

# Copper Ferrite Nanoparticles Catalyzed Challenging Diels-Alder Reaction of Aromatic Chalcones with Cyclopentadiene

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## 1. EXPERIMENTAL SECTION

### 1.1 Materials & Methods

Cyclopentadiene, isoprene and metal ferrites ( $\text{CuFe}_2\text{O}_4$ , particle size  $<100$  nm;  $\text{CoFe}_2\text{O}_4$ , particle size = 30 nm) were purchased from Sigma Aldrich. All the other metal salts were purchased from AVRA and were used as such without further purification. Chalcones were synthesized as per the procedure reported in literature.<sup>1,2</sup> Solvents were dried and purified according to standard procedures before use. Melting points were obtained on a Thomas-Hoover apparatus in open capillaries and are uncorrected. FTIR spectra were recorded using Bruker alpha Eco-ATR spectrometer in the spectral region of  $4000\text{-}650\text{ cm}^{-1}$ .  $^1\text{H-NMR}$  spectra were recorded on Bruker Avance Neo 500 MHz spectrometer in  $\text{CDCl}_3$  solvent. Spectroscopic data are represented as follows: chemical shift (ppm), multiplicity (s = singlet, d = doublet, t = triplet, dd = doublet of doublets m = multiplet, br = broad singlet, ddd = doublet of doublet of doublet, dddd = doublet of doublet of doublet of doublet, td = triplet of doublet, dt = doublet of triplet, qd = quartet of doublet), integration, coupling constants in Hertz (Hz).  $^{13}\text{C}$  NMR spectra were recorded at 125 MHz in  $\text{CDCl}_3$  relative to trimethylsilane as internal standard. Crude products were isolated and purified by column chromatography over 230-400 mesh size silica gel using hexane:ethyl acetate as eluents. The progress of the reaction was monitored by thin layer chromatography (TLC) on silica coated aluminum plates F<sub>254</sub> and visualized under UV chamber.

### 1.2 Characterization Data

Phenyl(3-phenylbicyclo[2.2.1]hept-5-en-2-yl)methanone (**3a**)

**Results:** 89% yield, pale-yellow oily liquid, dr = 65:35 (*endo:exo*); **IR (ATR):**  $\nu_{\text{max}}$  3058, 3022, 2992, 2970, 1668, 1596, 1447, 1333, 1215, 1014, 745, 692, 665  $\text{cm}^{-1}$ ;  **$^1\text{H-NMR}$  (500 MHz,  $\text{CDCl}_3$ ):**  $\delta$  7.96-7.92 (m, 1.36H (*endo*)), 7.91-7.88 (m, 0.70H (*exo*)), 7.56-7.49 (m, 1H), 7.46-7.37 (m, 2H), 7.31-7.27 (m, 3H), 7.25-7.15 (m, 2H), 6.49-6.46 (m, 1H), 6.17 (dd,  $J = 2.5$  Hz, 5.5 Hz, 0.35H (*exo*)), 5.87 (dd,  $J = 3.0$  Hz, 6.0 Hz, 0.65H (*endo*)), 3.91 (dd,  $J = 3.5$  Hz, 5.0 Hz, 1H), 3.47 (dd,  $J = 1.5$  Hz, 5.0 Hz, 0.65H (*endo*)), 3.44 (dd,  $J = 1.5$  Hz, 5.0 Hz, 0.35H (*exo*)), 3.34 (s, 0.65H

(endo)), 3.18 (s, 0.35H (exo)), 3.11-3.15 (m, 1H), 2.03 (d,  $J = 8.5$  Hz, 0.65H (endo)), 1.90 (d,  $J = 8.5$  Hz, 0.35H (exo)), 1.65 (dq,  $J = 2.0, 8.5$  Hz, 0.65H (endo)), 1.54 (dq,  $J = 1.5$  Hz, 8.5 Hz, 0.35H (exo)) ppm;  $^{13}\text{C NMR}$  (125 MHz,  $\text{CDCl}_3$ ):  $\delta$  201.3, 200.1, 144.8, 143.6, 139.3, 137.3, 137.0, 136.9, 136.6, 133.1, 133.0, 132.9, 128.7, 128.6, 128.5, 128.2, 128.1, 127.6, 126.3, 126.1, 56.3, 54.6, 49.0, 48.9, 48.7, 48.6, 48.1, 47.9, 47.8, 45.9 ppm.

#### 4-Fluorophenyl-(3-phenylbicyclo[2.2.1]hept-5-en-2-yl)methanone (**3b**)

**Results:** 68% yield, colorless oily liquid, dr = 70:30 (endo:exo); **IR (ATR):**  $\nu_{\text{max}}$  3059, 3027, 2986, 1676, 1495, 1454, 1333, 1219, 1016, 834, 746, 700  $\text{cm}^{-1}$ ;  **$^1\text{H-NMR}$  (500 MHz,  $\text{CDCl}_3$ ):**  $\delta$  8.12 (dd,  $J = 5.5$  Hz, 8.5 Hz, 1.47H (endo)), 8.05 (dd,  $J = 5.5$  Hz, 8.5 Hz, 0.63H (exo)), 7.48-7.38 (m, 4H), 7.37-7.29 (m, 1H), 7.26 (t,  $J = 8.5$  Hz, 1.39H (endo)), 7.20 (t,  $J = 8.5$  Hz, 0.66H (exo)), 6.63 (dd,  $J = 3.0$  Hz, 5.0 Hz, 1H), 6.33 (dd,  $J = 3.0$  Hz, 5.5 Hz, 0.30H (exo)), 6.04 (dd,  $J = 2.5$  Hz, 5.5 Hz, 0.70H (endo)), 4.02 (dd,  $J = 3.5$  Hz, 5.0 Hz, 0.70H (endo)), 3.99 (dd,  $J = 5.0$  Hz, 8.5 Hz, 0.30H (exo)), 3.60 (d,  $J = 4.0$  Hz, 0.70H (endo)), 3.53 (d,  $J = 4.5$  Hz, 0.30H (exo)), 3.49 (s, 0.70H (endo)), 3.32 (s, 0.30H (exo)), 3.29 (s, 0.30H), 3.28 (s, 0.70H), 2.19 (d,  $J = 8.5$  Hz, 0.70H (endo)), 2.05 (d,  $J = 9.0$  Hz, 0.30H (exo)), 1.82 (dd,  $J = 1.5$  Hz, 8.5 Hz, 0.70H (endo)), 1.72 (dd,  $J = 1.0$  Hz, 8.5 Hz, 0.30H (exo)) ppm;  $^{13}\text{C NMR}$  (125 MHz,  $\text{CDCl}_3$ ):  $\delta$  199.8, 198.5, 165.7(d,  $J = 250$  Hz) 165.7(d,  $J = 250$  Hz), 144.6, 143.4, 139.4, 137.0, 136.6, 133.7 (d,  $J = 2.5$  Hz), 133.4 (d,  $J = 2.5$  Hz), 133.0, 131.2 (d,  $J = 10.0$  Hz), 131.0 (d,  $J = 10.0$  Hz), 128.7, 128.3, 128.1, 127.6, 126.5, 126.2, 115.7(d,  $J = 12.5$  Hz), 115.7 (d,  $J = 15$  Hz), 115.6, 115.6, 56.3, 54.6, 49.1, 48.8, 48.7, 48.7, 48.2, 48.1, 46.2 ppm.

#### 4-Chlorophenyl-(3-phenylbicyclo[2.2.1]hept-5-en-2-yl)methanone (**3c**)

**Results:** 70% yield, colorless oily liquid, dr = 75:25 (endo:exo); **IR (ATR):**  $\nu_{\text{max}}$  3058, 3022, 2992, 2970, 1668, 1596, 1447, 1214, 1014, 745, 692, 665  $\text{cm}^{-1}$ ;  **$^1\text{H-NMR}$  (500 MHz,  $\text{CDCl}_3$ ):**  $\delta$  7.85 (d,  $J = 8.5$  Hz, 1.56H (endo)), 7.78 (d,  $J = 8.5$  Hz, 0.53H (exo)), 7.38 (d,  $J = 8.5$  Hz, 1.57H (endo)), 7.33 (d,  $J = 8.5$  Hz, 0.59H (exo)), 7.30-7.11 (m, 5H), 6.45 (dd,  $J = 3.5$  Hz, 5.0 Hz, 1H), 6.15 (dd,  $J = 2.5$  Hz, 5.5 Hz, 0.25H (exo)), 5.86 (dd,  $J = 2.5$  Hz, 5.5 Hz, 0.75H (endo)), 3.84 (dd,  $J = 3.5$  Hz, 5.0 Hz, 0.75H (endo)), 3.81 (dd,  $J = 4.0$  Hz, 5.0 Hz, 0.25H (exo)), 3.42 (d,  $J = 4.0$  Hz, 0.75H (endo)), 3.35 (d,  $J = 4.5$  Hz, 0.25H (exo)), 3.30 (s, 0.75H (endo)), 3.15 (s, 0.25H (exo)), 3.12 (s, 0.25H), 3.10 (s, 0.75H), 2.01 (d,  $J = 8.5$  Hz, 0.75H

(endo)), 1.86 (d,  $J = 8.5$  Hz, 0.25H (*exo*)), 1.64 (dd,  $J = 8.5$  Hz, 1.0 Hz, 0.75H (*endo*)), 1.54 (dd,  $J = 8.5$  Hz, 1.5 Hz, 0.25H (*exo*)) ppm;  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ ):  $\delta$  200.6, 199.3, 144.9, 143.7, 139.9, 139.8, 139.7, 137.4, 137.0, 136.0, 135.7, 133.4, 130.4, 130.3, 129.4, 129.3, 129.1, 128.7, 128.5, 128.0, 126.9, 126.6, 56.7, 49.1, 49.0, 48.6, 48.5, 46.5 ppm.

#### 4-Bromophenyl(3-phenylbicyclo[2.2.1]hept-5-en-2-yl)methanone (3d)

**Results:** 68% yield, colorless oily liquid, dr = 75:25 (*endo:exo*); **IR (ATR):**  $\nu_{\text{max}}$  3057, 3025, 2966, 1740, 1674, 1451, 1366, 1221, 1013, 797, 718, 699  $\text{cm}^{-1}$ ;  **$^1\text{H}$ -NMR (500 MHz,  $\text{CDCl}_3$ ):**  $\delta$  7.78 (dd,  $J = 2.0$  Hz, 7.0 Hz, 1.60H (*endo*)), 7.72 (dd,  $J = 2.0$  Hz, 7.0 Hz, 0.57H (*exo*)), 7.56 (dd,  $J = 2.0$  Hz, 6.5 Hz, 1.54H (*endo*)), 7.51 (dd,  $J = 1.5$  Hz, 6.5 Hz, 0.52H (*exo*)), 7.32-7.27 (m, 3H), 7.25-7.12 (m, 2H), 6.48-6.44 (m, 1H), 6.16 (dd,  $J = 3.0$  Hz, 5.5 Hz, 0.25H (*exo*)), 5.87 (dd,  $J = 3.0$  Hz, 6.0 Hz, 0.75H (*endo*)), 3.84 (dd,  $J = 3.5$  Hz, 5.0 Hz, 0.75H (*endo*)), 3.81 (dd,  $J = 5.0$  Hz, 3.5 Hz, 0.25H (*exo*)), 3.43 (d,  $J = 3.5$  Hz, 0.75H (*endo*)), 3.35 (dd,  $J = 1.5$  Hz, 5.5 Hz, 0.25H (*exo*)), 3.31 (s, 0.75H (*endo*)), 3.16 (s, 0.25H (*exo*)), 3.12 (s, 0.25H (*exo*)), 3.11 (s, 0.75H (*endo*)), 2.02 (d,  $J = 8.5$  Hz, 0.75H (*endo*)), 1.87 (d,  $J = 8.5$  Hz, 0.25H (*exo*)), 1.65 (dd,  $J = 1.5$  Hz, 8.5 Hz, 0.75H (*endo*)), 1.55 (dd,  $J = 2.0$  Hz, 9.0 Hz, 0.25H (*exo*)) ppm;  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ ):  $\delta$  200.3, 199.1, 144.4, 143.2, 139.3, 136.9, 136.5, 135.9, 135.6, 132.9, 131.9, 131.8, 130.0, 129.9, 128.6, 128.2, 128.0, 127.9, 127.5, 126.4, 126.1, 56.2, 54.5, 49.0, 48.7, 48.6, 48.5, 48.2, 48.1, 48.0, 46.1 ppm.

#### (3-Phenylbicyclo[2.2.1]hept-5-en-2-yl)(*p*-tolyl)methanone (3e)

**Results:** 52% yield, yellow oily liquid, dr = 70:30 (*endo:exo*); **IR (ATR):**  $\nu_{\text{max}}$  3060, 3024, 2967, 1668, 1598, 1455, 1330, 1256, 1219, 1019, 836, 745, 715  $\text{cm}^{-1}$ ;  **$^1\text{H}$ -NMR (500 MHz,  $\text{CDCl}_3$ ):**  $\delta$  7.84 (d,  $J = 8.0$  Hz, 1.47H (*endo*)), 7.79 (d,  $J = 8.5$  Hz, 0.64H (*exo*)), 7.31-7.15 (m, 7H), 6.46 (dd,  $J = 4.0$  Hz, 7.5 Hz, 1H), 6.16 (dd,  $J = 3.0$  Hz, 5.5 Hz, 0.30H (*exo*)), 5.87 (dd,  $J = 2.5$  Hz, 5.5 Hz, 0.70H (*endo*)), 3.93-3.87 (m, 1H), 3.48 (d,  $J = 3.5$  Hz, 0.70H (*endo*)), 3.41 (d,  $J = 4.5$  Hz, 0.30H (*exo*)), 3.33 (s,  $J = 4.5$  Hz, 0.70H (*endo*)), 3.17 (s, 0.30H (*exo*)), 3.12 (s, 1H), 2.40 (s, 2H,  $\text{CH}_3$  (*endo*)), 2.38 (s, 1H,  $\text{CH}_3$  (*exo*)), 2.02 (d,  $J = 8.0$  Hz, 0.70H (*endo*)), 1.90 (d,  $J = 8.5$  Hz, 0.30H (*exo*)), 1.64 (dd,  $J = 1.5$  Hz, 8.0 Hz, 1.06H (*endo*)),

1.53 (dd,  $J = 1.0$  Hz, 8.5 Hz, 0.48H (*exo*)) ppm;  $^{13}\text{C NMR}$  (125 MHz,  $\text{CDCl}_3$ ):  $\delta$  199.7, 198.4, 163.3, 139.0, 130.7, 128.5, 128.2, 128.1, 127.5, 125.9, 113.8, 113.7, 55.8, 55.5, 48.8, 48.5, 45.9, 32.0, 27.1, 26.4, 24.2 ppm.

4-Methoxyphenyl(3-phenylbicyclo[2.2.1]hept-5-en-2-yl)methanone (**3f**)

**Results:** 62% yield, yellow oily liquid, dr = 92:8 (*endo:exo*); **IR (ATR):**  $\nu_{\text{max}}$  3023, 2954, 2925, 1740, 1669, 1603, 1449, 1367, 1223, 1017, 817, 746, 698  $\text{cm}^{-1}$ ;  **$^1\text{H-NMR}$  (500 MHz,  $\text{CDCl}_3$ ):**  $\delta$  7.93 (dt,  $J = 3.0$  Hz, 10.0 Hz, 1.90H (*endo*)) 7.86 (dd,  $J = 2.0$  Hz, 7.0 Hz, 0.18H (*exo*)), 7.31-7.25 (m, 4H), 7.23-7.15 (m, 1H), 6.90 (dd,  $J = 2.0$  Hz, 7.0 Hz, 1.90H (*endo*)), 6.85 (dd,  $J = 2.5$  Hz, 7.0 Hz, 0.21H (*exo*)), 6.47-6.44 (m, 1H), 6.16 (dd,  $J = 2.5$  Hz, 5.5 Hz, 0.08H (*exo*)), 5.88 (dd,  $J = 2.5$  Hz, 5.5 Hz, 0.92H (*endo*)), 3.88-3.84 (m, 4H), 3.46 (dd,  $J = 2.0$  Hz, 5.0 Hz, 0.92H (*endo*)), 3.38 (dd,  $J = 1.5$  Hz, 5.5 Hz, 0.08H (*exo*)), 3.32 (s, 0.92H (*endo*)), 3.16 (s, 0.08H (*exo*)), 3.13-3.10 (m, 1H), 2.02 (d,  $J = 10.0$  Hz, 1H), 1.63 (dd,  $J = 1.5$  Hz, 8.5 Hz, 1H) ppm;  $^{13}\text{C NMR}$  (125 MHz,  $\text{CDCl}_3$ ):  $\delta$  198.5, 193.4, 163.4, 144.9, 139.1, 133.1, 130.8, 130.7, 130.3, 128.6, 127.6, 126.0, 113.8, 55.9, 55.6, 48.8, 48.6, 48.1, 46.0 ppm.

(3-(4-Fluorophenyl)bicyclo[2.2.1]hept-5-en-2-yl)(phenyl)methanone (**3g**)

**Results:** 58% yield, colorless oily liquid, dr = 55:45 (*endo:exo*); **IR (ATR):**  $\nu_{\text{max}}$  3059, 3027, 2986, 1676, 1495, 1454, 1333, 1219, 1016, 834, 746, 700  $\text{cm}^{-1}$ ;  **$^1\text{H-NMR}$  (500 MHz,  $\text{CDCl}_3$ ):**  $\delta$  7.93 (dd,  $J = 1.5$  Hz, 8.5 Hz, 1H (*endo*)), 7.88 (dd,  $J = 1.5$  Hz, 8.5 Hz, 1H (*exo*)), 7.57-7.52 (m, 1H), 7.47-7.39 (m, 2H), 7.24-7.21 (m, 1H), 7.00-6.90 (m, 2H), 6.50-6.44 (m, 1H), 6.15 (dd,  $J = 3.0$  Hz, 5.5 Hz, 0.45H (*exo*)), 5.87 (dd,  $J = 3.0$  Hz, 5.5 Hz, 0.55H (*endo*)), 3.88 (dd,  $J = 3.5$  Hz, 5.0 Hz, 0.45H (*exo*)), 3.84 (dd,  $J = 3.5$  Hz, 5.0 Hz, 0.55H (*endo*)), 3.45 (d,  $J = 4.0$  Hz, 0.55H (*endo*)), 3.38 (dd,  $J = 1.5$  Hz, 5.5 Hz, 0.45H (*exo*)), 3.35 (s, 0.55H (*endo*)), 3.15-3.13 (m, 1H), 3.08 (s, 0.55H (*endo*)), 2.00 (d,  $J = 8.5$  Hz, 0.55H (*endo*)), 1.88 (d,  $J = 9.0$  Hz, 0.45H (*exo*)), 1.66 (dd,  $J = 1.5$  Hz, 10.0 Hz, 0.55H (*endo*)), 1.54 (dd,  $J = 1.5$  Hz, 3.5 Hz, 0.45H (*exo*)) ppm;  $^{13}\text{C NMR}$  (125 MHz,  $\text{CDCl}_3$ ):  $\delta$  201.1, 200.0, 140.4, 139.2, 136.9, 136.8, 136.7, 133.1, 133.0 (d,  $J = 2.5$  Hz), 129.5, 129.4, 128.9, 128.9, 128.7 (d,  $J = 10.0$  Hz), 128.6, 128.4, 115.4, 115.3, 115.0, 114.9, 56.5, 54.9, 49.0, 48.8, 48.7, 48.1, 48.0, 47.0, 45.2 ppm.

(3-(4-Chlorophenyl)bicyclo[2.2.1]hept-5-en-2-yl)(phenyl)methanone (**3h**)

**Results:** 55% yield, yellow oily liquid, dr = 65:35 (*endo:exo*); **IR (ATR):**  $\nu_{\max}$  2958, 2923, 1735, 1678, 1451, 1258, 1013, 793, 731, 695  $\text{cm}^{-1}$ ;  **$^1\text{H-NMR}$  (500 MHz,  $\text{CDCl}_3$ ):**  $\delta$  7.92 (dd,  $J = 1.5$  Hz, 8.5 Hz, 1.30H (*endo*)), 7.88 (dd,  $J = 1.5$  Hz, 8.5 Hz, 0.72H (*exo*)), 7.68- 7.51 (m, 1H), 7.47-7.39 (m, 2H), 7.25-7.18 (m, 3.49H), 7.08 (d,  $J = 8.0$  Hz, 0.70H), 6.50-6.43 (m, 1H), 6.14-6.12 (m, 0.35H (*exo*)), 5.86 (dd,  $J = 3.0$  Hz, 5.5 Hz, 0.65H (*endo*)), 3.88 (dd,  $J = 3.5$  Hz, 5.0 Hz, 0.35H), 3.83 (dd,  $J = 3.0$  Hz, 4.5 Hz, 0.65H (*endo*)), 3.44 (dd,  $J = 1.5$  Hz, 5.0 Hz, 0.65H (*endo*)), 3.37 (dd,  $J = 1.5$  Hz, 5.5 Hz, 0.35H (*exo*)), 3.34 (s, 0.65H), 3.14 (m, 0.70H (*exo*)), 3.09-3.07 (m, 0.65H), 1.96 (d,  $J = 8.5$  Hz, 0.65H (*endo*)), 1.87 (d,  $J = 9.0$  Hz, 0.35H (*exo*)), 1.65 (dd,  $J = 3.5$  Hz, 8.5 Hz 0.65H (*endo*)), 1.54 (dd,  $J = 1.5$  Hz, 8.5 Hz, 0.35H (*exo*)) ppm;  **$^{13}\text{C NMR}$  (125 MHz,  $\text{CDCl}_3$ ):**  $\delta$  200.9, 199.8, 143.3, 142.1, 139.2, 137.2, 136.9, 136.6, 133.1, 133.0, 133.0, 132.0, 131.8, 129.4, 128.9, 128.7, 128.5, 128.4, 128.3, 56.4, 54.6, 49.0, 48.9, 48.7, 48.5, 48.1, 47.9, 47.1, 45.3 ppm.

(3-(4-Bromophenyl)bicyclo[2.2.1]hept-5-en-2-yl)(phenyl)methanone (**3i**)

**Results:** 65% yield, yellow oily liquid, dr = 65:35 (*endo:exo*); **IR (ATR):**  $\nu_{\max}$  3061, 2968, 2927, 1676, 1595, 1448, 1330, 1259, 1214, 1011, 818, 759, 724, 692  $\text{cm}^{-1}$ ;  **$^1\text{H-NMR}$  (500 MHz,  $\text{CDCl}_3$ ):**  $\delta$  7.93 (dd,  $J = 1.0$  Hz, 8.0 Hz, 1.33H (*endo*)), 7.89 (dd,  $J = 1.5$  Hz, 8.5 Hz, 0.72H (*exo*)), 7.57-7.51 (m, 1H), 7.47-7.33 (m, 4H), 7.14 (dd,  $J = 1.0$  Hz, 6.5 Hz 1.30H), 7.03 (dd,  $J = 2.5$  Hz, 9.5 Hz, 0.70H), 6.48 (dd,  $J = 3.5$  Hz, 5.5 Hz, 0.35H (*exo*)), 6.45 (dd,  $J = 3.5$  Hz, 6.0 Hz, 0.65H (*endo*)), 6.13 (dd,  $J = 3.0$  Hz, 5.5 Hz, 0.35H (*exo*)), 5.86 (dd,  $J = 3.0$  Hz, 6.0 Hz, 0.65H (*endo*)), 3.87 (dd,  $J = 3.5$  Hz, 5.0 Hz, 0.35H (*exo*)), 3.83 (dd,  $J = 3.5$  Hz, 5.0 Hz, 0.65H (*endo*)), 3.44 (d,  $J = 3.5$  Hz, 0.65H (*endo*)), 3.38 (dd,  $J = 1.5$  Hz, 5.5 Hz, 0.35H (*exo*)), 3.35 (s, 0.70H (*exo*)), 3.14 (dd,  $J = 1.5$  Hz, 3.0 Hz, 0.70H (*exo*)), 3.08 (d,  $J = 1.5$  Hz, 0.65H (*endo*)), 1.97 (d,  $J = 8.5$  Hz, 0.65H (*endo*)), 1.88 (d,  $J = 8.5$  Hz, 0.35H (*exo*)), 1.66 (dq,  $J = 1.5$  Hz, 8.5 Hz, 0.65H (*endo*)), 1.54 (dq,  $J = 1.5$  Hz, 8.5 Hz, 0.35H (*exo*)) ppm;  **$^{13}\text{C NMR}$  (125 MHz,  $\text{CDCl}_3$ ):**  $\delta$  200.7, 199.7, 143.7, 142.6, 139.1, 137.1, 136.8, 136.5, 133.0, 132.9, 131.6, 131.2, 129.7, 129.2, 128.6, 128.5, 128.3, 120.0, 119.7, 56.3, 54.5, 48.9, 48.8, 48.7, 48.3, 48.0, 47.8, 47.1, 45.3 ppm.

Phenyl-(3-(*p*-tolyl)bicyclo[2.2.1]hept-5-en-2-yl)methanone (**3j**)

**Results:** 58% yield, yellow oily liquid dr = 55:45 (*endo:exo*); **IR (ATR):**  $\nu_{\max}$  3058, 2970, 1676, 1596, 1448, 1329, 1209, 1016, 804, 760, 791, 664  $\text{cm}^{-1}$ ;  **$^1\text{H-NMR}$  (500 MHz,  $\text{CDCl}_3$ ):**  $\delta$  7.94 (dd,  $J = 1.0$  Hz, 8.0 Hz, 1.10H (*endo*)), 7.90 (dd,  $J = 1.0$  Hz, 8.0 Hz, 0.90H (*exo*)), 7.57-7.49 (m, 1H), 7.48-7.37 (m, 2H), 7.18 (d,  $J = 5.0$  Hz, 1H), 7.11 (d,  $J = 5.0$  Hz, 1H), 7.06 (s, 2H), 6.50 - 6.45 (m, 1H), 6.18 (dd,  $J = 3.0$  Hz, 5.5 Hz, 0.45H (*exo*)), 5.88 (dd,  $J = 2.5$  Hz, 8.5 Hz, 0.55H (*endo*)), 3.90 (dd,  $J = 3.5$  Hz, 5.0 Hz, 0.55H (*endo*)), 3.88 (dd,  $J = 3.0$  Hz, 5.0 Hz, 0.45H (*exo*)), 3.44 (d,  $J = 4.0$  Hz, 0.55H (*endo*)), 3.42 (dd,  $J = 1.0$  Hz, 5.0 Hz, 0.45H (*exo*)), 3.34 (s, 0.55H (*endo*)), 3.16 (s, 0.45H (*exo*)), 3.13 (s, 0.45H (*exo*)), 3.09 (d,  $J = 1.5$  Hz, 0.55H (*endo*)), 2.33 (s, 2H,  $\text{CH}_3$  (*endo*)), 2.31 (s, 1H,  $\text{CH}_3$  (*exo*)), 2.03 (d,  $J = 8.5$  Hz, 0.55H (*endo*)), 1.90 (d,  $J = 8.5$  Hz, 0.45H (*exo*)), 1.64 (dd,  $J = 1.5$  Hz, 8.5 Hz, 0.45H (*exo*)), 1.53 (dd,  $J = 1.5$  Hz, 8.5 Hz, 0.55H (*endo*)) ppm;  **$^{13}\text{C NMR}$  (125 MHz,  $\text{CDCl}_3$ ):**  $\delta$  201.3, 200.1, 141.6, 140.4, 139.2, 137.3, 137.0, 136.9, 136.5, 135.7, 135.5, 132.9, 132.8, 132.7, 129.2, 128.8, 128.6, 128.5, 128.4, 127.9, 127.4, 56.2, 54.5, 48.9, 48.8, 48.7, 48.6, 48.0, 47.8, 47.4, 45.5, 21.0, 20.9 ppm.

(3-(4-Nitrophenyl)bicyclo[2.2.1]hept-5-en-2-yl)(phenyl)methanone (**3k**)

**Results:** 79% yield, yellow oily liquid, dr = >99:1 (*endo:exo*); **IR (ATR):**  $\nu_{\max}$  3059, 2922, 2853, 1667, 1598, 1449, 1214, 1014, 843, 724, 693  $\text{cm}^{-1}$ ;  **$^1\text{H-NMR}$  (500 MHz,  $\text{CDCl}_3$ ):**  $\delta$  8.08 (dt,  $J = 2.5$  Hz, 4.0 Hz, 2H), 7.92 (dd,  $J = 0.5$  Hz, 8.0 Hz, 2H), 7.58- 7.53 (m, 1H), 7.46-7.40 (m, 2H), 7.31 (d,  $J = 2.0$  Hz, 8.5 Hz), 6.54 (dd,  $J = 3.0$  Hz, 5.5 Hz, 1H), 6.13 (dd,  $J = 3.0$  Hz, 6.0 Hz, 1H), 4.10 (dd,  $J = 3.5$  Hz, 5.0 Hz, 1H), 3.45 (dd,  $J = 1.0$  Hz, 5.0 Hz, 1H), 3.22 (s, 1H), 3.18 (s, 1H), 1.89 (d,  $J = 8.5$  Hz, 1H), 1.58 (dd,  $J = 1.5$  Hz, 9.0 Hz, 1H) ppm;  **$^{13}\text{C NMR}$  (125 MHz,  $\text{CDCl}_3$ ):**  $\delta$  199.2, 152.9, 146.4, 139.1, 136.9, 133.2, 133.2, 128.8, 128.5, 128.4, 128.3, 123.9, 56.7, 48.9, 48.2, 48.1, 45.7 ppm.

4-(3-Benzoylbicyclo[2.2.1]hept-5-en-2-yl)benzotrile (**3l**)

**Results:** 75% yield, yellow oily liquid, dr = > 99:1 (*endo:exo*); **IR (ATR):**  $\nu_{\max}$  3061, 2967, 2226, 1675, 1448, 1329, 1209, 1016, 756, 694, 660  $\text{cm}^{-1}$ ;  **$^1\text{H-NMR}$  (500 MHz,  $\text{CDCl}_3$ ):**  $\delta$  7.90 (dd,  $J = 1.0$  Hz, 8.5 Hz, 2H), 7.55 (tt,  $J = 7.0$  Hz, 14.5 Hz, 1H), 7.51(dt,  $J = 2.0$  Hz, 6.5 Hz, 2H) 7.46-7.41 (m, 2H), 7.27-7.24 (m, 2H), 6.51 (dd,  $J = 3.0$  Hz, 5.5 Hz, 1H), 6.12 (dd,  $J = 3.0$  Hz, 5.5 Hz, 1H), 4.04 (dd,  $J = 3.5$  Hz, 5.0 Hz, 1H), 3.41 (dd,

$J = 1.0$  Hz,  $5.0$  Hz,  $1$ H),  $3.20$  (s,  $1$ H),  $3.17$  (s,  $1$ H),  $1.88$  (d,  $J = 8.5$  Hz,  $1$ H),  $1.56$  (dd,  $J = 2.0$  Hz,  $9.0$  Hz,  $1$ H) ppm;  $^{13}\text{C}$  NMR (**125 MHz**,  $\text{CDCl}_3$ ):  $\delta$  200.0, 149.3, 137.1, 136.5, 136.2, 133.2, 131.9, 128.6, 128.4, 118.9, 110.0, 54.4, 49.1, 48.6, 47.7, 47.5 ppm.

(4-Fluorophenyl)(3-(*p*-tolyl)bicyclo[2.2.1]hept-5-en-2-yl)methanone (**3m**)

**Results:** 70% yield, yellow oily liquid, dr = 65:35 (*endo:exo*); **IR (ATR):**  $\nu_{\text{max}}$  3063, 2966, 2926, 1740, 1678, 1451, 1368, 1221, 1018, 802, 714, 677  $\text{cm}^{-1}$ ;  **$^1\text{H}$ -NMR (500 MHz,  $\text{CDCl}_3$ ):**  $\delta$  7.97-7.93 (m,  $1.33$ H (*endo*)), 7.90-7.86 (m,  $0.71$ H (*exo*)), 7.17-7.02 (m,  $6$ H), 6.48-6.43 (m,  $1$ H), 6.16 (dd,  $J = 2.5$  Hz,  $5.5$  Hz,  $0.35$ H (*exo*)), 5.87 (dd,  $J = 3.0$  Hz,  $6.0$  Hz,  $0.65$ H (*endo*)), 3.83 (dd,  $J = 3.5$  Hz,  $5.0$  Hz,  $0.65$ H (*endo*)), 3.78 (dd,  $J = 3.5$  Hz,  $5.5$  Hz,  $0.35$ H (*exo*)), 3.38 (d,  $J = 4.0$  Hz,  $0.65$ H (*endo*)), 3.34 (dd,  $J = 1.0$  Hz,  $5.0$  Hz,  $0.35$ H (*exo*)), 3.30 (s,  $0.35$ H (*exo*)), 3.15-3.10 (m,  $0.70$ H (*exo*)), 3.09- 3.06 (m,  $0.65$ H (*endo*)), 2.31 (s,  $2$ H  $\text{CH}_3$  (*endo*)), 2.30 (s,  $1$ H  $\text{CH}_3$  (*exo*)), 2.02 (d,  $J = 8.5$  Hz,  $0.65$ H (*endo*)), 1.88 (d,  $J = 8.5$  Hz,  $0.35$ H (*exo*)), 1.63 (dq,  $J = 1.5$  Hz,  $3.5$  Hz,  $0.65$ H (*endo*)), 1.53 (m,  $0.35$ H (*exo*)) ppm;  **$^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ ):**  $\delta$  199.8, 198.5, 139.2, 136.9, 136.4, 135.6, 133.6 (d,  $J = 3.75$  Hz), 133.3 (d,  $J = 2.5$  Hz), 132.8, 131.1 (d,  $J = 8.75$  Hz), 130.9 (d,  $J = 8.75$  Hz), 129.2, 128.8, 127.8, 127.3, 115.7, 115.5 (d,  $J = 21.2$  Hz), 115.5 (d,  $J = 21.2$  Hz), 115.4, 56.1, 54.5, 48.8 (d,  $J = 42.5$  Hz), 48.7 (d,  $J = 38.75$  Hz), 48.0, 47.9, 47.6, 45.7, 20.9 ppm.

(4-Chlorophenyl)(3-(*p*-tolyl)bicyclo[2.2.1]hept-5-en-2-yl)methanone (**3n**)

**Results:** 70% yield, yellow oily liquid, dr = 72:28 (*endo:exo*); **IR (ATR):**  $\nu_{\text{max}}$  3059, 2966, 2926, 1734, 1678, 1588, 1369, 1214, 1013, 803, 716, 676  $\text{cm}^{-1}$ ;  **$^1\text{H}$ -NMR (500 MHz,  $\text{CDCl}_3$ ):**  $\delta$  7.85 (dt,  $J = 2.5$  Hz,  $9.0$  Hz,  $1.46$ H (*endo*)), 7.78 (dt,  $J = 2.5$  Hz,  $9.5$  Hz,  $0.57$ H (*exo*)), 7.39 (dt,  $J = 2.5$  Hz,  $9.5$  Hz,  $1.41$ H (*endo*)), 7.33 (dt,  $J = 2.5$  Hz,  $9.5$  Hz,  $0.56$ H (*exo*)), 7.19- 7.09 (m,  $3$ H), 7.07 - 7.00 (m,  $1$ H), 6.45 (m,  $1$ H), 6.16 (dd,  $J = 3.0$  Hz,  $5.5$  Hz,  $0.28$ H (*exo*)) 5.86 (dd,  $J = 3.0$  Hz,  $6.0$  Hz,  $0.72$ H (*endo*)), 3.82 (dd,  $J = 3.5$  Hz,  $5.0$  Hz,  $0.72$ H (*endo*)), 3.76 (dd,  $J = 3.0$  Hz,  $5.5$  Hz,  $0.28$ H (*exo*)), 3.37 (d,  $J = 4.0$  Hz,  $0.72$ H (*endo*)), 3.32 (dd,  $J = 1.5$  Hz,  $5.5$  Hz,  $0.28$ H (*exo*)), 3.30 (s,  $0.72$ H (*endo*)), 3.14-3.10 (m,  $0.56$ H), 3.08-3.06 (m,  $0.72$ H (*endo*)), 2.32 (s,  $2.23$ H,  $\text{CH}_3$  (*endo*)), 2.30 (s,  $0.89$ H,  $\text{CH}_3$  (*exo*)), 2.01 (d,  $J = 8.5$  Hz,  $0.72$ H (*endo*)), 1.87 (d,  $J = 9.0$  Hz,  $0.28$ H (*exo*)), 1.63 (dd,  $J = 3.5$  Hz,  $10.5$  Hz,  $0.72$ H (*endo*)), 1.54-1.52 (m,  $0.28$ H (*exo*)) ppm;  **$^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ ):**  $\delta$  200.8, 199.5, 141.9, 140.7, 139.8,



139.8, 139.7, 137.4, 136.9, 136.4, 136.2, 136.0, 135.8, 135.8, 133.4, 130.4, 130.3, 129.8, 129.4, 129.3, 129.3, 128.4, 127.9, 56.7, 55.1, 49.5, 49.3, 49.1, 48.9, 48.5, 48.4, 48.2, 46.2, 21.4 ppm.

#### 4-Bromophenyl-(3-(*p*-tolyl)bicyclo[2.2.1]hept-5-en-2-yl)methanone (**3o**)

**Results:** 65% yield, yellow oily liquid, dr = 55:45 (*endo:exo*); **IR (ATR):**  $\nu_{\max}$  2952, 2921, 2852, 1740, 1584, 1458, 1373, 1214, 1023, 804, 720, 684  $\text{cm}^{-1}$ ;  **$^1\text{H-NMR}$  (500 MHz,  $\text{CDCl}_3$ ):**  $\delta$  7.77 (dt,  $J = 2.0$  Hz, 9.0 Hz, 1.21H (*endo*)), 7.70 (dt,  $J = 2.0$  Hz, 9.0 Hz, 0.92H (*exo*)), 7.56 (dt,  $J = 2.5$  Hz, 9.5 Hz, 1.18H (*endo*)), 7.50 (dt,  $J = 2.0$  Hz, 9.0 Hz, 0.94H (*exo*)), 7.17-7.09 (m, 2H), 7.06- 7.01 (m, 2H), 6.47-6.42 (m, 1H), 6.16 (dd,  $J = 2.5$  Hz, 5.5 Hz, 0.45H (*exo*)), 5.86 (dd,  $J = 3.0$  Hz, 6.0 Hz, 0.55H (*endo*)), 3.81 (dd,  $J = 3.5$  Hz, 5.0 Hz, 0.55H), 3.75 (dd,  $J = 3.5$  Hz, 5.5 Hz, 0.45H), 3.37 (d,  $J = 3.5$  Hz, 0.55H (*endo*)), 3.31 (dd,  $J = 1.5$  Hz, 5.5 Hz, 0.45H (*exo*)), 3.29 (s, 0.55H (*endo*)), 3.11 (d,  $J = 8.0$  Hz, 0.90H (*exo*)), 3.06 (s, 0.55H (*endo*)), 2.31 (s, 1.70H,  $\text{CH}_3$  (*endo*)), 2.30 (s, 1.35H,  $\text{CH}_3$  (*exo*)), 2.01 (d,  $J = 8.5$  Hz, 0.55H (*endo*)), 1.86 (d,  $J = 8.5$  Hz, 0.45H (*exo*)), 1.63(dd,  $J = 3.5$  Hz, 10.5 Hz, 0.55H), 1.53(dd,  $J = 1.5$  Hz, 3.0 Hz, 0.45H) ppm;  **$^{13}\text{C NMR}$  (125 MHz,  $\text{CDCl}_3$ ):**  $\delta$  200.6, 199.3, 141.4, 140.2, 139.4, 137.0, 136.5, 135.8, 132.9, 131.9, 131.8, 130.1, 130.0, 129.4, 129.0, 129.2, 128.1, 128.0, 127.4, 56.3, 54.7, 49.1, 48.9, 48.6, 48.5, 48.1, 48.0, 47.8, 45.8 21.0 ppm.

#### 4-Methoxyphenyl(3-(*p*-tolyl)bicyclo[2.2.1]hept-5-en-2-yl)methanone (**3p**)

**Results:** 71% yield, yellow oily liquid, dr = 45:55 (*endo:exo*); **IR (ATR):**  $\nu_{\max}$  3011, 2964, 2924, 1738, 1671, 1599, 1453, 1369, 1220, 1021, 838, 714, 680  $\text{cm}^{-1}$ ;  **$^1\text{H-NMR}$  (500 MHz,  $\text{CDCl}_3$ ):**  $\delta$  7.92 (dt,  $J = 2.0$ , 10.0 Hz, 0.92H (*endo*)), 7.86 (dt,  $J = 2.5$  Hz, 9.5 Hz, 1.12H (*exo*)), 7.19-7.08 (m, 2H), 7.04 (s, 2H), 6.90 (dd,  $J = 2.0$  Hz, 7.0 Hz, 0.96H (*endo*)), 6.86 (dd,  $J = 2.5$  Hz, 7.0 Hz, 1.16H (*exo*)), 6.47-6.43 (m, 1H), 6.16 (dd,  $J = 3.0$  Hz, 5.5 Hz, 0.55H (*exo*)), 5.88 (dd,  $J = 2.5$  Hz, 5.5 Hz, 0.45H (*endo*)), 3.86 (s, 1.20H,  $\text{OCH}_3$  (*endo*)), 3.84 (s, 2.20H,  $\text{OCH}_3$  (*exo*)) 3.42 (d,  $J = 4.5$  Hz, 0.45H (*endo*)), 3.35 (dd,  $J = 1.5$  Hz, 5.0 Hz, 0.55H (*exo*)), 3.31 (s, 0.45H (*endo*)), 3.13 (s, 0.55H (*exo*)), 3.07 (d,  $J = 1.5$  Hz, 1H), 2.31 (s, 1.30H,  $\text{CH}_3$  (*endo*)), 2.29 (s, 1.70H,  $\text{CH}_3$  (*exo*)), 2.01 (d,  $J = 8.5$  Hz, 0.45H (*endo*)), 1.90 (d,  $J = 8.5$  Hz, 0.55H (*exo*)), 1.62 (dd,  $J = 3.0$  Hz, 8.5 Hz, 1H), 1.52 (dd,  $J = 3.5$  Hz, 9.0 Hz, 1H) ppm;  **$^{13}\text{C NMR}$  (125 MHz,  $\text{CDCl}_3$ ):**  $\delta$  199.9, 198.6, 163.4, 141.9, 140.7, 139.1, 136.9, 136.6, 135.7, 135.5,

133.1, 130.8, 130.7, 130.3, 130.1, 129.3, 128.9, 127.5, 113.7, 112.5, 113.8, 113.7, 55.9, 55.5, 54.2, 49.0, 48.8, 48.7, 48.1, 48.0, 47.5, 45.6, 21.1, 21.0 ppm.

4-Chlorophenyl(5-methyl-1,2,3,6-tetrahydro-[1,1'-biphenyl]-2-yl)methanone (**5c** and **5c'**)

**Results:** 56% yield, yellow oily liquid, *Regio* isomers = 70:30 (*para:meta*); **IR (ATR):**  $\nu_{\max}$  3063, 3026, 2952, 2923, 1740, 1679, 1588, 1450, 1370, 1227, 1011, 839, 797, 699  $\text{cm}^{-1}$ ; **<sup>1</sup>H-NMR (500 MHz, CDCl<sub>3</sub>):**  $\delta$  7.72 (dd,  $J = 2.0$  Hz, 8.5 Hz, 2H), 7.32 (dd,  $J = 2.0$  Hz, 6.5 Hz, 2H), 7.17-7.13 (m, 4H), 7.08-7.04 (m, 1H), 5.57-5.53 (m, 0.30H), 5.52-5.47 (m, 0.70H) 3.97- 3.92 ( m, 0.30H), 3.89-3.82 (m, 0.70H), 3.34-3.26 (m, 0.70H), 3.24-3.17 (m, 0.30H), 2.35-2.27 (m, 4H), 1.73 (s, 3H) ppm; **<sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>):**  $\delta$  202.7, 202.6, 144.4, 144.2, 139.3, 139.2, 135.7, 134.2, 129.4, 128.8, 128.5, 128.4, 127.6, 127.5, 126.4, 120.9, 119.1, 47.2, 46.7, 42.9, 42.6, 38.8, 35.1, 34.0, 30.8, 29.7, 23.2 ppm.

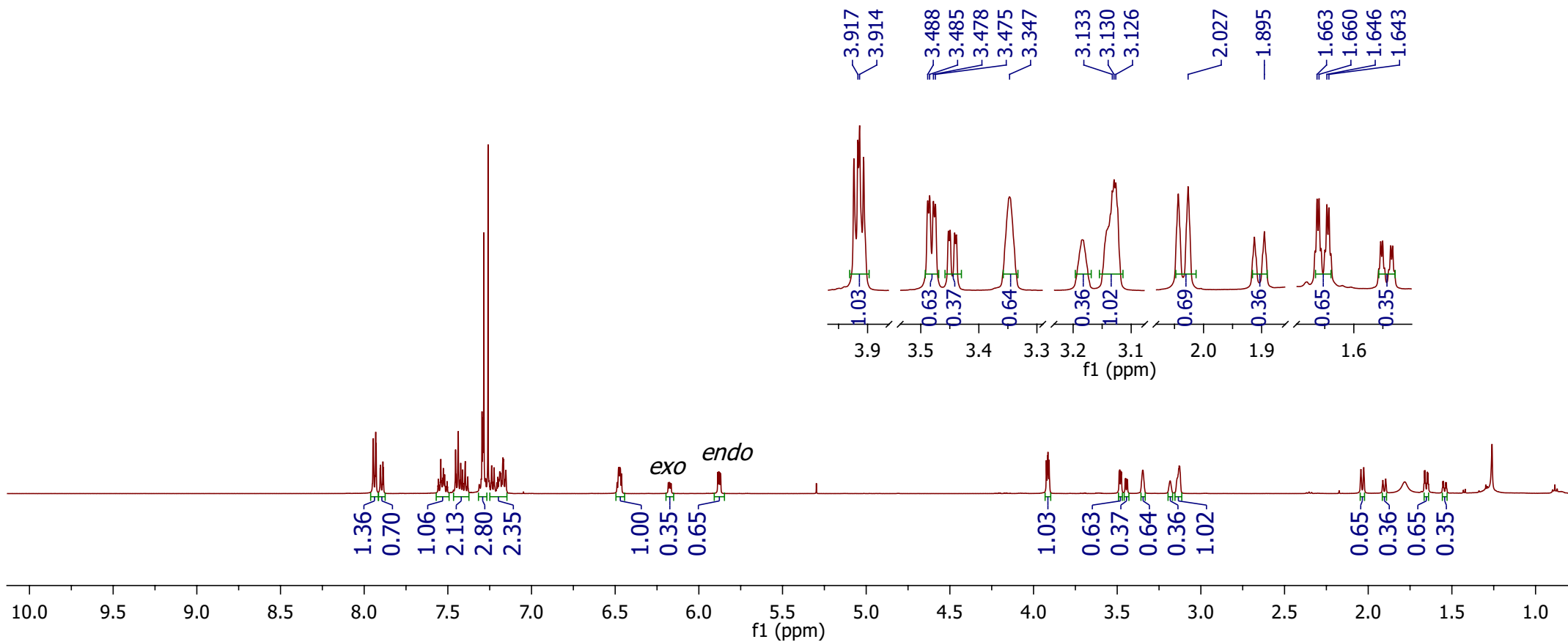
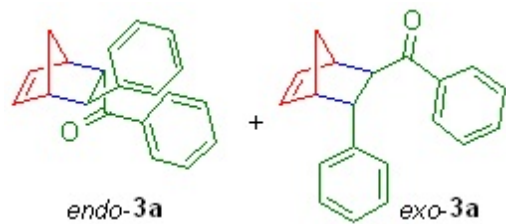
4-Bromophenyl(5-methyl-1,2,3,6-tetrahydro-[1,1'-biphenyl]-2-yl)methanone (**5d** and **5d'**)

**Results:** 58% yield, yellow oily liquid, *Regio* isomers = 70:30 (*para:meta*); **IR (ATR):**  $\nu_{\max}$  3063, 2923, 2853, 1734, 1584, 1451, 1228, 1007, 837, 742, 679  $\text{cm}^{-1}$ ; **<sup>1</sup>H-NMR (500 MHz, CDCl<sub>3</sub>):**  $\delta$  7.64 (dd,  $J = 2.0$  Hz, 7.0 Hz, 2H), 7.49 (dd,  $J = 2.0$  Hz, 7.0 Hz, 2H), 7.17-7.14 (m, 4H), 7.09-7.04 (m, 1H), 5.57-5.53 (m, 0.30H), 5.52-5.45 (m, 0.70H), 3.97-3.91 (m, 0.30H), 3.88-3.82 (m, 0.70H), 3.33-3.26 (m, 0.70H), 3.24-3.16 (m, 0.30H), 2.37-2.17 (m, 4H), 1.73(s, 3H) ppm; **<sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>):**  $\delta$  202.8, 144.4, 136.1, 134.2, 131.8, 129.6, 128.5, 128.4, 127.9, 127.5, 127.4, 126.4, 121.0, 119.1, 47.2, 46.7, 42.9, 42.6, 38.8, 38.2, 35.1, 34.0, 30.8, 29.7, 29.4, 23.2 ppm.

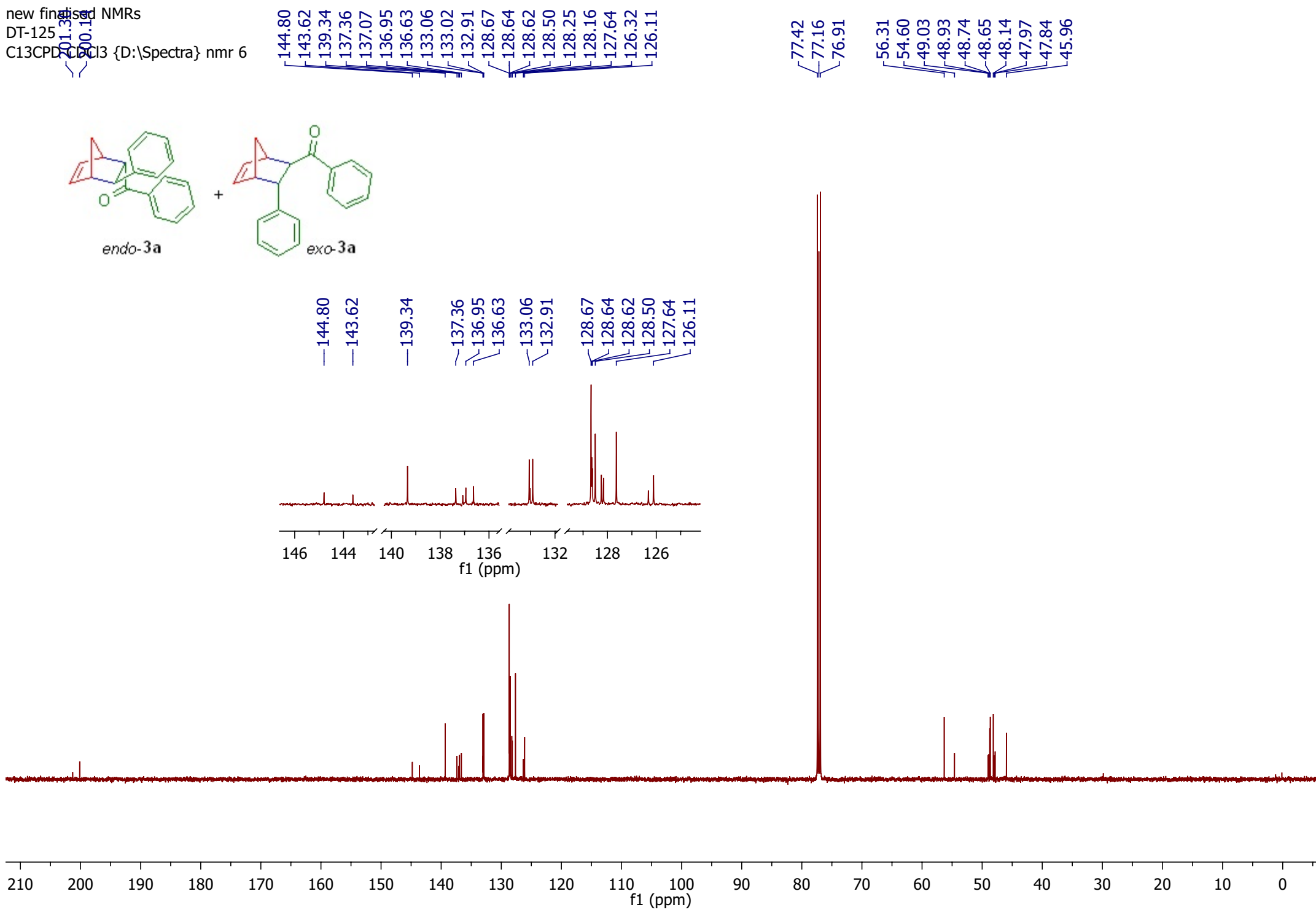
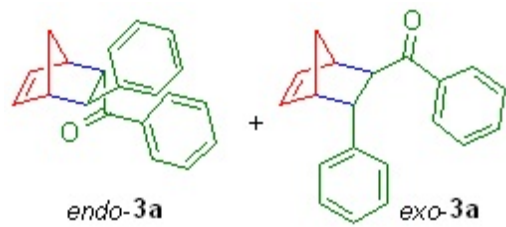
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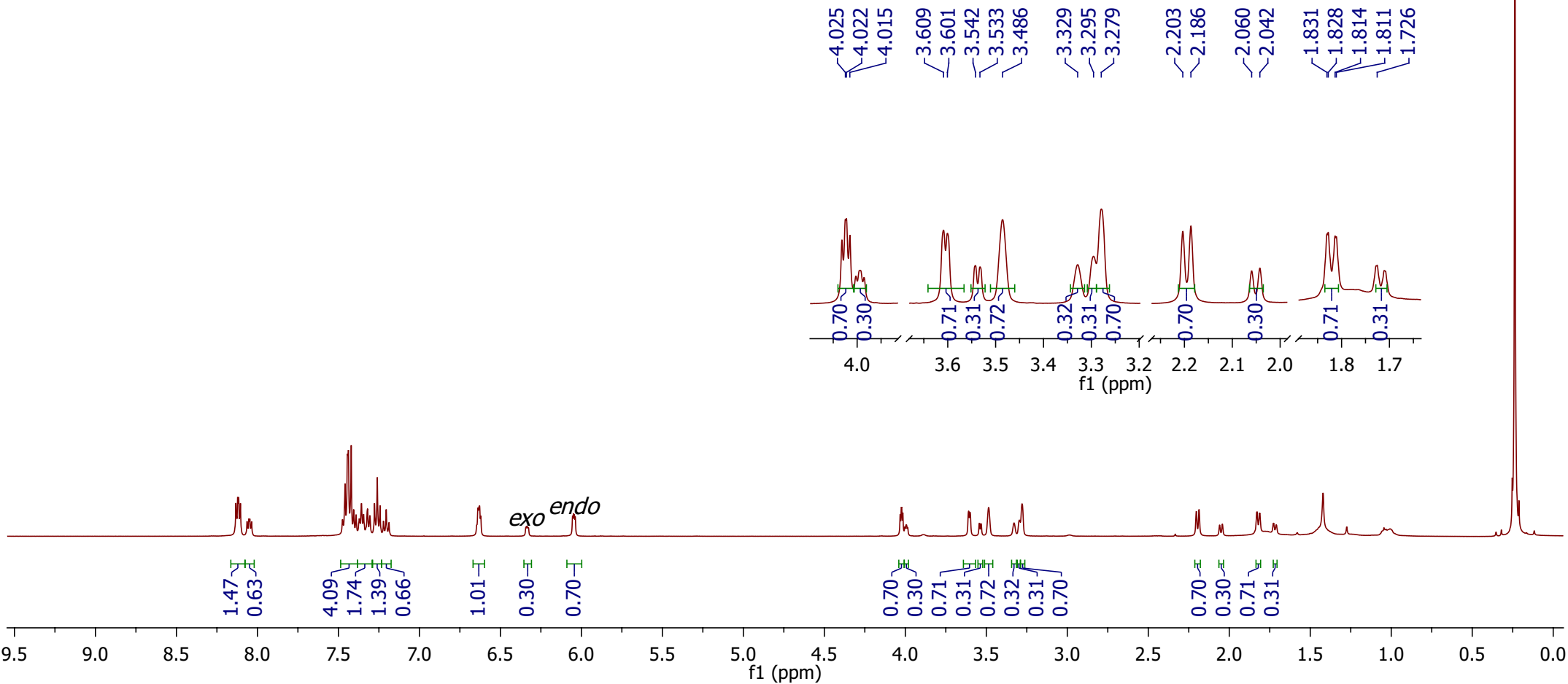
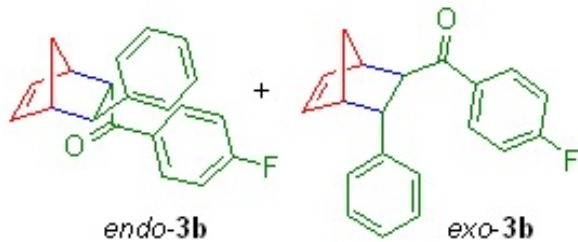
Mar 24 17:52:02  
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 7.914 7.902 7.888 7.885 7.852 7.530 7.527 7.524 7.519 7.454 7.451 7.438 7.423 7.412 7.396 7.381 7.301 7.296 7.291 7.285 7.260 7.238 7.224 7.202 7.190 7.186 7.185 7.171 7.168 7.153 7.153 6.479 6.473 6.469 6.462 5.887 5.881 5.875 5.870 3.924 3.917 3.914 3.914 3.907 3.488 3.485 3.478 3.475 3.347 3.133 3.130 3.126 2.027 1.895 1.663 1.660 1.646 1.643



new finalised NMRs  
DT-125  
C13CPD CDCl3 {D:\Spectra} nmr 6



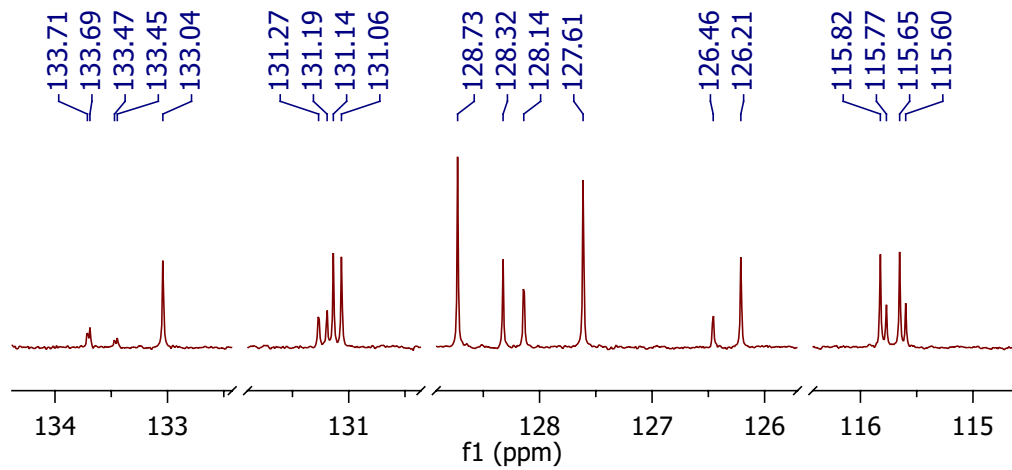
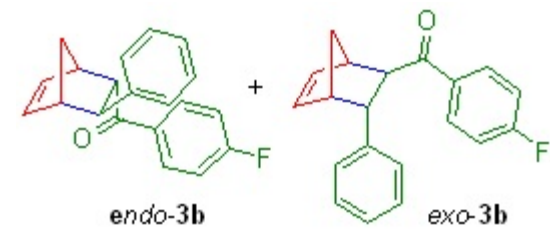
Apr 26 2022  
 D:\Spectra\hmr50  
 1H scan CDCl3  
 8.102  
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 8.047  
 8.036  
 7.475  
 7.459  
 7.444  
 7.438  
 7.421  
 7.406  
 7.391  
 7.371  
 7.357  
 7.344  
 7.320  
 7.306  
 7.277  
 7.260  
 7.243  
 7.222  
 7.205  
 7.187  
 6.638  
 6.632  
 6.628  
 6.621  
 6.343  
 6.337  
 6.332  
 6.054  
 6.049  
 6.043  
 6.038  
 4.032  
 4.025  
 4.022  
 4.015  
 4.003  
 3.993  
 3.986  
 3.609  
 3.601  
 3.542  
 3.533  
 3.486  
 3.329  
 3.295  
 3.279  
 2.203  
 2.186  
 2.060  
 2.042  
 1.831  
 1.828  
 1.814  
 1.811  
 1.726  
 1.708



Apr27-2022

DT-49

C13CPD, CDCl3 {D:\Spectra} nmr

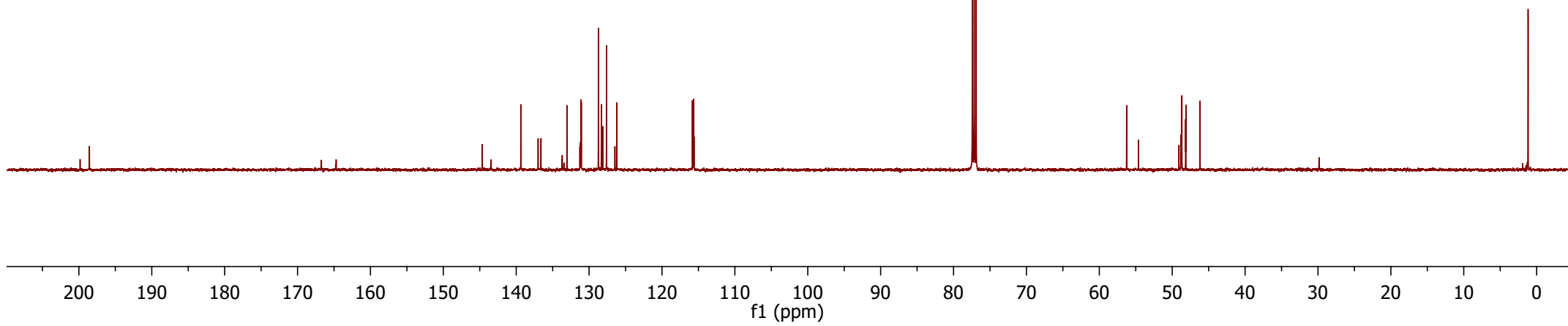


166.79  
166.72  
164.76  
164.70  
139.36  
137.00  
136.60  
133.04  
131.14  
131.06  
128.73  
128.32  
128.14  
127.61  
126.21  
115.82  
115.77  
115.65  
115.60

77.41  
77.16  
76.91

56.26  
54.62  
49.07  
48.80  
48.72  
48.67  
48.16  
48.12  
46.19

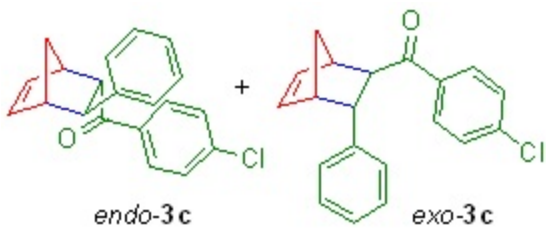
—1.17



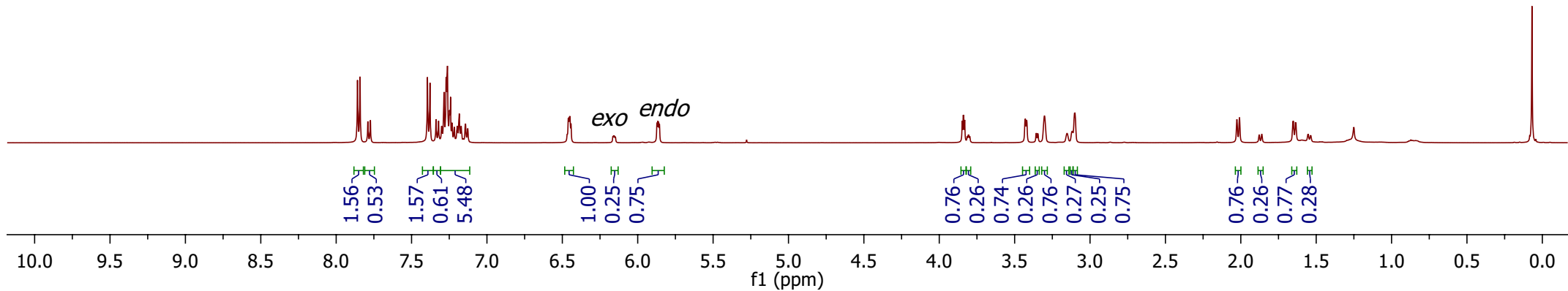
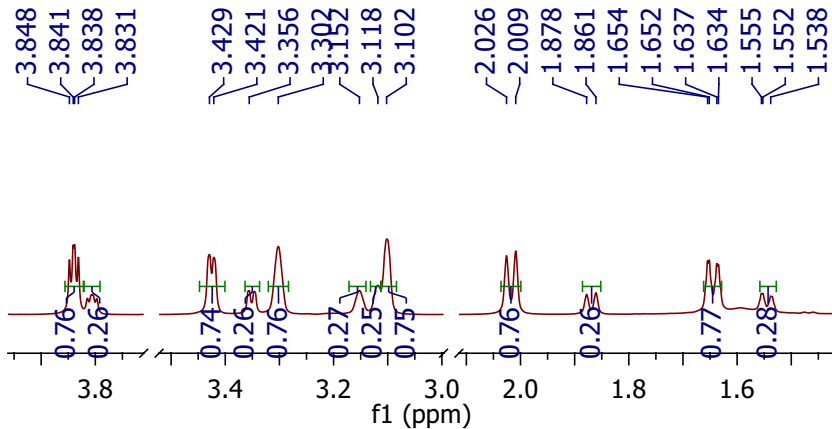
May05-2022

DT-52 4-CL

1H\_8scan CDCl3 {D:\Spectra} nmr 40



7.859, 7.842, 7.790, 7.773, 7.395, 7.378, 7.271, 7.262, 7.260, 6.453, 6.450, 6.443, 6.164, 6.159, 6.153, 6.148, 5.872, 5.867, 5.861, 5.856, 3.848, 3.841, 3.838, 3.831, 3.815, 3.807, 3.805, 3.429, 3.421, 3.356, 3.302, 3.118, 3.102, 2.026, 2.009, 1.878, 1.861, 1.654, 1.652, 1.637, 1.634, 1.555, 1.552, 1.538, 1.535



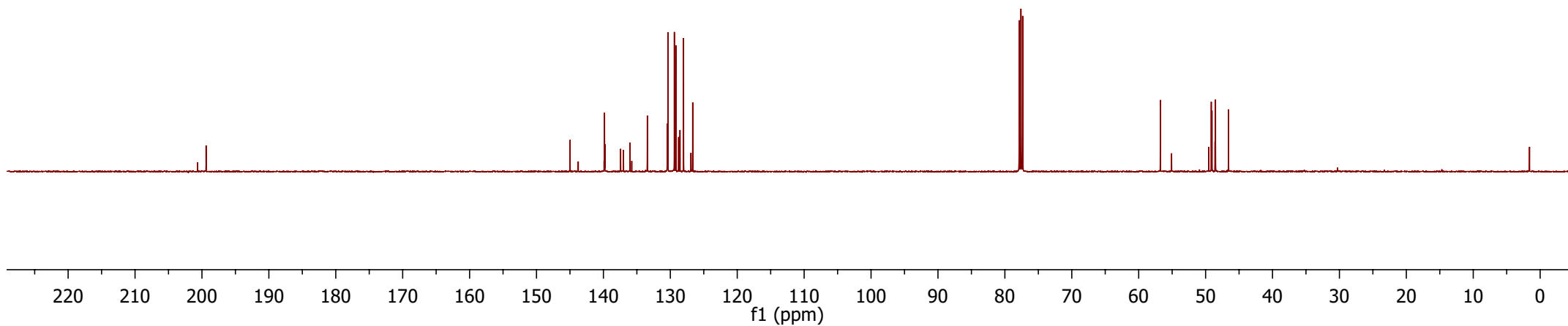
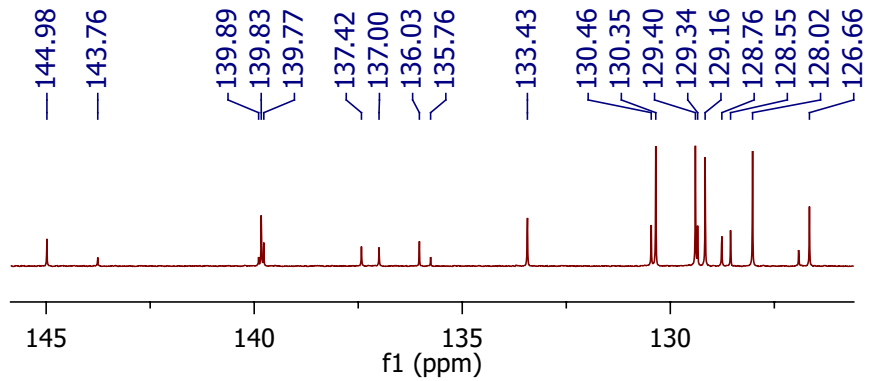
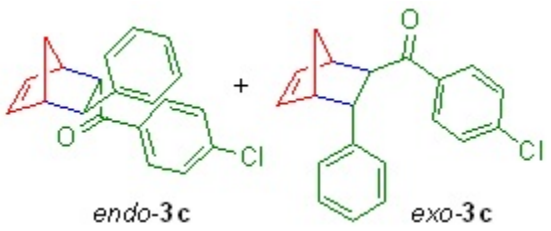
May05-2022  
DT-52 4-CL  
C13CPD CDCI3 {D:\Spectra}

100.65  
77.38

144.98  
143.76  
139.89  
139.83  
139.77  
137.42  
137.00  
136.03  
135.76  
133.43  
130.46  
130.35  
129.40  
129.34  
129.16  
128.76  
128.55  
128.02  
126.91  
126.66

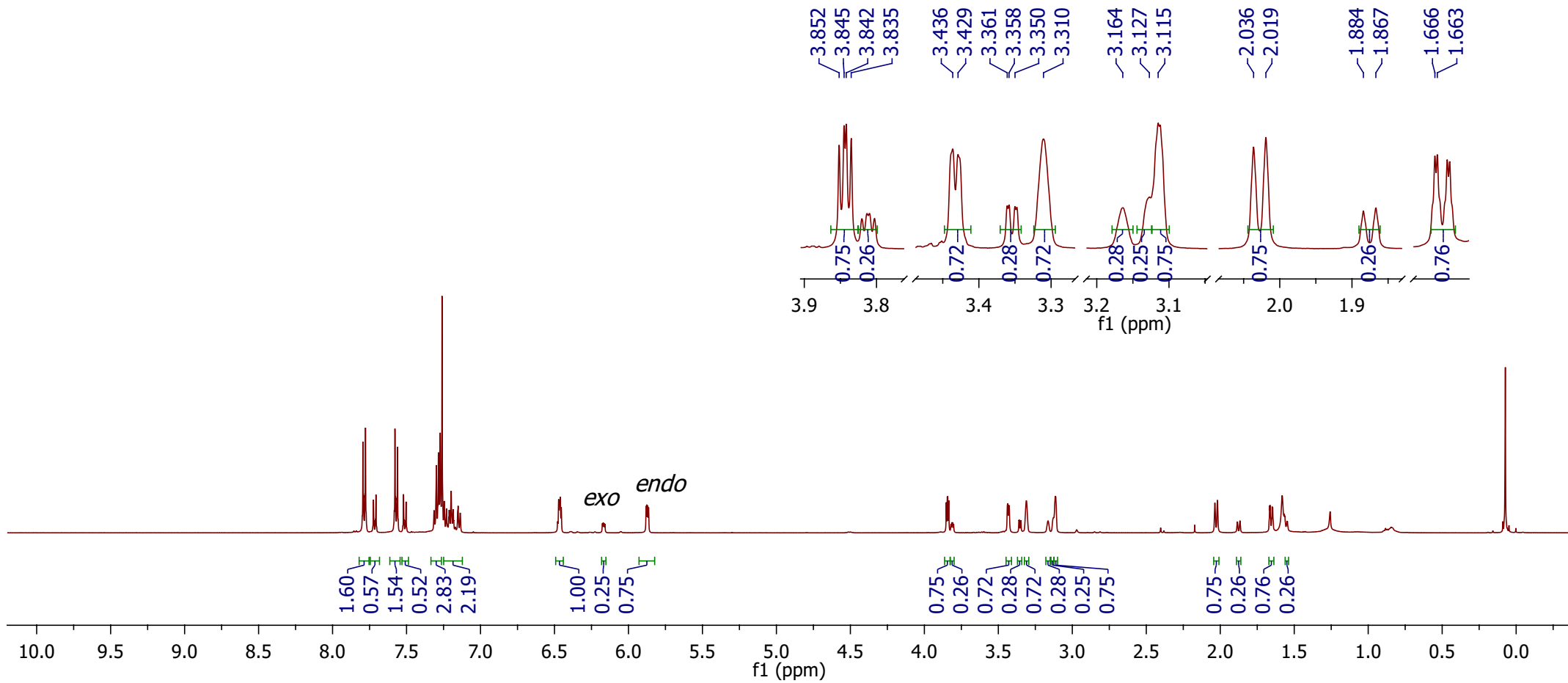
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77.59  
77.34

56.76  
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48.52  
46.58

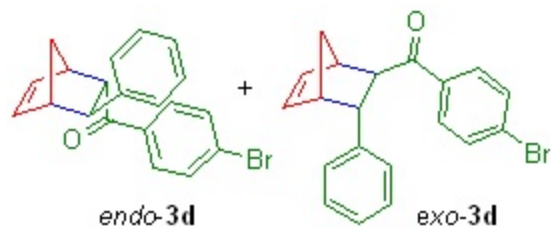




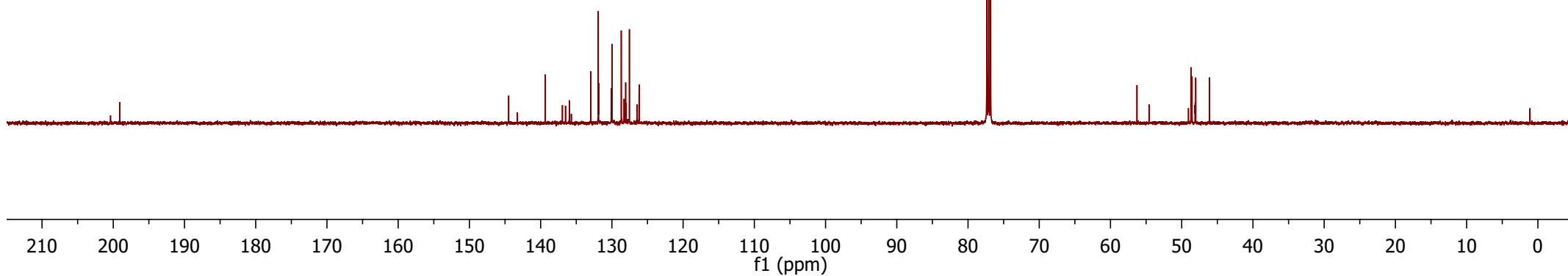
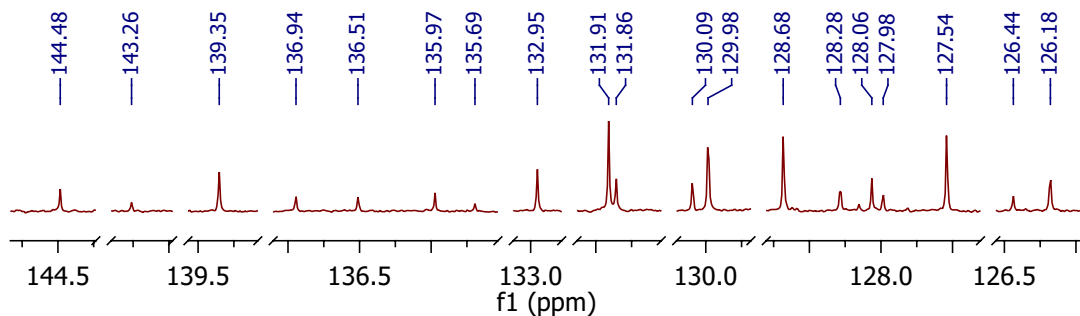
A 7.709 26-2022  
 D 7.709 48022  
 1H 8scan CDCl3 (DMSO-d6) Spectra pmr 51  
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 7.710  
 7.707  
 7.578  
 7.574  
 7.565  
 7.561  
 7.520  
 7.517  
 7.507  
 7.503  
 7.314  
 7.298  
 7.289  
 7.284  
 7.275  
 7.272  
 7.260  
 7.245  
 7.230  
 7.212  
 7.208  
 7.198  
 7.185  
 7.181  
 7.151  
 7.137  
 6.472  
 6.466  
 6.461  
 6.454  
 5.881  
 5.875  
 5.869  
 5.864  
 3.852  
 3.852  
 3.845  
 3.842  
 3.835  
 3.436  
 3.429  
 3.361  
 3.358  
 3.350  
 3.310  
 3.164  
 3.127  
 3.115  
 2.036  
 2.019  
 1.884  
 1.867  
 1.666  
 1.663  
 1.649  
 1.646  
 1.567  
 1.563  
 1.549



Apr27-2022  
DT-55 4-Br  
C13CPD CDCl<sub>3</sub> {D:\Spectra} nmr 7

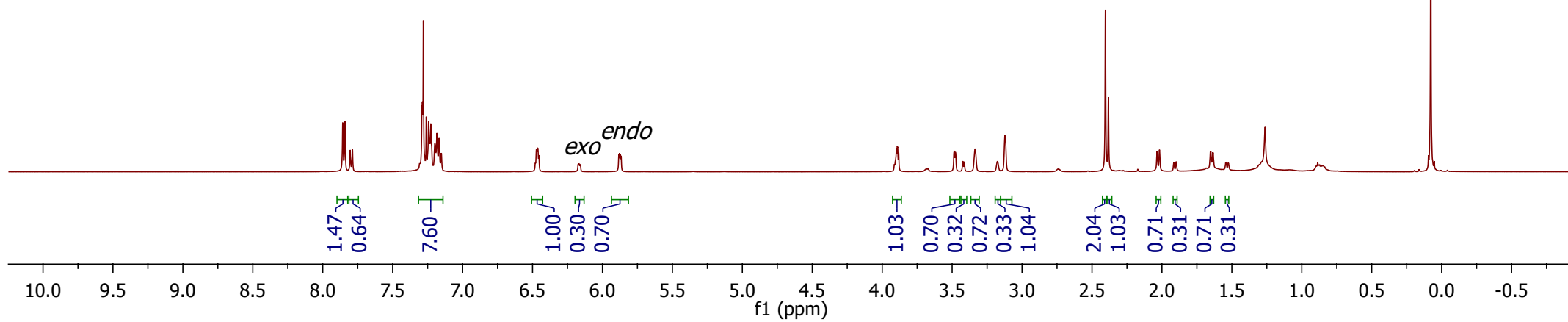
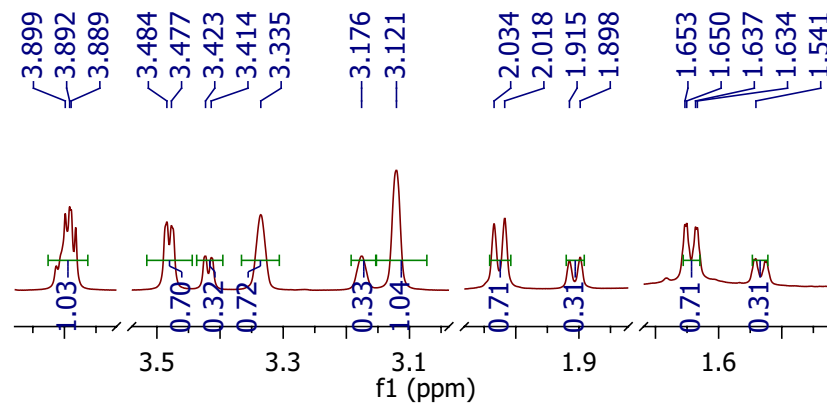
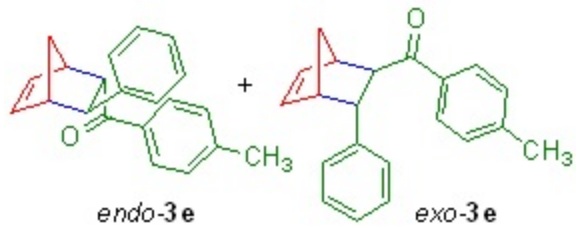


144.48  
143.26  
139.35  
136.94  
136.51  
135.97  
135.69  
132.95  
131.91  
131.86  
130.09  
129.98  
128.68  
128.28  
128.06  
127.98  
127.54  
126.44  
126.18  
  
77.35  
77.09  
76.84  
  
56.28  
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48.65  
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48.13  
48.10  
48.03  
46.10

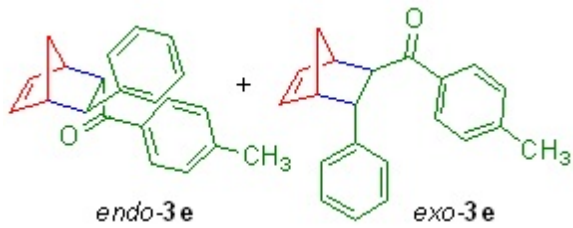


Apr29-2022  
DT-53 OCH3  
1H\_8scan CDCl3 {D:\Spectra} nmr

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7.804  
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7.291  
7.287  
7.281  
7.260  
6.480  
6.472  
6.465  
6.455  
6.174  
6.168  
6.163  
6.157  
5.883  
5.878  
5.872  
5.867  
3.913  
3.899  
3.892  
3.889  
3.882  
3.484  
3.477  
3.423  
3.335  
3.211  
2.404  
2.383  
2.034  
2.018  
1.915  
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1.653  
1.650  
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1.634  
1.543  
1.541  
1.526  
1.524

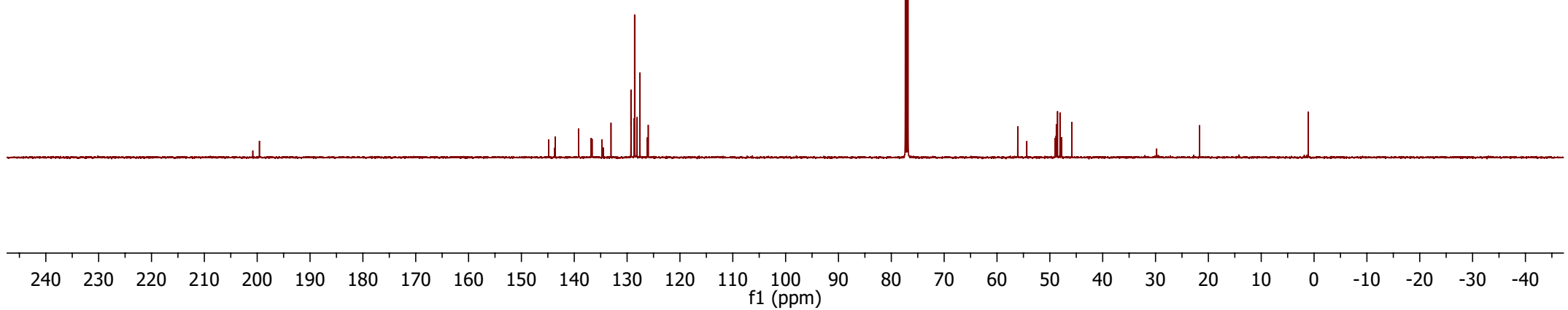
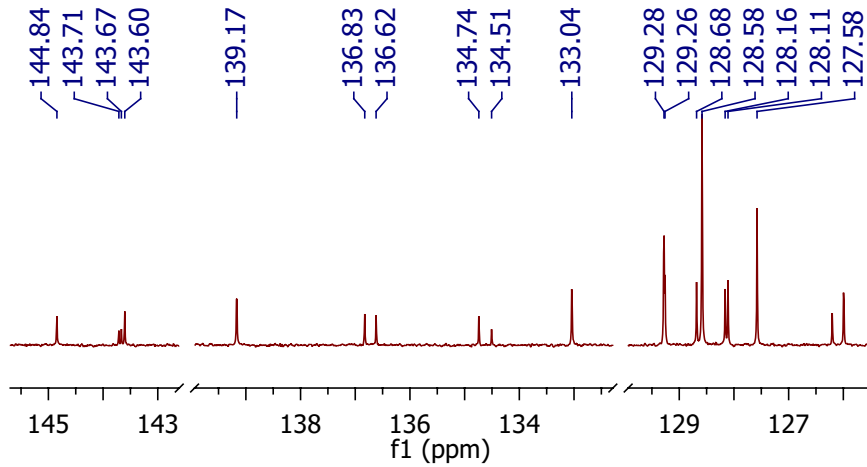


Apr29-2022  
DT-53 OCH3  
C13CPD CDCI3 {D:\Spectra\mfr 30



144.84  
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143.67  
143.60  
139.17  
136.83  
136.62  
134.74  
134.51  
133.04  
129.28  
129.26  
128.68  
128.58  
128.16  
128.11  
127.58  
126.20  
125.99  
77.35  
77.09  
76.84  
56.08  
54.36  
49.00  
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48.77  
48.54  
48.08  
47.91  
47.77  
45.84  
-21.67

-1.10



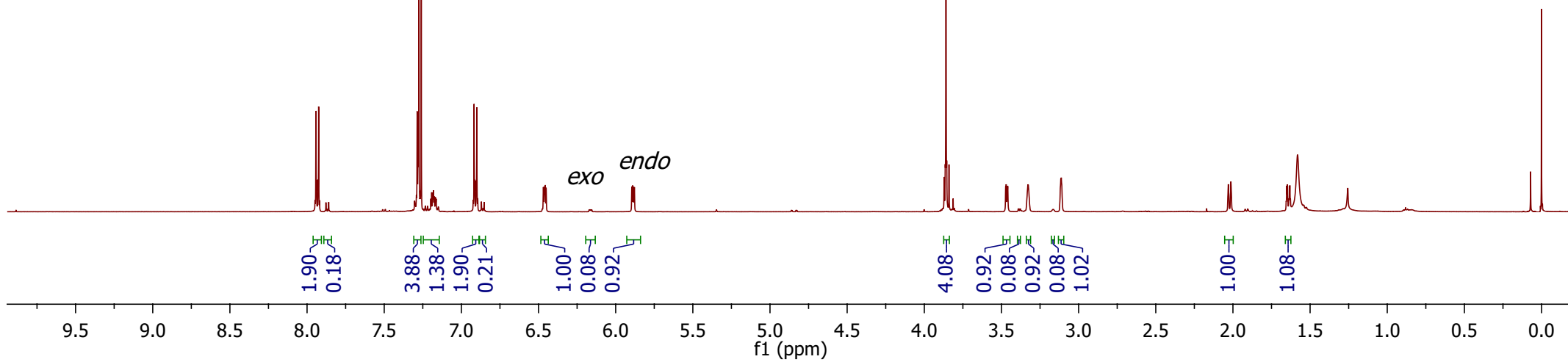
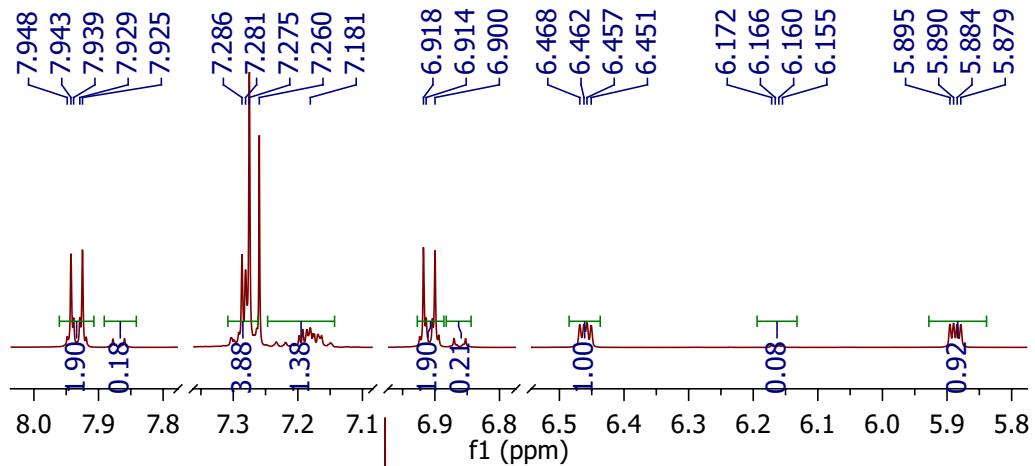
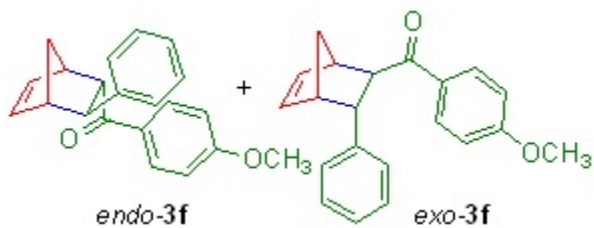
Desktop  
DT-53  
1H\_8scan CDC3-(D)-Spectra

7.948  
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7.919  
7.878  
7.874  
7.864  
7.860

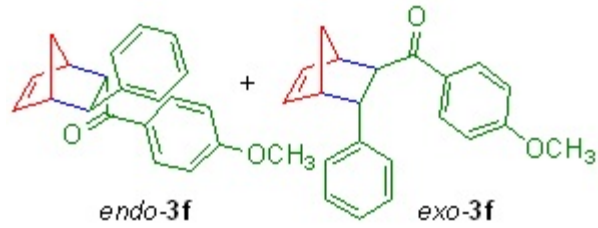
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6.900  
6.468  
6.462  
6.457  
6.451  
6.172  
6.166  
6.160  
6.155  
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5.890  
5.884  
5.879

3.871  
3.864  
3.860  
3.855  
3.840

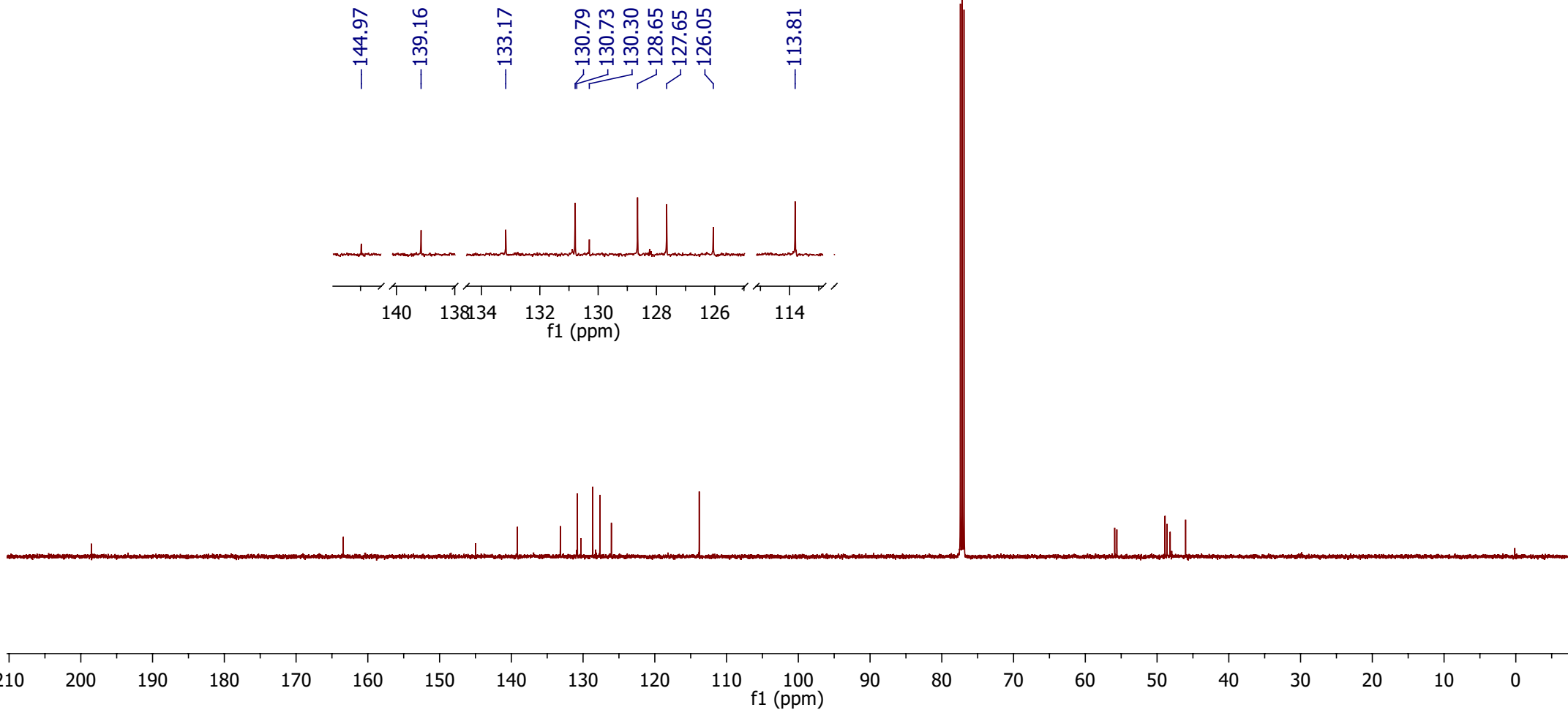
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3.459  
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3.328  
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2.030  
2.013  
1.651  
1.648  
1.634  
1.631



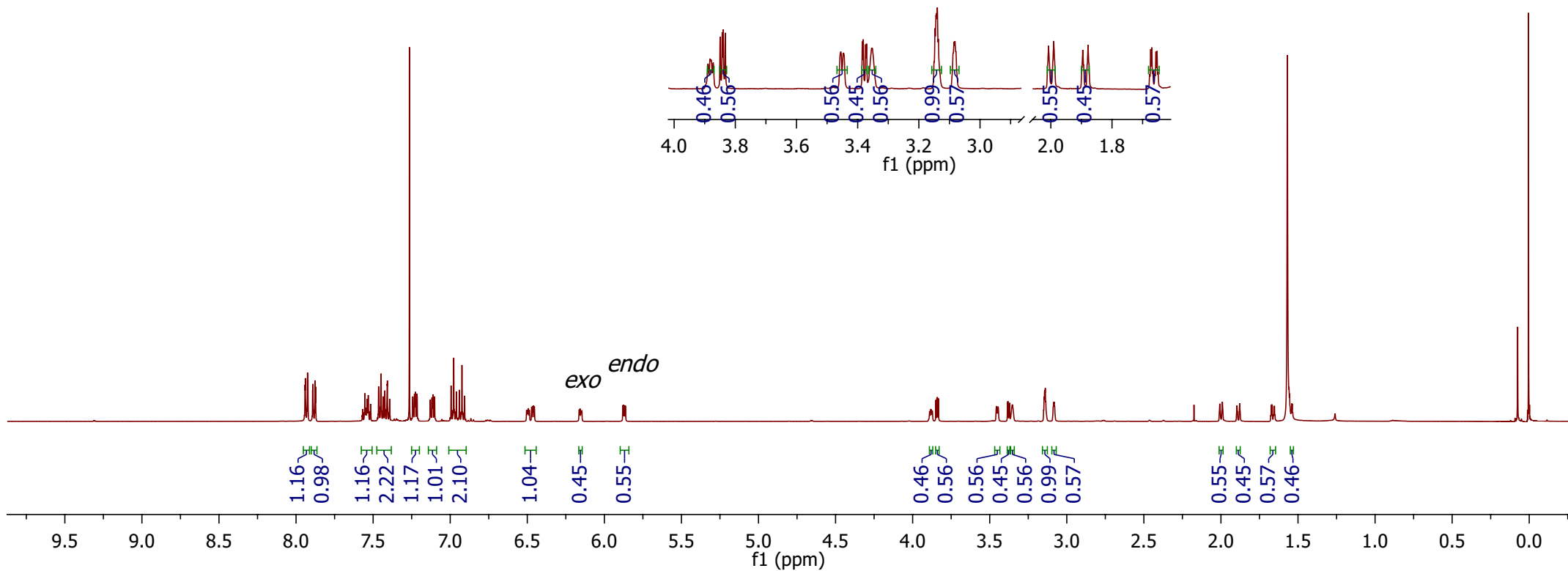
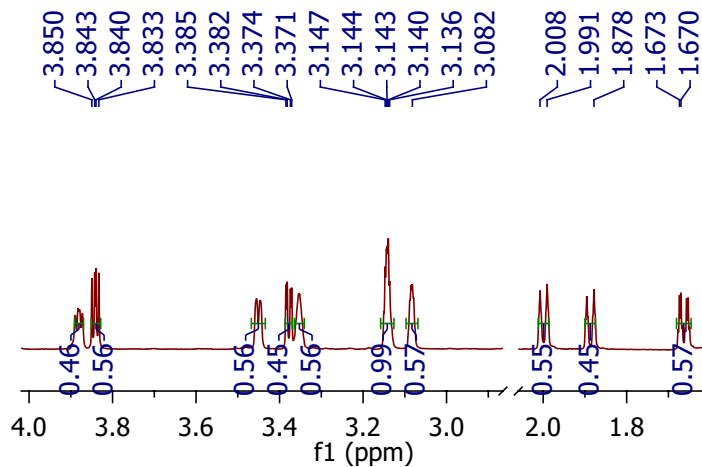
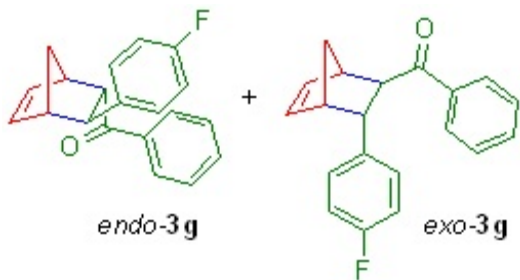
Desktop  
DT-53  
C13CPD CDCl<sub>3</sub> {D:\Spectra} nmr 8



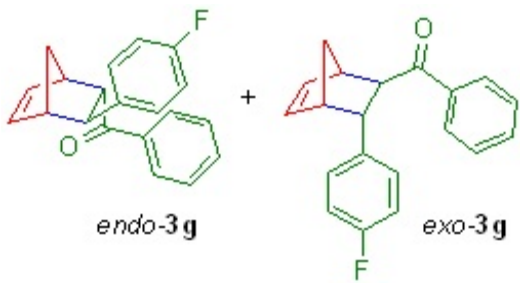
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130.30  
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127.65  
126.05  
113.81  
77.41  
77.16  
76.91  
55.90  
55.60  
48.89  
48.61  
48.17  
46.02



17.7412  
 17.5416  
 17.5416  
 17.9216  
 17.923  
 17.893  
 17.890  
 17.876  
 17.873  
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 17.464  
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 17.409  
 17.408  
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 17.243  
 17.232  
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 1.670  
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 1.541  
 1.537

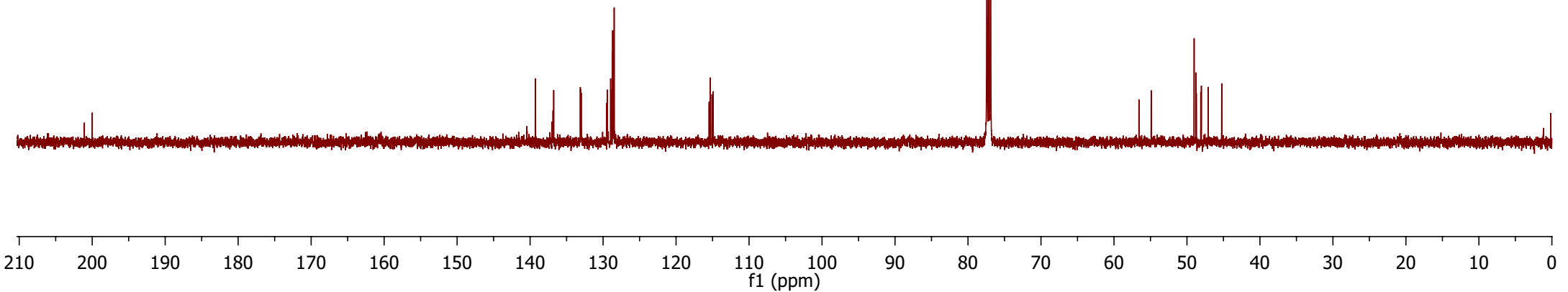
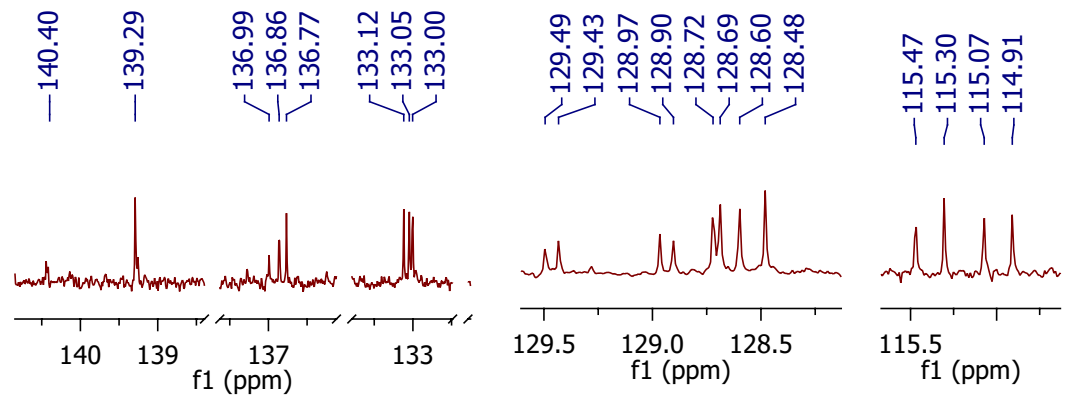


Jul27-2023  
DT-59  
C13CPD



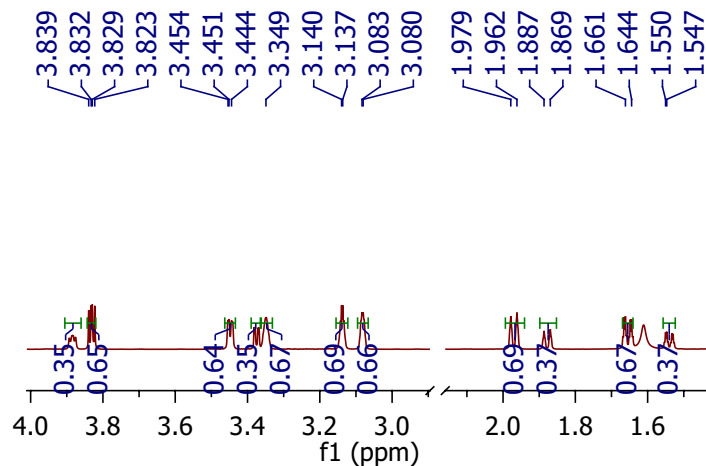
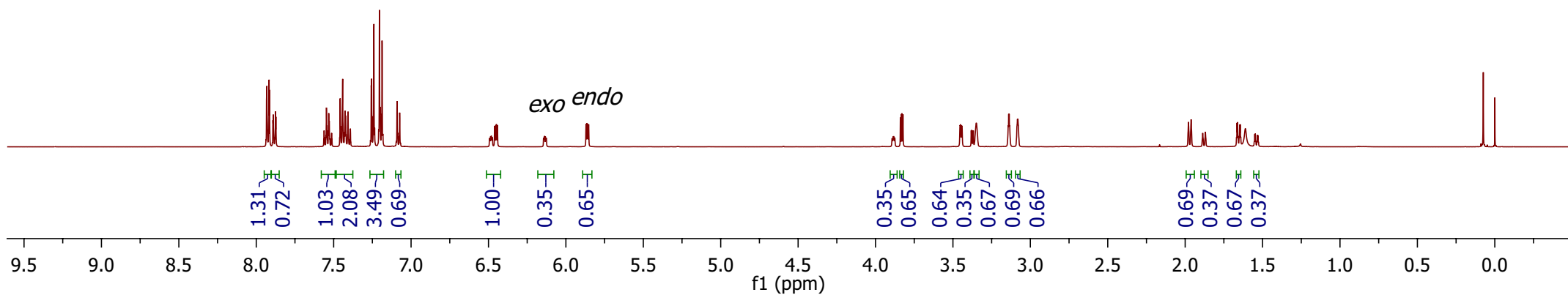
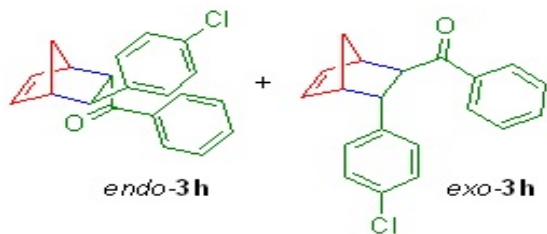
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136.99  
136.86  
136.77  
133.12  
133.05  
133.00  
129.49  
129.43  
128.97  
128.90  
128.72  
128.69  
128.60  
128.48  
115.47  
115.30  
115.07  
114.91

77.41  
77.16  
76.90  
56.58  
54.90  
49.02  
48.76  
48.72  
48.11  
48.03  
47.08  
45.24

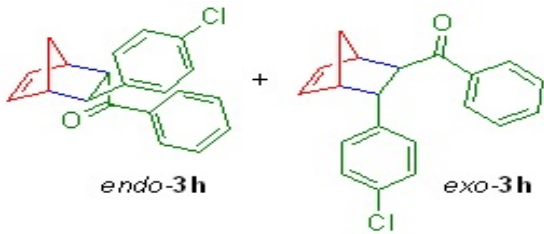




J:\8scan\CDCl3(DMSO-d6)\Spectra\hmr27



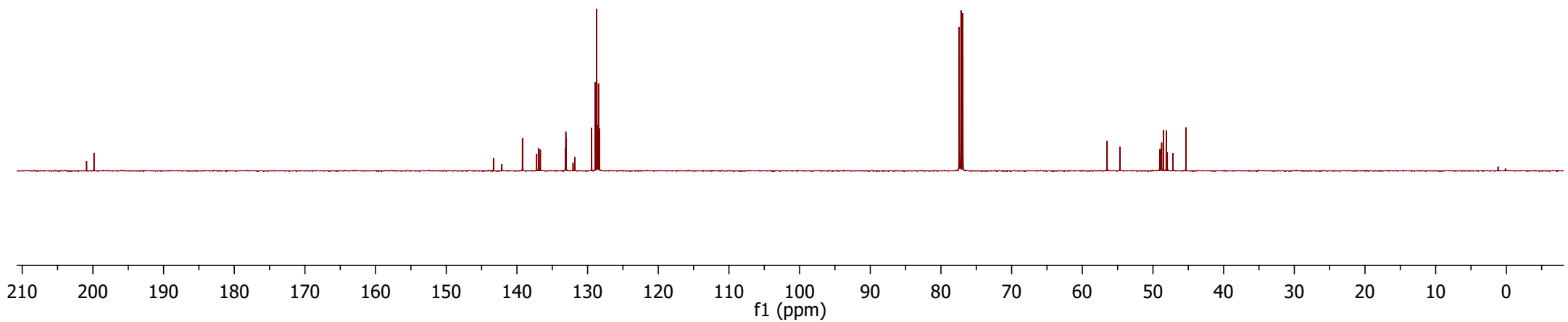
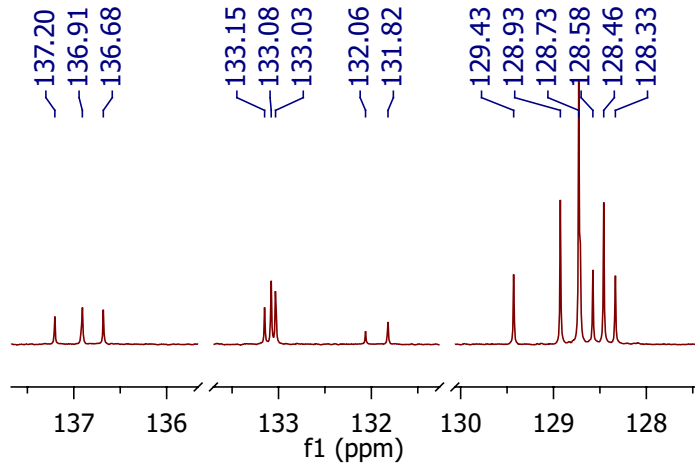
Jul26-2025  
DT-61  
C13CP1 CDCl3 {D:\Spectra} nmr 27



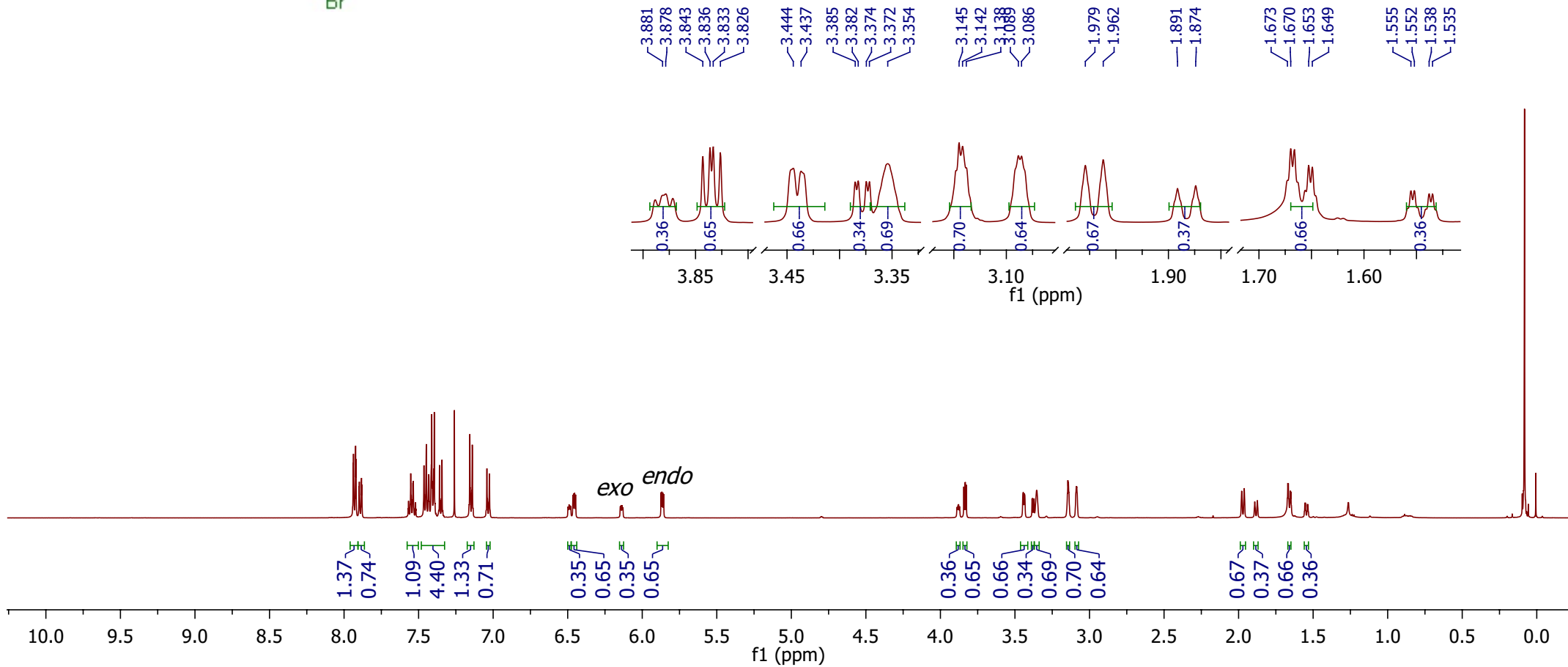
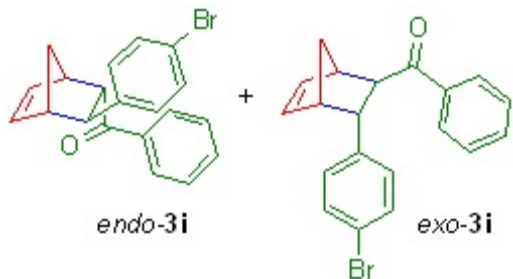
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133.03  
132.06  
131.82  
129.43  
128.93  
128.73  
128.58  
128.46  
128.33

77.41  
77.16  
76.91

56.49  
54.69  
49.05  
48.91  
48.77  
48.52  
48.12  
47.97  
47.17  
45.34



17.7861  
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 1.535



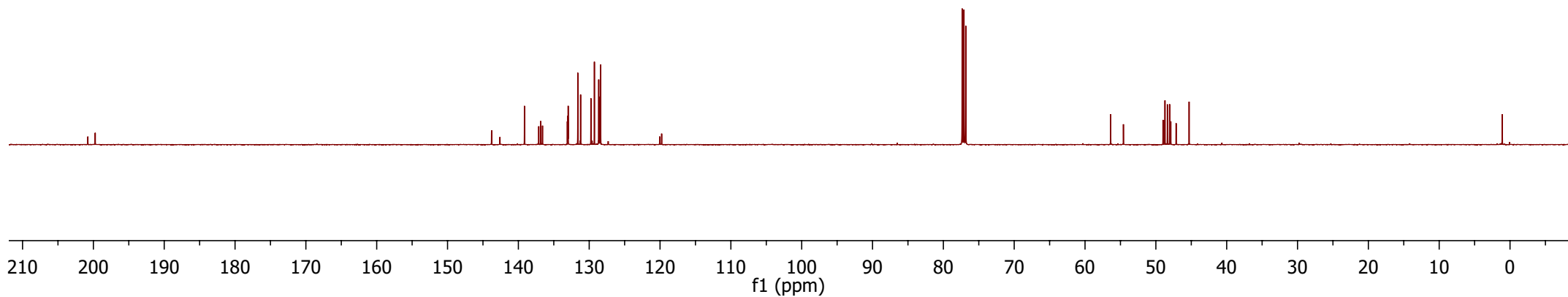
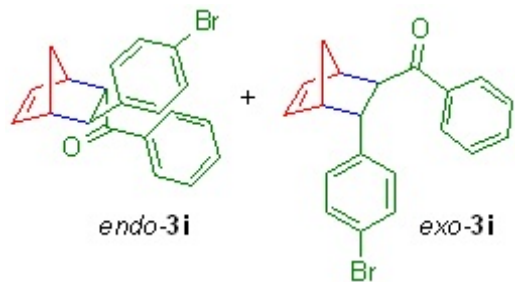
Jul19-2022  
DT-66 4B  
C13CPD CDCl3 {D:\Spectra\}

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139.14  
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136.85  
136.83  
136.59  
133.09  
133.01  
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119.77

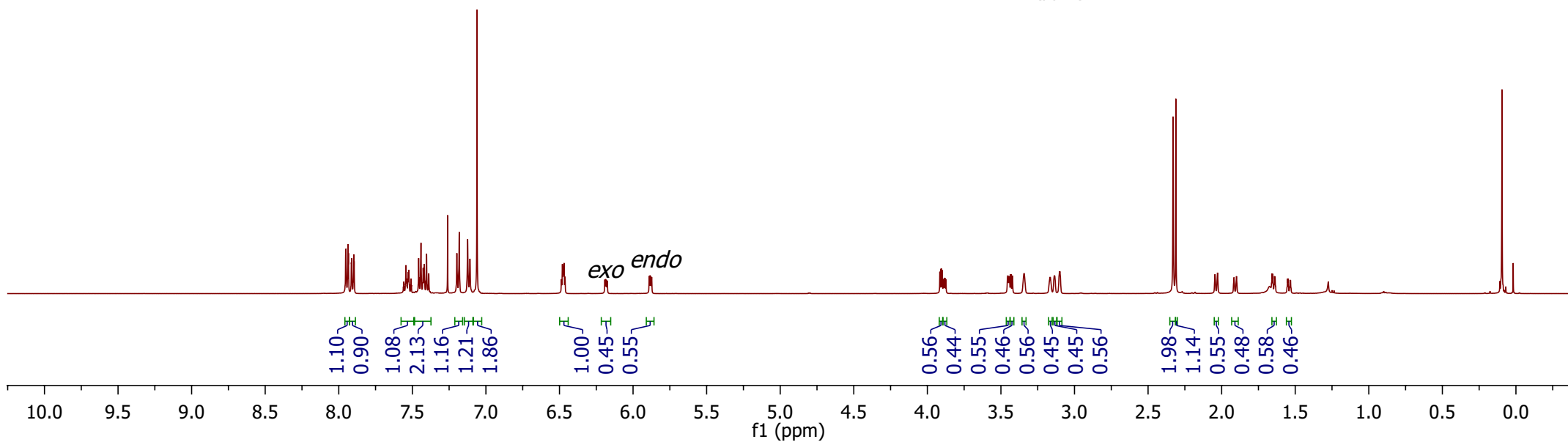
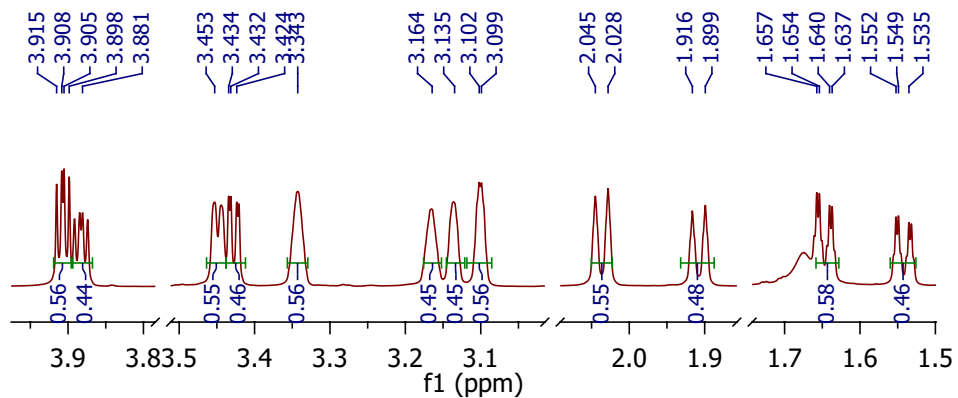
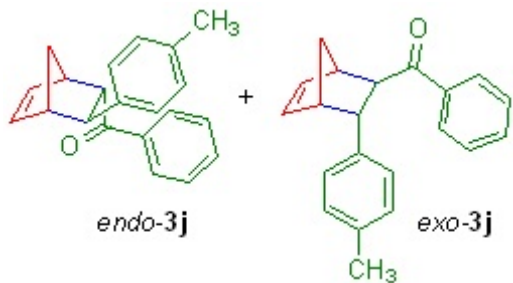
77.35  
77.09  
76.84

56.38  
54.58  
48.99  
48.79  
48.71  
48.37  
48.06  
47.89  
47.14  
45.31

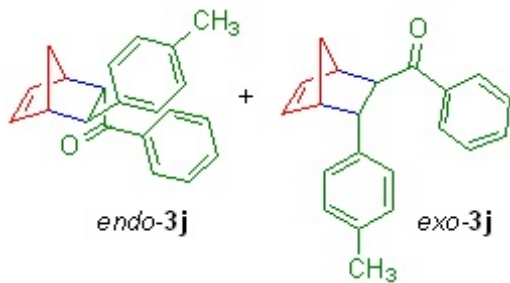
—1.09



J: 17.75519  
 D5: 17.75519  
 F1: 8 scan CDCl3 (D) Spectra hmr 13  
 17.75519  
 7.912  
 7.912  
 7.898  
 7.895  
 7.544  
 7.540  
 7.529  
 7.527  
 7.523  
 7.508  
 7.457  
 7.454  
 7.441  
 7.426  
 7.419  
 7.403  
 7.388  
 7.260  
 7.197  
 7.181  
 7.124  
 7.108  
 7.061  
 6.480  
 6.474  
 6.469  
 6.463  
 5.890  
 5.885  
 5.879  
 5.873  
 3.915  
 3.908  
 3.905  
 3.898  
 3.881  
 3.453  
 3.434  
 3.432  
 3.424  
 3.421  
 3.415  
 3.402  
 3.395  
 3.388  
 3.381  
 3.164  
 3.135  
 3.102  
 3.099  
 2.045  
 2.028  
 1.916  
 1.899  
 1.657  
 1.654  
 1.640  
 1.637  
 1.552  
 1.549  
 1.535  
 1.549  
 1.552  
 1.637  
 1.640  
 1.654  
 1.657  
 1.899  
 1.916  
 2.028  
 2.045  
 3.099  
 3.102  
 3.135  
 3.164  
 3.415  
 3.421  
 3.424  
 3.432  
 3.434  
 3.445  
 3.453



Jul19-2022  
DT-67 4-CH3  
C13CPD-CDCI3 {D:\Spectra} nmr 13



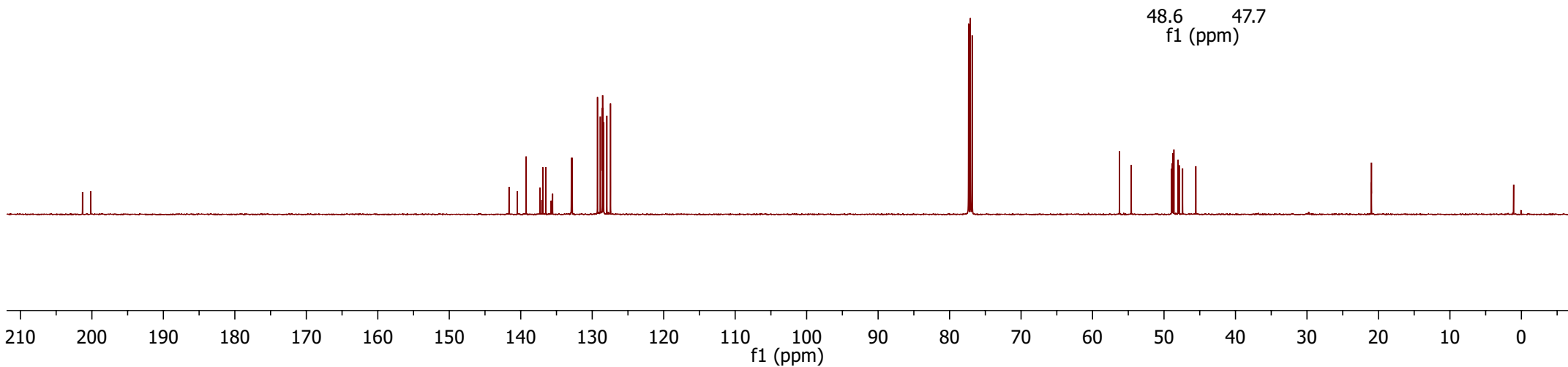
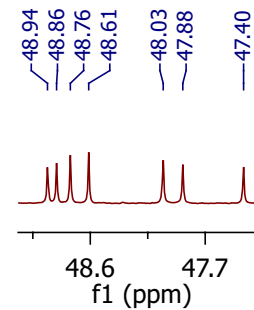
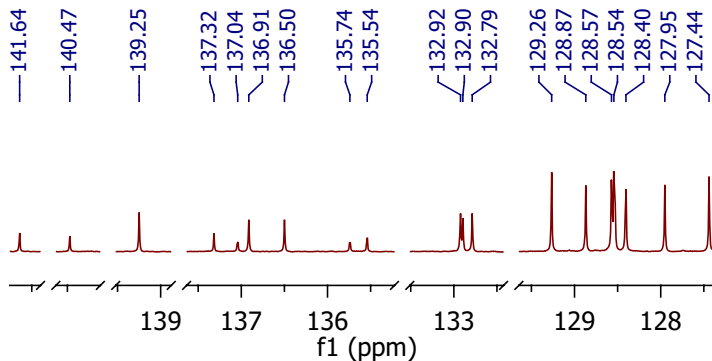
141.64  
140.47  
139.25  
137.32  
137.04  
136.91  
136.50  
135.74  
135.54  
132.92  
132.90  
132.79  
129.26  
128.87  
128.57  
128.54  
128.40  
127.95  
127.44

77.35  
77.09  
76.84

56.23  
54.58  
48.94  
48.86  
48.76  
48.61  
48.03  
47.88  
47.40  
45.55

21.00  
20.98

1.09



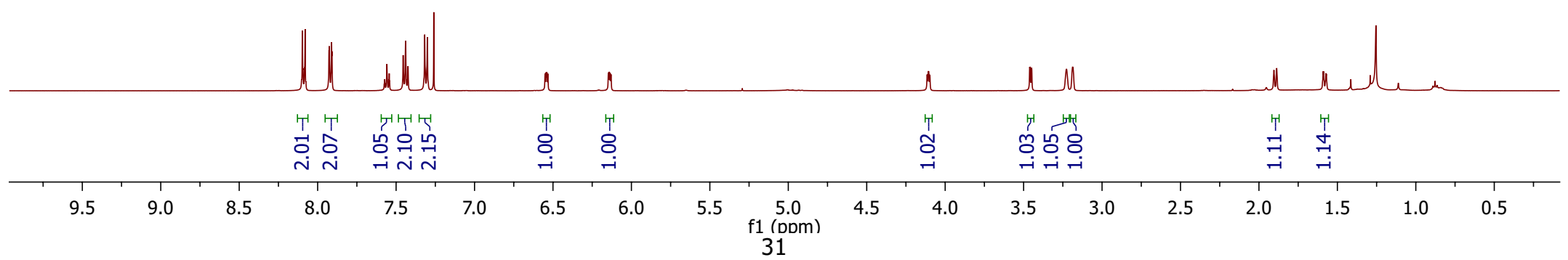
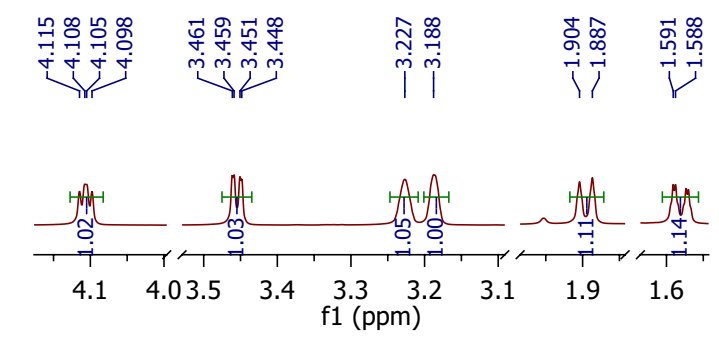
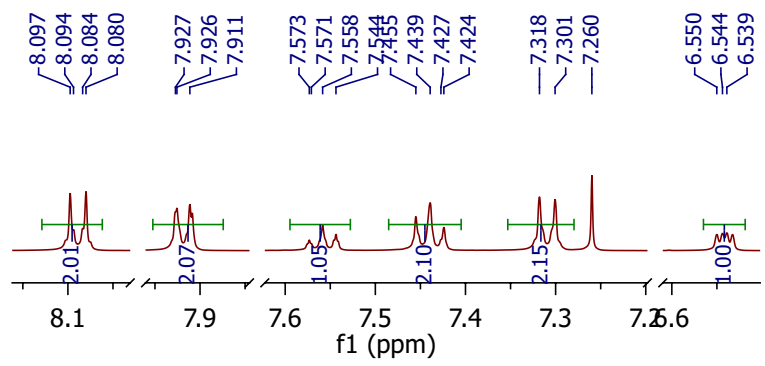
Aug01-2022  
 DT-69  
 1H\_8scan CDCl3 (DMSO-d6) nmr



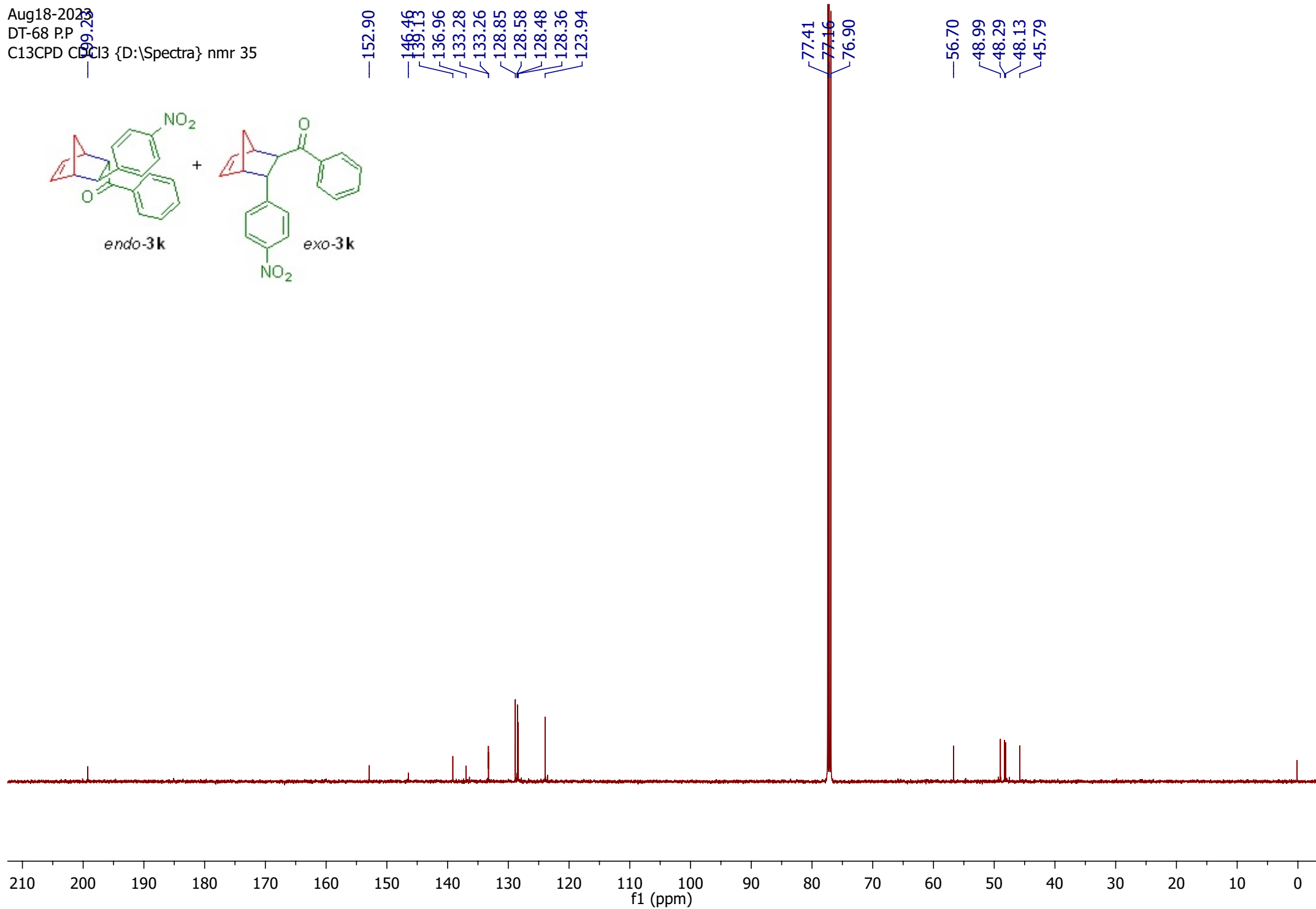
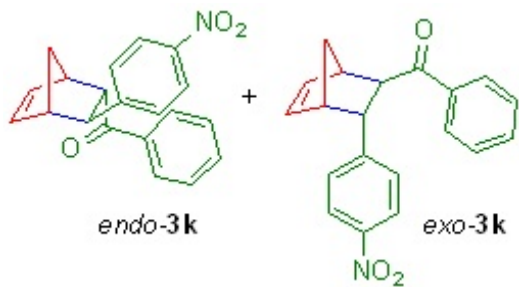
8.102  
 8.097  
 8.094  
 8.084  
 8.080  
 8.075  
 7.927  
 7.926  
 7.911  
 7.909  
 7.455  
 7.439  
 7.318  
 7.301  
 7.260  
 6.550  
 6.544  
 6.539  
 6.529  
 6.147  
 6.141  
 6.135  
 6.130

4.115  
 4.108  
 4.105  
 4.098  
 3.461  
 3.459  
 3.451  
 3.448  
 3.227  
 3.188

1.904  
 1.887  
 1.591  
 1.588  
 1.573  
 1.570

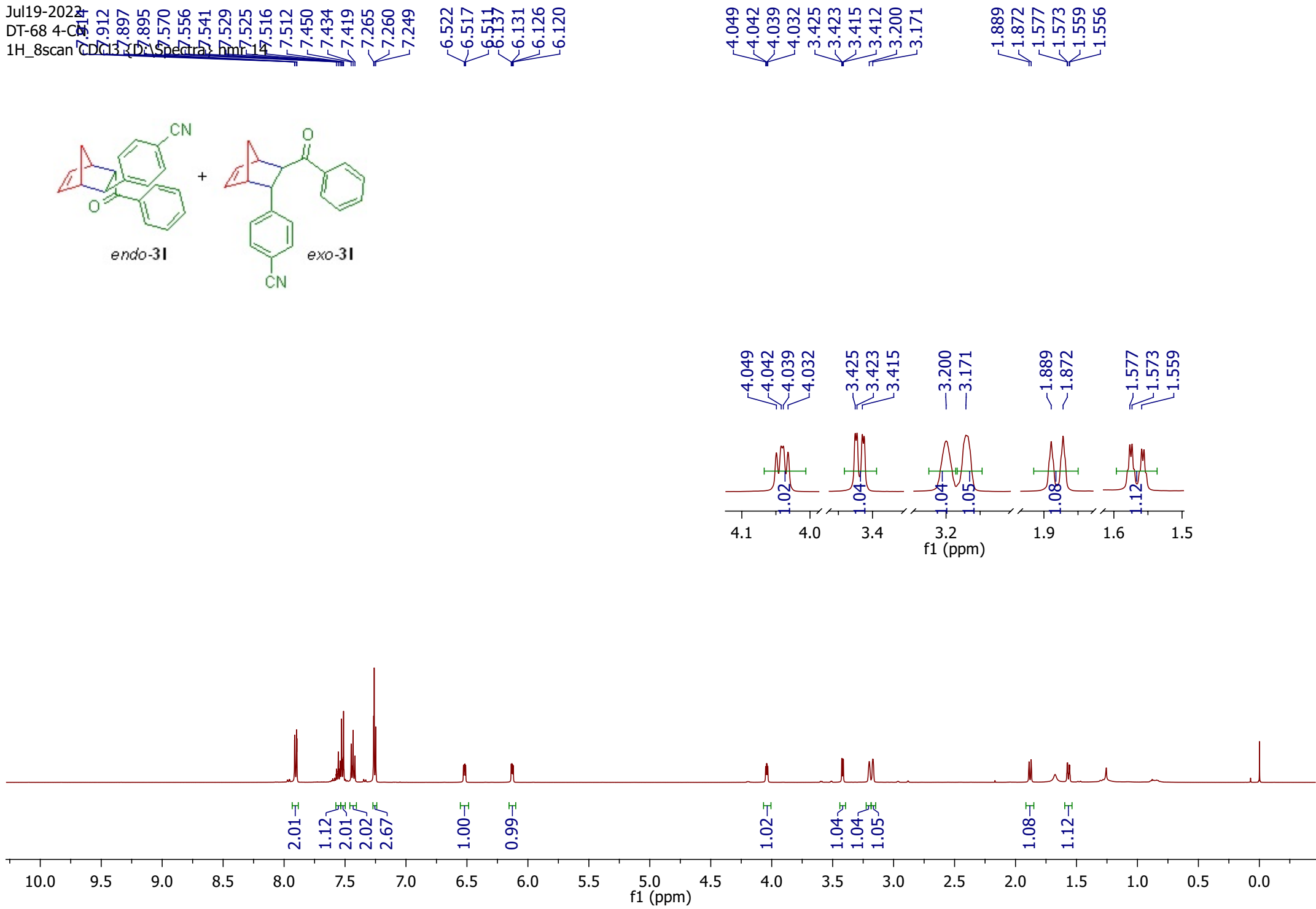


Aug18-2023  
DT-68 P.P  
C13CPD CDCl3 {D:\Spectra} nmr 35

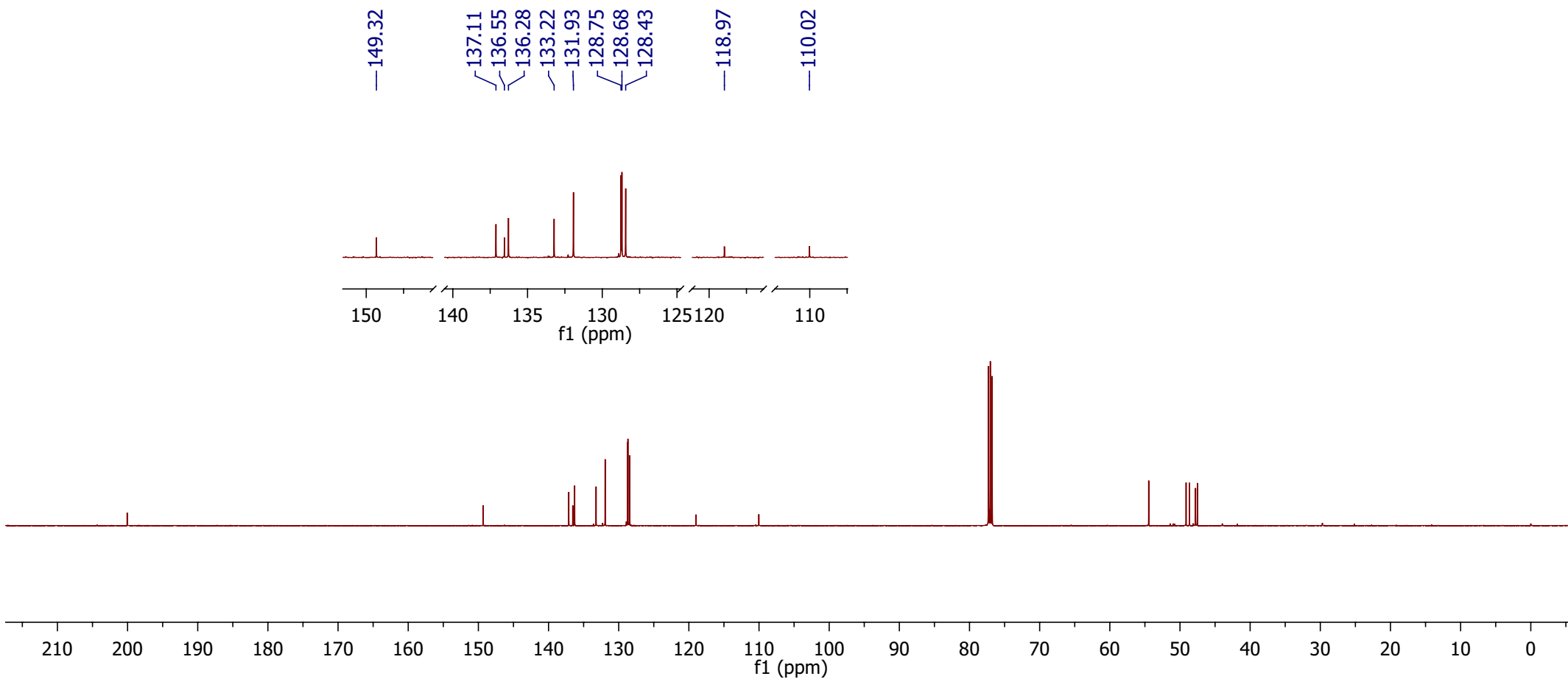
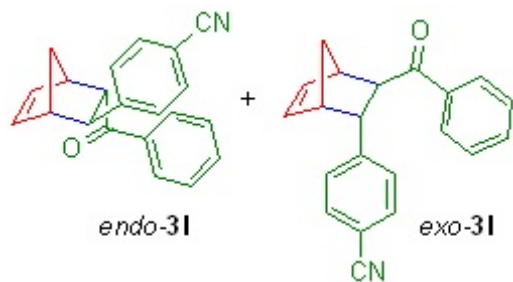




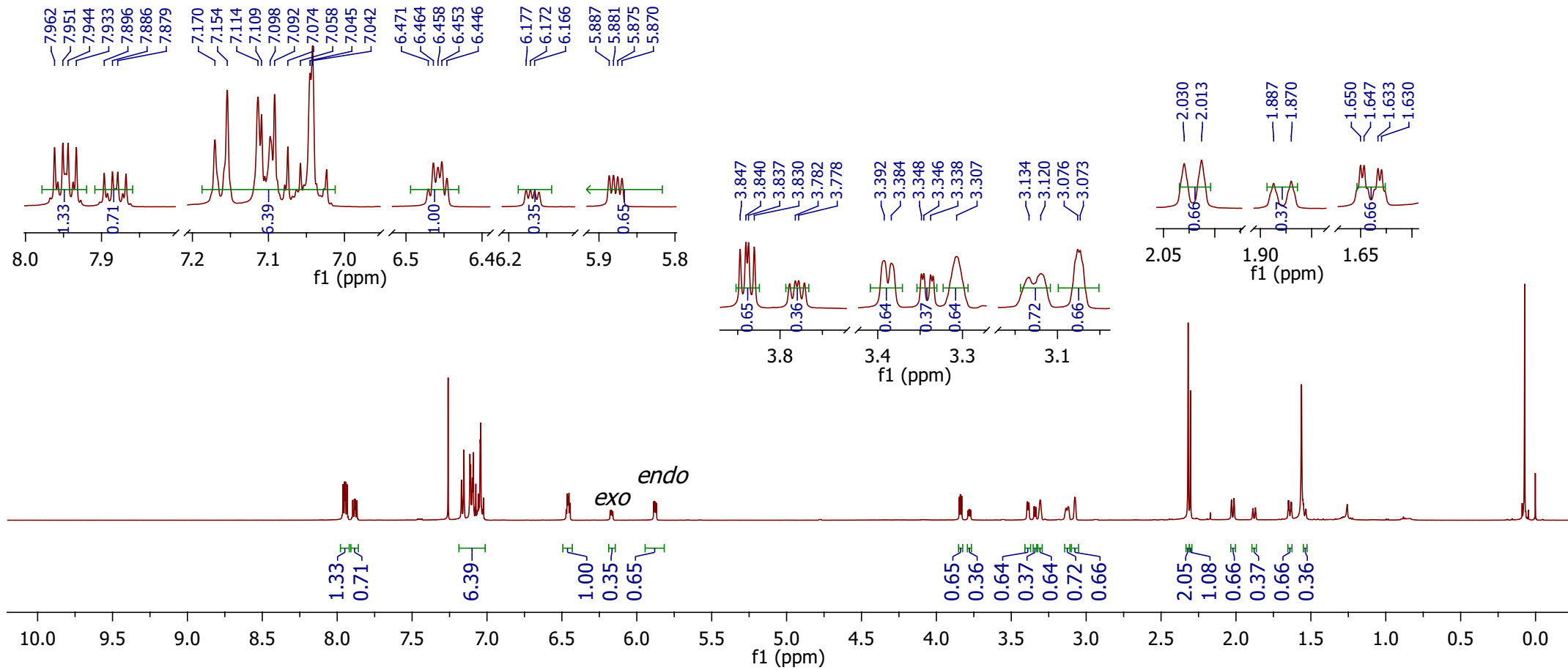
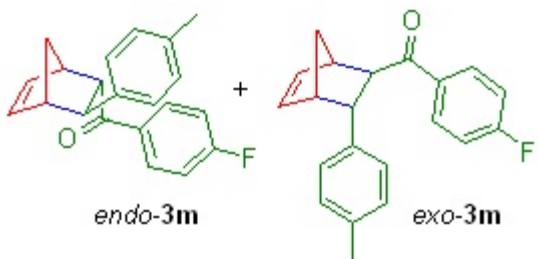
Jul19-2022  
DT-68 4-CN  
1H\_8scan CDCl3 (DMSO-d6) Spectra hmr 14



Jul19-2022  
DT-68 4-CN  
C13CPD CDCl3 {D:\Spectra} nmr 14



Sc 17-76pp-2022  
 1H-Scan CDCl3-D\Spectra\ nmr 6



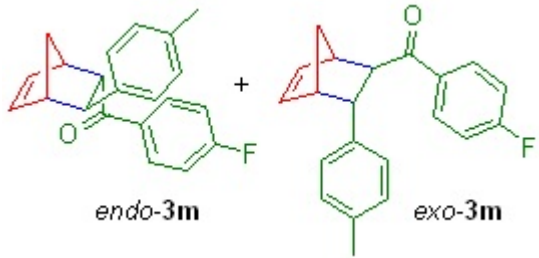
Sep30-2022  
DT-86  
C13CPD CDCI3 {D:\Spectra}

99.84  
98.54

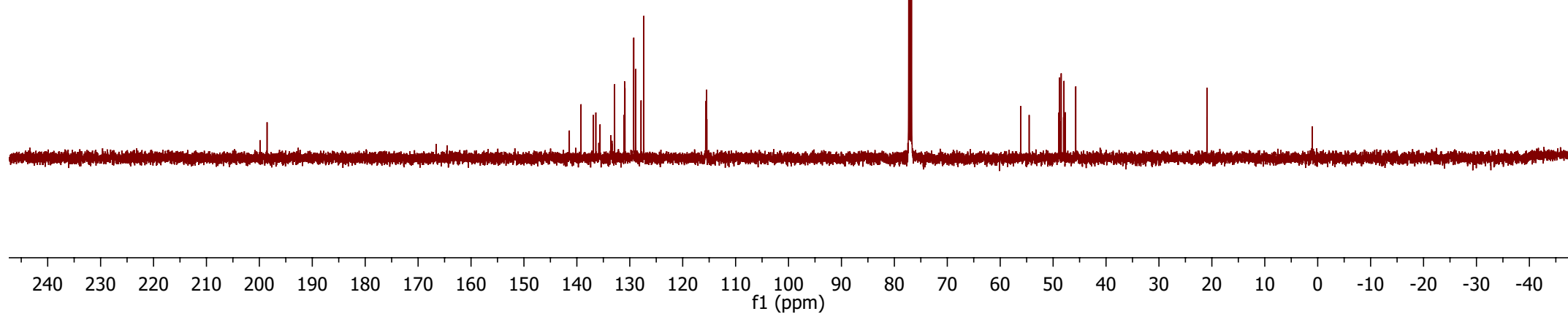
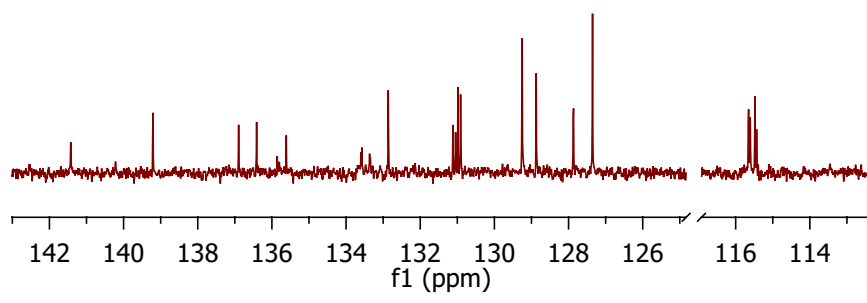
141.42  
139.21  
136.90  
136.41  
135.61  
133.57  
132.86  
131.12  
131.05  
130.98  
130.91  
129.25  
128.87  
127.87  
127.35  
115.65  
115.61  
115.48  
115.44

77.27  
77.01  
76.76  
56.12  
54.53  
48.96  
48.78  
48.62  
48.47  
48.02  
47.94  
47.68  
45.72  
20.92

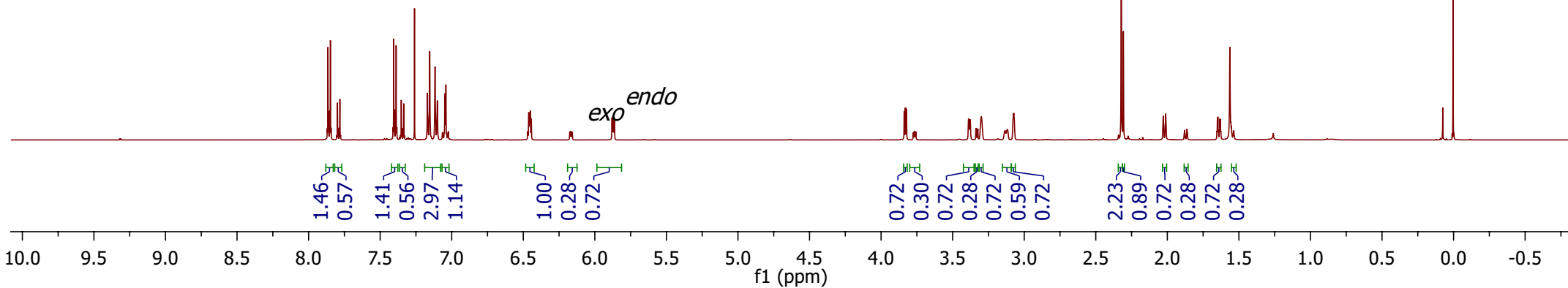
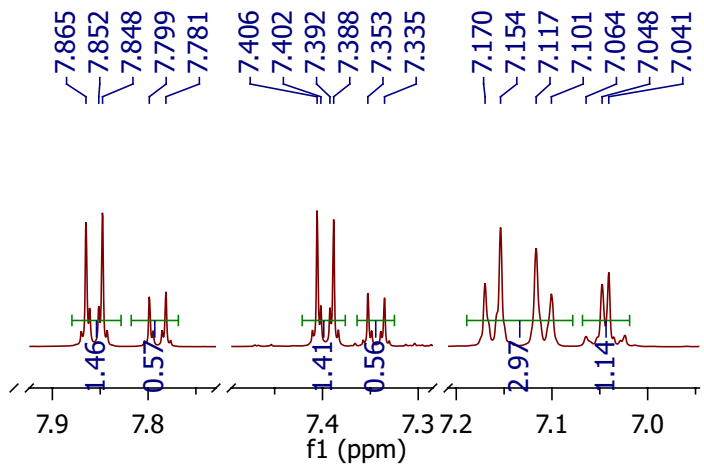
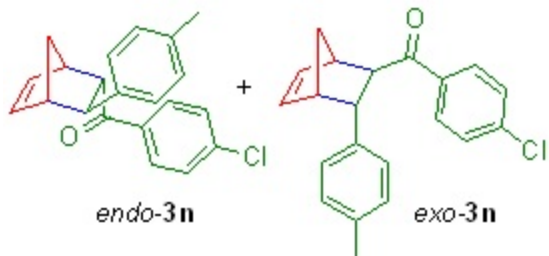
1.02



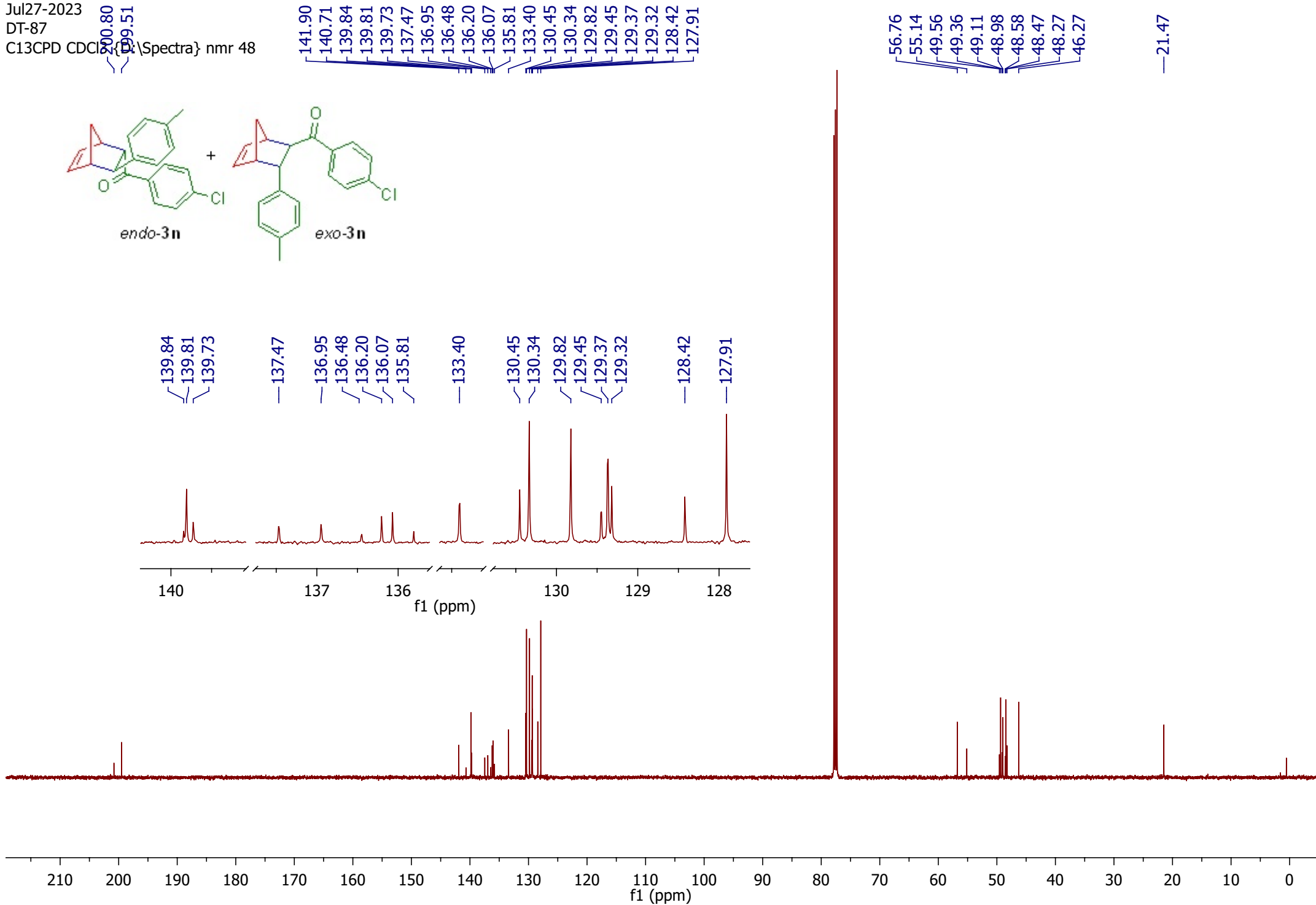
141.42  
139.21  
136.90  
136.41  
135.61  
133.60  
133.57  
132.86  
131.12  
131.05  
130.98  
130.91  
129.25  
128.87  
127.87  
127.35  
115.65  
115.61  
115.48  
115.44



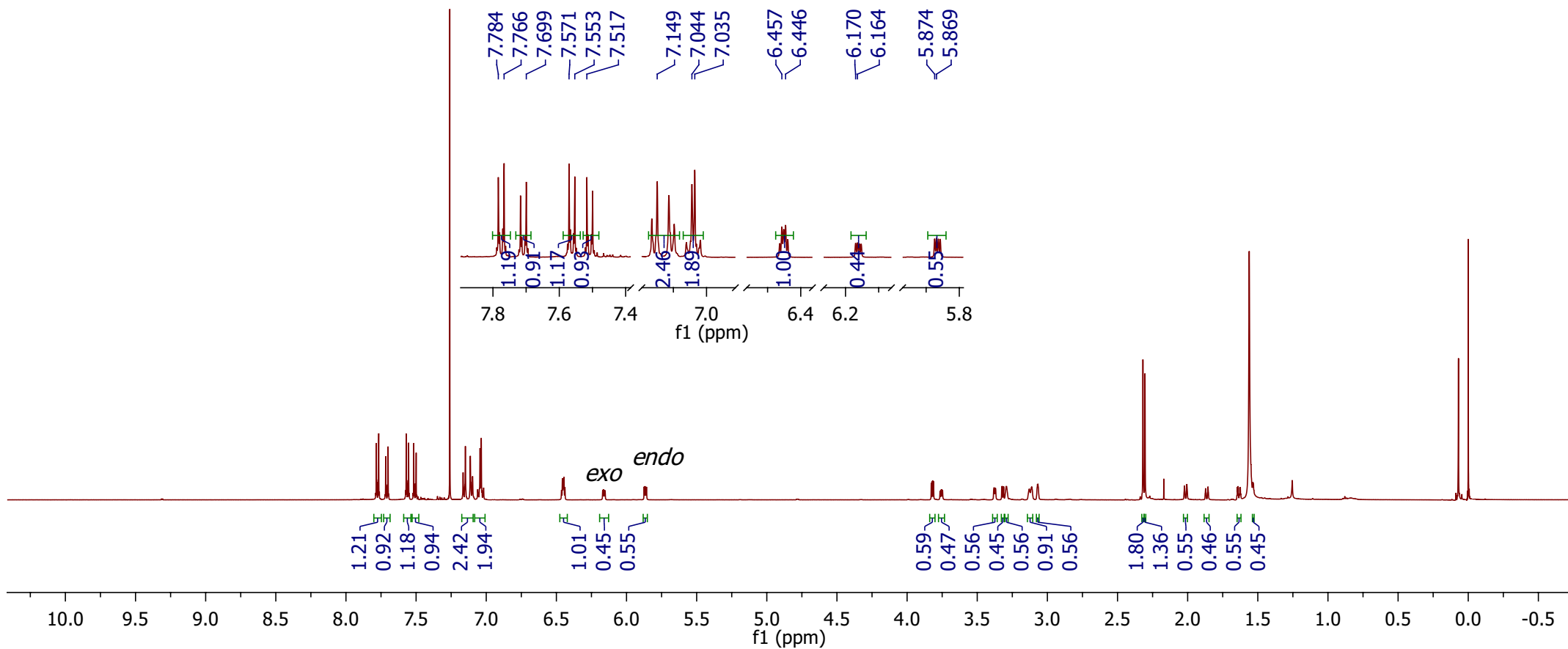
1H NMR spectrum (CDCl3) of compound 3n. The x-axis represents the chemical shift in ppm, ranging from 10.0 to -0.5. The spectrum shows several peaks, with integration values provided below the peaks. The chemical shift values are listed at the top of the image.



Jul27-2023  
DT-87  
C13CPD CDCl<sub>3</sub> (Spectra) nmr 48



17.7847  
 17.7826  
 17.7799  
 17.7772  
 17.7723  
 17.7666  
 17.717  
 17.713  
 17.703  
 17.699  
 17.571  
 17.567  
 17.557  
 17.553  
 17.517  
 17.513  
 17.503  
 17.499  
 17.260  
 17.165  
 17.149  
 17.113  
 17.097  
 17.061  
 17.044  
 17.035  
 16.463  
 16.457  
 16.451  
 16.446  
 16.439  
 16.170  
 16.164  
 15.874  
 15.869  
 15.863  
 15.857  
 3.828  
 3.821  
 3.818  
 3.811  
 3.758  
 3.754  
 3.379  
 3.372  
 3.325  
 3.322  
 3.314  
 3.311  
 3.292  
 3.128  
 3.112  
 3.067  
 2.319  
 2.304  
 2.023  
 2.006  
 1.872  
 1.855  
 1.645  
 1.642  
 1.628  
 1.538  
 1.534  
 1.531  
 1.528



Jul26-2023  
DT-91  
C13CPD CDCI3

100.63  
77.16  
76.90

Spectra

nmr 26

141.47  
140.24  
139.41  
137.06  
136.53  
136.06  
135.80  
132.99  
131.95  
131.90  
130.16  
130.05  
129.42  
129.05  
128.17  
128.00  
127.49

77.41  
77.16  
76.90

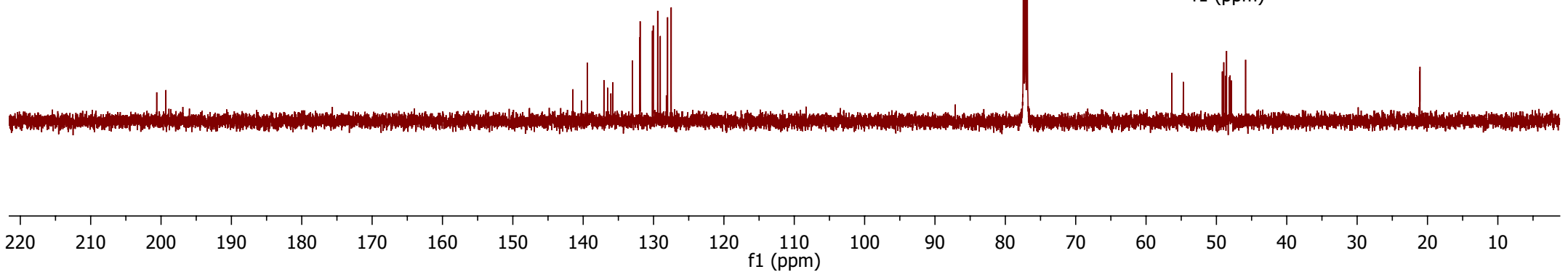
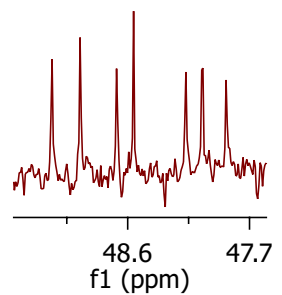
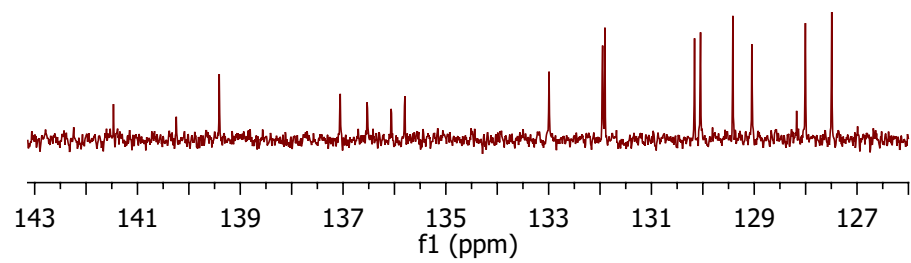
56.34  
54.70  
49.16  
48.95  
48.68  
48.56  
48.17  
48.05  
47.87  
45.85

21.06



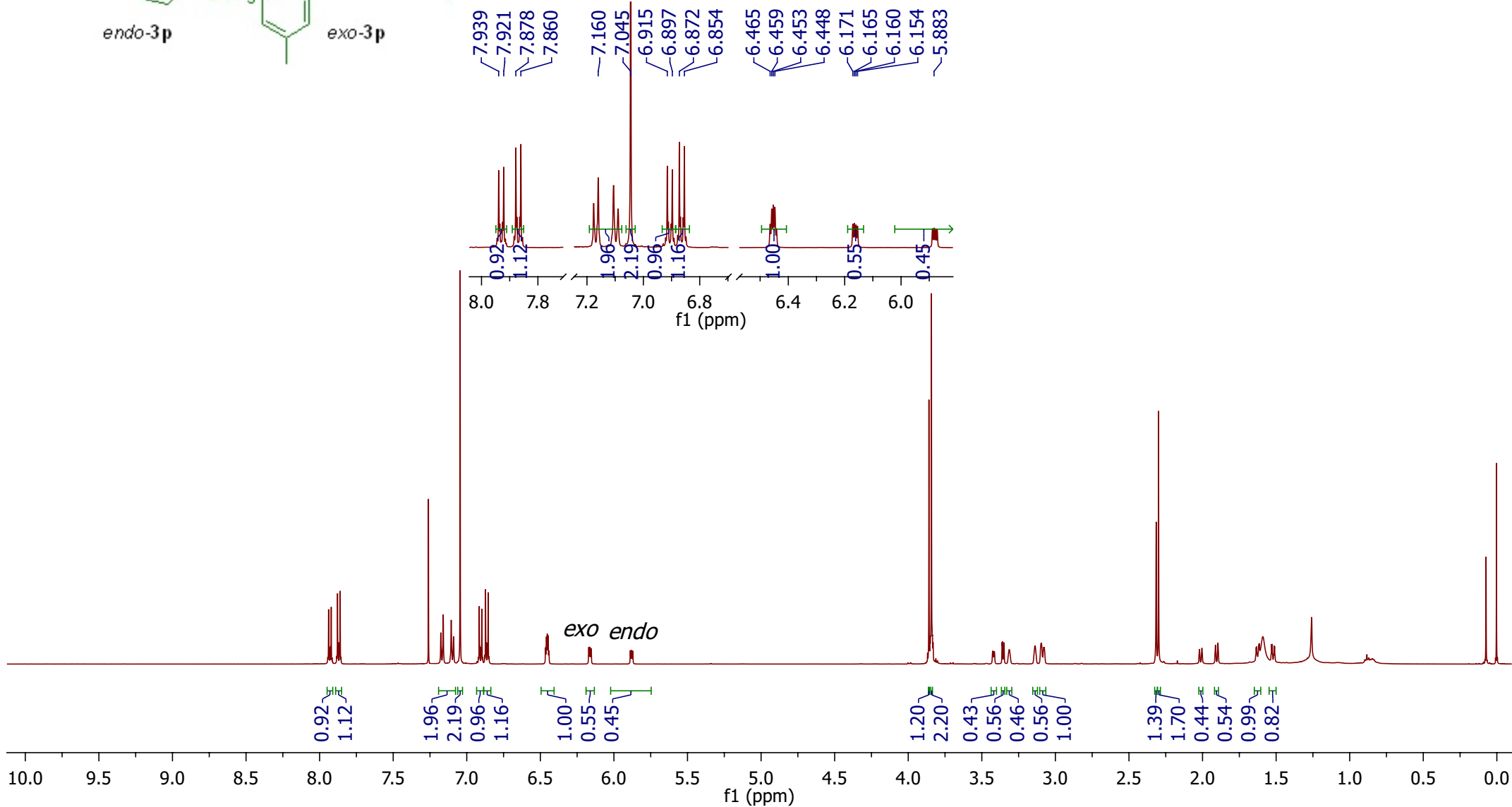
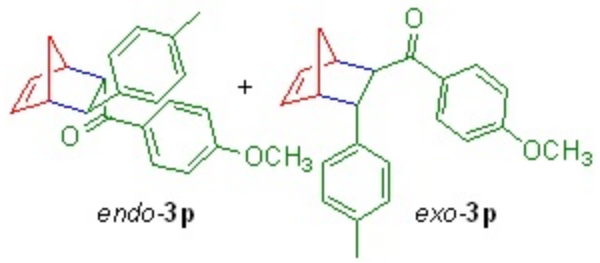
141.47  
140.24  
139.41  
137.06  
136.53  
136.06  
135.80  
132.99  
131.95  
131.90  
130.16  
130.05  
129.42  
129.05  
128.17  
128.00  
127.49

49.16  
48.95  
48.68  
48.56  
48.17  
48.05  
47.87

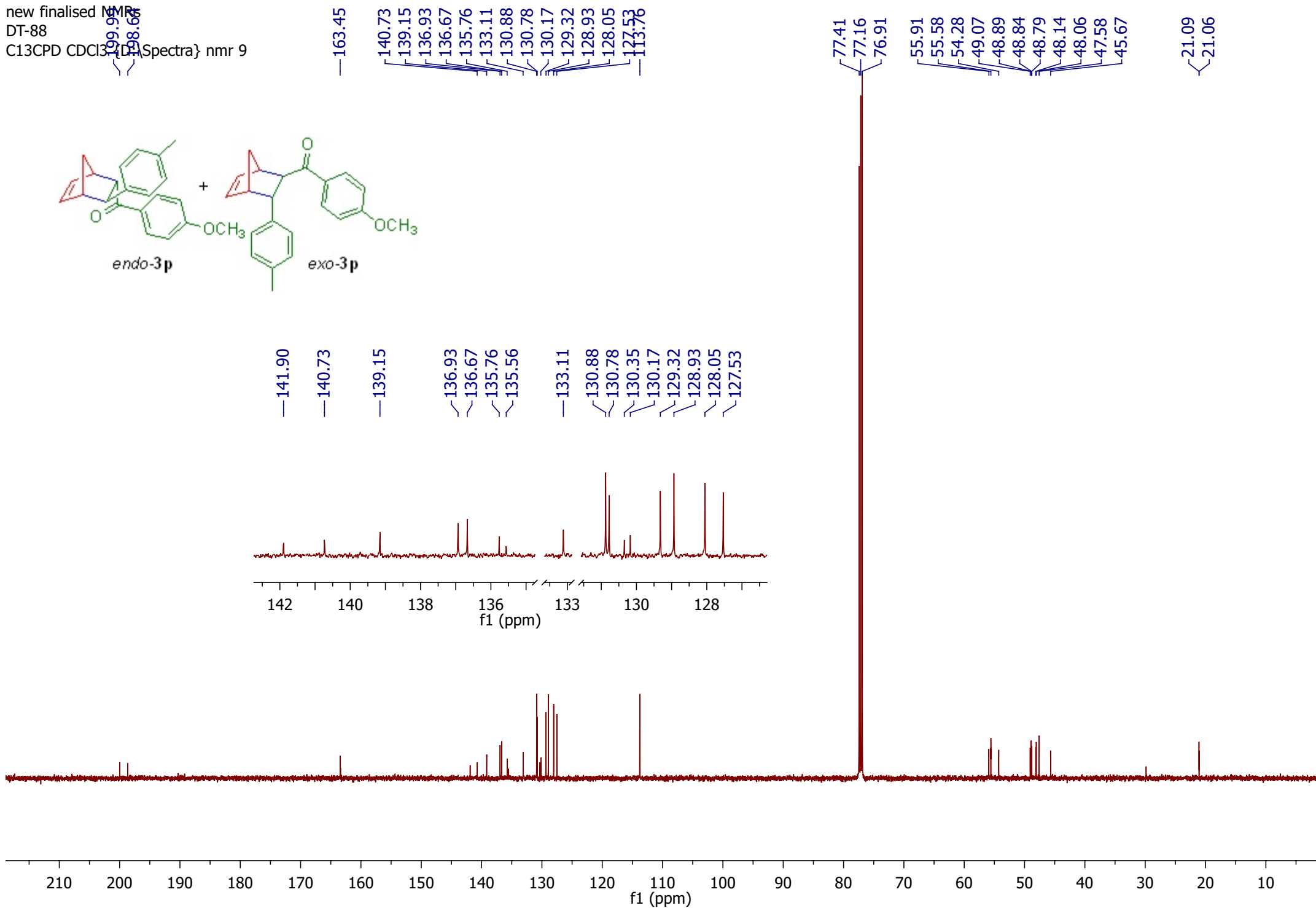
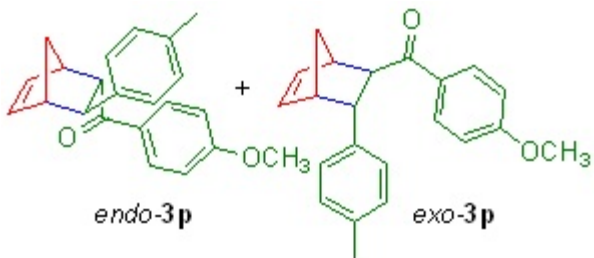




new finalised NMR  
D:\1H scan CDCl3 (D)\Spectra\hmr\_9  
17.748  
7.933  
7.921  
7.921  
7.889  
7.878  
7.874  
7.865  
7.860  
7.855  
7.260  
7.176  
7.160  
7.106  
7.090  
7.045  
6.915  
6.911  
6.901  
6.897  
6.872  
6.868  
6.859  
6.854  
6.465  
6.459  
6.453  
6.448  
6.442  
6.171  
6.165  
6.160  
6.154  
5.889  
5.883  
5.877  
5.872  
3.869  
3.842  
3.425  
3.416  
3.362  
3.359  
3.352  
3.349  
3.313  
3.138  
3.079  
3.076  
2.315  
2.299  
2.021  
2.004  
1.912  
1.895  
1.635  
1.629  
1.618  
1.612  
1.534  
1.528  
1.517  
1.510



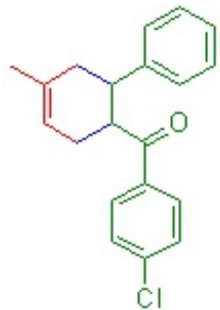
new finalised NMRs  
DT-88  
C13CPD CDC13-D<sub>2</sub> (Spectra) nmr 9



Oct13-2022

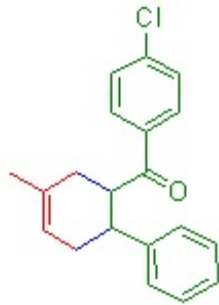
DT-89

<sup>1</sup>H\_8scan CDCl<sub>3</sub> {D:\Spectra} nmr 41

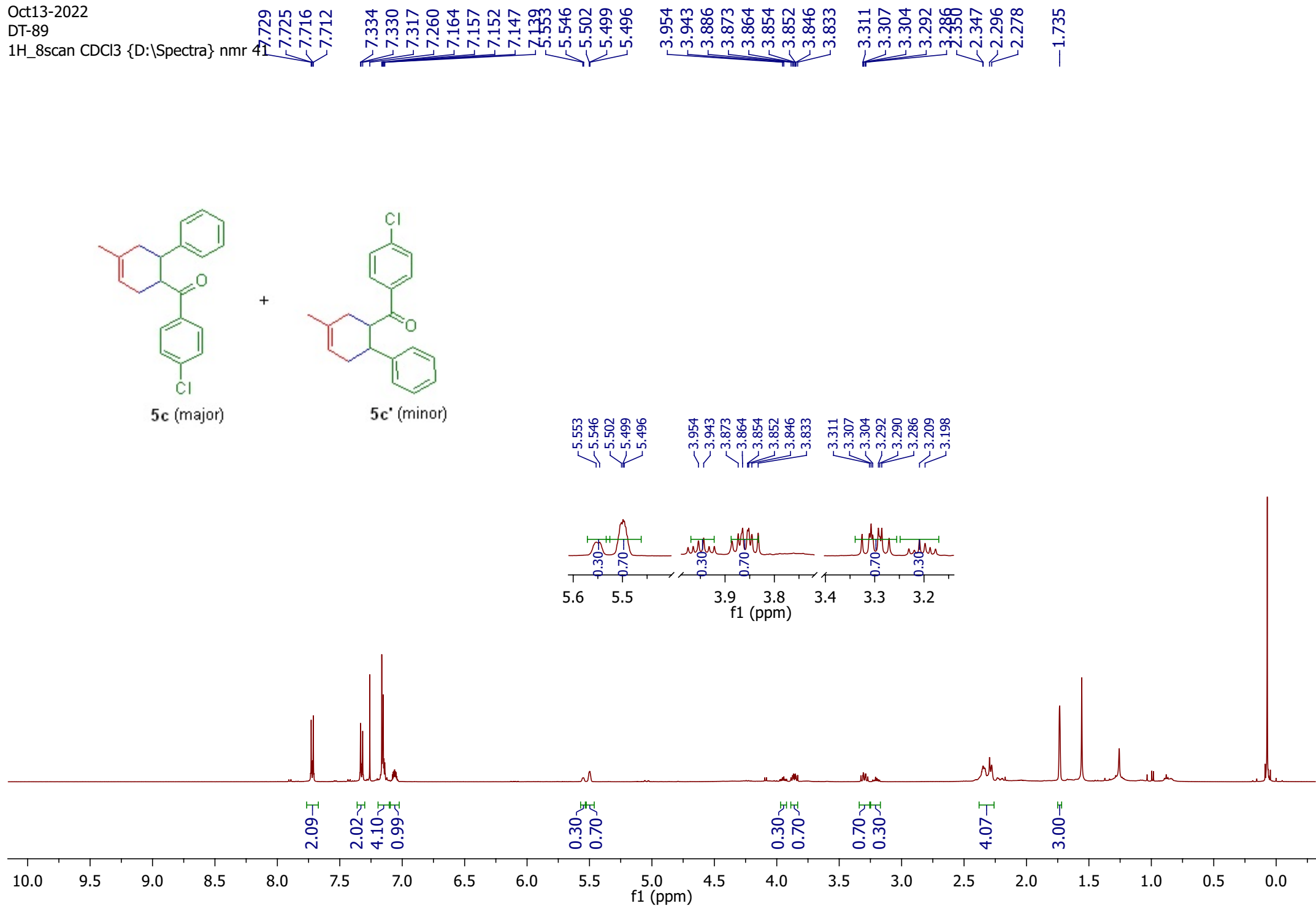


5c (major)

+



5c' (minor)

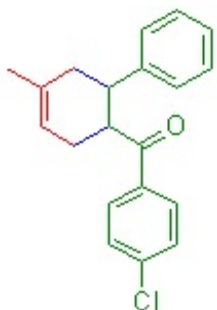


Oct13-2022  
DT-89  
C13CPD-GD-13 {D:\Spectra} nmr 41

144.45  
144.28  
139.26  
139.24  
135.74  
134.20  
129.49  
128.82  
128.47  
128.42  
127.54  
127.49  
126.40  
120.97  
119.17

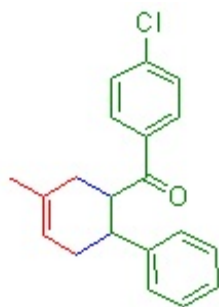
77.35  
77.09  
76.84

47.29  
46.77  
42.99  
42.65  
38.86  
35.12  
34.02  
30.80  
29.79  
23.23



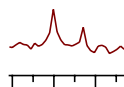
5c (major)

+

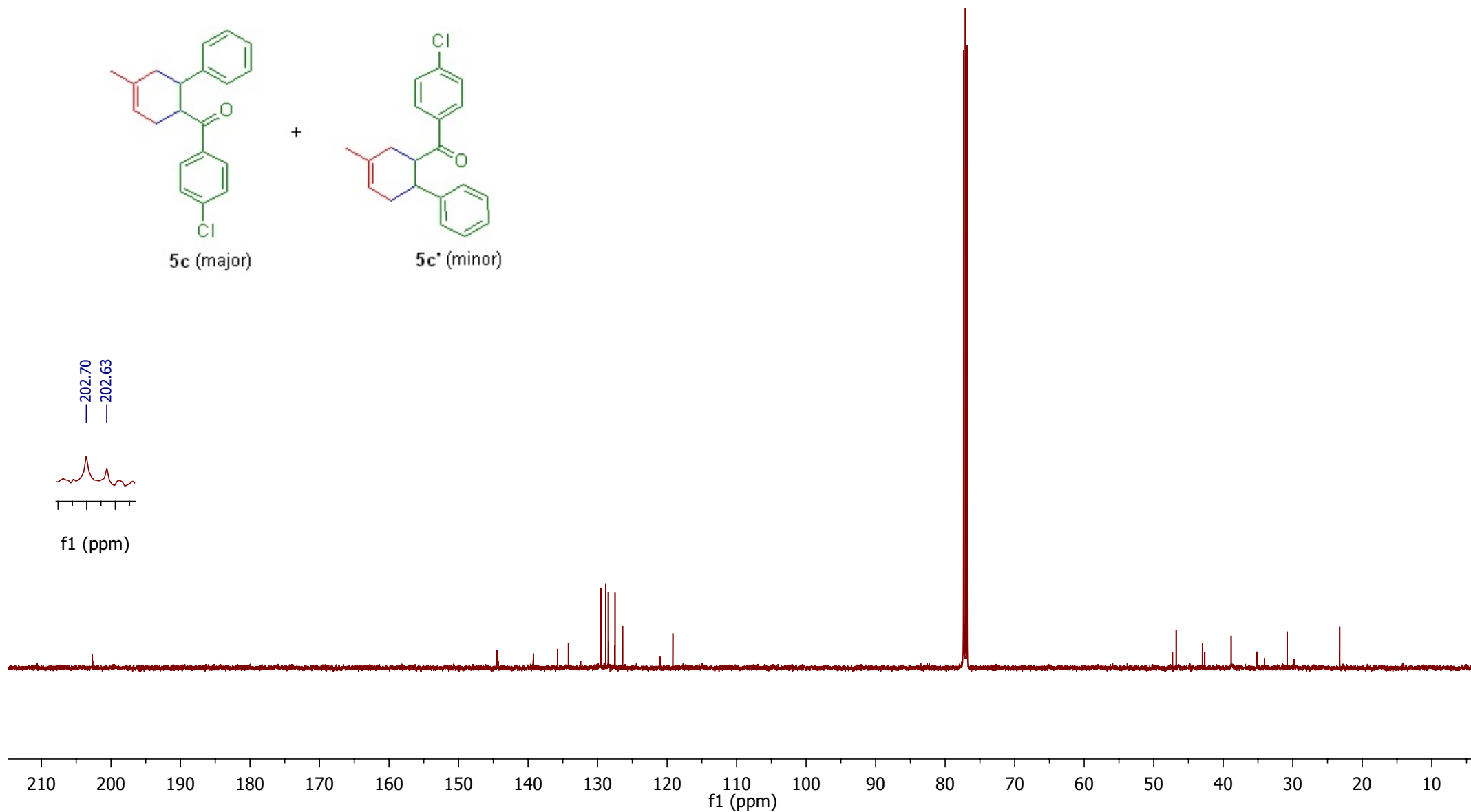


5c' (minor)

202.70  
202.63

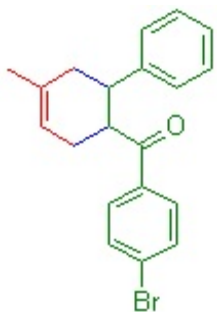


f1 (ppm)



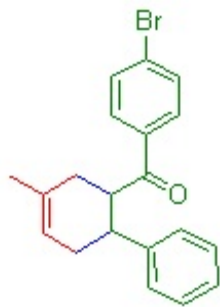
Dec08-2022  
DT-90-Br  
1H\_8scan CDCl3 (D) Spectra

7.652 7.648 7.638 7.634 7.502 7.498 7.488 7.485 7.260 7.163 7.155 7.153 7.151 7.145 7.141 7.080 7.073 7.070 7.063 7.059 7.055 7.052 5.554 5.545 5.500 5.497 5.494 3.946 3.936 3.878 3.866 3.857 3.847 3.844 3.838 3.825 3.324 3.305 3.291 3.284 2.344 2.341 2.294 2.278 1.733

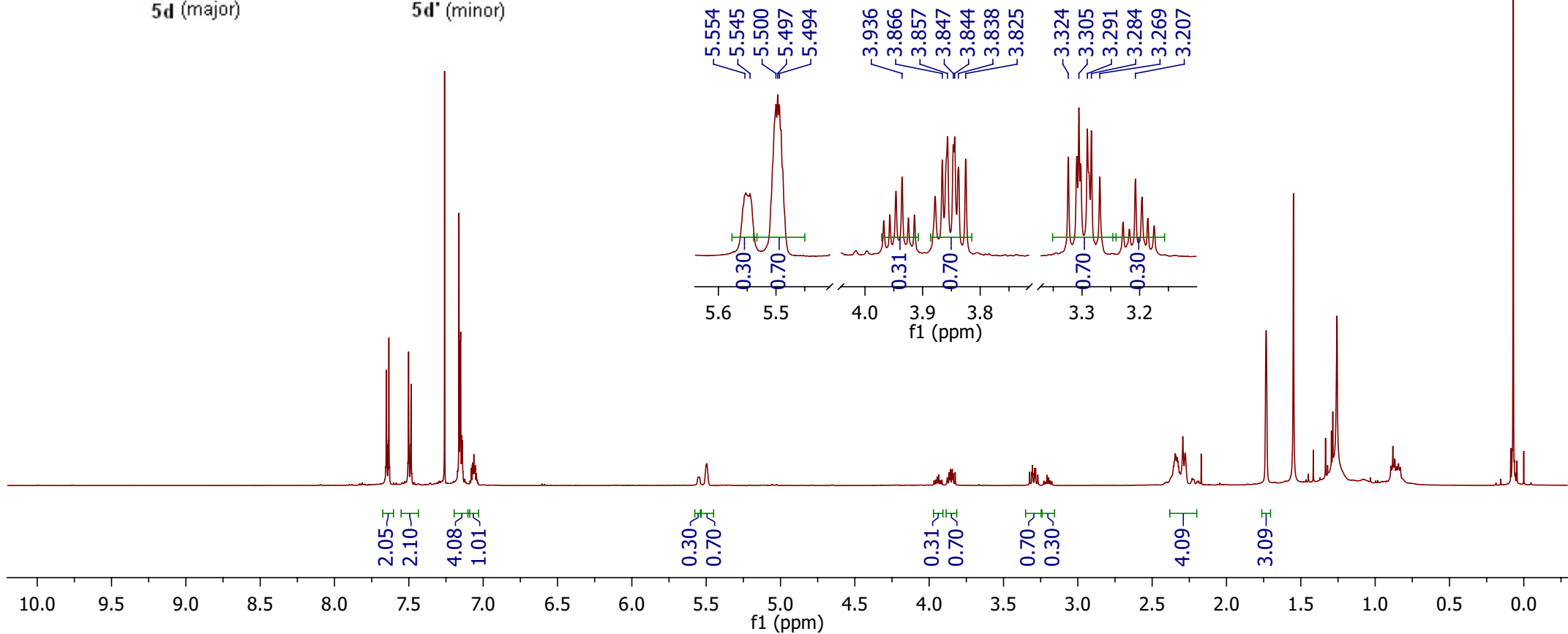


5d (major)

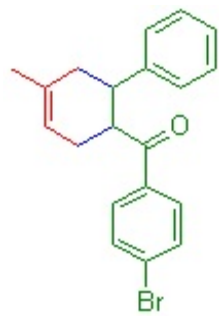
+



5d' (minor)

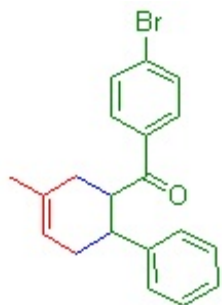


Dec08-2022  
DT-90-Br  
C13CPD\_003 {D:\Spectra} nmr 18



5d (major)

+



5d' (minor)

144.44  
136.15  
134.21  
131.82  
129.60  
128.48  
128.43  
127.97  
127.54  
127.48  
126.41  
121.03  
119.16

77.35  
77.09  
76.84

47.20  
46.77  
42.98  
42.61  
38.86  
38.20  
35.15  
34.00  
30.80  
29.79  
29.47  
23.24

