

Supporting Information

Gold(I)-Catalyzed Synthesis of Indenes and Cyclopentadienes: Access to (±)-Laurokamurene B and the Skeletons of the Cycloaurenones and Dysiherbols

*Xiang Yin, Mauro Mato, and Antonio M. Echavarren**

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1. General Considerations

All gold-catalyzed reactions were performed using HPLC-grade solvents, without a protective inert atmosphere. Unless otherwise stated, the rest of the reactions reported herein were carried out under argon atmosphere in solvents dried by passing through an activated alumina column on a PureSolv™ Solvent Purification System (SPS, Innovative Technologies, Inc., MA). Yields refer to chromatographically and spectroscopically pure (¹H NMR) homogeneous material, unless otherwise stated. Thin layer chromatography was carried out using TLC aluminum sheets coated with 0.2 mm of silica gel (Merck Gf234) using short-wave UV light as visualizing agent and phosphomolybdic acid, KMnO₄ or acidic vanillin followed by heat as developing agents. Chromatographic purifications were carried out using flash grade silica gel (SDS Chromatogel 60 ACC, 40-60 μm) as the stationary phase manually, or using a CombiFlash®R_f instrument with normal phase disposable columns of different sizes (Teledyne Isco). Preparative TLC was performed on 20 cm x 20 cm silica gel plates (2.0 mm thick, catalogue number 02015, Analtech or 1.0 mm thick, catalogue number P02013 Analtech). NMR spectra were recorded at 23 °C on a Bruker Avance 300, 400 Ultrashield or Bruker Avance 500 Ultrashield apparatus. Chemical shifts are reported in parts per million (ppm) downfield from tetramethylsilane, using the residual undeuterated solvent (CHCl₃ at 7.28 ppm ¹H NMR, 77.00 ppm ¹³C NMR) or tetramethylsilane as reference. Coupling constants are reported in hertz (Hz). The following abbreviations were used to explain multiplicities: s = singlet, d = doublet, t = triplet, q = quartet, quint = quintuplet, m = multiplet, br = broad. Mass spectra were recorded on a Waters LCT Premier Spectrometer (ESI and APCI) or on a Autoflex Bruker Daltonics (MALDI and LDI). Melting points were determined using a MP70 Melting Point System (Mettler Toledo). Unless otherwise stated, all reagents were purchased from commercial sources and used without further purification. Tropylium tetrafluoroborate was purchased from Fluorochem.

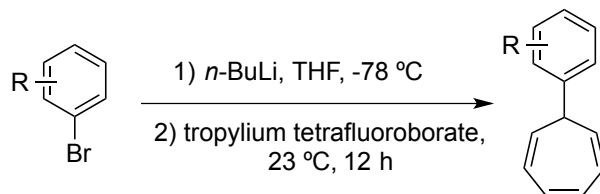
Handling of Gold(I) Catalysts

All gold complexes were synthesized according to our previously reported procedures^[1] or purchased from Sigma Aldrich, such as (acetonitrile)[(2-biphenyl)di-*tert*-butylphosphine]gold(I) hexafluoroantimonate (**A**) and (Acetonitrile)[2-di-*tert*-butyl(2',4',6'-triiso-propylbiphenyl)phosphine]gold(I) hexafluoroantimonate (**B**). The bottles were not stored under inert atmosphere.

¹ (a) C. Nieto-Oberhuber, S. López, M. P. Muñoz, D. J. Cárdenas, E. Buñuel, C. Nevado, A. M. Echavarren, *Angew. Chem. Int. Ed.* **2005**, *44*, 6146-6148; (b) S. López, E. Herrero-Gómez, P. Pérez-Galán, C. Nieto-Oberhuber, A. M. Echavarren, *Angew. Chem. Int. Ed.* **2006**, *45*, 6029-6032; (c) C. H. M. Amijs, V. López-Carrillo, M. Raducan, P. Pérez-Galán, C. Ferrer, A. M. Echavarren, *J. Org. Chem.* **2008**, *73*, 7721-7730.

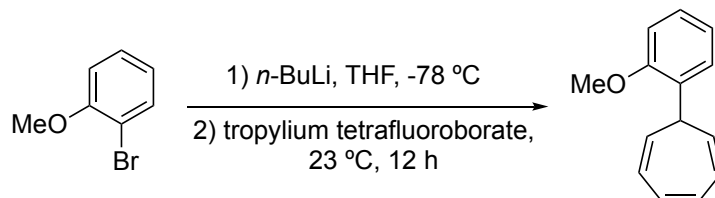
2. Preparation of 7-Aryl Cycloheptatrienes

7-Aryl-1,3,5-cycloheptatrienes (**1**) were prepared according to our previously reported literature procedures. Characterization data can be found below for all the new substrates.^[2]



n-BuLi (2.5 M in hexanes, 1.2 equiv) was added dropwise to a solution of the corresponding aryl bromide (1.0 equiv) in dry THF (0.4 M) at $-78\text{ }^{\circ}\text{C}$ under argon. The mixture was stirred for 30 min at $-78\text{ }^{\circ}\text{C}$, and then tropylium tetrafluoroborate (1.3 equiv) was added in one portion. The cooling bath was removed and the reaction was stirred at room temperature ($23\text{ }^{\circ}\text{C}$) for 12 h. The reaction was quenched by the addition of water. The aqueous phase was extracted with diethyl ether, the combined organic extracts were dried over MgSO_4 , and the solvent was evaporated. The crude reaction mixture was purified by column chromatography on silica gel with cyclohexane as eluent unless otherwise stated.

7-(2-Methoxyphenyl)cyclohepta-1,3,5-triene (**1c**)



This compound (yellow oil, 1.5 g, yield: 76%) was prepared according to the general procedure from 1-bromo-2-methoxybenzene (1.87 g, 10 mmol), *n*-BuLi (2.5 M, 4.8 mL, 12 mmol) and tropylium tetrafluoroborate (2.3 g, 13 mmol).

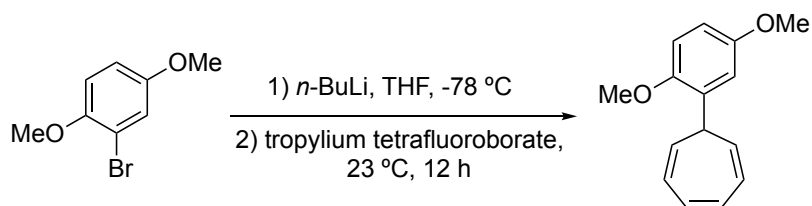
¹H NMR (400 MHz, CDCl_3) δ 7.39-7.34 (m, 1H), 7.33-7.27 (m, 1H), 7.06-6.99 (m, 1H), 6.98-6.94 (m, 1H), 6.79-6.69 (m, 2H), 6.30-6.23 (m, 2H), 5.48-5.41 (m, 2H), 3.83 (d, $J = 2.0\text{ Hz}$, 3H), 3.19-3.12 (m, 1H).

¹³C NMR (101 MHz, CDCl_3) δ 157.36, 131.80, 130.78, 128.92, 127.79, 127.18, 124.14, 120.76, 110.93, 55.40, 40.49.

HRMS-APCI: calculated for $\text{C}_{14}\text{H}_{15}\text{O}[\text{M}+\text{H}]^+$: 199.1117; found: 199.1114.

² Unless otherwise noted, all of the 7-aryl cycloheptatrienes were described already: (a) C. R. Solorio- Alvarado, Y. Wang, A. M. Echavarren, *J. Am. Chem. Soc.* **2011**, *133*, 11952- 11955; (b) Y. Wang, P. R. McGonigal, B. Herlé, M. Besora, A. M. Echavarren, *J. Am. Chem. Soc.* **2014**, *136*, 801-809; (c) Y. Wang, M. E. Muratore, Z. Rong, A. M. Echavarren, *Angew. Chem. Int. Ed.* **2014**, *53*, 14022-14026.

7-(2,5-Dimethoxyphenyl)cyclohepta-1,3,5-triene (**1f**)



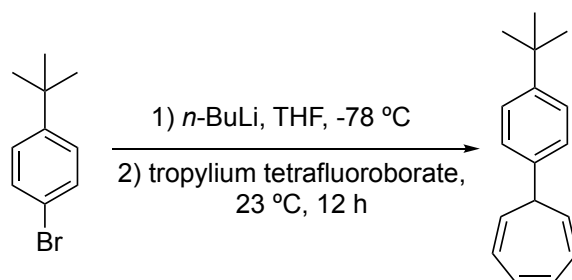
This compound (yellow oil, 2.0 g, yield: 88%) was prepared according to the general procedure from 2-bromo-1,4-dimethoxybenzene (2.2 g, 10 mmol), *n*-BuLi (2.5 M, 4.8 mL, 12 mmol) and tropylium tetrafluoroborate (2.3 g, 13 mmol).

¹H NMR (400 MHz, CDCl₃) δ 6.96 (d, *J* = 3.0 Hz, 1H), 6.89 (d, *J* = 8.9 Hz, 1H), 6.82 (dd, *J* = 8.9, 3.0 Hz, 1H), 6.74 (dd, *J* = 3.7, 2.7 Hz, 2H), 6.28-6.24 (m, 2H), 5.52-5.34 (m, 2H), 3.82 (s, 3H), 3.78 (s, 3H), 3.15-3.12 (m, 1H).

¹³C NMR (101 MHz, CDCl₃) δ 153.73, 151.63, 133.09, 130.79, 126.94, 124.27, 115.26, 112.10, 111.83, 56.15, 55.73, 40.42.

HRMS-APCI: calculated for C₁₅H₁₆O₂ [M+H]⁺: 229.1223; found: 229.1219.

7-(4-(*tert*-Butyl)phenyl)cyclohepta-1,3,5-triene (**1j**)



This compound (colorless oil, 1.8 g, yield: 80%) was prepared according to the general procedure from 1-bromo-4-(*tert*-butyl)benzene (2.1 g, 10 mmol), *n*-BuLi (2.5 M, 4.8 mL, 12 mmol) and tropylium tetrafluoroborate (2.3 g, 13 mmol).

¹H NMR (400 MHz, CDCl₃) δ 7.41 (d, *J* = 8.3 Hz, 2H), 7.33 (d, *J* = 0.8 Hz, 2H), 6.77-6.73 (m, 2H), 6.29-6.23 (m, 2H), 5.48-5.39 (m, 2H), 2.72-2.66 (m, 1H), 1.35 (s, 9H).

¹³C NMR (101 MHz, CDCl₃) δ 149.43, 140.83, 130.90, 127.19, 126.40, 125.57, 124.28, 44.83, 34.45, 31.41.

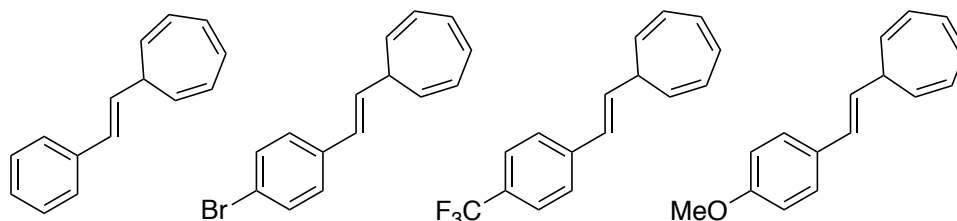
HRMS-APCI: calculated for C₁₇H₂₁ [M+H]⁺: 225.1638; found: 225.1635.

3. Preparation of 7-Styryl Cycloheptatrienes

(*E*)-7-Styrylcyclohepta-1,3,5-triene (**2a**) and (*E*)-7-(4-Methylstyryl)cyclohepta-1,3,5-triene (**2b**) were prepared by reaction of the corresponding potassium organotrifluoroborate with tropylium tetrafluoroborate according to published literature procedures and characterization data matched the previously reported ones (for a representative procedure check **2b**). (*E*)-7-(4-(trifluoromethyl)styryl)cyclohepta-1,3,5-

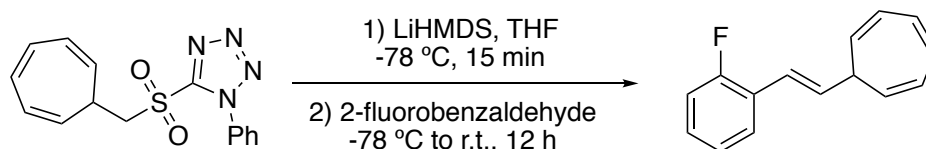
triene (**2c**), (*E*)-7-(4-methoxystyryl)cyclohepta-1,3,5-triene (**2d**) and (*E*)-7-(4-Bromostyryl)cyclohepta-1,3,5-triene (**2e**) were prepared by olefination of the corresponding aldehyde with a Julia-Kocienski reagent according to published literature procedures and characterization data matched the previously reported ones.

We have previously reported the synthesis of the styryl-cycloheptatrienes shown below.^[3]



(*E*)-7-(2-Fluorostyryl)cyclohepta-1,3,5-triene (**2f**) and (*E*)-2-(2-(cyclohepta-2,4,6-trien-1-yl)vinyl)naphthalene (**2g**) were prepared following the exact same reported Julia-Kocienski procedure, and its characterization data is listed below.

(*E*)-7-(2-Fluorostyryl)cyclohepta-1,3,5-triene (2f)



This compound (68 mg, 84%, 17:1 *E/Z* ratio) was obtained as a colorless oil from 2-fluorobenzaldehyde (95 mg, 0.763 mmol, 2.0 equiv) and 5-((cyclohepta-2,4,6-trien-1-yl)methyl)sulfonyl-1-phenyl-1H-tetrazole (120 mg, 0.382 mmol, 1.0 equiv).

¹H NMR (400 MHz, CDCl₃) δ 7.53 (td, *J* = 7.7, 1.7 Hz, 1H), 7.27-7.21 (m, 1H), 7.15 (td, *J* = 7.6, 1.3 Hz, 1H), 7.08 (ddd, *J* = 10.8, 8.1, 1.3 Hz, 1H), 6.78-6.73 (m, 3H), 6.68-6.61 (m, 1H), 6.32-6.28 (m, 2H), 5.40 (dd, *J* = 10.0, 5.8 Hz, 2H), 2.54 (q, *J* = 6.2 Hz, 1H) ppm.

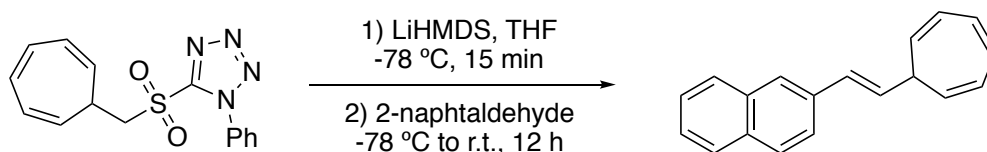
¹³C NMR (101 MHz, CDCl₃) δ 160.2 (d, *J*_{C-F} = 248 Hz), 133.5 (d, *J*_{C-F} = 4.6 Hz), 131.1, 128.5 (d, *J*_{C-F} = 8.3 Hz), 127.2 (d, *J*_{C-F} = 3.8 Hz), 124.7, 124.1, 124.0, 123.0 (d, *J*_{C-F} = 3.7 Hz), 115.8, 115.6, 42.4 ppm.

¹⁹F NMR (376 MHz, CDCl₃) δ -118.39 ppm.

HRMS (APCI Positive): calculated for C₁₅H₁₄F [M+H]⁺: 213.1074; found: 213.1072.

(*E*)-2-(2-(Cyclohepta-2,4,6-trien-1-yl)vinyl)naphthalene (2g)

³ For 7-styryl-1,3,5-cycloheptatrienes using the Julia-Kocienski olefination and from potassium styryl trifluoroborates: B. Herlé, P. M. Holstein, A. M. Echavarren, *ACS Catal.* **2017**, 7, 3668-3675.



This compound (62 mg, 80%, >20:1 *E/Z* ratio) was obtained as a white solid from 2-naphthaldehyde (99 mg, 0.636 mmol, 2.0 equiv) and 5-((cyclohepta-2,4,6-trien-1-ylmethyl)sulfonyl)-1-phenyl-1H-tetrazole (100 mg, 0.318 mmol, 1.0 equiv).

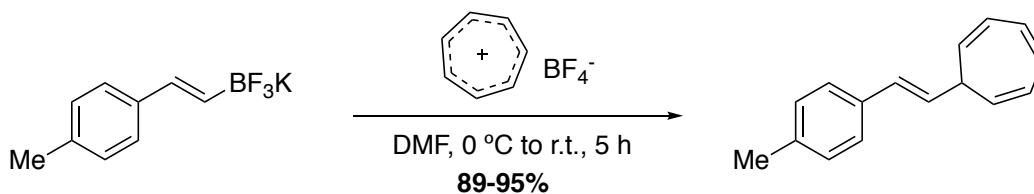
¹H NMR (500 MHz, CDCl₃) δ 7.85-7.82 (m, 3H), 7.76 (br, 1H), 7.67 (dd, *J* = 8.7, 1.7 Hz, 1H), 7.48 (quintuplet of doublets, *J* = 7.6, 1.6 Hz, 2H), 6.78-6.72 (m, 3H), 6.71-6.66 (m, 1H), 6.32-6.28 (m, 2H), 5.43 (dd, *J* = 9.2, 5.8 Hz, 2H), 2.55 (q, *J* = 6.0 Hz, 1H) ppm.

¹³C NMR (126 MHz, CDCl₃) δ 134.8, 133.6, 132.8, 131.4, 131.1, 130.6, 128.1, 127.9, 127.6, 126.2, 125.9, 125.7, 124.6, 124.3, 123.5, 77.2, 42.2 ppm.

HRMS (APCI Positive): calculated for C₁₉H₁₇ [M+H]⁺: 245.1325; found: 245.1323.

M.p.: 69-71 °C.

(*E*)-7-(4-Methylstyryl)cyclohepta-1,3,5-triene (2b)



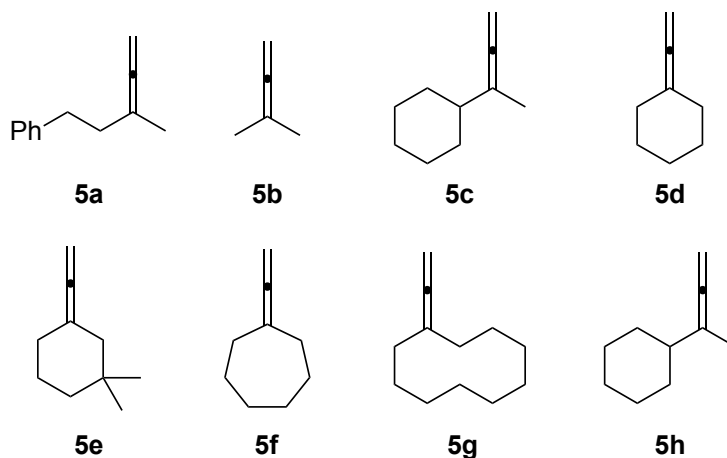
A 100 mL round-bottomed flask with a magnetic stirring bar was charged with potassium (*E*)-stryryltrifluoroborate (2.0 g, 8.93 mmol, 1.0 equiv) and it was dissolved in 35 mL of DMF. The solution was cooled down to 0 °C and then tropylium tetrafluoroborate (1.67 g, 9.37 mmol, 1.05 equiv) was added in one portion. The resulting yellow mixture was allowed to warm slowly to room temperature and further stirred for 5 h, then it was quenched by the addition of water and Et₂O and the aqueous phase was extracted three times with Et₂O. Combined organic fractions were washed with water three times, once with brine, and dried over anhydrous MgSO₄. After removal of the solvent, the product was purified by flash column chromatography in SiO₂ (eluent cyclohexane or pentane) to give (*E*)-7-(4-methylstyryl)cyclohepta-1,3,5-triene (1.76 g, 8.45 mmol, 95 % yield) as a pale yellow oil that solidifies upon cooling in the fridge.

¹H NMR (500 MHz, CDCl₃) δ 7.33-7.26 (m, 2H), 7.16-7.12 (m, 2H), 6.71 (br, 2 H), 6.54-6.46 (m, 2H), 6.34 (d, *J* = 7.6 Hz, 2H), 5.35 (quint, *J* = 4.7 Hz, 2H), 2.43 (quint, *J* = 4.7 Hz, 1H), 2.36 (s, 3H) ppm.

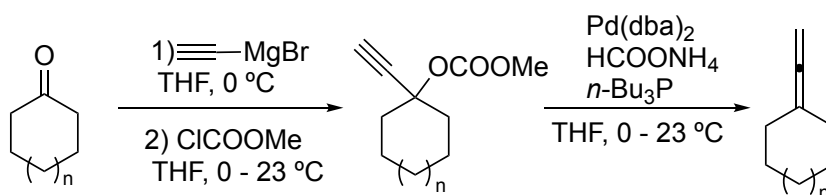
¹³C NMR (126 MHz, CDCl₃) δ 137.0, 134.6, 131.0, 130.4, 130.0, 129.2, 126.1, 124.6, 124.5, 42.1, 21.2 ppm.

HRMS (APCI Positive): calculated for C₁₆H₁₇ [M+H]⁺: 209.1325; found: 209.1323.

4. Procedure for the Preparation of Allenes



Allenenes **5a**^[4a], **5c**^[4b], **5f**^[4c] were known compounds and the obtained spectral data were in agreement with literature values. **5b**, **5d**, **5h** were purchased from Aldrich. **5e**, **5g** were prepared according to the same literature procedure.^[4a]



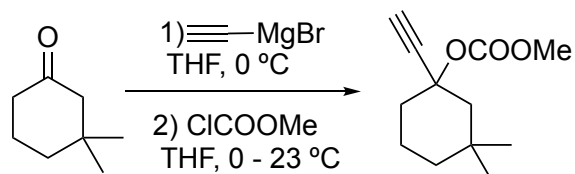
Ethynylmagnesium bromide (0.5 M in THF, 1.1 equiv) was added dropwise to a solution of the corresponding ketone (1.0 equiv) in dry THF (0.2 M) at 0 °C under argon. The mixture was stirred for 2 h at 0 °C, the disappearance of the ketone was confirmed by TLC and then methyl chloroformate (1.3 equiv) was added. The cooling bath was removed and the reaction was stirred at room temperature (23 °C) for 12 h. The reaction was quenched by addition of water. The aqueous phase was extracted with ethyl acetate, the combined organic extracts were dried over MgSO₄, and the solvent was evaporated. The crude reaction mixture was purified by column chromatography on silica gel with a mixture of cyclohexane and ethyl acetate as eluent unless otherwise stated, to give the corresponding carbonate.

n-Bu₃P (0.2 equiv) was added dropwise to a stirred mixture of carbonate (1.0 equiv), ammonium formate (2.0 equiv) and Pd(dba)₂ (0.05 equiv) in THF (0.2 M) at 0 °C. After 12 h, the disappearance of carbonate was confirmed by TLC and the reaction mixture was filtered through a short pad of Celite. The solvent was evaporated and the residue

⁴ (a) J. Takaya, N. Iwasawa, *J. Am. Chem. Soc.* **2008**, *130*, 15254-15255; (b) Y. Tani, T. Fujihara, J. Terao, Y. Tsuji, *J. Am. Chem. Soc.* **2014**, *136*, 17706-17709; (c) M. Aoki, S. Izumi, M. Kaneko, K. Ukai, J. Takaya, N. Iwasawa, *Org. Lett.* **2007**, *9*, 1251-1253.

was purified by column chromatography on silica gel with pentane as eluent.

1-Ethynyl-3,3-dimethylcyclohexyl methyl carbonate



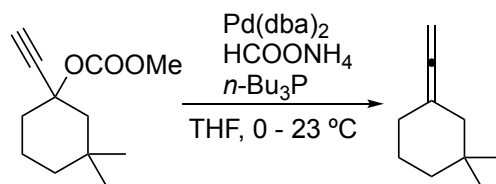
This compound (colorless oil, 1.8 g, yield: 54%) was prepared according to the general procedure from cyclodecanone (2.0 g, 15.9 mmol), ethynylmagnesium bromide (0.5 M in THF, 35 ml, 17.4 mmol) and methyl chloroformate (1.9 g, 1.6 ml, 20.6 mmol).

$^1\text{H NMR}$ (400 MHz, CDCl_3) δ 3.78 (s, 3H), 2.60 (s, 1H), 2.13-1.83 (m, 4H), 1.78-1.57 (m, 2H), 1.39-1.23 (m, 2H), 1.03 (s, 3H), 0.97 (s, 3H).

$^{13}\text{C NMR}$ (101 MHz, CDCl_3) δ 153.50, 84.43, 76.66, 73.57, 54.32, 46.95, 38.34, 37.53, 31.08, 30.43, 29.00, 18.59.

HRMS-ESI: calculated for $\text{C}_{12}\text{H}_{18}\text{NaO}_3$ $[\text{M}+\text{Na}]^+$: 233.1148; found: 233.1155.

1,1-Dimethyl-3-(1 λ^5 -vinylidene)cyclohexane (5e)



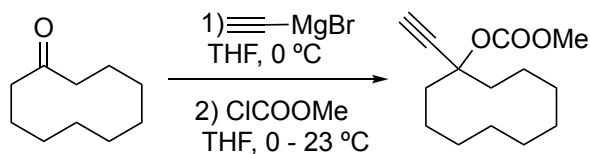
This compound (colorless oil, 800 mg, yield: 82%) was prepared according to the general procedure from 1-ethynyl-3,3-dimethylcyclohexyl methyl carbonate (2.0 g, 9.5 mmol), *n*- Bu_3P (385 mg, 0.46 ml, 1.9 mmol) and ammonium formate (1.2 g, 19 mmol) and $\text{Pd}(\text{dba})_2$ (273 mg, 0.48 mol).

$^1\text{H NMR}$ (500 MHz, CDCl_3) δ 4.61-4.51 (m, 2H), 2.13-2.04 (m, 2H), 1.95-1.88 (m, 2H), 1.66-1.58 (m, 2H), 1.36-1.29 (m, 2H), 0.95 (s, 6H).

$^{13}\text{C NMR}$ (101 MHz, CDCl_3) δ 204.47, 99.13, 72.15, 44.23, 38.94, 31.90, 30.63, 28.34, 22.76.

HRMS-APCI: calculated for $\text{C}_{10}\text{H}_{17}$ $[\text{M}+\text{H}]^+$: 137.1325; found: 137.1323.

1-Ethynylcyclodecyl methyl carbonate



This compound (white solid, 1.7 g, yield: 71%) was prepared according to the general procedure from cyclodecanone (1.54 g, 10 mmol), ethynylmagnesium bromide (0.5 M

in THF, 22 ml, 11 mmol) and methyl chloroformate (1.23 g, 1.0 ml, 13 mmol).

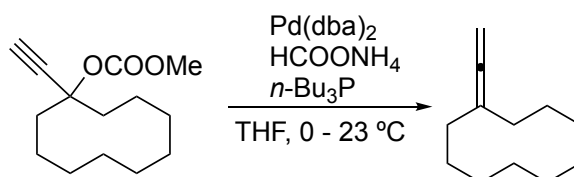
$^1\text{H NMR}$ (300 MHz, CDCl_3) δ 3.78 (s, 3H), 2.62 (s, 1H), 2.32 (dt, $J = 14.6, 7.0$ Hz, 2H), 2.08 (dt, $J = 14.9, 6.5$ Hz, 2H), 1.78 – 1.45 (m, 14H).

$^{13}\text{C NMR}$ (75 MHz, CDCl_3) δ 153.36, 83.52, 81.01, 74.18, 54.32, 32.64, 26.17, 25.53, 23.54, 20.87.

HRMS-ESI: calculated for $\text{C}_{14}\text{H}_{22}\text{NaO}_3[\text{M}+\text{Na}]^+$: 261.1461; found: 261.1452.

M.p.: 59-61 °C.

Vinylidenecyclodecane (5g)



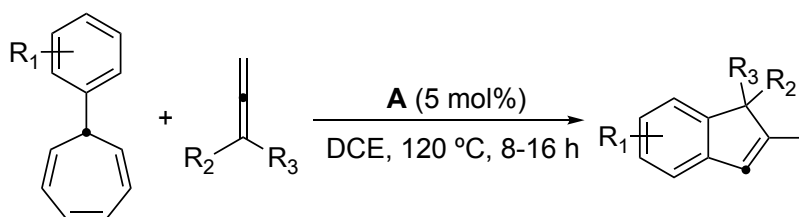
This compound (brown oil, 980 mg, yield: 84%) was prepared according to the general procedure from 1-ethynylcyclodecyl methyl carbonate (1.7 g, 7.1 mmol), $n\text{-Bu}_3\text{P}$ (290 mg, 0.35 ml, 1.4 mmol) and ammonium formate (900 mg, 14 mmol) and $\text{Pd}(\text{dba})_2$ (205mg, 0.36 mol).

$^1\text{H NMR}$ (300 MHz, CDCl_3) δ 4.65-4.59 (m, 2H), 2.20-2.05 (m, 4H), 1.69-1.36 (m, 14H).

$^{13}\text{C NMR}$ (75 MHz, CDCl_3) δ 207.31, 101.89, 74.37, 30.69, 25.62, 24.61, 24.48, 24.38.

HRMS-APCI: calculated for $\text{C}_{12}\text{H}_{19}[\text{M}-\text{H}]^+$: 163.1481; found: 163.1477.

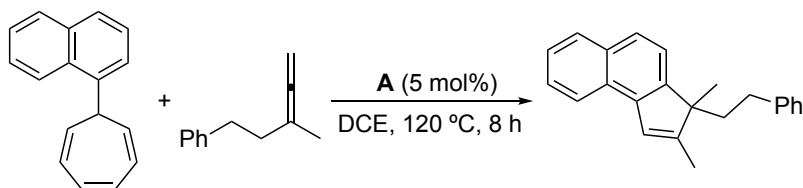
5. General Procedure A for the Gold(I)-Catalyzed Synthesis of Indenes



A solution of the 7-aryl-1,3,5-cycloheptatriene **1** (0.2 mmol), allene **5** (0.4 mmol, 2.0 equiv) and gold complex **A** (7.7 mg, 0.01 mmol, 5 mol%) in 1,2-dichloroethane (DCE, 2 mL, 0.1 M) was stirred at 120 °C in a sealed tube (in a heating block, covering the vial completely) until the starting material had been fully consumed (8 h). After that time, the reaction mixture was allowed to cool down to room temperature, the solvent was removed in vacuum and the crude residue was purified by column chromatography on silica gel. The reaction was performed under an air atmosphere with no special precautions taken to exclude water or oxygen.

Characterization Data for the Different Indenes

2,3-Dimethyl-3-phenethyl-3*H*-cyclopenta[*a*]naphthalene (6a)



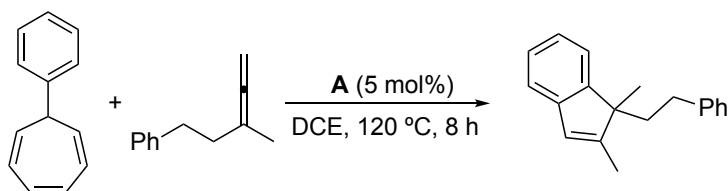
The title compound (light yellow oil, 39.5 mg, yield: 66%) was synthesized according to the General Procedure A from 1-(cyclohepta-2,4,6-trien-1-yl)naphthalene (44 mg, 0.2 mmol) and (3-methylpenta-3,4-dien-1-yl)benzene (63 mg, 0.4 mmol).

¹H NMR (400 MHz, CDCl₃) δ 8.16 (d, *J* = 8.2 Hz, 1H), 7.97 (d, *J* = 8.3 Hz, 1H), 7.78 (d, *J* = 8.2 Hz, 1H), 7.61-7.55 (m, 2H), 7.55-7.49 (m, 1H), 7.31 – 7.24 (m, 2H), 7.23-7.16 (m, 1H), 7.14-7.05 (m, 3H), 2.33 (td, *J* = 12.8, 4.6 Hz, 1H), 2.21-2.03 (m, 5H), 1.84 (td, *J* = 13.3, 5.1 Hz, 1H), 1.38 (s, 3H).

¹³C NMR (75 MHz, CDCl₃) δ 153.37, 148.44, 142.73, 139.73, 133.10, 128.48, 128.25, 128.22, 127.38, 125.61, 125.42, 124.89, 124.39, 124.08, 123.14, 120.16, 54.96, 38.94, 30.34, 23.61, 13.06.

HRMS-APCI: calculated for C₂₃H₂₃ [M+H]⁺: 299.1794; found: 299.1795.

1,2-Dimethyl-1-phenethyl-1*H*-indene (6b)



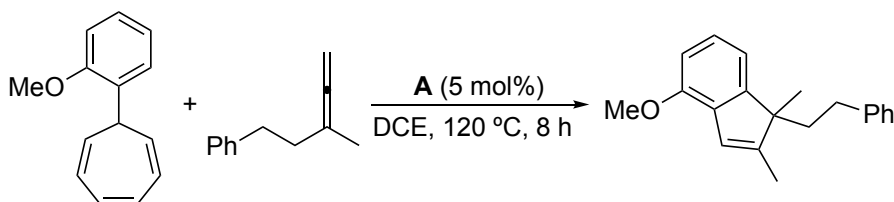
The title compound (colorless oil, 33.4 mg, yield: 67%) was synthesized according to the General Procedure A from 7-phenylcyclohepta-1,3,5-triene (34 mg, 0.2 mmol) and (3-methylpenta-3,4-dien-1-yl)benzene (63 mg, 0.4 mmol).

¹H NMR (400 MHz, CDCl₃) δ 7.36-7.12 (m, 7H), 7.07-7.02 (m, 2H), 6.49 (d, *J* = 1.6 Hz, 1H), 2.23-2.12 (m, 1H), 2.09-1.96 (m, 5H), 1.89-1.78 (m, 1H), 1.27 (s, 3H).

¹³C NMR (101 MHz, CDCl₃) δ 152.62, 151.36, 143.87, 142.75, 128.20, 128.18, 126.50, 125.77, 125.55, 124.04, 121.25, 119.98, 53.92, 39.31, 30.34, 23.93, 12.69.

HRMS-APCI: calculated for C₁₉H₂₁ [M+H]⁺: 249.1638; found: 249.1641.

4-Methoxy-1,2-dimethyl-1-phenethyl-1*H*-indene (6c)



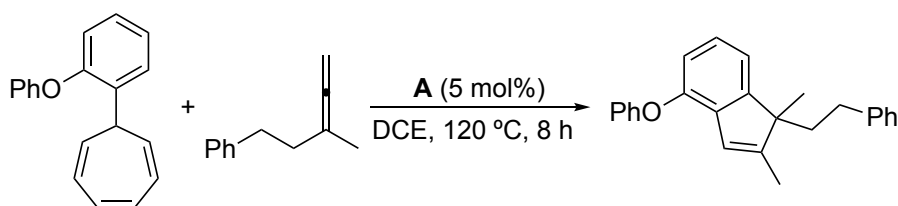
The title compound (colorless oil, 30 mg, yield: 54%) was synthesized according to the General Procedure A from 7-(2-methoxyphenyl)cyclohepta-1,3,5-triene (40 mg, 0.2 mmol) and (3-methylpenta-3,4-dien-1-yl)benzene (63 mg, 0.4 mmol).

¹H NMR (500 MHz, CDCl₃) δ 7.30-7.22 (m, 2H), 7.21-7.13 (m, 2H), 7.08-7.04 (m, 2H), 6.99 (dt, *J* = 7.4, 0.5 Hz, 1H), 6.81 (d, *J* = 8.0 Hz, 1H), 6.65 (d, *J* = 1.6 Hz, 1H), 3.93 (s, 3H), 2.20-2.11 (m, 1H), 2.08-1.97 (m, 5H), 1.90-1.81 (m, 1H), 1.27 (s, 3H).

¹³C NMR (126 MHz, CDCl₃) δ 153.51, 152.27, 150.95, 142.84, 131.92, 128.20, 125.53, 125.39, 121.70, 114.40, 108.84, 55.39, 54.47, 39.32, 30.35, 23.99, 12.74.

HRMS-APCI: calculated for C₂₀H₂₃O [M+H]⁺: 279.1743; found: 279.1752.

1,2-Dimethyl-1-phenethyl-4-phenoxy-1*H*-indene (6d)



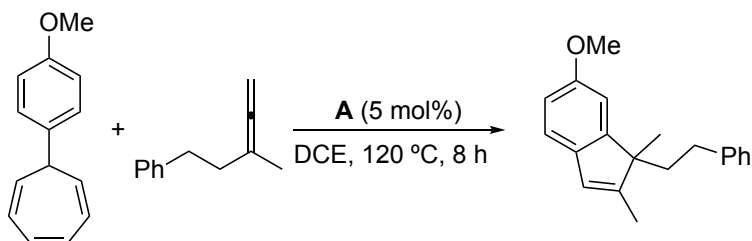
The title compound (yellow oil, 28 mg, yield: 41%) was synthesized according to the General Procedure A from 7-(2-phenoxyphenyl)cyclohepta-1,3,5-triene (52 mg, 0.2 mmol) and (3-methylpenta-3,4-dien-1-yl)benzene (63 mg, 0.4 mmol).

¹H NMR (400 MHz, CDCl₃) δ 7.40-7.33 (m, 2H), 7.32-7.25 (m, 2H), 7.24-7.15 (m, 3H), 7.14-7.07 (m, 3H), 7.07-7.02 (m, 2H), 6.93 (dd, *J* = 7.2, 1.7 Hz, 1H), 6.48 (d, *J* = 1.7 Hz, 1H), 2.27-2.17 (m, 1H), 2.14-2.02 (m, 2H), 1.99 (d, *J* = 1.6 Hz, 3H), 1.92 (td, *J* = 14.3, 4.5 Hz, 1H), 1.33 (s, 3H).

¹³C NMR (126 MHz, CDCl₃) δ 158.38, 154.26, 152.37, 148.27, 142.66, 135.23, 129.64, 128.29, 128.25, 125.68, 125.55, 122.31, 121.87, 118.04, 117.42, 117.39, 54.57, 39.46, 30.37, 23.97, 12.80.

HRMS-APCI: calculated for C₂₅H₂₅O [M+H]⁺: 341.1900; found: 341.1902.

6-Methoxy-1,2-dimethyl-1-phenethyl-1*H*-indene (6e)



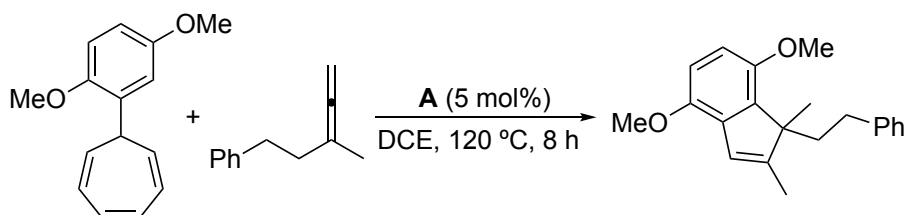
The title compound (colorless oil, 38 mg, yield: 68%) was synthesized according to the General Procedure A from 7-(4-methoxyphenyl)cyclohepta-1,3,5-triene (40 mg, 0.2 mmol) and (3-methylpenta-3,4-dien-1-yl)benzene (63 mg, 0.4 mmol).

¹H NMR (400 MHz, CDCl₃) δ 7.32-7.21 (m, 2H), 7.19-7.13 (m, 2H), 7.06 (d, *J* = 7.1 Hz, 2H), 6.92 (d, *J* = 2.4 Hz, 1H), 6.80 (dd, *J* = 8.2, 2.4 Hz, 1H), 6.42 (d, *J* = 1.8 Hz, 1H), 3.87 (s, 3H), 2.18-2.00 (m, 3H), 1.97 (d, *J* = 1.6 Hz, 3H), 1.92-1.80 (m, 1H), 1.26 (s, 3H).

¹³C NMR (101 MHz, CDCl₃) δ 157.83, 153.61, 150.69, 143.10, 137.27, 128.54, 128.43, 125.88, 125.46, 120.44, 111.42, 109.03, 55.91, 54.32, 39.79, 30.70, 24.56, 12.98.

HRMS-APCI: calculated for C₂₀H₂₃O [M+H]⁺: 279.1743; found: 279.1749.

4,7-Dimethoxy-1,2-dimethyl-1-phenethyl-1*H*-indene (6f)



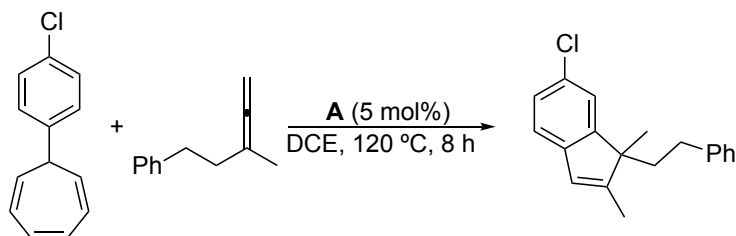
The title compound (colorless oil, 33 mg, yield: 53%) was synthesized according to the General Procedure A from 7-(2,5-dimethoxyphenyl)cyclohepta-1,3,5-triene (46 mg, 0.2 mmol) and (3-methylpenta-3,4-dien-1-yl)benzene (63 mg, 0.4 mmol).

¹H NMR (400 MHz, CDCl₃) δ 7.26-7.21 (m, 2H), 7.18-7.11 (m, 1H), 7.07-7.03 (m, 2H), 6.74 (d, *J* = 8.7 Hz, 1H), 6.63 (d, *J* = 8.7 Hz, 1H), 6.58 (d, *J* = 1.6 Hz, 1H), 3.87 (s, 3H), 3.86 (s, 3H), 2.70-2.62 (m, 1H), 2.03-1.95 (m, 4H), 1.92-1.83 (m, 2H), 1.35 (s, 3H).

¹³C NMR (101 MHz, CDCl₃) δ 152.31, 150.39, 146.89, 143.22, 138.70, 133.58, 128.26, 128.08, 125.35, 121.43, 109.78, 107.26, 56.02, 55.56, 55.55, 36.36, 30.73, 21.54, 12.45.

HRMS-APCI: calculated for C₂₁H₂₅O₂ [M+H]⁺: 309.1849; found: 309.1851.

6-Chloro-1,2-dimethyl-1-phenethyl-1*H*-indene (6g)



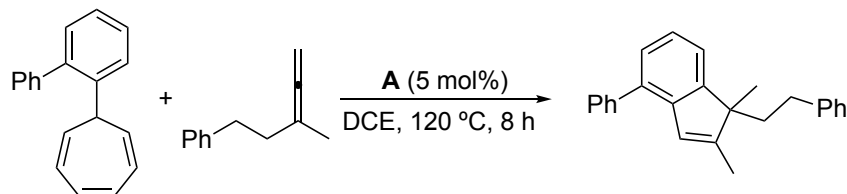
The title compound (colorless oil, 31 mg, yield: 55%) was synthesized according to the General Procedure A from 7-(4-chlorophenyl)cyclohepta-1,3,5-triene (41 mg, 0.2 mmol) and (3-methylpenta-3,4-dien-1-yl)benzene (63 mg, 0.4 mmol).

¹H NMR (400 MHz, CDCl₃) δ 7.29-7.21 (m, 4H), 7.18 (d, *J* = 7.8 Hz, 2H), 7.07-7.04 (m, 2H), 6.44 (d, *J* = 1.6 Hz, 1H), 2.18-2.10 (m, 1H), 2.08-1.97 (m, 5H), 1.89-1.81 (m, 1H), 1.26 (s, 3H).

¹³C NMR (126 MHz, CDCl₃) δ 153.25, 142.33, 142.29, 130.09, 128.74, 128.26, 128.16, 126.67, 125.70, 125.09, 121.89, 120.75, 54.30, 39.08, 30.26, 23.81, 12.71.

HRMS-APCI: calculated for C₁₉H₂₀Cl [M+H]⁺: 283.1248; found: 283.1248.

1,2-Dimethyl-1-phenethyl-4-phenyl-1*H*-indene (6h)



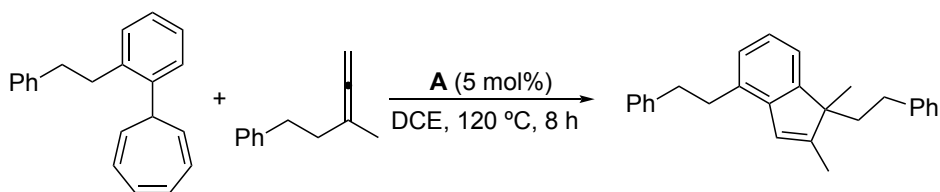
The title compound (colorless oil, 33.3 mg, yield: 51%) was synthesized according to the General Procedure A from 2-(cyclohepta-2,4,6-trien-1-yl)-1,1'-biphenyl (49 mg, 0.2 mmol) and (3-methylpenta-3,4-dien-1-yl)benzene (63 mg, 0.4 mmol).

¹H NMR (400 MHz, CDCl₃) δ 7.60-7.55 (m, 2H), 7.53-7.46 (m, 2H), 7.42-7.36 (m, 1H), 7.34-7.22 (m, 5H), 7.20-7.13 (m, 1H), 7.09-7.04 (m, 2H), 6.68 (d, *J* = 1.6 Hz, 1H), 2.27-2.16 (m, 1H), 2.13-1.98 (m, 5H), 1.96-1.86 (m, 1H), 1.32 (s, 3H).

¹³C NMR (101 MHz, CDCl₃) δ 153.12, 152.09, 142.74, 141.41, 141.08, 134.16, 128.97, 128.38, 128.23, 127.05, 126.76, 125.60, 124.82, 124.47, 120.30, 54.12, 39.45, 30.43, 24.09, 12.82.

HRMS-APCI: calculated for C₂₅H₂₅ [M+H]⁺: 325.1951; found: 325.1947.

1,2-Dimethyl-1,4-diphenethyl-1*H*-indene (6i)



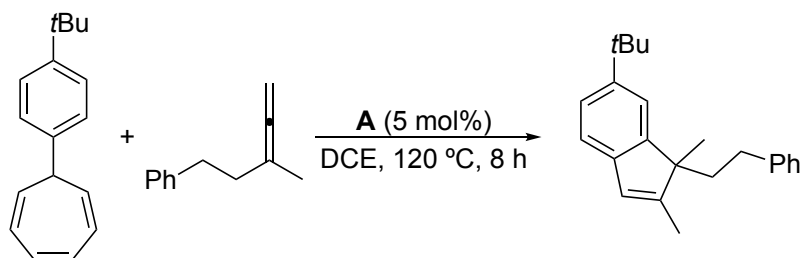
The title compound (colorless oil, 42 mg, yield: 59%) was synthesized according to the General Procedure A from 7-(2-phenethylphenyl)cyclohepta-1,3,5-triene (54 mg, 0.2 mmol) and (3-methylpenta-3,4-dien-1-yl)benzene (63 mg, 0.4 mmol).

¹H NMR (400 MHz, CDCl₃) δ 7.35-7.03 (m, 13H), 6.53 (d, *J* = 1.6 Hz, 1H), 3.10-3.03 (m, 2H), 3.02-2.95 (m, 2H), 2.22-2.09 (m, 1H), 2.07-1.95 (m, 5H), 1.90-1.75 (m, 1H), 1.27 (s, 3H).

¹³C NMR (101 MHz, CDCl₃) δ 152.16, 151.49, 142.85, 142.23, 142.05, 133.07, 128.52, 128.31, 128.22, 126.79, 125.84, 125.55, 124.27, 123.68, 119.15, 54.04, 39.43, 37.70, 35.24, 30.42, 24.05, 12.79.

HRMS-APCI: calculated for C₂₇H₂₉ [M+H]⁺: 353.2264; found: 353.2262.

6-(*tert*-Butyl)-1,2-dimethyl-1-phenethyl-1*H*-indene (6j)



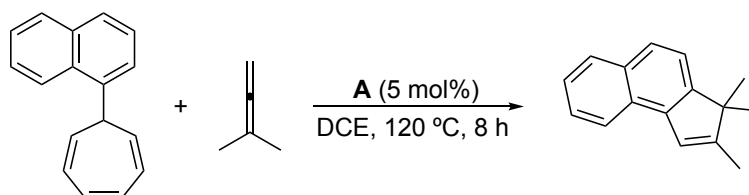
The title compound (colorless oil, 35 mg, yield: 58%) was synthesized according to the General Procedure A from 7-(4-(*tert*-butyl)phenyl)cyclohepta-1,3,5-triene (45 mg, 0.2 mmol) and (3-methylpenta-3,4-dien-1-yl)benzene (63 mg, 0.4 mmol).

¹H NMR (400 MHz, CDCl₃) δ 7.38-7.35 (m, 1H), 7.31-7.13 (m, 5H), 7.06-7.01 (m, 2H), 6.46 (d, *J* = 1.5 Hz, 1H), 2.20-2.11 (m, 1H), 2.11-2.01 (m, 2H), 2.00 (d, *J* = 1.6 Hz, 3H), 1.87-1.77 (m, 1H), 1.41 (s, 9H), 1.28 (s, 3H).

¹³C NMR (101 MHz, CDCl₃) δ 151.96, 151.21, 147.20, 142.97, 141.28, 128.24, 128.21, 128.18, 125.52, 125.40, 123.27, 119.21, 118.41, 77.35, 77.03, 76.71, 53.91, 39.52, 34.73, 31.80, 30.45, 24.01, 12.72.

HRMS-APCI: calculated for C₂₃H₂₉ [M+H]⁺: 305.2264; found: 305.2268.

2,3,3-Trimethyl-3*H*-cyclopenta[*a*]naphthalene (6k)



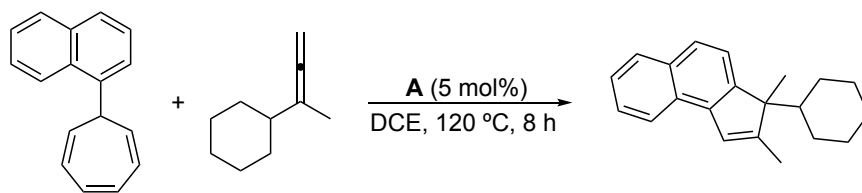
The title compound (colorless oil, 30 mg, yield: 72%) was synthesized according to the General Procedure A from 1-(cyclohepta-2,4,6-trien-1-yl)naphthalene (44 mg, 0.2 mmol) and 3-methylbuta-1,2-diene (27 mg, 0.4 mmol).

¹H NMR (400 MHz, CDCl₃) δ 8.08 (d, *J* = 8.4 Hz, 1H), 7.90 (d, *J* = 8.2 Hz, 1H), 7.70 (d, *J* = 8.2 Hz, 1H), 7.56-7.42 (m, 3H), 6.96 (d, *J* = 1.7 Hz, 1H), 2.11 (d, *J* = 1.6 Hz, 3H), 1.32 (s, 6H).

¹³C NMR (101 MHz, CDCl₃) δ 155.85, 150.73, 138.47, 132.98, 128.41, 127.42, 125.31, 124.76, 124.12, 124.06, 121.08, 120.18, 51.03, 23.40, 12.81.

HRMS-APCI: calculated for C₁₆H₁₇ [M+H]⁺: 209.1325; found: 209.1329.

3-Cyclohexyl-2,3-dimethyl-3*H*-cyclopenta[*a*]naphthalene (6l)



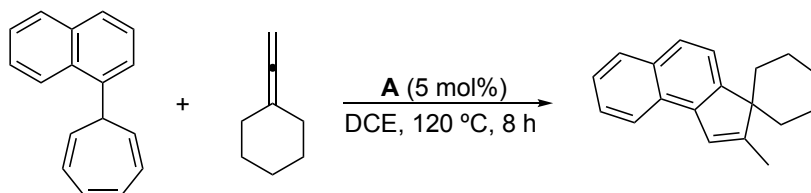
The title compound (colorless oil, 27 mg, yield: 49%) was synthesized according to the General Procedure A from 1-(cyclohepta-2,4,6-trien-1-yl)naphthalene (44 mg, 0.2 mmol) and buta-2,3-dien-2-ylcyclohexane (55 mg, 0.4 mmol).

$^1\text{H NMR}$ (500 MHz, CDCl_3) δ 8.06 (d, $J = 8.3$ Hz, 1H), 7.87 (d, $J = 8.3$ Hz, 1H), 7.63 (d, $J = 8.3$ Hz, 1H), 7.54 (d, $J = 8.2$ Hz, 1H), 7.48 (ddd, $J = 8.2, 6.8, 1.4$ Hz, 1H), 7.43 (ddd, $J = 8.1, 6.8, 1.3$ Hz, 1H), 6.97 (d, $J = 1.7$ Hz, 1H), 2.05 (d, $J = 1.5$ Hz, 3H), 2.01-1.94 (m, 1H), 1.85-1.77 (m, 1H), 1.71 (tt, $J = 12.0, 3.0$ Hz, 1H), 1.64-1.54 (m, 2H), 1.44-1.33 (m, 2H), 1.30 (s, 3H), 1.27-1.19 (m, 1H), 1.15 (tt, $J = 13.0, 3.6$ Hz, 1H), 1.02 (tt, $J = 12.8, 3.7$ Hz, 1H), 0.48 (ddd, $J = 25.3, 13.1, 3.7$ Hz, 1H).

$^{13}\text{C NMR}$ (126 MHz, CDCl_3) δ 155.09, 148.40, 139.96, 132.77, 128.27, 127.17, 125.14, 124.70, 124.04, 123.34, 122.74, 121.80, 57.91, 44.14, 28.31, 27.40, 27.10, 26.95, 26.55, 20.79, 13.95.

HRMS-APCI: calculated for $\text{C}_{21}\text{H}_{25}$ $[\text{M}+\text{H}]^+$: 277.1951; found: 277.1957.

2'-Methylspiro[cyclohexane-1,3'-cyclopenta[*a*]naphthalene] (6m)



The title compound (white solid, 36 mg, yield: 72%) was synthesized according to the General Procedure A from 1-(cyclohepta-2,4,6-trien-1-yl)naphthalene (44 mg, 0.2 mmol) and vinylidenecyclohexane (43 mg, 0.4 mmol).

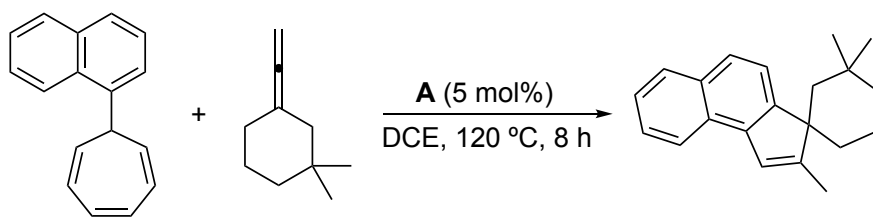
$^1\text{H NMR}$ (500 MHz, CDCl_3) δ 8.09 (d, $J = 8.5$ Hz, 1H), 7.99 (d, $J = 8.4$ Hz, 1H), 7.91-7.85 (m, 1H), 7.63 (d, $J = 8.4$ Hz, 1H), 7.49 (ddd, $J = 8.3, 6.8, 1.4$ Hz, 1H), 7.44 (ddd, $J = 8.1, 6.8, 1.3$ Hz, 1H), 7.00 (d, $J = 1.8$ Hz, 1H), 2.18-2.06 (m, 5H), 2.05-1.97 (m, 1H), 1.90-1.77 (m, 4H), 1.58-1.46 (m, 1H), 1.35-1.28 (m, 2H).

$^{13}\text{C NMR}$ (126 MHz, CDCl_3) δ 156.08, 150.07, 139.24, 132.56, 128.11, 127.28, 125.14, 124.82, 124.09, 123.23, 122.81, 121.96, 54.63, 31.79, 25.64, 22.60, 13.92.

HRMS-APCI: calculated for $\text{C}_{19}\text{H}_{21}$ $[\text{M}+\text{H}]^+$: 249.1638; found: 249.1638.

M.p.: 45-47 °C.

2',3,3-Trimethylspiro[cyclohexane-1,3'-cyclopenta[*a*]naphthalene] (6n)



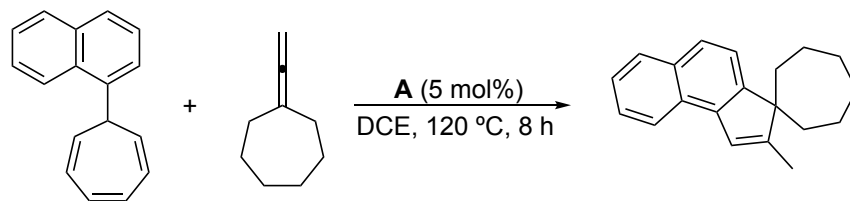
The title compound (colorless oil, 34 mg, yield: 62%) was synthesized according to the General Procedure A from 1-(cyclohepta-2,4,6-trien-1-yl)naphthalene (44 mg, 0.2 mmol) and 1,1-dimethyl-3-vinylidenecyclohexane (55 mg, 0.4 mmol).

$^1\text{H NMR}$ (400 MHz, CDCl_3) δ 8.07-7.98 (m, 2H), 7.86-7.82 (m, 1H), 7.59 (d, $J = 8.5$ Hz, 1H), 7.49-7.38 (m, 2H), 6.98-6.94 (m, 1H), 2.22-2.06 (m, 4H), 1.88-1.78 (m, 1H), 1.74-1.63 (m, 3H), 1.48-1.33 (m, 2H), 1.20 (s, 3H), 1.11 (dt, $J = 14.3, 1.7$ Hz, 1H), 1.04 (s, 3H).

$^{13}\text{C NMR}$ (126 MHz, CDCl_3) δ 156.60, 150.94, 139.50, 132.43, 127.94, 127.17, 125.11, 124.86, 124.10, 123.36, 122.75, 122.23, 55.62, 43.64, 38.91, 35.42, 30.52, 30.43, 28.73, 20.20, 14.05.

HRMS-APCI: calculated for $\text{C}_{21}\text{H}_{25}$ $[\text{M}+\text{H}]^+$: 277.1951; found: 277.1960.

2'-Methylspiro[cycloheptane-1,3'-cyclopenta[*a*]naphthalene] (6o)



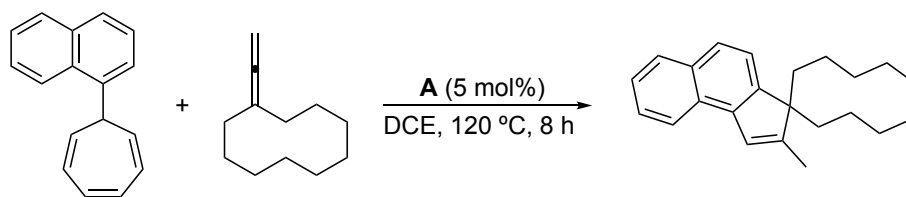
The title compound (colorless oil, 33 mg, yield: 63%) was synthesized according to the General Procedure A from 1-(cyclohepta-2,4,6-trien-1-yl)naphthalene (44 mg, 0.2 mmol) and vinylidenecycloheptane (49 mg, 0.4 mmol).

$^1\text{H NMR}$ (500 MHz, CDCl_3) δ 8.03 (d, $J = 8.3$ Hz, 1H), 7.86 (d, $J = 8.1$ Hz, 1H), 7.74 (d, $J = 8.3$ Hz, 1H), 7.65 (d, $J = 8.3$ Hz, 1H), 7.47 (ddd, $J = 8.2, 6.8, 1.4$ Hz, 1H), 7.42 (ddd, $J = 8.1, 6.8, 1.3$ Hz, 1H), 6.85 (d, $J = 1.7$ Hz, 1H), 2.18 (d, $J = 1.5$ Hz, 3H), 2.03-1.90 (m, 2H), 1.89-1.64 (m, 10H).

$^{13}\text{C NMR}$ (126 MHz, CDCl_3) δ 157.62, 152.42, 138.34, 132.72, 128.20, 127.26, 125.22, 124.72, 124.07, 123.74, 121.29, 121.10, 57.44, 35.53, 32.32, 25.47, 14.66.

HRMS-APCI: calculated for $\text{C}_{20}\text{H}_{23}$ $[\text{M}+\text{H}]^+$: 263.1794; found: 263.1805.

2'-Methylspiro[cyclodecane-1,3'-cyclopenta[*a*]naphthalene] (6p)



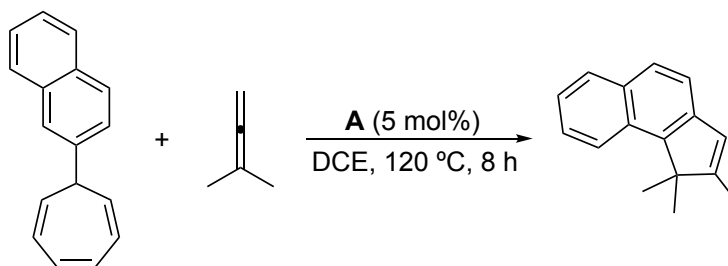
The title compound (colorless oil, 32 mg, yield: 52%) was synthesized according to the General Procedure A from 1-(cyclohepta-2,4,6-trien-1-yl)naphthalene (44 mg, 0.2 mmol) and vinylidenecyclodecane (66 mg, 0.4 mmol).

$^1\text{H NMR}$ (400 MHz, CDCl_3) δ 8.03 (d, $J = 8.2$ Hz, 1H), 7.85 (d, $J = 8.2$ Hz, 1H), 7.63-7.53 (m, 2H), 7.48-7.37 (m, 2H), 6.89 (d, $J = 1.6$ Hz, 1H), 2.16 (d, $J = 1.5$ Hz, 3H), 2.09-1.94 (m, 2H), 1.92-1.58 (m, 16H).

$^{13}\text{C NMR}$ (126 MHz, CDCl_3) δ 157.33, 150.34, 138.45, 132.69, 128.19, 127.27, 125.14, 124.72, 124.04, 123.26, 121.86, 121.74, 57.91, 29.35, 28.66, 28.13, 23.78, 22.94, 15.86.

HRMS-APCI: calculated for $\text{C}_{23}\text{H}_{29}$ $[\text{M}+\text{H}]^+$: 305.2264; found: 305.2268.

1,1,2-Trimethyl-1*H*-cyclopenta[*a*]naphthalene (6q)



The title compound (white solid, 17 mg, yield: 41%) was synthesized according to the General Procedure A from 2-(cyclohepta-2,4,6-trien-1-yl)naphthalene (44 mg, 0.2 mmol) and 3-methylbuta-1,2-diene (27 mg, 0.4 mmol).

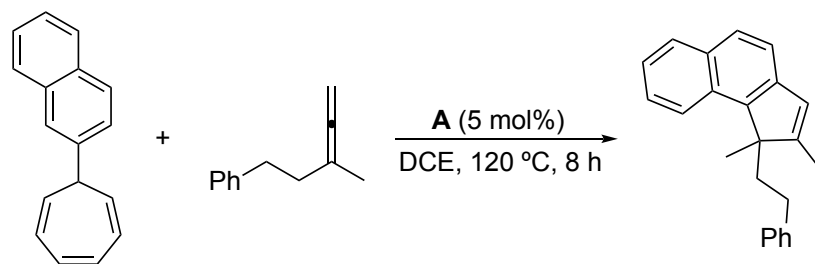
$^1\text{H NMR}$ (400 MHz, CDCl_3) δ 8.15 (d, $J = 8.6$ Hz, 1H), 7.94 (d, $J = 8.2$ Hz, 1H), 7.79 (d, $J = 8.2$ Hz, 1H), 7.57-7.51 (m, 2H), 7.42 (ddd, $J = 8.1, 6.8, 1.2$ Hz, 1H), 6.52 (d, $J = 1.6$ Hz, 1H), 2.11 (d, $J = 1.6$ Hz, 3H), 1.49 (s, 6H).

$^{13}\text{C NMR}$ (101 MHz, CDCl_3) δ 157.02, 146.88, 140.21, 131.93, 129.58, 128.97, 127.63, 125.58, 123.96, 123.44, 122.81, 120.18, 51.80, 23.51, 12.40.

HRMS-APCI: calculated for $\text{C}_{16}\text{H}_{17}$ $[\text{M}+\text{H}]^+$: 209.1325; found: 209.1333.

M.p.: 73-75 °C.

1,2-Dimethyl-1-phenethyl-1*H*-cyclopenta[*a*]naphthalene (6r)



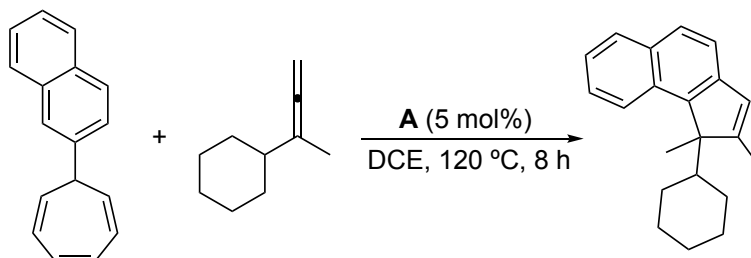
The title compound (colorless oil, 41 mg, yield: 69%) was synthesized according to the General Procedure A from 2-(cyclohepta-2,4,6-trien-1-yl)naphthalene (44 mg, 0.2 mmol) and (3-methylpenta-3,4-dien-1-yl)benzene (63 mg, 0.4 mmol).

¹H NMR (400 MHz, CDCl₃) δ 8.18 (d, *J* = 8.5 Hz, 1H), 7.99 (d, *J* = 8.2 Hz, 1H), 7.84 (d, *J* = 8.2 Hz, 1H), 7.61-7.54 (m, 2H), 7.50-7.44 (m, 1H), 7.22 (tq, *J* = 7.1, 1.2 Hz, 2H), 7.17-7.11 (m, 1H), 6.98 (d, *J* = 7.0 Hz, 2H), 6.67 (s, 1H), 2.69 (td, *J* = 13.1, 5.2 Hz, 1H), 2.28-2.18 (m, 1H), 2.14 (s, 3H), 1.95 (td, *J* = 13.1, 4.5 Hz, 1H), 1.69 (td, *J* = 13.1, 4.8 Hz, 1H), 1.52 (s, 3H).

¹³C NMR (101 MHz, CDCl₃) δ 154.29, 144.49, 142.66, 141.51, 131.98, 129.68, 129.33, 128.23, 128.16, 127.87, 126.12, 125.89, 125.54, 123.63, 122.43, 120.14, 56.06, 39.37, 30.48, 24.00, 12.60.

HRMS-APCI: calculated for C₂₃H₂₃ [M+H]⁺: 299.1794; found: 299.1799.

1-Cyclohexyl-1,2-dimethyl-1*H*-cyclopenta[*a*]naphthalene (6s)



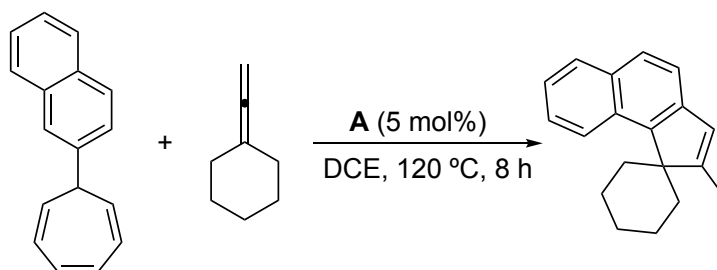
The title compound (colorless oil, 26 mg, yield: 47%) was synthesized according to the General Procedure A from 2-(cyclohepta-2,4,6-trien-1-yl)naphthalene (44 mg, 0.2 mmol) and buta-2,3-dien-2-ylcyclohexane (55 mg, 0.4 mmol).

¹H NMR (400 MHz, CDCl₃) δ 8.16 (d, *J* = 9.1 Hz, 1H), 7.93 (d, *J* = 8.2 Hz, 1H), 7.77 (d, *J* = 8.1 Hz, 1H), 7.52 (ddd, *J* = 8.5, 6.8, 1.4 Hz, 1H), 7.47 (d, *J* = 8.2 Hz, 1H), 7.40 (ddd, *J* = 8.1, 6.8, 1.2 Hz, 1H), 6.55 (d, *J* = 1.7 Hz, 1H), 2.35-2.25 (m, 1H), 2.14 (d, *J* = 1.5 Hz, 3H), 1.91-1.83 (m, 1H), 1.67-1.44 (m, 6H), 1.37-1.24 (m, 2H), 1.14-0.78 (m, 4H).

¹³C NMR (101 MHz, CDCl₃) δ 155.21, 146.82, 141.33, 132.16, 129.67, 128.94, 127.61, 126.83, 125.25, 123.45, 123.22, 119.76, 59.24, 44.93, 27.85, 27.67, 26.95, 26.64, 20.46, 16.00.

HRMS-APCI: calculated for C₂₁H₂₅ [M+H]⁺: 277.1951; found: 277.1957.

2'-Methylspiro[cyclohexane-1,1'-cyclopenta[a]naphthalene] (6t)



The title compound (yellow solid, 26 mg, yield: 52%) was synthesized according to the General Procedure A from 2-(cyclohepta-2,4,6-trien-1-yl)naphthalene (44 mg, 0.2 mmol) and vinylidenecyclohexane (44 mg, 0.4 mmol).

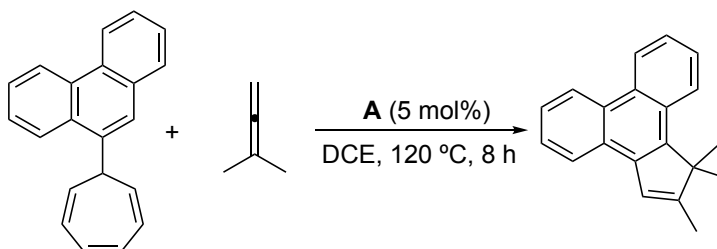
$^1\text{H NMR}$ (400 MHz, CDCl_3) δ 8.26 (d, $J = 8.6$ Hz, 1H), 7.93 (d, $J = 8.7$ Hz, 1H), 7.77 (d, $J = 7.8$ Hz, 1H), 7.55 (ddd, $J = 8.5, 6.8, 1.4$ Hz, 1H), 7.46 (d, $J = 8.2$ Hz, 1H), 7.41 (ddd, $J = 8.1, 6.8, 1.1$ Hz, 1H), 6.48 (d, $J = 1.6$ Hz, 1H), 2.58 (ddd, $J = 14.5, 12.8, 6.0$ Hz, 2H), 2.43 (d, $J = 1.6$ Hz, 3H), 2.07-1.88 (m, 5H), 1.76-1.63 (m, 1H), 1.49-1.42 (m, 2H).

$^{13}\text{C NMR}$ (126 MHz, CDCl_3) δ 159.39, 146.80, 139.96, 132.44, 129.95, 128.01, 125.67, 125.31, 123.19, 122.90, 119.85, 54.77, 31.90, 25.37, 23.01, 19.69.

HRMS-APCI: calculated for $\text{C}_{19}\text{H}_{21}$ $[\text{M}+\text{H}]^+$: 249.1638; found: 249.1647.

M.p.: 122-124 °C.

1,1,2-Trimethyl-1*H*-cyclopenta[*l*]phenanthrene (6u)



The title compound (white solid, 25.5 mg, yield: 50%) was synthesized according to the General Procedure A from 9-(cyclohepta-2,4,6-trien-1-yl)phenanthrene (54 mg, 0.2 mmol) and 3-methylbuta-1,2-diene (27 mg, 0.4 mmol).

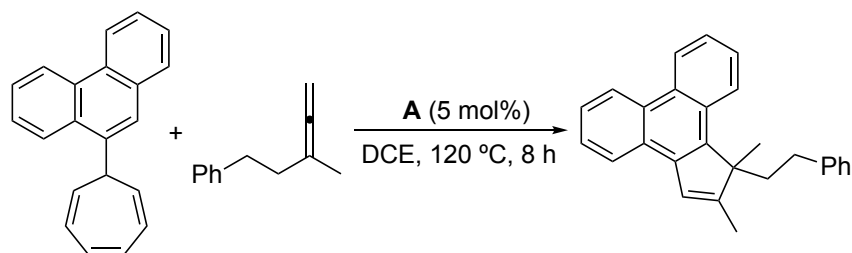
$^1\text{H NMR}$ (400 MHz, CDCl_3) δ 9.04-8.59 (m, 2H), 8.40-8.06 (m, 2H), 7.79-7.54 (m, 4H), 7.05 (d, $J = 1.6$ Hz, 1H), 2.20 (d, $J = 1.6$ Hz, 3H), 1.56 (s, 6H).

$^{13}\text{C NMR}$ (101 MHz, CDCl_3) δ 157.72, 144.58, 137.06, 130.25, 129.13, 128.73, 127.52, 126.34, 126.27, 125.67, 124.62, 124.17, 123.88, 123.42, 123.16, 120.93, 52.97, 23.45, 12.65.

HRMS-APCI: calculated for $\text{C}_{20}\text{H}_{19}$ $[\text{M}+\text{H}]^+$: 259.1481; found: 259.1486.

M.p.: 125-127 °C.

1,2-Dimethyl-1-phenethyl-1*H*-cyclopenta[*l*]phenanthrene (6v)



The title compound (white solid, 49.3 mg, yield: 71%) was synthesized according to the General Procedure A from 9-(cyclohepta-2,4,6-trien-1-yl)phenanthrene (54 mg, 0.2 mmol) and (3-methylpenta-3,4-dien-1-yl)benzene (63 mg, 0.4 mmol).

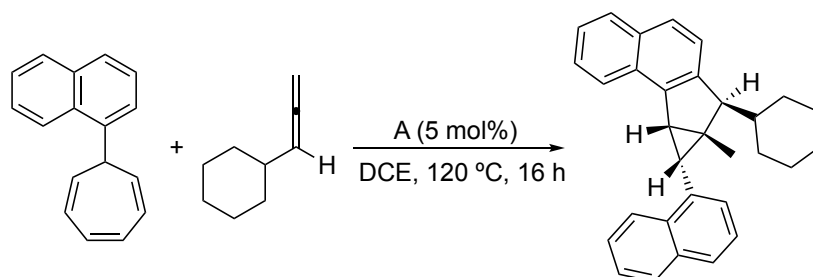
¹H NMR (400 MHz, CDCl₃) δ 8.87 (d, *J* = 8.2 Hz, 1H), 8.85-8.80 (m, 1H), 8.28-8.22 (m, 2H), 7.75 – 7.62 (m, 4H), 7.23-7.16 (m, 3H), 7.15-7.10 (m, 1H), 6.99-6.93 (m, 2H), 2.74 (td, *J* = 13.2, 4.8 Hz, 1H), 2.32-2.17 (m, 4H), 1.97 (ddd, *J* = 13.9, 12.5, 4.5 Hz, 1H), 8.87 (td, *J* = 12.8, 4.9 Hz, 1H), 1.56 (s, 3H).

¹³C NMR (101 MHz, CDCl₃) δ 155.07, 142.65, 142.32, 138.53, 130.44, 129.16, 129.06, 128.26, 128.20, 127.47, 126.61, 126.45, 125.85, 125.59, 124.67, 124.44, 124.01, 123.27, 123.11, 123.01, 57.28, 39.28, 30.61, 24.01, 12.88.

HRMS-APCI: calculated for C₂₇H₂₅ [M+H]⁺: 349.1591; found: 349.1596.

M.p.: 97-99 °C.

7-Cyclohexyl-7a-methyl-8-(naphthalen-1-yl)-7,7a,8,8a-tetrahydrocyclopropa[4,5]cyclopenta[1,2-*a*]naphthalene (11)



A solution of the 1-(cyclohepta-2,4,6-trien-1-yl)naphthalene (44 mg, 0.2 mmol), buta-2,3-dien-2-ylcyclohexane (55 mg, 0.4 mmol) and gold complex A (7.7 mg, 5 mol%) in 1,2-dichloroethane (DCE, 2 mL) was heated at 120 °C in a sealed tube until the starting material had been fully consumed (16 h). After the reaction mixture had been allowed to cool to room temperature, the solvent was removed in vacuo and the crude residue was purified by preparative TLC to give **11** (11 mg, 28% yield) as a yellow solid.

¹H NMR (400 MHz, CDCl₃) δ 8.29 (d, *J* = 7.6 Hz, 2H), 7.88-7.81 (m, 1H), 7.77 (d, *J* = 8.1 Hz, 1H), 7.64 (ddd, *J* = 8.2, 6.8, 1.3 Hz, 1H), 7.60-7.38 (m, 5H), 6.90 (d, *J* = 8.4 Hz, 1H), 6.69 (dd, *J* = 8.2, 7.2 Hz, 1H), 6.20 (dt, *J* = 7.3, 1.3 Hz, 1H), 3.32 (dd, *J* = 7.6, 1.8

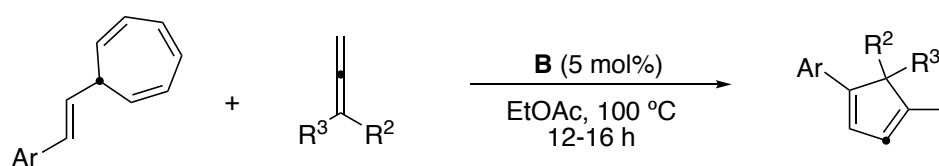
Hz, 1H), 2.74 (d, $J = 7.5$ Hz, 1H), 2.61 (t, $J = 2.1$ Hz, 1H), 1.93 (s, 4H), 1.79-1.71 (m, 1H), 1.67-1.45 (m, 5H), 1.39-1.17 (m, 2H), 1.08-0.91 (m, 1H), 0.52-0.38 (m, 1H).

^{13}C NMR (101 MHz, CDCl_3) δ 141.93, 139.74, 133.94, 133.43, 132.86, 132.42, 130.89, 128.69, 128.40, 128.02, 125.97, 125.80, 125.69, 125.10, 125.00, 124.84, 124.65, 124.48, 124.39, 123.51, 52.30, 40.65, 35.68, 33.69, 32.85, 32.82, 29.17, 27.61, 26.62, 26.45, 20.85.

HRMS-APCI: calculated for $\text{C}_{31}\text{H}_{31}$ $[\text{M}+\text{H}]^+$: 403.2420; found: 403.2417.

M.p.: 205-207 °C.

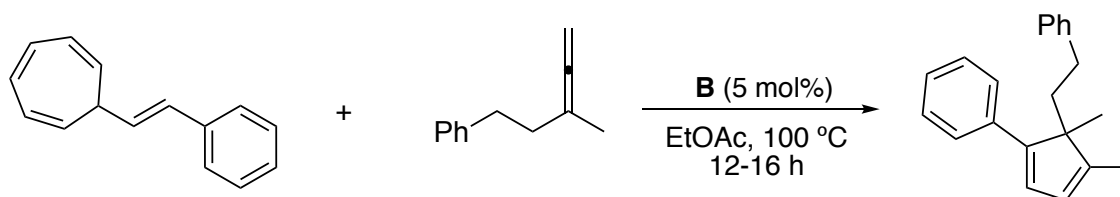
6. General Procedure B for the Gold(I)-Catalyzed Synthesis of Cyclopentadienes



Under air, a 2.0-5.0 mL microwave vial was charged with a Teflon-coated magnetic stirring bar and an allene **5** (1.5-3.0 equiv) and it was dissolved in EtOAc (HPLC grade, 0.1 M). Then, 7-styryl-1,3,5-cycloheptatriene **2** (1.0 equiv) was added as a solid by spatula or as a liquid by glass pipette and finally gold catalyst **B** (5 mol%) was added. The vial was sealed with its corresponding cap and the resulting solution was stirred at 100 °C in a heating block (covering the vial completely) for 12-16 h. The yellow-orange solution was concentrated under vacuum and the obtained residue was purified by flash column chromatography (SiO_2 , pentane or gradients of pentane/ Et_2O).

6.1. Characterization Data for the Different Cyclopentadienes

(4,5-Dimethyl-5-phenethylcyclopenta-1,3-dien-1-yl)benzene (**7a**)



This compound was obtained, following General Procedure B, from (*E*)-7-styrylcyclohepta-1,3,5-triene (50 mg, 0.257 mmol, 1.0 equiv) and (3-Methylpenta-3,4-dien-1-yl)benzene (61 mg, 0.386 mmol, 1.5 equiv) using gold catalyst **B** (11.6 mg, 0.013 mmol, 5 mol%) after purification by flash column (SiO_2 , eluent: pentane) as a colorless oil (35 mg, 0.128 mmol, 50%).

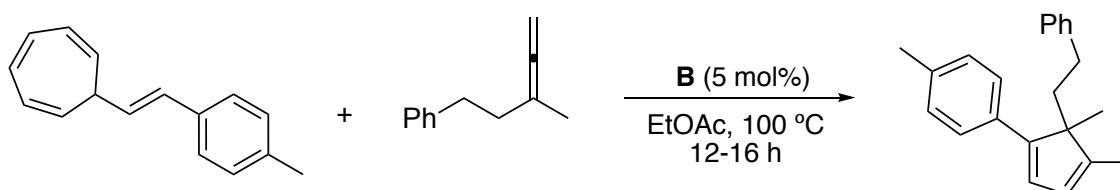
^1H NMR (500 MHz, CDCl_3) δ 7.56 (dt, $J = 7.4, 1.4$ Hz, 2H), 7.37 (tt, $J = 7.5, 1.6$ Hz, 2H), 7.26-7.20 (m, 3H), 7.13 (tt, $J = 7.5, 1.6$ Hz, 1H), 7.02 (d, $J = 7.5$ Hz, 2H), 6.75 (d,

$J = 2.2$ Hz, 1H), 2.24 (td, $J = 12.9, 4.7$ Hz, 1H), 2.12 (td, $J = 13.0, 4.7$ Hz, 1H), 2.02-1.88 (m, 2H), 1.96 (d, $J = 1.6$ Hz, 3 H) ppm.

^{13}C NMR (126 MHz, CDCl_3) δ 153.6, 151.2, 142.8, 136.6, 128.5, 128.3, 128.2, 128.0, 126.3, 125.8, 125.6, 125.4, 57.2, 37.9, 30.3, 22.9, 12.7 ppm.

HRMS (APCI Positive): calculated for $\text{C}_{21}\text{H}_{23}$ $[\text{M}+\text{H}]^+$: 275.1794; found: 275.1788.

1-(4,5-Dimethyl-5-phenethylcyclopenta-1,3-dien-1-yl)-4-methylbenzene (7b)



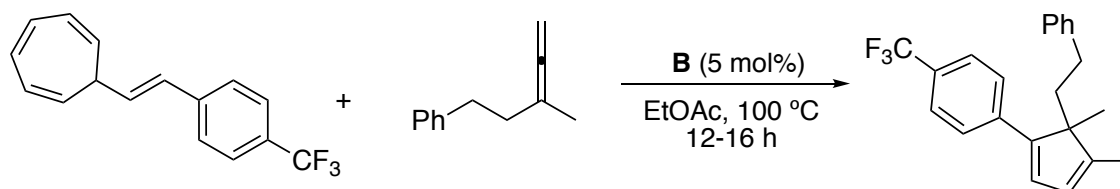
This compound was obtained, following General Procedure B, from (*E*)-7-(4-methylstyryl)cyclohepta-1,3,5-triene (70 mg, 0.340 mmol, 1.0 equiv) and (3-methylpenta-3,4-dien-1-yl)benzene (80 mg, 0.504 mmol, 1.5 equiv) using gold catalyst **B** (15 mg, 0.017 mmol, 5 mol%) after purification by flash column (SiO_2 , eluent: pentane) as a colorless oil (36 mg, 0.125 mmol, 37%).

^1H NMR (500 MHz, CDCl_3) δ 7.49 (d, $J = 8.3$ Hz, 2H), 7.24 (t, $J = 7.3$ Hz, 2H), 7.21 (d, $J = 8.1$ Hz, 2H), 7.16 (t, $J = 7.3$ Hz, 2H), 7.05 (d, $J = 8.1$ Hz, 2H), 6.73 (d, $J = 2.3$ Hz, 1H), 6.18 (quint, $J = 1.7$ Hz, 1H), 2.40 (s, 3H), 2.26 (td, $J = 12.6, 4.6$ Hz, 1H), 2.15 (td, $J = 12.6, 4.6$ Hz, 1H), 1.98 (d, $J = 1.6$ Hz, 3H), 2.04-1.90 (m, 2H), 1.28 (s, 3H) ppm.

^{13}C NMR (126 MHz, CDCl_3) δ 153.1, 151.2, 142.9, 136.0, 133.8, 129.2, 128.3, 128.2, 127.2, 125.7, 125.5, 125.4, 57.1, 37.9, 30.3, 22.9, 21.1, 12.7 ppm.

HRMS (APCI Positive): calculated for $\text{C}_{22}\text{H}_{25}$ $[\text{M}+\text{H}]^+$: 289.1951; found: 289.1949.

1-(4,5-Dimethyl-5-phenethylcyclopenta-1,3-dien-1-yl)-4-(tri-fluoromethyl)benzene (7c)



This compound was obtained, following General Procedure B, from (*E*)-7-(4-(trifluoromethyl)styryl)cyclohepta-1,3,5-triene (40 mg, 0.153 mmol, 1.0 equiv) and (3-methylpenta-3,4-dien-1-yl)benzene (48 mg, 0.305 mmol, 2.0 equiv) using gold catalyst **B** (6.9 mg, 7.6 μmol , 5 mol%) after purification by flash column (SiO_2 , eluent: pentane) as a colorless oil (23 mg, 0.153 mmol, 44%).

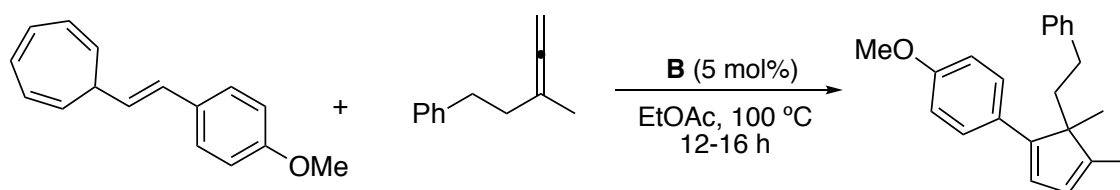
$^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.66 (d, $J = 8.6$ Hz, 2H), 7.61 (d, $J = 8.6$ Hz, 2H), 7.23 (tt, $J = 7.0, 1.4$ Hz, 2H), 7.15 (tt, $J = 7.2, 1.4$ Hz, 1H), 7.03-6.99 (m, 2H), 6.90 (d, $J = 2.4$ Hz, 1H), 6.21 (quint, $J = 1.7$ Hz, 1H), 2.28-2.20 (m, 1H), 2.08-1.94 (m, 3H), 1.99 (d, $J = 1.5$ Hz, 3H), 1.28 (s, 3H) ppm.

$^{13}\text{C NMR}$ (101 MHz, CDCl_3) δ 155.4, 149.5, 142.4, 130.2, 129.0, 128.4, 128.4, 128.3, 128.2, 125.7, 125.5, 125.4 (q, $J_{\text{C-F}} = 3.8$ Hz), 57.3, 37.9, 30.2, 22.9, 12.7 ppm.

$^{19}\text{F NMR}$ (376 MHz, CDCl_3) δ -62.50 ppm.

HRMS (APCI Positive): calculated for $\text{C}_{22}\text{H}_{22}\text{F}_3$ $[\text{M}+\text{H}]^+$: 343.1668; found: 343.1662.

1-(4,5-Dimethyl-5-phenethylcyclopenta-1,3-dien-1-yl)-4-methoxybenzene (7d)



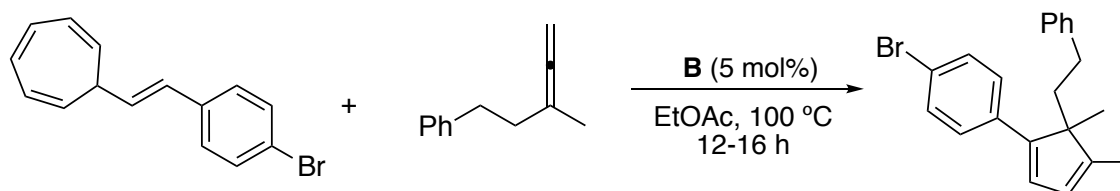
This compound was obtained, following General Procedure B, from (*E*)-7-(4-methoxystyryl)cyclohepta-1,3,5-triene (50 mg, 0.223 mmol, 1.0 equiv) and (3-methylpenta-3,4-dien-1-yl)benzene (71 mg, 0.446 mmol, 2.0 equiv) using gold catalyst **B** (10 mg, 11 μmol , 5 mol%) after purification by flash column (SiO_2 , eluent: pentane/ Et_2O 99:1) as a pale yellow syrup (27 mg, 0.089 mmol, 39%).

$^1\text{H NMR}$ (500 MHz, CDCl_3) δ 7.52 (d, $J = 8.9$ Hz, 2H), 7.24 (t, $J = 7.7$ Hz, 2H), 7.15 (t, $J = 7.5$ Hz, 1H), 7.04 (d, $J = 7.9$ Hz, 2H), 6.93 (d, $J = 7.9$ Hz, 2H), 6.64 (d, $J = 2.2$ Hz, 1H), 6.16 (quint, $J = 1.8$ Hz, 1H), 3.87 (s, 3H), 2.21 (td, $J = 12.9, 4.7$ Hz, 1H), 2.12 (td, $J = 12.9, 4.5$ Hz, 1H), 2.00 (td, $J = 13.0, 4.5$ Hz, 1H), 1.96 (d, $J = 1.5$ Hz, 3H), 1.91 (td, $J = 12.9, 4.5$ Hz, 1H), 1.26 (s, 3H) ppm.

$^{13}\text{C NMR}$ (126 MHz, CDCl_3) δ 158.2, 152.5, 150.9, 142.9, 129.6, 128.3, 128.2, 126.9, 126.4, 125.5, 125.4, 113.9, 77.3, 57.1, 55.3, 37.9, 30.3, 23.0, 12.6 ppm.

HRMS (APCI Positive): calculated for $\text{C}_{22}\text{H}_{25}\text{O}$ $[\text{M}+\text{H}]^+$: 305.1900; found: 305.1904.

1-Bromo-4-(4,5-dimethyl-5-phenethylcyclopenta-1,3-dien-1-yl)-benzene (7e)



This compound was obtained, following General Procedure B, from (*E*)-7-(4-bromostyryl)cyclohepta-1,3,5-triene (60 mg, 0.220 mmol, 1.0 equiv) and (3-methylpenta-3,4-dien-1-yl)benzene (70 mg, 0.439 mmol, 2.0 equiv) using gold catalyst

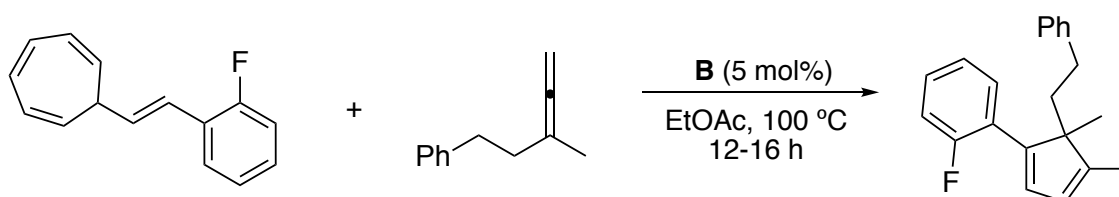
B (9.9 mg, 11 μ mol, 5 mol%) after purification by flash column (SiO₂, eluent: pentane) as a white syrup (39 mg, 0.110 mmol, 50%).

¹H NMR (400 MHz, CDCl₃) δ 7.50 (dt, J = 8.7, 2.2 Hz, 2H), 7.44 (dt, J = 8.6, 2.2 Hz, 2H), 7.24 (t, J = 7.2 Hz, 2H), 7.16 (tt, J = 7.2, 2.1 Hz, 1H), 7.02 (d, J = 7.2 Hz, 2H), 6.78 (d, J = 2.3), 6.18 (quint, J = 1.8 Hz, 1H), 2.19 (td, J = 12.4, 4.8 Hz, 1H), 2.08-1.90 (m, 3H), 1.97 (d, J = 1.5 Hz, 3H), 1.26 (s, 3H) ppm.

¹³C NMR (101 MHz, CDCl₃) δ 154.3, 149.9, 142.6, 135.4, 131.6, 128.6, 128.3, 128.2, 127.2, 125.7, 125.5, 120.0, 57.2, 37.9, 30.2, 22.9, 12.7 ppm.

HRMS (APCI Positive): calculated for C₂₁H₂₂Br [M+H]⁺: 353.0899; found: 353.0895.

1-(4,5-Dimethyl-5-phenethylcyclopenta-1,3-dien-1-yl)-2-fluoro-benzene (7f)



This compound was obtained, following General Procedure B, from (*E*)-7-(2-fluorostyryl)cyclohepta-1,3,5-triene (40 mg, 0.188 mmol, 1.0 equiv) and (3-methylpenta-3,4-dien-1-yl)benzene (60 mg, 0.377 mmol, 2.0 equiv) using gold catalyst **B** (8.5 mg, 9.4 μ mol, 5 mol%) after filtering through silica gel and further purification by preparative TLC (1000 micron SiO₂, eluent: pentane) as a colorless viscous oil (28 mg, 0.096 mmol, 48%).

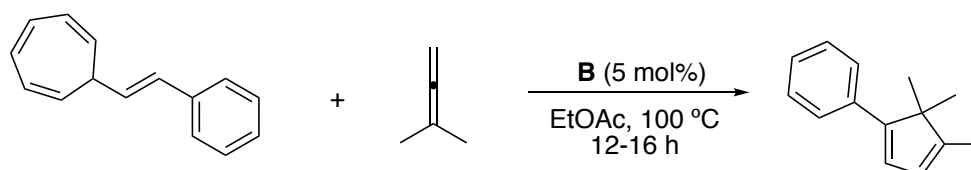
¹H NMR (400 MHz, CDCl₃) δ 7.47 (td, J = 7.9, 1.9 Hz, 1H), 7.26-7.21 (m, 3H), 7.18-7.12 (m, 3H), 7.08-7.04 (m, 2H), 6.79 (t, J = 2.2 Hz, 1H), 6.20 (quint, J = 1.7 Hz, 1H), 2.25-2.17 (m, 1H), 2.12-2.03 (m, 2H), 1.97 (d, J = 1.6 Hz, 3H), 1.90-1.84 (m, 1H) ppm.

¹³C NMR (101 MHz, CDCl₃) δ 160.4 (d, J_{C-F} = 248.1 Hz), 153.4, 144.6, 142.8, 132.7 (d, J_{C-F} = 9.7 Hz), 128.6 (d, J_{C-F} = 3.8 Hz), 128.2, 128.2, 127.6 (d, J_{C-F} = 8.7 Hz), 125.7, 125.6, 123.7 (d, J_{C-F} = 4.8 Hz), 116.2, 116.0, 58.3, 37.5, 30.1, 22.6, 12.8 ppm.

¹⁹F NMR (376 MHz, CDCl₃) δ -111.30 ppm.

HRMS (APCI Positive): calculated for C₂₁H₂₂F [M+H]⁺: 293.1700; found: 293.1701.

(4,5,5-Trimethylcyclopenta-1,3-dien-1-yl)benzene (7g)



This compound was obtained, following General Procedure B, from (*E*)-styrylcyclohepta-1,3,5-triene (0.26 g, 1.34 mmol, 1.0 equiv) and 3-methylbuta-1,2-diene

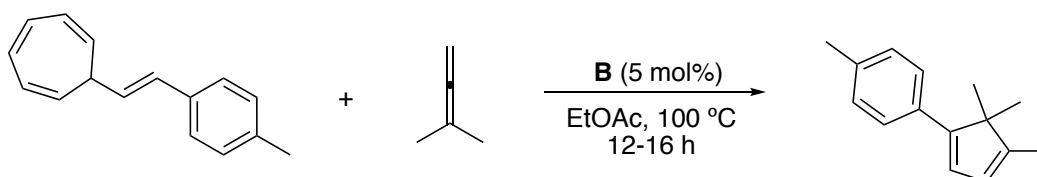
(0.27 g, 4.01 mmol, 3.0 equiv) using gold catalyst **B** (60 mg, 0.05 mmol, 5 mol%) after purification by flash column (SiO₂, eluent: pentane) as a colorless low boiling point oil (121 mg, 0.66 mmol, 49%).

¹H NMR (500 MHz, CDCl₃) δ 7.51 (d, *J* = 8.0 Hz, 2H), 7.32 (t, *J* = 7.9 Hz, 2H), 7.19 (t, *J* = 7.9 Hz, 1H), 6.63 (d, *J* = 2.3 Hz, 1H), 6.02 (quint, *J* = 1.4 Hz, 1 H), 1.92 (d, *J* = 1.4 Hz, 3H), 1.22 (s, 3H) ppm.

¹³C NMR (126 MHz, CDCl₃) δ 156.3, 153.6, 136.5, 128.3, 126.1, 126.1, 126.0, 123.3, 53.1, 22.5, 12.5 ppm.

HRMS (APCI Positive): calculated for C₁₅H₁₉ [M+H]⁺: 185.1325; found: 185.1321.

1-Methyl-4-(4,5,5-trimethylcyclopenta-1,3-dien-1-yl)benzene (7h)



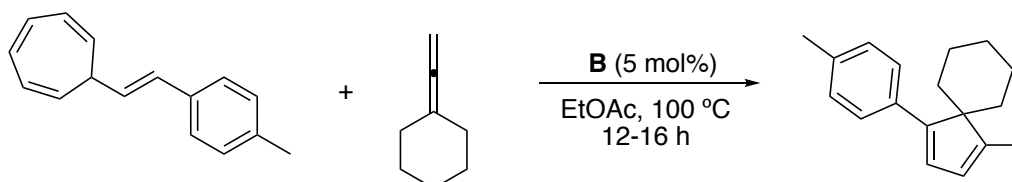
This compound was obtained, following General Procedure B, from (*E*)-7-(4-methylstyryl)cyclohepta-1,3,5-triene (0.21 g, 1.01 mmol, 1.0 equiv) and 3-methylbuta-1,2-diene (0.21 g, 3.02 mmol, 3.0 equiv) using gold catalyst **B** (45 mg, 0.05 mmol, 5 mol%) after purification by flash column (SiO₂, eluent: pentane) as a colorless low boiling point oil (95 mg, 0.48 mmol, 43-48%).

¹H NMR (400 MHz, CDCl₃) δ 7.45 (d, *J* = 8.1 Hz, 2H), 7.18 (d, *J* = 8.1 Hz, 2H), 6.62 (d, *J* = 2.1 Hz, 1H), 6.04 (quint, *J* = 1.5 Hz, 1H), 2.38 (s, 3H), 1.95 (d, *J* = 1.4 Hz, 3H), 1.25 (d, *J* = 0.6 Hz, 6H) ppm.

¹³C NMR (101 MHz, CDCl₃) δ 155.8, 153.6, 135.8, 133.6, 129.0, 125.9, 125.3, 123.3, 53.0, 22.5, 21.1, 12.5 ppm.

HRMS (APCI Positive): calculated for C₁₅H₁₉ [M+H]⁺: 199.1481; found: 199.1482.

1-Methyl-4-(*p*-tolyl)spiro[4.5]deca-1,3-diene (7i)



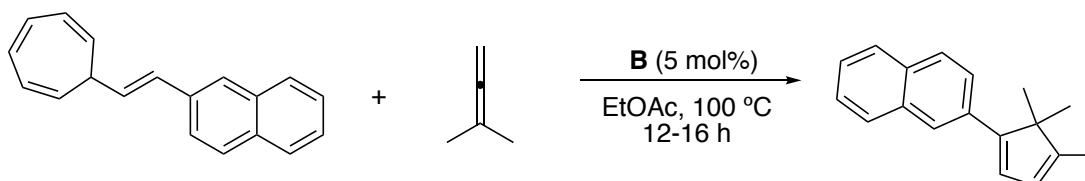
This compound was obtained, following General Procedure B, from (*E*)-7-(4-methylstyryl)-cyclohepta-1,3,5-triene (67 mg, 0.32 mmol, 1.0 equiv) and vinylidenecyclohexane (77 mg, 0.643 mmol, 2.0 equiv) using gold catalyst **B** (14 mg, 0.016 mmol, 5 mol%) after purification by flash column (SiO₂, eluent: pentane) as a colorless oil (28 mg, 0.117 mmol, 37%).

¹H NMR (500 MHz, CDCl₃) δ 7.29 (t, *J* = 4.1 Hz, 2H), 7.16 (d, *J* = 7.6 Hz, 2H), 6.28 (d, *J* = 2.2 Hz, 1H), 6.00 (quint, *J* = 1.7 Hz, 1H), 2.38 (s, 3H), 2.16 (d, *J* = 1.6 Hz, 3H), 1.91-1.85 (m, 2H), 1.80-1.72 (m, 2H), 1.67-1.59 (m, 3H), 1.50-1.42 (m, 3H) ppm.

¹³C NMR (126 MHz, CDCl₃) δ 155.9, 155.4, 135.8, 135.7, 128.5, 128.1, 126.6, 124.7, 56.9, 30.5, 25.4, 22.4, 21.1, 17.3 ppm.

HRMS (APCI Positive): calculated for C₁₈H₂₃ [M+H]⁺: 239.1794; found: 239.1788.

2-(4,5,5-Trimethylcyclopenta-1,3-dien-1-yl)naphthalene (7j)



This compound was obtained, following General Procedure B, from (*E*)-2-(cyclohepta-2,4,6-trien-1-yl)vinyl naphthalene (65 mg, 0.266 mmol, 1.0 equiv) and 3-methylbuta-1,2-diene (54 mg, 0.798 mmol, 3.0 equiv) using gold catalyst **B** (12 mg, 13 μmol, 5 mol%) after purification by flash column (SiO₂, eluent: pentane) as a pale yellow solid (35 mg, 0.149 mmol, 56%).

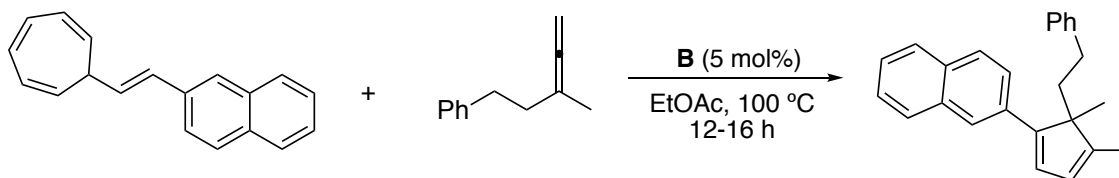
¹H NMR (400 MHz, CDCl₃) δ 7.95 – 7.89 (m, 1H), 7.89 – 7.70 (m, 4H), 7.46 (dq, *J* = 9.4, 6.9, 1.5 Hz, 2H), 6.84 (dd, *J* = 27.7, 2.3 Hz, 1H), 6.17 – 6.08 (m, 1H), 2.01 (d, *J* = 1.6 Hz, 3H), 1.36 (s, 6H).

¹³C NMR (101 MHz, CDCl₃) δ 157.0, 153.3, 133.6, 133.5, 132.0, 128.1, 127.7, 127.5, 126.9, 126.0, 125.3, 125.2, 123.5, 123.4, 53.2, 22.8, 12.5.

HRMS (APCI Positive): calculated for C₁₈H₁₉ [M+H]⁺: 235.1481; found: 235.1485.

M.p.: 58-62 °C.

2-(4,5-Dimethyl-5-phenethylcyclopenta-1,3-dien-1-yl)naphthalene (7k)



This compound was obtained, following General Procedure B, from (*E*)-2-(cyclohepta-2,4,6-trien-1-yl)vinyl naphthalene (30 mg, 0.123 mmol, 1.0 equiv) and (3-methylpenta-3,4-dien-1-yl)benzene (29 mg, 0.184 mmol, 1.5 equiv) using gold catalyst **B** (5.5 mg, 6.1 μmol, 5 mol%) after filtering through silica gel and further purification by preparative TLC (1000 micron SiO₂, eluent: pentane) as a pale yellow syrup (22 mg, 0.068 mmol, 55%).

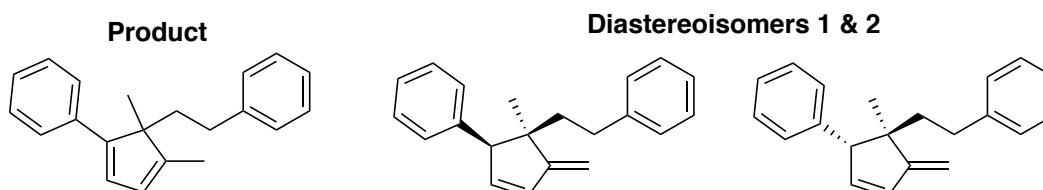
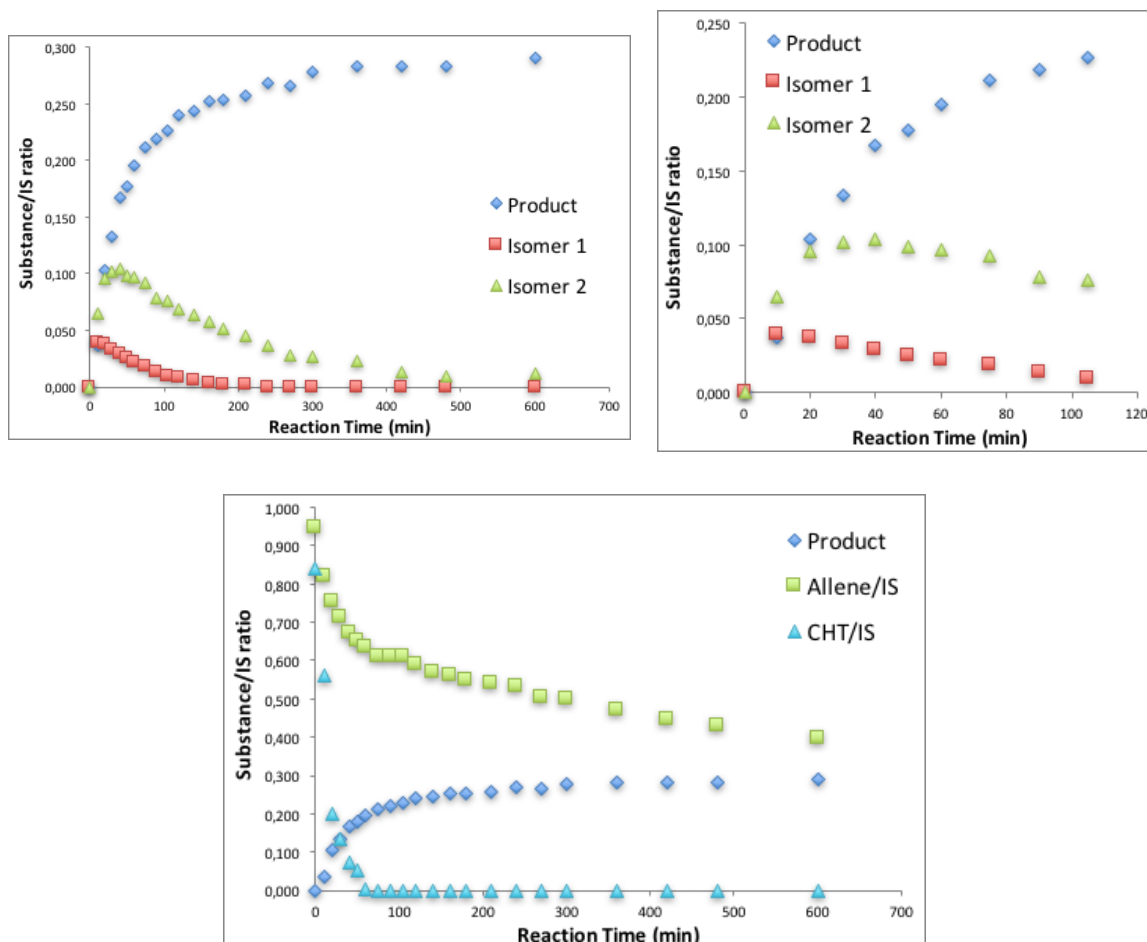
^1H NMR (400 MHz, CDCl_3) δ 7.96 (br, 1H), 7.86-7.76 (m, 4H), 7.47 (quint, $J = 7.3$ Hz, 2H), 7.20 (t, $J = 7.3$ Hz, 2H), 7.13 (t, $J = 7.2$ Hz, 1H), 7.04-7.00 (m, 2H), 6.93 (d, $J = 2.3$ Hz, 1H), 6.24 (quint, $J = 1.7$ Hz), 2.43-2.36 (m, 1H), 2.19-2.10 (m, 1H), 2.06-1.95 (m, 2H), 2.01 (d, $J = 1.5$ Hz, 3H), 1.37 (s, 3H) ppm.

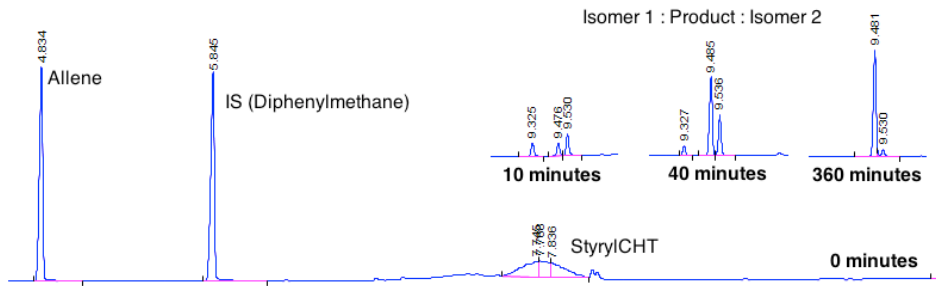
^{13}C NMR (101 MHz, CDCl_3) δ 154.3, 150.8, 142.8, 133.8, 133.7, 132.2, 128.8, 128.3, 128.3, 128.2, 128.0, 127.5, 126.1, 125.6, 125.6, 125.5, 125.1, 123.1, 57.3, 38.4, 30.4, 23.3, 12.8 ppm.

HRMS (APCI Positive): calculated for $\text{C}_{25}\text{H}_{25}$ $[\text{M}+\text{H}]^+$: 325.1951; found: 325.1949.

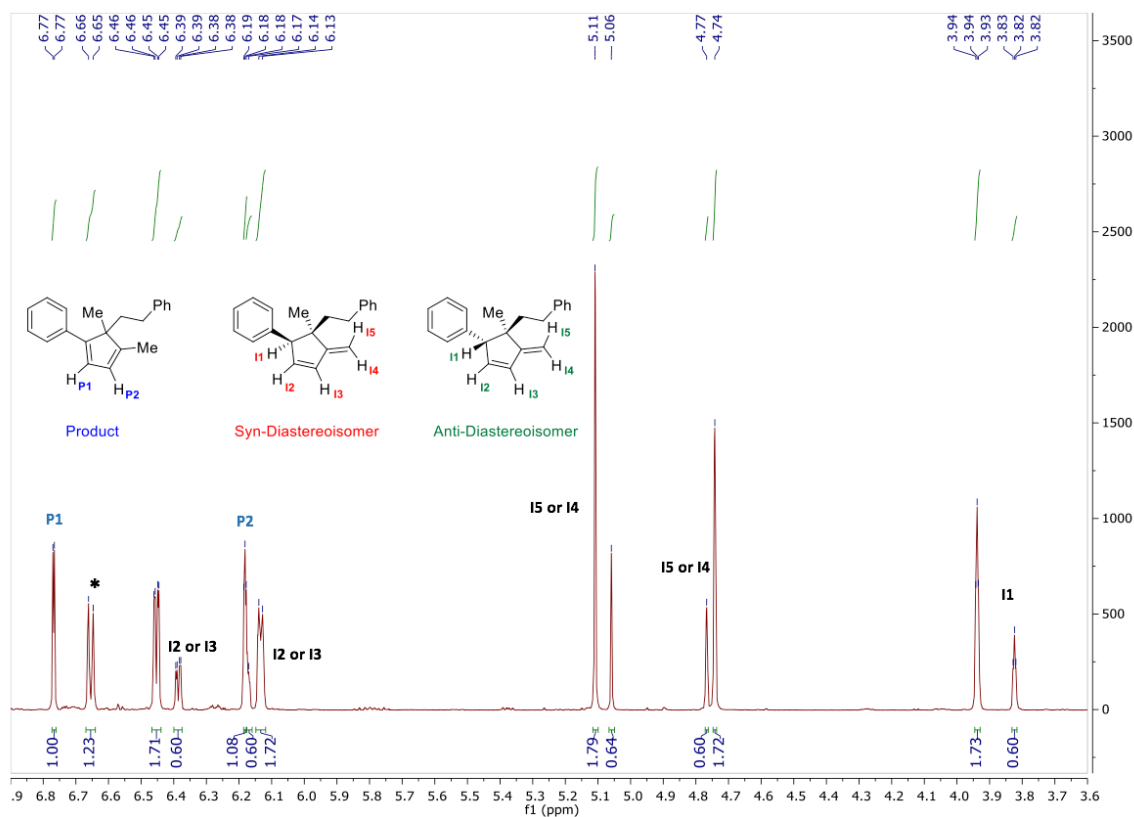
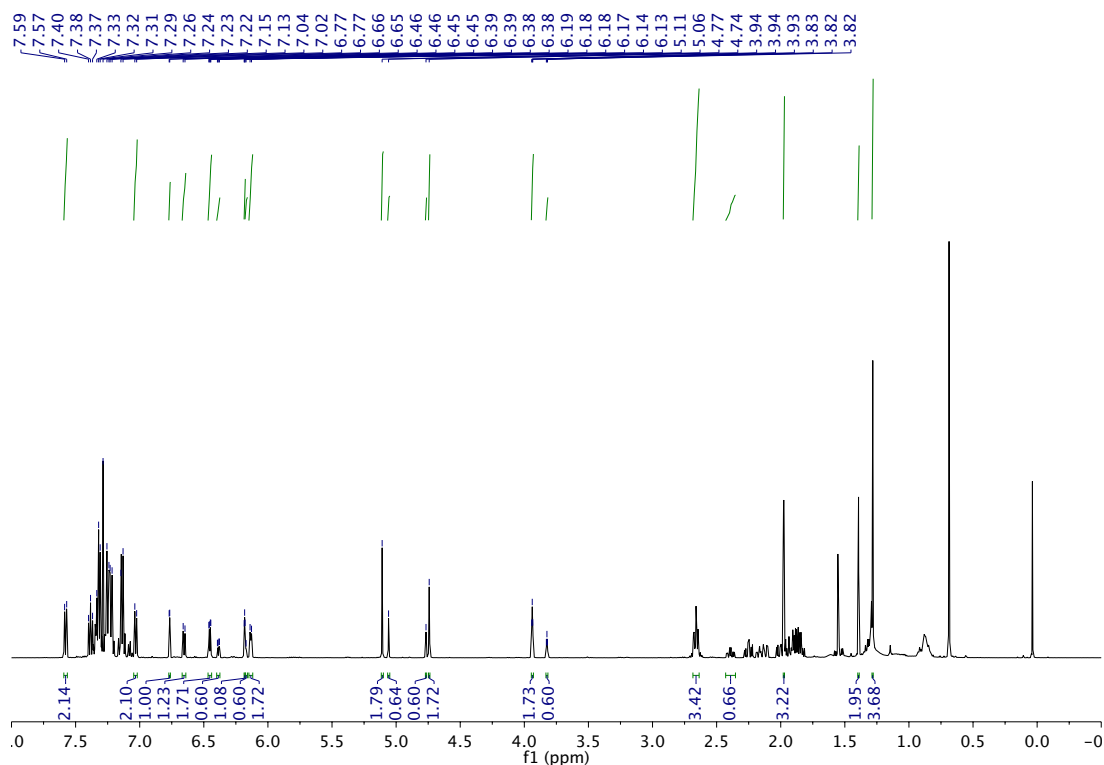
6.2. Kinetic and Mechanistic Studies

The synthesis of cyclopentadiene **7a** was followed by GC-FID using diphenylmethane as internal standard.





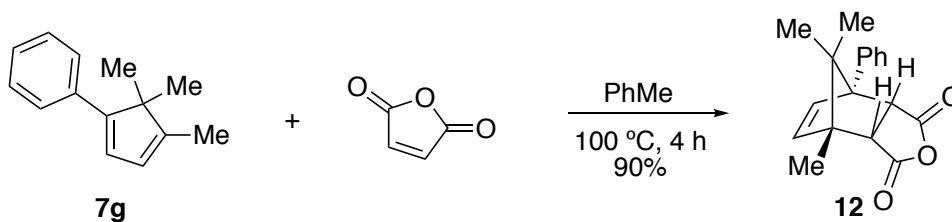
¹H NMR of the Mixture of Product and Diastereoisomers 1 & 2 (intermediates IIb)



* Two aromatic protons from the minor diastereoisomer, confirmed by integration, coupling constant and COSY.

For the NMR analysis, the reaction was stopped after 25 min and immediate flash column chromatography in SiO₂ with pentane afforded the mixture of the product and the two diastereomeric intermediates.

7. Diels-Alder Reaction of Highly Substituted Cyclopentadienes with Maleic Anhydride



To a solution of (4,5,5-trimethylcyclopenta-1,3-dien-1-yl)benzene **7g** (58 mg, 0.315 mmol, 1.0 equiv) in 1.5 mL of anhydrous toluene (0.2 M) open to air was added maleic anhydride (40 mg, 0.409 mmol, 1.3 equiv) and the resulting yellow mixture was stirred at 100 °C for 4 h. The obtained colorless suspension was cooled to room temperature and the solvent was removed under reduced pressure. Purification by flash column chromatography on SiO₂ (eluent pentane/Et₂O from 8:2 to 7:3) afforded *endo*-4,8,8-trimethyl-7-phenyl-3a,4,7,7a-tetrahydro-4,7-methano-isobenzofuran-1,3-dione **12** (80 mg, 90%⁵) as a white solid. Slow evaporation overnight of a solution of **12** in heptane/DCM afforded crystals suitable for X-ray analysis.

¹H NMR (500 MHz, CDCl₃) δ 7.47-7.42 (m, 2H), 7.38 (dd, *J* = 8.2, 2.2 Hz, 3H), 6.39 (d, *J* = 5.8 Hz, 1H), 6.20 (d, *J* = 5.8 Hz, 1H), 4.30 (d, *J* = 7.8 Hz, 1H), 3.49 (d, *J* = 7.8 Hz, 1H), 1.45 (s, 3H), 0.78 (s, 3H), 0.72 (s, 3H). ppm.

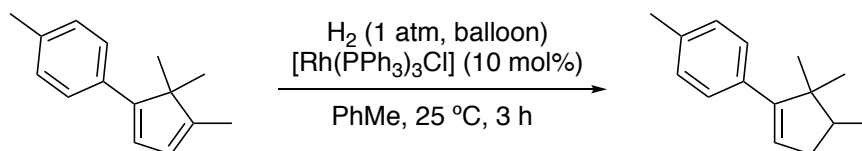
¹³C NMR (126 MHz, CDCl₃) δ 171.5, 170.6, 139.3, 136.8, 135.0, 128.5, 127.7, 127.7, 68.9, 67.9, 60.8, 52.5, 49.1, 17.42, 17.36, 12.8. ppm.

HRMS (ESI Positive): calculated for C₁₈H₁₈NaO₃ [M+Na+CH₃OH]⁺: 337.1410; found: 337.1413.

M.p.: 185-187 °C.

8. Total Synthesis of Laurokamurene B (10)

The synthesis of (±)-laurokamurene B was achieved in one step directly from cyclopentadiene **7h**, (1-methyl-4-(4,5,5-trimethylcyclopenta-1,3-dien-1-yl)benzene, see above for preparation).



To a stirred solution of 1-methyl-4-(4,5,5-trimethylcyclopenta-1,3-dien-1-yl)benzene (50 mg, 0.252 mmol, 1.0 equiv) in 1.5 mL of anhydrous toluene (0.17 M) under Ar atmosphere, was added Wilkinson's Catalyst, [Rh(PPh₃)₃Cl] (23 mg, 0.025 mmol, 10

⁵ *Endo* configuration confirmed by NOESY NMR experiments and single crystal X-ray diffraction. *Exo* diastereoisomer was not detected.

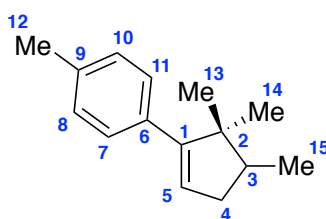
mol%, prepared following a reported procedure⁶). The Ar atmosphere was exchanged for an H₂ atmosphere through 3 vacuum/H₂ cycles using a H₂ balloon which was finally left attached to the flask. The reaction mixture was allowed to stir at room temperature for 3 h. The reaction was followed using both TLC and GC/MS (the later allowed the separation of the starting cyclopentadiene, the desired product and the double hydrogenation byproduct) and it was found that longer reaction times were detrimental to the desired product yield, as the second olefin gets also hydrogenated. After that time, the reaction was filtered through silica gel, and then purified by slow flash column in SiO₂ (eluent pentane, careful evaporation of pentane under 150-200 mbar at 20 °C was performed, since the product is relatively volatile) to afford (±)-laurokamurene B (43 mg, 0.220 mmol, 86%).

¹H NMR (500 MHz, CDCl₃) δ 7.23 (d, *J* = 8.0 Hz, 2H), 7.12 (d, *J* = 8.0 Hz, 2H), 5.71 (br, 1H), 2.45-2.40 (m, 1H), 2.35 (s, 3H), 2.07-1.99 (m, 2H), 1.11 (s, 3H), 1.02 (d, *J* = 6.7 Hz, 3H), 1.00 (s, 3H) ppm.

¹³C NMR (126 MHz, CDCl₃) δ 152.8, 136.2, 135.5, 128.6, 127.5, 126.2, 47.7, 45.8, 37.9, 26.3, 21.1, 20.7, 14.1 ppm.

HRMS (APCI Positive): calculated for C₁₅H₂₁ [M+H]⁺: 201.1638; found: 201.1636.

Table S2. Laurokamurene B Spectra Comparison



laurokamurene B

Position	¹ H NMR (δ) Natural Sample (400 MHz, CDCl ₃)	¹ H NMR (δ) Synthetic Sample (500 MHz, CDCl ₃)	¹³ C NMR (δ) Natural Sample (400 MHz, CDCl ₃)	¹³ C NMR (δ) Synthetic Sample (500 MHz, CDCl ₃)
1	-	-	152.8 (C)	152.83 (C)
2	-	-	47.7 (C)	47.73 (C)
3	2.01 (m)	2.03 (m)	45.8 (CH)	45.80 (CH)
4	2.01 (m)	2.03 (m)	37.8 (CH ₂)	37.86 (CH ₂)
	2.41 (ddd, 11.5, 9.7, 2.9)	2.43 (m)	-	-
5	5.69 (br)	5.71 (br)	126.1 (CH)	126.15 (CH)
6	-	-	135.5 (C)	135.48 (C)

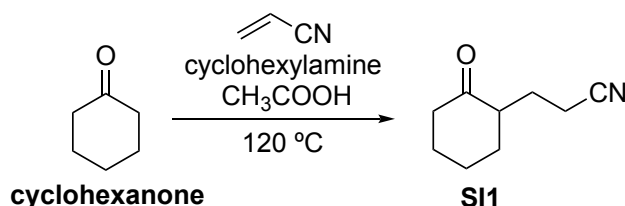
⁶ J. A. Osborn, G. Wilkinson, *Inorg. Syn.* **1967**, *10*, 67.

7	7.21 (d, 7.9)	7.23 (d, 8.0)	127.5 (CH)	127.46 (CH)
8	7.10 (d, 7.9)	7.12 (d, 8.0)	128.6 (CH)	128.60 (CH)
9	-	-	136.1 (C)	136.16 (C)
10	7.10 (d, 7.9)	7.12 (d, 8.0)	128.6 (CH)	128.60 (CH)
11	7.21 (d, 7.9)	7.23 (d, 8.0)	127.5 (CH)	127.46 (CH)
12	2.33 (s)	2.35 (s)	21.1 (CH ₃)	21.11 (CH ₃)
13	0.97 (s)	1.00 (s)	20.6 (CH ₃)	20.67 (CH ₃)
14	1.09 (s)	1.11 (s)	26.2 (CH ₃)	26.26 (CH ₃)
15	0.99 (d, 6.6)	1.02 (d, 6.7)	14.0 (CH ₃)	14.07 (CH ₃)

Chemical shifts (ppm) referenced to CDCl₃ ($\delta_{\text{H}} = 7.26$; $\delta_{\text{C}} = 77.0$). Proton coupling constants (J) in Hz are given in parentheses. Assignments were based on the comparison with the reported natural sample.⁷

9. Procedures for the Synthesis of the Tetracyclic Carbon Skeleton of Cycloaurenones

3-(2-Oxocyclohexyl)propanenitrile (SI1)



The title compound was synthesized according to a literature procedure.^[8] To a stirred mixture of cyclohexanone (35g, 37 mL, 0.36 mol) and acrylonitrile (28 g, 35 mL, 0.54 mol) was added cyclohexylamine (3.5 g, 4.1 mL, 36 mmol) and acetic acid (214 mg, 0.2 mL, 3.6 mmol). The reaction mixture was heated at 120 °C for 3 h. The resulting liquid was purified by column chromatography on silica gel (eluent cyclohexane/ethyl acetate 90/10) to result in a colorless oil (46.5 g, 86% yield).

¹H NMR (400 MHz, CDCl₃) δ 2.56-2.27 (m, 5H), 2.18-2.01 (m, 3H), 1.94-1.85 (m, 1H), 1.79-1.60 (m, 2H), 1.56-1.46 (m, 1H), 1.45-1.32 (m, 1H).

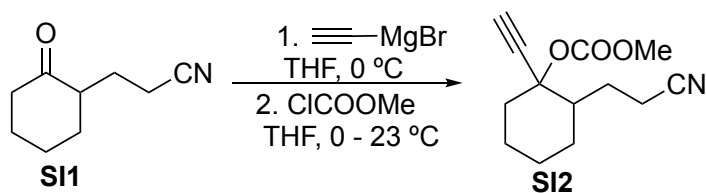
¹³C NMR (101 MHz, CDCl₃) δ 211.75, 119.72, 48.87, 42.25, 34.30, 28.00, 25.61, 25.18, 15.26.

HRMS-ESI: calculated for C₉H₁₃NNaO [M+Na]⁺: 174.0895; found: 174.0889.

2-(2-Cyanoethyl)-1-ethynylcyclohexyl methyl carbonate (SI2)

⁷ S.-C. Mao, Y.-W. Guo, *J. Nat. Prod.* **2006**, *69*, 1209-1211.

⁸ D. H. Woodmansee, M.-A. Muller, M. Neuburger, A. Pfaltz, *Chem. Sci.* **2010**, *1*, 72-78.



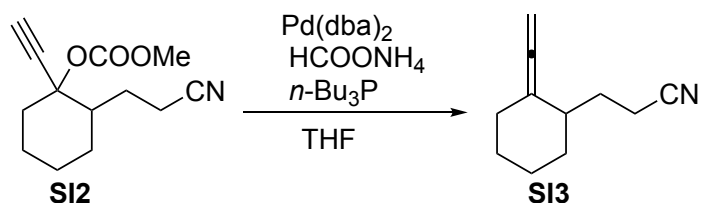
Ethynylmagnesium bromide (32 mL, 15.9 mol, 0.5 M in THF) was added dropwise to a solution of 3-(2-oxocyclohexyl)propanenitrile **SI1** (2 g, 13.2 mmol) in dry THF (30 mL) at 0 °C under argon. The mixture was stirred for 2 h at 0 °C, the disappearance of ketone was confirmed by TLC and then methyl chloroformate (1.6 g, 1.3 mL, 17.2 mmol) was added. The cooling bath was removed and the reaction was stirred at room temperature (23 °C) for 12 h. The reaction was quenched by the addition of water. The aqueous phase was extracted with ethyl acetate, the combined organic extracts were dried over MgSO₄, and the solvent was evaporated. The crude reaction mixture was purified by column chromatography on silica gel (cyclohexane/ethyl acetate 90:10) to give carbonate **SI2** (2.65g, 85% yield, *d.r.* = 1:1) as a colorless oil.

¹H NMR (400 MHz, CDCl₃) δ 3.77 (d, *J* = 4.2 Hz, 6H), 2.92-2.78 (m, 2H), 2.70 (s, 1H), 2.66 (s, 1H), 2.55-2.14 (m, 6H), 1.85-1.18 (m, 18H).

¹³C NMR (101 MHz, CDCl₃) δ 153.26, 153.13, 119.73, 119.55, 82.69, 81.45, 79.54, 78.14, 77.62, 74.97, 54.50, 54.42, 45.20, 45.15, 35.95, 34.73, 28.59, 26.83, 26.24, 25.63, 24.73, 24.24, 23.10, 20.57, 15.53, 15.35.

HRMS-ESI: calculated for C₁₃H₁₇NNaO₃ [M+Na]⁺: 258.1101; found: 258.1099.

3-(2-(1-Vinylidene)cyclohexyl)propanenitrile (**SI3**)



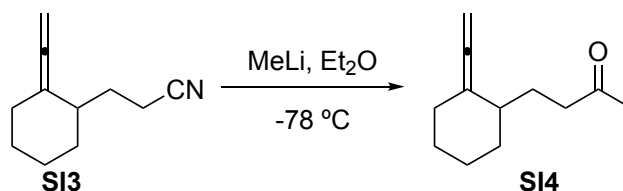
n-Bu₃P (340 mg, 0.4 ml, 1.7 mmol) was added dropwise to a stirred mixture of carbonate **SI2** (2.0 g, 8.5 mmol), ammonium formate (1.1 g, 17 mmol) and Pd(dba)₂ (244 mg, 0.4 mmol) in THF (50 mL) at 0 °C under argon. After 12 h, the disappearance of carbonate **7** was confirmed by TLC and the reaction mixture was filtered through a short pad of Celite. The solvent was evaporated, the residue was purified by column chromatography on silica gel (cyclohexane/ethyl acetate 50:1) to give allene **SI3** (1.1 g, 80% yield) as a colorless oil.

¹H NMR (400 MHz, CDCl₃) δ 4.75-4.68 (m, 2H), 2.46-2.39 (m, 2H), 2.35-2.27 (m, 1H), 2.09-1.72 (m, 6H), 1.69-1.58 (m, 1H), 1.48-1.35 (m, 2H), 1.25-1.12 (m, 1H).

¹³C NMR (101 MHz, CDCl₃) δ 202.42, 120.05, 104.25, 75.83, 38.32, 33.45, 31.34, 29.29, 27.20, 25.43, 15.17.

HRMS-ESI: calculated for $C_{11}H_{15}NNa$ $[M+Na]^+$: 184.1102; found: 184.1099.

4-(Vinylidene)cyclohexyl)butan-2-one (SI4)



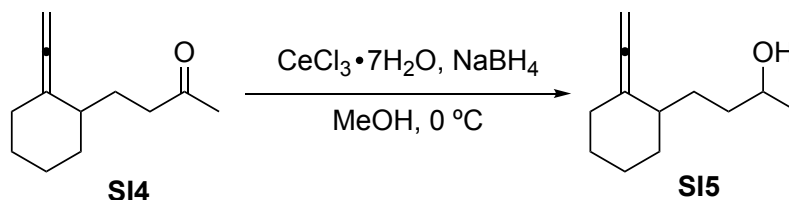
MeLi (30 mL, 48 mmol, 1.6 M in Et₂O) was added dropwise to a stirred solution of **SI3** (2.2 g, 13.6 mmol) in Et₂O (90 mL) at -78 °C under argon. The mixture was allowed to warm to 0 °C during 4 h. Thereafter, a saturated solution of NH₄Cl (20 mL) was added dropwise while stirring at 0 °C. The aqueous phase was extracted with Et₂O, the combined organic extracts were dried over MgSO₄. The solvent was evaporated, the residue was purified by column chromatography on silica gel (cyclohexane/ethyl acetate 50:1) to give ketone **SI4** (1.9 g, 78% yield) as a colorless oil.

¹H NMR (500 MHz, CDCl₃) δ 4.64 (t, *J* = 3.3 Hz, 2H), 2.58-2.39 (m, 2H), 2.31-2.22 (m, 1H), 2.13 (s, 3H), 2.01-1.68 (m, 6H), 1.61-1.51 (m, 1H), 1.48-1.28 (m, 2H), 1.23-1.12 (m, 1H).

¹³C NMR (101 MHz, CDCl₃) δ 206.40, 199.94, 102.10, 72.03, 38.86, 35.99, 30.72, 28.36, 26.97, 24.53, 24.41, 22.42.

HRMS-ESI: calculated for $C_{12}H_{18}NaO$ $[M+Na]^+$: 201.1250; found: 201.1254.

4-(Vinylidene)cyclohexyl)butan-2-ol (SI5)



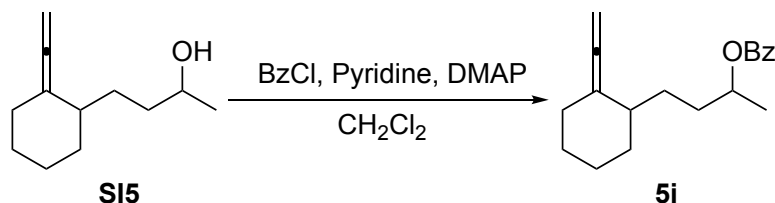
Cerium(III) chloride heptahydrate (12.5 g, 33.7 mmol) was added to a solution of **SI4** (1.5 g, 8.4 mmol) in MeOH (100 mL) at 0 °C. The mixture was stirred 10 min and then NaBH₄ (350 mg, 9.3 mmol) was added. After 1 h, the disappearance of ketone was confirmed by TLC and MeOH was removed. To the residue was added water and it was extracted with ethyl acetate, the combined organic extracts were dried over MgSO₄. The solvent was evaporated, the residue was purified by column chromatography on silica gel (cyclohexane/ethyl acetate 10:1) to give alcohol **SI5** (1.2 g, 79% yield, *d.r.* = 1:1) as a colorless oil.

¹H NMR (500 MHz, CDCl₃) δ 4.63-4.62 (m, 2H), 3.81-3.73 (m, 1H), 2.34-2.21 (m, 1H), 2.04-1.10 (m, 16H).

^{13}C NMR (101 MHz, CDCl_3) δ 203.06, 203.03, 105.68, 105.57, 74.79, 74.76, 68.46, 68.38, 39.40, 39.26, 37.19, 37.10, 33.66, 33.64, 31.50, 31.44, 29.68, 29.50, 27.43, 25.56, 25.51, 23.50, 23.46.

HRMS-APCI: calculated for $\text{C}_{12}\text{H}_{21}\text{O}$ $[\text{M}+\text{H}]^+$: 181.1587; found: 181.1582.

4-(Vinylidene)cyclohexyl)butan-2-yl benzoate (**5i**)



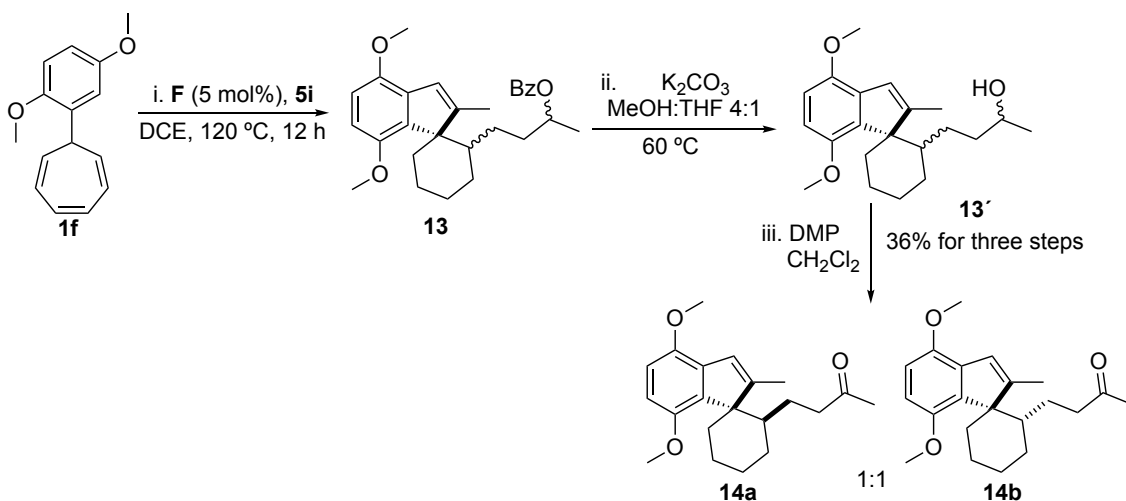
To a solution of **SI5** (1.0 g, 5.6 mmol) in CH_2Cl_2 (60 mL) was added pyridine (1.3 mL, 16.6 mmol) at 0 °C. The mixture was kept at 0 °C for 10 min and then benzoyl chloride (1.0 mL, 8.3 mmol) was added dropwise. After stirring for 24 h at 23 °C and **SI5** was no longer detected by TLC, water (50 ml) was added. The residue was extracted with CH_2Cl_2 , the combined organic extracts were dried over MgSO_4 . The solvent was evaporated, the residue was purified by column chromatography on silica gel (cyclohexane/ethyl acetate 20:1) to give compound **5i** (1.3 g, 83% yield, *d.r.* = 1:1) as a colorless oil.

^1H NMR (500 MHz, CDCl_3) δ 8.16-8.02 (m, 2H), 7.62-7.53 (m, 1H), 7.51-7.41 (m, 2H), 5.26-5.04 (m, 1H), 4.71-4.54 (m, 2H), 2.29 (dd, J = 13.4, 4.6 Hz, 1H), 2.08-1.52 (m, 8H), 1.51-1.26 (m, 6H), 1.25-1.08 (m, 1H).

^{13}C NMR (101 MHz, CDCl_3) δ 202.91, 166.22, 132.64, 130.98, 129.51, 128.24, 105.45, 105.42, 74.93, 72.08, 71.90, 39.35, 39.16, 33.93, 33.81, 33.77, 33.72, 31.50, 31.48, 29.33, 29.20, 27.42, 25.57, 25.55, 20.06.

HRMS-ESI: calculated for $\text{C}_{19}\text{H}_{24}\text{NaO}_2$ $[\text{M}+\text{Na}]^+$: 307.1669; found: 307.1672.

Procedure for synthesis of compounds **14a** and **14b**.

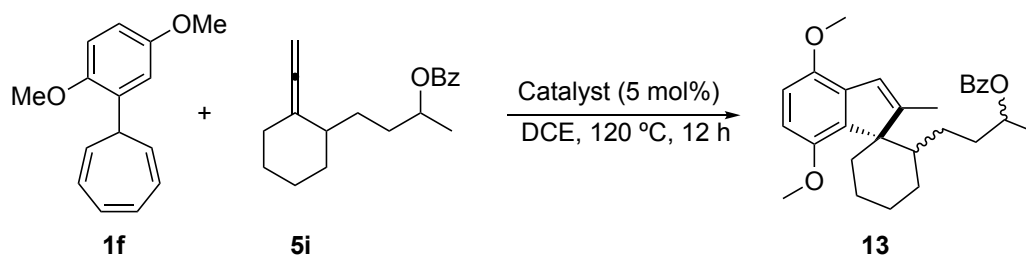


Step i:

A solution of the 7-(2,5-dimethoxyphenyl)cyclohepta-1,3,5-triene **1f** (913 mg, 4 mmol), 4-(2-(1 λ^5 -vinylidene)cyclohexyl)butan-2-yl benzoate **5i** (284 mg, 1 mmol) and gold complex **F**, [IPrAu(PhCN)]SbF₆, (46 mg, 0.05 mmol) in 1,2-dichloroethane (DCE, 20 mL) was heated at 120 °C in a sealed tube under nitrogen. After 8 h, the reaction mixture was allowed to cool to room temperature, the solvent was removed in vacuum and the crude residue was passed through a short pad of silica to provide crude product **13** with all (4) isomers together, which was used directly for the next step.

Note: The procedure was developed after the following optimization.

Table S1. Optimization of the key (3 + 2) cycloaddition.



Entry	catalyst (5 mol%)	yield (%) ^a
1 ^b	A	15
2 ^c	A	21
3 ^{c,d}	A	25
4 ^{c,d}	F	41(59) ^e
5 ^f	F	39(55) ^e

^a Yields determined by ¹H NMR using 1,3,5-trimethoxybenzene as internal standard. ^b Reaction at 120 °C (0.1 M in 1,2-dichloroethane), 2 equiv of **5i**, catalyst **A** (5 mol%), 12 h. ^c 2 equiv of **1f**. ^d Reaction under Argon. ^e Yield based on recovered starting material. ^f 1 mmol scale.

Step ii:

To a solution of crude **13** in MeOH/THF (4:1, 40:10 mL) was added K₂CO₃ (276 mg, 2 mmol). The reaction mixture stirred for 18 h at 50 °C and was quenched by saturated aqueous solution of NH₄Cl. The residue was extracted with ethyl acetate and the combined organic extracts were dried over MgSO₄. The solvent was evaporated to provide the crude deprotected alcohol **13'**, which was used directly for the next step.

Step iii:

To a solution of crude product **13'** in CH₂Cl₂ (50 mL) was added DMP (466 mg, 1.1 mmol) at 0 °C. The reaction mixture stirred for 2 h and was quenched with saturated aqueous Na₂S₂O₃ (10 mL) at 0 °C. The layers were separated and aqueous layer was extracted with CH₂Cl₂ (3×25 mL), the combined organic extracts were dried over

MgSO₄. The solvent was evaporated, the residue was purified by preparative TLC (pentane/ethyl ether 10:1) to give alcohol **14a** (60 mg, 18% for 3 steps) as colorless oil and **14b** (60 mg, 18% for 3 steps) as a colorless oil as well.

4-((1*R,2*S**)-4',7'-Dimethoxy-2'-methylspiro[cyclohexane-1,1'-inden]-2-yl)butan-2-one (**14a**)**

¹H NMR (500 MHz, CDCl₃) δ 6.68 (d, *J* = 8.7 Hz, 1H), 6.57 (d, *J* = 8.7 Hz, 1H), 6.52-6.47 (m, 1H), 3.83 (s, 3H), 3.81 (s, 3H), 2.67-2.53 (m, 2H), 2.29-2.19 (m, 4H), 2.07 (ddd, *J* = 16.0, 8.7, 7.3 Hz, 1H), 1.95-1.66 (m, 7H), 1.56-1.44 (m, 2H), 1.36-1.27 (m, 1H), 1.21-1.10 (m, 1H), 1.05-0.96 (m, 1H).

¹³C NMR (126 MHz, CDCl₃) δ 209.76, 153.09, 149.64, 146.47, 140.49, 133.08, 123.86, 109.67, 107.67, 59.27, 55.91, 55.30, 42.43, 37.31, 31.26, 29.08, 27.70, 25.90, 25.78, 22.53, 20.56.

HRMS-ESI: calculated for C₂₁H₂₈NaO₃ [M+Na]⁺: 351.1931; found: 351.1936.

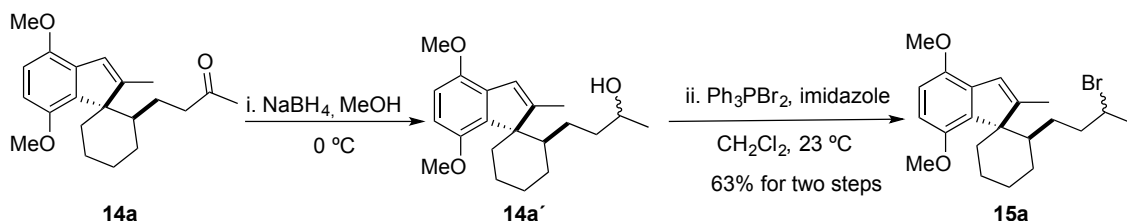
4-((1*R,2*R**)-4',7'-dimethoxy-2'-methylspiro[cyclohexane-1,1'-inden]-2-yl)butan-2-one (**14b**)**

¹H NMR (500 MHz, CDCl₃) δ 6.72 (d, *J* = 8.7 Hz, 1H), 6.62 (d, *J* = 8.7 Hz, 1H), 6.55-6.54 (m, 1H), 3.84 (s, 3H), 3.80 (s, 3H), 2.35-2.06 (m, 4H), 2.01 (s, 3H), 1.97-1.91 (m, 4H), 1.77-1.56 (m, 4H), 1.46-1.32 (m, 1H), 1.21-1.15 (m, 1H), 1.11-1.02 (m, 1H), 0.95-0.86 (m, 1H).

¹³C NMR (126 MHz, CDCl₃) δ 209.65, 153.48, 150.23, 147.05, 138.34, 135.07, 121.48, 109.75, 107.45, 61.45, 55.94, 54.83, 41.71, 38.42, 34.35, 29.62, 26.84, 26.26, 25.59, 22.64, 13.65.

HRMS-APCI: calculated for C₂₁H₂₈NaO₃ [M+Na]⁺: 351.1931; found: 351.1933.

(1*R,2*S**)-2-(3-Bromobutyl)-4',7'-dimethoxy-2'-methylspiro[cyclohexane-1,1'-indene] (**15a**).**



Step i:

To a solution of the **14a** (60 mg, 0.18 mmol) in MeOH (10 mL) was added NaBH₄ (10.3 mg, 0.27 mmol) at 0 °C. After 30 min, the disappearance of the ketone was confirmed by TLC and MeOH was removed. To the residue was added water and it was extracted with ethyl acetate, the combined organic extracts were dried over MgSO₄. The solvent was evaporated to provide crude alcohol **14a'**, which was used directly for the next step.

Step ii:

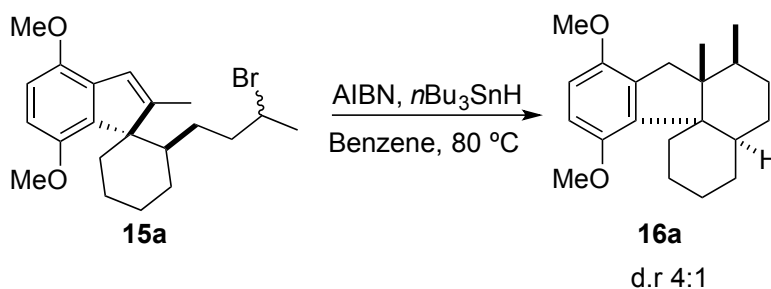
To a mixture of alcohol **14a'** and imidazole (15 mg, 0.22 mmol) in CH₂Cl₂ (4 mL) was added Ph₃PBr₂ (92 mg, 0.22 mmol) in the glove box. The reaction was stirred for 12 h and the solvent was removed, the residue was purified by column chromatography on silica gel (cyclohexane/ethyl acetate 20:1) to give compound **15a** (45 mg, 63% yield for two steps, *d.r.* = 1:1) as a colorless oil.

¹H NMR (500 MHz, CDCl₃) δ 6.69 (dd, *J* = 8.7, 2.4 Hz, 1H), 6.58 (dd, *J* = 8.7, 4.4 Hz, 1H), 6.52-6.47 (m, 1H), 4.01-3.81 (m, 7H), 2.72-2.48 (m, 2H), 2.26 (dd, *J* = 4.8, 1.6 Hz, 3H), 1.97-1.31 (m, 13H), 1.11-0.89 (m, 1H), 0.86-0.74 (m, 1H).

¹³C NMR (126 MHz, CDCl₃) δ 153.23, 153.20, 149.75, 149.63, 146.48, 146.43, 140.58, 140.56, 133.13, 133.10, 123.75, 123.74, 109.69, 109.64, 107.79, 107.70, 59.41, 59.36, 55.96, 55.42, 55.37, 52.08, 51.30, 39.67, 39.51, 37.36, 36.83, 31.30, 31.27, 29.29, 28.93, 28.03, 27.67, 26.67, 26.03, 26.02, 25.34, 22.62, 22.57, 20.61, 20.60.

HRMS-APCI: calculated for C₂₁H₃₀BrO₂ [M+H]⁺: 393.1424; found: 393.1422.

(4a*S,7*R**,7a*S**,12*bR**)-9,12-Dimethoxy-7,7a-dimethyl-1,2,3,4,4a,5,6,7,7a,8-decahydrobenzo[*d*]fluorine (16a).**



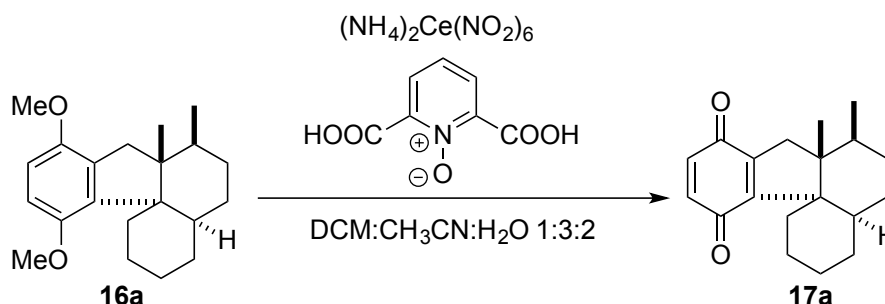
To a refluxing solution of **15a** (45 mg, 0.11 mmol) and AIBN (3.8 mg, 0.02 mmol) in benzene (8 mL) was added over 2 h a solution of *n*Bu₃SnH (0.154 ml, 0.57 mmol) in benzene (8 mL). The resulting solution was heated at reflux for 2 h, then the solvent was evaporated under vacuum. The residue was purified by column chromatography on silica gel (cyclohexane/ethyl acetate 20:1) to give compound **16a** (12 mg, 33% yield, *d.r.* = 4:1) as a yellow solid.

M.p.: 102-104 °C

¹H NMR (400 MHz, CDCl₃) δ 6.67-6.64 (m, 1H), 6.61 (d, *J* = 8.7 Hz, 1H), 3.78 (s, 6H), 3.16 (d, *J* = 12.9 Hz, 1H), 2.78 (d, *J* = 15.8 Hz, 1H), 2.53 (dd, *J* = 15.8, 0.9 Hz, 1H), 1.92-1.33 (m, 12H), 1.23 (s, 3H), 1.19-1.12 (m, 1H), 0.87 (d, *J* = 6.4 Hz, 3H).

¹³C NMR (101 MHz, CDCl₃) δ 150.98, 150.48, 141.47, 131.18, 110.14, 108.16, 55.84, 55.52, 55.16, 49.06, 39.94, 37.25, 35.60, 33.11, 30.86, 29.10, 26.27, 26.20, 24.12, 19.51, 18.13.

HRMS-APCI: calculated for $C_{21}H_{31}O_2$ $[M+H]^+$: 315.2319; found: 315.2317.
(4a*S,7*R**,7a*S**,12b*R**)-7,7a-Dimethyl-1,2,3,4,4a,5,6,7,7a,8-decahydrobenzo[*d*]fluorene-9,12-dione (17a).**



An ice-cold solution of cerium ammonium nitrate (87 mg, 0.16 mmol) in 1:1 MeCN/water (0.4 mL) was added slowly to a stirred and cooled (0 °C) solution of **16a** (10 mg, 0.032 mmol) in 1:2:1 $CH_2Cl_2/MeCN/water$ (0.8 mL) containing 2,6-dicarboxypyridine 1-oxide (14.6 mg, 0.08 mmol). After 40 min, the mixture was diluted with water (5 mL), and extracted with CH_2Cl_2 . The combined organic extracts were dried ($MgSO_4$) and evaporated. The residue was purified by preparative TLC (pentane/ethyl ether 10:1) to give compound **17a** (6.2 mg, 68% yield) as a yellow oil.

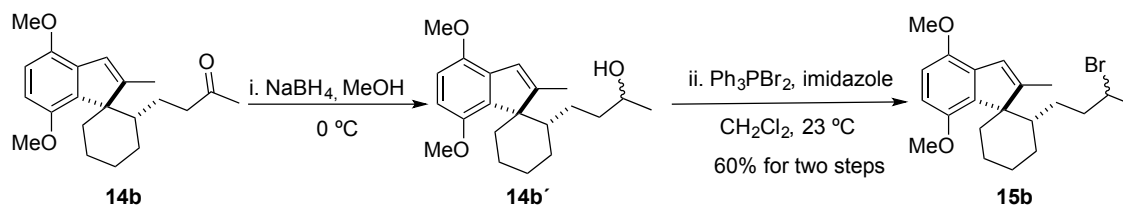
1H NMR (500 MHz, $CDCl_3$) δ 6.61 (d, $J = 10.0$ Hz, 1H), 6.57 (d, $J = 10.0$ Hz, 1H), 2.94 (d, $J = 12.8$ Hz, 1H), 2.62 (d, $J = 18.0$ Hz, 1H), 2.38 (d, $J = 18.0$ Hz, 1H), 1.82-1.75 (m, 2H), 1.71-1.56 (m, 4H), 1.50-1.34 (m, 7H), 1.21 (s, 3H), 0.88 (d, $J = 6.1$ Hz, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 187.14, 186.83, 153.77, 147.55, 138.11, 135.14, 56.02, 48.33, 39.85, 37.81, 34.50, 31.46, 31.36, 28.60, 25.55, 25.47, 23.38, 18.76, 17.94.

HRMS-ESI: calculated for $C_{19}H_{24}NaO_2$ $[M+H]^+$: 307.1699; found: 307.1676.

10. Procedures for the Synthesis of the Tetracyclic Carbon Skeleton of Dysiherbols

(1*R,2*R**)-2-(3-Bromobutyl)-4',7'-dimethoxy-2'-methylspiro[cyclohexane-1,1'-indene] (15b).**



Step i:

To a solution of the **14b** (60 mg, 0.18 mmol) in MeOH (10 mL) was added $NaBH_4$ (10.3 mg, 0.27 mmol) at 0 °C. After 30 min, the disappearance of ketone was confirmed by TLC and MeOH was removed. To the residue was added water and extracted with ethyl acetate, the combined organic extracts were dried over $MgSO_4$. The solvent was

evaporated to provide crude product **14b'**, which was used directly for the next step.

Step ii:

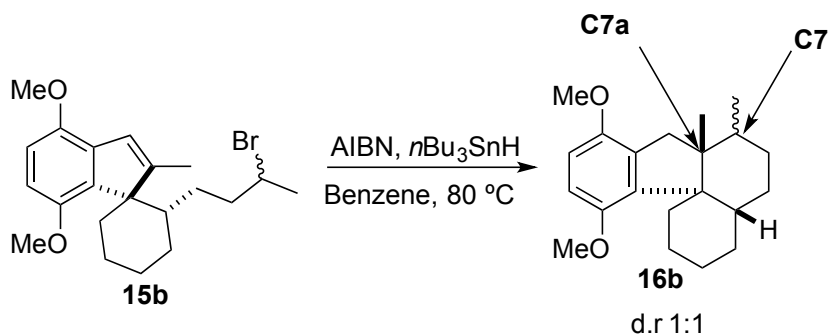
In a glovebox, to a mixture of **14b'** and imidazole (15 mg, 0.22 mmol) in CH₂Cl₂ (4 mL) was added Ph₃PBr₂ (92 mg, 0.22 mmol). The reaction stirred for 12 h and the solvent was removed, the residue was purified by column chromatography on silica gel (cyclohexane/ethyl acetate 20:1) to give compound **15b** (43 mg, 60% yield for two steps, *d.r.* = 1:1) as a colorless oil.

¹H NMR (400 MHz, CDCl₃) δ 6.73 (d, *J* = 8.7 Hz, 1H), 6.63 (dd, *J* = 8.7, 2.1 Hz, 1H), 6.57-6.53 (m, 1H), 3.94-3.75 (m, 7H), 2.23-2.06 (m, 2H), 1.95 (dd, *J* = 7.7, 1.5 Hz, 3H), 1.86-1.50 (m, 10H), 1.49-1.26 (m, 1H), 1.24-1.13 (m, 1H), 0.98-0.63 (m, 2H).

¹³C NMR (101 MHz, CDCl₃) δ 153.46, 153.39, 150.29, 150.27, 147.02, 147.00, 138.54, 138.49, 135.10, 135.07, 121.46, 121.40, 109.72, 109.70, 107.56, 107.49, 61.53, 55.97, 55.95, 54.95, 54.90, 51.92, 51.85, 39.67, 39.18, 39.00, 38.34, 34.38, 34.32, 29.05, 28.92, 27.11, 26.86, 26.54, 26.37, 26.36, 26.00, 22.68, 22.66, 13.75, 13.68.

HRMS-APCI: calculated for C₂₁H₃₀BrO₂ [M+H]⁺: 393.1424; found: 393.1425.

(4a*R,7a*S**)-9,12-Dimethoxy-7,7a-dimethyl-1,2,3,4,4a,5,6,7,7a,8-decahydrobenzo[d]fluorine (16b).**



To a refluxing solution of **15b** (43 mg, 0.11 mmol) and AIBN (3.6 mg, 0.02 mmol) in benzene (8 mL) was added over 2 h a solution of Bu₃SnH (0.147 mL, 0.55 mmol) in benzene (8 mL). The resulting solution was heated at reflux for 2 h, then the solvent was evaporated under vacuum. The residue was purified by column chromatography in silica gel (cyclohexane/ethyl acetate 20:1) to give compound **16b** (28 mg, 81% yield, *d.r.* = 1:1) as a yellow oil.

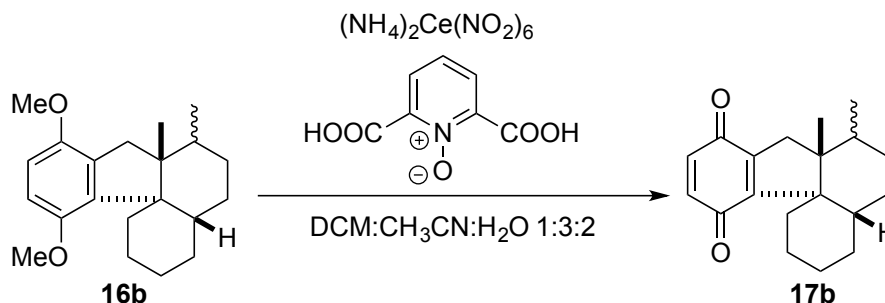
¹H NMR (400 MHz, CDCl₃) δ 6.80-6.59 (m, 4H), 3.84-3.74 (m, 12H), 2.92 (d, *J* = 16.5 Hz, 1H), 2.77 (d, *J* = 15.9 Hz, 1H), 2.54-2.40 (m, 3H), 2.32 (qd, *J* = 12.6, 5.1 Hz, 1H), 1.85-1.61 (m, 3H), 1.57-1.23 (m, 22H), 1.14 (s, 3H), 1.02 (s, 3H), 0.95-0.82 (m, 1H), 0.79 (d, *J* = 6.2 Hz, 3H), 0.65 (d, *J* = 7.1 Hz, 3H).

^{13}C NMR (101 MHz, CDCl_3) δ 151.10, 151.06, 150.24, 149.69, 140.36, 139.73, 133.66, 132.84, 109.82, 109.62, 108.86, 108.64, 59.35, 56.86, 55.68, 55.65, 55.05, 54.88, 50.46, 49.85, 38.73, 38.40, 37.31, 36.22, 35.98, 35.45, 35.29, 32.24, 31.25, 29.64, 28.96, 27.79, 26.80, 26.73, 23.65, 22.53, 22.14, 18.45, 17.98, 13.30.

HRMS-APCI: calculated for $\text{C}_{21}\text{H}_{31}\text{O}_2$ $[\text{M}+\text{H}]^+$: 315.2319; found: 315.2324.

Note: The title compound was obtained as 1:1 mixture of diastereoisomers at **C7**. The configuration at **C7a** was assumed based on simple structure modelling and geometry considerations, as the radical cyclization is expected to occur much easier from the same face of the substituent than from the opposite one.

(4a*R,7a*S**)-7,7a-Dimethyl-1,2,3,4,4a,5,6,7,7a,8-decahydrobenzo[*d*]fluorene-9,12-dione (**17b**).**



An ice-cold solution of cerium ammonium nitrate (87 mg, 0.16 mmol) in 1:1 MeCN/water (0.4 mL) was added slowly to a stirred and cooled (0 °C) solution of **16b** (10 mg, 0.032 mmol) in 1:2:1 $\text{CH}_2\text{Cl}_2/\text{MeCN}/\text{water}$ (0.8 mL) containing 2,6-dicarboxypyridine 1-oxide (14.6 mg, 0.08 mmol). After 40 min, the mixture was diluted with water (5 mL), and extracted with CH_2Cl_2 . The combined organic extracts were dried (MgSO_4) and evaporated. The residue was purified by preparative TLC (pentane/ethyl ether 10:1) to give compound **17b** (5.5 mg, 61% yield) as a yellow oil.

^1H NMR (400 MHz, CDCl_3) δ 6.64 (s, 4H), 4.49-3.66 (m, 1H), 2.89 (d, $J = 19.2$ Hz, 1H), 2.74-2.58 (m, 2H), 2.45-2.27 (m, 3H), 1.90-1.75 (m, 2H), 1.68-1.04 (m, 27H), 1.01 (s, 3H), 0.83 (dd, $J = 6.7, 4.9$ Hz, 6H).

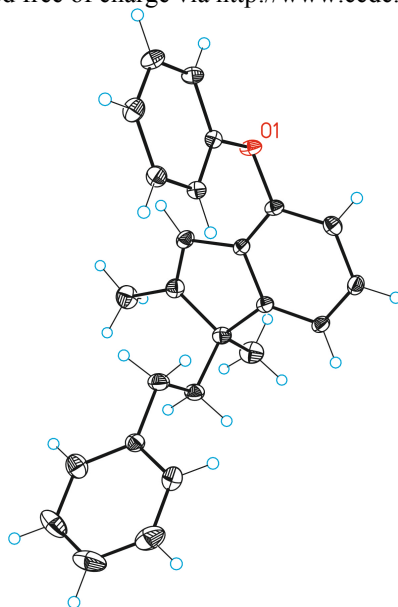
^{13}C NMR (101 MHz, CDCl_3) δ 187.21, 186.93, 186.74, 156.25, 155.29, 151.42, 151.17, 138.74, 138.58, 134.34, 134.22, 61.30, 58.85, 49.67, 48.68, 38.96, 38.04, 37.80, 36.01, 35.77, 35.59, 35.43, 35.03, 31.69, 29.38, 29.31, 27.95, 27.78, 26.40, 26.17, 23.35, 23.11, 22.43, 18.33, 17.88, 12.99.

HRMS-ESI: calculated for $\text{C}_{19}\text{H}_{24}\text{NaO}_2$ $[\text{M}+\text{H}]^+$: 307.1699; found: 307.1671.

11. Crystal Data and Structure Refinement

11.1. 1,2-dimethyl-1-phenethyl-4-phenoxy-1H-indene (6d)

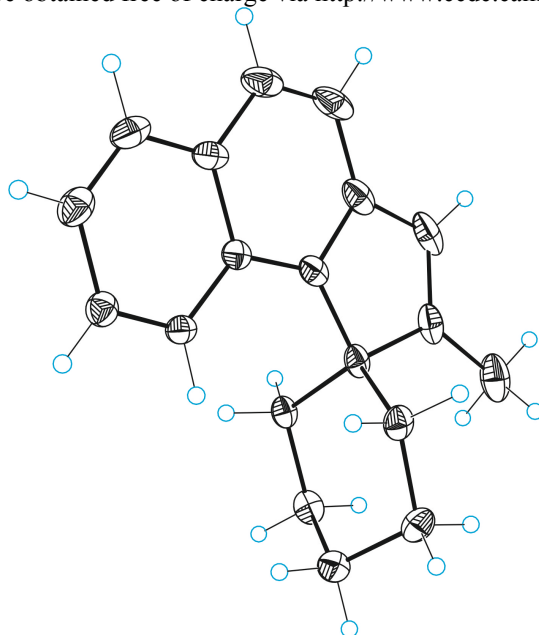
The single crystals of compound **6d** suitable for X-ray diffraction analysis were obtained from a solution of dichloromethane. The crystal structure information for this compound has been deposited at the Cambridge Crystallographic Data Centre. CCDC 1571036 contains the crystal structure information of this compound and can be obtained free of charge via <http://www.ccdc.cam.ac.uk>.



Identification code	XY-TMR173
Empirical formula	C ₂₅ H ₂₄ O
Formula weight	340.44
Temperature	100(2) K
Wavelength	0.71073 Å
Crystal system	Monoclinic
Space group	P2(1)/c
Unit cell dimensions	a = 17.9170(4)Å a = 90°. b = 7.7642(2)Å b = 92.617(2)°. c = 13.8078(3)Å g = 90°.
Volume	1918.82(8) Å ³
Z	4
Density (calculated)	1.178 Mg/m ³
Absorption coefficient	0.070 mm ⁻¹
F(000)	728
Crystal size	0.01 x 0.01 x 0.01 mm ³
Theta range for data collection	2.860 to 30.737°.
Index ranges	-24<=h<=25,-11<=k<=11,-19<=l<=19
Reflections collected	31032
Independent reflections	5478[R(int) = 0.0301]
Completeness to theta =30.737°	91.7%
Absorption correction	Multi-scan
Max. and min. transmission	0.999 and 0.768
Refinement method	Full-matrix least-squares on F ²
Data / restraints / parameters	5478/ 0/ 237
Goodness-of-fit on F ²	1.031
Final R indices [I>2sigma(I)]	R1 = 0.0470, wR2 = 0.1102
R indices (all data)	R1 = 0.0581, wR2 = 0.1154
Largest diff. peak and hole	0.394 and -0.203 e.Å ⁻³

11.2. 2'-methylspiro[cyclohexane-1,1'-cyclopenta[a]naphthalene] (6t)

The single crystals of compound **6t** suitable for X-ray diffraction analysis were obtained from a solution of cyclohexane/ethyl acetate. The crystal structure information for this compound has been deposited at the Cambridge Crystallographic Data Centre. CCDC 1571032 contains the crystal structure information of this compound and can be obtained free of charge via <http://www.ccdc.cam.ac.uk>.

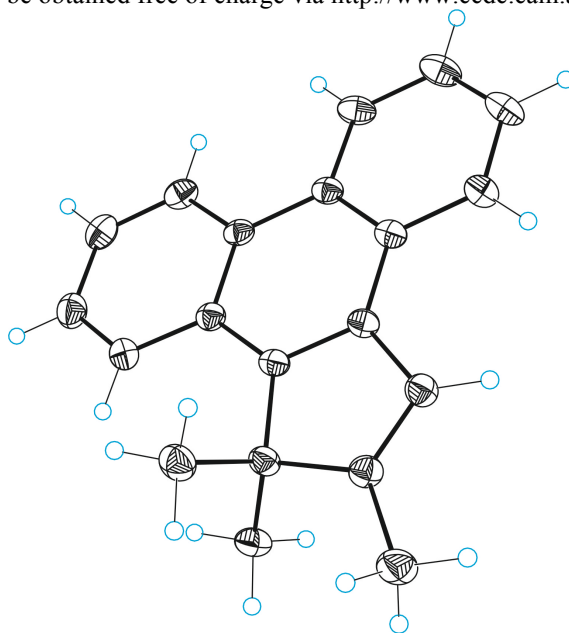


Identification code	mo_XYTMR10_0m
Empirical formula	C ₁₉ H ₂₀
Formula weight	248.35
Temperature	100(2) K
Wavelength	0.71073 Å
Crystal system	Orthorhombic
Space group	P2(1)2(1)2(1)
Unit cell dimensions	a = 7.4471(5)Å a = 90°. b = 14.2495(11)Å b = 90°. c = 26.067(2)Å g = 90°.
Volume	2766.1(4) Å ³
Z	8
Density (calculated)	1.193 Mg/m ³
Absorption coefficient	0.067 mm ⁻¹
F(000)	1072
Crystal size	0.40 x 0.40 x 0.40 mm ³
Theta range for data collection	1.629 to 30.466°.
Index ranges	-6<=h<=9,-10<=k<=20,-37<=l<=33
Reflections collected	18432
Independent reflections	7871[R(int) = 0.0324]
Completeness to theta =30.466°	97.5%
Absorption correction	Multi-scan
Max. and min. transmission	0.974 and 0.749
Refinement method	Full-matrix least-squares on F ²
Data / restraints / parameters	7871/ 441/ 467
Goodness-of-fit on F ²	1.049
Final R indices [I>2sigma(I)]	R1 = 0.0560, wR2 = 0.1344
R indices (all data)	R1 = 0.0693, wR2 = 0.1438
Flack parameter	x = -4.9(10)
Largest diff. peak and hole	0.309 and -0.294 e.Å ⁻³

11.3. 1,1,2-trimethyl-1H-cyclopenta[*l*]phenanthrene (**6u**)

The single crystals of compound **6u** suitable for X-ray diffraction analysis were obtained from a solution of cyclohexane/isopropanol. The crystal structure information for this compound has been deposited at

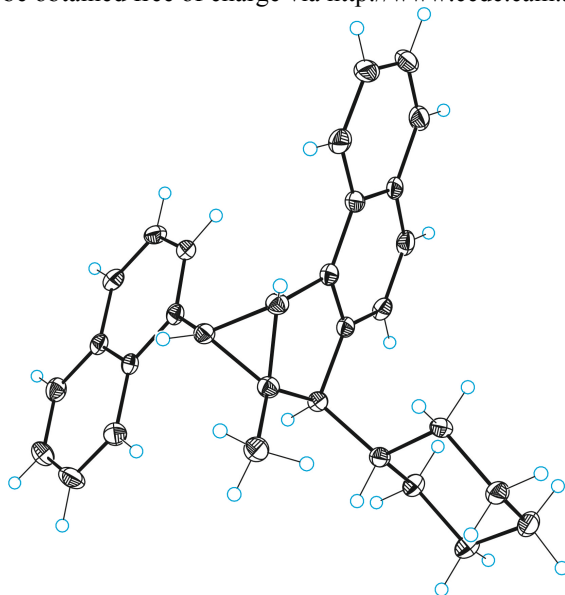
the Cambridge Crystallographic Data Centre. CCDC 1571033 contains the crystal structure information of this compound and can be obtained free of charge via <http://www.ccdc.cam.ac.uk>.



Identification code	mo_XYTMR76
Empirical formula	C ₂₀ H ₁₈
Formula weight	258.34
Temperature	100(2) K
Wavelength	0.71073 Å
Crystal system	Orthorhombic
Space group	Iba2
Unit cell dimensions	a = 20.2195(6) Å a = 90°. b = 31.6626(10) Å b = 90°. c = 8.7280(2) Å g = 90°.
Volume	5587.7(3) Å ³
Z	16
Density (calculated)	1.228 Mg/m ³
Absorption coefficient	0.069 mm ⁻¹
F(000)	2208
Crystal size	0.30 x 0.30 x 0.20 mm ³
Theta range for data collection	1.195 to 31.531°.
Index ranges	-29 ≤ h ≤ 20, -46 ≤ k ≤ 45, -12 ≤ l ≤ 7
Reflections collected	23162
Independent reflections	7300 [R(int) = 0.0281]
Completeness to theta = 31.531°	96.5%
Absorption correction	Multi-scan
Max. and min. transmission	0.986 and 0.758
Refinement method	Full-matrix least-squares on F ²
Data / restraints / parameters	7300 / 1 / 367
Goodness-of-fit on F ²	1.021
Final R indices [I > 2σ(I)]	R1 = 0.0391, wR2 = 0.1008
R indices (all data)	R1 = 0.0446, wR2 = 0.1054
Flack parameter	x = 0.3(10)
Largest diff. peak and hole	0.344 and -0.225 e. Å ⁻³

11.4. (7*S,7*aR**,8*R**,8*aS**)-7-cyclohexyl-7*a*-methyl-8-(naphthalen-1-yl)-7,7*a*,8,8*a*-tetrahydrocyclopropa[4,5]cyclopenta[1,2-*a*]naphthalene (11)**

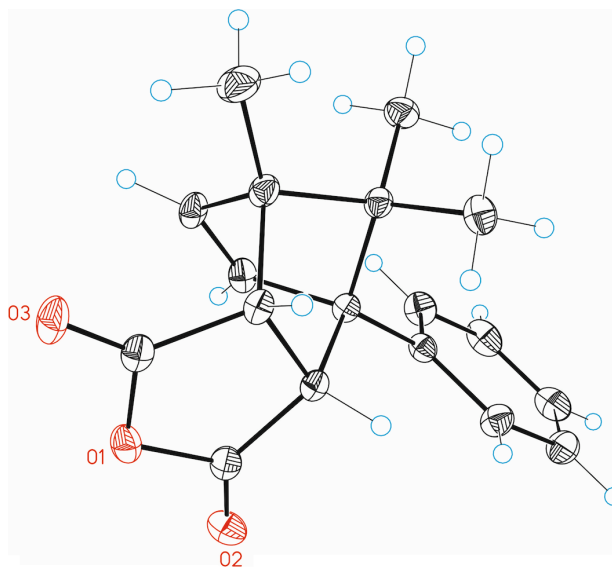
The single crystals of compound **11** suitable for X-ray diffraction analysis were obtained from a solution of cyclohexane/isopropanol. The crystal structure information for this compound has been deposited at the Cambridge Crystallographic Data Centre. CCDC 1571035 contains the crystal structure information of this compound and can be obtained free of charge via <http://www.ccdc.cam.ac.uk>.



Identification code	mo_XY_TMR15_0m
Empirical formula	C ₃₁ H ₃₀
Formula weight	402.55
Temperature	100(2) K
Wavelength	0.71073 Å
Crystal system	Orthorhombic
Space group	Pca2(1)
Unit cell dimensions	a = 21.3313(10)Å a = 90°. b = 6.0491(2)Å b = 90°. c = 34.2679(15)Å g = 90°.
Volume	4421.8(3) Å ³
Z	8
Density (calculated)	1.209 Mg/m ³
Absorption coefficient	0.068 mm ⁻¹
F(000)	1728
Crystal size	0.45 x 0.08 x 0.04 mm ³
Theta range for data collection	2.000 to 27.501°.
Index ranges	-27<=h<=27,-7<=k<=7,-44<=l<=44
Reflections collected	72531
Independent reflections	10136[R(int) = 0.0381]
Completeness to theta =27.501°	99.9%
Absorption correction	Empirical
Max. and min. transmission	0.997 and 0.95
Refinement method	Full-matrix least-squares on F ²
Data / restraints / parameters	10136/ 1/ 561
Goodness-of-fit on F ²	1.031
Final R indices [I>2sigma(I)]	R1 = 0.0379, wR2 = 0.0907
R indices (all data)	R1 = 0.0455, wR2 = 0.0950
Flack parameter	x = -2.9(10)
Largest diff. peak and hole	0.236 and -0.235 e.Å ⁻³

11.5. endo-4,8,8-trimethyl-7-phenyl-3a,4,7,7a-tetrahydro-4,7-methano-isobenzofuran-1,3-dione (12)

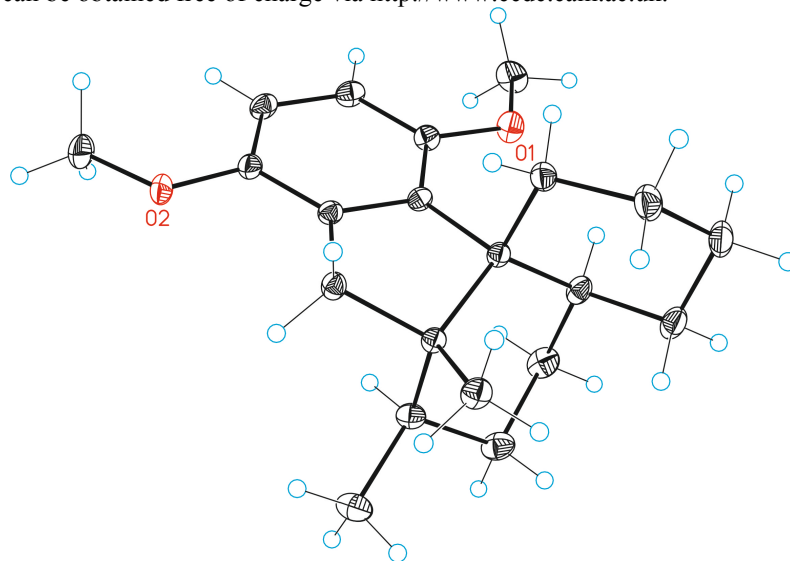
The single crystals of compound **12** suitable for X-ray diffraction analysis were obtained from a solution of heptane/dichloromethane. The crystal structure information for this compound has been deposited at the Cambridge Crystallographic Data Centre. CCDC 1571037 contains the crystal structure information of this compound and can be obtained free of charge via <http://www.ccdc.cam.ac.uk>.



Identification code	mo_MM143F_0m
Empirical formula	C18 H18 O3
Formula weight	282.32
Temperature	100(2) K
Wavelength	0.71073 Å
Crystal system	Orthorhombic
Space group	P2(1)2(1)2(1)
Unit cell dimensions	a = 6.4200(5)Å a = 90°. b = 12.0907(9)Å b = 90°. c = 18.3454(14)Å g = 90°.
Volume	1424.01(19) Å ³
Z	4
Density (calculated)	1.317 Mg/m ³
Absorption coefficient	0.089 mm ⁻¹
F(000)	600
Crystal size	0.20 x 0.10 x 0.02 mm ³
Theta range for data collection	2.017 to 29.904°.
Index ranges	-8<=h<=9,-10<=k<=16,-24<=l<=25
Reflections collected	22310
Independent reflections	093[R(int) = 0.0436]
Completeness to theta =29.904°	99.8%
Absorption correction	Multi-scan
Max. and min. transmission	0.998 and 0.768
Refinement method	Full-matrix least-squares on F ²
Data / restraints / parameters	4093/ 0/ 193
Goodness-of-fit on F ²	1.044
Final R indices [I>2sigma(I)]	R1 = 0.0408, wR2 = 0.0931
R indices (all data)	R1 = 0.0529, wR2 = 0.0995
Flack parameter	x =0.3(5)
Largest diff. peak and hole	0.300 and -0.233 e.Å

11.6. (4a*S,7*R**,7a*S**,12b*R**)-9,12-dimethoxy-7,7a-dimethyl-1,2,3,4,4a,5,6,7,7a,8-decahydrobenzo[*d*]fluorine (16a)**

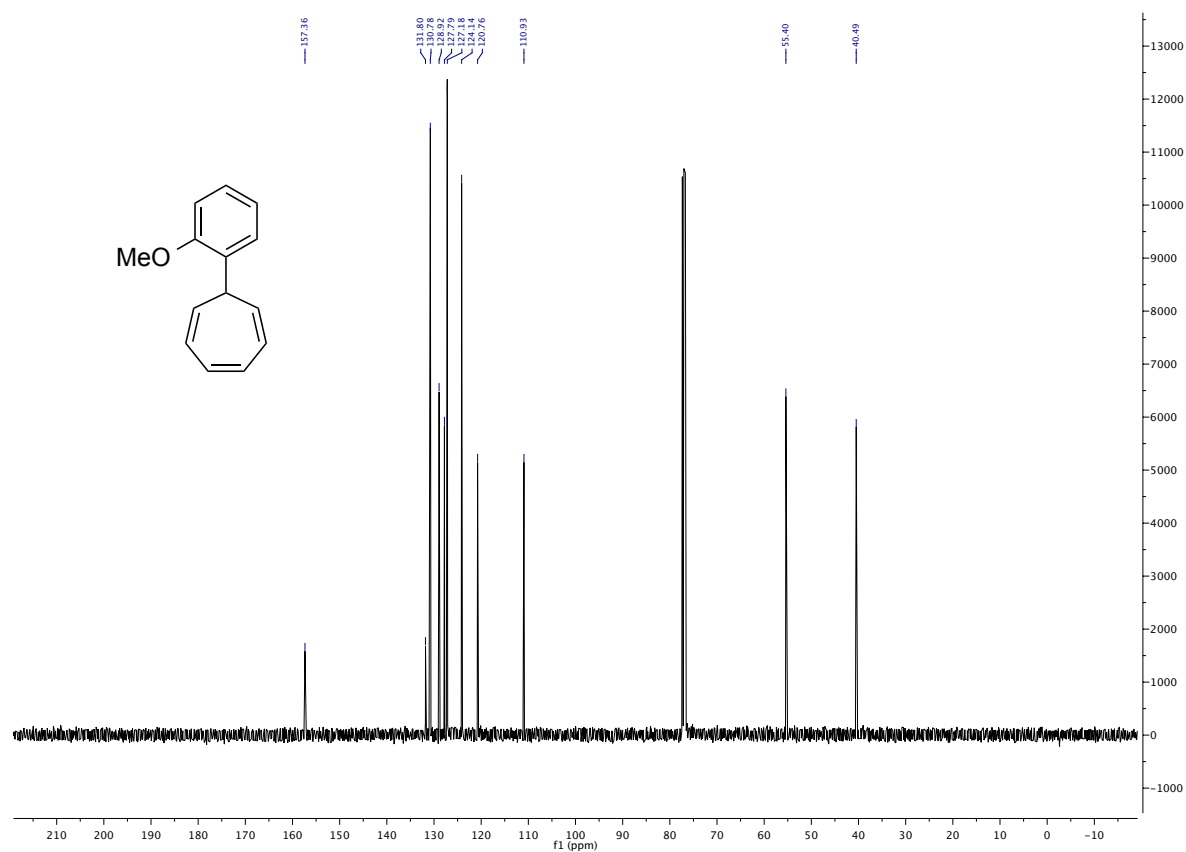
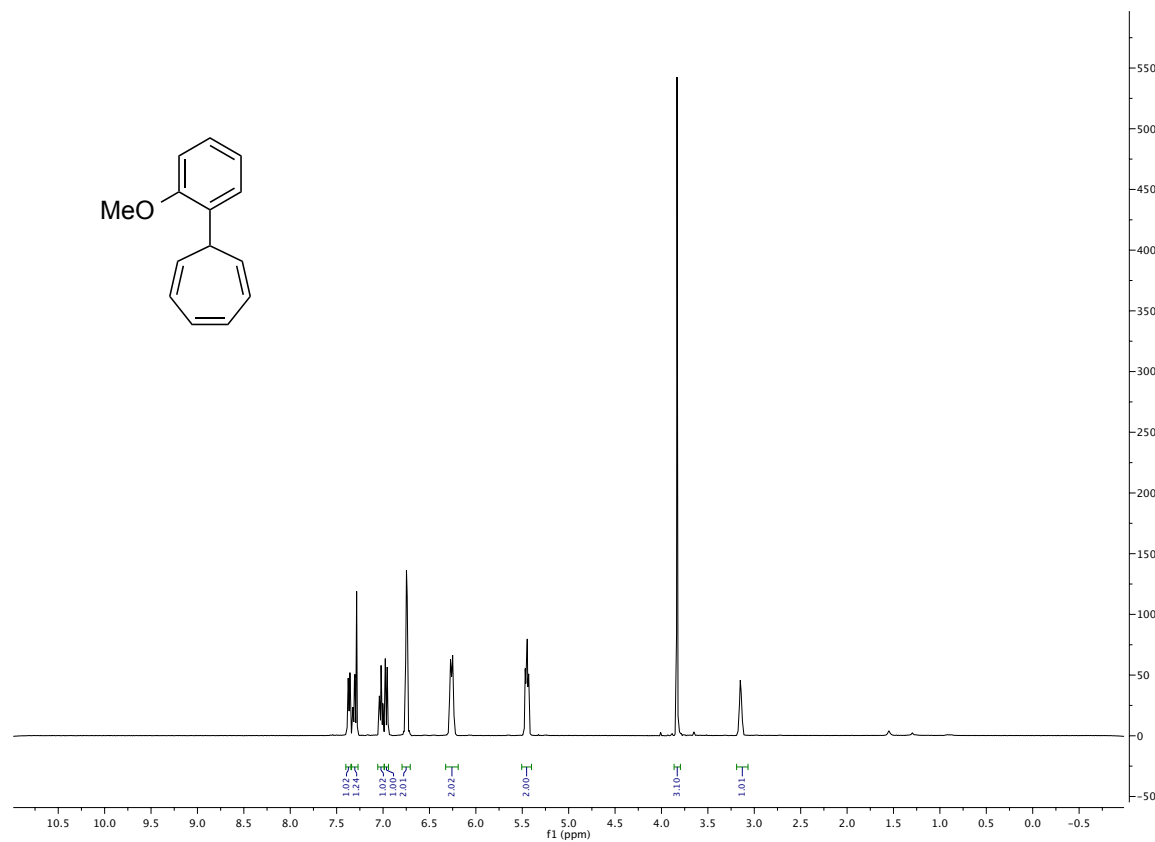
The single crystals of compound **16a** suitable for X-ray diffraction analysis were obtained from a solution of CDCl_3 . The crystal structure information for this compound has been deposited at the Cambridge Crystallographic Data Centre. CCDC 1571034 contains the crystal structure information of this compound and can be obtained free of charge via <http://www.ccdc.cam.ac.uk>.



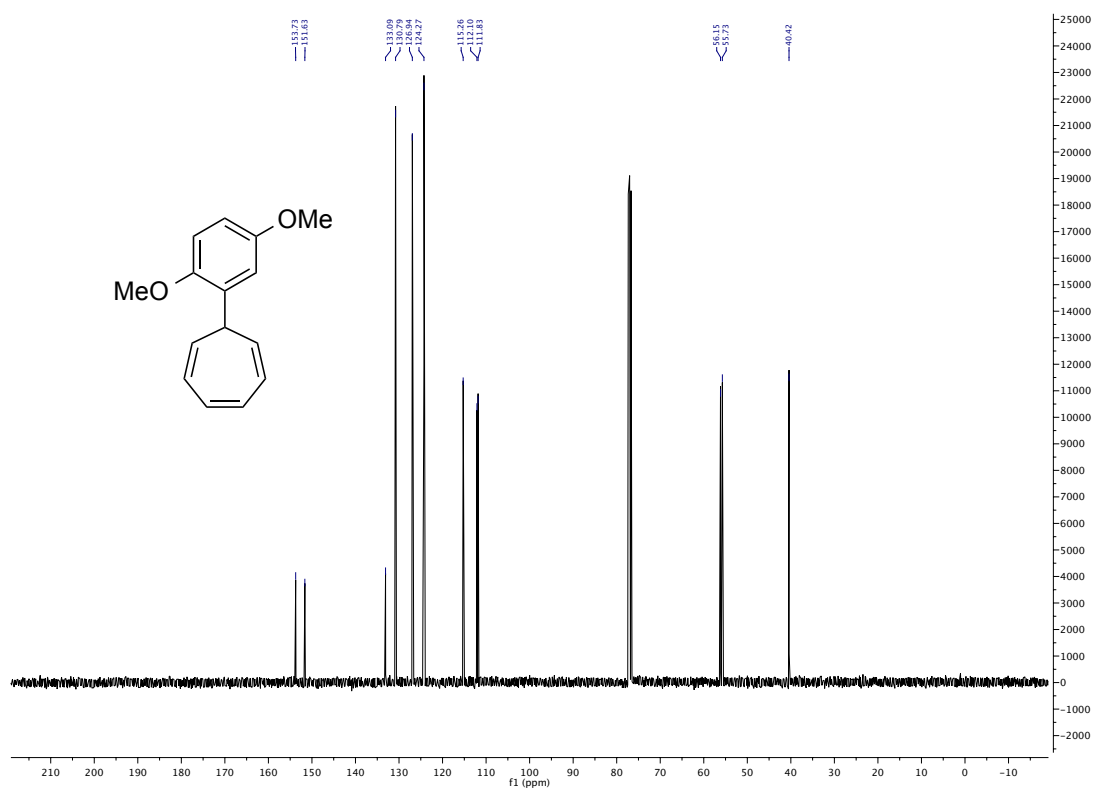
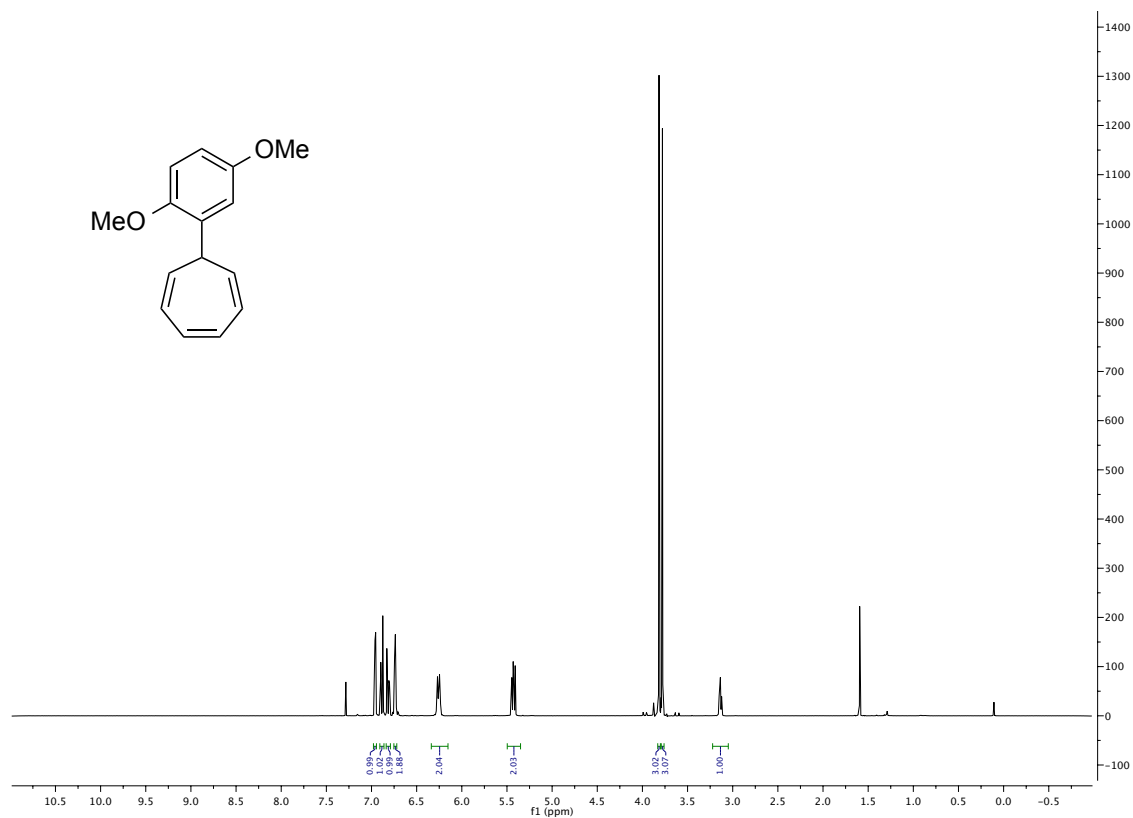
Identification code	mo_XYTS184D_0m
Empirical formula	C ₂₁ H ₃₀ O ₂
Formula weight	314.45
Temperature	100(2) K
Wavelength	0.71073 Å
Crystal system	Triclinic
Space group	P-1
Unit cell dimensions	a = 9.1291(4)Å a = 70.1811(9)° b = 9.5424(3)Å b = 85.6475(11)° c = 11.2264(4)Å g = 69.8209(10)°
Volume	862.64(6) Å ³
Z	2
Density (calculated)	1.211 Mg/m ³
Absorption coefficient	0.075 mm ⁻¹
F(000)	344
Crystal size	0.30 x 0.20 x 0.20 mm ³
Theta range for data collection	2.379 to 30.535°
Index ranges	-7<=h<=13, -12<=k<=13, -16<=l<=15
Reflections collected	10347
Independent reflections	5004[R(int) = 0.0154]
Completeness to theta =30.535°	94.8%
Absorption correction	Multi-scan
Max. and min. transmission	0.985 and 0.955
Refinement method	Full-matrix least-squares on F ²
Data / restraints / parameters	5004/ 0/ 212
Goodness-of-fit on F ²	1.046
Final R indices [I>2sigma(I)]	R1 = 0.0406, wR2 = 0.1098
R indices (all data)	R1 = 0.0468, wR2 = 0.1151
Largest diff. peak and hole	0.424 and -0.194 e.Å ⁻³

11. NMR Spectra

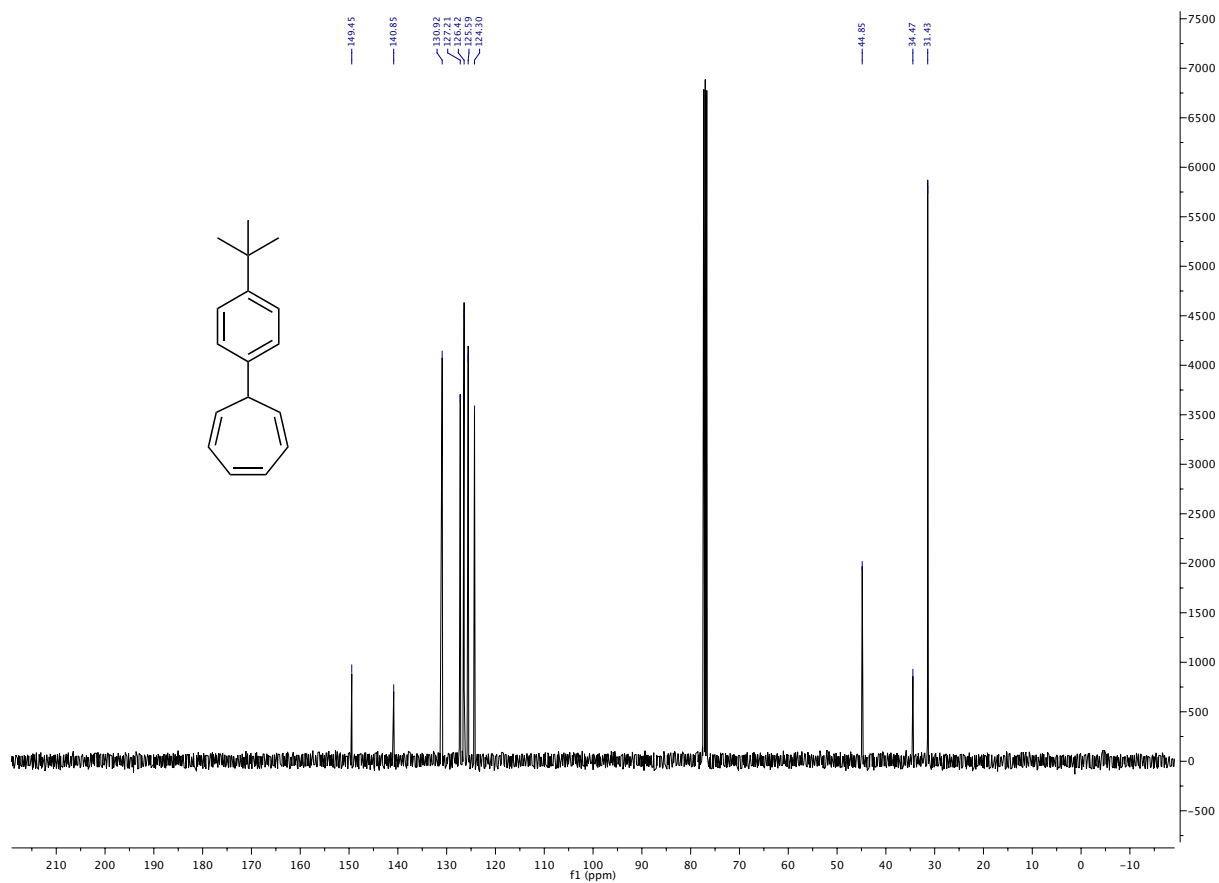
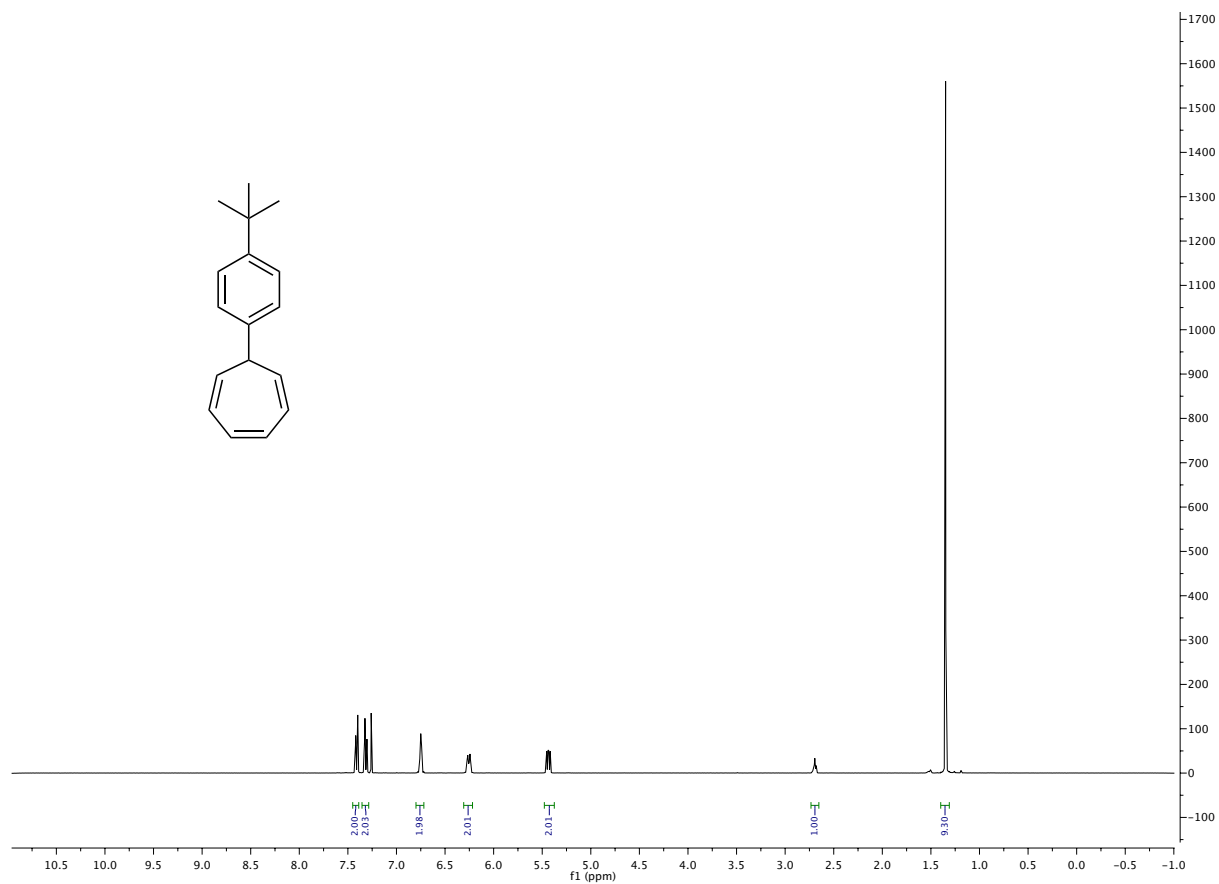
7-(2-Methoxyphenyl)cyclohepta-1,3,5-triene (1c)



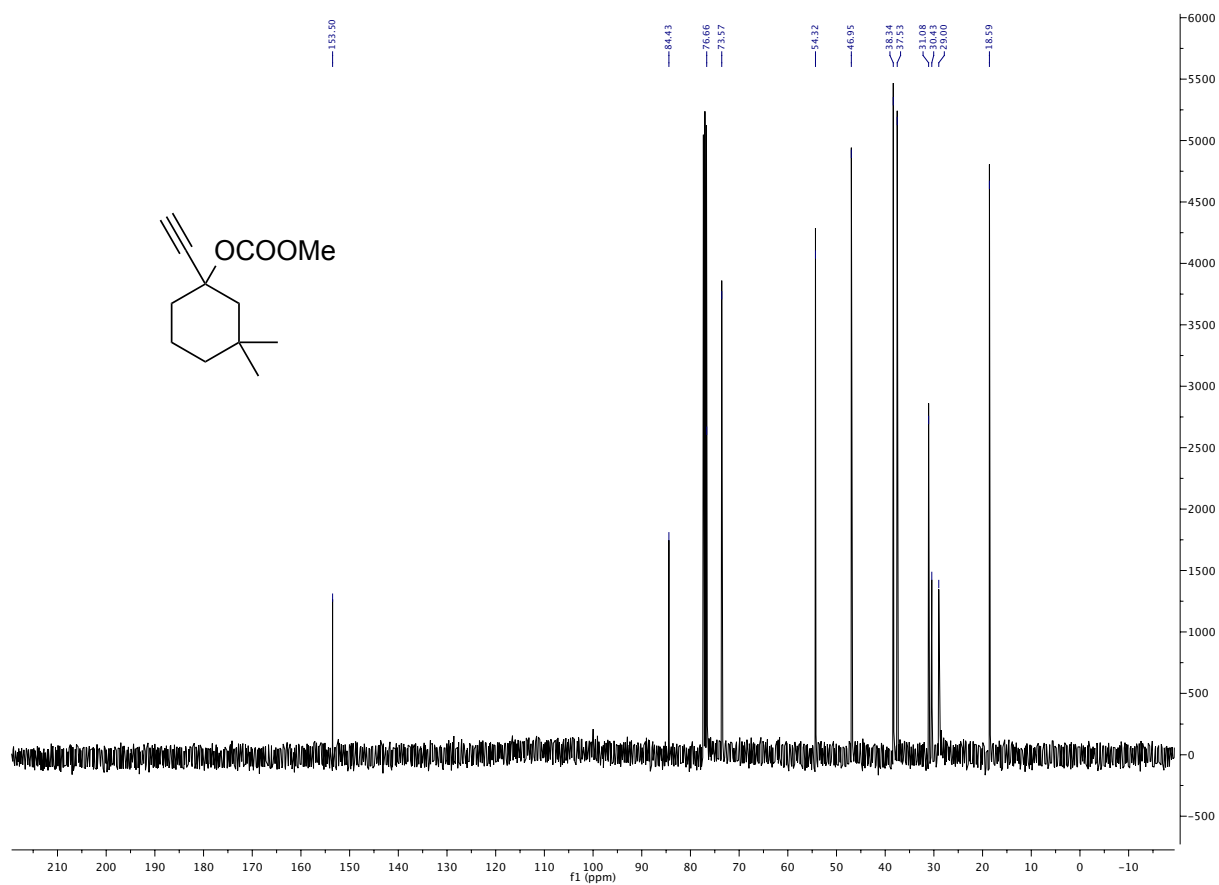
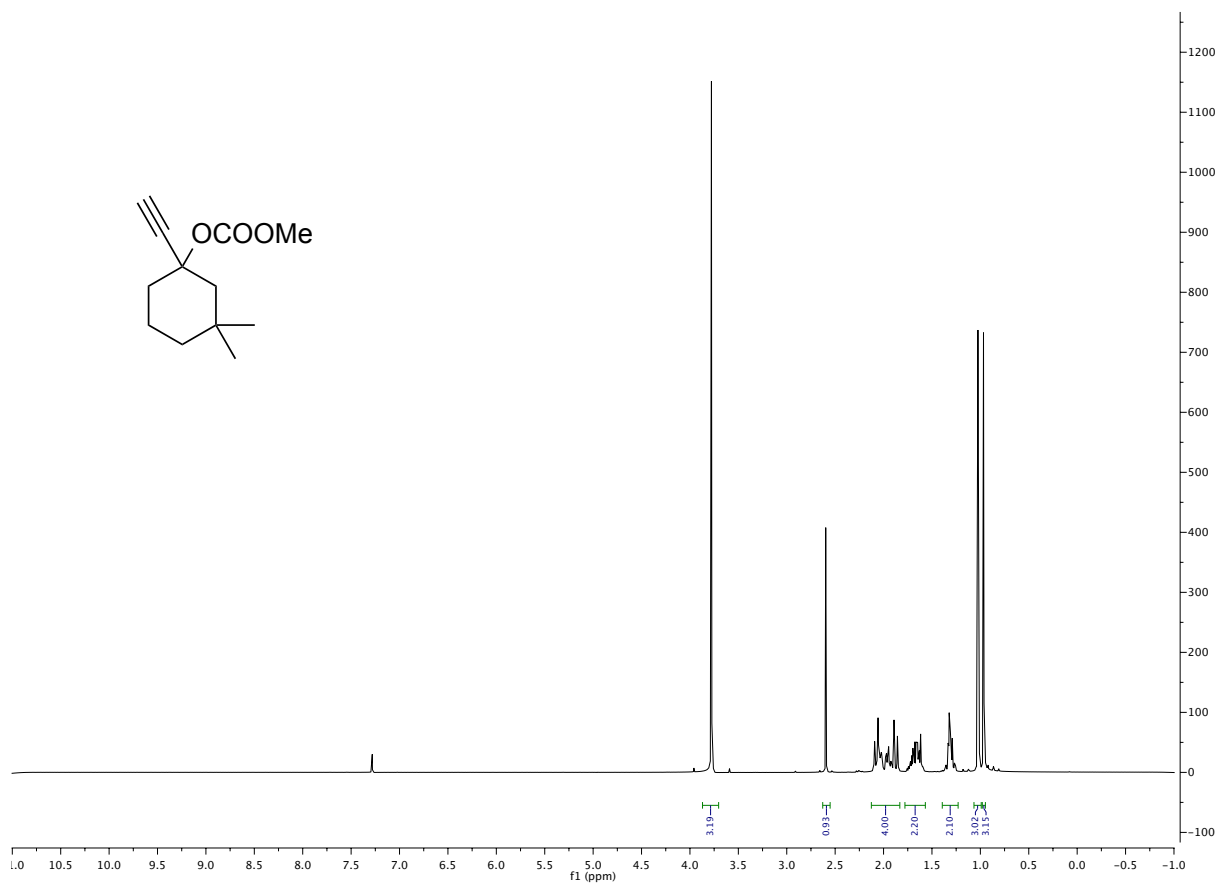
7-(2,5-Dimethoxyphenyl)cyclohepta-1,3,5-triene (1f)



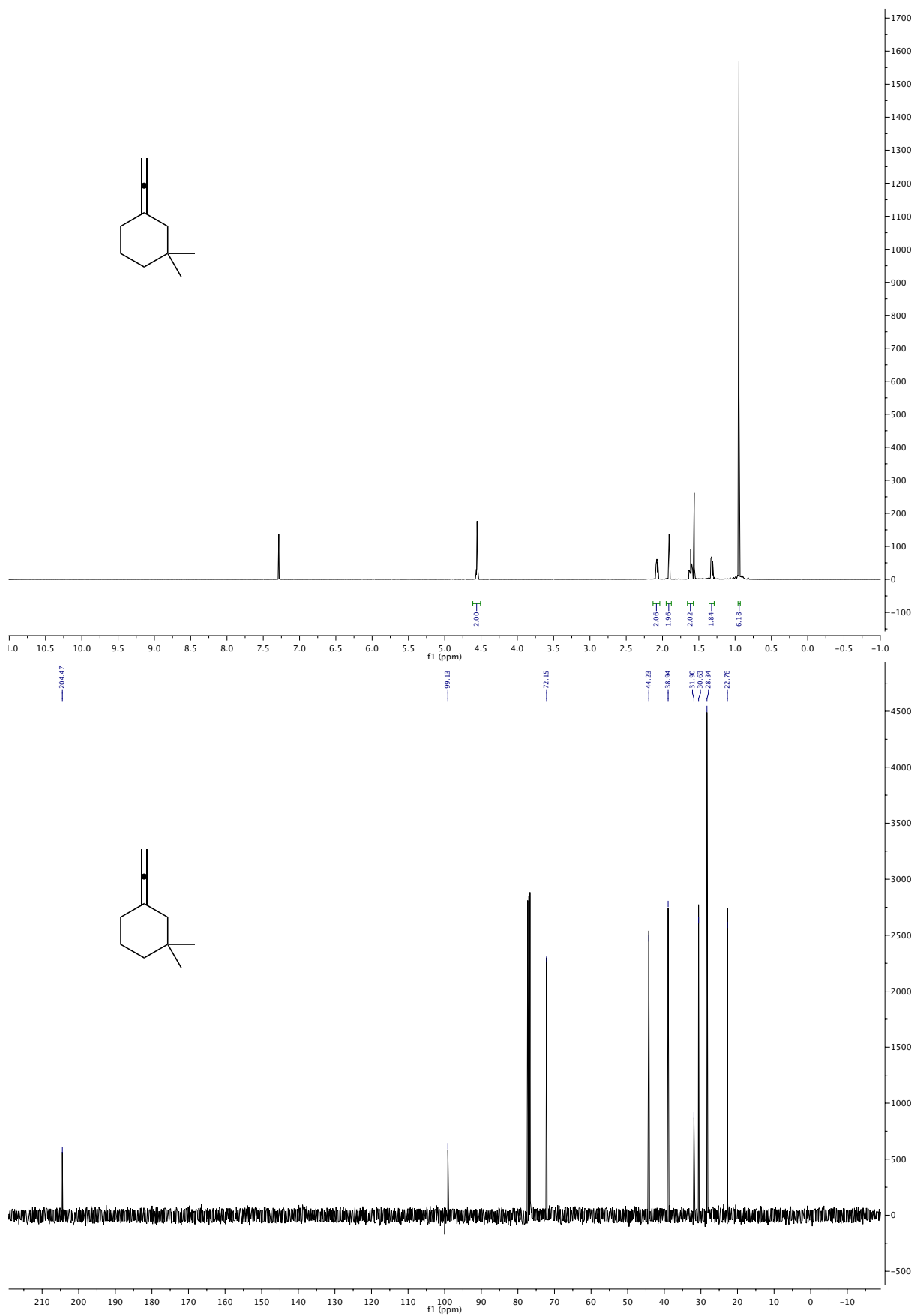
7-(4-(*Tert*-butyl)phenyl)cyclohepta-1,3,5-triene (1j)



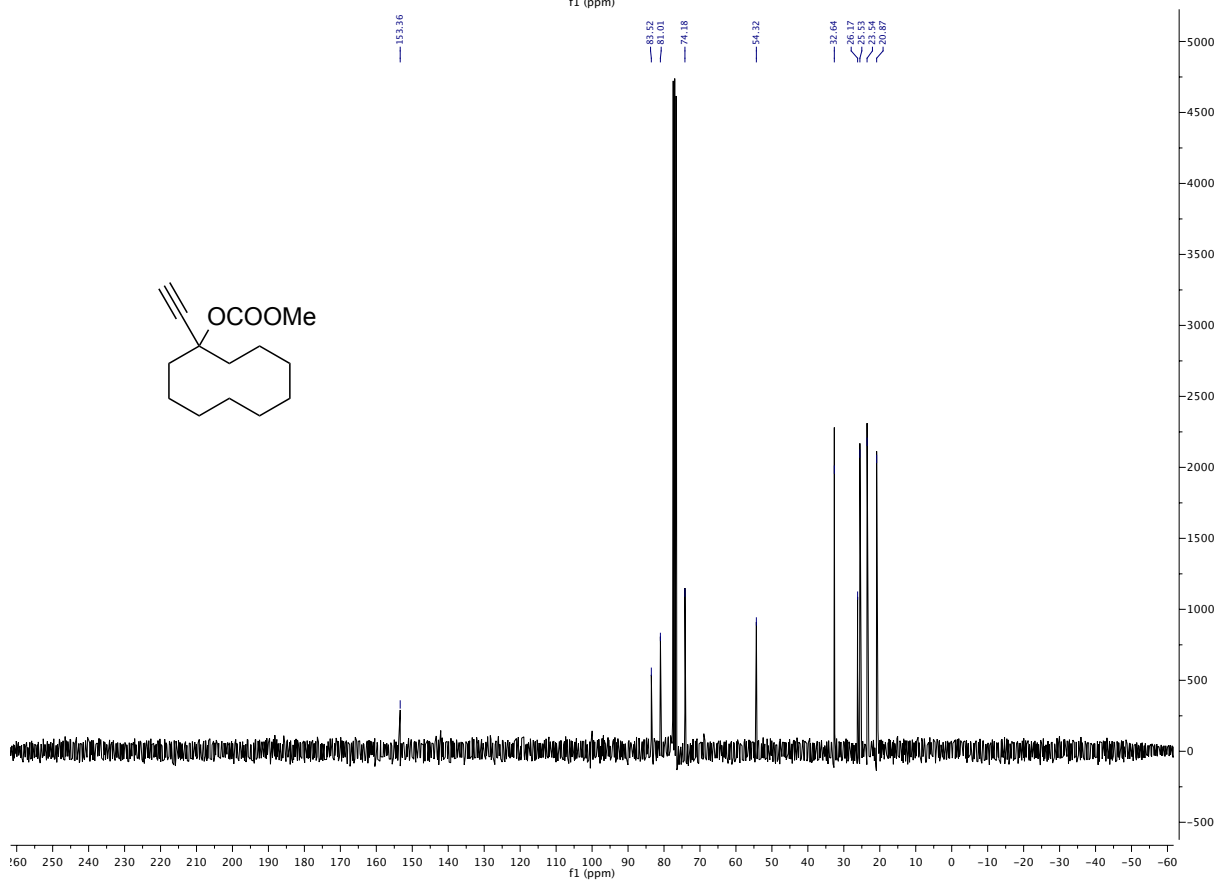
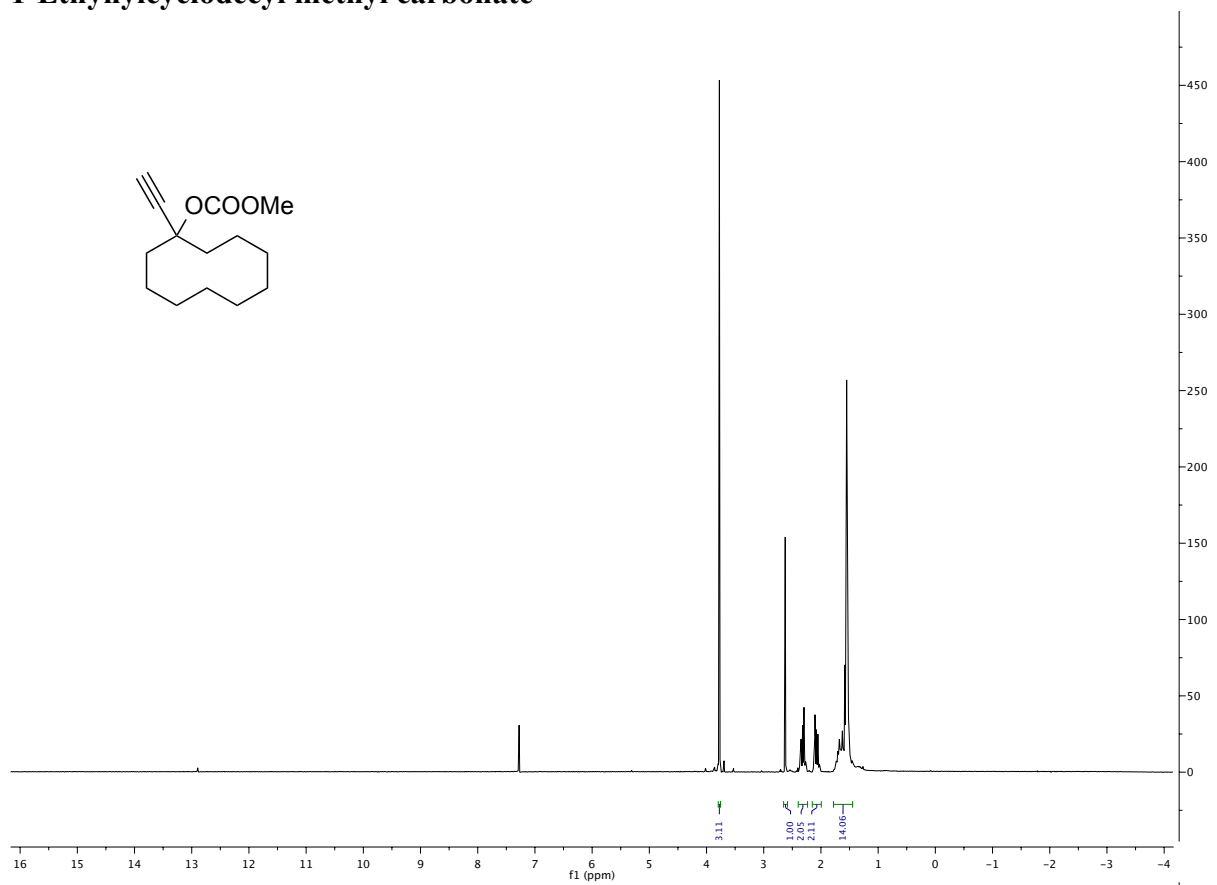
1-Ethynyl-3,3-dimethylcyclohexyl methyl carbonate



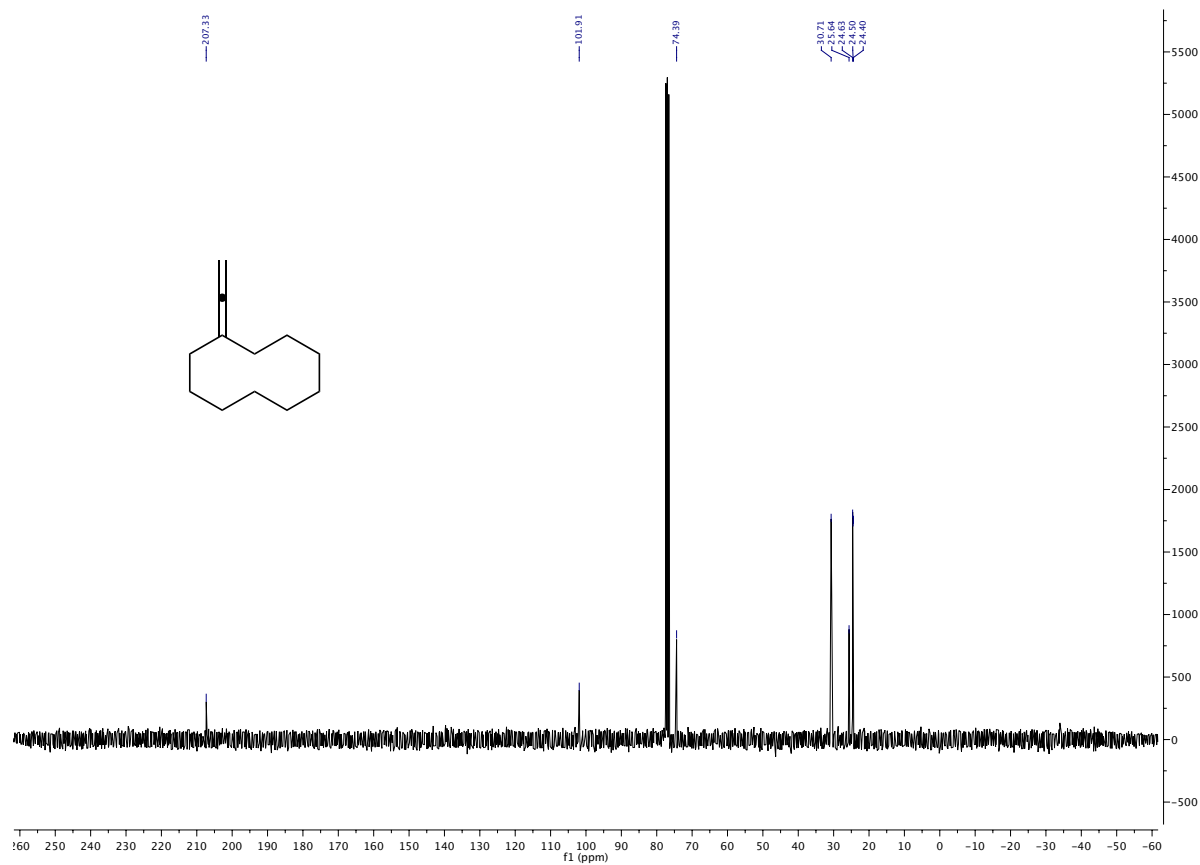
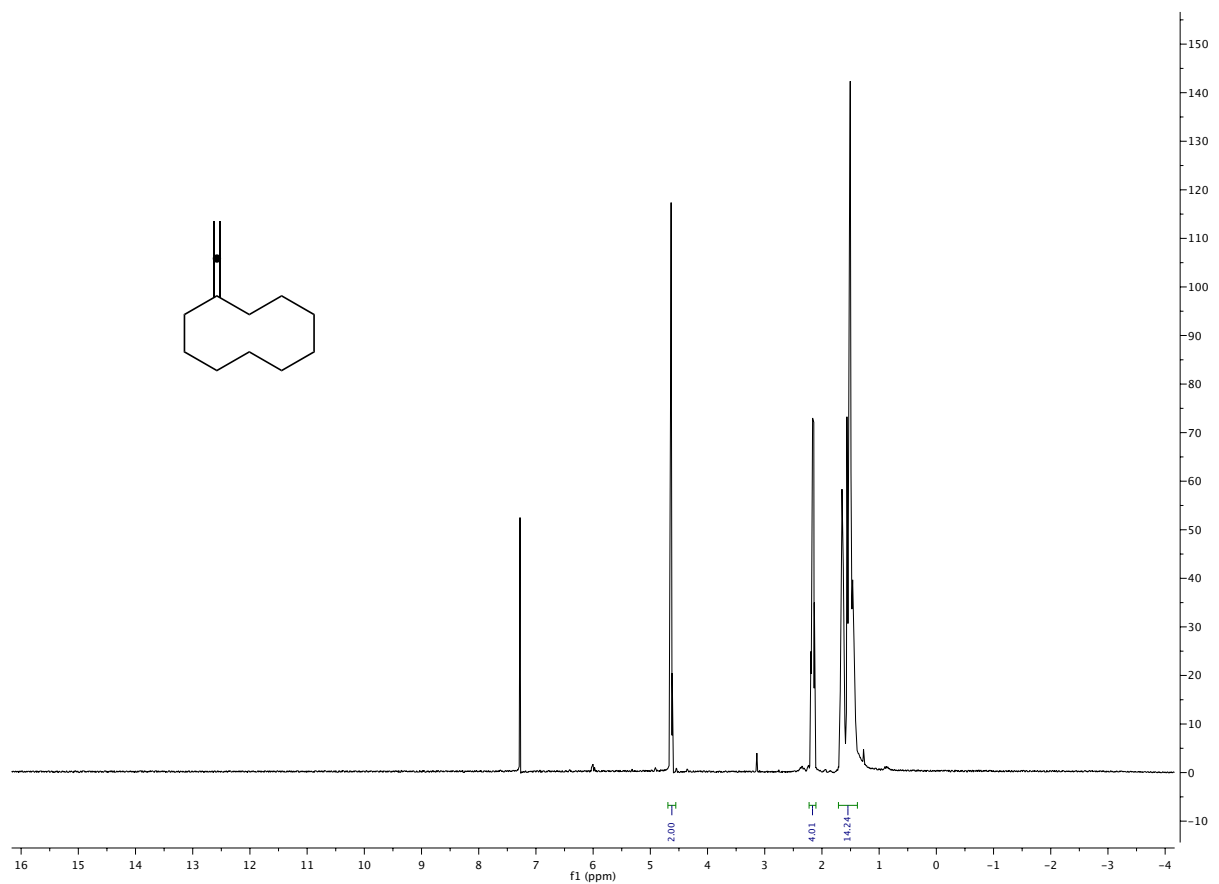
1,1-Dimethyl-3-(1 λ^5 -vinylidene)cyclohexane (5e)



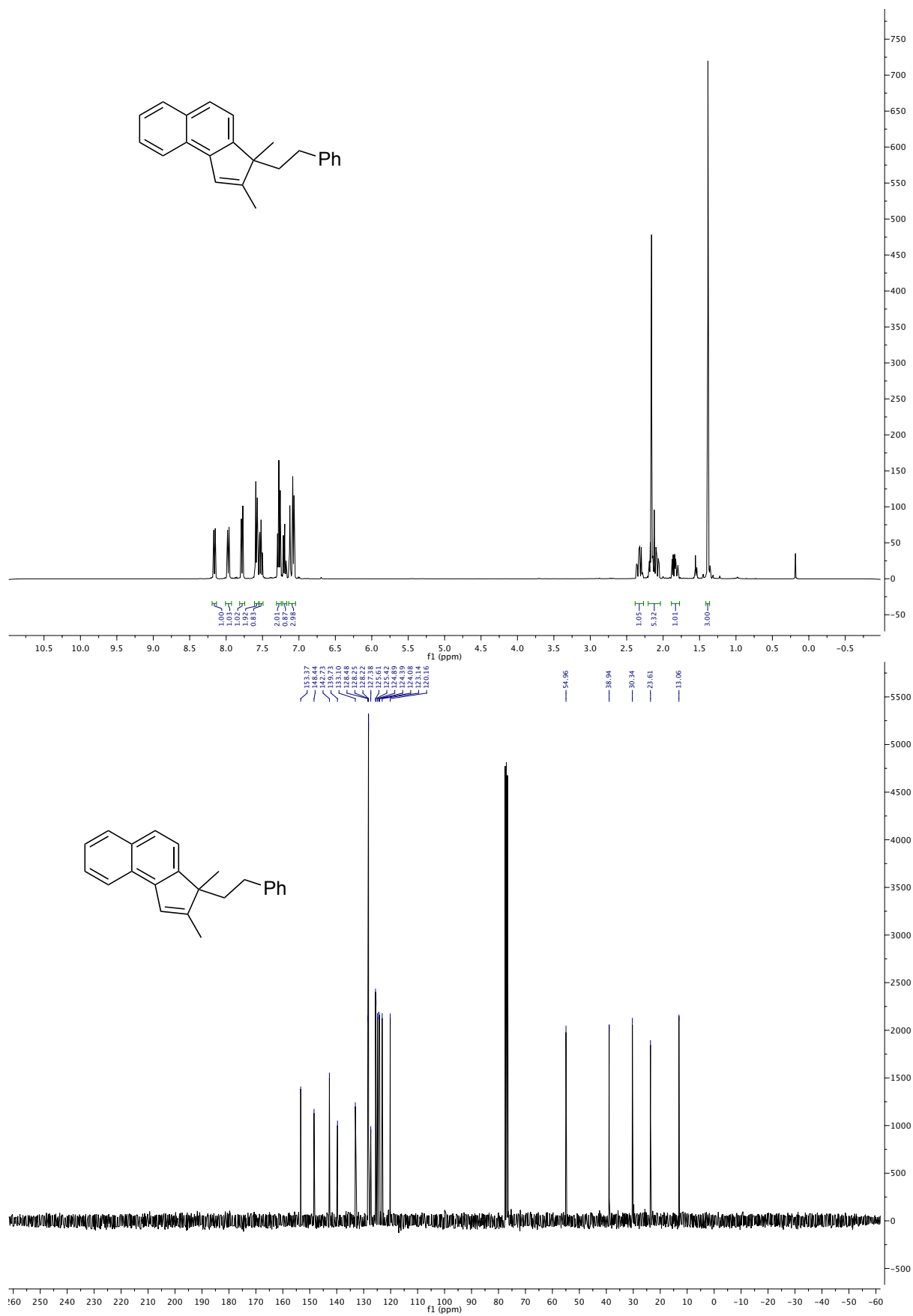
1-Ethynylcyclodecyl methyl carbonate



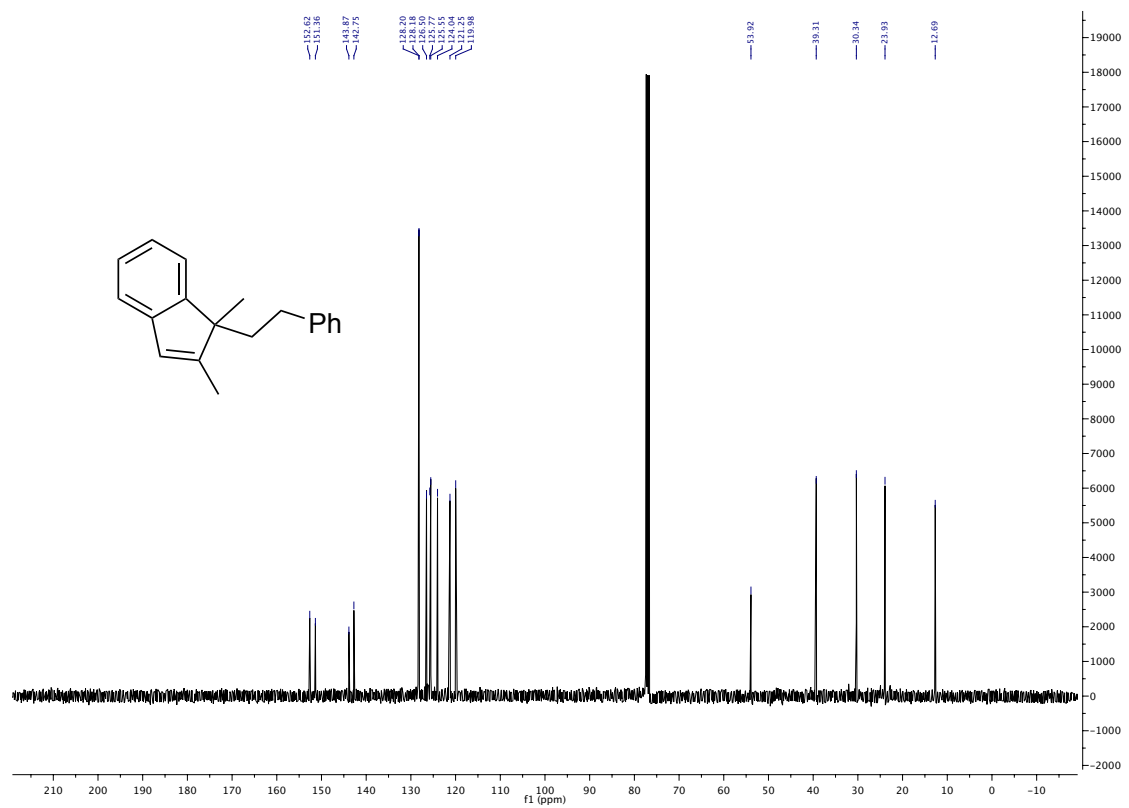
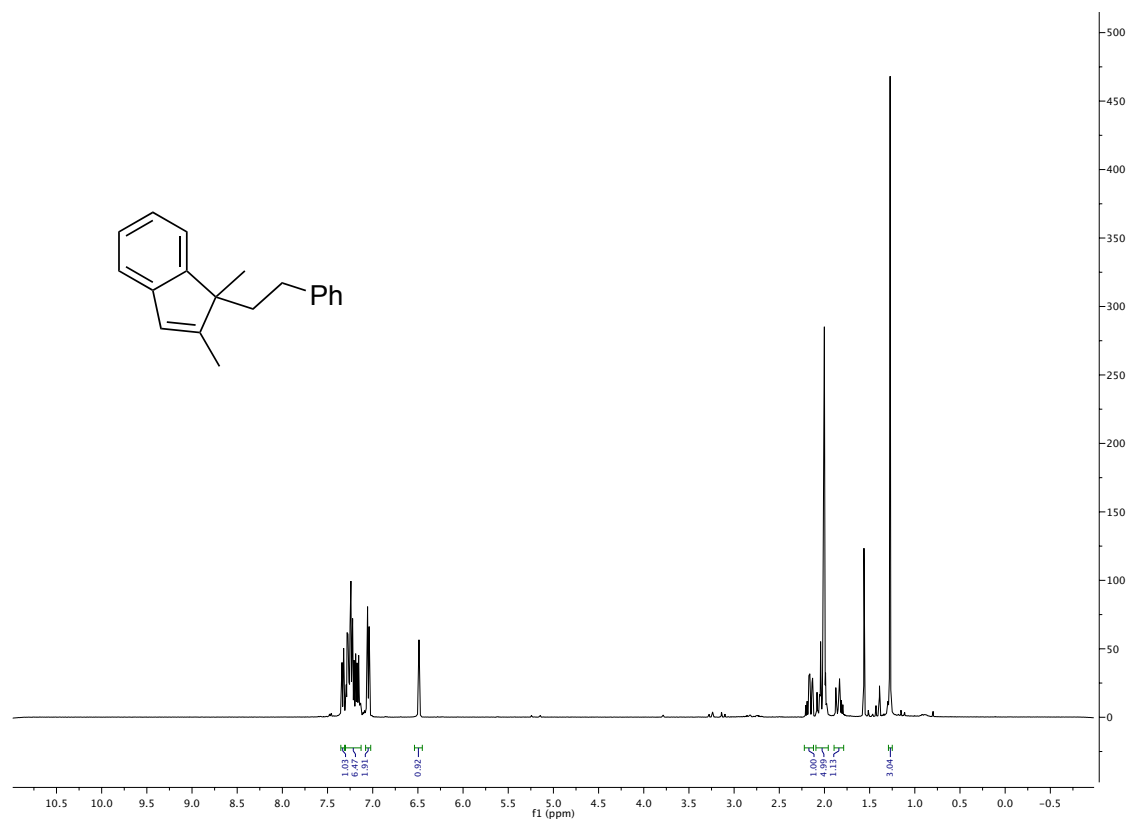
(1 λ^5 -Vinylidene)cyclodecane (5g)



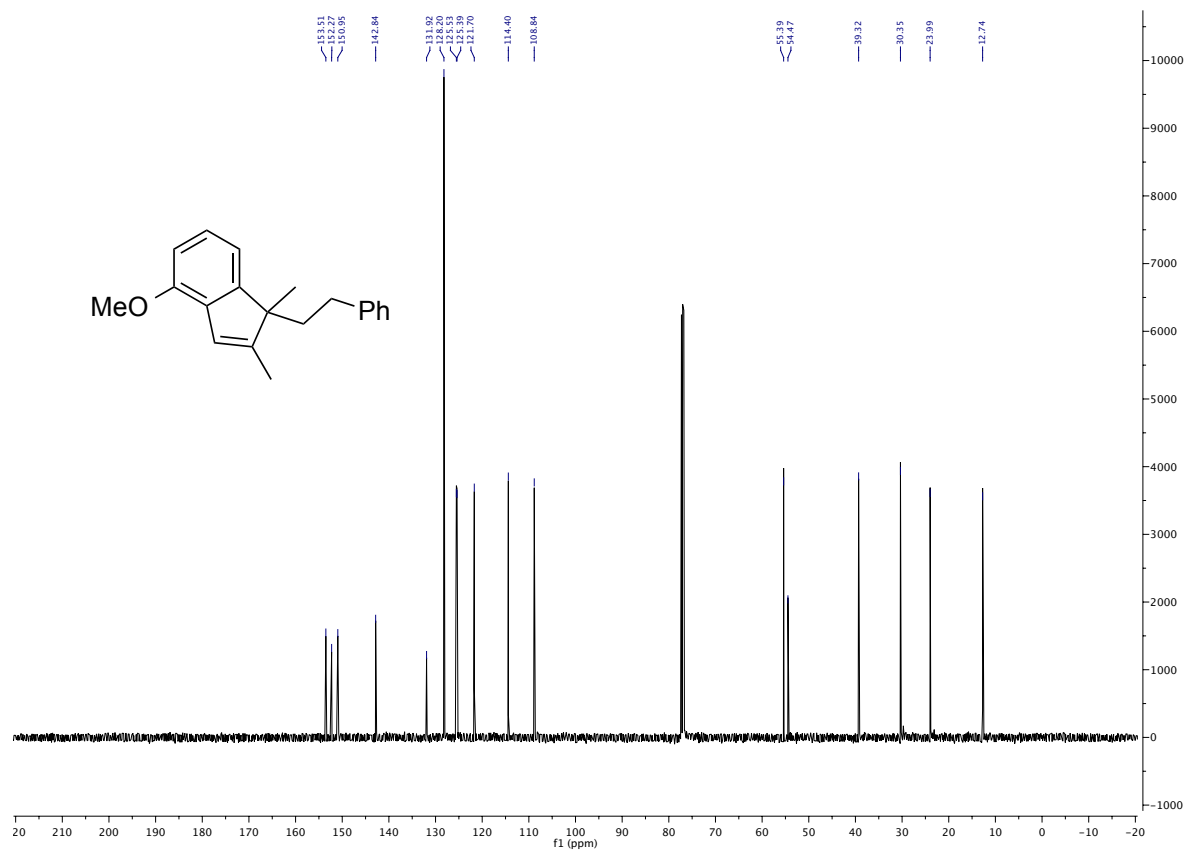
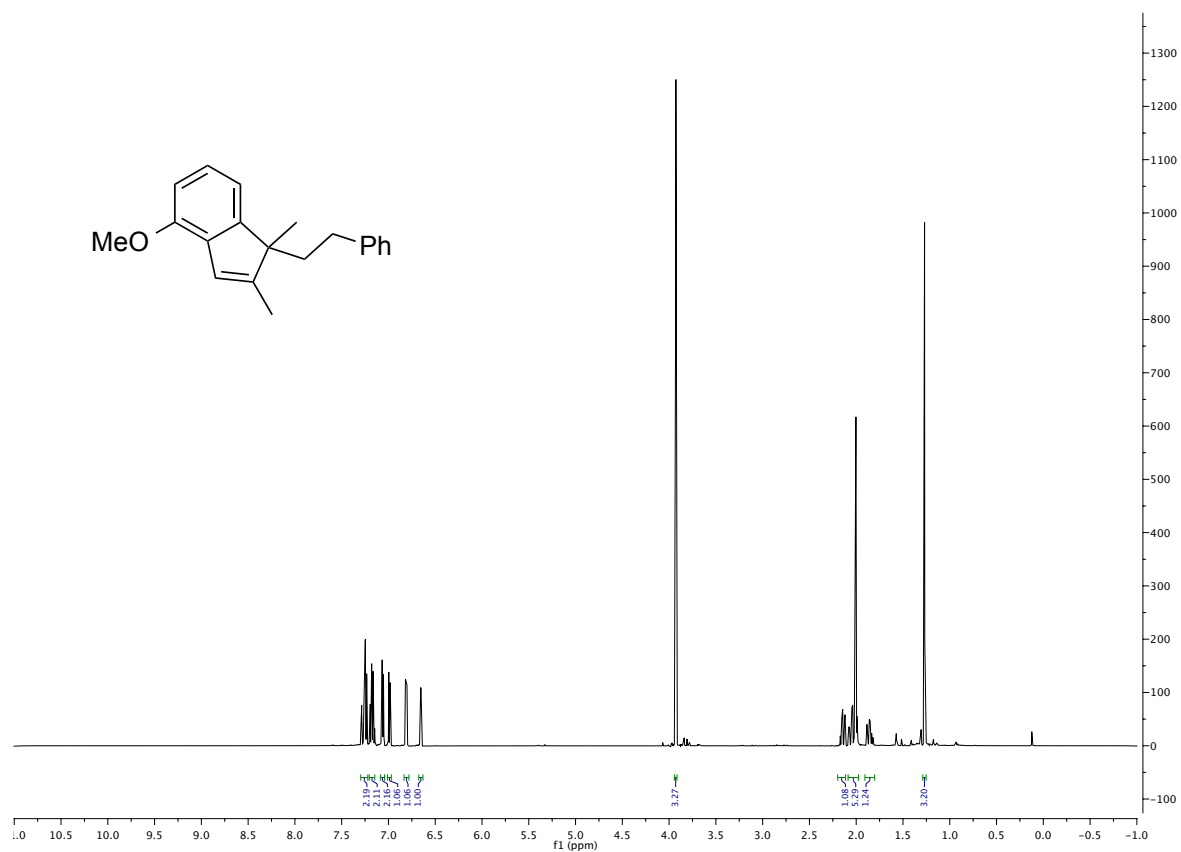
2,3-Dimethyl-3-phenethyl-3H-cyclopenta[*a*]naphthalene (6a)



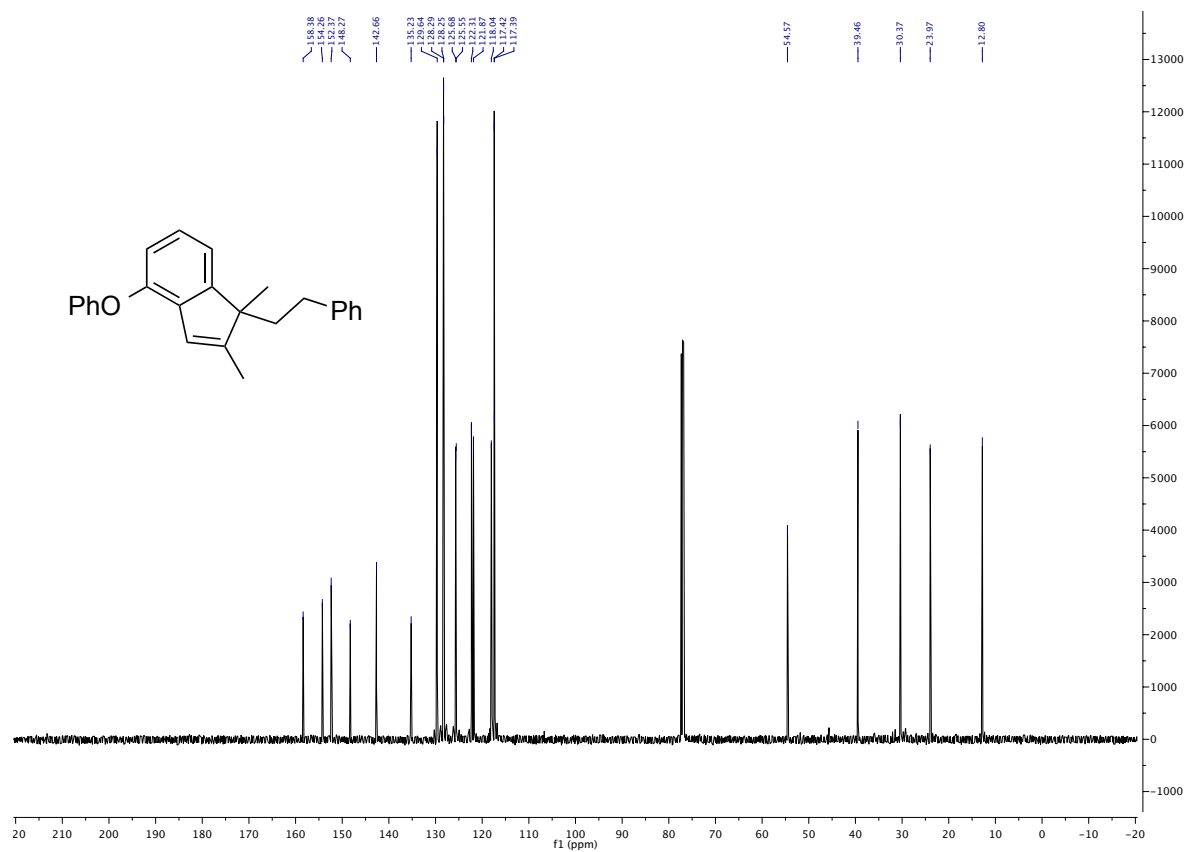
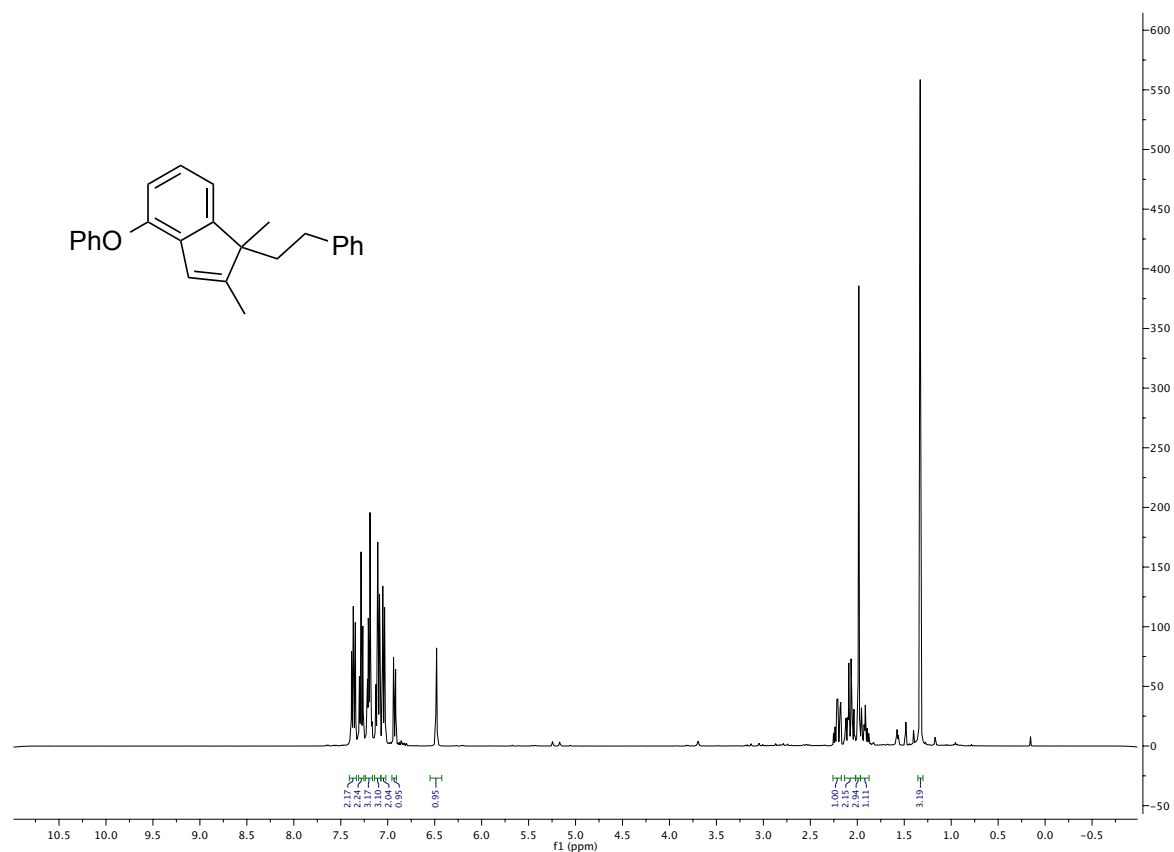
1,2-Dimethyl-1-phenethyl-1*H*-indene (6b)



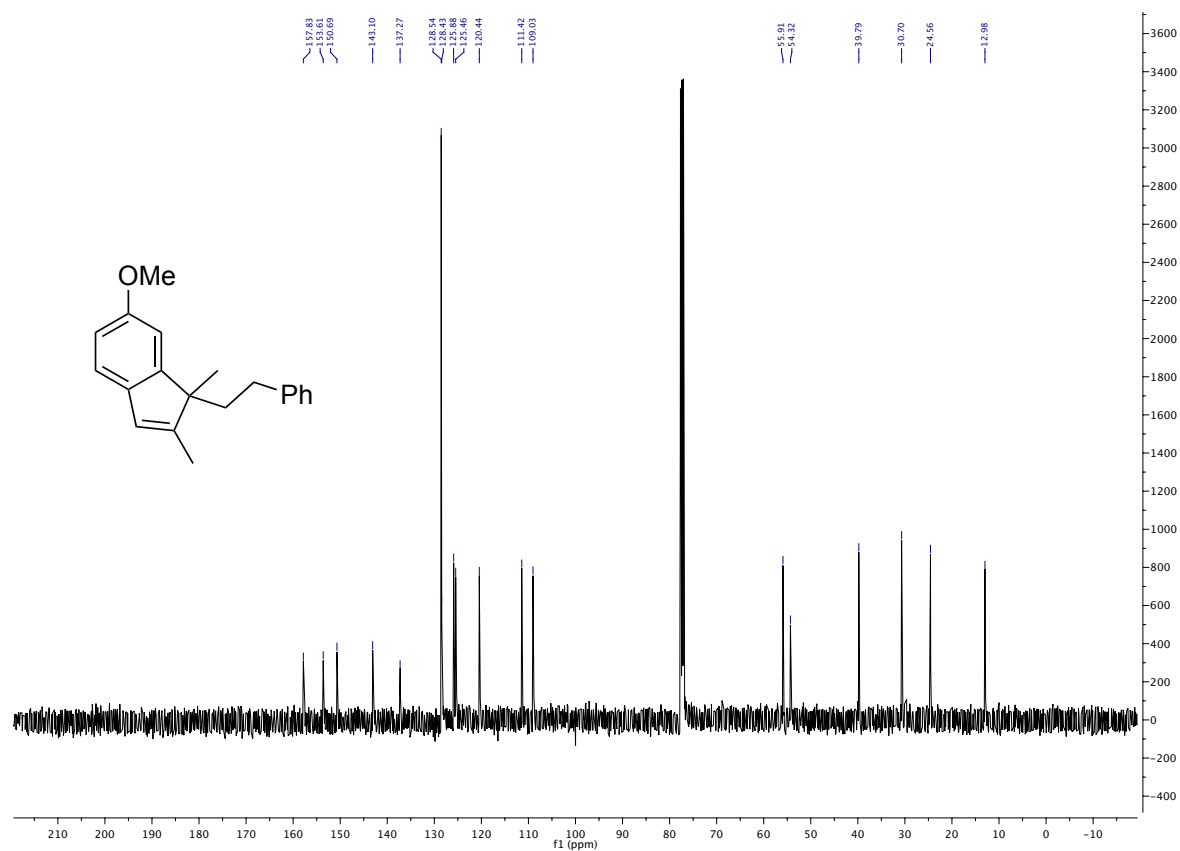
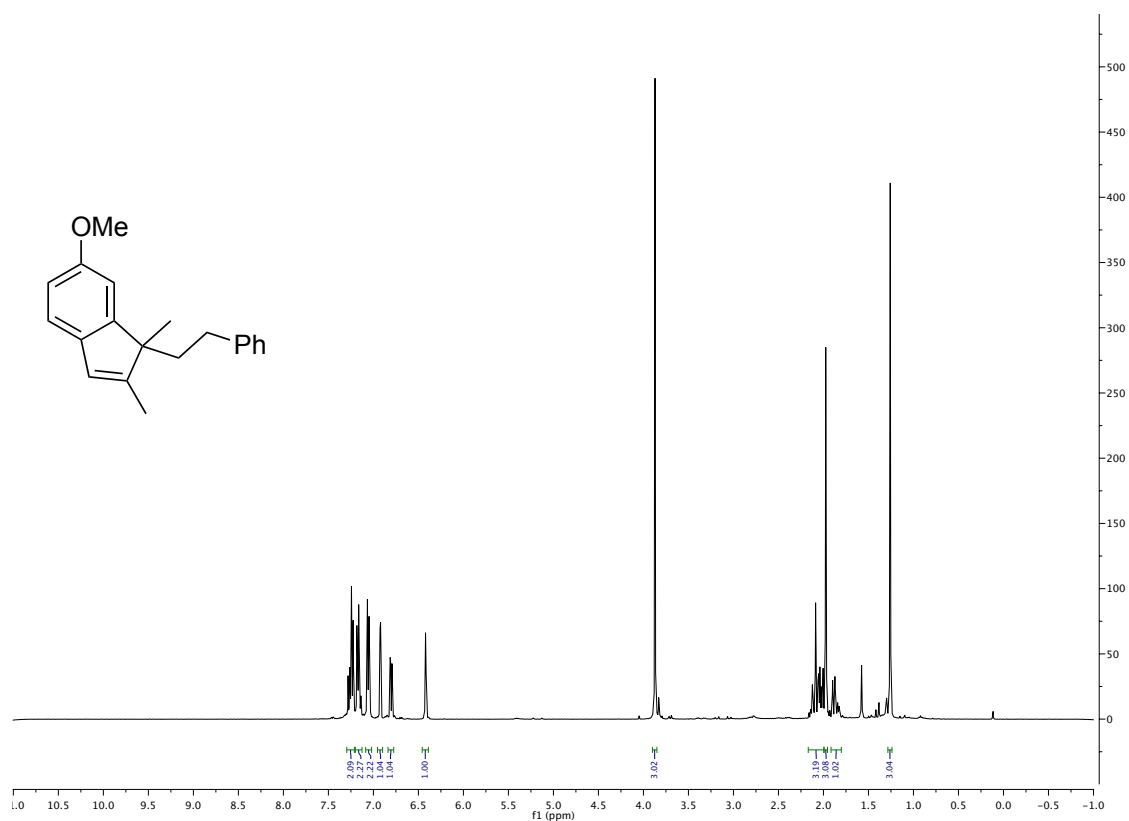
4-Methoxy-1,2-dimethyl-1-phenethyl-1H-indene (6c)



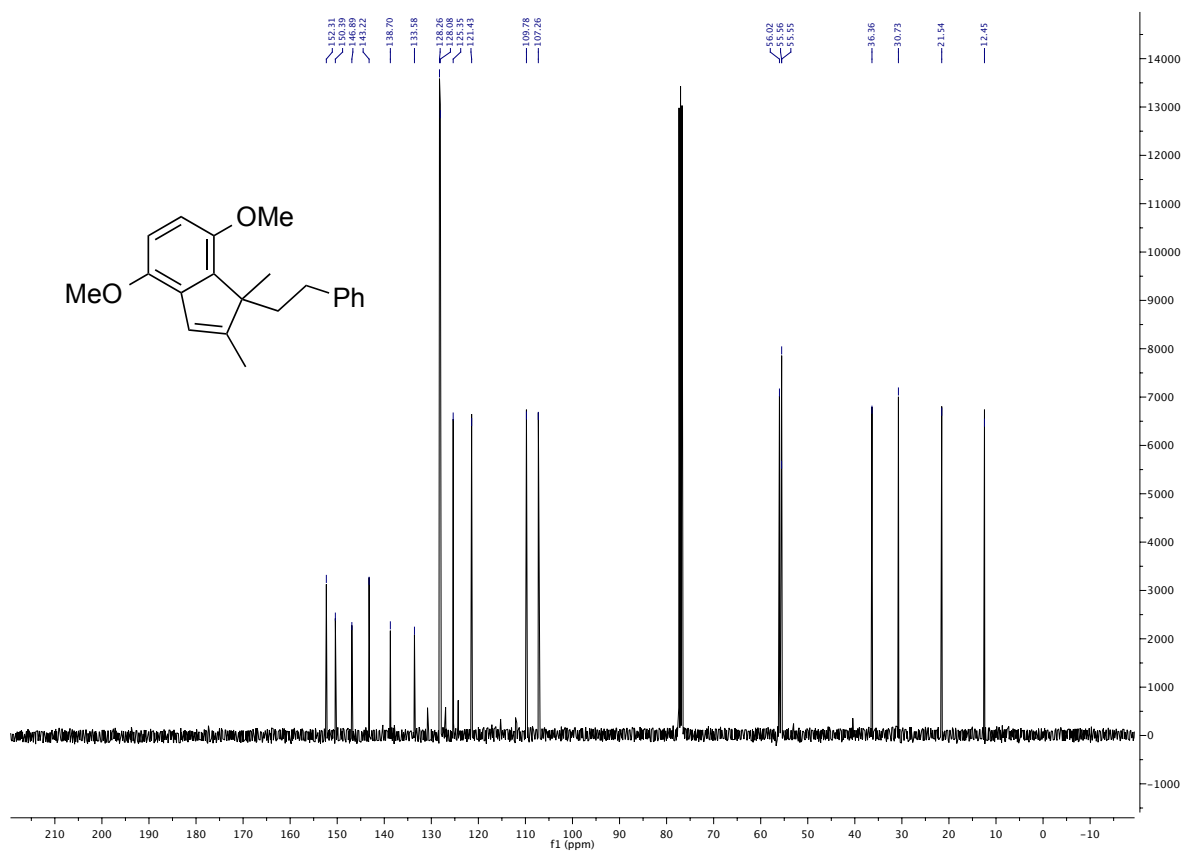
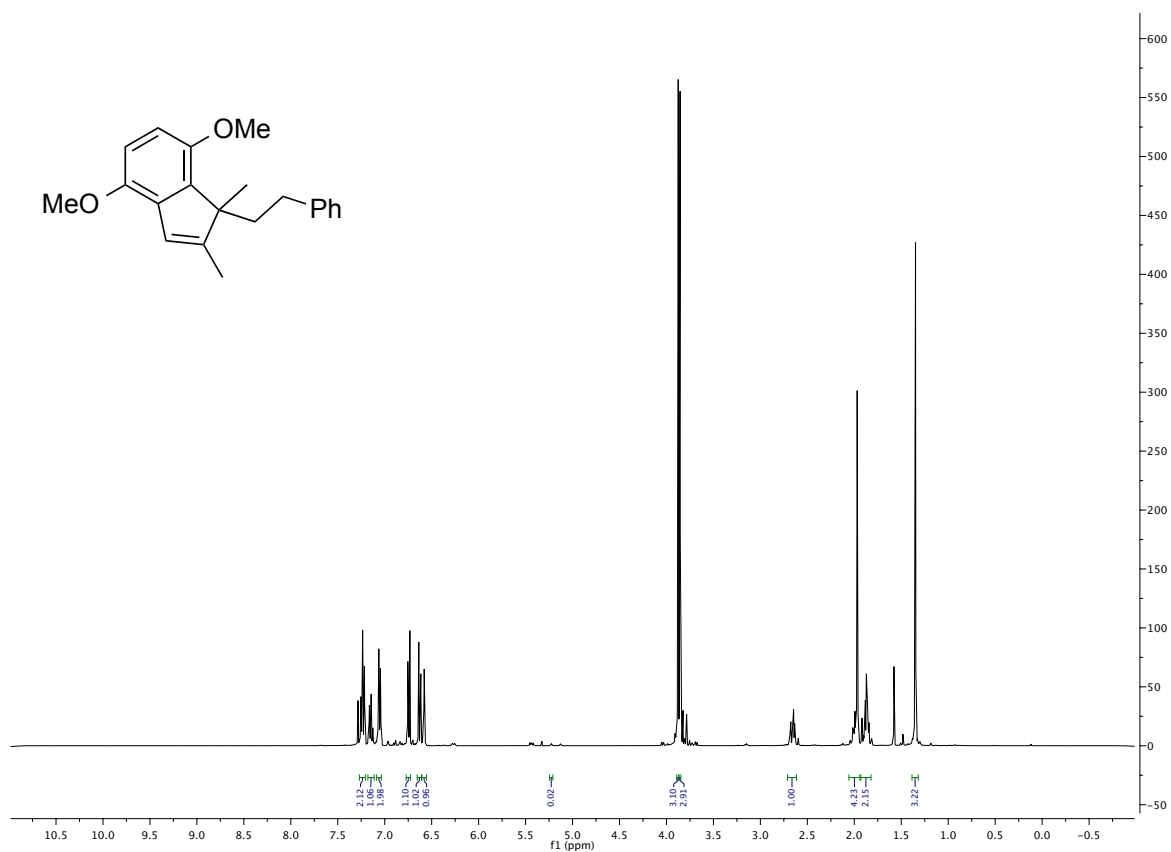
1,2-Dimethyl-1-phenethyl-4-phenoxy-1*H*-indene (6d)



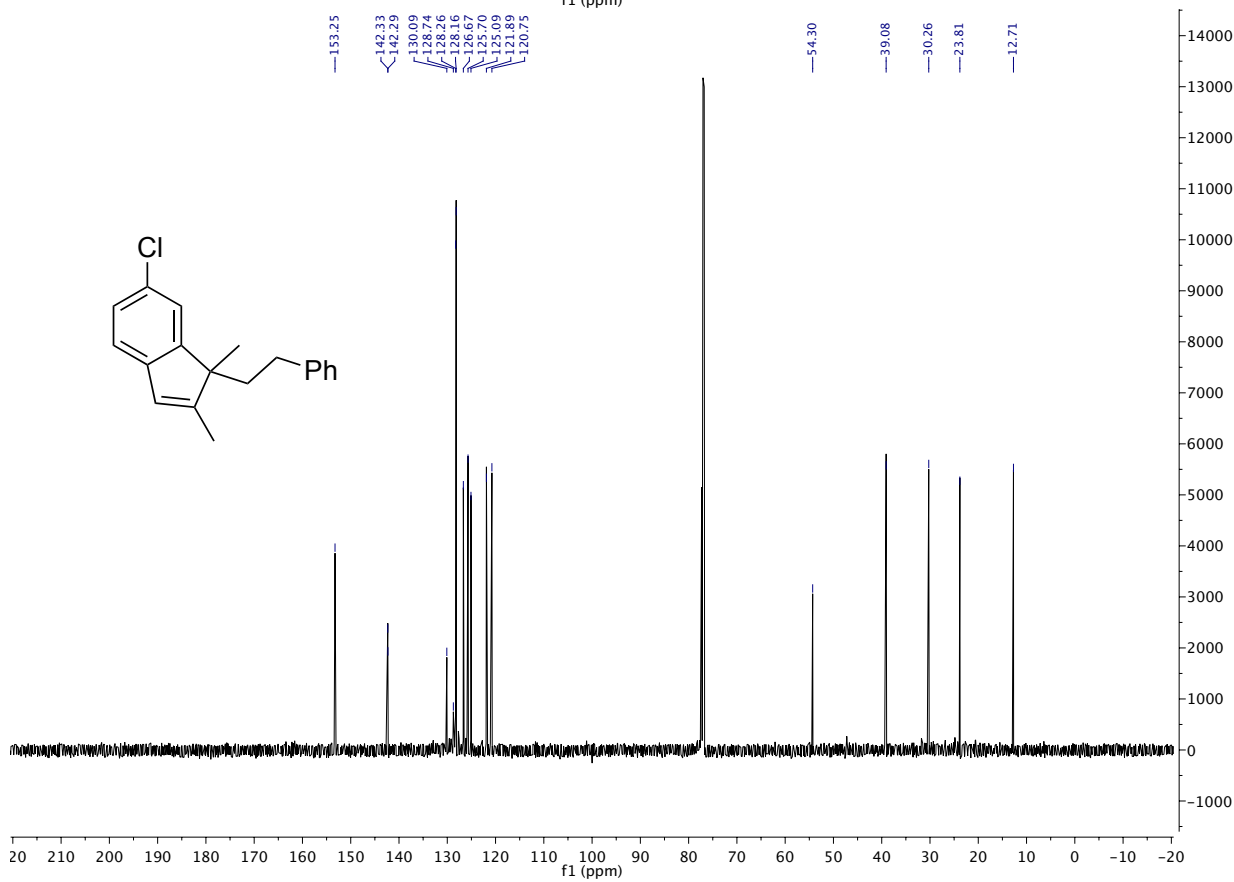
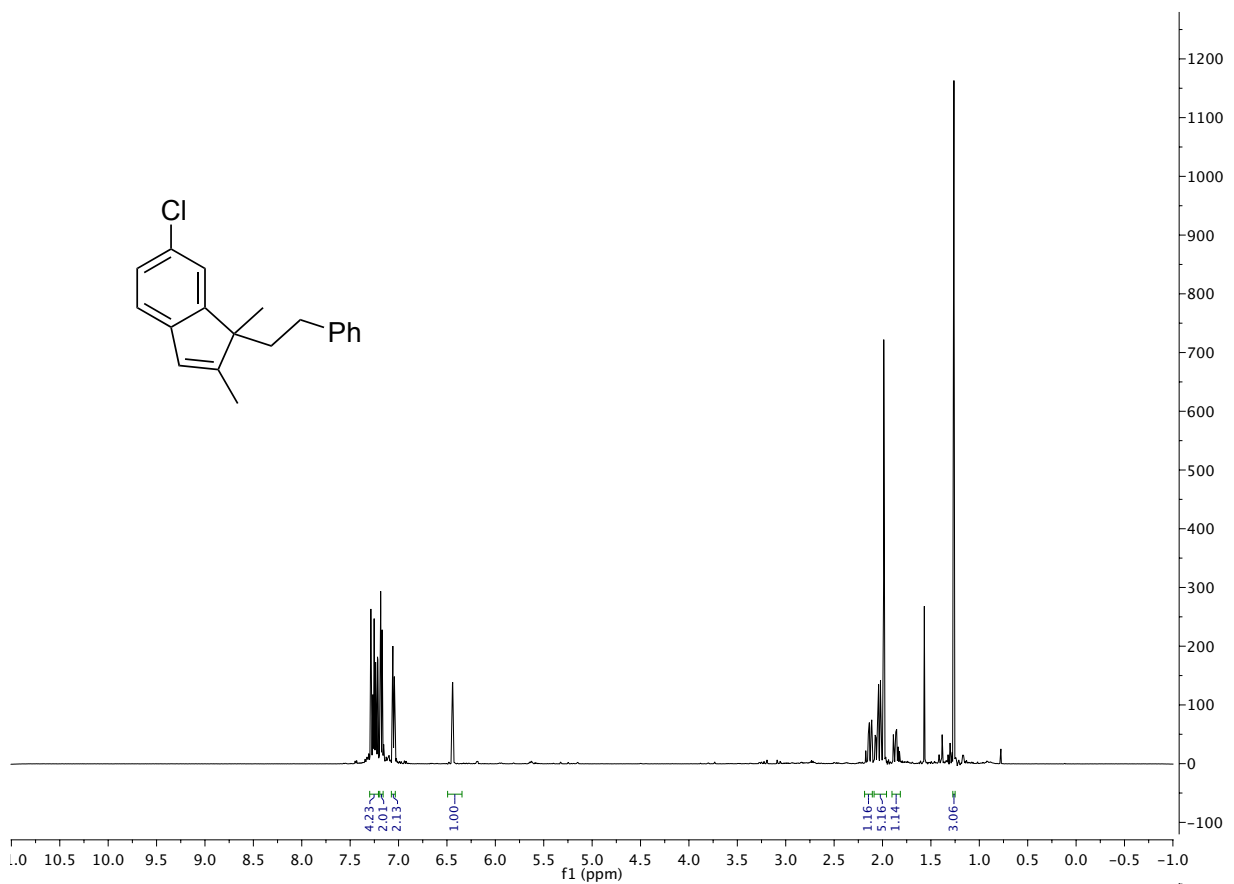
6-Methoxy-1,2-dimethyl-1-phenethyl-1H-indene (6e)



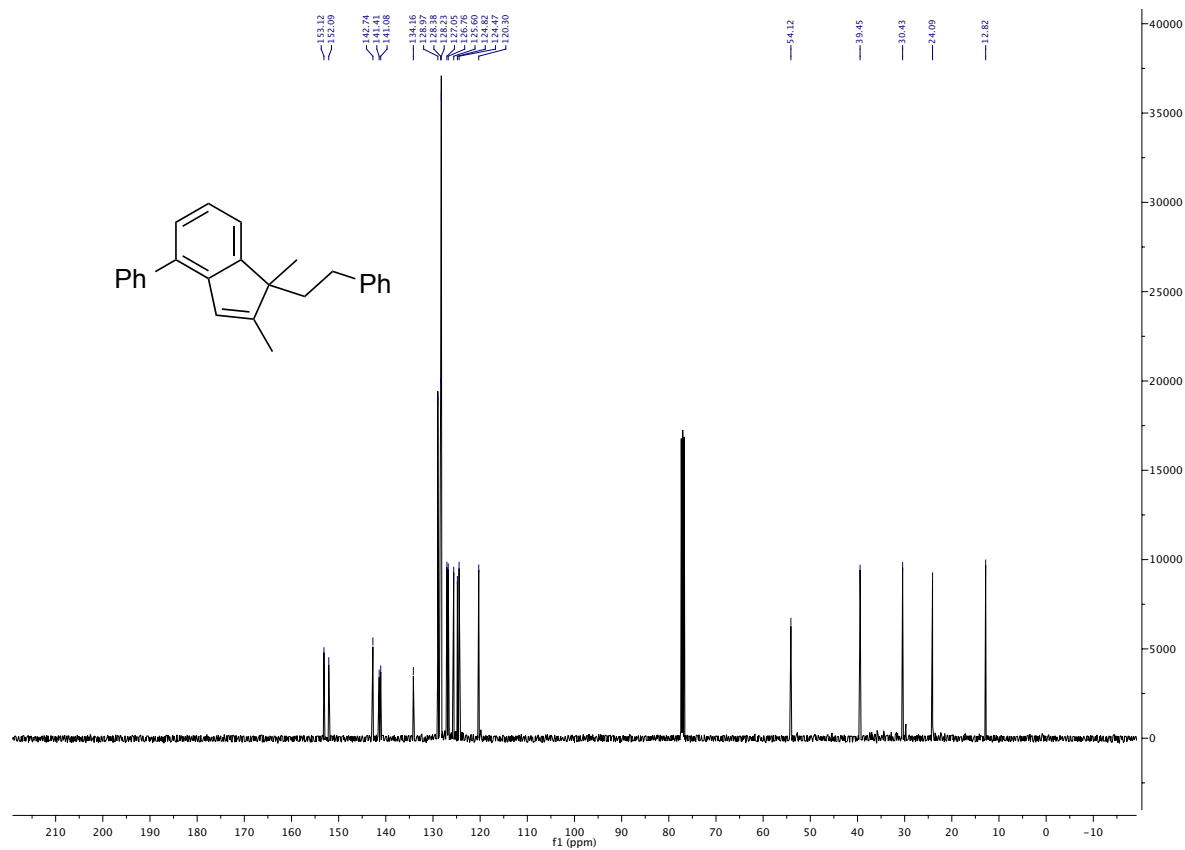
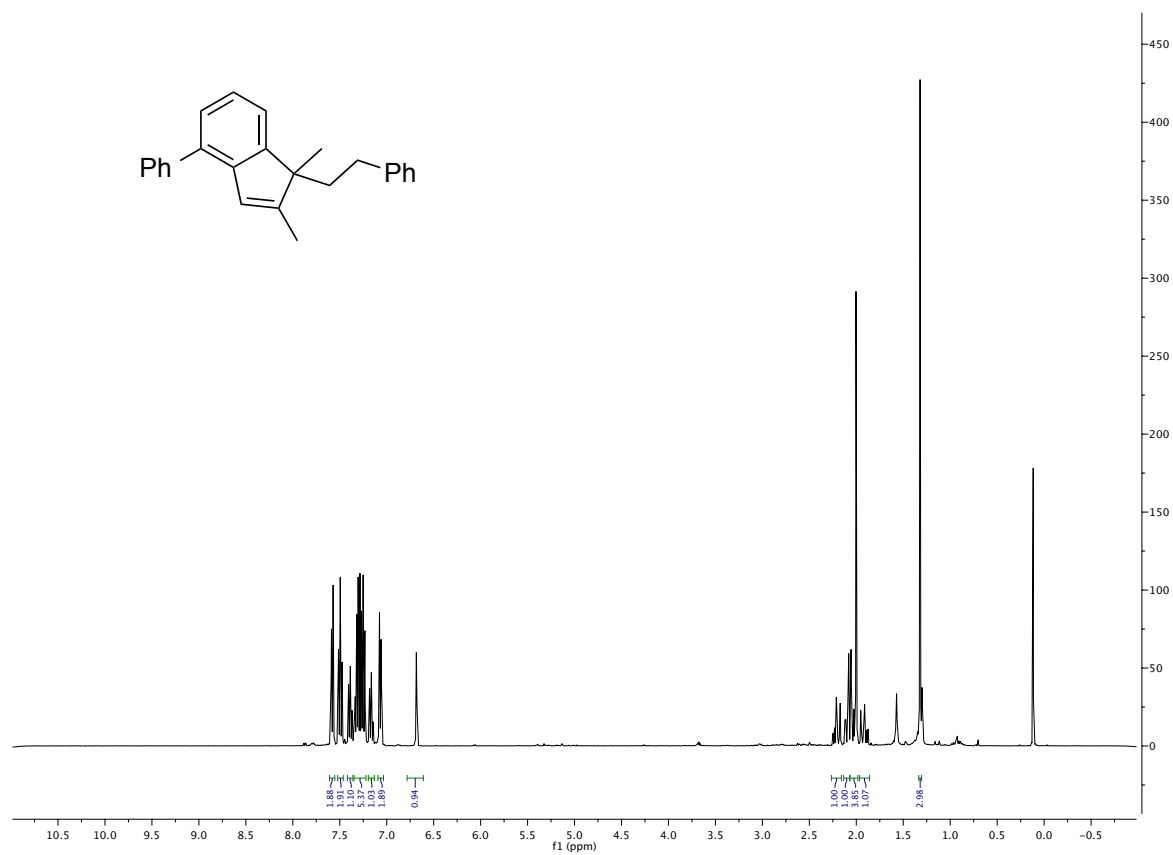
4,7-Dimethoxy-1,2-dimethyl-1-phenethyl-1H-indene (6f)



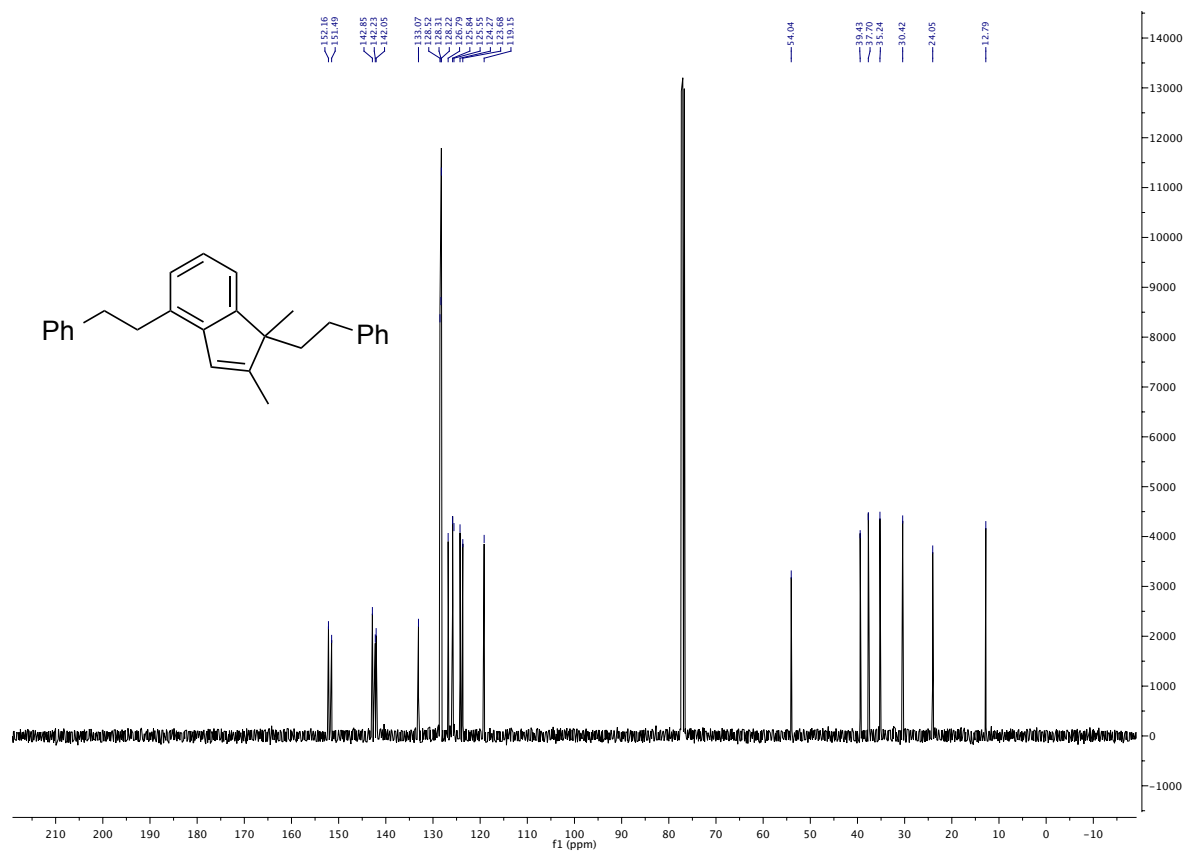
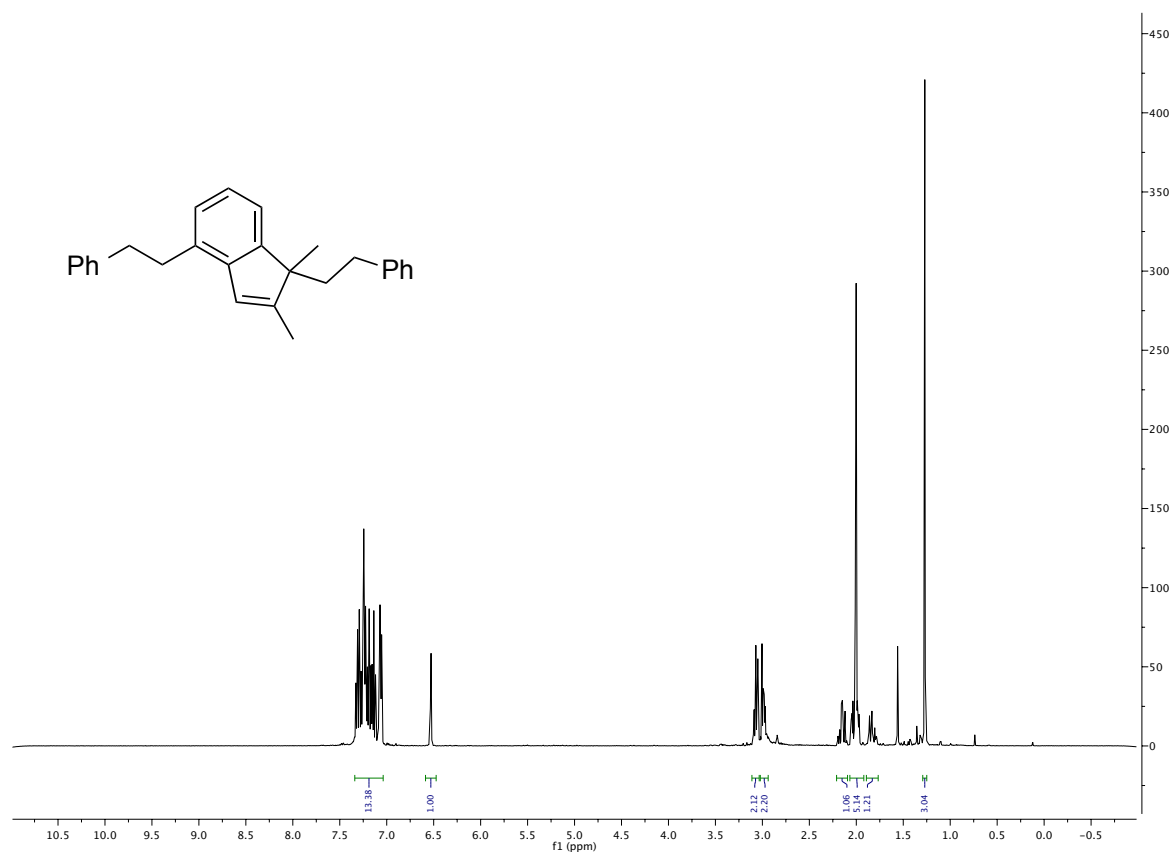
6-Chloro-1,2-dimethyl-1-phenethyl-1H-indene (6g)



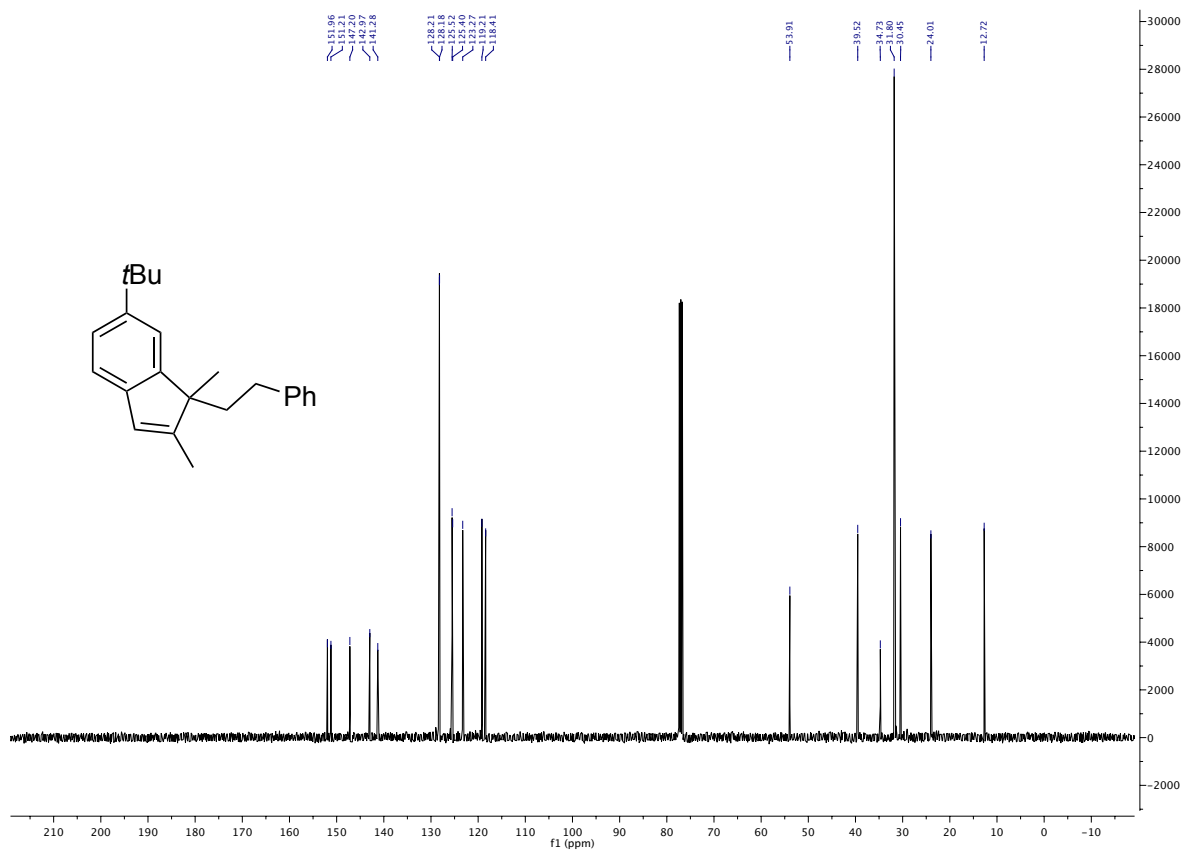
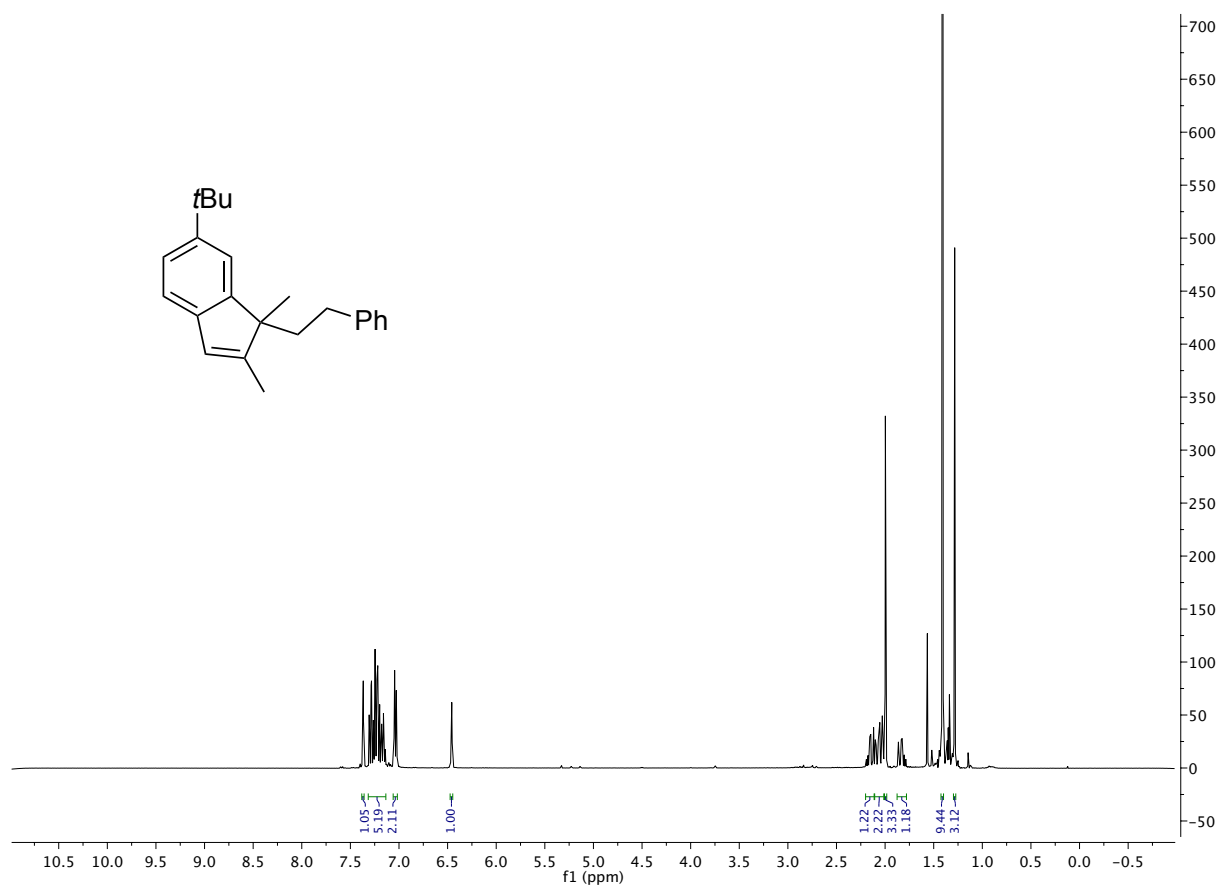
1,2-Dimethyl-1-phenethyl-4-phenyl-1*H*-indene (6h)



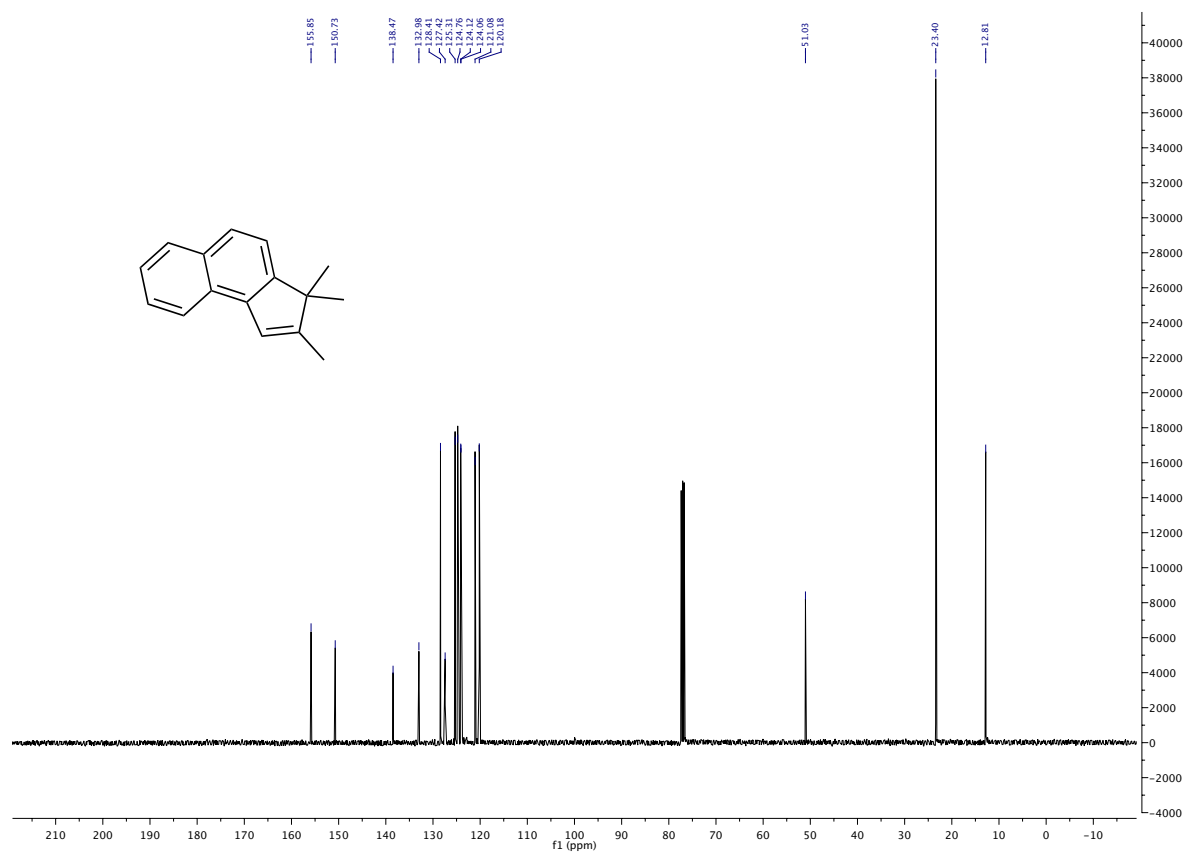
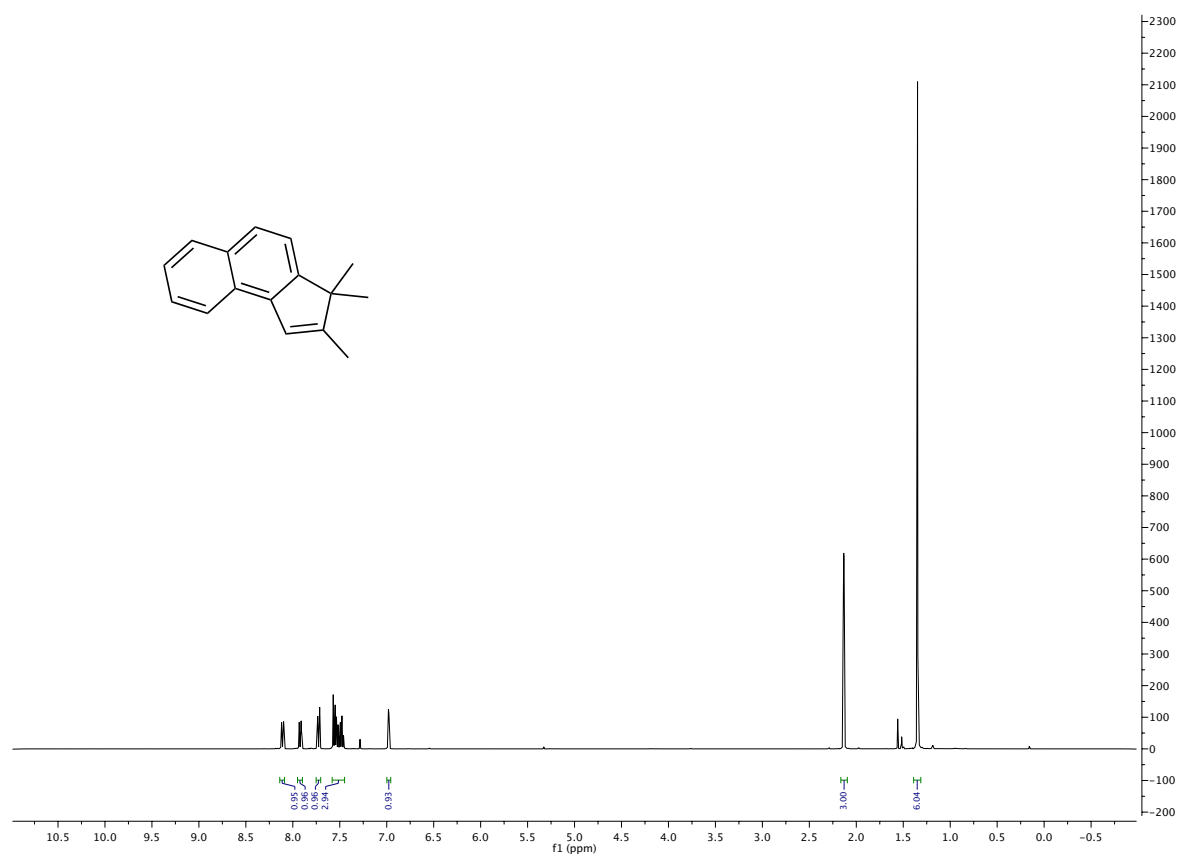
1,2-Dimethyl-1,4-diphenethyl-1*H*-indene (6i)



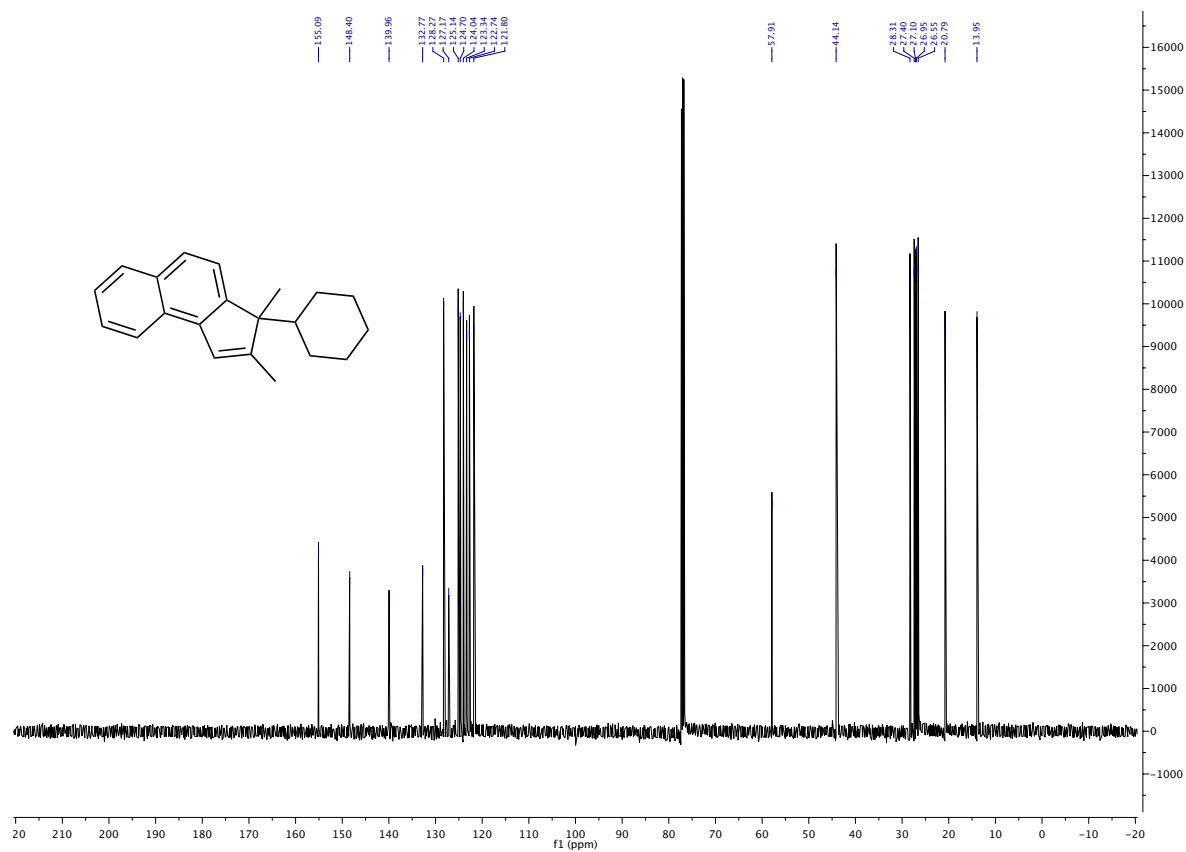
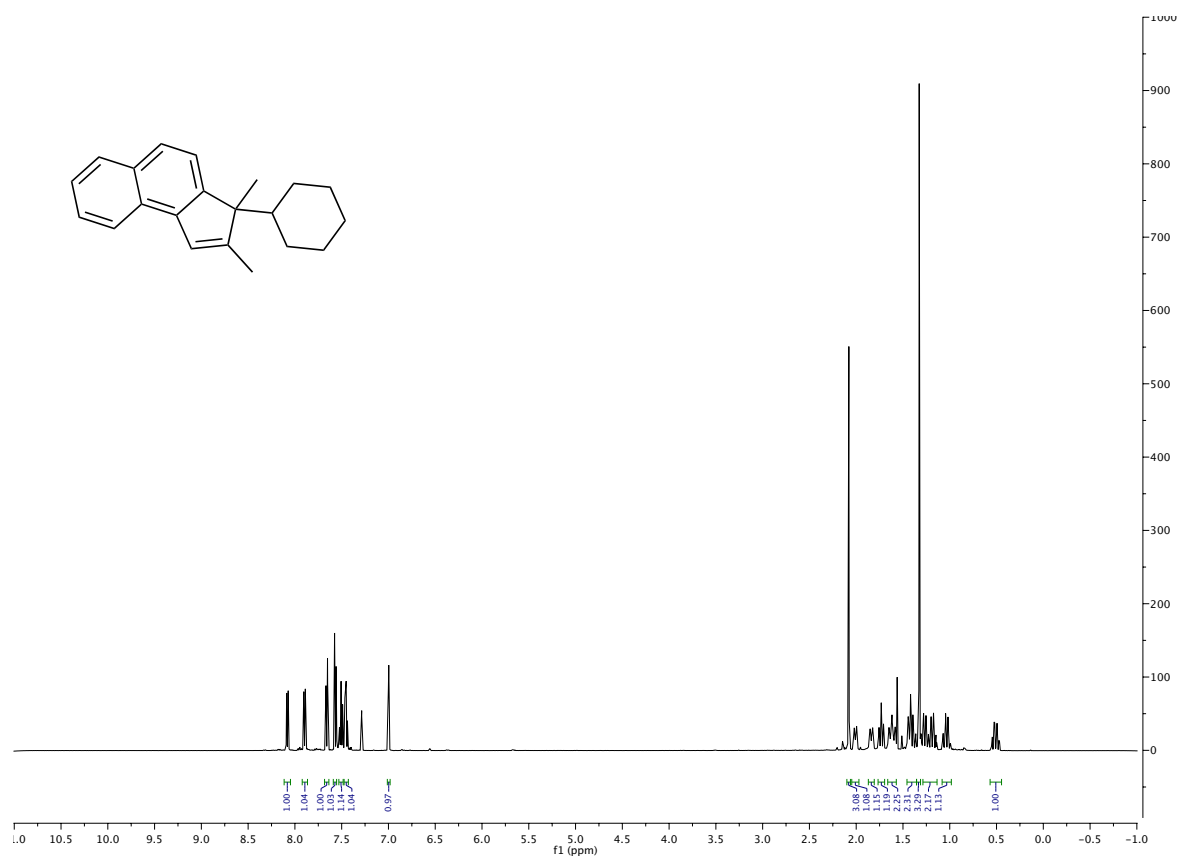
6-(*Tert*-butyl)-1,2-dimethyl-1-phenethyl-1*H*-indene (6j)



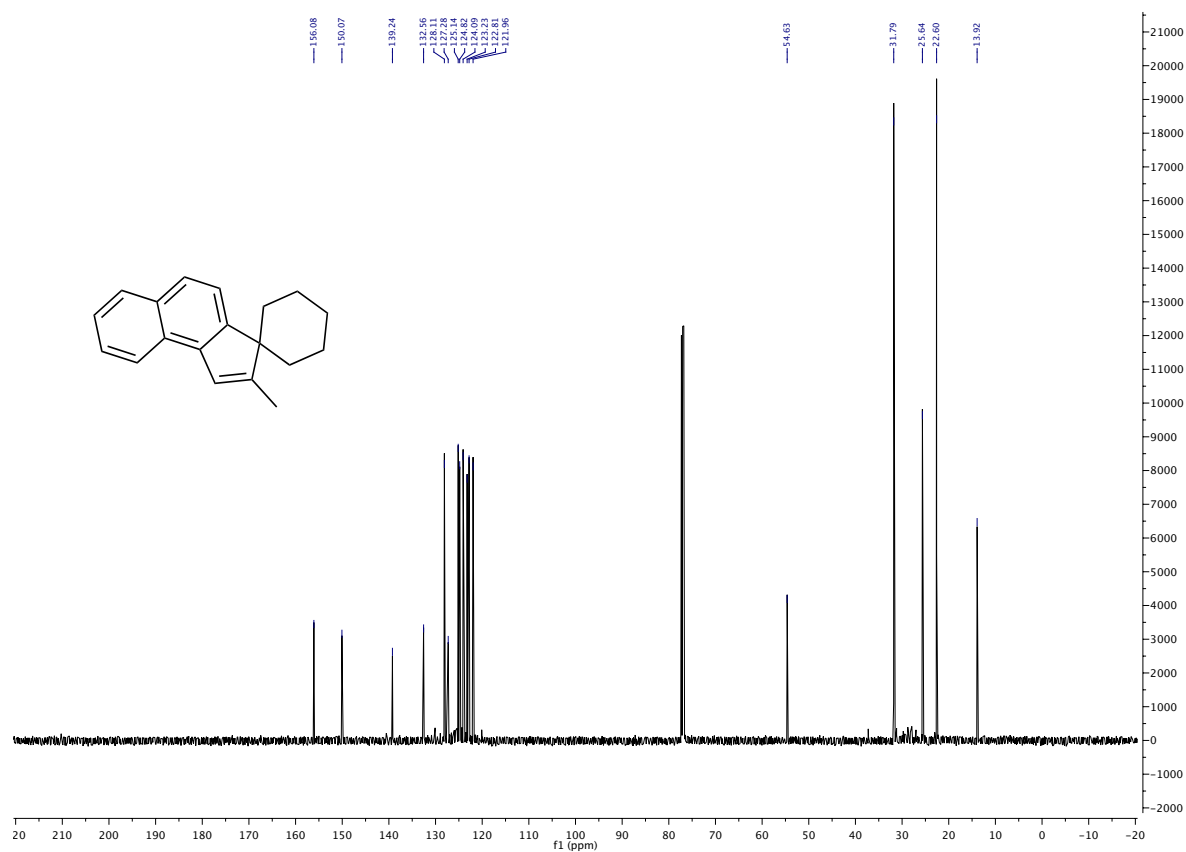
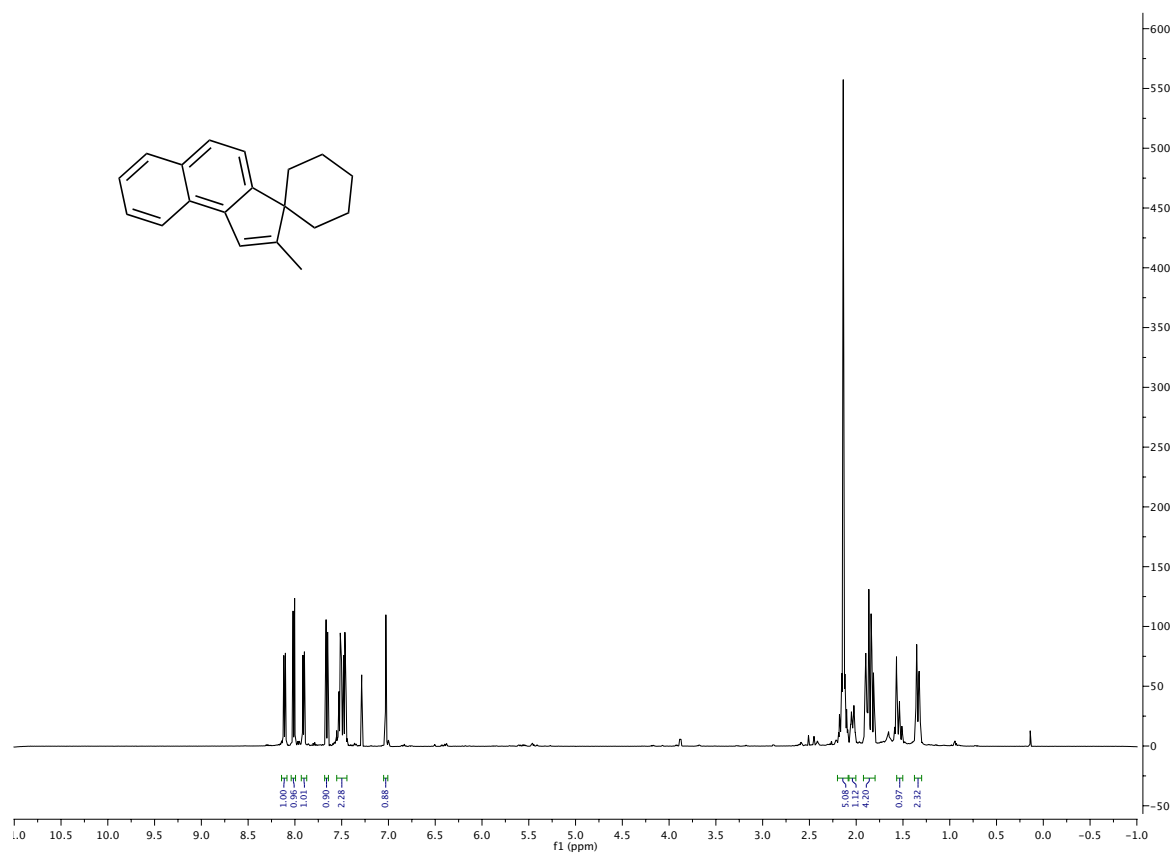
2,3,3-Trimethyl-3H-cyclopenta[*a*]naphthalene (6k)



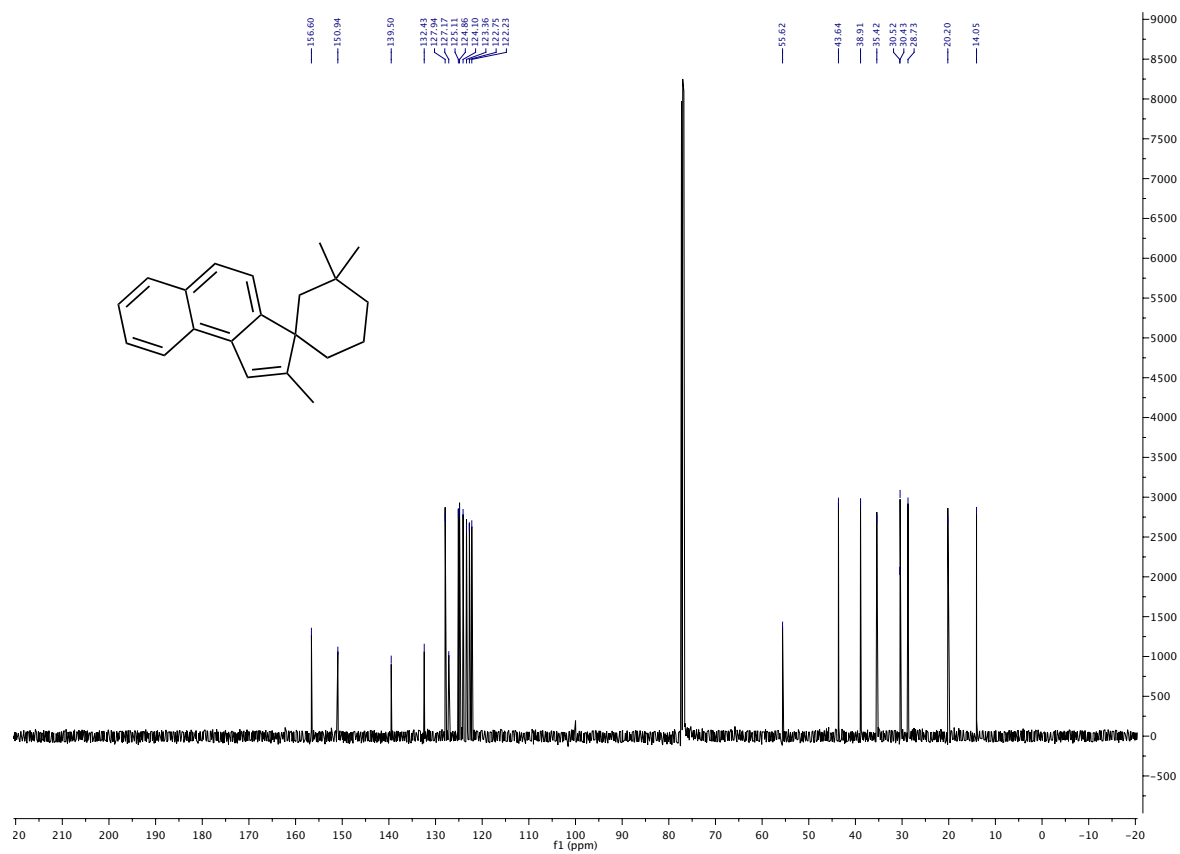
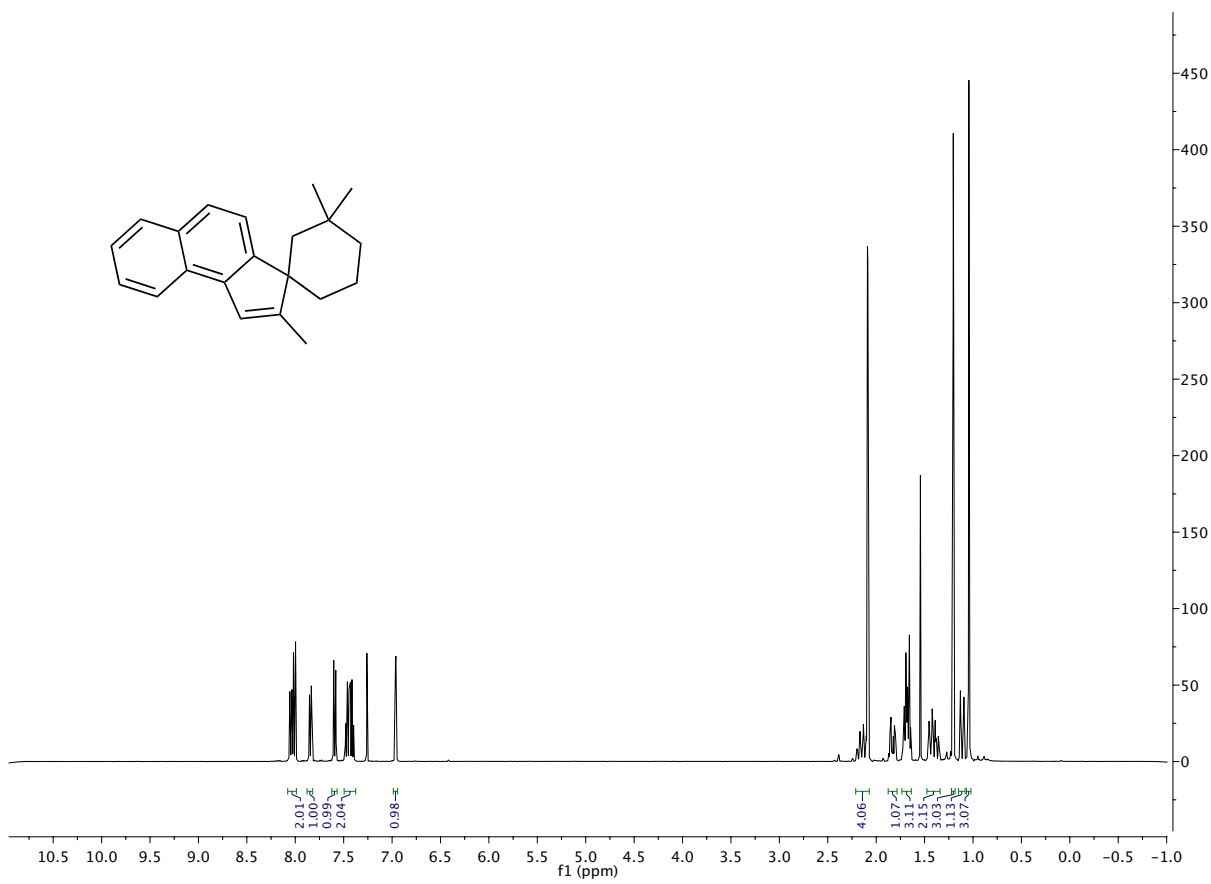
3-Cyclohexyl-2,3-dimethyl-3H-cyclopenta[*a*]naphthalene (6l)



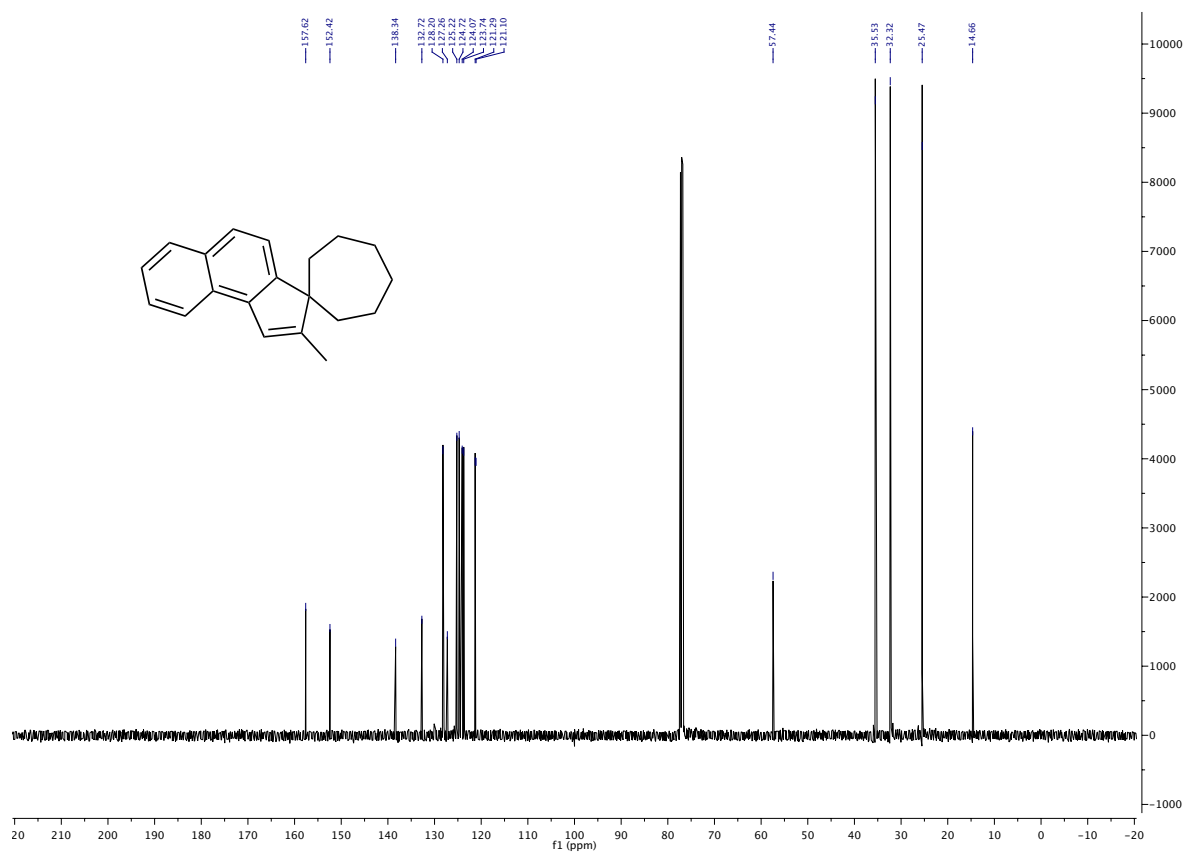
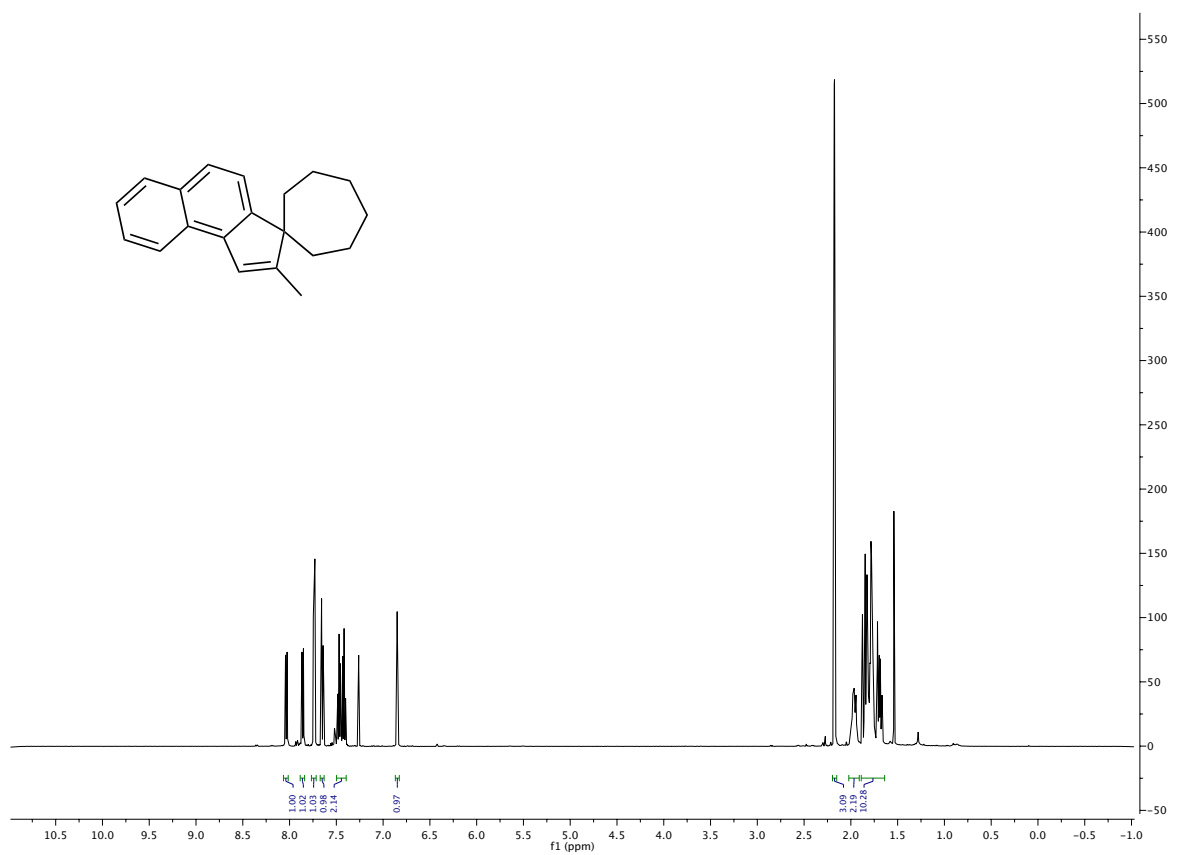
2'-Methylspiro[cyclohexane-1,3'-cyclopenta[*a*]naphthalene] (6m)



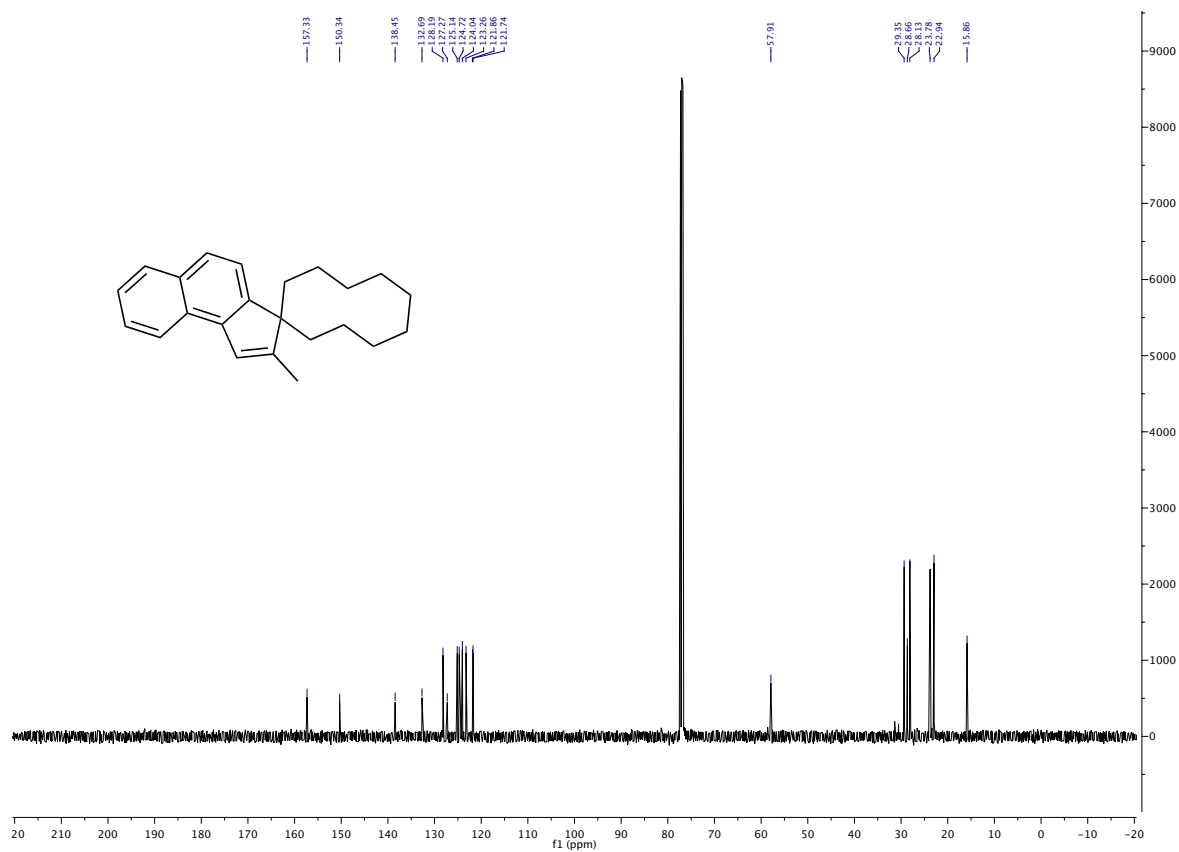
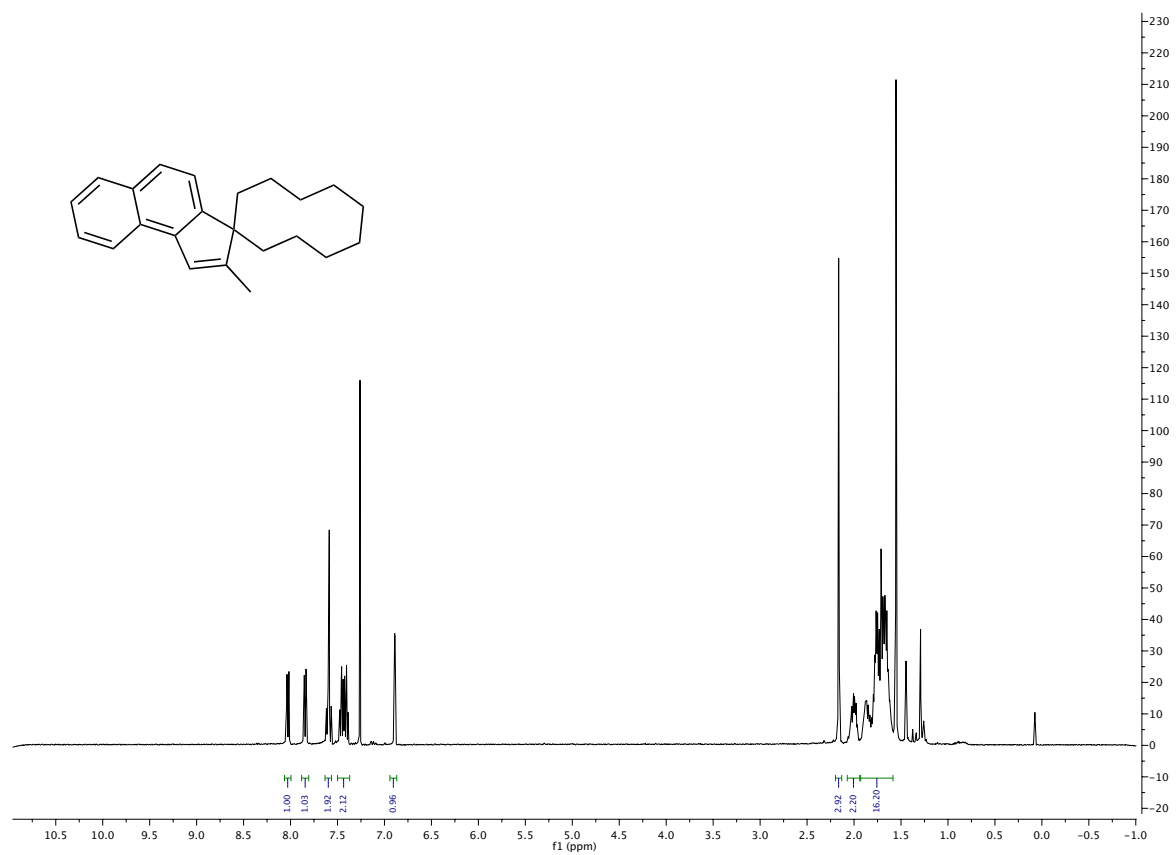
2',3,3-Trimethylspiro[cyclohexane-1,3'-cyclopenta[*a*]naphthalene] (6n)



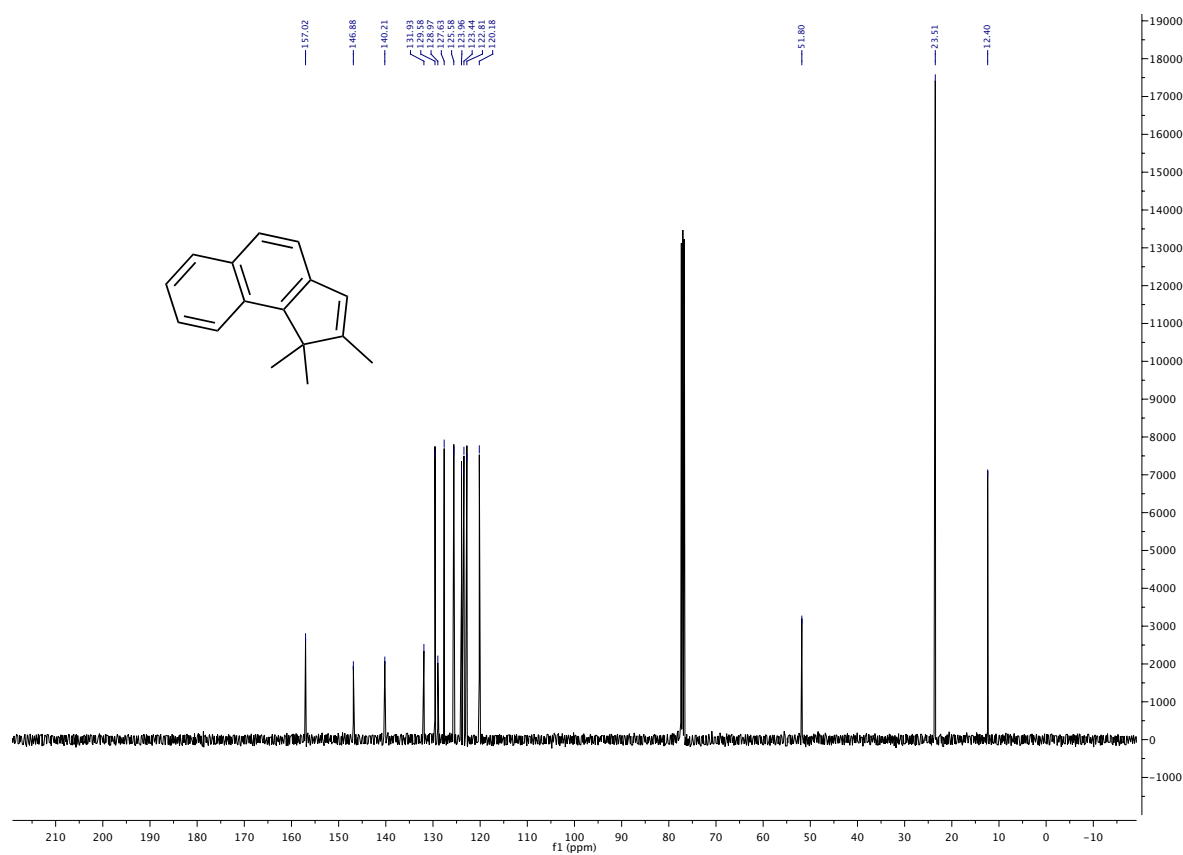
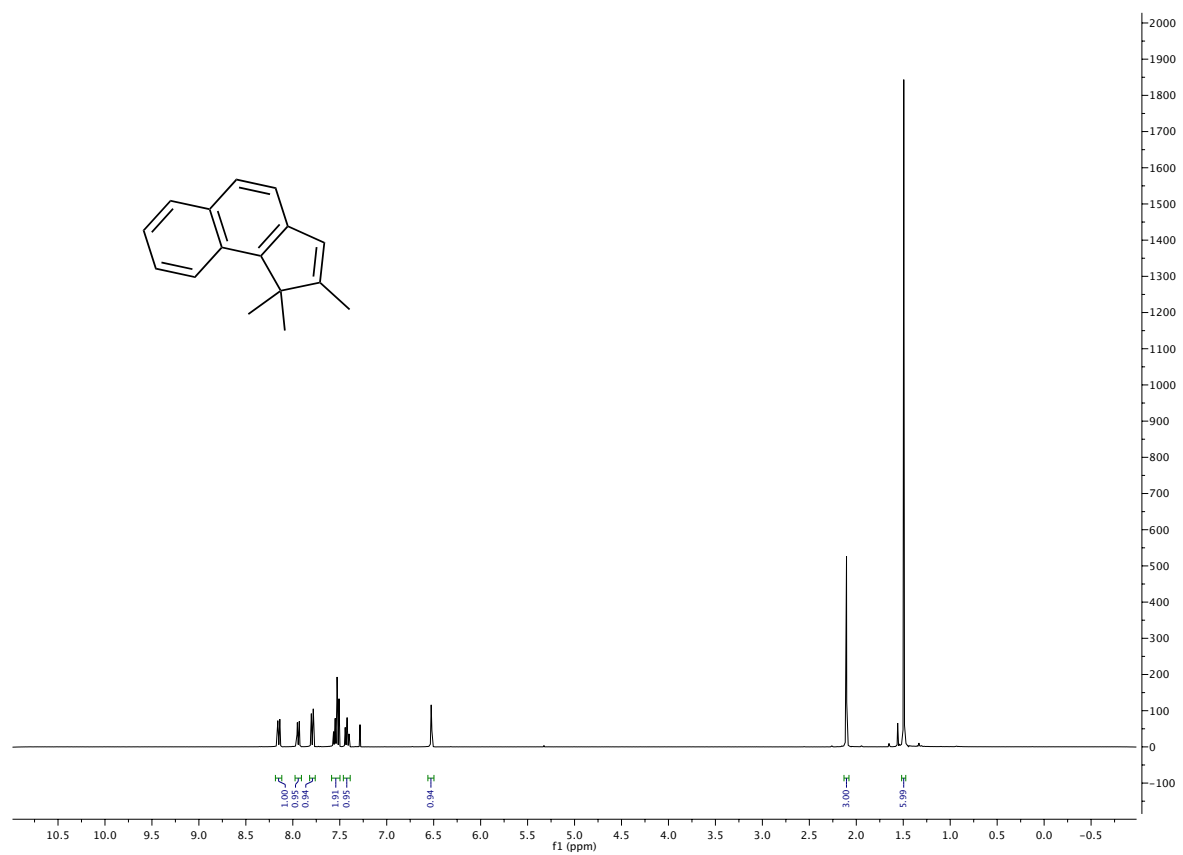
2'-Methylspiro[cycloheptane-1,3'-cyclopenta[*a*]naphthalene] (6o)



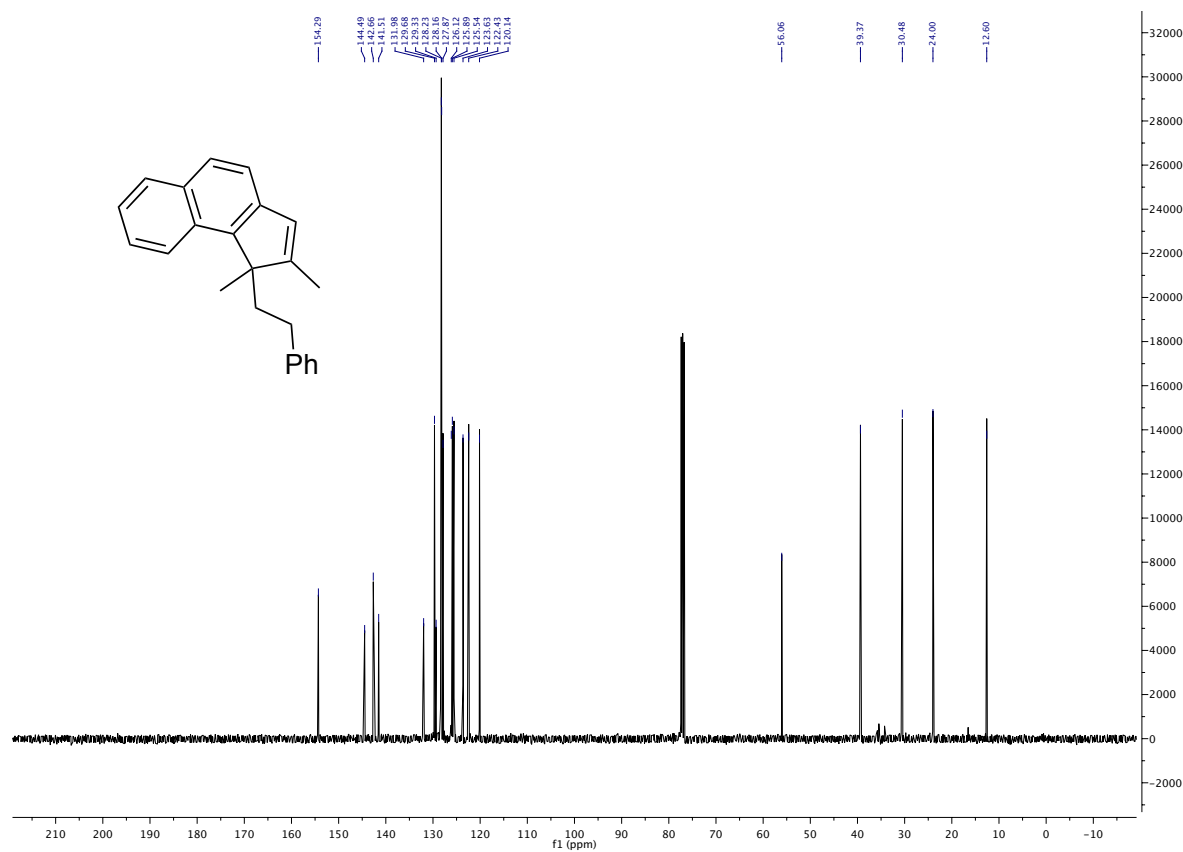
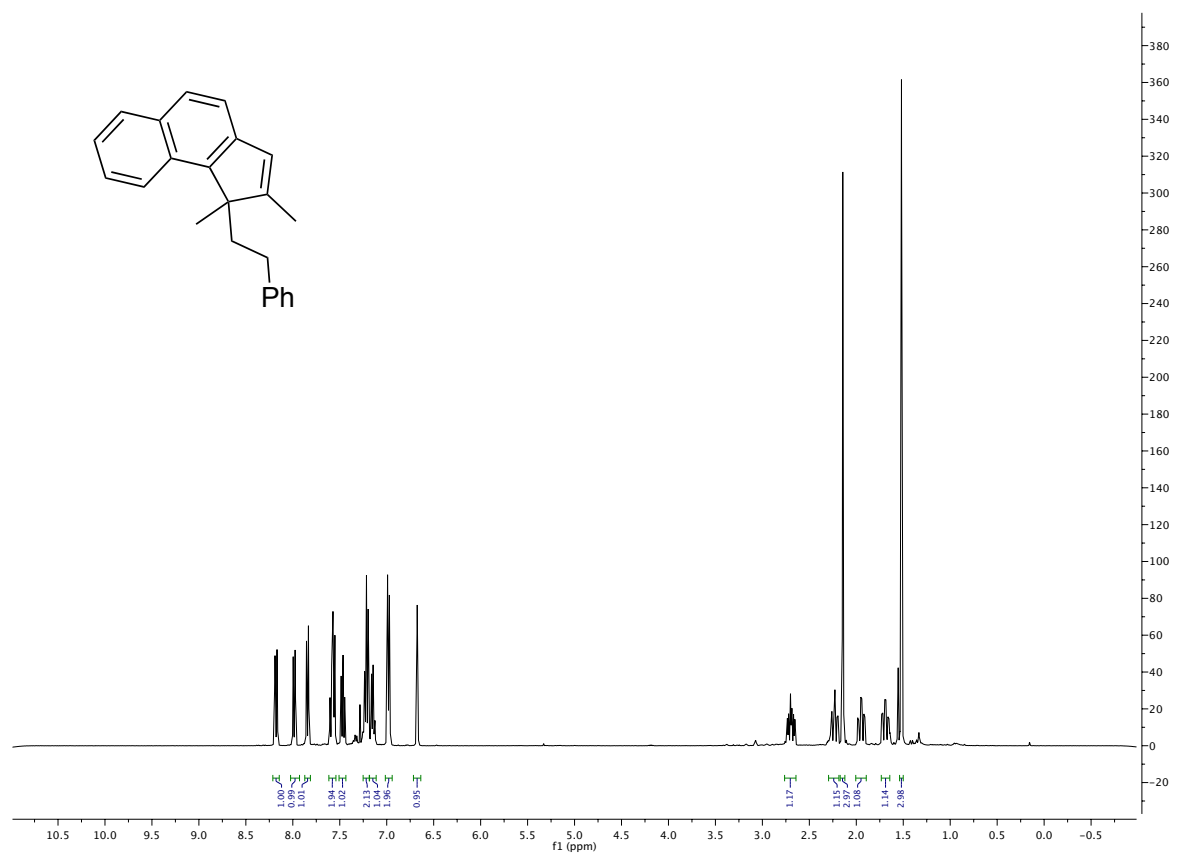
2'-Methylspiro[cyclodecane-1,3'-cyclopenta[*a*]naphthalene] (6p)



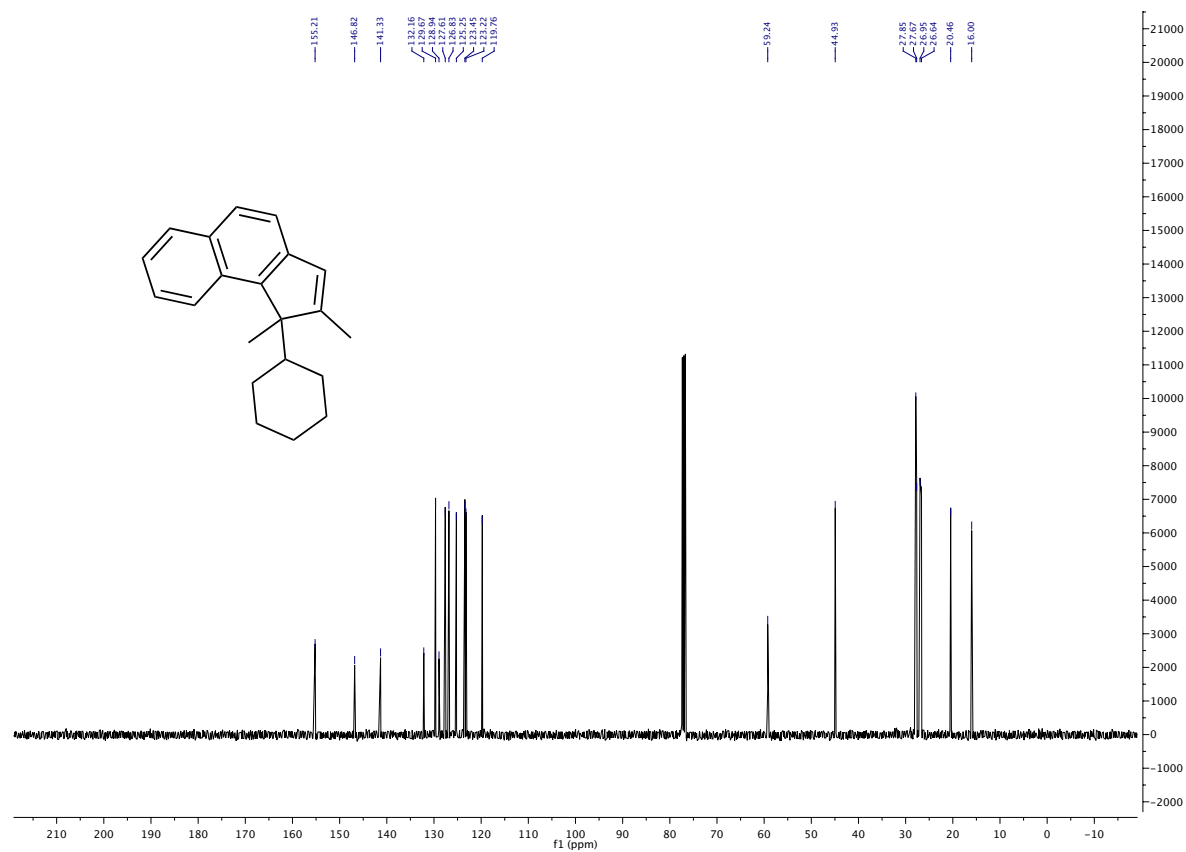
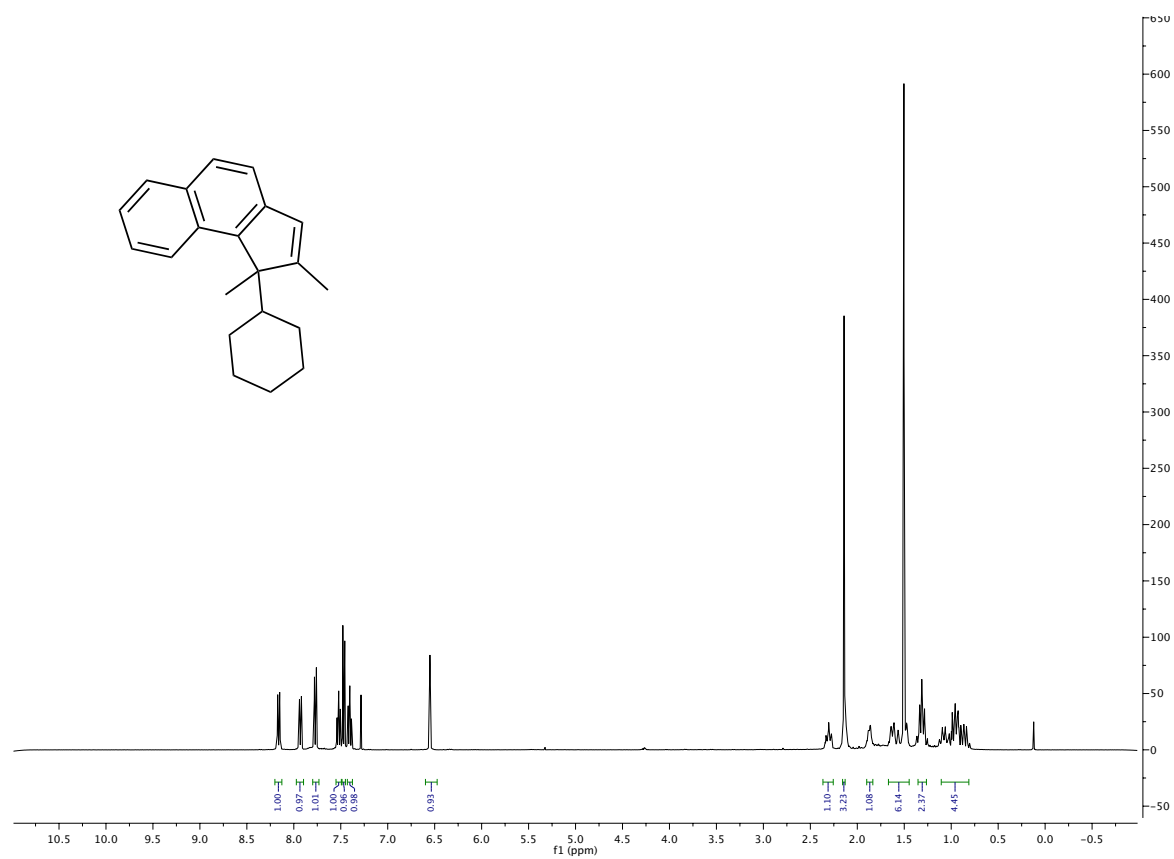
1,1,2-Trimethyl-1*H*-cyclopenta[*a*]naphthalene (6q)



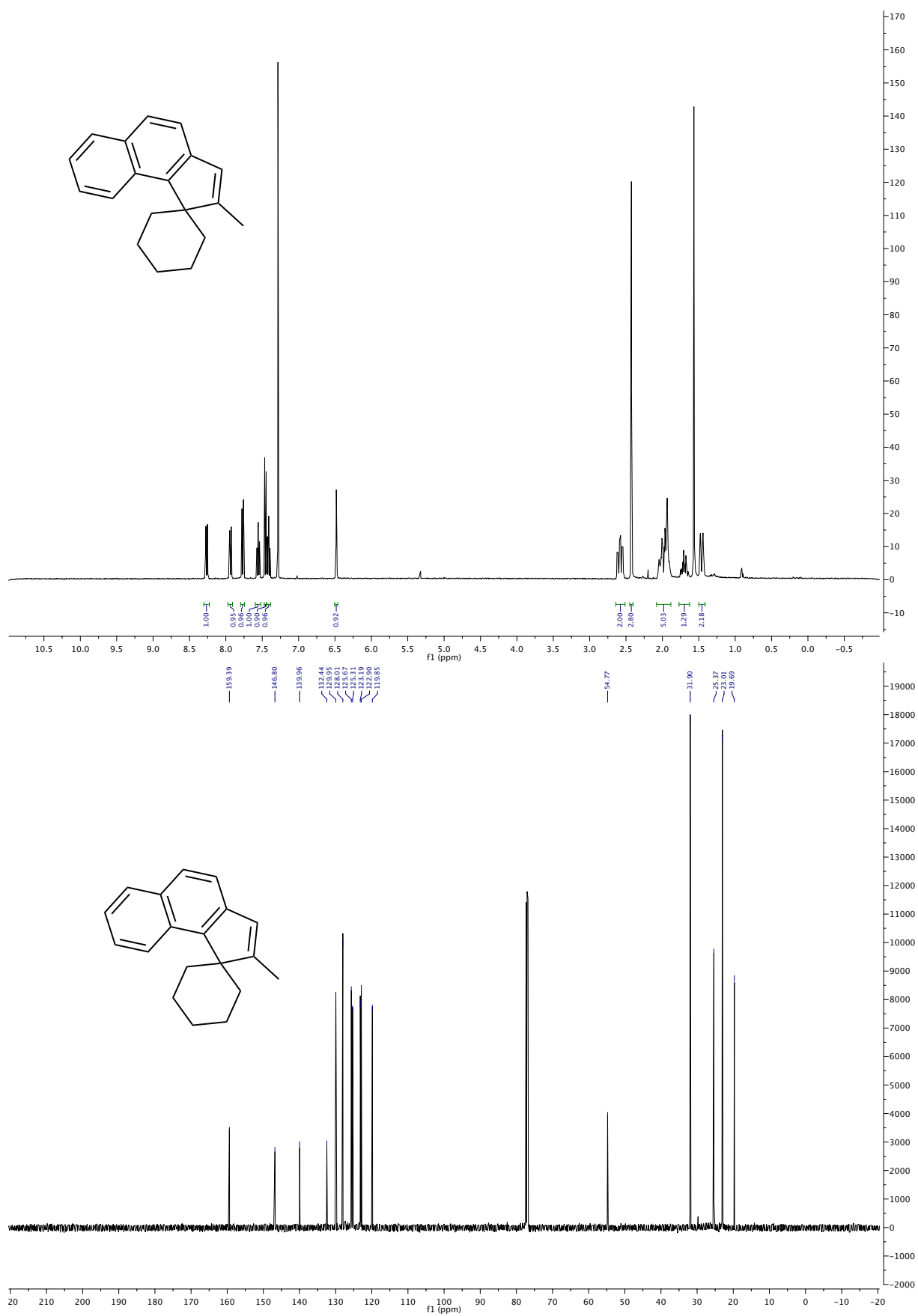
1,2-Dimethyl-1-phenethyl-1*H*-cyclopenta[*a*]naphthalene (6r)



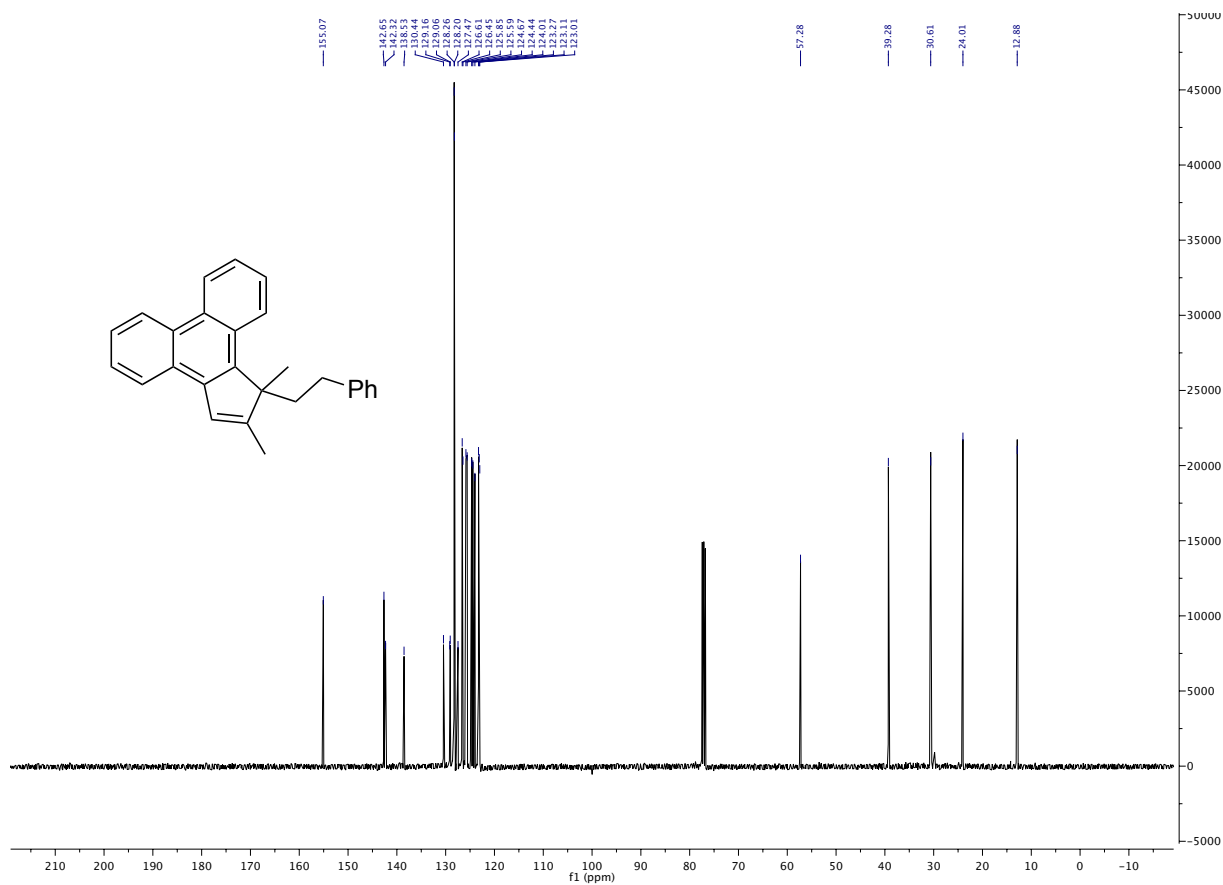
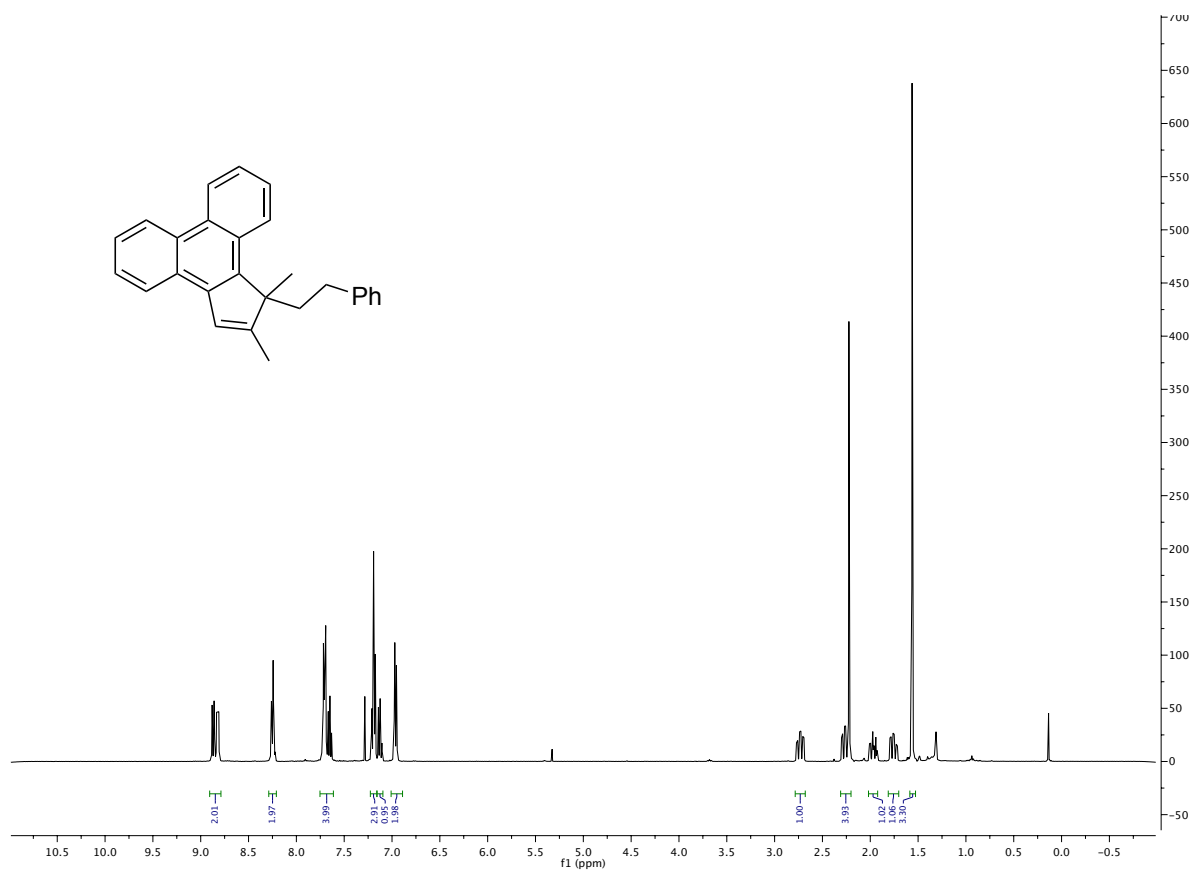
1-Cyclohexyl-1,2-dimethyl-1*H*-cyclopenta[*a*]naphthalene (6s)



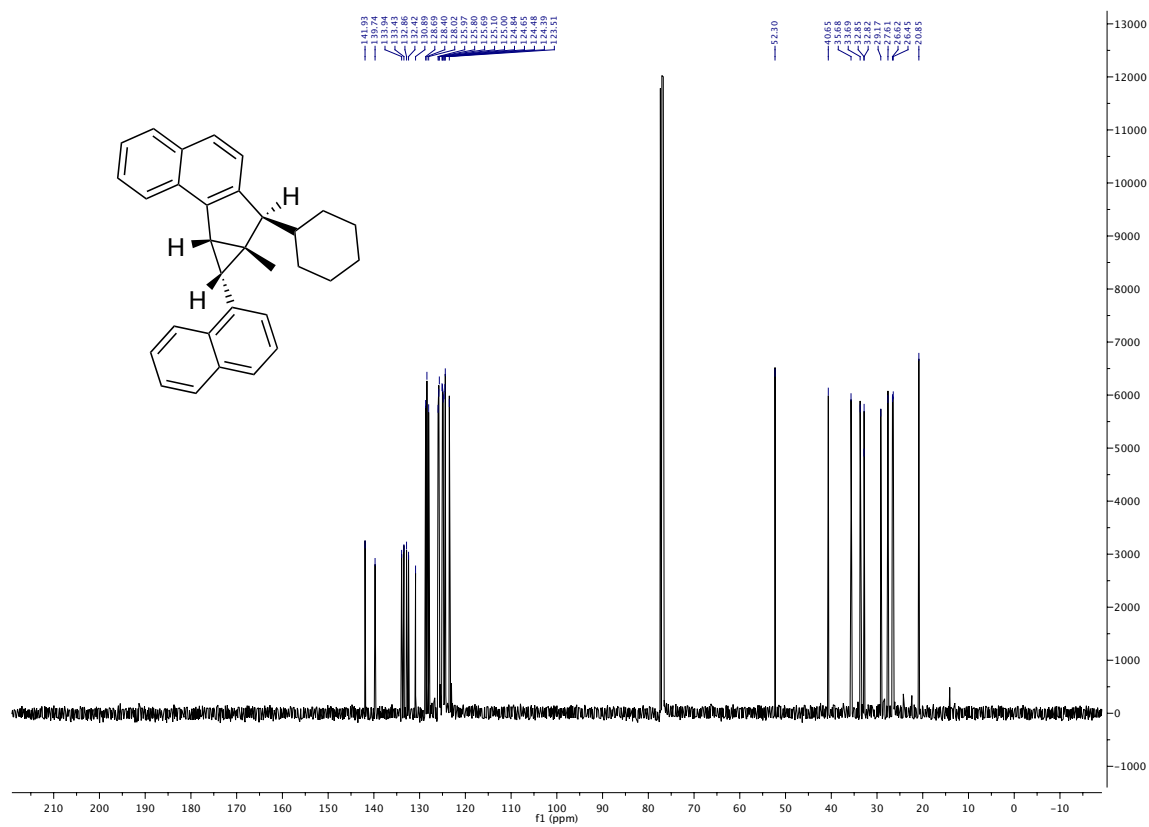
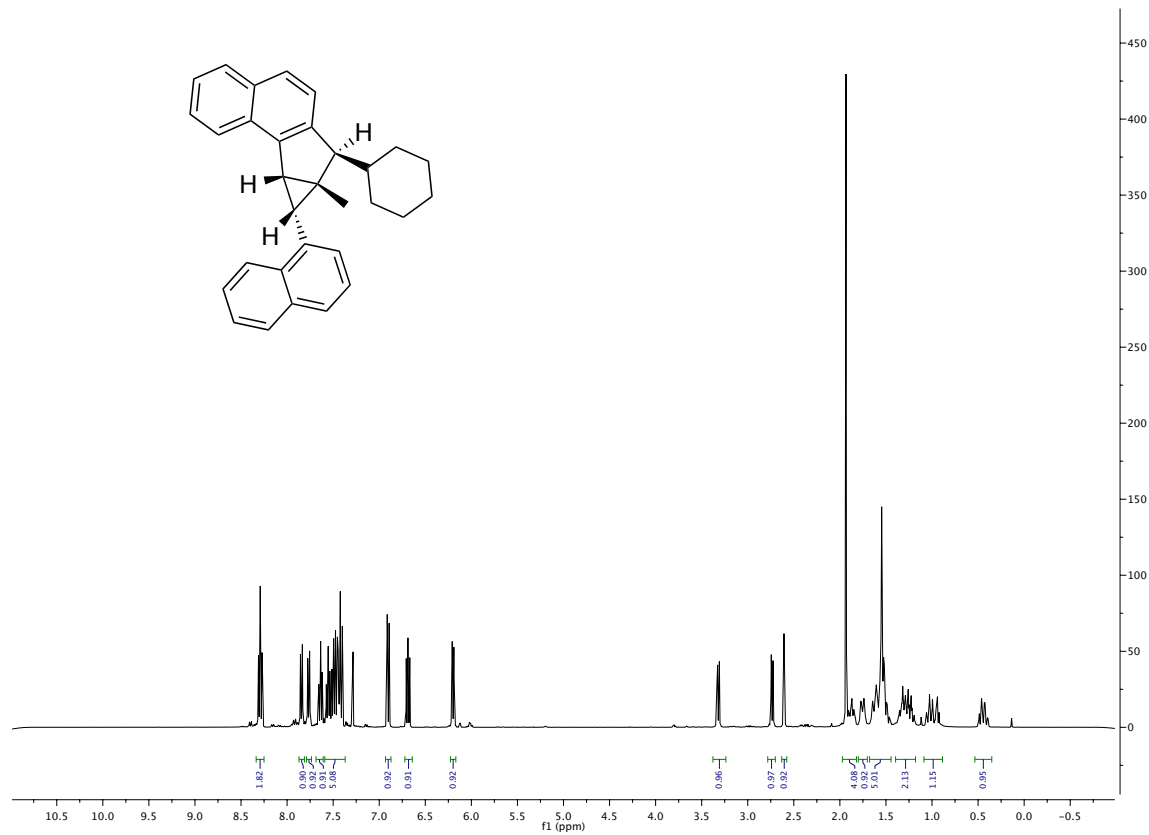
2'-Methylspiro[cyclohexane-1,1'-cyclopenta[a]naphthalene] (6t)



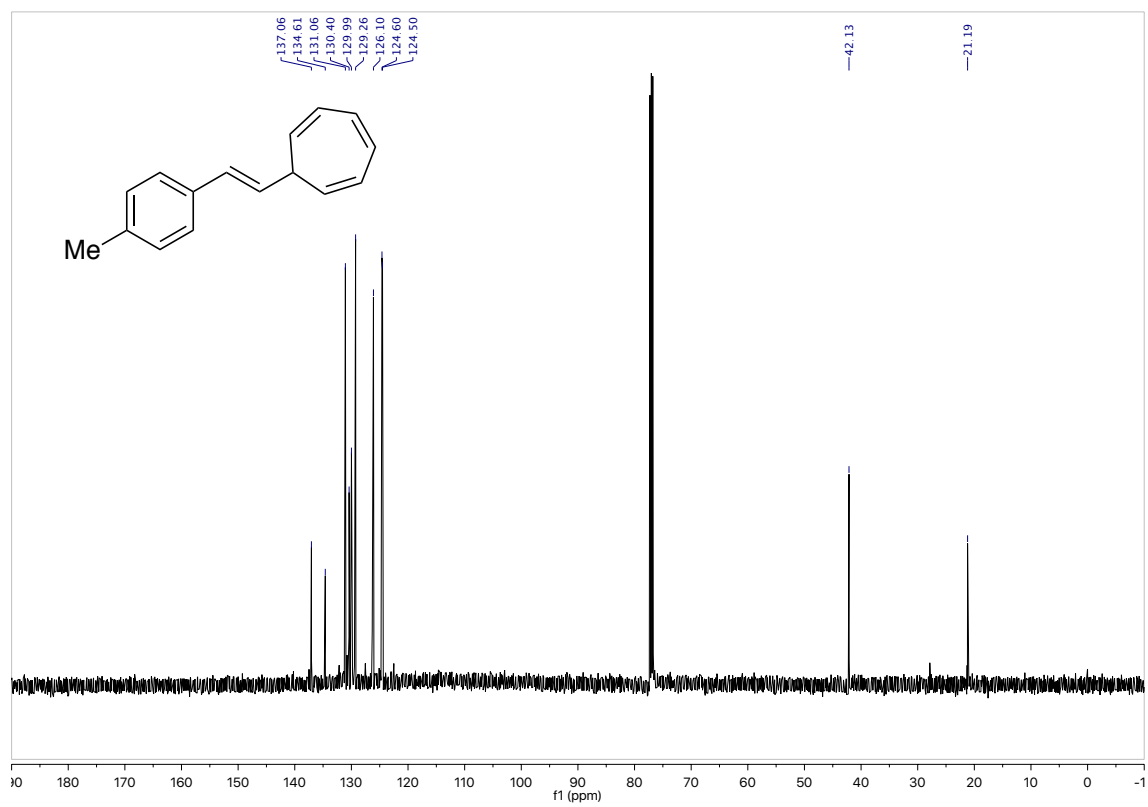
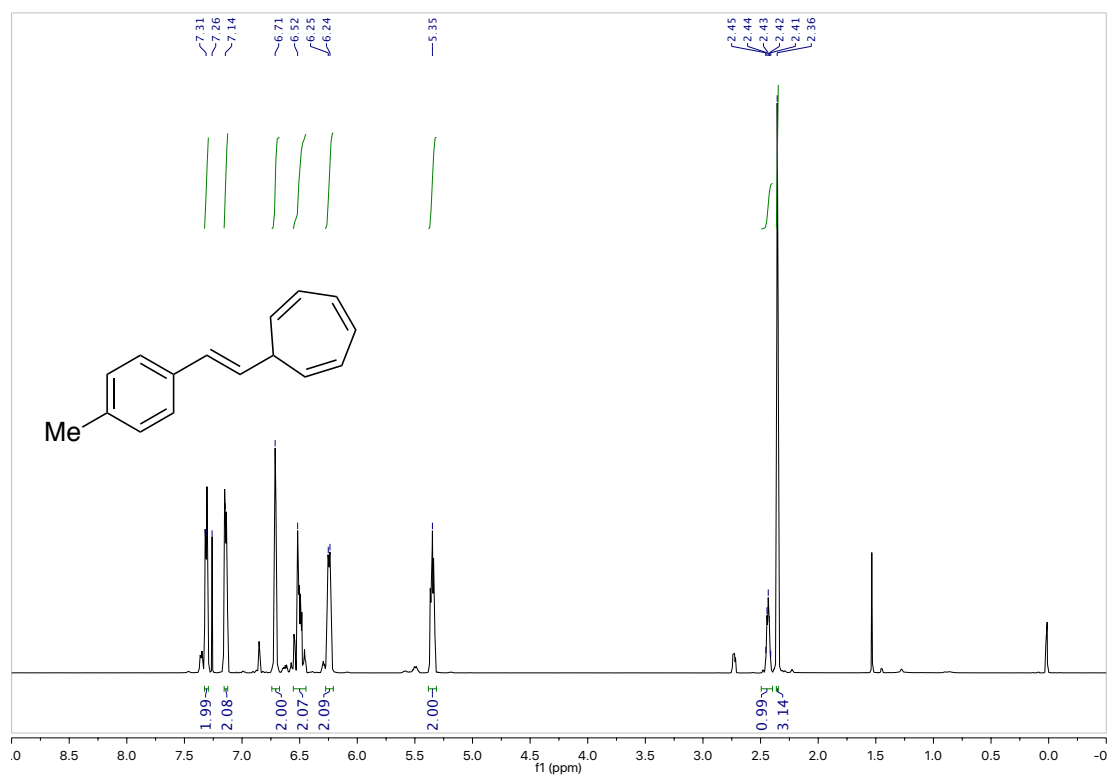
1,2-Dimethyl-1-phenethyl-1*H*-cyclopenta[*l*]phenanthrene (6v)



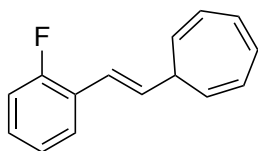
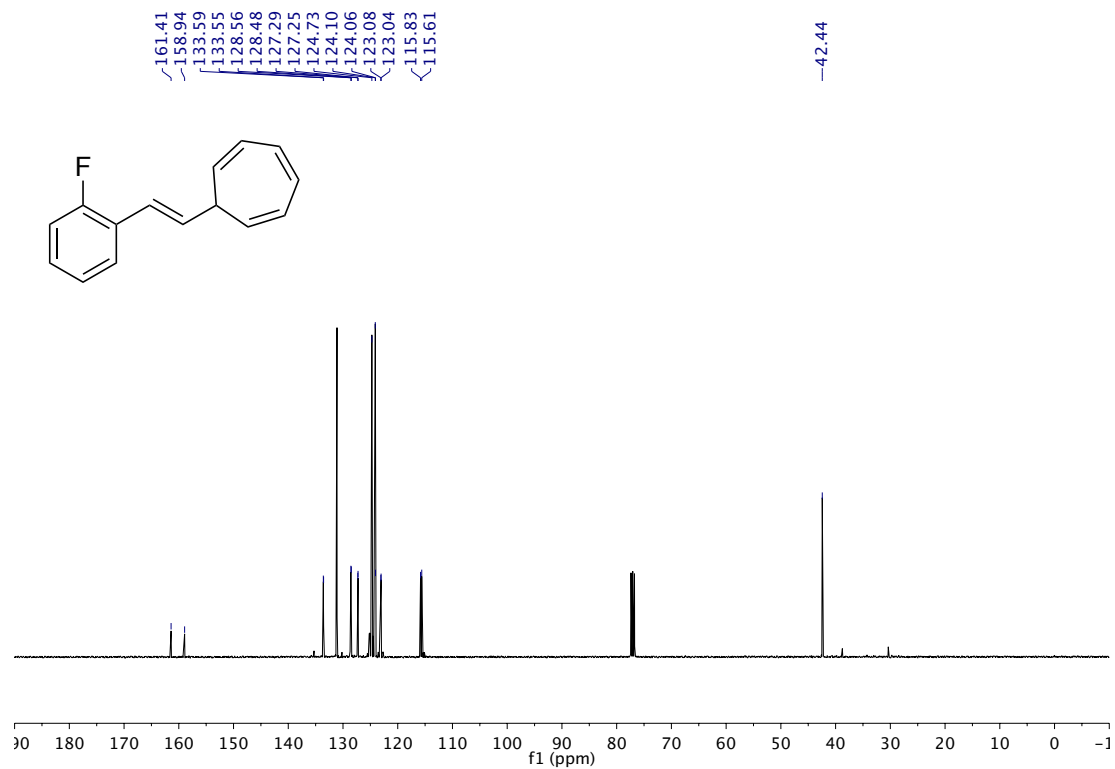
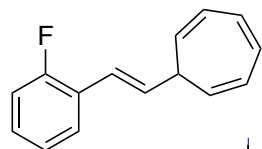
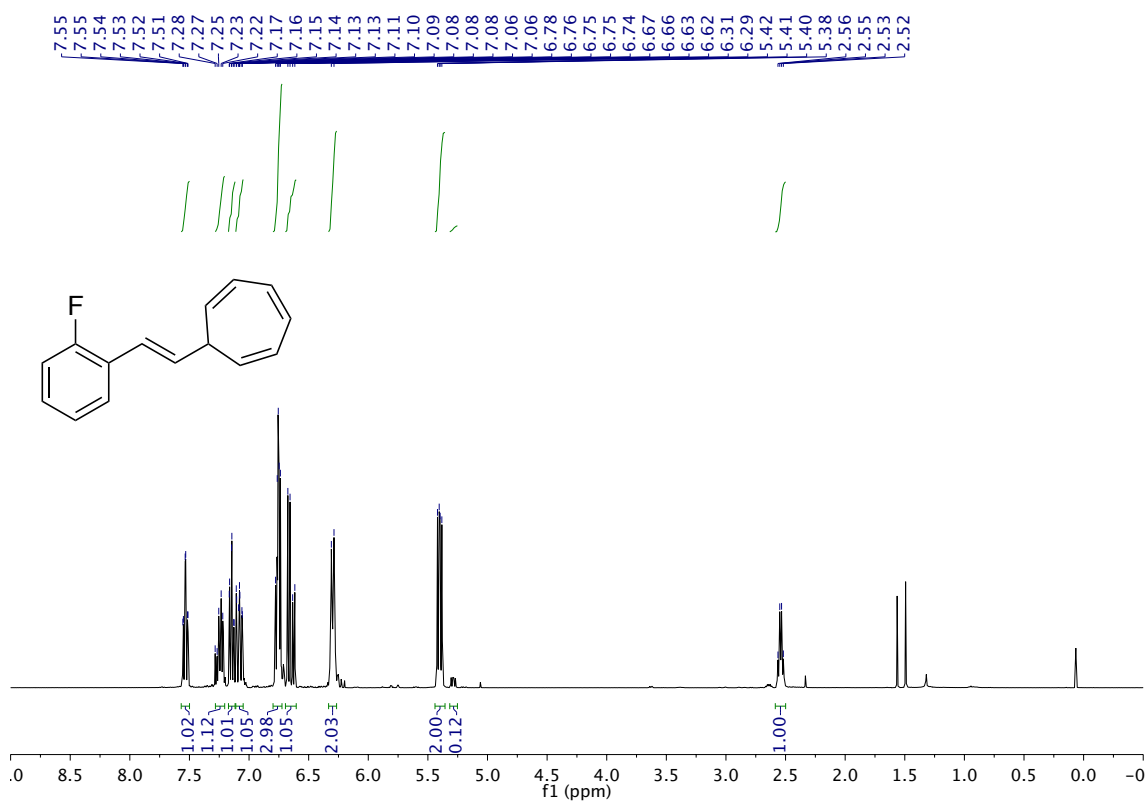
7-Cyclohexyl-7a-methyl-8-(naphthalen-1-yl)-7,7a,8,8a-tetrahydrocyclopropa[4,5]cyclopenta[1,2-*a*]naphthalene (11)



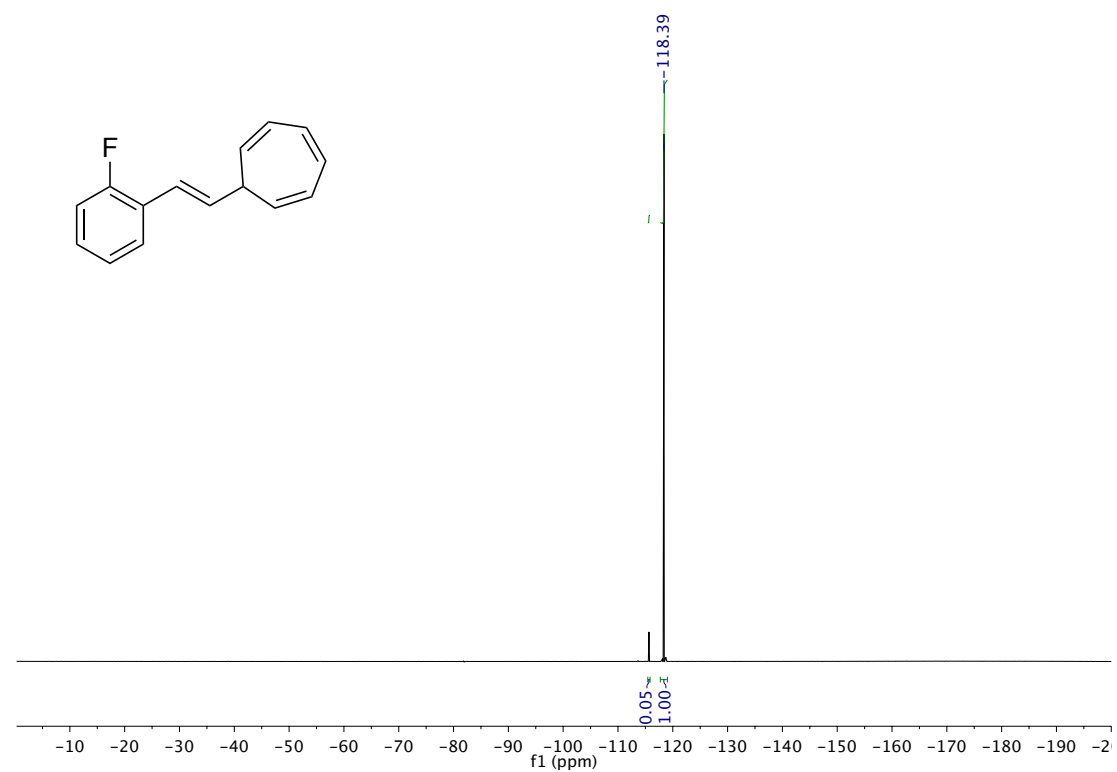
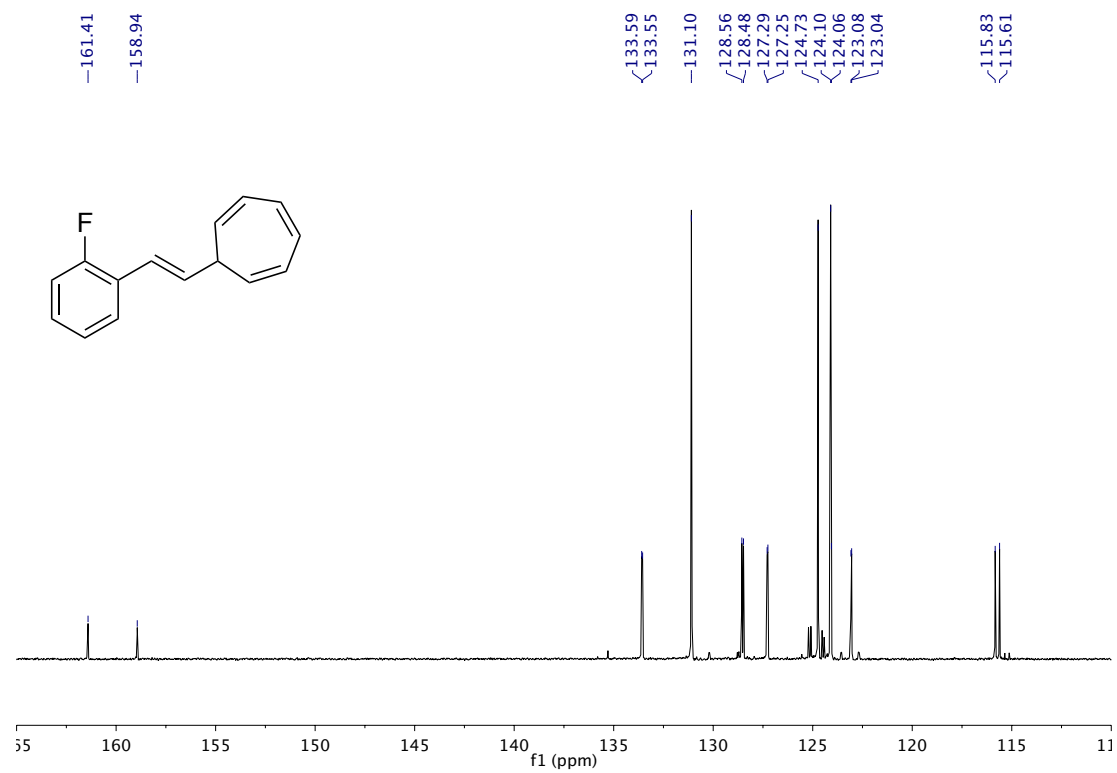
(E)-7-(4-methylstyryl)cyclohepta-1,3,5-triene (2b)



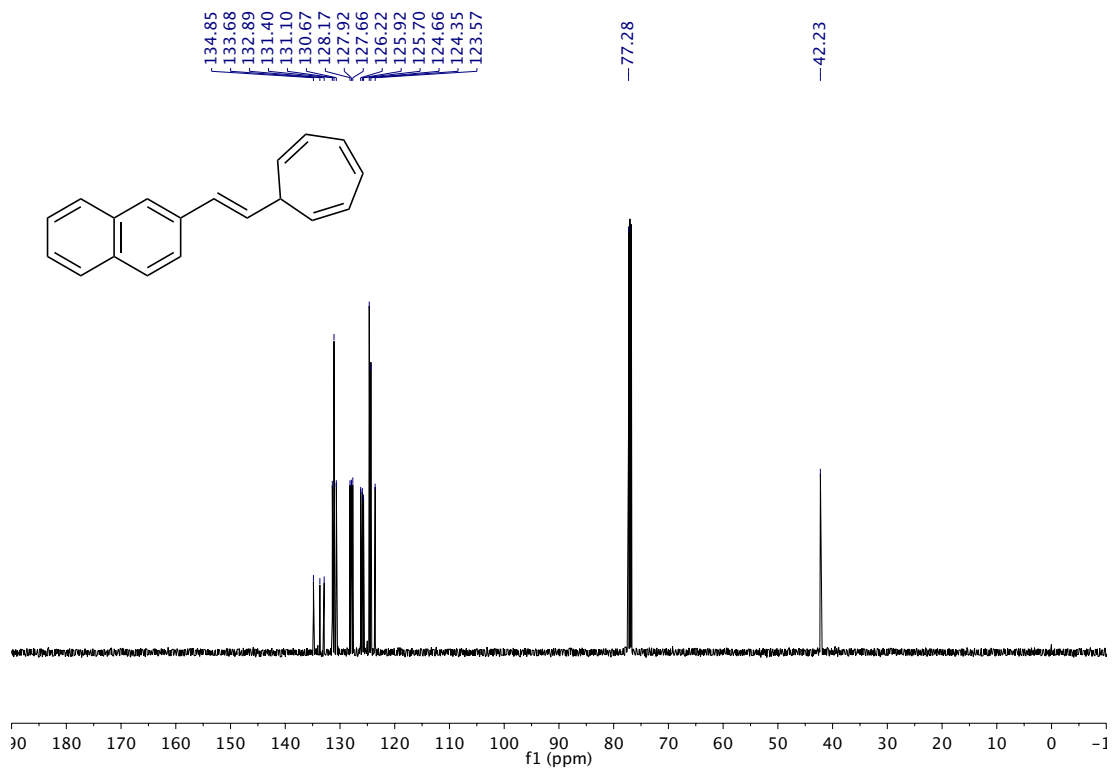
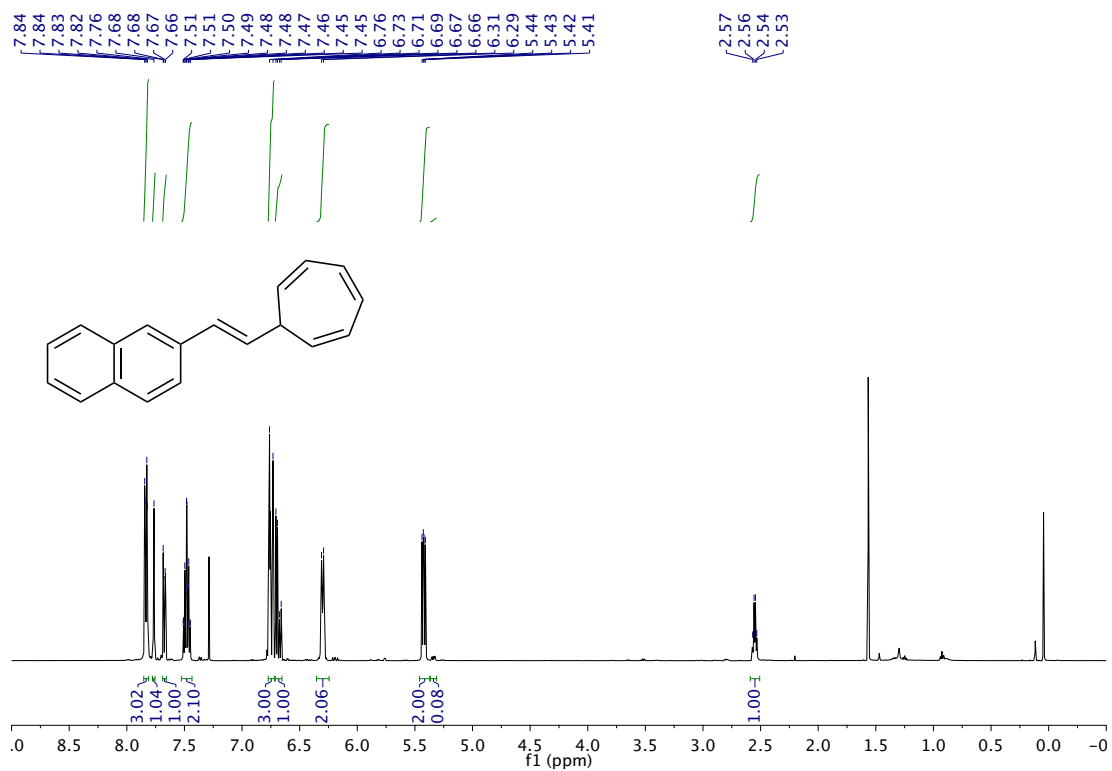
(E)-7-(2-Fluorostyryl)cyclohepta-1,3,5-triene (2f)



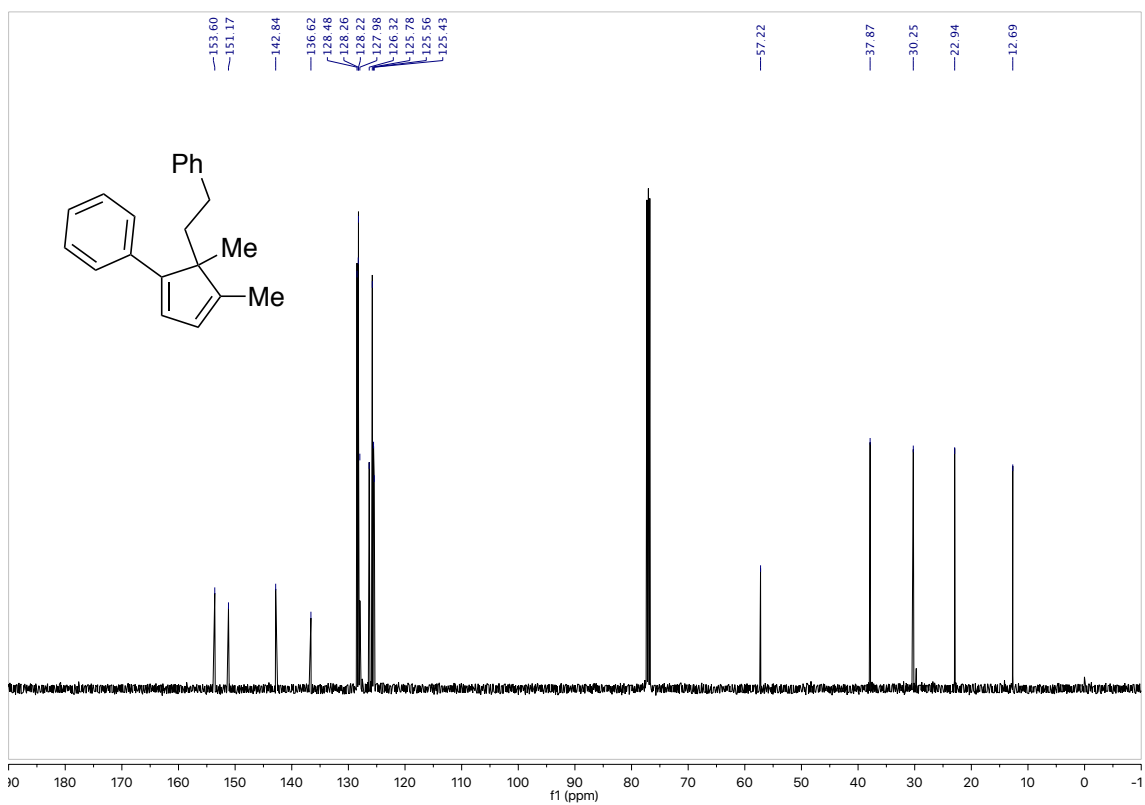
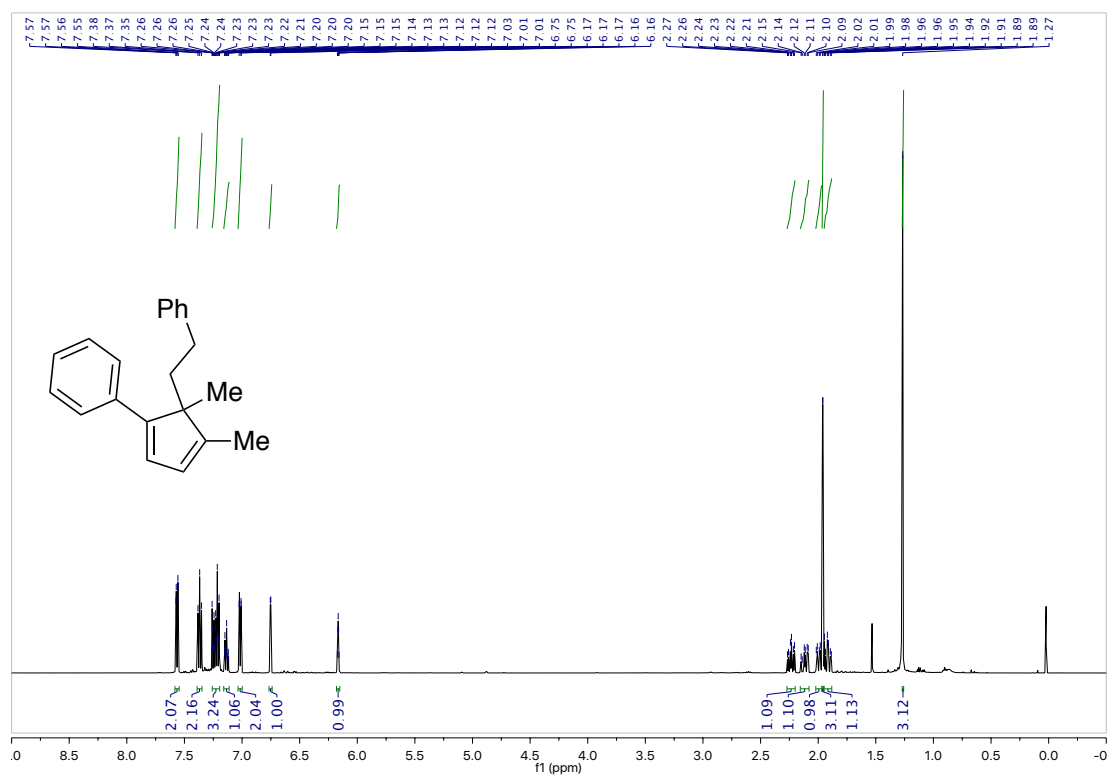
¹³C NMR Detail and ¹⁹F NMR



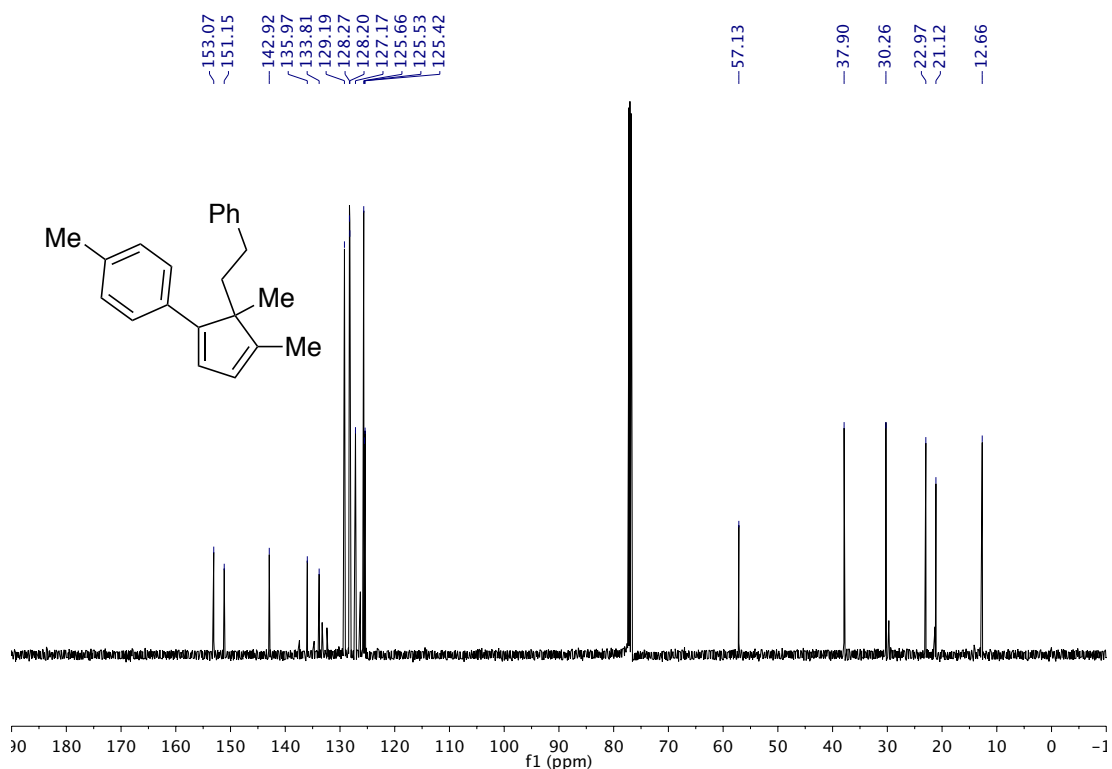
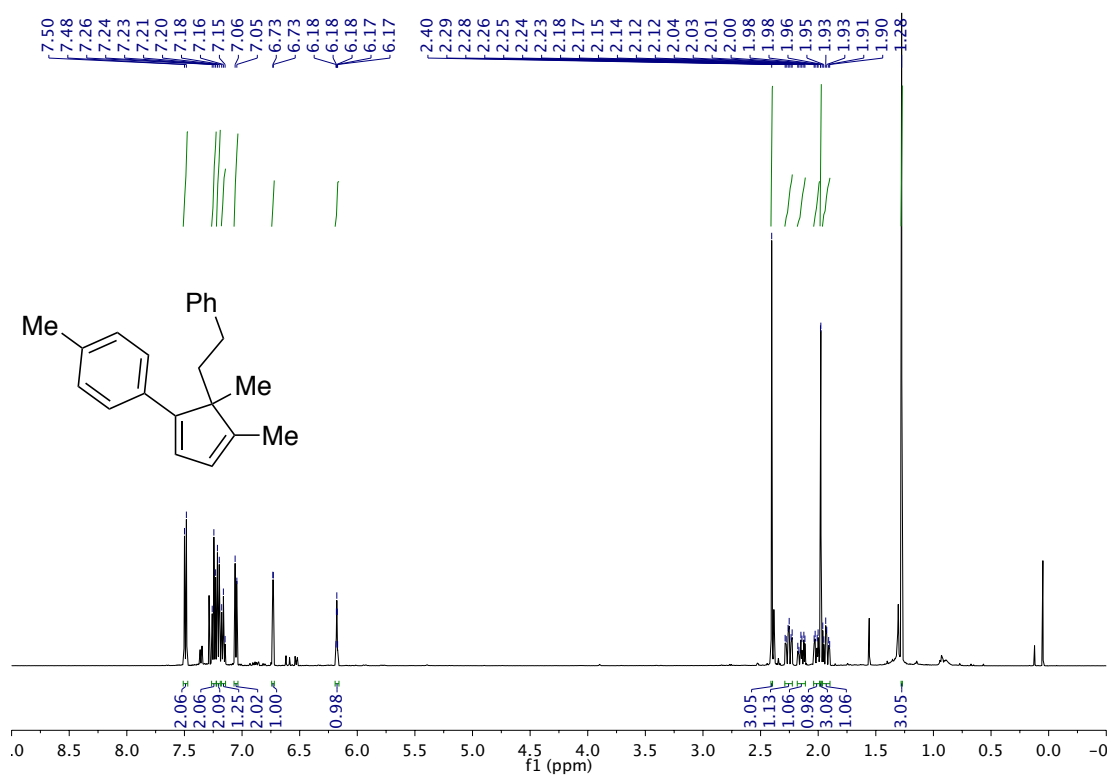
(E)-2-(2-(cyclohepta-2,4,6-trien-1-yl)vinyl)naphthalene (2g)



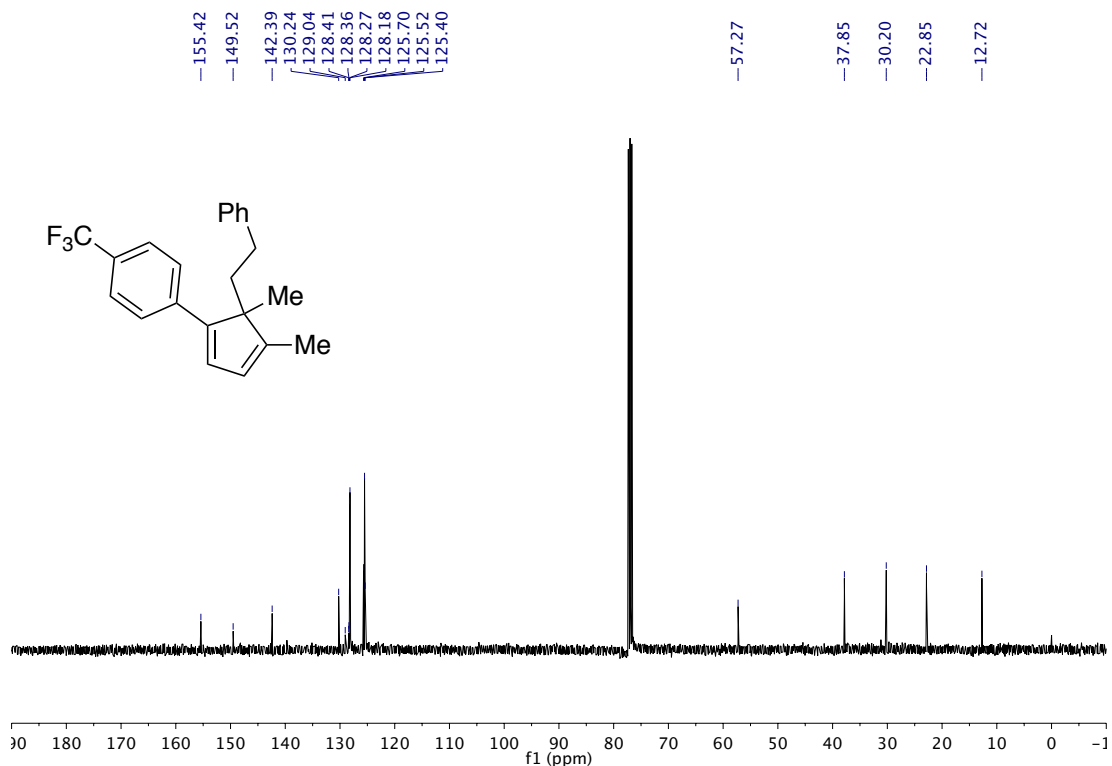
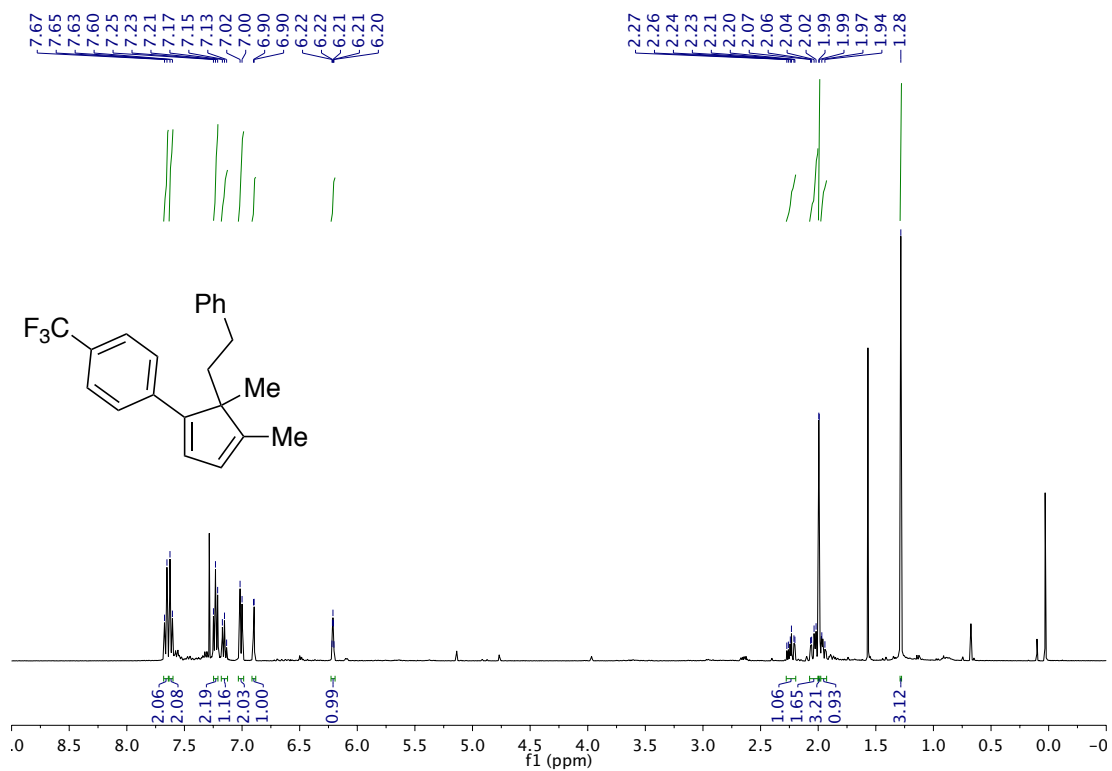
(4,5-dimethyl-5-phenethylcyclopenta-1,3-dien-1-yl)benzene (7a)



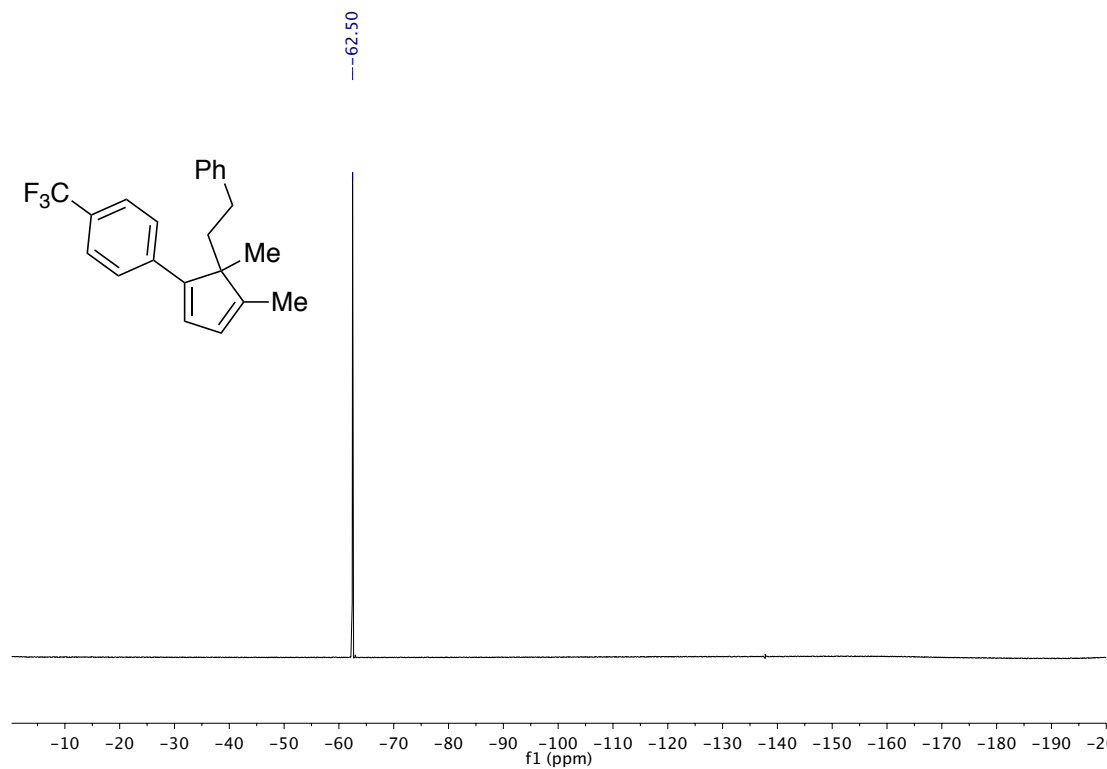
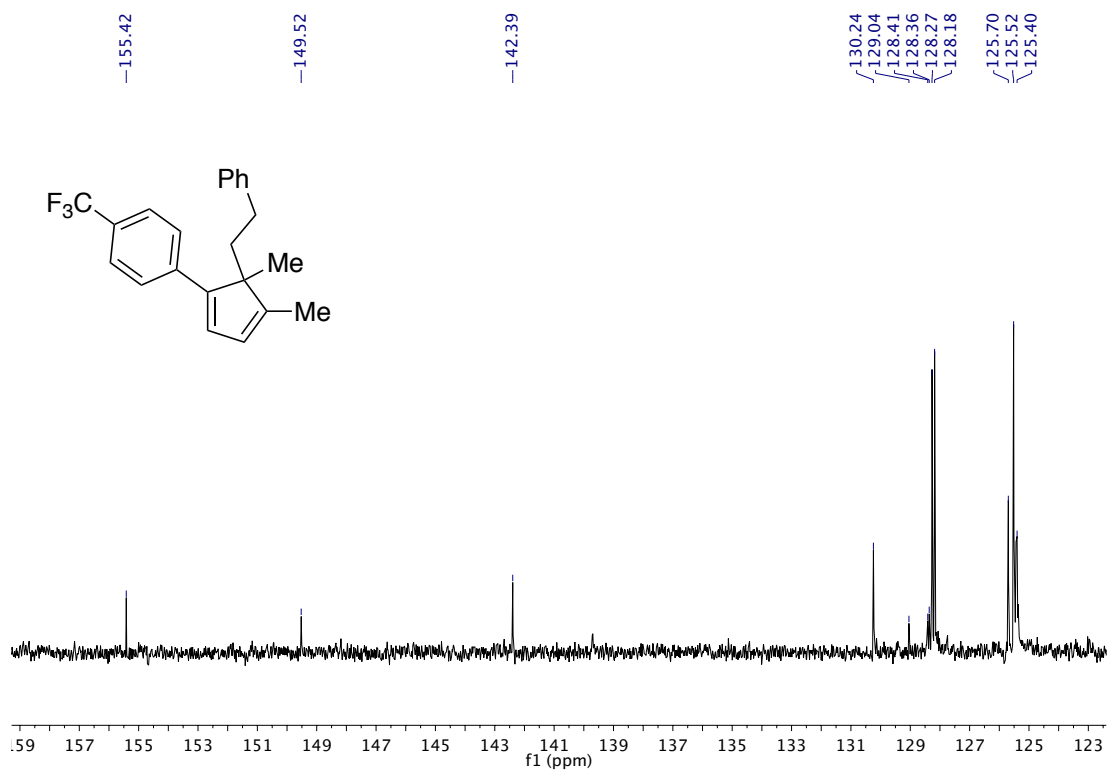
1-(4,5-dimethyl-5-phenethylcyclopenta-1,3-dien-1-yl)-4-methylbenzene (7b)



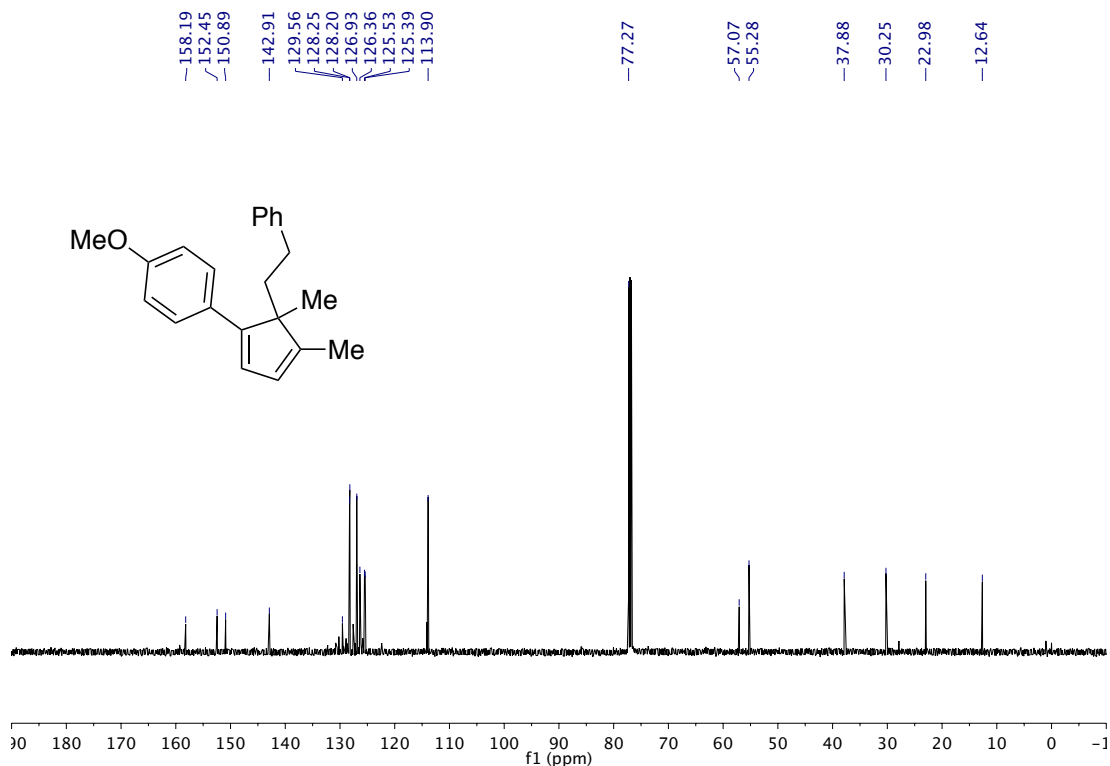
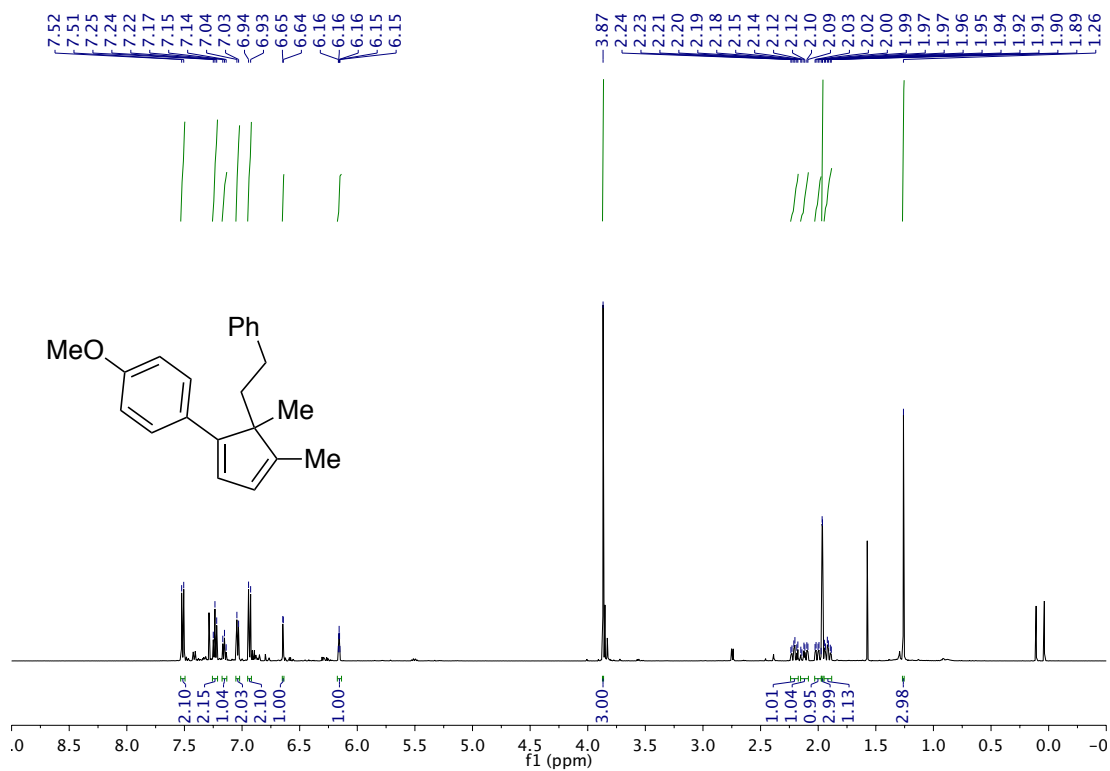
(4,5-dimethyl-5-phenethylcyclopenta-1,3-dien-1-yl)-4-(trifluoromethyl)benzene (7c)



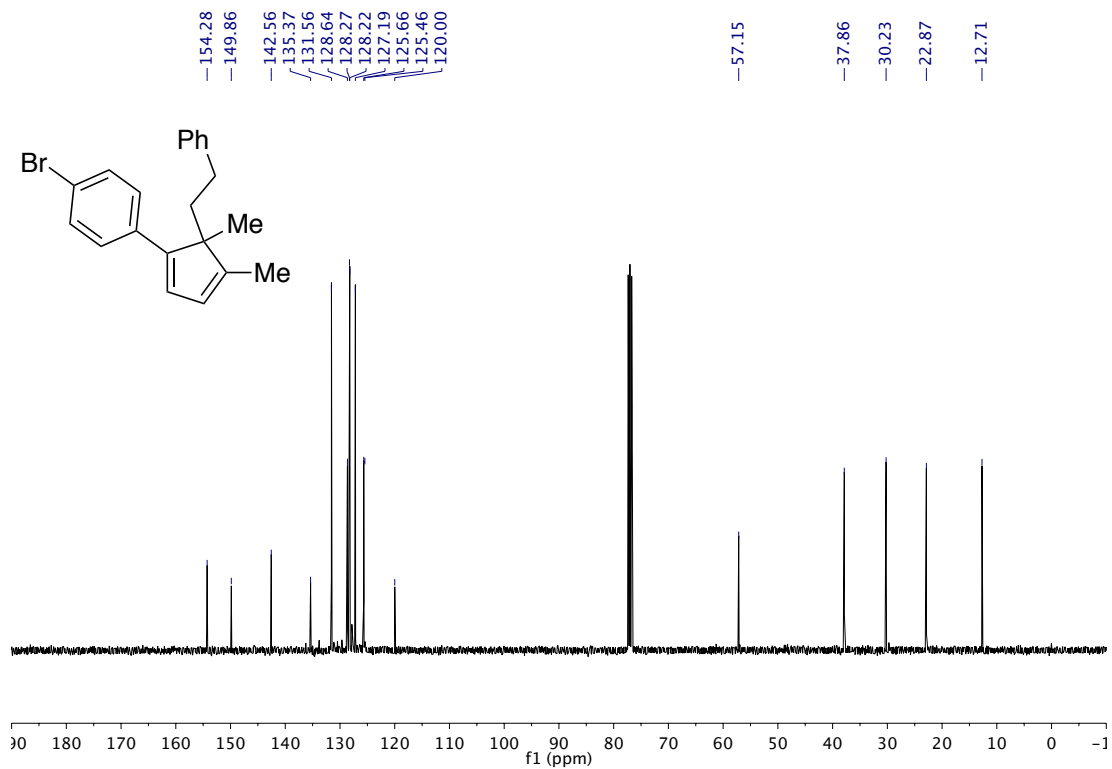
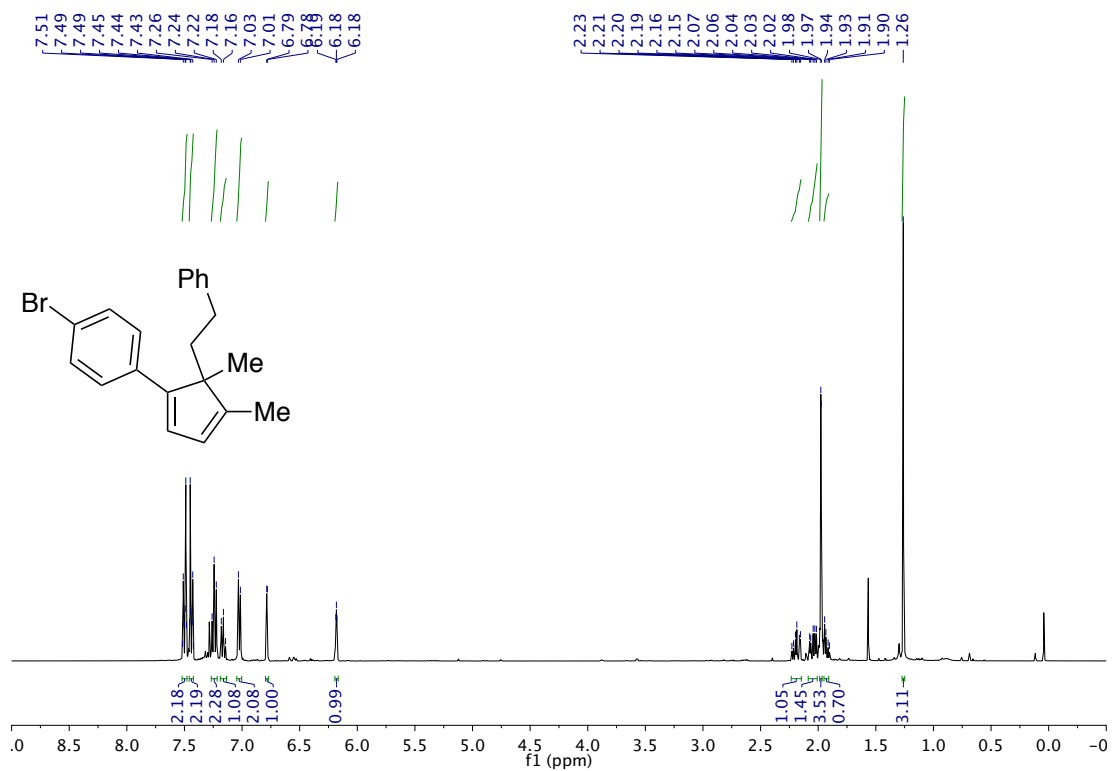
¹³C NMR Detail and ¹⁹F NMR



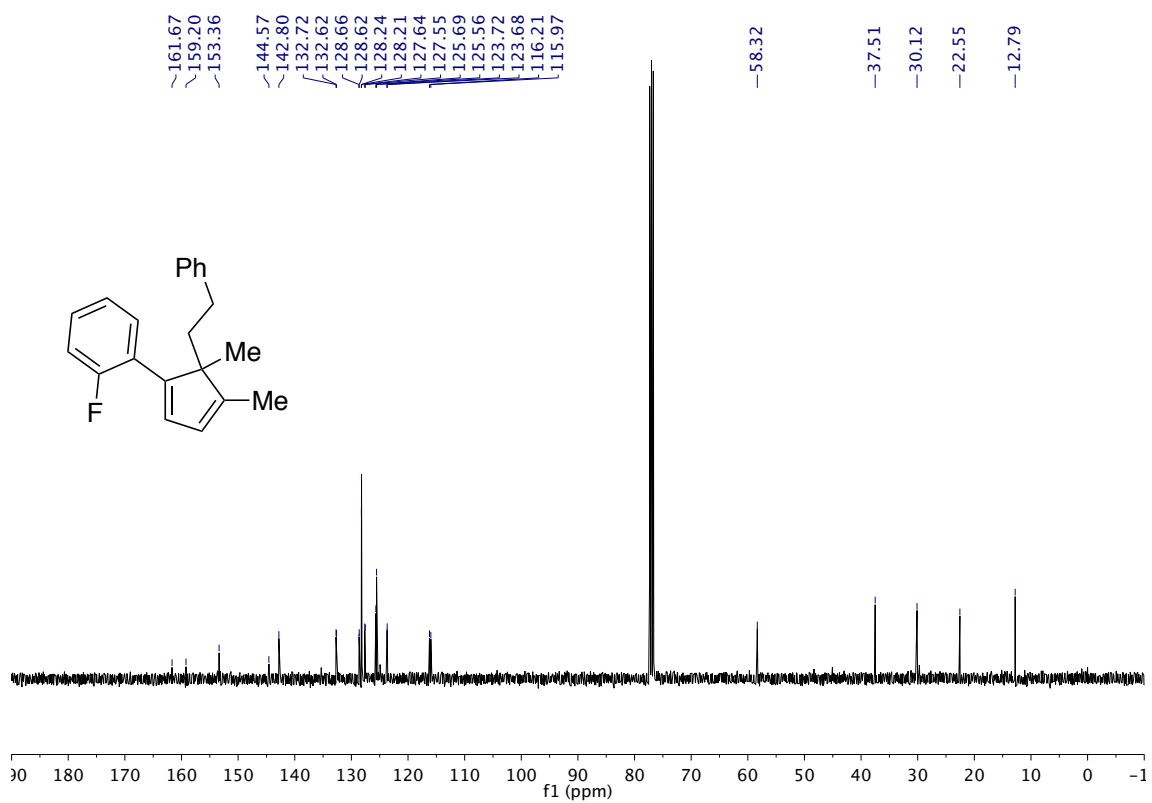
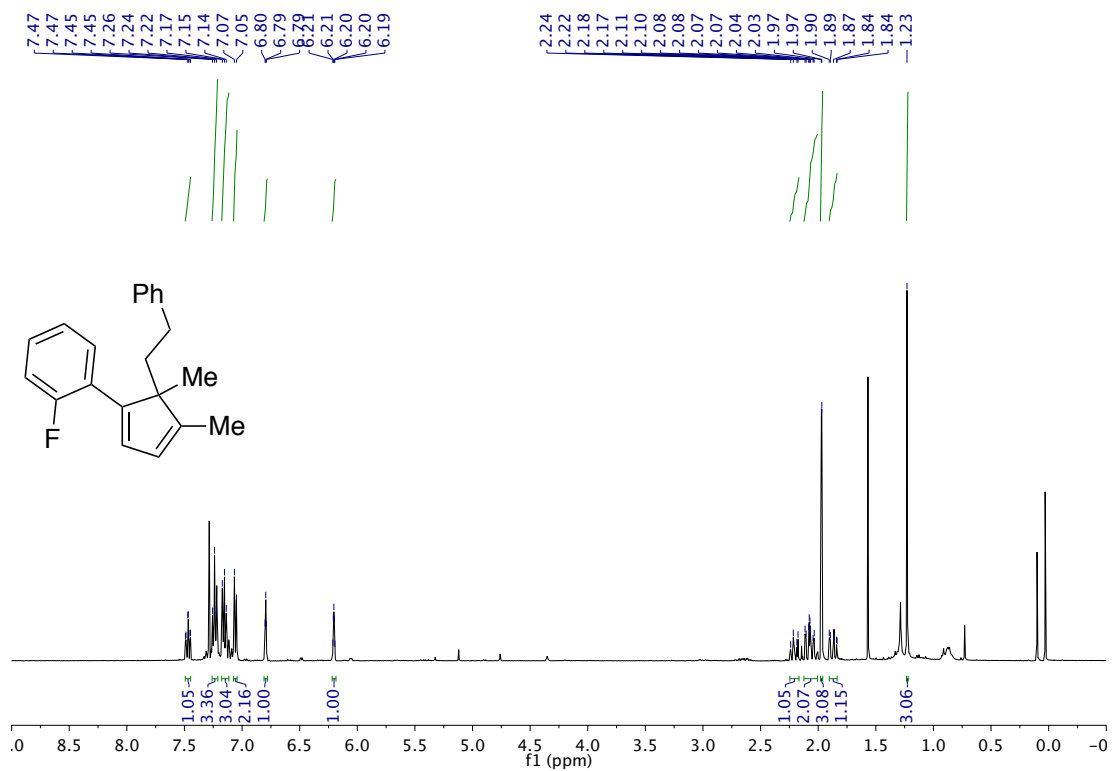
1-(4,5-dimethyl-5-phenethylcyclopenta-1,3-dien-1-yl)-4-methoxybenzene (7d)



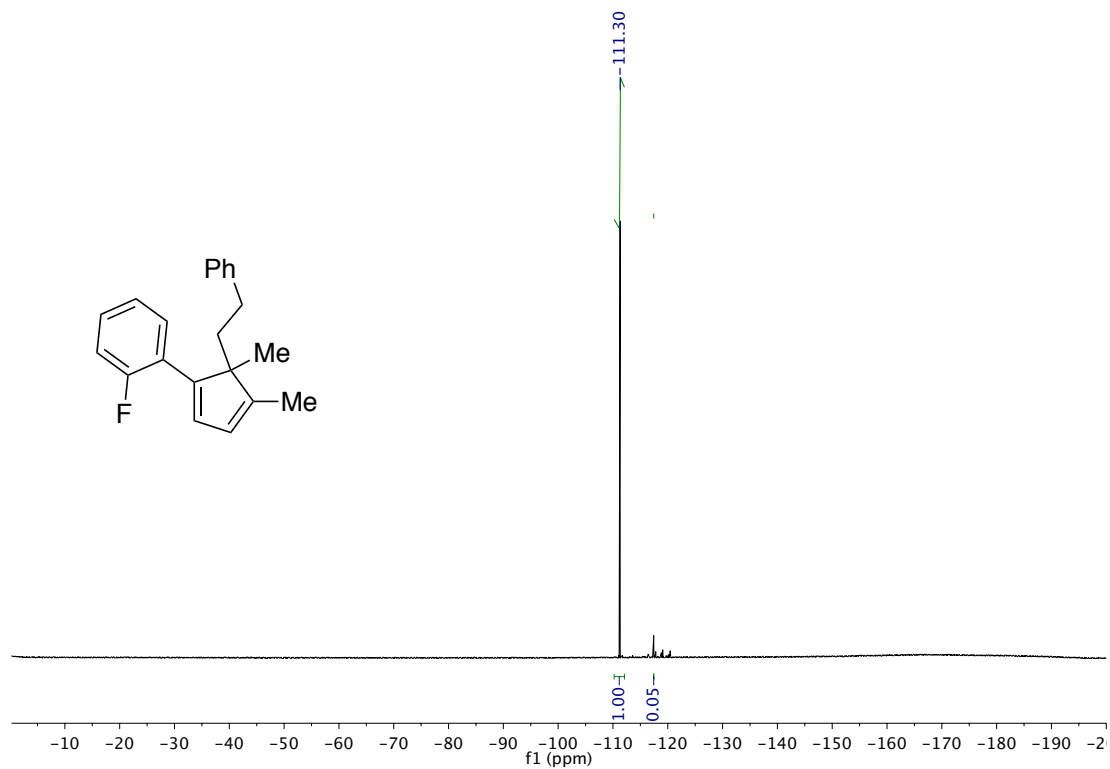
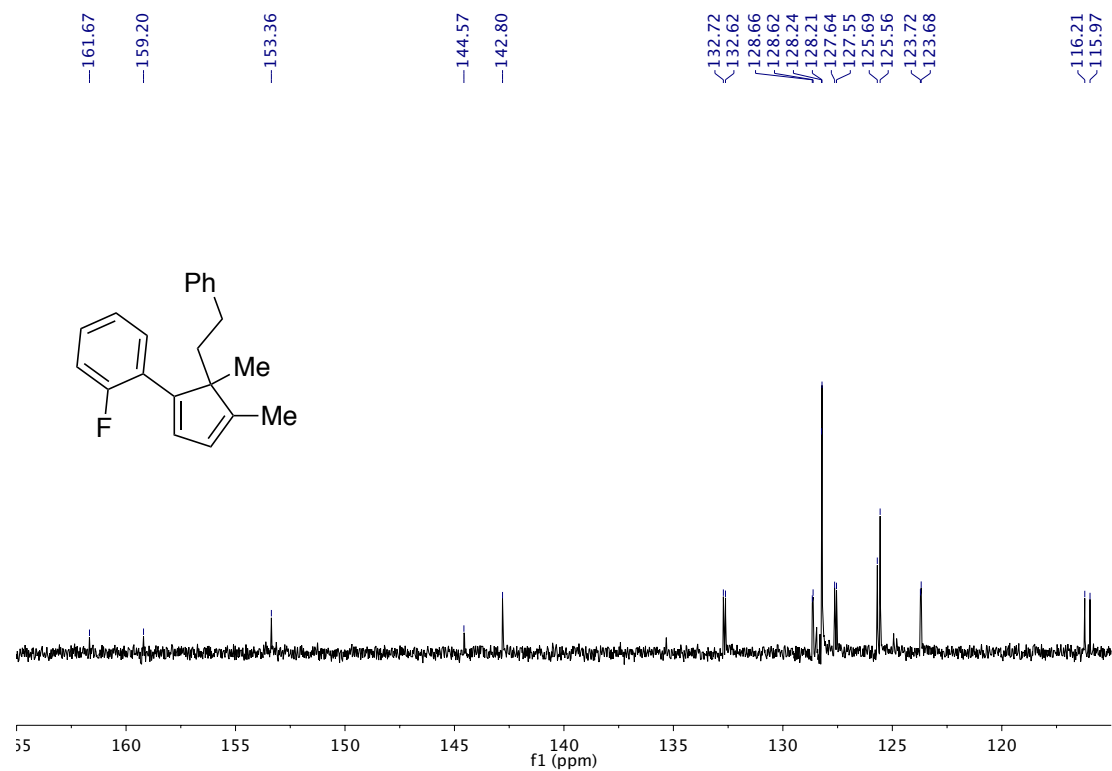
1-bromo-4-(4,5-dimethyl-5-phenethylcyclopenta-1,3-dien-1-yl)-benzene (7e)



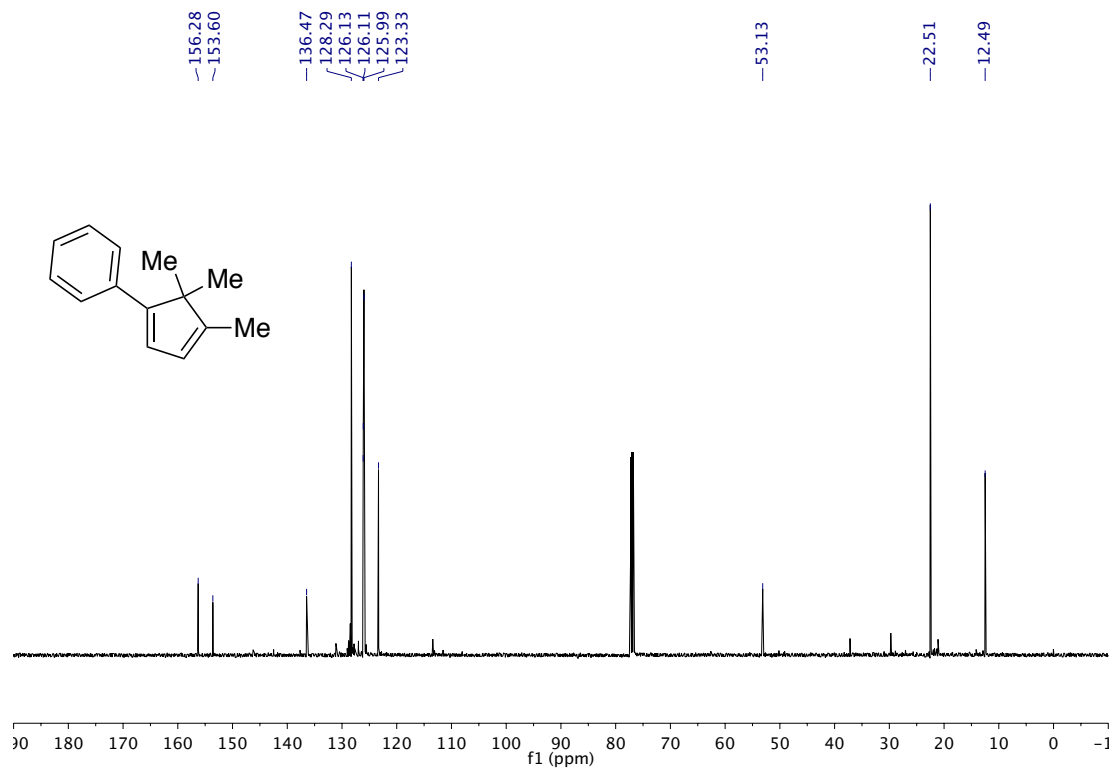
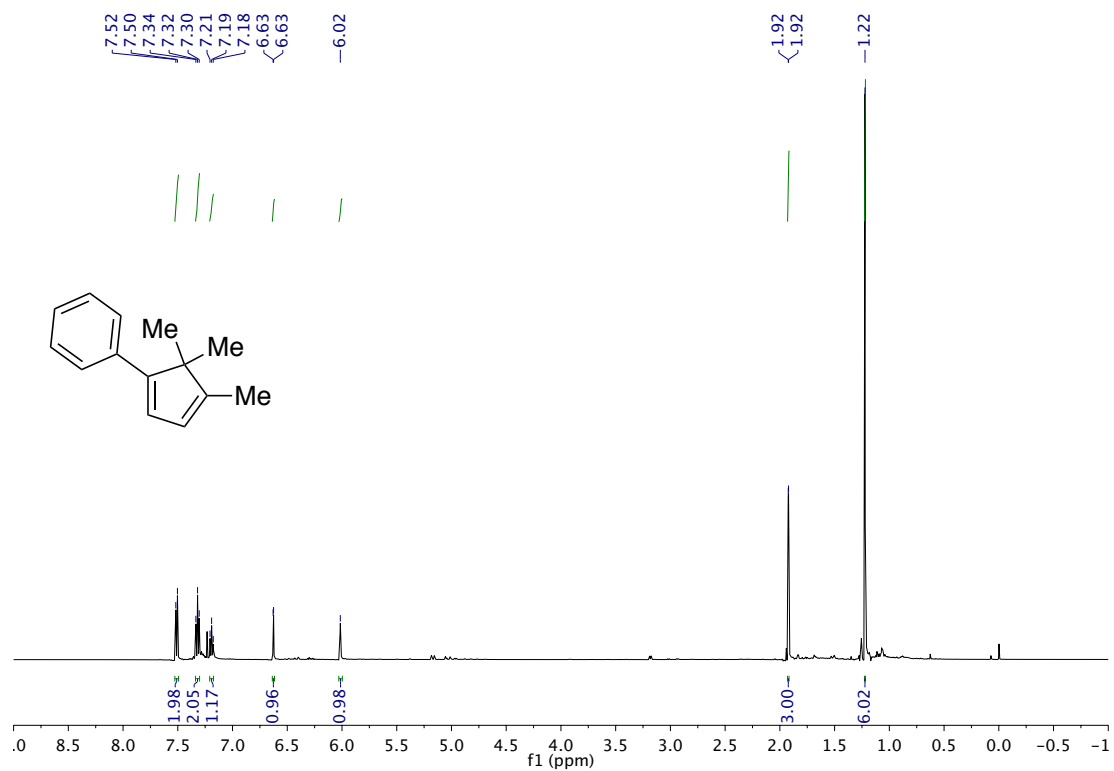
1-(4,5-dimethyl-5-phenethylcyclopenta-1,3-dien-1-yl)-2-fluorobenzene (7f)



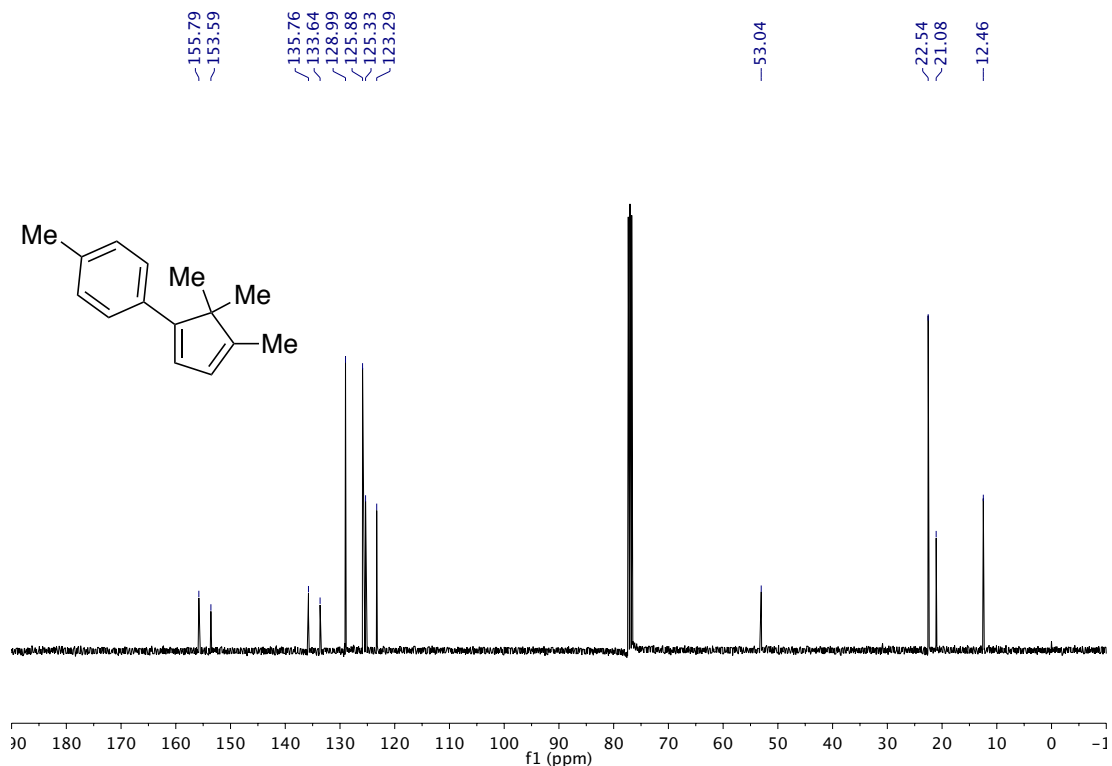
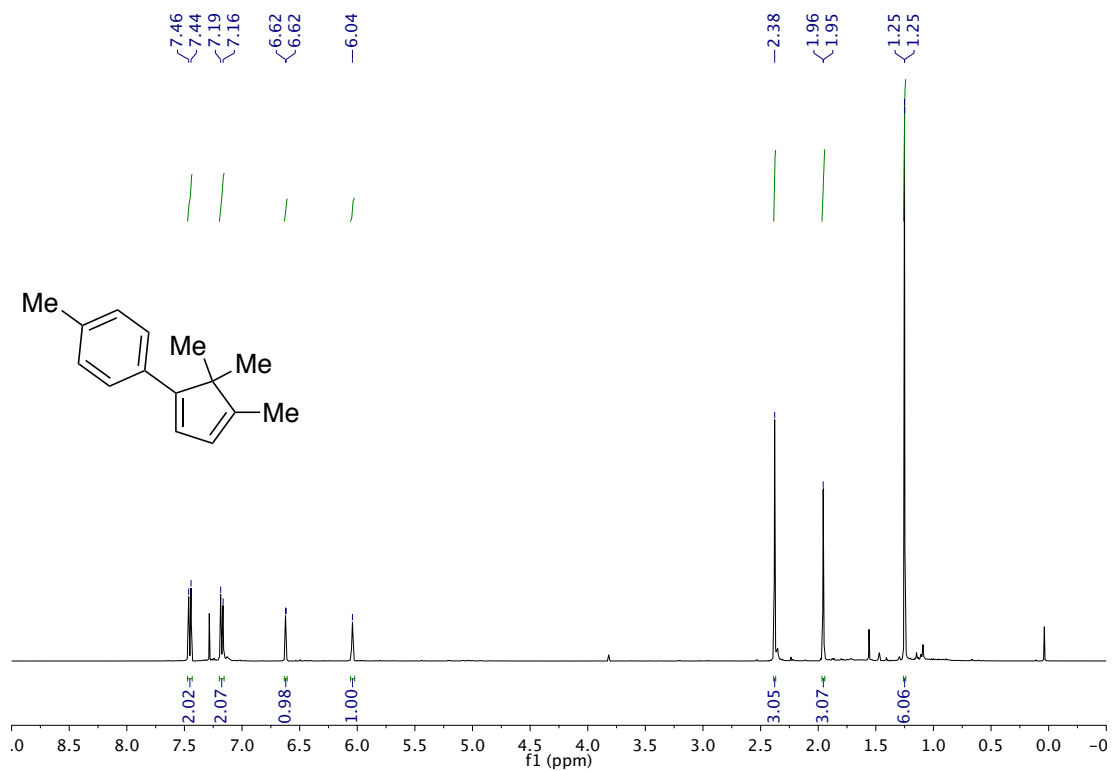
¹³C NMR Detail and ¹⁹F NMR



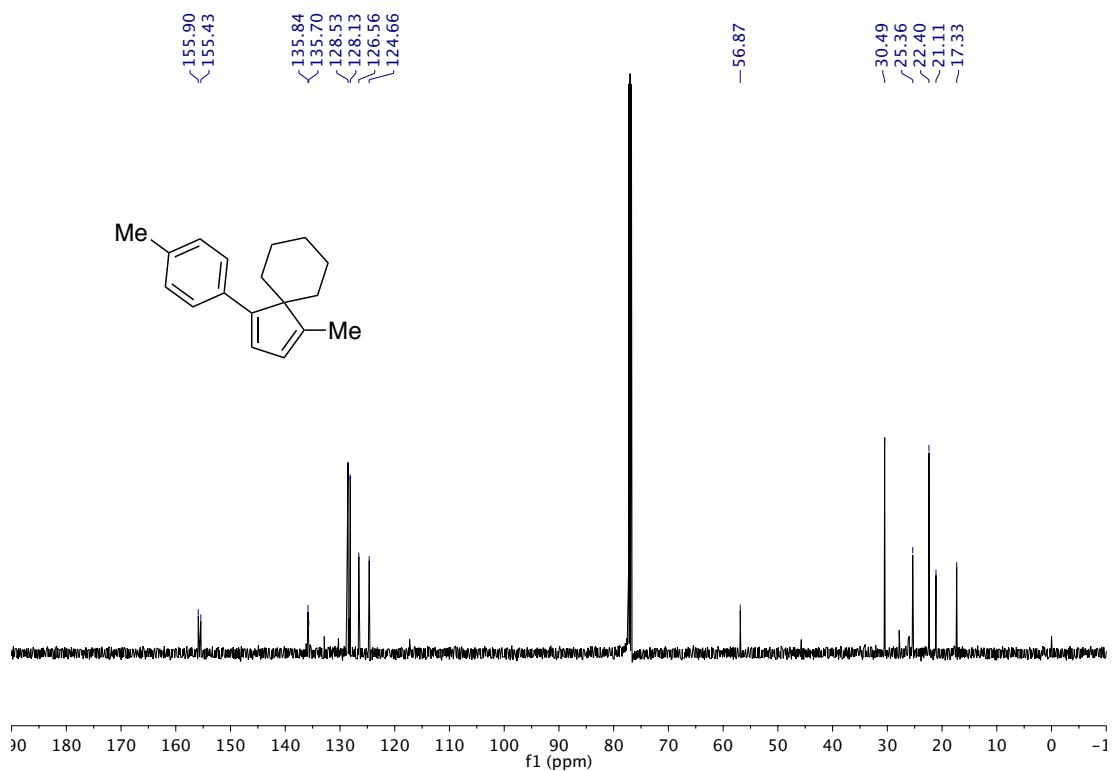
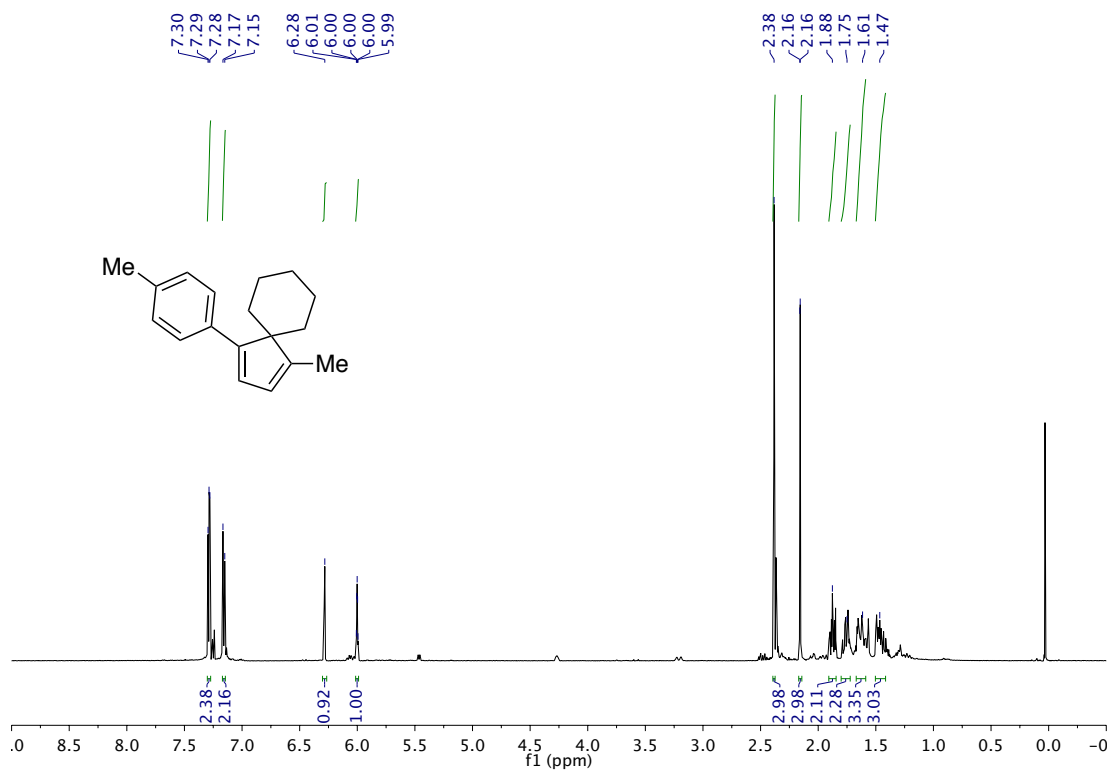
(4,5,5-trimethylcyclopenta-1,3-dien-1-yl)benzene (7g)



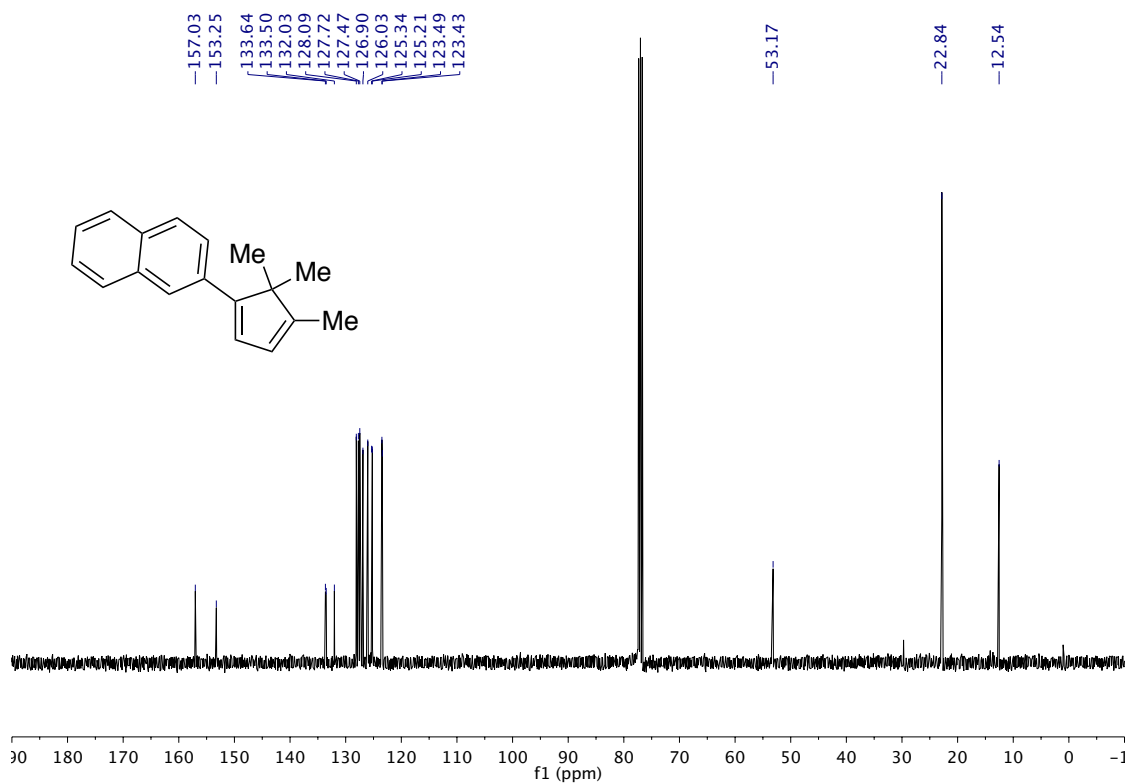
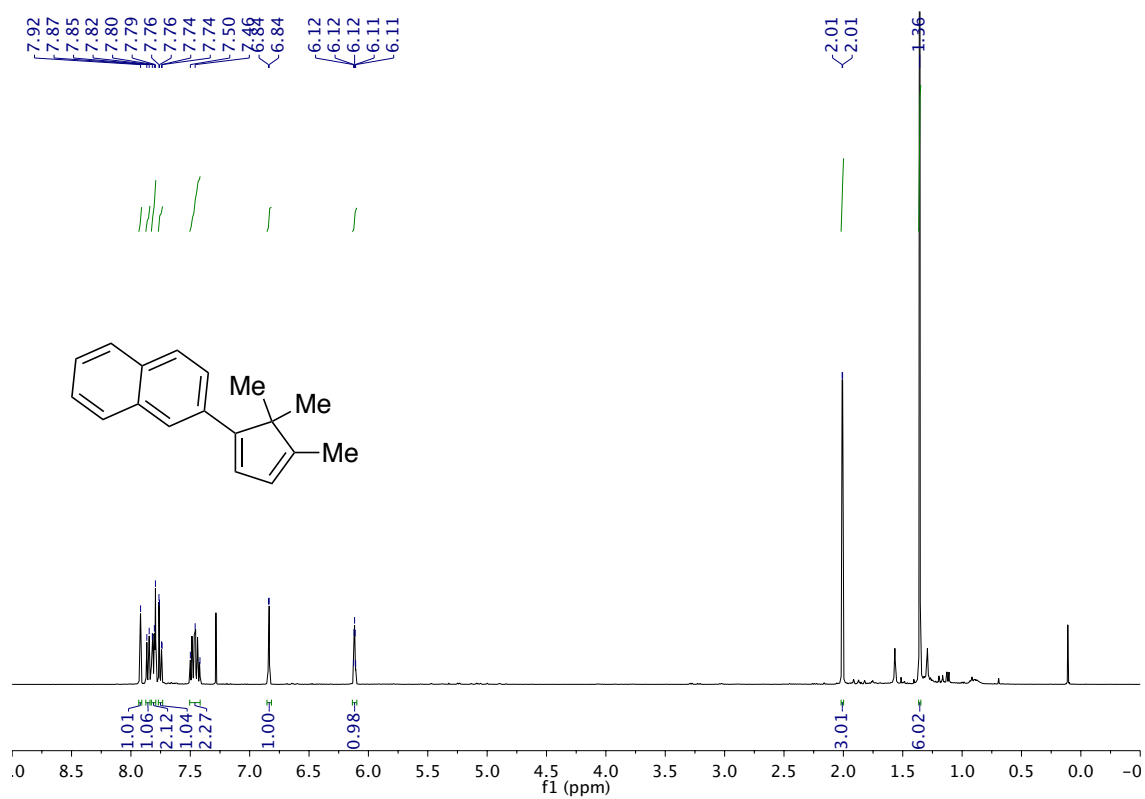
1-methyl-4-(4,5,5-trimethylcyclopenta-1,3-dien-1-yl)benzene (7h)



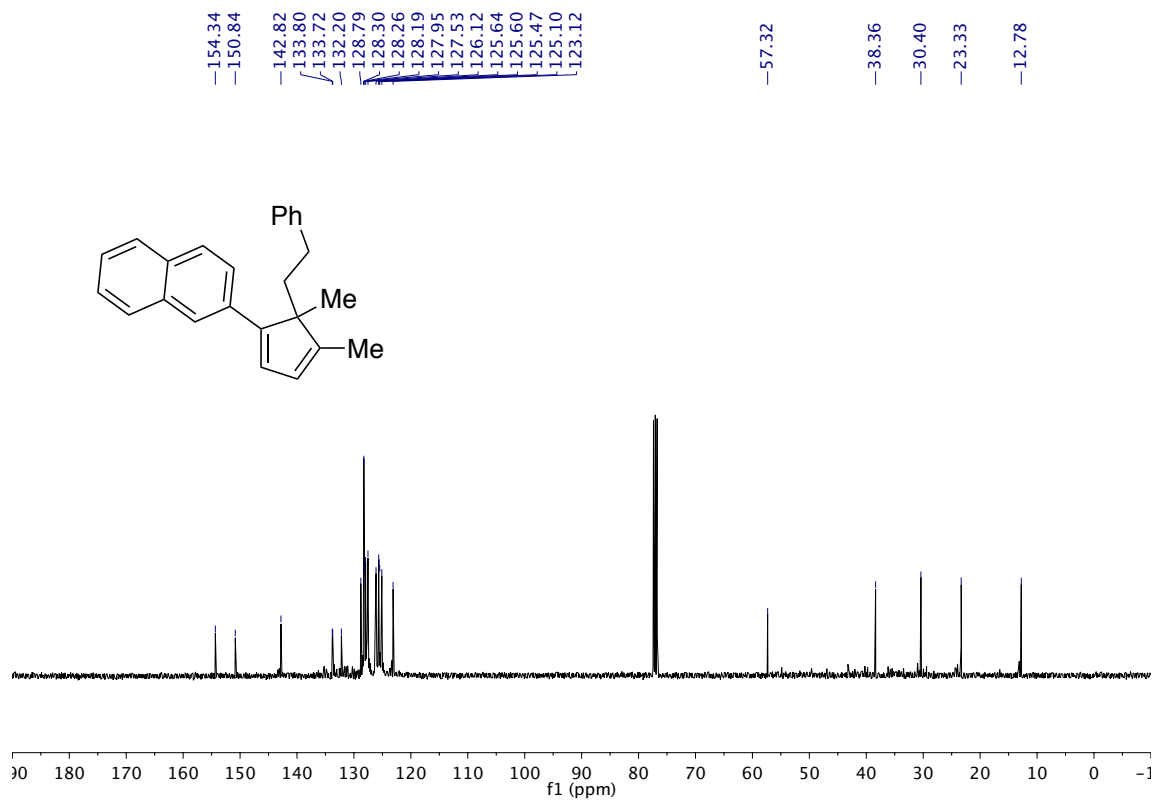
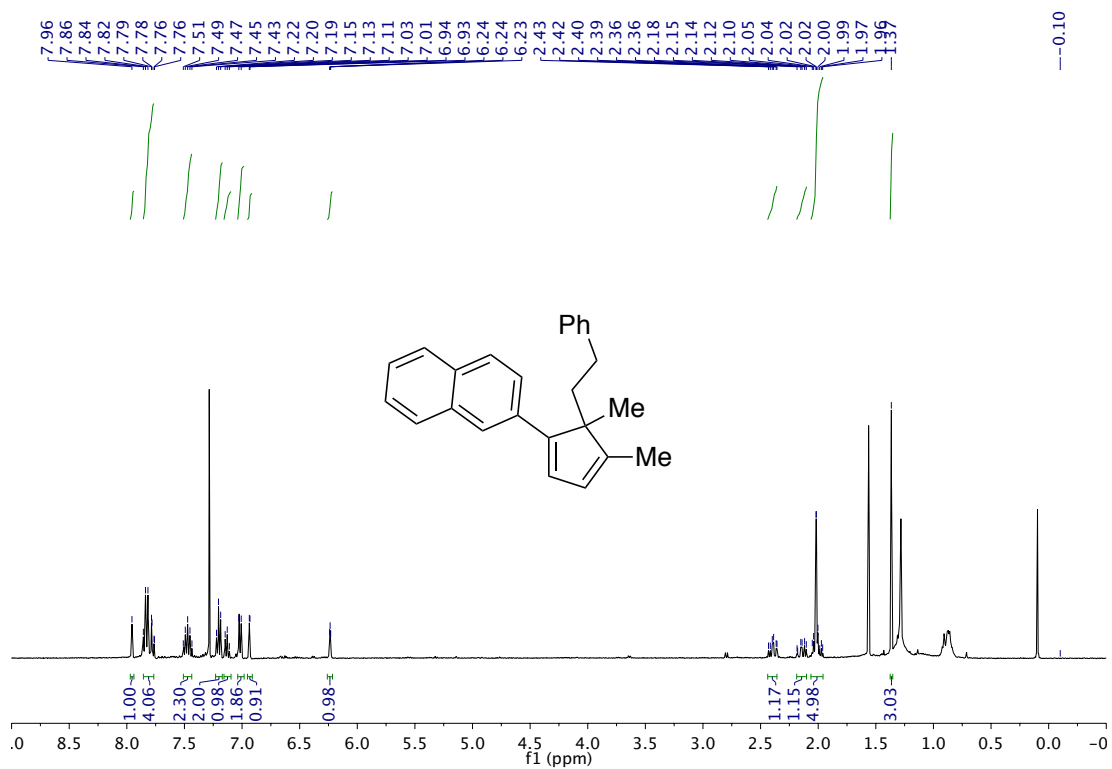
1-methyl-4-(p-tolyl)spiro[4.5]deca-1,3-diene (7i)



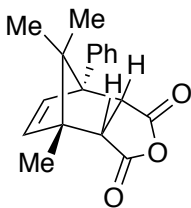
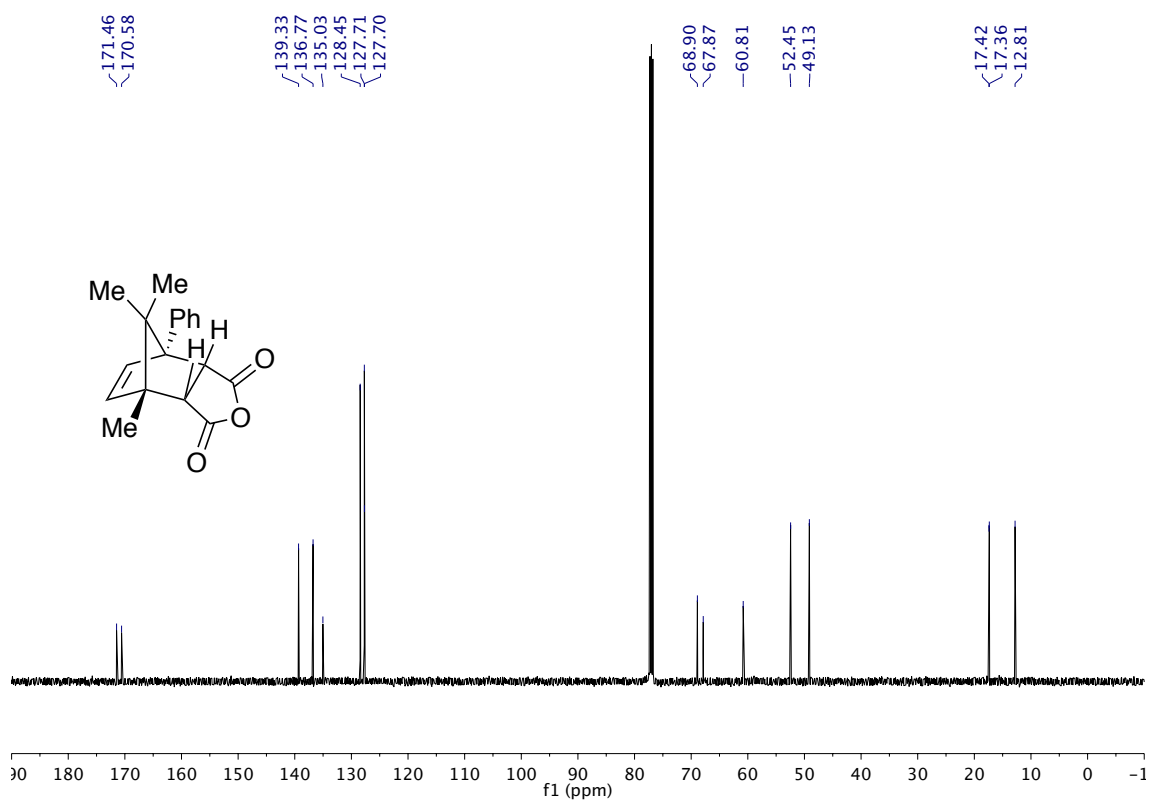
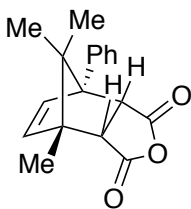
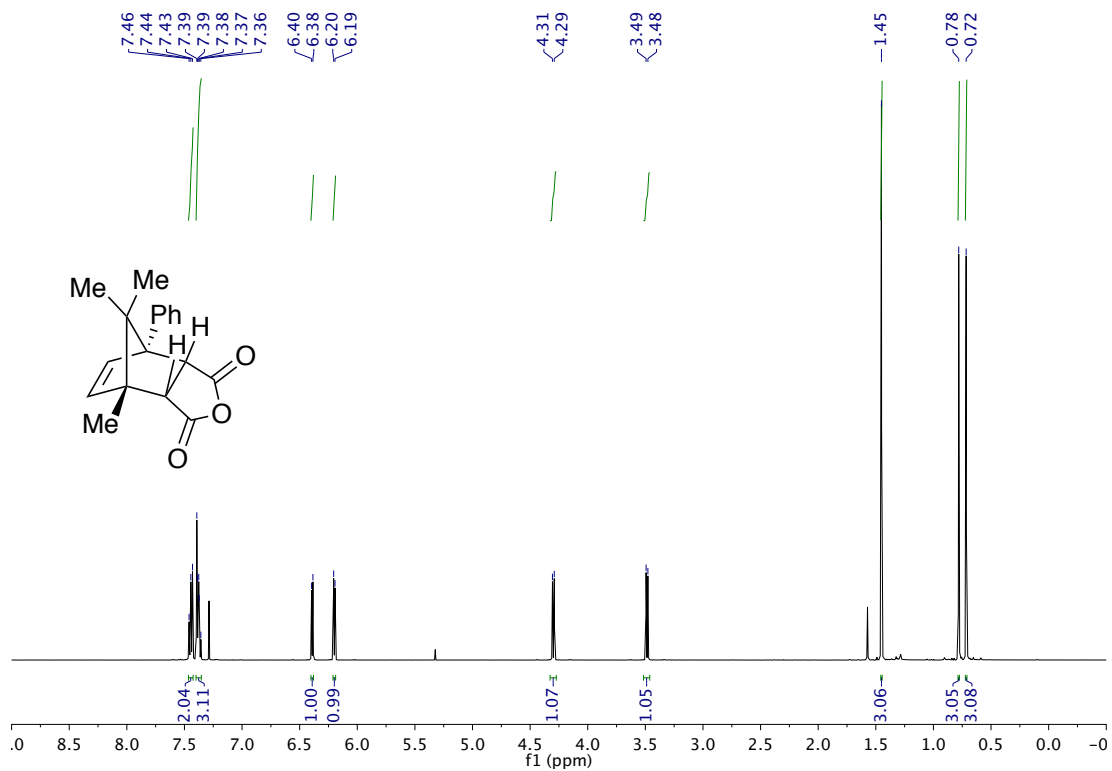
2-(4,5,5-trimethyl-cyclopenta-1,3-dien-1-yl)naphthalene (7j)



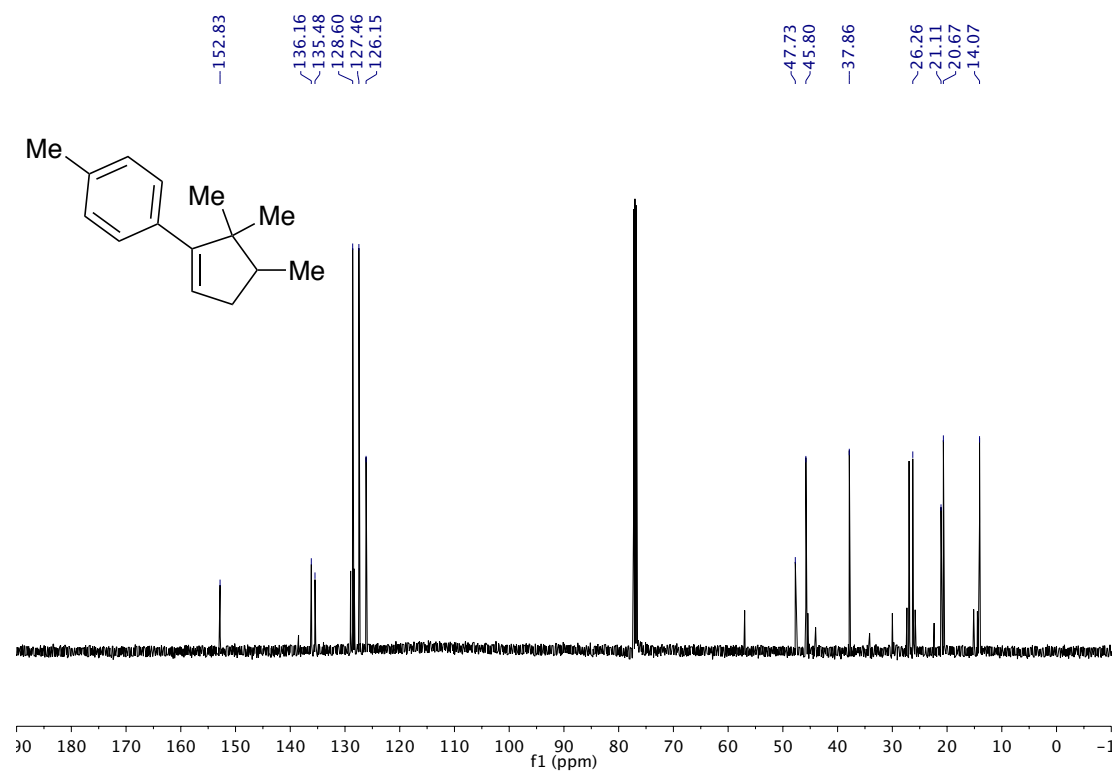
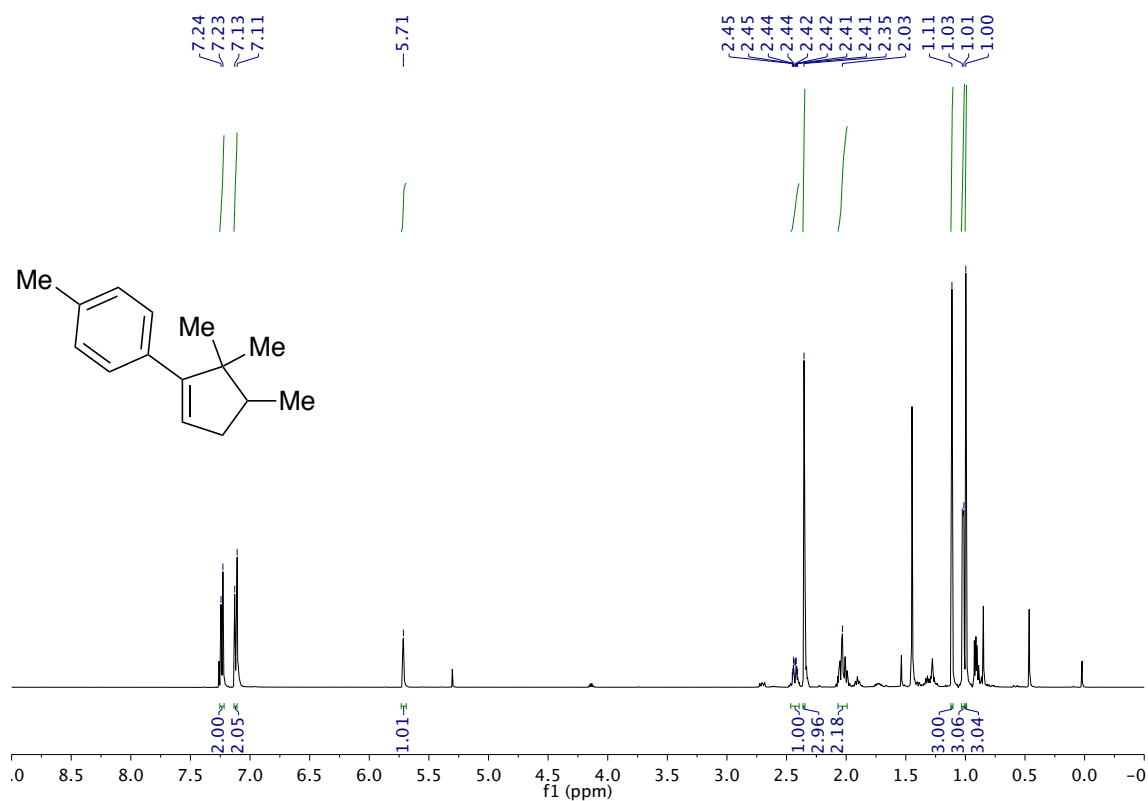
2-(4,5-dimethyl-5-phenethylcyclopenta-1,3-dien-1-yl)naphthalene (7k)



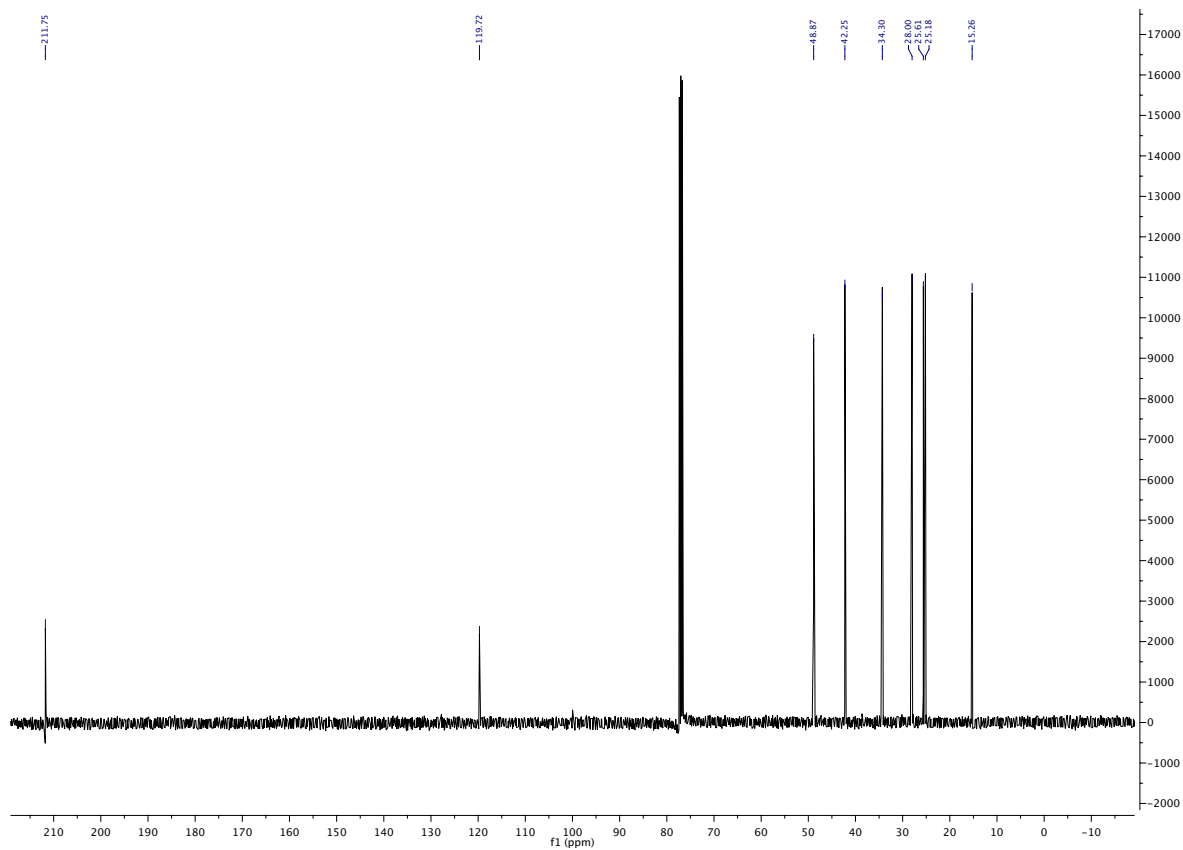
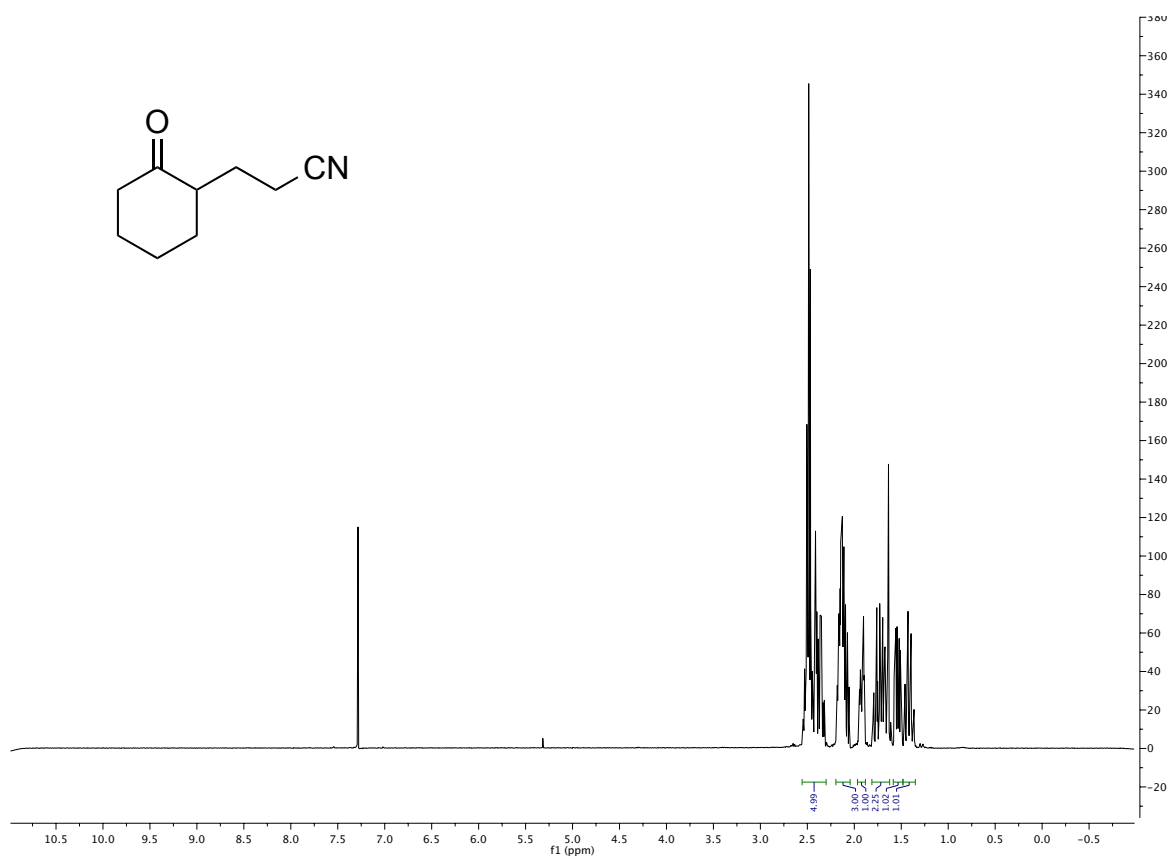
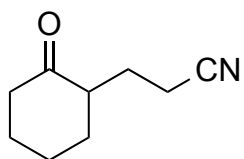
Endo-4,8,8-trimethyl-7-phenyl-3a,4,7,7a-tetrahydro-4,7-methano-isobenzofuran-1,3-dione (12)



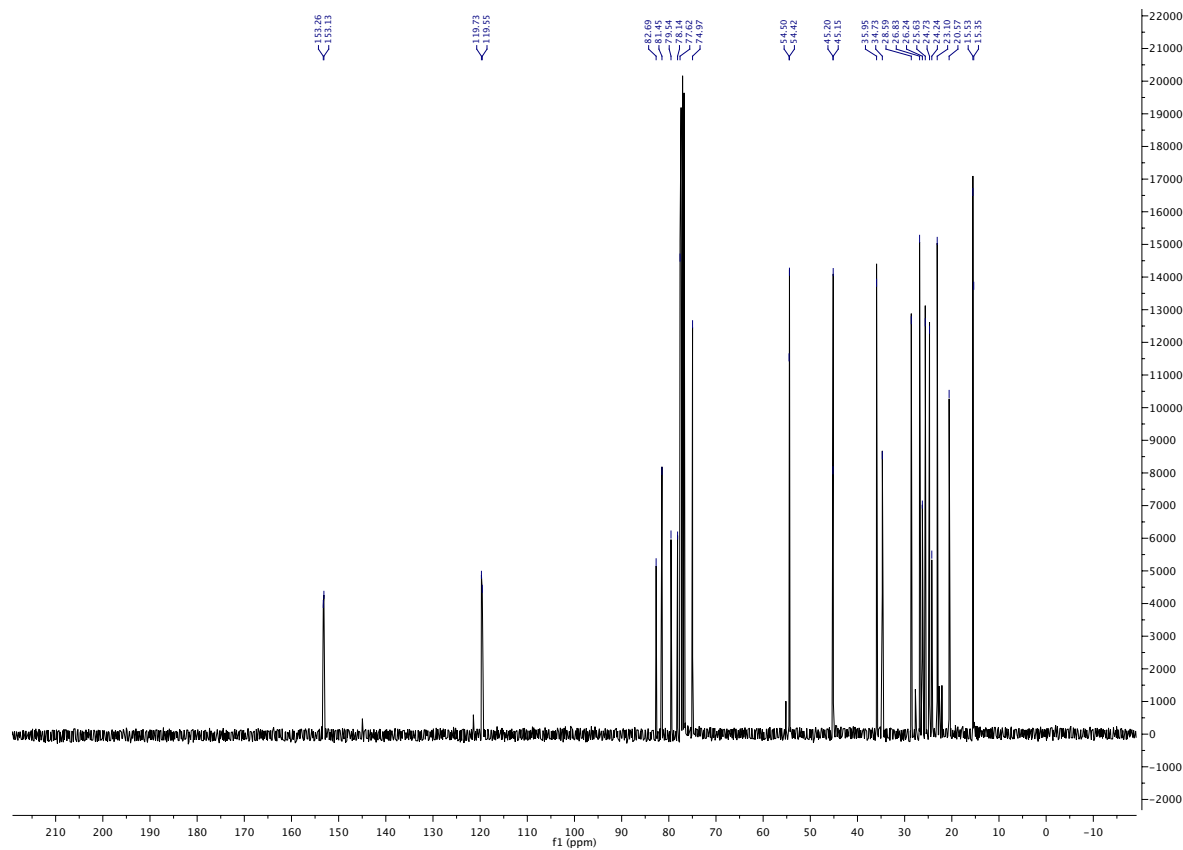
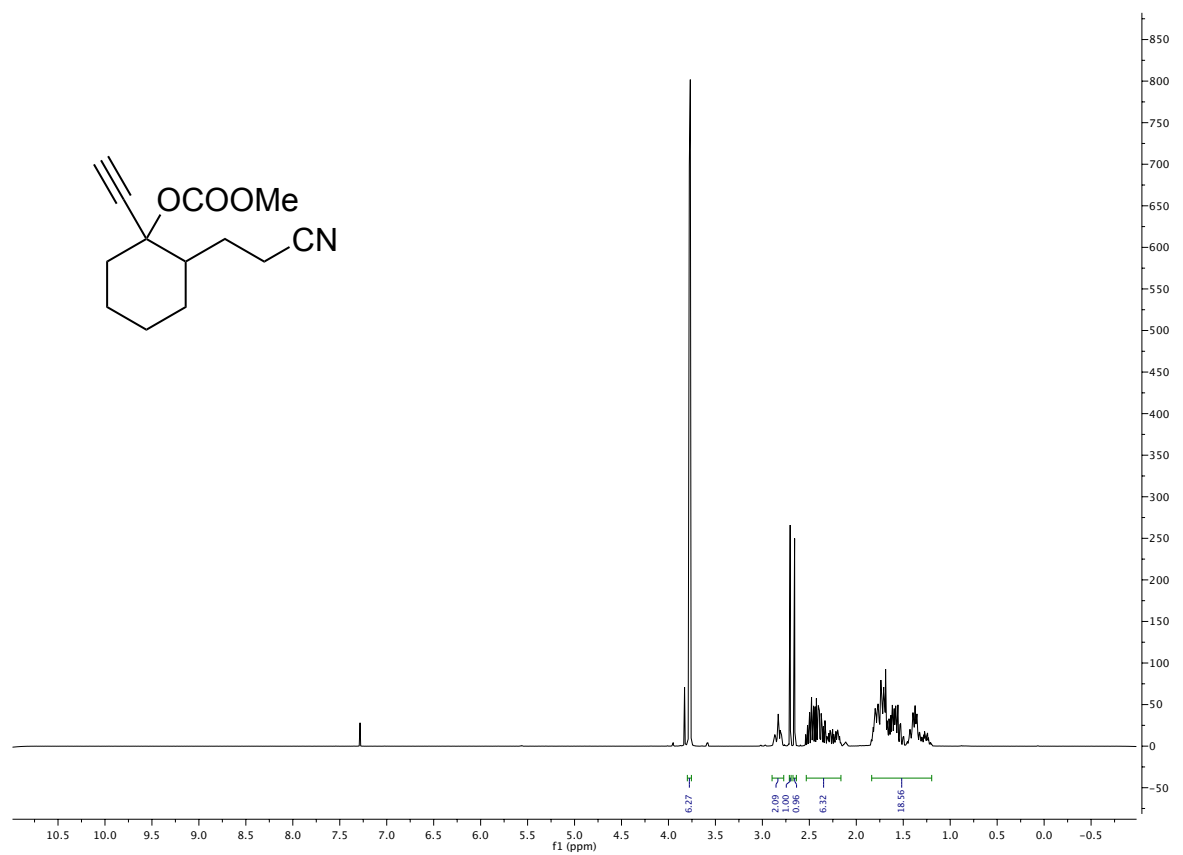
Laurokamurene B (10)



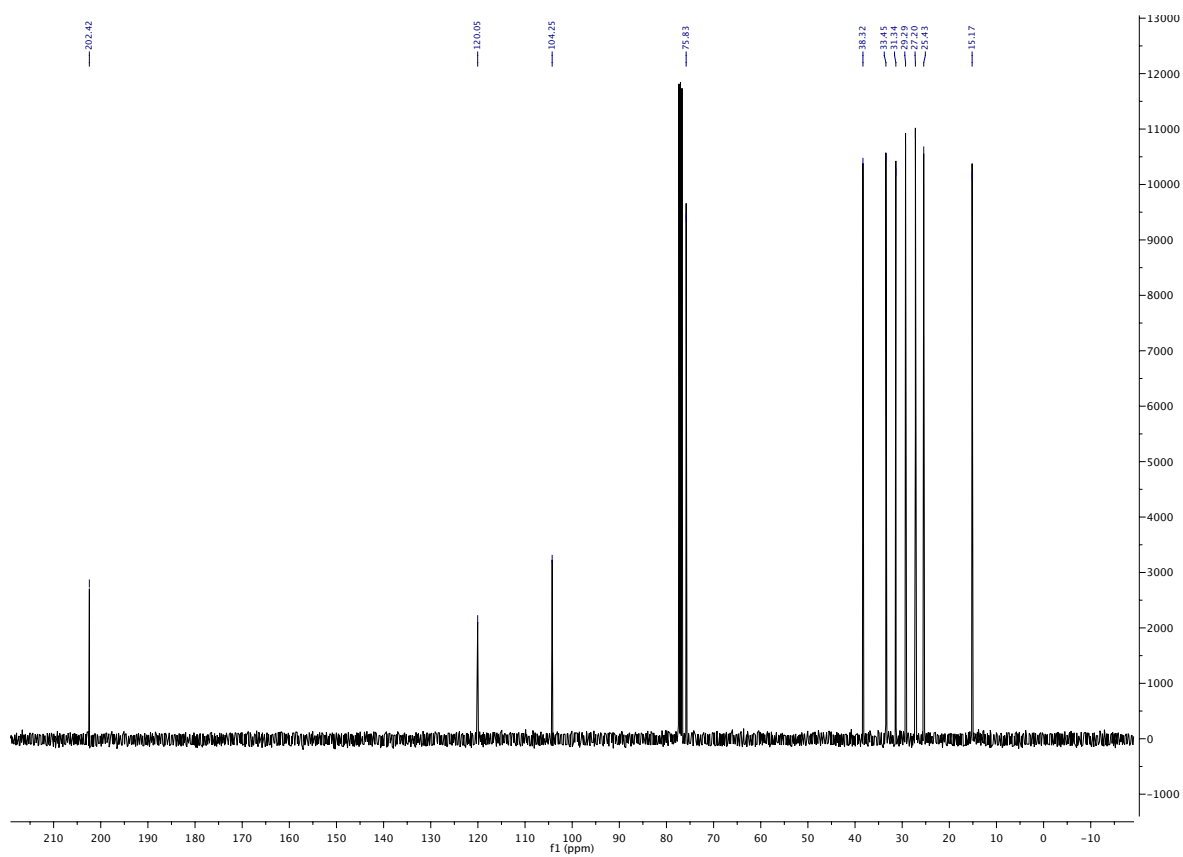
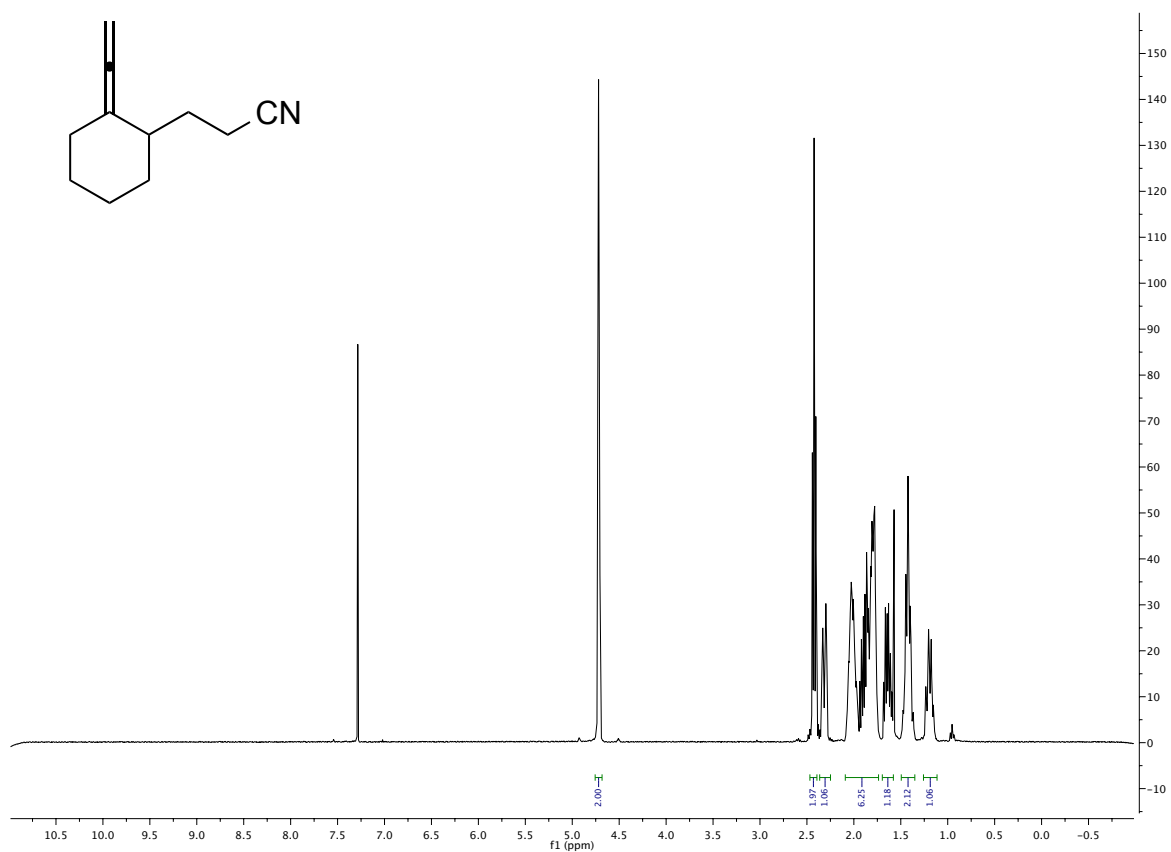
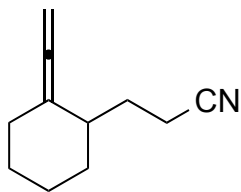
3-(2-Oxocyclohexyl)propanenitrile (SI1)



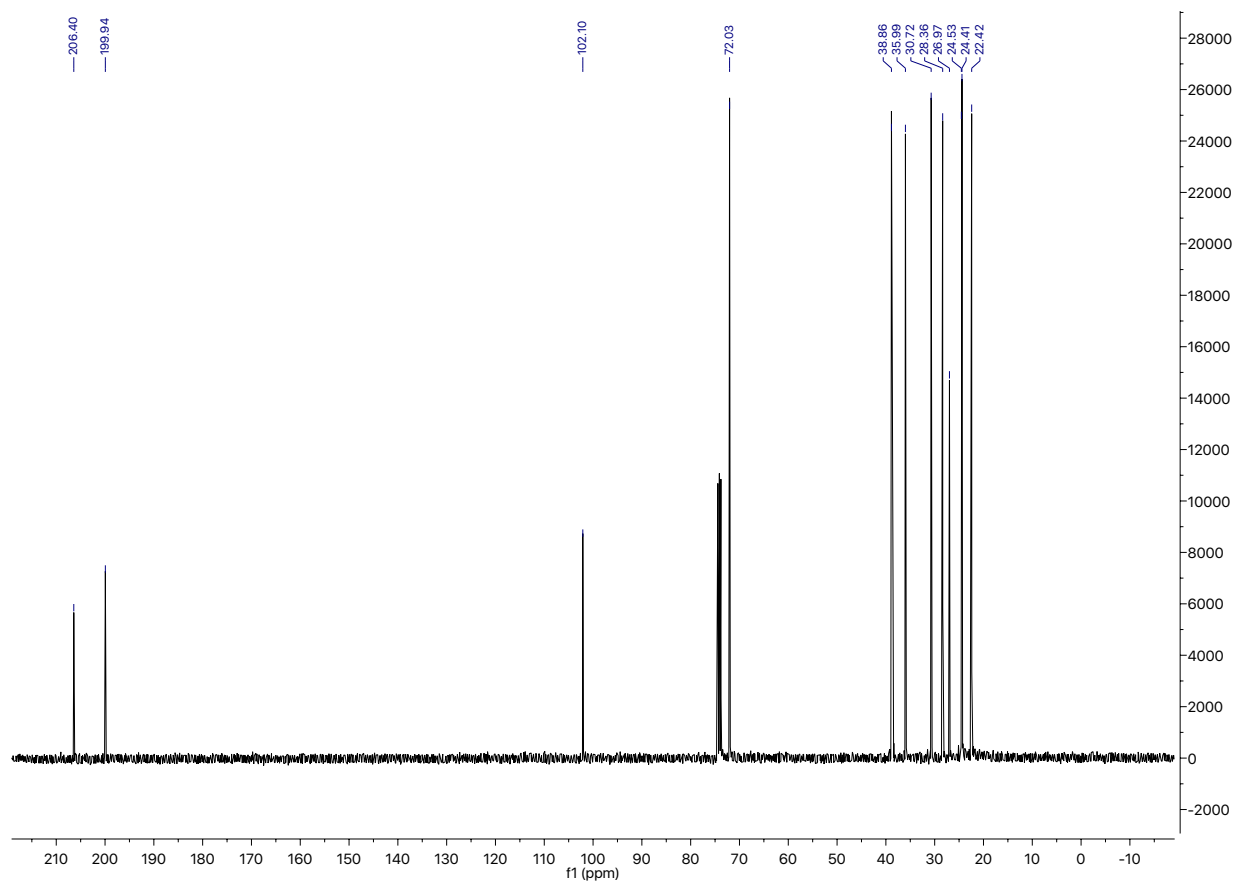
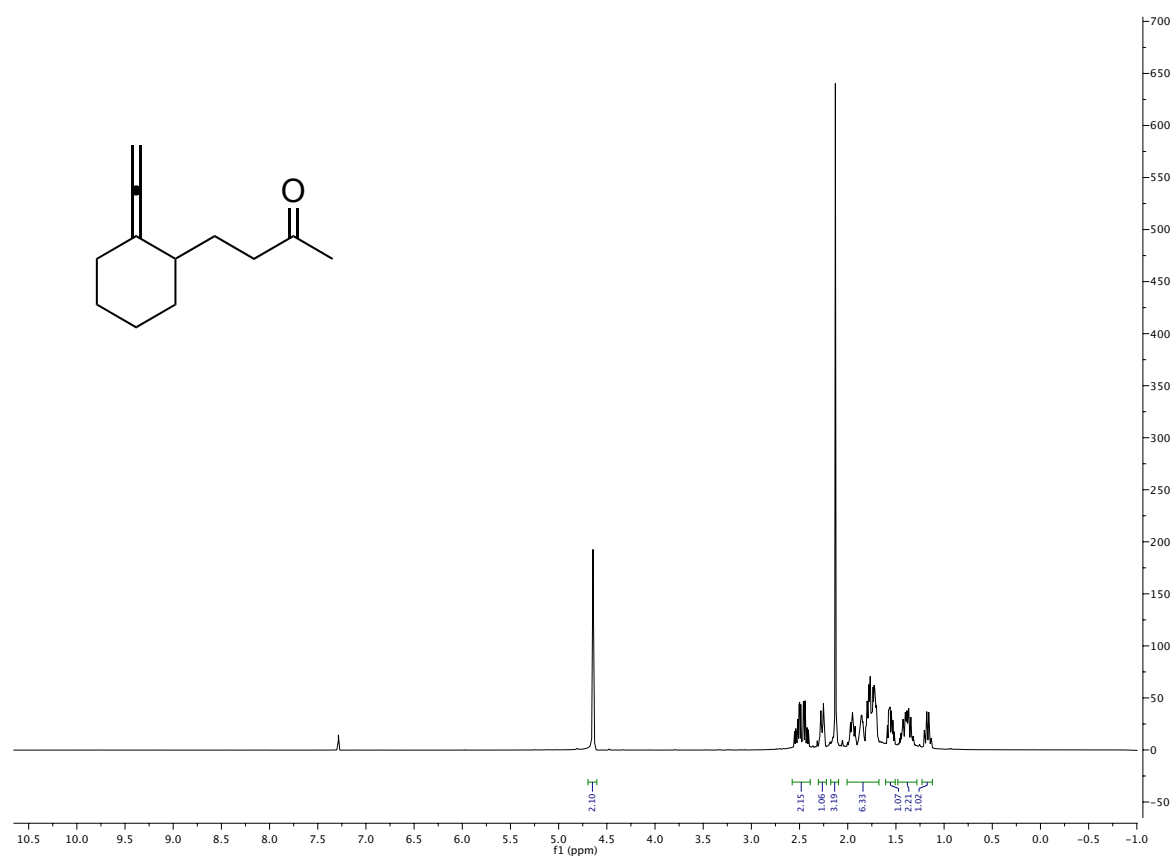
2-(2-Cyanoethyl)-1-ethynylcyclohexyl methyl carbonate (SI2)



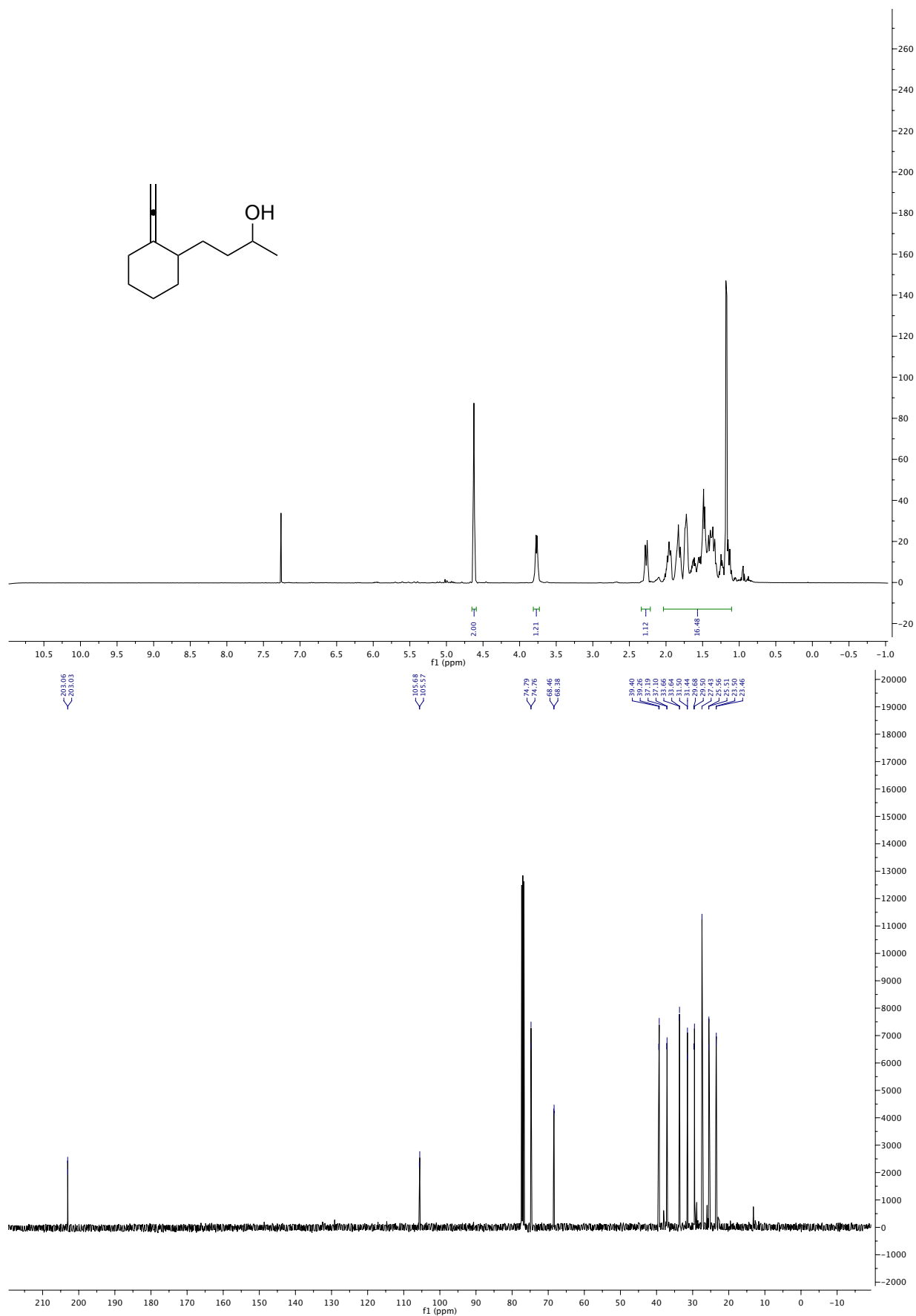
3-(2-(1 λ^5 -Vinylidene)cyclohexyl)propanenitrile (SI3)



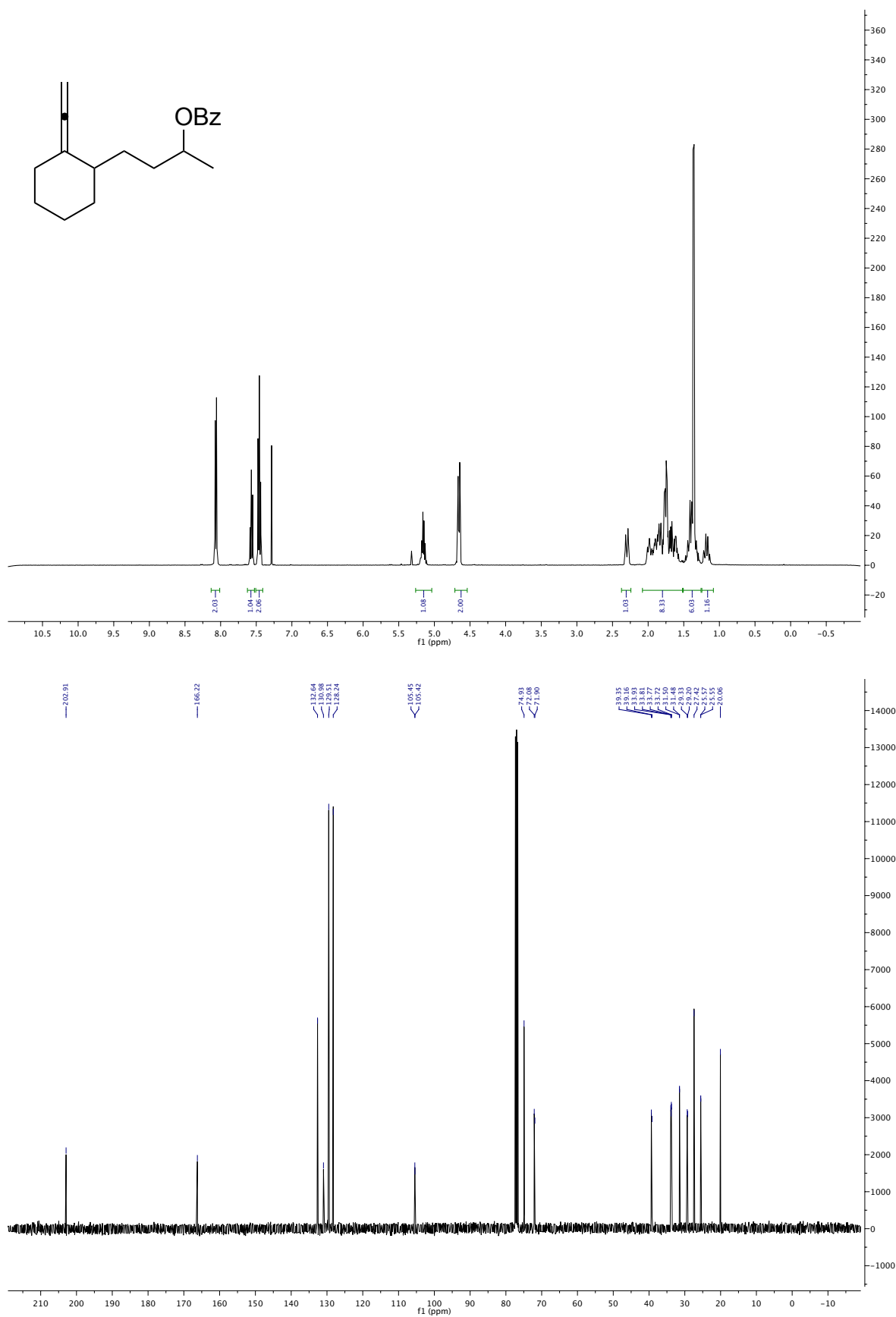
4-(2-(1 λ 5-Vinylidene)cyclohexyl)butan-2-one (SI4)



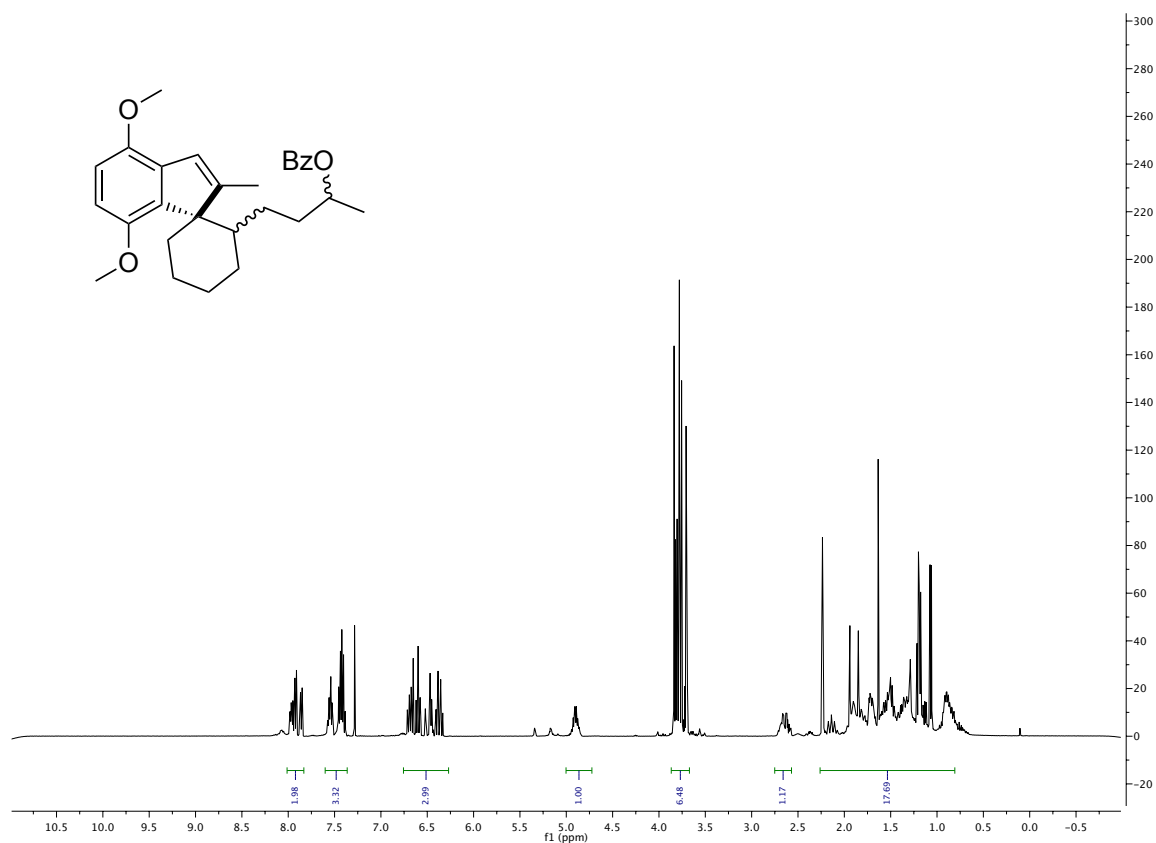
4-(2-(1λ⁵-Vinylidene)cyclohexyl)butan-2-ol (SI5)



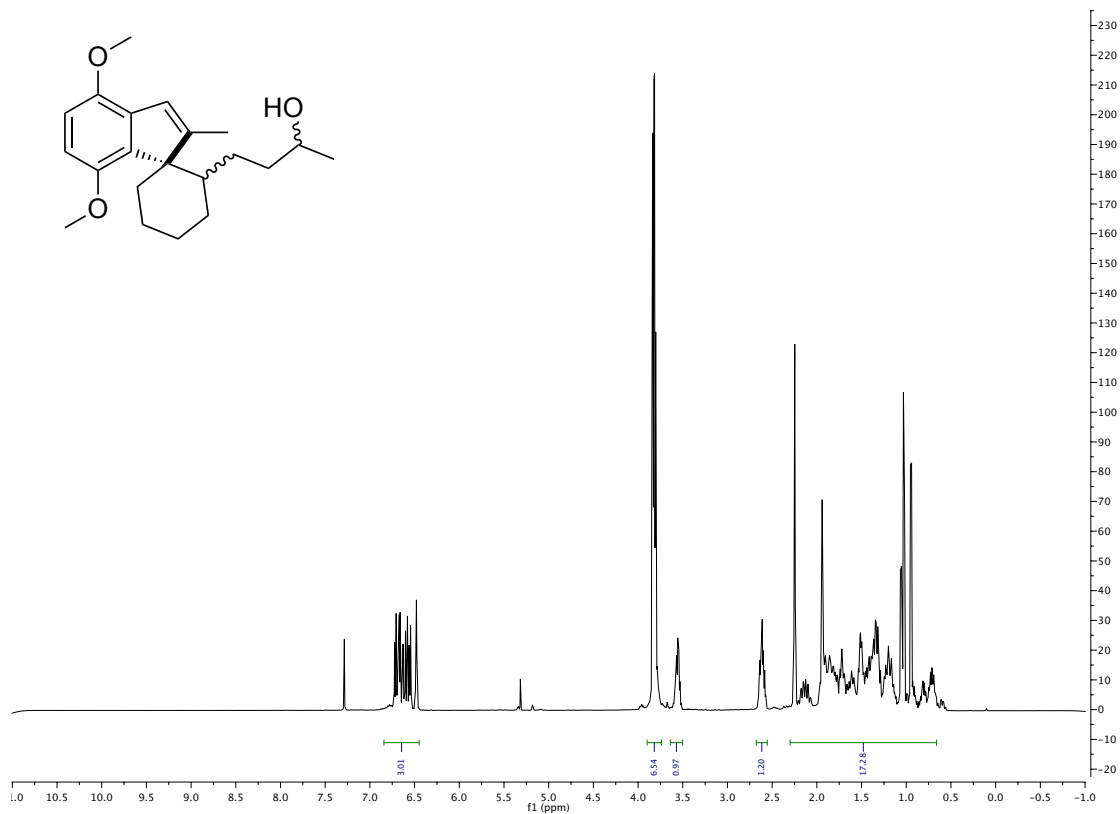
4-(2-(1 λ^5 -Vinylidene)cyclohexyl)butan-2-yl benzoate (5i)



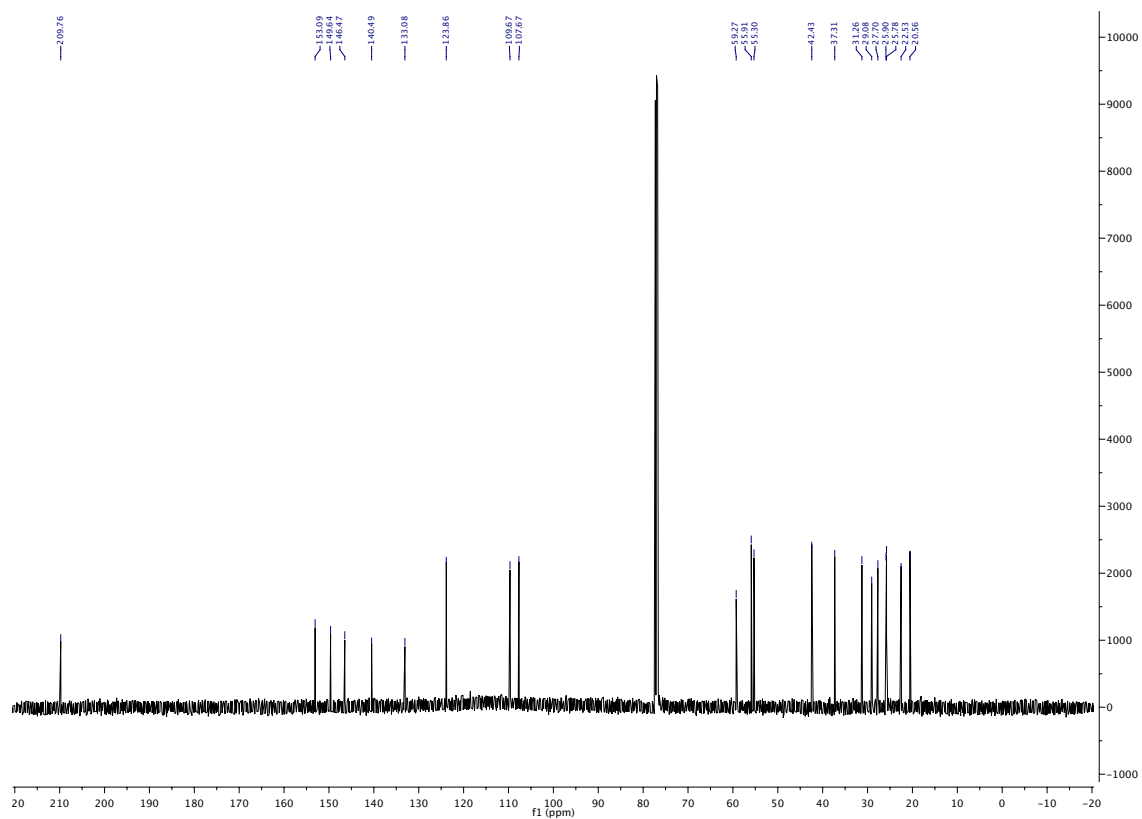
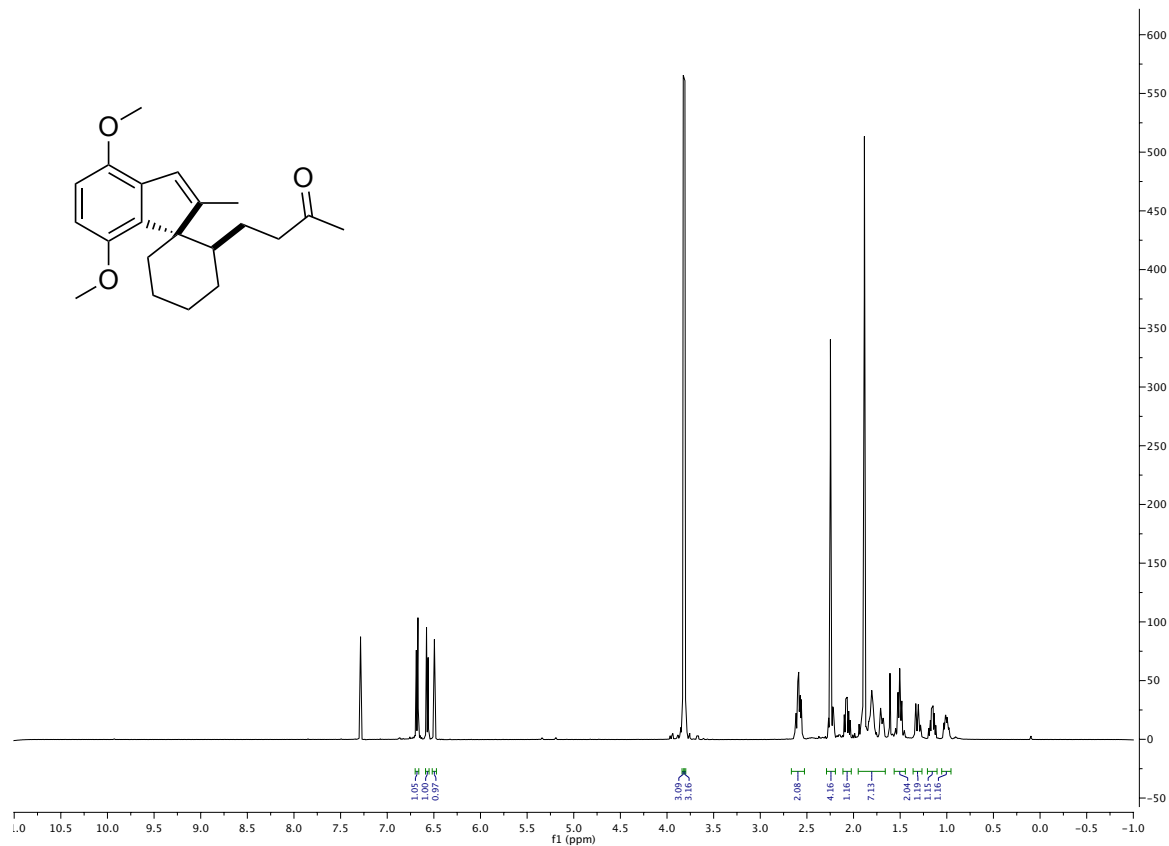
4-((1*R**)-4',7'-dimethoxy-2'-methylspiro[cyclohexane-1,1'-inden]-2-yl)butan-2-yl benzoate (13)



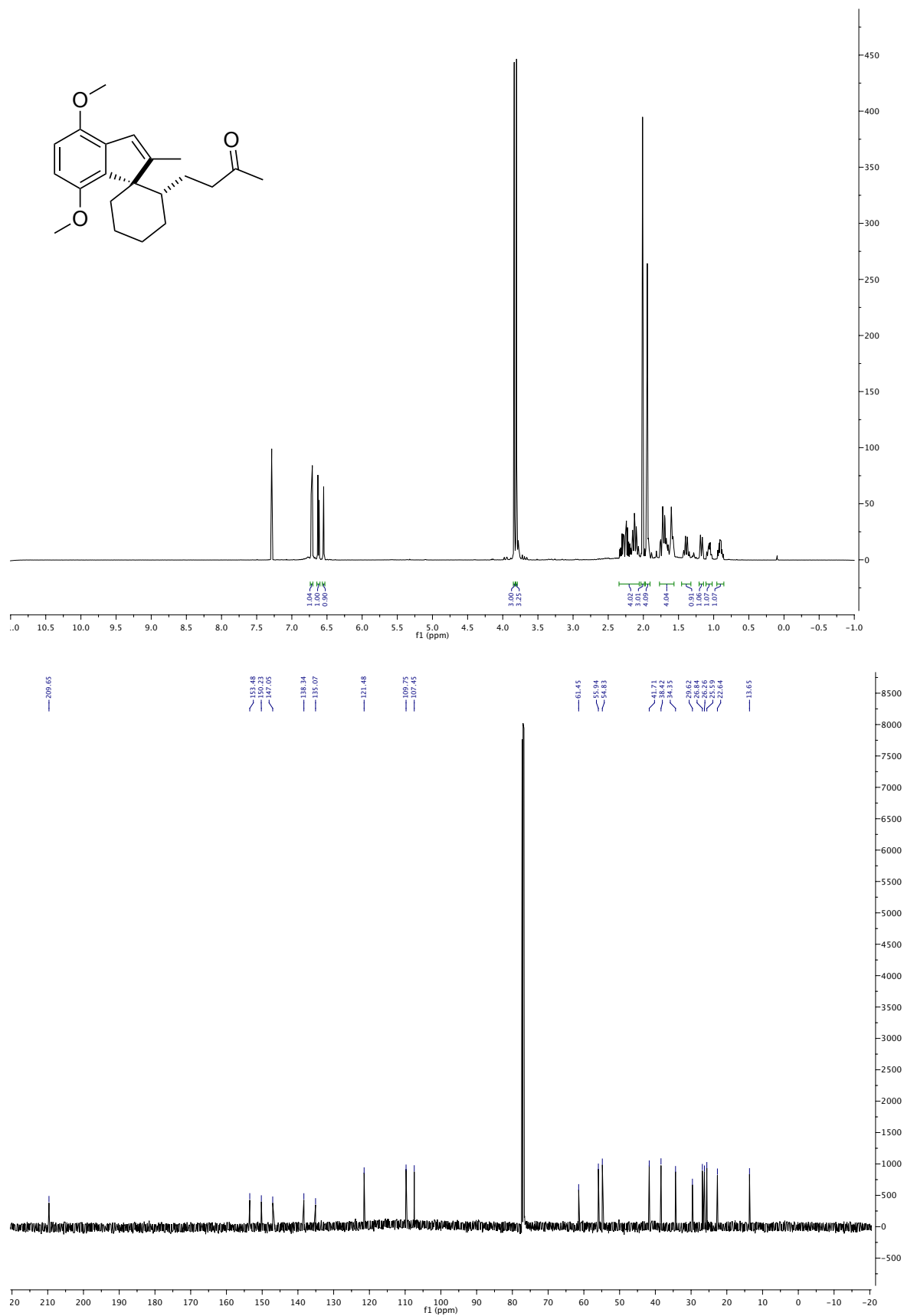
4-((1*R*)-4',7'-dimethoxy-2'-methylspiro[cyclohexane-1,1'-inden]-2-yl)butan-2-ol (13')



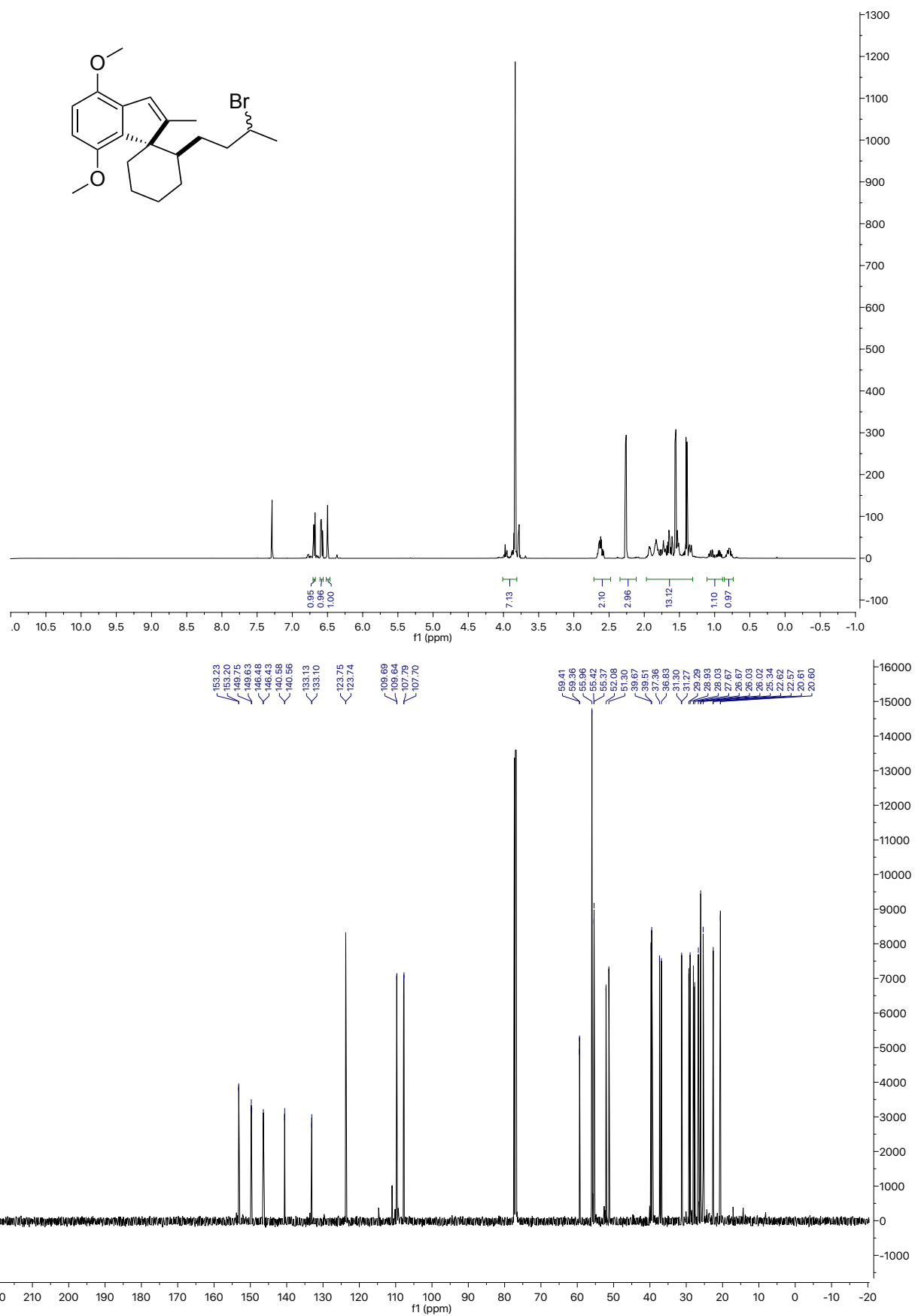
4-((1*R,2*S**)-4',7'-Dimethoxy-2'-methylspiro[cyclohexane-1,1'-inden]-2-yl)butan-2-one (14a)**



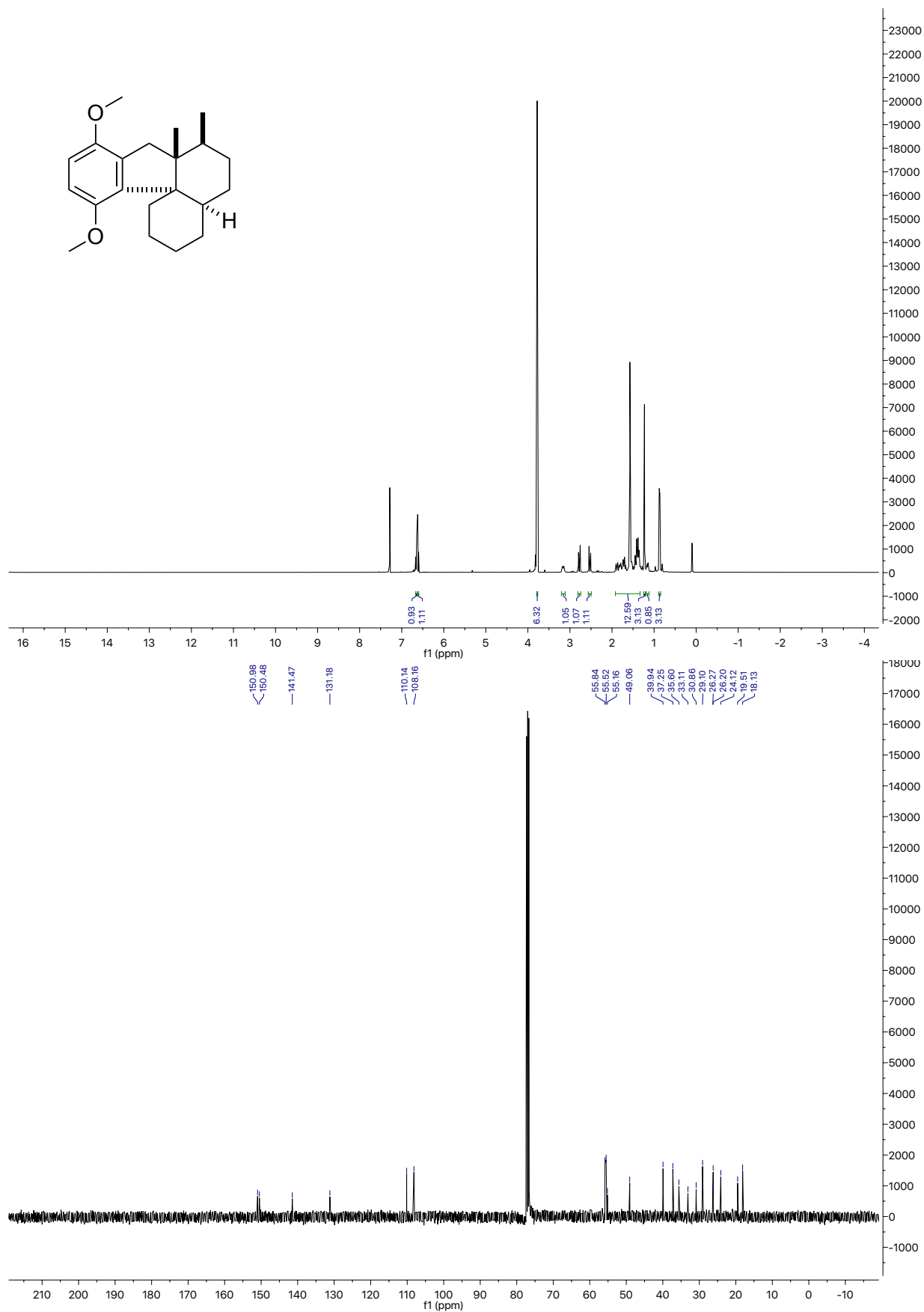
4-((1*R**,2*R**)-4',7'-dimethoxy-2'-methylspiro[cyclohexane-1,1'-inden]-2-yl)butan-2-one (14b)



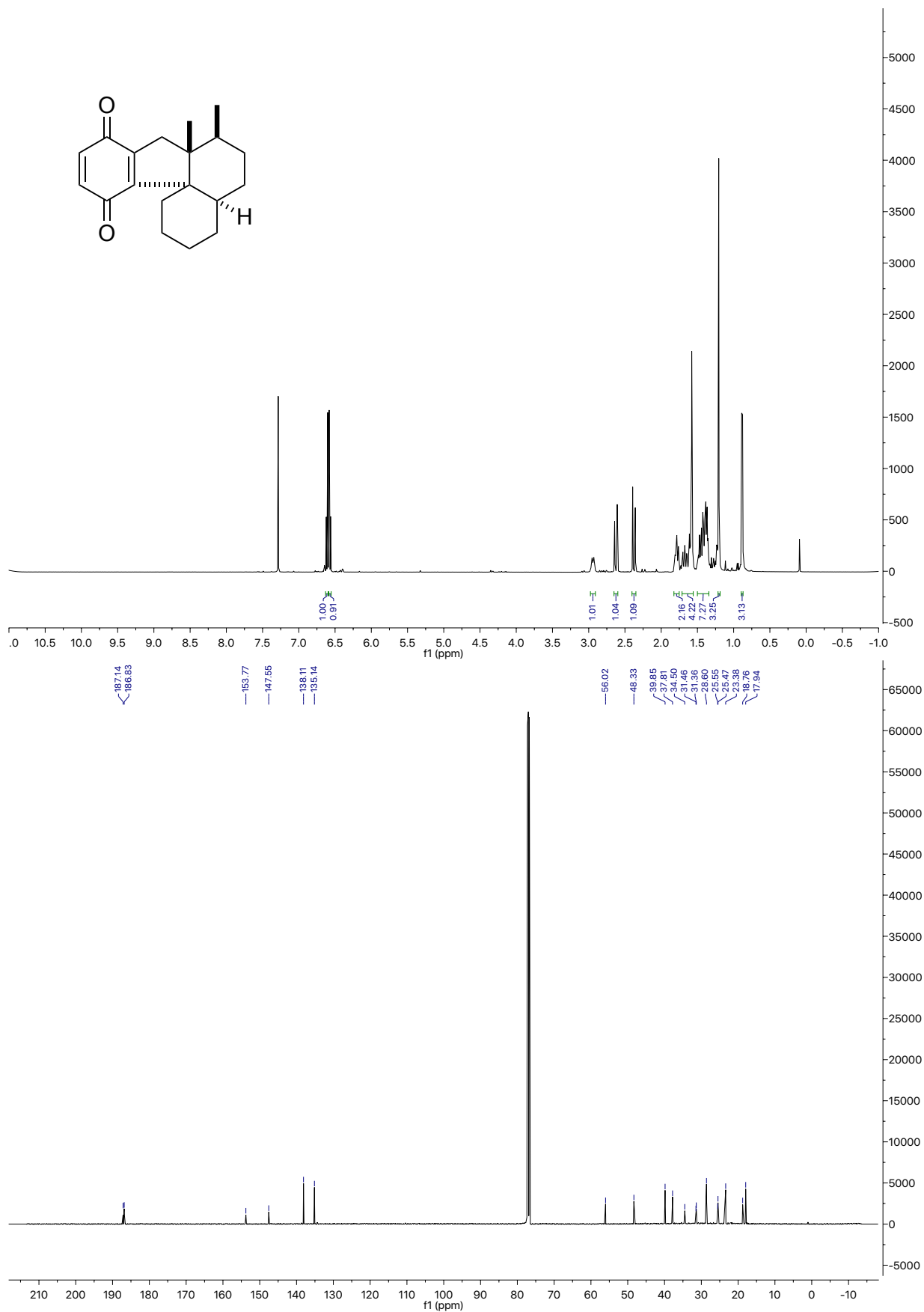
(1*R,2*S**)-2-(3-Bromobutyl)-4',7'-dimethoxy-2'-methylspiro[cyclohexane-1,1'-indene] (15a)**



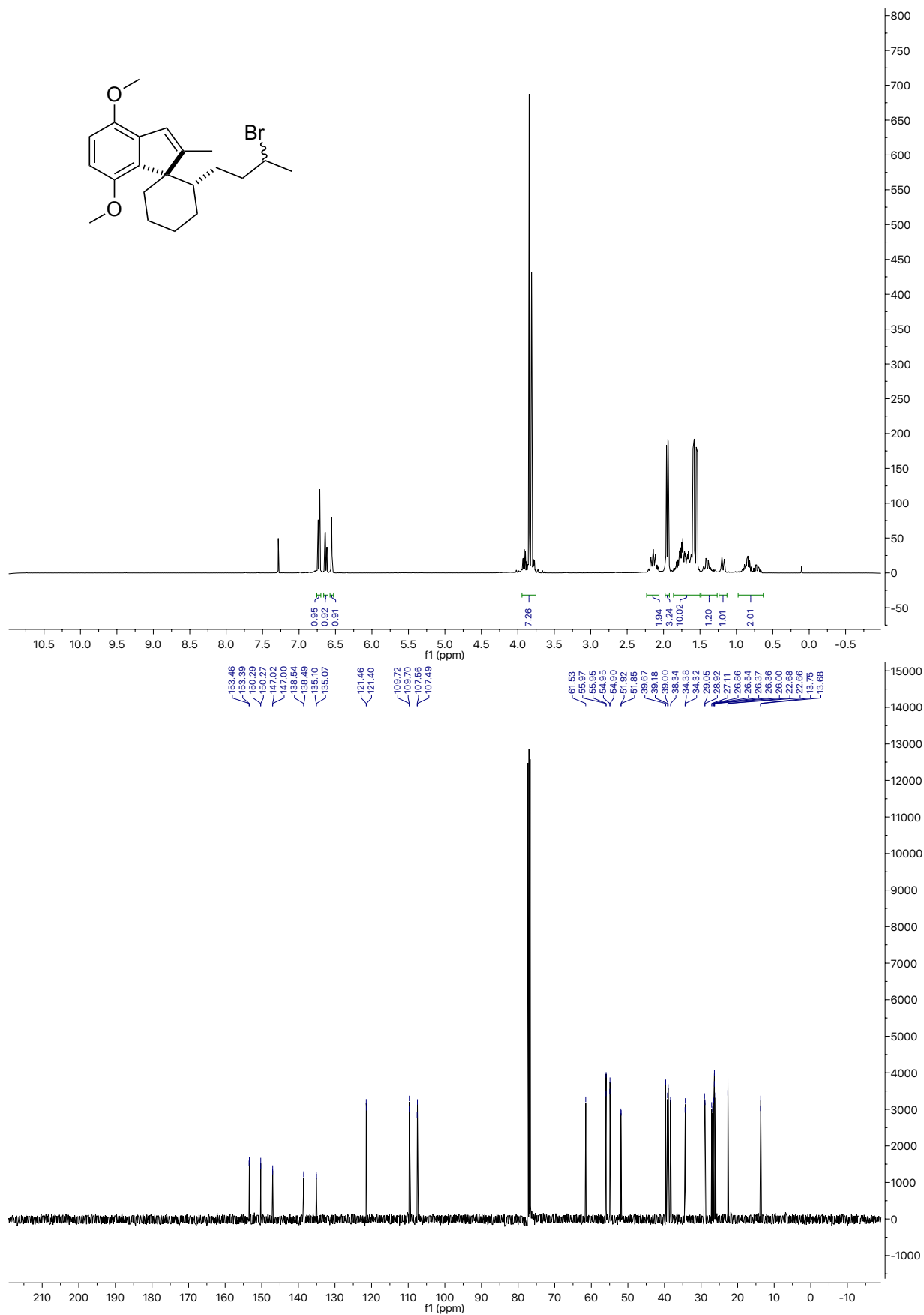
(4a*S,7*R**,7a*S**,12b*R**)-9,12-Dimethoxy-7,7a-dimethyl-1,2,3,4,4a,5,6,7,7a,8-decahydrobenzo[*d*]fluorine (16a)**



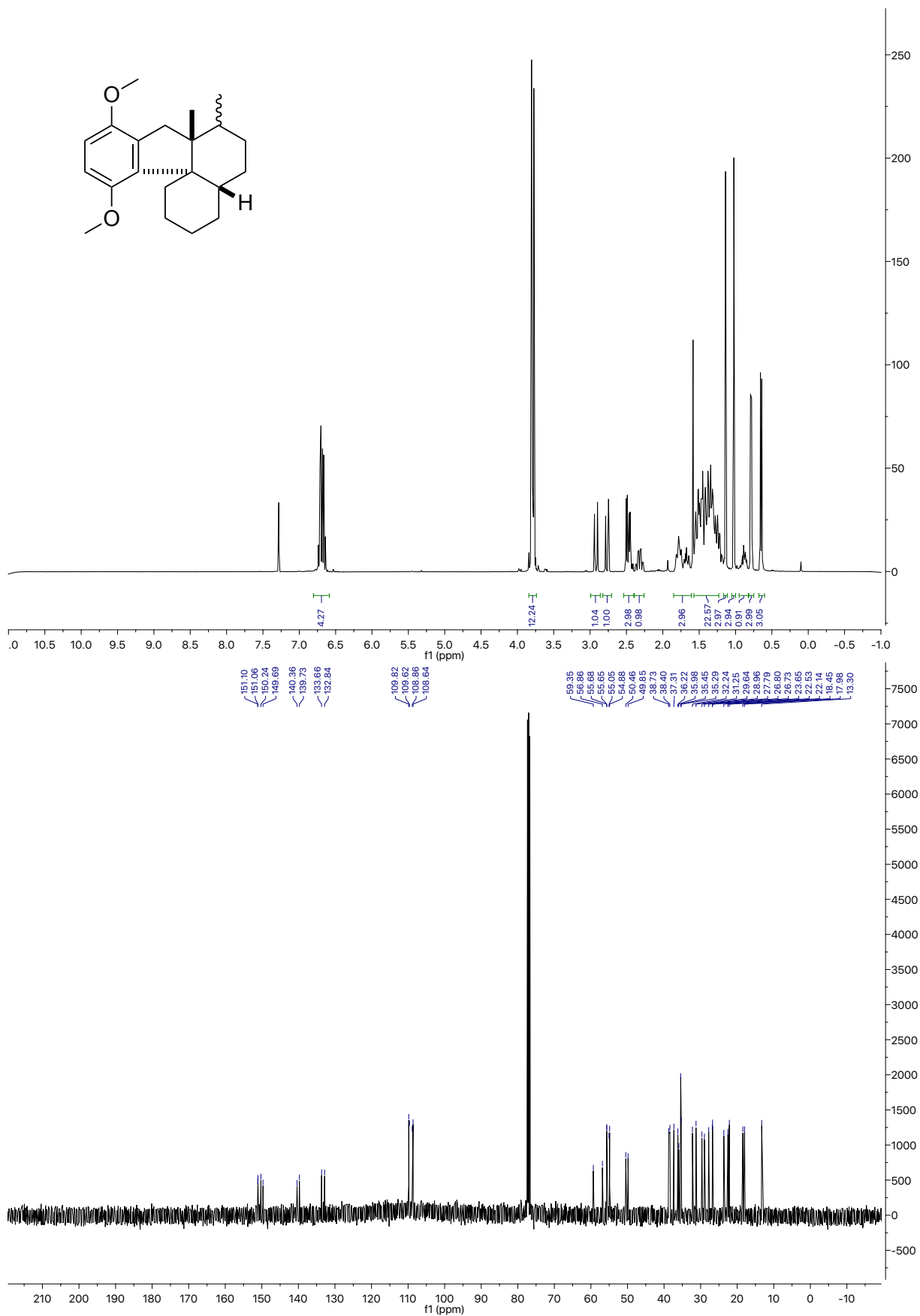
(4a*S,7*R**,7a*S**,12b*R**)-7,7a-Dimethyl-1,2,3,4,4a,5,6,7,7a,8-decahydrobenzo[*d*]fluorene-9,12-dione (17a) – Cycloaurenones Carbon Skeleton**



(1*R,2*R**)-2-(3-Bromobutyl)-4',7'-dimethoxy-2'-methylspiro[cyclohexane-1,1'-indene] (15b).**



(4a*R,7a*S**)-9,12-Dimethoxy-7,7a-dimethyl-1,2,3,4,4a,5,6,7,7a,8-decahydrobenzo [d]fluorine (16b) – Dysiherbols Carbon Skeleton**



(4a*R,7a*S**)-7,7a-dimethyl-1,2,3,4,4a,5,6,7,7a,8-decahydrobenzo[*d*]fluorene-9,12-dione (17b).**

