Neutral Chiral Cyclopentadienyl Ru(II)Cl Catalysts Enable Enantioselective [2+2]-Cycloadditions

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Supplementary Information

Table of Content:

General Methods

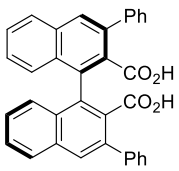
All reactions were carried out under an atmosphere of nitrogen in oven-dried glassware with magnetic stirring, unless otherwise indicated. THF and dichloromethane were purified by a Innovative Technology Solvent Delivery System. Chemicals were used as obtained from the suppliers. Flash chromatography was performed with Silicycle silica gel 60 (0.040-0.063 μm grade) or neutral alumina (Fluka, Brockmann activity 1). Analytical thin-layer chromatography was performed with commercial glass plates coated with 0.25 mm silica gel (E. Merck, Kieselgel 60 F254). Compounds were either visualised under UV-light at 254 nm or by dipping the plates in an aqueous potassium permanganate solution followed by heating. Proton nuclear magnetic resonance (^{1}H-NMR) data were acquired at 400 MHz on a Bruker AV400 and Bruker DRX600 (600 MHz) spectrometer. Chemical shifts (δ) are reported in parts per million (ppm) relative to residual chloroform (s, 7.26 ppm), CD_2Cl_2 (t, 5.32 ppm) and CD_3CN (quint, 1.94 ppm). Splitting patterns are designated as s, singlet; d, doublet; t, triplet; q, quartet; sept, septet; m, multiplet, br, broad. Proton decoupled Carbon-13 nuclear magnetic resonance (^{13}C-NMR) data were acquired at 100 MHz on a Bruker AV400 spectrometer. Chemical shifts are reported in ppm relative to $CDCl_3$ (77.16 ppm), CD_2Cl_2 (54.0 ppm) and CD_3CN (1.32 ppm). Proton decoupled Phosphorus-31 nuclear magnetic resonance (^{31}P-NMR) were acquired at 160 MHz on a Bruker AV400 spectrometer. Infrared (IR) data were recorded on an Alpha-P Bruker FT-IR Spectrometer. Absorbance frequencies are reported in reciprocal centimeters (cm^{-1}). HRMS measurements were performed by an Agilent LC-MS TOF. High resolution mass are given in *m/z*. Optical rotations were measured on a Polartronic M polarimeter using a 0.5 cm cell with a Na 589 nm filter. X-ray analysis was performed by Dr. R. Scopelliti at the EPF Lausanne.

Experimental procedures and characterization data

Phenyl-Ligand synthesis:

3,3'-diphenyl-[1,1'-binaphthalene]-2,2'-dicarboxylic acid (**7**):

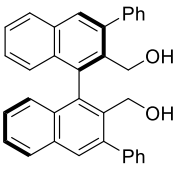
In an oven dried vial were weighted **6** (50 mg, 146 µmol, 1.0 equiv.), $Pd(OAc)_2$ (3.28 mg, 15.0 µmol, 10 mol%), Ac-Gly-OH (3.42 mg, 29.0 µmol, 20 mol%), Ag_2CO_3 (44.3 mg, 161 µmol, 1.1 equiv.) and K_2CO_3 (20.2 mg, 146 µmol, 1.0 equiv.). The vial was stoppered, evacuated and backfilled with nitrogen. Iodobenzene (98.0 µL, 876 µmol, 6.0 equiv.) and acetic acid (50.2 µL, 876 µmol, 6.0 equiv.) were added *via* syringe and the resulting mixture degassed by three pump-freeze-thaw cycles. The mixture was heated to 90 °C for 30 h protected from light, and monitored by negative mass spec analysis of an aliquot. After cooling down to 23 °C, 1 M HCl was added and the mixture filtered over a pad of silica eluting with ethyl acetate to remove metal particles. The filtrate was extracted with ethyl acetate (3x), the combined organic layer was dried over Na_2SO_4 and the solvent was removed under reduced pressure. Purification by silica gel column chromatography (pentane/EtOAc 3:1 to pentane/EtOAc 1:2 with 1% AcOH) delivered **7** (49.8 mg, 69% yield) as brown solid.



^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) = 8.00 (s, 2H), 7.92 (d, *J* = 8.2 Hz, 2H), 7.55 – 7.48 (m, 6H), 7.42 (t, *J* = 7.4 Hz, 4H), 7.40 – 7.36 (m, 2H), 7.29 – 7.25 (m, 2H), 7.08 (d, *J* = 8.6 Hz, 2H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ (ppm) = 172.1, 140.0, 136.4, 133.8, 133.0, 132.2, 131.3, 130.5, 128.8, 128.7, 128.3, 128.2, 128.0, 127.8, 126.8; **IR (ATR):** $\tilde{\nu}$ 3025, 2924, 1655, 1370, 1267, 1231, 751, 699 cm^{-1}; **HRMS (ESI)** calculated for $[C_{34}H_{22}O_4\text{-}H]^-$: 493.1445, found: 493.1443; **R_f:** 0.10 (pentane/EtOAc 1:1 + 1% AcOH); **m.p.:** 193 °C; **$[\alpha]_D^{20}$:** + 23.3° (c = 0.3, $CHCl_3$).

(3,3'-diphenyl-[1,1'-binaphthalene]-2,2'-diyl)dimethanol (**7-OH**):

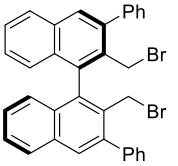
7 (400 mg, 806 µmol, 1.0 equiv.) was weighted in an oven dried vial. The vial was stoppered, evacuated and backfilled with nitrogen. THF (5 mL) was added followed by slow addition of BH_3-THF (1 M in THF, 4.0 mL, 4.0 mmol, 5.0 equiv) at 0 °C. The mixture was stirred at 65 °C for 18 h. After cooling down to 0 °C, water was added carefully, followed by 1 M HCl. The aqueous layer was extracted with ethyl acetate (3x), the combined organic layer was dried over Na_2SO_4 and the solvent was removed under reduced pressure. Purification by silica gel column chromatography (pentane/EtOAc 4:1) delivered **7-OH** (339 mg, 90% yield) as white solid.



^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) = 7.95 (s, 2H), 7.93 (d, *J* = 8.2 Hz, 2H), 7.71 – 7.66 (m, 4H), 7.49 (ddd, *J* = 8.1, 6.8, 1.2 Hz, 2H), 7.46 – 7.36 (m, 6H), 7.29 – 7.24 (m, 2H), 7.05 (dd, *J* = 8.6, 1.1 Hz, 2H), 4.39 (d, *J* = 11.3 Hz, 2H), 4.15 (d, *J* = 11.3 Hz, 2H), 3.06 (s, 2H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ (ppm) = 141.6, 141.2, 136.7, 135.9, 133.1, 132.6, 130.0, 129.9, 128.3, 128.2, 127.5, 126.8, 126.7, 126.4, 60.1; **IR (ATR):** $\tilde{\nu}$ 3211, 3057, 1493, 1026, 1018, 892, 766, 750, 702 cm^{-1}; **HRMS (ESI)** calculated for $[M\text{-}OH]^+$ equals to $[C_{34}H_{25}O]^+$: 449.1900, found: 449.1866; **R_f:** 0.50 (pentane/EtOAc 4:1); **m.p.:** 181-182°C; **$[\alpha]_D^{20}$:** + 76.8° (c = 1.0, $CHCl_3$).

2,2'-bis(bromomethyl)-3,3'-diphenyl-1,1'-binaphthalene (**8**):

7-OH (284 mg, 609 µmol, 1.0 equiv.) was weighted in an oven dried flask. The vial was stoppered, evacuated and backfilled with nitrogen. THF (6 mL) was added followed by slow addition of PBr_3 (57.4 µL, 609 µmol, 1.0 equiv) at 0 °C. The mixture was stirred at this temperature for 5 h. Aq. sat. $NaHCO_3$ solution was added and diluted with ethyl acetate. The aqueous layer was extracted with ethyl acetate (3x), the combined organic layer was dried over Na_2SO_4 and the solvent was removed under reduced pressure to yield pure **8** (358 mg, 99% yield) as white solid. Purification by silica gel column chromatography (dry load, pentane/EtOAc 15:1) was performed for characterisation.

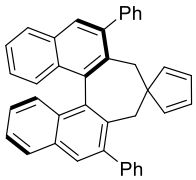


^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) = 7.97 – 7.89 (m, 4H), 7.68 – 7.61 (m, 4H), 7.56 – 7.42 (m, 8H), 7.30 (ddd, *J* = 8.2, 6.8, 1.3 Hz, 2H), 7.23 – 7.14 (m, 2H), 4.34 – 4.25 (m, 4H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ (ppm) = 141.1, 140.6, 136.5, 133.3, 132.5, 132.0, 130.5, 129.7, 128.3, 128.0, 127.7, 127.5, 127.4, 126.7, 32.2; **IR (ATR):** $\tilde{\nu}$ 3056, 1494, 1217, 752, 702, 491 cm^{-1}; **HRMS (ESI)** calculated for $[M\text{-}Br]^+$ equals to $[C_{34}H_{24}Br]^+$: 511.1056, found: 511.1032; **R_f:** 0.70 (pentane/EtOAc 6:1); **m.p.:** 173-175°C; **$[\alpha]_D^{20}$:** + 64.2° (c = 1.0, $CHCl_3$).

In a flame dried schlenk flask were weighted **8** (358 mg, 604 µmol, 1.0 equiv.), NaH (60 % in mineral oil, 26.6 mg, 665 µmol, 1.1 equiv.) and 15-Crown-5 (266 µL, 1.33 mmol, 2.2 equiv). The vial was stoppered, evacuated and backfilled with nitrogen. THF (6 mL) was added followed by slow addition of NaCp (2 M in THF 332 µL, 665 µmol, 1.1 equiv) at 0 °C. The mixture was stirred at for 30 min, then aq. sat. NH_4Cl solution was added carefully. The aqueous layer was extracted with ethyl acetate (3x), the combined organic layer was dried over Na_2SO_4 and the solvent was removed under reduced pressure. Purification by silica gel column chromatography (dry load, pentane/EtOAc 30:1) delivered a 1.2:1 mixture of literature known compounds **9':9** (210 mg, 70% yield) as white solid (*JACS* 2013, **135**, 636, SI pages 7-8, 11). This mixture can be used for the ruthenium complexation described previously (*JACS*

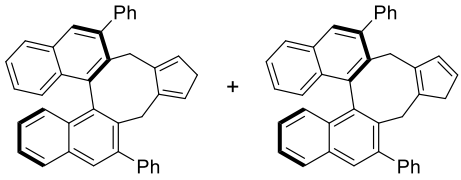
2015, **137**, 12478, SI pages 14, 20-21) and the spiro compound **9'** re-isolated from the first DCM fractions of acidic alumina column after complexation.

2,6-Diphenyl-3,5-dihydrospiro[cyclohepta[1,2-a:7,6-a']dinaphthalene-4,1'-cyclopenta-[2,4]diene] (**9'**):



^{1}H NMR (400 MHz, C_6D_6) δ (ppm) = 7.87 (s, 2H), 7.81 (d, *J* = 8.1 Hz, 2H), 7.64 (d, *J* = 8.5 Hz, 2H), 7.33 - 7.25 (m, 6H), 7.15 - 7.04 (m, 5H), 5.98 - 5.95 (m, 2H), 5.72 - 5.67 (m, 2H), 2.82 (d, *J* = 13.2 Hz, 2H), 2.59 (d, *J* = 13.2 Hz, 2H); **^{13}C NMR** (101 MHz, C_6D_6) δ (ppm) = 142.9, 142.0, 140.9, 136.2, 135.7, 133.0, 132.2, 130.4, 129.7, 128.7, 128.4, 128.4, 127.6, 127.2, 126.3, 125.9, 68., 33.02; **IR (ATR):** $\tilde{\nu}$ 3051, 2923, 2856, 1600, 1588, 1493, 1445, 1422, 1403, 1369, 1329, 1244, 1214, 1140, 1075, 1052, 1023, 965, 955, 924, 893, 867, 854, 840, 817, 785, 763, 750, 743, 702 cm^{-1}; **HRMS (ESI)** calculated for $[C_{39}H_{29}]^+$: 497.2264, found: 497.2266; **R_f:** 0.13 (pentane/EtOAc 40:1); **$[\alpha]_D^{20}$:** - 30.0° (c = 0.3, CH_2Cl_2).

5,16-Diphenyl-4,17-dihydro-1H-cyclopenta[6,7]cycloocta[2,1-a:3,4-a']dinaphthalene (**9**):

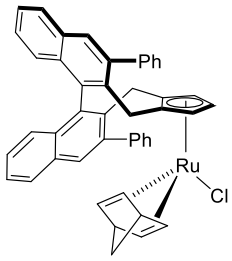


Double-bond isomers, ratio = 1.3:1.

^{1}H NMR (400 MHz, C_6D_6) δ (ppm) = 7.89 – 7.77 (m, 3H), 7.75 – 7.69 (m, 3H), 7.64 – 7.50 (m, 2H), 7.48 – 7.19 (m, 8H), 7.08 – 6.87 (m, 4H), 6.08 (d, *J* = 5.5 Hz, 0.6H), 6.04 (d, *J* = 5.3 Hz, 0.6H), 5.60 – 5.57 (m, 0.8H), 3.90 – 3.83 (m, 1.6H), 3.52 – 3.45 (m, 1H), 3.35 – 3.22 (m, 1.4H), 2.60 – 2.54 (m, 2H); **^{13}C NMR** (101 MHz, C_6D_6) δ (ppm) = 148.50, 145.28, 143.80, 142.64, 142.47, 142.15, 141.96, 141.75, 141.03, 140.87, 140.79, 140.45, 139.81, 137.94, 137.34, 136.87, 136.79, 136.28, 135.75, 135.43, 134.85, 134.47, 134.18, 133.55, 133.24, 132.89, 132.81, 132.66, 132.45, 132.38, 132.08, 132.03, 130.62, 130.51, 130.45, 130.24, 130.20, 130.03, 129.88, 129.25, 129.10, 127.54, 127.35, 127.29, 127.19, 126.61, 126.58, 126.53, 126.32, 126.09, 125.92, 125.71, 118.71, 46.19, 38.85, 33.42, 32.79, 31.55, 31.40; **IR (ATR):** $\tilde{\nu}$ 3054, 2970, 2923, 2900, 2205, 2161, 1493, 1446, 1407, 1393, 1379, 1258, 1221, 1074, 1066, 1055, 1027, 892, 868, 854, 803, 791, 763, 749, 701 cm^{-1}; **HRMS (ESI)** calculated for $[C_{39}H_{29}]^+$: 495.2118, found: 495.2109; ***R_f***: 0.10 (hexane:EtOAc, 40:1); **$[\alpha]_D^{20}$** = + 220 (*c* = 0.3, CH_2Cl_2).

Complexes:

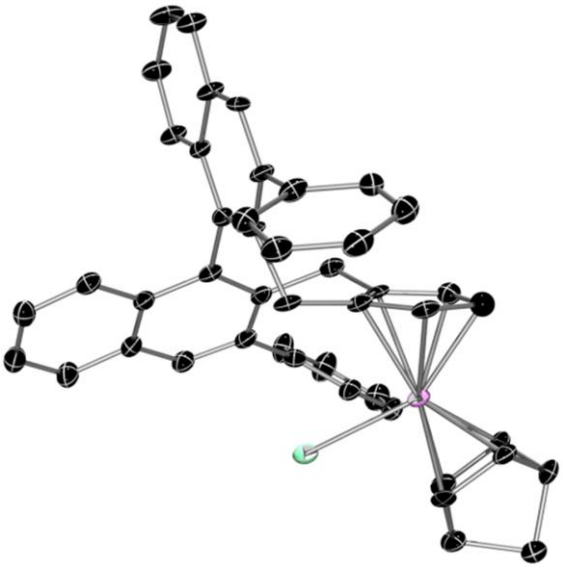
Complex Cp^X(Ph)Ru(nbd)Cl (**11**):



^{1}H NMR (600 MHz, CD_2Cl_2) δ (ppm) = 8.01 – 7.98 (m, 2H), 7.90 (d, *J* = 8.2 Hz, 1H), 7.87 (s, 1H), 7.64 (d, *J* = 7.6 Hz, 2H), 7.52 – 7.47 (m, 5H), 7.47 – 7.41 (m, 4H), 7.38 (td, *J* = 7.3, 1.3 Hz, 1H), 7.28 (ddd, *J* = 8.4, 6.8, 1.4 Hz, 1H), 7.19 (ddd, *J* = 8.4, 6.7, 1.4 Hz, 1H), 7.10 (d, *J* = 8.5 Hz, 1H), 6.86 (d, *J* = 8.6 Hz, 1H), 4.53 – 4.50 (m, 1H), 4.29 – 4.26 (m, 1H), 4.24 (t, *J* = 4.0 Hz, 1H), 4.19 – 4.15 (m, 2H), 3.93 – 3.89 (m, 1H), 3.73 (d, *J* = 15.7 Hz, 1H), 3.53 (t, *J* = 4.2 Hz, 1H), 3.46 (s, 1H), 3.41 – 3.31 (m, 2H), 3.19 (s, 1H), 3.15 (d, *J* = 15.6 Hz, 1H), 1.10 (dt, *J* = 8.9, 1.6 Hz, 1H), 1.03 (dt, *J* = 8.7, 1.6 Hz, 1H); **^{13}C NMR** (101 MHz, CD_2Cl_2) δ (ppm) = 141.7, 141.4, 141.3, 140.6, 137.9, 136.6, 134.5, 134.4, 132.9, 132.8, 132.6, 132.3, 131.4, 130.5, 130.0, 128.8, 128.7, 128.7, 128.5, 128.0, 127.7, 127.1, 126.8, 126.6, 126.4, 104.7, 92.8, 92.4, 90.1, 78.4, 75.3, 71.1, 62.4, 50.1, 48.3, 47.0, 30.6, 29.7; **IR (ATR):** $\tilde{\nu}$ 3058, 2924, 2852, 1493, 1446, 1026, 891, 762, 703, 429, 396 cm^{-1}; **HRMS (ESI)** calculated for $[M\text{-}Cl]^+$ equals to $[C_{46}H_{35}Ru]^+$ 689.1777, found: 689.1756; **R_f:** 0.30 (pentane/EtOAc 1:1) **$[\alpha]_D^{20}$:** + 152.6 (c = 0.1, CH_2Cl_2).

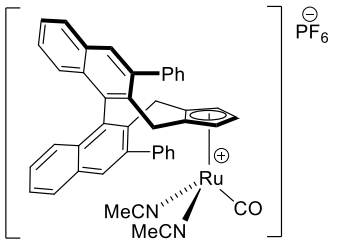
Crystals suitable for X-Ray analysis were grown by slow evaporation from THF under inert atmosphere.

X-Ray structure: CCDC 1499171



Complex $[Cp^X(Ph)Ru(CO)(MeCN)_2]PF_6$ (**1a-CO**):

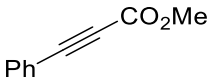
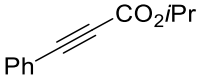
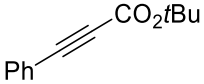
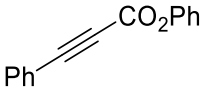
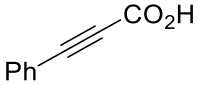
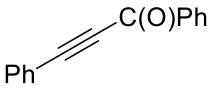
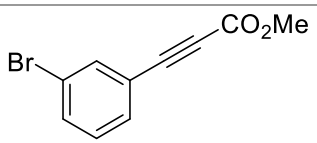
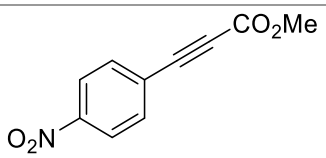
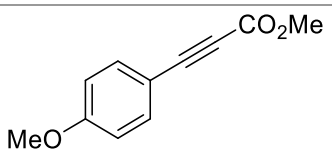
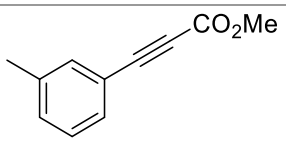
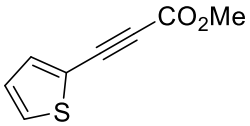
1a (4.0 mg, 4.63 µmol, 1.0 equiv.) was weighted in an oven dried vial. The vial was stoppered, evacuated and backfilled with nitrogen. Degassed acetonitrile (200 µL) was added and carbon monoxide bubbled through the mixture for 1 min. The mixture was stirred at 23 °C for 60 min. The solvent was removed under reduced pressure yielding **1a-CO** in quantitative yield as bright yellow solid.

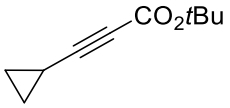
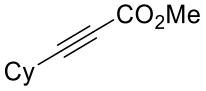


^{1}H NMR (600 MHz, CD_3CN) δ (ppm) = 8.02 – 8.01 (m, 1H), 8.01 – 7.99 (m, 2H), 7.96 – 7.95 (m, 1H), 7.62 – 7.59 (m, 2H), 7.56 – 7.44 (m, 8H), 7.42 – 7.38 (m, 2H), 7.35 – 7.30 (m, 2H), 7.05 – 7.00 (m, 2H), 4.73 – 4.69 (m, 1H), 4.38 – 4.35 (m, 1H), 4.16 (t, *J* = 2.4 Hz, 1H), 3.77 (d, *J* = 15.5 Hz, 1H), 3.36 (d, *J* = 14.2 Hz, 1H), 3.12 (d, *J* = 15.5 Hz, 1H), 2.99 (d, *J* = 14.2 Hz, 1H); **^{13}C NMR** (151 MHz, CD_3CN) δ (ppm) = 199.2, 142.1, 141.8, 141.6, 138.5, 137.1, 133.3, 132.5, 132.2, 131.1, 130.6, 130.4, 129.5, 129.2, 128.8, 128.6, 128.2, 127.7, 127.7, 127.6, 127.5, 127.2, 127.1, 100.9, 90.8, 90.3, 89.9, 64.9, 29.4, 28.6; **^{31}P NMR** (162 MHz, CD_3CN) δ (ppm) = -144.65 (hept, *J* = 706.2 Hz); **IR (ATR):** $\tilde{\nu}$ 1992, 1674, 1494, 1448, 838, 763, 705, 558 cm^{-1}; **HRMS (ESI)** calculated for $[M\text{-}MeCN\text{-}PF_6]^+$ equals to $[C_{42}H_{30}NORu]^+$ 666.1365, found: 666.1358; **$[\alpha]_D^{20}$:** + 5.6 (c = 0.3, CH_3CN).

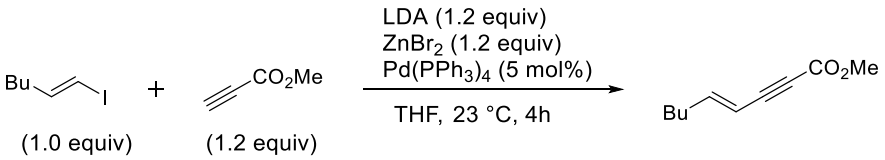
Substrates: Alkynes

Alkynes **4a**-**4k** and **4m**-**4n** are either commercially available or literature know compounds and were prepared according to the procedures in the given references. All spectra were in good agreement with the reported data.

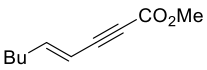
Number	Structure	Reference
4a		Supplier: TCI CAS number: 4891-38-7
4b		*Nature Chemistry*, 2015, **7**, 171-177; (SI page 34, 191-192)
4c		*Chem. Commun.*, 2015, **51**, 13004-13007; (SI page 6-7; 29-30)
4d		*Chem. Eur. J.*, 2015, **21**, 1468-1473; (SI page 4, 15)
4e		Supplier: Fluorochem CAS number: 637-44-5
4f		*J. Org. Chem.*, 2004, **69**, 1615-1619; (SI page 3; 11-14)
4g		*Org. Lett.*, 2001, **3**, 3111-3113; (SI page 1; 11-14)
4h		*Org. Lett.*, 2015, **17**, 520-523; (SI page 13; 82-83)
4i		*Org. Lett.*, 2015, **15**, 4742–4745; (SI page 2; 33)
4j		*J. Org. Chem.*, 1958,**23**, 885–890;
4k		*J. Org. Chem.*, 1987,**52**, *3662-3668*;

4m		*Chem. Commun.*, 2015, **51**, 13004-13007; (SI page 9; 49-50)
4n		*Chem.-Eur. J.*, 2014, **20**, 1834-1838; (SI page 7; 22)

Methyl (*E*)-non-4-en-2-ynoate (**4l**):



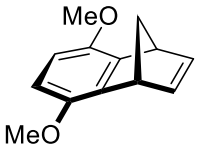
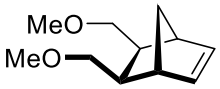
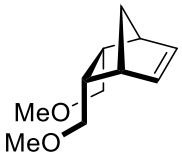
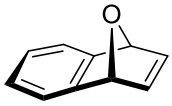
In a flame dried schlenk flask was diisopropylamine (285 µL, 2.00 mmol, 1.2 equiv.) in dry THF (4.1 mL). *n*BuLi (2.5 M in hexane, 800 µL, 2.00 mmol, 1.2 equiv.) was added dropwise at 0 °C under nitrogen atmosphere. After 30 min the solution was cooled down to -78 °C and methyl propiolate (179 µL, 2.00 mmol, 1.2 equiv) in THF (0.8 mL) was added slowly. After 30 min at this temperature zinc bromide (450 mg, 2.00 mmol, 1.2 equiv) in THF (1.7 mL) was added and the mixture gradually warmed to 0 °C over a period of 30 min. (*E*)-1-iodohex-1-ene (350 mg, 1.67 mmol, 1.0 equiv) in THF (1.7 mL) was added followed by $Pd(PPh_3)_4$ (96.0 mg, 83 µmol, 5 mol%) under counter flow of nitrogen. The mixture was allowed to warm to 23 °C and stirred at this temperature for 4 h. Aq. Sat. NH_4Cl solution was added and diluted with diethyl ether. The organic layer was washed with aq. sat. $NaHCO_3$ solution, dried over Na_2SO_4 and the solvent was removed under reduced pressure. Purification by silica gel column chromatography (pentane/EtOAc 15:1) yielded **4l** (70.0 mg, 25% yield) as colorless oil.



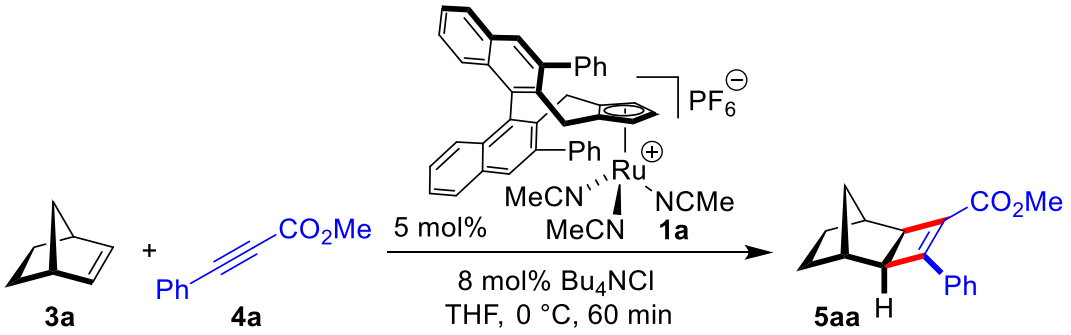
^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) = 6.52 (dt, *J* = 15.7, 7.0 Hz, 1H), 5.56 (dt, *J* = 16.0, 1.6 Hz, 1H), 3.78 (s, 3H), 2.23 – 2.13 (m, 2H), 1.46 – 1.22 (m, 4H), 0.90 (t, *J* = 7.1 Hz, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ (ppm) = 154.7, 152.9, 107.1, 86.2, 79.2, 52.8, 33.3, 30.4, 22.3, 13.9; **IR (ATR):** $\tilde{\nu}$ 2957, 2931, 2216, 1713, 1434, 1254, 1101, 962, 749 cm^{-1}; **HRMS (ESI)** calculated for $[C_{10}H_{14}O_2+H]^+$: 167.1067, found: 167.1072; **R_f:** 0.32 (pentane/Et_2O 15:1).

Substrates: Alkynes

All alkenes are either commercially available or literature know compounds and were prepared according to the procedures in the given references. All spectra were in good agreement with the reported data

Number	Struture	Reference
5a		Supplier: Fluka CAS number: 498-66-8
5b		Supplier: Alfa Aesar CAS number: 121-46-0
5c		*Organometallics*, 2008*,* **27**, 3622-3625; (SI page 9-10)
5d		*Organometallics*, 2008*,* **27**, 3622-3625; (SI page 10-11)
5e		*Organometallics*, 2008*,* **27**, 3622-3625; (SI page 6-7)
5f		*Organometallics*, 2008*,* **27**, 3622-3625; (SI page 5-6)
5g		Supplier: TCI CAS number: 573-57-9

Additional Optimization table:

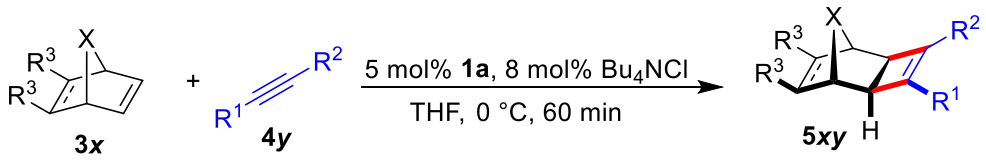


entry	deviation from standard conditions	conv. (%)[b]	**5aa** (%)[b]	er[c]
1	none	100	98	96.5:3.5
2	no (Bu_4N)Cl, 23 °C	100	80	47.5:52.5
3	6 mol % (Bu_4N)Cl, 23 °C	100	100	94.5:5.5
4	20 mol % (Bu_4N)Cl	100	100	96.5:3.5
5	Acetone instead of THF	100	87	95.5:4.5
6	THF + 1.0 equiv. H_2O	100	100	96:4
7	SbF_6^- instead of PF_6^-	100	92	96:4
8	-25 °C	9	3	94:6
9	1 mol% **1a**, 2 mol % (Bu_4N)Cl, 23°C, 24h	86	79	94.5:5.5

[a] Conditions: 37.5 µmol **3a**, 25 µmol **4a,** 2.0 µmol additive, 1.25 µmol **1a**, 0.3 M in THF, 0 °C, 60 min. [b] Determined by ^{1}H-NMR with an internal standard. [c] Determined by HPLC with a chiral stationary phase.

Products:

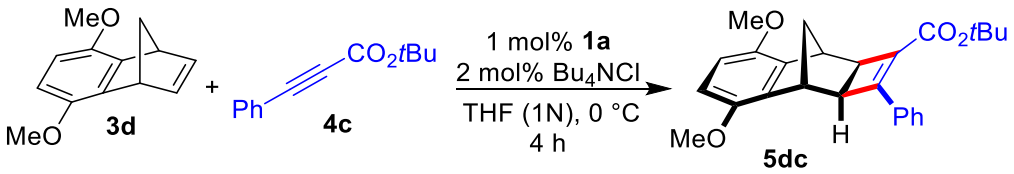
General procedure for the Ru-catalyzed synthesis of cyclobutenes:



1a (4.33 mg, 5.00 µmol, 5 mol%), Bu_4NCl (2.22 mg, 8.00 µmol, 8 mol%) and alkene **3** (150 µmol, 1.5 equiv.) were weighed in an oven dried tube containing a magnetic stirring bar. The tube was sealed with a rubber septum, evacuated and backfilled with nitrogen. At 23 °C dry THF (133 µL) was added and the mixture was stirred for two minutes. The color changed from brown to deep red. After cooling down to 0 °C alkyne **4** (100 µmol, 1.0 equiv.) in THF (200 µL, reaching 0.3 M) was added *via* syringe. After completion of the reaction the mixture was purified directly by silica gel chromatography eluting with pentane/Et_2O 20:1 to afford the cyclobutene product **5**.

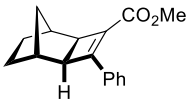
Optional, to recover the catalyst, after full conversion norbornadiene (20.3 µL, 200 µmol, 2.0 equiv.) was added and the solution stirred for 20 min at 23 °C. To prevent precipitation of the catalyst, some DCM is added to the reaction mixture when loading onto the column. Eluting with pentane/EtOAc 1:1 delivered complex **12**. This compound can be further purified by eluting through a pad of neutral alox with DCM.

Procedure for the big scale synthesis of cyclobutene 5dc:



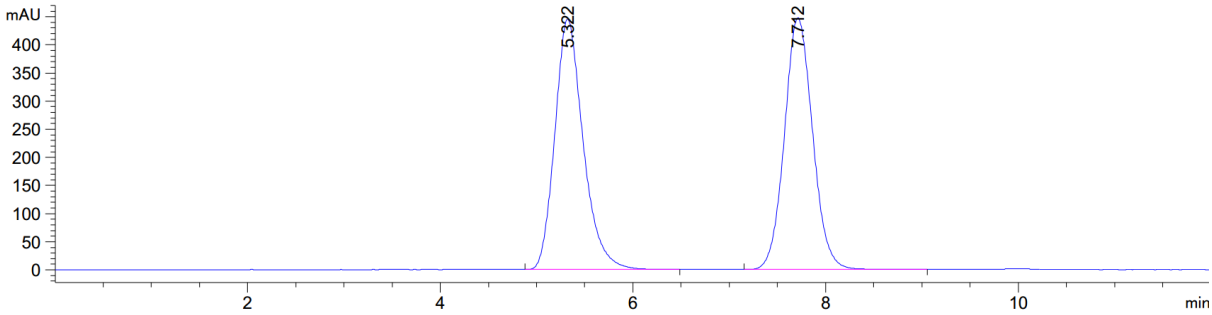
1a (21.7 mg, 25.00 µmol, 1 mol%), Bu_4NCl (13.9 mg, 50.0 µmol, 2 mol%) and alkene **3d** (107 mg, 0.5 mmol, 0.2 equiv.) were weighed in an oven dried tube containing a magnetic stirring bar. The tube was sealed with a rubber septum, evacuated and backfilled with nitrogen. At 23 °C dry THF (0.5 mL) was added and the mixture was stirred for two minutes. The color changed from brown to deep red. After cooling down to 0° a solution of alkene **3d** (500 mg, 2.0 mmol, 1.0 equiv.) and alkyne **4c** (506 mg, 2.0 mmol, 1.0 equiv.) in THF (2.0 mL) were added. After completion of the reaction the mixture was purified directly by silica gel chromatography eluting with pentane/Et_2O 20:1 to afford the cyclobutene product **5dc**.

(−)-Methyl (1*S*,5*S*,6*R*)-4-phenyltricyclo[4.2.1.02,5]non-3-ene-3-carboxylate (**5aa**):

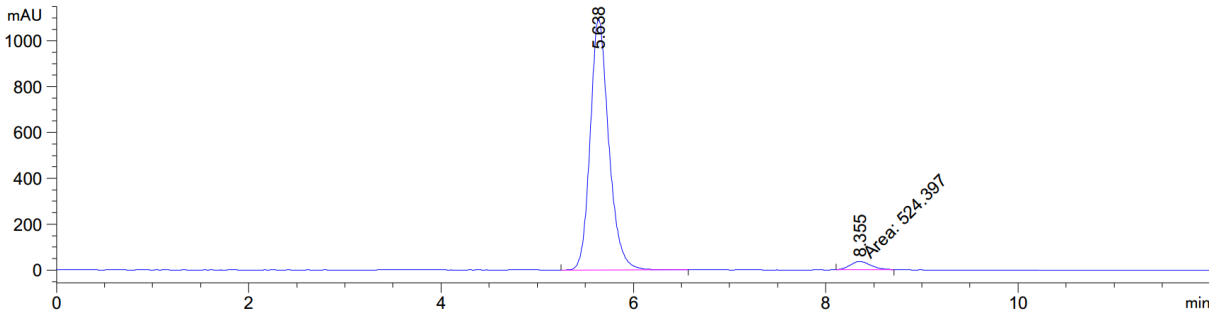


Obtained as colorless oil in 97% yield (25.3 mg). **^{1}H NMR** (400 MHz, $CDCl_3$) δ (ppm) = 8.08 – 7.98 (m, 2H), 7.46 – 7.32 (m, 3H), 3.79 (s, 3H), 2.81 (d, *J* = 3.7 Hz, 1H), 2.70 (d, *J* = 3.7 Hz, 1H), 2.34 – 2.16 (m, 2H), 1.71 – 1.59 (m, 2H), 1.44 – 1.33 (m, 1H), 1.26 – 1.15 (m, 2H), 1.09 – 0.99 (m, 1H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ (ppm) = 163.6, 156.2, 132.8, 130.0, 129.0, 128.5, 128.4, 51.3, 46.8, 46.1, 34.9, 34.4, 30.7, 28.5, 28.5; **IR (ATR):** $\tilde{\nu}$ 2950, 2870, 1707, 1220, 1204, 1132, 770 cm^{-1}; **HRMS (ESI)** calculated for $[C_{17}H_{18}O_2+H]^+$: 255.1380, found: 255.1385; **R_f:** 0.70 (pentane/EtOAc 6:1); **$[\alpha]_D^{20}$:** - 24.2° (c = 1.0, $CHCl_3$) ; **m.p.:** 64 °C.

Chiral HPLC: Chiralpak IA, 4.6 x 250 mm; 1% *i*-PrOH / hexane, 1.0 mL/min, 234 nm; t_R (major) = 5.6 min, t_R (minor) = 8.4 min, 96.5:3.5 er.

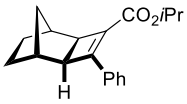


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	5.322	BB	0.3084	9094.88770	445.13443	49.9828
2	7.712	BB	0.3153	9101.16016	447.39795	50.0172



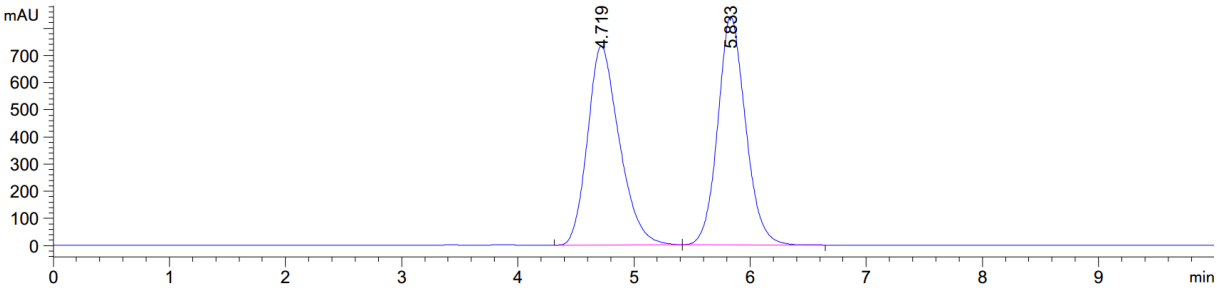
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	5.638	BB	0.2042	1.46746e4	1096.05530	96.5498
2	8.355	MM	0.2464	524.39691	35.47718	3.4502

(−)-Isopropyl (1*S*,5*S*,6*R*)-4-phenyltricyclo[4.2.1.02,5]non-3-ene-3-carboxylate (**5ab**):

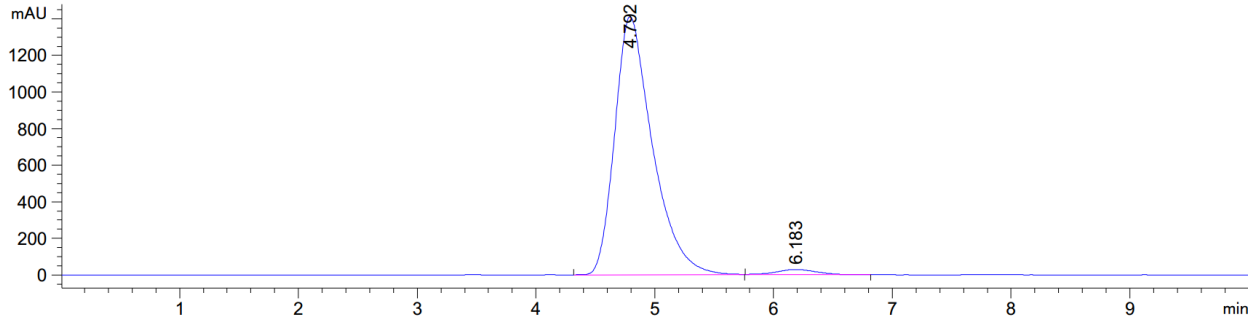


Obtained as colorless oil in 86% yield (24.2 mg). **^{1}H NMR** (400 MHz, $CDCl_3$) δ (ppm) = 8.10 – 7.98 (m, 2H), 7.43 – 7.30 (m, 3H), 5.11 (hept, *J* = 6.3 Hz, 1H), 2.79 (d, *J* = 3.7 Hz, 1H), 2.69 (d, *J* = 3.6 Hz, 1H), 2.30 – 2.25 (m, 1H), 2.25 – 2.21 (m, 1H), 1.70 – 1.61 (m, 2H), 1.43 – 1.36 (m, 1H), 1.32 (d, *J* = 6.2 Hz, 3H), 1.31 (d, *J* = 6.3 Hz, 3H), 1.25 – 1.18 (m, 2H), 1.07 – 1.00 (m, 1H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ (ppm) = 162.8, 155.3, 132.9, 129.8, 129.4, 129.0, 128.4, 67.4, 46.6, 46.2, 34.9, 34.4, 30.7, 28.5, 28.5, 22.1; **IR (ATR):** $\tilde{\nu}$ 2952, 2870, 1698, 1614, 1219, 1203, 1103, 770, 692 cm^{-1}; **HRMS (ESI)** calculated for $[C_{19}H_{22}O_2+H]^+$: 283.1693, found: 283.1691; **R_f:** 0.90 (pentane/EtOAc 5:1); **$[\alpha]_D^{20}$:** - 19.8° (c = 1.0, $CHCl_3$).

Chiral HPLC: Chiralpak IA, 4.6 x 250 mm; 1% *i*-PrOH / hexane, 1.0 mL/min, 290 nm; t_R (major) = 4.8 min, t_R (minor) = 6.2 min, 98:2 er.

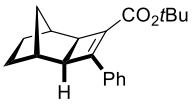


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	4.719	BB	0.2837	1.39336e4	733.19507	49.9696
2	5.833	BB	0.2519	1.39506e4	839.47131	50.0304



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	4.792	BB	0.3253	3.10645e4	1408.65967	98.0848
2	6.183	BB	0.3157	606.55957	27.46069	1.9152

(−)-*tert*-butyl (1*S*,5*S*,6*R*)-4-phenyltricyclo[4.2.1.02,5]non-3-ene-3-carboxylate (**5ac**):

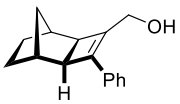


Obtained as colorless oil in 80% yield (23.6 mg). **^{1}H NMR** (400 MHz, $CDCl_3$) δ (ppm) = 8.05 – 7.96 (m, 2H), 7.43 – 7.30 (m, 3H), 2.75 (d, *J* = 3.5 Hz, 1H), 2.65 (d, *J* = 3.4 Hz, 1H), 2.26 (dt, *J* = 2.9, 1.5 Hz, 1H), 2.23 (dt, *J* = 2.9, 1.5 Hz, 1H), 1.71 – 1.57 (m, 2H), 1.54 (s, 9H), 1.43 – 1.36 (m, 1H), 1.25 – 1.15 (m, 2H), 1.06 – 0.99 (m, 1H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ (ppm) = 162.8, 154.3, 133.0, 130.7, 129.7, 128.9, 128.3, 80.4, 46.5, 46.4, 34.9, 34.4, 30.7, 28.6, 28.5, 28.5; **IR (ATR):** $\tilde{\nu}$ 2953, 2870, 1697, 1367, 1227, 1172, 1161, 1134, 770, 692 cm^{-1}; **HRMS (APCI)** calculated for $[C_{20}H_{24}O_2]^+$: 296.1771, found: 296.1776; **R_f:** 0.90 (pentane/EtOAc 5:1); **m.p.:** 40-41 °C; **$[\alpha]_D^{20}$:** - 17.7° (c = 1.0, $CHCl_3$, 98:2 er).

The enantiomeric excess was determined after reduction to the corresponding alcohol:

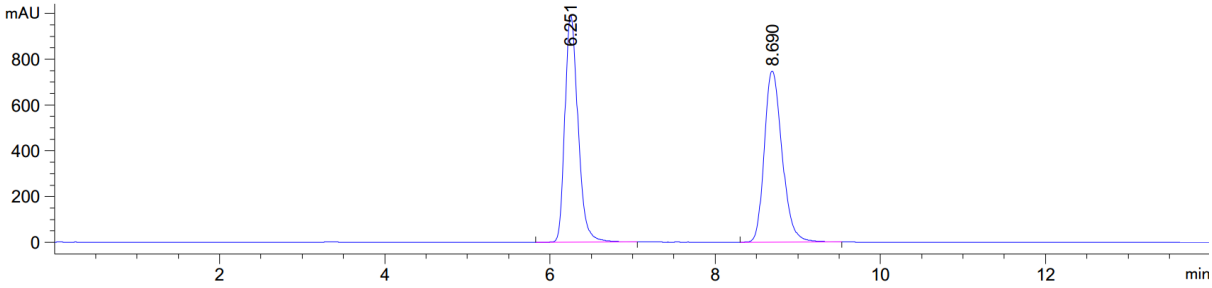
(−)-((1*S*,5*S*,6*R*)-4-phenyltricyclo[4.2.1.02,5]non-3-en-3-yl)methanol (**5ac-OH**):

To a solution of **5ac** (10.5 mg, 35 µmol, 1.0 equiv.) in toluene was added DIBAL-H (1.2 M in toluene, 62 µL, 74 µmol, 2.1 equiv.) at -78 °C under nitrogen atmosphere. The solution was stirred at this temperature for 30 min and then gradually warmed to 0°C. Water, aq. sat. rochelle salt solution and ethyl acetate were added. The layers were separated, the aqueous layer was extracted with ethyl acetate (3x), combined organic layers were dried over $MgSO_4$ and the solvent was removed under reduced pressure. Purification by column chromatography over silica gel delivered allylic alcohol **5ac-OH** (6.8 mg, 30 µmol, 85% yield).



^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) = 7.37 – 7.30 (m, 4H), 7.25 – 7.18 (m, 1H), 4.47 (d, *J* = 14.0 Hz, 1H), 4.40 (d, *J* = 14.0 Hz, 1H), 2.77 – 2.69 (m, 1H), 2.59 (d, *J* = 3.6 Hz, 1H), 2.20 (dt, *J* = 3.1, 1.5 Hz, 1H), 2.14 (dt, *J* = 3.0, 1.5 Hz, 1H), 1.62 (dt, *J* = 6.4, 2.0 Hz, 2H), 1.44 (dt, *J* = 10.2, 2.1 Hz, 1H), 1.39 (s, 1H), 1.23 – 1.08 (m, 2H), 1.02 (dt, *J* = 10.2, 1.4 Hz, 1H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ (ppm) = 140.8, 140.3, 134.6, 128.6, 127.4, 126.7, 59.2, 46.7, 46.5, 34.7, 34.4, 30.8, 28.7, 28.4; **IR (ATR):** $\tilde{\nu}$ 2948, 2921, 2868, 1492, 1446, 1297, 1034, 990, 769, 692 cm^{-1}; **HRMS (APCI)** calculated for $[C_{16}H_{18}O]^+$: 226.1352, found: 226.1345; **R_f:** 0.30 (pentane/EtOAc 6:1); **$[\alpha]_D^{20}$:** - 23.3° (c = 0.35, $CHCl_3$).

Chiral HPLC: Chiralpak OJH, 4.6 x 250 mm; 10% *i*-PrOH / hexane, 1.0 mL/min, 264 nm; t_R (major) = 6.3 min, t_R (minor) = 8.8 min, 98:2 er.



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
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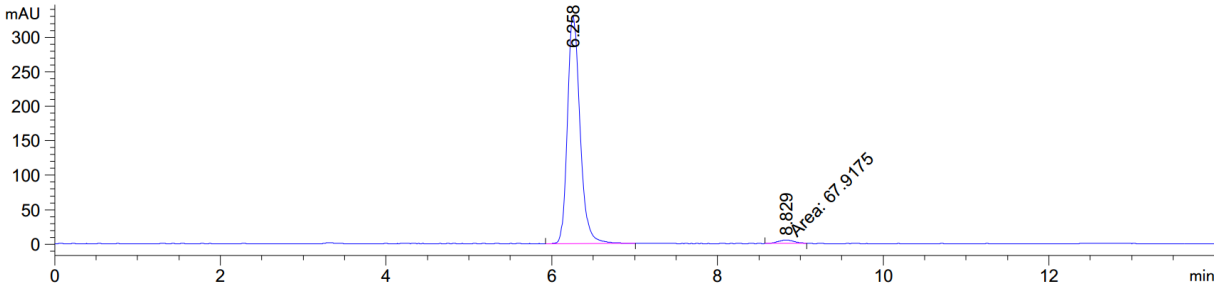
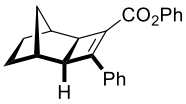
2	8.690	BB	0.2330	1.11877e4	745.92792	50.4990

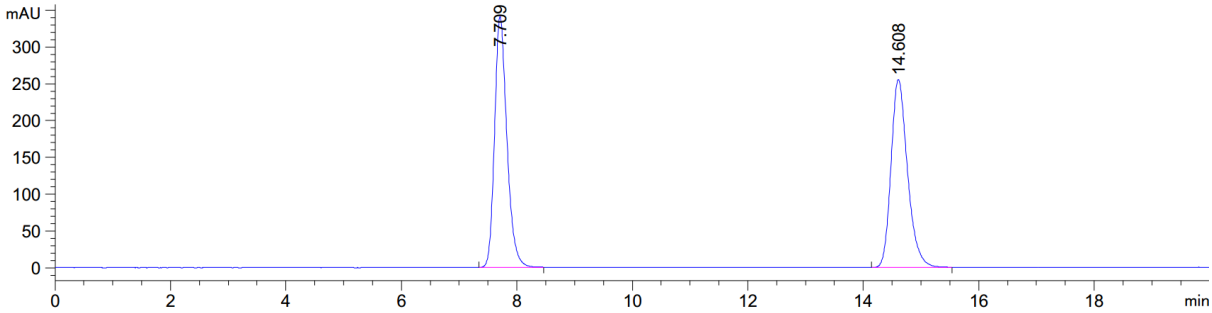


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	6.258	BB	0.1613	3489.35034	330.28983	98.0907
2	8.829	MM	0.2258	67.91749	5.01325	1.9093

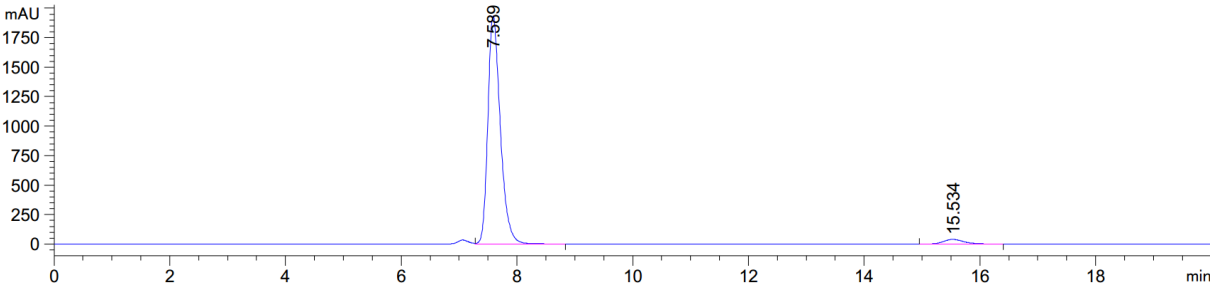
(−)-Phenyl (1*S*,5*S*,6*R*)-4-phenyltricyclo[4.2.1.02,5]non-3-ene-3-carboxylate (**5ad**):



Obtained as colorless oil in 76% yield (24.1 mg). **^{1}H NMR** (400 MHz, $CDCl_3$) δ (ppm) = 8.12 – 8.03 (m, 2H), 7.46 – 7.34 (m, 5H), 7.25 – 7.21 (m, 1H), 7.21 – 7.13 (m, 2H), 2.91 (d, *J* = 3.7 Hz, 1H), 2.87 (d, *J* = 3.8 Hz, 1H), 2.44 – 2.39 (m, 1H), 2.34 – 2.28 (m, 1H), 1.75 – 1.63 (m, 2H), 1.53 – 1.46 (m, 1H), 1.34 – 1.18 (m, 2H), 1.15 – 1.09 (m, 1H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ (ppm) = 161.3, 158.9, 150.8, 132.6, 130.4, 129.5, 129.3, 128.5, 127.6, 125.8, 121.9, 47.1, 46.3, 35.1, 34.5, 30.8, 28.5; **IR (ATR):** $\tilde{\nu}$ 2952, 1720, 1489, 1191, 1163, 1122, 689 cm^{-1}; **HRMS (ESI)** calculated for $[C_{22}H_{20}O_2+H]^+$: 317.1536, found: 317.1563; **R_f:** 0.50 (pentane/Et_2O 8:1); **m.p.:** 44-45 °C; **$[\alpha]_D^{20}$**: - 6.0° (c = 1.0, $CHCl_3$). Chiral HPLC: Chiralpak IA, 4.6 x 250 mm; 1% *i*-PrOH / hexane, 1.0 mL/min, 296 nm; t_R (major) = 7.6 min, t_R (minor) = 15.5 min, 97:3 er.

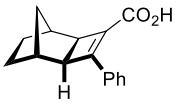


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	7.709	BB	0.2246	5038.44727	340.47116	49.8953
2	14.608	BB	0.3034	5059.59668	255.08295	50.1047



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	7.589	VB	0.2264	2.89055e4	1933.49231	96.7558
2	15.534	BB	0.3596	969.20050	39.32123	3.2442

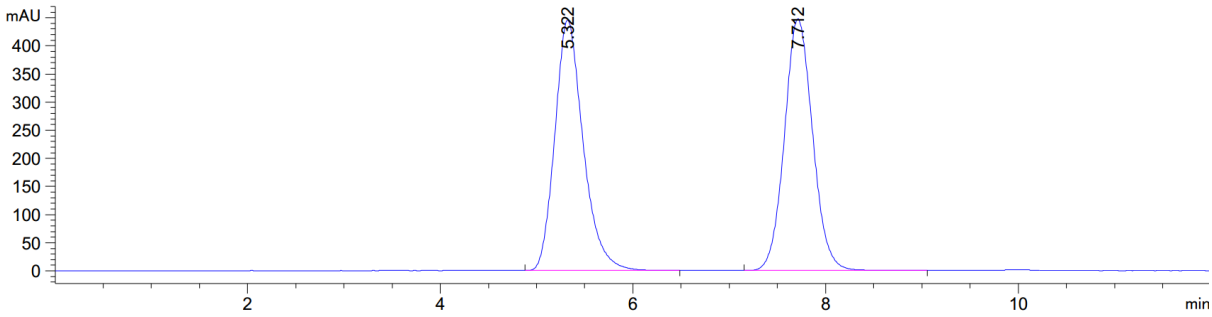
(−)-(1*S*,5*S*,6*R*)-4-phenyltricyclo[4.2.1.02,5]non-3-ene-3-carboxylic acid (**5ae**):



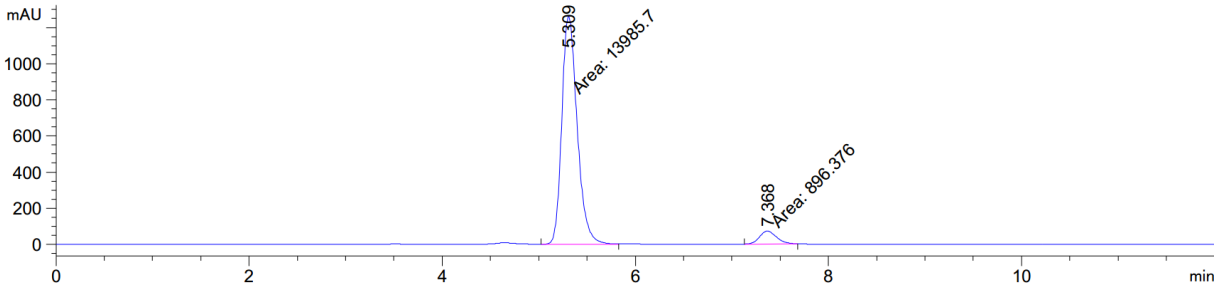
Obtained as white soild in 89% yield (21.5 mg). **^{1}H NMR** (400 MHz, $CDCl_3$) δ (ppm) = 12.17 (bs, 1H), 8.10 – 8.01 (m, 2H), 7.46 – 7.35 (m, 3H), 2.85 (d, *J* = 3.7 Hz, 1H), 2.76 (d, *J* = 3.6 Hz, 1H), 2.42 – 2.31 (m, 1H), 2.30 – 2.24 (m, 1H), 1.74 – 1.59 (m, 2H), 1.47 – 1.38 (m, 1H), 1.31 – 1.16 (m, 2H), 1.13 – 1.04 (m, 1H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ (ppm) = 167.6, 158.8, 132.6, 130.4, 129.3, 128.5, 127.7, 47.0, 46.0, 35.0, 34.3, 30.8, 28.5, 28.5; **IR (ATR):** $\tilde{\nu}$ 953, 2870, 1670, 1609, 1492, 1234, 771, 690 cm^{-1}; **HRMS (ESI)** calculated for $[C_{16}H_{16}O_2\text{-}H]^-$: 239.1078, found: 239.1072; **R_f:** 0.90 (pentane/EtOAc 1:1 + 1% AcOH); **m.p.:** 149 °C; **$[\alpha]_D^{20}$:** - 40.4° (c = 1.0, $CHCl_3$, 94:6 er).

The enantiomeric excess was determined after conversion to the corresponding methylester:

To a solution of **5ae** (2.6 mg, 11 µmol, 1.0 equiv.) in a mixture of toluene (32 µL) and methanol (22 µL) was added TMS-diazomethane (2 M in Et_2O, 22.6 µL, 43 µmol, 4.0 equiv.) at 23 °C under nitrogen atmosphere. The solution was stirred at this temperature for 30 min and then all volatiles were removed under reduced pressure. Purification by column chromatography over silica gel delivered methyl ester **5aa** in quantitative yield. (Characterization see page 14). Chiral HPLC: Chiralpak IA, 4.6 x 250 mm; 1% *i*-PrOH / hexane, 1.0 mL/min, 234 nm; t_R (major) = 5.3 min, t_R (minor) = 7.4 min, 94:6 er.

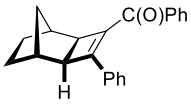


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	5.322	BB	0.3084	9094.88770	445.13443	49.9828
2	7.712	BB	0.3153	9101.16016	447.39795	50.0172



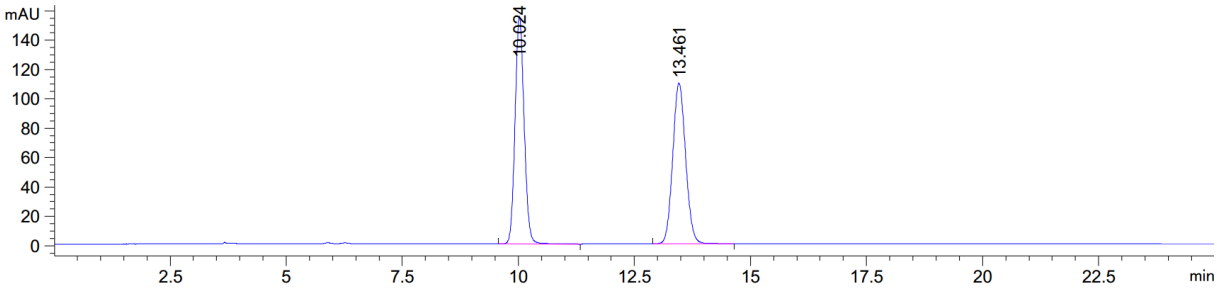
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	5.309	MM	0.1842	1.39857e4	1265.47058	93.9768
2	7.368	MM	0.2059	896.37610	72.56498	6.0232

(−)-Phenyl((1*S*,5*S*,6*R*)-4-phenyltricyclo[4.2.1.02,5]non-3-en-3-yl)methanone (**5af**):

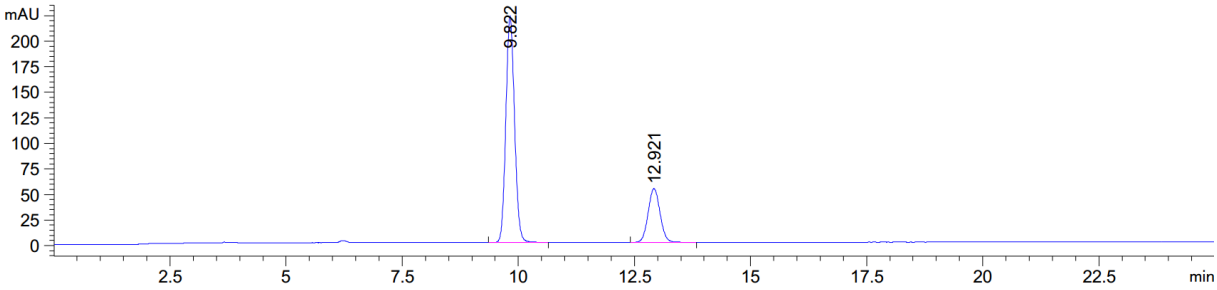


Obtained as colorless oil in 98% yield (30.0 mg). **^{1}H NMR** (400 MHz, $CDCl_3$) δ (ppm) = 7.91 – 7.84 (m, 2H), 7.64 – 7.56 (m, 2H), 7.51 – 7.44 (m, 1H), 7.37 (dd, *J* = 8.3, 7.0 Hz, 2H), 7.31 – 7.21 (m, 3H), 2.97 – 2.92 (m, 2H), 2.29 – 2.23 (m, 1H), 2.23 – 2.17 (m, 1H), 1.69 – 1.56 (m, 2H), 1.50 (dt, *J* = 10.5, 2.1 Hz, 1H), 1.30 – 1.15 (m, 2H), 1.05 (dt, *J* = 10.5, 1.5 Hz, 1H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ (ppm) = 191.2, 154.3, 138.3, 136.5, 133.0, 132.5, 129.8, 129.0, 128.9, 128.5, 128.3, 48.2, 47.4, 35.4, 35.0, 31.0, 28.6, 28.5; **IR (ATR):** $\tilde{\nu}$ 2951, 2869, 1636, 1597, 1579, 1558, 1489, 1447, 1228, 899, 734, 692 cm^{-1}; **HRMS (APCI)** calculated for $[C_{22}H_{20}O]^+$: 300.1509, found: 300.1514; **R_f:** 0.50 (pentane/Et_2O 10:1); **$[\alpha]_D^{20}$:** - 12.0° (c = 1.0, $CHCl_3$).

Chiral HPLC: Chiralpak IC, 4.6 x 250 mm; 2% *i*-PrOH / hexane, 1.0 mL/min, 288 nm; t_R (major) = 9.8 min, t_R (minor) = 12.9 min, 75.5:24.5 er.

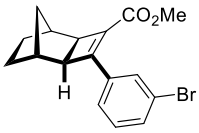


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	10.024	BB	0.2126	2106.53027	154.92740	50.0325
2	13.461	BB	0.3006	2103.79419	109.28017	49.9675



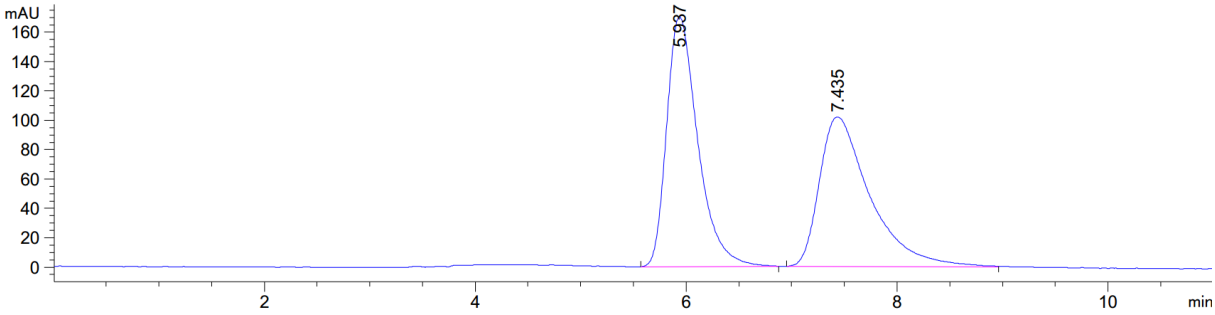
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	9.822	BB	0.2013	2867.83740	221.13652	75.5503
2	12.921	BB	0.2759	928.09247	52.58828	24.4497

(−)-Methyl (1*S*,5*S*,6*R*)-4-(3-bromophenyl)tricyclo[4.2.1.02,5]non-3-ene-3-carboxylate (**5ag**):

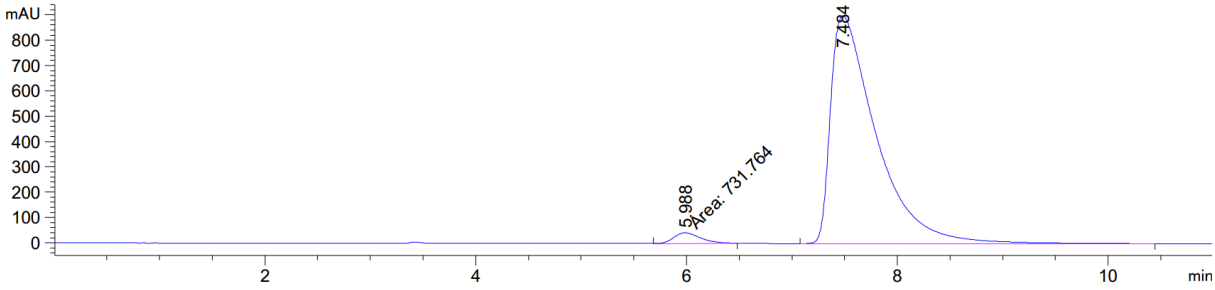


Obtained as colorless oil in 85% yield (28.4 mg). **^{1}H NMR** (400 MHz, $CDCl_3$) δ (ppm) = 8.16 (t, *J* = 1.7 Hz, 1H), 7.99 (dt, *J* = 7.9, 1.3 Hz, 1H), 7.49 (ddd, *J* = 8.0, 2.0, 1.0 Hz, 1H), 7.31 – 7.21 (m, 1H), 3.80 (s, 3H), 2.79 (d, *J* = 3.7 Hz, 1H), 2.71 (d, *J* = 3.7 Hz, 1H), 2.30 – 2.26 (m, 1H), 2.26 – 2.21 (m, 1H), 1.70 – 1.62 (m, 2H), 1.36 (dt, *J* = 10.6, 2.0 Hz, 1H), 1.25 – 1.18 (m, 2H), 1.11 – 1.03 (m, 1H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ (ppm) = 163.3, 154.3, 134.6, 132.8, 131.7, 130.0, 127.5, 122.6, 51.5, 46.8, 46.3, 34.8, 34.3, 30.7, 28.4, 28.4; **IR (ATR):** $\tilde{\nu}$ 2948, 2870, 1706, 1616, 1556, 1471, 1217, 1204, 1185, 1132, 1105, 780 cm^{-1}; **HRMS (APCI)** calculated for $[C_{17}H_{17}BrO_2+H]^+$: 333.0485, found: 333.0487; **R_f:** 0.65 (pentane/EtOAc 8:1); **$[\alpha]_D^{20}$:** - 14.1° (c = 1.0, $CHCl_3$).

Chiral HPLC: Chiralpak AYH, 4.6 x 250 mm; 1% *i*-PrOH / hexane, 1.0 mL/min, 288 nm; t_R (minor) = 6.0 min, t_R (major) = 7.5 min, 97.5:2.5 er.



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	5.937	BB	0.3113	3488.84058	170.10147	50.7214
2	7.435	BV	0.4829	3389.60059	101.69250	49.2786

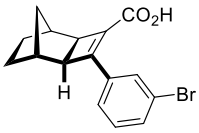


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	5.988	MM	0.2913	731.76373	41.86873	2.6294
2	7.484	BV	0.4474	2.70978e4	899.71820	97.3706

The absolute configuration of **5ag** was determined by single crystal X-Ray analysis after saponification to the corresponding carboxylic acid:

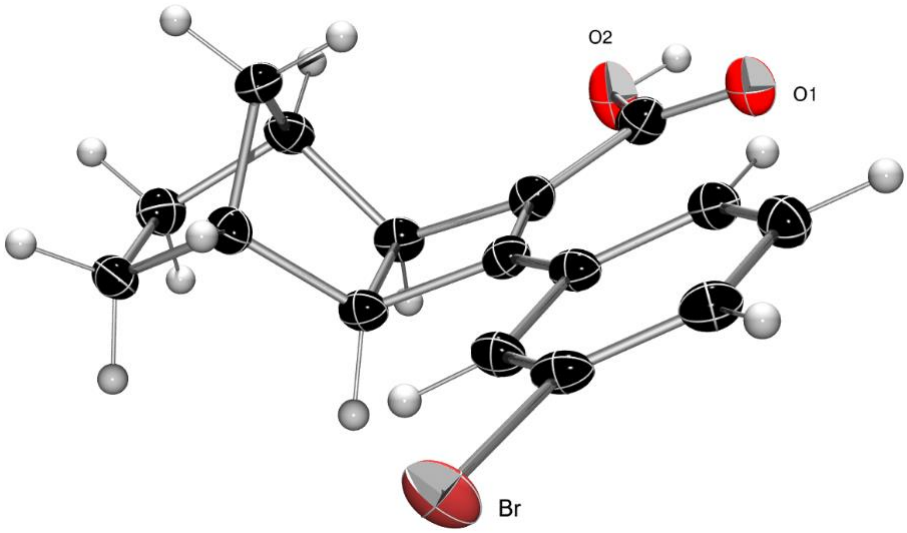
To a solution of **5ag** (16.0 mg, 48 µmol, 1.0 equiv.) in a THF (240 µL) was added a 5% aq. LiOH solution (180 µL) at 23 °C. The solution was stirred at 40 °C for 30 h and then diluted with ethyl acetate and acidified with 1 M HCl. The layers were separated, the aqueous layer was extracted with ethyl acetate (3x), combined organic layers were dried over $MgSO_4$ and the solvent was removed under reduced pressure. Purification by column chromatography over silica gel (pentane/EtOAc 8:1 + 1% AcOH) delivered acid **5ag-CO_2H** (14.2 mg, 44 µmol, 93% yield).

(−)-(1*S*,5*S*,6*R*)-4-(3-bromophenyl)tricyclo[4.2.1.02,5]non-3-ene-3-carboxylic acid (**5ag-CO_2H**):

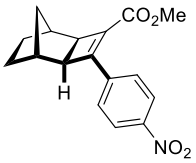


^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) = 8.09 (t, *J* = 1.8 Hz, 1H), 8.02 (dt, *J* = 7.8, 1.3 Hz, 1H), 7.50 (ddd, *J* = 8.0, 2.0, 1.0 Hz, 1H), 7.31 – 7.24 (m, 1H), 2.82 (d, *J* = 3.7 Hz, 1H), 2.76 (d, *J* = 3.7 Hz, 1H), 2.37 – 2.31 (m, 1H), 2.28 – 2.23 (m, 1H), 1.73 – 1.57 (m, 2H), 1.42 – 1.34 (m, 1H), 1.27 – 1.20 (m, 2H), 1.12 – 1.06 (m, 1H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ (ppm) = 167.6, 156.9, 134.4, 133.2, 131.9, 130.1, 129.3, 127.9, 122.7, 47.0, 46.2, 34.9, 34.3, 30.7, 28.4, 28.4; **IR (ATR):** $\tilde{\nu}$ 2953, 2870, 1672, 1612, 1556, 1233, 785 cm^{-1}; **HRMS (APCI)** calculated for $[C_{16}H_{15}BrO_2\text{-}H]^-$: 317.0183, found: 317.0190; **R_f:** 0.50 (pentane/EtOAc 4:1 + 1% AcOH); **m.p.:** 113 °C; **$[\alpha]_D^{20}$:** - 25.3° (c = 1.0, $CHCl_3$, 97.5:2.5 er).

X-Ray: CCDC 1499170

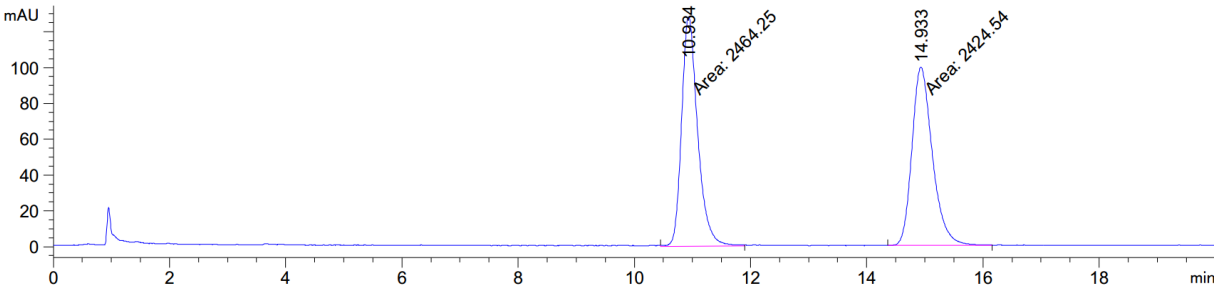


(−)-Methyl (1*S*,5*S*,6*R*)-4-(4-nitrophenyl)tricyclo[4.2.1.02,5]non-3-ene-3-carboxylate (**5ah**):

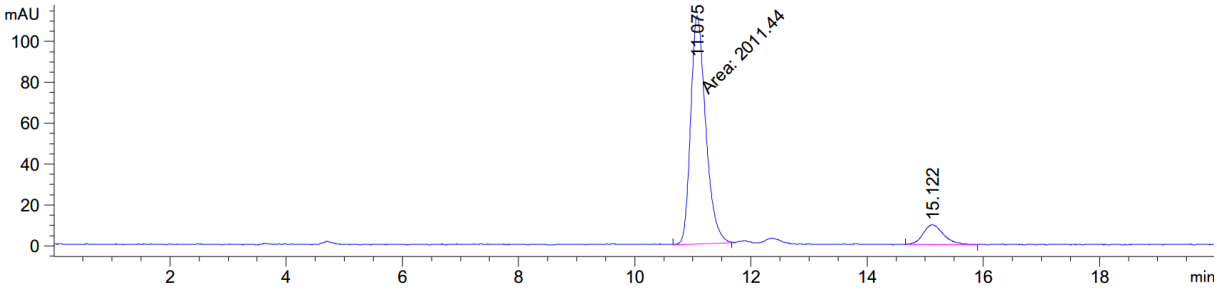


Obtained as yellow solid in 40% yield (12.1 mg). **^{1}H NMR** (400 MHz, $CDCl_3$) δ (ppm) = 8.25 – 8.20 (m, 2H), 8.20 – 8.15 (m, 2H), 3.81 (s, 3H), 2.88 – 2.82 (m, 1H), 2.76 (d, *J* = 3.7 Hz, 1H), 2.30 (dt, *J* = 3.2, 1.4 Hz, 1H), 2.25 (dt, *J* = 3.0, 1.4 Hz, 1H), 1.73 – 1.63 (m, 2H), 1.38 – 1.30 (m, 1H), 1.28 – 1.19 (m, 2H), 1.13 – 1.05 (m, 1H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ (ppm) = 163.1, 153.1, 148.1, 138.3, 133.2, 129.7, 123.8, 51.7, 47.0, 46.8, 34.7, 34.3, 30.7, 28.4, 28.3; **IR (ATR):** $\tilde{\nu}$ 2952, 2871, 1708, 1518, 1347, 1223, 1206, 854 cm^{-1}; **HRMS (APCI)** calculated for $[C_{17}H_{17}NO_4]^+$: 299.1152, found: 299.1157; **R_f:** 0.70 (pentane/EtOAc 6:1); **m.p.:** 91 °C; **$[\alpha]_D^{20}$:** - 53.3° (c = 0.3, $CHCl_3$).

Chiral HPLC: Chiralpak IA, 4.6 x 250 mm; 1% *i*-PrOH / hexane, 1.0 mL/min, 320 nm; t_R (major) = 11.0 min, t_R (minor) = 15.1 min, 89.5:10.5 er.

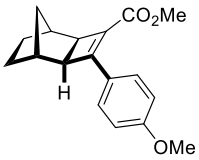


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	10.934	MM	0.3203	2464.25073	128.21194	50.4061
2	14.933	MM	0.4062	2424.54346	99.47559	49.5939



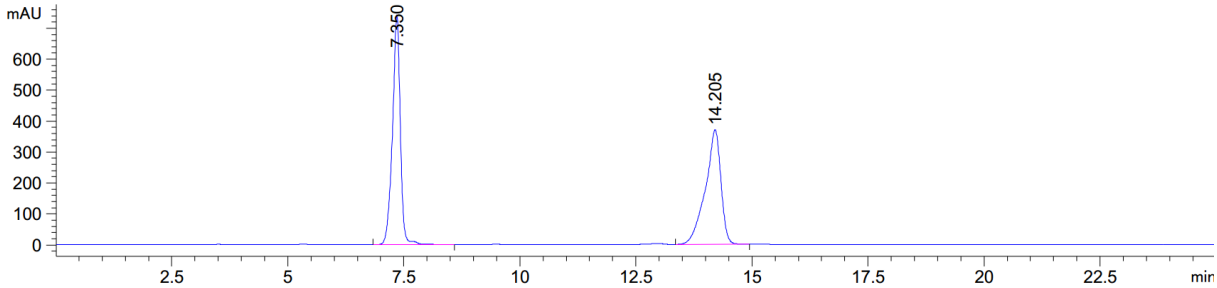
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	11.075	MM	0.3000	2011.44055	111.75826	89.5075
2	15.122	BV	0.3589	235.79160	9.58869	10.4925

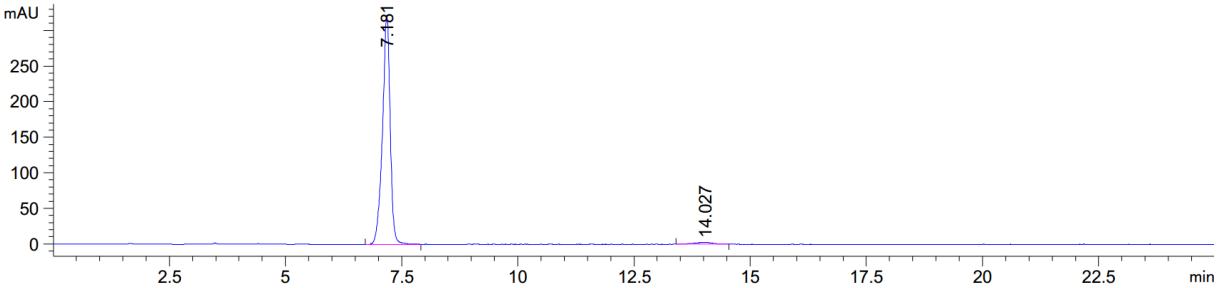
(−)-Methyl (1*S*,5*S*,6*R*)-4-(4-methoxyphenyl)tricyclo[4.2.1.02,5]non-3-ene-3-carboxylate (**5ai**):



Obtained as yellow oil in 91% yield (26.0 mg). **^{1}H NMR** (400 MHz, $CDCl_3$) δ (ppm) = 8.02 (d, *J* = 8.4 Hz, 2H), 6.90 (d, *J* = 8.4 Hz, 2H), 3.83 (s, 3H), 3.77 (s, 3H), 2.76 (d, *J* = 3.6 Hz, 1H), 2.67 (d, *J* = 3.6 Hz, 1H), 2.25 (s, 1H), 2.21 (s, 1H), 1.69 – 1.56 (m, 2H), 1.38 (d, *J* = 10.5 Hz, 1H), 1.23 – 1.15 (m, 2H), 1.02 (d, *J* = 10.4 Hz, 1H);**^{13}C NMR** (101 MHz, $CDCl_3$) δ (ppm) = 163.8, 161.0, 156.2, 130.9, 125.9, 125.6, 113.8, 55.4, 51.2, 46.7, 45.9, 35.0, 34.5, 30.8, 28.5; **IR (ATR):** $\tilde{\nu}$ 2952, 1702, 1604, 1508, 1255, 1220, 1204, 1175, 1133 cm^{-1}; **HRMS (APCI)** calculated for $[C_{18}H_{20}O_3]^+$: 284.1407, found: 284.1409; **R_f:** 0.70 (pentane/EtOAc 6:1); **$[\alpha]_D^{20}$:** - 40.3° (c = 1.0, $CHCl_3$).

Chiral HPLC: Chiralpak IA, 4.6 x 250 mm; 5% *i*-PrOH / hexane, 1.0 mL/min, 310 nm; t_R (major) = 7.2 min, t_R (minor) = 14.0 min, 98:2 er.

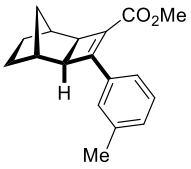




Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	7.350	BB	0.1755	8726.60547	740.42865	50.3549
2	14.205	BB	0.3333	8603.60938	369.92816	49.6451

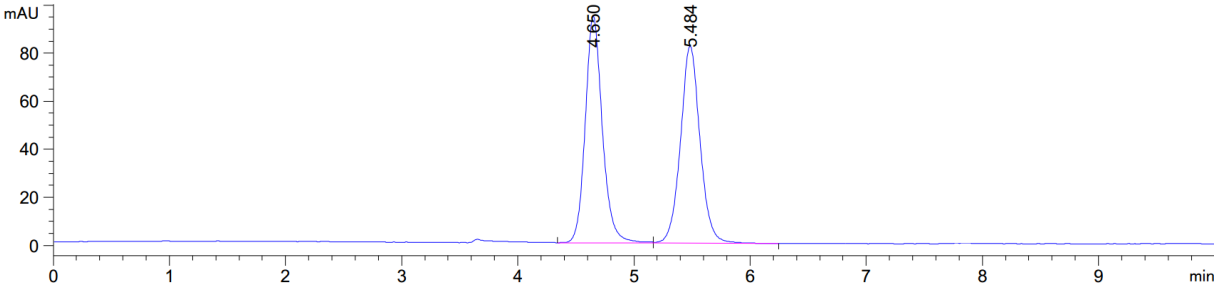
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	7.181	BB	0.1712	3735.11304	322.28958	97.9553
2	14.027	BB	0.3385	77.96602	2.87376	2.0447

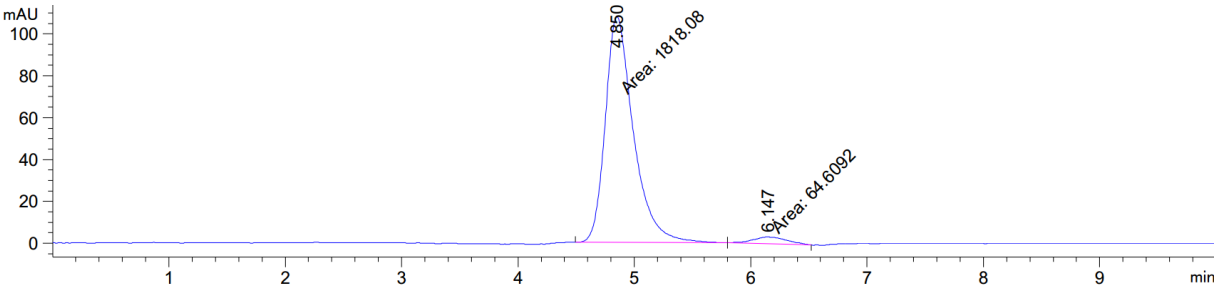
(−)-Methyl (1*S*,5*S*,6*R*)-4-(m-tolyl)tricyclo[4.2.1.02,5]non-3-ene-3-carboxylate (**5aj**):



Obtained as yellow oil in 93% yield (25.0 mg). **^{1}H NMR** (400 MHz, $CDCl_3$) δ (ppm) = 7.89 – 7.81 (m, 2H), 7.28 (t, *J* = 7.5 Hz, 1H), 7.18 (d, *J* = 7.6 Hz, 1H), 3.78 (s, 3H), 2.79 (d, *J* = 3.6 Hz, 1H), 2.68 (d, *J* = 3.6 Hz, 1H), 2.38 (s, 3H), 2.25 (d, *J* = 8.0 Hz, 2H), 1.69 – 1.58 (m, 2H), 1.39 (d, *J* = 10.5 Hz, 1H), 1.24 – 1.17 (m, 2H), 1.03 (d, *J* = 10.4 Hz, 1H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ (ppm) = 163.6, 156.4, 138.0, 132.7, 130.9, 129.5, 128.4, 128.2, 126.2, 51.3, 46.8, 46.1, 34.9, 34.4, 30.7, 28.5, 28.5, 21.6; **IR (ATR):** $\tilde{\nu}$ 2949, 2869, 1706, 1613, 1233, 1204, 1130, 780 cm^{-1}; **HRMS (APCI)** calculated for $[C_{18}H_{20}O_2+H]^+$: 269.1536, found: 269.1529; **R_f:** 0.70 (pentane/EtOAc 6:1); **$[\alpha]_D^{20}$:** - 24.0° (c = 1.0, $CHCl_3$).

Chiral HPLC: Chiralpak IA, 4.6 x 250 mm; 1% *i*-PrOH / hexane, 1.0 mL/min, 292 nm; t_R (major) = 4.8 min, t_R (minor) = 6.1 min, 96.5:3.5 er.

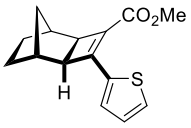




Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	4.650	BV	0.1554	967.53998	94.57198	50.1501
2	5.484	VB	0.1770	961.74982	81.87630	49.8499

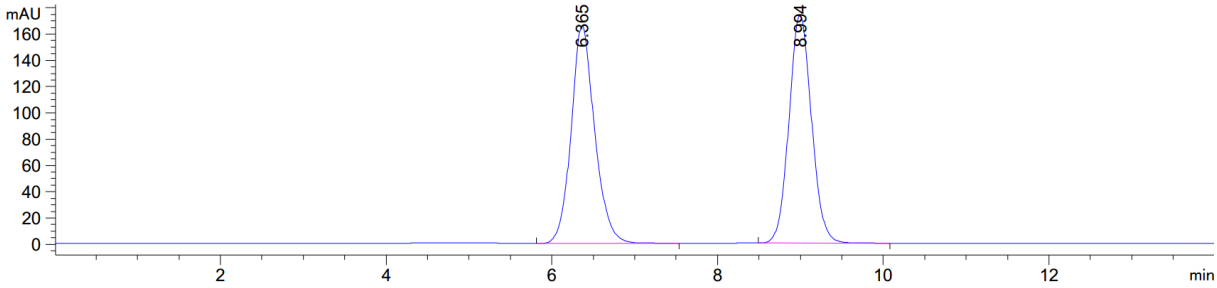
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	4.850	MM	0.2798	1818.07642	108.29026	96.5682
2	6.147	MM	0.3361	64.60916	3.20357	3.4318

(−)-Methyl (1*S*,5*S*,6*R*)-4-(thiophen-2-yl)tricyclo[4.2.1.02,5]non-3-ene-3-carboxylate (**5ak**):

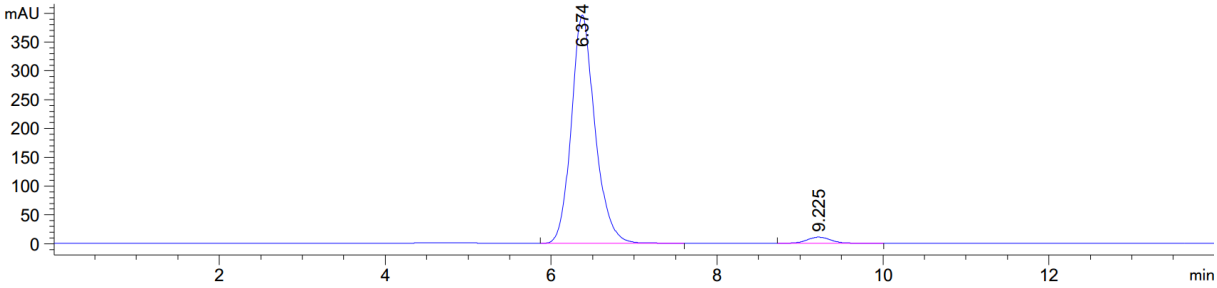


Obtained as colorless oil in 96% yield (25.0 mg). **^{1}H NMR** (400 MHz, $CDCl_3$) δ (ppm) = 7.58 (dd, *J* = 3.7, 1.2 Hz, 1H), 7.46 (dd, *J* = 5.1, 1.2 Hz, 1H), 7.07 (dd, *J* = 5.1, 3.7 Hz, 1H), 3.79 (s, 3H), 2.79 (d, *J* = 3.4 Hz, 1H), 2.73 (d, *J* = 3.7 Hz, 1H), 2.30 – 2.24 (m, 2H), 1.66 – 1.60 (m, 2H), 1.43 – 1.35 (m, 1H), 1.22 – 1.13 (m, 2H), 1.09 – 1.02 (m, 1H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ (ppm) = 163.5, 148.8, 136.0, 130.4, 130.1, 127.4, 124.2, 51.2, 47.9, 46.4, 34.9, 34.5, 30.9, 28.4, 28.2; **IR (ATR):** $\tilde{\nu}$ 2949, 2869, 1701, 1612, 1233, 1223, 1200, 1131, 1044, 708 cm^{-1}; **HRMS (ESI)** calculated for $[C_{15}H_{16}O_2S+H]^+$: 261.0944, found: 261.0949; **R_f:** 0.50 (pentane/Et_2O 8:1); **$[\alpha]_D^{20}$:** - 32.0° (c = 1.0, $CHCl_3$).

Chiral HPLC: Chiralpak IA, 4.6 x 250 mm; 1% *i*-PrOH / hexane, 1.0 mL/min, 316 nm; t_R (major) = 6.4 min, t_R (minor) = 9.2 min, 97.5:2.5 er.

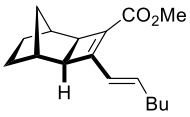


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	6.365	BB	0.2939	3265.51538	165.72089	49.8962
2	8.994	BB	0.2949	3279.10059	173.19914	50.1038



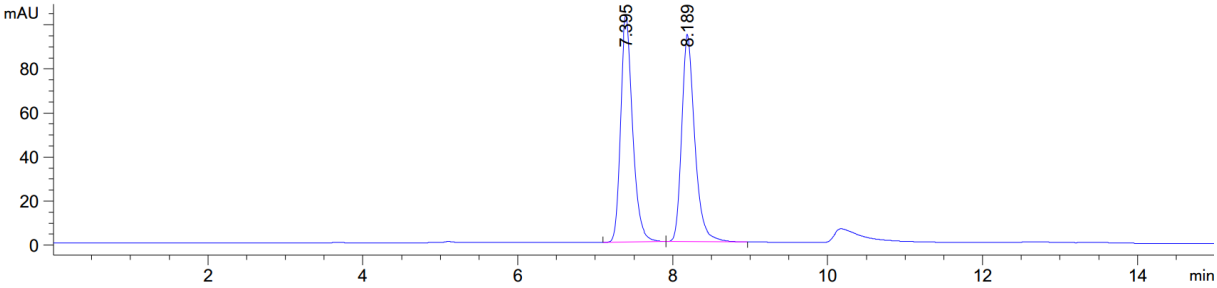
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	6.374	BB	0.2948	7835.24951	396.09171	97.4131
2	9.225	BB	0.3014	208.07501	10.58330	2.5869

(+)-Methyl (1*S*,5*S*,6*R*)-4-((*E*)-hex-1-en-1-yl)tricyclo[4.2.1.02,5]non-3-ene-3-carboxylate (**5al**):

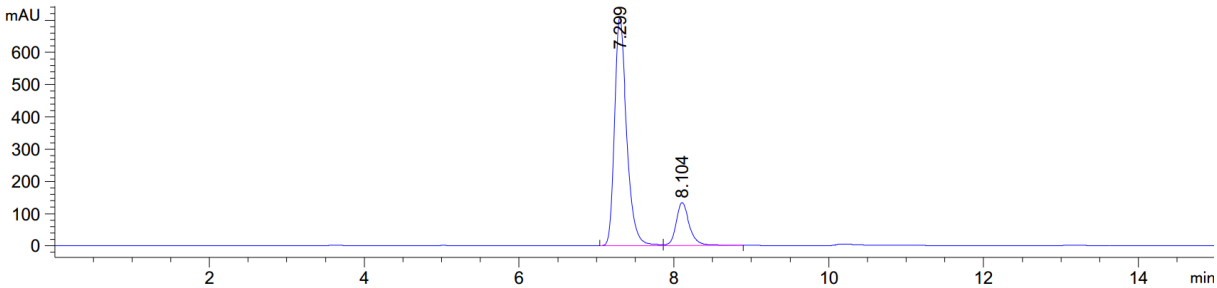


Obtained as colorless oil in 88% yield (23.0 mg). **^{1}H NMR** (400 MHz, $CDCl_3$) δ (ppm) = 6.56 (d, *J* = 15.8 Hz, 1H), 6.18 – 5.97 (m, 1H), 3.71 (s, 3H), 2.59 (d, *J* = 3.6 Hz, 1H), 2.56 (d, *J* = 3.6 Hz, 1H), 2.23 – 2.13 (m, 3H), 2.09 (d, *J* = 3.4 Hz, 1H), 1.64 – 1.50 (m, 2H), 1.46 – 1.24 (m, 5H), 1.17 – 1.05 (m, 2H), 1.01 (d, *J* = 10.4 Hz, 1H), 0.90 (t, *J* = 7.2 Hz, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ (ppm) = 163.9, 156.3, 141.1, 126.5, 123.4, 51.0, 46.4, 46.0, 34.7, 34.2, 32.8, 31.1, 30.9, 28.4, 28.3, 22.5, 14.1; **IR (ATR):** $\tilde{\nu}$ 2952, 2871, 1709, 1644, 1434, 1227, 1192, 1117, 973 cm^{-1}; **HRMS (APCI)** calculated for $[C_{17}H_{24}O_2]^+$: 260.1771, found: 260.1764; **R_f:** 0.20 (pentane/DCM 3:1); **$[\alpha]_D^{20}$:** + 35.5° (c = 1.0, $CHCl_3$).

Chiral HPLC: Chiralpak IA, 4.6 x 250 mm; 0.5% *i*-PrOH / hexane, 1.0 mL/min, 272 nm; t_R (minor) = 9.6 min, t_R (major) = 12.0 min, 83:17 er.

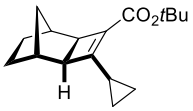


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	7.395	BB	0.1637	1109.27661	102.93884	50.0095
2	8.189	BB	0.1796	1108.85583	94.03324	49.9905



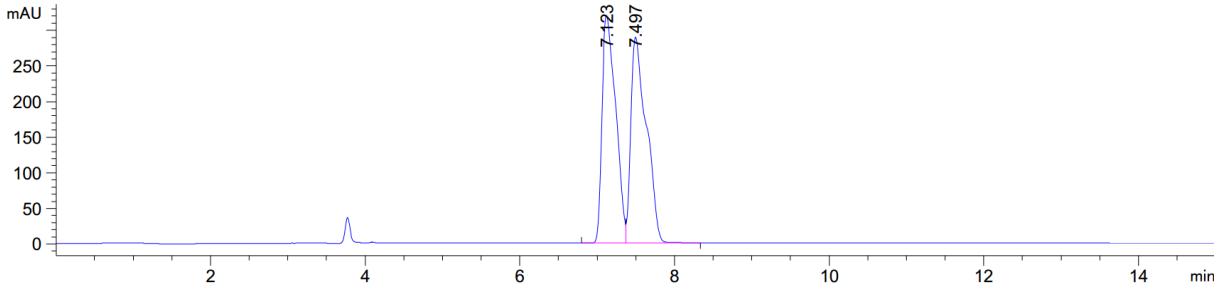
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	7.299	BV	0.1642	7657.50244	707.94055	82.9698
2	8.104	VB	0.1778	1571.75830	133.02415	17.0302

(+)-*tert*-butyl (1*S*,5*S*,6*R*)-4-cyclopropyltricyclo[4.2.1.02,5]non-3-ene-3-carboxylate (**5am**):

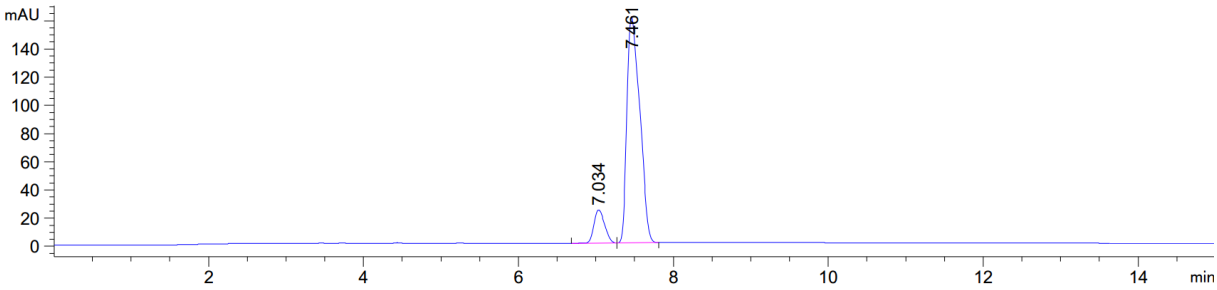


Obtained as colorless oil in 91% yield (23.8 mg). **^{1}H NMR** (400 MHz, $CDCl_3$) δ (ppm) = 2.46 (d, *J* = 3.5 Hz, 1H), 2.21 – 2.07 (m, 3H), 1.91 – 1.84 (m, 1H), 1.54 – 1.50 (m, 2H), 1.49 (s, 9H), 1.39 (dt, *J* = 10.4, 2.0 Hz, 1H), 1.10 – 0.92 (m, 3H), 0.89 – 0.76 (m, 2H), 0.76 – 0.61 (m, 2H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ (ppm) = 163.4, 163.3, 130.7, 79.7, 45.6, 45.4, 34.7, 34.4, 30.6, 28.5, 28.4, 28.2, 11.5, 7.4, 7.1; **IR (ATR):** $\tilde{\nu}$ 2952, 2870, 1698, 1643, 1365, 1236, 1172, 1137, 1121, 1031 cm^{-1}; **HRMS (APCI)** calculated for $[C_{17}H_{24}O_2+Na]^+$: 283.1669, found: 283.1672; **R_f:** 0.50 (pentane/Et_2O 8:1); **$[\alpha]_D^{20}$:** + 39.9° (c = 1.0, $CHCl_3$).

Chiral HPLC: Chiralpak IC, 4.6 x 250 mm; 0.5% *i*-PrOH / hexane, 1.0 mL/min, 244 nm; t_R (minor) = 7.0 min, t_R (major) = 7.5 min, 89:11 er.

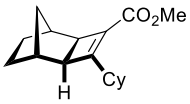


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	7.123	BV	0.1773	3929.10889	319.84192	49.4598
2	7.497	VB	0.1960	4014.94385	289.15137	50.5402



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	7.034	BB	0.1575	229.62617	23.59650	11.1153
2	7.461	BB	0.1655	1836.22375	160.42242	88.8847

(−)-Methyl (1*S*,5*S*,6*R*)-4-cyclohexyltricyclo[4.2.1.02,5]non-3-ene-3-carboxylate (**5an**):

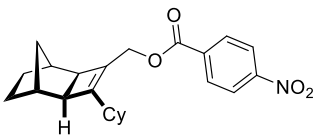


Obtained as yellow oil in 70% yield (18.3 mg). **^{1}H NMR** (400 MHz, $CDCl_3$) δ (ppm) = δ 3.70 (s, 3H), 2.75 (dt, *J* = 12.1, 6.4 Hz, 1H), 2.49 (d, *J* = 3.4 Hz, 1H), 2.41 (d, *J* = 3.4 Hz, 1H), 2.15 (s, 1H), 2.08 (s, 1H), 1.80 – 1.63 (m, 5H), 1.55 (d, *J* = 9.0 Hz, 2H), 1.38 – 1.32 (m, 1H), 1.33 – 1.10 (m, 5H), 1.12 – 1.01 (m, 2H), 0.98 (d, *J* = 10.3 Hz, 1H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ (ppm) = 168.7, 163.6, 128.0, 50.9, 47.4, 45.7, 39.1, 34.7, 34.1, 31.0, 30.6, 30.6, 28.5, 28.1, 26.1, 26.1, 25.9; **IR (ATR):** $\tilde{\nu}$ 2926, 2869, 2852, 1715, 1641, 1448, 1434, 1339, 1263, 1215, 1191, 1119 cm^{-1}; **HRMS (APCI)** calculated for $[C_{17}H_{24}O_2+H]^+$: 261.1849, found: 261.1837; **R_f:** 0.70 (pentane/EtOAc 6:1); **$[\alpha]_D^{20}$:** - 17.2° (c = 1.0, $CHCl_3$).

The enantiomeric excess was determined after reduction to the corresponding alcohol and esterification:

(+)-((1*S*,5*S*,6*R*)-4-cyclohexyltricyclo[4.2.1.02,5]non-3-en-3-yl)methyl 4-nitrobenzoate (**5an-benzoate**):

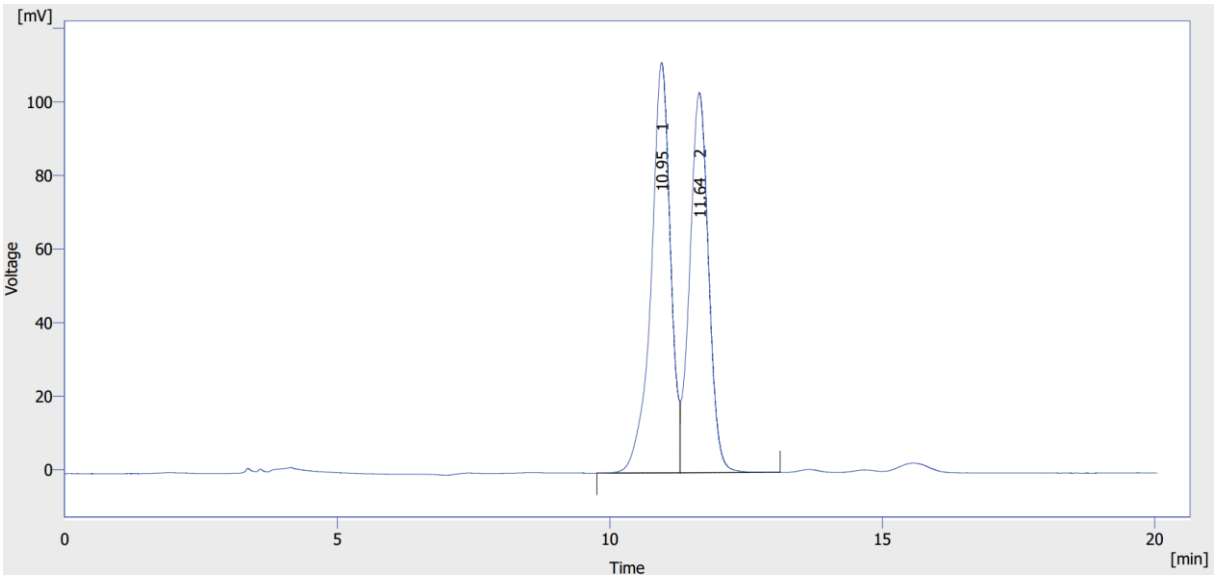
To a solution of **5an** (10.5 mg, 40 µmol, 1.0 equiv.) in toluene (202 µL) was added DIBAL-H (1.2 M in toluene, 70.6 µL, 85 µmol, 2.1 equiv.) at -78 °C under nitrogen atmosphere. The solution was stirred at this temperature for 30 min and then gradually warmed to 0°C. Water, aq. sat. rochelle salt solution and ethyl acetate were added. The layers were separated, the aqueous layer was extracted with ethyl acetate (3x), combined organic layers were dried over Na_2SO_4 and the solvent was removed under reduced pressure. The crude alcohol was passed through a short silica plug and dissolved in dry DCM (32 µL). Triethylamine (22.5 µL, 161 µmol, 4.0 equiv.) and 4-nitrobenzoyl chloride (22.5 mg, 121 µmol, 3.0 equiv.) were added at 23 °C under nitrogen atmosphere. After 30 min aq. sat. $NaHCO_3$ solution and DCM were added. The layers were separated, the aqueous layer was extracted with DCM (3x), combined organic layers were dried over $MgSO_4$ and the solvent was removed under reduced pressure. Purification by column chromatography over silica gel (pentane/Et_2O 40:1) delivered nitrobenzoate **5an-benzoate** as colorless oil (14.2 mg, 37 µmol, 92% yield over both steps).

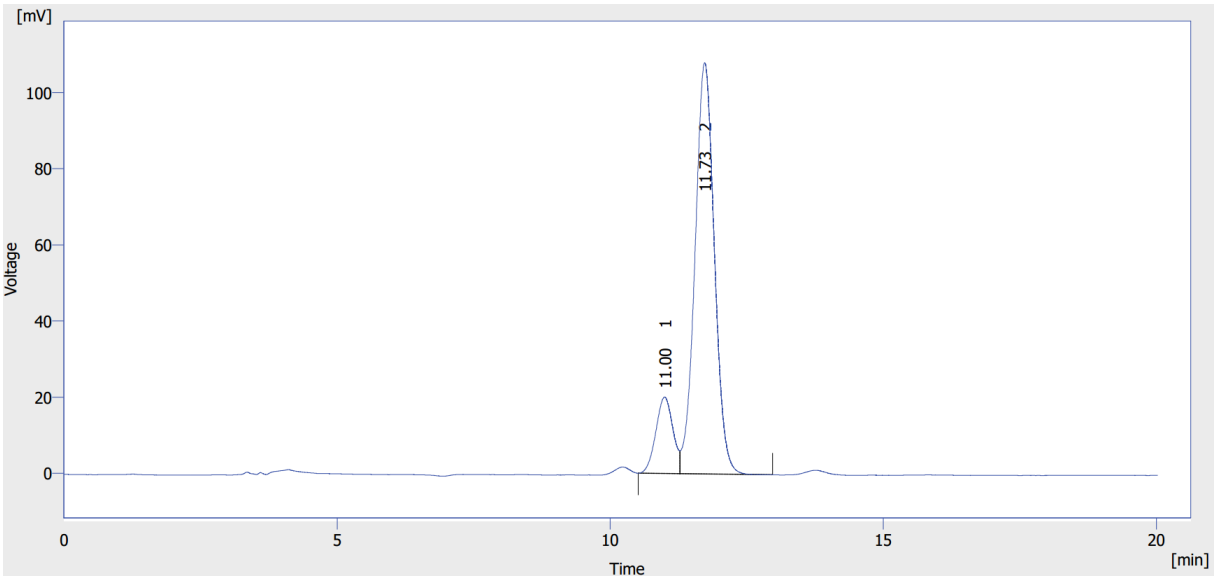


^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) = 8.30 (d, *J* = 8.5 Hz, 2H), 8.21 (d, *J* = 8.5 Hz, 2H), 4.85 (d, *J* = 12.9 Hz, 1H), 4.78 (d, *J* = 12.9 Hz, 1H), 2.39 (d, *J* = 3.4 Hz, 1H), 2.35 (d, *J* = 3.4 Hz, 1H), 2.26 – 2.16 (m, 1H), 2.02 (s, 1H), 1.98 (s, 1H), 1.78 – 1.69 (m, 4H), 1.65 (d, *J* = 11.2 Hz, 1H), 1.61 – 1.41 (m, 3H), 1.32 – 1.16 (m, 5H), 1.06 – 0.98 (m, 2H), 0.95 (d, *J* = 10.0 Hz, 1H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ (ppm) = 164.8, 152.7, 150.6, 136.0, 132.0, 130.8, 123.7, 61.0, 47.4, 46.8, 38.3, 34.9, 34.2, 31.8, 31.3, 30.5, 28.5, 28.4, 26.3, 26.2, 26.2; **IR (ATR):** $\tilde{\nu}$ 2924, 2852, 1726, 1530, 1347,

1269, 1101, 719 cm^{-1}; **HRMS (ESI)** calculated for $[C_{16}H_{23}]^+$: 215.1794, found: 215.1792; **R_f:** 0.70 (pentane/EtOAc 5:1); **$[\alpha]_D^{20}$:** + 6.5° (c = 1.0, $CHCl_3$).

Chiral HPLC: Chiralpak OZH, 4.6 x 250 mm; 0.5% *i*-PrOH / hexane, 1.0 mL/min, 254 nm; t_R (minor) = 11.0 min, t_R (major) = 11.7 min, 86:14 er.

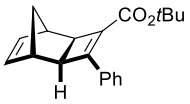




	Reten. Time [min]	Area [mV.s]	Height [mV]	Area [%]	Height [%]	W05 [min]
1	10.952	2740.677	111.553	52.4	51.9	0.36
2	11.643	2489.118	103.382	47.6	48.1	0.37
	Total	5229.795	214.936	100.0	100.0	

	Reten. Time [min]	Area [mV.s]	Height [mV]	Area [%]	Height [%]	W05 [min]
1	10.999	437.569	20.082	14.1	15.7	0.35
2	11.731	2668.055	108.040	85.9	84.3	0.38
	Total	3105.624	128.122	100.0	100.0	

(−)-*tert*-butyl (1*R*,5*S*,6*S*)-4-phenyltricyclo[4.2.1.02,5]nona-3,7-diene-3-carboxylate (**5bc**):

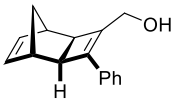


Obtained as colorless oil in 81% yield (23.7 mg). **^{1}H NMR** (400 MHz, $CDCl_3$) δ (ppm) = 8.08 – 8.01 (m, 2H), 7.45 – 7.32 (m, 3H), 6.24 (dd, *J* = 5.5, 2.9 Hz, 1H), 6.21 (dd, *J* = 5.6, 2.9 Hz, 1H), 2.76 – 2.69 (m, 2H), 2.64 (d, *J* = 3.9 Hz, 1H), 2.54 (d, *J* = 3.6 Hz, 1H), 1.56 (s, 9H), 1.42 – 1.37 (m, 1H), 1.37 – 1.31 (m, 1H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ (ppm) = ^{13}C NMR (101 MHz, $CDCl_3$) δ 162.9, 156.3, 136.8, 135.6, 132.8, 132.8, 129.9, 128.9, 128.4, 80.6, 43.2, 42.9, 40.0, 39.3, 39.1, 28.5; **IR (ATR):** $\tilde{\nu}$ 2974, 1696, 1367, 1230, 1216, 1167, 1130, 692 cm^{-1}; **HRMS (APCI)** calculated for $[C_{20}H_{22}O_2]^+$: 294.1614, found: 294.1620; **R_f:** 0.70 (pentane/Et_2O 8:1); **$[\alpha]_D^{20}$:** - 32.5° (c = 1.0, $CHCl_3$, 97:3 er).

The enantiomeric excess was determined after reduction to the corresponding alcohol:

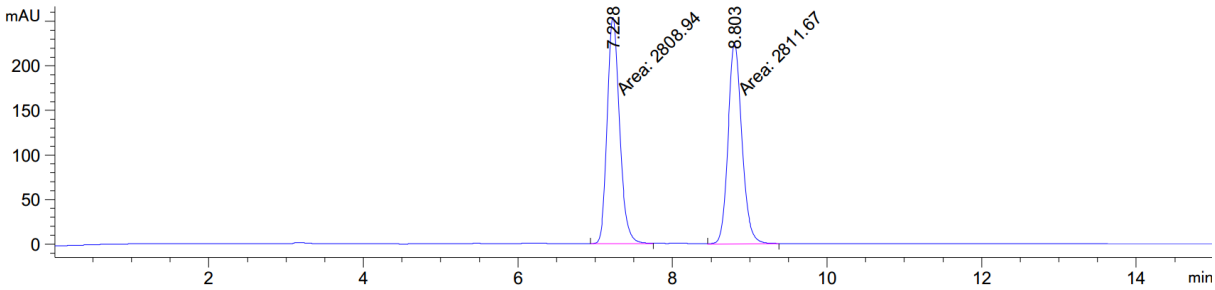
(−)-((1*R*,5*S*,6*S*)-4-phenyltricyclo[4.2.1.02,5]nona-3,7-dien-3-yl)methanol (**5bc-OH**):

To a solution of **5bc** (17.6 mg, 60 µmol, 1.0 equiv.) in toluene was added DIBAL-H (1.2 M in toluene, 105 µL, 126 µmol, 2.1 equiv.) at -78 °C under nitrogen atmosphere. The solution was stirred at this temperature for 30 min and then gradually warmed to 0°C. Water, aq. sat. rochelle salt solution and ethyl acetate were added. The layers were separated, the aqueous layer was extracted with ethyl acetate (3x), combined organic layers were dried over $MgSO_4$ and the solvent was removed under reduced pressure. Purification by column chromatography over silica gel (pentane/EtOAc 8:1) delivered allylic alcohol **5bc-OH** (9.1 mg, 41 µmol, 68% yield).

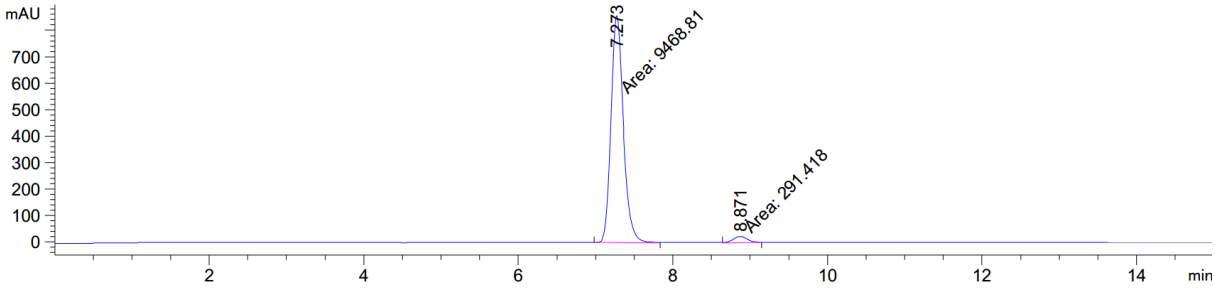


^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) = 7.43 – 7.33 (m, 4H), 7.28 – 7.22 (m, 1H), 6.23 – 6.15 (m, 2H), 4.57 (d, *J* = 14.2 Hz, 1H), 4.51 (d, *J* = 14.2 Hz, 1H), 2.68 (s, 1H), 2.66 – 2.59 (m, 2H), 2.47 (d, *J* = 3.7 Hz, 1H), 1.50 – 1.43 (m, 2H), 1.34 (dt, *J* = 9.1, 1.6 Hz, 1H);**^{13}C NMR** (101 MHz, $CDCl_3$) δ (ppm) = 142.7, 142.0, 136.1, 135.7, 134.3, 128.7, 127.6, 126.7, 59.4, 43.2, 42.9, 40.1, 39.2, 39.1; **IR (ATR):** $\tilde{\nu}$ 2968, 1654, 1448, 1321, 1036, 1023, 758, 695 cm^{-1}; **HRMS (APCI)** calculated for $[C_{16}H_{16}O]^+$: 224.1196, found: 224.1197; **R_f:** 0.50 (pentane/EtOAc 3:1); **$[\alpha]_D^{20}$:** - 45.0° (c = 0.3, $CHCl_3$).

Chiral HPLC: Chiralpak IA, 4.6 x 250 mm; 10% *i*-PrOH / hexane, 1.0 mL/min, 270 nm; t_R (major) = 7.3 min, t_R (minor) = 8.8 min, 97:3 er.

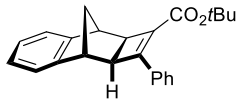


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	7.228	MM	0.1839	2808.93579	254.61382	49.9756
2	8.803	MM	0.2076	2811.67358	225.72432	50.0244



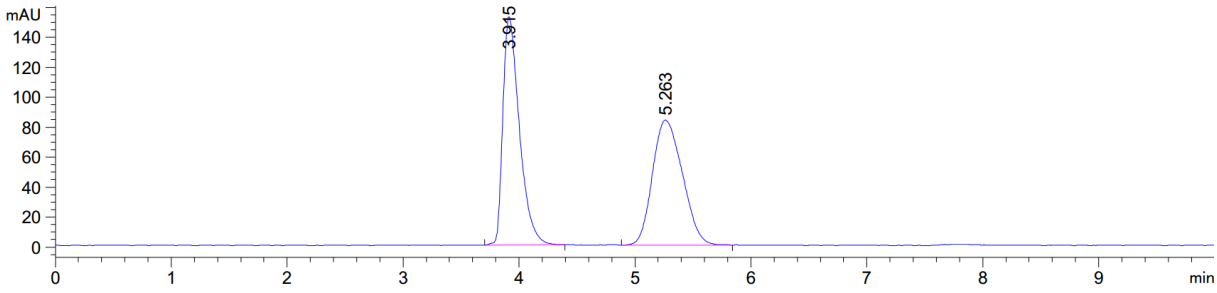
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	7.273	MM	0.1838	9468.80957	858.49847	97.0142
2	8.871	MM	0.2057	291.41776	23.61640	2.9858

(−)-*tert*-butyl (2*aS*,3*R*,8*S*)-2-phenyl-2a,3,8,8a-tetrahydro-3,8-methanocyclobuta[b]naphthalene-1-carboxylate (**5cc**):

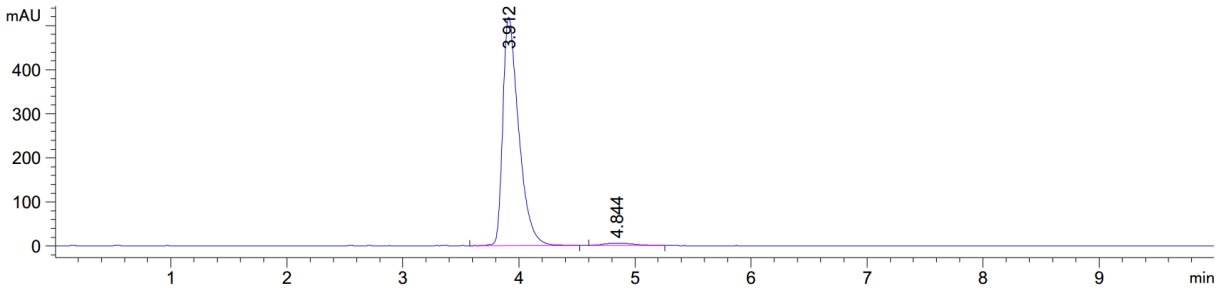


Obtained as white solid in 91% yield (31.5 mg). **^{1}H NMR** (400 MHz, $CDCl_3$) δ (ppm) = 8.13 – 8.06 (m, 2H), 7.47 – 7.35 (m, 3H), 7.30 – 7.22 (m, 2H), 7.14 – 7.07 (m, 2H), 3.26 (s, 1H), 3.24 (s, 1H), 2.81 (d, *J* = 3.5 Hz, 1H), 2.71 (d, *J* = 3.7 Hz, 1H), 1.81 (dt, *J* = 9.9, 1.5 Hz, 1H), 1.72 (dt, *J* = 9.8, 1.5 Hz, 1H), 1.59 (s, 9H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ (ppm) = 162.8, 154.5, 148.0, 147.4, 132.6, 131.2, 130.1, 129.1, 128.5, 125.9, 125.7, 121.7, 121.4, 80.9, 45.2, 44.9, 41.4, 41.3, 41.0, 28.5; **IR (ATR):** $\tilde{\nu}$ 2973, 1696, 1229, 1166, 1145, 1128, 766, 727, 691 cm^{-1}; **HRMS (APCI)** calculated for $[C_{24}H_{24}O_2]^+$: 344.1771, found: 344.1776; **R_f:** 0.60 (pentane/EtOAc 8:1); **m.p.:** 92-94 °C; **$[\alpha]_D^{20}$:** - 128.2° (c = 1.0, $CHCl_3$).

Chiral HPLC: Chiralpak IB, 4.6 x 250 mm; 1% *i*-PrOH / hexane, 1.0 mL/min, 298 nm; t_R (major) = 3.9 min, t_R (minor) = 4.8 min, 98:2 er.

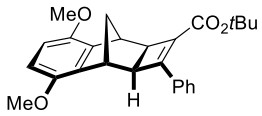


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	3.915	BB	0.1514	1506.86121	152.34244	50.2238
2	5.263	BB	0.2830	1493.42932	83.38171	49.7762



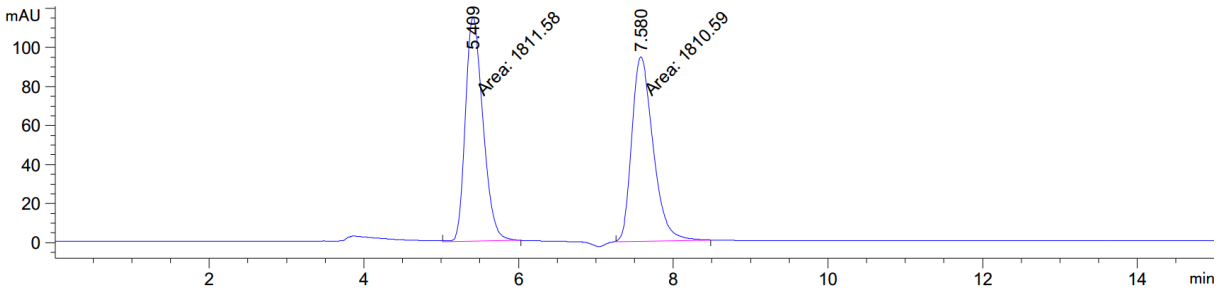
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	3.912	BB	0.1433	4945.11768	518.33606	98.0517
2	4.844	BB	0.2217	98.25859	5.41429	1.9483

(−)-*tert*-butyl (2*aS*,3*R*,8*S*)-4,7-dimethoxy-2-phenyl-2a,3,8,8a-tetrahydro-3,8-methanocyclobuta[b]naphthalene-1-carboxylate (**5dc**):

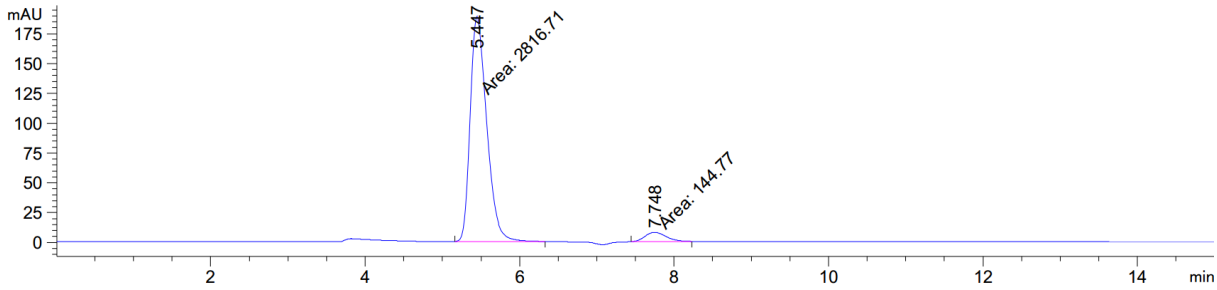


Obtained as colorless oil in 96% yield (38.9 mg). **^{1}H NMR** (400 MHz, $CDCl_3$) δ (ppm) = 8.15 – 8.08 (m, 2H), 7.46 – 7.35 (m, 3H), 6.69 – 6.59 (m, 2H), 3.84 (s, 3H), 3.82 (s, 3H), 3.56 – 3.51 (m, 1H), 3.51 – 3.47 (m, 1H), 2.82 (d, *J* = 3.4 Hz, 1H), 2.73 (d, *J* = 3.7 Hz, 1H), 1.79 (dt, *J* = 10.0, 1.5 Hz, 1H), 1.66 (dt, *J* = 9.8, 1.5 Hz, 1H), 1.59 (s, 9H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ (ppm) = 162.7, 154.7, 148.7, 148.7, 137.1, 136.2, 132.6, 131.5, 130.1, 129.1, 128.5, 110.6, 109.7, 80.8, 56.6, 56.2, 44.7, 44.3, 40.8, 38.0, 38.0, 28.5; **IR (ATR):** $\tilde{\nu}$ 2978, 2944, 2832, 1696, 1496, 1279, 1253, 1229, 1163, 1130, 1082, 764 cm^{-1}; **HRMS (APCI)** calculated for $[C_{26}H_{28}O_4]^+$: 404.1982, found: 404.1979; **R_f:** 0.40 (pentane/EtOAc 6:1); **$[\alpha]_D^{20}$:** - 105.3° (c = 1.0, $CHCl_3$).

Chiral HPLC: Chiralpak IB, 4.6 x 250 mm; 1% *i*-PrOH / hexane, 1.0 mL/min, 294 nm; t_R (major) = 5.4 min, t_R (minor) = 7.7 min, 95:5 er.

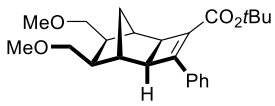


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	5.409	MM	0.2636	1811.57556	114.52752	50.0135
2	7.580	MM	0.3199	1810.59485	94.31976	49.9865



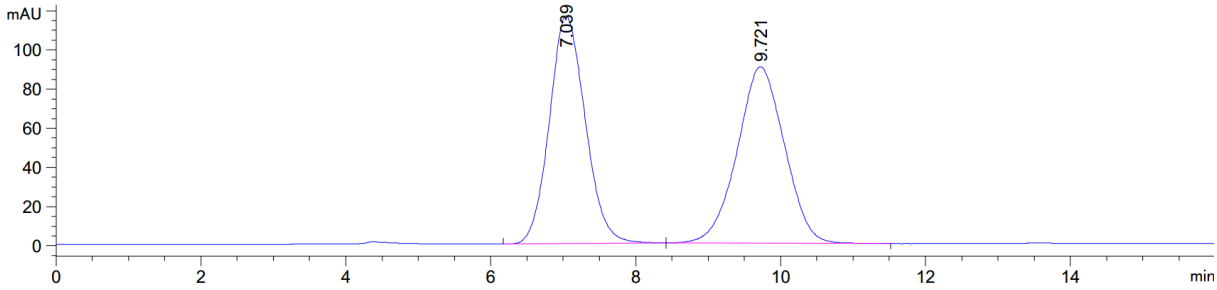
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	5.447	MM	0.2485	2816.70898	188.91588	95.1116
2	7.748	MM	0.3151	144.76997	7.65801	4.8884

(−)-*tert*-butyl (1*S*,5*S*,6*R*,7*R*,8*S*)-7,8-bis(methoxymethyl)-4-phenyltricyclo[4.2.1.02,5]non-3-ene-3-carboxylate (**5ec**):

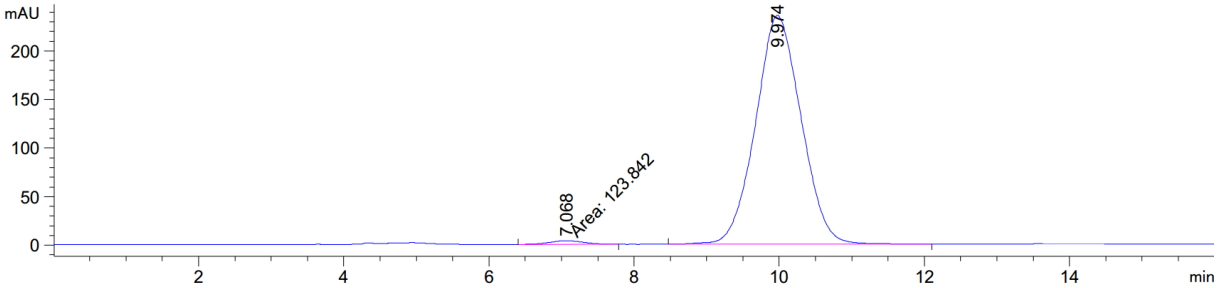


Obtained as white solid in 97% yield (37.3 mg). **^{1}H NMR** (400 MHz, $CDCl_3$) δ (ppm) = ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.05 – 7.95 (m, 2H), 7.40 – 7.30 (m, 3H), 3.53 – 3.47 (m, 1H), 3.44 – 3.37 (m, 1H), 3.34 (s, 3H), 3.32 (s, 3H), 3.32 – 3.23 (m, 2H), 2.82 (d, *J* = 3.3 Hz, 1H), 2.71 (d, *J* = 3.4 Hz, 1H), 2.25 (s, 1H), 2.22 – 2.17 (m, 1H), 1.94 – 1.84 (m, 2H), 1.53 (s, 9H), 1.27 (s, 2H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ (ppm) = 162.7, 154.1, 132.9, 130.4, 129.8, 129.0, 128.3, 80.6, 77.5, 77.2, 76.8, 73.0, 72.7, 58.9, 58.7, 46.3, 46.1, 44.7, 44.4, 38.4, 38.1, 28.5, 26.4; **IR (ATR):** $\tilde{\nu}$ 2974, 2924, 1695, 1226, 1172, 1136, 1104, 693 cm^{-1}; **HRMS (APCI)** calculated for $[C_{24}H_{32}O_4]^+$: 384.2295, found: 384.2295; **R_f:** 0.50 (pentane/EtOAc 6:1); **m.p.:** 96 °C; **$[\alpha]_D^{20}$:** - 13.7° (c = 1.0, $CHCl_3$).

Chiral HPLC: Chiralpak IA, 4.6 x 250 mm; 1% *i*-PrOH / hexane, 1.0 mL/min, 288 nm; t_R (minor) = 7.0 min, t_R (major) = 9.9 min, 99:1 er.

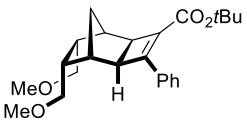


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	7.039	BB	0.5296	4004.96118	116.35474	49.5128
2	9.721	BB	0.6782	4083.78394	90.20544	50.4872



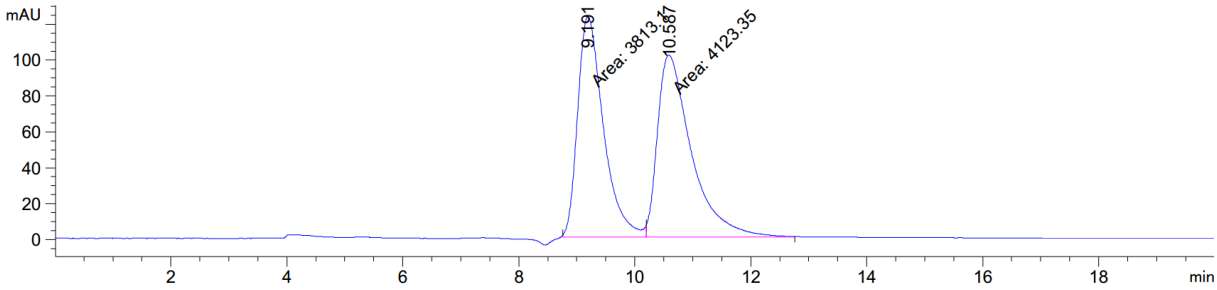
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	7.068	MM	0.5540	123.84190	3.72540	1.1915
2	9.974	BB	0.6668	1.02700e4	235.48444	98.8085

(−)-*tert*-butyl (1*S*,5*S*,6*R*,7*S*,8*R*)-7,8-bis(methoxymethyl)-4-phenyltricyclo[4.2.1.02,5]non-3-ene-3-carboxylate (**5fc**):

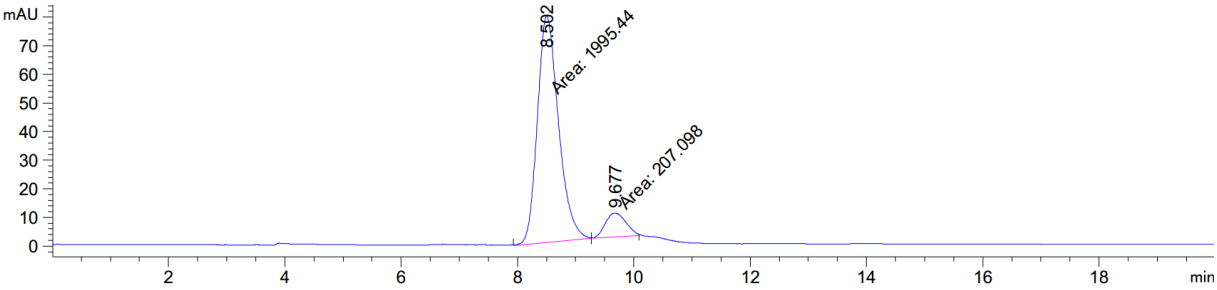


Obtained as colorless oil in 39% yield (14.8 mg). **^{1}H NMR** (400 MHz, $CDCl_3$) δ (ppm) = 8.02 – 7.94 (m, 2H), 7.41 – 7.29 (m, 3H), 3.55 – 3.48 (m, 2H), 3.45 (d, *J* = 5.8 Hz, 2H), 3.40 (s, 3H), 3.36 (s, 3H), 3.07 (d, *J* = 3.5 Hz, 1H), 2.89 (d, *J* = 3.5 Hz, 1H), 2.40 (d, *J* = 2.0 Hz, 4H), 1.57 – 1.54 (m, 1H), 1.53 (s, 9H), 1.17 – 1.10 (m, 1H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ (ppm) = 162.4, 153.8, 132.8, 129.8, 129.6, 129.0, 128.4, 80.5, 70.4, 69.9, 59.1, 58.9, 40.8, 40.1, 40.0, 39.9, 37.9, 37.8, 32.0, 28.4; **IR (ATR):** $\tilde{\nu}$ 2972, 2918, 1695, 1228, 1172, 1139, 1101, 771 cm^{-1}; **HRMS (APCI)** calculated for $[C_{24}H_{32}O_4]^+$: 384.2295, found: 384.2293; **R_f:** 0.40 (pentane/EtOAc 6:1); **$[\alpha]_D^{20}$:** - 30.1° (c = 1.0, $CHCl_3$).

Chiral HPLC: Chiralpak ID, 4.6 x 250 mm; 1% *i*-PrOH / hexane, 1.0 mL/min, 290 nm; t_R (minor) = 8.5 min, t_R (major) = 9.7 min, 90.5:9.5 er.

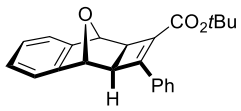


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	9.191	MF	0.5165	3813.10107	123.04875	48.0454
2	10.587	FM	0.6772	4123.34766	101.48427	51.9546



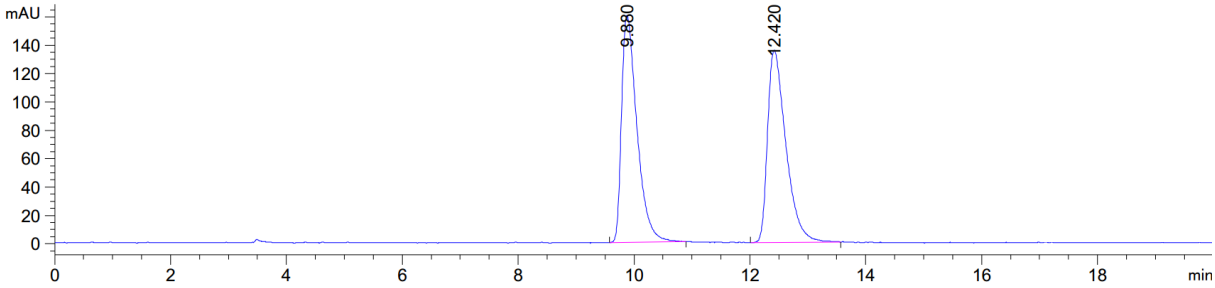
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	8.502	MM	0.4202	1995.43848	79.15076	90.5973
2	9.677	MM	0.4122	207.09776	8.37307	9.4027

(−)-*tert*-butyl (2*aS*,3*R*,8*S*)-2-phenyl-2a,3,8,8a-tetrahydro-3,8-epoxycyclobuta[b]naphthalene-1-carboxylate (**5gc**):

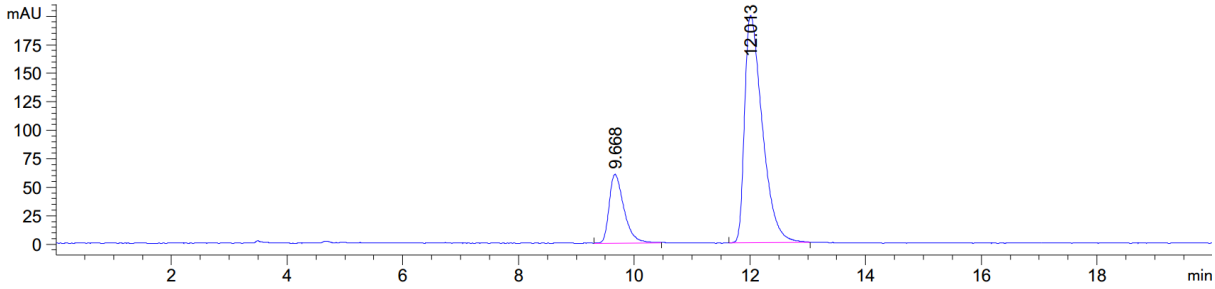


Obtained as colorless oil in 87% yield (30.2 mg). **^{1}H NMR** (400 MHz, $CDCl_3$) δ (ppm) = 8.13 – 8.05 (m, 2H), 7.48 – 7.40 (m, 3H), 7.39 – 7.32 (m, 2H), 7.24 – 7.17 (m, 2H), 5.20 (s, 1H), 5.15 (s, 1H), 3.00 (d, *J* = 3.6 Hz, 1H), 2.89 (d, *J* = 3.6 Hz, 1H), 1.60 (s, 9H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ (ppm) = 162.4, 153.3, 144.9, 144.5, 132.2, 130.3, 130.1, 129.0, 128.5, 127.0, 126.9, 120.1, 119.8, 81.3, 76.4, 76.3, 45.0, 44.6, 28.5; **IR (ATR):** $\tilde{\nu}$ 2974, 1696, 1249, 1219, 1161, 1125, 775, 738 cm^{-1}; **HRMS (APCI)** calculated for $[C_{23}H_{22}O_3]^+$: 346.1563, found: 346.1568; **R_f:** 0.50 (pentane/EtOAc 8:1); **m.p.:** 149-151 °C; **$[\alpha]_D^{20}$:** - 41.3.1° (c = 0.5, $CHCl_3$).

Chiral HPLC: Chiralpak IB, 4.6 x 250 mm; 2% *i*-PrOH / hexane, 1.0 mL/min, 292 nm; t_R (minor) = 9.6 min, t_R (major) = 12.0 min, 80:20 er.



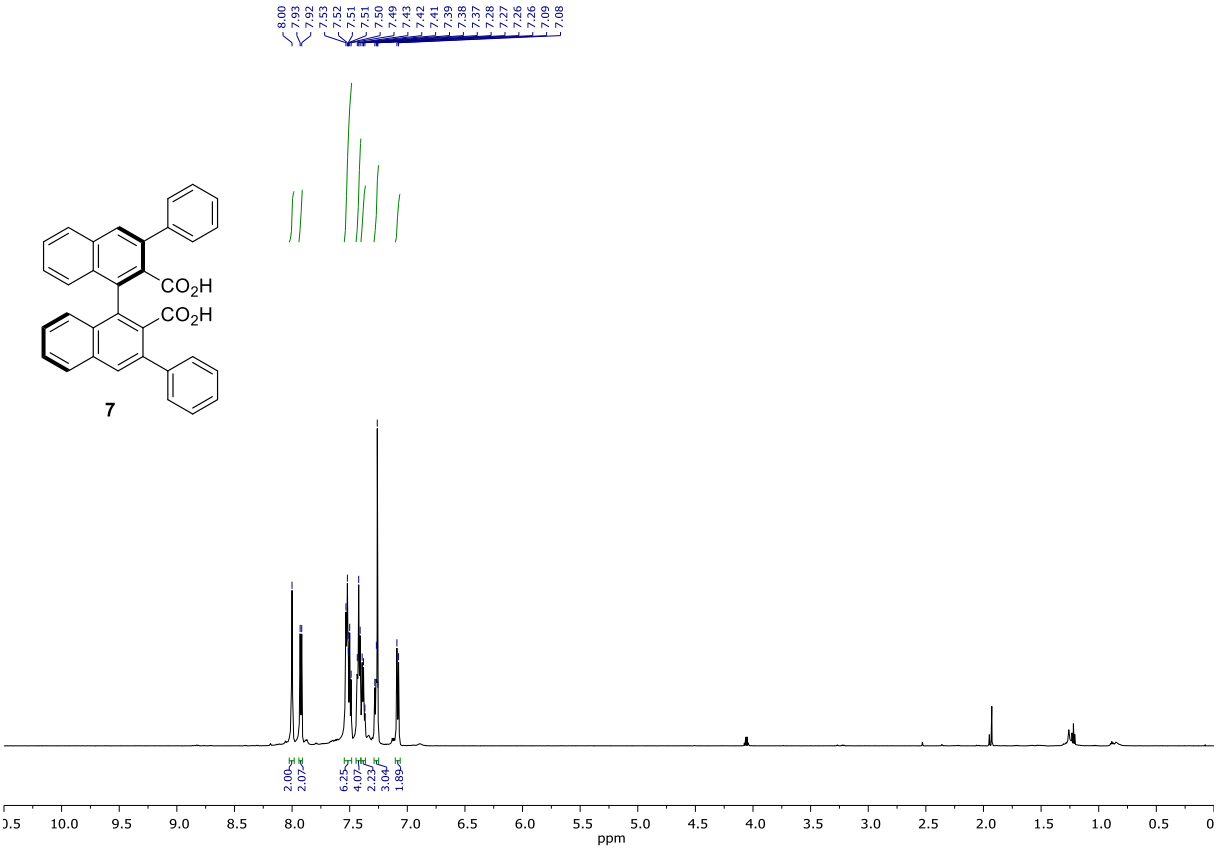
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	9.880	BB	0.2798	2962.73877	160.17528	49.7913
2	12.420	BV	0.3290	2987.57983	135.62543	50.2087

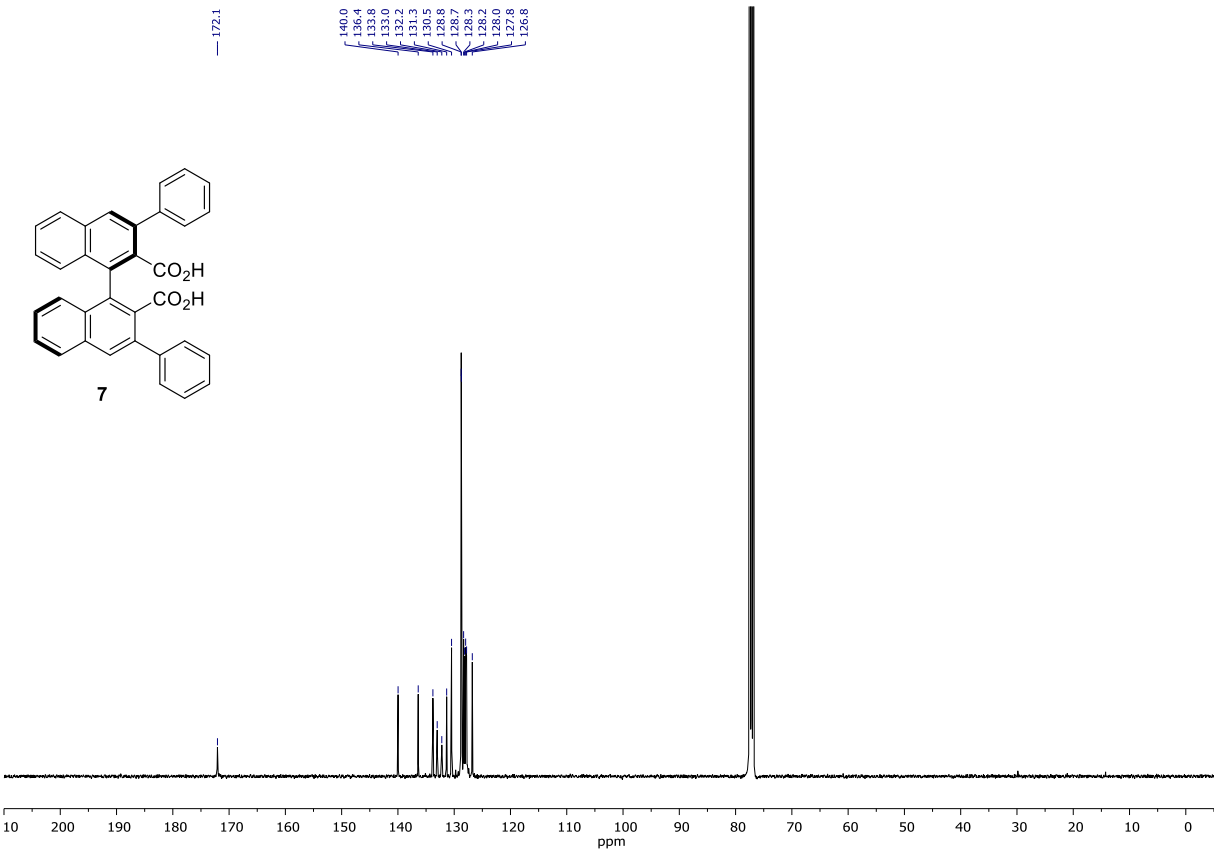


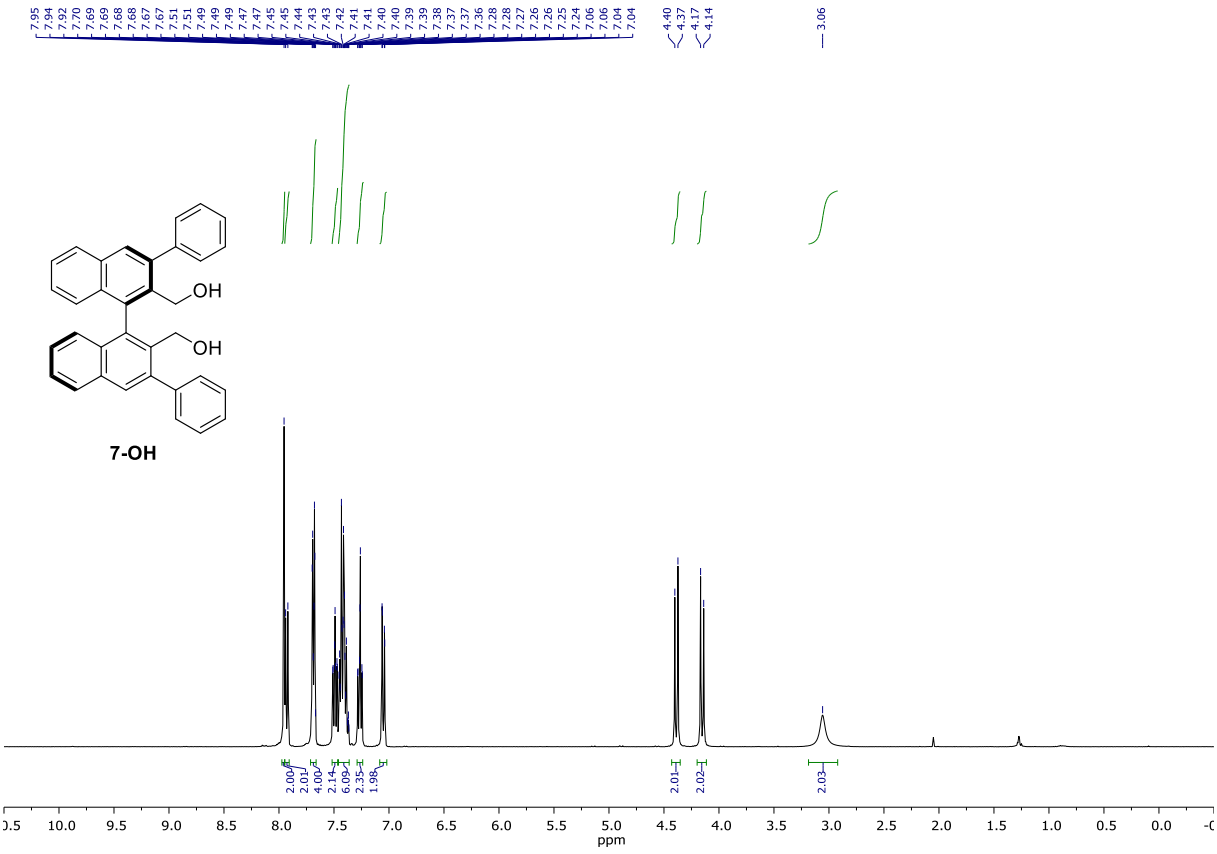
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	9.668	BV	0.2619	1063.95435	60.27497	20.0261
2	12.013	BB	0.3124	4248.89404	199.52237	79.9739

NMR Spectra

Ligand synthesis



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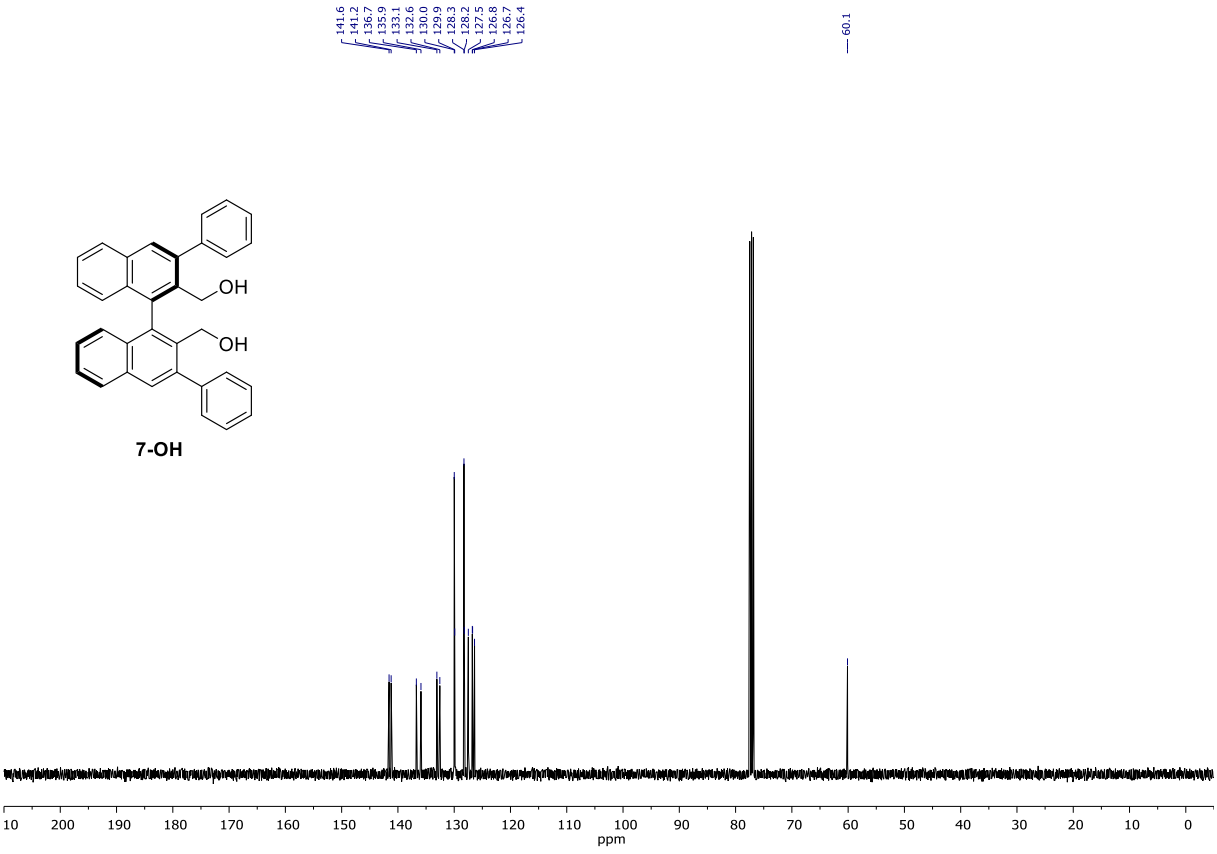
ppm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126.4
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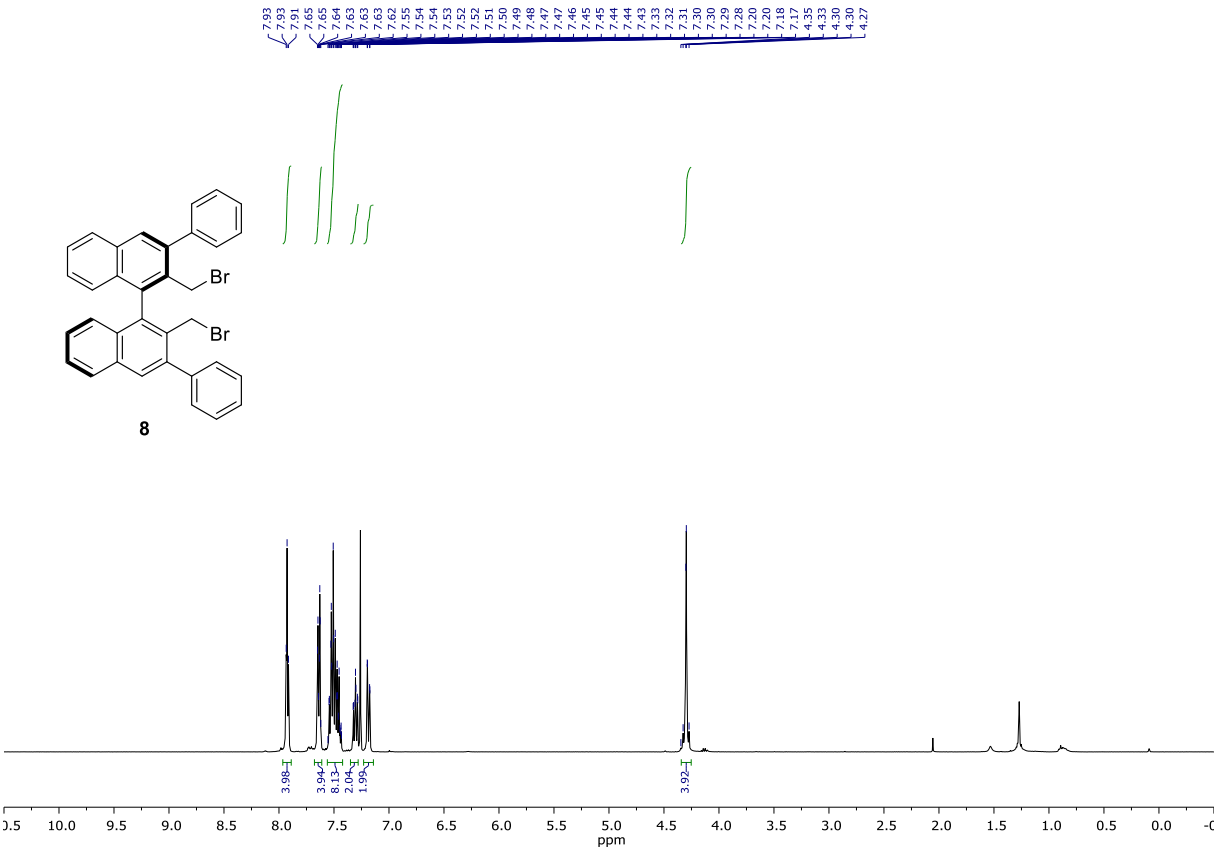
OH
7-OH
ppm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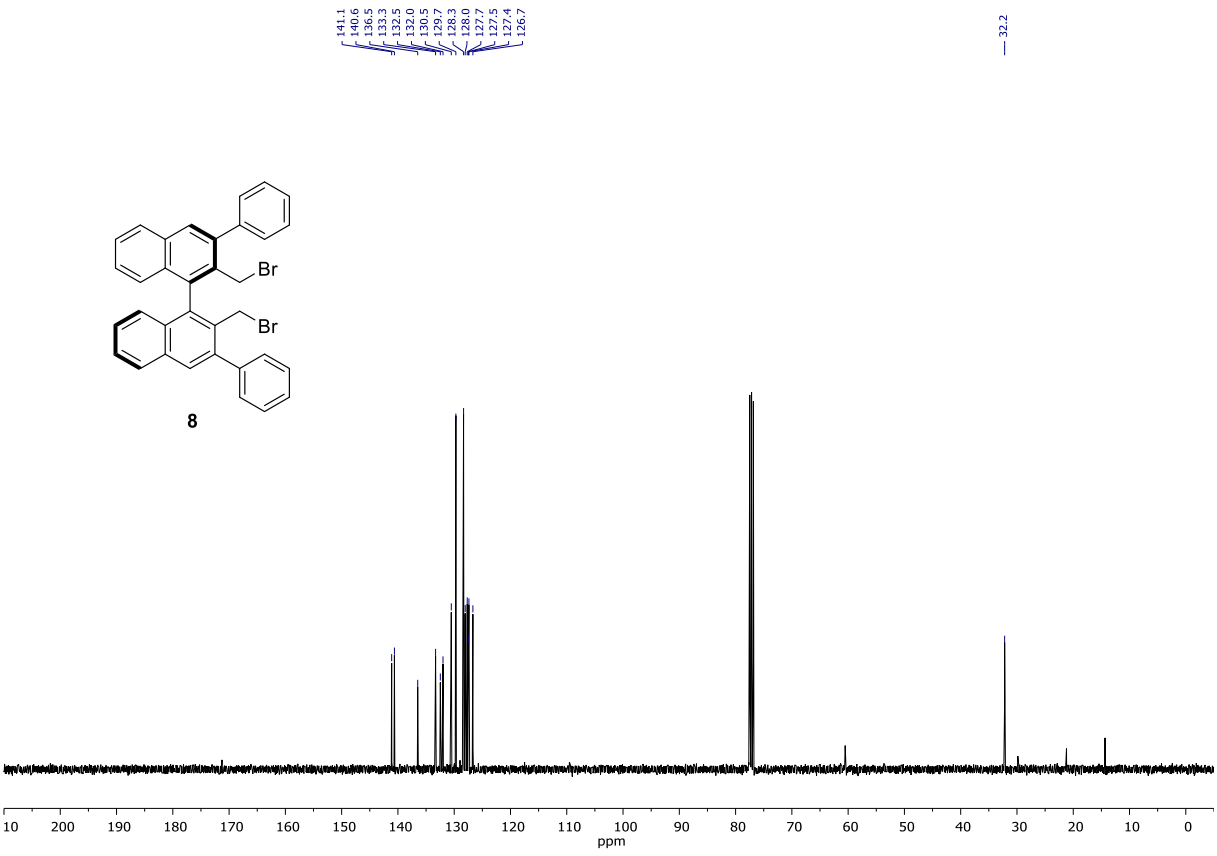
7.51
7.50
7.49
7.48
7.47
7.47
7.46
7.45
7.44
7.43
7.33
7.32
7.31
7.30
7.30
7.29
7.28
7.20
7.20
7.18
7.17
4.35
4.33
4.30
4.30
4.27
Br
Br
3.98
3.94
8.13
2.04
1.99
3.92
ppm

8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140.6
136.5
133.3
132.5
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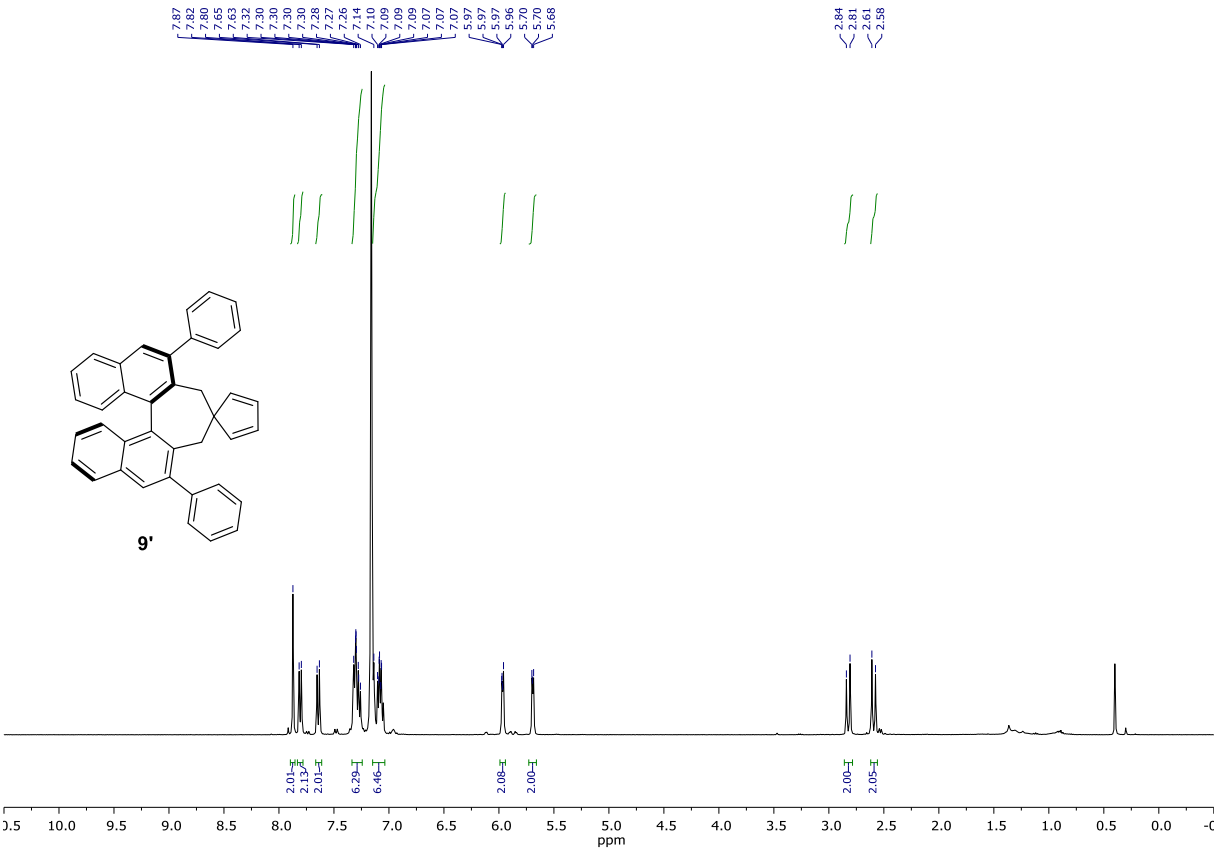
128.3
128.0
127.7
127.5
127.4
126.7
32.2
Br
Br
ppm

8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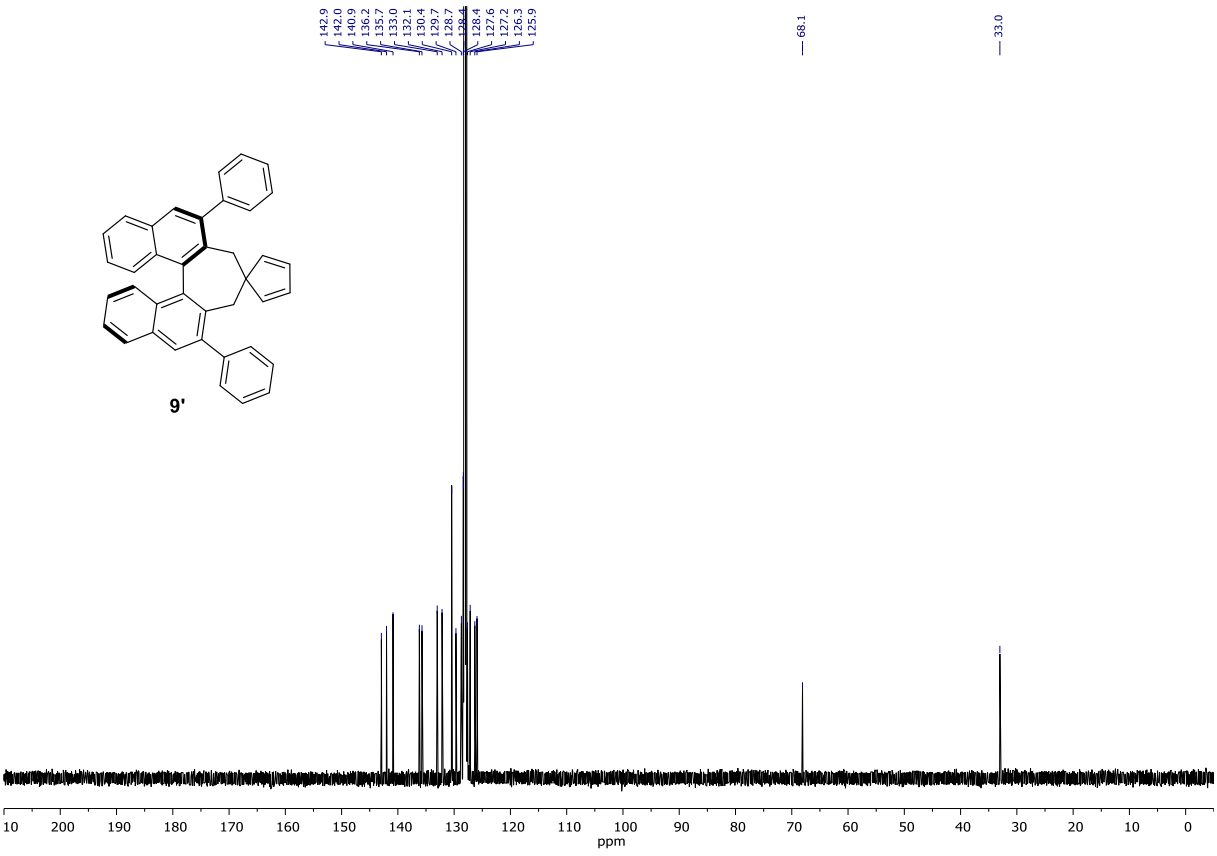
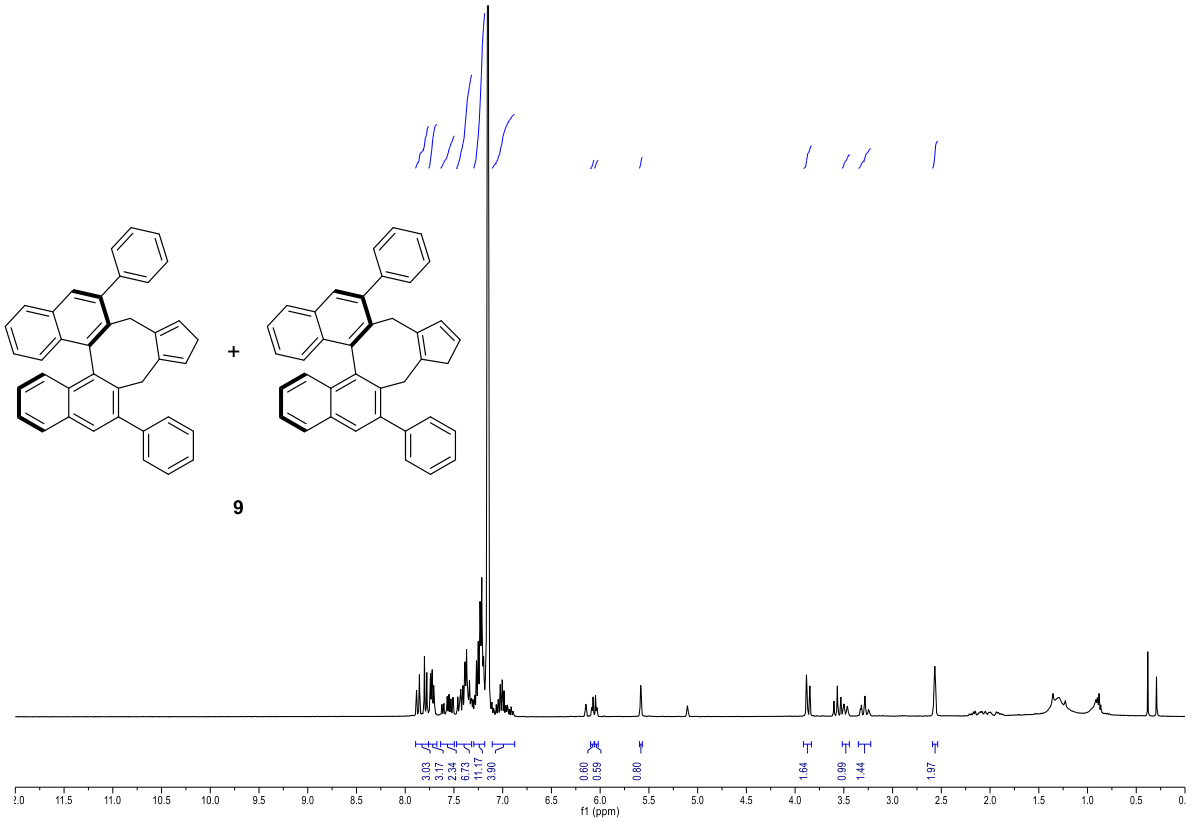
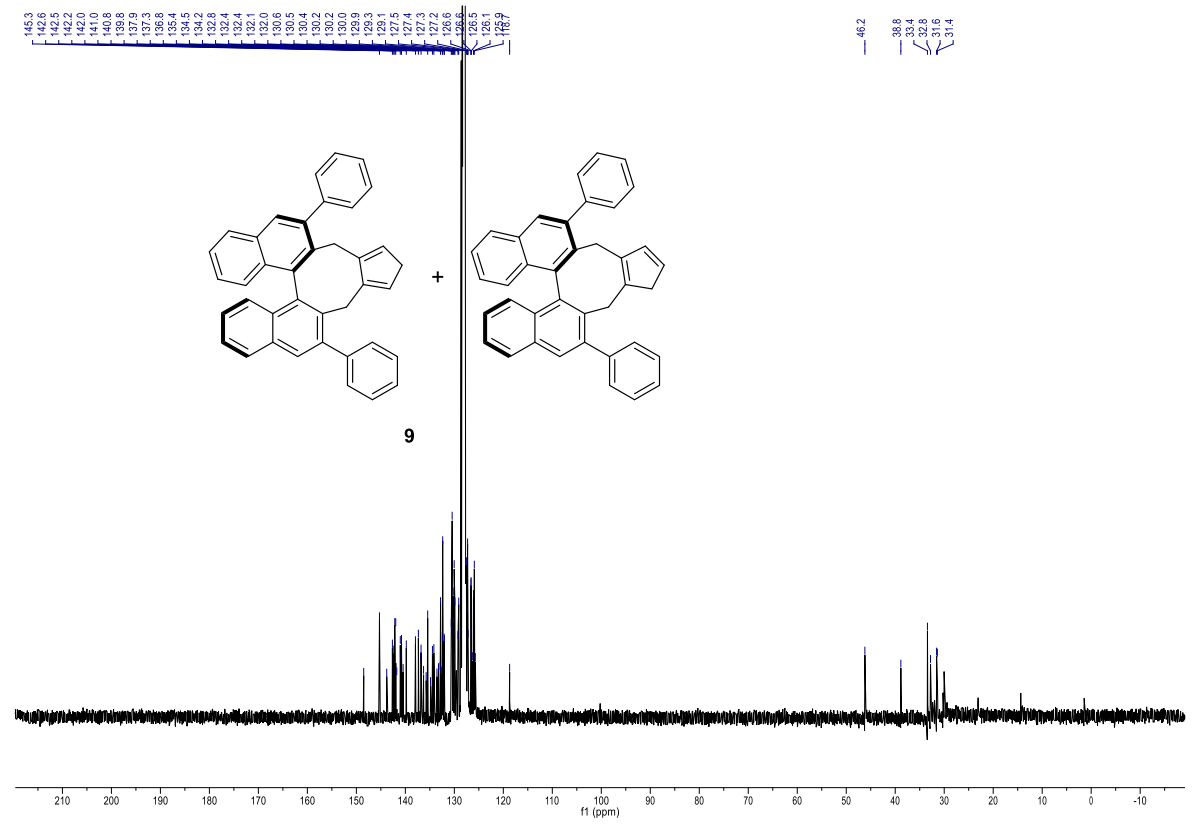
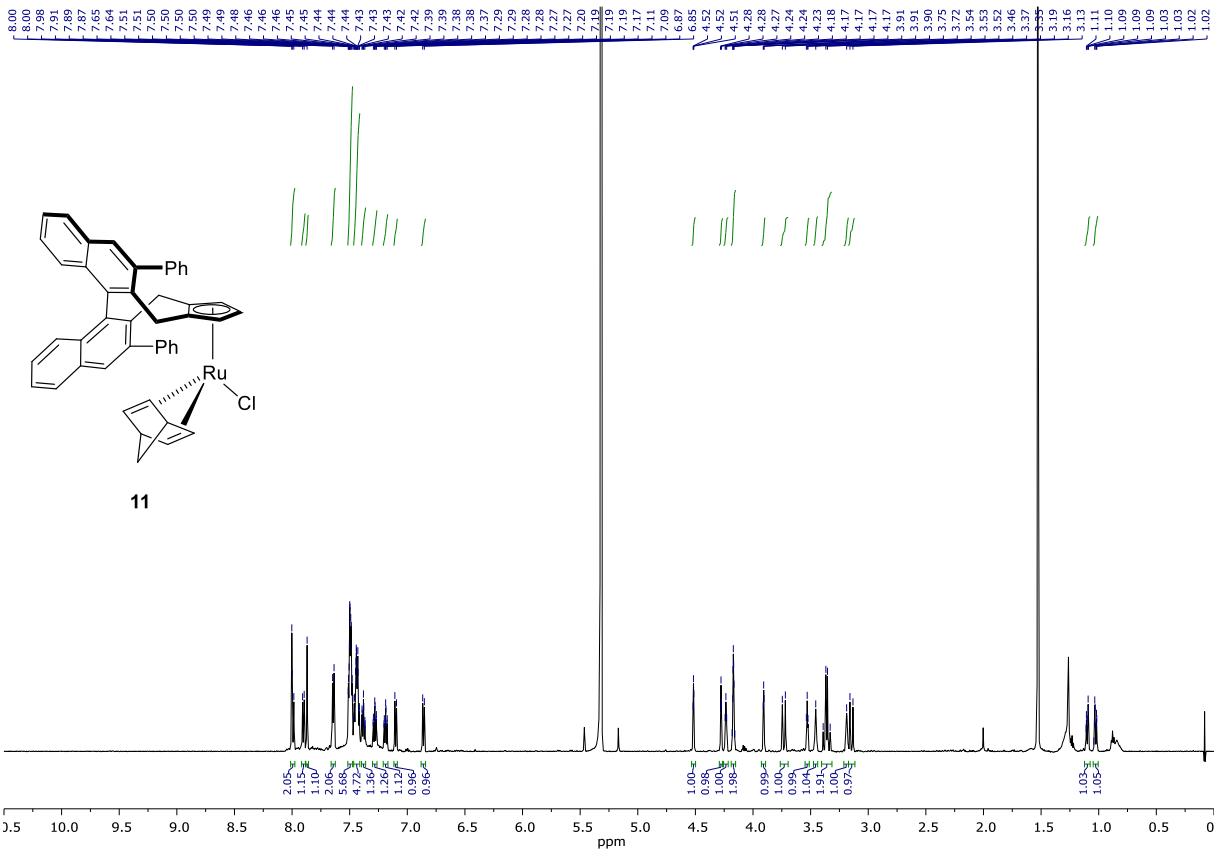
7.82
7.80
7.65
7.63
7.32
7.30
7.30
7.30
7.28
7.27
7.26
7.14
7.10
7.09
7.09
7.09
7.07
7.07
7.07
5.97
5.97
5.97
5.96
5.70
5.70
5.68
2.84
2.81
2.61
2.58
9'
2.01
2.13
2.01
6.29
6.46
2.08
2.00
2.00
2.05
ppm

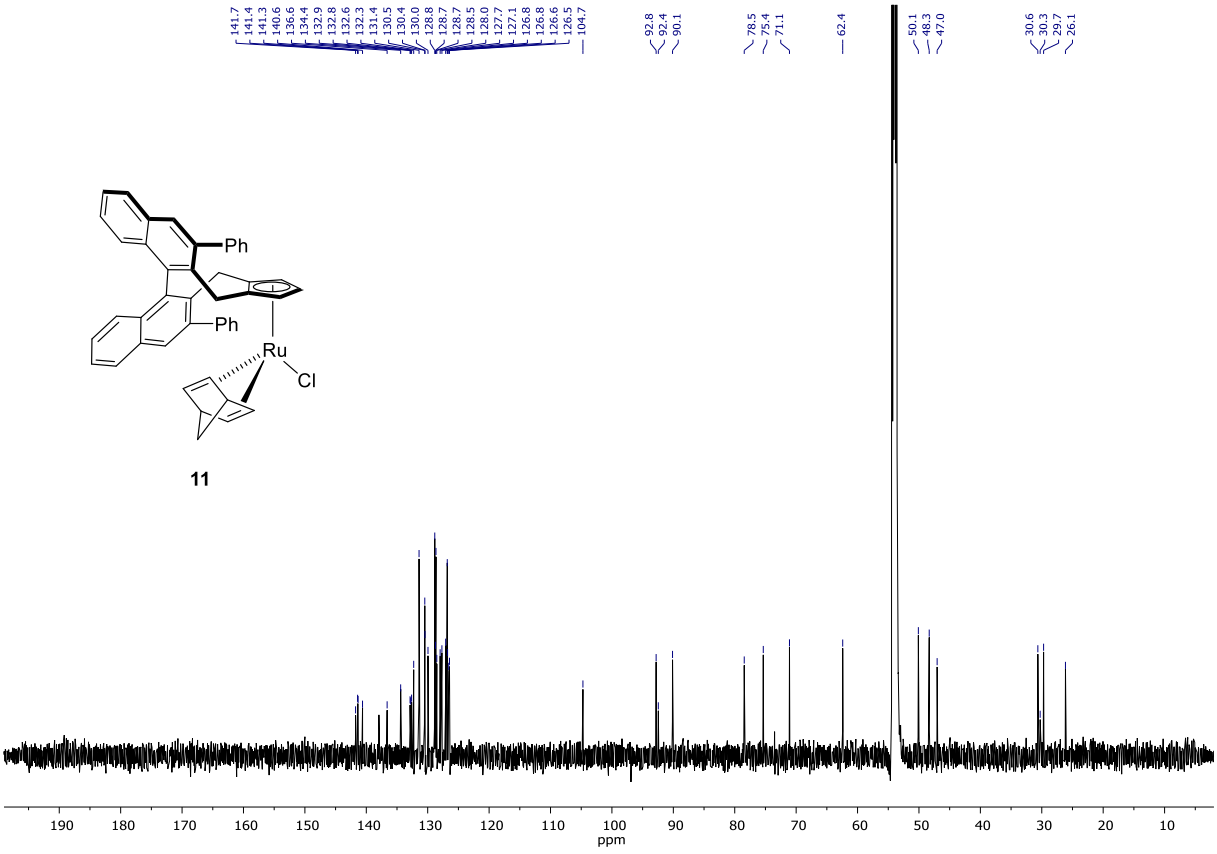

142.9
142.0
140.9
136.2
135.7
133.0
132.1
130.4
129.7
128.7
128.4
127.6
127.2
126.3
125.9
68.1
33.0
9'
ppm

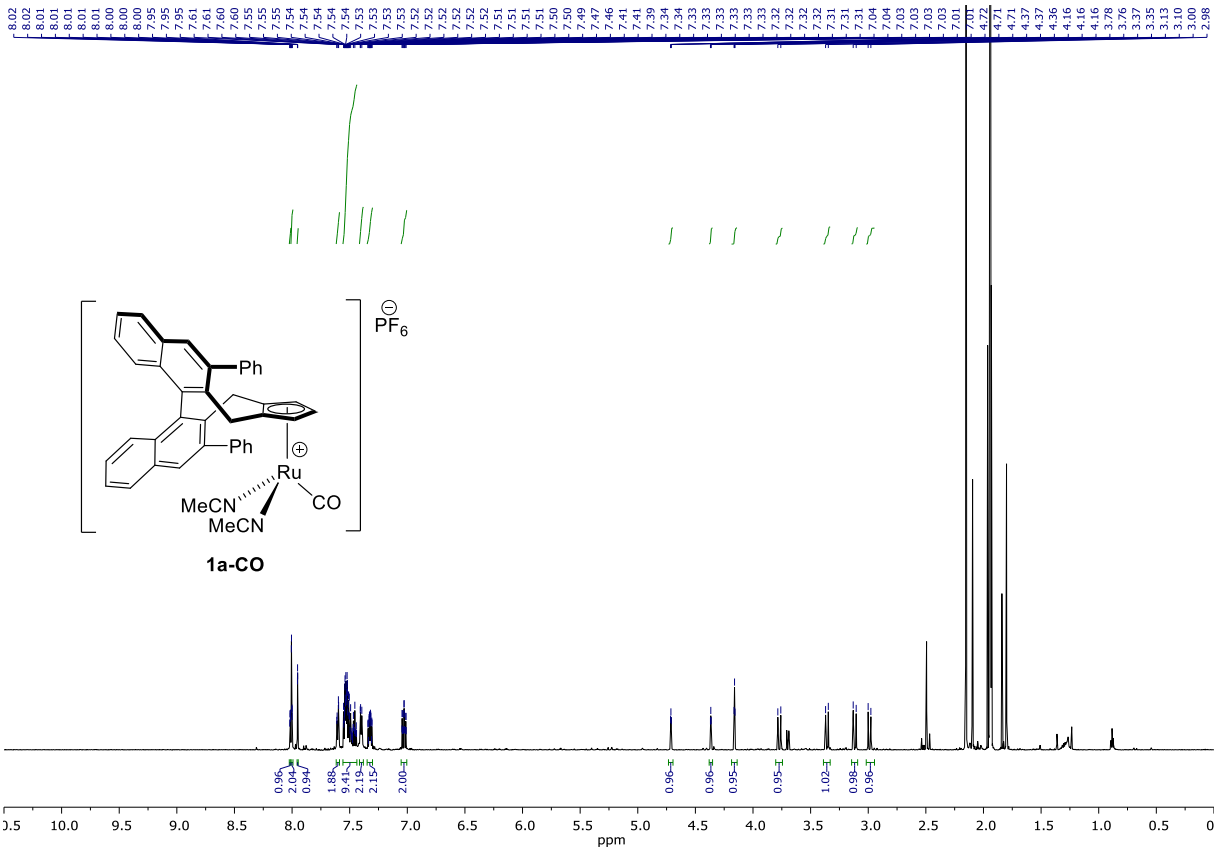

9
3.03
3.17
2.34
6.73
11.17
3.90
0.60
0.59
0.80
1.64
0.99
1.44
1.97
f1 (ppm)


9
f1 (ppm)

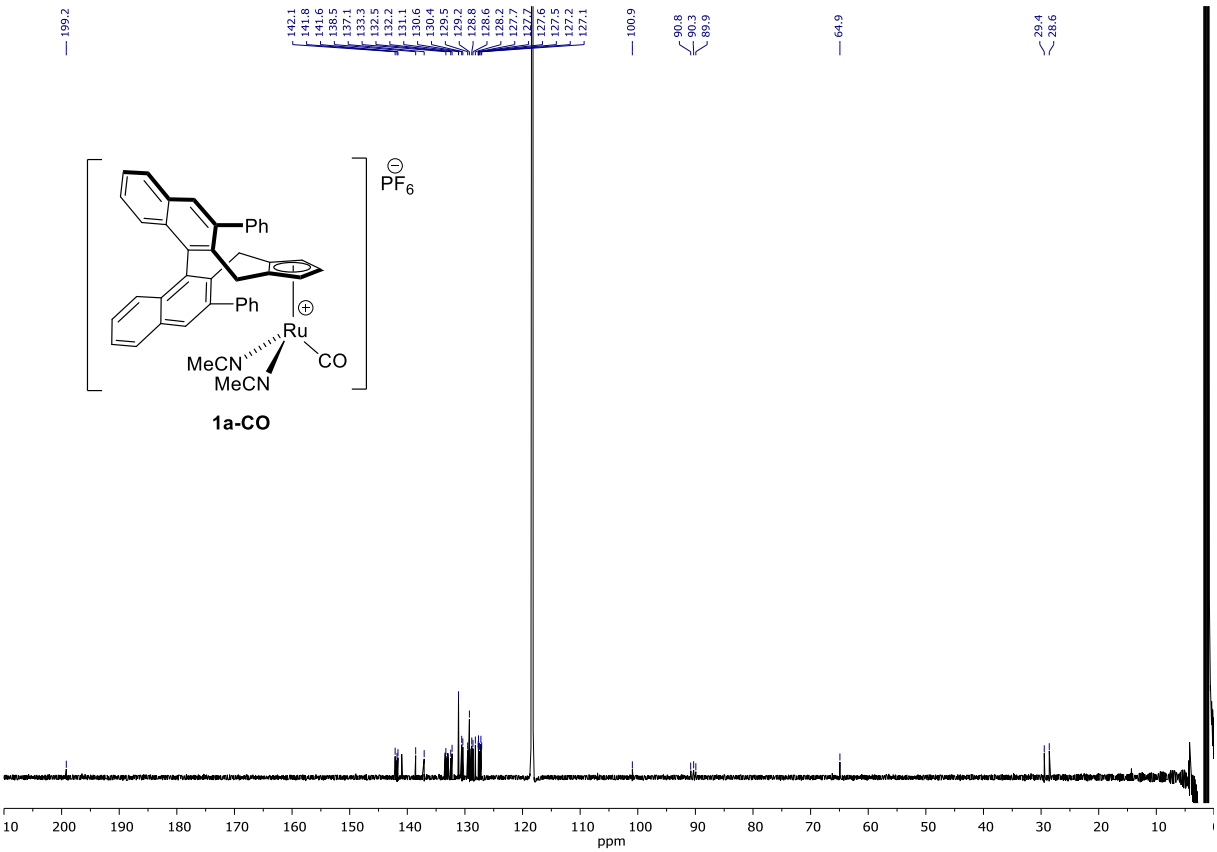
Catalysts:





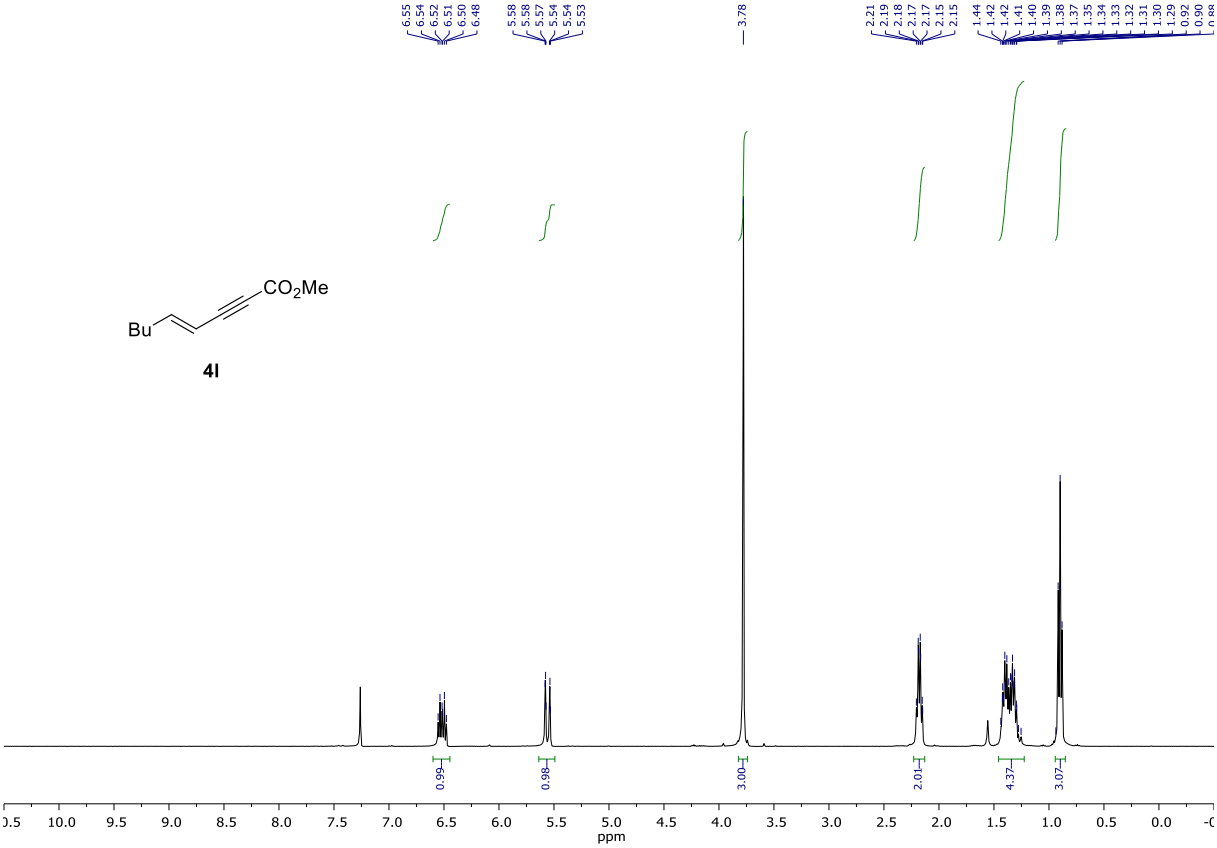


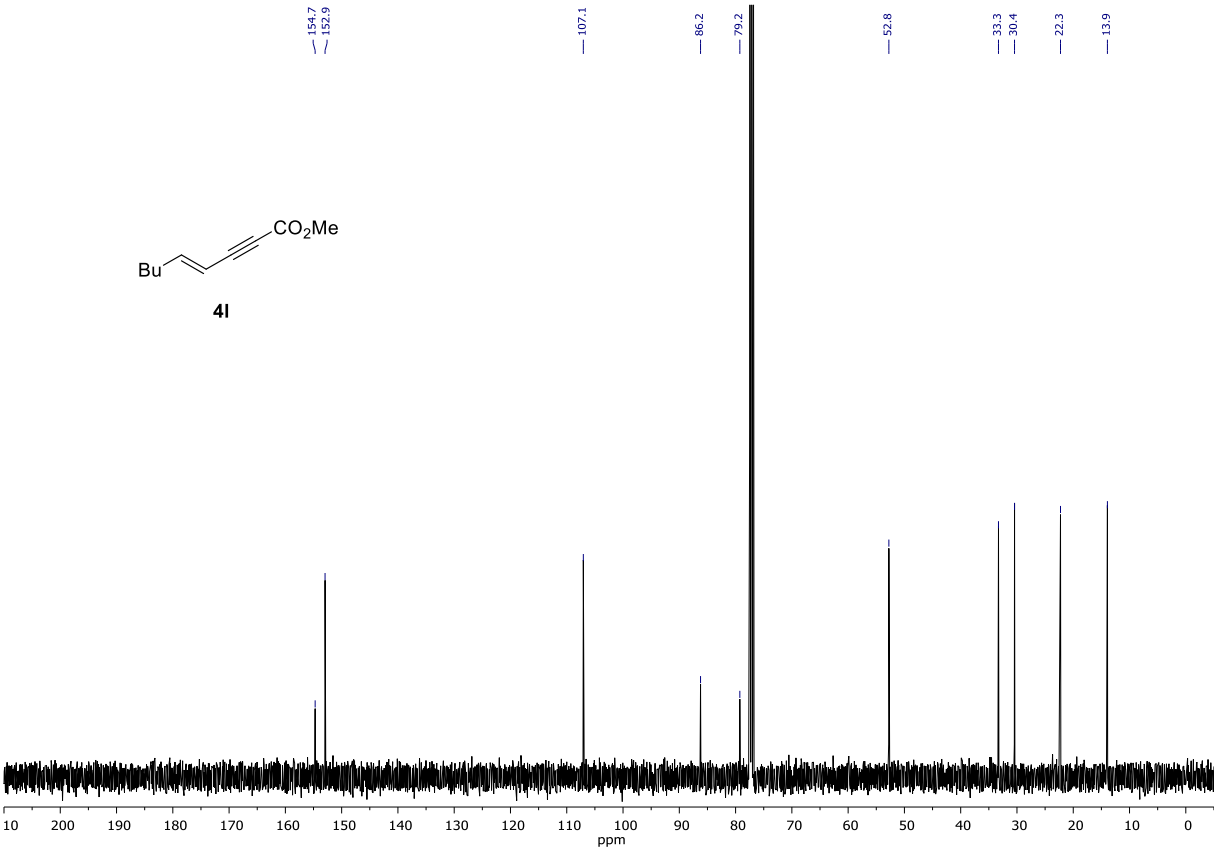
1a-CO



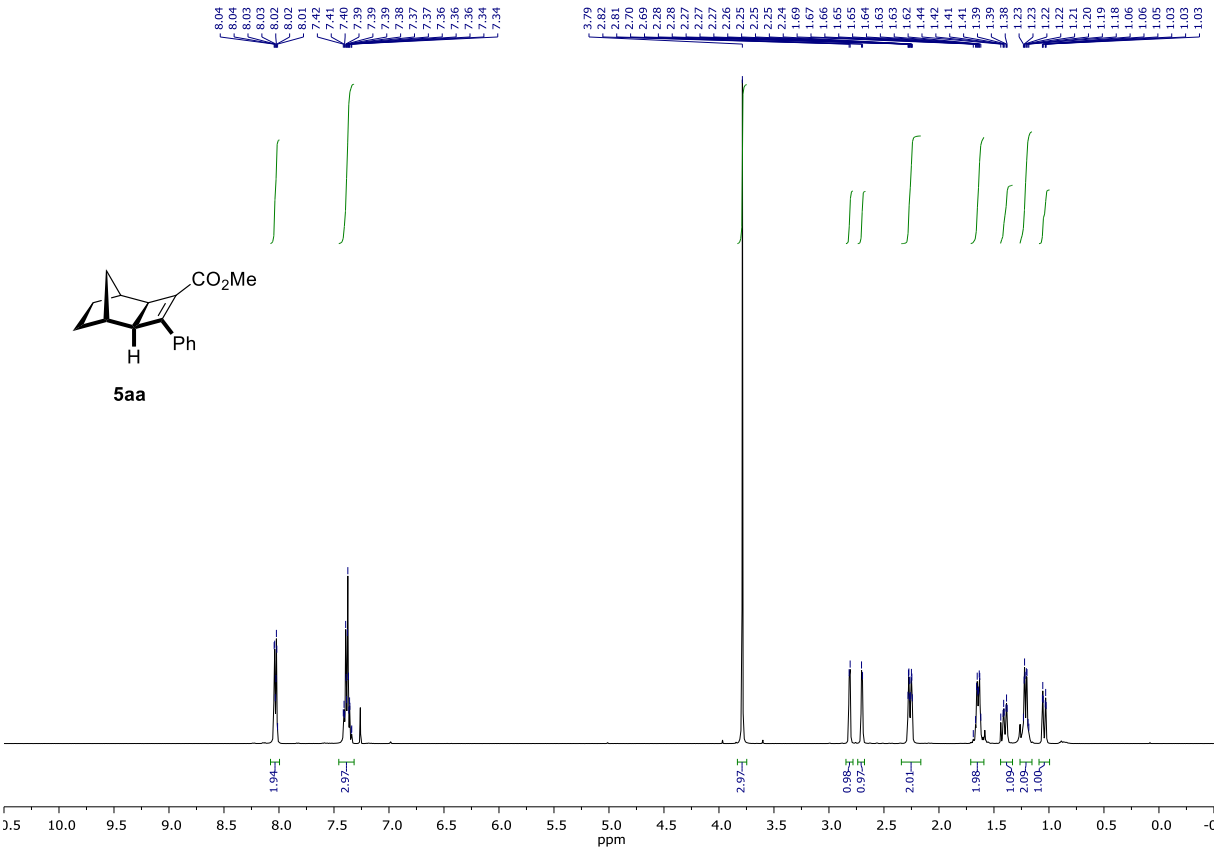
1a-CO

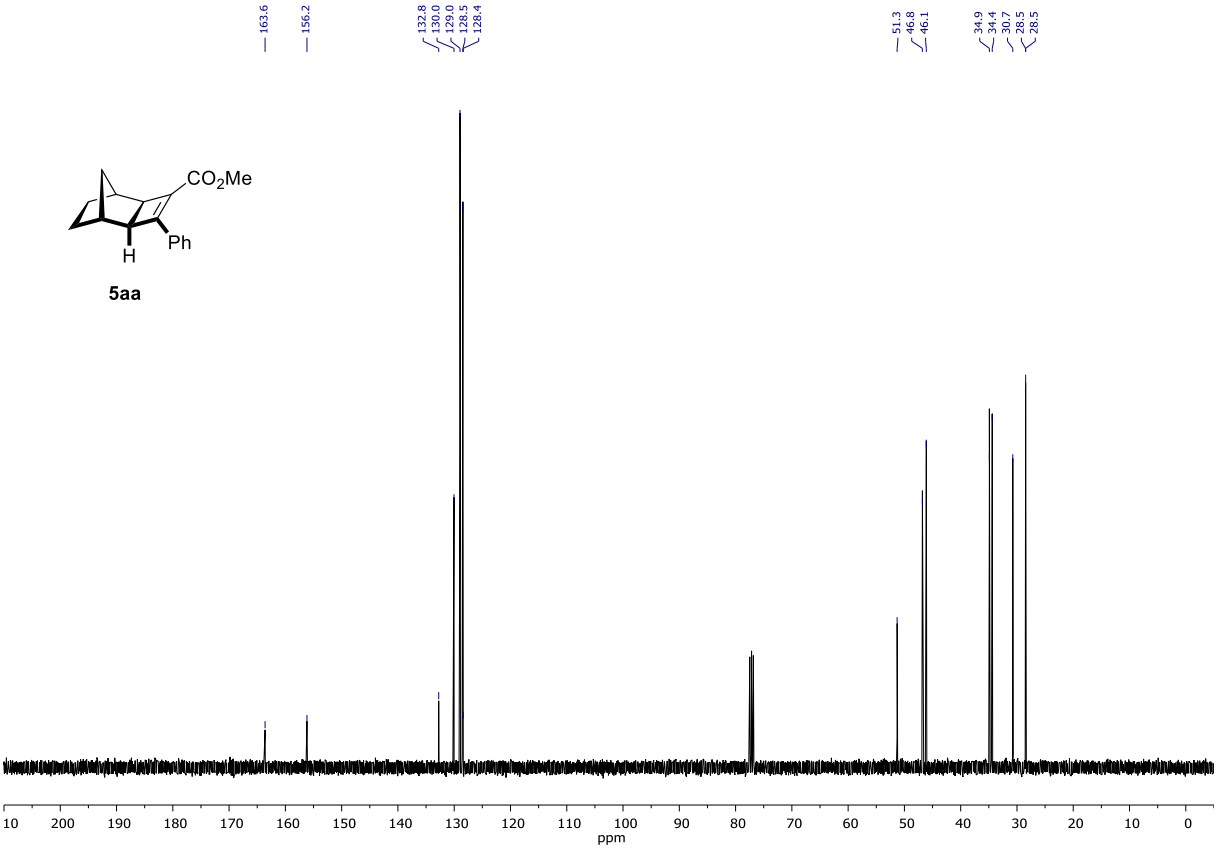
Starting alkyne:

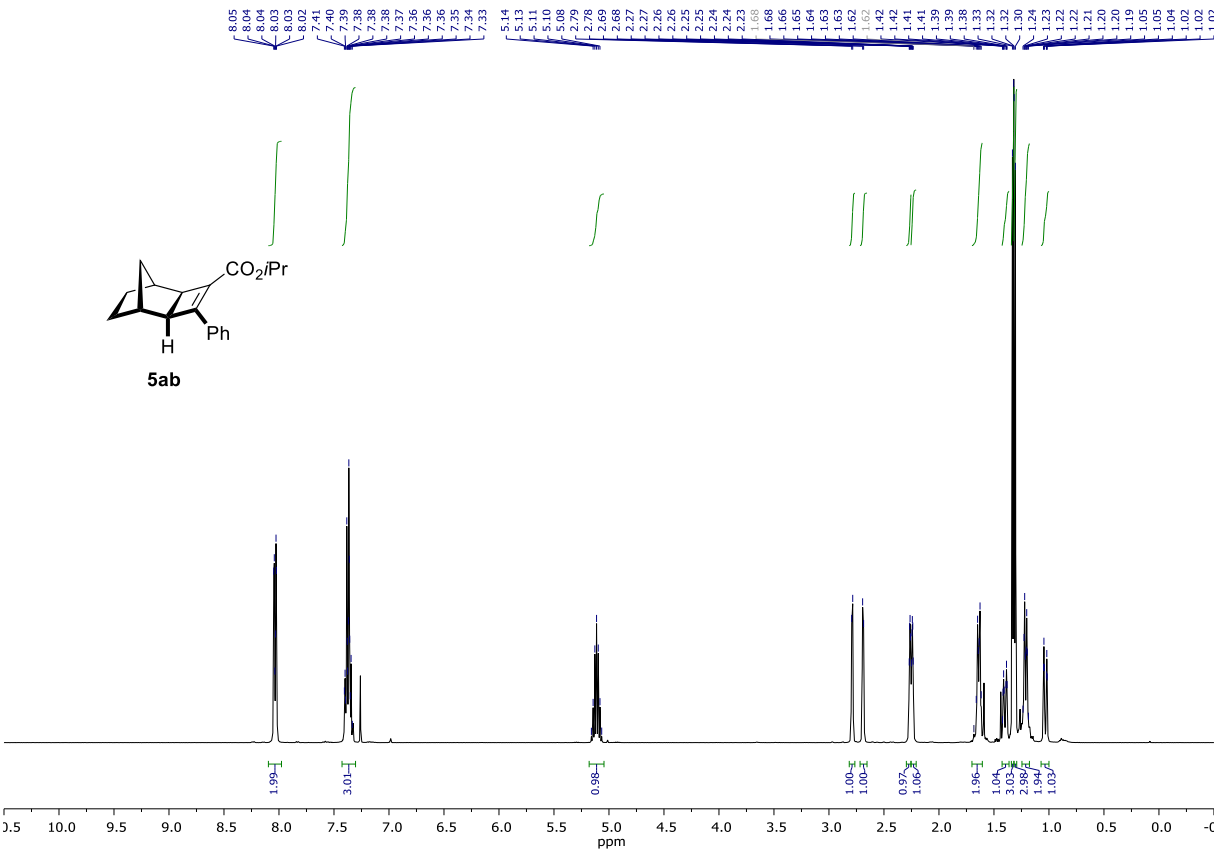


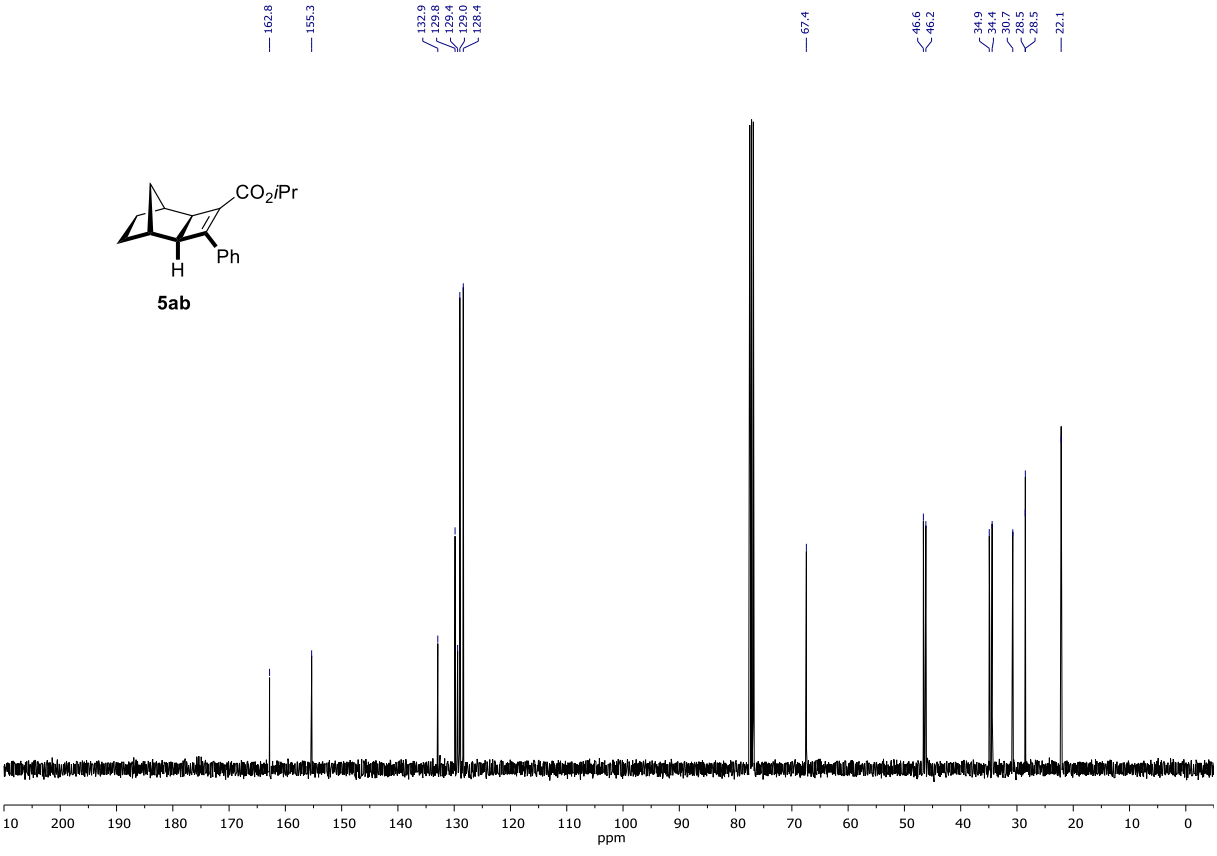


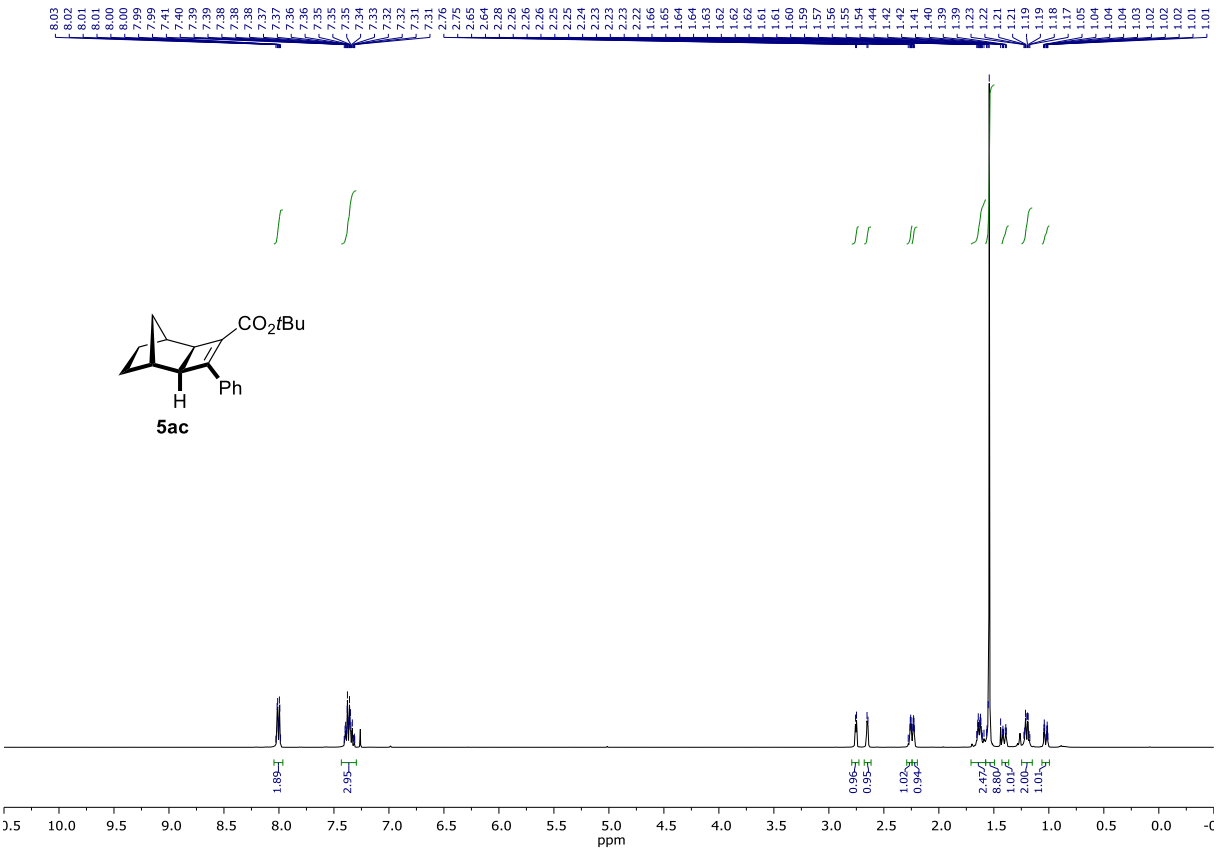
Cyclobutenes:

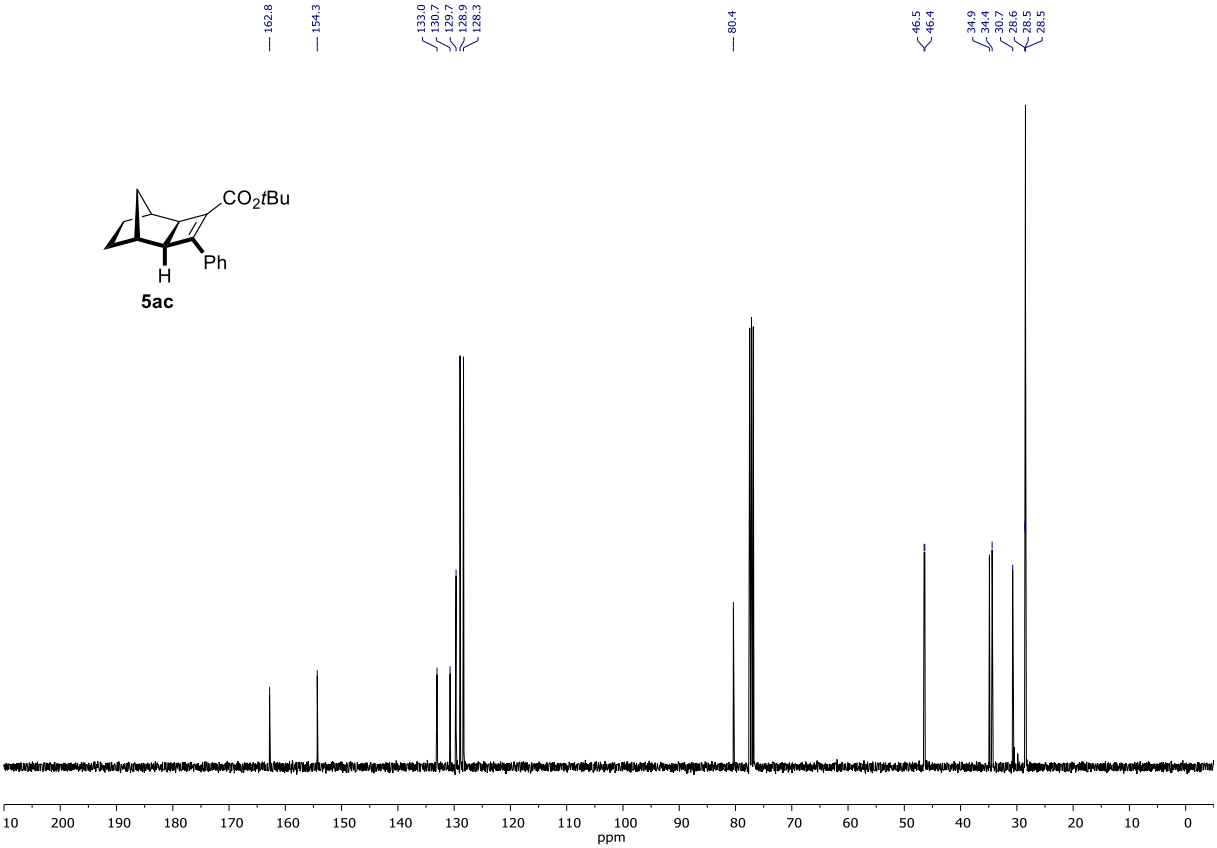


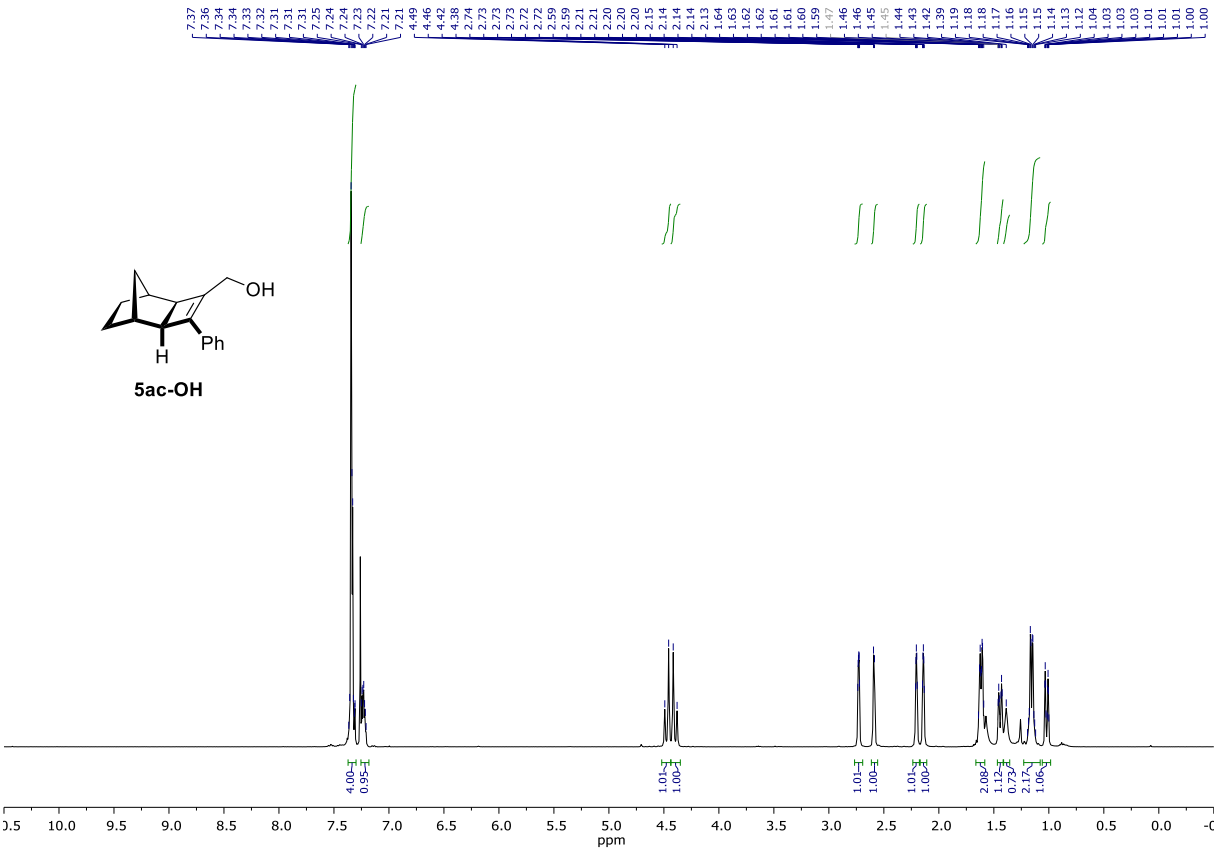


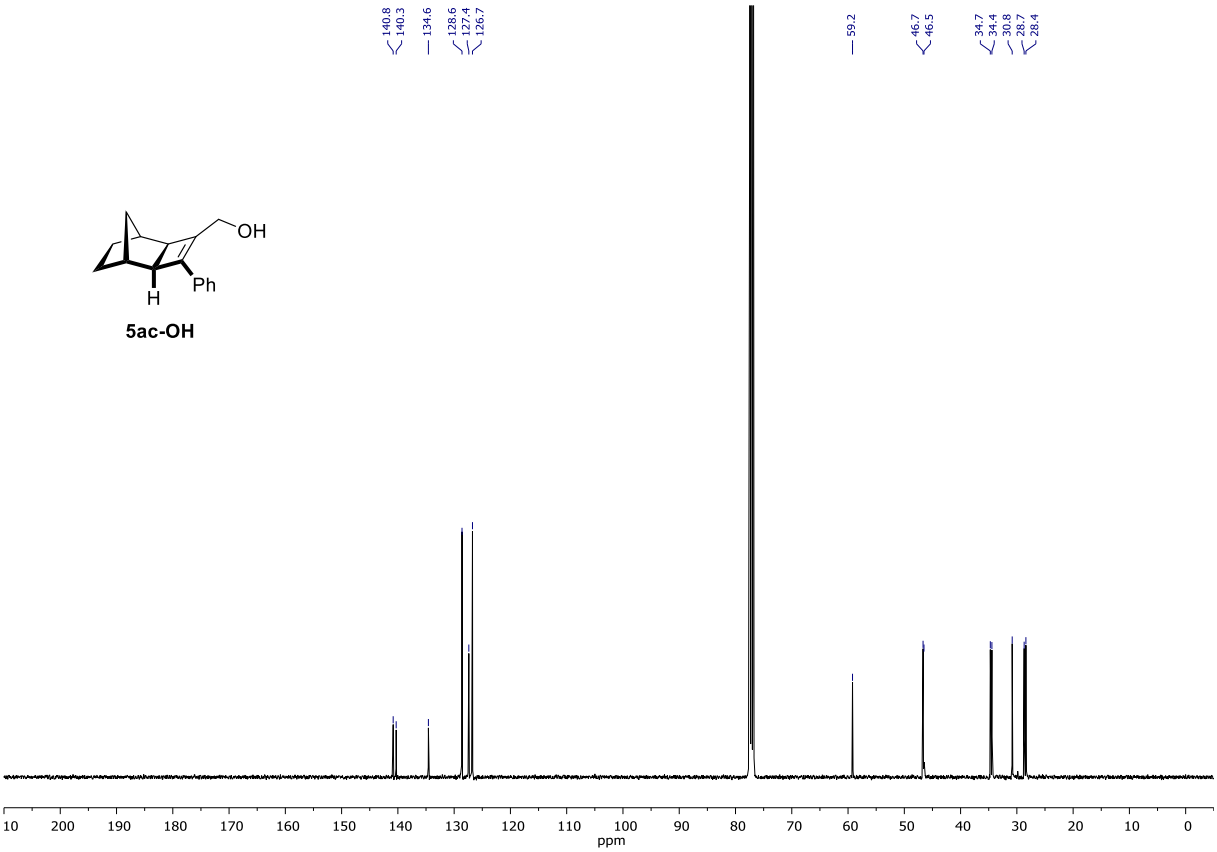

CO2iPr
Ph
H
5ab
ppm

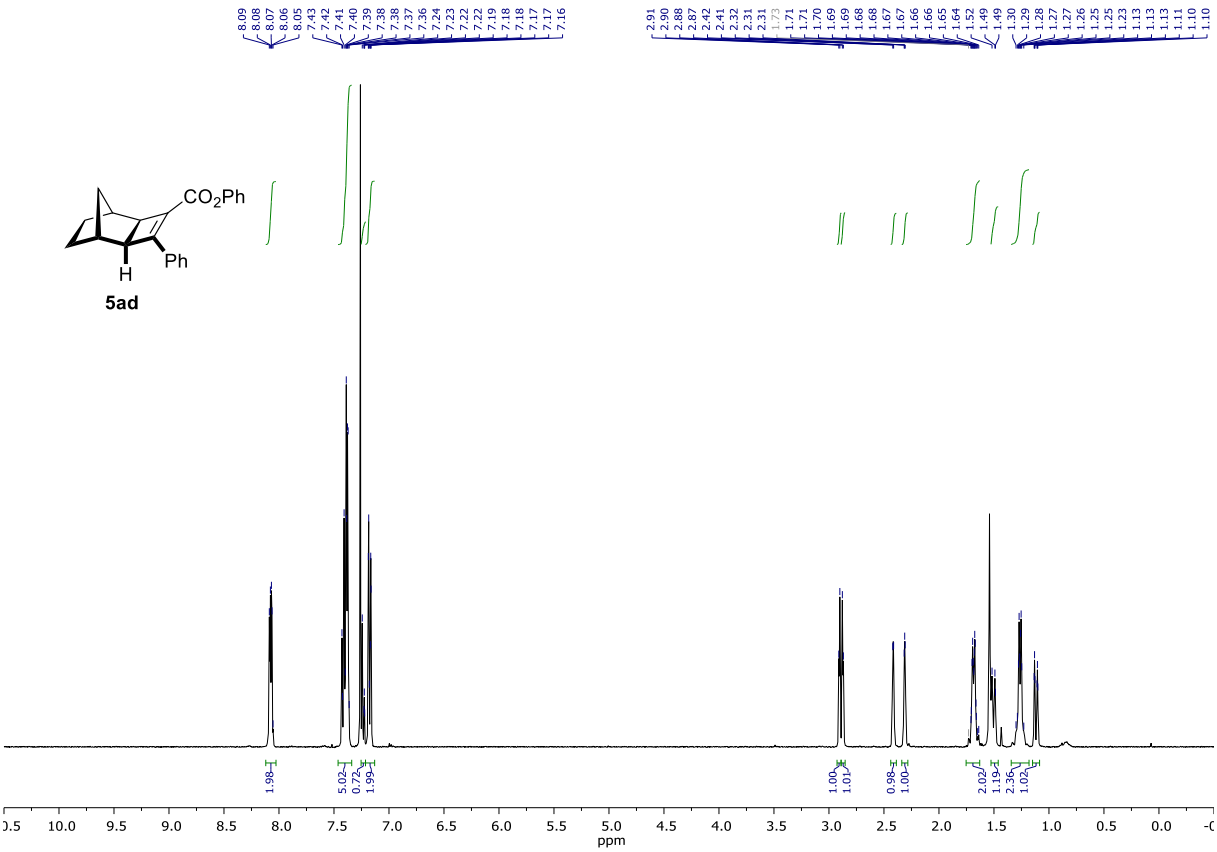

CO2iPr
Ph
H
5ab
ppm

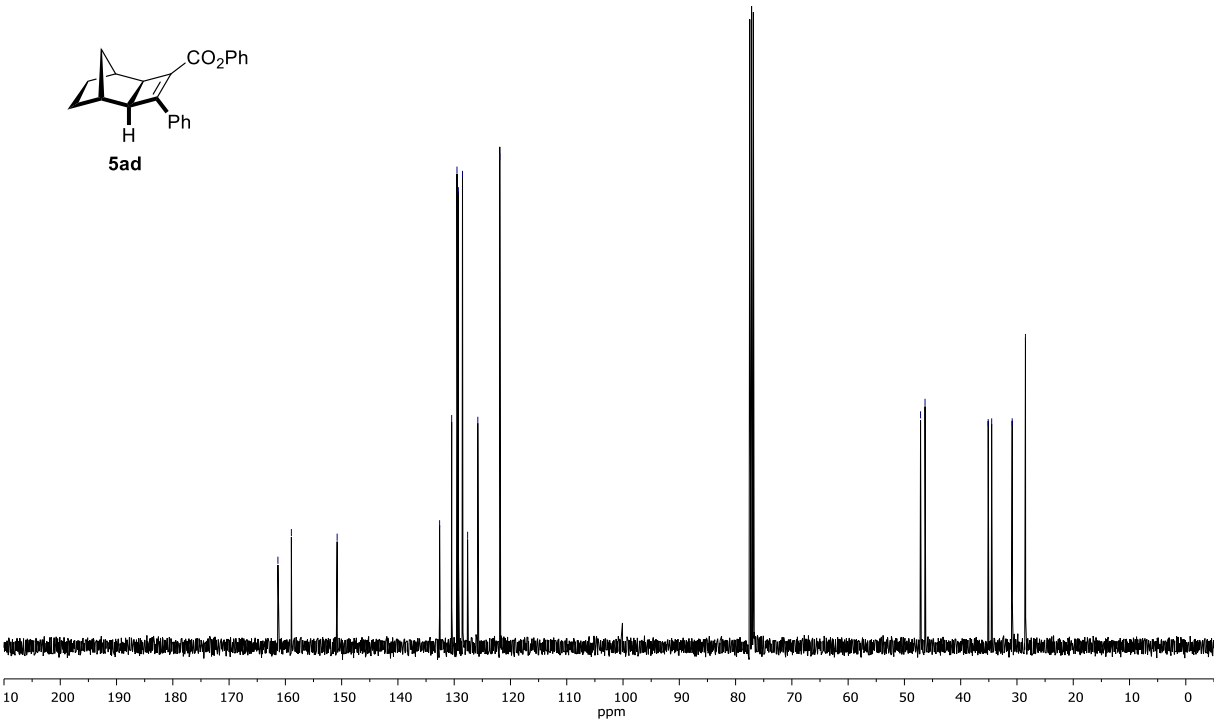

CO2tBu
Ph
H
5ac
ppm

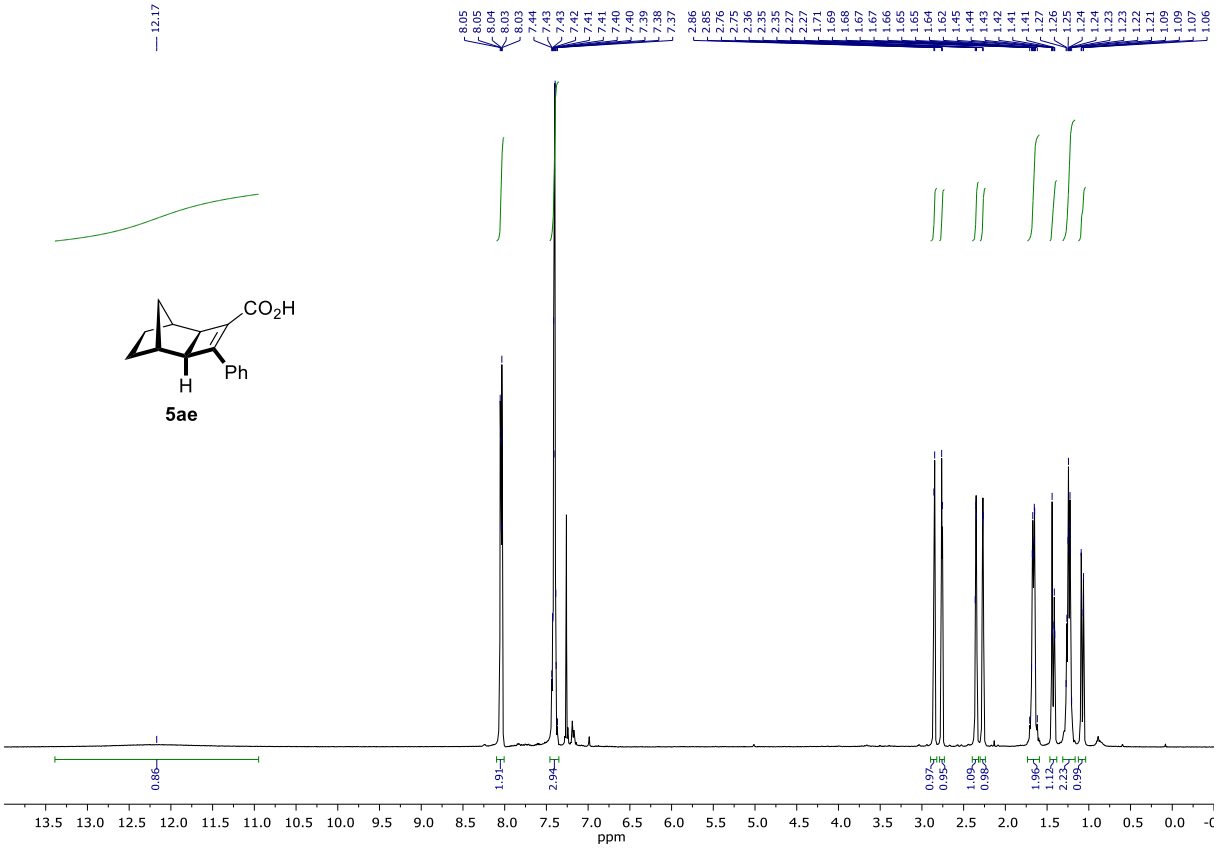

CO2tBu
Ph
H
5ac
ppm

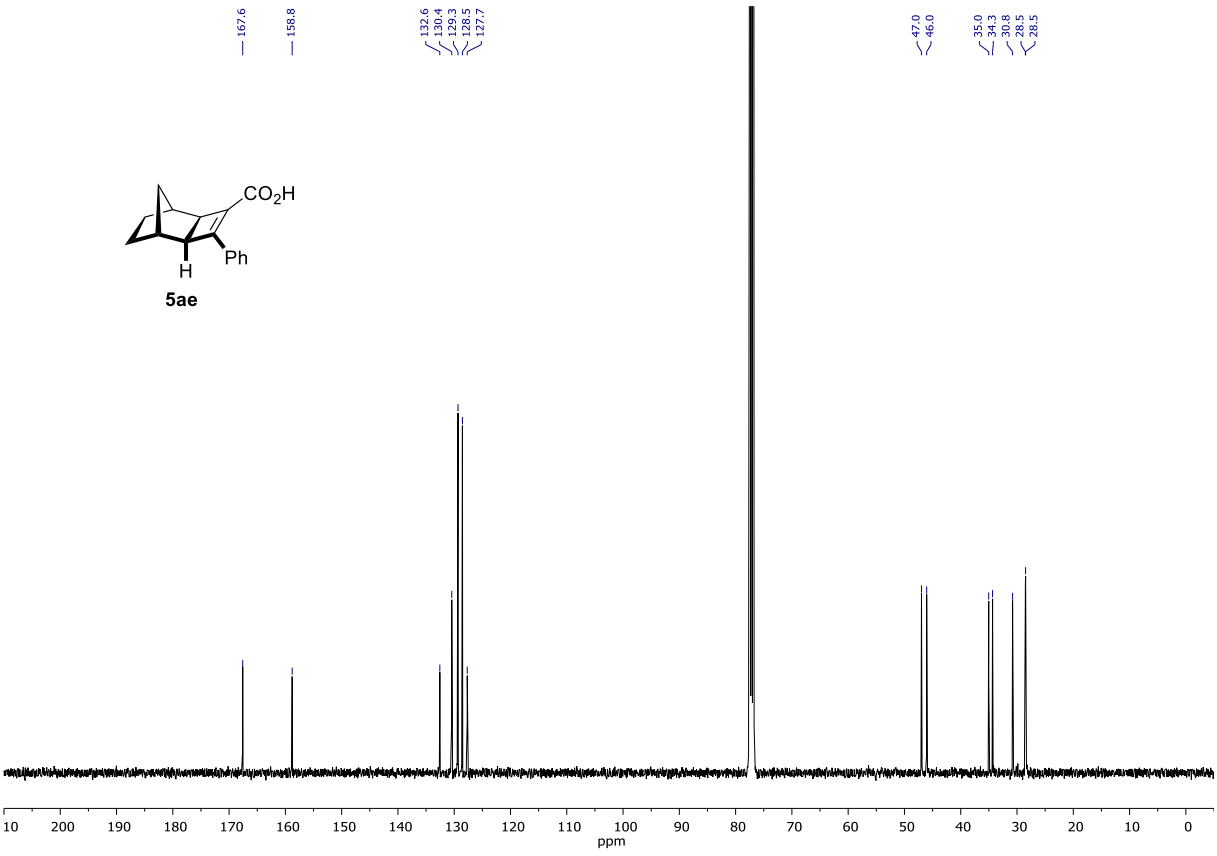

OH
Ph
H
5ac-OH
ppm

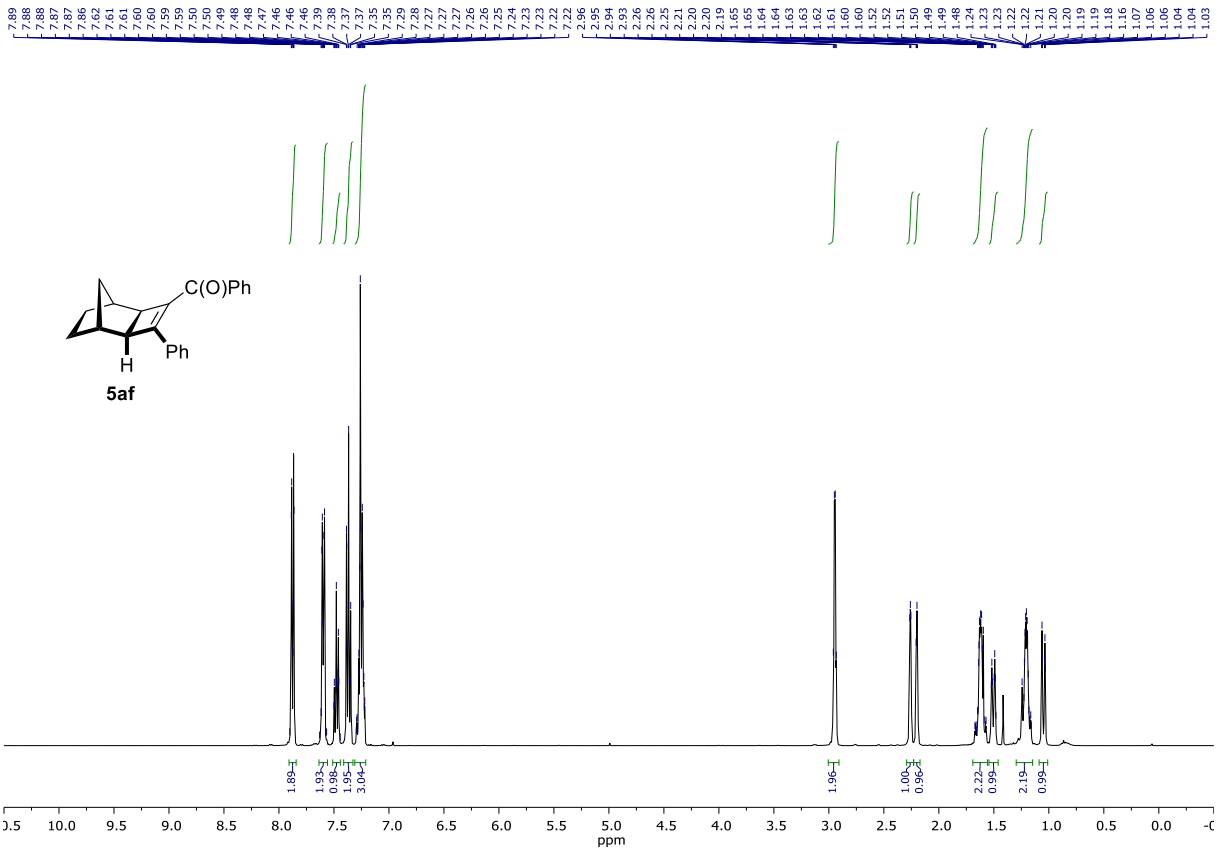

OH
Ph
H
5ac-OH
ppm

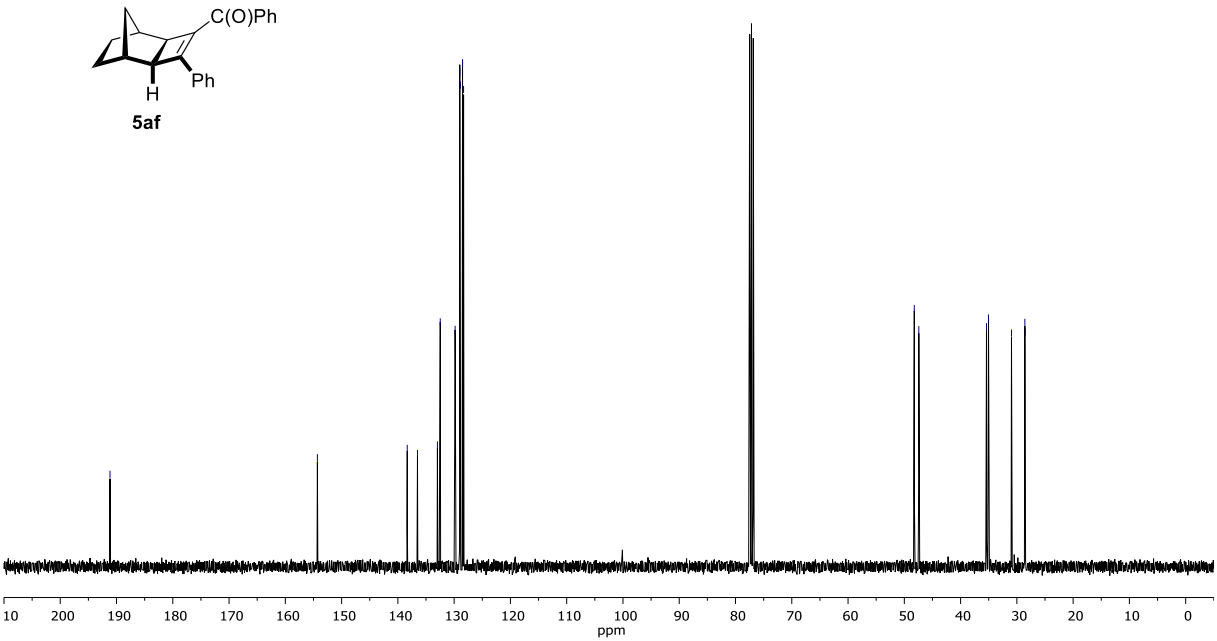

CO2Ph
Ph
H
5ad
ppm

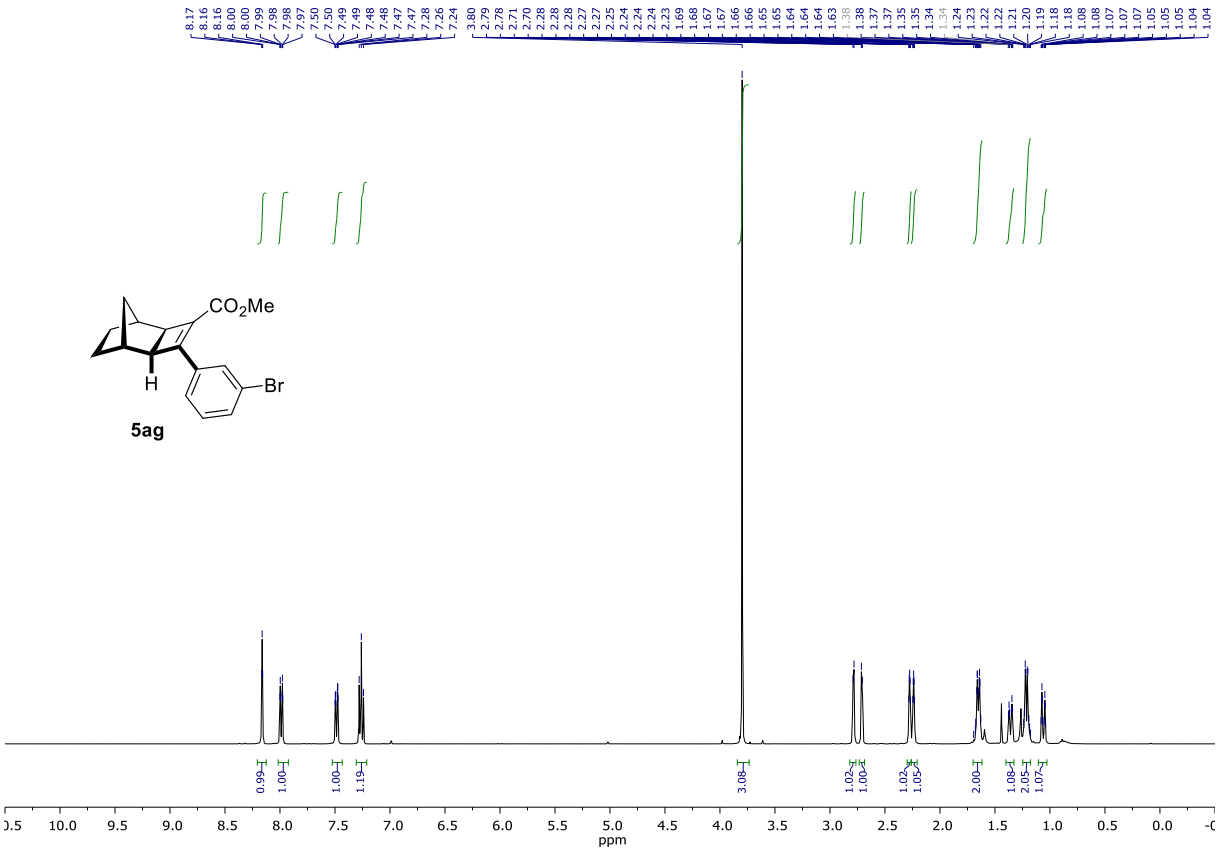

CO2Ph
Ph
H
5ad
ppm

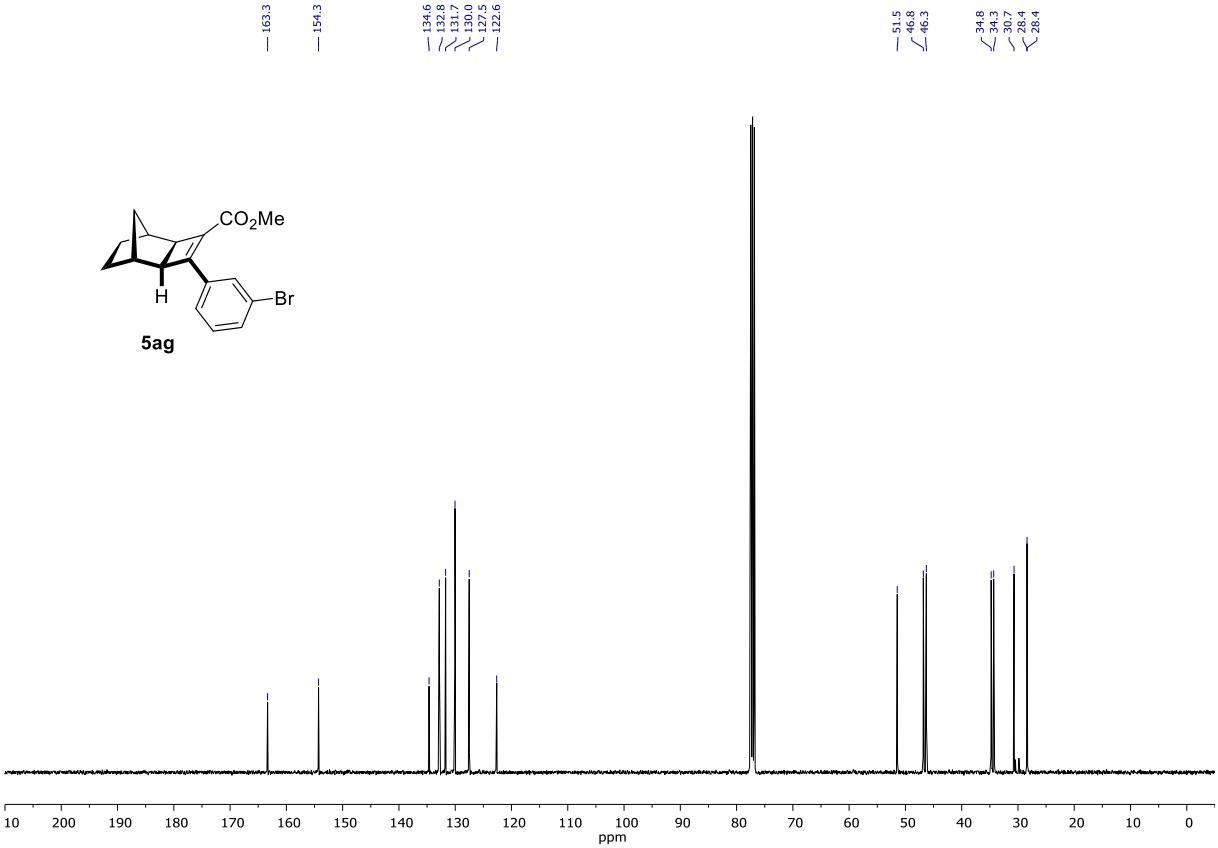

12.17
8.05 8.05 8.04 8.03 8.03 7.44 7.43 7.43 7.42 7.41 7.41 7.40 7.40 7.39 7.38 7.37
2.86 2.85 2.76 2.75 2.36 2.35 2.27 2.27 1.71 1.69 1.68 1.67 1.67 1.66 1.65 1.65 1.64 1.62 1.45 1.44 1.43 1.42 1.41 1.41 1.27 1.26 1.25 1.24 1.24 1.23 1.23 1.22 1.21 1.09 1.09 1.07 1.06
CO2H
Ph
H
5ae
0.86
1.91
2.94
0.97
0.95
1.09
0.98
1.96
1.12
2.23
0.99
ppm

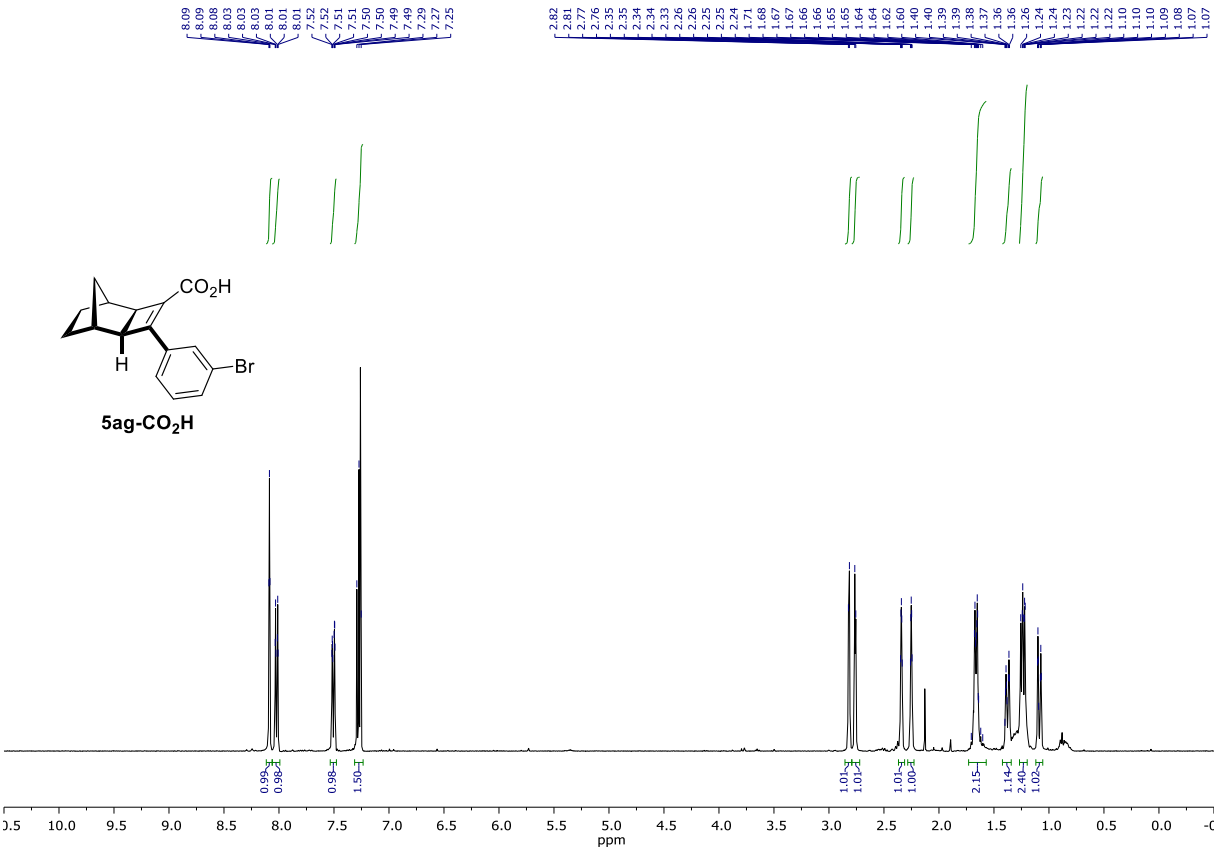

167.6
158.8
132.6
130.4
129.3
128.5
127.7
47.0
46.0
35.0
34.3
30.8
28.5
28.5
CO2H
Ph
H
5ae
ppm

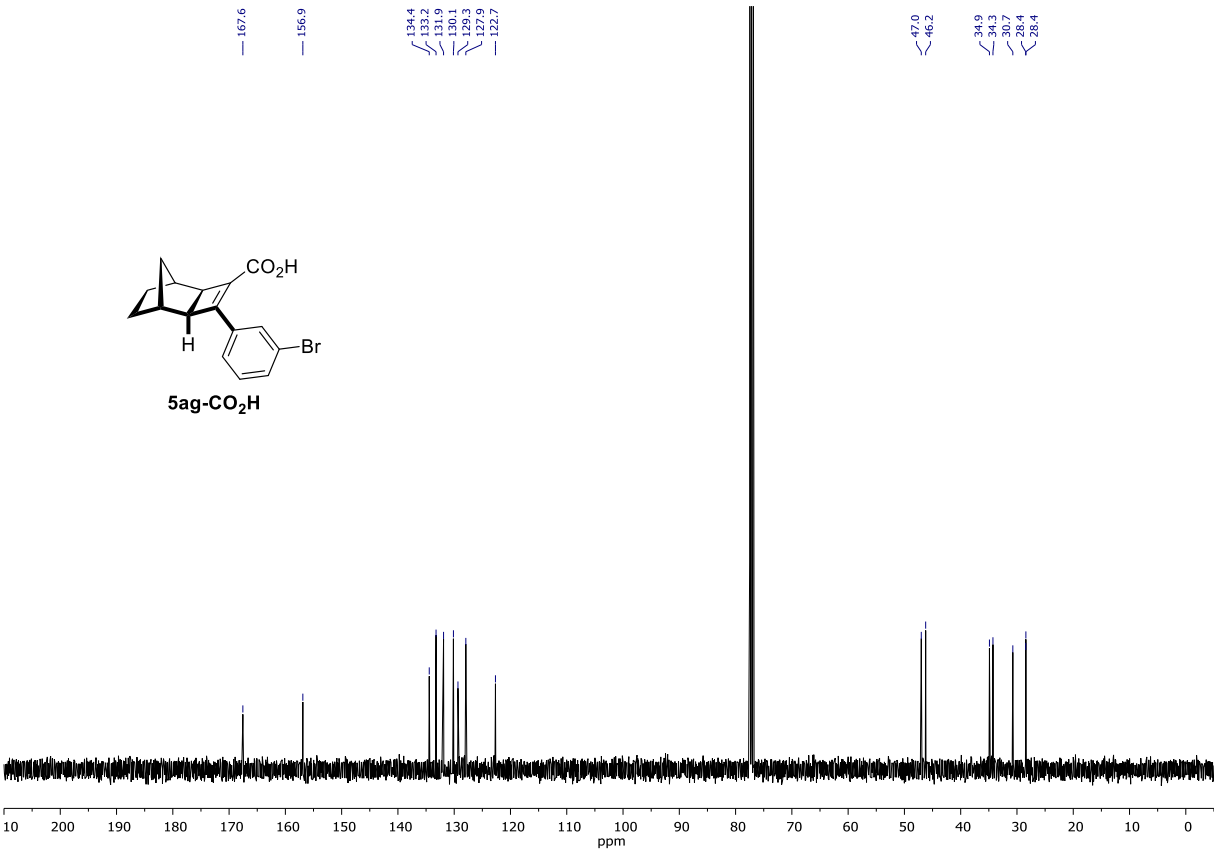

C(O)Ph
Ph
H
5af
ppm

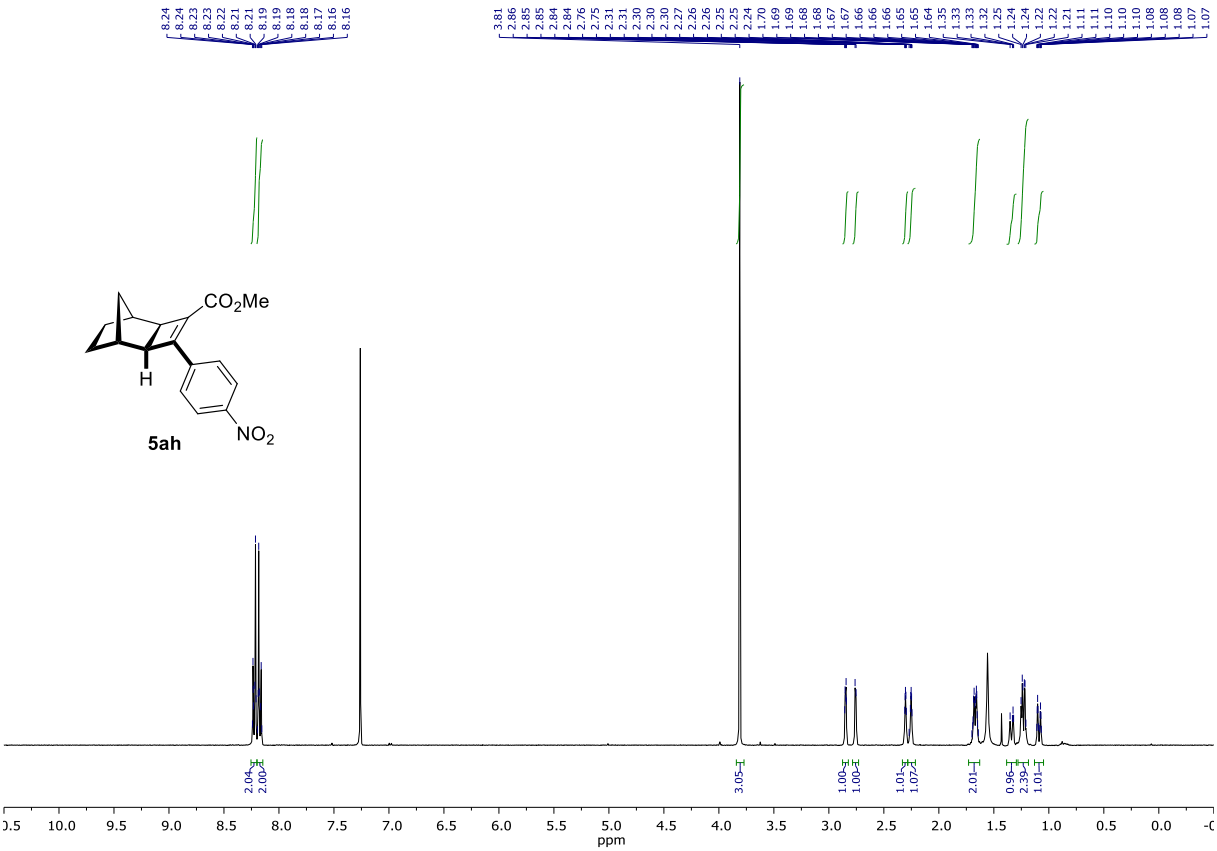

C(O)Ph
Ph
H
5af
ppm

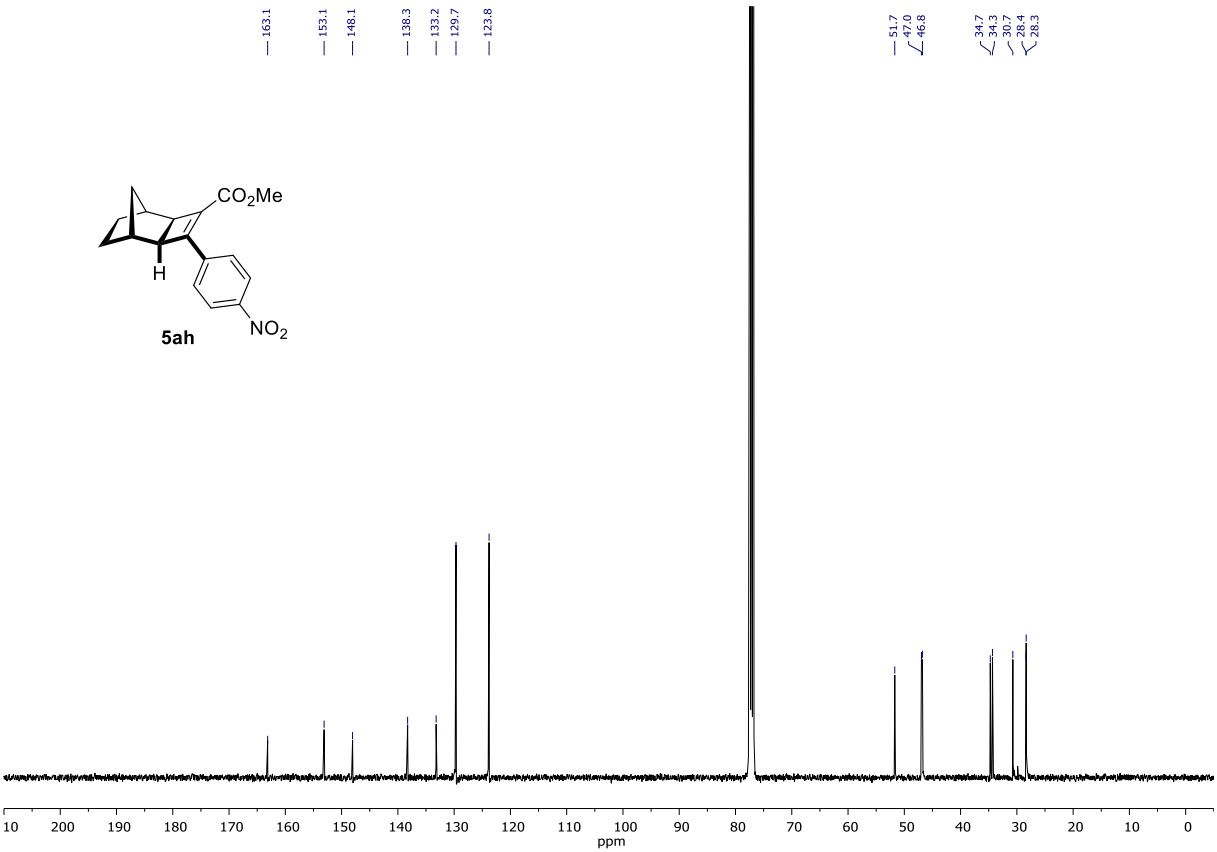

CO2Me
H
Br
5ag
ppm

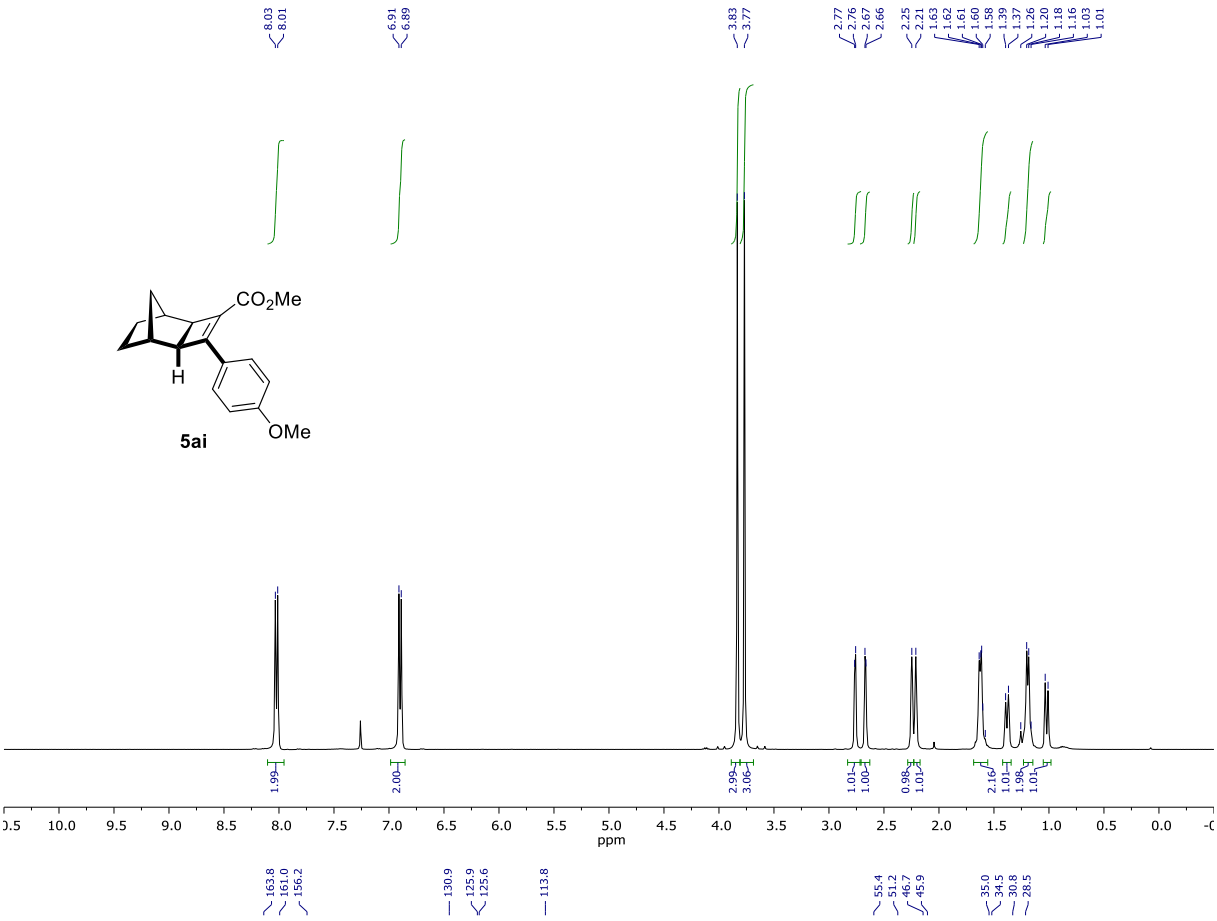

CO2Me
H
Br
5ag
ppm

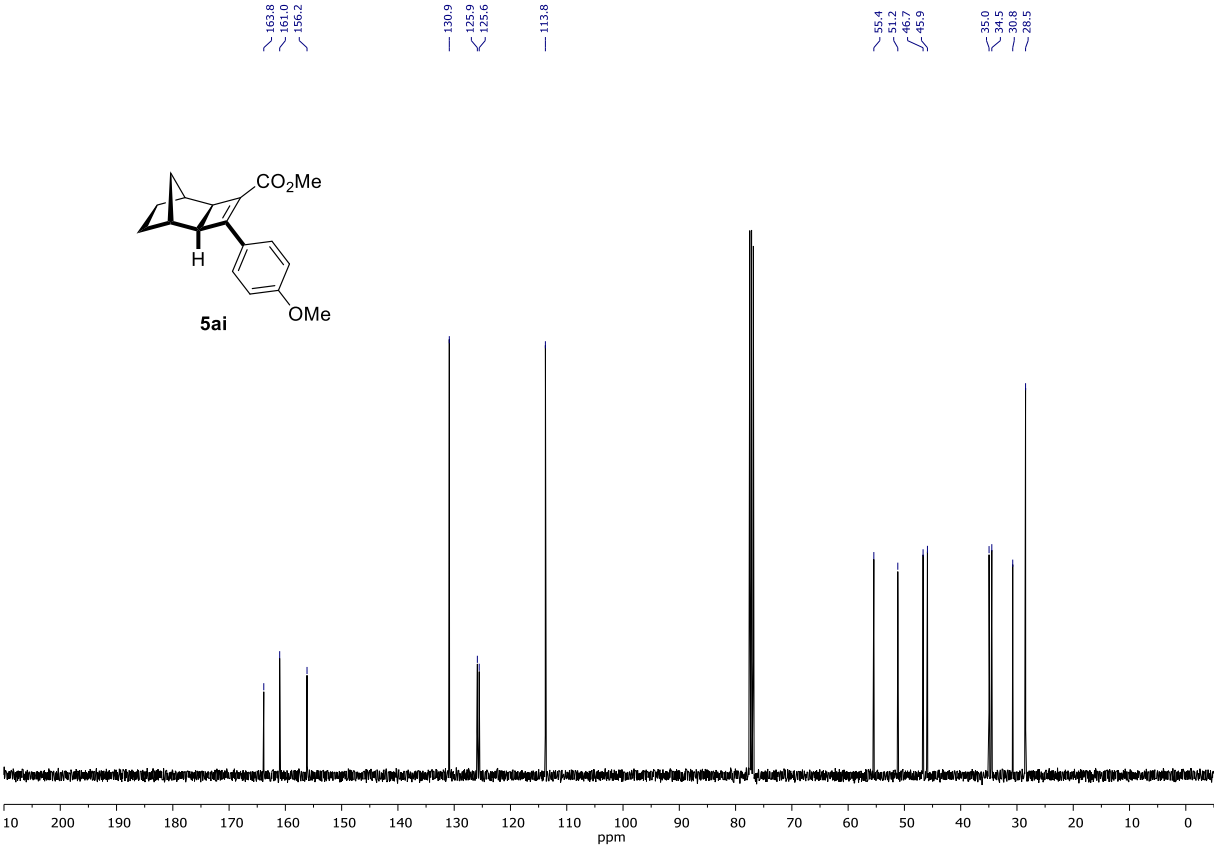

CO2H
H
Br
5ag-CO2H
ppm

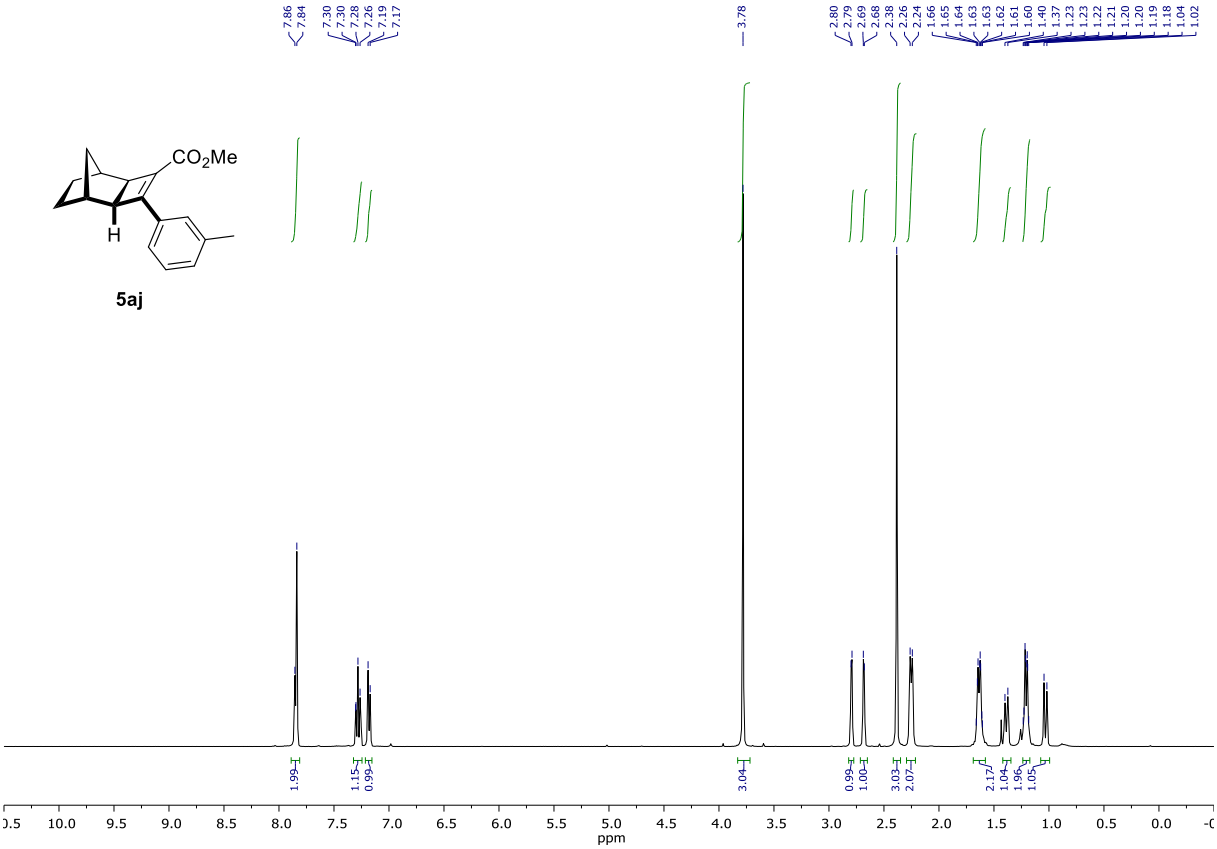

CO2H
H
Br
5ag-CO2H
ppm

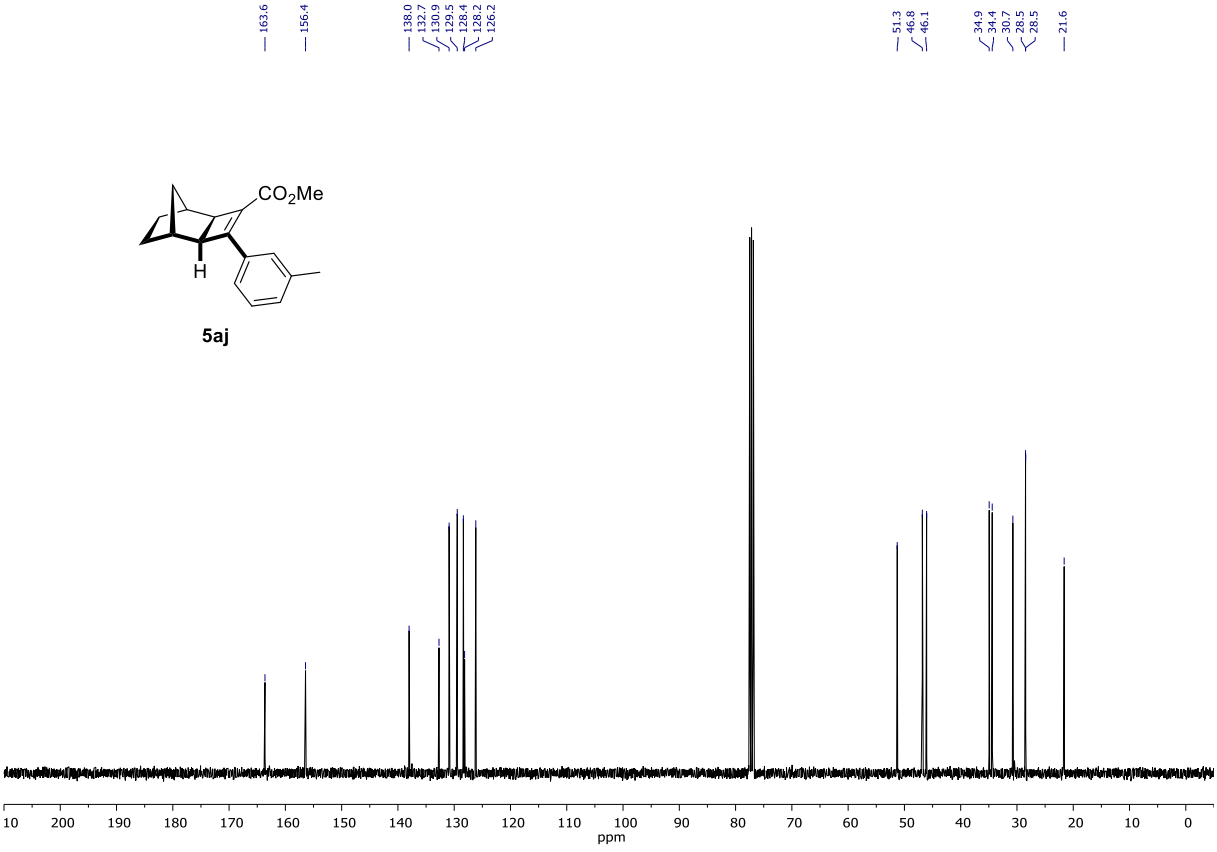

CO2Me
H
NO2
5ah
ppm

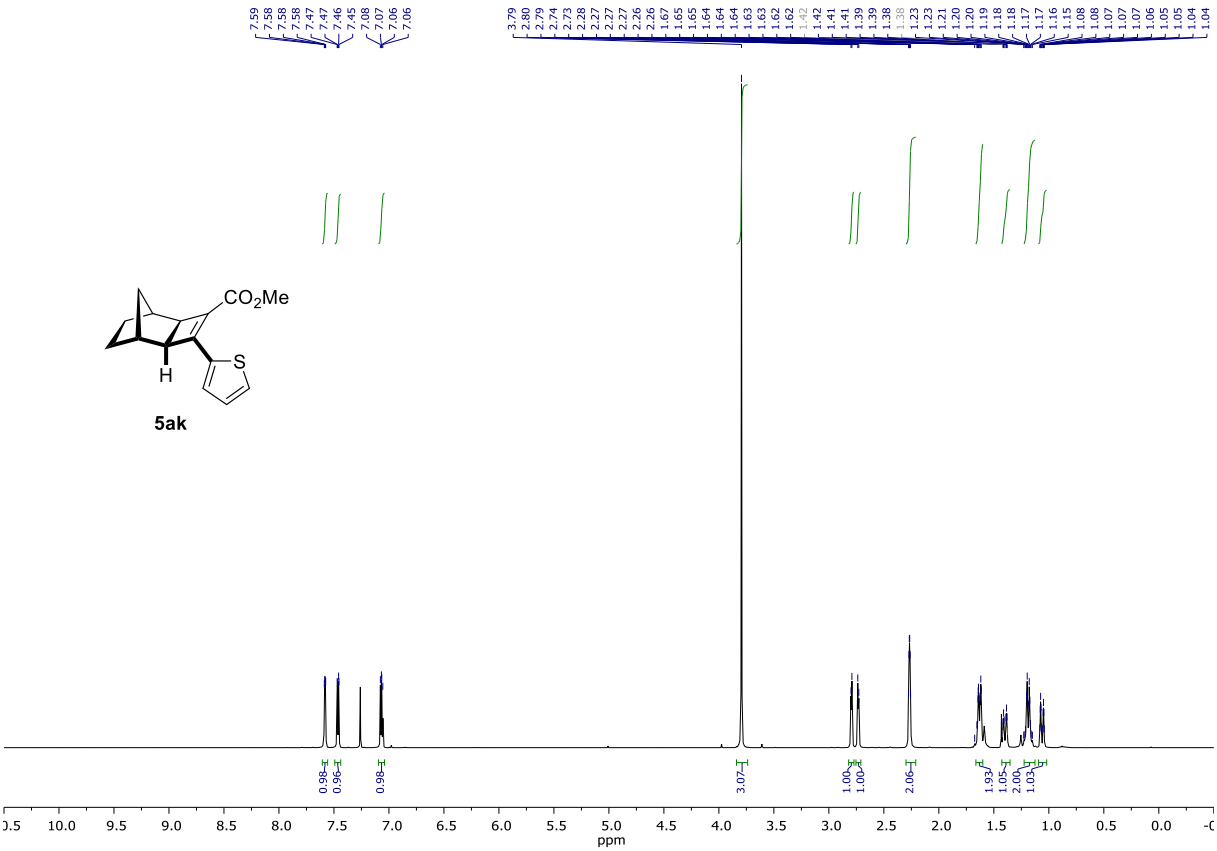

CO2Me
H
NO2
5ah
ppm

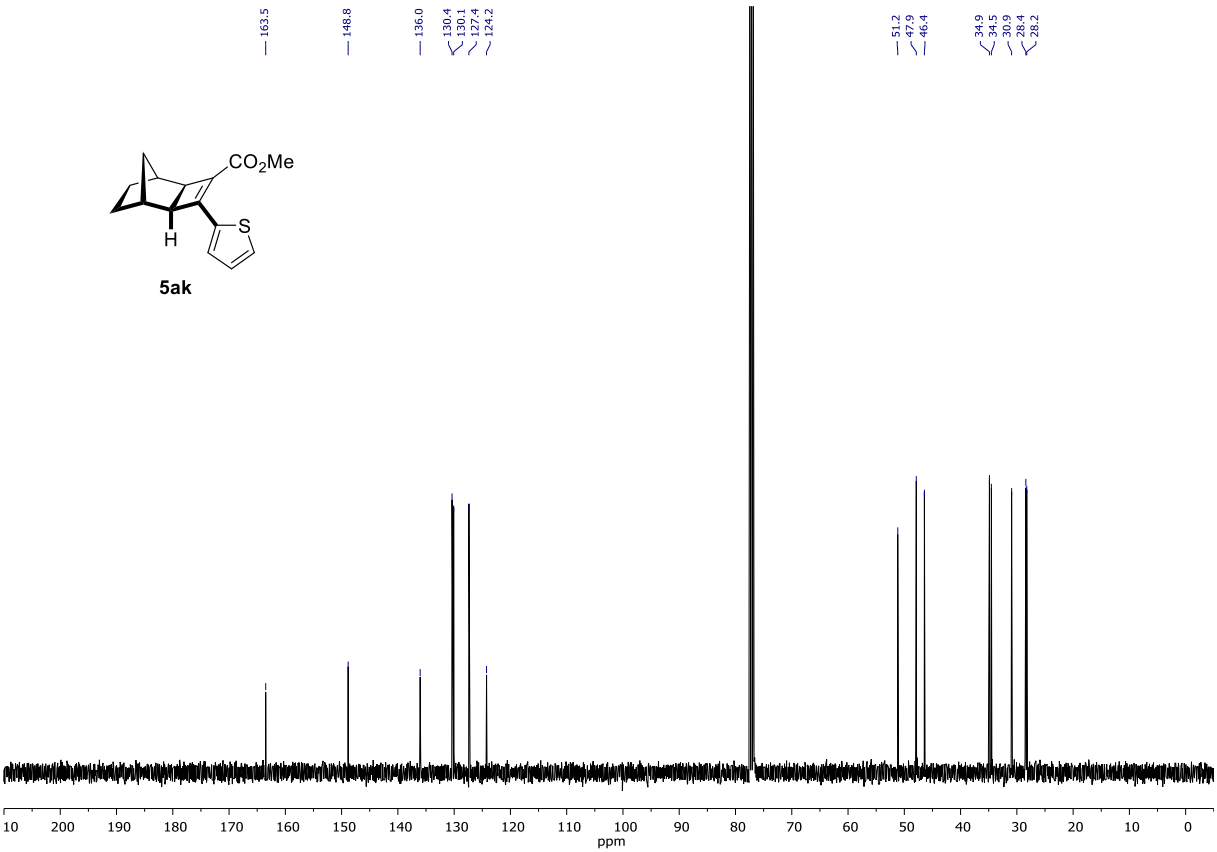

8.03
8.01
6.91
6.89
3.83
3.77
2.77
2.76
2.67
2.66
2.25
2.21
1.63
1.62
1.61
1.60
1.58
1.39
1.37
1.26
1.20
1.18
1.16
1.03
1.01
CO2Me
H
OMe
5ai
1.99
2.00
2.99
3.06
1.01
1.00
0.98
1.01
2.16
1.01
1.98
1.01
ppm

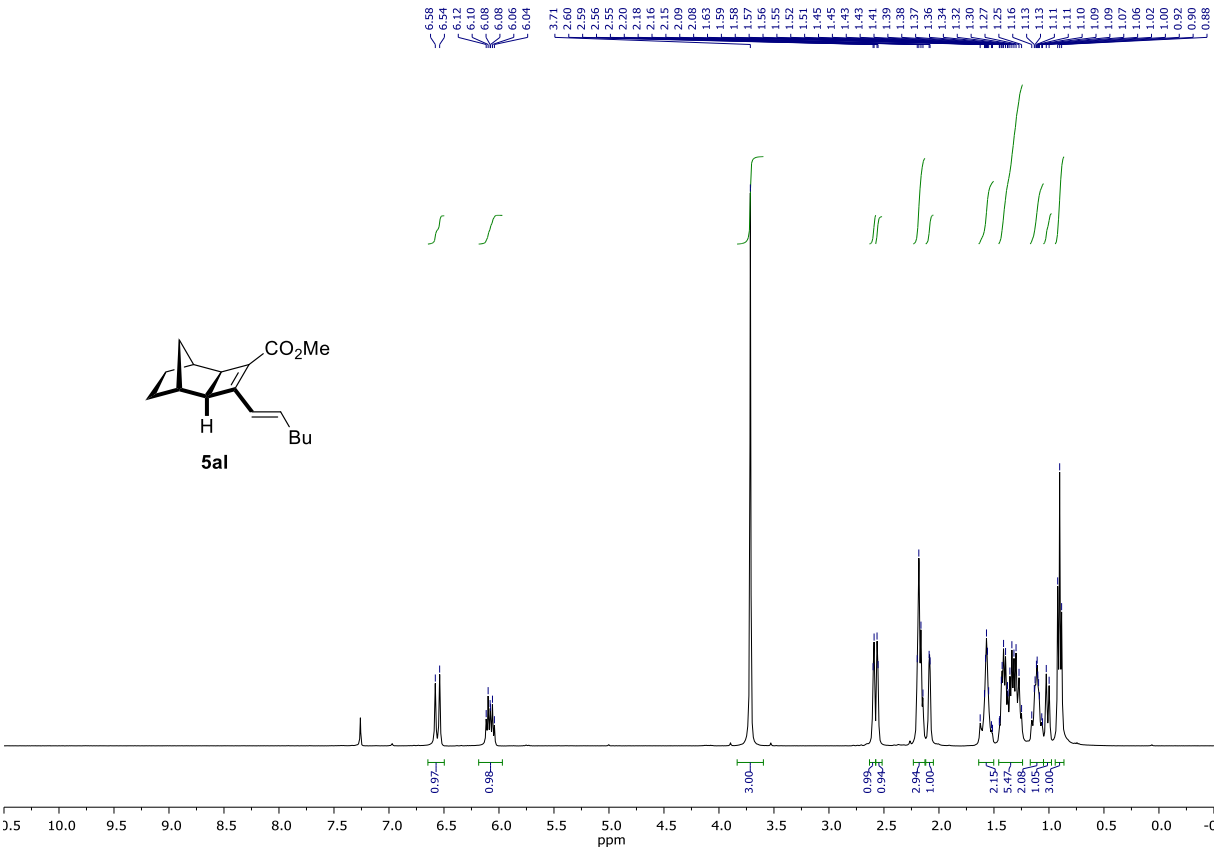

163.8
161.0
156.2
130.9
125.9
125.6
113.8
55.4
51.2
46.7
45.9
35.0
34.5
30.8
28.5
CO2Me
H
OMe
5ai
ppm


7.86
7.84
7.30
7.30
7.28
7.26
7.19
7.17
3.78
2.80
2.79
2.69
2.68
2.38
2.26
2.24
1.66
1.65
1.64
1.63
1.63
1.62
1.61
1.60
1.40
1.37
1.23
1.23
1.22
1.21
1.20
1.20
1.19
1.18
1.04
1.02
CO2Me
H
5aj
1.99
1.15
0.99
3.04
0.99
1.00
3.03
2.07
2.17
1.04
1.96
1.05
ppm


163.6
156.4
138.0
132.7
130.9
129.5
128.4
128.2
126.2
51.3
46.8
46.1
34.9
34.4
30.7
28.5
28.5
21.6
CO2Me
H
5aj
ppm


CO2Me
S
H
5ak
ppm


CO2Me
S
H
5ak
ppm


6.58
6.54
6.12
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6.08
6.08
6.06
6.04
3.71
2.60
2.59
2.56
2.55
2.20
2.18
2.16
2.15
2.09
2.08
1.63
1.59
1.58
1.57
1.56
1.55
1.52
1.51
1.45
1.45
1.43
1.43
1.41
1.39
1.38
1.37
1.36
1.34
1.32
1.30
1.27
1.25
1.16
1.13
1.13
1.11
1.11
1.10
1.09
1.09
1.07
1.06
1.02
1.00
0.92
0.90
0.88
CO2Me
H
Bu
5al
0.97
0.98
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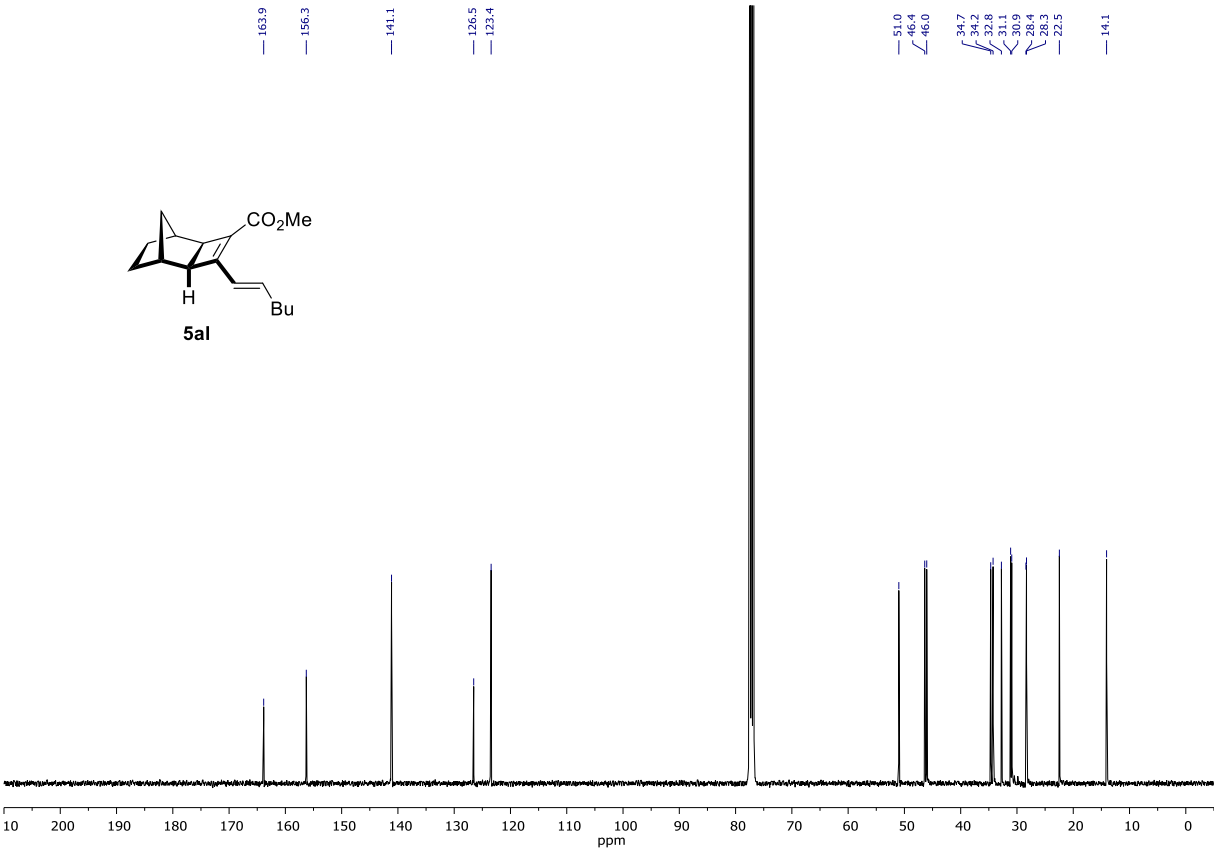
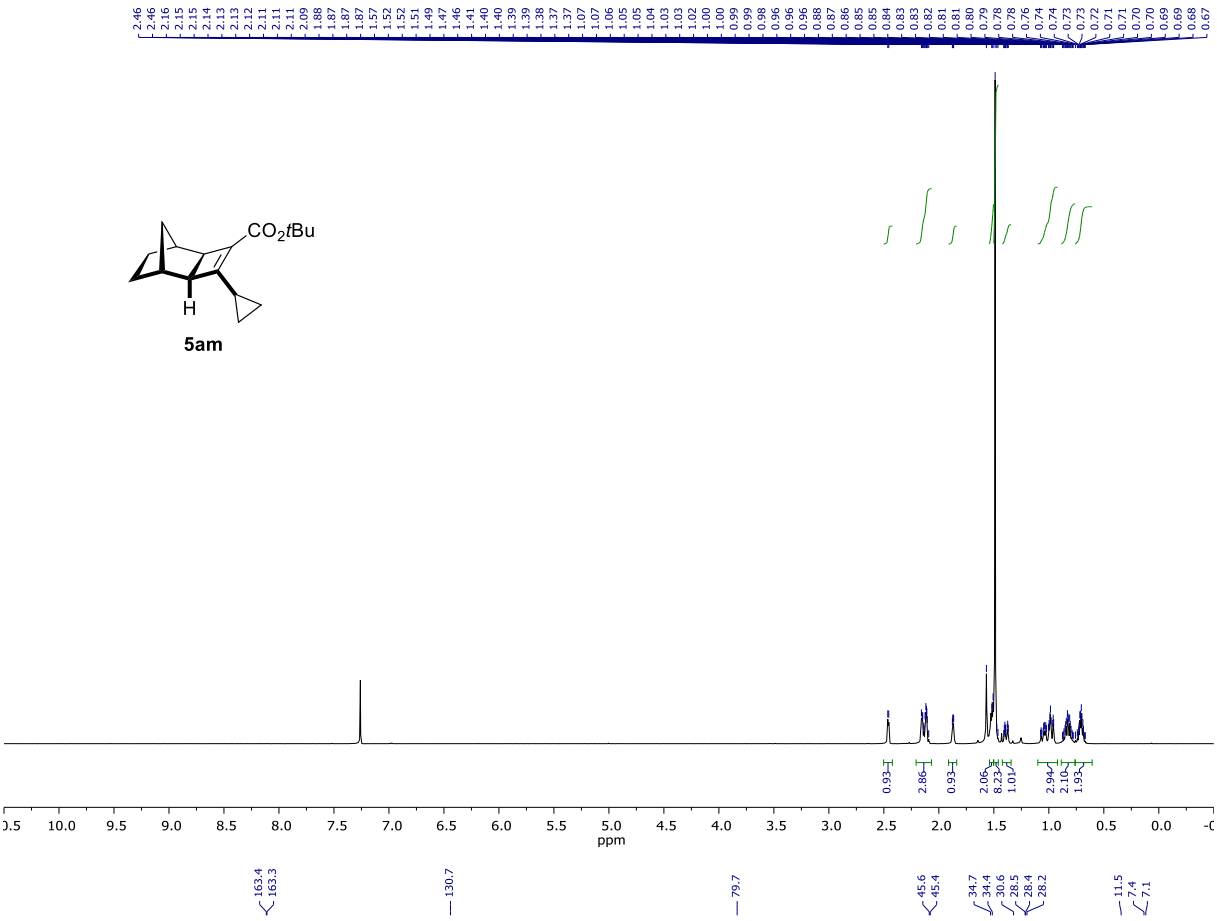
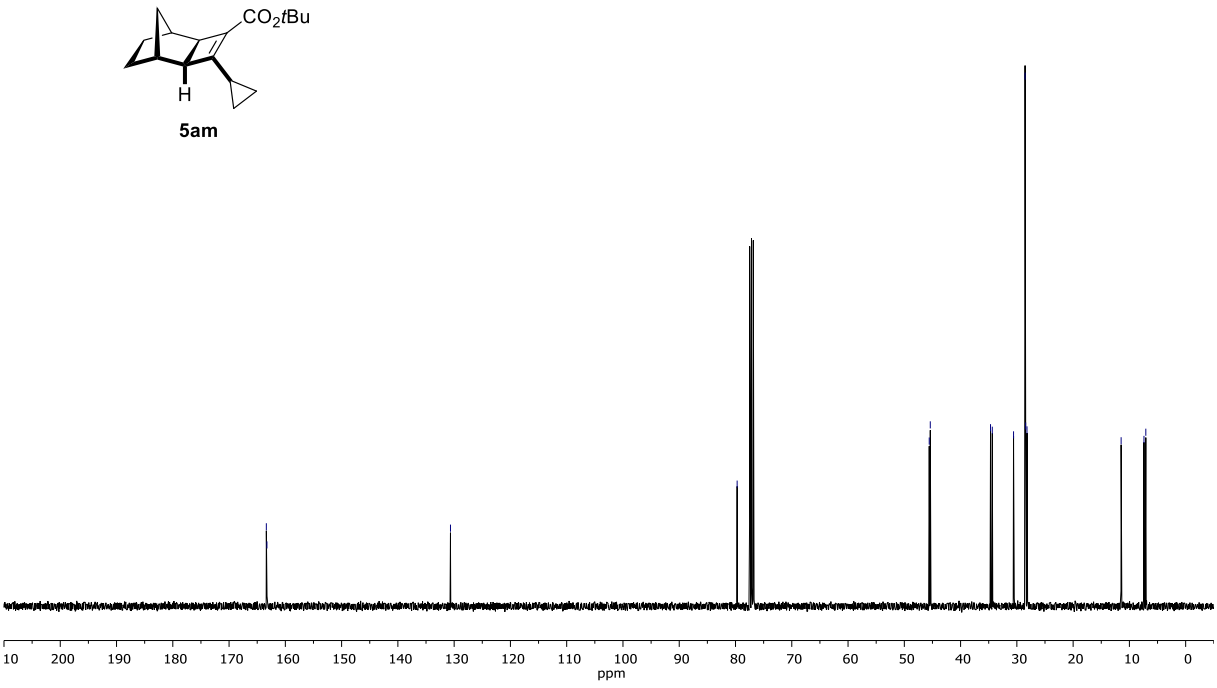
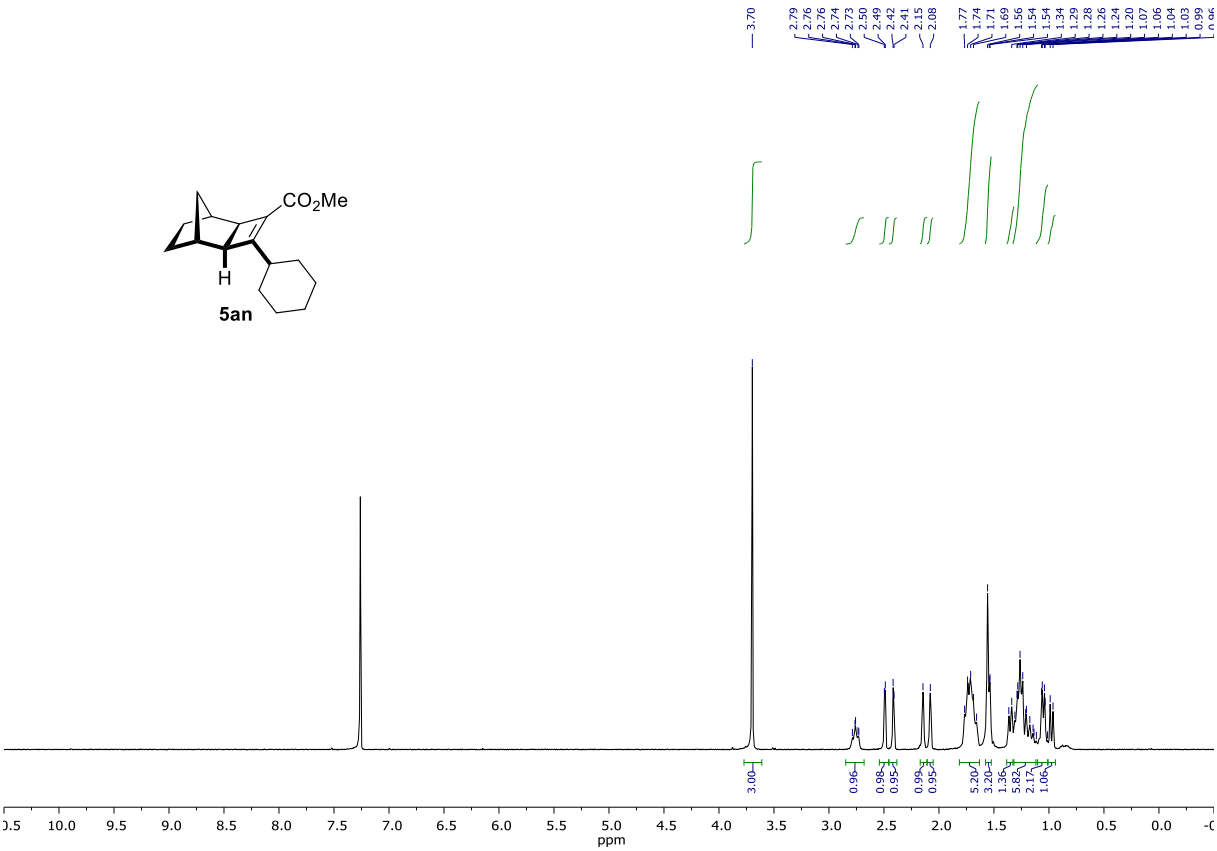
0.99
0.94
2.94
1.00
2.15
5.47
2.08
1.05
3.00
ppm


163.9
156.3
141.1
126.5
123.4
51.0
46.4
46.0
34.7
34.2
32.8
31.1
30.9
28.4
28.3
22.5
14.1
CO2Me
H
Bu
5al
ppm


CO2tBu
H
5am
ppm


CO2tBu
H
5am
ppm


CO2Me
H
5an
3.70
2.79
2.76
2.74
2.73
2.50
2.49
2.42
2.41
2.15
2.08
1.77
1.74
1.71
1.69
1.56
1.54
1.34
1.29
1.28
1.26
1.24
1.20
1.07
1.06
1.04
1.03
0.99
3.00
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0.95
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0.95
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3.20
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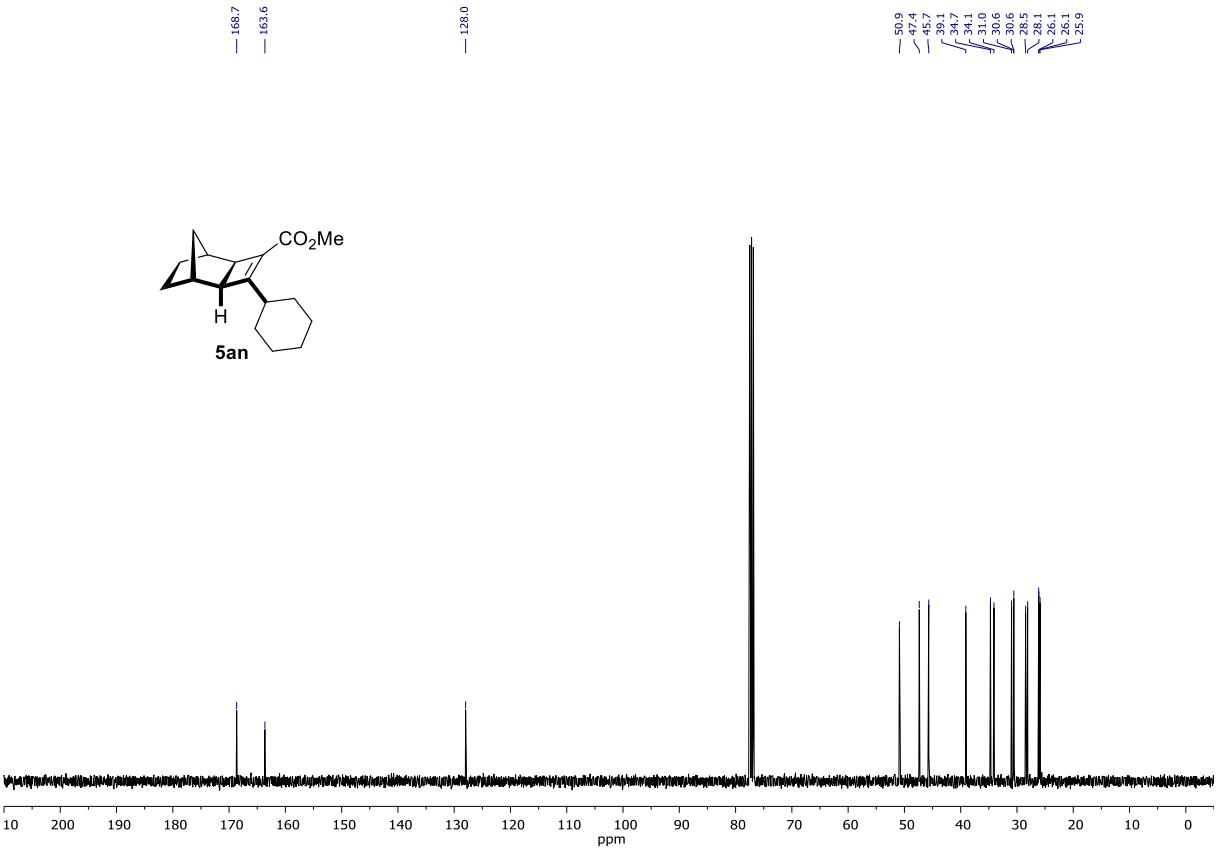
2.17
1.06
ppm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163.6
128.0
50.9
47.4
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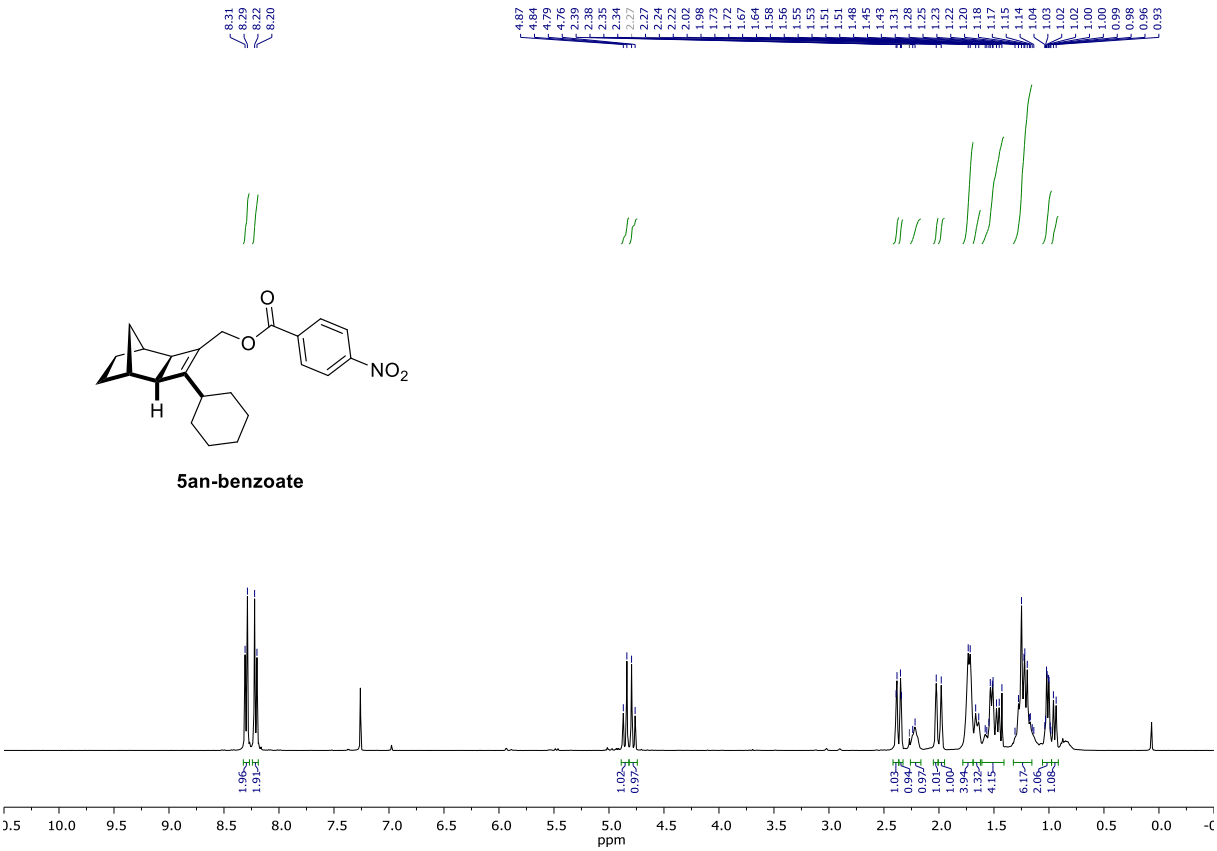
28.1
26.1
26.1
25.9
ppm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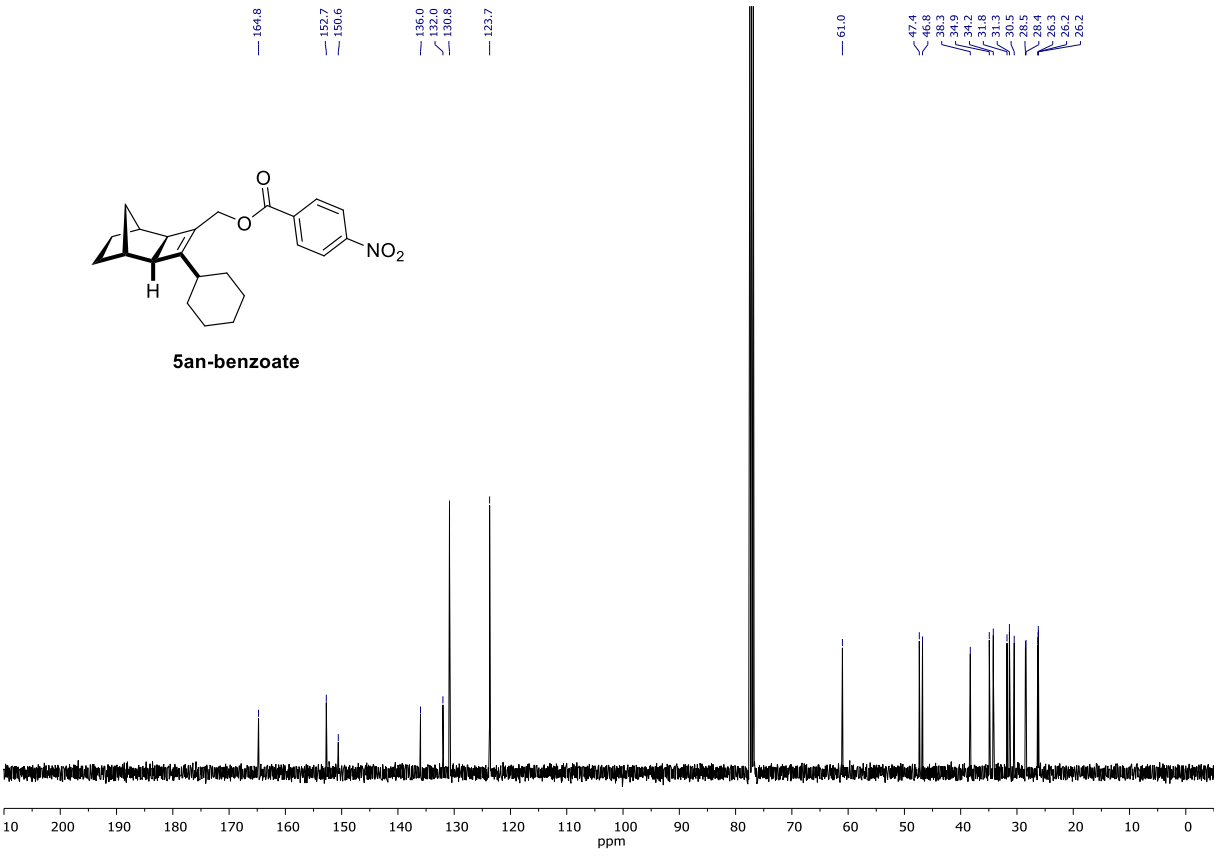
ppm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NO2
H
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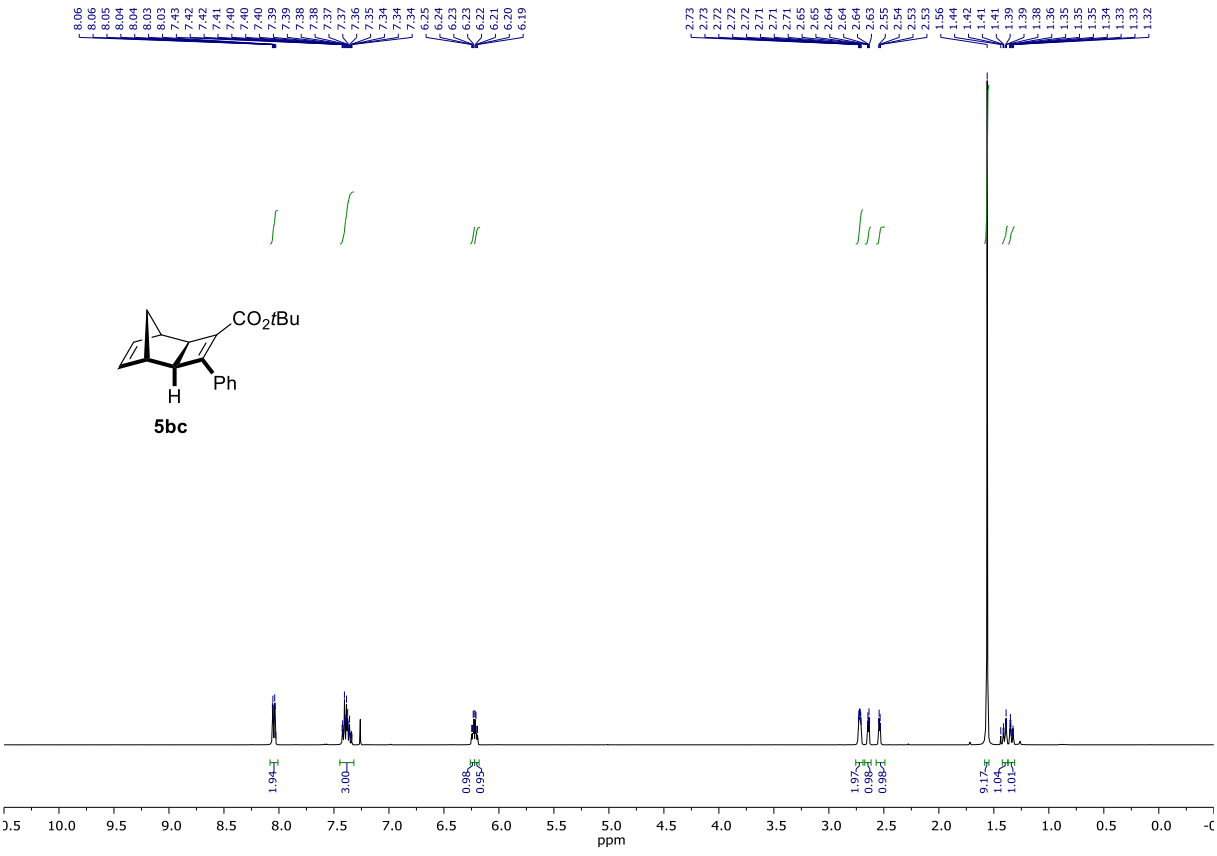
ppm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2.73 2.73 2.72 2.72 2.72 2.71 2.71 2.71 2.65 2.65 2.64 2.64 2.64 2.63 2.55 2.54 2.53 2.53 1.56 1.44 1.42 1.41 1.41 1.39 1.39 1.38 1.36 1.35 1.35 1.34 1.33 1.33 1.32
CO2tBu
Ph
H
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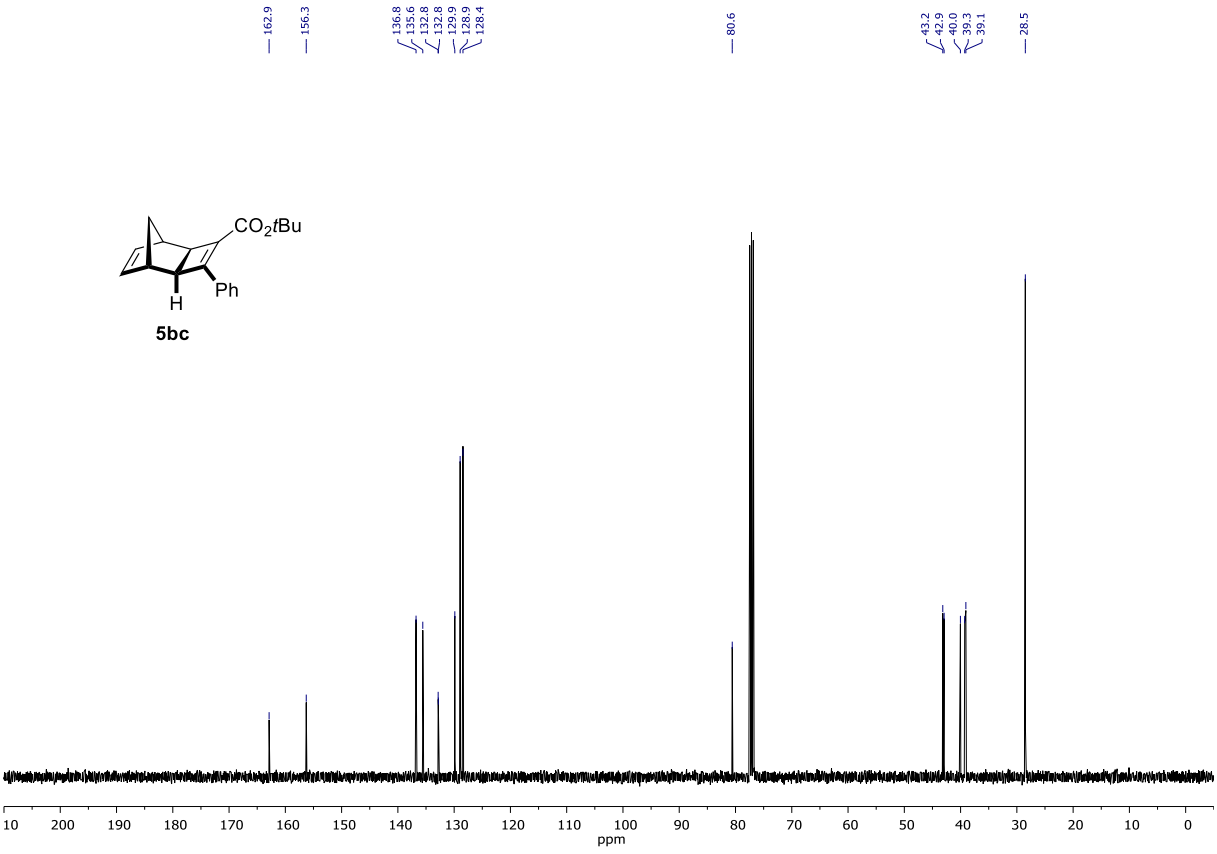
ppm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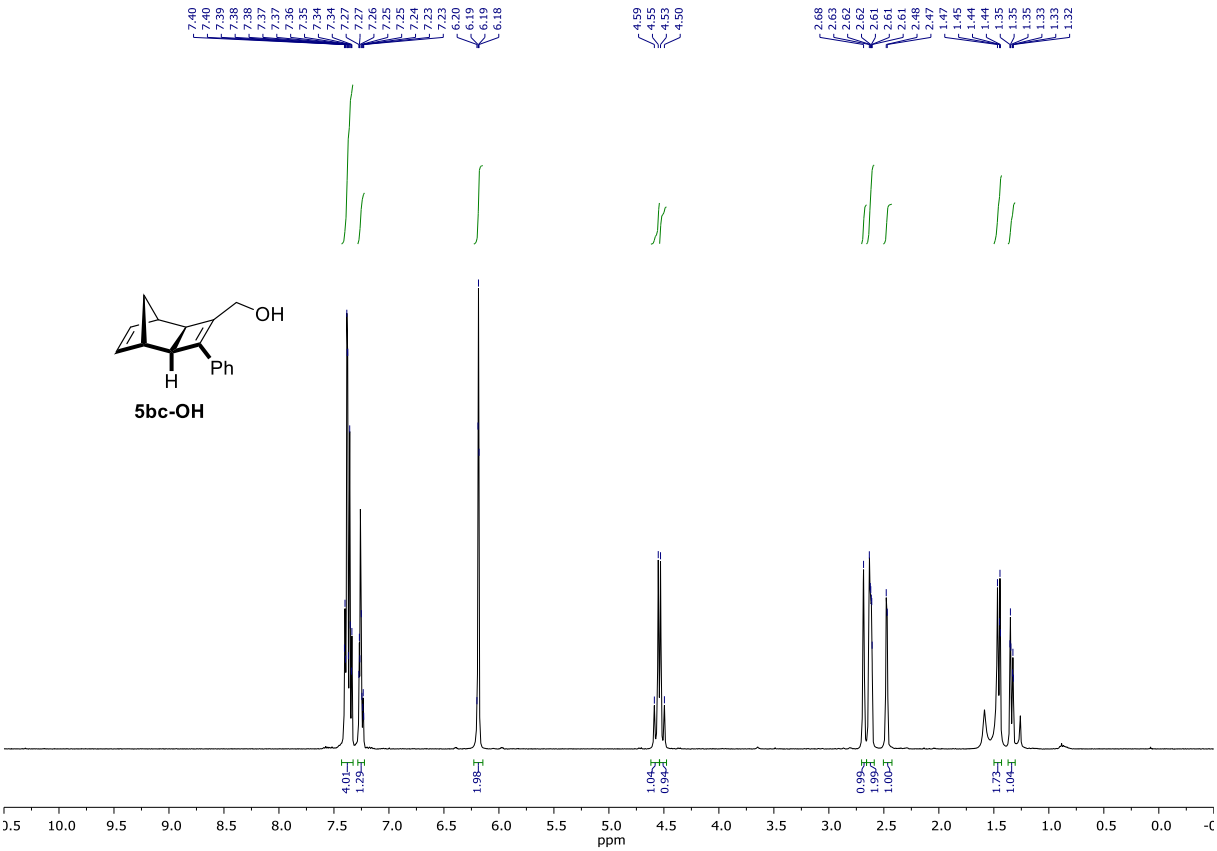
CO2tBu
Ph
H
5bc
ppm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4.59 4.55 4.53 4.50
2.68 2.63 2.62 2.62 2.61 2.61 2.61 2.48 2.47 1.47 1.45 1.44 1.44 1.35 1.35 1.35 1.33 1.33 1.32
OH
Ph
H
5bc-OH
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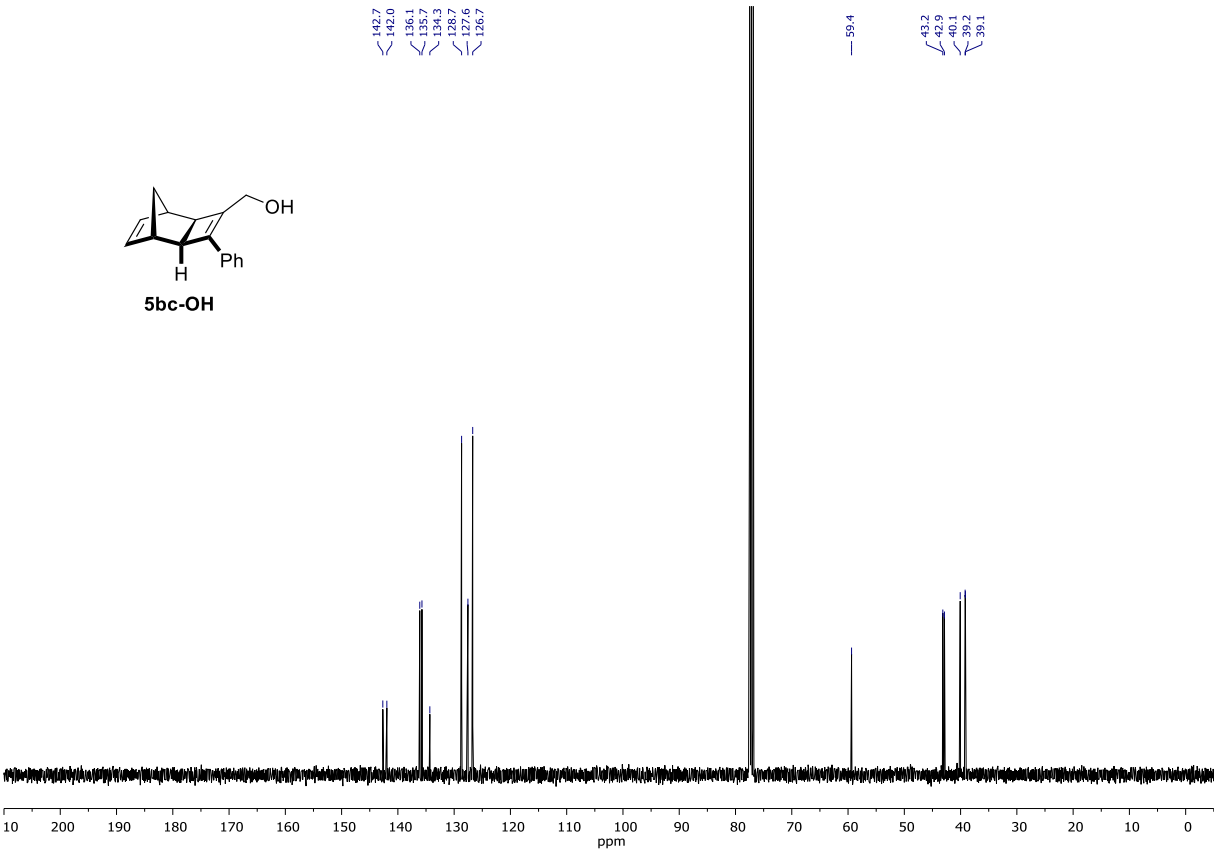
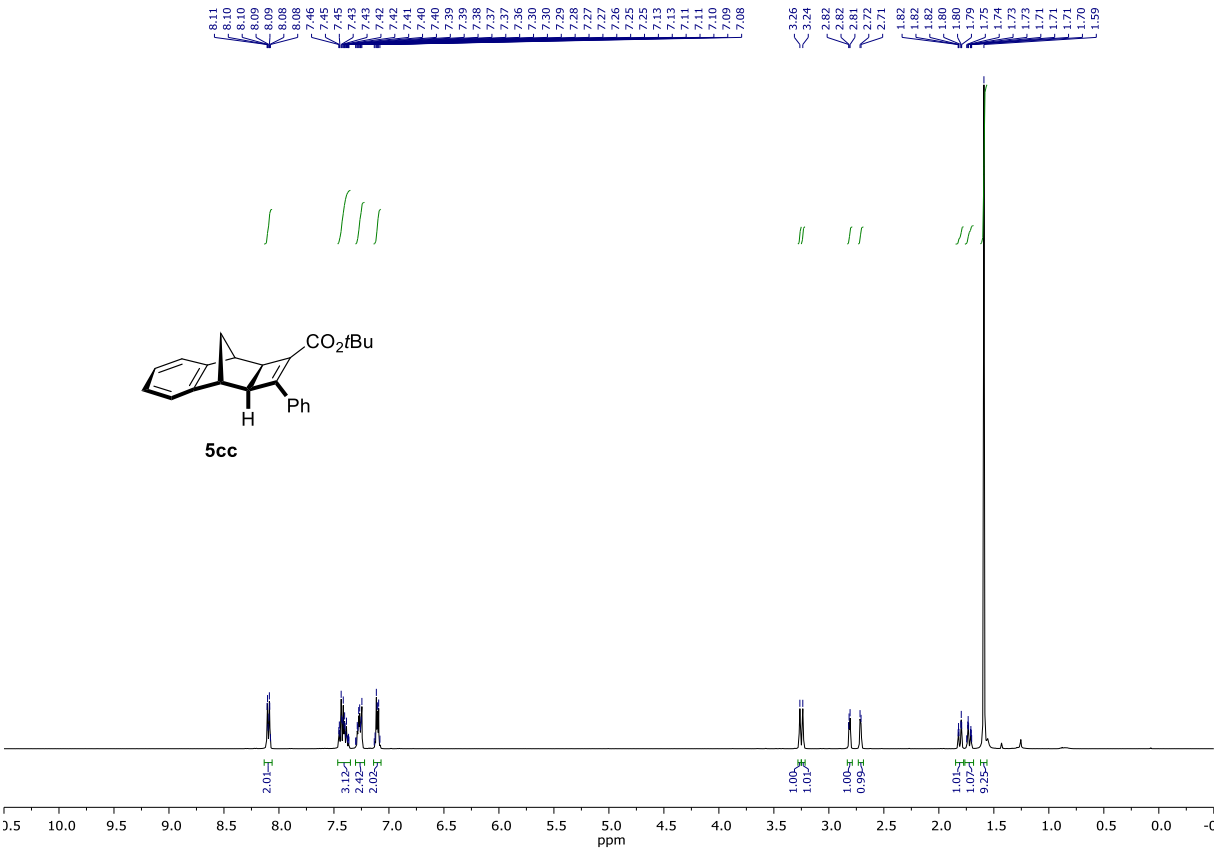
ppm


142.7 142.0 136.1 135.7 134.3 128.7 127.6 126.7
59.4
43.2 42.9 40.1 39.2 39.1
OH
Ph
H
5bc-OH
ppm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3.26 3.24 2.82 2.82 2.81 2.72 2.71 1.82 1.82 1.82 1.80 1.80 1.79 1.75 1.74 1.73 1.73 1.71 1.71 1.71 1.70 1.59
CO2tBu
Ph
H
5cc
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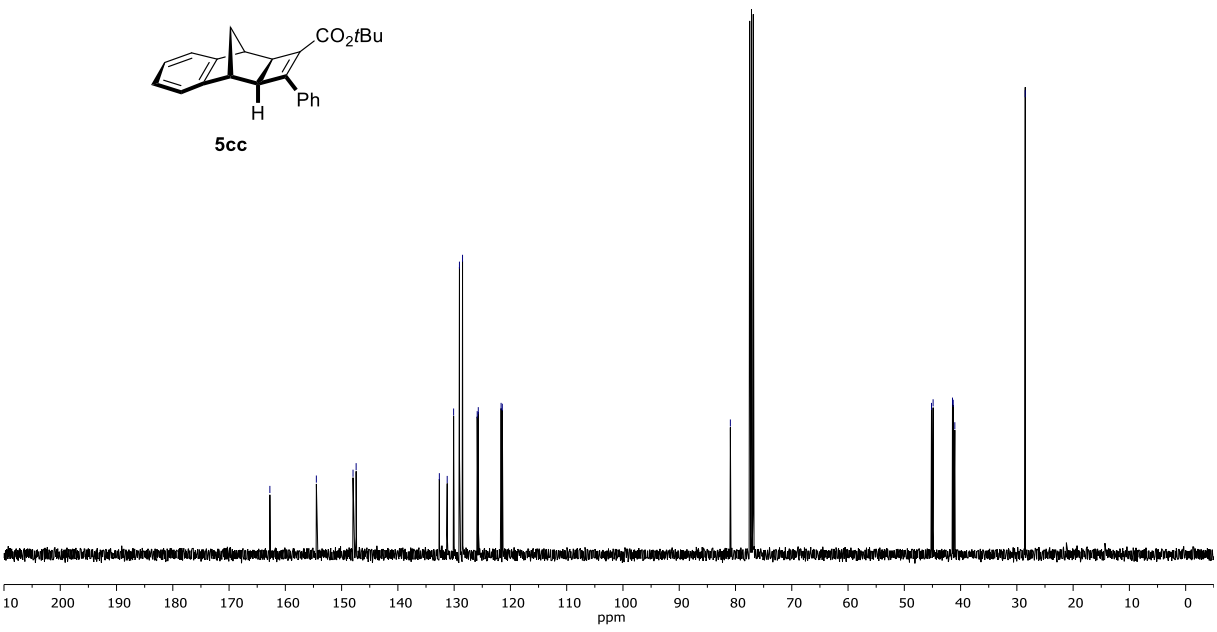
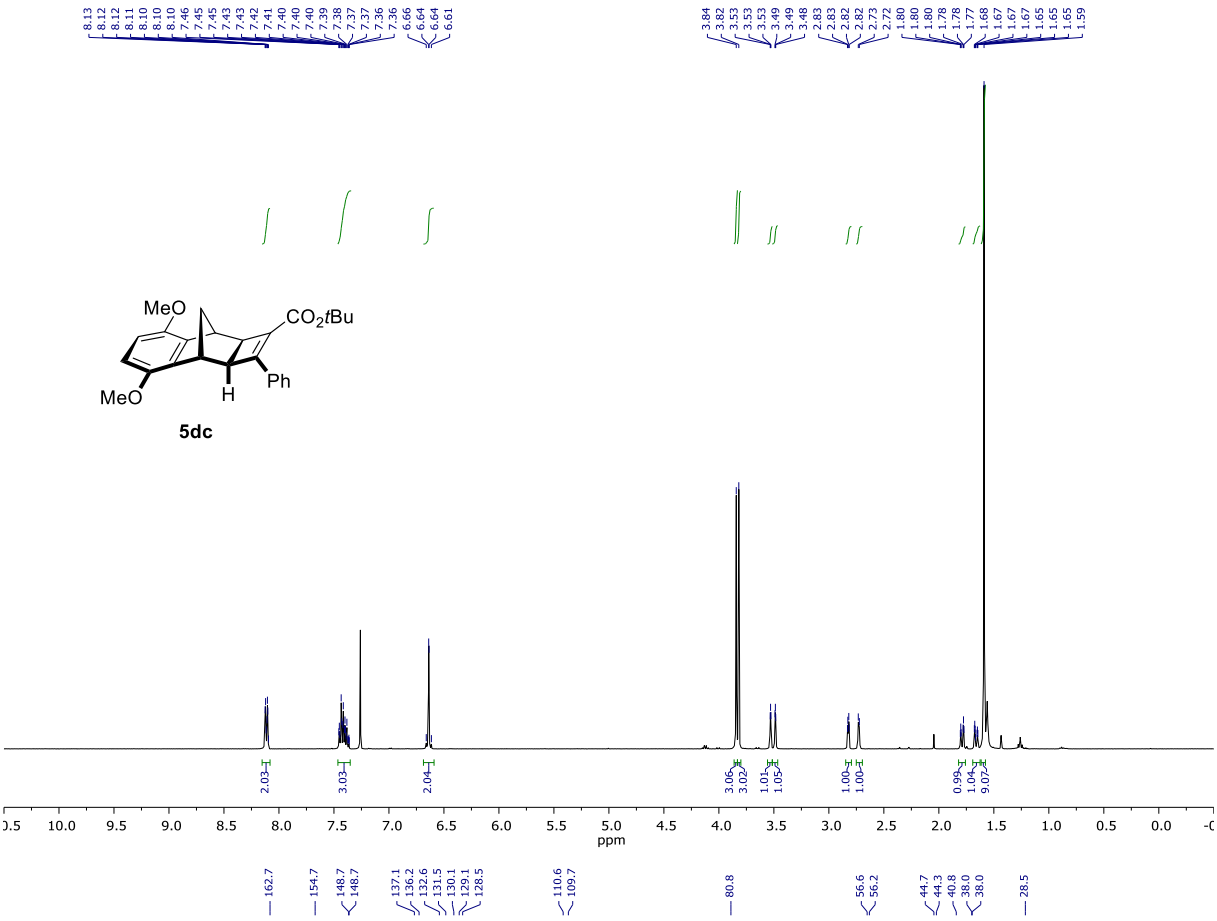
ppm


162.8 154.5 148.0 147.4 132.6 131.2 130.1 129.1 128.5 125.9 125.7 121.7 121.4 80.9 45.2 44.9 41.4 41.3 41.0 28.5
CO2tBu
Ph
H
5cc
ppm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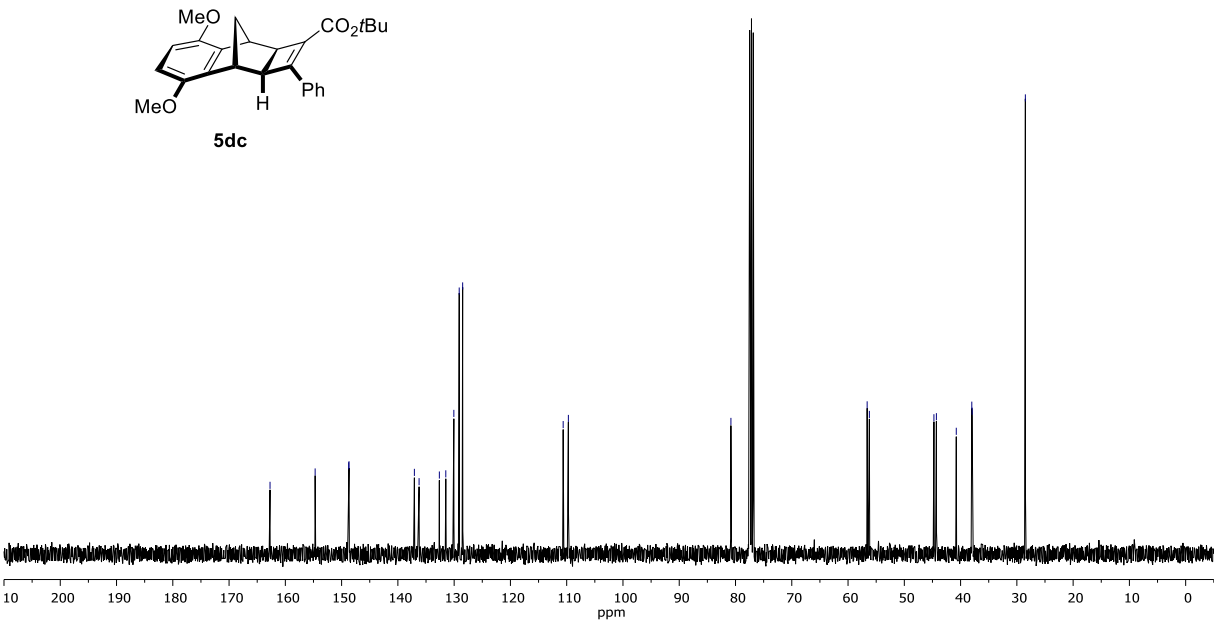
CO2tBu
Ph
H
MeO
5dc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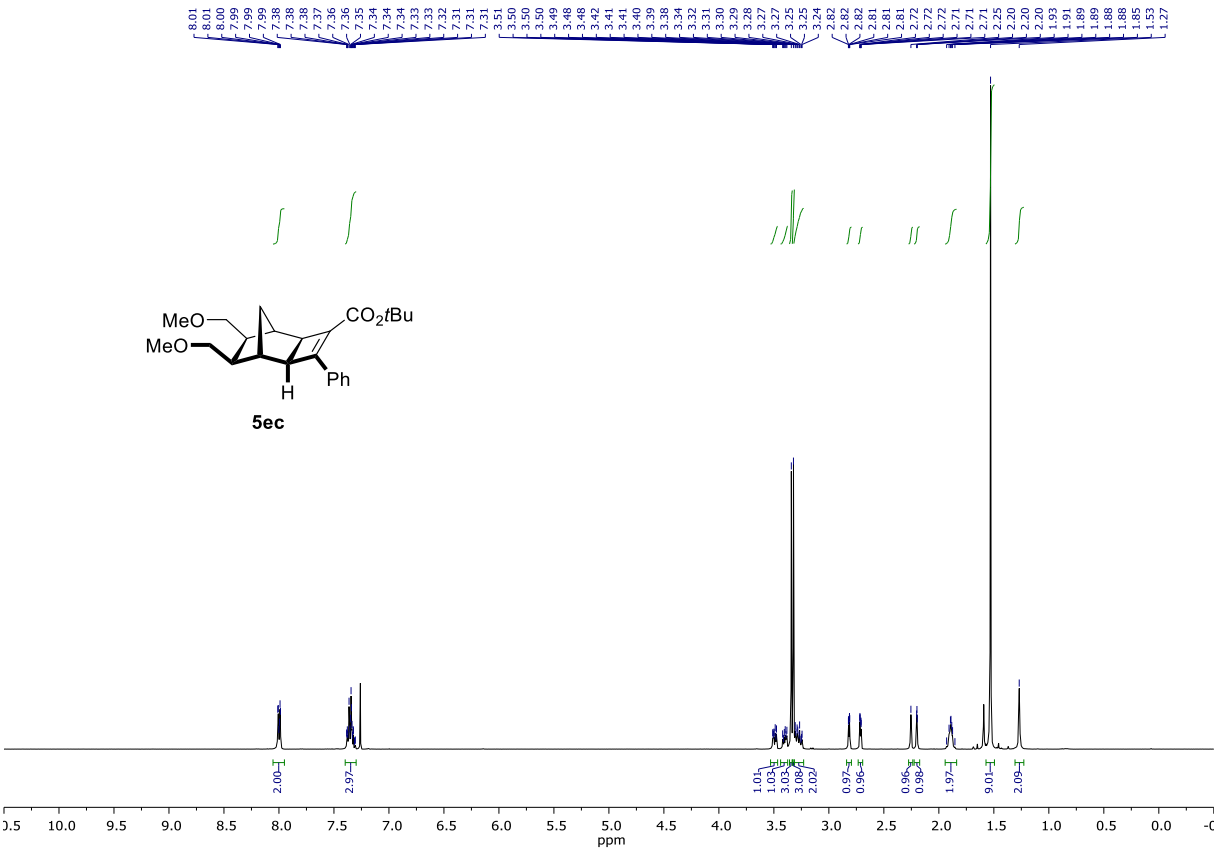
CO2tBu
Ph
H
MeO
5dc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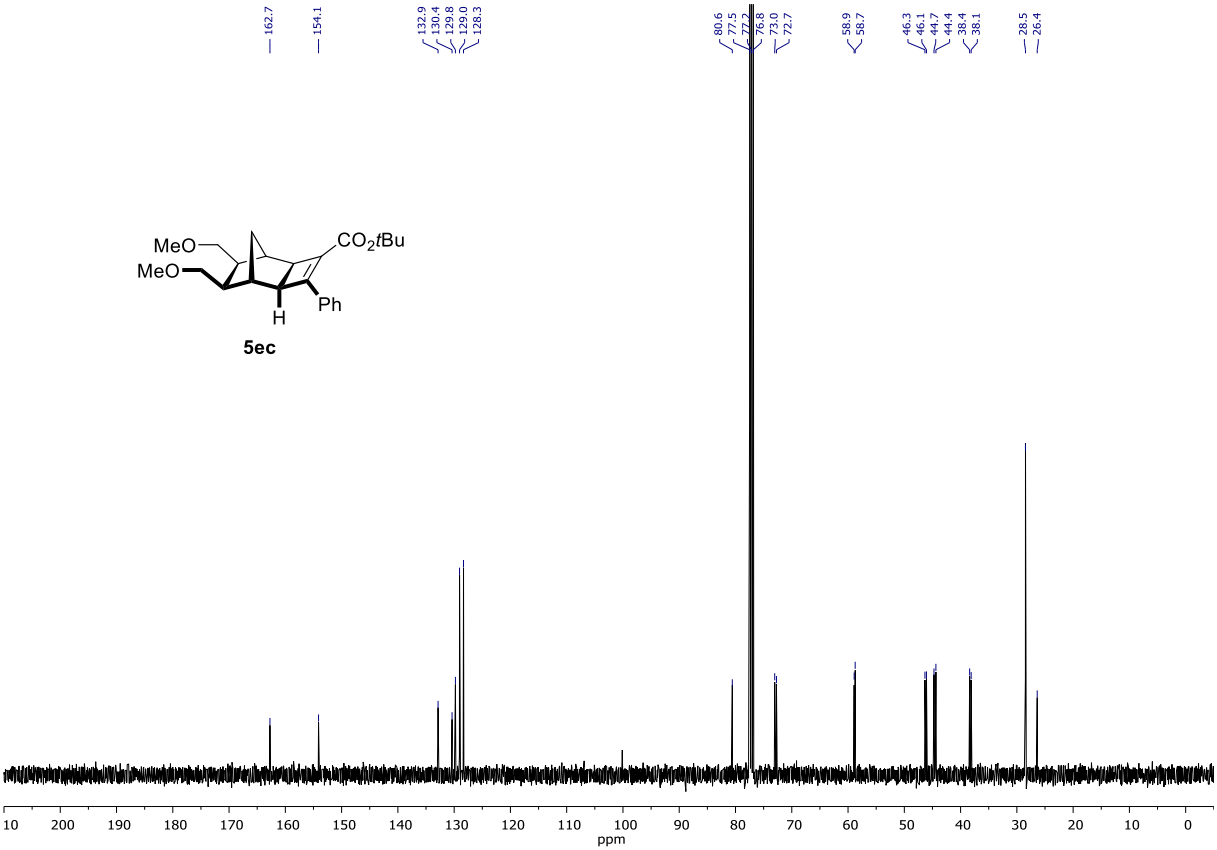
MeO
CO2tBu
Ph
H
5ec
ppm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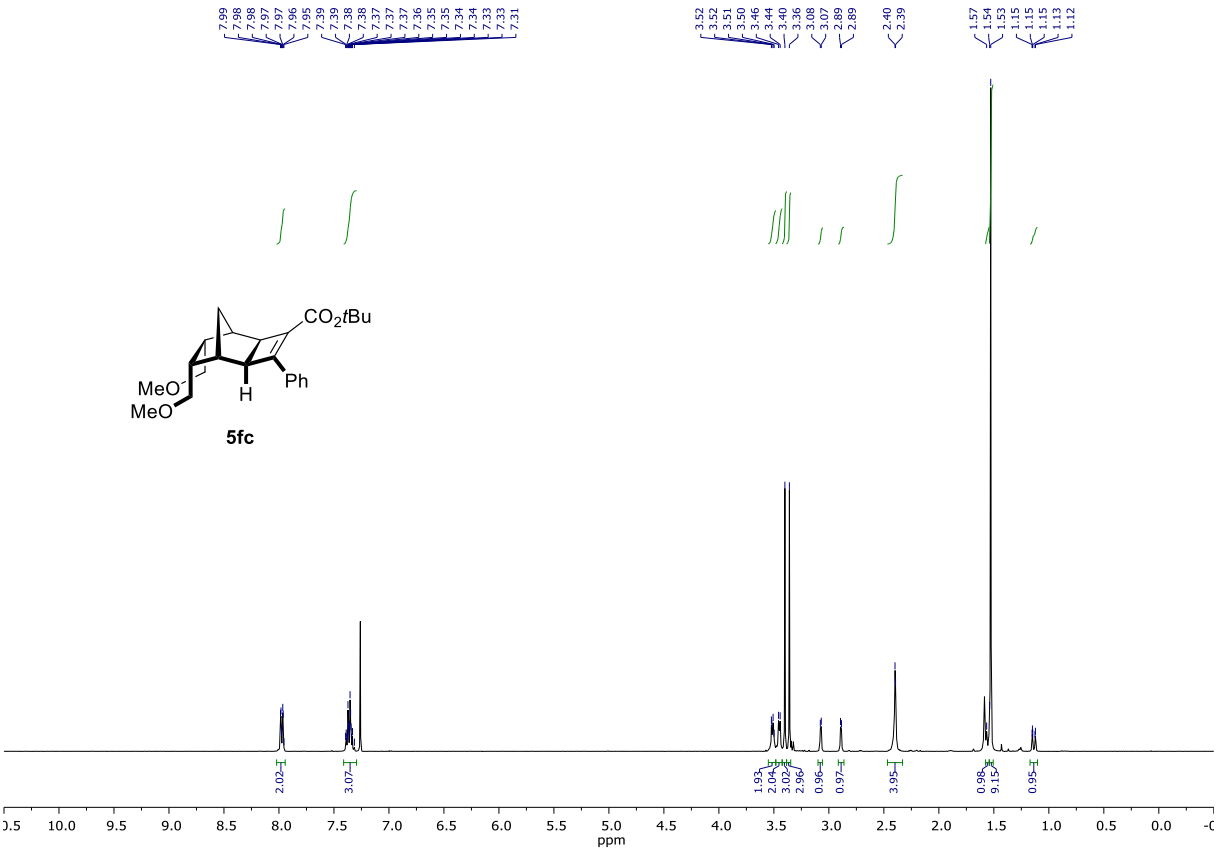
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2.40
2.39
1.57
1.54
1.53
1.15
1.15
1.15
1.13
1.12
CO2tBu
Ph
H
MeO
MeO
5fc
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2.04
3.02
2.96
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3.95
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9.15
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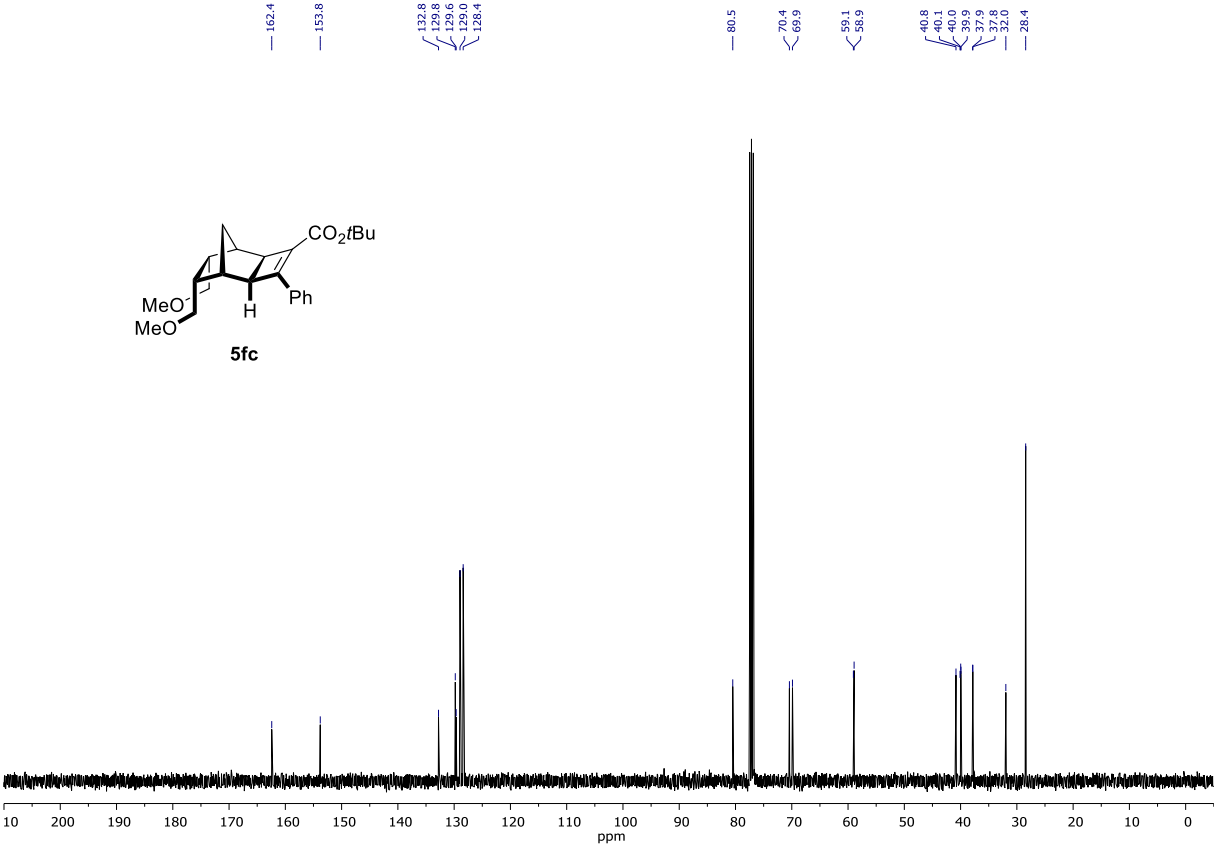
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128.4
80.5
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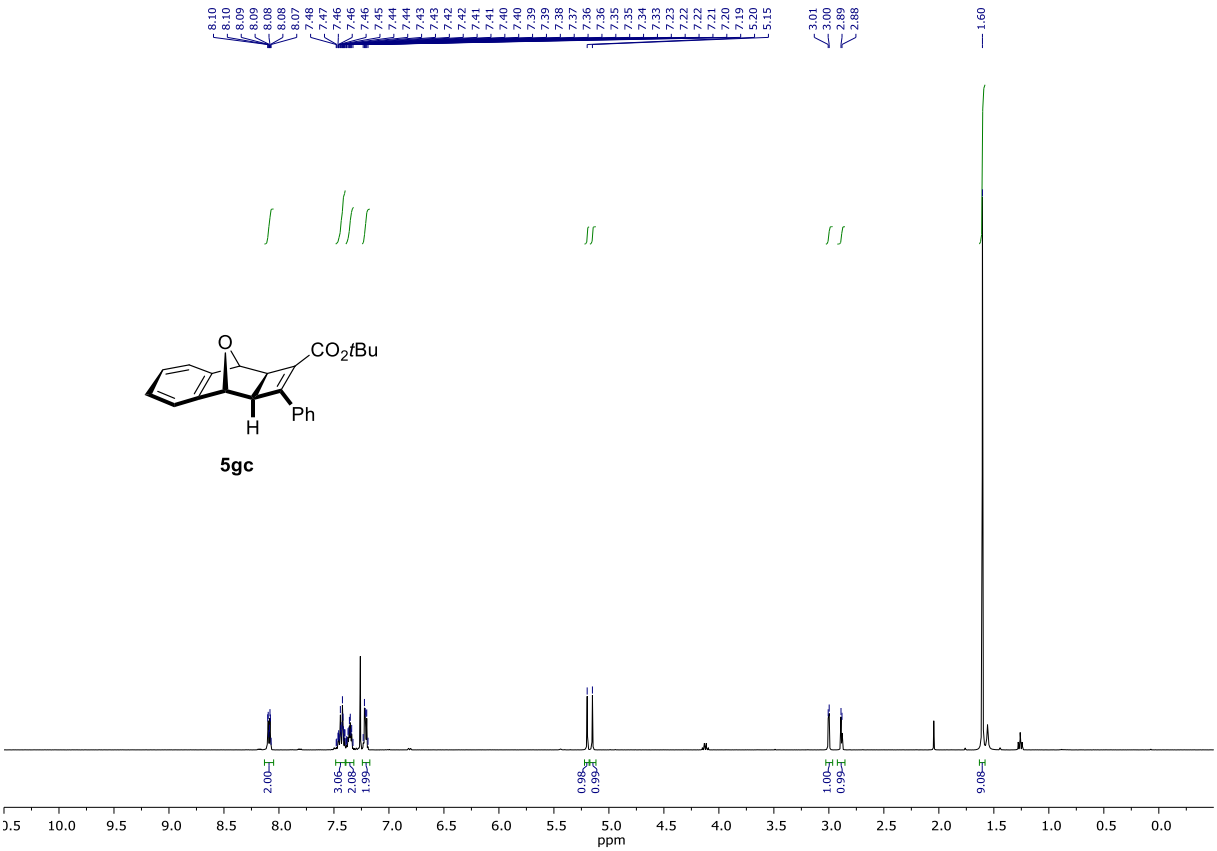
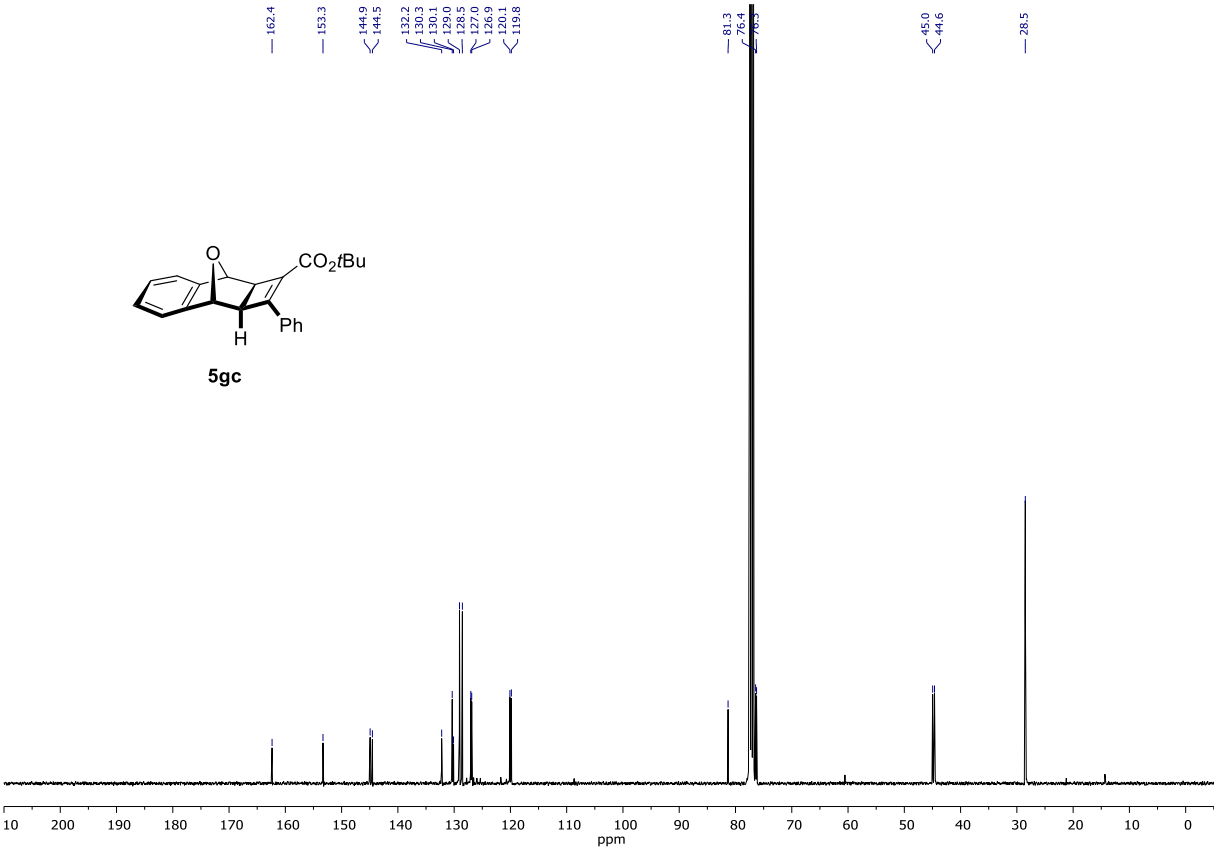
69.9
59.1
58.9
40.8
40.1
40.0
39.9
37.9
37.8
32.0
28.4
CO2tBu
Ph
H
MeO
MeO
5fc
ppm



5gc



5gc