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Supporting Information

Merging Gold and Organocatalysis: A Facile Asymmetric Synthesis of Annulated Pyrroles

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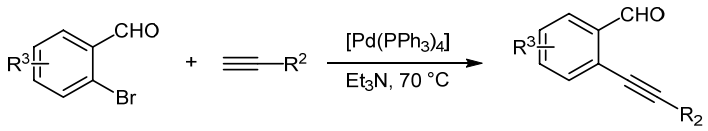
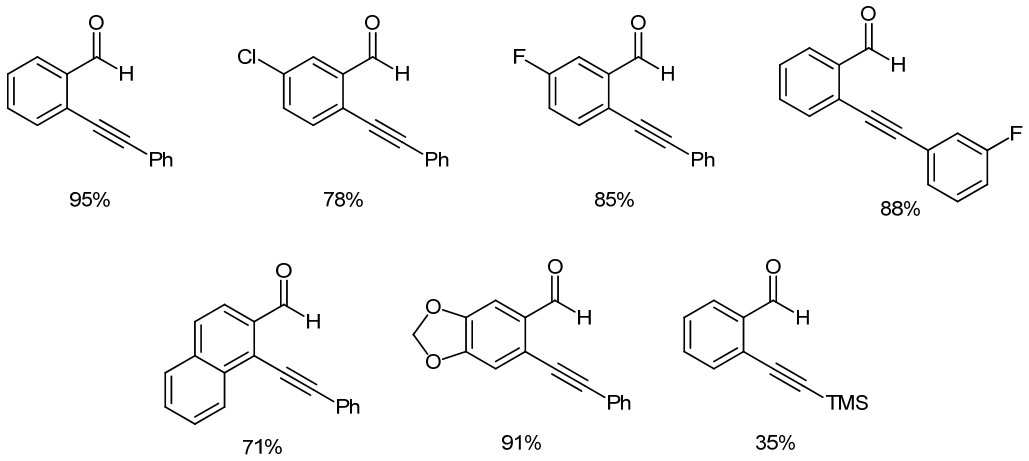
General Information

Unless otherwise noted, all commercially available compounds were used without further purification. Catalyst **10** was prepared according to the previously described procedure. For preparative column chromatography SIL G-25 UV252 from Macherey-Nagel, particle size 0.040-0.063 nm (230-240 mesh. flash) was used. Visualization of the developed TLC plates was performed with UV irradiation (254 nm) or by staining with ninhydrin. Optical rotations were measured on a Perkin-Elmer 241 polarimeter. Mass spectra were recorded on a Finnigan SSQ7000 (EI 70 eV) spectrometer and high-resolution mass spectra on a Thermo Fisher Scientific Orbitrap XL spectrometer. IR spectra were recorded on a Perkin-Elmer FT-IR Spectrum 100 using ATR-Unit. ^{1}H, ^{13}C and ^{19}F spectra were recorded at ambient temperature on Varian Mercury 300, Inova 400, Varian VNMRS-400, or Varian VNMRS-600 spectrometers with TMS as an internal standard. Analytical HPLC was performed on a Hewlett-Packard 1100 Series instrument using chiral stationary phases (Daicel AD, Daicel AS, Daicel IA, Daicel OD, Daicel OJ or Chiralpak IC).

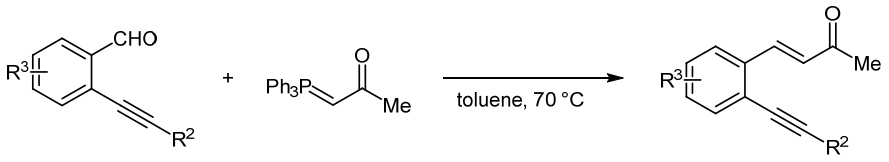
General Procedure A: Sonogashira-Ogihara-Crosscoupling



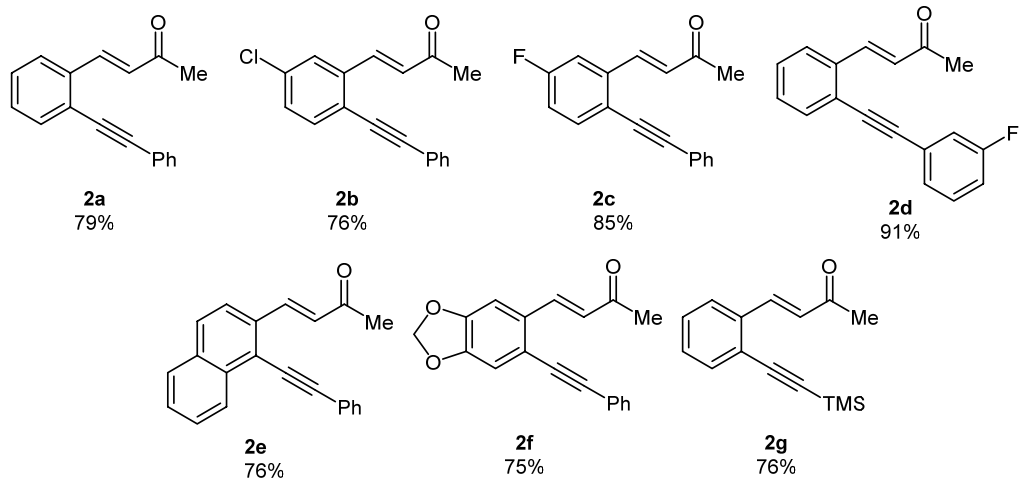
To a mixture of aryl bromide, copper(I) iodide (0.02 equiv.) and $[Pd(PPh_3)_4]$ (0.01 equiv.) under argon was added degassed triethylamine (2 mL per mmol). The suspension was stirred for five minutes and the alkyne (1.10 equiv.) was added. The reaction mixture was heated to 70 °C. When the reaction was completed as determined by TLC, the dark suspension was allowed to cool to ambient temperature. Water (50 mL) was added and the resulting slurry was extracted three times with dichloromethane (50 mL). The combined organic phases were dried with magnesium sulfate and the solvent was removed *in vacuo*. Column chromatography of the crude product over silica gel using pentane/Et_2O as eluant yielded the corresponding arylalkyne.



General Procedure B: Wittig Olefination



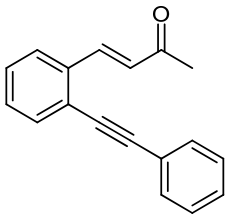
A suspension of the aldehyde and 1-(triphenylphosphoranylidene)propan-2-one (1.1 equiv.) in toluene (0.5 M) was heated with stirring to 70 °C, dissolving any residual solid reactant. When the reaction was completed as determined by TLC, the solution was left to cool to ambient temperature, and the toluene was removed *in vacuo*. Pentane/Et_2O was added and the resulting suspension was filtered. The yellowish filtrate was collected and the solvent removed *in vacuo*. Column chromatography of the crude product over silica gel using pentane/Et_2O as solvent afforded the corresponding enone.



General Procedure C: Sequential catalysis

Freshly distilled pyrrole (69 µL, 1.00 mmol) or 2-arylpyrrole (0.55 mmol) was added to a solution of 9-amino(9-deoxy)*epi* cinchonine **10** (29 mg, 0.20 mmol), TFA (16 µL, 0.15 mmol) and enone (0.50 mmol) in toluene (3 mL) at 0 °C. The reaction was stirred at 0 °C and the progress of the reaction was monitored by TLC analysis. After complete consumption of the starting material, a suspension of $AgNTf_2$ (10 mg, 0.10 mmol) and catalyst **13** (13 mg, 0.10 mmol) in toluene (1 mL) was added to the reaction mixture at room temperature. After complete conversion, the crude product was directly subjected to flash chromatography (silica gel, pentane/Et_2O).

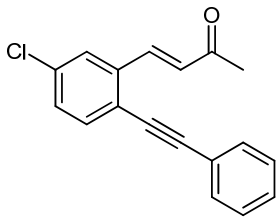
(*E*)-4-(2-(Phenylethynyl)phenyl)but-3-en-2-one (2a)



2a

Compound **2a** was isolated after flash chromatography (SiO_2, Pentane/Et_2O 10:1) as yellow crystals (1.891 g, 79%). **Molecular formula:** $C_{18}H_{14}O$. **Molecular mass** 246.303 g mol^{-1}. $\mathbf{R_f}$(Pentane/Et_2O 15:1) = 0.14. **Mp:** 62-65 °C. **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 2.44 (s, 3 H, Me), 6.75 (d, J = 16.4 Hz, 1 H, CH), 7.33-7.44 (m, 5 H, Ar), 7.54-7.71 (m, 3 H, ArH), 7.65-7.71 (m, 1 H, ArH), 8.15 (d, J = 16.5 Hz, 1 H, CH). **^{13}C NMR** (150 MHz, $CDCl_3$): δ = 27.2 (q), 87.0 (s), 95.9 (s), 122.9 (s), 124.4 (s), 126.3 (d), 128.7 (d, 2 C), 128.8 (d), 128.9 (d, 2 C), 130.1 (d), 131.7 (d, 2 C), 133.0 (d), 135.9 (s), 141.7 (d), 198.7 (s). **IR** (ATR): $\tilde{\nu}$ = 3921, 3294, 3031, 2920, 2655, 2331, 2215, 2064, 1935, 1820, 1736, 1659, 1490, 1438, 1359, 1256, 1199, 1070, 1012, 968, 914, 840, 755, 689 cm^{-1}. **MS (EI$^+$)** *m*/*z* (%): 246.2 (73) $[M]^+ = [C_{18}H_{14}O]^+$, 231.2 (67) $[M-CH_3]^+ = [C_{17}H_{11}O]^+$, 203.1 (67) $[M-C_2H_3O]^+ = [C_{16}H_{11}]^+$, 202.1 (100) $[M-C_2H_4O]^+ = [C_{16}H_{10}]^+$. **MS (CI$^+$, methane)** *m*/*z* (%): 247.1 (100) $[M+H]^+ = [C_{18}H_{15}O]^+$, 246.1 (16) $[M]^+ = [C_{18}H_{14}O]^+$, 105.1 (73). **EA** calcd. for $C_{18}H_{14}O$: C 87.78%, H 5.73%; found: C 87.91%, H 6.00%.

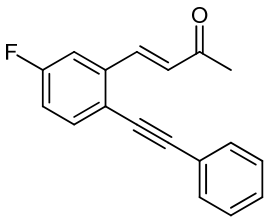
(*E*)-4-(5-Chloro-2-(phenylethynyl)phenyl)but-3-en-2-one (2b)



2b

Compound **2b** was isolated after flash chromatography (SiO_2, Pentane/Et_2O 5:1) as yellow solid (0.354 g, 76%). **Molecular formula:** $C_{18}H_{13}ClO$. **Molecular mass** 280.748 g mol^{-1}. **R_f**(Pentane/Et_2O 10:1) = 0.27. **Mp:** 64-66 °C **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 2.41 (s, 3 H, Me), 6.75 (d, J = 16.4 Hz, 1 H, CH), 7.30-7.38 (m, 4 H, ArH), 7.48-7.62 (m, 4 H, ArH), 8.03 (d, J = 16.4 Hz, 1 H, CH). **^{13}C NMR** (100 MHz, $CDCl_3$): δ = 27.6 (q), 86.1 (s), 96.7 (s), 122.6 (s), 122.8 (s), 126.3 (d), 128.7 (d, 2 C), 129.1 (d), 129.5 (d), 130.3 (d), 131.7 (d, 2 C), 134.0 (d), 134.8 (d), 137.4 (s), 140.0 (d), 198.1 (s). **IR** (ATR): $\tilde{\nu}$ = 3062, 2921, 2648, 2327, 2215, 2093, 1898, 1818, 1660, 1540, 1491, 1467, 1434, 1359, 1260, 1187, 1105, 1012, 973, 909, 818, 755, 719, 688 cm^{-1}. **MS (EI$^+$)** *m/z* (%): 282.2 (10) [M, ^{37}Cl]$^+$ = $[C_{18}H_{13}ClO]^+$, 280.3 (29) [M, ^{35}Cl]$^+$ = $[C_{18}H_{13}ClO]^+$, 265.2 (28) $[M-CH_3]^+$ = $[C_{17}H_{10}ClO]^+$, 245.3 (51) $[M-Cl]^+$ = $[C_{18}H_{13}O]^+$, 203.2 (24), 202.2 (100) $[M-Cl-C_2H_3O]^+$ = $[C_{16}H_{10}]^+$, 201.2 (22), 200.2 (29.0), 101.1 (17.2) $[C_8H_5]^+$, 100.2 (12). **EA** calcd. for $C_{18}H_{13}ClO$: C 77.01%, H 4.67%; found: C 77.09%, H 4.67%.

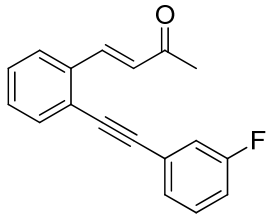
(*E*)-4-(5-Fluoro-2-(phenylethynyl)phenyl)but-3-en-2-one (2c)



2c

Compound **2c** was isolated after flash chromatography (SiO_2, Pentane/Et_2O 5:1) as pale yellow crystals (0.998 g, 85%). **Molecular formula:** $C_{18}H_{13}FO$. **Molecular mass:** 264.294 g mol^{-1}. **R_f** (pentane/Et_2O 5:1): 0.56. **Mp**: 60-63 °C. **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 2.42 (s, 3 H, Me), 6.73 (d, J = 16.4 Hz, 1 H, CH), 7.08 (td, J = 2.6 Hz, J = 8.3 Hz, 1 H, ArH), 7.32-7.39 (m, 4 H, ArH), 7.53-7.58 (m, 3 H, ArH), 8.07 (dd, J = 1.5 Hz, J = 16.4 Hz, 1 H, CH). **^{13}C{^{19}F} NMR** (100MHz, $CDCl_3$): δ = 27.6 (q), 86.1 (s), 95.6 (s), 113.0 (d), 117.8 (d, 2 C), 120.7 (s), 128.8 (d, 2 C), 129.1 (d), 129.7 (d), 131.7 (d, 2 C), 134.9 (d), 138.3 (s), 140.5 (d), 162.7 (d), 198.4 (s). **^{19}F{^{1}H} NMR** (376 MHz, $CDCl_3$): δ = −110.0. **IR** (ATR): $\tilde{\nu}$ = 3826, 3292, 3033, 2660, 2335, 2211, 2092, 1903, 1808, 1734, 1657, 1567, 1490, 1422, 1358, 1316, 1257, 1200, 1154, 1073, 1014, 910, 833, 754, 686 cm^{-1}. **MS (EI$^+$)** *m/z* (%): 265.2 (28), 264.1 (91) $[M]^+$ = $[C_{18}H_{13}FO]^+$, 250.1 (18), 249.1 (89) $[M-CH_3]^+$ = $[C_{17}H_{10}FO]^+$, 222.2 (17), 221.2 (77) $[M-C_2H_3O]^+$ = $[C_{16}H_{10}F]^+$, 220.1 (100) $[M-C_2H_4O]^+$ = $[C_{16}H_9F]^+$, 219.1 (15), 218.1 (20), 200.1 (12) $[M-C_2H_4FO]^+$ = $[C_{16}H_9]^+$, 110.1 (20), 105.1 (20). **MS (CI$^+$, methane)** *m/z* (%): 266.2 (22), 265.2 (100) $[M+H]^+$ = $[C_{18}H_{14}FO]^+$, 264.2 (14) $[M]^+$ = $[C_{18}H_{13}FO]^+$, 105.1 (56). **EA:** calcd. for $C_{18}H_{13}FO$: C 81.80 %, H 4.96 %; found: C 81.98 %, H 4.93 %.

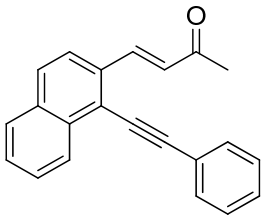
(*E*)-4-(2-((3-Fluorophenyl)ethynyl)phenyl)but-3-en-2-one (2d)



2d

Compound **2d** was isolated after flash chromatography (SiO_2, Pentane/Et_2O 5:1) as pale yellow crystals (0.325 g, 91%). **Molecular formula:** $C_{18}H_{13}FO$. **Molecular mass:** 264.294 g mol^{-1}. **R_f** (pentane/EtO_2 10:1): 0.19. **Mp:** 60-62 °C. **^{1}H NMR** (400MHz, $CDCl_3$): δ = 2.41 (s, 3 H, Me), 6.76 (d, *J* = 16.4 Hz, 1 H, CH), 7.04-7.09 (m, 1 H, ArH), 7.22-7.24 (m, 1 H, ArH), 7.31-7.38 (m, 4 H, ArH), 7.57 (dd, *J* = 3.5 Hz, *J* = 5.6 Hz, 1 H, ArH), 7.65 (dd, *J* = 3.6 Hz, *J* = 5.6 Hz, 1 H, ArH), 8.08 (d, *J* = 16.4 Hz, 1 H, CH). **^{13}C{^{19}F} NMR** (100 MHz, $CDCl_3$): δ = 27.3 (q), 87.8 (s), 94.3 (d), 116.2 (d), 118.3 (d), 123.8 (s), 124.7 (s), 126.3 (d), 127.5 (d), 128.9 (d), 129.1 (d), 130.1 (d), 130.2 (d), 133.1 (d), 136.0 (s), 141.2 (d), 162.5 (d), 198.5 (s). **^{19}F{^{1}H} NMR** (376MHz, $CDCl_3$): δ = –112.5. **IR** (ATR): $\tilde{\nu}$ = 3826, 3293, 3061, 2922, 2854, 2663, 2336, 2200, 2086, 1994, 1938, 1794, 1732, 1657, 1575, 1481, 1426, 1359, 1318, 1256, 1205, 1164, 1120, 1069, 1012, 966, 942, 864, 789, 753, 678 cm^{-1}. **MS (EI$^+$)** *m/z* (%): 265.1 (15), 264.1 (74) $[M]^+ = [C_{18}H_{13}FO]^+$, 250.1 (14), 249.1 (76) $[M–CH_3]^+ = [C_{17}H_{10}FO]^+$, 222.1 (15), 221.1 (74) $[M–C_3H_5O]^+ = [C_{15}H_8F]^+$, 220.1 (100) $[M–C_3H_6O]^+ = [C_{15}H_7F]^+$, 219.1 (14), 200.1 (11) $[M– C_3H_6FO]^+ = [C_{15}H_7]^+$, 123.0 (11), 110.2 (24). **MS (CI$^+$, methane)** *m/z* (%): 266.2 (27), 265.2 (100) $[M+H]^+ = [C_{18}H_{14}FO]^+$, 264.2 (22) $[M]^+ = [C_{18}H_{13}FO]^+$, 123.1 (56). **EA:** calcd. for $C_{18}H_{13}FO$: C 81.80 %, H 4.96 %; found: C 81.80 %, H 5.35 %.

(*E*)-4-(1-(Phenylethynyl)naphthalen-2-yl)but-3-en-2-one (2e)

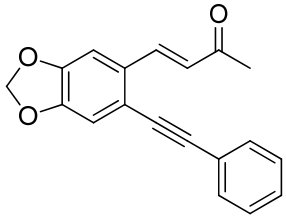


2e

Compound **2e** was isolated after flash chromatography (SiO_2, Pentane/Et_2O 5:1) as yellow powder (1.312 g, 76%). **Molecular formula:** $C_{22}H_{16}O$. **Molecular mass:** 296.362 g mol^{-1}. **R_f** (pentane/Et_2O 5:1): 0.31. **Mp:** 114-116 °C. **^{1}H NMR** (600 MHz, $CDCl_3$): δ = 2.47 (s, 3 H, Me), 6.82 (d, *J* = 16.4 Hz, 1 H, CH), 7.39-7.47 (m, 3 H, ArH), 7.55 (t, *J* = 7.3 Hz, 1 H, ArH), 7.61 (t, *J* = 7.2 Hz, 1 H, ArH), 7.66-7.73 (m, 3 H, ArH), 7.78 (d, *J* = 8.7 Hz, 1 H, ArH), 7.82 (d, *J* = 8.0 Hz, 1 H, ArH), 8.41 (d, *J* = 16.4 Hz, 1 H, CH), 8.48 (d, *J* = 8.4 Hz, 1 H, ArH). **^{13}C NMR** (150 MHz, $CDCl_3$): δ = 27.2 (q), 85.1 (s), 101.9 (s), 122.4 (d), 123.0 (s, 2 C), 127.3 (d), 127.7 (d), 127.8 (d), 128.4 (d), 128.8 (d, 2

C), 128.9 (d), 129.0 (d), 129.1 (d), 131.7 (d, 2 C), 133.5 (s), 133.9 (s), 134.2 (s), 142.1 (d), 198.7 (s). **IR** (ATR): $\tilde{\nu}$ = 3825, 3287, 3051, 2924, 2668, 2322, 2200, 2105, 1923, 1814, 1657, 1610, 1490, 1436, 1349, 1258, 1067, 1009, 962, 908, 864, 807, 746, 681 cm^{-1}. **MS (EI$^+$)** *m/z* (%): 295.9 (13) $[M]^+ = [C_{22}H_{16}O]^+$, 295.1 (21) $[M–H]^+ = [C_{22}H_{15}O]^+$, 281.6 (23) $[M–CH_3]^+ = [C_{21}H_{13}O]^+$, 280.6 (16), 279.6 (16), 253.9 (18), 252.8 (77) $[M–C_2H_3O]^+ = [C_{20}H_{13}]^+$, 251.8 (62) $[M–C_2H_4O]^+ = [C_{20}H_{12}]^+$, 251.0 (14), 250.3 (100), 248.6 (40), 226.4 (15) $[M–C_4H_5O]^+ = [C_{18}H_{11}]^+$. **EA:** calcd. for $C_{22}H_{16}O$: C 89.16 %, H 5.44 %; found: C 88.90 %, H 5.29 %.

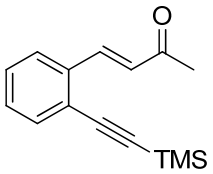
(*E*)-4-(6-(Phenylethynyl)benzo[*d*][1,3]dioxol-5-yl)but-3-en-2-one (2f)



2f

Compound **2f** was isolated after flash chromatography (SiO_2, Pentane/Et_2O 3:1) as yellow powder (1.313 g, 75%). **Molecular formula:** $C_{19}H_{14}O_3$. **Molecular mass:** 290.313 g mol^{-1}. **R_f** (pentane/Et_2O 3:1): 0.21. **Mp:** 135-136 °C. **^{1}H NMR** (600 MHz, $CDCl_3$): δ = 2.42 (s, 3 H, Me), 6.04 (s, 2 H, CH_2), 6.59 (d, *J* = 16.3 Hz, 1 H, CH), 7.00 (s, 1 H, ArH), 7.11 (s, 1 H, ArH), 7.36-7.39 (m, 3 H, ArH), 7.53-7.55 (m, 2 H, ArH), 8.13 (d, *J* = 16.3 Hz, 1 H, CH). **^{13}C NMR** (150 MHz, $CDCl_3$): δ = 27.1 (q), 87.0 (s), 94.9 (s), 102.2 (t), 105.3 (d), 111.9 (d), 119.5 (s), 122.9 (s), 127.1 (d), 128.7 (d, 2 C), 128.8 (d, 2 C), 131.1 (s), 131.6 (d), 141.6 (d), 148.8 (s), 149.6 (s), 198.7 (s). **IR** (ATR): $\tilde{\nu}$ = 3808, 3262, 3054, 3001, 2915, 2773, 2661, 2321, 2189, 2106, 1982, 1923, 1844, 1708, 1635, 1603, 1478, 1432, 1365, 1318, 1295, 1246, 1221, 1140, 1026, 971, 922, 857, 787, 750, 685 cm^{-1}. **MS (ESI$^+$)** *m/z* (%): 276.1 (48) $[M–CH_3]^+ = [C_{18}H_{11}O_3]^+$, 273.1 (43), 272.1 (71), 263.1 (14), 261.1 (22), 249.1 (19), 248.1 (15) $[M–C_2H_3O]^+ = [C_{17}H_{11}O_2]^+$, 246.1 (100), 244.1 (12), 233.1 (23), 105.0 (37). **HR-MS (ESI$^+$)** *m/z* (%): calcd. for $[M+H]^+ = [C_{19}H_{15}O_3]^+$: 291.1016; found: 291.1008. **EA:** calcd. for $C_{19}H_{14}O_3$: C 78.61 %, H 4.86 %; found: C 78.34 %, H 4.91 %.

(*E*)-4-(2-((Trimethylsilyl)ethynyl)phenyl)but-3-en-2-one (2g)



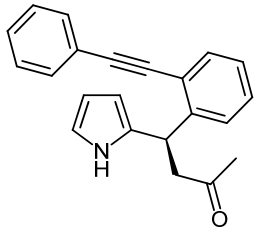
2g

Compound **2g** was isolated after flash chromatography (SiO_2, Pentane/Et_2O 3:1) as colorless powder (1,650 g, 76%). **Molecular formula:** $C_{15}H_{18}OSi$. **Molecular mass:** 242.388 g mol^{-1}. **R_f**

(pentane/Et_2O 5:1): 0.63. **Mp**: 65–67 °C. **^{1}H NMR** (600 MHz, $CDCl_3$): δ = 0.29 (s, 9 H, Me), 2.41 (s, 3 H, Me), 6.72 (d, J = 16.5 Hz, 1 H, CH), 7.31-7.36 (m, 2 H, ArH), 7.50-7.52 (m, 1 H, ArH), 7.62-7.65 (m, 1 H, ArH), 8.06 (d, J = 16.6 Hz, 1 H, CH). **^{13}C NMR** (150 MHz, $CDCl_3$): δ = 0.1 (q, 3 C), 26.7 (q), 101.4 (s), 102.5 (s), 124.2 (s), 126.1 (d), 129.0 (d, 2 C), 130.0 (d), 133.2 (d), 136.3 (s), 141.8 (d), 198.9 (s). **IR** (ATR): $\tilde{\nu}$ = 3290, 3060, 2960, 2323, 2153, 1984, 1938, 1658, 1468, 1414, 1354, 1291, 1245, 1091, 971, 834, 756 cm^{-1}. **MS (EI$^+$)** *m/z* (%): 242.9 (15), 242.1 (15) $[M]^+ = [C_{15}H_{18}OSi]^+$, 227.8 (57), 226.9 (50) $[M-CH_3]^+ = [C_{14}H_{15}OSi]^+$, 199.0 (22) $[M-C_2H_5O]^+ = [C_{13}H_{13}Si]^+$, 197.7 (73), 168.9 (21) $[M-TMS]^+ = [C_{12}H_9O]^+$, 167.9 (41). **MS (CI$^+$, methane)** *m/z* (%): 242.8 (29) $[M+H]^+ = [C_{15}H_{19}OSi]^+$, 226.4 (64) $[M-CH_3]^+ = [C_{14}H_{15}OSi]^+$, 199.5 (29) $[M-C_2H_5O]^+ = [C_{13}H_{13}Si]^+$. **EA:** calcd. for $C_{15}H_{18}OSi$: C 74.33 %, H 7.49 %; found: C 74.23 %, H 7.26 %.

Characterization of the Michael product 3

(*R*)-4-(2-(Phenylethynyl)phenyl)-4-(1H-pyrrol-2-yl)butan-2-one (3)

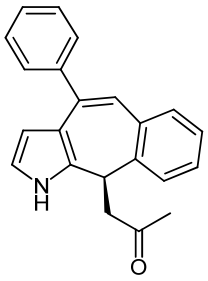


3

Compound **3** was isolated after flash chromatography (SiO_2, Pentane/Et_2O 5:1) as colorless oil (149.1 mg, 95%). **Molecular formula:** $C_{22}H_{19}NO$. **Molecular mass:** 313.392 g mol^{-1}. **R_f**(Pentane/EtOAc 4:1) = 0.30. **HPLC:** AS, 9/1 *n*-Heptane/EtOH, 1.0 ml/min, λ = 230 nm, τ_{minor} = 6.2 min, τ_{major} = 7.0 min. $[\alpha]_D^{20}$ = −210.6 (*c* = 0.75, $CHCl_3$, 93% ee). **^{1}H NMR** (600 MHz, $CDCl_3$): δ = 2.13 (s, 3 H, Me), 3.07 (dd, J = 4.9 Hz, J = 17.0 Hz, 1 H, CH_2), 3.26 (dd, J = 9.4 Hz, J = 17.0 Hz, 1 H, CH_2), 5.23 (dd, J = 4.9 Hz, J = 9.4 Hz, 1 H, CH), 5.90-5.93 (m, 1 H, ArH), 6.10 (dd, J = 2.8 Hz, J = 6.0 Hz, 1 H, ArH), 6.61-6.64 (m, 1 H, ArH), 7.13 (dd, J = 1.1 Hz, J = 7.7 Hz, 1 H, ArH), 7.19 (dt, J = 1.4 Hz, J = 7.5 Hz, 1 H, ArH), 7.24 (dt, J = 1.4 Hz, J = 7.6 Hz, 1 H, ArH), 7.30-7.36 (m, 3 H, ArH), 7.50-7.55 (m, 3 H, ArH), 8.30 (s, 1 H, NH). **^{13}C NMR** (150 MHz, $CDCl_3$): δ = 30.3 (q), 37.4 (d), 49.1 (t), 87.7 (s), 94.4 (s), 105.4 (d), 108.0 (d), 117.3 (d), 122.2 (s), 123.1 (s), 126.7 (d), 127.5 (d), 128.5 (d, 2 C), 128.6 (d, C), 128.9 (d), 131.7 (d, 2 C), 132.6 (d), 133.4 (s), 144.9 (s), 207.4 (s). **IR** (ATR): $\tilde{\nu}$ = 3730, 3340, 3134, 3095, 2997, 2905, 2848, 2650, 2452, 2331, 2113, 2016, 1825, 1696, 1597, 1568, 1492, 1440, 1356, 1287, 1240, 1186, 1154, 1118, 1096, 1022, 951, 914, 878, 799, 753, 722, 688 cm^{-1}. **MS (EI$^+$)** *m/z* (%): 313.3 (11) $[M]^+ = [C_{22}H_{19}NO]^+$, 270.1 (42) $[M-C_2H_3O]^+ = [C_{20}H_{16}NO]^+$, 256.3 (60) $[M-C_3H_5O]^+ = [C_{19}H_{14}N]^+$, 255.1 (100), 254.1 (84), 203.0 (25). **MS (CI$^+$, methane)** *m/z* (%): 314.3 (54) $[M+H]^+ = [C_{22}H_{20}NO]^+$, 313.3 (12) $[M]^+ = [C_{22}H_{19}NO]^+$, 257.2 (100), 256.3 (100) $[M-C_3H_5O]^+ =$

$[C_{19}H_{14}N]^+$. **HR-MS (ESI$^+$)** *m*/*z* (%): calcd. for $[M+Na]^+ = [C_{22}H_{19}NaNO_3]^+$: 336.13589; found: 336.13568.

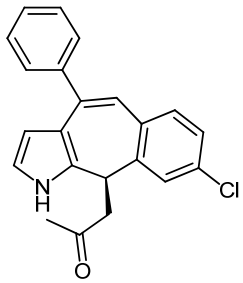
(*R*)-1-(4-Phenyl-1,10-dihydrobenzo[5,6]cyclohepta[1,2-*b*]pyrrol-10-yl)propan-2-one (17a)



17a

Compound **17a** was isolated after flash chromatography (SiO_2, Pentane/Et_2O 2:1) as pale yellow foam (139.0 mg, 89%). **Molecular formula:** $C_{22}H_{19}NO$. **Molecular mass:** 313.392 g mol^{-1}. **R_f**(Pentane/Et_2O 2:1) = 0.19. **Mp:** 150-152 °C. **HPLC:** OD, 95/5 *n*-Heptane/*i*PrOH, 1.0 ml/min, λ = 230 nm, τ_{minor} = 5.9 min, τ_{major} = 7.6 min. $[\alpha]_D^{20} = -9.9$ (*c* = 0.5, $CHCl_3$, 94% ee). **^{1}H NMR** (600 MHz, CD_2Cl_2): δ = 1.90 (s, 3 H, Me), 2.52-2.62 (m, 1 H, CH_2), 3.07 (dd, *J* = 9.5 Hz, *J* = 17.4 Hz, 1 H, CH_2), 4.59 (dd, *J* = 4.9 Hz, *J* = 9.3 Hz, 1 H, CH), 5.93 (t, *J* = 2.7 Hz, 1 H, ArH), 6.63 (d, *J* = 2.7 Hz, 1 H, ArH), 6.90 (s, 1 H, CH), 7.21-7.31 (m, 3 H, ArH), 7.33-7.38 (m, 1 H, ArH), 7.39-7.46 (m, 3 H, ArH), 7.58-7.63 (m, 2 H, ArH), 8.50 (s, 1 H, NH). **^{13}C NMR** (150 MHz, CD_2Cl_2): δ = 31.0 (q), 41.7 (d), 45.4 (t), 109.9 (d), 116.7 (d), 117.3 (s), 124.9 (d), 126.7 (d), 128.0 (d), 128.5 (d), 128.6 (d, 2 C), 129.2 (d, 3 C), 131.3 (d), 132.2 (s), 136.1 (s), 138.5 (s, 2 C), 143.6 (s), 208.2 (s). **IR** (ATR): $\tilde{\nu}$ = 3852, 3748, 3649, 3407, 3055, 2923, 2879, 2671, 2480, 2325, 2210, 2170, 2114, 2033, 1986, 1955, 1892, 1813, 1704, 1598, 1563, 1487, 1396, 1360, 1295, 1264, 1215, 1163, 1121, 1081, 1031, 950, 892, 843, 765, 697, 660 cm^{-1}. **MS (EI$^+$)** *m*/*z* (%): 313.3 (13) $[M]^+ = [C_{22}H_{19}NO]^+$, 256.3 (100) $[M-C_3H_5O]^+ = [C_{19}H_{14}N]^+$. **MS (CI$^+$, methane)** *m*/*z* (%): 314.3 (38) $[M+H]^+ = [C_{22}H_{20}NO]^+$, 313.3 (25) $[M]^+ = [C_{22}H_{19}NO]^+$, 256.3 (100) $[M-C_3H_5O]^+ = [C_{19}H_{14}N]^+$. **HR-MS (ESI$^+$)** *m*/*z* (%): calcd. for $[M+Na]^+ = [C_{22}H_{19}NNaO]^+$: 336.1359; found: 336.1359.

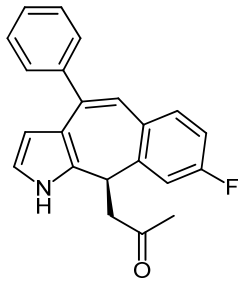
(*R*)-1-(8-Chloro-4-phenyl-1,10-dihydrobenzo[5,6]cyclohepta[1,2-*b*]pyrrol-10-yl)propan-2-one (17b)



17b

Compound **17b** was isolated after flash chromatography (SiO_2, Pentane/Et_2O 2:1) as pale yellow foam (173.0 mg, 99%). **Molecular formula:** $C_{22}H_{18}ClNO$. **Molecular mass:** 347.837 g mol^{-1}. **R_f**(Pentane/Et_2O 2:1) = 0.29. **Mp:** 58-60 °C. **HPLC:** IA, 9/1 *n*-Heptane/EtOH, 0.7 ml/min, λ = 230 nm, τ_{minor} = 10.5 min, τ_{major} = 8.3 min. $[\alpha]_D^{20}$ = +14.6 (*c* = 0.5, $CHCl_3$, 91% ee). **^{1}H NMR** (600 MHz, $CDCl_3$): δ = 1.98 (s, 3 H, Me), 2.58 (dd, *J* = 3.7 Hz, *J* = 17.4 Hz, 1 H, CH_2), 3.15 (dd, *J* = 9.7 Hz, *J* = 17.4 Hz, 1 H, CH_2), 4.61 (dd, *J* = 4.6 Hz, *J* = 9.7 Hz, 1 H, CH), 6.02 (t, *J* = 2.7 Hz, 1 H, ArH), 6.64 (d, *J* = 2.7 Hz, 1 H, ArH), 6.68 (s, 1 H, CH), 7.17-7.32 (m, 2 H, ArH), 7.35-7.43 (m, 2 H, ArH), 7.46 (t, *J* = 7.4, 2 H, ArH), 7.60-7.69 (m, 2 H, ArH), 8.64 (s, 1 H, NH). **^{13}C NMR** (150 MHz, $CDCl_3$): 30.9 (q), 40.9 (d), 44.9 (t), 109.8 (d), 116.7 (d), 117.0 (s), 123.3 (d), 126.4 (d), 127.8 (d), 128.3 (d, 2 C), 128.5 (d), 128.7 (d, 2 C), 131.0 (s), 132.2 (d), 133.6 (s), 134.3 (s), 138.5 (s), 139.0 (s), 142.9 (s), 208.0 (s). **IR** (ATR): $\tilde{\nu}$ = 3854, 3629, 3370, 3057, 3024, 2979, 2891, 2670, 2486, 2324, 2175, 2035, 1992, 1952, 1893, 1703, 1590, 1547, 1486, 1357, 1291, 1244, 1158, 1124, 1089, 955, 866, 814, 760, 698 cm^{-1}. **MS (EI$^+$)** *m*/*z* (%): 347.3 (13) [M, $^{35}Cl]^+$ = $[C_{22}H_{18}ClNO]^+$, 292.3 (32) [M−C_3H_5O, $^{37}Cl]^+$ = $[C_{19}H_{13}ClN]^+$, 290.2 (100) [M−C_3H_5O, $^{35}Cl]^+$ = $[C_{19}H_{13}ClN]^+$. **HR-MS (ESI$^+$)** *m*/*z* (%): calcd. for $[M+H]^+$ = $[C_{22}H_{19}ClNO]^+$: 348.1150; found: 348.1149.

(*R*)-1-(8-Fluoro-4-phenyl-1,10-dihydrobenzo[5,6]cyclohepta[1,2-*b*]pyrrol-10-yl)propan-2-one (17c)

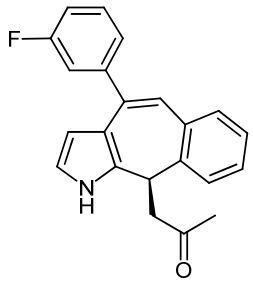


17c

Compound **17c** was isolated after flash chromatography (SiO_2, Pentane/Et_2O 2:1) as white foam (159.0 mg, 96%). **Molecular formula:** $C_{22}H_{18}FNO$. **Molecular mass:** 331.383 g mol^{-1}. **R_f**(Pentane/Et_2O 2:1) = 0.27. **HPLC:** AS, 9/1 *n*-Heptane/EtOH, 0.7 ml/min, λ = 230 nm, τ_{minor} = 10.4 min, τ_{major} = 8.3 min. $[\alpha]_D^{20}$ = +22.2 (*c* = 0.5, $CHCl_3$, 90% ee). **^{1}H NMR** (400 MHz, CD_2Cl_2): δ = 1.92

(s, 3 H, Me), 2.60 (m, 1 H, CH_2), 3.07 (dd, J = 9.5 Hz, J = 17.4 Hz, 1 H, CH_2), 4.54 (dd, J = 5.1 Hz, J = 9.3 Hz, 1 H, CH), 5.93 (t, J = 2.8 Hz, 1 H, ArH), 6.64 (t, J = 2.6 Hz, 1 H, ArH), 6.86 (s, 1 H, CH), 6.93-7.02 (m, 2 H, ArH), 7.31-7.46 (m, 4 H, ArH), 7.55-7.63 (m, 2 H, ArH), 8.47 (s, 1 H, NH). **^{13}C{^{19}F} NMR** (100.572 MHz, CD_2Cl_2): δ = 30.9 (q), 41.3 (d), 45.1 (t), 110.0 (d), 113.7 (d), 115.5 (s), 117.0 (d), 117.4 (s), 123.8 (d), 128.1 (d), 128.7 (d, 2 C), 129.1 (d, 2 C), 131.4 (s), 132.5 (s), 133.0 (d), 138.1 (d), 140.4 (s), 143.4 (s), 163.2 (s), 207.8 (s). **^{19}F{^{1}H} NMR** (375 MHz, CD_2Cl_2): δ = −116.12. **IR** (ATR): $\tilde{\nu}$ = 3373, 3056, 3026, 2892, 2328, 2197, 2164, 2109, 1994, 1965, 1886, 1811, 1704, 1599, 1565, 1492, 1395, 1357, 1266, 1147, 1082, 1028, 975, 941, 867, 813, 763, 699 cm^{-1}. **MS (EI$^+$)** *m/z* (%): 331.3 (16) $[M]^+ = [C_{22}H_{18}FNO]^+$, 274.3 (100) $[M-C_3H_5O]^+ = [C_{19}H_{13}FN]^+$. **MS (CI$^+$, methane)** *m/z* (%): 332.3 (38) $[M+H]^+ = [C_{22}H_{19}FNO]^+$, 331.3 (36) $[M]^+ = [C_{22}H_{18}FNO]^+$, 312.4 (14) $[M-F]^+ = [C_{22}H_{18}NO]^+$, 274.2 (100) $[M-C_3H_5O]^+ = [C_{19}H_{13}FN]^+$. **HR-MS (ESI$^+$)** *m/z* (%): calcd. for $[M+Na]^+ = [C_{22}H_{18}FNNaO]^+$: 354.1262; found: 354.1261.

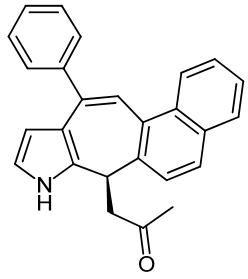
(*R*)-1-(4-(3-Fluorophenyl)-1,10-dihydrobenzo[5,6]cyclohepta[1,2-*b*]pyrrol-10-yl)propan-2-one (17d)



17d

Compound **17d** was isolated after flash chromatography (SiO_2, Pentane/Et_2O 2:1) as white foam (158.0 mg, 95%). **Molecular formula:** $C_{22}H_{18}FNO$. **Molecular mass:** 331.383 g mol^{-1}. **R_f**(Pentane/Et_2O 2:1) = 0.23. **HPLC:** AS, 9/1 *n*-Heptane/EtOH, 1.0 ml/min, λ = 230 nm, τ_{minor} = 7.9 min, τ_{major} = 5.8 min. $[\alpha]_D^{20}$ = +12.9 (*c* = 0.75, $CHCl_3$, 93% ee). **^{1}H NMR** (400 MHz, CD_2Cl_2): δ = 1.90 (s, 3 H, Me), 2.56 (dd, J = 4.7 Hz, J = 17.5 Hz, 1 H, CH_2), 3.04 (dd, J = 9.5 Hz, J = 17.4 Hz, 1 H, CH_2), 4.60 (dd, J = 5.0 Hz, J = 9.4 Hz, 1 H, CH), 5.95 (t, J = 2.7 Hz, 1 H, ArH), 6.64 (t, J = 2.7 Hz, 1 H, ArH), 6.91 (s, 1 H, CH), 7.01-7.11 (m, 1 H, ArH), 7.22-7.48 (m, 7 H, ArH), 8.54 (s, 1 H, NH). **^{13}C{^{19}F} NMR** (100 MHz, CD_2Cl_2): δ = 30.9 (q), 41.6 (d), 45.5 (t), 109.8 (d), 114.7 (d), 116.0 (d), 116.8 (s), 117.0 (d), 125.0 (d), 125.4 (d), 126.8 (d), 128.8 (d), 129.2 (d), 130.1 (d), 131.4 (d), 132.5 (s), 135.8 (s), 137.3 (s), 138.6 (s), 146.0 (s), 163.3 (s), 208.1 (s). **^{19}F{^{1}H} NMR** (375 MHz, CD_2Cl_2): δ = −114.69. **IR** (ATR): $\tilde{\nu}$ = 3362, 3018, 2925, 2645, 2322, 2099, 1930, 1700, 1577, 1475, 1373, 1173, 1091, 1018, 956, 857, 701 cm^{-1}. **MS (EI$^+$)** *m/z* (%): 331.3 (12) $[M]^+ = [C_{22}H_{18}FNO]^+$, 274.1 (100) $[M-C_3H_5O]^+ = [C_{19}H_{13}FN]^+$. **MS (CI$^+$, methane)** *m/z* (%): 332.4 (21) $[M+H]^+ = [C_{22}H_{19}FNO]^+$, 331.4 (12) $[M]^+ = [C_{22}H_{18}FNO]^+$, 275.4 (23), 274.3 (100) $[M-C_3H_5O]^+ = [C_{19}H_{13}FN]^+$. **HR-MS (ESI$^+$)** *m/z* (%): calcd. for $[M+Na]^+ = [C_{22}H_{18}FNNaO]^+$: 354.1262; found: 354.1262.

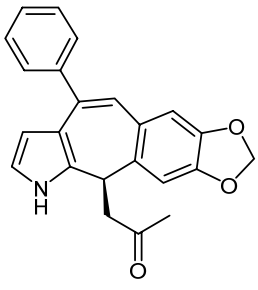
(*R*)-1-(4-Phenyl-1,12-dihydronaphtho[2',3':5,6]cyclohepta[1,2-*b*]pyrrol-12-yl)propan-2-one (17e)



17e

Compound **17e** was isolated after flash chromatography (SiO_2, Pentane/Et_2O 2:1) as pale yellow foam (147.0 mg, 81%). **Molecular formula:** $C_{26}H_{21}NO$. **Molecular mass:** 363.451 g mol^{-1}. **R_f**(Pentane/Et_2O 2:1) = 0.17. **Mp:** 73-75 °C. **HPLC:** IA, 95/5 *n*-Heptane/*i*PrOH, 0.7 ml/min, λ = 230 nm, τ_{minor} = 16.1 min, τ_{major} = 11.0 min. $[\alpha]_D^{20}$ = +37.3 (*c* = 0.5, $CHCl_3$, 93% ee). **^{1}H NMR** (600 MHz, CD_2Cl_2): δ = 1.91 (s, 3 H, Me), 2.70 (dd, *J* = 2.9 Hz, *J* = 17.1 Hz, 1 H, CH_2), 3.15 (dd, *J* = 9.0 Hz, *J* = 17.5 Hz, 1 H, CH_2), 4.68-4.75 (m, 1 H, CH), 6.01 (m, 1 H, ArH), 6.66 (d, *J* = 2.5 Hz, 1 H, ArH), 7.40 (t, *J* = 7.3 Hz, 2 H, ArH), 7.45-7.51 (m, 3 H, ArH), 7.60 (t, *J* = 7.6 Hz, 1 H, ArH), 7.71 (s, 1 H, CH), 7.75 (d, *J* = 7.9 Hz, 2 H, ArH), 7.78 (d, *J* = 8.0 Hz, 1 H, ArH), 7.84 (d, *J* = 8.0 Hz, 1 H, ArH), 8.46-8.55 (m, 2 H, Ar, NH). **^{13}C NMR** (150 MHz, CD_2Cl_2): 30.9 (q), 41.8 (d), 44.3 (t), 109.8 (d), 117.0 (d), 117.5 (s), 120.7 (d), 124.9 (d), 125.8 (d), 126.9 (d), 128.3 (d), 128.6 (d), 128.8 (d, 2 C), 128.9 (d), 129.2 (d), 129.4 (d, 2 C), 130.7 (s), 133.8 (s, 2 C), 133.4 (s), 137.7 (s), 139.7 (s), 144.1 (s), 208.2 (s). **IR** (ATR): $\tilde{\nu}$ = 3854, 3749, 3633, 3411, 3053, 2922, 2675, 2490, 2302, 2221, 2177, 2149, 2125, 2056, 2028, 1986, 1944, 1895, 1847, 1816, 1703, 1590, 1551, 1489, 1391, 1355, 1269, 1236, 1154, 1080, 1031, 945, 889, 810, 767, 699 cm^{-1}. **MS (EI$^+$)** *m/z* (%): 363.2 (16) $[M]^+ = [C_{26}H_{21}NO]^+$, 307.2 (24), 306.2 (100) $[M-C_3H_5O]^+ = [C_{23}H_{16}N]^+$. **MS (CI$^+$, methane)** *m/z* (%): 364.4 (41) $[M+H]^+ = [C_{26}H_{22}NO]^+$, 363.2 (24) $[M]^+ = [C_{26}H_{21}NO]^+$, 307.2 (25), 306.4 (100) $[M-C_3H_5O]^+ = [C_{23}H_{16}N]^+$. **MS (ESI$^+$)** *m/z* (%): 364.2 (40) $[M+H]^+ = [C_{26}H_{22}NO]^+$, 306.1 (100) $[M-C_3H_5O]^+ = [C_{23}H_{16}N]^+$. **HR-MS (ESI$^+$)** *m/z* (%): calcd. for $[M+H]^+ = [C_{26}H_{22}NO]^+$: 364.1696; found: 364.1712.

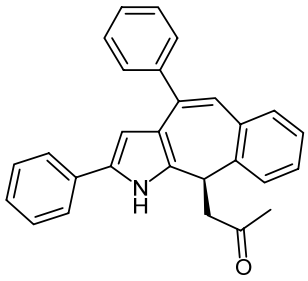
(*R*)-1-(9-Phenyl-5,6-dihydro-[1,3]dioxolo[4'',5'':4',5']benzo[1',2':5,6]cyclohepta[1,2-*b*]pyrrol-5-yl)propan-2-one (17f)



17f

Compound **17f** was isolated after flash chromatography (SiO_2, Pentane/Et_2O 2:1) as pale orange foam (172.1 mg, 96%). **Molecular formula:** $C_{23}H_{19}NO_3$. **Molecular mass:** 357.402 g mol^{-1}. $\mathbf{R_f}$(Pentane/Et_2O 2:1) = 0.22. **Mp:** 67-70 °C. **HPLC:** OD, 9/1 *n*-Heptane/EtOH, 0.7 ml/min, λ = 230 nm, τ_{minor} = 12.2 min, τ_{major} = 16.1 min. $[\alpha]_D^{20}$ = −3.30 (*c* = 1.1, $CHCl_3$, 92% ee). **^{1}H NMR** (600 MHz, $CDCl_3$): δ = 1.93 (s, 3 H, Me), 2.50-2.63 (m, 1 H, CH_2), 3.06 (dd, *J* = 9.4 Hz, *J* = 17.3 Hz, 1 H, CH_2), 4.47 (dd, *J* = 4.8 Hz, *J* = 8.5 Hz, 1 H, CH), 5.91 (s, 1 H, CH_2), 5.95 (s, 1 H, CH_2), 5.97-6.00 (m, 1 H, ArH), 6.57-6.65 (m, 1 H, ArH), 6.71 (s, 1 H, ArH), 6.76 (s, 1 H, ArH), 6.87 (s, 1 H, CH), 7.31-7.47 (m, 3 H, ArH), 7.53-7.65 (m, 2 H, ArH), 8.32 (s, 1 H, NH). **^{13}C NMR** (150 MHz, CD_2Cl_2): 31.0 (q), 41.8 (d), 45.2 (t), 101.4 (t), 108.9 (d), 109.7 (d), 110.3 (d), 116.4 (d), 117.0 (s), 124.2 (d), 127.5 (d), 128.3 (d, 2 C), 128.7 (d, 2 C), 129.9 (s), 131.2 (s), 131.9 (s), 136.7 (s), 143.1 (s), 146.3 (s), 148.0 (s), 208.4 (s). **IR** (ATR): $\tilde{\nu}$ = 3396, 3056, 2921, 2769, 2659, 2333, 2144, 1863, 1703, 1621, 1597, 1564, 1482, 1371, 1278, 1221, 1155, 1123, 1081, 1035, 932, 877, 760 cm^{-1}. **MS (EI$^+$)** *m*/*z* (%): 357.2 (19) $[M]^+$ = $[C_{23}H_{19}NO_3]^+$, 301.2 (22), 300.2 (100) $[M-C_3H_5O]^+$ = $[C_{20}H_{14}NO_2]^+$. **MS (CI$^+$, methane)** *m*/*z* (%): 359.4 (17), 358.3 (42) $[M+H]^+$ = $[C_{23}H_{20}NO_3]^+$, 301.3 (23), 300.3 (100) $[M-C_3H_5O]^+$ = $[C_{20}H_{14}NO_2]^+$. **MS (ESI$^+$)** *m*/*z* (%): 380.1 (44) $[M+Na]^+$ = $[C_{23}H_{19}NNaO]^+$, 358.1 (100) $[M+H]^+$ = $[C_{23}H_{20}NO_3]^+$, 328.1 (36) $[M-CHO]^+$ = $[C_{22}H_{18}N]^+$, 300.1 (48) $[M-C_3H_5O]^+$ = $[C_{20}H_{14}N]^+$. **HR-MS (ESI$^+$)** *m*/*z* (%): calcd. for $[M+H]^+$ = $[C_{23}H_{20}NO_3]^+$: 358.1438; found: 358.1453.

(*R*)-1-(2,4-Diphenyl-1,10-dihydrobenzo[5,6]cyclohepta[1,2-*b*]pyrrol-10-yl)propan-2-one (17g)

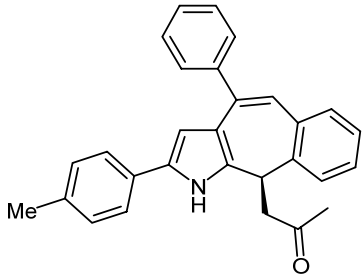


17g

Compound **17g** was isolated after flash chromatography (SiO_2, Pentane/Et_2O 2:1) as pale orange foam (186.1 mg, 96%). **Molecular formula:** $C_{28}H_{23}NO$. **Molecular mass:** 389.488 g mol^{-1}. $\mathbf{R_f}$(Pentane/Et_2O 2:1) = 0.29. **Mp:** 59-62 °C. **HPLC:** OD, 9/1 *n*-Heptane/EtOH, 1.0 ml/min, λ = 230 nm, τ_{minor} = 5.2 min, τ_{major} = 7.5 min. $[\alpha]_D^{20}$ = +5.5 (*c* = 0.5, $CHCl_3$, 85% ee). **^{1}H NMR** (500 MHz, $CDCl_3$): δ = 1.96 (s, 3 H, Me), 2.60 (dd, *J* = 4.5 Hz, *J* = 17.6 Hz, 1 H, CH_2), 3.16 (dd, *J* = 9.6 Hz, *J* = 17.5 Hz, 1 H, CH_2), 4.68 (dd, *J* = 4.7 Hz, *J* = 9.5 Hz, 1 H, CH), 6.28 (d, *J* = 2.6 Hz, 1 H, ArH), 6.93 (s, 1 H, CH), 7.10-7.20 (m, 1 H, ArH), 7.22-7.34 (m, 5 H, ArH), 7.35-7.49 (m, 6 H, ArH), 7.65 (dd, *J* = 1.2 Hz, *J* = 8.1 Hz, 2 H, ArH), 8.70 (s, 1 H, NH). **^{13}C NMR** (150 MHz, CD_3Cl): δ = 31.0 (q), 41.4 (d), 45.4 (t), 107.1 (d), 118.7 (d), 123.8 (d, 2 C), 125.1 (d), 126.3 (d), 126.5 (d), 127.7 (d), 128.4 (d, 3 C), 128.9 (d, 5 C), 130.7 (s), 131.1 (d), 132.5 (s), 133.0 (s), 135.7 (s), 137.6 (s), 137.8 (s), 143.0 (s), 208.3 (s). **IR** (ATR): $\tilde{\nu}$ = 3350, 3056, 3022, 2925, 2660, 2322, 2087, 1929, 1702, 1600, 1559, 1522, 1481,

1448, 1358, 1297, 1240, 1208, 1163, 1122, 1076, 1028, 946, 946, 907, 881, 849, 812, 756, 694 cm^{-1}. **MS (EI$^+$)** *m/z* (%): 389.2 (14) $[M]^+ = [C_{28}H_{23}NO]^+$, 333.2 (27), 332.2 (100) $[M-C_3H_5O]^+ = [C_{25}H_{18}N]^+$. **HR-MS (ESI$^+$)** *m/z* (%): calcd. for $[M+H]^+ = [C_{28}H_{24}NO]^+$: 390.1857; found: 390.1868.

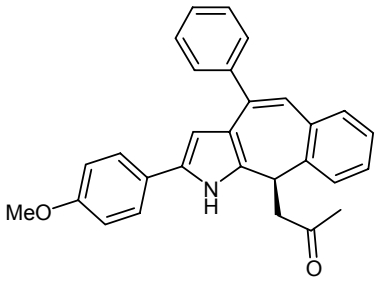
(*R*)-1-(4-Phenyl-2-(p-tolyl)-1,10-dihydrobenzo[5,6]cyclohepta[1,2-*b*]pyrrol-10-yl)propan-2-one (17h)



17h

Compound **17h** was isolated after flash chromatography (SiO_2, Pentane/Et_2O 2:1) as pale orange foam (171.0 mg, 85%). **Molecular formula:** $C_{29}H_{25}NO$. **Molecular mass:** 403.515 g mol^{-1}. **R_f**(Pentane/Et_2O 2:1) = 0.29. **Mp:** 185-187 °C. **HPLC:** AD, 7/3 *n*-Heptane/*i*PrOH, 1.0 ml/min, λ = 230 nm, τ_{minor} = 7.7 min, τ_{major} = 4.5 min. $[\alpha]_D^{20}$ = −5.4 (*c* = 0.5, $CHCl_3$, 78% ee). **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 1.95 (s, 3 H, Me), 2.31 (s, 3 H, Me), 2.60 (dd, *J* = 4.7 Hz, *J* = 17.3 Hz, 1 H, CH_2), 3.15 (dd, *J* = 9.6 Hz, *J* = 17.4 Hz, 1 H, CH_2), 4.67 (dd, *J* = 4.7 Hz, *J* = 9.5 Hz, 1 H, CH), 6.22 (d, *J* = 2.6 Hz, 1 H, ArH), 6.92 (s, 1 H, CH), 7.11 (d, *J* = 7.9 Hz, 2 H, ArH), 7.20-7.34 (m, 5 H, ArH), 7.34-7.49 (m, 4 H, ArH), 7.60-7.71 (m, 2 H, ArH), 8.64 (s, 1 H, NH). **^{13}C NMR** (100 MHz, $CDCl_3$): δ = 21.2 (q), 31.0 (q), 41.5 (d), 45.4 (t), 106.6 (d), 118.6 (s), 123.8 (d, 2 C), 125.0 (d), 126.5 (d), 127.7 (d), 128.4 (d, 3 C), 128.9 (d, 3 C), 129.6 (d, 2 C), 129.8 (s), 130.9 (s), 131.1 (d), 132.6 (s), 135.7 (s), 136.0 (s), 137.6 (s), 137.9 (s), 143.1 (s), 208.3 (s). **IR** (ATR): $\tilde{\nu}$ = 3852, 3341, 3058, 3022, 2921, 2861, 2672, 2330, 2217, 2082, 1991, 1892, 1800, 1695, 1595, 1532, 1484, 1440, 1350, 1244, 1214, 1161, 1112, 1027, 941, 879, 850, 801, 747, 695 cm^{-1}. **MS (EI$^+$)** *m/z* (%): 403.4 (17) $[M]^+ = [C_{29}H_{25}NO]^+$, 347.4 (29), 346.3 (100) $[M-C_3H_5O]^+ = [C_{26}H_{20}N]^+$. **MS (ESI$^+$)** *m/z* (%): 404.2 (50) $[M+H]^+ = [C_{29}H_{26}NO]^+$, 346.2 (100) $[M-C_3H_5O]^+ = [C_{26}H_{20}N]^+$. **HR-MS (ESI$^+$)** *m/z* (%): calcd. for $[M+H]^+ = [C_{29}H_{26}NO]^+$: 404.2009; found: 404.2019.

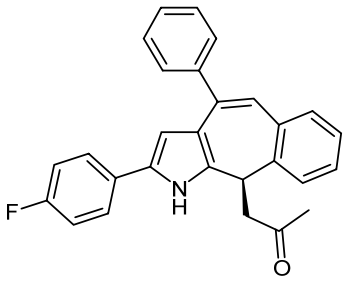
(*R*)-1-(2-(4-Methoxyphenyl)-4-phenyl-1,10-dihydrobenzo[5,6]cyclohepta[1,2-*b*]pyrrol-10-yl)propan-2-one (17i)



17i

Compound **17i** was isolated after flash chromatography (SiO_2, Pentane/Et_2O 2:1) as orange solid (185.0 mg, 73%). **Molecular formula:** $C_{29}H_{25}NO_2$. **Molecular mass:** 419.514 g mol^{-1}. **R_f**(Pentane/Et_2O 2:1) = 0.16. **Mp:** 98-102 °C. **HPLC:** AD, 7/3 *n*-Heptane/*i*PrOH, 1.0 ml/min, λ = 230 nm, τ_{minor} = 11.2 min, τ_{major} = 5.4 min. $[\alpha]_D^{20}$ = −8.8 (*c* = 0.6, $CHCl_3$, 73% ee). **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 1.93 (s, 3 H, Me), 2.62 (dd, *J* = 4.5 Hz, *J* = 17.5 Hz, 1 H, CH_2), 3.12 (dd, *J* = 9.4 Hz, *J* = 17.5 Hz, 1 H, CH_2), 3.77 (s, 3 H, OMe), 4.65 (dd, *J* = 4.9 Hz, *J* = 9.2 Hz, 1 H, CH), 6.13 (d, *J* = 2.7 Hz, 1 H, ArH), 6.84-6.88 (m, 2 H, ArH), 6.92 (s, 1 H, CH), 7.23-7.49 (m, 9 H, ArH), 7.63-7.68 (m, 2 H, ArH), 8.74 (s, 1 H, NH). **^{13}C NMR** (100 MHz, $CDCl_3$): δ = 31.0 (q), 41.7 (d), 45.9 (t), 55.8 (q), 106.1 (d), 114.8 (d, 2 C), 118.8 (s), 125.2 (d), 125.5 (d, 2 C), 125.9 (s), 126.7 (d), 128.0 (d), 128.6 (d), 128.7 (d, 2 C), 129.2 (d, 3 C), 131.0 (s), 131.4 (d), 133.0 (s), 136.1 (s), 138.3 (s, 2 C), 143.5 (s), 158.9 (s), 208.4 (s). **IR** (ATR): $\tilde{\nu}$ = 3856, 3610, 3351, 3054, 3015, 2934, 2834, 2673, 2330, 2176, 2088, 1915, 1702, 1582, 1528, 1487, 1438, 1357, 1276, 1244, 1176, 1109, 1028, 946, 913, 880, 856, 831, 798, 760, 699, 671 cm^{-1}. **MS (EI$^+$)** *m*/*z* (%): 419.2 (16) $[M]^+ = [C_{29}H_{25}NO_2]^+$, 363.2 (27), 362.2 (100) $[M\text{-}C_3H_5O]^+ = [C_{26}H_{20}NO]^+$. **MS (ESI$^+$)** *m*/*z* (%): 420.2 (72) $[M+H]^+ = [C_{29}H_{26}NO_2]^+$, 362.2 (100) $[M\text{-}C_3H_5O]^+ = [C_{26}H_{20}N]^+$. **HR-MS (ESI$^+$)** *m*/*z* (%): calcd. for $[M+H]^+ = [C_{29}H_{26}NO_2]^+$: 420.1958; found: 420.1966.

***(R)*-1-(2-(4-fluorophenyl)-4-phenyl-1,10-dihydrobenzo[5,6]cyclohepta[1,2-*b*]pyrrol-10-yl)propan-2-one (17j)**

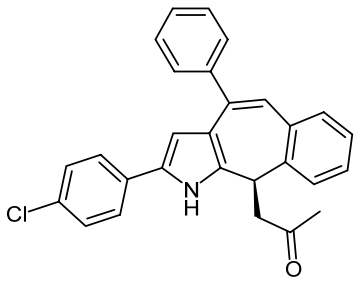


17j

Compound **17j** was isolated after flash chromatography (SiO_2, Pentane/Et_2O 2:1) as yellow foam (173.0 mg, 85%). **Molecular formula:** $C_{28}H_{22}FNO$. **Molecular mass:** 407.479g mol^{-1}. **R_f**(Pentane/Et_2O 2:1) = 0.26. **Mp:** 87-91 °C. **HPLC:** AD, 7/3 *n*-Heptane/*i*PrOH, 1.0 ml/min, λ = 230

nm, τ_{minor} = 6.9 min, τ_{major} = 4.4 min. $[\alpha]_D^{20}$ = +25.9 (*c* = 0.7, $CHCl_3$, 84% ee). **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 1.96 (s, 3 H, Me), 2.63 (dd, *J* = 4.7 Hz, *J* = 17.4 Hz, 1 H, CH_2), 3.17 (dd, *J* = 9.5 Hz, *J* = 17.4 Hz, 1 H, CH_2), 4.74 (dd, *J* = 4.8 Hz, *J* = 9.4 Hz, 1 H, CH), 6.19 (d, *J* = 2.6 Hz, 1 H, ArH), 6.88-7.00 (m, 3 H, ArH, CH), 7.18-7.35 (m, 5 H, ArH), 7.35-7.50 (m, 4 H, ArH), 7.61-7.70 (m, 2 H, ArH), 9.03 (s, 1 H, NH). **^{13}C{^{19}F} NMR** (100 MHz, $CDCl_3$): δ = 31.0 (q), 41.4 (d), 45.3 (t), 106.9 (d), 115.7 (d, 2 C), 118.6 (s), 125.1 (d), 125.4 (d, 2 C), 126.5 (d), 127.7 (d), 128.3 (d), 128.4 (d, 2 C), 128.8 (d, 3 C), 128.9 (s), 129.9 (s), 131.4 (d), 132.9 (s), 135.6 (s), 137.5 (s), 137.8 (s), 143.0 (s), 161.5 (s), 208.8 (s). **^{19}F{^{1}H} NMR** (375MHz, $CDCl_3$): δ = −116.33. **IR** (ATR): $\tilde{\nu}$ = 3637, 3368, 3054, 2922, 2669, 2327, 2218, 2087, 1887, 1816, 1700, 1582, 1526, 1484, 1428, 1359, 1299, 1225, 1158, 1097, 1026, 946, 913, 880, 813, 759, 698 cm^{-1}. **MS (EI$^+$)** *m*/*z* (%): 407.2 (14) $[M]^+ = [C_{28}H_{22}FNO]^+$, 351.2 (26), 350.2 (100) $[M-C_3H_5O]^+ = [C_{25}H_{17}FN]^+$. **MS (ESI$^+$)** *m*/*z* (%): 408.2 (90) $[M+H]^+ = [C_{28}H_{23}FNO]^+$, 350.1 (100) $[M-C_3H_5O]^+ = [C_{25}H_{17}FN]^+$. **HR-MS (ESI$^+$)** *m*/*z* (%): calcd. for $[M+H]^+ = [C_{28}H_{23}FNO]^+$: 408.1764; found: 408.1772.

(*R*)-1-(2-(4-Chlorophenyl)-4-phenyl-1,10-dihydrobenzo[5,6]cyclohepta[1,2-*b*]pyrrol-10-yl)propan-2-one (17k)

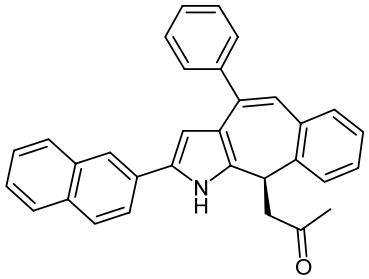


17k

Compound **17k** was isolated after flash chromatography (SiO_2, Pentane/Et_2O 2:1) as yellow foam (162.1 mg, 76%). **Molecular formula:** $C_{28}H_{22}ClNO$. **Molecular mass:** 423.933 g mol^{-1}. **R_f**(Pentane/Et_2O 2:1) = 0.27. **Mp:** 195-198 °C. **HPLC:** IA, 7/3 *n*-Heptane/*i*PrOH, 0.7 ml/min, λ = 230 nm, τ_{minor} = 8.5 min, τ_{major} = 6.9 min. $[\alpha]_D^{20}$ = +6.6° (*c* = 0.5, $CHCl_3$, 86% ee). **^{1}H NMR** (400 MHz, CD_2Cl_2): δ = 1.95 (s, 3 H, Me), 2.65 (dd, *J* = 4.0 Hz, *J* = 16.0 Hz, 1 H, CH_2), 3.17 (dd, *J* = 9.5 Hz, *J* = 17.6 Hz, 1 H, CH_2), 4.74 (dd, *J* = 4.7 Hz, *J* = 9.0 Hz, 1 H, CH), 6.23 (d, *J* = 2.2 Hz, 1 H, ArH), 6.96 (s, 1 H, CH), 7.18-7.31 (m, 7 H, ArH), 7.34-7.41 (m, 1 H, ArH), 7.45 (t, *J* = 7.3 Hz, 3 H, ArH), 7.65 (d, *J* = 7.3 Hz, 2 H, ArH), 9.28 (s, 1 H, NH). **^{13}C NMR** (100 MHz, CD_2Cl_2): δ = 31.2 (q), 41.7 (d), 45.5 (t), 107.7 (d), 119.2 (s), 125.3 (d, 2 C), 125.5 (d), 126.9 (d), 128.2 (d), 128.8 (d, 3 C), 129.2 (d, 3 C), 129.3 (d, 2 C), 130.0 (s), 131.5 (d), 131.6 (s), 131.8 (s), 134.1 (s), 136.1 (s), 138.1 (s), 138.2 (s), 143.3 (s), 209.1 (s). **IR** (ATR): $\tilde{\nu}$ = 3857, 3632, 3344, 3054, 3021, 2924, 2668, 2326, 2088, 1984, 1917, 1701, 1595, 1518, 1479, 1418, 1357, 1298, 1211, 1164, 1090, 1013, 945, 911, 880, 811, 757, 697 cm^{-1}. **MS (EI$^+$)** *m*/*z* (%): 423.2 (13) [M, ^{35}Cl]$^+ = [C_{28}H_{22}ClNO]^+$, 368.1 (28) [M−$C_3H_5O$, ^{37}Cl]$^+ = [C_{25}H_{17}ClN]^+$, 366.1 (100) [M−$C_3H_5O$, ^{35}Cl]$^+ = [C_{25}H_{17}ClN]^+$. **MS (CI$^+$, methane)** *m*/*z* (%): 426.4 (43) [M+H, ^{37}Cl]$^+$

= $[C_{28}H_{23}ClNO]^+$, 425.4 (41) [M, $^{37}Cl]^+$ = $[C_{28}H_{22}ClNO]^+$, 424.4 (100) [M+H, $^{35}Cl]^+$ = $[C_{28}H_{23}ClNO]^+$, 423.3 (50) [M, $^{35}Cl]^+$ = $[C_{28}H_{23}ClNO]^+$, 368.3 (33) [M−C_3H_5O, $^{37}Cl]^+$ = $[C_{25}H_{18}ClN]^+$, 366.3 (94) [M−C_3H_5O, $^{35}Cl]^+$ = $[C_{25}H_{18}ClN]^+$. **MS (ESI$^+$)** *m*/*z* (%): 462.1 (8) [M+K, $^{35}Cl]^+$ = $[C_{28}H_{22}ClKNO]^+$, 446.1 (32) [M+Na, $^{35}Cl]^+$ = $[C_{28}H_{22}ClNNaO]^+$, 424.1 (81) [M+H, $^{35}Cl]^+$ = $[C_{28}H_{23}ClNO]^+$, 366.1 (100) [M−C_3H_5O, $^{35}Cl]^+$ = $[C_{25}H_{17}ClN]^+$. **HR-MS (ESI$^+$)** *m*/*z* (%): calcd. for $[M+H]^+$ = $[C_{28}H_{23}ClNO]^+$: 424.1463; found: 424.1480.

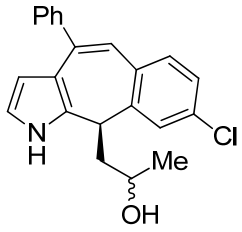
(*R*)-1-(2-(Naphthalen-2-yl)-4-phenyl-1,10-dihydrobenzo[5,6]cyclohepta[1,2-*b*]pyrrol-10-yl)propan-2-one (17l)



17l

Compound **17l** was isolated after flash chromatography (SiO_2, Pentane/Et_2O 2:1) as red foam (154.3 mg, 70%). **Molecular formula:** $C_{32}H_{25}NO$. **Molecular mass:** 439.547 g mol^{-1}. **R_f**(Pentane/Et_2O 2:1) = 0.31. **Mp:** 128-132 °C. **HPLC:** IA, 7/3 *n*-Heptane/*i*PrOH, 1.0 ml/min, λ = 230 nm, τ_{minor} = 7.5 min, τ_{major} = 4.7 min. $[\alpha]_D^{20}$ = −3.9 (*c* = 0.5, $CHCl_3$, 81% ee). **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 1.98 (s, 3 H, Me), 2.63 (dd, *J* = 4.5 Hz, *J* = 17.6 Hz, 1 H, CH_2), 3.20 (dd, *J* = 9.7 Hz, *J* = 17.5 Hz, 1 H, CH_2), 4.74 (dd, *J* = 4.7 Hz, *J* = 9.7 Hz, 1 H, CH), 6.40 (d, *J* = 2.6 Hz, 1 H, ArH), 6.95 (s, 1 H, CH), 7.25-7.33 (m, 3 H, ArH), 7.35-7.50 (m, 6 H, ArH), 7.51-7.57 (m, 1 H, ArH), 7.65-7.70 (m, 2 H, ArH), 7.72-7.82 (m, 4 H, ArH), 9.28 (s, 1 H, NH). **^{13}C NMR** (100 MHz, $CDCl_3$): δ = 31.0 (q), 41.5 (d), 45.4 (t), 107.8 (d), 118.9 (s), 121.0 (d), 123.1 (d), 125.2 (d), 125.4 (d), 126.5 (d, 2 C), 127.8 (d, 3 C), 128.4 (d, 3 C), 128.6 (d), 128.9 (d, 3 C), 129.9 (s), 130.8 (s), 131.2 (d), 132.2 (s), 133.4 (s), 133.9 (s), 135.7 (s), 137.5 (s), 137.8 (s), 143.0 (s), 208.3 (s). **IR** (ATR): $\tilde{\nu}$ = 3890, 3728, 3636, 3347, 3047, 2923, 2657, 2547, 2324, 2222, 2057, 1928, 1703, 1601, 1481, 1359, 1240, 1161, 1026, 945, 854, 806, 752, 697 cm^{-1}. **MS (EI$^+$)** *m*/*z* (%): 439.3 (10) $[M]^+$ = $[C_{32}H_{25}NO]^+$, 383.2 (21), 382.2 (100) [M−$C_3H_5O]^+$ = $[C_{29}H_{20}N]^+$. **MS (ESI$^+$)** *m*/*z* (%): 440.2 (32) $[M+H]^+$ = $[C_{32}H_{26}NO]^+$: 382.2 (100) [M−$C_3H_5O]^+$ = $[C_{29}H_{20}N]^+$. **HR-MS (ESI$^+$)** *m*/*z* (%): calcd. for $[M+H]^+$ = $[C_{32}H_{26}NO]^+$: 440.2009; found: 440.2017.0078

(*R*)-1-((*R/S*)-8-Chloro-4-phenyl-1,10-dihydrobenzo[5,6]cyclohepta[1,2-b]pyrrol-10-yl)propan-2-ol (18)



18

A solution of **17b** (157.1 mg, 0.45 mmol) in MeOH (2 mL) was added slowly to a solution of sodium borohydride (17.2 mg, 0.45 mmol) in MeOH (3 mL) at −78 °C. The reaction was allowed to warm to room temperature, water was added, and the layers were separated. The organic layer was extracted with DCM, the combined organic layers dried over $MgSO_4$, and the solvent was removed *in vacuo*. The crude product was purified by flash chromatography (SiO_2, Pentane/Et_2O 1:2) to yield**18** (150 mg, 95%, 64:36 d.r) as white foam.

Molecular formula: $C_{22}H_{20}ClNO$. **Molecular mass:** 349.853 g mol^{-1}. **R_f**(Pentane/Et_2O 1:2) = 0.31. **Mp**: 80-82 °C (main diastereomer). **HPLC:** IC, 97/3 *n*-Heptane/*i*PrOH, 0.3 ml/min, λ = 230 nm, main diasteromer: τ_{minor} = 12.6 min, τ_{major} = 21.2 min; minor diasteromer: τ_{minor} = 10.0 min, τ_{major} = 11.7 min. $[\alpha]_D^{20}$ = +120.2 (*c* = 0.5, $CHCl_3$, 92% ee). **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 1.05 (d, *J*= 6.2 Hz 3 H, Me), 1.55-1.91 (m, 2 H, CH_2, OH), 1.92-2.03 (m, 1 H, CH_2), 3.41-3.54 (m, 1 H, CH), 4.27 (dd, *J*= 17.4 Hz, *J*= 6.4 Hz, 1 H, CH), 6.01 (t, *J*= 2.7 Hz, 1 H, ArH), 6.62 (t, *J*= 2.7 Hz, 1 H, ArH), 6.80 (s, 1 H, CH). 7.18-7.22 (dd, *J*= 8.2 Hz,*J*= 2.2 Hz, 1 H, ArH), 7.24-7.26 (m, 1 H, ArH), 7.32-7.38 (m, 2 H, ArH), 7.38-7.44 (m, 2 H, ArH), 7.58-7.64 (m, 2 H, ArH), 8.44 (s, 1 H, NH). **^{13}C NMR** (100 MHz, $CDCl_3$): δ = 24.4 (q), 39.6 (t), 42.7 (d), 65.6 (d), 110.2 (d), 116.3 (d), 117.5 (s), 123.3 (d), 126.2 (d), 127.7 (d), 128.3 (d, 2 C), 128.8 (d, 3 C), 131.8 (s), 132.4 (d), 133.3 (s), 134.2 (s), 138.5 (s), 139.5 (s), 143.0 (s). **IR** (ATR): $\tilde{\nu}$ = 3838, 3558, 3410, 3020, 2963, 2658, 2324, 2102, 1896, 1739, 1588, 1477, 1373, 1213, 1074, 1011, 927, 864, 814, 757, 698 cm^{-1}. **HR-MS (ESI$^+$)** *m*/*z* (%): calcd. for $[M+H]^+$ = $[C_{22}H_{21}ClNO]^+$: 350.1306; found: 350.1304.

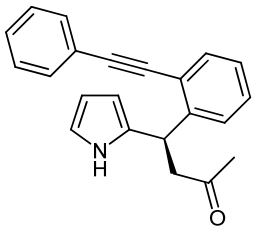
Sample Name: DH 133 rac
Data file: D:\ERNIE\DH\133RAS.D
Sample Info: Laufmittel: n-Heptan/EtOH 9:1;
Die Probe ist in DCM/1M gelöst

Agilent Technologies

Säule: DAICELAS.M
Säuleninfo: Chiralpak AS (250 x 4.6)mm 10µ

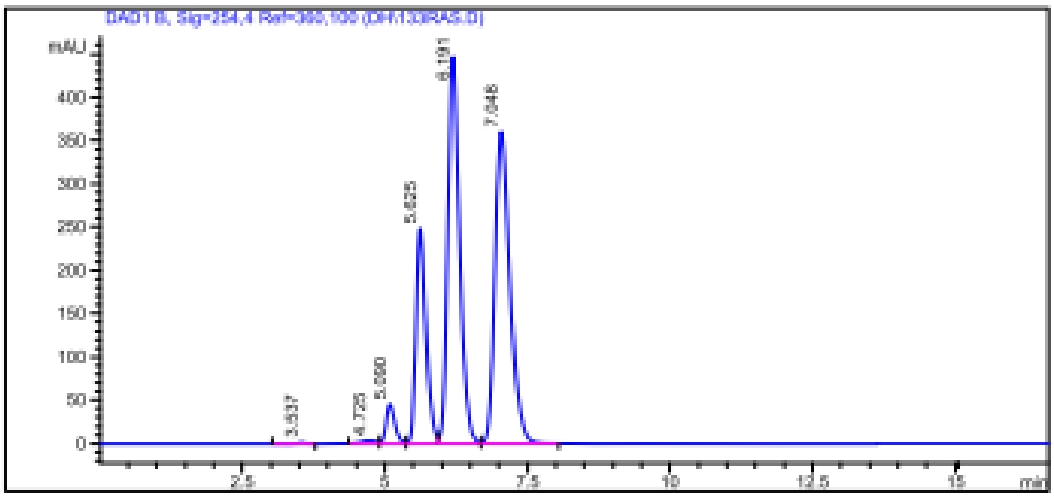
Operator: Analytik Labor AKEN

Injektion Time: 14:55:16
Injektion Date: 28.01.2013



3

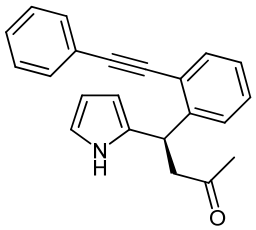
Instrument Conditions:	At Start	At Stop
Temperature in°C:	30.0	30.0
Pressure in bar:	32.0	31.6
Flow in ml/min:	1.0	1.0



#	Ret. Time (min)	Width	Height (mAU)	Area (mAU*s)	Area %
1	3.54	0.11	1.87	14.22	0.09
2	4.73	0.31	3.68	74.26	0.45
3	5.09	0.16	44.85	487.55	2.93
4	5.62	0.18	247.88	2953.65	17.78
5	6.19	0.23	447.78	6544.70	39.40
6	7.05	0.28	359.67	6538.16	39.36
Total				16612.54	100.00

Sample Name: DH 328
Data file: D:\ERNIE\DH\328AS.D
Sample Info: Laufmittel: n-Heptan/EtOH 9:1;
Die Probe ist in DCM/LM gelöst

Agilent Technologies



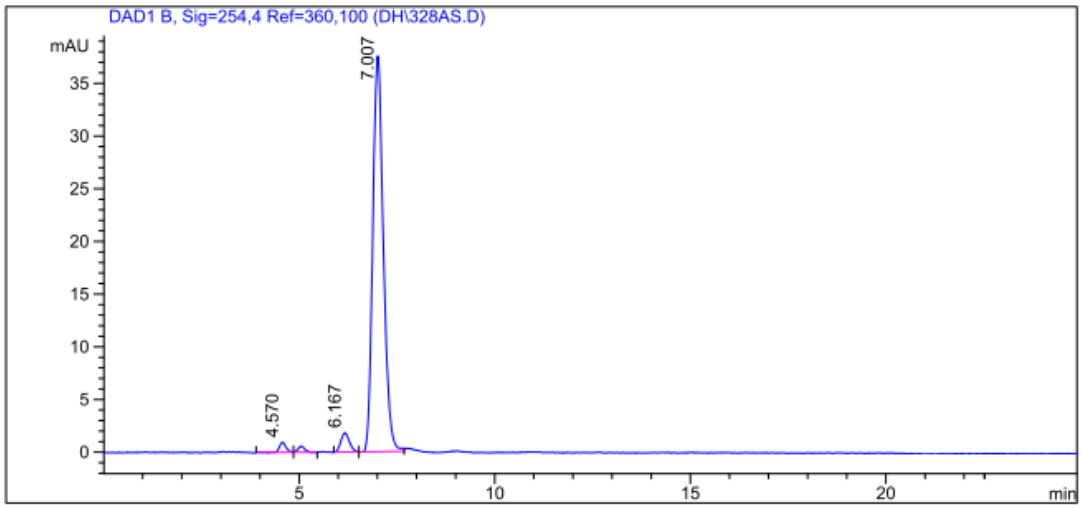
3

Säule: DAICELAS.M
Säuleninfo: Chiralpak AS (250 x 4.6)mm 10µ

Operator: Analytik Labor AKEN

Injektion Time: 13:28:50
Injektion Date: 08.07.2013

Instrument Conditions:	At Start	At Stop
Temperature in°C:	30.0	30.0
Pressure in bar:	30.8	30.8
Flow in ml/min:	1.0	1.0



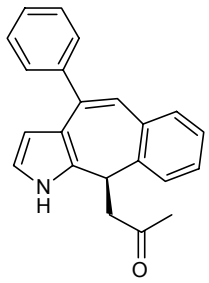
#	Ret. Time (min)	Width	Height (mAU)	Area (mAU*s)	Area %
1	4.57	0.17	0.95	11.28	1.50
2	5.04	0.16	0.59	6.94	0.92
3	6.17	0.24	1.83	27.92	3.71
4	7.01	0.29	37.56	706.21	93.87
Total				752.35	100.00

Sample Name: DH 195 rac
Data file: D:\GONZO\DH\195R1OD.D
Sample Info: Laufmittel: n-Heptan/IP 9:1;
Die Probe ist in DCM/LM gelöst.

Säule: DAICELOD.M
Säuleninfo: Chiralcel OD (250x4,6)mm
Operator: Analytik Labor AKEN

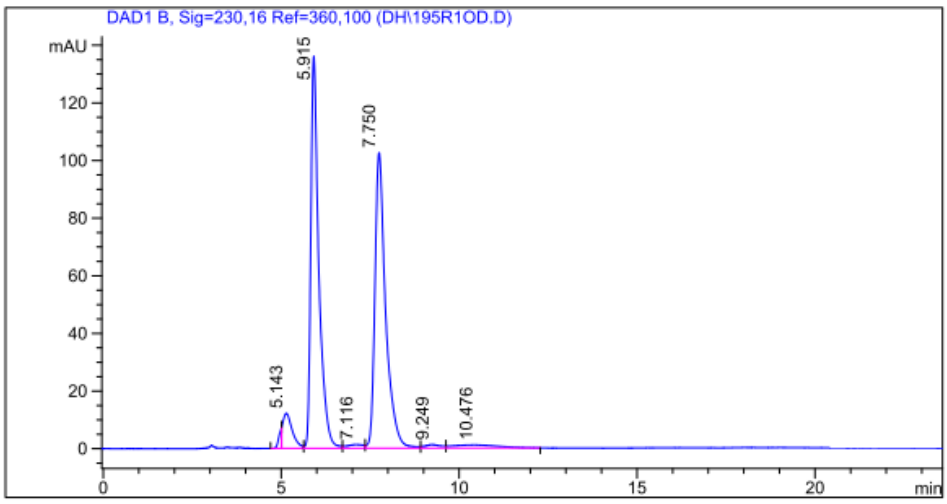
Injektion Time: 15:13:38
Injektion Date: 01.03.2013

Instrument Conditions:	At Start	At Stop
Temperature in°C:	30.0°C	30.0°C
Pressure in bar:	32.9	34.1
Flow in ml/min:	1.00	1.00



->

17a



#	Ret. Time (min)	Width	Height (mAU)	Area (mAU*s)	Area %
1	4.95	0.11	4.62	37.04	0.79
2	5.14	0.28	12.19	225.51	4.78
3	5.91	0.23	136.10	2128.30	45.11
4	7.12	0.42	1.28	40.64	0.86
5	7.75	0.31	102.56	2151.49	45.60
6	9.25	0.41	1.22	37.79	0.80
7	10.48	1.05	1.10	97.54	2.07
Total				4718.31	100.00

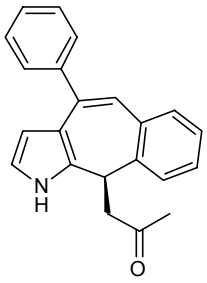
Sample Name: DH 338
Data file: D:\GONZO\DH\338OD.D
Sample Info: Laufmittel: n-Heptan/IP 9:1;
Die Probe ist in DCM/LM gelöst.

Säule: DAICELOD.M
Säuleninfo: Chiralcel OD (250x4,6)mm
Operator: Analytik Labor AKEN

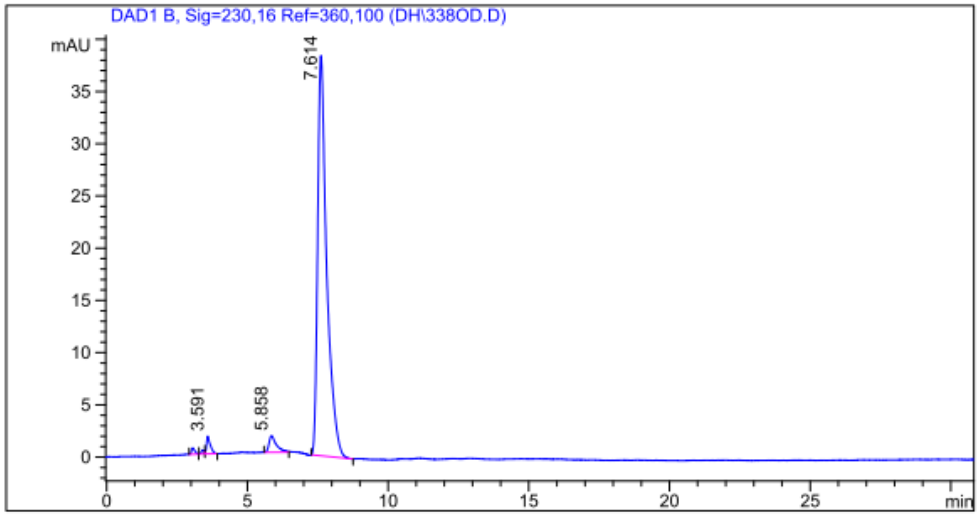
Injektion Time: 13:34:38
Injektion Date: 23.07.2013

Instrument Conditions:	At Start	At Stop
Temperature in°C:	30.0°C	30.0°C
Pressure in bar:	26.1	26.8
Flow in ml/min:	1.00	1.00

->



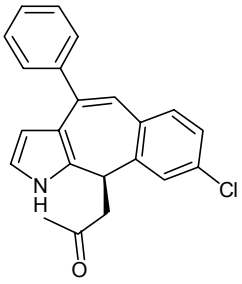
17a



#	Ret. Time (min)	Width	Height (mAU)	Area (mAU*s)	Area %
1	3.06	0.13	0.62	5.33	0.58
2	3.41	0.12	0.39	2.96	0.32
3	3.59	0.13	1.71	15.78	1.73
4	5.86	0.26	1.59	29.13	3.20
5	7.61	0.33	38.32	858.42	94.17
Total				911.61	100.00

Sample Name: DH JH 42 rac
Data file: D:\ERNIE\DH\JH42RAS.D
Sample Info: Laufmittel: n-Heptan/EtOH 9:1;
Die Probe ist in DCM/LM gelöst

Agilent Technologies



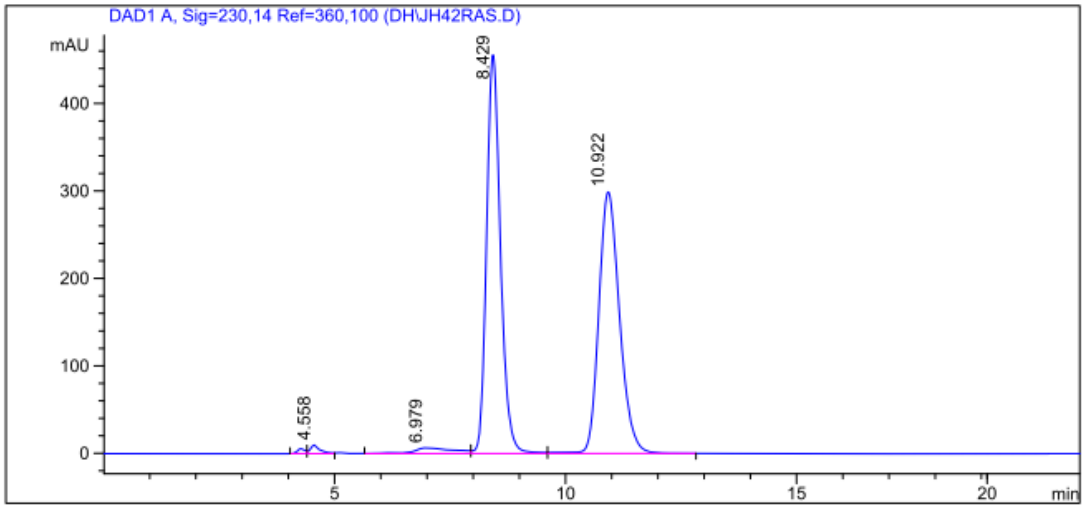
17b

Säule: DAICELAS.M
Säuleninfo: Chiralpak AS (250 x 4.6)mm 10µ

Operator: Analytik Labor AKEN

Injektion Time: 08:07:42
Injektion Date: 05.07.2013

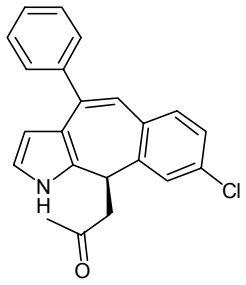
Instrument Conditions:	At Start	At Stop
Temperature in°C:	30.0	30.0
Pressure in bar:	21.8	22.0
Flow in ml/min:	0.7	0.7



#	Ret. Time (min)	Width	Height (mAU)	Area (mAU*s)	Area %
1	4.27	0.18	5.66	65.50	0.34
2	4.56	0.21	9.94	147.07	0.76
3	6.98	0.89	6.52	404.56	2.08
4	8.43	0.32	456.00	9517.98	48.90
5	10.92	0.48	299.16	9327.79	47.93
Total				19462.91	100.00

Sample Name: DH 339
Data file: D:\ERNIE\DH\339AS.D
Sample Info: Laufmittel: n-Heptan/EtOH 9:1;
Die Probe ist in DCM/LM gelöst

Agilent Technologies



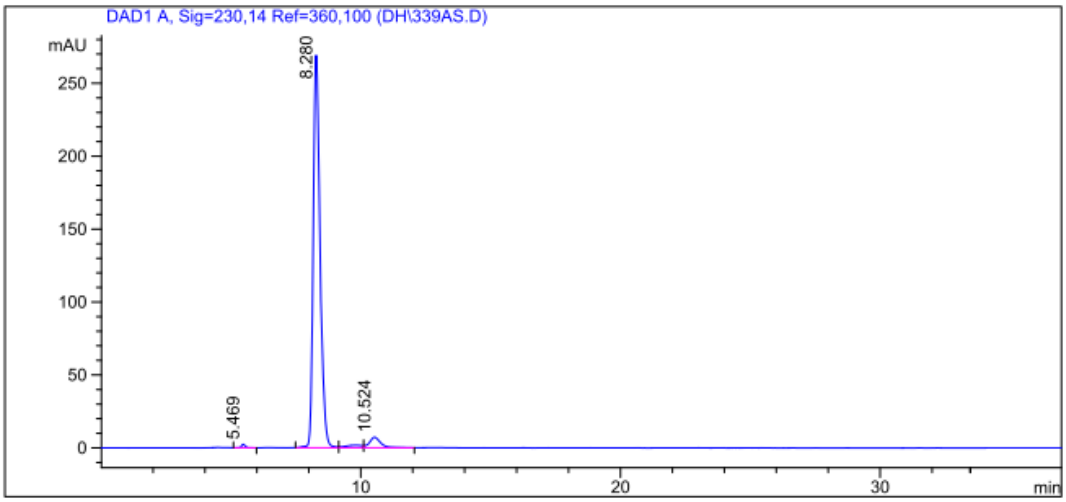
17b

Säule: DAICELAS.M
Säuleninfo: Chiralpak AS (250 x 4.6)mm 10µ

Operator: Analytik Labor AKEN

Injektion Time: 10:39:13
Injektion Date: 23.07.2013

Instrument Conditions:	At Start	At Stop
Temperature in°C:	31.1	31.4
Pressure in bar:	21.8	21.6
Flow in ml/min:	0.7	0.7



#	Ret. Time (min)	Width	Height (mAU)	Area (mAU*s)	Area %
1	5.47	0.16	2.43	25.21	0.48
2	8.28	0.28	269.29	4895.85	93.73
3	9.79	0.55	1.76	78.60	1.50
4	10.52	0.45	7.27	223.61	4.28
Total				5223.27	100.00

Sample Name: DH JH 43 rac
Data file: D:\ERNIE\DH\JH43R1AS.D
Sample Info: Laufmittel: n-Heptan/EtOH 9:1;
Die Probe ist in DCM/LM gelöst

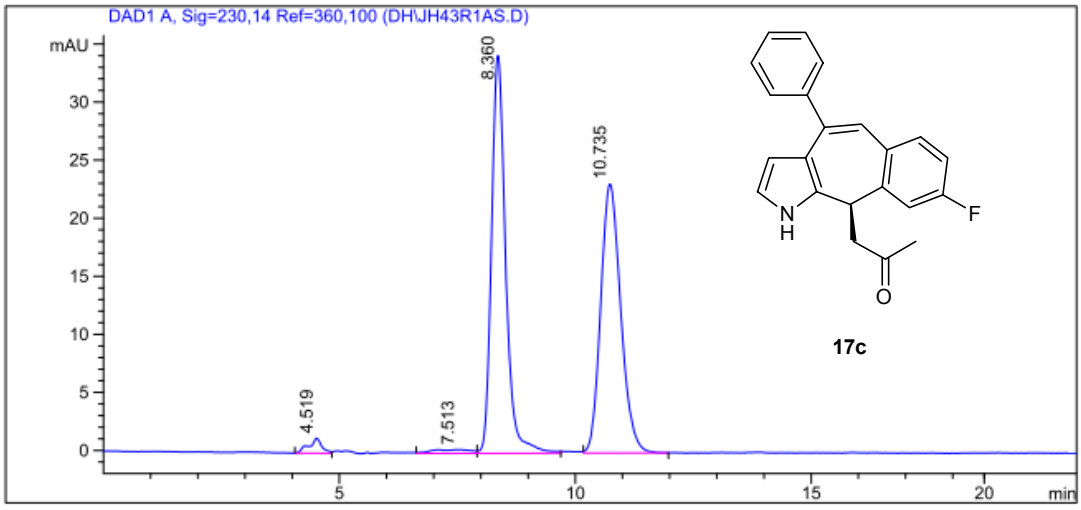
Agilent Technologies

Säule: DAICELAS.M
Säuleninfo: Chiralpak AS (250 x 4.6)mm 10µ

Operator: Analytik Labor AKEN

Injektion Time: 08:50:44
Injektion Date: 05.07.2013

Instrument Conditions:	At Start	At Stop
Temperature in°C:	30.0	30.0
Pressure in bar:	22.4	21.6
Flow in ml/min:	0.7	0.7



17c

#	Ret. Time (min)	Width	Height (mAU)	Area (mAU*s)	Area %
1	4.52	0.26	1.28	24.63	1.71
2	7.51	0.69	0.33	18.89	1.31
3	8.36	0.31	34.25	710.64	49.45
4	10.74	0.46	23.15	682.94	47.52
Total				1437.10	100.00

Sample Name: DH 340
Data file: D:\ERNIE\DH\340AS.D
Sample Info: Laufmittel: n-Heptan/EtOH 9:1;
Die Probe ist in DCM/LM gelöst

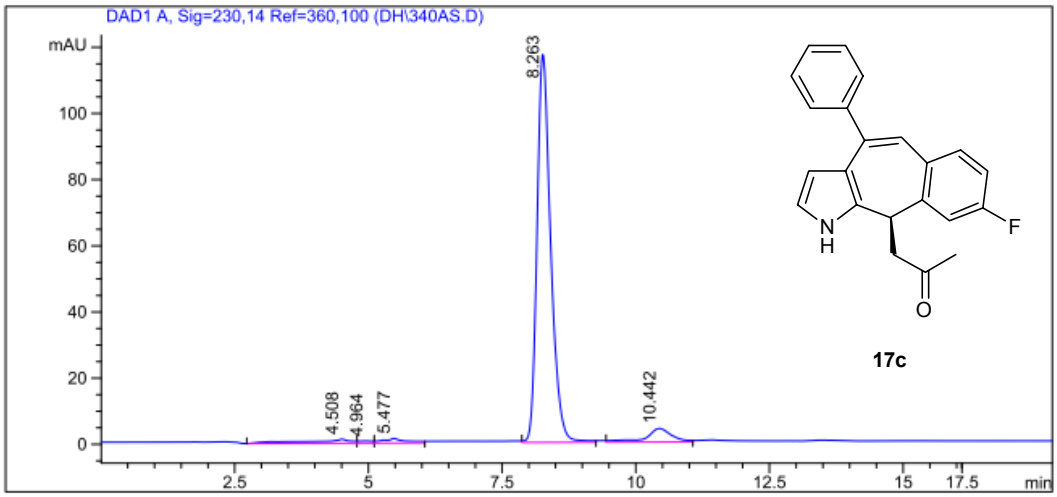
Agilent Technologies

Säule: DAICELAS.M
Säuleninfo: Chiralpak AS (250 x 4.6)mm 10µ

Operator: Analytik Labor AKEN

Injektion Time: 09:37:47
Injektion Date: 23.07.2013

Instrument Conditions:	At Start	At Stop
Temperature in°C:	30.5	30.7
Pressure in bar:	22.2	21.8
Flow in ml/min:	0.7	0.7



17c

#	Ret. Time (min)	Width	Height (mAU)	Area (mAU*s)	Area %
1	4.51	0.73	1.22	73.32	3.12
2	4.96	0.24	0.68	12.35	0.53
3	5.48	0.40	1.37	43.28	1.84
4	8.26	0.27	117.36	2081.04	88.64
5	10.44	0.47	4.11	137.83	5.87
Total				2347.82	100.00

Sample Name: DH 38 rac
Data file: D:\ERNIE\DH\38RAS.D
Sample Info: Laufmittel: n-Heptan/EtOH 9:1;
Die Probe ist in DCM/LM gelöst

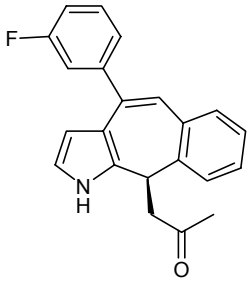
Agilent Technologies

Säule: DAICELAS.M
Säuleninfo: Chiralpak AS (250 x 4.6)mm 10µ

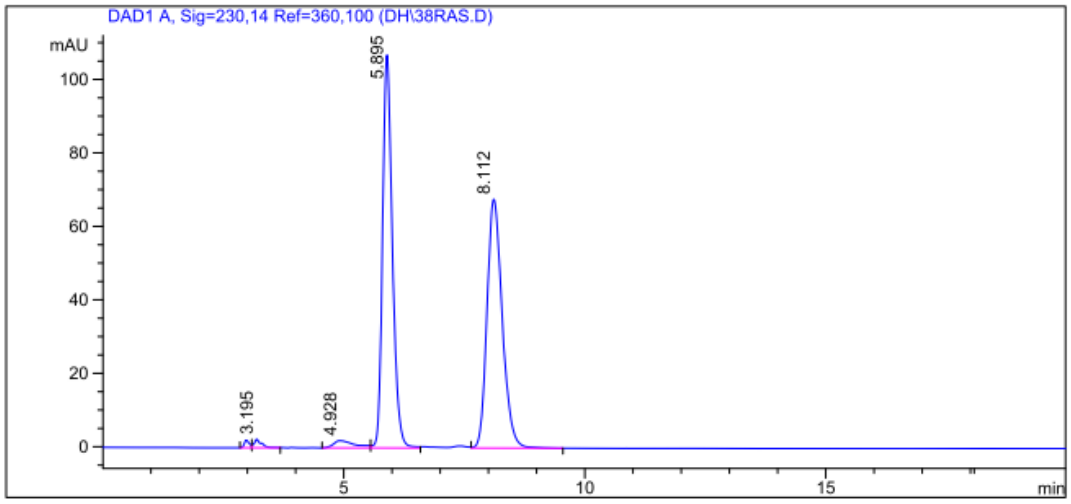
Operator: Analytik Labor AKEN

Injektion Time: 08:58:45
Injektion Date: 03.07.2013

Instrument Conditions:	At Start	At Stop
Temperature in°C:	30.0	30.0
Pressure in bar:	31.4	32.0
Flow in ml/min:	1.0	1.0



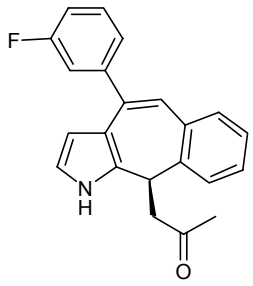
17d



#	Ret. Time (min)	Width	Height (mAU)	Area (mAU*s)	Area %
1	2.98	0.11	2.09	15.15	0.49
2	3.19	0.15	2.35	24.82	0.80
3	4.93	0.41	2.01	59.94	1.94
4	5.89	0.22	106.95	1510.00	48.81
5	8.11	0.34	67.77	1483.91	47.96
Total				3093.83	100.00

Sample Name: DH 341
Data file: D:\ERNIE\DH\341AS.D
Sample Info: Laufmittel: n-Heptan/EtOH 9:1;
Die Probe ist in DCM/LM gelöst

Agilent Technologies



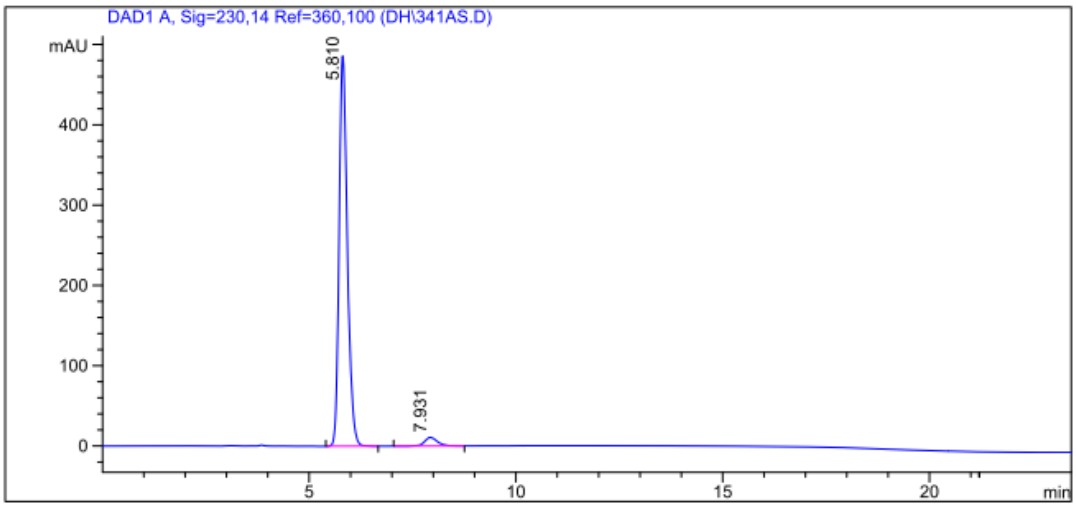
17d

Säule: DAICELAS.M
Säuleninfo: Chiralpak AS (250 x 4.6)mm 10µ

Operator: Analytik Labor AKEN

Injektion Time: 08:22:56
Injektion Date: 29.07.2013

Instrument Conditions:	At Start	At Stop
Temperature in°C:	30.0	30.0
Pressure in bar:	31.4	30.6
Flow in ml/min:	1.0	1.0

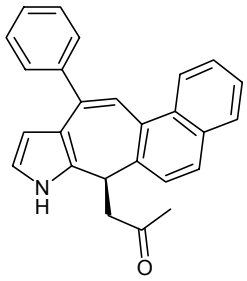


#	Ret. Time (min)	Width	Height (mAU)	Area (mAU*s)	Area %
1	5.81	0.21	486.34	6689.80	96.54
2	7.93	0.33	10.86	239.89	3.46
Total				6929.69	100.00

Sample name: **DH JH 36 rac**

Data file: C:\SNOOPY\DH\DH JH 36 RAC IA.D

Description: Laufmittel: n-Heptan/IP 9:1; Die Probe ist in EtOH/LM gelöst.

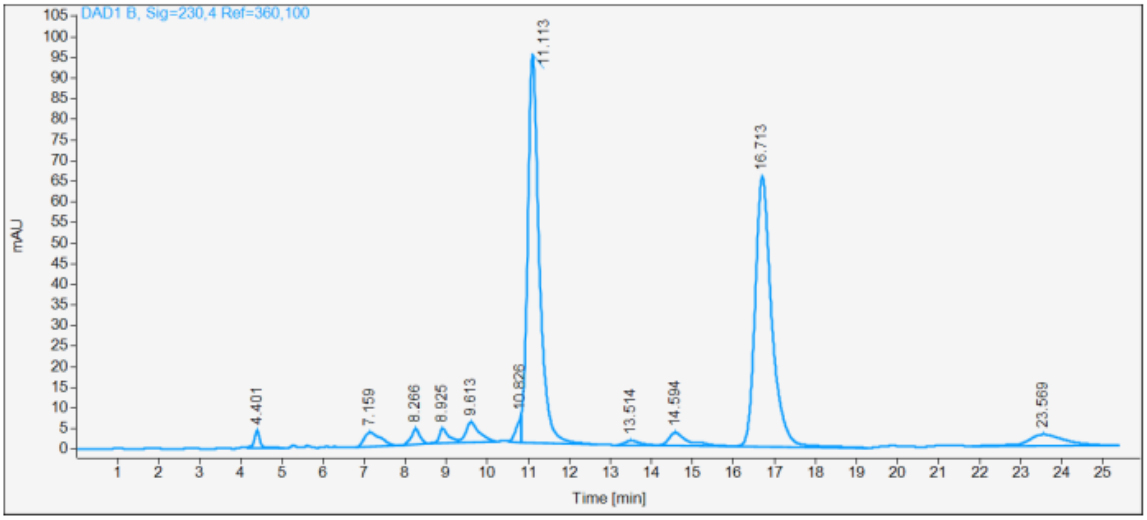


Injection date: 6/27/2013 10:32:25 AM

Acq. Analysis method: CHIRALPAKIARNP.M

Column: Chiralpak IA (250 x 4,6) mm, 5µ, SN: IA00CE-RC036

Pressure at start: 47 bar **Start flow:** 0.700 ml/min **Column oven:** 29.98 °C **17e**



Name DH JH 36 rac

RT [min]	Type	Area%	Area	Height	Width [min]
4.40	VB	1.00	44.02	4.29	0.15
7.16	BB	2.23	98.53	3.50	0.40
8.27	BB	1.28	56.48	3.83	0.21
8.92	BV	1.34	59.21	3.61	0.23
9.61	VB	2.52	111.07	4.91	0.32
10.83	MF	1.10	48.55	6.16	0.13
11.11	FM	41.89	1848.95	94.19	0.33
13.51	BV	0.67	29.44	1.11	0.39
14.59	VB	2.29	101.21	3.14	0.46
16.71	BB	41.59	1835.43	65.42	0.42
23.57	BBA	4.09	180.53	2.76	0.95
	Sum	100.00	4413.42		

Sample name: DH 342

Data file: C:\SNOOPY\DH\DH 342 IA.D

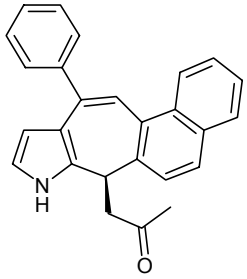
Description: Laufmittel: n-Heptan/IP 9:1; Die Probe ist in EtOH/LM gelöst.

Injection date: 7/31/2013 8:28:34 AM

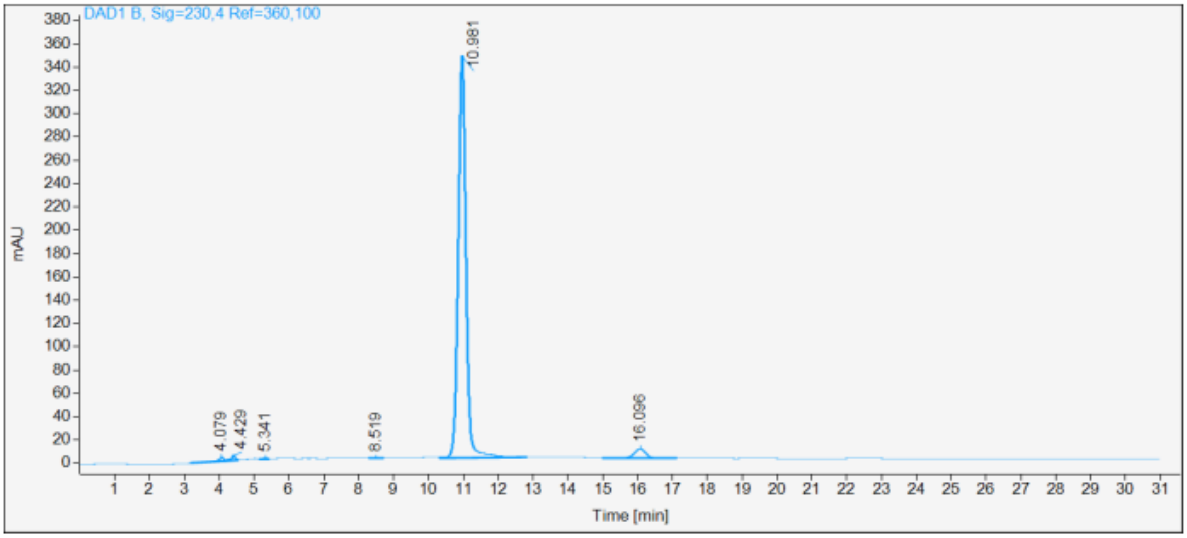
Acq. Analysis method: CHIRALPAKIARNP.M

Column: Chiralpak IA (250 x 4,6) mm, 5µ, SN: IA00CE-RC036

Pressure at start: 34 bar **Start flow:** 0.700 ml/min **Column oven:** 30 °C



17e



Name DH 342

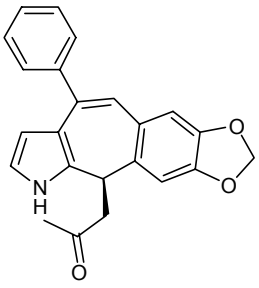
RT [min]	Type	Area%	Area	Height	Width [min]
4.08	BV	0.73	41.01	3.72	0.15
4.43	VB	0.76	43.07	4.58	0.13
5.34	VB	0.20	11.31	1.32	0.12
8.52	VV	0.21	11.67	0.58	0.28
10.98	VB	94.72	5340.94	344.92	0.23
16.10	BB	3.38	190.43	8.10	0.35
	Sum	100.00	5638.42		

Sample Name: DH JH 35 rac
Data file: D:\GONZO\DH\JH35ROD.D
Sample Info: Laufmittel: n-Heptan/EtOH 9:1;
Die Probe ist in DCM/LM gelöst.

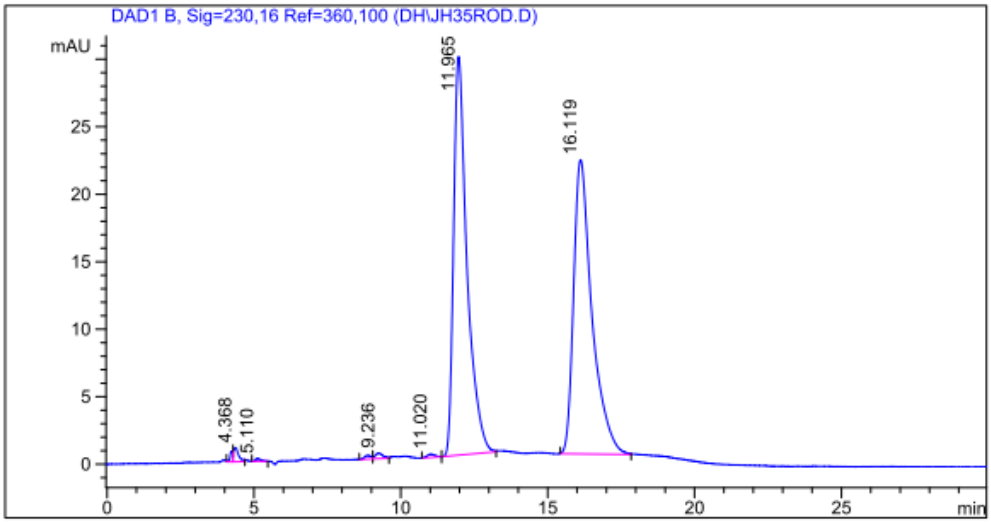
Säule: DAICELOD.M
Säuleninfo: Chiralcel OD (250x4,6)mm
Operator: Analytik Labor AKEN

Injektion Time: 08:26:36
Injektion Date: 27.06.2013

Instrument Conditions:	At Start	At Stop
Temperature in°C:	30.0°C	30.0°C
Pressure in bar:	18.1	18.2
Flow in ml/min:	0.70	0.70



17f



#	Ret. Time (min)	Width	Height (mAU)	Area (mAU*s)	Area %
1	4.22	0.09	0.75	5.17	0.27
2	4.37	0.18	1.04	12.66	0.66
3	5.11	0.20	0.21	2.55	0.13
4	8.88	0.23	0.28	4.25	0.22
5	9.24	0.27	0.41	7.53	0.39
6	11.02	0.24	0.24	4.35	0.23
7	11.97	0.47	29.54	938.33	48.88
8	16.12	0.64	21.79	944.74	49.22
Total				1919.57	100.00

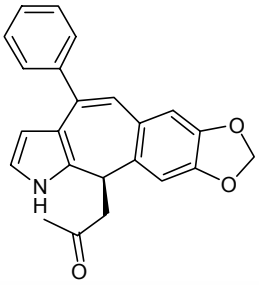
Sample Name: DH 344-2
Data file: D:\GONZO\DH\344-2OD.D
Sample Info: Laufmittel: n-Heptan/EtOH 9:1;
Die Probe ist in LM/EtOH gelöst.

Säule: DAICELOD.M
Säuleninfo: Chiralcel OD (250x4,6)mm
Operator: Analytik Labor AKEN

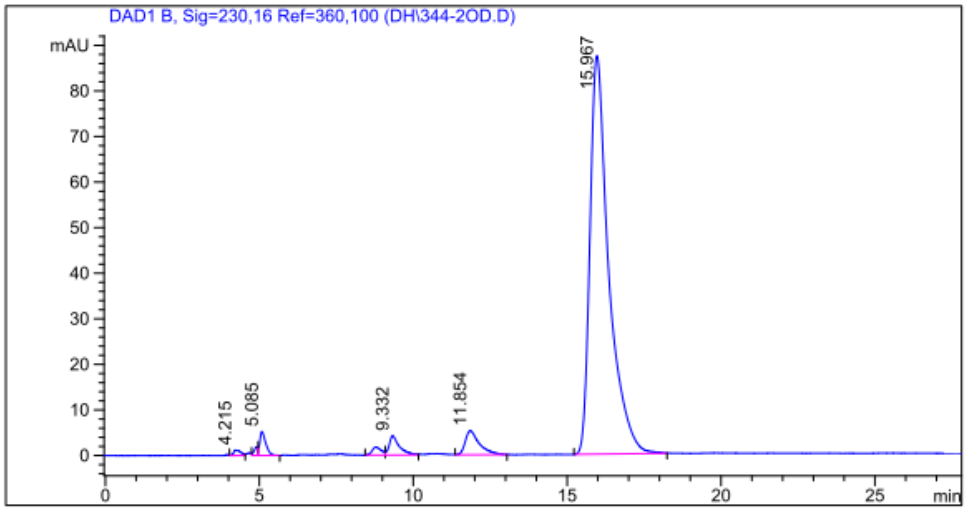
Injektion Time: 13:13:55
Injektion Date: 18.09.2013

Instrument Conditions:	At Start	At Stop
Temperature in°C:	30.0°C	30.0°C
Pressure in bar:	19.1	19.4
Flow in ml/min:	0.70	0.70

->



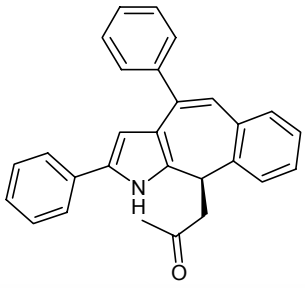
17f



#	Ret. Time (min)	Width	Height (mAU)	Area (mAU*s)	Area %
1	4.22	0.21	1.23	20.08	0.49
2	4.92	0.13	1.96	16.58	0.40
3	5.08	0.20	5.29	71.34	1.73
4	8.79	0.31	1.75	35.93	0.87
5	9.33	0.33	4.22	97.54	2.37
6	11.85	0.47	5.28	168.78	4.10
7	15.97	0.62	87.43	3702.80	90.03
Total				4113.04	100.00

Sample Name: DH JH 31 rac
Data file: D:\GONZO\DH\JH31ROD.D
Sample Info: Laufmittel: n-Heptan/EtOH 9:1;
Die Probe ist in DCM/LM gelöst.

HEWLETT PACKARD



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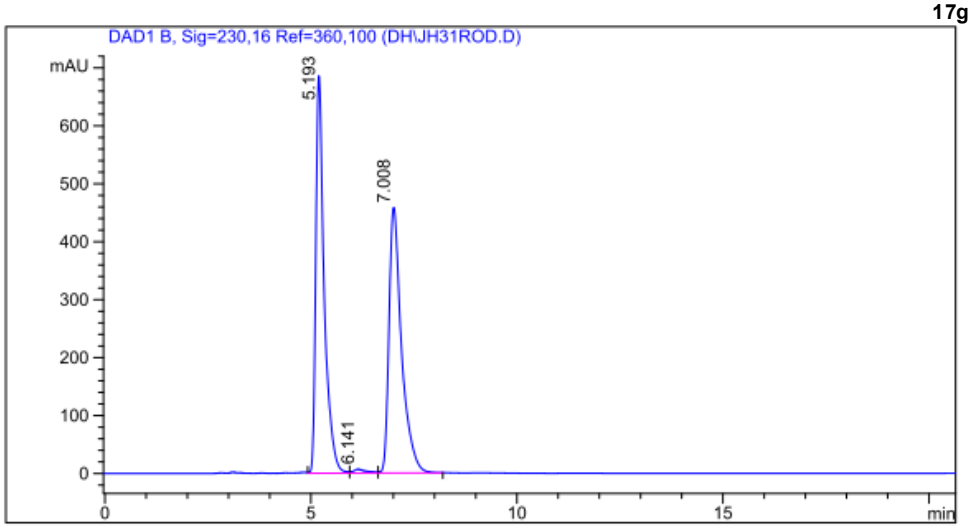
Säule: DAICELOD.M
Säuleninfo: Chiralcel OD (250x4,6)mm
Operator: Analytik Labor AKEN

Injektion Time: 10:26:34
Injektion Date: 20.06.2013

Instrument Conditions:	At Start	At Stop
Temperature in°C:	30.0°C	30.0°C
Pressure in bar:	27.0	27.3
Flow in ml/min:	1.00	1.00

17g



#	Ret. Time (min)	Width	Height (mAU)	Area (mAU*s)	Area %
1	5.19	0.21	685.74	9720.87	49.74
2	6.14	0.31	6.78	149.62	0.77
3	7.01	0.31	457.64	9674.29	49.50
Total				19544.78	100.00

Sample Name: DH 345
Data file: D:\GONZO\DH\345OD.D
Sample Info: Laufmittel: n-Heptan/EtOH 9:1;
Die Probe ist in DCM/LM gelöst.

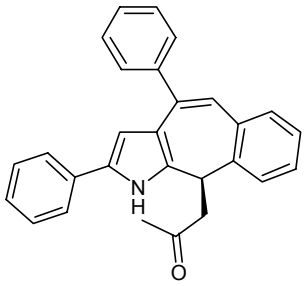
Säule: DAICELOD.M
Säuleninfo: Chiralcel OD (250x4,6)mm
Operator: Analytik Labor AKEN

Injektion Time: 09:41:26
Injektion Date: 30.07.2013

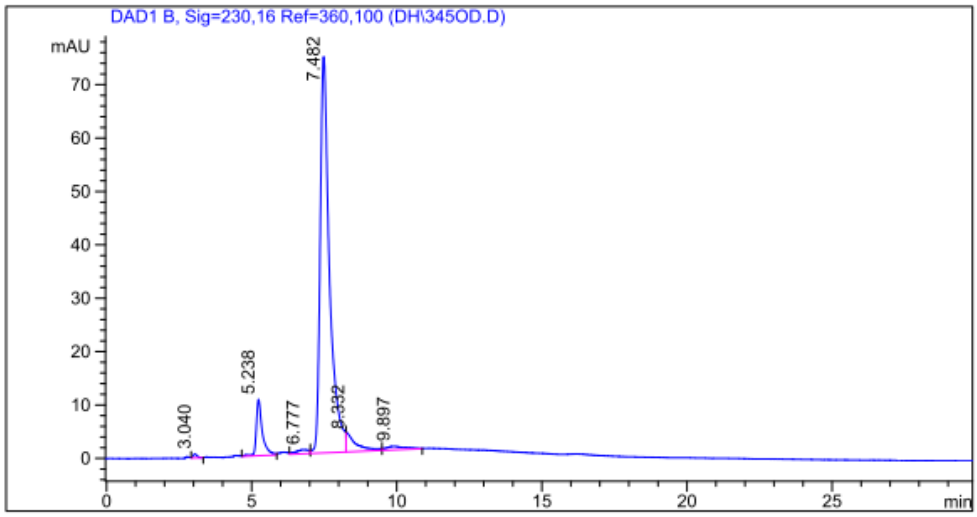
Instrument Conditions:	At Start	At Stop
Temperature in°C:	30.0°C	30.0°C
Pressure in bar:	26.7	27.3
Flow in ml/min:	1.00	1.00

HEWLETT PACKARD

->



17g



#	Ret. Time (min)	Width	Height (mAU)	Area (mAU*s)	Area %
1	3.04	0.14	0.77	7.43	0.38
2	5.24	0.21	10.55	153.15	7.74
3	6.78	0.41	0.79	24.48	1.24
4	7.48	0.33	74.23	1673.50	84.59
5	8.33	0.35	3.31	87.01	4.40
6	9.90	0.64	0.69	32.83	1.66
Total				1978.41	100.00

Sample Name: DH 352 rac
Data file: D:\GONZO\DH\352R2AD.D
Sample Info: Laufmittel: n-Heptan/IP 7:3;
Die Probe ist in DCM/LM gelöst.

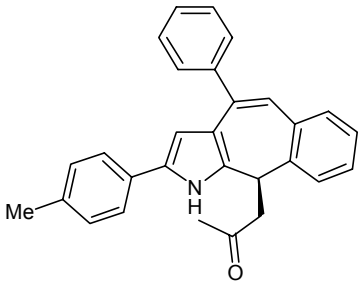
Säule: DAICELAD.M
Säuleninfo: Chiralpak AD (250x4,6)mm
Operator: Analytik Labor AKEN

Injektion Time: 13:14:19
Injektion Date: 02.08.2013

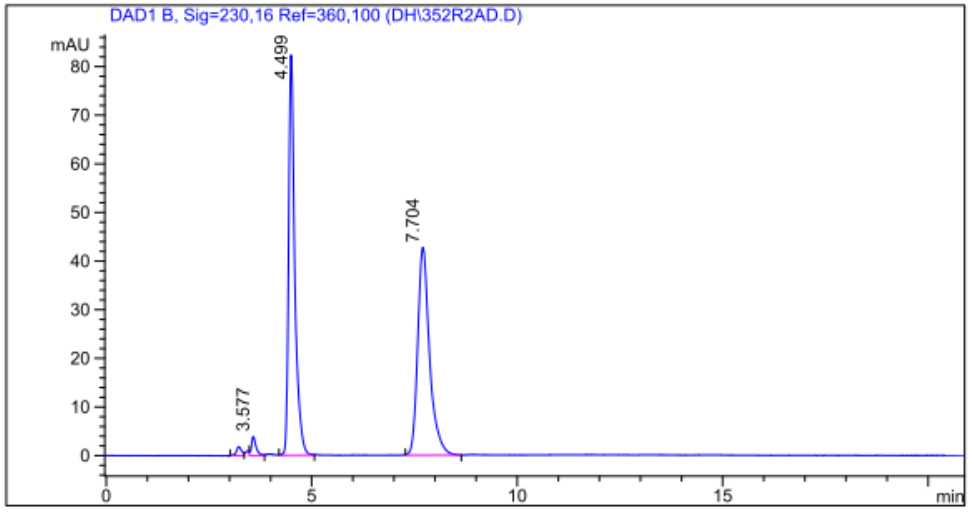
Instrument Conditions:	At Start	At Stop
Temperature in°C:	30.0°C	30.0°C
Pressure in bar:	29.9	30.2
Flow in ml/min:	1.00	1.00

HEWLETT PACKARD

->



17h



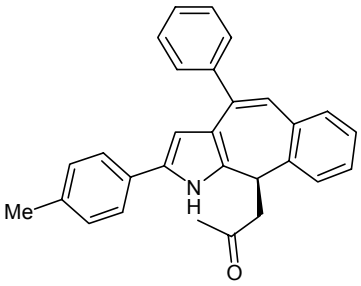
#	Ret. Time (min)	Width	Height (mAU)	Area (mAU*s)	Area %
1	3.22	0.13	1.83	16.34	0.93
2	3.58	0.12	3.92	30.66	1.74
3	4.50	0.15	82.26	858.73	48.72
4	7.70	0.30	42.67	856.91	48.62
Total				1762.65	100.00

Sample Name: DH 346
Data file: D:\GONZO\DH\346AD.D
Sample Info: Laufmittel: n-Heptan/IP 7:3;
Die Probe ist in LM/DCM gelöst

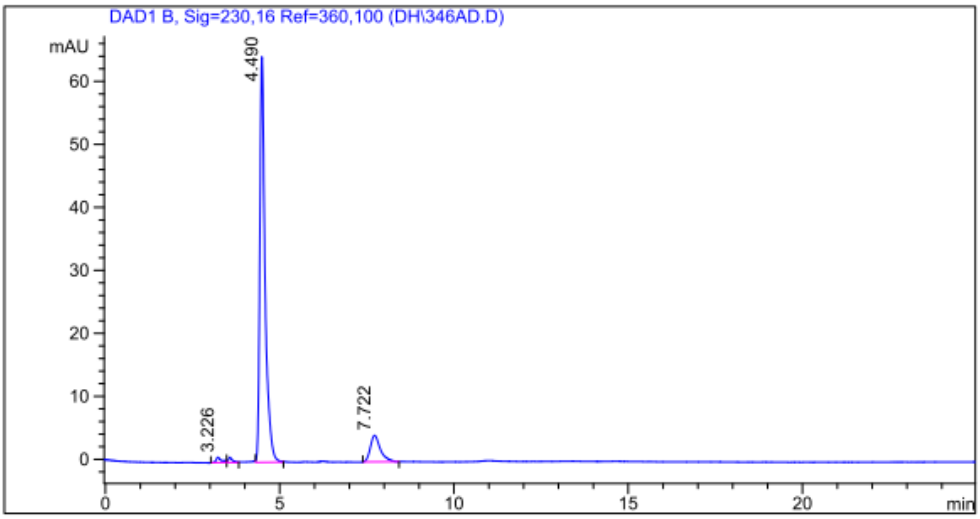
Säule: DAICELAD.M
Säuleninfo: Chiralpak AD (250x4,6)mm
Operator: Analytik Labor AKEN

Injektion Time: 09:56:29
Injektion Date: 06.08.2013

Instrument Conditions:	At Start	At Stop
Temperature in°C:	30.0°C	30.0°C
Pressure in bar:	30.0	30.7
Flow in ml/min:	1.00	1.00



17h



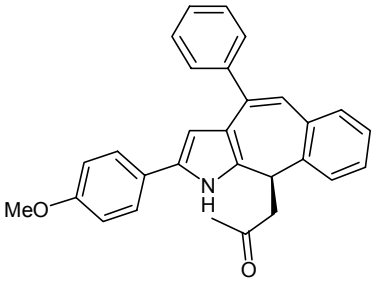
#	Ret. Time (min)	Width	Height (mAU)	Area (mAU*s)	Area %
1	3.23	0.16	0.85	9.44	1.22
2	3.57	0.12	0.84	7.13	0.92
3	4.49	0.15	64.25	674.07	86.94
4	7.72	0.30	4.20	84.70	10.92
Total				775.34	100.00

Sample Name: DH 353 rac
Data file: D:\GONZO\DH\353R2AD.D
Sample Info: Laufmittel: n-Heptan/IP 7:3;
Die Probe ist in DCM/LM gelöst.

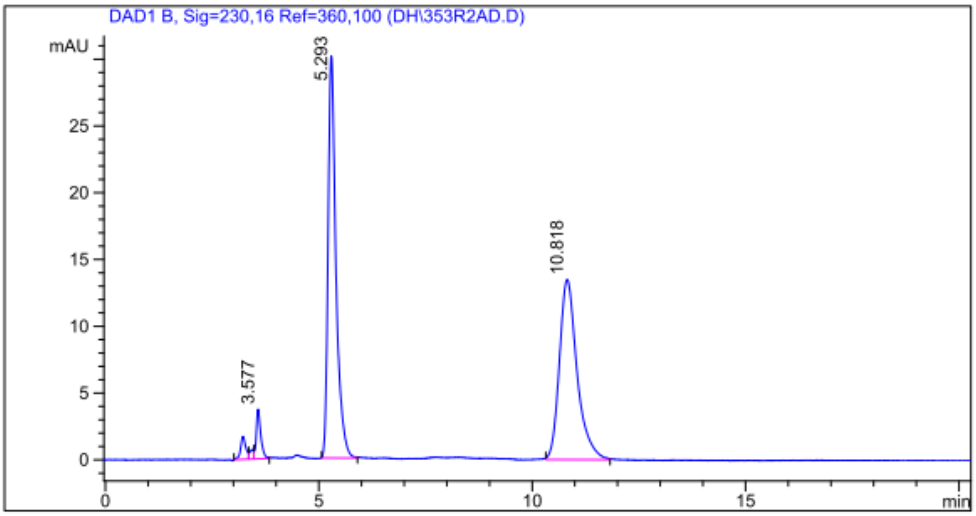
Säule: DAICELAD.M
Säuleninfo: Chiralpak AD (250x4,6)mm
Operator: Analytik Labor AKEN

Injektion Time: 12:24:53
Injektion Date: 02.08.2013

Instrument Conditions:	At Start	At Stop
Temperature in°C:	30.0°C	30.0°C
Pressure in bar:	29.8	30.2
Flow in ml/min:	1.00	1.00



17i



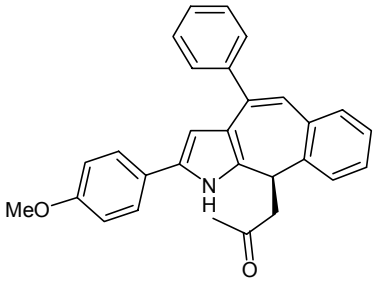
#	Ret. Time (min)	Width	Height (mAU)	Area (mAU*s)	Area %
1	3.22	0.12	1.71	14.76	1.80
2	3.43	0.09	0.71	4.36	0.53
3	3.58	0.11	3.72	27.39	3.34
4	5.29	0.19	30.07	386.64	47.09
5	10.82	0.44	13.48	387.88	47.24
Total				821.03	100.00

Sample Name: DH 347-2
Data file: D:\GONZO\DH\347-2AD.D
Sample Info: Laufmittel: n-Heptan/IP 7:3;
Die Probe ist in LM/DCM gelöst

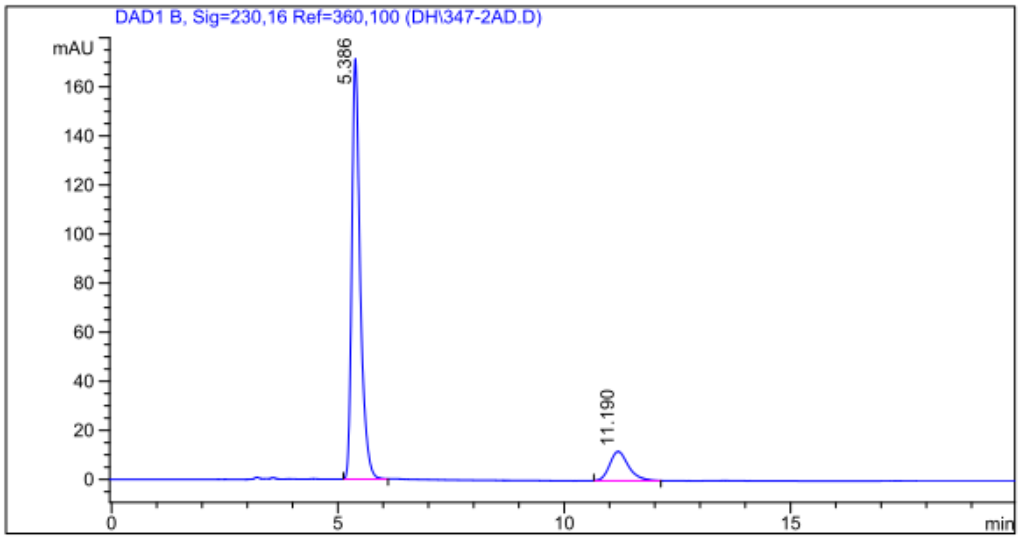
Säule: DAICELAD.M
Säuleninfo: Chiralpak AD (250x4,6)mm
Operator: Analytik Labor AKEN

Injektion Time: 11:50:25
Injektion Date: 11.09.2013

Instrument Conditions:	At Start	At Stop
Temperature in°C:	30.0°C	30.0°C
Pressure in bar:	32.4	33.2
Flow in ml/min:	1.00	1.00



17i



#	Ret. Time (min)	Width	Height (mAU)	Area (mAU*s)	Area %
1	5.39	0.19	171.06	2207.90	86.38
2	11.19	0.44	11.97	348.06	13.62
Total				2555.96	100.00

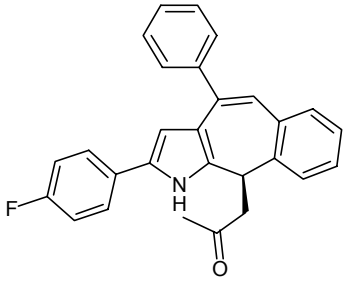
Sample Name: DH 354 rac
Data file: D:\GONZO\DH\354R2AD.D
Sample Info: Laufmittel: n-Heptan/IP 7:3;
Die Probe ist in DCM/LM gelöst.

Säule: DAICELAD.M
Säuleninfo: Chiralpak AD (250x4,6)mm
Operator: Analytik Labor AKEN

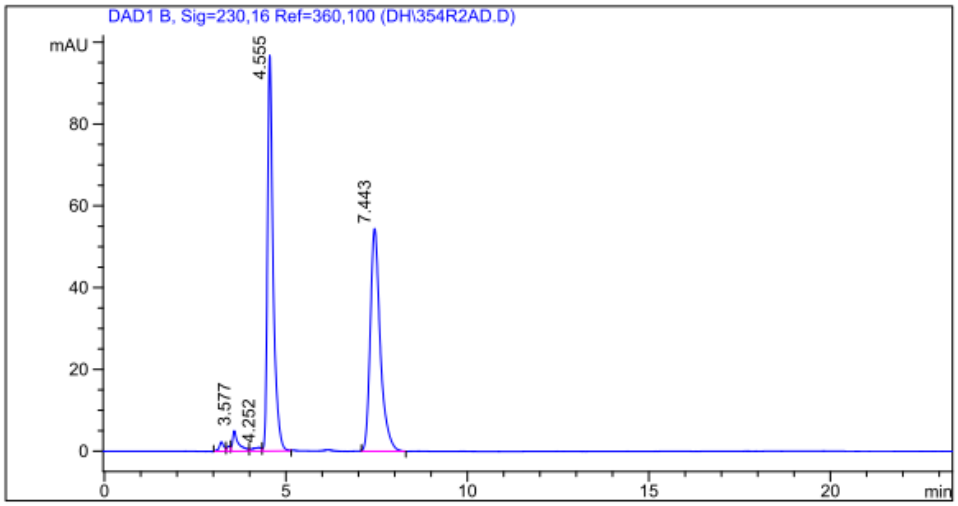
Injektion Time: 12:48:54
Injektion Date: 02.08.2013

Instrument Conditions:	At Start	At Stop
Temperature in°C:	30.0°C	30.0°C
Pressure in bar:	29.7	30.3
Flow in ml/min:	1.00	1.00

->



17j



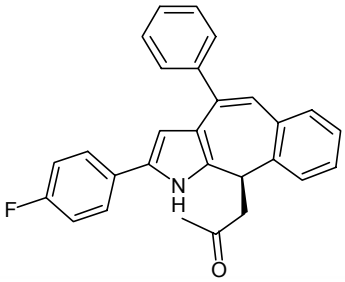
#	Ret. Time (min)	Width	Height (mAU)	Area (mAU*s)	Area %
1	3.22	0.13	2.29	20.31	0.93
2	3.44	0.10	1.27	8.29	0.38
3	3.58	0.15	4.99	55.86	2.55
4	4.25	0.23	0.88	14.64	0.67
5	4.55	0.16	96.55	1050.32	47.97
6	7.44	0.29	54.45	1040.16	47.51
Total				2189.59	100.00

Sample Name: DH 348-2
Data file: D:\GONZO\DH\348-2AD.D
Sample Info: Laufmittel: n-Heptan/IP 7:3;
Die Probe ist in LM/DCM gelöst

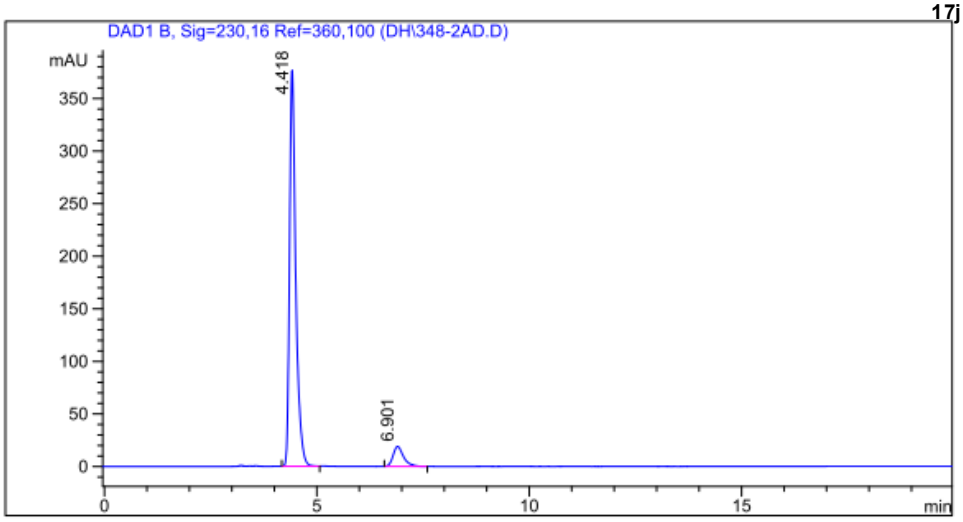
Säule: DAICELAD.M
Säuleninfo: Chiralpak AD (250x4,6)mm
Operator: Analytik Labor AKEN

Injektion Time: 12:11:37
Injektion Date: 11.09.2013

Instrument Conditions:	At Start	At Stop
Temperature in°C:	30.0°C	30.0°C
Pressure in bar:	32.5	33.2
Flow in ml/min:	1.00	1.00



17j



#	Ret. Time (min)	Width	Height (mAU)	Area (mAU*s)	Area %
1	4.42	0.15	376.25	3836.22	92.19
2	6.90	0.26	18.99	325.16	7.81
Total				4161.38	100.00

Sample name: DH 355 rac

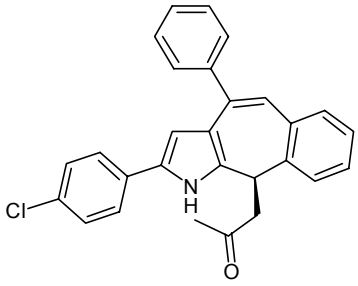
Data file: C:\SNOOPY\DH\DH 355 RAC IA.D

Description: Laufmittel: n-Heptan/IP 7:3; Die Probe ist in EtOH/LM gelöst.

Injection date: 8/8/2013 8:55:00 AM

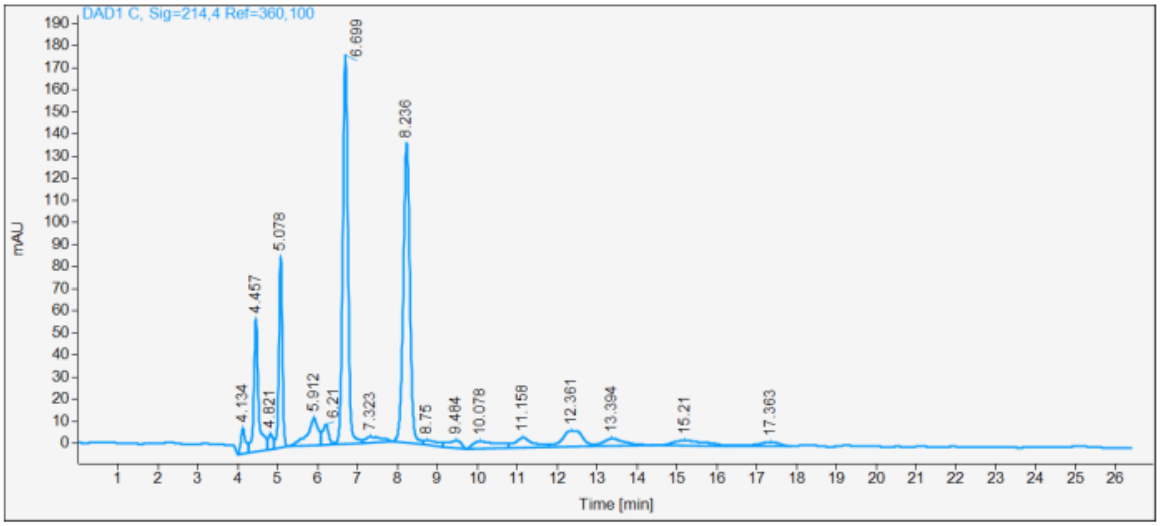
Acq. Analysis method: CHIRALPAKIARNP.M

Column: Chiralpak IA (250 x 4,6) mm, 5µ, SN: IA00CE-RC036



17k

Pressure at start: 43 bar **Start flow:** 0.700 ml/min **Column oven:** 30 °C



Name DH 355 rac

RT [min]	Type	Area%	Area	Height	Width [min]
4.13	BV	1.62	93.57	11.15	0.13
4.46	VV	8.47	488.20	58.51	0.13
4.82	VV	1.07	61.76	6.81	0.13
5.08	VB	9.05	522.03	84.87	0.10
5.91	BV	4.09	236.02	12.14	0.27
6.21	VV	1.74	100.24	9.07	0.16
6.70	VV	27.24	1570.89	174.41	0.15
7.32	VB	1.29	74.32	2.51	0.39
8.24	BV	27.08	1561.23	134.45	0.18
8.75	VV	0.99	57.27	2.17	0.36
9.48	VB	1.33	76.57	3.27	0.34
10.08	BV	2.57	148.39	3.36	0.61
11.16	VV	2.74	158.18	4.67	0.47
12.36	VV	4.62	266.30	7.25	0.49
13.39	VB	2.37	136.56	3.47	0.55
15.21	BV	2.26	130.21	2.39	0.77
17.36	VV	1.46	84.22	1.97	0.63
	Sum	100.00	5765.96		

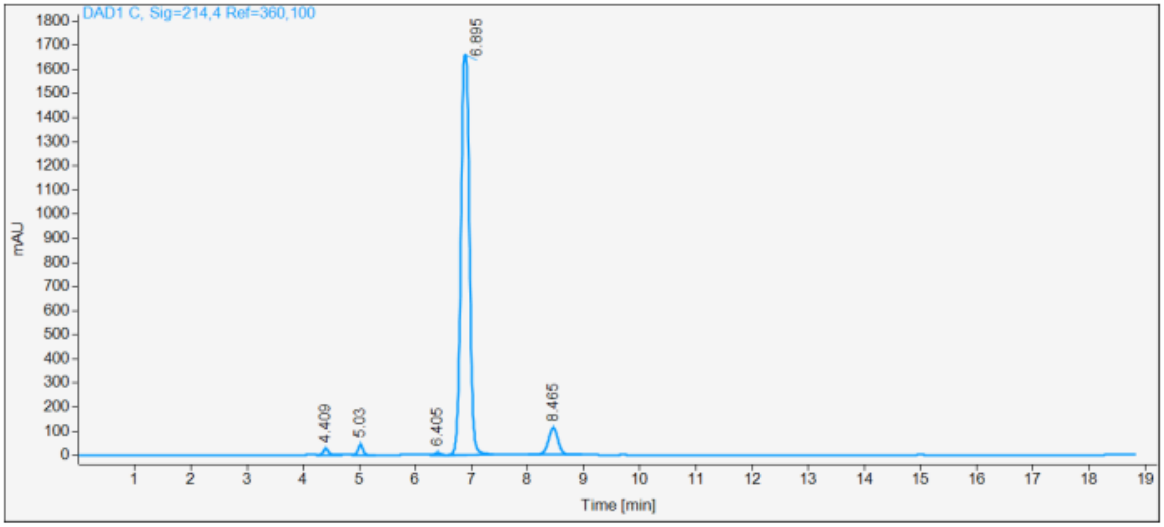
Sample name: **DH 349-2**

Data file: C:\SNOOPY\DH\DH 349-2 IA.D
Description: Laufmittel: n-Heptan/IP 7:3 Die Probe ist in DCM/EtOH/LM gelöst.

Injection date: 9/13/2013 10:09:05 AM
Acq. Analysis method: CHIRALPAKIARNP.M

Column: Chiralpak IA (250 x 4,6) mm, 5µ, SN: IA00CE-RC036

Pressure at start: 44 bar **Start flow:** 0.700 ml/min **Column oven:** 29.97 °C



Name DH 349-2

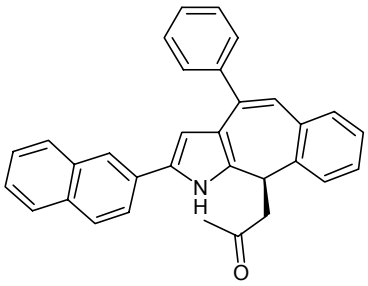
RT [min]	Type	Area%	Area	Height	Width [min]
4.41	VV	1.12	217.77	27.55	0.12
5.03	VB	1.41	273.25	45.17	0.09
6.40	VB	0.34	65.71	8.69	0.12
6.90	BB	90.25	17536.81	1658.41	0.17
8.46	BB	6.89	1338.52	112.15	0.18
	Sum	100.00	19432.07		

Sample Name: DH 356 rac
Data file: D:\GONZO\DH\356R1AD.D
Sample Info: Laufmittel: n-Heptan/IP 7:3;
Die Probe ist in LM/DCM gelöst

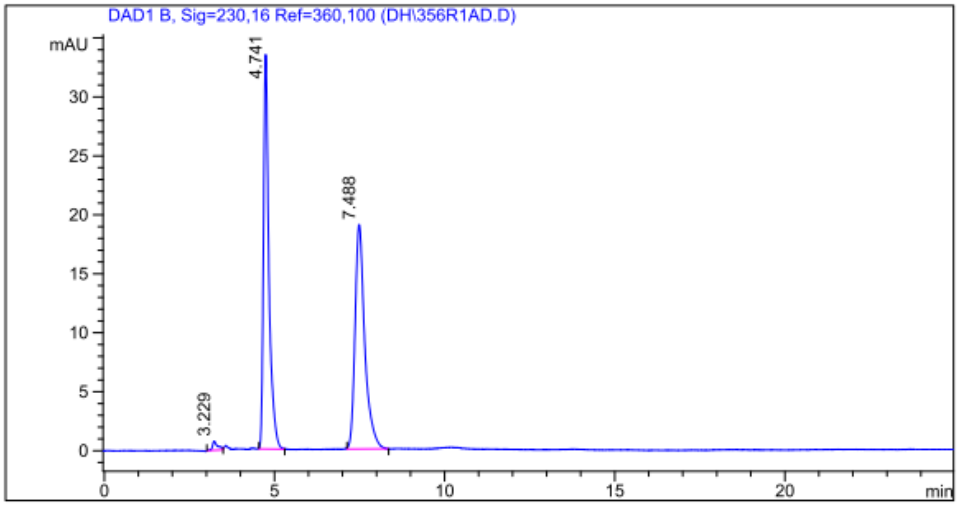
Säule: DAICELAD.M
Säuleninfo: Chiralpak AD (250x4,6)mm
Operator: Analytik Labor AKEN

Injektion Time: 10:48:55
Injektion Date: 06.08.2013

Instrument Conditions:	At Start	At Stop
Temperature in°C:	30.0°C	30.0°C
Pressure in bar:	30.2	30.5
Flow in ml/min:	1.00	1.00



17l



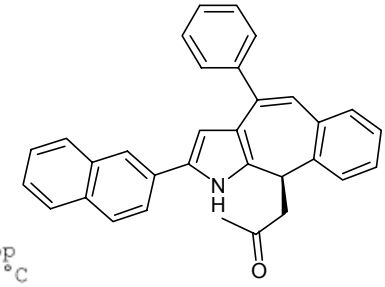
#	Ret. Time (min)	Width	Height (mAU)	Area (mAU*s)	Area %
1	3.23	0.15	0.77	8.48	1.12
2	4.74	0.16	33.37	372.49	49.08
3	7.49	0.30	19.02	377.97	49.80
Total				758.93	100.00

Sample Name: DH 350-2
Data file: D:\GONZO\DH\350-1AD.D
Sample Info: Laufmittel: n-Heptan/IP 7:3;
Die Probe ist in LM/EtOH gelöst.

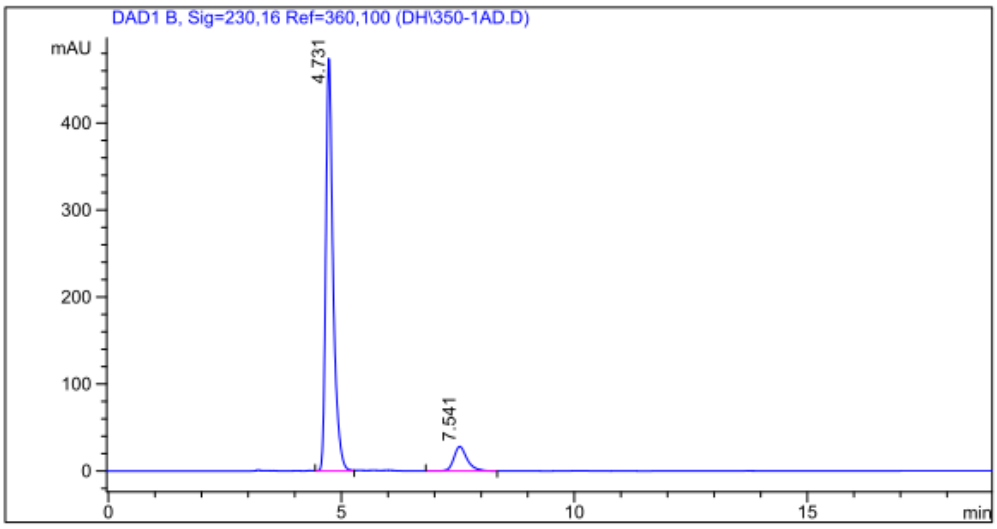
Säule: DAICELAD.M
Säuleninfo: Chiralpak AD (250x4,6)mm
Operator: Analytik Labor AKEN

Injektion Time: 09:31:06
Injektion Date: 13.09.2013

Instrument Conditions:	At Start	At Stop
Temperature in°C:	30.0°C	30.0°C
Pressure in bar:	33.0	33.8
Flow in ml/min:	1.00	1.00



17l



#	Ret. Time (min)	Width	Height (mAU)	Area (mAU*s)	Area %
1	4.73	0.16	473.77	5170.78	90.26
2	7.54	0.30	28.09	558.05	9.74
Total				5728.83	100.00

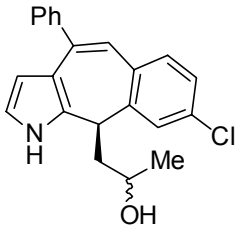
Sample name: **DH 375 rac**

Data file: C:\SNOOPY\DH\375R3IC.D

Description: Laufmittel: n-Heptan/IP 97:3;
Die Probe ist im LM/DCM gelöst.

Injection date: 10/22/2013 11:29:05 AM

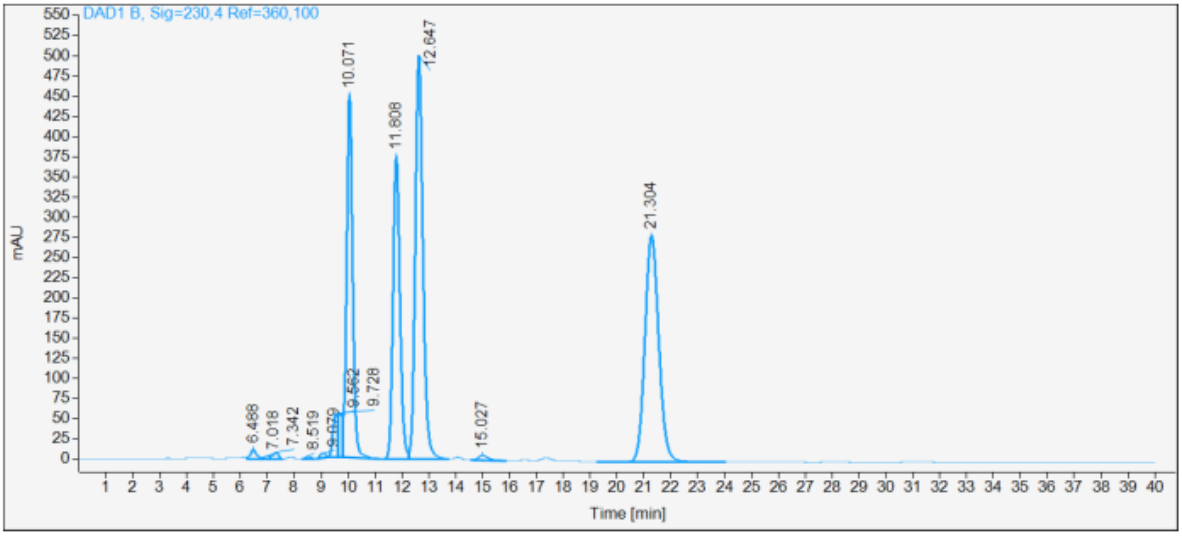
Acq. Analysis method: CHIRALPAKIC1-6LNP.M



18

Column: Chiralpak IC, (150 x 4,6) mm, 5µ, SN: IC00CD-QF015

Pressure at start: 9 bar **Start flow:** 0.300 ml/min **Column oven:** 29.98 °C



Name DH 375 rac

RT [min]	Type	Area%	Area	Height	Width [min]
6.49	VV	0.52	184.58	11.87	0.22
7.02	VV	0.17	61.94	4.43	0.19
7.34	VB	0.35	125.10	8.61	0.21
8.52	BB	0.13	45.54	3.27	0.22
9.08	BB	0.20	70.22	5.39	0.22
9.56	BV	1.81	640.52	53.48	0.18
9.73	VV	1.58	559.69	54.54	0.15
10.07	VB	19.67	6976.03	450.02	0.24
11.81	BV	18.84	6683.89	374.93	0.28
12.65	VB	27.96	9915.77	500.16	0.31
15.03	BB	0.45	161.28	6.18	0.40
21.30	BB	28.32	10045.18	280.10	0.55
	Sum	100.00	35469.74		

Sample name: DH 373

Data file: C:\SNOOPY\DH\373IC.D

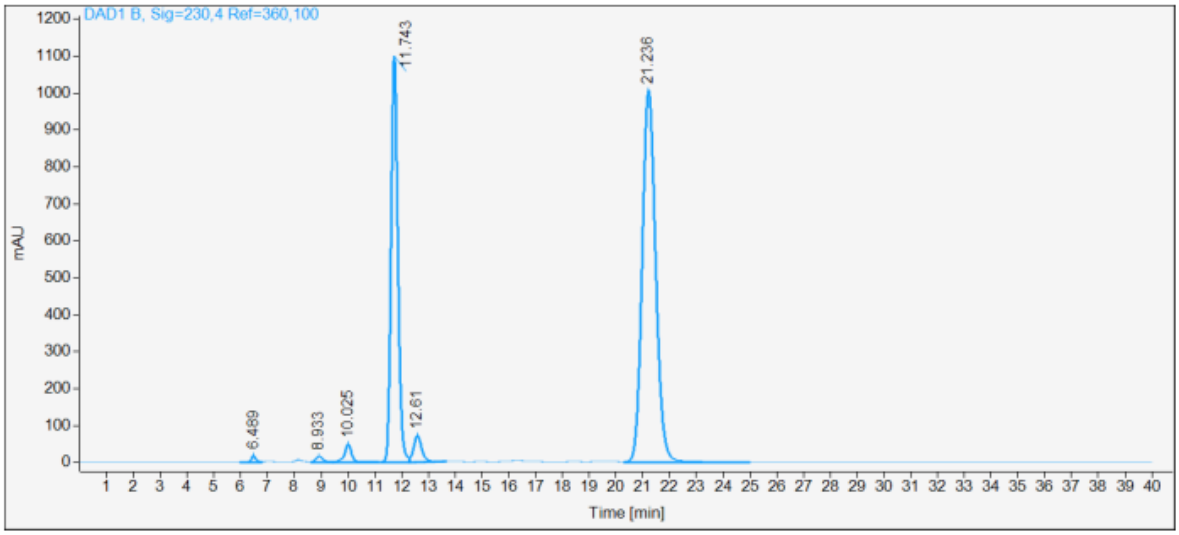
Description: Laufmittel: n-Heptan/IP 97:3;
Die Probe ist im LM/DCM gelöst.

Injection date: 10/22/2013 12:10:14 PM

Acq. Analysis method: CHIRALPAKIC1-6LNP.M

Column: Chiralpak IC, (150 x 4,6) mm, 5µ, SN: IC00CD-QF015

Pressure at start: 9 bar **Start flow:** 0.300 ml/min **Column oven:** 30 °C



Name DH 373

RT [min]	Type	Area%	Area	Height	Width [min]
6.49	BV	0.35	201.93	17.63	0.17
8.93	VV	0.49	279.76	15.21	0.28
10.03	VB	1.50	859.88	48.55	0.26
11.74	BV	33.77	19329.81	1097.97	0.27
12.61	VB	2.61	1494.24	70.54	0.32
21.24	BB	61.28	35078.64	1005.01	0.54
	Sum	100.00	57244.26		

Sample Name: DH 371
Data file: D:\ERNIE\DH\371AS.D
Sample Info: Laufmittel: n-Heptan/EtOH 9:1;
Die Probe ist in DCM/LM gelöst

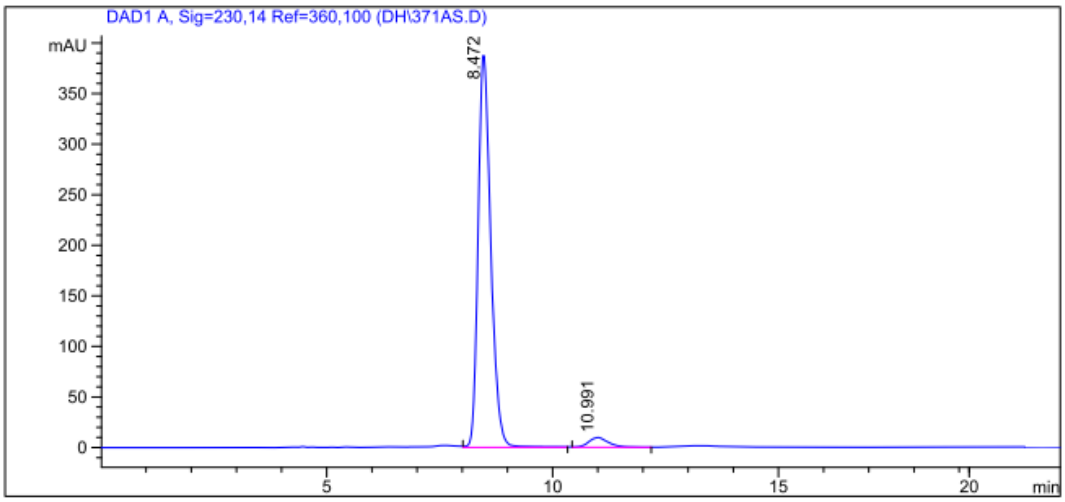
Agilent Technologies

Säule: DAICELAS.M
Säuleninfo: Chiralpak AS (250 x 4.6)mm 10µ

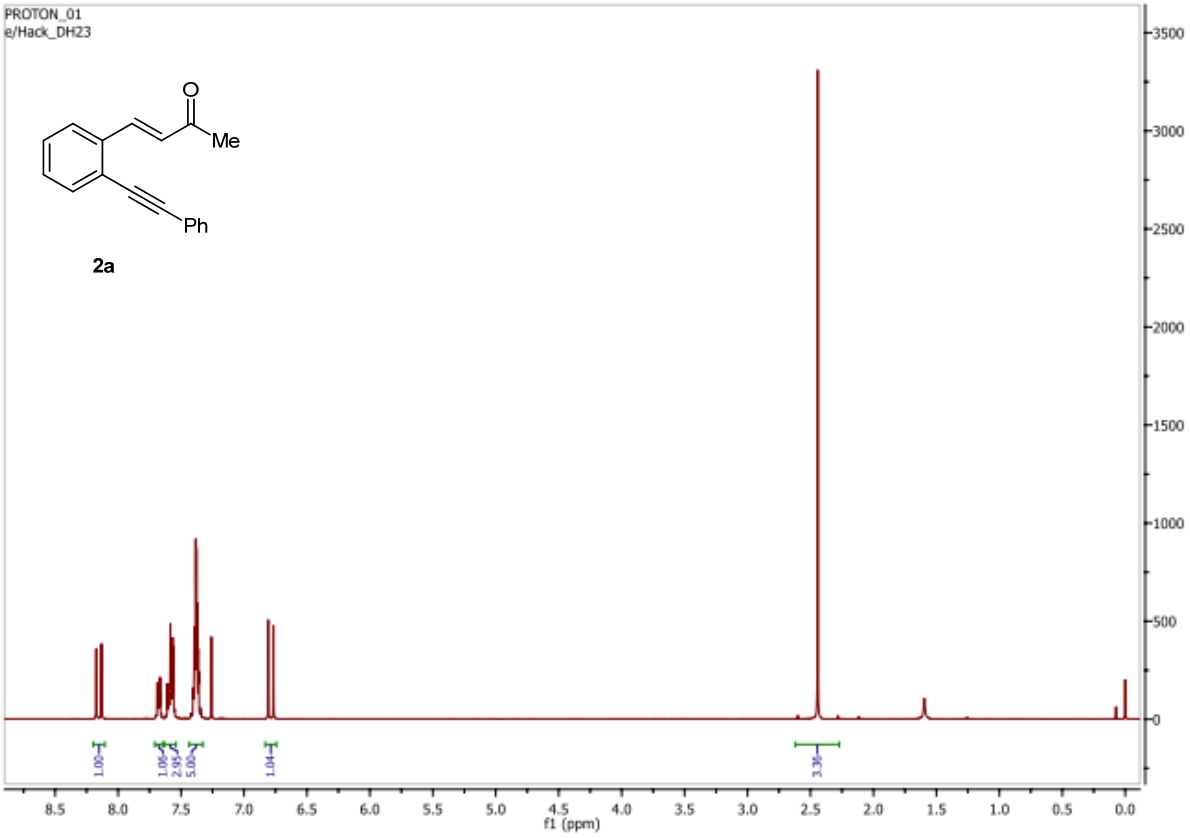
Operator: Analytik Labor AKEN

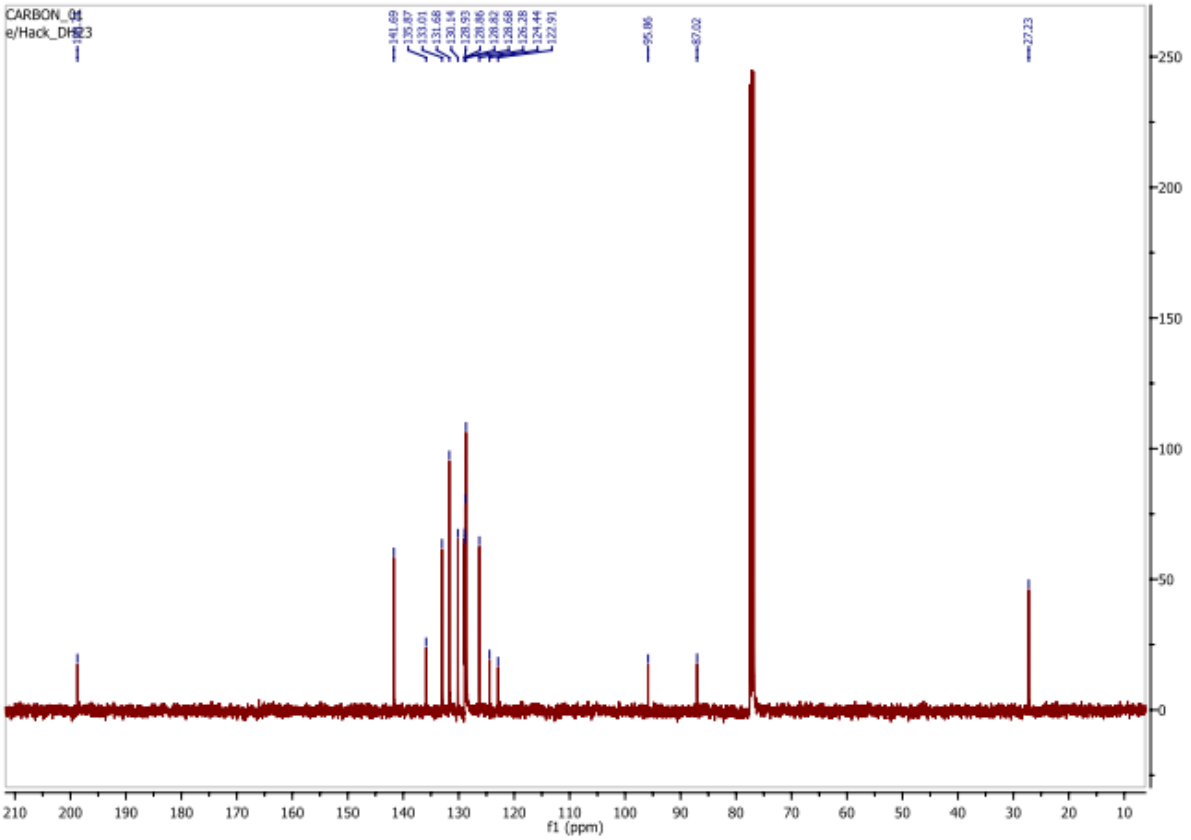
Injektion Time: 09:31:28
Injektion Date: 14.10.2013

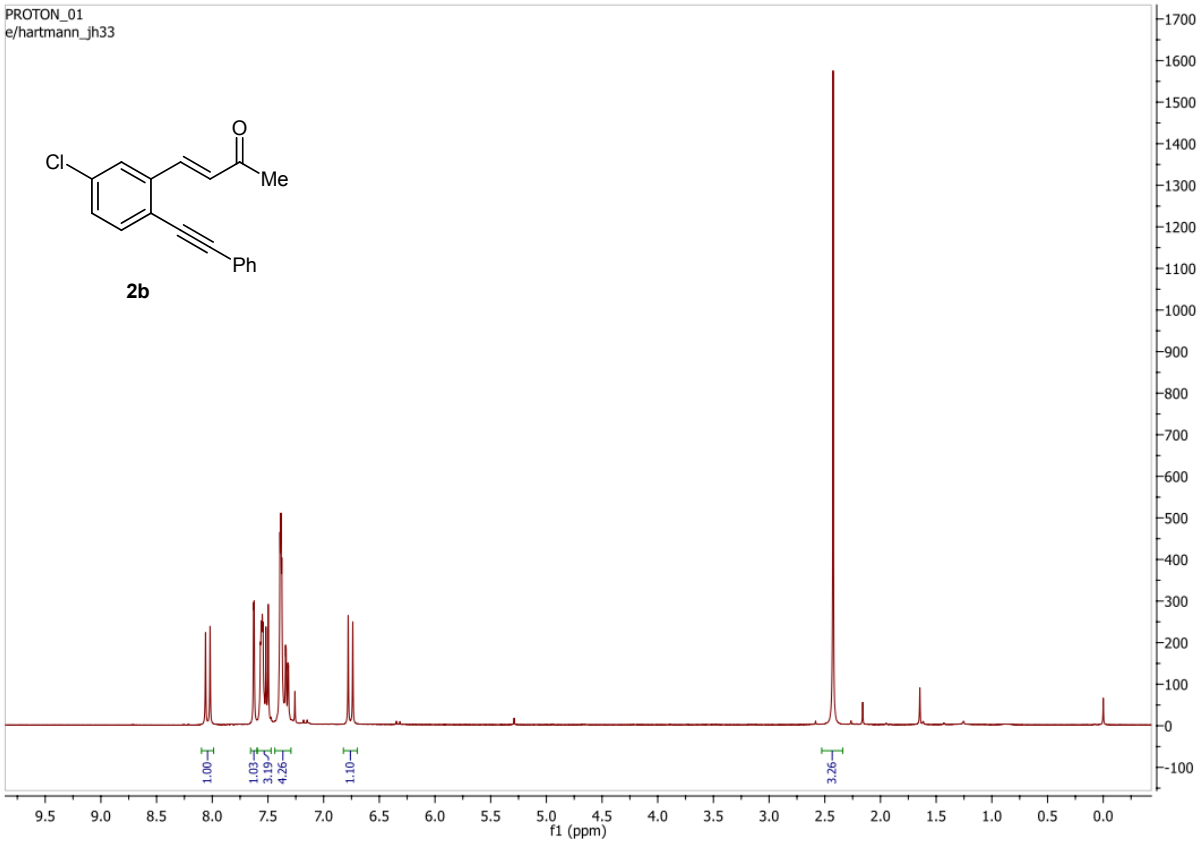
Instrument Conditions:	At Start	At Stop
Temperature in°C:	30.0	30.0
Pressure in bar:	21.2	20.8
Flow in ml/min:	0.7	0.7

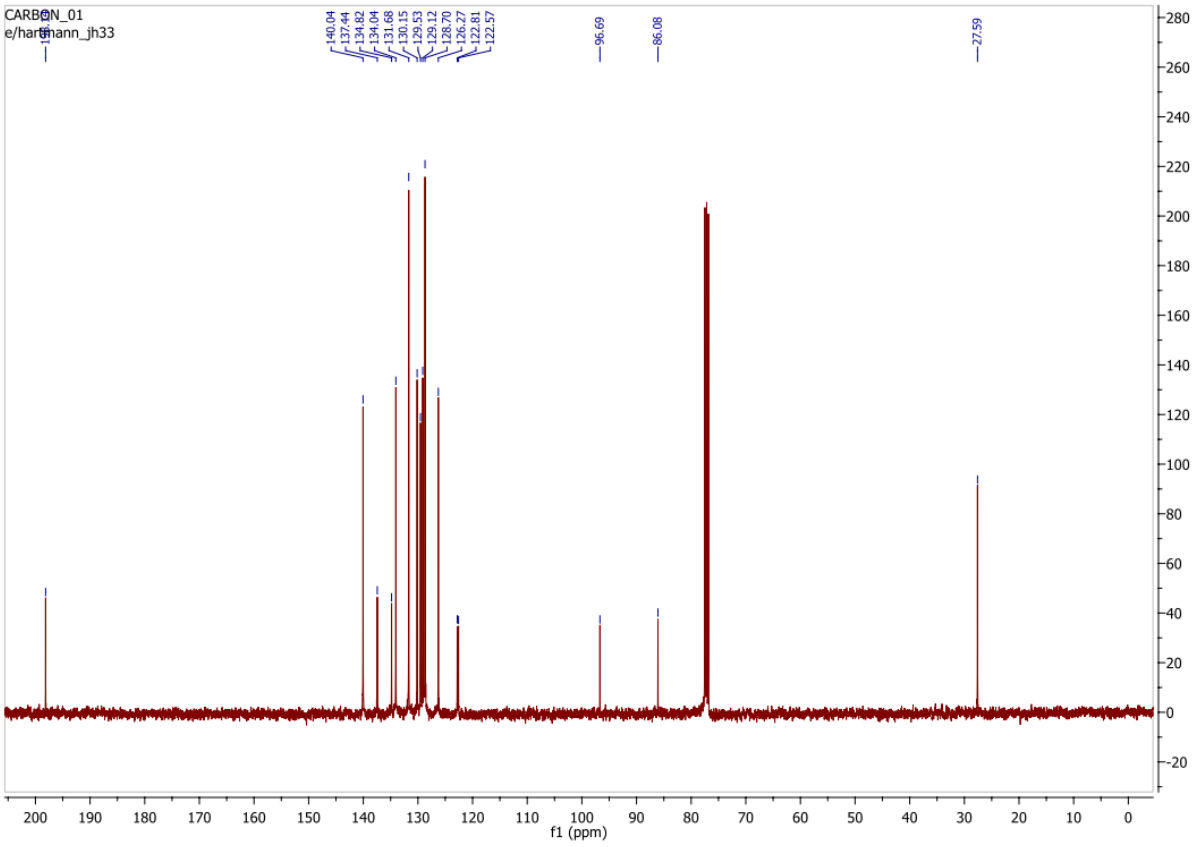


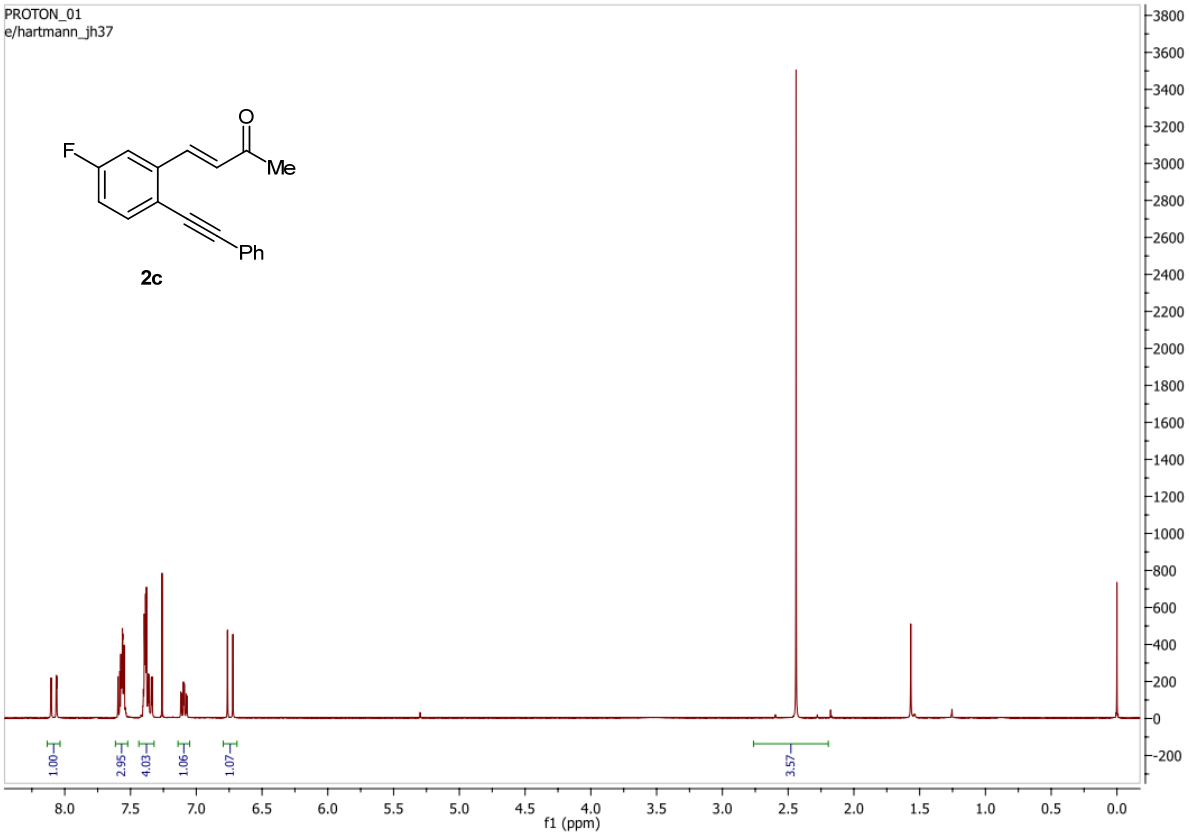
#	Ret. Time (min)	Width	Height (mAU)	Area (mAU*s)	Area %
1	8.47	0.30	388.04	7540.75	96.09
2	10.99	0.47	9.77	307.02	3.91
Total				7847.77	100.00

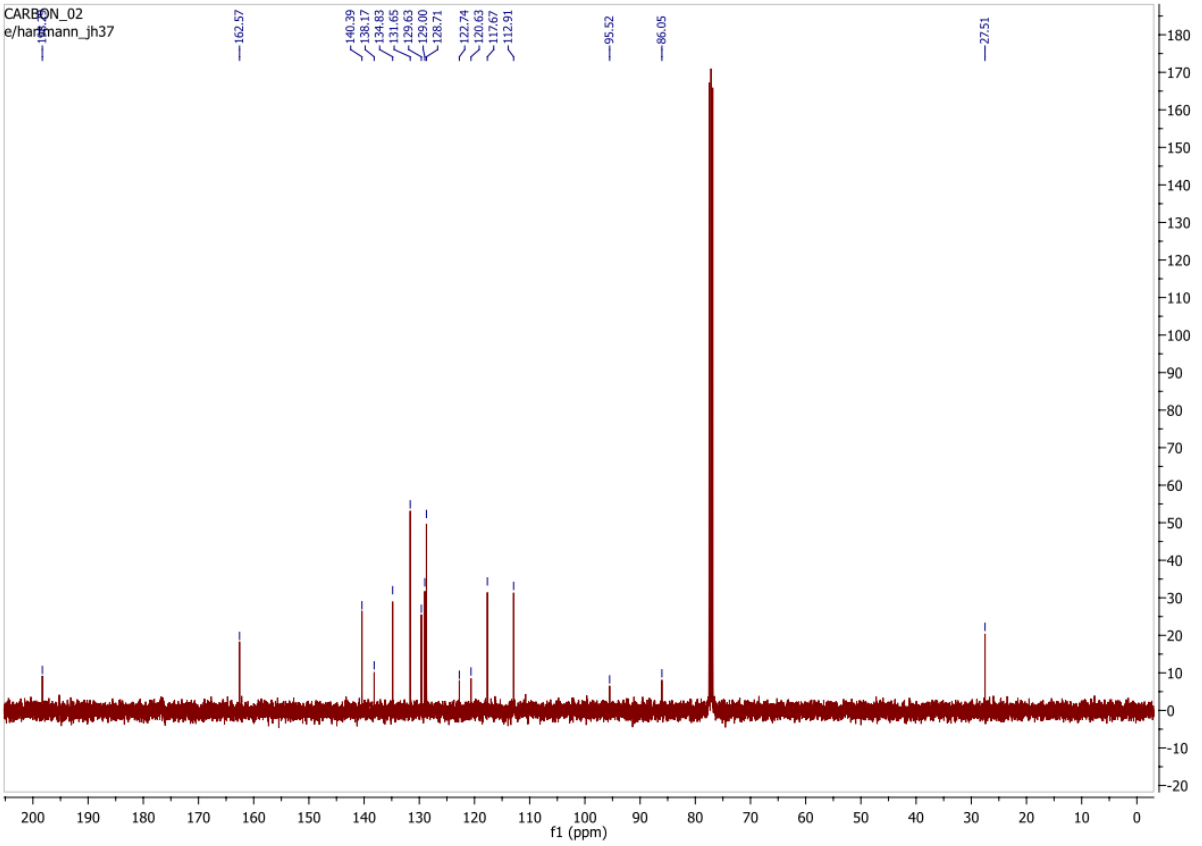

PROTON_01
e/Hack_DH23
O
Me
Ph
2a
1.00
1.06
2.95
5.00
1.04
3.36
f1 (ppm)

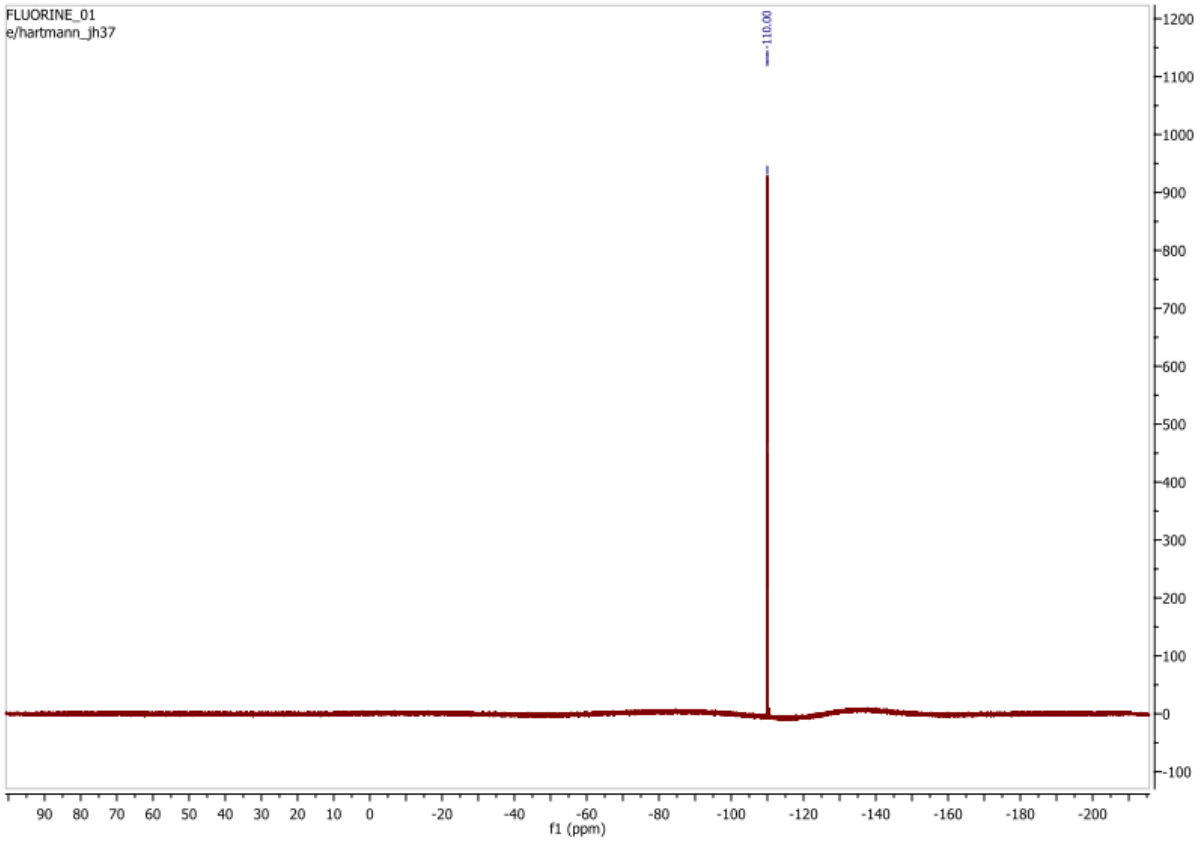

CARBON_01
e/Hack_DH23
141.69
135.67
133.01
131.68
130.14
128.93
128.86
128.62
128.58
126.28
124.44
122.91
95.86
87.02
27.23
f1 (ppm)

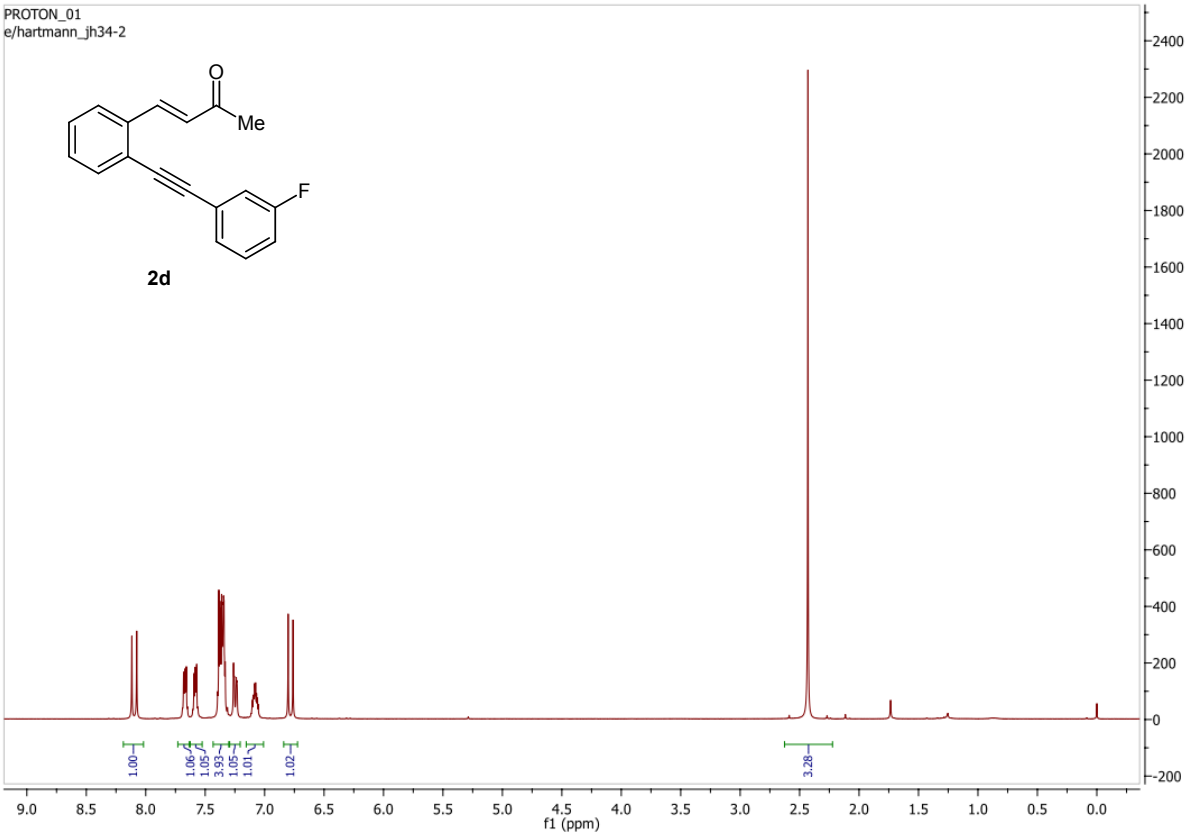

PROTON_01
e/hartmann_jh33
Cl
O
Me
Ph
2b
1.00
1.03
3.19
4.26
1.10
3.26
f1 (ppm)

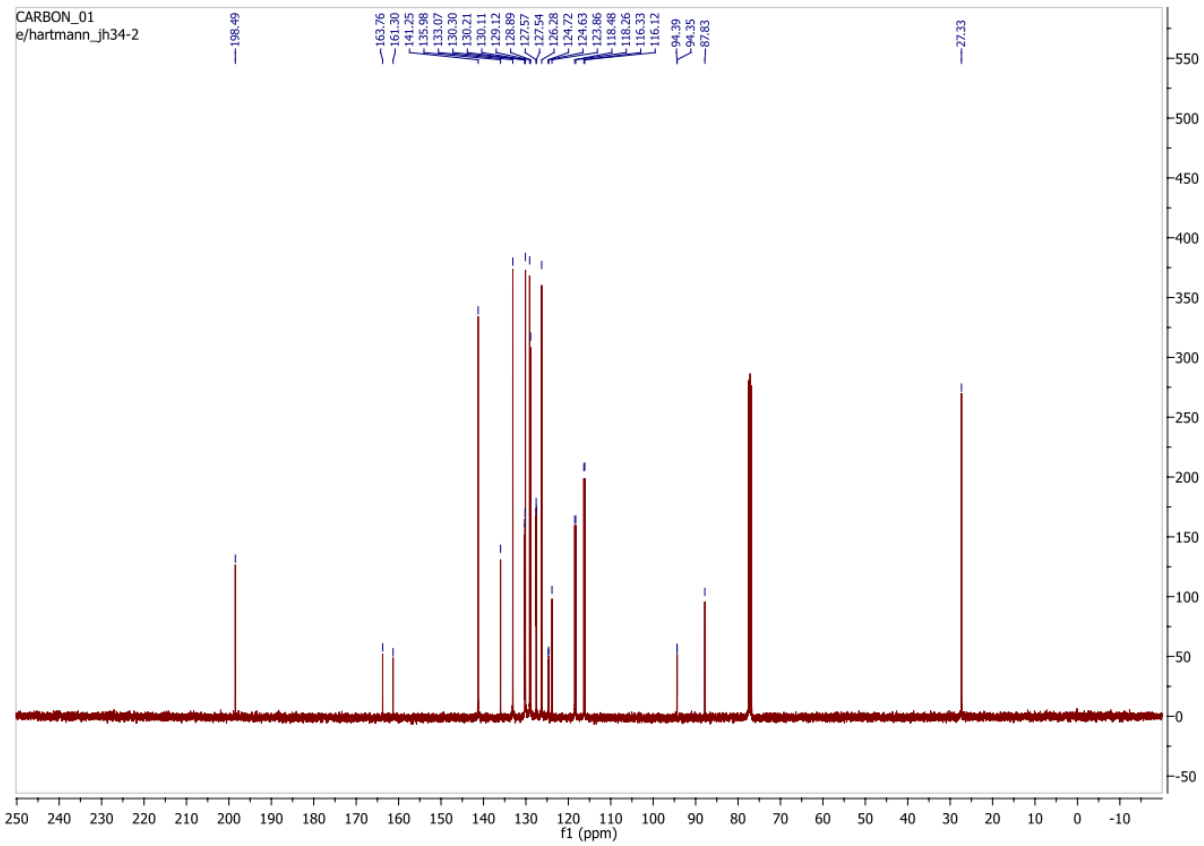

CARBON_01
e/hartmann_jh33
140.04
137.44
134.82
134.04
131.68
130.15
129.53
129.12
128.70
126.27
122.81
122.57
96.69
86.08
27.59
f1 (ppm)

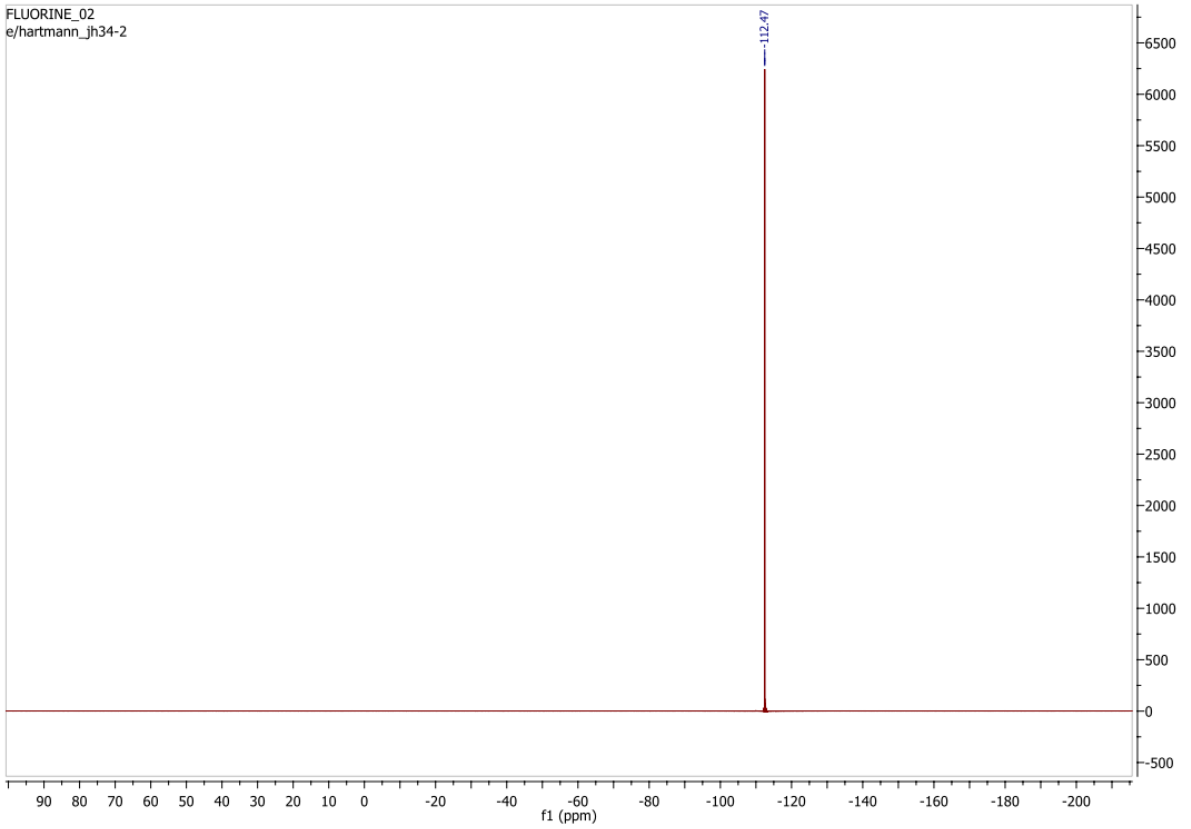

PROTON_01
e/hartmann_jh37
F
O
Me
Ph
2c
1.00
2.95
4.03
1.06
1.07
3.57
f1 (ppm)

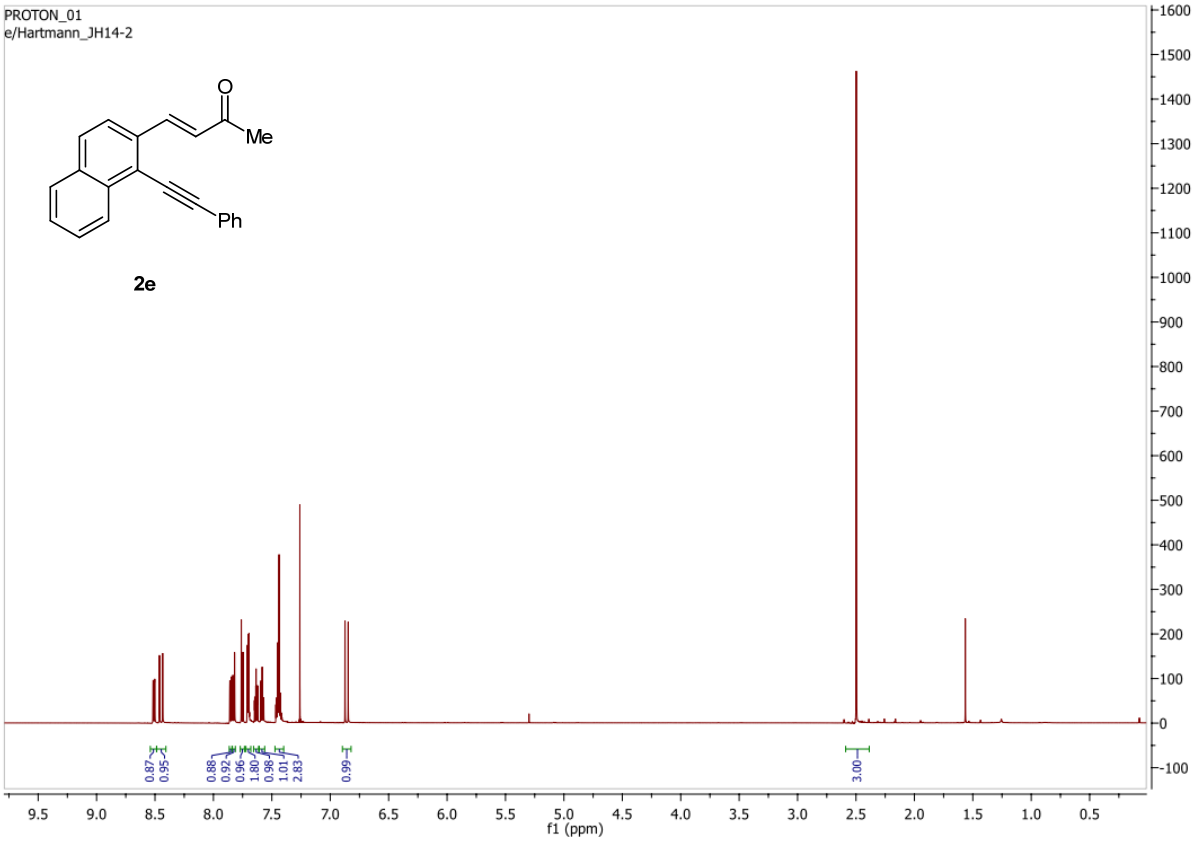

CARBON_02
e/hartmann_jh37
162.57
140.39
138.17
134.83
131.65
129.63
129.00
128.71
122.74
120.63
117.67
112.91
95.52
86.05
27.51
f1 (ppm)

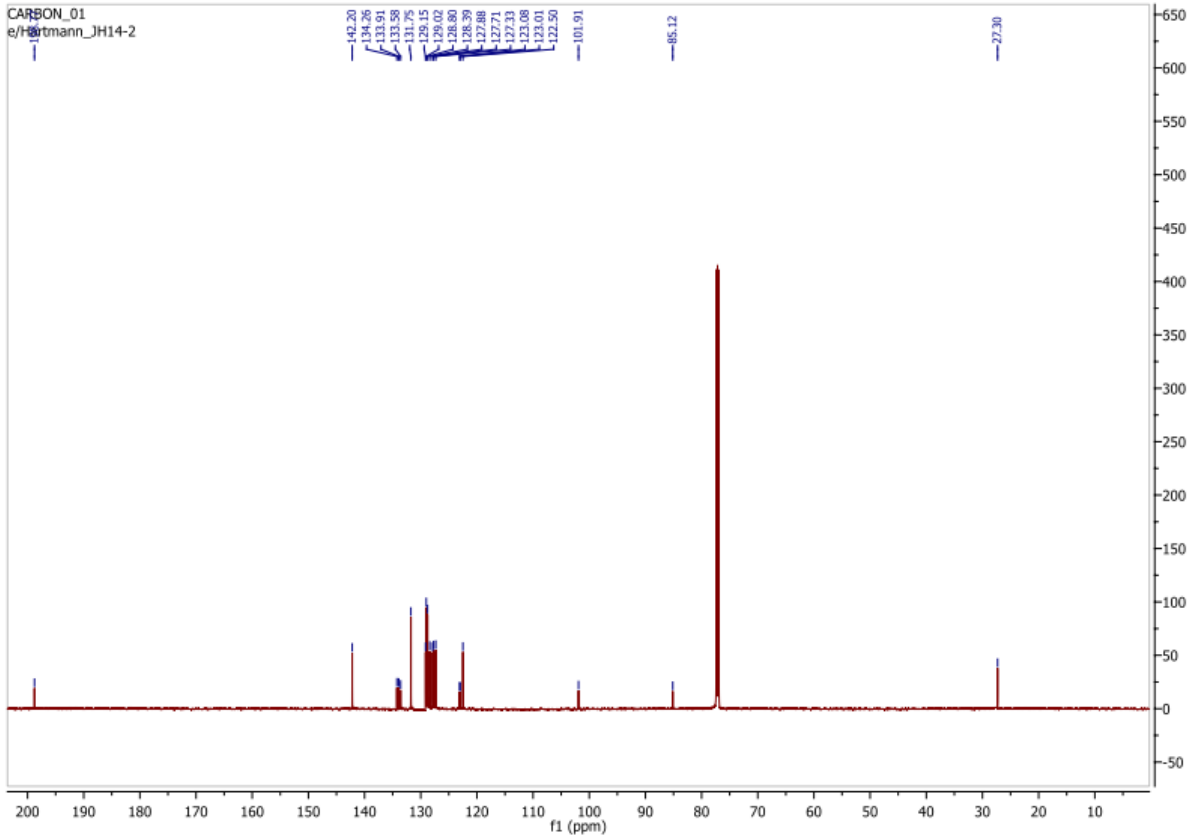

FLUORINE_01
e/hartmann_jh37
-110.00
f1 (ppm)

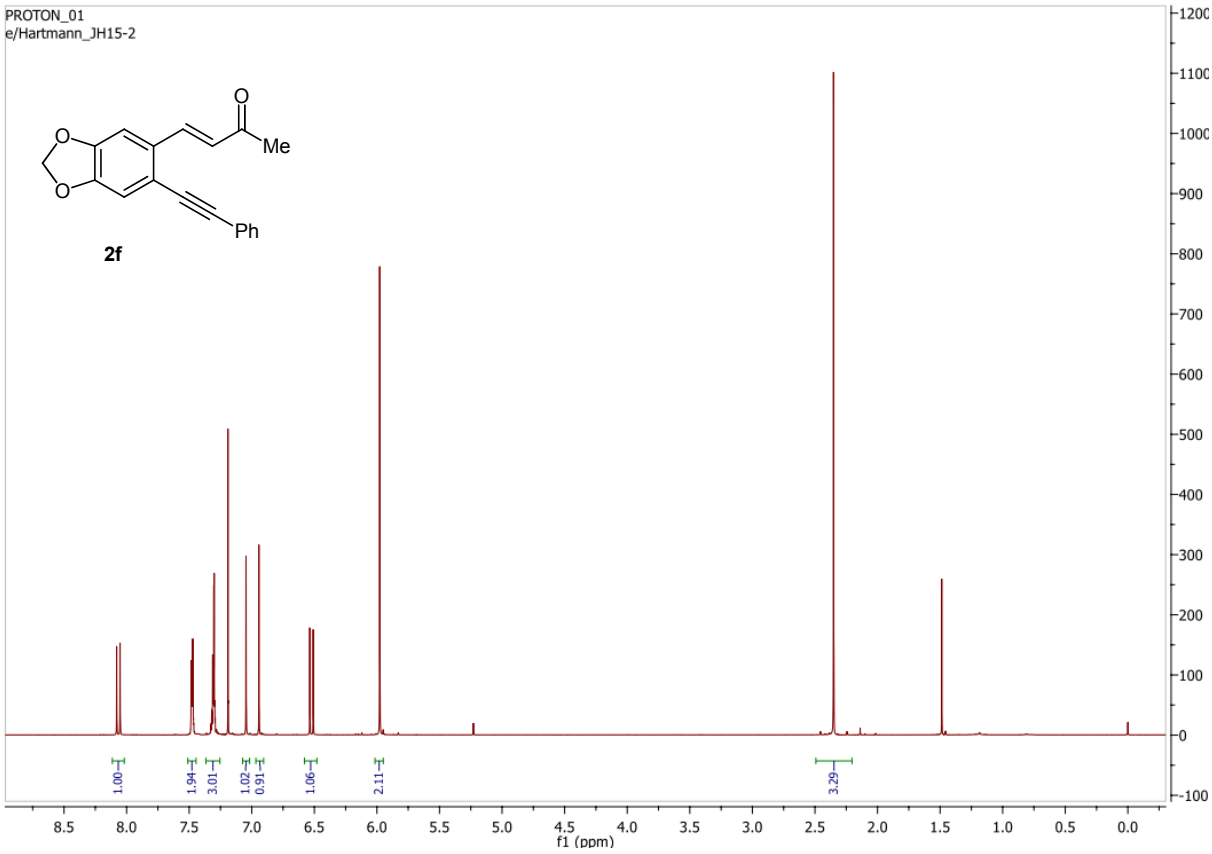

PROTON_01
e/hartmann_jh34-2
O
Me
F
2d
1.00
1.06
1.05
3.93
1.05
1.01
1.02
3.28
f1 (ppm)

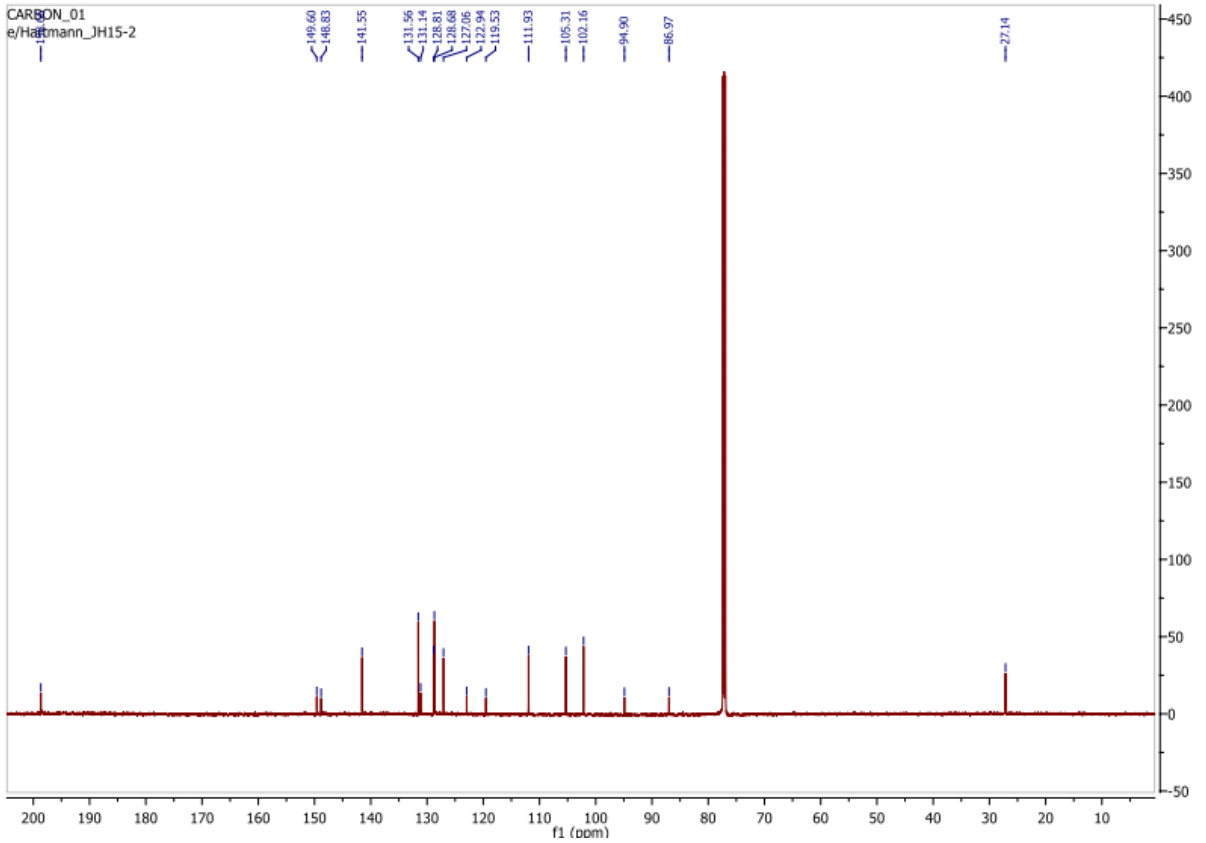

CARBON_01
e/hartmann_jh34-2
198.49
163.76
161.30
141.25
135.98
133.07
130.30
130.21
130.11
129.12
128.89
127.57
127.54
126.28
124.72
124.63
123.86
118.48
118.26
116.33
116.12
94.39
94.35
87.83
27.33
f1 (ppm)

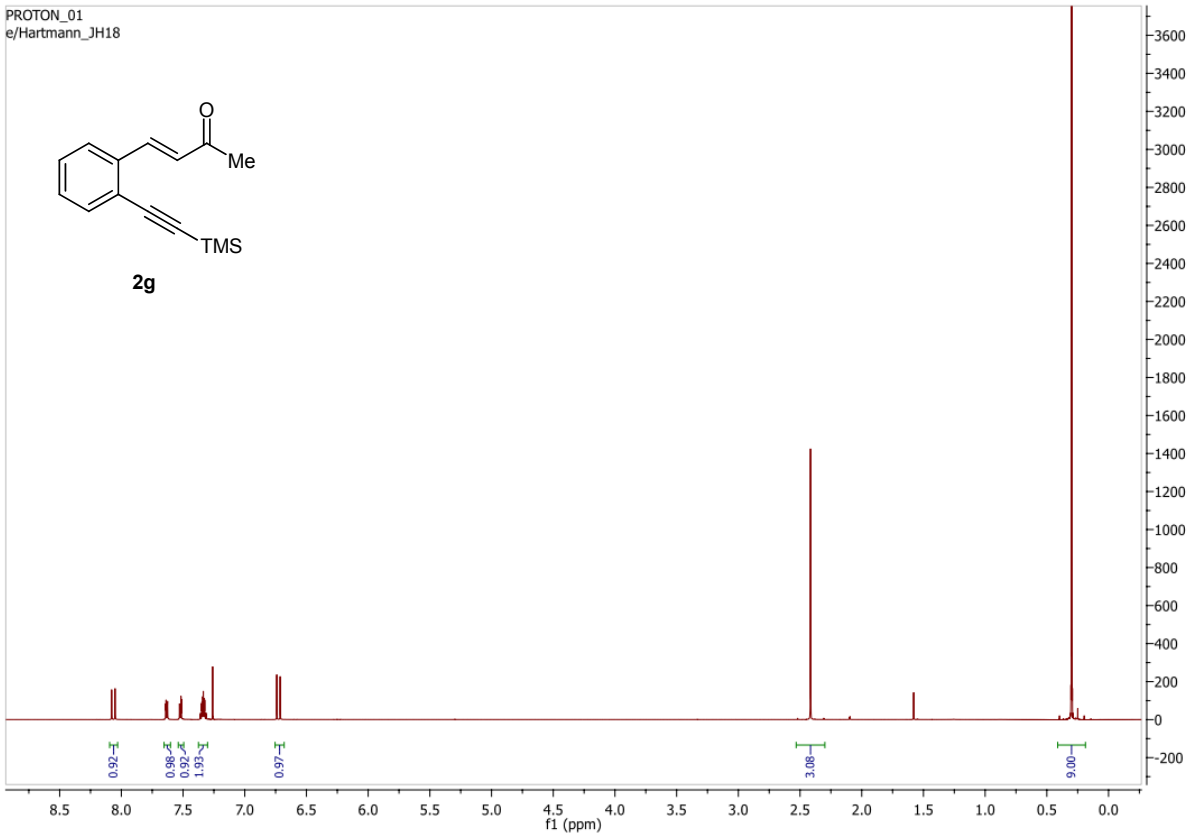

FLUORINE_02
e/hartmann_jh34-2
-112.47
f1 (ppm)

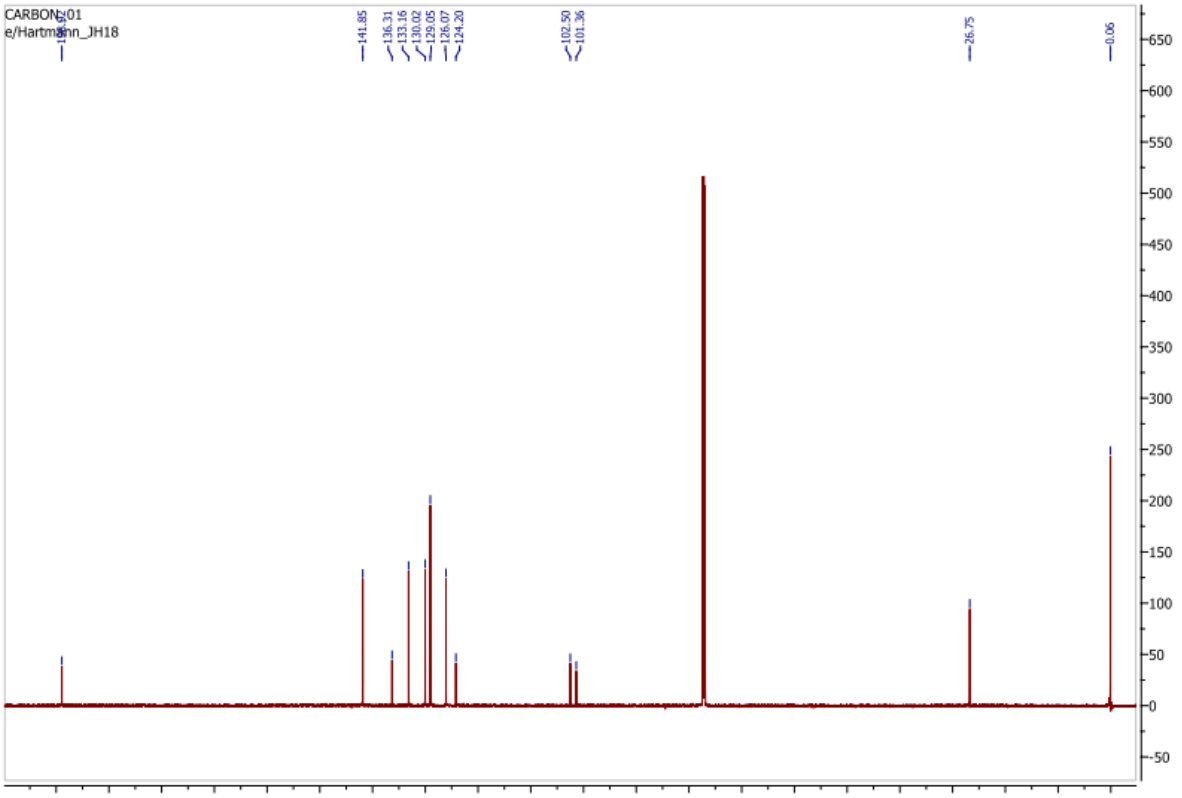

PROTON_01
e/Hartmann_JH14-2
O
Me
Ph
2e
0.87
0.95
0.88
0.92
0.96
1.80
0.98
1.01
2.83
0.99
3.00
f1 (ppm)

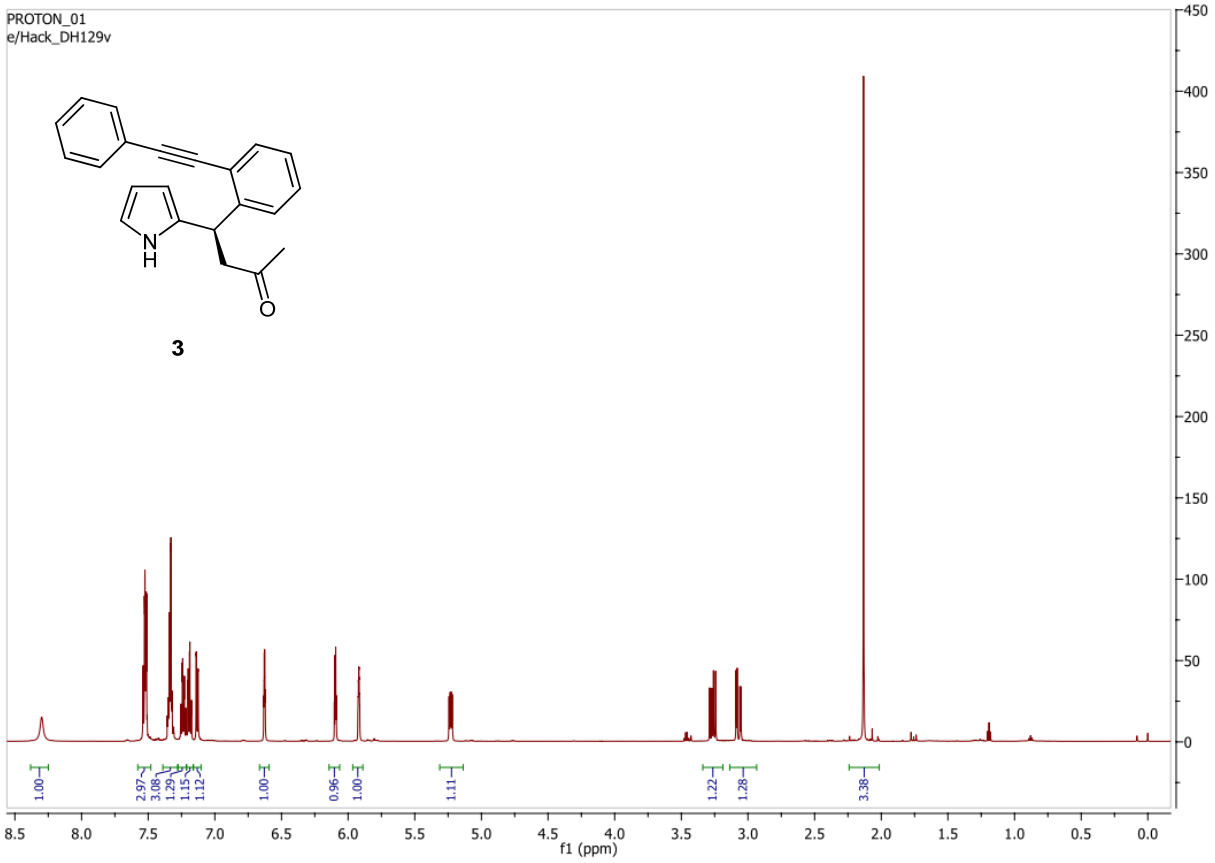

CARBON_01
e/Hartmann_JH14-2
142.20
134.26
133.91
133.58
131.75
129.15
129.02
128.80
128.39
127.88
127.71
127.33
123.08
123.01
122.50
101.91
85.12
27.30
f1 (ppm)

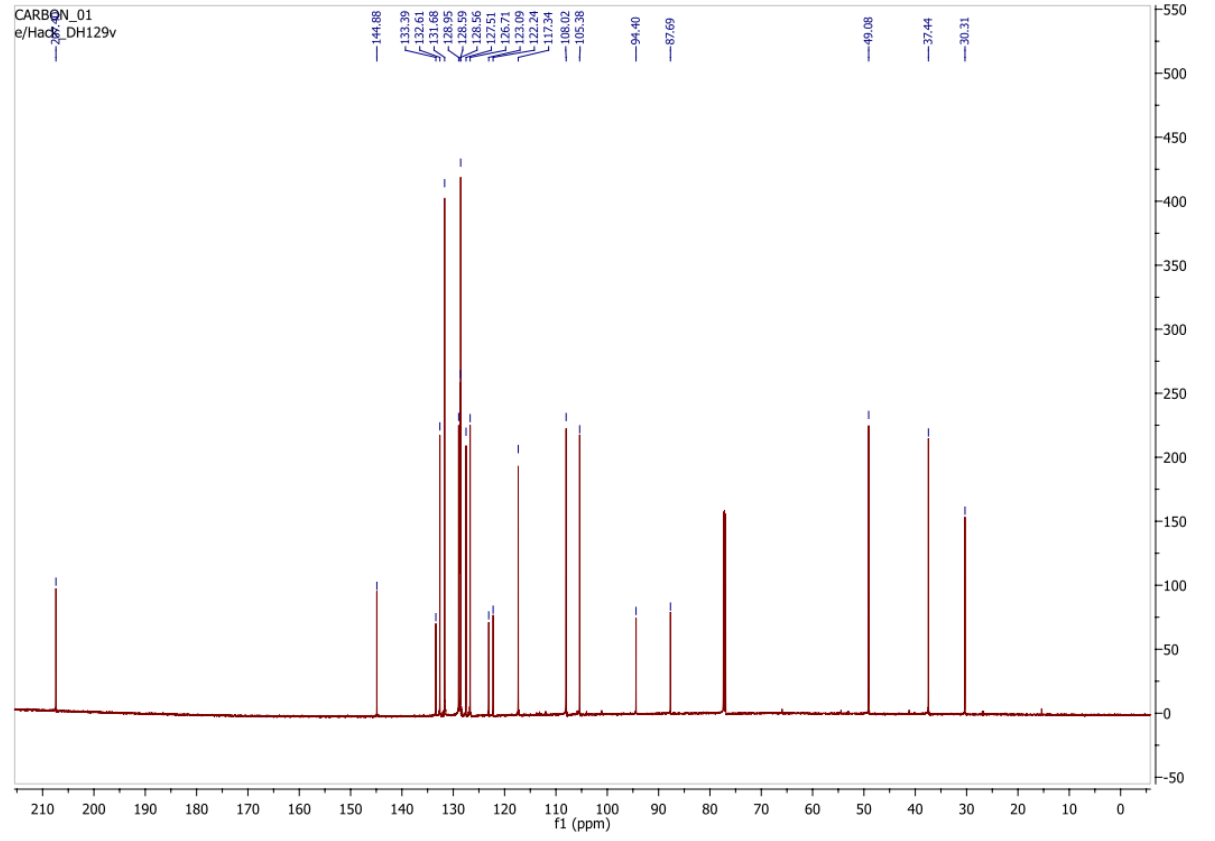

PROTON_01
e/Hartmann_JH15-2
O
Me
O
O
Ph
2f
1.00
1.94
3.01
1.02
0.91
1.06
2.11
3.29
f1 (ppm)

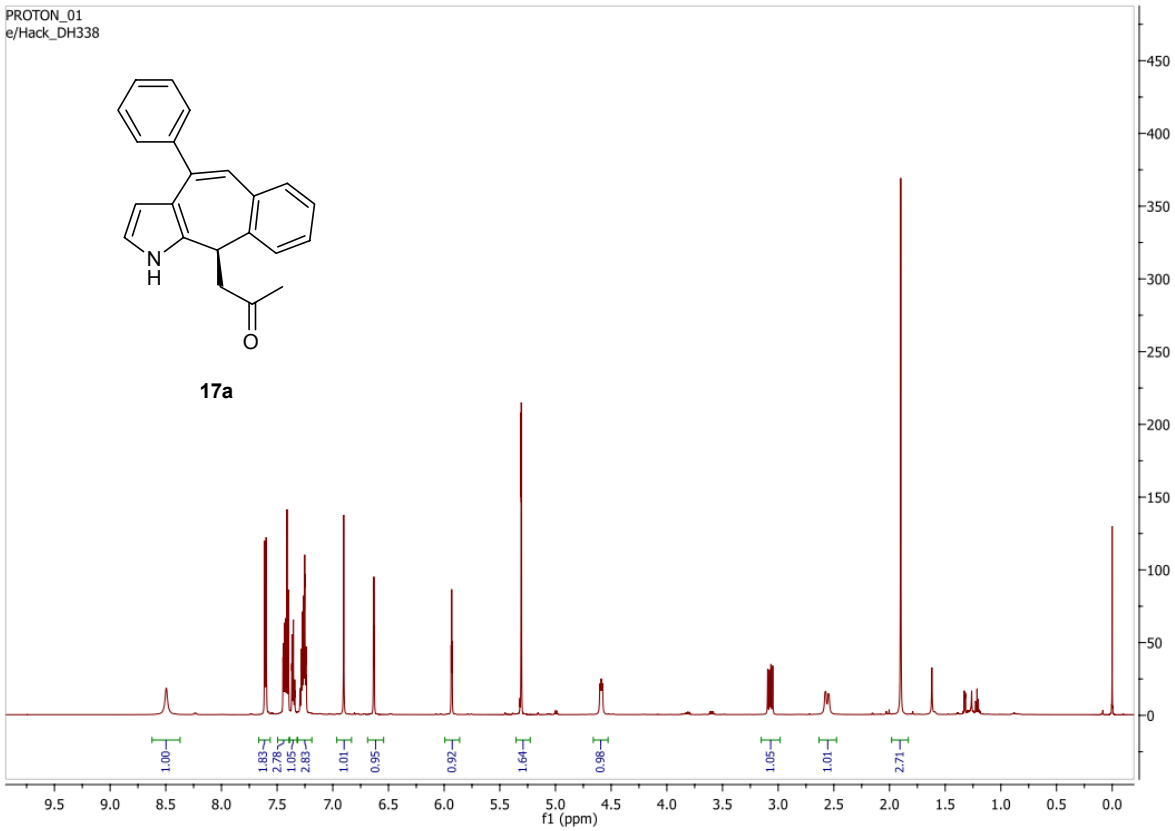

CARBON_01
e/Hartmann_JH15-2
149.60
148.83
141.55
131.56
131.14
128.81
128.68
127.06
122.94
119.53
111.93
105.31
102.16
94.90
86.97
27.14
f1 (ppm)

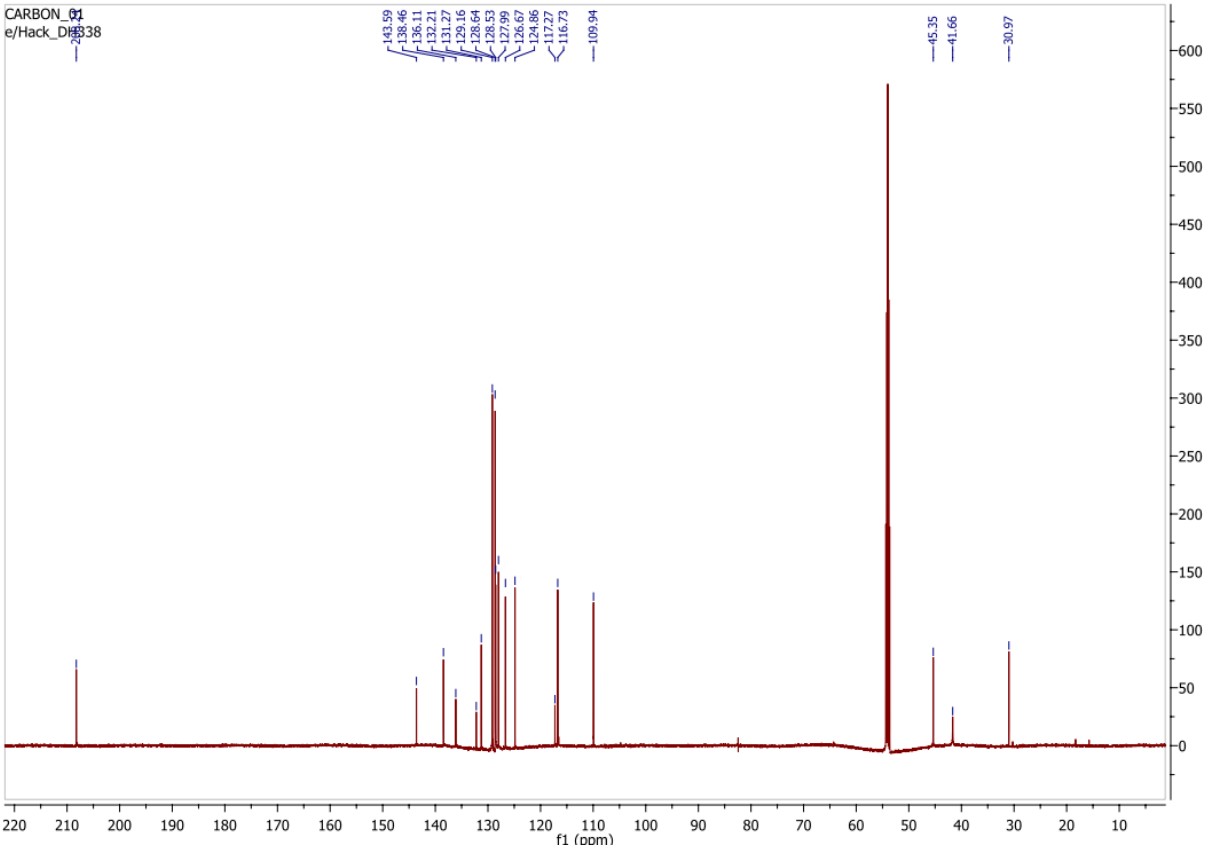

PROTON_01
e/Hartmann_JH18
O
Me
TMS
2g
0.92
0.98
0.92
1.93
0.97
3.08
9.00
f1 (ppm)

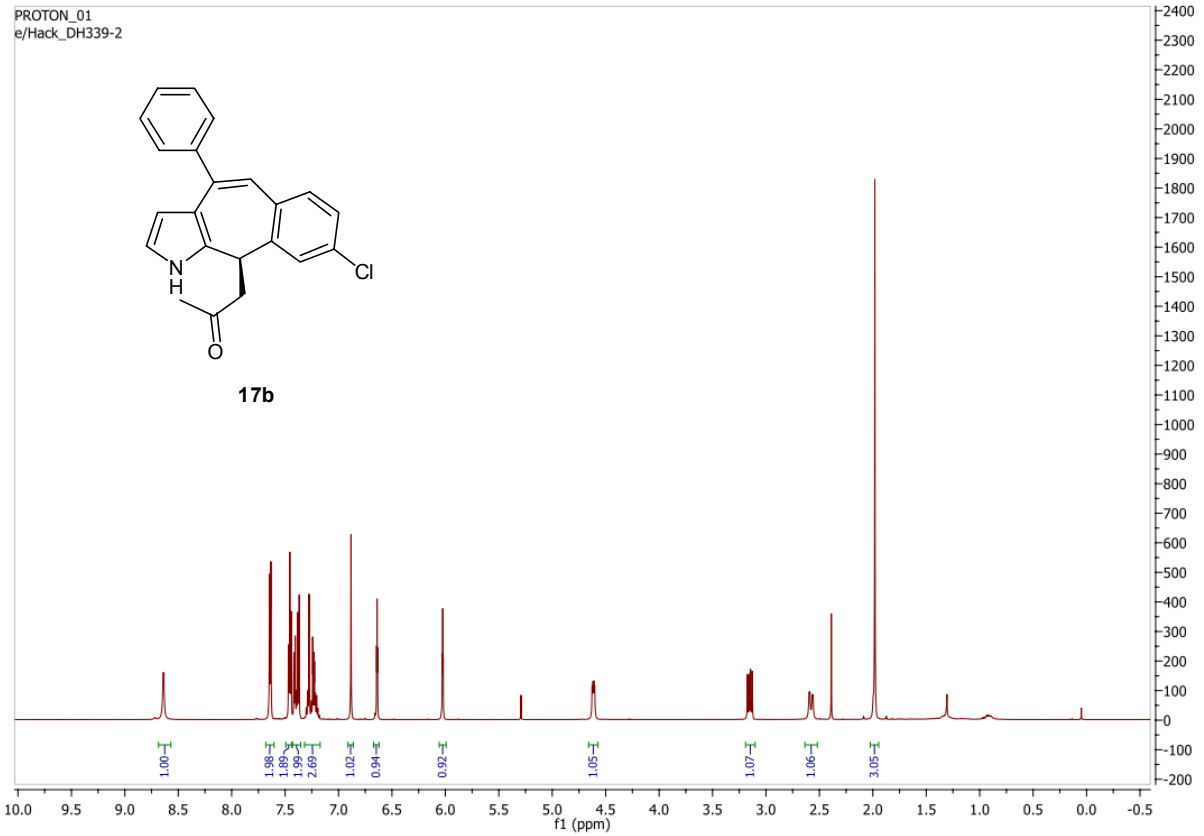

CARBON_01
e/Hartmann_JH18
141.85
136.31
133.16
130.02
129.05
126.07
124.20
102.50
101.36
26.75
0.06


PROTON_01
e/Hack_DH129v
3
1.00
2.97
3.08
1.29
1.15
1.12
1.00
0.96
1.00
1.11
1.22
1.28
3.38
f1 (ppm)

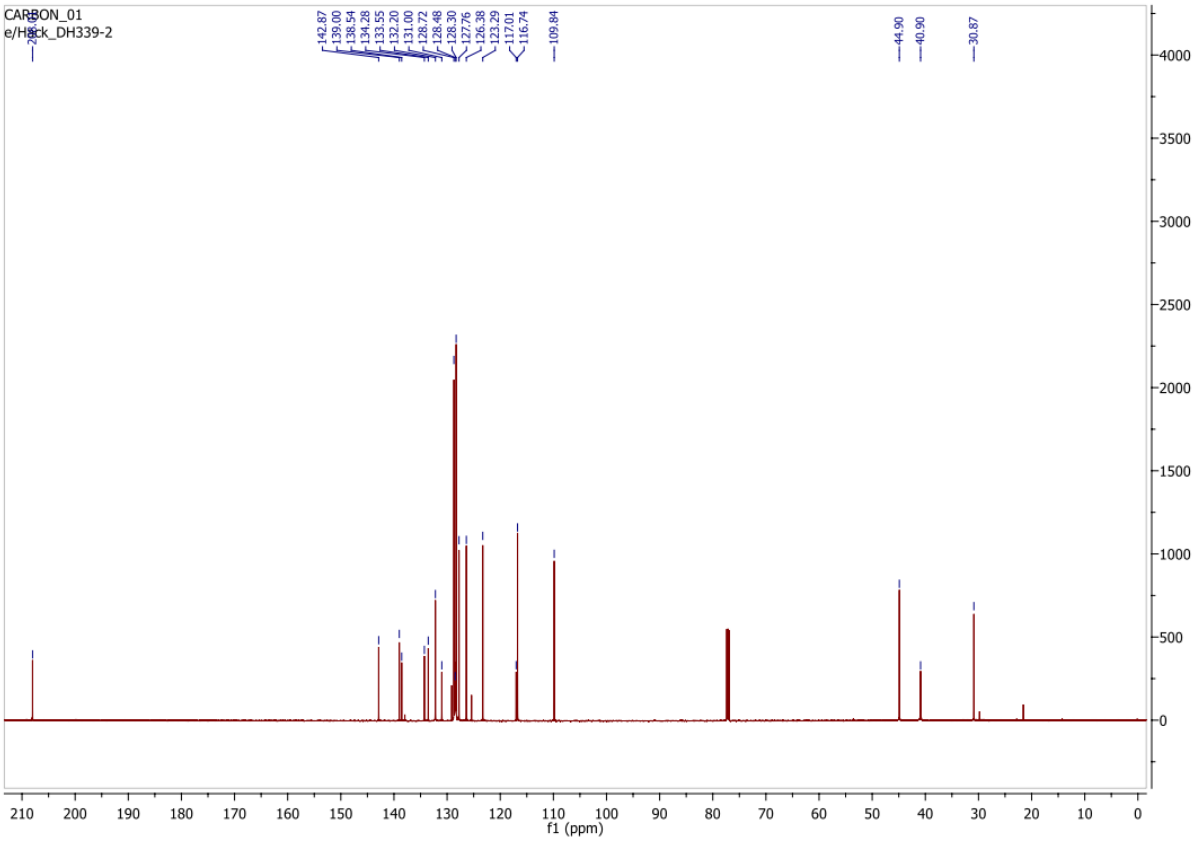

CARBON_01
e/Hack_DH129v
144.88
133.39
132.61
131.68
128.95
128.59
128.56
127.51
126.71
123.09
122.24
117.34
108.02
105.38
94.40
87.69
49.08
37.44
30.31
f1 (ppm)

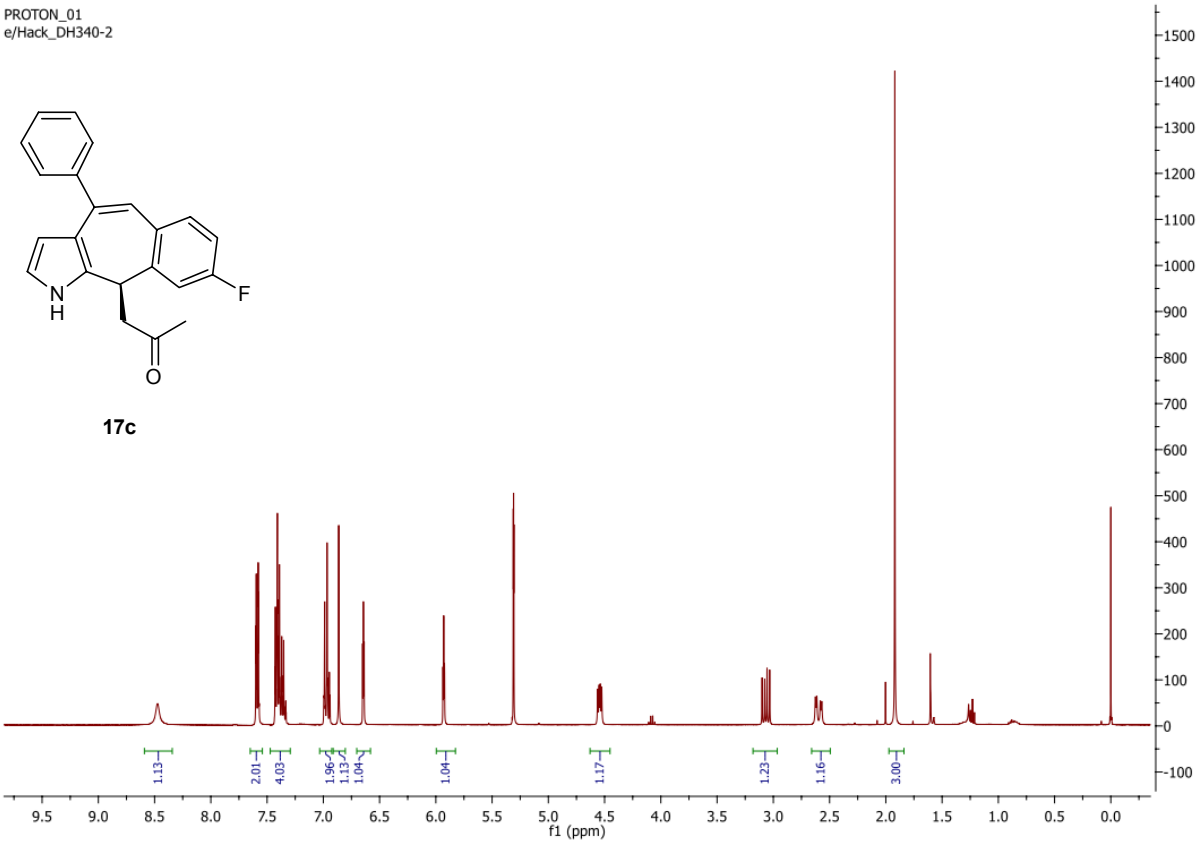

PROTON_01
e/Hack_DH338
N
H
O
17a
1.00
1.83
2.78
1.05
2.83
1.01
0.95
0.92
1.64
0.98
1.05
1.01
2.71
f1 (ppm)


CARBON_01
e/Hack_DH338
143.59
138.46
136.11
132.21
131.27
129.16
128.64
128.53
127.99
126.67
124.86
117.27
116.73
109.94
45.35
41.66
30.97
f1 (ppm)

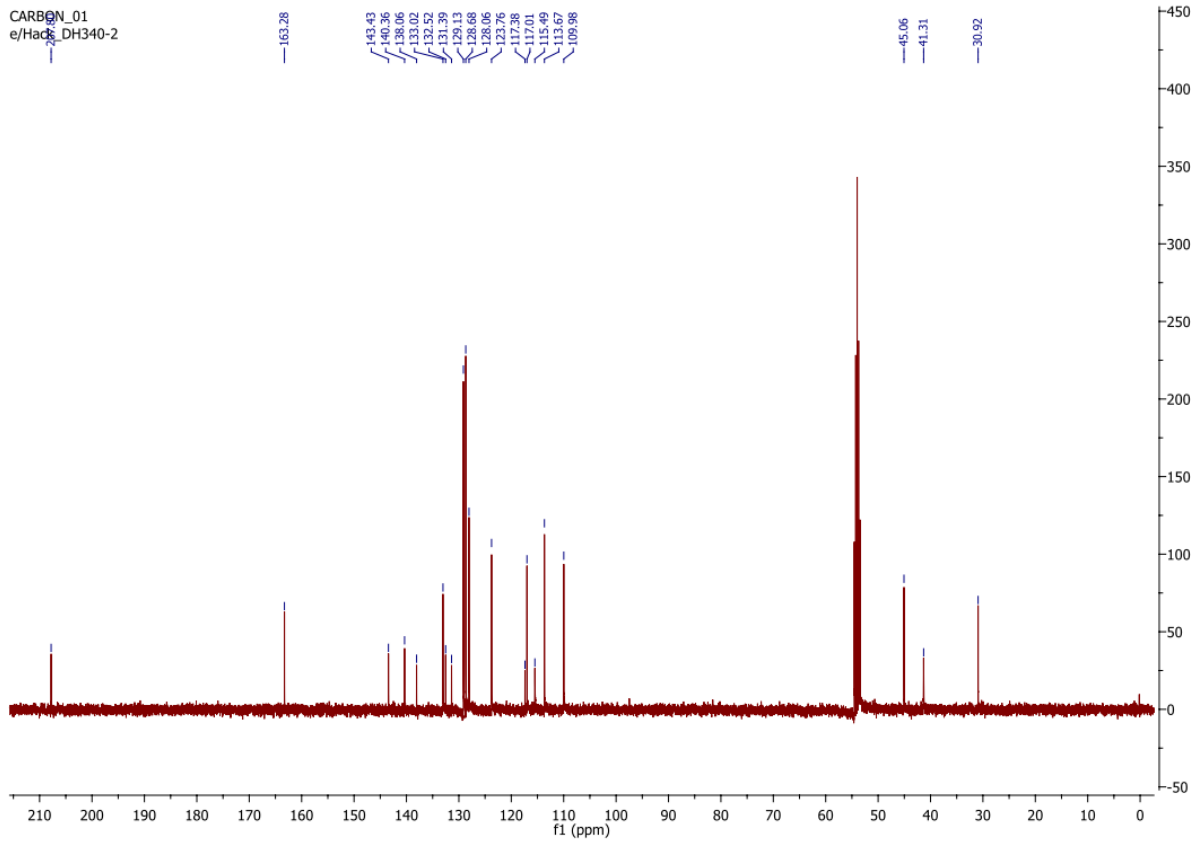

PROTON_01
e/Hack_DH339-2
N
H
Cl
O
1.00
1.98
1.89
1.99
2.69
1.02
0.94
0.92
1.05
1.07
1.06
3.05
f1 (ppm)

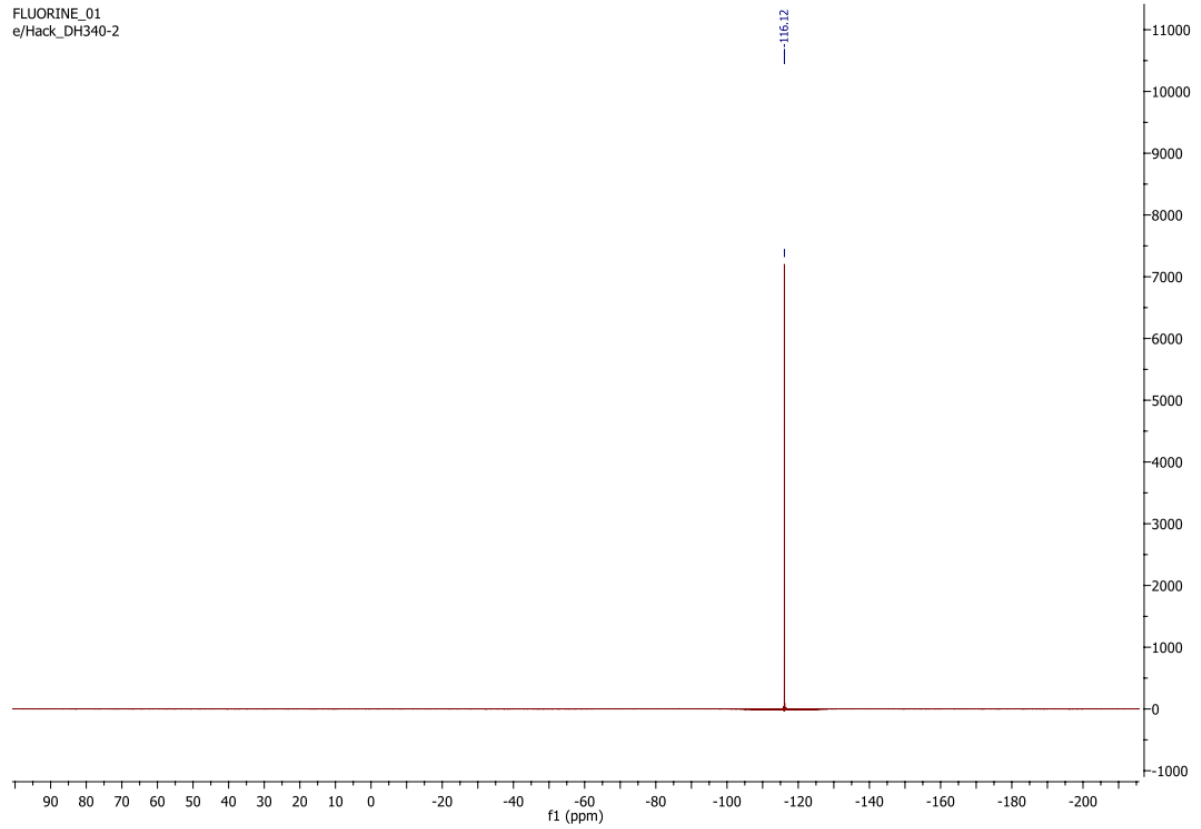
17b

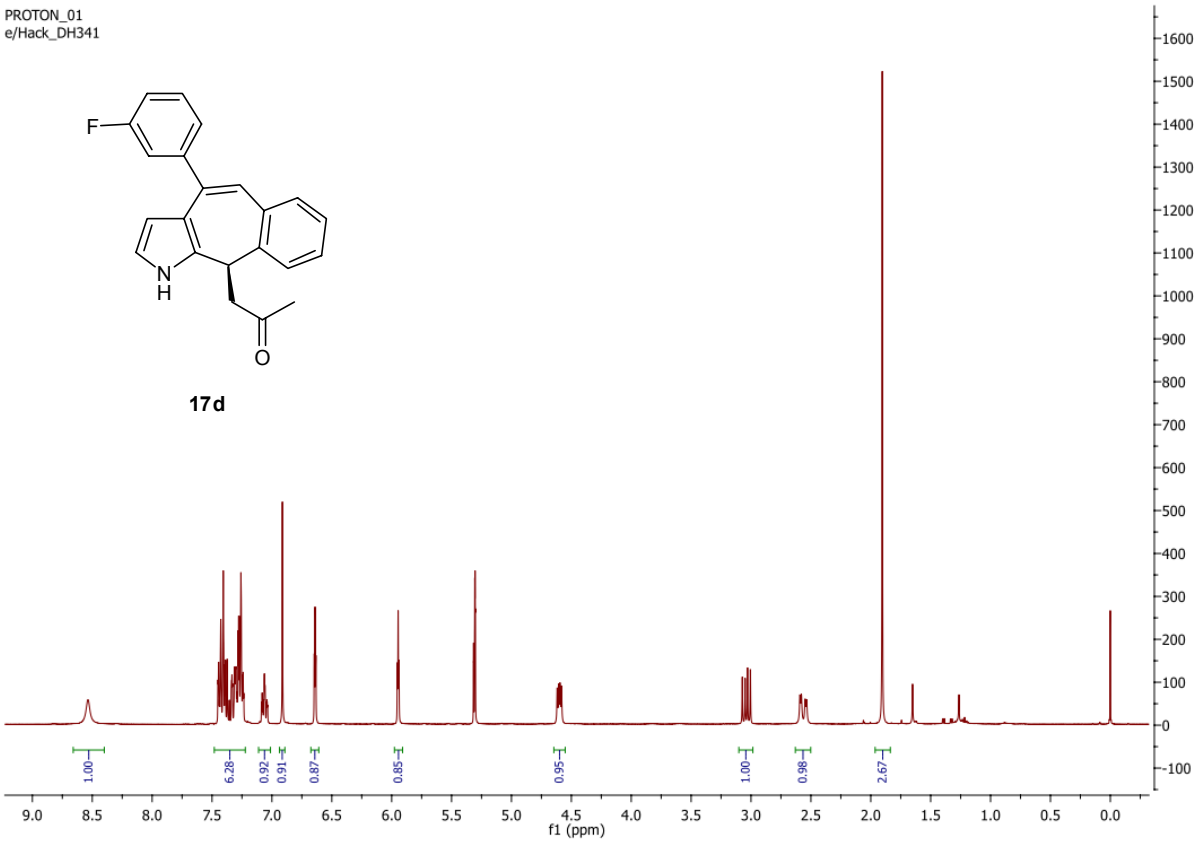

CARBON_01
e/Hack_DH339-2
142.87
139.00
138.54
134.28
133.55
132.20
131.00
128.72
128.48
128.30
127.76
126.38
123.29
117.01
116.74
109.84
44.90
40.90
30.87
f1 (ppm)


PROTON_01
e/Hack_DH340-2
N
H
F
O
1.13
2.01
4.03
1.96
1.13
1.04
1.04
1.17
1.23
1.16
3.00
f1 (ppm)

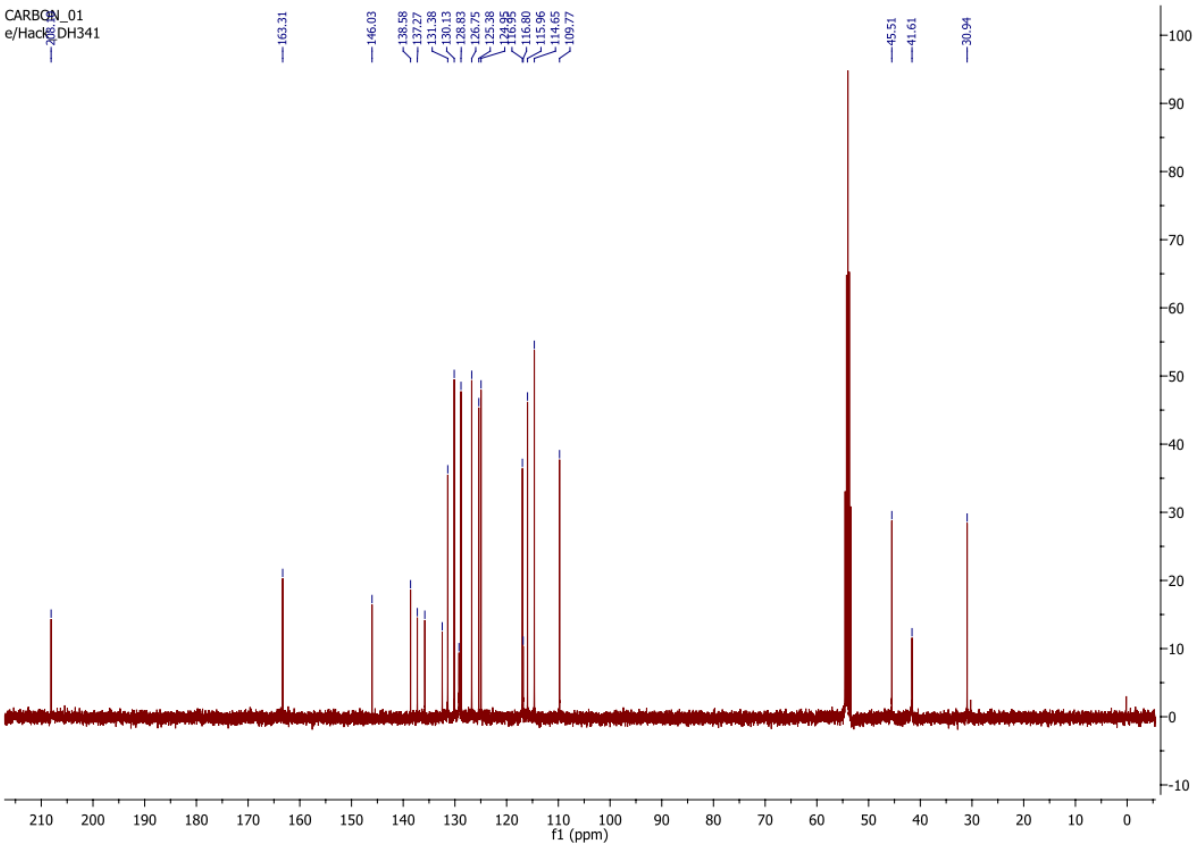
17c

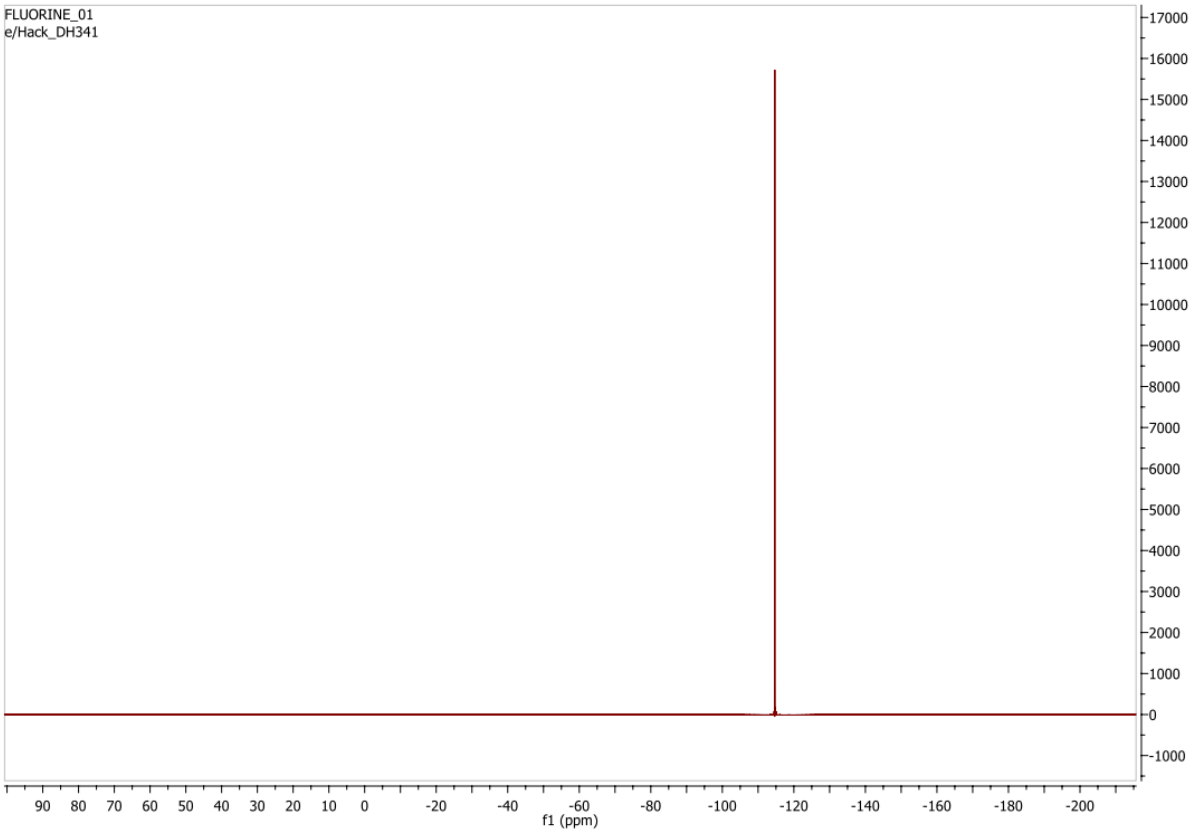

CARBON_01
e/Hack_DH340-2
163.28
143.43
140.36
138.06
133.02
132.52
131.39
129.13
128.68
128.06
123.76
117.38
117.01
115.49
113.67
109.98
45.06
41.31
30.92
f1 (ppm)

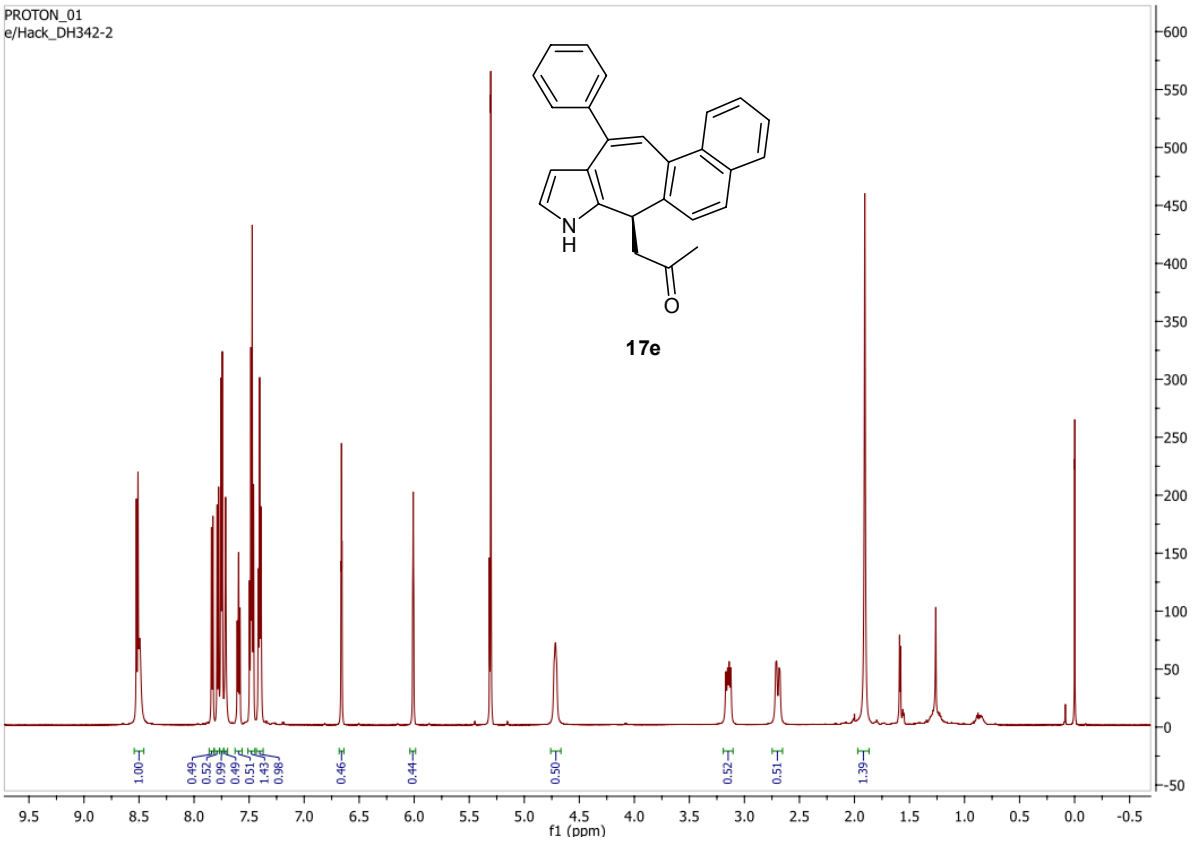

FLUORINE_01
e/Hack_DH340-2
-116.12
f1 (ppm)

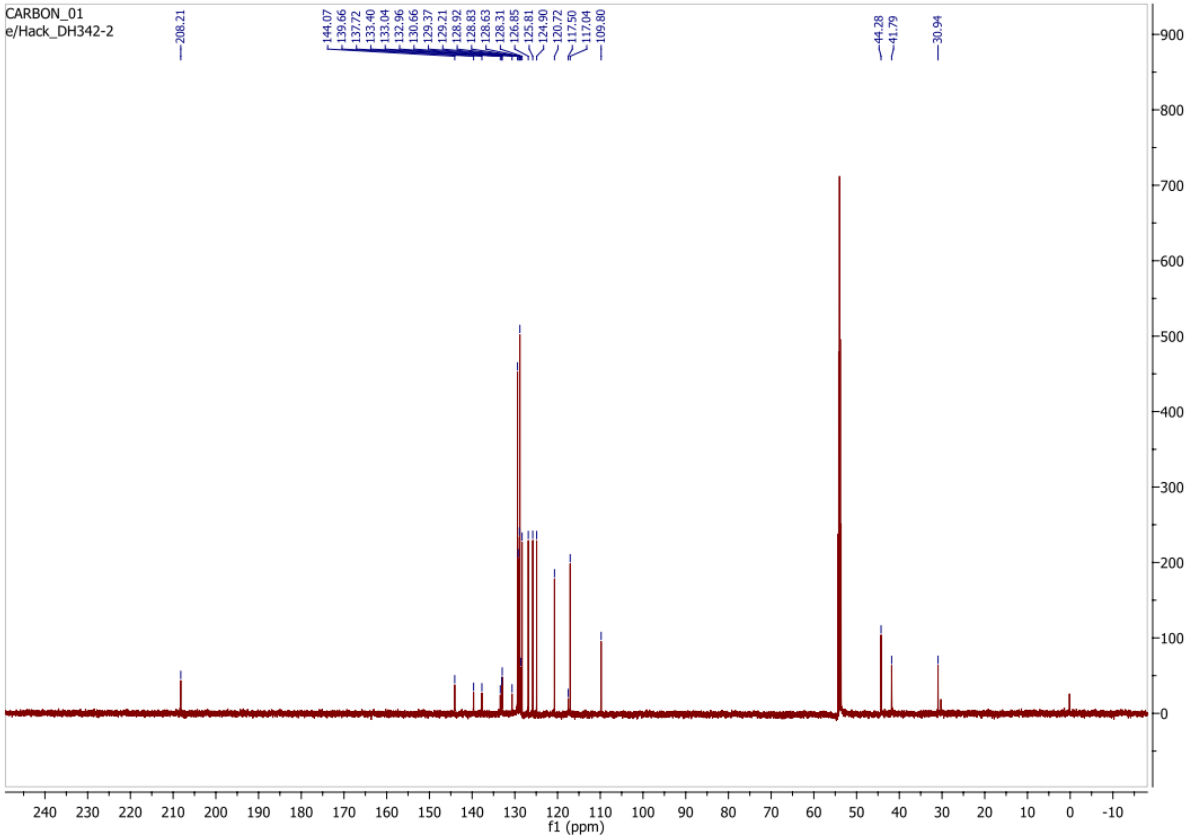

PROTON_01
e/Hack_DH341
F
N
H
O
1.00
6.28
0.92
0.91
0.87
0.85
0.95
1.00
0.98
2.67
f1 (ppm)

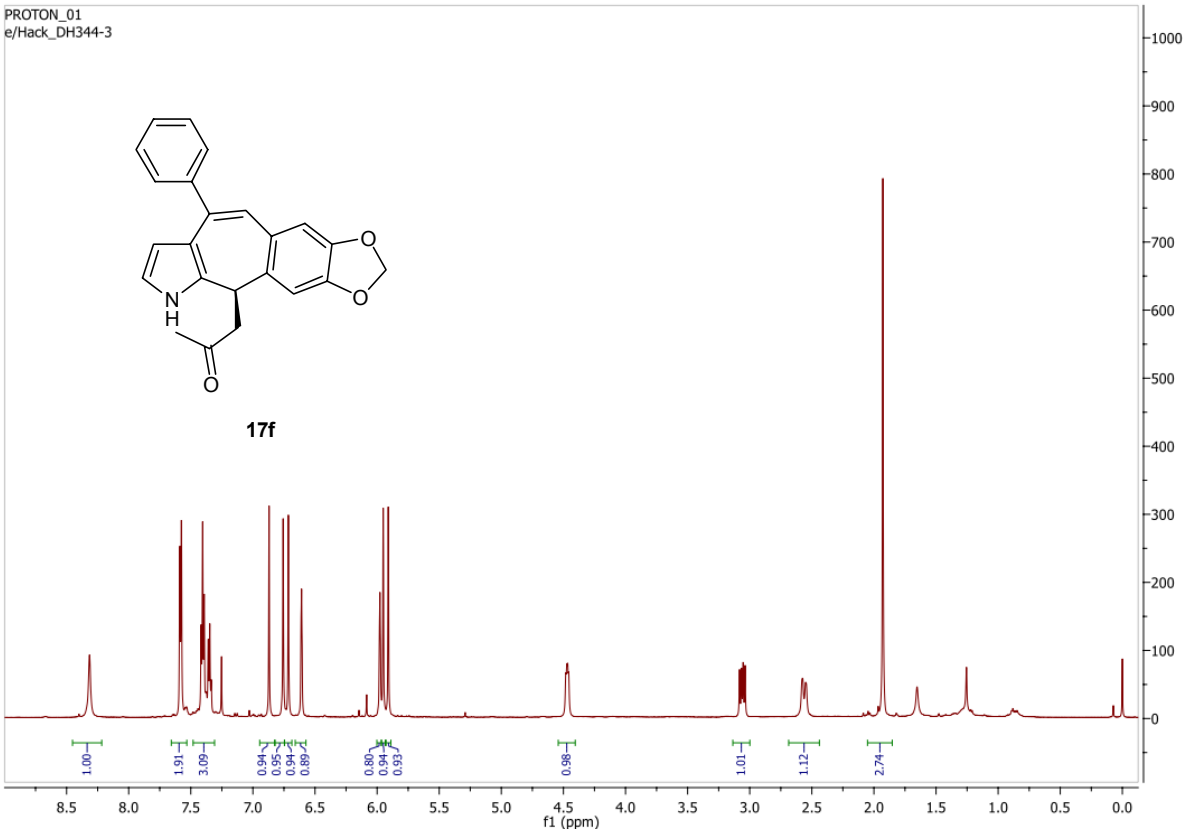
17d


CARBON_01
e/Hack_DH341
163.31
146.03
138.58
137.27
131.38
130.13
128.83
126.75
125.38
116.80
115.96
114.65
109.77
45.51
41.61
30.94
f1 (ppm)

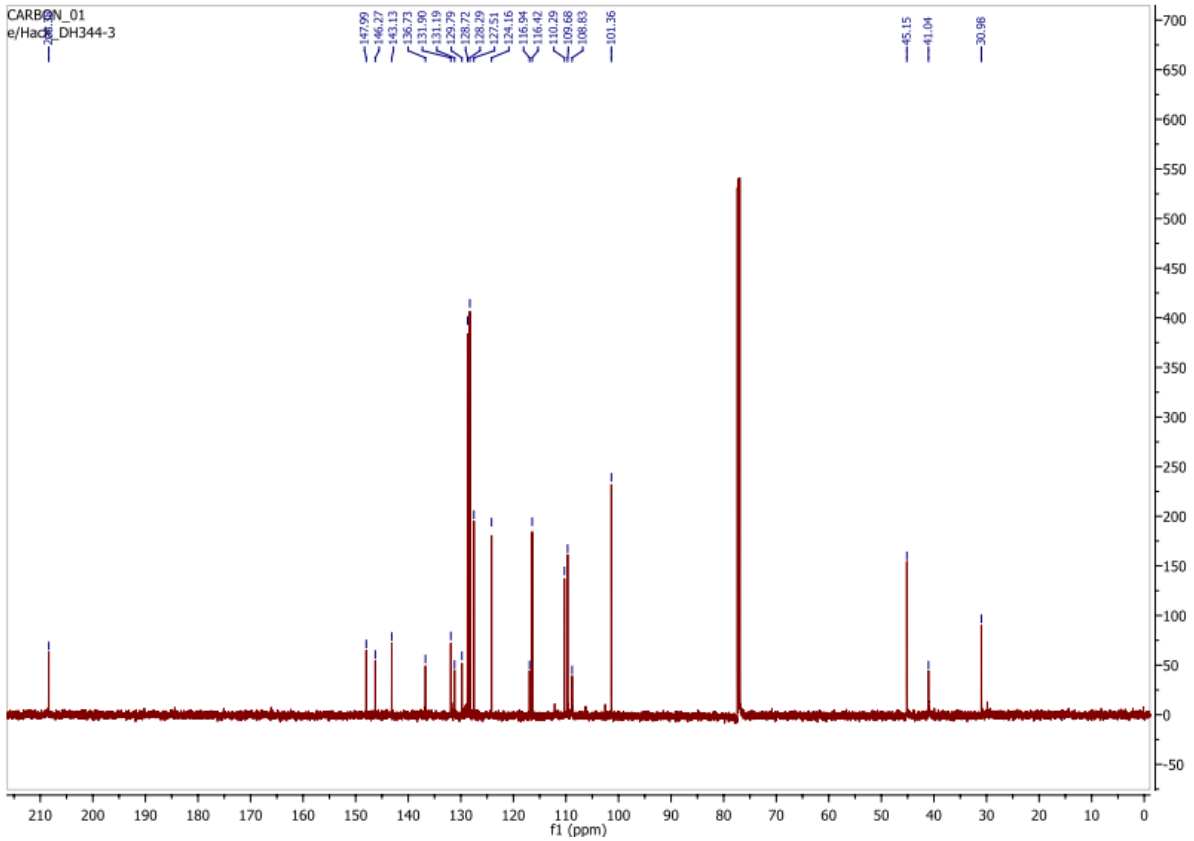

FLUORINE_01
e/Hack_DH341
f1 (ppm)

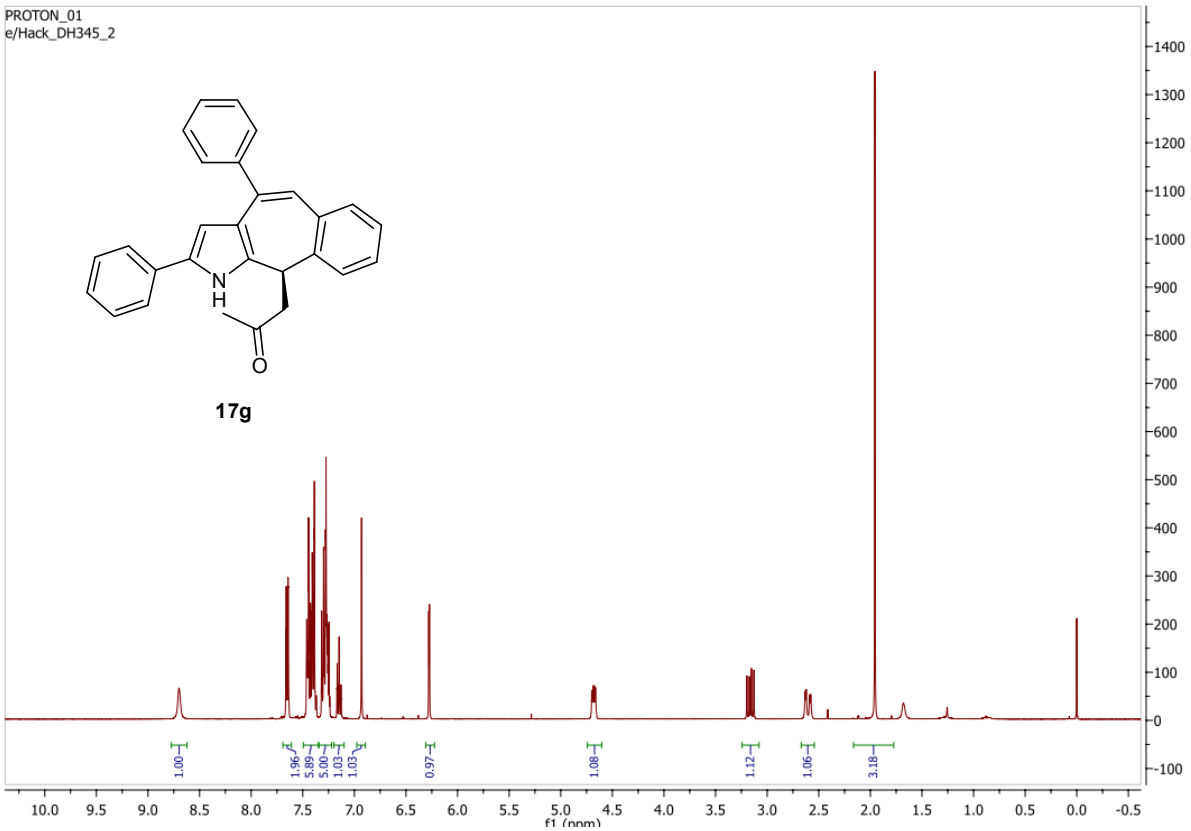

PROTON_01
e/Hack_DH342-2
N
H
O
17e
1.00
0.49
0.52
0.99
0.49
0.51
1.43
0.98
0.46
0.44
0.50
0.52
0.51
1.39
f1 (ppm)

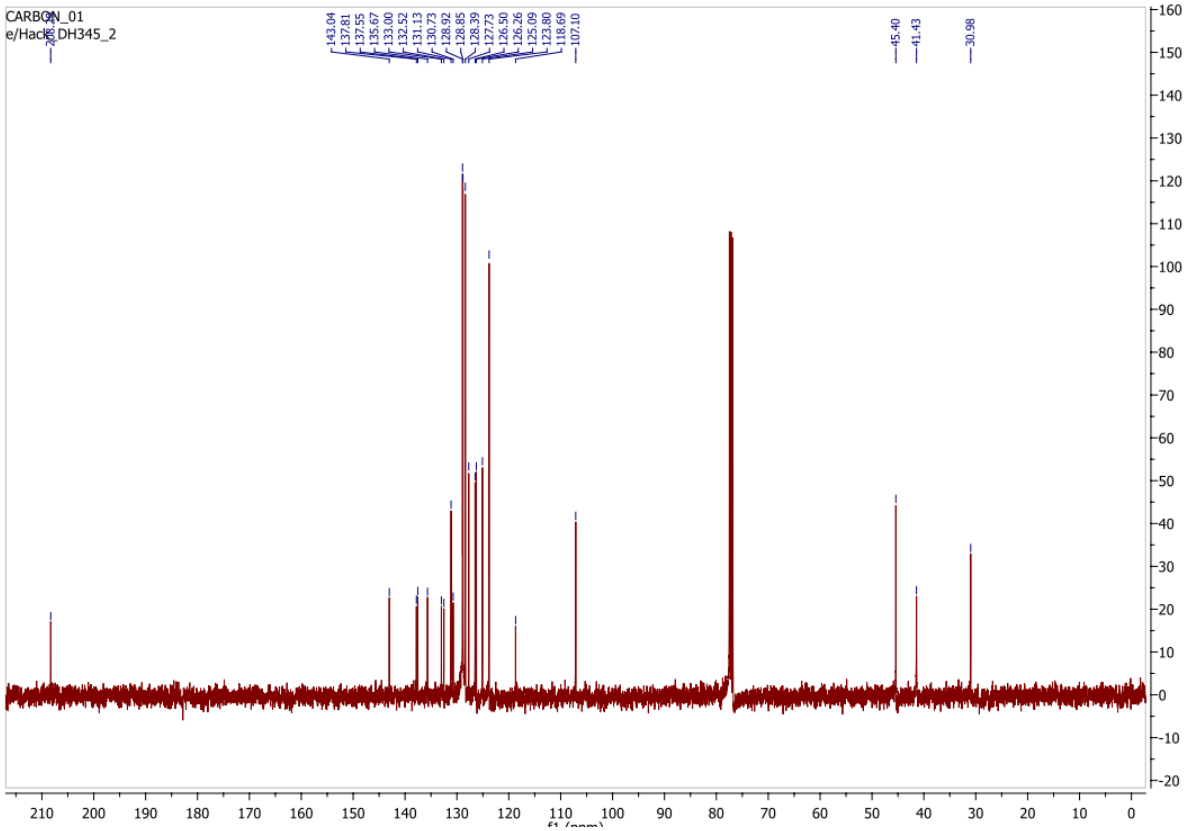

CARBON_01
e/Hack_DH342-2
208.21
144.07
139.66
137.72
133.40
133.04
132.96
130.66
129.37
129.21
128.92
128.83
128.63
128.31
126.85
125.81
124.90
120.72
117.50
117.04
109.80
44.28
41.79
30.94
f1 (ppm)

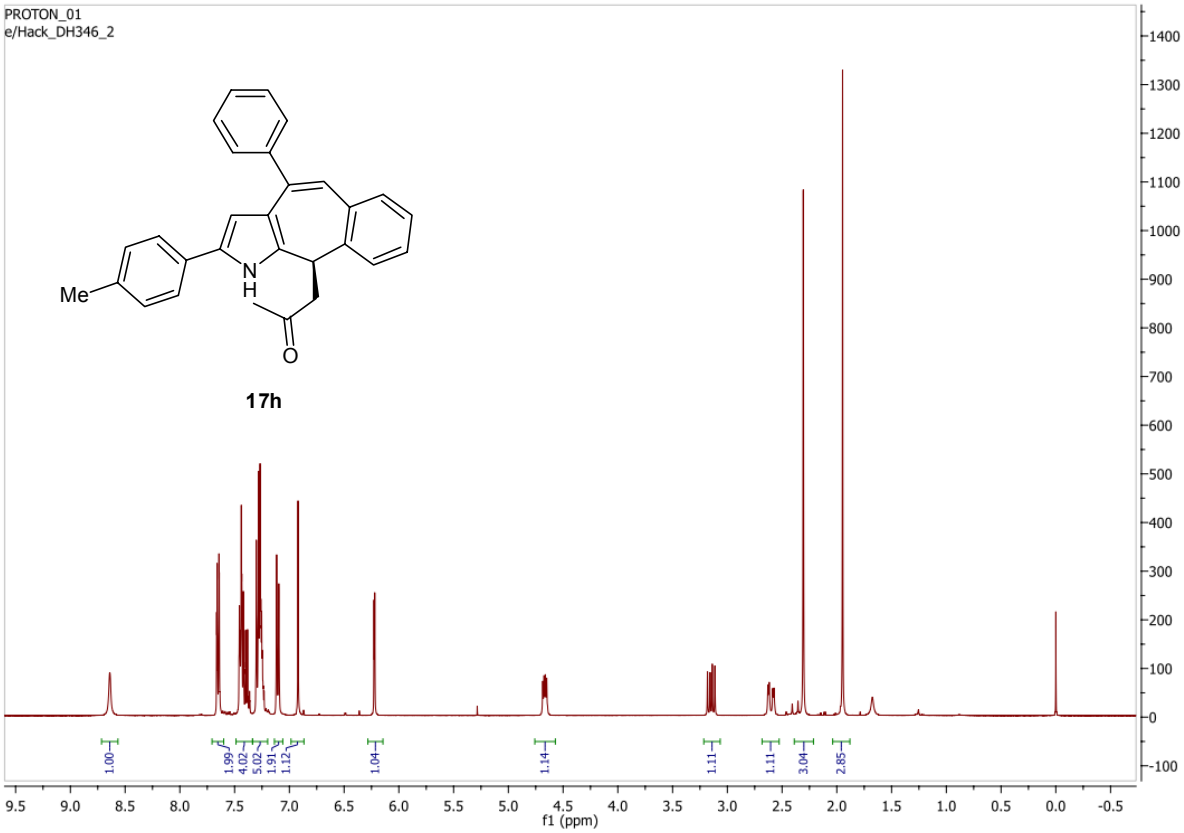

PROTON_01
e/Hack_DH344-3
O
O
N
H
O
1.00
1.91
3.09
0.94
0.95
0.94
0.89
0.80
0.94
0.93
0.98
1.01
1.12
2.74
f1 (ppm)

17f

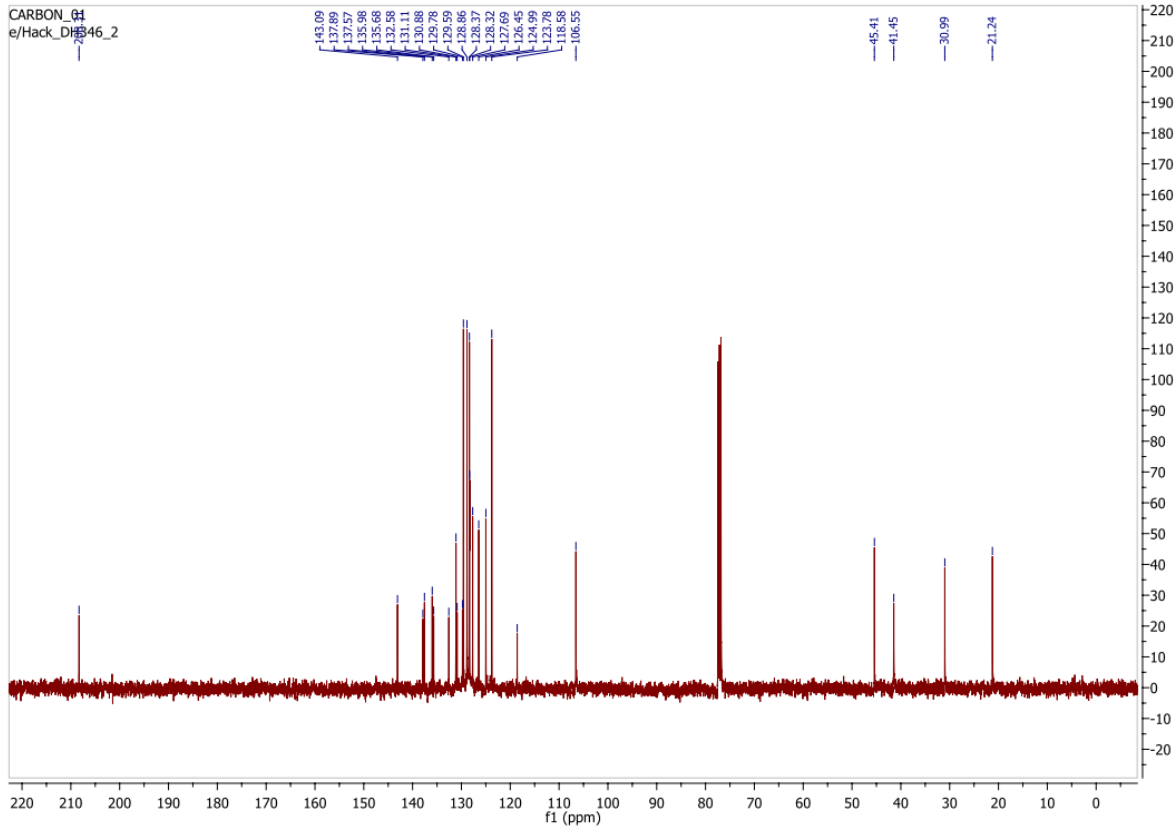

CARBON_01
e/Hack_DH344-3
147.99
146.27
143.13
136.73
131.90
131.19
129.79
128.72
128.29
127.51
124.16
116.94
116.42
110.29
109.68
108.83
101.36
45.15
41.04
30.98
f1 (ppm)

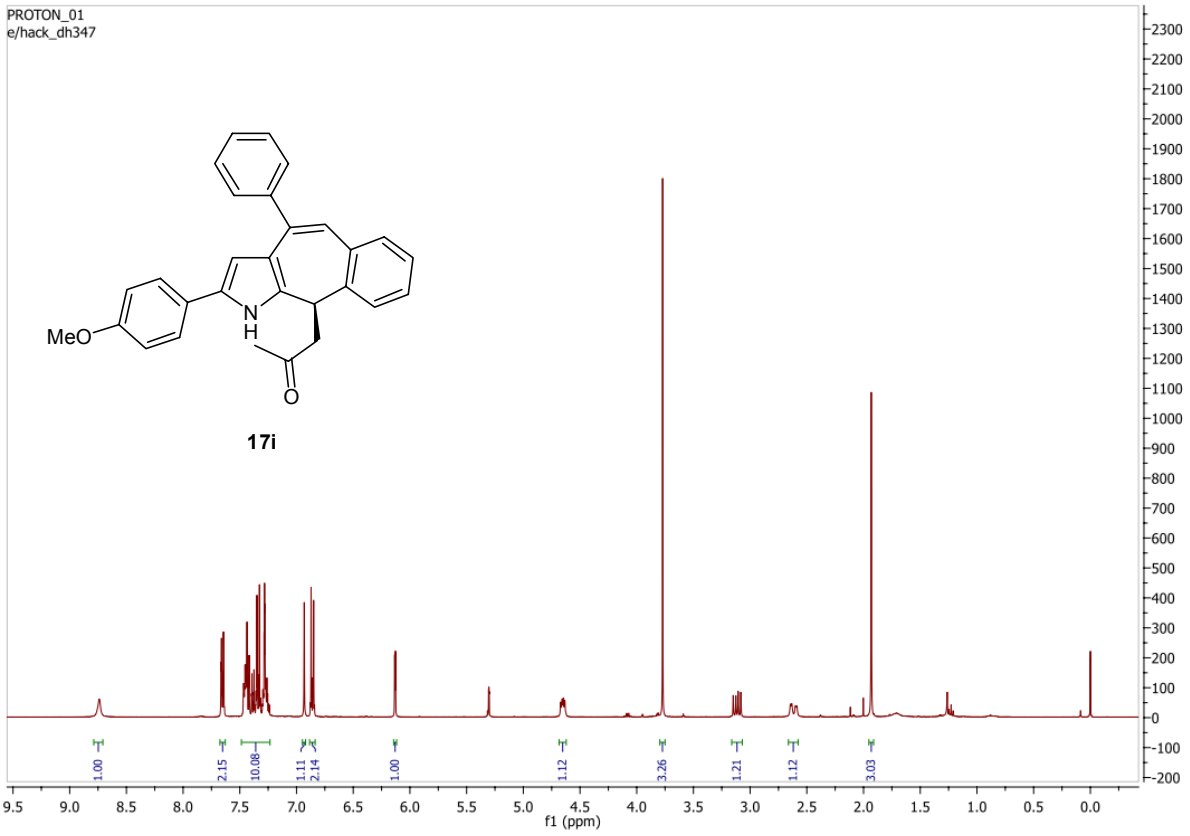

PROTON_01
e/Hack_DH345_2
N
H
O
17g
1.00
1.96
5.89
5.00
1.03
1.03
0.97
1.08
1.12
1.06
3.18
f1 (ppm)

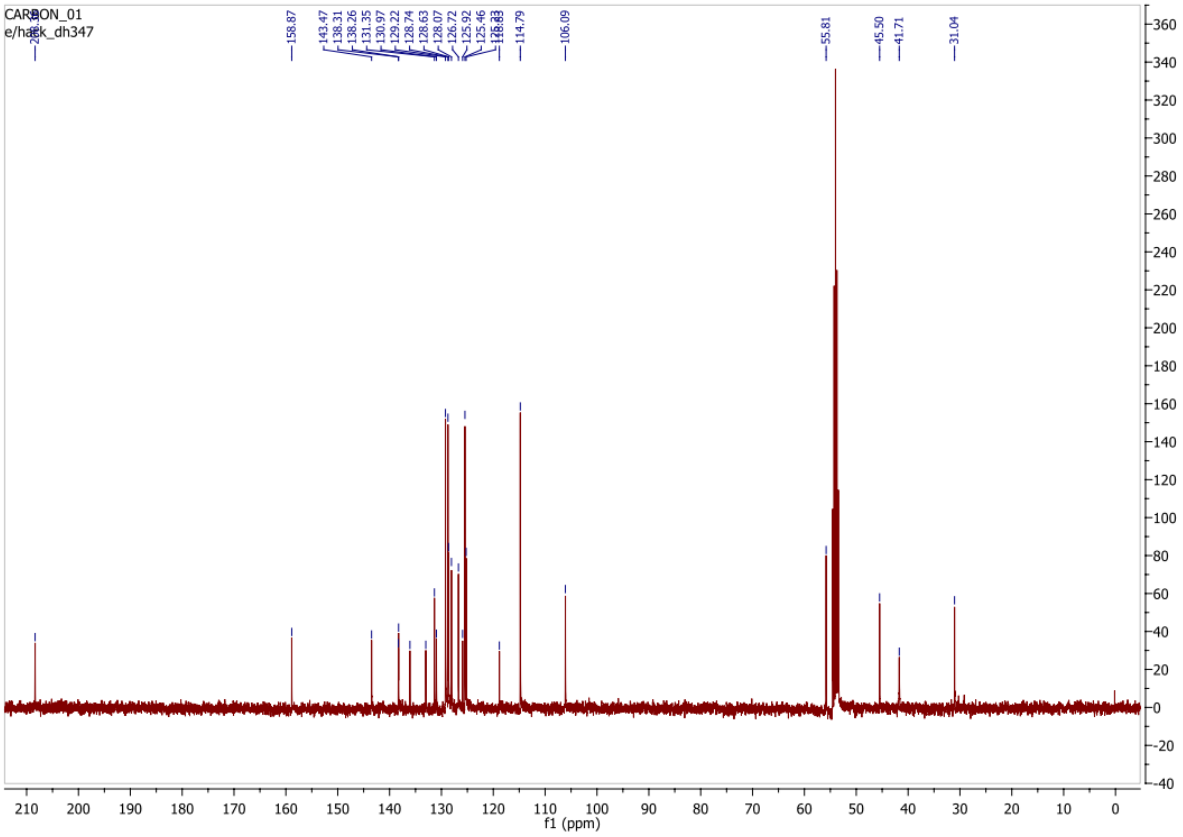

CARBON_01
e/Hack_DH345_2
143.04
137.81
137.55
135.67
133.00
132.52
131.13
130.73
128.92
128.85
128.39
127.73
126.50
126.26
125.09
123.80
118.69
107.10
45.40
41.43
30.98
f1 (ppm)

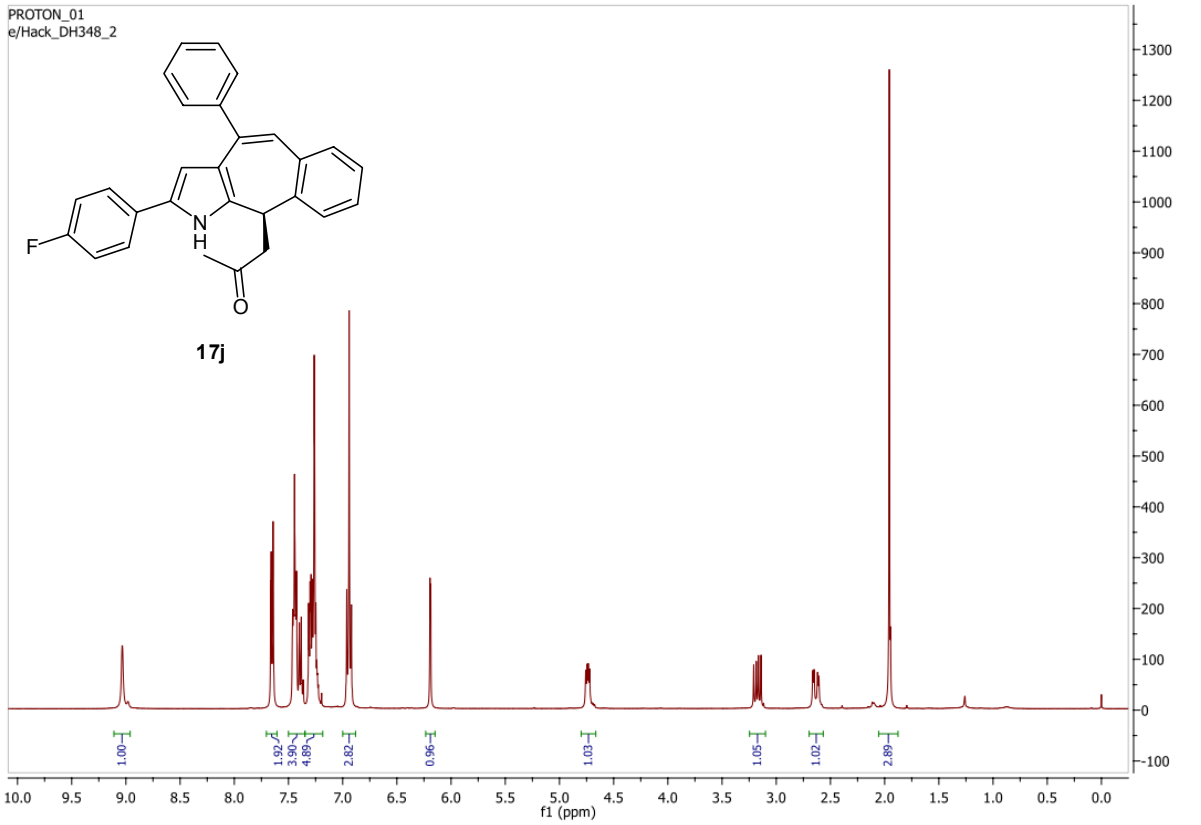

PROTON_01
e/Hack_DH346_2
Me
N
H
O
f1 (ppm)

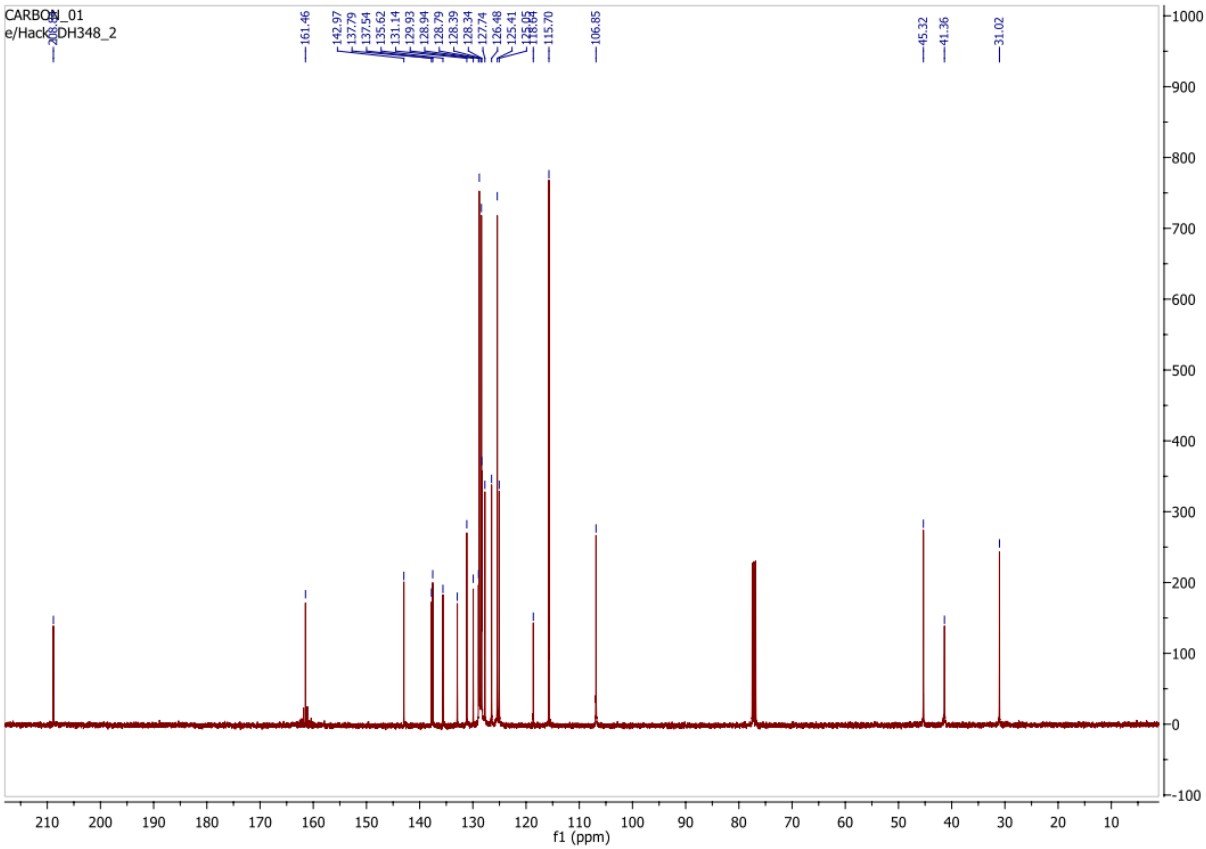
17h

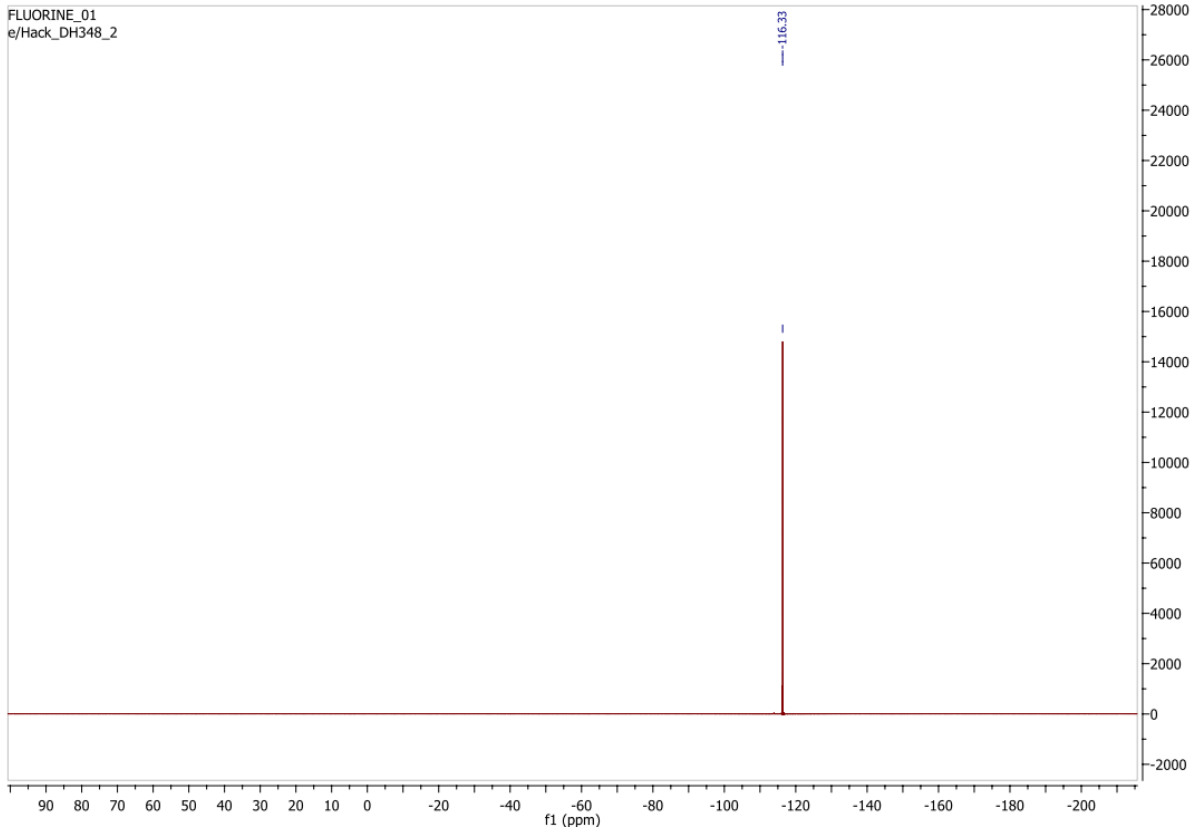

CARBON_01
e/Hack_DH346_2
143.09
137.89
137.57
135.98
135.68
132.58
131.11
130.88
129.78
129.59
128.86
128.37
128.32
127.69
126.45
124.99
123.78
118.58
106.55
45.41
41.45
30.99
21.24
f1 (ppm)

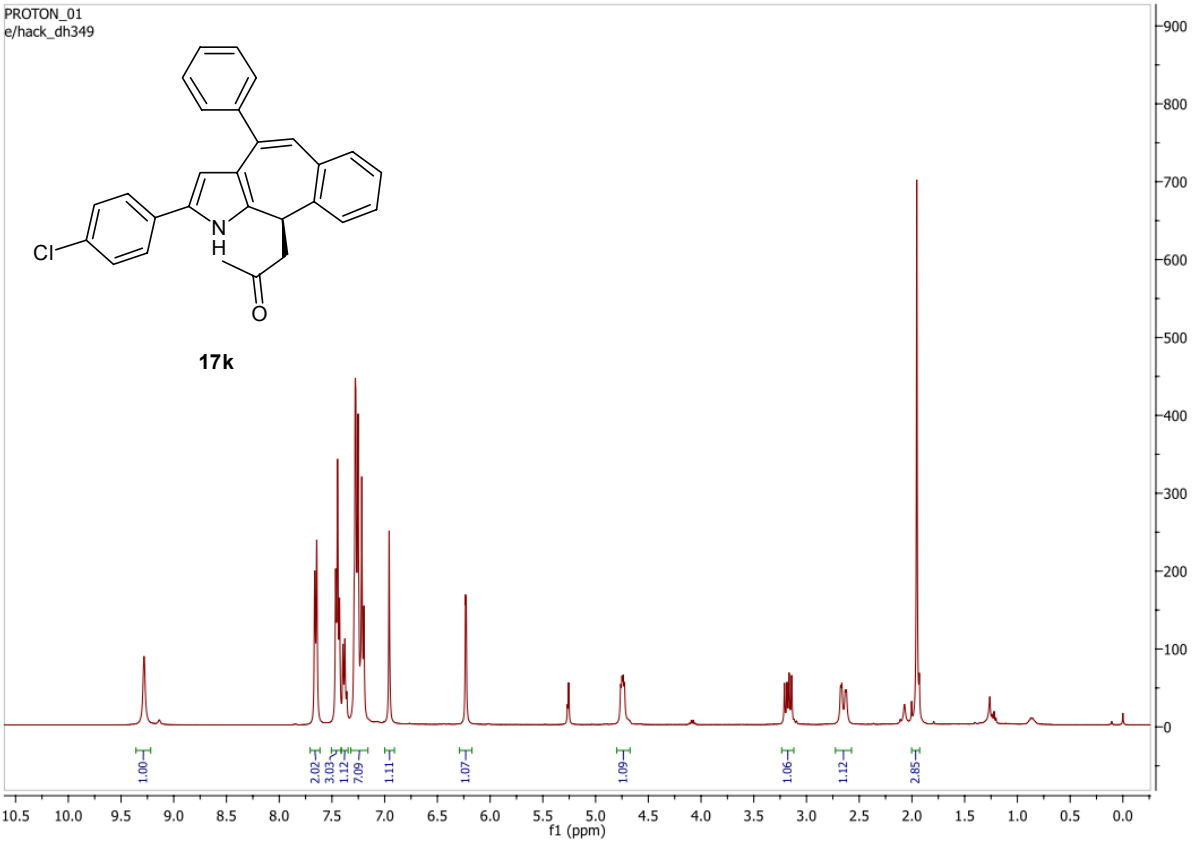

PROTON_01
e/hack_dh347
MeO
N
H
O
17i
1.00
2.15
10.08
1.11
2.14
1.00
1.12
3.26
1.21
1.12
3.03
f1 (ppm)

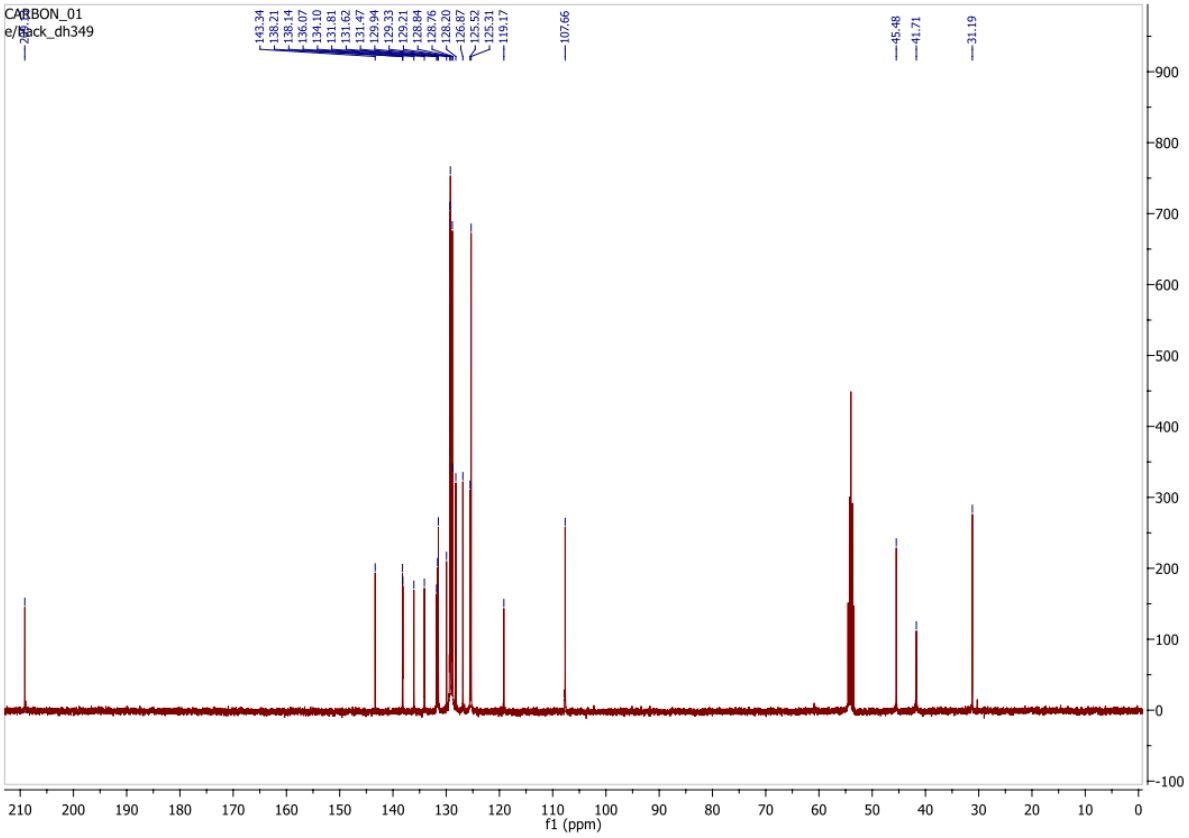

CARBON_01
e/hack_dh347
158.87
143.47
138.31
138.26
131.35
130.97
129.22
128.74
128.63
128.07
126.72
125.92
125.46
114.79
106.09
55.81
45.50
41.71
31.04
f1 (ppm)

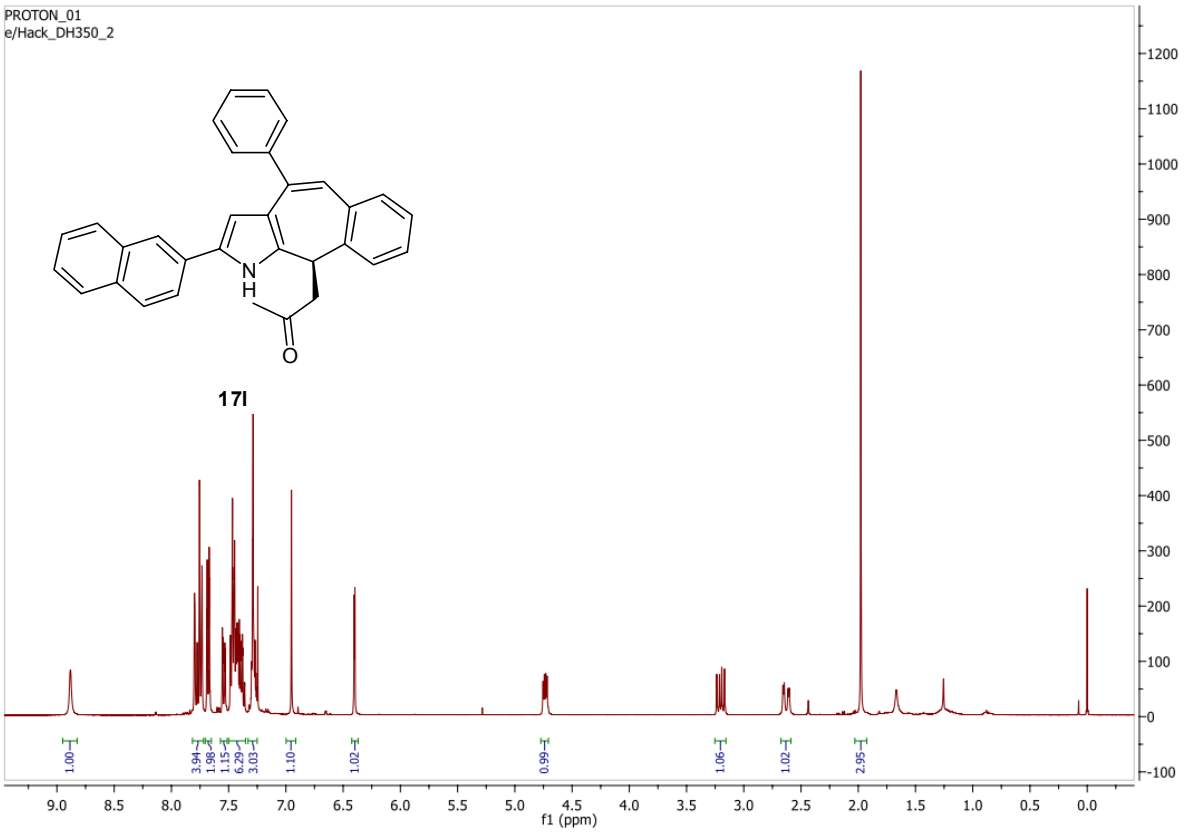

PROTON_01
e/Hack_DH348_2
F
N
H
O
17j
1.00
1.92
3.90
4.89
2.82
0.96
1.03
1.05
1.02
2.89
f1 (ppm)

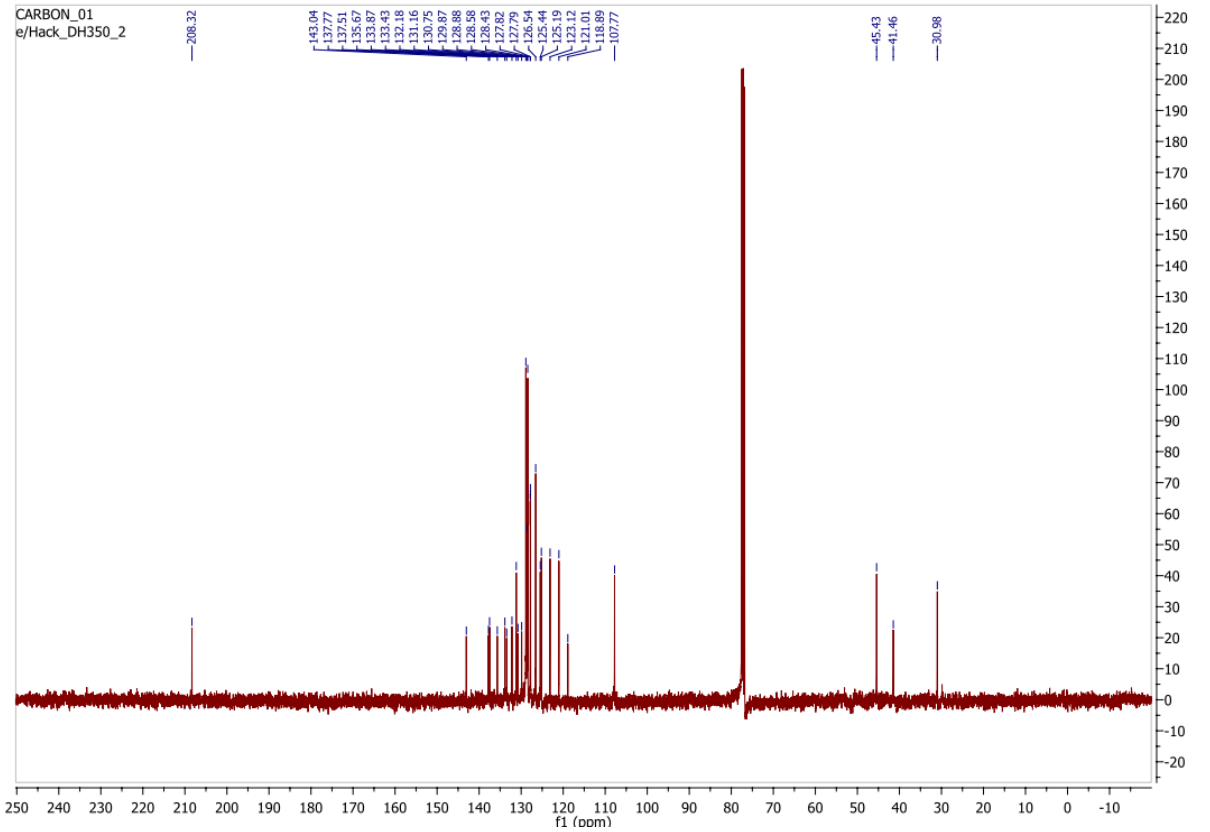

CARBON_01
e/Hack_DH348_2
161.46
142.97
137.79
137.54
135.62
131.14
129.93
128.94
128.79
128.39
128.34
127.74
126.48
125.41
115.70
106.85
45.32
41.36
31.02
f1 (ppm)

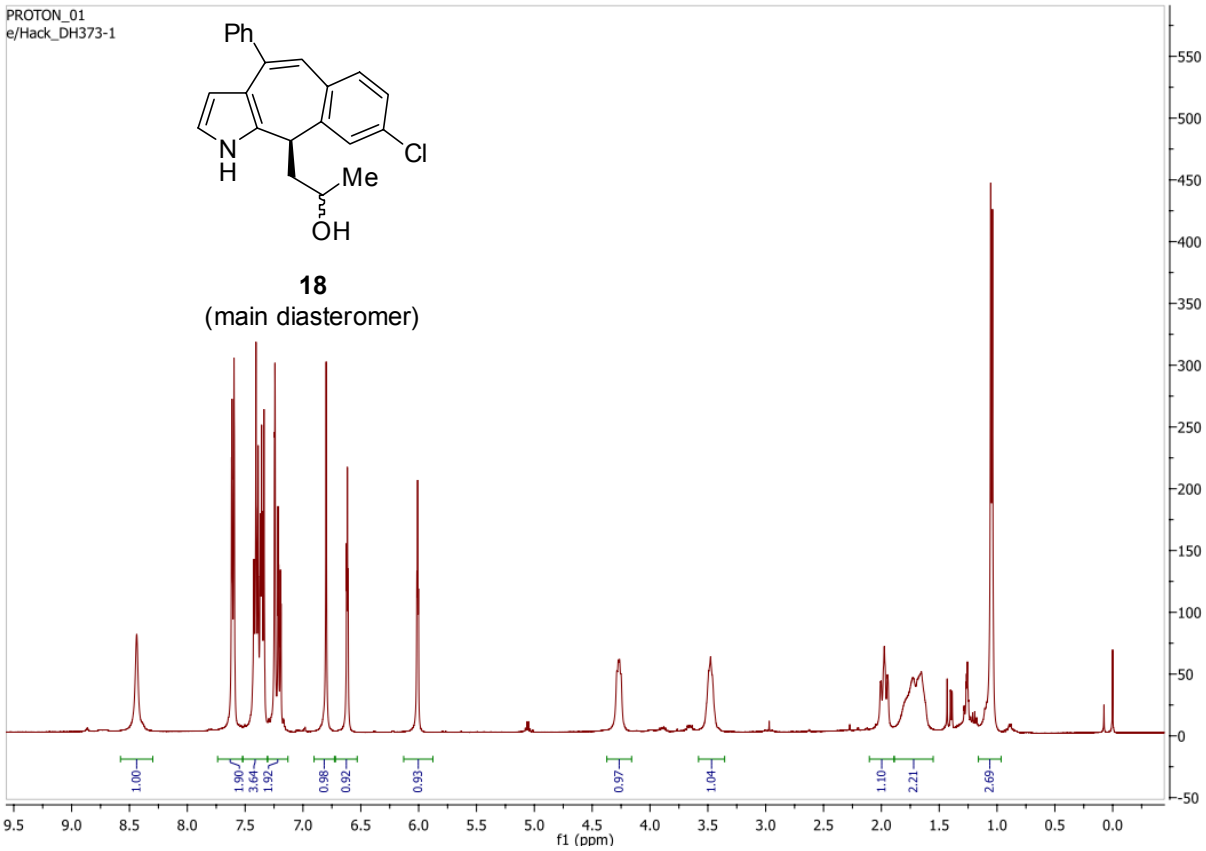

FLUORINE_01
e/Hack_DH348_2
-116.33
f1 (ppm)

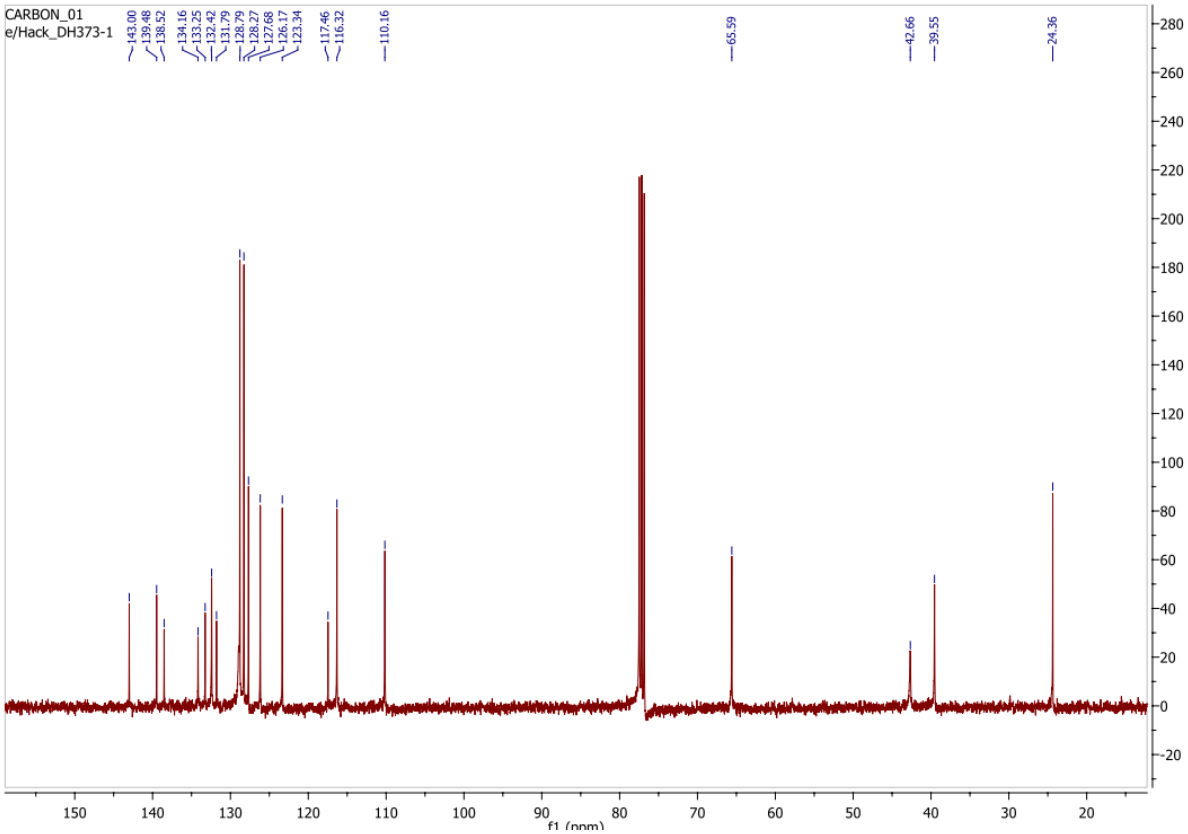

PROTON_01
e/hack_dh349
Cl
N
H
O
17k
1.00
2.02
3.03
1.12
7.09
1.11
1.07
1.09
1.06
1.12
2.85
f1 (ppm)


CARBON_01
e/Hack_dh349
143.34
138.21
138.14
136.07
134.10
131.81
131.62
131.47
129.94
129.33
129.21
128.84
128.76
128.20
126.87
125.52
125.31
119.17
107.66
45.48
41.71
31.19
f1 (ppm)


PROTON_01
e/Hack_DH350_2
N
H
O
17l
1.00
3.94
1.98
1.15
6.29
3.03
1.10
1.02
0.99
1.06
1.02
2.95
f1 (ppm)


CARBON_01
e/Hack_DH350_2
208.32
143.04
137.77
137.51
135.67
133.87
133.43
132.18
131.16
130.75
129.87
128.88
128.58
128.43
127.82
127.79
126.54
125.44
125.19
123.12
121.01
118.89
107.77
45.43
41.46
30.98
f1 (ppm)


PROTON_01
e/Hack_DH373-1
Ph
N
H
Cl
Me
OH
18
(main diasteromer)
1.00
1.90
3.64
1.92
0.98
0.92
0.93
0.97
1.04
1.10
2.21
2.69
f1 (ppm)


CARBON_01
e/Hack_DH373-1
143.00
139.48
138.52
134.16
133.25
132.42
131.79
128.79
128.27
127.68
126.17
123.34
117.46
116.32
110.16
65.59
42.66
39.55
24.36
f1 (ppm)