Electronic Supplementary Material (ESI) for Organic & Biomolecular Chemistry.

Supporting Information

Carbene-Controlled Regioselectivity in Photochemical Cascades

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1. Materials and Methods

Unless otherwise stated, all solvents were purchased from Fisher Scientific and Merck, and used without further purification. Substrates and reagents were purchased from Fluorochem or Sigma Aldrich and used as received.

^{1}H-NMR spectra were recorded on 400 MHz and 500 MHz instruments and are reported relative to residual solvent: $CHCl_3$ (δ 7.26 ppm) or the indicated deuterated solvent. ^{13}C-NMR spectra were recorded on the same instruments (100 and 125 MHz) and are reported relative to $CHCl_3$ (δ 77.16 ppm) or the indicated deuterated solvent. Data for ^{1}H-NMR are reported as follows: chemical shift (δ/ ppm) (multiplicity, coupling constant (Hz), integration). Multiplicities are reported as follows: s = singlet, d = doublet, t = triplet, q = quartet, p = pentet, m = multiplet, br. s = broad singlet, app = apparent. Data for 13C{1H} NMR are reported in terms of chemical shift (δ/ ppm) and multiplicity (C, CH, CH_2 or CH_3). COSY, HSQC, HMBC and NOESY experiments were used in the structural assignment. IR spectra were obtained by use of a Bruker Platinum spectrometer (neat, ATR sampling) with the intensities of the characteristic signals being reported as weak (w, <20% of tallest signal), medium (m, 21-70% of tallest signal) or strong (s, >71% of tallest signal).

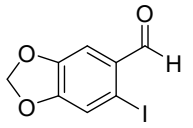
High-resolution mass spectrometry was performed using the indicated techniques on a micromass LCT orthogonal time-of-flight mass spectrometer with leucine-enkephalin (Tyr-Gly-Phe-Leu) as an internal lock mass.

For UV-Vis measurements a Shimadzu UV-1800 UV spectrophotometer was used. Melting points were recorded on a Stuart SMP10 melting point apparatus and are uncorrected.

Continuous flow experiments were performed on a Vapourtec E-series system with the UV150 photoreactor that is equipped with a high-power LED array (50-100 W tuneable, λ_{max} 365 nm, see page SI19)

2. Experimental Procedures and Spectroscopic Data of all Compounds

6-Iodobenzo[d][1,3]dioxole-5-carbaldehyde (SM-1) [SI1]



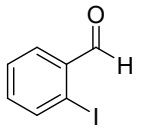
Chemical Formula: $C_8H_5IO_3$
Exact Mass: 275.93

Yield: 87% (4.6 g, 16.6 mmol)
Appearance: beige powder.

^{1}H-NMR (500 MHz, $CDCl_3$) δ/ppm 9.89 (s, 1H), 7.37 (s, 1H), 7.34 (s, 1H), 6.09 (s, 2H). **^{13}C-NMR (125 MHz, $CDCl_3$)** δ/ppm 194.4 (C), 153.5 (C), 149.2 (C), 129.7 (C), 119.4 (CH), 108.9 (CH), 102.7 (CH_2), 93.3 (C). **IR (neat)** ν/cm^{-1}: 2902 (w), 2857 (w), 1660 (s), 1608 (m), 1487 (s), 1404 (s), 1384 (s), 1253 (s), 1112 (s), 1034 (s), 924 (s), 882 (s), 605 (s). **HR-MS** (TOF ES+) calcd for $C_8H_6O_3I$ 276.9356, found 276.9357 ($M+H^+$).

[SI1] Tang, H.-J.; Zhang, Y.-F.; Jiang, Y.-W.; Feng, C. *Org. Lett.* **2018**, *20*, 5190-5193.

2-Iodobenzaldehyde (SM-1')[SI2]



Chemical Formula: C_7H_5IO
Exact Mass: 231.94

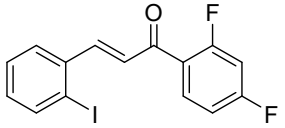
Yield: 91% (2.12 g, 9.1 mmol)
Appearance: white solid.

^{1}H-NMR (400 MHz, $CDCl_3$) δ/ppm 10.07 (d, *J* = 0.8 Hz, 1H), 7.95 (dd, *J* = 8.0, 1.0 Hz, 1H), 7.88 (dd, *J* = 7.7, 2.0 Hz, 1H), 7.46 (t, *J* = 7.7 Hz, 1H), 7.28 (td, *J* = 7.8, 1.9 Hz, 1H). **^{13}C-NMR (100 MHz, $CDCl_3$)** δ/ppm 195.7 (C), 140.6 (CH), 135.4 (CH), 135.1 (C), 130.2 (CH), 128.7 (CH), 100.7 (C). **IR (neat)** ν/cm^{-1}: 2848 (w), 1681 (s), 1577 (s), 1387 (m), 1287 (m), 1199 (s), 1015 (s), 820 (m), 748 (s), 670 (m), 627 (m). **HR-MS** (TOF ES+) calcd for C_7H_6IO 232.9458, found 232.9457 ($M+H^+$).

[SI2] Hoover, J. M.; Stahl, S. S. *J. Am. Chem. Soc.*, **2011**, *133*, 16901-16910.

Synthesis of iodo-chalcones:
To a solution of the desired iodobenzaldehyde (1.0 equiv.) and the corresponding ketone partner (1.0 equiv.) in a mixture i-PrOH (0.5 M)/MeCN (1.5 M), was added a second solution of aq. NaOH (4M) dropwise. The reaction mixture was left to stir at room temperature until a slurry is formed. Crude NMR was used to confirm the end of the reaction. The precipitate was filtered under vacuum and washed with a mixture of i-PrOH/H_2O 8:2. No further purification was required.

(*E*)-1-(2,4-Difluorophenyl)-3-(2-iodophenyl)prop-2-en-1-one:



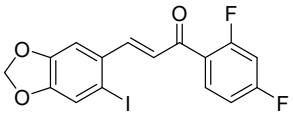
Chemical Formula: $C_{15}H_9F_2IO$
Exact Mass: 369.97

Yield: 39% (230 mg, 0.62 mmol)
Appearance: white powder.
Melting point range: 43-47 °C

^{1}H-NMR (500 MHz, $CDCl_3$) δ/ppm 7.97 – 7.88 (m, 3H), 7.67 (dd, *J* = 7.8, 1.6 Hz, 1H), 7.38 (t, *J* = 7.3 Hz, 1H), 7.23 (dd, *J* = 15.5, 2.9 Hz, 1H), 7.08 (dt, *J* = 7.7, 1.6 Hz, 1H), 7.02 – 6.99 (m, 1H), 6.91 (dddd, *J* = 10.9, 8.7, 2.4 Hz, 1H). **^{13}C-NMR (125 MHz, $CDCl_3$)** δ/ppm 186.7 (d, *J* = 3.2 Hz, C), 165.5 (dd, *J* = 255.1, 12.2 Hz, CF), 163.0 (dd, *J* = 255.3, 12.2 Hz, CF), 148.0 (CH), 140.1 (CH), 137.9 (C), 133.0 (dd, *J* = 9.9, 3.8 Hz, CH), 131.6 (CH), 128.6 (CH), 127.9 (d, *J* = 7.0 Hz, CH), 127.5 (CH), 123.2 (dd, *J* = 12.7, 4.2 Hz, C), 112.3 (dd, *J* = 21.0, 3.9 Hz, CH), 104.8 (dd, *J* = 27.1, 25.0 Hz, CH), 102.0 (C). **^{19}F-NMR (376 MHz, $CDCl_3$)** δ/ppm -102.1, -105.4. **IR (neat)** ν/cm^{-1}: 2987

(w), 1652 (m), 1595 (s), 1493 (m), 1427 (m), 1262 (s), 1096 (s), 970 (s), 846 (s), 735 (s), 521 (m). **HR-MS** (TOF ES+) calcd for $C_{15}H_{10}F_2IO$ 370.9739, found 370.9742 ($M+H^+$).

(*E*)-1-(2,4-Difluorophenyl)-3-(6-iodobenzo[d][1,3]dioxol-5-yl)prop-2-en-1-one:

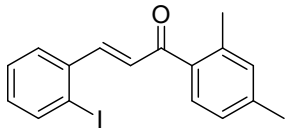


Chemical Formula: $C_{16}H_9F_2IO_3$
Exact Mass: 413.96

Yield: 70% (518 mg, 1.25 mmol)
Appearance: yellow powder.
Melting point range: 137-139 °C

^{1}H-NMR (400 MHz, $CDCl_3$) δ/ppm 7.93 – 7.84 (m, 2H), 7.33 (s, 1H), 7.17 (s, 1H), 7.08 (dd, *J* = 15.3, 2.9 Hz, 1H), 7.01 – 6.96 (m, 1H), 6.89 (m, 1H), 6.03 (s, 2H). **^{13}C-NMR (125 MHz, $CDCl_3$)** δ/ppm 186.9 (d, *J* = 3.3 Hz, C), 165.4 (dd, *J* = 254.8, 12.1 Hz, CF), 161.9 (dd, *J* = 254.6, 12.4 Hz, CF), 150.4 (C), 149.0 (C), 148.2 (CH), 133.0 (dd, *J* = 10.4, 4.3 Hz, CH), 131.2 (C), 126.1 (d, *J* = 7.2 Hz, CH), 123.4 (dd, *J* = 13.3, 3.6 Hz, C), 119.3 (d, *J* = 1.7 Hz, CH), 112.2 (dd, *J* = 21.3, 3.4 Hz, CH), 106.6 (CH), 104.7 (dd, *J* = 27.1, 25.4 Hz, CH), 102.2 (CH_2), 93.0 (C). **^{19}F-NMR (376 MHz, $CDCl_3$)** δ/ppm -102.6, -105.7. **IR (neat)** ν/cm^{-1}: 1609 (s), 1495 (s), 1406 (m), 1261 (s), 1105 (s), 1035 (s), 967 (s), 923 (s), 842 (s), 575 (s). **HR-MS** (TOF ES+) calcd for $C_{16}H_{10}F_2IO_3$ 414.9637, found 414.9639 ($M+H^+$).

(*E*)-1-(2,4-Dimethylphenyl)-3-(2-iodophenyl)prop-2-en-1-one:

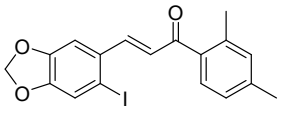


Chemical Formula: $C_{17}H_{15}IO$
Exact Mass: 362.02

Yield: 65% (195 mg, 0.54 mmol)
Appearance: light yellow oil.

^{1}H-NMR (500 MHz, $CDCl_3$) δ/ppm 7.89 (dd, *J* = 7.9, 1.0 Hz, 1H), 7.71 (d, *J* = 15.8 Hz, 1H), 7.62 (dd, *J* = 7.8, 1.5 Hz, 1H), 7.51 (d, *J* = 7.7 Hz, 1H), 7.37 (t, *J* = 7.8 Hz, 1H), 7.10 – 7.08 (m, 2H), 7.05 (dt, *J* = 7.8, 1.6 Hz, 1H), 7.00 (d, *J* = 15.8 Hz, 1H), 2.48 (s, 3H), 2.38 (s, 3H). **^{13}C-NMR (125 MHz, $CDCl_3$)** δ/ppm 195.3 (C), 148.4 (CH), 141.3 (C), 140.0 (CH), 138.2 (C), 137.8 (C), 135.6 (C), 132.4 (CH), 131.3 (CH), 129.4 (CH), 129.0 (CH), 128.6 (CH), 127.4 (CH), 126.1 (CH), 101.7 (C), 21.4 (CH_3), 20.6 (CH_3). **IR (neat)** ν/cm^{-1}: 2920 (w), 1661 (m), 1598 (s), 1497 (m), 1310 (m), 1262 (s), 1207 (s), 1008 (s), 973 (s), 816 (m), 758 (s), 577 (m). **HR-MS** (TOF ES+) calcd for $C_{17}H_{16}IO$ 363.0240, found 363.0240 ($M+H^+$).

(*E*)-1-(2,4-Dimethylphenyl)-3-(6-iodobenzo[d][1,3]dioxol-5-yl)prop-2-en-1-one:

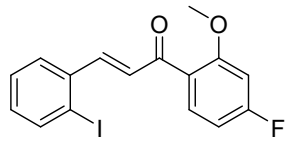


Chemical Formula: $C_{18}H_{15}IO_3$
Exact Mass: 406.01

Yield: 63% (333 mg, 0.82 mmol)
Appearance: white powder.
Melting point range: 115-118 °C

^{1}H-NMR (500 MHz, $CDCl_3$) δ/ppm 7.66 (d, *J* = 15.7 Hz, 1H), 7.46 (d, *J* = 7.7 Hz, 1H), 7.31 (s, 1H), 7.14 (s, 1H), 7.09 – 7.07 (m, 2H), 6.87 (d, *J* = 15.7 Hz, 1H), 6.03 (s, 2H), 2.45 (s, 3H), 2.37 (s, 3H). **^{13}C-NMR (125 MHz, $CDCl_3$)** δ/ppm 195.4 (C), 150.2 (C), 148.9 (C), 148.4 (CH), 141.1 (C), 137.6 (C), 135.8 (C), 132.3 (CH), 131.5 (C), 128.8 (CH), 127.8 (CH), 126.1 (CH), 119.2 (CH), 106.5 (CH), 102.2 (CH_2), 92.3 (C), 21.4 (CH_3), 20.5 (CH_3). **IR (neat)** ν/cm^{-1}: 2920 (w), 1631 (s), 1485 (s), 1405 (m), 1303 (m), 1254 (s), 1228 (s), 1115 (s), 1031 (s), 982 (m), 922 (s), 848 (s). **HR-MS** (TOF ES+) calcd for $C_{18}H_{16}IO_3$ 407.0139, found 407.0142 ($M+H^+$).

(*E*)-1-(4-Fluoro-2-methoxyphenyl)-3-(2-iodophenyl)prop-2-en-1-one:

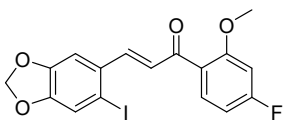


Chemical Formula: $C_{16}H_{12}FIO_2$
Exact Mass: 381.99

Yield: 69% (413 mg, 1.10 mmol)
Appearance: white powder.
Melting point range: 99-102 °C

^{1}H-NMR (400 MHz, $CDCl_3$) δ/ppm 7.89 (dd, *J* = 8.0, 1.1 Hz, 1H), 7.79 (d, *J* = 15.7 Hz, 1H), 7.68 (dd, *J* = 8.6, 6.9 Hz, 1H), 7.62 (dd, *J* = 7.8, 1.5 Hz, 1H), 7.36 (t, *J* = 7.8 Hz, 1H), 7.20 (d, *J* = 15.7 Hz, 1H), 7.04 (dt, *J* = 7.8, 1.6 Hz, 1H), 6.76 – 6.68 (m, 2H), 3.89 (s, 3H). **^{13}C-NMR (100 MHz, $CDCl_3$)** δ/ppm 190.9 (C), 165.8 (d, *J* = 251.3 Hz, CF), 160.0 (d, *J* = 9.8 Hz, C), 146.5 (CH), 140.1 (CH), 138.4 (C), 132.6 (d, *J* = 11.2 Hz, CH), 131.1 (CH), 129.5 (CH), 128.5 (CH), 127.4 (CH), 125.0 (d, *J* = 3.1 Hz, C), 107.7 (d, *J* = 21.3 Hz, CH), 101.8 (C), 99.7 (d, *J* = 26.0 Hz, CH), 56.0 (CH_3). **^{19}F-NMR (376 MHz, $CDCl_3$)** δ/ppm -104.4. **IR (neat)** ν/cm^{-1}: 2972 (w), 1650 (m), 1577 (s), 1412 (m), 1320 (m), 1278 (s), 1197 (s), 1015 (s), 842 (m), 757 (s), 739 (s). **HR-MS** (TOF ES+) calcd for $C_{16}H_{13}FIO_2$ 382.9939, found 382.9942 ($M+H^+$).

(*E*)-1-(4-Fluoro-2-methoxyphenyl)-3-(6-iodobenzo[d][1,3]dioxol-5-yl)prop-2-en-1-one:

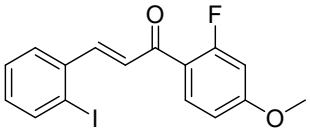


Chemical Formula: $C_{17}H_{12}FIO_4$
Exact Mass: 425.98

Yield: 86% (730 mg, 1.72 mmol)
Appearance: yellow powder.
Melting point range: 149-152 °C

^{1}H-NMR (400 MHz, $CDCl_3$) δ/ppm 7.75 (d, *J* = 15.6 Hz, 1H), 7.66 (dd, *J* = 8.6, 6.9 Hz, 1H), 7.30 (s, 1H), 7.12 (s, 1H), 7.07 (d, *J* = 15.6 Hz, 1H), 6.75 – 6.67 (m, 2H), 6.01 (s, 2H), 3.88 (s, 3H). **^{13}C-NMR (100 MHz, $CDCl_3$)** δ/ppm 190.8 (C), 165.8 (d, *J* = 251.4 Hz, CF), 159.9 (d, *J* = 9.9 Hz, C), 150.0 (C), 148.9 (C), 146.6 (CH), 132.5 (d, *J* = 11.2 Hz, CH), 131.6 (C), 127.8 (CH), 125.1 (d, *J* = 3.2 Hz, C), 119.23 (CH), 107.7 (d, *J* = 21.3 Hz, CH), 106.5 (CH), 102.1 (CH_2), 99.6 (d, *J* = 25.0 Hz, CH), 92.4 (C), 56.0 (CH_3). **^{19}F-NMR (376 MHz, $CDCl_3$)** δ/ppm -104.7. **IR (neat)** ν/cm^{-1}: 2912 (w), 1648 (m), 1600 (s), 1465 (m), 1405 (m), 1247 (s), 1195 (m), 1026 (s), 833 (s), 508 (m). **HR-MS** (TOF ES+) calcd for $C_{17}H_{13}FIO_4$ 426.9837, found 426.9837 ($M+H^+$).

(*E*)-1-(2-Fluoro-4-methoxyphenyl)-3-(2-iodophenyl)prop-2-en-1-one:

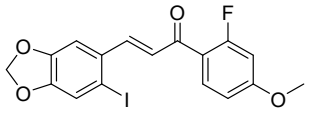


Chemical Formula: $C_{16}H_{12}FIO_2$
Exact Mass: 381.99

Yield: 83% (474 mg, 1.24 mmol)
Appearance: white powder.
Melting point range: 107-109 °C

^{1}H-NMR (400 MHz, $CDCl_3$) δ/ppm 7.95 (dd, *J* = 15.5, 2.0 Hz, 1H), 7.92 – 7.87 (m, 2H), 7.67 (dd, *J* = 7.8, 1.6 Hz, 1H), 7.37 (t, *J* = 7.3 Hz, 1H), 7.30 (dd, *J* = 15.5, 2.9 Hz, 1H), 7.05 (dt, *J* = 7.8, 1.6 Hz, 1H), 6.79 (dd, *J* = 8.8, 2.4 Hz, 1H), 6.64 (dd, *J* = 13.0, 2.4 Hz, 1H), 3.87 (s, 3H). **^{13}C-NMR (100 MHz, $CDCl_3$)** δ/ppm 186.8 (d, *J* = 3.8 Hz, C), 164.8 (d, *J* = 11.9 Hz, C), 163.3 (d, *J* = 253.0 Hz, CF), 147.0 (CH), 140.2 (CH), 138.5 (C), 132.9 (d, *J* = 4.1 Hz, CH), 131.3 (CH), 128.6 (CH), 128.5 (d, *J* = 8.2 Hz, CH), 127.6 (CH), 119.5 (d, *J* = 12.8 Hz, C), 110.9 (d, *J* = 3.4 Hz, CH), 102.0 (d, *J* = 5.8 Hz, CH), 101.8 (C), 56.0 (CH_3). **^{19}F-NMR (376 MHz, $CDCl_3$)** δ/ppm -106.4. **IR (neat)** ν/cm^{-1}: 2970 (w), 1651 (m), 1591 (s), 1439 (m), 1329 (s), 1306 (s), 1208 (s), 1092 (s), 1007 (s), 952 (s), 864 (m), 755 (s), 578 (m). **HR-MS** (TOF ES+) calcd for $C_{16}H_{13}FIO_2$ 382.9939, found 382.9941 ($M+H^+$).

(*E*)-1-(2-Fluoro-4-methoxyphenyl)-3-(6-iodobenzo[d][1,3]dioxol-5-yl)prop-2-en-1-one:

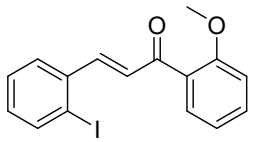


Chemical Formula: $C_{17}H_{12}FIO_4$
Exact Mass: 425.98

Yield: 89% (567 mg, 1.33 mmol)
Appearance: yellow powder.
Melting point range: 130-134 °C

^{1}H-NMR (400 MHz, $CDCl_3$) δ/ppm 7.91 (dd, *J* = 17.6, 2.2 Hz, 1H), 7.88 (t, *J* = 8.4 Hz, 1H), 7.32 (s, 1H), 7.18 (s, 1H), 7.17 (dd, *J* = 15.2, 2.8 Hz, 1H), 6.78 (dd, *J* = 8.8, 2.4 Hz, 1H), 6.64 (dd, *J* = 13.0, 2.3 Hz, 1H), 6.02 (s, 2H), 3.87 (s, 3H). **^{13}C-NMR (100 MHz, $CDCl_3$)** δ/ppm 186.7 (d, *J* = 3.6 Hz, C), 164.7 (d, *J* = 11.7 Hz, C), 163.2 (d, *J* = 253.4 Hz, CF), 150.2 (C), 149.0 (C), 147.0 (d, *J* = 1.0 Hz, CH), 132.8 (d, *J* = 4.1 Hz, CH), 131.7 (C), 126.7 (d, *J* = 8.0 Hz, CH), 119.6 (d, *J* = 12.7 Hz, C), 119.4 (CH), 110.9 (d, *J* = 3.1 Hz, CH), 106.7 (CH), 102.2 (CH_2), 101.9 (d, *J* = 27.0 Hz, CH), 92.7 (C), 56.0 (CH_3). **^{19}F-NMR (376 MHz, $CDCl_3$)** δ/ppm -106.5. **IR (neat)** ν/cm^{-1}: 2909 (w), 1609 (s), 1459 (m), 1330 (m), 1232 (s), 1095 (m), 1013 (m), 854 (m), 557 (m), 427 (m). **HR-MS** (TOF ES+) calcd for $C_{17}H_{13}FIO_4$ 426.9837, found 426.9842 ($M+H^+$).

(*E*)-3-(2-Iodophenyl)-1-(2-methoxyphenyl)prop-2-en-1-one:

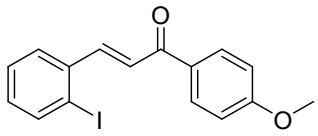


Chemical Formula: $C_{16}H_{13}IO_2$
Exact Mass: 364.00

Yield: 92% (671 mg, 1.84 mmol)
Appearance: white powder.
Melting point range: 80-82 °C

^{1}H-NMR (500 MHz, $CDCl_3$) δ/ppm 7.90 (d, *J* = 8.0 Hz, 1H), 7.79 (d, *J* = 15.8 Hz, 1H), 7.65 – 7.63 (m, 2H), 7.48 (t, *J* = 8.8 Hz, 1H), 7.37 (t, *J* = 7.4 Hz, 1H), 7.21 (d, *J* = 15.7 Hz, 1H), 7.05 (t, *J* = 7.7 Hz, 2H), 7.00 (d, *J* = 8.4 Hz, 1H), 3.91 (s, 3H). **^{13}C-NMR (100 MHz, $CDCl_3$)** δ/ppm 192.8 (C), 158.1 (C), 146.5 (CH), 140.0 (CH), 138.5 (C), 133.0 (CH), 131.1 (CH), 130.5 (CH), 129.8 (CH), 128.9 (C), 128.5 (CH), 127.4 (CH), 120.8 (CH), 111.6 (CH), 101.8 (C), 55.8 (CH_3). **IR (neat)** ν/cm^{-1}: 2980 (w), 1652 (m), 1584 (s), 1484 (m), 1434 (s), 1323 (s), 1248 (s), 1031 (s), 755 (s), 736 (s). **HR-MS** (TOF ES+) calcd for $C_{16}H_{14}IO_2$ 365.0033, found 365.0036 ($M+H^+$).

(*E*)-3-(2-Iodophenyl)-1-(4-methoxyphenyl)prop-2-en-1-one:[SI3]



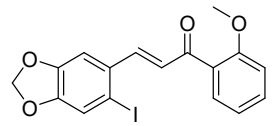
Chemical Formula: $C_{16}H_{13}IO_2$
Exact Mass: 364.00

Yield: 90% (653 mg, 1.79 mmol)
Appearance: white powder.
Melting point range: 106-107 °C

^{1}H-NMR (500 MHz, $CDCl_3$) δ/ppm 8.06 – 8.02 (m, 2H), 7.94 (d, *J* = 16.0 Hz, 1H), 7.92 (d, *J* = 7.9 Hz, 1H), 7.68 (dd, *J* = 8.4, 1.9 Hz, 1H), 7.39 (t, *J* = 7.2 Hz, 1H), 7.34 (d, *J* = 15.7 Hz, 1H), 7.07 (dt, *J* = 7.8, 1.5 Hz, 1H), 7.00 – 6.97 (m, 2H), 3.89 (s, 3H). **^{13}C-NMR (100 MHz, $CDCl_3$)** δ/ppm 188.6 (C), 163.5 (C), 147.0 (CH), 140.1 (CH), 138.6 (C), 131.1 (CH), 131.0 (2CH), 130.8 (C), 128.5 (CH), 127.4 (CH), 125.2 (CH), 113.9 (2CH), 101.6 (C), 55.5 (CH_3). **IR (neat)** ν/cm^{-1}: 2975 (w), 1652 (m), 1590 (s), 1455 (m), 1332 (m), 1258 (m), 1008 (s), 967 (s), 758 (s), 571 (m). **HR-MS** (TOF ES+) calcd for $C_{16}H_{14}IO_2$ 365.0033, found 365.0035 ($M+H^+$).

[SI3] Karuppasamy, M.; Vachan, B. S.; Jandial, T.; Babiola Annes, S.; Bhuvanesh, N.; Uma Maheswari, C.; Sridharan, V. *Adv. Synth. Catal.*, **2020**, *13*, 2716-2724.

(*E*)-3-(6-Iodobenzo[d][1,3]dioxol-5-yl)-1-(2-methoxyphenyl)prop-2-en-1-one:

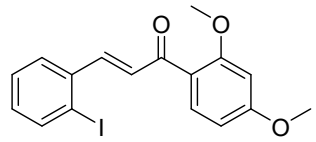


Chemical Formula: $C_{17}H_{13}IO_4$
Exact Mass: 407.99

Yield: 82% (670 mg, 1.64 mmol)
Appearance: off-white powder.
Melting point range: 151-153 °C

^{1}H-NMR (400 MHz, $CDCl_3$) δ/ppm 7.75 (d, *J* = 15.6 Hz, 1H), 7.60 (dd, *J* = 7.6, 1.9 Hz, 1H), 7.47 (t, *J* = 8.4 Hz, 1H), 7.32 (s, 1H), 7.15 (s, 1H), 7.07 (d, *J* = 15.5 Hz, 1H), 7.04 - 6.98 (m, 2H), 6.02 (s, 2H), 3.90 (s, 3H). **^{13}C-NMR (100 MHz, $CDCl_3$)** δ/ppm 192.7 (C), 158.0 (C), 150.0 (C), 148.9 (C), 146.6 (CH), 132.8 (CH), 131.7 (C), 130.4 (CH), 129.1 (C), 128.1 (CH), 120.7 (CH), 119.2 (CH), 111.5 (CH), 106.5 (CH), 102.1 (CH_2), 92.3 (C), 55.7 (CH_3). **IR (neat)** ν/cm^{-1}: 2909 (w), 1651 (m), 1579 (s), 1475 (s), 1241 (s), 1111 (m), 1031 (s), 839 (m), 762 (s), 517.9 (m). **HR-MS** (TOF ES+) calcd for $C_{17}H_{14}IO_4$ 408.9931, found 408.9963 ($M+H^+$).

(*E*)-1-(2,4-Dimethoxyphenyl)-3-(2-iodophenyl)prop-2-en-1-one:

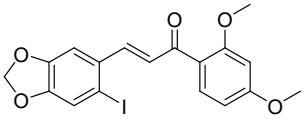


Chemical Formula: $C_{17}H_{15}IO_3$
Exact Mass: 394.01

Yield: 87% (1.33 g, 3.4 mmol)
Appearance: white powder.
Melting point range: 107-110 °C

^{1}H-NMR (500 MHz, $CDCl_3$) δ/ppm 7.90 (dd, *J* = 7.9, 1.0 Hz, 1H), 7.84 (d, *J* = 15.6 Hz, 1H), 7.78 (d, *J* = 8.6, 1H), 7.64 (dd, *J* = 7.8, 1.5 Hz, 1H), 7.38 – 7.34 (m, 2H), 7.04 (dt, *J* = 7.7, 1.6 Hz, 1H), 6.57 (dd, *J* = 8.6, 2.2 Hz, 1H), 6.49 (d, *J* = 2.2 Hz, 1H), 3.90 (s, 3H), 3.87 (s, 3H). **^{13}C-NMR (125 MHz, $CDCl_3$)** δ/ppm 190.1 (C), 164.3 (C), 160.4 (C), 145.1 (CH), 140.0 (CH), 138.9 (C), 133.1 (CH), 130.8 (CH), 130.0 (CH), 128.4 (CH), 127.4 (CH), 121.9 (C), 105.2 (CH), 101.7 (C), 98.6 (CH), 55.7 (CH_3), 55.5 (CH_3). **IR (neat)** ν/cm^{-1}: 2978 (w), 1584 (s), 1459 (m), 1429 (m), 1248 (s), 1203 (s), 1104 (s), 1013 (s), 961 (s), 844 (m), 742 (s). **HR-MS** (TOF ES+) calcd for $C_{17}H_{16}IO_3$ 395.0139, found 395.0138 ($M+H^+$).

(*E*)-1-(2,4-Dimethoxyphenyl)-3-(6-iodobenzo[d][1,3]dioxol-5-yl)prop-2-en-1-one:



Chemical Formula: $C_{18}H_{15}IO_5$
Exact Mass: 438.00

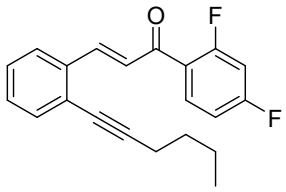
Yield: 58% (459 mg, 1.05 mmol)
Appearance: light yellow solid
Melting point range: 129-133 °C

^{1}H-NMR (400 MHz, $CDCl_3$) δ/ppm 7.78 (d, *J* = 15.5 Hz, 1H), 7.73 (d, *J* = 8.6 Hz, 1H), 7.29 (s, 1H), 7.21 (d, *J* = 15.5 Hz, 1H), 7.12 (s, 1H), 6.54 (dd, *J* = 8.6, 2.2 Hz, 1H), 6.46 (d, *J* = 2.2 Hz, 1H), 5.99 (s, 2H), 3.87 (s, 3H), 3.84 (s, 3H). **^{13}C-NMR (100 MHz, $CDCl_3$)** δ/ppm 190.0 (C), 164.2 (C), 160.3 (C), 149.8 (C), 148.8 (C), 145.1 (CH), 132.9 (CH), 132.1 (C), 128.3 (CH), 122.0 (C), 119.1 (CH), 106.5 (CH), 105.2 (CH), 102.0 (CH_2), 98.6 (CH), 92.1 (C), 55.8 (CH_3), 55.5 (CH_3). **IR (neat)** ν/cm^{-1}: 2917 (w), 1577 (s), 1470 (s), 1409 (m), 1248 (s), 1211 (s), 1106 (m), 1021 (s), 974 (m), 823 (s). **HR-MS** (TOF ES+) calcd for $C_{18}H_{16}IO_5$ 439.0037, found 439.0035 ($M+H^+$).

Synthesis of alkynylated-chalcones:

To a solution of the desired iodo-chalcone (1.0 equiv.) in MeCN (0.2 M) was added in quick succession the alkyne coupling partner (1.5 equiv.), Et_3N (20 equiv.), CuI (15 mol%), $Pd(OAc)_2$ (7.5 mol%) and PPh_3 (15 mol%). The reaction mixture changed colour to black and was left to stir at room temperature for 1h when tlc (10% Et_2O in pentane) indicated full conversion of substrate. The crude product mixture was filtered through a pad of celite (ca. 2 cm) before evaporation of all volatiles. The resulting residue was purified by silica gel column chromatography (10% Et_2O in pentane) to yield the desired Sonogashira reaction products.

(*E*)-1-(2,4-Difluorophenyl)-3-(2-(hex-1-yn-1-yl)phenyl)prop-2-en-1-one, 1a:

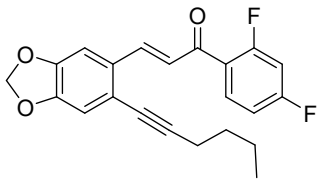


Chemical Formula: $C_{21}H_{18}F_2O$
Exact Mass: 324.13

Yield: 96% (165 mg, 0.51 mmol)
Appearance: red oil.
UV-Vis (MeCN) λ_{max} = 307 nm.

^{1}H-NMR (400 MHz, $CDCl_3$) δ/ppm 8.23 (dd, *J* = 15.8, 1.7 Hz, 1H), 7.89 – 7.85 (m, 1H), 7.70 – 7.69 (m, 1H), 7.46 – 7.44 (m, 1H), 7.41 (dd, *J* = 15.8, 2.9 Hz, 1H), 7.33 – 7.28 (m, 2H), 7.01 – 6.97 (m, 1H), 6.89 (dddd, *J* = 11.1, 8.8, 2.3 Hz, 1H), 2.46 (t, *J* = 7.1 Hz, 2H), 1.62 – 1.57 (m, 2H), 1.52 – 1.54 (m, 2H), 0.95 (t, *J* = 7.2 Hz, 3H). **^{13}C-NMR (100 MHz, $CDCl_3$)** δ/ppm 187.8 (d, *J* = 3.2 Hz, C), 165.4 (dd, *J* = 255.0, 12.9 Hz, CF), 161.9 (dd, *J* = 254.8, 12.4 Hz, CF), 143.7 (d, *J* = 12.9 Hz, CH), 135.8 (C), 133.1 (CH), 133.0 (dd, *J* = 10.3, 4.3 Hz, CH), 130.2 (CH), 127.9 (CH), 126.5 (CH), 126.4 (d, *J* = 6.7 Hz, CH), 125.8 (C), 123.7 (dd, *J* = 13.4, 3.7 Hz, C), 112.2 (dd, *J* = 21.3, 3.6 Hz, CH), 104.7 (dd, *J* = 27.0, 25.2 Hz, CH), 97.6 (C), 78.3 (C), 30.8 (CH_2), 22.1 (CH_2), 19.4 (CH_2), 13.7 (CH_3). **^{19}F-NMR (376 MHz, $CDCl_3$)** δ/ppm -102.8, -105.8. **IR (neat)** ν/cm^{-1}: 2931 (w), 2225 (w), 1664 (m), 1607 (s), 1425 (m), 1265 (s), 1095 (s), 970 (s), 851 (s), 820 (s), 761 (s). **HR-MS** (TOF ES+) calcd for $C_{21}H_{19}F_2O$ 325.1398, found 325.1401 ($M+H^+$).

(*E*)-1-(2,4-Difluorophenyl)-3-(6-(hex-1-yn-1-yl)benzo[d][1,3]dioxol-5-yl)prop-2-en-1-one, 1b:



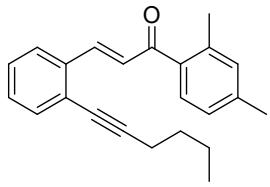
Chemical Formula: $C_{22}H_{18}F_2O_3$
Exact Mass: 368,1224

Yield: 85% (200 mg, 0.54 mmol)
Appearance: orange solid.
UV-Vis (MeCN) λ_{max} = 377, 322 nm.
Melting point range: 48-49 °C

^{1}H-NMR (400 MHz, $CDCl_3$) δ/ppm 8.19 (dd, *J* = 15.8, 2.0 Hz, 1H), 7.86 – 7.80 (m, 1H), 7.17 (dd, *J* = 15.8, 2.7 Hz, 1H), 7.12 (s, 1H), 6.99 – 6.94 (m, 1H), 6.90 – 6.84 (m, 2H), 5.99 (s, 2H), 2.41 (t, *J* = 7.0 Hz, 2H), 1.59 – 1.52 (m, 2H), 1.49 – 1.40 (m, 2H), 0.93 (t, *J* = 7.3 Hz, 3H). **^{13}C-NMR (100 MHz, $CDCl_3$)** δ/ppm 187.7 (C), 165.1 (dd, *J* = 254.0, 12.0 Hz, CF), 161.7 (dd, *J* = 254.4, 12.4 Hz, CF), 149.6 (C), 147.9 (C), 143.5 (CH), 132.7 (dd, *J* = 102.7, 4.4 Hz, CH), 130.7 (C), 124.4 (d, *J* = 6.5 Hz, CH), 123.8 (dd, *J* = 13.5, 3.6 Hz, C), 121.3 (C), 112.0 (dd, *J* = 21.3, 3.5 Hz, CH), 112.1 (CH), 105.1 (CH), 104.6 (dd, *J* = 27.1, 25.3 Hz, CH), 101.8 (CH_2), 96.4 (C), 77.9 (C), 30.7 (CH_2), 22.0 (CH_2), 19.3 (CH_2), 13.6 (CH_3). **^{19}F-NMR (376 MHz, $CDCl_3$)** δ/ppm -103.4 (s, F), -106.9 (s, F). **IR (neat)** ν/cm^{-1}: 2929 (w), 1608 (s), 1478 (s), 1294 (s), 1263

(m), 1198 (s), 1096 (m), 1036 (s), 822 (m), 519 (w). **HR-MS** (TOF ES+) calcd for $C_{22}H_{19}F_2O_3$ 369.1297, found 369.1296 ($M+H^+$).

(*E*)-1-(2,4-Dimethylphenyl)-3-(2-(hex-1-yn-1-yl)phenyl)prop-2-en-1-one, 1c:

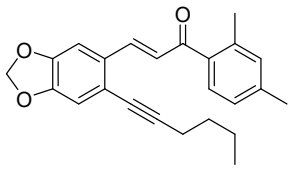


Chemical Formula: $C_{23}H_{24}O$
Exact Mass: 316.18

Yield: 86% (108 mg, 0.34 mmol)
Appearance: yellow oil.
UV-Vis (MeCN) λ_{max} = 300 nm.

^{1}H-NMR (400 MHz, $CDCl_3$) δ/ppm 7.94 (d, *J* = 16.2 Hz, 1H), 7. 67– 7.63 (m, 1H), 7.44 – 7.40 (m, 2H), 7.30 – 7.26 (m, 2H), 7.15 (d, *J* = 16.2 Hz, 1H), 7.07 – 7.04 (m, 2H), 7.01 – 6.97 (m, 1H), 2.42 (s, 3H), 2.36 (t, *J* = 7.1 Hz, 1H), 2.35 (s, 3H), 1.52 – 1.44 (m, 2H), 1.43 – 1.35 (m, 2H), 0.90 (t, *J* = 7.2 Hz, 3H). **^{13}C-NMR (100 MHz, $CDCl_3$)** δ/ppm 196.7 (C), 144.1 (CH), 140.6 (C), 137.3 (C), 136.2 (C), 136.0 (C), 132.8 (CH), 132.0 (CH), 129.8 (CH), 128.7 (CH), 128.0 (CH), 127.8 (CH), 126.1 (CH), 125.9 (CH), 125.3 (C), 97.2 (C), 78.1 (C), 30.6 (CH_2), 22.0 (CH_2), 21.3 (CH_3), 20.4 (CH_3), 19.2 (CH_2), 13.5 (CH_3). **IR (neat)** ν/cm^{-1}: 2927 (m), 2222 (w), 1664 (s), 1593 (s), 1448 (m), 1267 (s), 986 (m), 752 (s), 588 (m). **HR-MS** (TOF ES+) calcd for $C_{23}H_{24}ONa$ 339.1719, found 339.1719 ($M+Na^+$).

(*E*)-1-(2,4-Dimethylphenyl)-3-(6-(hex-1-yn-1-yl)benzo[d][1,3]dioxol-5-yl)prop-2-en-1-one, 1d:

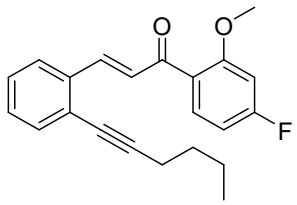


Chemical Formula: $C_{24}H_{24}O_3$
Exact Mass: 360.17

Yield: 78% (280 mg, 0.78 mmol)
Appearance: light yellow powder.
UV-Vis (MeCN) λ_{max} = 366, 320 nm.
Melting point range: 77-78 °C

^{1}H-NMR (400 MHz, $CDCl_3$) δ/ppm 7.92 (d, *J* = 16.2 Hz, 1H), 7.39 (d, *J* = 7.6 Hz, 1H), 7.11 (s, 1H), 7.07 – 7.04 (m, 2H), 6.96 (d, *J* = 16.1 Hz, 1H), 6.85 (s, 1H), 6.00 (s, 2H), 2.41 (s, 3H), 2.35 (s, 3H), 2.32 (t, *J* = 7.1 Hz, 2H), 1.50 – 1.33 (m, 4H), 0.91 (t, *J* = 7.2 Hz, 3H). **^{13}C-NMR (100 MHz, $CDCl_3$)** δ/ppm 196.9 (C), 149.3 (C), 147.9 (C), 144.3 (CH), 140.4 (C), 137.0 (C), 136.4 (C), 131.9 (CH), 131.0 (C), 128.5 (CH), 126.2 (CH), 125.9 (CH), 120.6 (C), 111.9 (CH), 105.0 (CH), 101.8 (CH2), 96.1 (C), 77.8 (C), 30.6 (CH_2), 22.0 (CH_2), 21.3 (CH_3), 20.3 (CH_3), 19.1 (CH_2), 13.5 (CH_3). **IR (neat)** ν/cm^{-1}: 2933 (w), 1631 (s), 1610 (s), 1488 (s), 1271 (s), 1197 (m), 1034 (s), 988 (s), 922 (s), 868 (s), 553 (m). **HR-MS** (TOF ES+) calcd for $C_{24}H_{25}O_3$ 361.1798, found 361.1800 ($M+H^+$).

(*E*)-1-(4-Fluoro-2-methoxyphenyl)-3-(2-(hex-1-yn-1-yl)phenyl)prop-2-en-1-one, 1e:



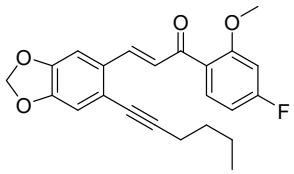
Chemical Formula: $C_{22}H_{21}FO_2$
Exact Mass: 336.15

Yield: 60% (200 mg, 0.6 mmol)
Appearance: red oil.
UV-Vis (MeCN) λ_{max} = 305 nm.

^{1}H-NMR (400 MHz, $CDCl_3$) δ/ppm 8.09 (d, *J* = 16.0 Hz, 1H), 7.67 – 7.62 (m, 2H), 7.44 – 7.40 (m, 1H), 7.34 (d, *J* = 16.0 Hz, 1H), 7.29 – 7.24 (m, 2H), 6.74 – 6.66 (m, 2H), 3.86 (s, 3H), 2.41 (t, *J* = 7.1 Hz, 2H), 1.59 – 1.51 (m, 2H), 1.49 – 1.40 (m, 2H), 0.92 (t, *J* = 7.2 Hz, 3H). **^{13}C-NMR (100 MHz, $CDCl_3$)** δ/ppm 191.7 (C),

165.6 (d, *J* = 250.5 Hz, CF), 159.8 (d, *J* = 10.4 Hz, C), 142.0 (CH), 136.2 (C), 132.9 (CH), 132.3 (d, *J* = 10.8 Hz, CH), 129.7 (CH), 127.8 (CH), 127.7 (CH), 125.9 (CH), 125.5 (C), 125.4 (d, *J* = 3.0 Hz, C), 107.5 (d, *J* = 21.5 Hz, CH), 99.6 (d, *J* = 25.6 Hz, CH), 97.1 (C), 78.2 (C), 56.0 (CH_3), 30.7 (CH_2), 22.0 (CH_2), 19.3 (CH_2), 13.6 (CH_3). **^{19}F-NMR (376 MHz, $CDCl_3$)** δ/ppm -105.2. **IR (neat)** ν/cm^{-1}: 2931 (w), 2224 (w), 1655 (m), 1606 (s), 1589 (s), 1410 (m), 1321 (m), 1267 (s), 1195 (s), 1026 (s), 954 (s), 835 (s), 752 (s). **HR-MS** (TOF ES+) calcd for $C_{22}H_{22}FO_2$ 337.1598, found 337.1600 ($M+H^+$).

(*E*)-1-(4-Fluoro-2-methoxyphenyl)-3-(6-(hex-1-yn-1-yl)benzo[d][1,3]dioxol-5-yl)prop-2-en-1-one, 1f:

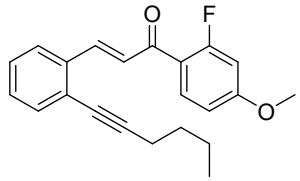


Chemical Formula: $C_{23}H_{21}FO_4$
Exact Mass: 380.14

Yield: 82% (484 mg, 1.27 mmol)
Appearance: orange powder.
UV-Vis (MeCN) λ_{max} = 368, 321 nm.
Melting point range: 49-51 °C

^{1}H-NMR (500 MHz, $CDCl_3$) δ/ppm 8.06 (d, *J* = 15.6 Hz, 1H), 7.62 (dd, *J* = 8.6, 6.9 Hz, 1H), 7.14 (d, *J* = 15.9 Hz, 1H), 7.11 (s, 1H), 6.85 (s, 1H), 6.74 – 6.67 (m, 2H), 5.98 (s, 2H), 3.87 (s, 3H), 2.39 (t, *J* = 7.1 Hz, 2H), 1.57 – 1.51 (m, 2H), 1.47 – 1.40 (m, 2H), 0.93 (t, *J* = 7.5 Hz, 3H). **^{13}C-NMR (125 MHz, $CDCl_3$)** δ/ppm 191.7 (C), 165.5 (d, *J* = 251.3 Hz, CF), 159.7 (d, *J* = 9.8 Hz, C), 149.2 (C), 147.8 (C), 142.1 (CH), 132.2 (d, *J* = 9.9 Hz, CH), 131.2 (C), 126.0 (CH), 125.6 (d, *J* = 3.1 Hz, C), 120.8 (C), 112.0 (CH), 107.4 (d, *J* = 22.3 Hz, CH), 104.9 (CH), 101.8 (CH_2), 99.6 (d, *J* = 25.0 Hz, CH), 96.0 (C), 78.0 (C), 56.0 (CH_3), 30.7 (CH_2), 22.0 (CH_2), 19.2 (CH_2), 13.6 (CH_3). **^{19}F-NMR (470 MHz, $CDCl_3$)** δ/ppm -105.5. **IR (neat)** ν/cm^{-1}: 2935 (w), 2230 (w), 1654 (m), 1584 (s), 1480 (s), 1290 (m),1257 (s), 1198 (s), 1029 (s), 849 (s), 519 (s). **HR-MS** (TOF ES+) calcd for $C_{23}H_{22}FO_4$ 381.1497, found 381.1499 ($M+H^+$).

(*E*)-1-(2-Fluoro-4-methoxyphenyl)-3-(2-(hex-1-yn-1-yl)phenyl)prop-2-en-1-one, 1g:

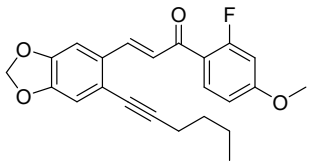


Chemical Formula: $C_{22}H_{21}FO_2$
Exact Mass: 336.15

Yield: 84% (330 mg, 0.98 mmol)
Appearance: red oil.
UV-Vis (MeCN) λ_{max} = 311 nm.

^{1}H-NMR (400 MHz, $CDCl_3$) δ/ppm 8.23 (dd, *J* = 15.8, 2.2 Hz, 1H), 7.86 (t, *J* = 8.7 Hz, 1H), 7.70 – 7.66 (m, 1H), 7.48 (dd, *J* = 15.8, 2.8 Hz, 1H), 7.45 – 7.41 (m, 1H), 7.29 – 7.25 (m, 2H), 6.76 (dd, *J* = 8.8, 2.4 Hz, 1H), 6.62 (dd, *J* = 12.9, 2.4 Hz, 1H), 3.84 (s, 3H), 2.46 (t, *J* = 7.1 Hz, 2H), 1.63 – 1.56 (m, 2H), 1.52 – 1.46 (m, 2H), 0.93 (t, *J* = 7.2 Hz, 3H). **^{13}C-NMR (100 MHz, $CDCl_3$)** δ/ppm 187.4 (d, *J* = 3.7 Hz, C), 164.4 (d, *J* = 11.5 Hz, C), 163.0 (d, *J* = 252.6 Hz, CF), 142.3 (CH), 136.1 (C), 133.0 (CH), 132.6 (d, *J* = 4.5 Hz, CH), 129.7 (CH), 127.7 (CH), 126.7 (d, *J* = 8.0 Hz, CH), 126.4 (CH), 125.5 (C), 119.7 (d, *J* = 12.9 Hz, C), 110.7 (d, *J* = 2.6 Hz, CH), 101.7 (d, *J* = 27.2 Hz, CH), 97.2 (C), 78.3 (C), 55.8 (CH_3), 30.7 (CH_2), 22.1 (CH_2), 19.3 (CH_2), 13.6 (CH_3).**^{19}F-NMR (376 MHz, $CDCl_3$)** δ/ppm -106.8. **IR (neat)** ν/cm^{-1}: 2931 (w), 2225 (w), 1658 (m), 1612 (s), 1456 (m), 1327 (s), 1266 (s), 1207 (s), 1014 (s), 983 (m), 836 (m), 759 (s). **HR-MS** (TOF ES+) calcd for $C_{22}H_{22}FO_2$ 337.1598, found 337.1599 ($M+H^+$).

(*E*)-1-(2-Fluoro-4-methoxyphenyl)-3-(6-(hex-1-yn-1-yl)benzo[d][1,3]dioxol-5-yl)prop-2-en-1-one, 1h:

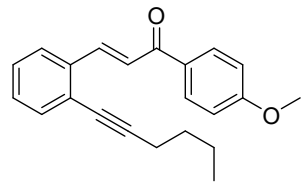


Chemical Formula: $C_{23}H_{21}FO_4$
Exact Mass: 380.14

Yield: 86% (436 mg, 1.15 mmol)
Appearance: orange powder.
UV-Vis (MeCN) λ_{max} = 373, 318 nm.
Melting point range: 59-62 °C

^{1}H-NMR (400 MHz, $CDCl_3$) δ/ppm 8.22 (dd, *J* = 15.7, 2.0 Hz, 1H), 7.83 (t, *J* = 8.7 Hz, 1H), 7.26 (dd, *J* = 15.7, 2.6 Hz, 1H), 7.14 (s, 1H), 6.85 (s, 1H), 6.76 (dd, *J* = 8.8, 2.4 Hz, 1H), 6.62 (dd, *J* = 12.9, 2.3 Hz, 1H), 5.98 (s, 2H), 3.85 (s, 3H), 2.43 (t, *J* = 7.1 Hz, 2H), 1.61 – 1.54 (m, 2H), 1.50 – 1.41 (m, 2H), 0.93 (t, *J* = 7.3 Hz, 3H). **^{13}C-NMR (125 MHz, $CDCl_3$)** δ/ppm 187.4 (d, *J* = 4 Hz, C), 164.3 (d, *J* = 12 Hz, C), 162.9 (d, *J* = 252 Hz, C), 149.3 (C), 147.8 (C), 142.3 (CH), 132.6 (d, *J* = 5 Hz, CH), 131.2 (C), 124.8 (d, *J* = 8 Hz, CH), 120.9 (C), 119.9 (d, *J* = 13 Hz, C), 112.1 (CH), 110.6 (CH), 105.2 (CH), 101.8 (d, *J* = 27 Hz, CH), 101.7 (CH_2), 96.2 (C), 78.1 (C), 55.8 (d, *J* = 3 Hz, CH_3), 30.7 (CH_2), 22.1 (CH_2), 19.3 (CH_2), 13.6 (CH_3). **^{19}F-NMR (376 MHz, $CDCl_3$)** δ/ppm -107.0. **IR (neat)** ν/cm^{-1}: 2908 (w), 2227 (w), 1650 (m), 1613 (s), 1579 (s), 1473 (s), 1294 (s),1230 (s), 1089 (s), 1010 (s), 839 (s), 523 (m). **HR-MS** (TOF ES+) calcd for $C_{23}H_{22}FO_4$ 381.1497, found 381.1499 ($M+H^+$).

(*E*)-3-(2-(Hex-1-yn-1-yl)phenyl)-1-(4-methoxyphenyl)prop-2-en-1-one 1j:

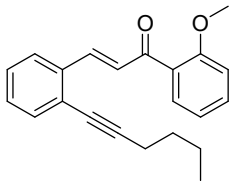


Chemical Formula: $C_{22}H_{22}O_2$
Exact Mass: 318.16

Yield: 75% (395 mg, 1.24 mmol)
Appearance: yellow oil.
UV-Vis (MeCN) λ_{max} = 317 nm.

^{1}H-NMR (400 MHz, $CDCl_3$) δ/ppm 8.23 (d, *J* = 15.8 Hz, 1H), 8.01 (d, *J* = 8.9 Hz, 2H), 7.71 – 7.68 (m, 1H), 7.58 (d, *J* = 15.8 Hz, 1H), 7.46 – 7.44 (m, 1H), 7.30 – 7.27 (m, 2H), 6.96 (d, *J* = 8.8 Hz, 2H), 3.87 (s, 3H), 2.47 (t, *J* = 7.1 Hz, 2H), 1.64 – 1.57 (m, 2H), 1.51 – 1.42 (m, 2H), 0.92 (t, *J* = 7.2 Hz, 3H). **^{13}C-NMR (100 MHz, $CDCl_3$)** δ/ppm 189.3 (C), 163.5 (C), 142.4 (CH), 136.4 (C), 133.2 (CH), 131.3 (C), 131.0 (2CH), 129.7 (CH), 127.8 (CH), 126.4 (CH), 125.4 (C), 123.6 (CH), 113.9 (2CH), 97.3 (C), 78.6 (C), 55.6 (CH_3), 30.8 (CH_2), 22.2 (CH_2), 19.5 (CH_2), 13.7 (CH_3). **IR (neat)** ν/cm^{-1}: 2930 (w), 2223 (w), 1657 (m), 1593 (s), 1330 (s), 1256 (s), 1215 (s), 1166 (s), 1018 (s), 832 (s), 760 (s), 581 (m). **HR-MS** (TOF ES+) calcd for $C_{22}H_{23}O_2$ 319.1693, found 319.1696 ($M+H^+$).

(*E*)-3-(2-(Hex-1-yn-1-yl)phenyl)-1-(2-methoxyphenyl)prop-2-en-1-one, 1k:



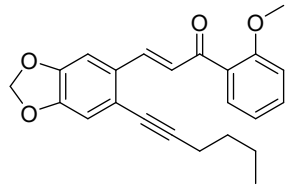
Chemical Formula: $C_{22}H_{22}O_2$
Exact Mass: 318.16

Yield: 96% (459 mg, 1.44 mmol)
Appearance: yellow oil.
UV-Vis (MeCN) λ_{max} = 340, 301 nm.

^{1}H-NMR (400 MHz, $CDCl_3$) δ/ppm 8.08 (d, *J* = 16.1 Hz, 1H), 7.69 – 7.65 (m, 1H), 7.58 (dd, *J* = 7.6, 1.8 Hz, 1H), 7.47 – 7.40 (m, 2H), 7.33 (d, *J* = 16.1 Hz, 1H), 7.29 – 7.25 (m, 2H), 7.02 (t, *J* = 7.5 Hz, 1H), 6.97 (d, *J* =8.4, 1H), 3.86 (s,

3H), 2.40 (t, *J* = 7.1 Hz, 2H), 1.57 – 1.50 (m, 2H), 1.48 – 1.39 (m, 2H), 0.93 (t, *J* = 7.2 Hz, 3H). **^{13}C-NMR (100 MHz, $CDCl_3$)** δ/ppm 193.7 (C), 158.1(C), 142.2 (CH), 136.4 (C), 132.9 (CH), 132.7 (C), 130.3 (CH), 129.7 (CH), 129.5 (C), 128.3 (CH), 127.8 (CH), 126.1 (CH), 125.6 (C), 120.7 (CH), 111.7 (CH), 97.2 (C), 78.3 (C), 55.8 (CH_3), 30.8 (CH_2), 22.1 (CH_2), 19.4 (CH_2), 13.7 (CH_3). **IR (neat)** ν/cm^{-1}: 2927 (w), 2222 (w), 1658 (m), 1587 (s), 1461 (s), 1328 (s), 1266 (s), 1161 (s), 1051 (s), 994 (s), 751 (s), 584 (m). **HR-MS** (TOF ES+) calcd for $C_{22}H_{23}O_2$ 319.1693, found 319.1692 ($M+H^+$).

(*E*)-3-(6-(Hex-1-yn-1-yl)benzo[d][1,3]dioxol-5-yl)-1-(2-methoxyphenyl)prop-2-en-1-one, 1l:

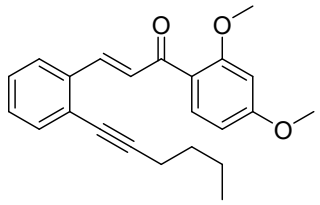


Chemical Formula: $C_{23}H_{22}O_4$
Exact Mass: 362.15

Yield: 89% (500 mg, 1.38 mmol)
Appearance: dark yellow powder.
UV-Vis (MeCN) λ_{max} = 367, 320 nm.
Melting point range: 64-66 °C

^{1}H-NMR (400 MHz, $CDCl_3$) δ/ppm 8.02 (d, *J* = 16.0 Hz, 1H), 7.54 (dd, *J* = 7.6, 1.8 Hz, 1H), 7.45 – 7.39 (m, 1H), 7.13 (d, *J* = 15.9 Hz, 1H), 7.10 (s, 1H), 7.00 (td, *J* = 7.5, 0.9 Hz, 1H), 6.96 (d, *J* = 8.3 Hz, 1H), 6.83 (s, 1H), 5.97 (s, 2H), 3.85 (s, 3H), 2.35 (t, *J* = 7.1 Hz, 2H), 1.54 – 1.46 (m, 2H), 1.45 – 1.36 (m, 2H), 0.91 (t, *J* = 7.2 Hz, 3H). **^{13}C-NMR (100 MHz, $CDCl_3$)** δ/ppm 193.6(C), 157.8 (C), 149.2 (C), 147.8 (C), 142.2 (CH), 132.3 (CH), 131.3 (C), 130.1 (CH), 129.5 (C), 126.3 (CH), 120.7 (C), 120.6 (CH), 111.9 (CH), 111.5 (CH), 105.0 (CH), 101.7 (CH), 95.9 (C), 77.9 (C), 55.7 (CH_3), 30.7 (CH_2), 22.0 (CH_2), 19.2 (CH_2), 13.6 (CH_3). **IR (neat)** ν/cm^{-1}: 2956 (w), 2225 (w), 1654 (m), 1596 (s), 1482 (s), 1289 (s), 1241 (s), 1017 (s), 864 (s), 763 (s). **HR-MS** (TOF ES+) calcd for $C_{23}H_{23}O_4$ 363.1591, found 363.1592 ($M+H^+$).

(*E*)-1-(2,4-Dimethoxyphenyl)-3-(2-(hex-1-yn-1-yl)phenyl)prop-2-en-1-one, 1m:

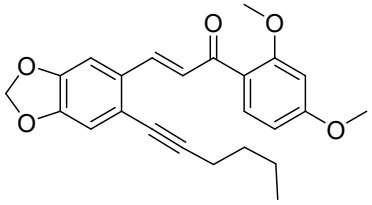


Chemical Formula: $C_{23}H_{24}O_3$
Exact Mass: 348.17

Yield: 85% (1.00 g, 2.9 mmol)
Appearance: red oil.
UV-Vis (MeCN) λ_{max} = 332, 304 nm.

^{1}H-NMR (500 MHz, $CDCl_3$) δ/ppm 8.15 (d, *J* = 15.9 Hz, 1H), 7.74 (d, *J* = 8.6 Hz, 1H), 7.70 – 7.67 (m, 1H), 7.49 (d, *J* = 15.9 Hz, 1H), 7.48 – 7.42 (m, 1H), 7.29 – 7.26 (m, 2H), 6.56 (dd, *J* = 8.6, 2.3 Hz, 1H), 6.50 (d, *J* = 2.2 Hz, 1H), 3.89 (s, 3H), 3.86 (s, 3H), 2.45 (t, *J* = 7.1 Hz, 2H), 1.63 – 1.57 (m, 2H), 1.51 – 1.44 (m, 2H), 0.94 (t, *J* = 7.2 Hz, 3H). **^{13}C-NMR (125 MHz, $CDCl_3$)** δ/ppm 190.9 (C), 164.0 (C), 160.3 (C), 140.6 (CH), 136.7 (C), 132.9 (CH), 132.8 (CH), 129.3 (CH), 128.3 (CH), 127.6 (CH), 125.9 (CH), 125.4 (C), 122.3 (C), 105.0 (CH), 98.7 (CH), 96.9 (C), 78.37 (C), 55.7 (CH_3), 55.5 (CH_3), 30.7 (CH_2), 22.1 (CH_2), 19.3 (CH_2), 13.6 (CH_3). **IR (neat)** ν/cm^{-1}: 2931 (w), 2222 (w), 1651 (m), 1602 (s), 1499 (m), 1322 (s), 1266 (s), 1208 (s),1124 (s), 1020 (s), 753 (s), 578 (m). **HR-MS** (TOF ES+) calcd for $C_{23}H_{25}O_3$ 349.1798, found 349.1803 ($M+H^+$).

(*E*)-1-(2,4-Dimethoxyphenyl)-3-(6-(hex-1-yn-1-yl)benzo[d][1,3]dioxol-5-yl)prop-2-en-1-one, 1n:



Chemical Formula: $C_{24}H_{24}O_5$
Exact Mass: 392,1624

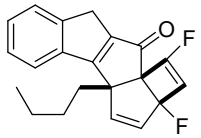
Yield: 91% (420 mg, 1.1 mmol)
Appearance: yellow oil.
UV-Vis (MeCN) λ_{max} = 371, 327 nm.

^{1}H-NMR (500 MHz, $CDCl_3$) δ/ppm 8.13 (d, *J* = 15.8 Hz, 1H), 7.72 (d, *J* = 8.6 Hz, 1H), 7.30 (d, *J* = 15.8 Hz, 1H), 7.13 (s, 1H), 6.86 (s, 1H), 6.55 (dd, *J* = 8.6, 2.3 Hz, 1H), 6.49 (d, *J* = 2.2 Hz, 1H), 5.99 (s, 2H), 3.88 (s, 3H), 3.86 (s, 3H), 2.43 (t, *J* = 7.1 Hz, 2H), 1.61 – 1.55 (m, 2H), 1.50 – 1.43 (m, 2H), 0.95 (t, *J* = 7.2 Hz, 3H). **^{13}C-NMR (125 MHz, $CDCl_3$)** δ/ppm 190.9 (C), 163.9 (C), 160.2 (C), 148.9 (C), 147.8 (C), 140.6 (CH), 132.7 (CH), 131.7 (C), 126.4 (CH), 122.4 (C), 120.5 (C), 112.1 (CH), 112.0 (CH), 105.0 (CH), 101.7 (CH_2), 98.6 (CH), 95.8 (C), 78.1 (C), 55.7 (d, *J* = 8.8 Hz, CH_3), 55.5 (d, *J* = 9.1 Hz, CH_3), 30.7 (CH_2), 22.1 (CH_2), 19.3 (CH_2), 13.6 (CH_3). **IR (neat)** ν/cm^{-1}: 2915 (w), 1639 (m), 1475 (m), 1329 (m), 1248 (s), 1192 (s), 1101 (s), 819 (s), 522 (m). **HR-MS** (TOF ES+) calcd for $C_{24}H_{25}O_5$ 393.1697, found 393.1698 ($M+H^+$).

Synthesis of photo-cascade products:

A solution of the chalcone substrate (**1a-n**) was prepared in MeCN (0.03 M) and pumped through a Vapourtec E-Series photoflow reactor (70 W, LED, 365 nm; FEP tubing 10 mL) with a flow rate of 1.2 mL/min (7 min residence time). The reaction mixture was collected and evaporated. The resulting residue was purified by silica gel column chromatography (10-20% EtOAc in cyclohexane) to furnish the desired photo-cascade product (**5a-n**).

Rac-(2aS,4aR,10aR)-4a-Butyl-1,2a-difluoro-4a,9-dihydrocyclobuta[3a,4]pentaleno[1,2-a]inden-10(2aH)-one, 5a:

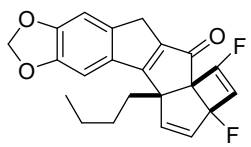


Chemical Formula: $C_{21}H_{18}F_2O$
Exact Mass: 324.13

Yield: 52% (60 mg, 0.18 mmol)
Appearance: off-white solid.
Melting point range: 145-149 °C

^{1}H-NMR (400 MHz, $CDCl_3$) δ/ppm 7.63 - 7.57 (m, 2H), 7.46 – 7.39 (m, 2H), 6.23 (dd, *J* = 5.7, 2.1 Hz, 1H), 6.04 (dd, *J* = 5.8, 1.2 Hz, 1H), 5.76 (dd, *J* = 9.1, 1.3 Hz, 1H), 3.61 (d, *J* = 23.9 Hz, 1H), 3.53 (d, *J* = 23.4 Hz, 1H), 2.09 – 2.01 (m, 1H), 1.76 – 1.69 (m, 1H), 1.26 – 1.14 (m, 3H), 0.95 – 0.86 (m, 1H), 0.77 (t, *J* = 7.4 Hz, 3H). **^{13}C-NMR (100 MHz, $CDCl_3$)** δ/ppm 192.1 (d, *J* = 4 Hz, C), 180.8 (d, *J* = 2 Hz, C), 153.6 (dd, *J* = 349, 22 Hz, C), 150.3 (C), 146.7 (C), 139.7 (d, *J* = 10 Hz, CH), 137.7 (C), 129.6 (CH), 129.4 (dd, *J* = 27, 9 Hz, CH), 127.4 (CH), 126.2 (CH), 122.6 (CH), 115.4 (d, *J* = 31.2 Hz, CH), 98.4 (dd, *J* = 235, 38 Hz, CF), 80.6 (dd, *J* = 23, 16, C), 57.8 (C), 32.6 (d, *J* = 4 Hz, CH_2), 32.1 (CH_2), 28.2 (d, *J* = 2 Hz, CH_2), 23.0 (CH_2), 13.7 (CH_3). **^{19}F-NMR (376 MHz, $CDCl_3$)** δ/ppm -88.2 (t, *J* = 8.7 Hz, 1F), -157.6 (dt, *J* = 8.9, 1.9 Hz, 1F). **IR (neat)** ν/cm^{-1}: 2930 (w), 1692 (s), 1643 (s), 1381 (m), 1332 (m), 1248 (m) 1011 (s), 845 (m), 794 (m), 732 (s). **HR-MS** (TOF ES+) calcd for $C_{21}H_{19}F_2O$ 325.1398, found 325.1399 ($M+H^+$).

Rac-(2aS,4aR,11aR)-4a-Butyl-1,2a-difluoro-4a,10-dihydrocyclobuta[3a',4']pentaleno[1',2':1,2]-indeno[5,6-d][1,3]dioxol-11(2aH)-one, 5b:



Chemical Formula: $C_{22}H_{18}F_2O_3$
Exact Mass: 368.12

Yield: 56% (28 mg, 0.08 mmol)

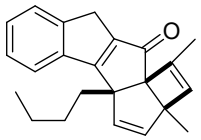
Appearance: light brown solid.

Crystal data (CCDC-2201533): P-1; a = 7.80430(10), b = 7.92550(10), c = 14.73430(10), α = 74.4540(10), β = 77.6380(10), γ = 88.2870(10).

Melting point range: 180-183 °C

^{1}H-NMR (500 MHz, $CDCl_3$) δ/ppm 7.06 (s, 1H), 7.02 (s, 1H), 6.17 (dd, *J* = 6.2, 2.0 Hz, 1H), 6.07 – 6.04 (m, 3H), 5.75 (dd, *J* = 8.8, 1H), 3.53 (d, *J* = 23.5 Hz, 1H), 3.46 (d, *J* = 23.7 Hz, 1H), 2.02 – 1.96 (m, 1H), 1.72 – 1.66 (m, 1H), 1.27 – 1.12 (m, 3H), 0.95 – 0.88 (m, 1H), 0.79 (t, *J* = 6.8 Hz, 3H). **^{13}C-NMR (125 MHz, $CDCl_3$)** δ/ppm 190.7 (d, *J* = 4 Hz, C), 180.6 (d, *J* = 3 Hz, C), 153.6 (dd, *J* = 350, 22 Hz, C), 149.8 (C), 147.7 (C), 146.1 (C), 145.4 (C), 139.3 (d, *J* = 9 Hz, CH), 131.3 (C), 129.4 (dd, *J* = 28, 10 CH), 115.2 (d, *J* = 31 Hz, CH), 107.0 (CH), 102.3 (CH), 101.9 (CH_2), 98.1 (dd, *J* = 239, 36 Hz, CF), 80.4 (dd, *J* = 23, 16 Hz, C), 57.5 (C), 32.4 (d, *J* = 4 Hz, CH_2), 32.1 (CH_2), 28.0 (d, *J* = 3 Hz, CH_2), 22.9 (CH_2), 13.6 (CH_3). **^{19}F-NMR (470 MHz, $CDCl_3$)** δ/ppm -89.2 (t, *J* = 9.2 Hz, 1F), -157.8 (dt, *J* = 8.9, 1.6 Hz, 1F). **IR (neat)** ν/cm^{-1}: 2865 (w), 1684 (s), 1645 (s), 1556 (m), 1459 (m), 1329 (s), 1150 (s), 1017 (s), 917 (s), 788 (m), 738 (m), 607 (m). **HR-MS** (TOF ES+) calcd for $C_{22}H_{19}F_2O_3$ 369.1297, found 369.1297 ($M+H^+$).

Rac-(2aR,4aR,10aR)-4a-Butyl-1,2a-dimethyl-4a,9-dihydrocyclobuta[3a,4]pentaleno[1,2-a]inden-10(2aH)-one, 5c:



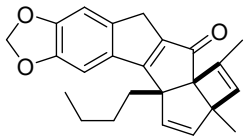
Chemical Formula: $C_{23}H_{24}O$
Exact Mass: 316.18

Yield: 74% (34 mg, 0.11 mmol)

Appearance: light yellow oil.

^{1}H-NMR (600 MHz, $CDCl_3$) δ/ppm 7.60 – 7.57 (m, 2H), 7.40 – 7.38 (m, 2H), 6.40 (m, 1H), 5.85 (d, *J* = 5.7 Hz, 1H), 5.75 (d, *J* = 5.4 Hz, 1H), 3.56 (d, *J* = 22.6 Hz, 1H), 3.48 (d, *J* = 22.6 Hz, 1H), 2.05 – 1.99 (m, 1H), 1.81 – 1.76 (m, 4H), 1.26 – 1.13 (m, 3H), 1.05 (s, 3H), 0.98 – 0.92 (m, 1H), 0.78 (t, *J* = 7.3 Hz, 3H). **^{13}C-NMR (125 MHz, $CDCl_3$)** δ/ppm 200.4 (C), 182.2 (C), 150.0 (C), 146.2 (C), 144.0 (CH), 142.1 (C), 138.5 (C), 138.4 (CH), 133.0 (CH), 128.6 (CH), 127.0 (CH), 125.9 (CH), 122.5 (CH), 77.6 (C), 60.9 (C), 59.3 (C), 34.1 (CH_2), 31.7 (CH_2), 28.8 (CH_2), 23.2 (CH_2), 17.7 (CH_3), 15.7 (CH_3), 13.8 (CH_3). **IR (neat)** ν/cm^{-1}: 2926 (m), 1726 (s), 1678 (s), 1605 (w), 1454 (m), 1378 (s), 833 (m), 731 (s). **HR-MS** (TOF ES+) calcd for $C_{24}H_{25}O$ 317.1900, found 317.1911 ($M+H^+$).

Rac-(2aR,4aR,11aR)-4a-Butyl-1,2a-dimethyl-4a,10-dihydrocyclobuta[3a',4']pentaleno[1',2':1,2]-indeno[5,6-d][1,3]dioxol-11(2aH)-one, 5d:



Chemical Formula: $C_{24}H_{24}O_3$
Exact Mass: 360.17

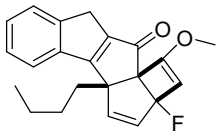
Yield: 73% (73 mg, 0.20 mmol)

Appearance: yellow solid.

Melting point range: 106-107 °C

^{1}H-NMR (500 MHz, $CDCl_3$) δ/ppm 7.05 (s, 1H), 7.01 (s, 1H), 6.39 (dd, *J* = 1.6, 1.4 Hz, 1H), 6.03 (dd, *J* = 7.7, 1.4 Hz, 2H), 5.79 (d, *J* = 6.0 Hz, 1H), 5.76 (d, *J* = 6.0 Hz, 1H), 3.49 (d, *J* = 22.4 Hz, 1H), 3.46 (d, *J* = 24.0 Hz, 1H), 1.99 – 1.96 (m, 1H), 1.78 – 1.75 (m, 4H), 1.27 – 1.14 (m, 3H), 1.05 (s, 3H), 0.98 – 0.86 (m, 1H), 0.79 (t, *J* = 7.2 Hz, 3H). **^{13}C-NMR (125 MHz, $CDCl_3$)** δ/ppm 199.2 (C), 182.1 (C), 149.0 (C), 147.4 (C), 145.6 (C), 145.1 (C), 143.9 (CH), 142.2 (C), 138.6 (CH), 132.8 (CH), 132.1 (C), 106.9 (CH), 102.5 (CH), 101.7 (CH_2), 77.4 (C), 60.8 (C), 59.1 (C), 34.0 (CH_2), 31.8 (CH_2), 28.7 (CH_2), 23.2 (CH_2), 17.6 (CH_3), 15.7 (CH_3), 13.8 (CH_3). **IR (neat)** ν/cm^{-1}: 2924 (w), 1656 (s), 1561 (m), 1499 (m), 1401 (s), 1290 (m), 1181 (m), 1037 (s), 911 (m), 850 (m), 839 (m). **HR-MS** (TOF ES+) calcd for $C_{24}H_{24}O_3Na$ 383.1618, found 383.1624 ($M+Na^+$).

Rac-(2aS,4aR,10aS)-4a-Butyl-2a-fluoro-1-methoxy-4a,9-dihydrocyclobuta[3a,4]pentaleno[1,2-a]inden-10(2aH)-one, 5e:

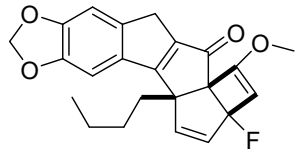


Chemical Formula: $C_{22}H_{21}FO_2$
Exact Mass: 336.15

Yield: 40% (40 mg, 0.12 mmol)
Appearance: light brown solid.
Melting point range: 80-85 °C

^{1}H-NMR (500 MHz, CD_3CN) δ/ppm 7.80 – 7.77 (m, 1H), 7.65 – 7.63 (m, 1H), 7.49 – 7.45 (m, 3H), 6.29 (dd, *J* = 5.6, 2.5 Hz, 1H), 6.10 (d, *J* = 5.6 Hz, 1H), 5.51 (d, *J* = 2.4 Hz, 1H), 3.75 (s, 3H), 3.56 (d, *J* = 22.9 Hz, 1H), 3.48 (d, *J* = 23.3 Hz, 1H), 2.10 – 2.04 (m, 1H), 1.68 – 1.62 (m, 1H), 1.30 – 1.18 (m, 3H), 0.85 – 0.77 (m, 4H). **^{13}C-NMR (125 MHz, CD_3CN)** δ/ppm 193.6 (d, *J* = 2 Hz, C), 180.8 (d, *J* = 3 Hz, C), 156.3 (d, *J* = 18 Hz, C), 150.1 (C), 146.6 (C), 138.7 (d, *J* = 10 Hz, CH), 137.7 (C), 130.4 (d, *J* = 31 Hz, CH), 129.3 (C), 127.2 (CH), 126.0 (CH), 122.7 (CH), 106.4 (d, *J* = 34 Hz, CH), 100.6 (d, *J* = 228 Hz, CF), 78.7 (d, *J* = 16 Hz, C), 58.0 (C), 56.8 (CH_3), 32.1 (CH_2), 31.3 (CH_2), 27.9 (CH_2), 22.6 (CH_2), 13.0 (CH_3). **^{19}F-NMR (470 MHz, CD_3CN)** δ/ppm -151.48 (t, *J* = 2.3 Hz, 1F). **IR (neat)** ν/cm^{-1}: 2929 (m), 1687 (s), 1625 (s), 1455 (m), 1380 (s), 1336 (m), 1193 (m), 1059 (s), 999 (s), 771 (s). **HR-MS** (TOF ES+) calcd for $C_{22}H_{22}FO_2$ 337.1598, found 337.1602 ($M+H^+$).

Rac-(2aS,4aR,11aS)-4a-Butyl-2a-fluoro-1-methoxy-4a,10-dihydrocyclobuta[3a',4']pentaleno-[1',2':1,2]indeno[5,6-d][1,3]dioxol-11(2aH)-one, 5f:

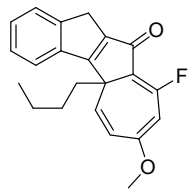


Chemical Formula: $C_{23}H_{21}FO_4$
Exact Mass: 380.14

Yield: 45% (48 mg, 0.13 mmol)
Appearance: dark solid.
Melting point range: 80-83 °C

^{1}H-NMR (500 MHz, acetone-d_6) δ/ppm 7.35 (s, 1H), 7.18 (s, 1H), 6.36 (dd, *J* = 5.8, 2.3 Hz, 1H), 6.11 (m, 2H), 6.07 (d, *J* = 4.6 Hz, 1H), 5.49 (d, *J* = 2.1 Hz, 1H), 3.76 (s, 3H), 3.48 (d, *J* = 22.7 Hz, 1H), 3.40 (d, *J* = 22.5 Hz, 1H), 2.12 – 2.07 (m, 1H), 1.61 (td, *J* = 12.4, 3.3 Hz, 1H), 1.32 – 1.19 (m, 3H), 0.89 – 0.82 (m, 1H), 0.77 (t, *J* = 7.2 Hz, 3H). **^{13}C-NMR (125 MHz, acetone-d_6)** δ/ppm 191.3 (d, *J* = 1 Hz, C), 179.8 (d, *J* = 2 Hz, C), 156.7 (C), 156.4 (C), 149.4 (C), 147.7 (C), 145.6 (d, *J* = 15 Hz, C), 138.4 (d, *J* = 10 Hz, CH), 131.6 (C), 130.6 (d, *J* = 31 Hz, CH), 106.7 (CH), 106.2 (d, *J* = 34 Hz, CH), 102.6 (CH), 101.9 (CH_2), 100.2 (d, *J* = 229 Hz, CF), 78.5 (d, *J* = 16 Hz, C), 57.8 (d, *J* = 2 Hz, C), 56.3 (CH_3), 32.1 (d, *J* = 4 Hz, CH_2), 31.4 (CH_2), 27.8 (CH_2), 22.7 (CH_2), 13.1 (CH_3). **^{19}F-NMR (470 MHz, acetone-d_6)** δ/ppm -152.1 (t, *J* = 2.2 Hz, 1F). **IR (neat)** ν/cm^{-1}: 2927 (m), 1687 (s), 1590 (m), 1481 (s), 1378 (s), 1247 (s), 1152 (s), 1033 (s), 918 (m), 799 (m). **HR-MS** (TOF ES+) calcd for $C_{23}H_{22}FO_4$ 381.1497, found 381.1496 ($M+H^+$).

Rac-4c-Butyl-9-fluoro-7-methoxy-4c,11-dihydro-10H-indeno[1,2-a]azulen-10-one, 5g:



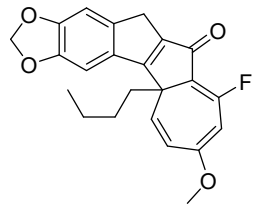
Chemical Formula: $C_{22}H_{21}FO_2$
Exact Mass: 336.15

Yield: 36% (24 mg, 0.07 mmol)
Appearance: yellow solid.
Melting point range: 151-153 °C

^{1}H-NMR (400 MHz, $CDCl_3$) δ/ppm 7.66 – 7.58 (m, 2H), 7.42 – 7.37 (m, 2H), 6.34 (d, *J* = 11.0 Hz, 1H), 5.99 (dd, *J* = 11.0, 2.1 Hz, 1H), 5.62 (dd, *J* = 12.7, 2.0

Hz,1H), 3.76 (s, 3H), 3.60 (d, *J* = 23.2 Hz, 1H), 3.53 (d, *J* = 23.2z Hz, 1H), 1.89 – 1.85 (m, 2H), 1.15 – 1.00 (m, 3H), 0.78 – 0.67 (m, 4H). **^{13}C-NMR (100 MHz, $CDCl_3$)** δ/ppm 185.8 (C), 174.7 (d, *J* = 4 Hz, C), 164.4 (d, *J* = 17 Hz, C), 157.4 (d, *J* = 259 Hz, CF), 150.0 (d, *J* = 2 Hz, C), 149.8 (C), 139.5 (CH), 137.4 (C), 128.7 (CH), 127.1 (CH), 126.0 (CH), 123.5 (CH), 121.7 (CH), 117.0 (d, *J* = 11 Hz, C), 95.8 (d, *J* = 38 Hz, C), 55.3 (CH_3), 46.2 (d, *J* = 7 Hz, C), 32.0 (CH_2), 31.5 (CH_2), 25.6 (CH_2), 22.7 (CH_2), 13.7 (CH_3). **^{19}F-NMR (376 MHz, $CDCl_3$)** δ/ppm -104.9 (d, *J* = 12.7 Hz, 1F). **IR (neat)** ν/cm^{-1}: 2922 (w), 1671 (s), 1623 (m), 1560 (s), 1384 (s), 1256 (s), 1195 (m), 1085 (m), 939 (m), 846 (m), 770 (m), 721 (m). **HR-MS** (TOF ES+) calcd for $C_{22}H_{22}FO_2$ 337.1598, found 337.1601 ($M+H^+$).

Rac-4c-Butyl-9-fluoro-7-methoxy-4c,11-dihydro-10H-azuleno[1',2':1,2]indeno[5,6-d][1,3]dioxol-10-one, 5h:

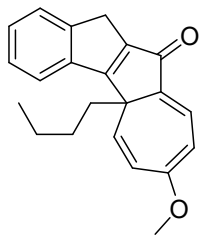


Chemical Formula: $C_{23}H_{21}FO_4$
Exact Mass: 380.14

Yield: 38% (38 mg, 0.10 mmol)
Appearance: dark solid.
Crystal data (CCDC-2201535): P_{-1}; a = 8.6257(3), b = 10.2667(3), c = 10.6007(3), α = 86.328(2), β = 76.801(3), γ = 87.255(3)
Melting point range: 103-107 °C

^{1}H-NMR (400 MHz, $CDCl_3$) δ/ppm 7.05 (s, 1H), 7.04 (s, 1H), 6.26 (d, *J* = 10.9 Hz, 1H), 6.03 (s, 2H), 5.97 (dd, *J* = 10.8, 2.0 Hz, 1H), 5.60 (dd, *J* = 12.7, 1.9 Hz,1H), 3.74 (s, 3H), 3.51 (d, *J* = 23.2 Hz, 1H), 3.44 (d, *J* = 23.0 Hz, 1H), 1.88 – 1.74 (m, 2H), 1.14 – 0.99 (m, 3H), 0.76 – 0.68 (m, 4H). **^{13}C-NMR (100 MHz, $CDCl_3$)** δ/ppm 184.9 (C), 174.9 (d, *J* = 4 Hz, C), 164.1 (d, *J* = 17 Hz, C), 157.1 (d, *J* = 258 Hz, CF), 149.1 (C), 148.8 (d, *J* = 2 Hz, C), 147.4 (C), 145.4 (C), 139.1 (CH), 131.0 (C), 123.6 (CH), 117.0 (d, *J* = 11 Hz, C), 107.1 (CH), 101.9 (CH), 101.8 (CH_2), 95.9 (d, *J* = 38 Hz, CH), 55.3 (CH_3), 46.1 (d, *J* = 7 Hz, C), 32.1 (CH_2), 31.4 (CH_2), 25.6 (CH_2), 22.7 (CH_2), 13.79 (CH_3). **^{19}F-NMR (376 MHz, $CDCl_3$)** δ/ppm -105.9 (m, 1F). **IR (neat)** ν/cm^{-1}: 2929 (w), 1673 (w), 1562 (w), 1481 (s), 1228 (s), 1119 (s), 980 (s), 803 (m), 745 (m). **HR-MS** (TOF ES+) calcd for $C_{23}H_{22}FO_4$ 381.1497, found 381.1499 ($M+H^+$).

Rac-4c-Butyl-7-methoxy-4c,11-dihydro-10H-indeno[1,2-a]azulen-10-one, 5i:



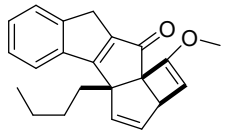
Chemical Formula: $C_{22}H_{22}O_2$
Exact Mass: 318.16

Yield: 67% (67 mg, 0.21 mmol)
Appearance: orange solid.
Melting point range: 137-138 °C

^{1}H-NMR (500 MHz, $CDCl_3$) δ/ppm 7.73 – 7.70 (m, 1H), 7.64 – 7.60 (m, 1H), 7.44 – 7.40 (m, 2H), 7.10 (d, *J* = 7.5 Hz, 1H), 6.18 (d, *J* = 10.7 Hz, 1H), 6.05 (dd, *J* = 10.4, 2.8 Hz, 1H), 5.82 (dd, *J* = 7.4, 2.3 Hz, 1H), 3.76 (s, 3H),

3.63 (d, *J* = 22.9 Hz, 1H), 3.57 (d, *J* = 22.9 Hz, 1H), 1.88 – 1.76 (m, 2H), 1.11 – 0.92 (m, 3H), 0.81 – 0.67 (m, 1H), 0.68 (t, *J* = 7.1 Hz, 3H). **^{13}C-NMR (125 MHz, $CDCl_3$)** δ/ppm 187.9 (C), 177.1 (C), 163.2 (C), 149.9 (C), 137.8 (C), 136.5 (CH), 135.7 (C), 128.8 (CH), 127.1 (CH), 126.0 (CH), 124.1 (CH), 123.0 (CH), 122.0 (CH), 100.7 (CH), 55.0 (CH_3), 48.7 (C), 32.0 (CH_2), 31.4 (CH_2), 25.8 (CH_2), 22.7 (CH_2), 13.8 (CH_3); one quaternary carbon resonance was not observed. **IR (neat)** ν/cm^{-1}: 2934 (m), 1666 (s), 1624 (m), 1544 (s), 1387 (m), 1222 (m), 1174 (m), 1061 (m), 1013 (m), 930 (m), 864 (m), 782 (s), 743 (s), 671 (s). **HR-MS** (TOF ES+) calcd for $C_{22}H_{23}O_2$ 319.1693, found 319.1694 ($M+H^+$).

Rac-(2aR,4aR,10aR)-4a-Butyl-1-methoxy-4a,9-dihydrocyclobuta[3a,4]pentaleno[1,2-a]inden-10(2aH)-one, 5k:

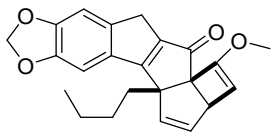


Chemical Formula: $C_{22}H_{22}O_2$
Exact Mass: 318.16

Yield: 41% (41 mg, 0.13 mmol)
Appearance: orange oil.

^{1}H-NMR (500 MHz, $CDCl_3$) δ/ppm 7.61 – 7.57 (m, 2H), 7.42 – 7.37 (m, 2H), 5.95 (d, *J* = 5.7 Hz, 1H), 5.88 (dd, *J* = 5.6, 2 Hz, 2H), 5.27 (d, *J* = 0.8 Hz, 1H), 3.67 (s, 3H), 3.57 (d, *J* = 22.9 Hz, 1H), 3.50 (d, *J* = 22.9 Hz, 1H), 3.20 (d, *J* = 1.7 Hz, 1H), 2.03 (td, *J* = 13.5, 4.8 Hz, 1H), 1.81 (td, *J* = 7.8, 3.7 Hz, 1H), 1.40 – 1.31 (m, 1H), 1.25 – 1.18 (m, 2H), 0.94 – 0.85 (m, 1H), 0.79 (t, *J* = 7.3 Hz, 3H). **^{13}C-NMR (125 MHz, $CDCl_3$)** δ/ppm 198.6 (C), 182.3 (C), 152.5 (C), 150.3 (C), 145.7 (C), 138.2 (C), 135.3 (CH), 134.5 (CH), 128.9 (CH), 127.0 (CH), 125.9 (CH), 122.5 (CH), 106.1 (CH), 76.1 (C), 57.9 (C), 55.6 (CH_3), 50.4 (CH), 34.6 (CH_2), 31.9 (CH_2), 27.8 (CH_2), 23.1 (CH_2), 13.6 (CH_3). **IR (neat)** ν/cm^{-1}: 2928 (m), 1732 (m), 1682 (s), 1629 (m), 1379 (s), 1336 (m), 1145 (m), 1021 (m), 713 (s). **HR-MS** (TOF ES+) calcd for $C_{22}H_{23}O_2$ 319.1693, found 319.1694 ($M+H^+$).

Rac-(2aR,4aR,11aR)-4a-Butyl-1-methoxy-4a,10-dihydrocyclobuta[3a',4']pentaleno[1',2':1,2]-indeno[5,6-d][1,3]dioxol-11(2aH)-one, 5l:

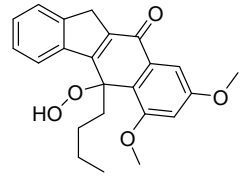


Chemical Formula: $C_{23}H_{22}O_4$
Exact Mass: 362.15

Yield: 38% (38 mg, 0.11 mmol)
Appearance: beige solid.
Melting point range: 187-190 °C

^{1}H-NMR (500 MHz, $CDCl_3$) δ/ppm 7.04 (s, 1H), 7.01 (s, 1H), 6.04 (dd, *J* = 5.8, 2.3 Hz, 2H), 5.90 – 5.88 (m, 2H), 5.25 (s, 1H), 3.66 (s, 3H), 3.48 (d, *J* = 22.8 Hz, 1H), 3.41 (d, *J* = 22.8 Hz, 1H), 3.18 (s, 1H), 1.97 (td, *J* = 13.4, 4.7 Hz, 1H), 1.76 (td, *J* = 12.8, 3.6 Hz, 1H), 1.38 – 1.30 (m, 1H), 1.23 (sext, *J* = 7.3 Hz, 2H), 0.92 – 0.84 (m, 1H), 0.79 (t, *J* = 7.3 Hz, 3H). **^{13}C-NMR (125 MHz, $CDCl_3$)** δ/ppm 197.3 (C), 182.2 (C), 152.6 (C), 149.2 (C), 147.4 (C), 146.0 (C), 144.4 (C), 135.1 (CH), 134.7 (CH), 131.8 (C), 106.8 (CH), 106.1 (CH), 102.5 (CH), 101.7 (CH_2), 76.0 (C), 57.7 (C), 55.6 (CH_3), 50.3 (CH), 34.5 (CH_2), 32.0 (CH_2), 27.8 (CH_2), 23.1 (CH_2), 13.7 (CH_3). **IR (neat)** ν/cm^{-1}: 2928 (w), 1672 (s), 1627 (m), 1561 (m), 1457 (m), 1385 (s), 1150 (s), 1027 (s), 927 (m), 805 (m), 719 (m). **HR-MS** (TOF ES+) calcd for $C_{23}H_{22}O_4Na$ 385.1410, found 385.1412 ($M+Na^+$).

Rac-5-Butyl-5-hydroperoxy-6,8-dimethoxy-5,5a,9a,11-tetrahydro-10H-benzo[b]fluoren-10-one, 5m:



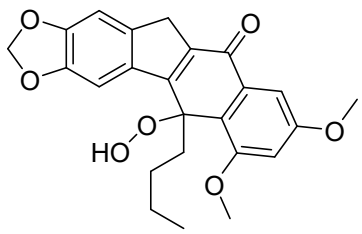
Chemical Formula: $C_{23}H_{24}O_5$
Exact Mass: 380.16

Yield: 50% (55 mg, 0.145 mmol)
Appearance: brown solid.
Crystal data (CCDC-2201534): P_{-1}; a = 9.14550(10), b = 9.46920(10), c =

11.22560(10), α = 102.2020(10), β = 91.5720(10), γ = 100.0760(10).
Melting point range: decomposition > 60 °C

^{1}H-NMR (500 MHz, $CDCl_3$) δ/ppm 8.11 – 8.09 (m, 1H), 8.00 (s, OH), 7.63 – 7.62 (m, 1H), 7.46 – 7.43 (m, 3H), 6.75 (d, *J* = 2.5 Hz, 1H), 3.94 (s, 3H), 3.89 (s, 3H), 3.88 (d, *J* = 23.2 Hz, 1H), 3.78 (d, *J* = 23.5 Hz, 1H), 2.72 (td, *J* = 12.0, 4.6 Hz, 1H), 2.16 (td, *J* = 12.3, 4.7 Hz, 1H), 1.03 (sext, *J* = 7.4 Hz, 2H), 0.73 – 0.65 (m, 1H), 0.64 – 0.56 (m, 4H). **^{13}C-NMR (125 MHz, $CDCl_3$)** δ/ppm 181.8 (C), 160.5 (C), 159.4 (C), 159.0 (C), 145.4 (C), 140.6 (C), 140.4 (C), 136.4 (C), 128.7 (CH), 127.2 (CH), 125.0 (CH), 124.4 (CH), 123.6 (C), 104.5 (CH), 101.3 (CH), 86.2 (C), 56.2 (CH_3), 55.6 (CH_3), 35.6 (CH_2), 34.1 (CH_2), 26.4 (CH_2), 22.4 (CH_2), 13.6 (CH_3). **IR (neat)** ν/cm^{-1}: 3294 (br. w), 2929 (w), 1637 (m), 1597 (s), 1460 (m), 1429 (m), 1312 (m), 1142 (m), 945 (w), 842 (m), 734 (s). **HR-MS** (TOF ES+) calcd for $C_{23}H_{25}O_5$ 381.1697, found 381.1697 ($M+H^+$).

Rac-5-Butyl-5-hydroperoxy-6,8-dimethoxy-5,5a,9a,11-tetrahydro-10H-benzo[6,7]fluoreno[2,3-d][1,3]dioxol-10-one, 5n:

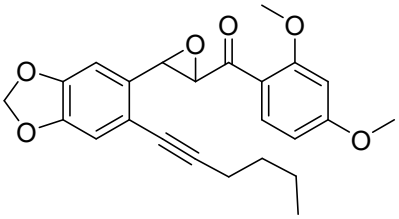


Chemical Formula: $C_{24}H_{24}O_7$
Exact Mass: 424.1522

Yield: 13% (66 mg, 0.15 mmol)
Appearance: brown solid.

^{1}H-NMR (600 MHz, $CDCl_3$) δ/ppm 7.97 (s, 1H), 7.54 (s, 1H), 7.43 (d, *J* = 2.7 Hz, 1H), 7.07 (s, 1H), 6.73 (d, *J* = 2.4 Hz, 1H), 6.04 (dd, *J* = 12.1, 1.7 Hz, 2H), 3.93 (s, 3H), 3.89 (s, 3H), 3.80 (d, *J* = 22.5 Hz, 1H), 3.71 (d, *J* = 23.9 Hz, 1H), 2.66 (td, *J* = 11.6, 4.4 Hz, 1H), 2.07 (td, *J* = 12.3, 5.1 Hz, 1H), 1.03 (sext, *J* = 7.4 Hz, 2H), 0.73 – 0.65 (m, 3H), 0.61 (t, *J* = 7.3 Hz, 3H), 0.62 – 0.57 (m, 1H). **^{13}C-NMR (125 MHz, $CDCl_3$)** δ/ppm 180.7 (C), 160.5 (C), 159.6 (C), 158.8 (C), 149.3 (C), 147.5 (C), 141.1 (C), 139.5 (C), 136.5 (C), 134.2 (C), 123.1 (C), 105.8 (CH), 104.4 (CH), 104.2 (CH), 101.6 (CH_2), 101.3 (CH), 86.2 (C), 56.1 (CH_3), 55.6 (CH_3), 35.6 (CH_2), 34.1 (CH_2), 26.4 (CH_2), 22.4 (CH_2), 13.6 (CH_3). **IR (neat)** ν/cm^{-1}: 3335 (br. w), 2930 (w), 1646 (m), 1595 (s), 1481 (s), 1293 (m), 1250 (s), 1211 (s), 1035 (s), 935 (m), 835 (m), 735 (m). **HR-MS** (TOF ES+) calcd for $C_{24}H_{25}O_7$ 425.1595, found 425.1597 ($M+H^+$).

Rac-(2,4-Dimethoxyphenyl)(3-(6-(hex-1-yn-1-yl)benzo[d][1,3]dioxol-5-yl)oxiran-2-yl)methanone, 6:



Chemical Formula: $C_{24}H_{24}O_6$
Exact Mass: 408.1573

Yield: 20% (16 mg, 0.04 mmol)

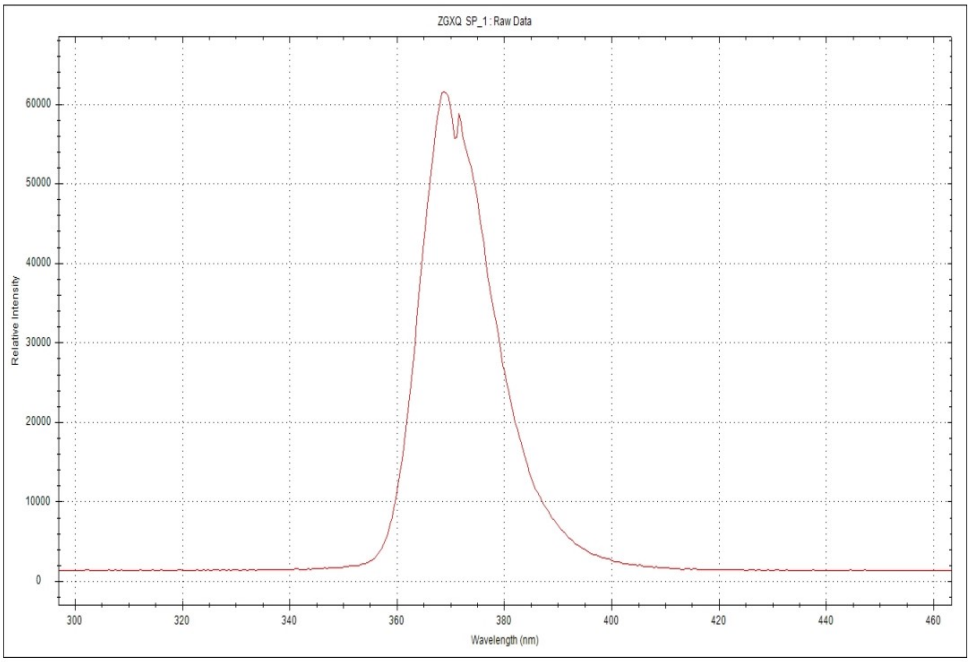
Appearance: red oil

^{1}H-NMR (400 MHz, $CDCl_3$) δ/ppm 7.72 (d, *J* = 9.7 Hz, 1H), 7.28 (s, 1H), 6.68 (s, 1H), 6.42 (d, *J* = 9.3 Hz, 1H), 6.22 (s, 1H), 5.88 (d, *J* = 16.6 Hz, 2H), 4.52-4.50 (m, 1H), 4.44-4.41 (m, 1H), 3.79 (s, 3H), 3.37 (s, 3H), 2.27-2.18 (m, 2H), 1.47-1.34 (m, 4H), 0.89 (t, *J* = 7.6 Hz, 3H). **^{13}C-NMR (125 MHz, $CDCl_3$)** δ/ppm 199.7 (C), 164.3 (C), 161.0 (C), 147.6 (C), 145.6 (C), 139.5 (C), 132.9 (CH), 121.1 (C), 116.9 (C), 111.2 (CH), 107.9 (CH), 104.8

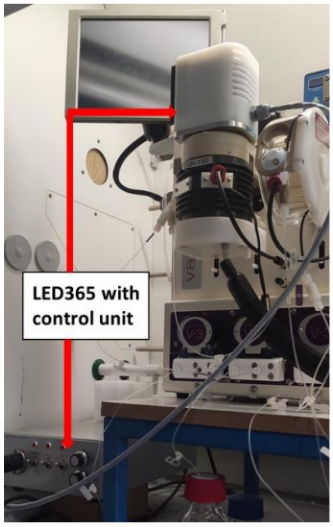
(CH), 101.1 (CH_2), 98.0 (CH), 93.3 (C), 79.1 (C), 55.5 (CH_3), 54.7 (CH_3), 51.7 (CH), 45.0 (CH), 30.8 (CH_2), 22.2 (CH_2), 19.3 (CH_2), 13.7 (CH_3). **IR (neat)** ν/cm^{-1}: 2957 (m), 1650 (m), 1598 (s), 1482 (s), 1252 (s), 1214 (s), 1036 (s), 935 (m), 866 (m). **HR-MS** (TOF ES+) calcd for $C_{24}H_{25}O_6$ 409.1646, found 409.1647 (M + H+).

3. Emission Spectrum of High-Power LED

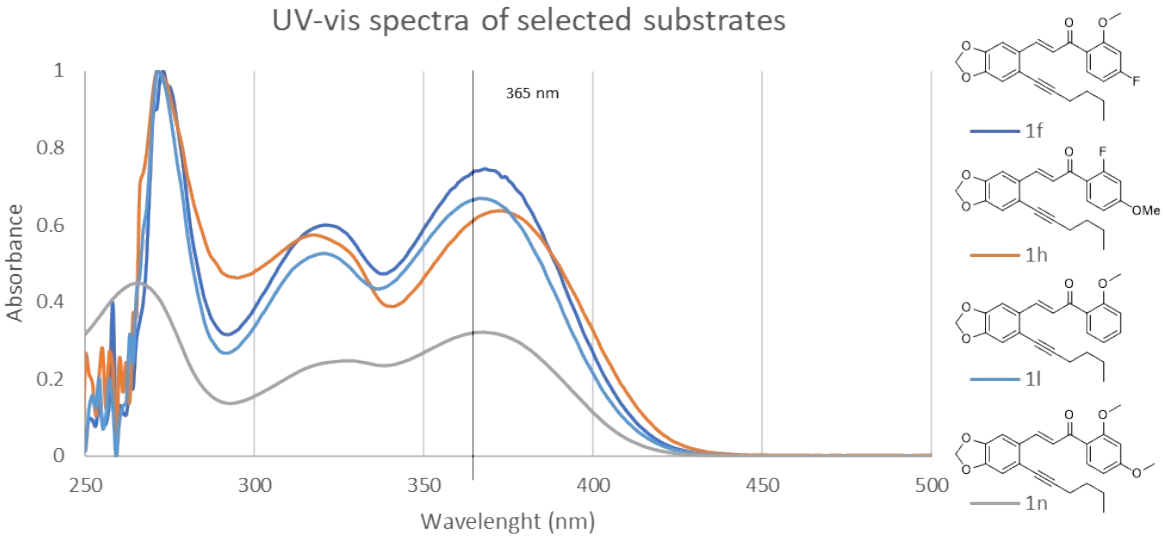
Spectrum Name: SP_1
System Model: BRC115P-U-ST1 C Code: ZGXQ Operator:
Exposure Time: 4 (ms) Laser Level: Date: 02/11/2021

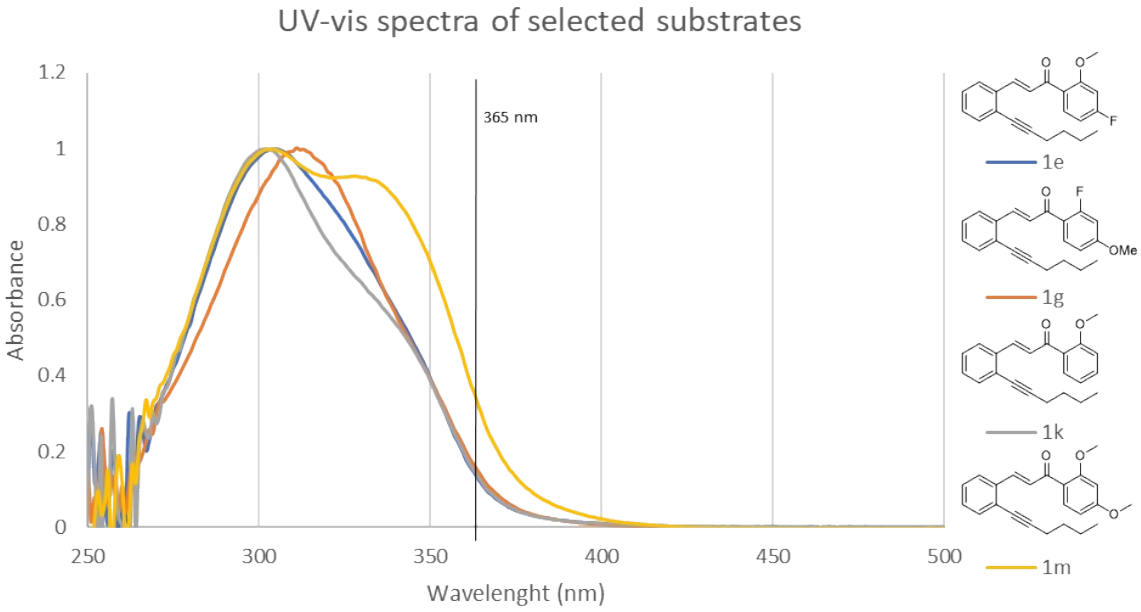


Flow Reactor Set-up:



4. Comparison of UV-vis Spectra





5. *Summary of X-ray data for compounds 5b, 5h and 5m*

For each sample, a suitable single crystal was removed from the growing vessel and manipulated in a perfluoropolyalkylether oil matrix (F06206K, ABCR company) on a standard glass microscope slide. The selected crystal was mounted in the end of a cactus fibre afixed to a copper pin magnetically attached to a standard goniometer head which was placed in the Euler cradle and flashed cooled with a cold blanket of N_2 gas using an Oxford Cryosystems cooling device. The mounted crystal was kept under a (<110 K) gaseous flow of N_2 during the entire collection process. A complete diffraction data set was collected on a 4-circle dual source Rigaku SuperNova A instrument equipped with a 140 mm Atlas-model CCD detector using mono-chromated Cu-Kα (λ=1.54184 Å, 50.0 kV, 0.8 mA) radiation generated by a microfocus source. For data collection, optimised ω-scans were employed and raw data treatment including cell indexing (using reflections measured from the entire data set), space group determination, raw data reduction and gaussian-based adsorption corrections[SI4] were performed with the CrysAlisPro application (version 42).[SI5] A small number of reflections where filtered out when the associated R_{int} value was particularly large. The structures were solved by intrinsic phasing using the SHELXT program.[SI6] Refinement was performed by full matrix least-squares minimisation on F^2 for all data using SHELX-LS.[SI7] Hydrogen atoms were added at calculated positions and refined using a riding model based on the connecting atom. Where electron density was sufficient, the hydrogen atoms were located manually from electron density map and the positions were allowed to ride to the attached atom. The associated isotropic thermal displacement parameters for the hydrogen atoms were fixed to 1.2 times (1.5 times for the methyl groups) to that of the attached atom. Anisotropic thermal displacement parameters were used for all non-hydrogen atoms. None of the structure reported displayed positional disorder. Structure solution, refinement and structural analysis were performed using the program Olex2 (version 1.5-ac).

[SI4] Coppens, P.; Hamilton, W. C. Anisotropic extinction corrections in the Zachariasen approximation. *Acta Cryst*. **1970**, A26, 71-83.

[SI5] Sheldrick, G. M. SHELXT − Integrated Space-Group and Crystal-Structure Determination. *Acta Crystallogr.* **2015**, A71 (1), 3-8.

[SI6] Sheldrick, G. M. Crystal Structure Refinement with SHELXL. *Acta Crystallogr*. **2015**, C71 (1), 3-8

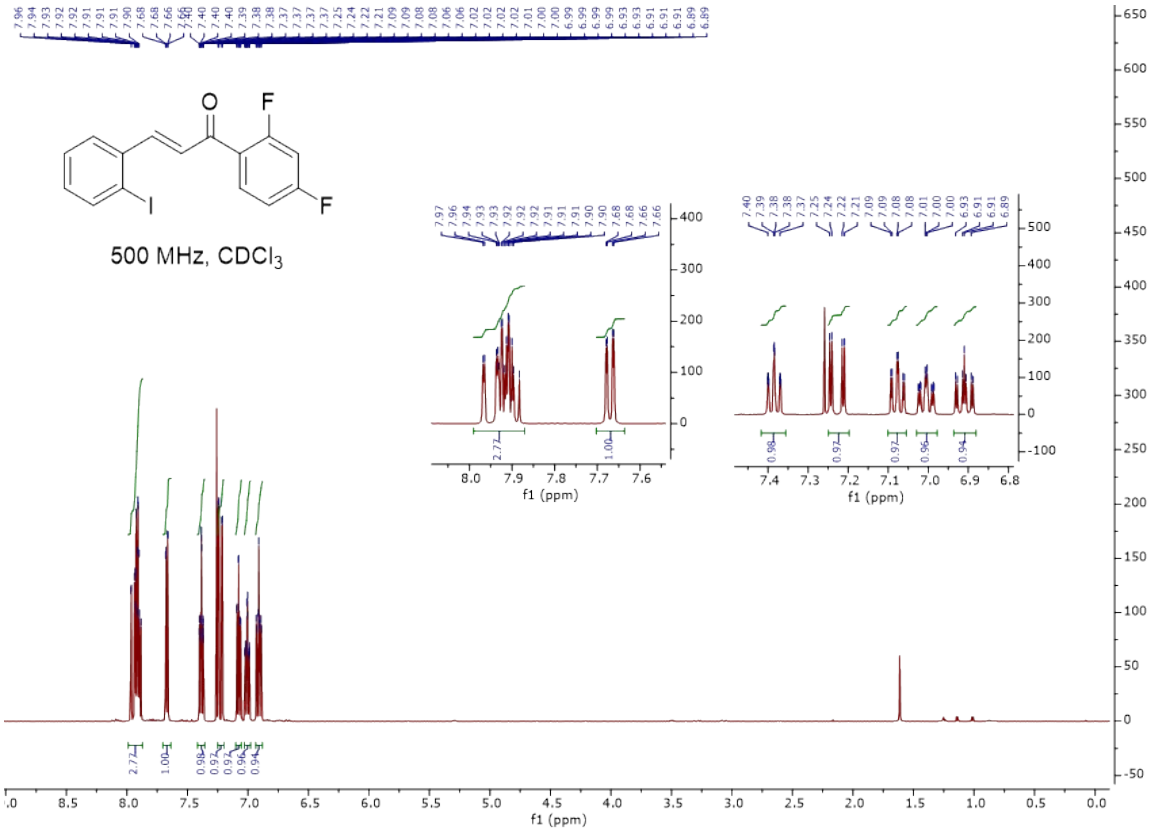
[SI7] Dolomanov, O.V.; Bourhis, L.J.; Gildea, R.J.; Howard, J.A.K.; Puschmann, H., OLEX2: A complete structure solution, refinement and analysis program. *J. Appl. Cryst.*, **2009**, 42, 339-341

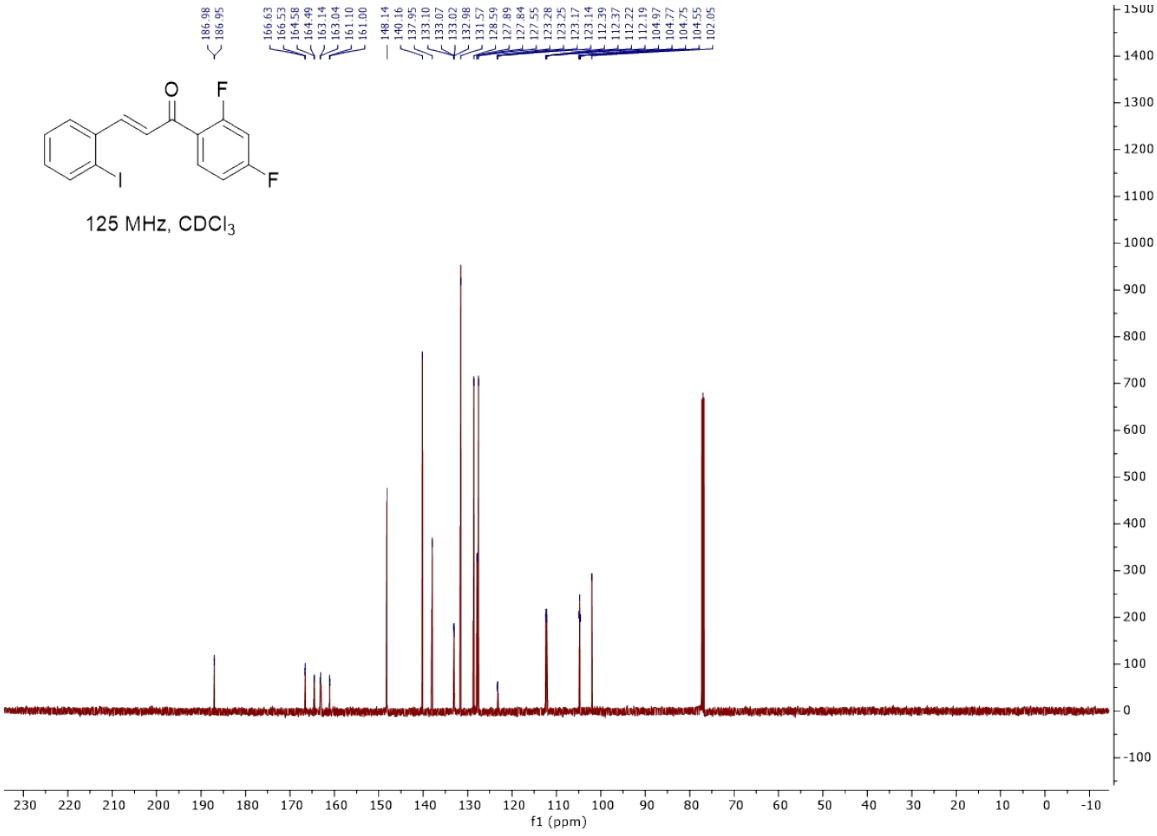
Table SI-1: Selected Crystallographic Information for Compounds Bau32, Bau45 and Bau47

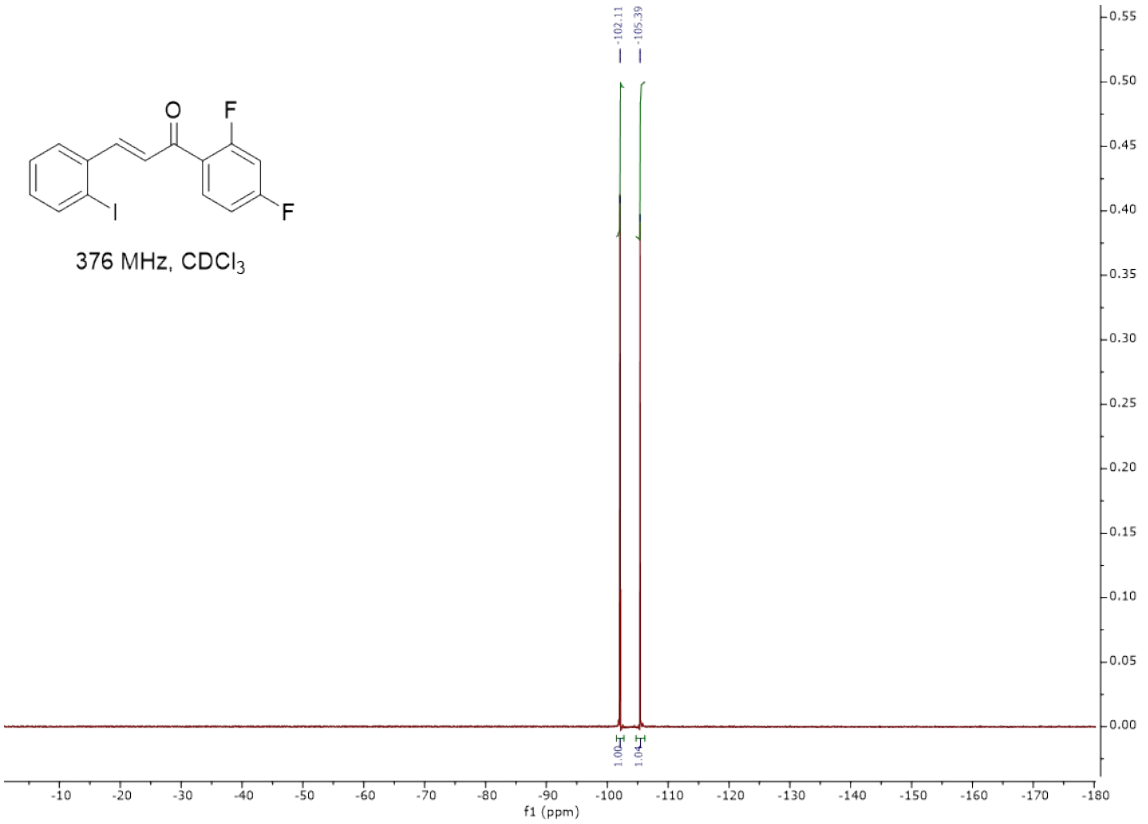
Identification Code	**Bau32 = 5b**	**Bau45 = 5m**	**Bau47 = 5h**
Empirical formula	$C_{22}H_{18}F_2O_3$	$C_{23}H_{24}O_5$	$C_{23}H_{21}FO_4$
Molecular formula	$C_{22}H_{18}F_2O_3$	$C_{23}H_{24}O_5$	$C_{23}H_{21}FO_4$
Formula weight (g mol^{-1})	368.36	380.42	380.40
Temperature (K)	100.55(10)	103.8(3)	103.3(2)
Radiation Wavelength	Cu-K_α (λ = 1.54184)	Cu-K_a (λ = 1.54184)	Cu-K_α (λ = 1.54184)
Crystal system	triclinic	triclinic	triclinic
Space group	P_{-1} (no. 2)	P_{-1} (no. 2)	P_{-1} (no. 2)
Unit cell dimensions			
a (Å)	7.80430(10)	9.14550(10)	8.6257(3)
b (Å)	7.92550(10)	9.46920(10)	10.2667(3)
c (Å)	14.73430(10)	11.22560(10)	10.6007(3)
α (°)	74.4540(10)	102.2020(10)	86.328(2)
β (°)	77.6380(10)	91.5720(10)	76.801(3)
γ (°)	88.2870(10)	100.0760(10)	87.255(3)
Volume (Å^3)	857.296(17)	933.428(17)	911.56(5)
Z	2	2	2
Density (calculated, g cm^{-3})	1.427	1.354	1.386
Absorption coefficient (mm^{-1})	0.909	0.772	0.833
F(000)	384.0	404.0	400.0
Crystal size (mm x mm x mm)	0.16 × 0.12 × 0.1	0.15 × 0.12 × 0.09	0.15 × 0.08 × 0.07
Theta range for data collection (°)	11.594 to 153.396	8.076 to 152.716	8.58 to 152.794
Index ranges	$-9 \le h \le 9$,	$-10 \le h \le 11$	$-10 \le h \le 10$
	$-10 \le k \le 9$	$-11 \le k \le 11$	$-11 \le k \le 12$
	$-18 \le l \le 18$	$-14 \le l \le 14$	$-13 \le l \le 13$
Reflections collected	33181	28164	14565
Independent reflections	3560	3882	3765
	R_{int} = 0.0259	R_{int} = 0.0280	R_{int} = 0.0320
	R_σ = 0.0120	R_σ = 0.0121	R_s = 0.0277
Completeness to theta (%)	99.0	98.9	98.6
Max. and min. transmission	0.868	0.893	0.885
	0.915	0.934	0.944
Refinement method	F^2	F^2	F^2
Data / restraints / parameters	3560/0/246	3882/0/260	3765/0/255
Goodness–of–fit on F^2	1.070	1.064	1.035
Final R indices [I>2σ(I)]	R_1 = 0.0359	R_1 = 0.0346	R_1 = 0.0366
	wR_2 = 0.0888	wR_2 = 0.0948	wR_2 = 0.0917
R indices (all data)	R_1 = 0.0403	R_1 = 0.0376	R_1 = 0.0486
	wR_2 = 0.0923	wR_2 = 0.0974	wR_2 = 0.0998
Absolute structure parameter	n/a	n/a	n/a
Extinction coefficient	0.0017(4)	0	0
Largest diff. peak and hole (e Å^{-3})	0.27/-0.18	0.30/-0.22	0.24/-0.19

6. Copies of NMR Spectra of all new Compounds:

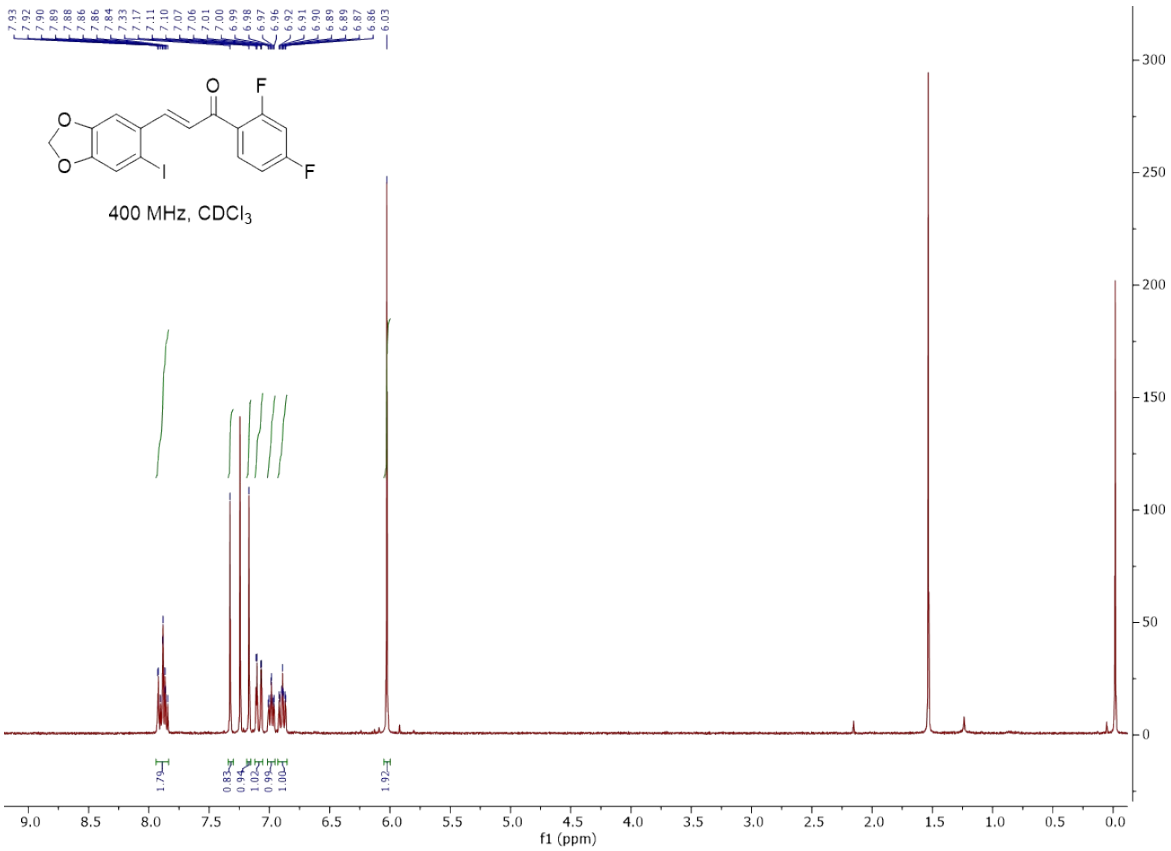
(E)-1-(2,4-Difluorophenyl)-3-(2-iodophenyl)prop-2-en-1-one

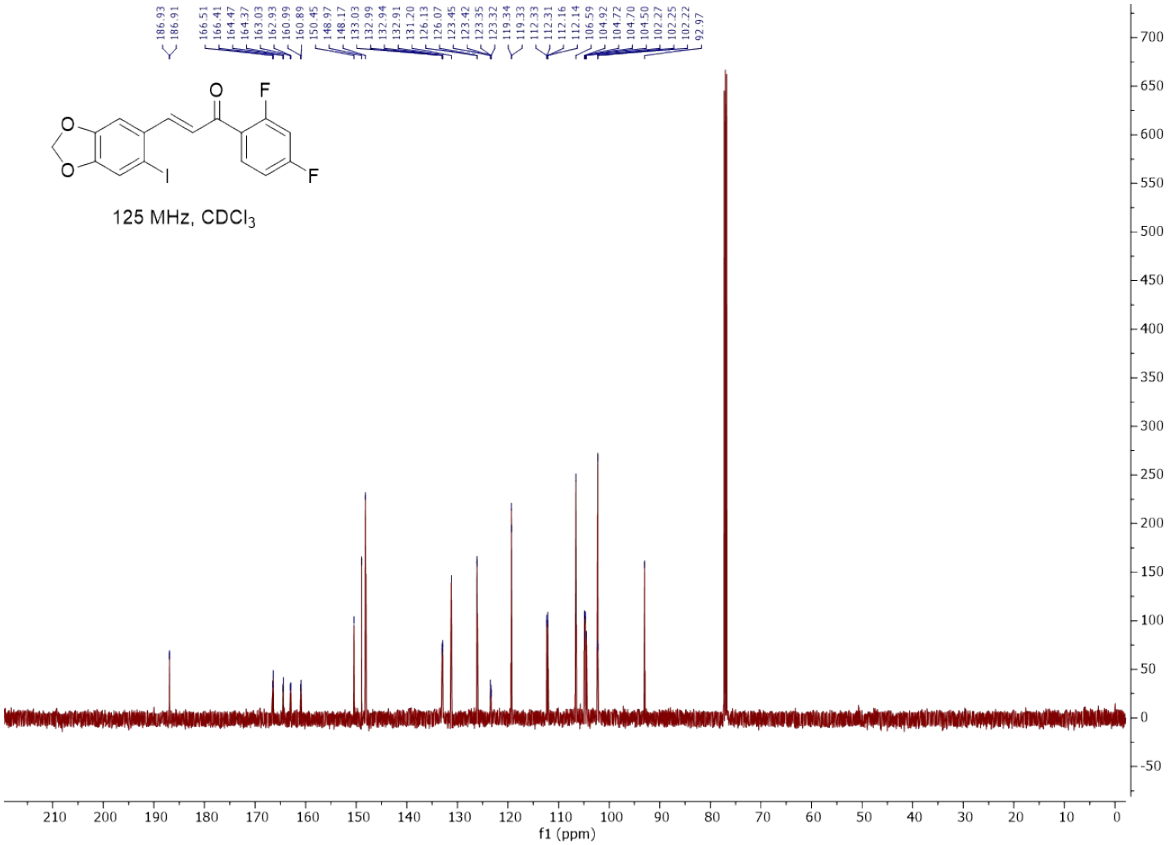






(E)-1-(2,4-Difluorophenyl)-3-(6-iodobenzo[d][1,3]dioxol-5-yl)prop-2-en-1-one

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166.41
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162.93
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160.89
150.45
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133.03
132.99
132.94
132.91
131.20
126.13
126.07
123.45
123.42
123.35
123.32
119.34
119.33
112.33
112.31
112.16
112.14
106.59
104.92
104.72
104.70
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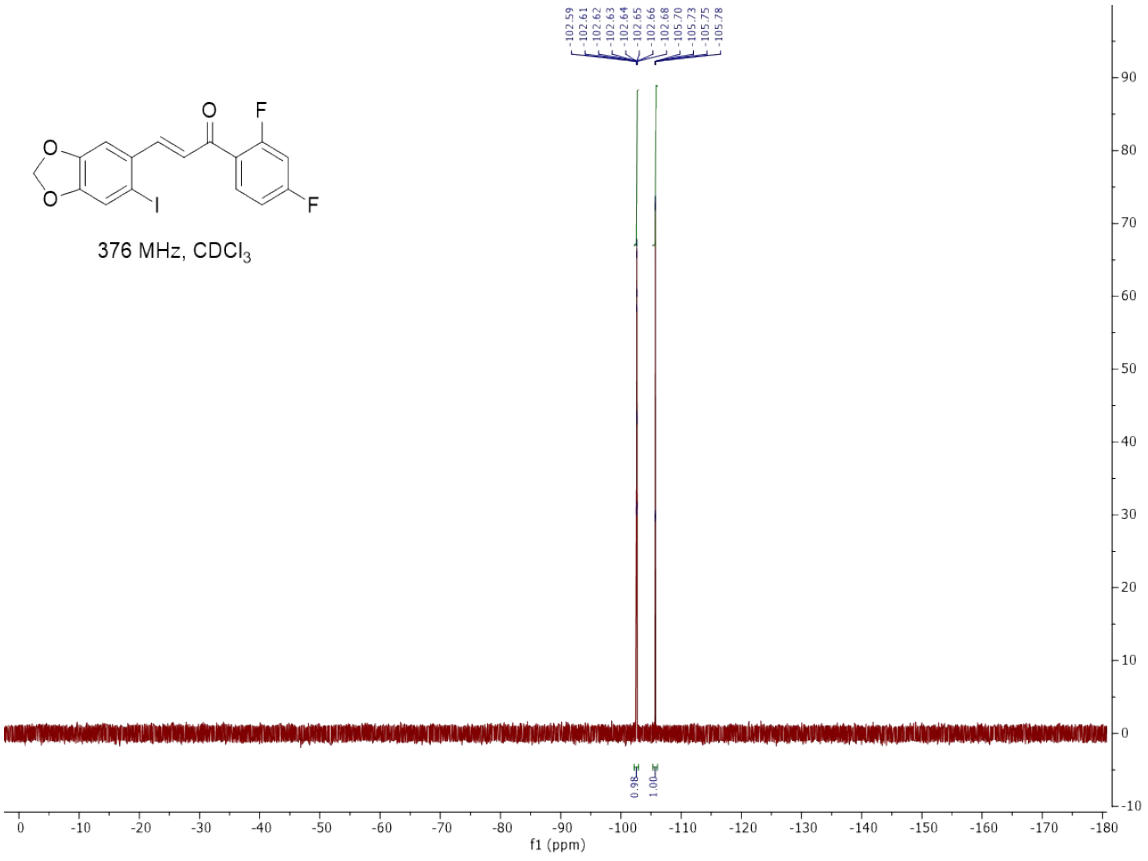
F
O
O
I
F
125 MHz, CDCl3
f1 (ppm)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-102.64
-102.65
-102.66
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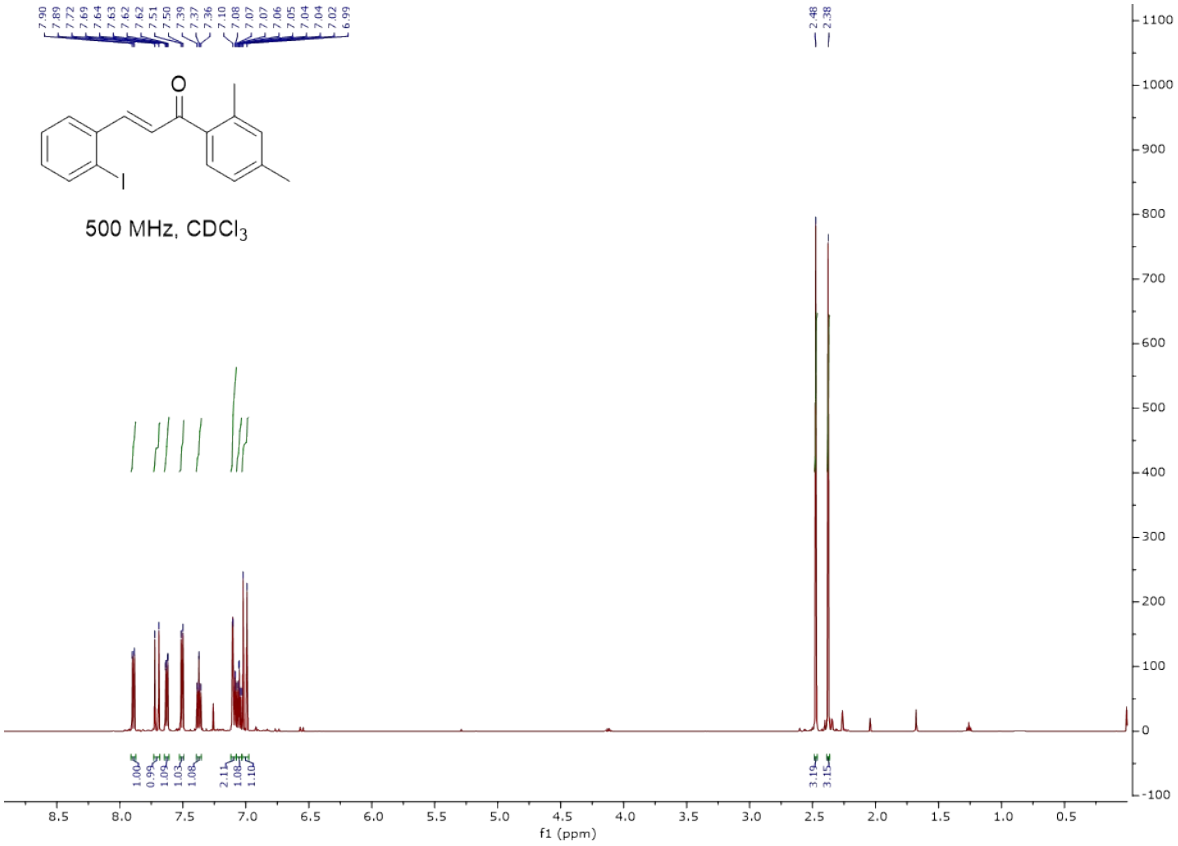
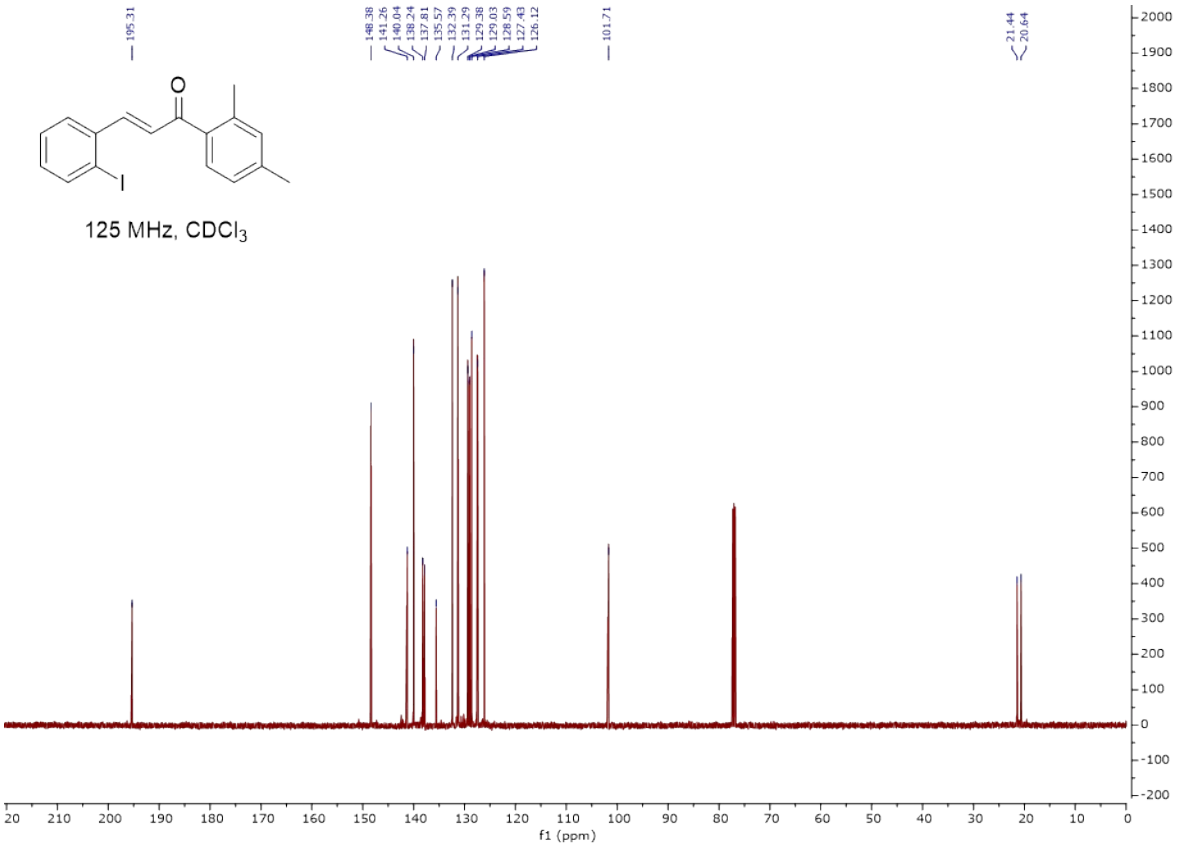
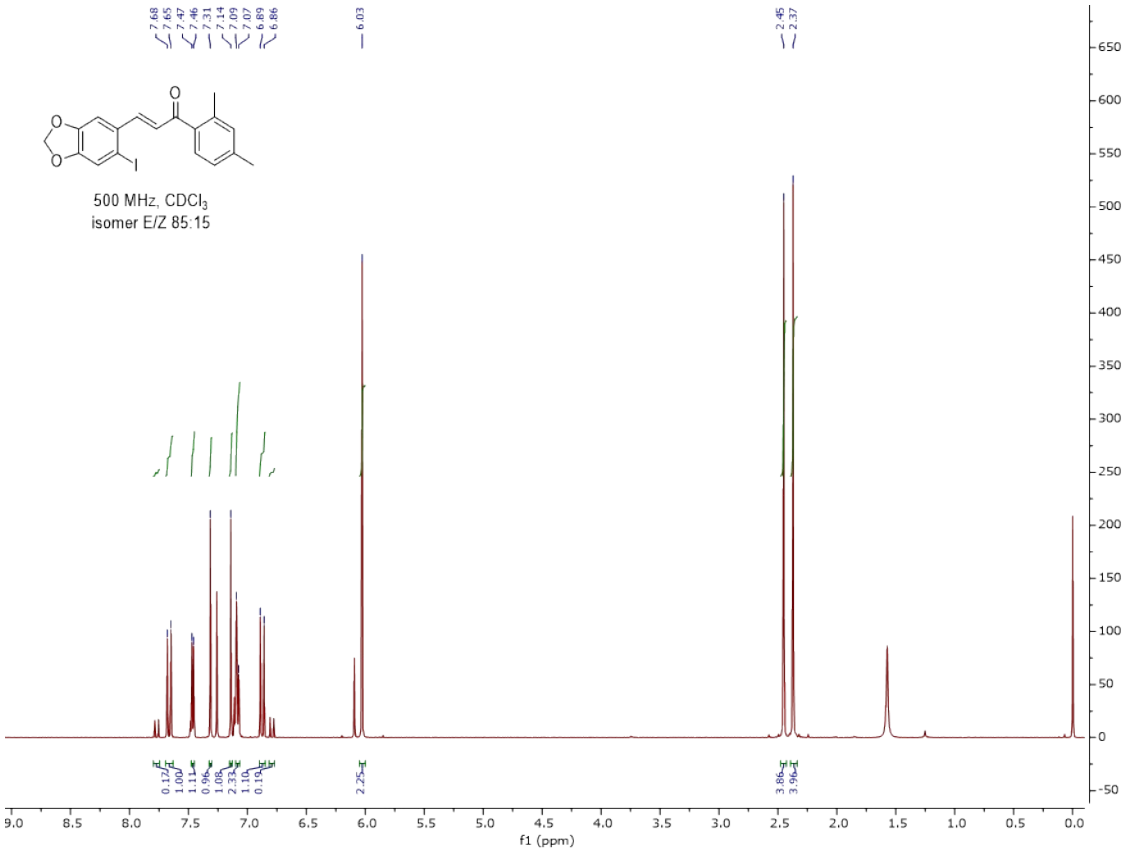
-105.78
O
F
O
O
I
F
376 MHz, CDCl3
0.98
1.00
f1 (ppm)

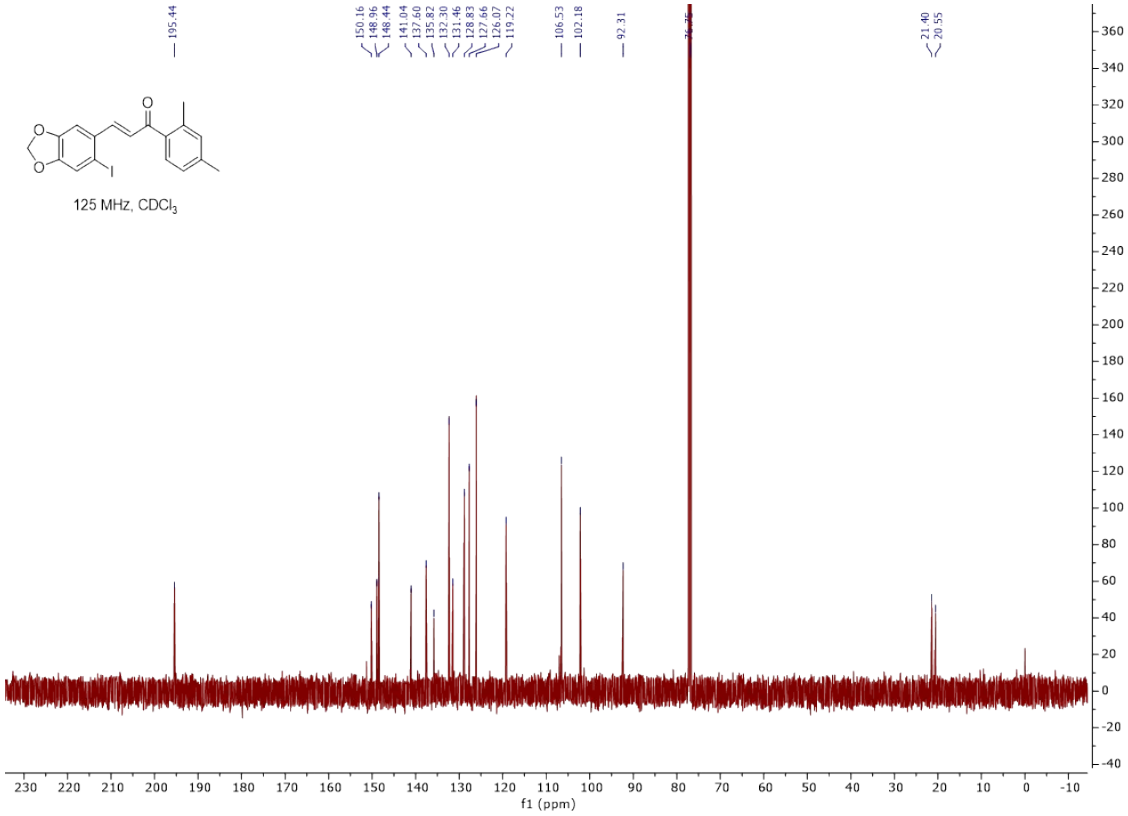
(E)-1-(2,4-Dimethylphenyl)-3-(2-iodophenyl)prop-2-en-1-one



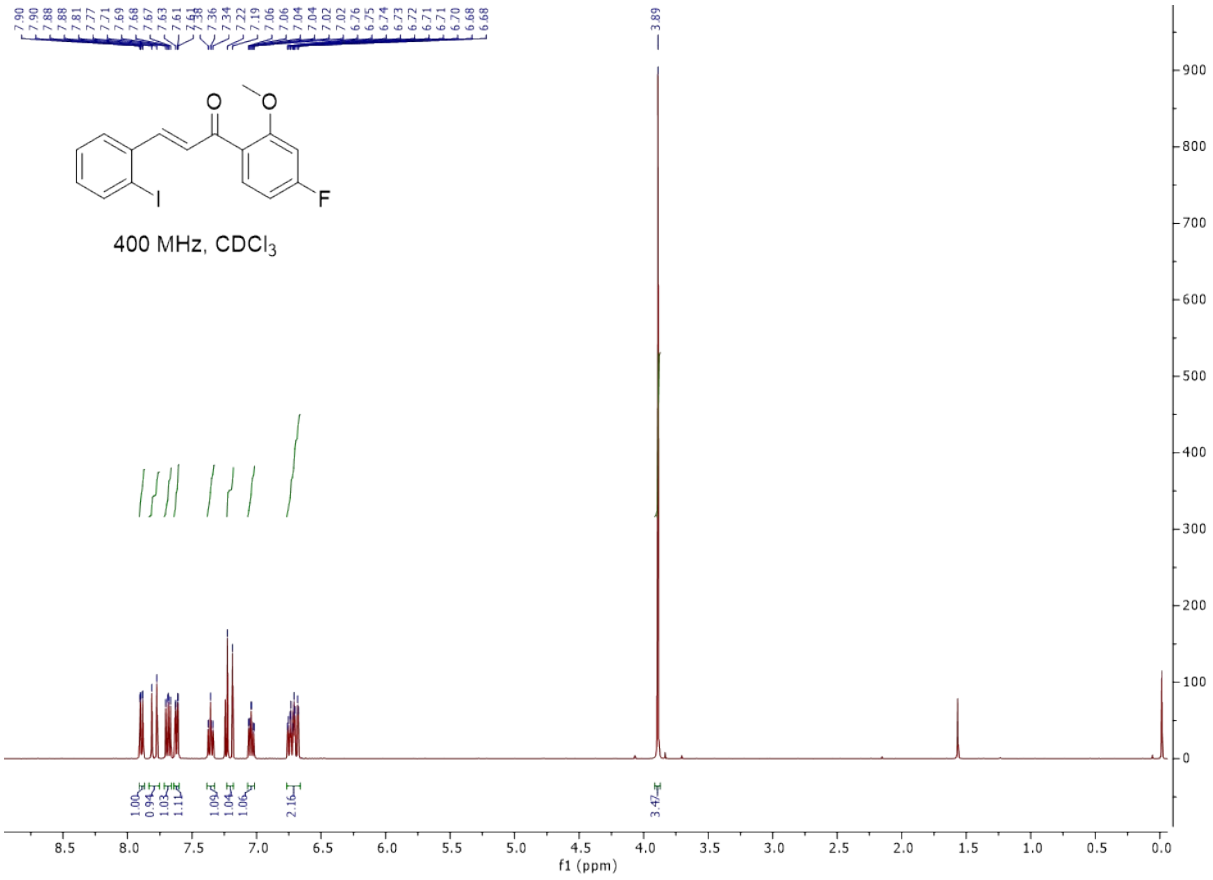


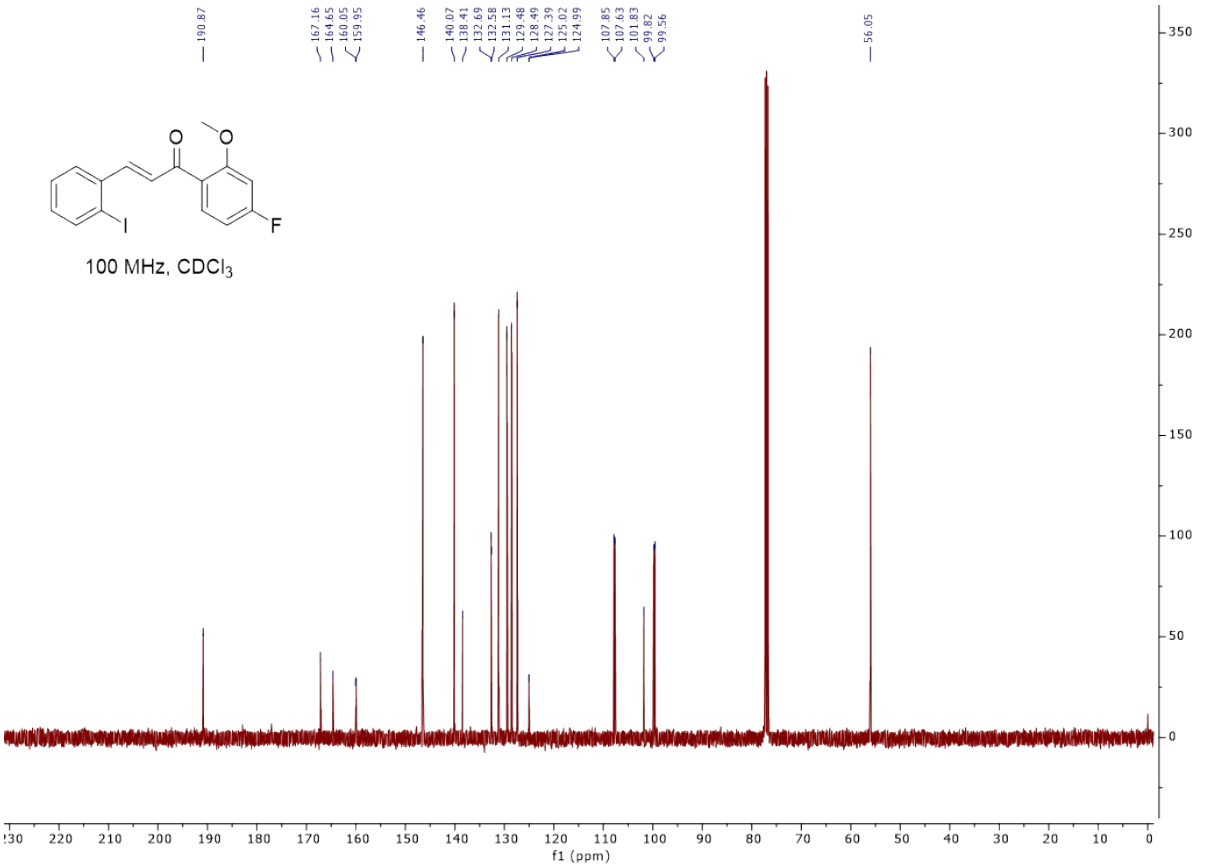
(E)-1-(2,4-Dimethylphenyl)-3-(6-iodobenzo[d][1,3]dioxol-5-yl)prop-2-en-1-one

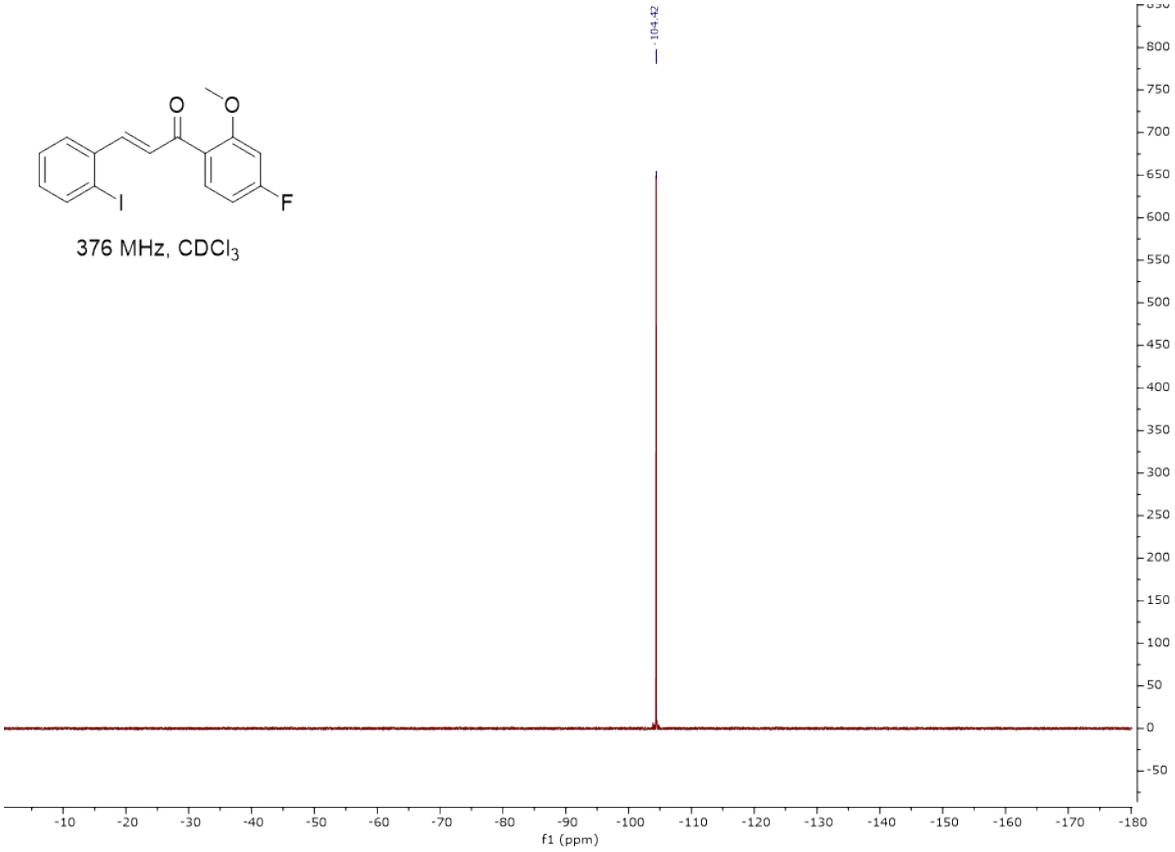




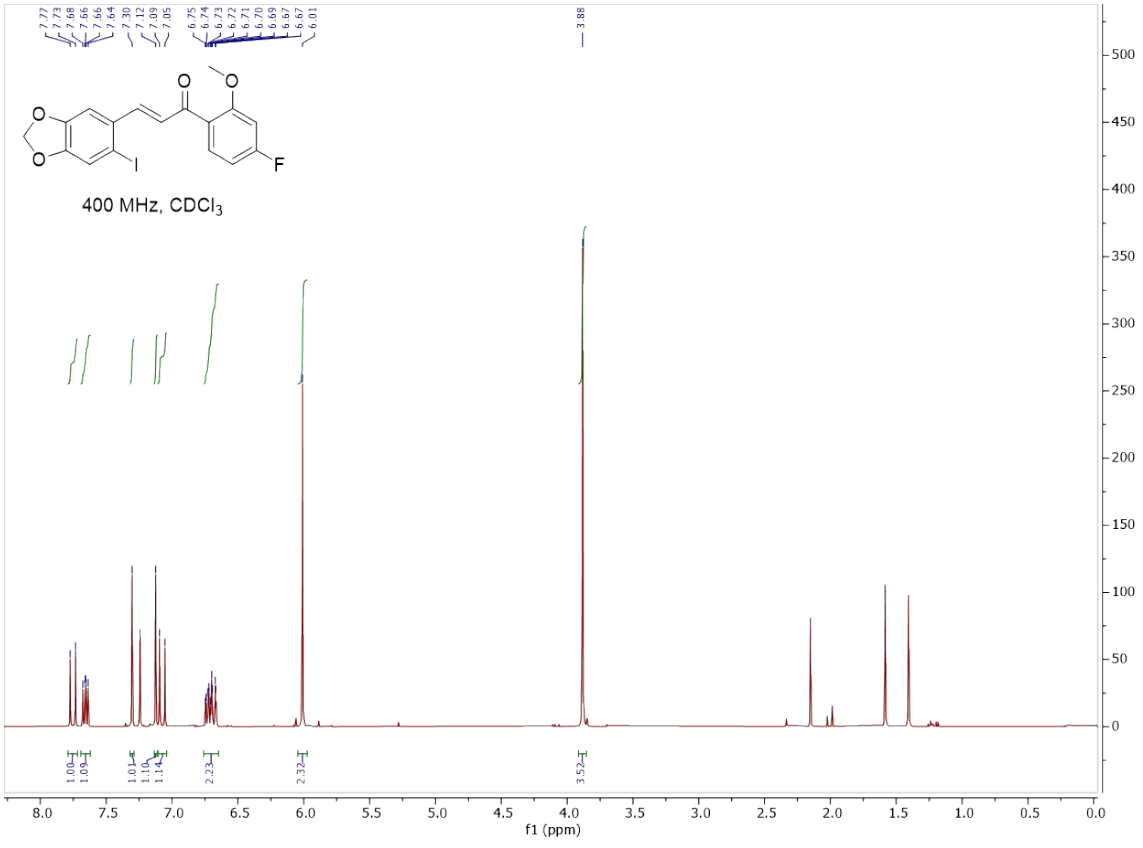
(E)-1-(4-Fluoro-2-methoxyphenyl)-3-(2-iodophenyl)prop-2-en-1-one

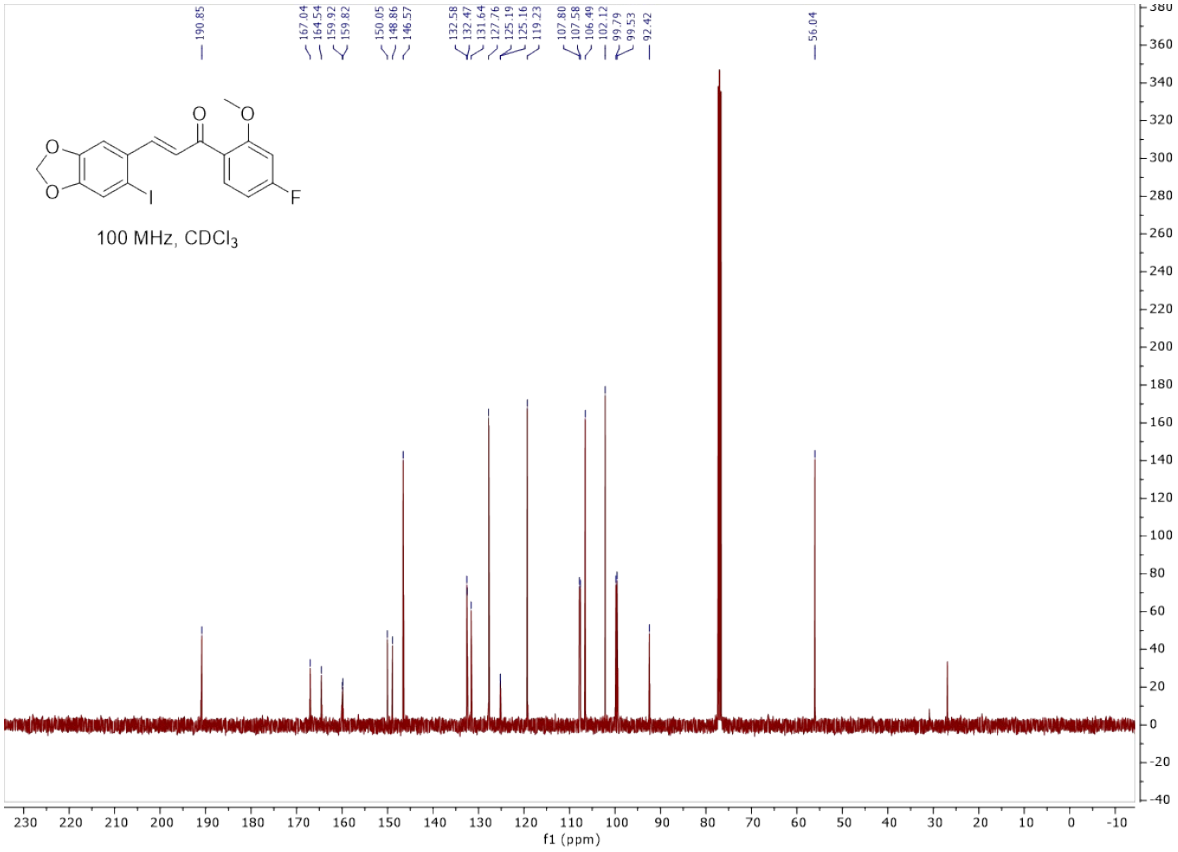






(E)-1-(4-Fluoro-2-methoxyphenyl)-3-(6-iodobenzo[d][1,3]dioxol-5-yl)prop-2-en-1-one

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146.57
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132.47
131.64
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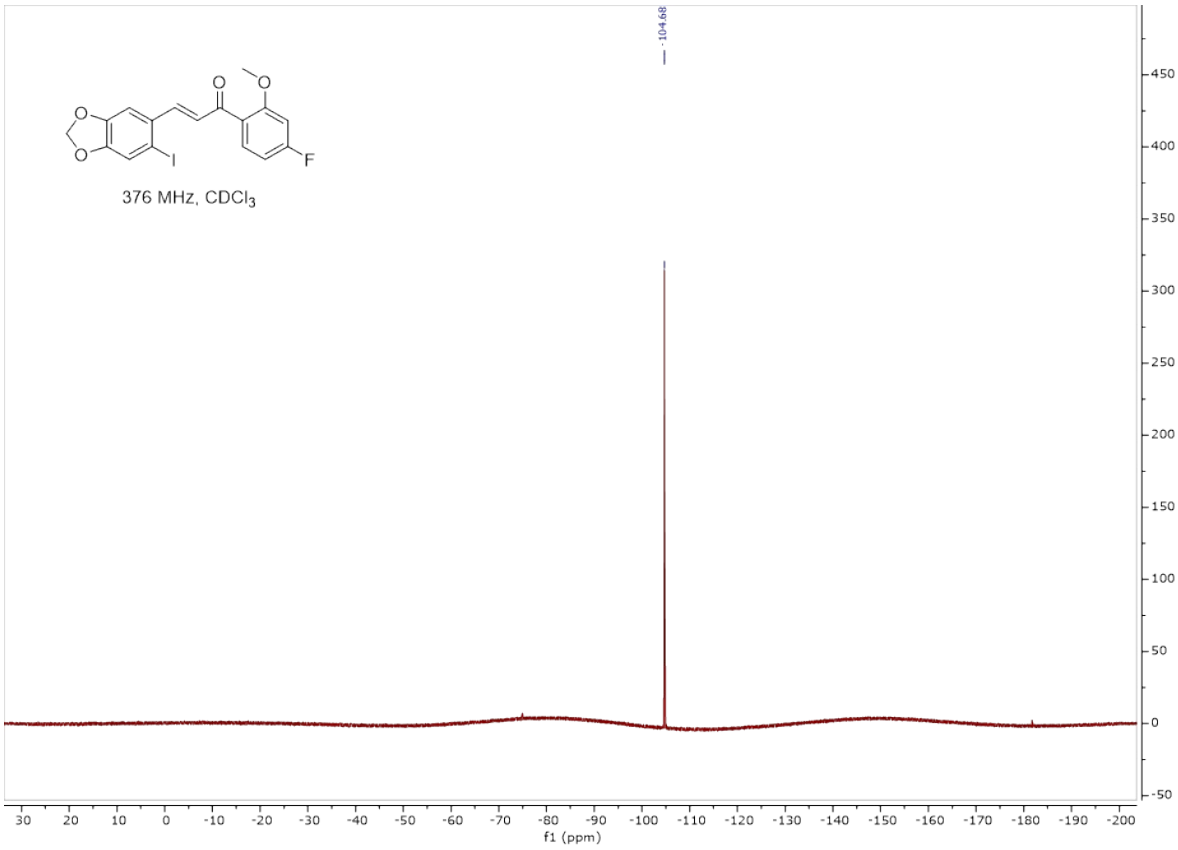
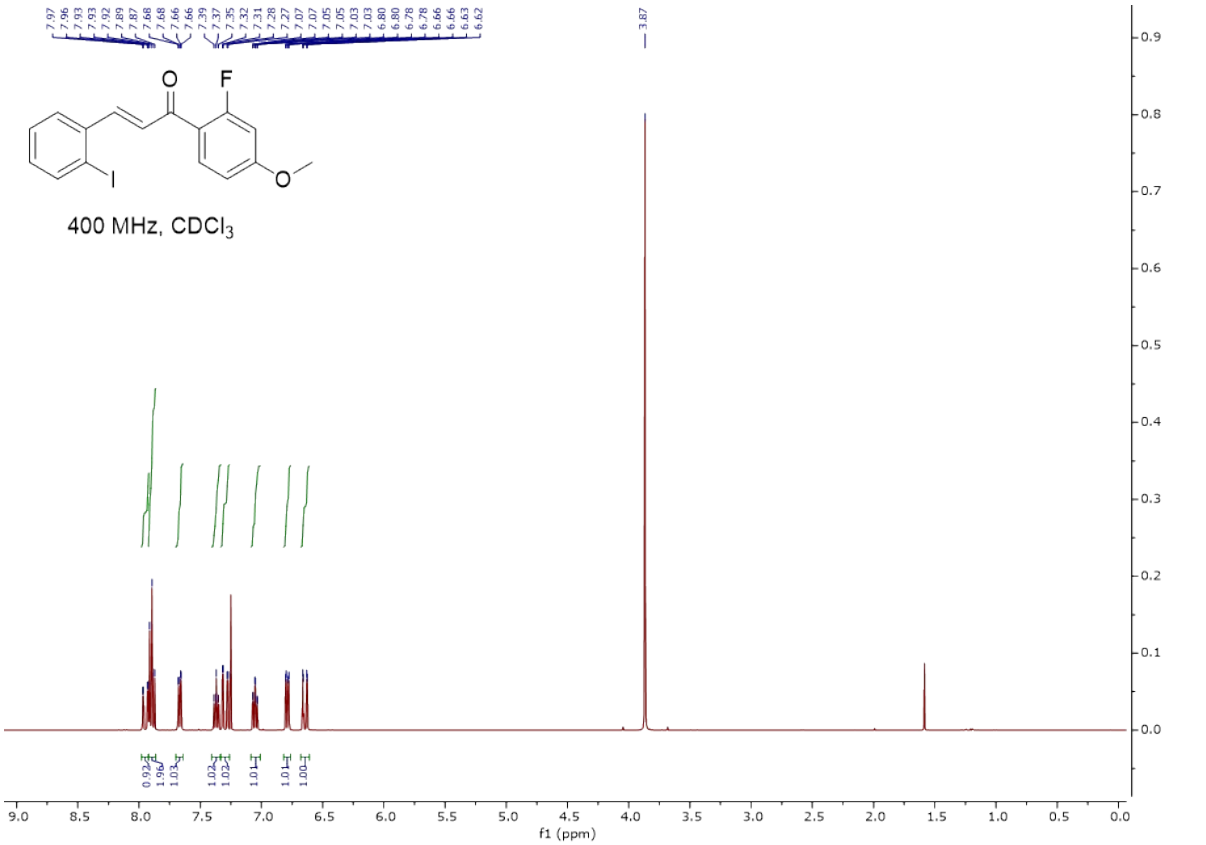
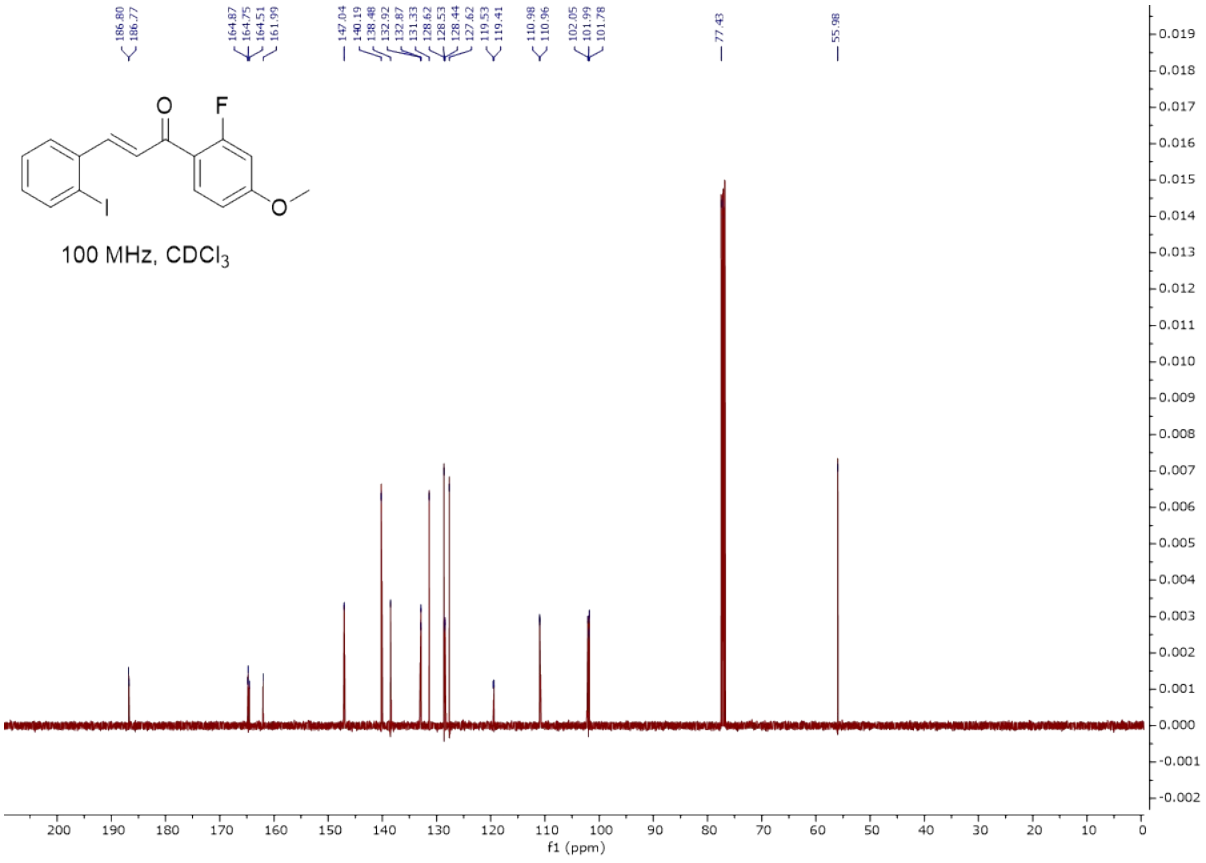
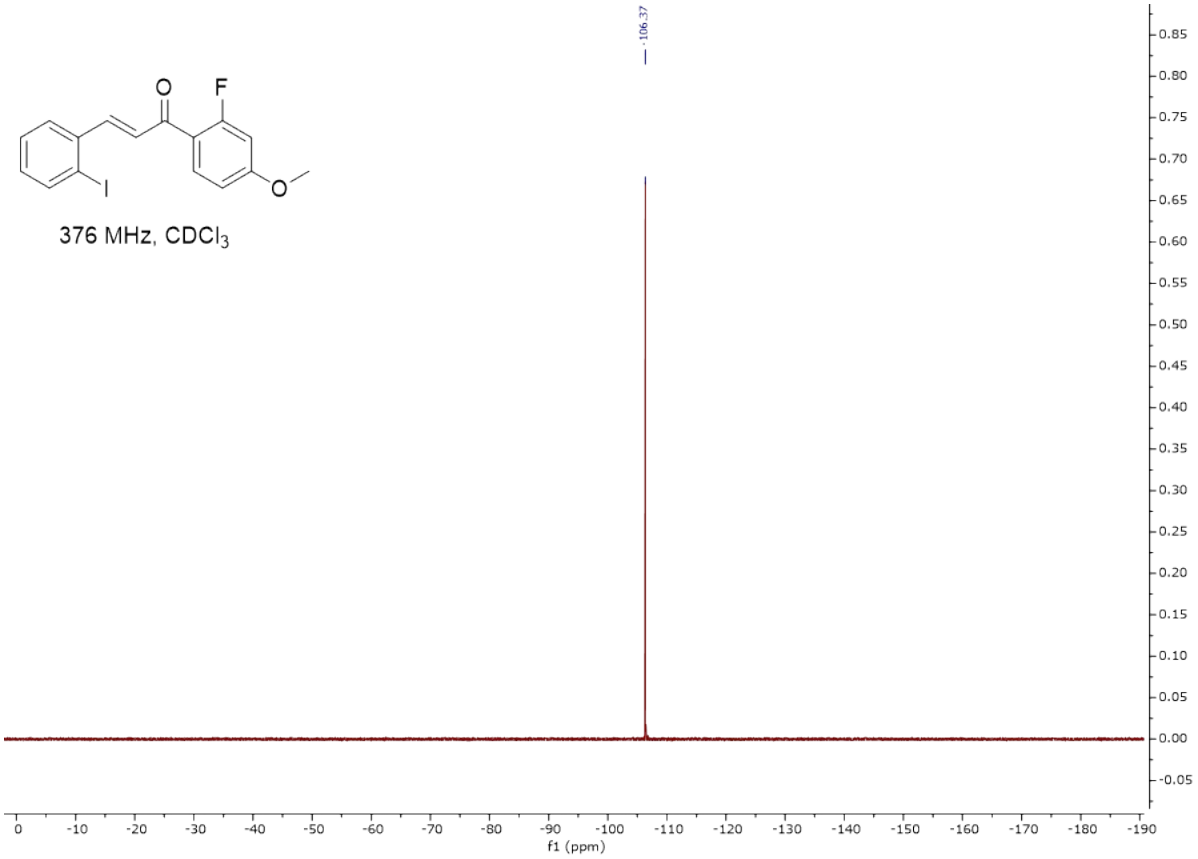
125.16
119.23
107.80
107.58
106.49
102.12
99.79
99.53
92.42
56.04
O
O
O
O
I
F
100 MHz, CDCl3
f1 (ppm)


-104.68
O
O
O
O
I
F
376 MHz, CDCl3
f1 (ppm)

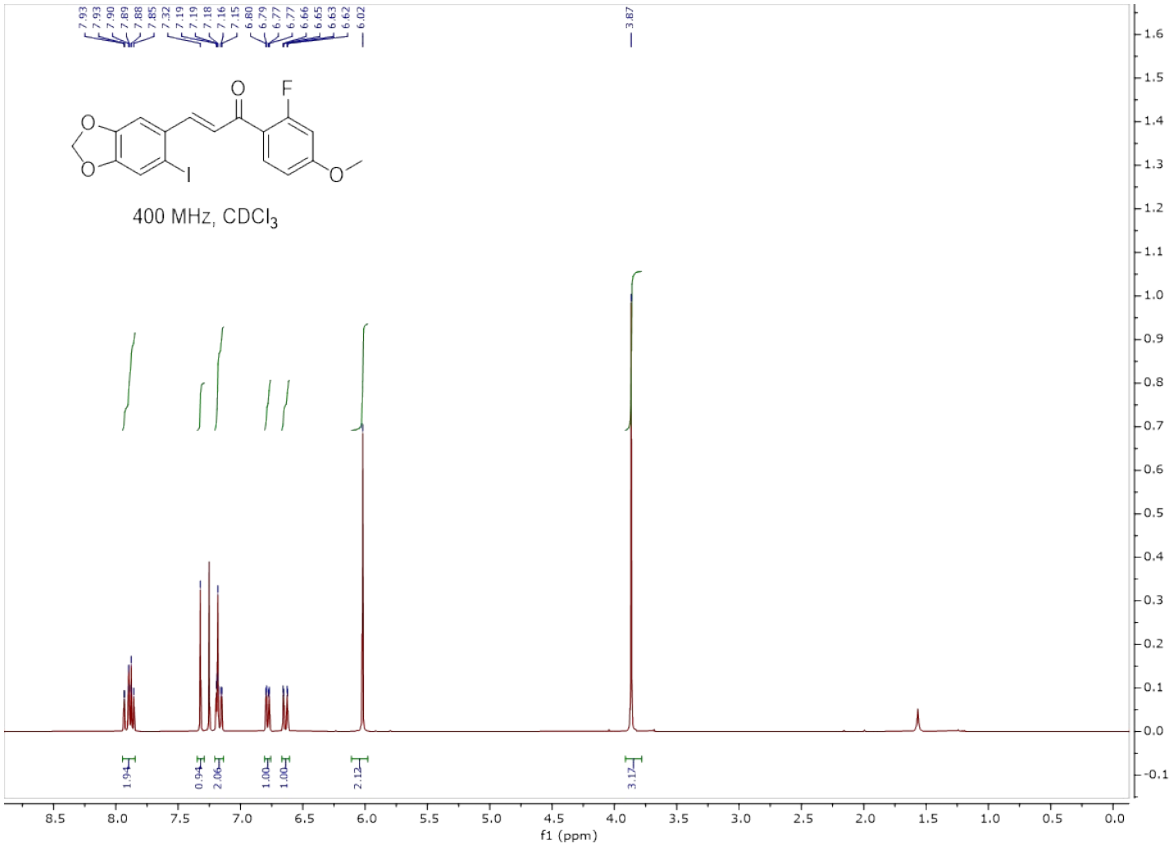
(E)-1-(2-Fluoro-4-methoxyphenyl)-3-(2-iodophenyl)prop-2-en-1-one

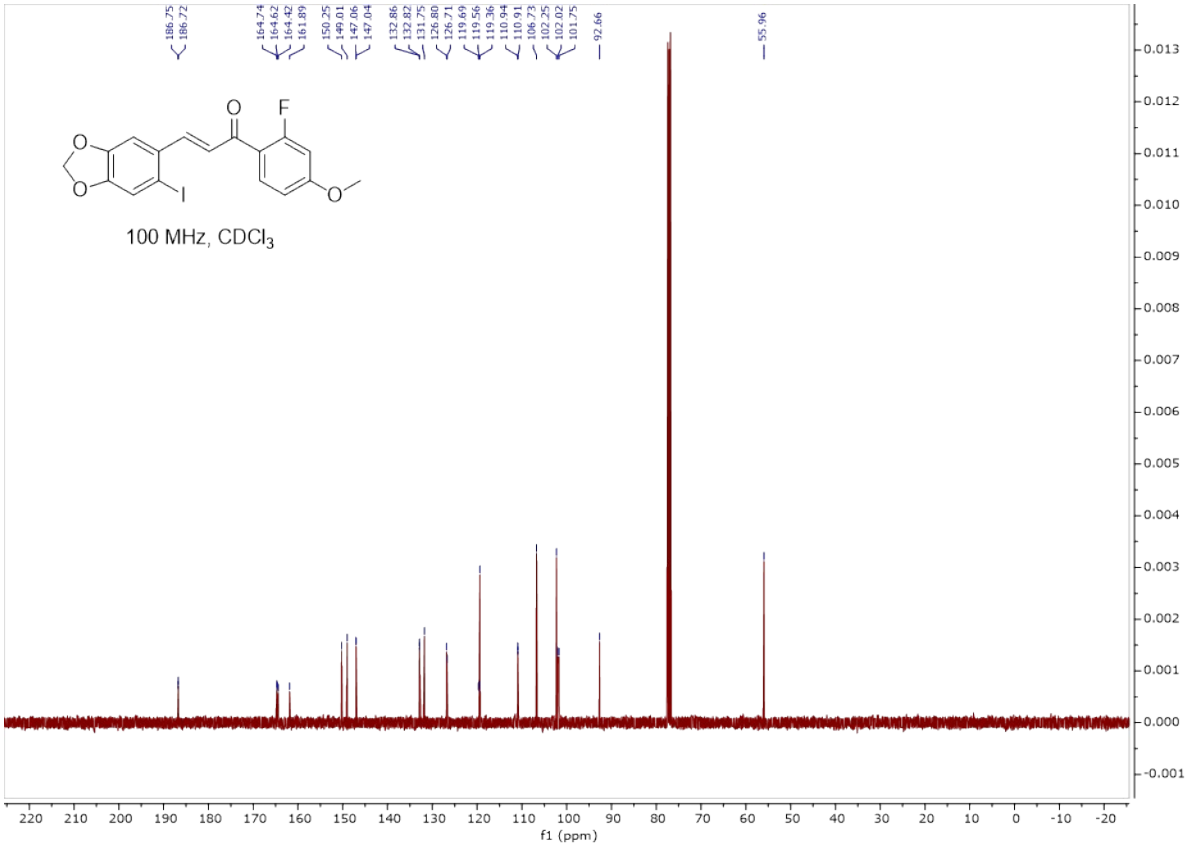






(E)-1-(2-Fluoro-4-methoxyphenyl)-3-(6-iodobenzo[d][1,3]dioxol-5-yl)prop-2-en-1-one




186.75
186.72
164.74
164.62
164.42
161.89
150.25
149.01
147.06
147.04
132.86
132.82
131.75
126.80
126.71
119.69
119.56
119.36
110.94
110.91
106.73
102.25
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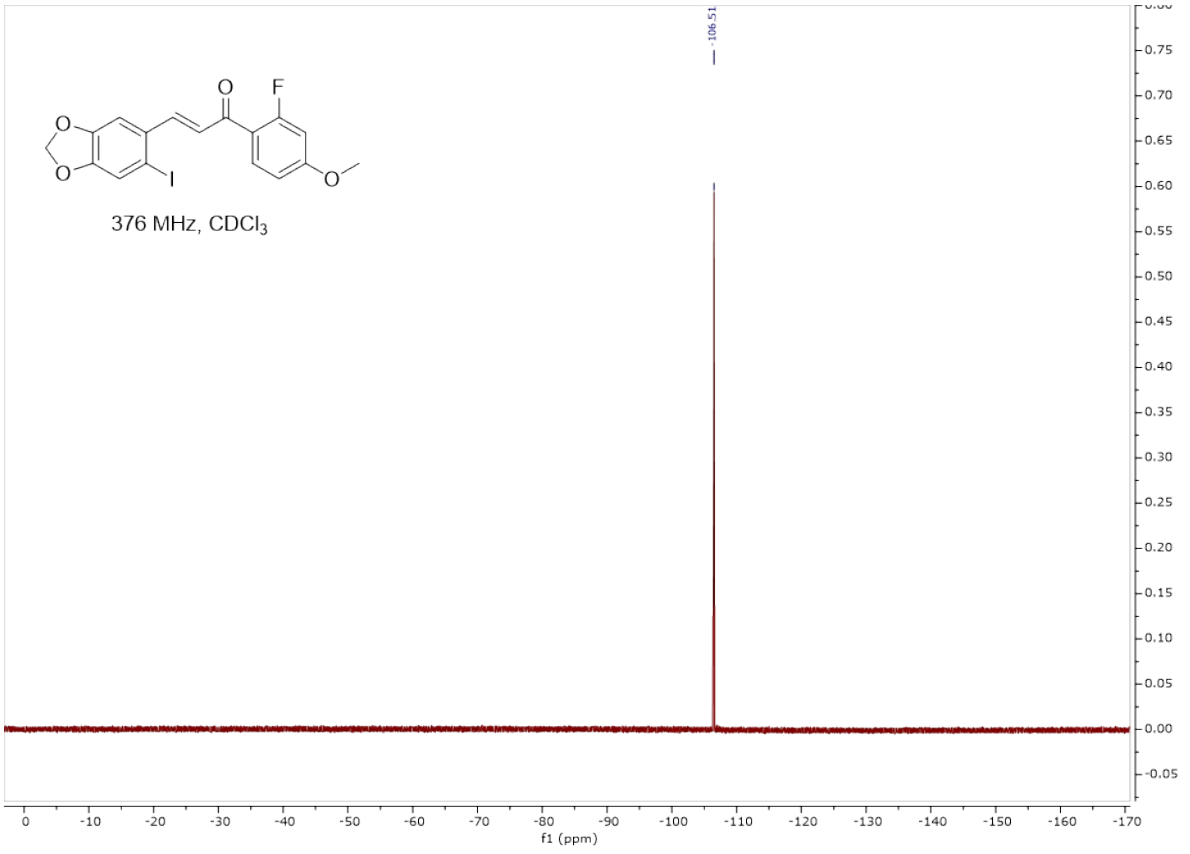
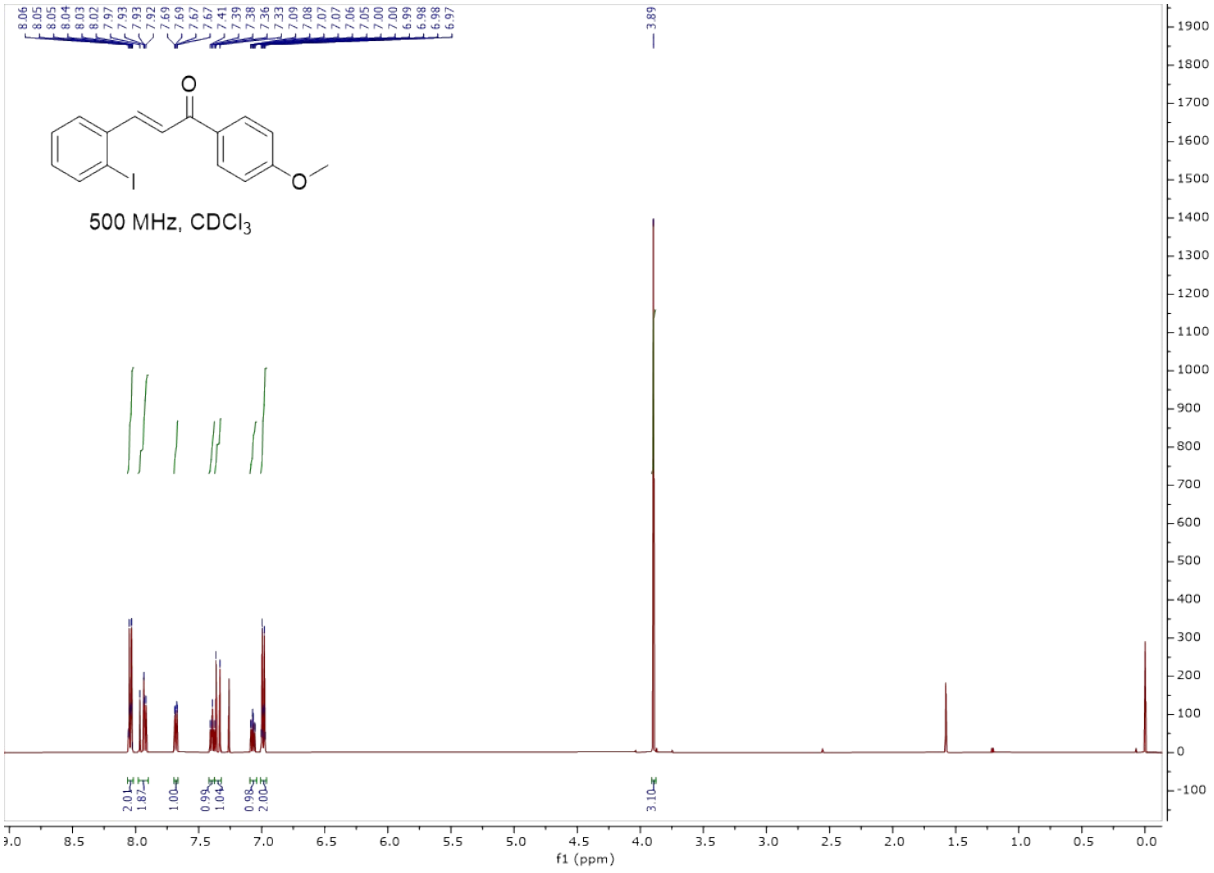
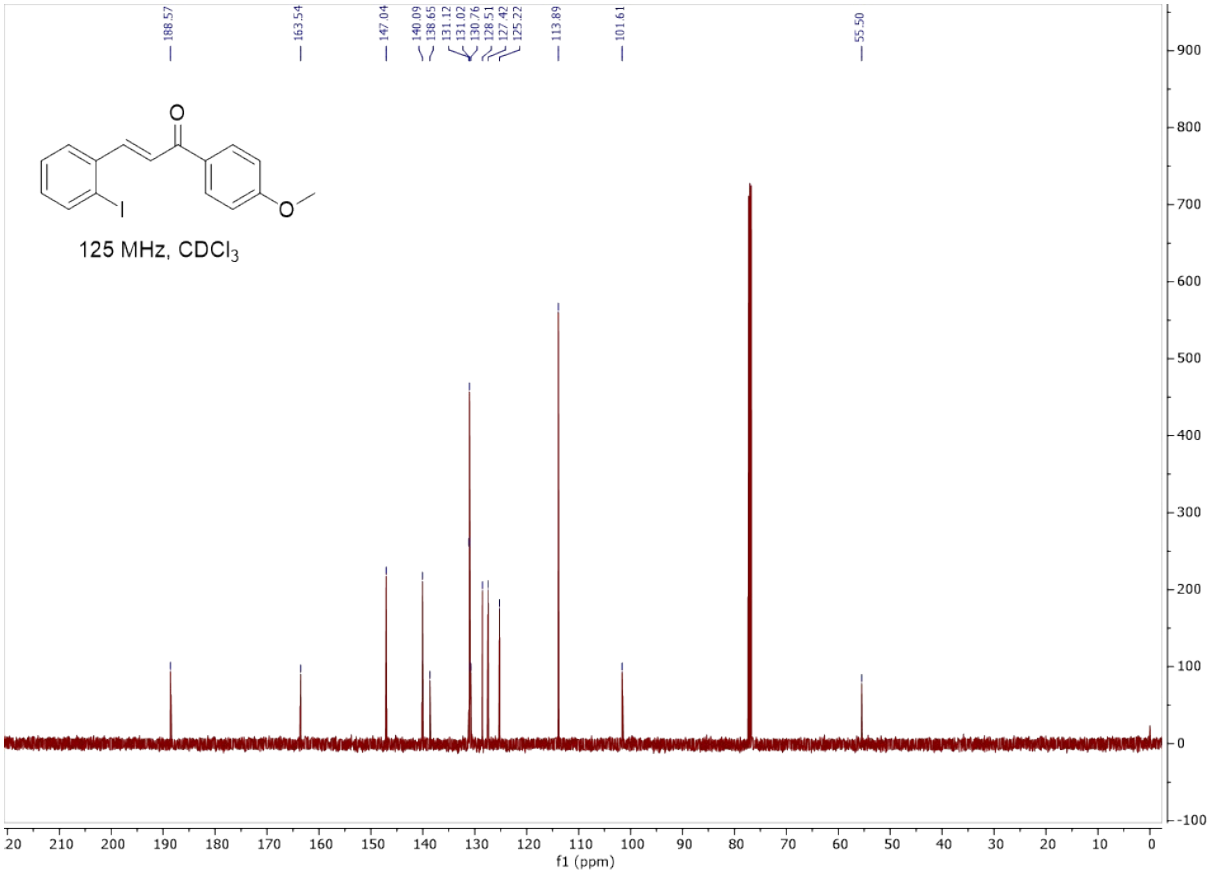
101.75
92.66
55.96
O
F
O
O
I
O
100 MHz, CDCl3
f1 (ppm)

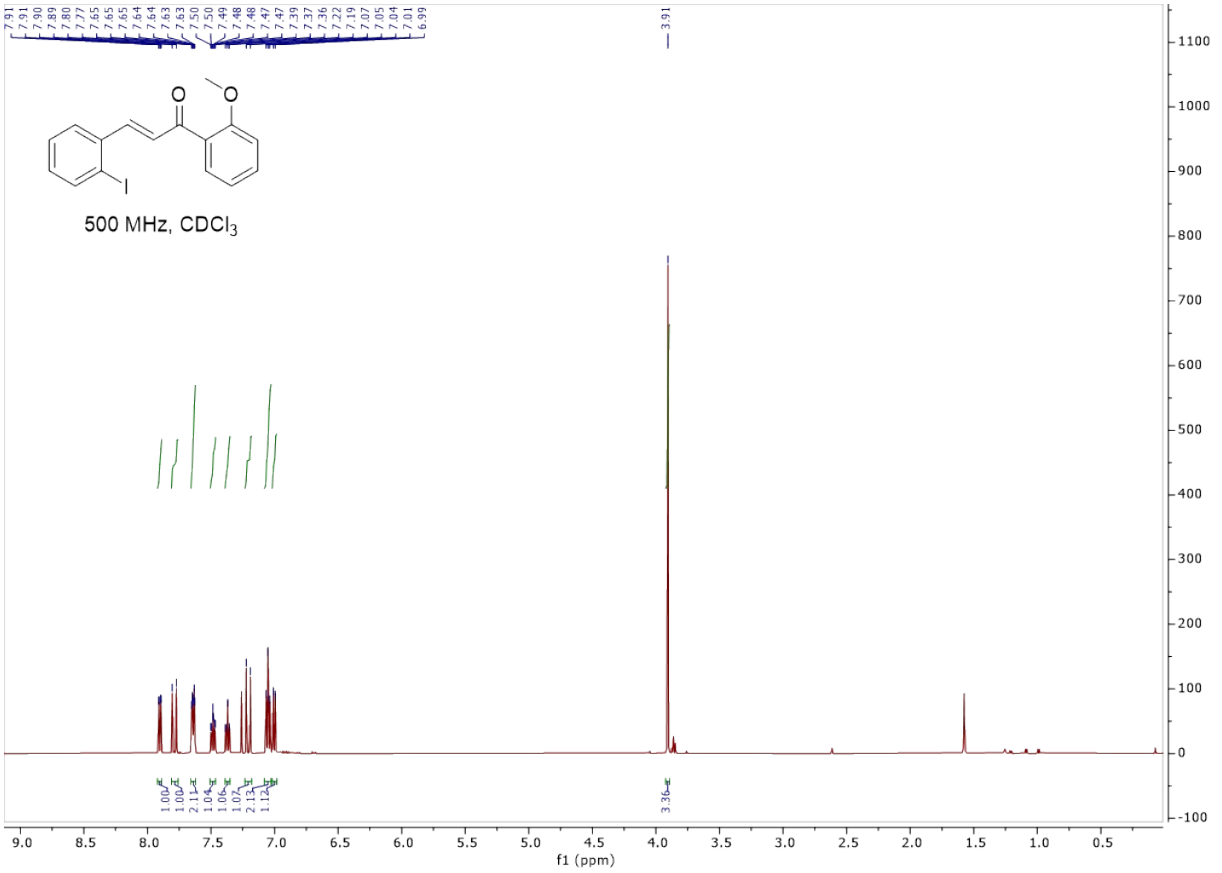

-106.51
O
F
O
O
I
O
376 MHz, CDCl3
f1 (ppm)

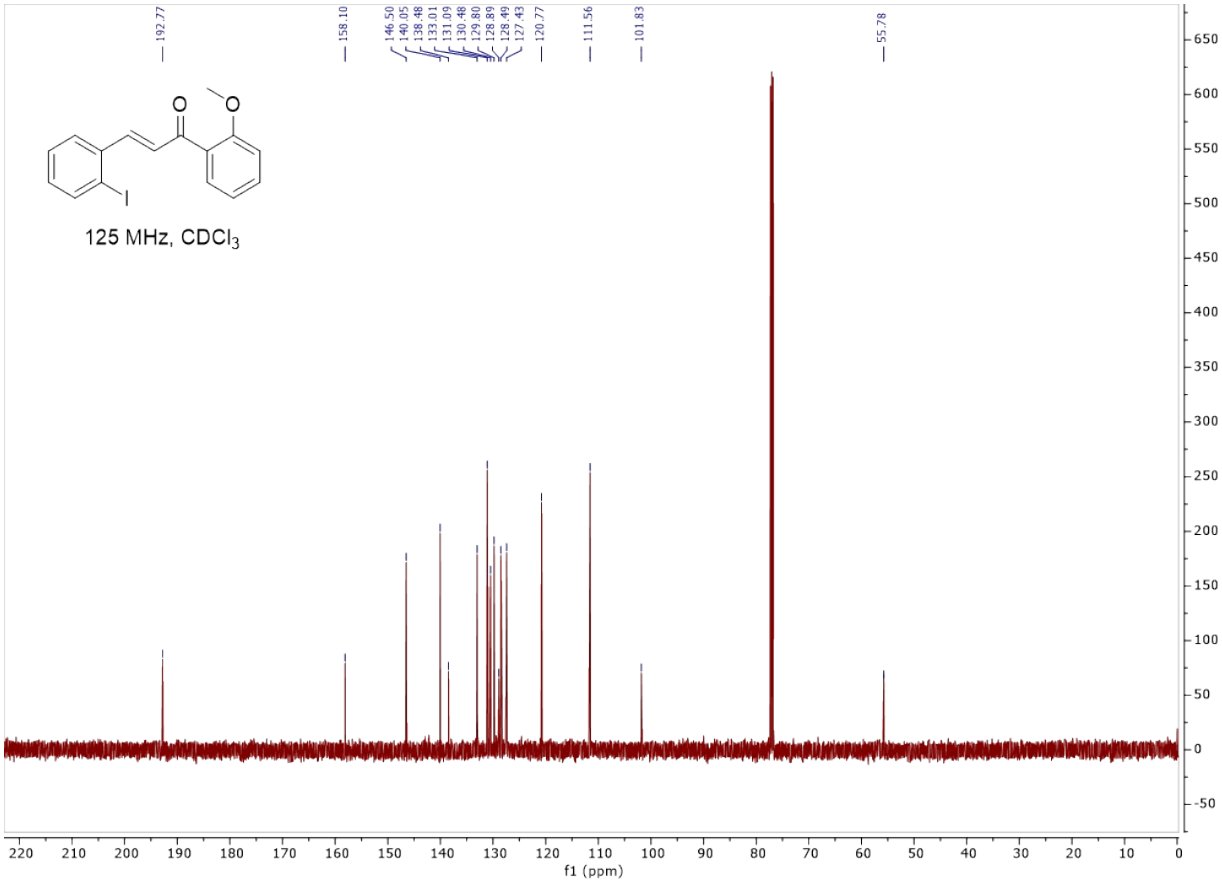
(E)-3-(2-Iodophenyl)-1-(4-methoxyphenyl)prop-2-en-1-one



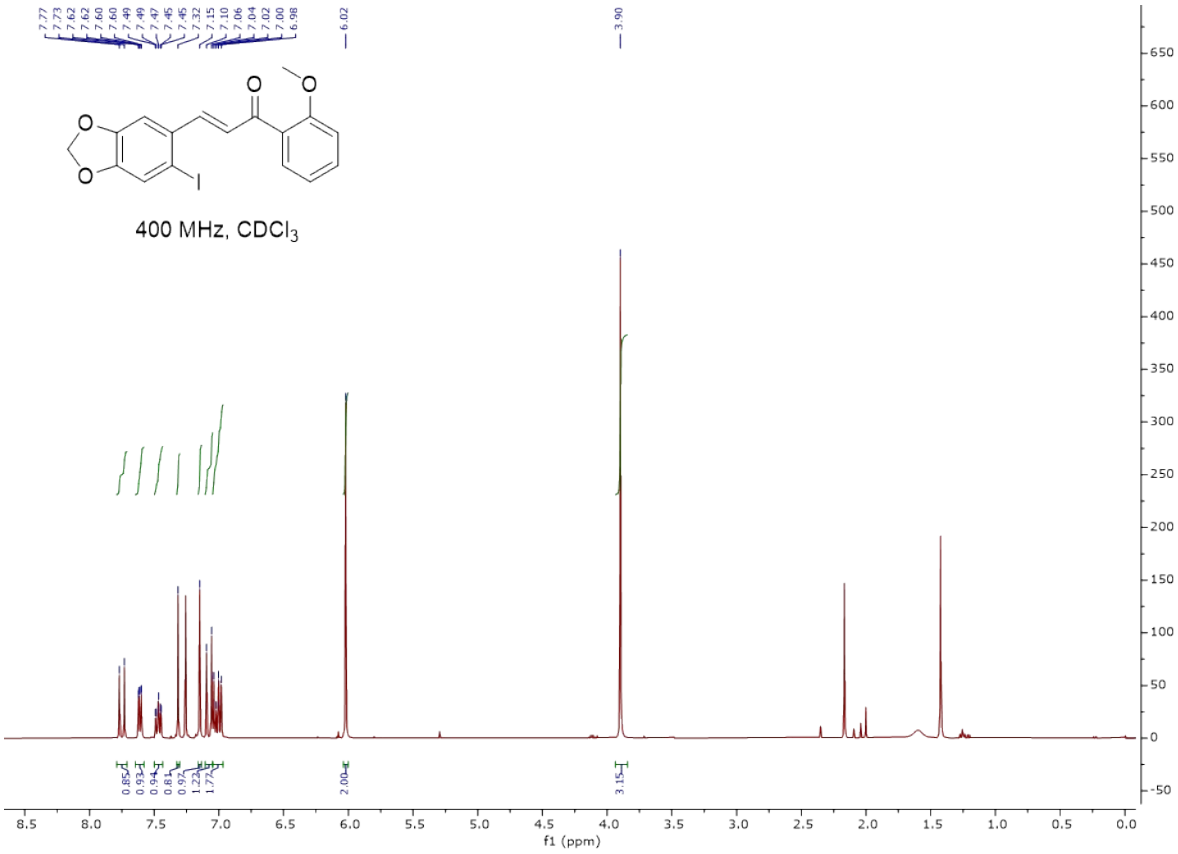


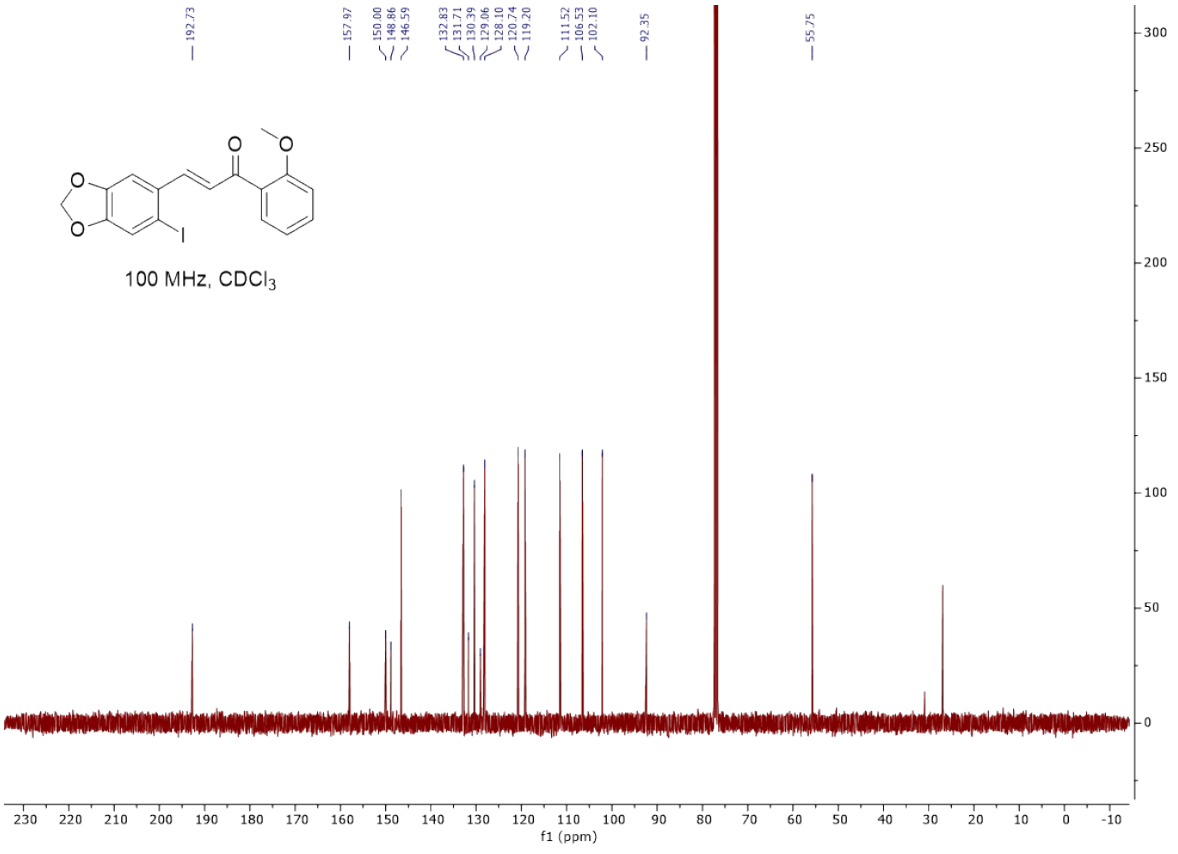
(E)-3-(2-Iodophenyl)-1-(2-methoxyphenyl)prop-2-en-1-one



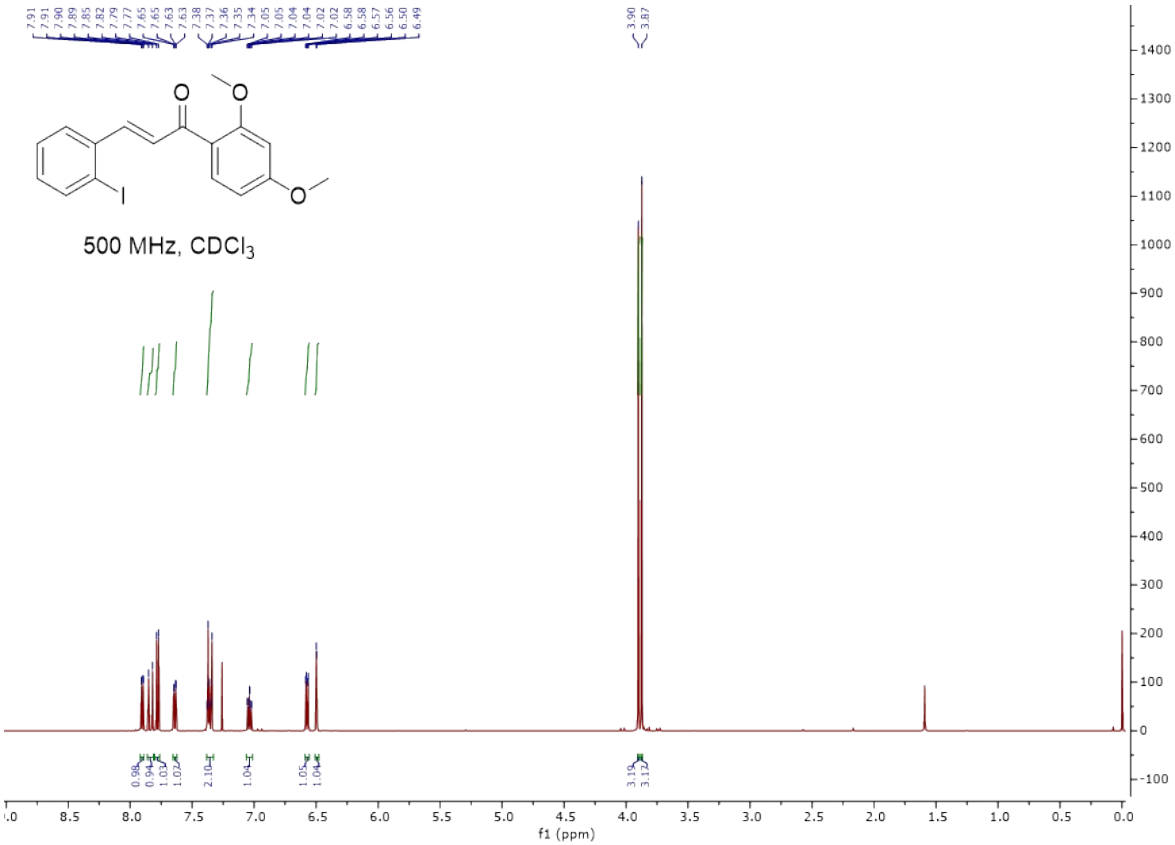


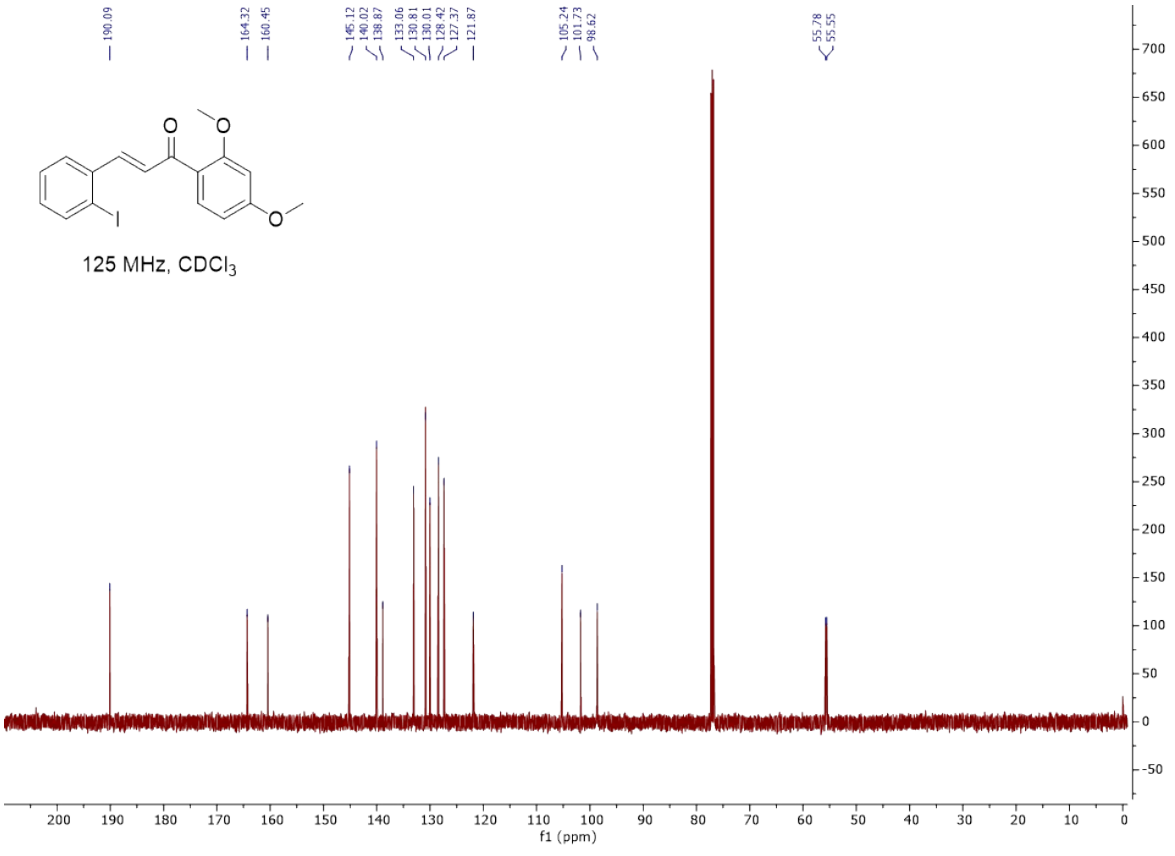
(E)-3-(6-Iodobenzo[d][1,3]dioxol-5-yl)-1-(2-methoxyphenyl)prop-2-en-1-one



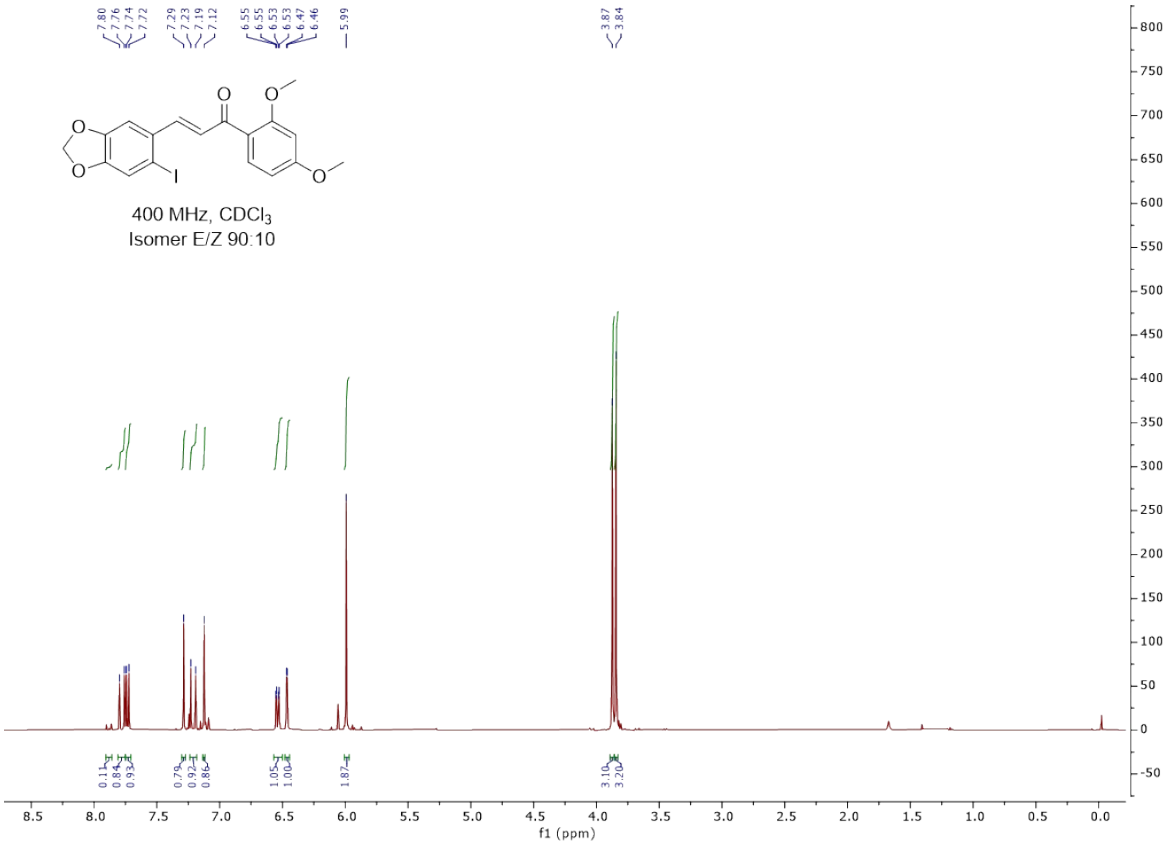


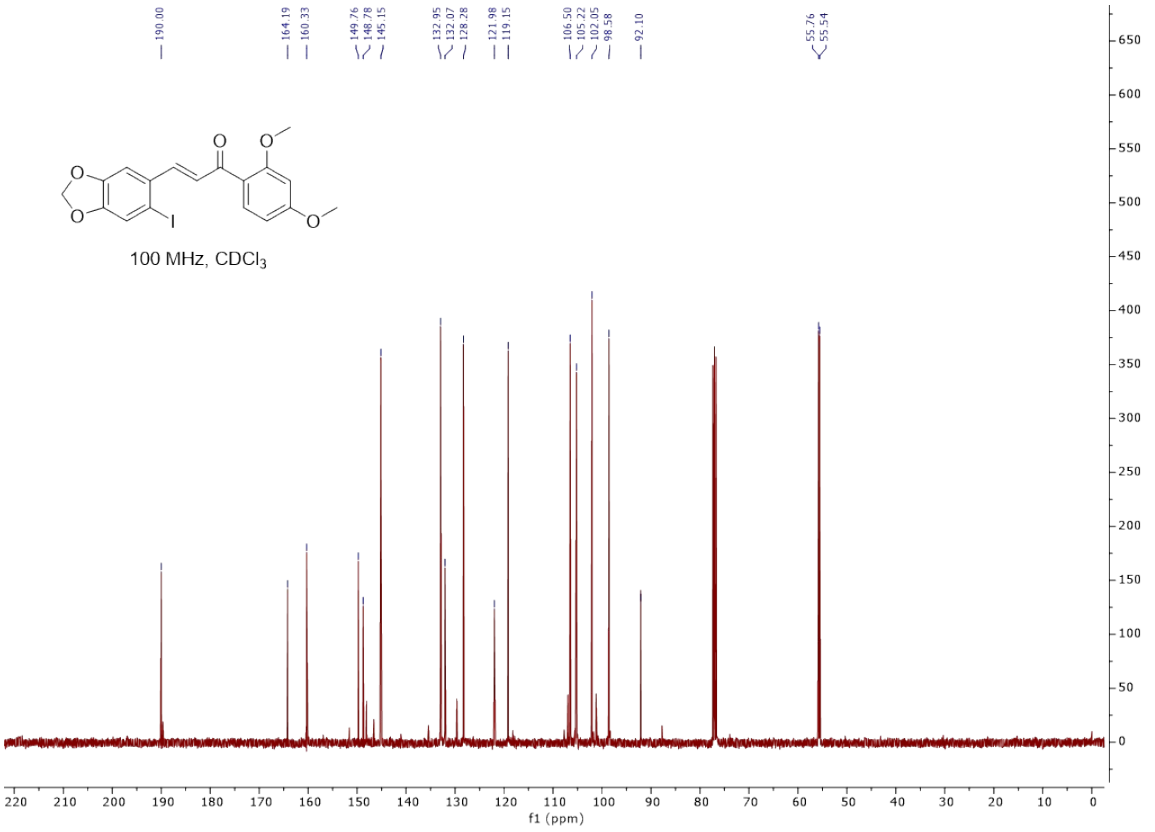
(E)-1-(2,4-Dimethoxyphenyl)-3-(2-iodophenyl)prop-2-en-1-one



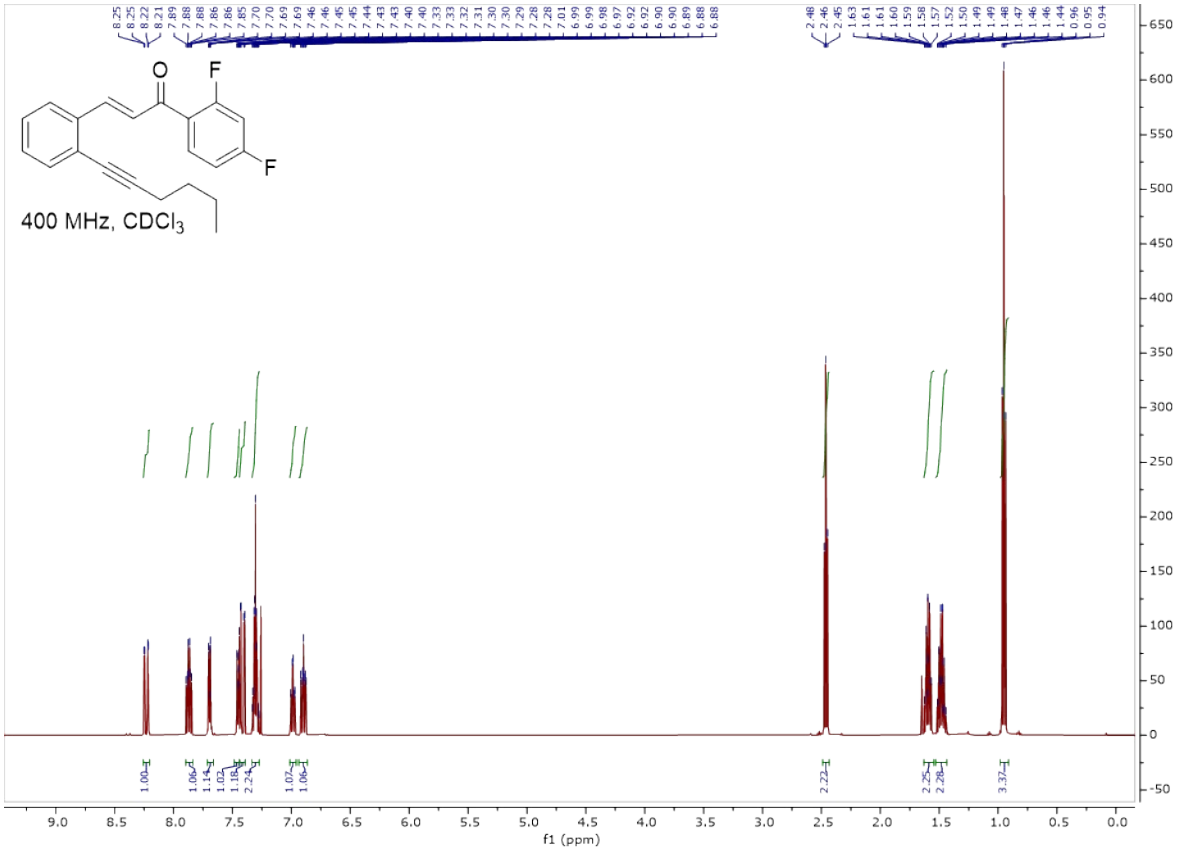


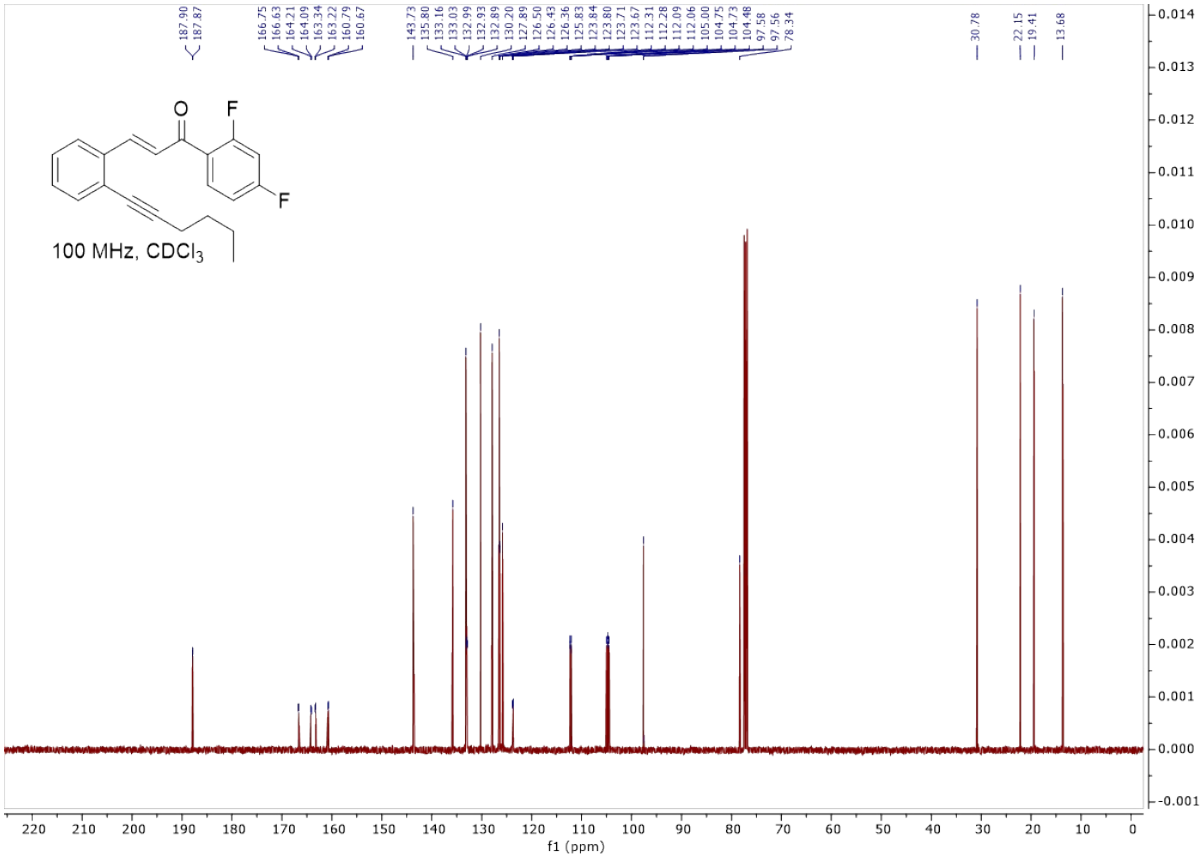
(E)-1-(2,4-Dimethoxyphenyl)-3-(6-iodobenzo[d][1,3]dioxol-5-yl)prop-2-en-1-one

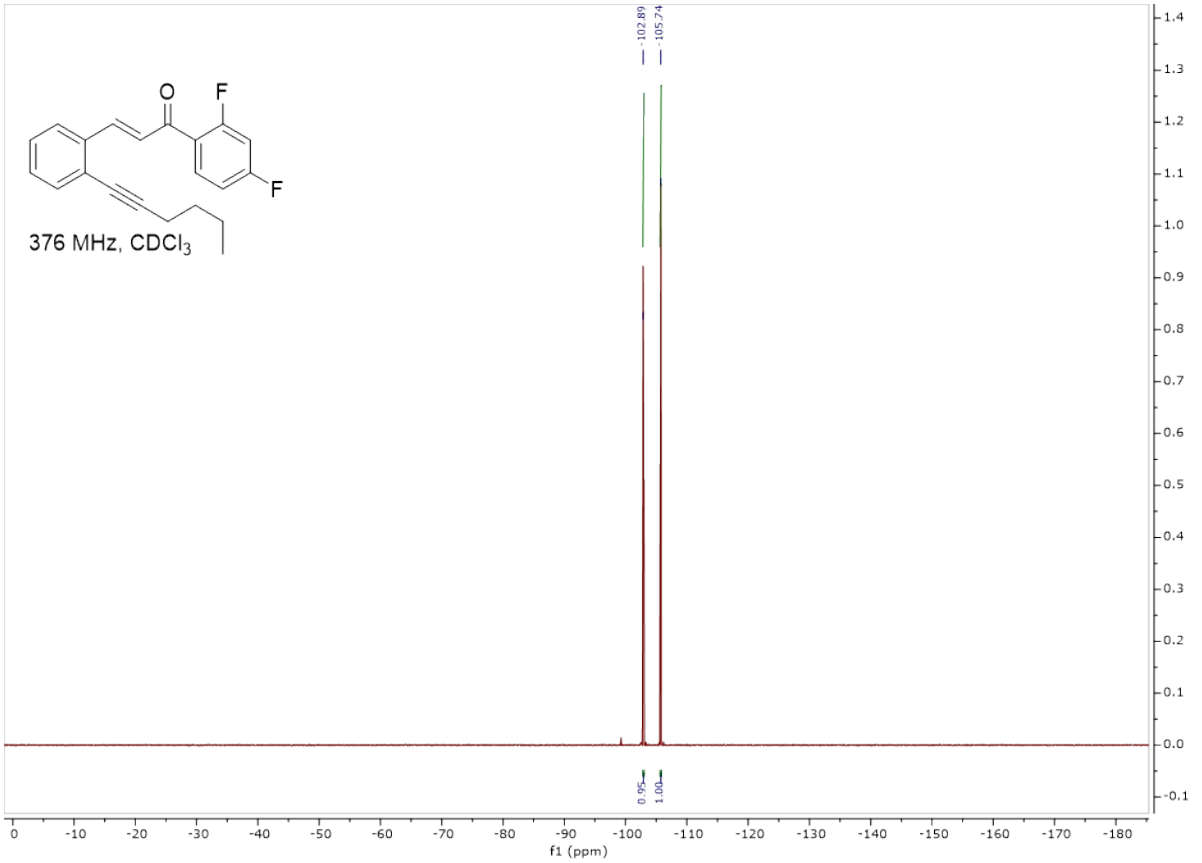




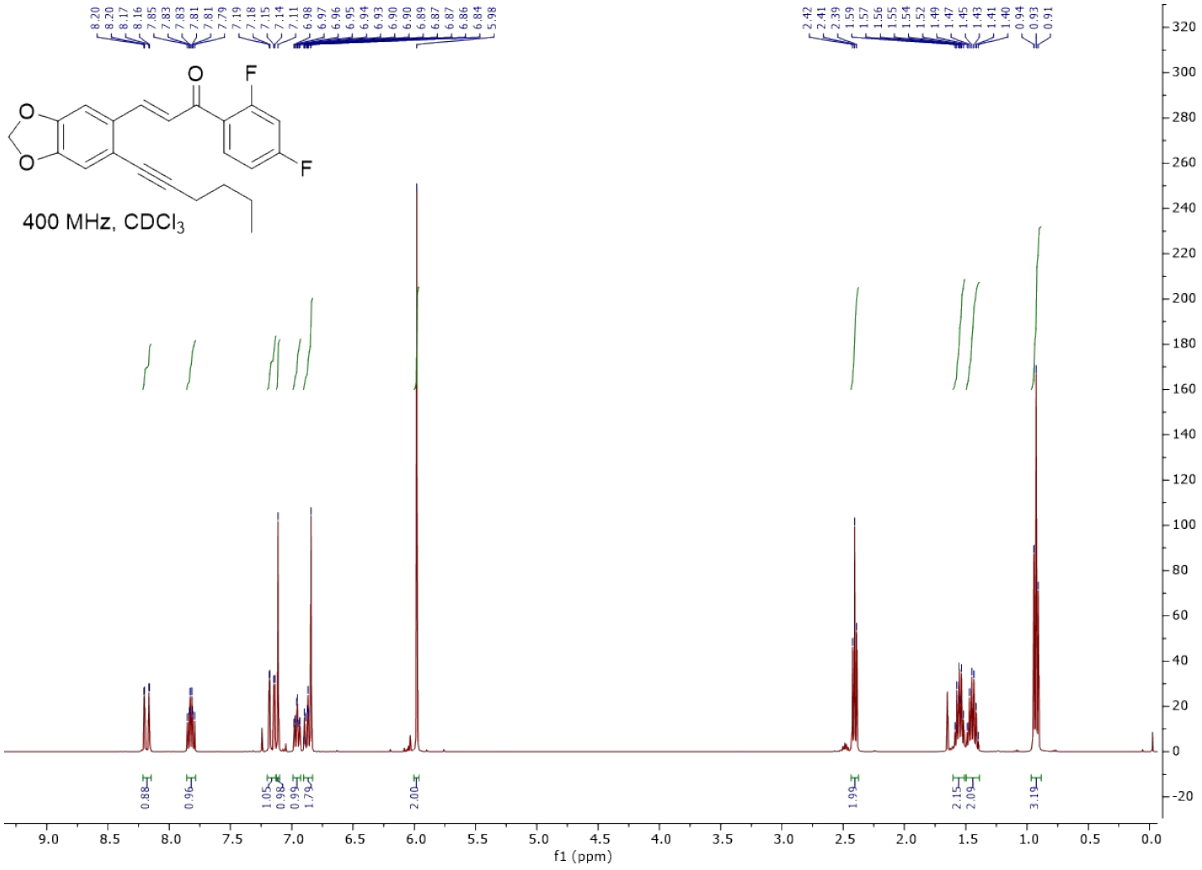
(E)-1-(2,4-Difluorophenyl)-3-(2-(hex-1-yn-1-yl)phenyl)prop-2-en-1-one, 1a

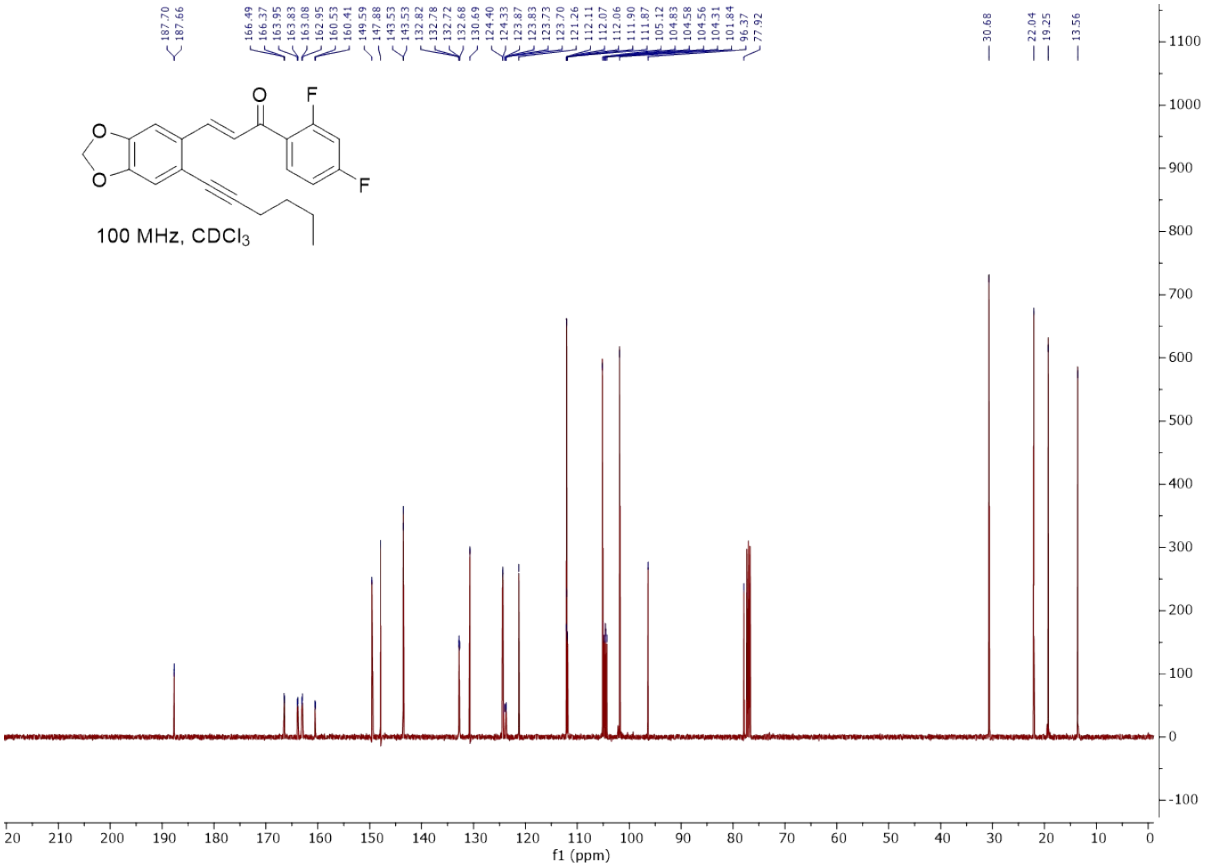


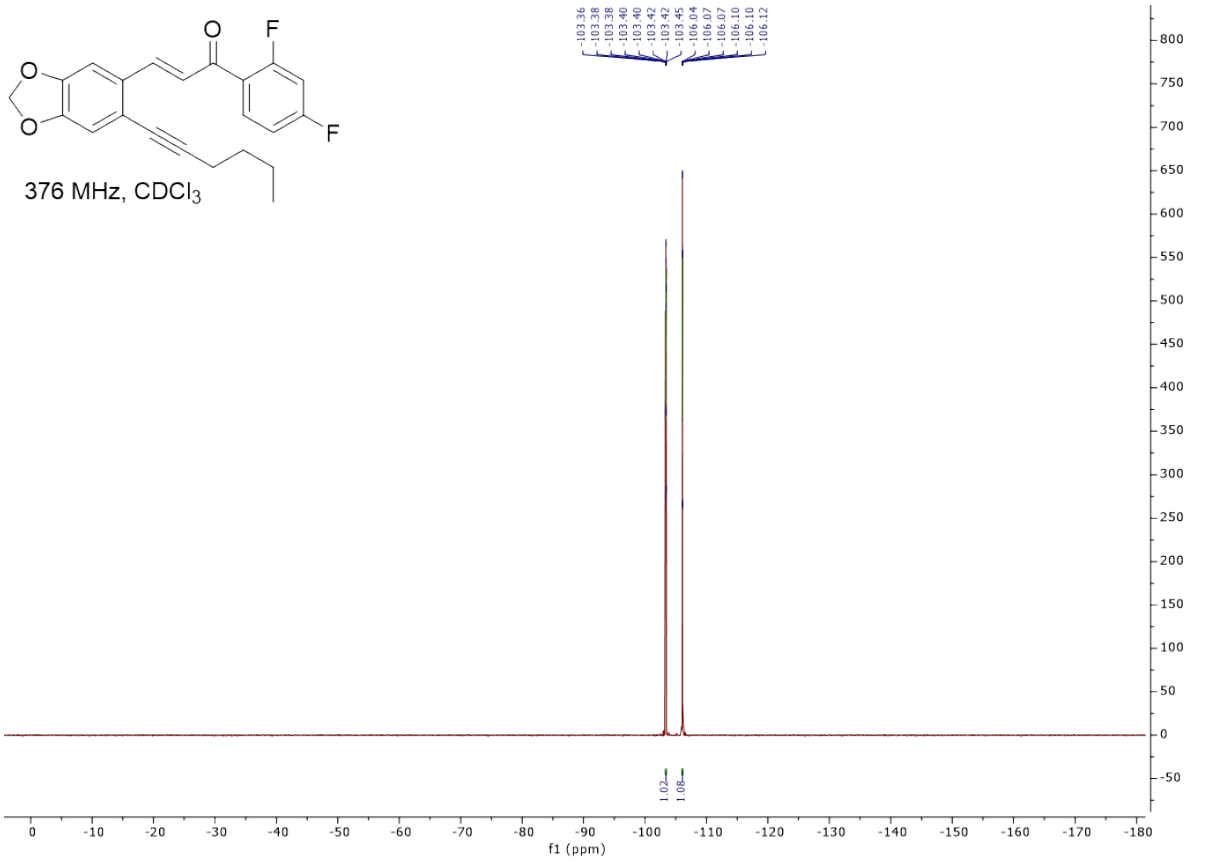




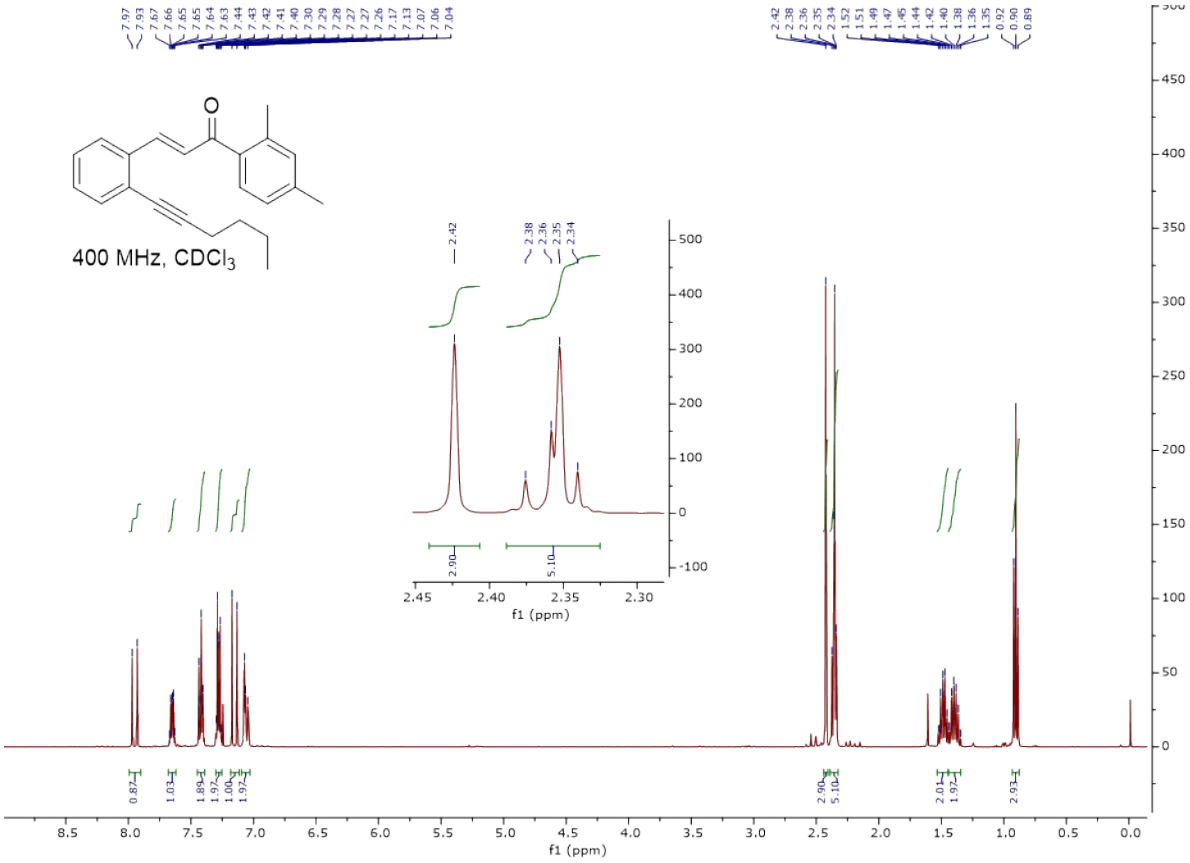
(*E*)-1-(2,4-Difluorophenyl)-3-(6-(hex-1-yn-1-yl)benzo[d][1,3]dioxol-5-yl)prop-2-en-1-one, 1b

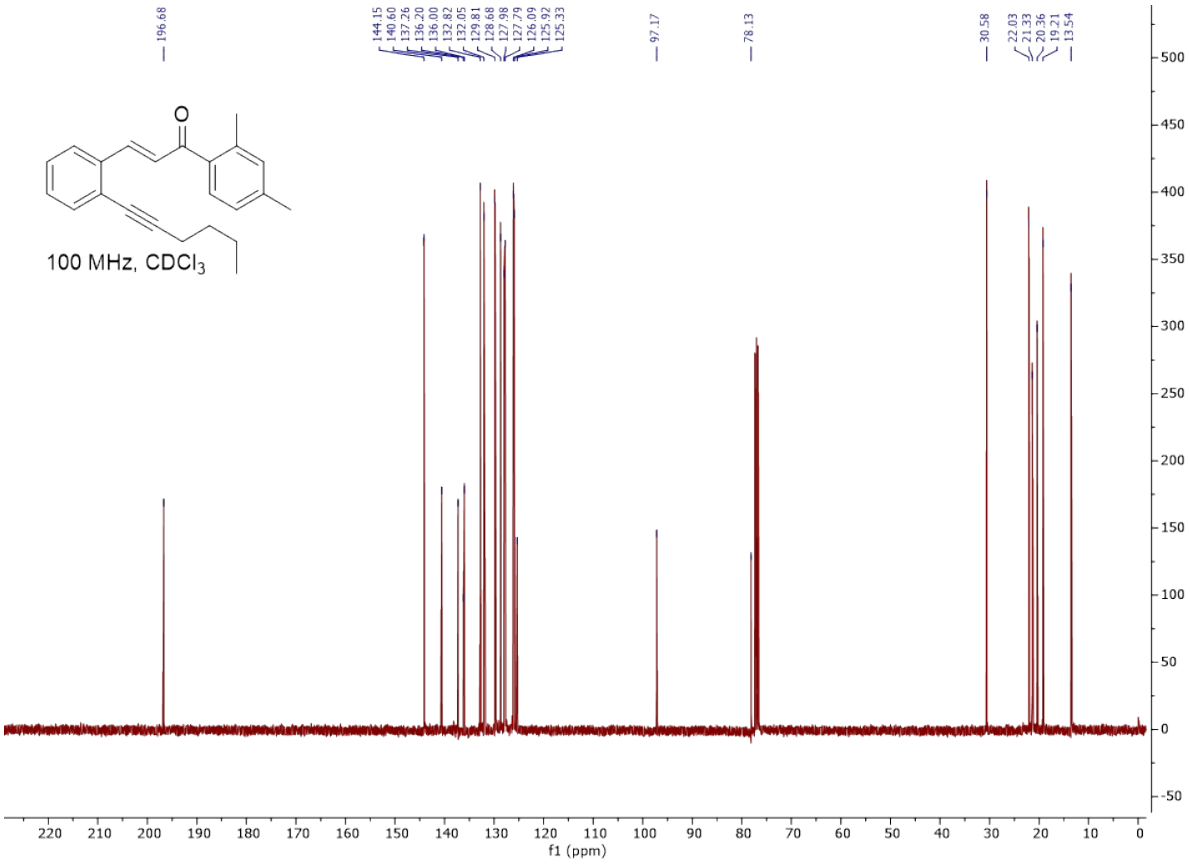



O
F
O
O
F
100 MHz, CDCl3
f1 (ppm)

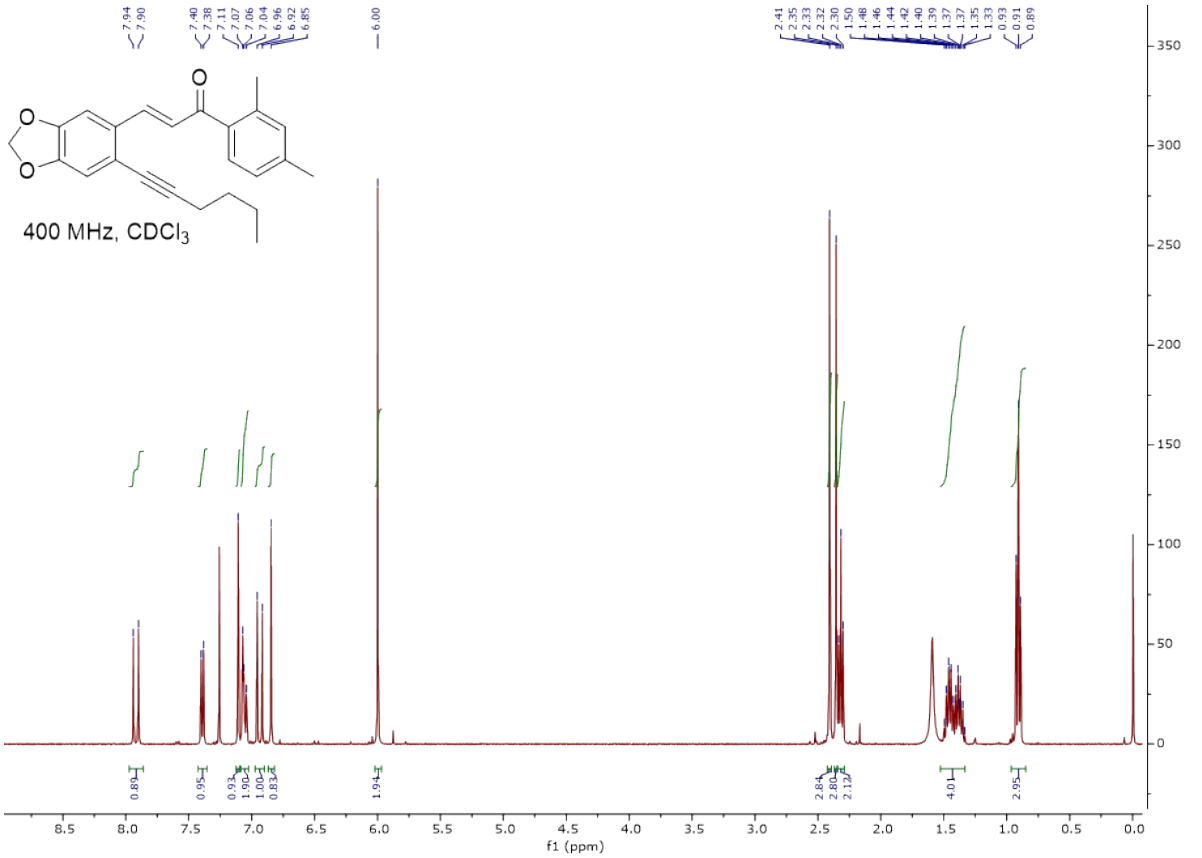

O
F
O
O
F
376 MHz, CDCl3
f1 (ppm)

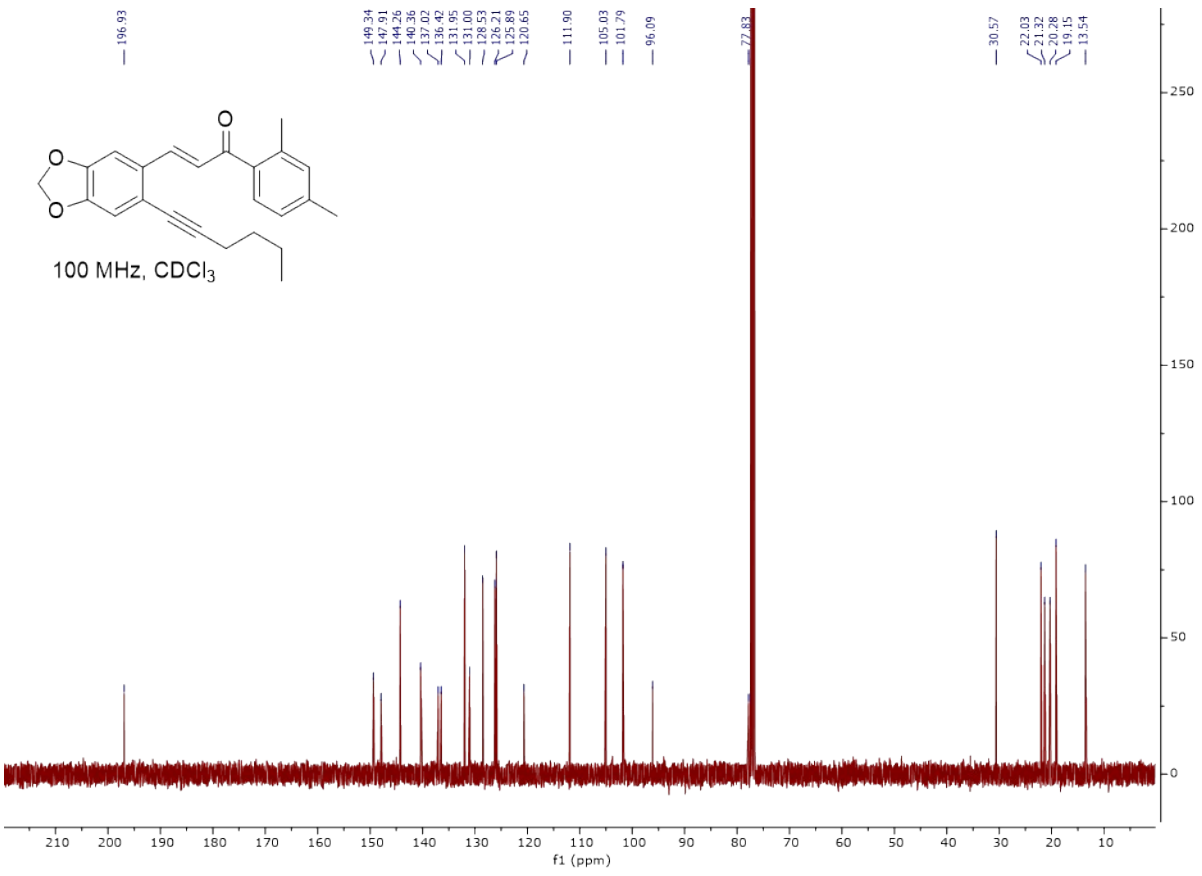
(E)-1-(2,4-Dimethylphenyl)-3-(2-(hex-1-yn-1-yl)phenyl)prop-2-en-1-one, 1c



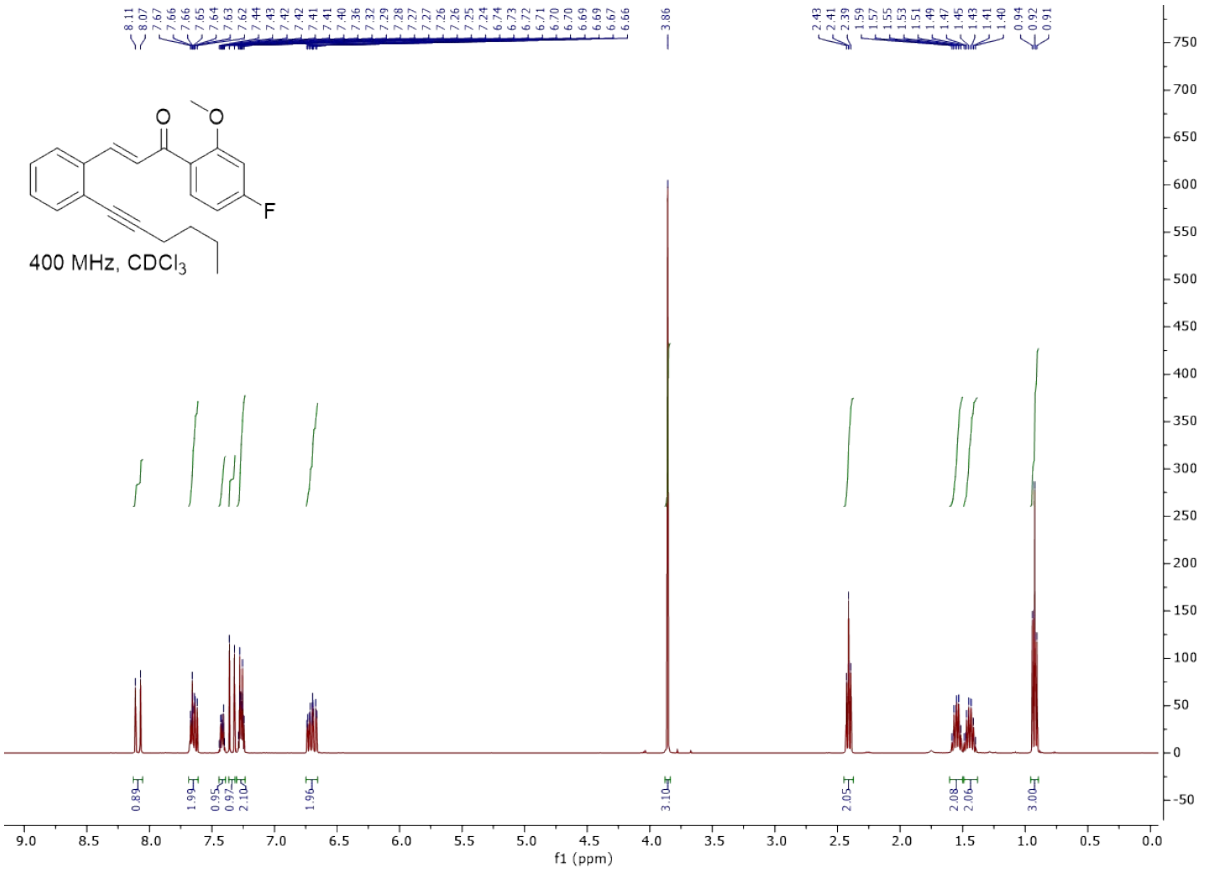


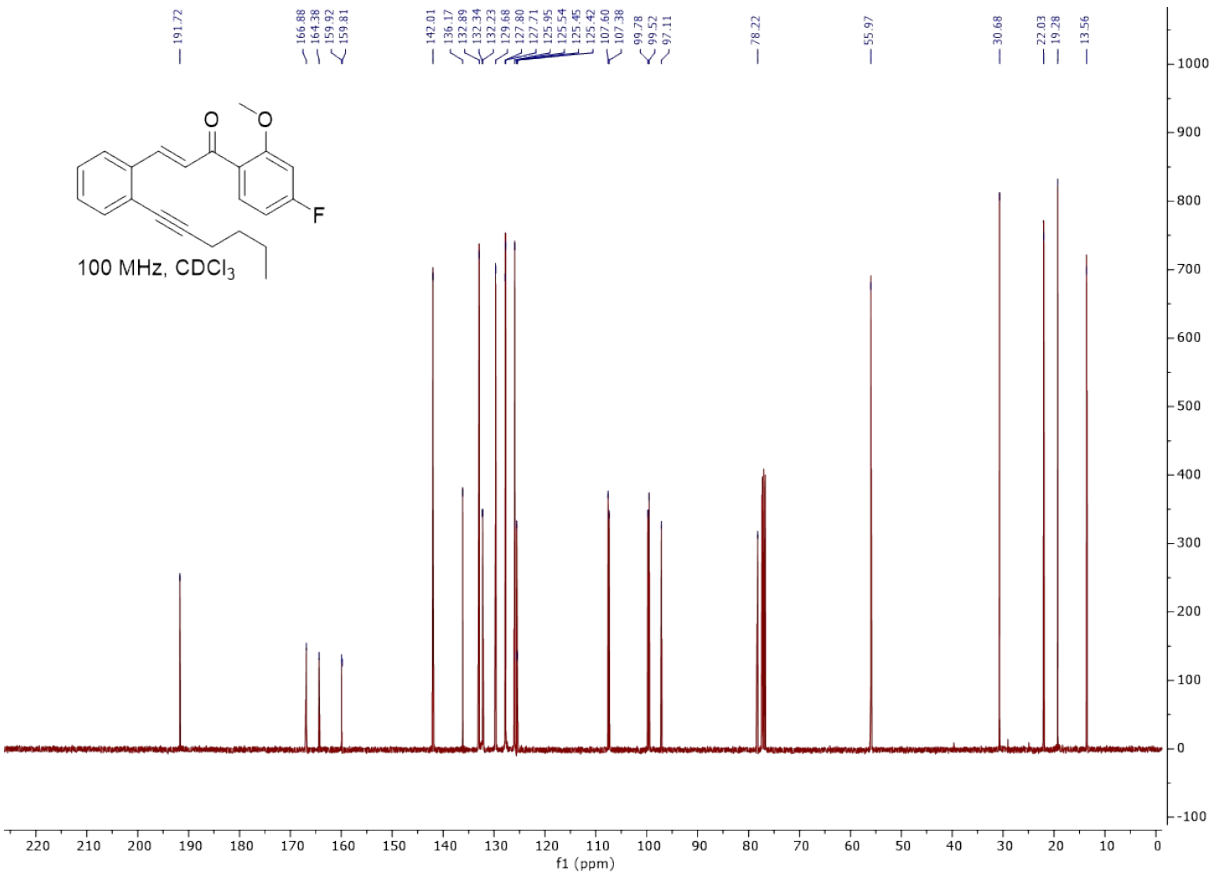
(E)-1-(2,4-Dimethylphenyl)-3-(6-(hex-1-yn-1-yl)benzo[d][1,3]dioxol-5-yl)prop-2-en-1-one, 1d

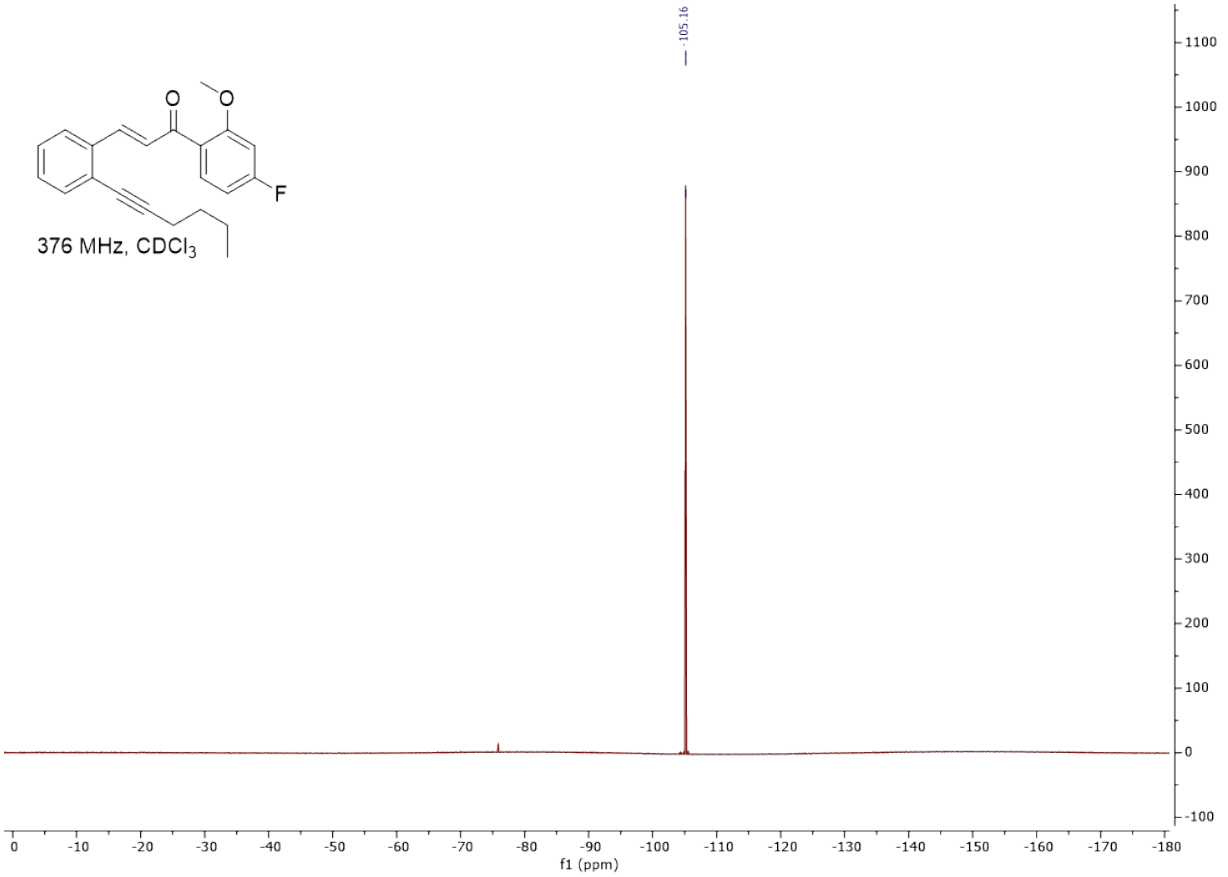




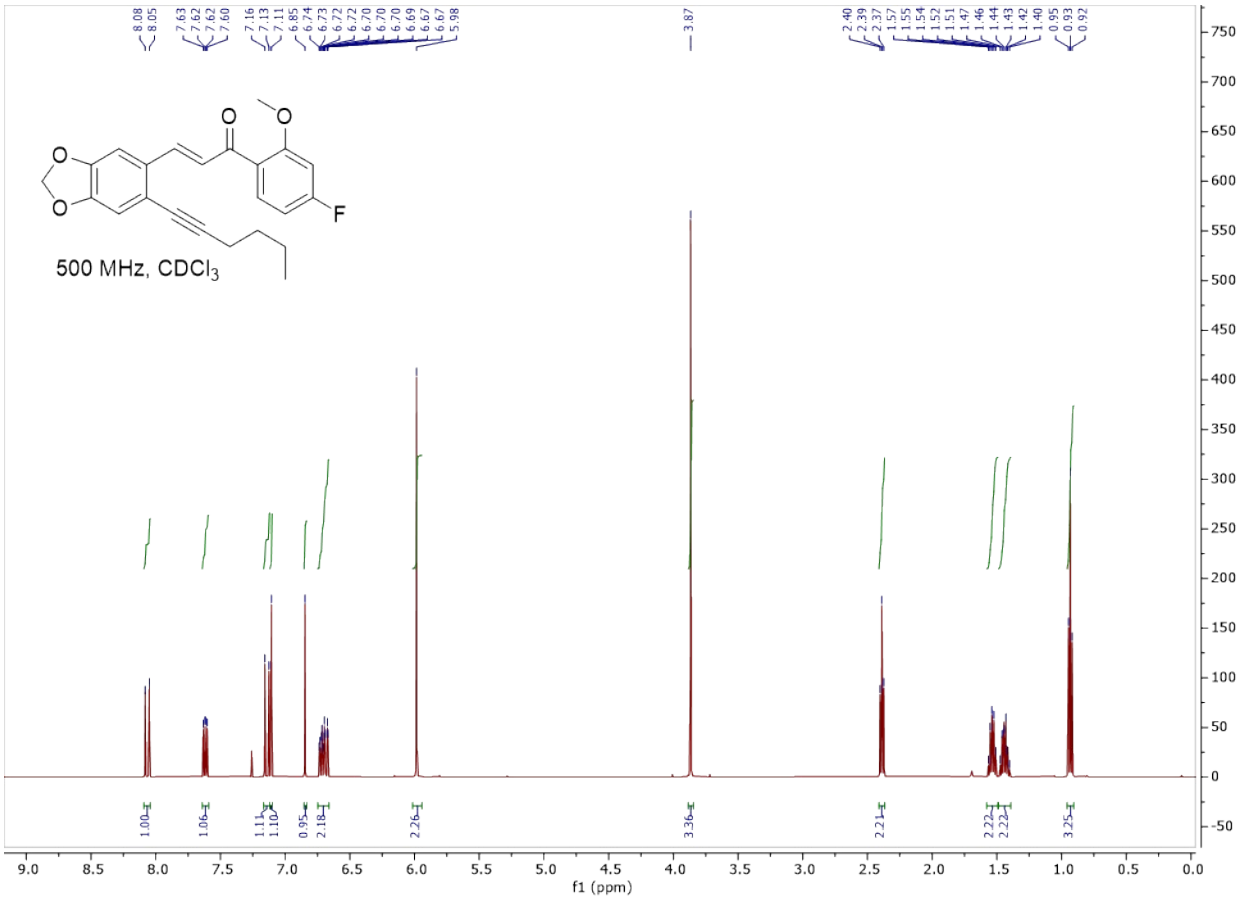
(E)-1-(4-Fluoro-2-methoxyphenyl)-3-(2-(hex-1-yn-1-yl)phenyl)prop-2-en-1-one, 1e

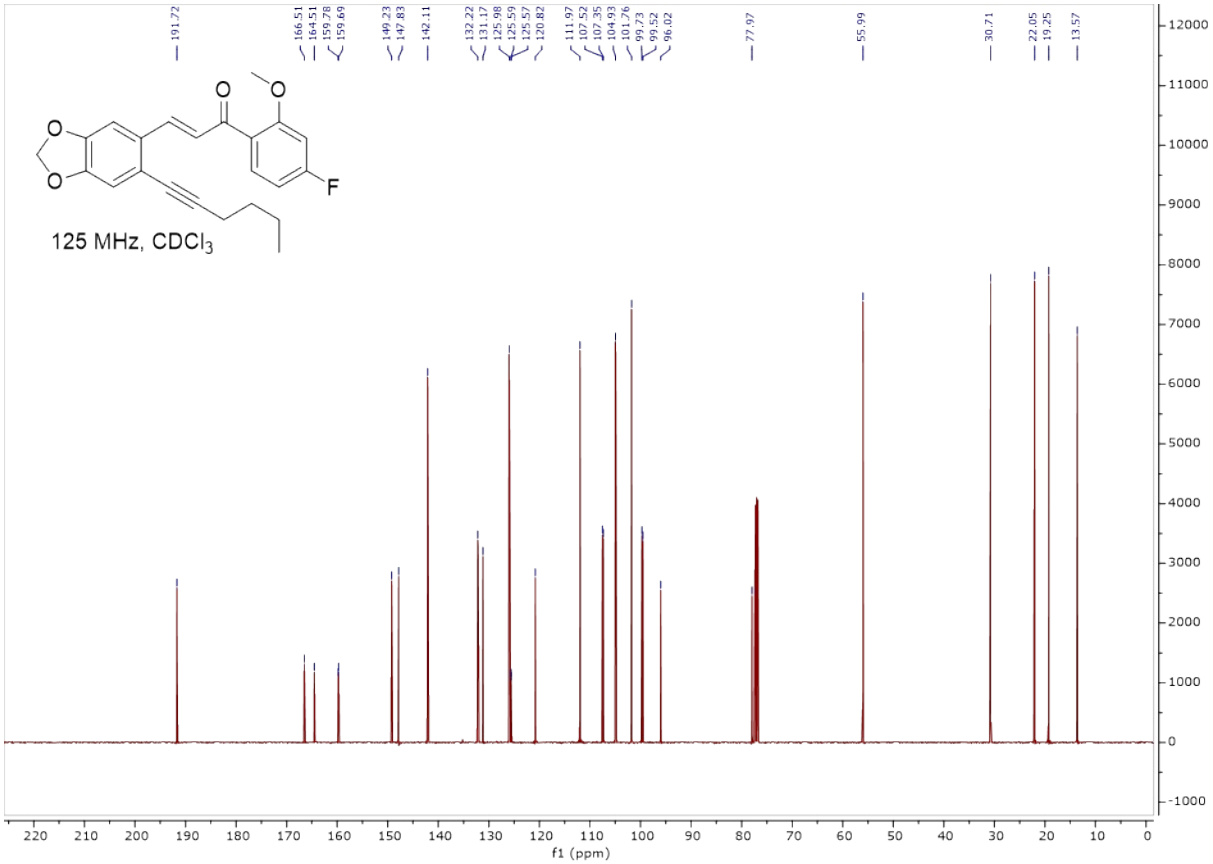






(E)-1-(4-Fluoro-2-methoxyphenyl)-3-(6-(hex-1-yn-1-yl)benzo[d][1,3]dioxol-5-yl)prop-2-en-1-one, 1f




191.72
166.51
164.51
159.78
159.69
149.23
147.83
142.11
132.22
131.17
125.98
125.59
125.57
120.82
111.97
107.52
107.35
104.93
101.76
99.73
99.52
96.02
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30.71
22.05
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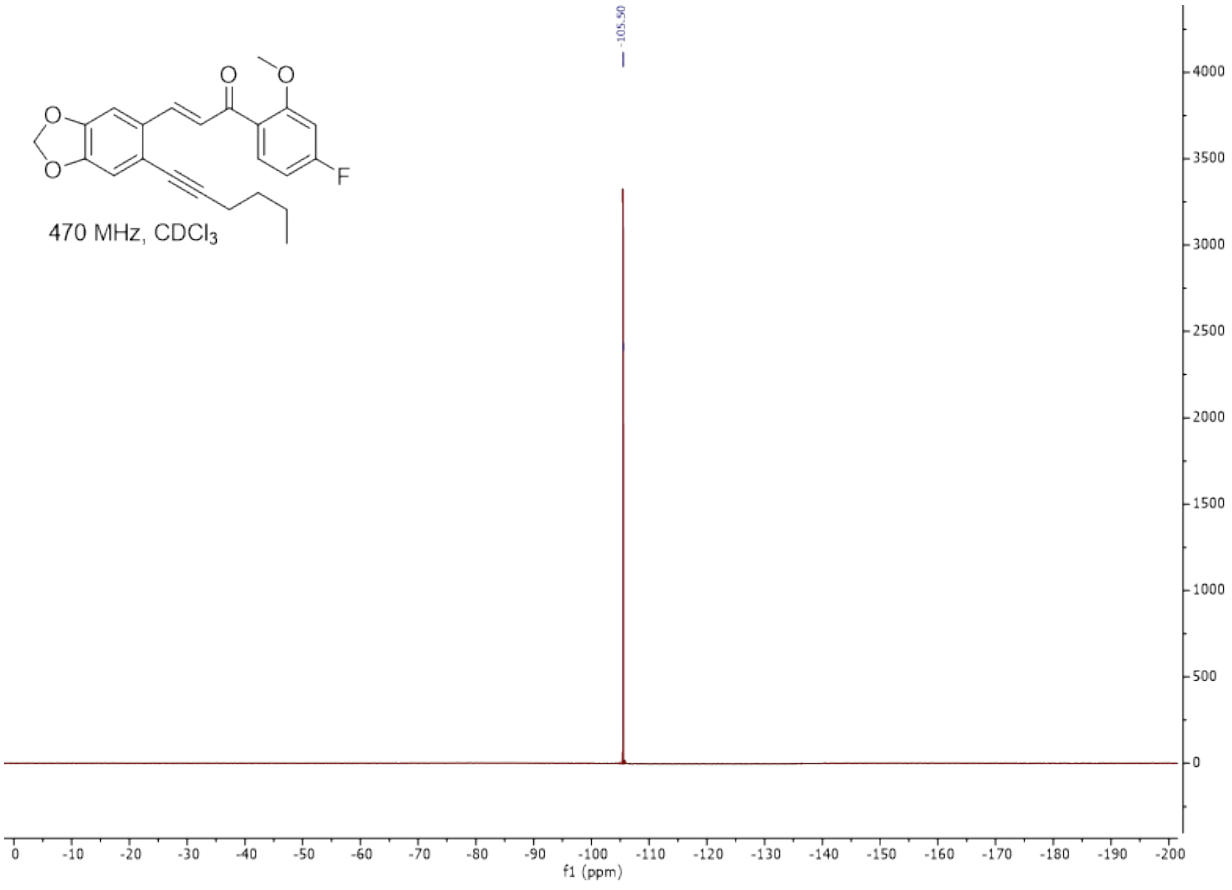
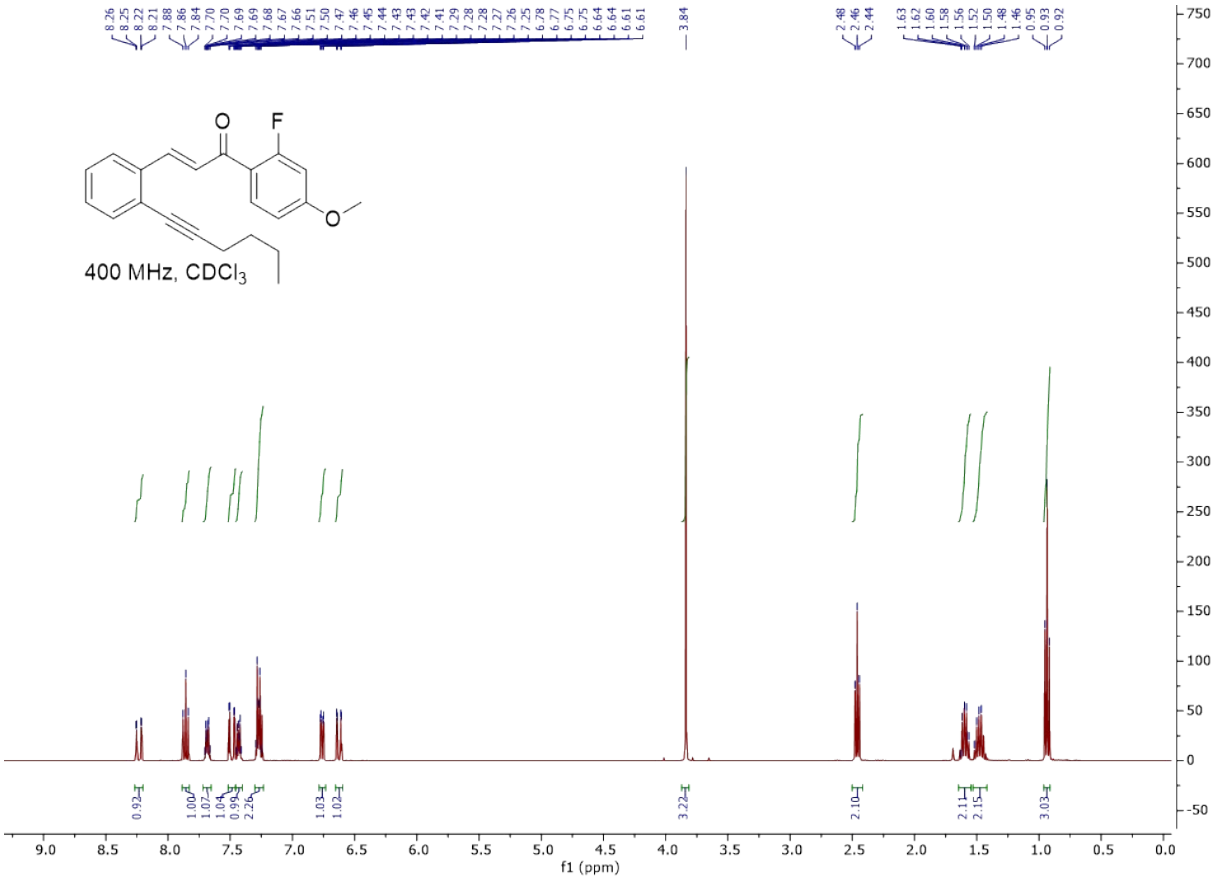
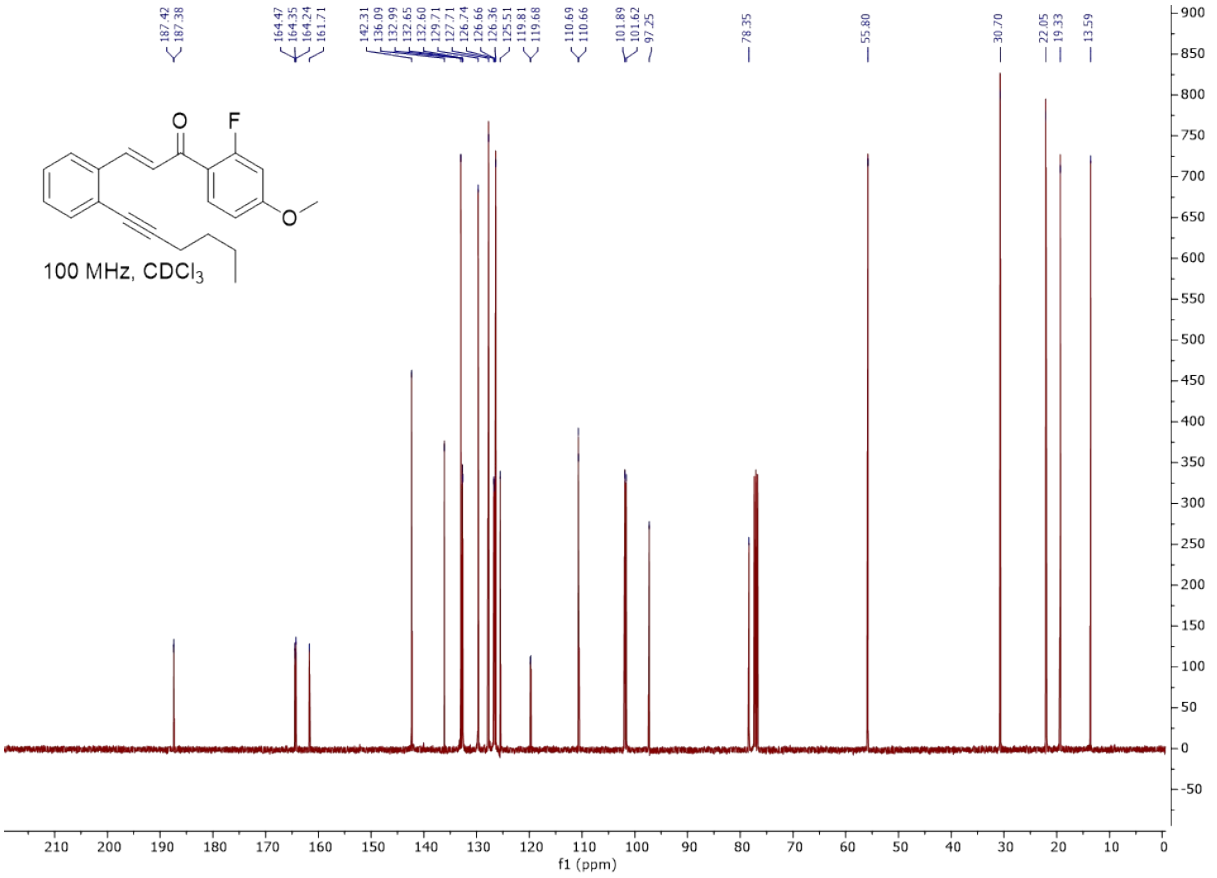
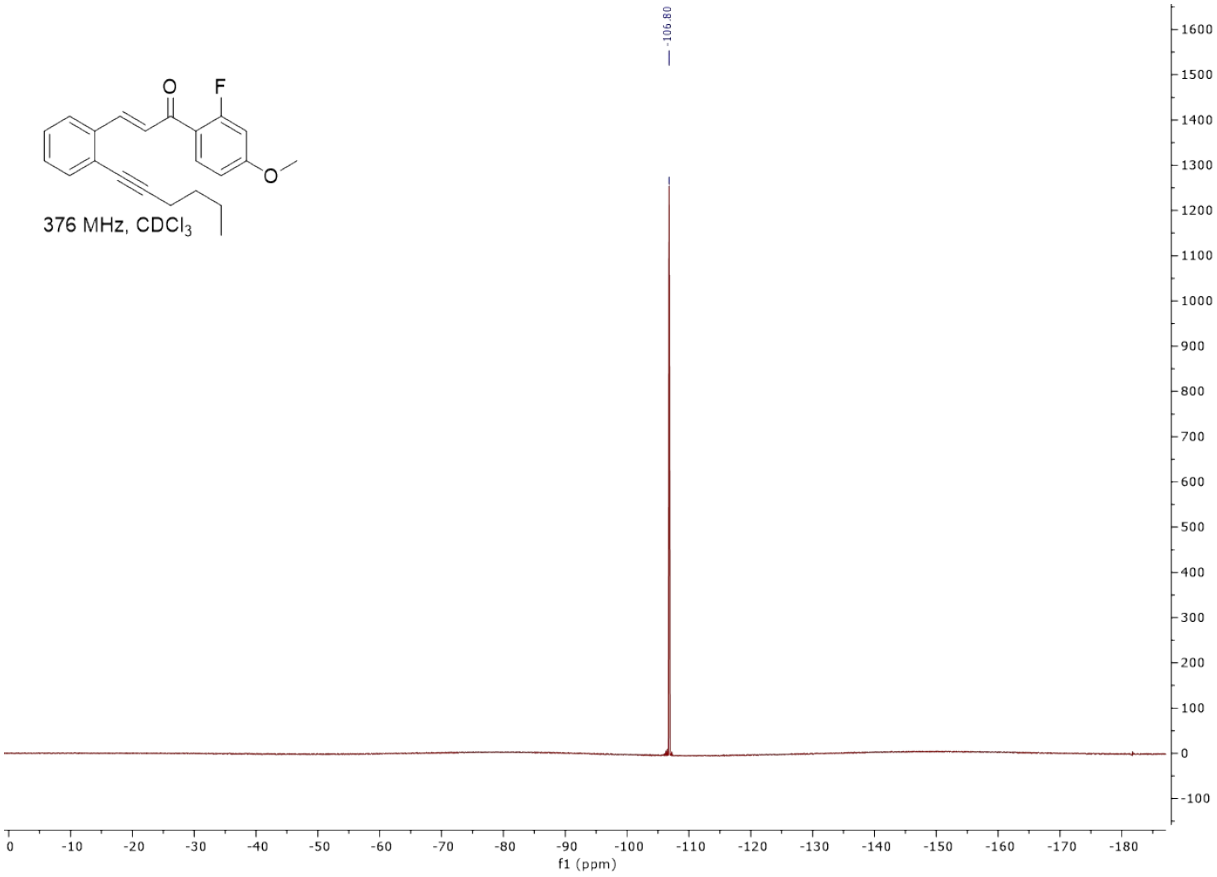
O
O
O
F
125 MHz, CDCl3
f1 (ppm)


-105.50
O
O
O
F
470 MHz, CDCl3
f1 (ppm)

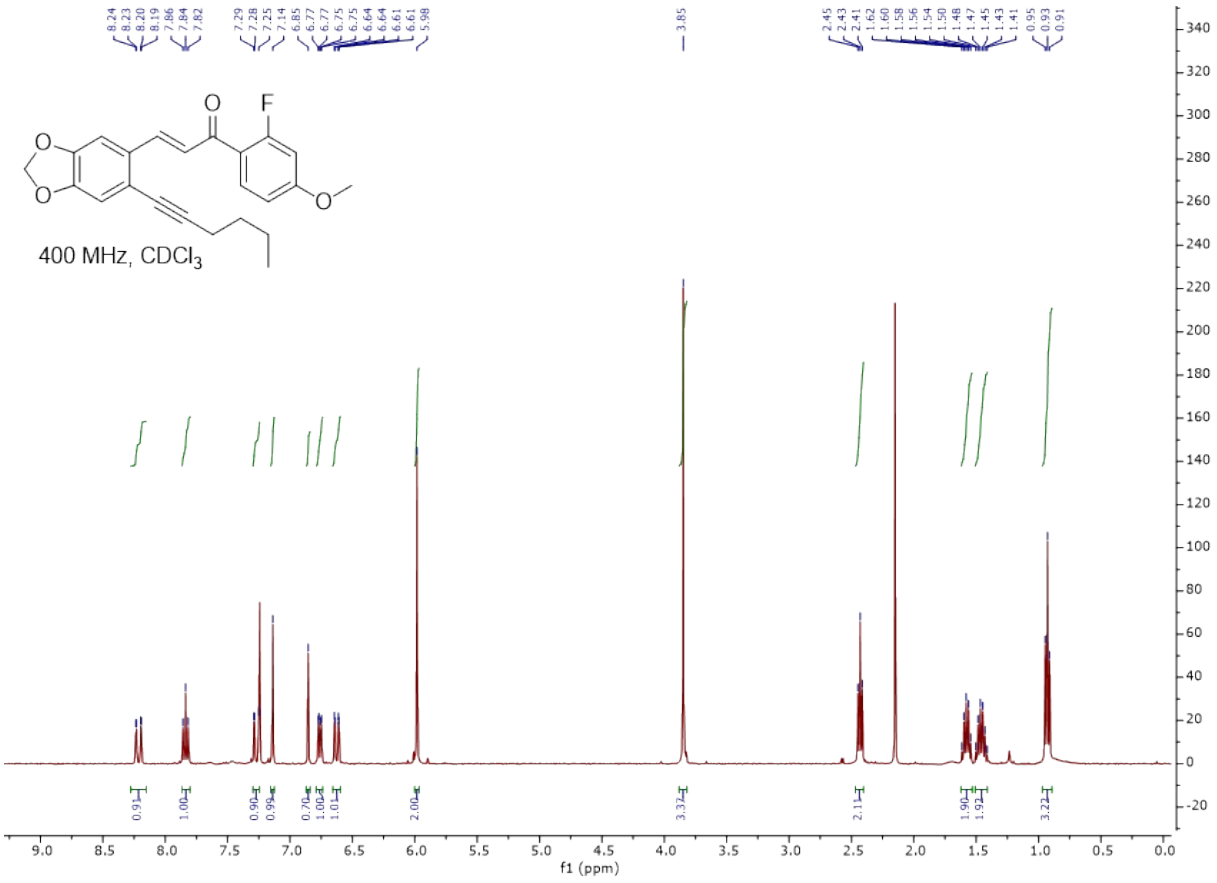
(E)-1-(2-Fluoro-4-methoxyphenyl)-3-(2-(hex-1-yn-1-yl)phenyl)prop-2-en-1-one, 1g

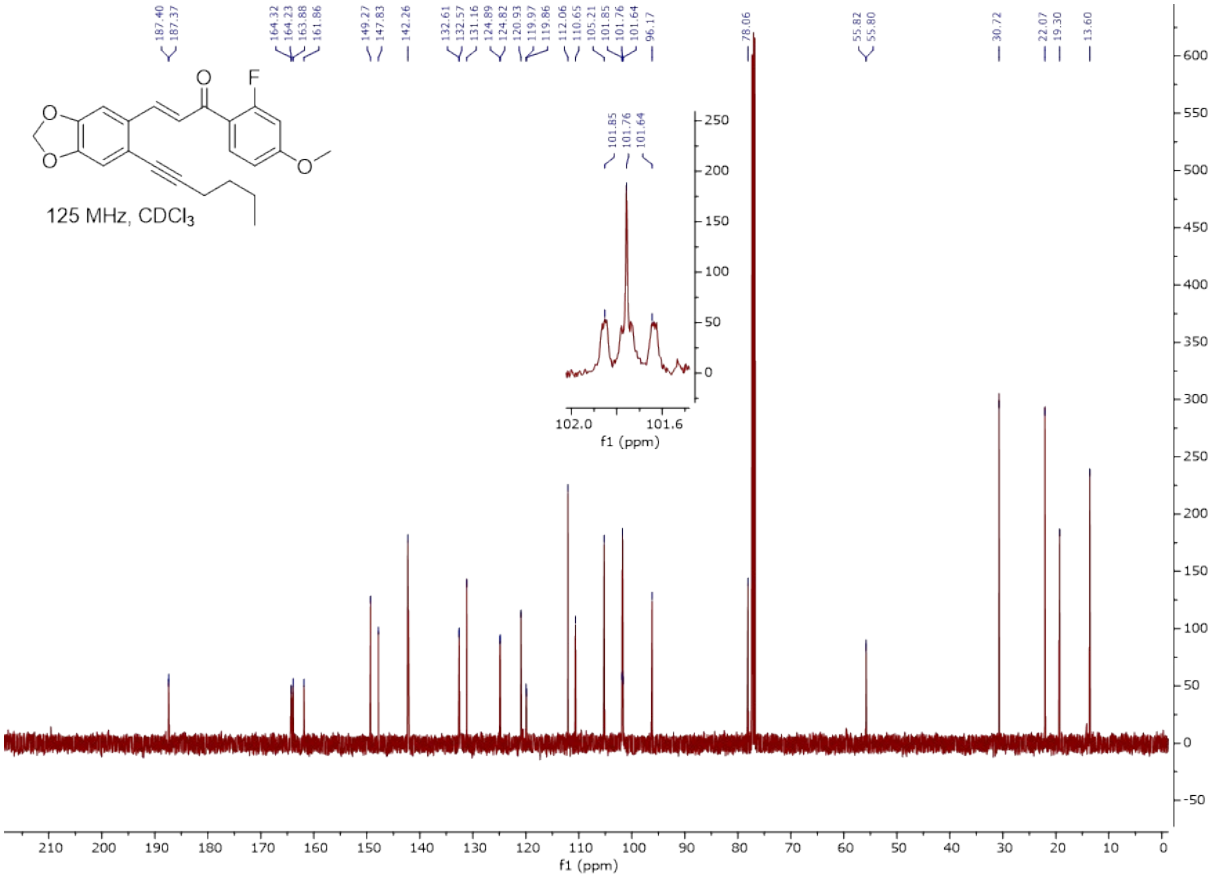






(E)-1-(2-Fluoro-4-methoxyphenyl)-3-(6-(hex-1-yn-1-yl)benzo[d][1,3]dioxol-5-yl)prop-2-en-1-one, 1h




187.40
187.37
164.32
164.23
163.88
161.86
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147.83
142.26
132.61
132.57
131.16
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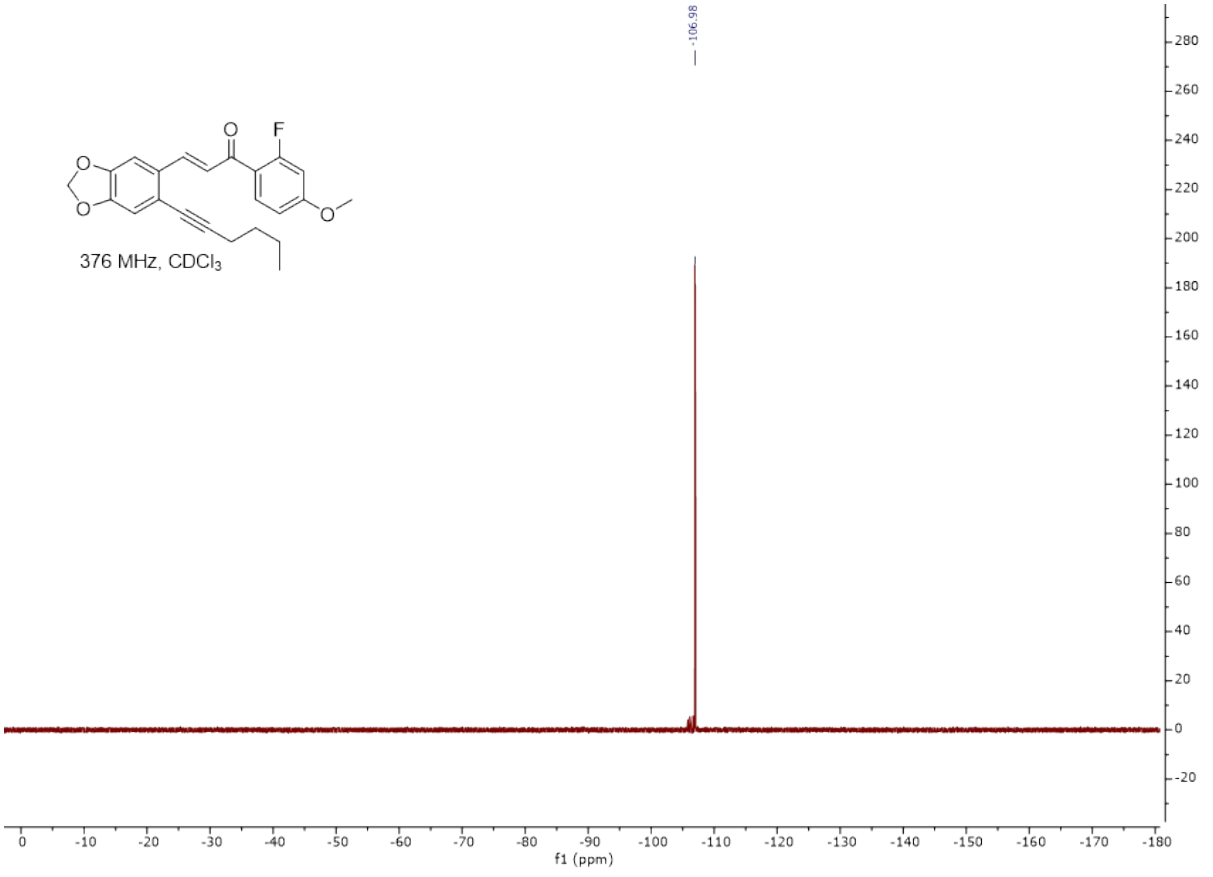
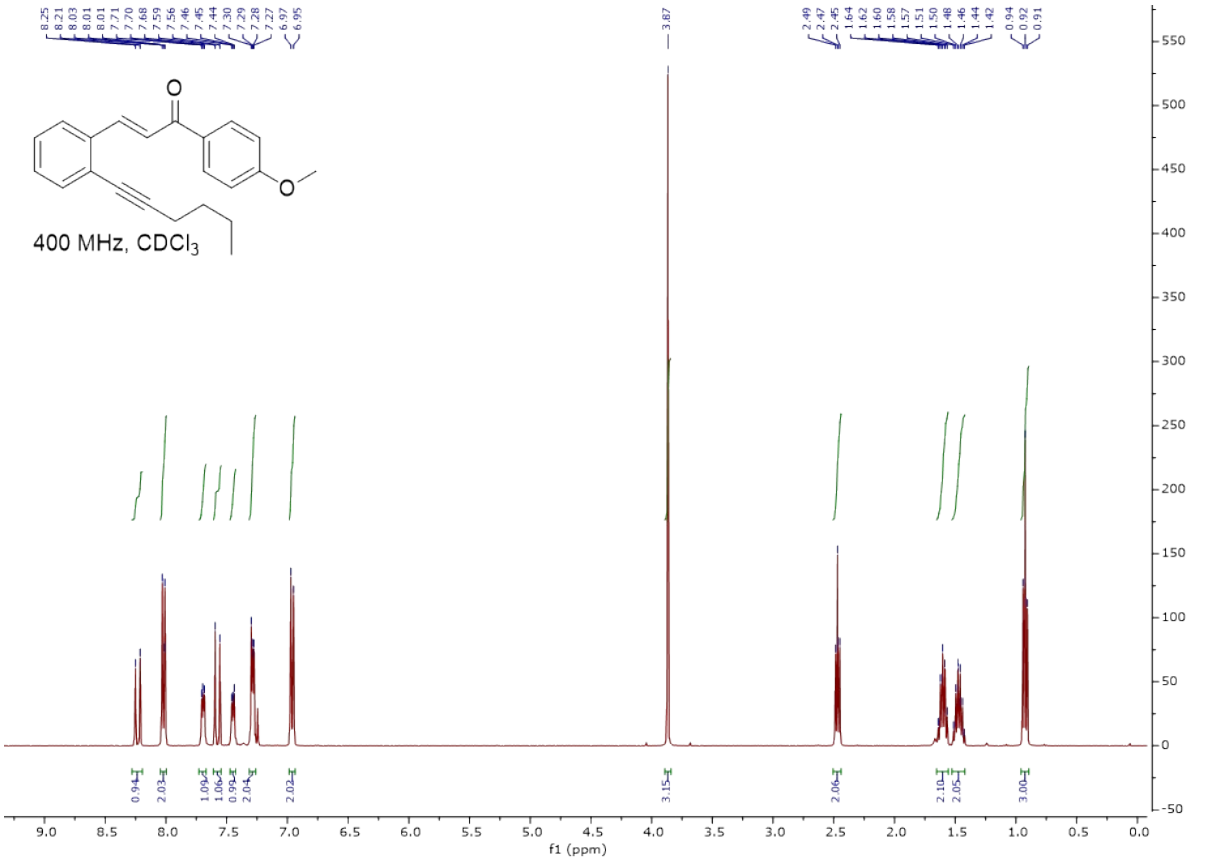
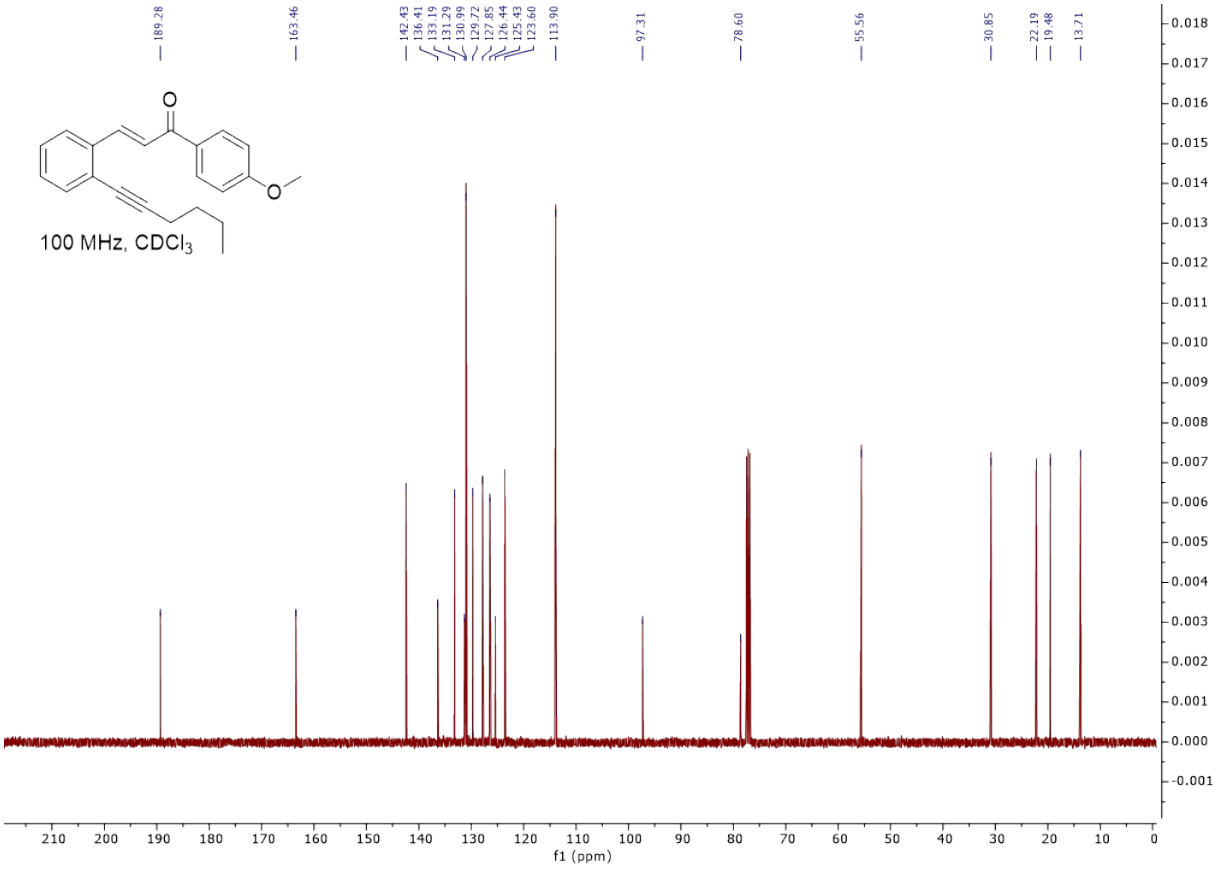
124.82
120.93
119.97
119.86
112.06
110.65
105.21
101.85
101.76
101.64
96.17
78.06
55.82
55.80
30.72
22.07
19.30
13.60
O
F
O
O
O
125 MHz, CDCl3
f1 (ppm)

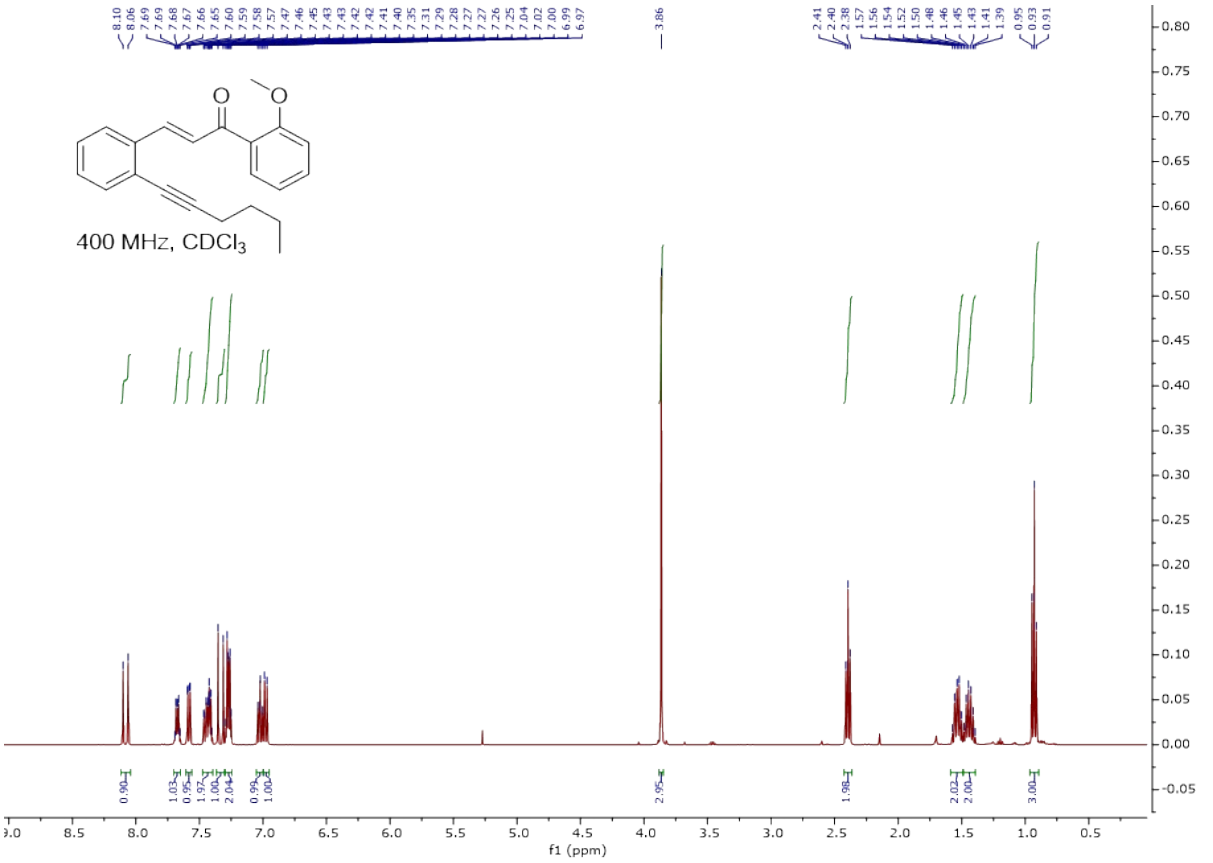

-106.98
O
F
O
O
O
376 MHz, CDCl3
f1 (ppm)

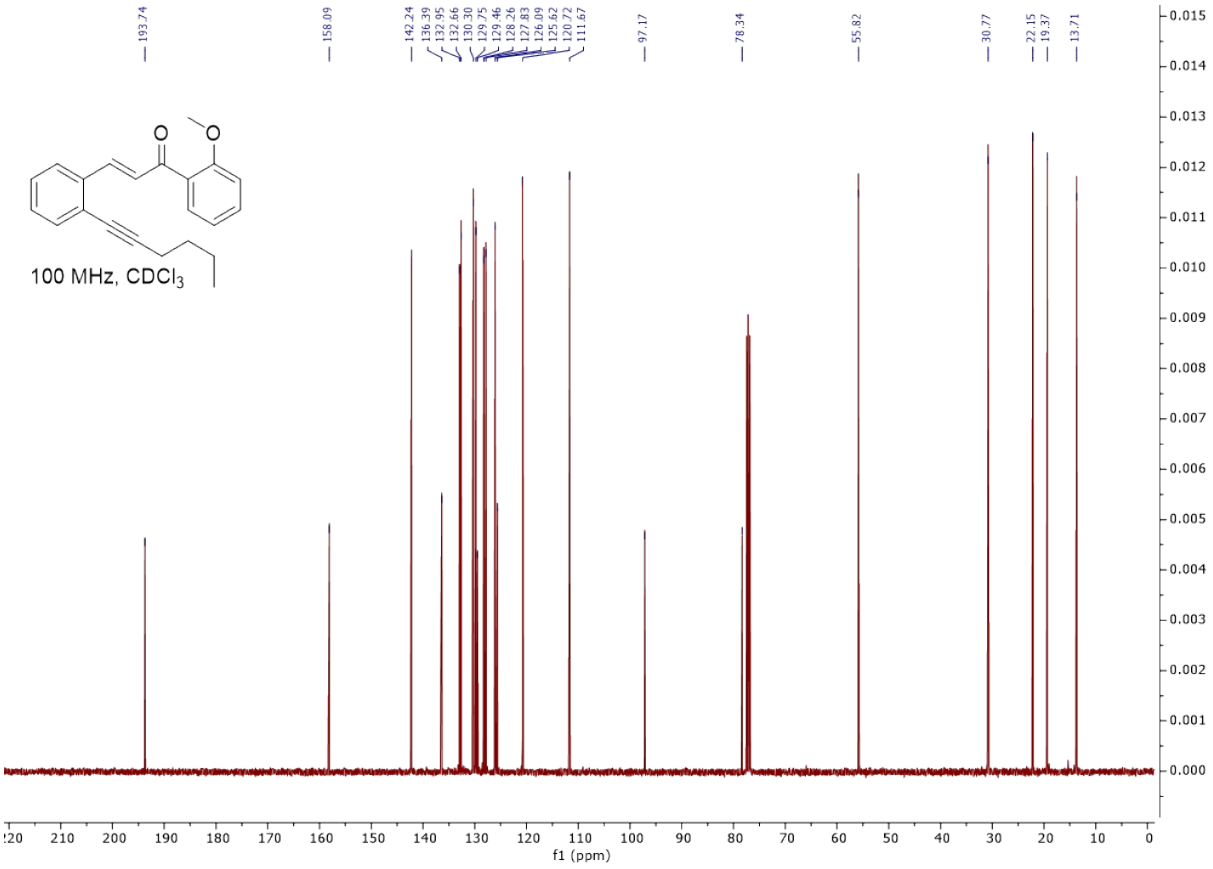
(E)-3-(2-(Hex-1-yn-1-yl)phenyl)-1-(4-methoxyphenyl)prop-2-en-1-one, 1j



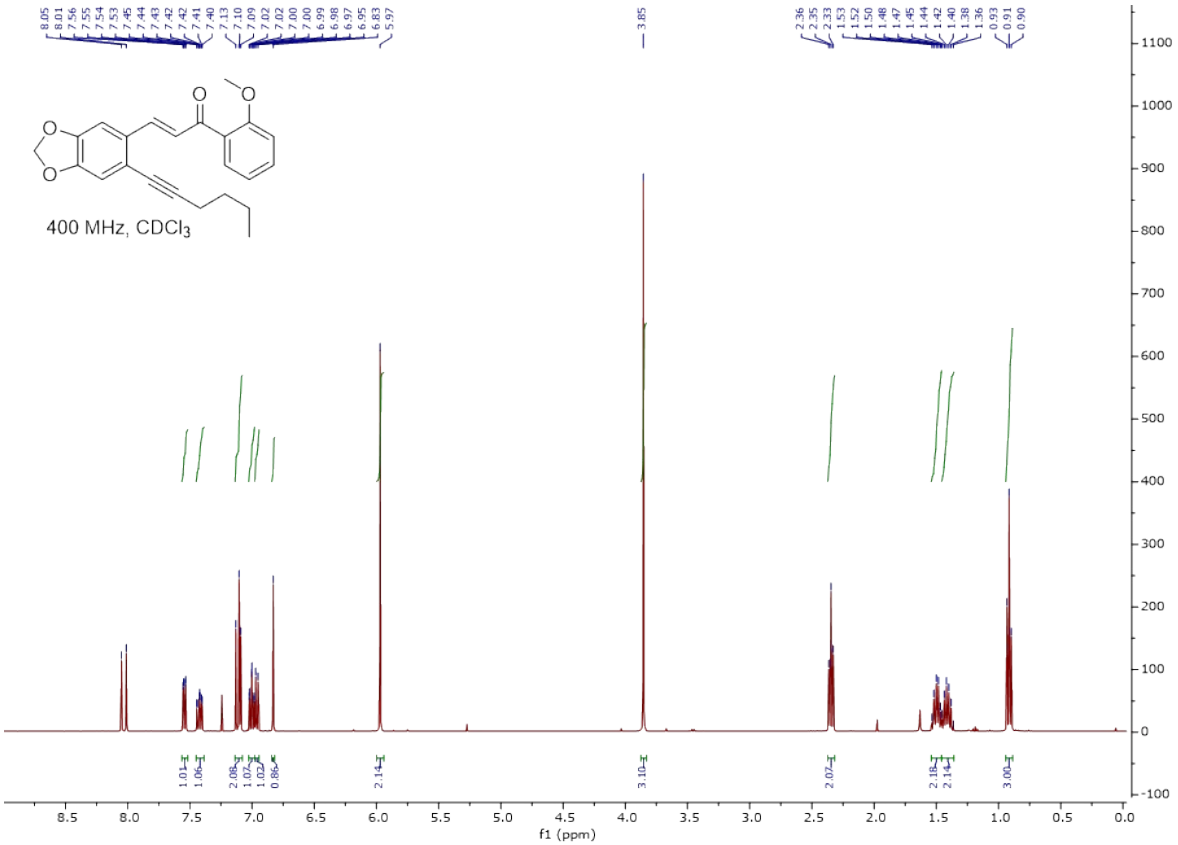


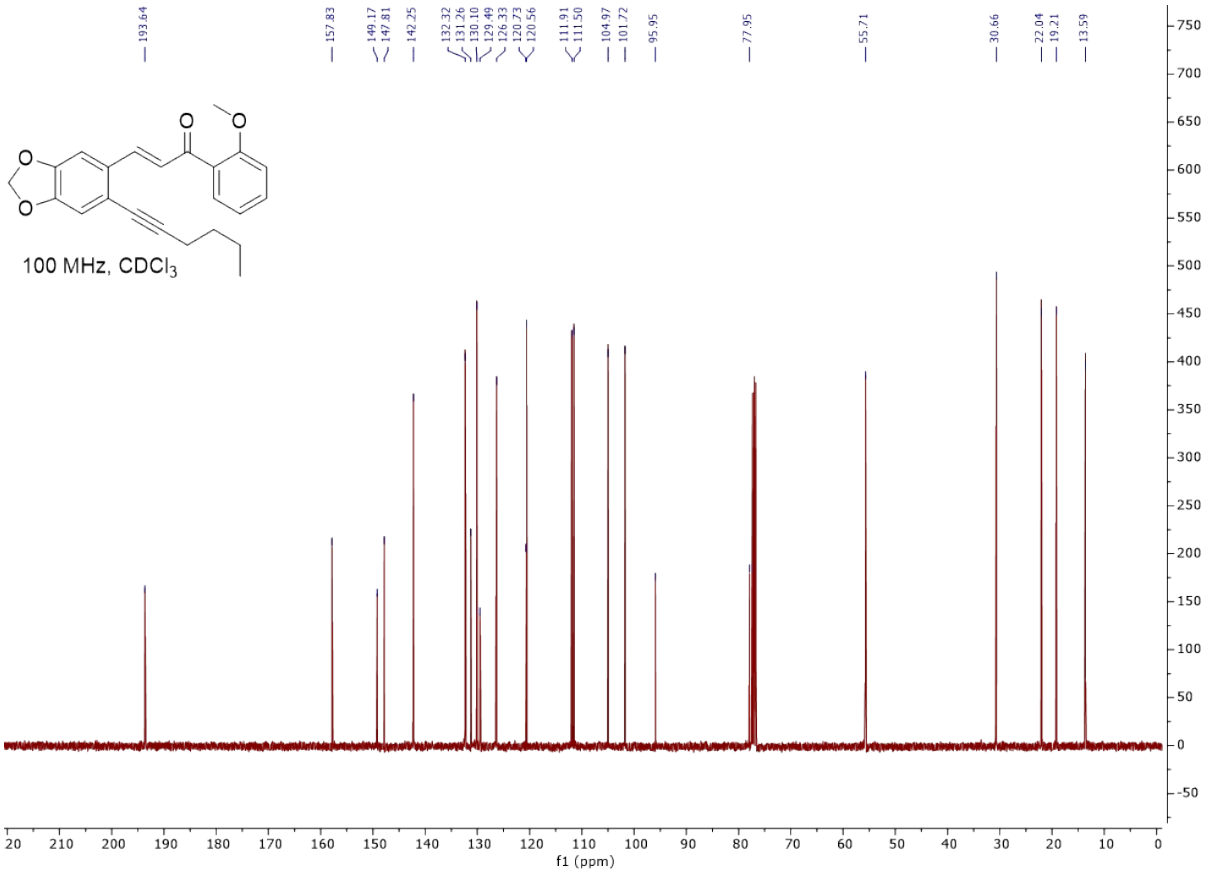
(E)-3-(2-(Hex-1-yn-1-yl)phenyl)-1-(2-methoxyphenyl)prop-2-en-1-one, 1k



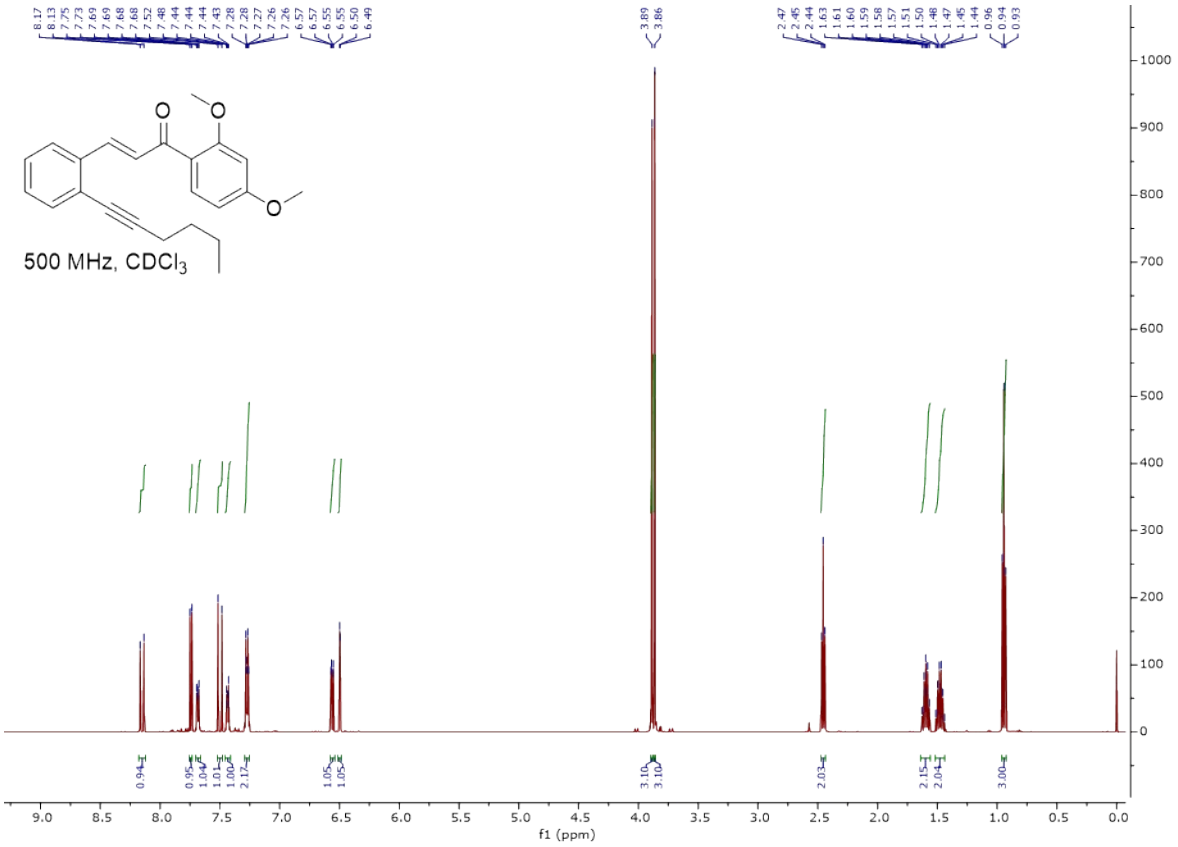


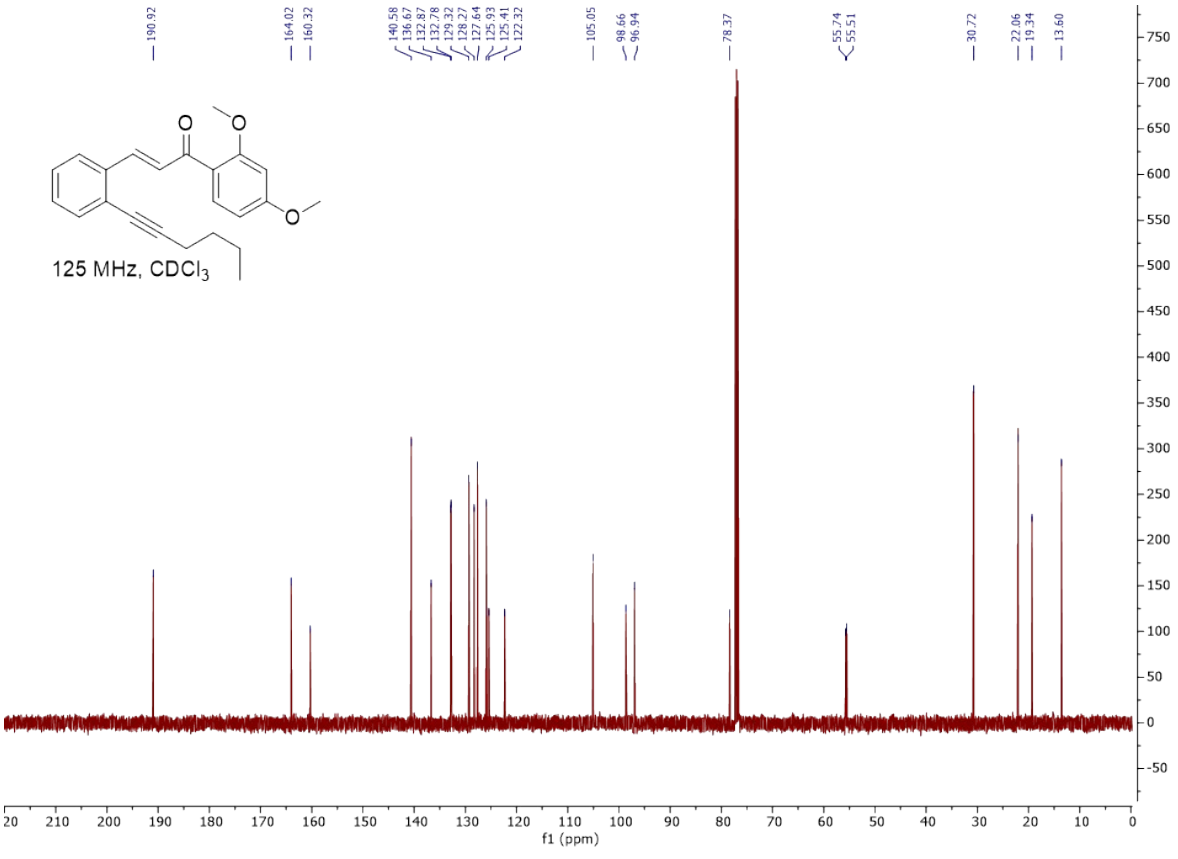
(E)-3-(6-(Hex-1-yn-1-yl)benzo[d][1,3]dioxol-5-yl)-1-(2-methoxyphenyl)prop-2-en-1-one, 1l



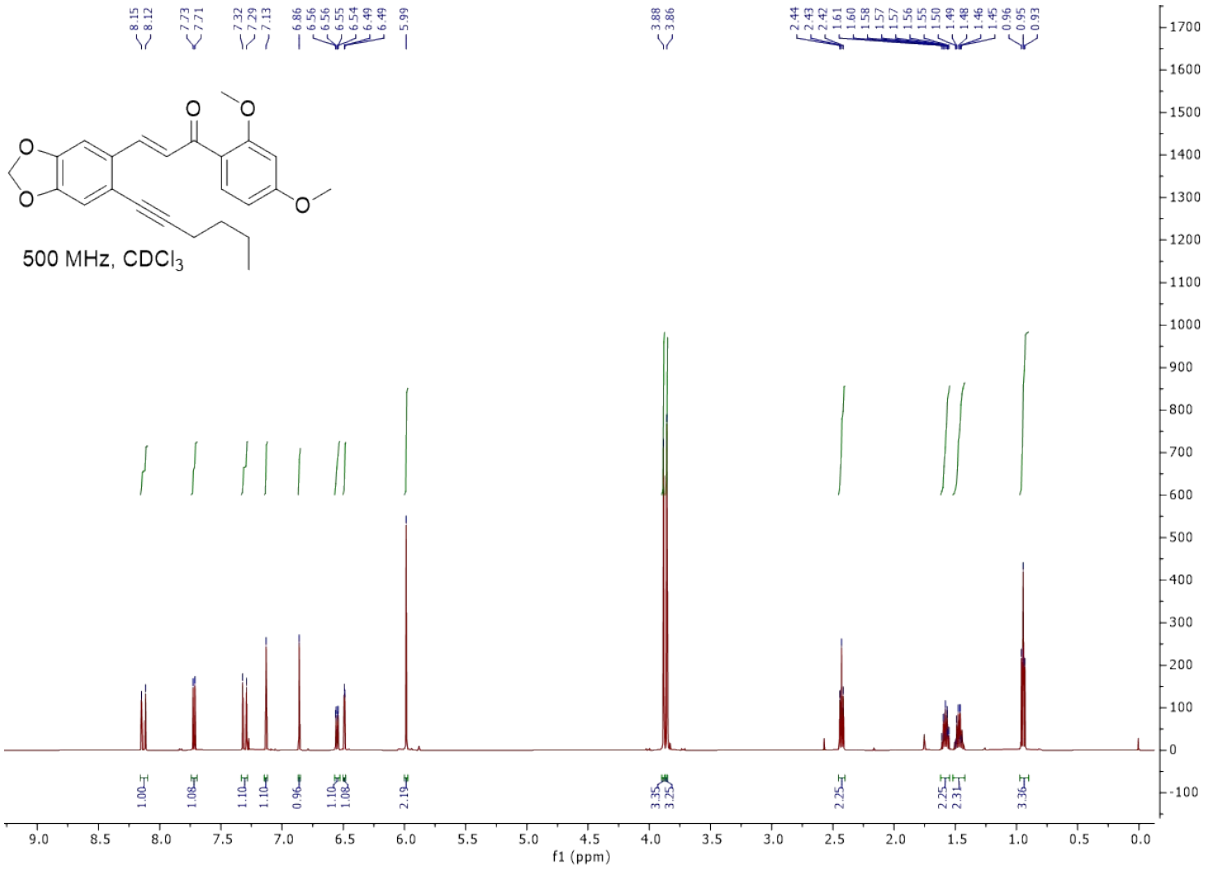


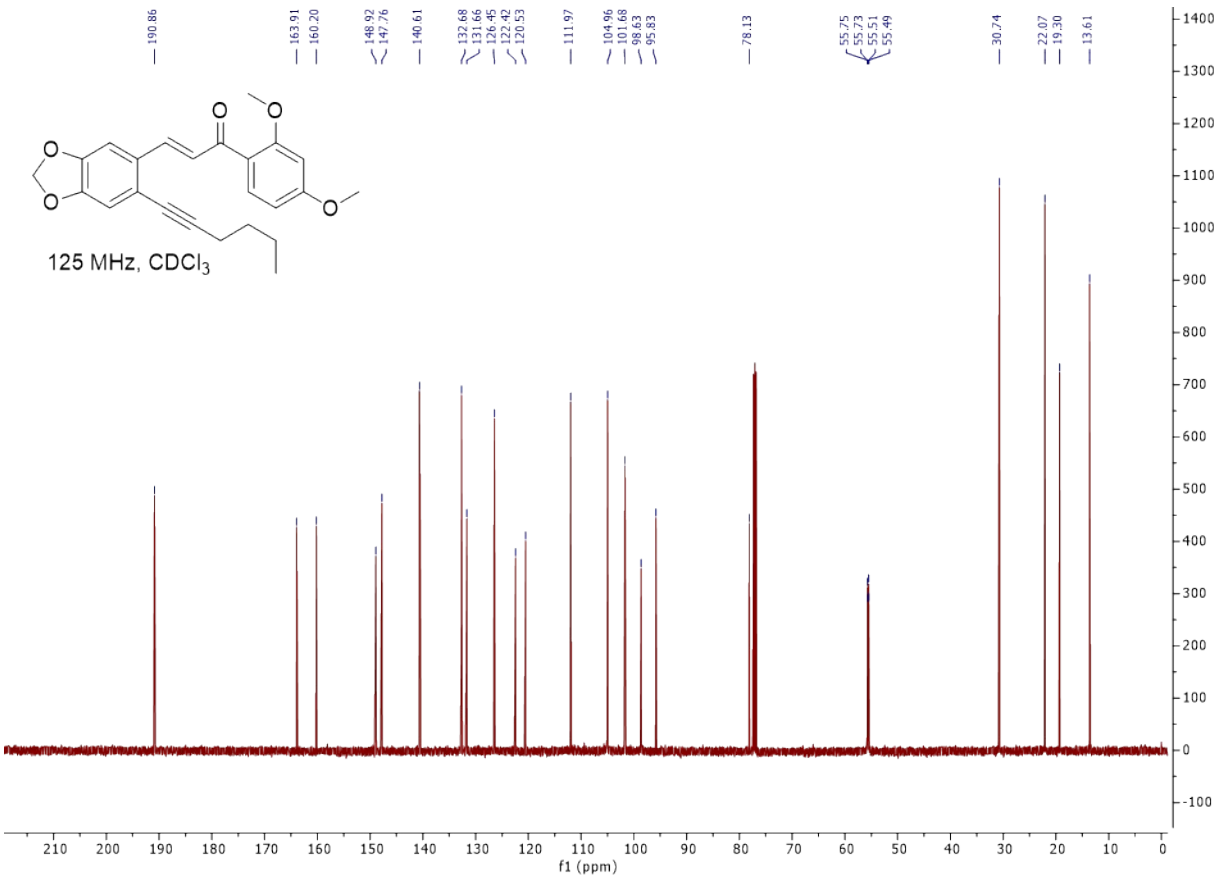
(E)-1-(2,4-Dimethoxyphenyl)-3-(2-(hex-1-yn-1-yl)phenyl)prop-2-en-1-one, 1m



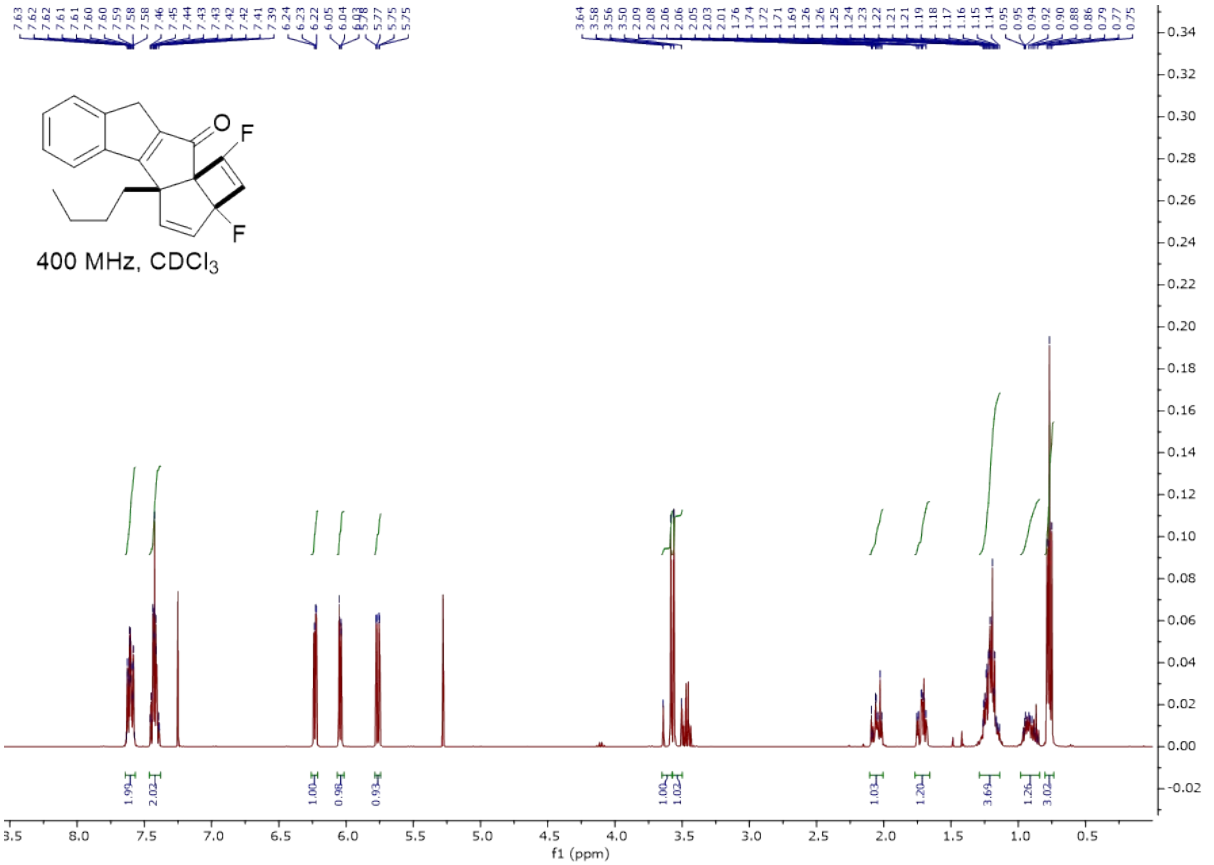


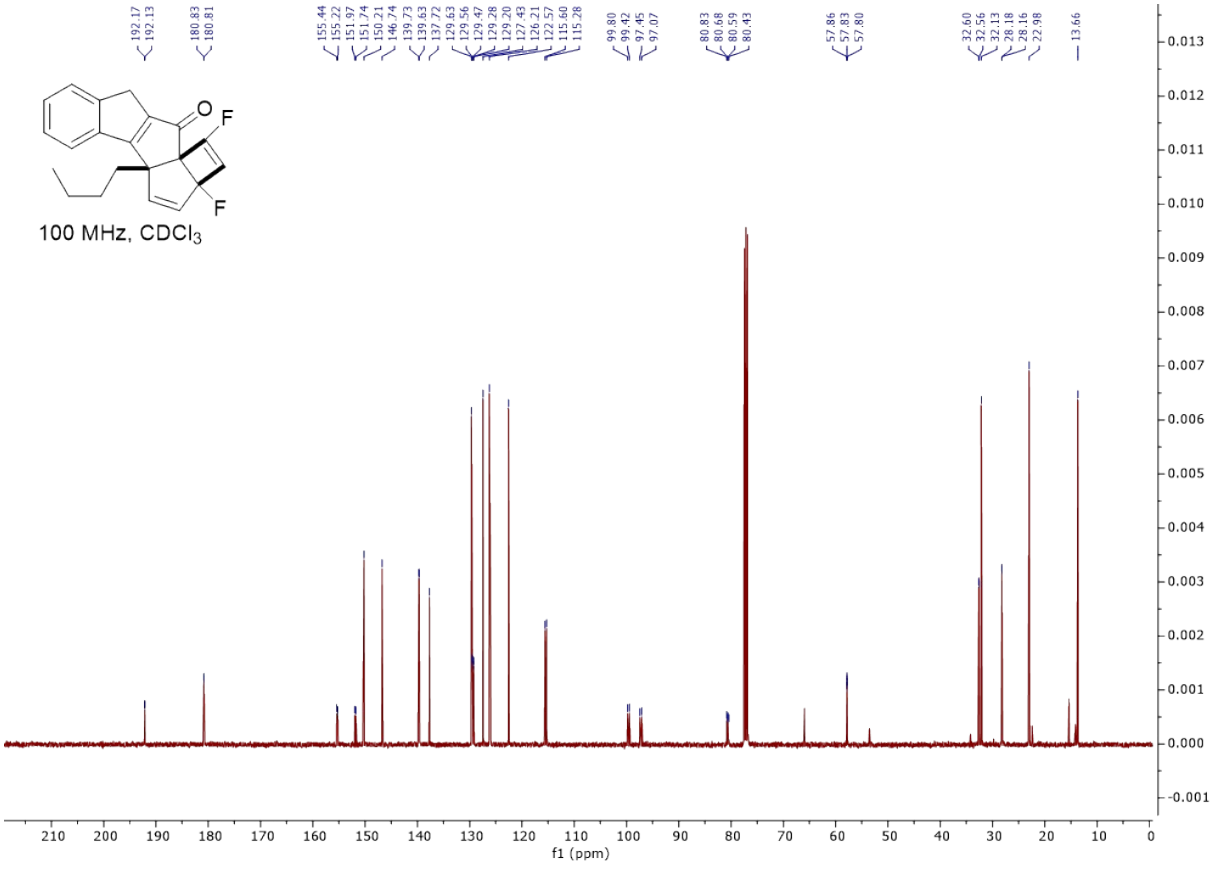
(E)-1-(2,4-Dimethoxyphenyl)-3-(6-(hex-1-yn-1-yl)benzo[d][1,3]dioxol-5-yl)prop-2-en-1-one, 1n

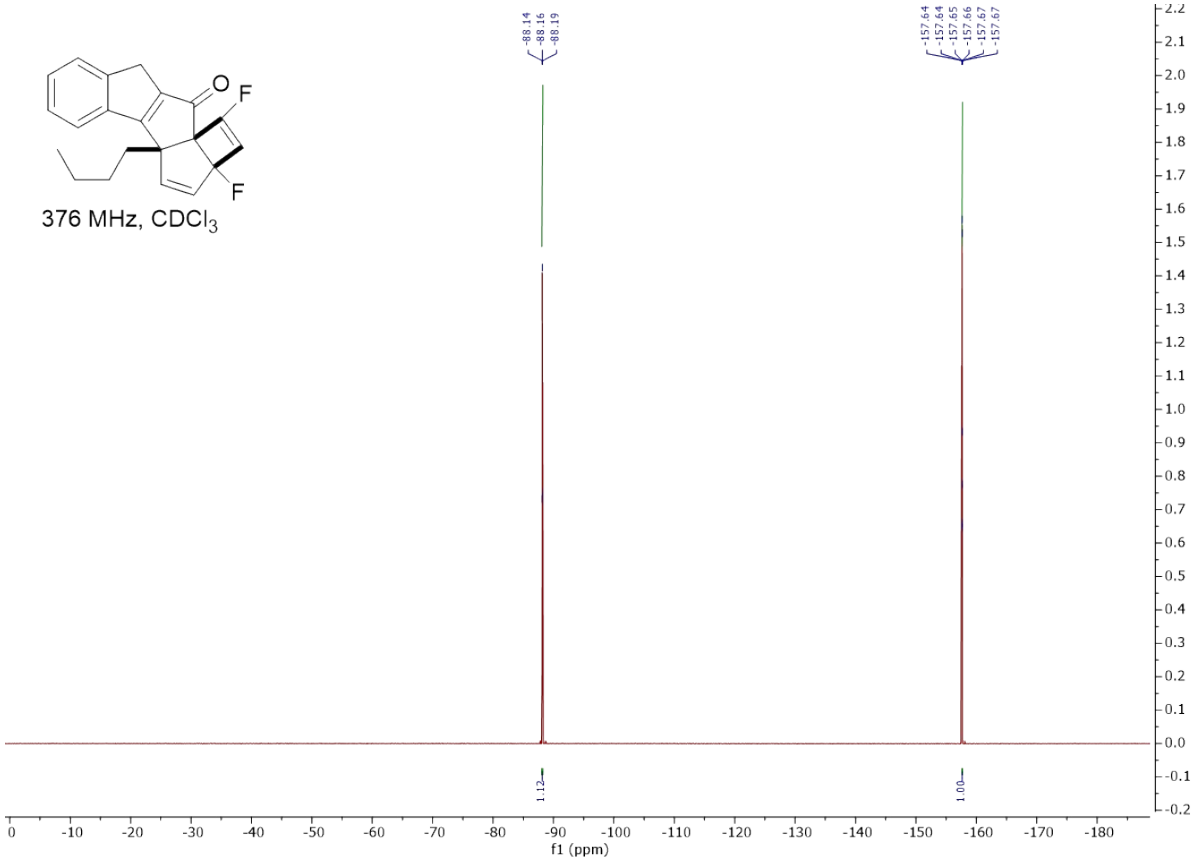


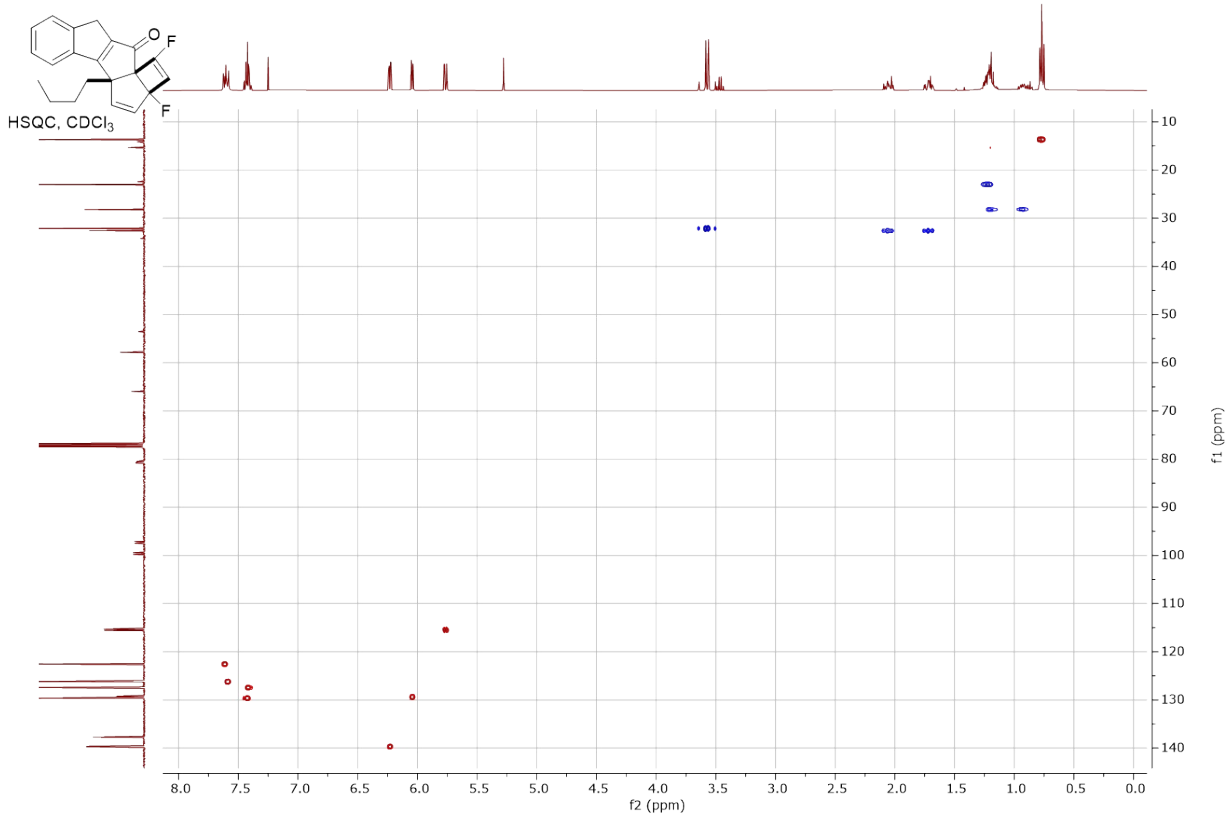


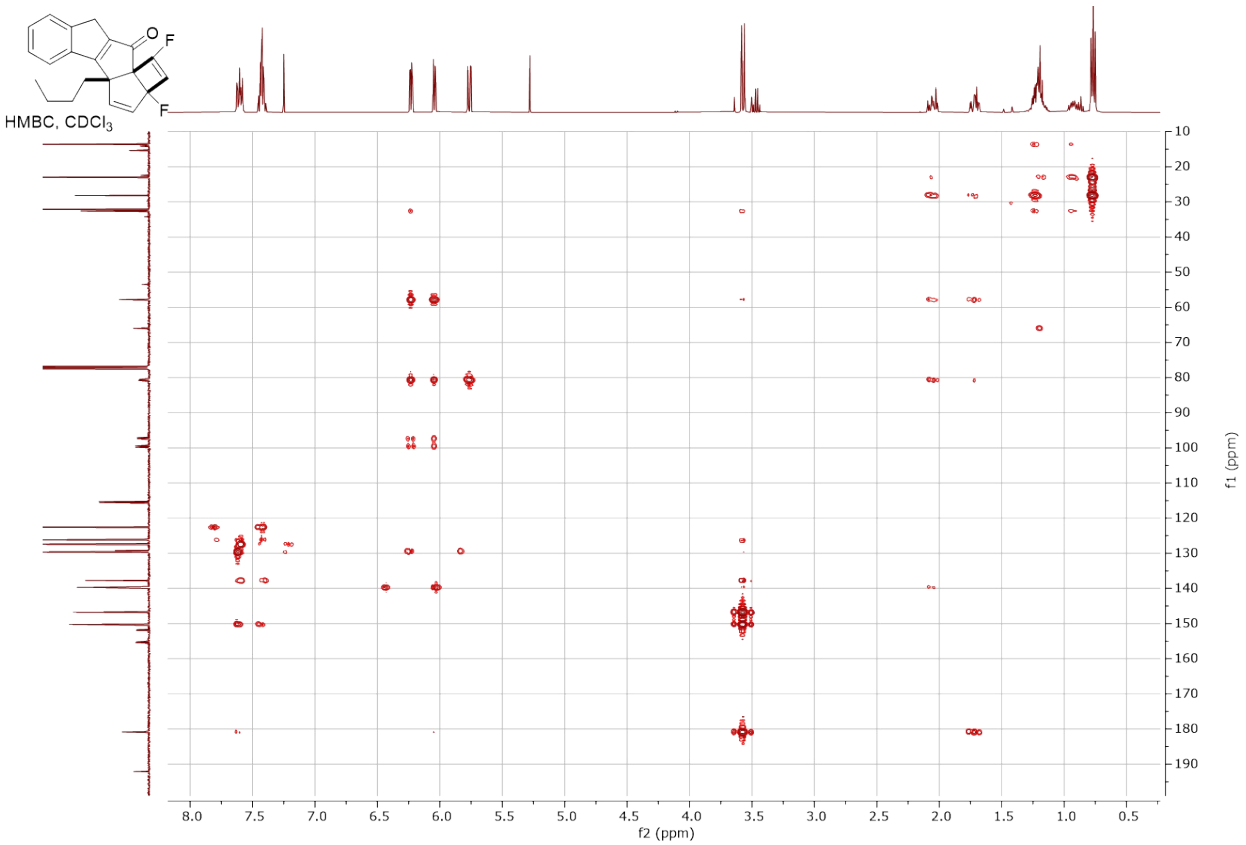
Rac-(2aS,4aR,10aR)-4a-Butyl-1,2a-difluoro-4a,9-dihydrocyclobuta[3a,4]pentaleno[1,2-a]inden-10(2aH)-one, 5a



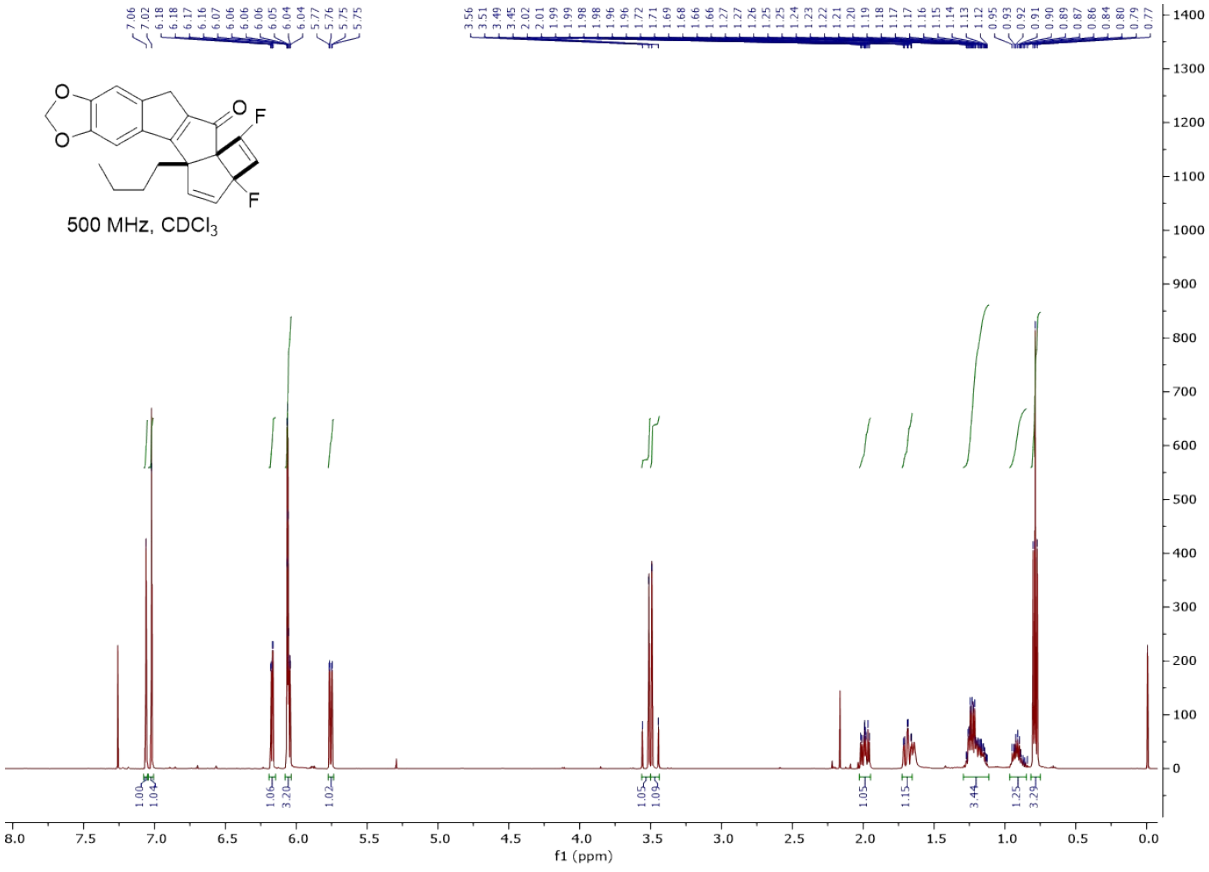


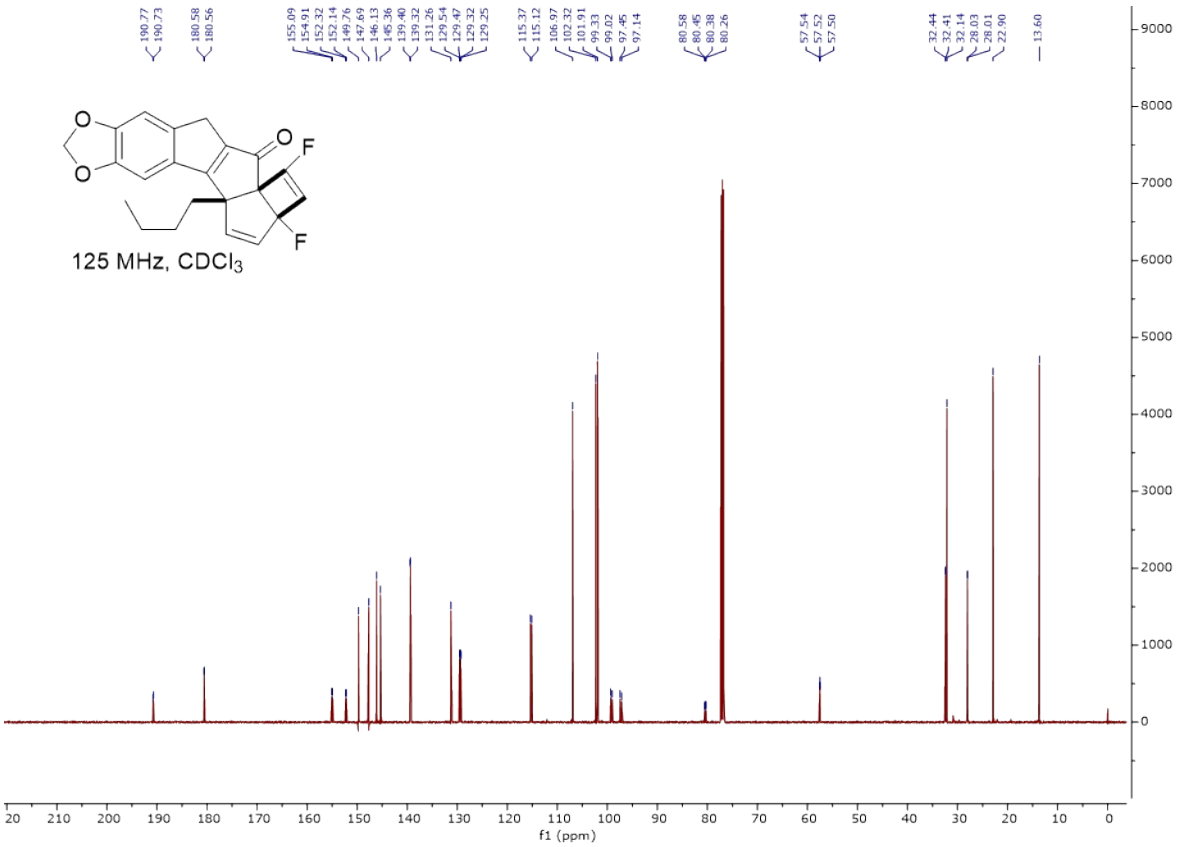

376 MHz, CDCl3
-88.14
-88.15
-88.19
-157.64
-157.64
-157.65
-157.66
-157.67
-157.67
1.12
1.00
f1 (ppm)

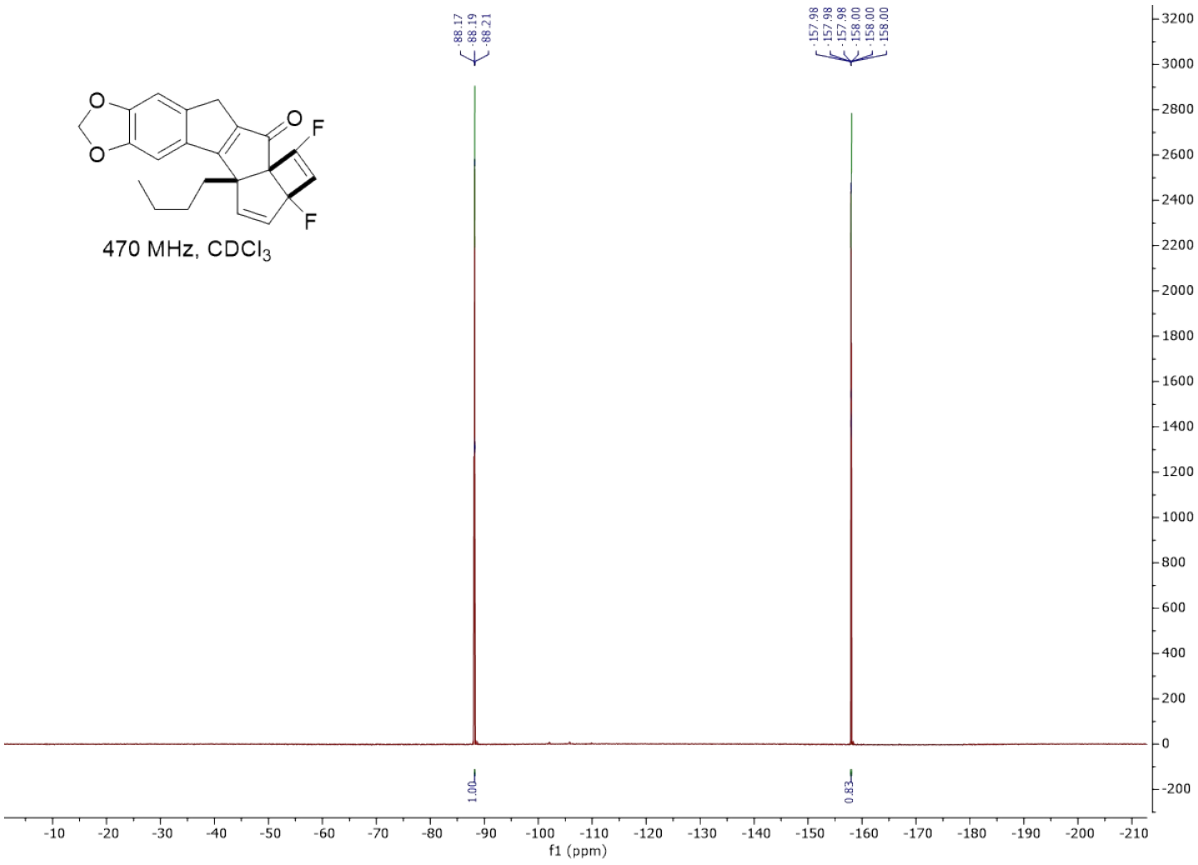

HSQC, CDCl3
f2 (ppm)
f1 (ppm)

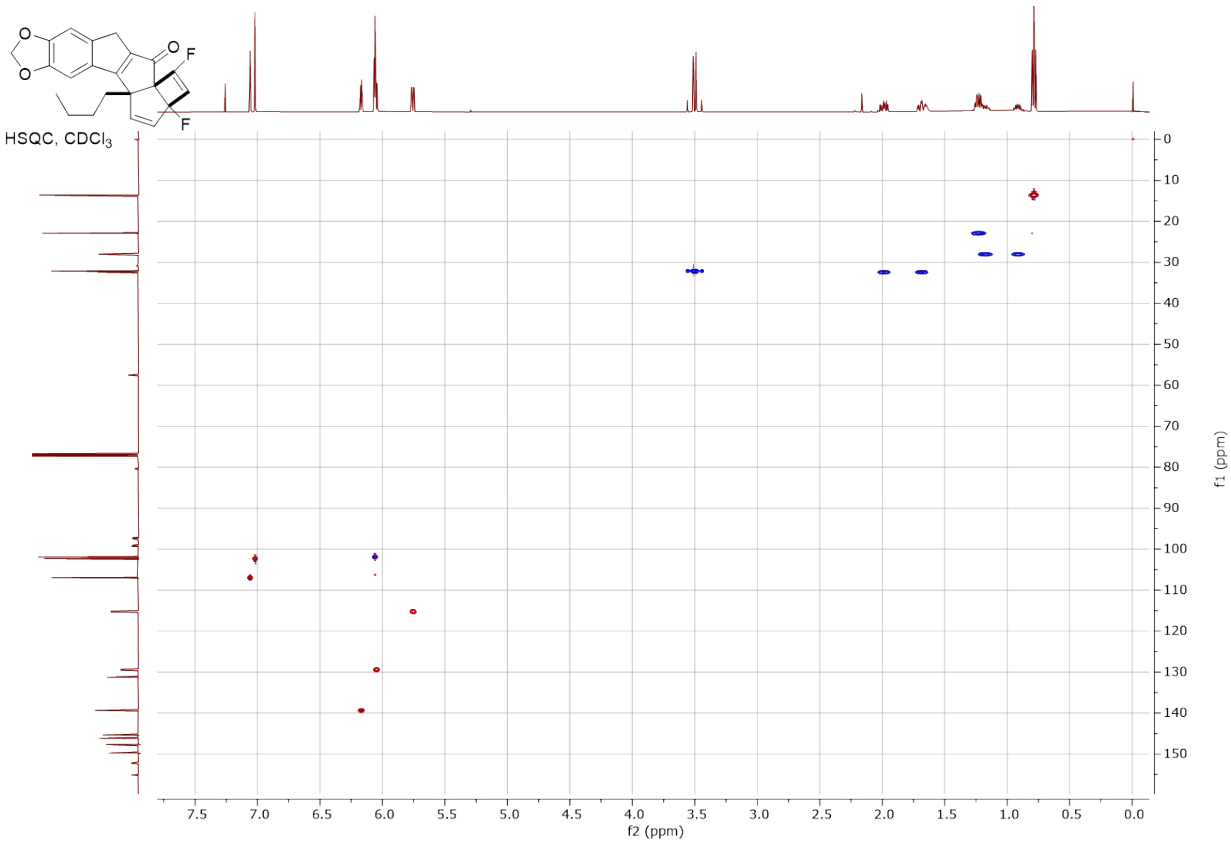


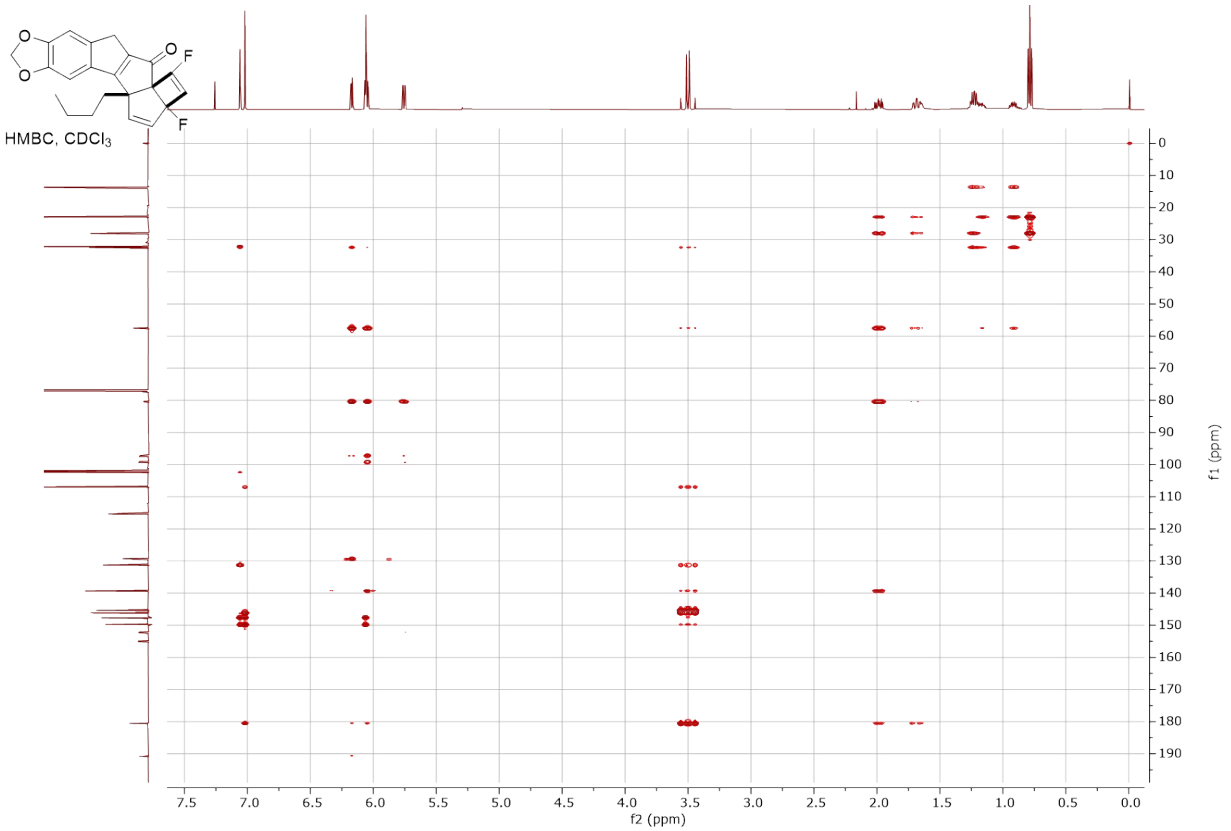
Rac-(2aS,4aR,11aR)-4a-Butyl-1,2a-difluoro-4a,10-dihydrocyclobuta[3a',4']pentaleno[1',2':1,2]-indeno[5,6-d][1,3]dioxol-11(2aH)-one, 5b



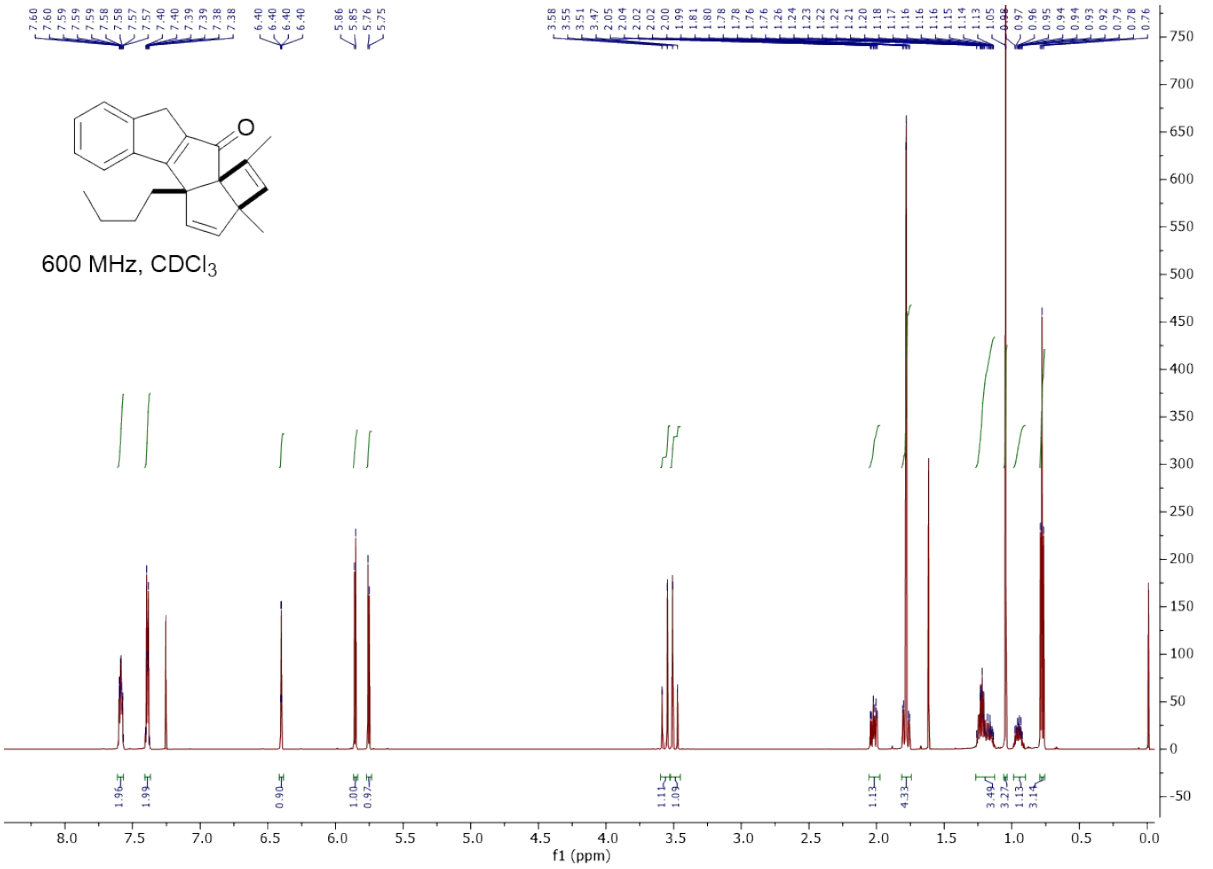

125 MHz, CDCl3
f1 (ppm)

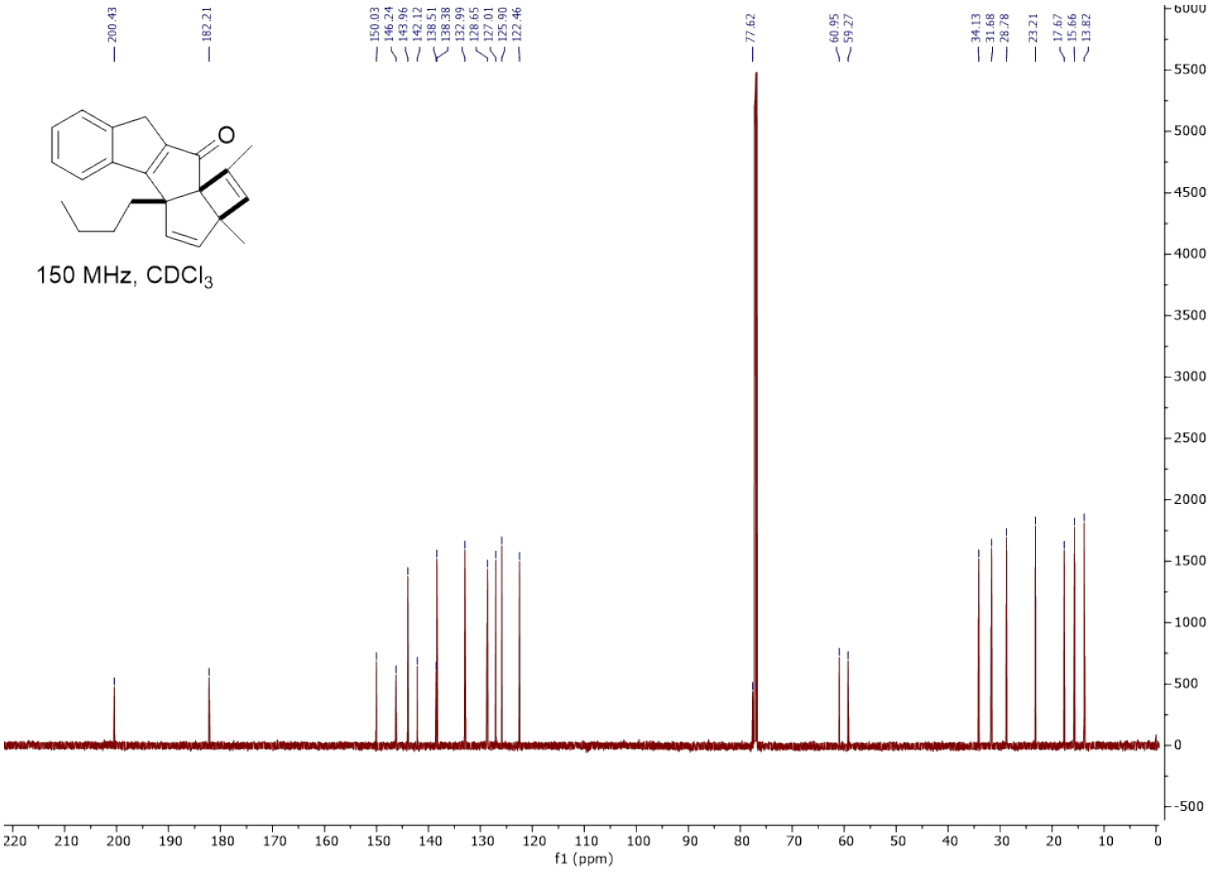

470 MHz, CDCl3
f1 (ppm)

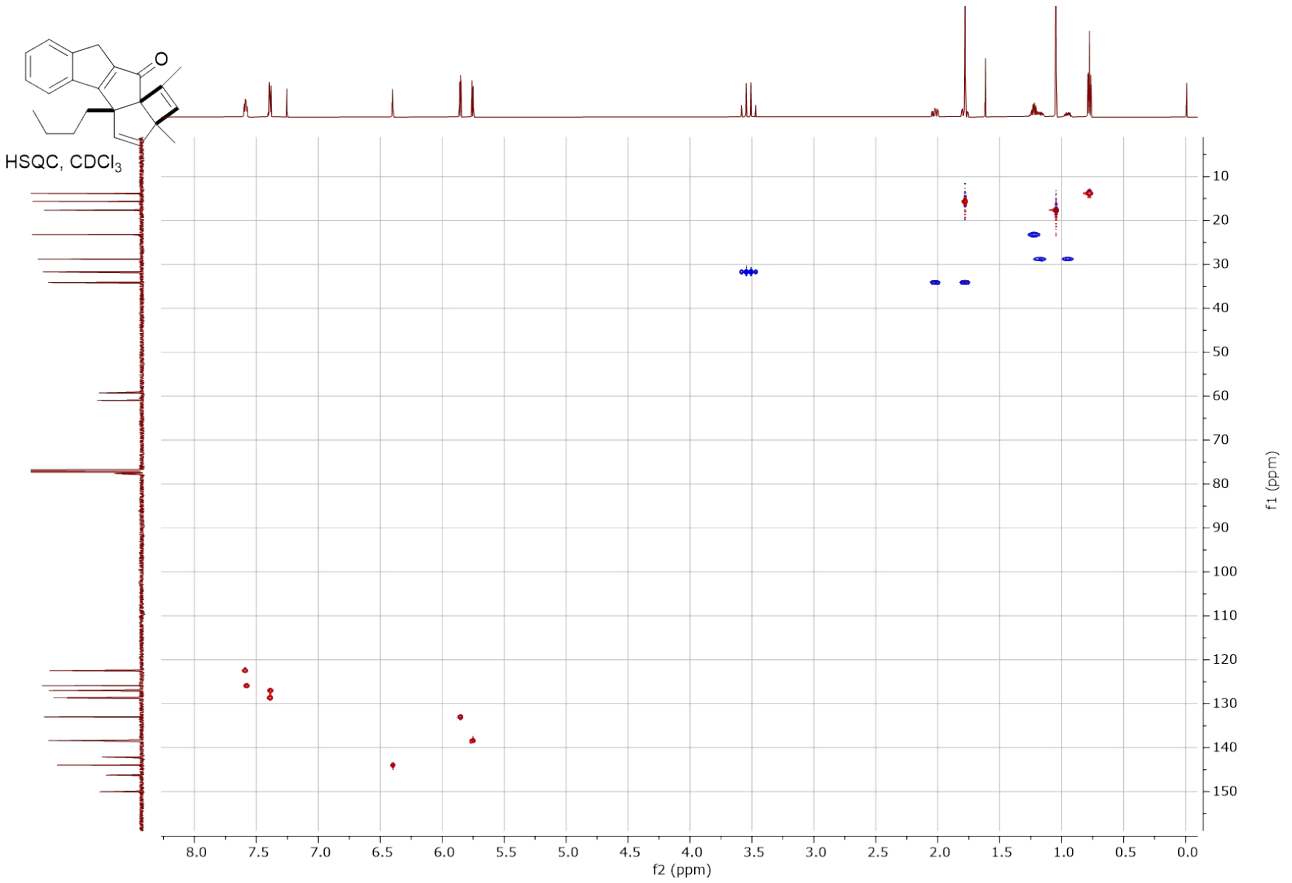

HSQC, CDCl3
f2 (ppm)
f1 (ppm)

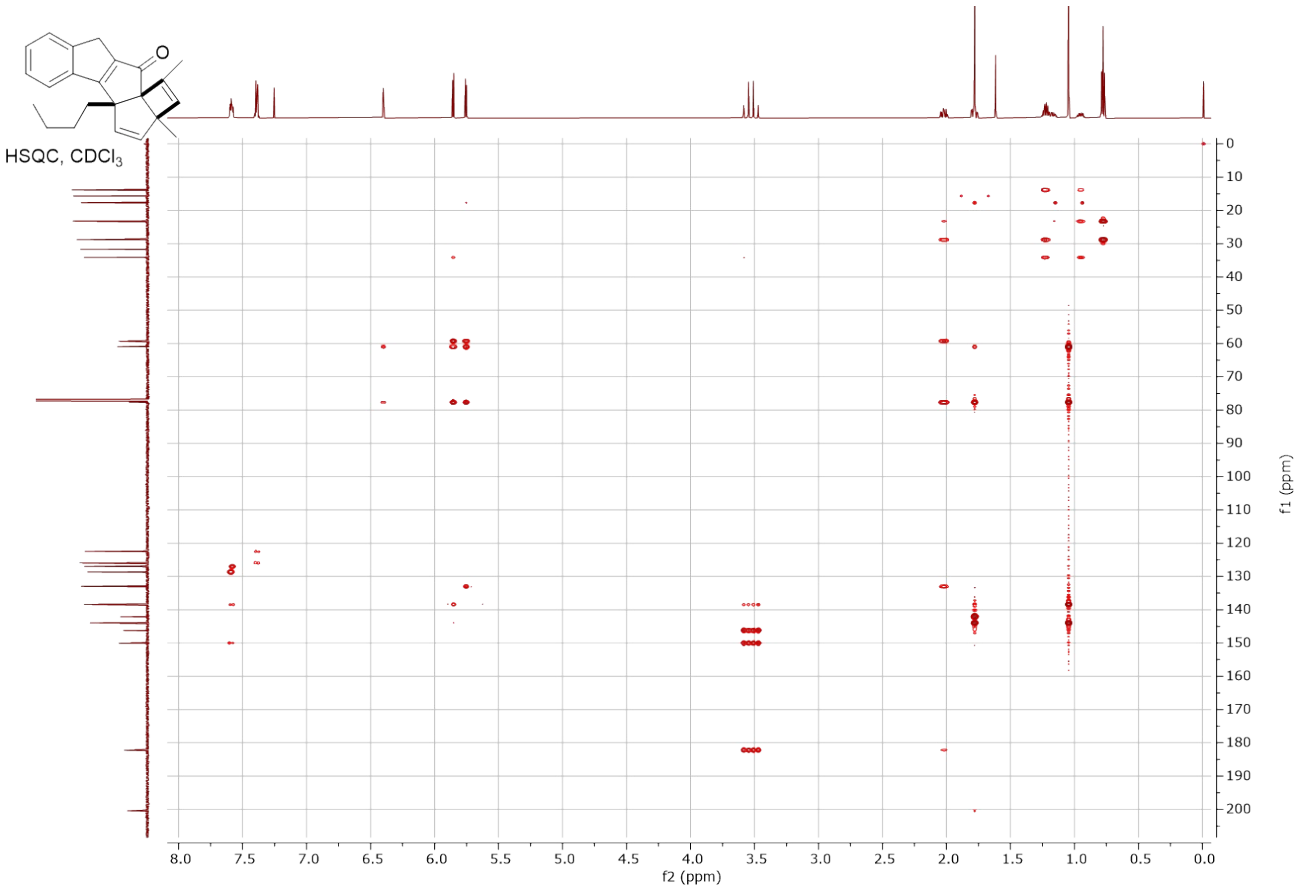

HMBC, CDCl3
f2 (ppm)
f1 (ppm)

Rac-(2aR,4aR,10aR)-4a-Butyl-1,2a-dimethyl-4a,9-dihydrocyclobuta[3a,4]pentaleno[1,2-a]inden-10(2aH)-one, 5c

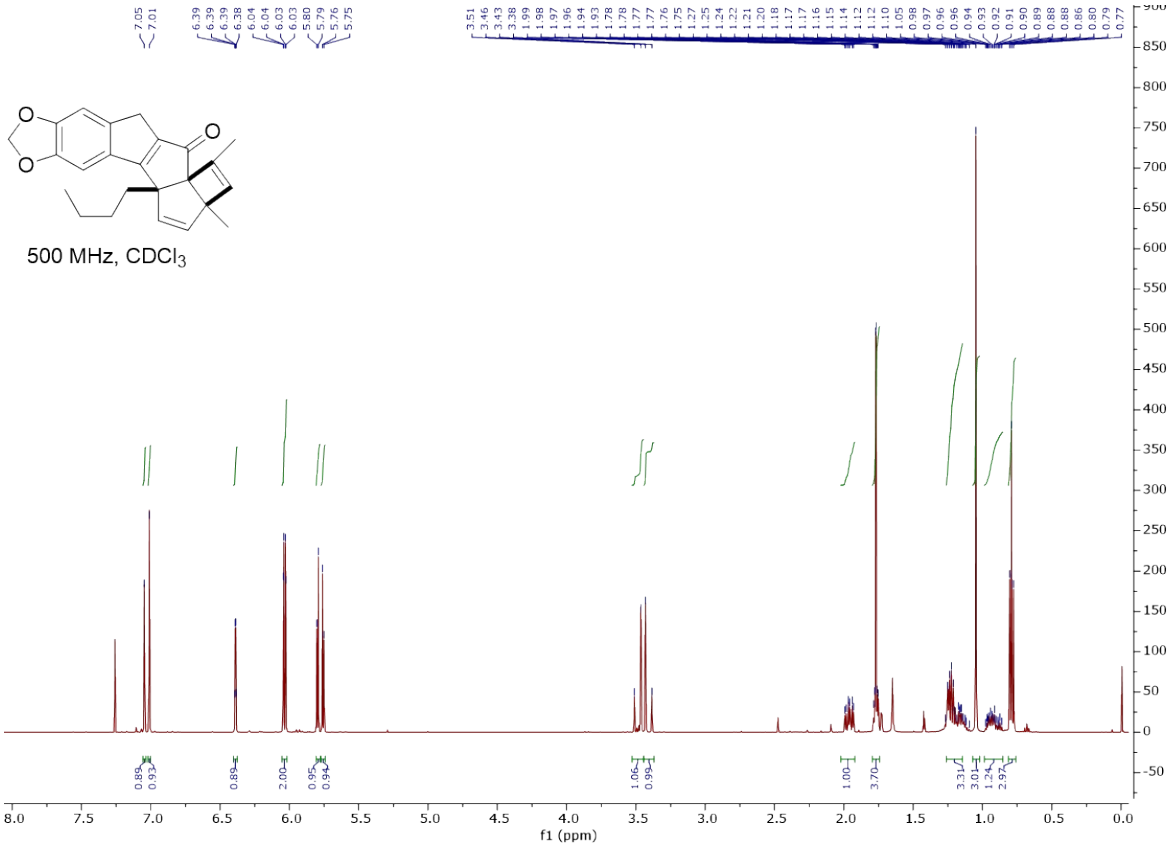


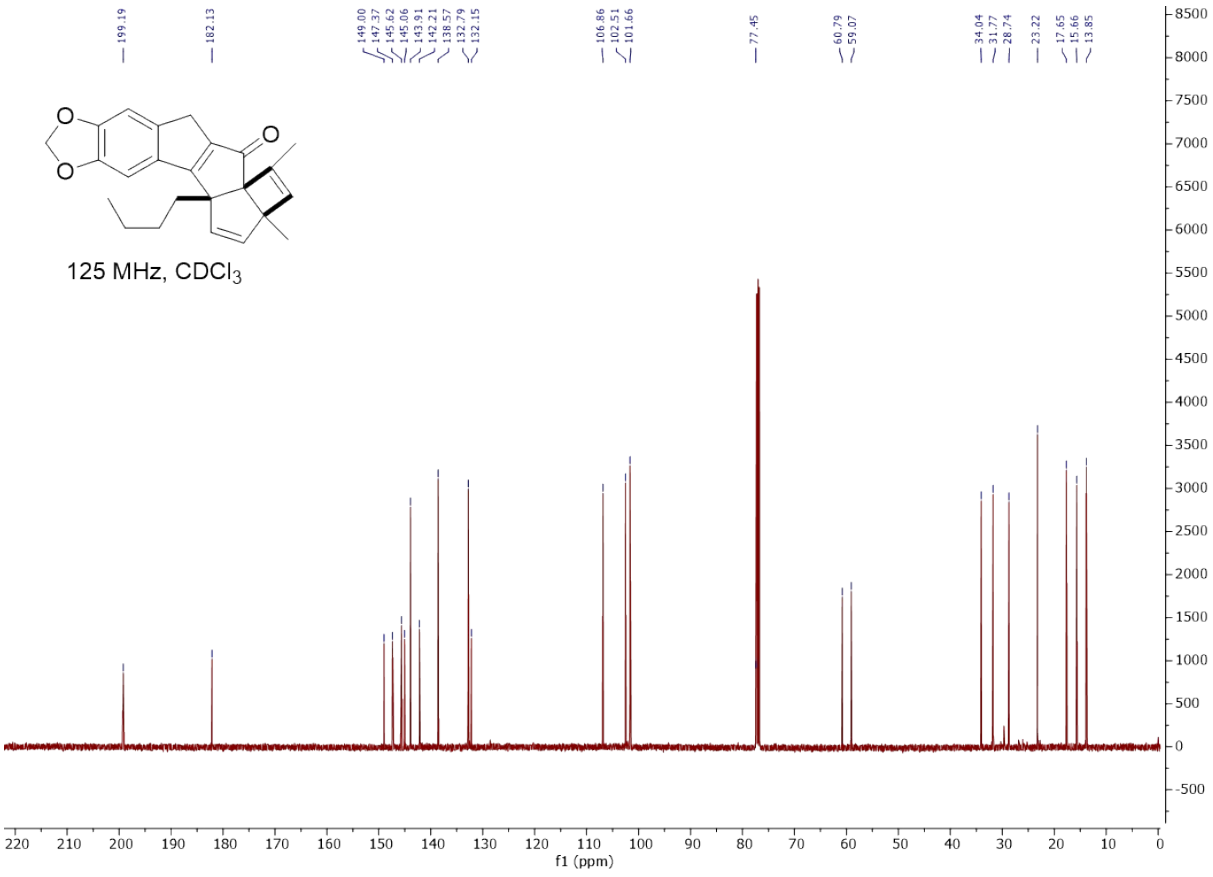


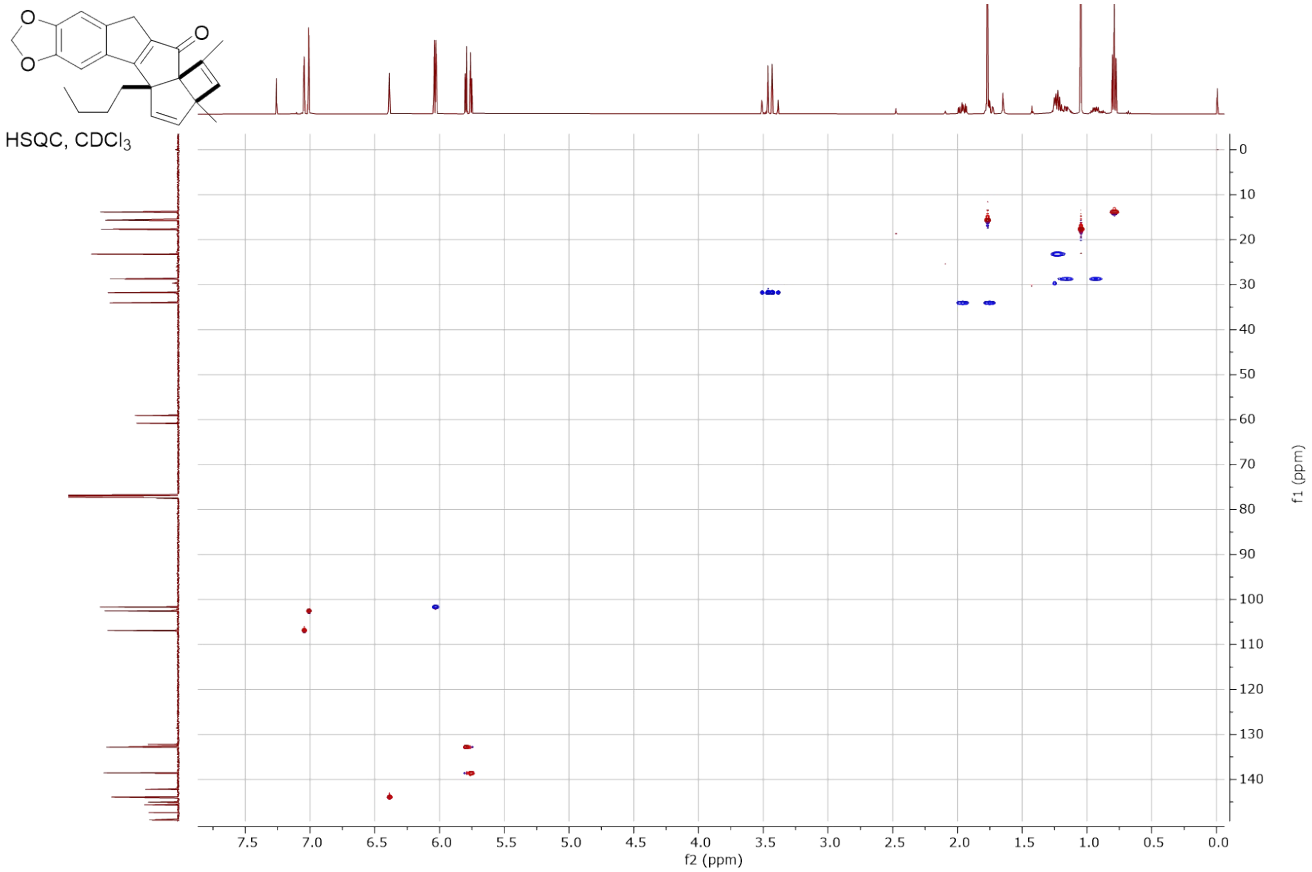

O
HSQC, CDCl3
f2 (ppm)
f1 (ppm)

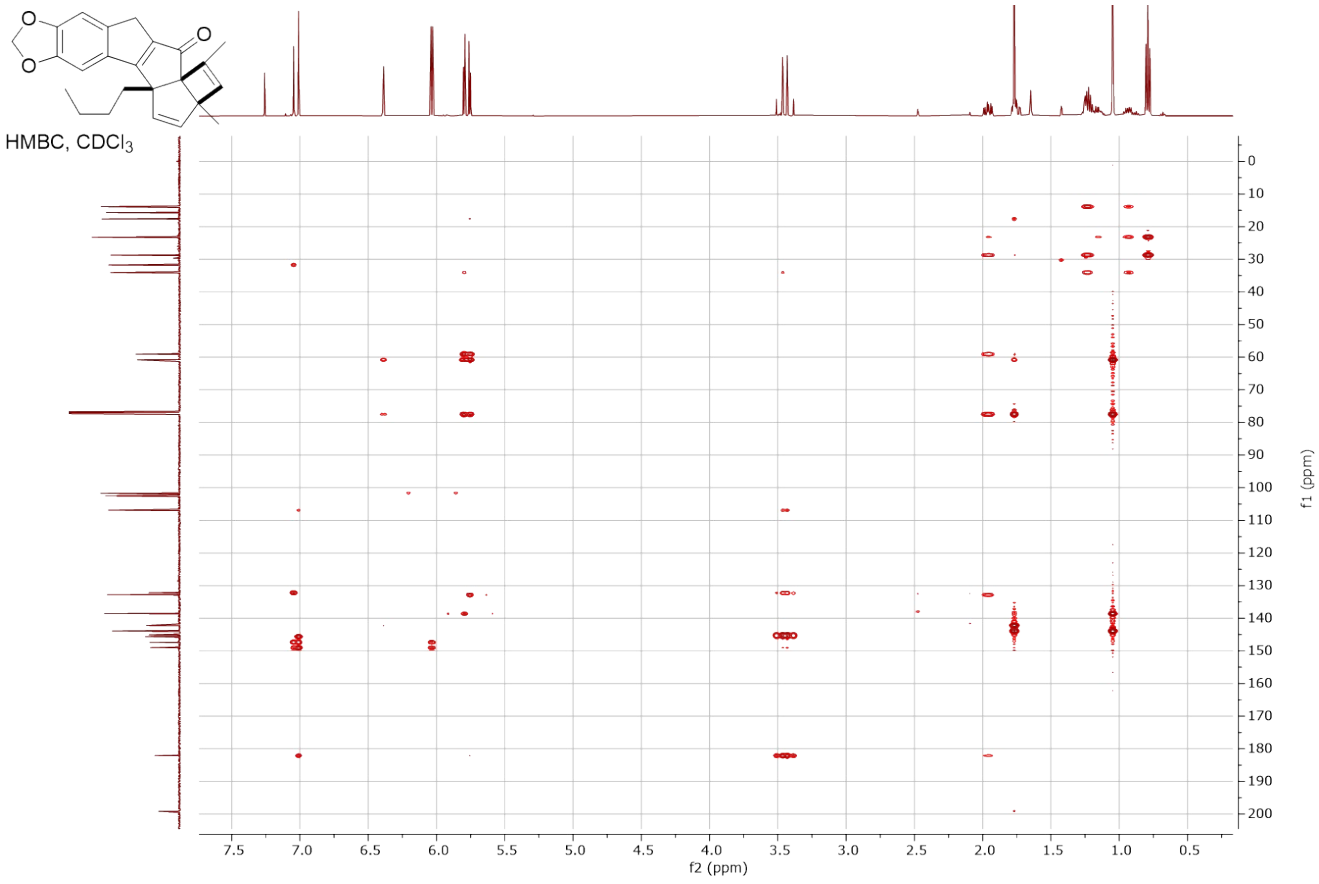

O
HSQC, CDCl3
f2 (ppm)
f1 (ppm)

Rac-(2aR,4aR,11aR)-4a-Butyl-1,2a-dimethyl-4a,10-dihydrocyclobuta[3a',4']pentaleno[1',2':1,2]-indeno[5,6-d][1,3]dioxol-11(2aH)-one, 5d

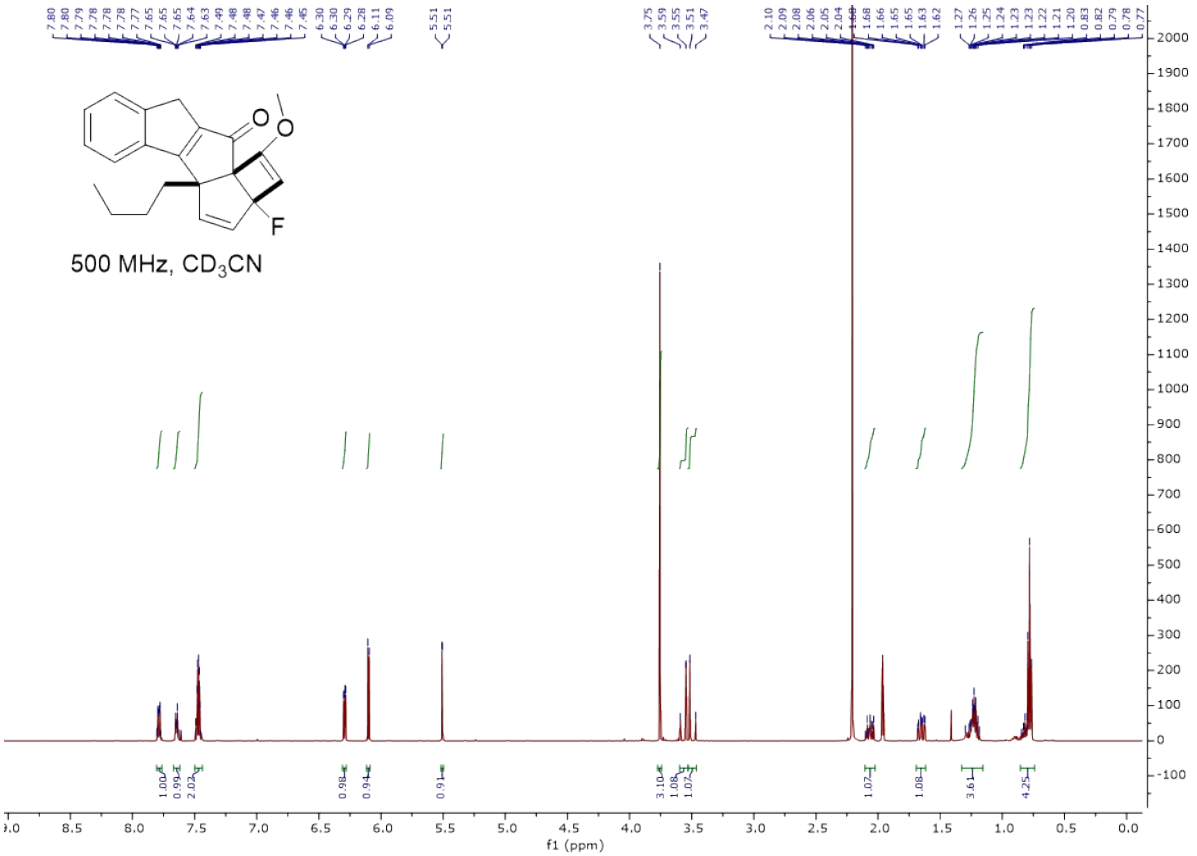


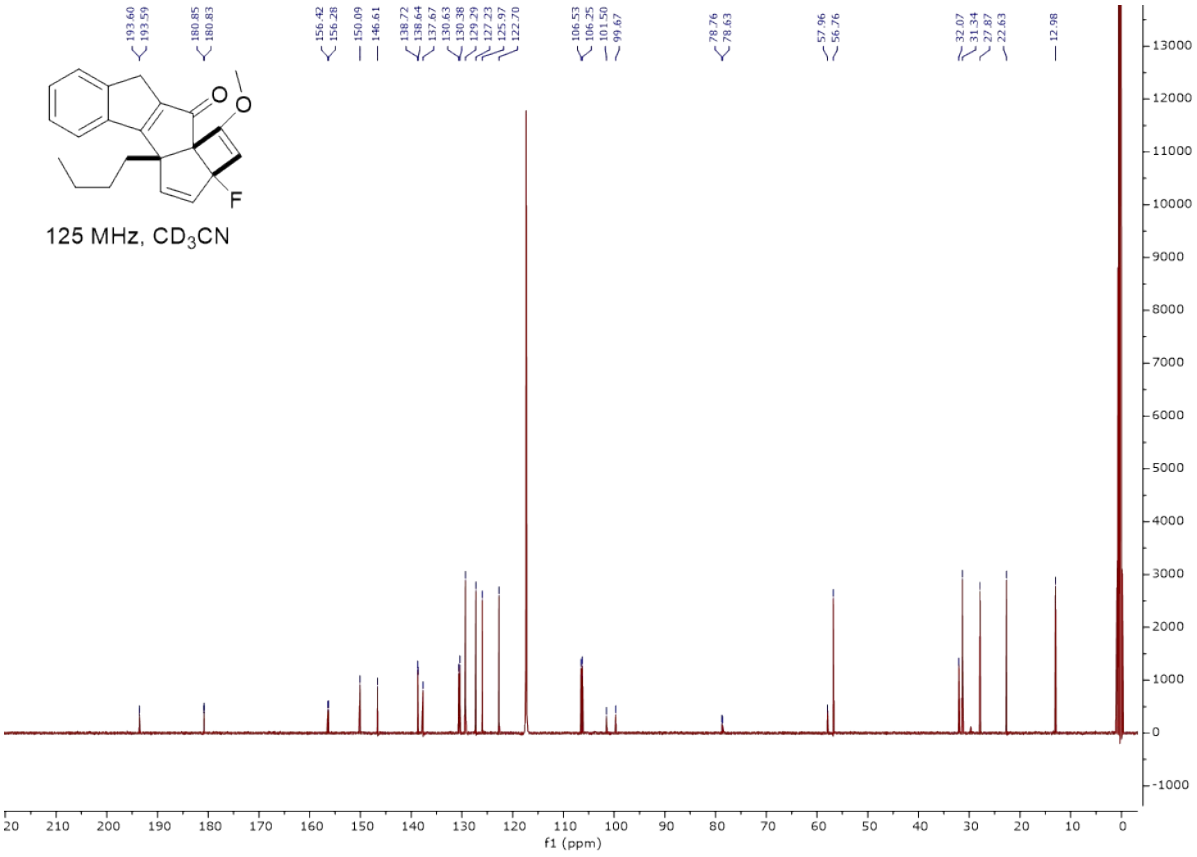


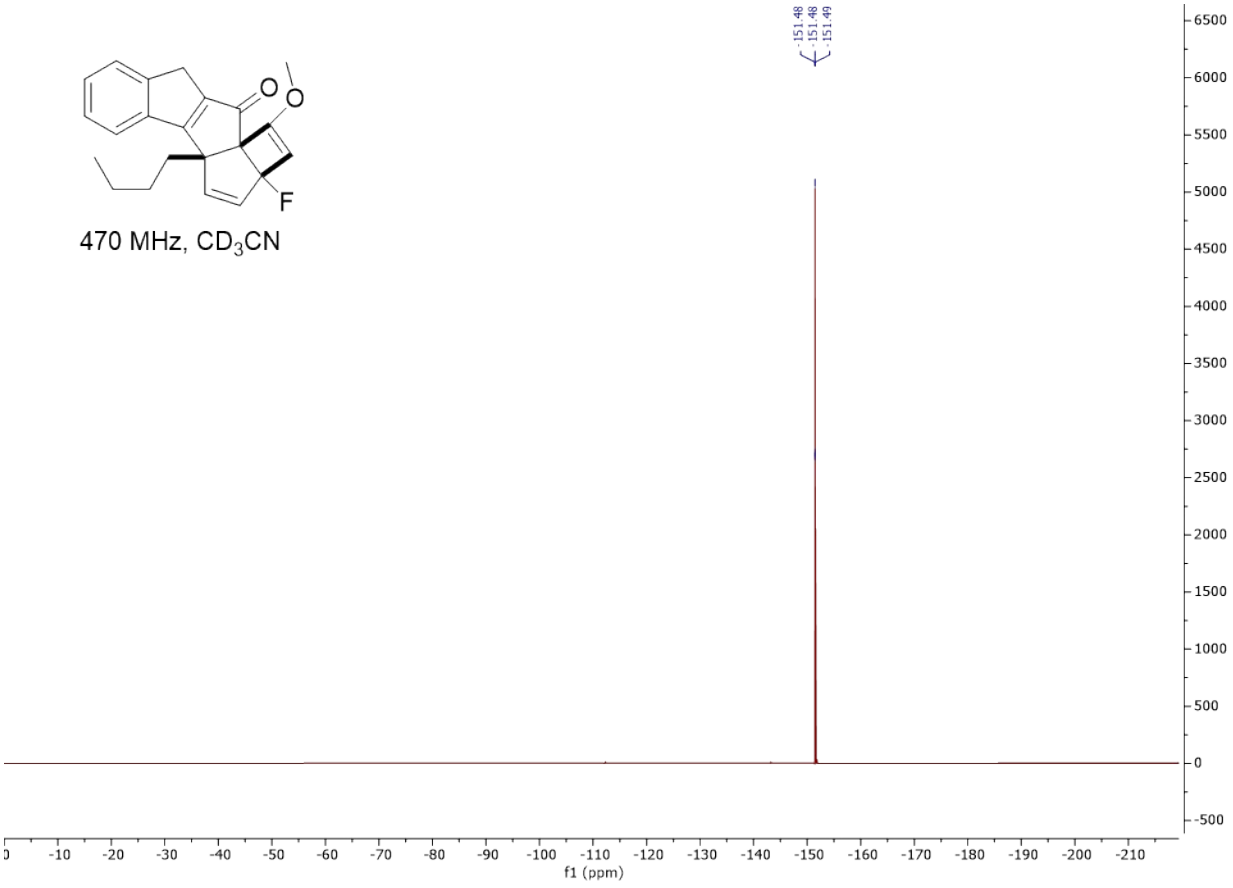

HSQC, CDCl3
f2 (ppm)
f1 (ppm)

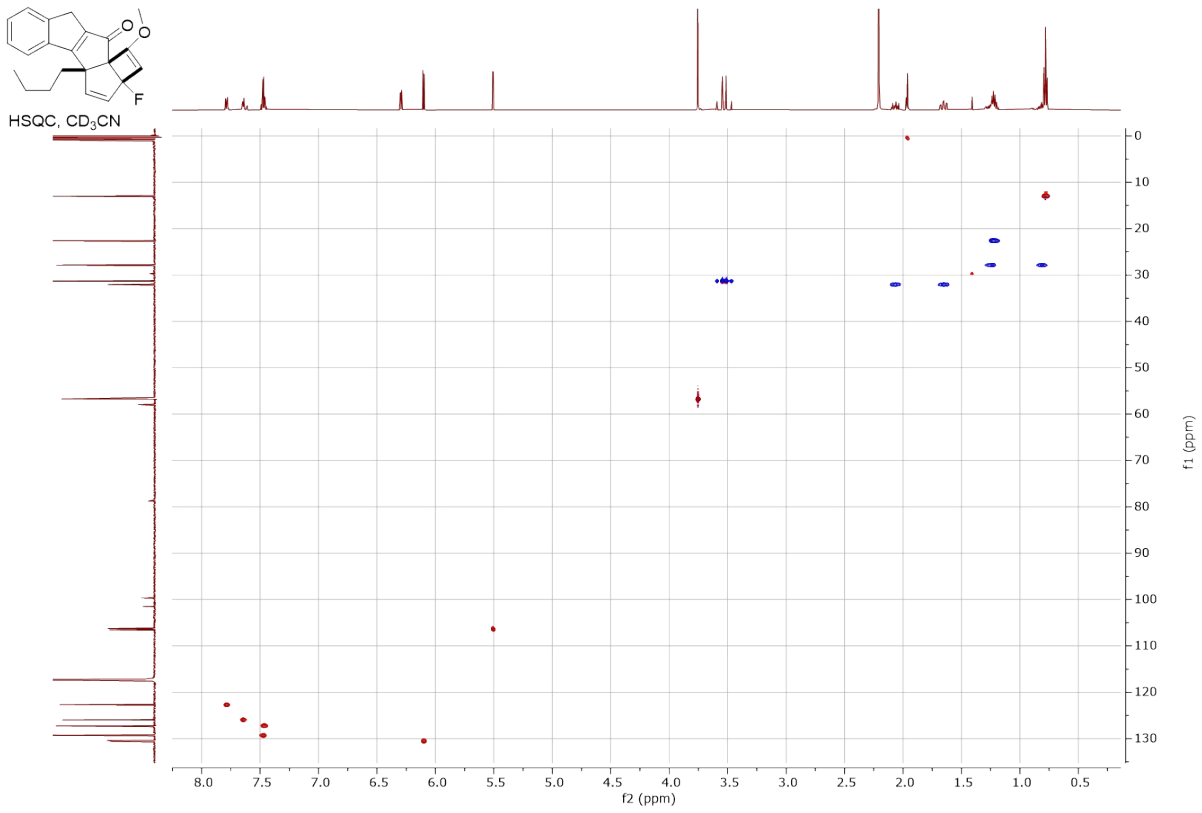

HMBC, CDCl3
f2 (ppm)
f1 (ppm)

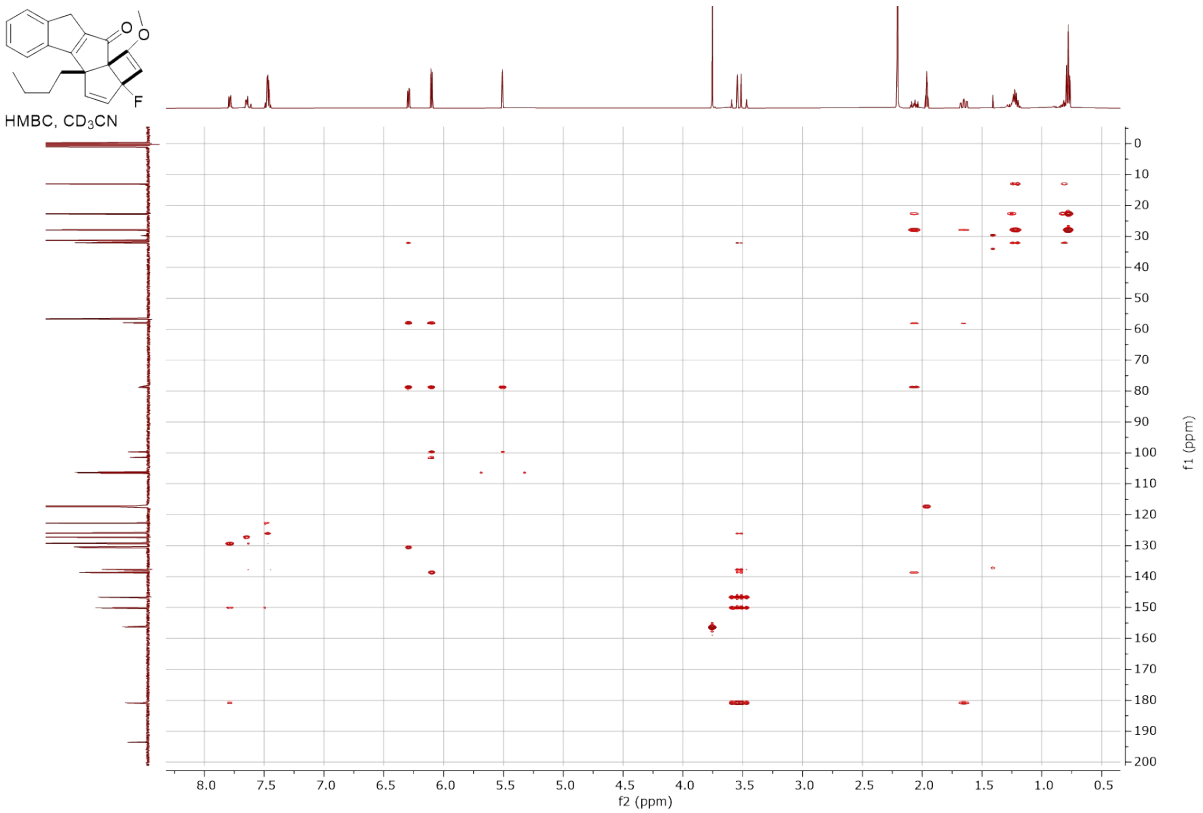
Rac-(2aS,4aR,10aS)-4a-Butyl-2a-fluoro-1-methoxy-4a,9-dihydrocyclobuta[3a,4]pentaleno[1,2-a]inden-10(2aH)-one, 5e



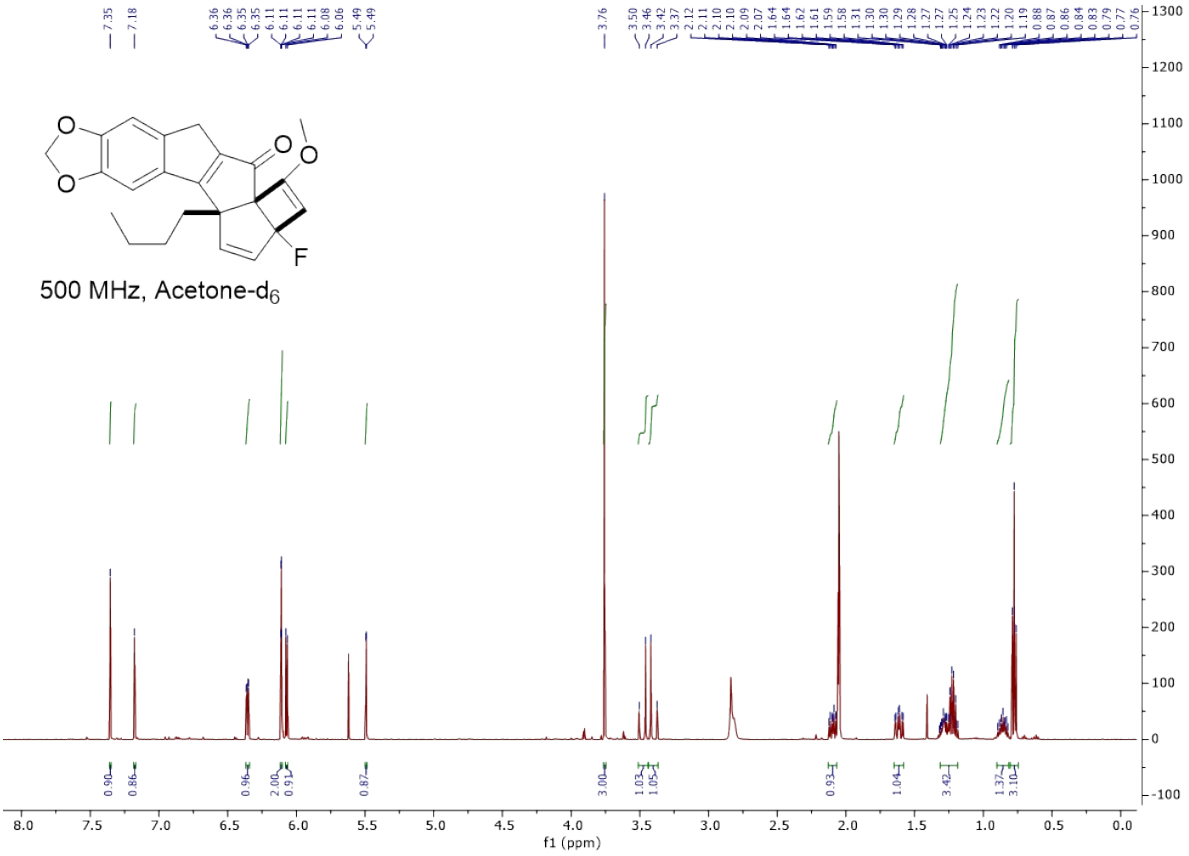


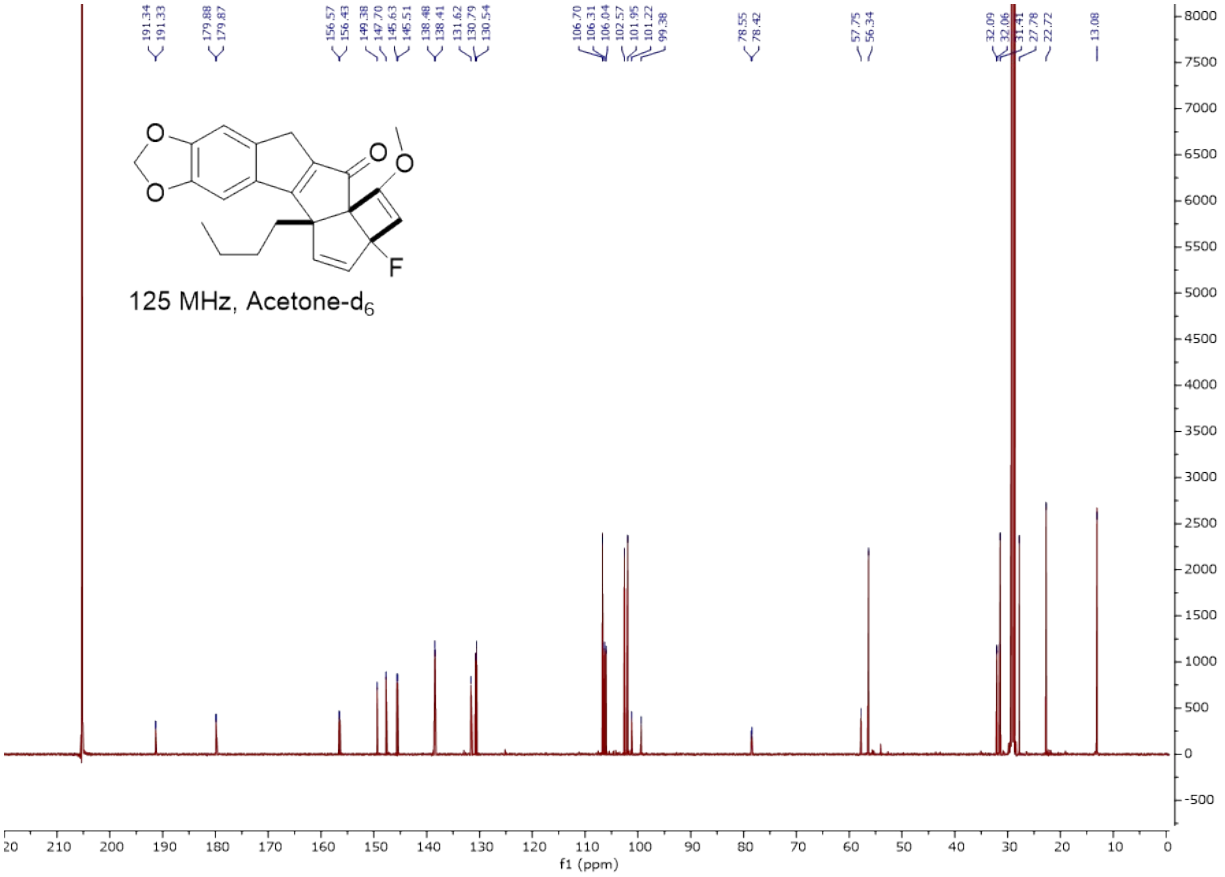

O
O
F
470 MHz, CD3CN
-151.48
-151.48
-151.49
f1 (ppm)

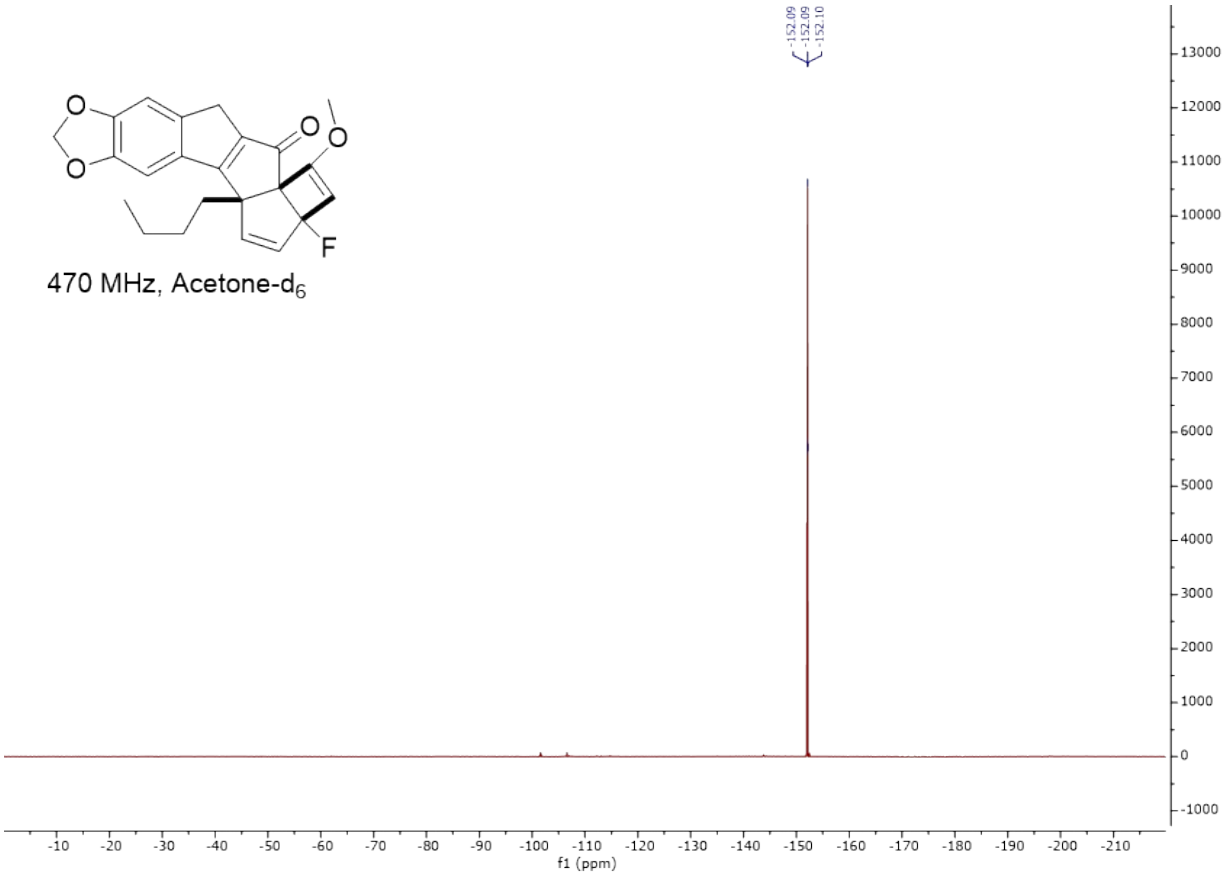

O
O
F
HSQC, CD3CN
f2 (ppm)
f1 (ppm)

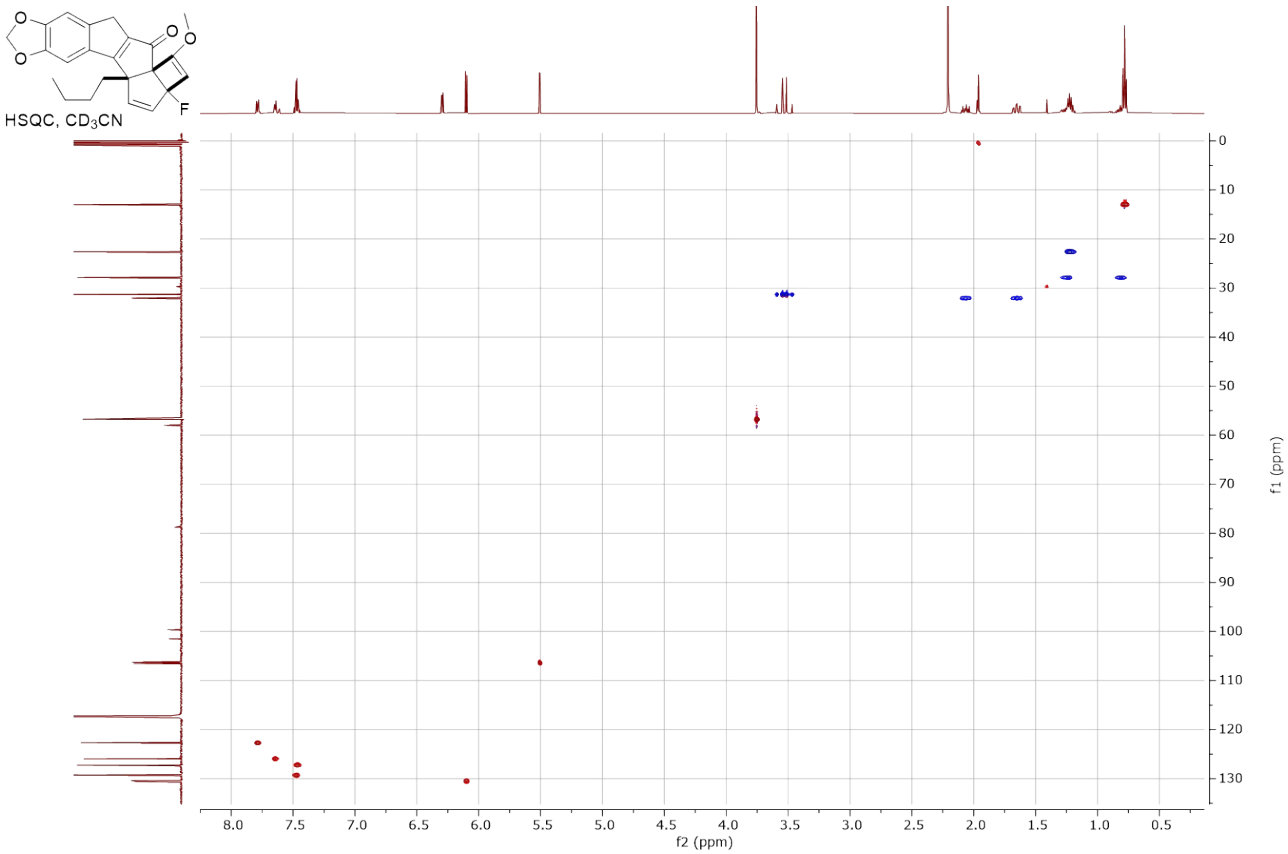


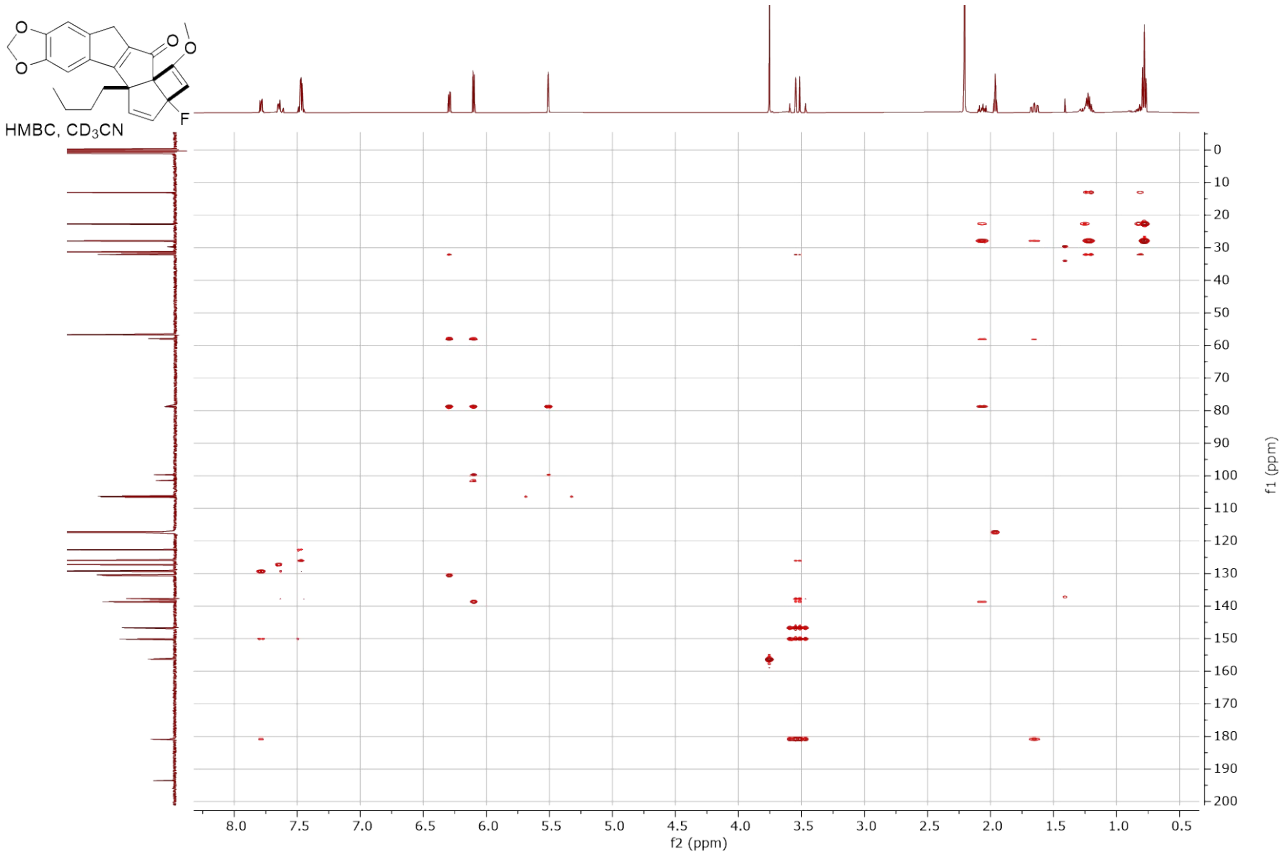
Rac-(2aS,4aR,11aS)-4a-Butyl-2a-fluoro-1-methoxy-4a,10-dihydrocyclobuta[3a',4']pentaleno-[1',2':1,2]indeno[5,6-d][1,3]dioxol-11(2aH)-one, 5f



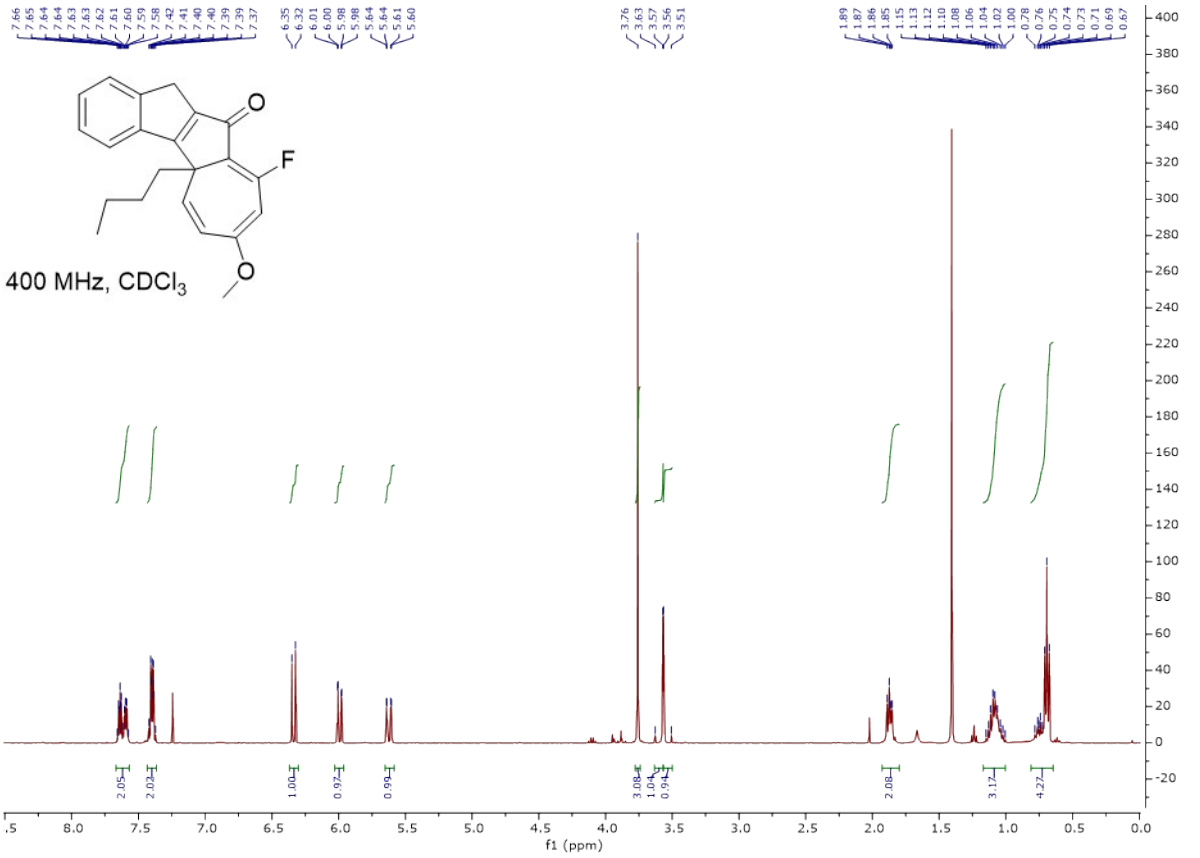

191.34
191.33
179.88
179.87
156.57
156.43
149.38
147.70
145.63
145.51
138.48
138.41
131.62
130.79
130.54
106.70
106.31
106.04
102.57
101.95
101.22
99.38
78.55
78.42
57.75
56.34
32.09
32.06
31.41
27.78
22.72
13.08
O
O
O
O
F
125 MHz, Acetone-d6
f1 (ppm)

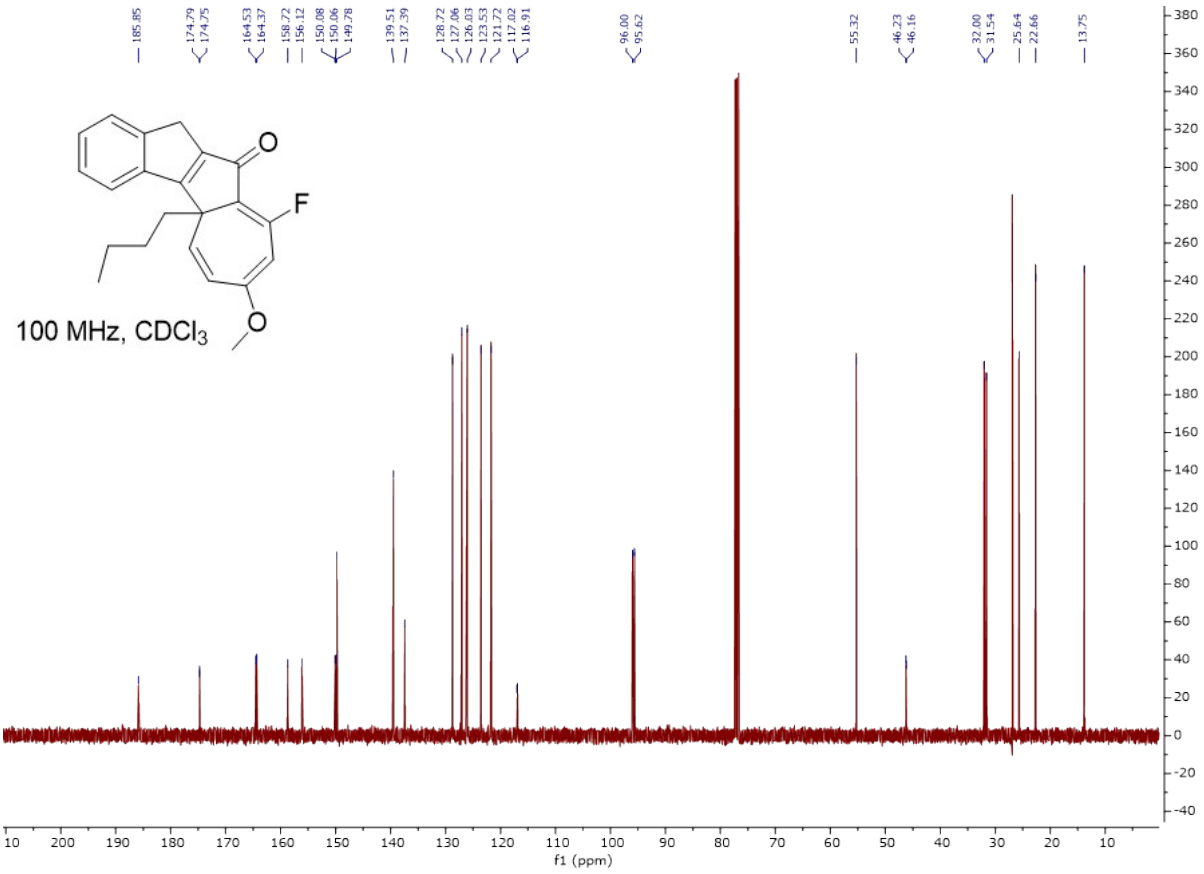

-152.09
-152.09
-152.10
O
O
O
O
F
470 MHz, Acetone-d6
f1 (ppm)

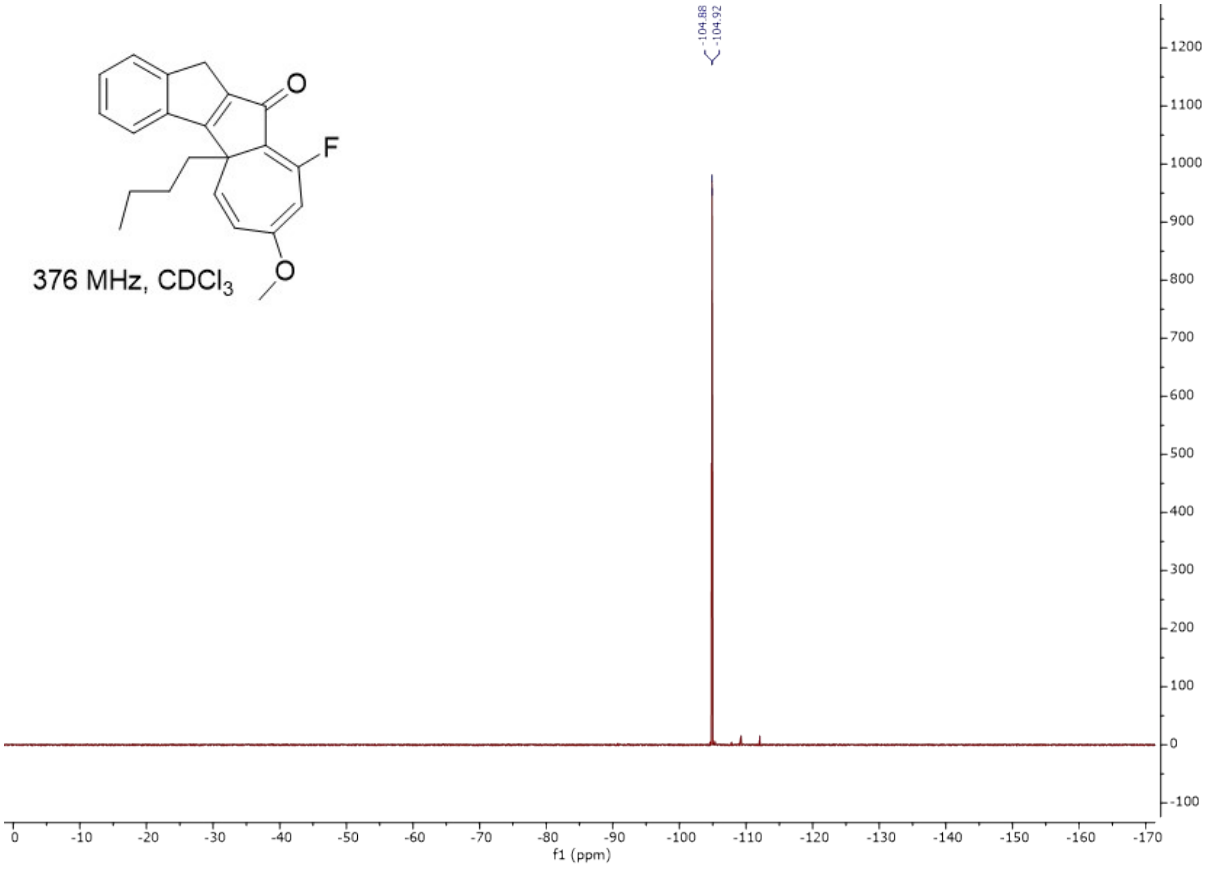

HSQC, CD3CN
F
f2 (ppm)
f1 (ppm)

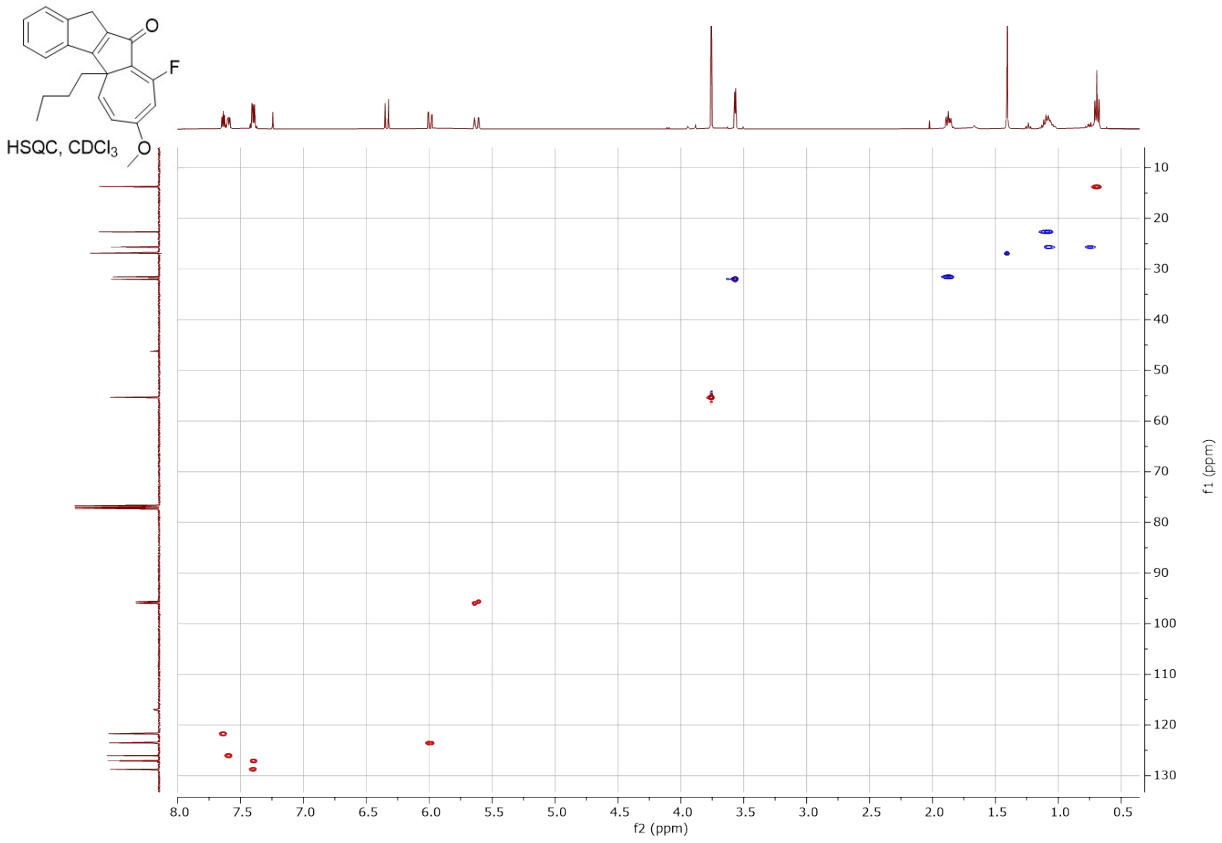

HMBC, CD3CN
F
f2 (ppm)
f1 (ppm)

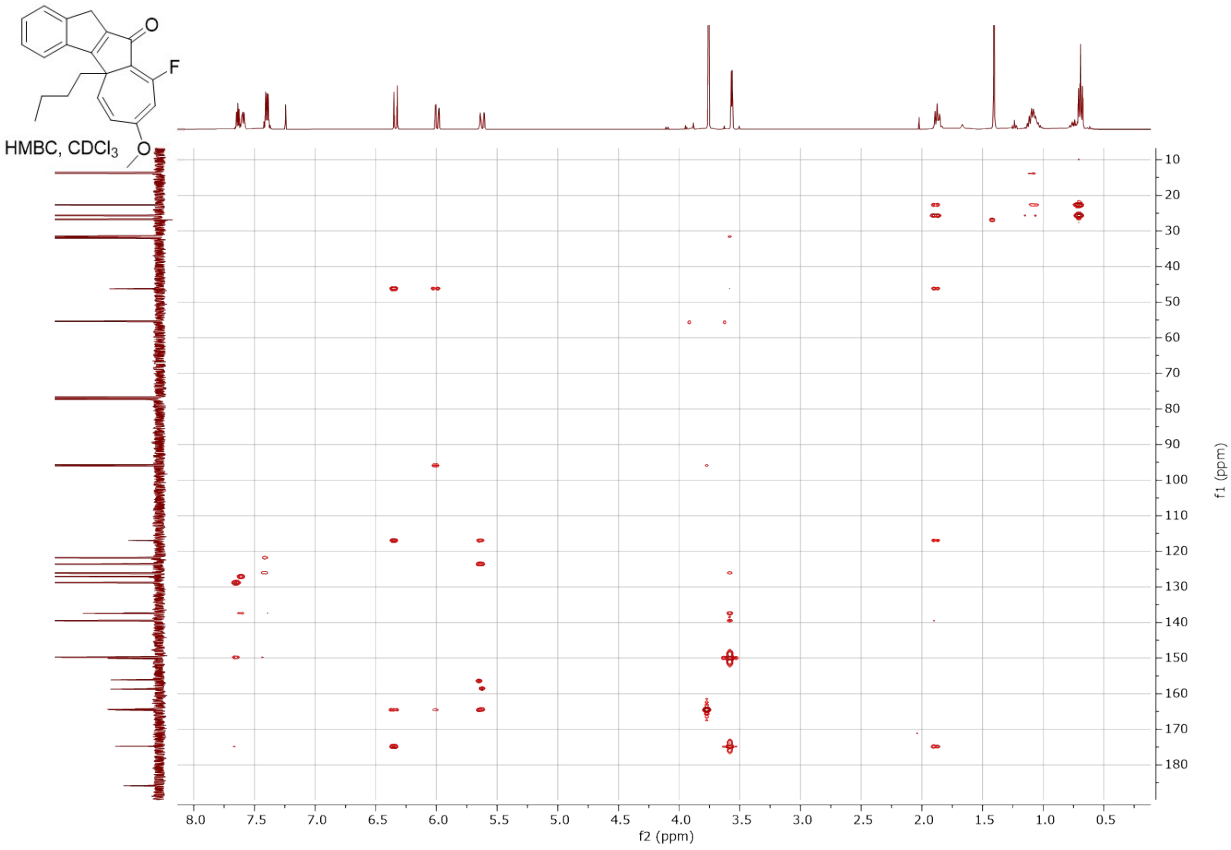
Rac-4c-Butyl-9-fluoro-7-methoxy-4c,11-dihydro-10H-indeno[1,2-a]azulen-10-one, 5g



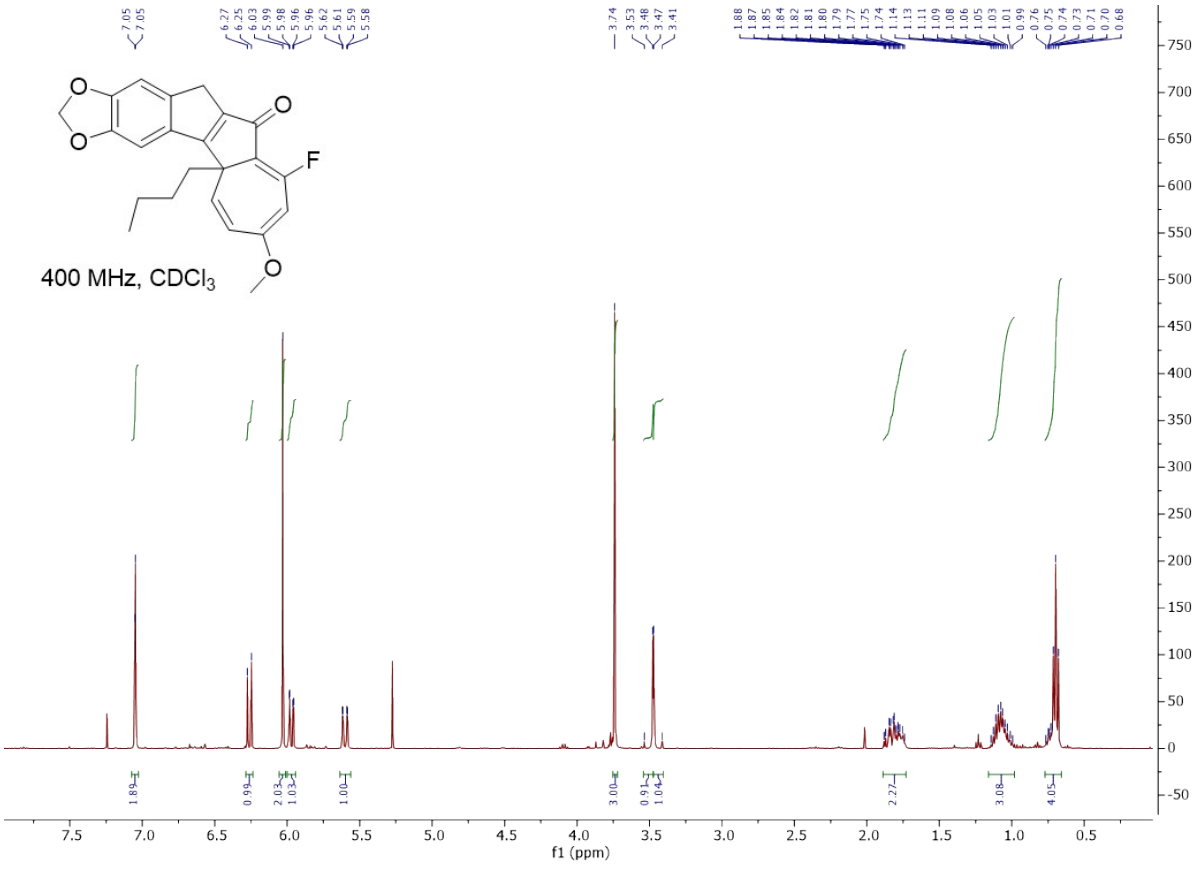


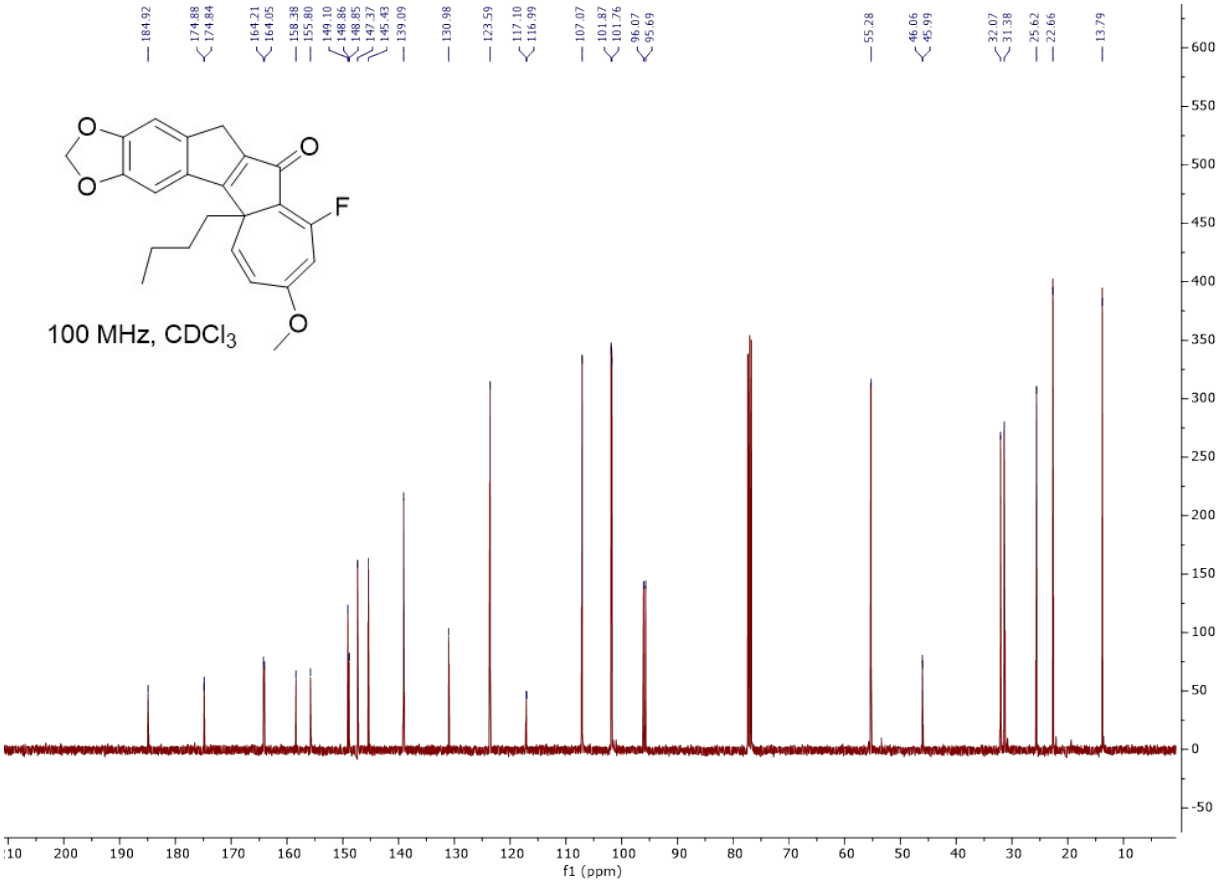

376 MHz, CDCl3
-104.88
-104.92
f1 (ppm)


HSQC, CDCl3
f2 (ppm)
f1 (ppm)



Rac-4c-Butyl-9-fluoro-7-methoxy-4c,11-dihydro-10H-azuleno[1',2':1,2]indeno[5,6-d][1,3]dioxol-10-one, 5h




184.92
174.88
174.84
164.21
164.05
158.38
155.80
149.10
148.86
148.85
147.37
145.43
139.09
130.98
123.59
117.10
116.99
107.07
101.87
101.76
96.07
95.69
55.28
46.06
45.99
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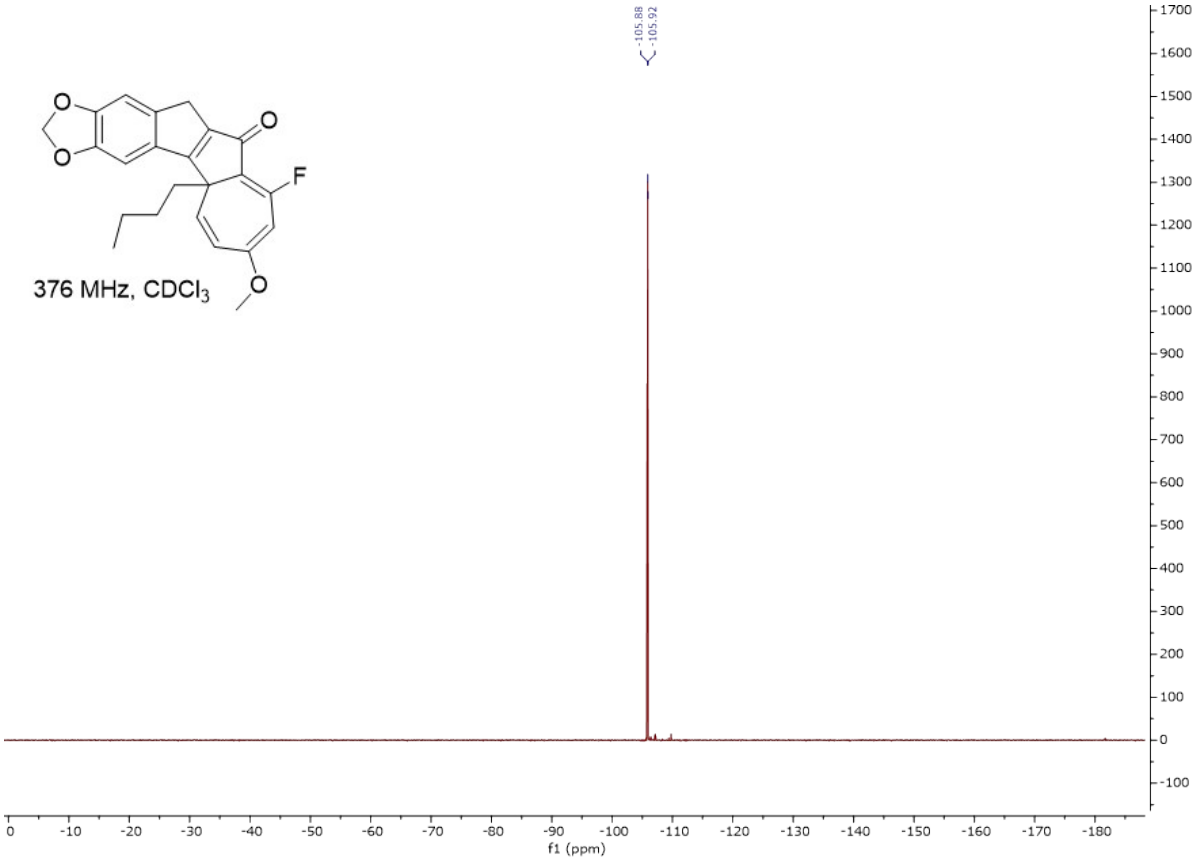
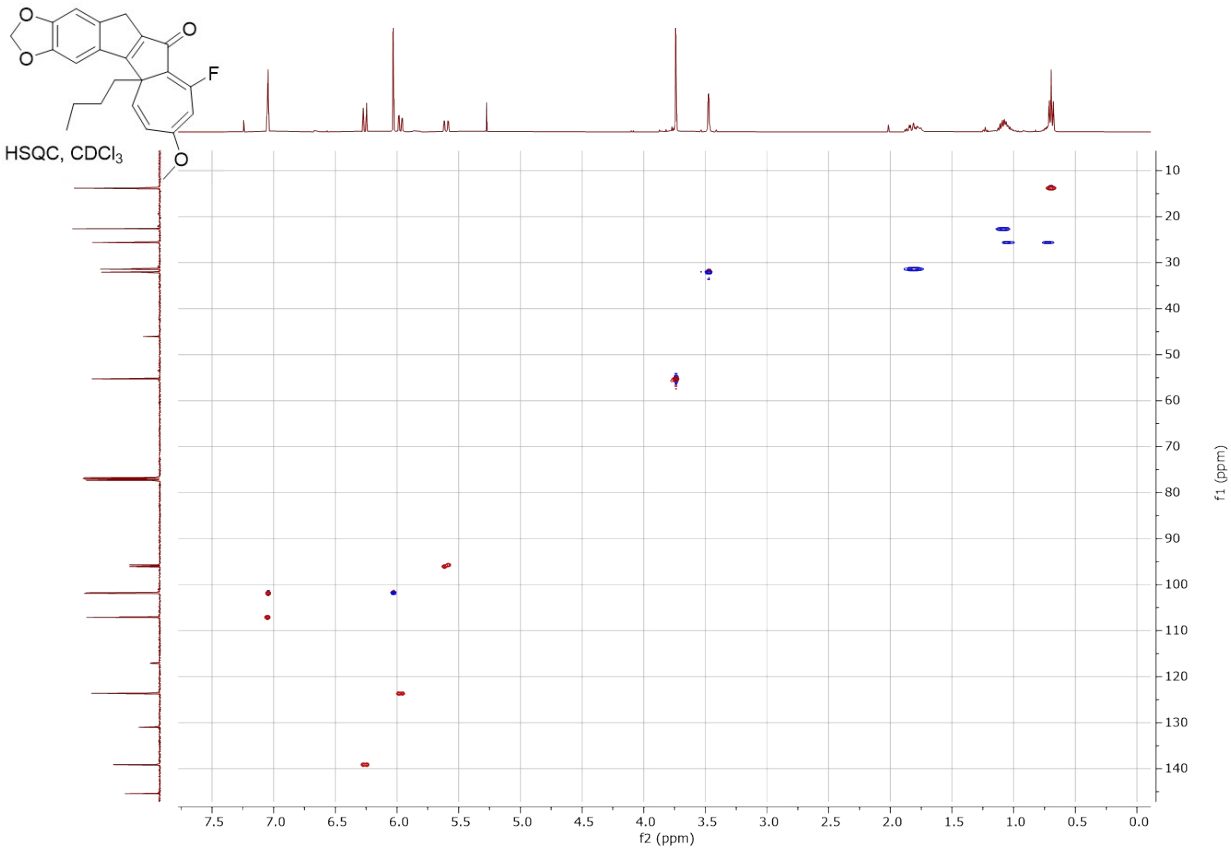
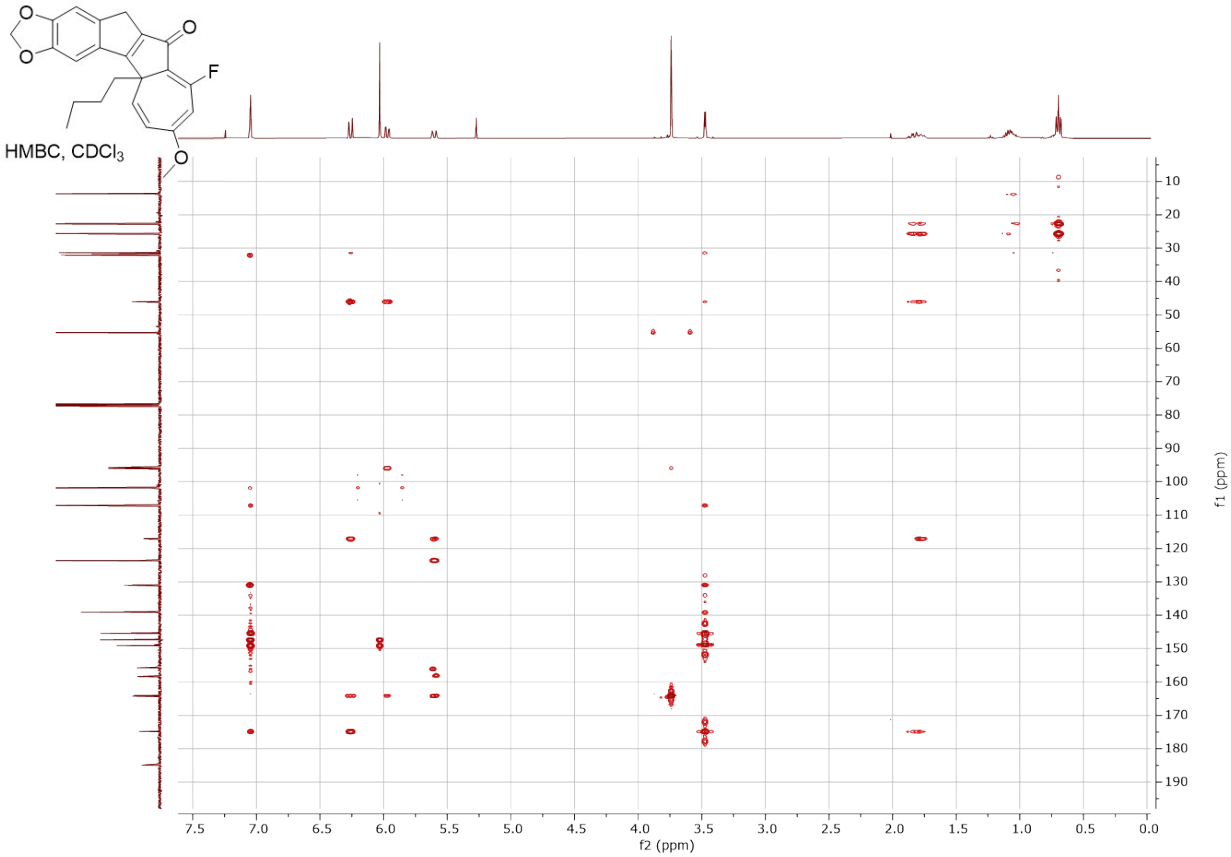
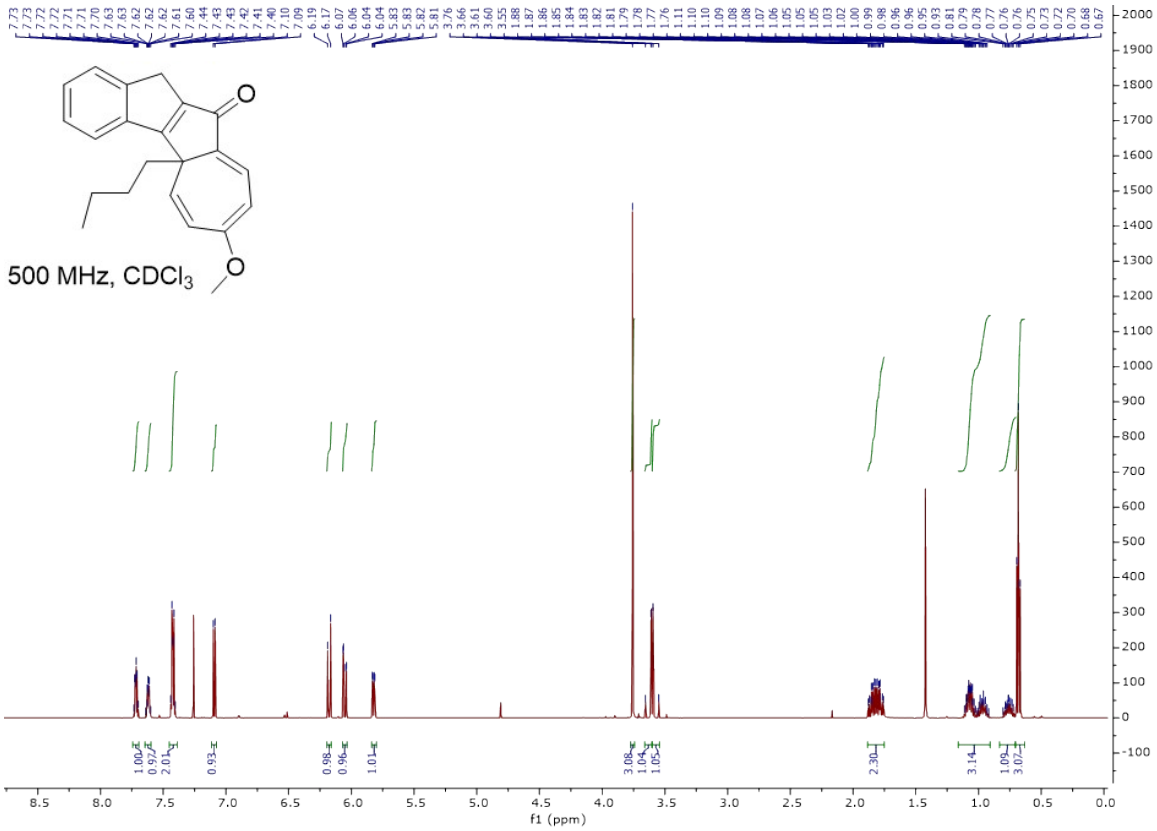
25.62
22.66
13.79
O
O
O
F
O
100 MHz, CDCl3
f1 (ppm)

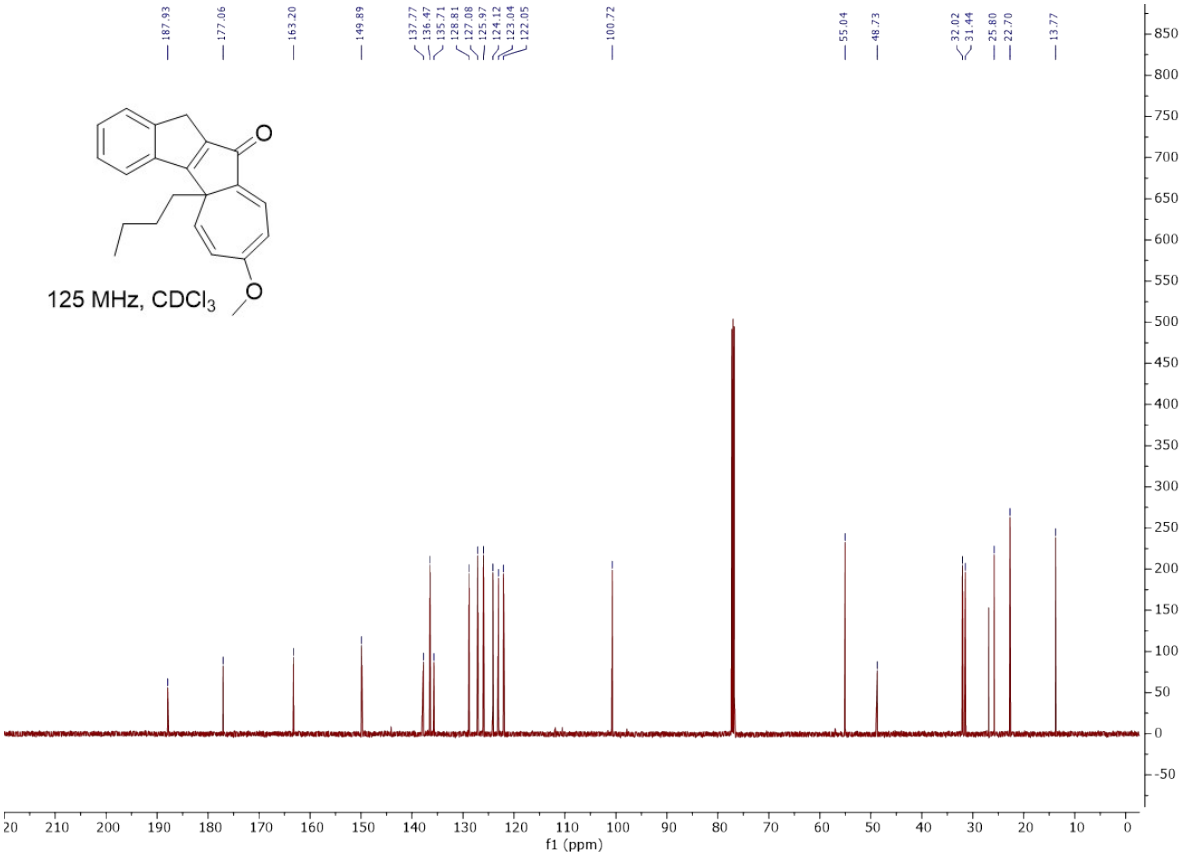

-105.88
-105.92
O
O
O
F
O
376 MHz, CDCl3
f1 (ppm)

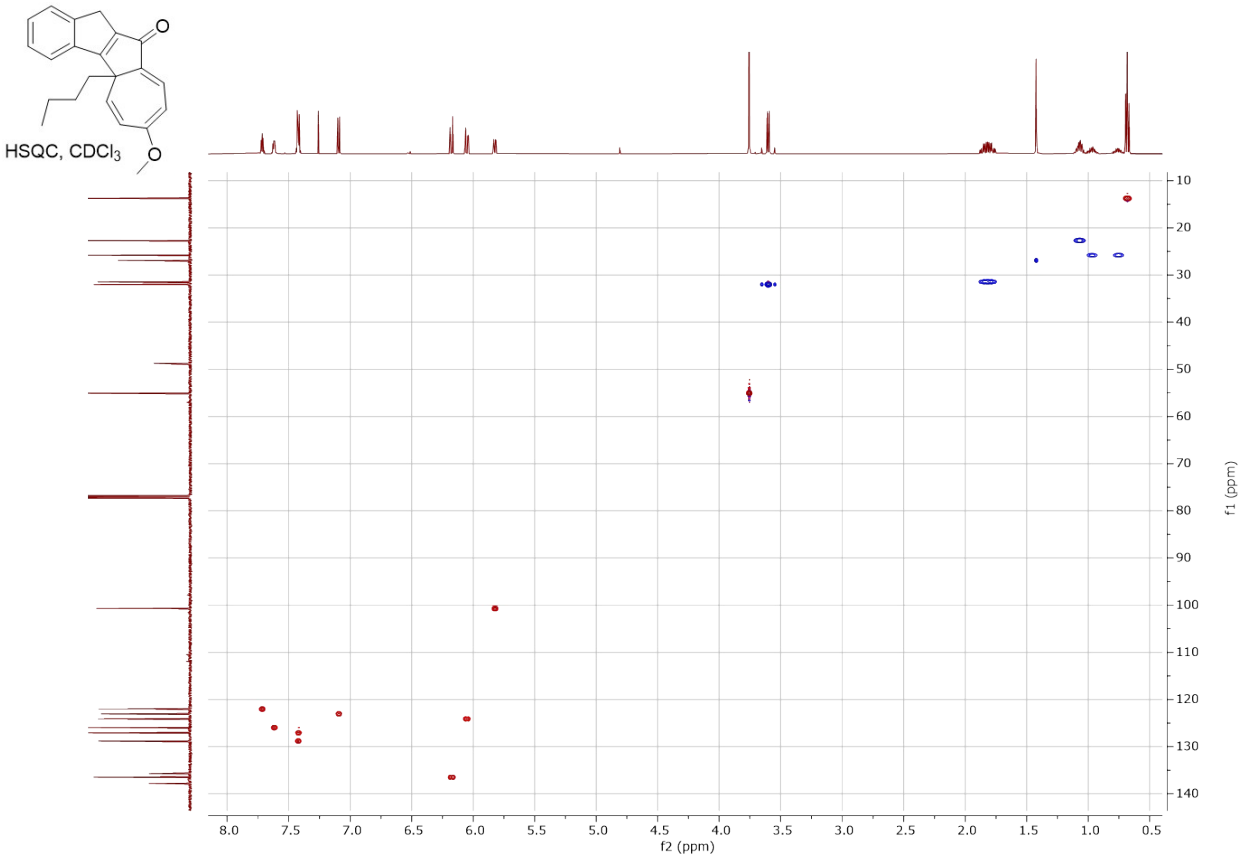

HSQC, CDCl3
f2 (ppm)
f1 (ppm)

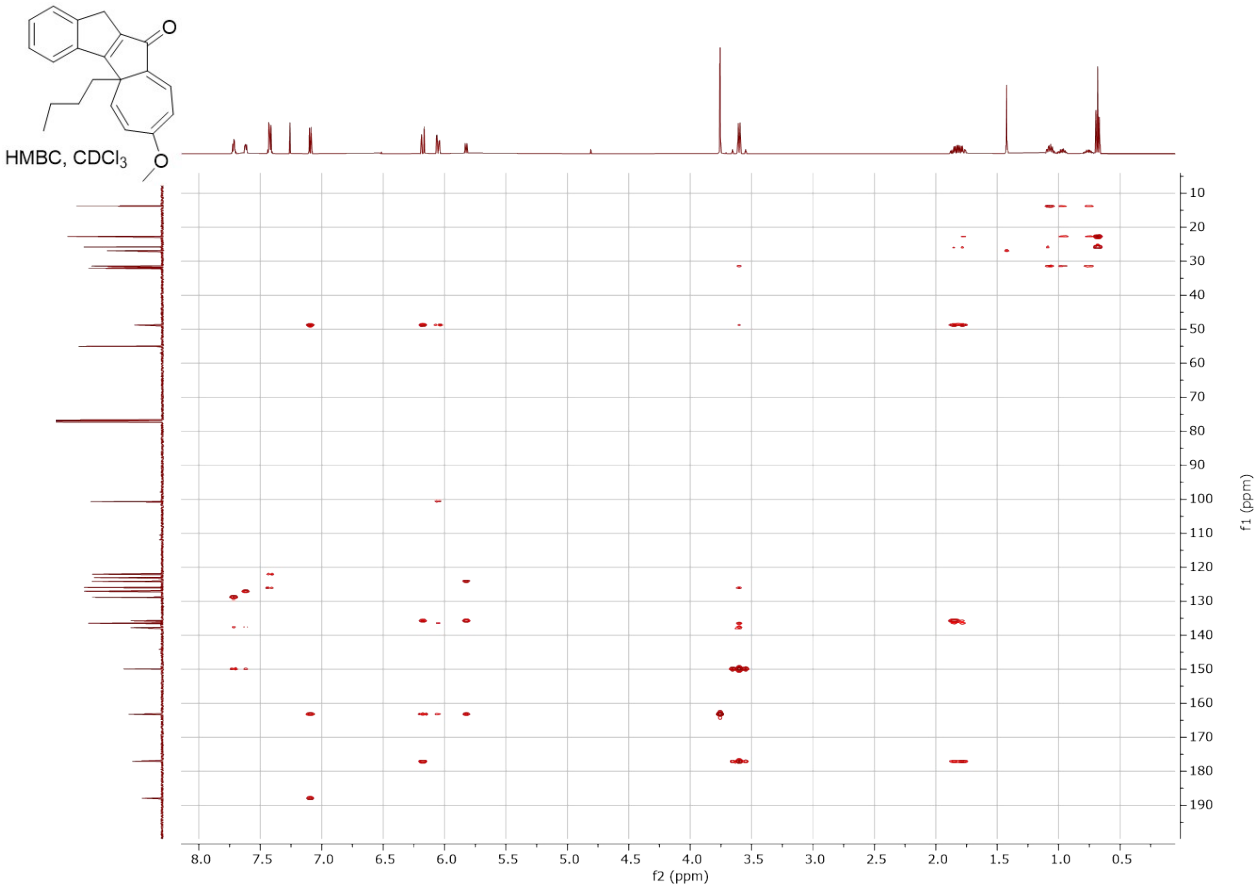

HMBC, CDCl3
f2 (ppm)
f1 (ppm)

Rac-4c-Butyl-7-methoxy-4c,11-dihydro-10H-indeno[1,2-a]azulen-10-one, 5i

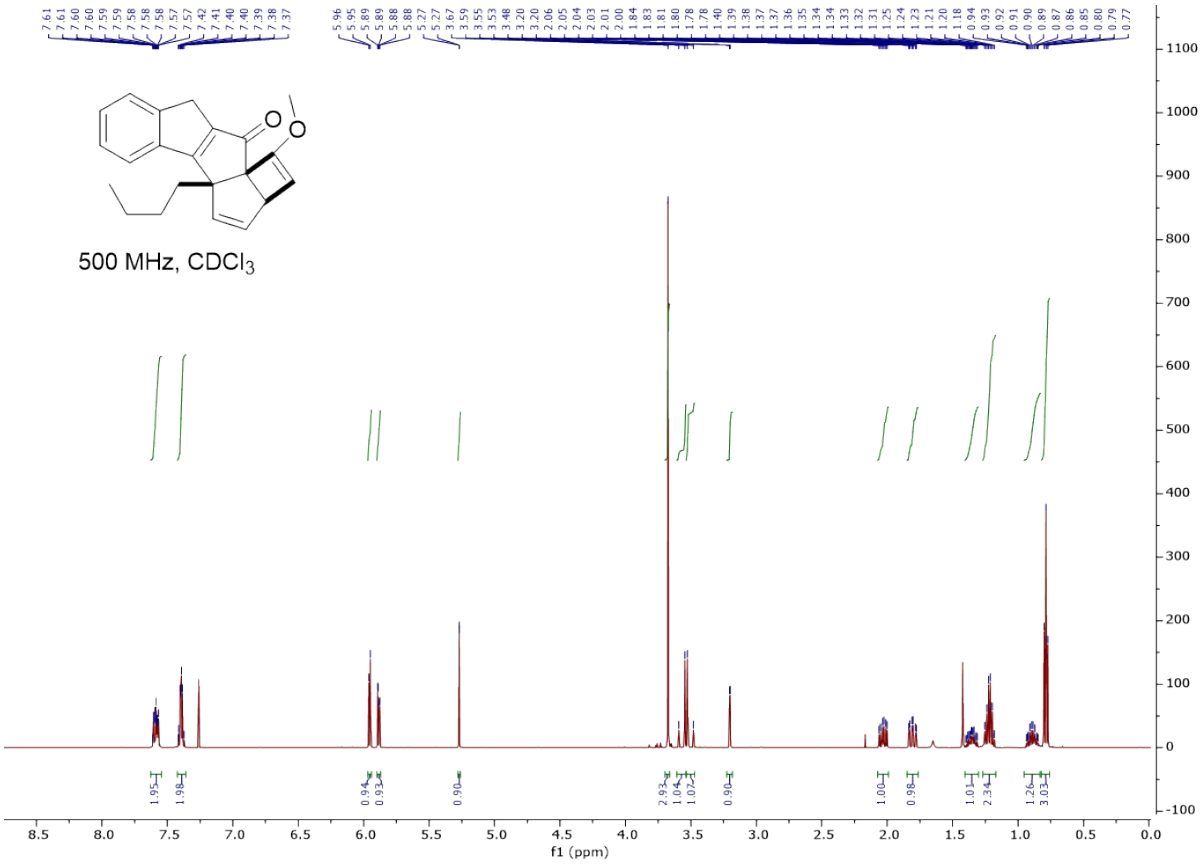


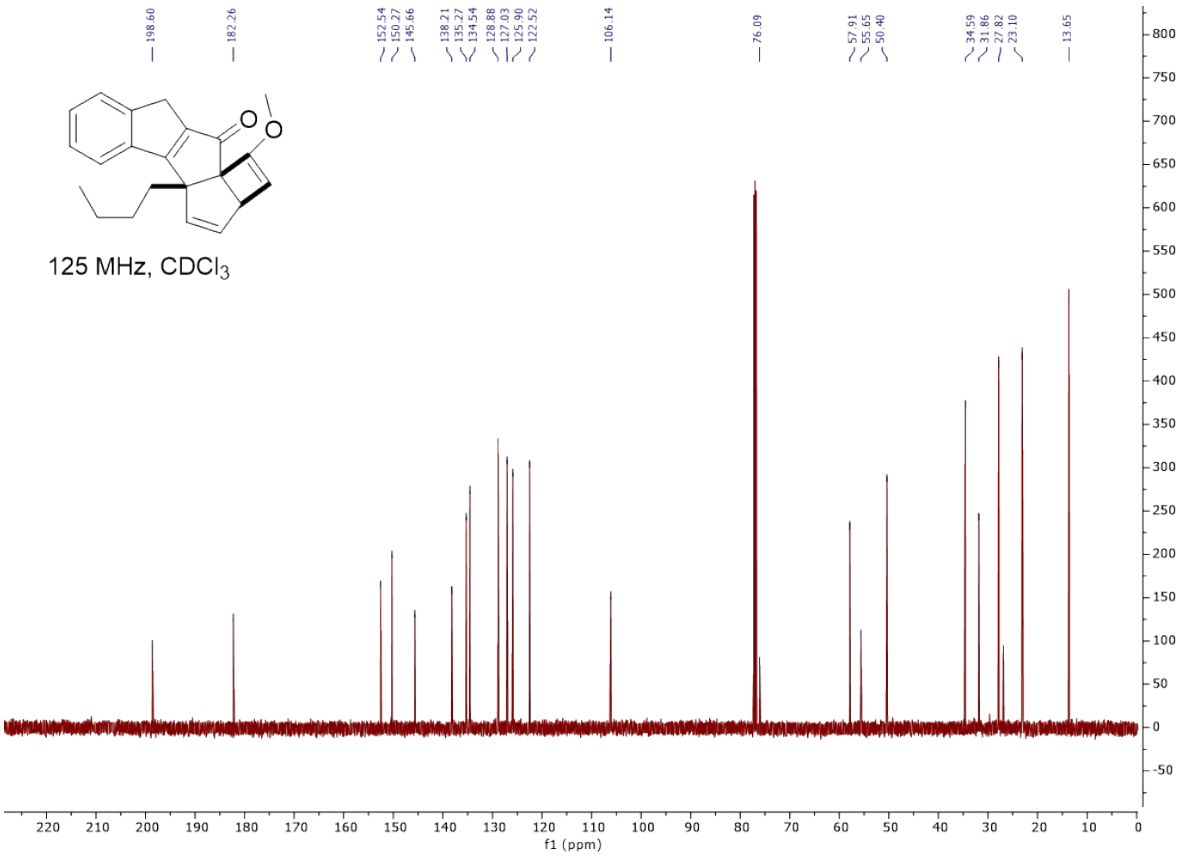


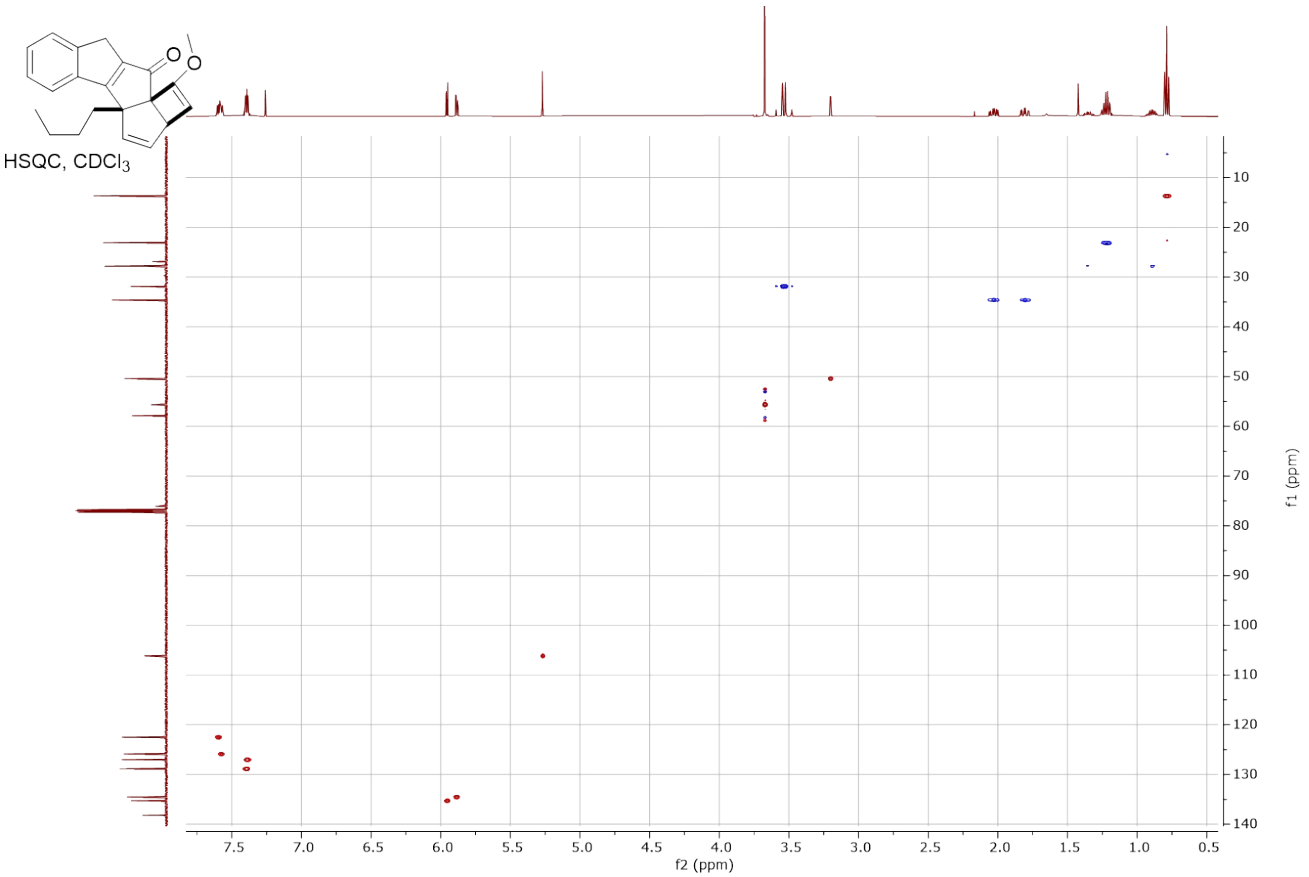

HSQC, CDCl3
f2 (ppm)
f1 (ppm)

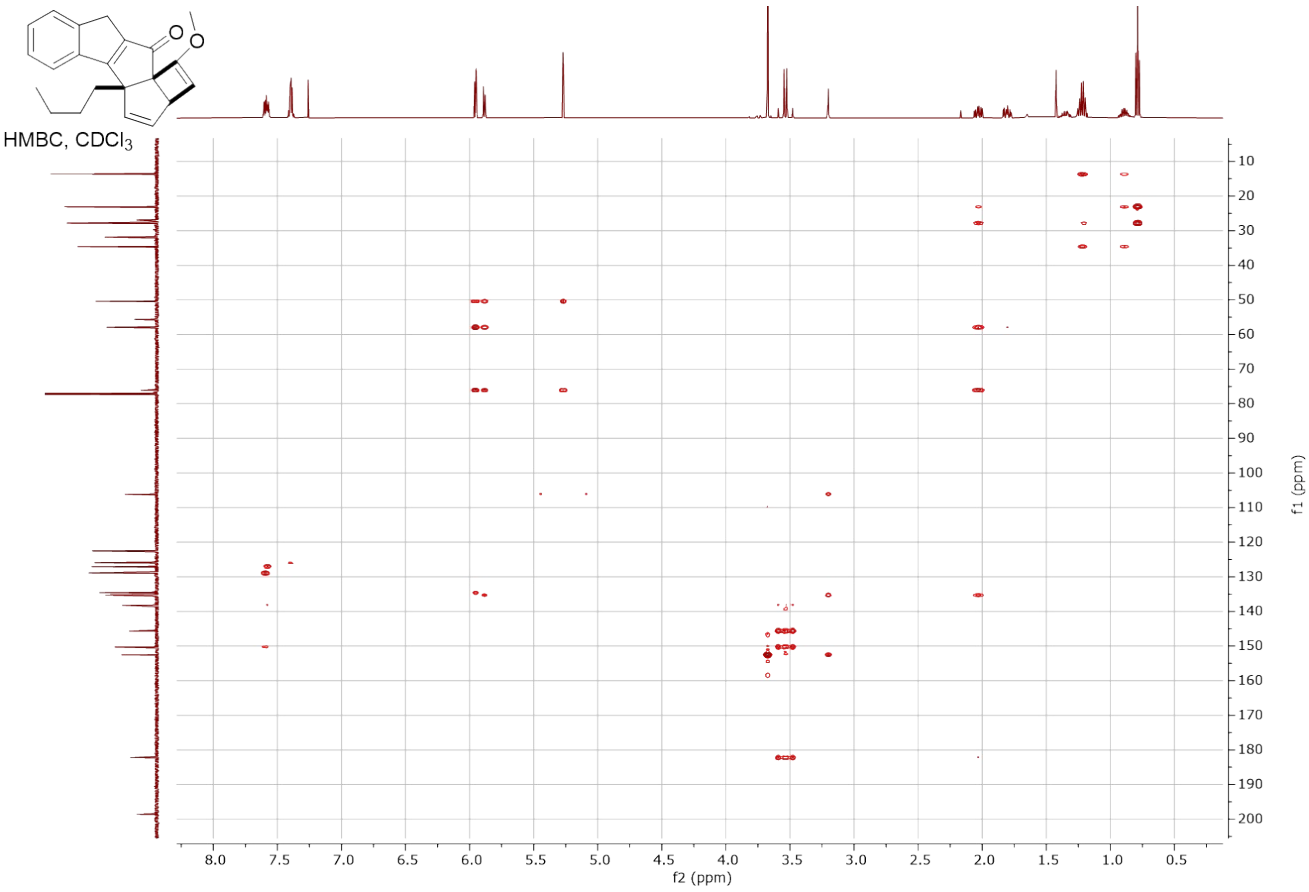

HMBC, CDCl3
f2 (ppm)
f1 (ppm)

Rac-(2aR,4aR,10aR)-4a-Butyl-1-methoxy-4a,9-dihydrocyclobuta[3a,4]pentaleno[1,2-a]inden-10(2aH)-one, 5k

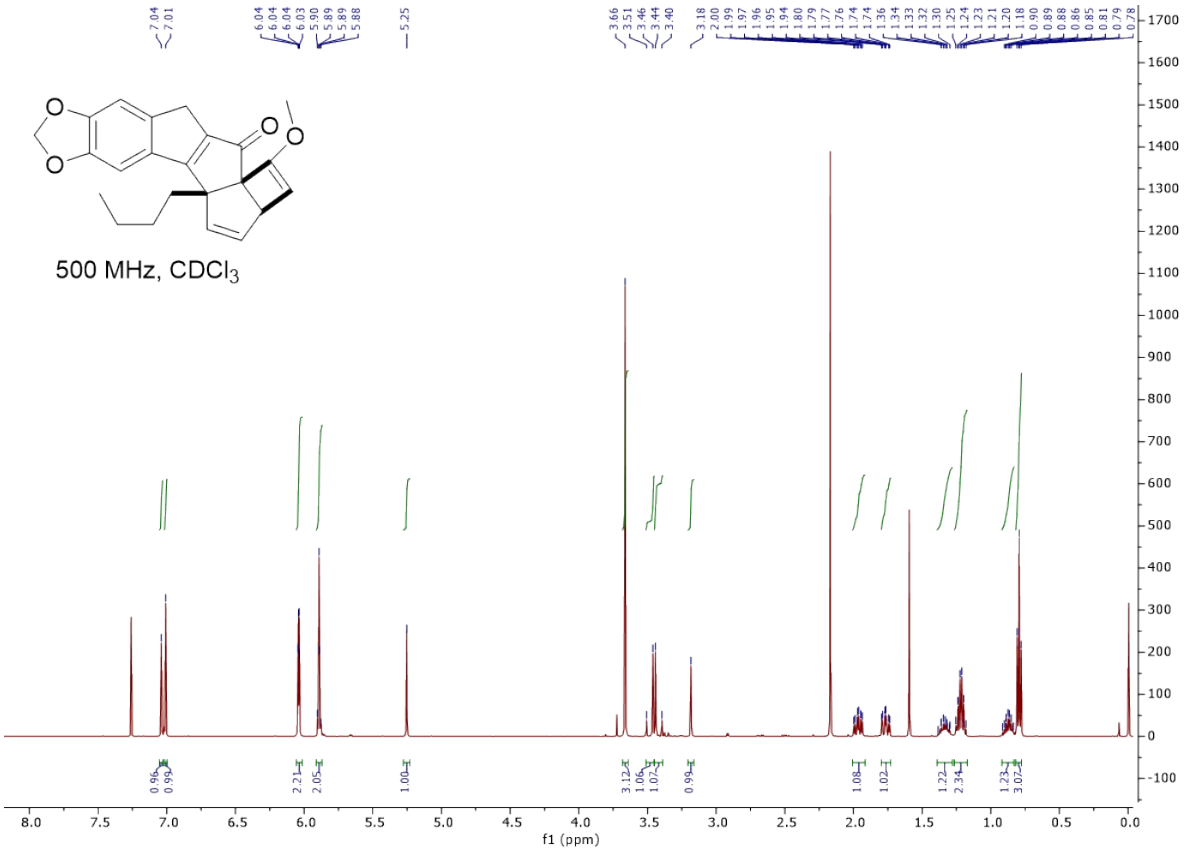


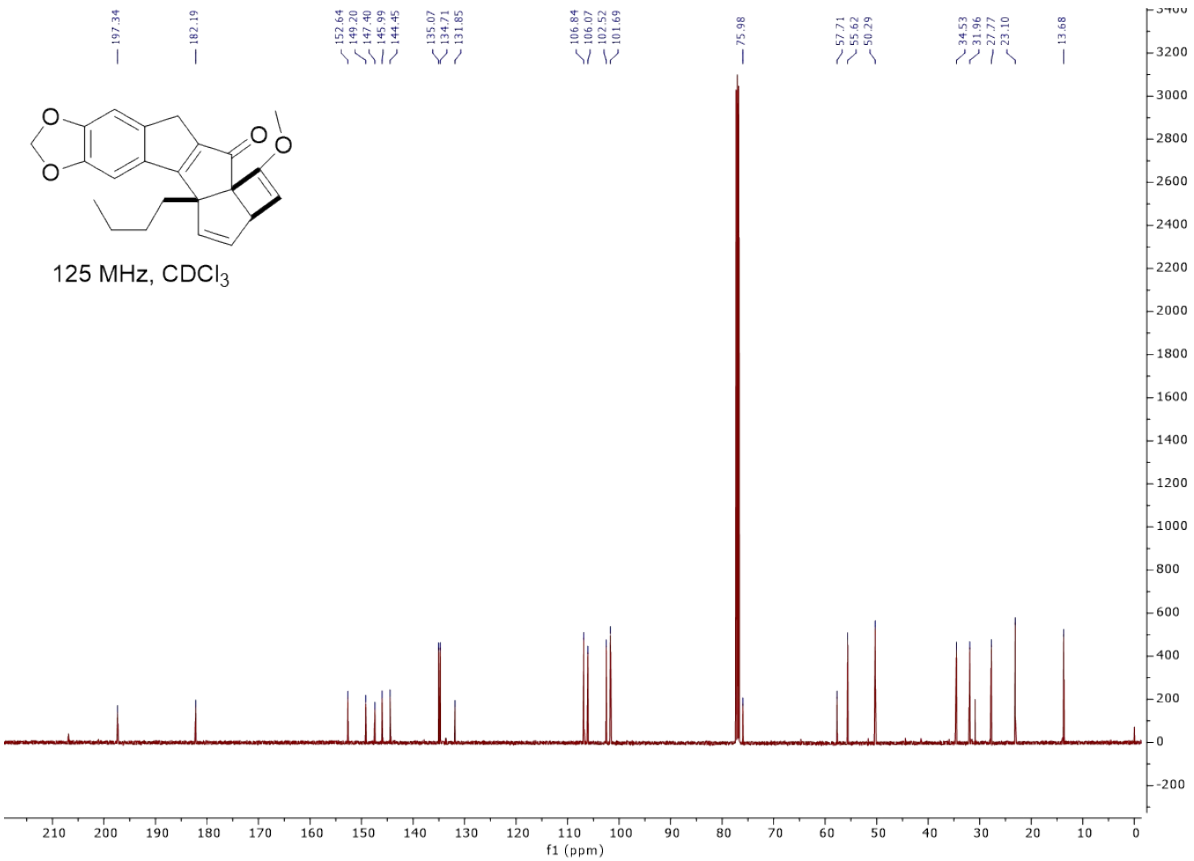


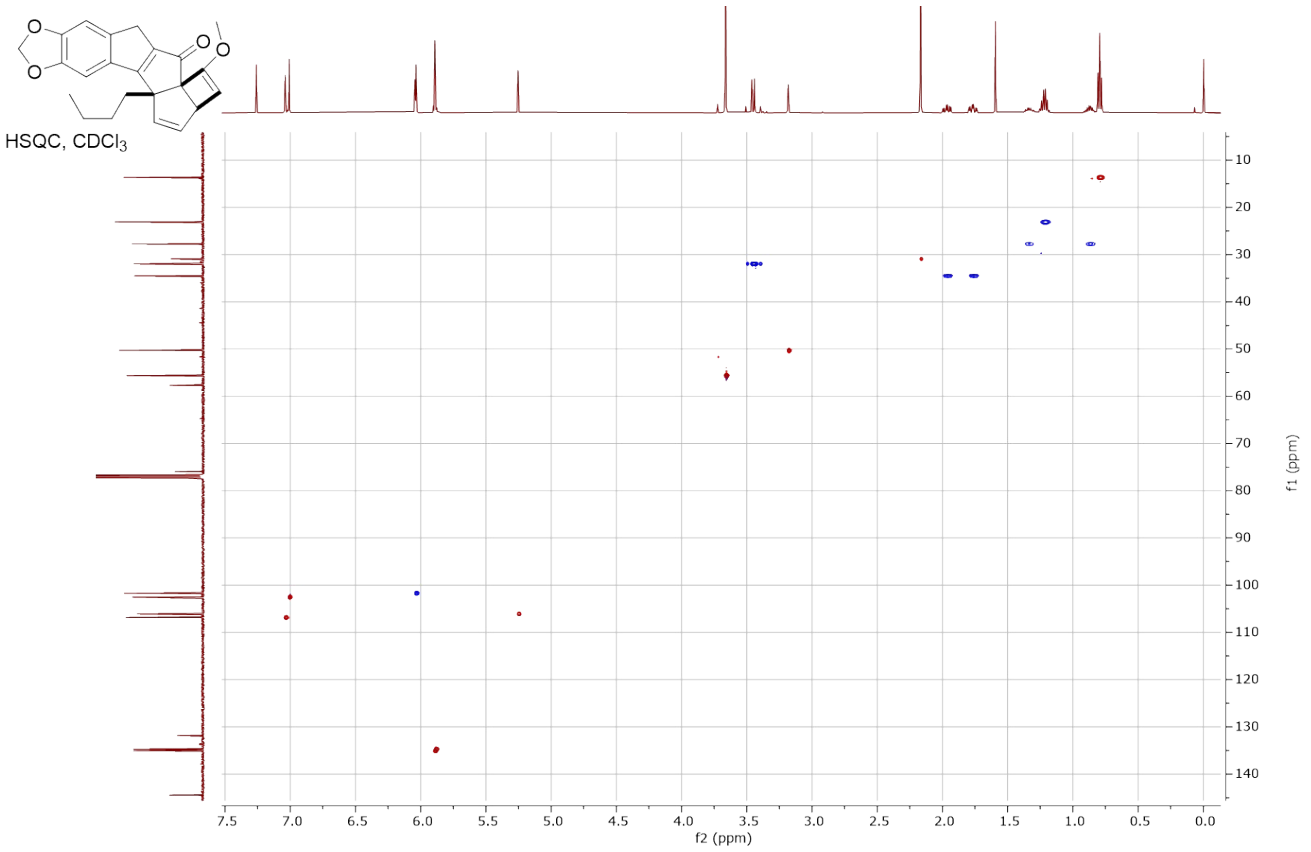

HSQC, CDCl3
f2 (ppm)
f1 (ppm)

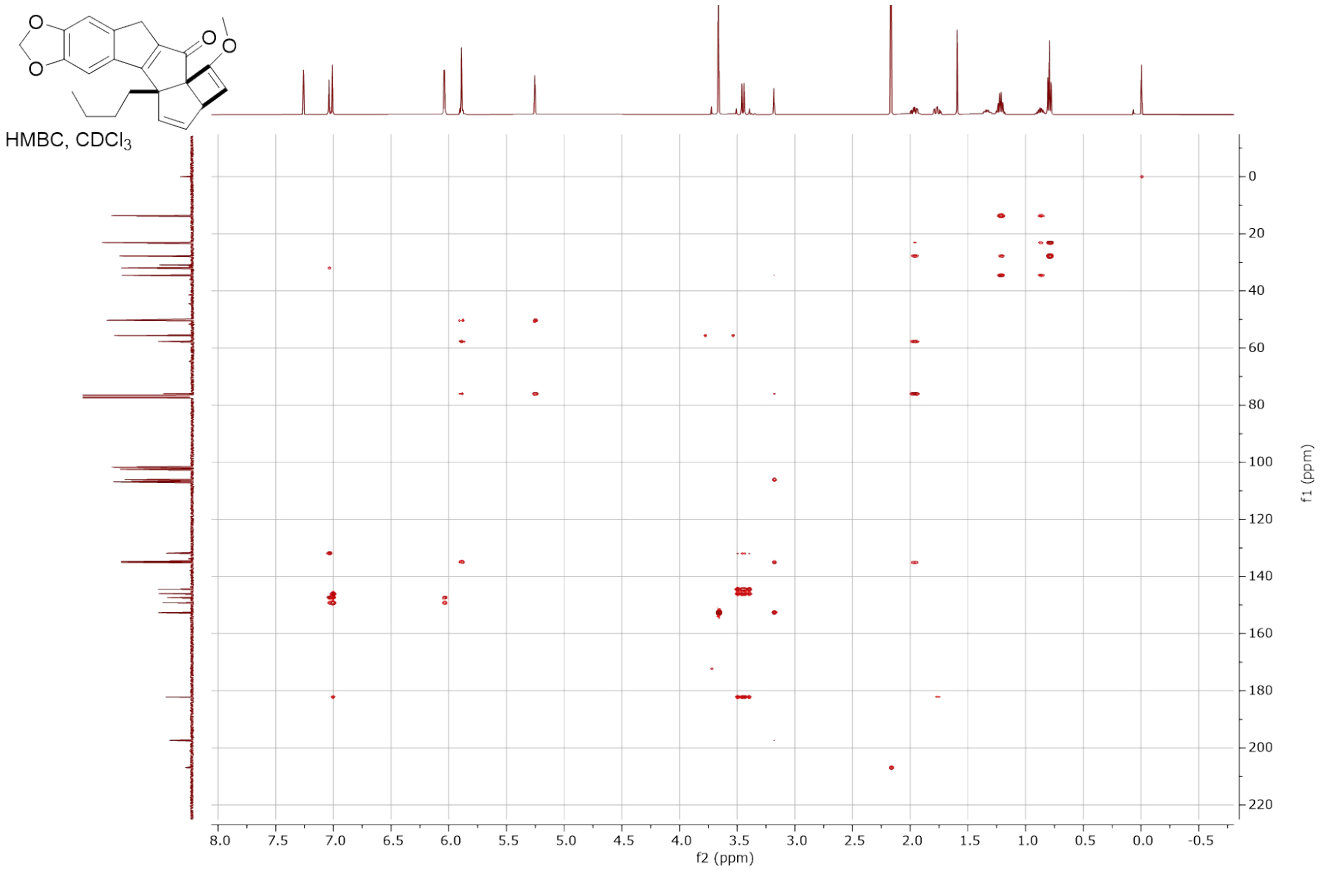

HMBC, CDCl3
f2 (ppm)
f1 (ppm)

Rac-(2aR,4aR,11aR)-4a-Butyl-1-methoxy-4a,10-dihydrocyclobuta[3a',4']pentaleno[1',2':1,2]-indeno[5,6-d][1,3]dioxol-11(2aH)-one, 5l

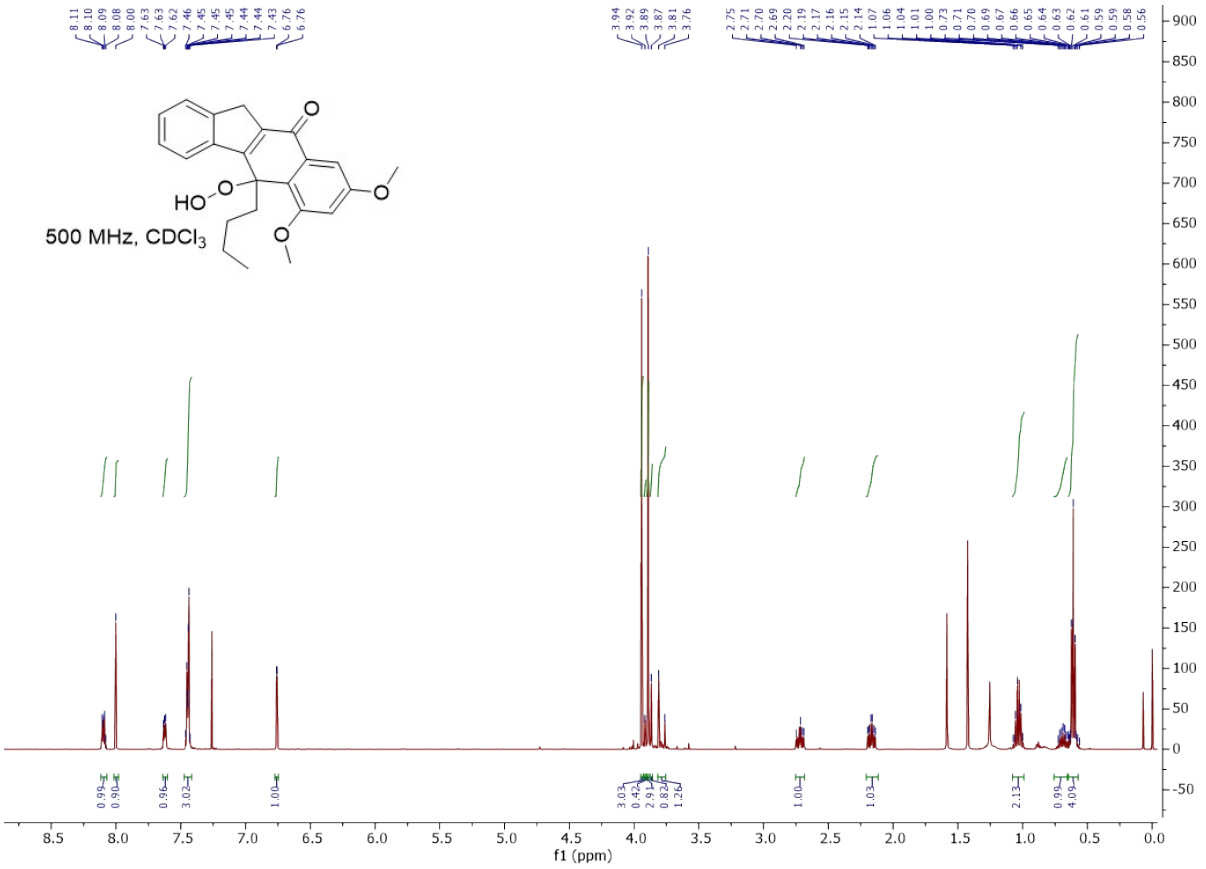


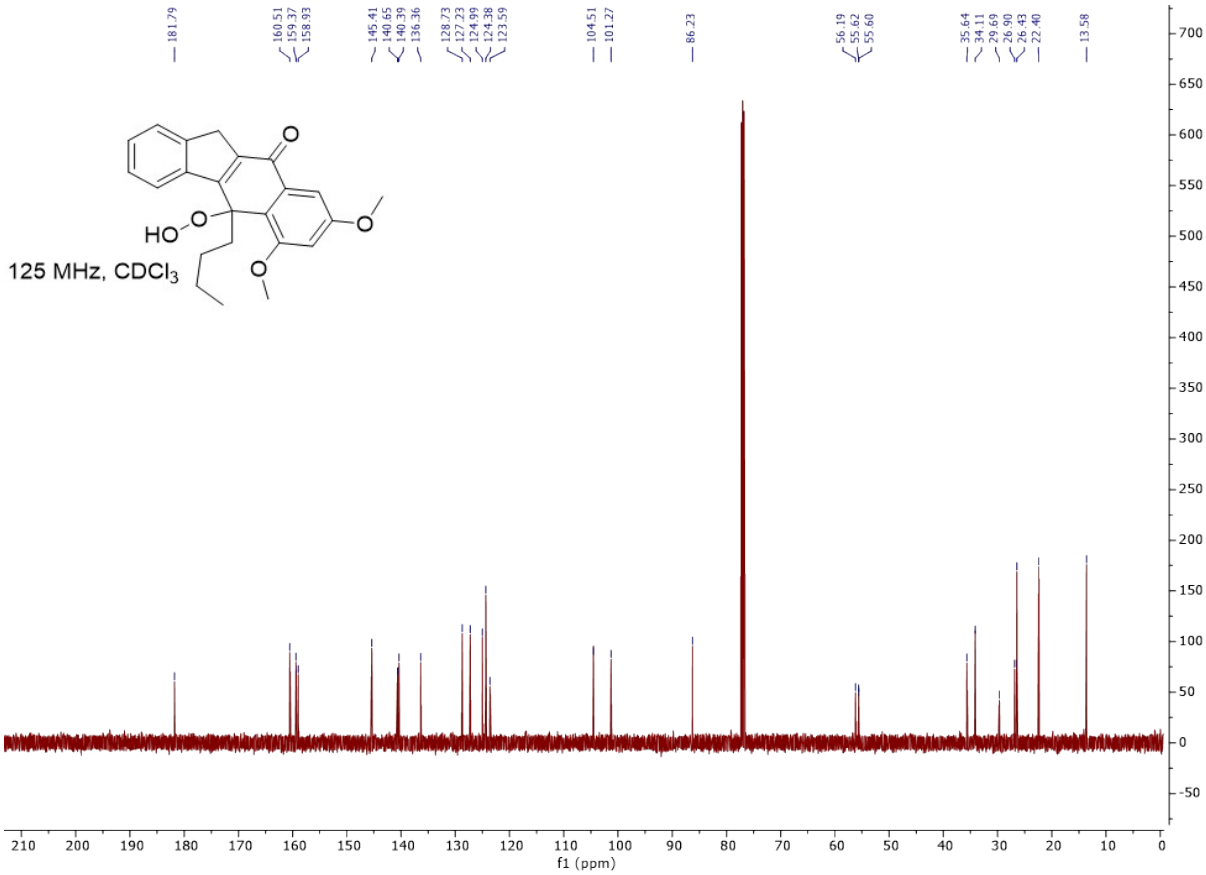


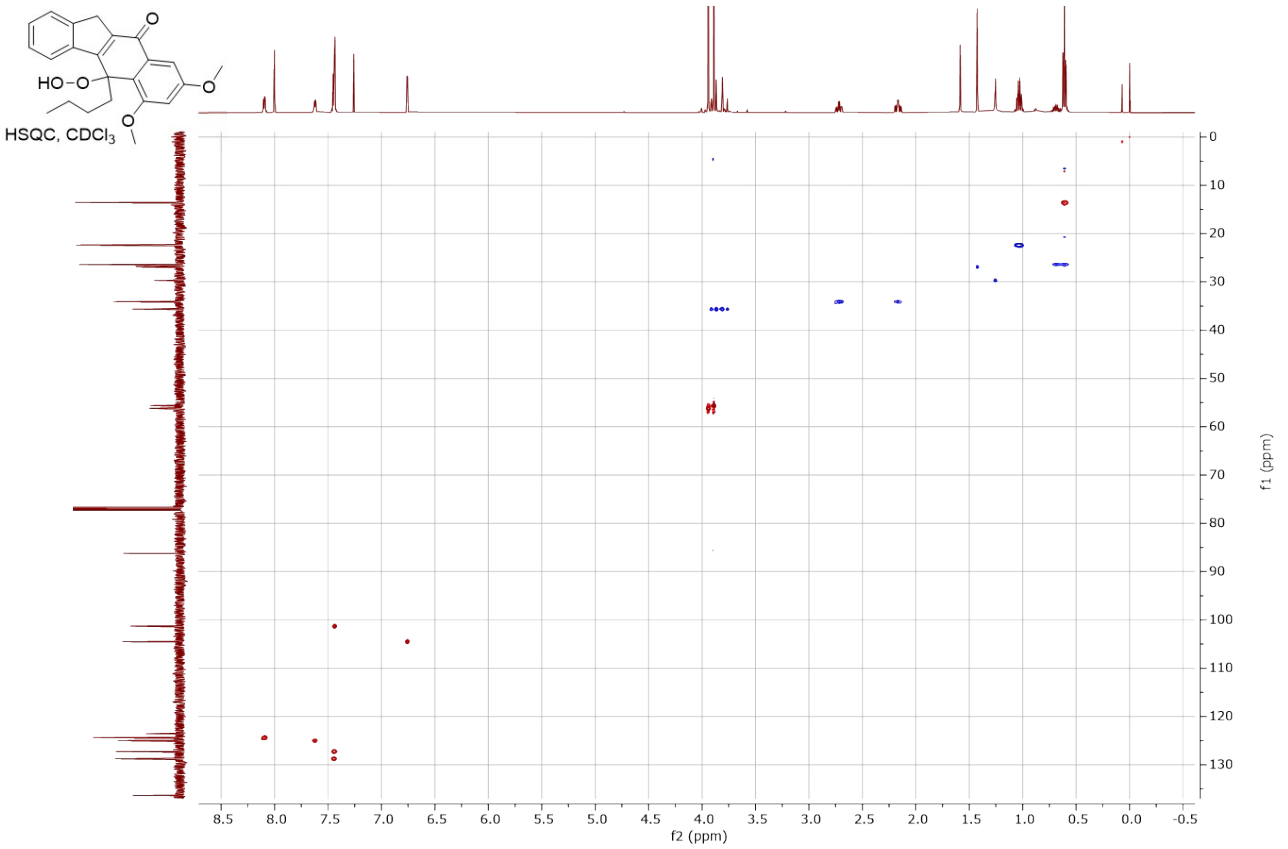

HSQC, CDCl3
f2 (ppm)
f1 (ppm)

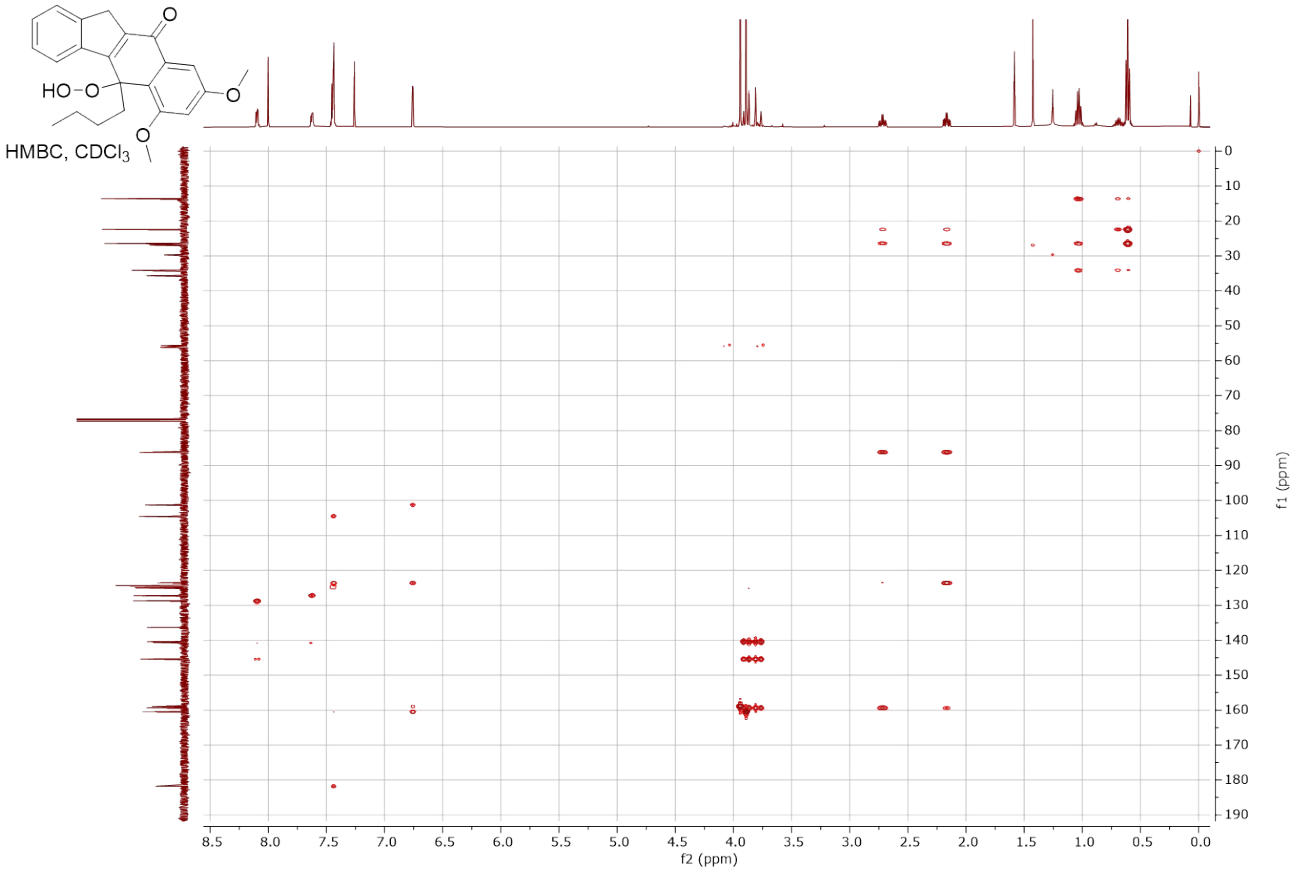

HMBC, CDCl3
f2 (ppm)
f1 (ppm)

Rac-5-Butyl-5-hydroperoxy-6,8-dimethoxy-5,5a,9a,11-tetrahydro-10H-benzo[b]fluoren-10-one, 5m

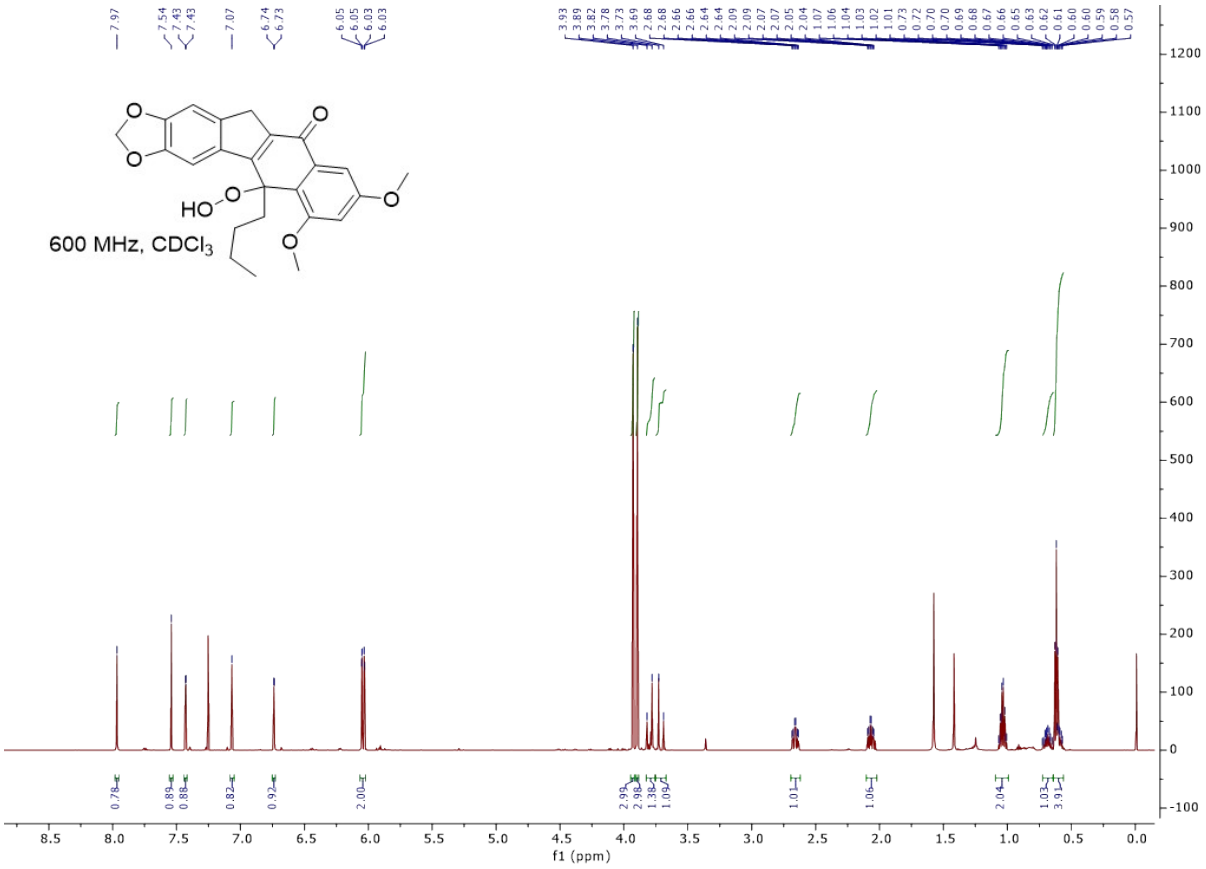


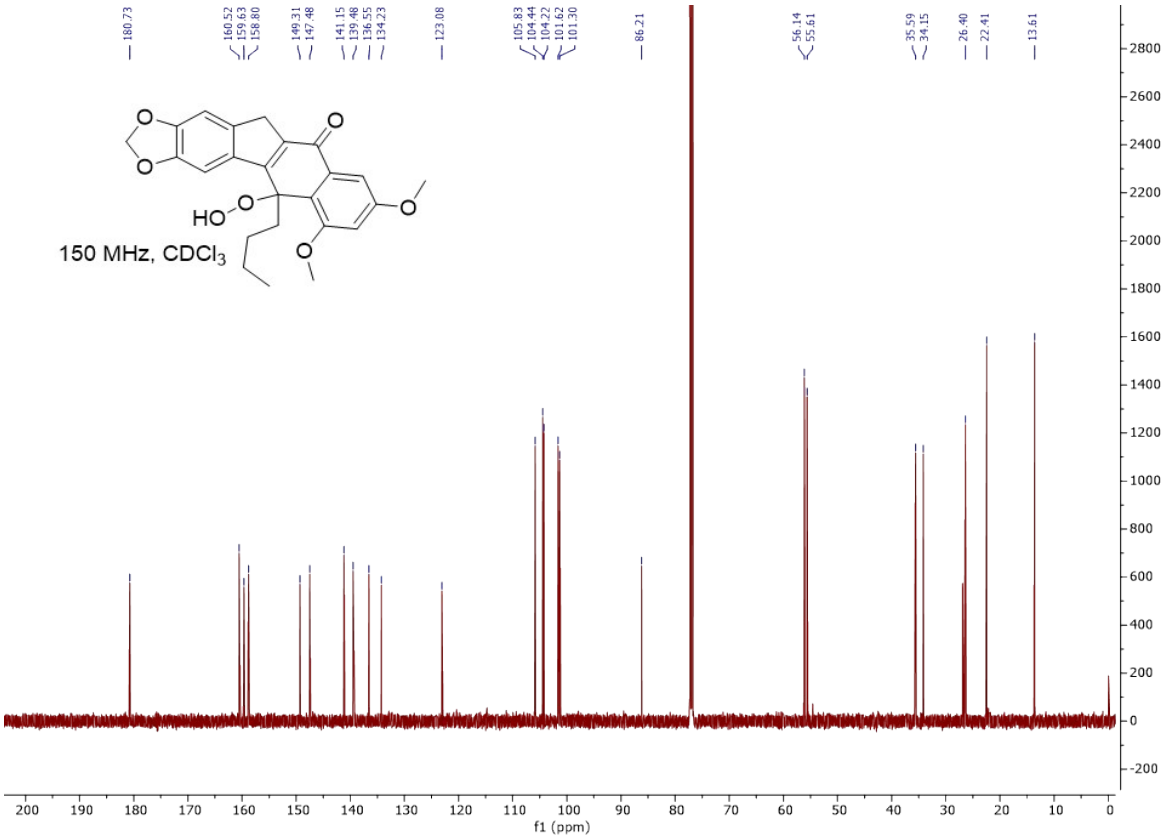


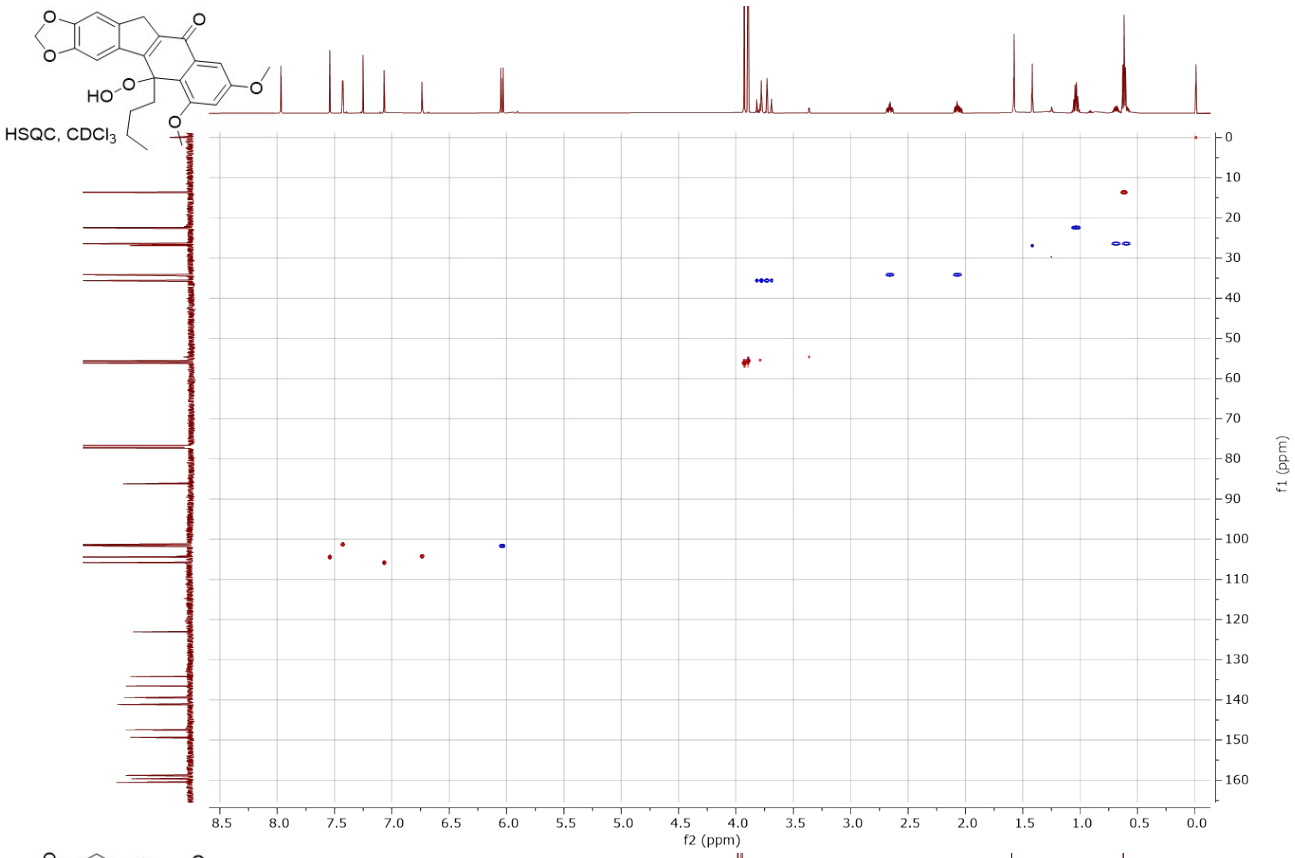

HO–O
O
O
O
HSQC, CDCl3
f2 (ppm)
f1 (ppm)

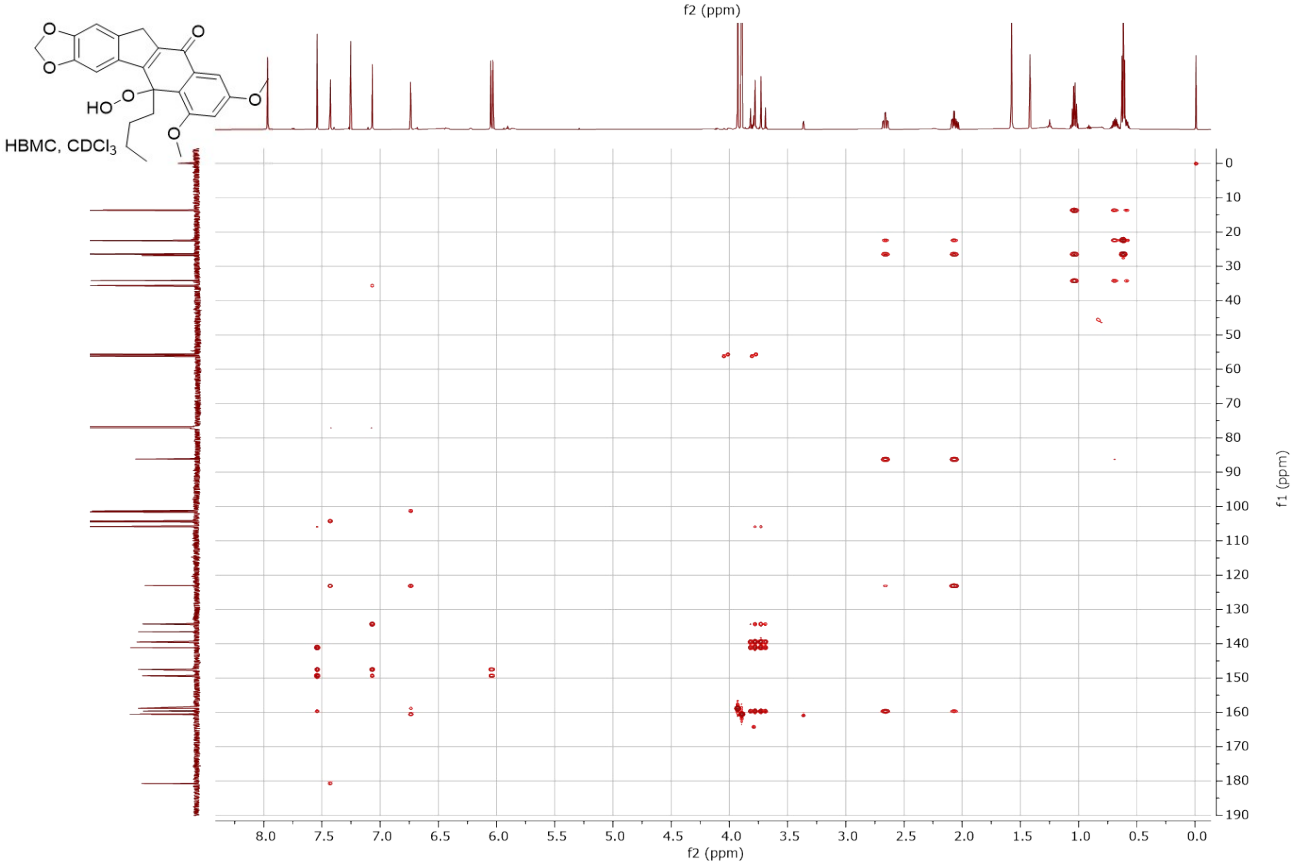

HO–O
O
O
O
HMBC, CDCl3
f2 (ppm)
f1 (ppm)

Rac-5-Butyl-5-hydroperoxy-6,8-dimethoxy-5,5a,9a,11-tetrahydro-10H-benzo[6,7]fluoreno[2,3-d][1,3]dioxol-10-one, 5n






HSQC, CDCl3
f2 (ppm)
f1 (ppm)


HBMC, CDCl3
f2 (ppm)
f1 (ppm)

Rac-(2,4-Dimethoxyphenyl)(3-(6-(hex-1-yn-1-yl)benzo[d][1,3]dioxol-5-yl)oxiran-2-yl)methanone, 6: