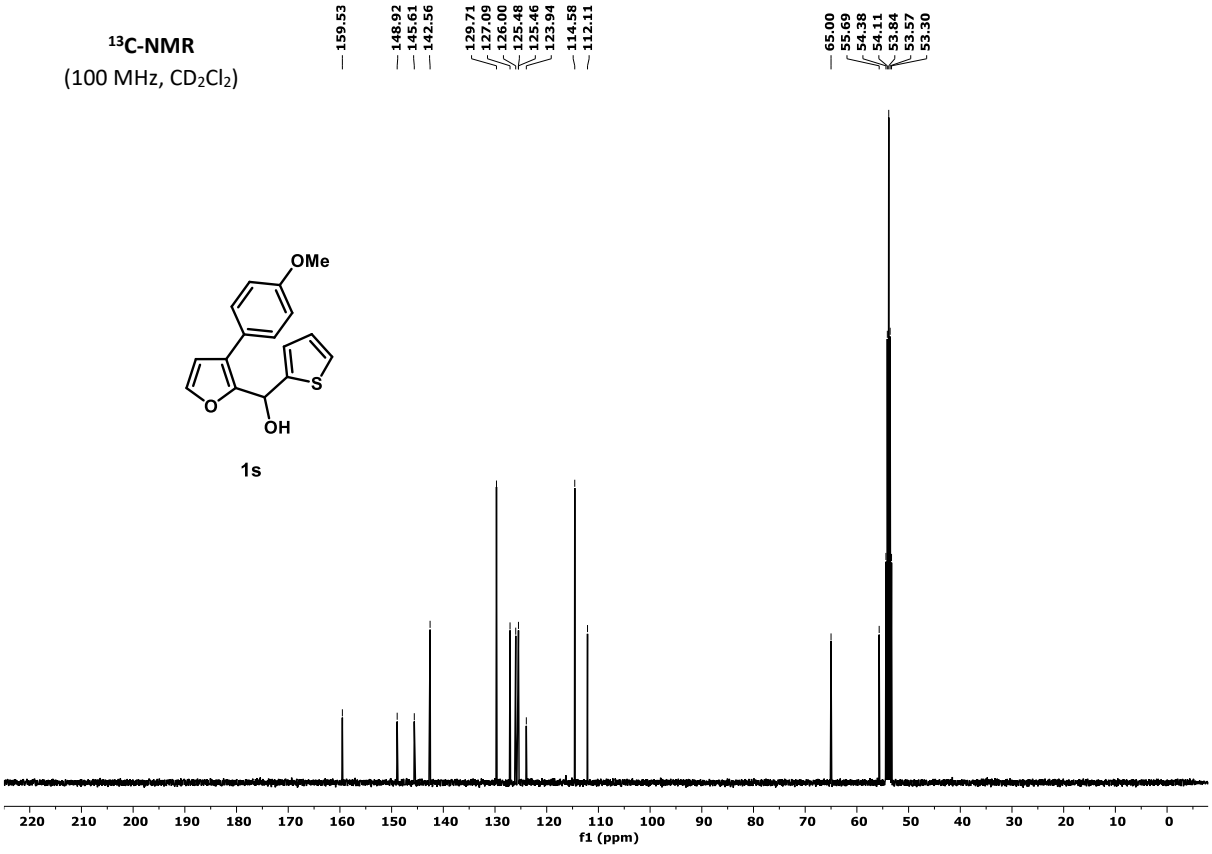
^{13}C-NMR
(75 MHz, CD_2Cl_2)



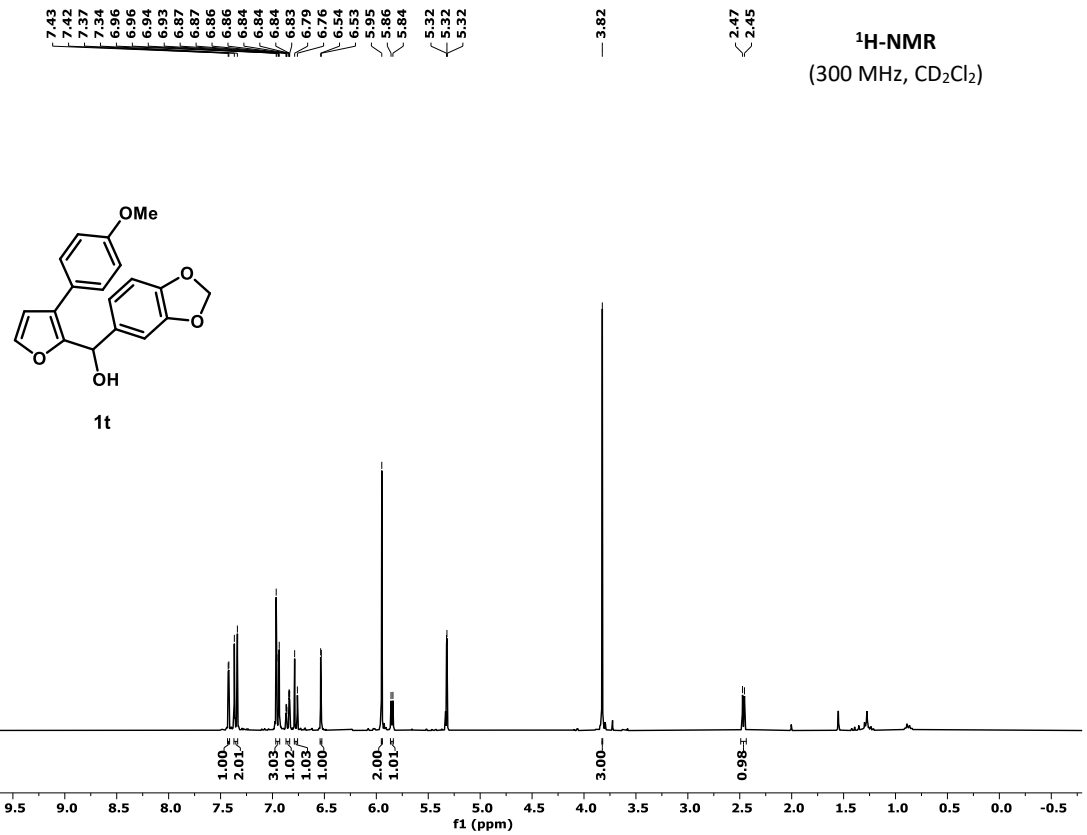
^{1}H-NMR
(400 MHz, CD_2Cl_2)



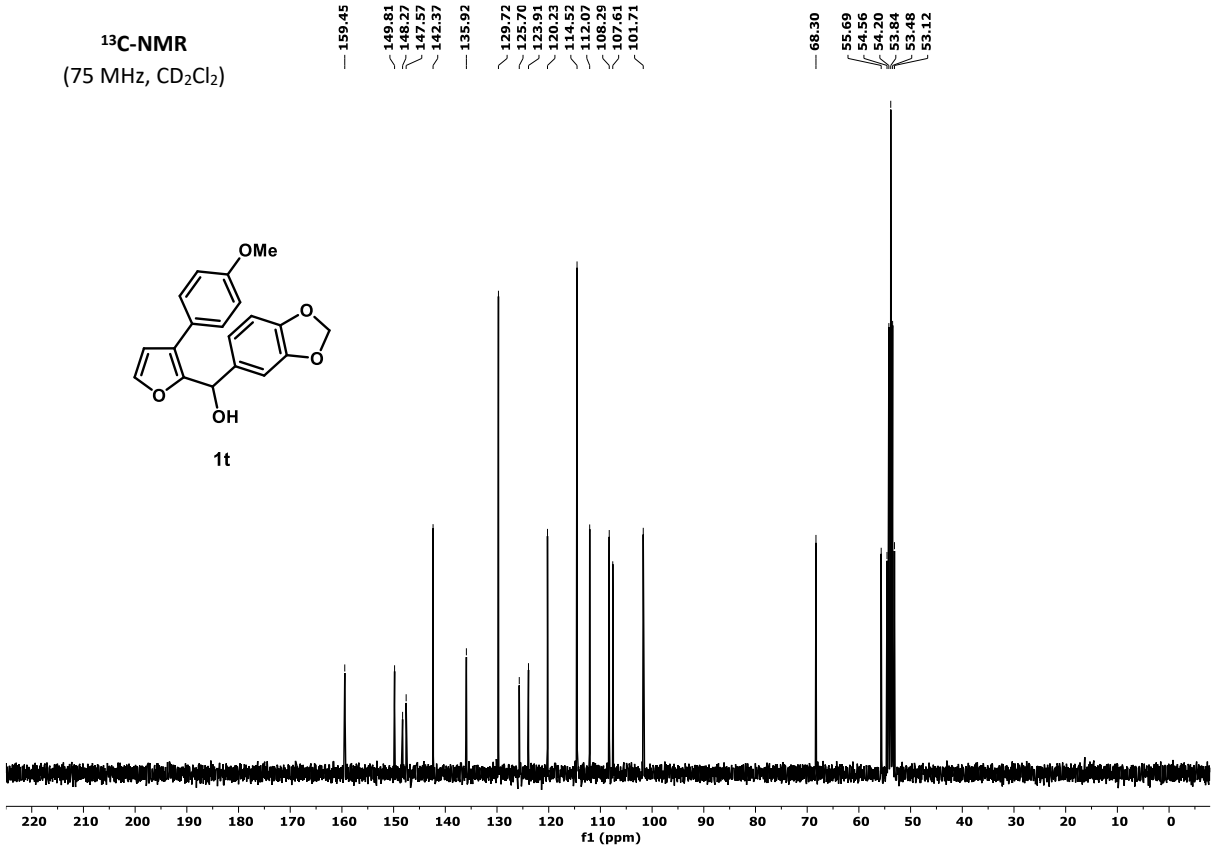
^{13}C-NMR
(100 MHz, CD_2Cl_2)



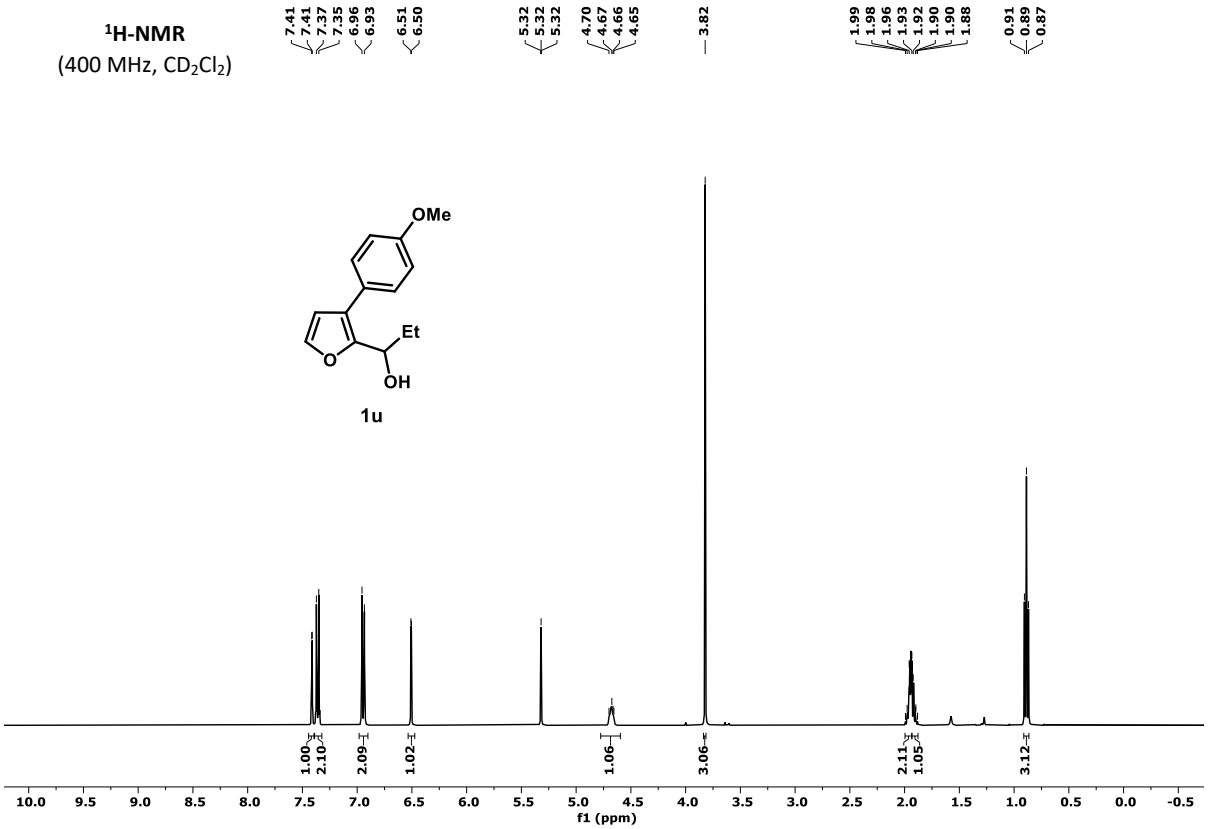
^{1}H-NMR
(300 MHz, CD_2Cl_2)



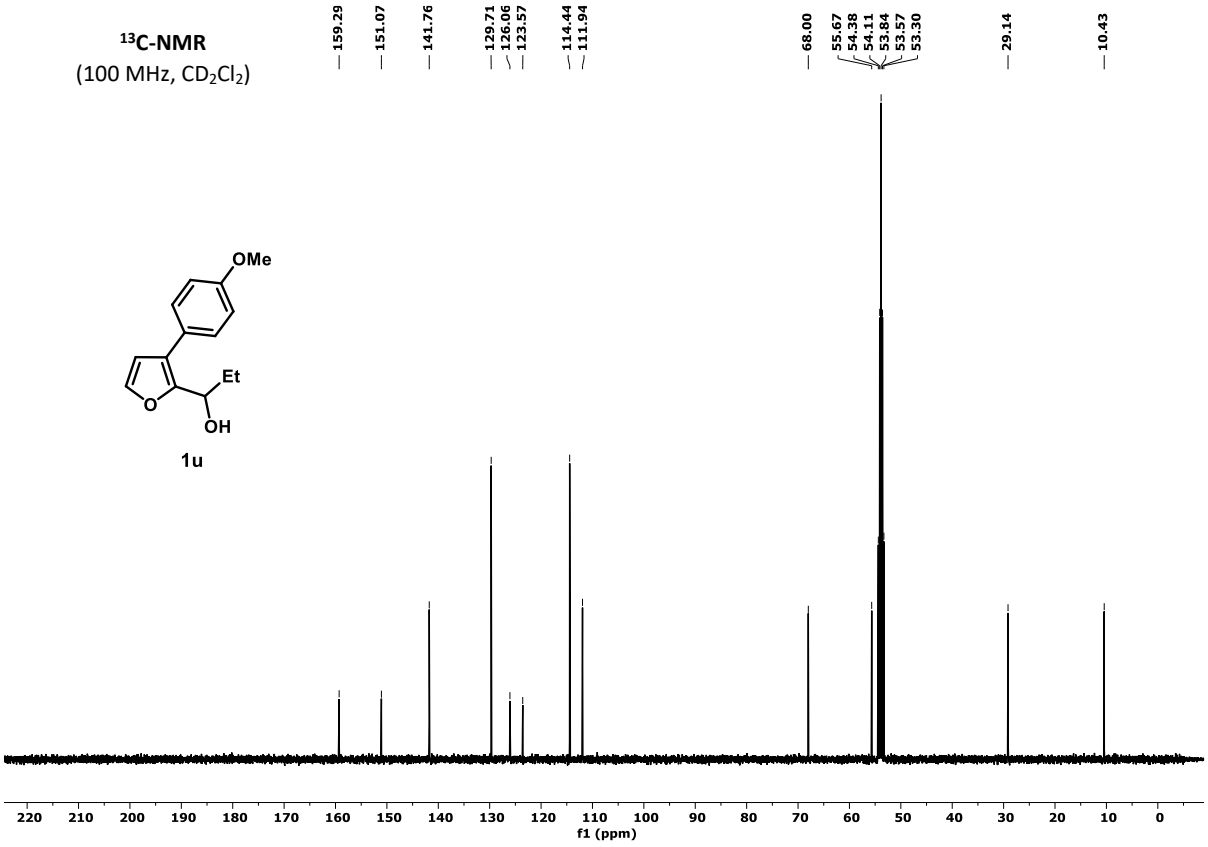
^{13}C-NMR
(75 MHz, CD_2Cl_2)



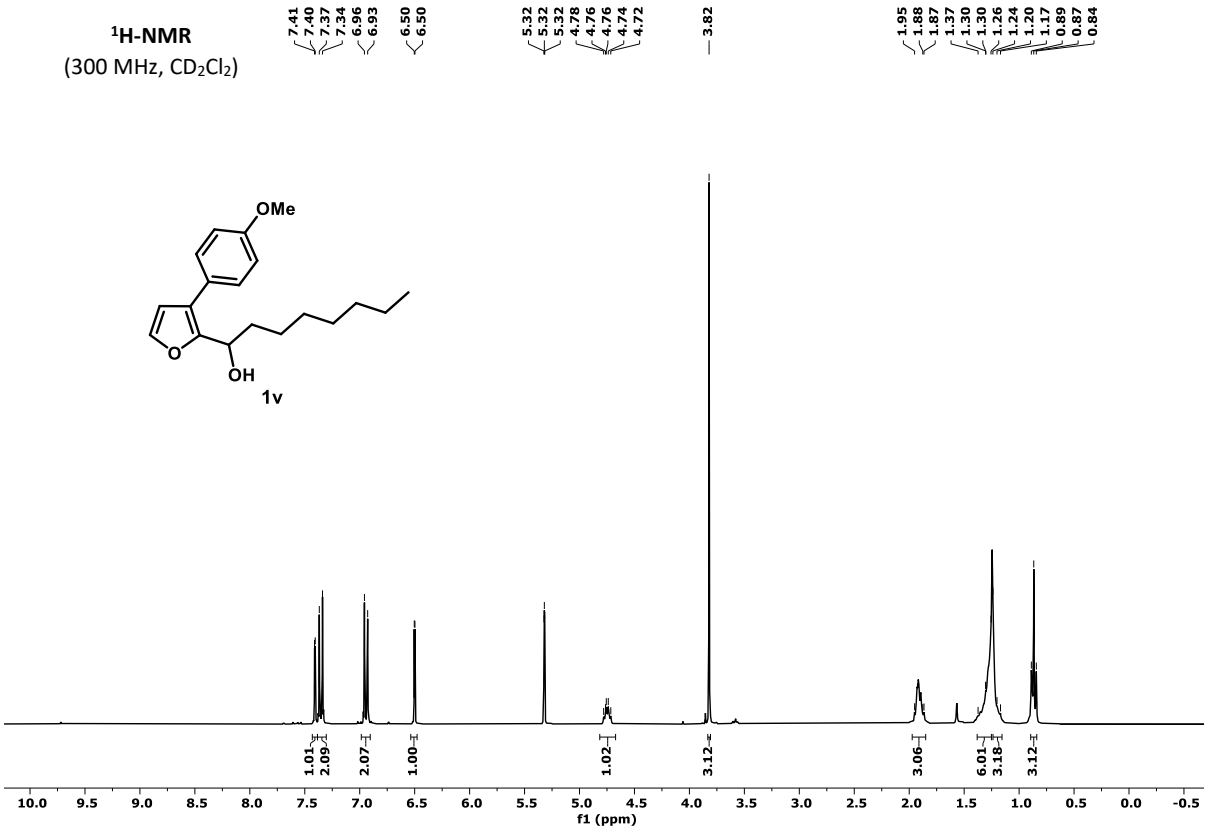
^{1}H-NMR
(400 MHz, CD_2Cl_2)



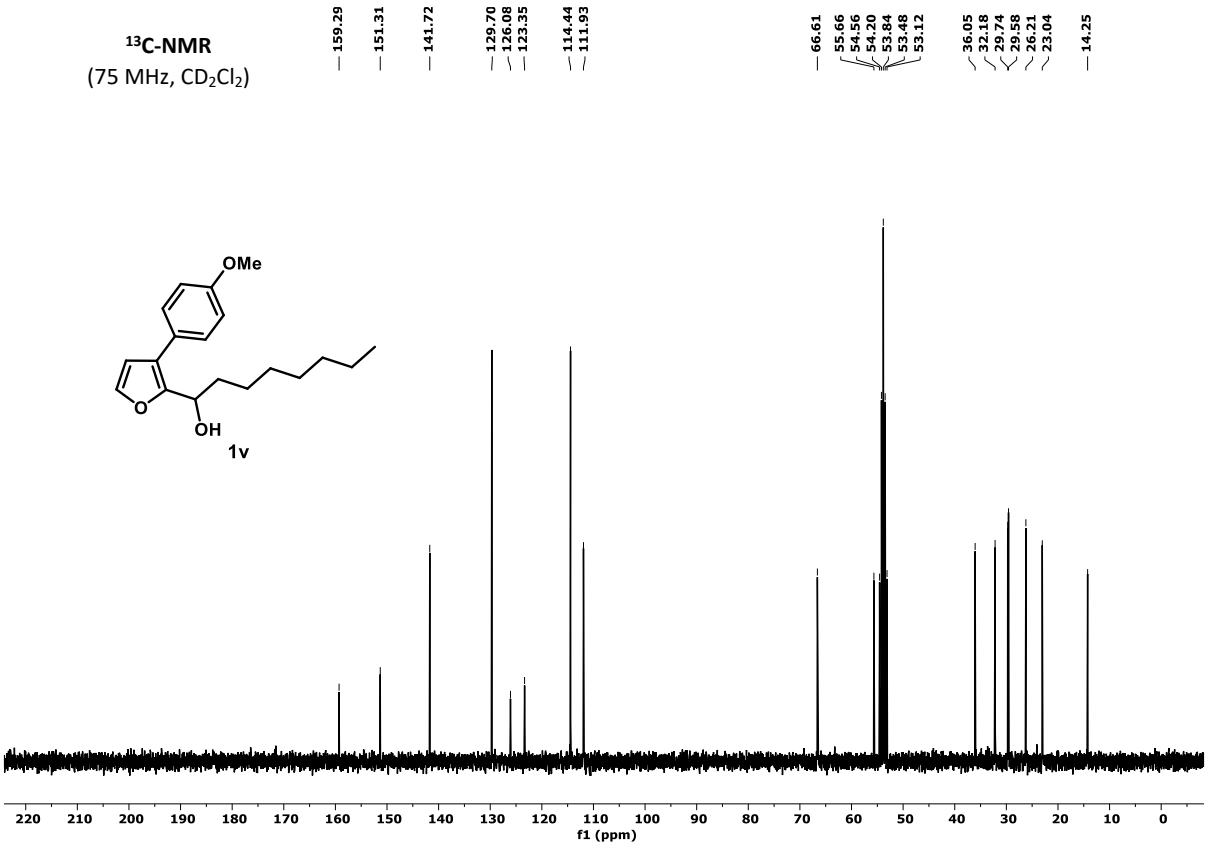
^{13}C-NMR
(100 MHz, CD_2Cl_2)



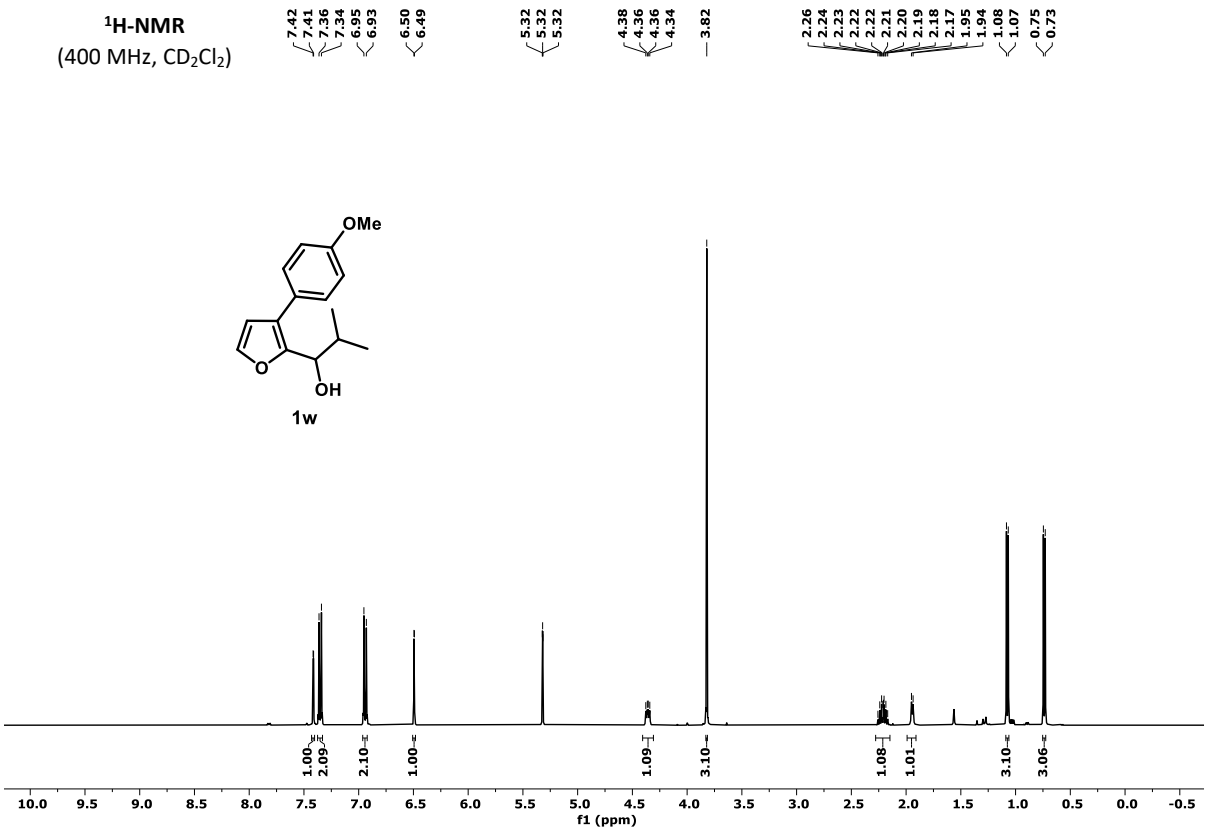
^{1}H-NMR
(300 MHz, CD_2Cl_2)



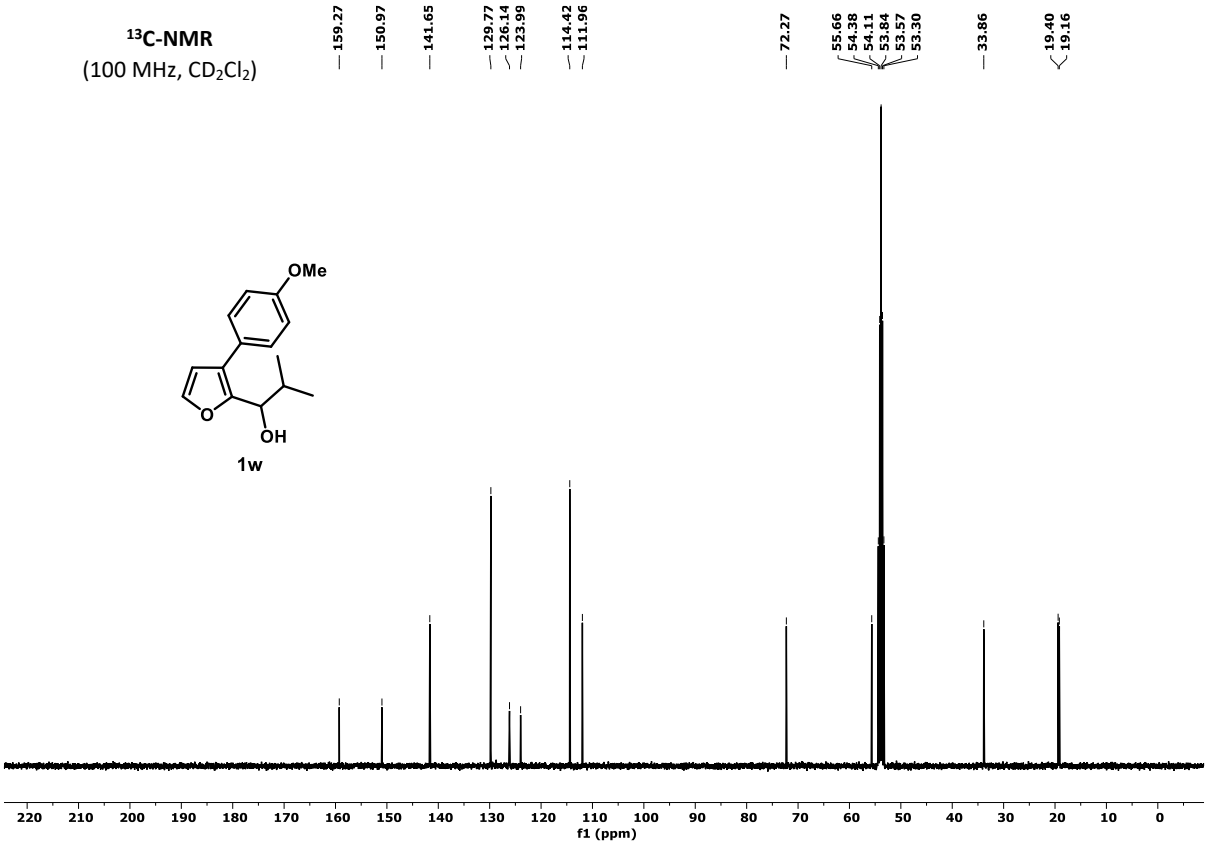
^{13}C-NMR
(75 MHz, CD_2Cl_2)



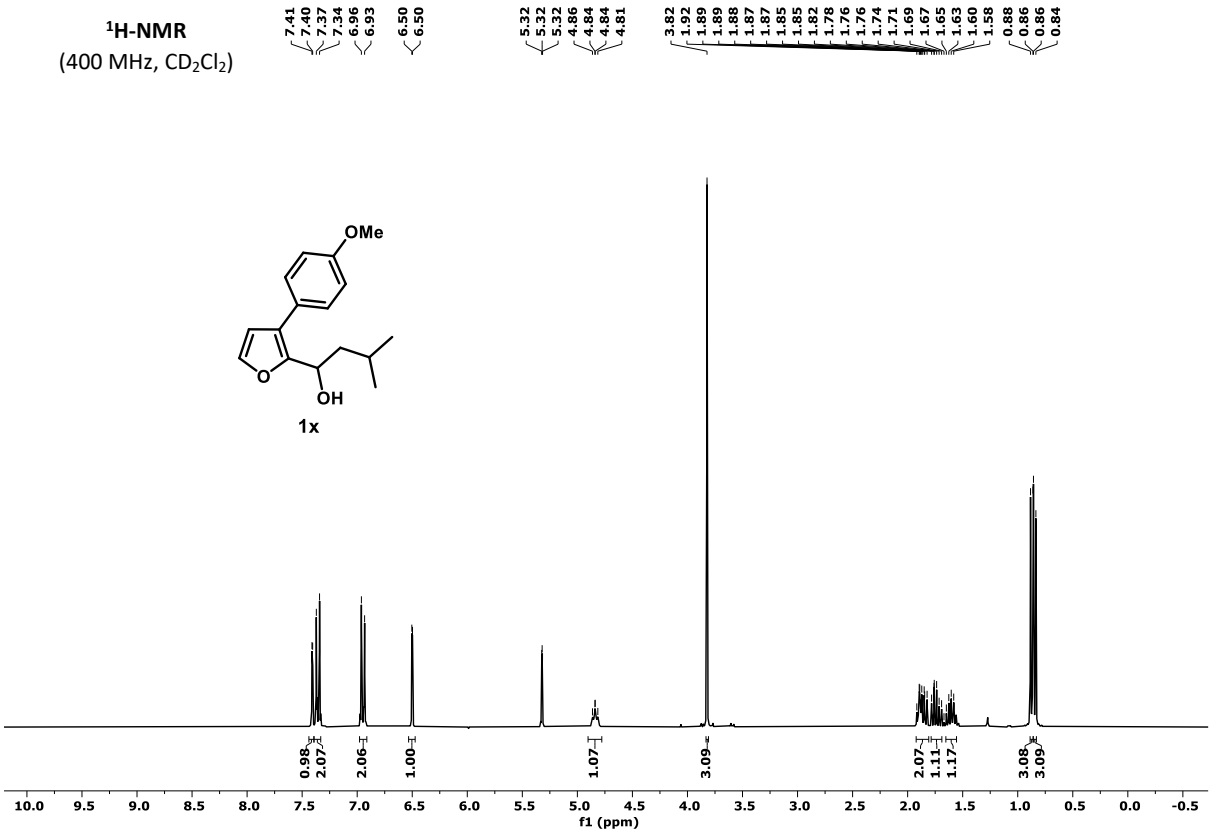
^{1}H-NMR
(400 MHz, CD_2Cl_2)

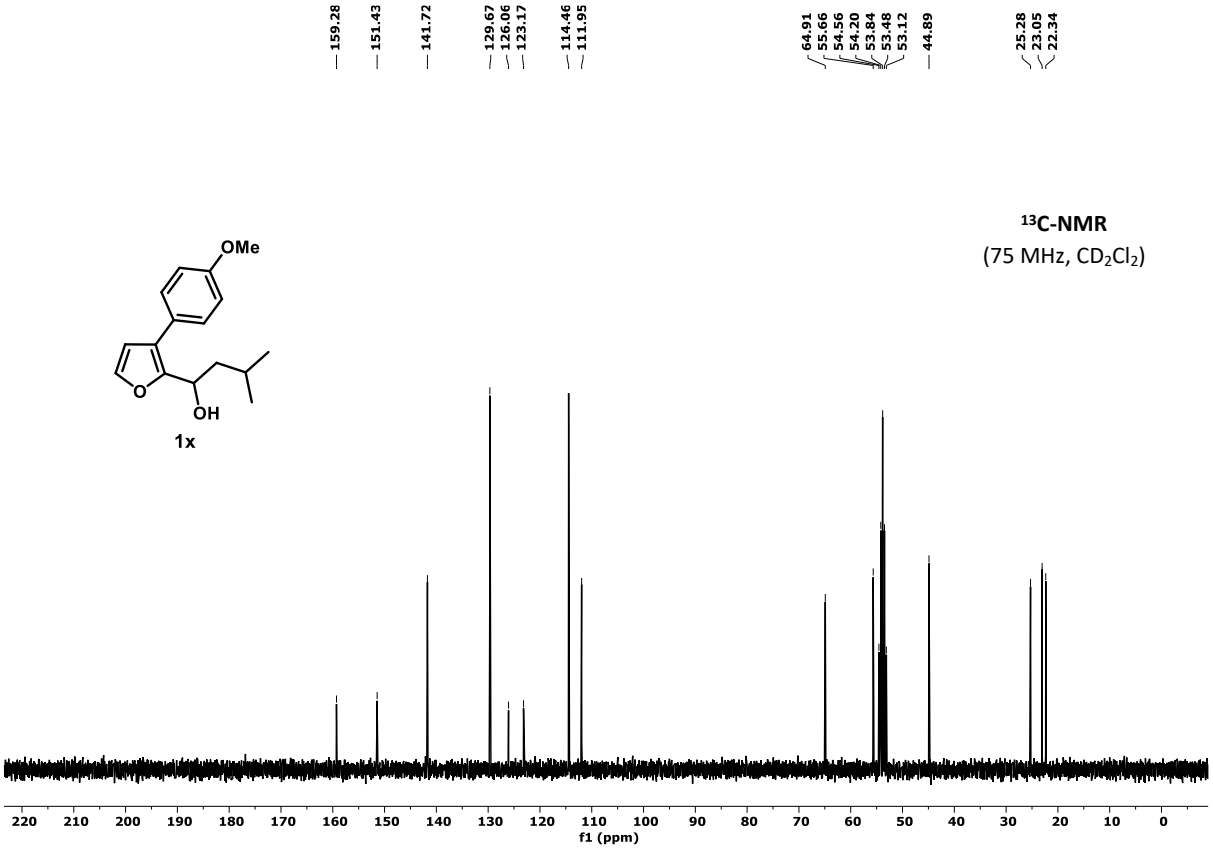


^{13}C-NMR
(100 MHz, CD_2Cl_2)



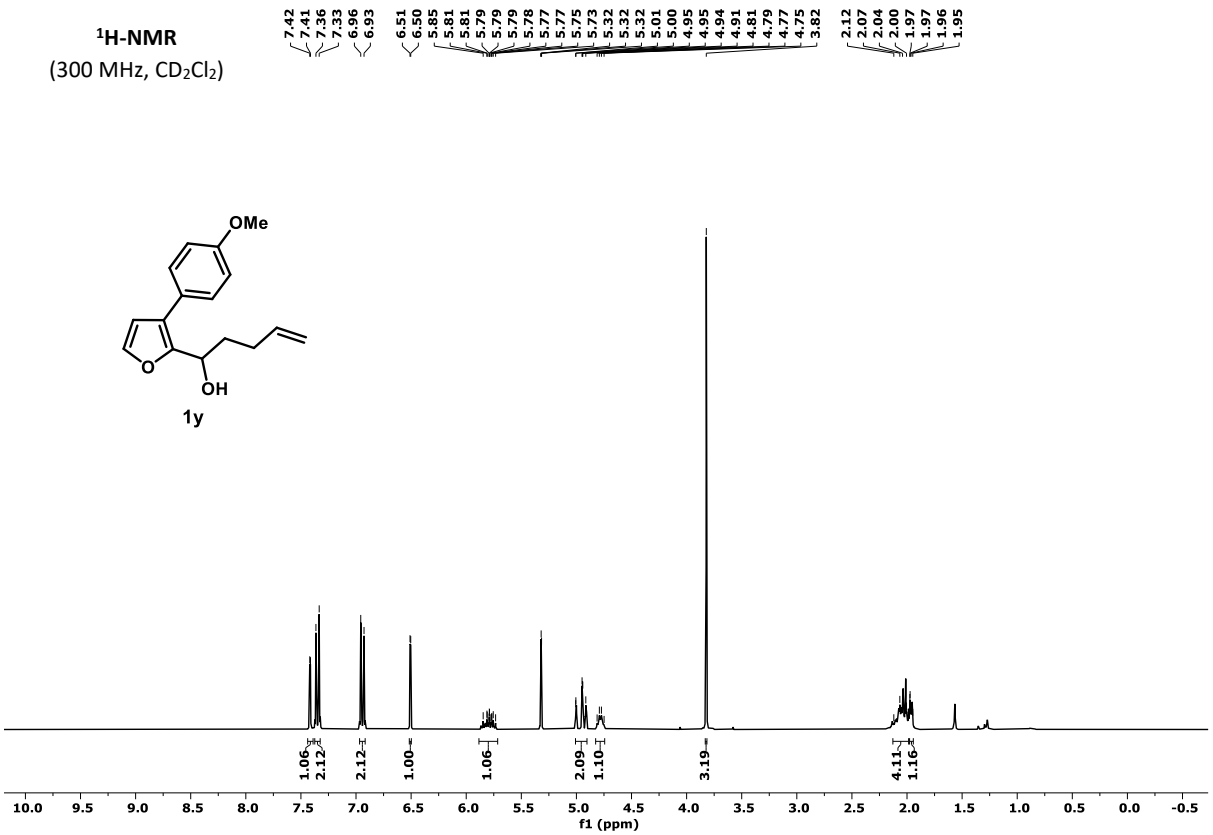
^{1}H-NMR
(400 MHz, CD_2Cl_2)





^{13}C-NMR
(75 MHz, CD_2Cl_2)

^{1}H-NMR
(300 MHz, CD_2Cl_2)



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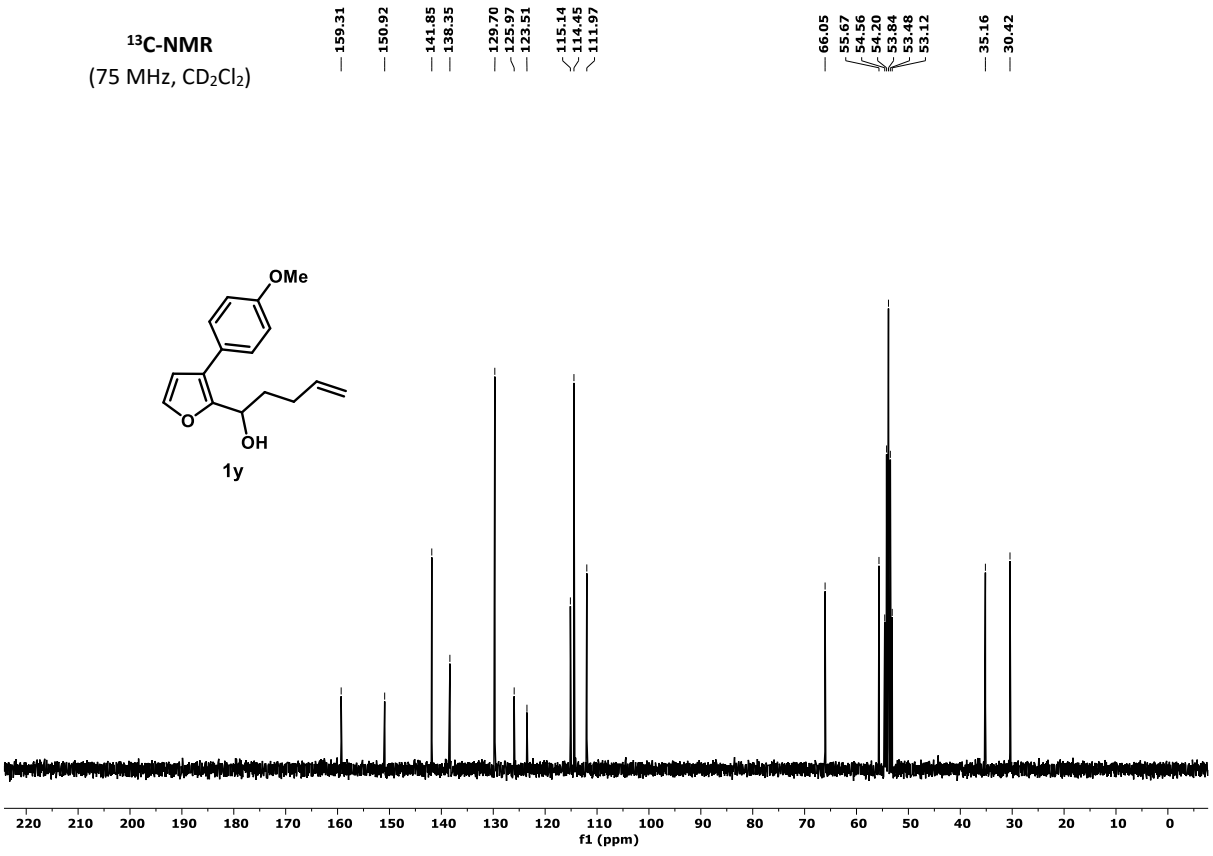
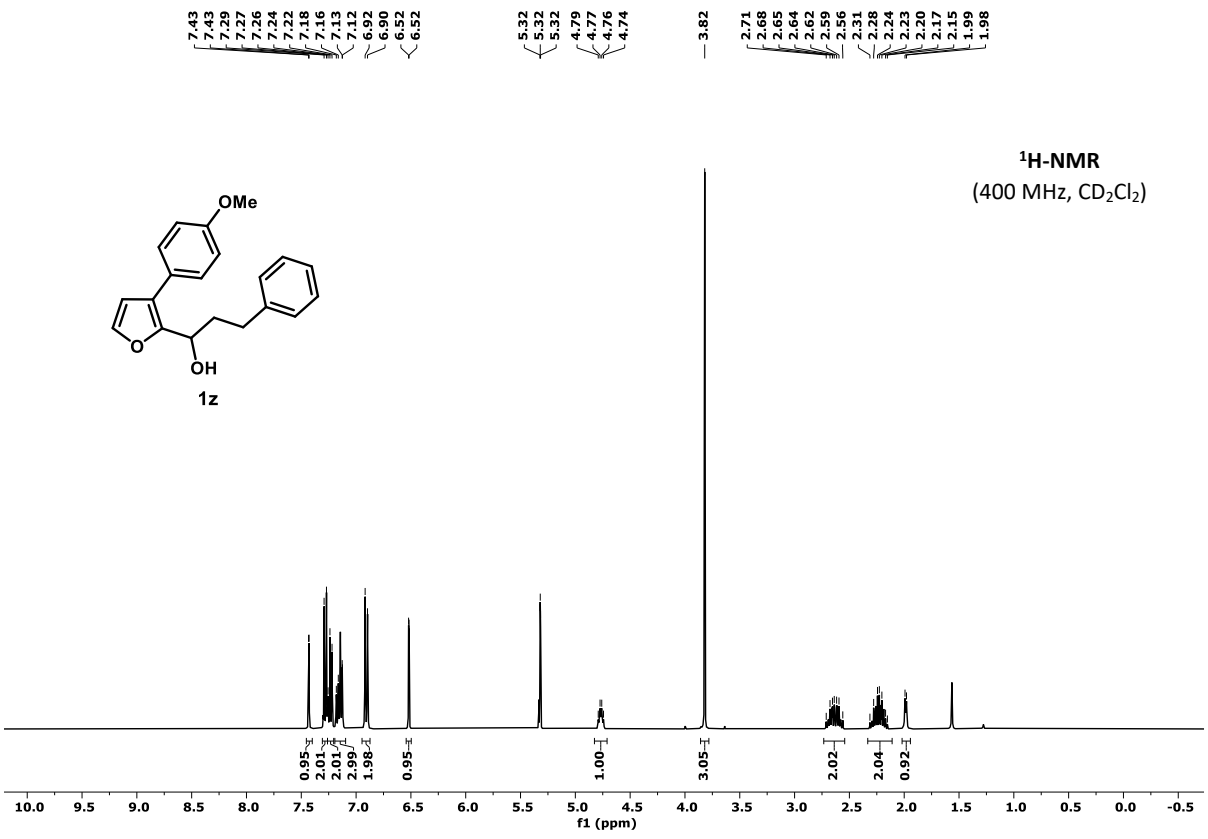
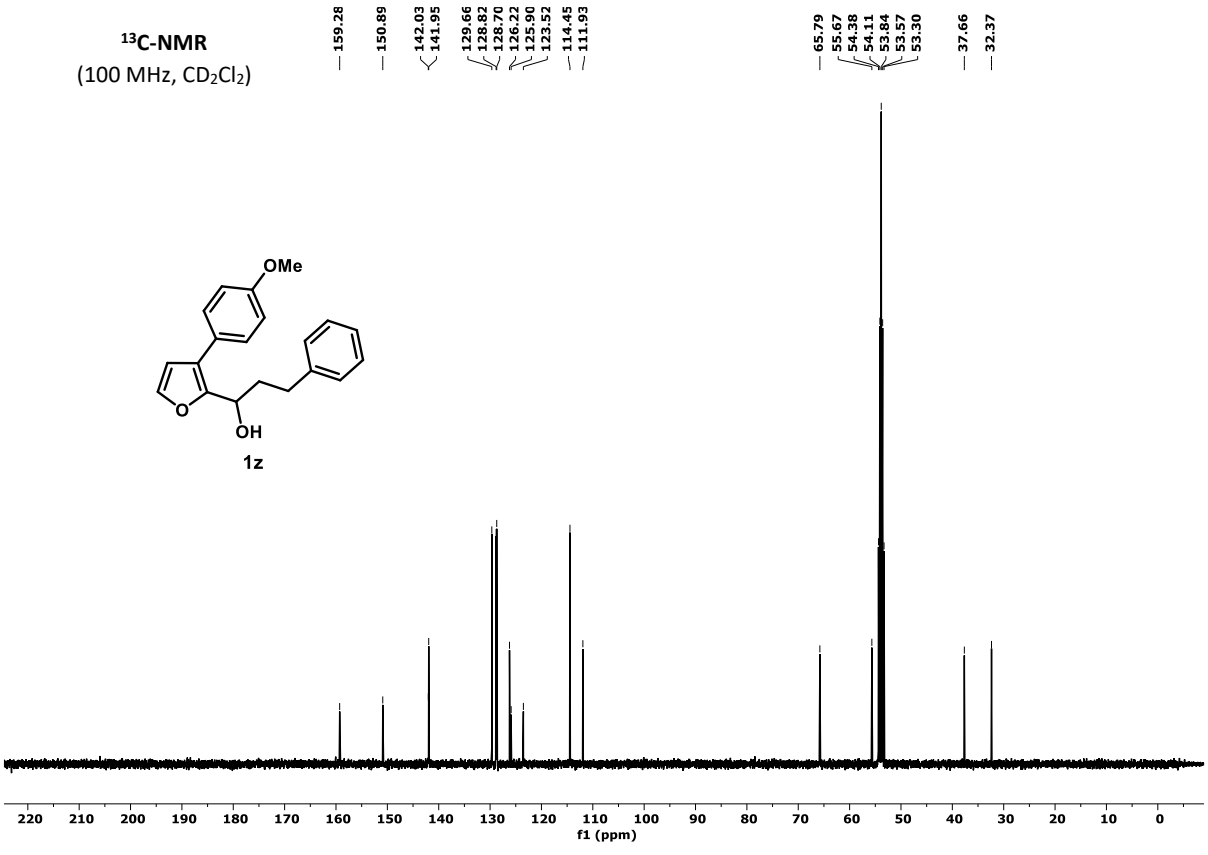
(75 MHz, CD_2Cl_2)





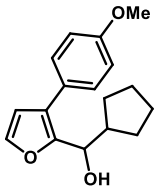
^{1}H-NMR
(400 MHz, CD_2Cl_2)



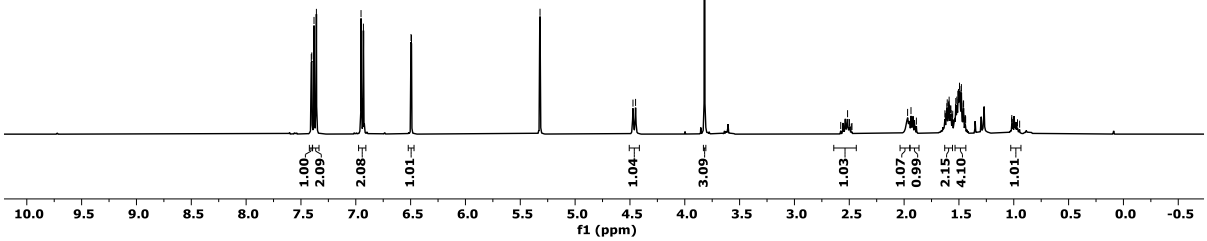
^{13}C-NMR
(100 MHz, CD_2Cl_2)

^{1}H-NMR

(400 MHz, CD_2Cl_2)

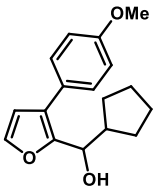


1aa



^{13}C-NMR

(100 MHz, CD_2Cl_2)



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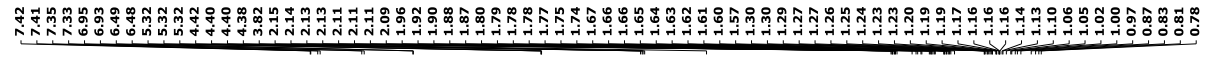
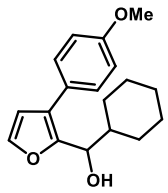
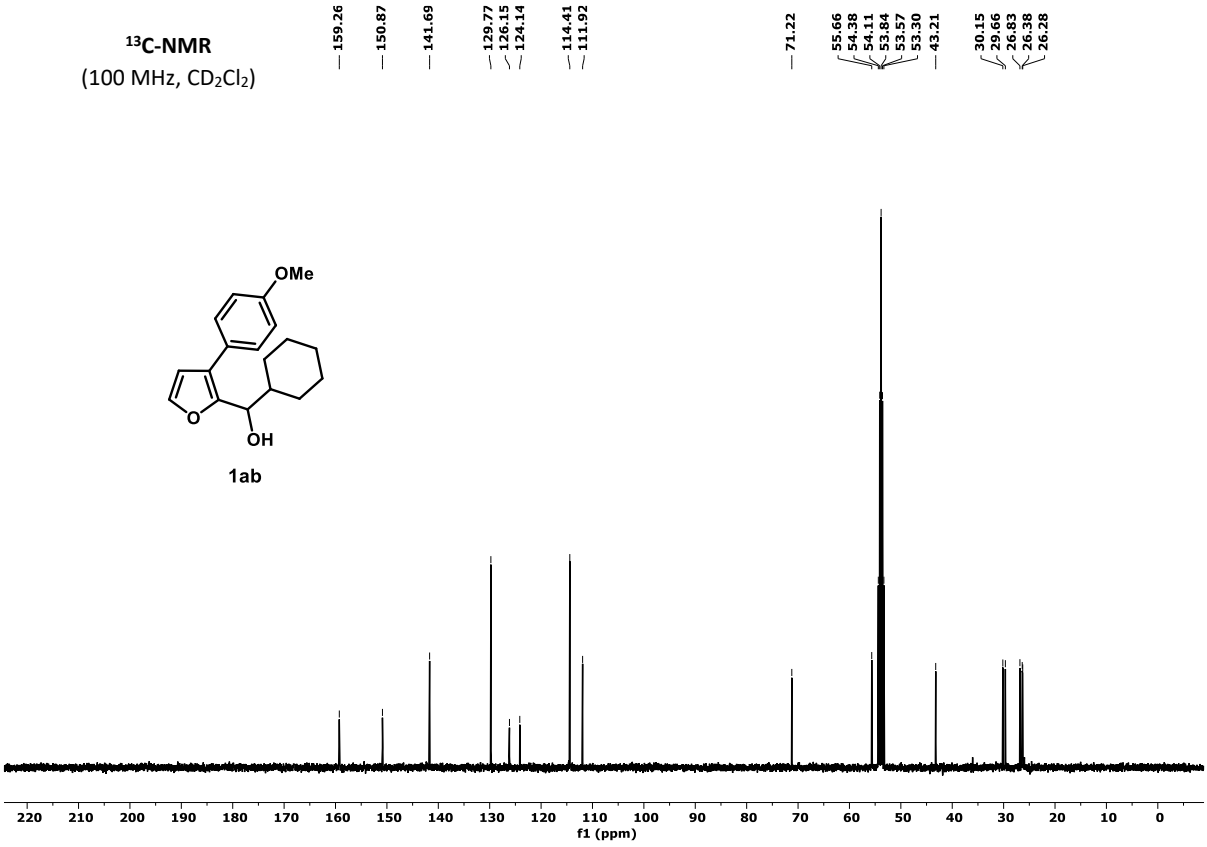


^{1}H-NMR
(400 MHz, CD_2Cl_2)



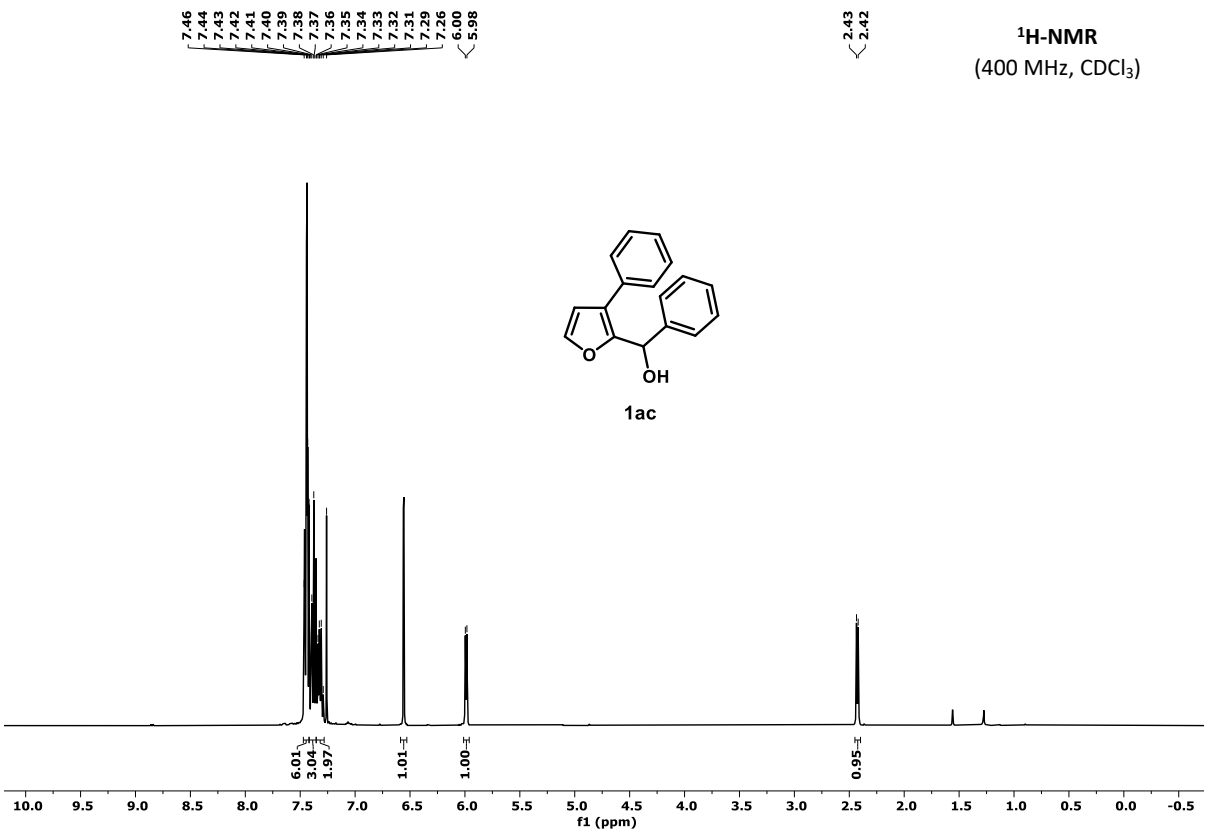
1ab

^{13}C-NMR
(100 MHz, CD_2Cl_2)

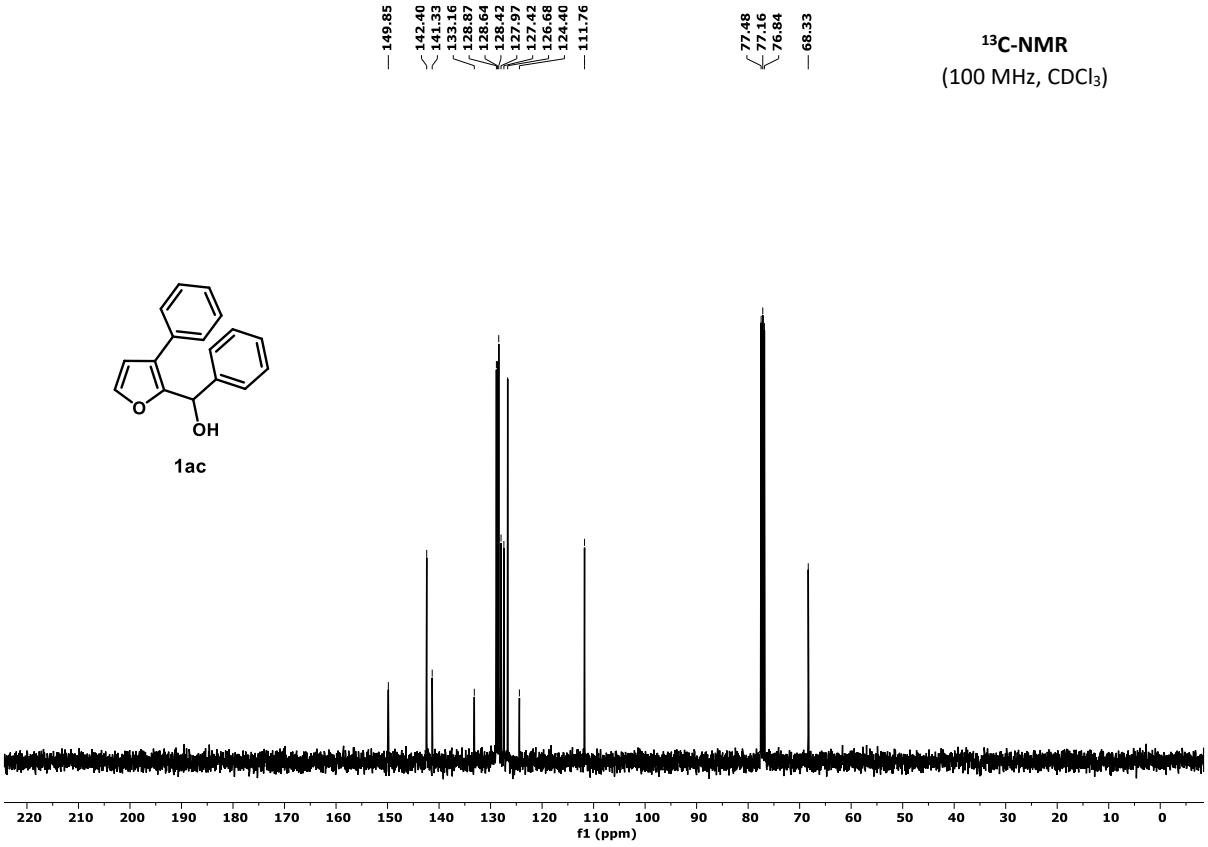


1ab

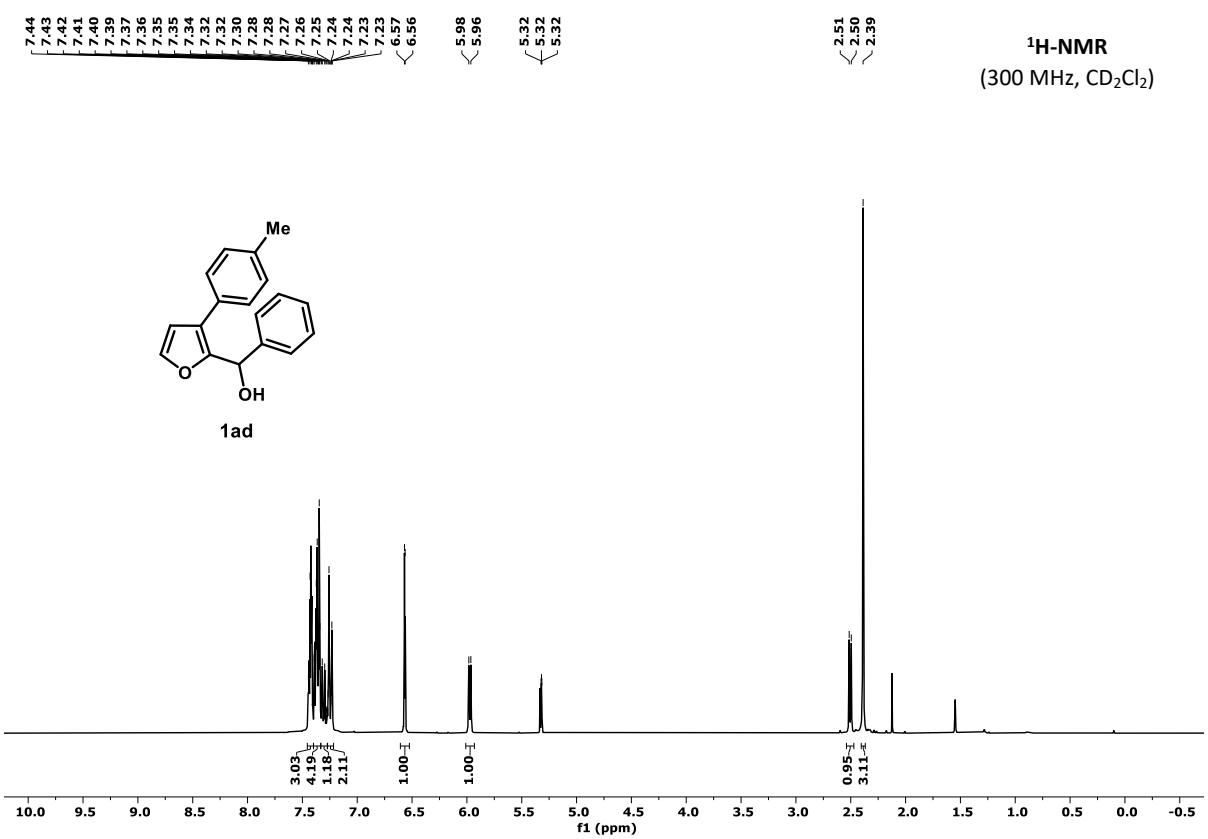
^{1}H-NMR
(400 MHz, $CDCl_3$)



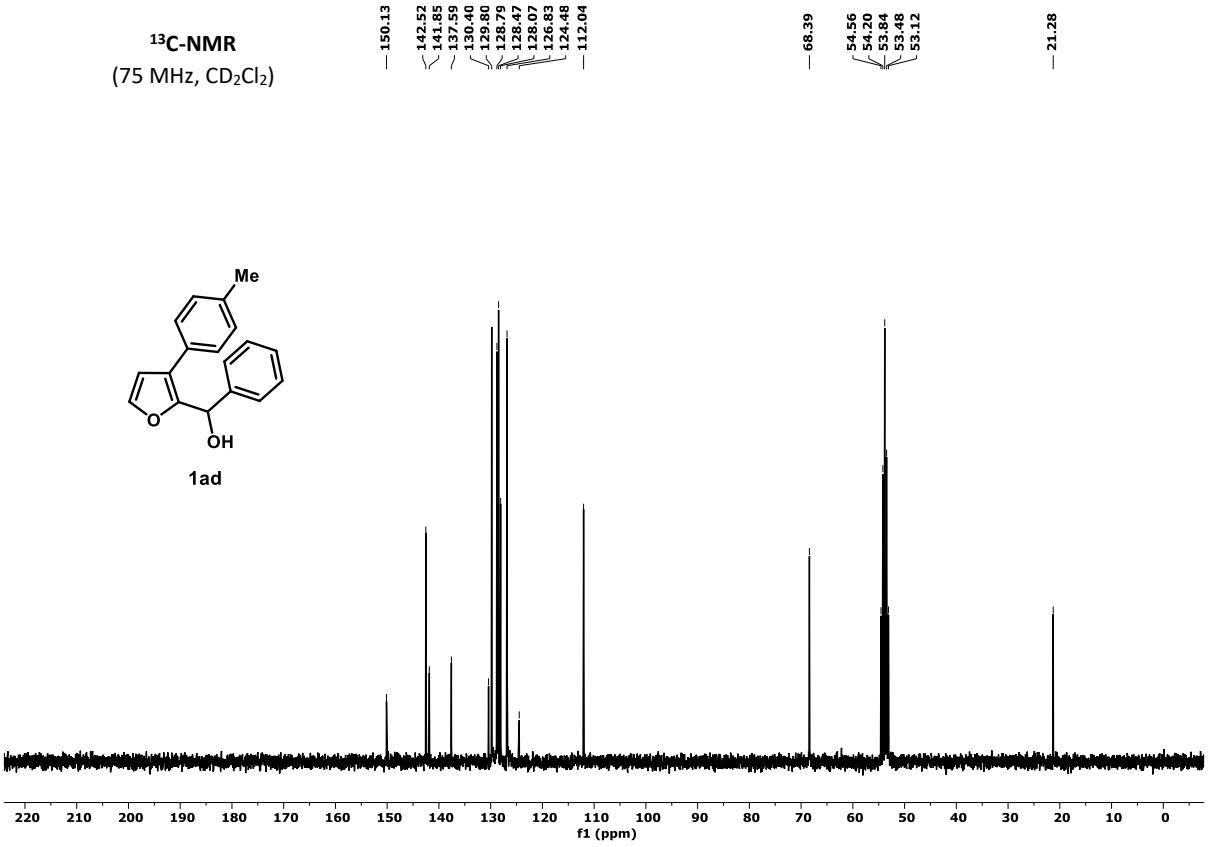
^{13}C-NMR
(100 MHz, $CDCl_3$)



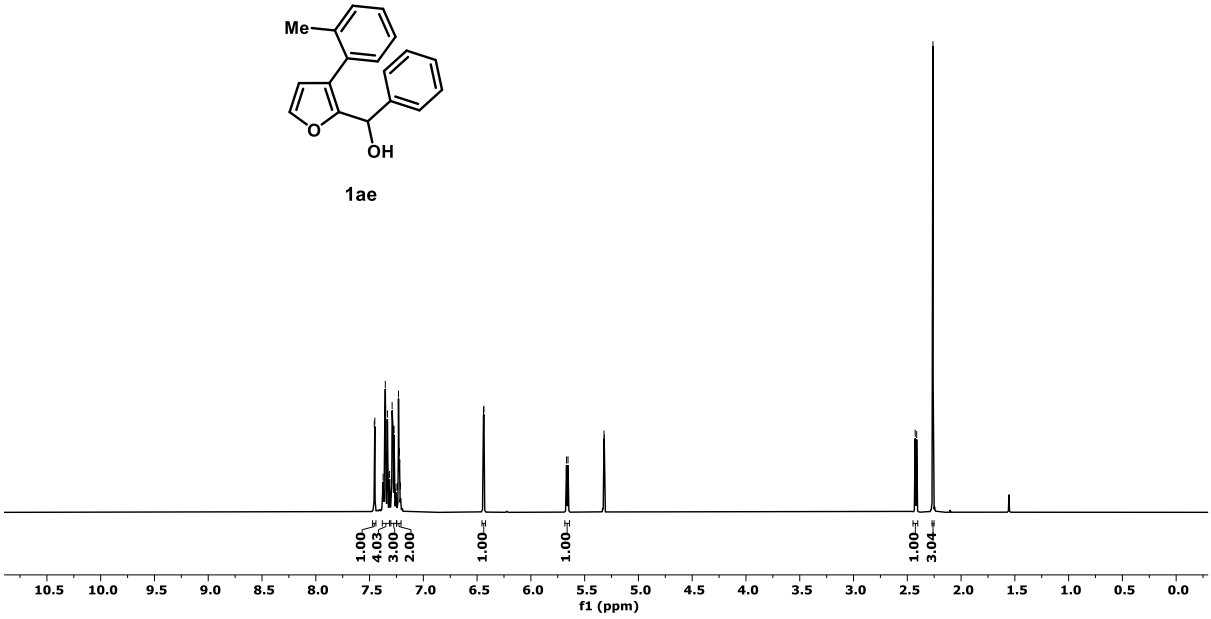
^{1}H-NMR
(300 MHz, CD_2Cl_2)



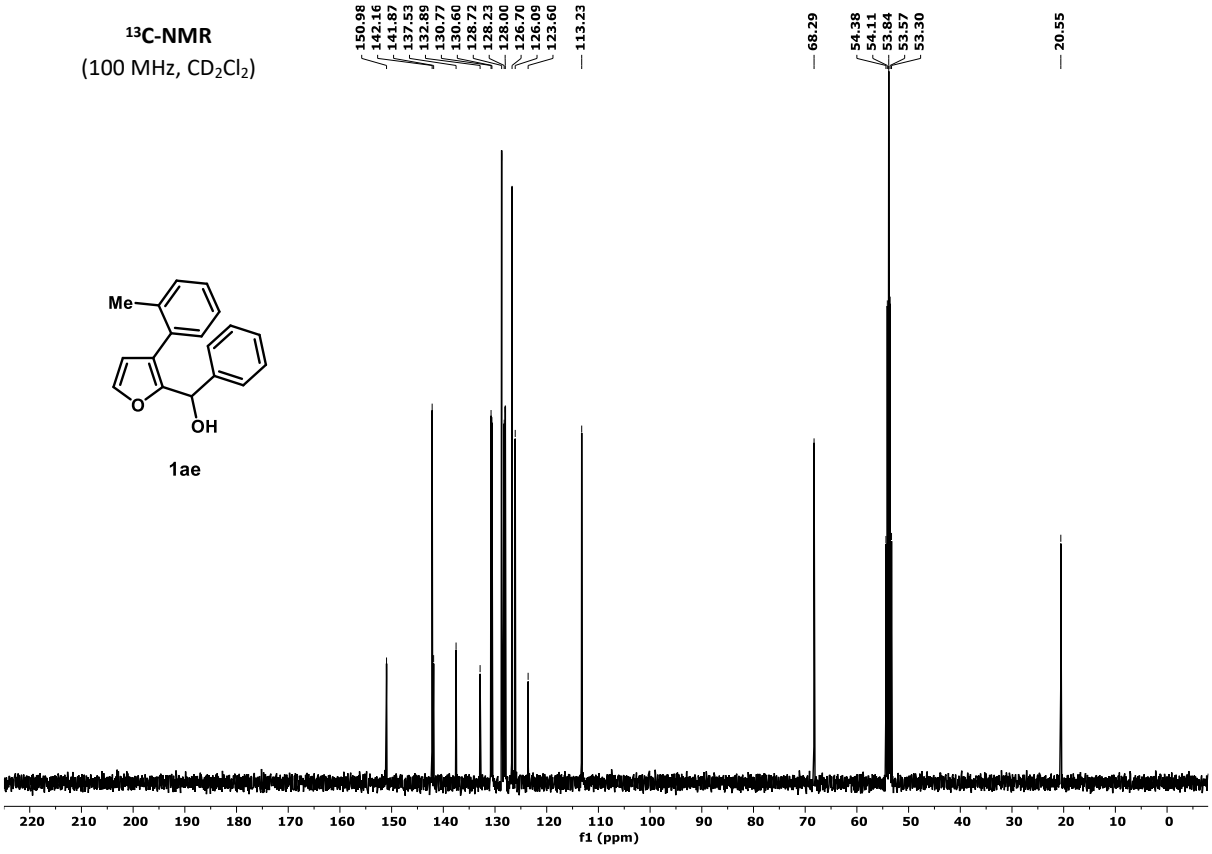
^{13}C-NMR
(75 MHz, CD_2Cl_2)



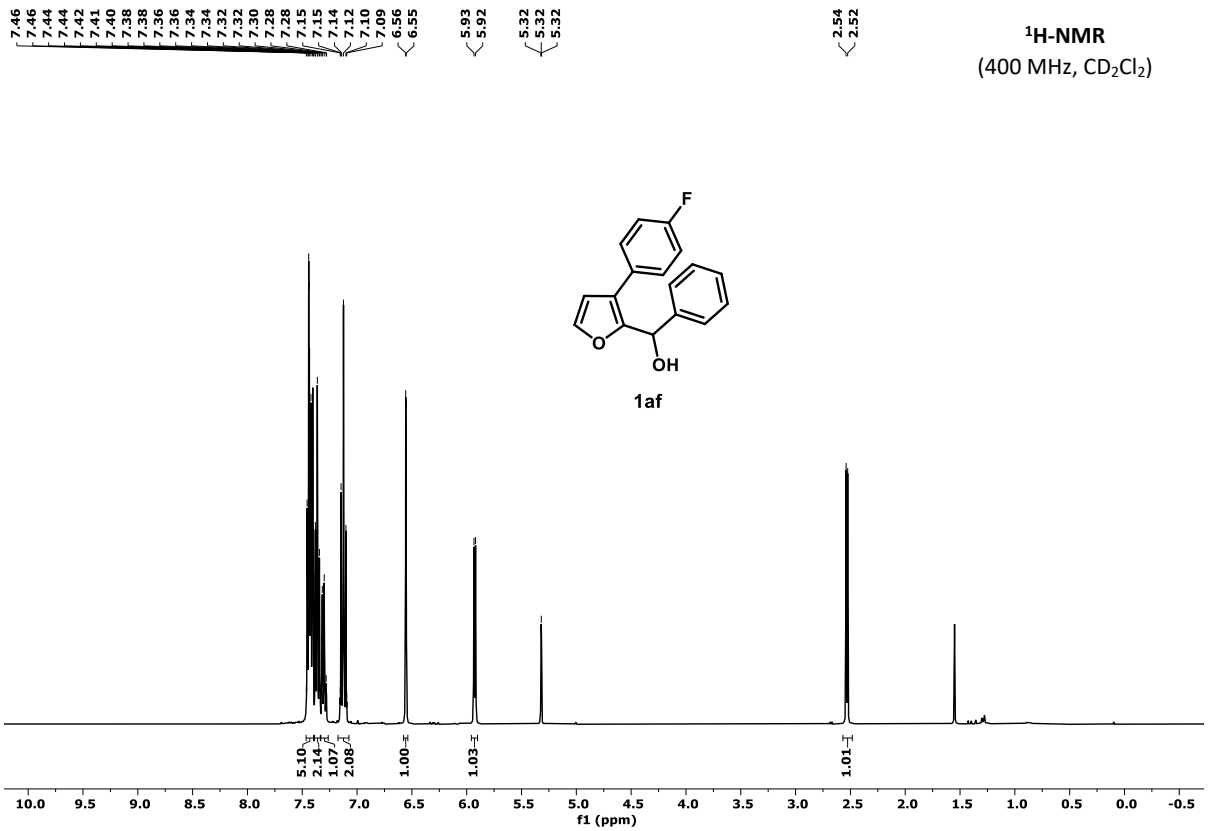
^{1}H-NMR
(400 MHz, CD_2Cl_2)



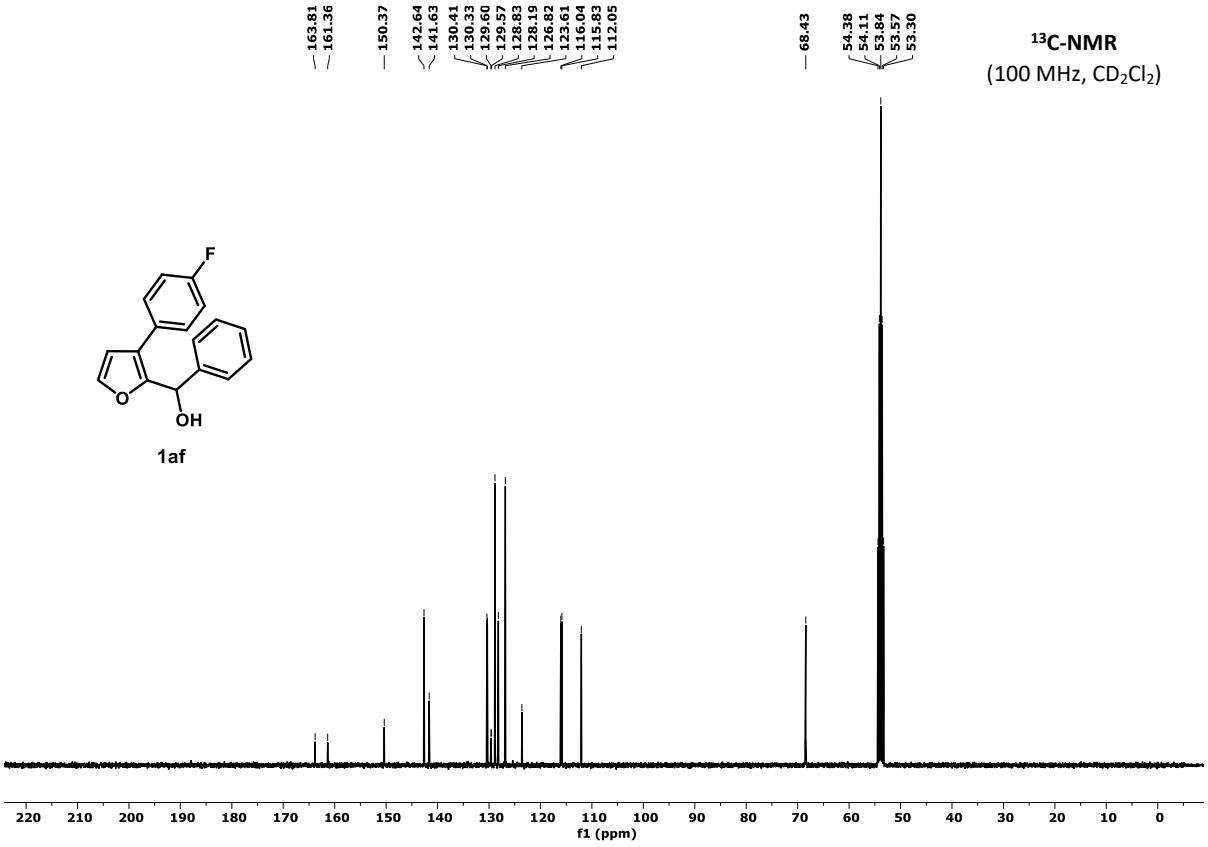
^{13}C-NMR
(100 MHz, CD_2Cl_2)



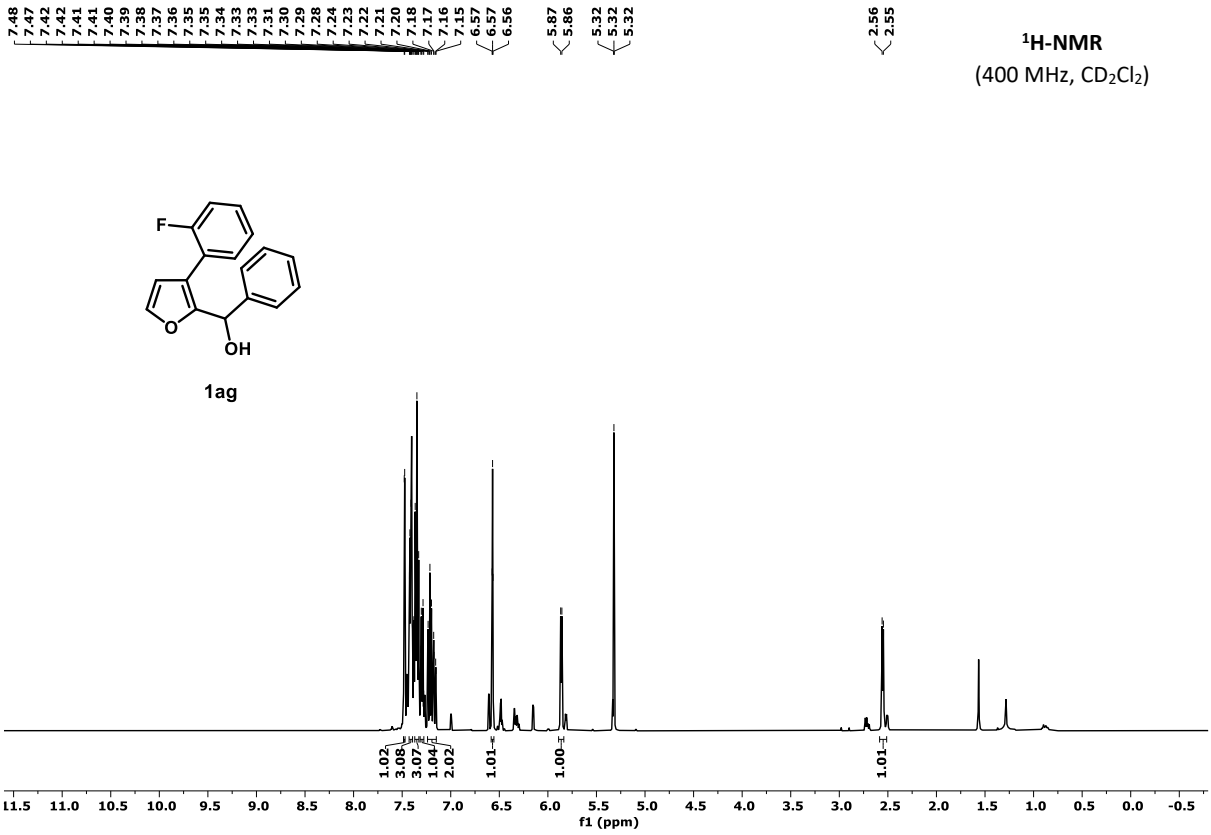
^{1}H-NMR
(400 MHz, CD_2Cl_2)



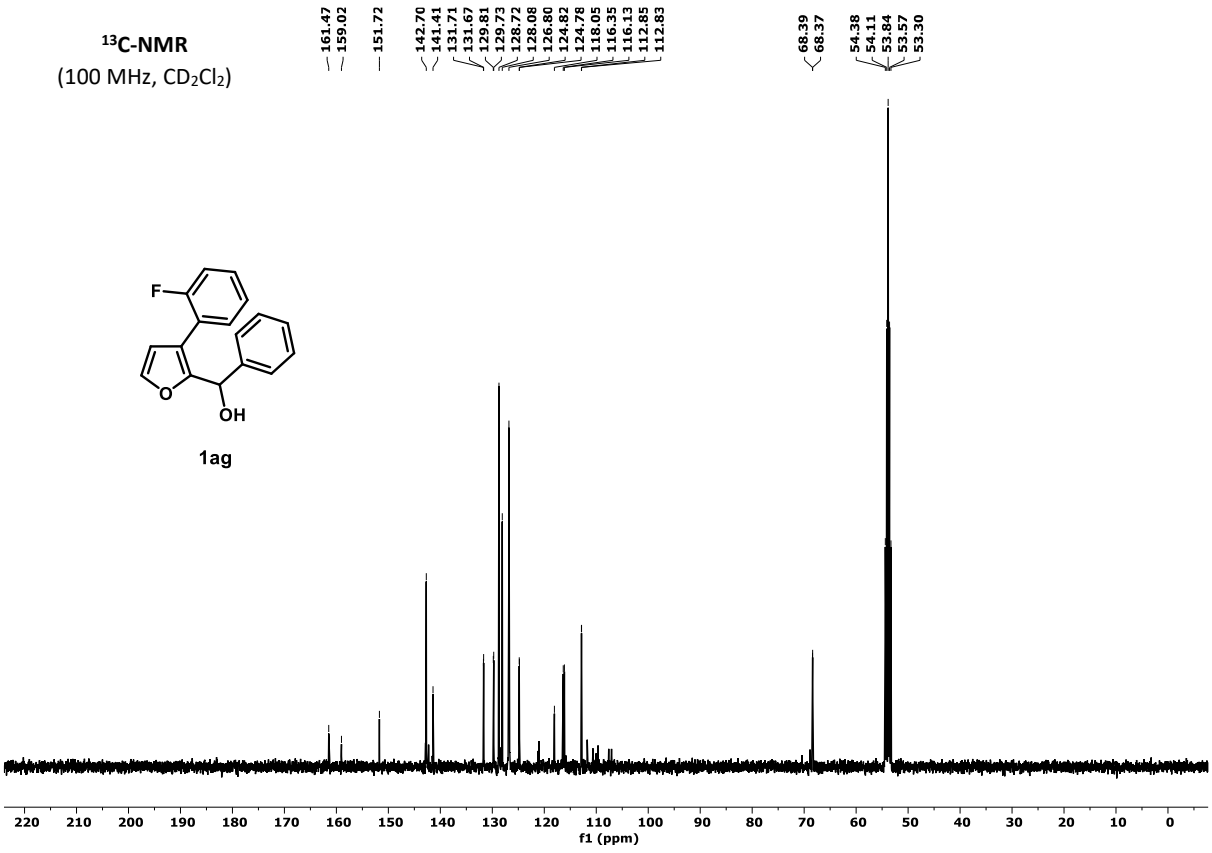
^{13}C-NMR
(100 MHz, CD_2Cl_2)



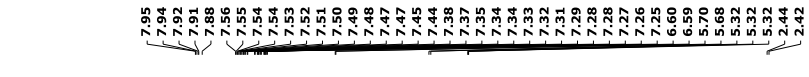
^{1}H-NMR
(400 MHz, CD_2Cl_2)

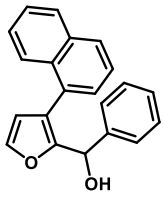


^{13}C-NMR
(100 MHz, CD_2Cl_2)

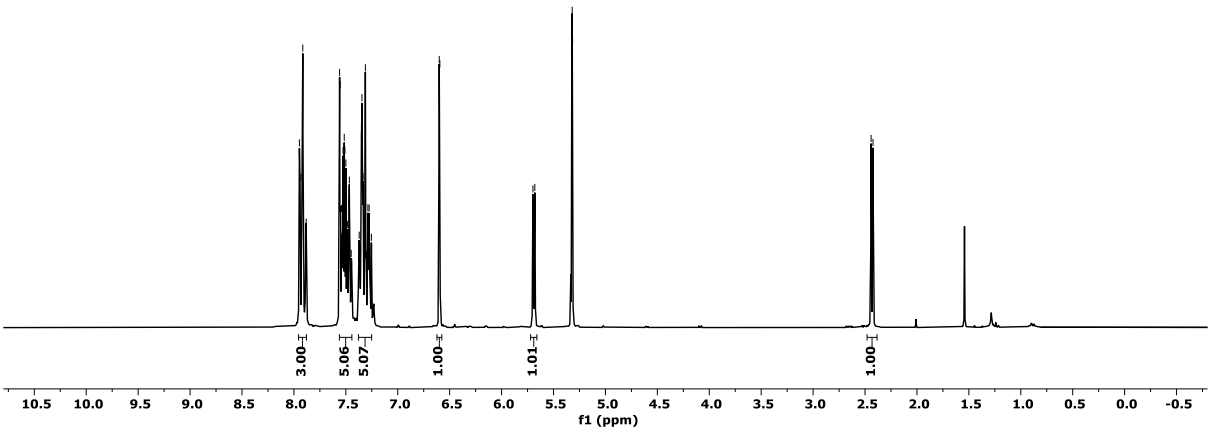


^{1}H-NMR
(300 MHz, CD_2Cl_2)

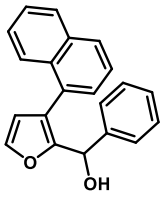




1ah

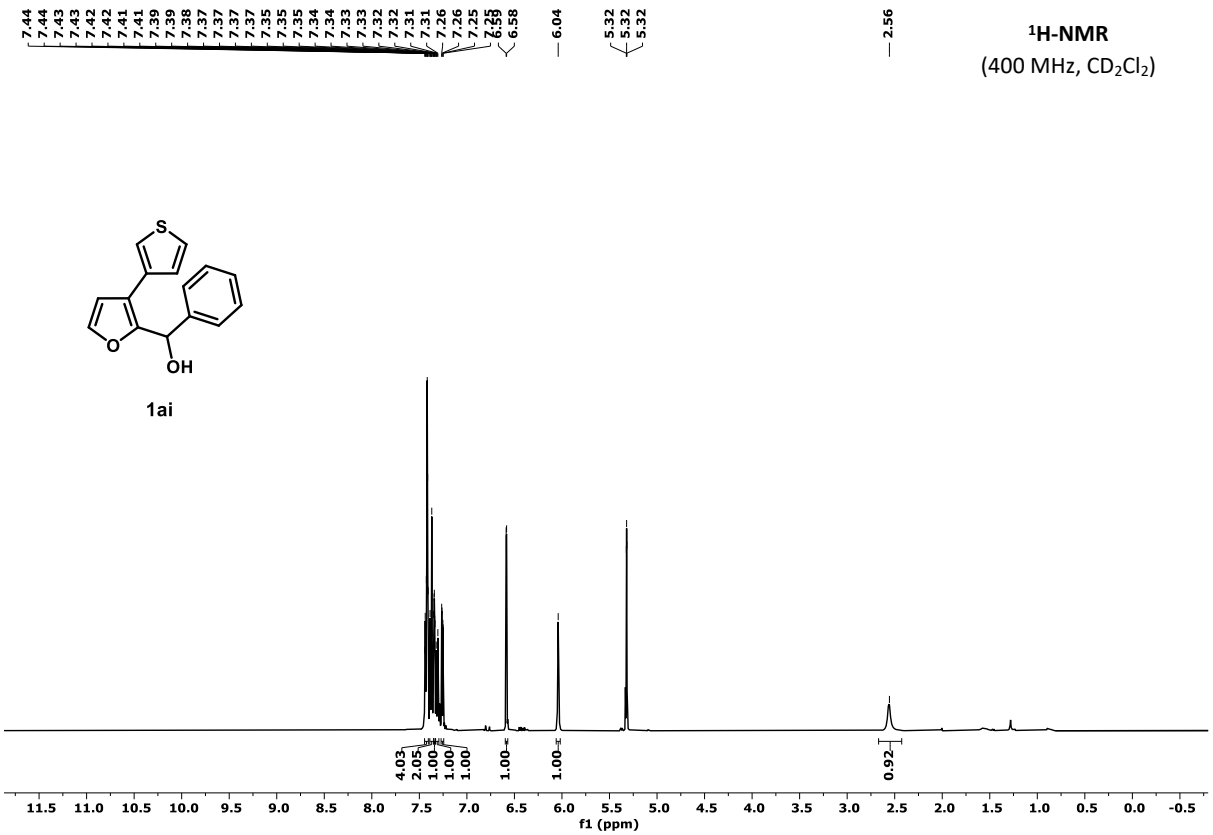


^{13}C-NMR
(75 MHz, CD_2Cl_2)

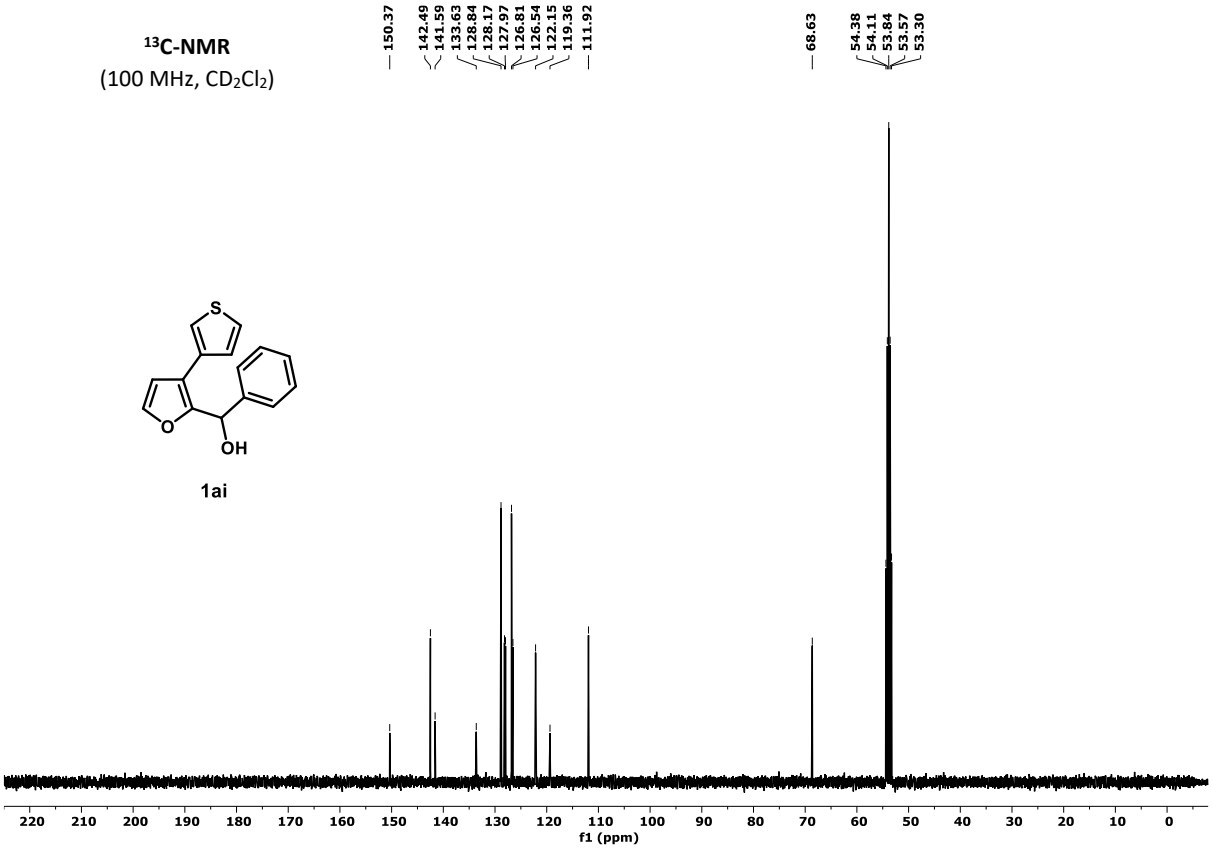


1ah

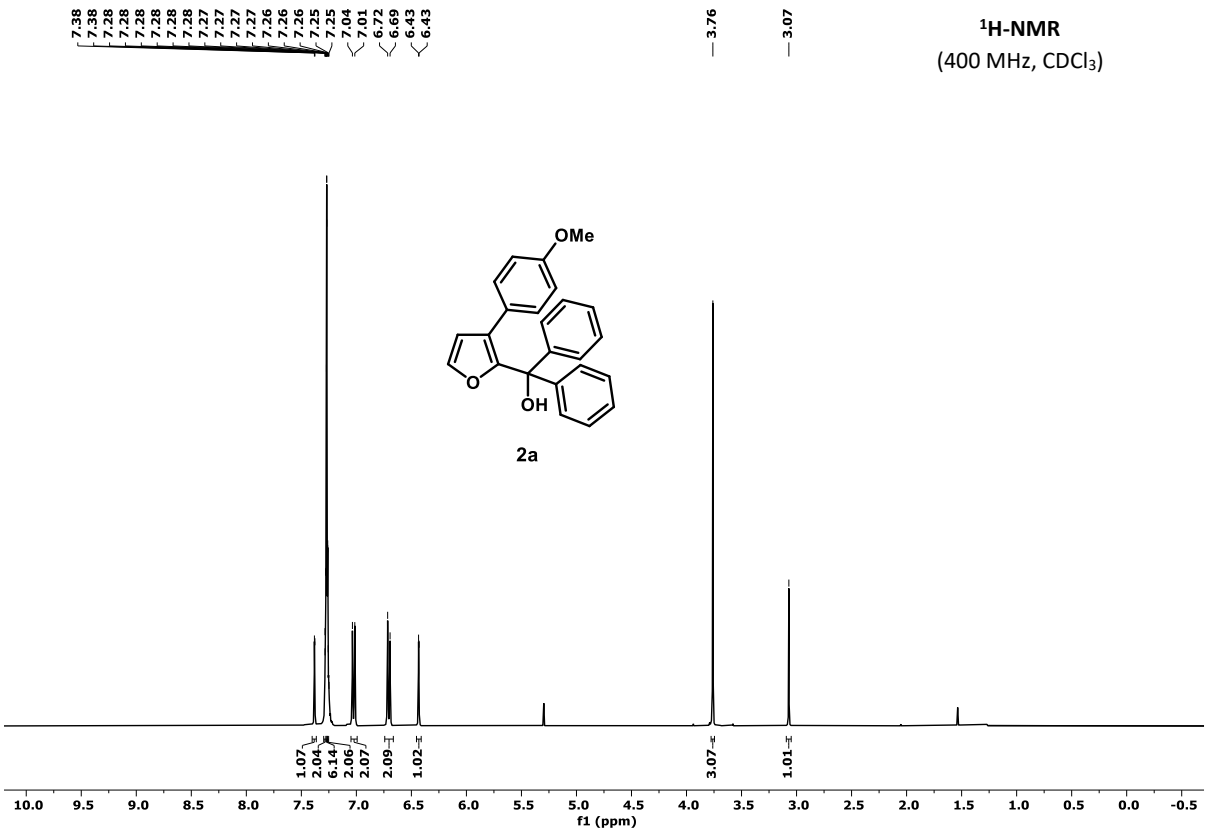
^{1}H-NMR
(400 MHz, CD_2Cl_2)



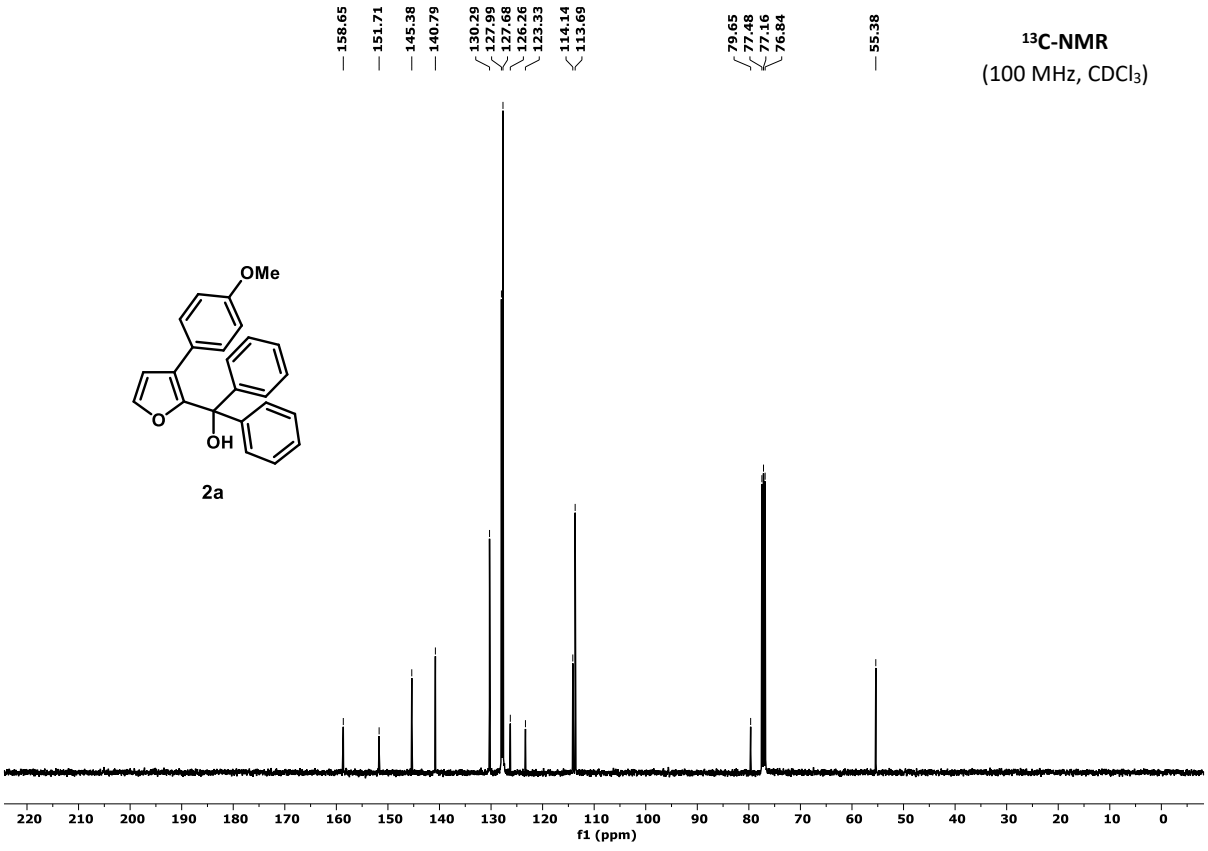
^{13}C-NMR
(100 MHz, CD_2Cl_2)



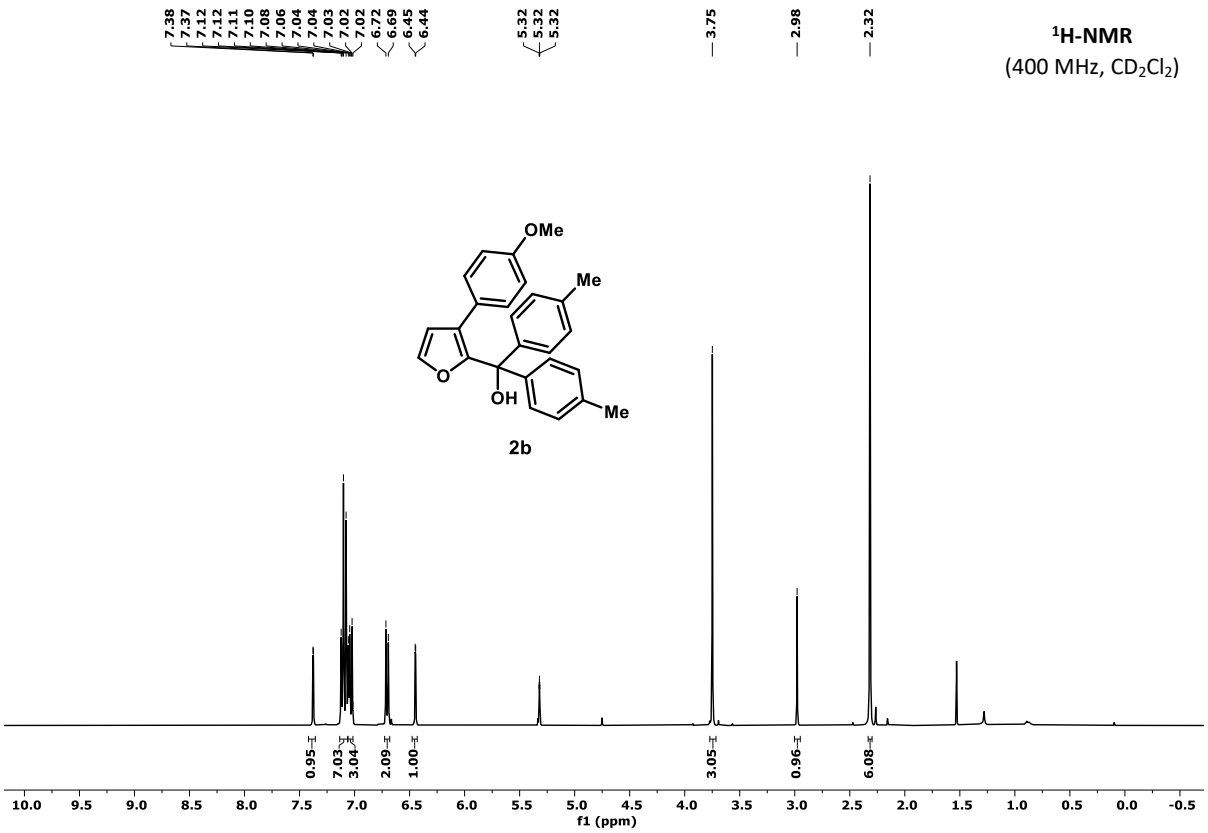
^{1}H-NMR
(400 MHz, $CDCl_3$)



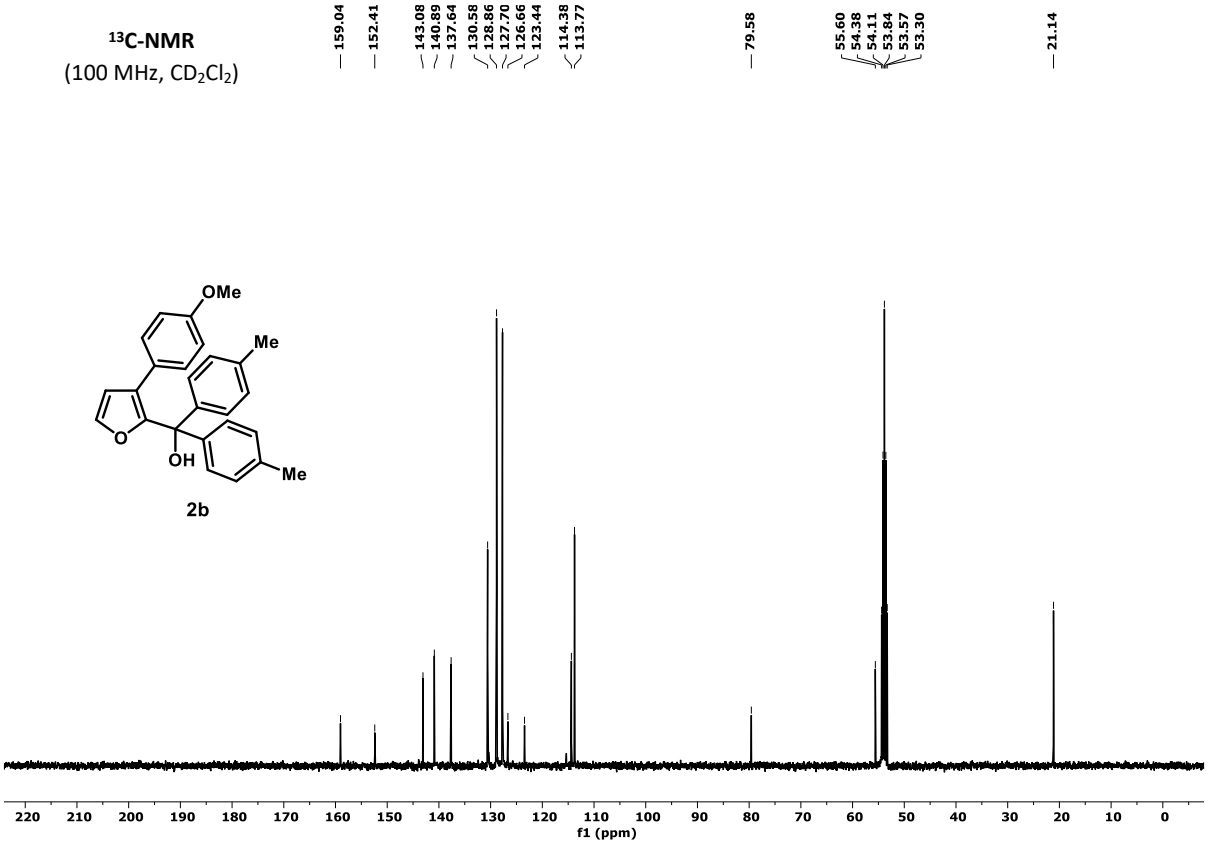
^{13}C-NMR
(100 MHz, $CDCl_3$)



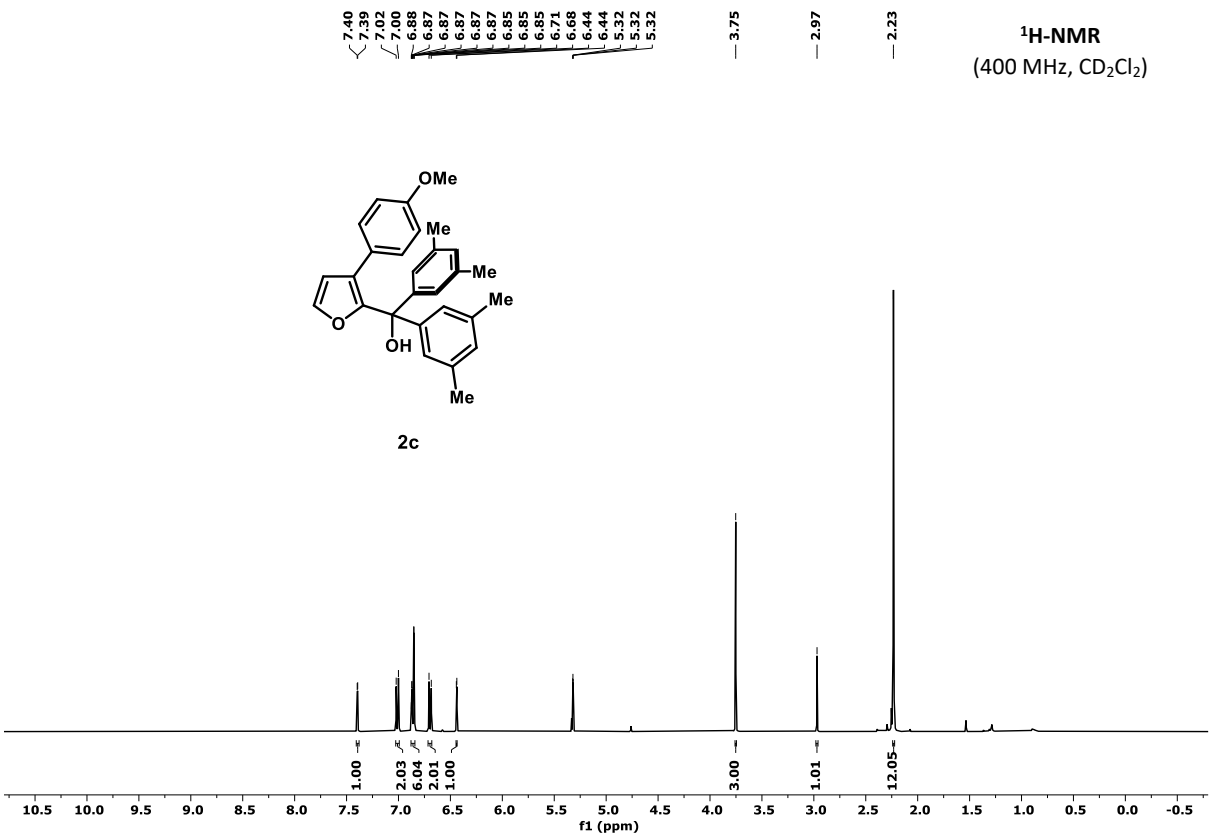
^{1}H-NMR
(400 MHz, CD_2Cl_2)



^{13}C-NMR
(100 MHz, CD_2Cl_2)

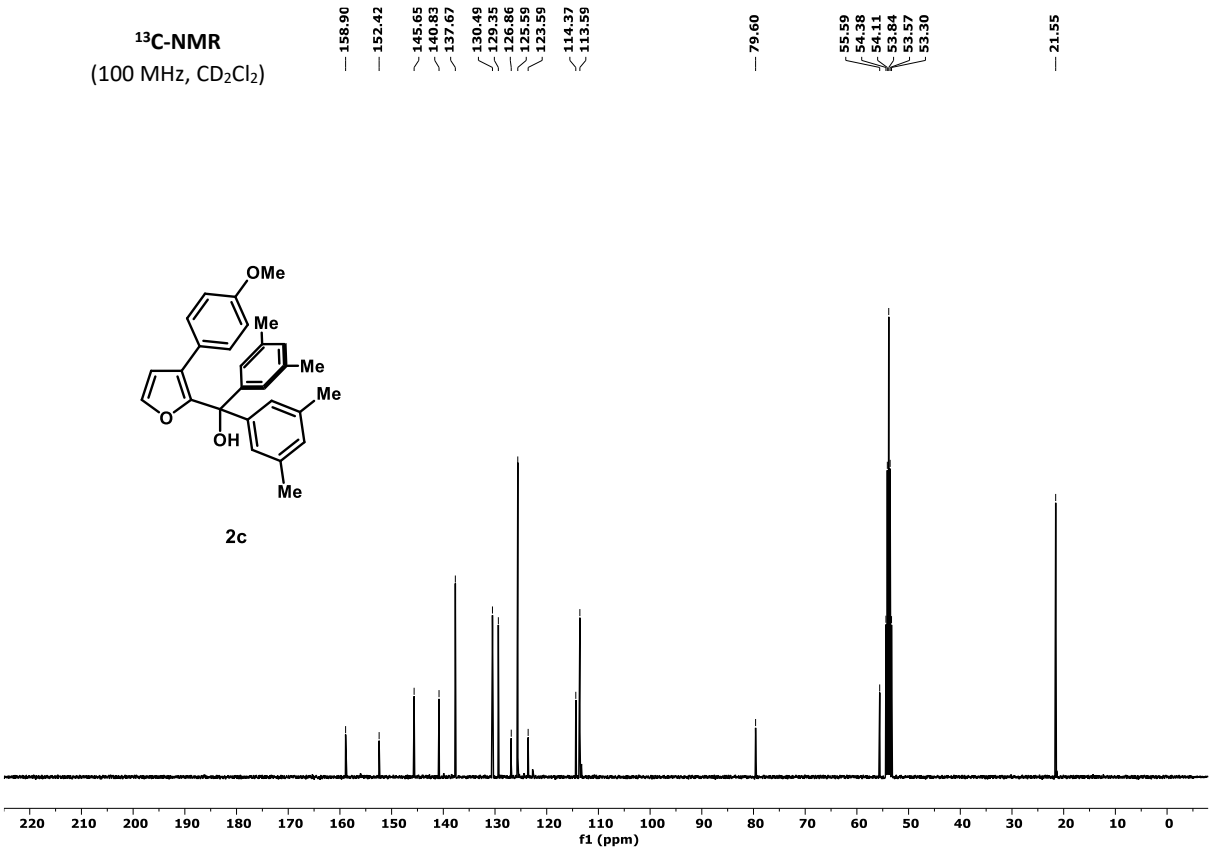


^{1}H-NMR
(400 MHz, CD_2Cl_2)



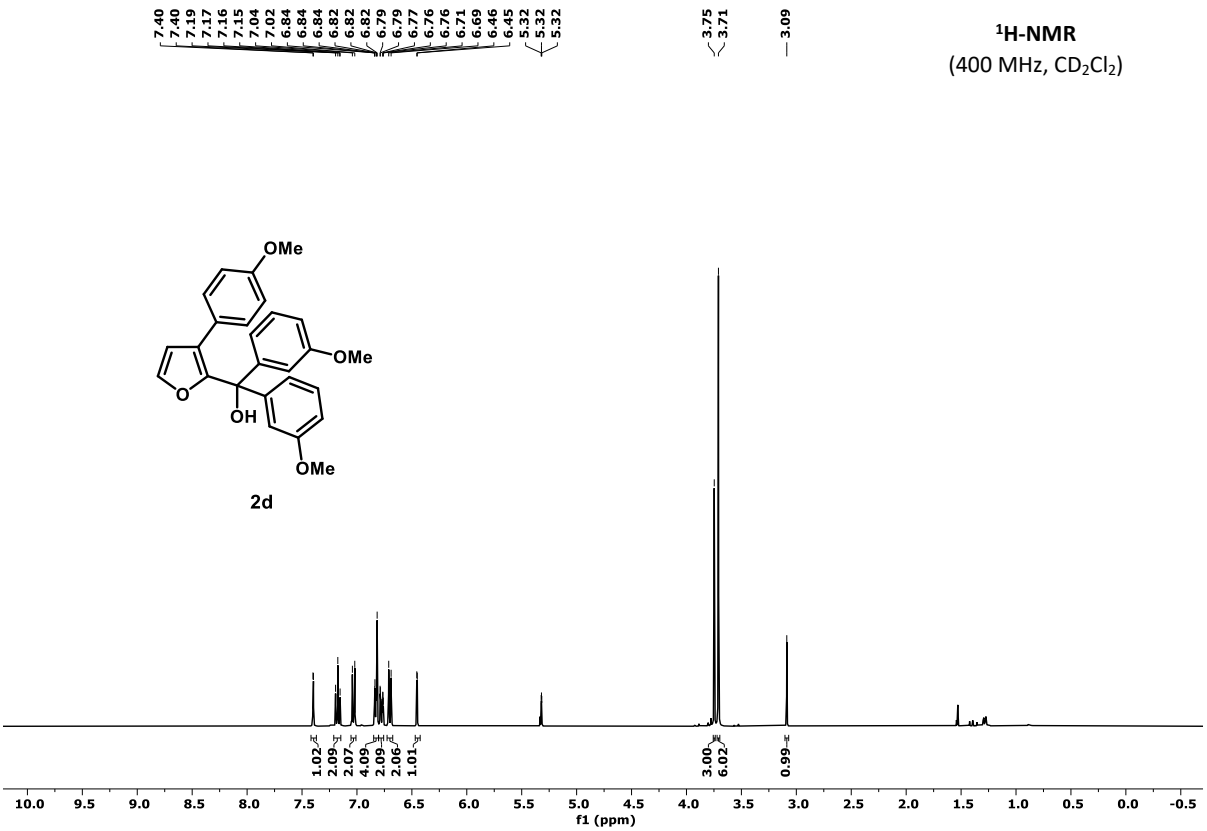
2c

^{13}C-NMR
(100 MHz, CD_2Cl_2)



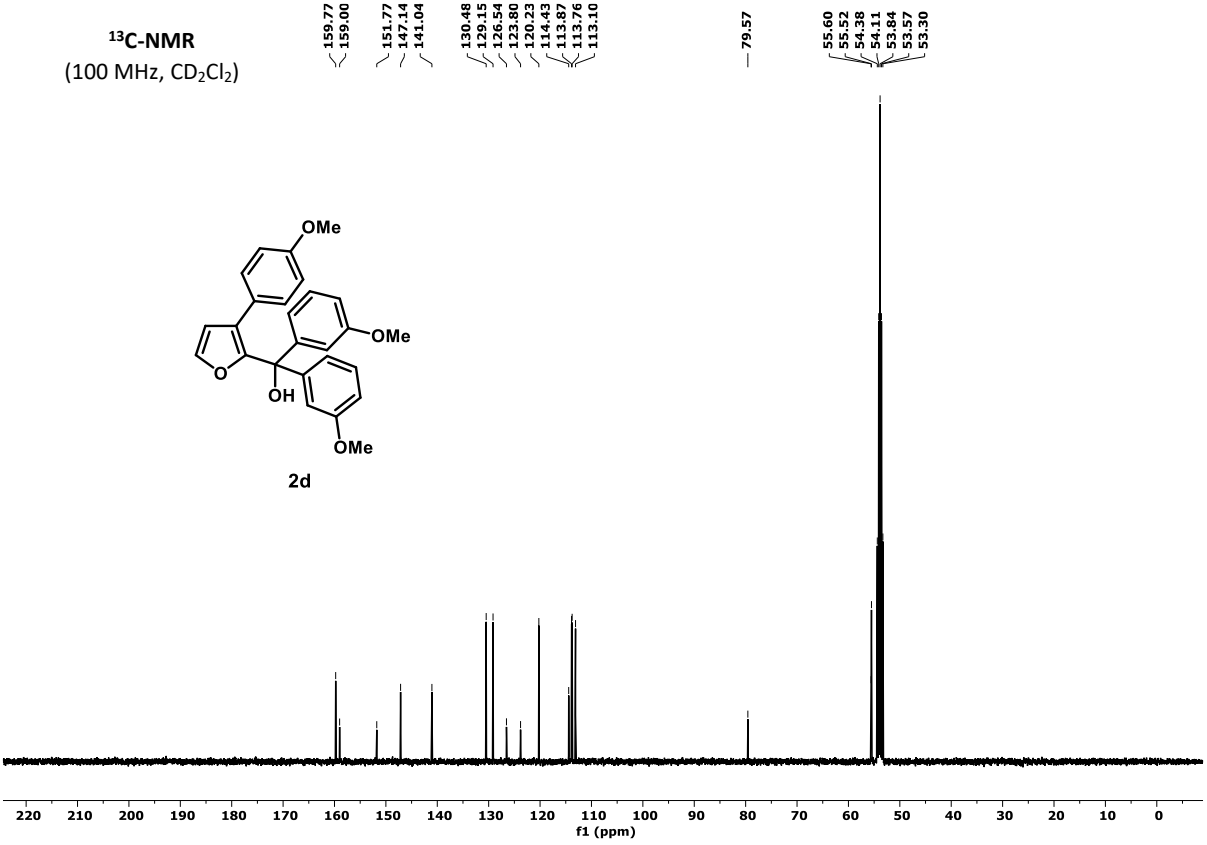
2c

^{1}H-NMR
(400 MHz, CD_2Cl_2)



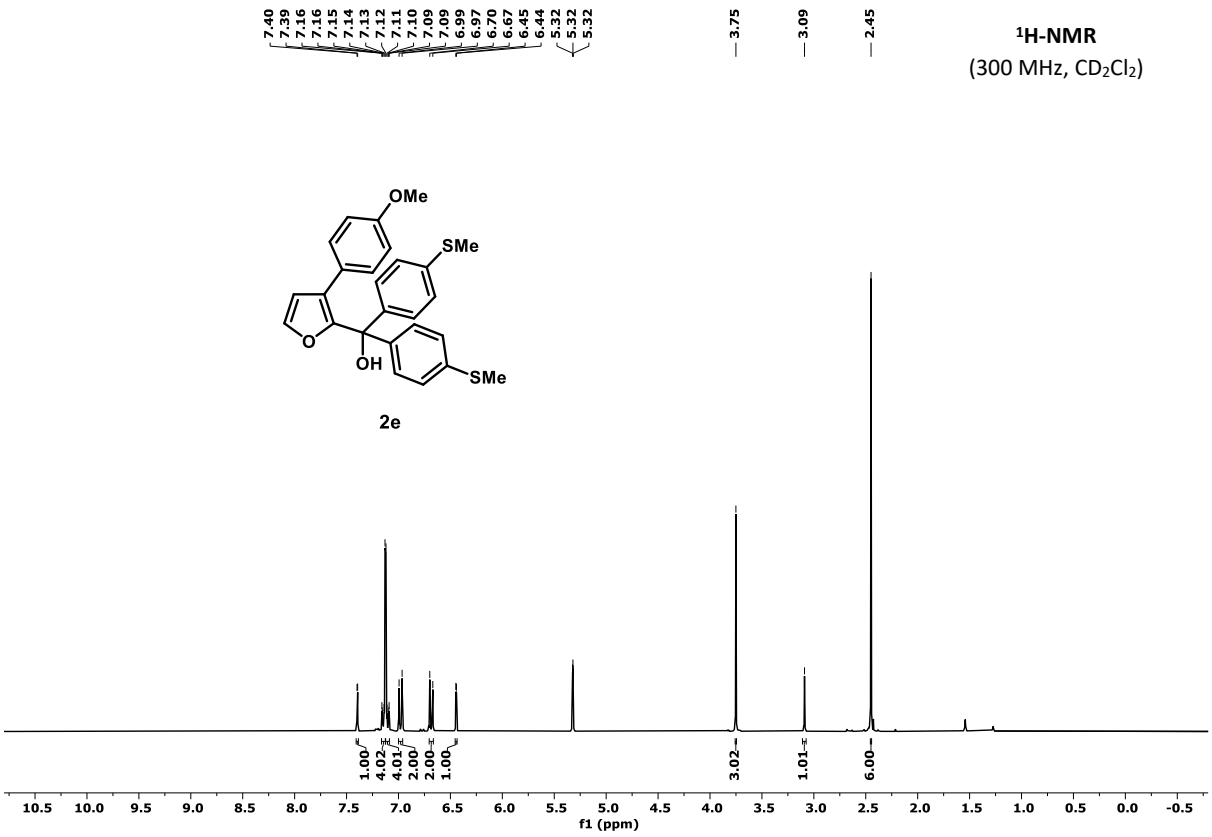
2d

^{13}C-NMR
(100 MHz, CD_2Cl_2)

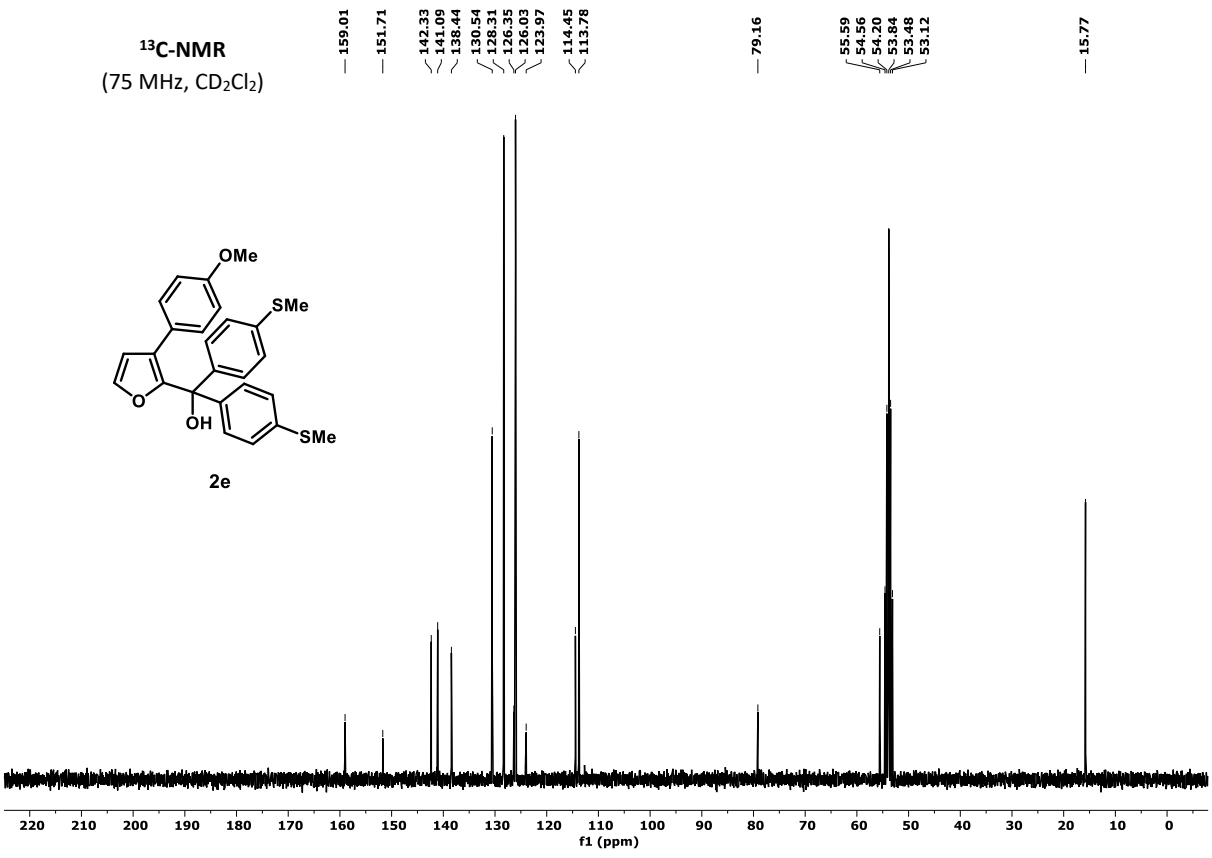


2d

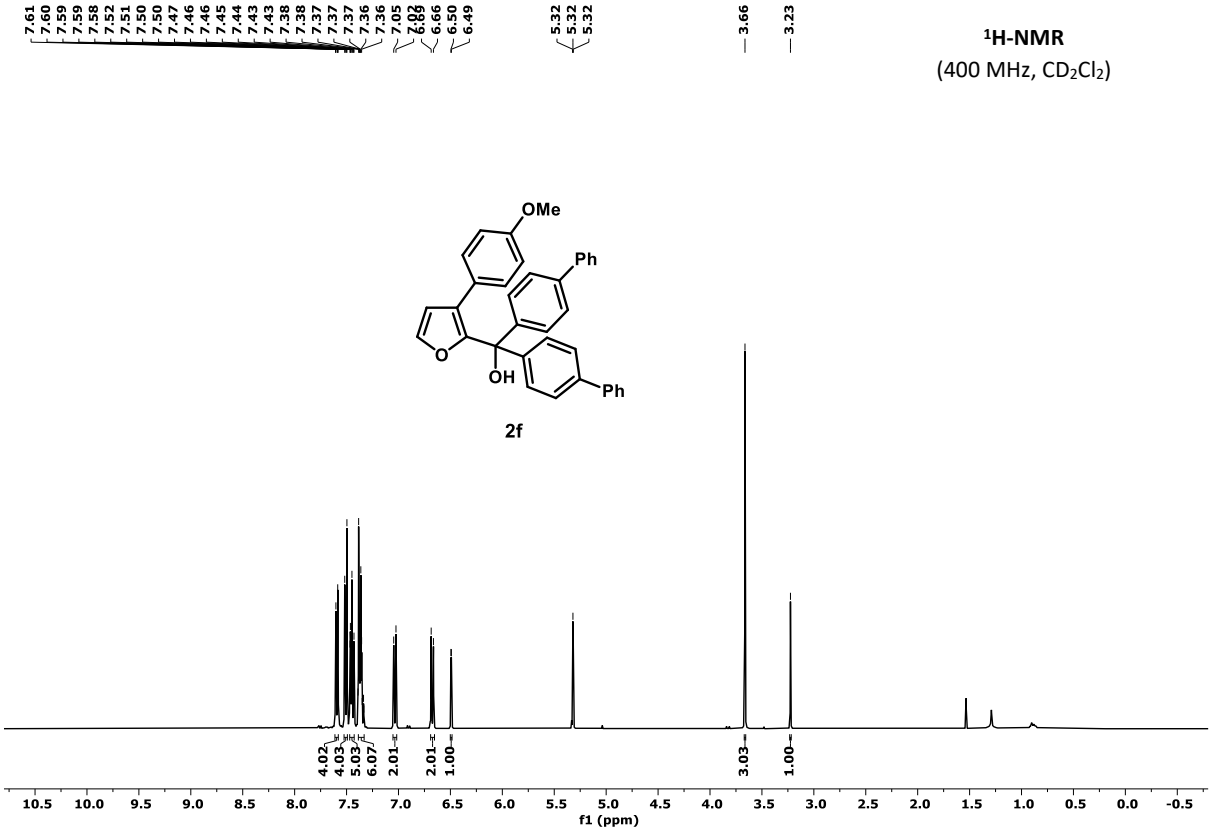
^{1}H-NMR
(300 MHz, CD_2Cl_2)



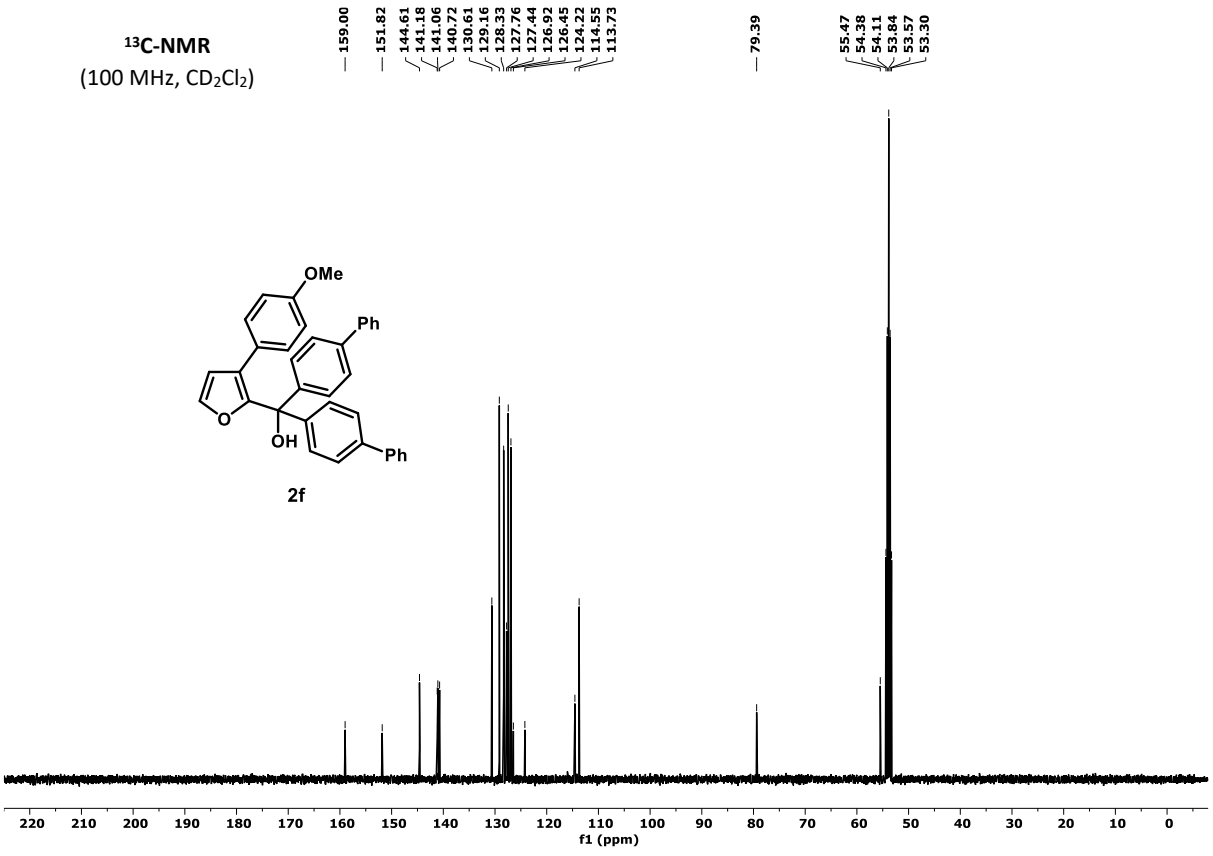
^{13}C-NMR
(75 MHz, CD_2Cl_2)



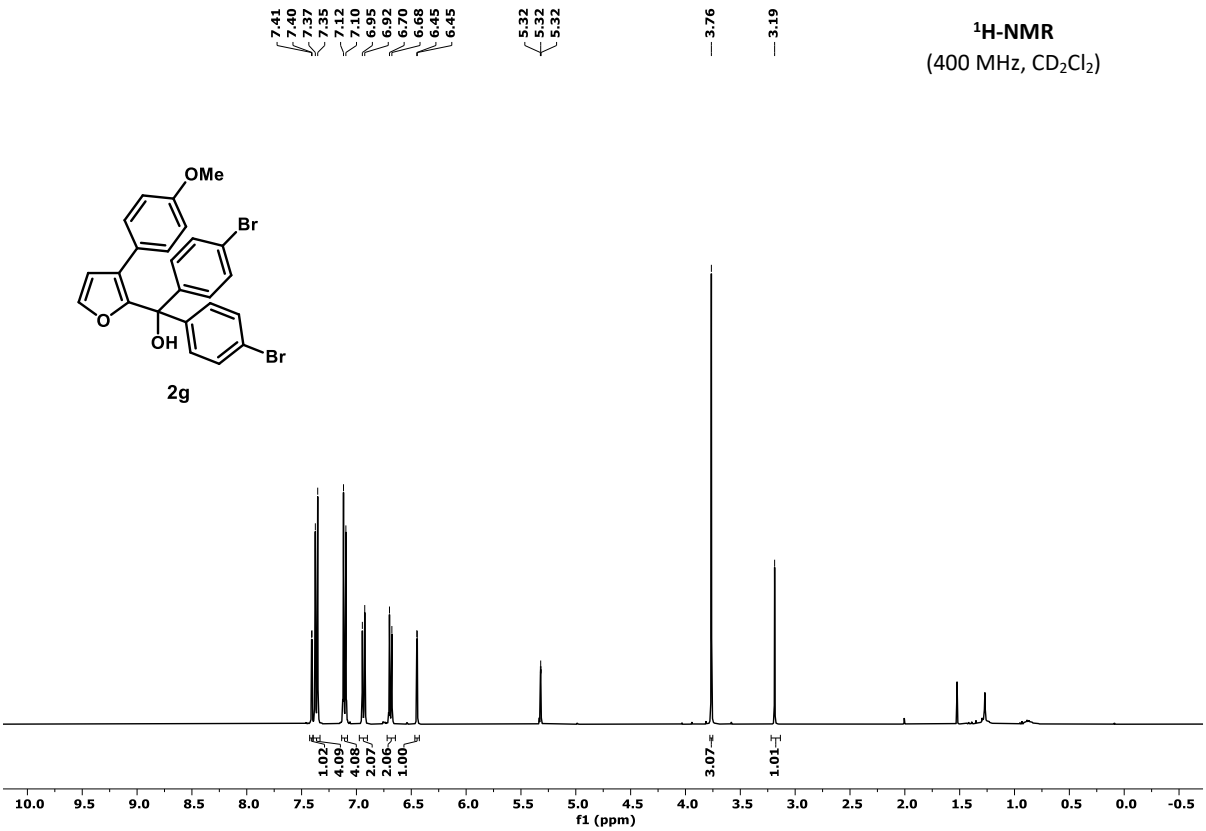
^{1}H-NMR
(400 MHz, CD_2Cl_2)



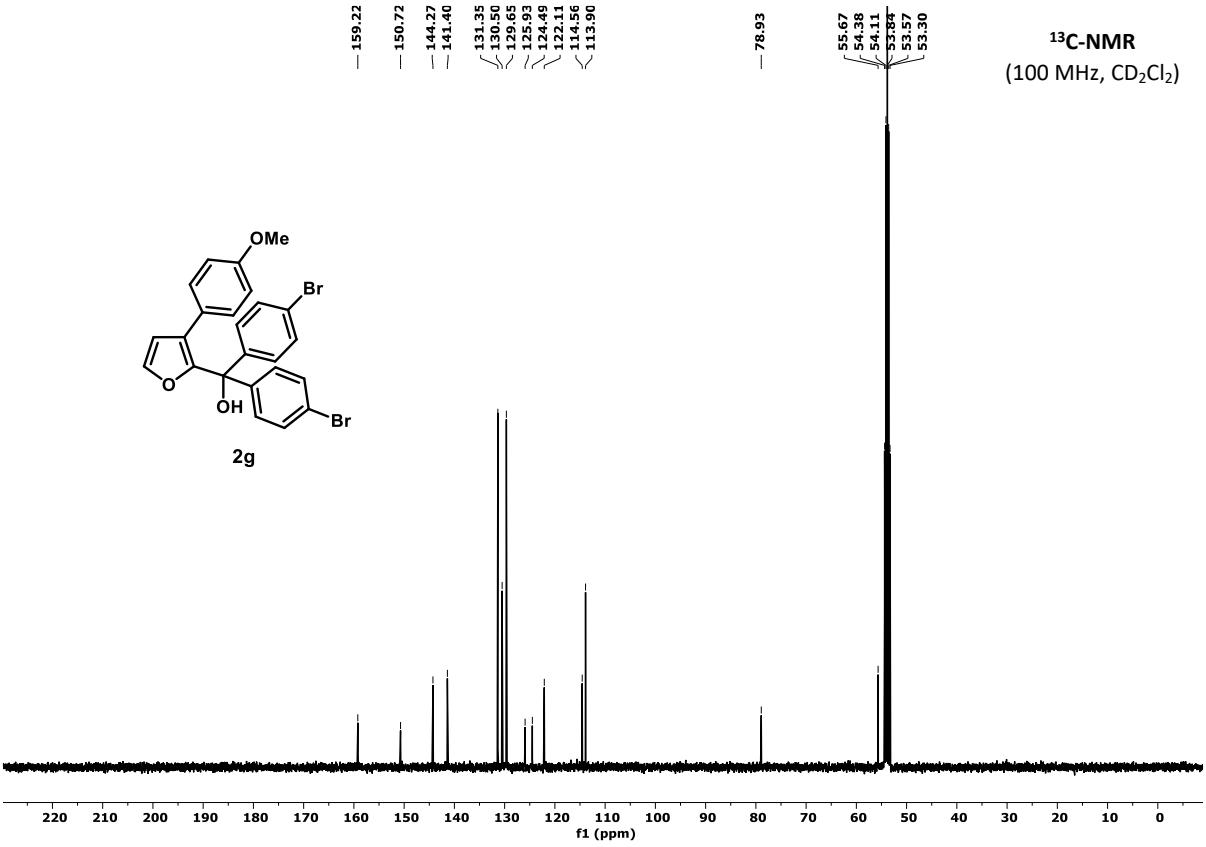
^{13}C-NMR
(100 MHz, CD_2Cl_2)



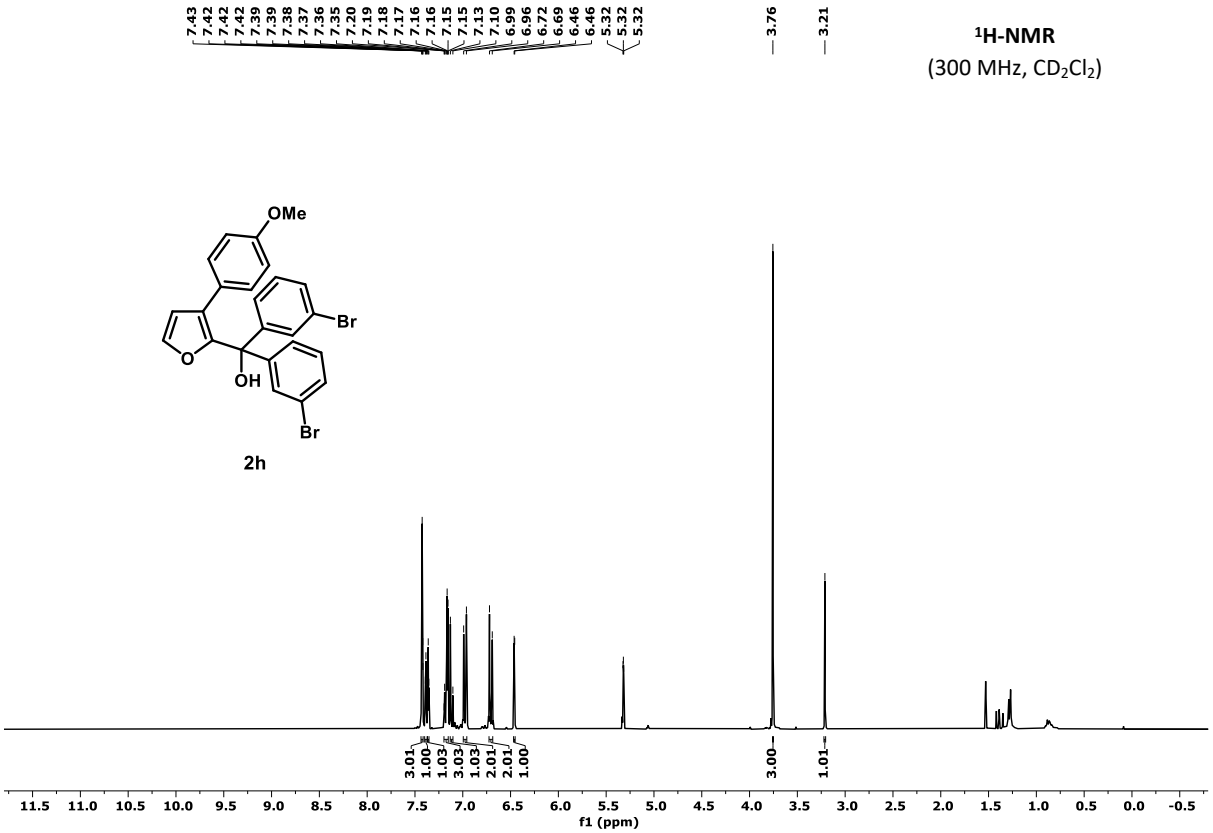
^{1}H-NMR
(400 MHz, CD_2Cl_2)



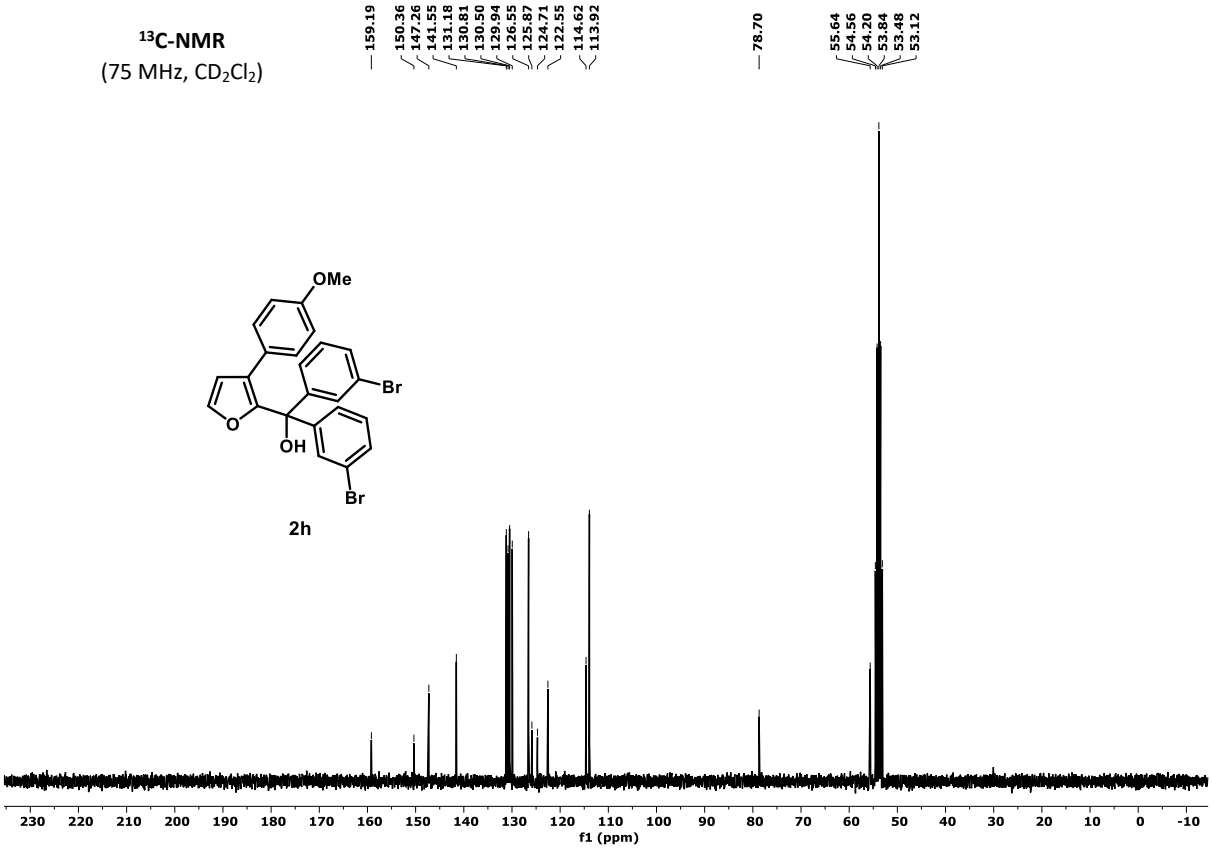
^{13}C-NMR
(100 MHz, CD_2Cl_2)

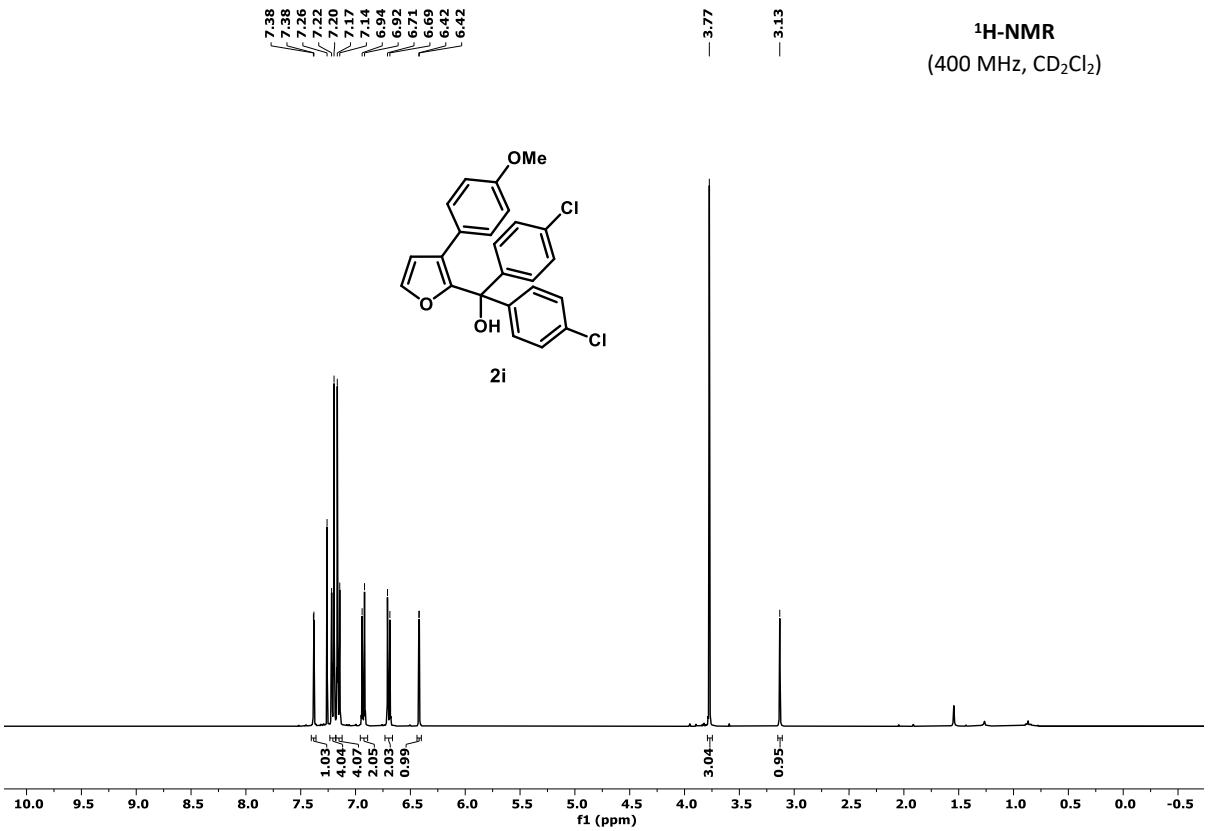


^{1}H-NMR
(300 MHz, CD_2Cl_2)

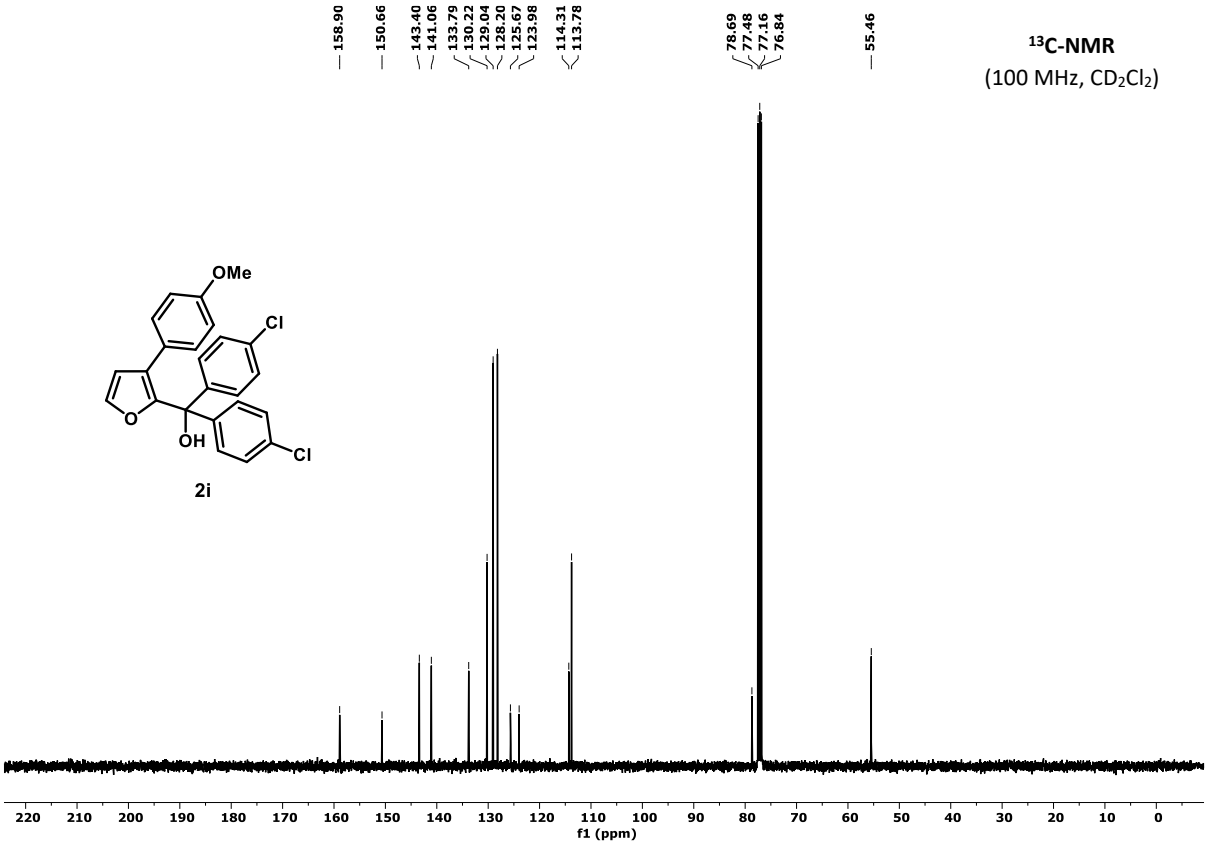


^{13}C-NMR
(75 MHz, CD_2Cl_2)



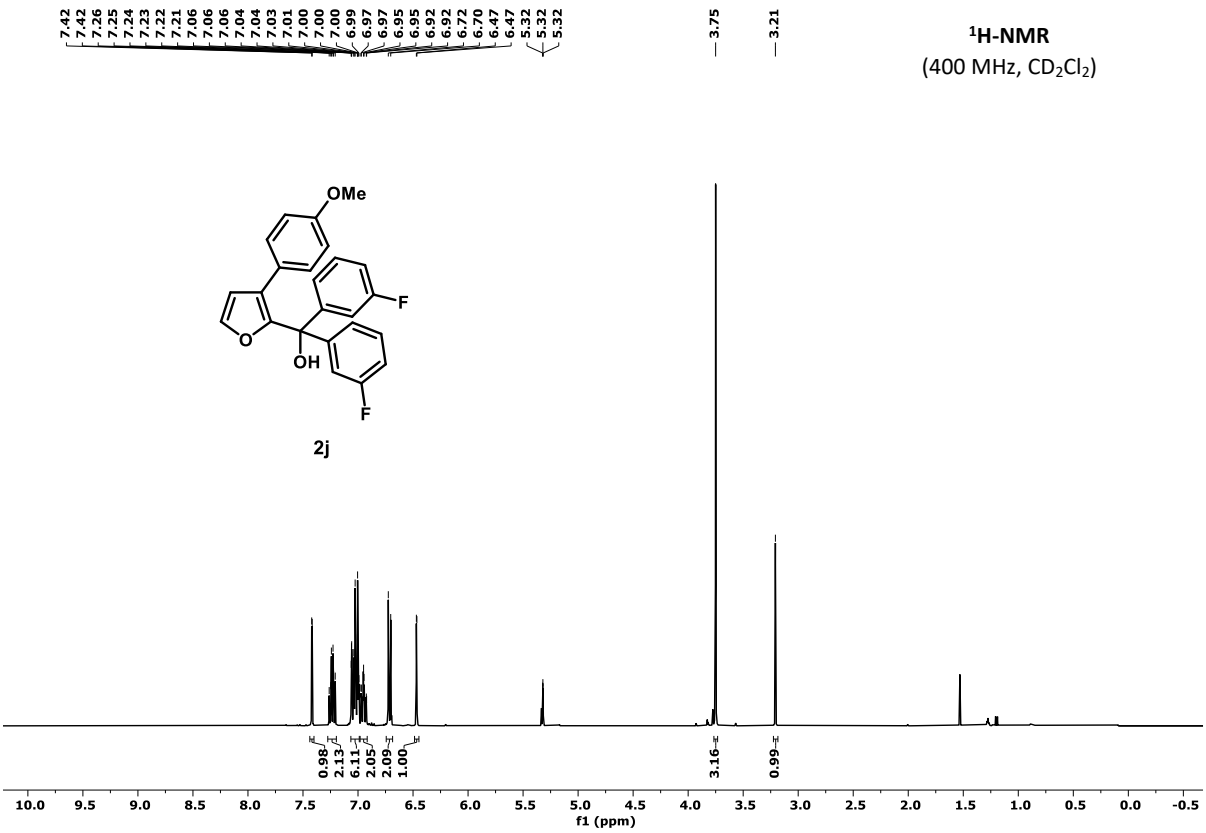


^{1}H-NMR
(400 MHz, CD_2Cl_2)

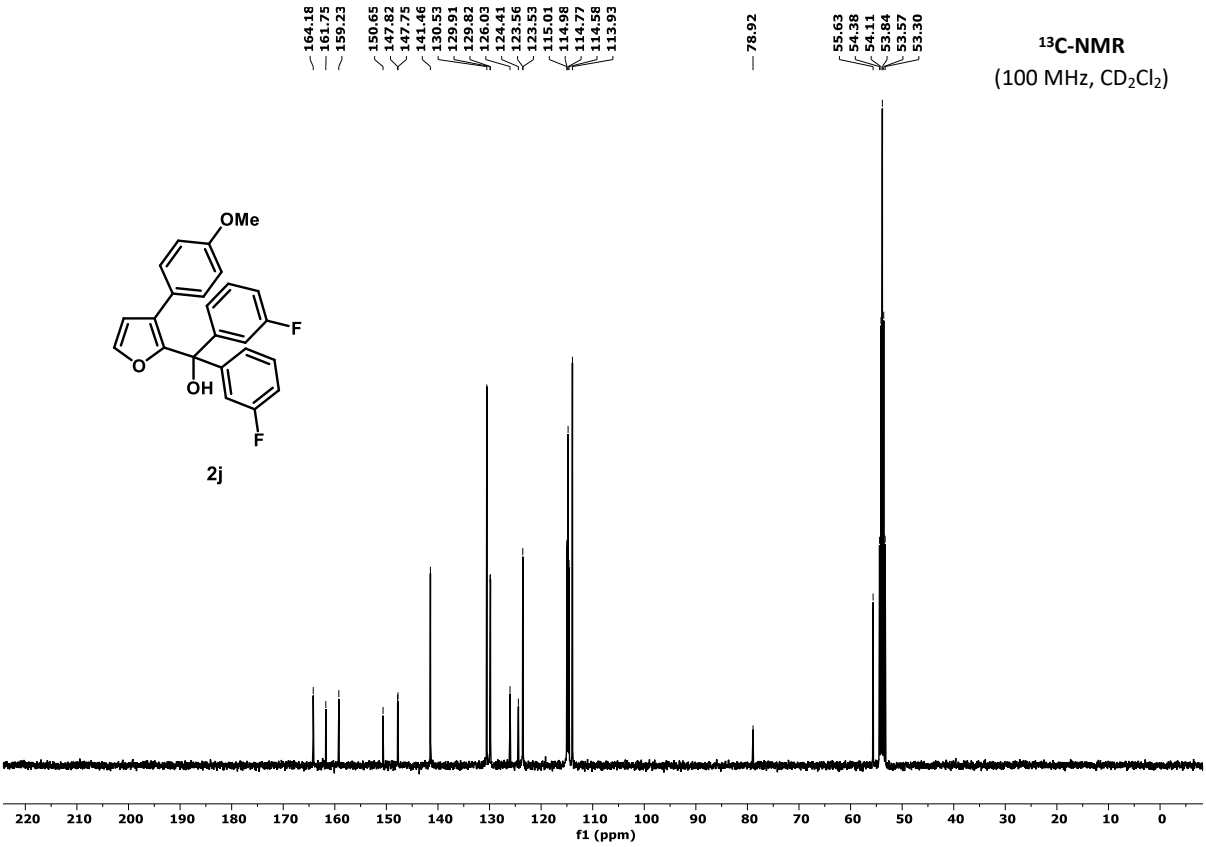


^{13}C-NMR
(100 MHz, CD_2Cl_2)

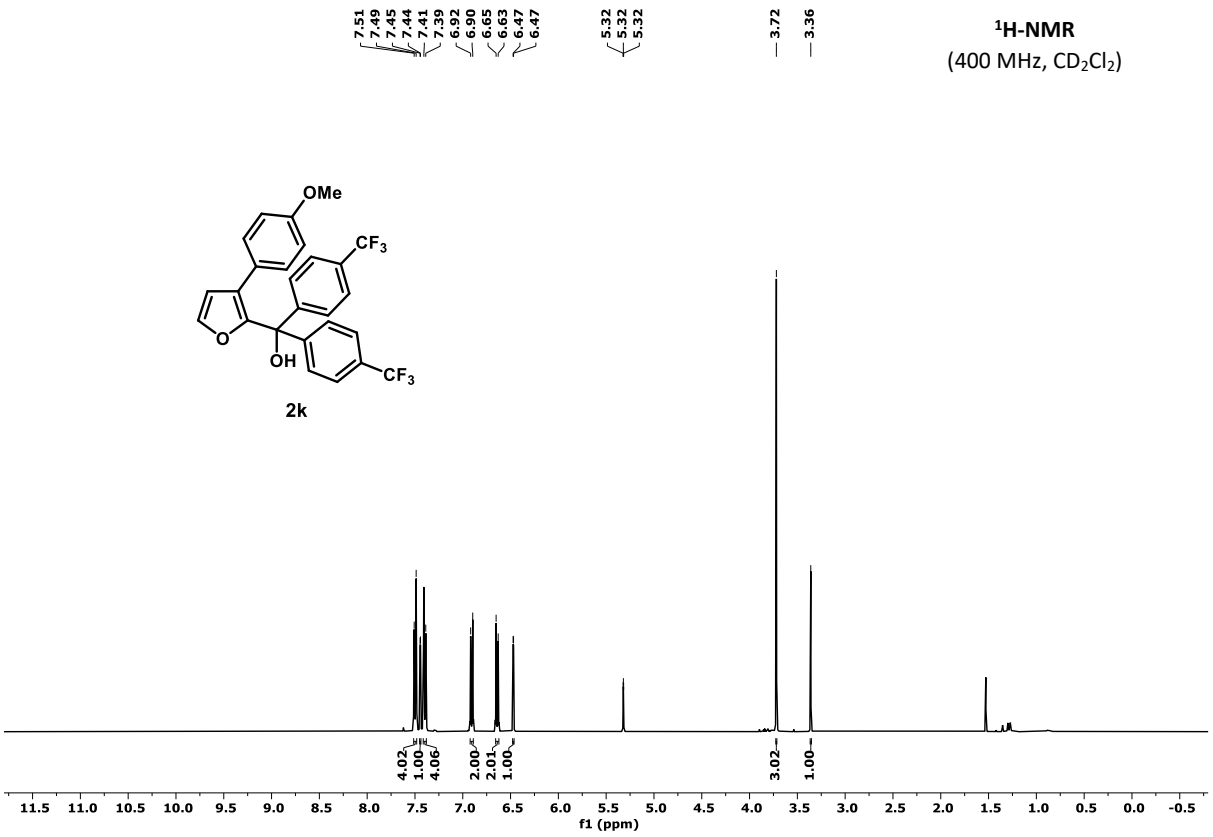
^{1}H-NMR
(400 MHz, CD_2Cl_2)



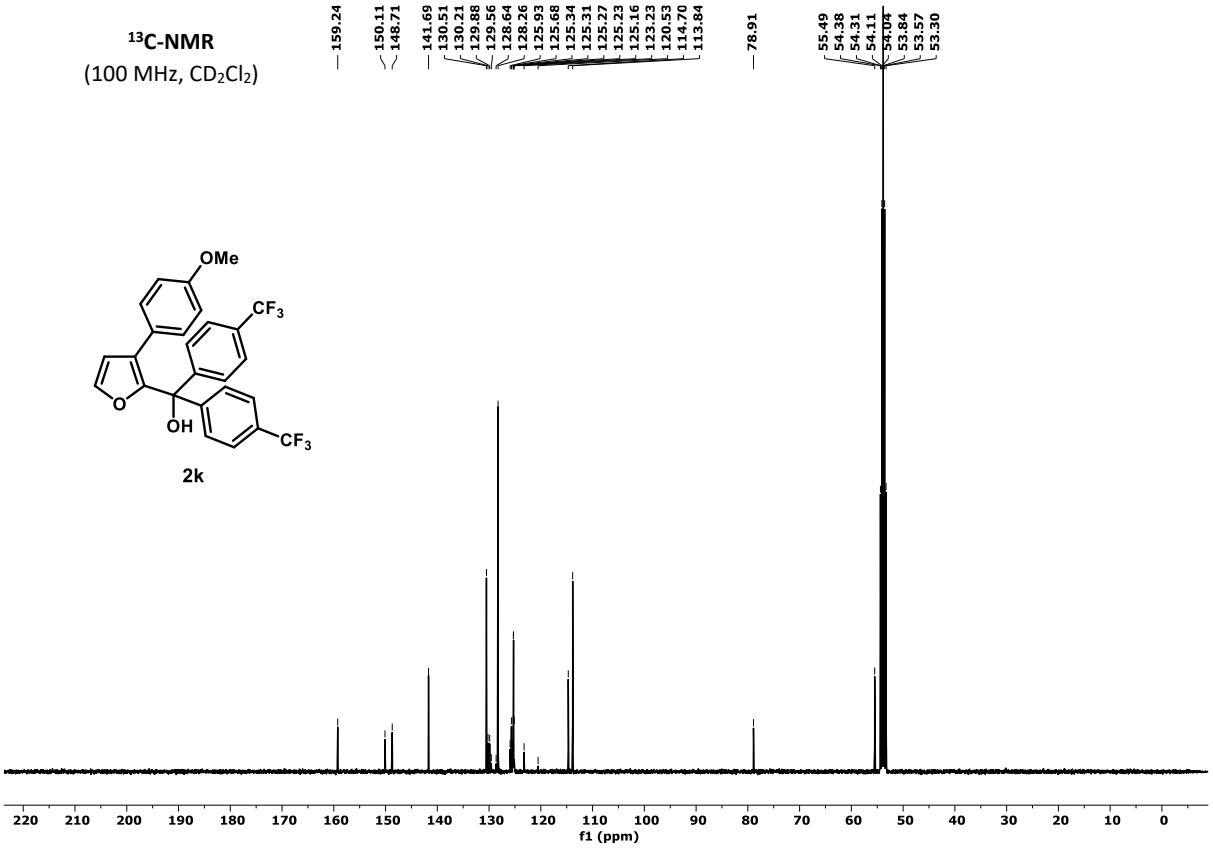
^{13}C-NMR
(100 MHz, CD_2Cl_2)



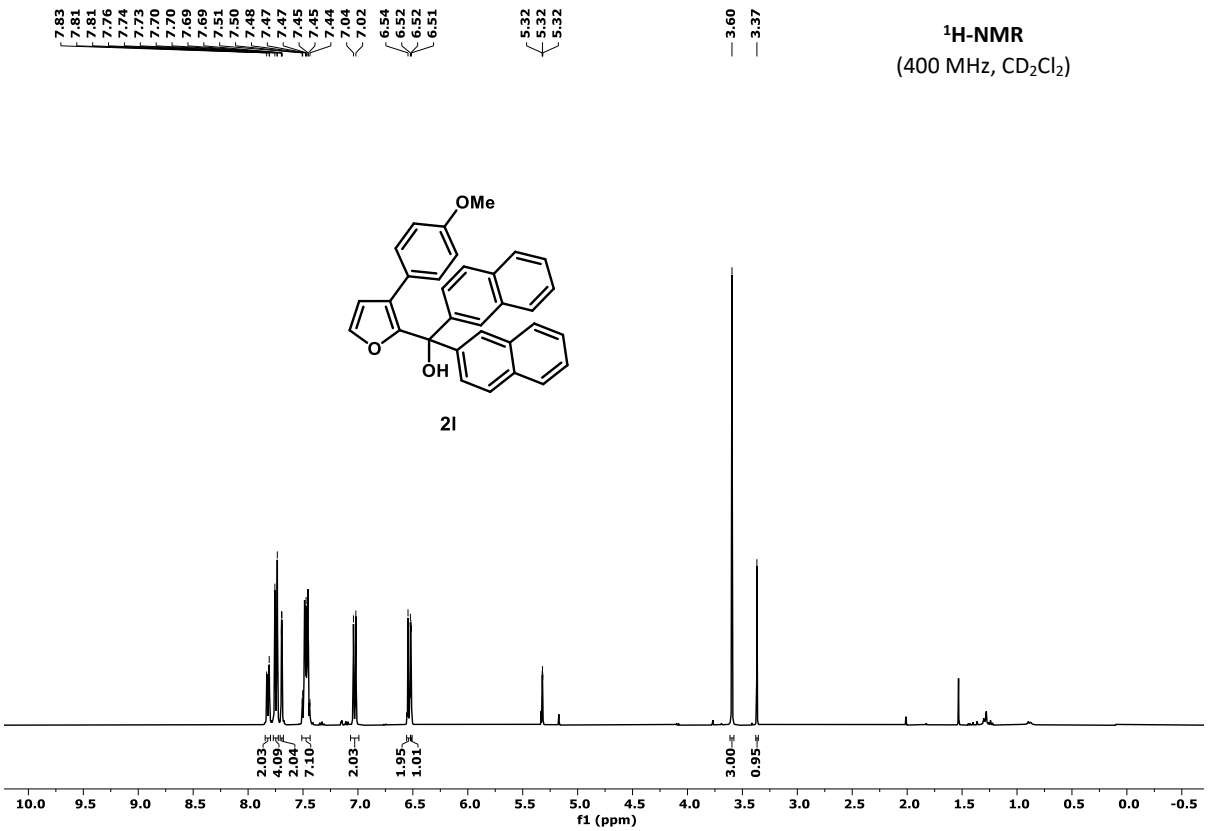
^{1}H-NMR
(400 MHz, CD_2Cl_2)



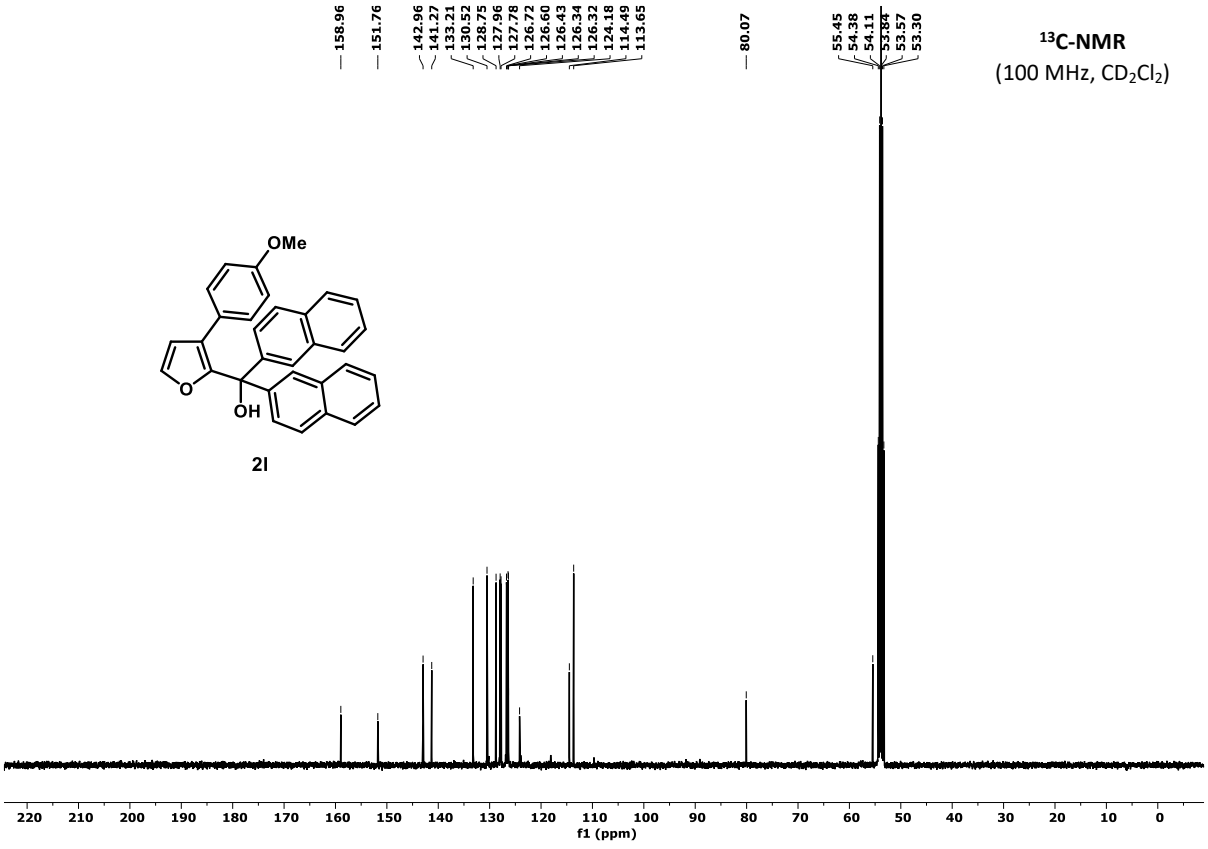
^{13}C-NMR
(100 MHz, CD_2Cl_2)

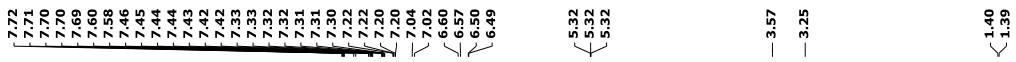


^{1}H-NMR
(400 MHz, CD_2Cl_2)



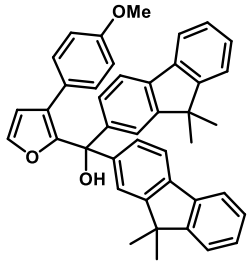
^{13}C-NMR
(100 MHz, CD_2Cl_2)



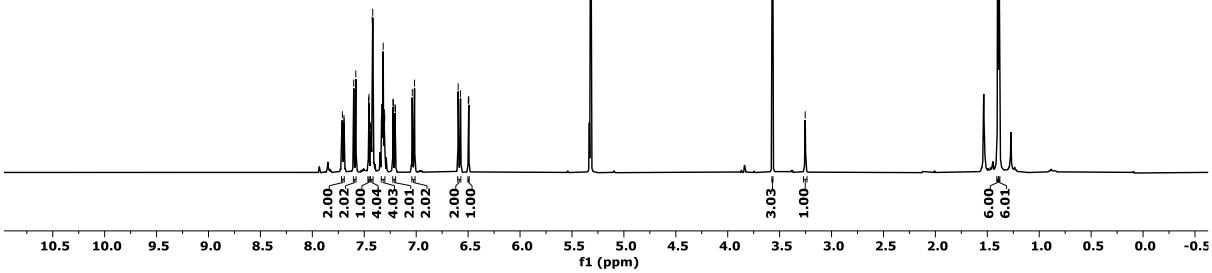


^{1}H-NMR

(400 MHz, CD_2Cl_2)

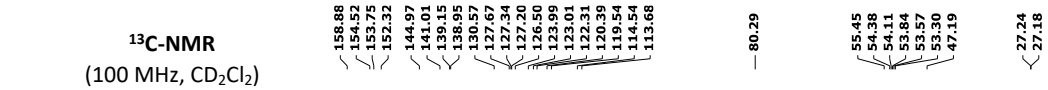


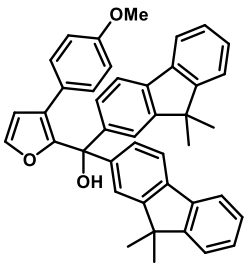
2m



^{13}C-NMR

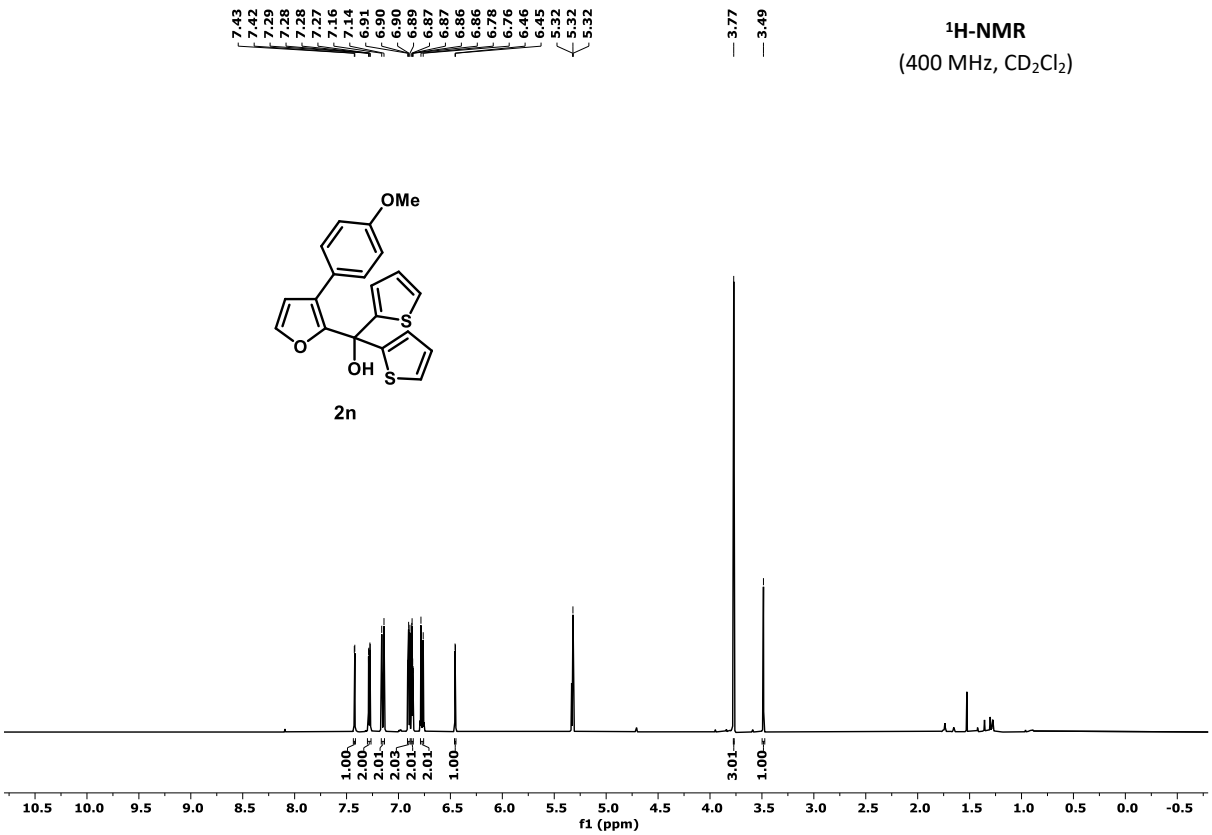
(100 MHz, CD_2Cl_2)



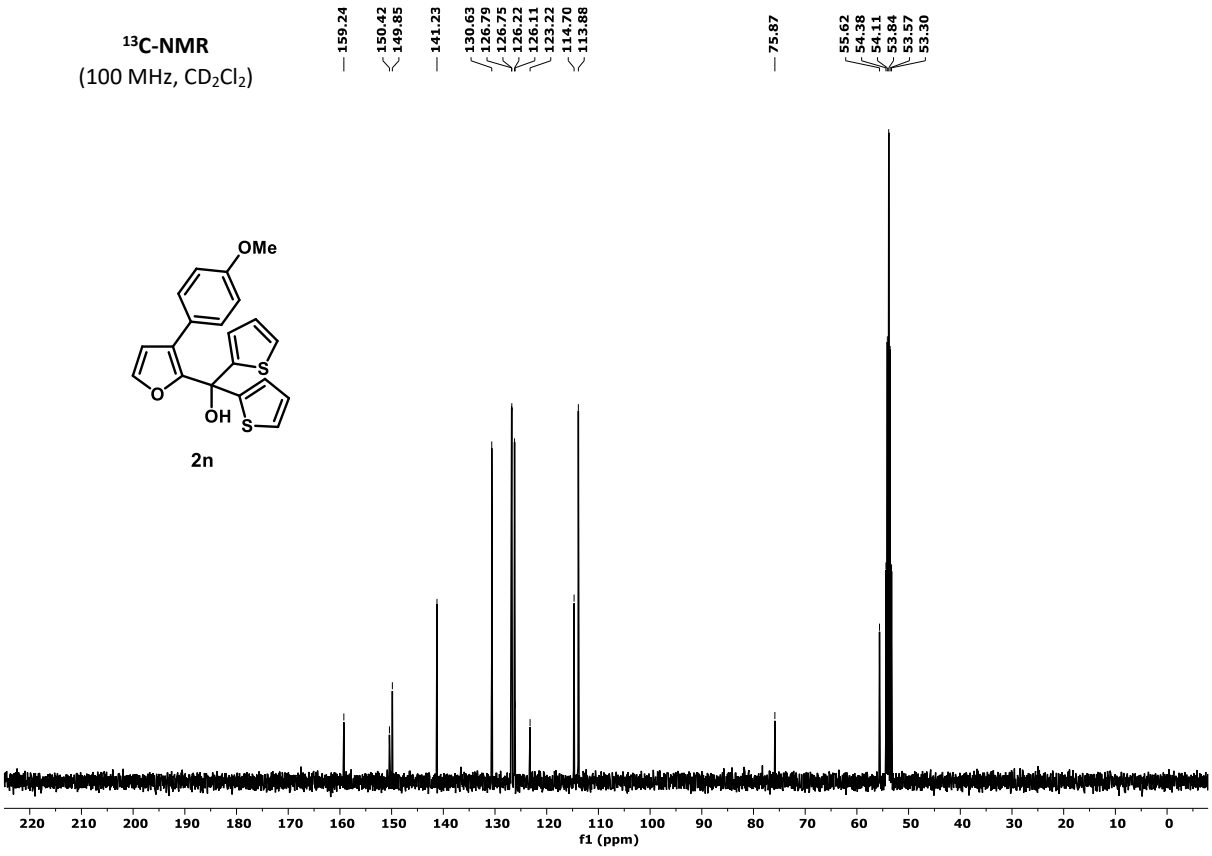


2m

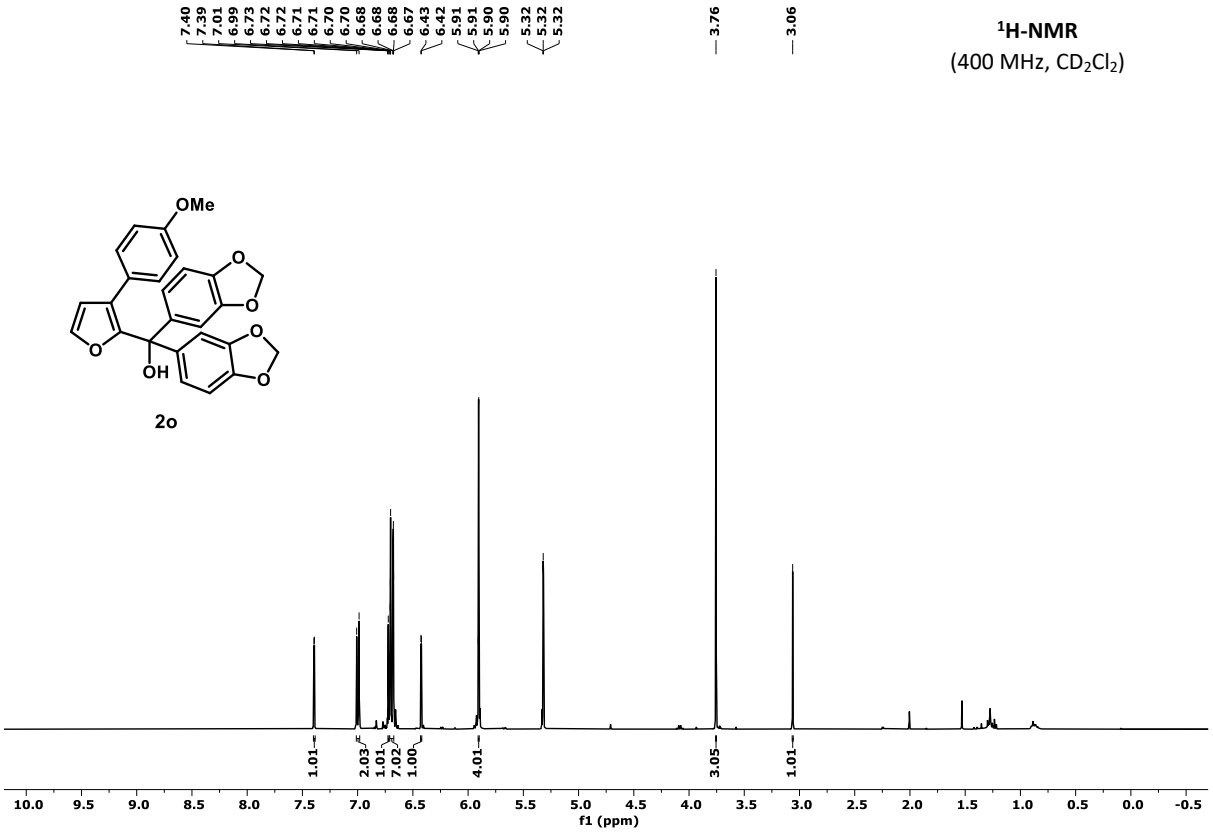
^{1}H-NMR
(400 MHz, CD_2Cl_2)



^{13}C-NMR
(100 MHz, CD_2Cl_2)

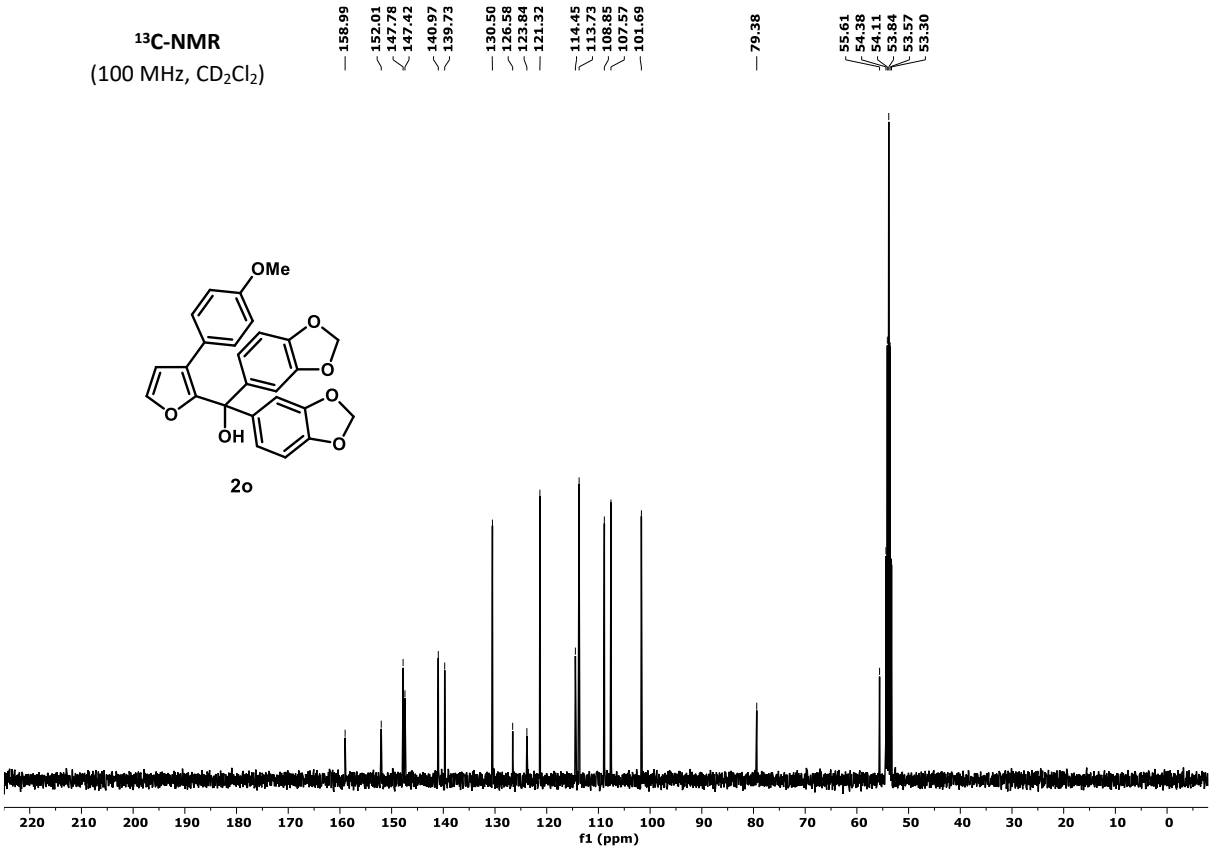


^{1}H-NMR
(400 MHz, CD_2Cl_2)



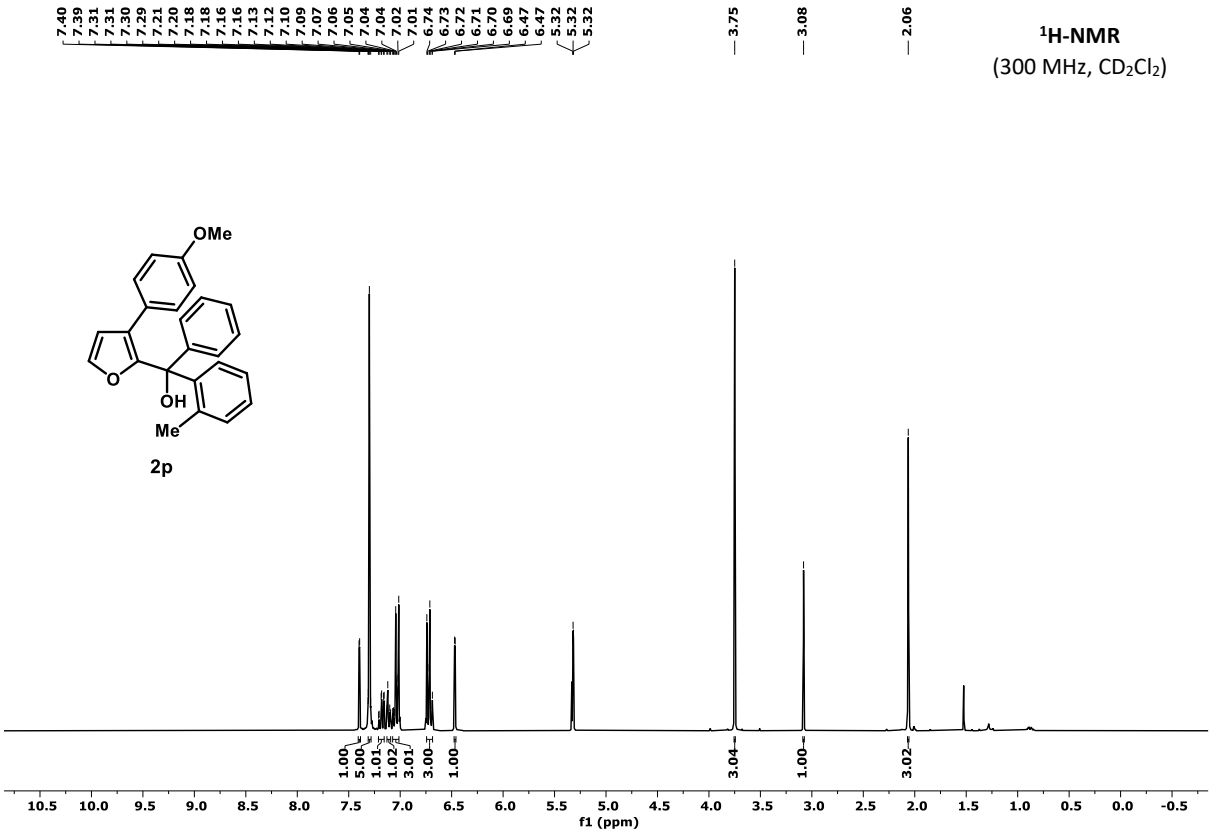
2o

^{13}C-NMR
(100 MHz, CD_2Cl_2)

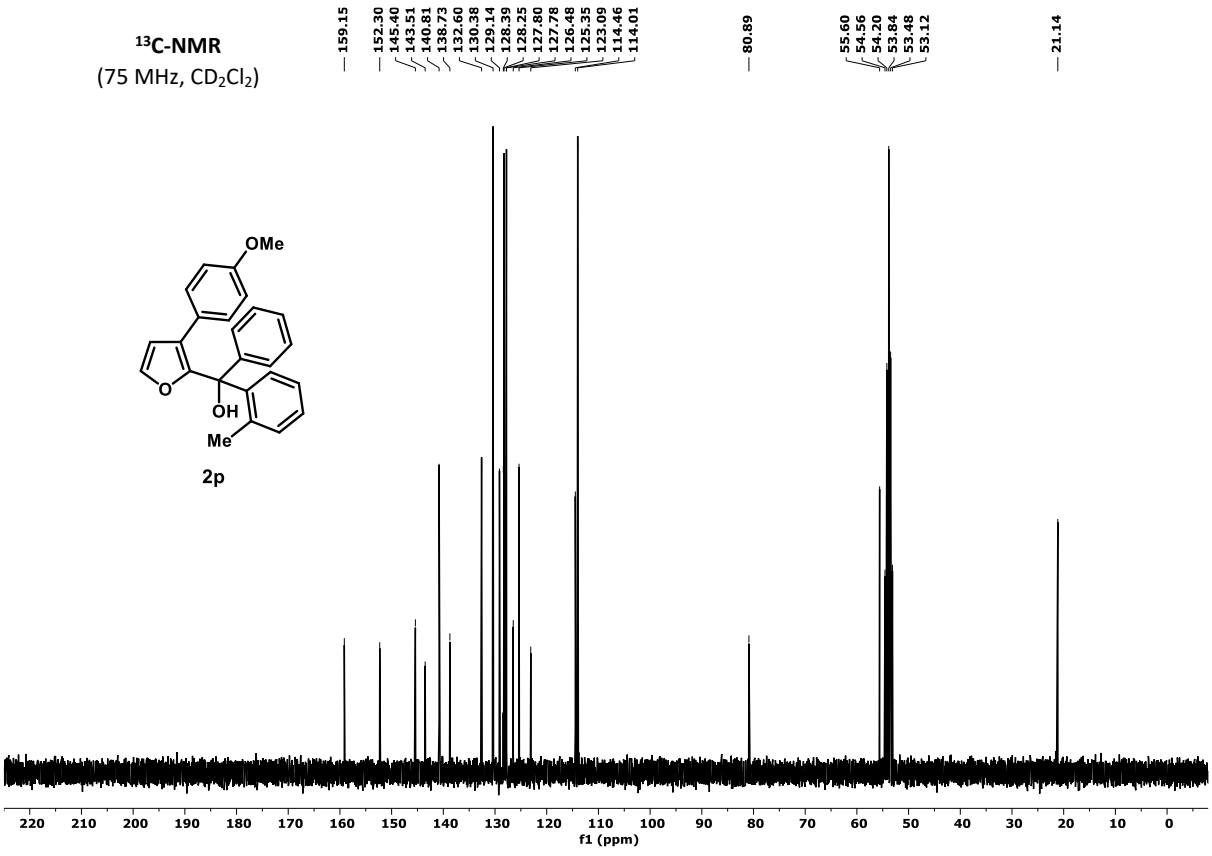


2o

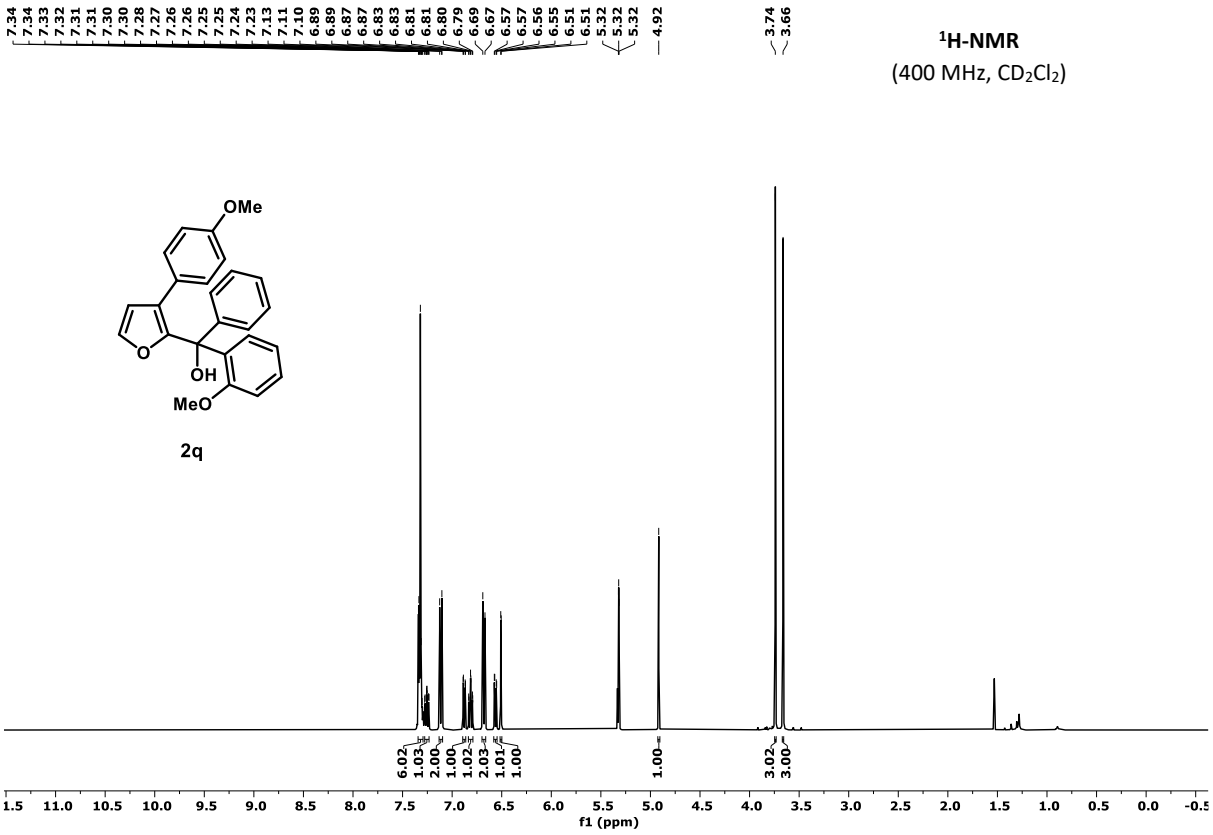
^{1}H-NMR
(300 MHz, CD_2Cl_2)



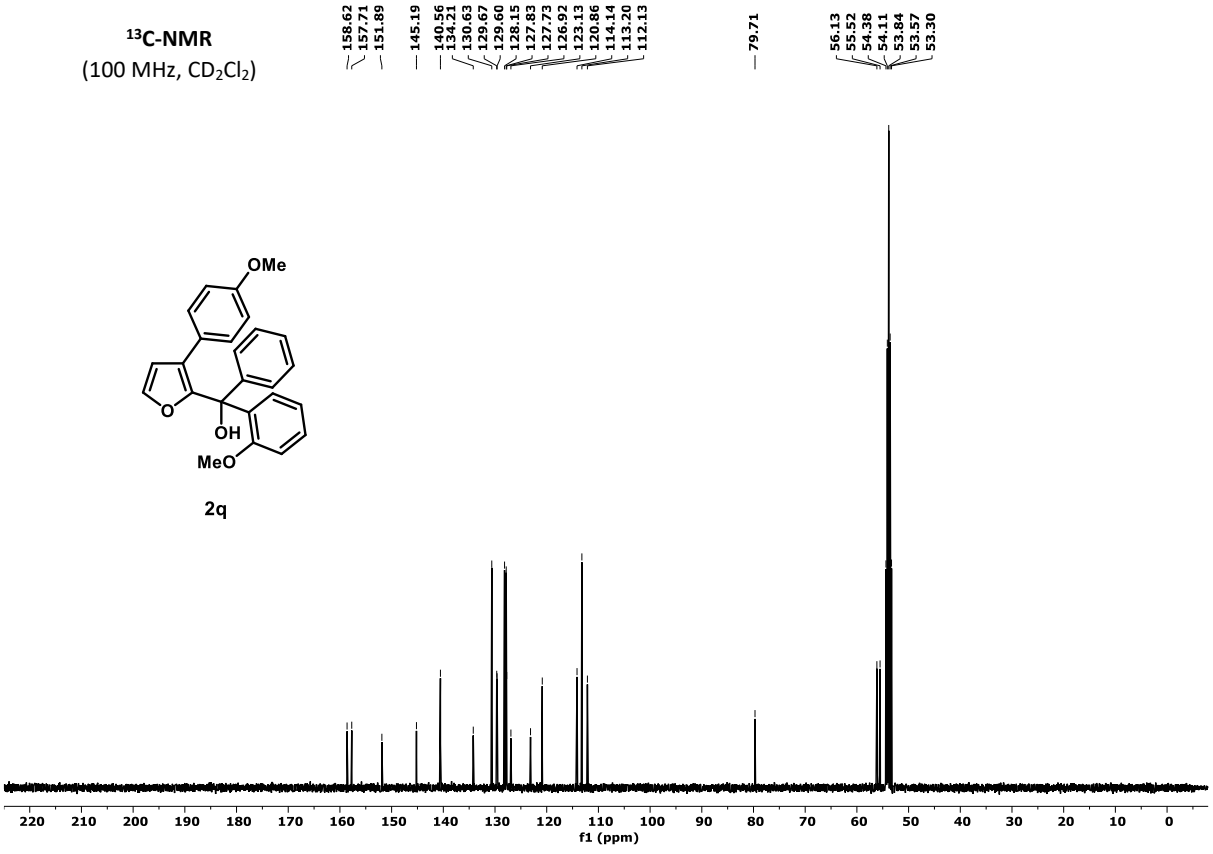
^{13}C-NMR
(75 MHz, CD_2Cl_2)



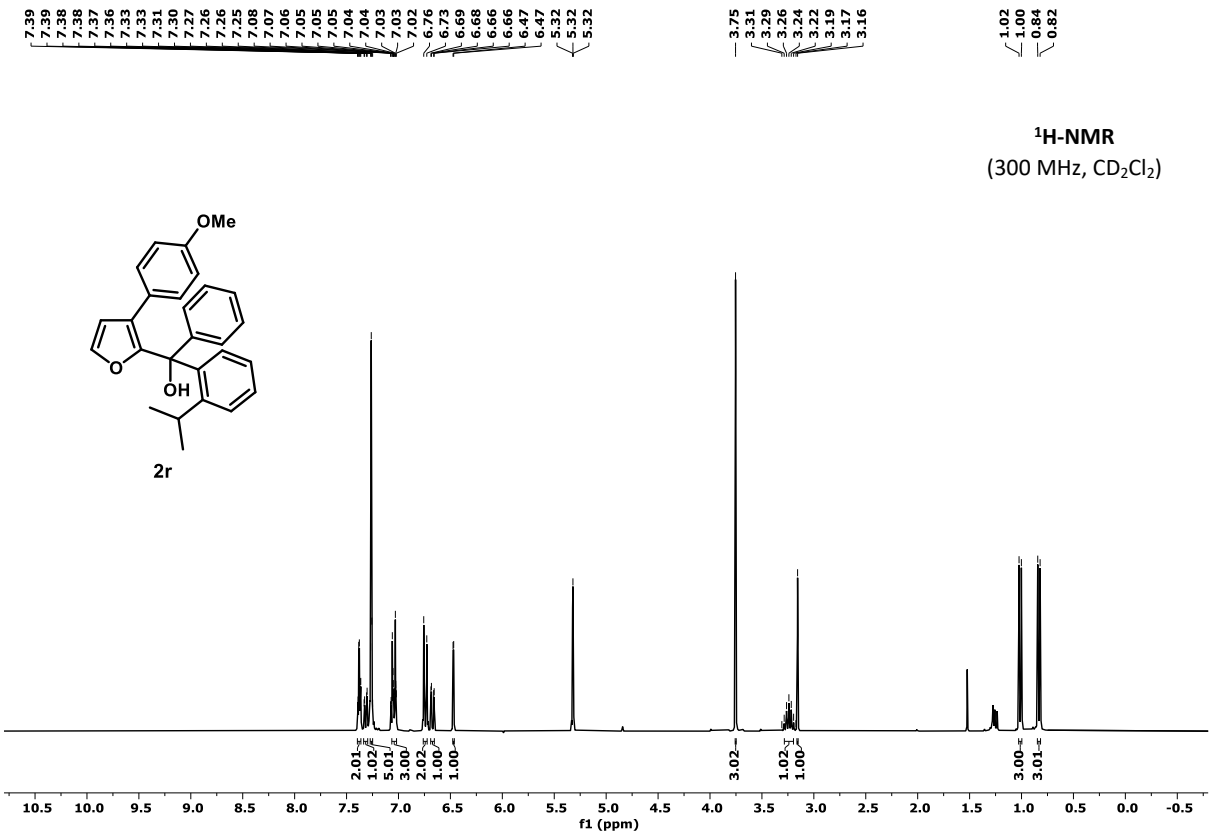
^{1}H-NMR
(400 MHz, CD_2Cl_2)



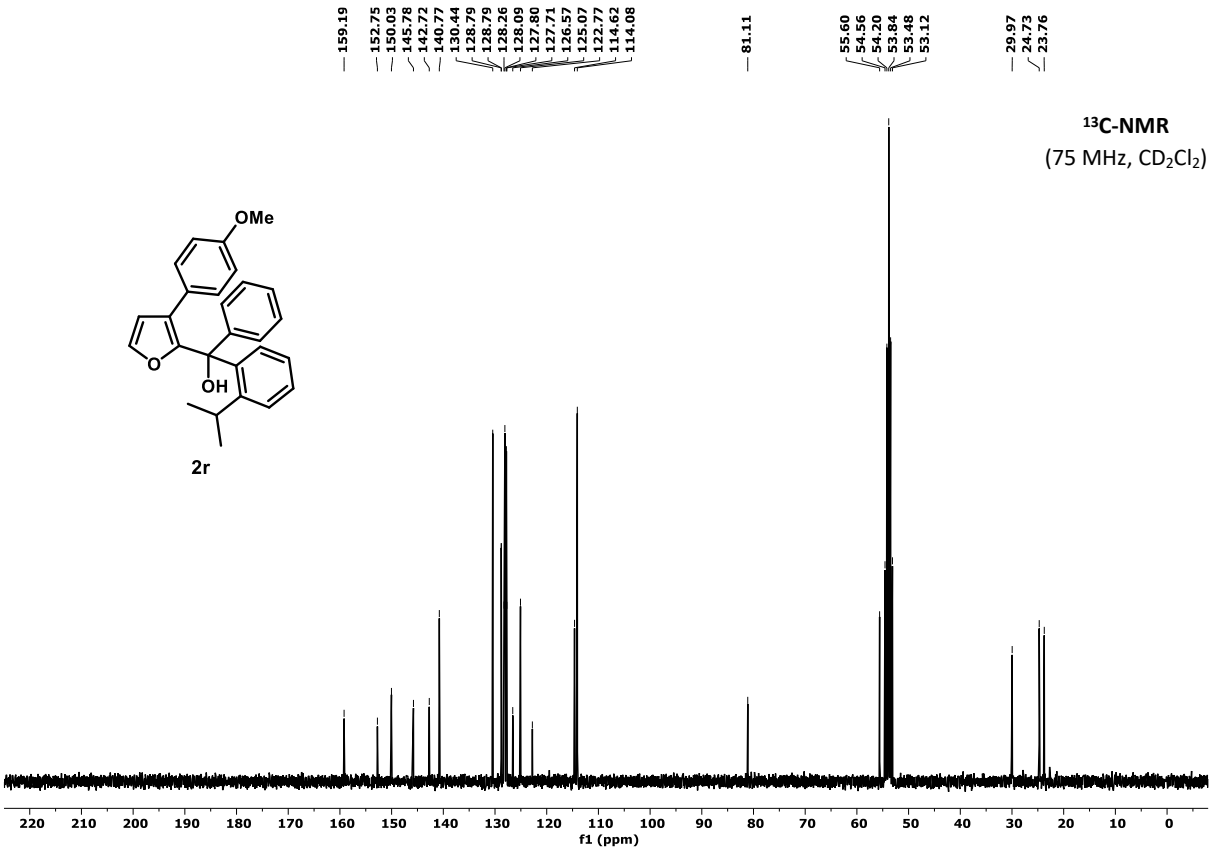
^{13}C-NMR
(100 MHz, CD_2Cl_2)



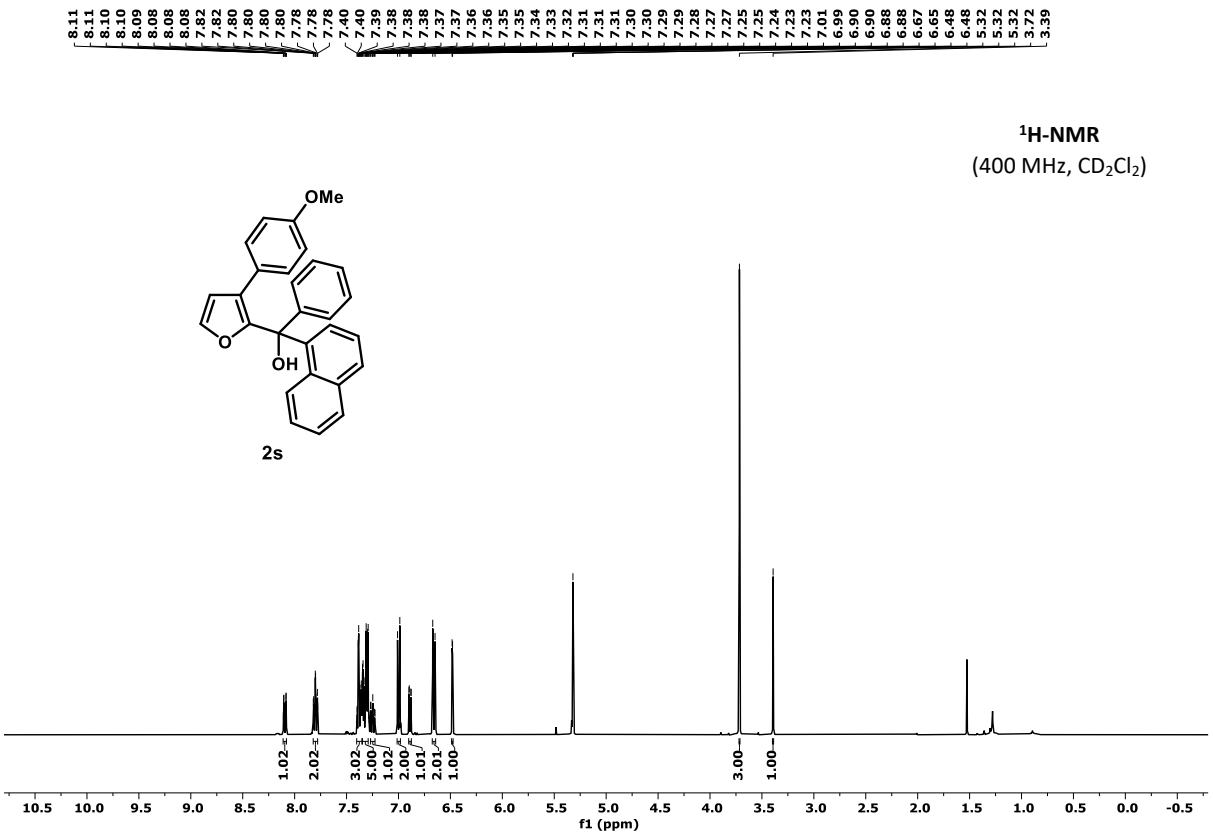
^{1}H-NMR
(300 MHz, CD_2Cl_2)



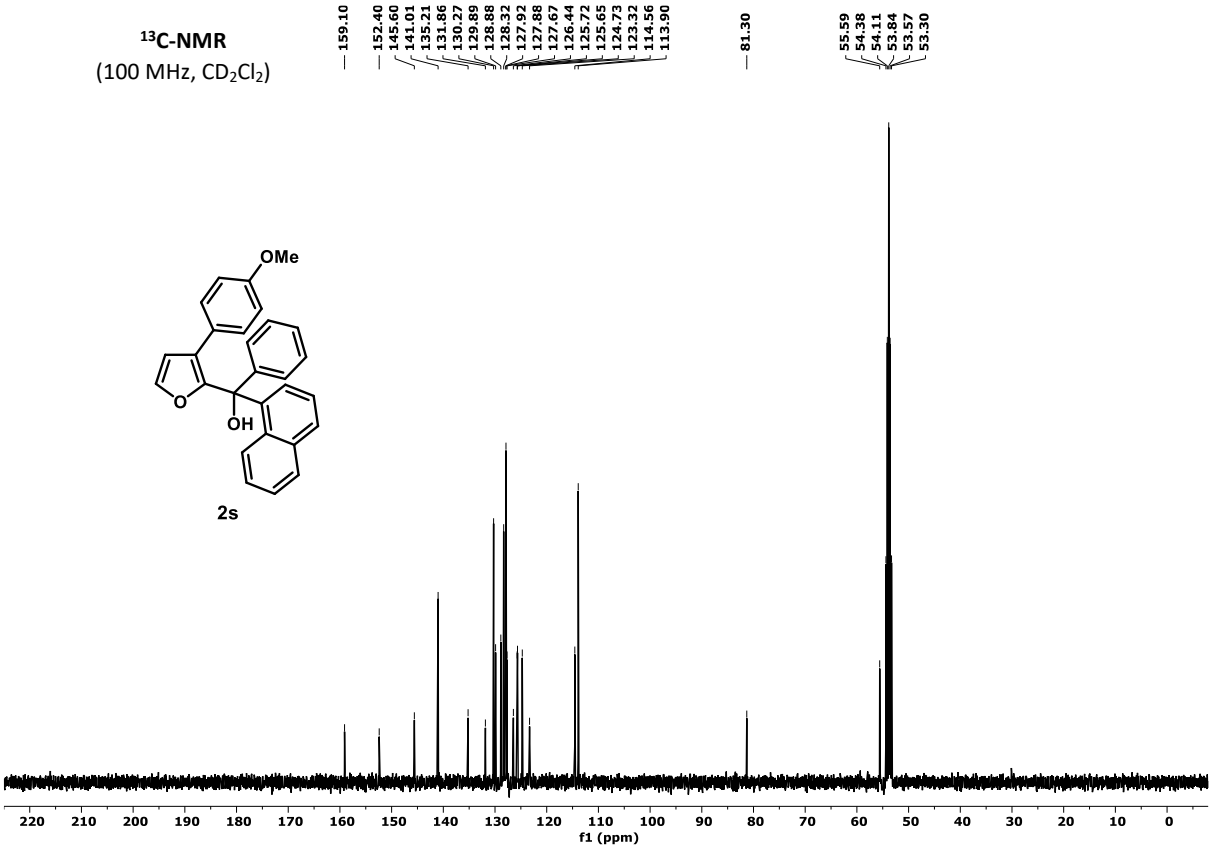
^{13}C-NMR
(75 MHz, CD_2Cl_2)



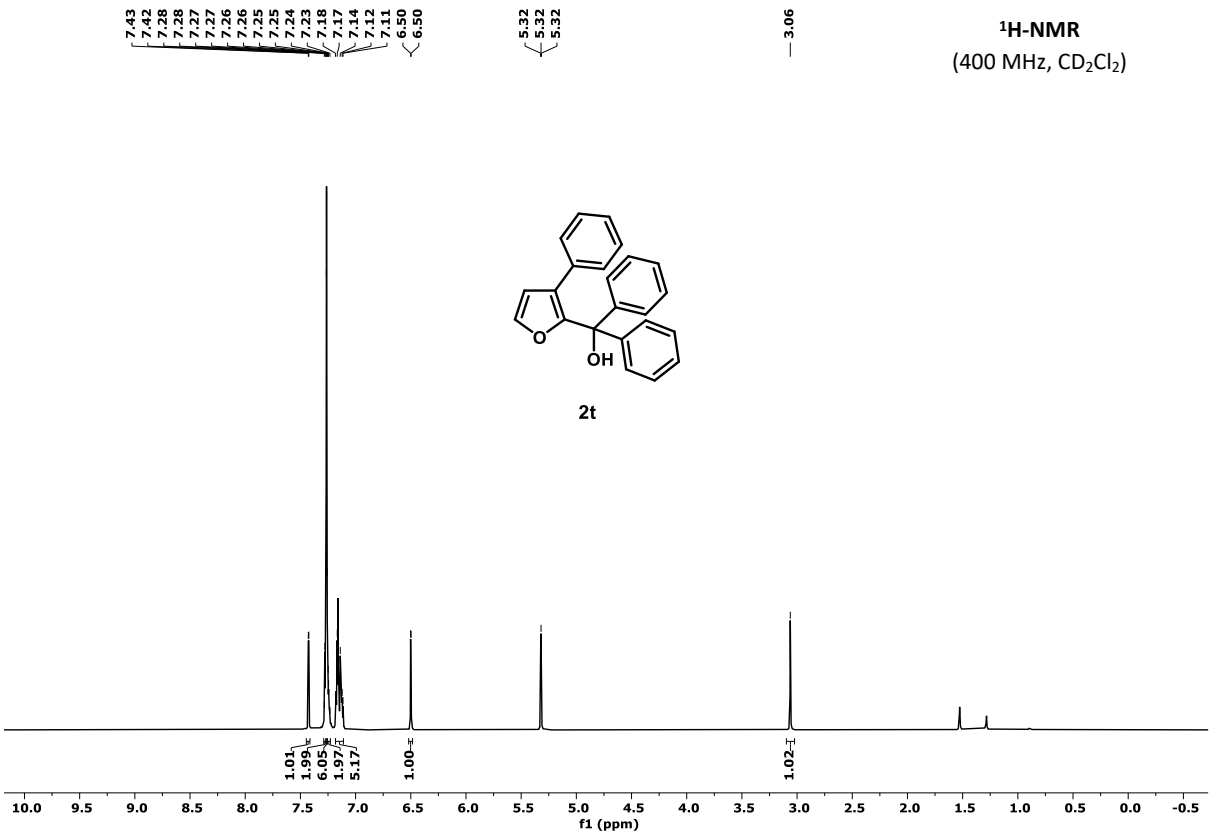
^{1}H-NMR
(400 MHz, CD_2Cl_2)



^{13}C-NMR
(100 MHz, CD_2Cl_2)

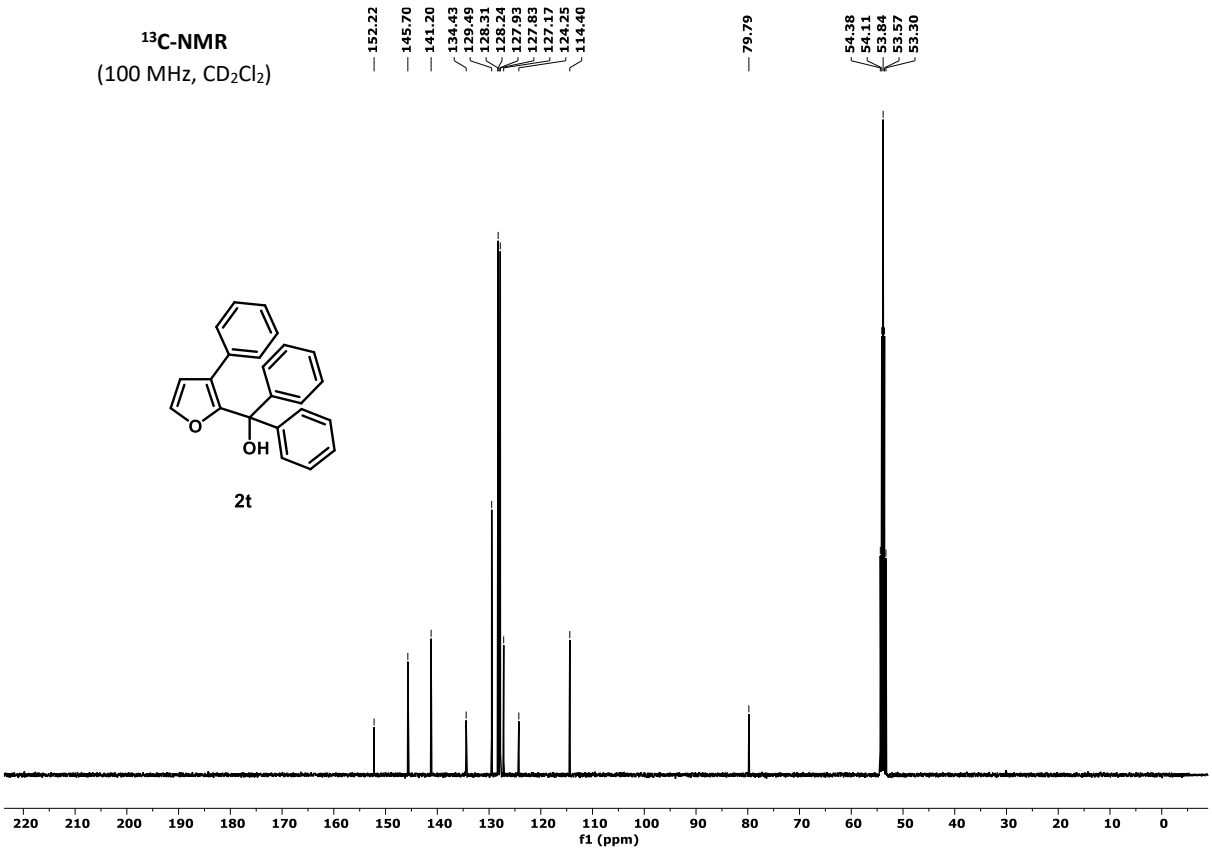


^{1}H-NMR
(400 MHz, CD_2Cl_2)



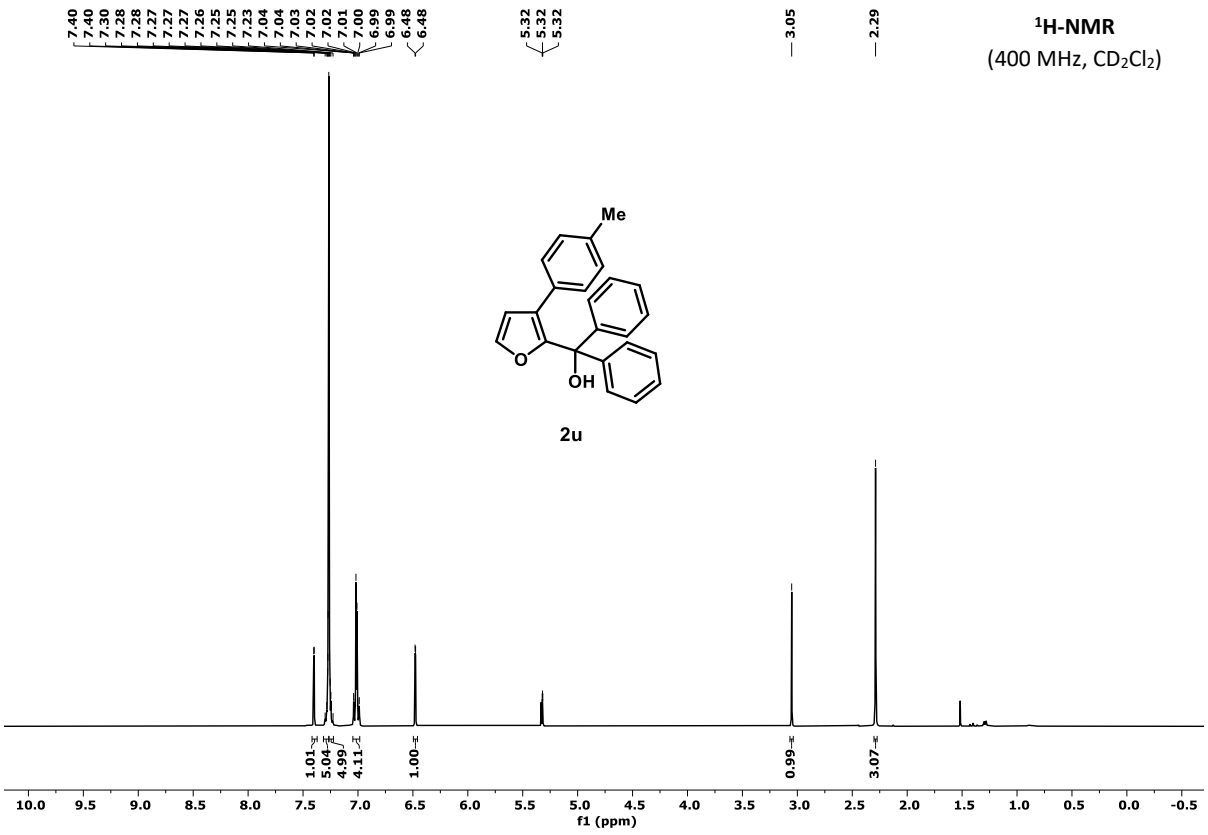
2t

^{13}C-NMR
(100 MHz, CD_2Cl_2)



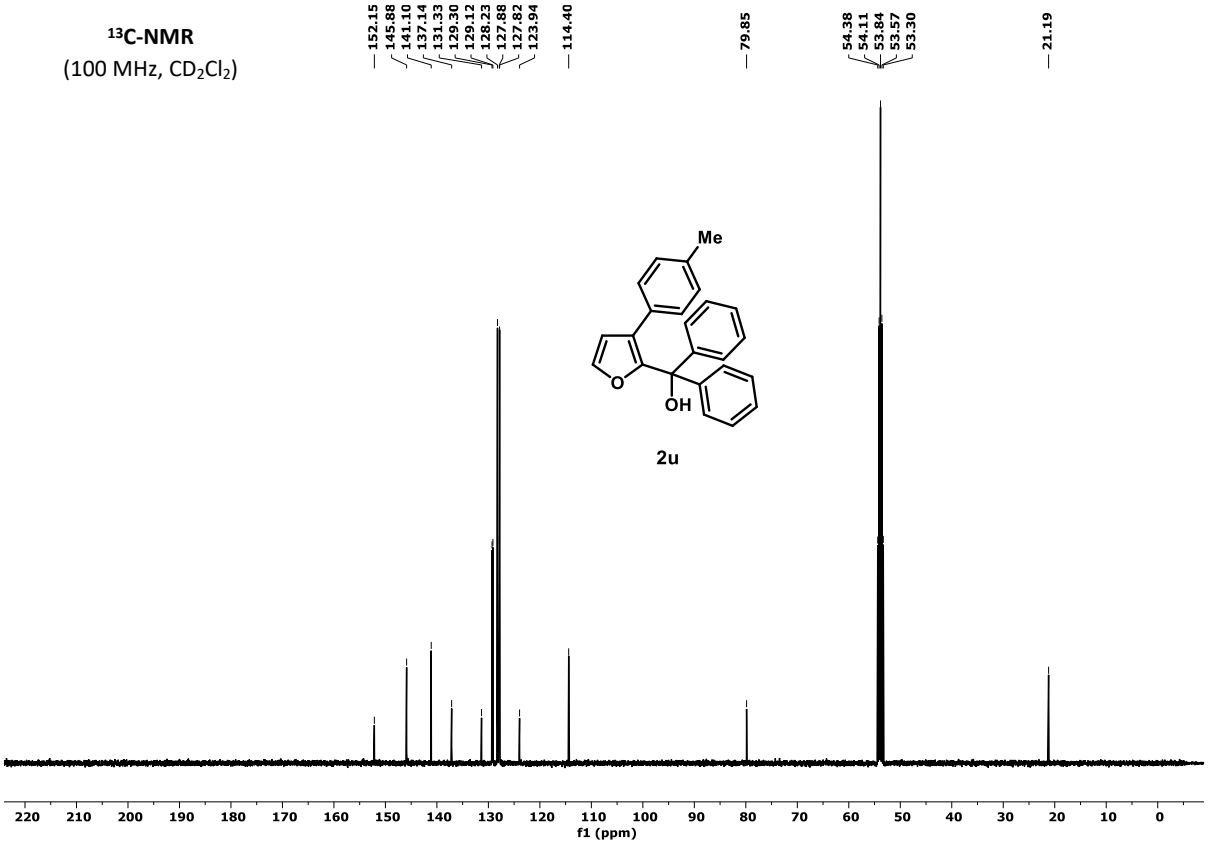
2t

^{1}H-NMR
(400 MHz, CD_2Cl_2)



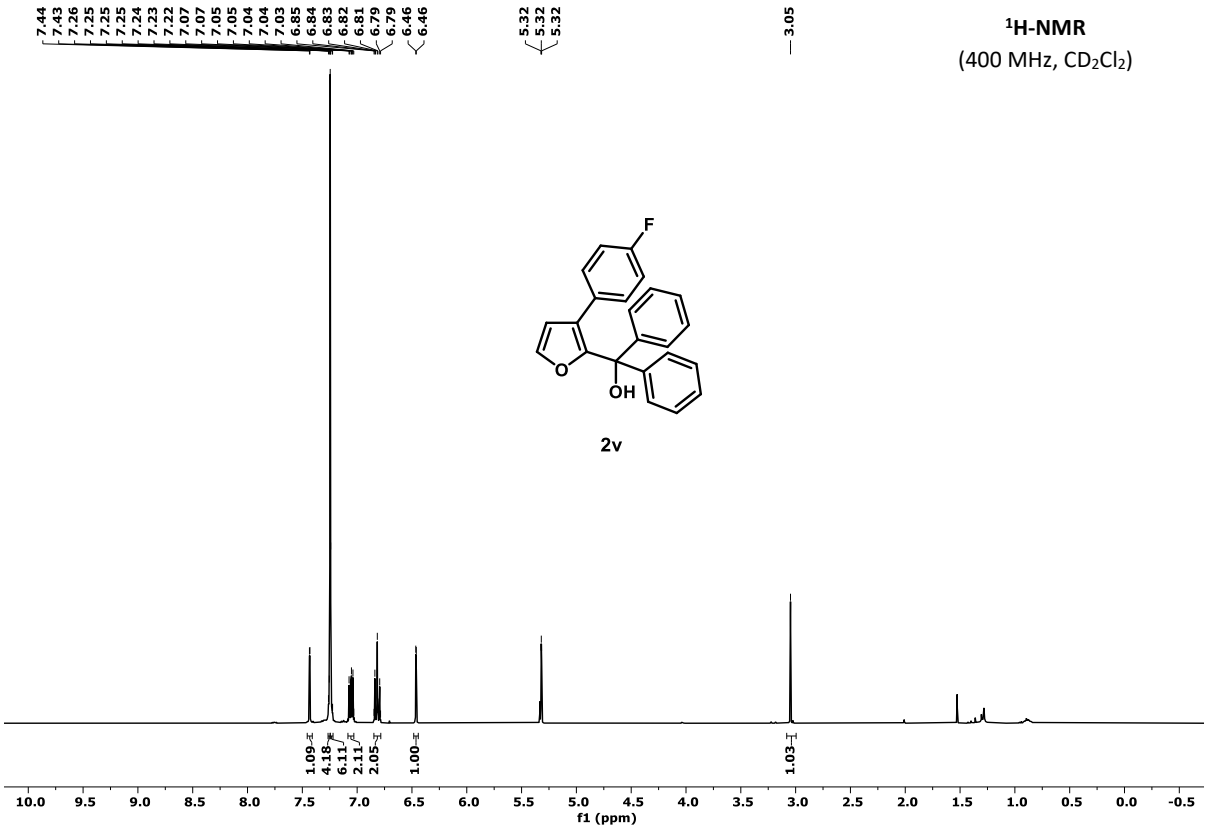
2u

^{13}C-NMR
(100 MHz, CD_2Cl_2)



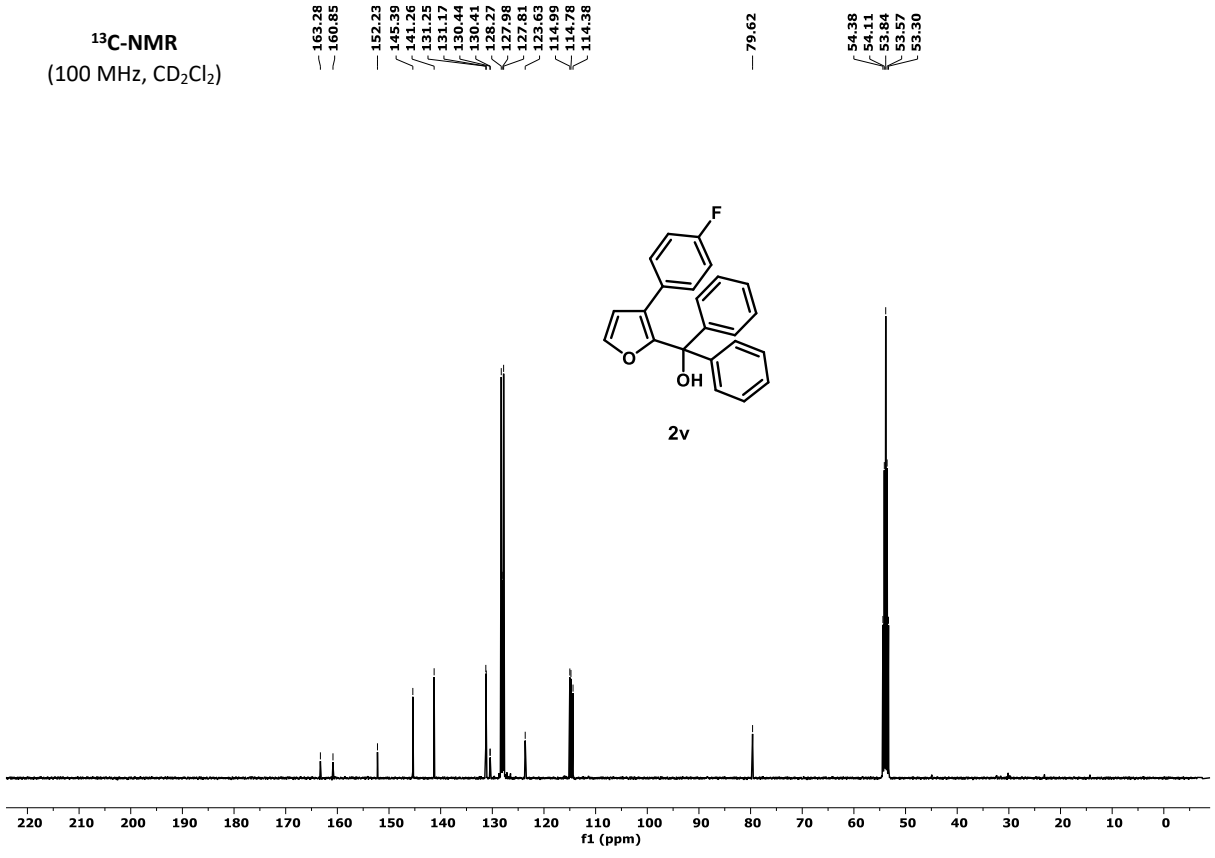
2u

^{1}H-NMR
(400 MHz, CD_2Cl_2)



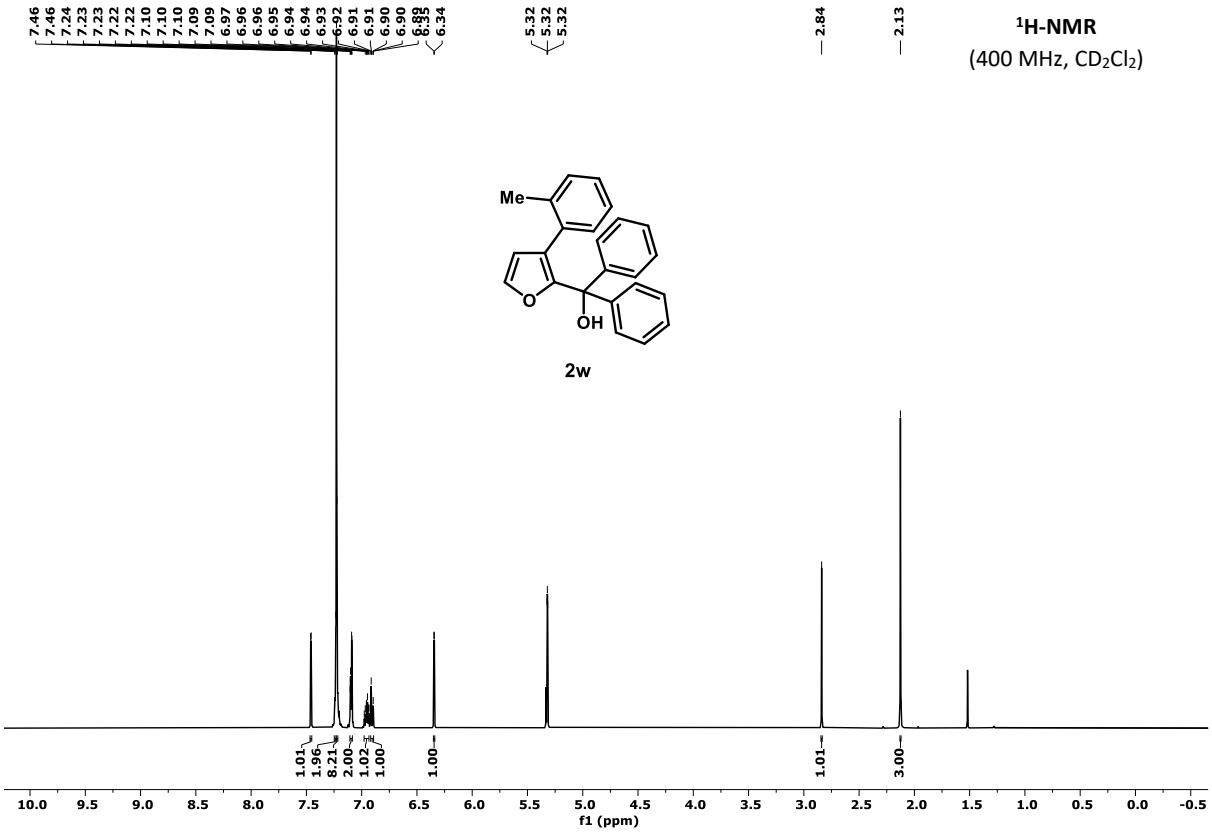
2v

^{13}C-NMR
(100 MHz, CD_2Cl_2)



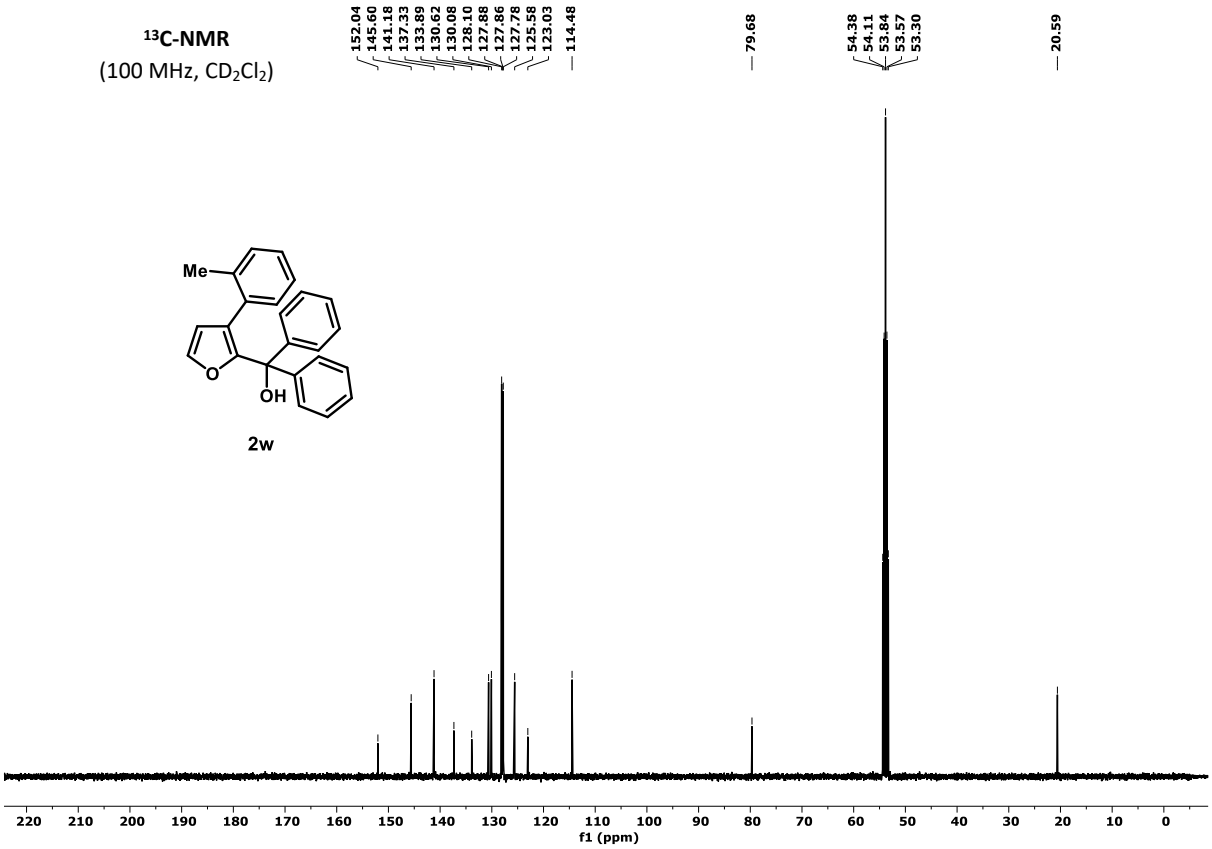
2v

^{1}H-NMR
(400 MHz, CD_2Cl_2)



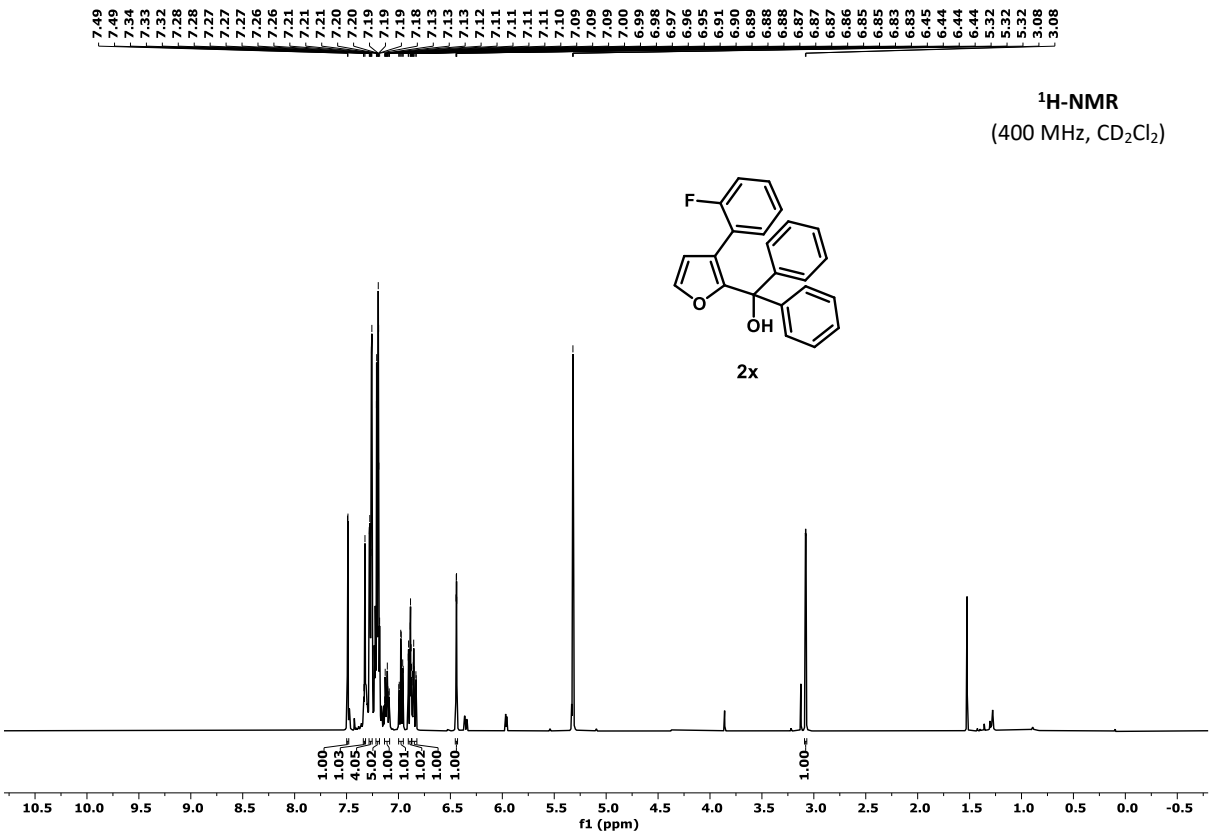
2w

^{13}C-NMR
(100 MHz, CD_2Cl_2)

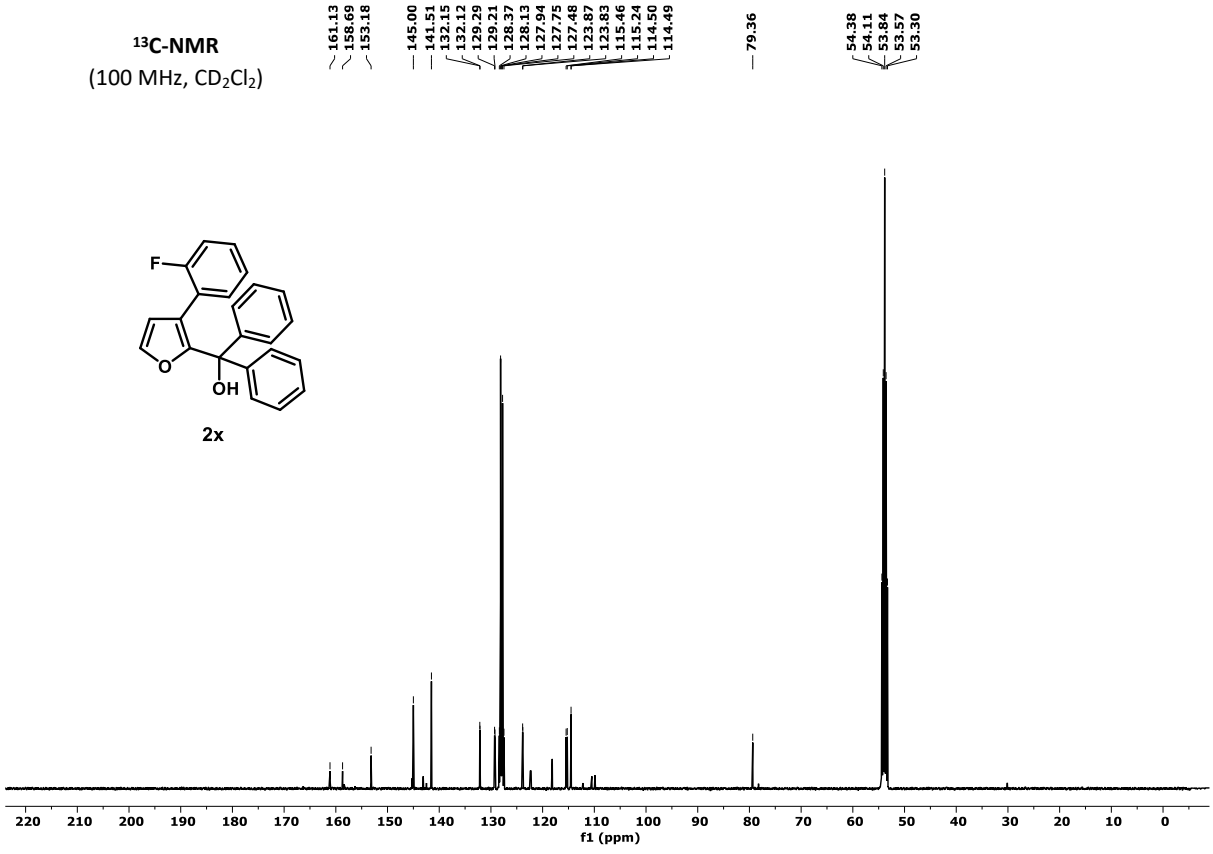


2w

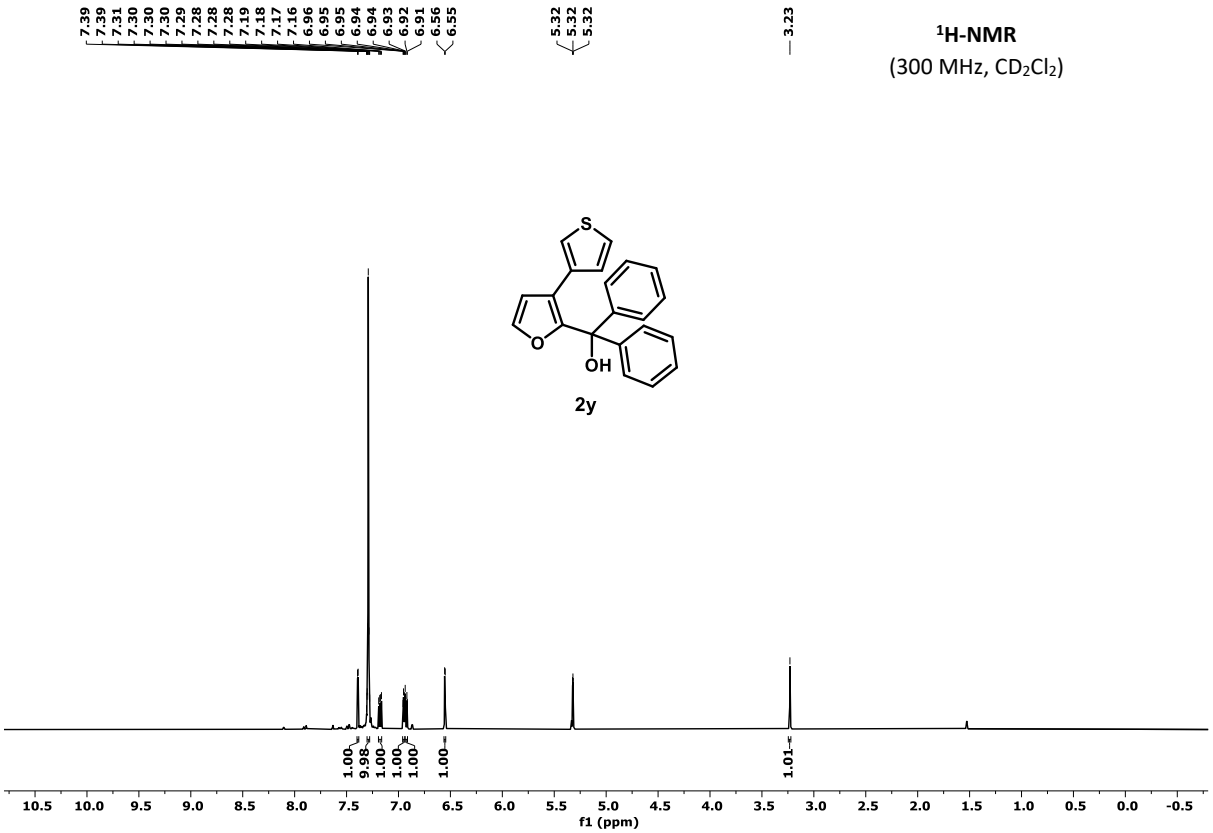
^{1}H-NMR
(400 MHz, CD_2Cl_2)



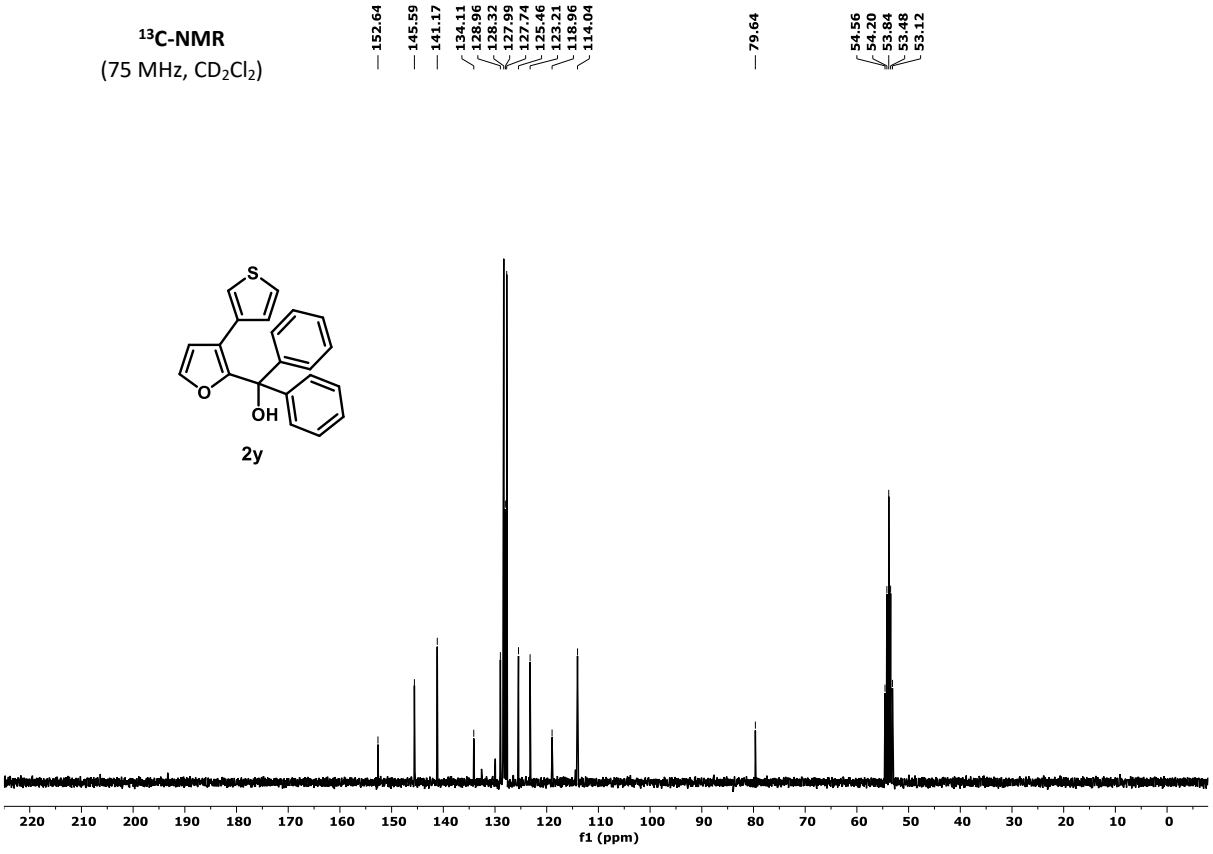
^{13}C-NMR
(100 MHz, CD_2Cl_2)



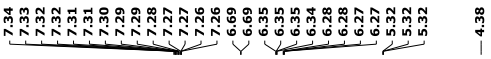
^{1}H-NMR
(300 MHz, CD_2Cl_2)

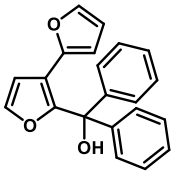


^{13}C-NMR
(75 MHz, CD_2Cl_2)

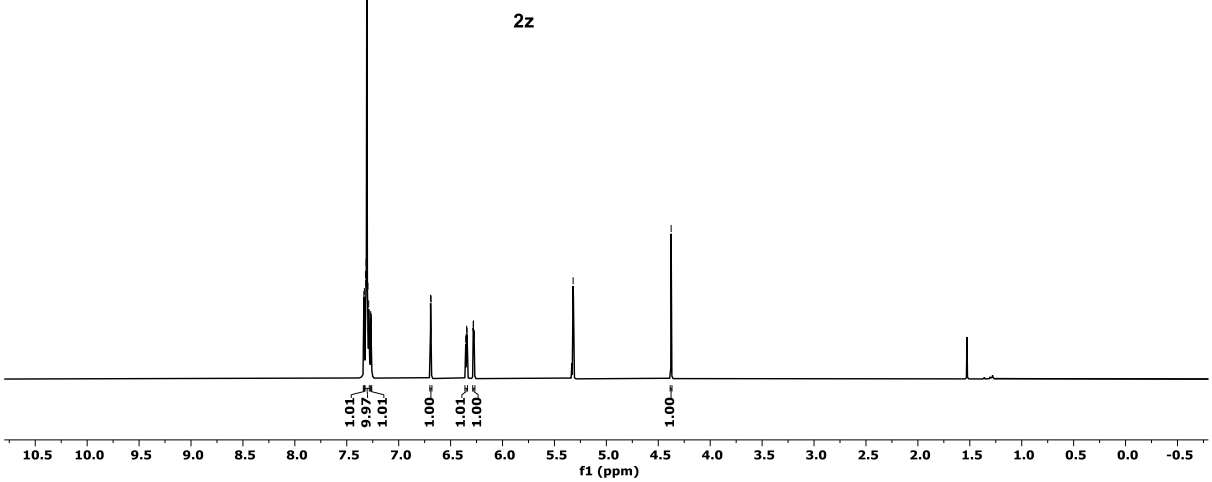


^{1}H-NMR
(400 MHz, CD_2Cl_2)

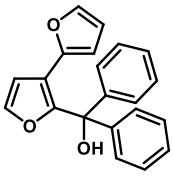




2z

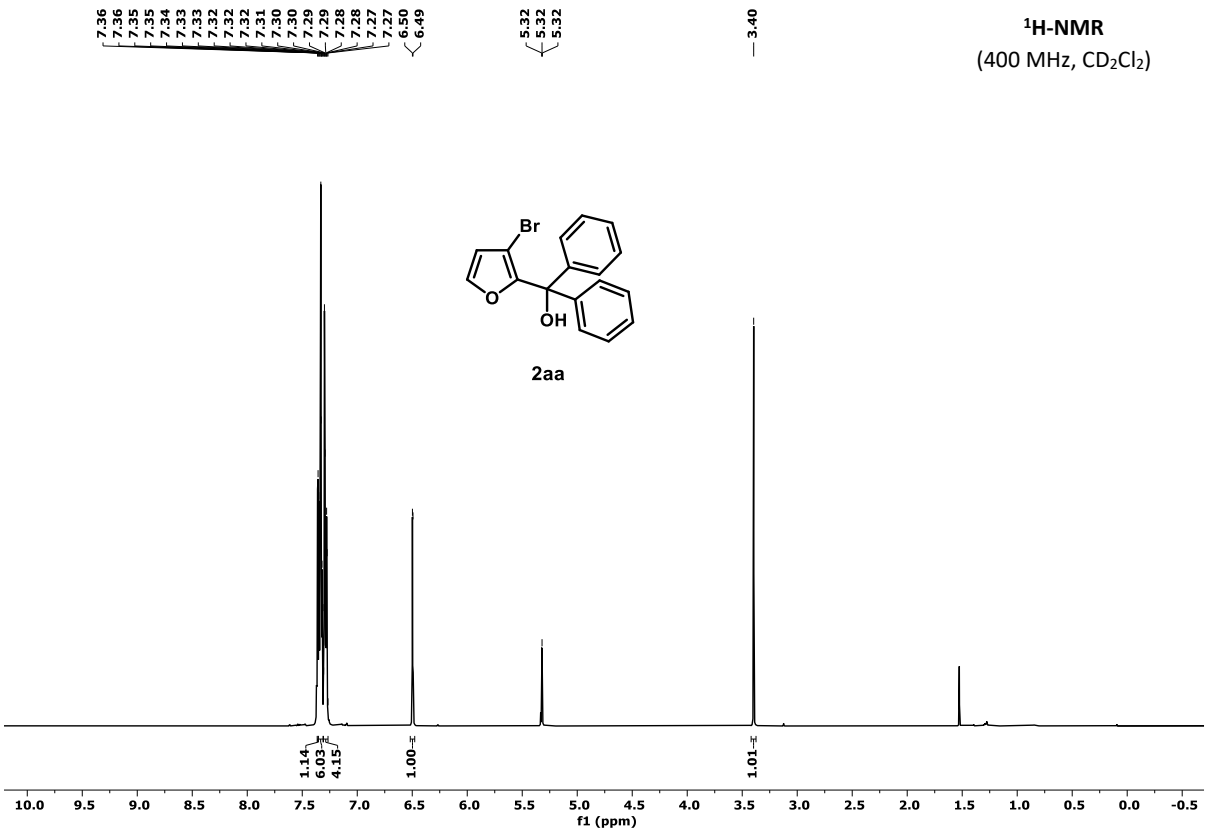


^{13}C-NMR
(100 MHz, CD_2Cl_2)

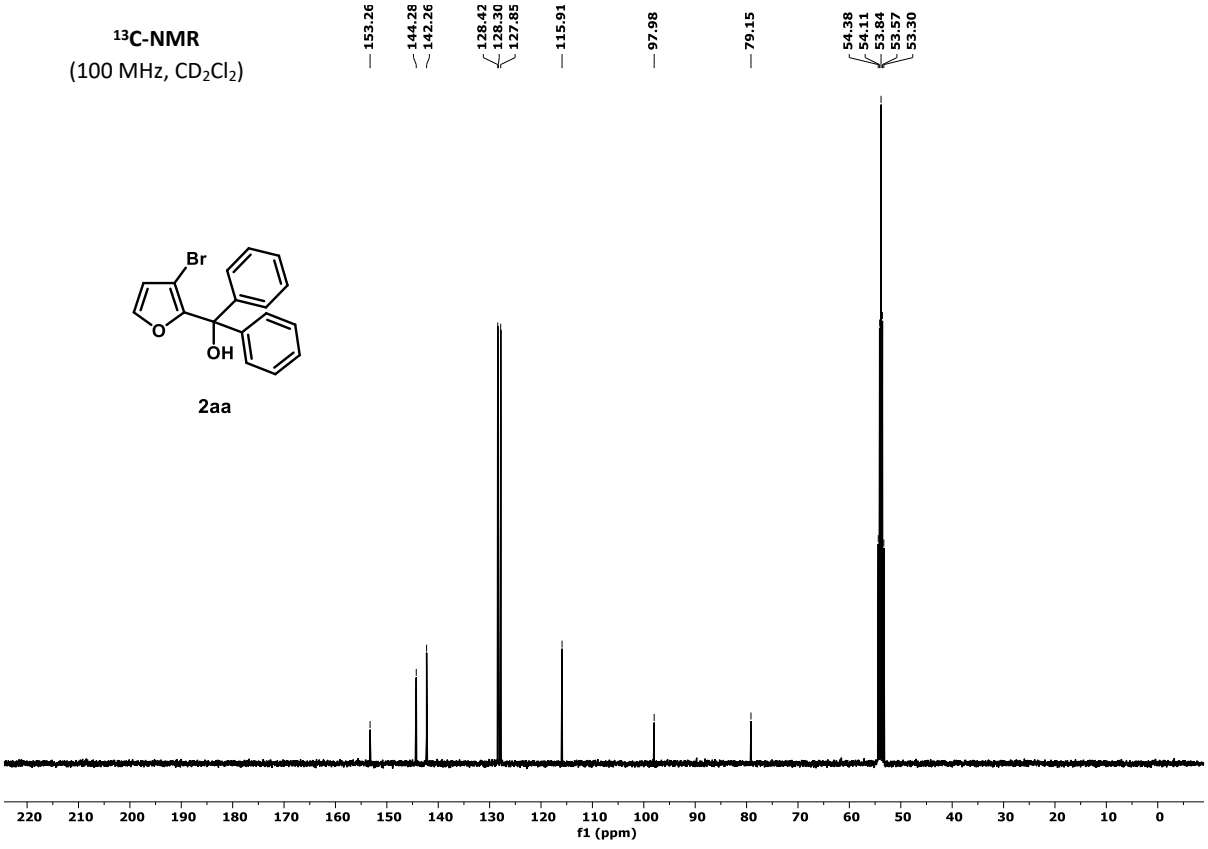


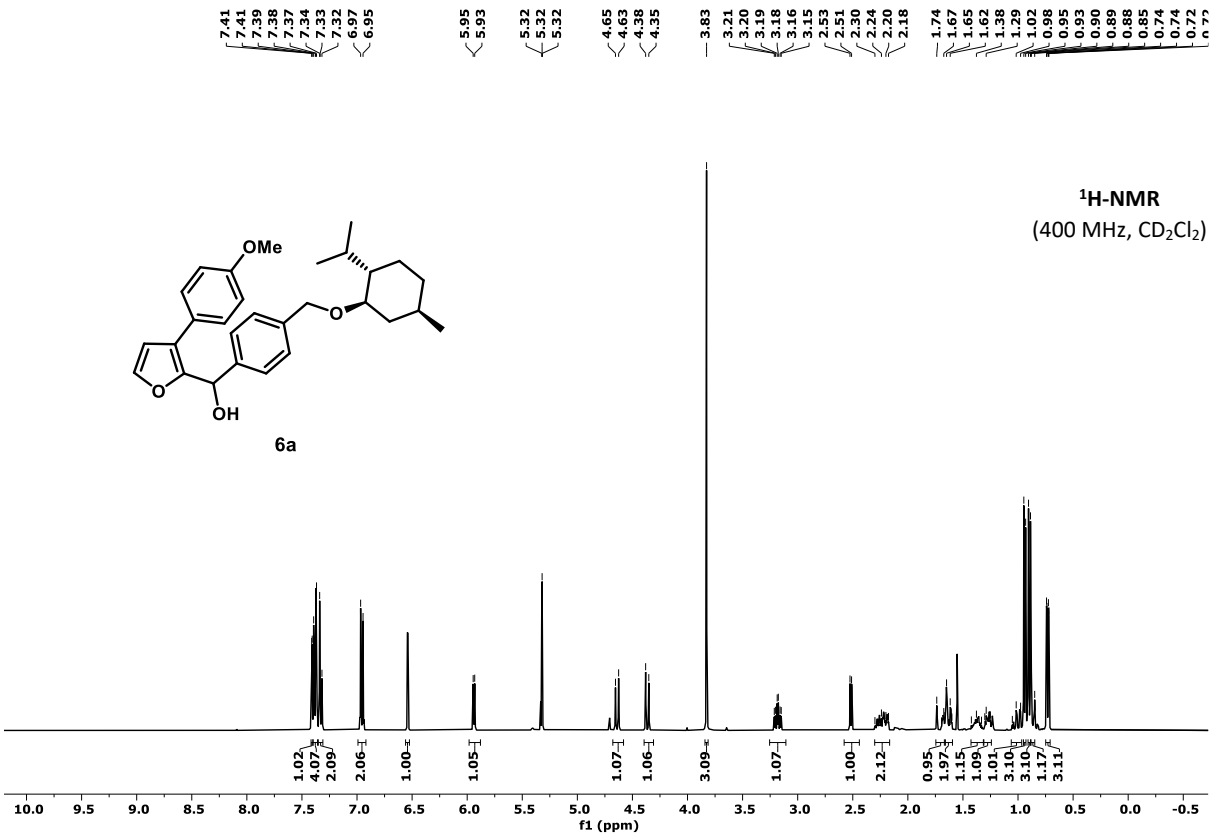
2z

^{1}H-NMR
(400 MHz, CD_2Cl_2)



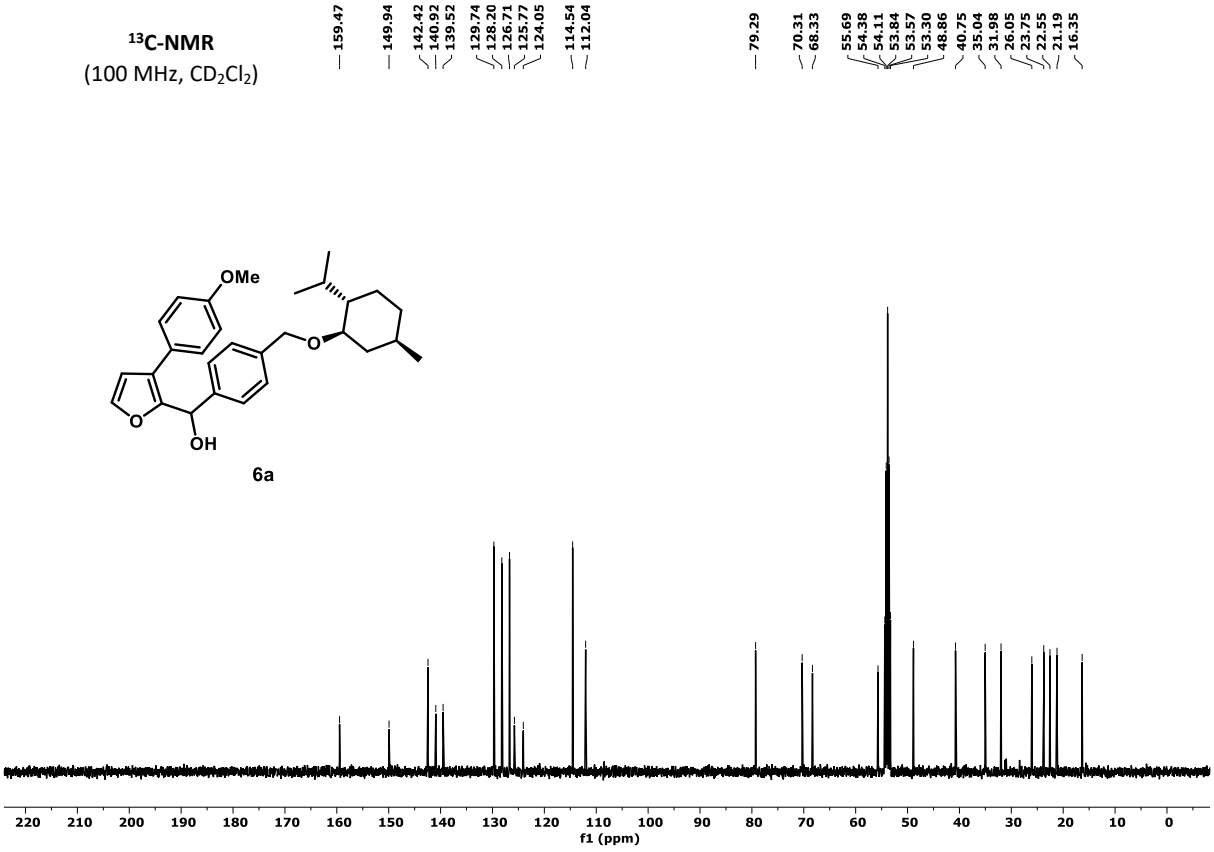
^{13}C-NMR
(100 MHz, CD_2Cl_2)

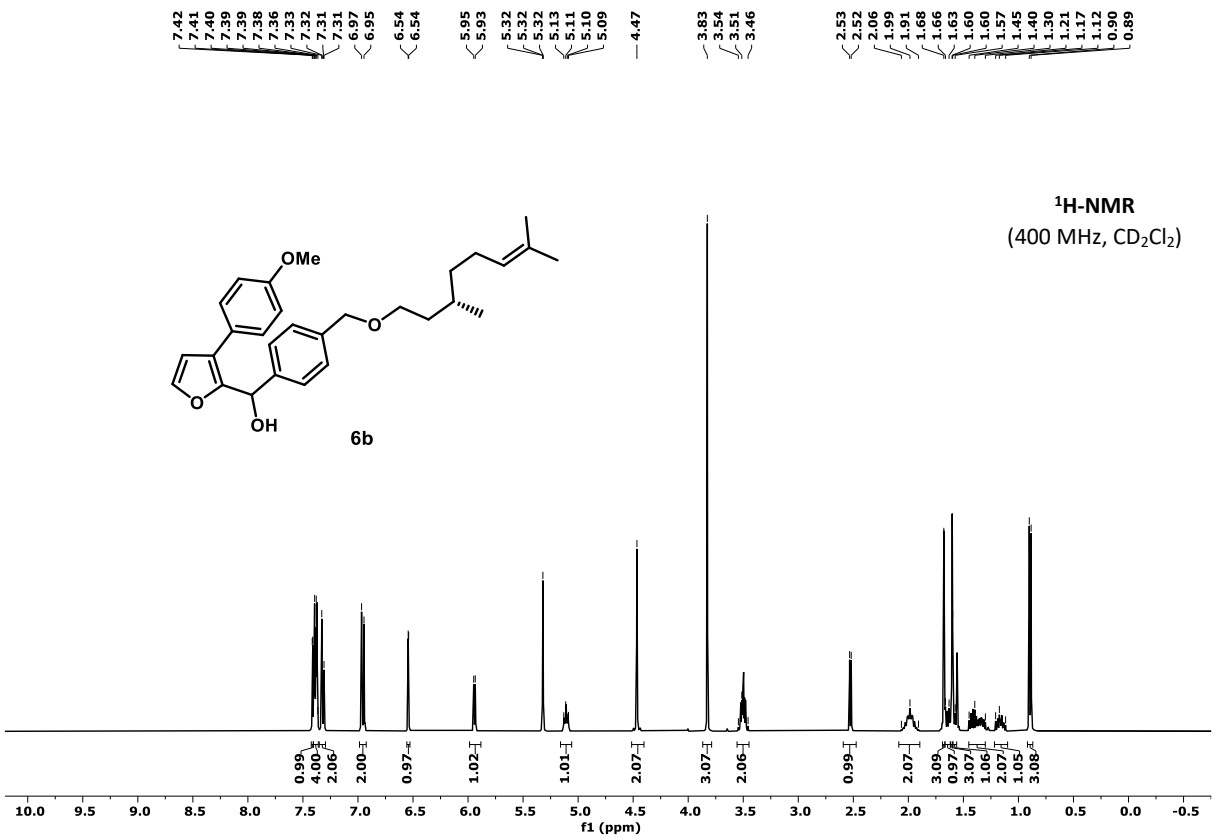


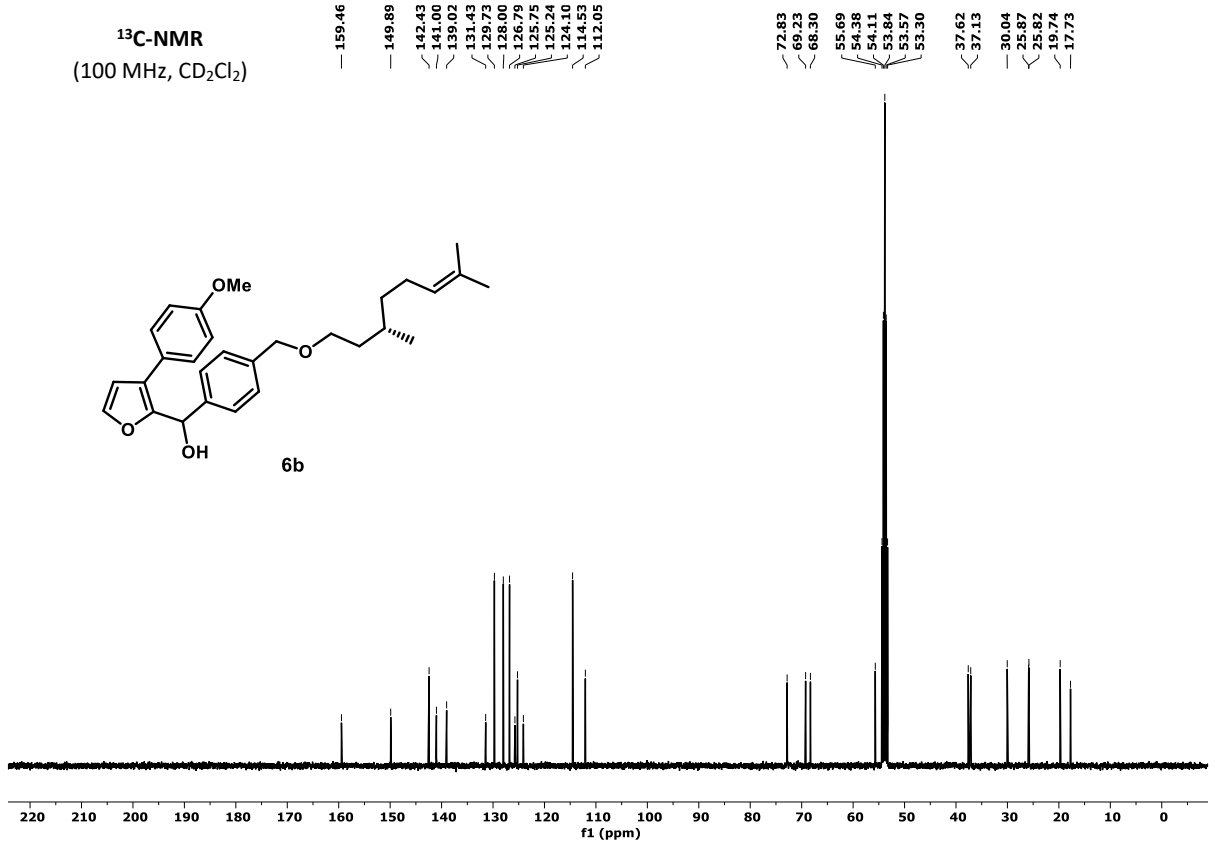


^{1}H-NMR
(400 MHz, CD_2Cl_2)

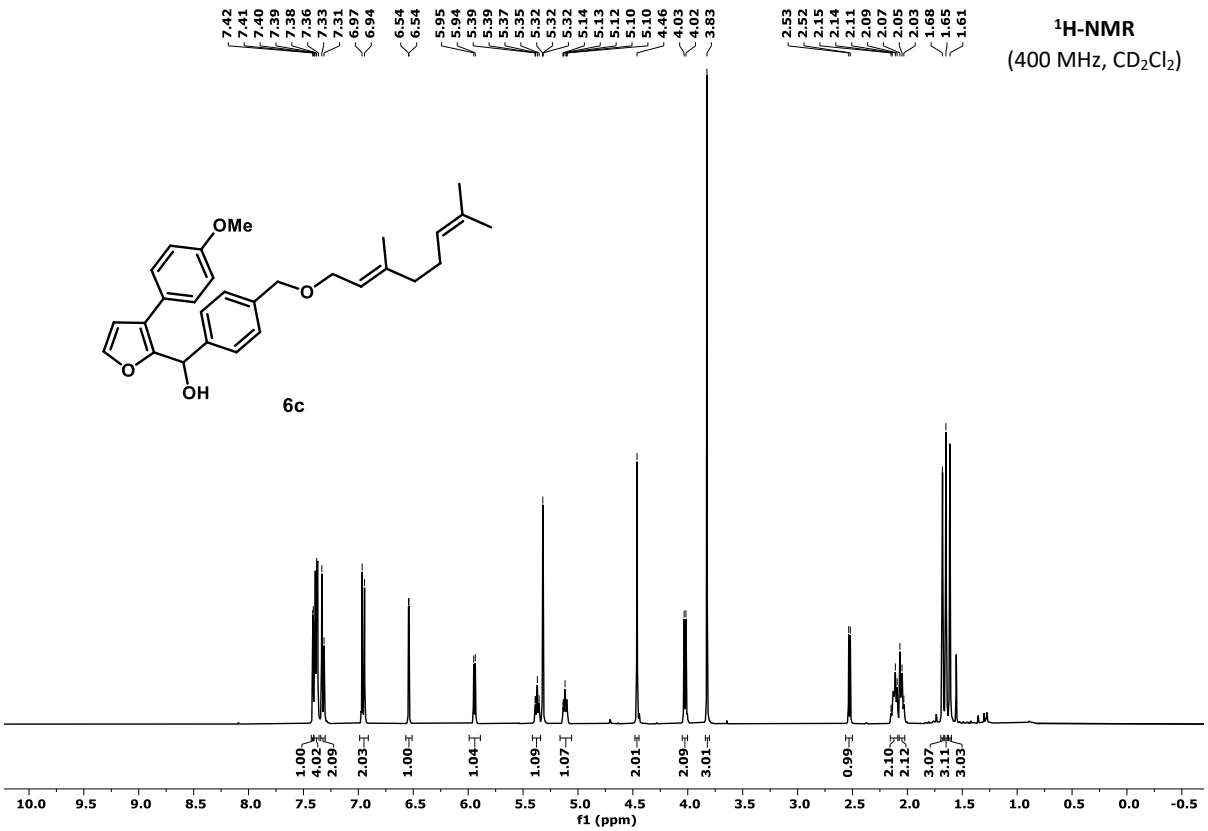
^{13}C-NMR
(100 MHz, CD_2Cl_2)



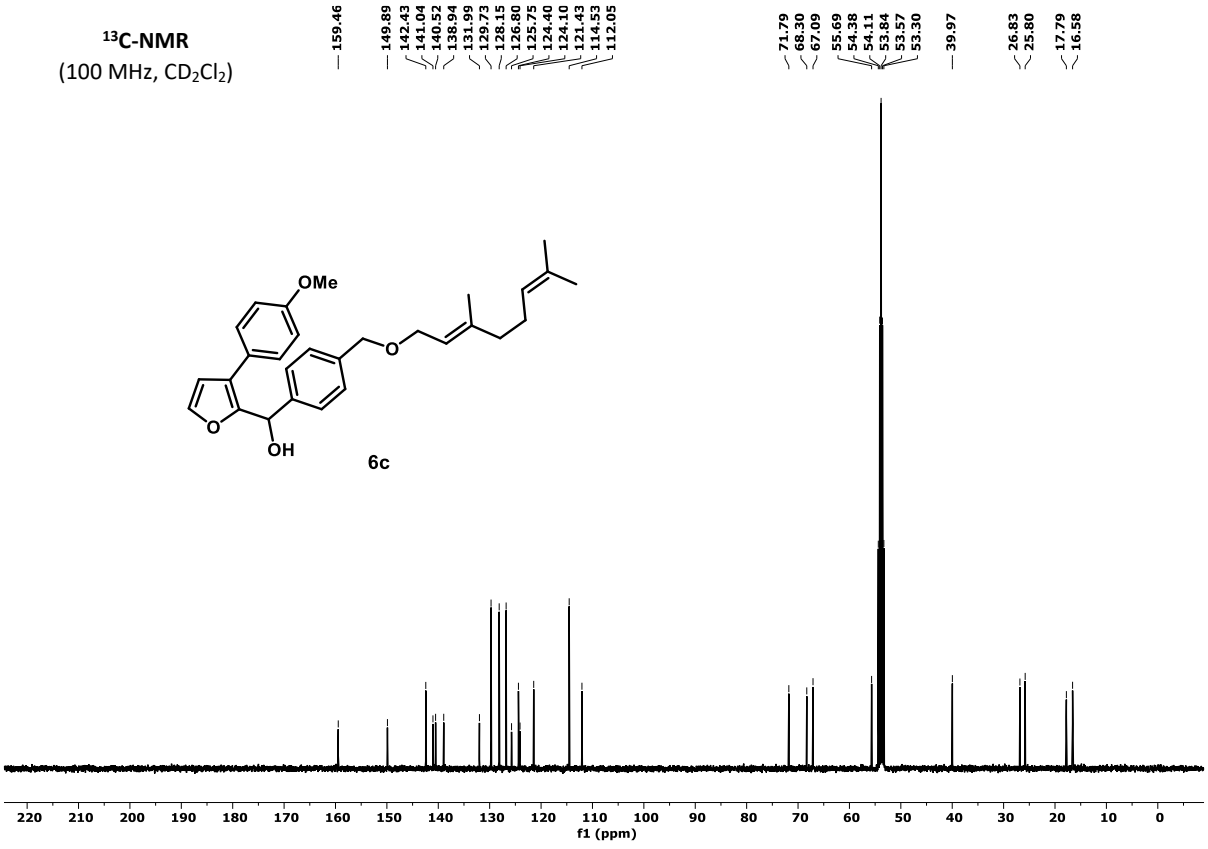

7.42 7.41 7.40 7.39 7.39 7.38 7.36 7.33 7.32 7.31 7.31 6.97 6.95 6.54 6.54 5.95 5.93 5.32 5.32 5.32 5.13 5.11 5.10 5.09 4.47 3.83 3.54 3.51 3.46 2.53 2.52 2.06 1.99 1.91 1.68 1.66 1.63 1.60 1.60 1.57 1.45 1.40 1.30 1.21 1.17 1.12 0.90 0.89
1H-NMR
(400 MHz, CD2Cl2)
OMe
O
O
OH
6b
0.99 4.00 2.06 2.00 0.97 1.02 1.01 2.07 3.07 2.06 0.99 2.07 3.09 0.97 3.07 1.06 2.07 1.05 3.08
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
f1 (ppm)


13C-NMR
(100 MHz, CD2Cl2)
159.46 149.89 142.43 141.00 139.02 131.43 129.73 128.00 126.79 125.75 125.24 124.10 114.53 112.05
72.83 69.23 68.30 55.69 54.38 54.11 53.84 53.57 53.30 37.62 37.13 30.04 25.87 25.82 19.74 17.73
OMe
O
O
OH
6b
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

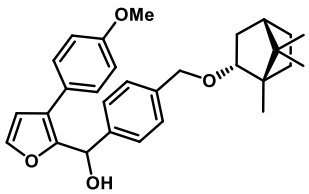
^{1}H-NMR
(400 MHz, CD_2Cl_2)



^{13}C-NMR
(100 MHz, CD_2Cl_2)

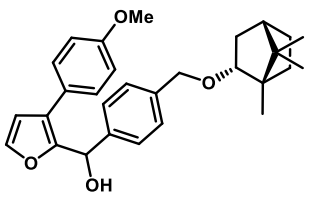


^{1}H-NMR
(300 MHz, CD_2Cl_2)



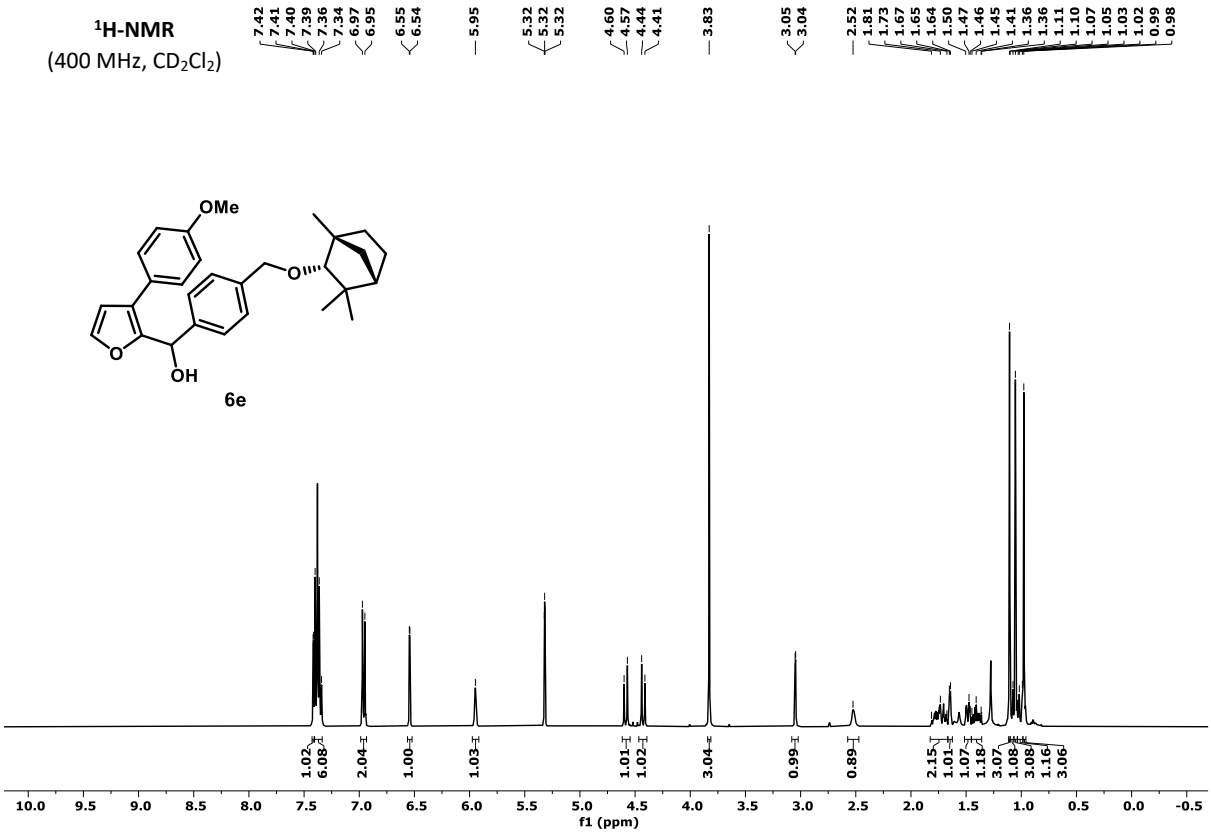
6d

^{13}C-NMR
(75 MHz, CD_2Cl_2)

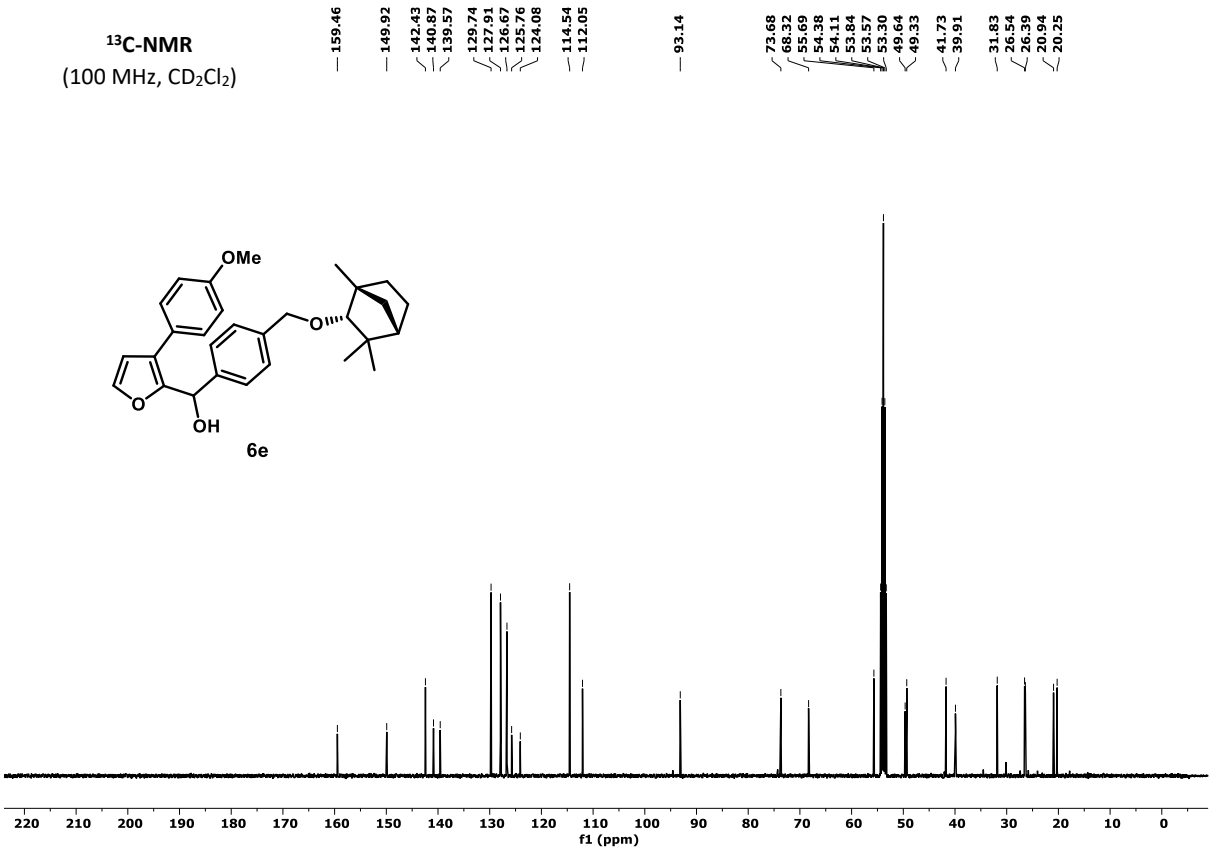


6d

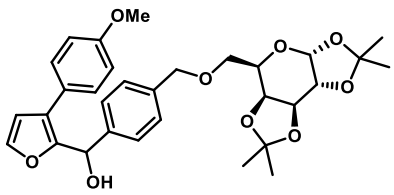
^{1}H-NMR
(400 MHz, CD_2Cl_2)



^{13}C-NMR
(100 MHz, CD_2Cl_2)

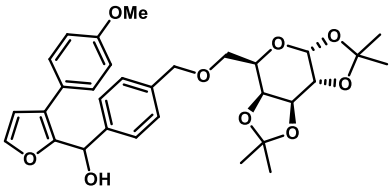


^{1}H-NMR
(400 MHz, CD_2Cl_2)



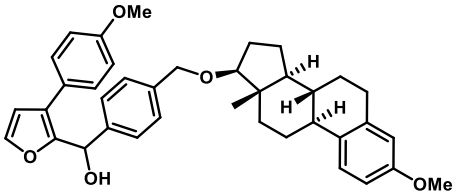
6f

^{13}C-NMR
(100 MHz, CD_2Cl_2)



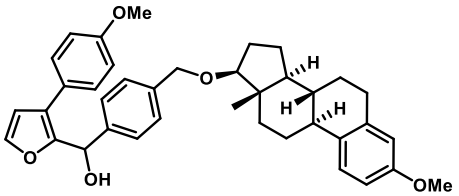
6f

^{1}H-NMR
(400 MHz, CD_2Cl_2)

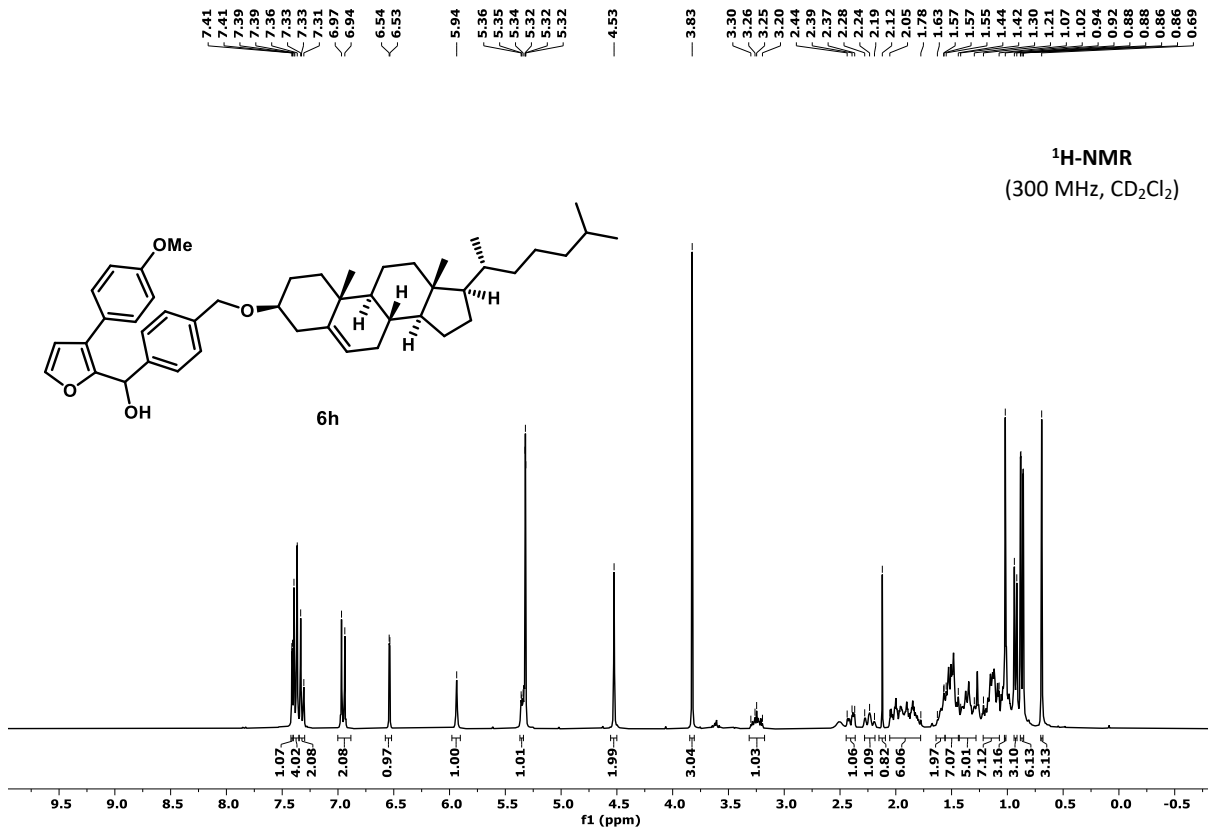


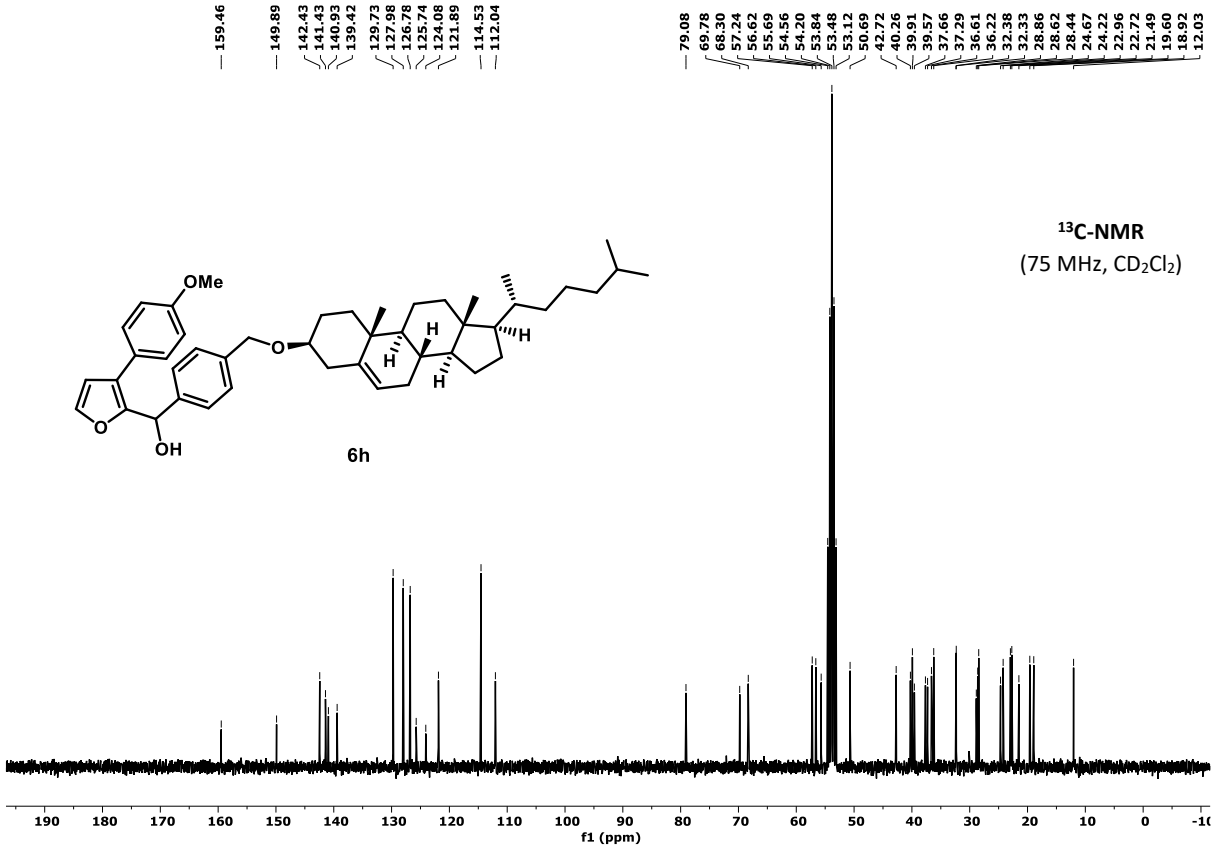
6g

^{13}C-NMR
(100 MHz, CD_2Cl_2)

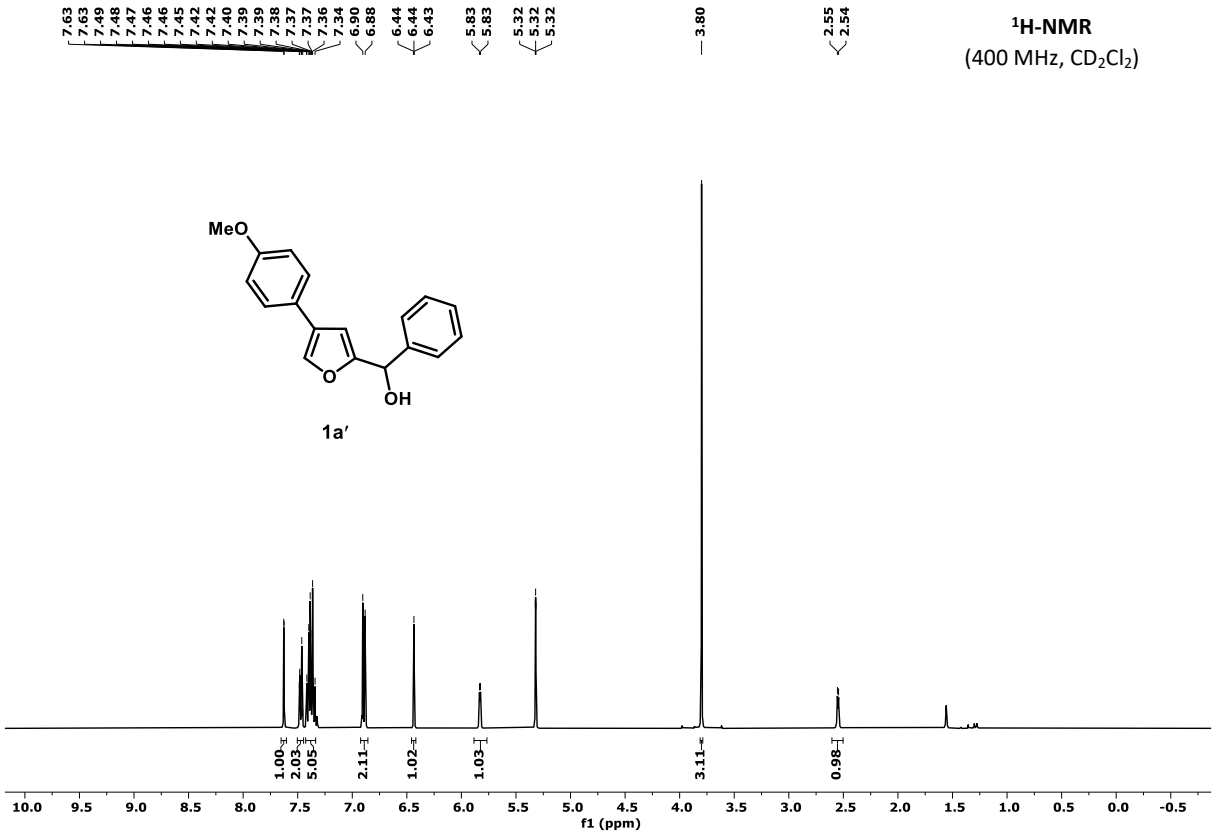


6g

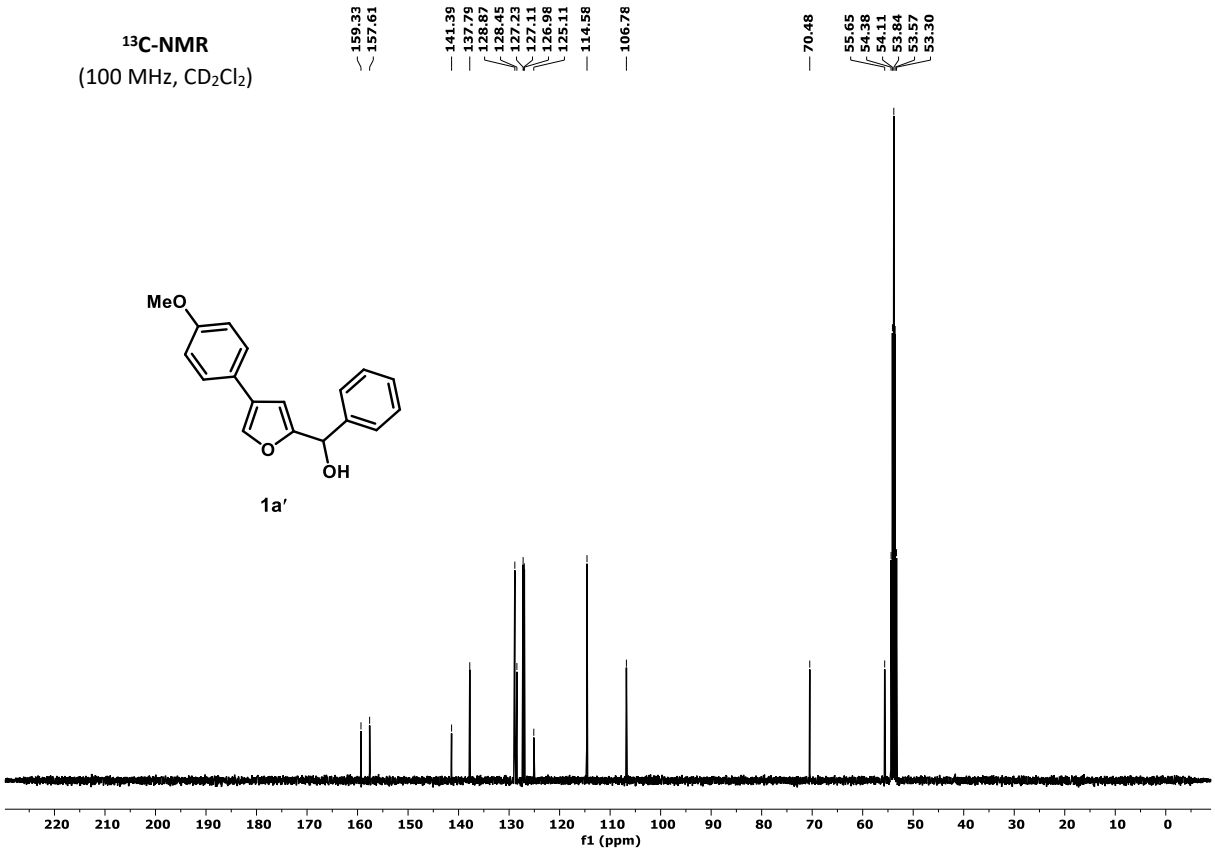

7.41 7.41 7.39 7.39 7.36 7.33 7.33 7.31 6.97 6.94 6.54 6.53 5.94 5.36 5.35 5.34 5.32 5.32 5.32 4.53 3.83 3.30 3.26 3.25 3.20 2.44 2.39 2.37 2.28 2.24 2.19 2.12 2.05 1.78 1.63 1.57 1.57 1.55 1.44 1.42 1.30 1.21 1.07 1.02 0.94 0.92 0.88 0.88 0.86 0.86 0.69
1H-NMR
(300 MHz, CD2Cl2)
OMe
O
OH
H
H
H
H
6h
1.07 4.02 2.08 2.08 0.97 1.00 1.01 1.99 3.04 1.03 1.06 1.09 0.82 6.06 1.97 7.07 5.01 7.12 3.16 3.10 6.13 3.13
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
f1 (ppm)

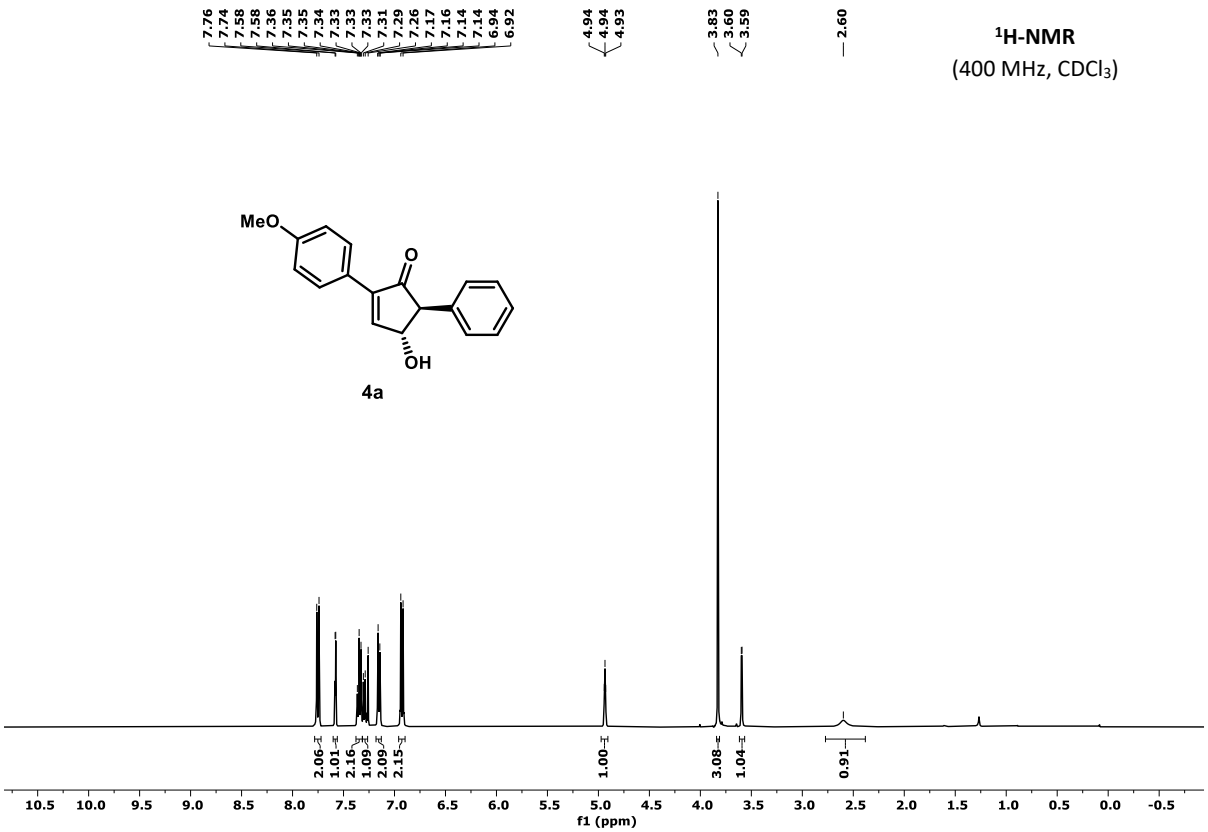

159.46 149.89 142.43 141.43 140.93 139.42 129.73 127.98 126.78 125.74 124.08 121.89 114.53 112.04 79.08 69.78 68.30 57.24 56.62 55.69 54.56 54.20 53.84 53.48 53.12 50.69 42.72 40.26 39.91 39.57 37.66 37.29 36.61 36.22 32.38 32.33 28.86 28.62 28.44 24.67 24.22 22.96 22.72 21.49 19.60 18.92 12.03
13C-NMR
(75 MHz, CD2Cl2)
OMe
O
OH
H
H
H
H
6h
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

^{1}H-NMR
(400 MHz, CD_2Cl_2)

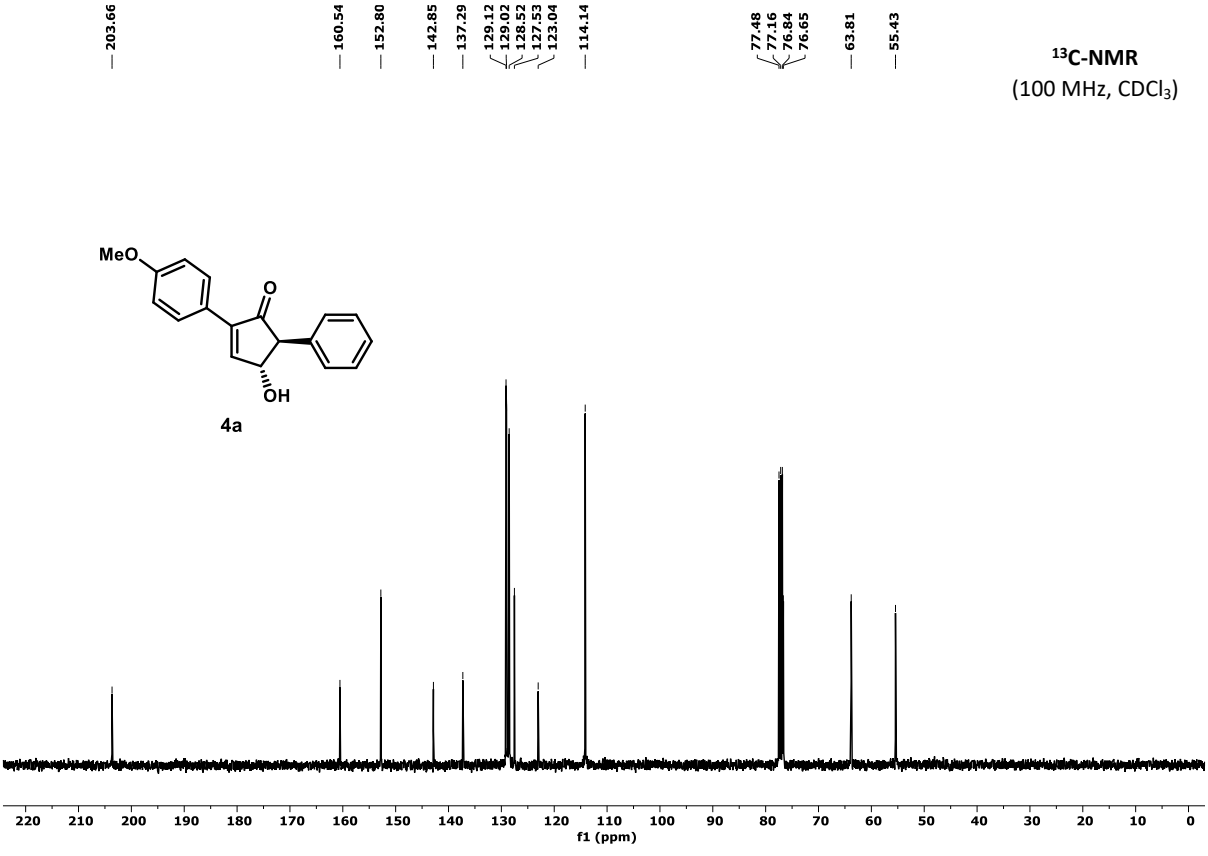


^{13}C-NMR
(100 MHz, CD_2Cl_2)

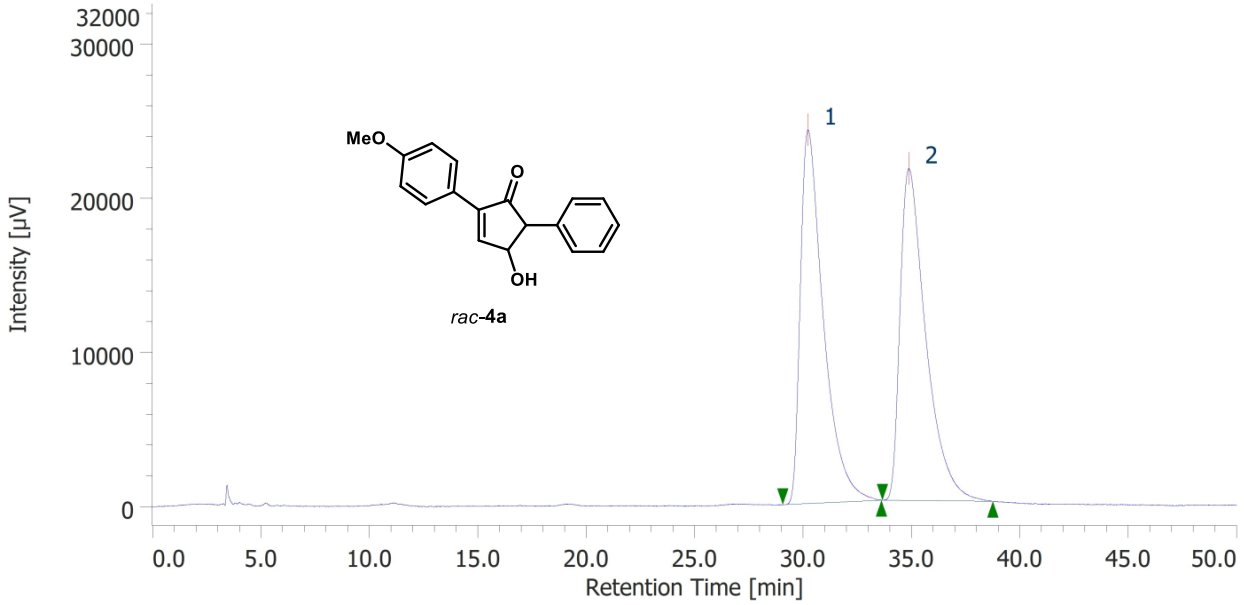




^{1}H-NMR
(400 MHz, $CDCl_3$)

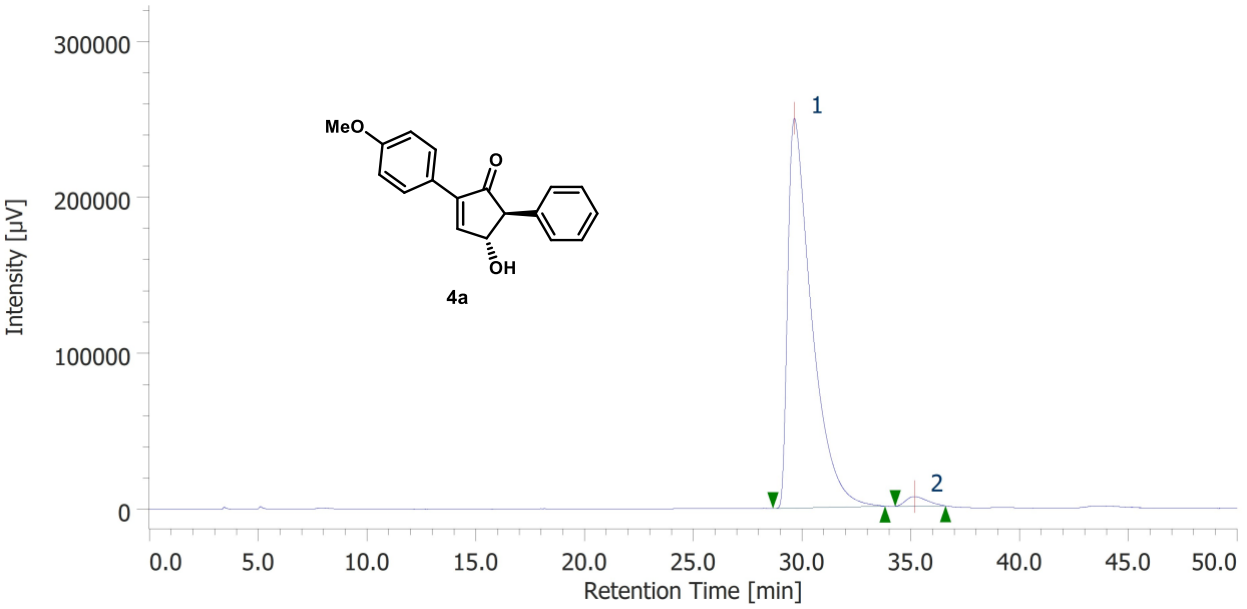


^{13}C-NMR
(100 MHz, $CDCl_3$)



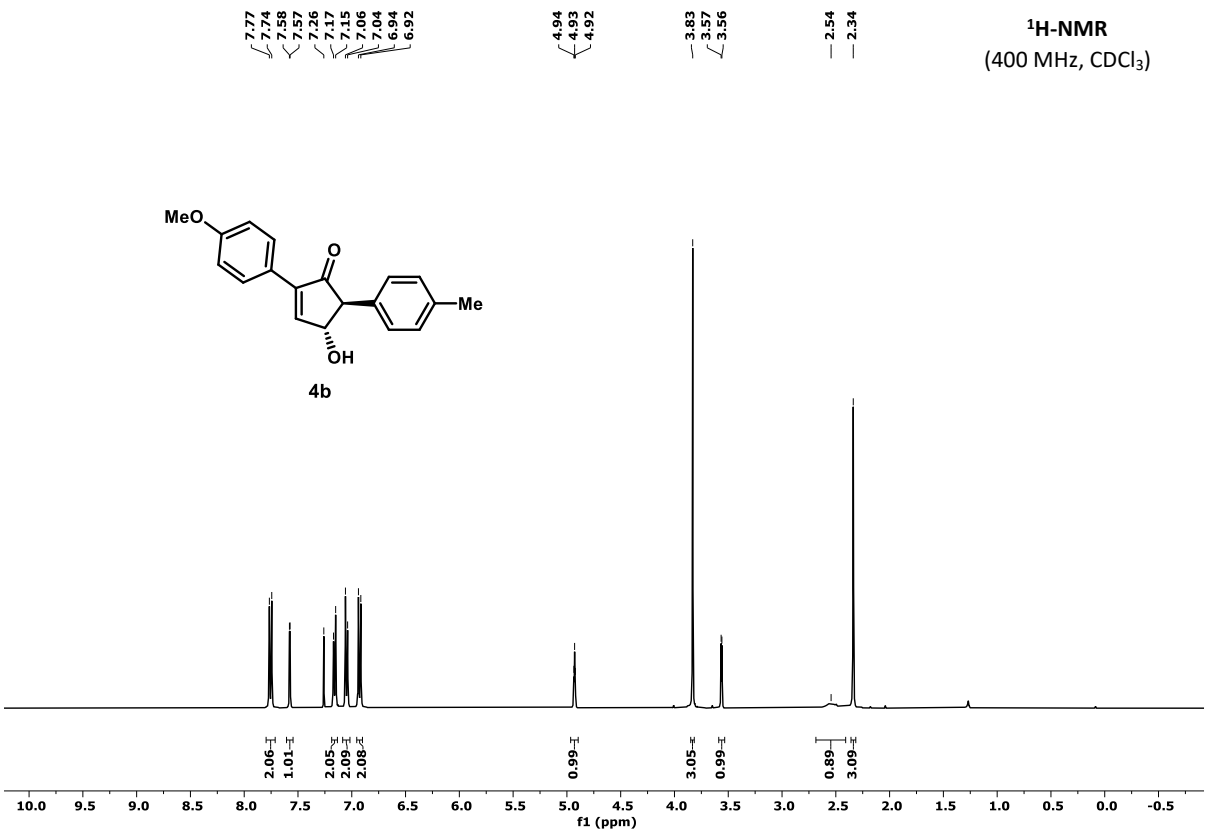
#	Peak Name	CH	tR [min]	Area [μV·sec]	Height [μV]	Area%	Height%	Quantity	NTP	Resolution	Symmetry Factor	Warning
1	Unknown	11	30.230	1785311	24225	50.132	52.950	N/A	4304	2.377	1.911	
2	Unknown	11	34.873	1775938	21526	49.868	47.050	N/A	4525	N/A	1.864	

Daicel Chiralpak IB column (90:10 *n*-Hexane/*i*-PrOH, 1.0 mL/min, 245 nm)

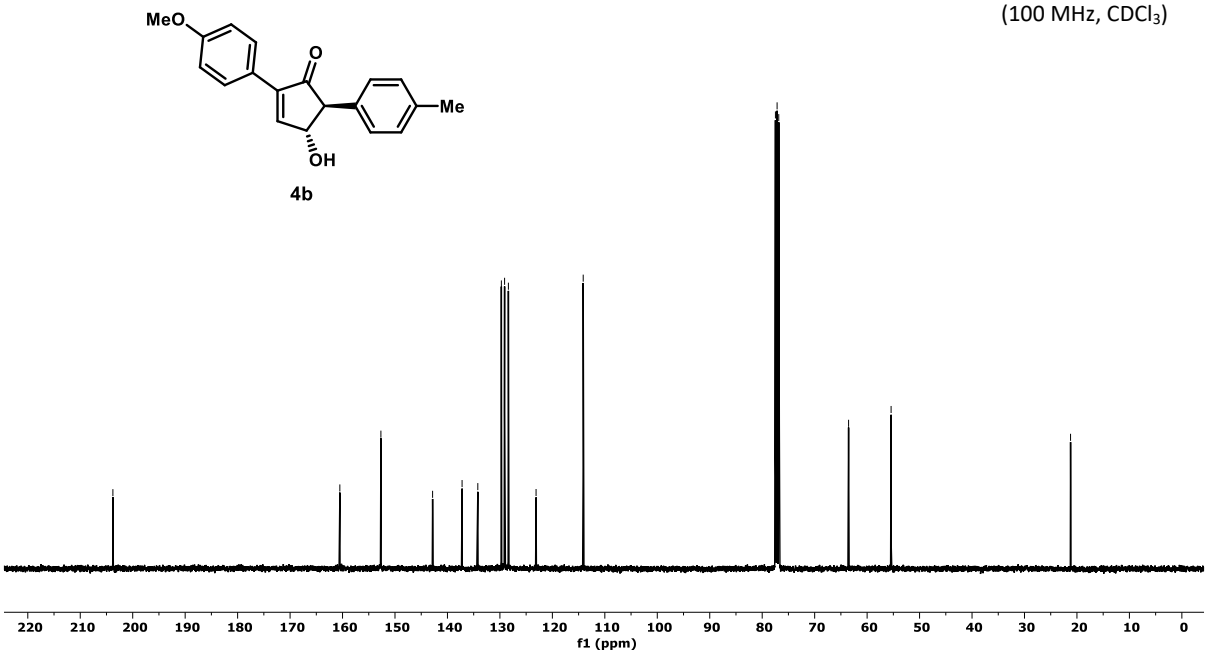


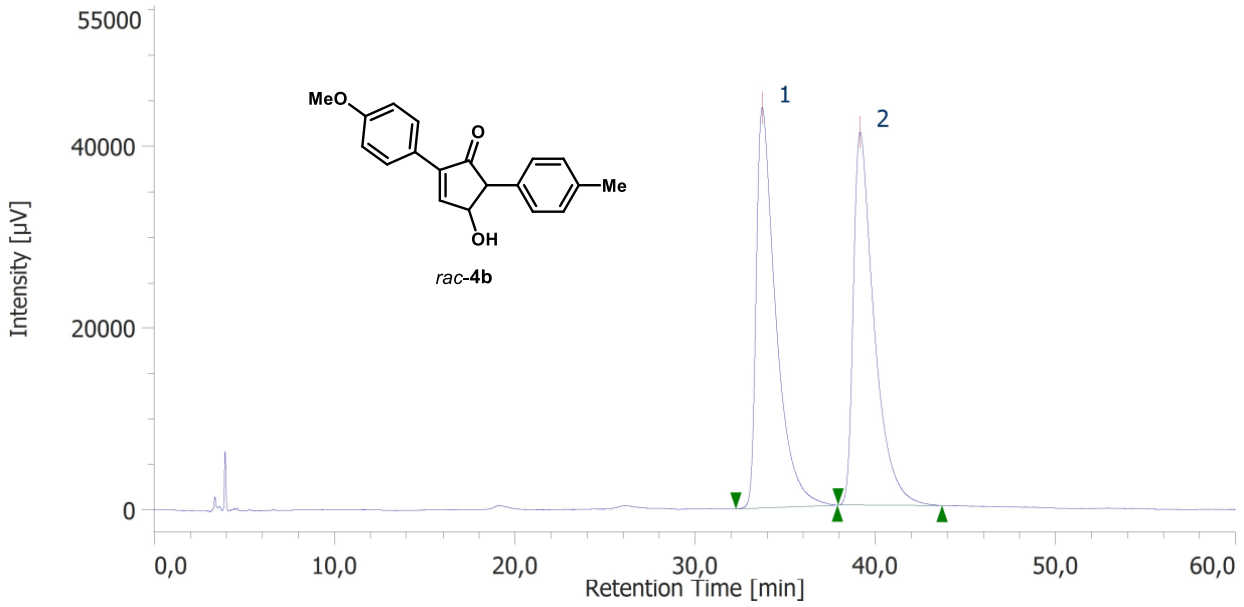
#	Peak Name	CH	tR [min]	Area [μV·sec]	Height [μV]	Area%	Height%	Quantity	NTP	Resolution	Symmetry Factor	Warning
1	Unknown	11	29.643	19011155	249703	97.854	97.599	N/A	3930	2.944	2.425	
2	Unknown	11	35.160	416914	6144	2.146	2.401	N/A	5679	N/A	1.342	

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



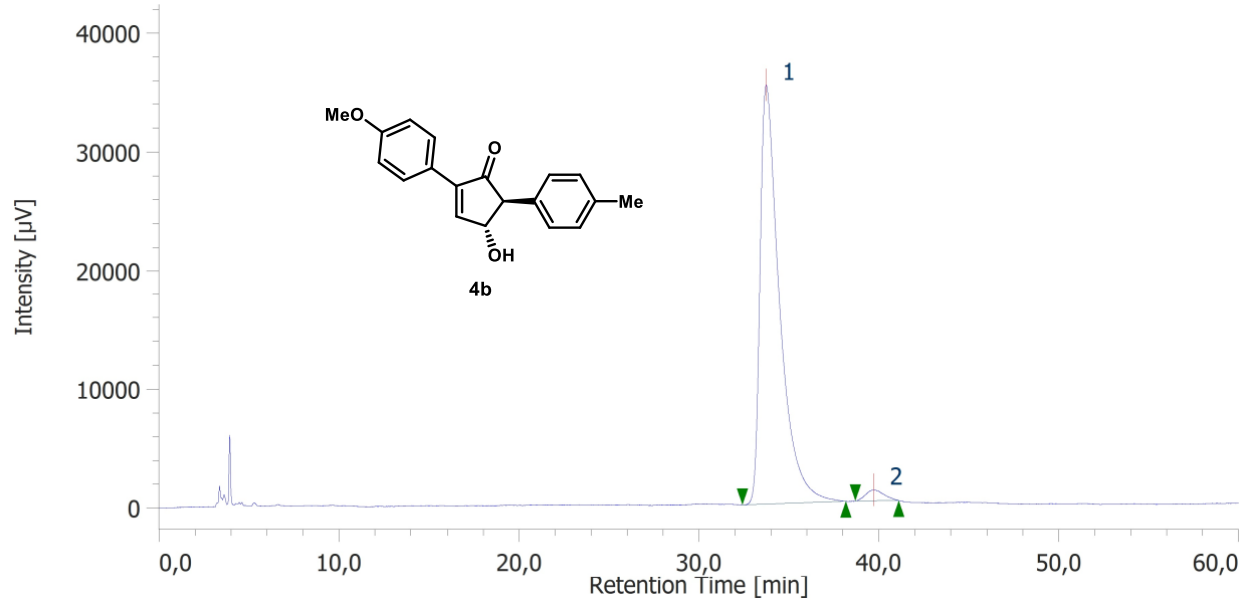
^{13}C-NMR
(100 MHz, $CDCl_3$)



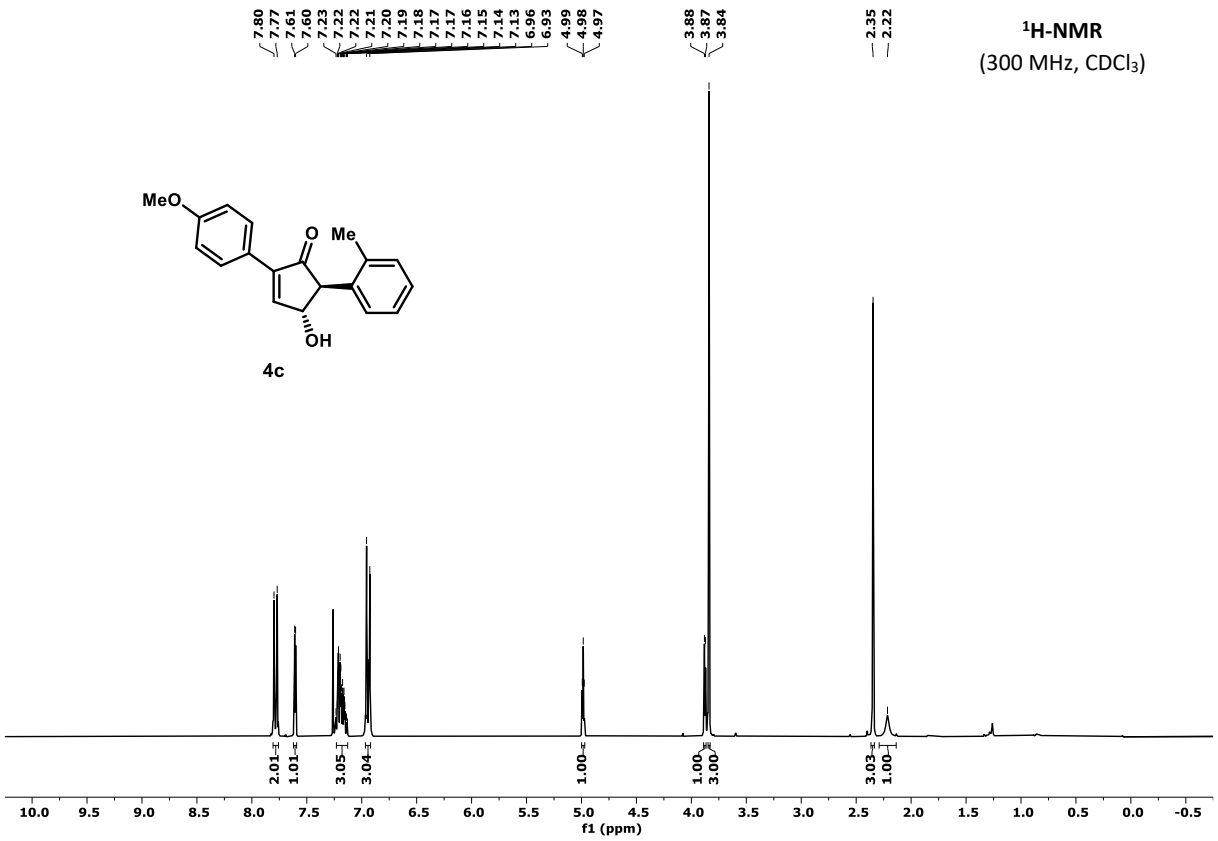


#	Peak Name	CH	tR [min]	Area [μV·sec]	Height [μV]	Area%	Height%	Quantity	NTP	Resolution	Symmetry Factor	Warning
1	Unknown	10	33,717	3324523	43990	50,292	51,771	N/A	5330	2,851	2,116	
2	Unknown	10	39,150	3285983	40980	49,708	48,229	N/A	6289	N/A	1,944	

Daicel Chiralpak IB column (90:10 *n*-Hexane/*i*-PrOH, 1.0 mL/min, 230 nm)

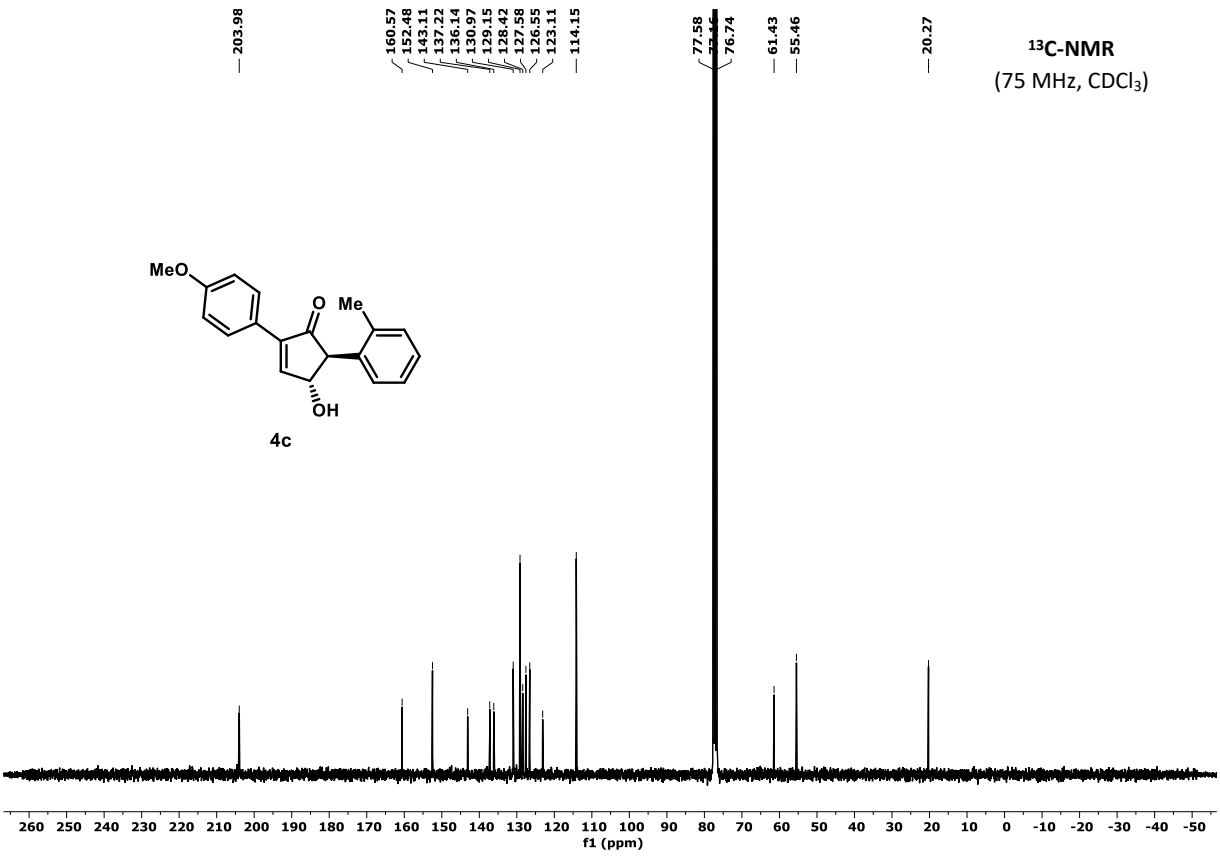


#	Peak Name	CH	tR [min]	Area [μV·sec]	Height [μV]	Area%	Height%	Quantity	NTP	Resolution	Symmetry Factor	Warning
1	Unknown	10	33,723	2657286	35284	97,619	97,489	N/A	5404	3,172	2,070	
2	Unknown	10	39,693	64817	909	2,381	2,511	N/A	6706	N/A	1,233	



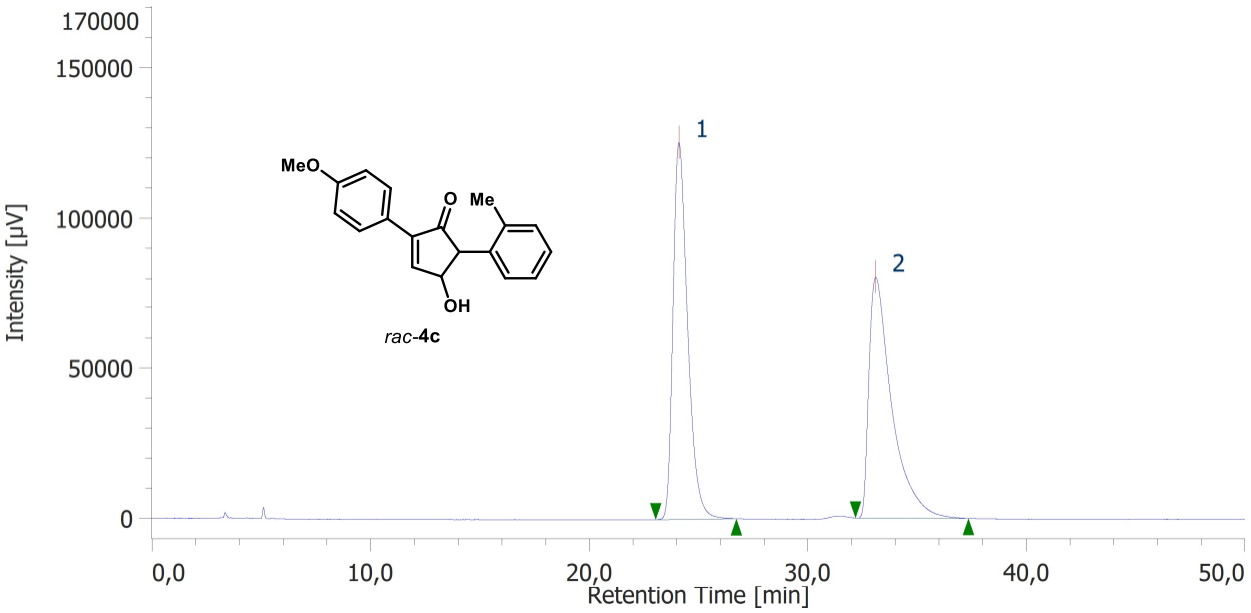
^{1}H-NMR
(300 MHz, $CDCl_3$)

4c



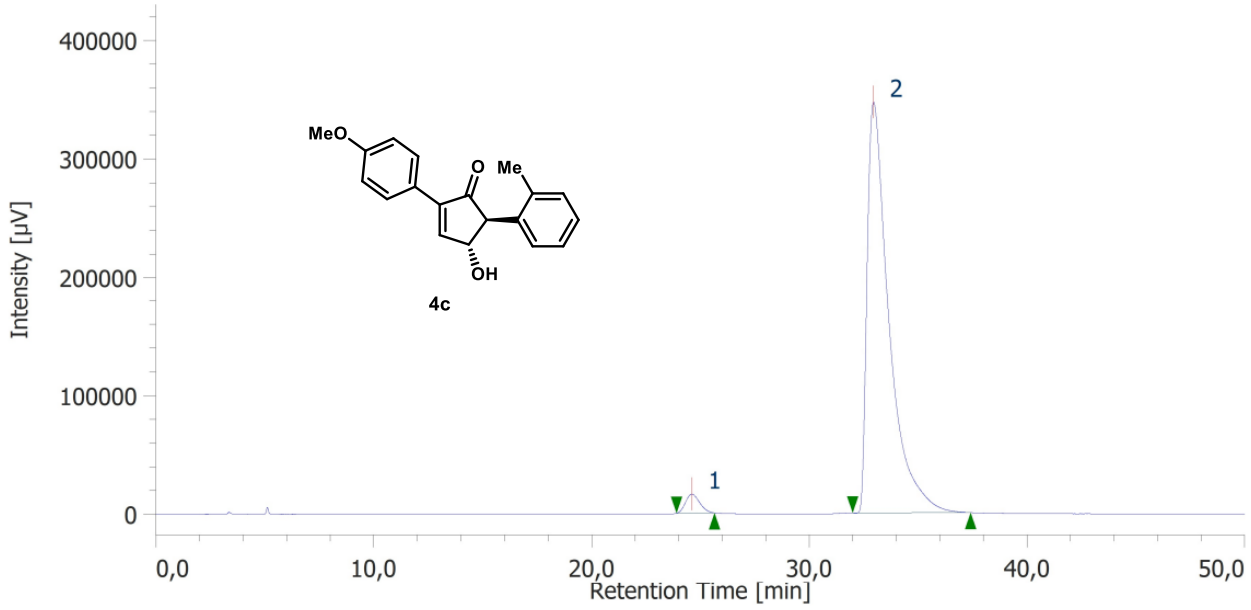
^{13}C-NMR
(75 MHz, $CDCl_3$)

4c

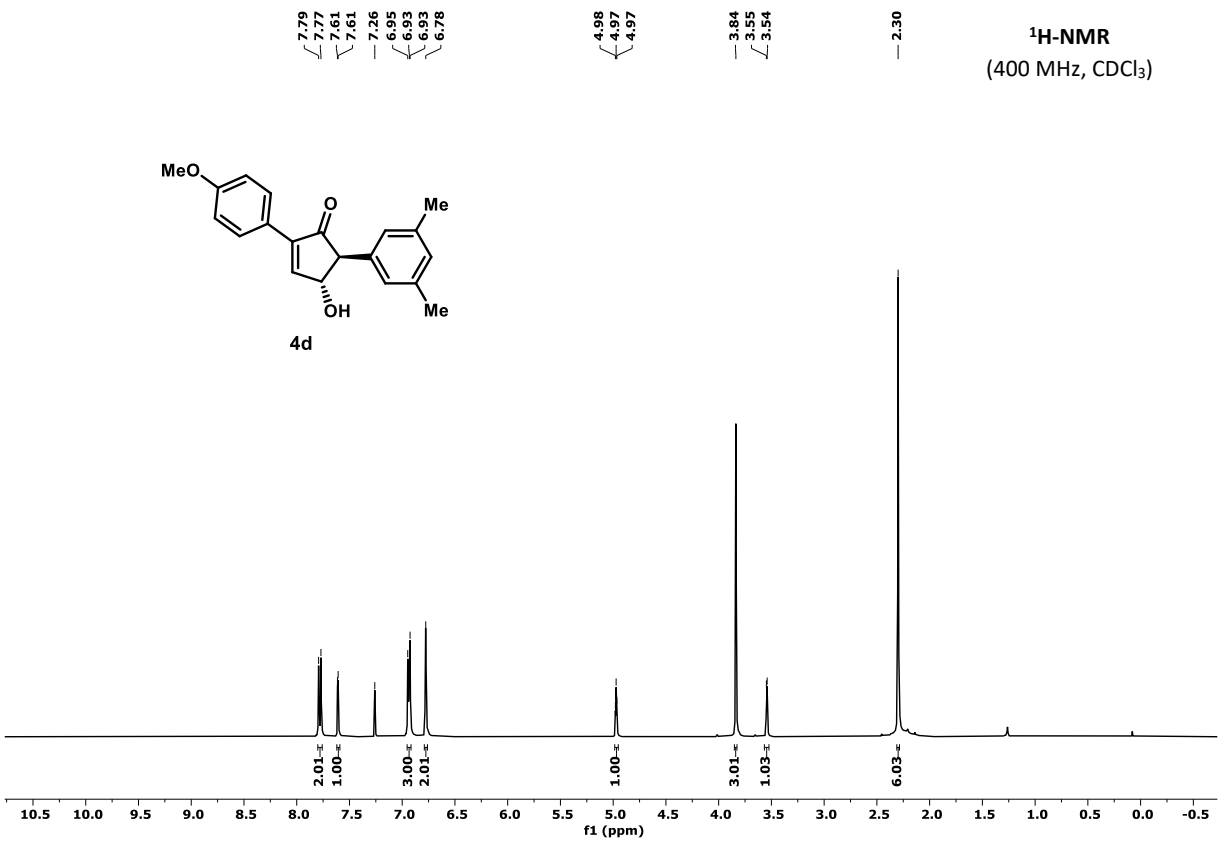


#	Peak Name	CH	tR [min]	Area [μV·sec]	Height [μV]	Area%	Height%	Quantity	NTP	Resolution	Symmetry Factor	Warning
1	Unknown	11	24,093	5821895	125410	50,031	60,931	N/A	6548	6,152	1,415	
2	Unknown	11	33,097	5814681	80414	49,969	39,069	N/A	5764	N/A	2,399	

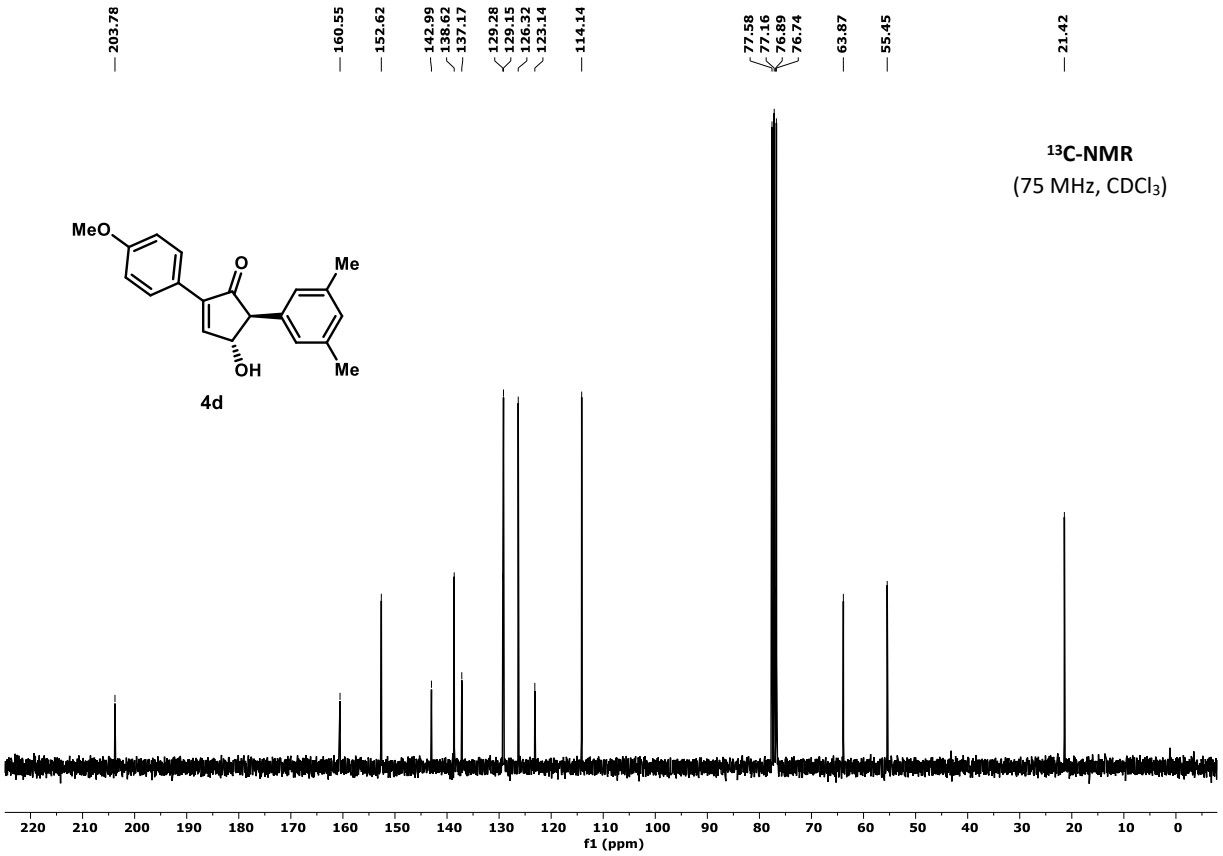
Daicel Chiralpak IC column (90:10 *n*-Hexane/*i*-PrOH, 1.0 mL/min, 232 nm)



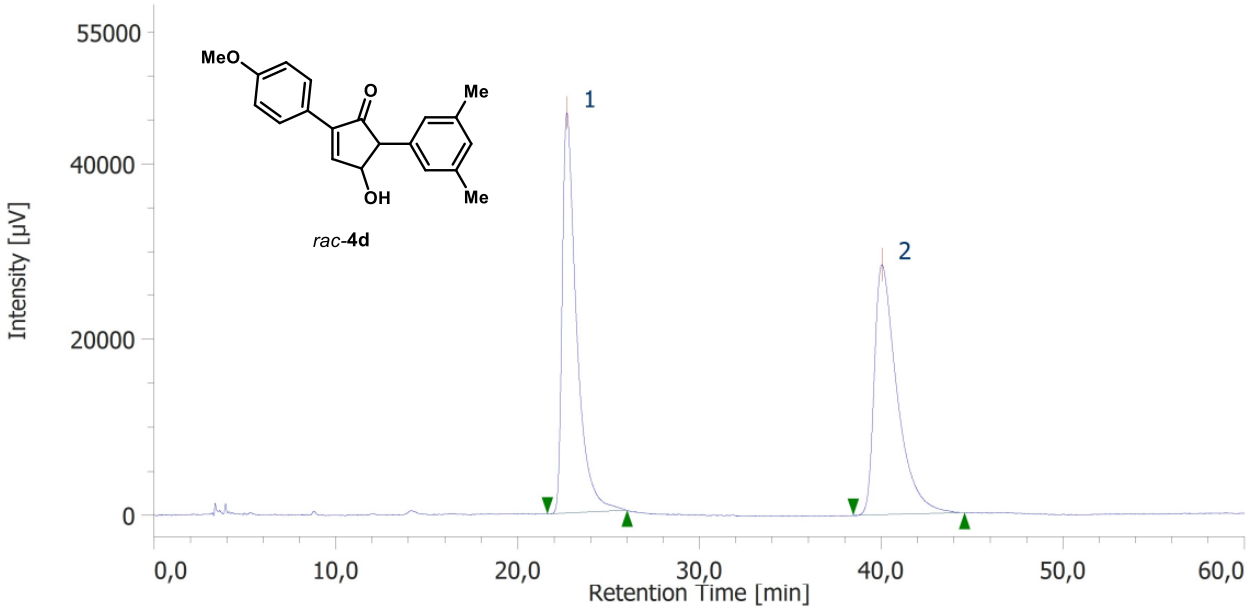
#	Peak Name	CH	tR [min]	Area [μV·sec]	Height [μV]	Area%	Height%	Quantity	NTP	Resolution	Symmetry Factor	Warning
1	Unknown	11	24,597	716462	15955	2,882	4,400	N/A	6703	5,802	1,208	
2	Unknown	11	32,947	24144232	346672	97,118	95,600	N/A	6121	N/A	2,529	



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

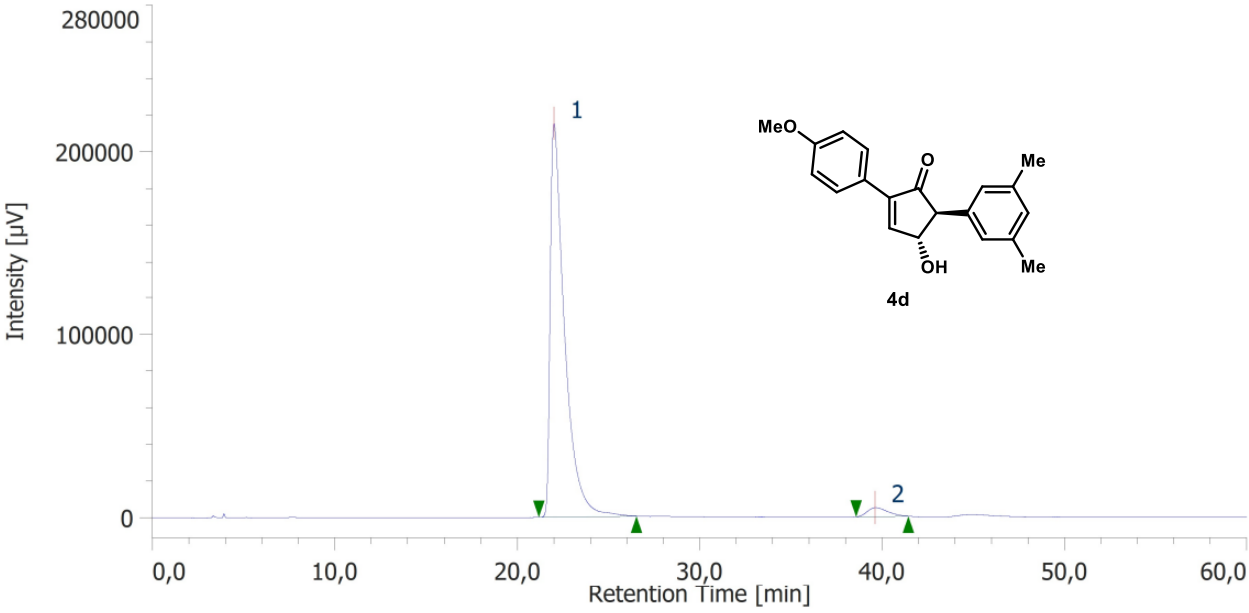


^{13}C-NMR
(75 MHz, $CDCl_3$)



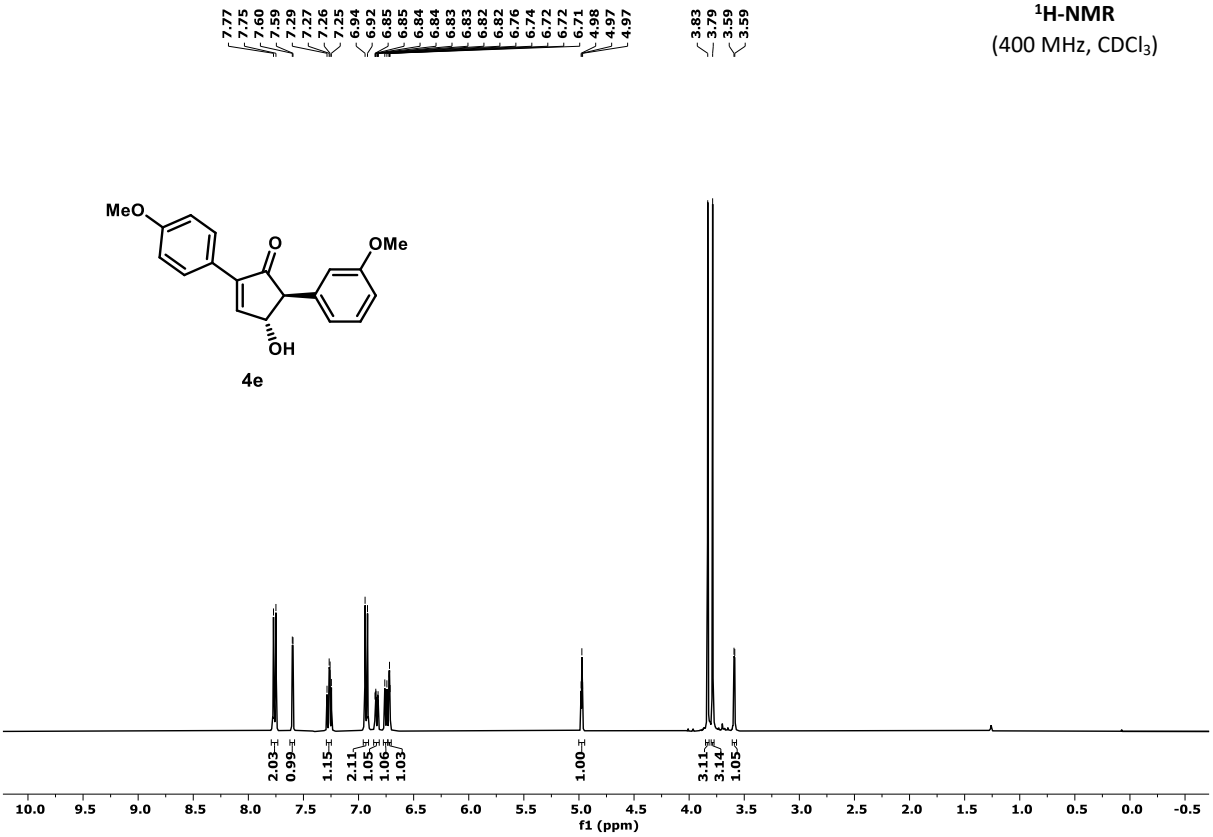
#	Peak Name	CH	tR [min]	Area [μV·sec]	Height [μV]	Area%	Height%	Quantity	NTP	Resolution	Symmetry Factor	Warning
1	Unknown	11	22,693	2484767	45541	50,091	61,486	N/A	4747	10,044	2,018	
2	Unknown	11	40,037	2475707	28526	49,909	38,514	N/A	5574	N/A	1,873	

Daicel Chiralpak IB column (90:10 *n*-Hexane/*i*-PrOH, 1.0 mL/min, 240 nm)

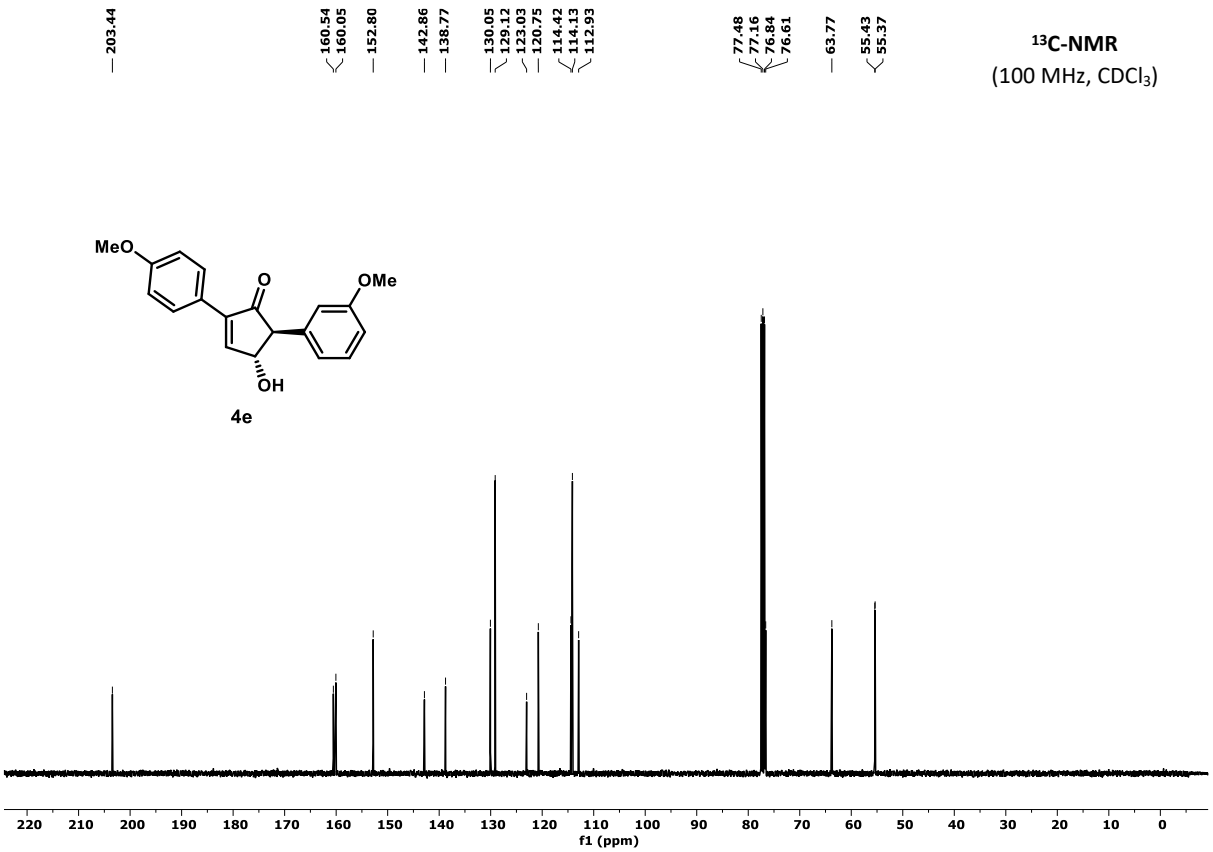


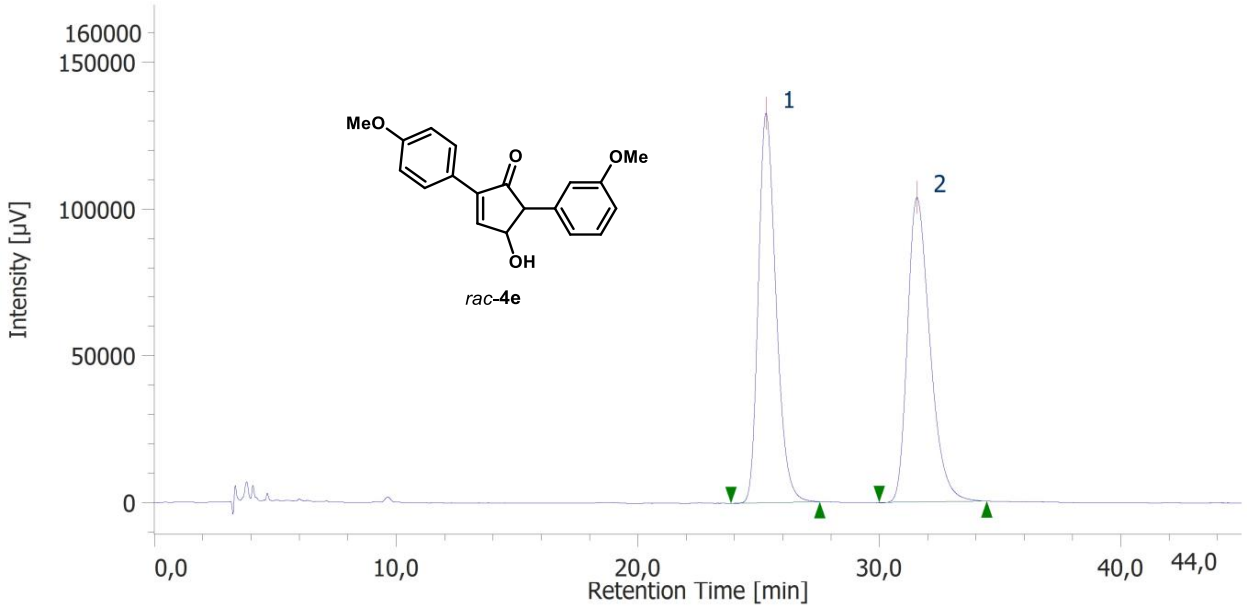
#	Peak Name	CH	tR [min]	Area [μV·sec]	Height [μV]	Area%	Height%	Quantity	NTP	Resolution	Symmetry Factor	Warning
1	Unknown	11	22,003	11754996	215015	96,890	97,791	N/A	4488	10,393	2,556	
2	Unknown	11	39,610	377259	4856	3,110	2,209	N/A	5784	N/A	1,376	

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



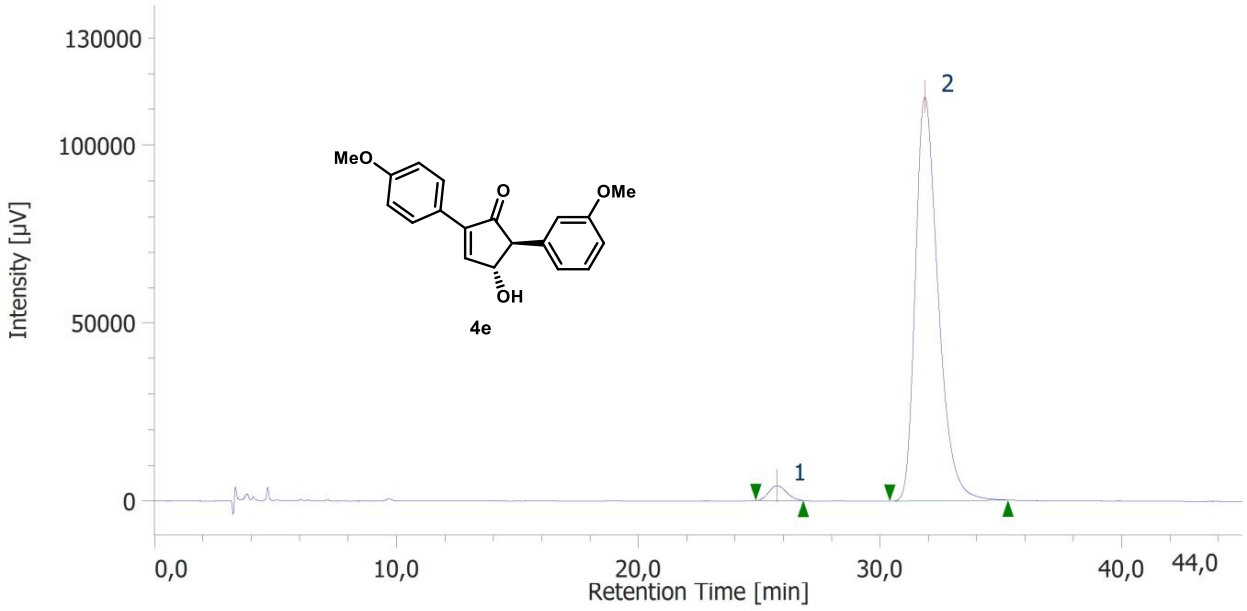
^{13}C-NMR
(100 MHz, $CDCl_3$)





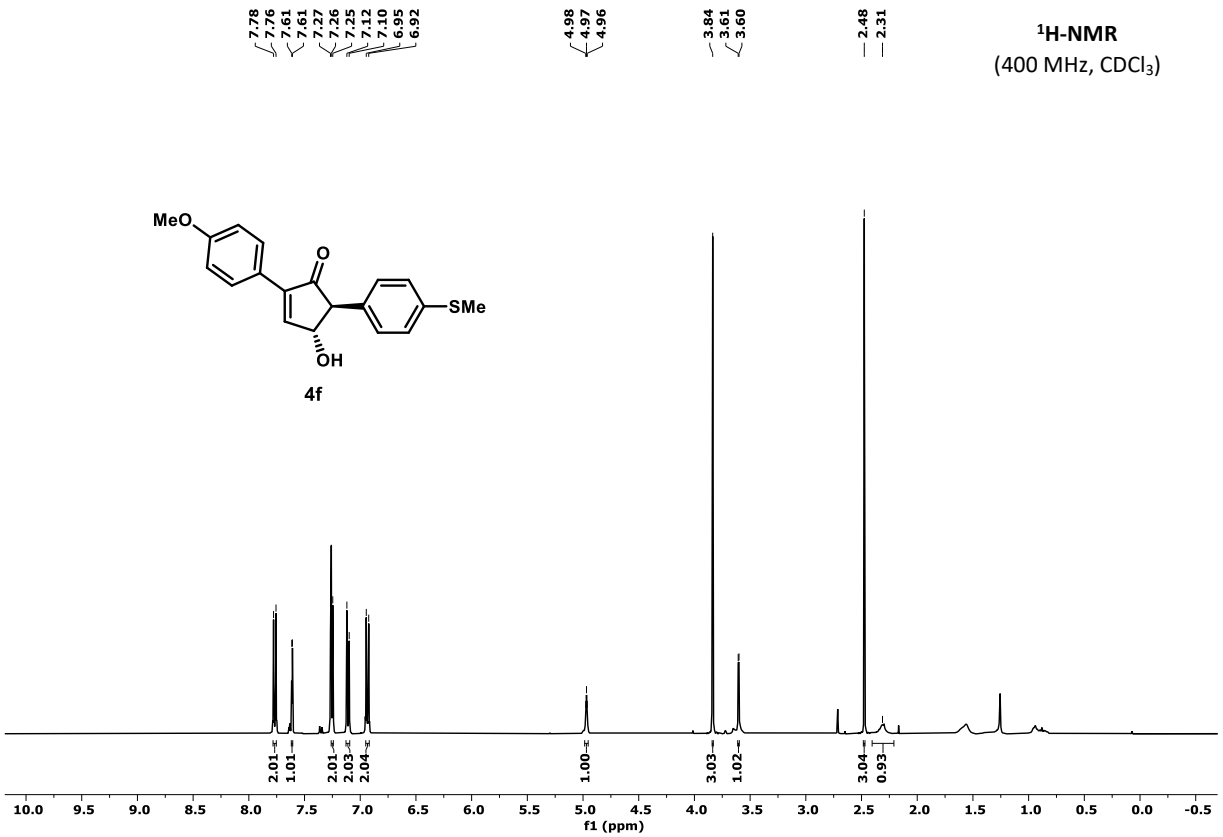
#	Peak Name	CH	tR [min]	Area [μV·sec]	Height [μV]	Area%	Height%	Quantity	NTP	Resolution	Symmetry Factor	Warning
1	Unknown	10	25,300	6724414	132551	50,039	56,088	N/A	5906	4,196	1,275	
2	Unknown	10	31,550	6713976	103776	49,961	43,912	N/A	5712	N/A	1,347	

Daicel Chiralpak IC column (80:20 *n*-Hexane/*i*-PrOH, 1.0 mL/min, 230 nm)

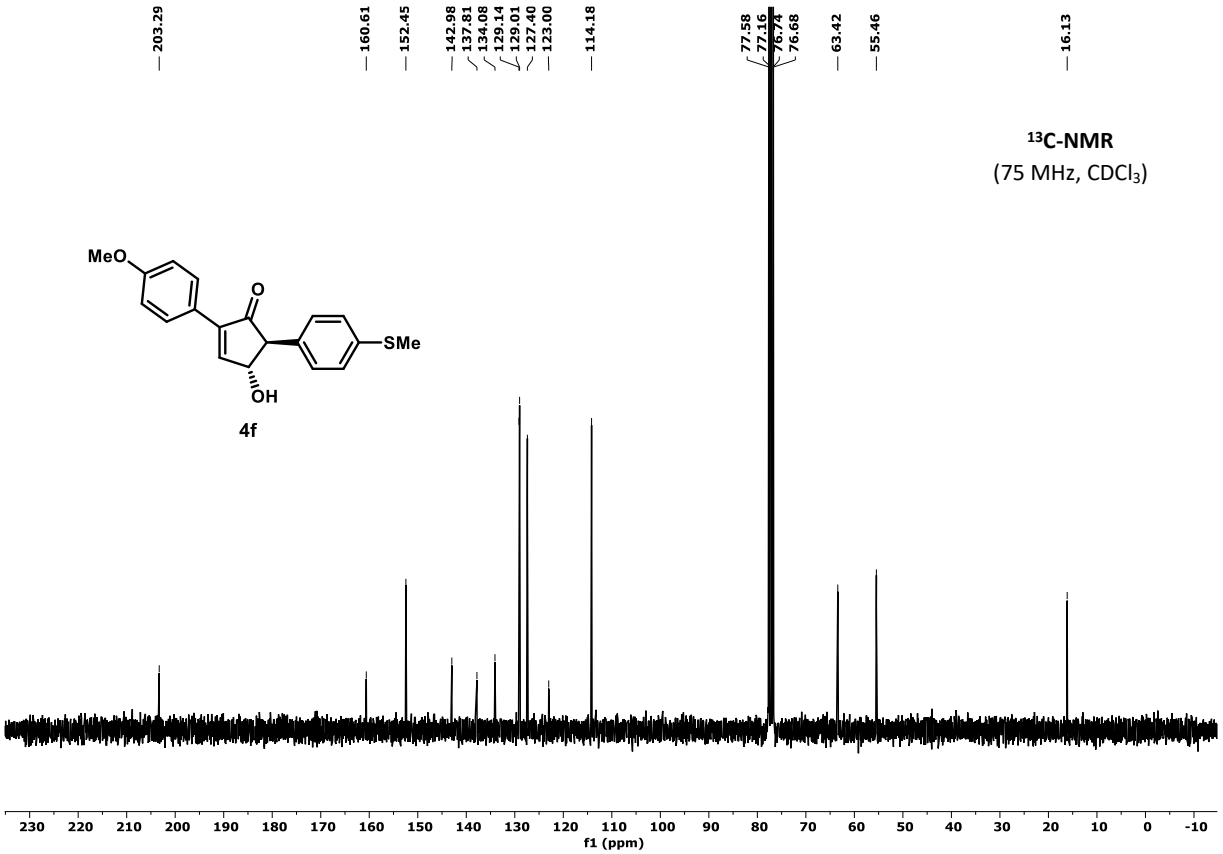


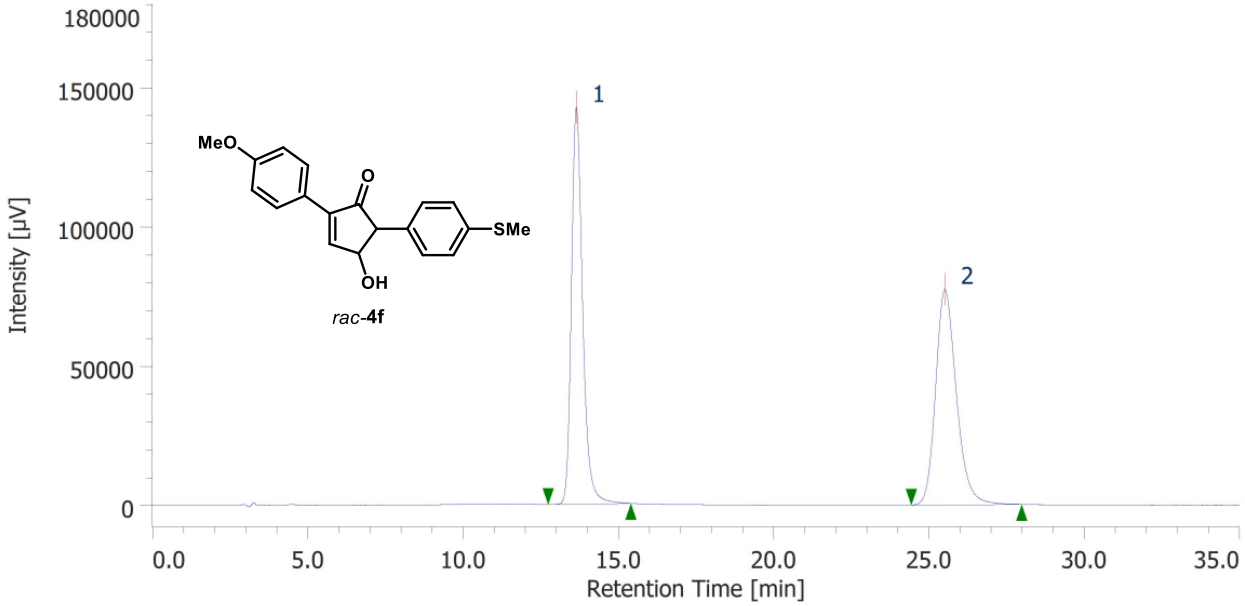
#	Peak Name	CH	tR [min]	Area [μV·sec]	Height [μV]	Area%	Height%	Quantity	NTP	Resolution	Symmetry Factor	Warning
1	Unknown	10	25,727	210552	4179	2,764	3,555	N/A	5813	4,054	1,137	
2	Unknown	10	31,847	7407402	113385	97,236	96,445	N/A	5764	N/A	1,369	

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



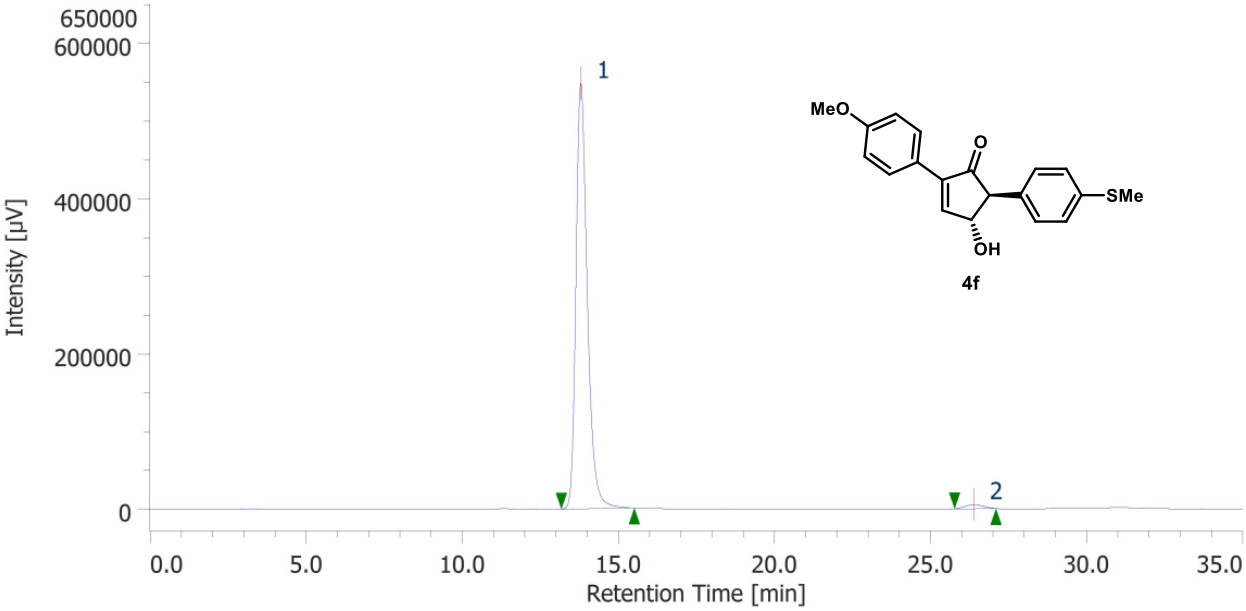
^{13}C-NMR
(75 MHz, $CDCl_3$)



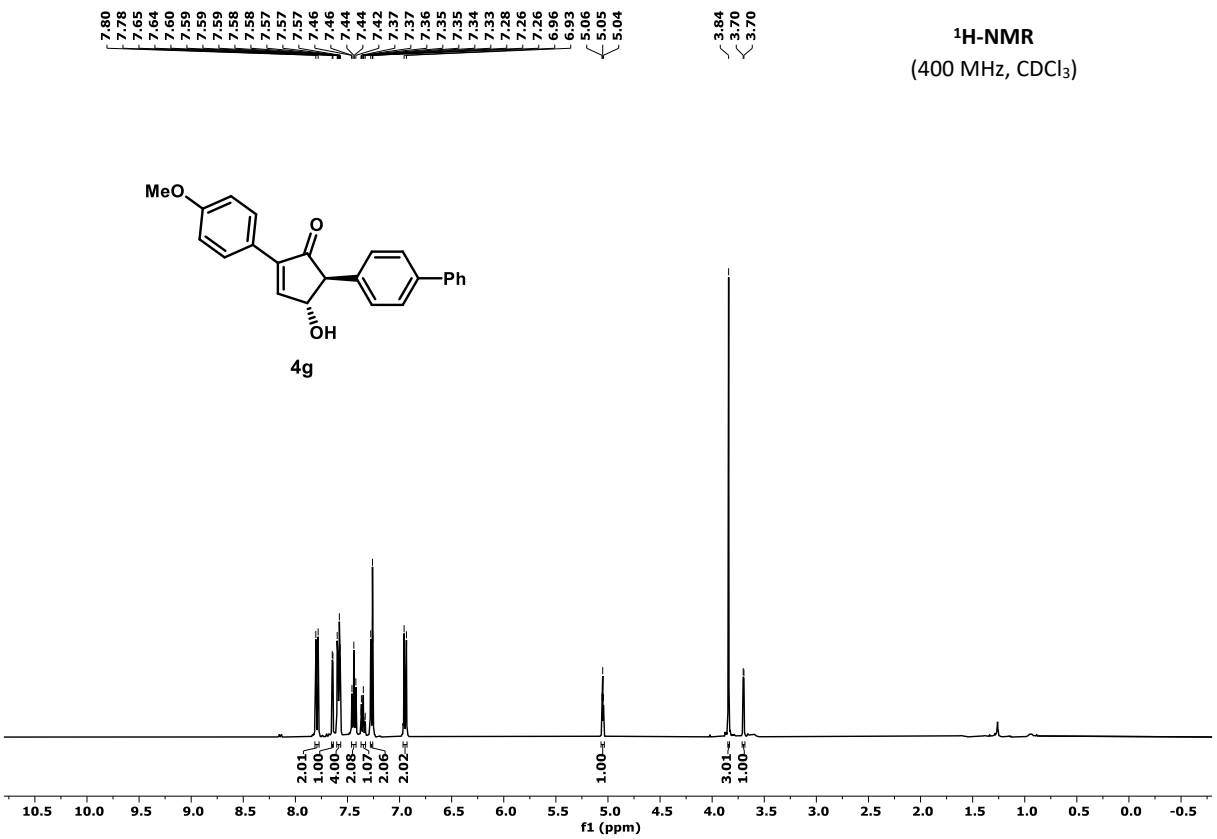


#	Peak Name	CH	tR [min]	Area [μV·sec]	Height [μV]	Area%	Height%	Quantity	NTP	Resolution	Symmetry Factor	Warning
1	Unknown	11	13.640	3559738	142469	49.750	64.798	N/A	7575	13.130	1.287	
2	Unknown	11	25.507	3595545	77398	50.250	35.202	N/A	7407	N/A	1.232	

Daicel Chiralpak IA column (70:30 *n*-Hexane/*i*-PrOH, 1.0 mL/min, 254 nm)

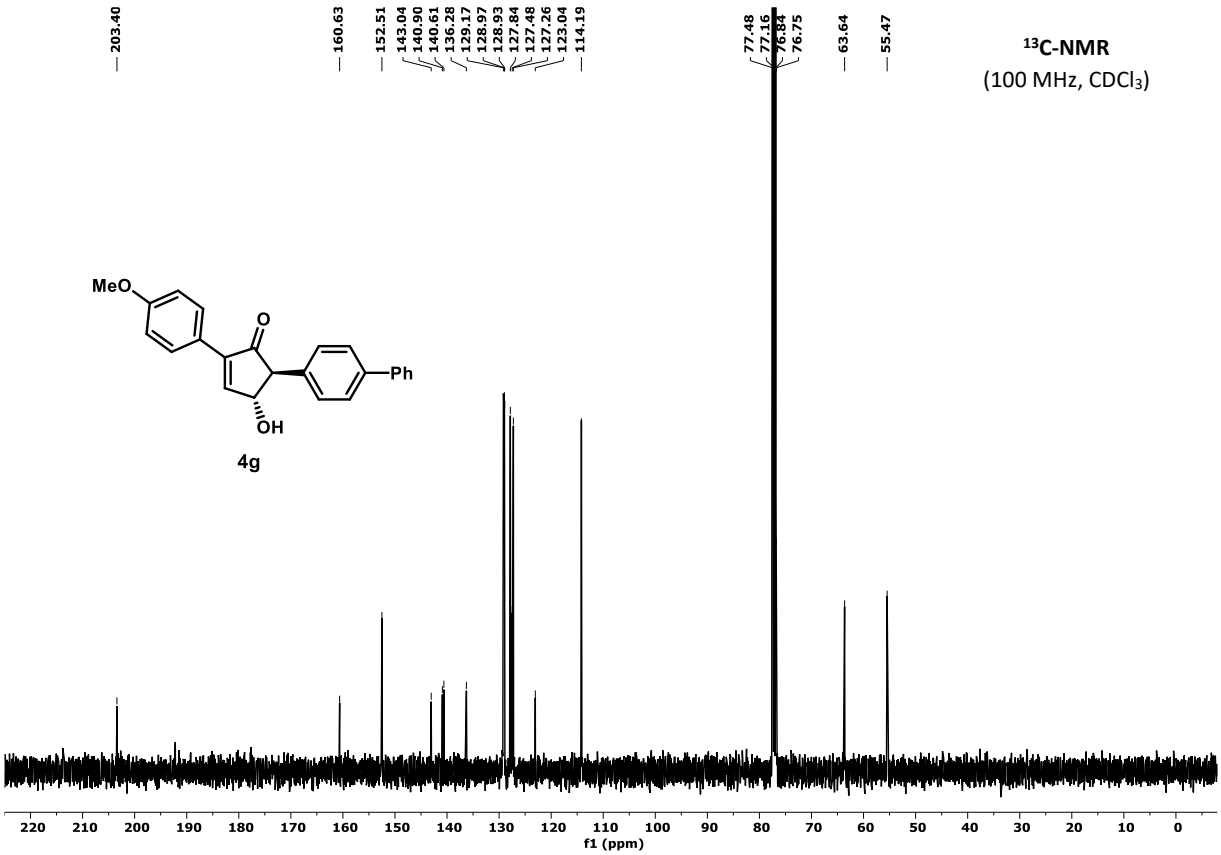


#	Peak Name	CH	tR [min]	Area [μV·sec]	Height [μV]	Area%	Height%	Quantity	NTP	Resolution	Symmetry Factor	Warning
1	Unknown	11	13.793	13803853	547794	98.486	99.064	N/A	7531	14.203	1.324	
2	Unknown	11	26.377	212241	5178	1.514	0.936	N/A	8552	N/A	1.084	



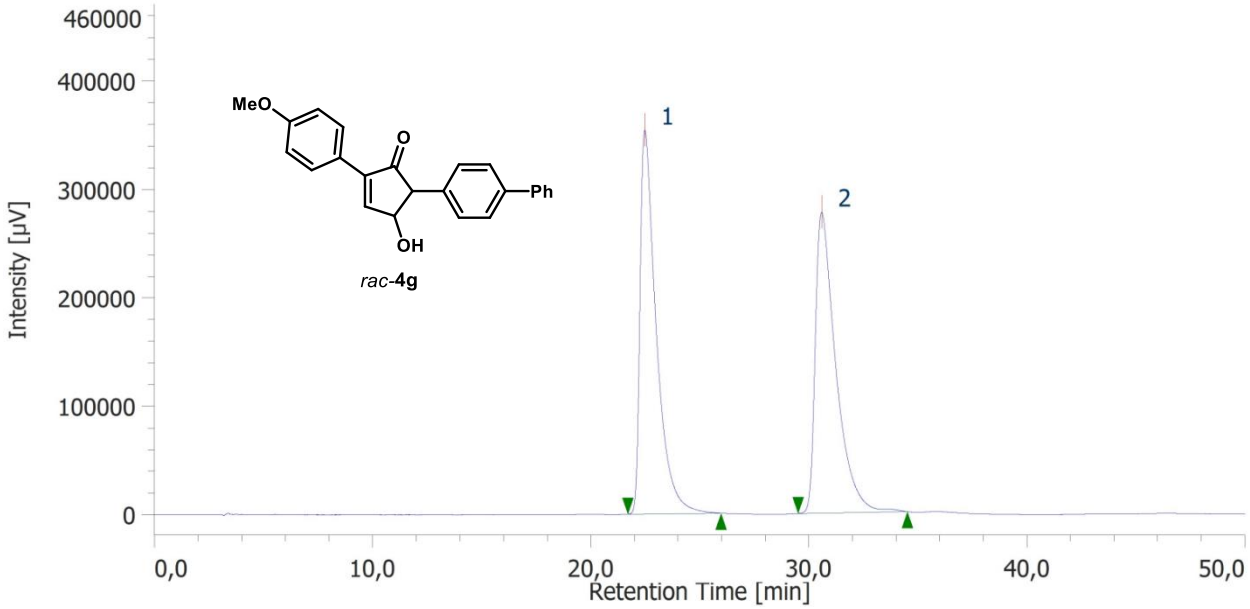
^{1}H-NMR
(400 MHz, $CDCl_3$)

4g



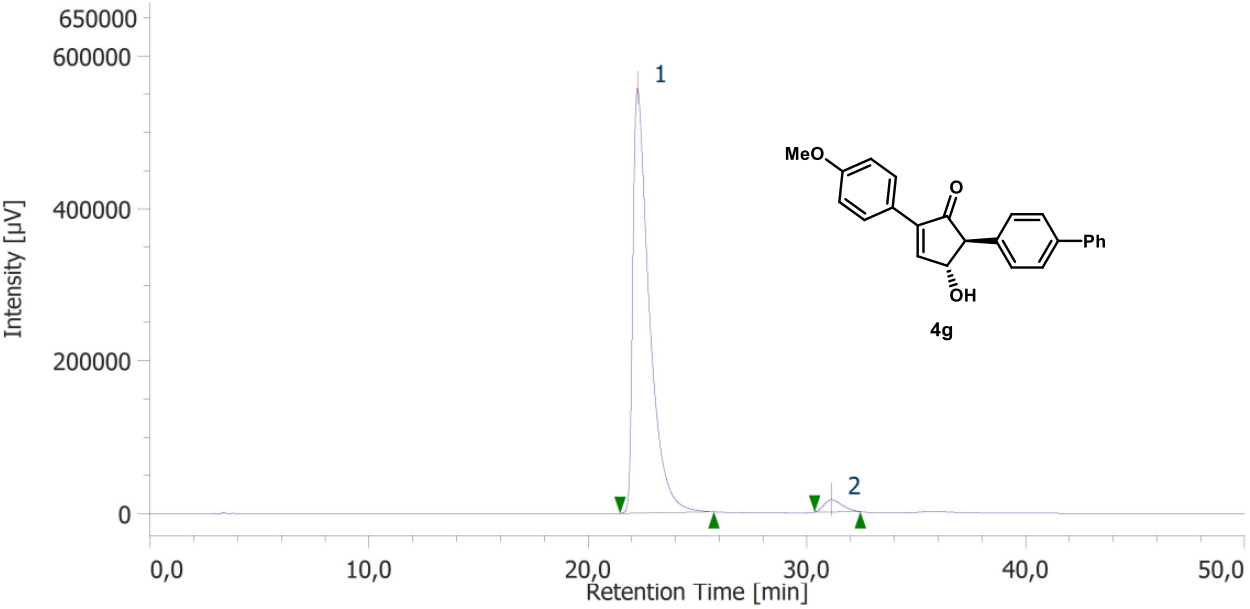
^{13}C-NMR
(100 MHz, $CDCl_3$)

4g



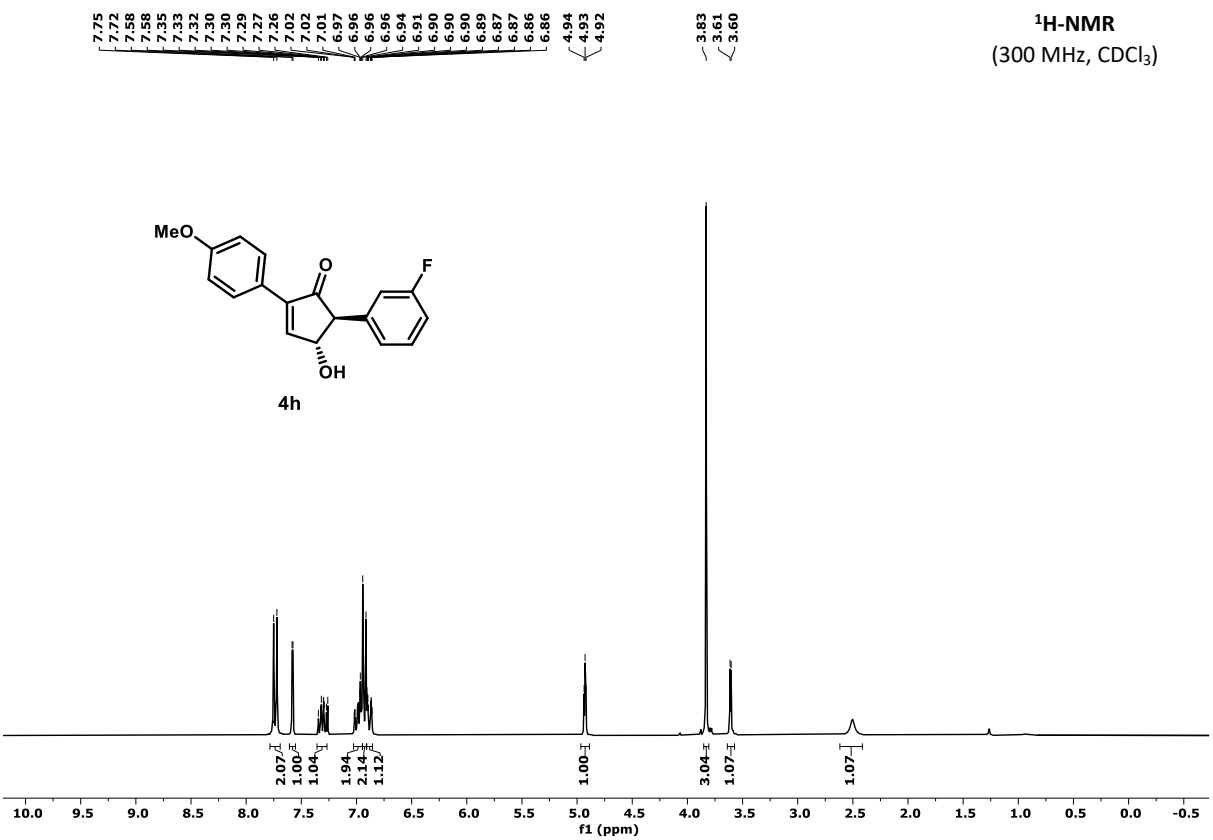
#	Peak Name	CH	tR [min]	Area [μV·sec]	Height [μV]	Area%	Height%	Quantity	NTP	Resolution	Symmetry Factor	Warning
1	Unknown	11	22,470	18267411	354272	50,162	56,027	N/A	5077	5,662	2,201	
2	Unknown	11	30,577	18149675	278046	49,838	43,973	N/A	5774	N/A	2,047	

Daicel Chiralpak IB column (80:20 *n*-Hexane/*i*-PrOH, 1.0 mL/min, 248 nm)



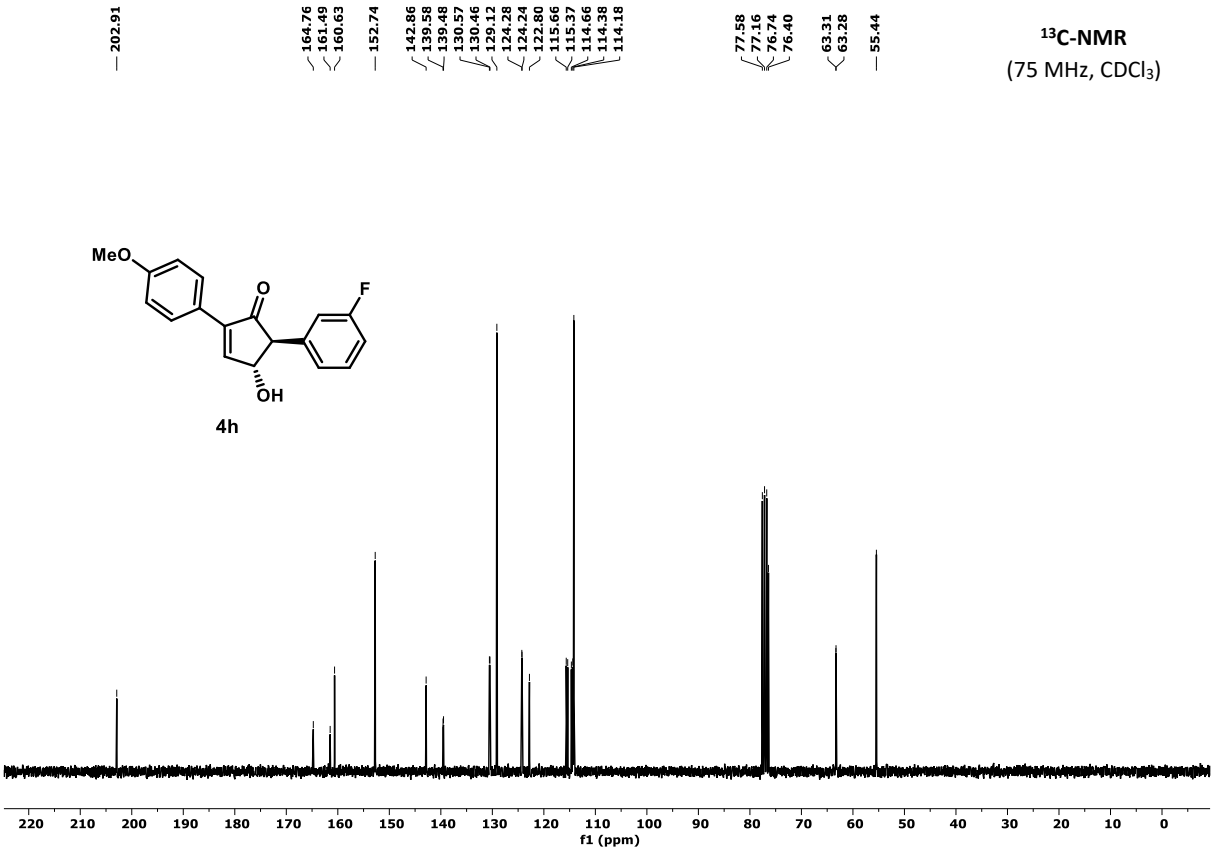
#	Peak Name	CH	tR [min]	Area [μV·sec]	Height [μV]	Area%	Height%	Quantity	NTP	Resolution	Symmetry Factor	Warning
1	Unknown	11	22,253	28851691	557441	96,900	97,232	N/A	4901	6,266	2,351	
2	Unknown	11	31,123	923076	15867	3,100	2,768	N/A	6311	N/A	1,323	

^{1}H-NMR
(300 MHz, $CDCl_3$)

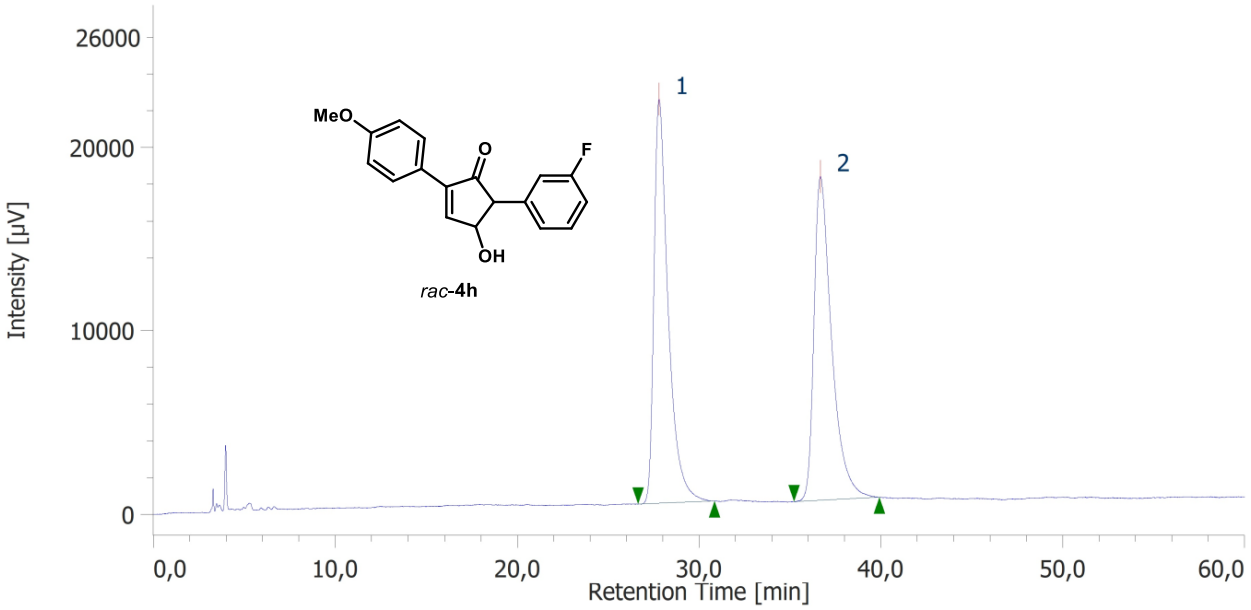


4h

^{13}C-NMR
(75 MHz, $CDCl_3$)

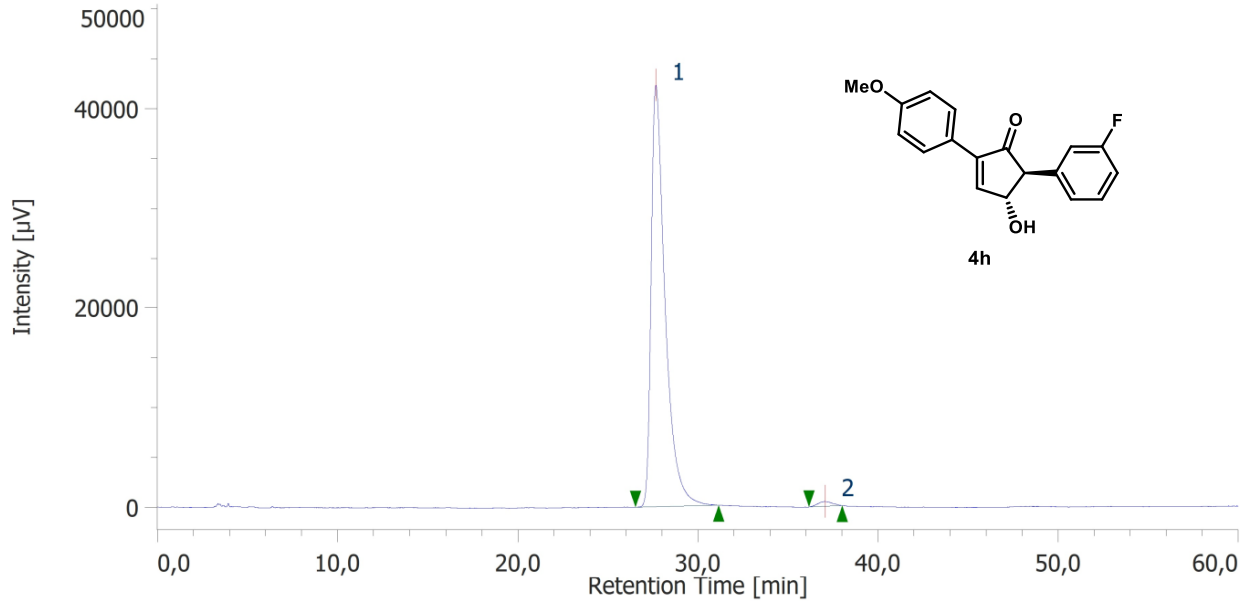


4h



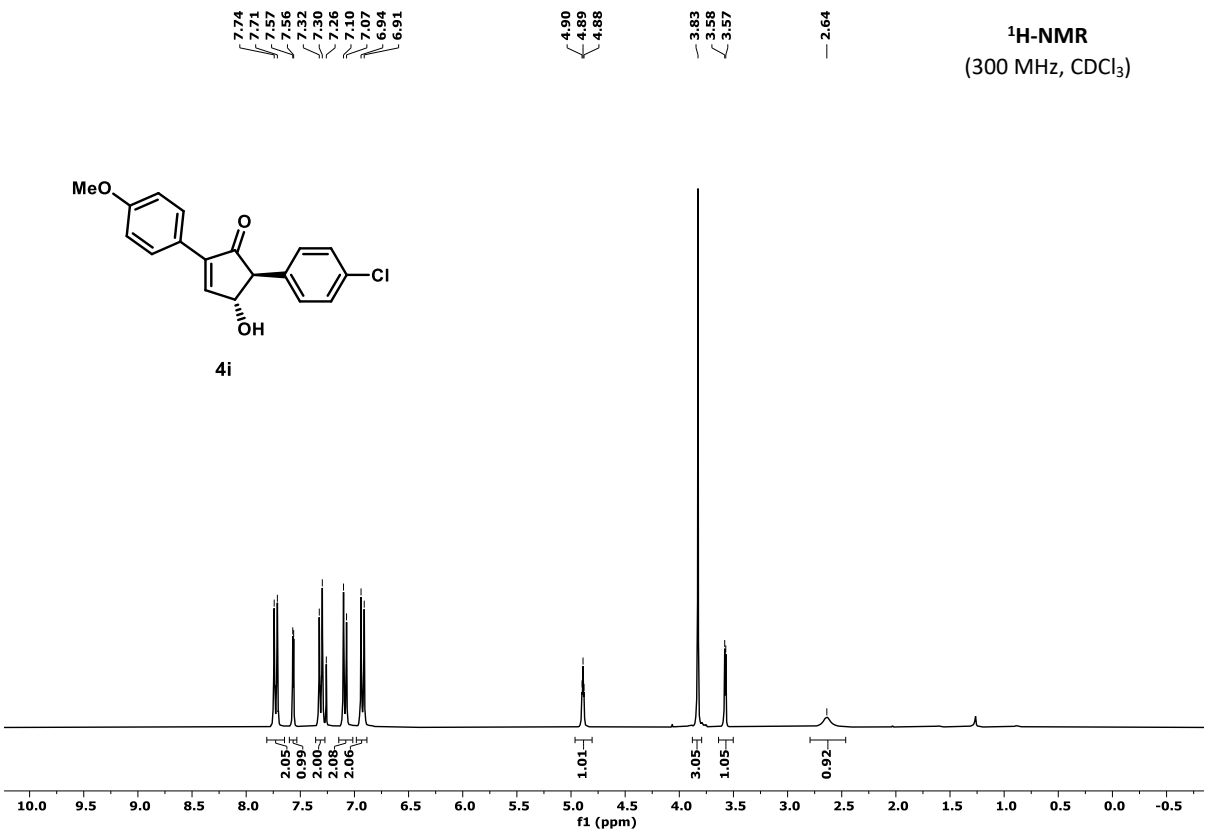
#	Peak Name	CH	tR [min]	Area [μV·sec]	Height [μV]	Area%	Height%	Quantity	NTP	Resolution	Symmetry Factor	Warning
1	Unknown	11	27.790	1191425	22004	50.068	55.509	N/A	6975	5.924	1.724	
2	Unknown	11	36.663	1188207	17637	49.932	44.491	N/A	7687	N/A	1.659	

Daicel Chiralpak IB column (90:10 *n*-Hexane/*i*-PrOH, 1.0 mL/min, 245 nm)

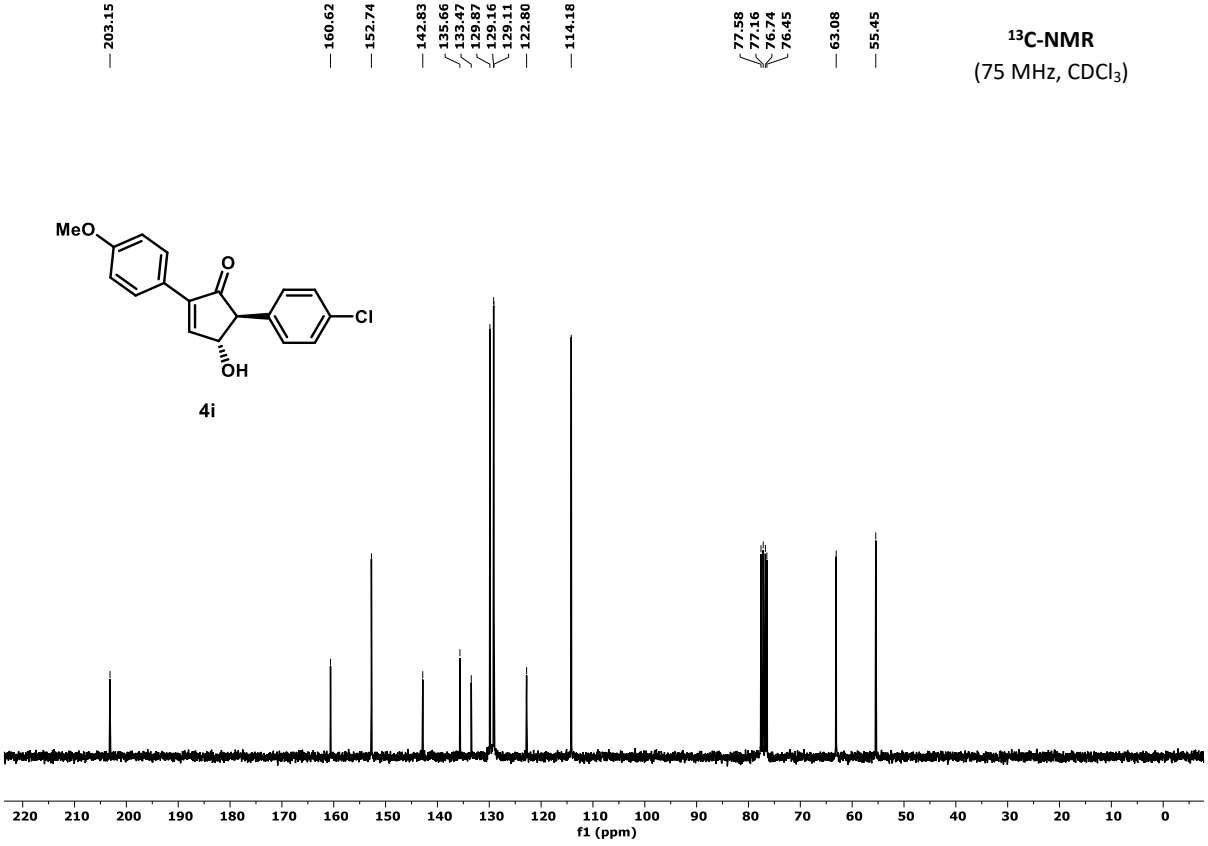


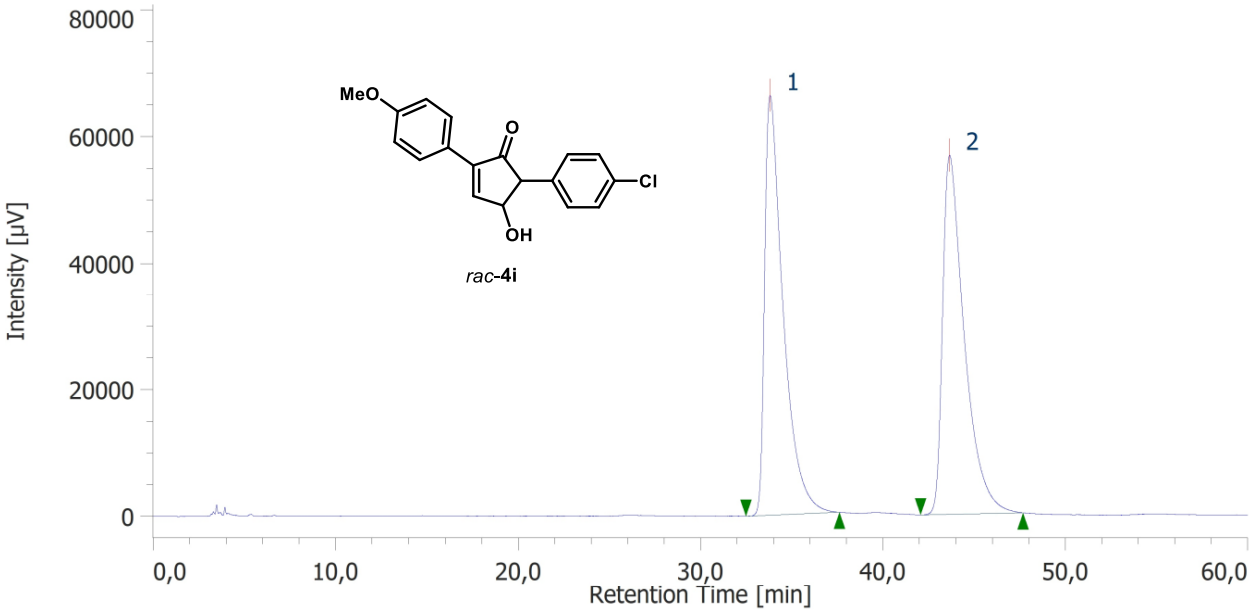
#	Peak Name	CH	tR [min]	Area [μV·sec]	Height [μV]	Area%	Height%	Quantity	NTP	Resolution	Symmetry Factor	Warning
1	Unknown	11	27.657	2278130	42314	98.850	98.900	N/A	7038	6.546	1.842	
2	Unknown	11	37.067	26512	470	1.150	1.100	N/A	8988	N/A	1.017	

^{1}H-NMR
(300 MHz, $CDCl_3$)



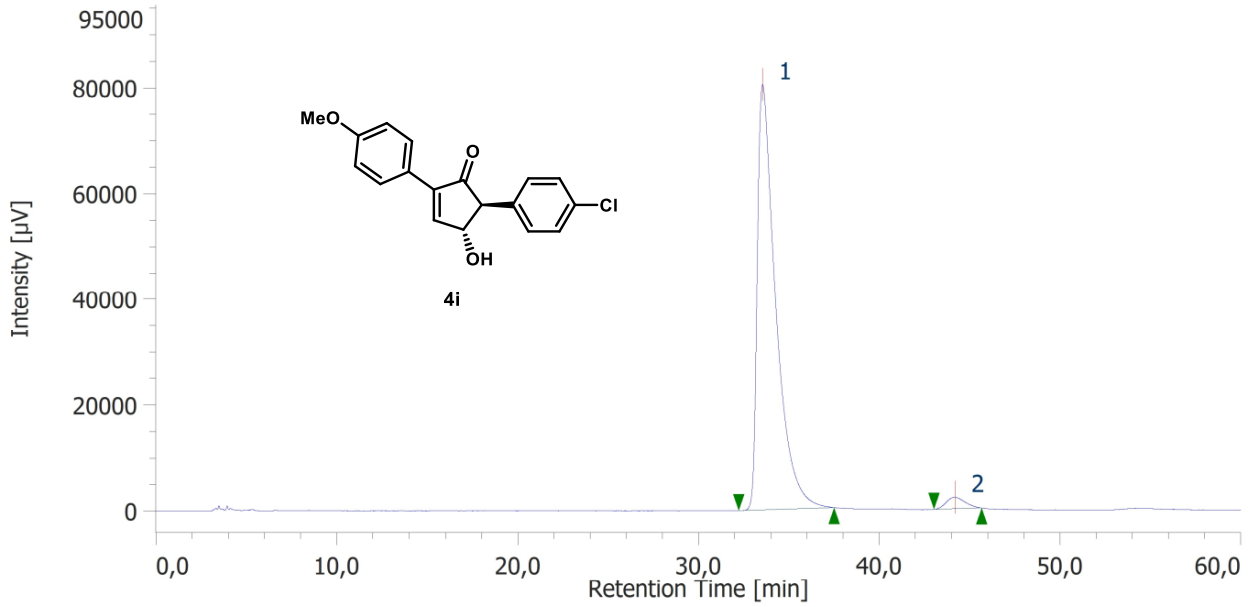
^{13}C-NMR
(75 MHz, $CDCl_3$)





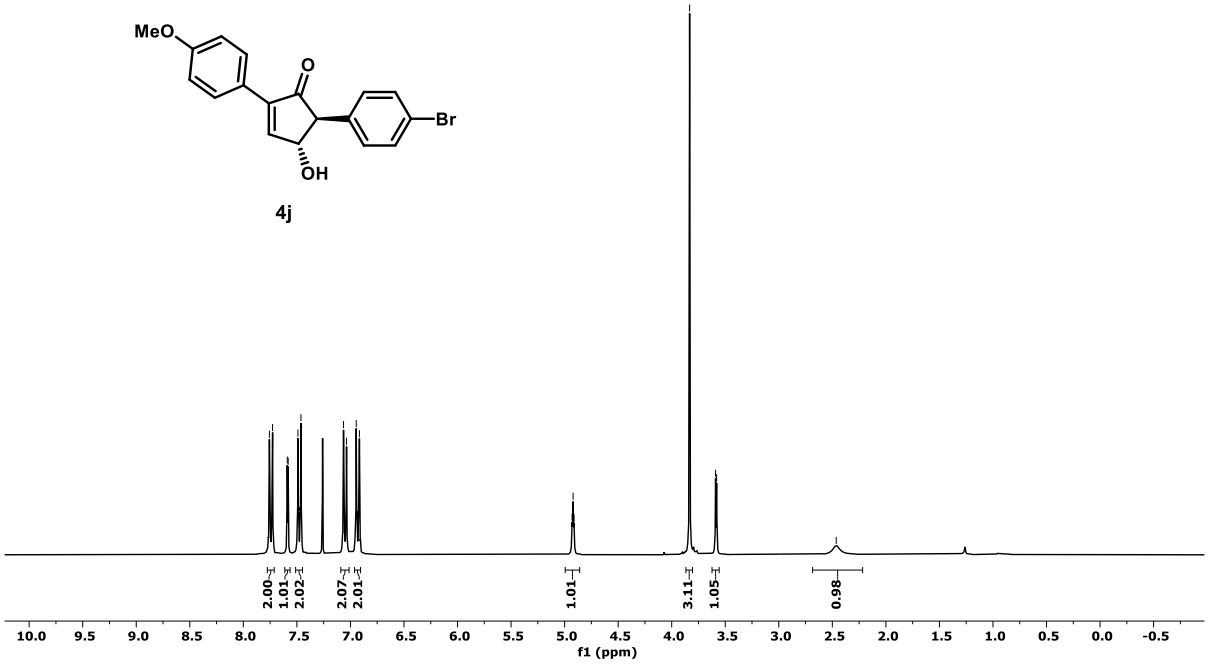
#	Peak Name	CH	tR [min]	Area [μV·sec]	Height [μV]	Area%	Height%	Quantity	NTP	Resolution	Symmetry Factor	Warning
1	Unknown	11	33,803	4673481	66308	49,916	53,904	N/A	6041	5,201	2,216	
2	Unknown	11	43,643	4689244	56702	50,084	46,096	N/A	7221	N/A	1,950	

Daicel Chiralpak IB column (90:10 *n*-Hexane/*i*-PrOH, 1.0 mL/min, 245 nm)

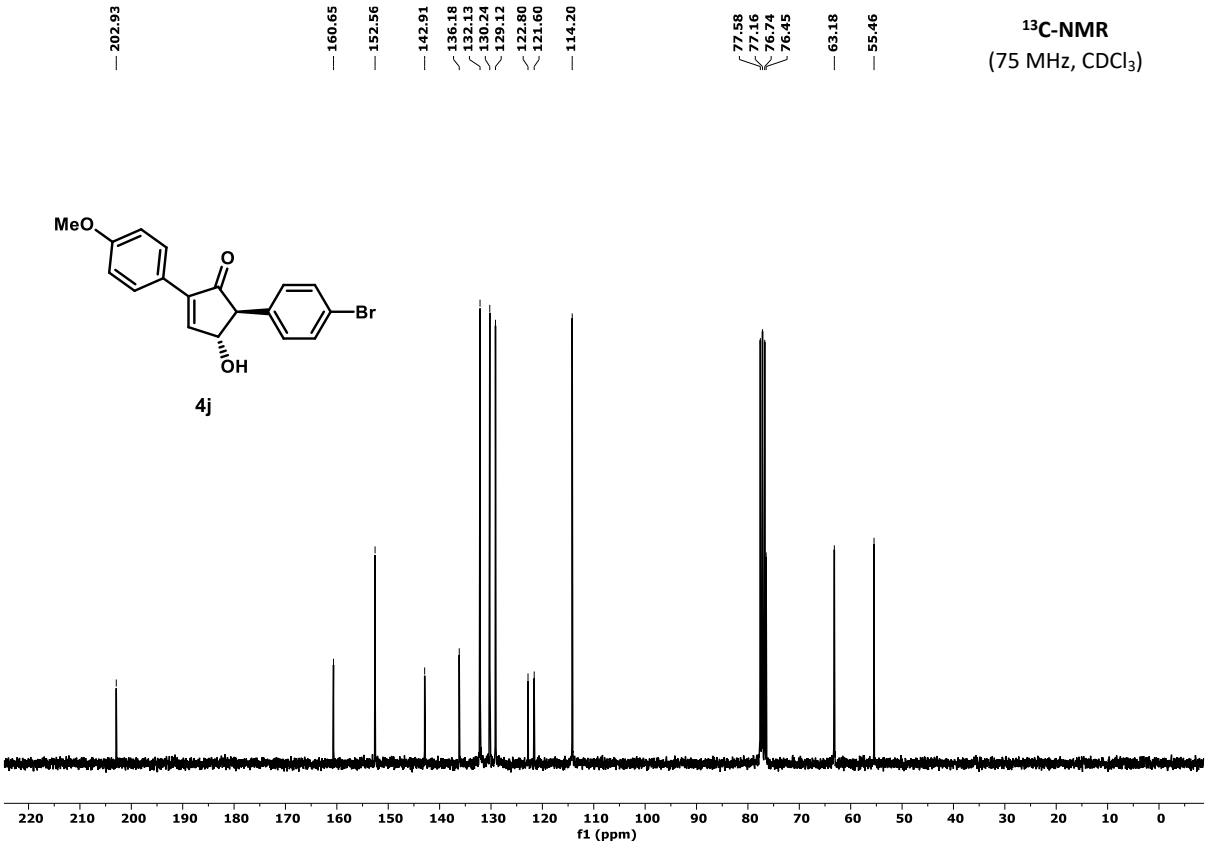


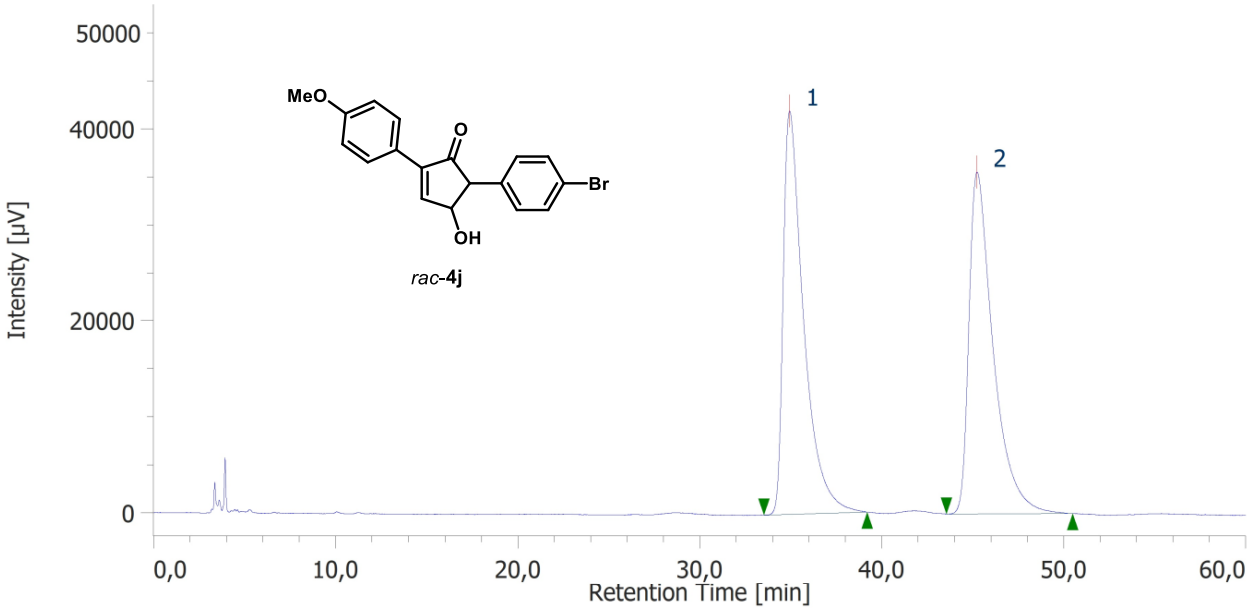
#	Peak Name	CH	tR [min]	Area [μV·sec]	Height [μV]	Area%	Height%	Quantity	NTP	Resolution	Symmetry Factor	Warning
1	Unknown	11	33,533	5672678	80353	97,279	97,378	N/A	5954	5,753	2,298	
2	Unknown	11	44,187	158698	2164	2,721	2,622	N/A	8009	N/A	1,164	

^{1}H-NMR
(300 MHz, $CDCl_3$)



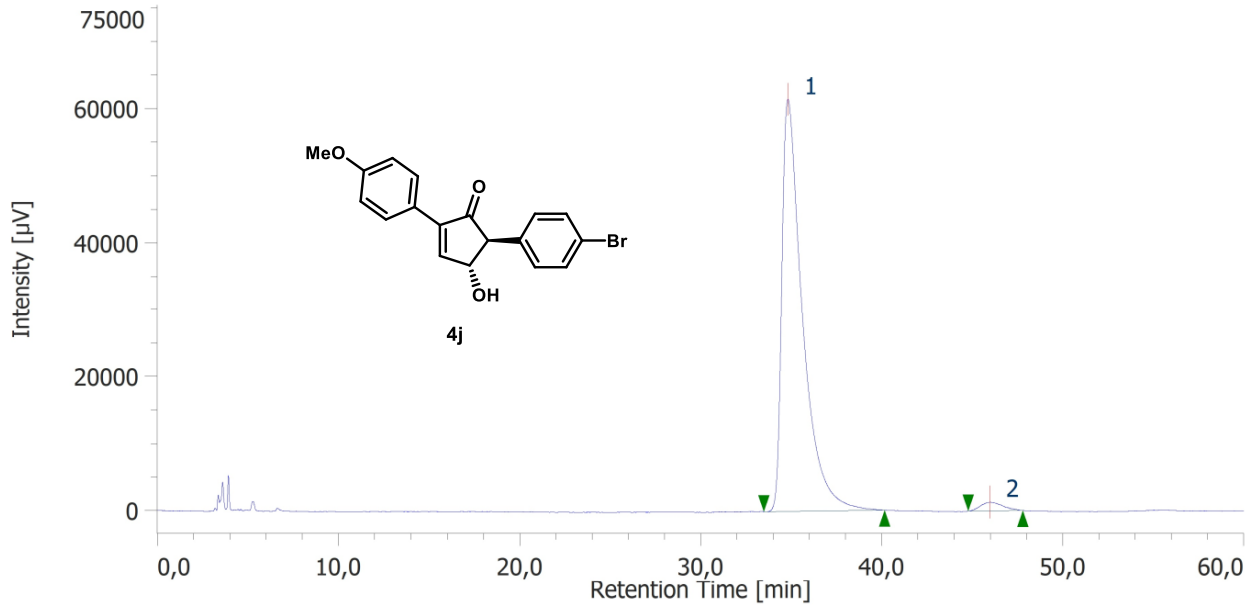
^{13}C-NMR
(75 MHz, $CDCl_3$)



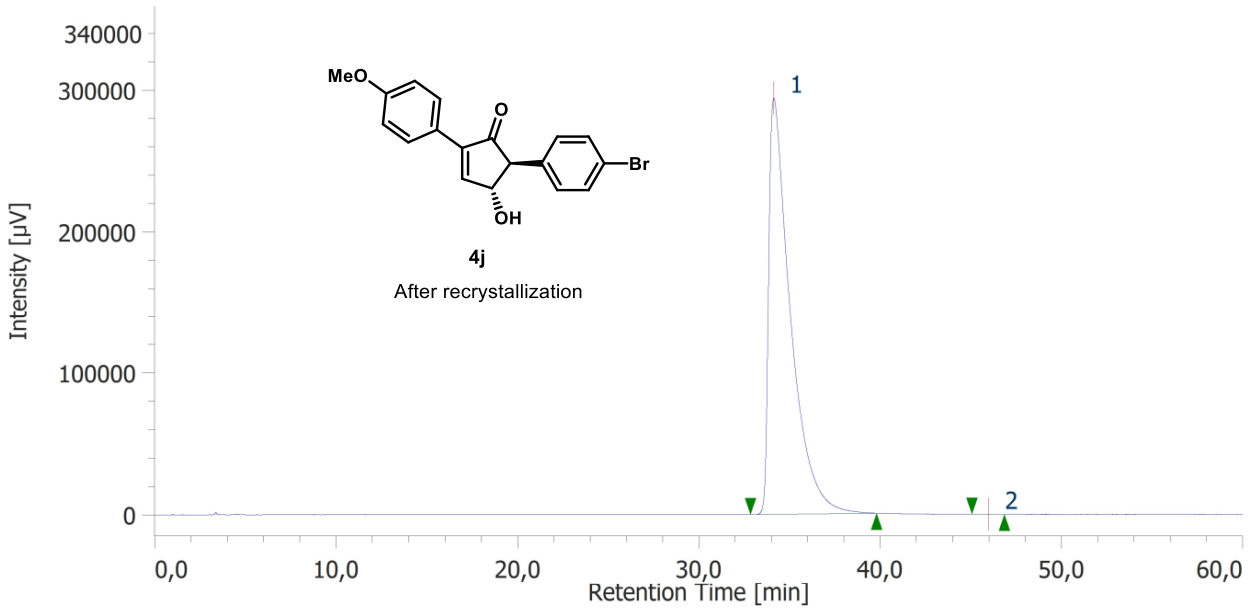


#	Peak Name	CH	tR [min]	Area [μV·sec]	Height [μV]	Area%	Height%	Quantity	NTP	Resolution	Symmetry Factor	Warning
1	Unknown	10	34,930	3277185	42004	49,912	54,109	N/A	5355	4,946	2,075	
2	Unknown	10	45,230	3288782	35624	50,088	45,891	N/A	6368	N/A	1,874	

Daicel Chiralpak IB column (90:10 *n*-Hexane/*i*-PrOH, 1.0 mL/min, 230 nm)

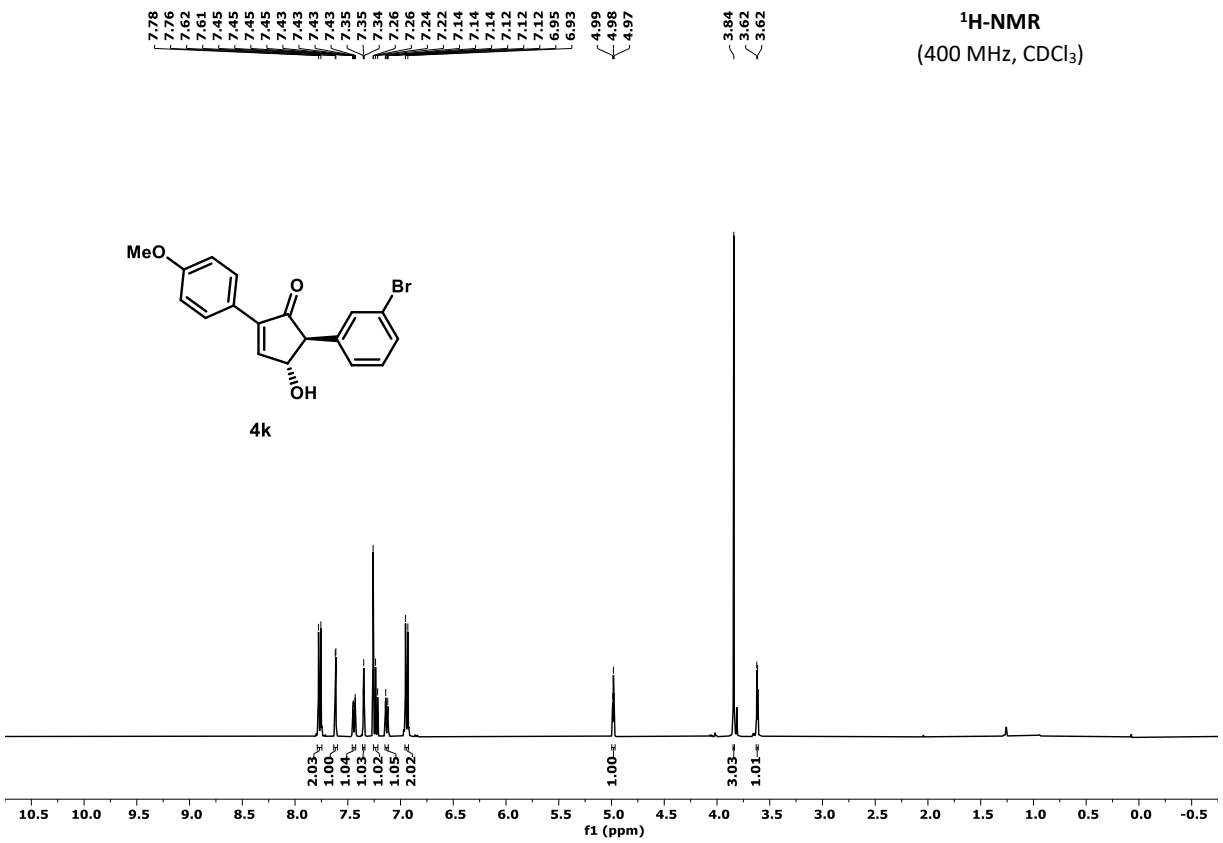


#	Peak Name	CH	tR [min]	Area [μV·sec]	Height [μV]	Area%	Height%	Quantity	NTP	Resolution	Symmetry Factor	Warning
1	Unknown	10	34,810	4864935	61430	97,820	97,969	N/A	5270	5,316	2,229	
2	Unknown	10	45,960	108416	1273	2,180	2,031	N/A	6457	N/A	1,309	

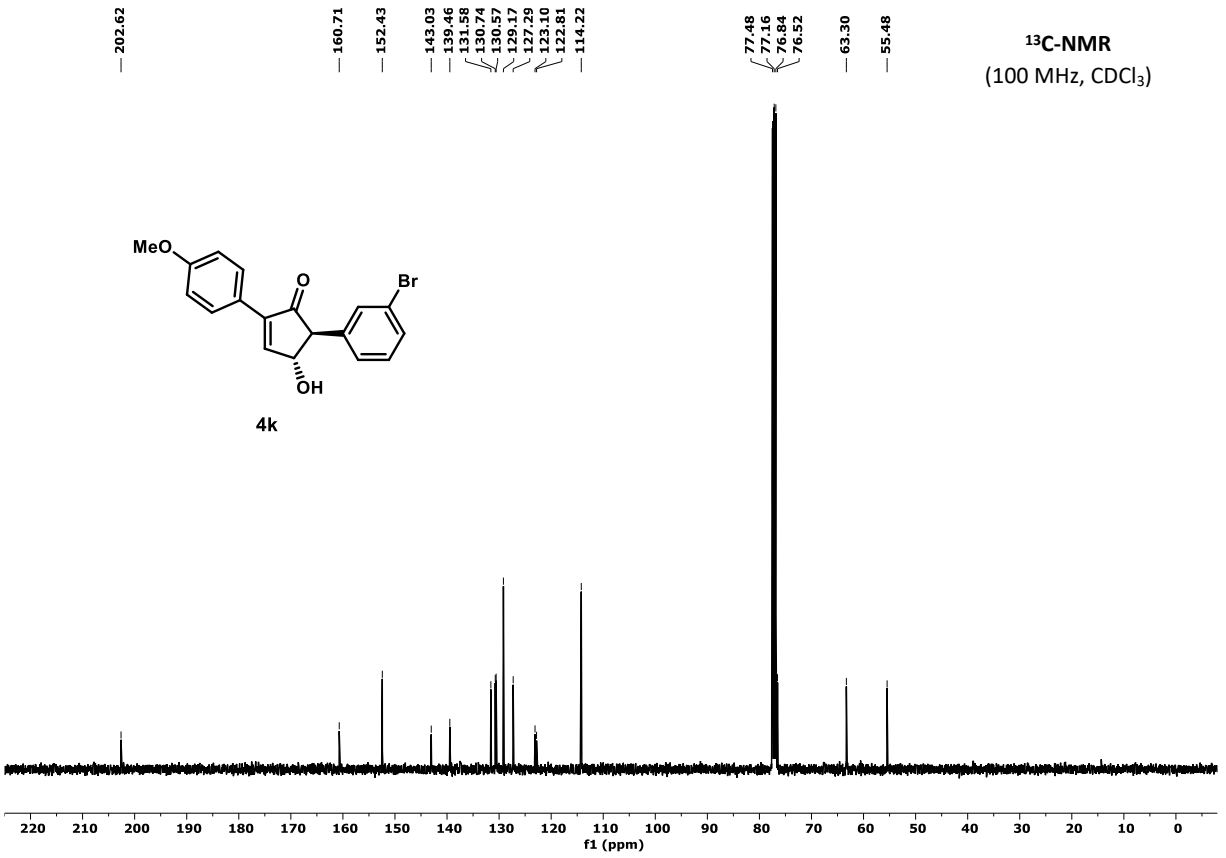


#	Peak Name	CH	tR [min]	Area [μV·sec]	Height [μV]	Area%	Height%	Quantity	NTP	Resolution	Symmetry Factor	Warning
1	Unknown	10	34,123	24399918	294025	99,985	99,979	N/A	4572	5,833	2,945	
2	Unknown	10	45,970	3641	63	0,015	0,021	N/A	8012	N/A	1,056	

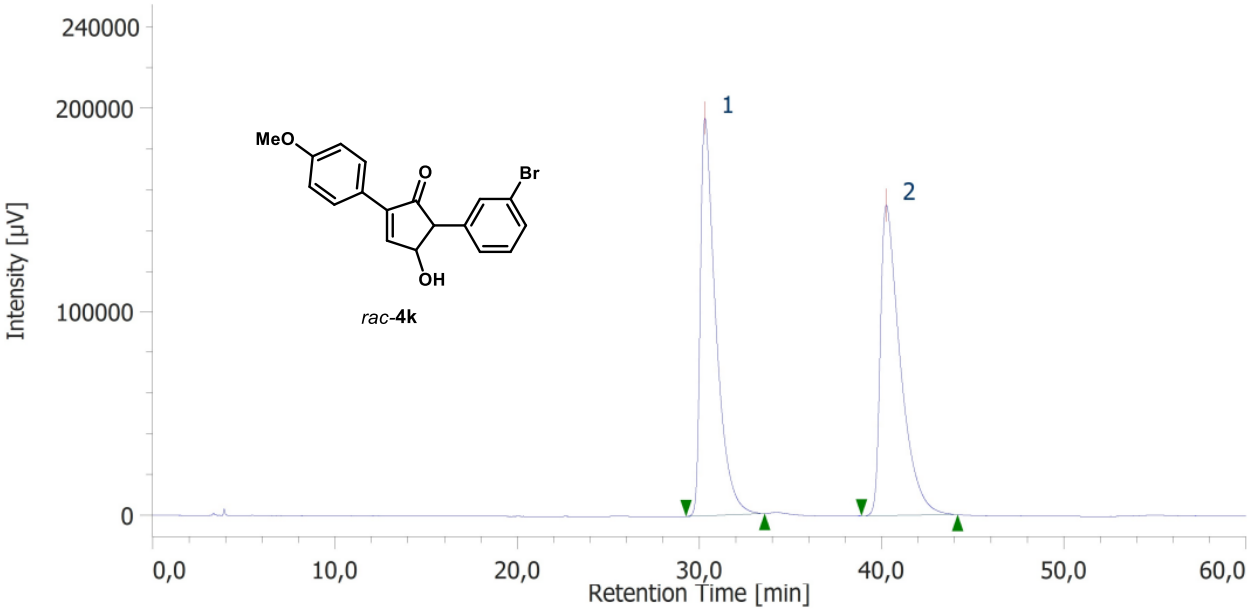
Daicel Chiralpak IB column (90:10 *n*-Hexane/*i*-PrOH, 1.0 mL/min, 230 nm)



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

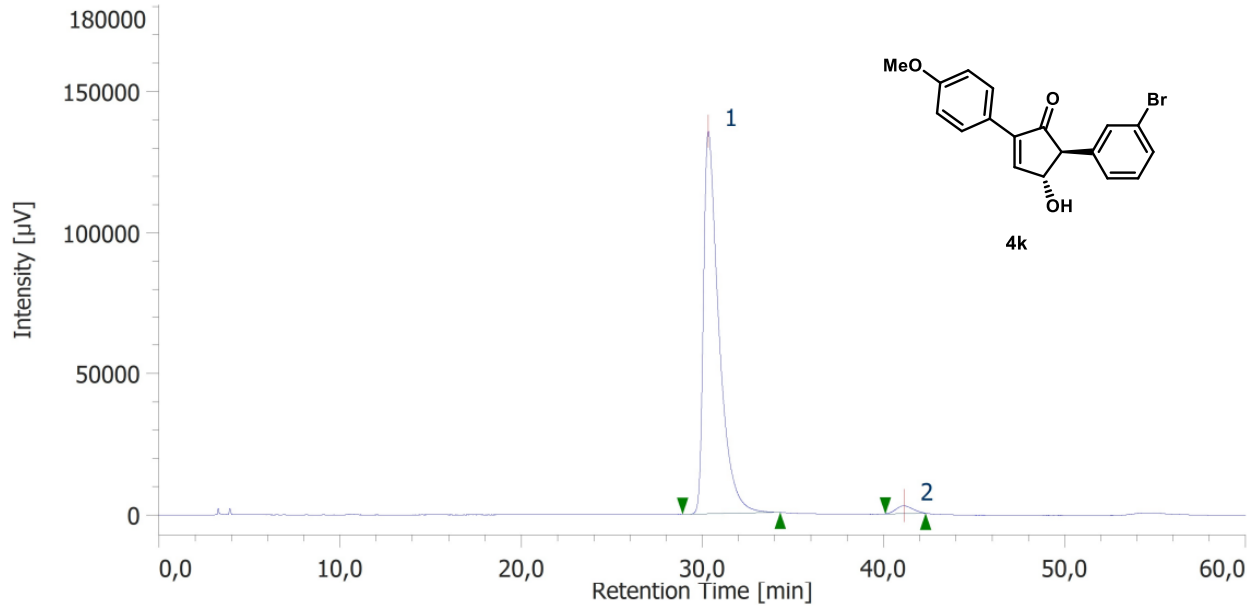


^{13}C-NMR
(100 MHz, $CDCl_3$)

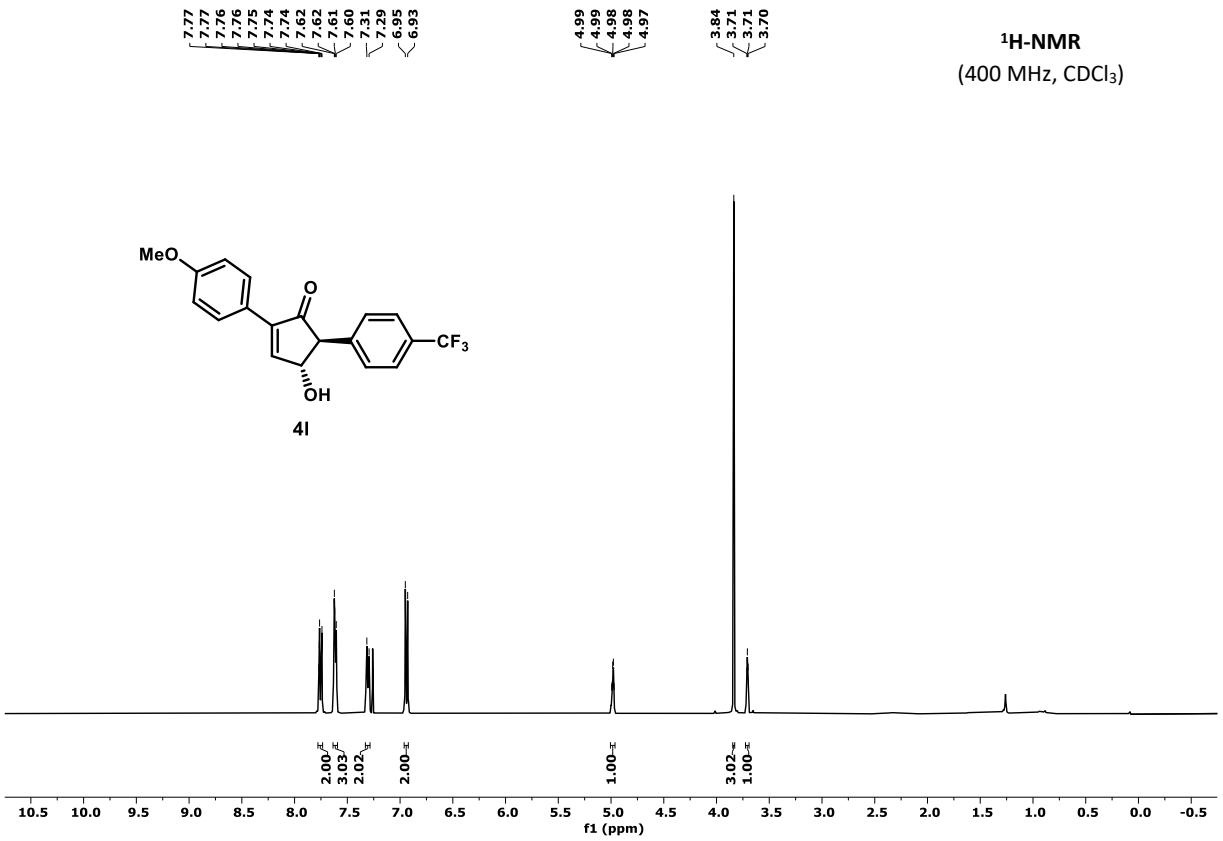


#	Peak Name	CH	tR [min]	Area [μV·sec]	Height [μV]	Area%	Height%	Quantity	NTP	Resolution	Symmetry Factor	Warning
1	Unknown	11	30,297	11562645	195228	49,858	56,104	N/A	6810	5,933	2,112	
2	Unknown	11	40,250	11628628	152748	50,142	43,896	N/A	7214	N/A	2,099	

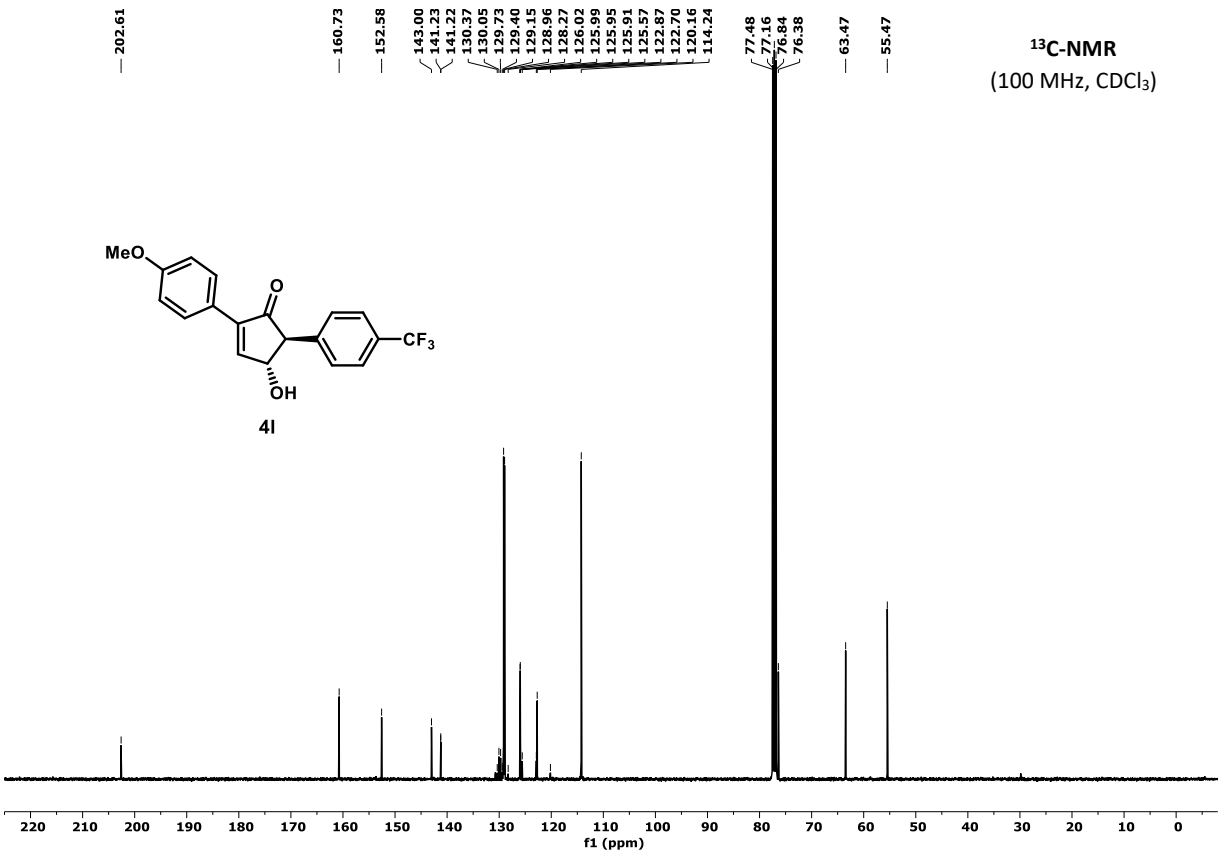
Daicel Chiralpak IA column (90:10 *n*-Hexane/*i*-PrOH, 1.0 mL/min, 240 nm)



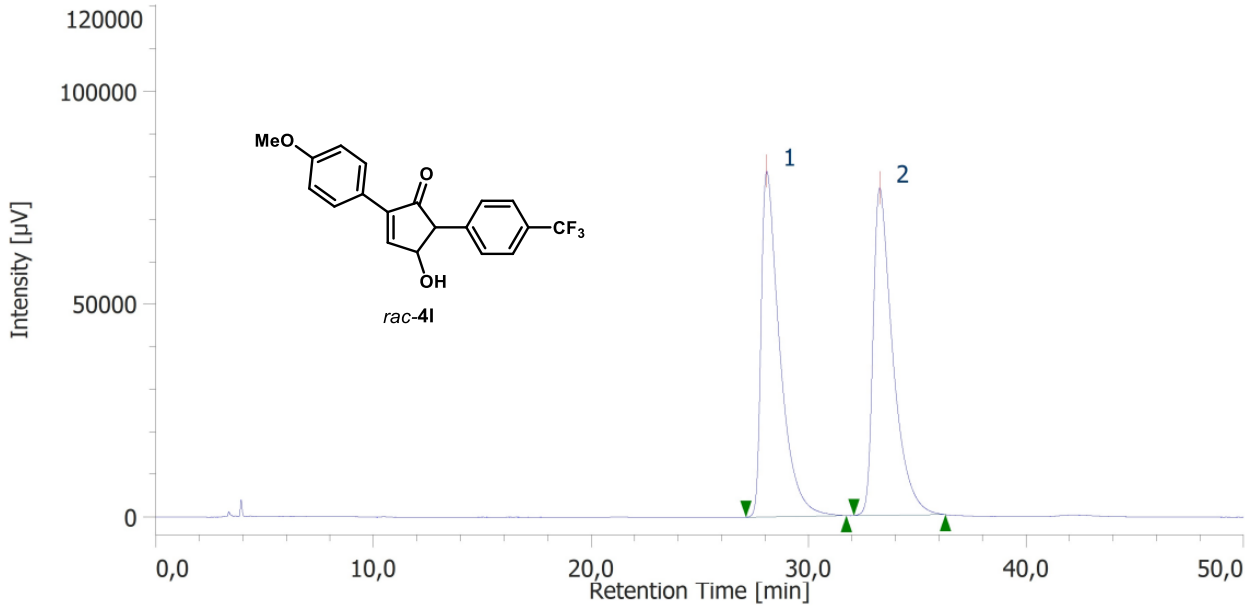
#	Peak Name	CH	tR [min]	Area [μV·sec]	Height [μV]	Area%	Height%	Quantity	NTP	Resolution	Symmetry Factor	Warning
1	Unknown	11	30,320	7996717	135438	97,859	98,024	N/A	6957	6,752	1,999	
2	Unknown	11	41,123	174948	2730	2,141	1,976	N/A	8789	N/A	1,102	



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

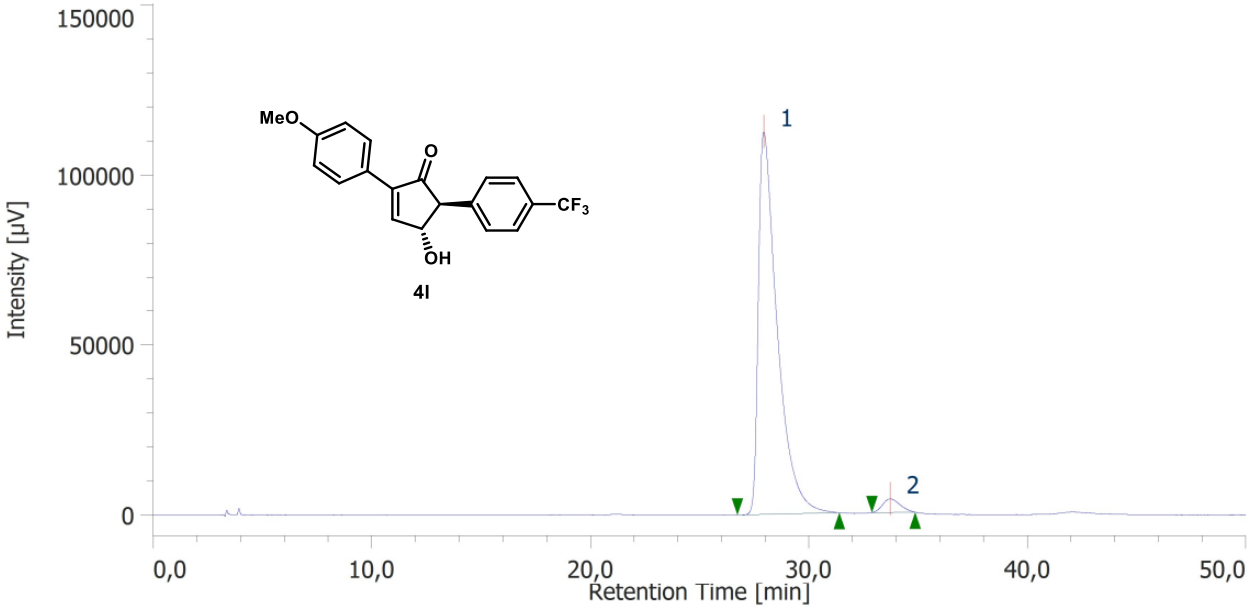


^{13}C-NMR
(100 MHz, $CDCl_3$)



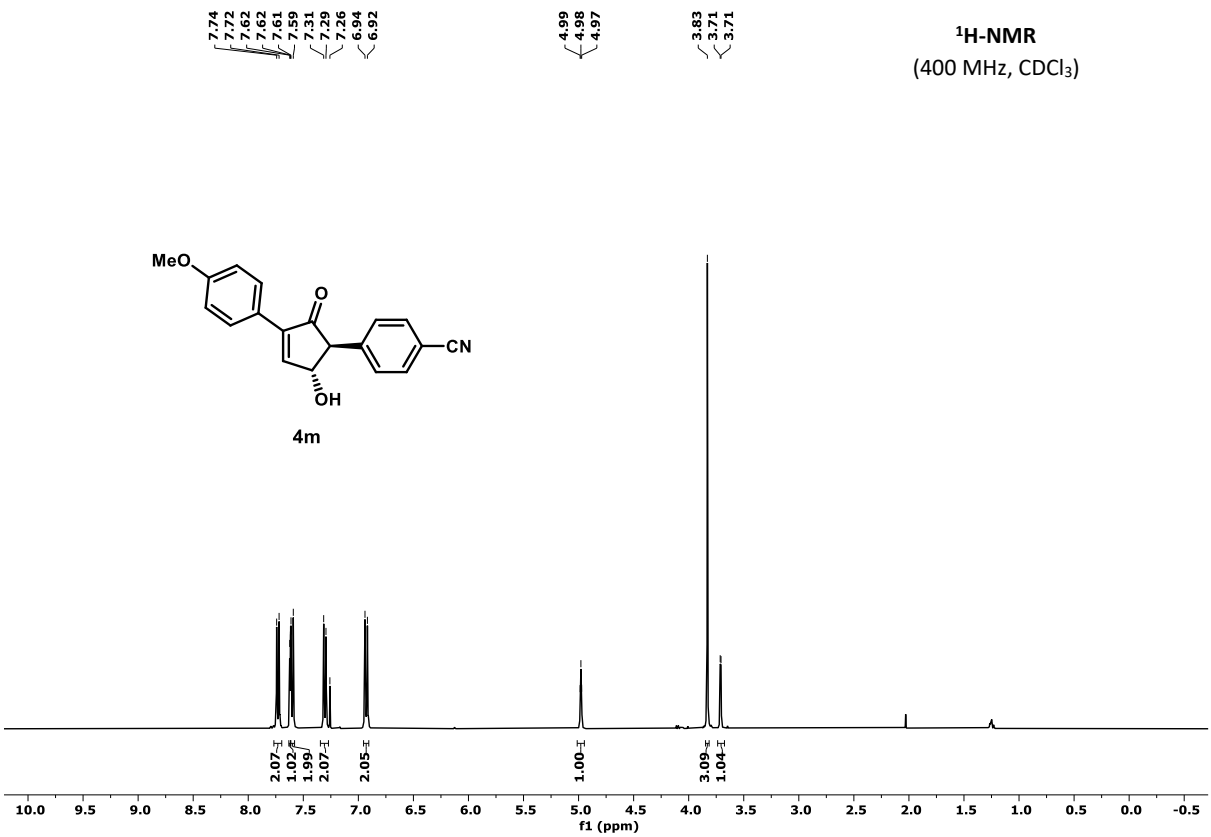
#	Peak Name	CH	tR [min]	Area [μV·sec]	Height [μV]	Area%	Height%	Quantity	NTP	Resolution	Symmetry Factor	Warning
1	Unknown	11	28,073	4836209	81226	49,931	51,340	N/A	5862	3,440	2,120	
2	Unknown	11	33,263	4849592	76986	50,069	48,660	N/A	7289	N/A	1,844	

Daicel Chiralpak IB column (90:10 *n*-Hexane/*i*-PrOH, 1.0 mL/min, 240 nm)

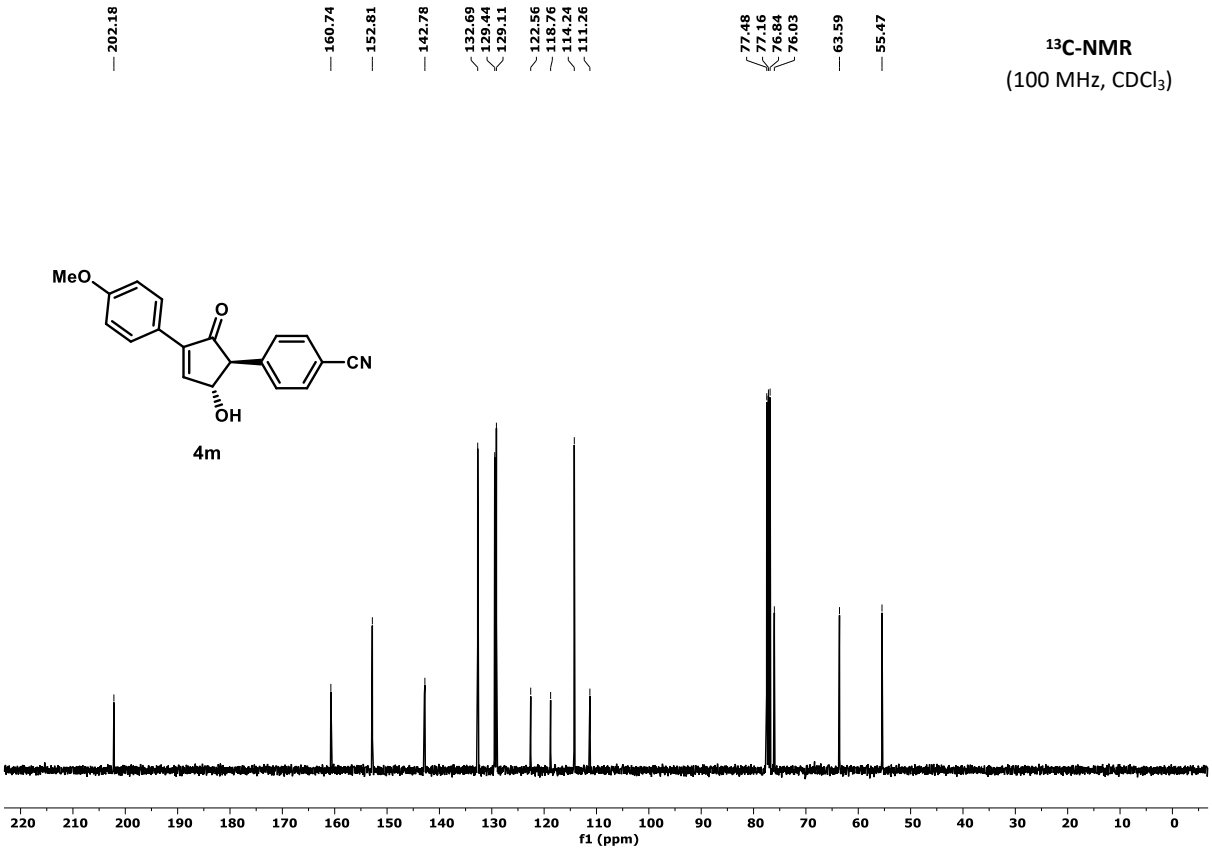


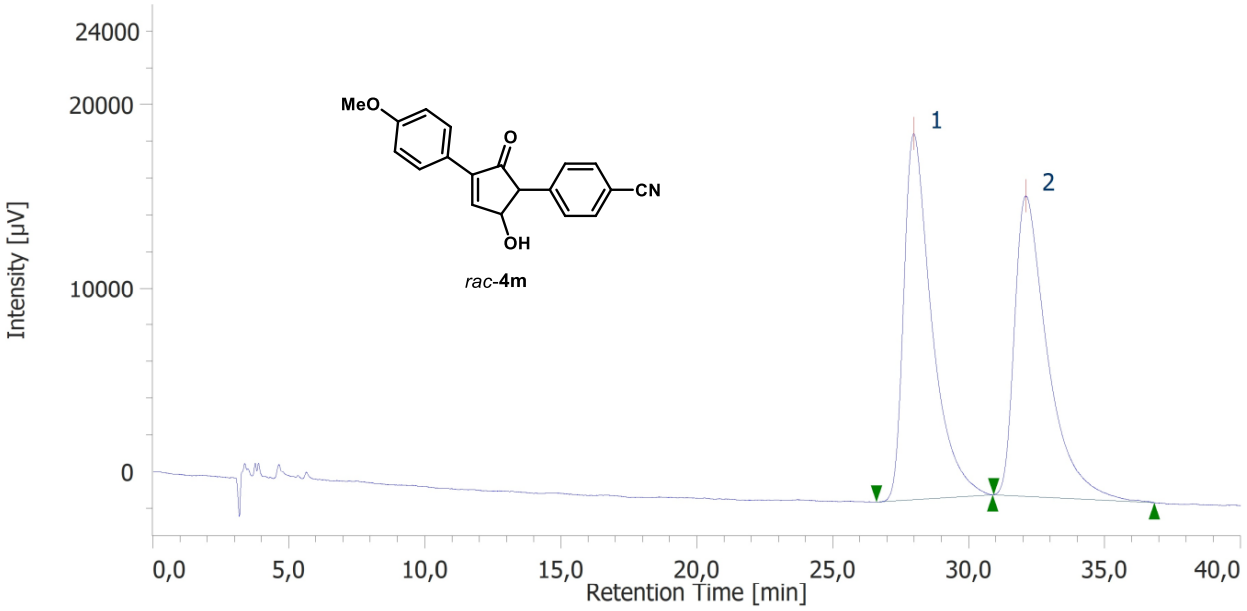
#	Peak Name	CH	tR [min]	Area [μV·sec]	Height [μV]	Area%	Height%	Quantity	NTP	Resolution	Symmetry Factor	Warning
1	Unknown	11	27,930	6743554	112513	96,846	96,600	N/A	5711	3,892	2,252	
2	Unknown	11	33,713	219621	3960	3,154	3,400	N/A	8065	N/A	1,207	

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



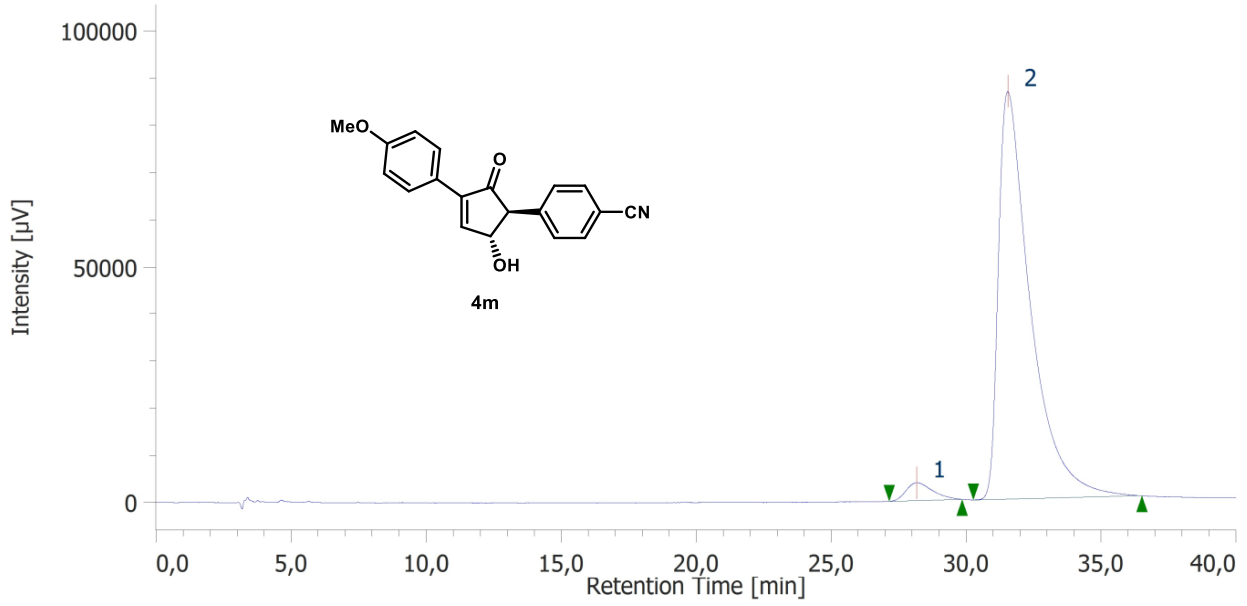
^{13}C-NMR
(100 MHz, $CDCl_3$)



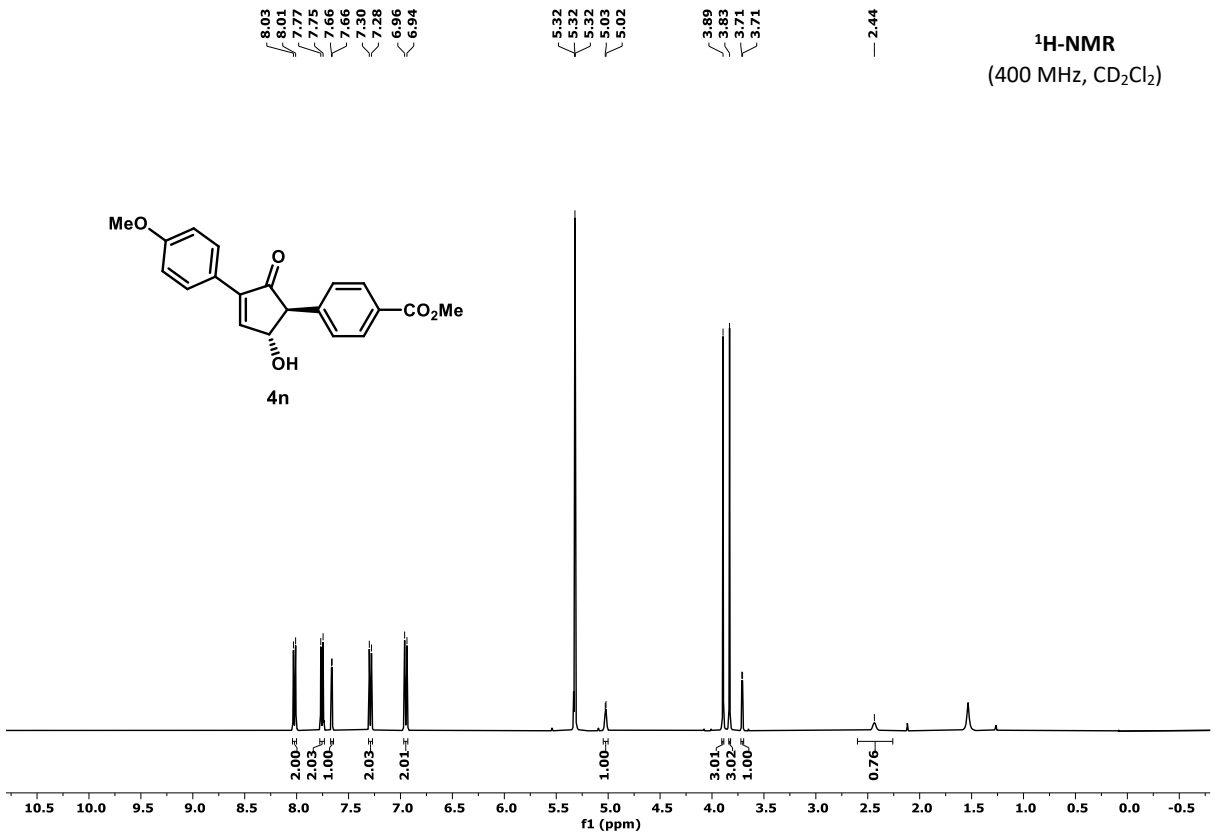


#	Peak Name	CH	tR [min]	Area [μV·sec]	Height [μV]	Area%	Height%	Quantity	NTP	Resolution	Symmetry Factor	Warning
1	Unknown	13	27,973	1423986	19928	50,788	54,888	N/A	4022	2,162	1,774	
2	Unknown	13	32,100	1379781	16379	49,212	45,112	N/A	3876	N/A	1,882	

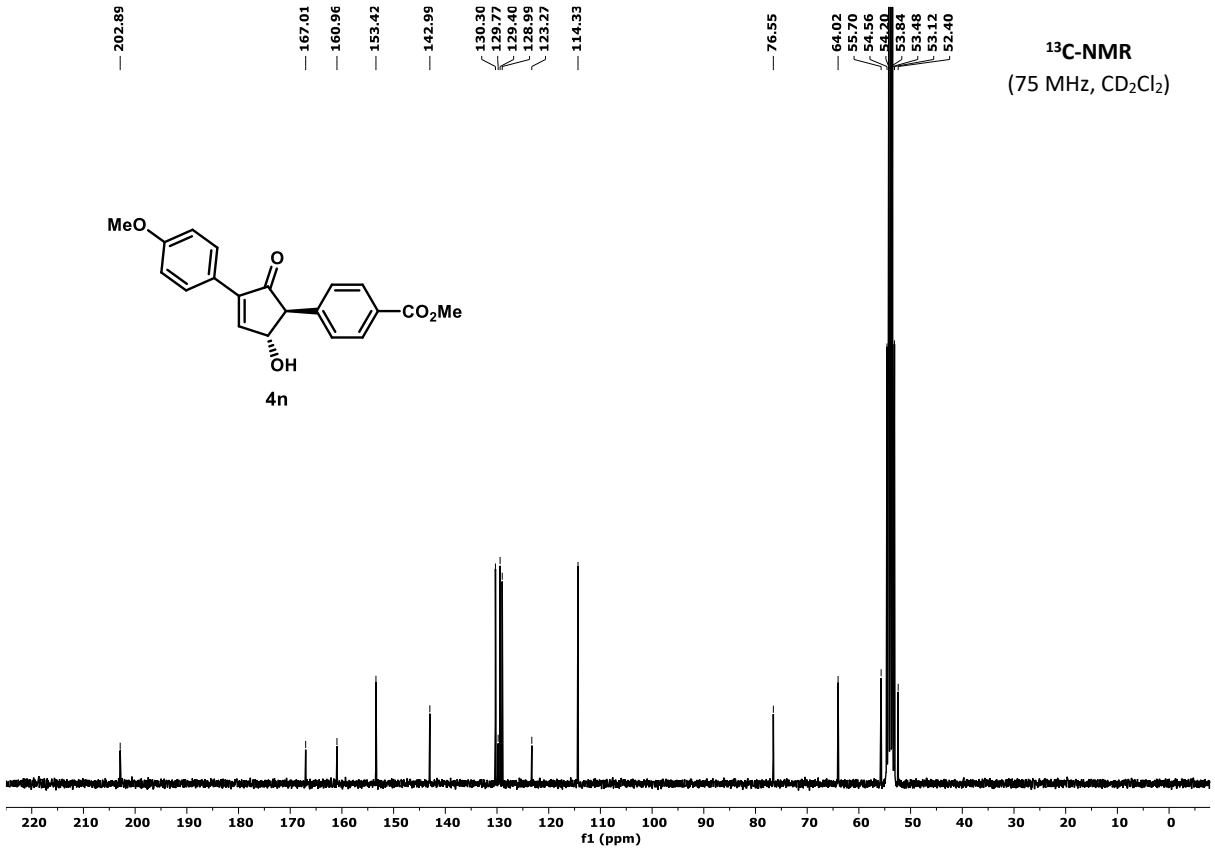
Daicel Chiralpak IB column (80:20 *n*-Hexane/*i*-PrOH, 1.0 mL/min, 245 nm)



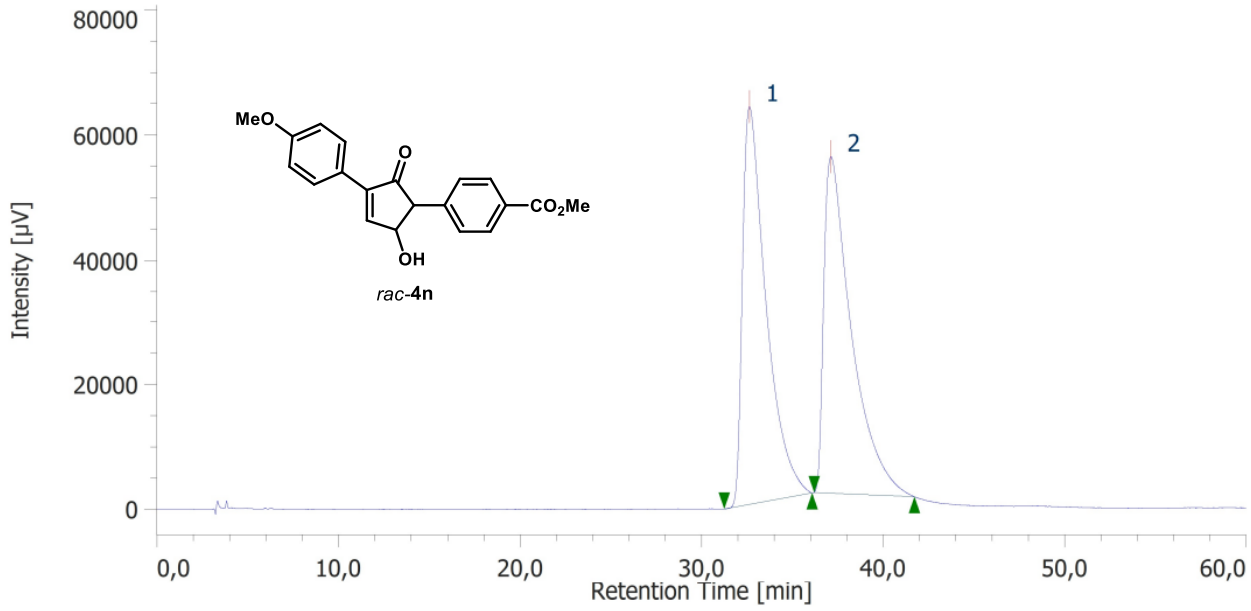
#	Peak Name	CH	tR [min]	Area [μV·sec]	Height [μV]	Area%	Height%	Quantity	NTP	Resolution	Symmetry Factor	Warning
1	Unknown	11	28,163	256615	3775	3,478	4,184	N/A	3919	1,782	1,393	
2	Unknown	11	31,537	7122180	86452	96,522	95,816	N/A	3992	N/A	2,318	



^{1}H-NMR
(400 MHz, CD_2Cl_2)

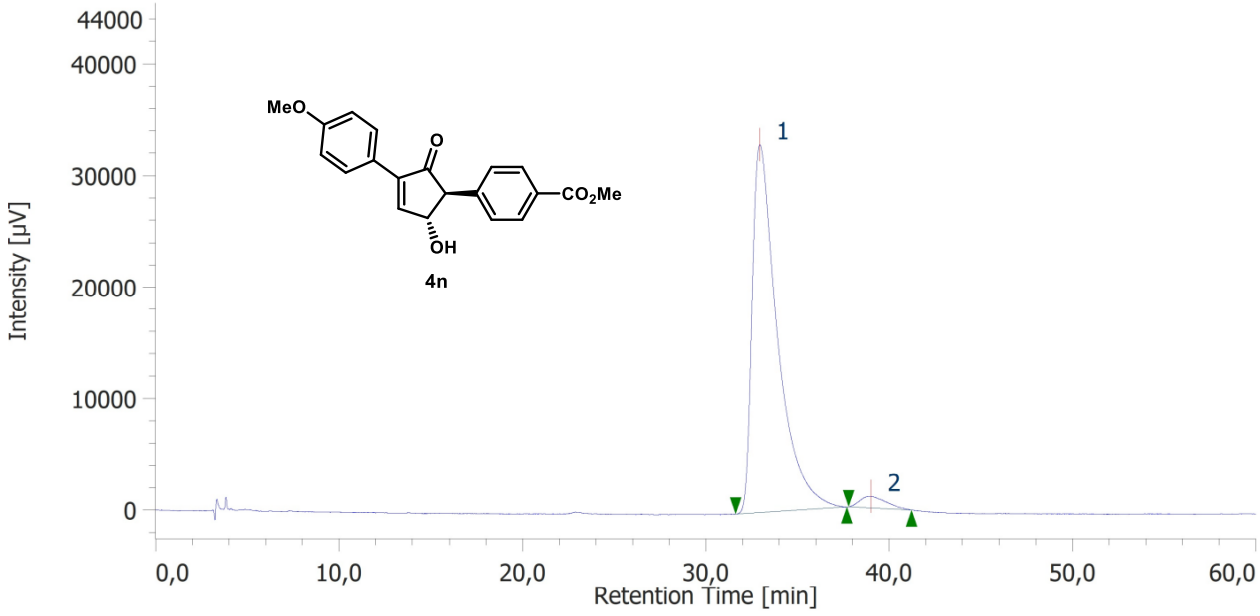


^{13}C-NMR
(75 MHz, CD_2Cl_2)

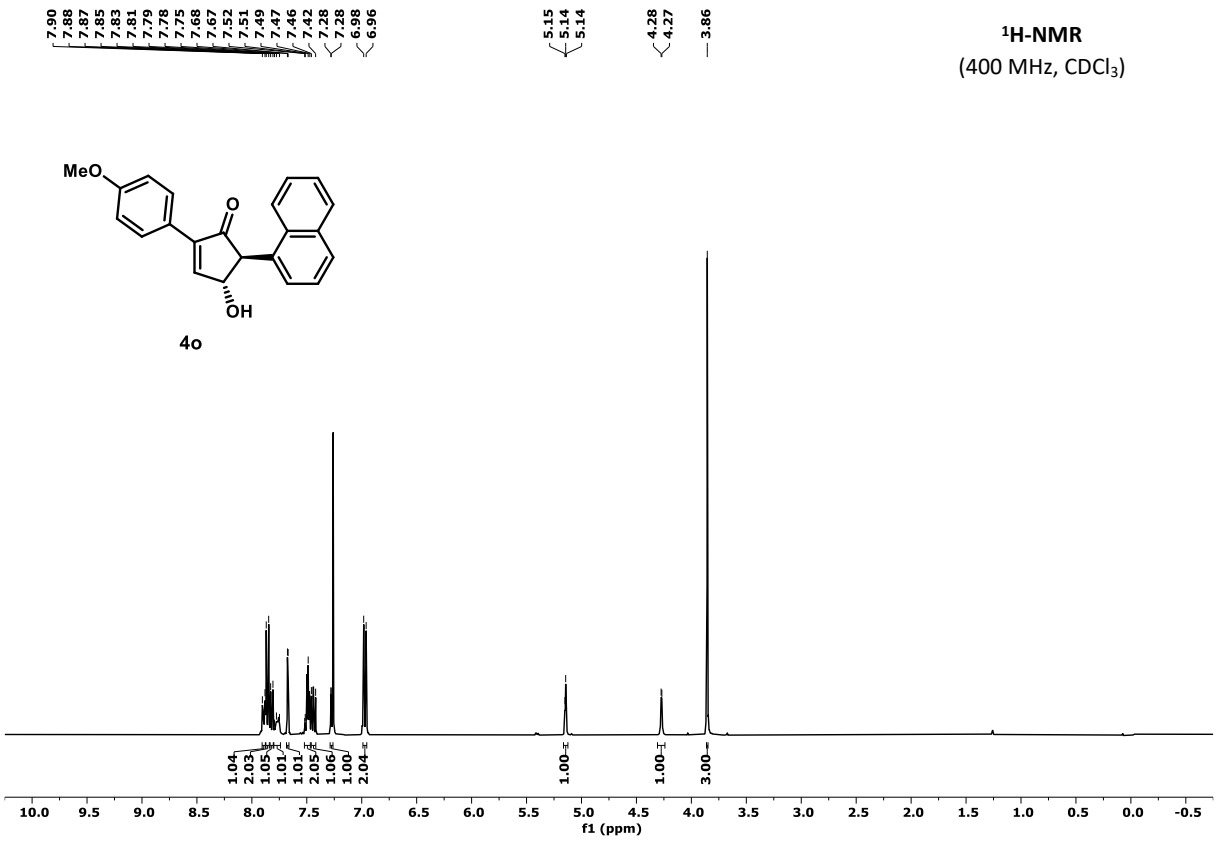


#	Peak Name	CH	tR [min]	Area [μV·sec]	Height [μV]	Area%	Height%	Quantity	NTP	Resolution	Symmetry Factor	Warning
1	Unknown	11	32,623	5766086	63739	50,166	54,151	N/A	3299	1,851	2,257	
2	Unknown	11	37,113	5727893	53966	49,834	45,849	N/A	3279	N/A	2,818	

Daicel Chiralpak IB column (85:15 *n*-Hexane/*i*-PrOH, 1.0 mL/min, 244 nm)

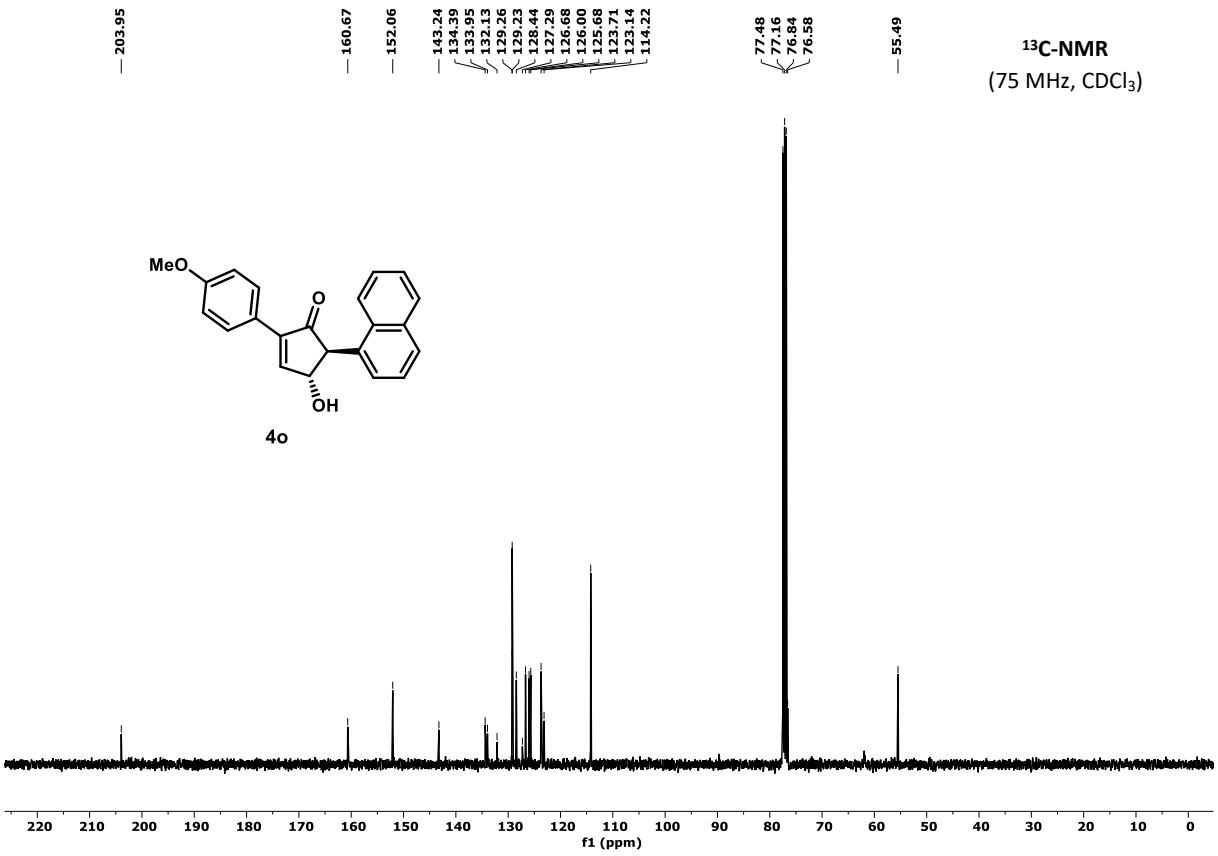


#	Peak Name	CH	tR [min]	Area [μV·sec]	Height [μV]	Area%	Height%	Quantity	NTP	Resolution	Symmetry Factor	Warning
1	Unknown	11	32,933	3172676	32969	96,818	96,952	N/A	3157	2,382	2,231	
2	Unknown	11	39,000	104274	1036	3,182	3,048	N/A	3186	N/A	1,401	



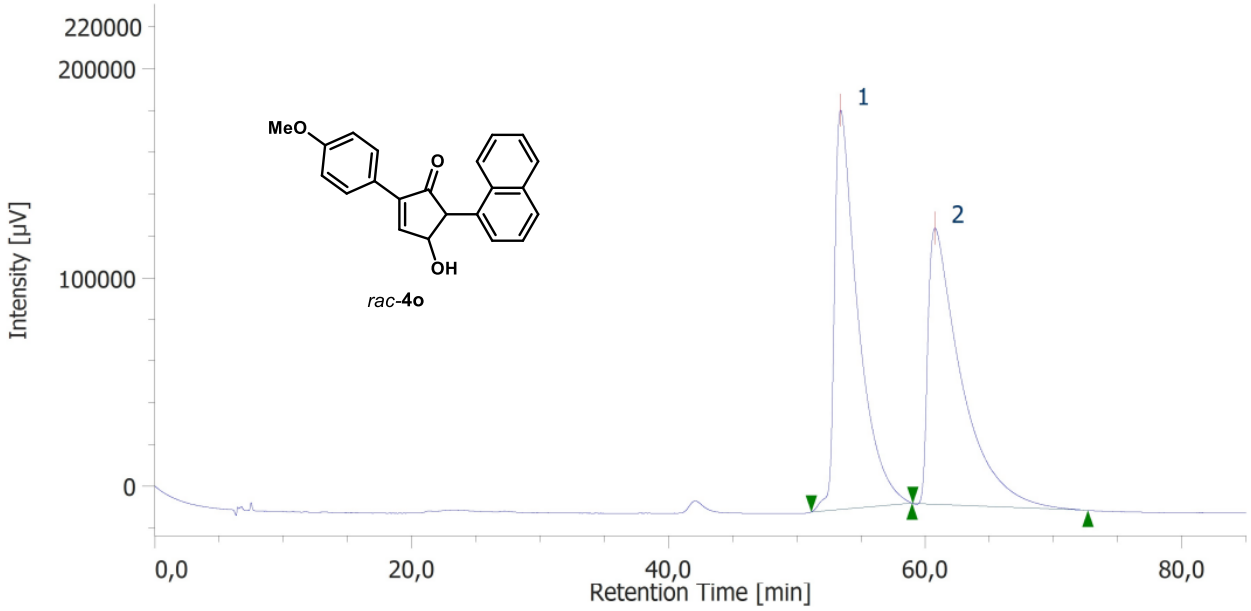
^{1}H-NMR
(400 MHz, $CDCl_3$)

4o



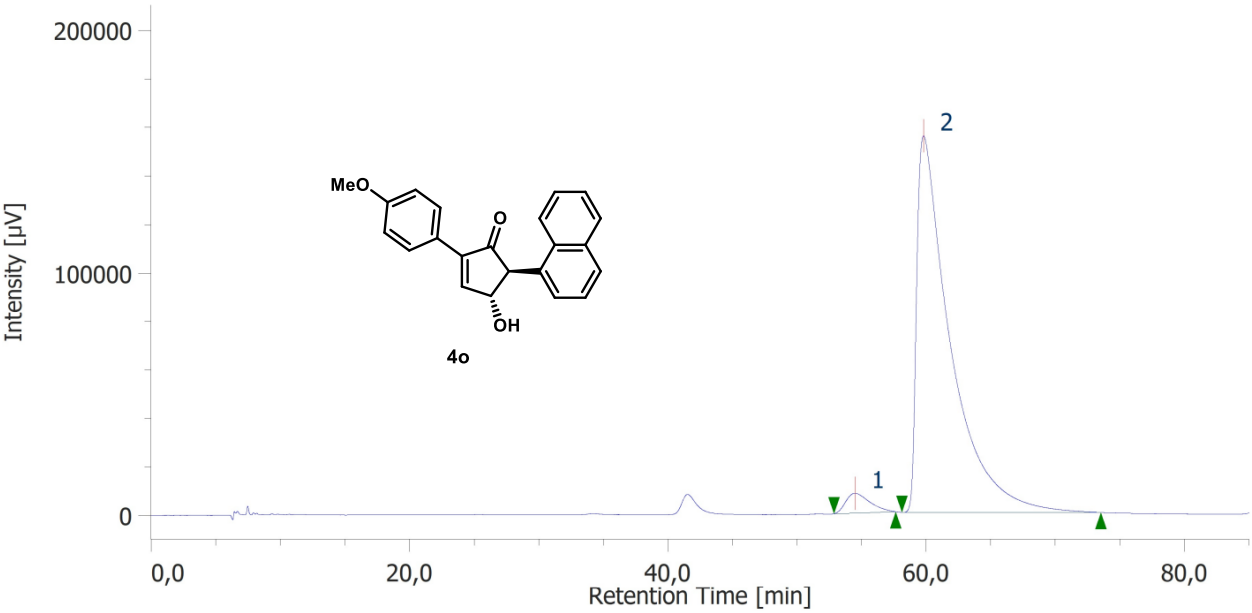
^{13}C-NMR
(75 MHz, $CDCl_3$)

4o



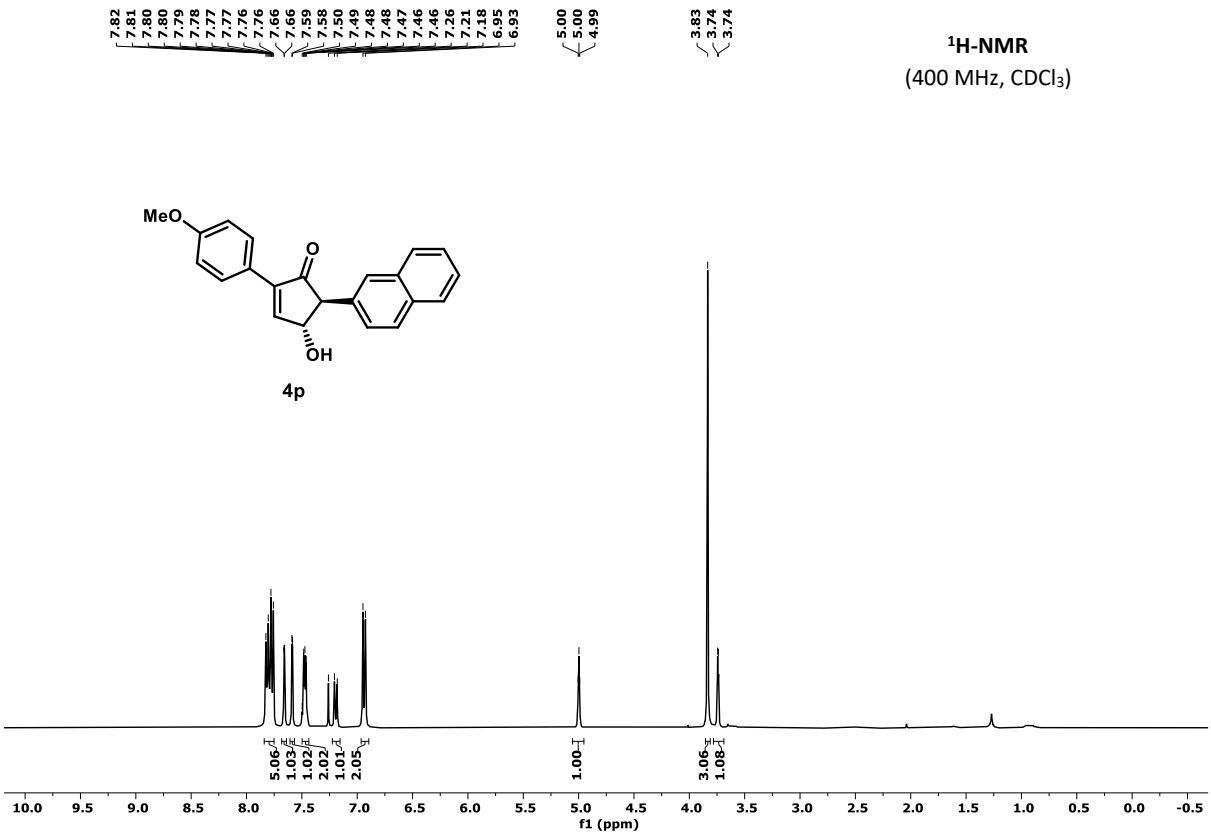
#	Peak Name	CH	tR [min]	Area [μV·sec]	Height [μV]	Area%	Height%	Quantity	NTP	Resolution	Symmetry Factor	Warning
1	Unknown	13	53,393	24467029	191044	50,736	59,049	N/A	4765	2,016	2,552	
2	Unknown	13	60,750	23757308	132489	49,264	40,951	N/A	3310	N/A	3,617	

Daicel Chiralpak IB column (80:20 *n*-Hexane/*i*-PrOH, 1.0 mL/min, 240 nm)

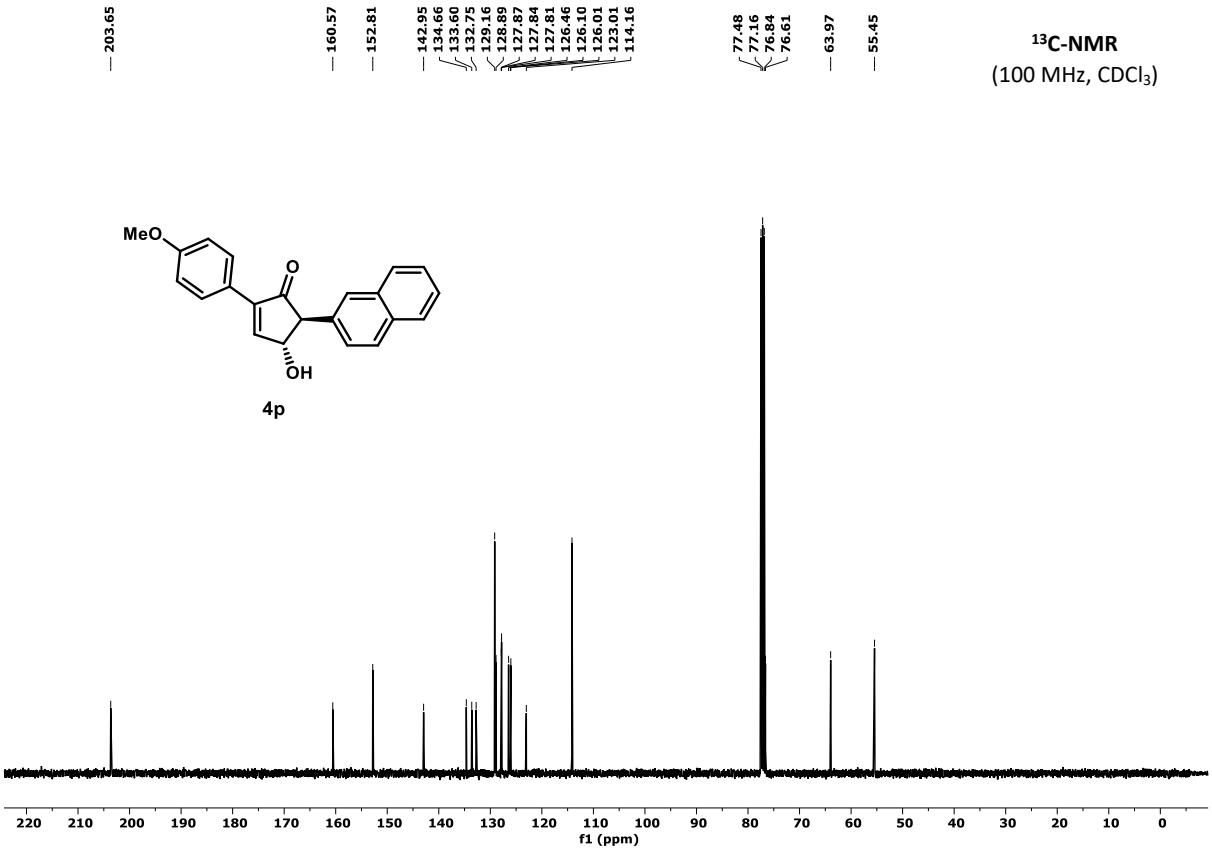


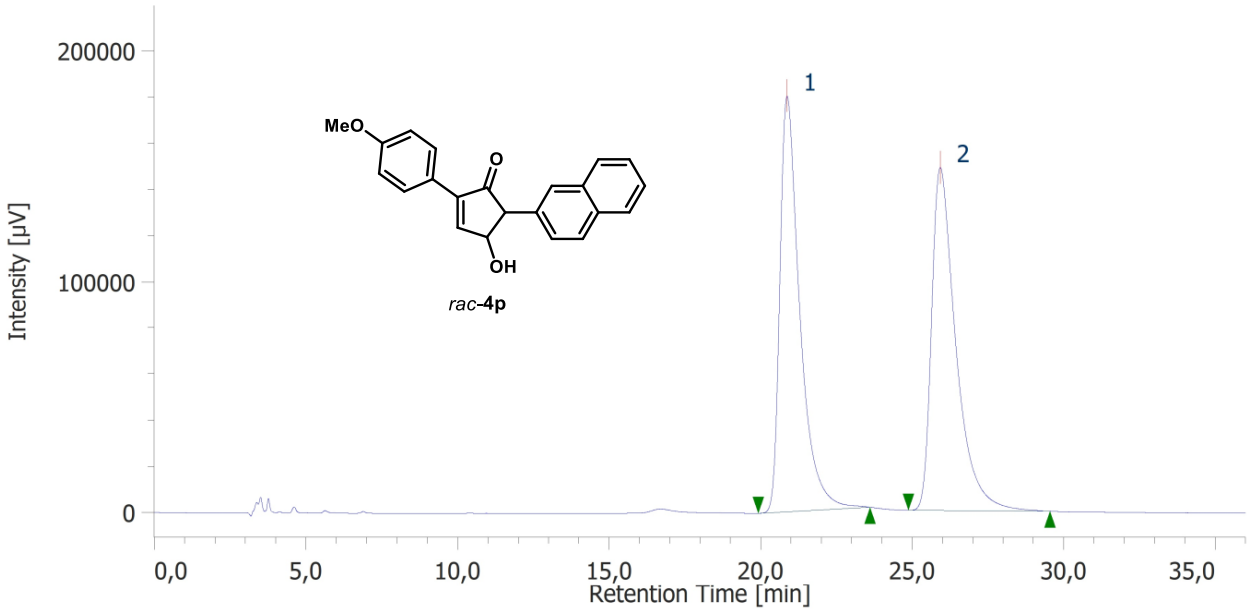
#	Peak Name	CH	tR [min]	Area [μV·sec]	Height [μV]	Area%	Height%	Quantity	NTP	Resolution	Symmetry Factor	Warning
1	Unknown	11	54,467	1046395	8107	3,609	4,965	N/A	4005	1,406	1,495	
2	Unknown	11	59,783	27944356	155181	96,391	95,035	N/A	3334	N/A	3,859	

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



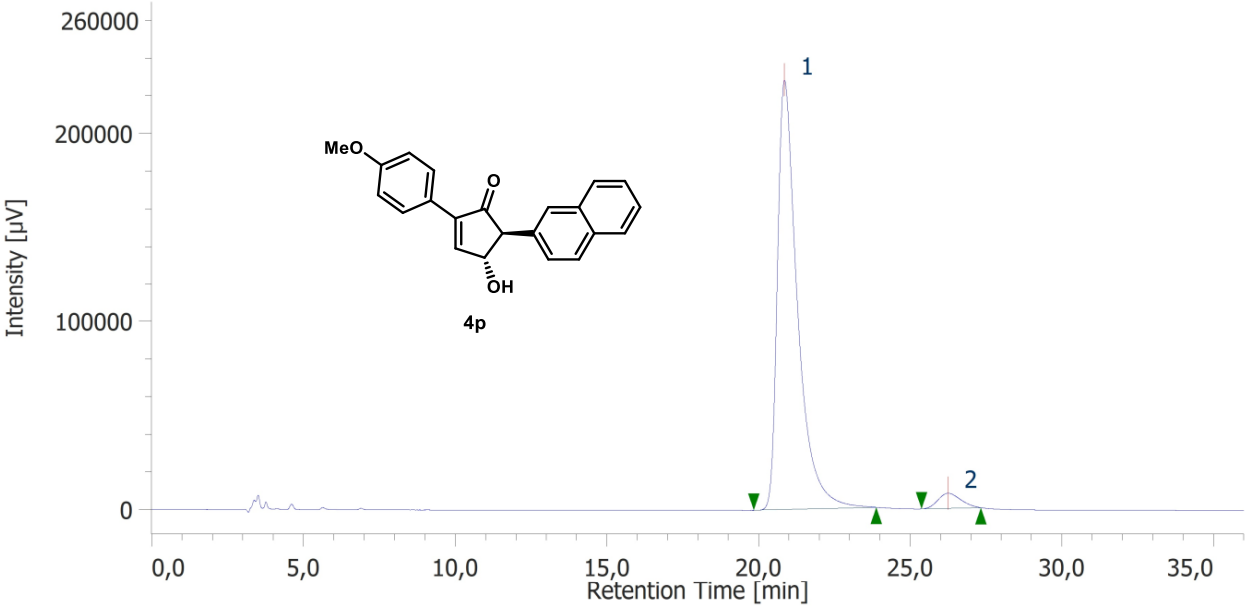
^{13}C-NMR
(100 MHz, $CDCl_3$)



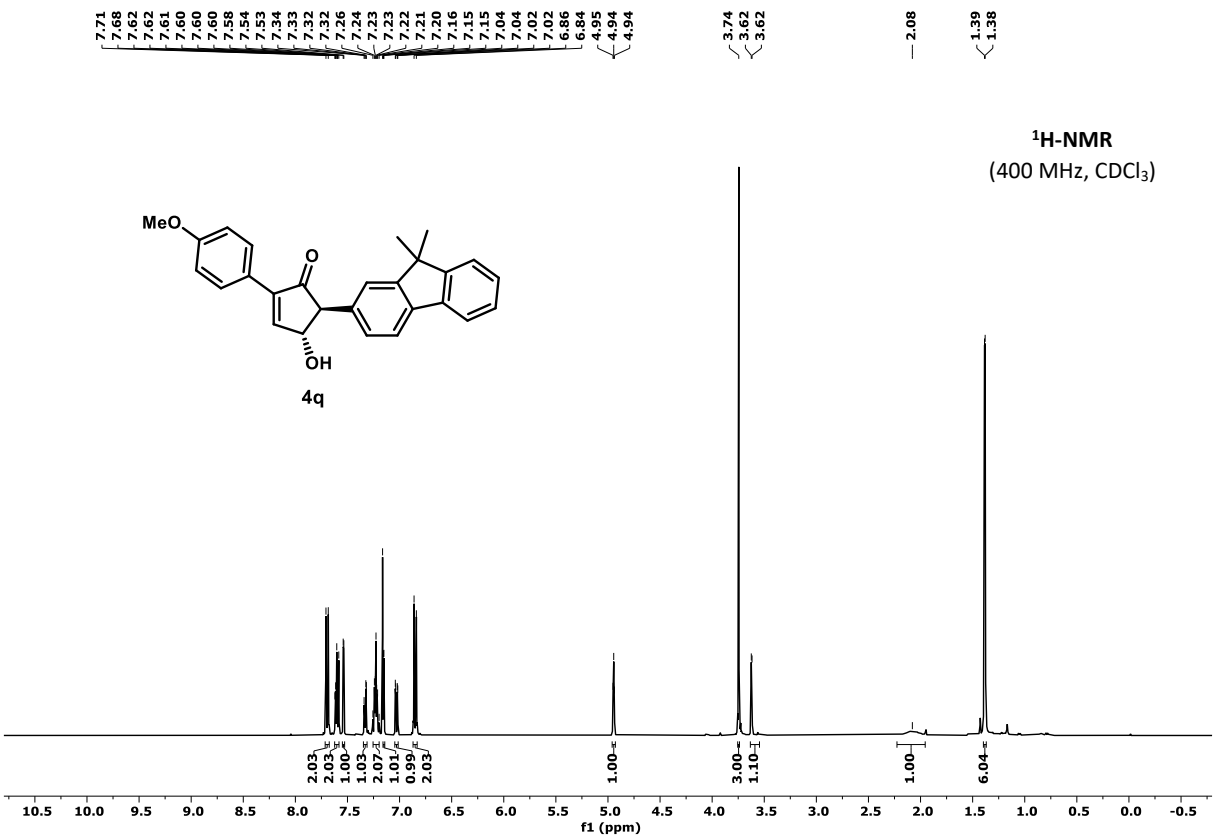


#	Peak Name	CH	tR [min]	Area [μV·sec]	Height [μV]	Area%	Height%	Quantity	NTP	Resolution	Symmetry Factor	Warning
1	Unknown	10	20,867	8219243	179995	49,779	54,780	N/A	5543	4,065	1,724	
2	Unknown	10	25,923	8292141	148586	50,221	45,220	N/A	5701	N/A	1,720	

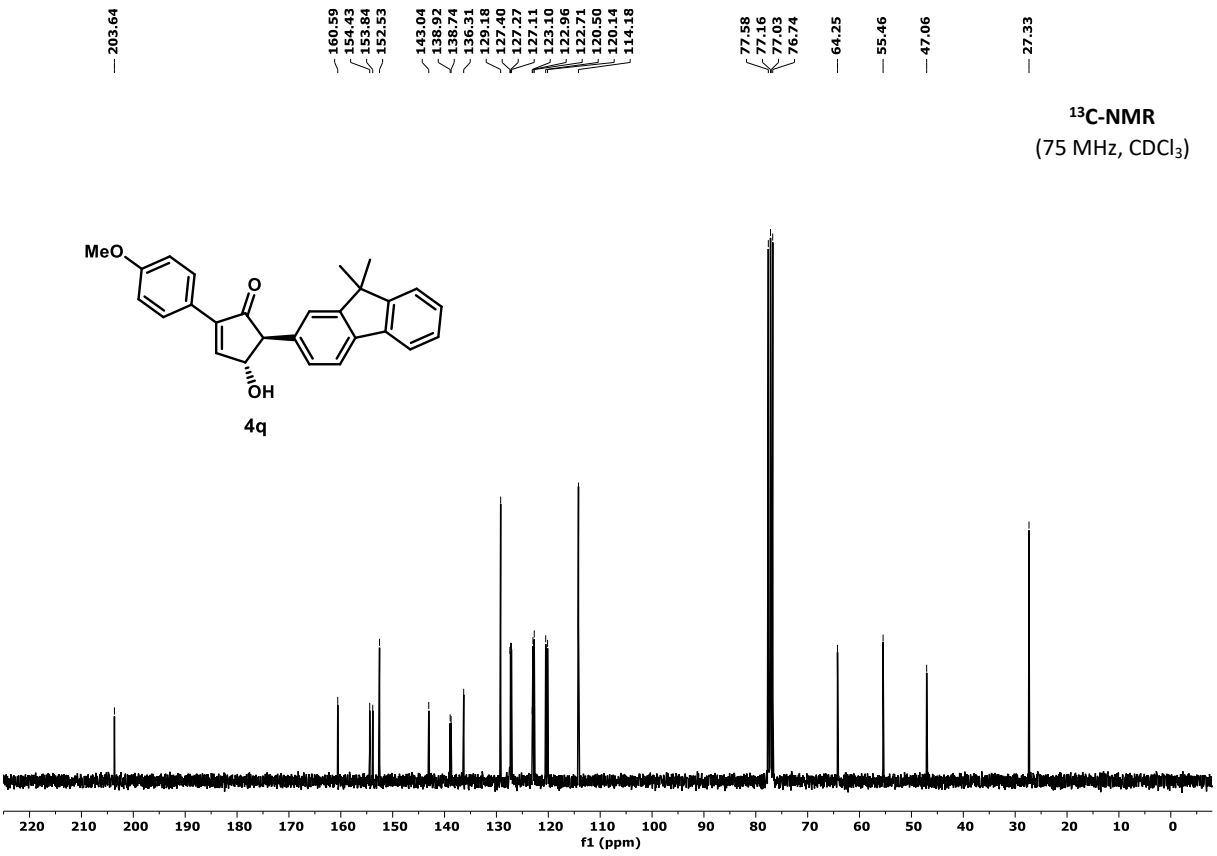
Daicel Chiralpak IB column (80:20 *n*-Hexane/*i*-PrOH, 1.0 mL/min, 230 nm)



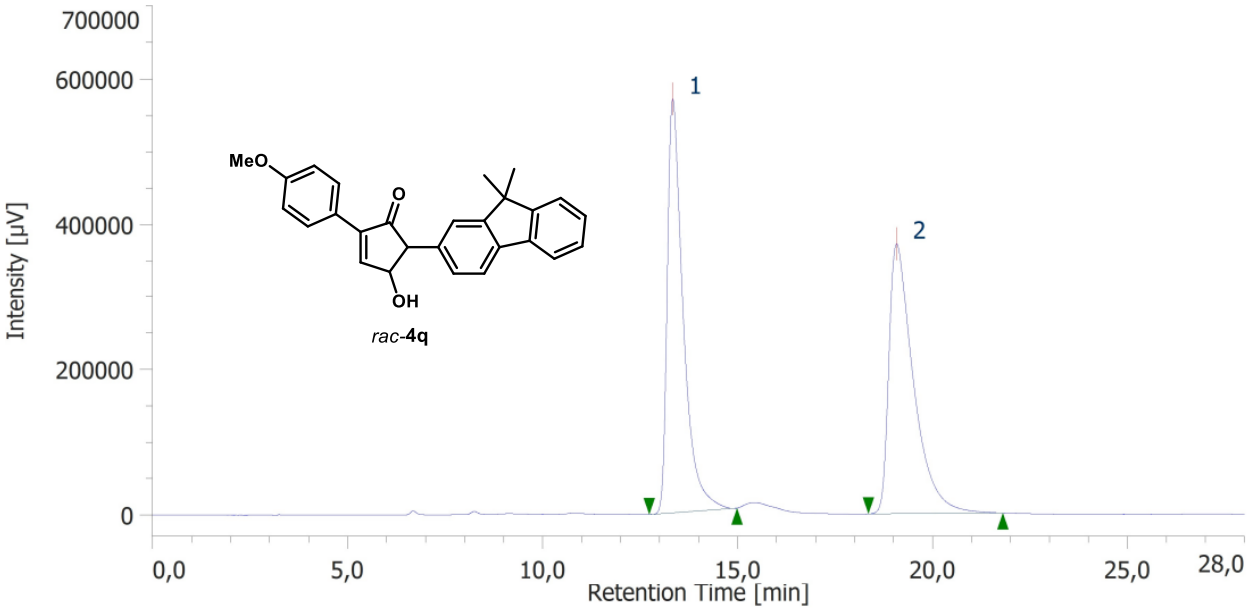
#	Peak Name	CH	tR [min]	Area [μV·sec]	Height [μV]	Area%	Height%	Quantity	NTP	Resolution	Symmetry Factor	Warning
1	Unknown	10	20,850	10470710	228281	96,184	96,617	N/A	5580	4,299	1,797	
2	Unknown	10	26,240	415409	7992	3,816	3,383	N/A	5638	N/A	1,200	



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

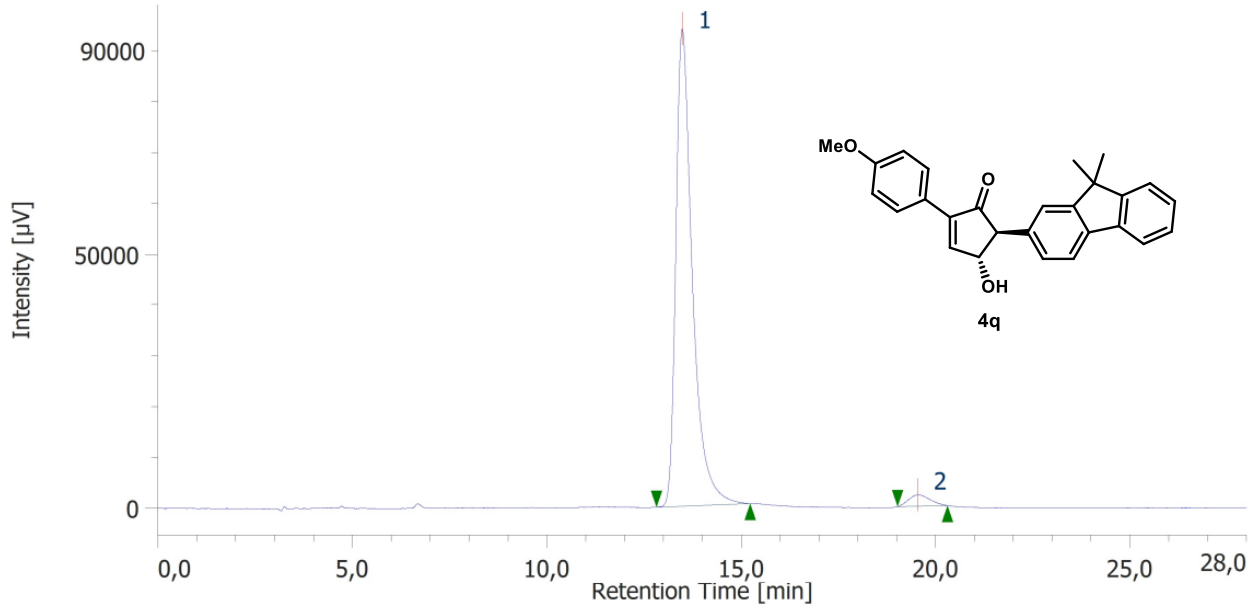


^{13}C-NMR
(75 MHz, $CDCl_3$)



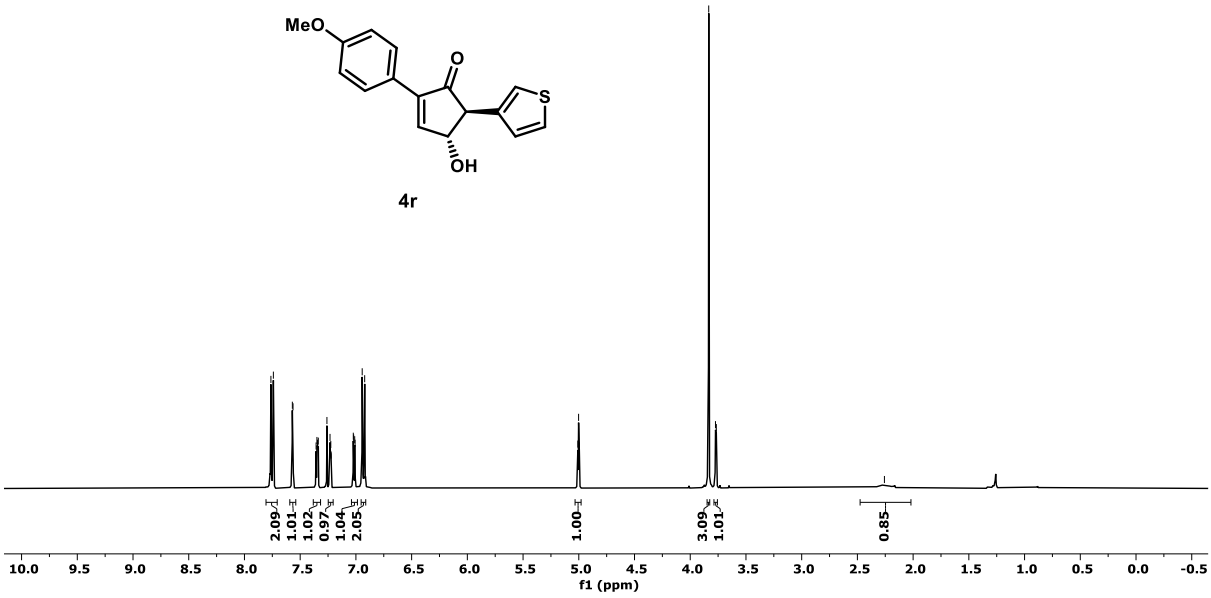
#	Peak Name	CH	tR [min]	Area [μV·sec]	Height [μV]	Area%	Height%	Quantity	NTP	Resolution	Symmetry Factor	Warning
1	Unknown	11	13,330	16106771	568817	49,696	60,477	N/A	5907	6,476	1,877	
2	Unknown	11	19,073	16304005	371736	50,304	39,523	N/A	4947	N/A	2,019	

Daicel Chiralpak IB column (80:20 *n*-Hexane/*i*-PrOH, 1.0 mL/min, 272 nm)



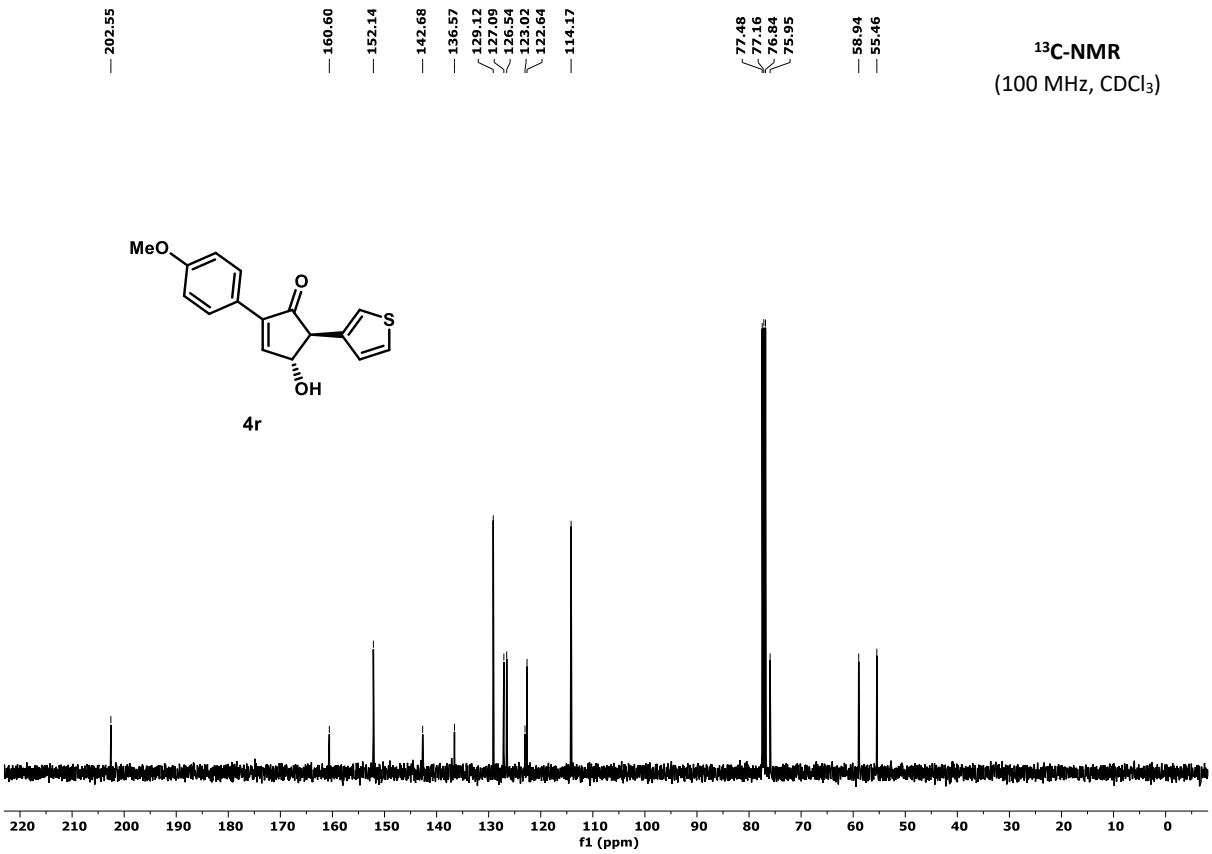
#	Peak Name	CH	tR [min]	Area [μV·sec]	Height [μV]	Area%	Height%	Quantity	NTP	Resolution	Symmetry Factor	Warning
1	Unknown	11	13,477	2769042	93765	97,057	97,716	N/A	5553	6,826	1,615	
2	Unknown	11	19,530	83978	2192	2,943	2,284	N/A	5485	N/A	1,260	

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

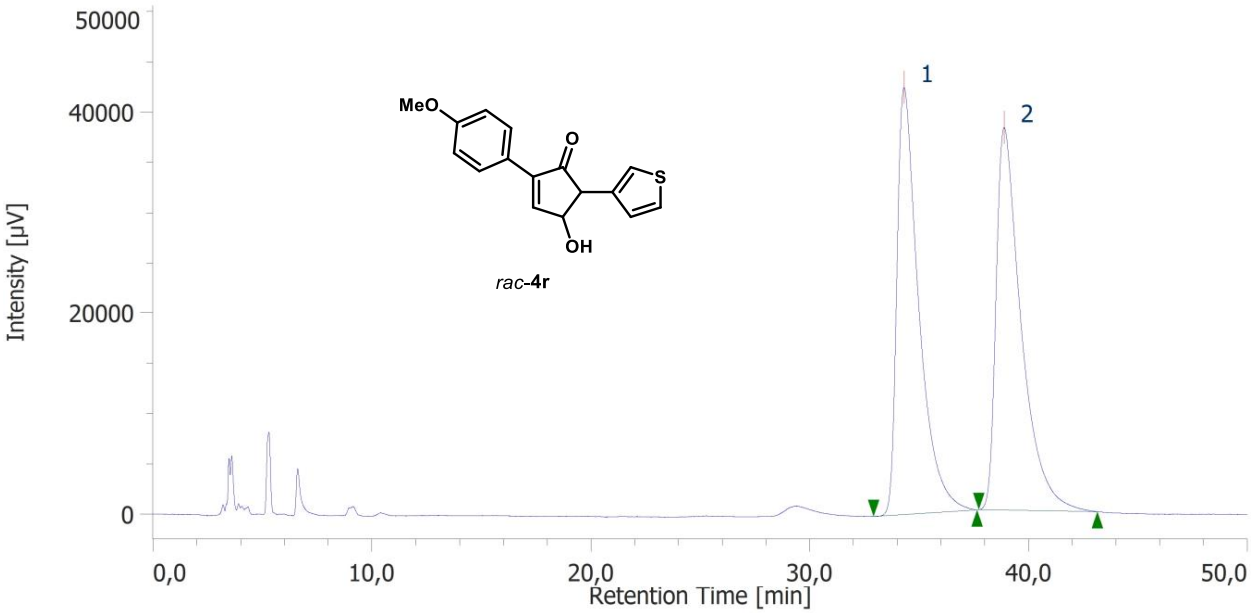


4r

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

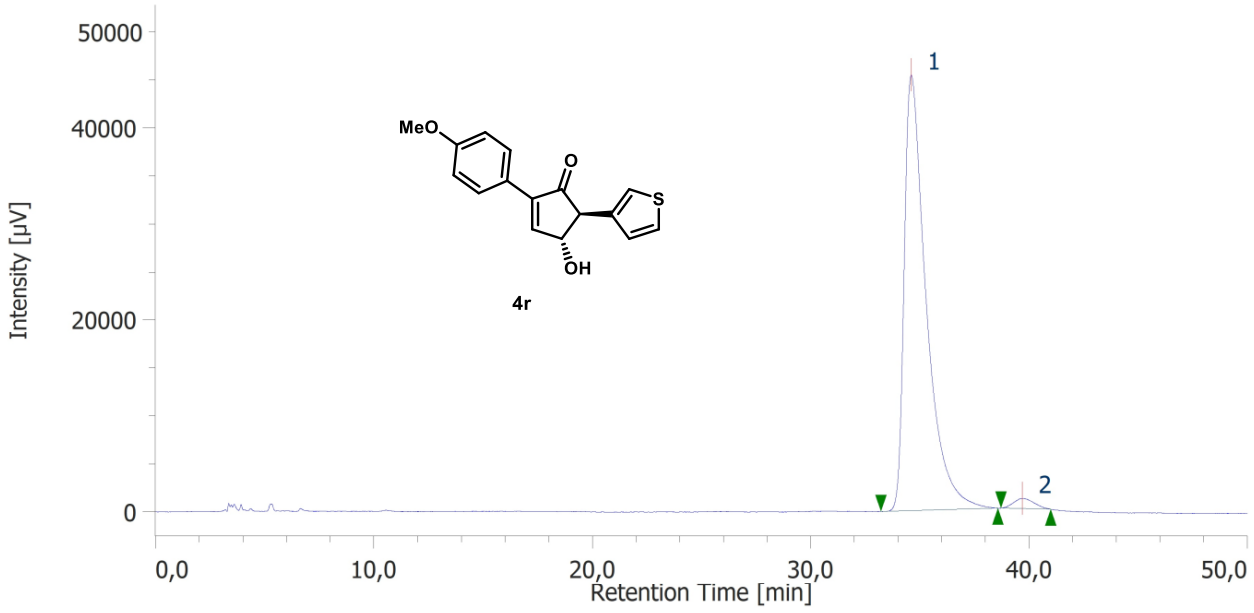


4r

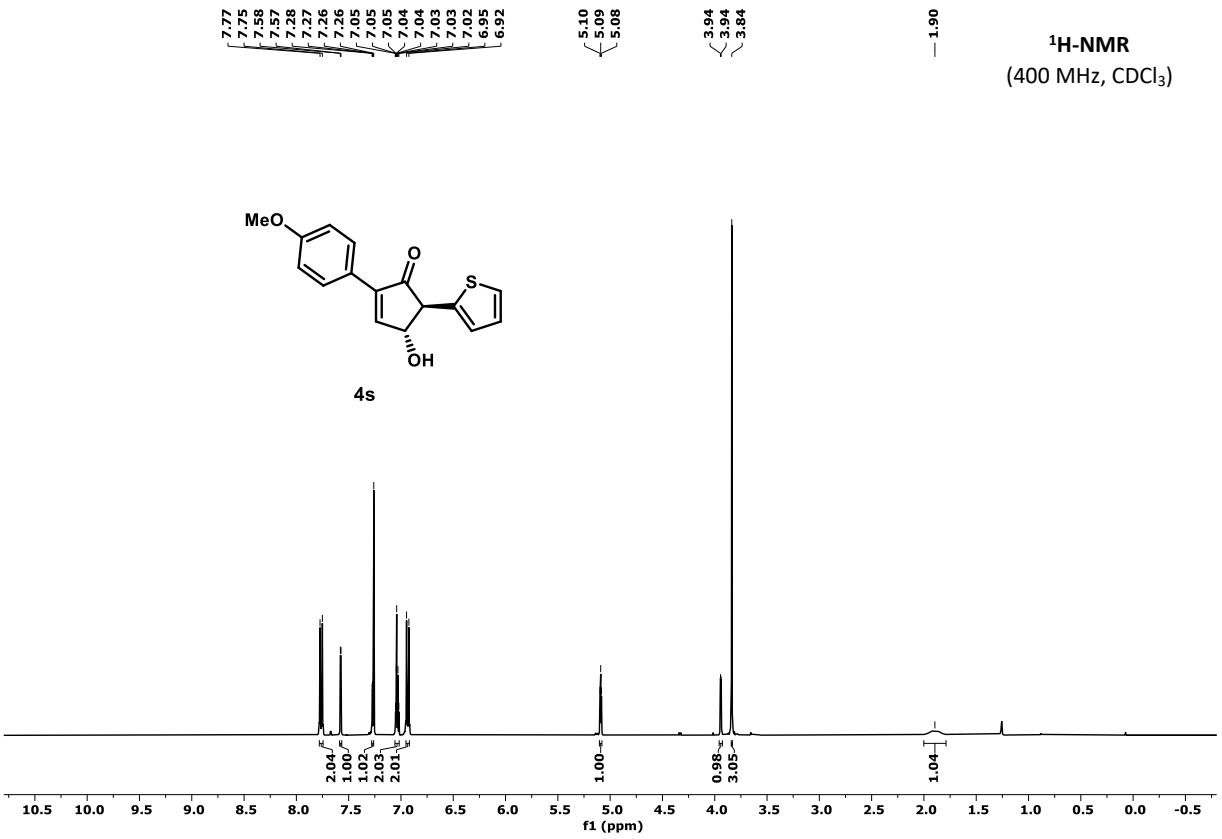


#	Peak Name	CH	tR [min]	Area [μV·sec]	Height [μV]	Area%	Height%	Quantity	NTP	Resolution	Symmetry Factor	Warning
1	Unknown	15	34,300	2949869	42494	49,316	52,749	N/A	6406	2,497	1,969	
2	Unknown	15	38,873	3031745	38066	50,684	47,251	N/A	6306	N/A	1,994	

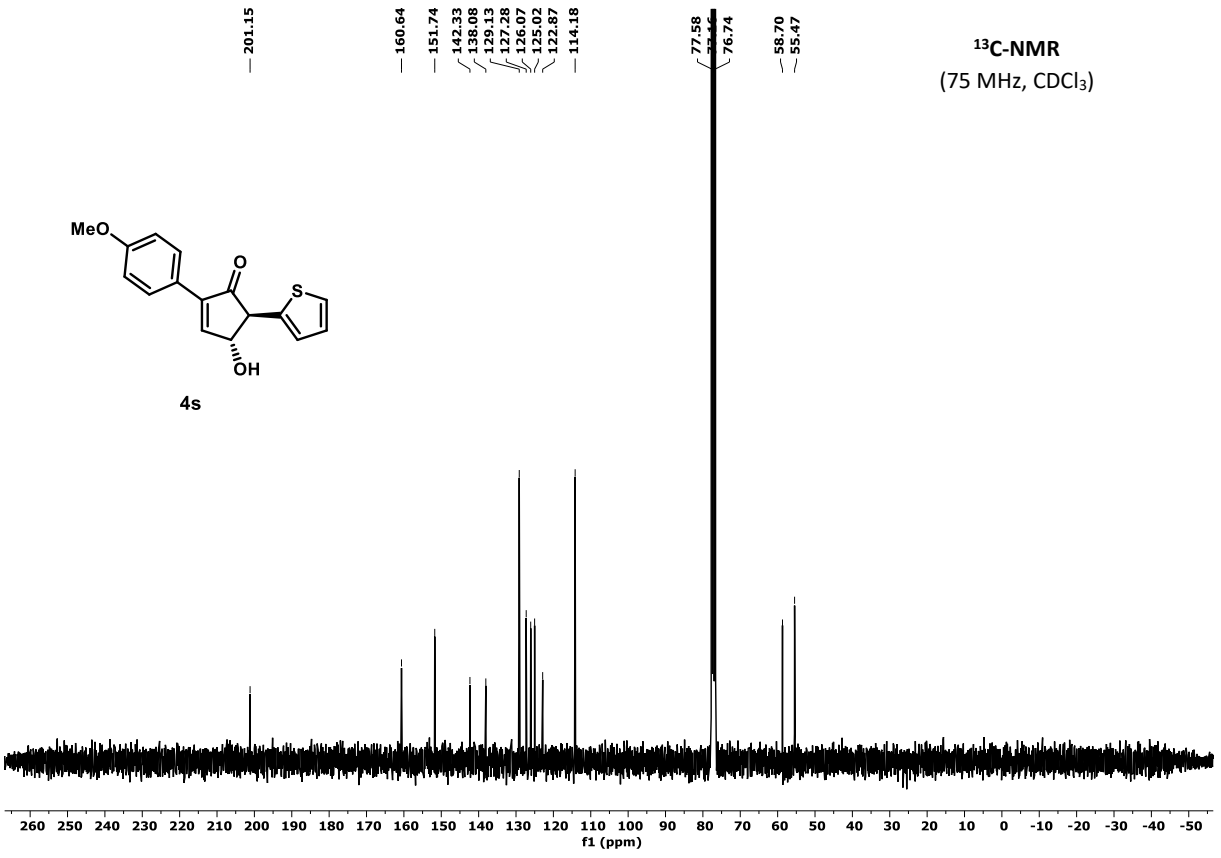
Daicel Chiralpak IB column (90:10 *n*-Hexane/*i*-PrOH, 1.0 mL/min, 245 nm)



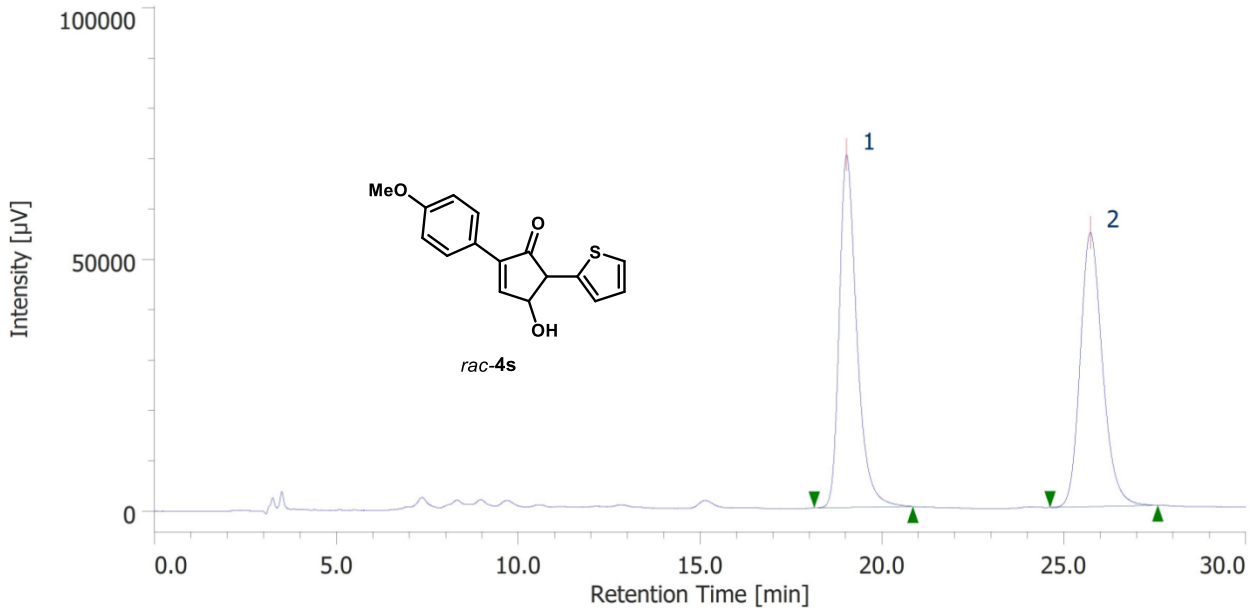
#	Peak Name	CH	tR [min]	Area [μV·sec]	Height [μV]	Area%	Height%	Quantity	NTP	Resolution	Symmetry Factor	Warning
1	Unknown	11	34,597	3171485	45372	97,881	97,731	N/A	6553	2,912	2,015	
2	Unknown	11	39,677	68671	1054	2,119	2,269	N/A	7876	N/A	1,201	



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

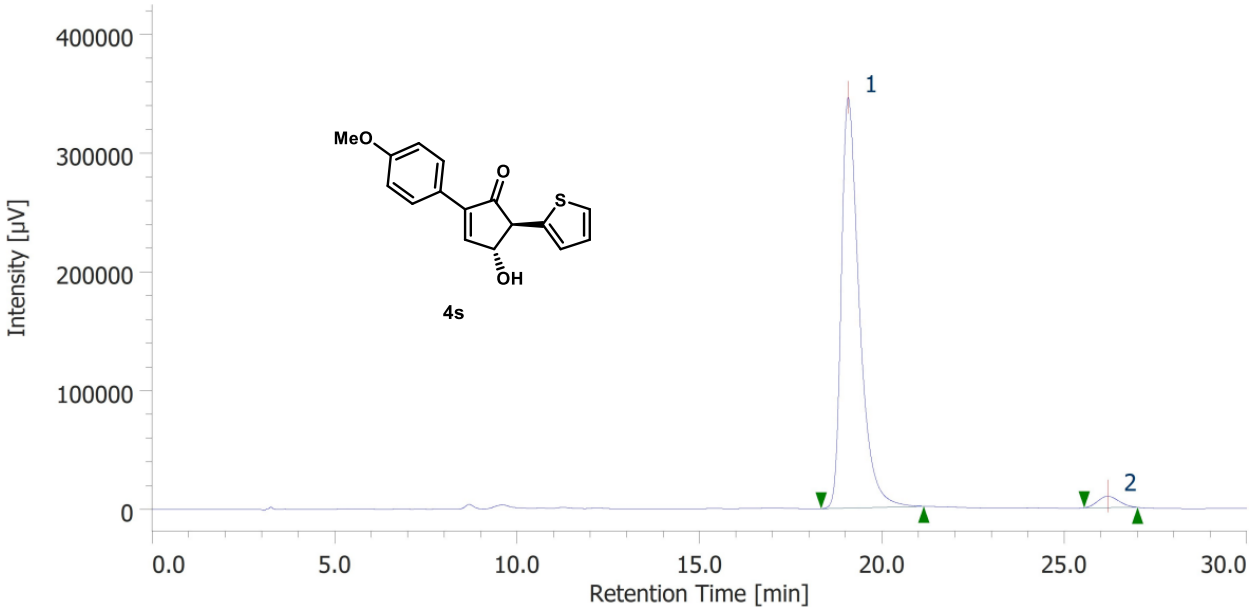


^{13}C-NMR
(75 MHz, $CDCl_3$)



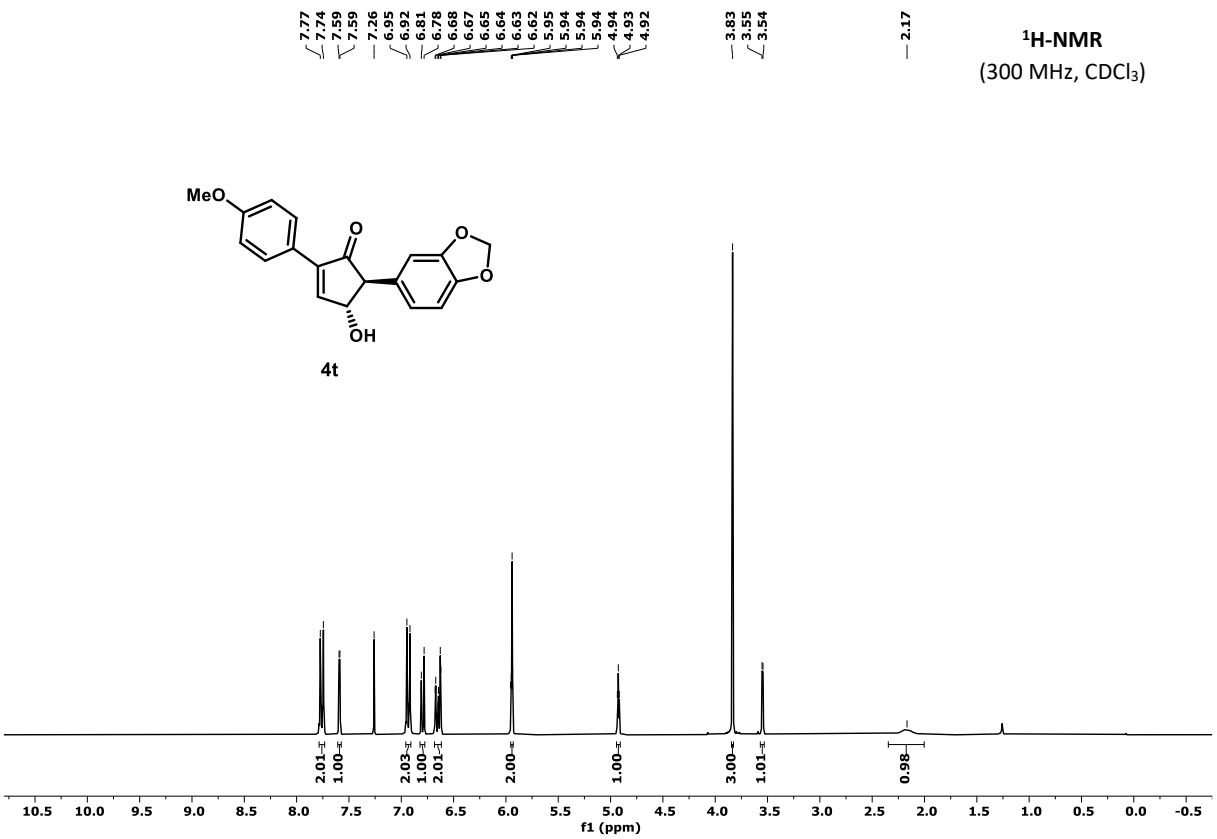
#	Peak Name	CH	tR [min]	Area [μV·sec]	Height [μV]	Area%	Height%	Quantity	NTP	Resolution	Symmetry Factor	Warning
1	Unknown	11	19.023	2339537	69983	50.257	56.264	N/A	8273	6.963	1.387	
2	Unknown	11	25.723	2315576	54400	49.743	43.736	N/A	8863	N/A	1.209	

Daicel Chiralpak IA column (80:20 *n*-Hexane/*i*-PrOH, 1.0 mL/min, 245 nm)

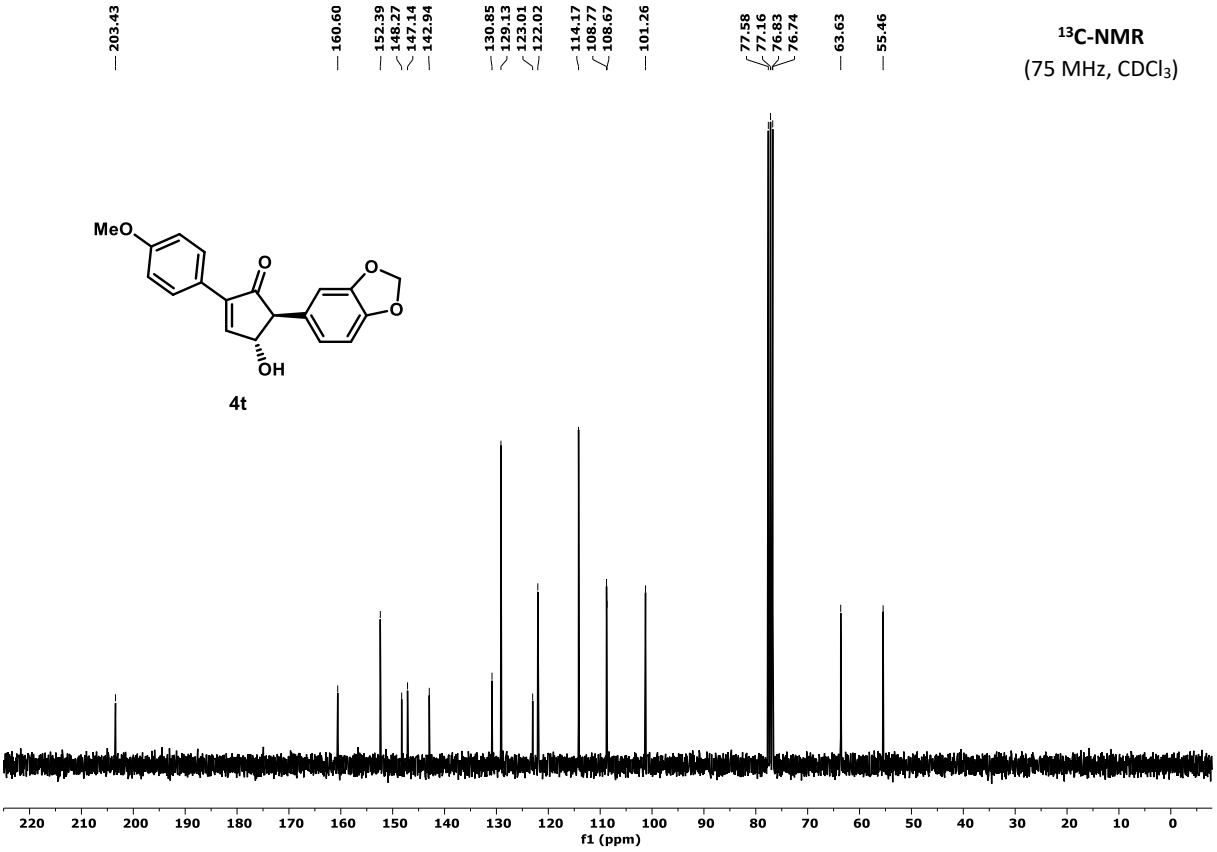


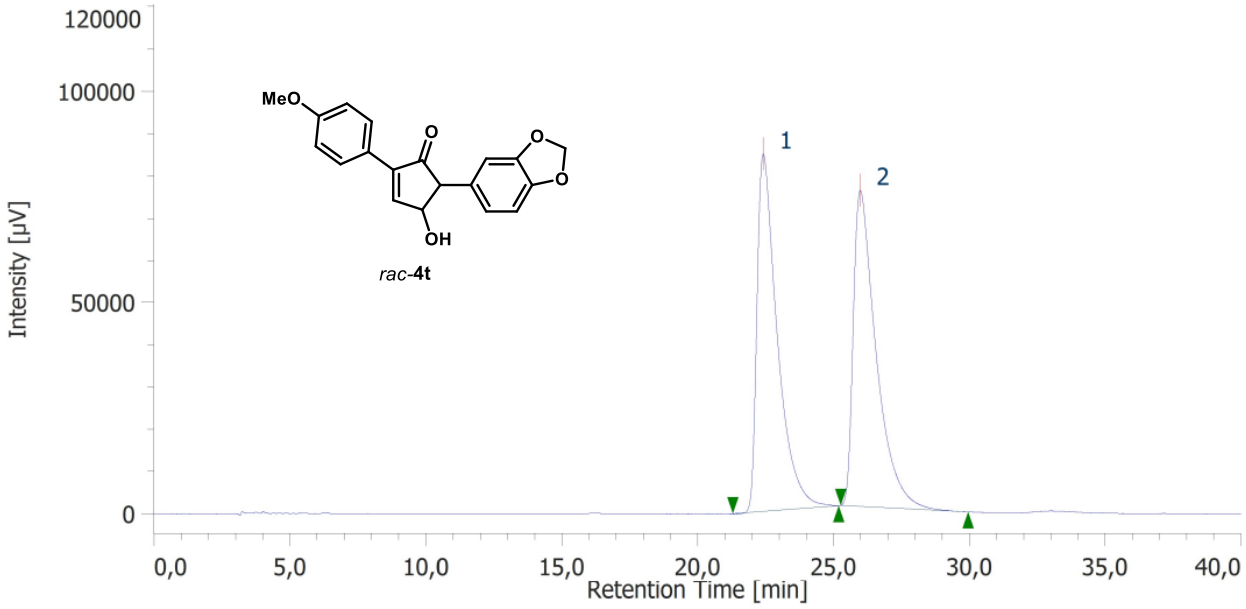
#	Peak Name	CH	tR [min]	Area [μV·sec]	Height [μV]	Area%	Height%	Quantity	NTP	Resolution	Symmetry Factor	Warning
1	Unknown	11	19.073	11843172	345514	96.834	97.306	N/A	7924	7.298	1.551	
2	Unknown	11	26.183	387245	9567	3.166	2.694	N/A	9122	N/A	1.121	

^{1}H-NMR
(300 MHz, $CDCl_3$)



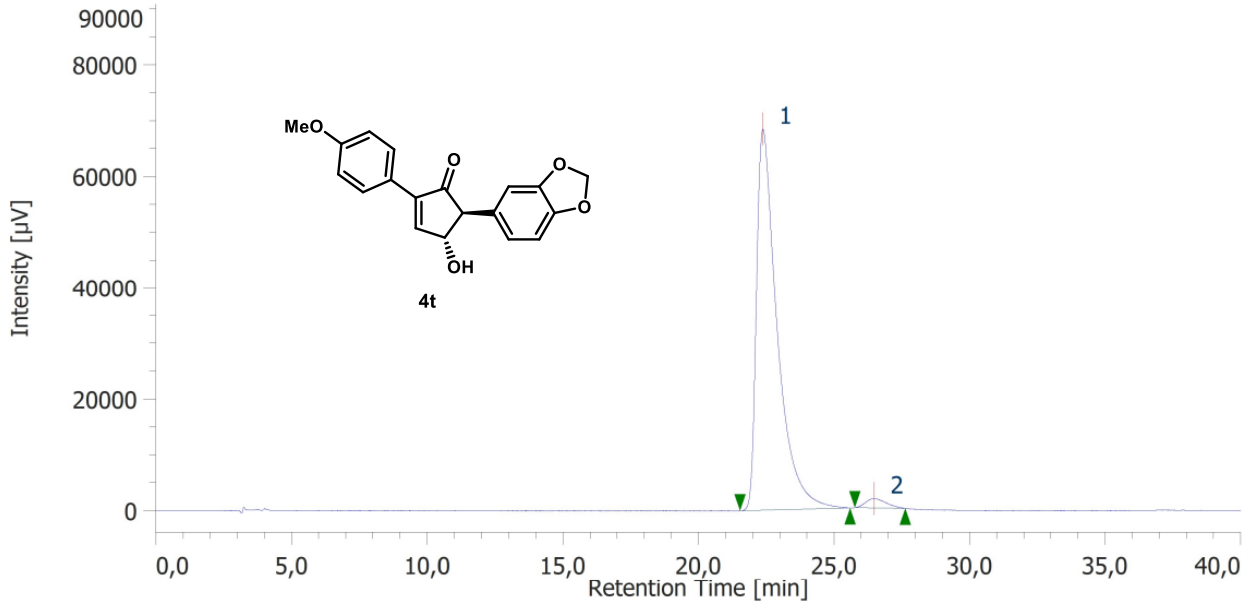
^{13}C-NMR
(75 MHz, $CDCl_3$)





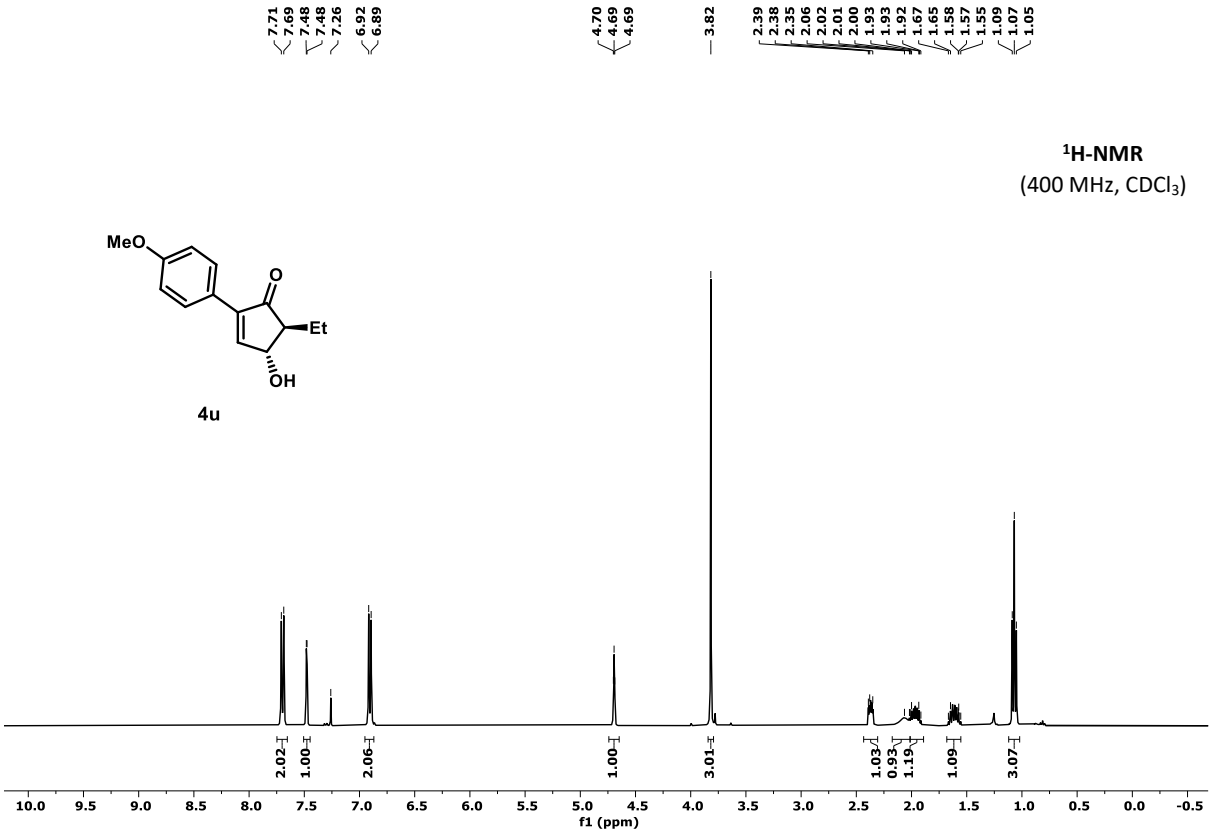
#	Peak Name	CH	tR [min]	Area [μV·sec]	Height [μV]	Area%	Height%	Quantity	NTP	Resolution	Symmetry Factor	Warning
1	Unknown	11	22,407	4400193	84655	50,117	53,049	N/A	4860	2,624	2,099	
2	Unknown	11	25,980	4379596	74925	49,883	46,951	N/A	5171	N/A	2,116	

Daicel Chiralpak IB column (80:20 *n*-Hexane/*i*-PrOH, 1.0 mL/min, 284 nm)

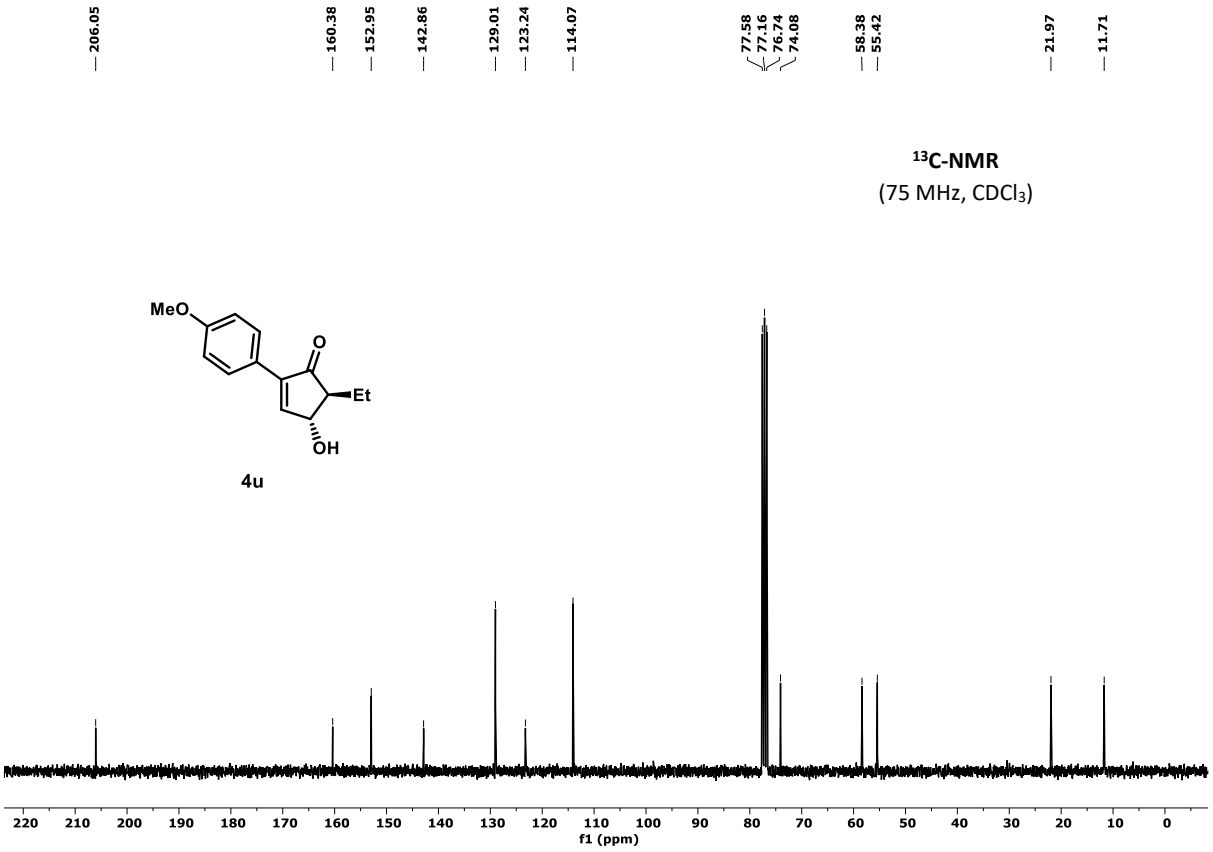


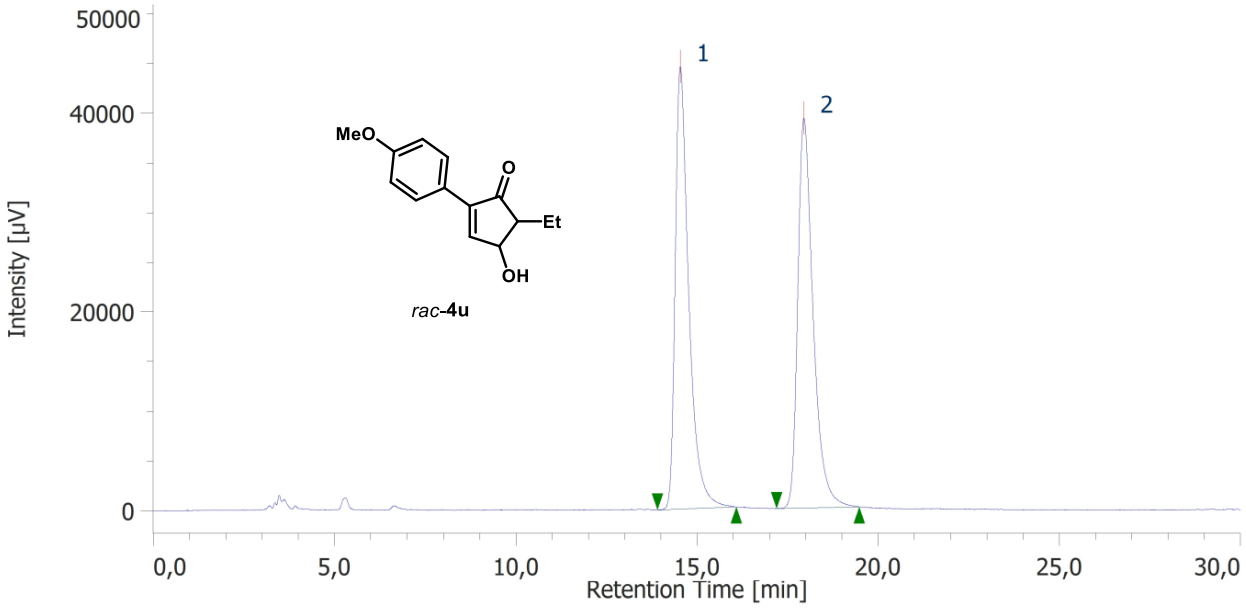
#	Peak Name	CH	tR [min]	Area [μV·sec]	Height [μV]	Area%	Height%	Quantity	NTP	Resolution	Symmetry Factor	Warning
1	Unknown	11	22,373	3618474	68328	97,612	97,601	N/A	4831	3,045	2,107	
2	Unknown	11	26,480	88520	1680	2,388	2,399	N/A	5585	N/A	1,300	

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



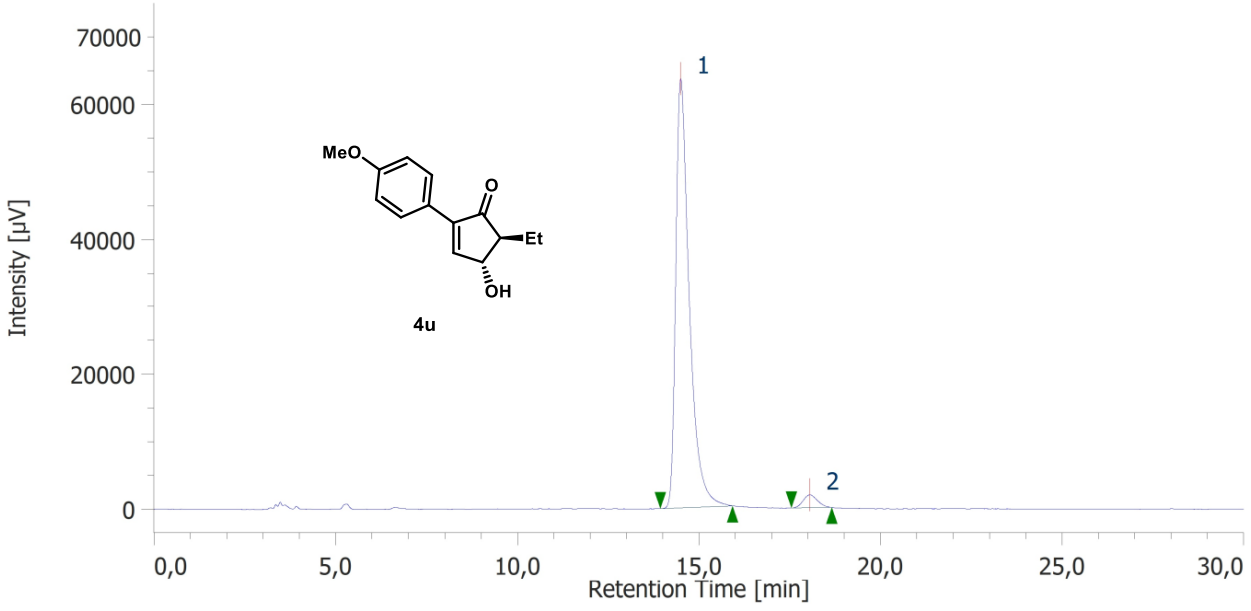
^{13}C-NMR
(75 MHz, $CDCl_3$)





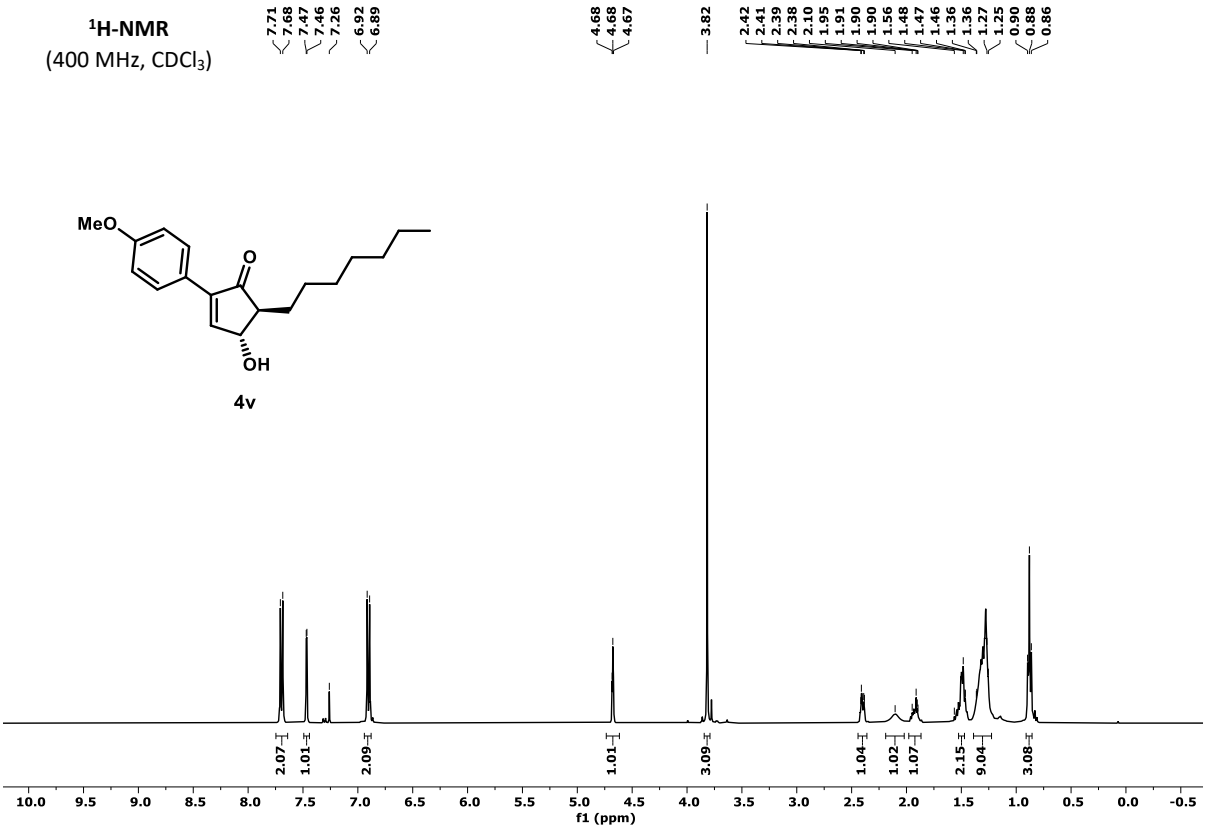
#	Peak Name	CH	tR [min]	Area [μV·sec]	Height [μV]	Area%	Height%	Quantity	NTP	Resolution	Symmetry Factor	Warning
1	Unknown	11	14,533	1152974	44503	50,007	53,163	N/A	8306	4,981	1,632	
2	Unknown	11	17,943	1152648	39208	49,993	46,837	N/A	9533	N/A	1,464	

Daicel Chiralpak IB column (90:10 *n*-Hexane/*i*-PrOH, 1.0 mL/min, 245 nm)

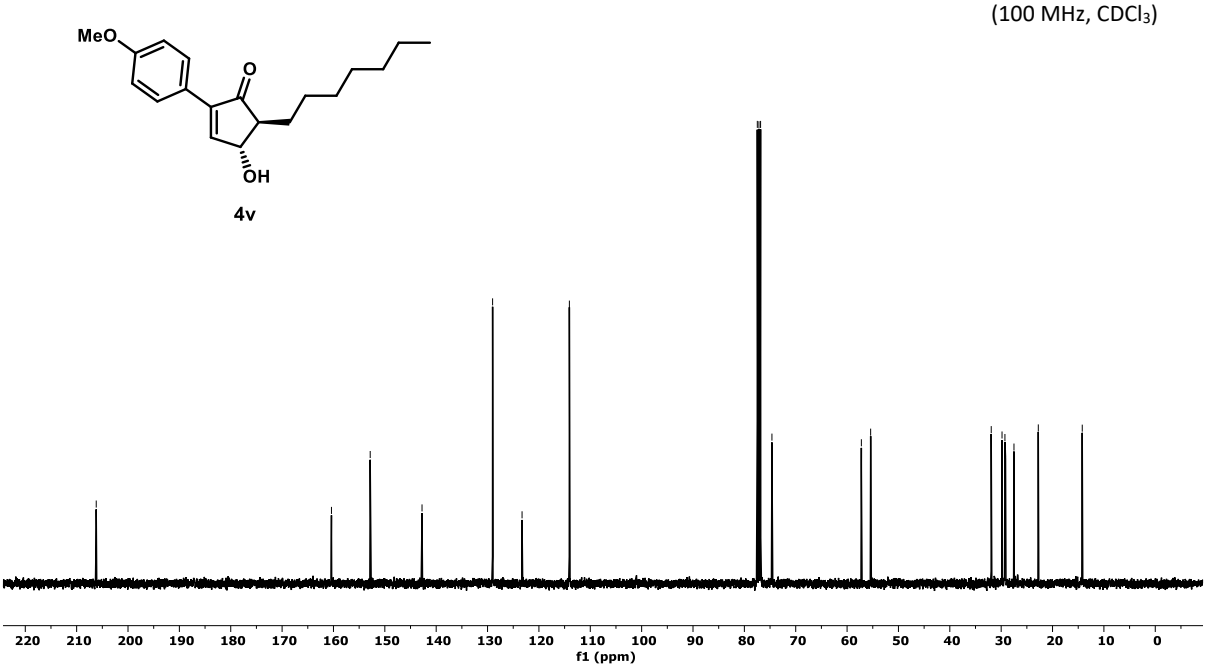


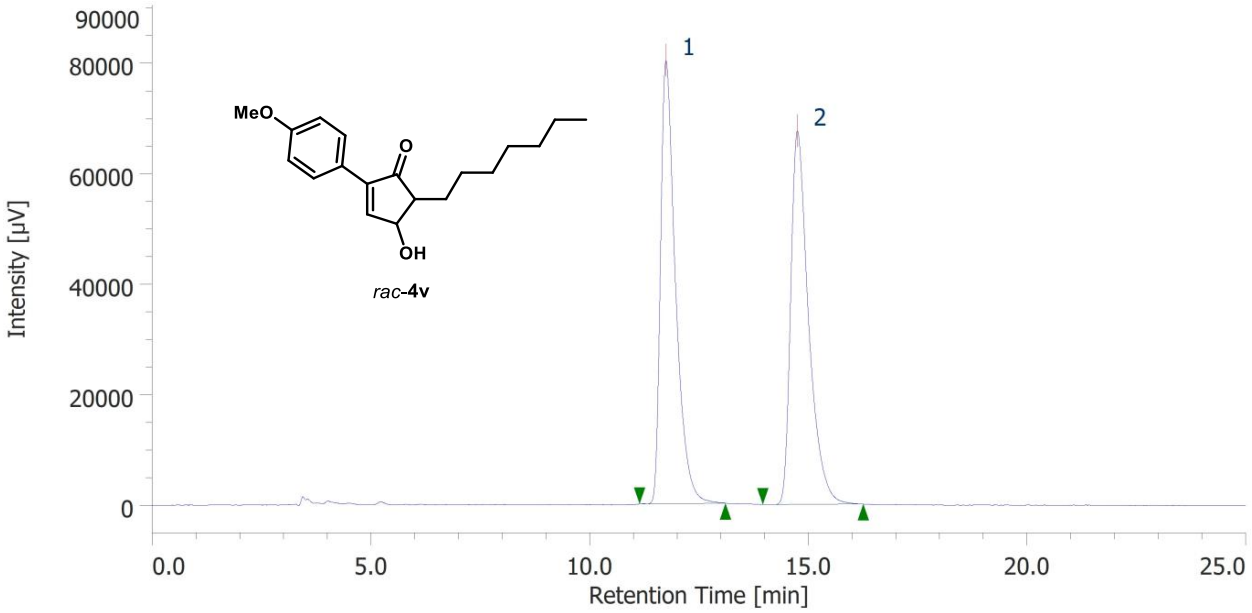
#	Peak Name	CH	tR [min]	Area [μV·sec]	Height [μV]	Area%	Height%	Quantity	NTP	Resolution	Symmetry Factor	Warning
1	Unknown	11	14,490	1639537	63574	96,949	97,102	N/A	8285	5,221	1,691	
2	Unknown	11	18,047	51591	1897	3,051	2,898	N/A	9797	N/A	1,148	

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



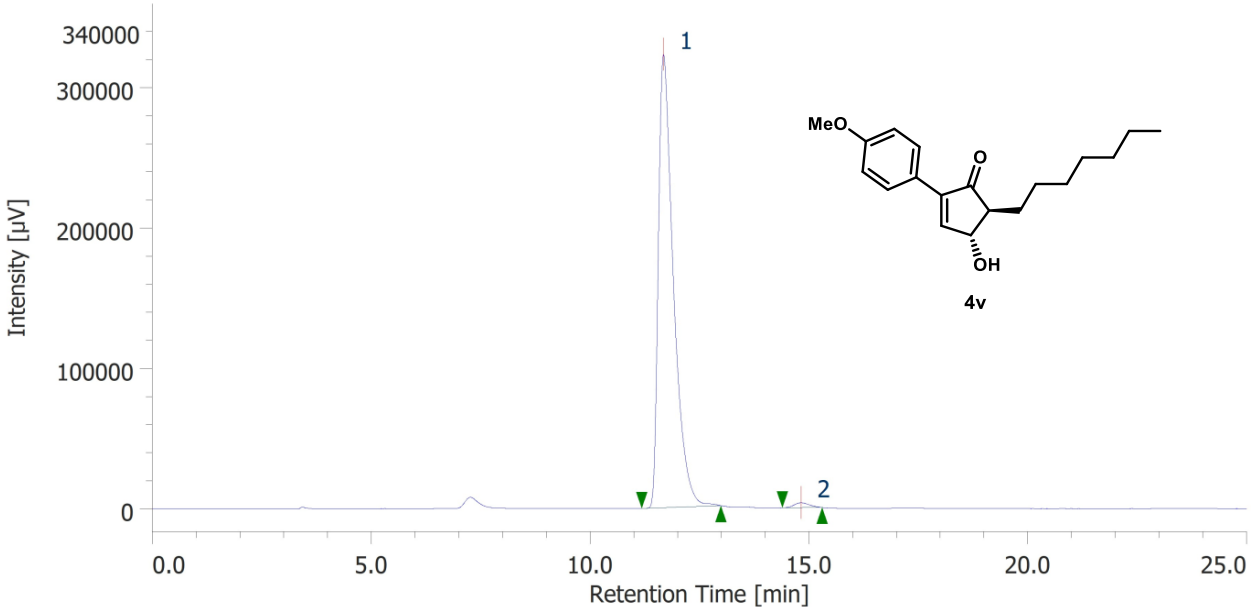
^{13}C-NMR
(100 MHz, $CDCl_3$)





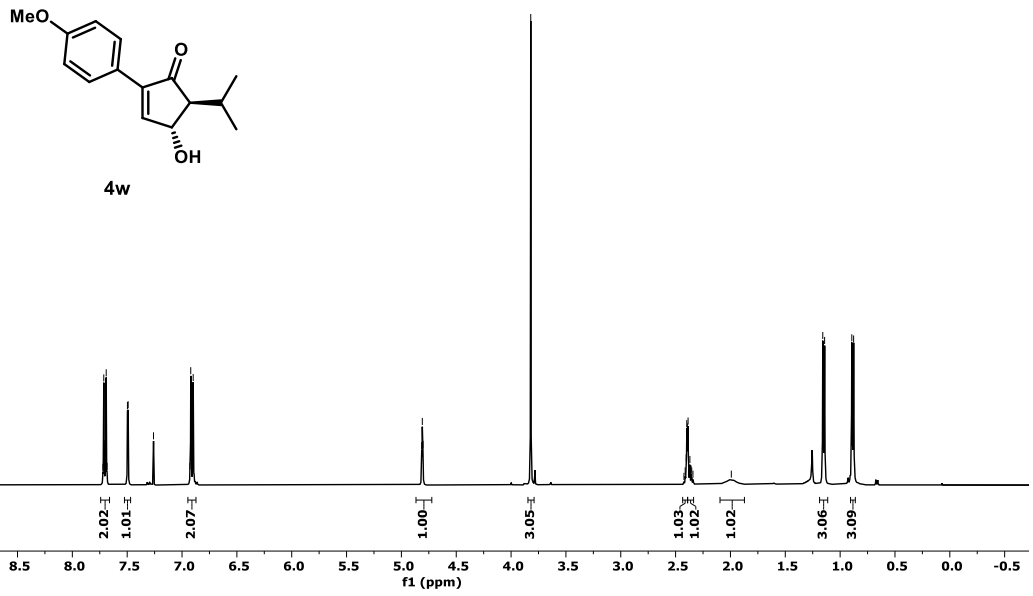
#	Peak Name	CH	tR [min]	Area [μV·sec]	Height [μV]	Area%	Height%	Quantity	NTP	Resolution	Symmetry Factor	Warning
1	Unknown	11	11.743	1906373	80173	49.902	54.266	N/A	6162	4.599	1.646	
2	Unknown	11	14.747	1913875	67569	50.098	45.734	N/A	6881	N/A	1.593	

Daicel Chiralpak IB column (90:10 *n*-Hexane/*i*-PrOH, 1.0 mL/min, 245 nm)



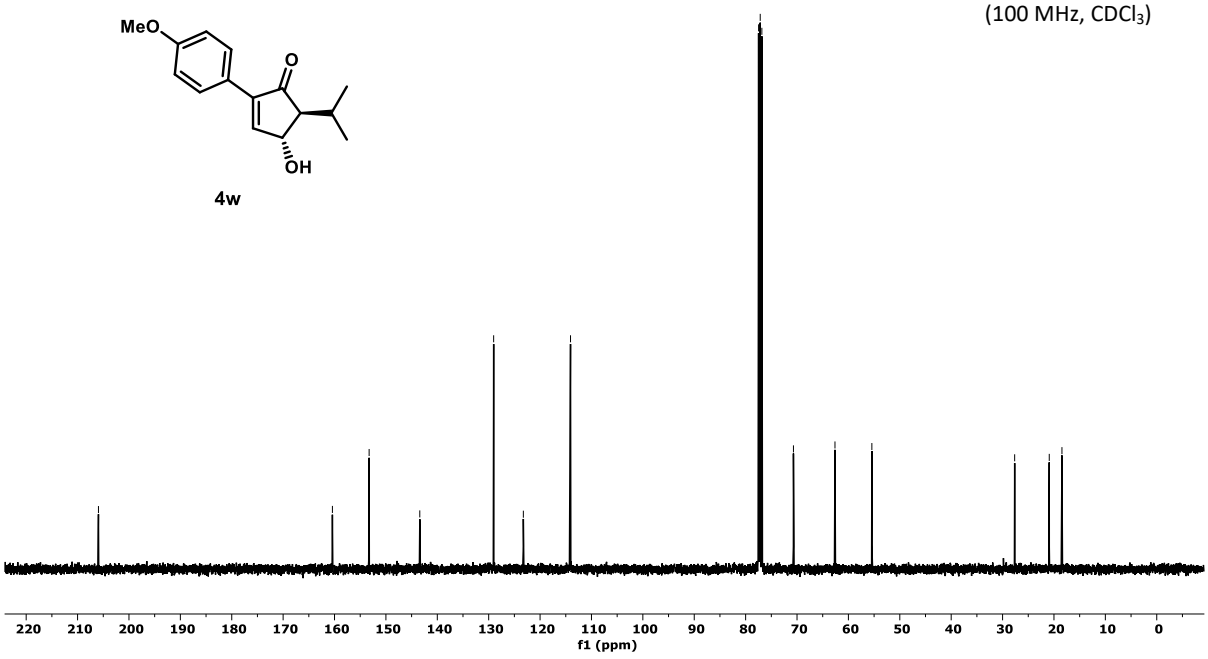
#	Peak Name	CH	tR [min]	Area [μV·sec]	Height [μV]	Area%	Height%	Quantity	NTP	Resolution	Symmetry Factor	Warning
1	Unknown	11	11.673	7711627	322750	98.894	98.921	N/A	5992	4.987	1.815	
2	Unknown	11	14.813	86269	3519	1.106	1.079	N/A	8073	N/A	1.140	

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

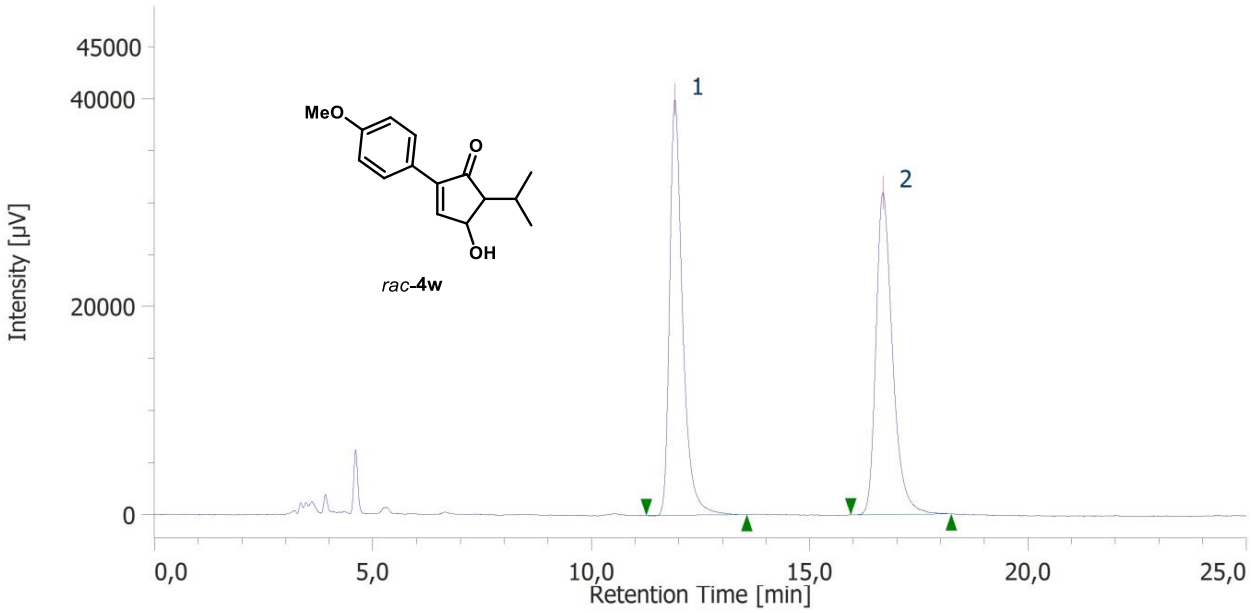


4w

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

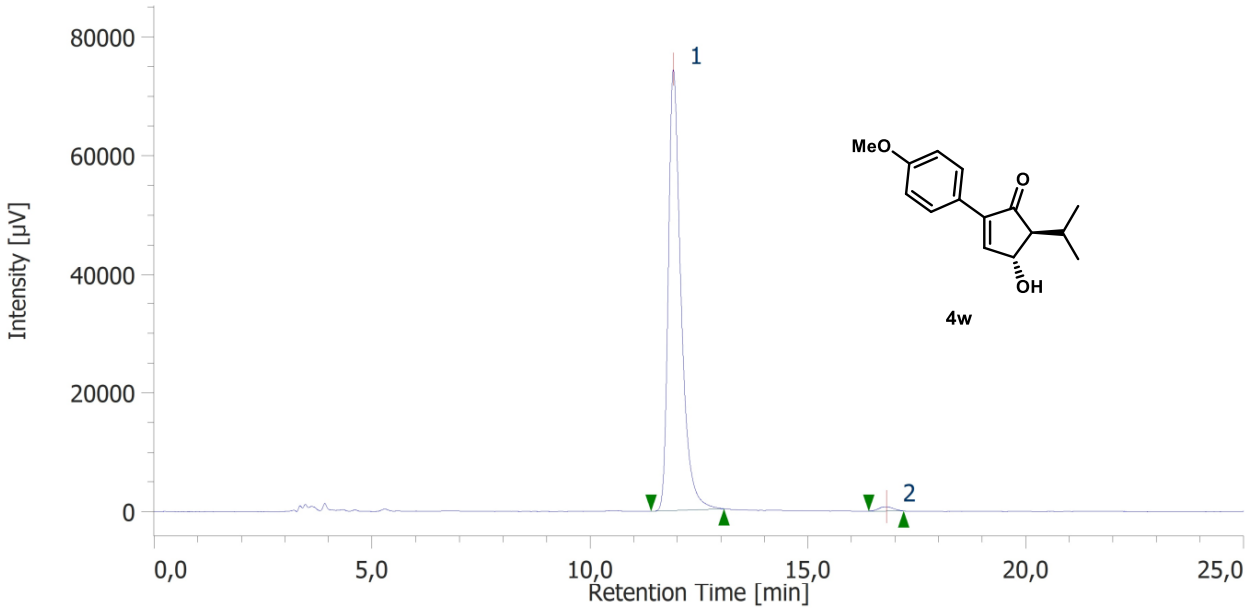


4w



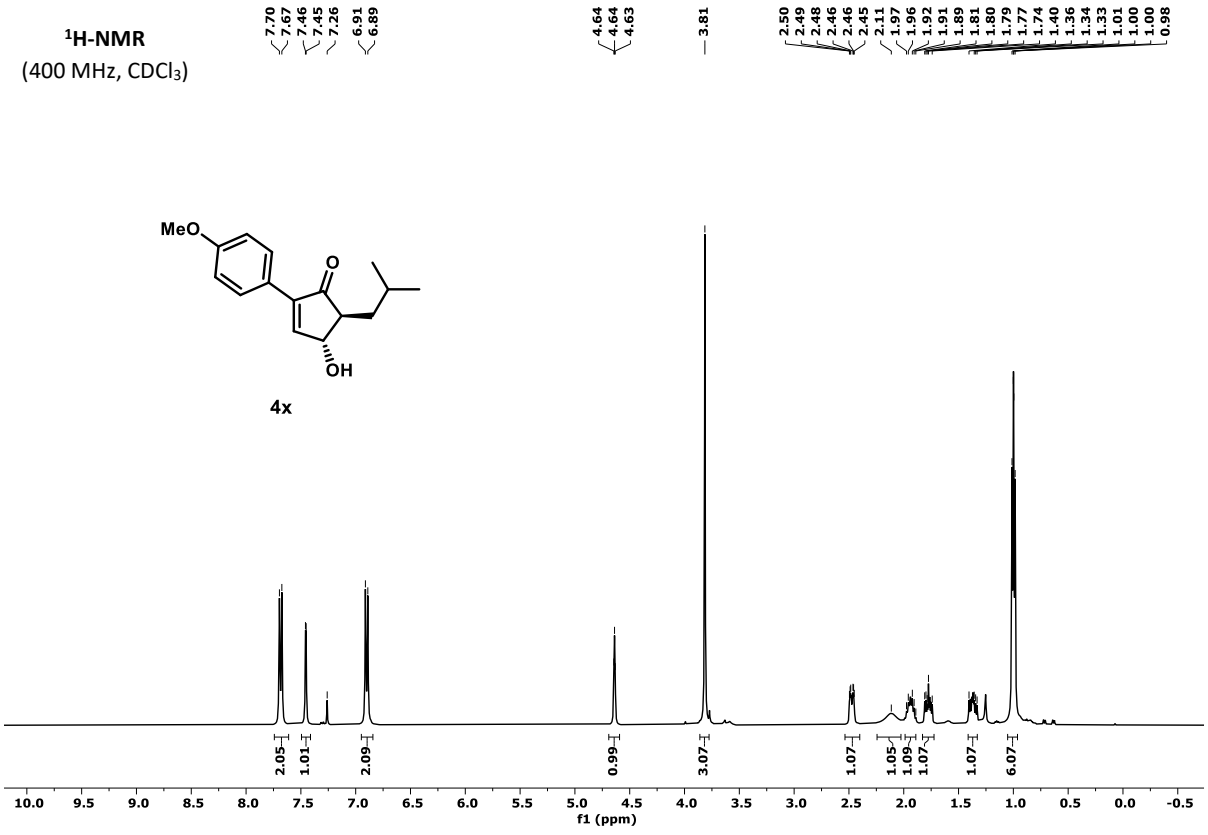
#	Peak Name	CH	tR [min]	Area [μV·sec]	Height [μV]	Area%	Height%	Quantity	NTP	Resolution	Symmetry Factor	Warning
1	Unknown	13	11,907	822865	39952	50,218	56,322	N/A	8785	8,168	1,466	
2	Unknown	13	16,673	815717	30983	49,782	43,678	N/A	10144	N/A	1,355	

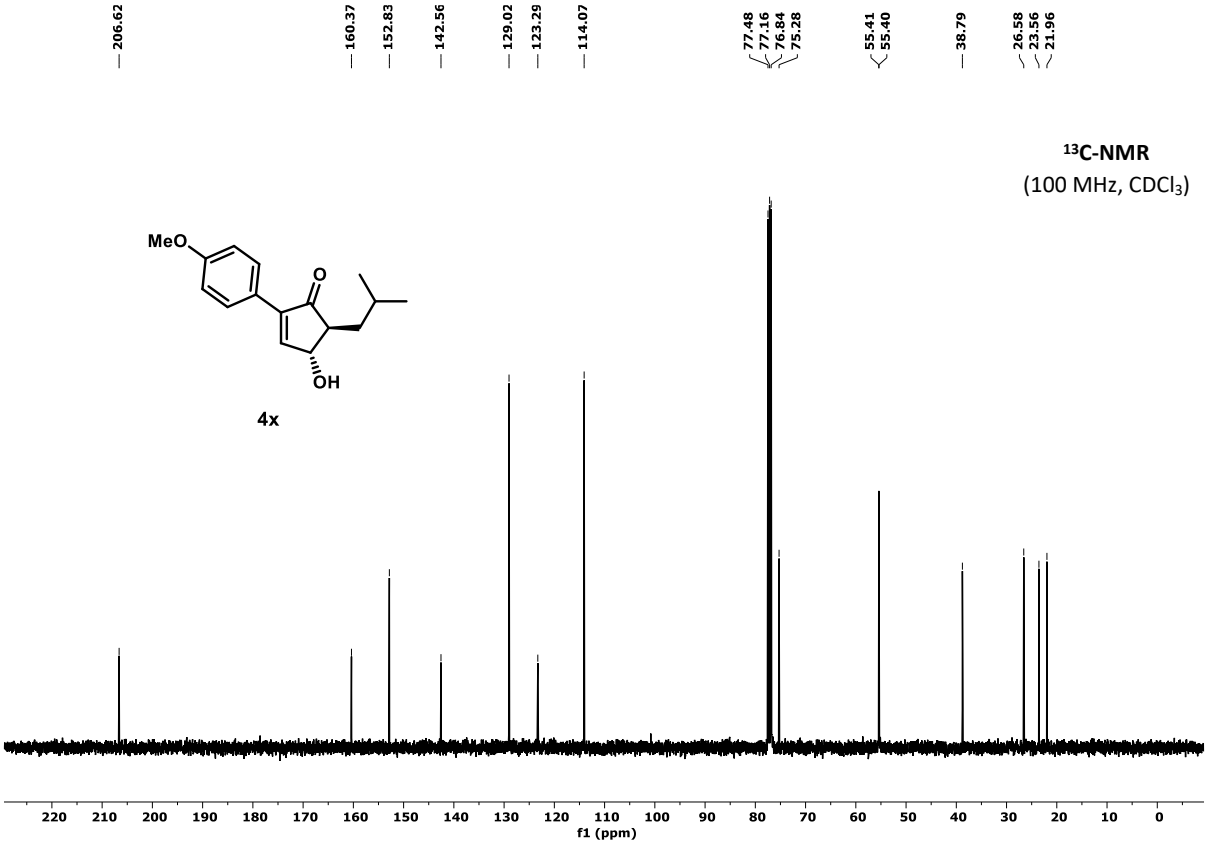
Daicel Chiralpak IB column (90:10 *n*-Hexane/*i*-PrOH, 1.0 mL/min, 240 nm)



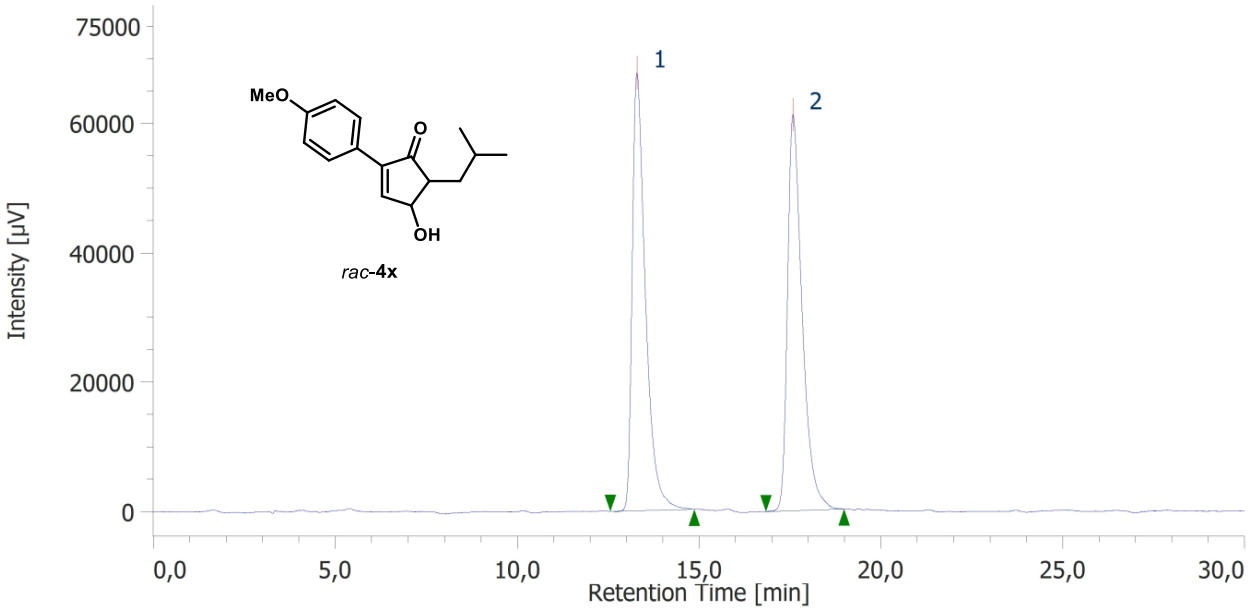
#	Peak Name	CH	tR [min]	Area [μV·sec]	Height [μV]	Area%	Height%	Quantity	NTP	Resolution	Symmetry Factor	Warning
1	Unknown	11	11,907	1505736	74297	98,918	99,046	N/A	8938	8,682	1,495	
2	Unknown	11	16,797	16470	716	1,082	0,954	N/A	11528	N/A	1,046	

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



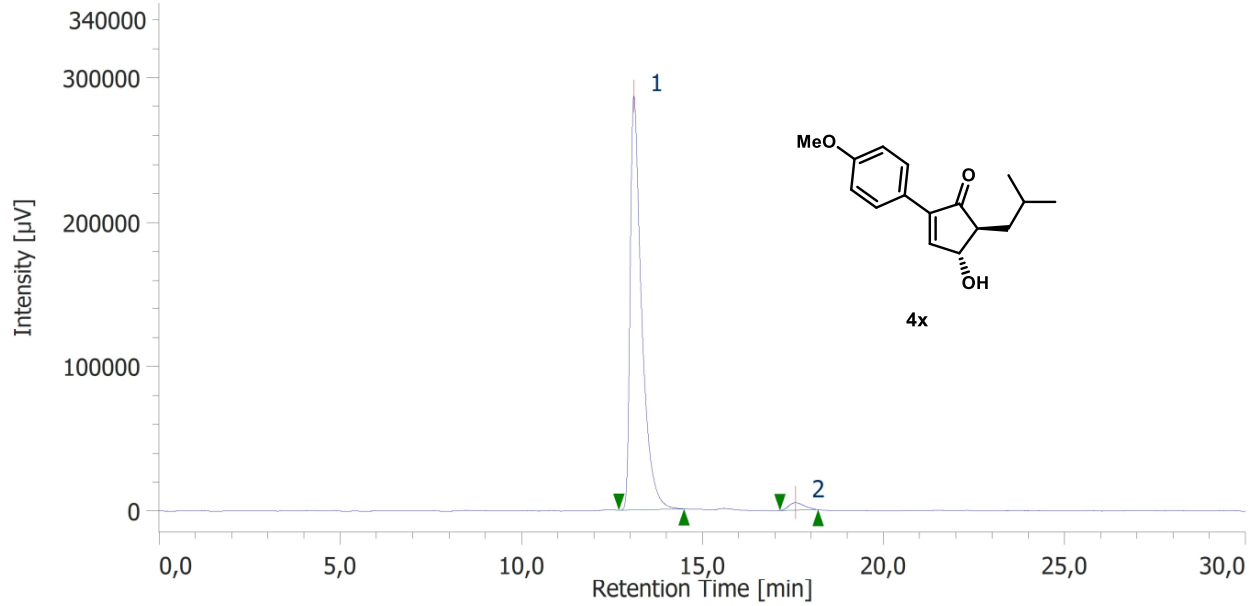


^{13}C-NMR
(100 MHz, $CDCl_3$)



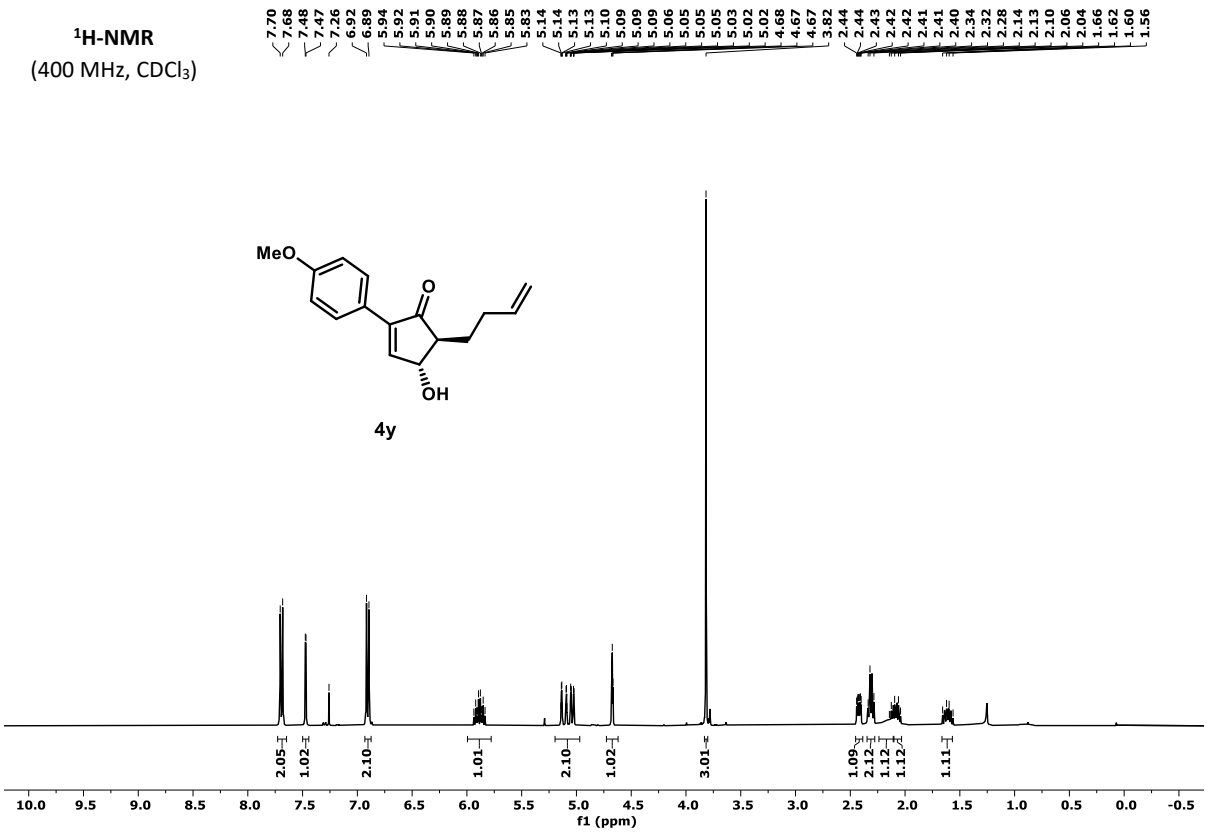
#	Peak Name	CH	tR [min]	Area [μV·sec]	Height [μV]	Area%	Height%	Quantity	NTP	Resolution	Symmetry Factor	Warning
1	Unknown	13	13,287	1704563	67652	49,971	52,536	N/A	7175	6,474	1,704	
2	Unknown	13	17,577	1706512	61120	50,029	47,464	N/A	10045	N/A	1,565	

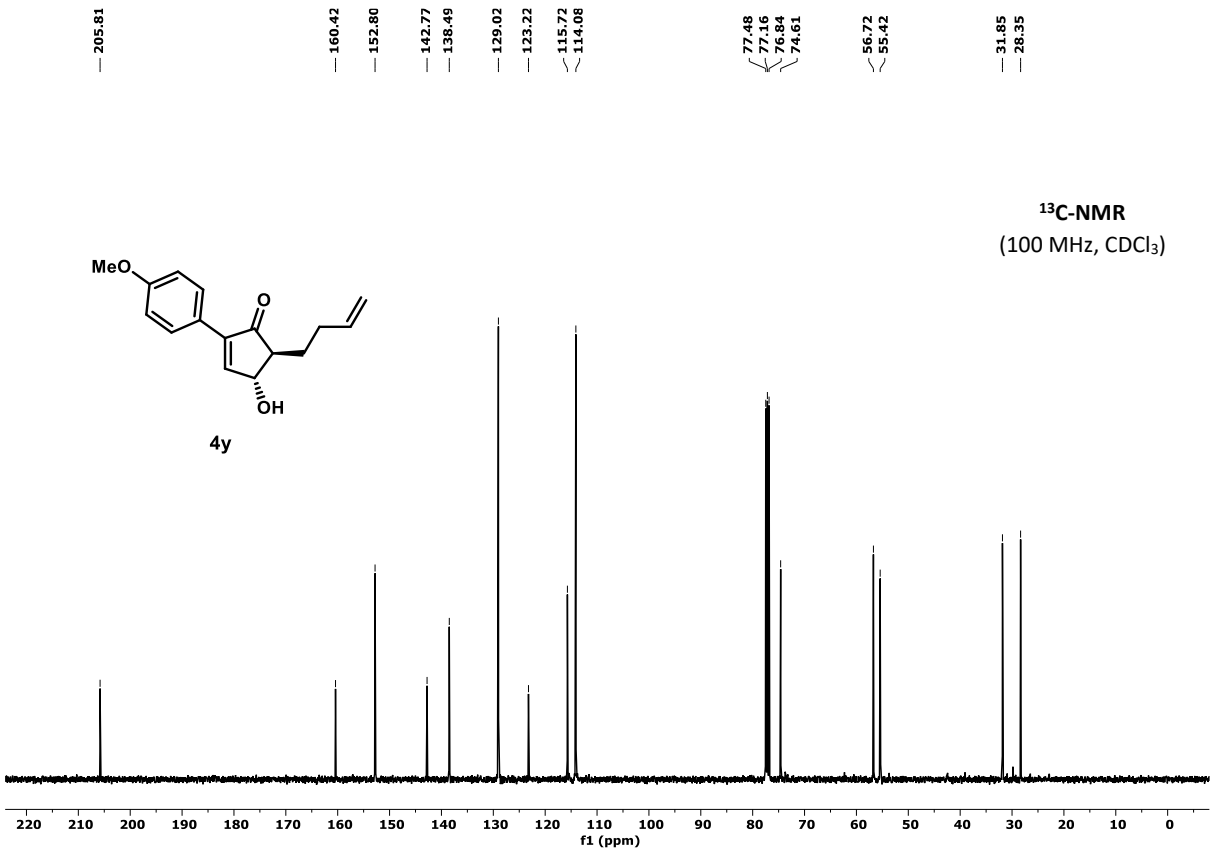
Daicel Chiralpak IB column (90:10 *n*-Hexane/*i*-PrOH, 1.0 mL/min, 290 nm)



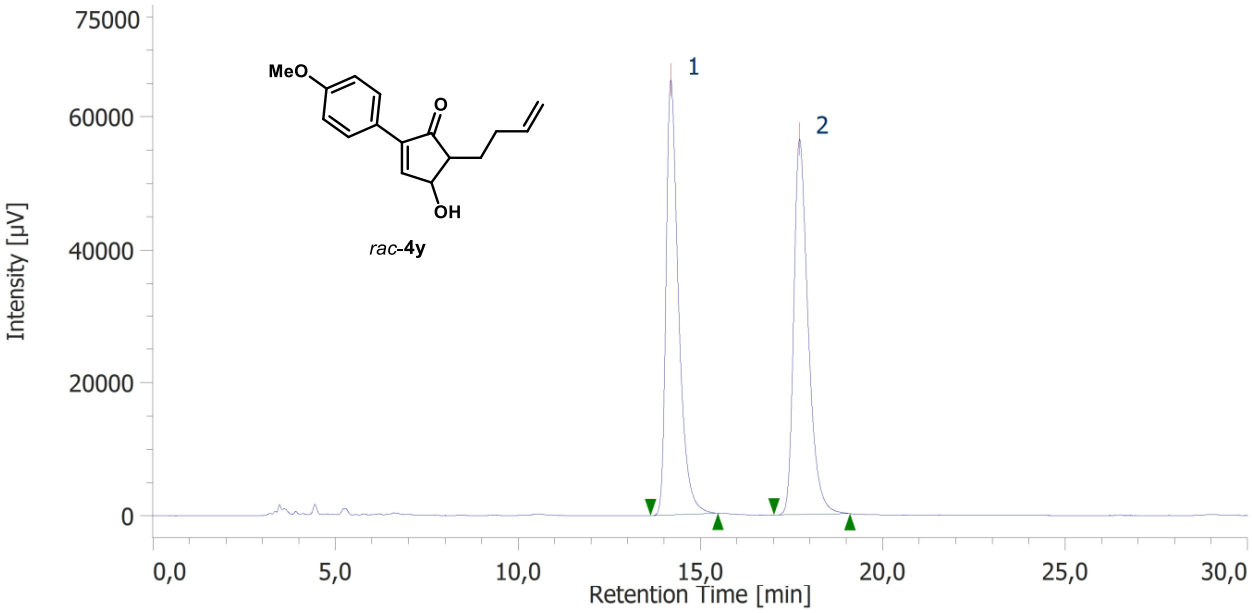
#	Peak Name	CH	tR [min]	Area [μV·sec]	Height [μV]	Area%	Height%	Quantity	NTP	Resolution	Symmetry Factor	Warning
1	Unknown	11	13,103	6284555	286294	97,565	98,209	N/A	9545	6,658	1,953	
2	Unknown	11	17,570	156847	5221	2,435	1,791	N/A	7550	N/A	1,235	

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



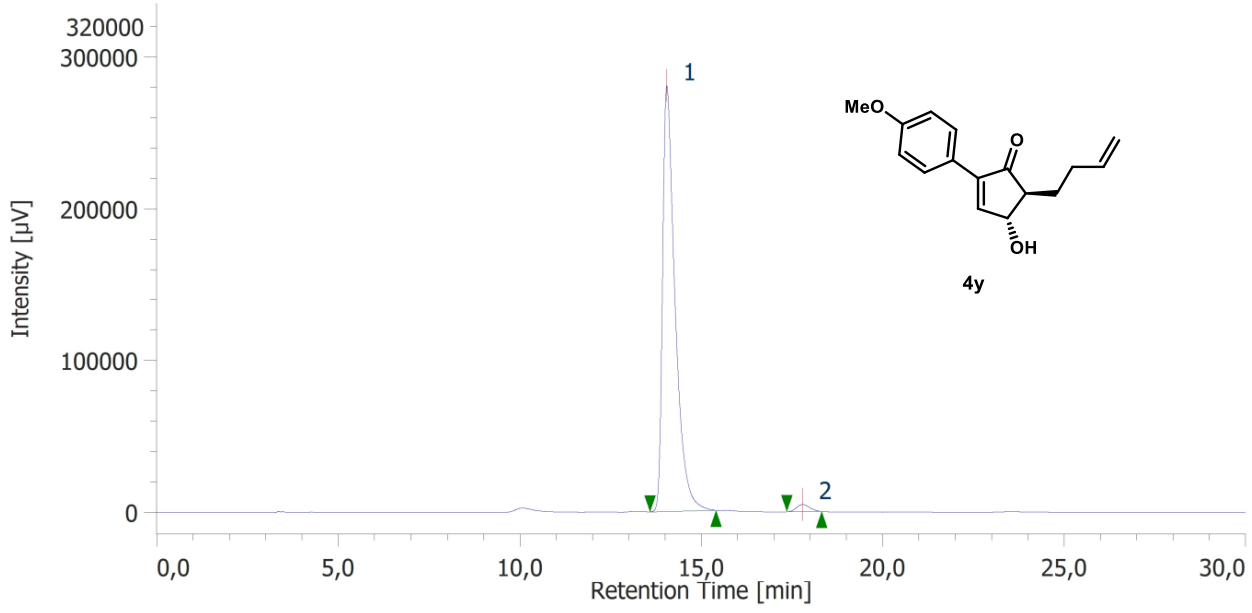


^{13}C-NMR
(100 MHz, $CDCl_3$)



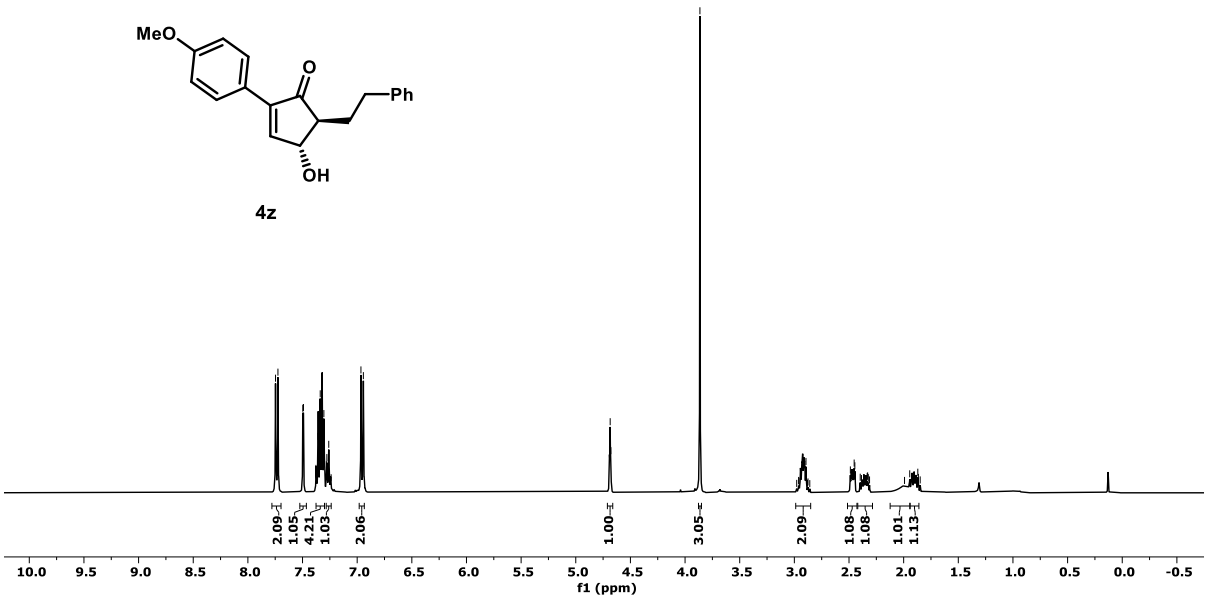
#	Peak Name	CH	tR [min]	Area [μV·sec]	Height [μV]	Area%	Height%	Quantity	NTP	Resolution	Symmetry Factor	Warning
1	Unknown	12	14,183	1548975	65359	50,004	53,662	N/A	9234	5,515	1,557	
2	Unknown	12	17,713	1548722	56438	49,996	46,338	N/A	10451	N/A	1,420	

Daicel Chiralpak IB column (90:10 *n*-Hexane/*i*-PrOH, 1.0 mL/min, 245 nm)

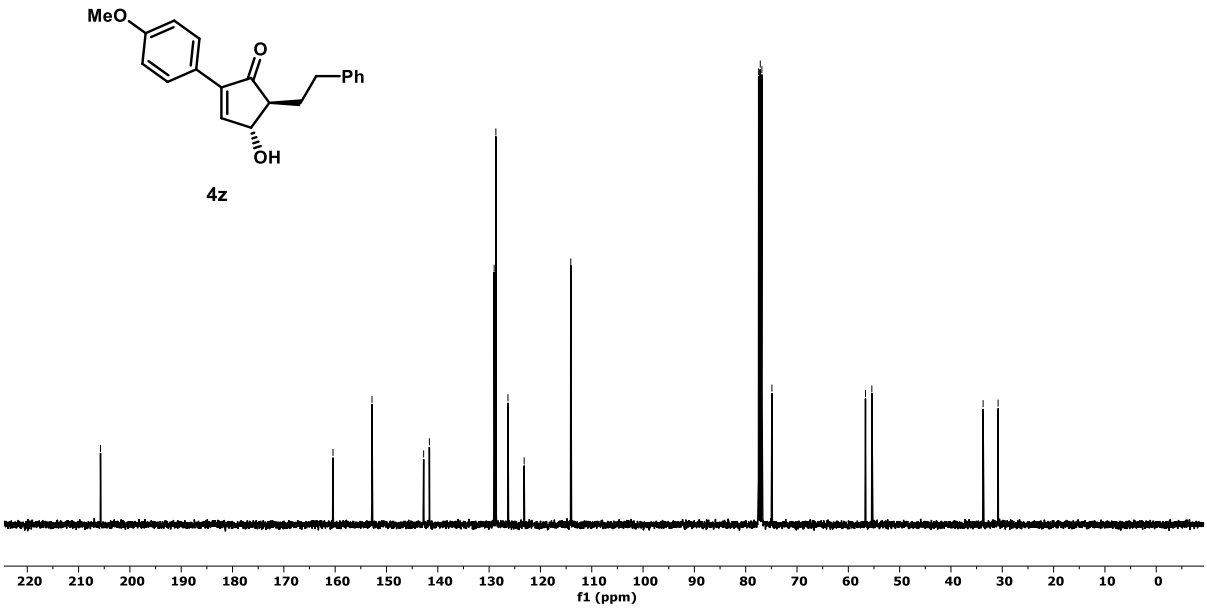


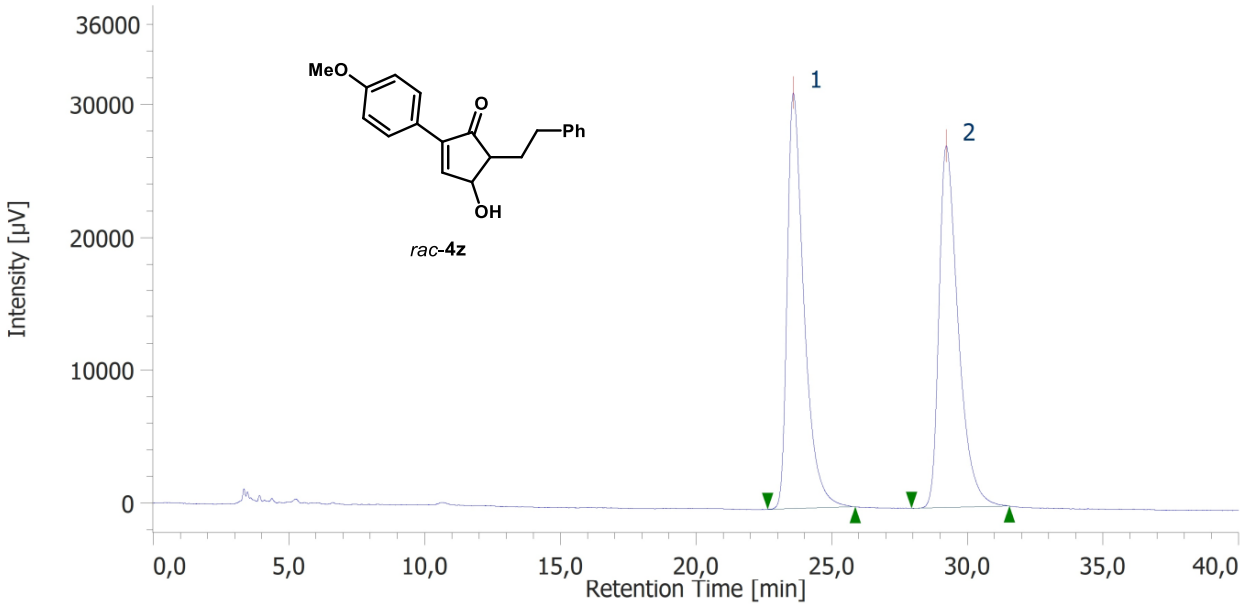
#	Peak Name	CH	tR [min]	Area [μV·sec]	Height [μV]	Area%	Height%	Quantity	NTP	Resolution	Symmetry Factor	Warning
1	Unknown	12	14,043	6701033	280383	98,257	98,350	N/A	8962	5,911	1,816	
2	Unknown	12	17,787	118870	4703	1,743	1,650	N/A	11058	N/A	1,142	

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



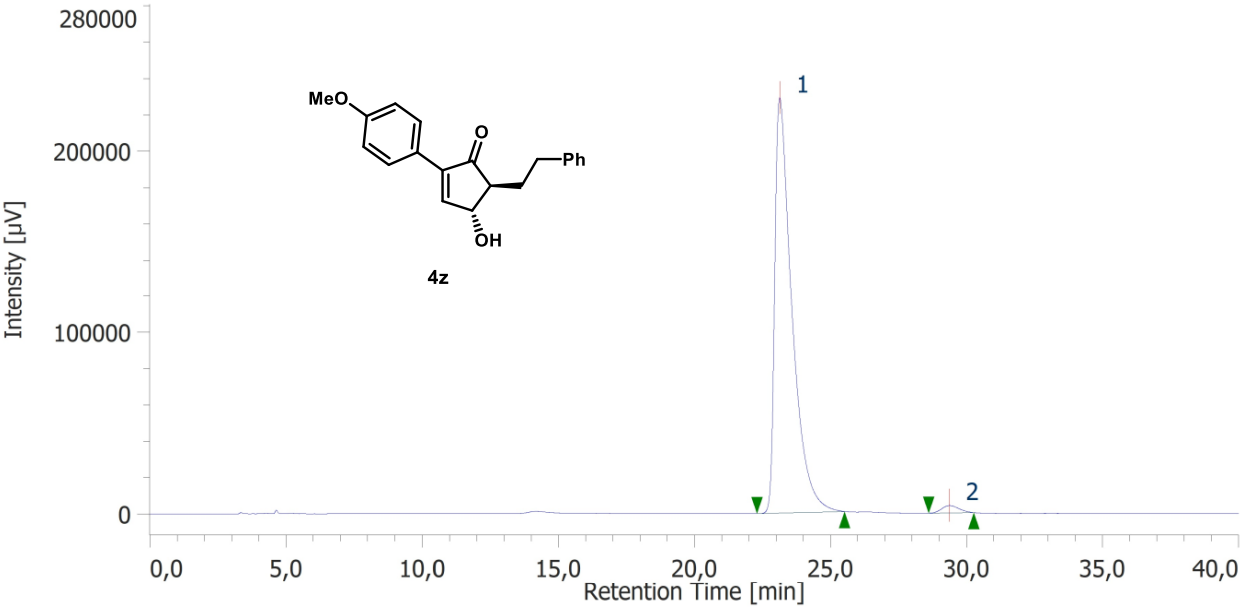
^{13}C-NMR
(100 MHz, $CDCl_3$)





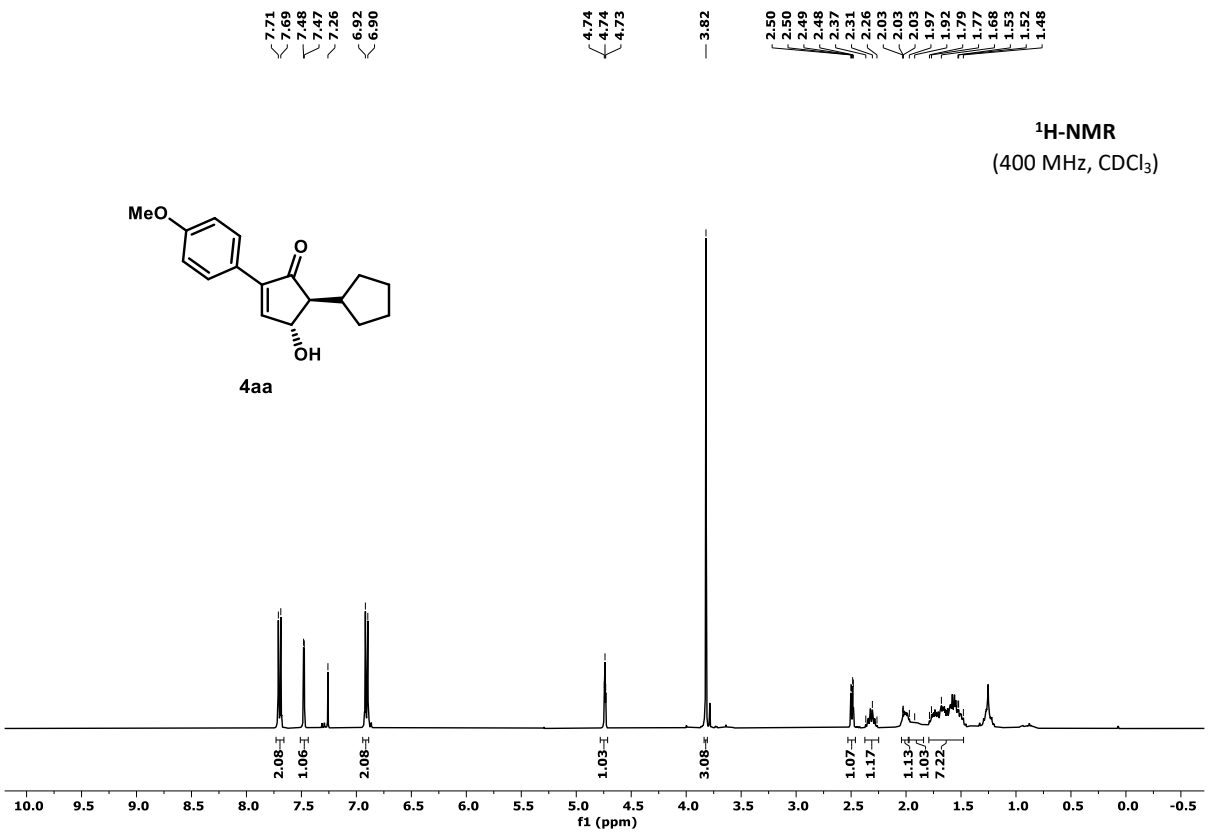
#	Peak Name	CH	tR [min]	Area [μV·sec]	Height [μV]	Area%	Height%	Quantity	NTP	Resolution	Symmetry Factor	Warning
1	Unknown	11	23.580	1338460	31239	49.974	53.465	N/A	7835	4.901	1.657	
2	Unknown	11	29.217	1339864	27189	50.026	46.535	N/A	8870	N/A	1.555	

Daicel Chiralpak IB column (90:10 *n*-Hexane/*i*-PrOH, 1.0 mL/min, 245 nm)

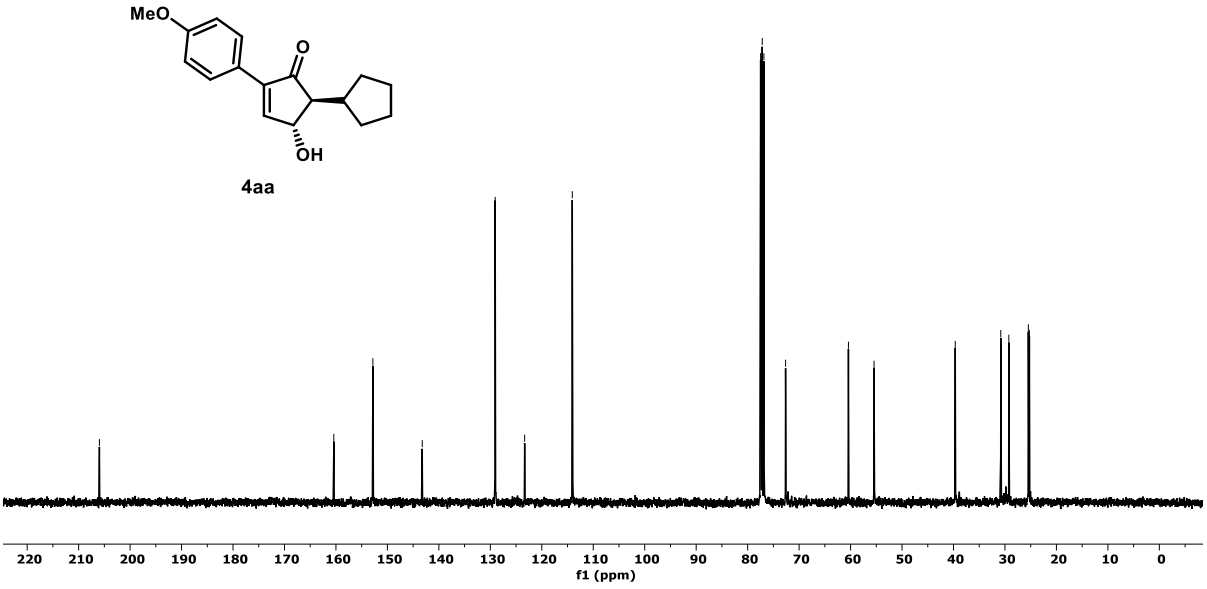


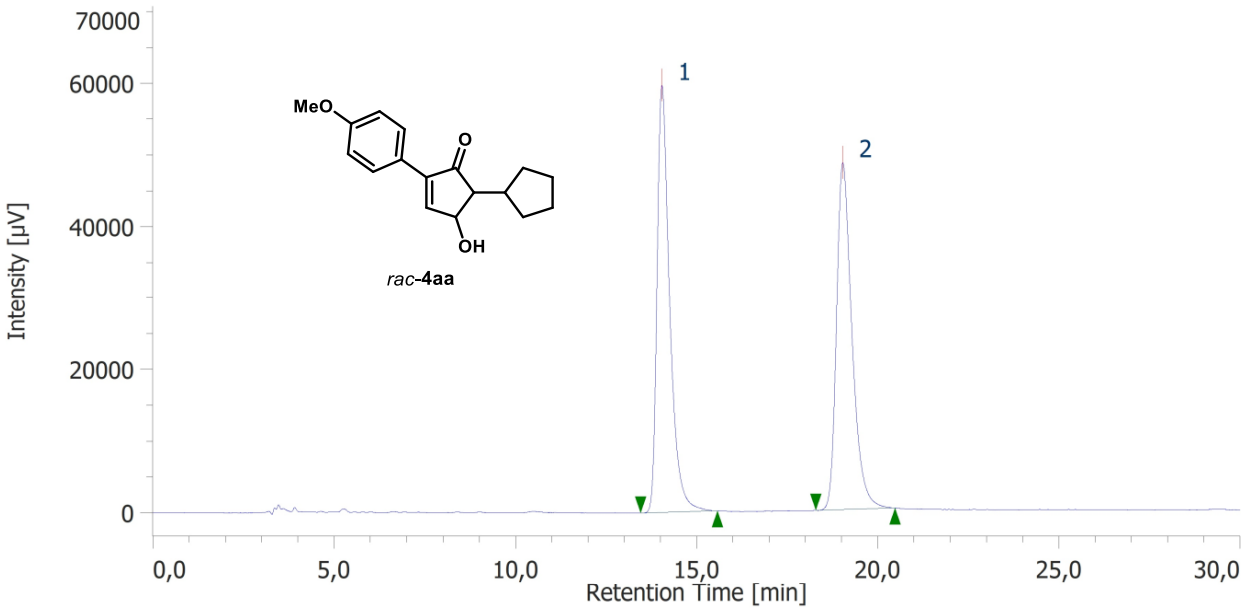
#	Peak Name	CH	tR [min]	Area [μV·sec]	Height [μV]	Area%	Height%	Quantity	NTP	Resolution	Symmetry Factor	Warning
1	Unknown	11	23.130	10033040	228857	98.243	98.259	N/A	7271	5.504	2.200	
2	Unknown	11	29.373	179476	4055	1.757	1.741	N/A	9757	N/A	1.150	

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



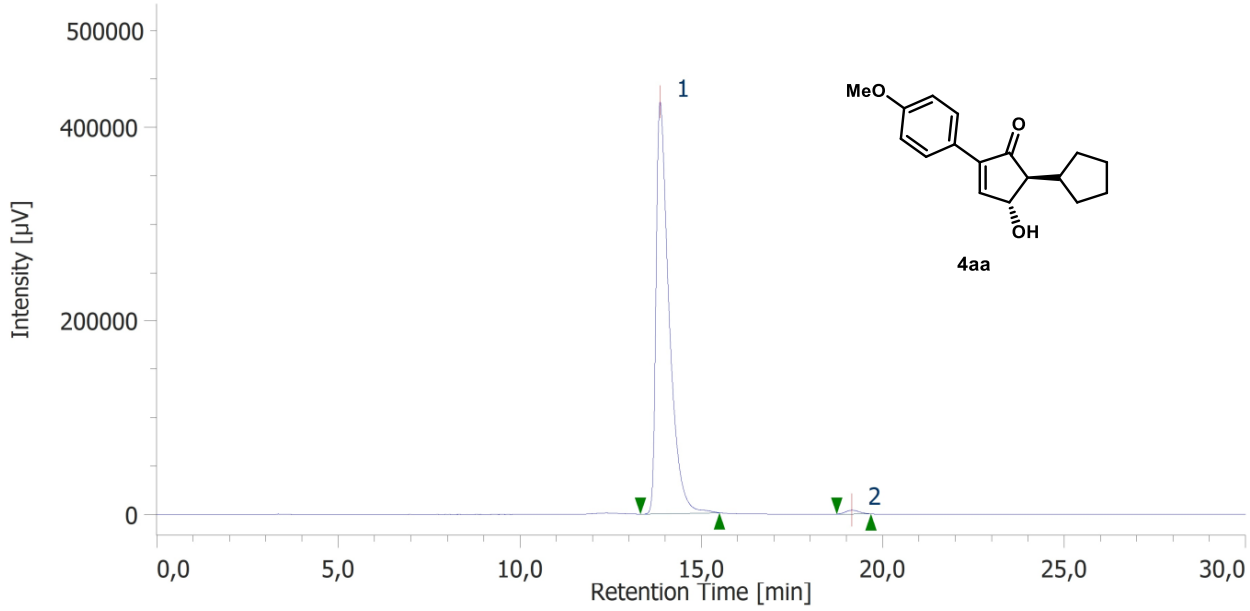
^{13}C-NMR
(100 MHz, $CDCl_3$)





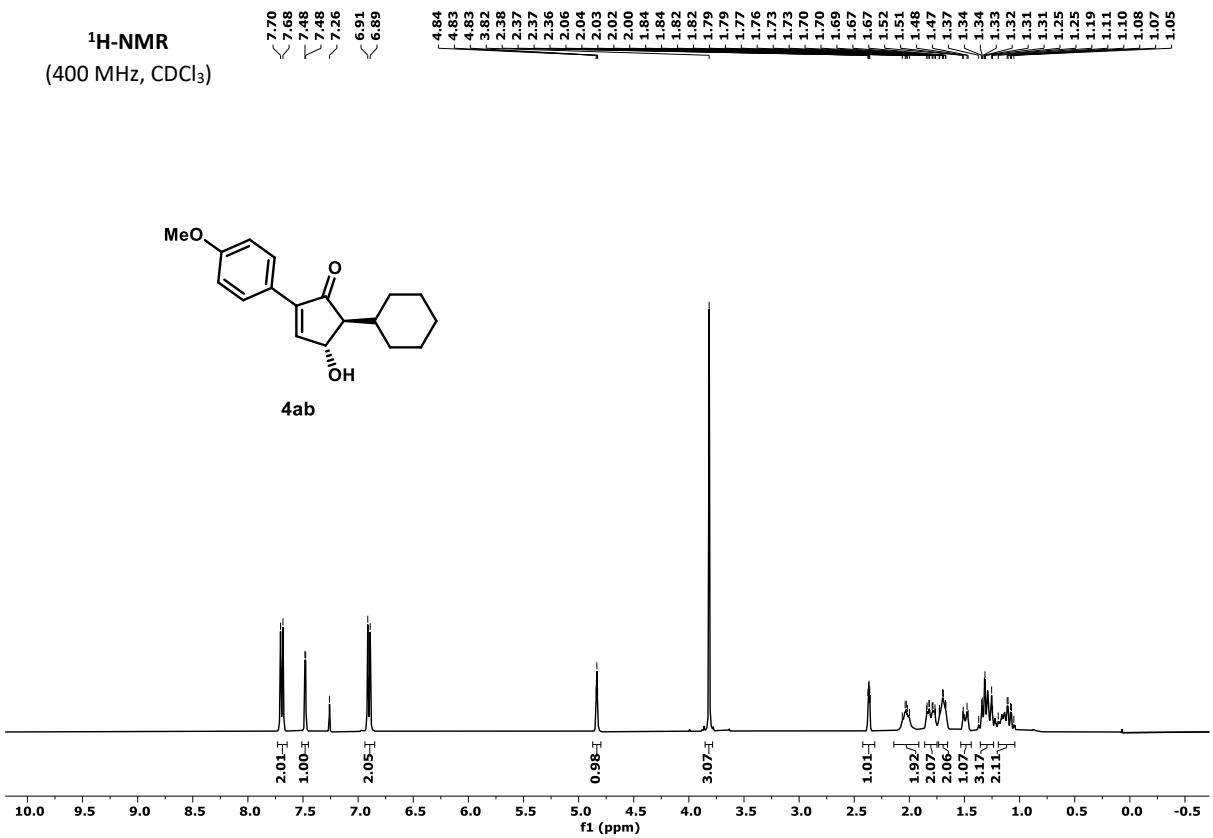
#	Peak Name	CH	tR [min]	Area [μV·sec]	Height [μV]	Area%	Height%	Quantity	NTP	Resolution	Symmetry Factor	Warning
1	Unknown	11	14,037	1440596	59647	50,086	55,179	N/A	8752	7,419	1,549	
2	Unknown	11	19,030	1435643	48450	49,914	44,821	N/A	10314	N/A	1,400	

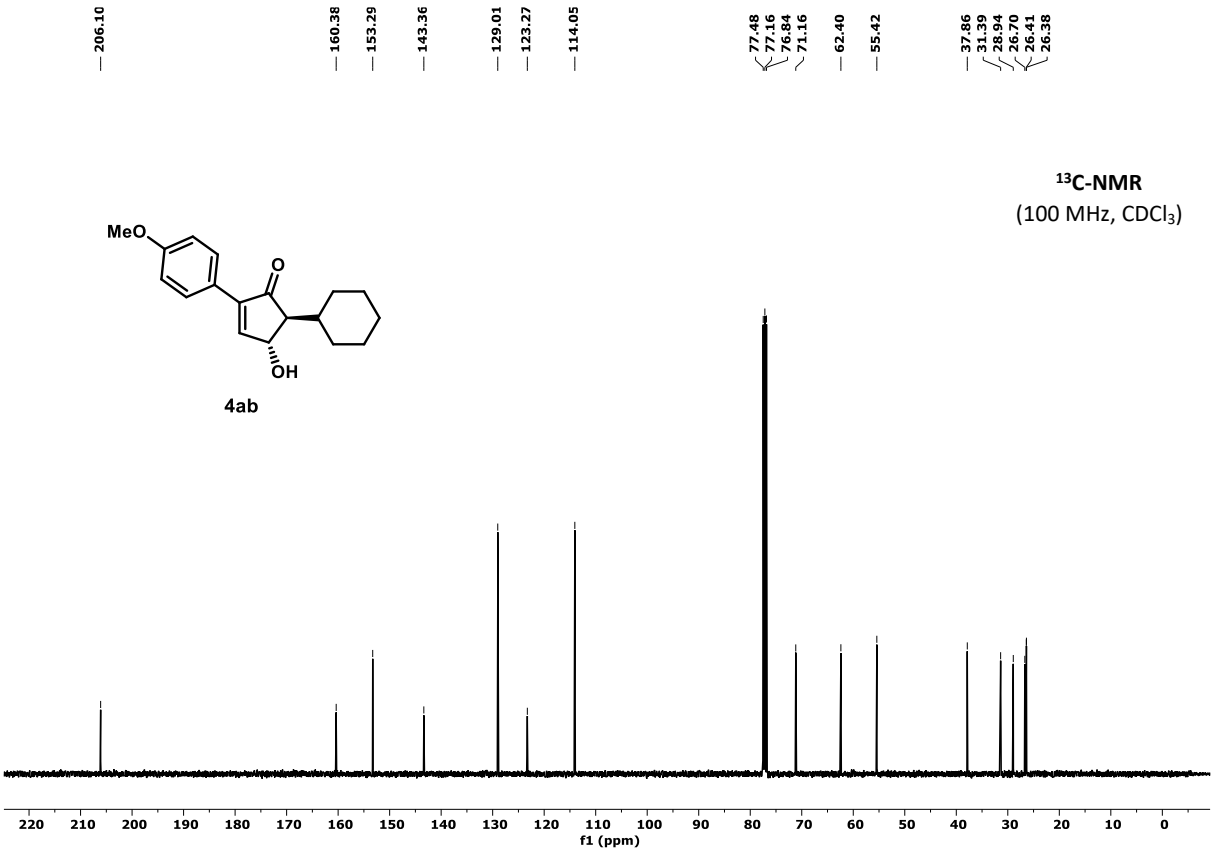
Daicel Chiralpak IB column (90:10 *n*-Hexane/*i*-PrOH, 1.0 mL/min, 245 nm)



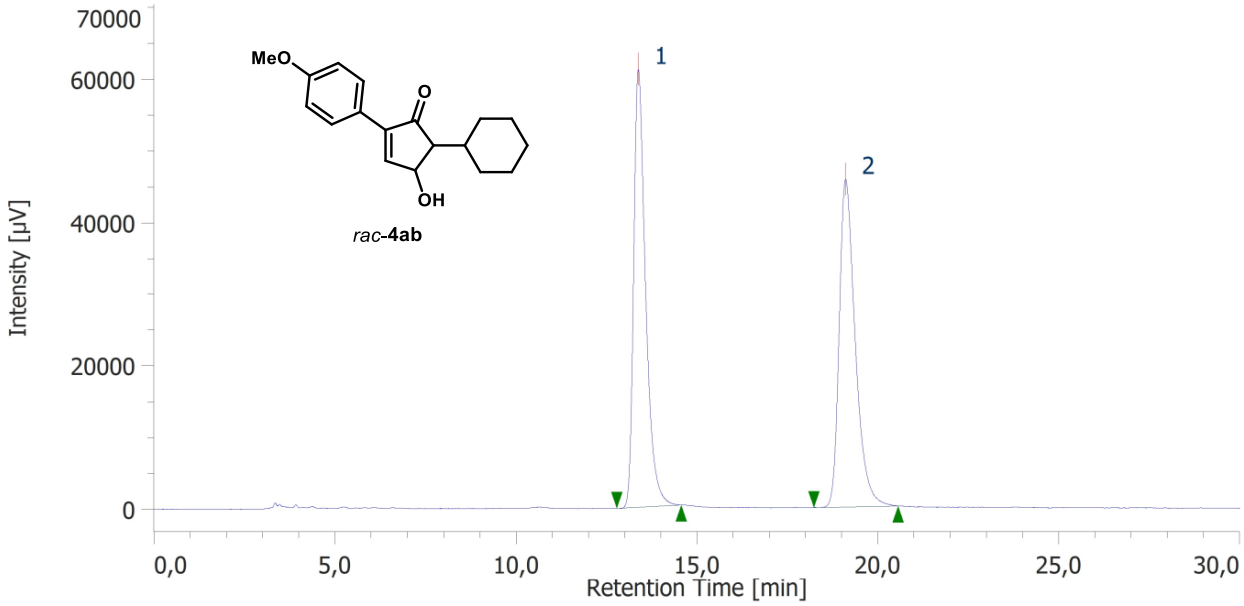
#	Peak Name	CH	tR [min]	Area [μV·sec]	Height [μV]	Area%	Height%	Quantity	NTP	Resolution	Symmetry Factor	Warning
1	Unknown	11	13,860	10558610	425149	99,036	99,097	N/A	8091	7,958	1,973	
2	Unknown	11	19,147	102747	3876	0,964	0,903	N/A	11446	N/A	1,134	

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



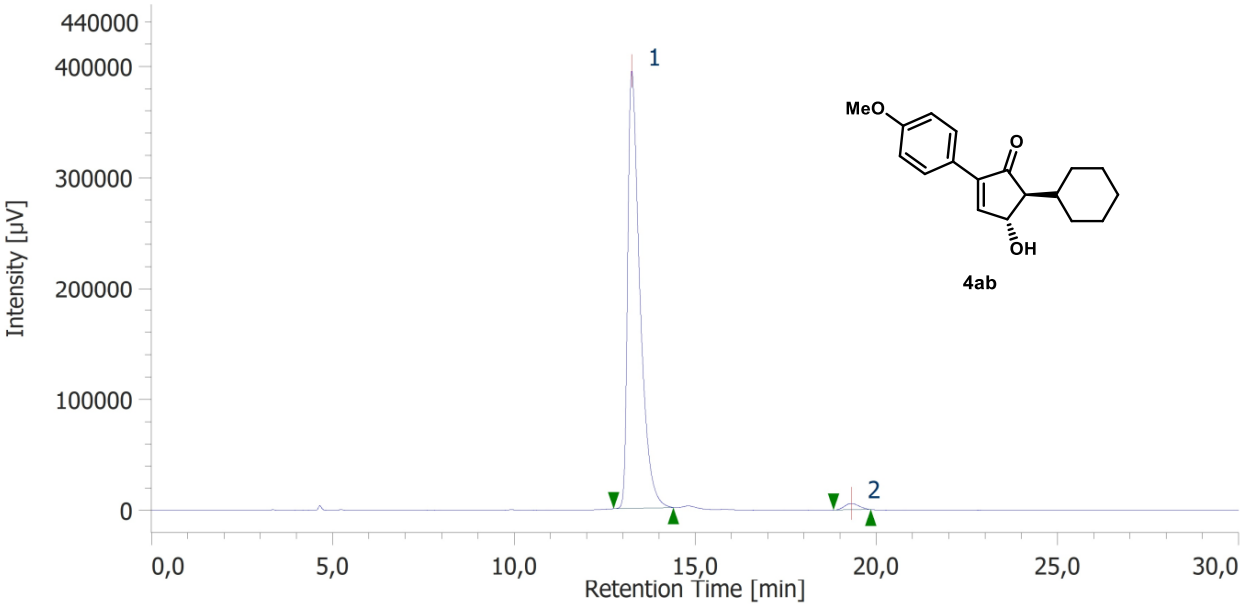


^{13}C-NMR
(100 MHz, $CDCl_3$)



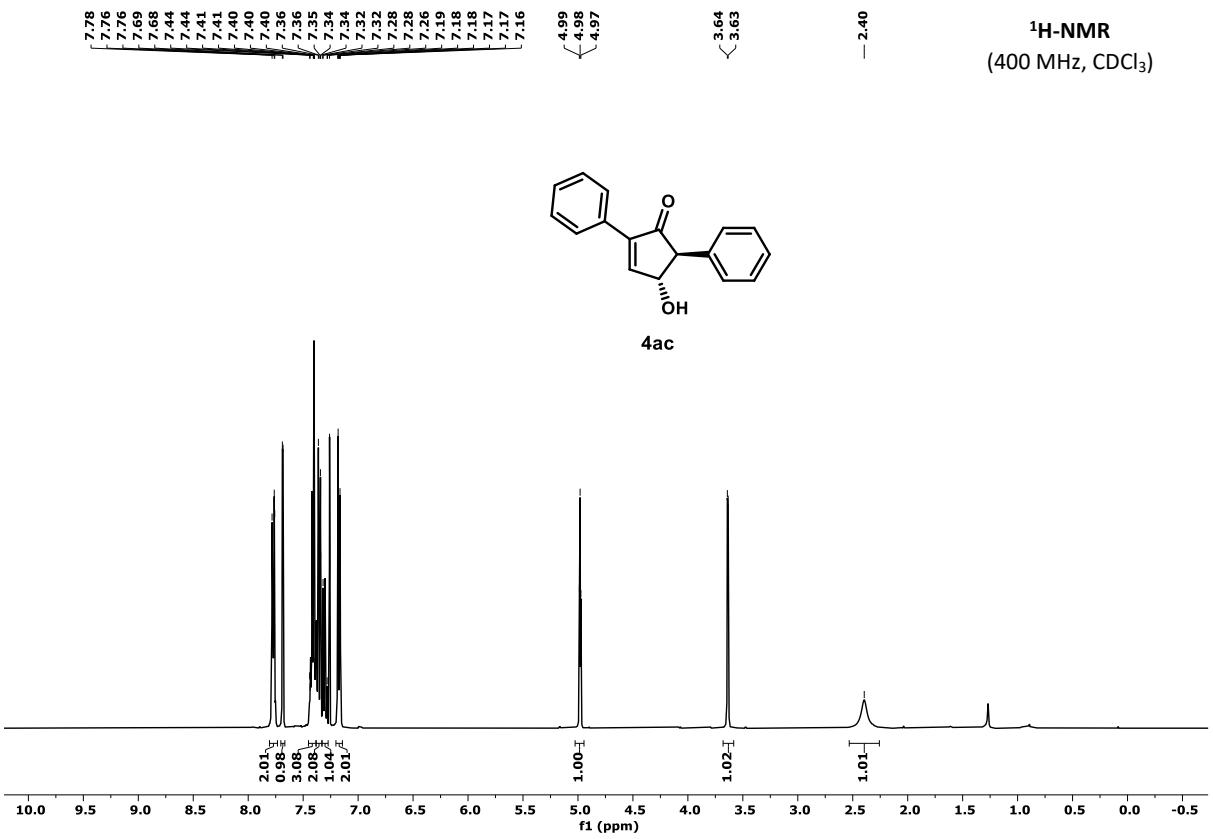
#	Peak Name	CH	tR [min]	Area [μV·sec]	Height [μV]	Area%	Height%	Quantity	NTP	Resolution	Symmetry Factor	Warning
1	Unknown	11	13,377	1395065	61050	49,799	57,184	N/A	8704	8,505	1,496	
2	Unknown	11	19,107	1406301	45710	50,201	42,816	N/A	9661	N/A	1,428	

Daicel Chiralpak IB column (90:10 *n*-Hexane/*i*-PrOH, 1.0 mL/min, 245 nm)

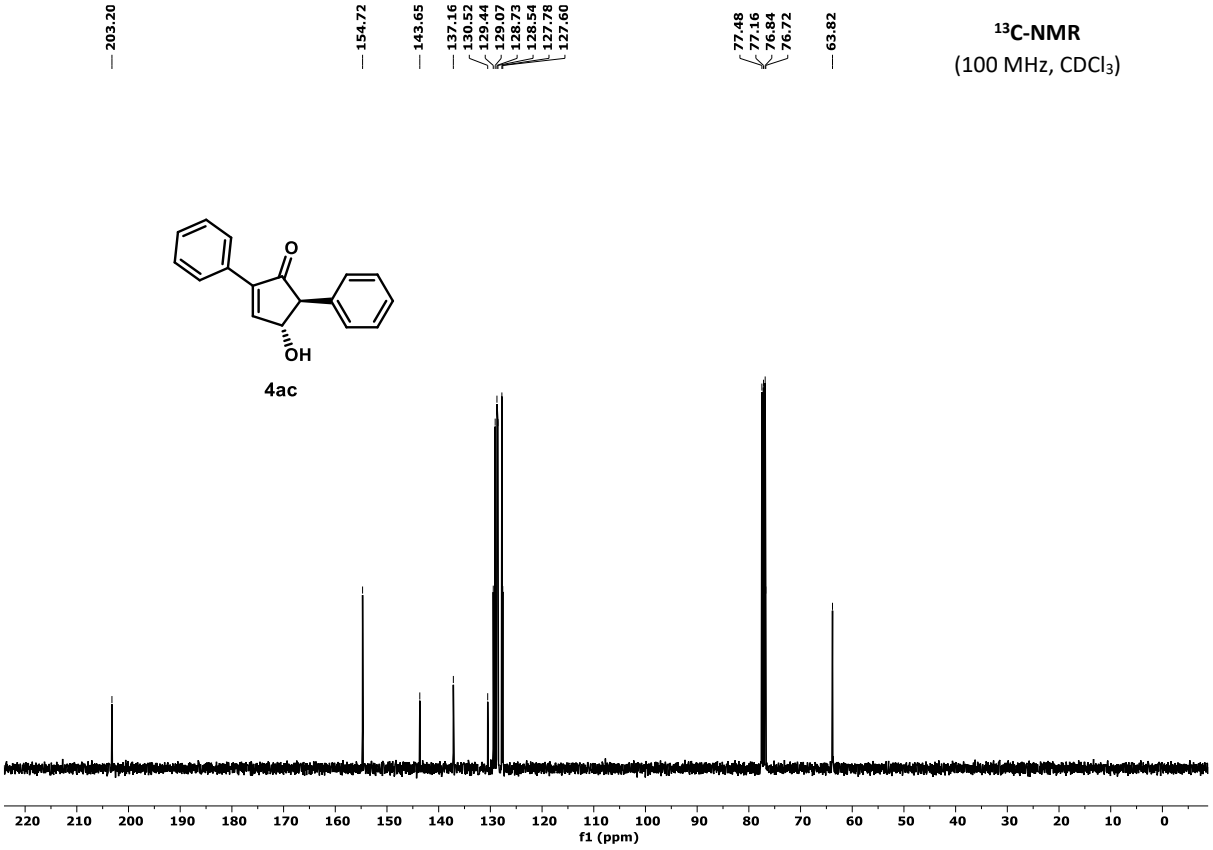


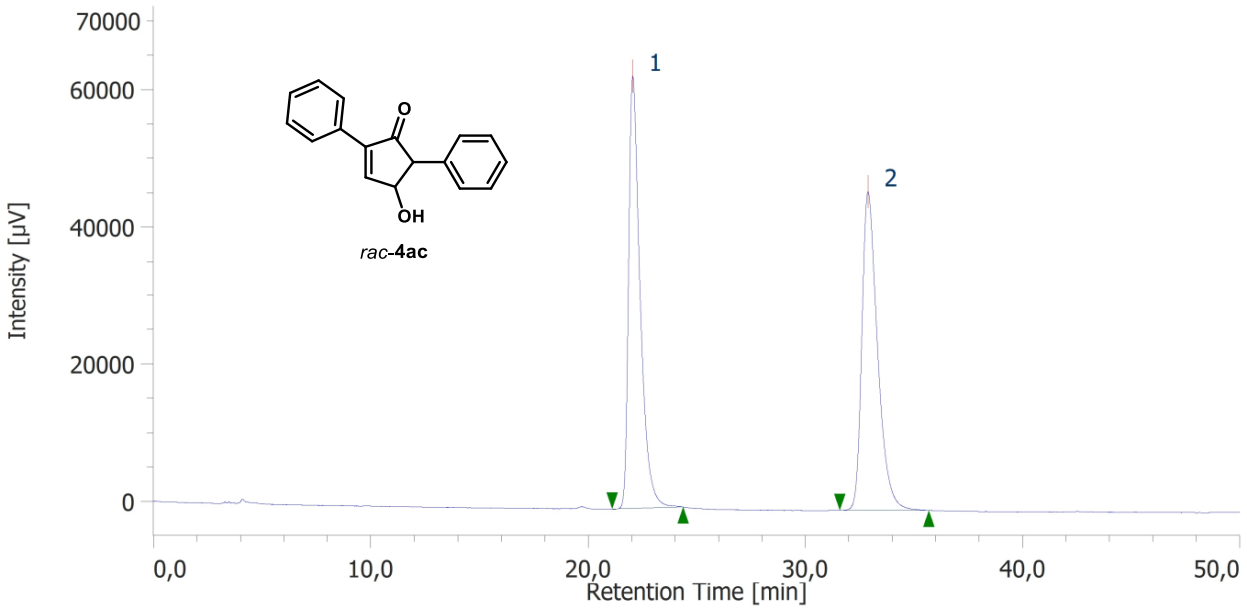
#	Peak Name	CH	tR [min]	Area [μV·sec]	Height [μV]	Area%	Height%	Quantity	NTP	Resolution	Symmetry Factor	Warning
1	Unknown	11	13,243	9156803	393869	98,256	98,549	N/A	8247	9,049	1,847	
2	Unknown	11	19,300	162511	5800	1,744	1,451	N/A	10347	N/A	1,110	

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



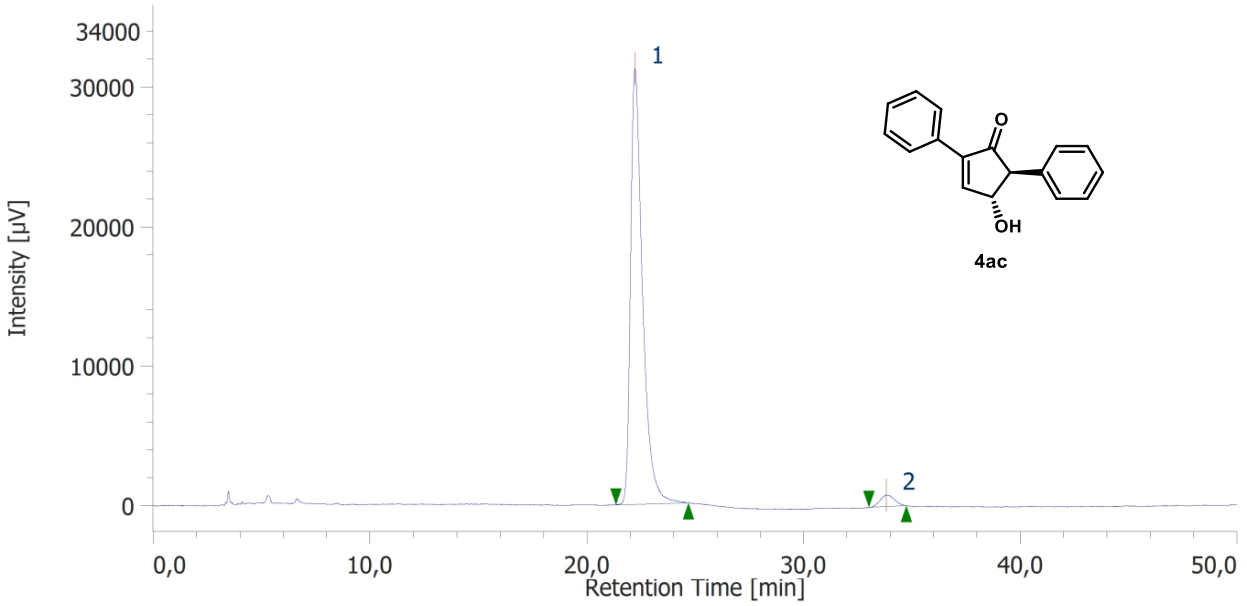
^{13}C-NMR
(100 MHz, $CDCl_3$)



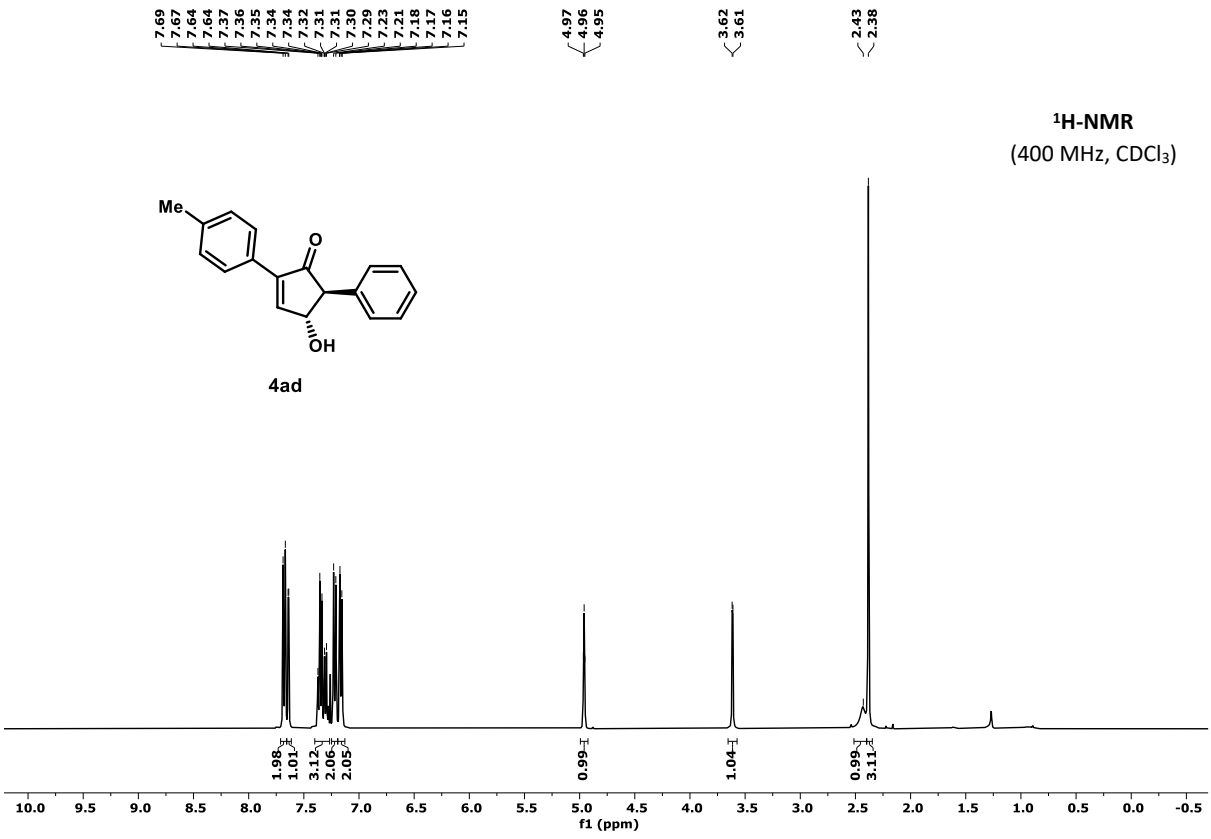


#	Peak Name	CH	tR [min]	Area [μV·sec]	Height [μV]	Area%	Height%	Quantity	NTP	Resolution	Symmetry Factor	Warning
1	Unknown	11	22,043	2318029	62979	49,891	57,559	N/A	9203	9,913	1,666	
2	Unknown	11	32,873	2328175	46437	50,109	42,441	N/A	10693	N/A	1,459	

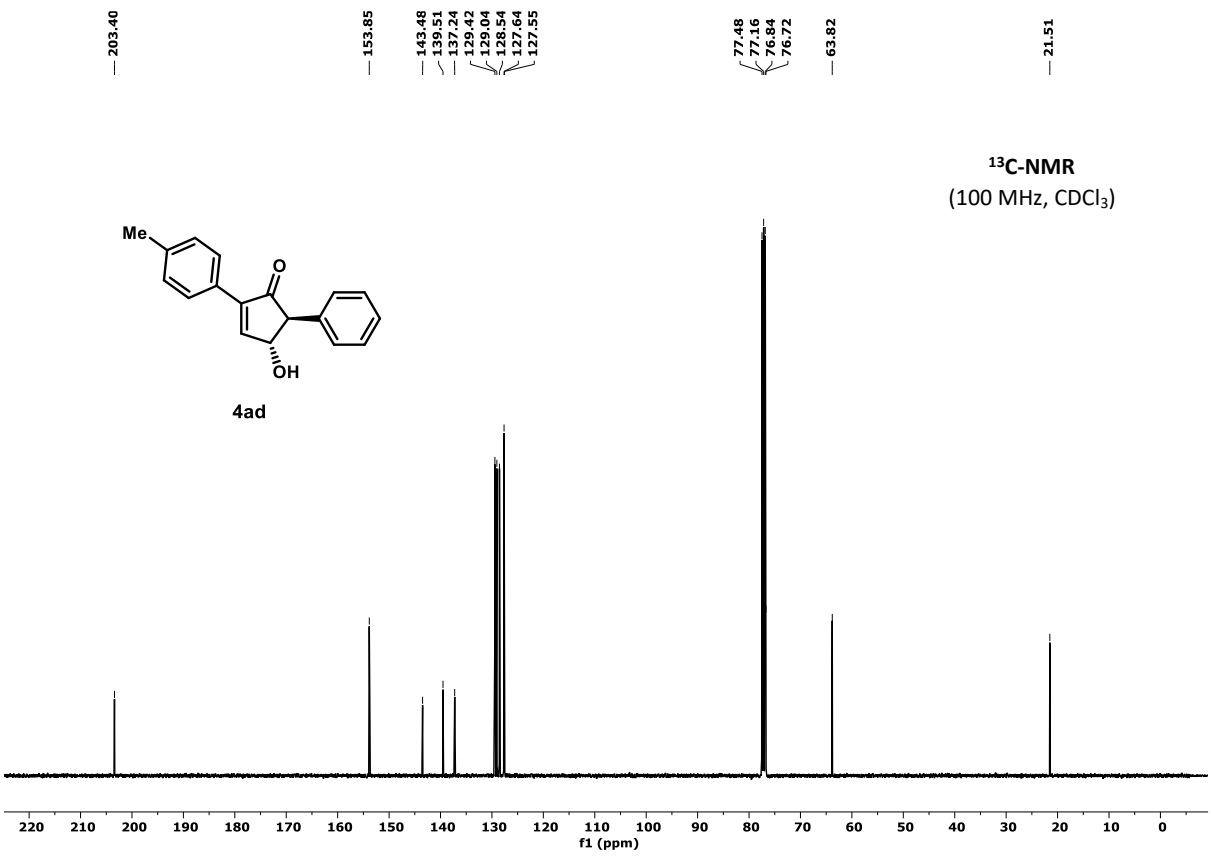
Daicel Chiralpak IB column (90:10 *n*-Hexane/*i*-PrOH, 1.0 mL/min, 254 nm)



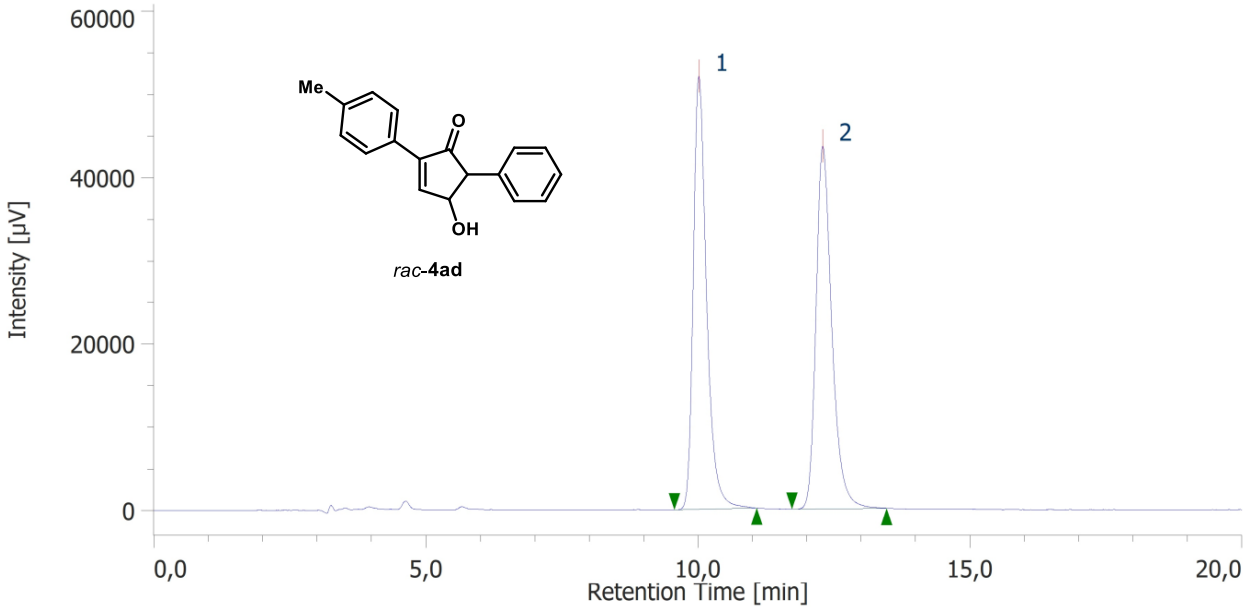
#	Peak Name	CH	tR [min]	Area [μV·sec]	Height [μV]	Area%	Height%	Quantity	NTP	Resolution	Symmetry Factor	Warning
1	Unknown	11	22,210	1194389	31192	96,938	97,404	N/A	8808	10,687	1,635	
2	Unknown	11	33,807	37731	831	3,062	2,596	N/A	12097	N/A	1,122	



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

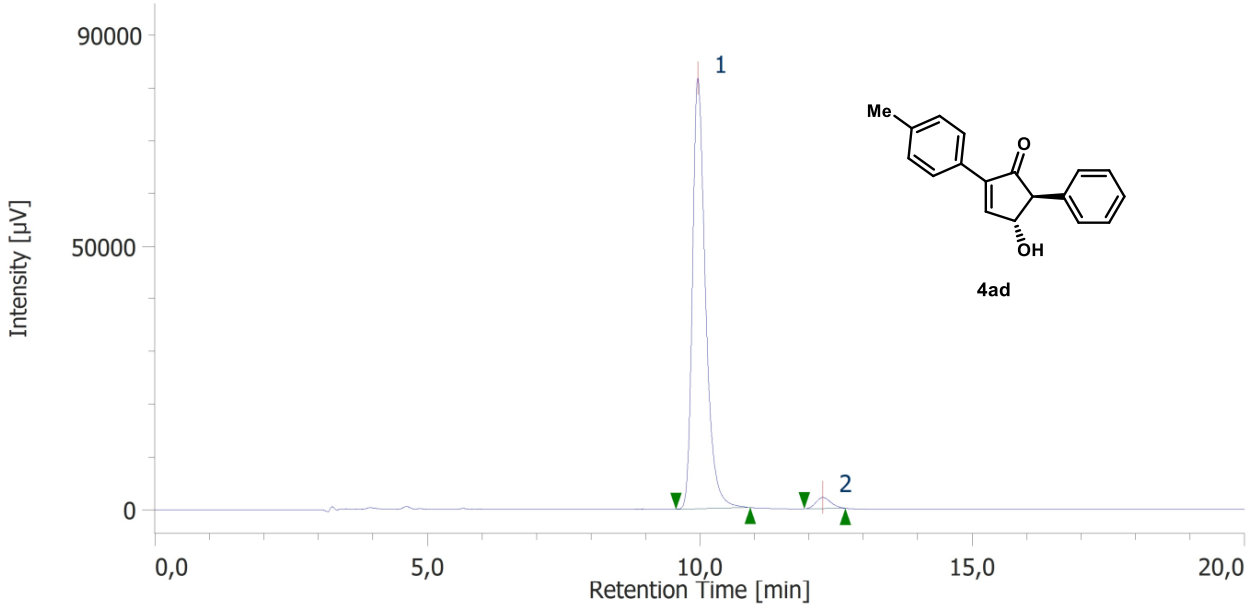


^{13}C-NMR
(100 MHz, $CDCl_3$)

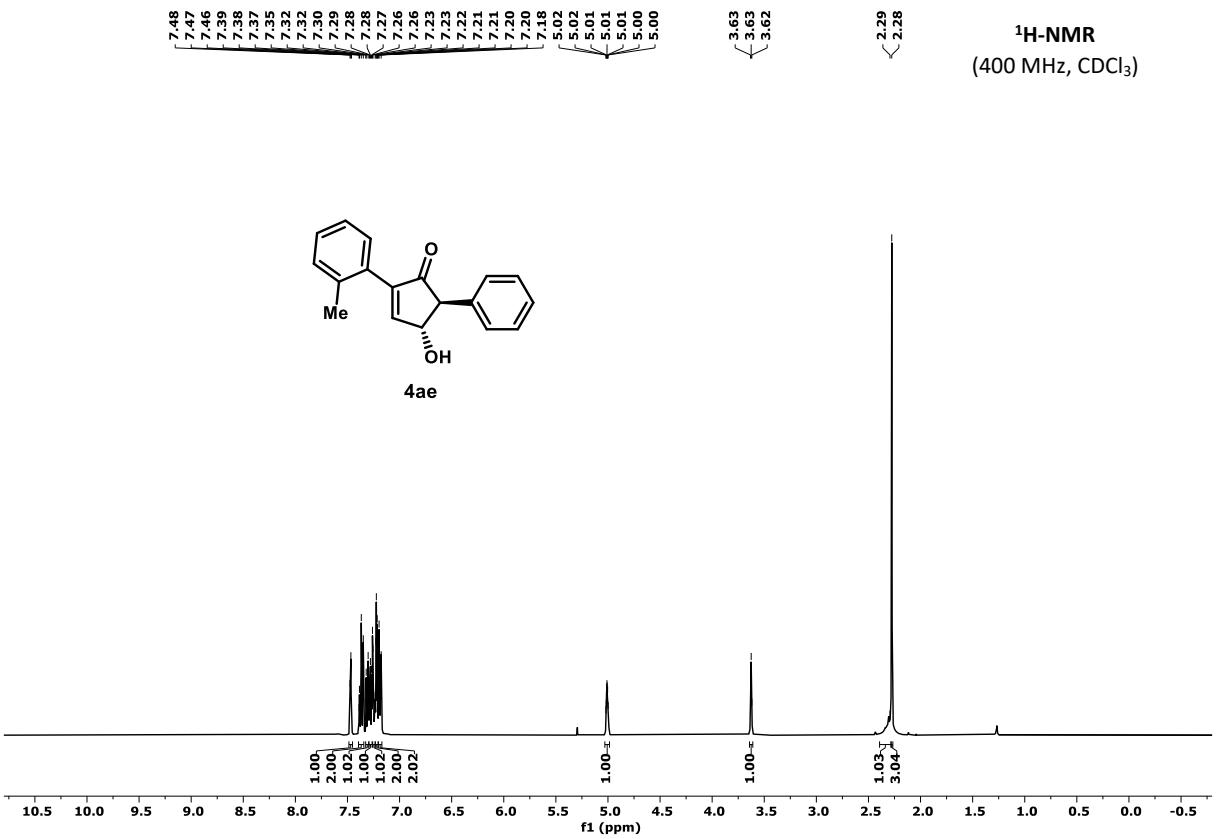


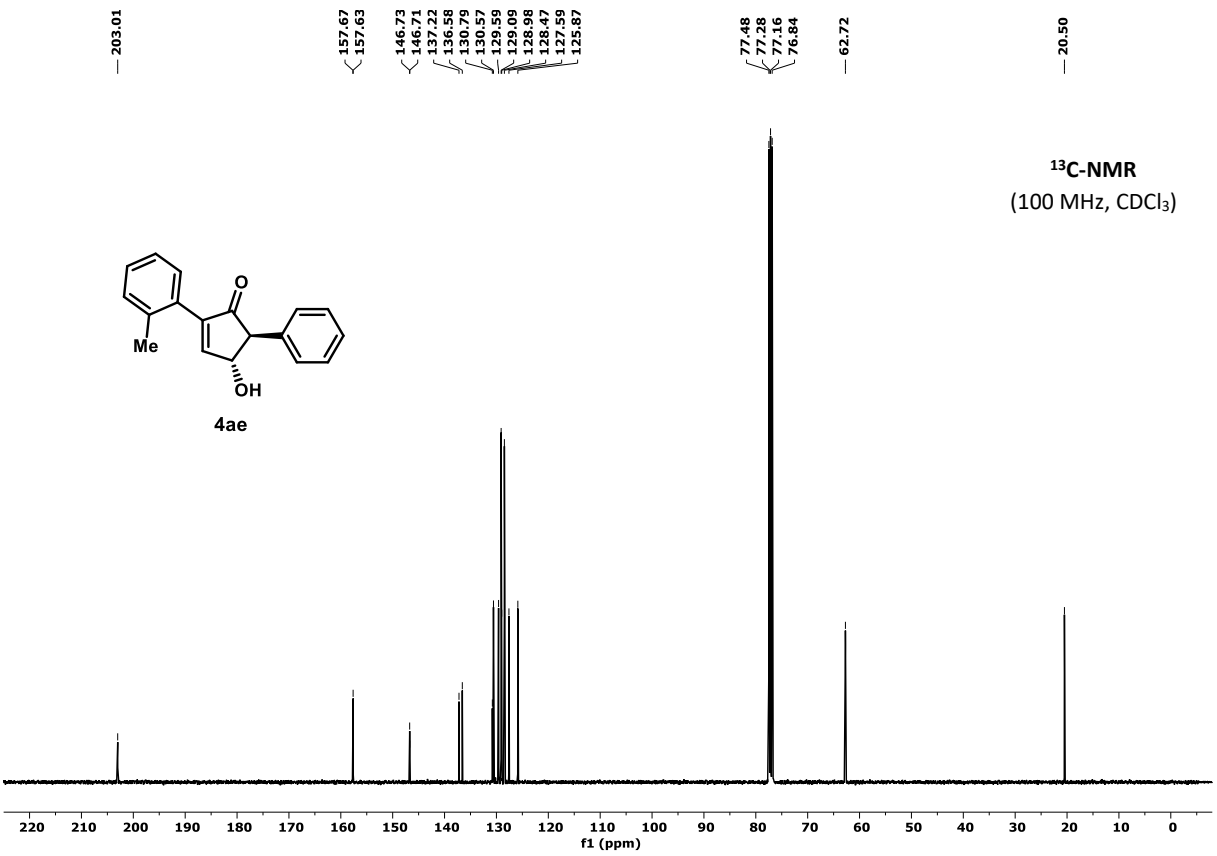
#	Peak Name	CH	tR [min]	Area [μV·sec]	Height [μV]	Area%	Height%	Quantity	NTP	Resolution	Symmetry Factor	Warning
1	Unknown	11	10,013	881374	52023	49,989	54,434	N/A	8955	4,894	1,375	
2	Unknown	11	12,290	881752	43547	50,011	45,566	N/A	9302	N/A	1,336	

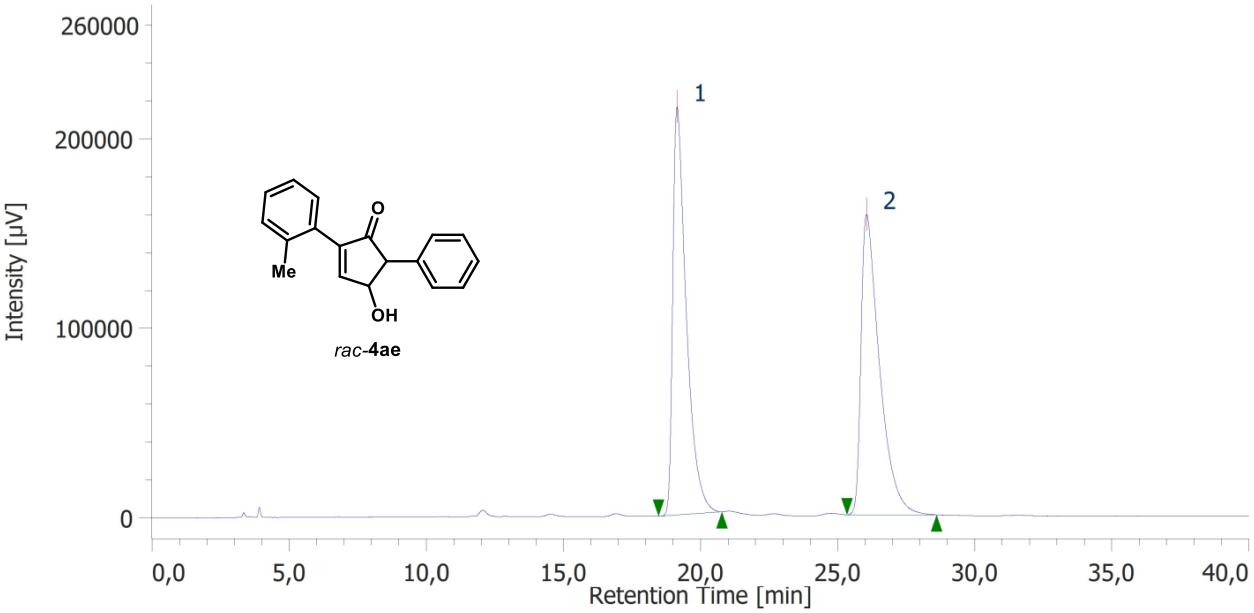
Daicel Chiralpak IB column (80:20 *n*-Hexane/*i*-PrOH, 1.0 mL/min, 275 nm)



#	Peak Name	CH	tR [min]	Area [μV·sec]	Height [μV]	Area%	Height%	Quantity	NTP	Resolution	Symmetry Factor	Warning
1	Unknown	11	9,960	1357625	81646	97,115	97,495	N/A	9118	4,968	1,387	
2	Unknown	11	12,253	40337	2098	2,885	2,505	N/A	9292	N/A	1,170	

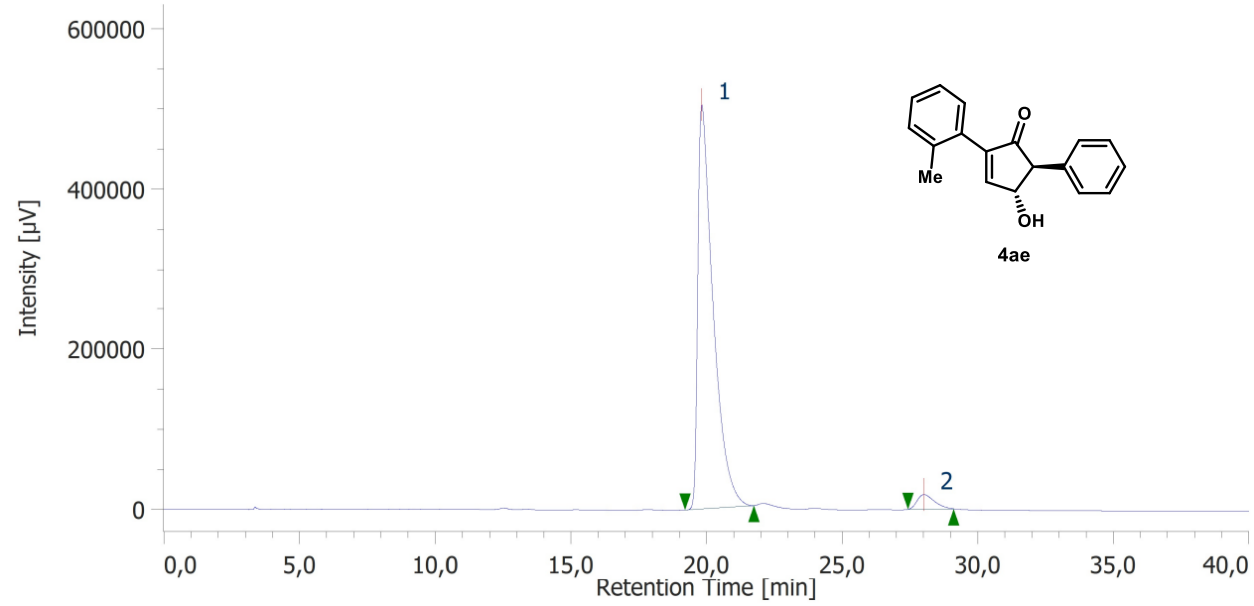

7.48 7.47 7.46 7.39 7.38 7.37 7.35 7.32 7.32 7.30 7.29 7.28 7.28 7.27 7.26 7.26 7.23 7.23 7.22 7.21 7.21 7.20 7.20 7.18 5.02 5.02 5.01 5.01 5.01 5.00 5.00
3.63 3.63 3.62
2.29 2.28
1H-NMR
(400 MHz, CDCl3)
O
Me
OH
4ae
1.00 2.00 1.00 1.02 2.00 2.02 1.00 1.00 1.03 3.04
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 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
f1 (ppm)


203.01
157.67 157.63 146.73 146.71 137.22 136.58 130.79 130.57 129.59 129.09 128.98 128.47 127.59 125.87
77.48 77.28 77.16 76.84
62.72
20.50
13C-NMR
(100 MHz, CDCl3)
O
Me
OH
4ae
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

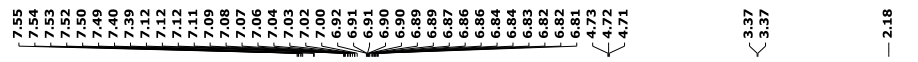


#	Peak Name	CH	tR [min]	Area [μV·sec]	Height [μV]	Area%	Height%	Quantity	NTP	Resolution	Symmetry Factor	Warning
1	Unknown	10	19.137	7361035	215301	49.839	57.584	N/A	8048	6.856	1.976	
2	Unknown	10	26.050	7408683	158591	50.161	42.416	N/A	7949	N/A	2.070	

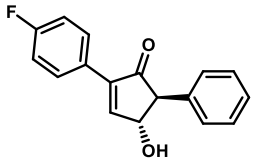
Daicel Chiralpak IB column (90:10 *n*-Hexane/*i*-PrOH, 1.0 mL/min, 230 nm)



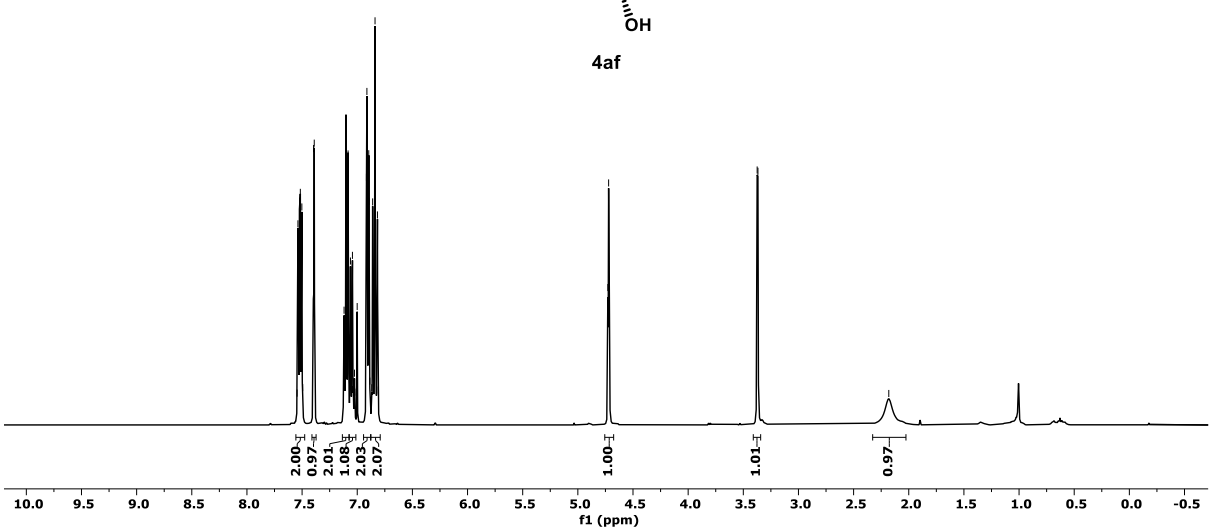
#	Peak Name	CH	tR [min]	Area [μV·sec]	Height [μV]	Area%	Height%	Quantity	NTP	Resolution	Symmetry Factor	Warning
1	Unknown	10	19.820	19794242	504171	96.121	96.528	N/A	6549	7.638	2.504	
2	Unknown	10	28.007	798845	18136	3.879	3.472	N/A	9173	N/A	1.429	



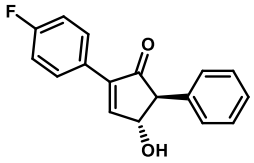
^{1}H-NMR
(400 MHz, $CDCl_3$)



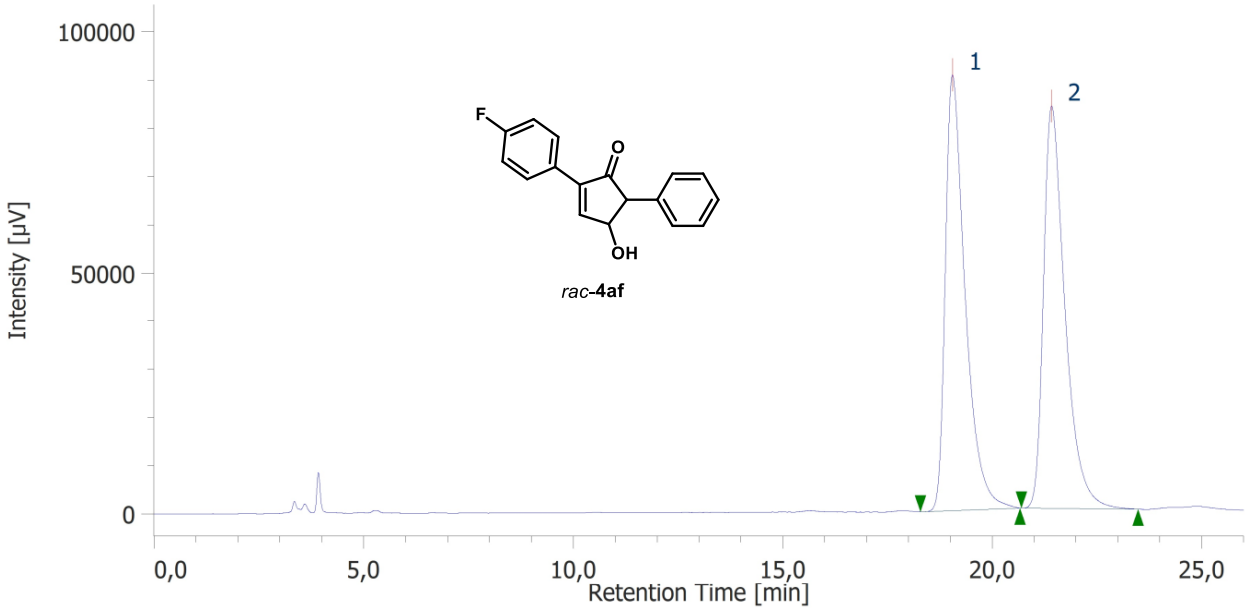
4af



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

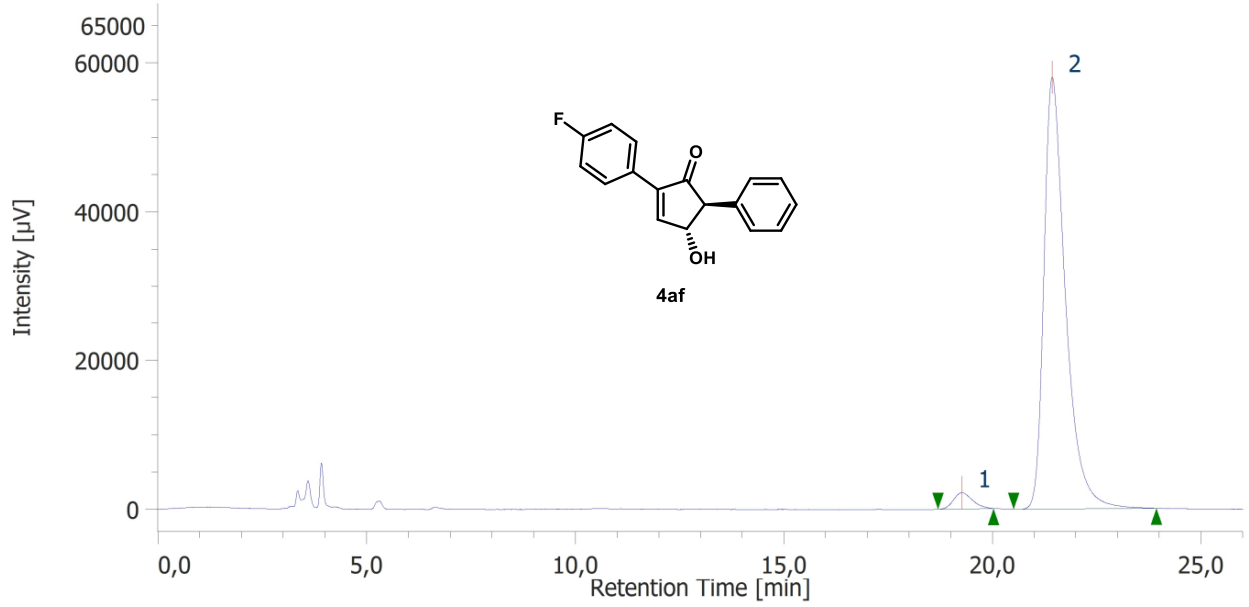


4af



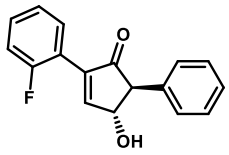
#	Peak Name	CH	tR [min]	Area [μV·sec]	Height [μV]	Area%	Height%	Quantity	NTP	Resolution	Symmetry Factor	Warning
1	Unknown	10	19,047	2970622	90341	49,970	51,992	N/A	8617	2,770	1,667	
2	Unknown	10	21,413	2974173	83419	50,030	48,008	N/A	9214	N/A	1,559	

Daicel Chiralpak IB column (90:10 *n*-Hexane/*i*-PrOH, 1.0 mL/min, 230 nm)

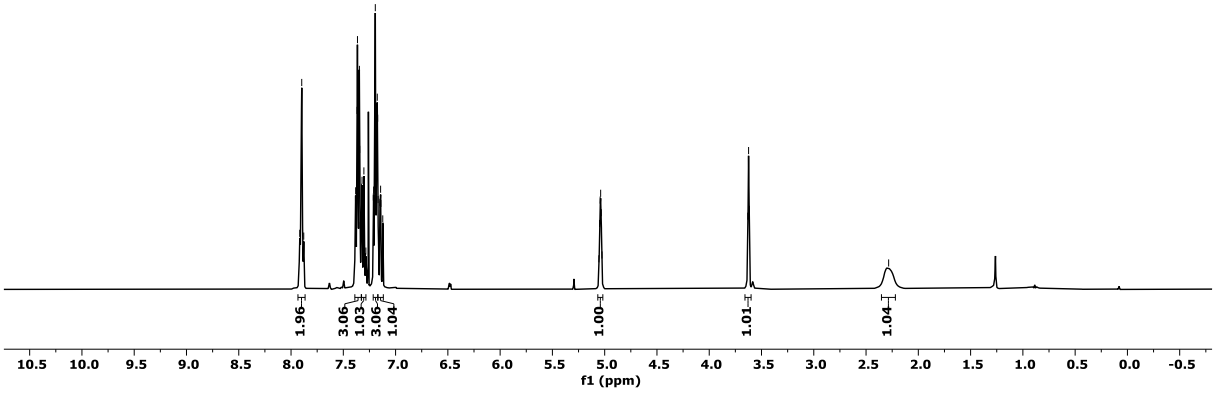


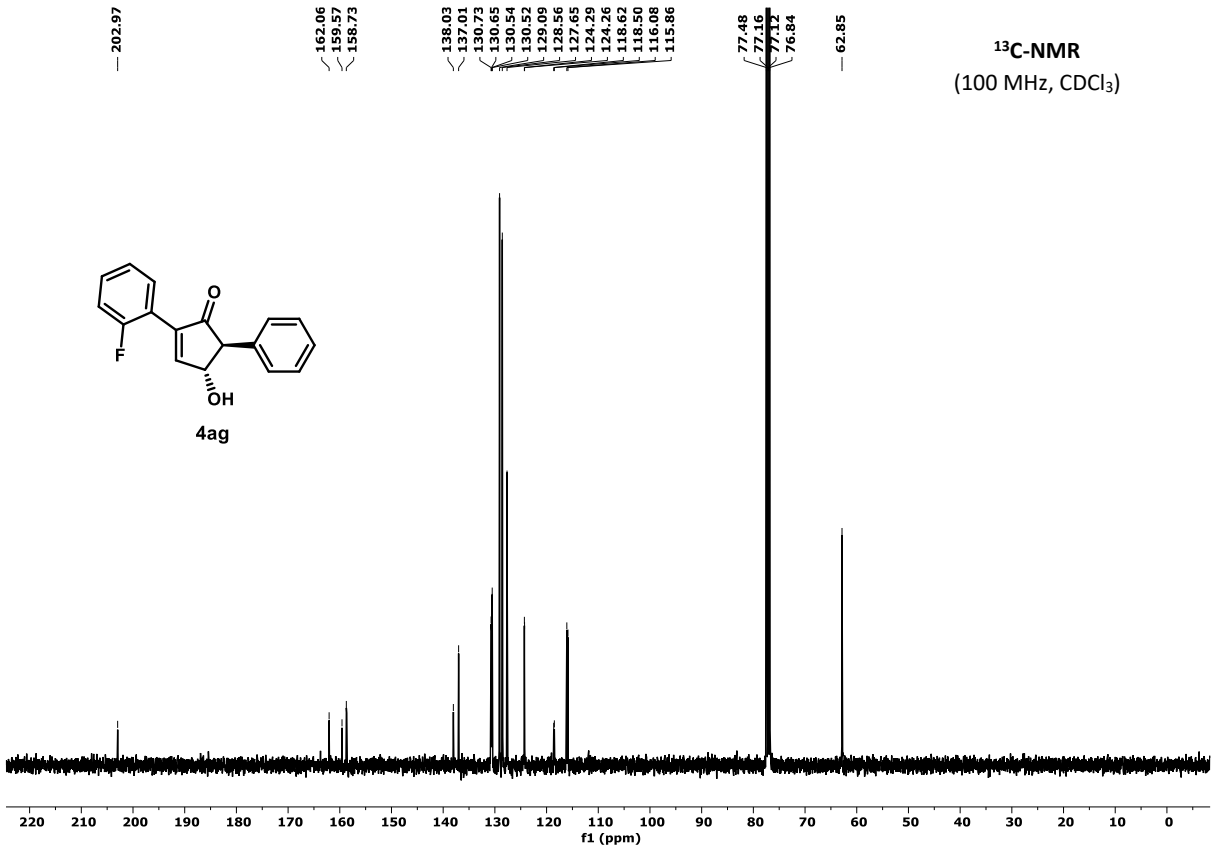
#	Peak Name	CH	tR [min]	Area [μV·sec]	Height [μV]	Area%	Height%	Quantity	NTP	Resolution	Symmetry Factor	Warning
1	Unknown	10	19,263	68972	2179	3,207	3,621	N/A	8528	2,514	1,225	
2	Unknown	10	21,427	2081635	57995	96,793	96,379	N/A	9246	N/A	1,533	

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



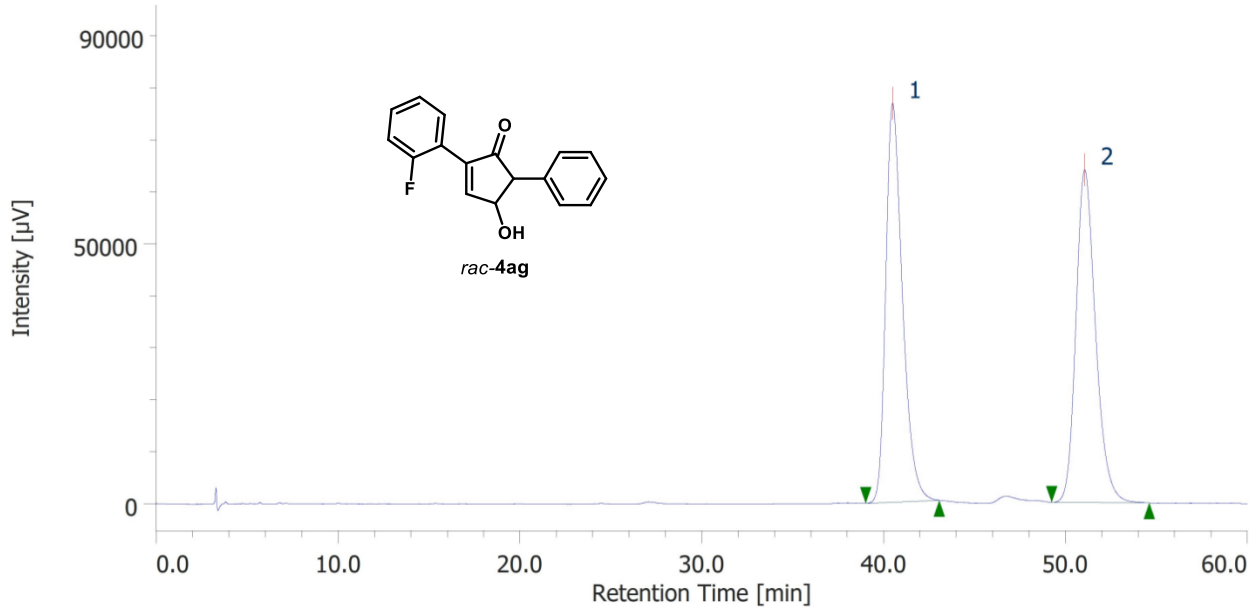
4ag





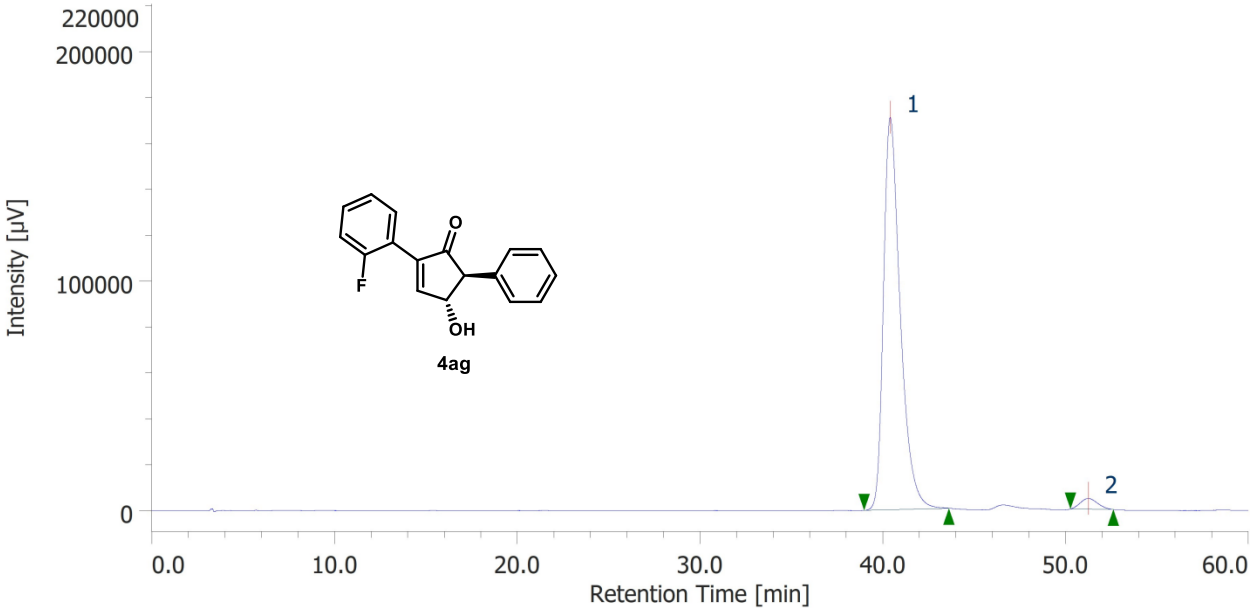
^{13}C-NMR
(100 MHz, $CDCl_3$)

4ag

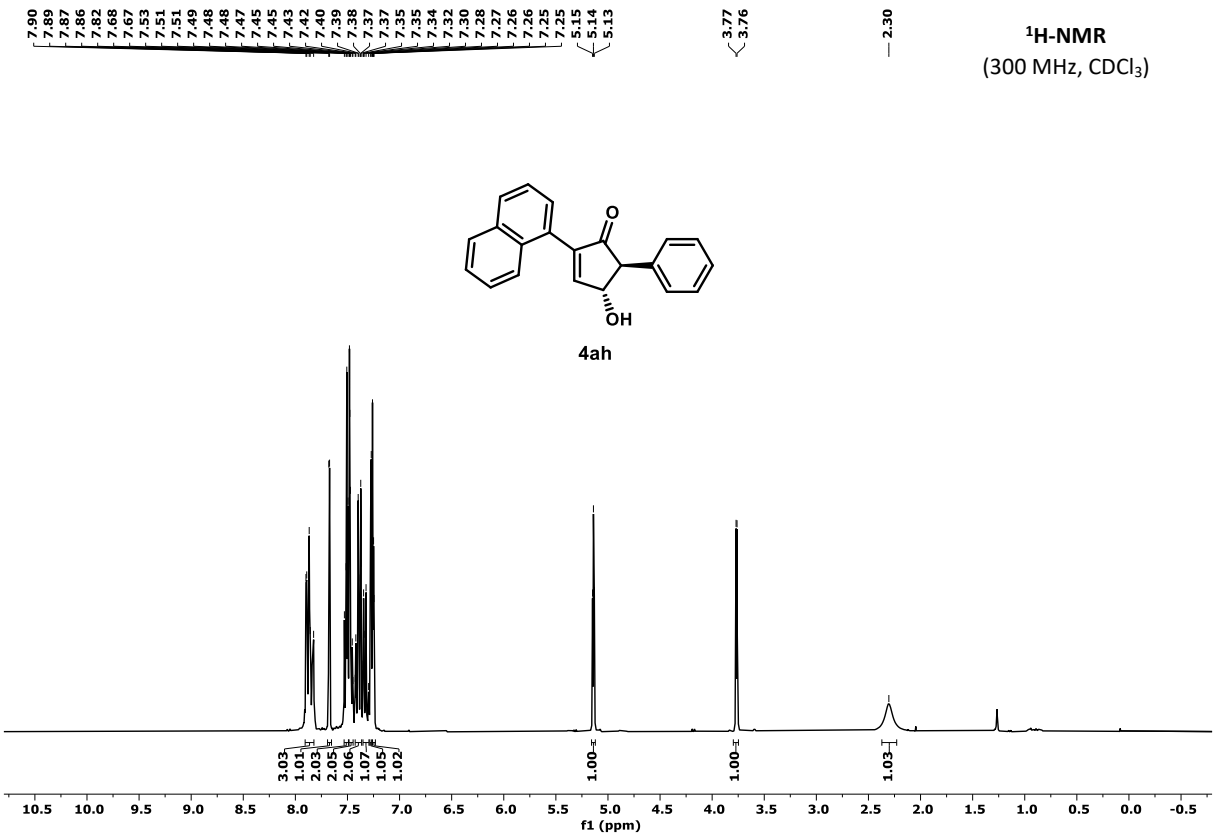


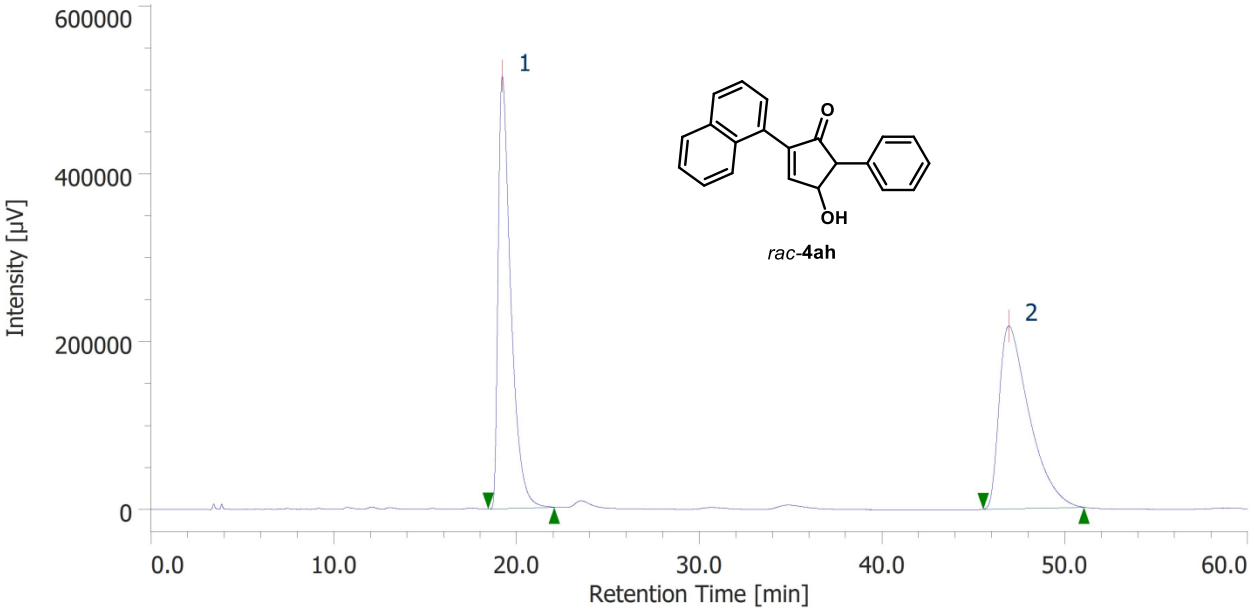
#	Peak Name	CH	tR [min]	Area [μV·sec]	Height [μV]	Area%	Height%	Quantity	NTP	Resolution	Symmetry Factor	Warning
1	Unknown	12	40.487	4894352	76727	50.501	54.523	N/A	9805	5.955	1.374	
2	Unknown	12	51.047	4797276	63997	49.499	45.477	N/A	11303	N/A	1.233	

Daicel Chiralpak IA column (95:5 *n*-Hexane/*i*-PrOH, 1.0 mL/min, 254 nm)



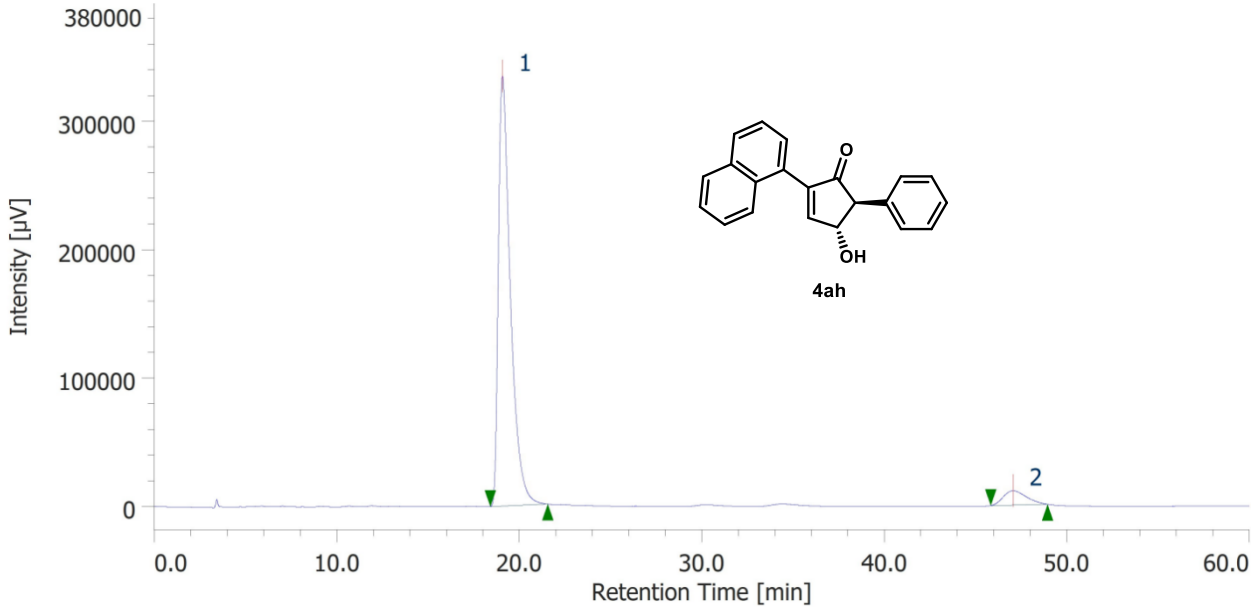
#	Peak Name	CH	tR [min]	Area [μV·sec]	Height [μV]	Area%	Height%	Quantity	NTP	Resolution	Symmetry Factor	Warning
1	Unknown	12	40.397	10903284	170847	97.243	97.327	N/A	9996	6.377	1.455	
2	Unknown	12	51.237	309157	4692	2.757	2.673	N/A	13068	N/A	1.159	


7.90
7.89
7.87
7.86
7.82
7.68
7.67
7.53
7.51
7.51
7.49
7.48
7.48
7.47
7.45
7.45
7.43
7.42
7.40
7.39
7.38
7.37
7.37
7.35
7.35
7.34
7.32
7.30
7.28
7.27
7.26
7.26
7.25
7.25
5.15
5.14
5.13
3.77
3.76
2.30
1H-NMR
(300 MHz, CDCl3)
O
OH
4ah
3.03
1.01
2.03
2.05
2.06
1.07
1.05
1.02
1.00
1.00
1.03
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
f1 (ppm)
203.23
158.80
145.16
137.16
133.84
131.39
129.43
129.15
128.73
128.61
128.52
127.66
127.47
126.57
126.16
125.30
125.00
77.58
77.32
77.16
76.74
62.92
13C-NMR
(75 MHz, CDCl3)
O
OH
4ah
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

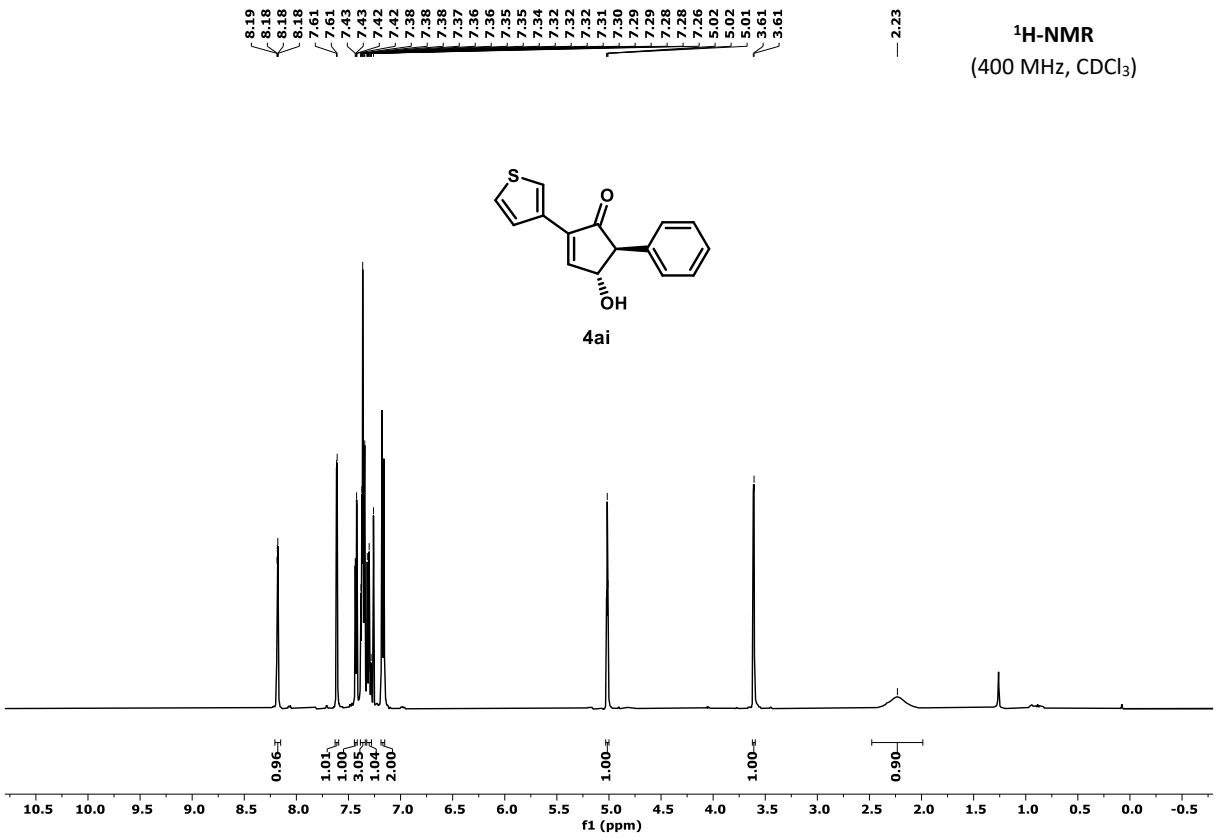


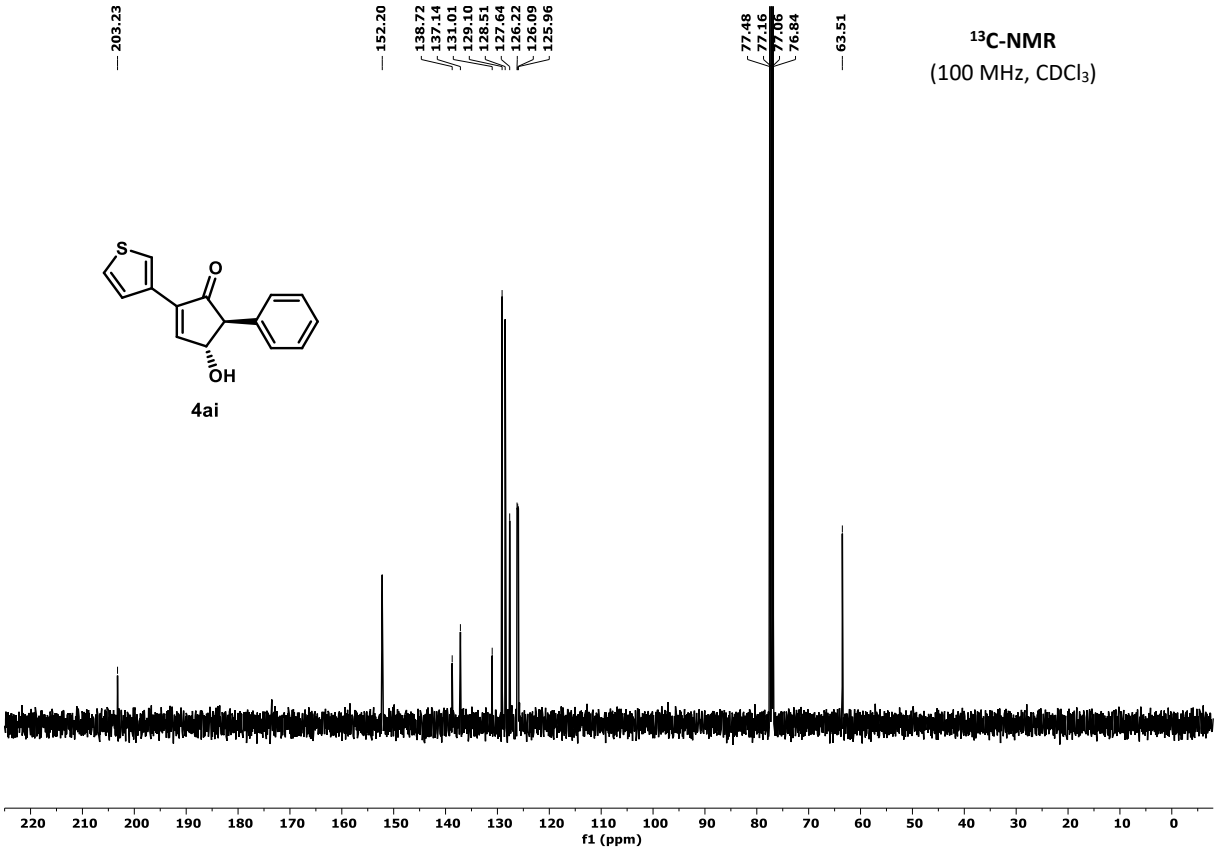
#	Peak Name	CH	tR [min]	Area [μV·sec]	Height [μV]	Area%	Height%	Quantity	NTP	Resolution	Symmetry Factor	Warning
1	Unknown	10	19.213	24685409	515088	49.669	70.272	N/A	4091	13.392	1.954	
2	Unknown	10	46.930	25013924	217907	50.331	29.728	N/A	4053	N/A	1.951	

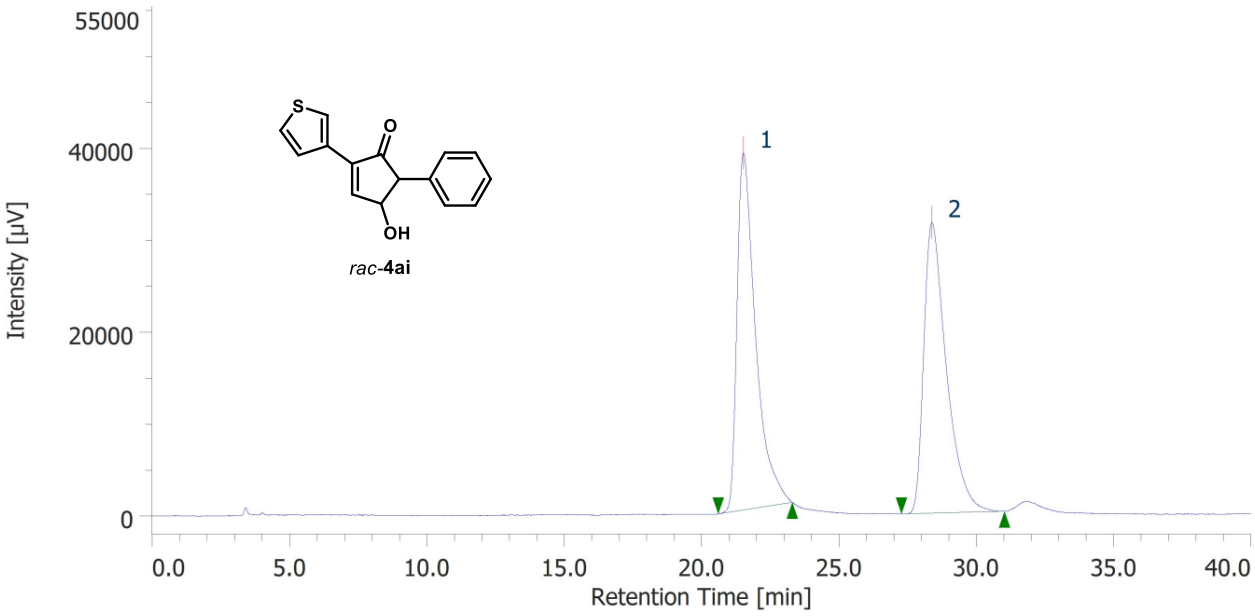
Daicel Chiralpak IB column (80:20 *n*-Hexane/*i*-PrOH, 1.0 mL/min, 230 nm)



#	Peak Name	CH	tR [min]	Area [μV·sec]	Height [μV]	Area%	Height%	Quantity	NTP	Resolution	Symmetry Factor	Warning
1	Unknown	10	19.070	15302512	334528	93.972	96.772	N/A	4439	15.923	1.853	
2	Unknown	10	47.047	981593	11159	6.028	3.228	N/A	6260	N/A	1.284	

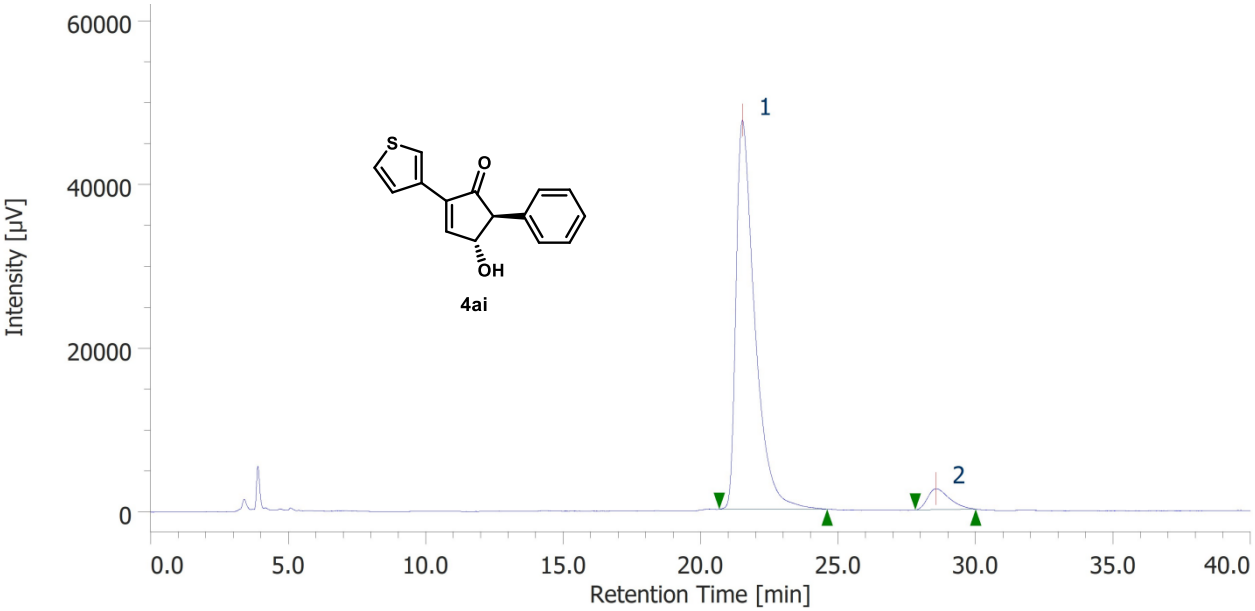

8.19
8.18
8.18
8.18
7.61
7.61
7.43
7.43
7.42
7.42
7.38
7.38
7.38
7.37
7.36
7.36
7.35
7.35
7.34
7.32
7.32
7.32
7.31
7.30
7.29
7.29
7.28
7.28
7.26
5.02
5.02
5.01
3.61
3.61
2.23
1H-NMR
(400 MHz, CDCl3)
S
O
OH
4ai
0.96
1.01
1.00
3.05
1.04
2.00
1.00
1.00
0.90
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)


203.23
152.20
138.72
137.14
131.01
129.10
128.51
127.64
126.22
126.09
125.96
77.48
77.16
77.06
76.84
63.51
13C-NMR
(100 MHz, CDCl3)
S
O
OH
4ai
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

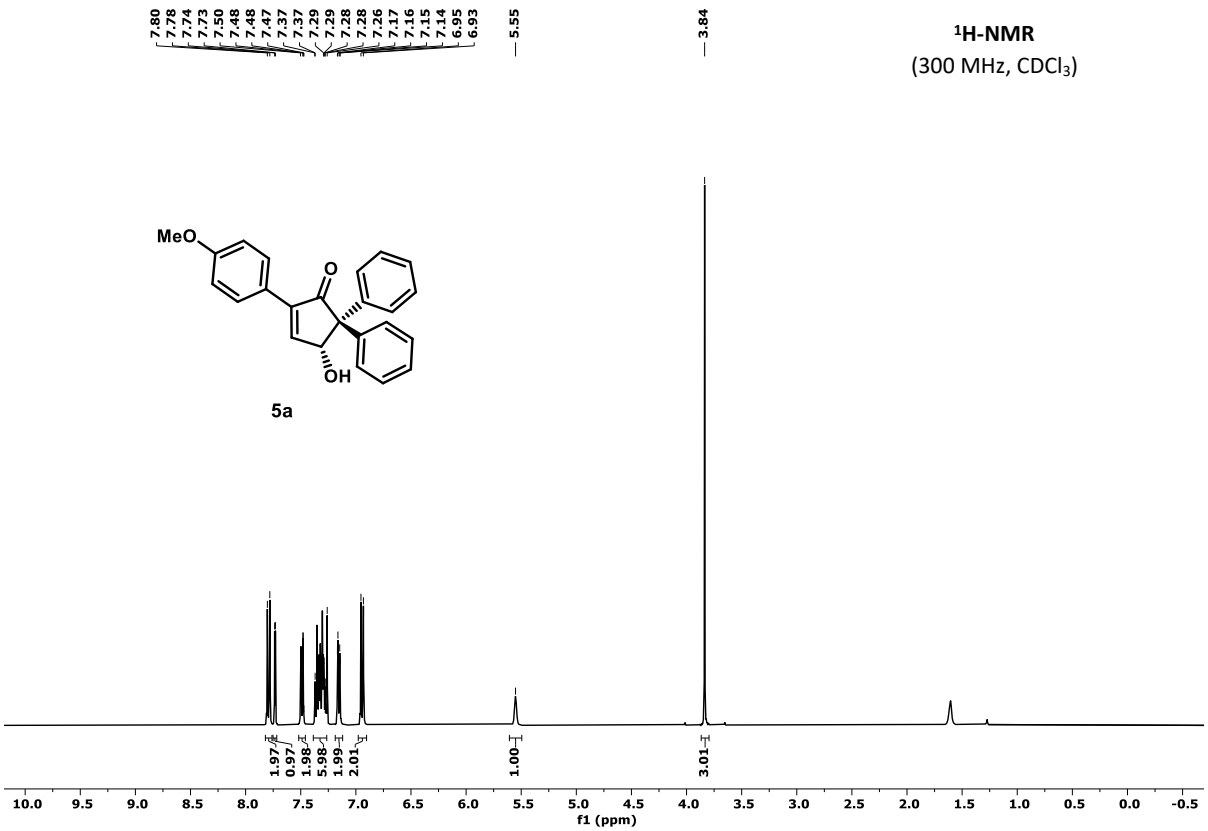


#	Peak Name	CH	tR [min]	Area [μV·sec]	Height [μV]	Area%	Height%	Quantity	NTP	Resolution	Symmetry Factor	Warning
1	Unknown	12	21.517	1824728	38818	50.273	55.119	N/A	5460	5.282	1.927	
2	Unknown	12	28.380	1804892	31608	49.727	44.881	N/A	6207	N/A	1.674	

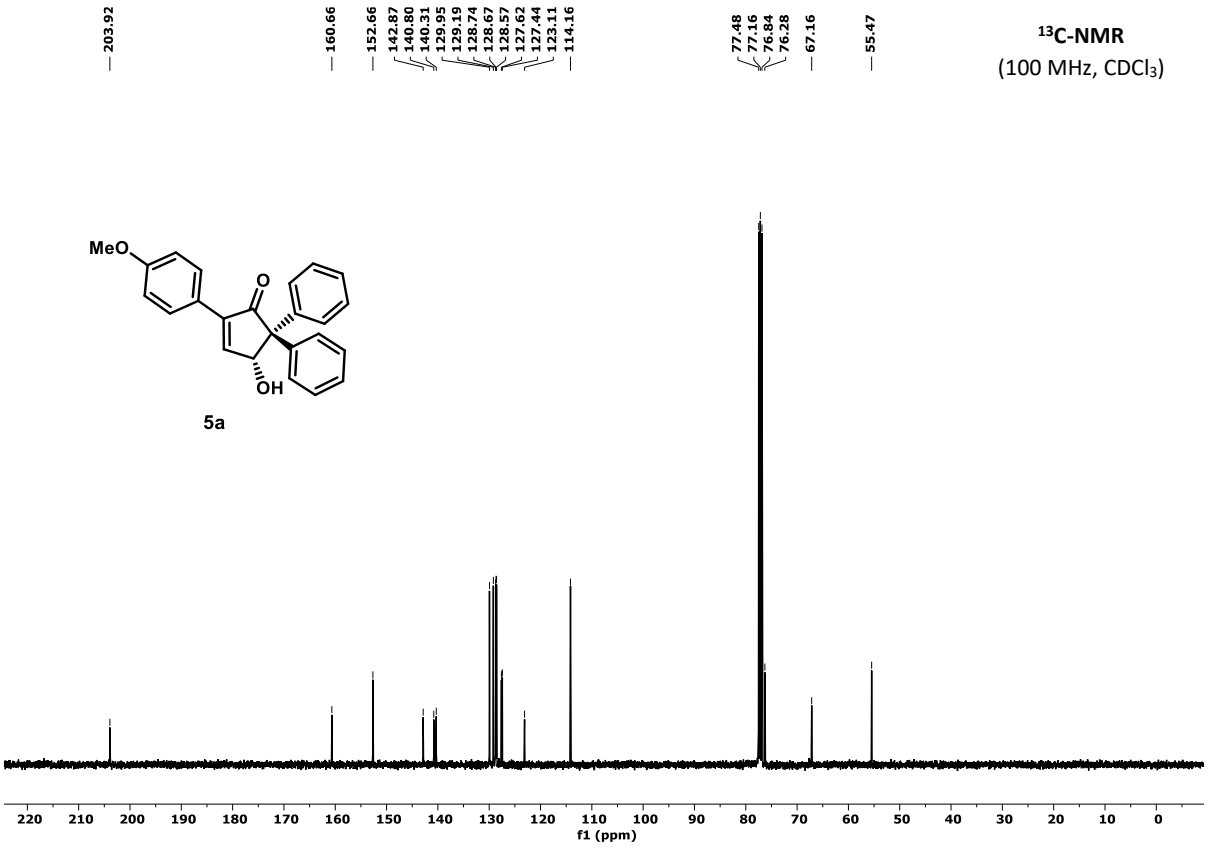
Daicel Chiralpak IB column (90:10 *n*-Hexane/*i*-PrOH, 1.0 mL/min, 250 nm)



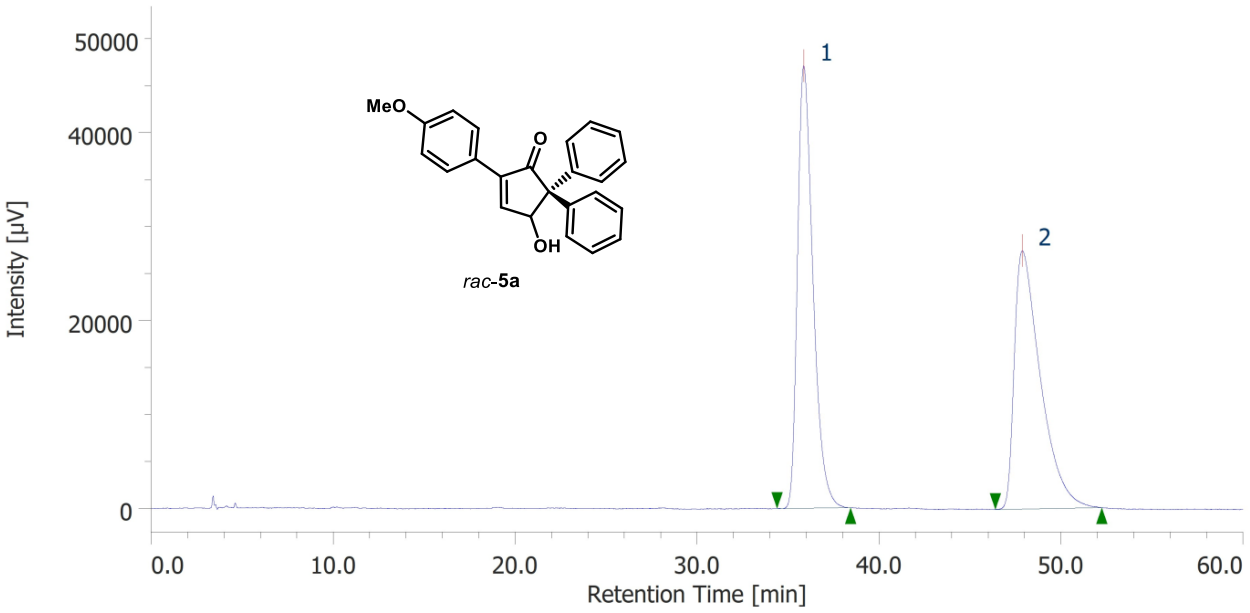
#	Peak Name	CH	tR [min]	Area [μV·sec]	Height [μV]	Area%	Height%	Quantity	NTP	Resolution	Symmetry Factor	Warning
1	Unknown	12	21.517	2245944	47455	94.003	94.843	N/A	5394	5.385	1.834	
2	Unknown	12	28.563	143269	2580	5.997	5.157	N/A	6190	N/A	1.465	



^{1}H-NMR
(300 MHz, $CDCl_3$)

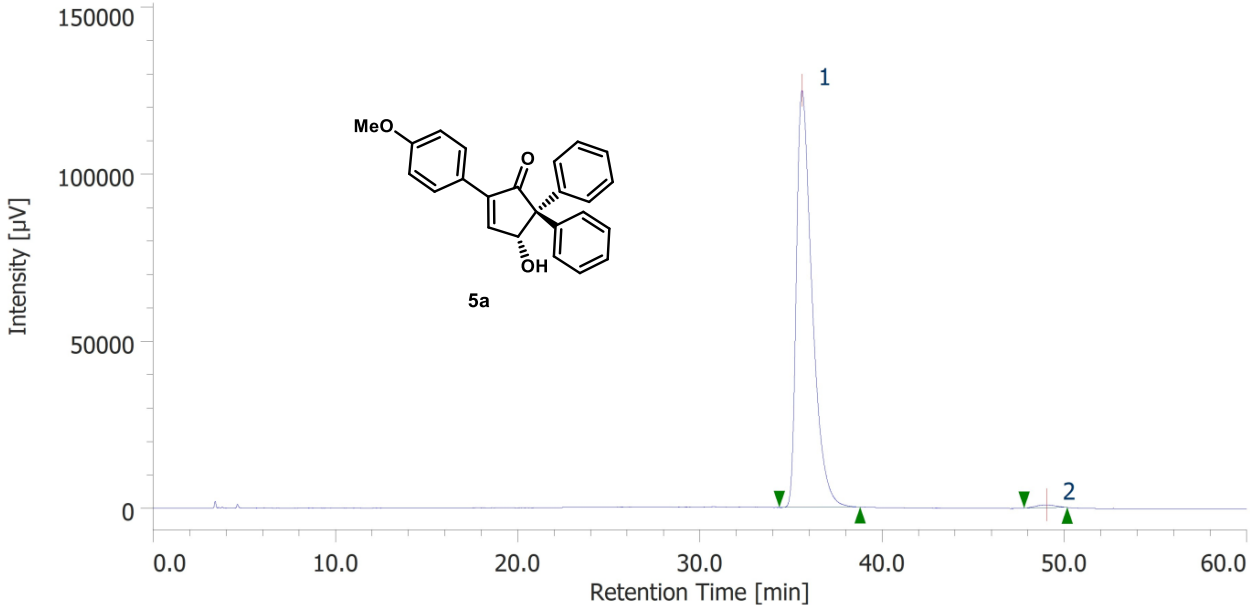


^{13}C-NMR
(100 MHz, $CDCl_3$)



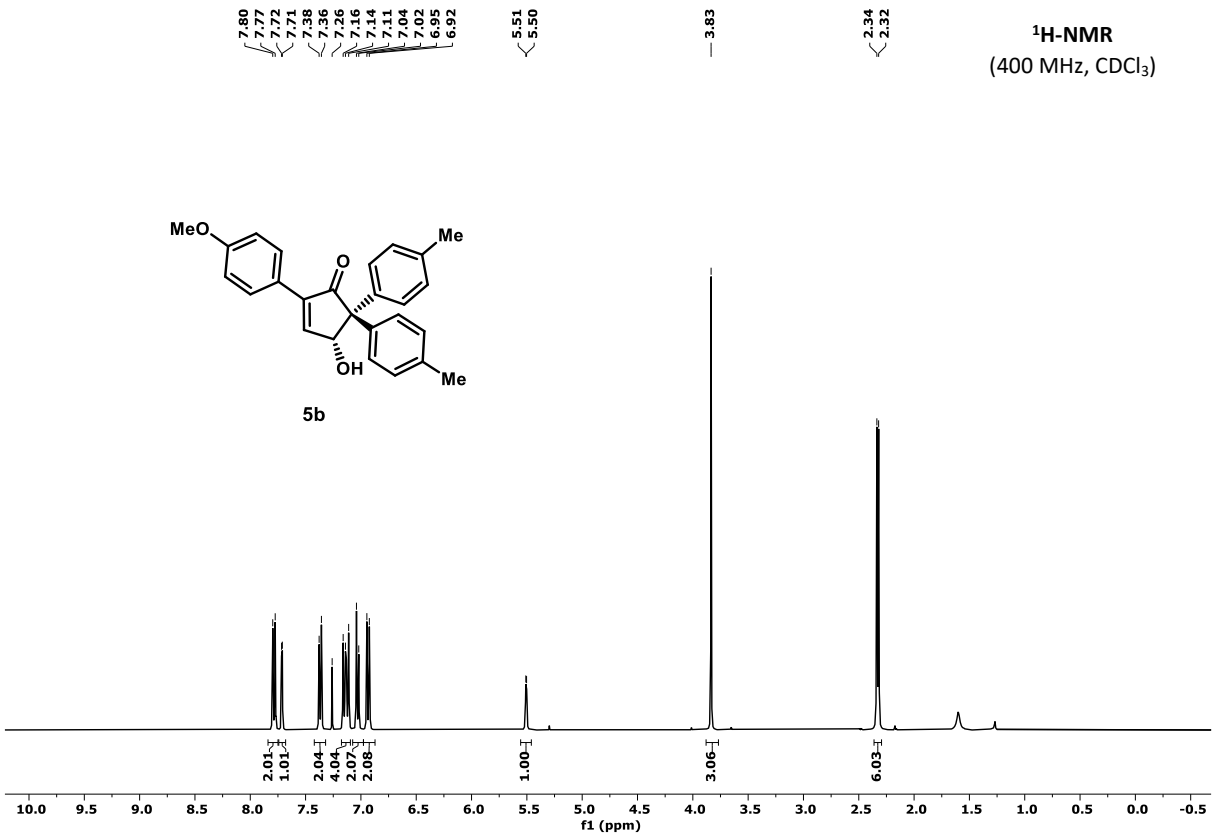
#	Peak Name	CH	tR [min]	Area [μV·sec]	Height [μV]	Area%	Height%	Quantity	NTP	Resolution	Symmetry Factor	Warning
1	Unknown	11	35.853	2780245	47061	50.382	63.129	N/A	8867	5.932	1.434	
2	Unknown	11	47.863	2738056	27487	49.618	36.871	N/A	5696	N/A	2.063	

Daicel Chiralpak IE column (90:10 *n*-Hexane/*i*-PrOH, 1.0 mL/min, 245 nm)

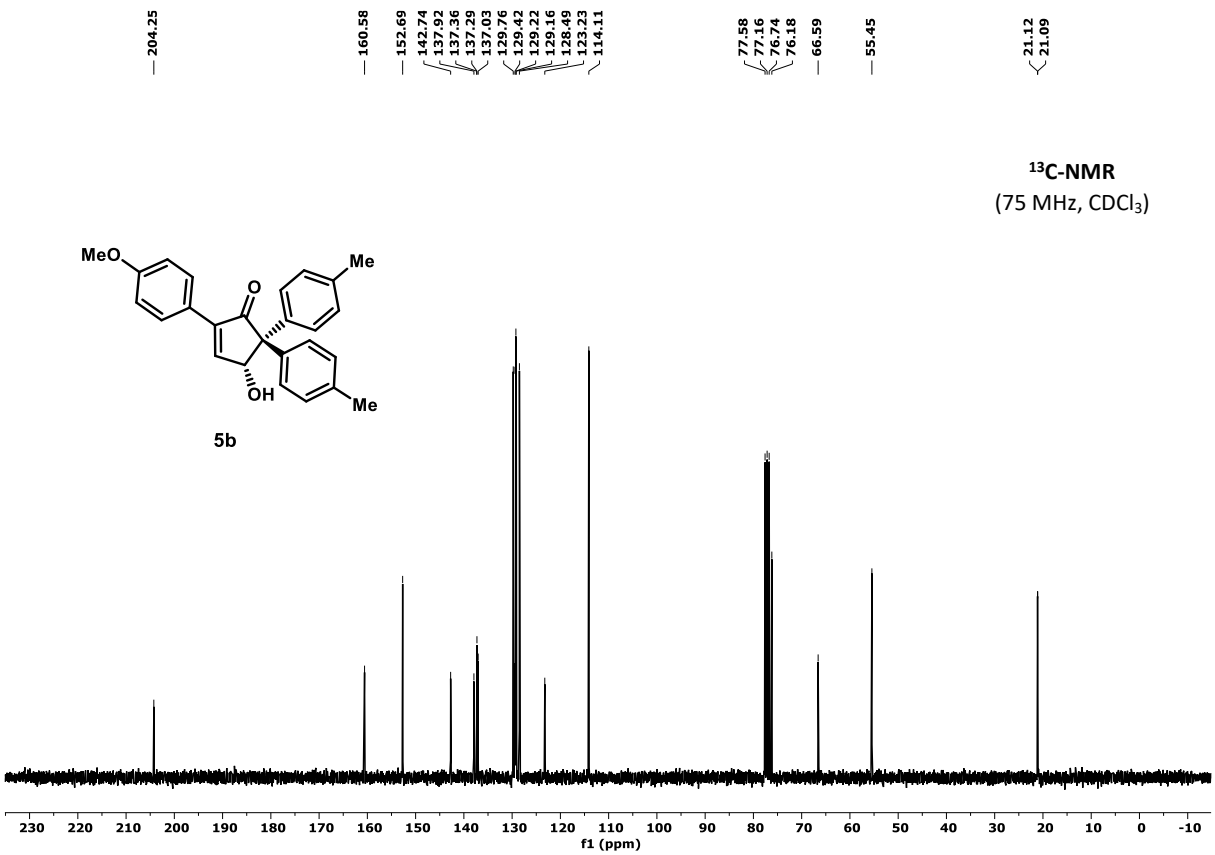


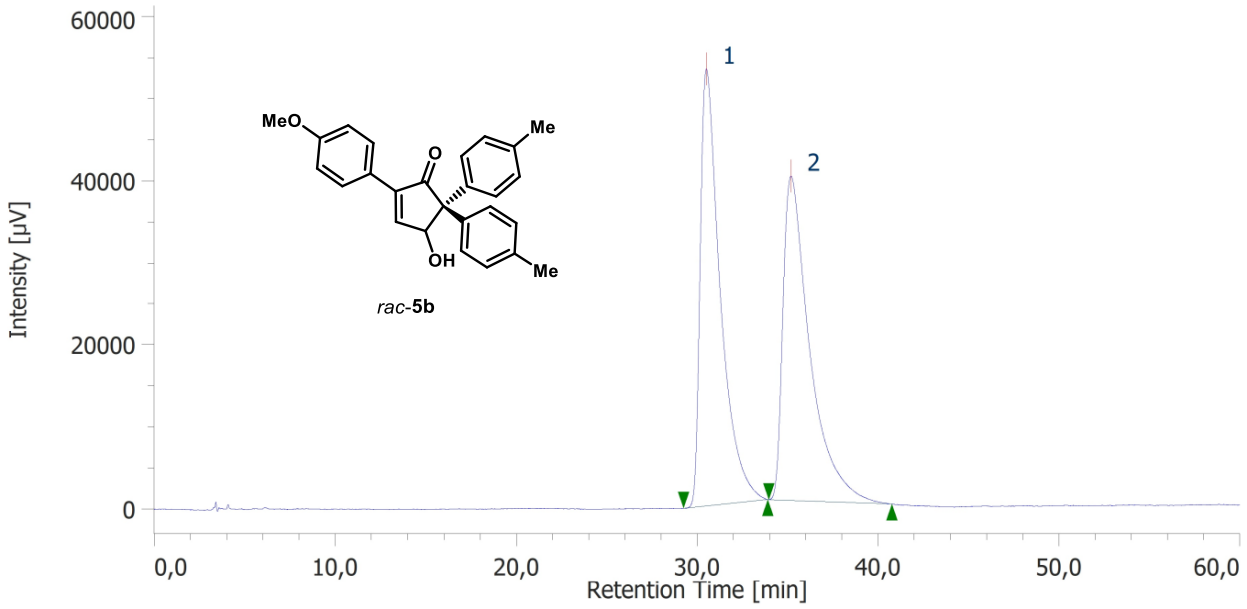
#	Peak Name	CH	tR [min]	Area [μV·sec]	Height [μV]	Area%	Height%	Quantity	NTP	Resolution	Symmetry Factor	Warning
1	Unknown	11	35.597	7456056	124689	99.143	99.316	N/A	8708	7.420	1.686	
2	Unknown	11	49.013	64474	859	0.857	0.684	N/A	8716	N/A	0.969	

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



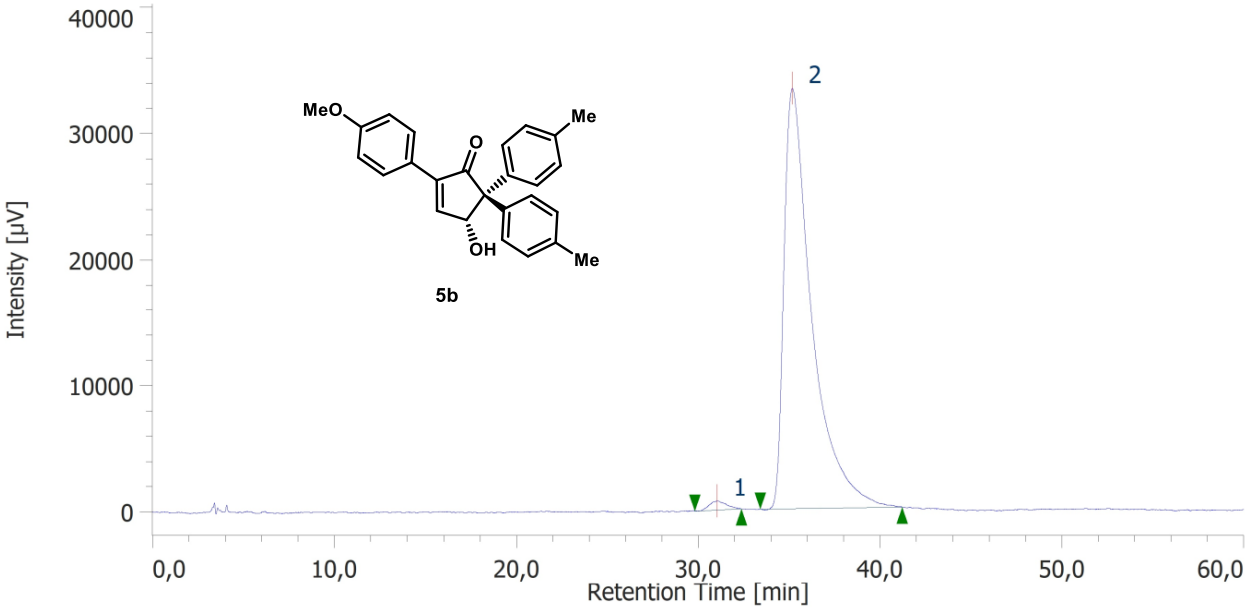
^{13}C-NMR
(75 MHz, $CDCl_3$)



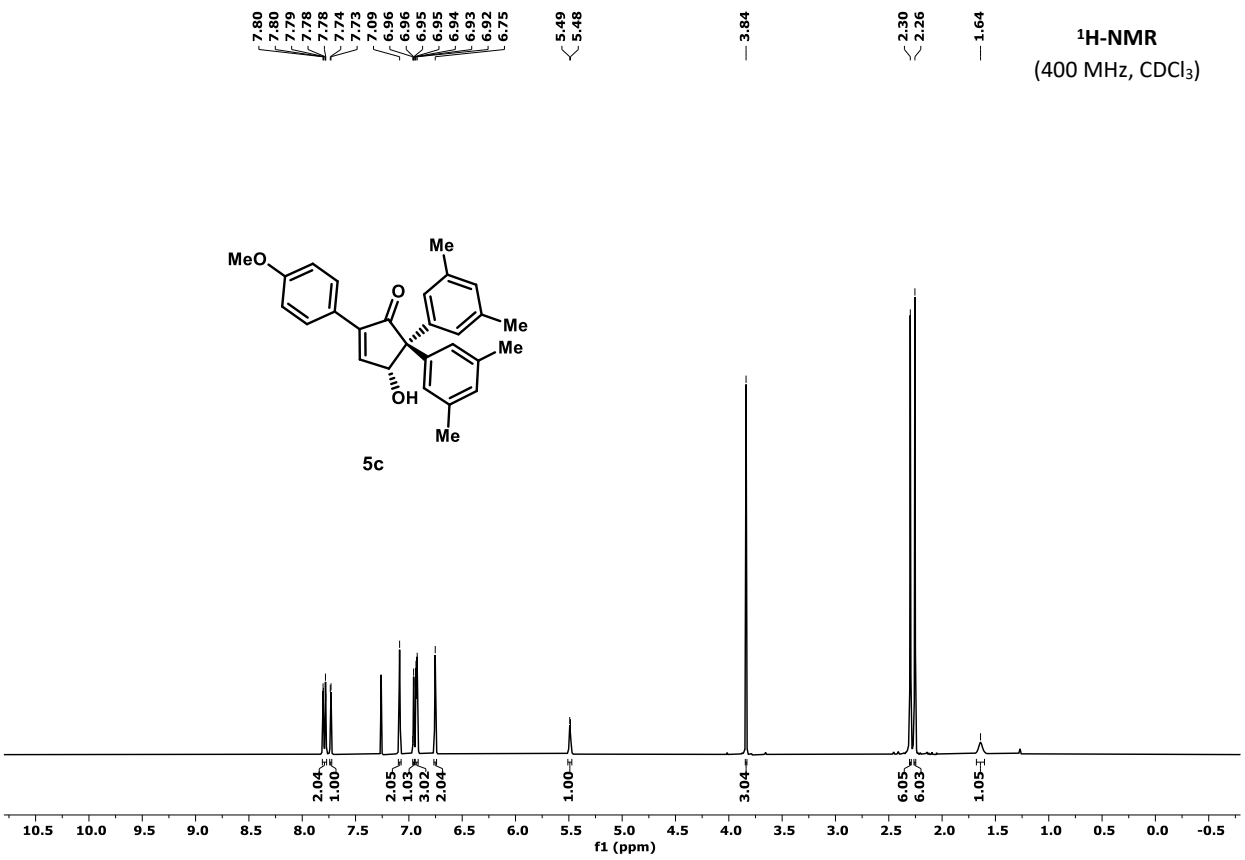


#	Peak Name	CH	tR [min]	Area [μV·sec]	Height [μV]	Area%	Height%	Quantity	NTP	Resolution	Symmetry Factor	Warning
1	Unknown	11	30,500	4107163	53212	50,260	57,387	N/A	4147	2,147	2,180	
2	Unknown	11	35,180	4064728	39513	49,740	42,613	N/A	3228	N/A	2,332	

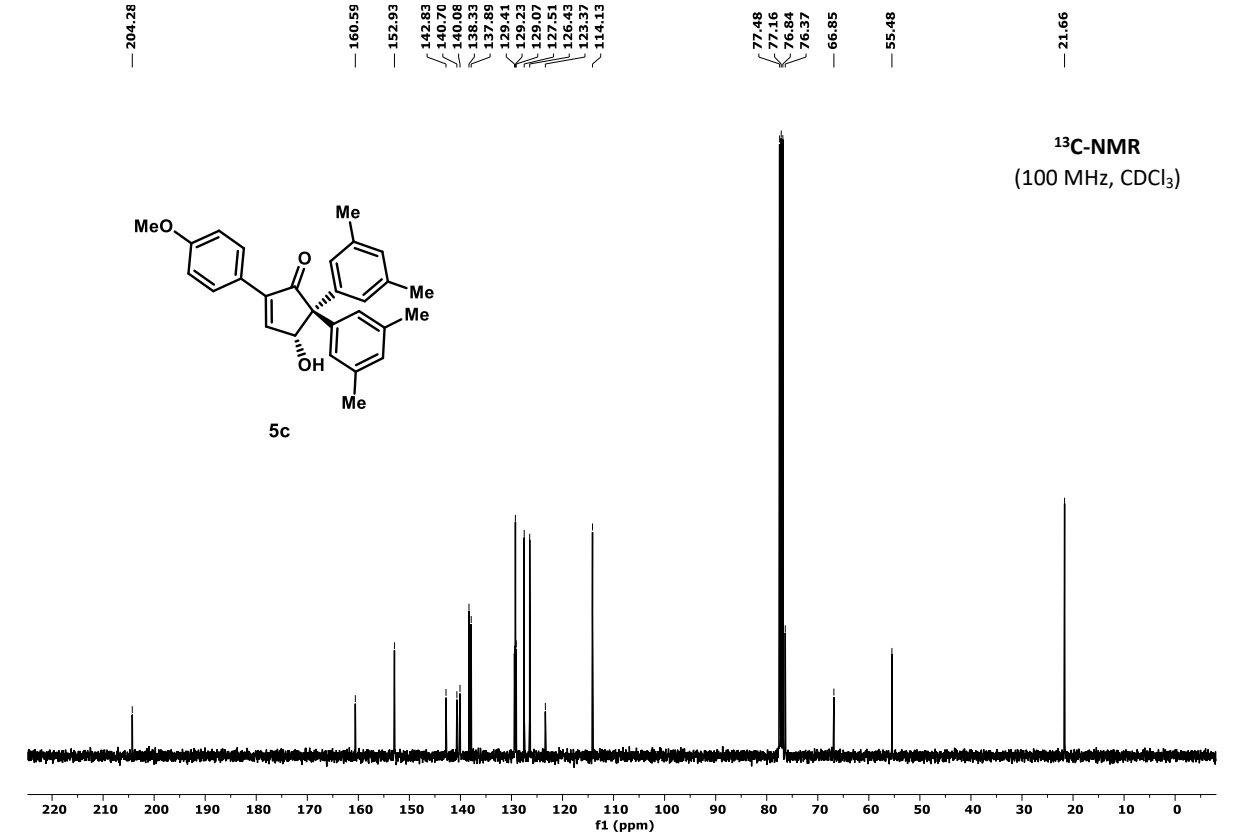
Daicel Chiralpak IB column (95:5 *n*-Hexane/*i*-PrOH, 1.0 mL/min, 245 nm)



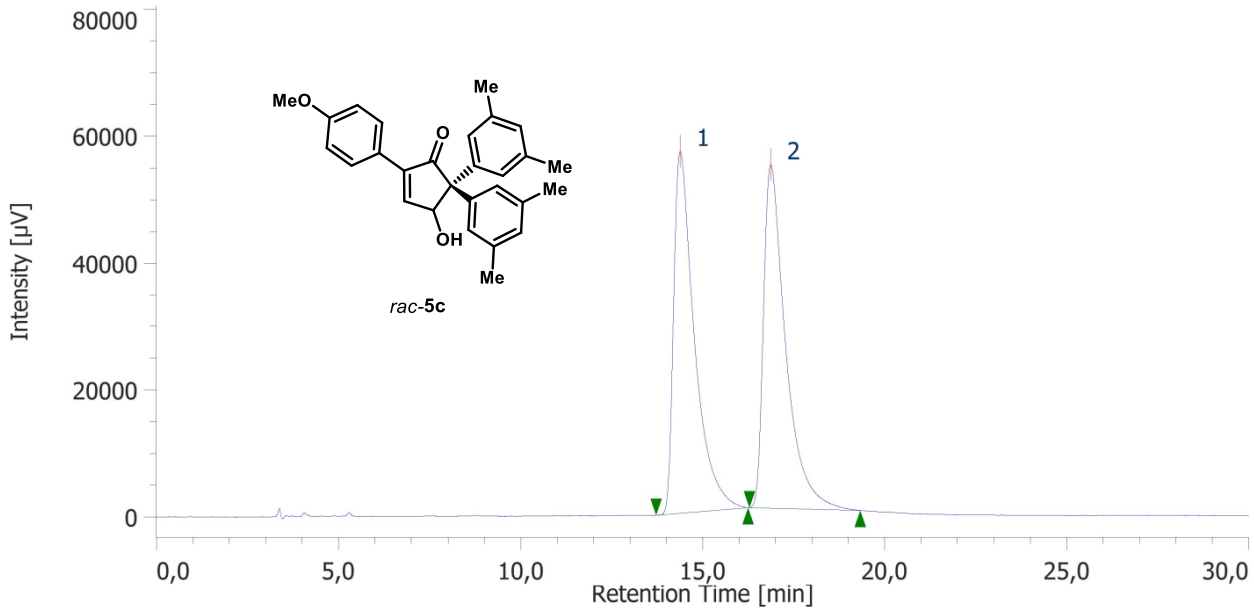
#	Peak Name	CH	tR [min]	Area [μV·sec]	Height [μV]	Area%	Height%	Quantity	NTP	Resolution	Symmetry Factor	Warning
1	Unknown	11	31,023	47306	718	1,322	2,110	N/A	4964	1,942	1,212	
2	Unknown	11	35,163	3531144	33311	98,678	97,890	N/A	3133	N/A	2,370	



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

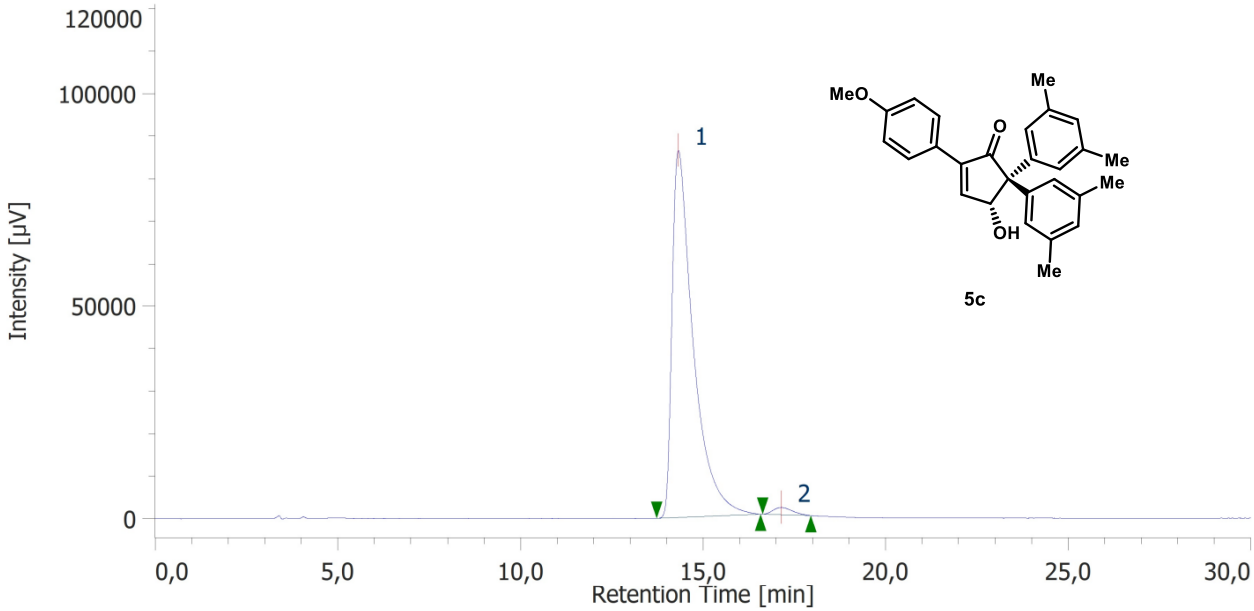


^{13}C-NMR
(100 MHz, $CDCl_3$)

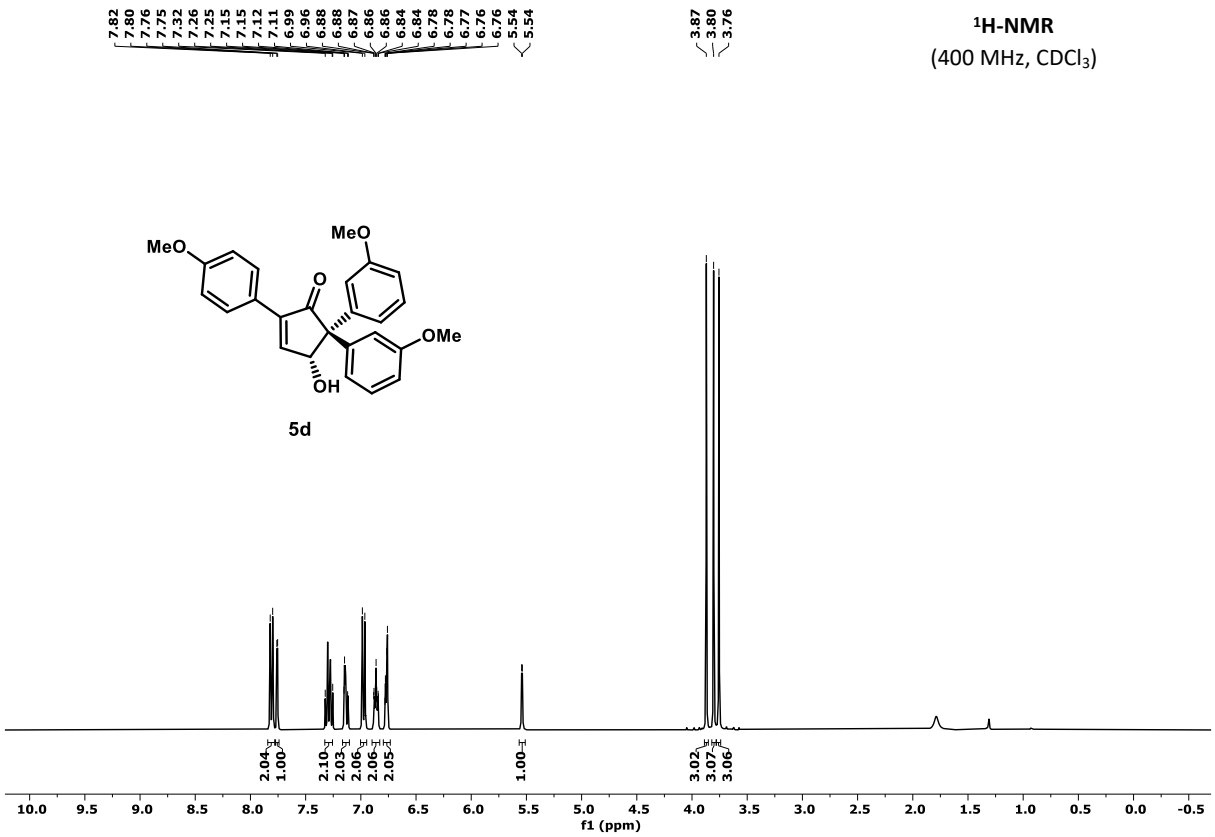


#	Peak Name	CH	tR [min]	Area [μV·sec]	Height [μV]	Area%	Height%	Quantity	NTP	Resolution	Symmetry Factor	Warning
1	Unknown	11	14,377	2266607	57032	49,815	51,299	N/A	3492	2,492	2,110	
2	Unknown	11	16,863	2283466	54145	50,185	48,701	N/A	4308	N/A	2,013	

Daicel Chiralpak IB column (95:5 *n*-Hexane/*i*-PrOH, 1.0 mL/min, 248 nm)

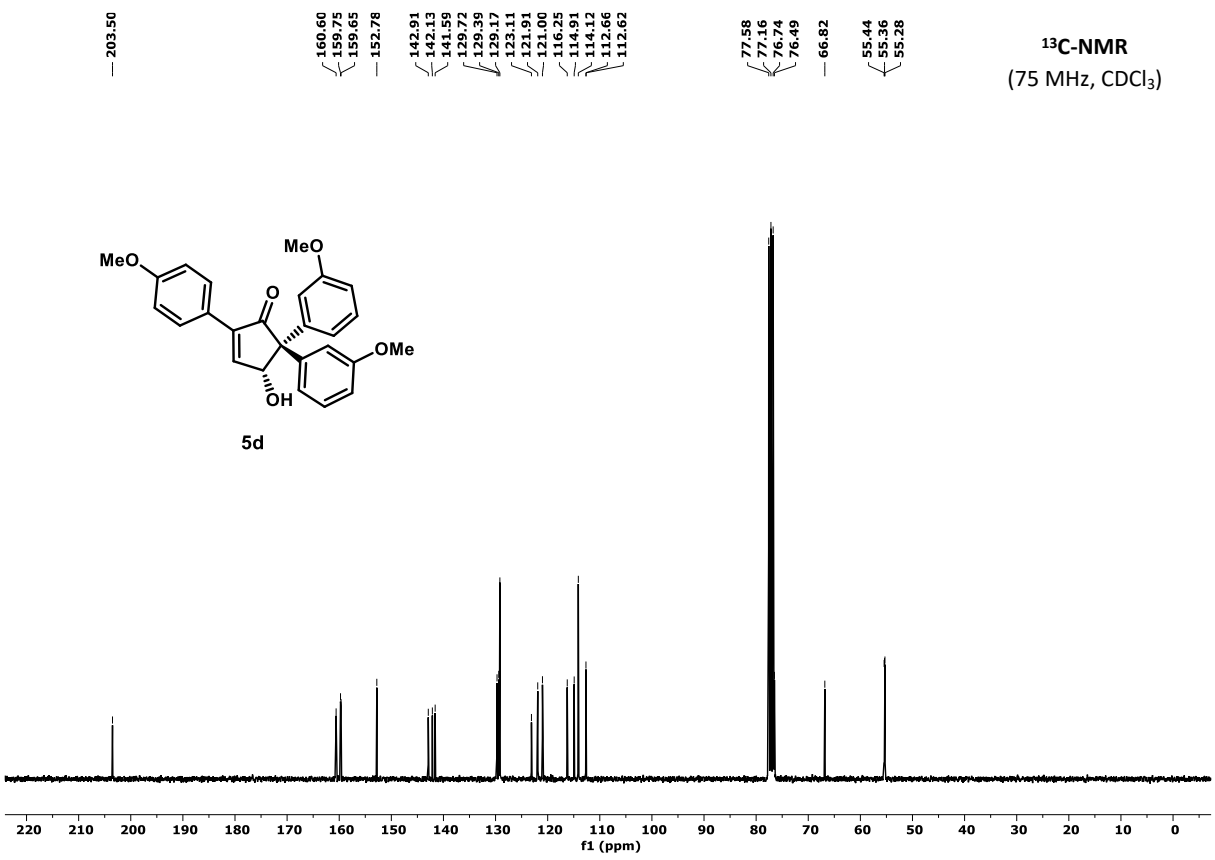


#	Peak Name	CH	tR [min]	Area [μV·sec]	Height [μV]	Area%	Height%	Quantity	NTP	Resolution	Symmetry Factor	Warning
1	Unknown	11	14,320	3475499	86311	98,219	98,049	N/A	3476	2,868	2,292	
2	Unknown	11	17,137	63015	1717	1,781	1,951	N/A	4719	N/A	1,275	



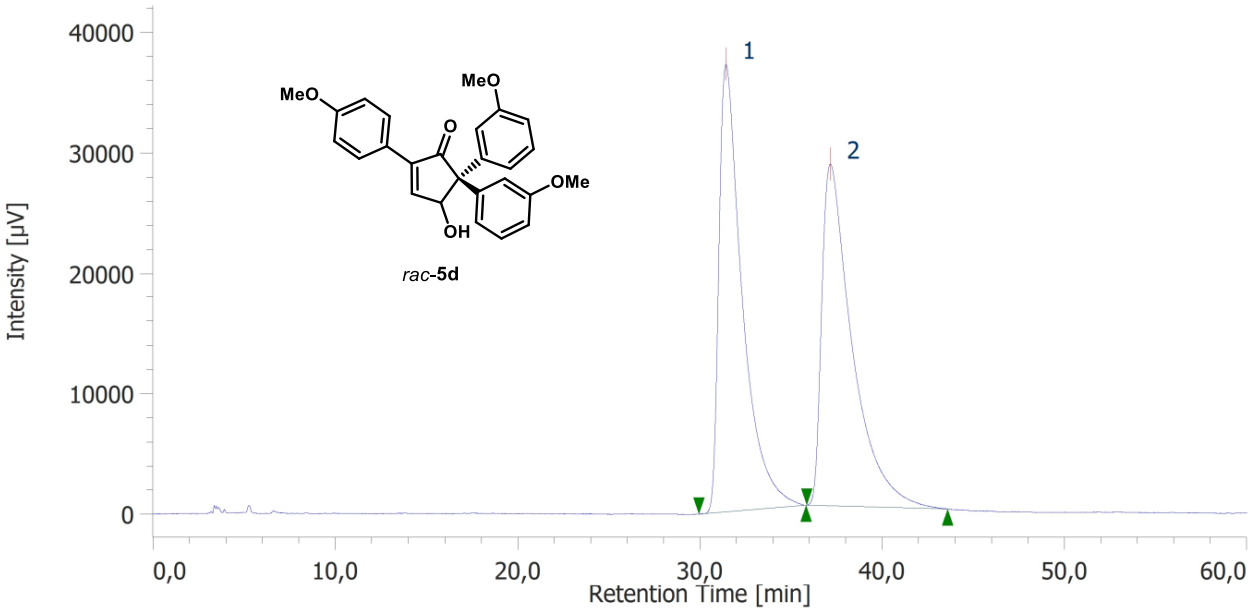
^{1}H-NMR
(400 MHz, $CDCl_3$)

5d



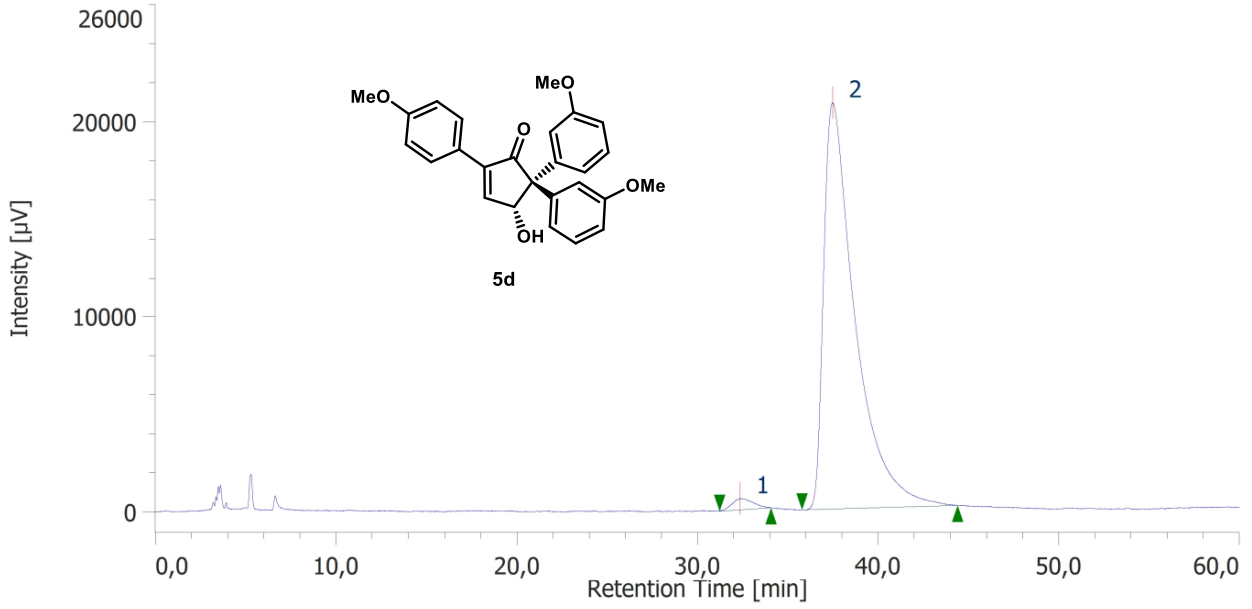
^{13}C-NMR
(75 MHz, $CDCl_3$)

5d

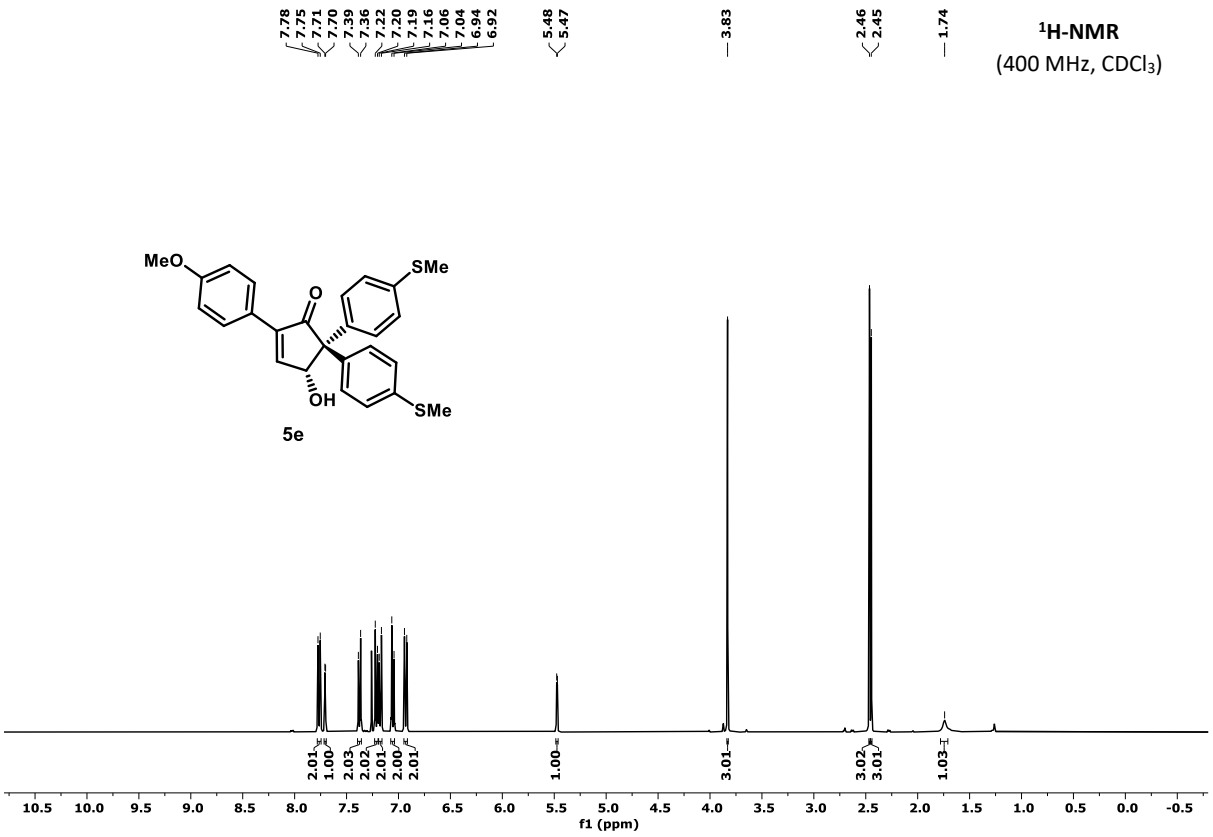


#	Peak Name	CH	tR [min]	Area [μV·sec]	Height [μV]	Area%	Height%	Quantity	NTP	Resolution	Symmetry Factor	Warning
1	Unknown	11	31,417	3306768	37146	50,202	56,712	N/A	3372	2,317	2,272	
2	Unknown	11	37,147	3280094	28353	49,798	43,288	N/A	2824	N/A	2,482	

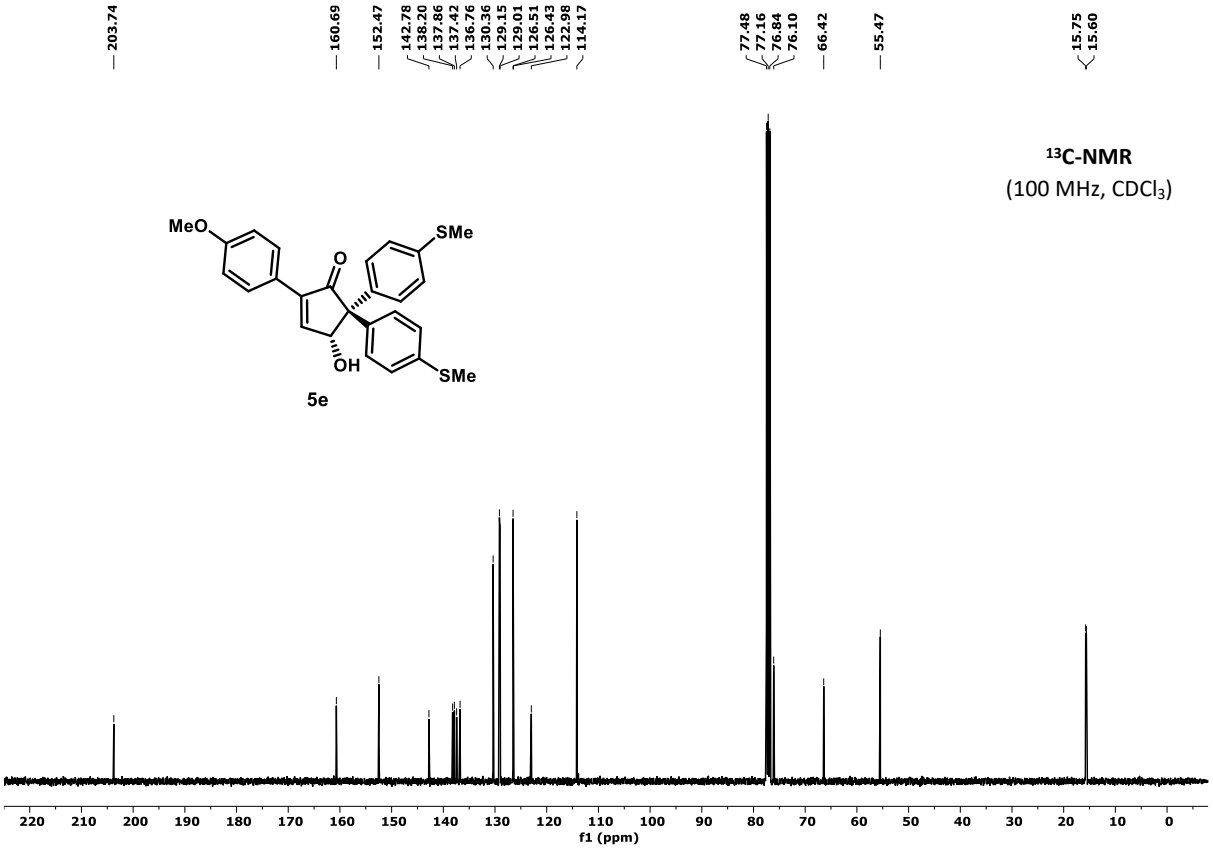
Daicel Chiralpak IB column (90:10 *n*-Hexane/*i*-PrOH, 1.0 mL/min, 245 nm)



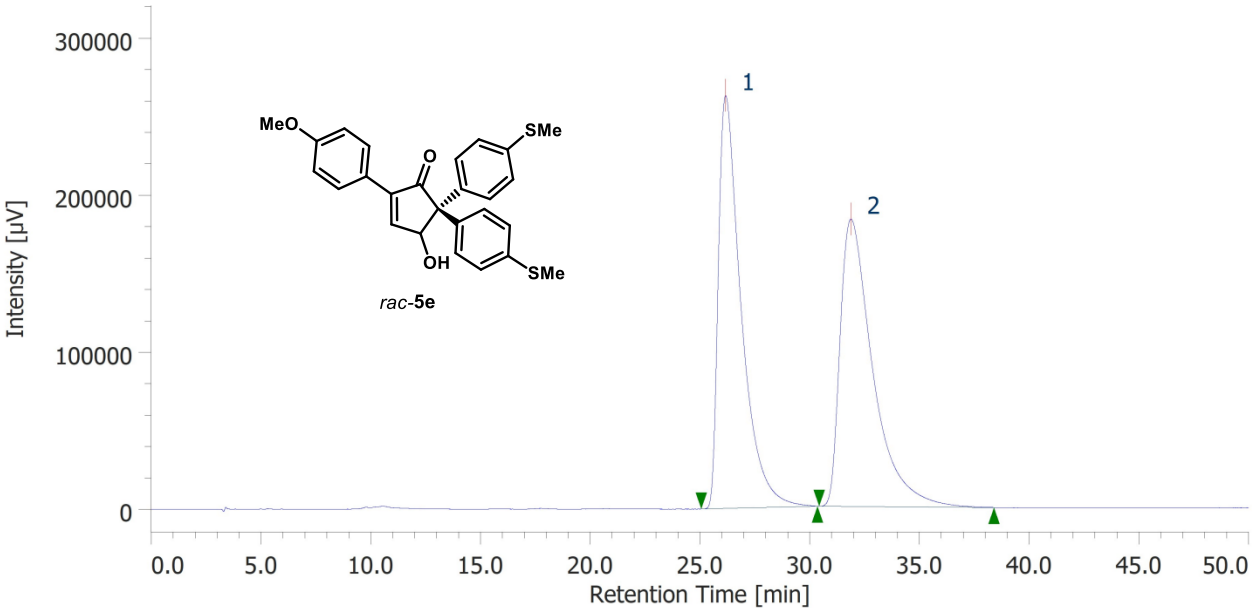
#	Peak Name	CH	tR [min]	Area [μV·sec]	Height [μV]	Area%	Height%	Quantity	NTP	Resolution	Symmetry Factor	Warning
1	Unknown	11	32,347	46122	570	1,801	2,668	N/A	3424	2,014	1,295	
2	Unknown	11	37,473	2515092	20811	98,199	97,332	N/A	2683	N/A	2,453	



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

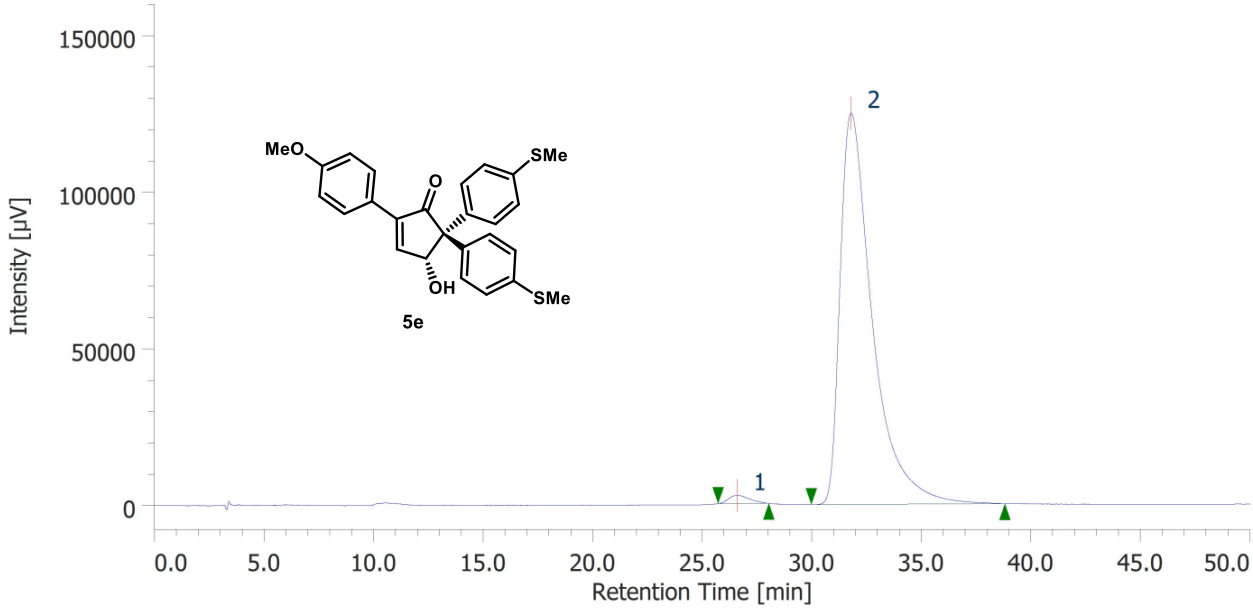


^{13}C-NMR
(100 MHz, $CDCl_3$)



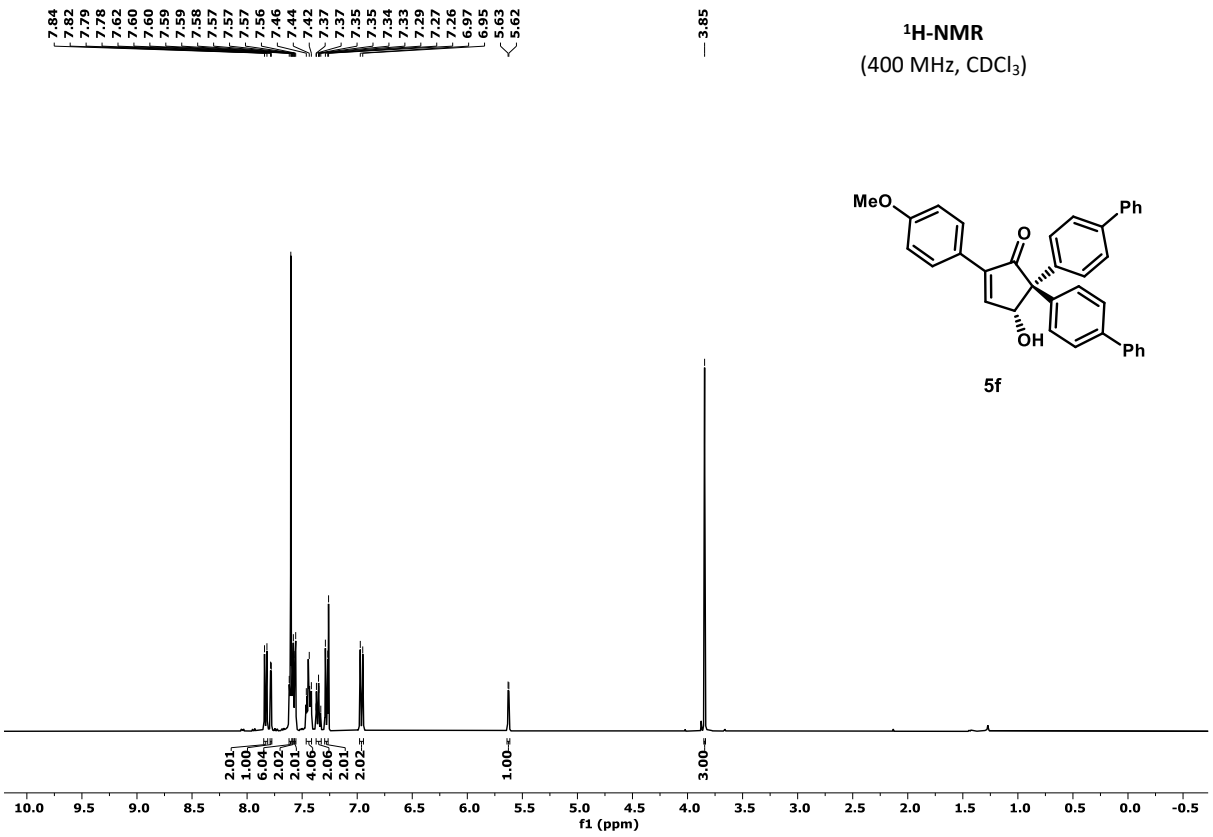
#	Peak Name	CH	tR [min]	Area [μV·sec]	Height [μV]	Area%	Height%	Quantity	NTP	Resolution	Symmetry Factor	Warning
1	Unknown	11	26.163	18977022	262986	50.074	58.979	N/A	3434	2.641	2.084	
2	Unknown	11	31.873	18921043	182914	49.926	41.021	N/A	2500	N/A	2.042	

Daicel Chiralpak IB column (85:15 *n*-Hexane/*i*-PrOH, 1.0 mL/min, 260 nm)



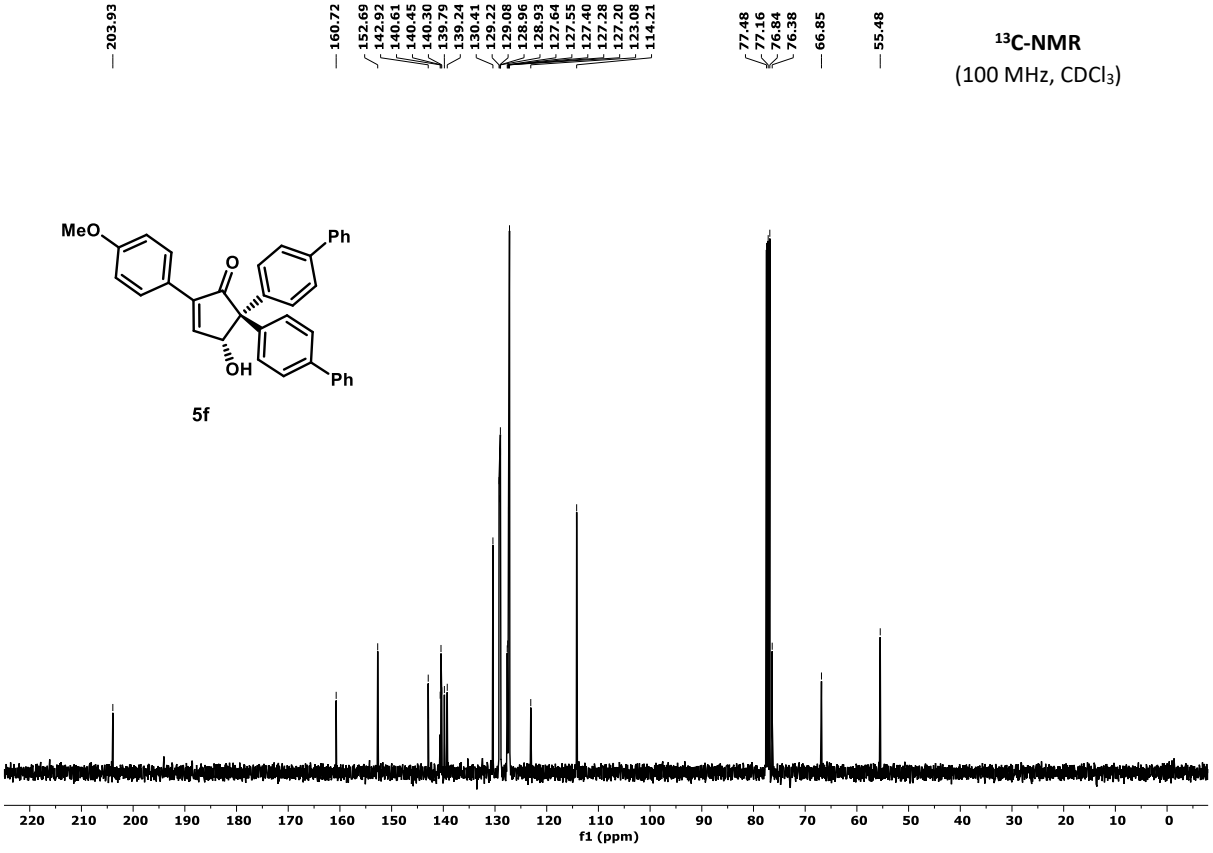
#	Peak Name	CH	tR [min]	Area [μV·sec]	Height [μV]	Area%	Height%	Quantity	NTP	Resolution	Symmetry Factor	Warning
1	Unknown	11	26.593	174065	2647	1.345	2.076	N/A	3475	2.428	1.349	
2	Unknown	11	31.793	12769407	124865	98.655	97.924	N/A	2606	N/A	1.981	

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

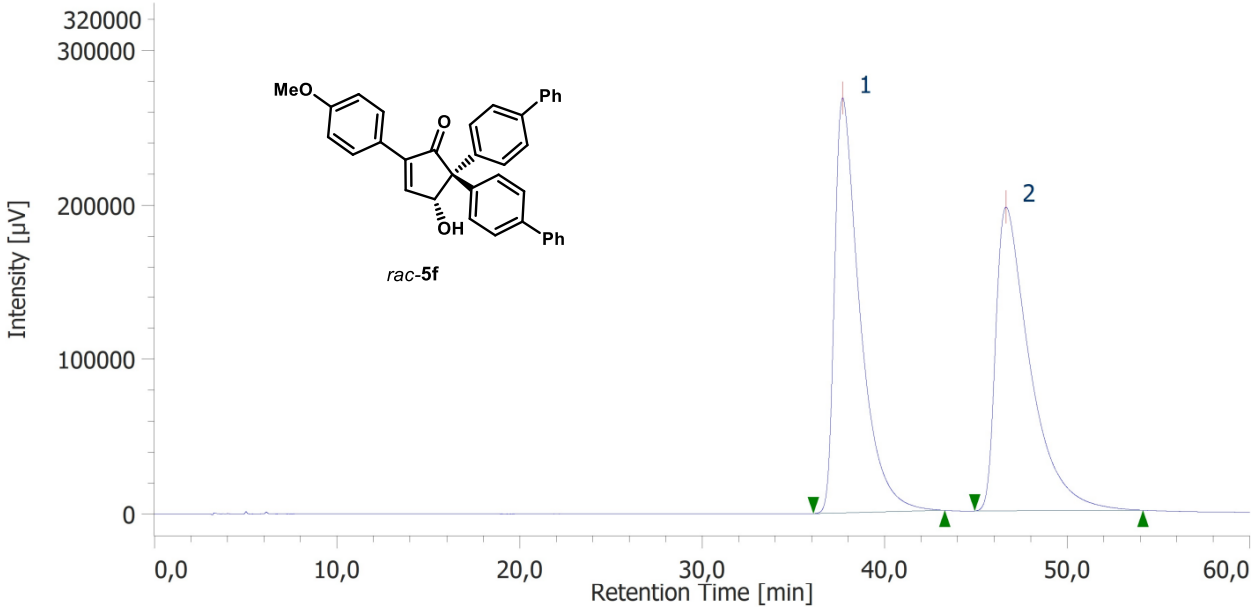


5f

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

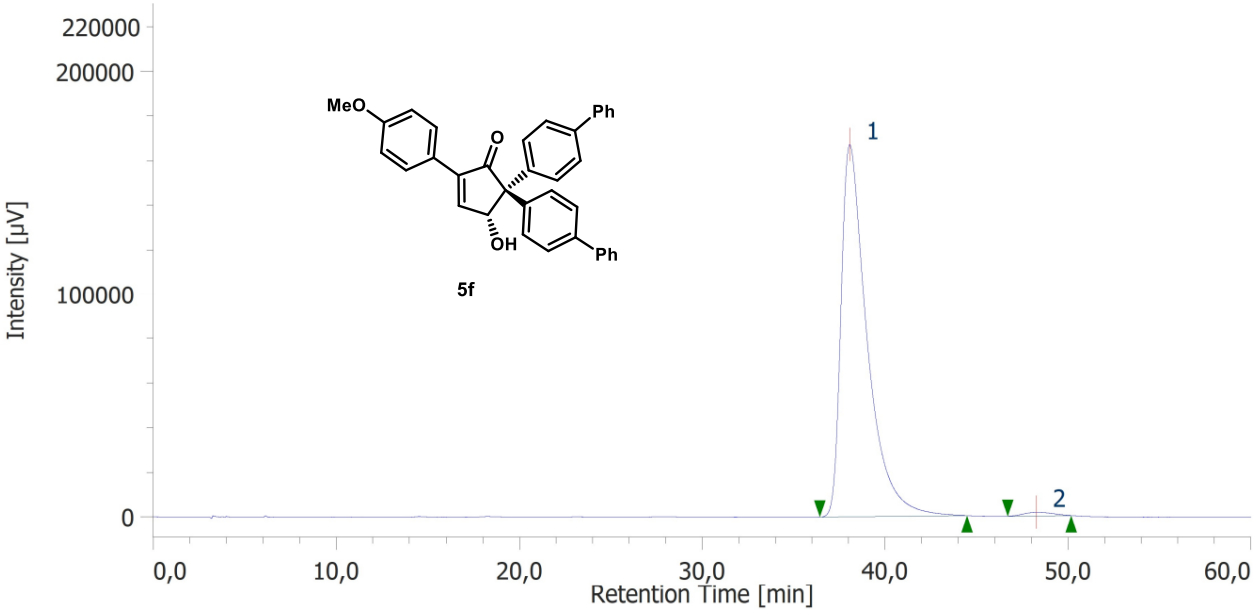


5f

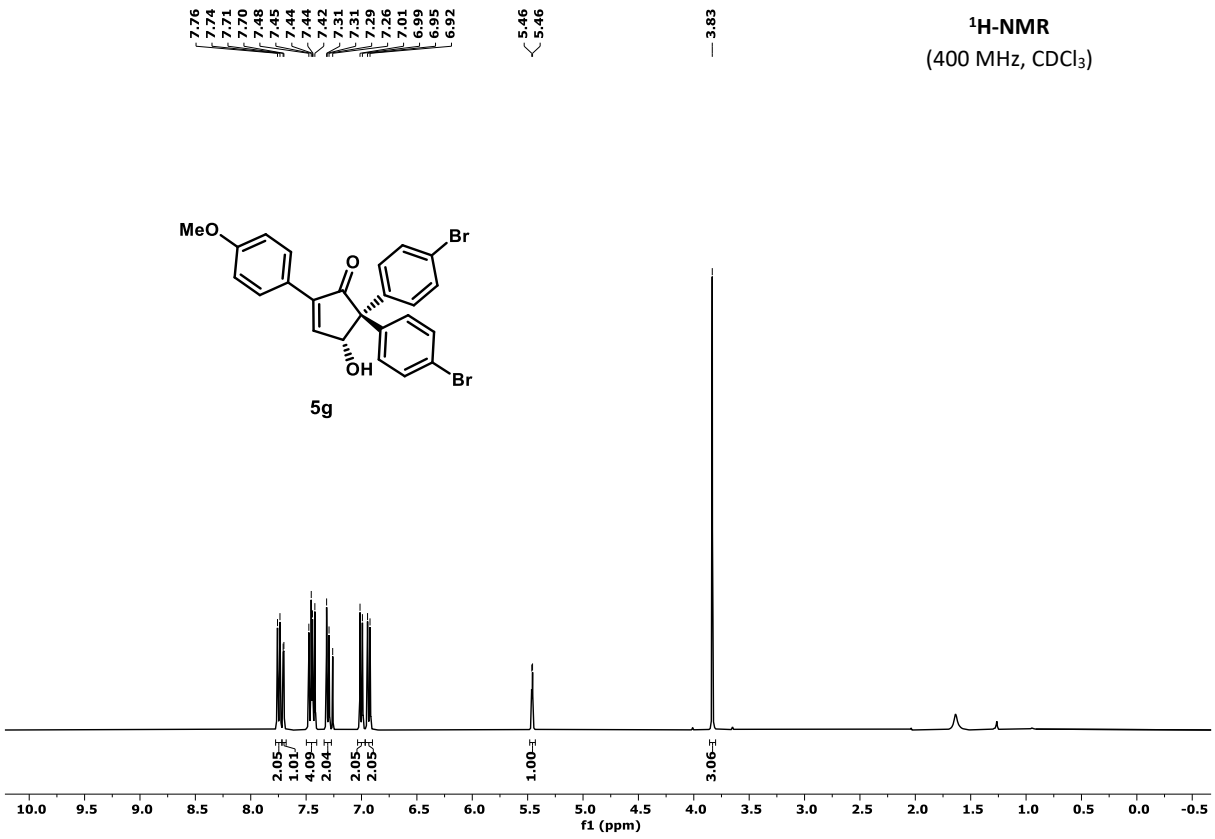


#	Peak Name	CH	tR [min]	Area [μV·sec]	Height [μV]	Area%	Height%	Quantity	NTP	Resolution	Symmetry Factor	Warning
1	Unknown	11	37,683	25913962	268192	50,248	57,698	N/A	4026	3,224	2,024	
2	Unknown	11	46,640	25658509	196627	49,752	42,302	N/A	3410	N/A	2,206	

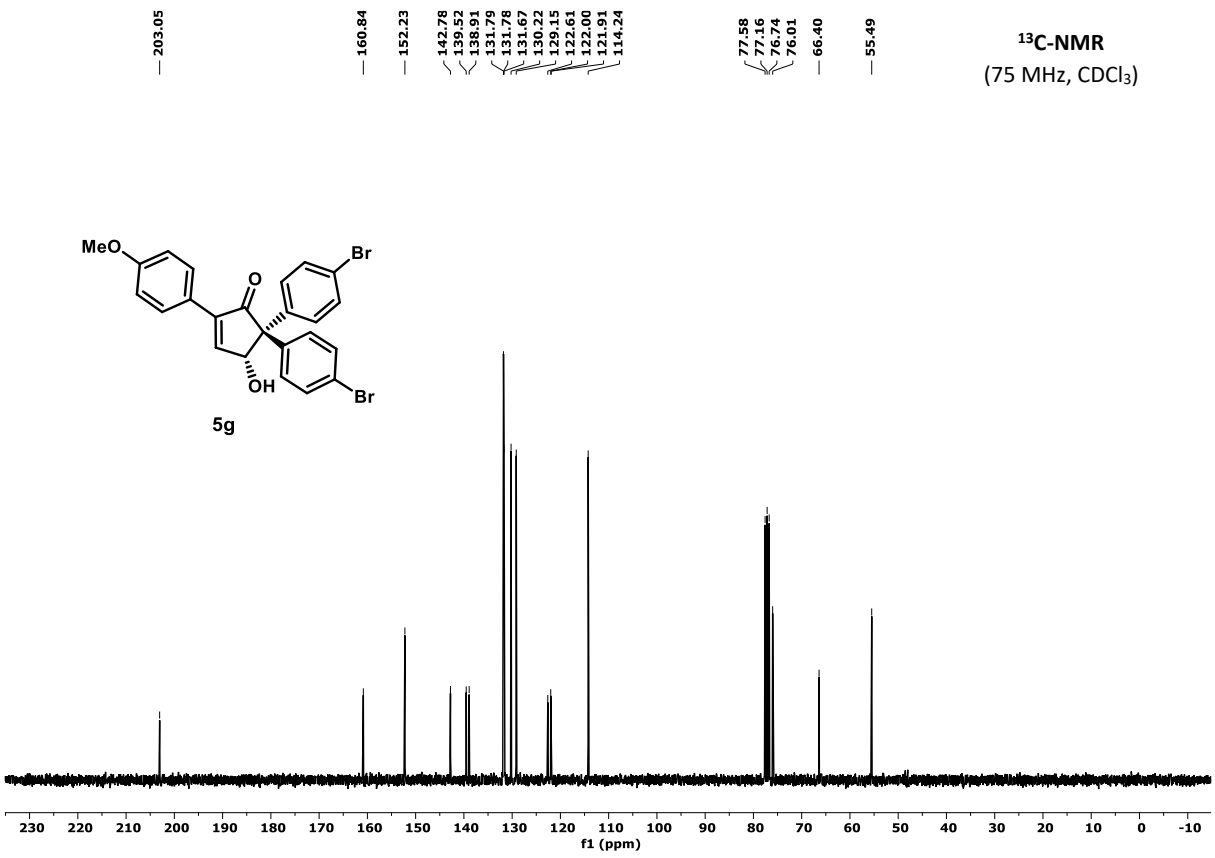
Daicel Chiralpak IB column (80:20 *n*-Hexane/*i*-PrOH, 1.0 mL/min, 256 nm)



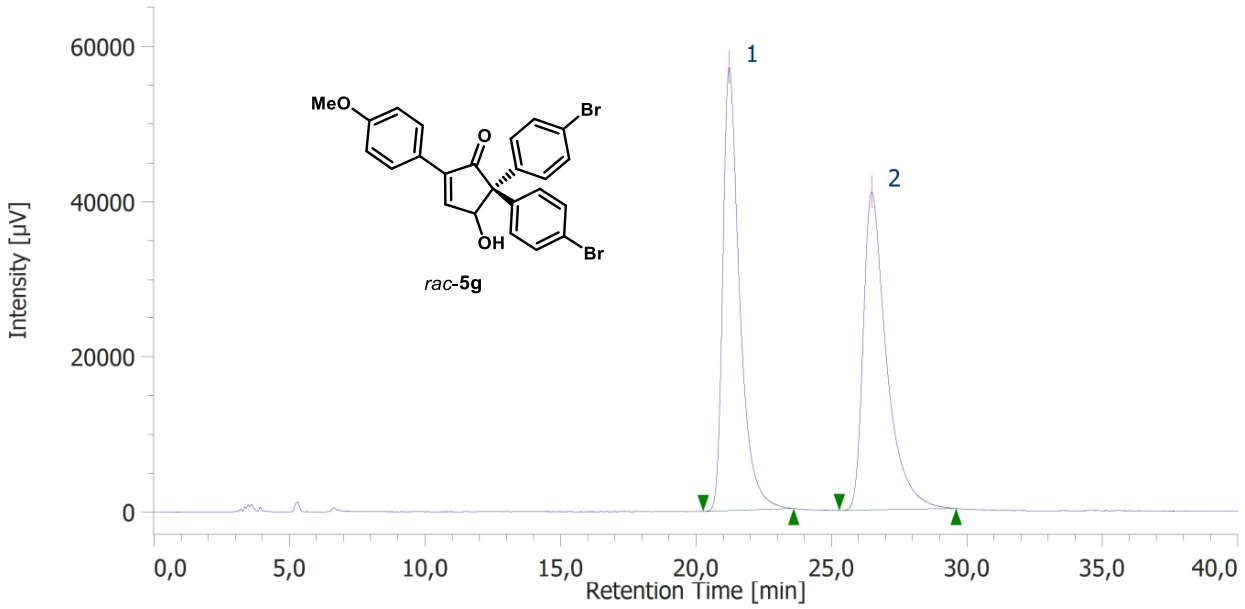
#	Peak Name	CH	tR [min]	Area [μV·sec]	Height [μV]	Area%	Height%	Quantity	NTP	Resolution	Symmetry Factor	Warning
1	Unknown	11	38,053	16594960	167056	98,911	99,005	N/A	3952	3,721	1,922	
2	Unknown	11	48,253	182655	1679	1,089	0,995	N/A	3936	N/A	1,140	



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

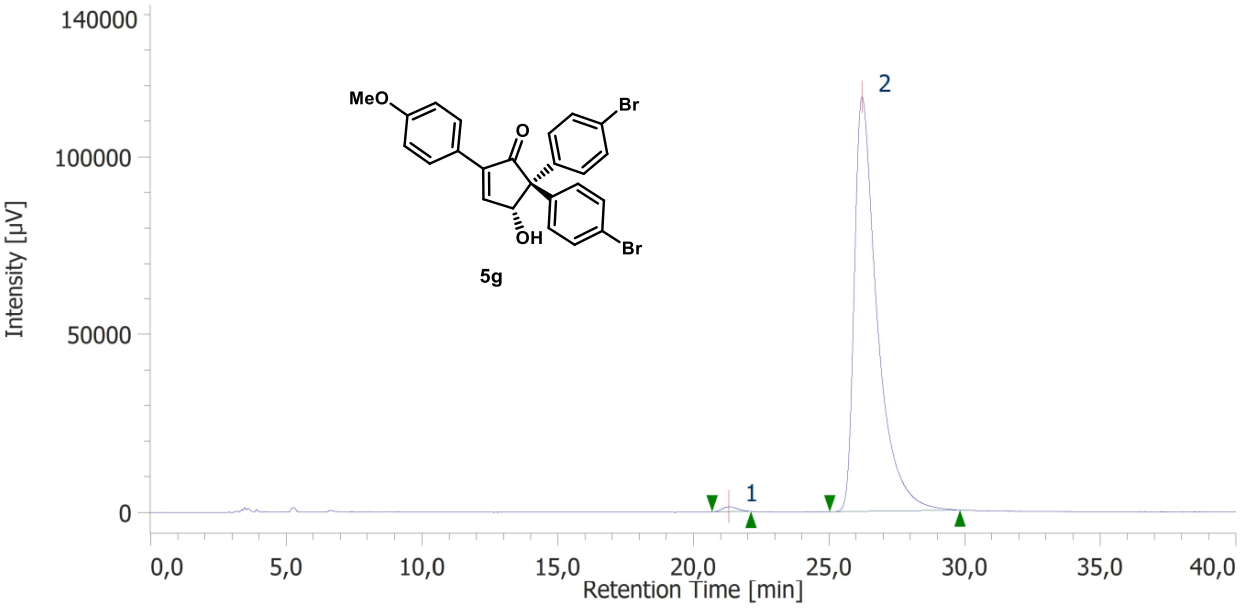


^{13}C-NMR
(75 MHz, $CDCl_3$)



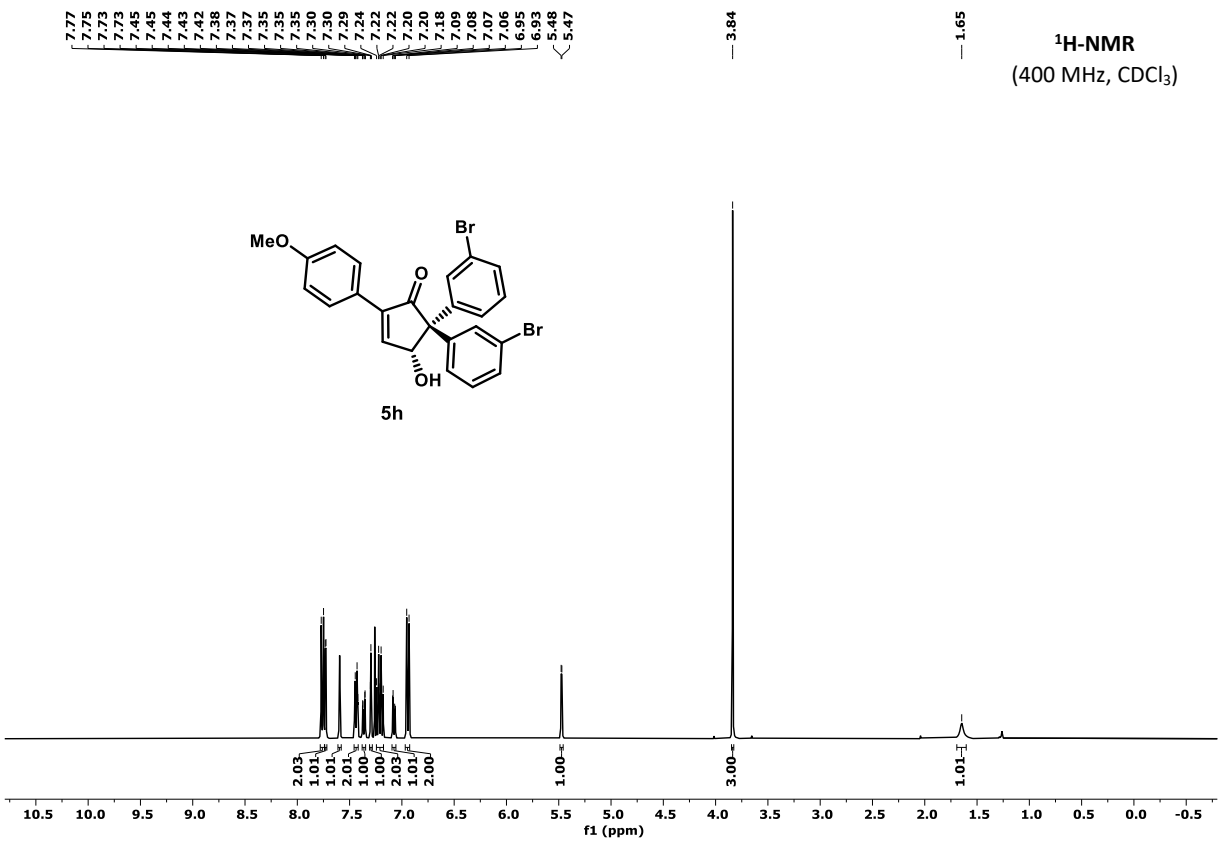
#	Peak Name	CH	tR [min]	Area [μV·sec]	Height [μV]	Area%	Height%	Quantity	NTP	Resolution	Symmetry Factor	Warning
1	Unknown	11	21.220	2464097	57096	50.179	58.209	N/A	6376	4.197	1.603	
2	Unknown	11	26.483	2446559	40992	49.821	41.791	N/A	5324	N/A	1.720	

Daicel Chiralpak IB column (90:10 *n*-Hexane/*i*-PrOH, 1.0 mL/min, 245 nm)

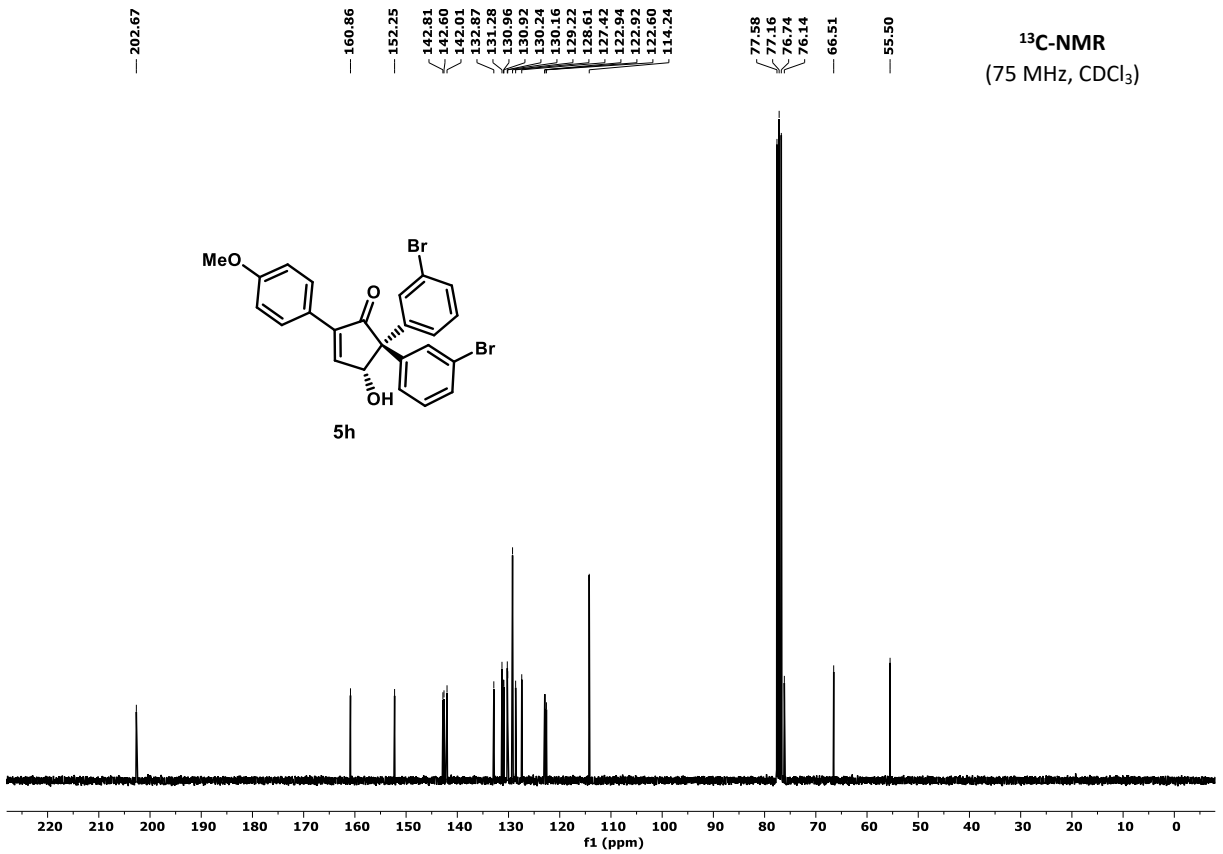


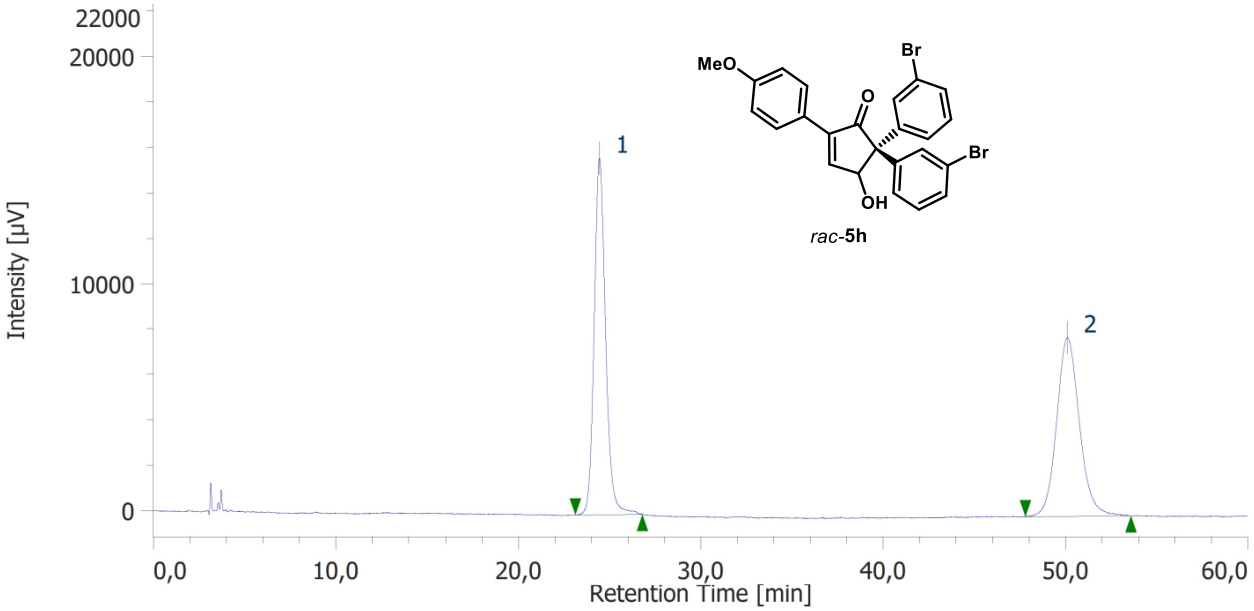
#	Peak Name	CH	tR [min]	Area [μV·sec]	Height [μV]	Area%	Height%	Quantity	NTP	Resolution	Symmetry Factor	Warning
1	Unknown	11	21.307	54903	1388	0.799	1.177	N/A	6143	3.937	1.187	
2	Unknown	11	26.213	6816766	116547	99.201	98.823	N/A	5513	N/A	1.909	

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



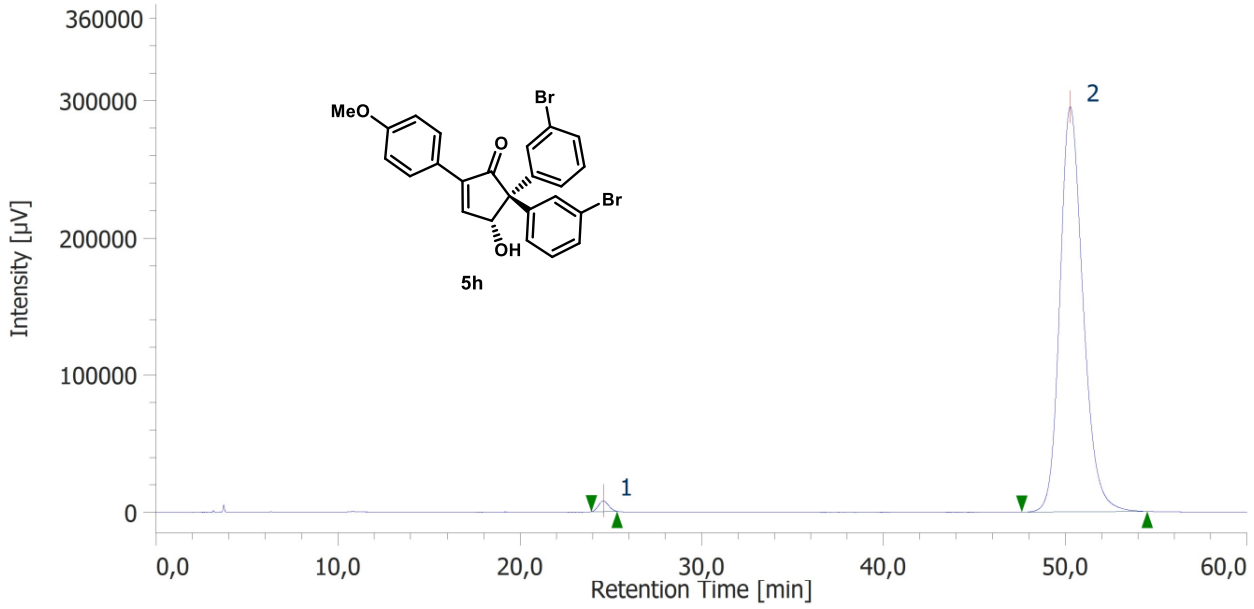
^{13}C-NMR
(75 MHz, $CDCl_3$)





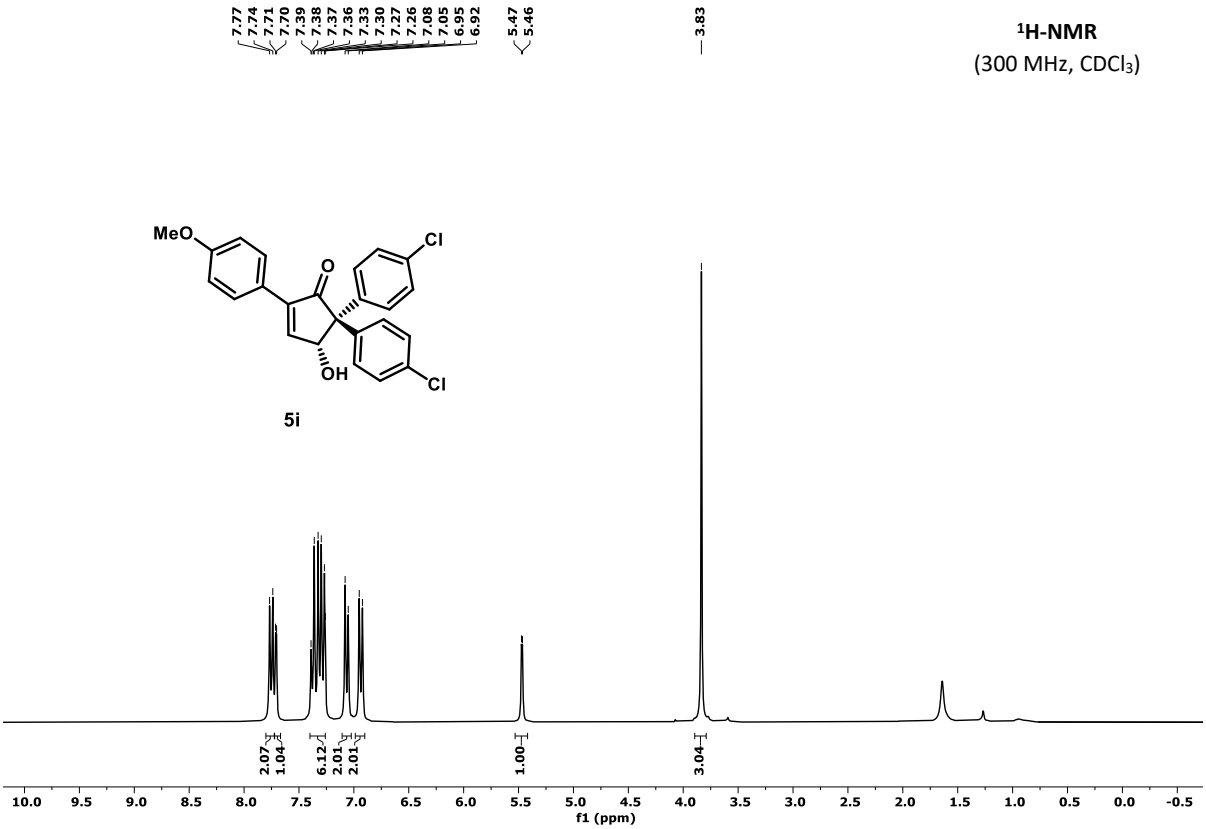
#	Peak Name	CH	tR [min]	Area [μV·sec]	Height [μV]	Area%	Height%	Quantity	NTP	Resolution	Symmetry Factor	Warning
1	Unknown	12	24.430	682324	15702	50.052	66.708	N/A	7973	15.535	1.159	
2	Unknown	12	50.090	680914	7836	49.948	33.292	N/A	8160	N/A	1.119	

Daicel Chiralpak IA column (90:10 *n*-Hexane/*i*-PrOH, 1.0 mL/min, 240 nm)

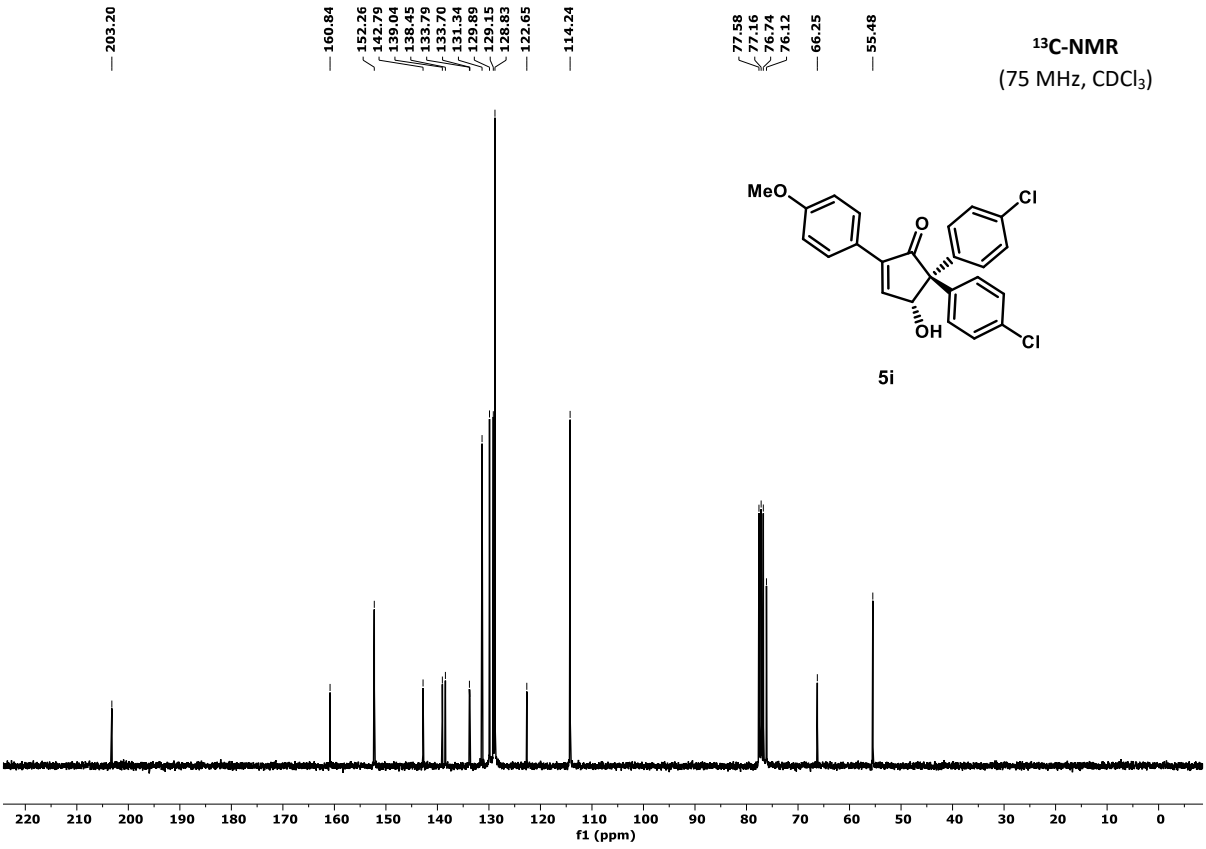


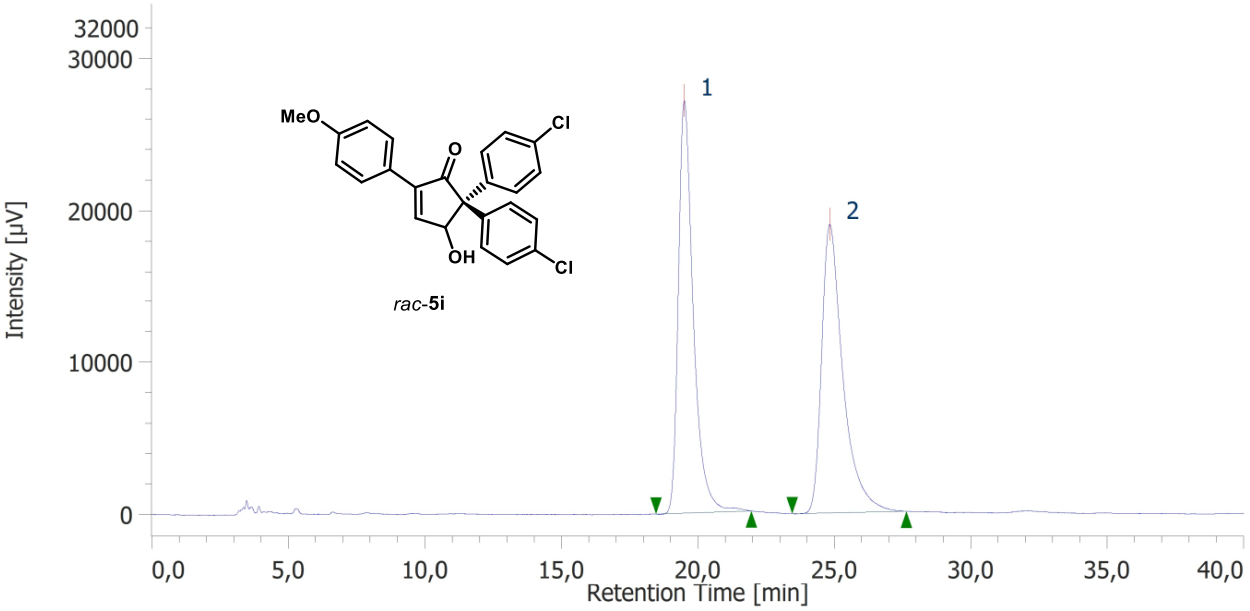
#	Peak Name	CH	tR [min]	Area [μV·sec]	Height [μV]	Area%	Height%	Quantity	NTP	Resolution	Symmetry Factor	Warning
1	Unknown	11	24.580	297420	7647	1.128	2.527	N/A	8702	15.522	1.076	
2	Unknown	11	50.260	26076925	294989	98.872	97.473	N/A	7888	N/A	1.212	

^{1}H-NMR
(300 MHz, $CDCl_3$)



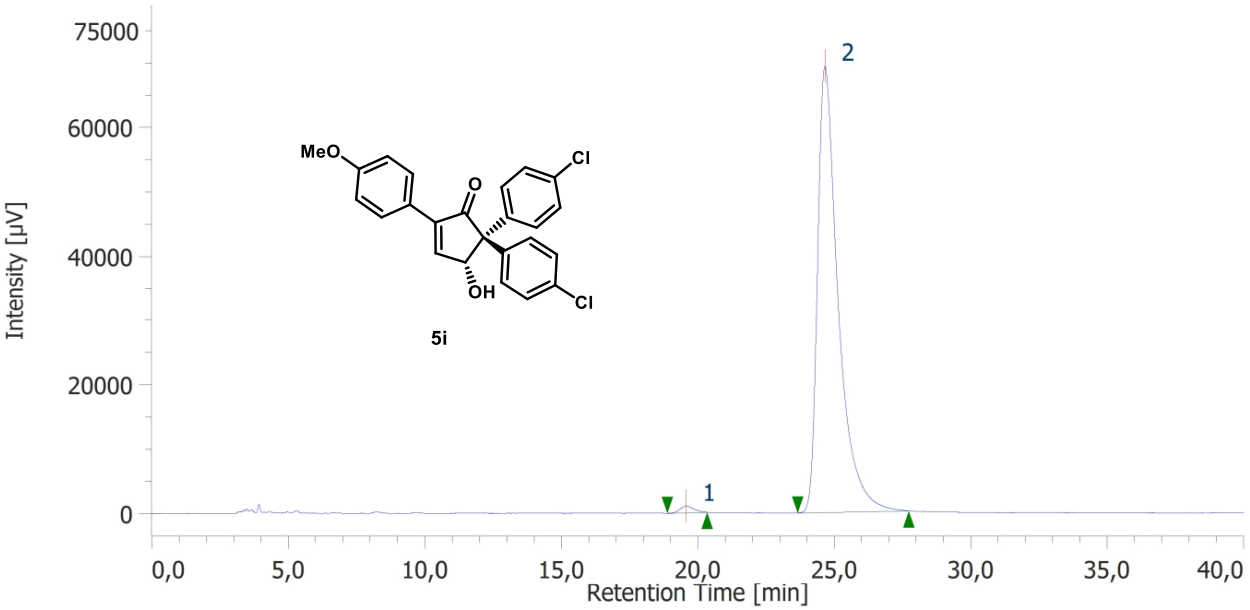
^{13}C-NMR
(75 MHz, $CDCl_3$)





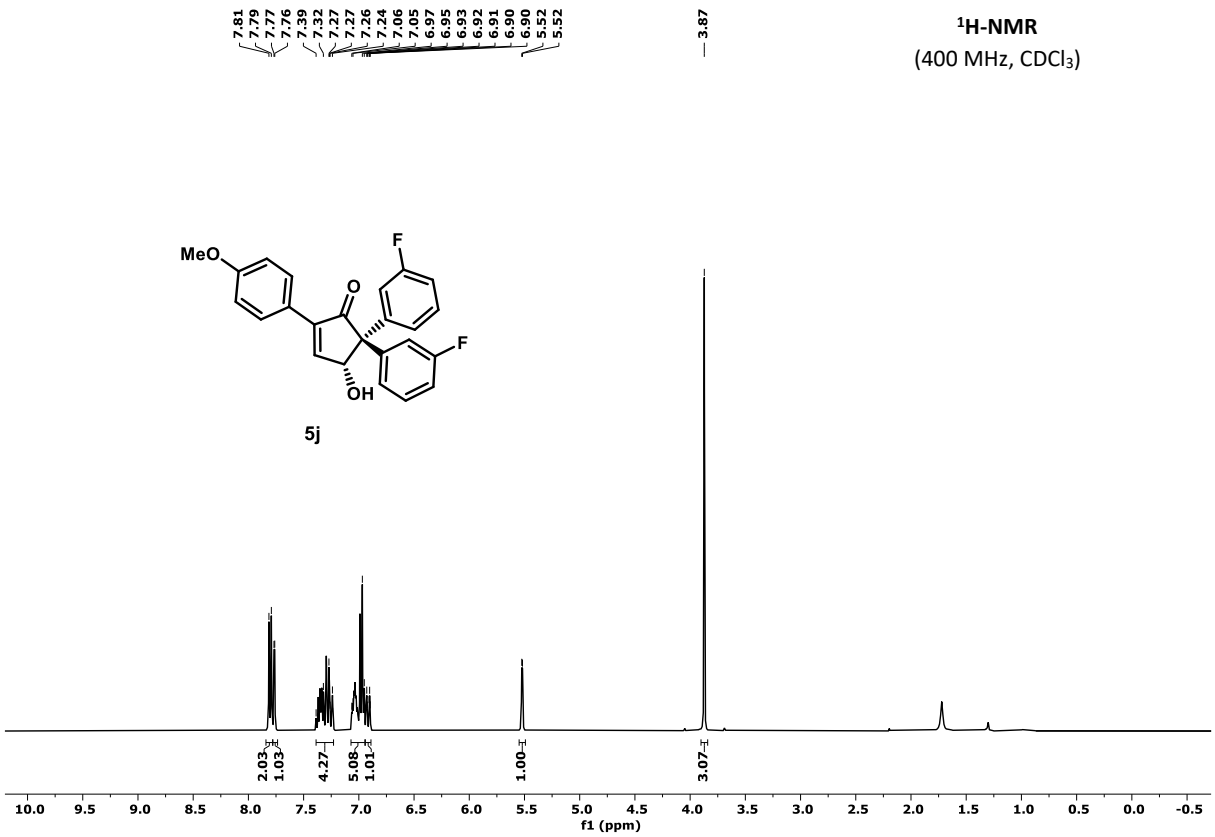
#	Peak Name	CH	tR [min]	Area [μV·sec]	Height [μV]	Area%	Height%	Quantity	NTP	Resolution	Symmetry Factor	Warning
1	Unknown	11	19,497	1032673	27118	50,087	58,811	N/A	6915	4,737	1,491	
2	Unknown	11	24,827	1029088	18992	49,913	41,189	N/A	5671	N/A	1,650	

Daicel Chiralpak IB column (90:10 *n*-Hexane/*i*-PrOH, 1.0 mL/min, 245 nm)

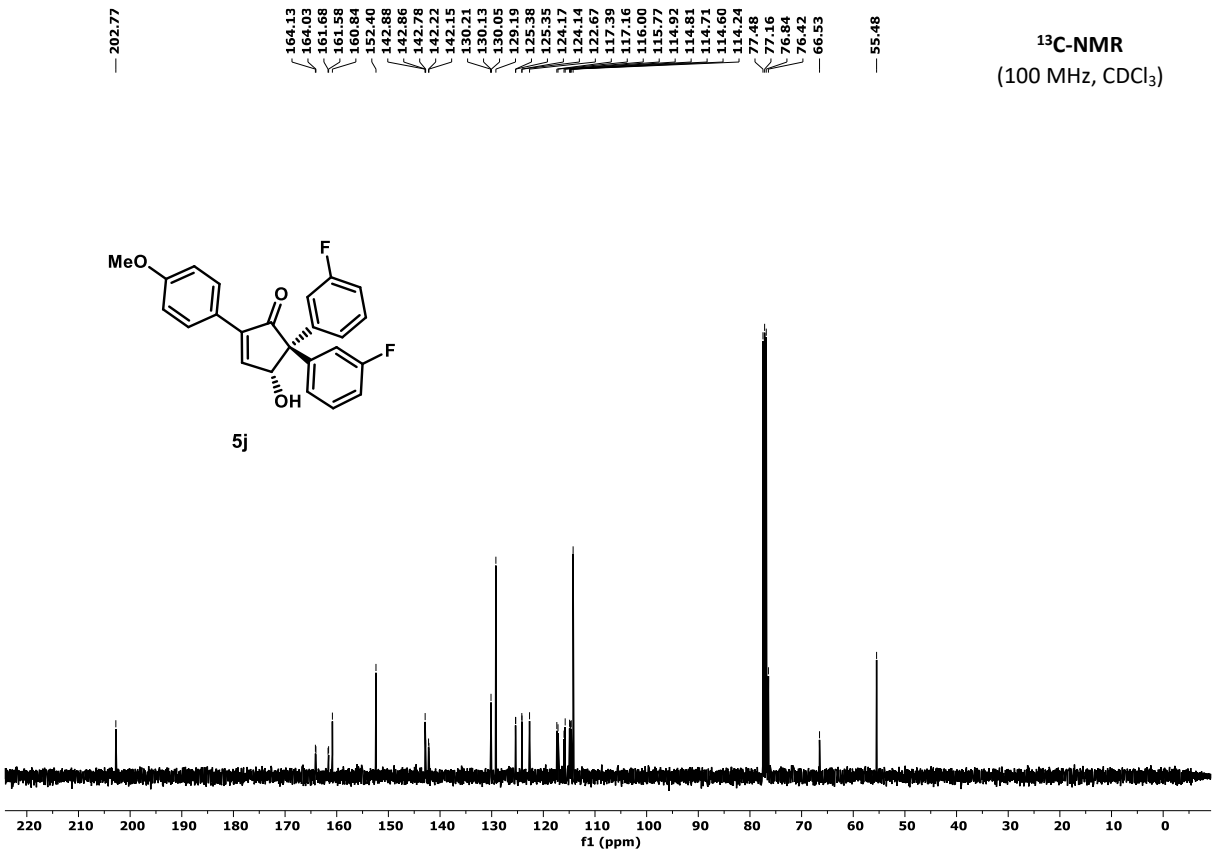


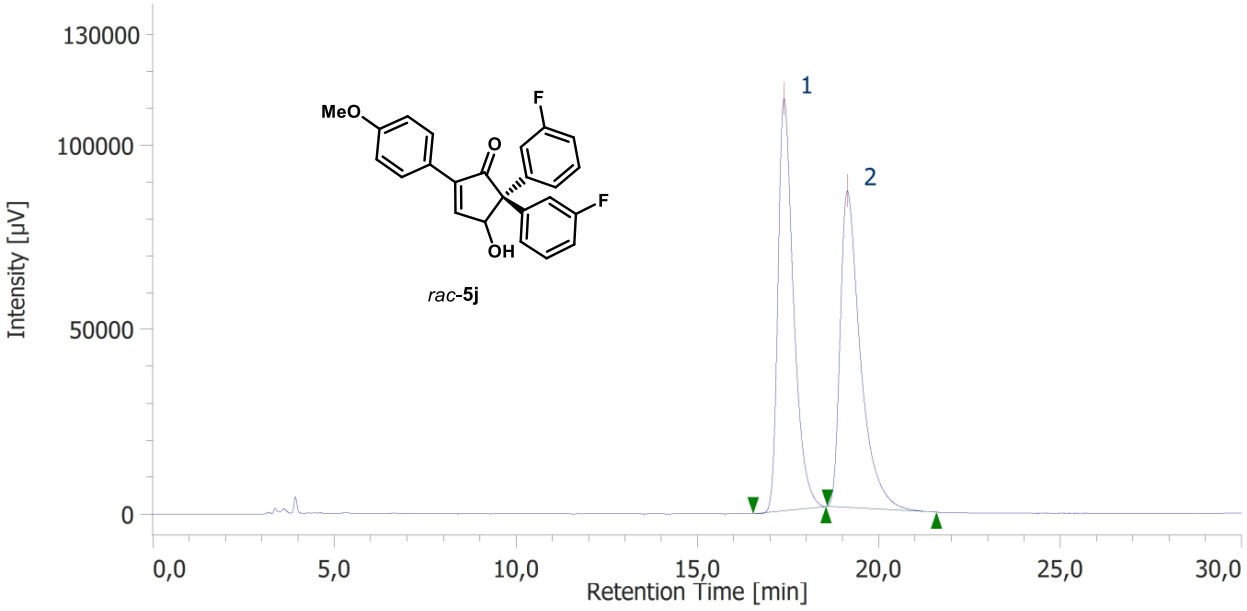
#	Peak Name	CH	tR [min]	Area [μV·sec]	Height [μV]	Area%	Height%	Quantity	NTP	Resolution	Symmetry Factor	Warning
1	Unknown	11	19,570	36830	1023	1,005	1,455	N/A	6729	4,578	1,187	
2	Unknown	11	24,650	3627222	69261	98,995	98,545	N/A	6018	N/A	1,779	

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



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

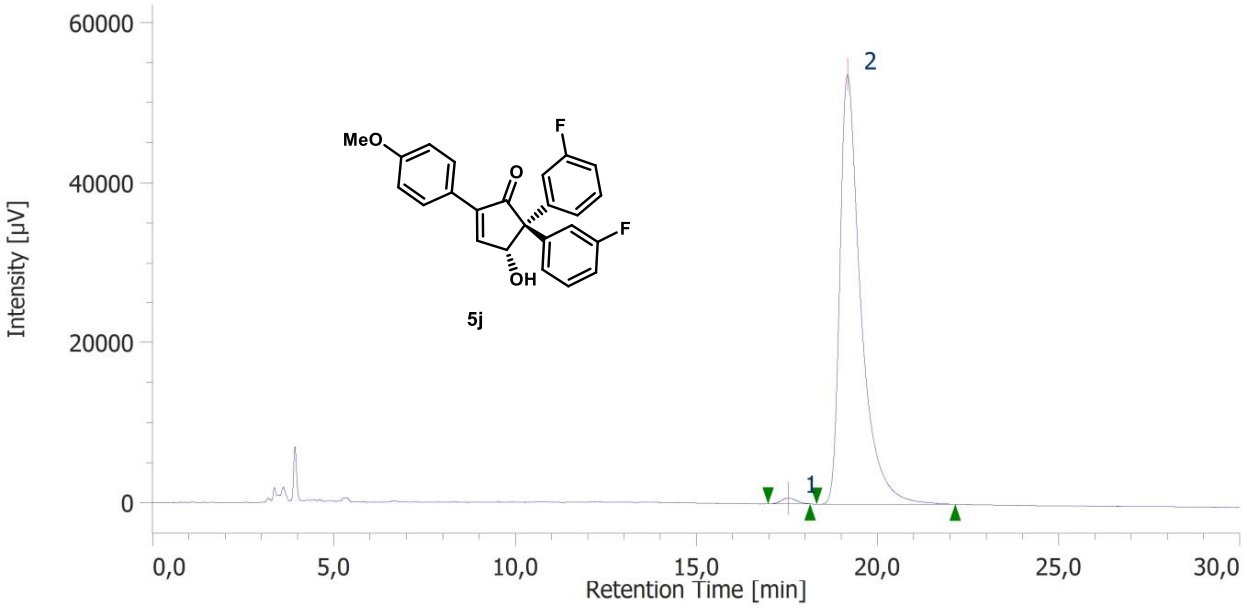




rac-**5j**

#	Peak Name	CH	tR [min]	Area [μV·sec]	Height [μV]	Area%	Height%	Quantity	NTP	Resolution	Symmetry Factor	Warning
1	Unknown	10	17,383	3327539	111600	50,114	56,527	N/A	8434	2,053	1,505	
2	Unknown	10	19,130	3312385	85829	49,886	43,473	N/A	6505	N/A	1,783	

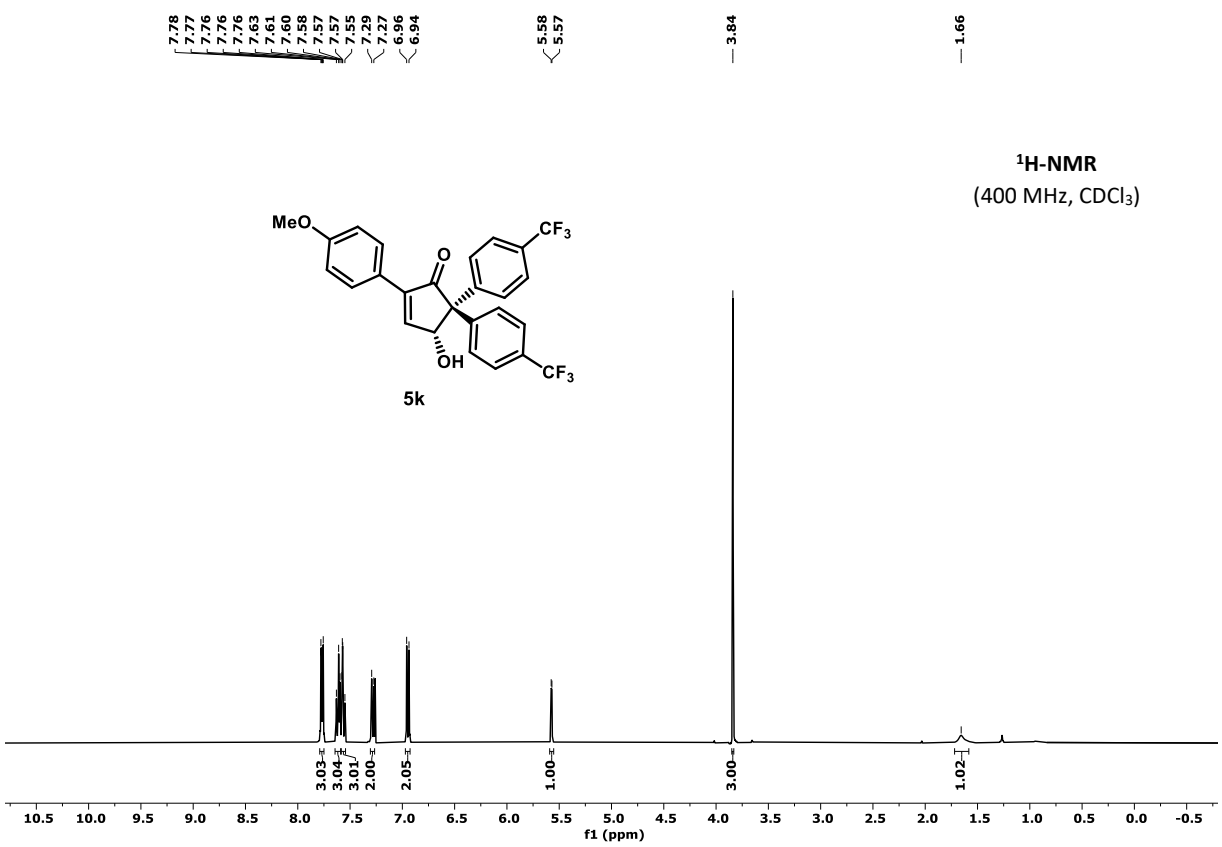
Daicel Chiralpak IB column (90:10 *n*-Hexane/*i*-PrOH, 1.0 mL/min, 230 nm)



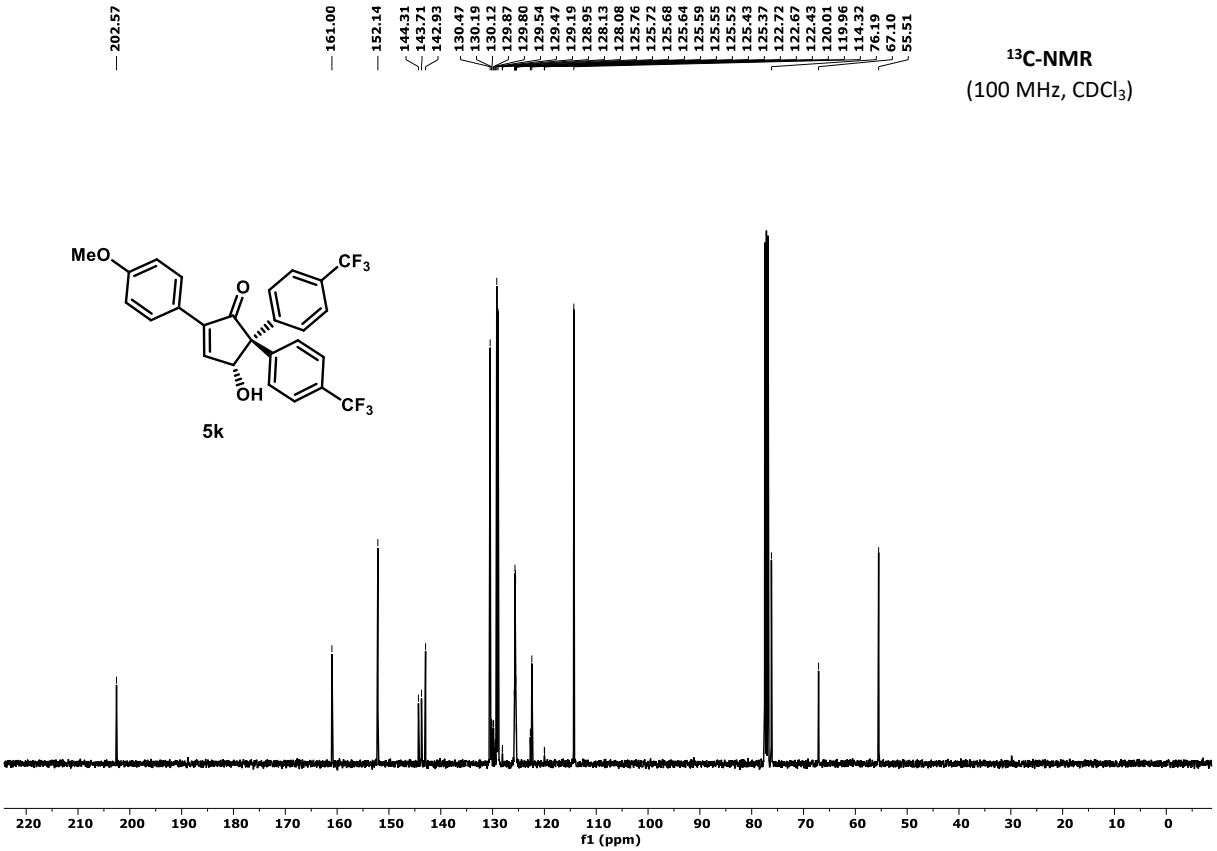
5j

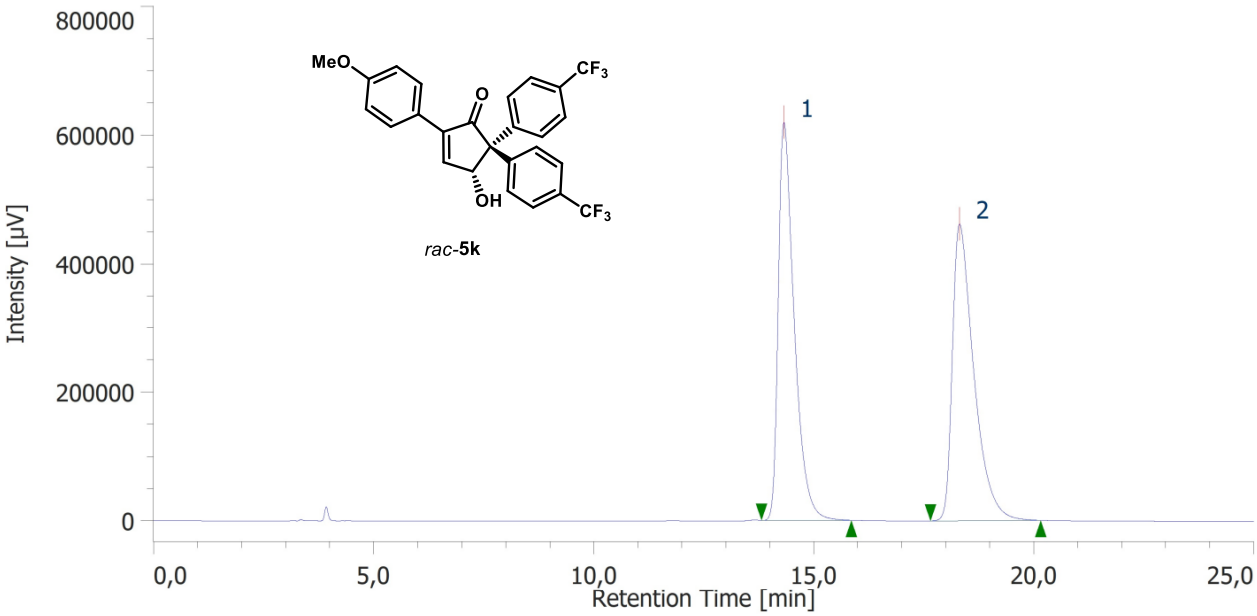
#	Peak Name	CH	tR [min]	Area [μV·sec]	Height [μV]	Area%	Height%	Quantity	NTP	Resolution	Symmetry Factor	Warning
1	Unknown	10	17,540	21176	732	0,974	1,345	N/A	8149	1,871	1,079	
2	Unknown	10	19,167	2153345	53696	99,026	98,655	N/A	6297	N/A	1,747	

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



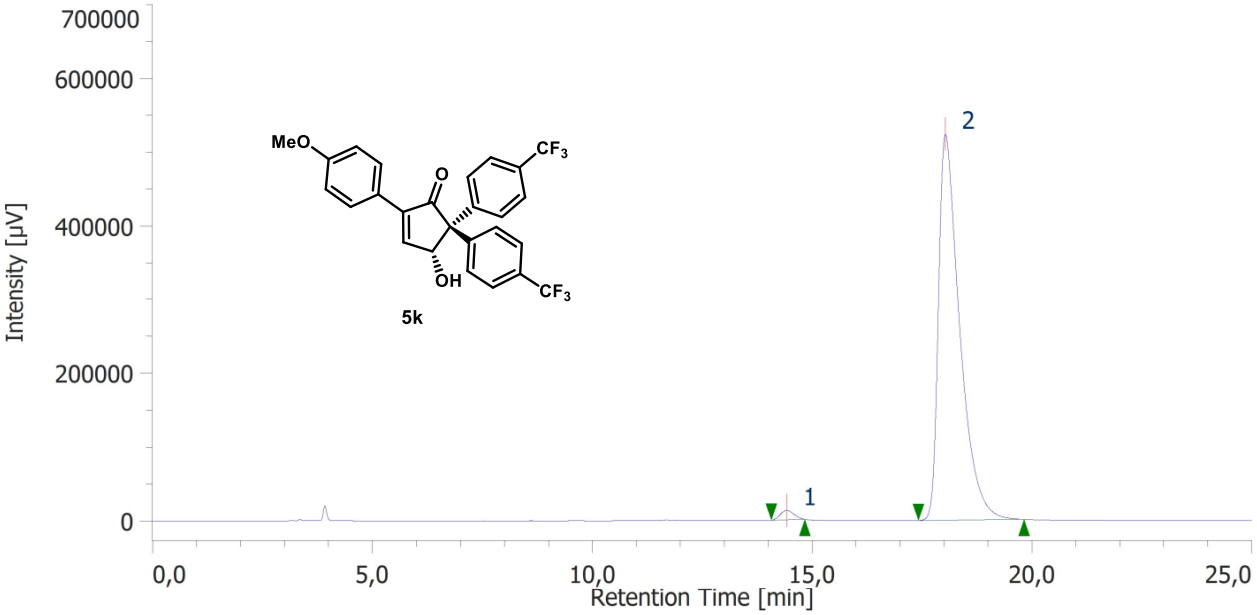
^{13}C-NMR
(100 MHz, $CDCl_3$)



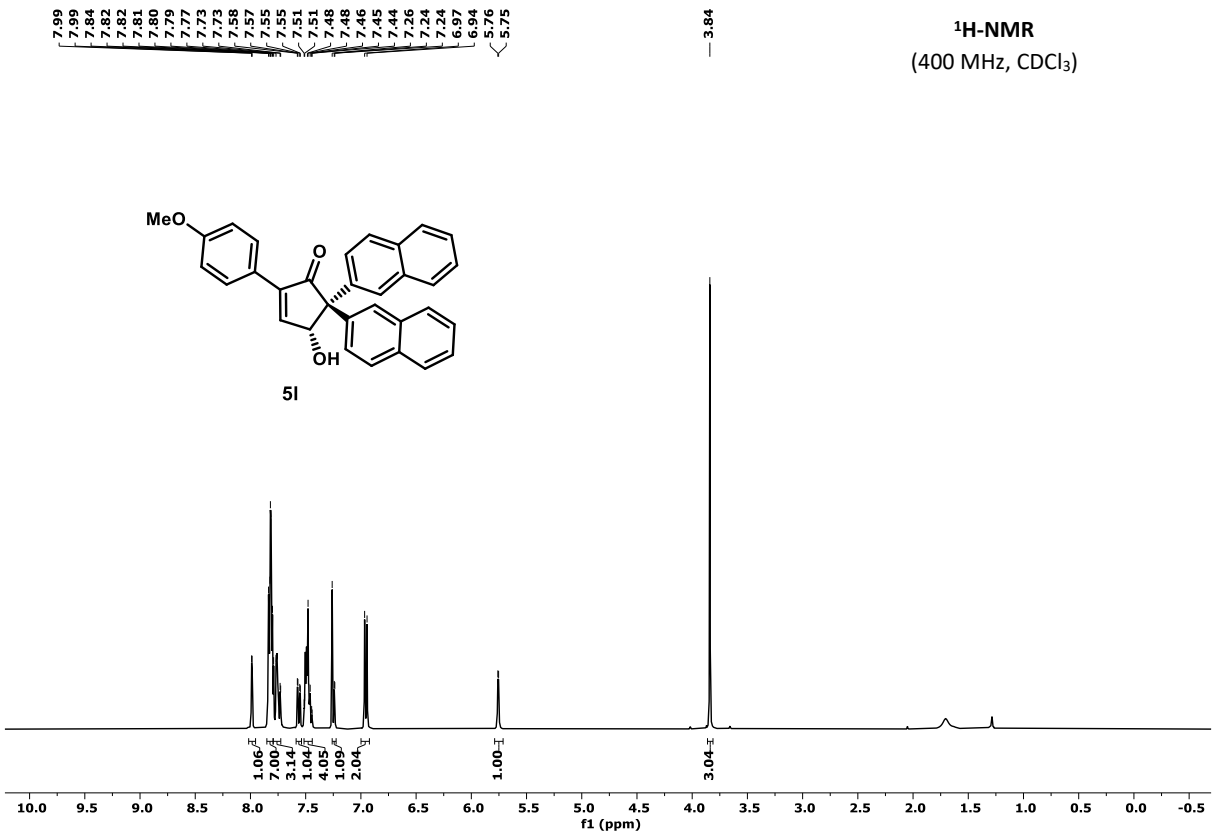


#	Peak Name	CH	tR [min]	Area [μV·sec]	Height [μV]	Area%	Height%	Quantity	NTP	Resolution	Symmetry Factor	Warning
1	Unknown	11	14,317	15554276	618924	49,905	57,249	N/A	8171	5,403	1,664	
2	Unknown	11	18,310	15613734	462190	50,095	42,751	N/A	7450	N/A	1,784	

Daicel Chiralpak IB column (90:10 *n*-Hexane/*i*-PrOH, 1.0 mL/min, 236 nm)

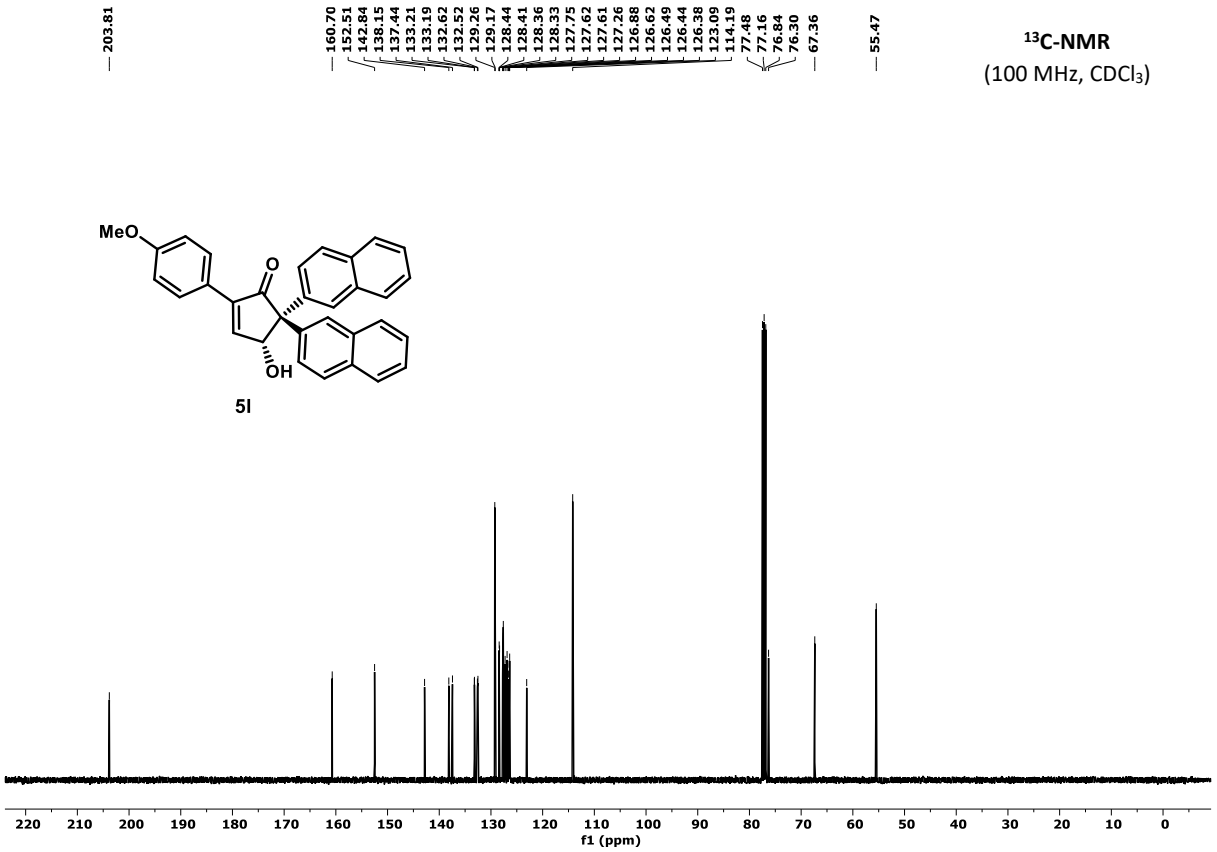


#	Peak Name	CH	tR [min]	Area [μV·sec]	Height [μV]	Area%	Height%	Quantity	NTP	Resolution	Symmetry Factor	Warning
1	Unknown	11	14,417	274809	12669	1,544	2,364	N/A	9498	5,055	1,112	
2	Unknown	11	18,027	17522540	523257	98,456	97,636	N/A	7360	N/A	1,845	



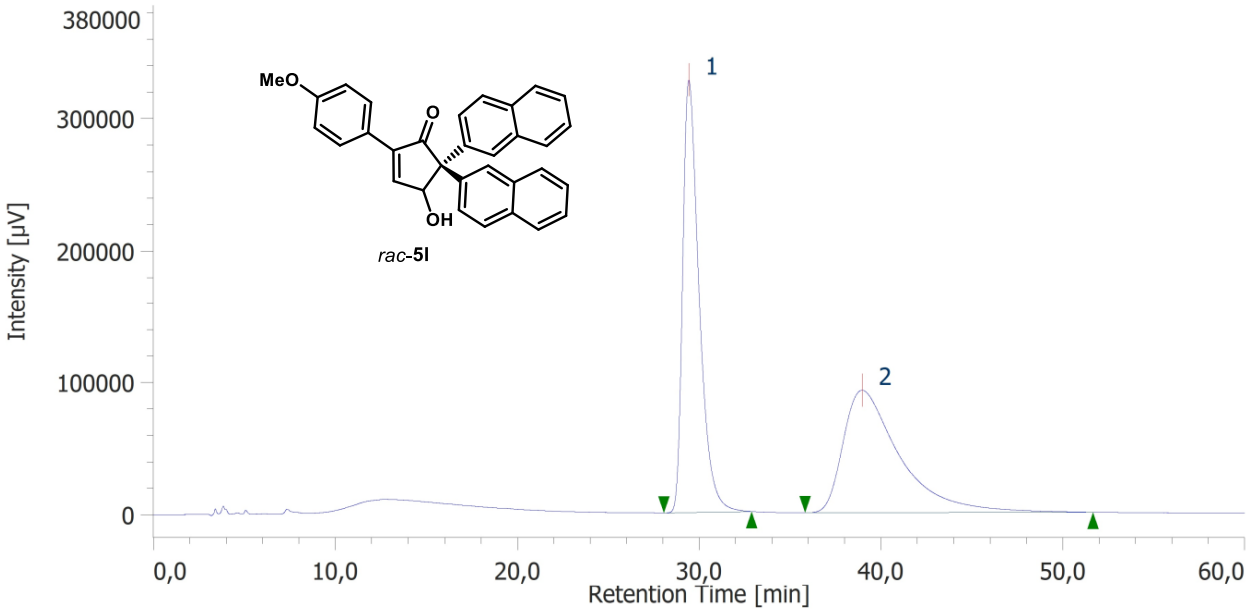
^{1}H-NMR
(400 MHz, $CDCl_3$)

5l



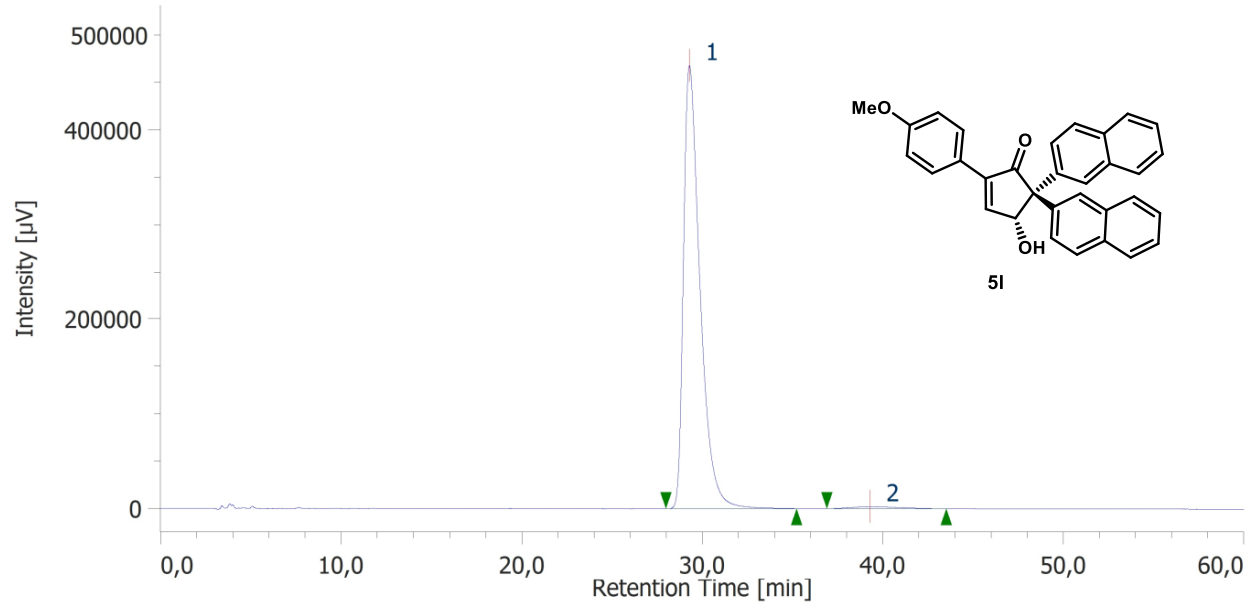
^{13}C-NMR
(100 MHz, $CDCl_3$)

5l

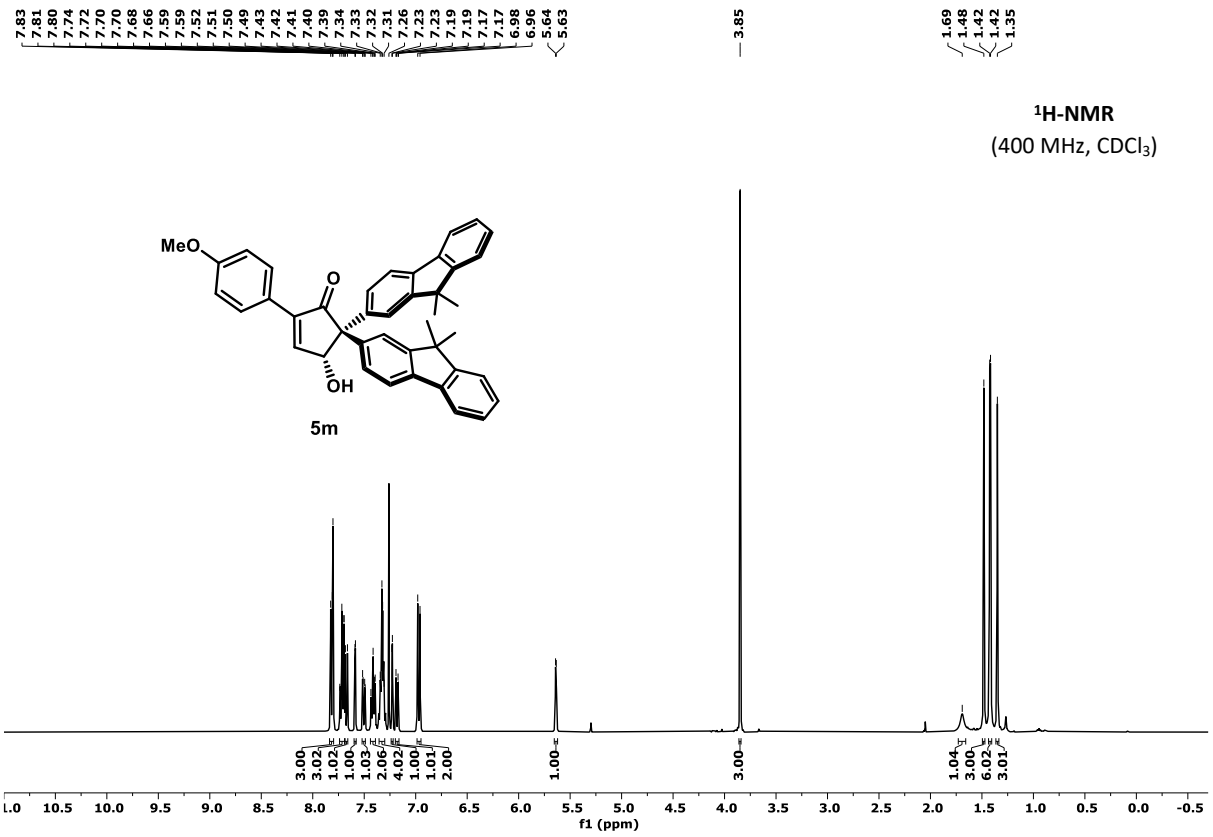


#	Peak Name	CH	tR [min]	Area [μV·sec]	Height [μV]	Area%	Height%	Quantity	NTP	Resolution	Symmetry Factor	Warning
1	Unknown	10	29,420	20540620	327411	50,650	77,960	N/A	5459	2,804	1,584	
2	Unknown	10	38,957	20013552	92561	49,350	22,040	N/A	889	N/A	1,998	

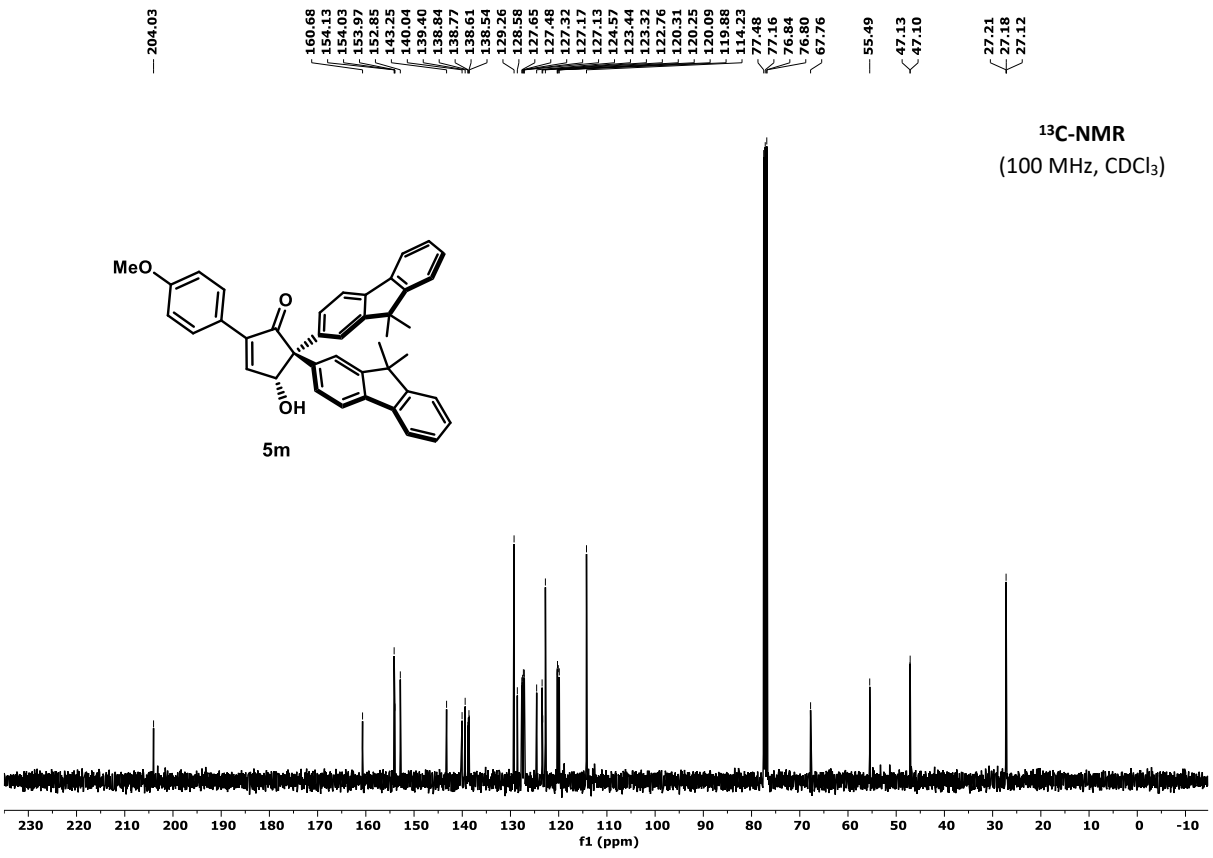
Daicel Chiralpak IF column (75:25 *n*-Hexane/*i*-PrOH, 1.0 mL/min, 230 nm)



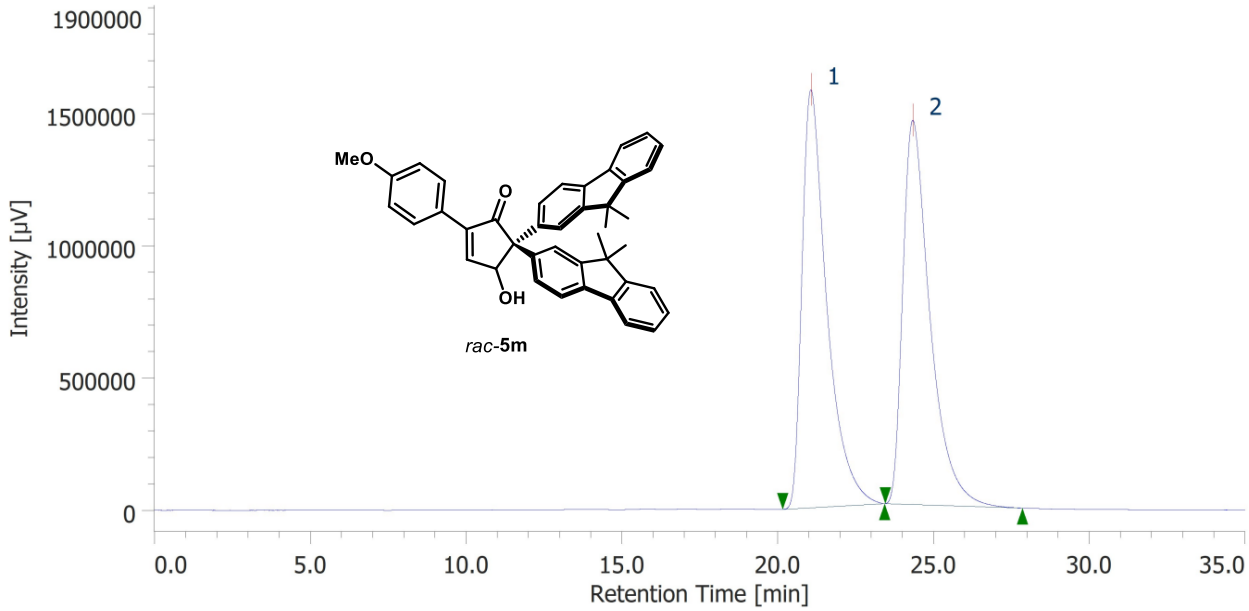
#	Peak Name	CH	tR [min]	Area [μV·sec]	Height [μV]	Area%	Height%	Quantity	NTP	Resolution	Symmetry Factor	Warning
1	Unknown	10	29,277	29788254	468183	98,781	99,571	N/A	5326	3,089	1,674	
2	Unknown	10	39,280	367498	2018	1,219	0,429	N/A	1033	N/A	1,360	



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

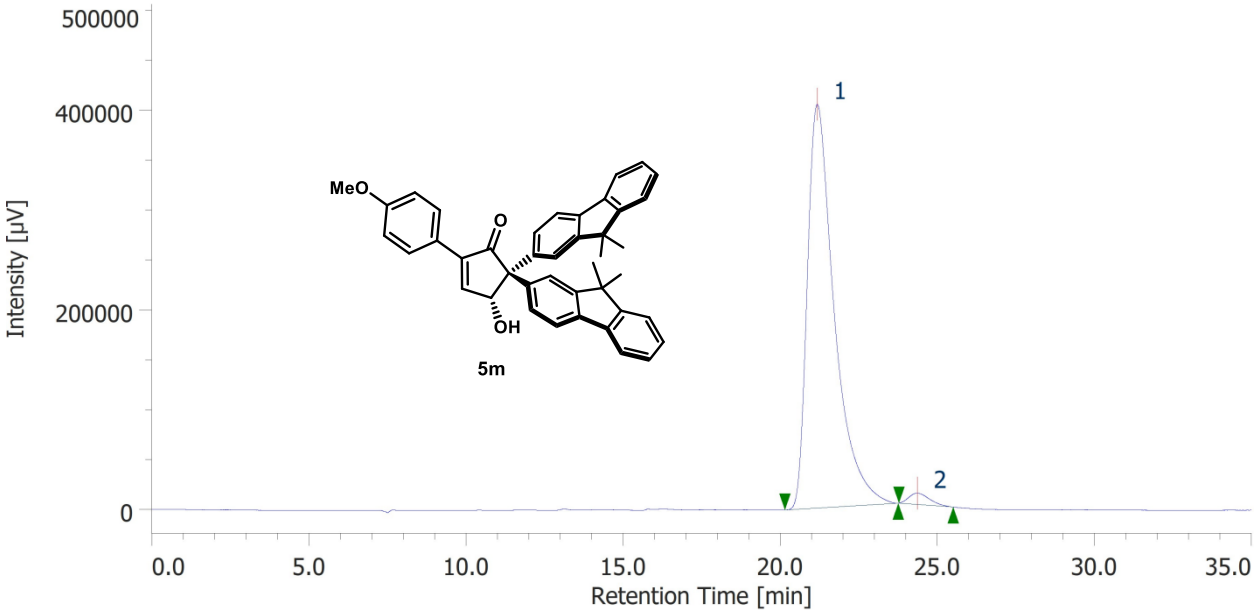


^{13}C-NMR
(100 MHz, $CDCl_3$)

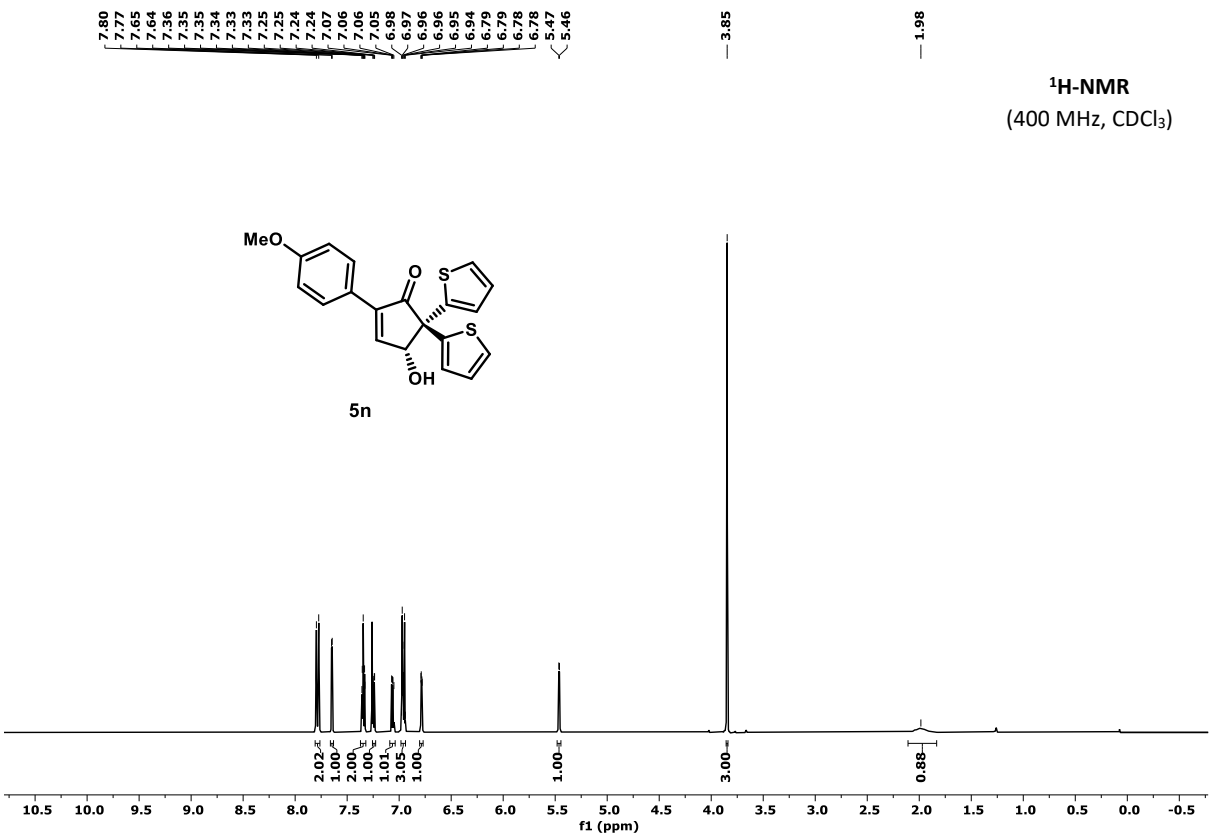


#	Peak Name	CH	tR [min]	Area [μV·sec]	Height [μV]	Area%	Height%	Quantity	NTP	Resolution	Symmetry Factor	Warning
1	Unknown	11	21.067	87351278	1580457	49.810	52.122	N/A	3774	2.267	1.774	
2	Unknown	11	24.337	88015984	1451751	50.190	47.878	N/A	4099	N/A	1.698	

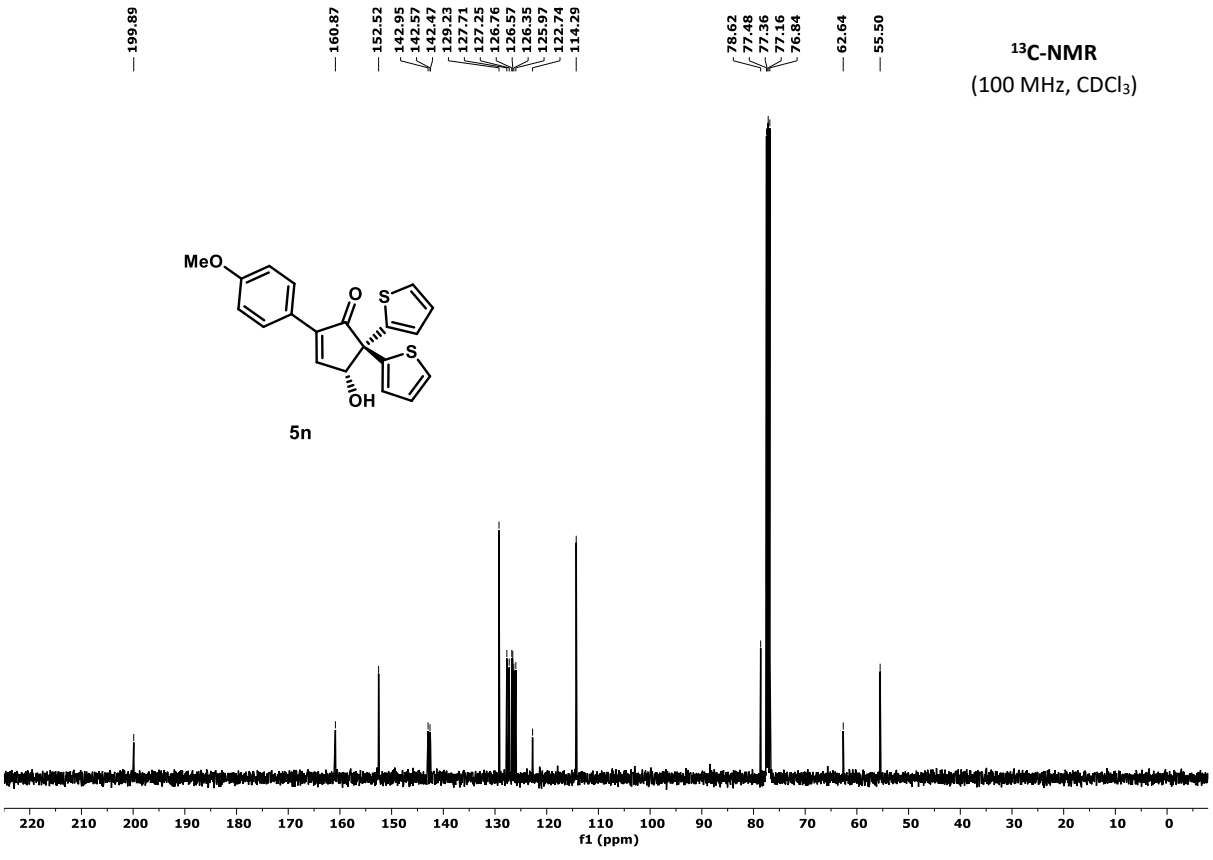
Daicel Chiralpak IC column (90:10 *n*-Hexane/EtOAc, 0.5 mL/min, 276 nm)



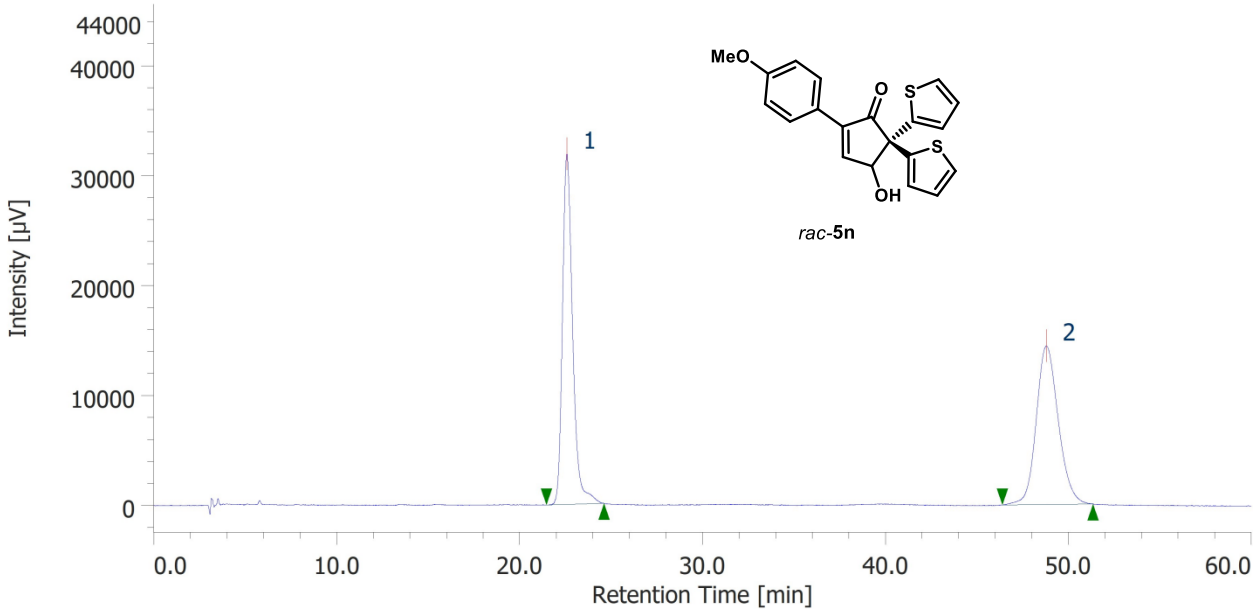
#	Peak Name	CH	tR [min]	Area [μV·sec]	Height [μV]	Area%	Height%	Quantity	NTP	Resolution	Symmetry Factor	Warning
1	Unknown	11	21.177	24091192	404286	97.903	97.280	N/A	3297	2.358	1.748	
2	Unknown	11	24.358	515922	11305	2.097	2.720	N/A	6271	N/A	1.371	



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

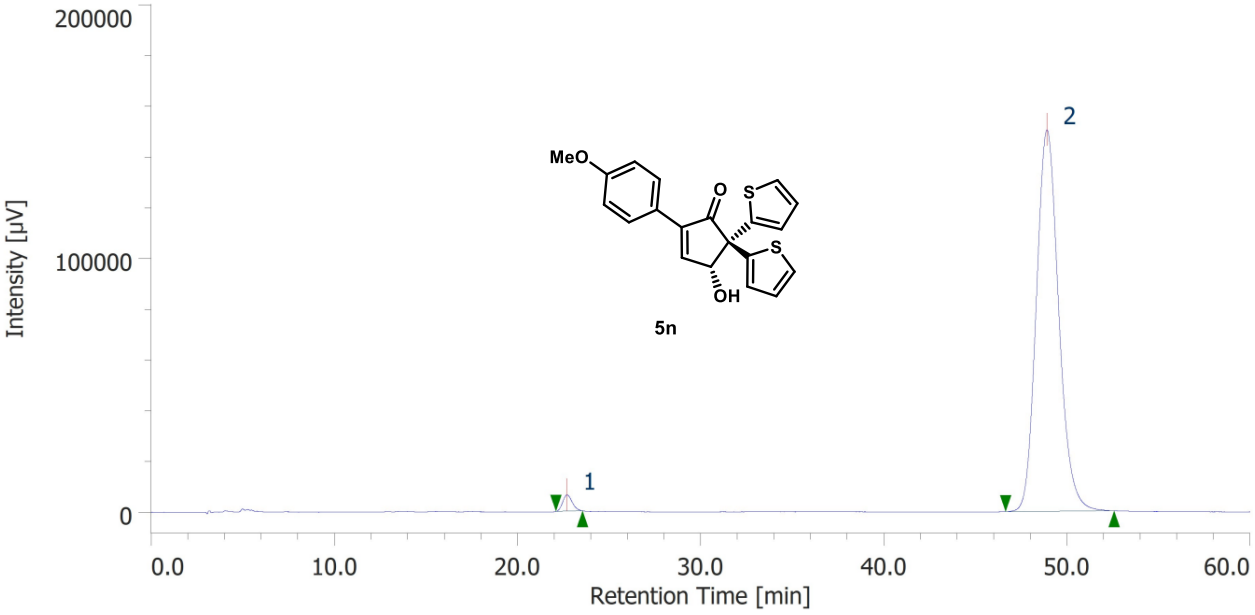


^{13}C-NMR
(100 MHz, $CDCl_3$)

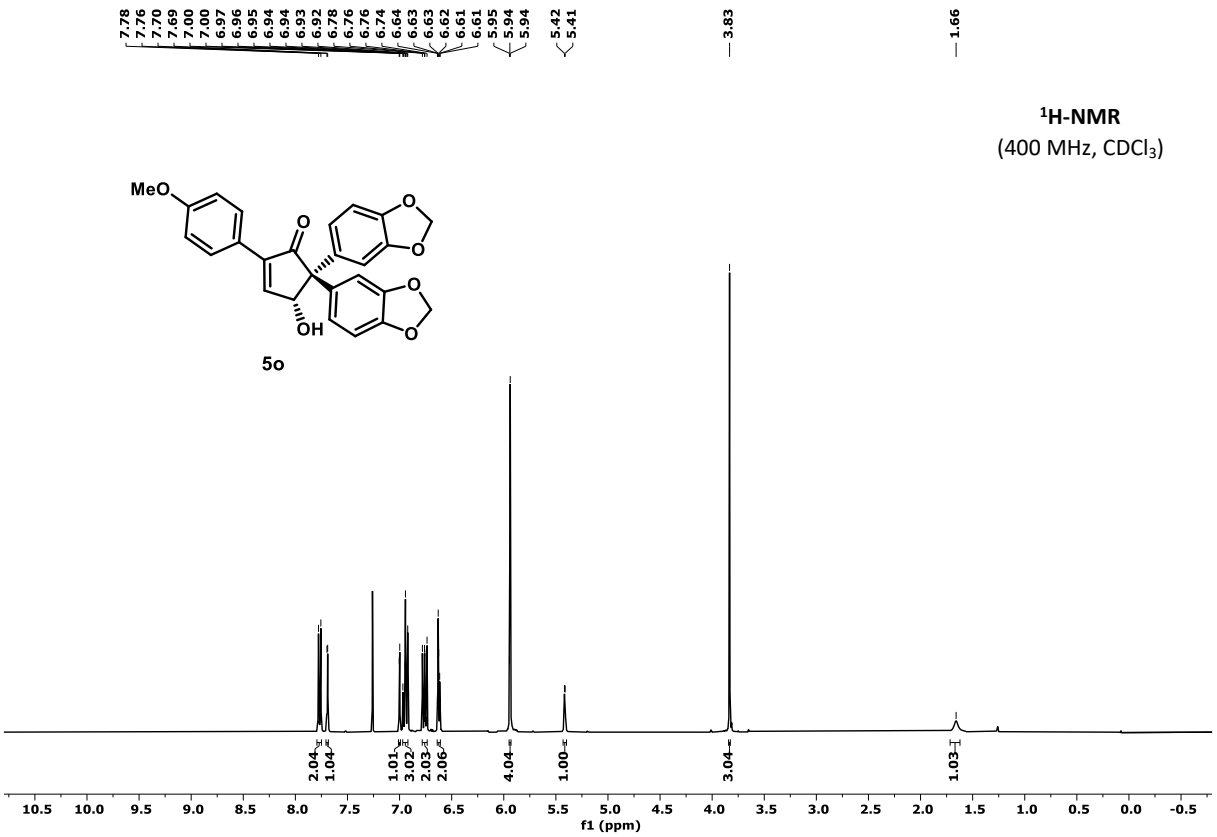


#	Peak Name	CH	tR [min]	Area [μV·sec]	Height [μV]	Area%	Height%	Quantity	NTP	Resolution	Symmetry Factor	Warning
1	Unknown	11	22.573	1230816	31870	50.446	68.835	N/A	8774	16.842	1.296	
2	Unknown	11	48.793	1209058	14429	49.554	31.165	N/A	8179	N/A	1.145	

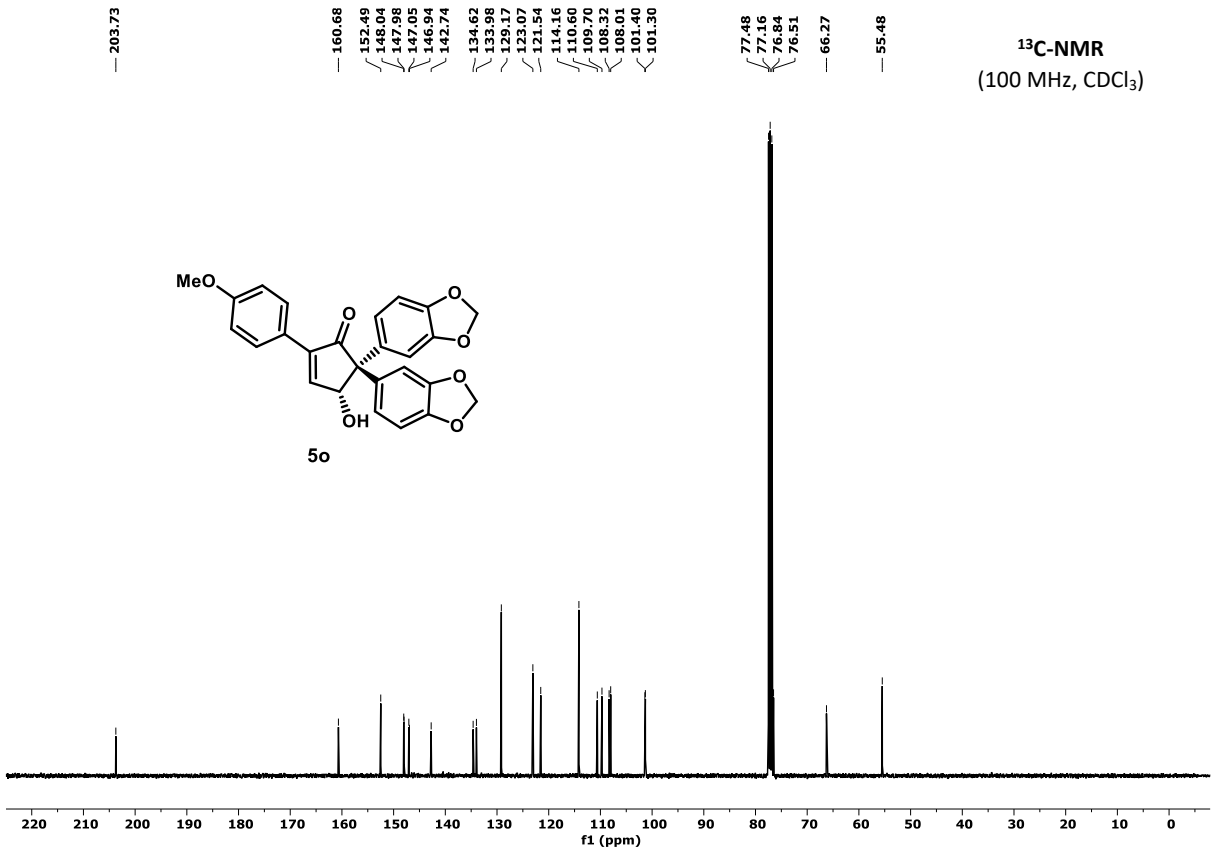
Daicel Chiralpak IA column (80:20 *n*-Hexane/*i*-PrOH, 1.0 mL/min, 290 nm)



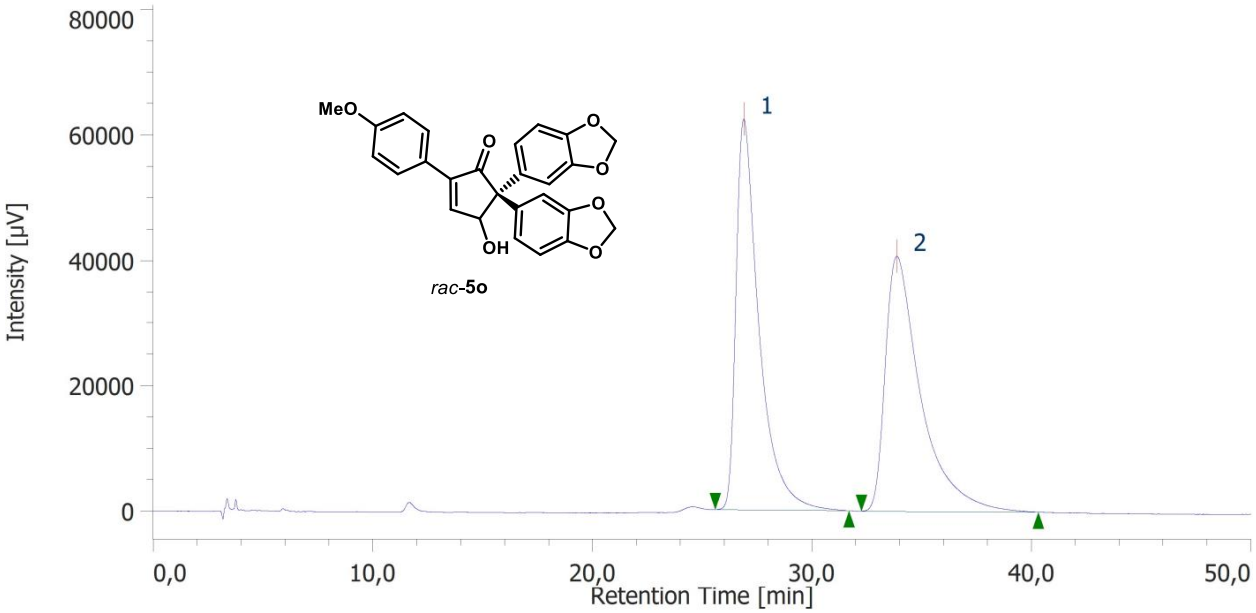
#	Peak Name	CH	tR [min]	Area [μV·sec]	Height [μV]	Area%	Height%	Quantity	NTP	Resolution	Symmetry Factor	Warning
1	Unknown	11	22.690	232499	6452	1.790	4.114	N/A	9021	16.646	1.207	
2	Unknown	11	48.903	12758724	150390	98.210	95.886	N/A	7889	N/A	1.155	



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

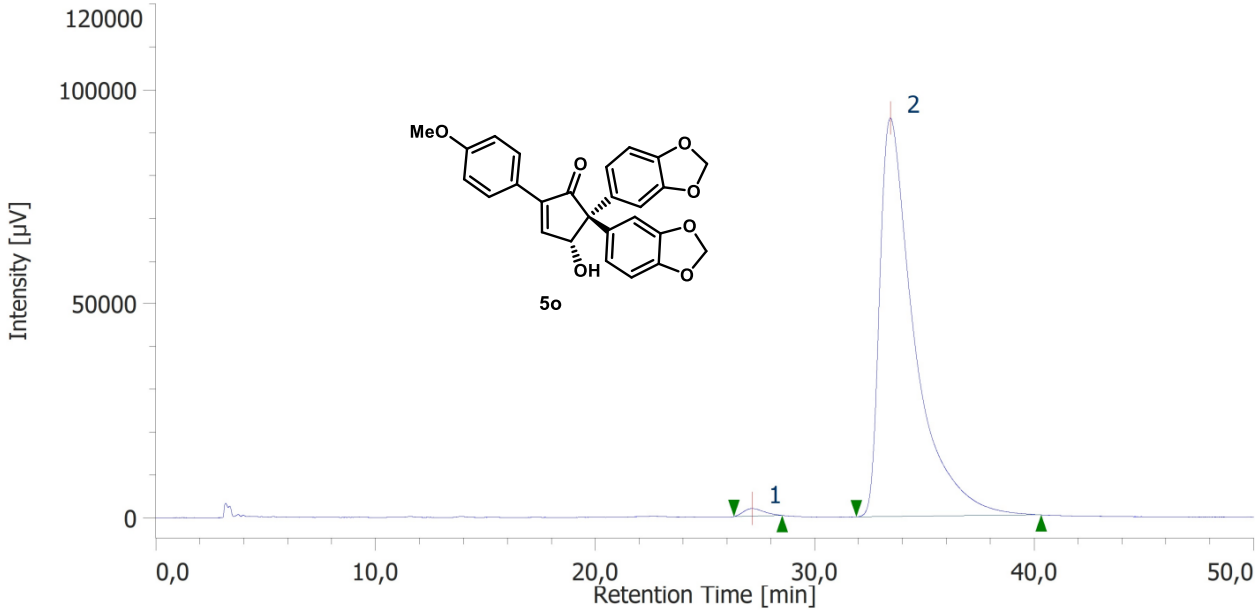


^{13}C-NMR
(100 MHz, $CDCl_3$)



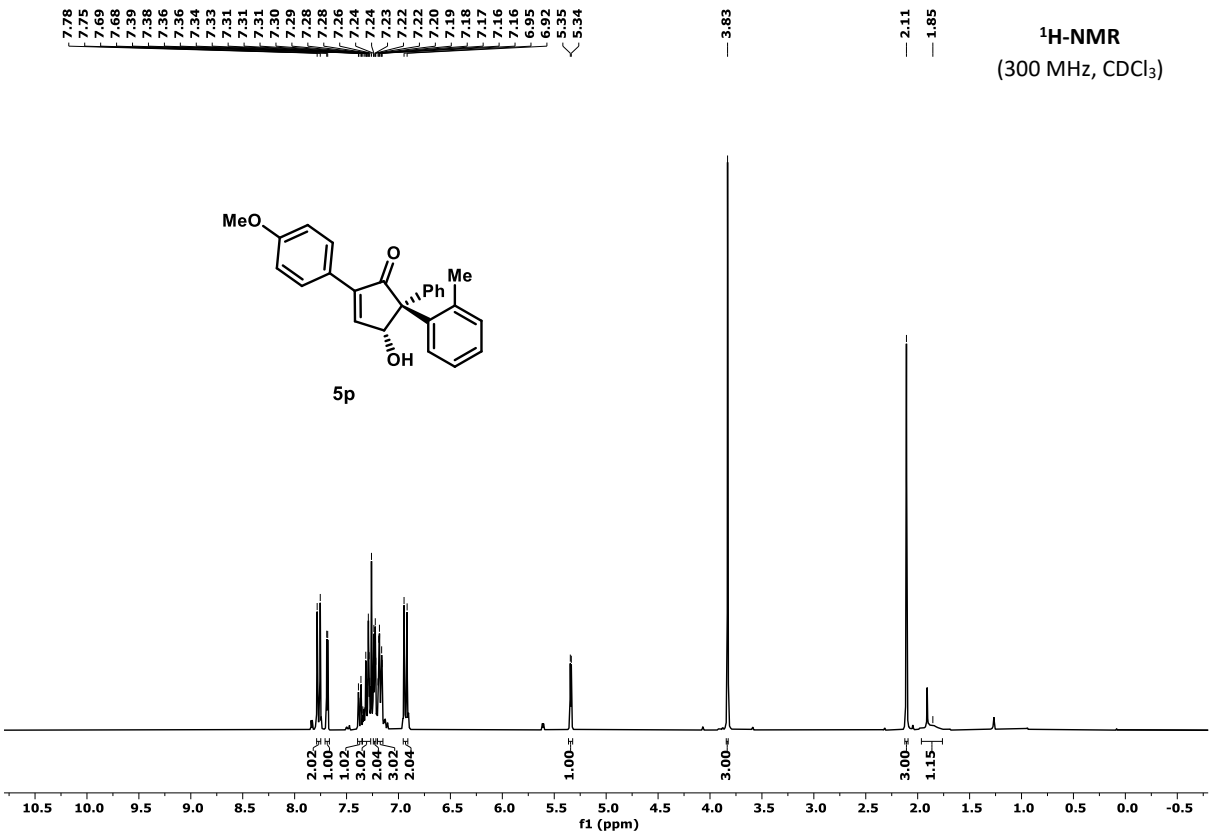
#	Peak Name	CH	tR [min]	Area [μV·sec]	Height [μV]	Area%	Height%	Quantity	NTP	Resolution	Symmetry Factor	Warning
1	Unknown	11	26.887	4528536	62315	49.879	60.445	N/A	3774	3.177	1.950	
2	Unknown	11	33.863	4550586	40778	50.121	39.555	N/A	2606	N/A	2.088	

Daicel Chiralpak IB column (80:20 *n*-Hexane/*i*-PrOH, 1.0 mL/min, 240 nm)

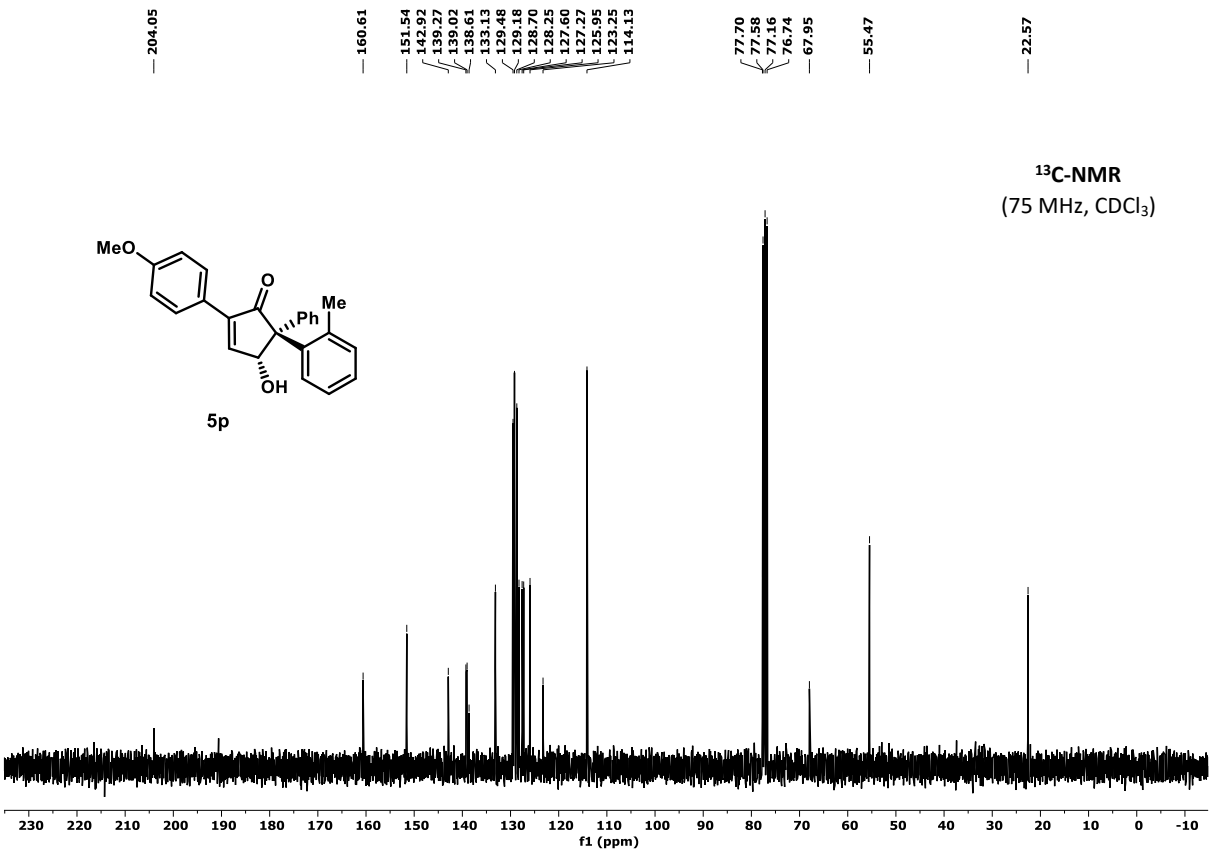


#	Peak Name	CH	tR [min]	Area [μV·sec]	Height [μV]	Area%	Height%	Quantity	NTP	Resolution	Symmetry Factor	Warning
1	Unknown	11	27.143	114628	1766	1.112	1.864	N/A	3764	2.908	1.316	
2	Unknown	11	33.437	10195302	93023	98.888	98.136	N/A	2709	N/A	2.349	

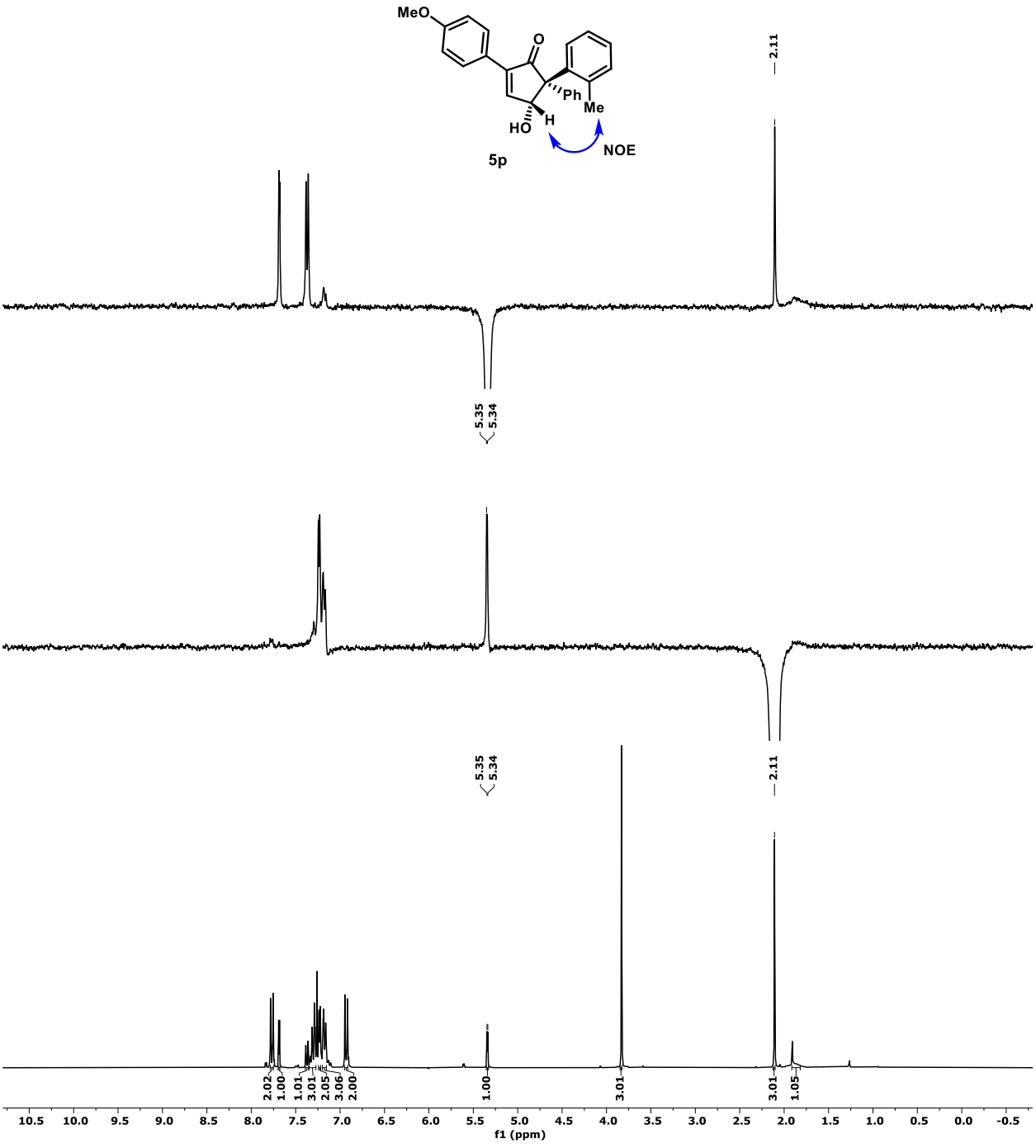
^{1}H-NMR
(300 MHz, $CDCl_3$)

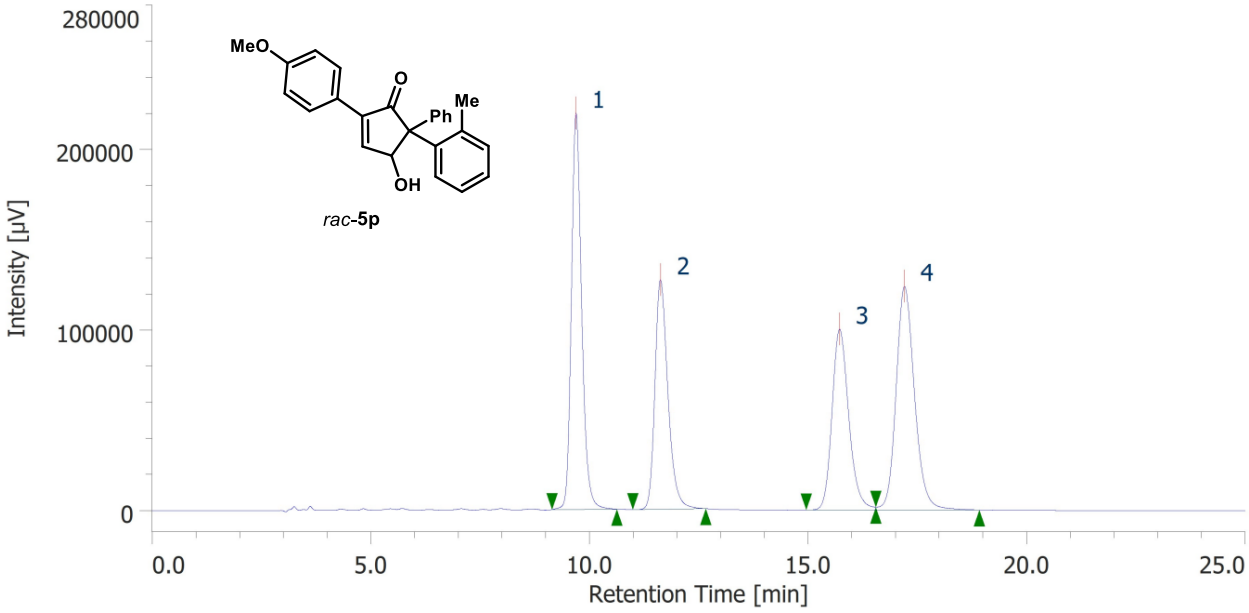


^{13}C-NMR
(75 MHz, $CDCl_3$)



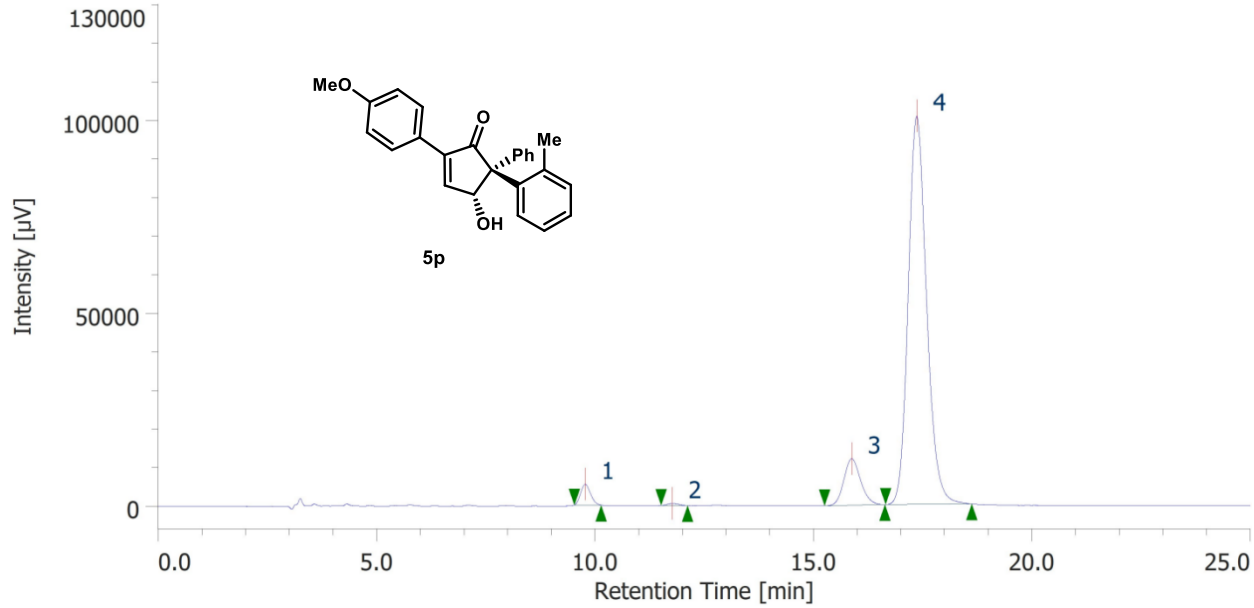
1D NOE of $3b_{16}$:



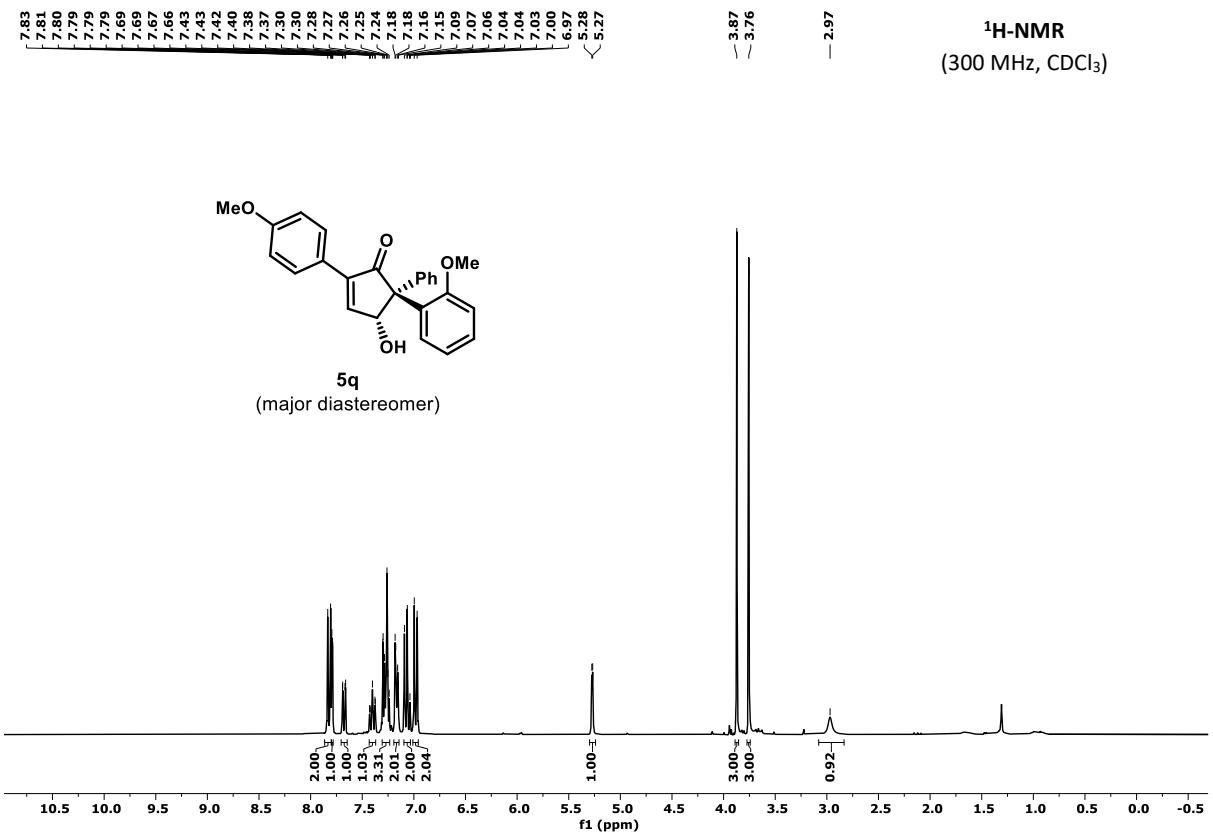


#	Peak Name	CH	tR [min]	Area [μV·sec]	Height [μV]	Area%	Height%	Quantity	NTP	Resolution	Symmetry Factor	Warning
1	Unknown	11	9.690	3577897	219443	28.639	38.467	N/A	8761	4.128	1.221	
2	Unknown	11	11.623	2627326	127059	21.030	22.273	N/A	7843	6.817	1.307	
3	Unknown	11	15.720	2664335	100167	21.327	17.559	N/A	8546	2.086	1.216	
4	Unknown	11	17.203	3623421	123802	29.004	21.702	N/A	8514	N/A	1.169	

Daicel Chiralpak IA column (80:20 *n*-Hexane/*i*-PrOH, 1.0 mL/min, 245 nm)

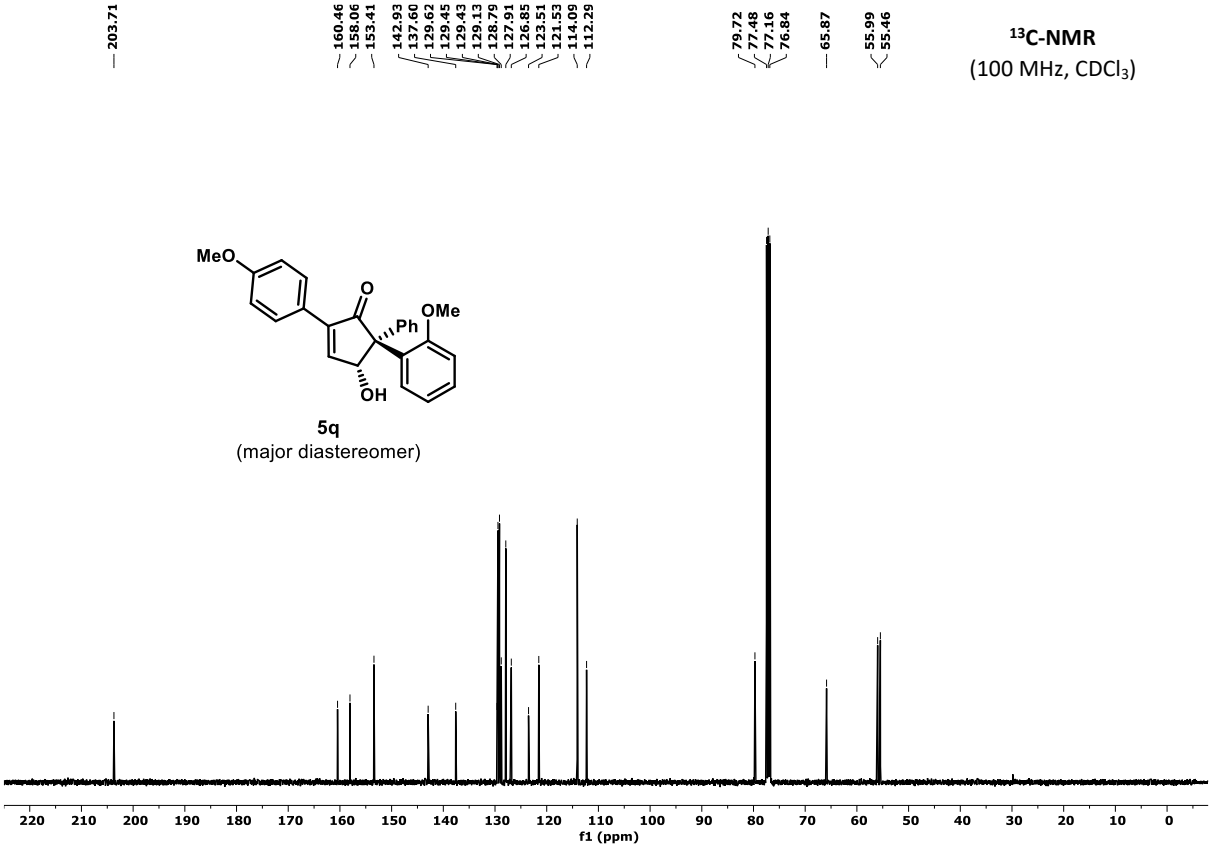


#	Peak Name	CH	tR [min]	Area [μV·sec]	Height [μV]	Area%	Height%	Quantity	NTP	Resolution	Symmetry Factor	Warning
1	Unknown	11	9.770	84384	5399	2.523	4.551	N/A	8783	4.380	1.174	
2	Unknown	11	11.767	9939	558	0.297	0.470	N/A	8964	6.918	1.183	
3	Unknown	11	15.873	321588	12075	9.616	10.178	N/A	8387	2.065	1.145	
4	Unknown	11	17.360	2928436	100602	87.564	84.800	N/A	8557	N/A	1.174	



^{1}H-NMR
(300 MHz, $CDCl_3$)

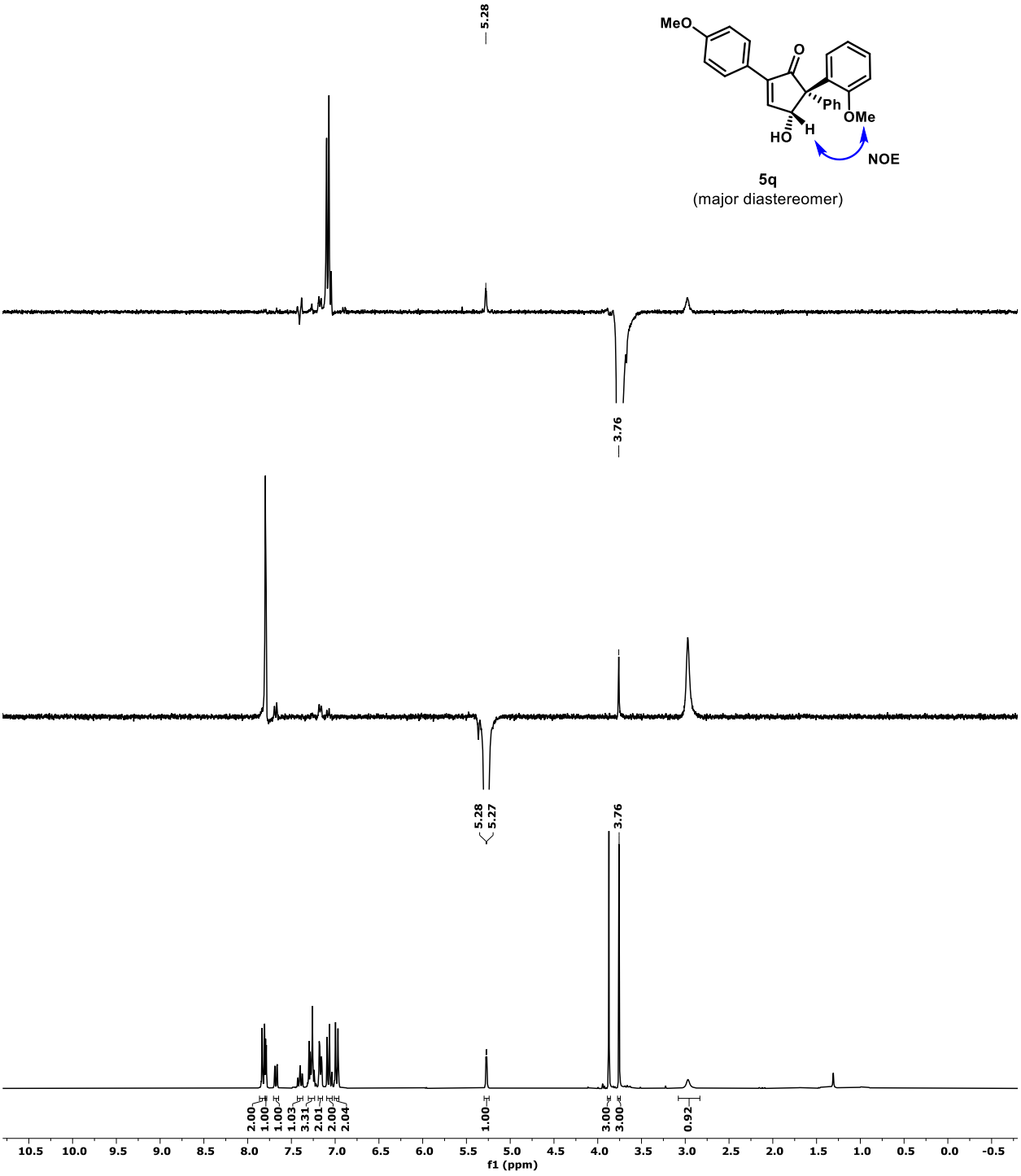
5q
(major diastereomer)

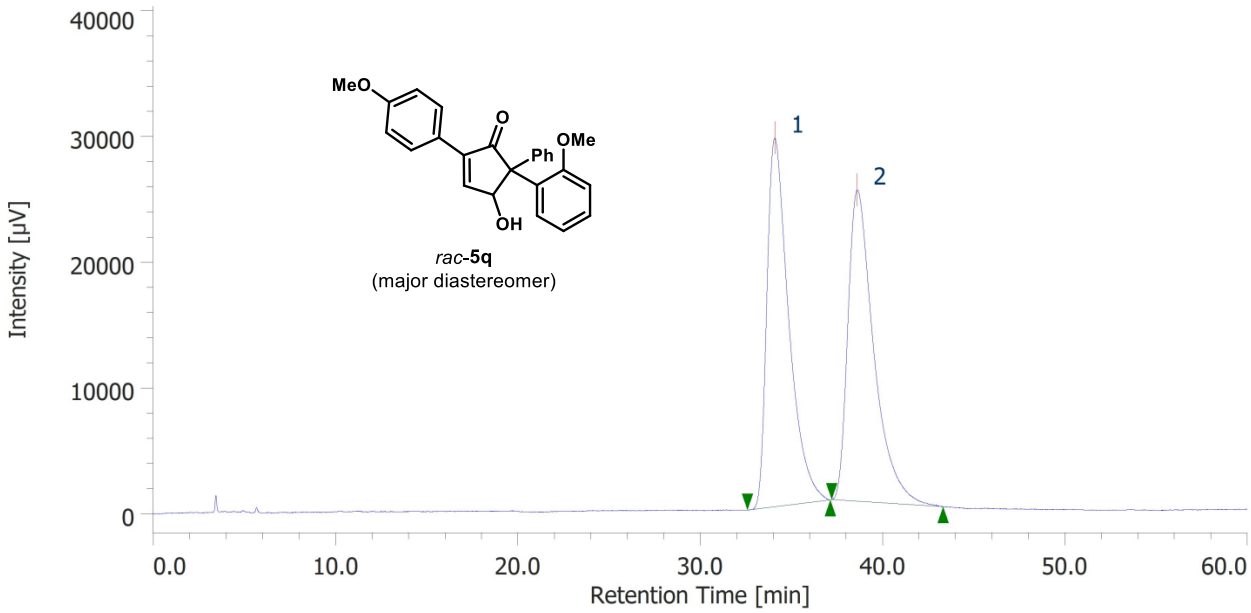


^{13}C-NMR
(100 MHz, $CDCl_3$)

5q
(major diastereomer)

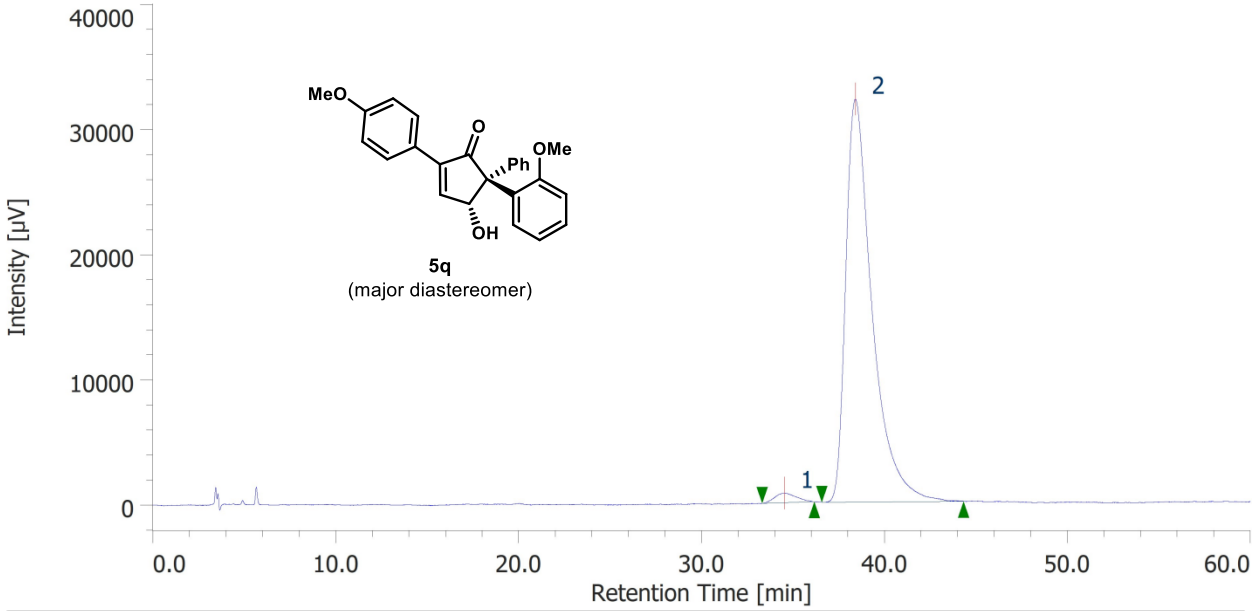
1D NOE of $3b_{17}$:



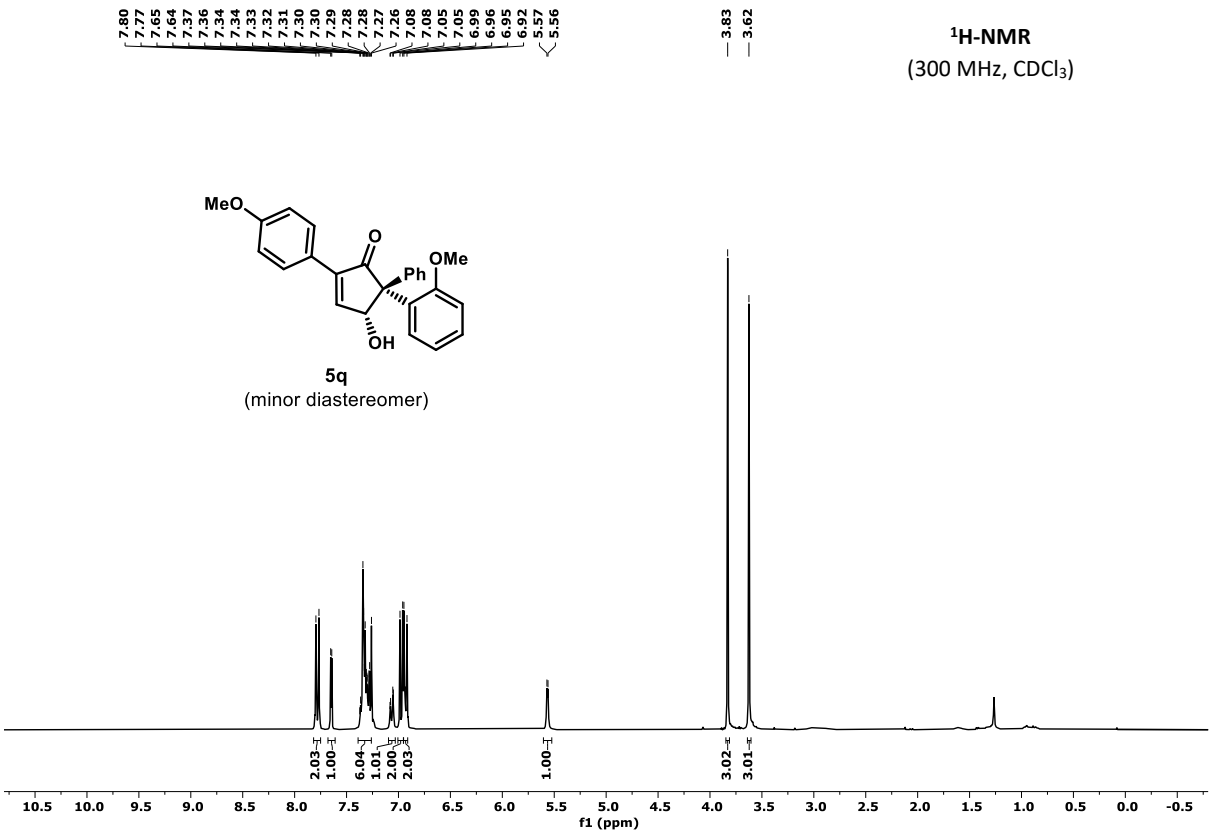


#	Peak Name	CH	tR [min]	Area [μV·sec]	Height [μV]	Area%	Height%	Quantity	NTP	Resolution	Symmetry Factor	Warning
1	Unknown	11	34.080	2441185	29293	50.064	54.221	N/A	4154	1.983	1.717	
2	Unknown	11	38.600	2434956	24732	49.936	45.779	N/A	3951	N/A	1.726	

Daicel Chiralpak IC column (95:5 *n*-Hexane/*i*-PrOH, 1.0 mL/min, 245 nm)

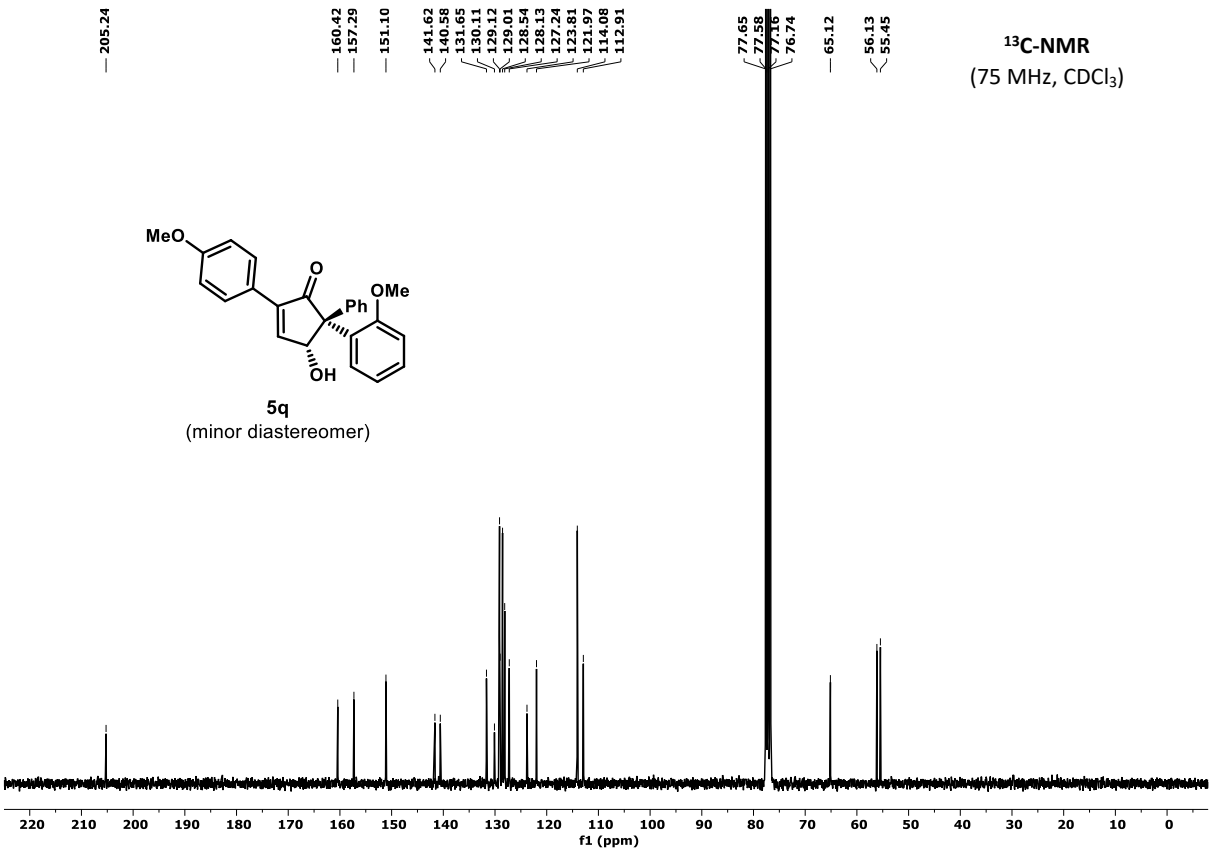


#	Peak Name	CH	tR [min]	Area [μV·sec]	Height [μV]	Area%	Height%	Quantity	NTP	Resolution	Symmetry Factor	Warning
1	Unknown	11	34.520	61313	756	1.869	2.298	N/A	3839	1.662	1.203	
2	Unknown	11	38.403	3218689	32162	98.131	97.702	N/A	3907	N/A	1.760	



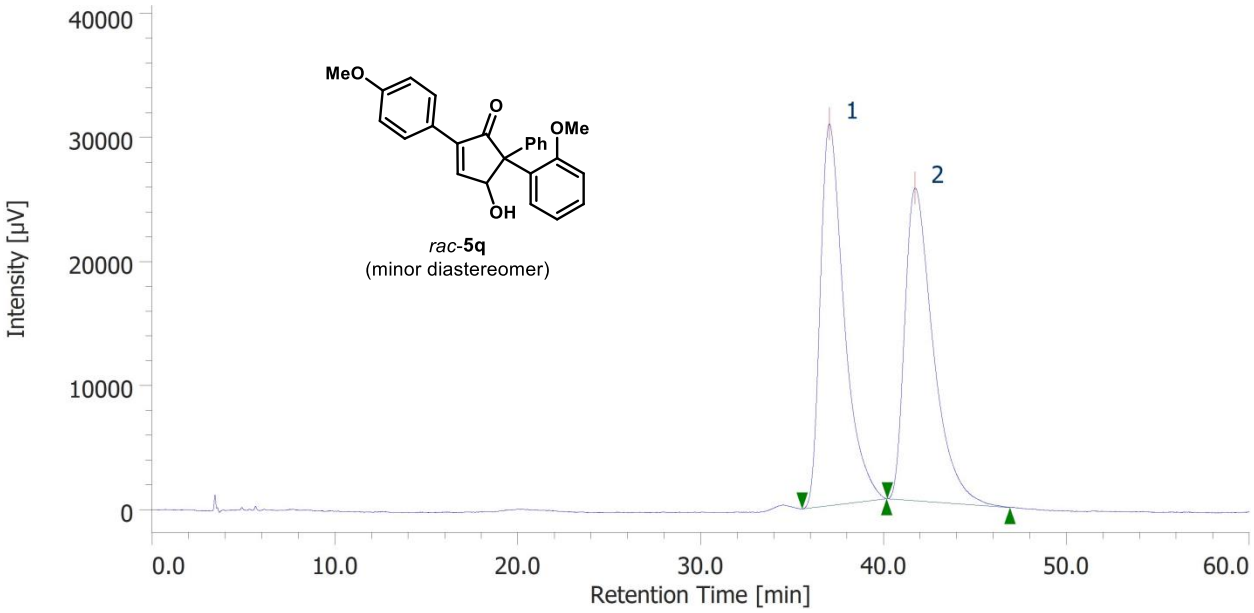
^{1}H-NMR
(300 MHz, $CDCl_3$)

5q
(minor diastereomer)



^{13}C-NMR
(75 MHz, $CDCl_3$)

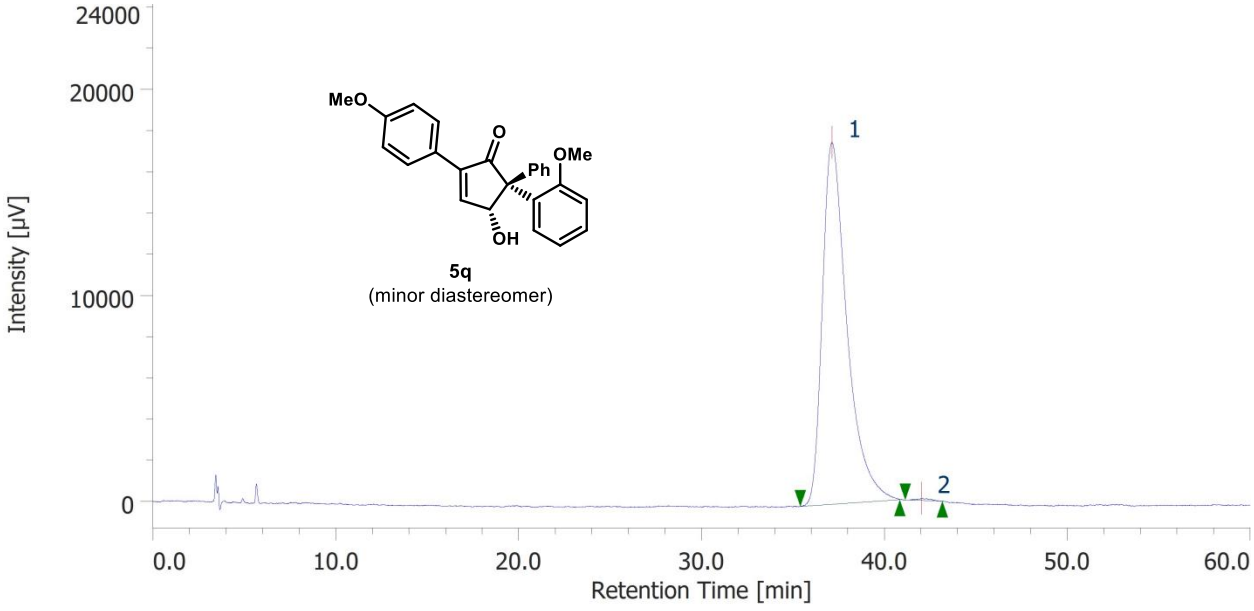
5q
(minor diastereomer)



rac-**5q**
(minor diastereomer)

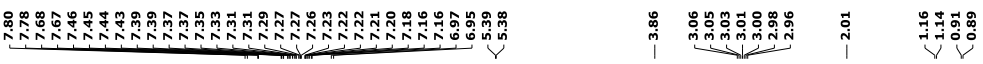
#	Peak Name	CH	tR [min]	Area [μV·sec]	Height [μV]	Area%	Height%	Quantity	NTP	Resolution	Symmetry Factor	Warning
1	Unknown	11	37.030	2786682	30755	50.646	54.976	N/A	4233	1.877	1.622	
2	Unknown	11	41.713	2715647	25188	49.354	45.024	N/A	3743	N/A	1.701	

Daicel Chiralpak IC column (95:5 *n*-Hexane/*i*-PrOH, 1.0 mL/min, 245 nm)



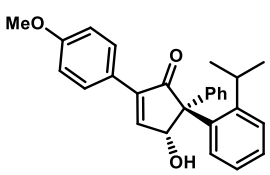
5q
(minor diastereomer)

#	Peak Name	CH	tR [min]	Area [μV·sec]	Height [μV]	Area%	Height%	Quantity	NTP	Resolution	Symmetry Factor	Warning
1	Unknown	11	37.117	1643985	17557	99.692	99.412	N/A	4040	2.602	1.602	
2	Unknown	11	42.007	5082	104	0.308	0.588	N/A	13764	N/A	1.176	



^{1}H-NMR

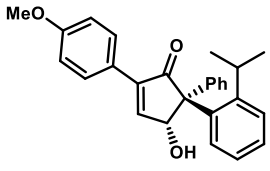
(400 MHz, $CDCl_3$)



5r

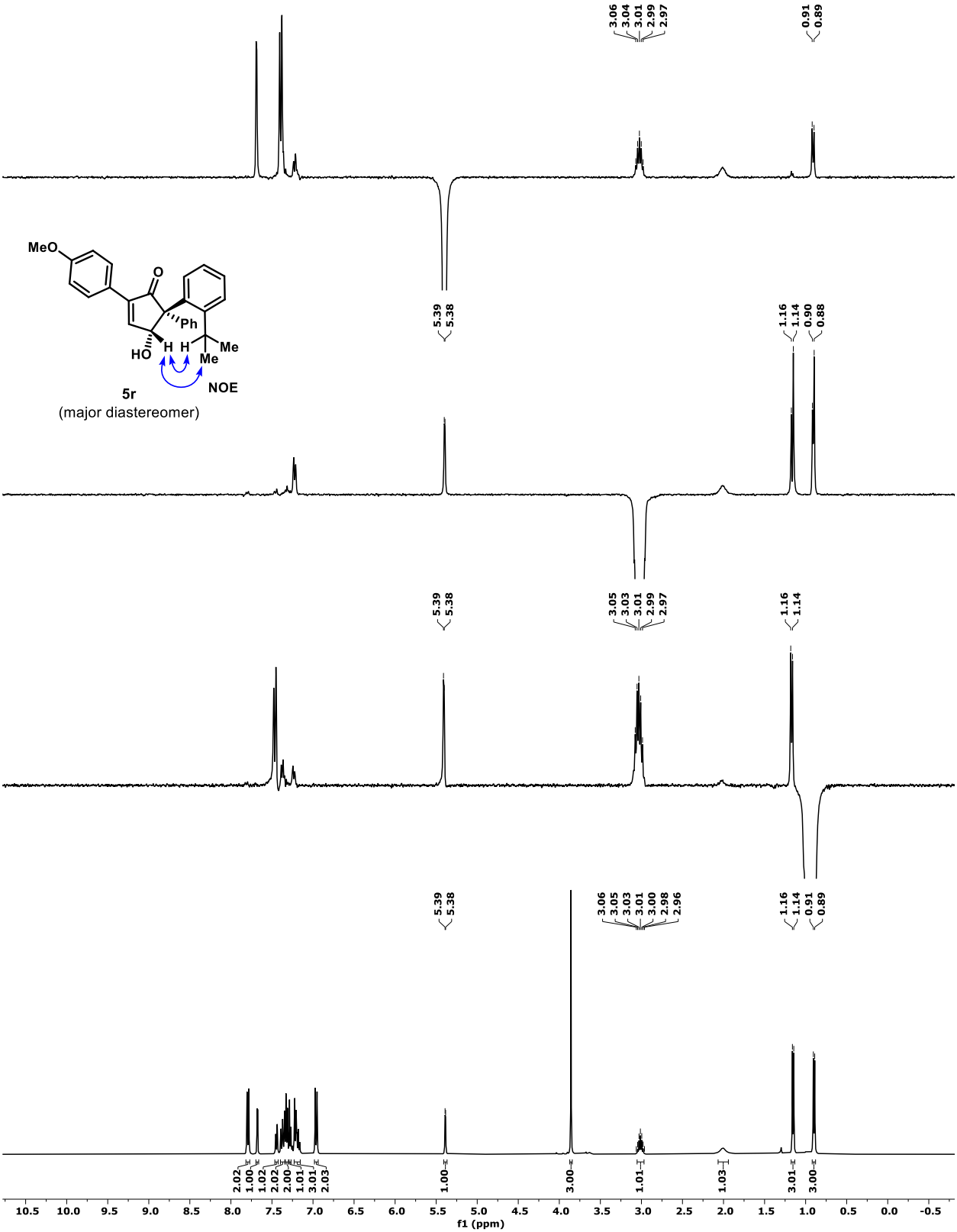
^{13}C-NMR

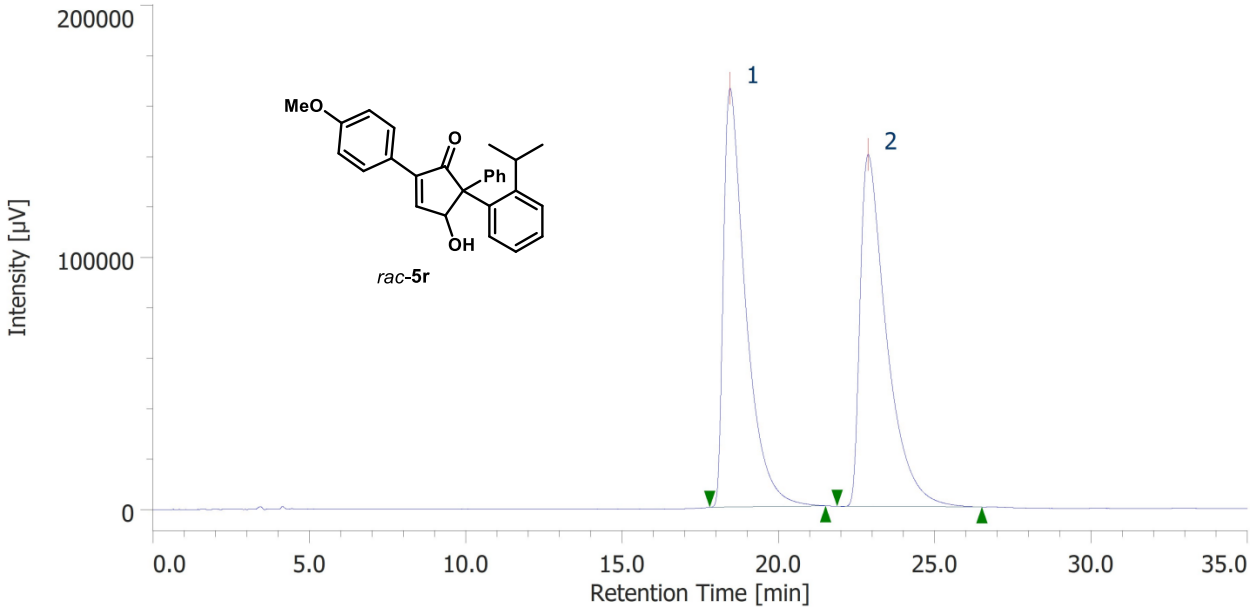
(100 MHz, $CDCl_3$)



5r

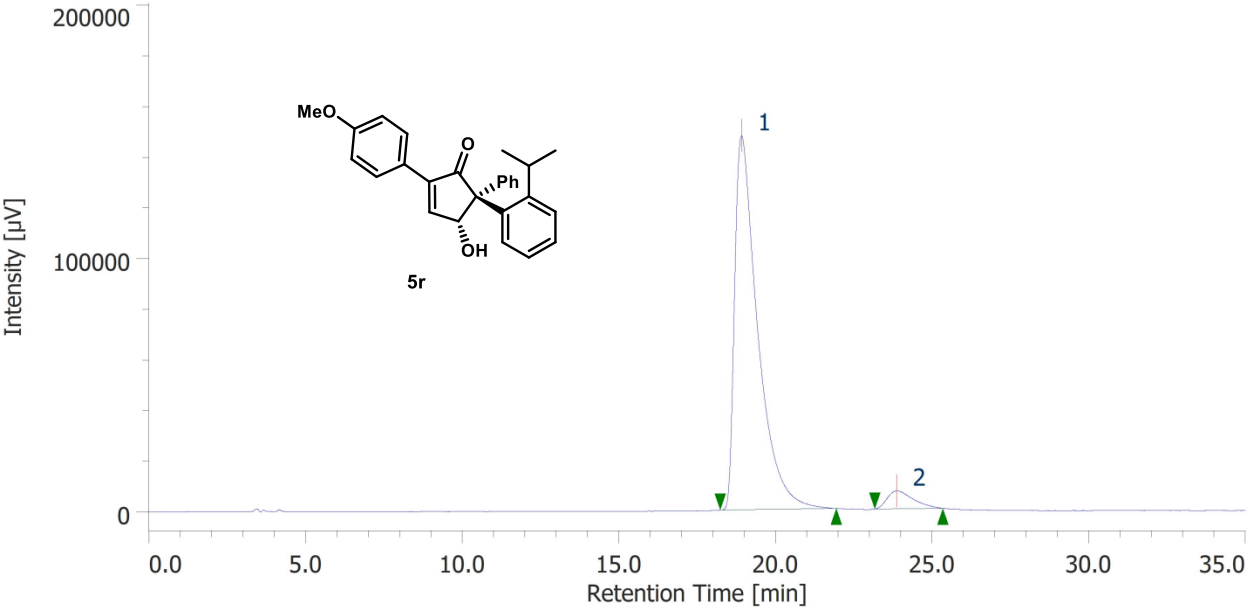
1D NOE of $3b_{19}$:



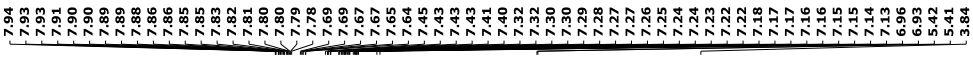


#	Peak Name	CH	tR [min]	Area [μV·sec]	Height [μV]	Area%	Height%	Quantity	NTP	Resolution	Symmetry Factor	Warning
1	Unknown	11	18.453	8187732	166023	49.930	54.336	N/A	3668	3.312	2.238	
2	Unknown	11	22.867	8210680	139527	50.070	45.664	N/A	3960	N/A	2.200	

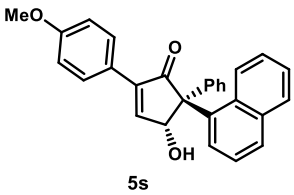
Daicel Chiralpak IB column (95:5 *n*-Hexane/*i*-PrOH, 1.0 mL/min, 245 nm)



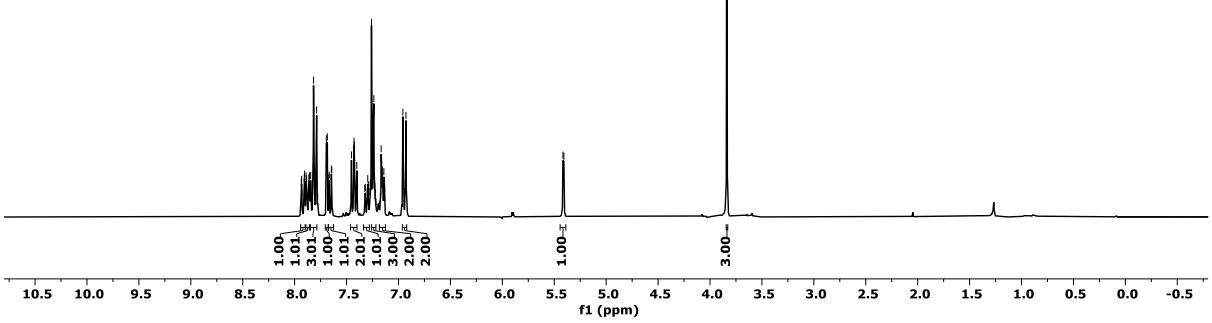
#	Peak Name	CH	tR [min]	Area [μV·sec]	Height [μV]	Area%	Height%	Quantity	NTP	Resolution	Symmetry Factor	Warning
1	Unknown	11	18.913	7535990	147596	94.854	95.433	N/A	3621	3.560	2.252	
2	Unknown	11	23.863	408825	7063	5.146	4.567	N/A	3887	N/A	1.582	



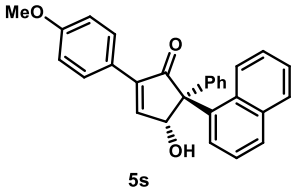
^{1}H-NMR
(300 MHz, $CDCl_3$)



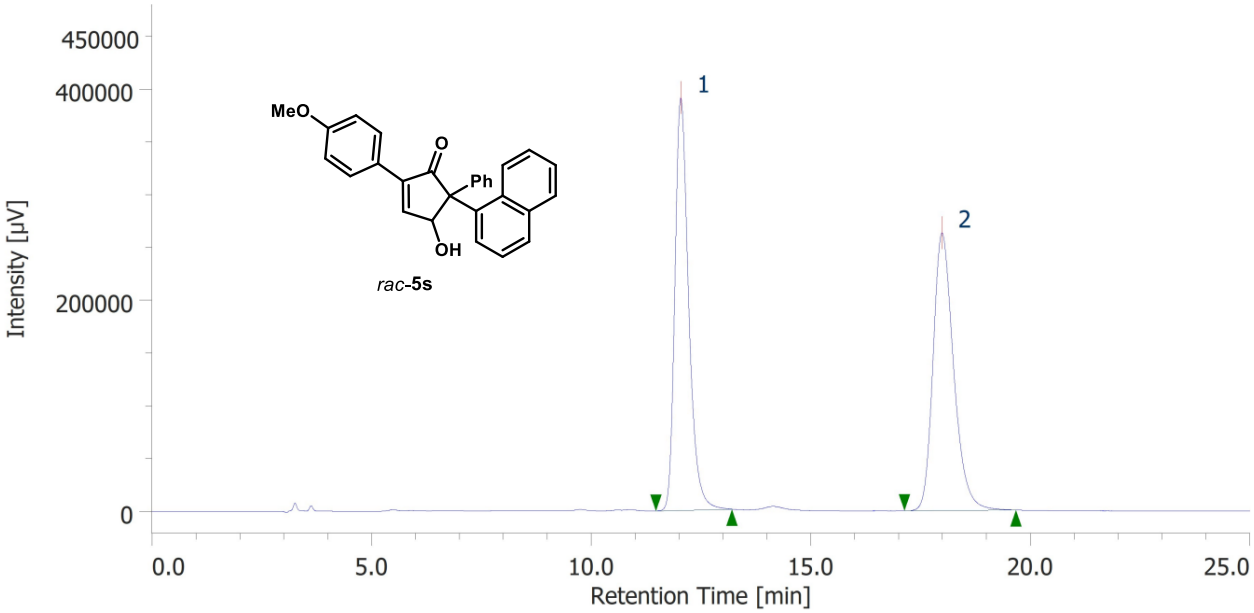
5s



^{13}C-NMR
(75 MHz, $CDCl_3$)

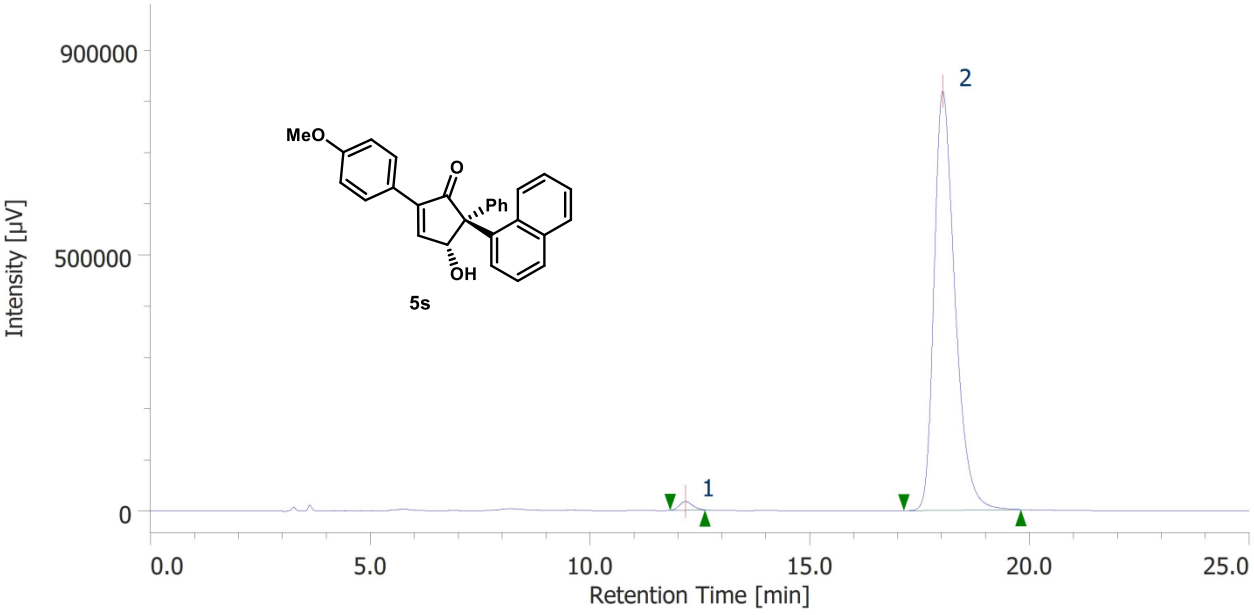


5s



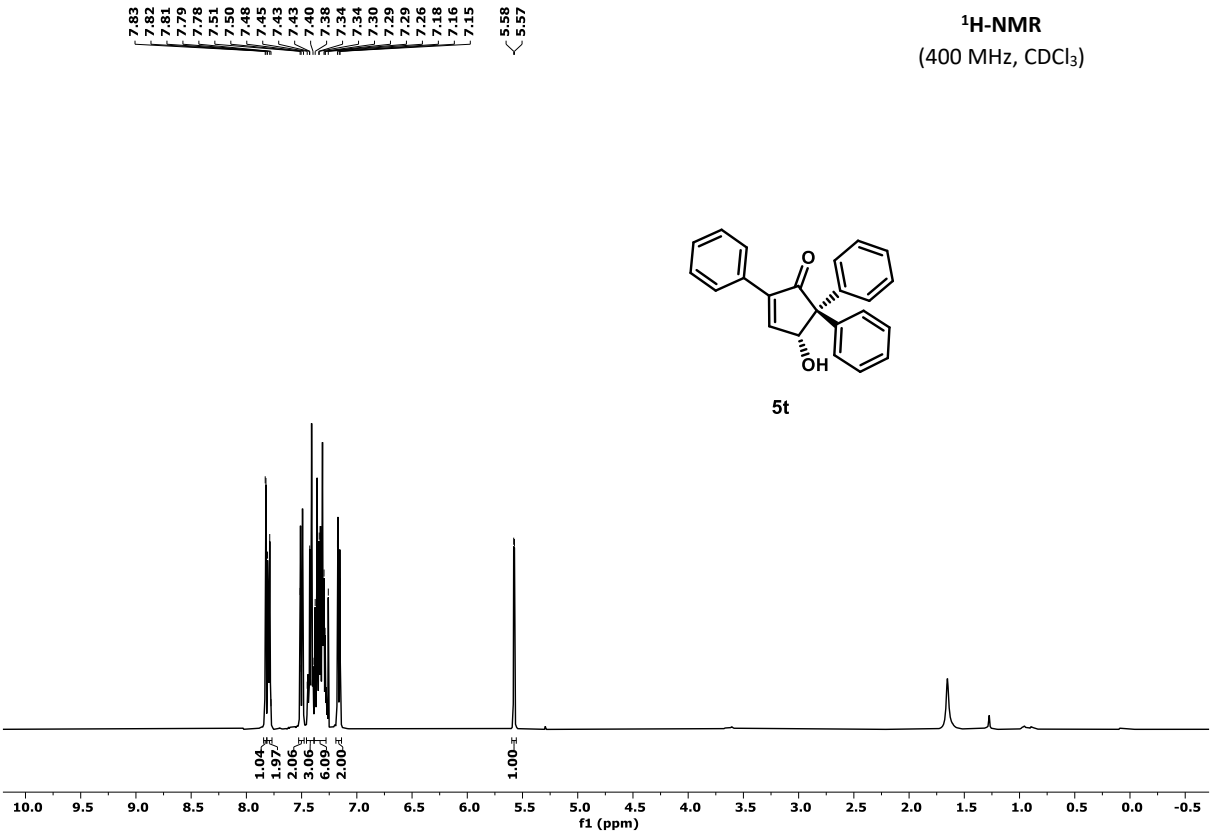
#	Peak Name	CH	tR [min]	Area [μV·sec]	Height [μV]	Area%	Height%	Quantity	NTP	Resolution	Symmetry Factor	Warning
1	Unknown	10	12.037	8490156	390377	49.837	59.765	N/A	7611	8.618	1.335	
2	Unknown	10	17.983	8545570	262813	50.163	40.235	N/A	7477	N/A	1.284	

Daicel Chiralpak IA column (80:20 *n*-Hexane/*i*-PrOH, 1.0 mL/min, 230 nm)

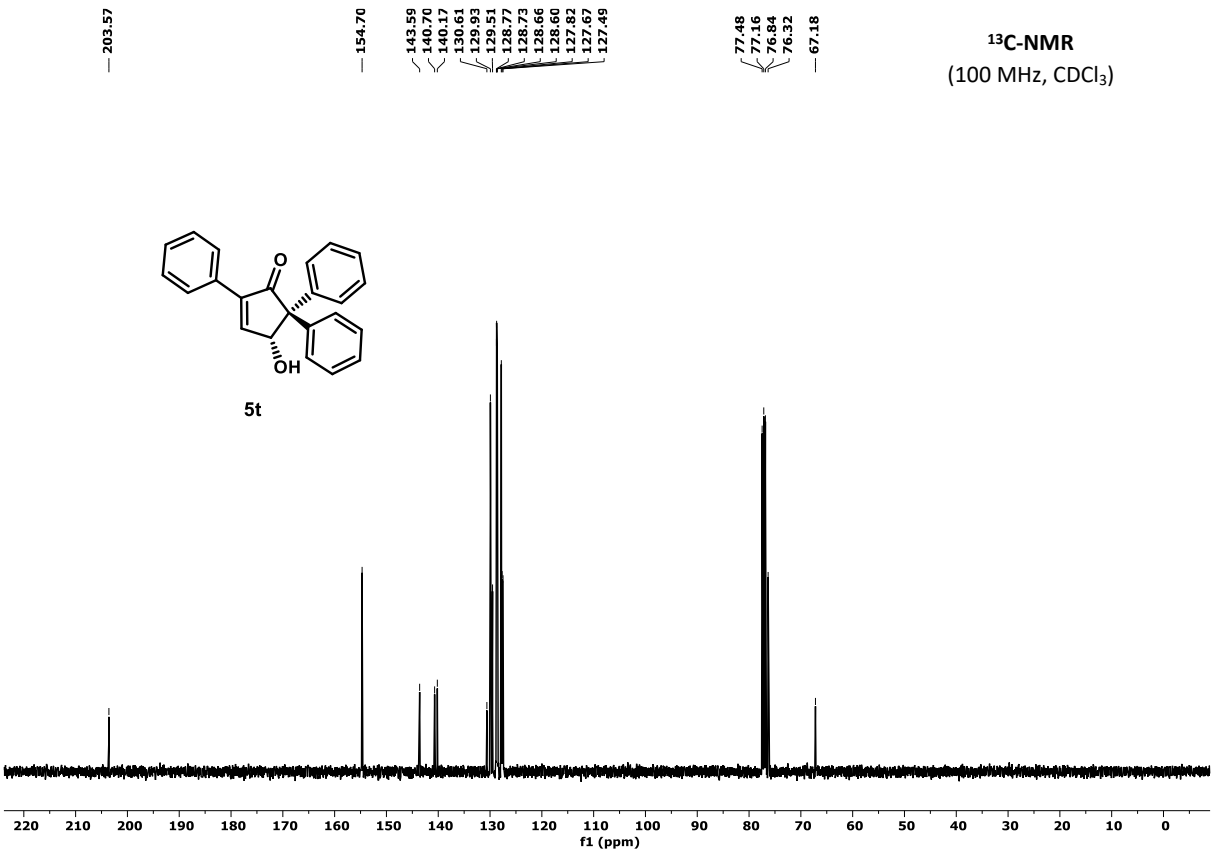


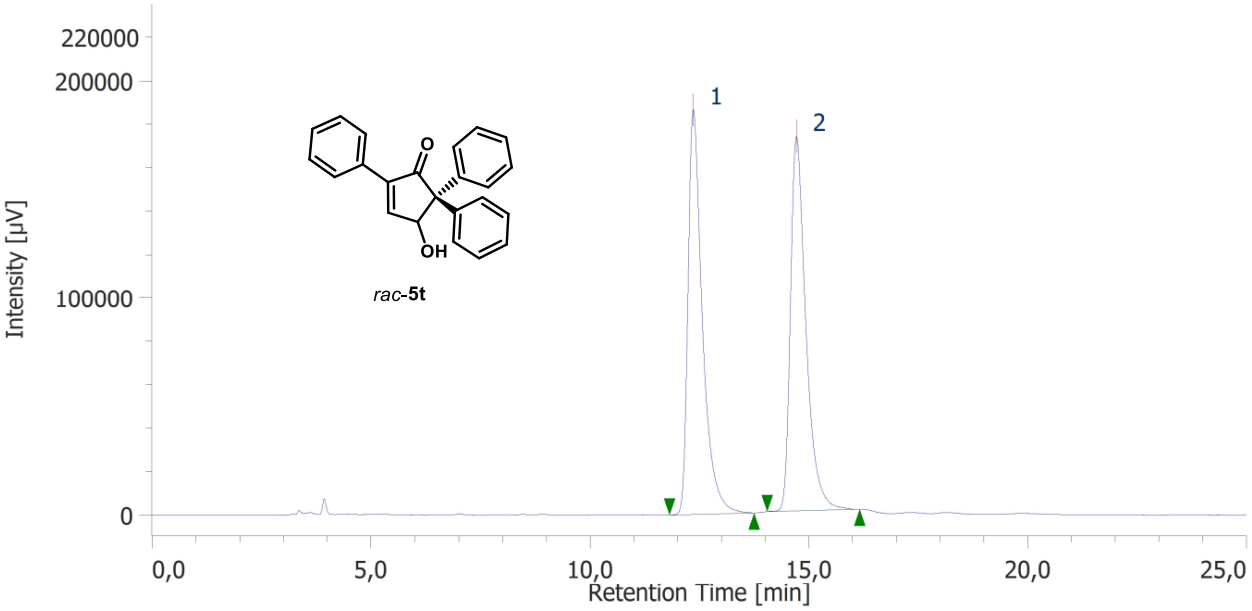
#	Peak Name	CH	tR [min]	Area [μV·sec]	Height [μV]	Area%	Height%	Quantity	NTP	Resolution	Symmetry Factor	Warning
1	Unknown	10	12.167	347431	16844	1.269	2.018	N/A	7850	8.422	1.170	
2	Unknown	10	18.020	27020765	817941	98.731	97.982	N/A	7285	N/A	1.381	

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



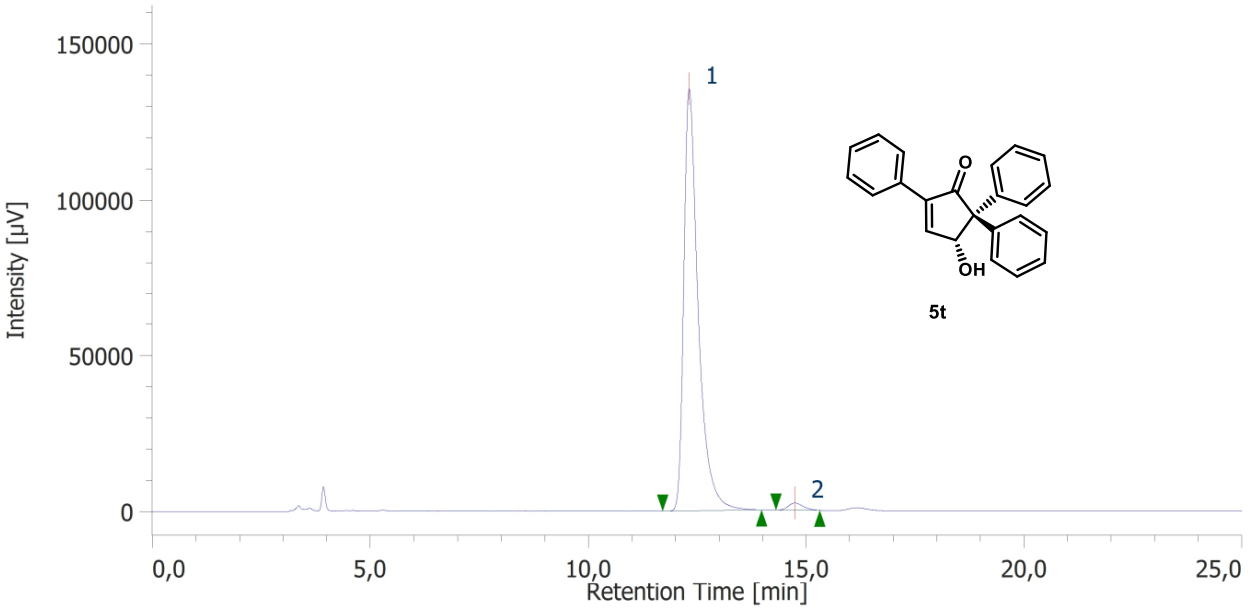
^{13}C-NMR
(100 MHz, $CDCl_3$)





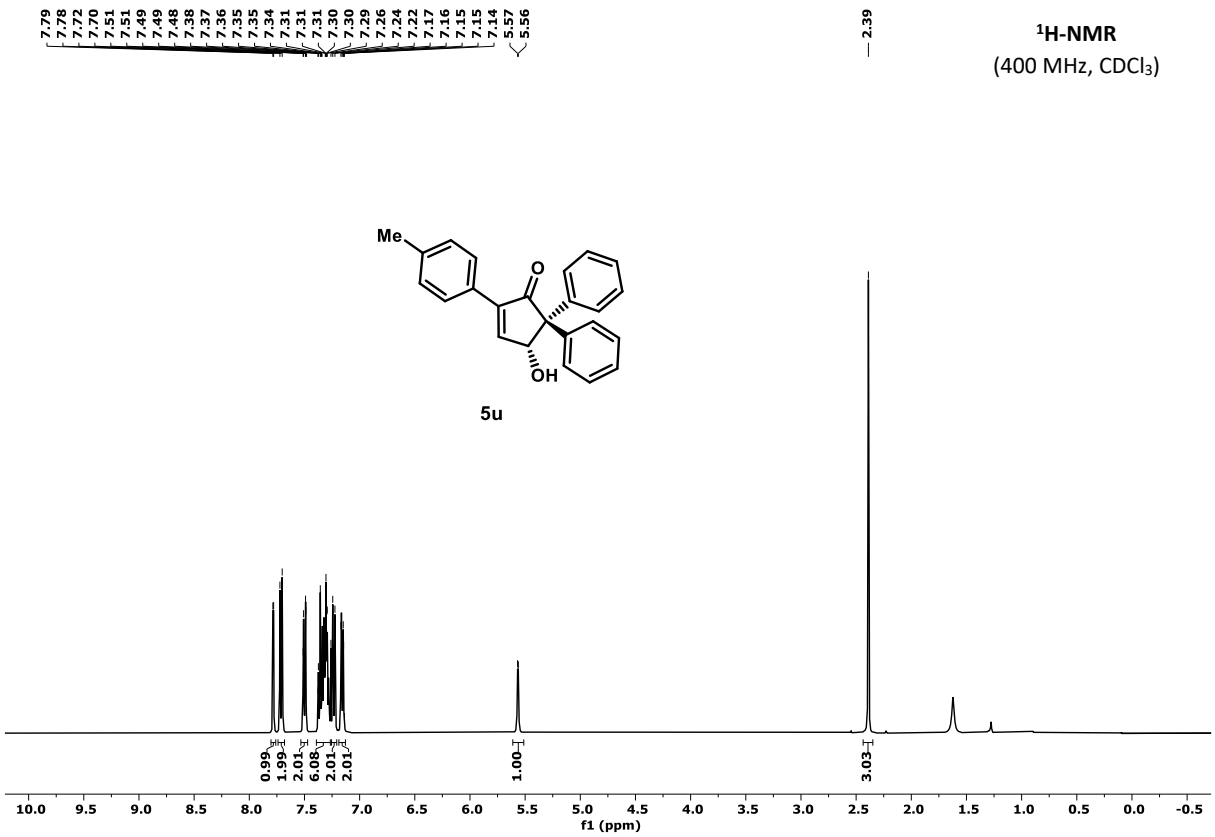
#	Peak Name	CH	tR [min]	Area [μV·sec]	Height [μV]	Area%	Height%	Quantity	NTP	Resolution	Symmetry Factor	Warning
1	Unknown	10	12,353	4251313	186269	50,254	51,941	N/A	7796	4,043	1,686	
2	Unknown	10	14,710	4208394	172345	49,746	48,059	N/A	9325	N/A	1,536	

Daicel Chiralpak IB column (90:10 *n*-Hexane/*i*-PrOH, 1.0 mL/min, 230 nm)

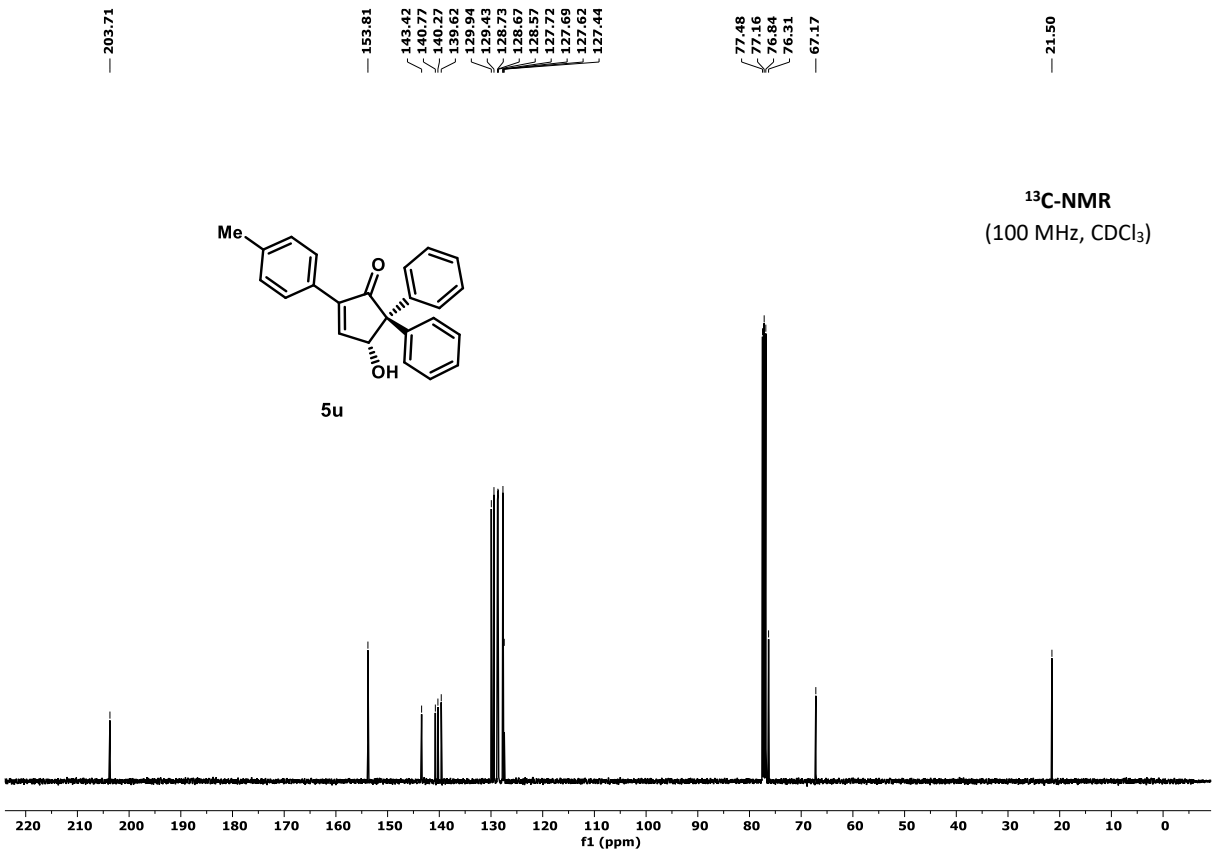


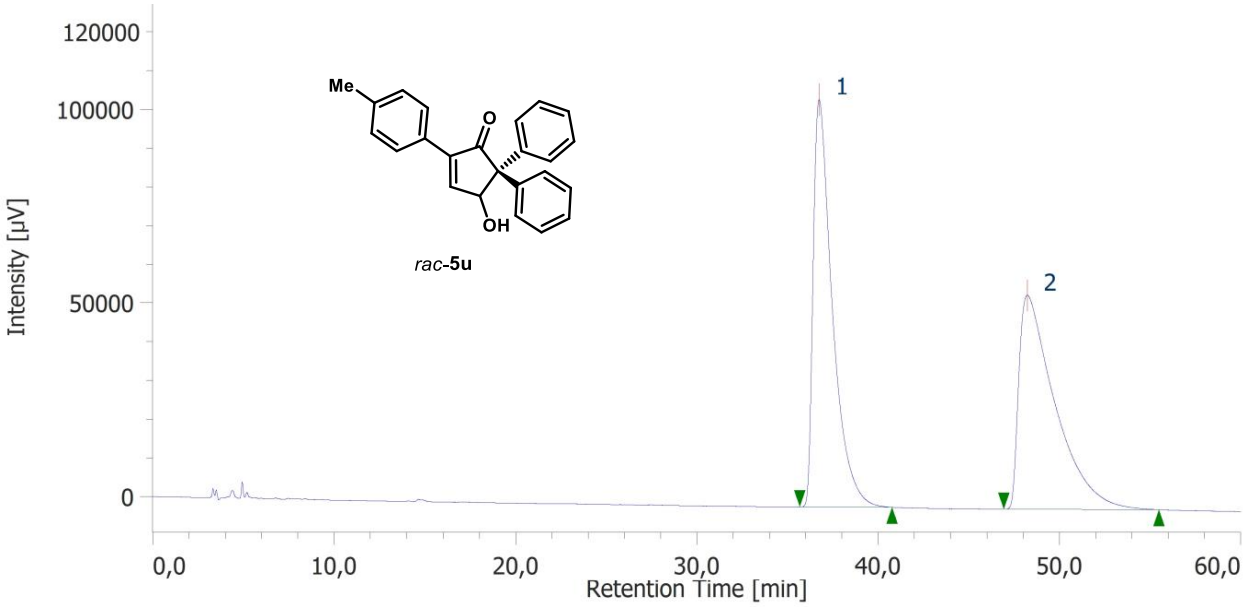
#	Peak Name	CH	tR [min]	Area [μV·sec]	Height [μV]	Area%	Height%	Quantity	NTP	Resolution	Symmetry Factor	Warning
1	Unknown	10	12,310	3103778	135350	98,270	98,325	N/A	7747	4,113	1,662	
2	Unknown	10	14,737	54648	2305	1,730	1,675	N/A	8934	N/A	1,227	

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



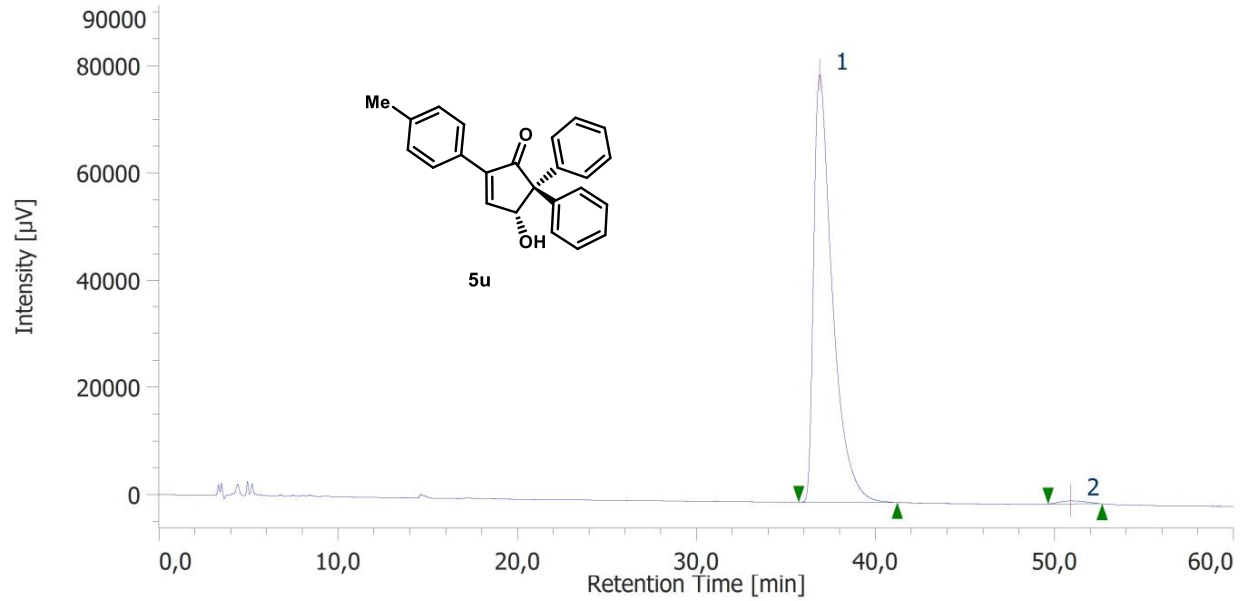
^{13}C-NMR
(100 MHz, $CDCl_3$)





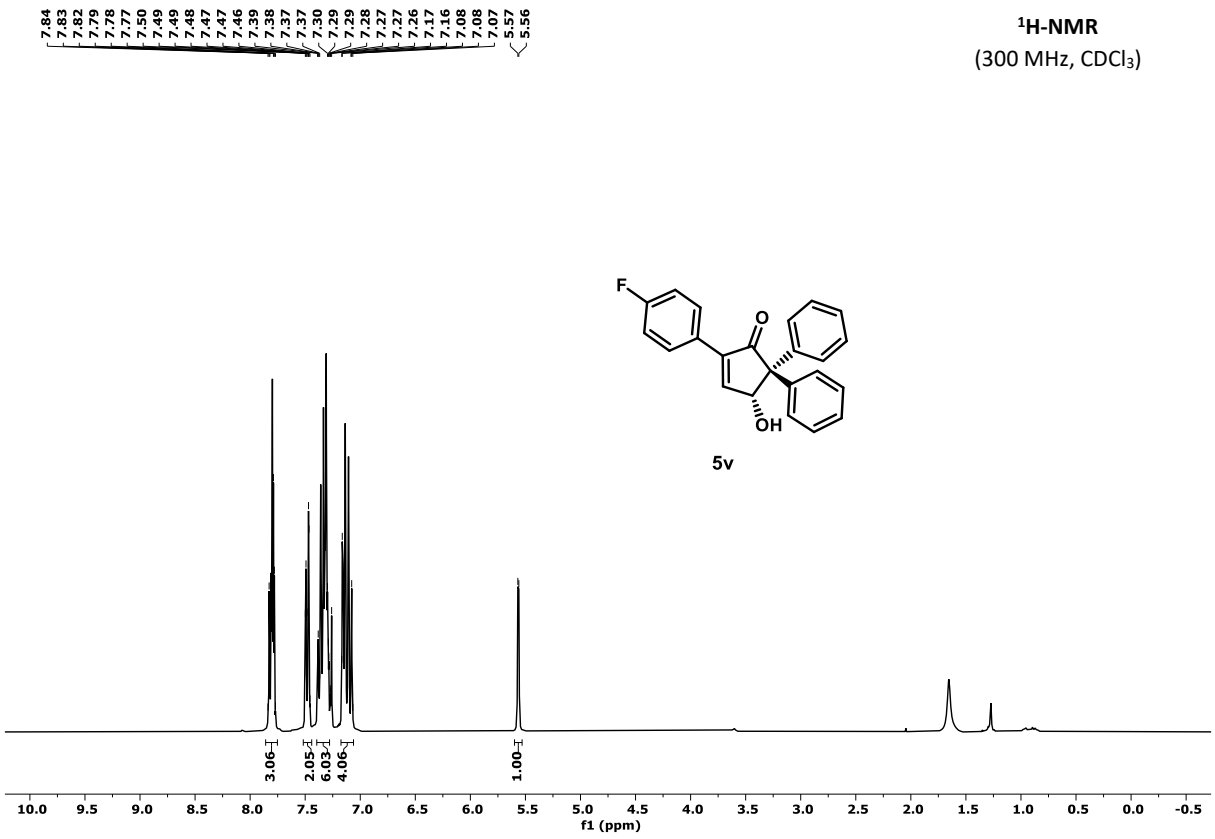
#	Peak Name	CH	tR [min]	Area [μV·sec]	Height [μV]	Area%	Height%	Quantity	NTP	Resolution	Symmetry Factor	Warning
1	Unknown	10	36,733	7731663	105075	50,281	65,593	N/A	6413	4,337	2,144	
2	Unknown	10	48,213	7645173	55118	49,719	34,407	N/A	3084	N/A	3,017	

Daicel Chiralpak IE column (95:5 *n*-Hexane/*i*-PrOH, 1.0 mL/min, 230 nm)

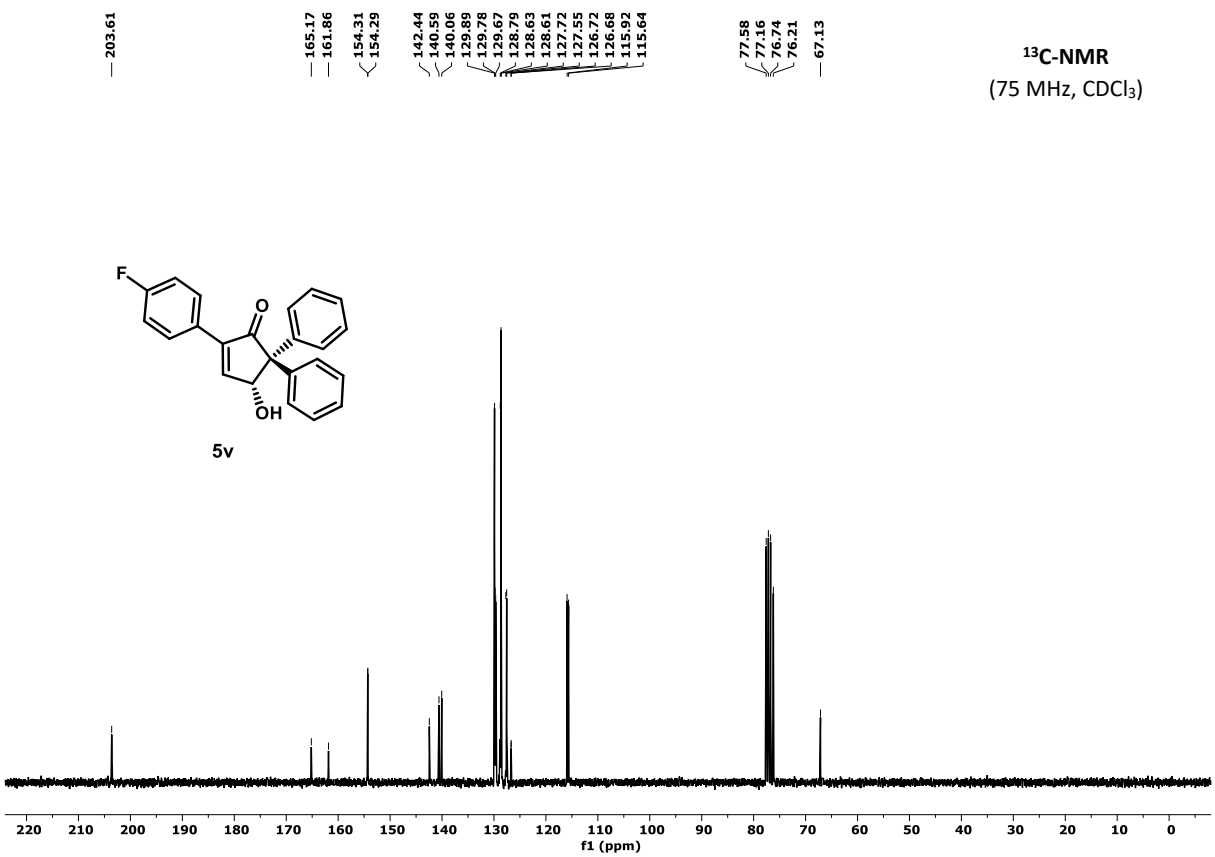


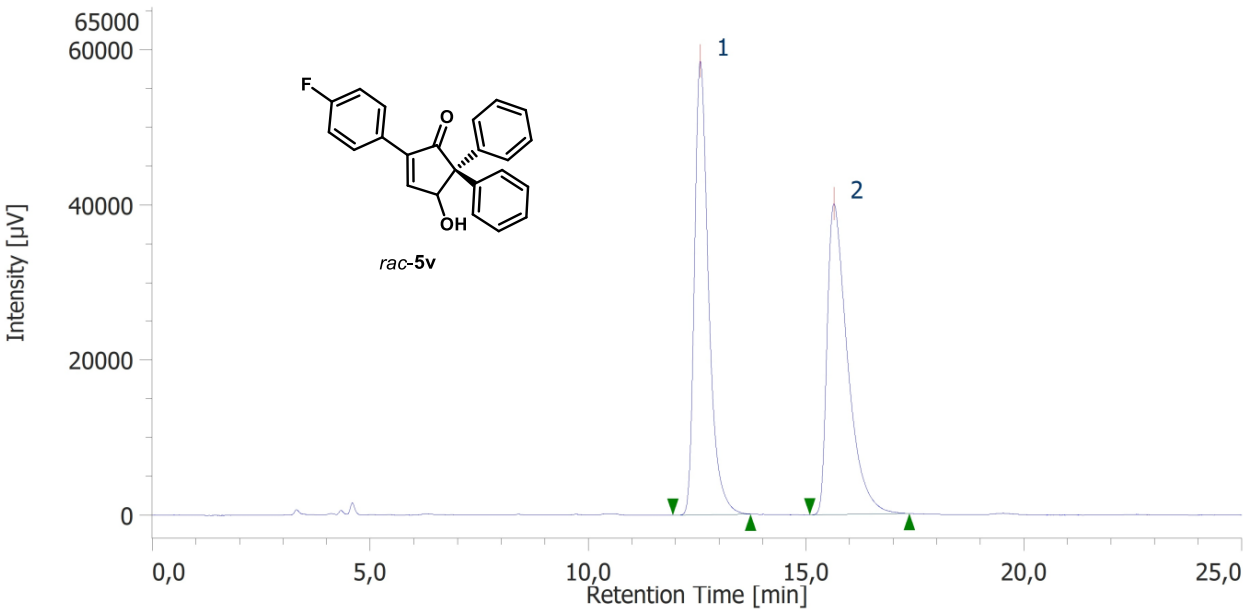
#	Peak Name	CH	tR [min]	Area [μV·sec]	Height [μV]	Area%	Height%	Quantity	NTP	Resolution	Symmetry Factor	Warning
1	Unknown	10	36,873	5780033	79690	99,001	99,268	N/A	6669	6,031	2,066	
2	Unknown	10	50,887	58336	588	0,999	0,732	N/A	5088	N/A	1,207	

^{1}H-NMR
(300 MHz, $CDCl_3$)



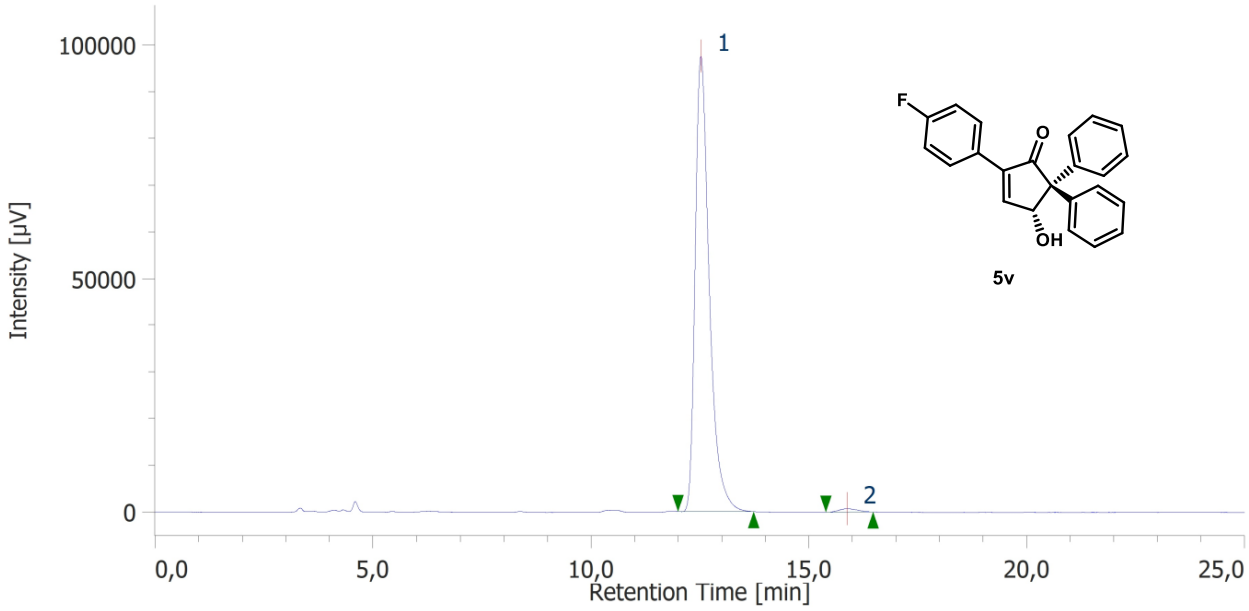
^{13}C-NMR
(75 MHz, $CDCl_3$)





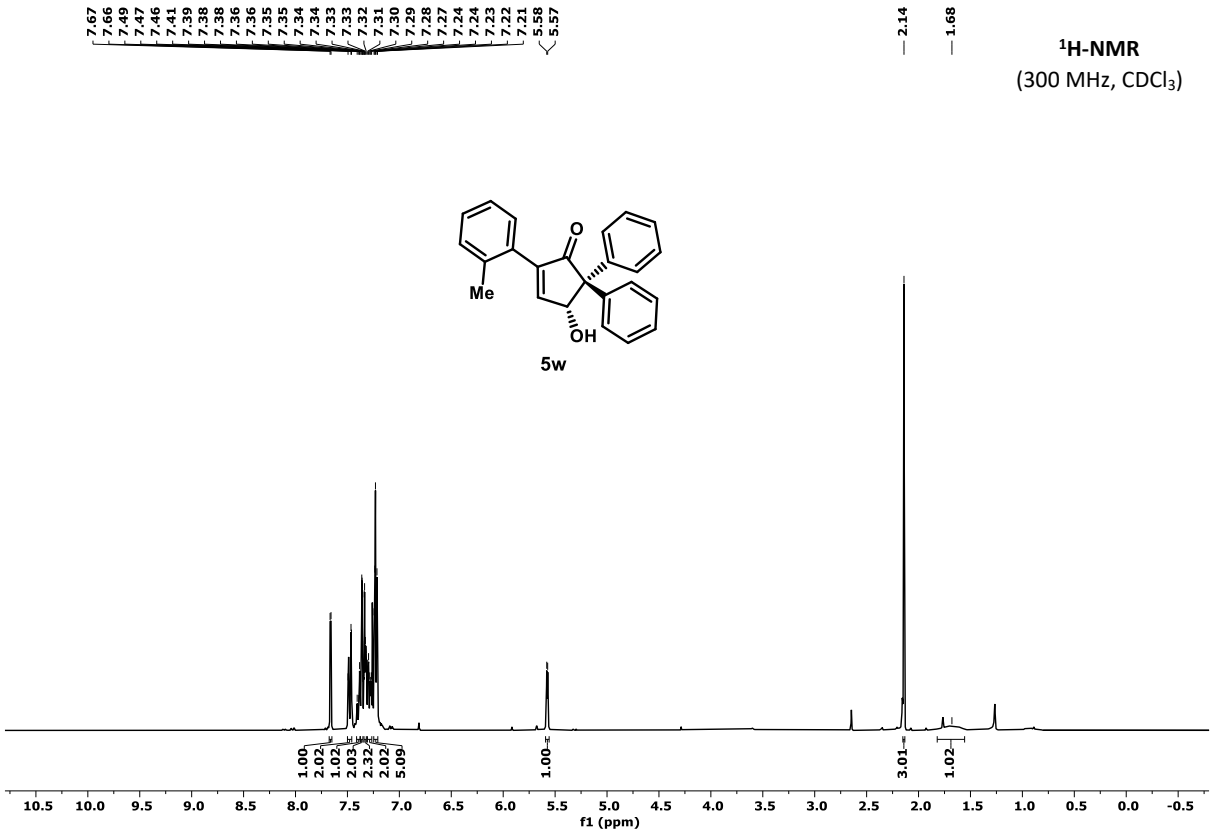
#	Peak Name	CH	tR [min]	Area [μV·sec]	Height [μV]	Area%	Height%	Quantity	NTP	Resolution	Symmetry Factor	Warning
1	Unknown	11	12,570	1315153	58461	50,181	59,341	N/A	7886	4,429	1,443	
2	Unknown	11	15,637	1305661	40055	49,819	40,659	N/A	5783	N/A	1,894	

Daicel Chiralpak IE column (90:10 *n*-Hexane/*i*-PrOH, 1.0 mL/min, 245 nm)

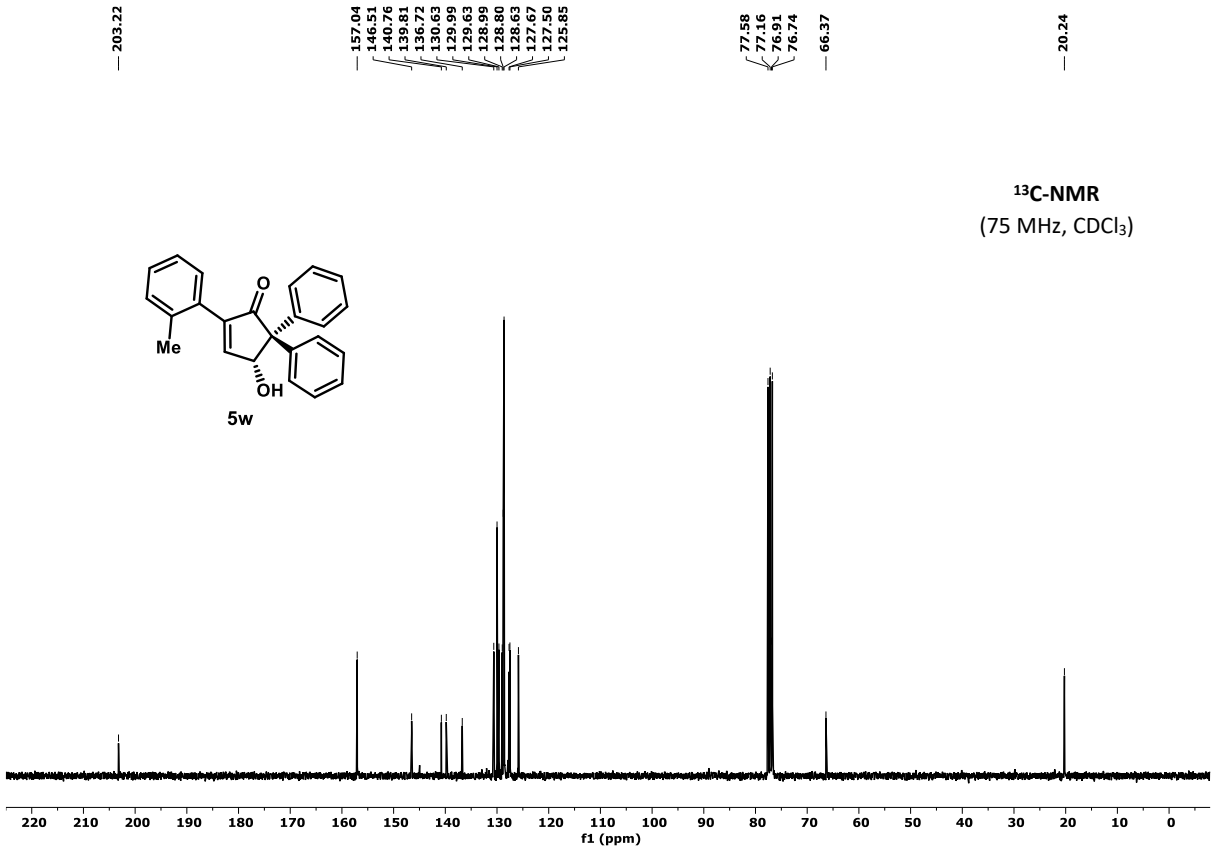


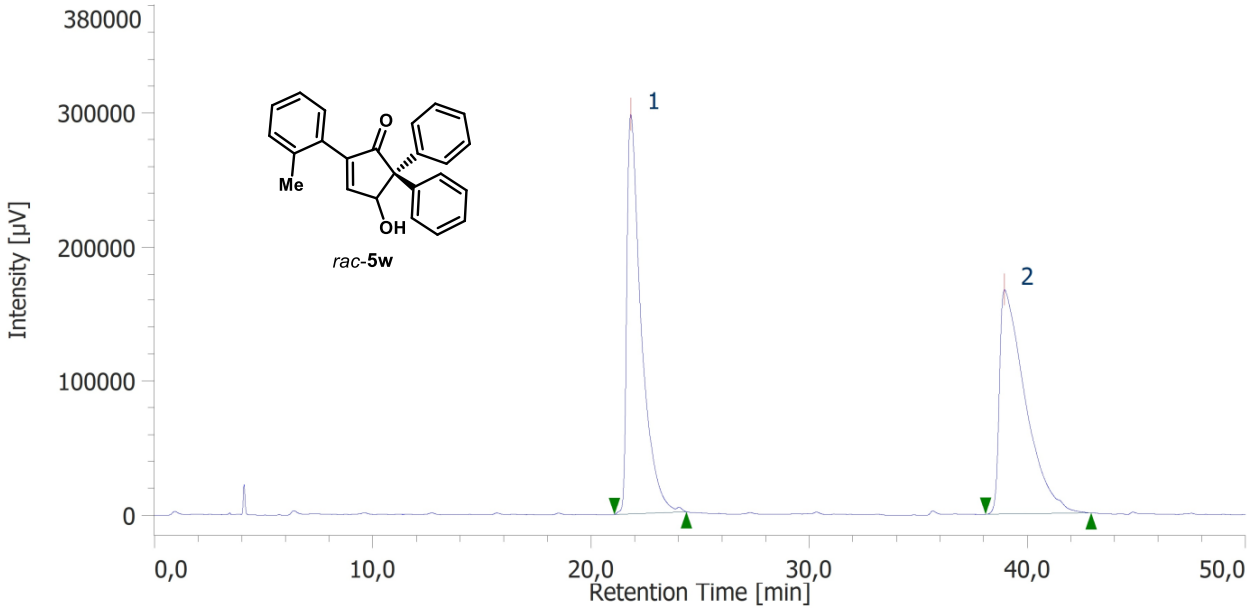
#	Peak Name	CH	tR [min]	Area [μV·sec]	Height [μV]	Area%	Height%	Quantity	NTP	Resolution	Symmetry Factor	Warning
1	Unknown	11	12,520	2192332	97448	99,019	99,247	N/A	7819	4,902	1,490	
2	Unknown	11	15,873	21728	739	0,981	0,753	N/A	6216	N/A	1,159	

^{1}H-NMR
(300 MHz, $CDCl_3$)



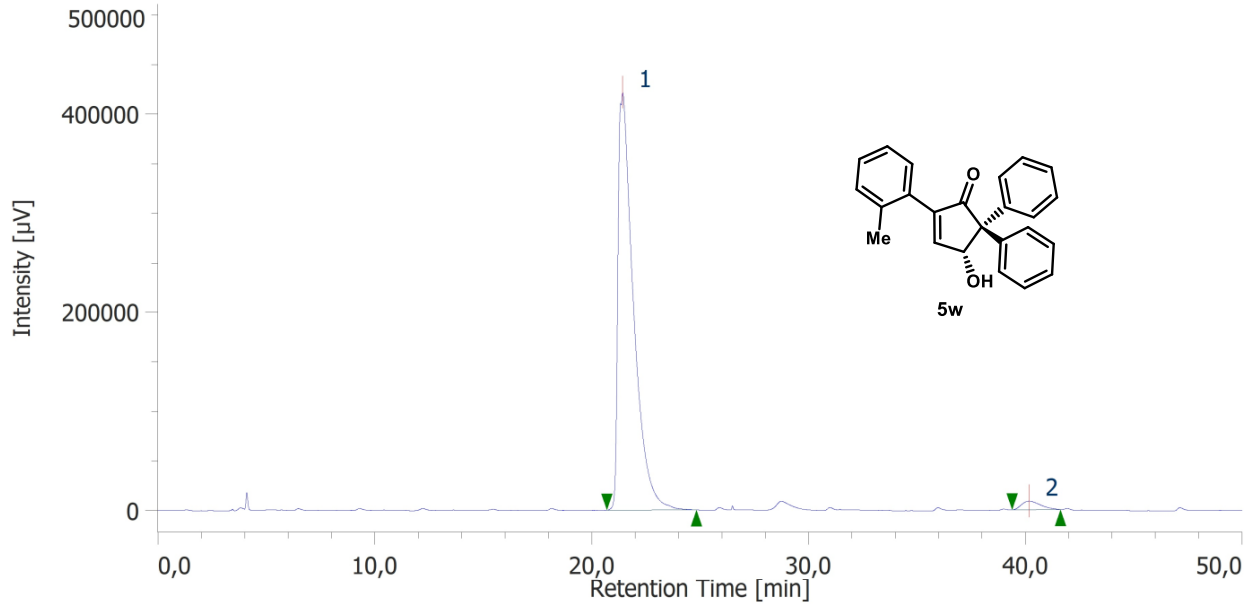
^{13}C-NMR
(75 MHz, $CDCl_3$)



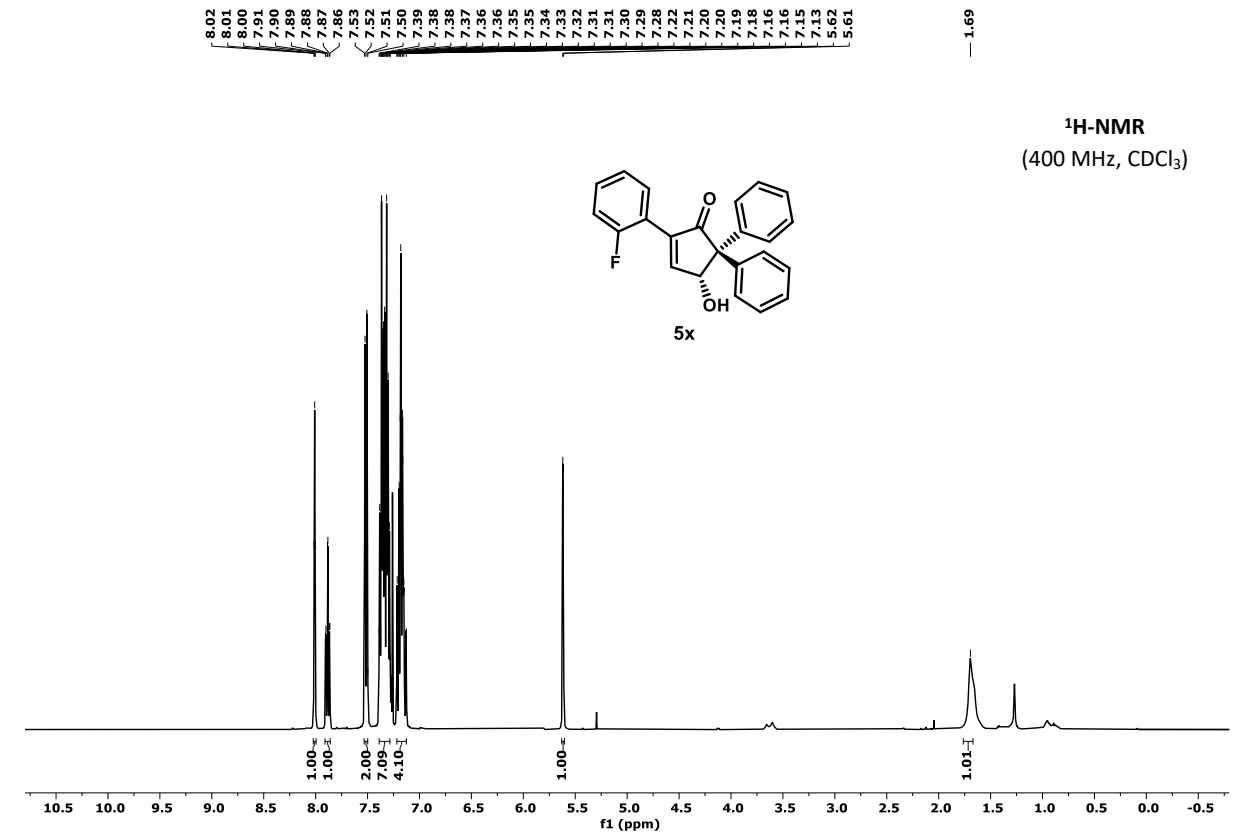


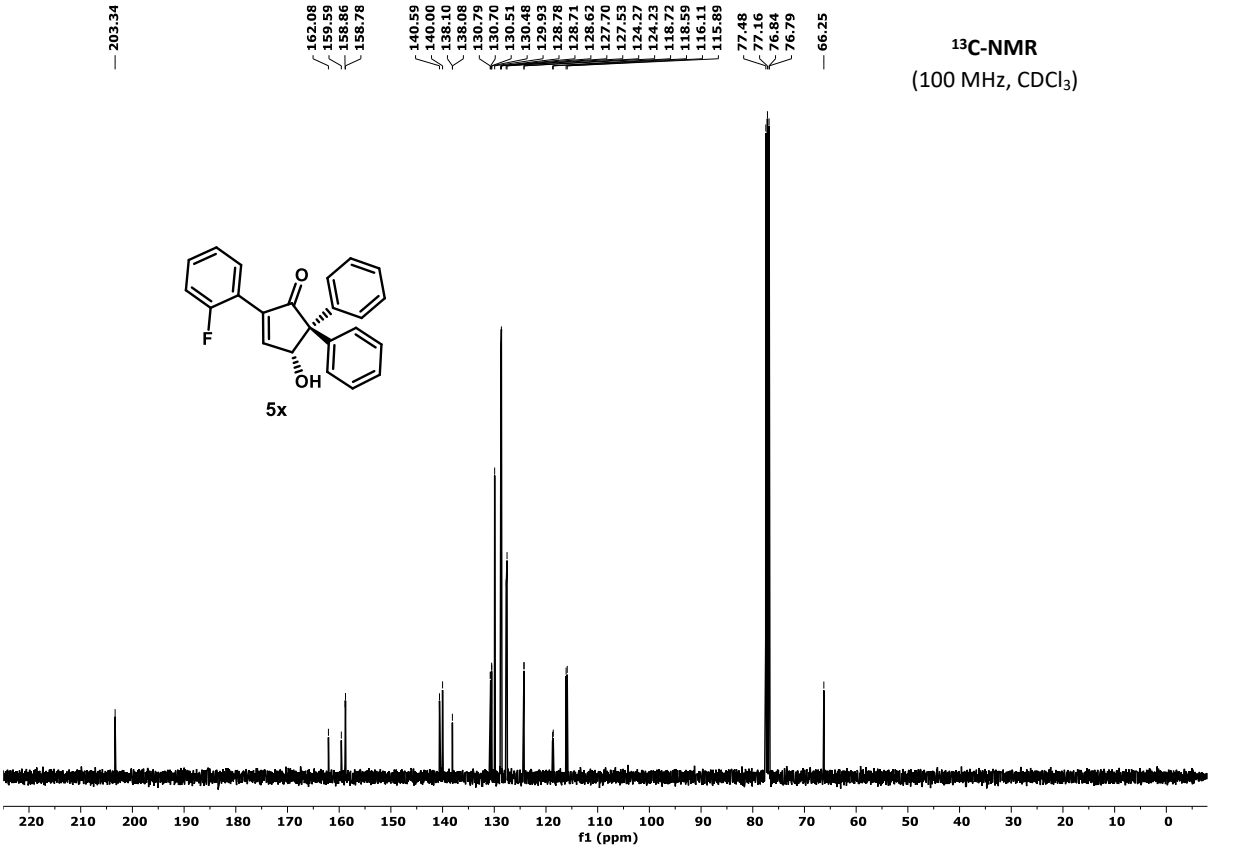
#	Peak Name	CH	tR [min]	Area [μV·sec]	Height [μV]	Area%	Height%	Quantity	NTP	Resolution	Symmetry Factor	Warning
1	Unknown	10	21.813	13742445	297744	49.980	63.998	N/A	6354	10.855	2.522	
2	Unknown	10	38.947	13753646	167498	50.020	36.002	N/A	5660	N/A	3.265	

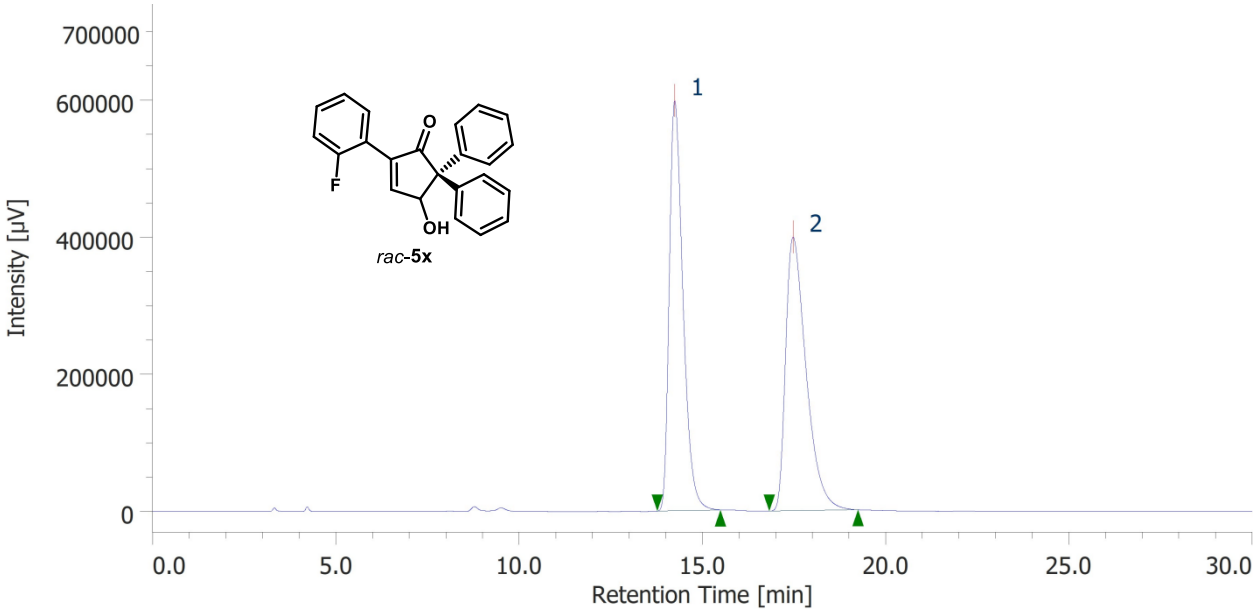
Daicel Chiralpak IB column (95:5 *n*-Hexane/*i*-PrOH, 1.0 mL/min, 230 nm)



#	Peak Name	CH	tR [min]	Area [μV·sec]	Height [μV]	Area%	Height%	Quantity	NTP	Resolution	Symmetry Factor	Warning
1	Unknown	10	21.417	20879897	421262	97.545	97.984	N/A	4831	13.125	2.385	
2	Unknown	10	40.163	525519	8668	2.455	2.016	N/A	9693	N/A	1.407	

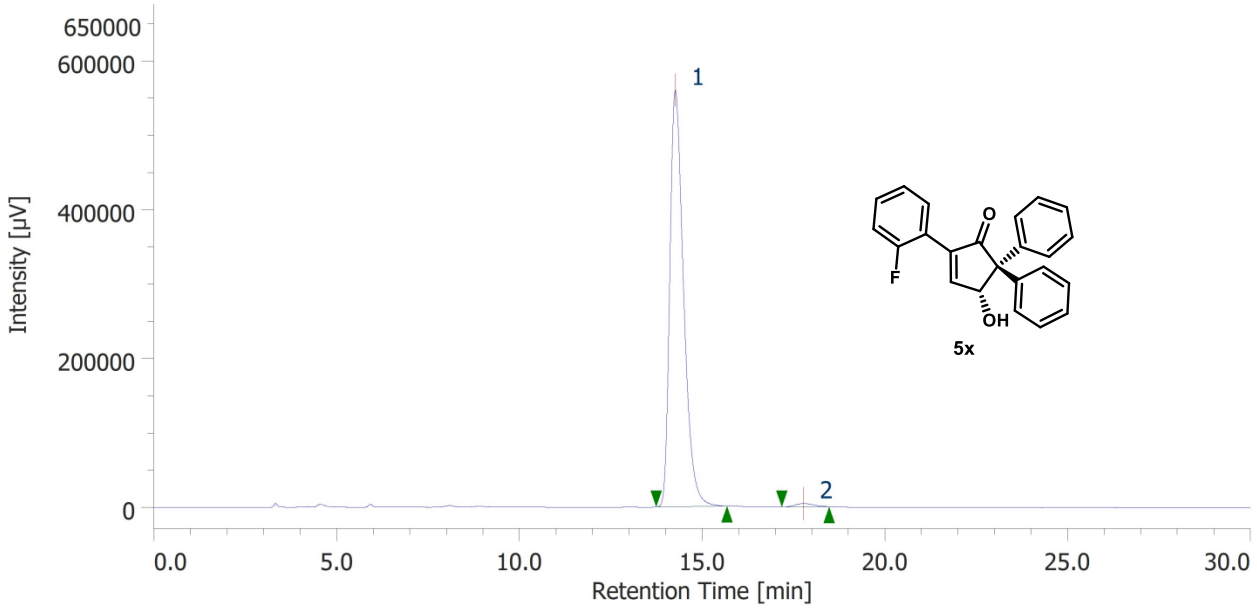

8.02 8.01 8.00 7.91 7.90 7.89 7.88 7.87 7.86 7.53 7.52 7.51 7.50 7.39 7.38 7.38 7.37 7.36 7.36 7.35 7.35 7.34 7.33 7.32 7.31 7.31 7.30 7.29 7.28 7.22 7.21 7.20 7.20 7.19 7.18 7.16 7.16 7.15 7.13 5.62 5.61
1.69
1H-NMR
(400 MHz, CDCl3)
O
F
OH
5x
1.00 1.00 2.00 7.09 4.10 1.00 1.01
10.5 10.0 9.5 9.0 8.5 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
f1 (ppm)


203.34
162.08 159.59 158.86 158.78 140.59 140.00 138.10 138.08 130.79 130.70 130.51 130.48 129.93 128.78 128.71 128.62 127.70 127.53 124.27 124.23 118.72 118.59 116.11 115.89 77.48 77.16 76.84 76.79 66.25
13C-NMR
(100 MHz, CDCl3)
O
F
OH
5x
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)



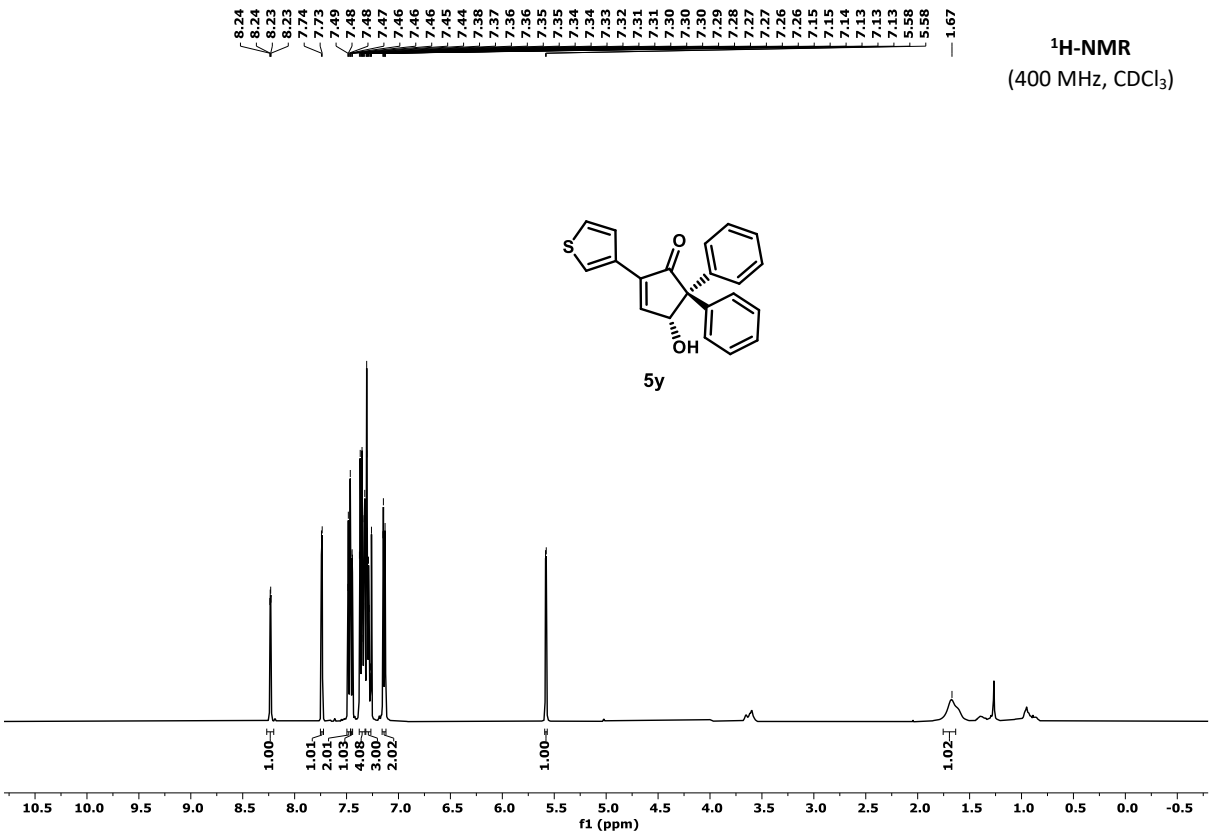
#	Peak Name	CH	tR [min]	Area [μV·sec]	Height [μV]	Area%	Height%	Quantity	NTP	Resolution	Symmetry Factor	Warning
1	Unknown	10	14.243	15511857	597910	50.020	59.978	N/A	7201	3.876	1.434	
2	Unknown	10	17.473	15499660	398972	49.980	40.022	N/A	4888	N/A	1.646	

Daicel Chiralpak IH column (90:10 *n*-Hexane/*i*-PrOH, 1.0 mL/min, 230 nm)

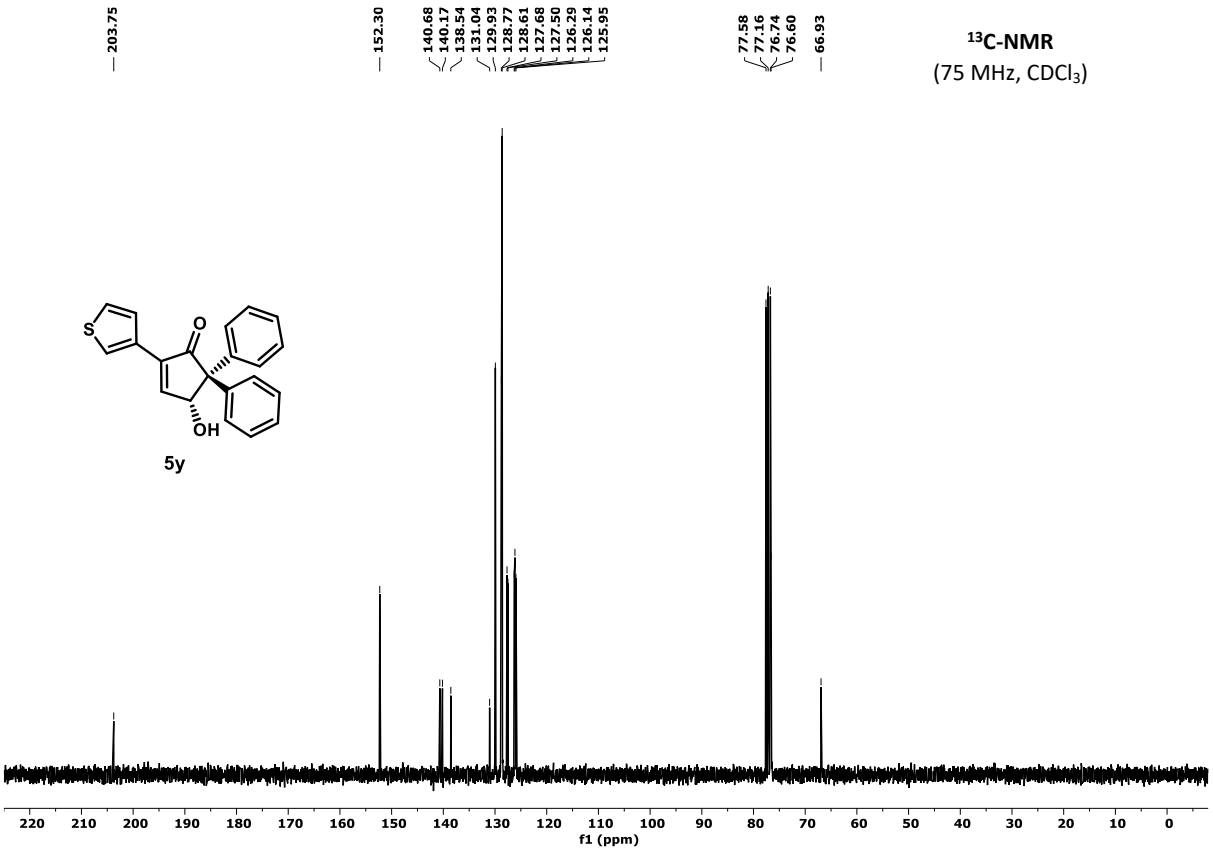


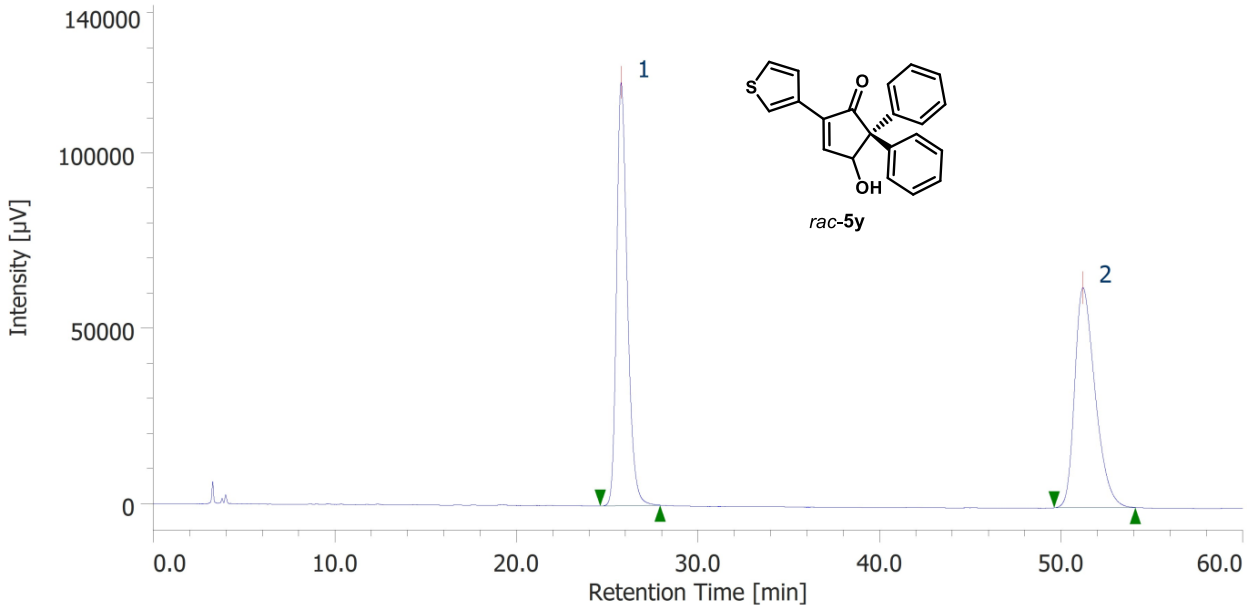
#	Peak Name	CH	tR [min]	Area [μV·sec]	Height [μV]	Area%	Height%	Quantity	NTP	Resolution	Symmetry Factor	Warning
1	Unknown	10	14.263	14639652	559582	98.916	99.190	N/A	7143	4.335	1.430	
2	Unknown	10	17.773	160500	4572	1.084	0.810	N/A	5617	N/A	1.146	

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



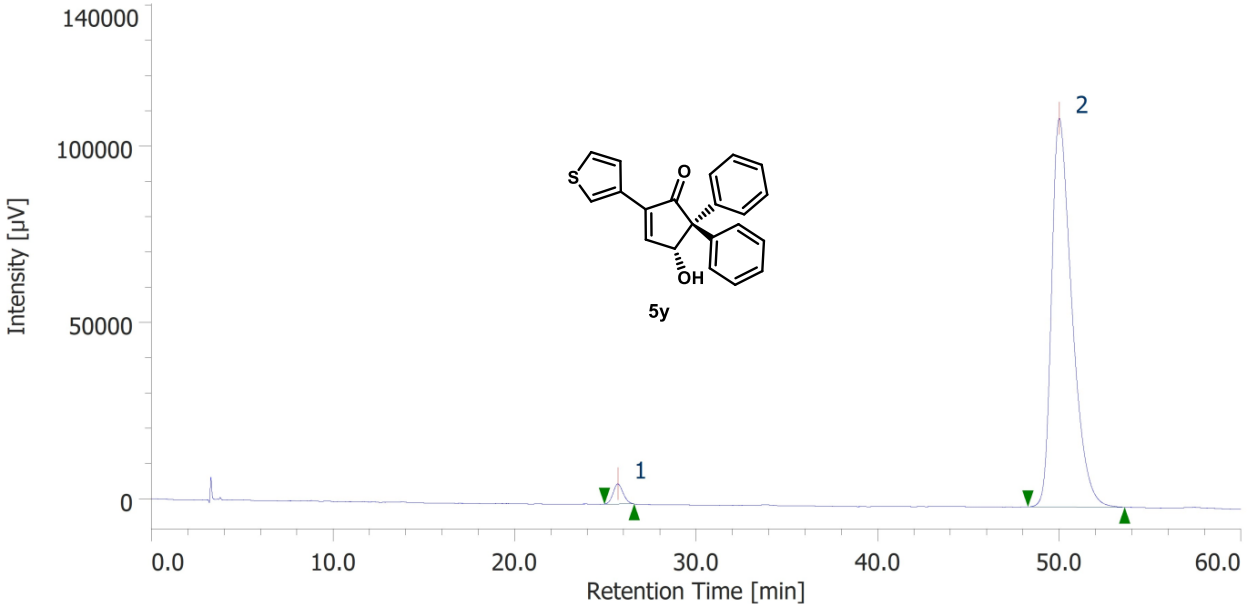
^{13}C-NMR
(75 MHz, $CDCl_3$)



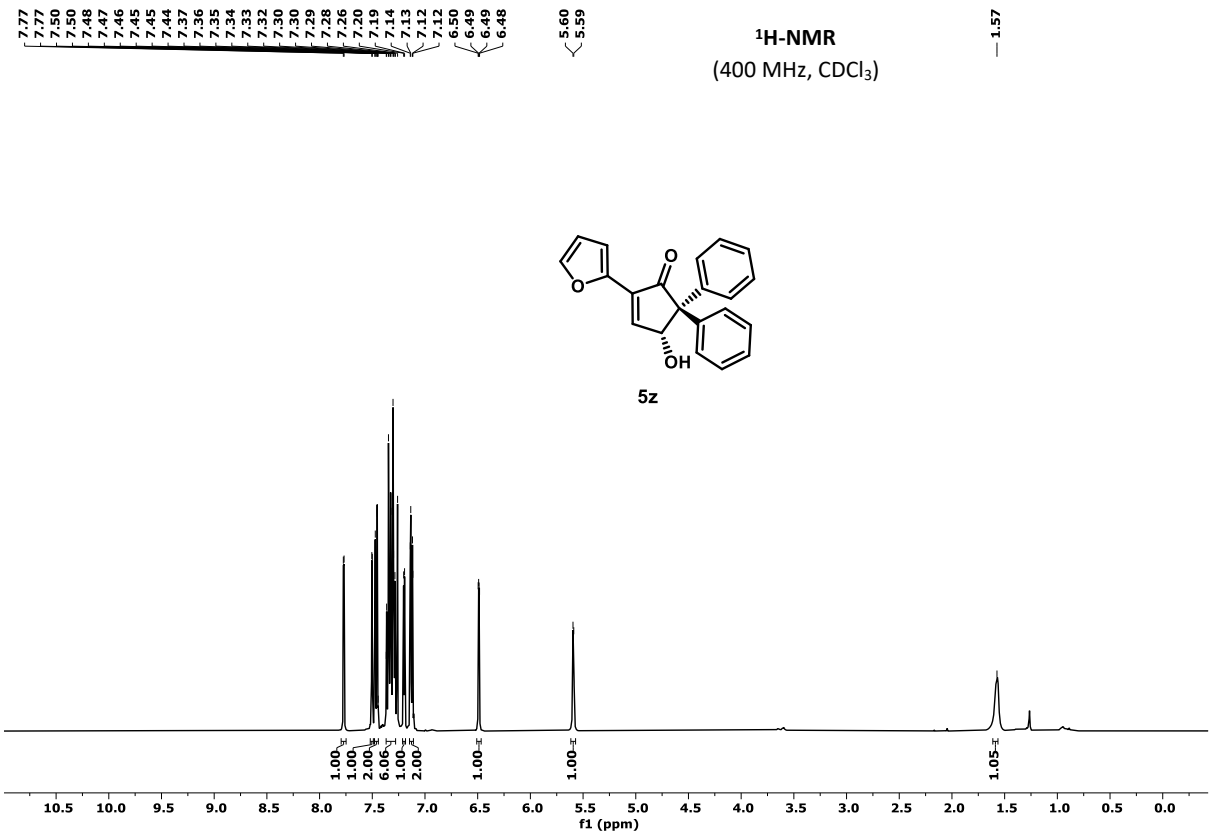


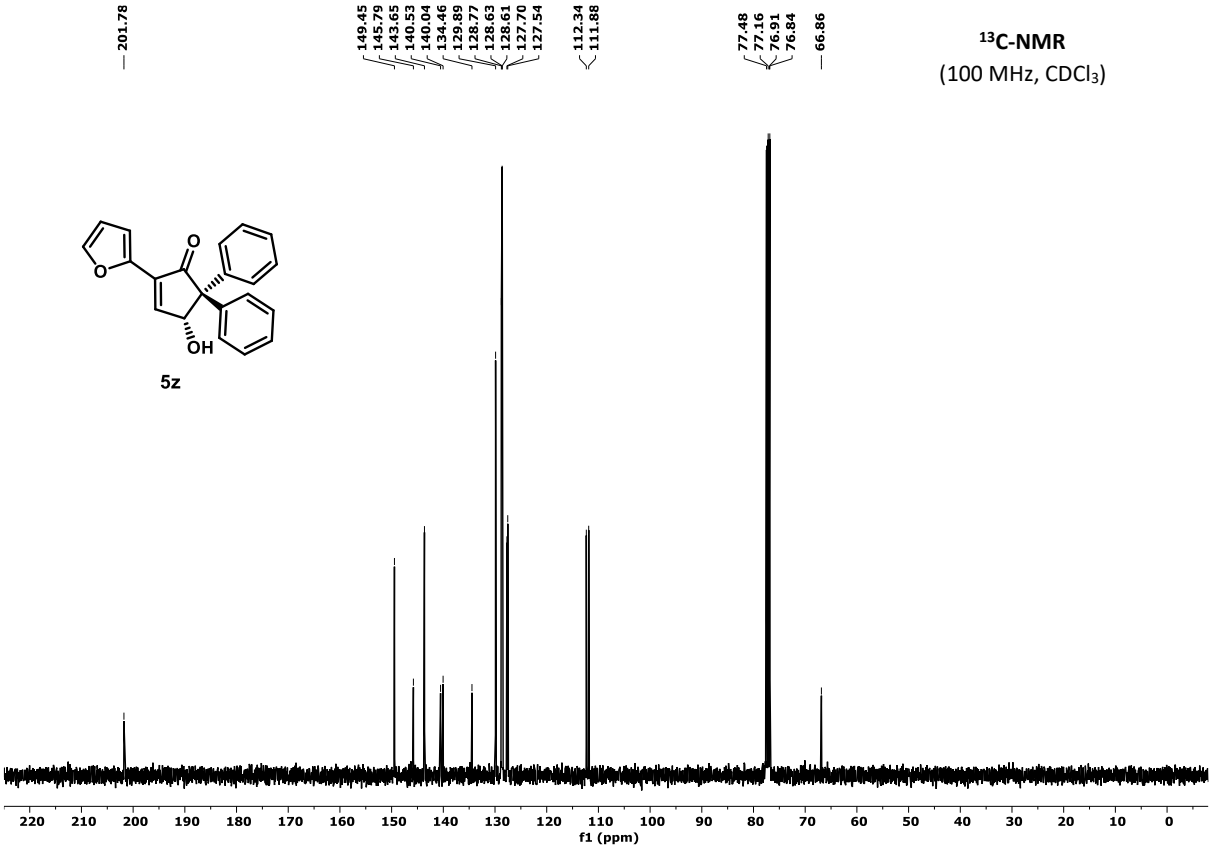
#	Peak Name	CH	tR [min]	Area [μV·sec]	Height [μV]	Area%	Height%	Quantity	NTP	Resolution	Symmetry Factor	Warning
1	Unknown	10	25.760	4943447	120691	50.124	65.800	N/A	9701	16.580	1.306	
2	Unknown	10	51.193	4918910	62730	49.876	34.200	N/A	10175	N/A	1.377	

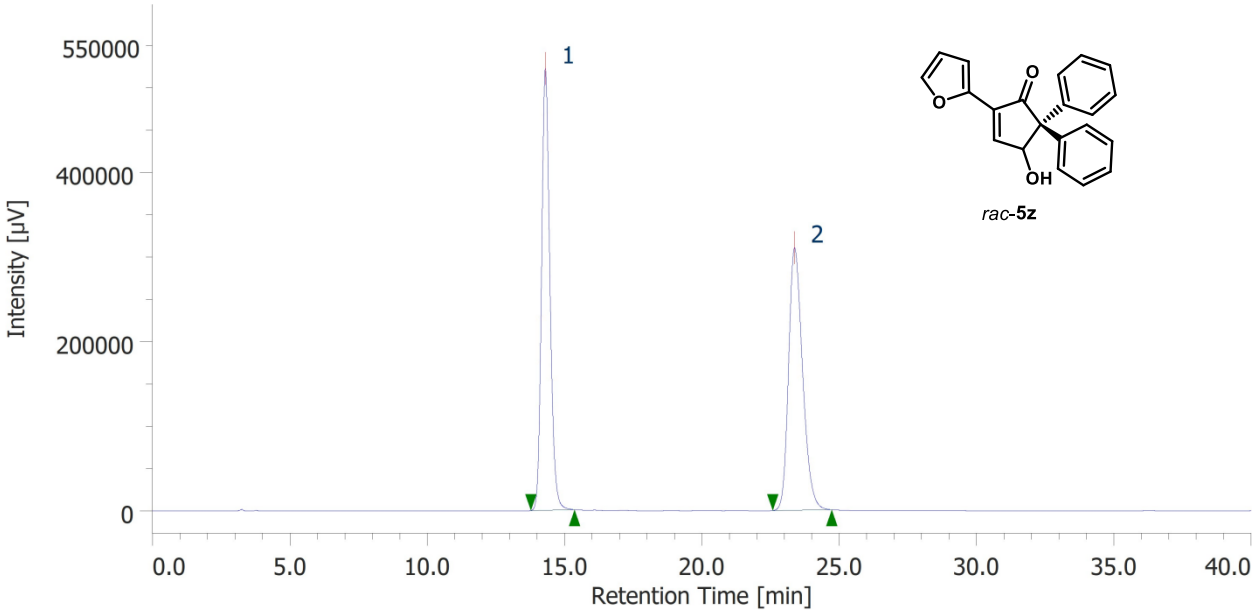
Daicel Chiralpak IA column (90:10 *n*-Hexane/*i*-PrOH, 1.0 mL/min, 230 nm)



#	Peak Name	CH	tR [min]	Area [μV·sec]	Height [μV]	Area%	Height%	Quantity	NTP	Resolution	Symmetry Factor	Warning
1	Unknown	10	25.680	218591	5706	2.486	4.926	N/A	10412	16.209	1.117	
2	Unknown	10	49.993	8573847	110119	97.514	95.074	N/A	9984	N/A	1.492	

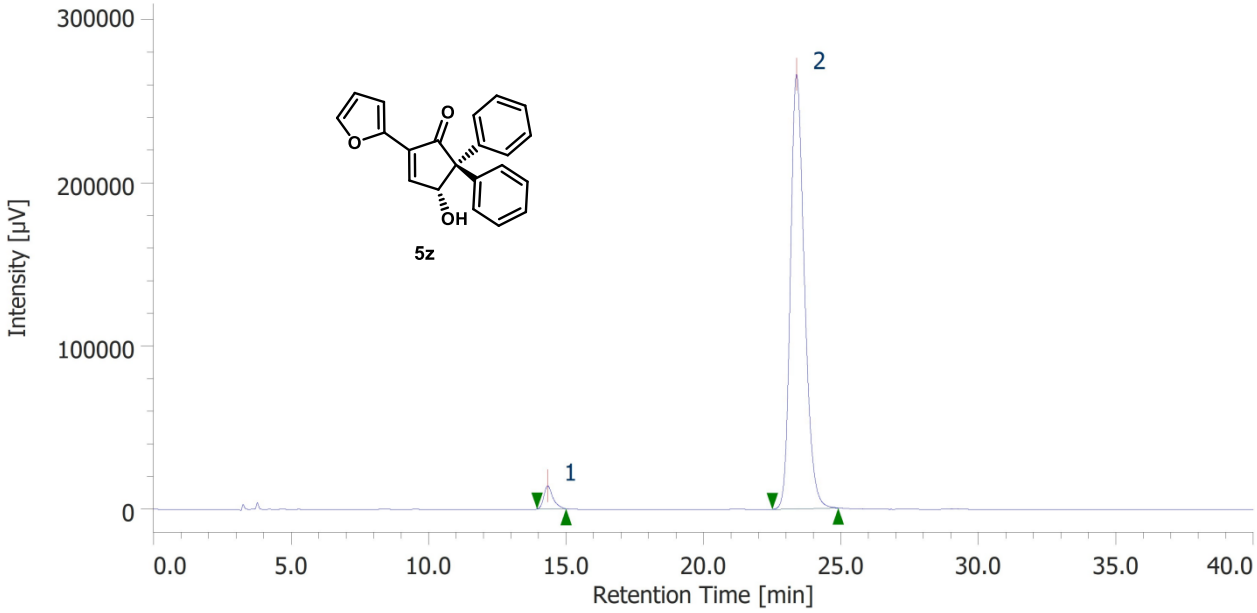

7.77
7.77
7.50
7.50
7.48
7.47
7.46
7.45
7.45
7.44
7.37
7.36
7.35
7.34
7.33
7.32
7.30
7.30
7.29
7.28
7.26
7.20
7.19
7.14
7.13
7.12
7.12
6.50
6.49
6.49
6.48
5.60
5.59
1.57
1H-NMR
(400 MHz, CDCl3)
O
O
OH
5z
1.00
1.00
2.00
6.06
1.00
2.00
1.00
1.00
1.05
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


201.78
149.45
145.79
143.65
140.53
140.04
134.46
129.89
128.77
128.63
128.61
127.70
127.54
112.34
111.88
77.48
77.16
76.91
76.84
66.86
13C-NMR
(100 MHz, CDCl3)
O
O
OH
5z
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

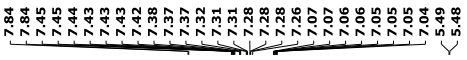


#	Peak Name	CH	tR [min]	Area [μV·sec]	Height [μV]	Area%	Height%	Quantity	NTP	Resolution	Symmetry Factor	Warning
1	Unknown	11	14.300	11016215	521509	50.074	62.719	N/A	11089	12.440	1.179	
2	Unknown	11	23.373	10983653	309992	49.926	37.281	N/A	10339	N/A	1.264	

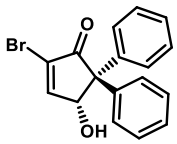
Daicel Chiralpak IA column (90:10 *n*-Hexane/*i*-PrOH, 1.0 mL/min, 240 nm)



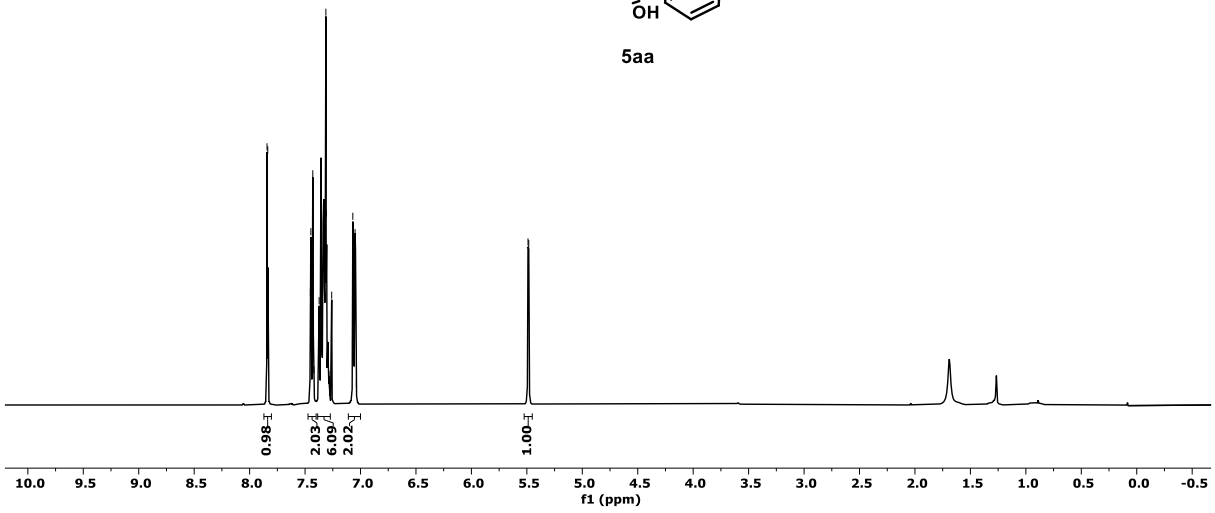
#	Peak Name	CH	tR [min]	Area [μV·sec]	Height [μV]	Area%	Height%	Quantity	NTP	Resolution	Symmetry Factor	Warning
1	Unknown	11	14.333	325943	14147	3.351	5.049	N/A	10001	12.198	1.359	
2	Unknown	11	23.380	9400695	266063	96.649	94.951	N/A	10469	N/A	1.254	



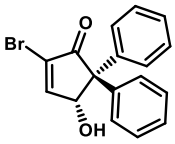
^{1}H-NMR
(400 MHz, $CDCl_3$)



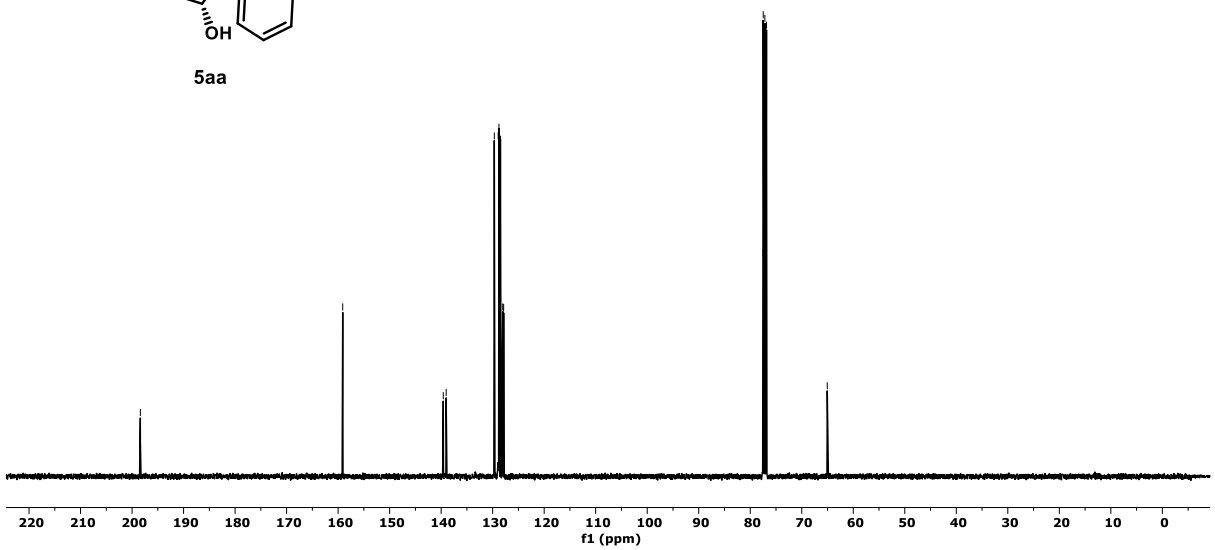
5aa

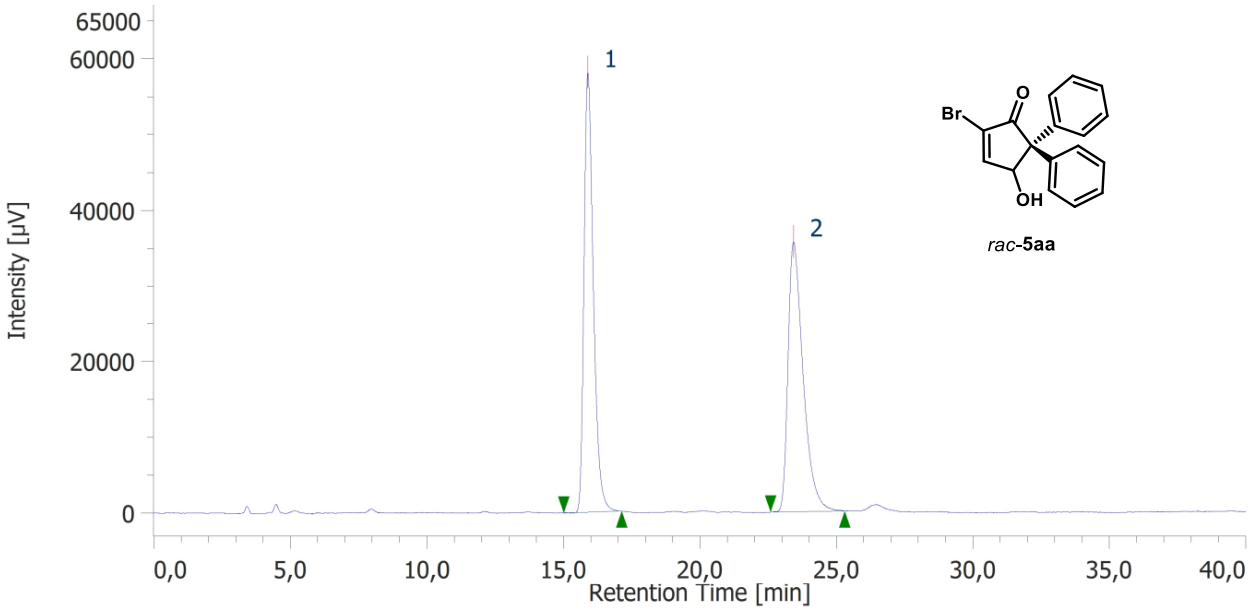


^{13}C-NMR
(100 MHz, $CDCl_3$)



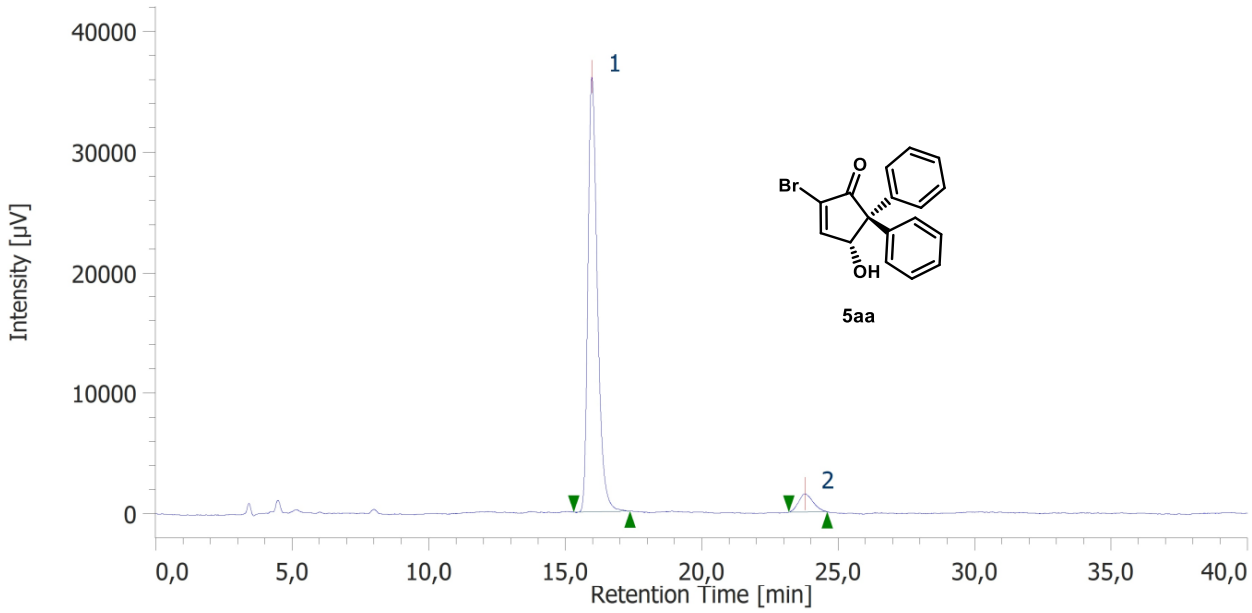
5aa





#	Peak Name	CH	tR [min]	Area [μV·sec]	Height [μV]	Area%	Height%	Quantity	NTP	Resolution	Symmetry Factor	Warning
1	Unknown	12	15,890	1380455	58034	50,217	61,927	N/A	10938	9,546	1,393	
2	Unknown	12	23,423	1368538	35679	49,783	38,073	N/A	9239	N/A	1,624	

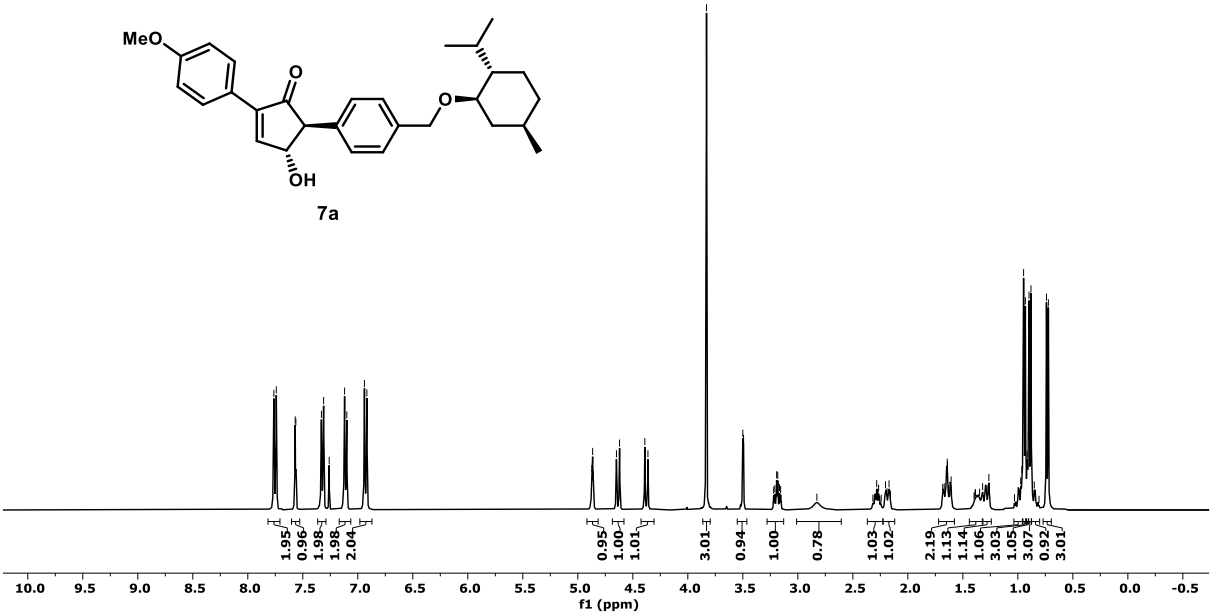
Daicel Chiralpak IF column (95:5 *n*-Hexane/*i*-PrOH, 1.0 mL/min, 245 nm)



#	Peak Name	CH	tR [min]	Area [μV·sec]	Height [μV]	Area%	Height%	Quantity	NTP	Resolution	Symmetry Factor	Warning
1	Unknown	12	15,970	864694	36059	93,981	96,024	N/A	10927	9,845	1,372	
2	Unknown	12	23,773	55376	1493	6,019	3,976	N/A	9449	N/A	1,174	

^{1}H-NMR

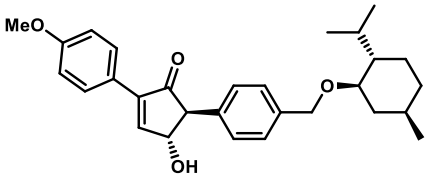
(400 MHz, $CDCl_3$)



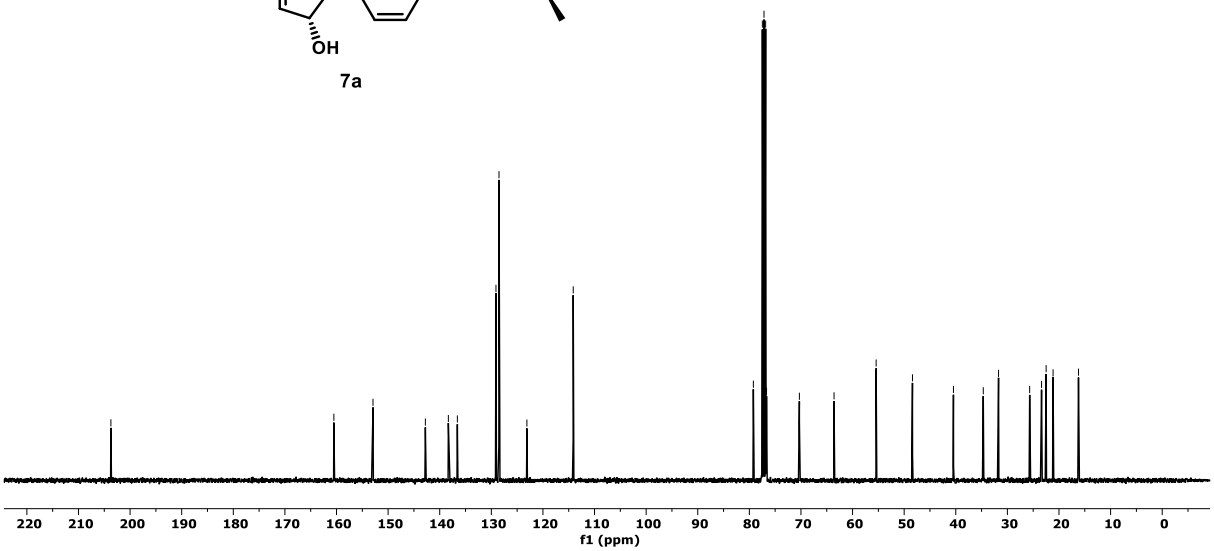
7a

^{13}C-NMR

(100 MHz, $CDCl_3$)

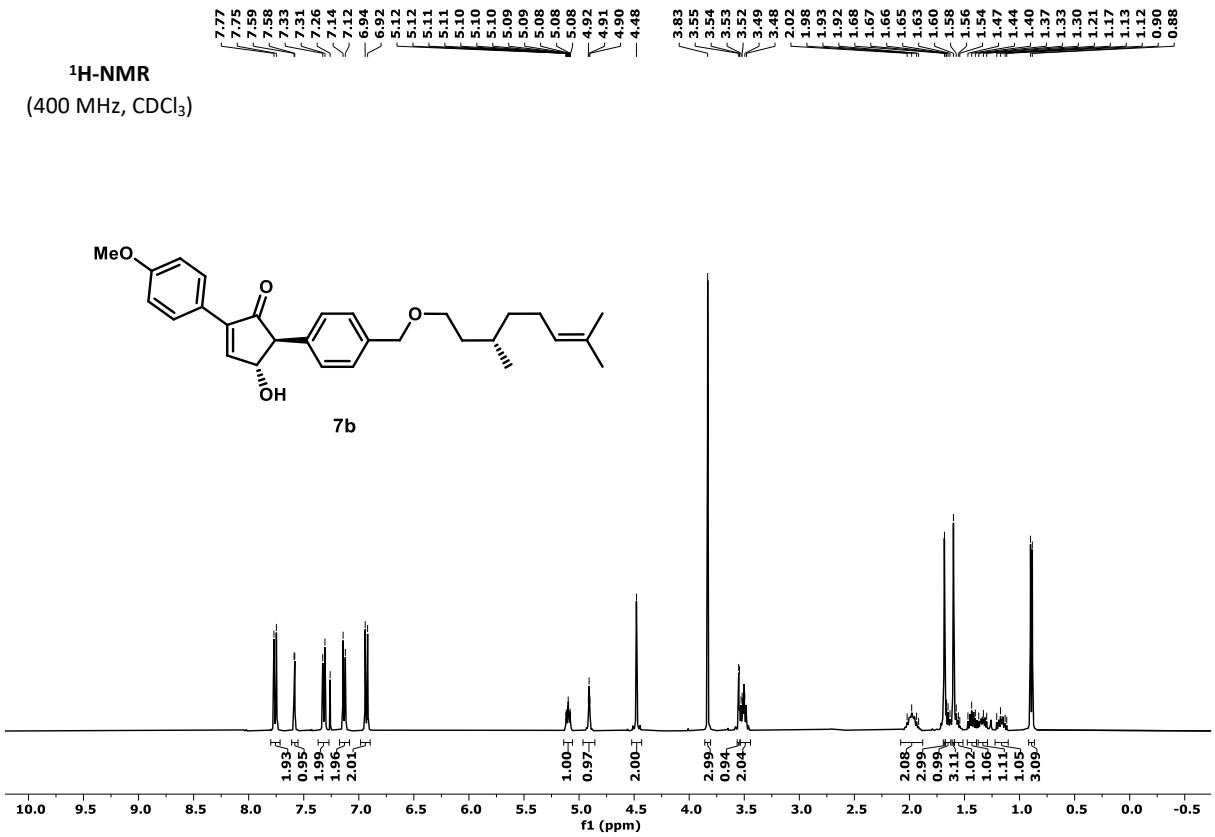


7a



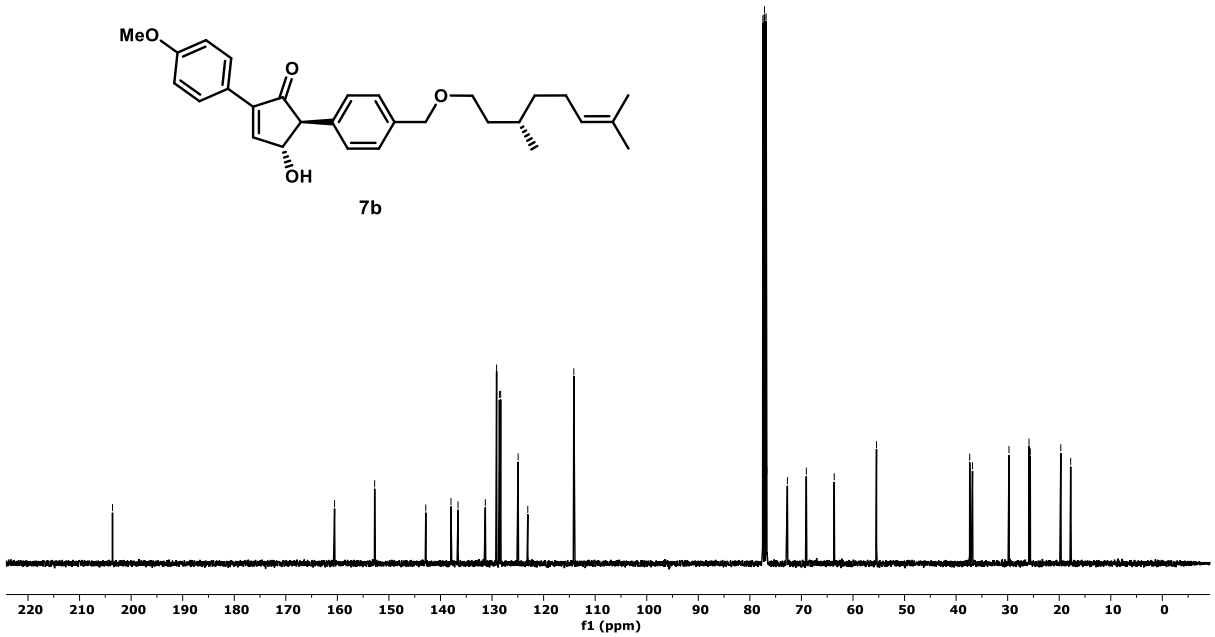
^{1}H-NMR

(400 MHz, $CDCl_3$)

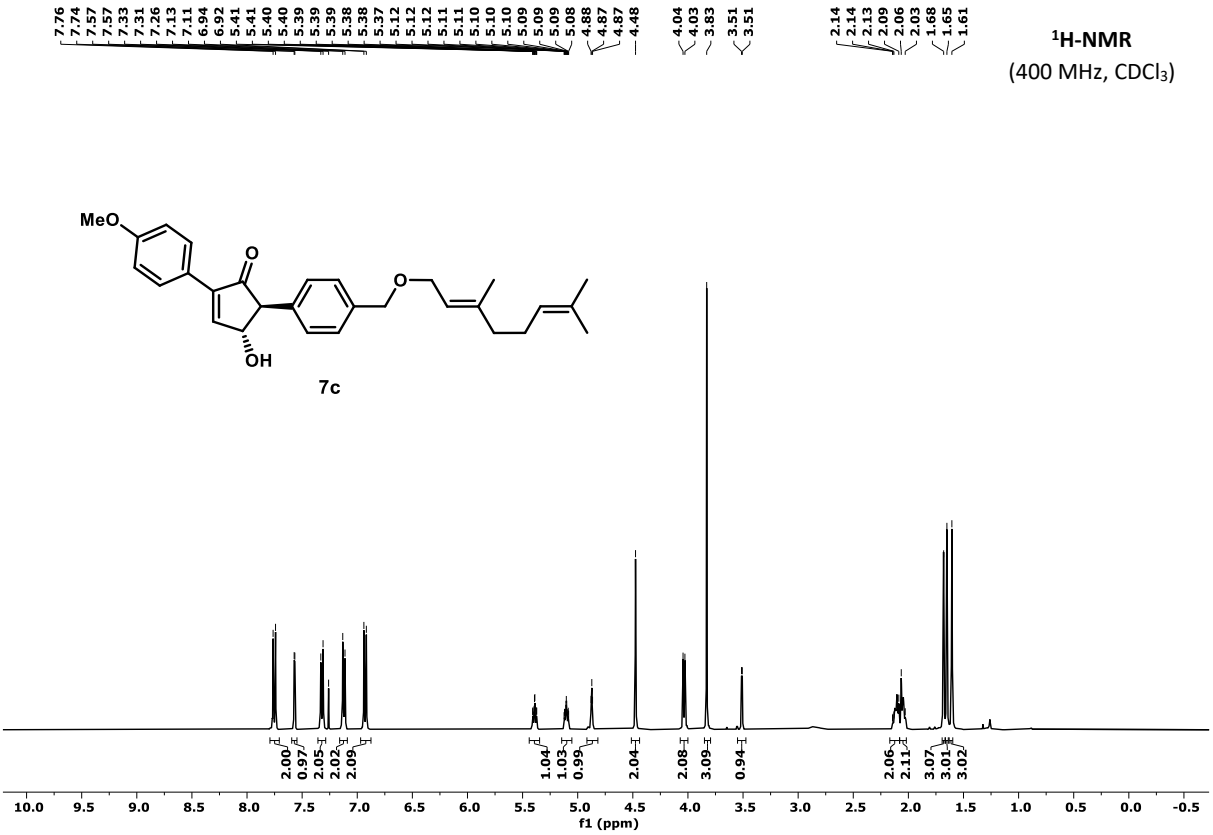


^{13}C-NMR

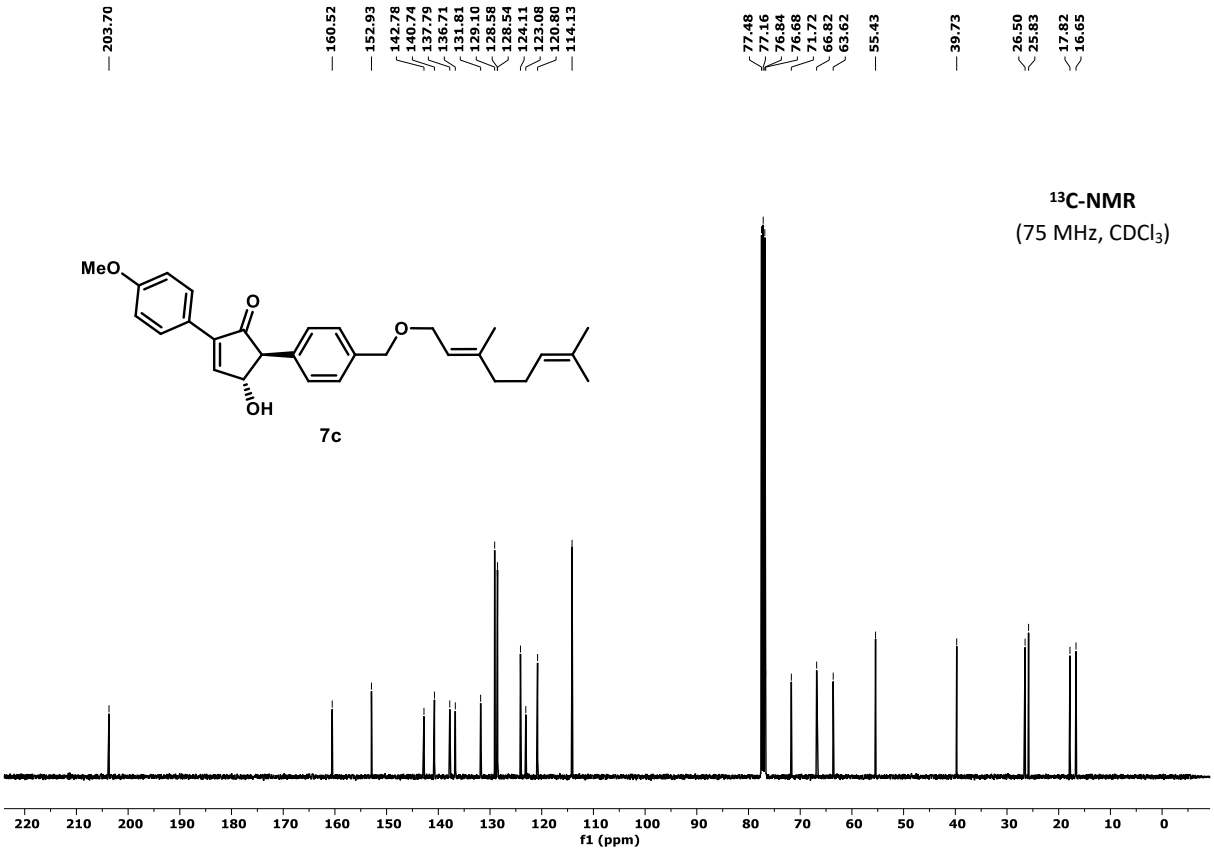
(100 MHz, $CDCl_3$)

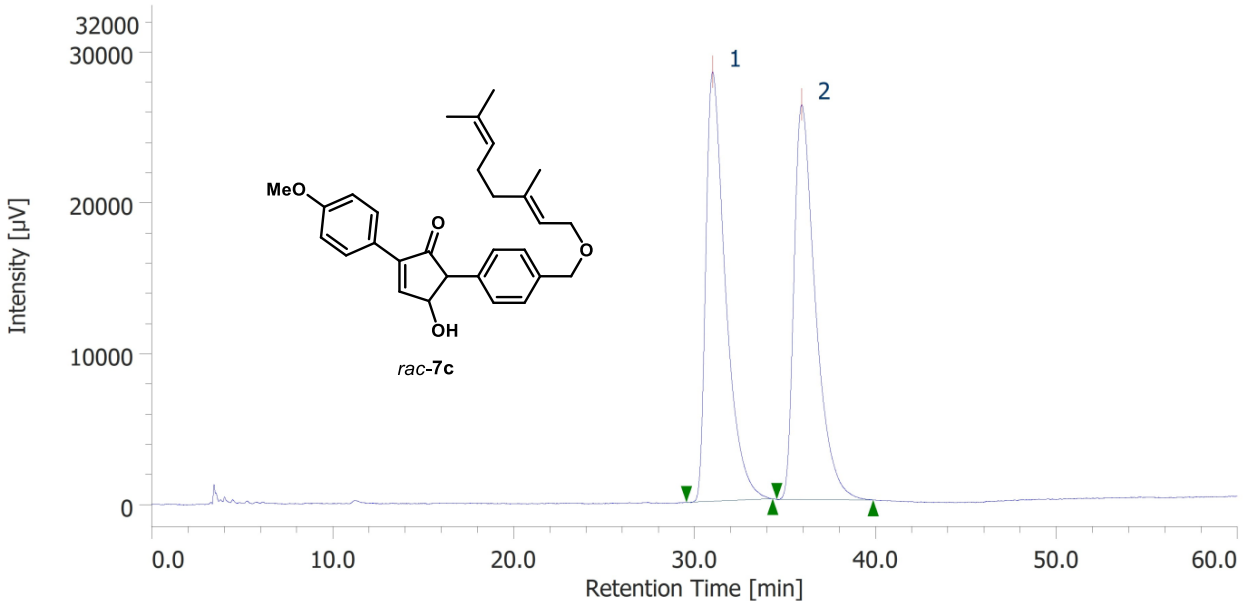


^{1}H-NMR
(400 MHz, $CDCl_3$)



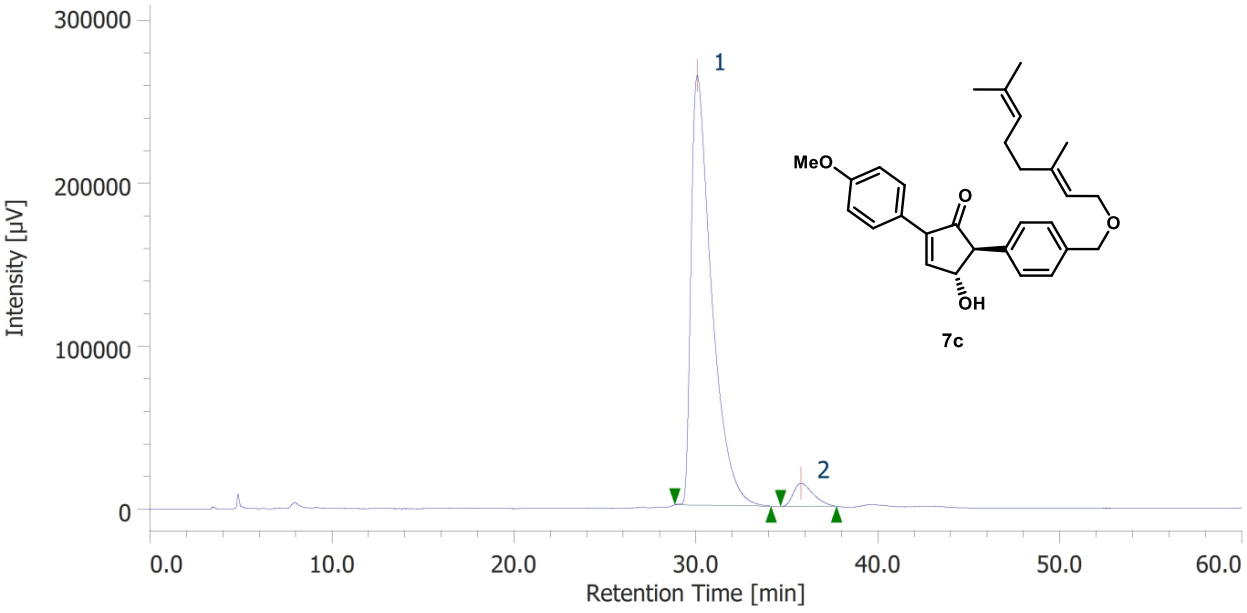
^{13}C-NMR
(75 MHz, $CDCl_3$)





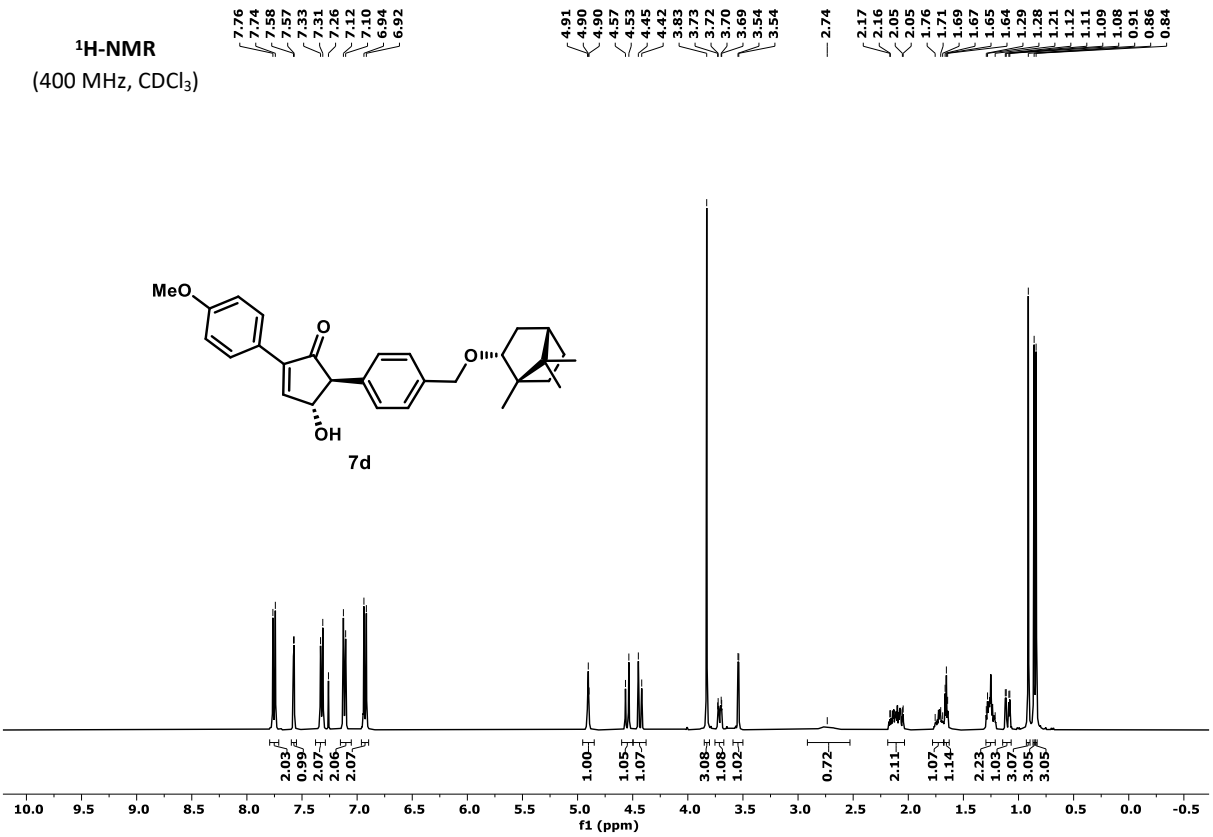
#	Peak Name	CH	tR [min]	Area [μV·sec]	Height [μV]	Area%	Height%	Quantity	NTP	Resolution	Symmetry Factor	Warning
1	Unknown	11	30.993	2145788	28454	49.951	52.093	N/A	4265	2.488	1.820	
2	Unknown	11	35.923	2149989	26167	50.049	47.907	N/A	4795	N/A	1.678	

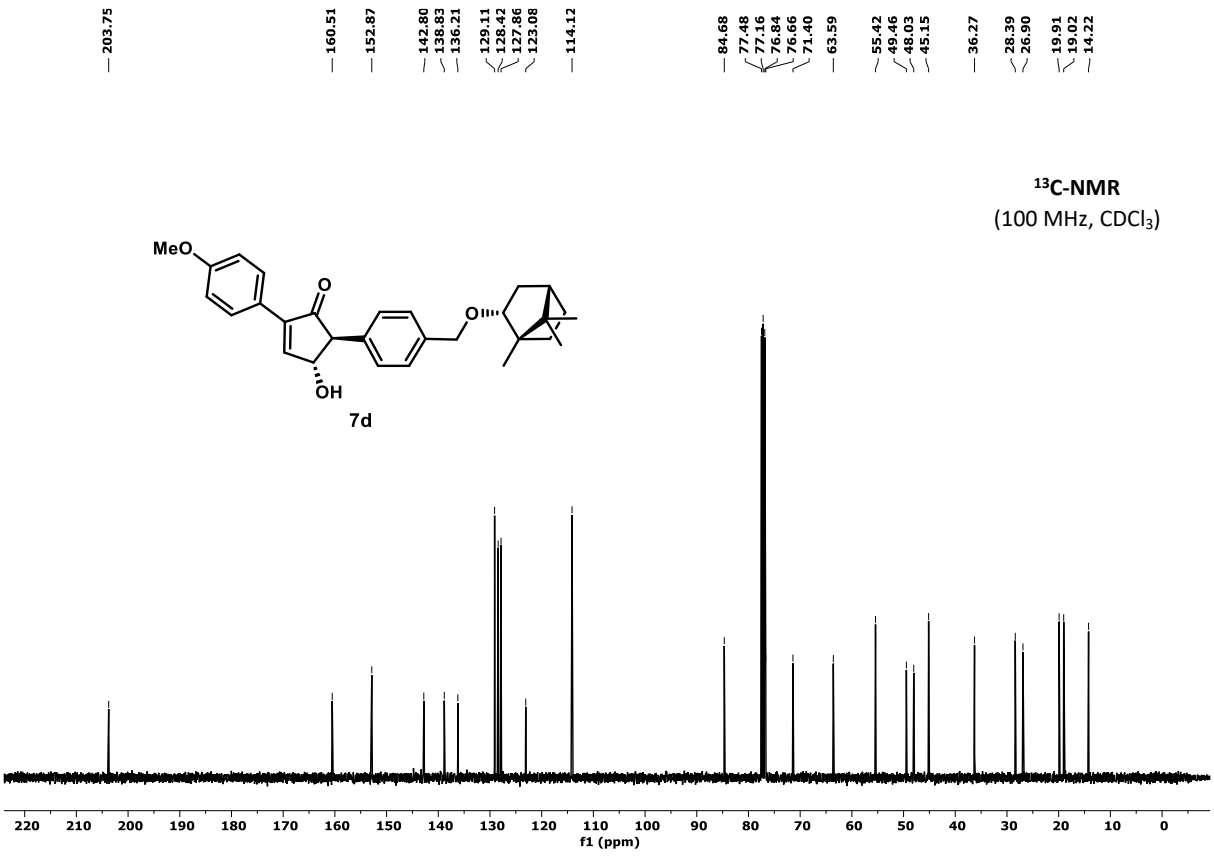
Daicel Chiralpak IB column (90:10 *n*-Hexane/*i*-PrOH, 1.0 mL/min, 245 nm)



#	Peak Name	CH	tR [min]	Area [μV·sec]	Height [μV]	Area%	Height%	Quantity	NTP	Resolution	Symmetry Factor	Warning
1	Unknown	11	30.067	20643434	263673	95.020	94.884	N/A	3744	2.873	2.185	
2	Unknown	11	35.763	1081821	14216	4.980	5.116	N/A	5064	N/A	1.474	

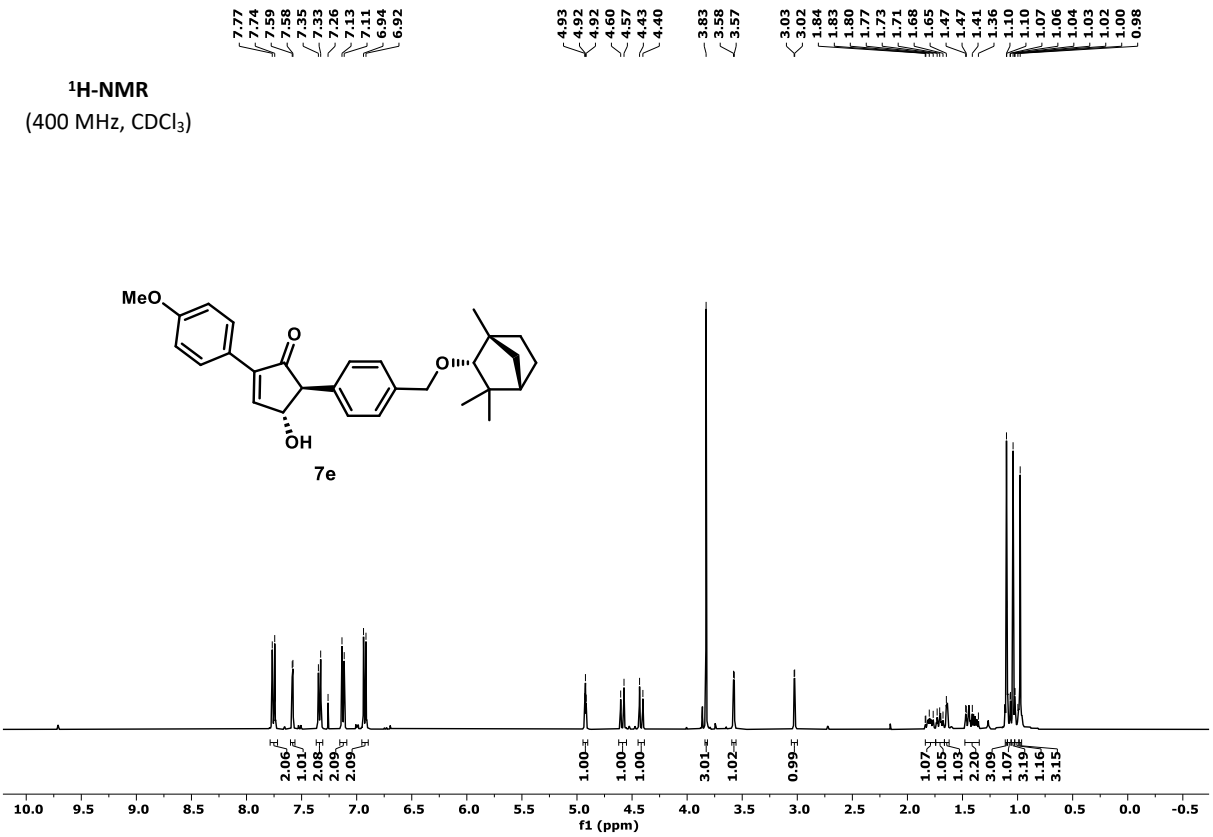
^{1}H-NMR
(400 MHz, $CDCl_3$)



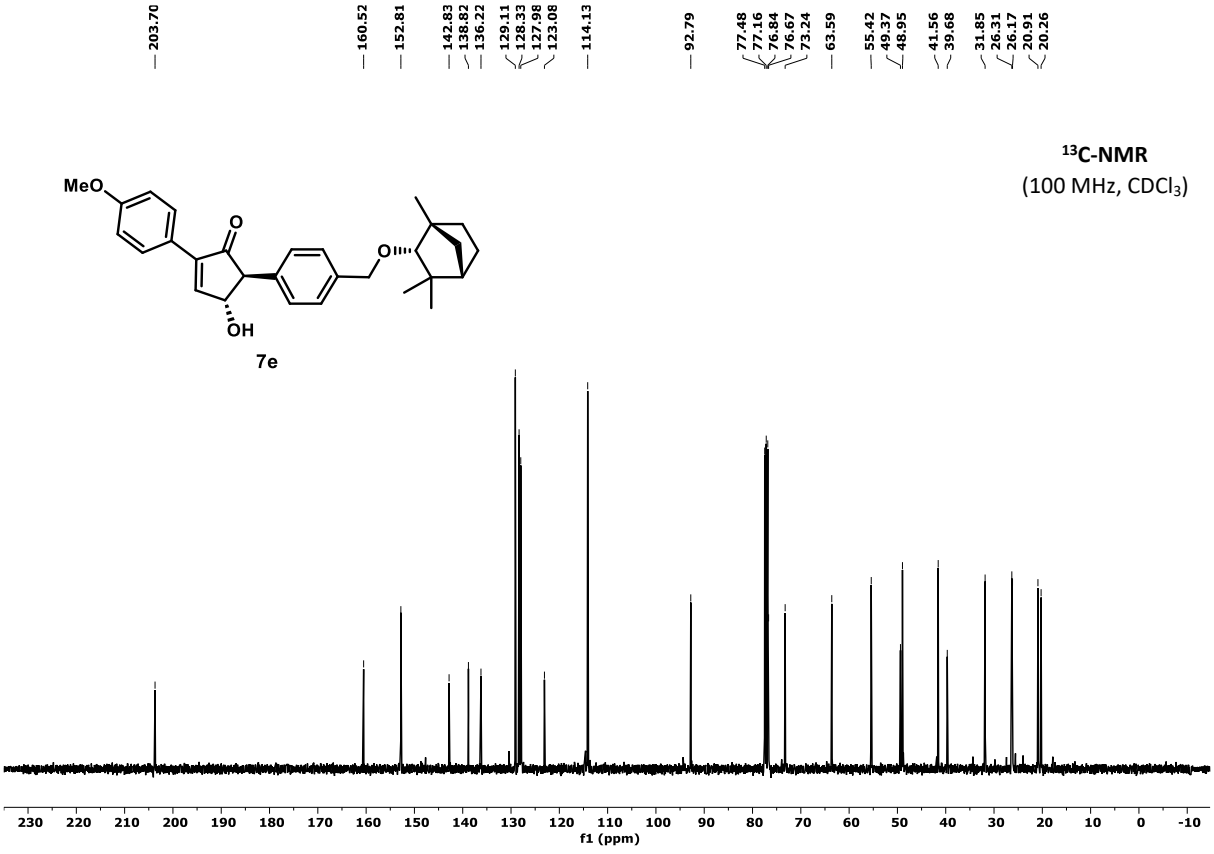


^{13}C-NMR
(100 MHz, $CDCl_3$)

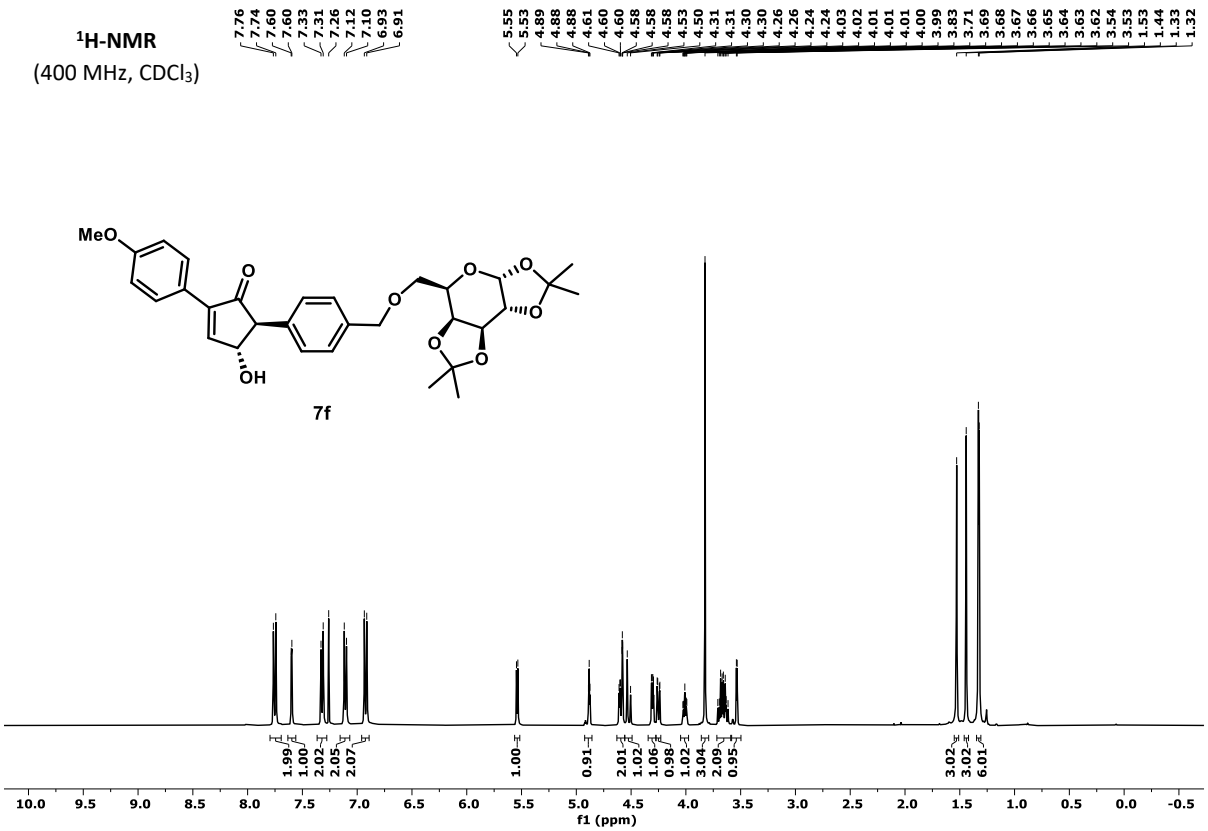
^{1}H-NMR
(400 MHz, $CDCl_3$)



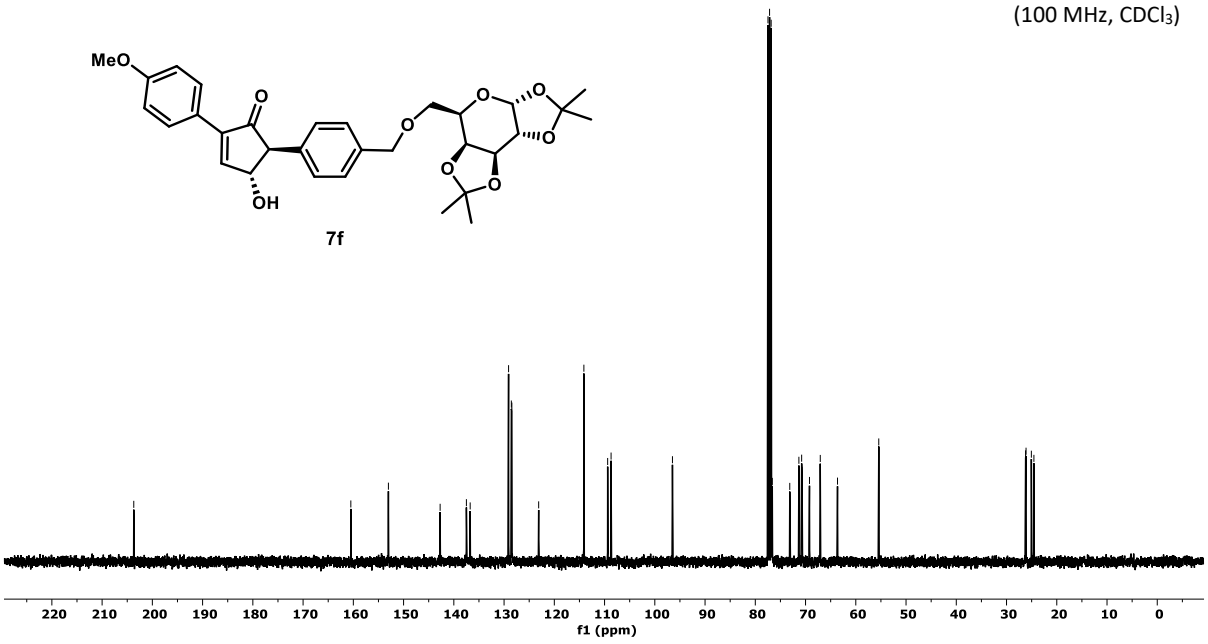
^{13}C-NMR
(100 MHz, $CDCl_3$)

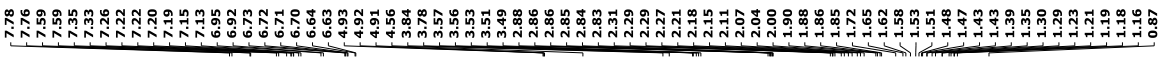


^{1}H-NMR
(400 MHz, $CDCl_3$)



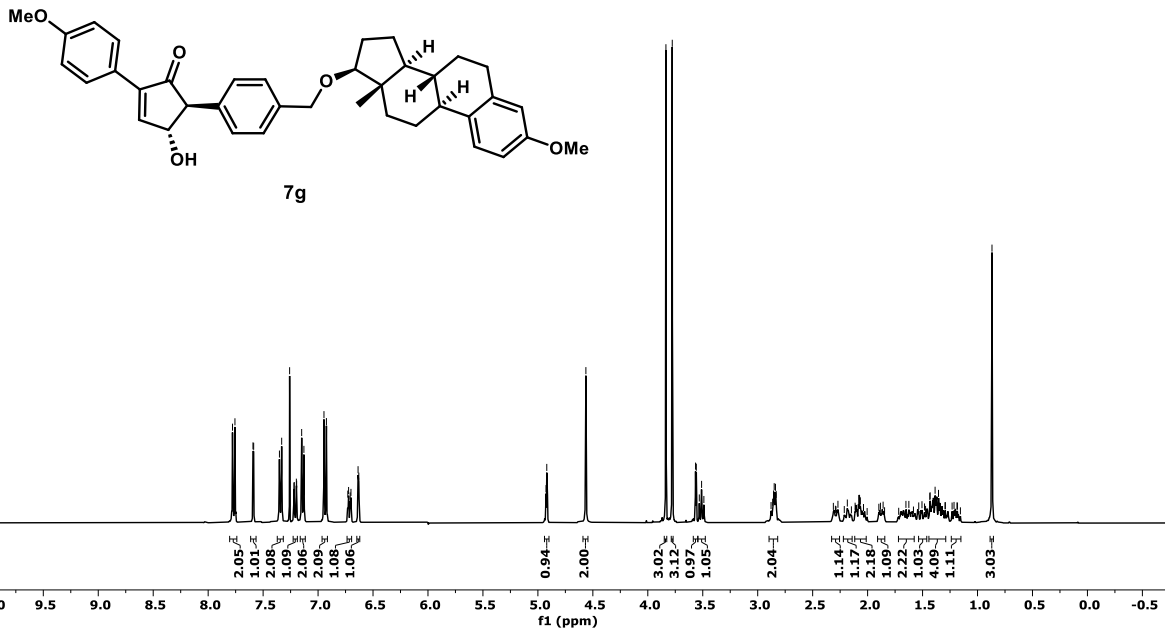
^{13}C-NMR
(100 MHz, $CDCl_3$)





^{1}H-NMR

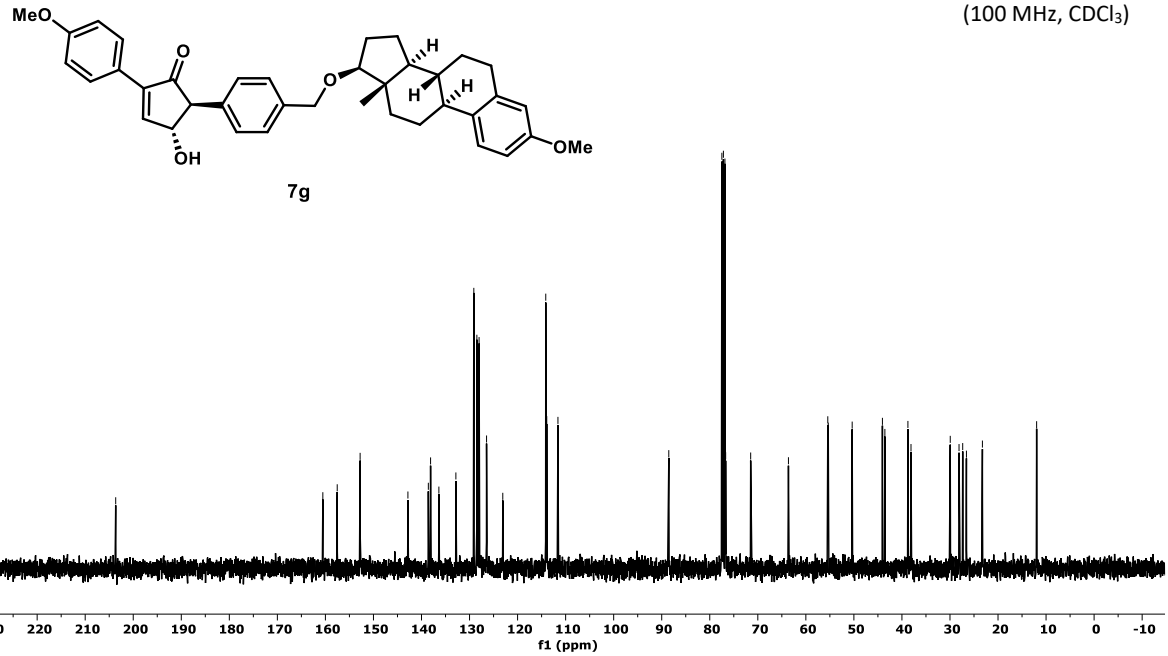
(400 MHz, $CDCl_3$)



7g

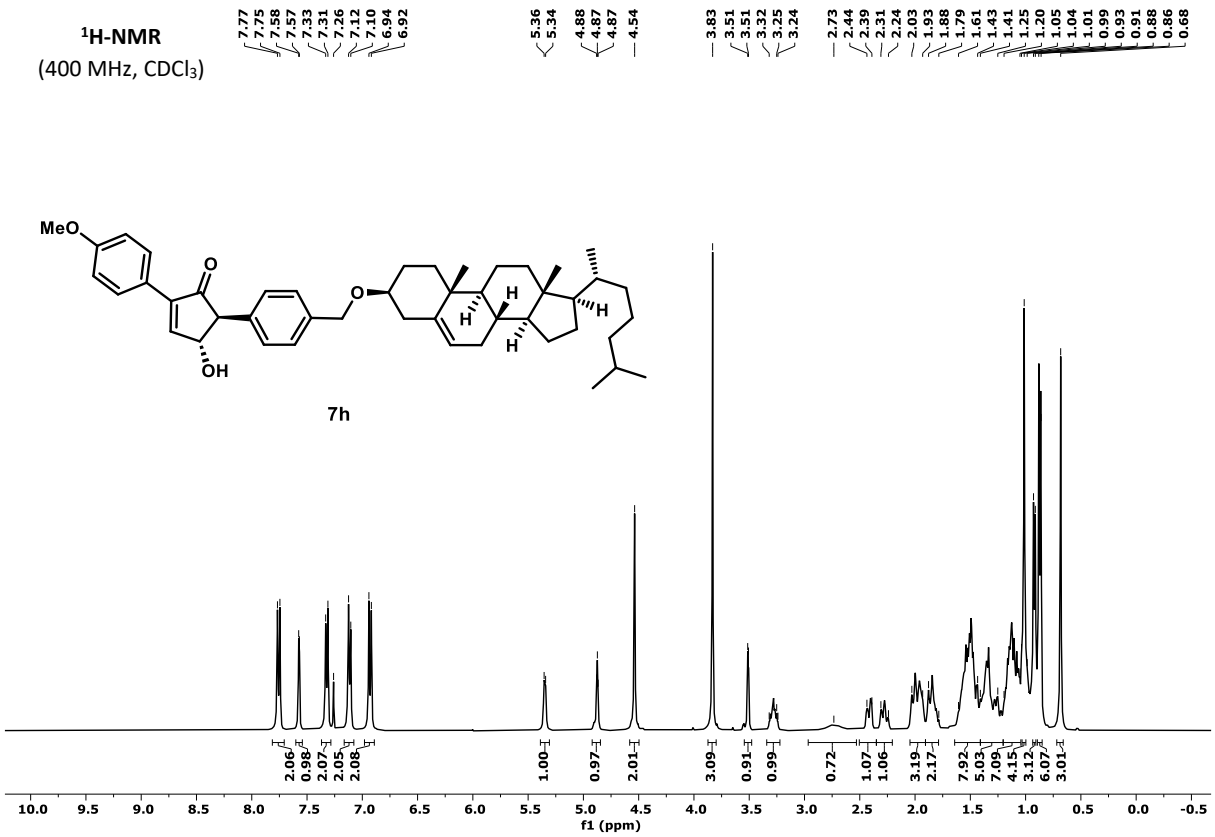
^{13}C-NMR

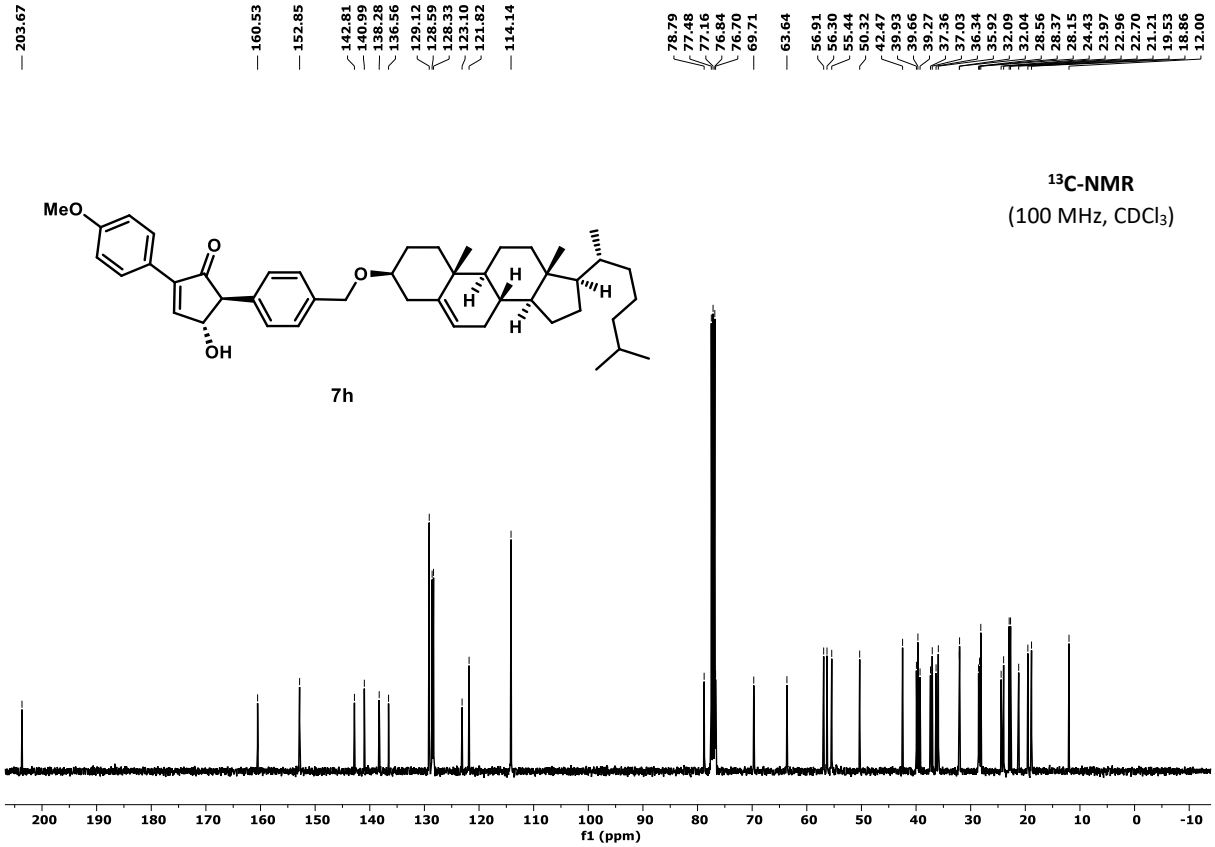
(100 MHz, $CDCl_3$)



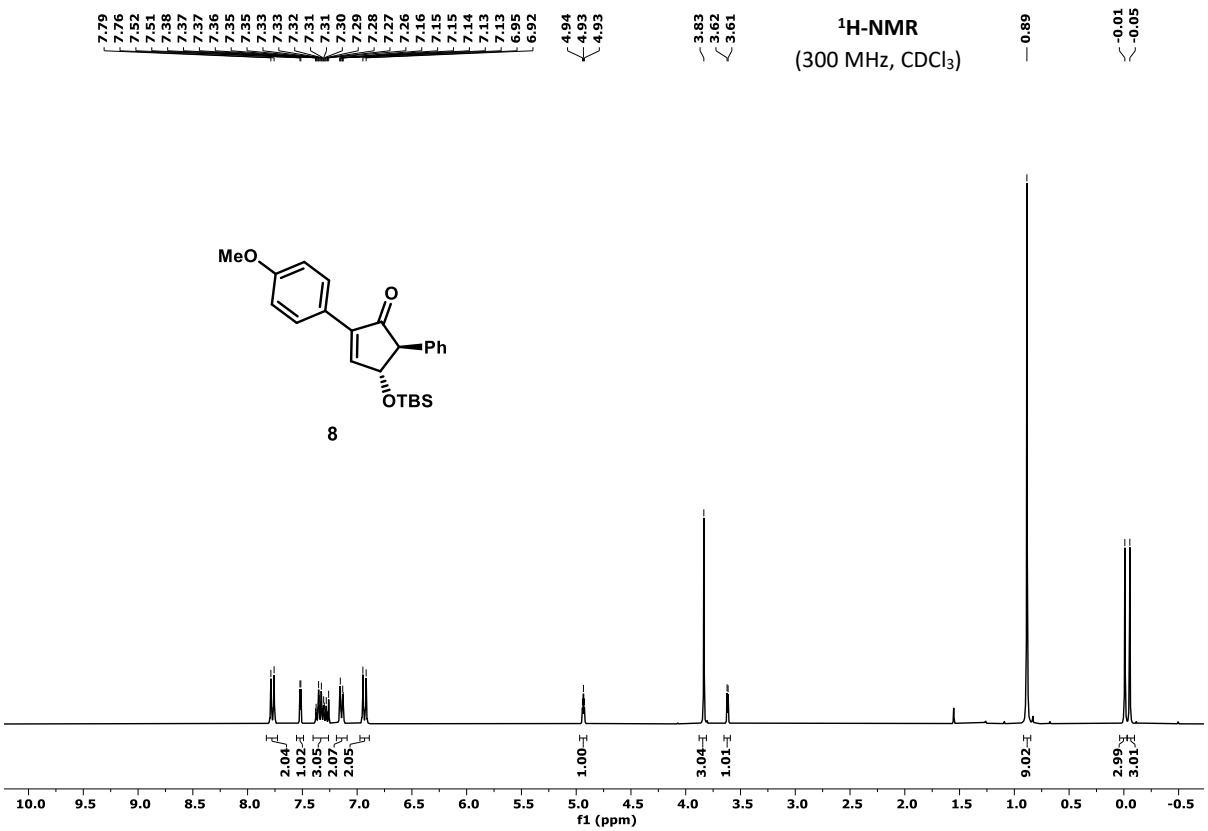
7g

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





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


7.79
7.76
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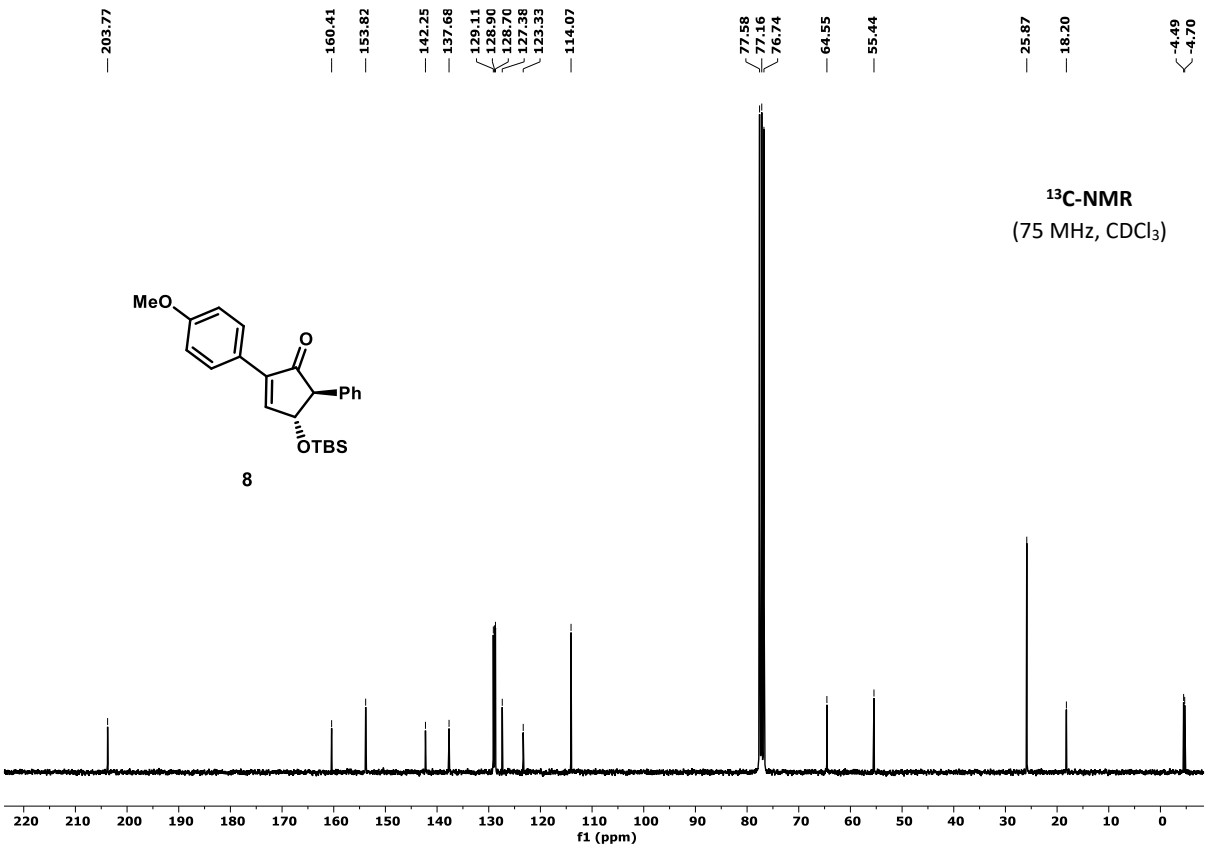
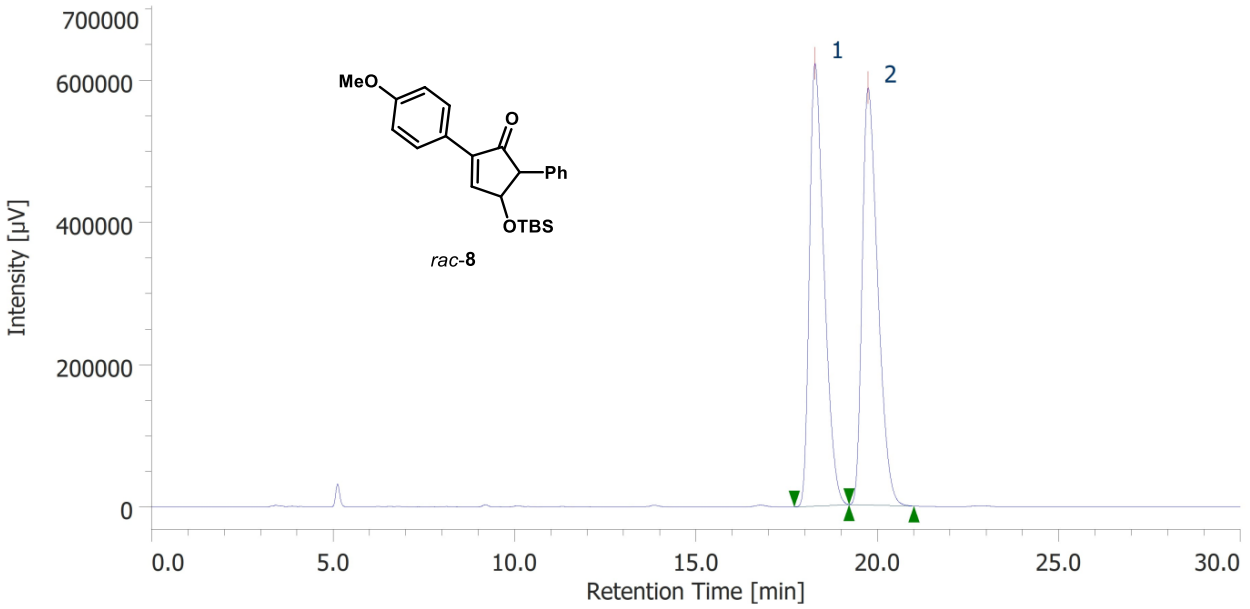
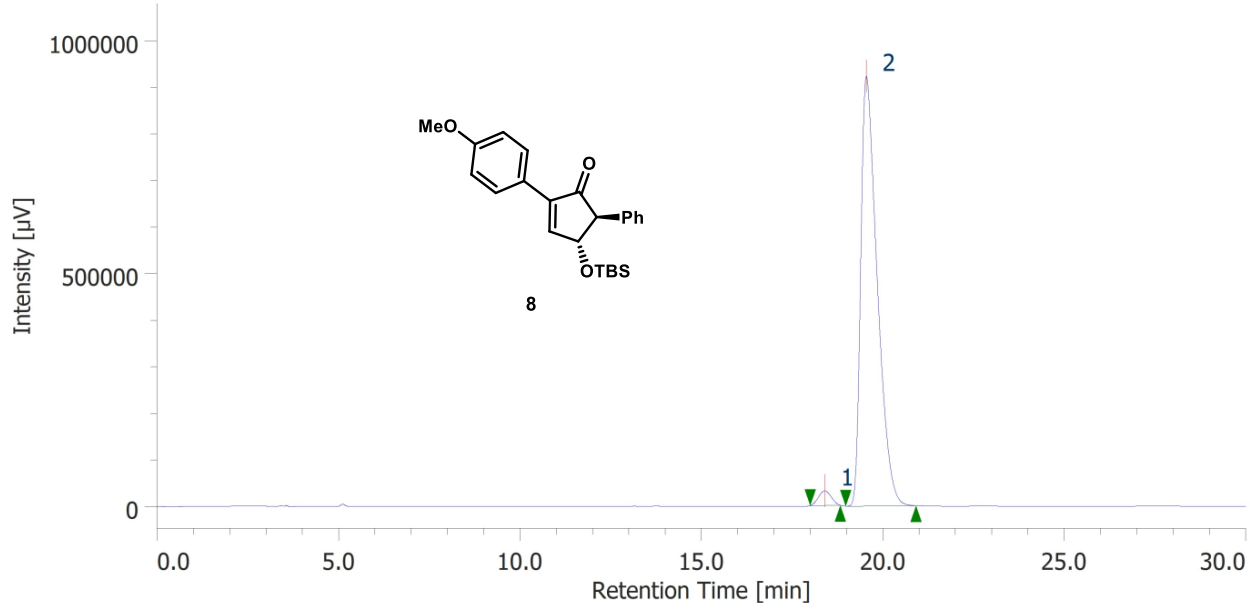
7.51
7.38
7.37
7.37
7.36
7.35
7.35
7.33
7.33
7.32
7.31
7.31
7.30
7.29
7.28
7.27
7.26
7.16
7.15
7.15
7.14
7.13
7.13
6.95
6.92
4.94
4.93
4.93
3.83
3.62
3.61
0.89
-0.01
-0.05
1H-NMR
(300 MHz, CDCl3)
MeO
O
Ph
OTBS
8
2.04
1.02
3.05
2.07
2.05
1.00
3.04
1.01
9.02
2.99
3.01
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 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
f1 (ppm)


203.77
160.41
153.82
142.25
137.68
129.11
128.90
128.70
127.38
123.33
114.07
77.58
77.16
76.74
64.55
55.44
25.87
18.20
-4.49
-4.70
13C-NMR
(75 MHz, CDCl3)
MeO
O
Ph
OTBS
8
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)



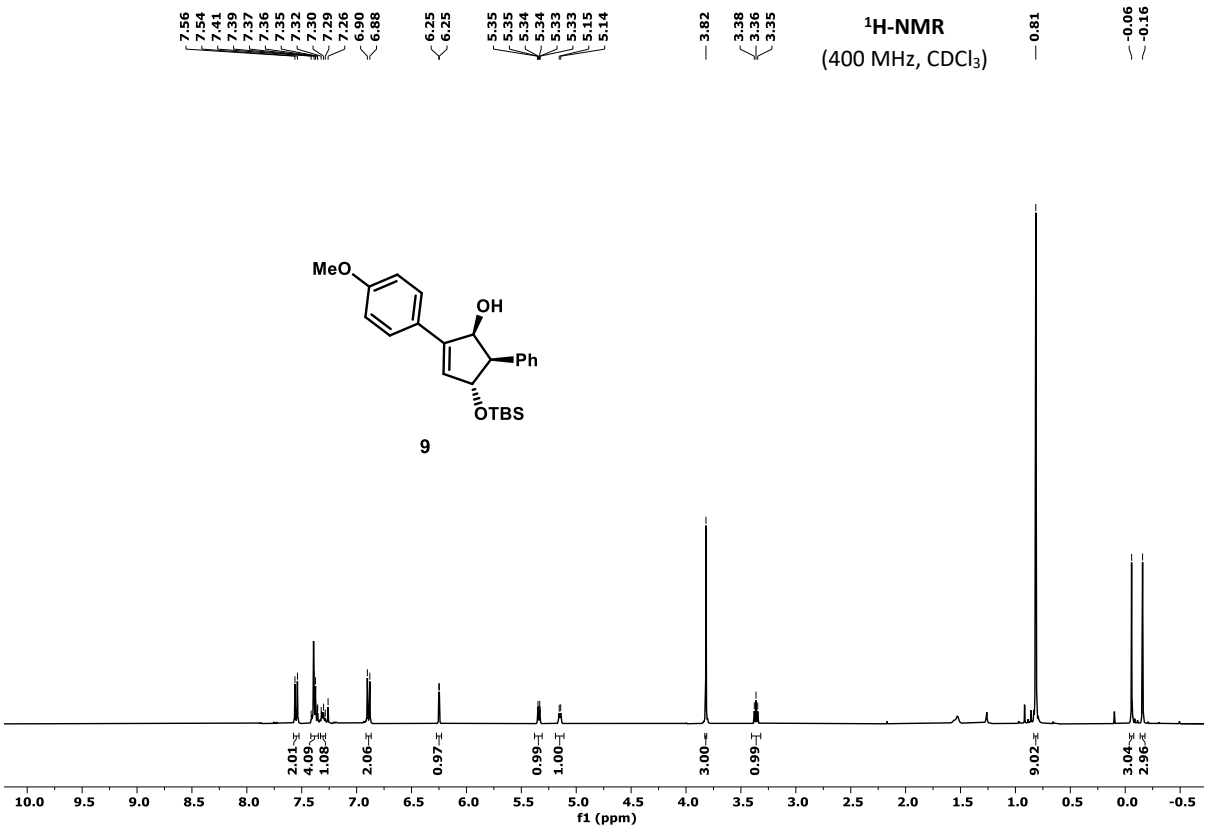
#	Peak Name	CH	tR [min]	Area [μV·sec]	Height [μV]	Area%	Height%	Quantity	NTP	Resolution	Symmetry Factor	Warning
1	Unknown	11	18.277	17433075	621495	49.936	51.466	N/A	9877	1.933	1.462	
2	Unknown	11	19.740	17477921	586100	50.064	48.534	N/A	10174	N/A	1.462	

Daicel Chiralpak IE column (95:5 *n*-Hexane/*i*-PrOH, 1.0 mL/min, 245 nm)



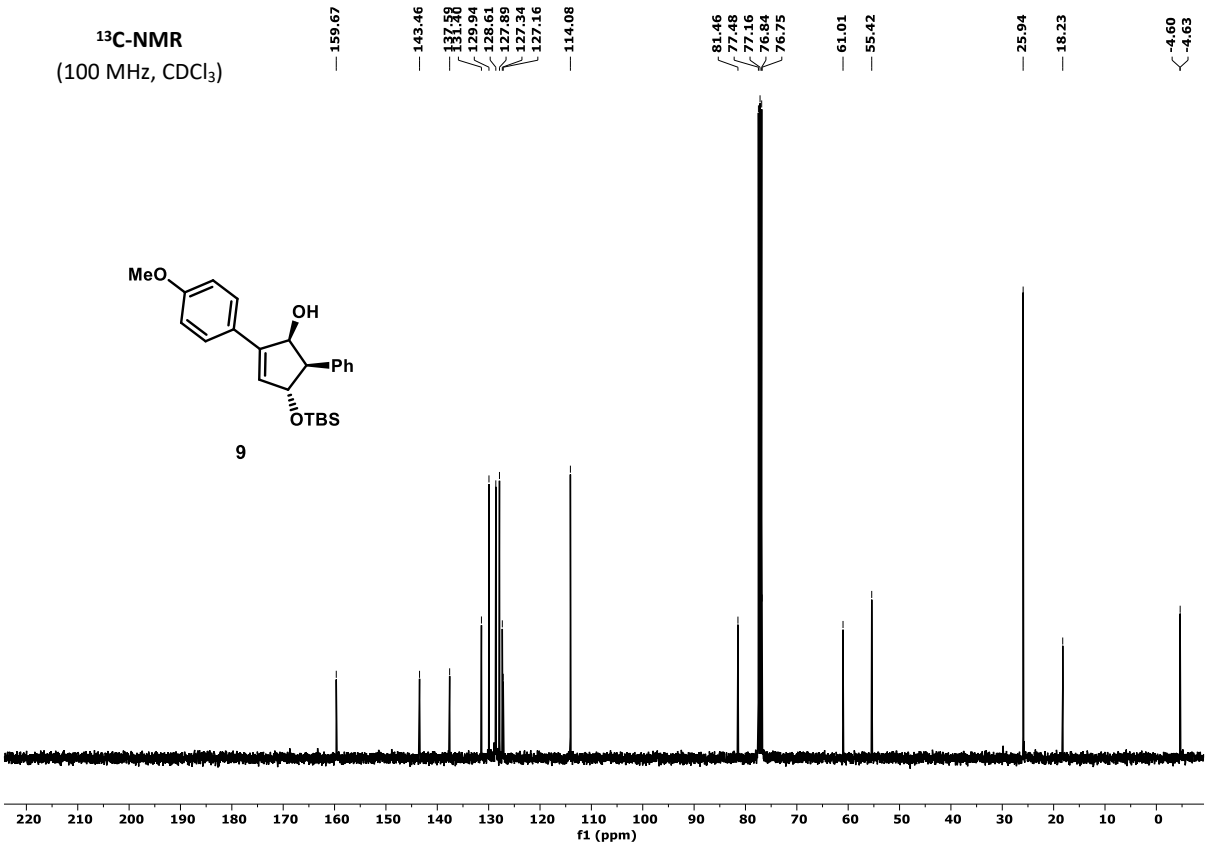
#	Peak Name	CH	tR [min]	Area [μV·sec]	Height [μV]	Area%	Height%	Quantity	NTP	Resolution	Symmetry Factor	Warning
1	Unknown	13	18.393	758922	31449	2.551	3.296	N/A	12312	1.551	1.041	
2	Unknown	13	19.540	28990974	922806	97.449	96.704	N/A	9090	N/A	1.683	

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



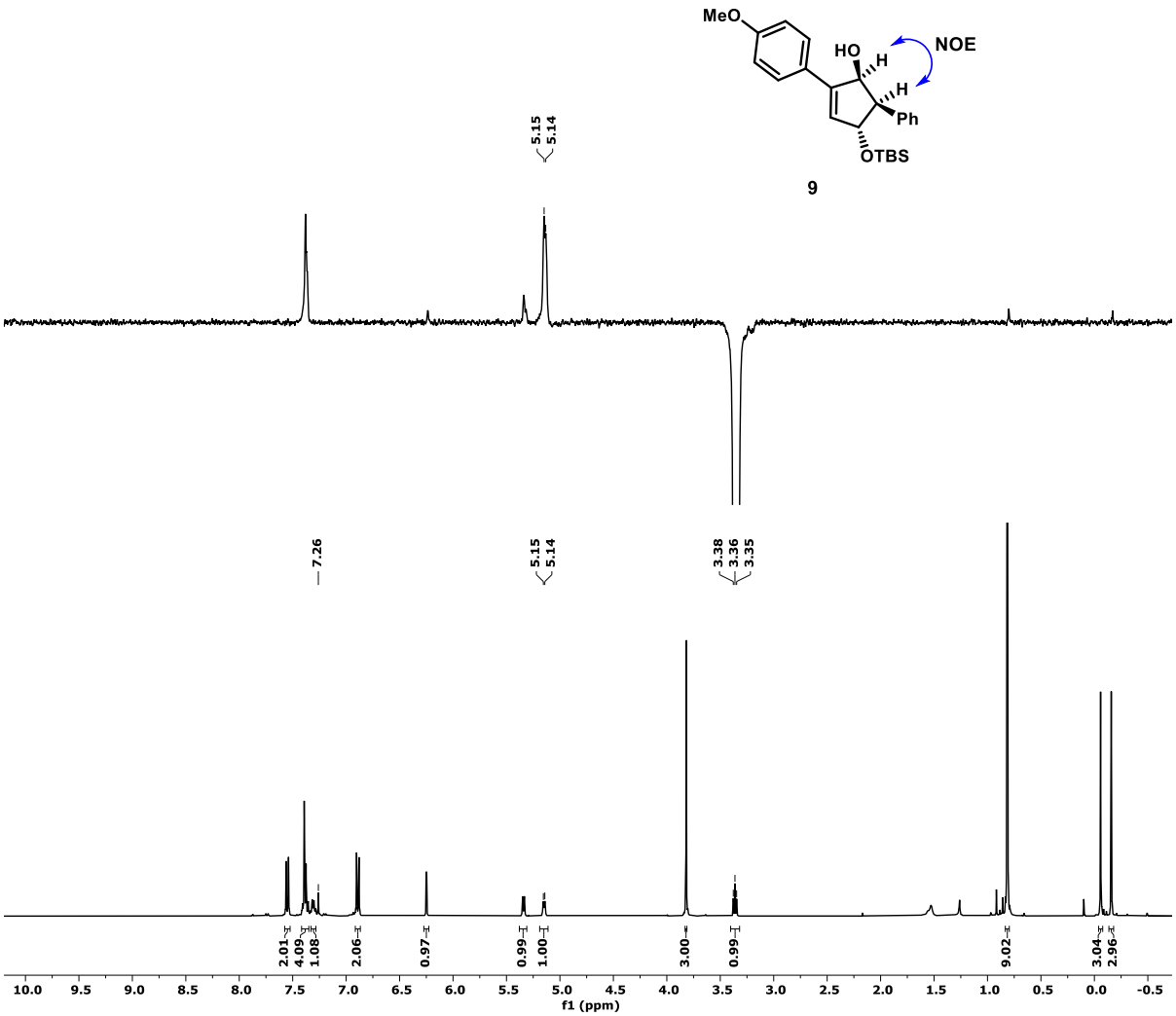
9

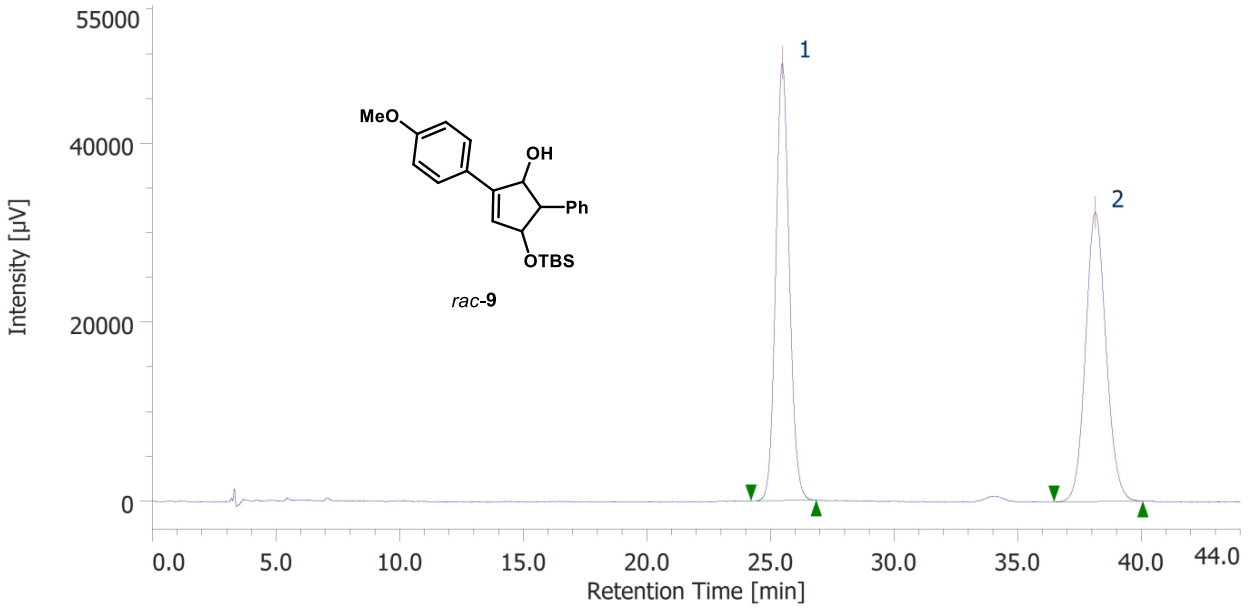
^{13}C-NMR
(100 MHz, $CDCl_3$)



9

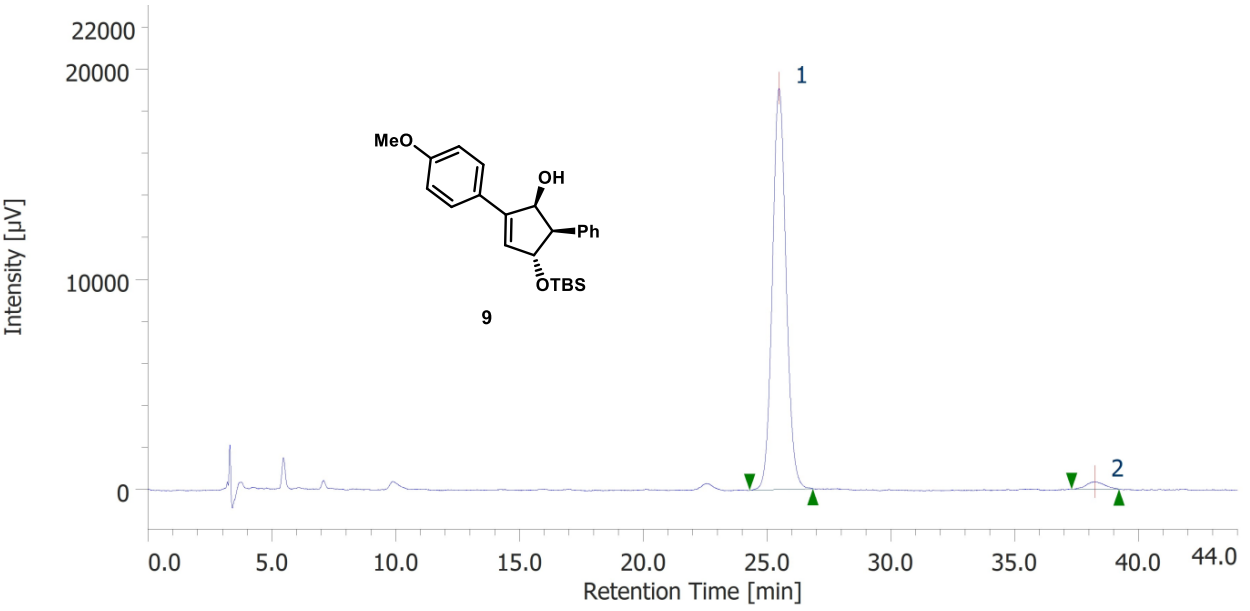
1D NOE of 5:


MeO
HO
H
NOE
H
Ph
OTBS
9
5.15
5.14
7.26
5.15
5.14
3.38
3.36
3.35
2.01
4.09
1.08
2.06
0.97
0.99
1.00
3.00
0.99
9.02
3.04
2.96
f1 (ppm)

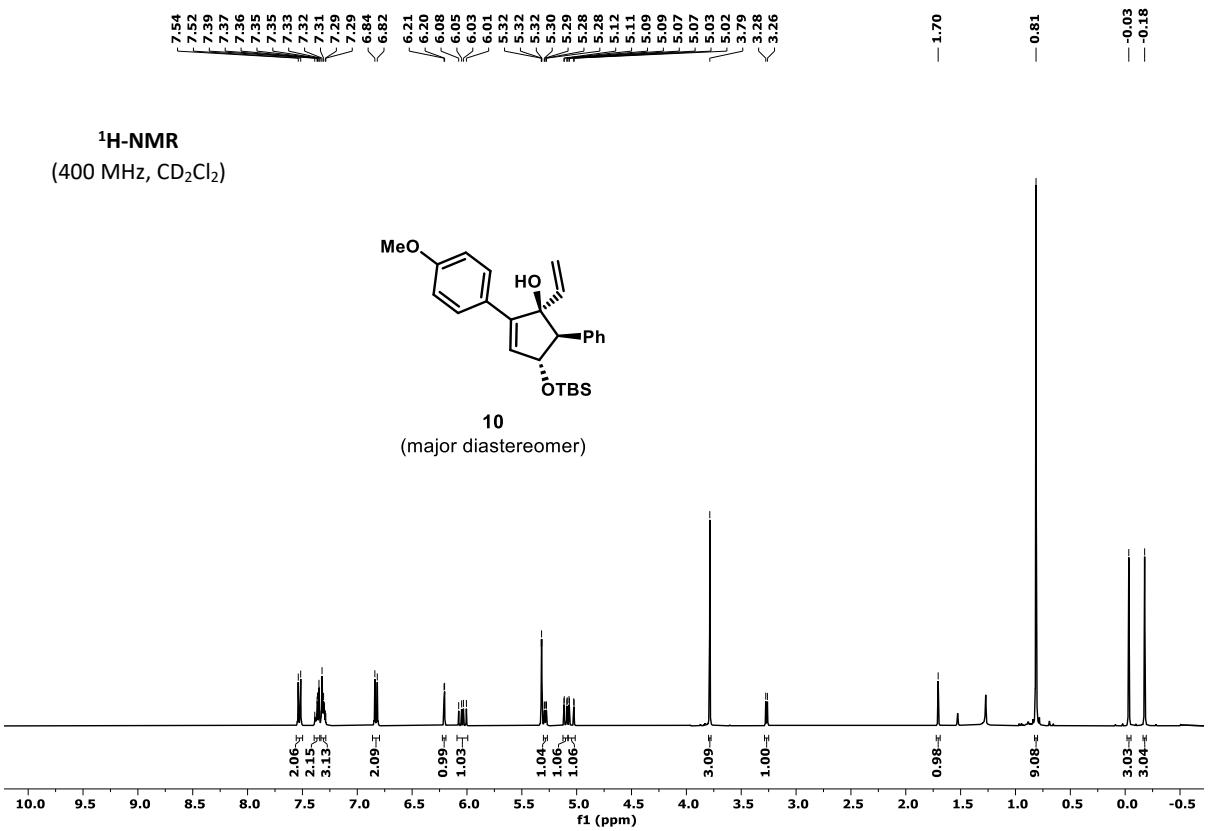


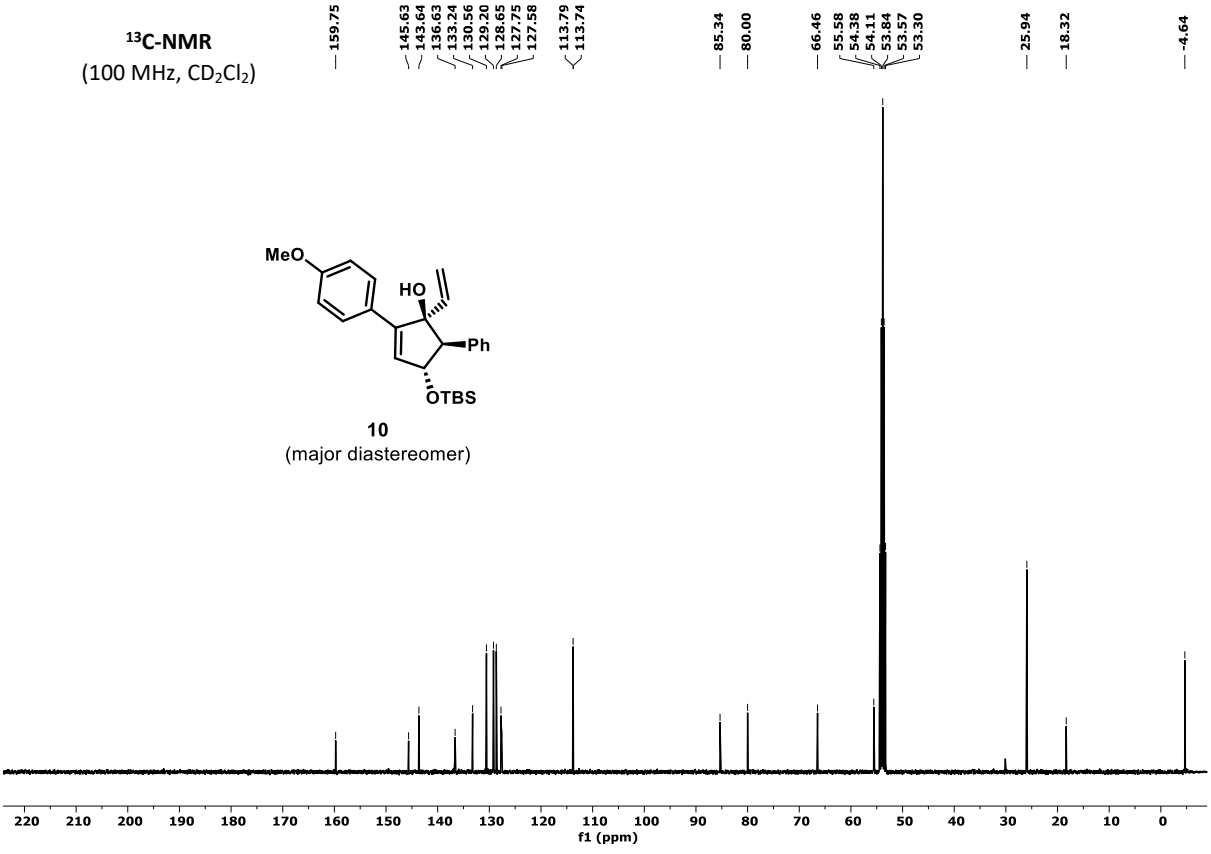
#	Peak Name	CH	tR [min]	Area [μV·sec]	Height [μV]	Area%	Height%	Quantity	NTP	Resolution	Symmetry Factor	Warning
1	Unknown	12	25.470	1861228	48910	49.959	60.217	N/A	10631	10.199	1.092	
2	Unknown	12	38.130	1864280	32313	50.041	39.783	N/A	10323	N/A	1.099	

Daicel Chiralpak IA column (95:5 *n*-Hexane/*i*-PrOH, 1.0 mL/min, 260 nm)

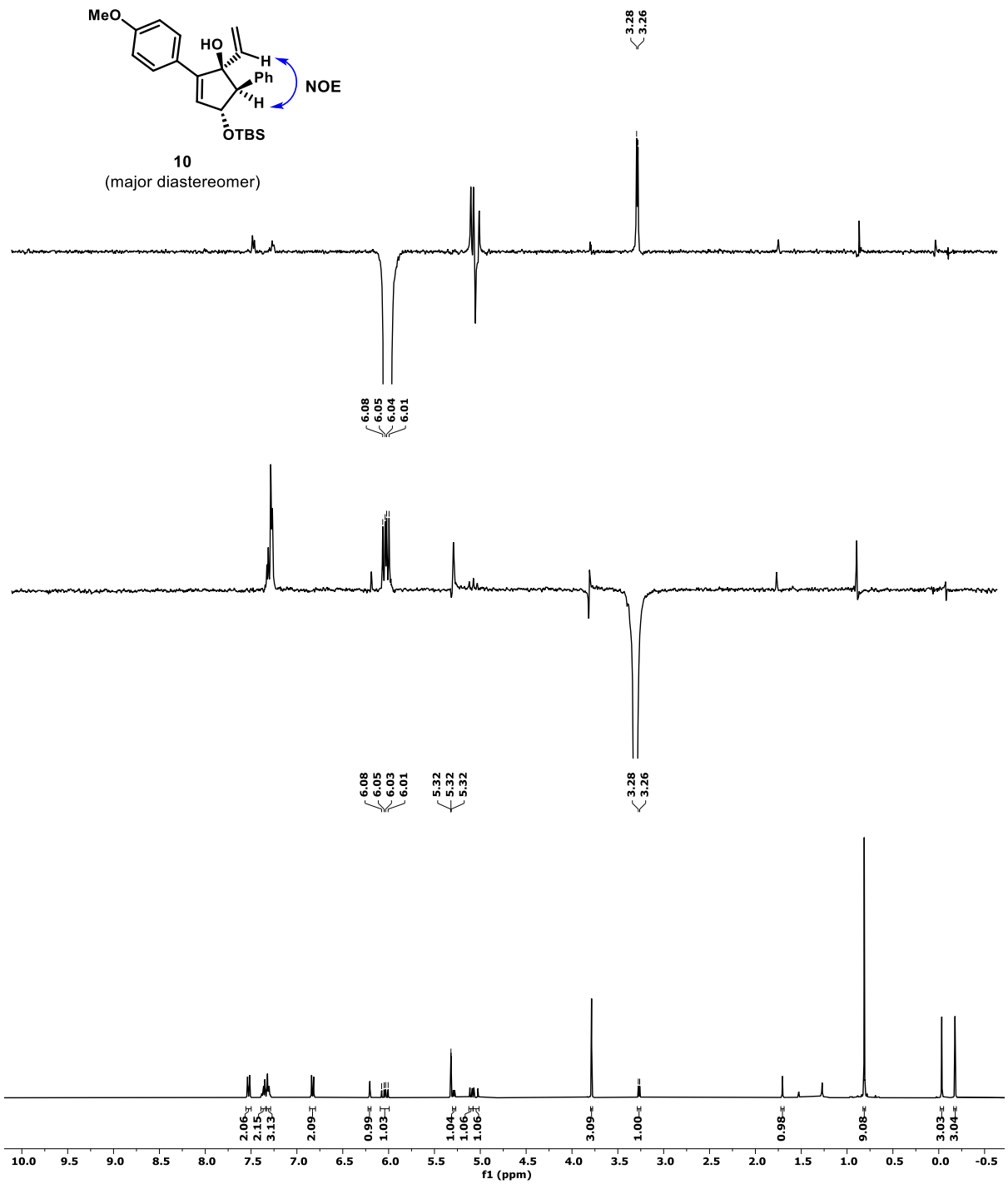


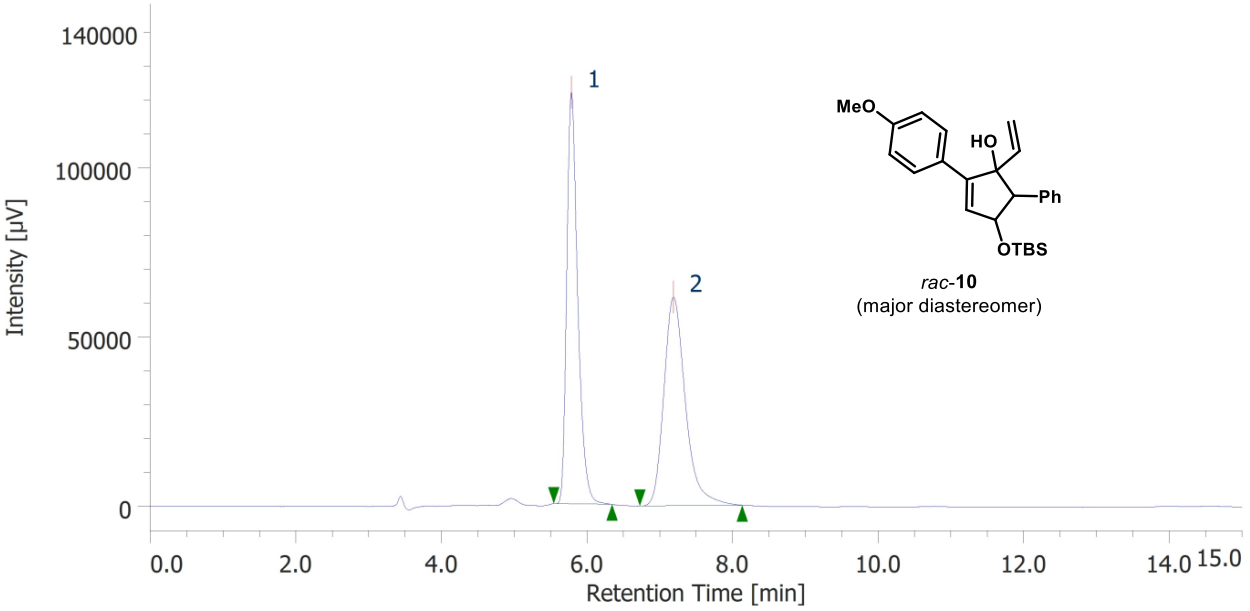
#	Peak Name	CH	tR [min]	Area [μV·sec]	Height [μV]	Area%	Height%	Quantity	NTP	Resolution	Symmetry Factor	Warning
1	Unknown	11	25.473	734636	19090	97.495	98.185	N/A	10419	10.692	1.085	
2	Unknown	11	38.237	18877	353	2.505	1.815	N/A	12010	N/A	1.073	


7.54
7.52
7.39
7.37
7.36
7.35
7.35
7.33
7.32
7.31
7.29
7.29
6.84
6.82
6.21
6.20
6.08
6.05
6.03
6.01
5.32
5.32
5.30
5.29
5.28
5.28
5.12
5.11
5.09
5.09
5.07
5.07
5.03
5.02
3.79
3.28
3.26
1.70
0.81
-0.03
-0.18
1H-NMR
(400 MHz, CD2Cl2)
MeO
HO
Ph
OTBS
10
(major diastereomer)
2.06
2.15
3.13
2.09
0.99
1.03
1.04
1.06
1.06
3.09
1.00
0.98
9.08
3.03
3.04
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
f1 (ppm)


13C-NMR
(100 MHz, CD2Cl2)
159.75
145.63
143.64
136.63
133.24
130.56
129.20
128.65
127.75
127.58
113.79
113.74
85.34
80.00
66.46
55.58
54.38
54.11
53.84
53.57
53.30
25.94
18.32
-4.64
MeO
HO
Ph
OTBS
10
(major diastereomer)
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

1D NOE of 6:

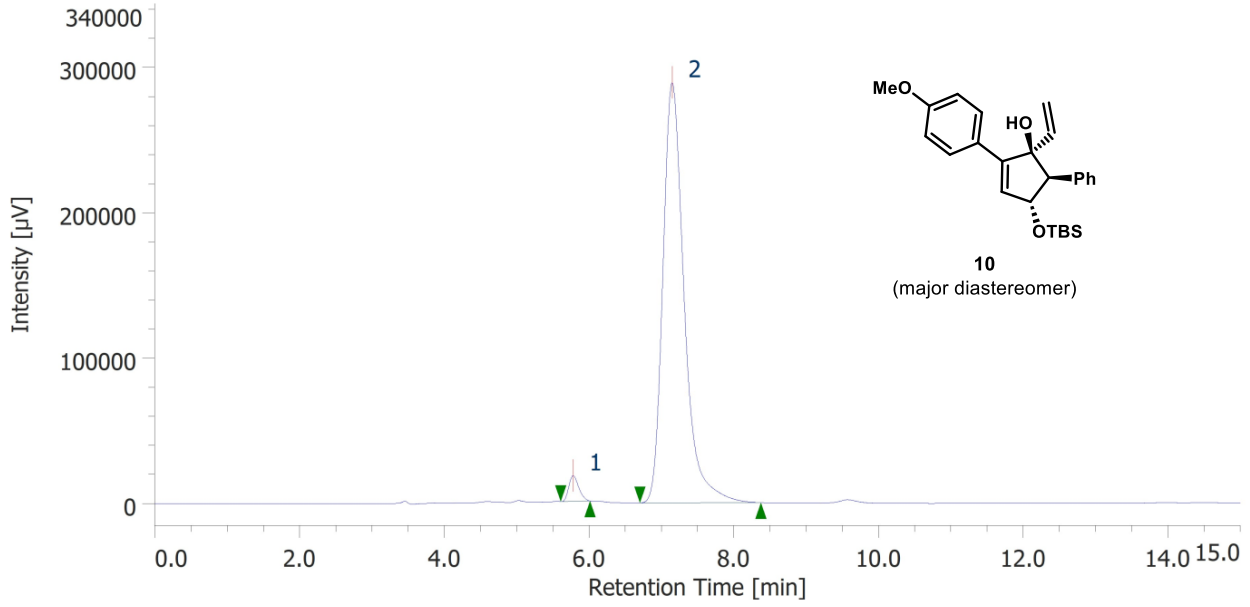

MeO
HO
H
Ph
H
NOE
OTBS
10
(major diastereomer)
3.28
3.26
6.08
6.05
6.04
6.01
6.08
6.05
6.03
6.01
5.32
5.32
5.32
3.28
3.26
2.06
2.15
3.13
2.09
0.99
1.03
1.04
1.06
1.06
3.09
1.00
0.98
9.08
3.03
3.04
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)



rac-**10**
(major diastereomer)

#	Peak Name	CH	tR [min]	Area [μV·sec]	Height [μV]	Area%	Height%	Quantity	NTP	Resolution	Symmetry Factor	Warning
1	Unknown	13	5.783	1272494	121512	50.112	66.357	N/A	7525	3.585	1.378	
2	Unknown	13	7.187	1266807	61607	49.888	33.643	N/A	3075	N/A	1.309	

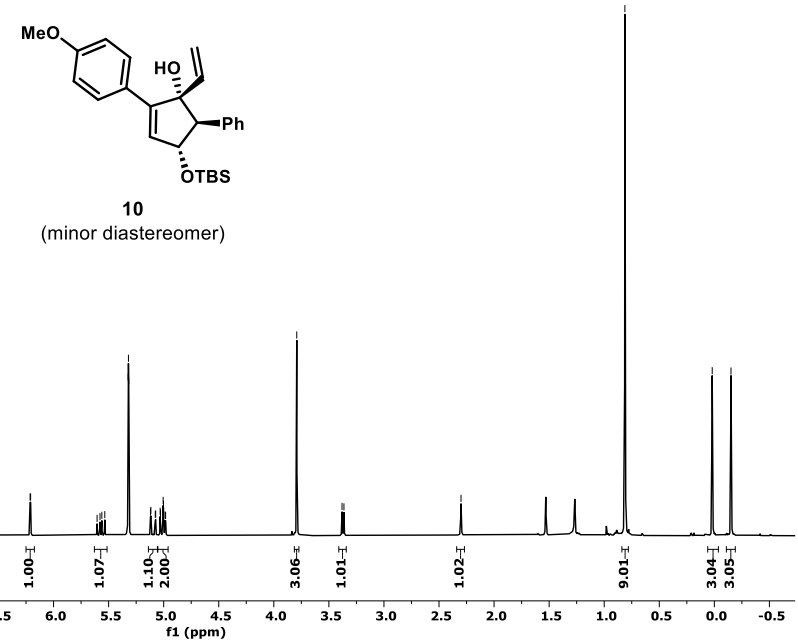
Daicel Chiralpak IB column (95:5 *n*-Hexane/*i*-PrOH, 1.0 mL/min, 264 nm)



10
(major diastereomer)

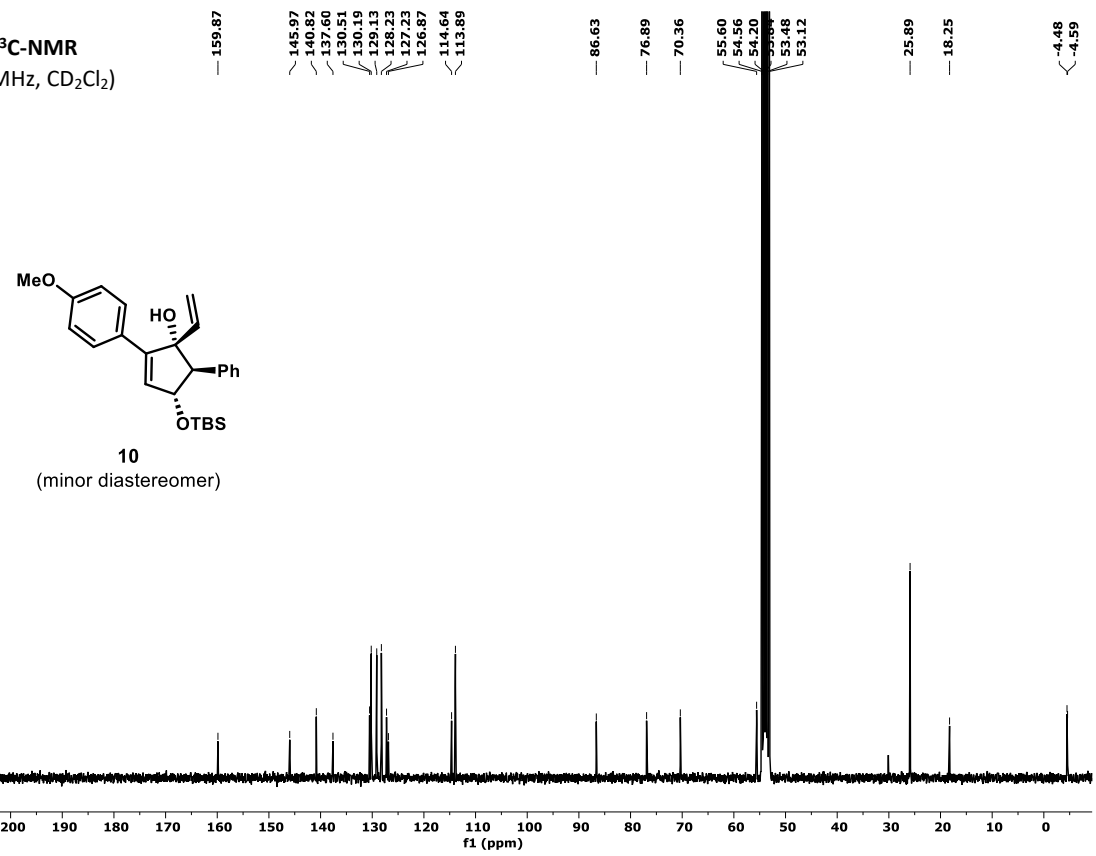
#	Peak Name	CH	tR [min]	Area [μV·sec]	Height [μV]	Area%	Height%	Quantity	NTP	Resolution	Symmetry Factor	Warning
1	Unknown	13	5.780	169198	17669	2.791	5.763	N/A	8276	3.592	1.251	
2	Unknown	13	7.147	5892972	288948	97.209	94.237	N/A	3157	N/A	1.366	

^{1}H-NMR
(400 MHz, CD_2Cl_2)

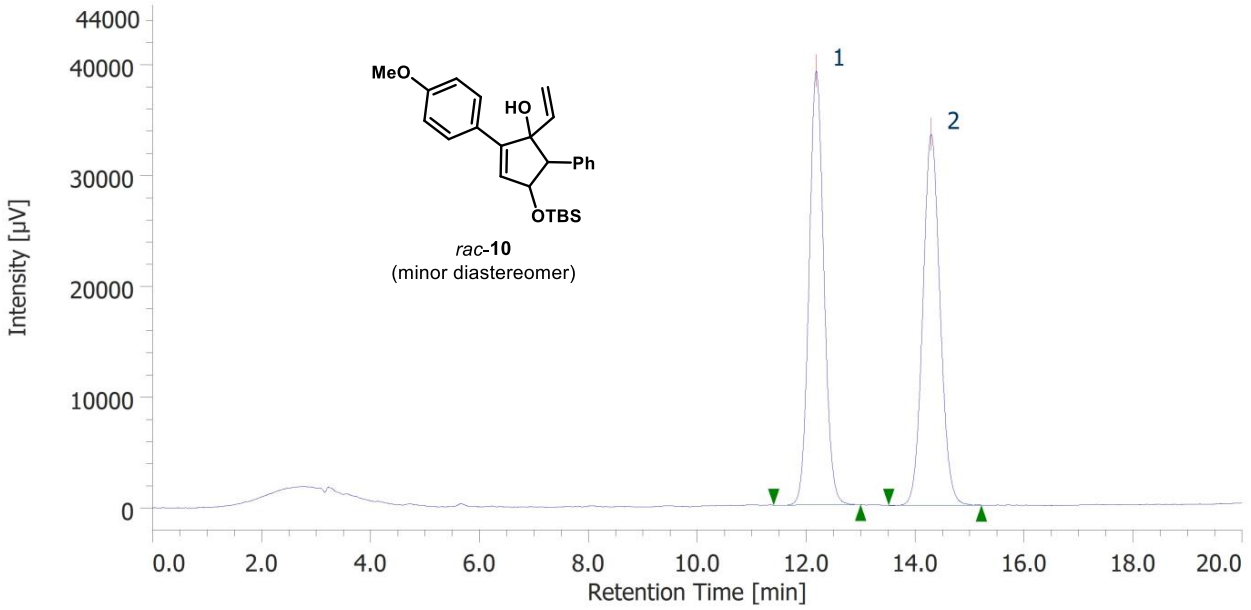


10
(minor diastereomer)

^{13}C-NMR
(75 MHz, CD_2Cl_2)

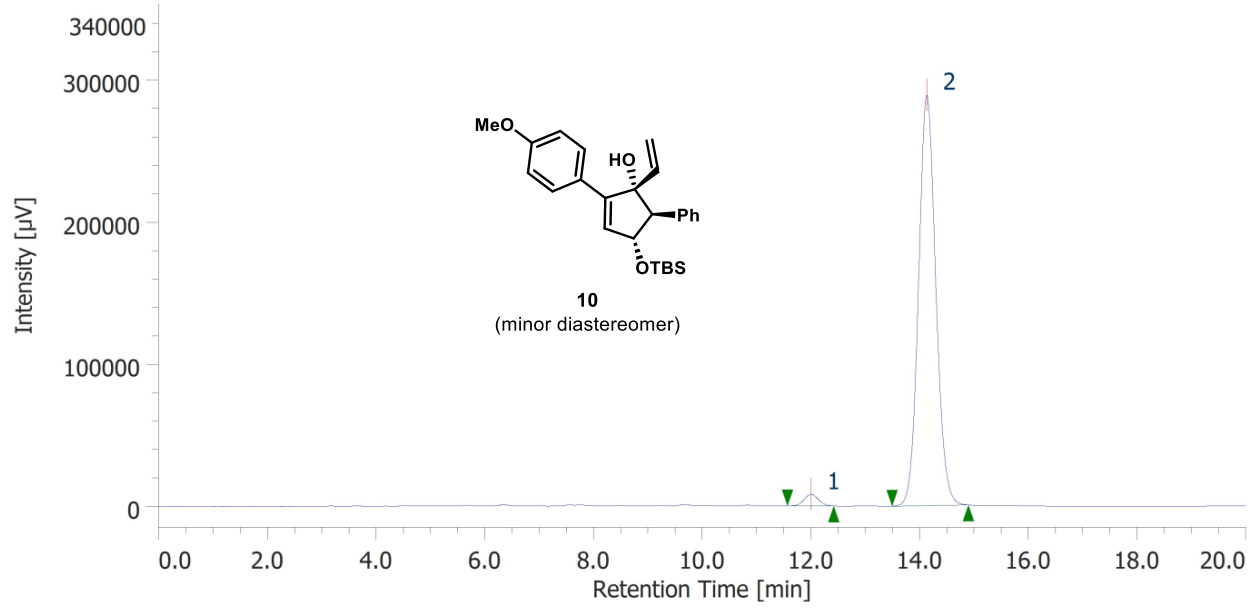


10
(minor diastereomer)

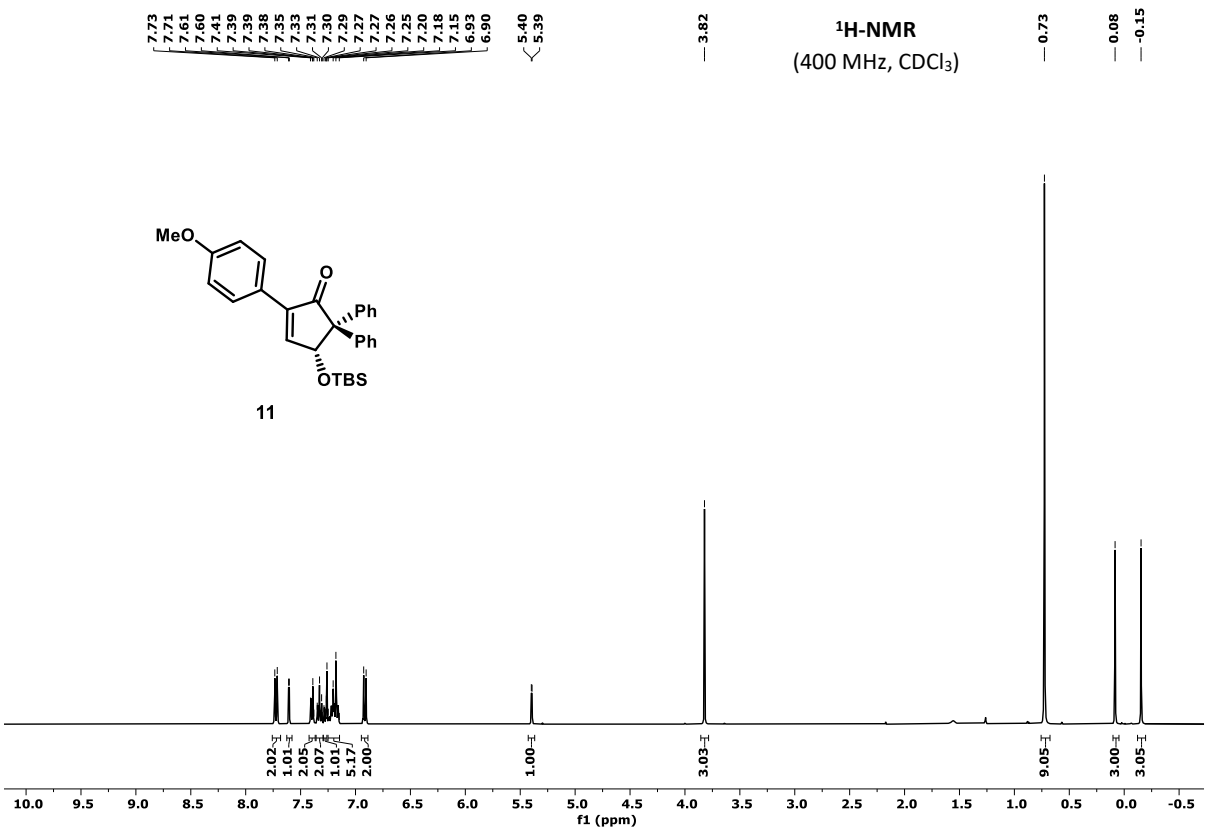


#	Peak Name	CH	tR [min]	Area [μV·sec]	Height [μV]	Area%	Height%	Quantity	NTP	Resolution	Symmetry Factor	Warning
1	Unknown	12	12.180	736839	39139	50.016	53.907	N/A	9867	3.976	1.081	
2	Unknown	12	14.290	736359	33466	49.984	46.093	N/A	9927	N/A	1.075	

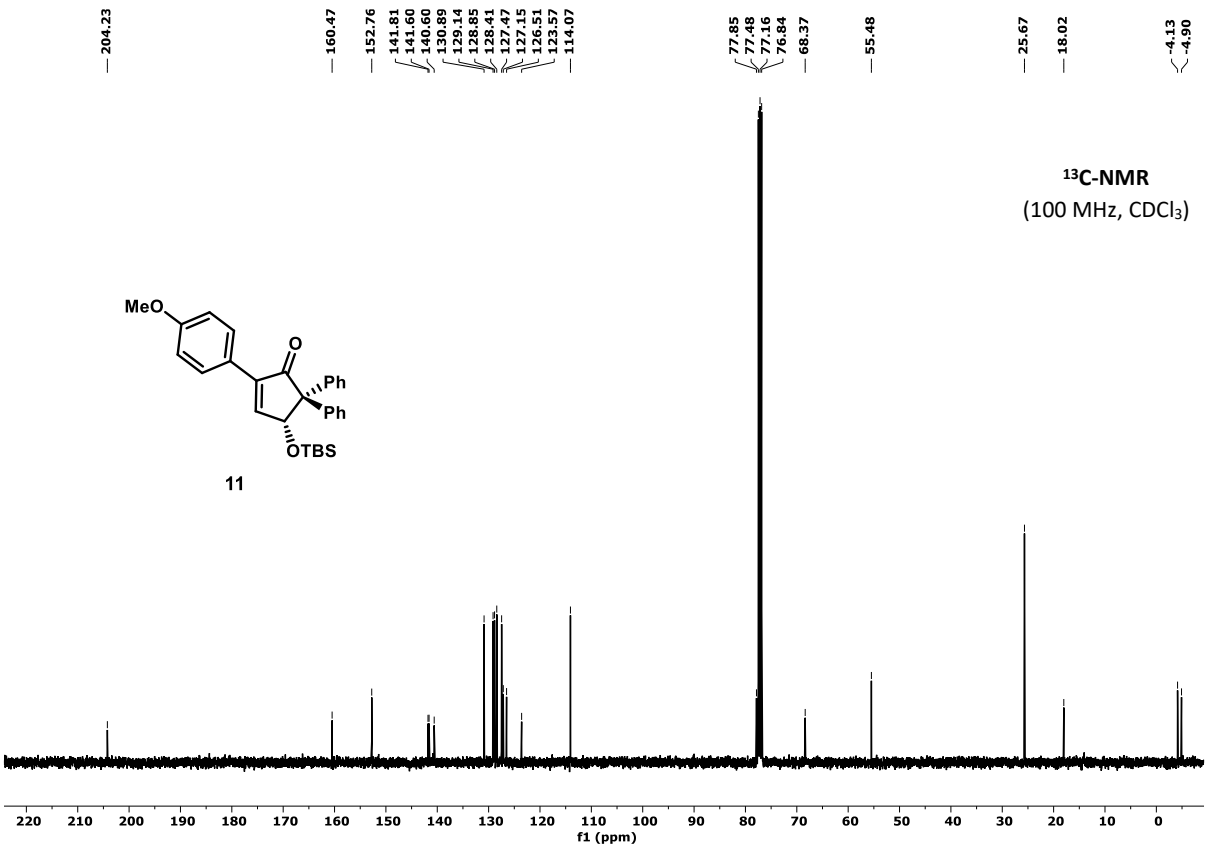
Daicel Chiralpak IA column (90:10 *n*-Hexane/*i*-PrOH, 1.0 mL/min, 265 nm)



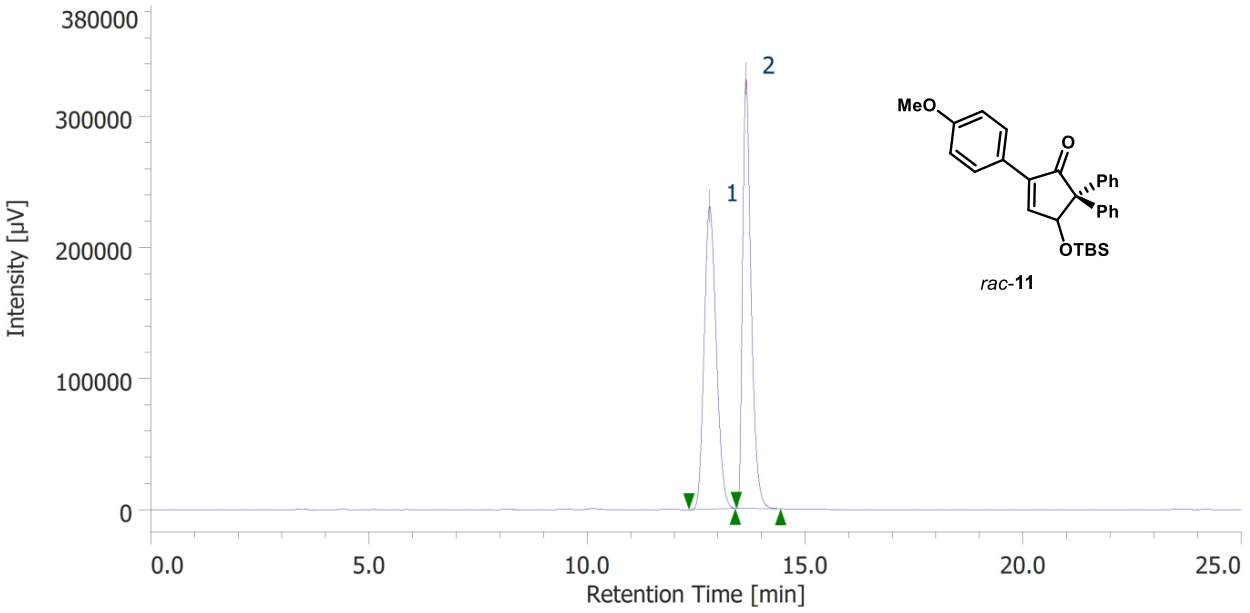
#	Peak Name	CH	tR [min]	Area [μV·sec]	Height [μV]	Area%	Height%	Quantity	NTP	Resolution	Symmetry Factor	Warning
1	Unknown	11	12.003	151126	8205	2.322	2.763	N/A	9768	4.027	1.041	
2	Unknown	11	14.130	6356368	288758	97.678	97.237	N/A	9726	N/A	1.094	



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

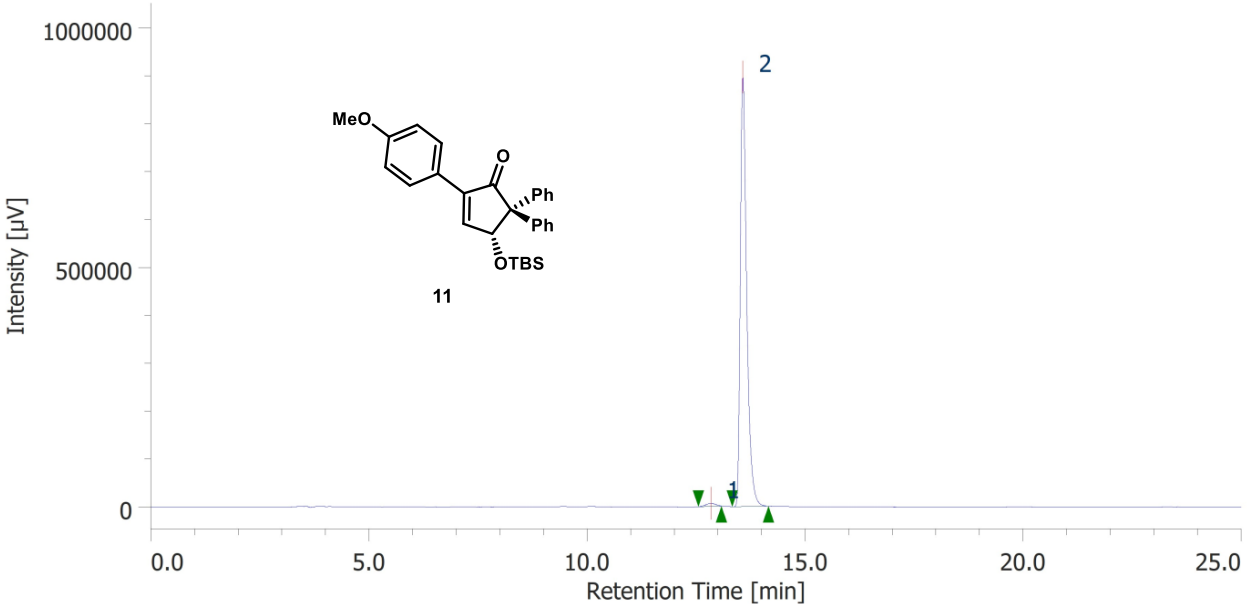


^{13}C-NMR
(100 MHz, $CDCl_3$)



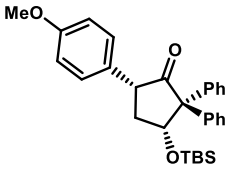
#	Peak Name	CH	tR [min]	Area [μV·sec]	Height [μV]	Area%	Height%	Quantity	NTP	Resolution	Symmetry Factor	Warning
1	Unknown	12	12.807	4470752	230900	50.147	41.346	N/A	10028	1.954	1.186	
2	Unknown	12	13.643	4444624	327558	49.853	58.654	N/A	24731	N/A	1.515	

Daicel Chiralpak IE column (95:5 *n*-Hexane/*i*-PrOH, 1.0 mL/min, 254 nm)



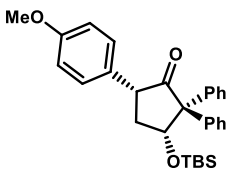
#	Peak Name	CH	tR [min]	Area [μV·sec]	Height [μV]	Area%	Height%	Quantity	NTP	Resolution	Symmetry Factor	Warning
1	Unknown	11	12.837	98575	6174	1.074	0.684	N/A	13333	2.109	0.957	
2	Unknown	11	13.570	9076071	895807	98.926	99.316	N/A	46120	N/A	1.505	

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



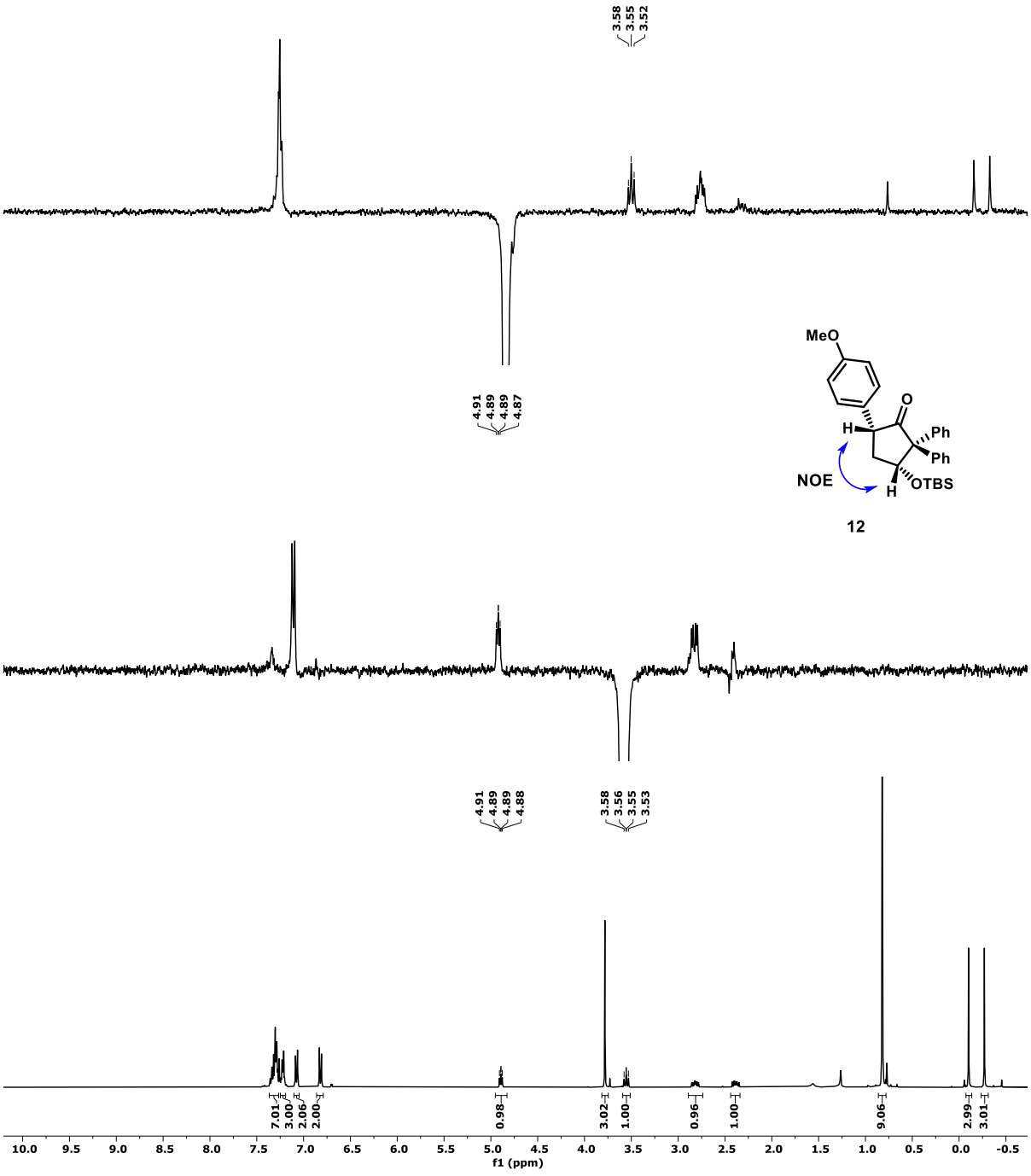
12

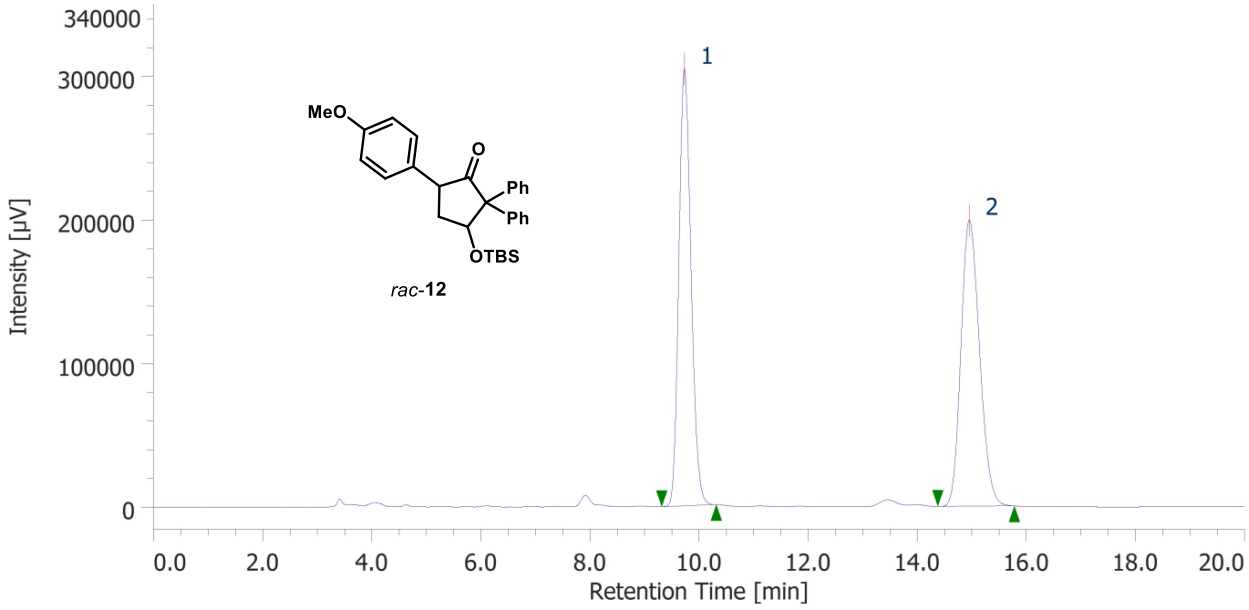
^{13}C-NMR
(100 MHz, $CDCl_3$)



12

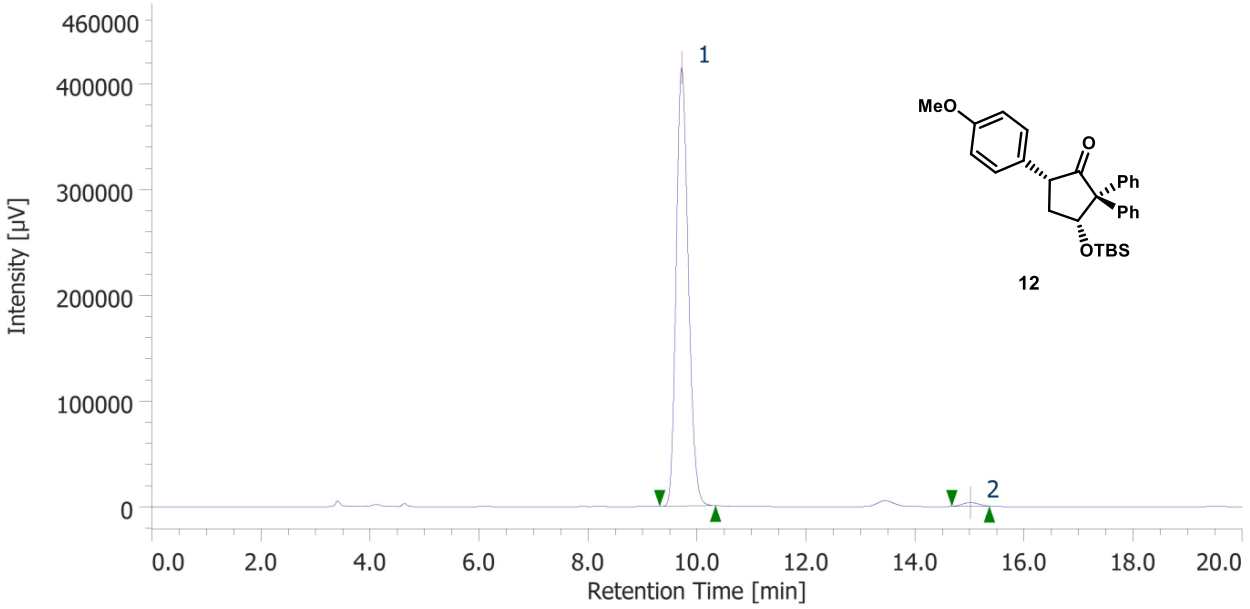
1D NOE of 8:


3.58
3.55
3.52
4.91
4.89
4.89
4.87
MeO
O
H
Ph
Ph
NOE
H
OTBS
12
4.91
4.89
4.89
4.88
3.58
3.56
3.55
3.53
7.01
3.00
2.06
2.00
0.98
3.02
1.00
0.96
1.00
9.06
2.99
3.01
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
f1 (ppm)



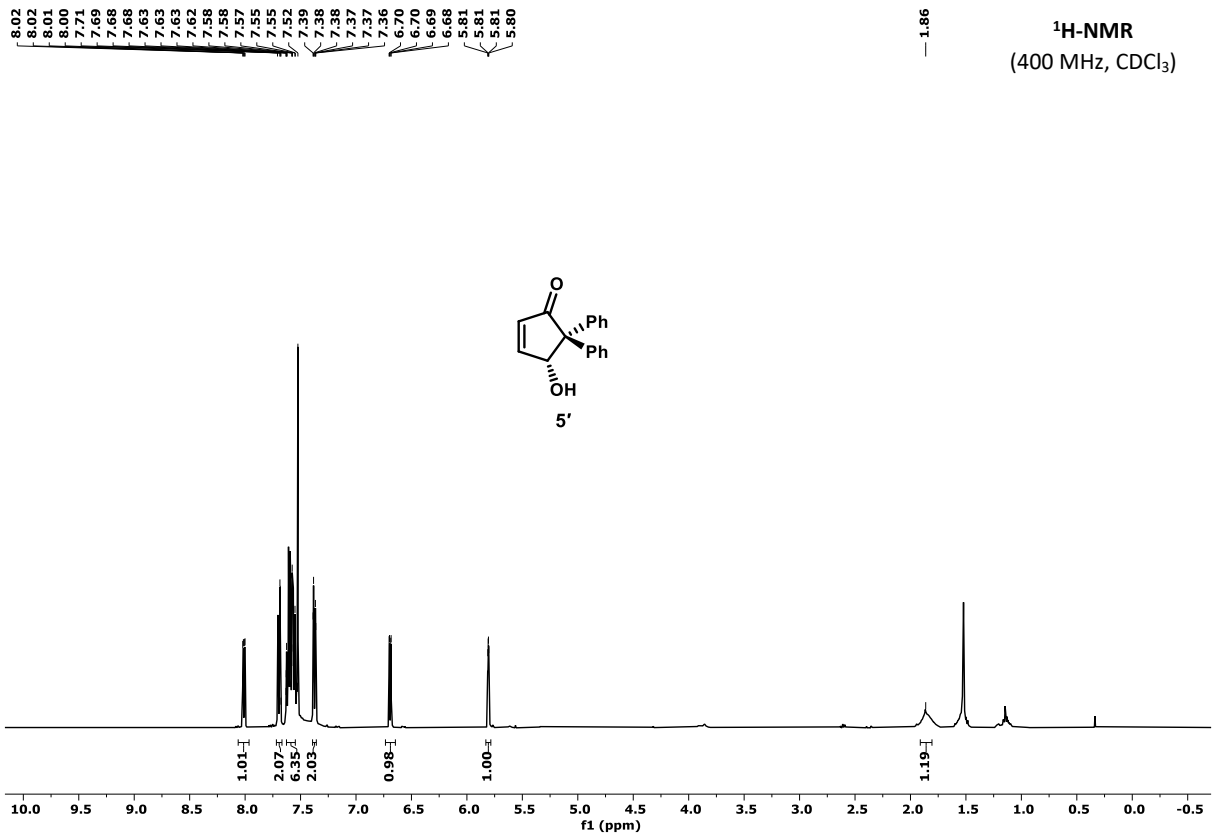
#	Peak Name	CH	tR [min]	Area [μV·sec]	Height [μV]	Area%	Height%	Quantity	NTP	Resolution	Symmetry Factor	Warning
1	Unknown	10	9.730	4717765	304041	49.945	60.408	N/A	9058	10.109	1.174	
2	Unknown	10	14.953	4728101	199271	50.055	39.592	N/A	9094	N/A	1.183	

Daicel Chiralpak IE column (90:10 *n*-Hexane/*i*-PrOH, 1.0 mL/min, 230 nm)



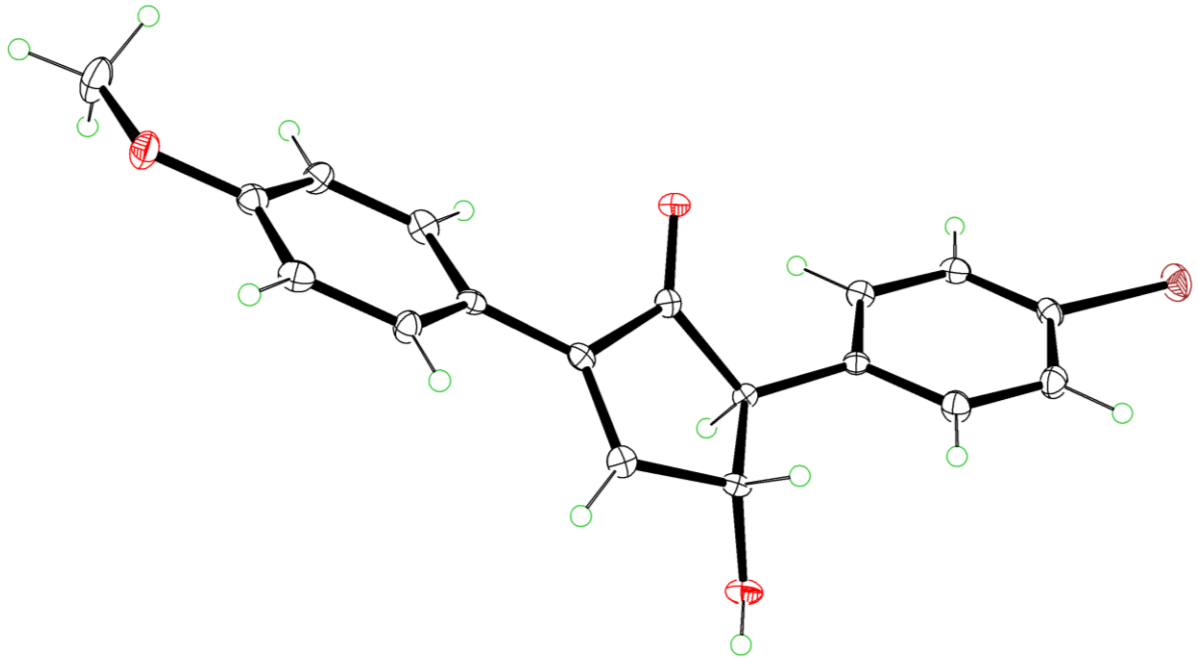
#	Peak Name	CH	tR [min]	Area [μV·sec]	Height [μV]	Area%	Height%	Quantity	NTP	Resolution	Symmetry Factor	Warning
1	Unknown	10	9.717	6394880	414199	98.867	99.162	N/A	9158	10.776	1.201	
2	Unknown	10	15.013	73302	3501	1.133	0.838	N/A	10740	N/A	1.023	

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



XVII. Single crystal X-ray diffraction analysis of 4j:

The crystal was prepared by liquid/liquid diffusion of a solution of **4j** in *n*-Hexane/CH_2Cl_2 (3:1) at 25 °C. A single crystal of **4j** was mounted and the diffraction data were collected on a Gemini diffractometer (Rigaku Oxford Diffraction) using Mo-Kα radiation (λ = 71.073 pm) and ω-scan rotation. The structure was solved with SHELXT-2018 (dual-space method). Anisotropic refinement of all non-hydrogen atoms with SHELXL-2018. All hydrogen atoms were calculated on idealized positions. Structure was drawn using Olex-2 and ORTEP-3.



ORTEP representation of the X-ray structure of enantiopure **4j** (thermal ellipsoids at 30% probability)

The crystallographic refinement parameters are given below:

Table S3. Crystal data and structure refinement for **4j**

Identification code	**4j**	
CCDC	2295678	
Empirical formula	$C_{18}H_{15}BrO_3$	
Formula weight	359.21	
Temperature/K	130(2) K	
Crystal system	monoclinic	
Space group	P 21	
Unit cell dimensions	a = 720.04(3) pm	α = 90°
	b = 686.61(3) pm	β = 100.880(4)°
	c = 1600.22(6) pm	γ = 90°
Volume	0.77691(6) nm^3	
Z	2	
Density (calculated)	1.536 Mg/m^3	
Absorption coefficient	2.655 mm^{-1}	
F(000)	364	
Crystal size	0.43 x 0.08 x 0.01 mm^3	
Radiation	MoKα (λ = 71.073 pm)	
Theta range for data collection	2.592 to 28.229°	
Index ranges	$-9 \leq h \leq 9$, $-9 \leq k \leq 8$, $-20 \leq l \leq 20$	
Reflections collected	6895	
Independent reflections	3263 [R(int) = 0.0358]	
Completeness to theta = 25.350°	99.9 %	
Absorption correction	Analytical	
Max. and min. transmission	0.973 and 0.621	
Refinement method	Full-matrix least-squares on F^2	
Data/restraints/parameters	3263/1/201	
Goodness-of-fit on F^2	1.046	
Final R indexes [I>=2σ (I)]	R_1 = 0.0409, wR_2 = 0.0727	
Final R indexes [all data]	R_1 = 0.0528, wR_2 = 0.0792	
Largest diff. peak and hole	0.721 and -0.470 e.$Å^{-3}$	
Flack parameter	-0.025(8)	

Comments: Structure solution with SHELXT-2018 (dual-space method). Anisotropic refinement of all non-hydrogen atoms with SHELXL-2018. All hydrogen atoms were calculated on idealized positions. With intermolecular OH-O hydrogen donor acceptor bonds (Table 6) chains along [010] are formed.

Table S4. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (pm^2x 10^{-1}) for **4j**. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
Br(1)	-283(1)	7524(1)	590(1)	33(1)
O(1)	2693(4)	7662(6)	4988(2)	20(1)
O(2)	1216(6)	1099(5)	4299(3)	24(1)
O(3)	5462(5)	7334(8)	9127(2)	28(1)
C(1)	1515(8)	4563(7)	4309(4)	14(1)
C(2)	2517(7)	5908(7)	5021(3)	17(1)
C(3)	3274(7)	4638(7)	5760(3)	16(1)
C(4)	3285(6)	2791(9)	5466(3)	20(1)
C(5)	2541(6)	2637(10)	4529(3)	16(1)
C(6)	1217(7)	5322(7)	3409(3)	17(1)
C(7)	1867(7)	4339(8)	2758(3)	23(1)
C(8)	1436(8)	4979(8)	1923(3)	25(1)
C(9)	348(7)	6653(7)	1735(3)	20(1)
C(10)	-304(6)	7654(11)	2365(3)	21(1)
C(11)	119(7)	6994(6)	3191(3)	20(1)
C(12)	3863(7)	5379(7)	6629(3)	17(1)
C(13)	3003(7)	7017(7)	6901(3)	23(1)
C(14)	3463(6)	7691(11)	7726(3)	22(1)
C(15)	4842(7)	6752(7)	8307(4)	22(1)
C(16)	5735(7)	5101(7)	8054(4)	23(1)
C(17)	5254(7)	4436(8)	7226(3)	21(1)
C(18)	4550(10)	8931(9)	9435(4)	38(2)

Table S5. Bond lengths [pm] and angles [°] for **4j**.

Br(1)-C(9)	189.9(5)
O(1)-C(2)	121.3(7)
O(2)-C(5)	142.4(7)
O(2)-H(1O)	84.00
O(3)-C(15)	136.4(6)
O(3)-C(18)	141.3(8)
C(1)-C(6)	150.8(8)
C(1)-C(5)	152.3(8)
C(1)-C(2)	153.7(7)
C(1)-H(1)	100.00
C(2)-C(3)	148.7(7)
C(3)-C(4)	135.3(8)
C(3)-C(12)	146.7(7)
C(4)-C(5)	149.8(6)
C(4)-H(4)	95.00
C(5)-H(5)	100.00
C(6)-C(7)	139.4(7)
C(6)-C(11)	140.0(7)
C(7)-C(8)	138.5(7)
C(7)-H(7)	95.00
C(8)-C(9)	139.1(7)
C(8)-H(8)	95.00
C(9)-C(10)	137.4(7)
C(10)-C(11)	137.6(7)
C(10)-H(10)	95.00
C(11)-H(11)	95.00
C(12)-C(13)	139.2(7)
C(12)-C(17)	140.5(7)
C(13)-C(14)	138.0(7)
C(13)-H(13)	95.00
C(14)-C(15)	138.5(7)
C(14)-H(14)	95.00
C(15)-C(16)	140.0(7)
C(16)-C(17)	138.1(7)

C(16)-H(16)	95.00
C(17)-H(17)	95.00
C(18)-H(18A)	98.00
C(18)-H(18B)	98.00
C(18)-H(18C)	98.00
C(5)-O(2)-H(1O)	109.5
C(15)-O(3)-C(18)	118.3(4)
C(6)-C(1)-C(5)	119.8(4)
C(6)-C(1)-C(2)	117.6(4)
C(5)-C(1)-C(2)	102.2(4)
C(6)-C(1)-H(1)	105.3
C(5)-C(1)-H(1)	105.3
C(2)-C(1)-H(1)	105.3
O(1)-C(2)-C(3)	126.2(5)
O(1)-C(2)-C(1)	127.1(5)
C(3)-C(2)-C(1)	106.7(4)
C(4)-C(3)-C(12)	129.4(5)
C(4)-C(3)-C(2)	107.4(5)
C(12)-C(3)-C(2)	123.2(4)
C(3)-C(4)-C(5)	112.9(6)
C(3)-C(4)-H(4)	123.6
C(5)-C(4)-H(4)	123.6
O(2)-C(5)-C(4)	114.0(5)
O(2)-C(5)-C(1)	108.2(4)
C(4)-C(5)-C(1)	103.7(5)
O(2)-C(5)-H(5)	110.2
C(4)-C(5)-H(5)	110.2
C(1)-C(5)-H(5)	110.2
C(7)-C(6)-C(11)	117.7(5)
C(7)-C(6)-C(1)	122.6(4)
C(11)-C(6)-C(1)	119.5(4)
C(8)-C(7)-C(6)	121.4(5)
C(8)-C(7)-H(7)	119.3
C(6)-C(7)-H(7)	119.3
C(7)-C(8)-C(9)	119.0(5)
C(7)-C(8)-H(8)	120.5

C(9)-C(8)-H(8)	120.5
C(10)-C(9)-C(8)	120.7(5)
C(10)-C(9)-Br(1)	119.8(4)
C(8)-C(9)-Br(1)	119.4(4)
C(9)-C(10)-C(11)	119.7(6)
C(9)-C(10)-H(10)	120.2
C(11)-C(10)-H(10)	120.2
C(10)-C(11)-C(6)	121.5(5)
C(10)-C(11)-H(11)	119.3
C(6)-C(11)-H(11)	119.3
C(13)-C(12)-C(17)	117.5(5)
C(13)-C(12)-C(3)	120.7(5)
C(17)-C(12)-C(3)	121.8(5)
C(14)-C(13)-C(12)	121.9(5)
C(14)-C(13)-H(13)	119.0
C(12)-C(13)-H(13)	119.0
C(13)-C(14)-C(15)	119.9(6)
C(13)-C(14)-H(14)	120.1
C(15)-C(14)-H(14)	120.1
O(3)-C(15)-C(14)	124.9(5)
O(3)-C(15)-C(16)	115.5(5)
C(14)-C(15)-C(16)	119.5(5)
C(17)-C(16)-C(15)	120.0(5)
C(17)-C(16)-H(16)	120.0
C(15)-C(16)-H(16)	120.0
C(16)-C(17)-C(12)	121.1(5)
C(16)-C(17)-H(17)	119.4
C(12)-C(17)-H(17)	119.4
O(3)-C(18)-H(18A)	109.5
O(3)-C(18)-H(18B)	109.5
H(18A)-C(18)-H(18B)	109.5
O(3)-C(18)-H(18C)	109.5
H(18A)-C(18)-H(18C)	109.5
H(18B)-C(18)-H(18C)	109.5

Symmetry transformations used to generate equivalent atoms:

Table S6. Anisotropic displacement parameters ($pm^2 x\ 10^{-1}$) for **4j**. The anisotropic displacement factor exponent takes the form: $-2\pi^2[\ h^2 a^{*2} U^{11} + ... + 2\ h\ k\ a^*\ b^*\ U^{12}]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
Br(1)	37(1)	40(1)	20(1)	6(1)	2(1)	0(1)
O(1)	20(2)	15(2)	24(2)	0(2)	2(1)	-2(2)
O(2)	24(2)	15(2)	32(3)	3(2)	1(2)	1(2)
O(3)	33(2)	31(2)	18(2)	-3(2)	1(1)	2(2)
C(1)	12(3)	15(3)	16(3)	0(2)	2(2)	2(2)
C(2)	12(2)	20(3)	19(3)	0(2)	5(2)	2(2)
C(3)	12(2)	18(3)	20(3)	3(2)	6(2)	1(2)
C(4)	15(2)	23(3)	22(2)	1(3)	4(2)	3(3)
C(5)	14(2)	13(2)	22(2)	3(3)	3(2)	0(3)
C(6)	13(2)	18(3)	18(3)	-2(2)	2(2)	-6(2)
C(7)	26(3)	22(3)	21(3)	4(2)	4(2)	7(2)
C(8)	25(3)	29(3)	23(3)	-3(2)	9(2)	0(3)
C(9)	18(3)	26(3)	16(3)	5(2)	0(2)	-3(2)
C(10)	21(2)	19(2)	24(2)	2(3)	1(2)	-2(3)
C(11)	18(2)	21(3)	22(3)	0(2)	4(2)	1(2)
C(12)	15(3)	16(2)	22(3)	2(2)	6(2)	-2(2)
C(13)	19(2)	27(4)	24(3)	5(2)	4(2)	4(2)
C(14)	21(2)	21(3)	24(2)	-4(3)	6(2)	5(3)
C(15)	20(3)	24(3)	23(3)	1(2)	4(2)	-3(2)
C(16)	19(3)	19(3)	29(3)	4(2)	2(2)	4(2)
C(17)	23(3)	21(3)	17(3)	0(2)	2(2)	4(2)
C(18)	48(4)	42(4)	23(4)	-10(3)	6(3)	9(3)

Table S7. Hydrogen coordinates (x 10^4) and isotropic displacement parameters (pm^2x 10^{-1}) for **4j**.

	x	y	z	U(eq)
H(1O)	1766	23	4405	36
H(1)	217	4361	4430	17
H(4)	3718	1705	5818	24
H(5)	3610	2508	4215	20
H(7)	2621	3205	2890	28
H(8)	1877	4285	1485	30
H(10)	-1044	8797	2231	26
H(11)	-345	7687	3622	24
H(13)	2072	7689	6506	28
H(14)	2835	8798	7896	26
H(16)	6670	4439	8451	27
H(17)	5875	3322	7058	25
H(18A)	4661	10081	9085	56
H(18B)	5147	9197	10026	56
H(18C)	3211	8622	9406	56

Table S8. Hydrogen bonds for **4j** [pm and °].

D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)
O(2)-H(1O)...O(1)#1	84	193	273.4(6)	160.8

Symmetry transformations used to generate equivalent atoms:
#1 x, y-1, z