Electronic Supplementary Material (ESI) for ChemComm.

Supporting Information

A Fast, Efficient and Simple Method for the Synthesis of Cyclic Alkenyl Fluorides by a Fluorinative Carbocyclization Reaction

Table of Contents:

1. General

^{1}H NMR spectra were recorded on a Bruker AV-600 (600 MHz), Bruker AV-400 (400 MHz), Bruker AV-300 (300 MHz) or Bruker DPX-300 (300 MHz). Chemical shifts are reported in ppm from tetramethylsilane with the residual solvent resonance as the internal standard ($CHCl_3$: δ 7.26). Data are reported as follows: chemical shift, multiplicity (s: singlet, d: doublet, dd: double doublet, ddd: double doublet of doublets, ddt: double doublet of triplets, t: triplet, td: triplet of doublets, tqd: triplet quartet of doublet, q: quartet, qd: quartet of doublets, br: broad, m: multiplet, app: apparent), coupling constants (*J* in Hz), integration and assignment. ^{13}C NMR spectra were recorded on a Bruker AV-600 (150 MHz), Bruker AV-400 (100 MHz), Bruker AV-300 (75 MHz) or Bruker DPX-300 (75 MHz) with complete proton decoupling. Chemical shifts are reported in ppm from tetramethylsilane with the solvent resonance as internal standard ($CDCl_3$: δ 76.95). ^{19}F NMR spectra were recorded on a Bruker AV-300 (282 MHz) or Bruker DPX-300 (282 MHz). Chemical shifts are reported in ppm from tetramethylsilane. Bi-dimensional NMR experiments (COSY, HSQCED, HMBC and NOESY) were recorded on a Bruker AV-600 (600 MHz), Bruker AV-400 (400 MHz), Bruker AV-300 (300 MHz) or Bruker DPX-300 (300 MHz). High-resolution mass spectrometry was carried out on a Finnigan-Mat 95 spectrometer.

All reactions were conducted in dried glassware under an inert atmosphere of argon and magnetic stirring. Hexane was dried and stored under a Nitrogen atmosphere using a PureSolv^{TM}-400-7 system before use. Tetrafluoroboric acid diethyl ether complex was used as received from Sigma-Aldrich.

Unless specified, all products were prepared using conventional procedures found in the literature.

2. Procedure for the synthesis of cyclohexenyl fluoride derivatives 4 and 7

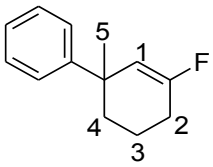
To a solution of the corresponding alkynol **1**, enyne **5** or dienyne **6** (0.3 mmol) in dry hexane (3 mL) tetrafluoroboric acid diethyl ether complex (0.3 mmol, 41 µL, 1 equiv.) was dropwise added under an Argon atmosphere. The reaction was then gently stirred at room temperature for 20 min (12 h for alkynols **1h**, **1i** and **1j** and 2 h for enynes **5a** and **5b**). After this time the mixture was diluted with hexane (5 ml), filtered and washed with hexane (30 mL). Volatile components were removed under reduced pressure. The crude was purified by flash column chromatography (hexane) to give cyclohexenyl fluorides **4** and **7** (in most cases, crude products were obtained in analytically pure form).

3. Procedure for the gram-scale synthesis of cyclohexenyl fluoride derivatives 4a

Tetrafluoroboric acid diethyl ether complex (15 mmol, 2.04 mL, 1 equiv.) was added dropwise to a solution of the alkynol **1a** (2.82 g, 15 mmol) in dry hexane (30 mL) under an argon atmosphere. The reaction was then gently stirred at room temperature for the stated time. Then, the mixture was diluted with hexane (10 mL), filtered and washed with hexane (50 mL). Volatile components were removed under reduced pressure. Cyclohexenyl fluoride **4a** was thus obtained in analytically pure form (2.60 g, 90 %).

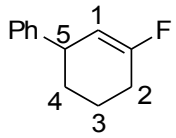
4. Characterization data for compounds 4 and 7

5-Fluoro-1-methyl-1,2,3,4-tetrahydro-1,1'-biphenyl (4a)



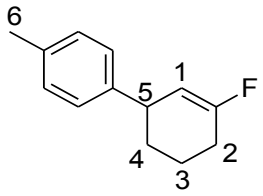
Colorless oil. R_f 0.45 (hexane). ^{1}H-NMR (300 MHz, $CDCl_3$) δ = 7.45–7.21 (m, 5H; Ar-H), 5.32 (dtd, *J* = 18.3, 1.5, 0.8 Hz, 1H; H_1), 2.27–2.19 (m, 2H; H_2), 1.90–1.48 (m, 4H; H_3, H_4), 1.44 (s, 3H; H_5). ^{13}C-NMR (75 MHz, $CDCl_3$) δ = 159.9 (d, *J* = 255.7 Hz), 148.9, 128.0, 126.4, 125.8, 110.4 (d, *J* = 13.8 Hz), 39.6 (d, *J* = 8.4 Hz), 38.4 (d, *J* = 2.0 Hz), 29.7, 25.4 (d, *J* = 23.4 Hz), 19.0 (d, *J* = 9.2 Hz). ^{19}F-NMR (282 MHz, $CDCl_3$) δ –102.4. HRMS calcd for $C_{13}H_{15}F$ $[M]^+$ 190.1153, found 190.1158.

5-Fluoro-1,2,3,4-tetrahydro-1,1'-biphenyl (4b)



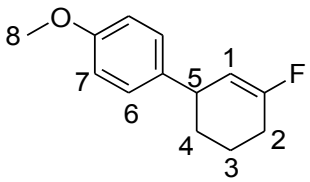
Colorless oil. R_f 0.55 (hexane). ^{1}H-NMR (300 MHz, $CDCl_3$) δ = 7.41–7.24 (m, 5H; Ar-*H*), 5.41–5.31 (m, 1H; H_1), 3.58 (ddt, *J* = 10.8, 5.5, 2.9 Hz, 1H; H_5), 2.40-2.22 (m, 2H; H_2), 2.09 – 1.70 (m, 3H; H_3, H_{4a}), 1.62–1.47 (m, 1H; H_{4b}). ^{13}C-NMR (75 MHz, $CDCl_3$) δ = 160.9 (d, *J* = 256.3 Hz), 145.5, 128.3, 127.5, 126.2, 105.4 (d, *J* = 15.6 Hz), 40.2 (d, *J* = 8.1 Hz), 32.1 (d, *J* = 1.7 Hz), 25.4 (d, *J* = 23.0), 20.8 (d, *J* = 9.2 Hz). ^{19}F-NMR (282 MHz, $CDCl_3$) δ = –100.5. HRMS calcd for $C_{12}H_{13}F$ $[M]^+$ 176.0996, found 176.1001.

5-Fluoro-4'-methyl-1,2,3,4-tetrahydro-1,1'-biphenyl (4c)



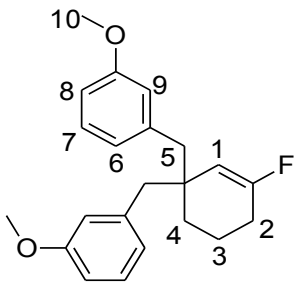
Colorless oil. R_f 0.55 (hexane). ^{1}H-NMR (300 MHz, $CDCl_3$) δ = 7.19–7.08 (m, 4H; Ar-*H*), 5.31 (ddt, *J* = 17.7, 2.9, 1.4 Hz, 1H; H_1), 3.58 (ddt, *J* = 10.8, 5.5, 2.9 Hz, 1H; H_5), 2.37 (s, 3H; H_6), 2.35 - 2.18 (m, 2H; H_2), 2.05–1.66 (m, 3H; H_3, H_{4a}), 1.57–1.43 (m, 1H; H_{4b}). ^{13}C-NMR (75 MHz, $CDCl_3$) δ = 160.8 (d, *J* = 256.1 Hz), 142.5, 135.8, 128.9, 127.4, 105.6 (d, *J* = 14.9 Hz), 39.7 (d, *J* = 8.1 Hz), 32.1 (d, *J* = 1.9 Hz), 25.4 (d, *J* = 23.0), 20.9, 20.8 (d, *J* = 9.2 Hz). ^{19}F-NMR (282 MHz, $CDCl_3$) δ = –100.7. HRMS calcd for $C_{13}H_{15}F$ $[M]^+$ 190.1153, found 190.1157.

5-Fluoro-4'-methoxy-1,2,3,4-tetrahydro-1,1'-biphenyl (4d)



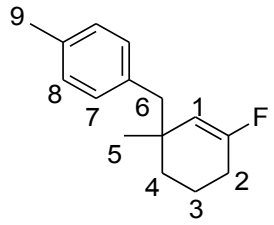
Colorless oil. R_f 0.30 (hexane). ^{1}H-NMR (300 MHz, $CDCl_3$) δ = 7.15 (d, *J* = 8.6 Hz, 2H; H_6), 6.87 (d, *J* = 8.6 Hz, 2H; H_7), 5.33–5.23 (m, 1H; H_1), 3.81 (s, 3H; H_8), 3.49 (ddt, *J* = 10.9, 5.4, 2.8 Hz, 1H; H_5), 2.35-2.20 (m, 2H; H_2), 2.01–1.63 (m, 3H; H_3, H_{4a}), 1.52–1.35 (m, 1H; H_{4b}). ^{13}C-NMR (75 MHz, $CDCl_3$) δ = 161.1 (d, *J* = 253.0 Hz), 158.2, 128.5, 127.6, 113.7, 105.7 (d, *J* = 14.1 Hz), 55.5, 39.4 (d, *J* = 8.3 Hz), 32.2, 25.5 (d, *J* = 23.0 Hz), 20.8 (d, *J* = 9.2 Hz). ^{19}F-NMR (282 MHz, $CDCl_3$) δ = –100.7. HRMS calcd for $C_{13}H_{15}FO$ $[M]^+$ 206.1102, found 206.1107.

3,3'-[(3-Fluorocyclohex-2-ene-1,1-diyl)bis(methylene)]bis(methoxybenzene) (4e)



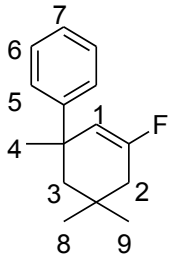
Colorless oil. R_f 0.35 (hexane:diethyl ether 10:1). ^{1}H-NMR (400 MHz, $CDCl_3$) δ = 7.18 (t, *J* = 7.9 Hz, 2H; H_7), 6.77 (dd, *J* = 7.9, 2.3 Hz, 2H; H_6), 6.73 (d, *J* = 7.9 Hz, 2H; H_8), 6.68 (br s, 2H; H_9), 5.13–5.03 (m, 1H; H_1), 3.79 (s, 6H; H_{10}), 2.69 (d, *J* = 13.2 Hz, 1H; H_{5a}), 2.63 (d, *J* = 13.2 Hz, 1H; H_{5b}), 1.95 (t, *J* = 6.1 Hz, 2H; H_2), 1.64–1.38 (m, 4H; H_3, H_4). ^{13}C-NMR (100 MHz, $CDCl_3$) δ = 159.7 (d, *J* = 257.4 Hz), 159.0, 139.8, 128.7, 123.3, 116.5, 111.4, 109.5 (d, *J* = 13.9 Hz), 55.1, 47.4, 40.2, 31.0, 25.0 (d, *J* = 23.4 Hz), 18.7 (d, *J* = 9.1 Hz). ^{19}F-NMR (282 MHz, $CDCl_3$) δ = –100.7. HRMS calcd for $C_{22}H_{25}FO_2$ $[M]^+$ 340.1834, found 340.1835.

1-[(1-Ethyl-3-fluorocyclohex-2-en-1-yl)methyl]-4-methylbenzene (4f)



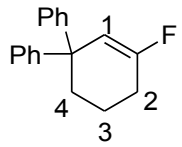
Colorless oil. R_f 0.32 (hexane). ^{1}H-NMR (400 MHz, $CDCl_3$) δ = 7.08 (d, *J* = 8.2 Hz, 2H; H_7), 7.02 (d, *J* = 8.2 Hz, 2H; H_8), 5.00 (d, *J* = 18.7 Hz, 1H; H_1), 2.62 (s, 2H; H_6), 2.33 (s, 3H; H_9), 2.12 (t; *J* = 6.4 Hz, 2H; H_2), 1.81-1.70 (m, 2H; H_3), 1.57–1.45 (m, 1H; H_{4a}), 1.35–1.26 (m, 1H; H_{4b}), 0.97 (s, 3H; H_5). ^{13}C-NMR (100 MHz, $CDCl_3$) δ = 158.9 (d, *J* = 253.2 Hz), 135.5, 135.2, 130.4, 128.4, 111.0 (d, *J* = 12.5 Hz), 48.3, 35.5 (d, *J* = 7.4 Hz), 34.5, 27.3, 25.4 (d, *J* = 23.5 Hz), 20.9, 18.9 (d, *J* = 8.9 Hz). ^{19}F-NMR (282 MHz, $CDCl_3$) δ = –103.0. HRMS calcd for $C_{15}H_{19}F$ $[M]^+$ 218.1466, found 218.1466.

5-Fluoro-1,3,3-trimethyl-1,2,3,4-tetrahydro-1,1'-biphenyl (4g)



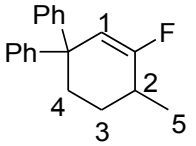
Colorless oil. R_f 0.44 (hexane). ^{1}H-NMR (300 MHz, $CDCl_3$) δ = 7.41-7.36 (m, 2H; H_5), 7.33-7.26 (m, 2H; H_6), 7.18 (tt, *J* = 7.2, 1.4 Hz, 1H; H_7), 5.55–5.45 (m, 1H; H_1), 2.12 (dd, *J* = 17.0, 1.6 Hz, 1H; H_{2a}), 2.02–1.9 (m, 2H; H_{2b}, H_{3a}), 1.61 (d, *J* = 13.8 Hz, 1H; H_{3b}), 1.38 (d, *J* = 1.0 Hz, 3H, H_4), 1.04 (d, *J* = 0.6 Hz, 3H, H_8), 0.54 (s, 3H, H_9). ^{13}C-NMR (75 MHz, $CDCl_3$) δ = 158.9 (d, *J* = 255.1 Hz), 149.9, 128.0, 126.0, 125.6, 108.7 (d, *J* = 14.7 Hz), 50.7 (d, *J* = 2.5 Hz), 39.7 (d, *J* = 9.4 Hz), 39.3 (d, *J* = 19.8 Hz), 33.4 (d, *J* = 2.0 Hz), 32.1 (d, *J* = 8.4 Hz), 31.4, 28.1. ^{19}F-NMR (282 MHz, $CDCl_3$) δ = –102.6. HRMS calcd for $C_{14}H_{16}F$ $[M\text{-}15]^+$ 203.1231, found 203.1236.

5'-Fluoro-3',4'-dihydro-2'H-1,1':1',1''-terphenyl (4h)



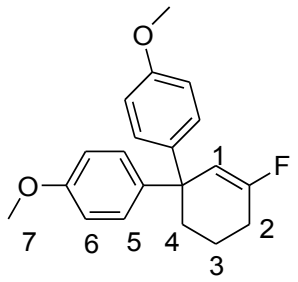
Yellow oil. R_f 0.22 (hexane). ^{1}H-NMR (300 MHz, $CDCl_3$) δ = 7.38–7.21 (m, 10H; Ar-*H*), 5.79 (d, *J* = 18.4 Hz, 1H; H_1), 2.36-2.28 (m, 4H; H_2, H_4), 1.83–1.73 (m, 2H; H_3). ^{13}C-NMR (75 MHz, $CDCl_3$) δ = 160.2 (d, *J* = 257.3 Hz), 148.4, 128.0, 127.5, 125.9, 110.6 (d, *J* = 15.9 Hz), 48.1 (d, *J* = 8.4 Hz), 35.7 (d, *J* = 1.5 Hz), 25.4 (d, *J* = 23.0 Hz), 18.9 (d, *J* = 9.5 Hz). ^{19}F-NMR (282 MHz, $CDCl_3$) δ = –100.7. HRMS calcd for $C_{18}H_{17}F$ $[M]^+$ 252.1309, found 252.1307.

5'-Fluoro-4'-methyl-3',4'-dihydro-2'H-1,1':1',1''-terphenyl (4i)



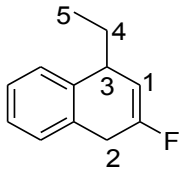
Colorless oil. R_f 0.15 (hexane). ^{1}H-NMR (300 MHz, $CDCl_3$) δ = 7.34-7.09 (m, 10H; Ar-*H*), 5.69 (d, *J* = 18.6 Hz, 1H; H_1), 2.50 (app sextuplet, *J* = 6.6 Hz, 1H; H_2), 2.38–2.19 (m, 2H; H_4), 1.94–1.80 (m, 1H; H_{3a}), 1.46–1.33 (m, 1H; H_{3b}), 1.16 (d, *J* = 6.6 Hz, 3H; H_5). ^{13}C-NMR (75 MHz, $CDCl_3$) δ = 163.8 (d, *J* = 259.8 Hz), 148.5, 143.9, 129.5, 128.3, 128.1, 127.6 (d, *J* = 14.9 Hz), 126.2, 126.0 (d, *J* = 2.7 Hz), 110.3 (d, *J* = 17.3 Hz), 48.7 (d, *J* = 8.3 Hz), 34.0, 30.7 (d, *J* = 22.3 Hz), 27.7 (d, *J* = 7.7 Hz), 17.3. ^{19}F-NMR (282 MHz, $CDCl_3$) δ = –108.7. HRMS calcd for $C_{19}H_{19}F$ $[M]^+$ 266.1466, found 266.1469.

5-Fluoro-4,4'-dimethoxy-3',4'-dihydro-2'*H*-1,1':1',1''-terphenyl (4j)



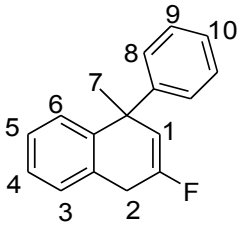
Colorless oil. R_f 0.27 (hexane:diethyl ether 10:1). ^{1}H-NMR (300 MHz, $CDCl_3$) δ = 7.19 (d, *J* = 8.9 Hz, 2H; H_5), 6.87 (d, *J* = 8.9 Hz, 2H; H_6), 5.71 (dt, *J* = 18.4, 1.5 Hz, 1H; H_1), 3.86 (s, 6H; H_7), 2.31 (tt, *J* = 6.3, 1.5 Hz, 2H; H_2), 2.27–2.20 (m, 2H; H_4), 1.79–1.69 (m, 2H; H_3). ^{13}C-NMR (75 MHz, $CDCl_3$) δ = 159.9 (d, *J* = 257.0 Hz), 157.6, 140.8 (d, *J* = 1.9 Hz), 128.5, 113.3, 110.9 (d, *J* = 15.3 Hz), 55.1, 46.8 (d, *J* = 8.4 Hz), 35.9 (d, *J*= 2.0 Hz), 25.4 (d, *J* = 23.0 Hz), 18.9 (d, *J* = 9.5 Hz). ^{19}F-NMR (282 MHz, $CDCl_3$) δ = –101.3. HRMS calcd for $C_{20}H_{21}FO_2$ $[M]^+$ 312.1521, found 312.1524.

1-Ethyl-3-fluoro-1,4-dihydronaphthalene (4k)



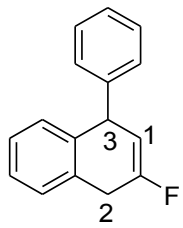
Colorless oil. R_f 0.51 (hexane). ^{1}H-NMR (600 MHz, $CDCl_3$) δ = 7.31-7.11 (m, 4H; Ar-*H*), 5,44–5.39 (m, 1H; H_1), 3.73–3.57 (m, 2H; $H_{2a,}$ H_3), 3.44 (app dt, *J* = 7.8, 3.5 Hz, 1H; H_{2b}), 1.86–1.69 (m, 2H; H_4), 0.82 (t, *J* = 7.4 Hz, 3H; H_5). ^{13}C-NMR (75 MHz, $CDCl_3$) δ = 157.0 (d, *J* = 251.7 Hz), 137.2, 132.6 (d, *J* = 11.4 Hz), 128.4, 127.8, 126.5, 126.0, 103.5 (d, *J* = 13.9 Hz), 40.3 (d, *J* = 7.5 Hz), 31.2, 30.2 (d, *J* = 27.3 Hz), 9.7. ^{19}F-NMR (282 MHz, $CDCl_3$) δ = –106.5. HRMS calcd for $C_{12}H_{13}F$ $[M]^+$ 176.0996, found 176.1000.

3-Fluoro-1-methyl-1-phenyl-1,4-dihydronaphthalene (4l)



Yellow oil. R_f 0.48 (hexane). ^{1}H-NMR (300 MHz, $CDCl_3$) δ = 7.33-7.04 (m, 8H; H_4, H_5, H_6, H_8, H_9, H_{10}), 6.95 (d, *J* = 7.9 Hz, 1H; H_3), 5.17 (dt, *J* = 18.7, 1.6 Hz, 1H; H_1), 3.41 (s, 2H; H_2), 1.34 (d, *J* = 1.6 Hz, 3H; H_7). ^{13}C-NMR (75 MHz, $CDCl_3$) δ = 155.7 (d, *J* = 253.5 Hz), 148.9, 142.3, 130.9 (d, *J* = 11.8 Hz), 128.8, 128.6, 128.4, 128.3, 127.2, 126.9, 126.2, 111.6 (d, *J* = 14.3 Hz), 45.6, 30.0 (d, *J* = 27.0 Hz), 29.9 (d, *J* = 2.1 Hz). ^{19}F-NMR (282 MHz, $CDCl_3$) δ = –109.7. HRMS calcd for $C_{15}H_{17}F$ $[M]^+$ 238.1153, found 238.1163.

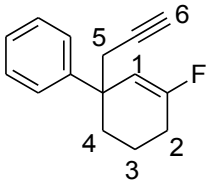
3-Fluoro-1-phenyl-1,4-dihydronaphthalene (4m)



White solid. mp 55-56 ºC. R_f 0.5 (hexane/ethyl acetate 40:1). ^{1}H NMR ($CDCl_3$, 300 MHz) *δ* ppm = 7.38-7.09 (m, 9H; Ar-H), 5.65–5.45 (m, 1H, H_1), 4.86 (app q, *J* = 4.7 Hz, 1H, H_3), 3.86 (ddd, *J* = 21.0, 5.2, 2.0, 1H, H_{2a}), 3.74–3.64 (m, 1H, H_{2b}). ^{13}C NMR ($CDCl_3$, 75 MHz) *δ* ppm = 157.4 (d, *J* = 253.5 Hz), 146.3 (*J* = 1.98 Hz), 137.1 (d, *J* = 2.43 Hz), 132.2 (d, *J* = 11.7 Hz), 130.2, 129.3,

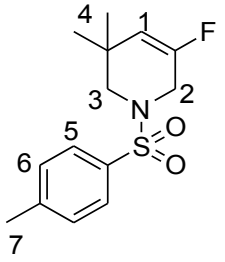
129.2, 128.9, 127.4, 127.3, 127.0, 105.8 (d, *J* = 15.5), 46.8 (d, *J* = 8.2), 30.7 (d, *J* = 26.9). ^{19}F NMR ($CDCl_3$, 282 MHz) δ ppm = –106.7. HRMS calcd for $C_{16}H_{13}F$ $[M]^+$ 224.0996, found 224.1003.

5-Fluoro-1-(prop-2-yn-1-yl)-1,2,3,4-tetrahydro-1,1'-biphenyl (4n)



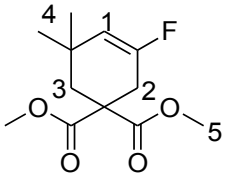
Colorless oil. R_f 0.5 (hexane/ethyl acetate 40:1). ^{1}H NMR ($CDCl_3$, 300 MHz) δ ppm = 7.46-7.27 (m, 5H, Ar-H), 5.66 (app d, *J* = 18.1 Hz 1H, H_1), 2.77 (ddd, *J* = 16.6, 2.6, 1.3, 1H, H_{5a}), 2.65 (ddd, *J* = 16.6, 2.6, 0.7, H_{5b}), 2.39-2.20 (m, 2H, H_2), 2.08-1.99 (m, 1H, H_{4a}), 1.96 (t, *J* = 2.6 Hz, 1H, H_6), 1.93 - 1.84 (m, 1H, H_{4b}), 1.83-1.71 (m, 1H, H_{3a}), 1.61-1.48 (m, 1H, H_{3b}). ^{13}C NMR ($CDCl_3$, 75 MHz) δ ppm = 161.1 (d, *J* = 257.5), 146.1, 128.2, 126.9, 126.4, 108.1 (d, *J* = 15.9 Hz), 81.3, 70.6, 43.2 (d, *J* = 8.6 Hz), 35.9, 32.7, 25.6 (d, *J* =23.1), 18.8 (d, *J* = 9.1). ^{19}F NMR ($CDCl_3$, 282 MHz) δ ppm = –100.1. HRMS calcd for $C_{15}H_{15}F$ $[M]^+$ 214.1153, found 214.1157.

5-Fluoro-3,3-dimethyl-1-tosyl-1,2,3,6-tetrahydropyridine (4o)



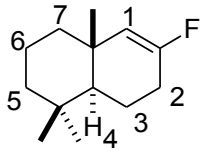
Colorless oil. R_f 0.3 in hexane/ethyl acetate 10:1. ^{1}H NMR ($CDCl_3$, 300 MHz) δ ppm = 7.68 (d, *J* = 8.3 Hz, 2H, H_5), 7.36 (d, *J* = 8.3 Hz, 2H, H_6) 5.11 (app dt, *J* = 16.2, 1.6 Hz, 1H, H_1), 3.57 (d, *J* = 1.6 Hz, 2H, H_2), 2.80 (s, 2H, H_3), 2.45 (s, 3H, H_7), 1.10 (d, *J* = 0.9 Hz, 6H, H_4). ^{13}C NMR ($CDCl_3$, 75 MHz) δ ppm = 154.3 (d, *J* = 254.4 Hz), 144.1, 133.1, 130.0, 127.8, 111.6 (d, *J* = 9.3 Hz), 55.1, 44.0 (d, *J* = 40.7 Hz), 32.9 (d, *J* = 6.8 Hz), 27.1 (d, *J* = 1.9 Hz), 21.7. ^{19}F NMR ($CDCl_3$, 282 MHz) δ ppm = –116.9. HRMS calcd for $C_{16}H_{13}FNO_2S$ $[M]^+$ 283.1037, found 283.1037.

Dimethyl 3-fluoro-5,5-dimethylcyclohex-3-ene-1,1-dicarboxylate (4p)



Colorless oil. R_f 0.3 in hexane/ethyl acetate 10:1. ^{1}H NMR ($CDCl_3$, 300 MHz) δ ppm = 5.03 (app dt, *J* = 17.4, 1.3 Hz, 1H, H_1), 3.73 (s, 6H, H_5), 2.80-2.49 (m, 2H, H_2), 2.08 (s, 2H, H_3), 0.98 (d, *J* = 0.9 Hz, 6H, H_4). ^{13}C NMR ($CDCl_3$, 75 MHz) δ ppm = 171.5, 155.2 (d, *J* = 254.0 Hz), 111.5 (d, *J* = 12.3 Hz), 53.2 (d, *J* = 6.6 Hz), 52.9, 40.9 (d, *J* = 2.0 Hz), 31.4 (d, *J* = 7.9 Hz), 30.6 (d, *J* = *2.2* Hz), 30.6 (*J* = 30.2 Hz). ^{19}F NMR ($CDCl_3$, 282 MHz) δ ppm = –106.6. HRMS calcd for $C_{12}H_{17}FO_4$ $[M]^+$ 244.1111, found 244.1156.

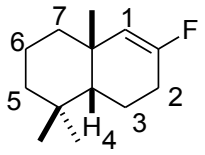
(4a*S,8a*S**)-7-Fluoro-4,4,8a-trimethyl-1,2,3,4,4a,5,6,8a-octahydronaphthalene (7a)**



Colorless oil. R_f 0.89 (hexane). ^{1}H-NMR (300 MHz, $CDCl_3$) δ = 4.95 (dt, *J* = 17.1, 1.5 Hz, 1H; H_1), 2,22 (ddd, *J* = 8.8, 4.6, 1.5 Hz, 2H; H_2), 1.86–1.77 (m, 1H; H_{3a}), 1.68–1.40 (m, 5H; H_{3b}, H_{5a}, H_6, H_{7a}), 1.29–1.18 (m, 2H; H_{5b}, H_{7b}), 1.11 (ddd, *J* = 12.7, 7.8, 2.1 Hz,

1H; H_4), 1.00 (s, 3H, Me), 0.91 (s, 3H, Me), 0.84 (s, 3H, Me). ^{13}C-NMR (75 MHz, $CDCl_3$) δ = 158.3 (d, *J* = 253.9 Hz), 115.8 (d, *J* = 10.7 Hz), 51.0, 42.0, 39.9, 34.4(d, *J* = 8.0 Hz), 33.1, 26.9 (d, *J* = 23.3 Hz), 32.8 22.0 (d, *J* = 2.9 Hz), 21.1, 18.9, 18.6 (d, *J* = 10.1 Hz). ^{19}F-NMR (282 MHz, $CDCl_3$) δ = –109.7. HRMS calcd for $C_{13}H_{12}F$ $[M]^+$ 196.1622, found 196.1621.

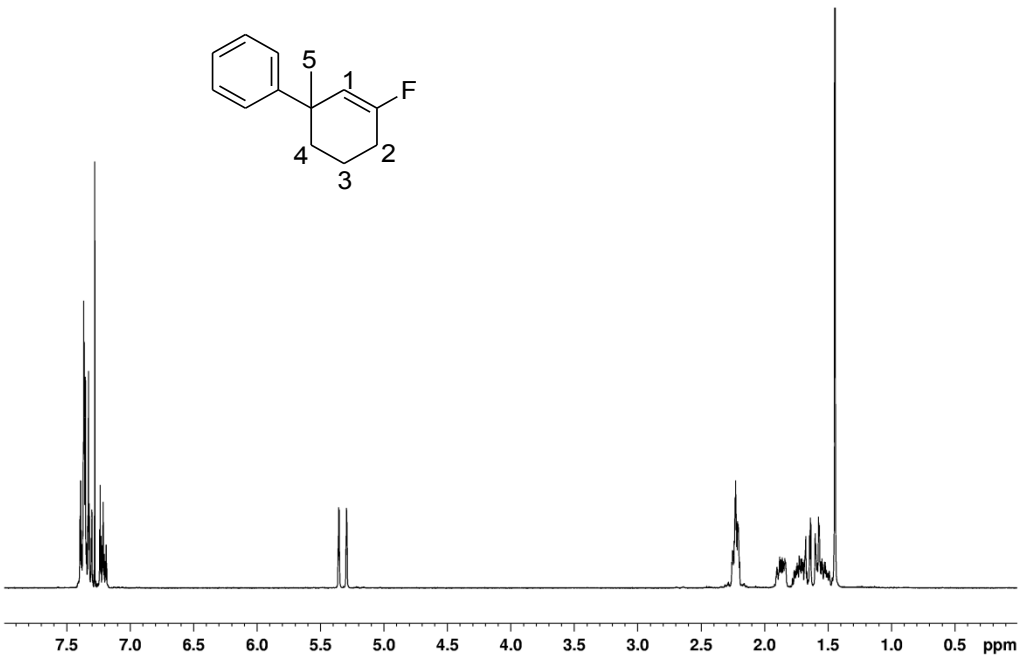
(4a*R,8a*S**)-7-Fluoro-4,4,8a-trimethyl-1,2,3,4,4a,5,6,8a-octahydronaphthalene (*diast*-7a)**



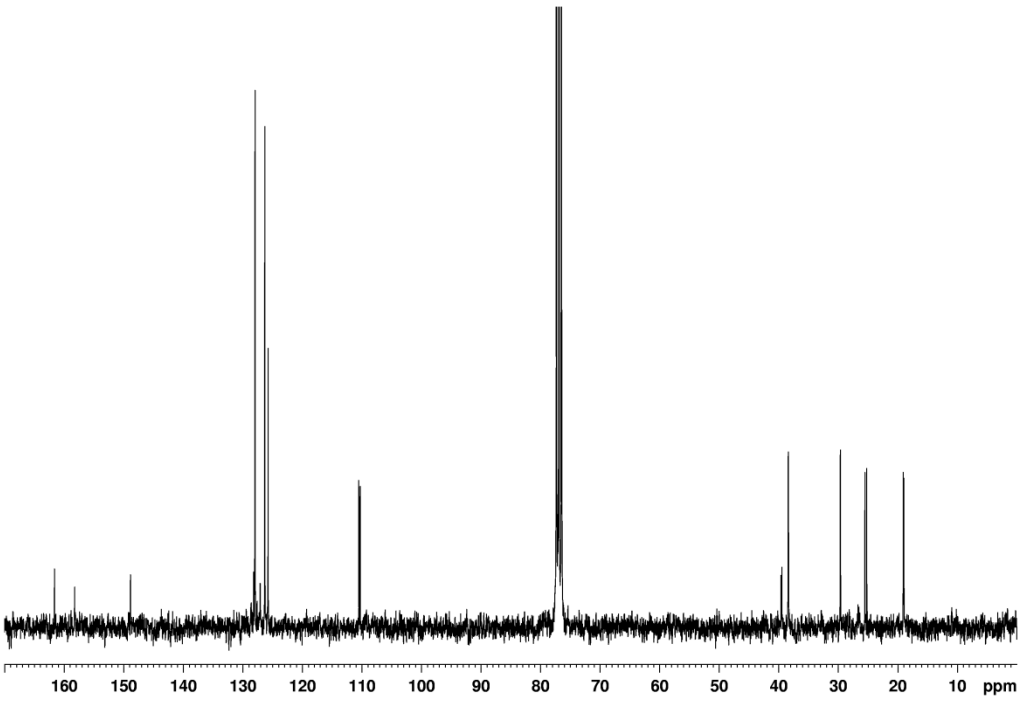
Colorless oil. R_f 0.89 (hexane). ^{1}H NMR ($CDCl_3$, 300 MHz) ***diast*-7a**/**7a** 5:1 *δ* ppm = 4.95 (**7a**, dt, *J* = 17.1, 1.3, 1H), 4.93 (***diast*-7a**, dt, *J* = 18.0, 1.5, 1H, *H1*), 2.40–1.15 (***diast*-7a**, **7a**, m, 11 H), 1.12 (***diast*-7a**, d, *J* = 0.9, 3H, Me), 1.02 (***diast*-7a**, s, 3H, Me), 0.99 (***diast*-7a**, s, 3H, Me), 0.92 (**7a**, s, 3H), 0.85 (**7a**, s, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz) *δ* ppm = 159.8 (***diast*-7a**, d, *J* = 253.9), 159.1 (**7a**, d, *J* = 254.0), 116.5 (**7a**, d, *J* = 10.7), 113.6 (***diast*-7a**, d, *J* = 11.0), 51.7 (**7a**, d, *J* = 1.8), 48.7 (***diast*-7a**), 42.8 (**7a**), 41.6 (***diast*-7a**), 40.7 (***diast*-7a**), 40.7 (**7a**), 36.0 (***diast*-7a**, d, *J* = 6.8), 35.2 (**7a**, d, *J* = 8.0), 34.7 (***diast*-7a**), 33.8 (**7a**), 33.6 (**7a**), 33.5 (***diast*-7a**, d, *J* = 2.0), 33.1 (***diast*-7a**), 27.7 (**7a**, d, *J* = 23.3), 26.8 (***diast*-7a**), 25.0 (***diast*-7a**, d, *J* = 23.0), 22.8 (**7a**, d, *J* = 2.8), 21.9 (**7a**), 20.7 (***diast*-7a**, d, *J* = 2.4), 20.2 (***diast*-7a**), 19.7 (**7a**), 19.4 (**7a**, d, *J* = 10.2). ^{19}F NMR ($CDCl_3$, 282 MHz) *δ* ppm = –105.1 (***diast*-7a**), –109.7 (**7a**). HRMS calcd for $C_{13}H_{12}F$ $[M]^+$ 196.1622, found 196.1634.

9. NMR spectra

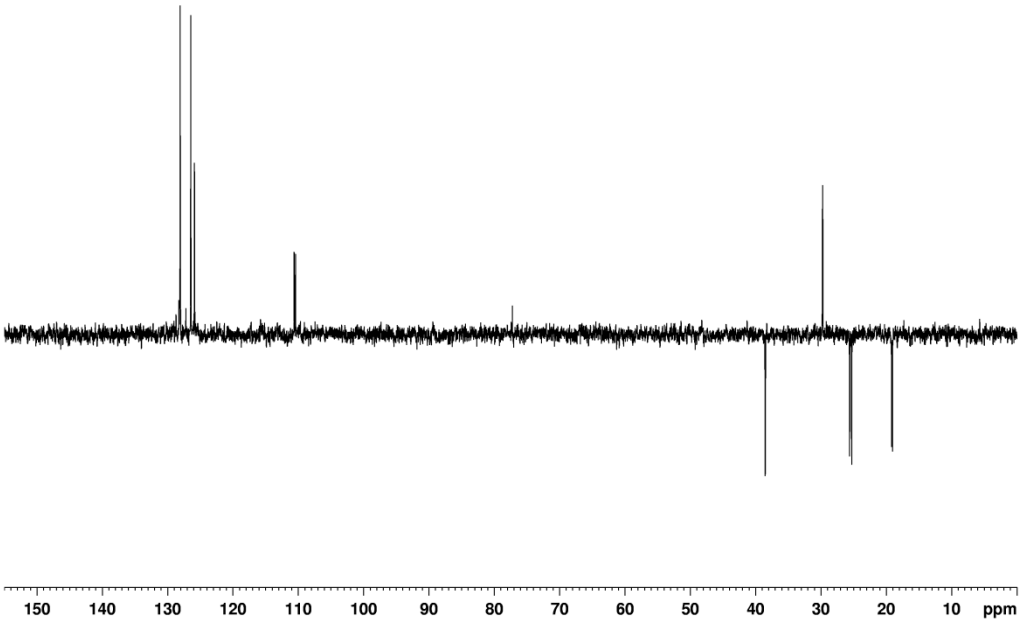
5-Fluoro-1-methyl-1,2,3,4-tetrahydro-1,1'-biphenyl (4a)



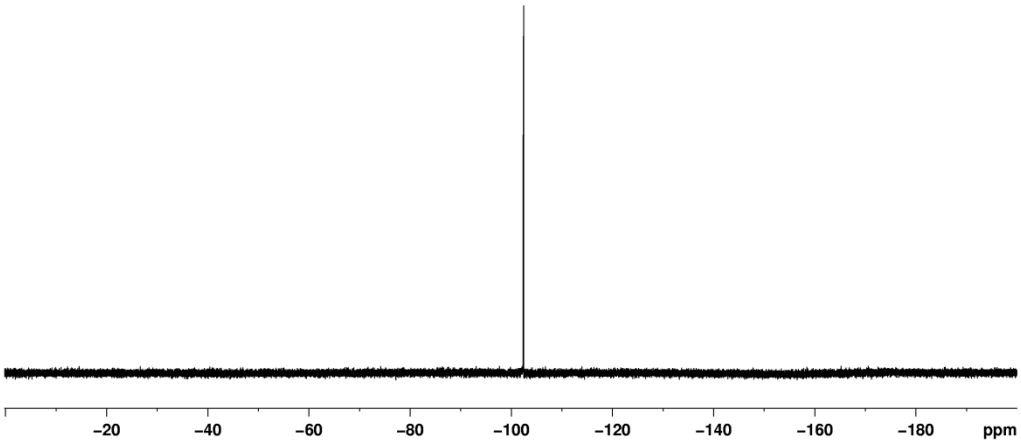
^{1}H NMR



^{13}C NMR

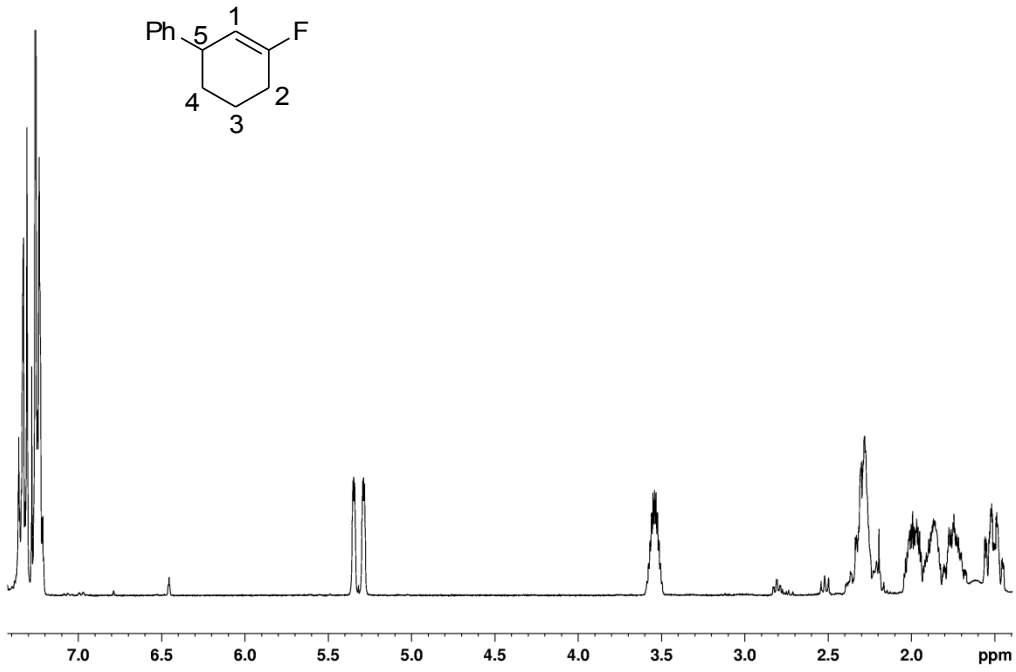


DEPT-135

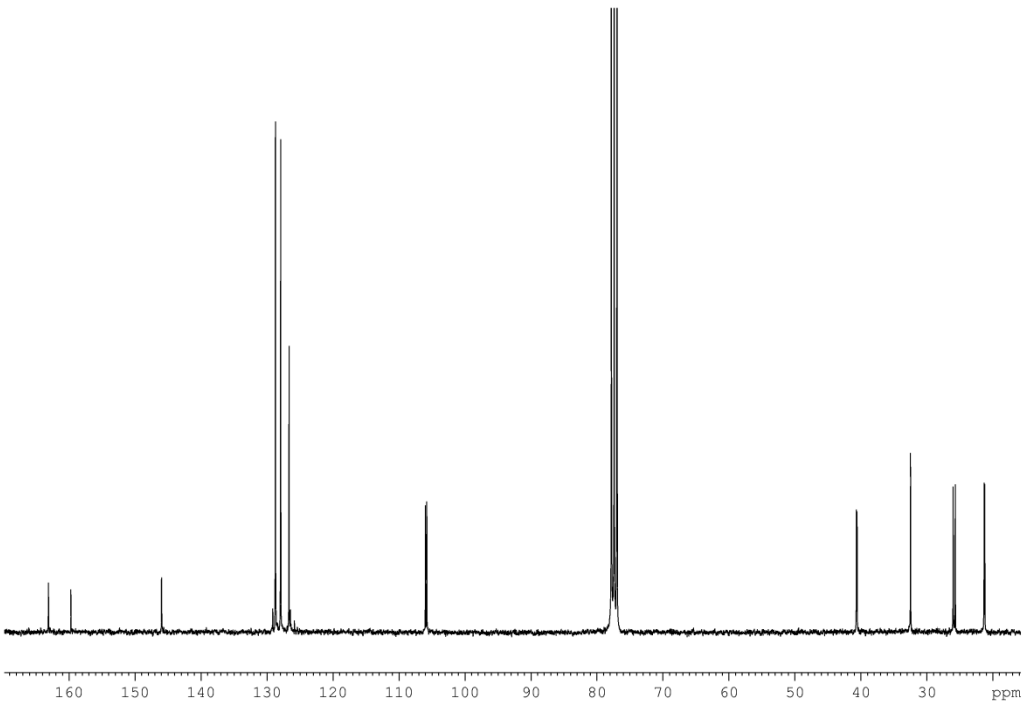


^{19}F NMR

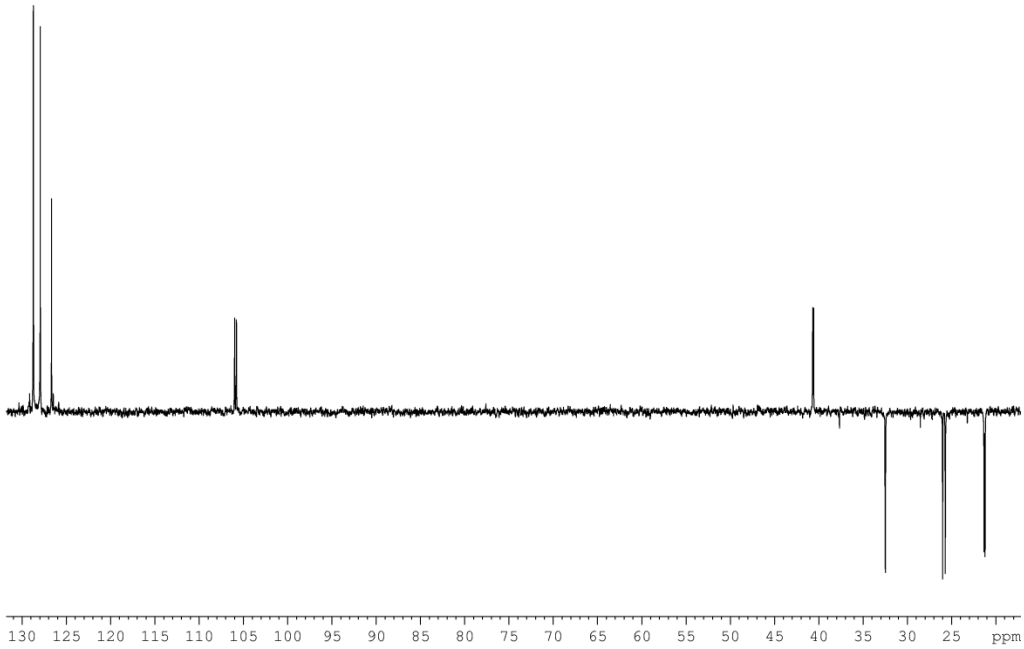
5-Fluoro-1,2,3,4-tetrahydro-1,1'-biphenyl (4b)



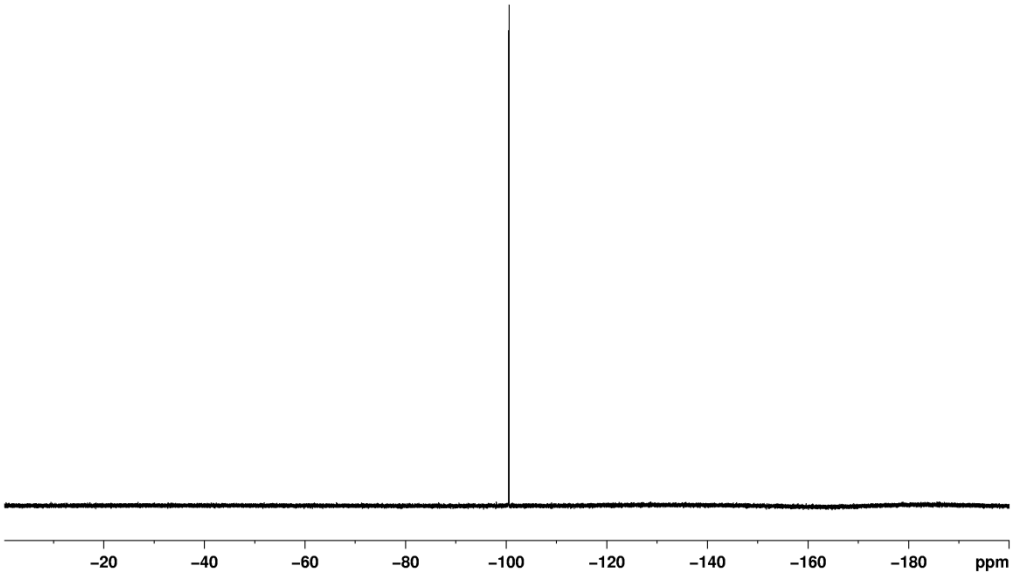
^{1}H NMR



^{13}C NMR

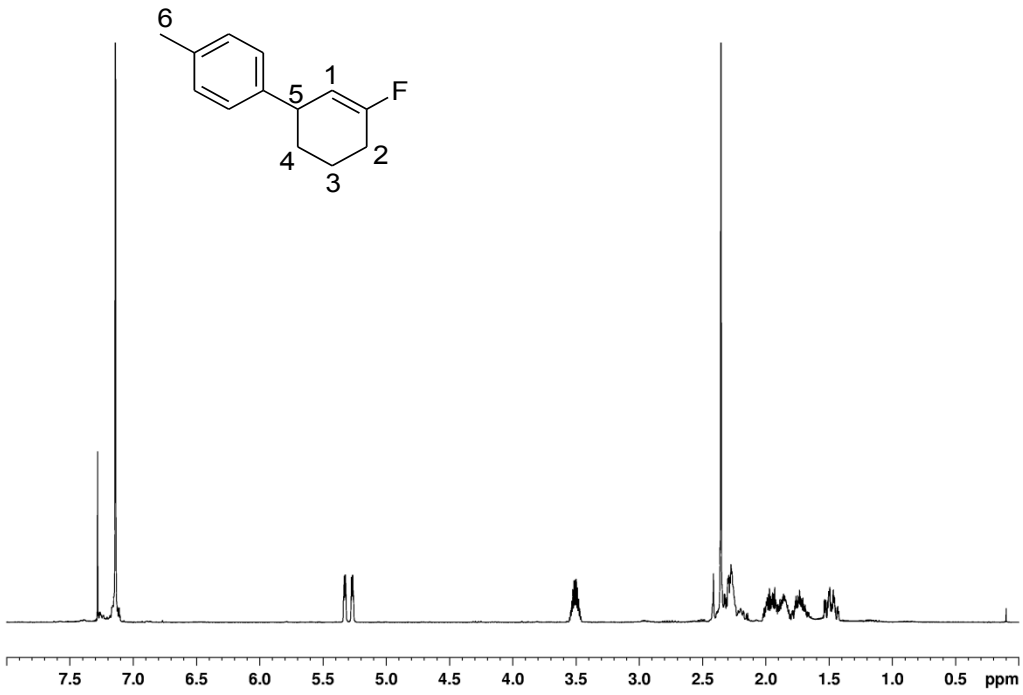


DEPT-135

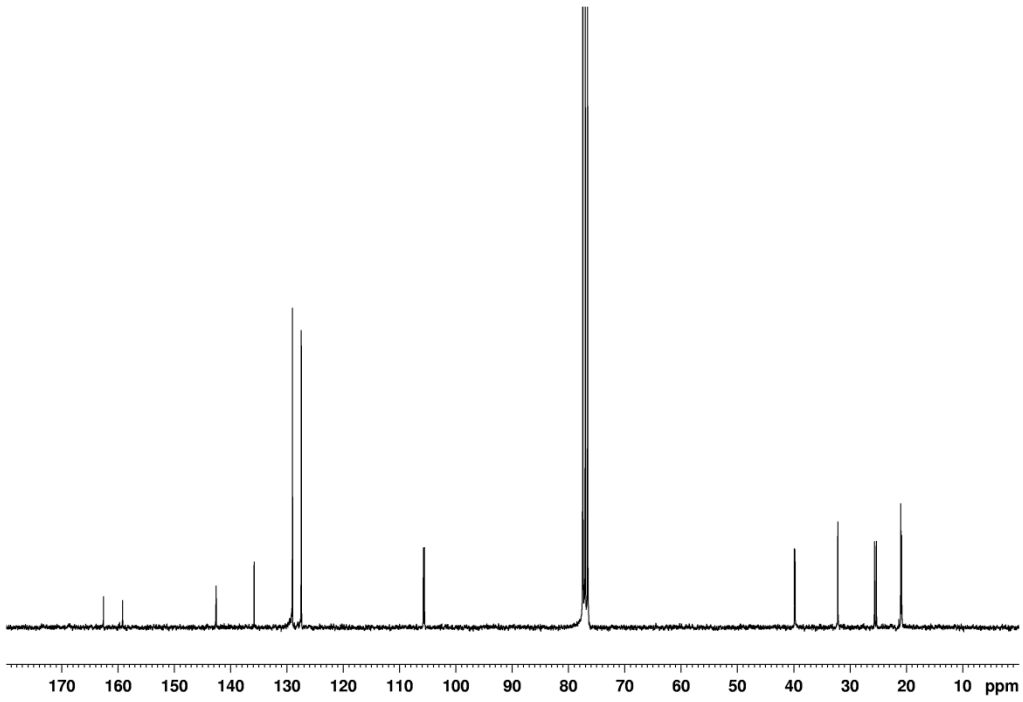


^{19}F NMR

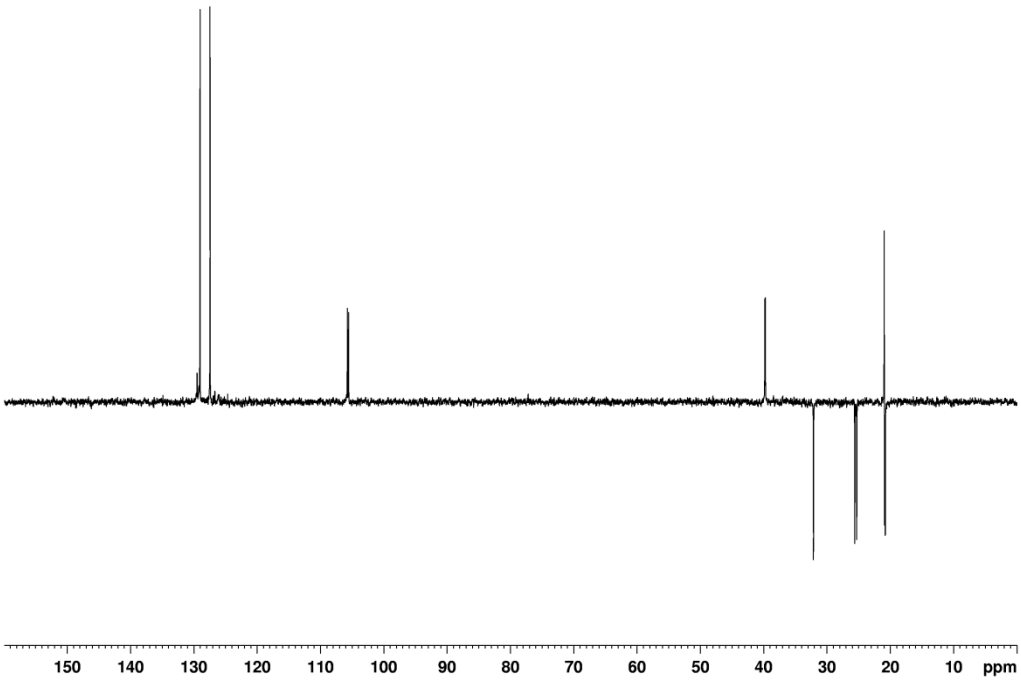
5-Fluoro-4'-methyl-1,2,3,4-tetrahydro-1,1'-biphenyl (4c)



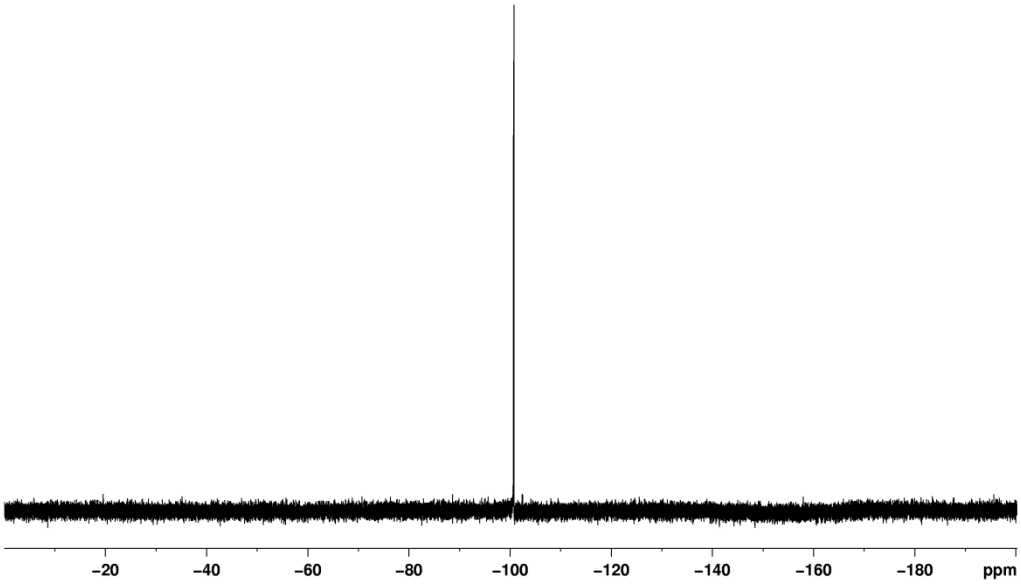
^{1}H NMR



^{13}C NMR

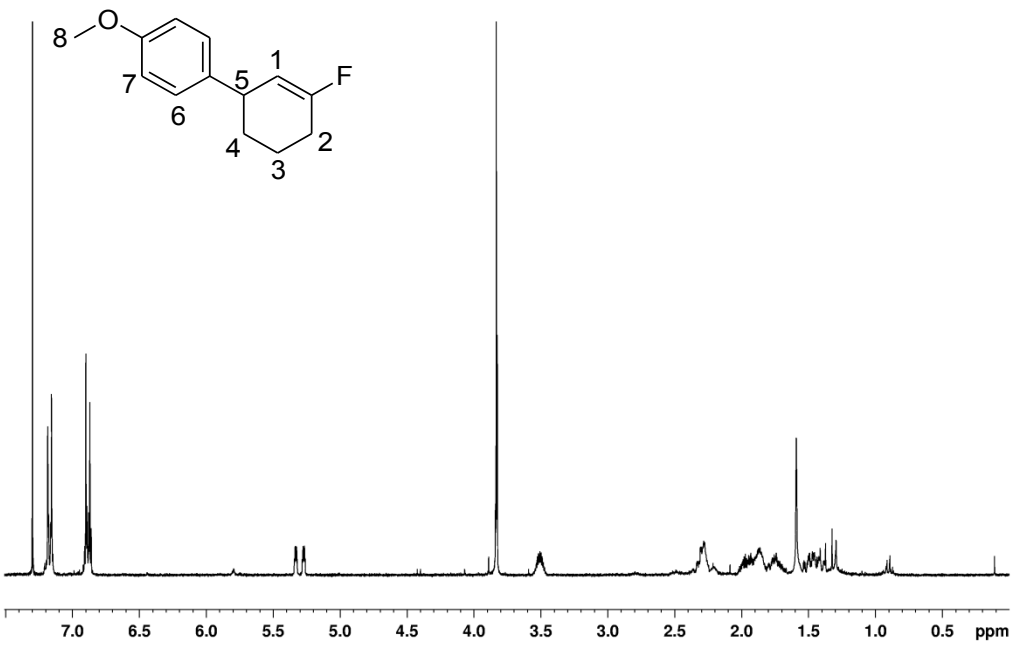


DEPT-135

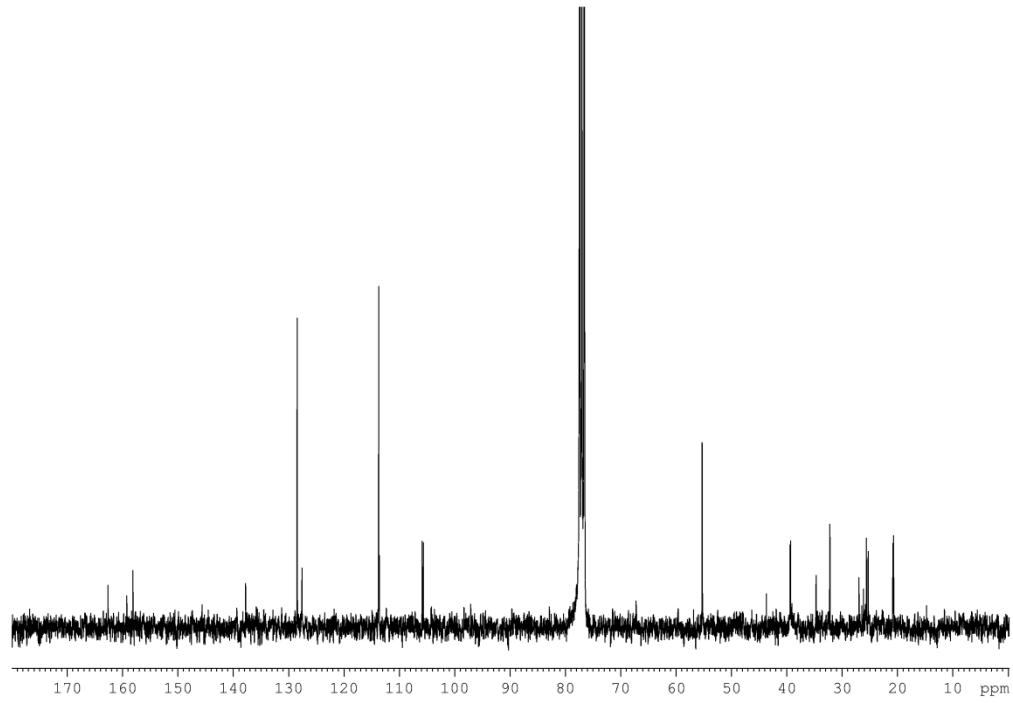


^{19}F NMR

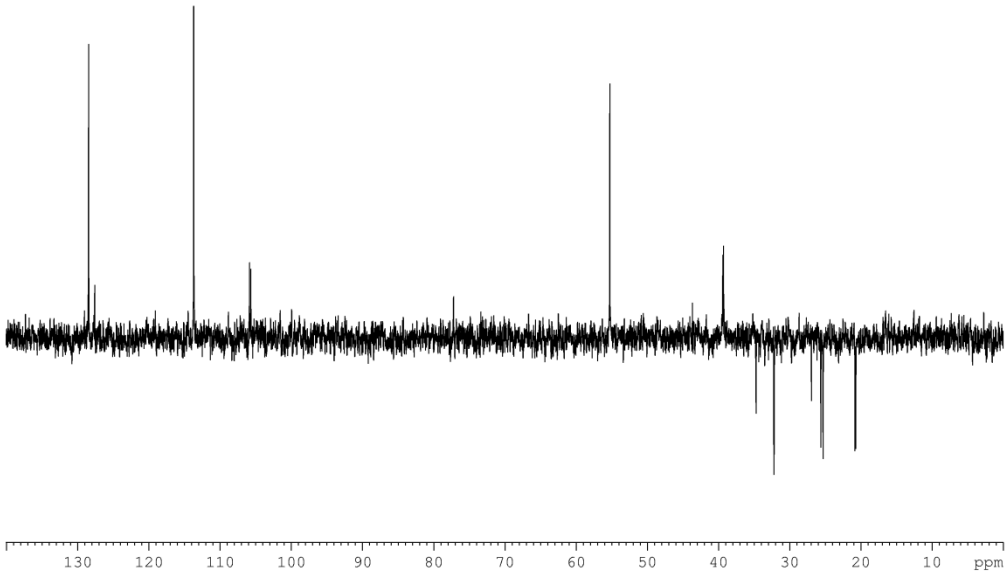
5-Fluoro-4'-methoxy-1,2,3,4-tetrahydro-1,1'-biphenyl (4d)



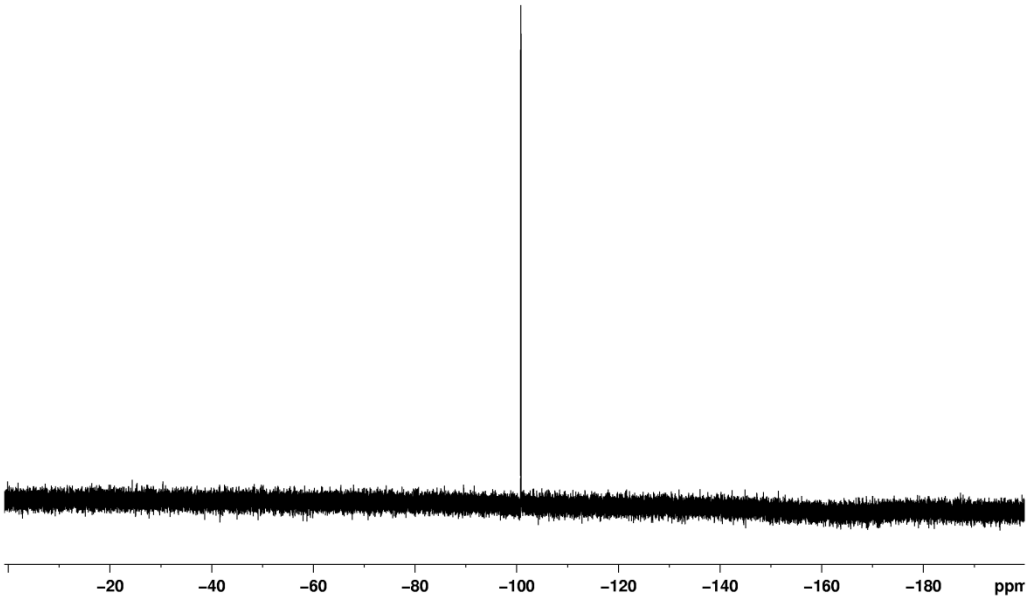
^{1}H NMR



^{13}C NMR

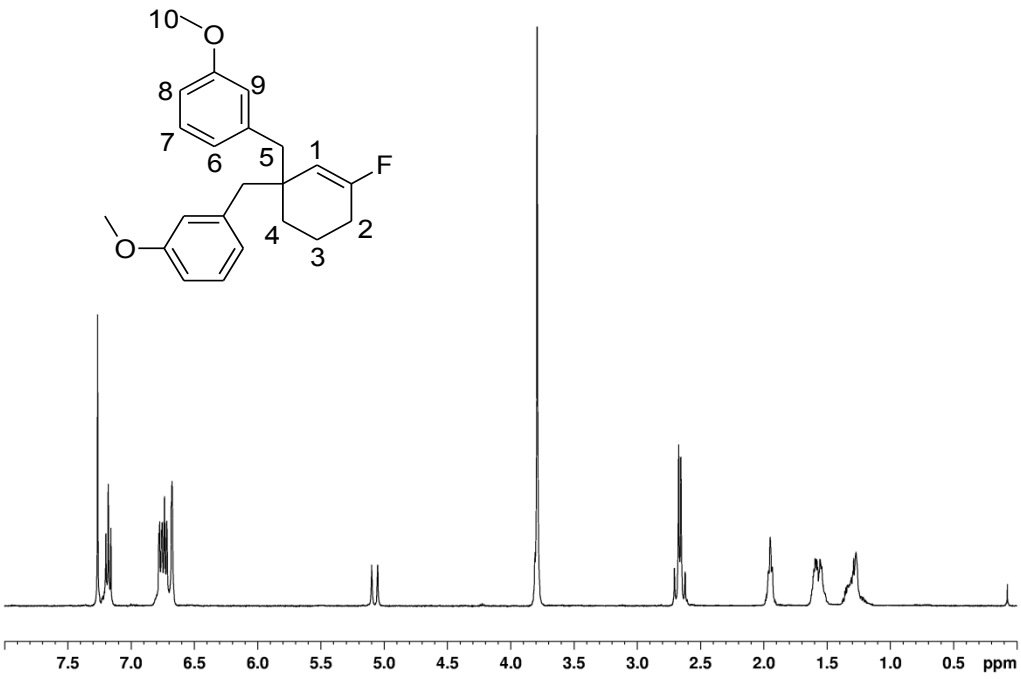


DEPT-135

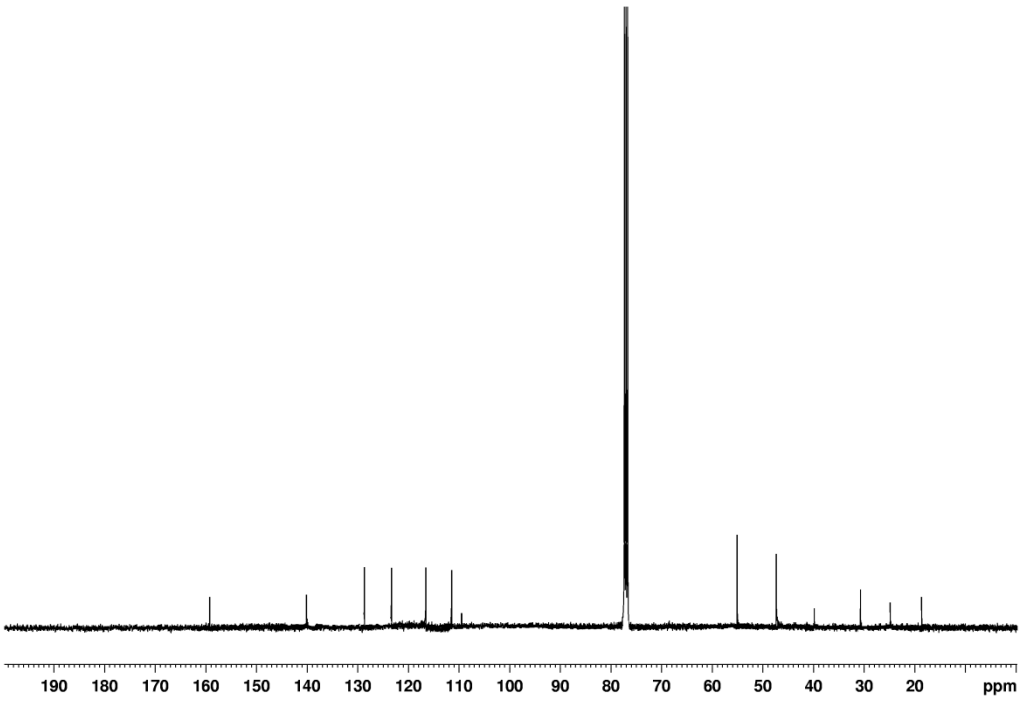


^{19}F NMR

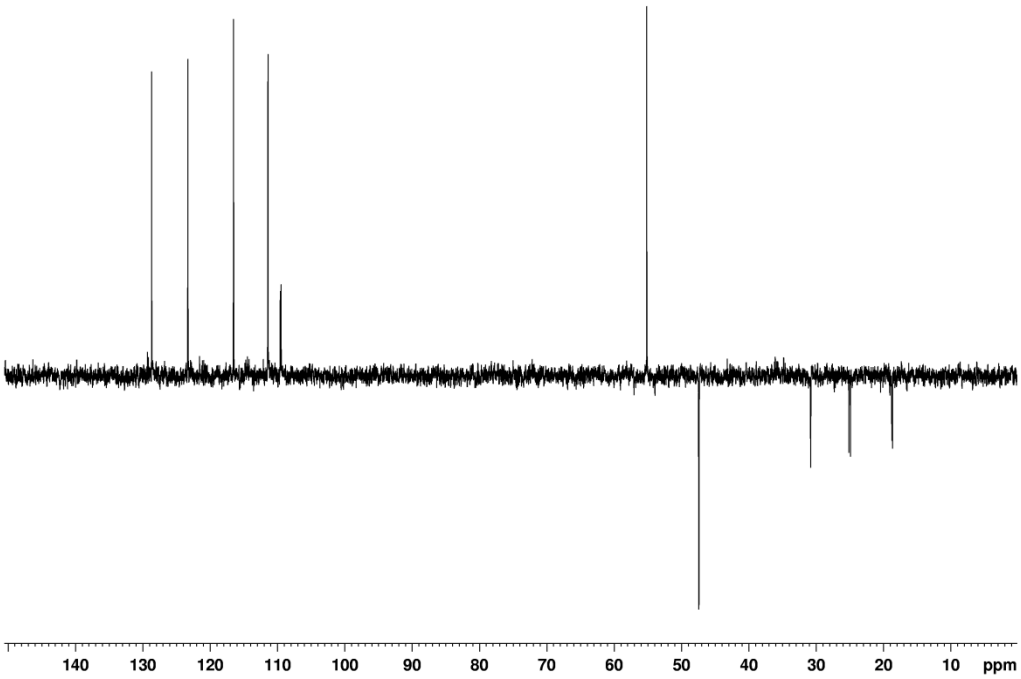
3,3'-[(3-Fluorocyclohex-2-ene-1,1-diyl)bis(methylene)]bis(methoxybenzene) (4e)



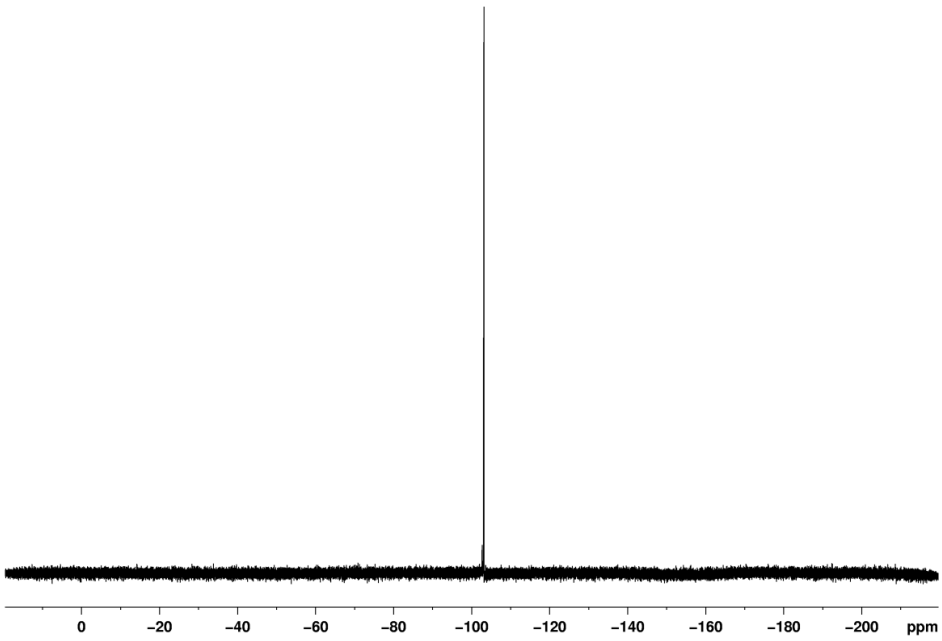
^{1}H NMR



^{13}C NMR

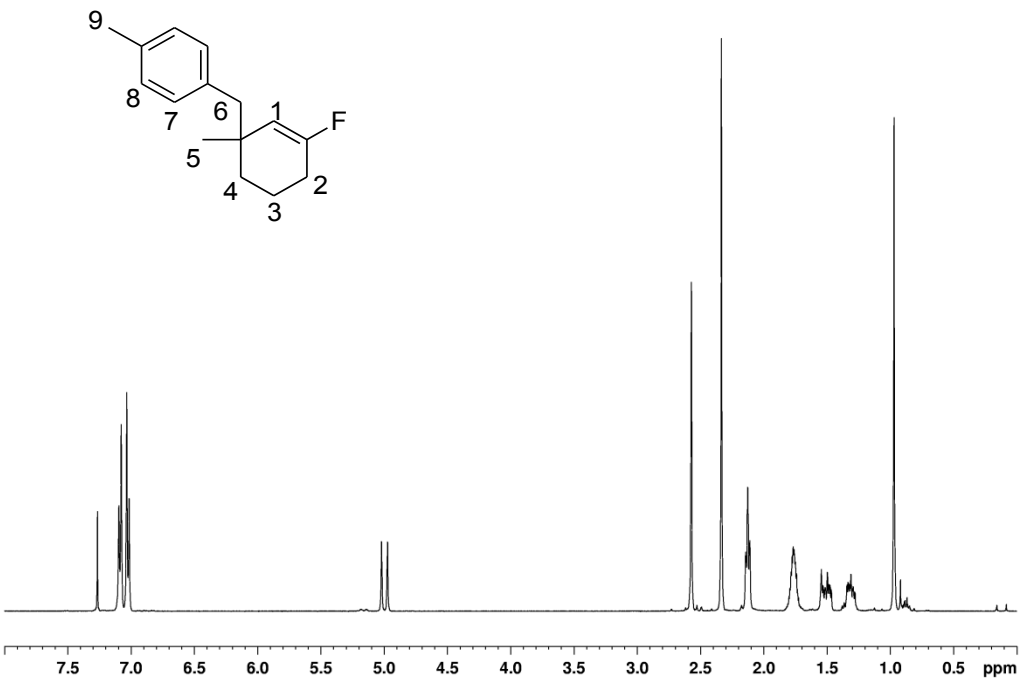


DEPT-135

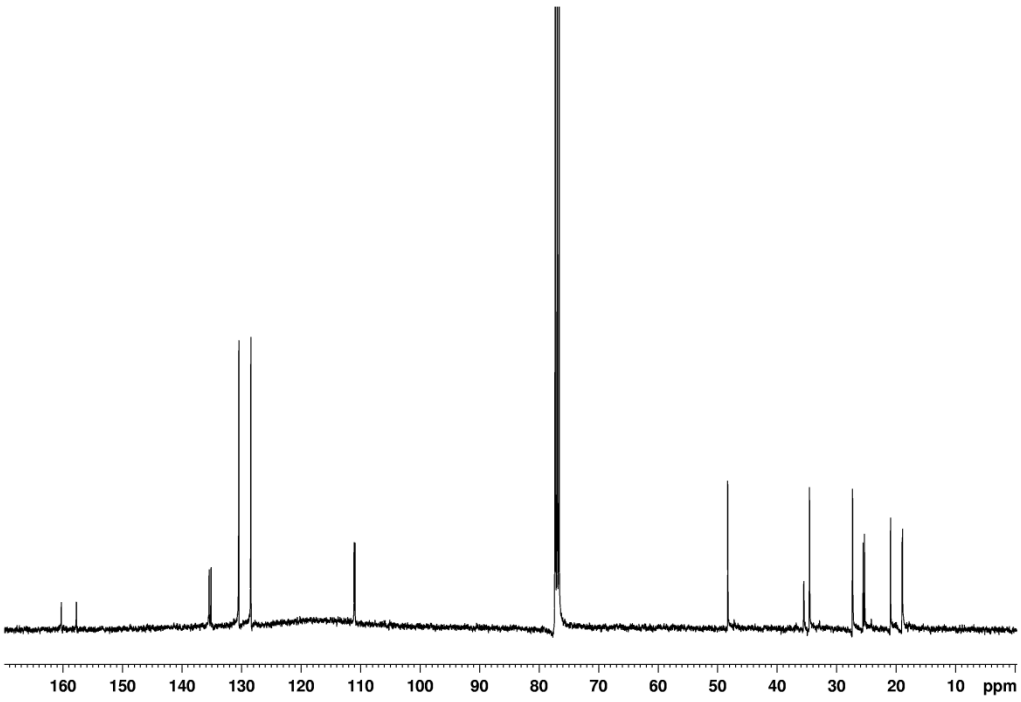


^{19}F NMR

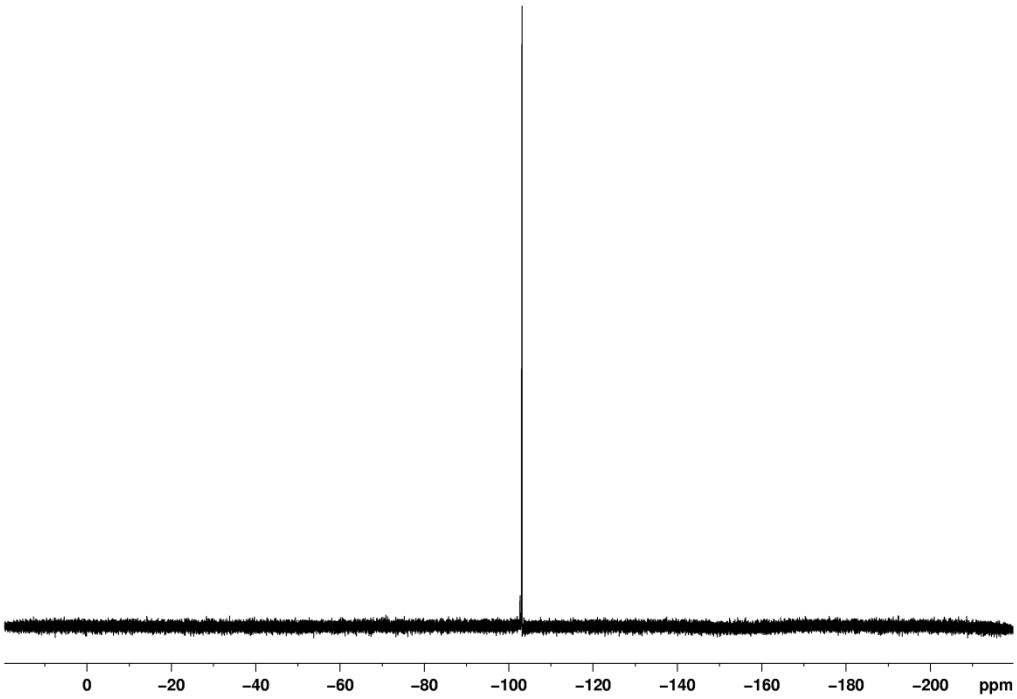
1-[(1-Ethyl-3-fluorocyclohex-2-en-1-yl)methyl]-4-methylbenzene (4f)



^{1}H NMR

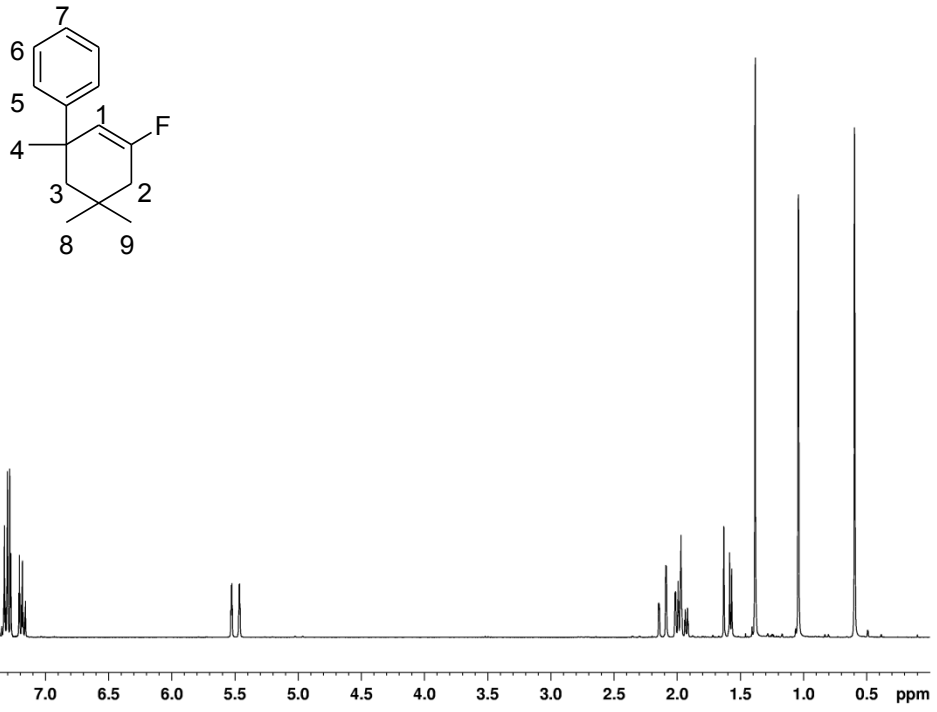


^{13}C NMR

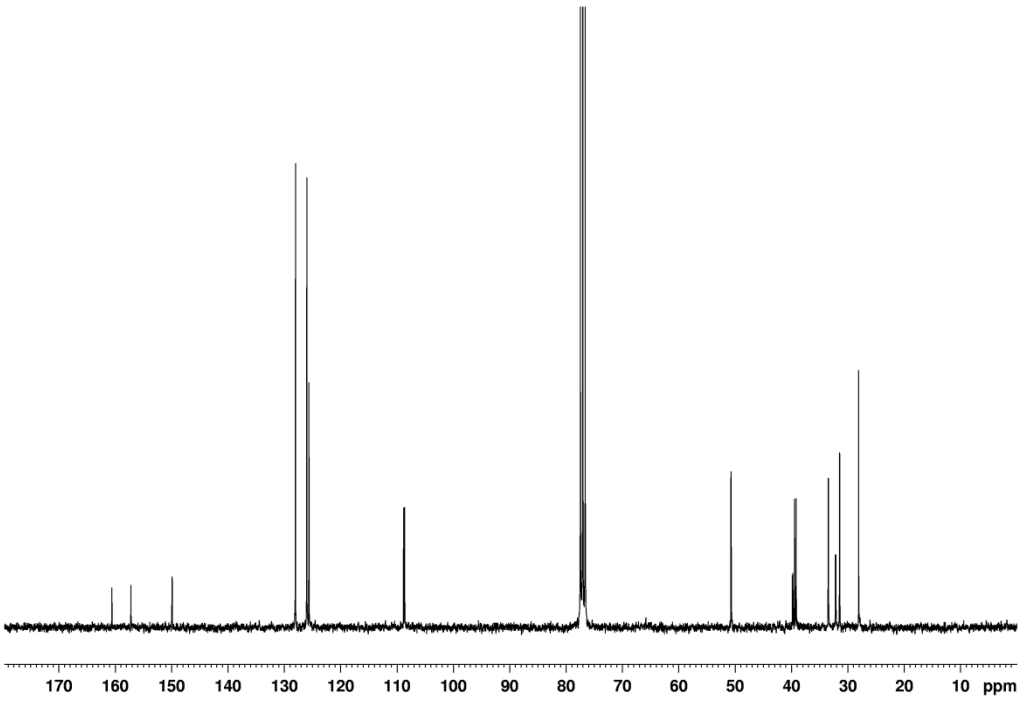


^{19}F NMR

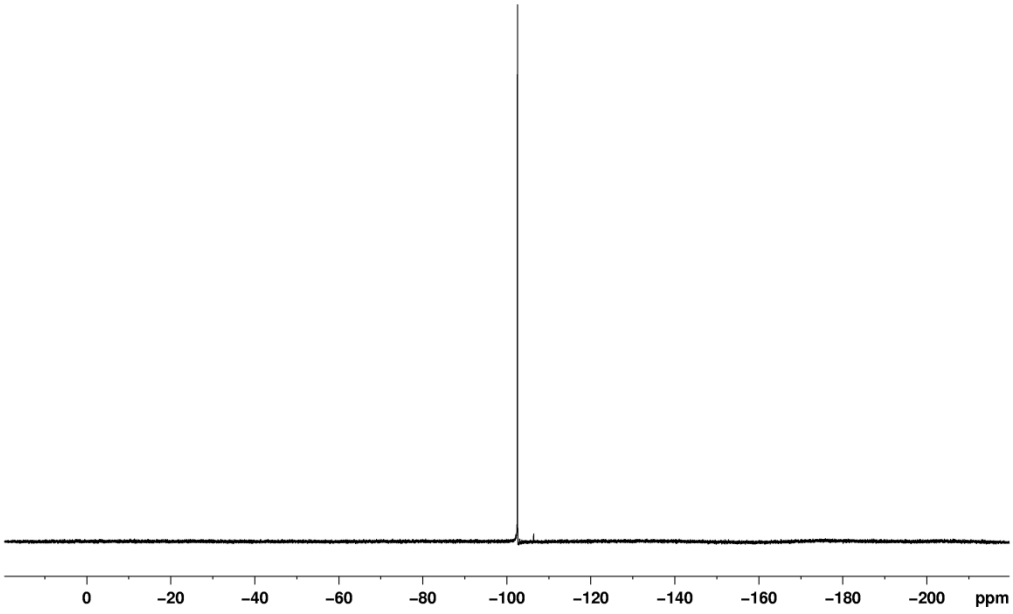
5-Fluoro-1,3,3-trimethyl-1,2,3,4-tetrahydro-1,1'-biphenyl (4g)



^{1}H NMR

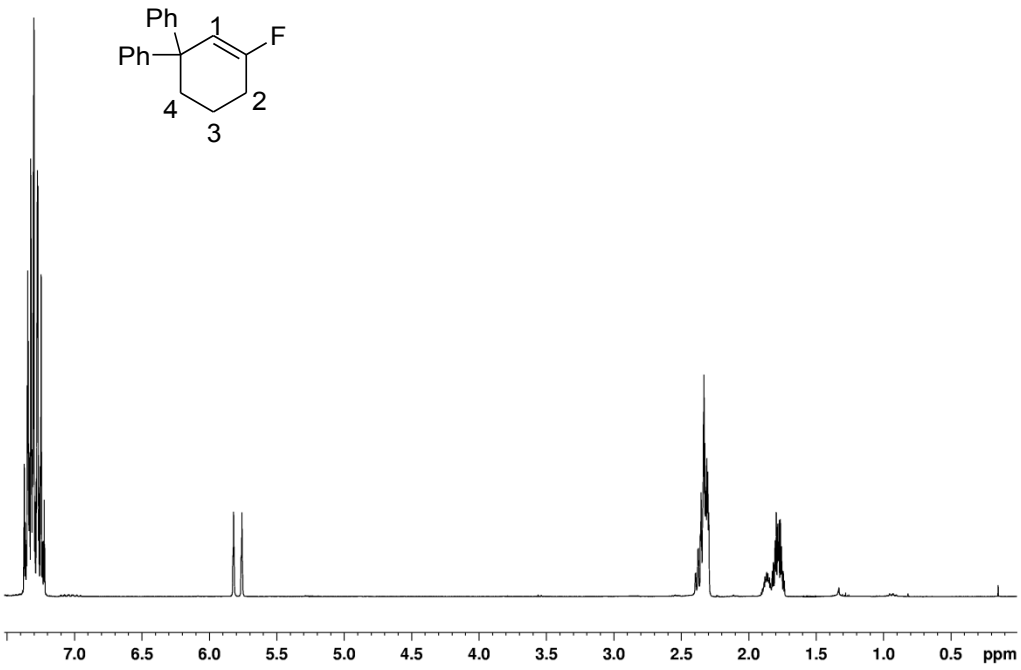


^{13}C NMR

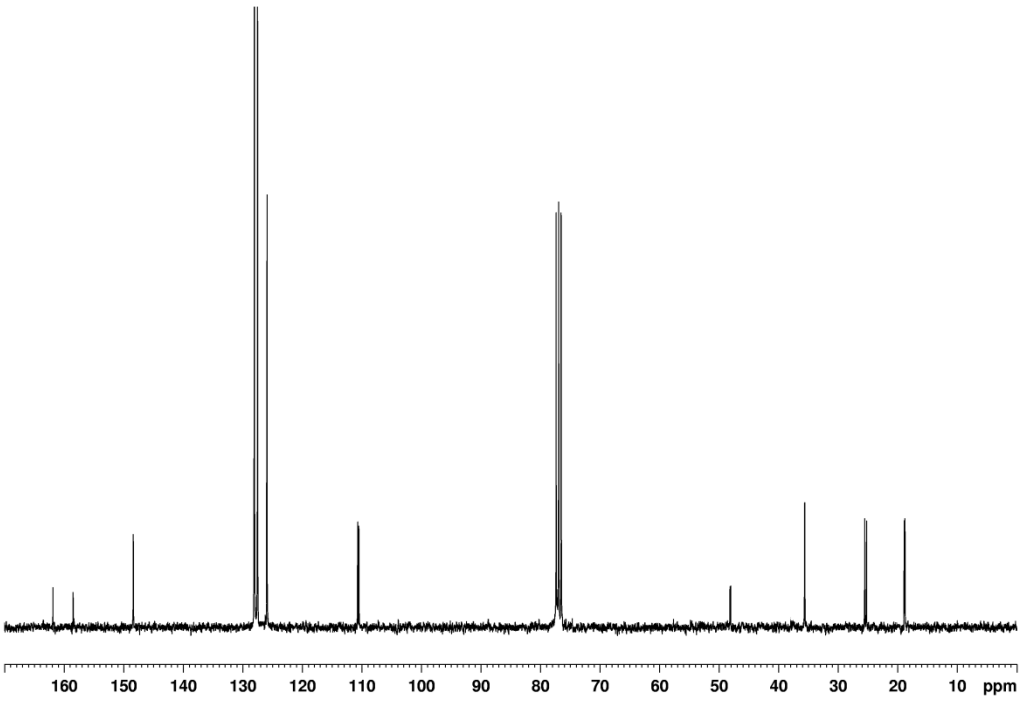


^{19}F NMR

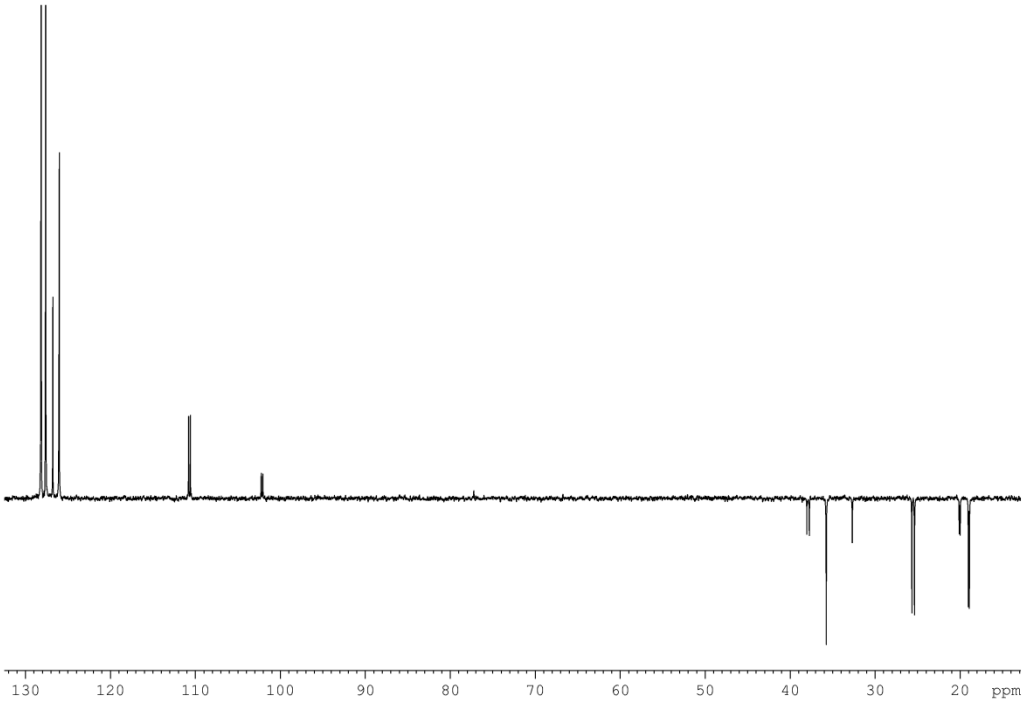
5'-Fluoro-3',4'-dihydro-2'H-1,1':1',1''-terphenyl (4h)



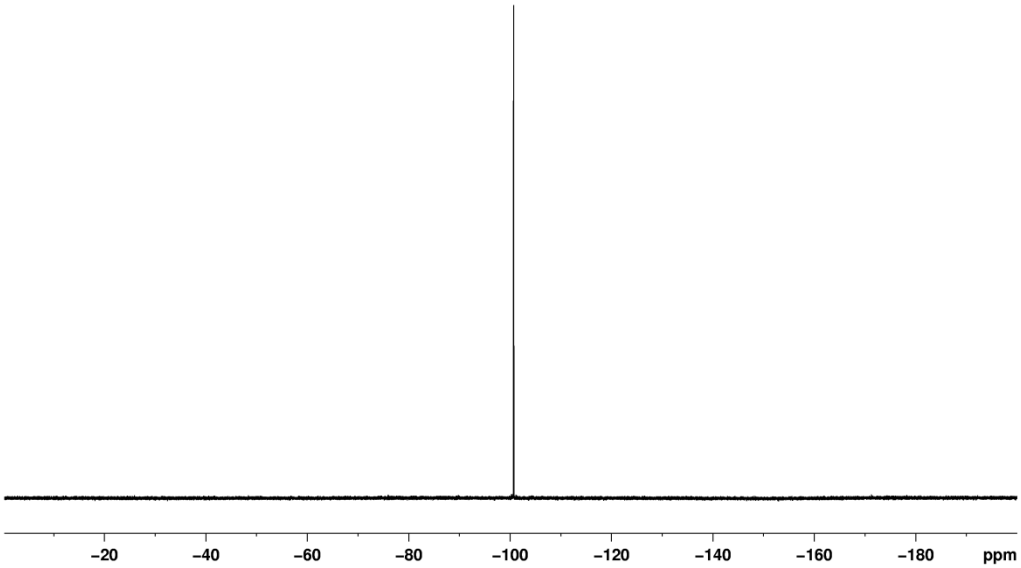
^{1}H NMR



^{13}C NMR

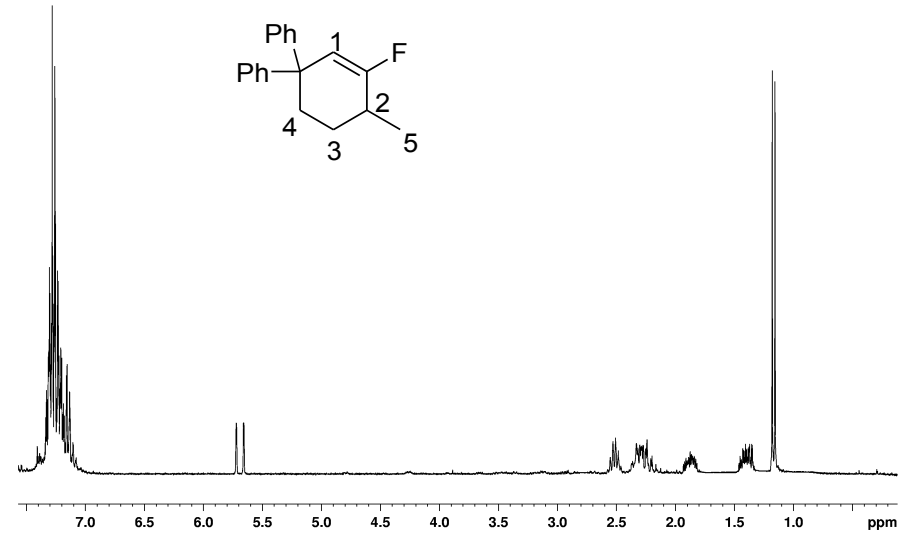


DEPT-135

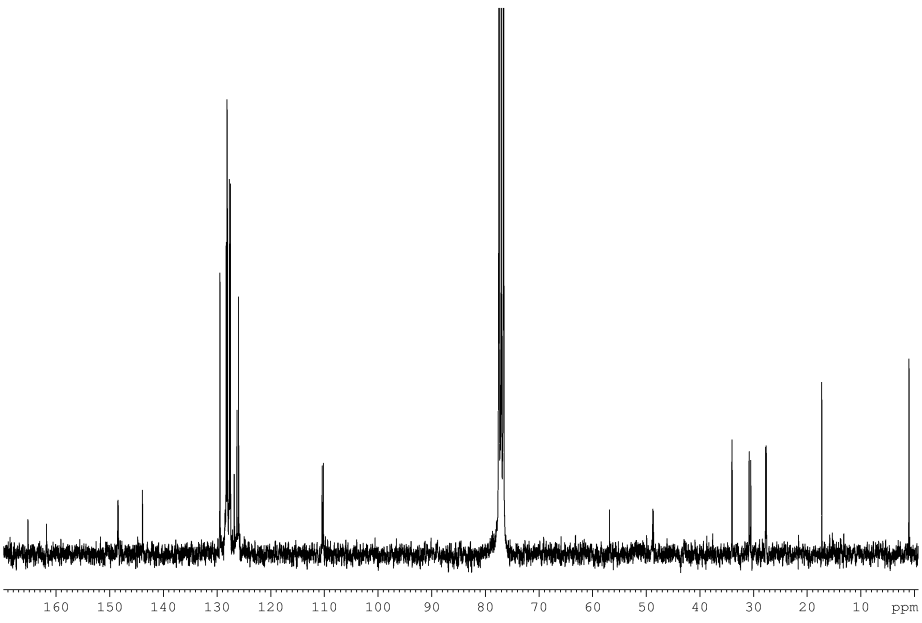


^{19}F NMR

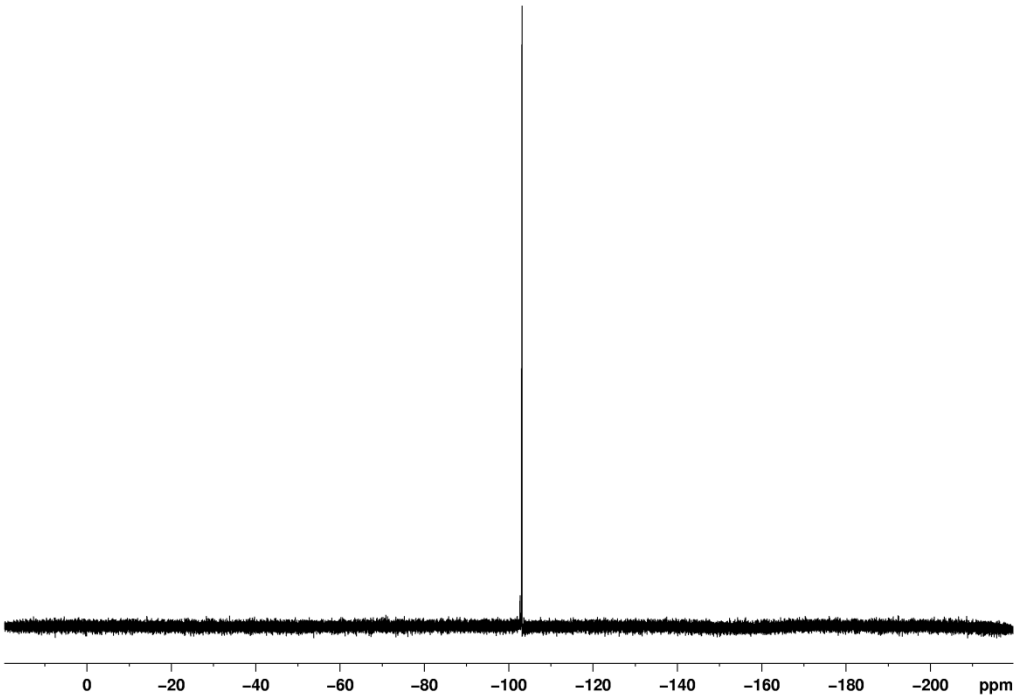
5'-Fluoro-4'-methyl-3',4'-dihydro-2'H-1,1':1',1''-terphenyl (4i)



^{1}H NMR

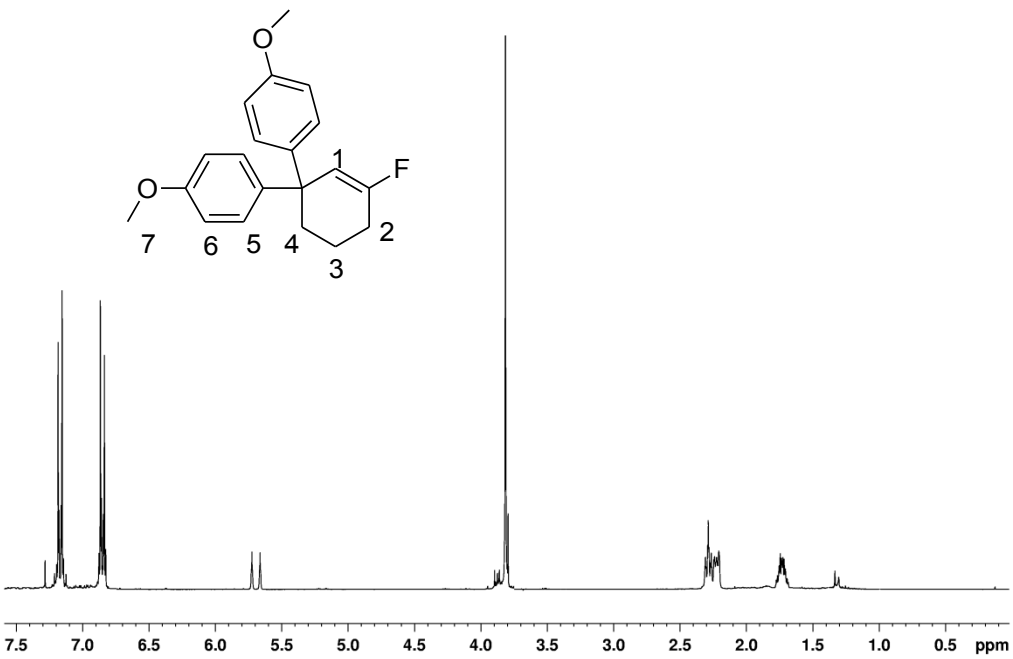


^{13}C NMR

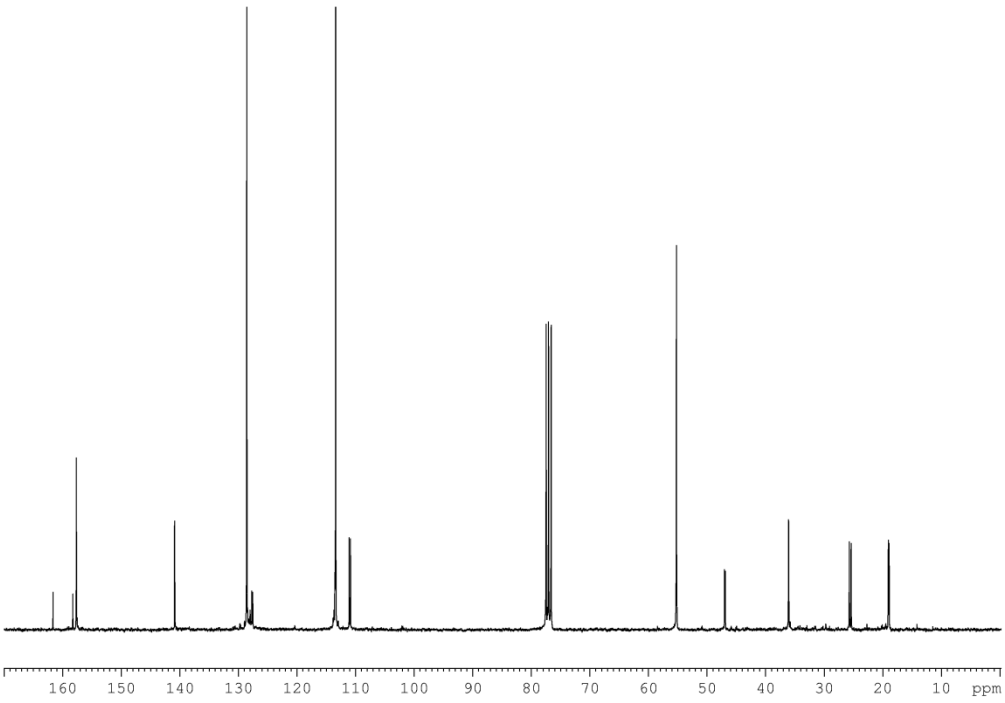


^{19}F NMR

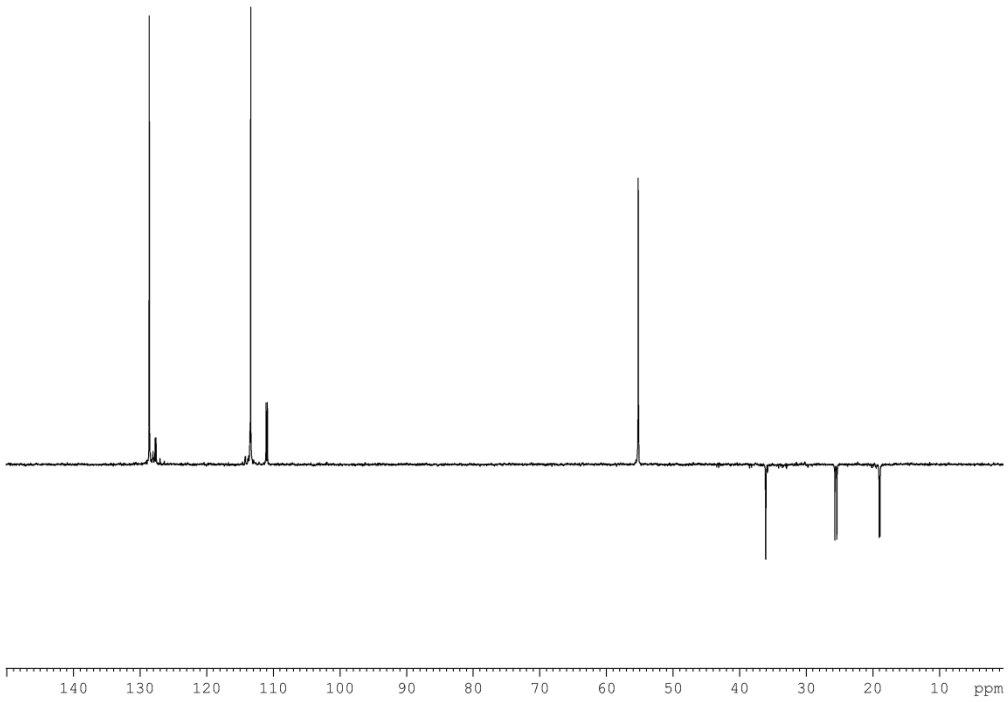
5'-Fluoro-4,4''-dimethoxy-3',4'-dihydro-2'H-1,1':1',1''-terphenyl (4j)



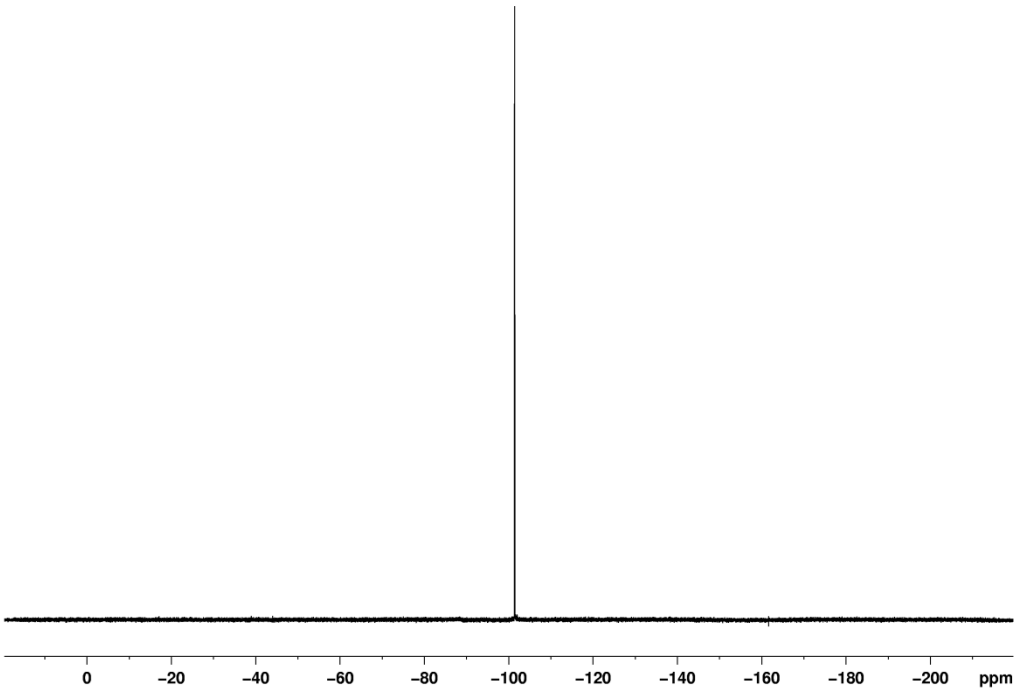
^{1}H NMR



^{13}C NMR

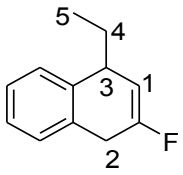


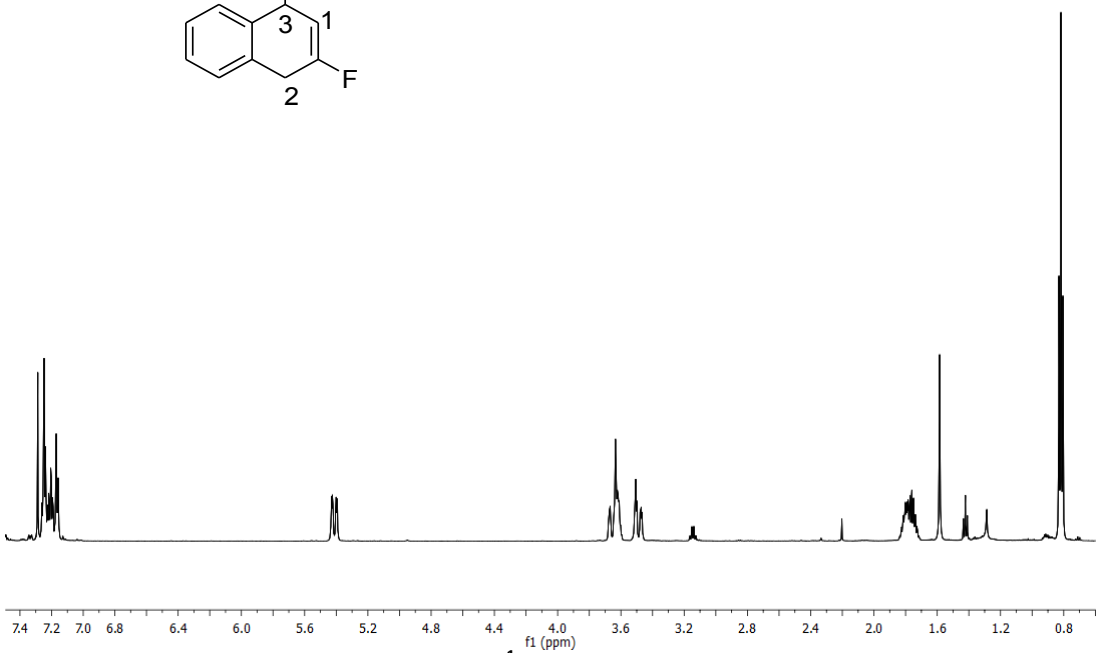
DEPT-135



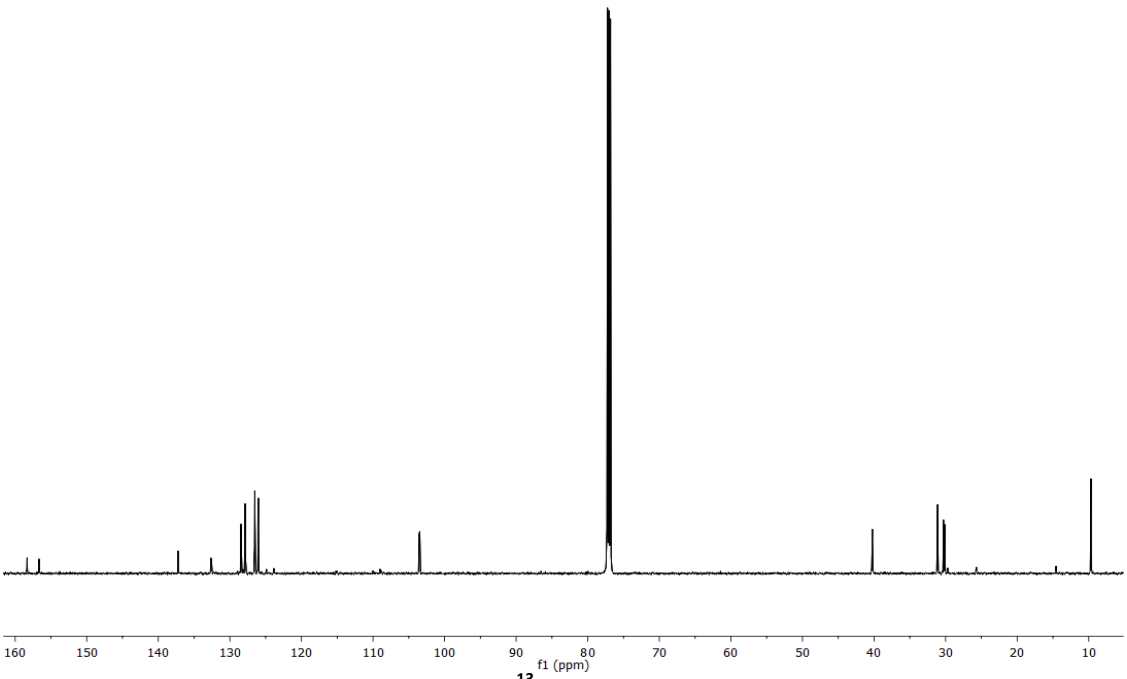
^{19}F NMR

1-Ethyl-3-fluoro-1,4-dihydronaphthalene (4k)

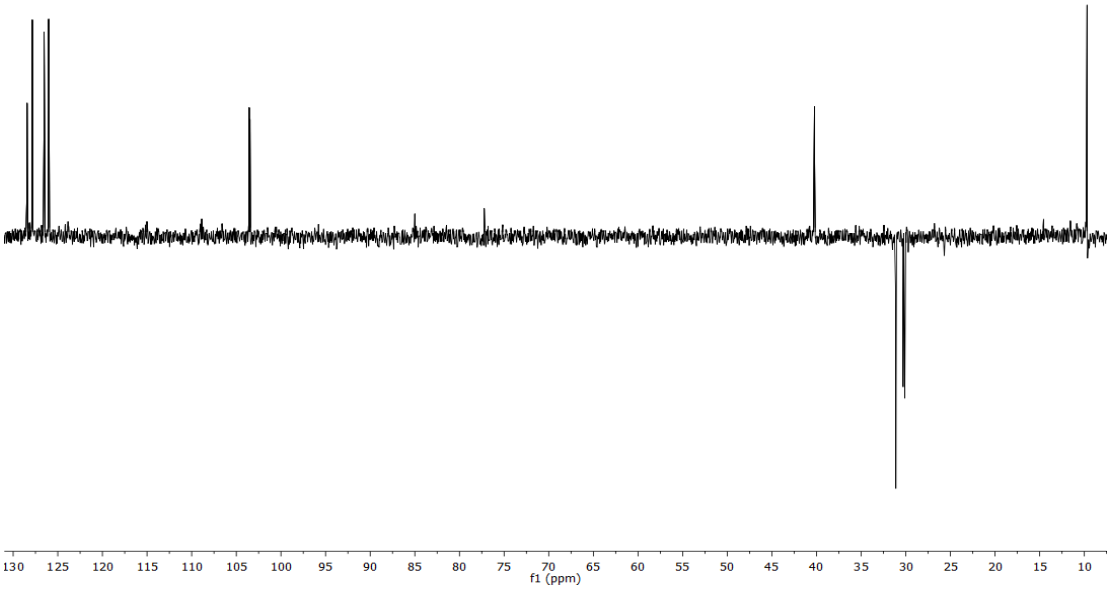




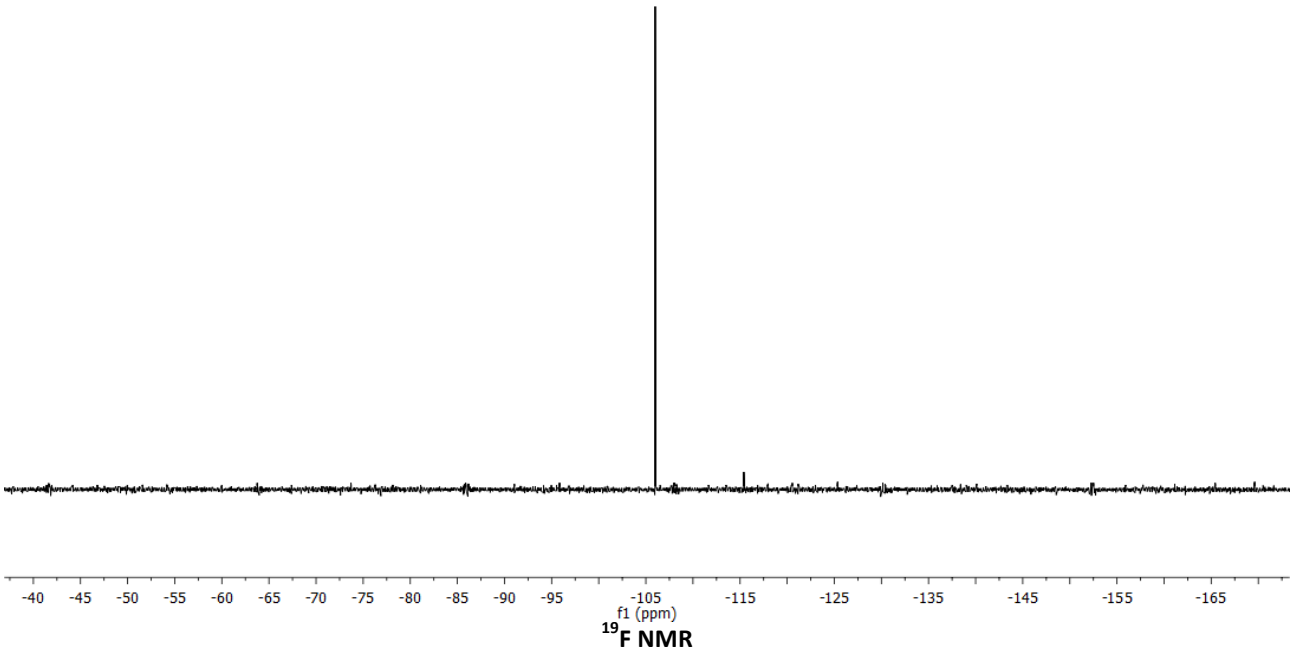
^{1}H NMR



^{13}C NMR

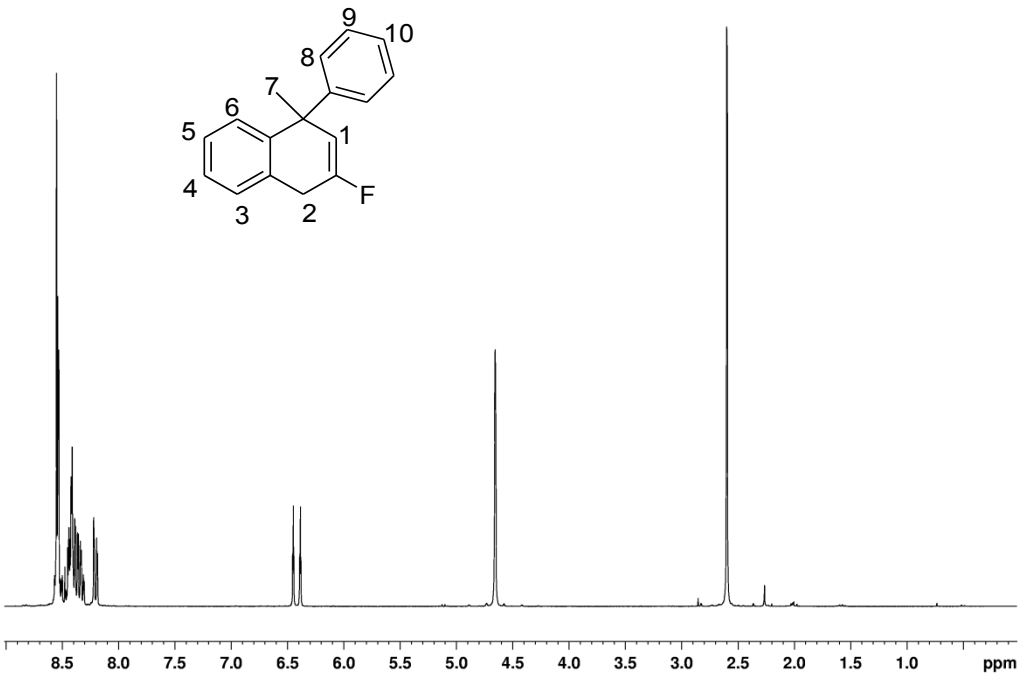


DEPT-135

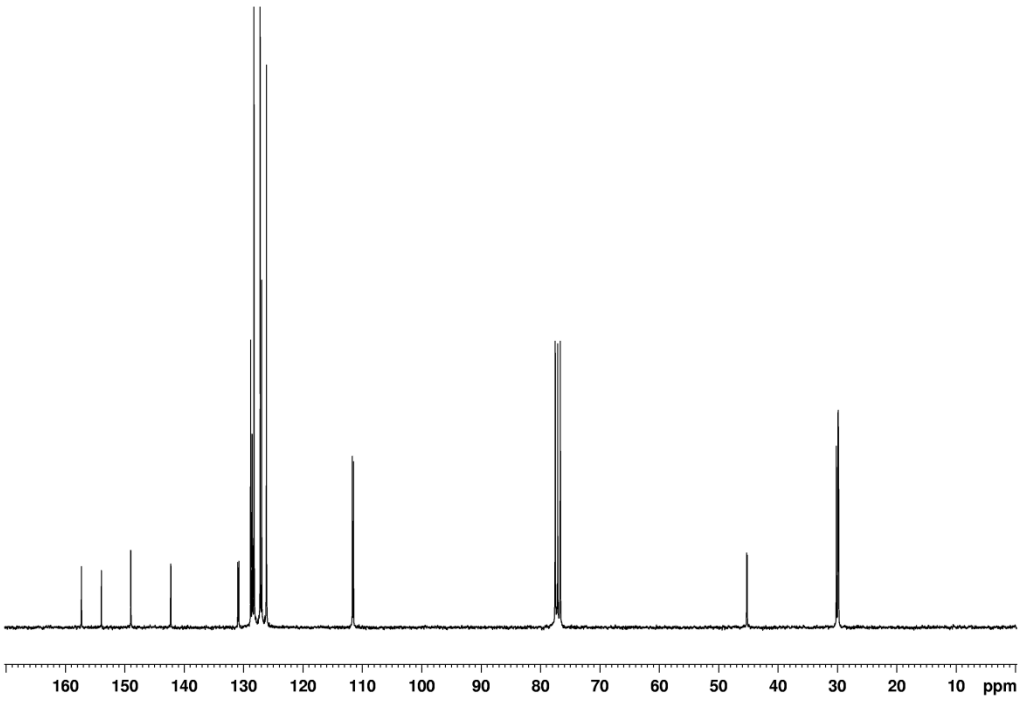


^{19}F NMR

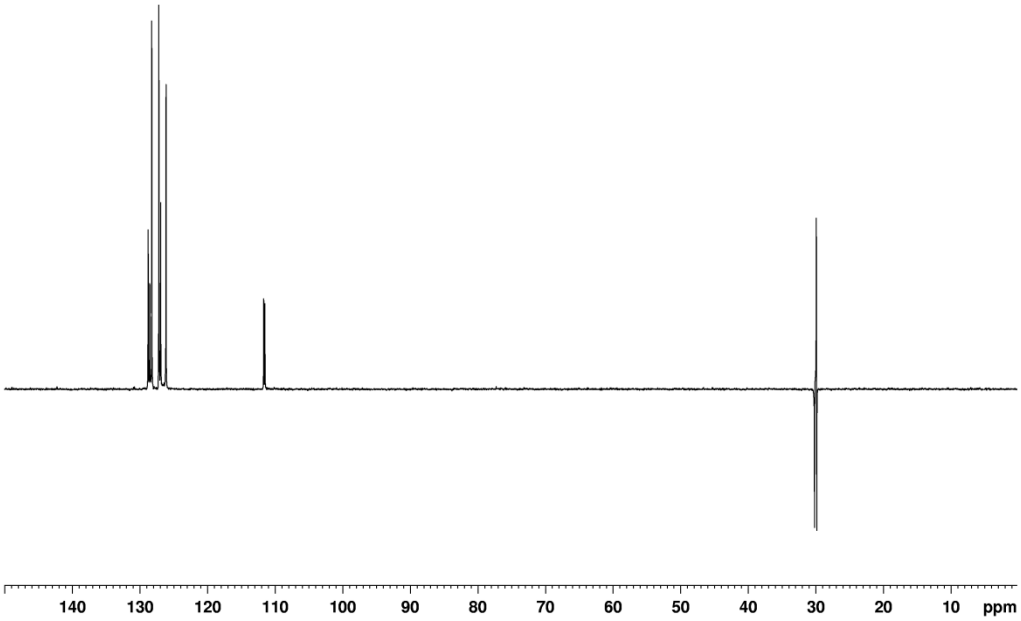
3-Fluoro-1-methyl-1-phenyl-1,4-dihydronaphthalene (4l)



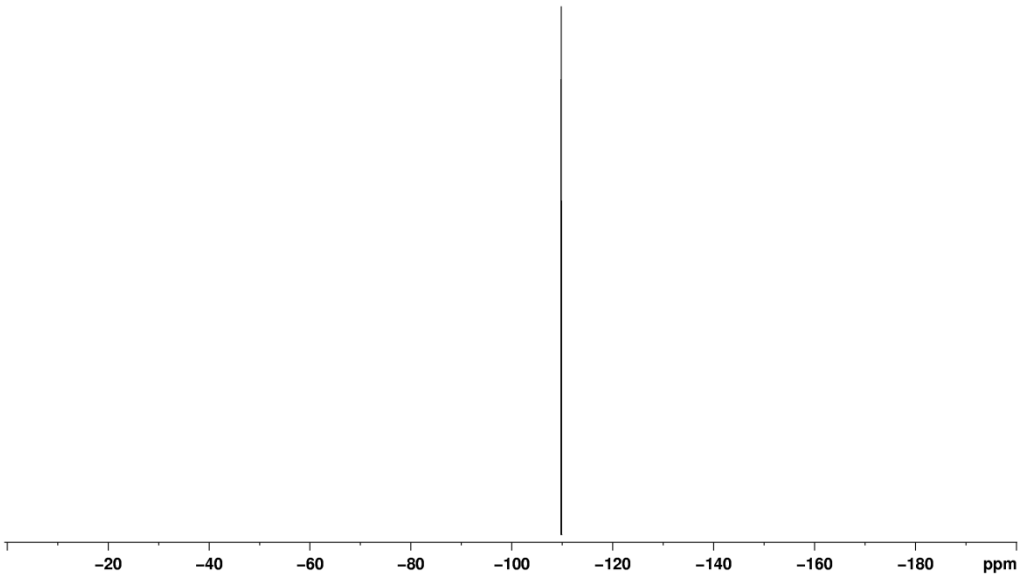
^{1}H NMR



^{13}C NMR

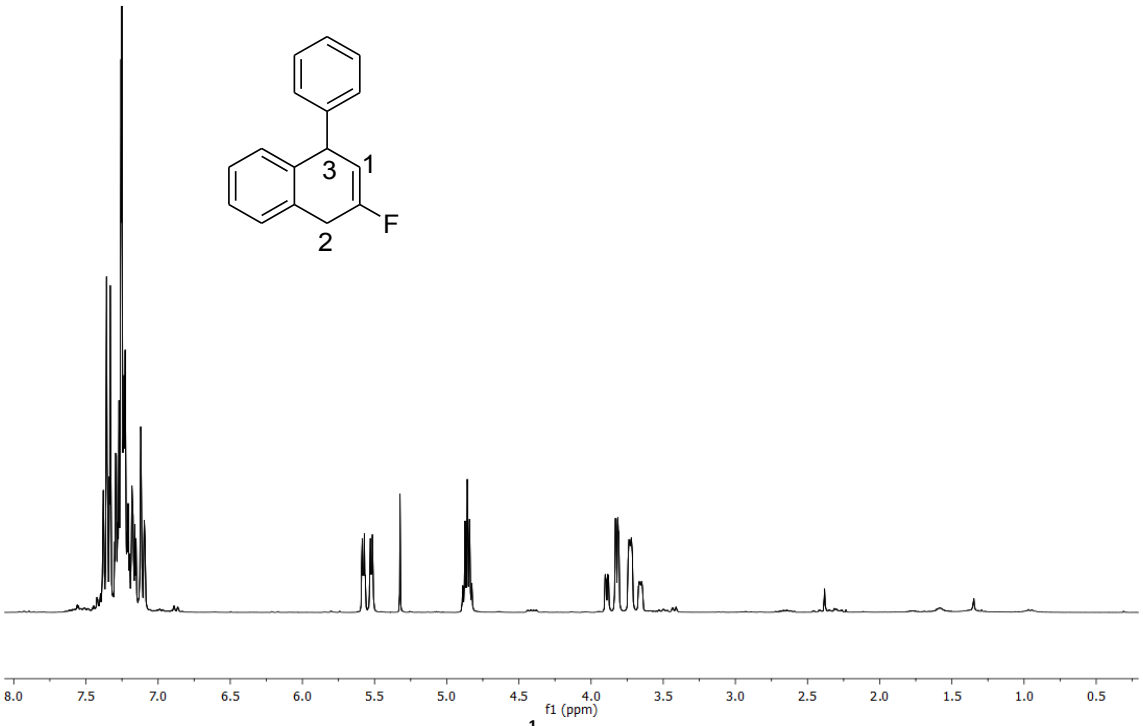


DEPT-135

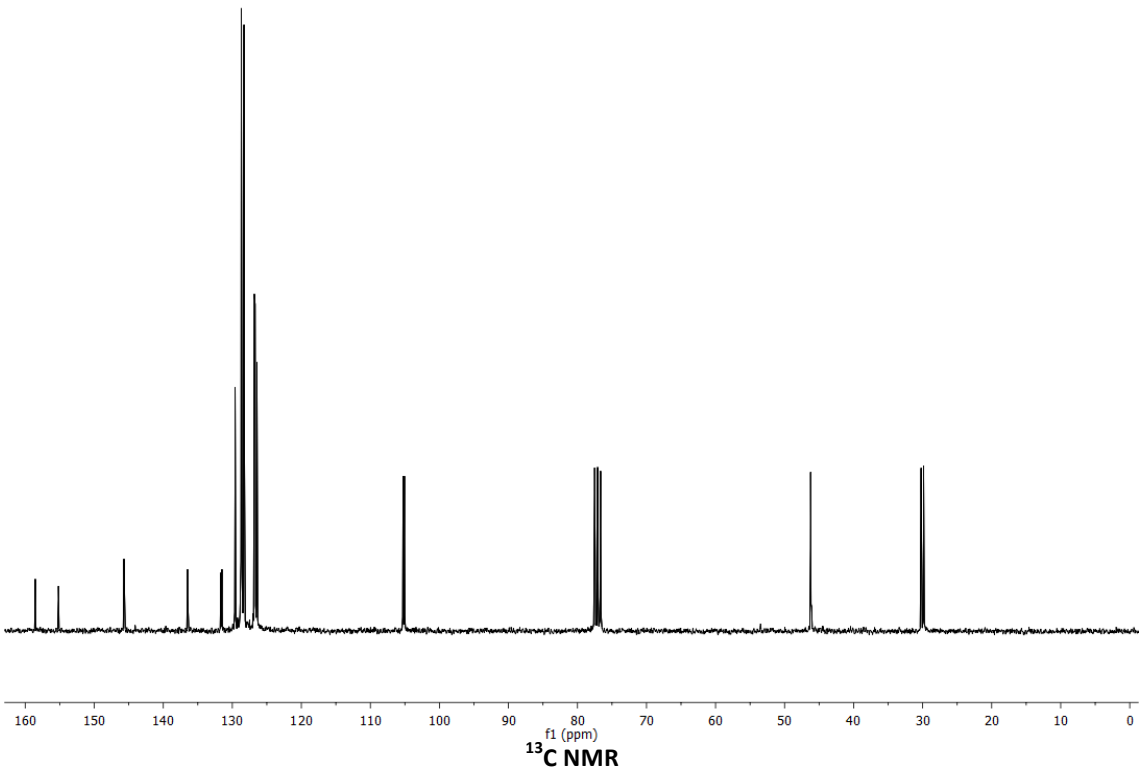


^{19}F NMR

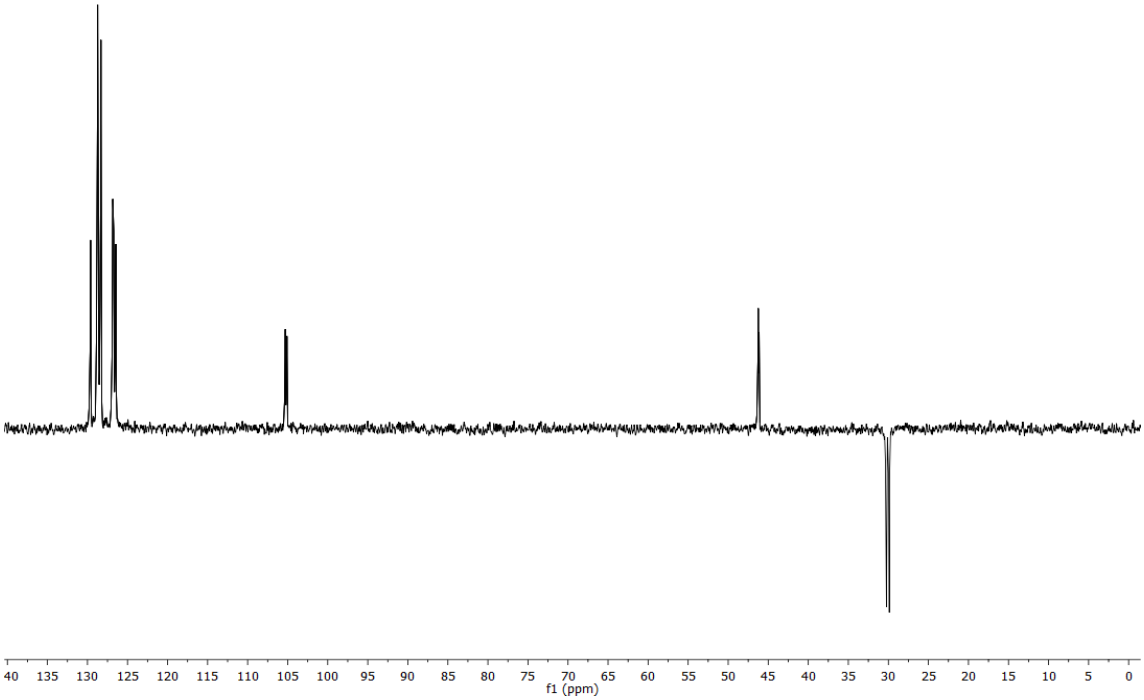
3-Fluoro-1-phenyl-1,4-dihydronaphthalene (4m)



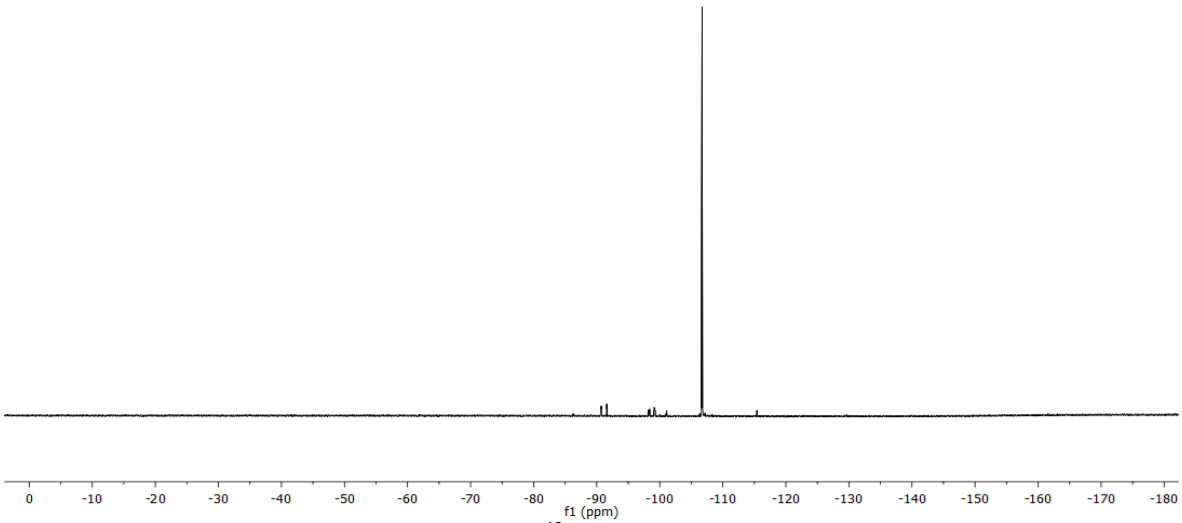
^{1}H NMR



^{13}C NMR

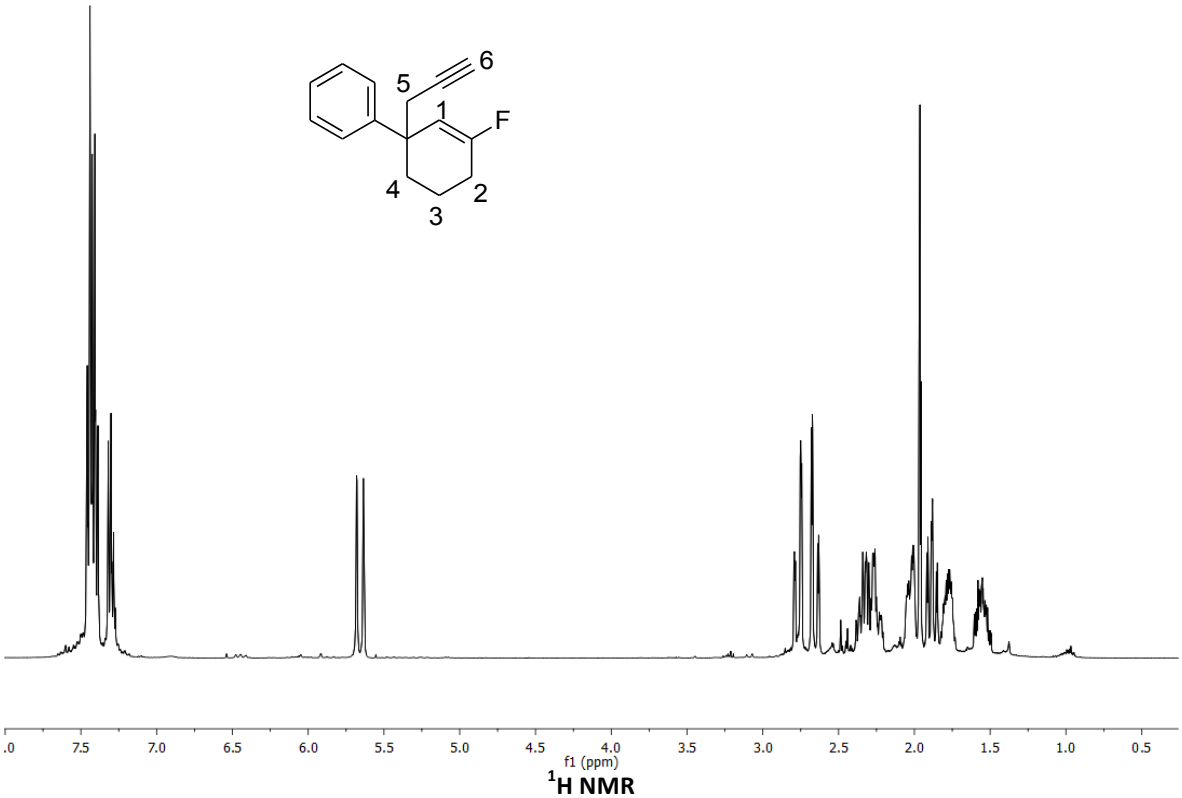


DEPT-135

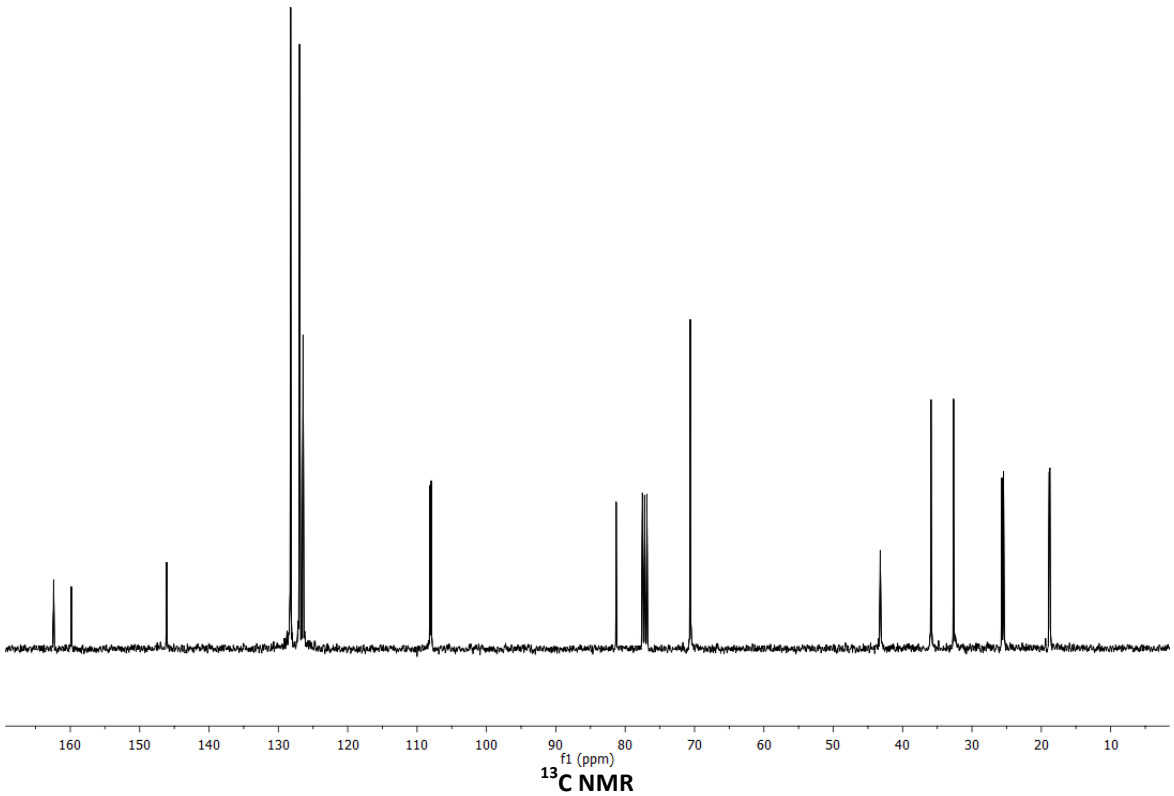


^{19}F NMR

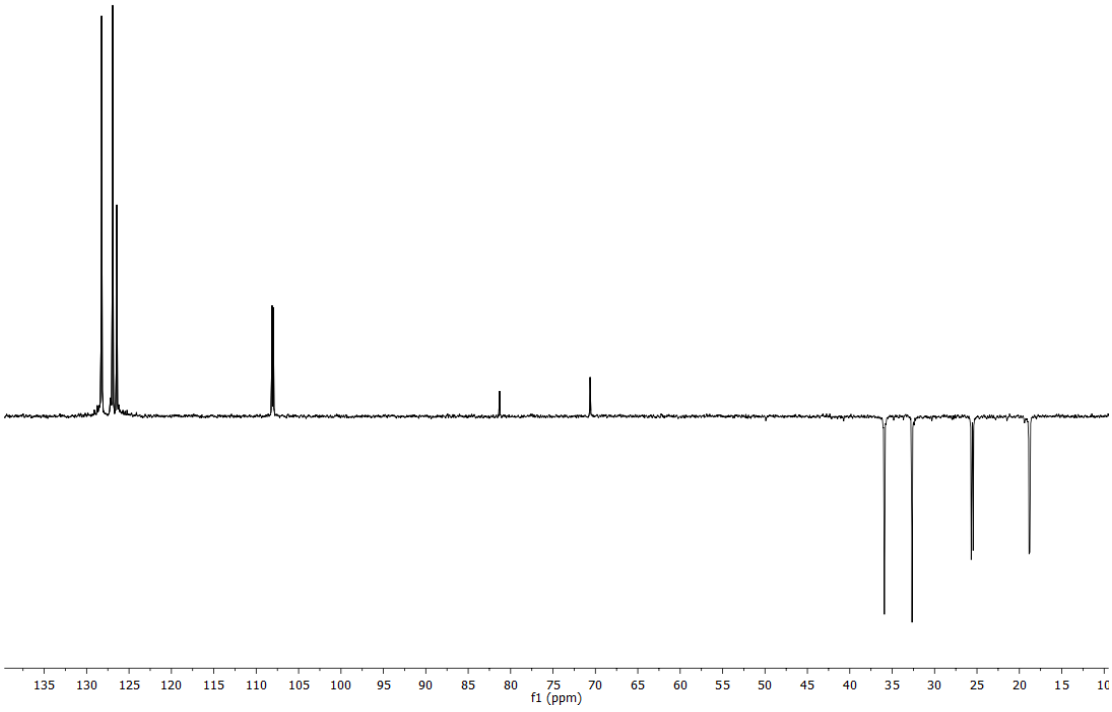
5-Fluoro-1-(prop-2-yn-1-yl)-1,2,3,4-tetrahydro-1,1'-biphenyl (4n)



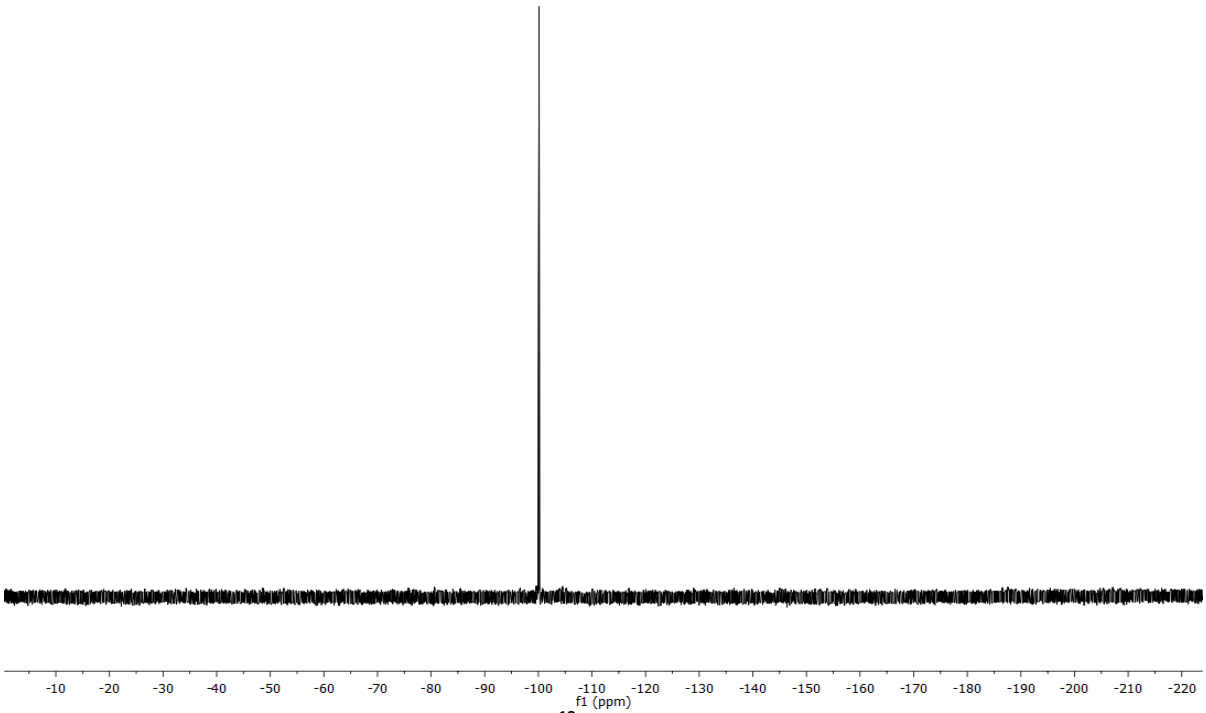
^{1}H NMR



^{13}C NMR

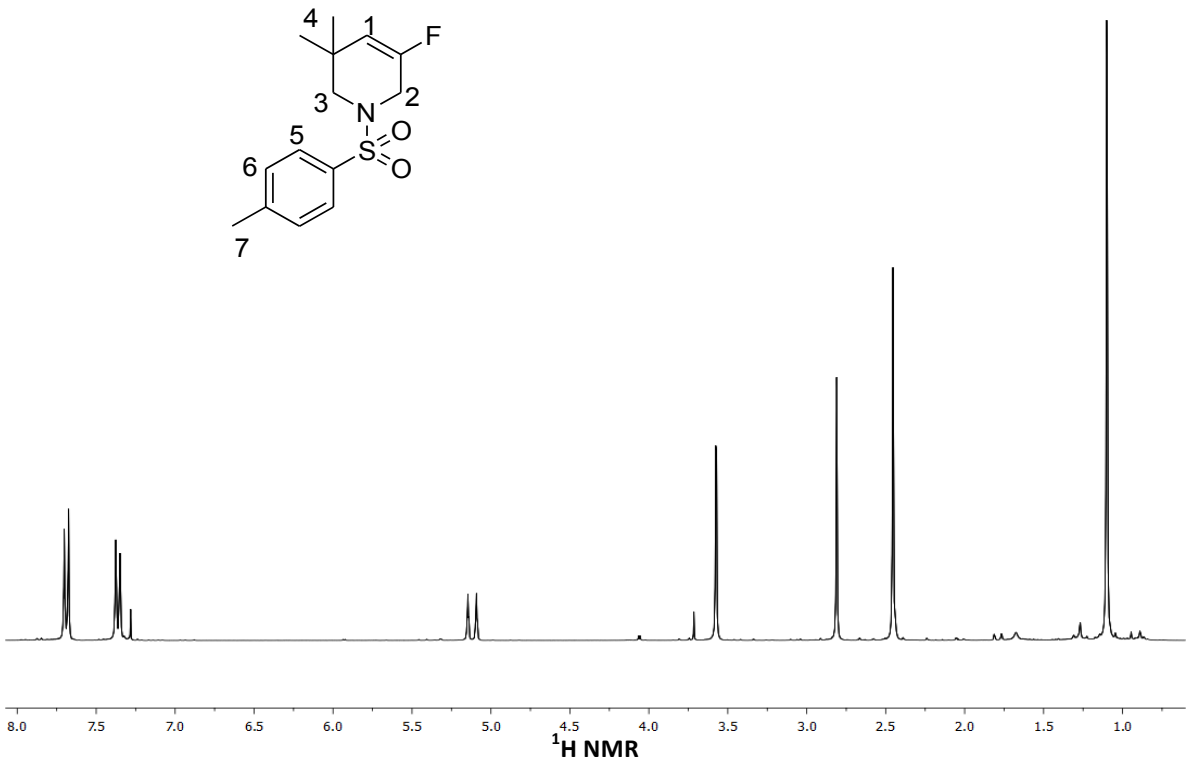


DEPT-135

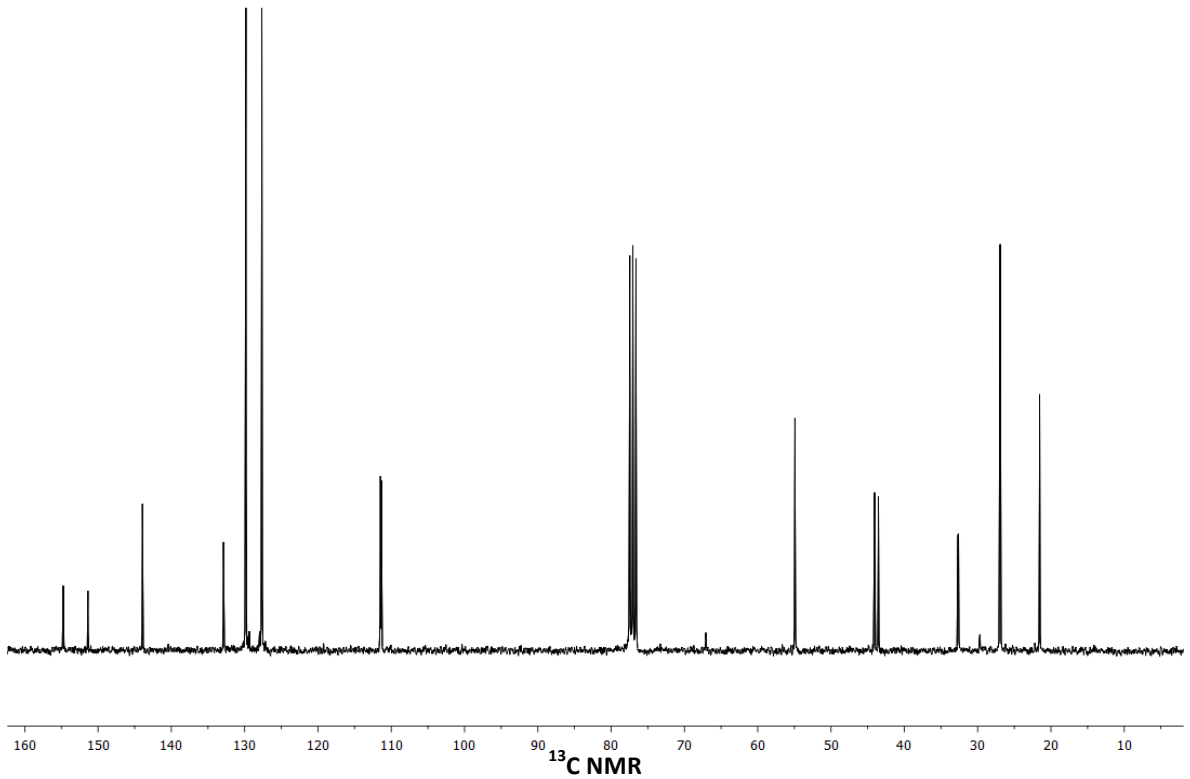


^{19}F NMR

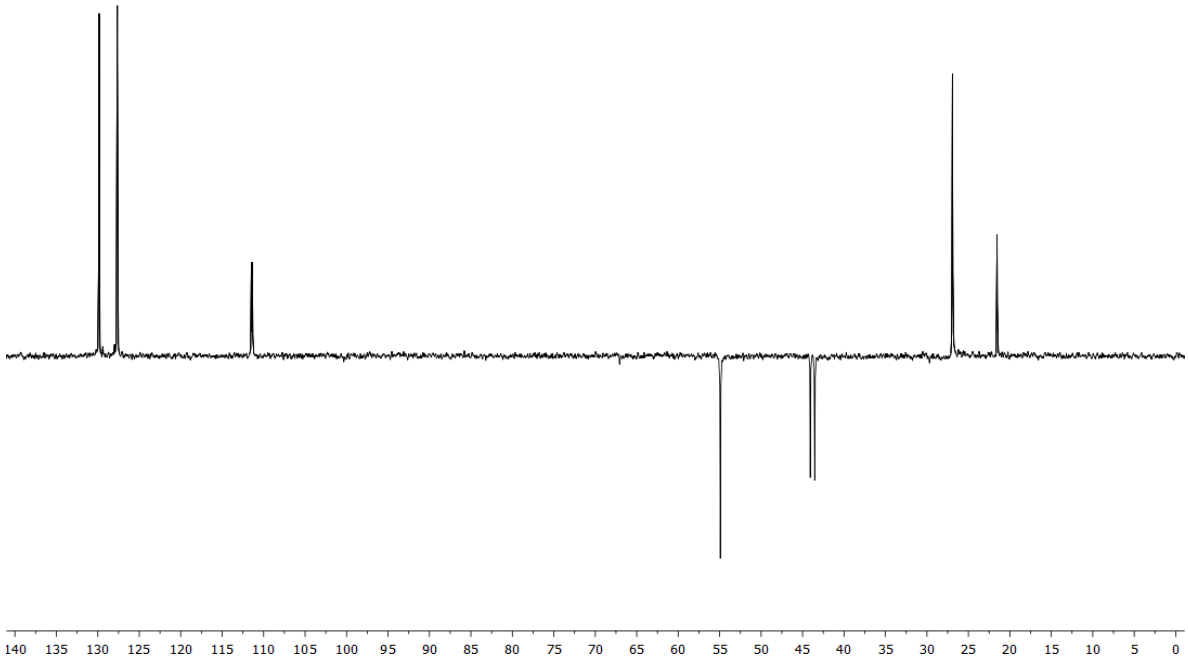
5-Fluoro-3,3-dimethyl-1-tosyl-1,2,3,6-tetrahydropyridine (4o)



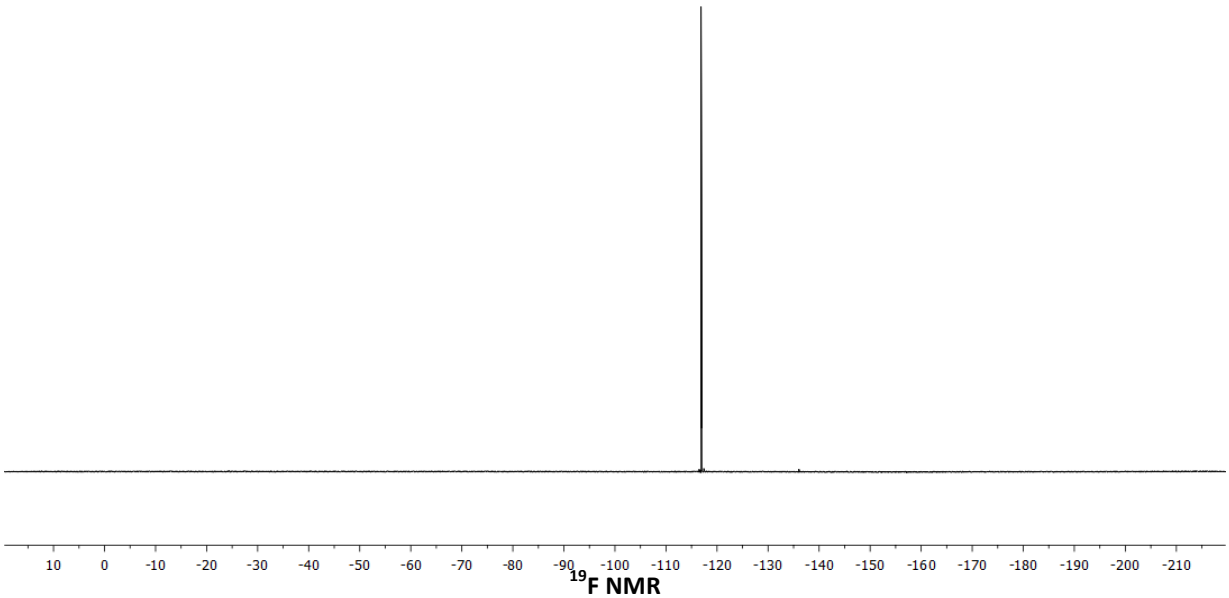
^{1}H NMR



^{13}C NMR

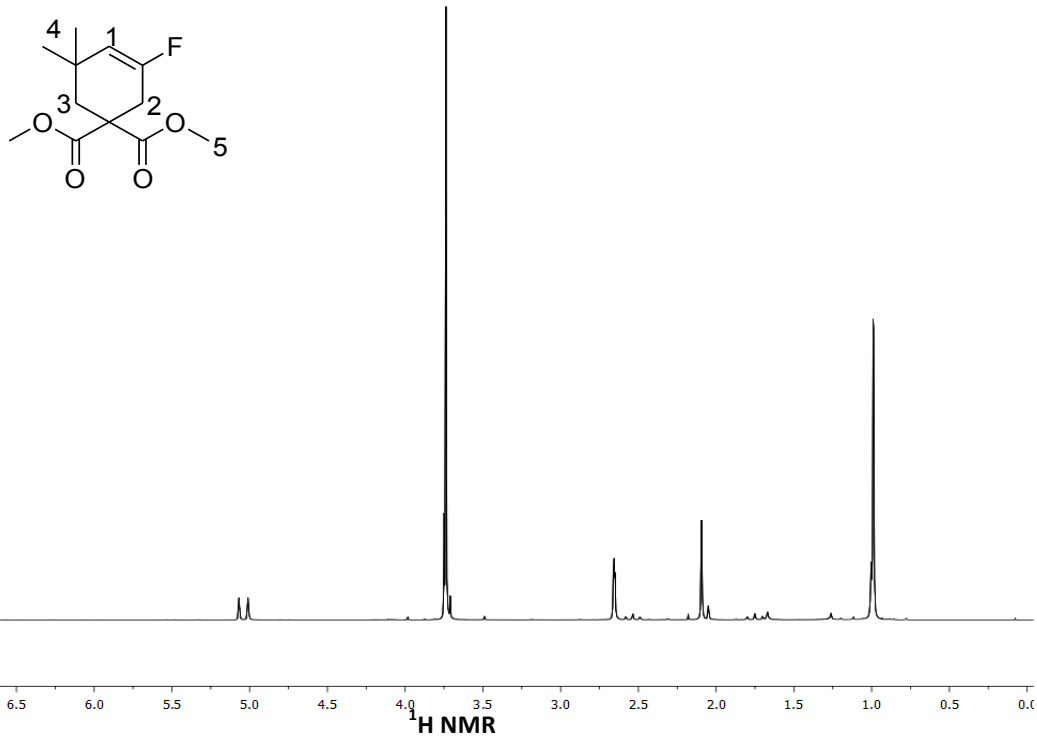


DEPT-135

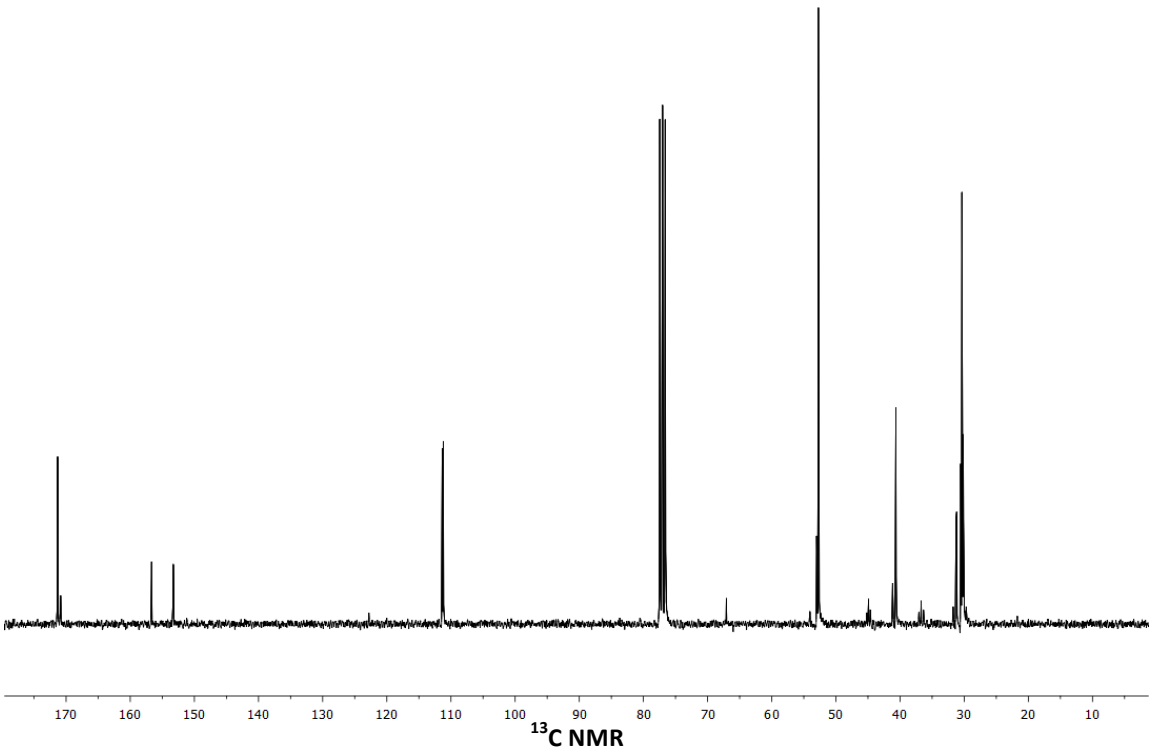


^{19}F NMR

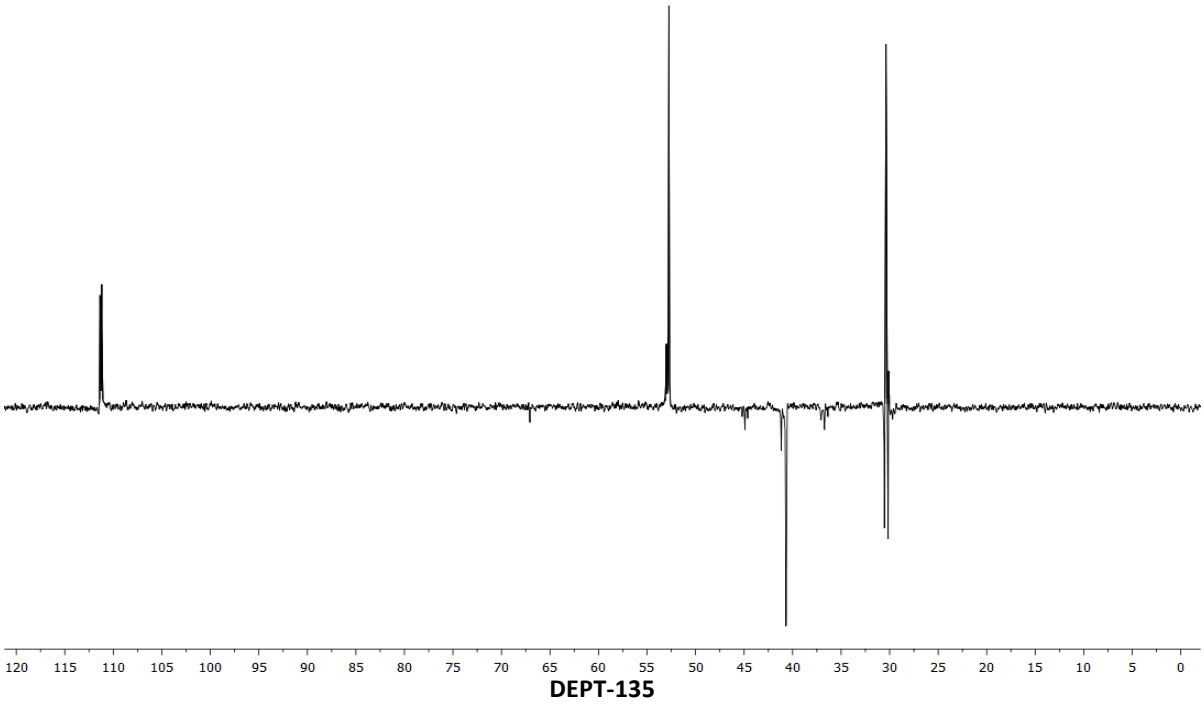
Dimethyl-3-fluoro-5,5-dimethylcyclohex-3-ene-1,1-dicarboxylate (4p)



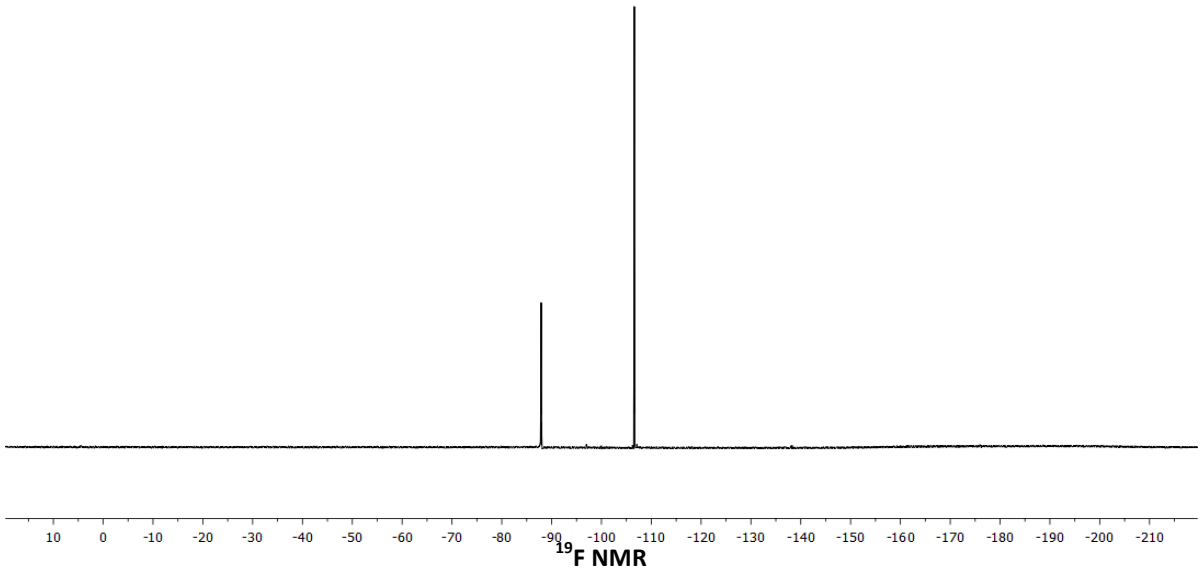
^{1}H NMR



^{13}C NMR

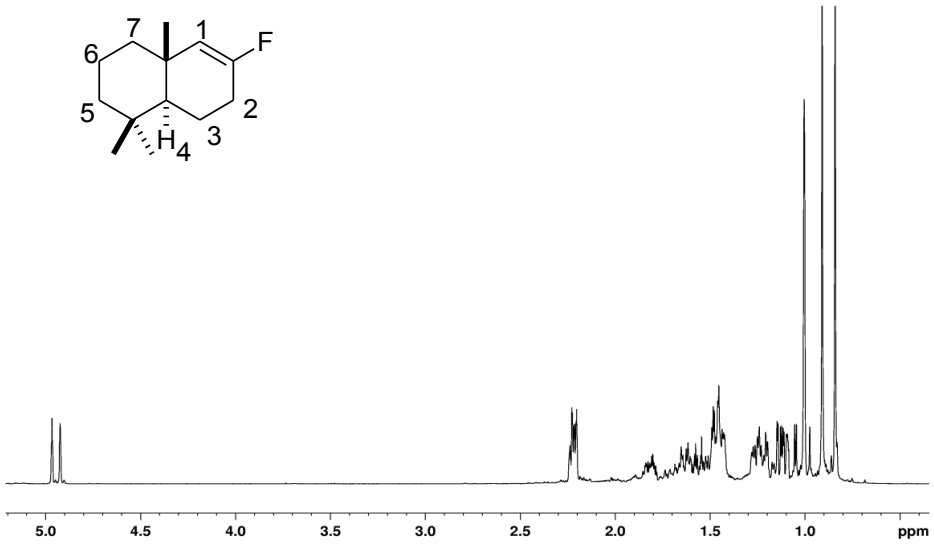


DEPT-135

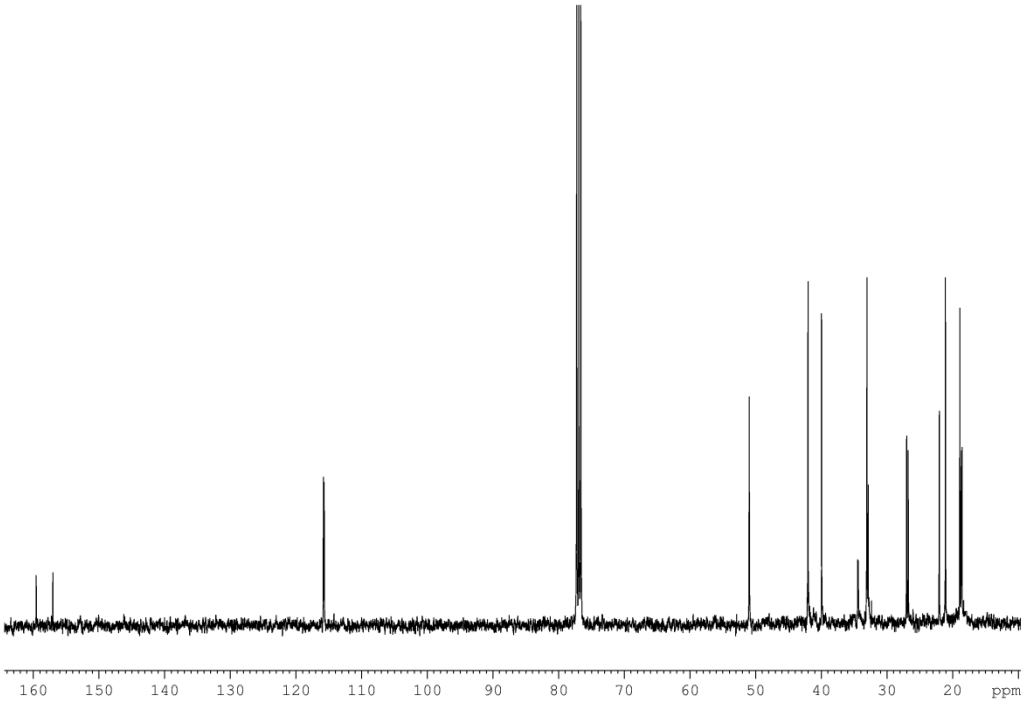


^{19}F NMR

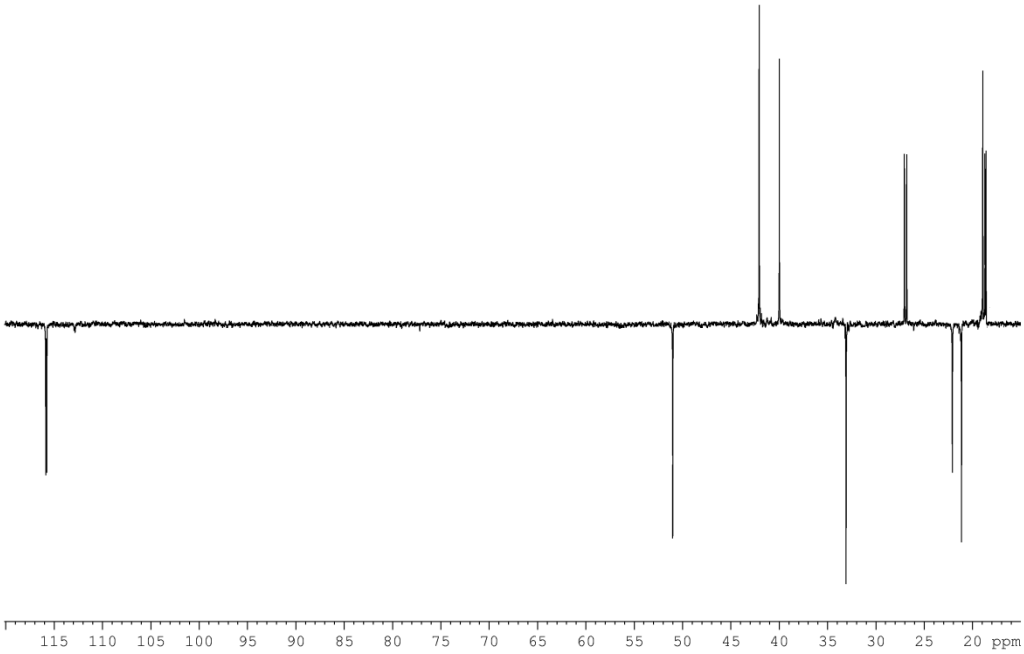
(4a*S,8a*S**)-7-Fluoro-4,4,8a-trimethyl-1,2,3,4,4a,5,6,8a-octahydronaphthalene (7a)**



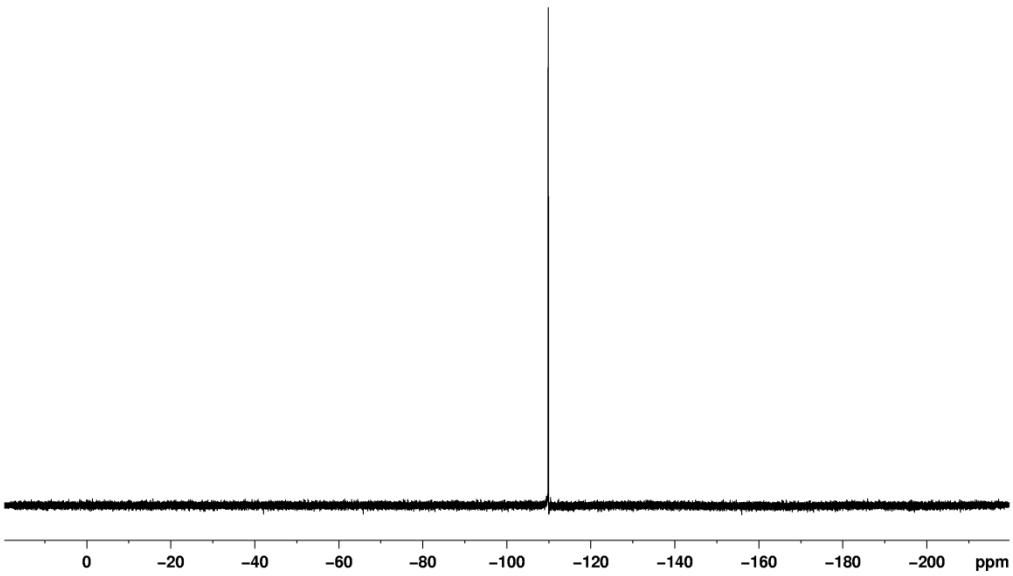
^{1}H NMR



^{13}C NMR

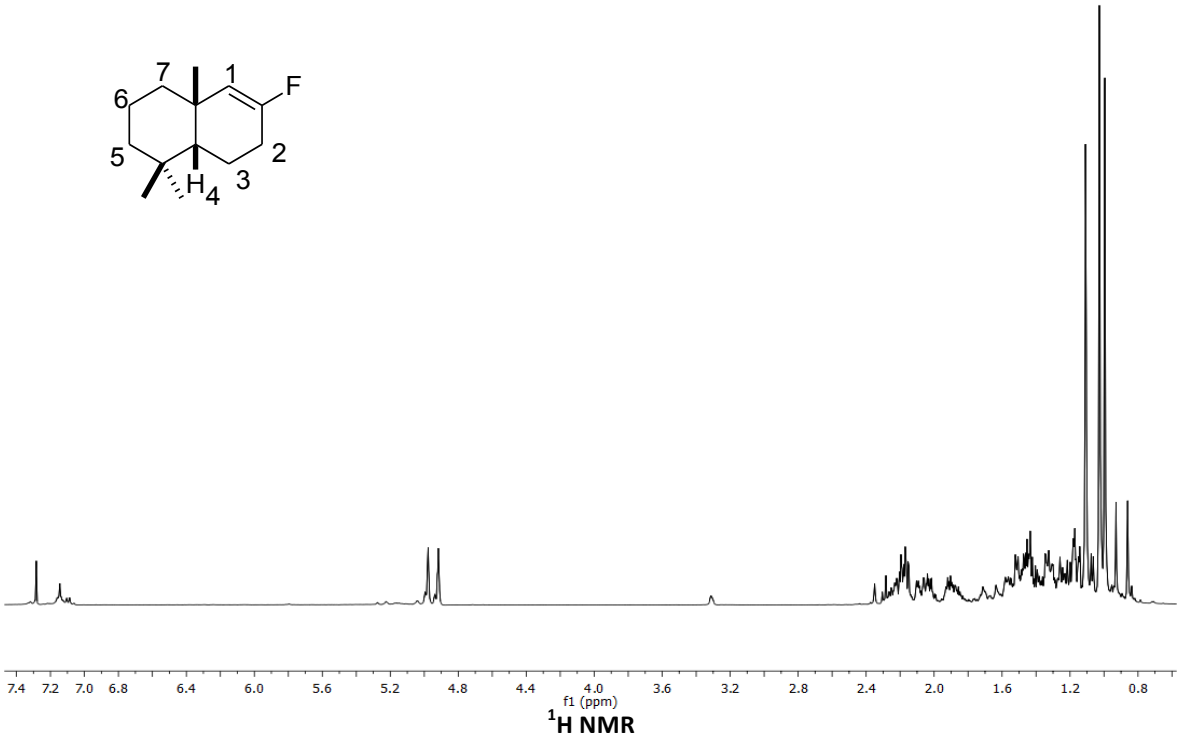


DEPT-135

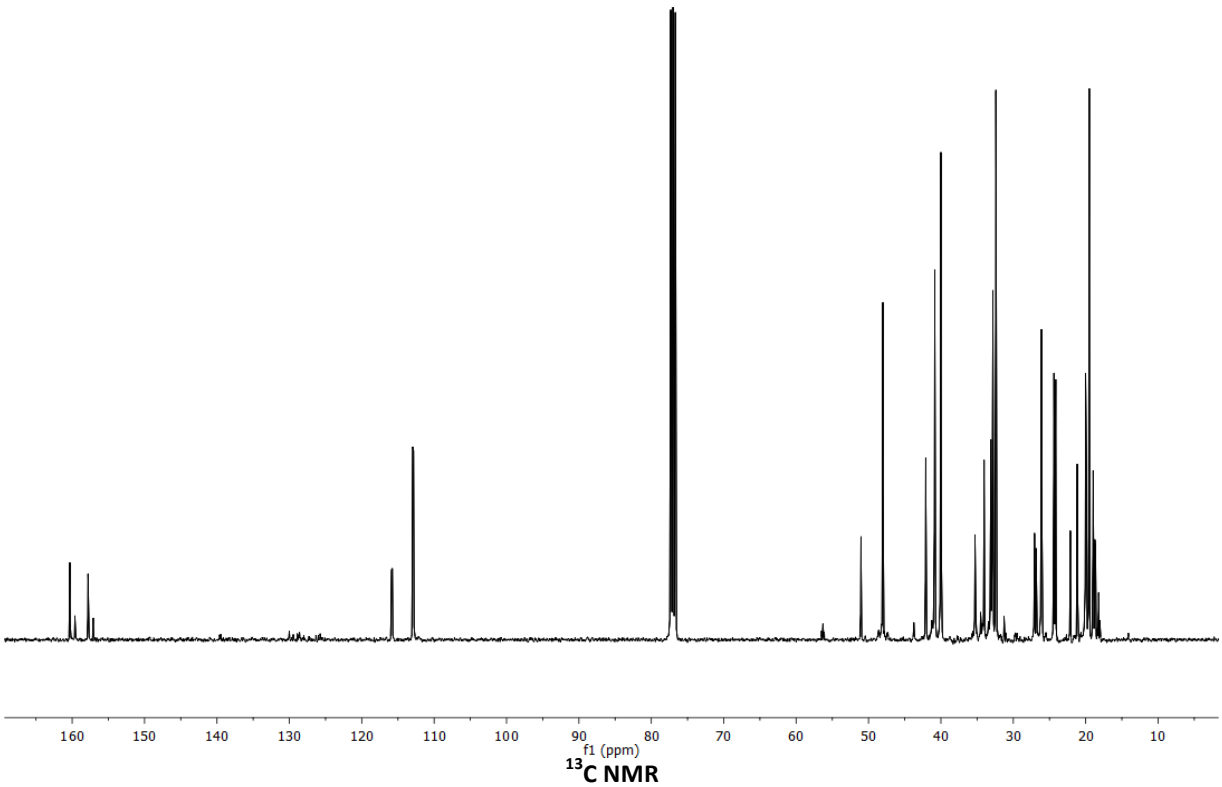


^{19}F NMR

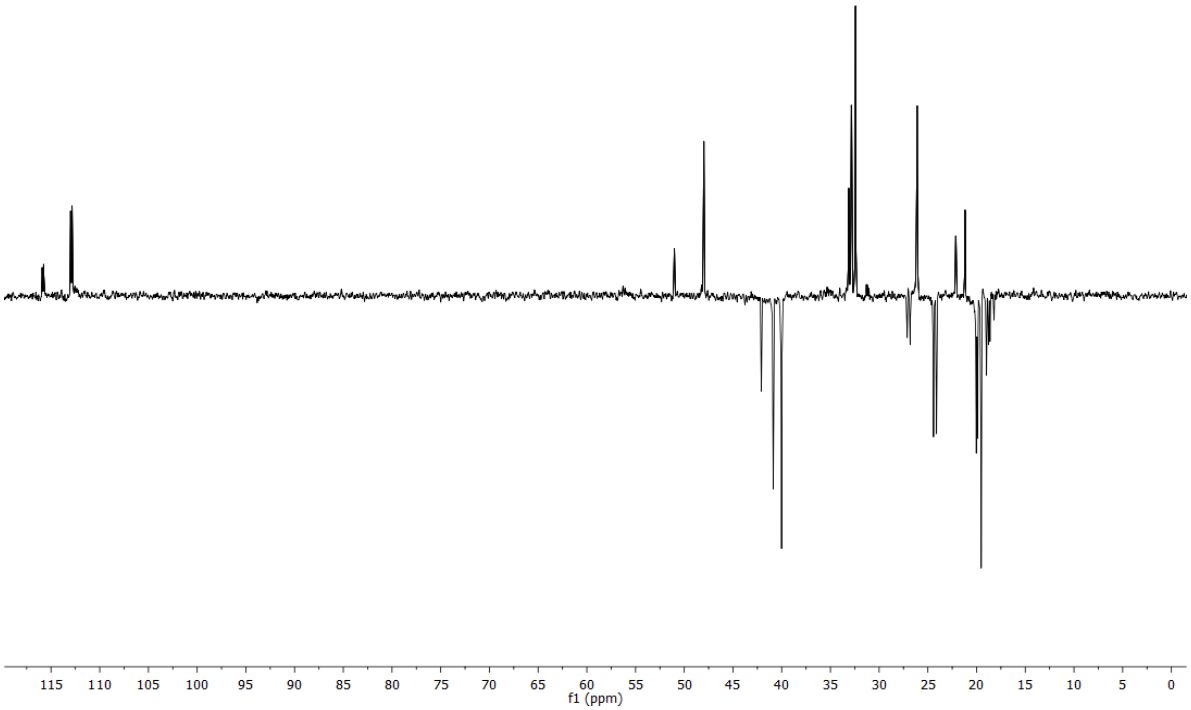
(4a*R,8a*S**)-7-Fluoro-4,4,8a-trimethyl-1,2,3,4,4a,5,6,8a-octahydronaphthalene (*diast*-7a)**



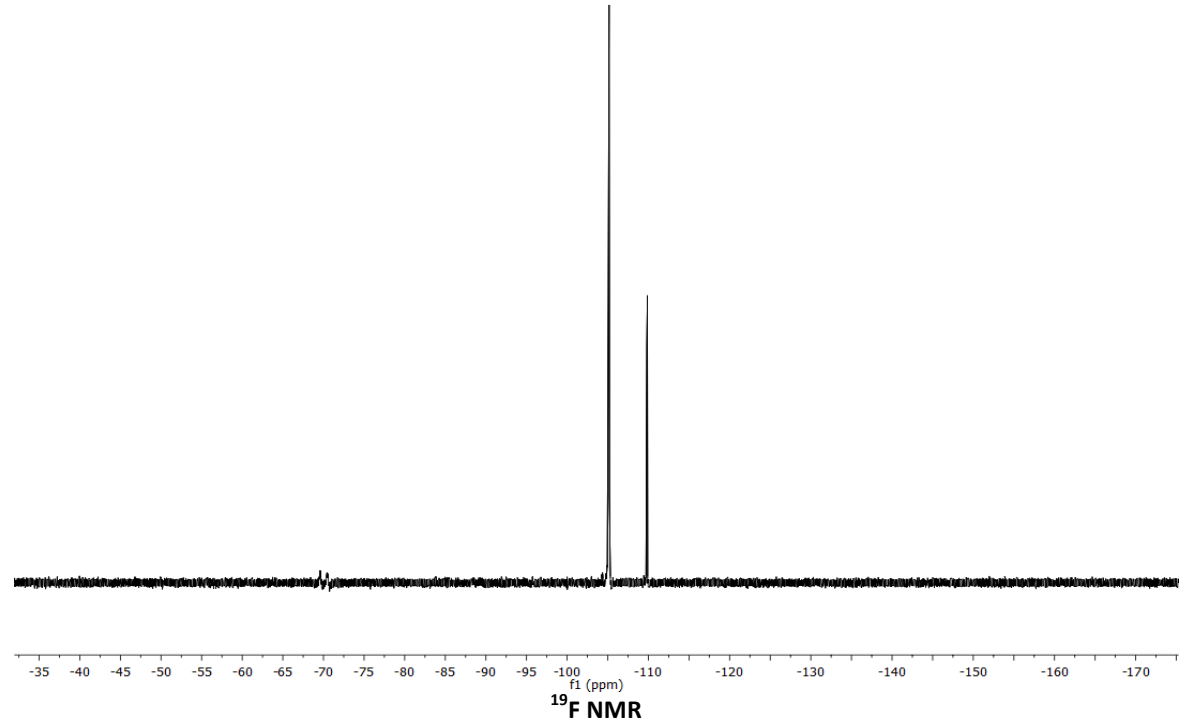
^{1}H NMR



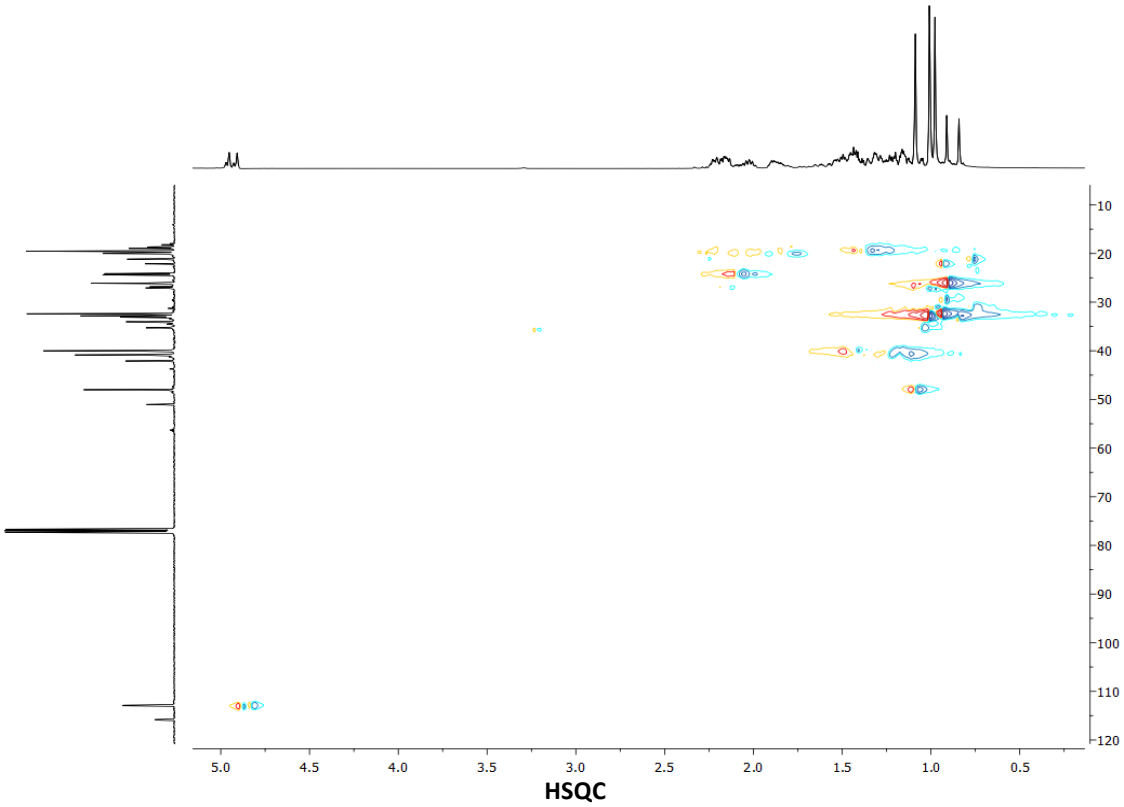
^{13}C NMR



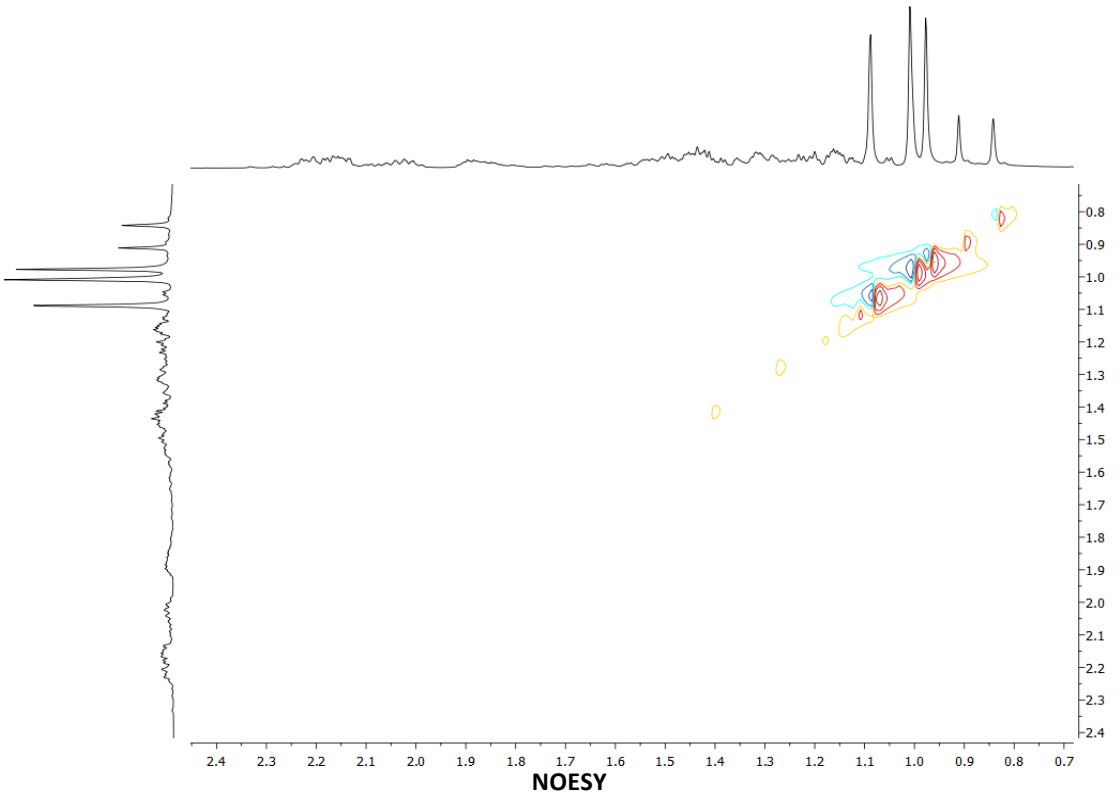
DEPT-135



^{19}F NMR


10
20
30
40
50
60
70
80
90
100
110
120
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5

HSQC


0.8
0.9
1.0
1.1
1.2
1.3
1.4
1.5
1.6
1.7
1.8
1.9
2.0
2.1
2.2
2.3
2.4
2.4
2.3
2.2
2.1
2.0
1.9
1.8
1.7
1.6
1.5
1.4
1.3
1.2
1.1
1.0
0.9
0.8
0.7

NOESY