Supporting Information for the Paper

Transition Metal-Free Cyclobutene Rearrangement in Fused Naphthalen-1-ones: Controlled Access to Functionalized Quinones§

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§In memory of Prof. Odón Arjona

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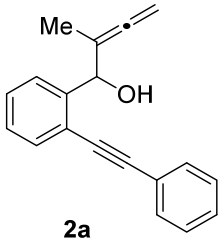
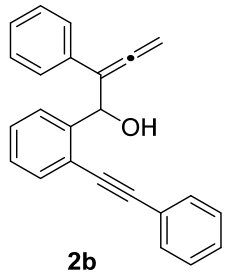
General Methods: ^{1}H NMR, ^{13}C NMR, and ^{19}F NMR spectra were recorded on a Bruker Avance AMX-700, Bruker AMX-500, or Bruker Avance-DPX 300. NMR spectra were recorded in $CDCl_3$ or C_6D_6, solutions, except otherwise stated. Chemical shifts are given in ppm relative to TMS (^{1}H, 0.0 ppm), or $CDCl_3$ (^{1}H, 7.27 ppm; ^{13}C, 76.9 ppm), or C_6D_6 (^{1}H, 7.16 ppm; 13C, 128.0 ppm). Low- and high-resolution mass spectra were taken on an AGILENT 6520 Accurate Mass QTOF LC/MS spectrometer using the electronic impact (EI) or electrospray modes (ES) unless otherwise stated. IR spectra were recorded on a Bruker Tensor 27 spectrometer. All commercially available compounds were used without further purification.

Indium-promoted reaction between 3-substituted prop-2-ynyl bromides and aldehydes; general procedure for the synthesis of allenynols 2a–k. 1-Bromo-2-butyne or (3-bromoprop-1-yn-1-yl)benzene (3.0 mmol) was added to a well stirred suspension of the corresponding aldehyde (1.0 mmol) and indium powder (6.0 mmol) in THF/NH_4Cl (aq. sat.) (1:5, 5 mL) at 0 ºC. After disappearance of the starting material (TLC) the mixture was extracted with ethyl acetate (3 x 5 mL). The organic extract was washed with brine, dried ($MgSO_4$) and concentrated under reduced pressure. Chromatography of the residue using hexanes/ethyl acetate mixtures or toluene gave analytically pure compounds. Spectroscopic and analytical data for allenynols **2** follow:



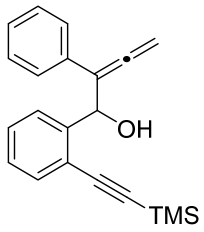
2a

Allenynol 2a. From 357 mg (1.70 mmol) of aldehyde **1a**, and after chromatography of the residue using hexanes/ethyl acetate (15:1) as eluent, gave compound **2a** (311 mg, 69%) as a pale yellow oil; ^{1}H-NMR (300 MHz, $CDCl_3$, 25 ºC) δ: 7.54 (m, 4H), 7.37 (m, 4H), 7.29 (m, 1H), 5.70 (s, 1H), 4.86 (m, 2H), 2.48 (m, 1H), 1.68 (t, J = 3.1 Hz, 3H); ^{13}C-NMR (75 MHz, $CDCl_3$, 25 ºC) δ: 205.0, 143.6, 132.3 (2C), 131.5, 128.5, 128.4 (2C), 128.4, 127.5, 126.4, 123.2, 121.6, 102.3, 94.3, 87.3, 77.9, 72.4, 14.9; IR ($CHCl_3$, cm^{-1}): ν 3303; HRMS (ES): calcd for $C_{19}H_{16}NaO$ $[M + Na]^+$: 283.1093; found: 283.1101.



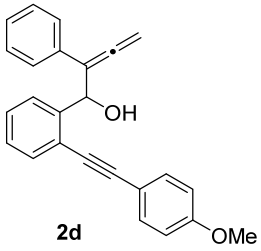
2b

Allenynol 2b. From 394 mg (1.90 mmol) of aldehyde **1a**, and after chromatography of the residue using hexanes/ethyl acetate (14:1) as eluent, gave compound **2a** (365 mg, 60%) as a pale yellow oil; ^{1}H-NMR (300 MHz, C_6D_6, 25 ºC) δ: 7.62 (3H), 7.53 (dd, *J* = 7.6, 1.4 Hz, 1H), 7.27 (m, 2H), 7.08 (m, 5H), 6.93 (m, 3H), 6.35 (s, 1H), 4.73 (m, 2H), 1.92 (br. s, 1H); ^{13}C-NMR (75 MHz, C_6D_6, 25 ºC) δ: 209.2, 145.4, 135.7, 132.2, 131.9 (2C), 128.8 (2C), 128.6 (2C), 128.6, 127.5, 127.4 (2C), 127.3, 127.2, 126.8, 123.7, 122.1, 110.7, 95.3, 88.1, 80.4, 71.4; IR (C_6D_6, cm^{-1}): ν 3416; HRMS (ES): calcd for $C_{24}H_{18}NaO$ [*M* + Na]$^{+}$: 343.1250; found: 345.1234.



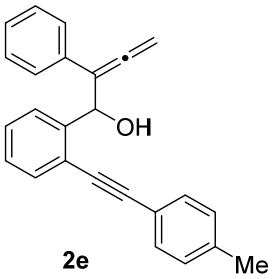
2c

Allenynol 2c. From 293 mg (1.40 mmol) of aldehyde **1b**, and after chromatography of the residue using hexanes/ethyl acetate (8:1) as eluent, gave compound **2c** (299 mg, 65%) as a yellow oil; ^{1}H-NMR (300 MHz, $CDCl_3$, 25 ºC) δ: 7.30 (m, 4H), 7.08 (m, 5H), 6.04 (s, 1H), 4.96 (m, 2H), 2.39 (br. s, 1H), 0.00 (s, 9H); ^{13}C-NMR (75 MHz, C_6D_6, 25 ºC) δ: 208.2, 144.3, 134.5, 132.4, 128.7, 128.4 (2C), 127.4, 127.0, 126.6 (2C), 126.4, 121.6, 109.8, 102.8, 99.8, 81.0, 70.3, –0.2 (3C); IR ($CHCl_3$, cm^{-1}): ν 3418; HRMS (ES): calcd for $C_{21}H_{23}OSi$ [*M* + H]$^{+}$: 319.1513; found: 319.1503.



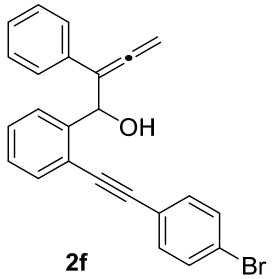
2d

Allenynol 2d. From 335 mg (1.50 mmol) of aldehyde **1c**, and after chromatography of the residue using hexanes/ethyl acetate (9:1) as eluent, gave compound **2d** (284 mg, 53%) as a pale yellow oil; ^{1}H-NMR (300 MHz, C_6D_6, 25 ºC) δ: 7.66 (3H), 7.55 (dd, *J* = 7.6, 1.4 Hz, 1H), 7.22 (d, *J* = 8.8 Hz, 2H), 7.08 (m, 5H), 6.56 (d, *J* = 8.8 Hz, 2H), 6.41 (m, 1H), 4.75 (m, 2H), 3.15 (s, 3H), 2.23 (d, *J* = 5.8 Hz, 1H); ^{13}C-NMR (75 MHz, C_6D_6, 25 ºC) δ: 209.3, 160.2, 145.1, 135.8, 133.4 (2C), 132.0, 128.8 (2C), 128.3, 127.5, 127.3 (2C), 127.2, 126.8, 122.5, 115.8, 114.4 (2C), 110.6, 95.5, 86.9, 80.5, 71.4, 54.8; IR (C_6D_6, cm^{-1}): ν 3379; HRMS (ES): calcd for $C_{25}H_{20}NaO_2$ [*M* + Na]$^+$: 375.1355; found: 375.1365.



2e

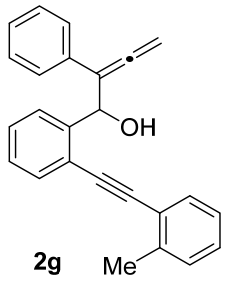
Allenynol 2e. From 493 mg (2.20 mmol) of aldehyde **1d**, and after chromatography of the residue using hexanes/ethyl acetate (7:1) as eluent, gave compound **2e** (504 mg, 67%) as a pale yellow oil; ^{1}H-NMR (300 MHz, C_6D_6, 25 ºC) δ: 7.64 (m, 2H), 7.53 (m, 3H), 7.21 (d, *J* = 8.1 Hz, 2H), 6.99 (m, 4H), 6.76 (d, *J* = 7.9 Hz, 2H), 6.38 (m, 1H), 4.74 (m, 2H), 1.95 (m, 4H); ^{13}C-NMR (75 MHz, C_6D_6, 25 ºC) δ: 209.3, 145.3, 138.5, 135.8, 132.1, 131.9 (2C), 129.4, 129.3 (2C), 128.8 (2C), 127.5, 127.4 (2C), 127.2, 126.8, 122.3, 120.7, 110.7, 95.6, 87.5, 80.4, 71.4, 21.3; IR (C_6D_6, cm^{-1}): ν 3354; HRMS (ES): calcd for $C_{25}H_{20}NaO$ [*M* + Na]$^+$: 359.1406; found: 359.1417.



2f

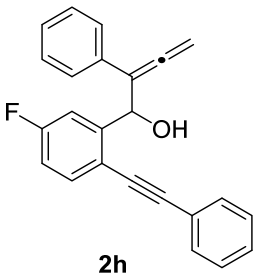
Allenynol 2f. From 441 mg (1.50 mmol) of aldehyde **1e**, and after chromatography of the residue using hexanes/ethyl acetate (9:1) as eluent, gave compound **2f** (304 mg, 49%) as a pale yellow oil; ^{1}H-NMR (300 MHz, C_6D_6, 25 ºC) δ: 7.65 (m, 1H), 7.57 (m, 2H), 7.48 (dd, *J* = 7.6, 1.4 Hz, 1H), 7.11

(m, 3H), 6.99 (m, 4H), 6.79 (d, J = 8.5 Hz, 2H), 6.27 (br. s, 1H), 4.70 (m, 2H), 2.52 (br. s, 1H); ^{13}C-NMR (75 MHz, C_6D_6, 25 ºC) δ: 209.3, 145.6, 135.7, 133.2 (2C), 132.0, 131.8 (2C), 128.9, 128.8(2C), 127.4, 127.3, 127.1 (2C), 126.7, 122.4 (2C), 121.6, 110.5, 94.2, 89.1, 80.6, 71.4; IR (C_6D_6, cm^{-1}): ν 3346; HRMS (ES): calcd for $C_{24}H_{17}BrNaO$ [M + Na]$^+$: 423.0355; found: 423.0357.



2g

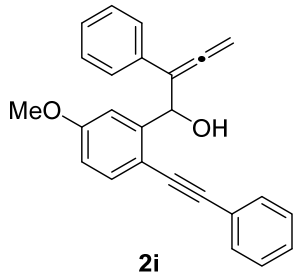
Allenynol 2g. From 270 mg (1.20 mmol) of aldehyde **1f** and after chromatography of the residue using toluene as eluent, gave compound **2g** (169 mg, 41%) as a pale yellow oil; ^{1}H-NMR (300 MHz, C_6D_6, 25 ºC) δ: 7.62 (m, 3H), 7.52 (m, 1H), 7.31 (d, J = 7.5 Hz, 1H), 7.11 (m, 3H), 6.94 (m, 5H), 6.40 (t, J = 2.0 Hz, 1H), 4.75 (d, J = 2.2 Hz, 2H), 2.33 (s, 3H); ^{13}C-NMR (75 MHz, C_6D_6, 25 ºC) δ: 209.1, 144.9, 140.3, 135.4, 132.4, 129.7, 128.8 (2C), 128.7, 128.6, 127.6, 127.4, 127.3 (2C), 127.2, 127.0, 125.9, 123.5, 122.5, 110.5, 94.1, 91.9, 80.6, 71.1, 20.9; IR (C_6D_6, cm^{-1}): ν 3330; HRMS (ES): calcd for $C_{25}H_{20}NaO$ [M + Na]$^+$: 359.1406; found: 359.1401.



2h

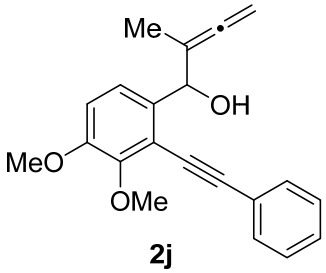
Allenynol 2h. From 647 mg (2.90 mmol) of aldehyde **1g**, and after chromatography of the residue using toluene as eluent, gave compound **2h** (344 mg, 35%) as a yellow oil; ^{1}H-NMR (300 MHz, C_6D_6, 25 ºC) δ: 7.57 (m, 2H), 7.48 (m, 1H), 7.28 (dd, J = 8.5, 5.6 Hz, 1H), 7.17 (m, 3H), 7.02 (m, 2H), 6.92 (m, 3H), 6.61 (td, J = 8.3, 2.8 Hz, 1H), 6.20 (br. s, 1H), 4.64 (d, J = 2.0 Hz, 2H), 1.77 (m, 1H); ^{13}C-NMR (75 MHz, C_6D_6, 25 ºC) δ: 209.2, 163.2 (d, J = 248.0 Hz), 148.5 (d, J = 7.5 Hz), 135.5, 133.8 (d, J = 8.2 Hz), 131.8 (2C), 128.9 (2C), 128.6 (2C), 128.4, 127.3, 127.2 (2C), 123.5, 117.8 (d, J = 3.3 Hz), 114.5 (d, J = 22.2 Hz), 114.1 (d, J = 23.3 Hz), 110.1, 94.9, 87.0, 80.5, 71.2; ^{19}F NMR

(282 MHz, C_6D_6, 25 °C): δ = −110.2 (s, 1F); IR (C_6D_6, cm^{-1}): ν 3437; HRMS (ES): calcd for $C_{24}H_{17}FNaO$ [*M* + Na]$^+$: 363.1156; found: 363.1157.



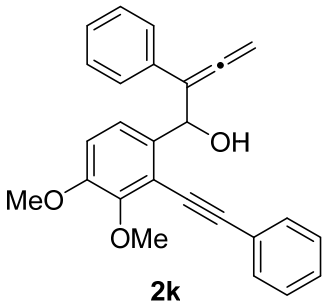
2i

Allenynol 2i. From 176 mg (0.75 mmol) of aldehyde **1h**, and after chromatography of the residue using hexanes/ethyl acetate (8:1) as eluent, gave compound **2i** (180 mg, 68%) as a pale yellow oil; ^{1}H-NMR (300 MHz, $CDCl_3$, 25 ºC) δ: 7.45 (m, 2H), 7.40 (d, *J* = 8.5 Hz, 1H), 7.30–7.14 (m, 8H), 7.07 (d, *J* = 2.7 Hz, 1H), 6.73 (dd, *J* = 8.5, 2.7 Hz, 1H), 6.19 (m, 1H), 5.08 (m, 2H), 3.73 (s, 3H), 2.51 (d, *J* = 5.7 Hz, 1H); ^{13}C-NMR (75 MHz, $CDCl_3$, 25 ºC) δ: 208.2, 159.8, 145.7, 134.5, 133.5, 131.3 (2C), 128.5 (2C), 128.2 (2C), 128.0, 127.0, 126.7 (2C), 123.3, 113.9, 113.2, 112.1, 109.7, 93.2, 87.2, 81.0, 70.6, 55.3; IR ($CHCl_3$, cm^{-1}): ν 3393; HRMS (ES): calcd for $C_{25}H_{20}NaO_2$ [*M* + Na]$^+$: 375.1356; found: 375.1356.



2j

Allenynol 2j. From 307 mg (1.15 mmol) of aldehyde **1i**, and after chromatography of the residue using hexanes/ethyl acetate (7:1) as eluent, gave compound **2j** (282 mg, 77%) as a pale yellow oil; ^{1}H-NMR (300 MHz, $CDCl_3$, 25 ºC) δ: 7.56 (m, 2H), 7.37 (m, 3H), 7.21 (d, *J* = 8.6 Hz, 1H), 6.93 (d, *J* = 8.6 Hz, 1H), 5.59 (m, 1H), 4.85 (m, 2H), 3.99 (s, 3H), 3.89 (s, 3H), 2.43 (d, *J* = 5.0 Hz, 1H), 1.66 (t, *J* = 3.1 Hz, 3H); ^{13}C-NMR (75 MHz, $CDCl_3$, 25 ºC) δ: 205.0, 152.0, 150.2, 136.5, 131.5 (2C), 128.4, 128.3 (2C), 123.4, 122.2, 117.0, 112.6, 102.4, 98.5, 83.2, 77.9, 72.1, 61.0, 56.0, 15.1; IR ($CHCl_3$, cm^{-1}): ν 3445; HRMS (ES): calcd for $C_{21}H_{20}NaO_3$ [*M* + Na]$^+$: 343.1305; found: 343.1304.



2k

Allenynol 2k. From 323 mg (1.21 mmol) of aldehyde **1i**, and after chromatography of the residue using hexanes/ethyl acetate (8:1) as eluent, gave compound **2k** (227 mg, 49%) as a pale yellow oil; ^{1}H-NMR (300 MHz, $CDCl_3$, 25 ºC) δ: 7.38 (m, 2H), 7.29 (m, 3H), 7.20 (m, 5H), 7.13 (m, 2H), 6.77 (d, *J* = 8.6 Hz, 1H), 6.10 (m, 1H), 5.09 (m, 2H), 3.83 (s, 3H), 3.76 (s, 3H); ^{13}C-NMR (75 MHz, $CDCl_3$, 25 ºC) δ: 208.1, 152.0, 150.2, 136.7, 134.5, 131.5 (2C), 128.5(2C), 128.4, 128.2 (2C), 127.0, 126.7 (2C), 123.1, 122.1, 117.1, 112.4, 109.8, 98.7, 83.1, 81.2, 70.1, 61.0, 55.9; IR ($CHCl_3$, cm^{-1}): ν 3438; HRMS (ES): calcd for $C_{26}H_{22}NaO_3$ $[M + Na]^+$: 405.1461; found: 405.1453.

General procedures for the synthesis of tricycles 3a–k.

Procedure A: Dess-Martin periodinane

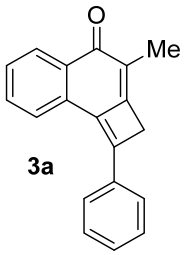
A flask was charged with Dess-Martin periodinane (1.16 mmol) in dichloromethane (4 mL). Then, the corresponding allenynol **2a**–**k** (1.0 mmol) in dichloromethane (3.6 mL) was added by syringe under an atmosphere of argon. The reaction mixture was stirred at RT until the starting material disappeared, as indicated by TLC. After completion of the reaction, diethyl ether (10 mL) and aqueous solution of NaOH (1M, 3 mL) were sequentially added. The product was extracted with dichloromethane (3×10 mL), and then washed with water. The combined organic extract was dried over MgSO4, and the desiccant was removed by filtration. After removal of the solvent in vacuum, the residue was purified by column chromatography on silica gel to give analytically pure compounds.

Procedure B: IBX

IBX (2.0 mmol) was added to a solution of the appropriate allenynol **2a**–**k** (1.0 mmol) in acetonitrile (3.3 mL). Then, the reaction was heated in a sealed tube at 80 ºC until disappearance of the starting

material (TLC). The solution was then cooled to room temperature, and the solvent was directly removed under vacuum. The crude product was purified by column chromatography on silica gel.

Spectroscopic and analytical data for products **3a**–**k** follow:



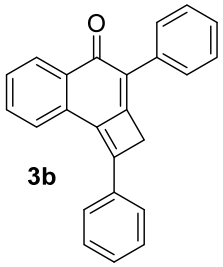
3a

Tricycle 3a

Procedure A: From 126 mg (0.48 mmol) of allenynol **2a**, and after chromatography of the residue using hexanes/ethyl acetate (10:1) as eluent, gave compound **3a** (85 mg, 69%) as a pale yellow oil.

Procedure B. From 159.4 mg (0.61 mmol) of allenynol **2a**, and after chromatography of the residue using hexanes/ethyl acetate (10:1) as eluent, gave compound **3a** (55.4 mg, 35%) as a pale yellow oil.

^{1}H-NMR (300 MHz, $CDCl_3$, 25 ºC) δ: 8.36 (d, J = 7.6 Hz, 1H), 7.96 (d, J = 7.5 Hz, 1H), 7.77 (d, J = 7.4 Hz, 2H), 7.52 (m, 5H), 3.76 (s, 2H), 2.02 (s, 3H); ^{13}C-NMR (75 MHz, $CDCl_3$, 25 ºC) δ: 185.4, 150.0, 146.8, 134.5, 134.3, 133.8, 131.2, 130.5, 131.0, 129.0 (2C), 128.9, 128.4 (2C), 128.3, 124.6, 121.9, 36.7, 10.2; IR ($CHCl_3$, cm^{-1}): ν 1694; HRMS (ES): calcd for $C_{19}H_{15}O$ [M + H]$^+$: 259.1117; found: 259.1118.



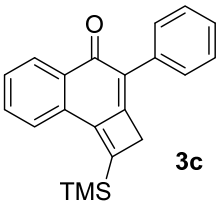
3b

Tricycle 3b

Procedure A: From 127 mg (0.39 mmol) of allenynol **2b**, and after chromatography of the residue using toluene as eluent, gave compound **3b** (102 mg, 82%) as a pale yellow oil.

Procedure B: From 62 mg (0.19 mmol) of allenynol **2b**, and after chromatography of the residue using toluene as eluent, gave compound **3b** (40 mg, 65%) as a pale yellow oil.

^{1}H-NMR (300 MHz, $CDCl_3$, 25 ºC) δ: 8.47 (dd, *J* = 7.9, 1.1 Hz, 1H), 8.07 (d, *J* = 7.5 Hz, 1H), 7.86 (m, 2H), 7.70 (m, 2H), 7.64 (dd, *J* = 7.6, 1.4 Hz, 1H), 7.57 (m, 4H), 7.45 (m, 2H), 7.35 (m, 1H), 4.01 (s, 2H); ^{13}C-NMR (75 MHz, $CDCl_3$, 25 ºC) δ: 183.4, 150.8, 149.5, 135.0, 134.8, 133.4, 133.3, 131.4, 130.9, 129.8, 129.3 (2C), 129.2, 129.0 (2C), 128.7, 128.5 (2C), 128.1 (2C), 127.5, 124.7, 124.4, 38.1; IR ($CHCl_3$, cm^{-1}): ν 1687; HRMS (ES): calcd for $C_{24}H_{17}O$ [*M* + H]$^+$: 321.1274; found: 321.1281.



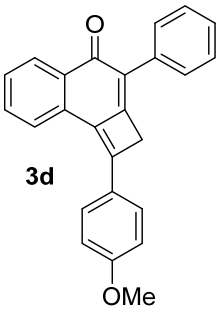
3c

Tricycle 3c

Procedure A: From 279 mg (0.88 mmol) of allenynol **2c**, and after chromatography of the residue using hexanes/ethyl acetate (11:1) as eluent, gave compound **3c** (234 mg, 85%) as a pale yellow oil.

Procedure B: From 250 mg (0.79 mmol) of allenynol **2c**, and after chromatography of the residue using hexanes/ethyl acetate (11:1) as eluent, gave compound **3c** (162 mg, 65%) as a pale yellow oil.

^{1}H-NMR (300 MHz, $CDCl_3$, 25 ºC) δ: 8.37 (m, 1H), 7.63 (m, 3H), 7.54 (m, 2H), 7.42 (m, 2H), 7.32 (m, 1H), 3.73 (s, 2H), 0.38 (s, 9H); ^{13}C-NMR (75 MHz, $CDCl_3$, 25 ºC) δ: 183.9, 160.6, 152.4, 150.6, 134.5, 132.9, 131.4, 130.7, 129.4 (2C), 129.2, 128.3, 128.1 (2C), 127.5, 123.7, 123.5, 40.1, 1.8 (3C); IR ($CHCl_3$, cm^{-1}): ν 1743; HRMS (ES): calcd for $C_{21}H_{21}OSi$ [*M* + H]$^+$: 317.1356; found: 317.1372.



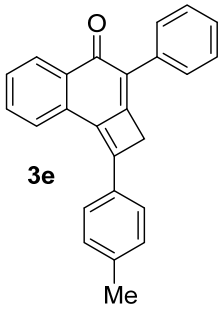
3d

Tricycle 3d

Procedure A: From 78 mg (0.22 mmol) of allenynol **2d**, and after chromatography of the residue using hexanes/toluene (1:10) as eluent, gave compound **3d** (68 mg, 88%) as a pale yellow oil.

Procedure B: From 391 mg (1.11 mmol) of allenynol **2d**, and after chromatography of the residue using hexanes/toluene (1:10) as eluent, gave compound **3d** (198 mg, 51%) as a pale yellow oil.

^{1}H-NMR (300 MHz, $CDCl_3$, 25 ºC) δ: 8.41 (dd, *J* = 7.8, 1.1 Hz, 1H), 7.88 (d, *J* = 7.4 Hz, 1H), 7.68 (d, *J* = 8.8 Hz, 2H), 7.64 (m, 2H), 7.54 (td, *J* = 7.5, 1.4 Hz, 1H), 7.47 (m, 1H), 7.39 (t, *J* = 7.4 Hz, 2H), 7.31 (d, *J* = 7.2 Hz, 1H), 6.95 (d, *J* = 8.8 Hz, 2H), 3.82 (m, 3H), 3.79 (m, 2H); ^{13}C-NMR (75 MHz, $CDCl_3$, 25 ºC) δ: 183.1, 161.9, 151.1, 149.9, 134.9, 133.6, 132.5, 131.2, 130.6 (2C), 129.9, 129.2 (2C), 128.6, 128.5, 128.0 (2C), 127.2, 126.0, 124.1, 123.8, 114.5 (2C), 55.4, 38.0; IR ($CHCl_3$, cm^{-1}): ν 1736; HRMS (ES): calcd for $C_{25}H_{19}O_2$ [*M* + H]$^+$: 351.1380; found: 351.1390.

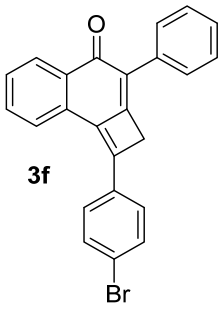


Tricycle 3e

Procedure A: From 64 mg (0.19 mmol) of allenynol **2e**, and after chromatography of the residue using toluene as eluent, gave compound **3e** (49 mg, 77%) as a pale yellow oil.

Procedure B: From 284 mg (0.84 mmol) of allenynol **2e**, and after chromatography of the residue using toluene as eluent, gave compound **3e** (194 mg, 69%) as a pale yellow oil.

^{1}H-NMR (300 MHz, $CDCl_3$, 25 ºC) δ: 8.38 (m, 1H), 7.89 (d, *J* = 7.7 Hz, 1H), 7.61 (m, 4H), 7.48 (m, 2H), 7.36 (t, *J* = 7.4 Hz, 2H), 7.28 (m, 1H), 7.23 (d, *J* = 8.2 Hz, 2H), 3.79 (s, 2H), 2.36 (s, 3H); ^{13}C-NMR (75 MHz, $CDCl_3$, 25 ºC) δ: 183.2, 151.0, 149.9, 141.8 (2C), 134.9, 133.9, 133.5, 131.3, 130.6, 129.9, 129.8 (2C), 129.3 (2C), 128.8, 128.6, 128.5 (2C), 128.1 (2C), 127.3, 124.4, 38.0, 21.7; IR ($CHCl_3$, cm^{-1}): ν 1690; HRMS (ES): calcd for $C_{25}H_{19}O$ [*M* + H]$^+$: 335.1430; found: 335.1445.

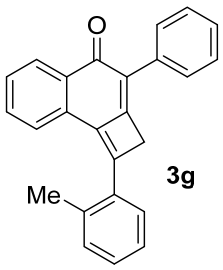


Tricycle 3f

Procedure A: From 125 mg (0.31 mmol) of allenynol **2f**, and after chromatography of the residue using hexanes/ethyl acetate (16:1) as eluent, gave compound **3f** (100 mg, 80%) as a pale yellow oil.

Procedure A: From 290 mg (0.72 mmol) of allenynol **2f**, and after chromatography of the residue using hexanes/ethyl acetate (16:1) as eluent, gave compound **3f** (167.5 mg, 58%) as a pale yellow oil.

^{1}H-NMR (300 MHz, $CDCl_3$, 25 ºC) δ: 8.04 (dd, *J* = 7.8, 1.2 Hz, 1H), 7.56 (d, *J* = 7.5 Hz, 1H), 7.24 (m, 3H), 7.20 (m, 1H), 7.16 (m, 1H), 7.03 (m, 3H), 6.96 (m, 2H), 6.86 (s, 1H), 3.56 (s, 2H); ^{13}C-NMR (75 MHz, $CDCl_3$, 25 ºC) δ: 183.4, 150.3, 147.8, 135.5, 135.0, 133.2, 132.4 (2C), 132.3, 131.6, 129.7 (2C), 129.6, 129.5, 129.3 (2C), 128.9, 128.2 (2C), 127.6, 125.3, 125.2, 124.4, 38.1; IR ($CHCl_3$, cm^{-1}): ν 1665; HRMS (ES): calcd for $C_{24}H_{16}BrO$ [*M* + H]$^+$: 401.0362; found: 401.0360.



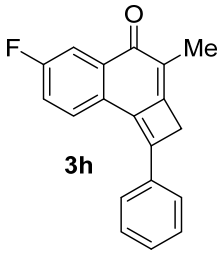
3g

Tricycle 3g

Procedure A: From 71 mg (0.21 mmol) of allenynol **2g**, and after chromatography of the residue using toluene as eluent, gave compound **3g** (58 mg, 82%) as a pale yellow oil.

Procedure B: From 251 mg (0.75 mmol) of allenynol **2g**, and after chromatography of the residue using toluene as eluent, gave compound **3g** (112.5 mg, 45%) as a pale yellow oil.

^{1}H-NMR (300 MHz, $CDCl_3$, 25 ºC) δ: 8.44 (m, 1H), 7.82 (m, 2H), 7.69 (m, 2H), 7.55 (m, 2H), 7.39 (m, 6H), 4.15 (s, 2H), 2.54 (s, 3H); ^{13}C-NMR (75 MHz, $CDCl_3$, 25 ºC) δ: 183.7, 151.3, 151.2, 137.7, 136.9, 134.9, 133.5, 133.3, 131.5, 131.4, 130.4, 129.9, 129.3 (2C), 129.2, 129.0, 128.5, 128.2 (2C), 127.5, 126.1, 124.5, 124.0, 42.0, 21.0; IR ($CHCl_3$, cm^{-1}): ν 1765; HRMS (ES): calcd for $C_{25}H_{19}O$ [*M* + H]$^+$: 335.1430; found: 335.1416.



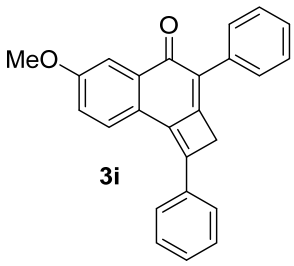
3h

Tricycle 3h

Procedure A: From 322 mg (0.95 mmol) of allenynol **2h**, and after chromatography of the residue using toluene as eluent, gave compound **3h** (257 mg, 80%) as a pale yellow oil.

Procedure B: From 115 mg (0.34 mmol) of allenynol **2h**, and after chromatography of the residue using toluene as eluent, gave compound **3h** (54 mg, 47%) as a pale yellow oil.

^{1}H-NMR (300 MHz, $CDCl_3$, 25 ºC) δ: 8.44 (m, 1H), 7.82 (m, 2H), 7.69 (m, 2H), 7.55 (m, 2H), 7.39 (m, 6H), 4.15 (s, 2H), 2.54 (s, 3H); ^{13}C-NMR (75 MHz, $CDCl_3$, 25 ºC) δ: 182.3 (d, J = 1.9 Hz), 163.1 (d, J = 250.9 Hz), 151.2, 149.3 (d, J = 2.2 Hz), 137.6 (d, J = 6.9 Hz), 134.0 (d, J = 1.1 Hz), 133.4, 133.1, 131.1, 129.3 (2C), 129.2 (2C), 128.5 (2C), 128.3 (2C), 127.7, 126.7 (d, J = 7.7 Hz), 126.4 (d, J = 3.3 Hz), 124.7, 119.1 (d, J = 23.2 Hz), 115.2 (d, J = 23.2 Hz), 38.2; ^{19}F NMR (282 MHz, $CDCl_3$, 25 °C): δ = −108.5 (s, 1F); IR ($CHCl_3$, cm^{-1}): ν 1695; HRMS (ES): calcd for $C_{24}H_{16}FO$ $[M + H]^+$: 339.1180; found: 339.1175.



3i

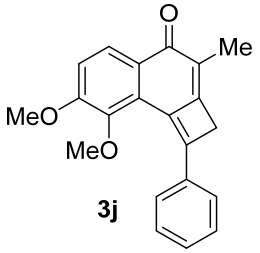
Tricycle 3i

Procedure A: From 98 mg (0.28 mmol) of allenynol **2i**, and after chromatography of the residue using hexanes/ethyl acetate (8:1) as eluent, gave compound **3i** (68 mg, 70%) as a pale yellow oil.

Procedure B. From 86 mg (0.24 mmol) of allenynol **2i**, and after chromatography of the residue using hexanes/ethyl acetate (8:1) as eluent, gave compound **3i** (43 mg, 52%) as a pale yellow oil.

^{1}H-NMR (300 MHz, $CDCl_3$, 25 ºC) δ: 8.01 (d, J = 8.7 Hz, 1H), 7.97 (d, J = 2.8 Hz, 1H), 7.83 (m, 2H), 7.69 (m, 2H), 7.64–7.39 (m, 5H), 7.37 (m, 1H), 7.22 (dd, J = 8.6, 2.8 Hz, 1H), 4.00 (s, 2H), 3.97

(s, 3H); ^{13}C-NMR (125 MHz, $CDCl_3$, 25 ºC) δ: 183.7, 160.8, 151.4, 147.9, 137.3, 135.1, 134.1, 133.9, 131.0, 129.8 (2C), 129.5 (2C), 128.8 (2C), 128.6 (2C), 127.9, 126.6, 125.0, 123.7, 120.2, 111.4, 56.0, 38.4; IR ($CHCl_3$, cm^{-1}): ν 1654; HRMS (ES): calcd for $C_{25}H_{19}O_2$ [*M* + H]$^+$: 351.1380; found: 351.1365.



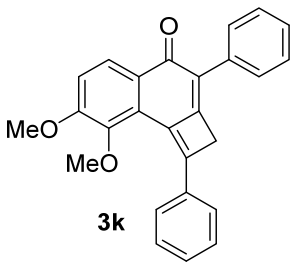
3j

Tricycle 3j

Procedure A: From 250 mg (0.78 mmol) of allenynol **2j**, and after chromatography of the residue using hexanes/ethyl acetate (8:1) as eluent, gave compound **3j** (140 mg, 56%) as a pale green solid; mp 116–118 ºC.

Procedure B. From 135 mg (0.42 mmol) of allenynol **2j**, and after chromatography of the residue using hexanes/ethyl acetate (8:1) as eluent, gave compound **3j** (43 mg, 39%) as a pale green solid; mp 116–118 ºC.

^{1}H-NMR (500 MHz, $CDCl_3$, 25 ºC) δ: 8.18 (d, *J* = 8.7 Hz, 1H), 7.81 (m, 2H), 7.47 (m, 3H), 7.11 (d, *J* = 8.9 Hz, 1H), 4.00 (s, 3H), 3.86 (s, 2H), 3.43 (s, 3H), 2.03 (s, 3H); ^{13}C-NMR (125 MHz, $CDCl_3$, 25 ºC) δ: 185.2, 155.0, 150.0, 147.6, 144.6, 134.2 (2C), 130.5 (2C), 129.9, 128.4, 128.0 (2C), 125.5, 125.4, 120.6, 112.1, 60.3, 56.0, 38.1, 10.0; IR ($CHCl_3$, cm^{-1}): ν 1695; HRMS (ES): calcd for $C_{21}H_{19}O_3$ [*M* + H]$^+$: 319.1329; found: 319.1337.



3k

Tricycle 3k

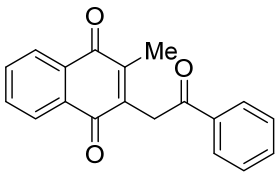
Procedure A: From 328 mg (0.86 mmol) of allenynol **2k**, and after chromatography of the residue using hexanes/ethyl acetate (10:1) as eluent, gave compound **3k** (266 mg, 81%) as a pale yellow oil.

Procedure B. From 138 mg (0.36 mmol) of allenynol **2k**, and after chromatography of the residue using hexanes/ethyl acetate (10:1) as eluent, gave compound **3k** (79 mg, 57%) as a yellow oil.

^{1}H-NMR (500 MHz, $CDCl_3$, 25 ºC) δ: 8.26 (d, *J* = 8.7 Hz, 1H), 7.84 (m, 2H), 7.67 (m, 2H), 7.50 (m, 3H), 7.43 (m, 2H), 7.35 (m, 1H), 7.16 (d, *J* = 8.7 Hz, 1H), 4.02 (s, 6H), 3.47 (s, 2H); ^{13}C-NMR (125 MHz, $CDCl_3$, 25 ºC) δ: 183.1, 155.2, 150.9, 150.5, 144.5, 134.0, 133.5, 130.9, 130.6 (2C), 130.3, 129.4 (2C), 129.0, 128.2 (2C), 128.1 (2C), 127.4, 125.9, 125.3, 123.8, 112.3, 60.4, 56.1, 39.6; IR ($CHCl_3$, cm^{-1}): ν 1657; HRMS (ES): calcd for $C_{26}H_{21}O_3$ [*M* + H]$^+$: 381.1485; found: 381.1503.

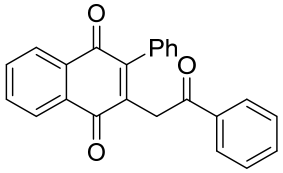
General procedure for the synthesis of naphthalene-1,4-diones 4a–j, 4a–Br and 4h–Br

N-Bromosuccinimide (0.4 mmol) and water (1.0 mmol) were sequentially added to a solution of the appropriate tricycle **3** (0.2 mmol) in acetonitrile (2 mL). The reaction mixture was stirred at room temperature until the starting material disappeared, as indicated by TLC. After completion of the reaction, the mixture was concentrated under reduced pressure, and purified by flash column chromatography on silica gel to give analytically pure compounds. Spectroscopic and analytical data for products **4a–j** follow:



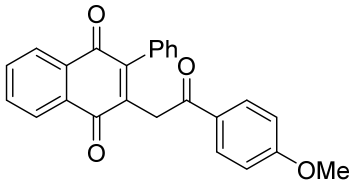
4a

Naphthalene-1,4-dione 4a. From 48 mg (0.19 mmol) of tricycle **3a**, and after chromatography of the residue using hexanes/ethyl acetate (9:1) as eluent, gave compound **4a** (40 mg, 72%) as a pale yellow oil; ^{1}H-NMR (300 MHz, $CDCl_3$, 25 ºC) δ: 7.62 (3H), 7.53 (dd, *J* = 7.6, 1.4 Hz, 1H), 7.27 (m, 2H), 7.08 (m, 5H), 6.93 (m, 3H), 6.35 (s, 1H), 4.73 (m, 2H), 1.92 (br s, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ: 195.1, 184.7, 184.1, 146.2, 141.1, 136.5, 133.6, 133.5, 133.5, 132.3, 131.9, 128.8 (2C), 128.3 (2C), 126.5 (2C), 37.0, 13.4; IR ($CHCl_3$, cm^{-1}): ν 1687, 1660, 1596; HRMS (ES): calcd for $C_{19}H_{15}O_3$ [*M* + H]$^+$: 291.1016; found: 291.1015.



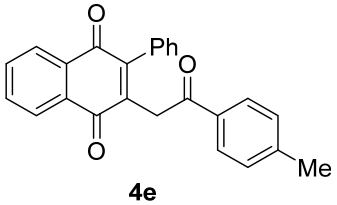
4b

Naphthalene-1,4-dione 4b. From 69 mg (0.22 mmol) of tricycle **3b**, and after chromatography of the residue using hexanes/ethyl acetate (12:1) as eluent, gave compound **4b** (47 mg, 61%) as a pale yellow oil; ^{1}H-NMR (300 MHz, $CDCl_3$, 25 ºC) δ: 8.07 (m, 2H), 7.86 (m, 2H), 7.69 (m, 2H), 7.50 (t, J = 7.4 Hz, 1H), 7.38 (t, J = 7.6 Hz, 2H),7.30 (m, 3H), 7.19 (m, 2H), 4.10 (s, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ: 196.4, 184.7, 184.1, 148.3, 142.3, 136.4, 133.9, 133.7, 133.4, 133.0, 132.2, 131.9, 129.0 (2C), 128.9, 128.6 (2C), 128.3 (4C), 126.8, 126.5, 38.9; IR ($CHCl_3$, cm^{-1}): ν 1685, 1661, 1594; HRMS (ES): calcd for $C_{24}H_{17}O_3$ [M + H]$^+$: 353.1172; found: 353.1174.



4d

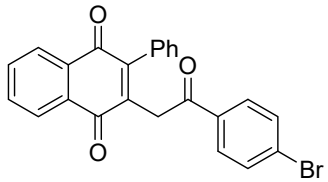
Naphthalene-1,4-dione 4d. From 127 mg (0.36 mmol) of tricycle **3d**, and after chromatography of the residue using hexanes/ethyl acetate (17:1) as eluent, gave compound **4d** (80 mg, 58%) as a pale yellow oil; ^{1}H-NMR (700 MHz, C_6D_6, 25 ºC) δ: 8.02 (m, 1H), 7.99 (m, 1H), 7.77 (m, 2H), 7.40 (m, 2H), 7.09 (m, 2H), 7.05 (m, 1H), 7.00 (m, 2H), 6.54 (m, 2H), 4.03 (s, 2H), 3.13 (s, 3H); ^{13}C NMR (175 MHz, C_6D_6) δ: 194.6, 184.8, 183.7, 163.8, 148.1, 143.1, 134.1, 133.5, 133.3, 132.7, 132.5, 130.8 (2C), 130.1, 129.7 (2C), 128.9, 128.3 (2C), 126.7, 126.4, 114.0 (2C), 54.9, 39.1; IR (C_6D_6, cm^{-1}): ν 1663, 1598; HRMS (ES): calcd for $C_{25}H_{19}O_4$ [M + H]$^+$: 383.1278; found: 383.1272.



4e

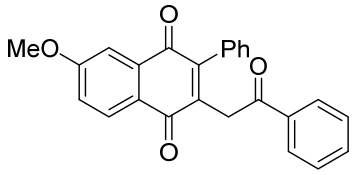
Naphthalene-1,4-dione 4e. From 65 mg (0.19 mmol) of tricycle **3e**, and after chromatography of the residue using toluene as eluent, gave compound **4e** (38 mg, 55%) as a pale yellow oil; ^{1}H-NMR (300

MHz, $CDCl_3$, 25 ºC) δ: 8.18 (m, 2H), 7.87 (d, *J* = 8.3 Hz, 2H), 7.79 (m, 2H), 7.45 (m, 3H), 7.31 (m, 4H), 4.19 (s, 2H), 2.44 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ: 196.0, 184.8, 184.1, 148.2, 144.3, 142.4, 133.9, 133.8, 133.7, 133.1, 132.2, 132.0, 129.3 (2C), 129.0 (2C), 128.9, 128.4 (2C), 128.2 (2C), 126.7, 126.5, 38.8, 21.6; IR ($CHCl_3$, cm^{-1}): ν 1660, 1599; HRMS (ES): calcd for $C_{25}H_{19}O_3$ [*M* + H]$^+$: 367.1329; found: 367.1332.



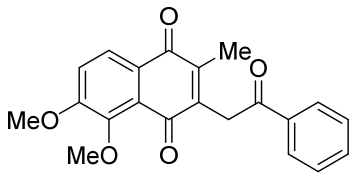
4f

Naphthalene-1,4-dione 4f. From 25.4 mg (0.06 mmol) of tricycle **3f**, and after chromatography of the residue using hexanes/ethyl acetate (10:1) as eluent, gave compound **4f** (16 mg, 60%) as a pale yellow oil; ^1H-NMR (300 MHz, $CDCl_3$, 25 ºC) δ: 8.15 (m, 2H), 7.78 (m, 4H), 7.61 (m, 2H), 7.42 (m, 4H), 7.28 (m, 1H), 4.13 (s, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ: 195.5, 184.7, 184.0, 148.4, 141.9, 135.1, 134.0, 133.8, 132.9, 132.2, 132.0 (2C), 131.9, 129.8 (2C), 129.0, 128.9 (2C), 128.7, 128.3 (2C), 126.8, 126.5, 38.8; IR ($CHCl_3$, cm^{-1}): ν 1687, 1664; HRMS (ES): calcd for $C_{24}H_{16}BrO_3$ [*M* + H]$^+$: 431.0277; found: 431.0263.



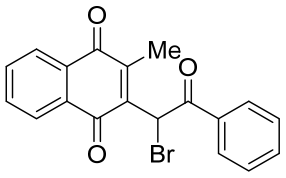
4i

Naphthalene-1,4-dione 4i. From 25 mg (0.07 mmol) of tricycle **3i**, and after chromatography of the residue using hexanes/ethyl acetate (9:1) as eluent, gave compound **4i** (13 mg, 53%) as a pale yellow oil; ^1H-NMR (500 MHz, $CDCl_3$, 25 ºC) δ: 8.08 (d, *J* = 8.6 Hz, 1H), 7.94 (dd, *J* = 8.3, 1.3 Hz, 2H), 7.58 (m, 2H), 7.46 (m, 2H), 7.41 (m, 3H), 7.27 (m, 2H), 7.22 (dd, *J* = 8.6, 2.7 Hz, 1H), 4.16 (s, 2H), 3.97 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ: 196.5, 184.2, 183.7, 164.2, 148.0, 142.5, 136.4, 134.3, 133.4, 133.2, 129.0 (2C), 128.9, 128.6 (2C), 128.3 (3C), 128.2 (2C), 125.6, 120.3, 110.0, 55.9, 38.9; IR ($CHCl_3$, cm^{-1}): ν 1699, 1598, 1581.



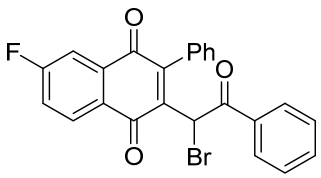
4j

Naphthalene-1,4-dione 4j. From 80 mg (0.25 mmol) of tricycle **3j**, and after chromatography of the residue using hexanes/ethyl acetate (10:1) as eluent, gave compound **4j** (50 mg, 57%) as a pale yellow oil; ^{1}H-NMR (300 MHz, $CDCl_3$, 25 ºC) δ: 8.05 (m, 2H), 7.97 (d, *J* = 8.6 Hz, 1H), 7.61(m, 1H), 7.51 (m, 2H), 7.19 (d, *J* = 8.6 Hz, 1H), 4.37 (s, 2H), 3.97 (s, 3H), 3.89 (s, 3H), 2.12 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ: 195.2, 183.9, 183.5, 158.6, 149.0, 144.7, 142.4, 136.2, 133.4, 128.7 (2C), 128.3 (2C), 126.2, 125.2, 124.4, 115.5, 61.2, 56.2, 37.2, 13.2; IR ($CHCl_3$, cm^{-1}): ν 1686, 1655, 1575; HRMS (ES): calcd for $C_{21}H_{19}O_5$ $[M + H]^+$: 351.1227; found: 351.1237.



4a-Br

Naphthalene-1,4-dione 4a-Br. From 34 mg (0.13 mmol) of tricycle **3a**, and after chromatography of the residue using hexanes/ethyl acetate (9:1) as eluent, gave compound **4a-Br** (31 mg, 65%) as a pale yellow oil; ^{1}H-NMR (300 MHz, $CDCl_3$, 25 ºC) δ: 8.17 (m, 1H), 8.08 (m, 1H), 7.81 (d, *J* = 7.5 Hz, 2H), 7.75 (m, 2H), 7.53 (t, *J* = 7.4 Hz, 1H), 7.40 (t, *J* = 7.6 Hz, 2H), 7.03 (s, 1H), 2.19 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ: 190.2, 184.5, 181.7, 147.8, 141.9, 134.3, 134.2, 134.0, 133.7, 131.9, 131.2, 128.9 (2C), 128.4 (2C), 127.1, 126.7, 46.9, 13.6; IR ($CHCl_3$, cm^{-1}): ν 1699, 1663, 1593; HRMS (ES): calcd for $C_{19}H_{14}BrO_3$ $[M + H]^+$: 369.0121; found: 369.0118.



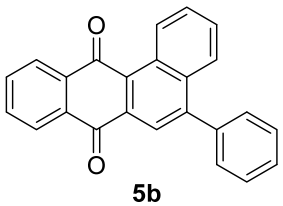
4h-Br

Naphthalene-1,4-dione 4h-Br. From 37 mg (0.11 mmol) of tricycle **3h**, and after chromatography of the residue using hexanes/ethyl acetate (6:1) as eluent, gave compound **4h-Br** (31 mg, 62%) as a

pale yellow oil; ^{1}H-NMR (300 MHz, $CDCl_3$, 25 ºC) δ: 8.14 (dd, *J* = 8.7, 5.2 Hz, 1H), 7.73 (dd, *J* = 8.4, 2.6 Hz, 1H), 7.59 (m, 5H), 7.45 (m, 4H), 7.36 (m, 2H), 6.08 (s, 1H); ^{13}C-NMR (75 MHz, $CDCl_3$, 25 ºC) δ: 189.6, 183.0 (d, *J* = 1.7 Hz), 181.1, 166.4 (d, *J* = 258.6 Hz), 146.3, 143.3, 134.7, 134.3 (d, *J* = 8.3 Hz), 133.1, 131.4, 130.3 (d, *J* = 8.8 Hz), 130.0, 128.7 (2C), 128.6 (2C), 128.5 (2C), 128.2, 128.2 (2C), 121.5 (d, *J* = 22.7 Hz), 113.5 (d, *J* = 23.2 Hz), 50.1; ^{19}F NMR (282 MHz, $CDCl_3$, 25 °C): δ = −127.5 (s, 1F); IR ($CHCl_3$, cm^{-1}): ν 1708, 1666, 1597; HRMS (ES): calcd for $C_{24}H_{15}BrFO_3$ [*M* + H]$^+$: 451.0166; found: 451.0150.

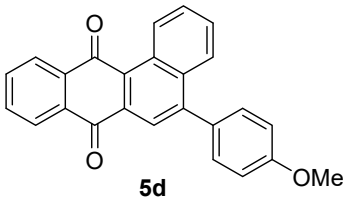
General procedure for the synthesis of tetraphene-7,12-diones 5b–i

The appropriate tricycle **3b–i** (1.0 mmol), Selectfluor (2.0 mmol) and $NaHCO_3$ (2.0 mmol) were mixed in acetonitrile (10 mL). The reaction mixture was stirred at room temperature until the starting material disappeared, as indicated by TLC. The crude reaction was concentrated under reduced pressure and purified by flash column chromatography on silica gel to give analytically pure compounds. Spectroscopic and analytical data for products **5b–i** follow:



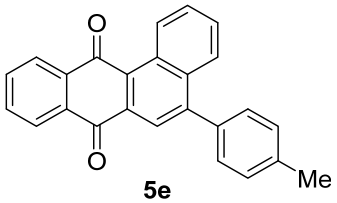
5b

Tetraphene-7,12-dione 5b. From 93 mg (0.29 mmol) of fused-cyclobutene **3b**, and after chromatography of the residue using hexanes/ethyl acetate (4:1) as eluent, gave compound **5b** (47 mg, 49%) as a pale yellow oil; ^{1}H-NMR (300 MHz, $CDCl_3$, 25 ºC) δ: 9.81 (d, *J* = 8.5 Hz, 1H), 8.35 (s, 1H), 8.33 (m, 1H), 8.27 (dd, *J* = 7.4, 1.3 Hz, 1H), 8.00 (d, *J* = 7.9 Hz, 1H), 7.78 (m, 3H), 7.58 (m, 6H); ^{13}C NMR (125 MHz, $CDCl_3$) δ: 186.0, 184.0, 147.5, 139.5, 135.2, 135.0, 134.3, 133.4 (2C), 133.3, 132.3, 131.3, 129.8 (2C), 129.6, 128.9, 128.7, 128.5 (2C), 128.3, 127.3, 126.9, 126.5, 123.5; IR ($CHCl_3$, cm^{-1}): ν 1663, 1584; HRMS (ES): calcd for $C_{24}H_{14}NaO_2$ [*M* + Na]$^+$: 357.0886; found: 357.0893.



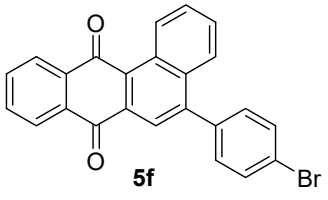
5d

Tetraphene-7,12-dione 5d. From 75 mg (0.21 mmol) of fused-cyclobutene **3d**, and after chromatography of the residue using toluene as eluent, gave compound **5d** (42 mg, 55%) as a pale yellow oil; ^{1}H-NMR (700 MHz, $CDCl_3$, 25 ºC) δ: 9.83 (d, *J* = 9.0 Hz, 1H), 8.36 (m, 2H), 8.29 (d, *J* = 7.4 Hz, 1H), 8.07 (d, *J* = 8.7 Hz, 1H), 7.84 (t, *J* = 7.3 Hz, 1H), 7.79 (m, 2H), 7.63 (t, *J* = 7.3 Hz, 1H), 7.50 (d, *J* = 8.7 Hz, 2H), 7.09 (d, *J* = 8.3 Hz, 2H), 3.94 (s, 3H); ^{13}C NMR (175 MHz, $CDCl_3$) δ: 186.0, 184.1, 159.7, 147.3, 135.3, 135.1, 134.3, 133.4, 133.3, 132.3, 131.8, 131.4, 131.1 (2C), 129.5, 128.9, 128.6, 128.2, 127.3, 127.0, 126.5, 123.5, 114.0 (2C), 55.4; IR ($CHCl_3$, cm^{-1}): ν 1668, 1607; HRMS (ES): calcd for $C_{25}H_{17}O_3$ [*M* + H]$^+$: 365.1172; found: 365.1184.



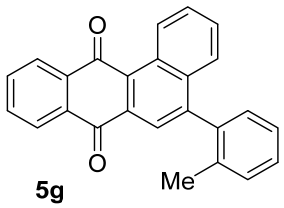
5e

Tetraphene-7,12-dione 5e. From 75 mg (0.14 mmol) of fused-cyclobutene **3e**, and after chromatography of the residue using toluene as eluent, gave compound **5e** (29 mg, 59%) as a pale yellow oil; ^{1}H-NMR (300 MHz, $CDCl_3$, 25 ºC) δ: 9.82 (d, *J* = 8.5 Hz, 1H), 8.35 (m, 2H), 8.28 (dd, *J* = 7.4, 1.3 Hz, 1H), 8.04 (d, *J* = 7.9 Hz, 1H), 7.80 (m, 3H), 7.61 (m, 1H), 7.44 (d, *J* = 8.1 Hz, 2H), 7.37 (d, *J* = 7.9 Hz, 2H), 2.50 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ: 186.0, 184.1, 147.6, 138.2, 136.5, 135.2, 135.1, 134.2, 133.4, 133.3, 132.3, 131.3, 129.8 (2C), 129.5, 129.2 (2C), 128.9, 128.6, 128.3, 127.3, 127.0, 126.4, 123.5, 21.3; IR ($CHCl_3$, cm^{-1}): ν 1665, 1586; HRMS (ES): calcd for $C_{25}H_{17}O_2$ [*M* + H]$^+$: 349.1223; found: 349.1208.



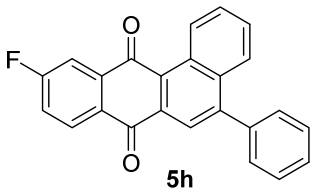
5f

Tetraphene-7,12-dione 5f. From 40.4 mg (0.10 mmol) of fused-cyclobutene **3f**, and after chromatography of the residue using toluene as eluent, gave compound **5f** (21.5 mg, 52%) as a pale yellow oil; ^{1}H-NMR (700 MHz, $CDCl_3$, 25 ºC) δ: 9.82 (d, *J* = 8.7 Hz, 1H), 8.35 (d, *J* = 7.7 Hz, 1H), 8.33 (s, 1H), 8.28 (d, *J* = 7.7 Hz, 1H), 7.94 (d, *J* = 8.3 Hz, 1H), 7.85 (t, *J* = 7.4 Hz, 1H), 7.80 (t, *J* = 7.7 Hz, 2H), 7.70 (d, *J* = 8.0 Hz, 2H), 7.63 (t, *J* = 7.4 Hz, 1H), 7.42 (d, *J* = 7.7 Hz, 2H); ^{13}C NMR (175 MHz, $CDCl_3$) δ: 185.9, 183.9, 146.0, 138.3, 135.2, 134.7, 134.4, 133.5, 133.2, 132.2, 131.8 (2C), 131.4 (2C), 131.2, 129.7, 129.0, 128.9, 128.8, 127.3, 126.6, 126.5, 123.4, 122.7; IR ($CHCl_3$, cm^{-1}): ν 1666, 1587.



5g

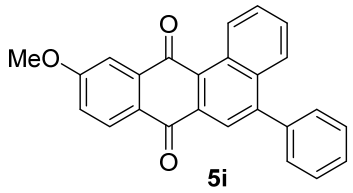
Tetraphene-7,12-dione 5g. From 68 mg (0.20 mmol) of fused-cyclobutene **3g**, and after chromatography of the residue using toluene as eluent, gave compound **5g** (37 mg, 54%) as a pale yellow oil; ^{1}H-NMR (300 MHz, $CDCl_3$, 25 ºC) δ: 9.82 (d, *J* = 8.8 Hz, 1H), 8.36 (m, 1H), 8.29 (m, 1H), 8.27 (m, 1H), 7.80 (m, 3H), 7.58 (m, 2H), 7.39 (m, 4H), 2.04 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ: 186.1, 184.1, 147.4, 139.0, 136.3 135.4, 135.2, 134.3, 133.5, 133.4, 132.3, 130.9, 130.2, 129.8, 129.6, 128.9, 128.8, 128.7, 128.4, 127.3, 126.9, 126.5, 125.8, 123.4, 20.0; IR ($CHCl_3$, cm^{-1}): ν 1723, 1668; HRMS (ES): calcd for $C_{25}H_{17}O_2$ $[M + H]^+$: 349.1223; found: 349.1234.



5h

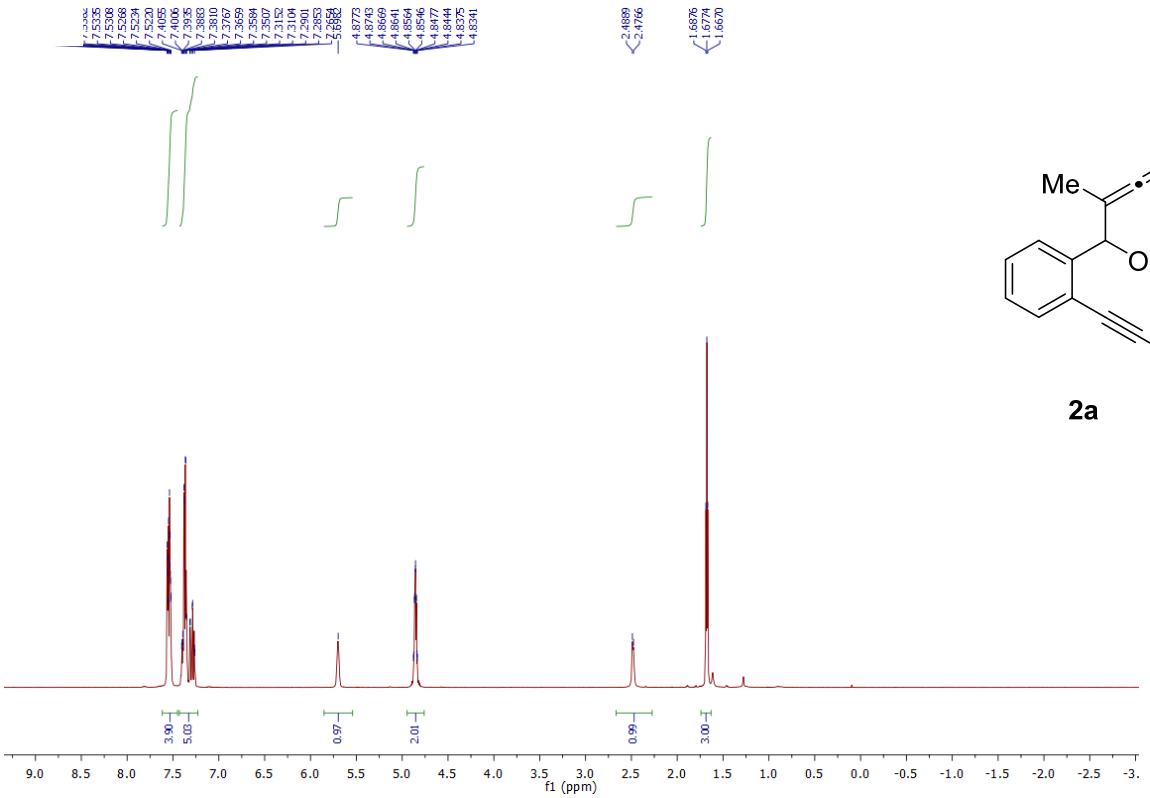
Tetraphene-7,12-dione 5h. From 45 mg (0.13 mmol) of fused-cyclobutene **3h**, and after chromatography of the residue using toluene as eluent, gave compound **5h** (27.5 mg, 60%) as a pale yellow oil; ^{1}H-NMR (300 MHz, $CDCl_3$, 25 ºC) δ: 9.80 (d, *J* = 8.8 Hz, 1H), 8.36 (s, 1H), 8.31 (dd, *J* = 8.6, 5.3 Hz, 1H), 8.00 (m, 2H), 7.80 (m, 1H), 7.63 (m, 1H), 7.54 (m, 5H), 7.44 (td, *J* = 8.3, 2.6 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ: 184.6 (d, *J* = 1.1 Hz), 182.7, 166.6 (d, *J* = 257.1 Hz), 147.9,

139.4, 137.9 (d, J = 8.0 Hz), 134.9, 133.2, 131.3, 129.9, 129.8 (2C), 129.7, 128.9, 128.9, 128.8, 128.7, 128.5 (2C), 128.4, 127.0, 123.6, 120.8 (d, J = 22.7 Hz), 114.0 (d, J = 23.2 Hz); ^{19}F NMR (282 MHz, $CDCl_3$, 25 °C): δ = −101.6 (s, 1F); IR ($CHCl_3$, cm^{-1}): ν 1669, 1590; HRMS (ES): calcd for $C_{24}H_{14}FO_2$ $[M + H]^+$: 353.0972; found: 353.0985.



5i

Tetraphene-7,12-dione 5i. From 35 mg (0.09 mmol) of fused-cyclobutene **3i**, and after chromatography of the residue using hexanes/ethyl acetate (9:1) as eluent, gave compound **5i** (16 mg, 48%) as a yellow solid; mp 196–198 ºC; ^{1}H-NMR (300 MHz, $CDCl_3$, 25 ºC) δ: 9.79 (m, 1H), 8.36 (s, 1H), 8.22 (d, J = 8.6 Hz, 1H), 7.99 (m, 1H), 7.76 (m, 2H), 7.61 (m, 1H), 7.57–7.50 (m, 5H), 7.24 (m, 1H), 4.03 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ: 185.9, 182.8, 164.6, 147.5, 139.5, 137.3, 134.7, 133.5, 131.3, 129.8 (2C), 129.5, 129.0, 128.7, 128.5 (3C), 128.4, 128.2, 126.9, 125.9, 123.6, 120.4, 110.3, 55.9; ^{19}F NMR (282 MHz, $CDCl_3$, 25 °C): δ = −101.6 (s, 1F); IR ($CHCl_3$, cm^{-1}): ν 1666, 1598; HRMS (ES): calcd for $C_{25}H_{17}O_3$ $[M + H]^+$: 365.1172; found: 365.1176.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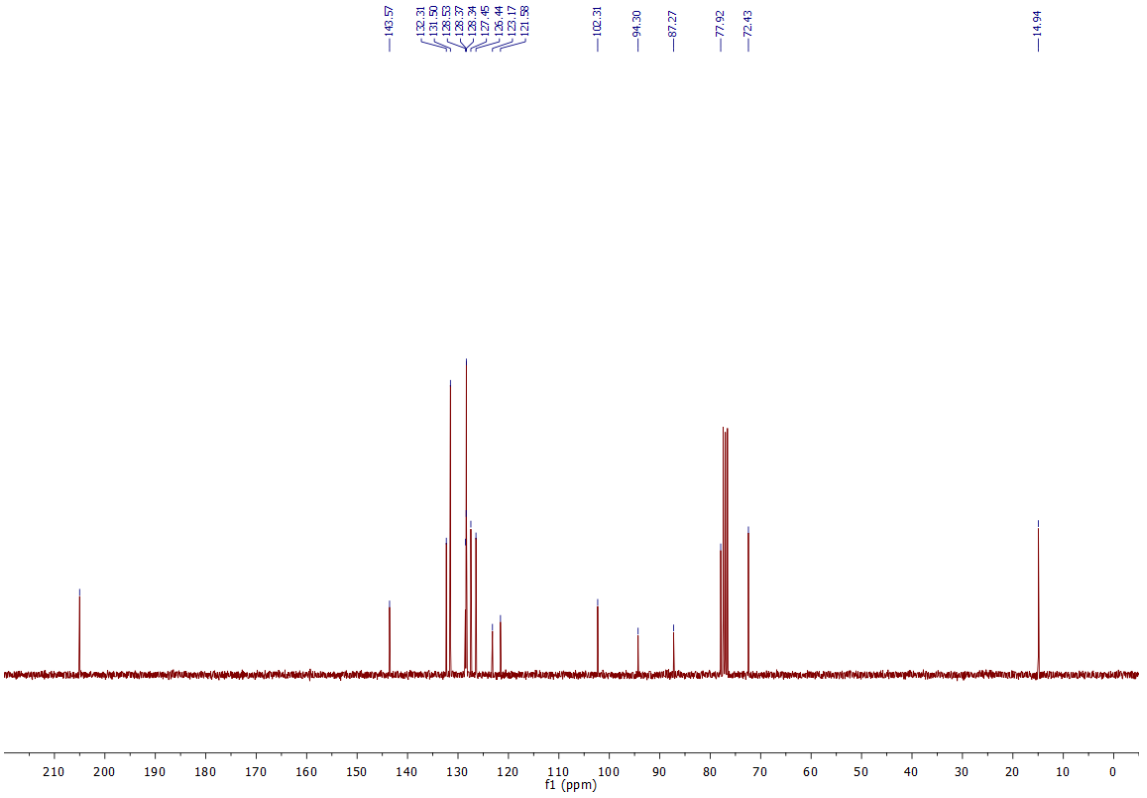
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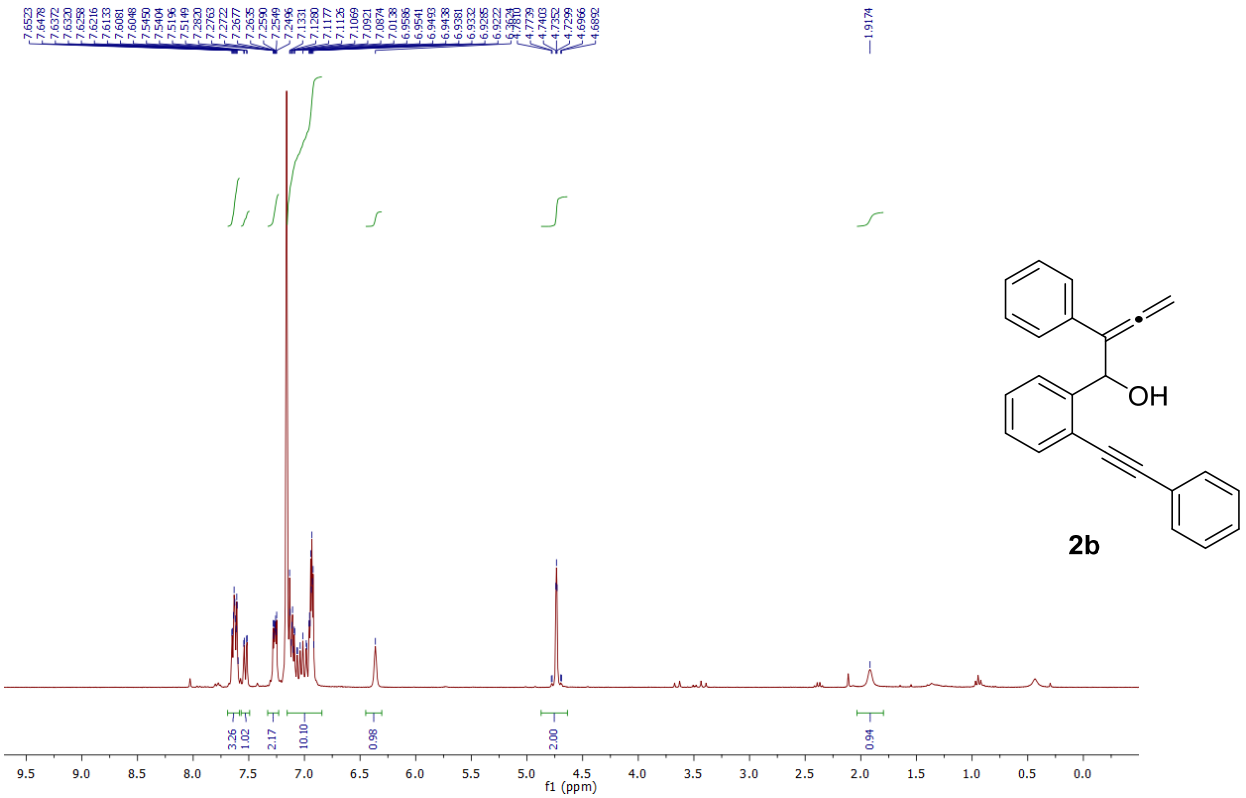
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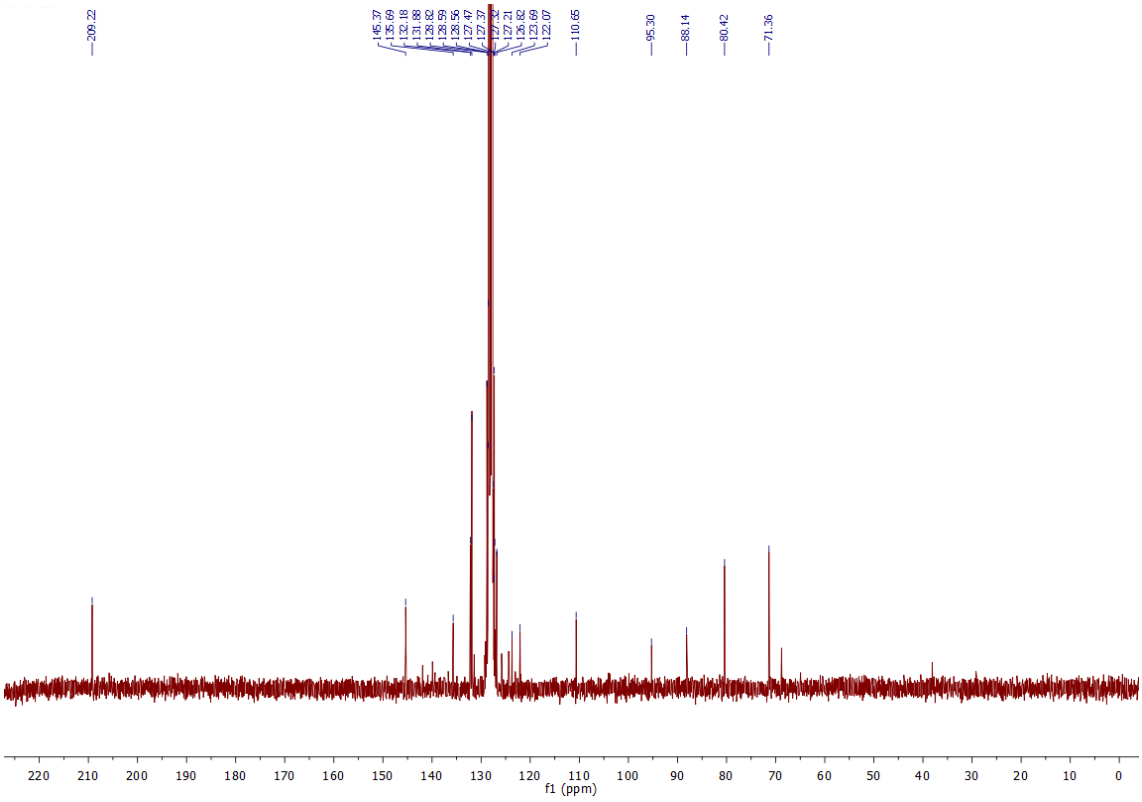
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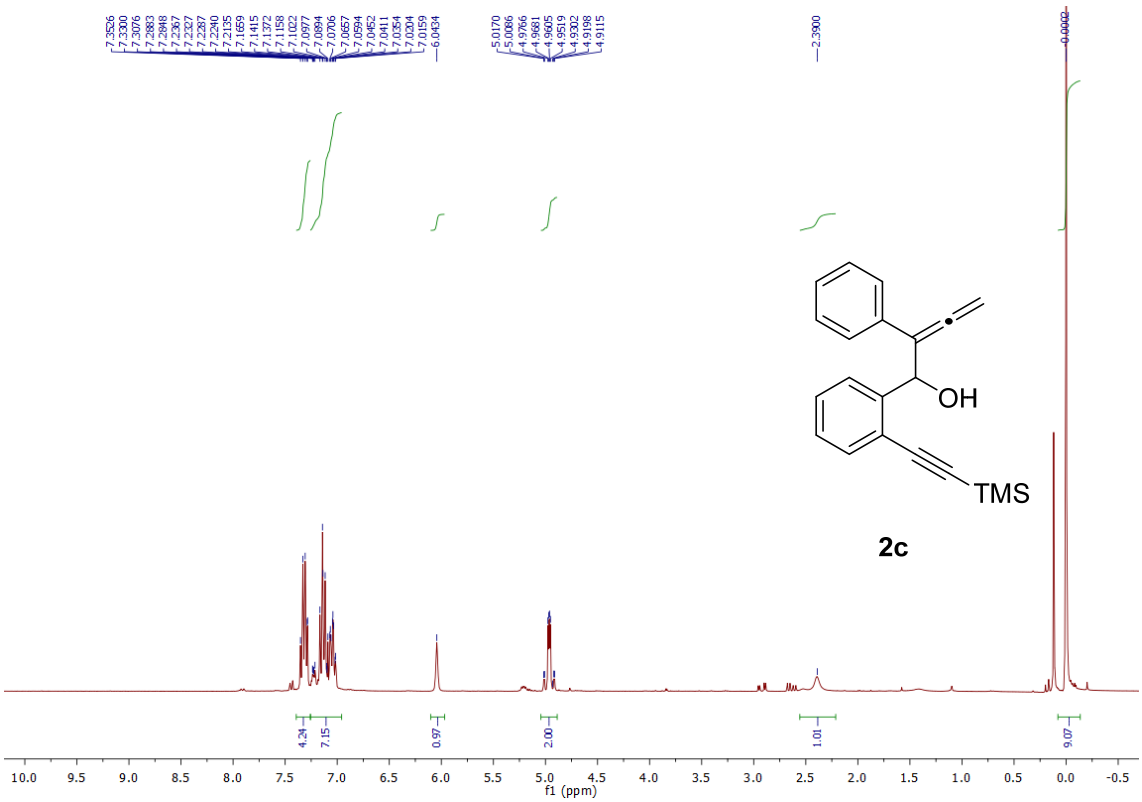
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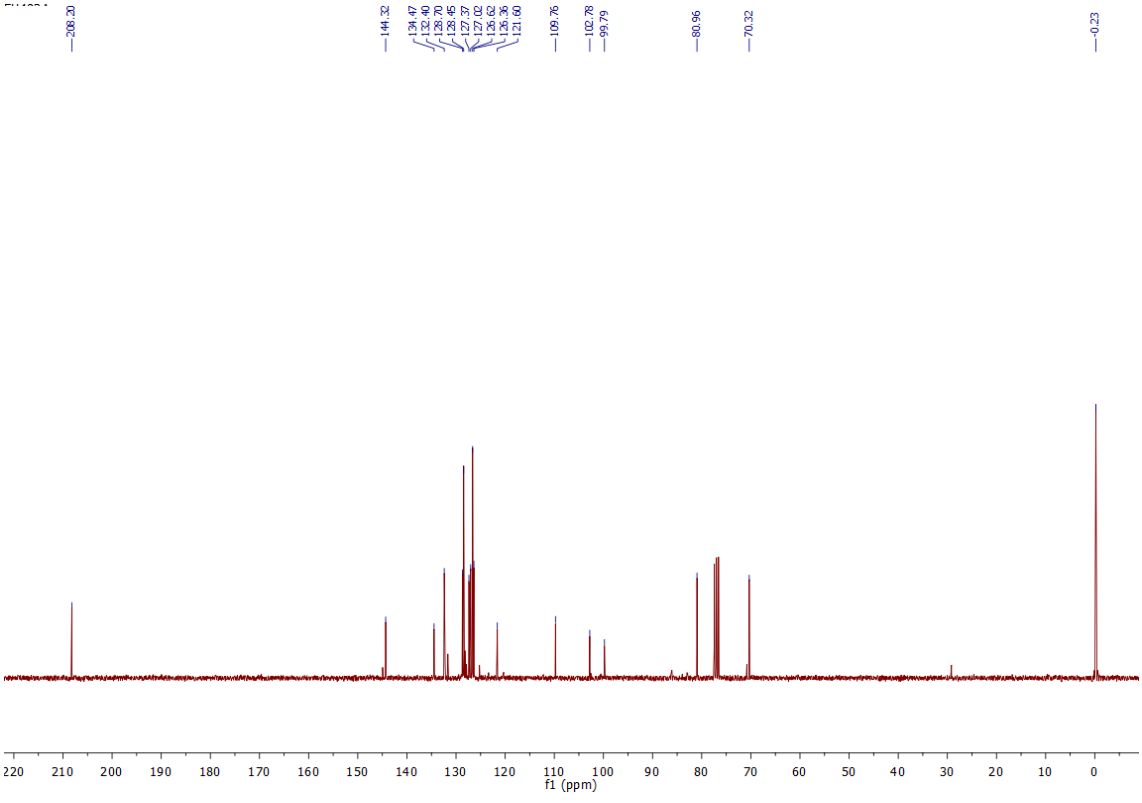
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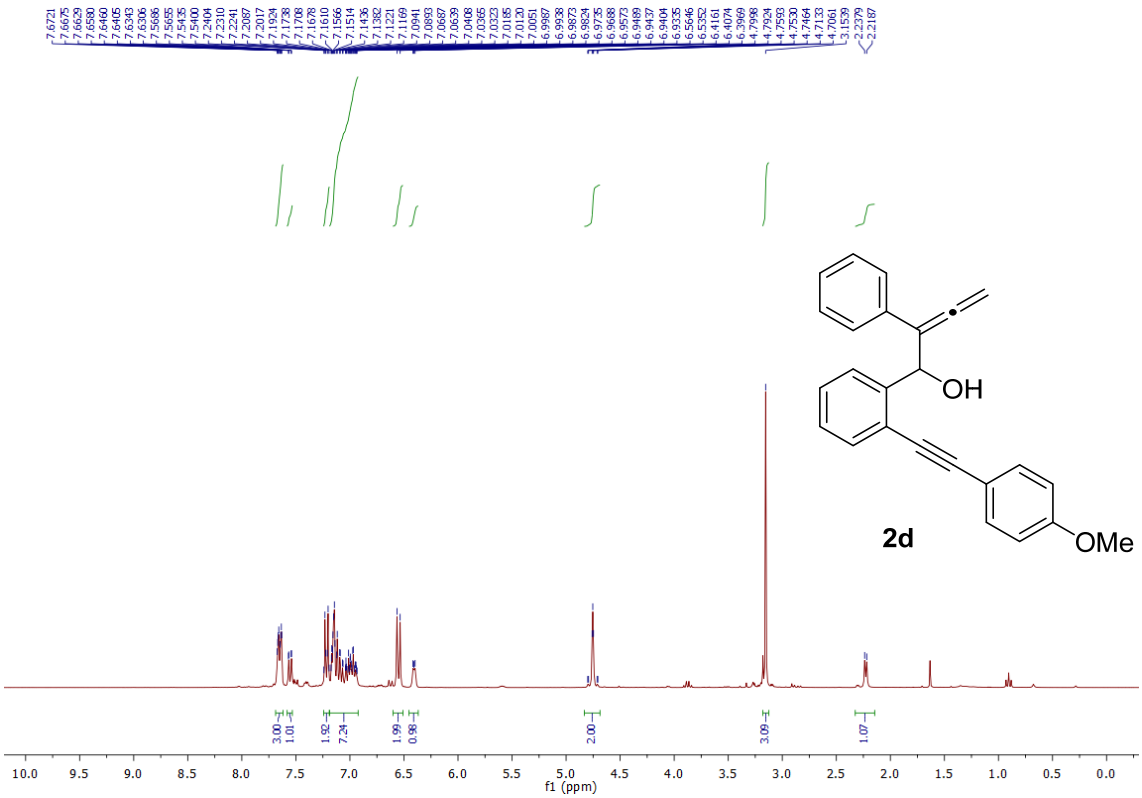
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2d
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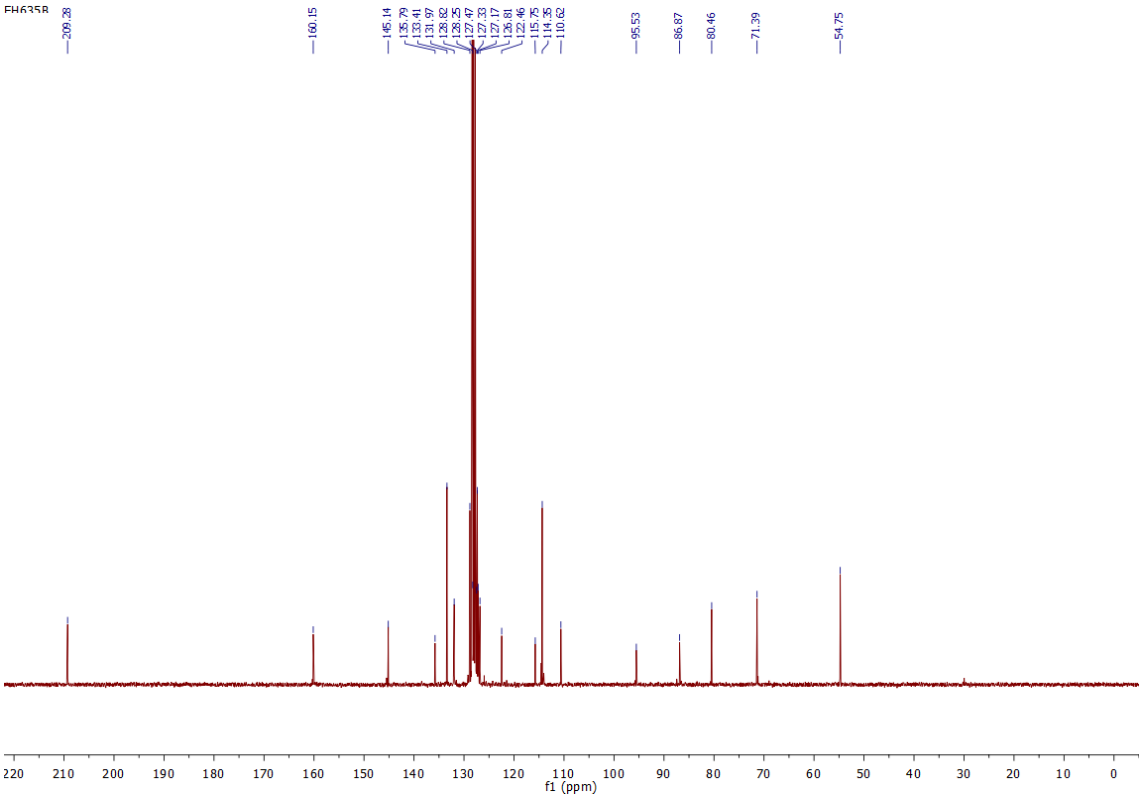
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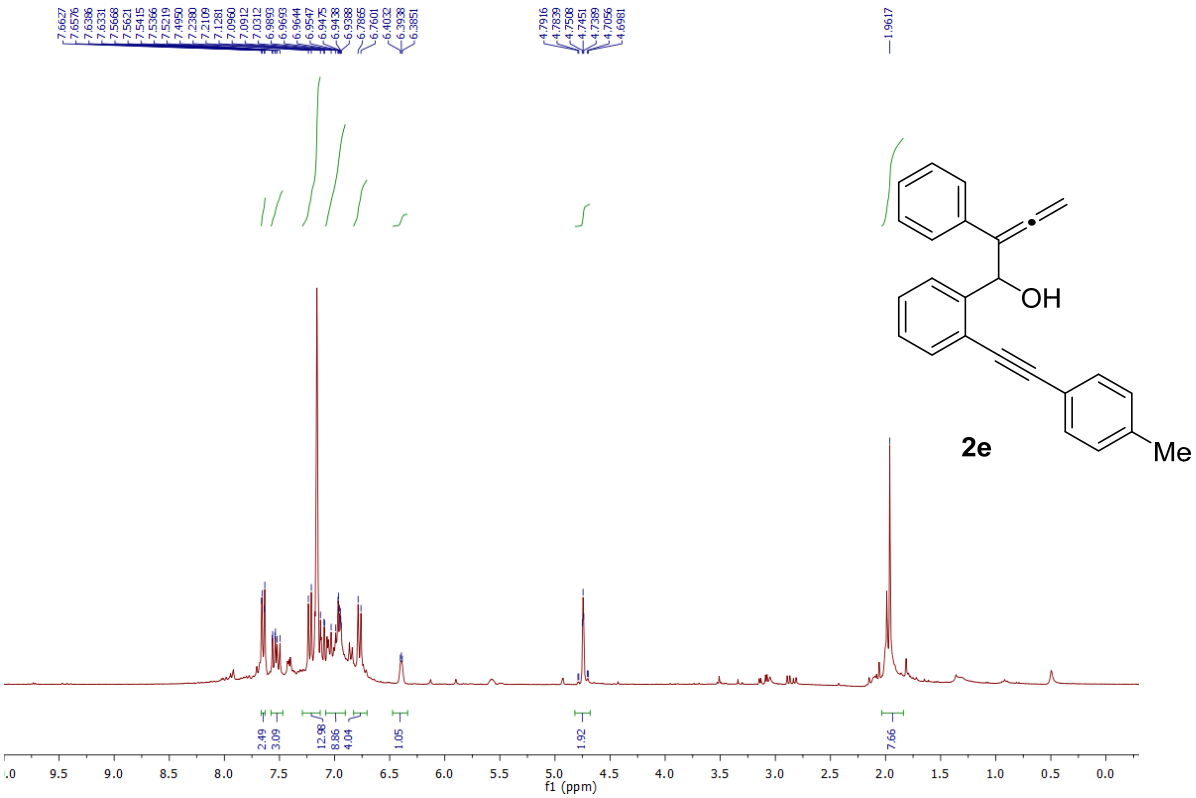
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2e
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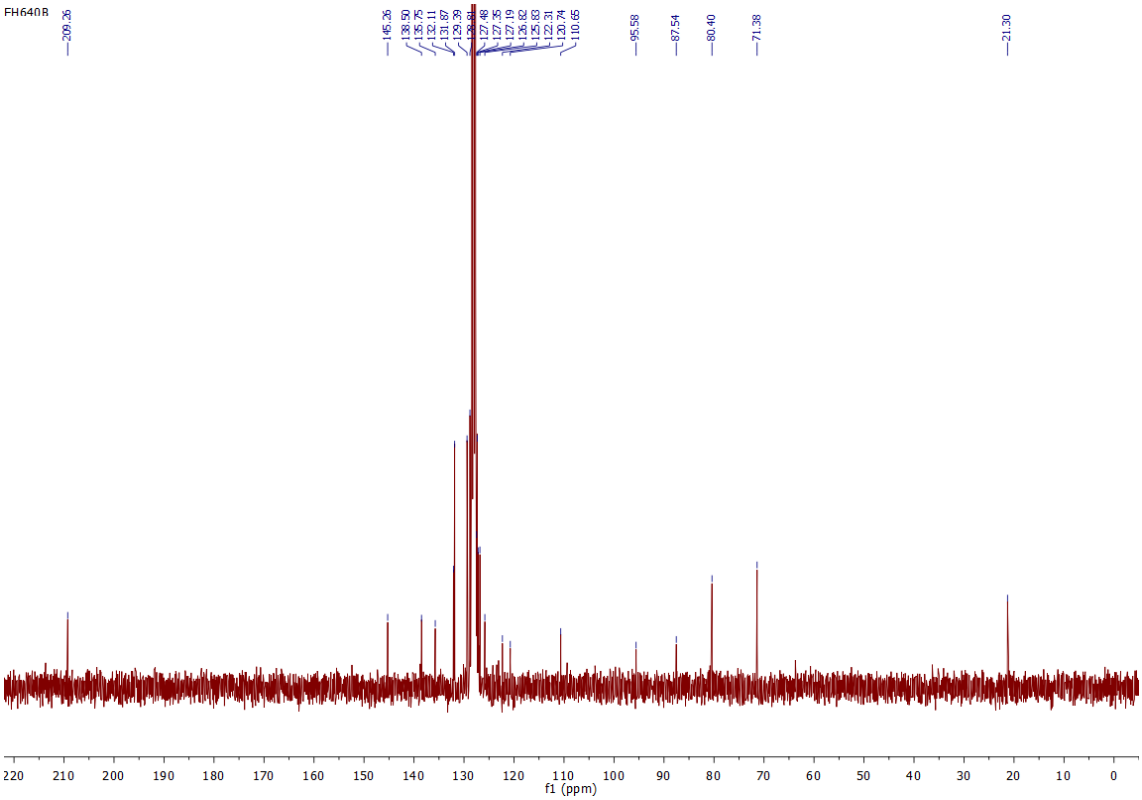
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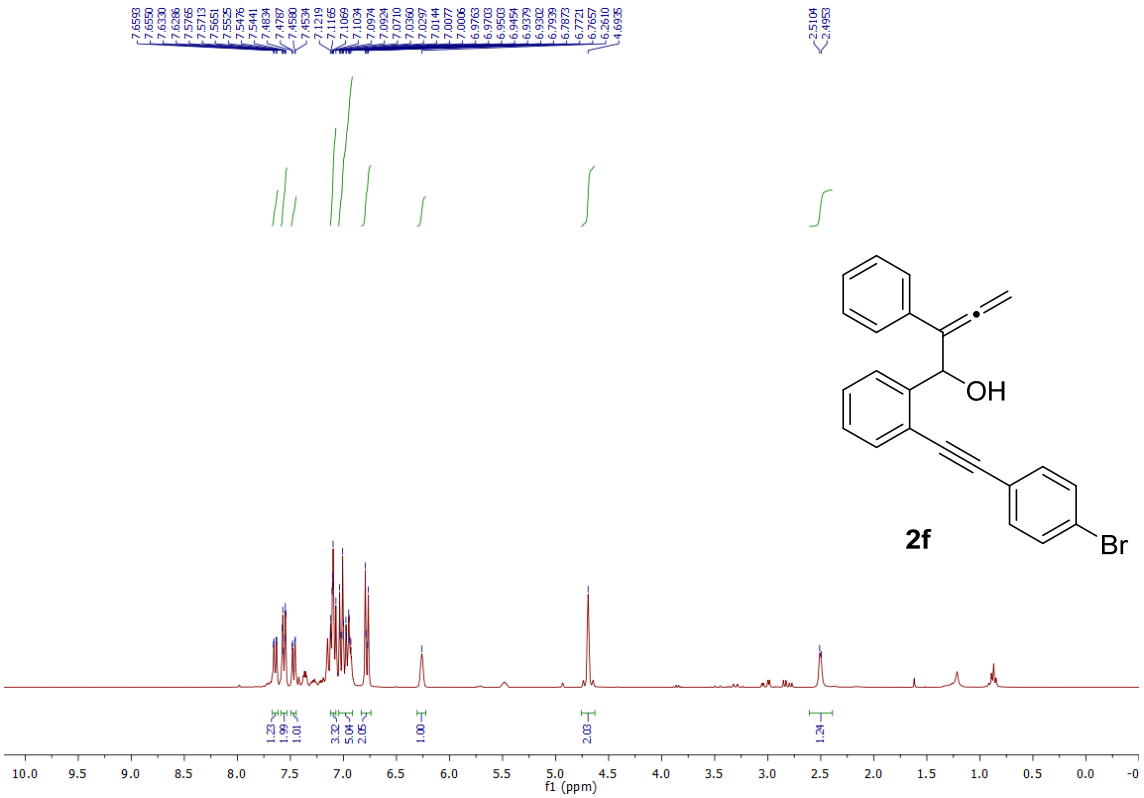
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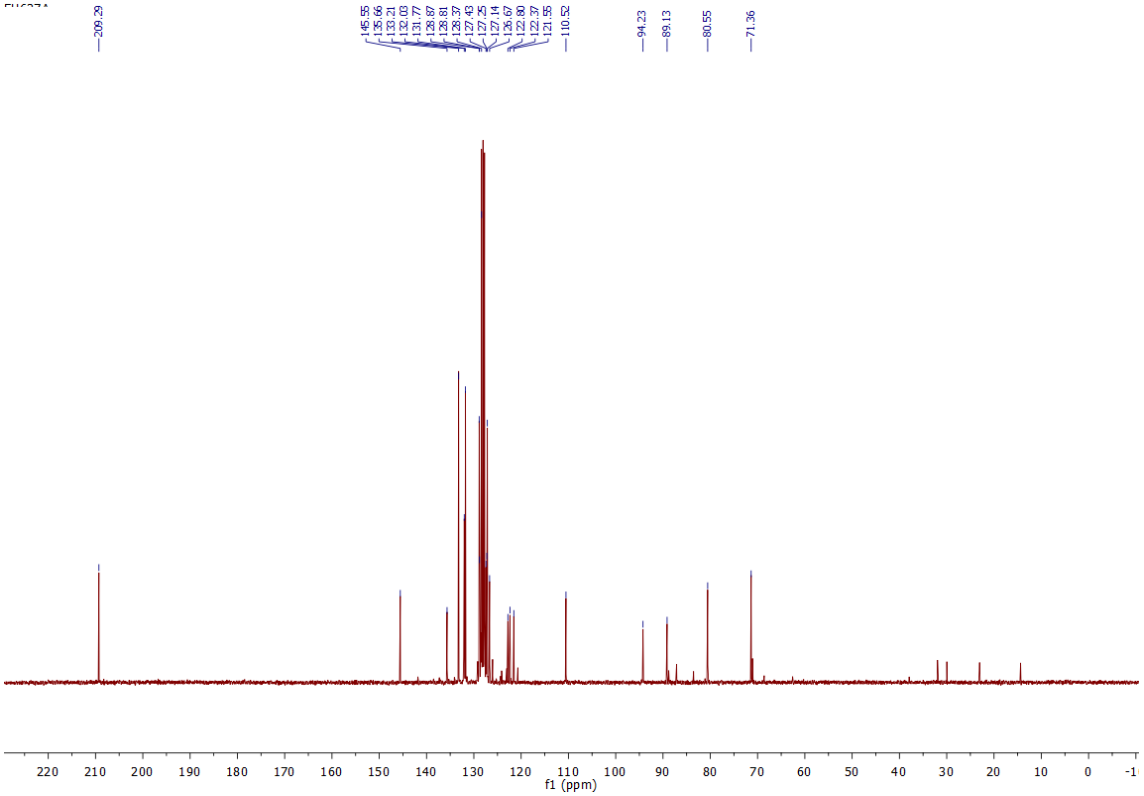
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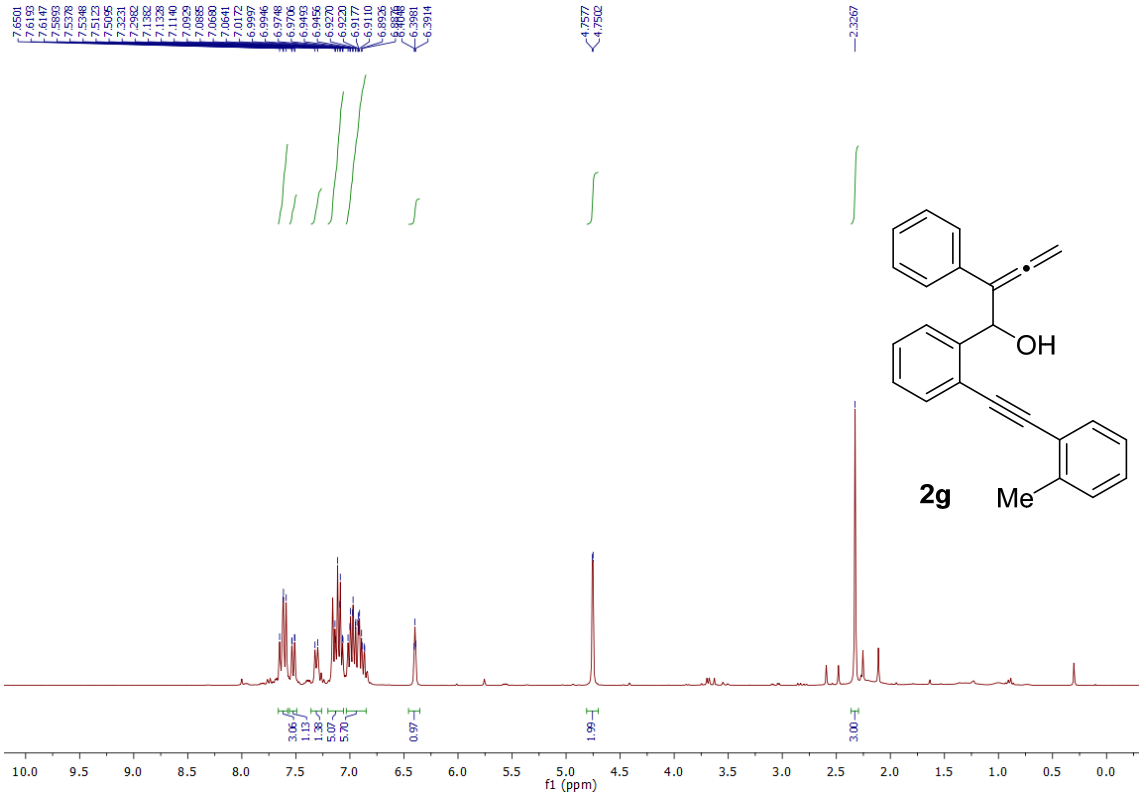
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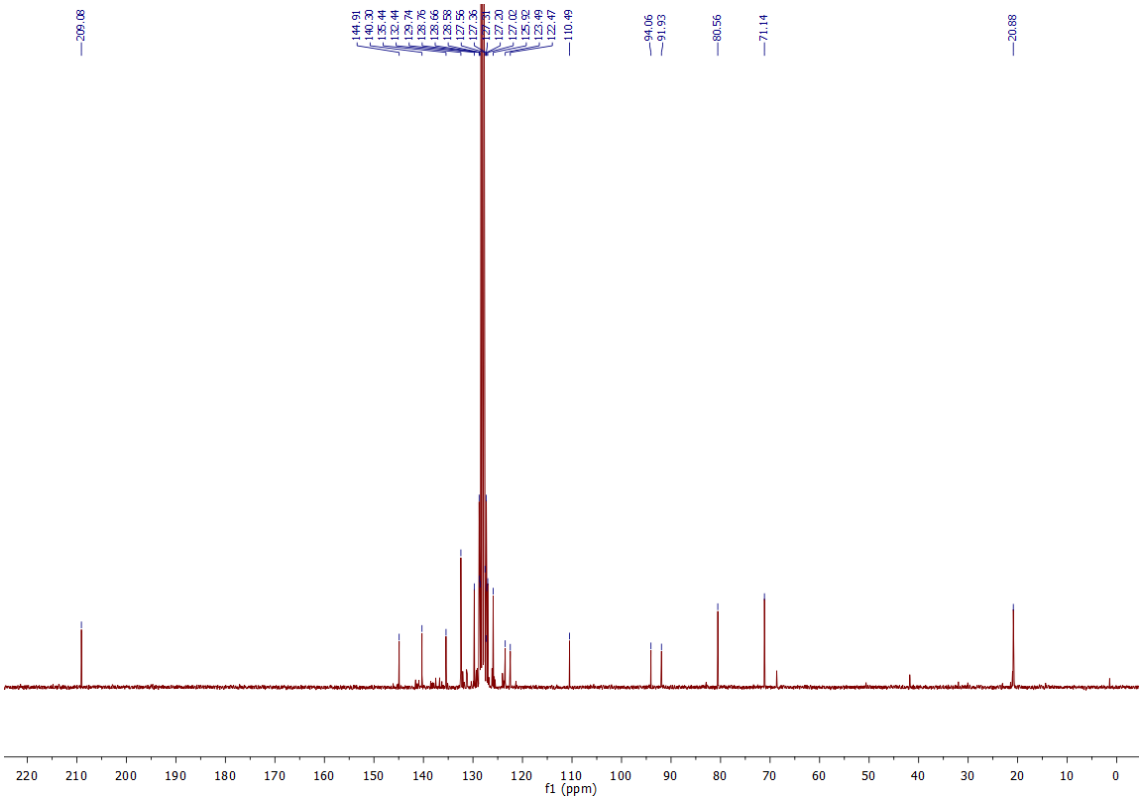
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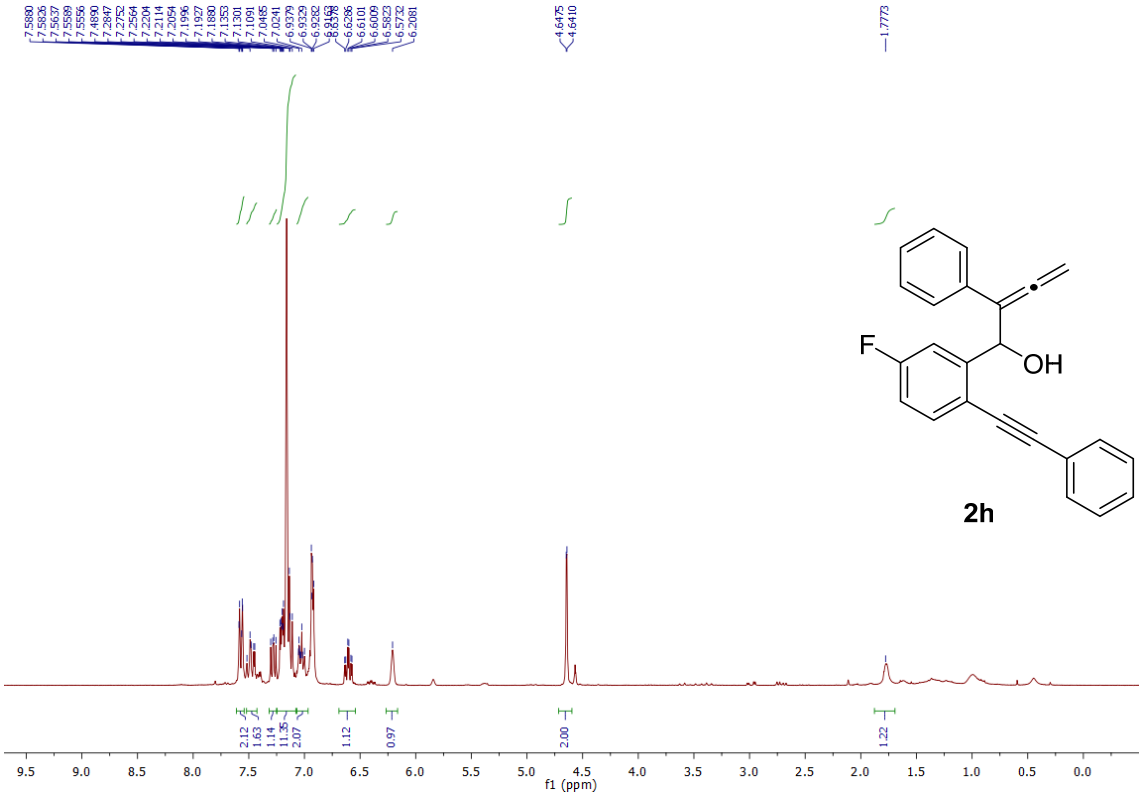
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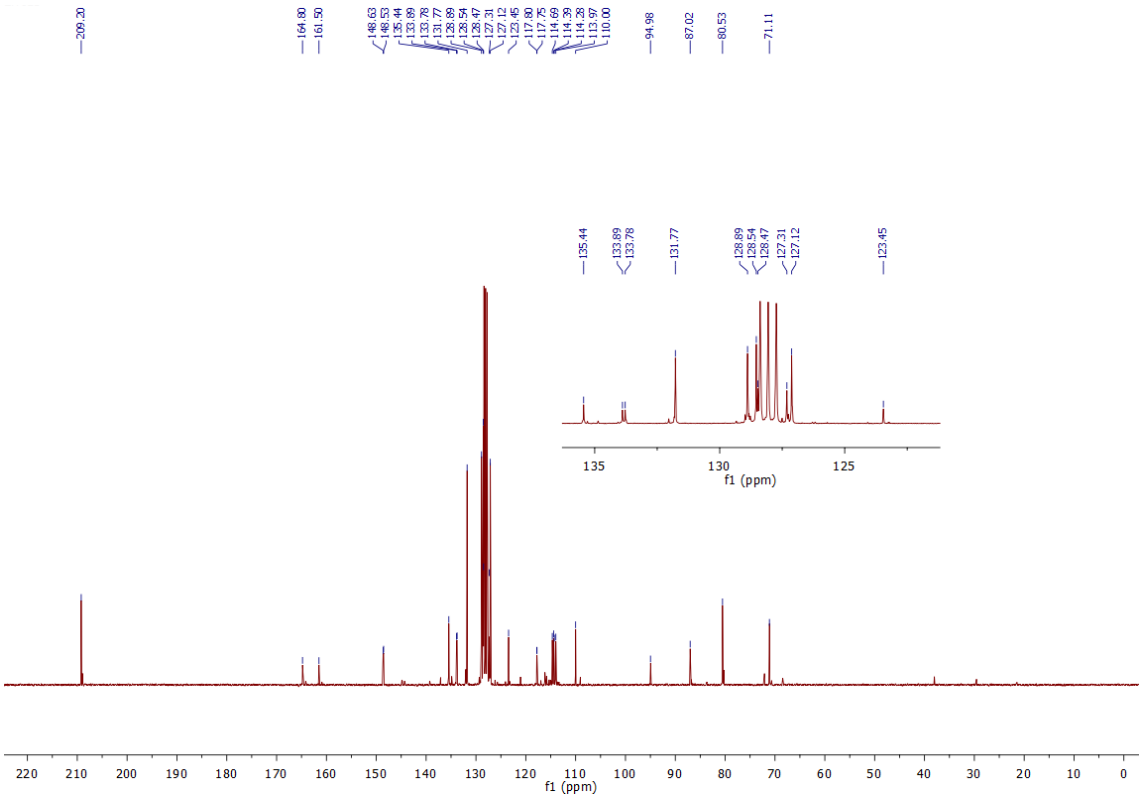
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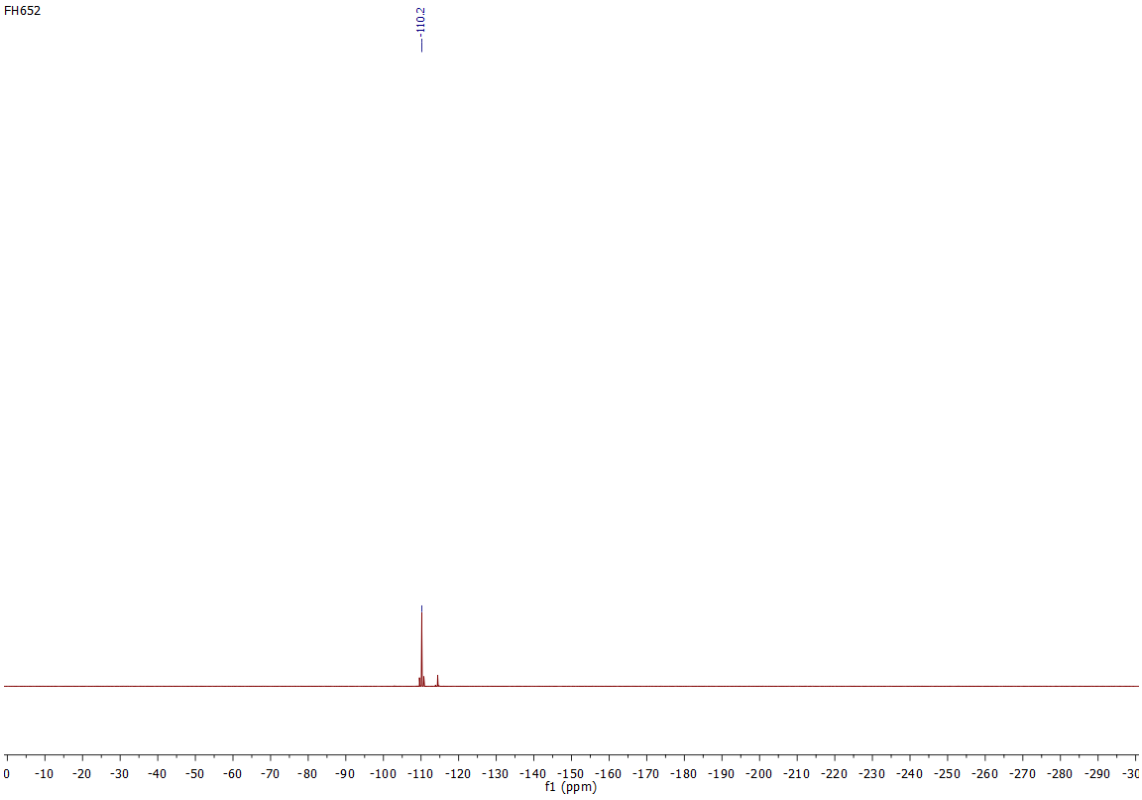
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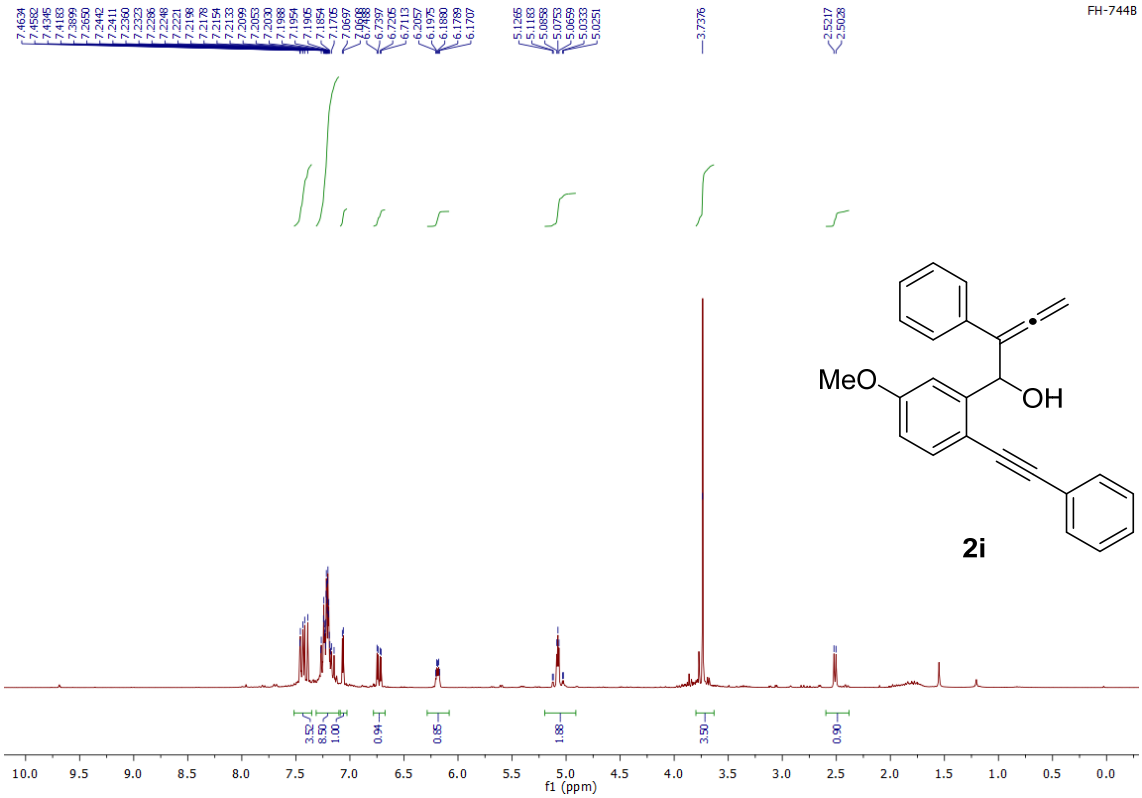
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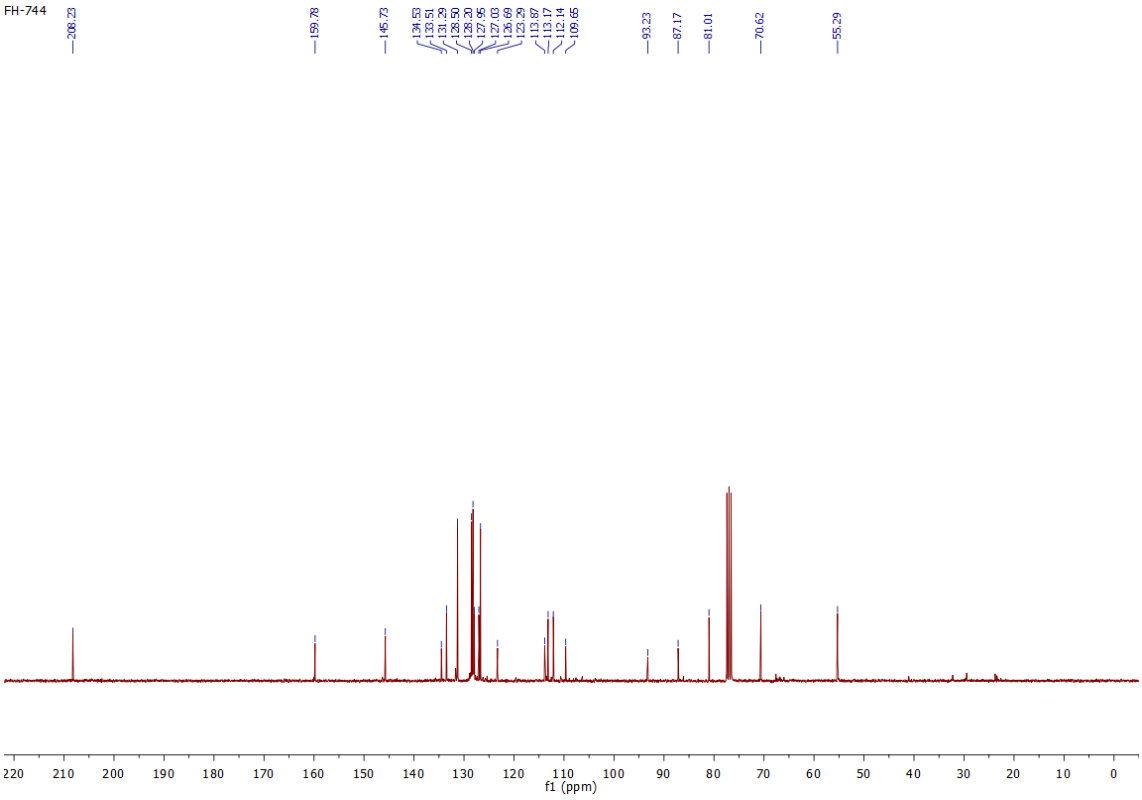
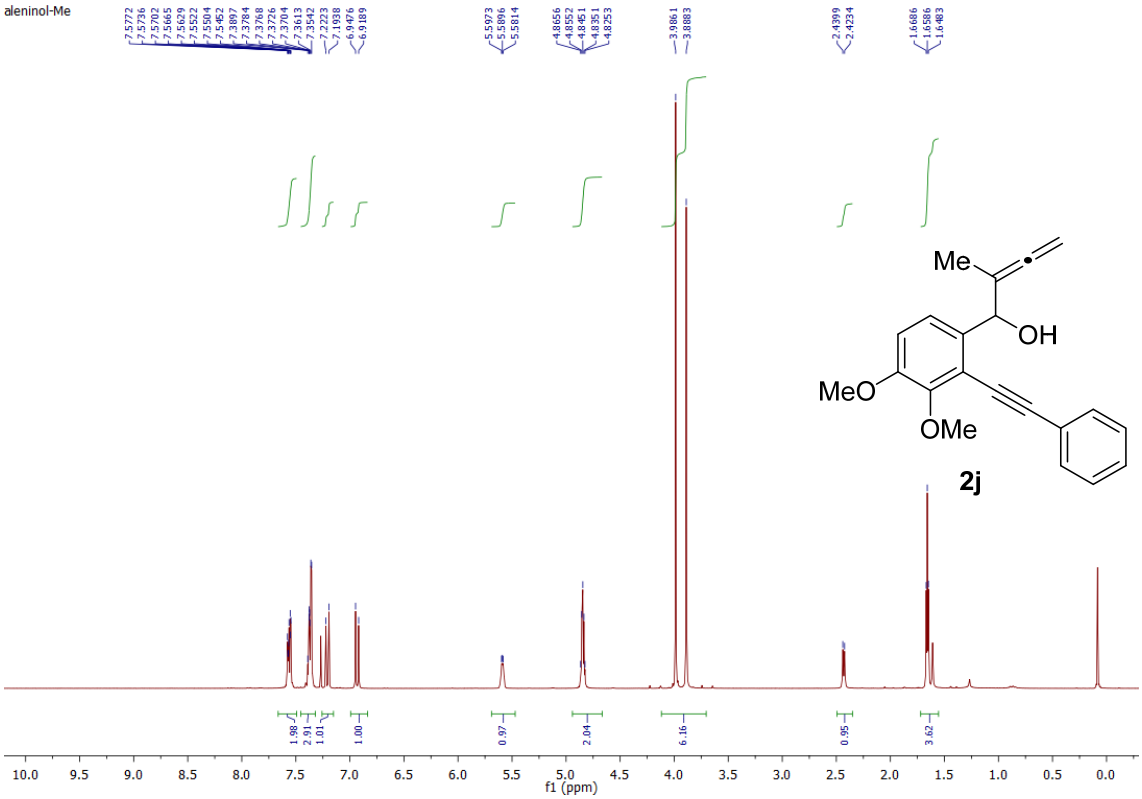
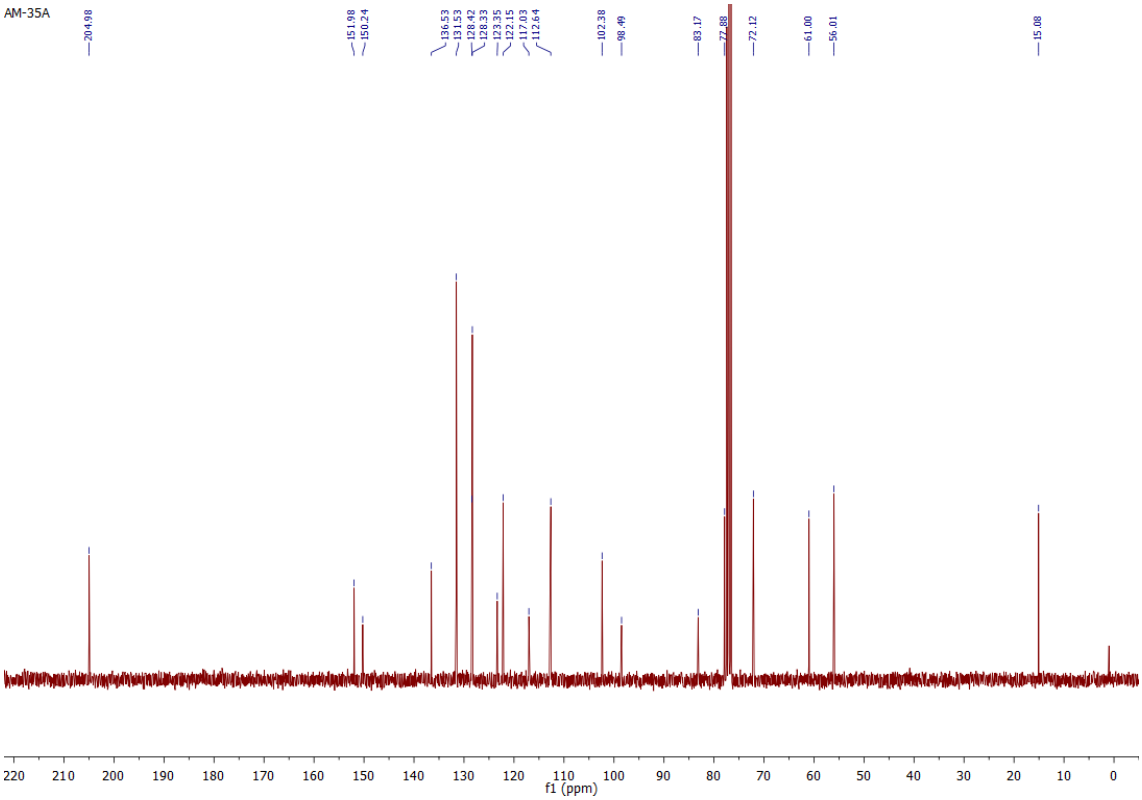
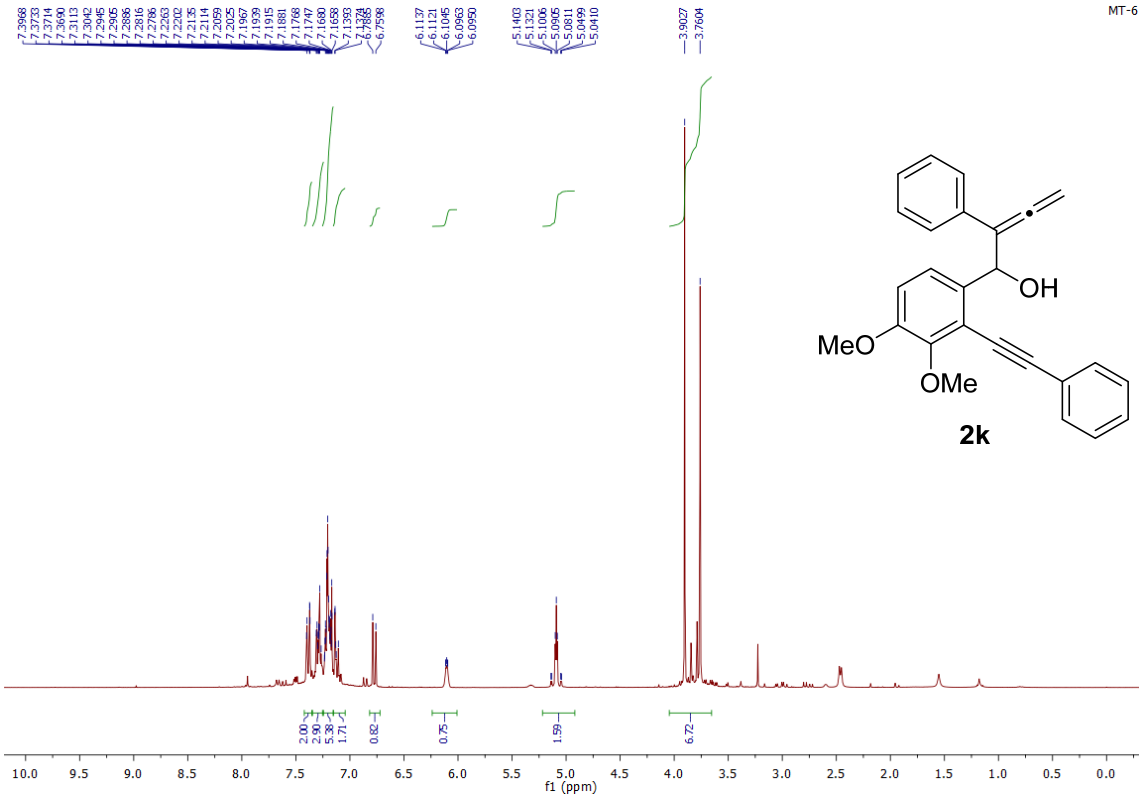
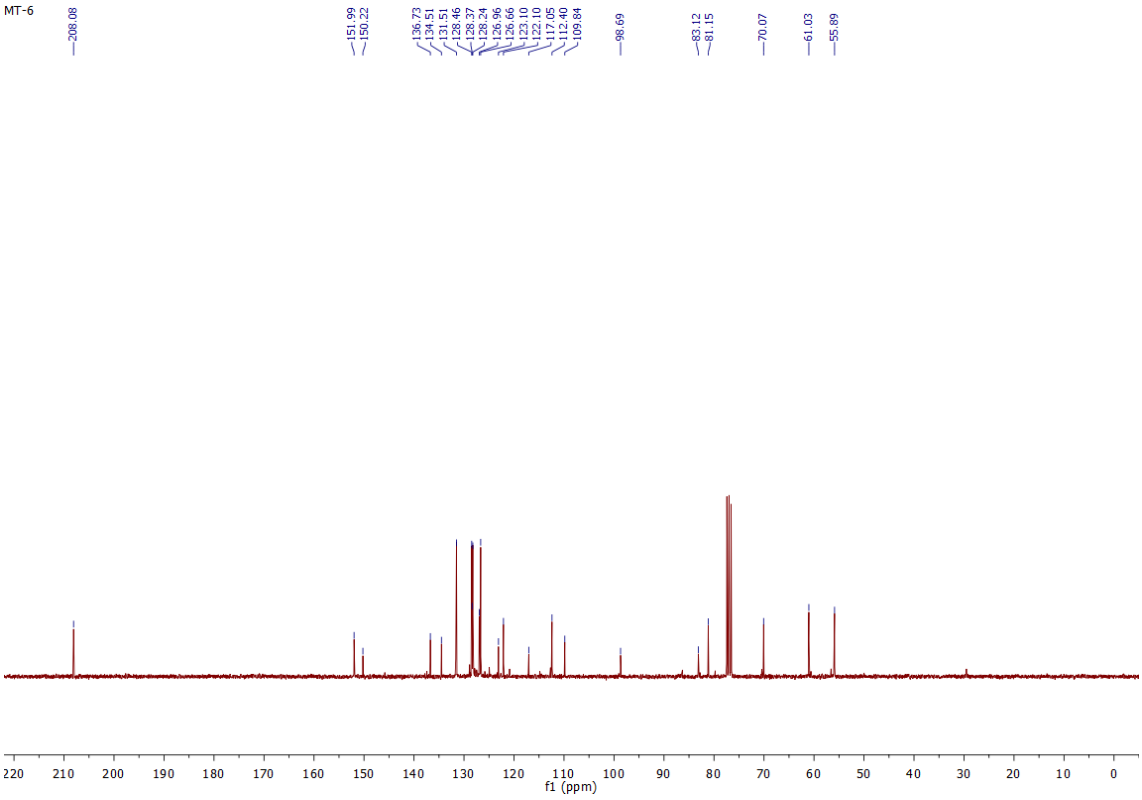
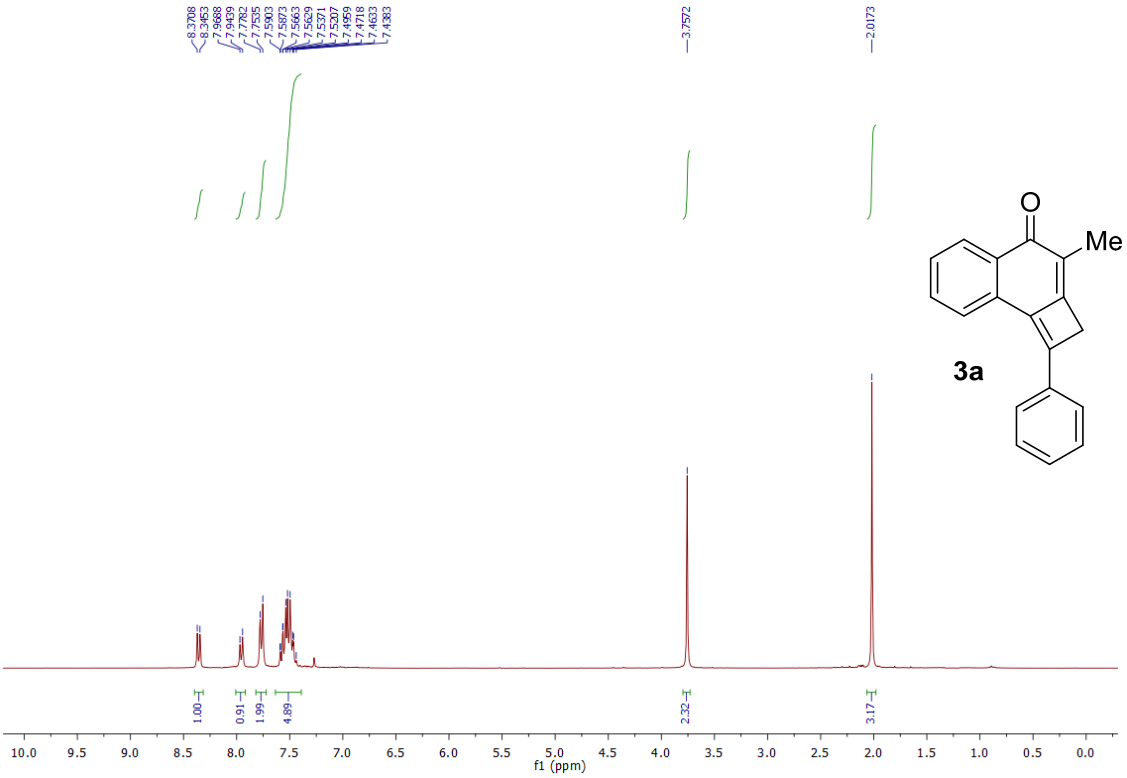

FH-744
f1 (ppm)


aleninol-Me
Me
OH
MeO
OMe
2j
f1 (ppm)


AM-35A
f1 (ppm)


MT-6
OH
MeO
OMe
2k
f1 (ppm)


MT-6
f1 (ppm)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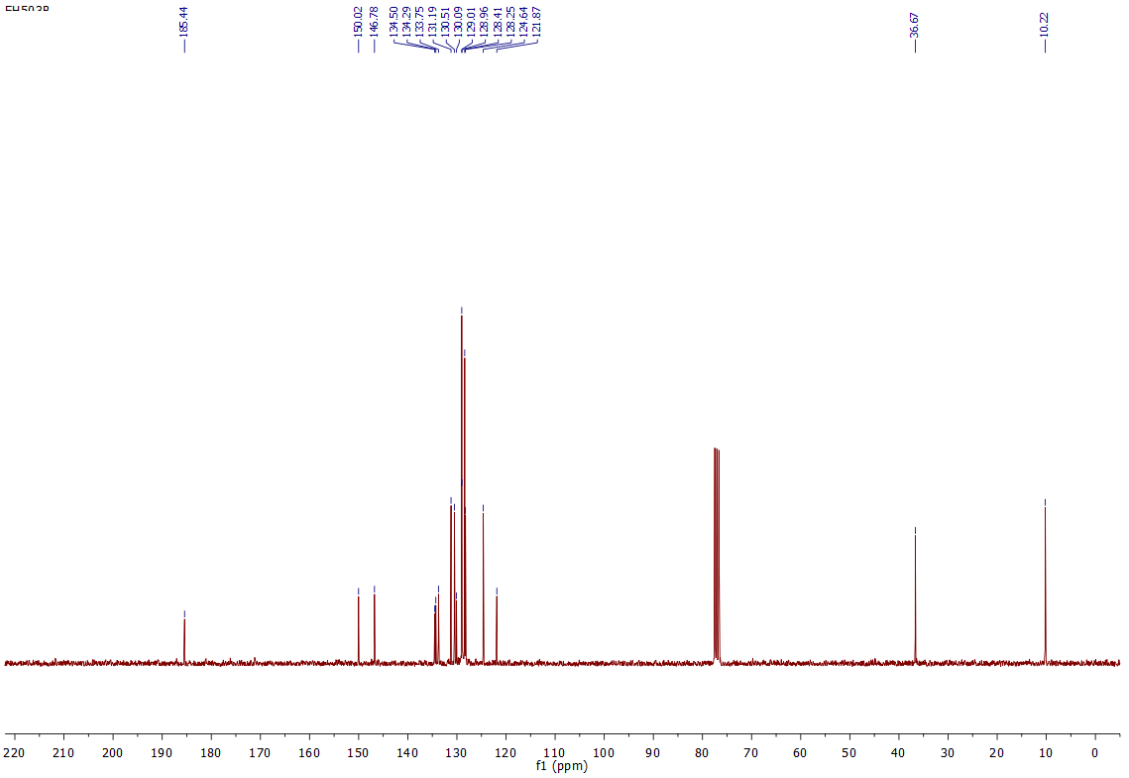
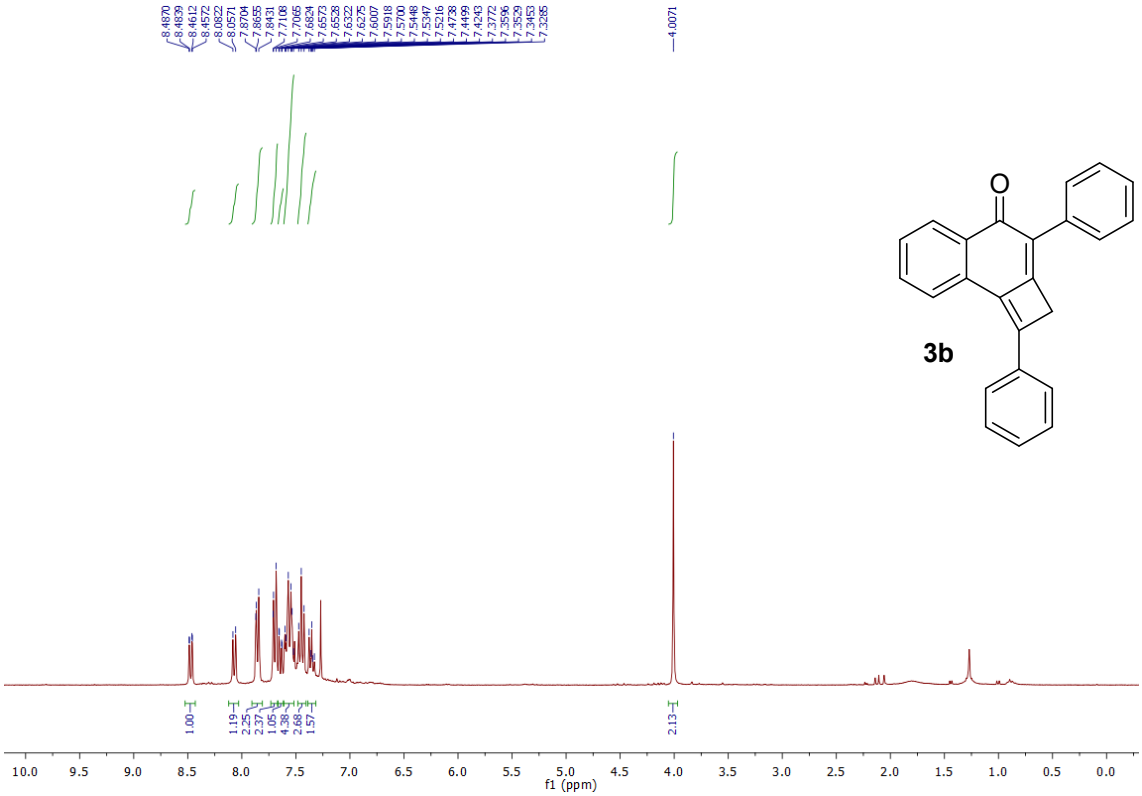
7.9439
7.7782
7.7535
7.5903
7.5873
7.5663
7.5629
7.5371
7.5307
7.4959
7.4718
7.4633
7.4383
3.7572
2.0173
O
Me
3a
1.00
0.91
1.99
4.89
2.32
3.17
f1 (ppm)


185.44
150.02
146.78
134.50
134.29
133.75
131.19
131.51
130.09
129.01
128.96
128.41
128.25
124.64
121.87
36.67
10.22
f1 (ppm)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8.0571
7.8704
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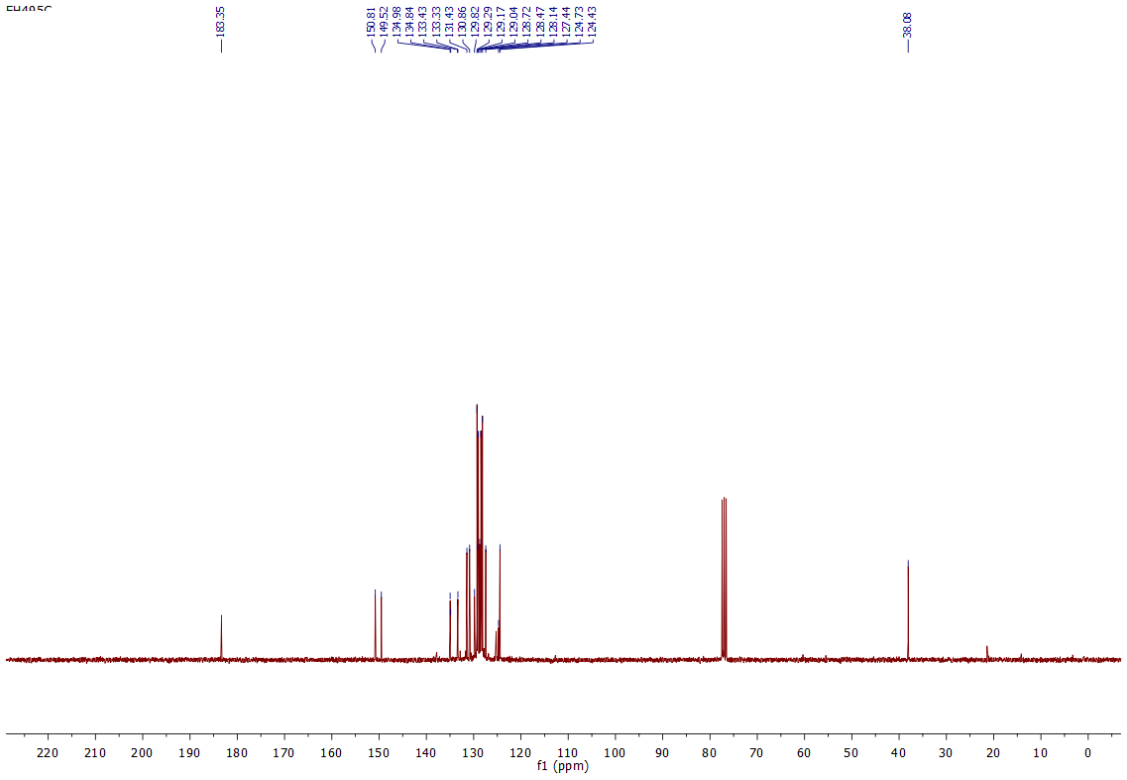
7.8431
7.7108
7.7065
7.6824
7.6573
7.6528
7.6322
7.6275
7.6007
7.5918
7.5700
7.5448
7.5397
7.5216
7.4738
7.4499
7.4243
7.3772
7.3596
7.3529
7.3453
7.3285
4.0071
O
3b
1.00
1.19
2.25
2.37
1.05
4.38
2.68
1.57
2.13
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)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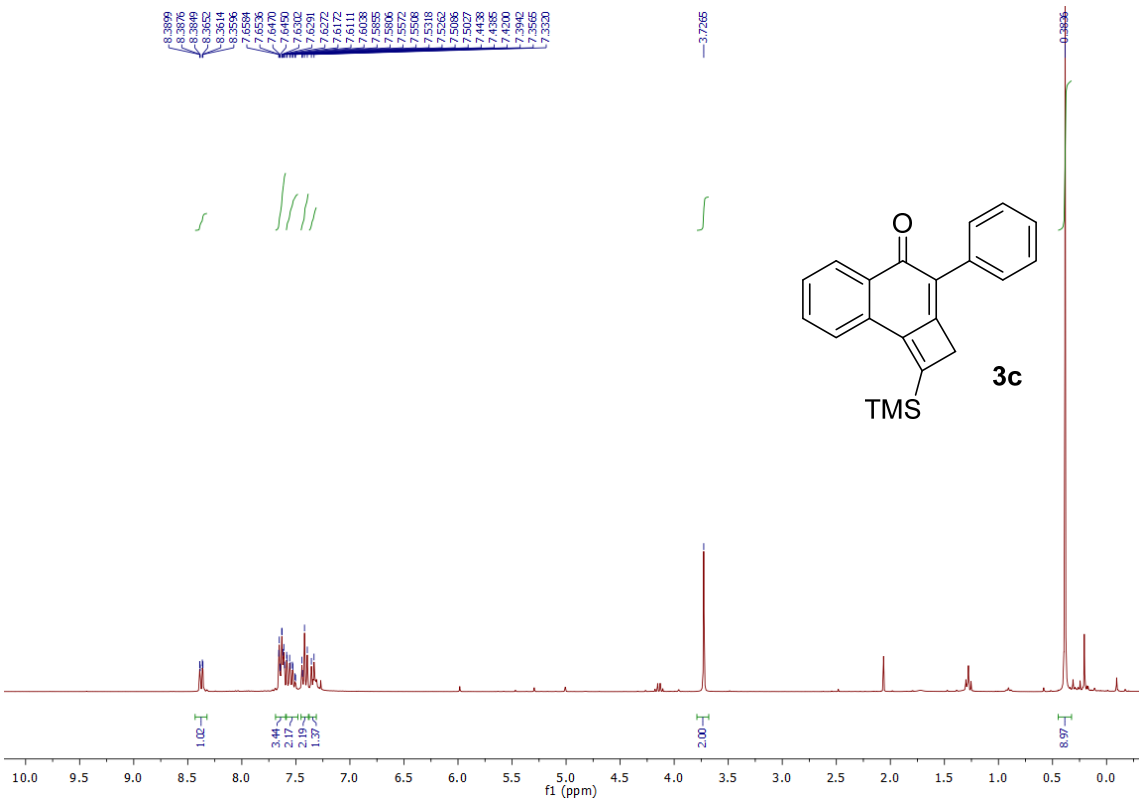
149.52
134.98
134.84
133.43
133.33
131.43
130.86
129.92
129.29
129.17
129.04
128.72
128.47
128.14
127.44
124.73
124.43
38.08
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)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8.3849
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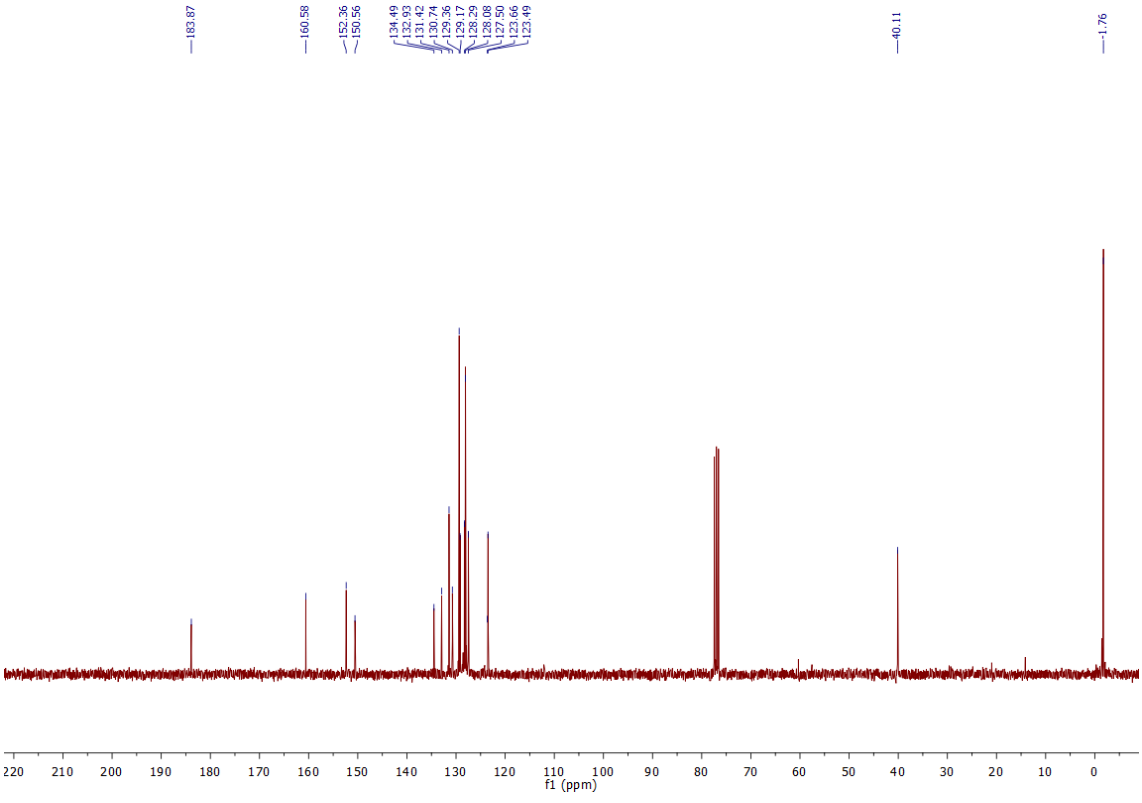
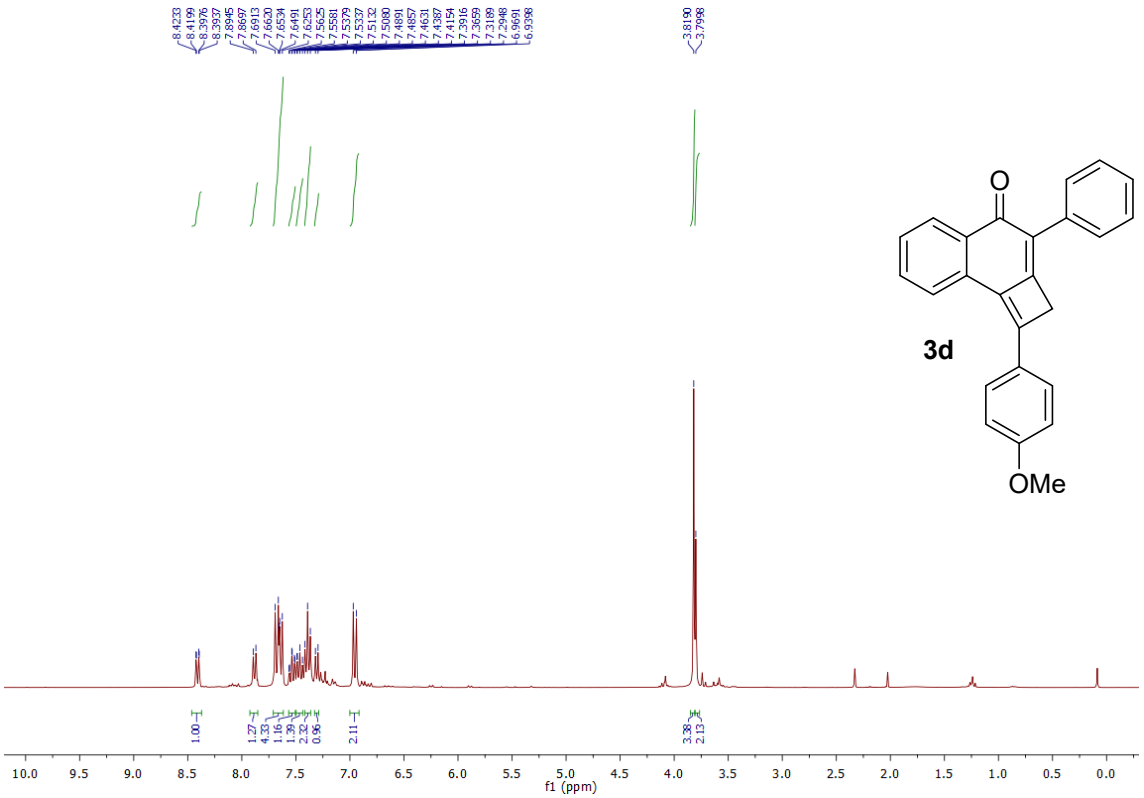
8.3614
8.3596
7.6594
7.6555
7.6470
7.6450
7.6302
7.6291
7.6272
7.6172
7.6111
7.6038
7.5895
7.5806
7.5572
7.5508
7.5318
7.5262
7.5095
7.5027
7.4438
7.4385
7.4200
7.3942
7.3565
7.3320
3.7265
0.3824
O
TMS
3c
1.02
3.44
2.17
2.19
1.37
2.00
8.97
f1 (ppm)


183.87
160.58
152.36
150.56
134.49
132.93
131.42
130.74
129.36
129.17
128.29
128.08
127.50
123.66
123.49
40.11
11.76
f1 (ppm)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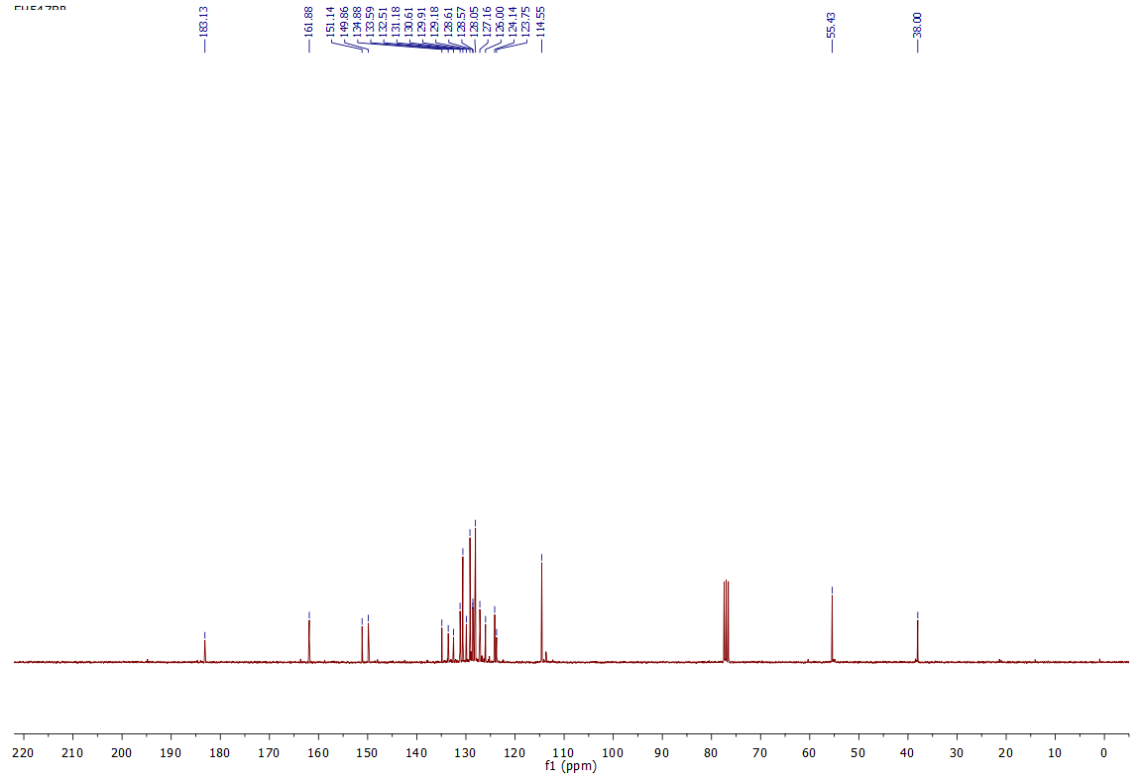
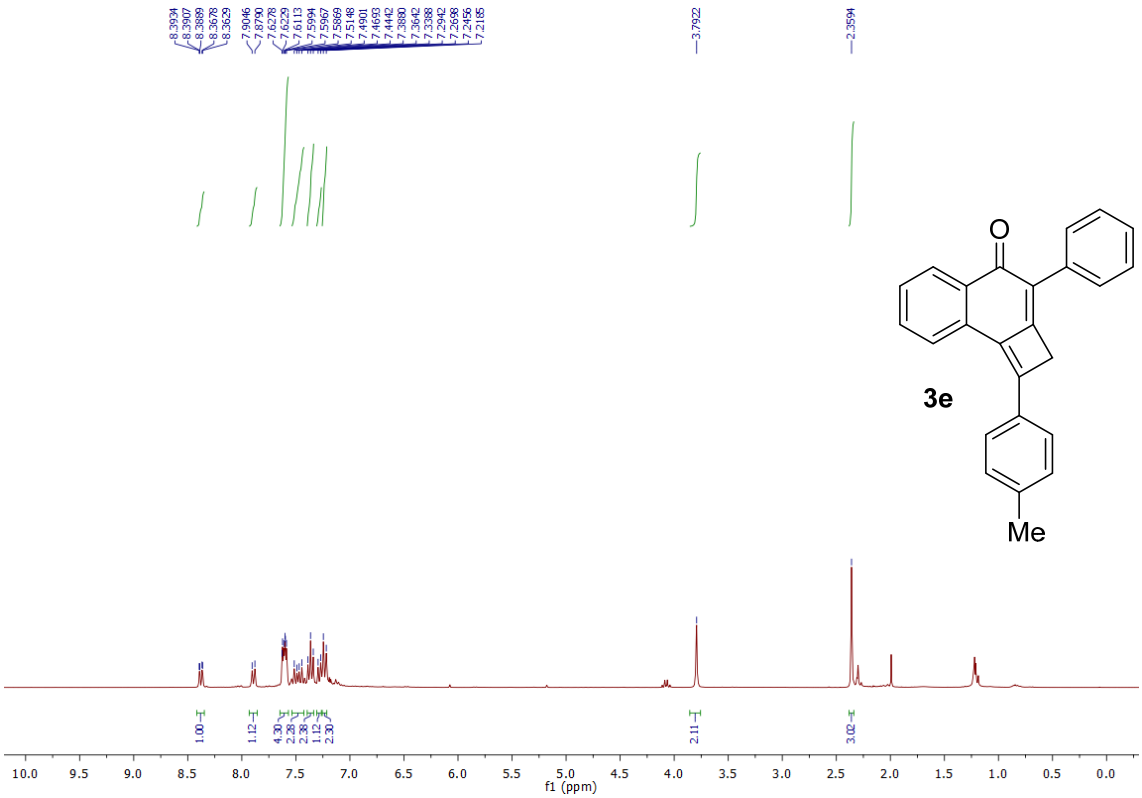
8.3976
8.3937
7.8945
7.8697
7.6913
7.6620
7.6524
7.6491
7.6253
7.5625
7.5581
7.5379
7.5337
7.5132
7.5080
7.4691
7.4657
7.4631
7.4387
7.4154
7.3916
7.3659
7.3189
7.2948
6.9691
6.9398
3.8190
3.7998
O
3d
OMe
1.00
1.27
4.33
1.16
1.39
2.22
0.98
2.11
3.38
2.13
f1 (ppm)


183.13
161.88
151.14
149.86
134.88
132.59
132.51
131.18
130.61
129.91
129.18
128.61
128.57
128.05
127.16
126.00
124.14
123.75
114.55
55.43
38.00
f1 (ppm)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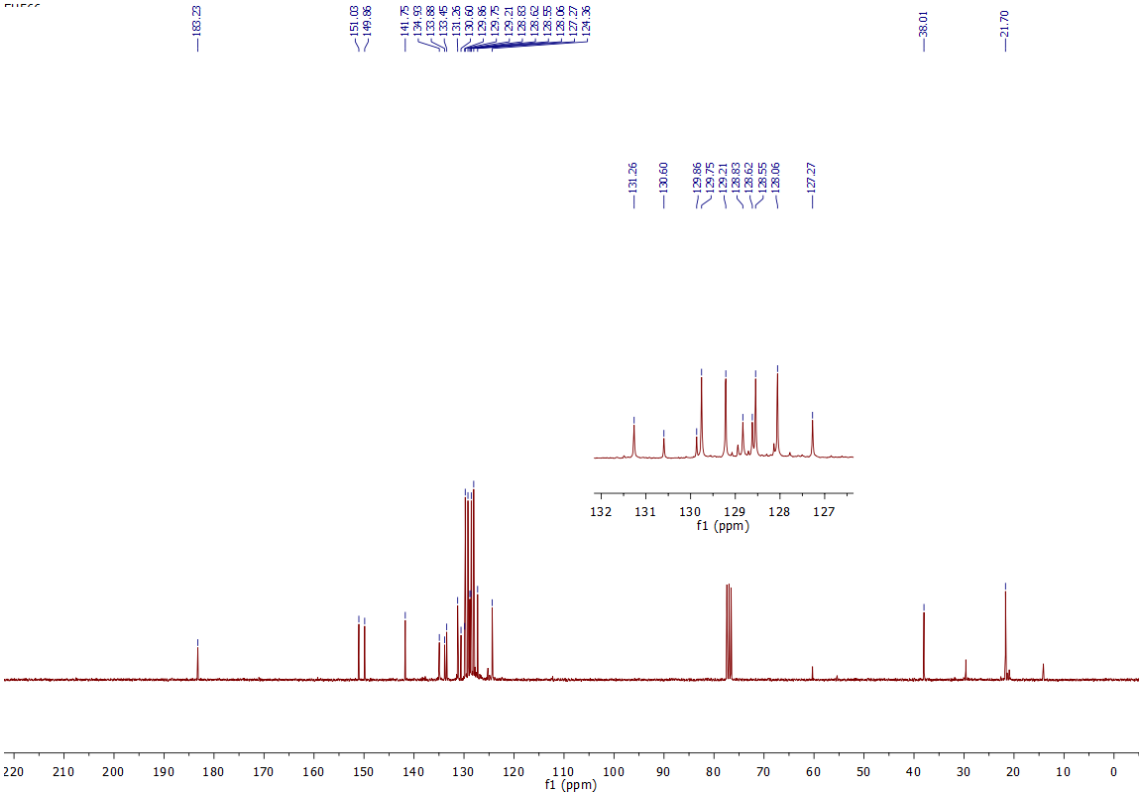
8.3889
8.3678
8.3629
7.9046
7.8990
7.8729
7.6229
7.6113
7.5994
7.5967
7.5869
7.5148
7.4901
7.4693
7.4442
7.3880
7.3642
7.3388
7.2942
7.2698
7.2456
7.2185
3.7922
2.3594
O
3e
Me
1.00
1.12
4.30
2.28
2.38
1.12
2.30
2.11
3.02
f1 (ppm)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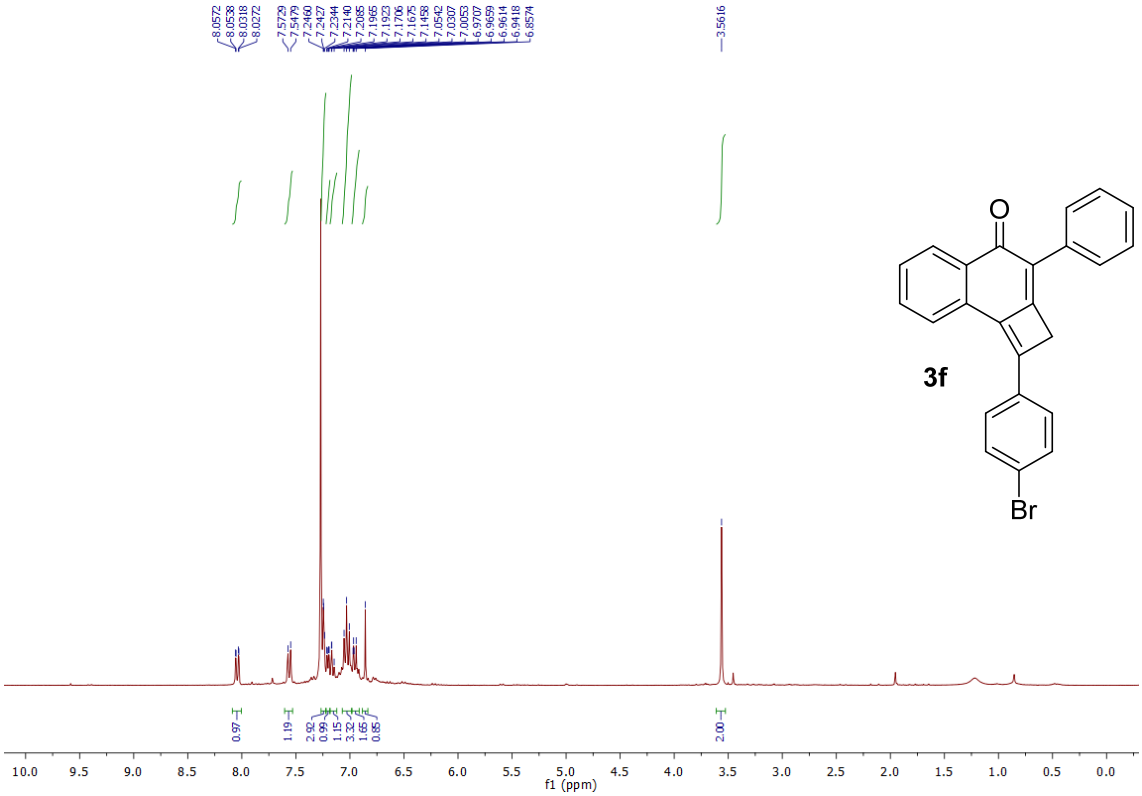
141.75
134.93
133.88
133.45
131.26
130.60
129.86
129.75
129.21
128.83
128.62
128.55
128.06
127.27
124.36
38.01
21.70
131.26
130.60
129.86
129.75
129.21
128.83
128.62
128.55
128.06
127.27
132
131
130
129
128
127
f1 (ppm)
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)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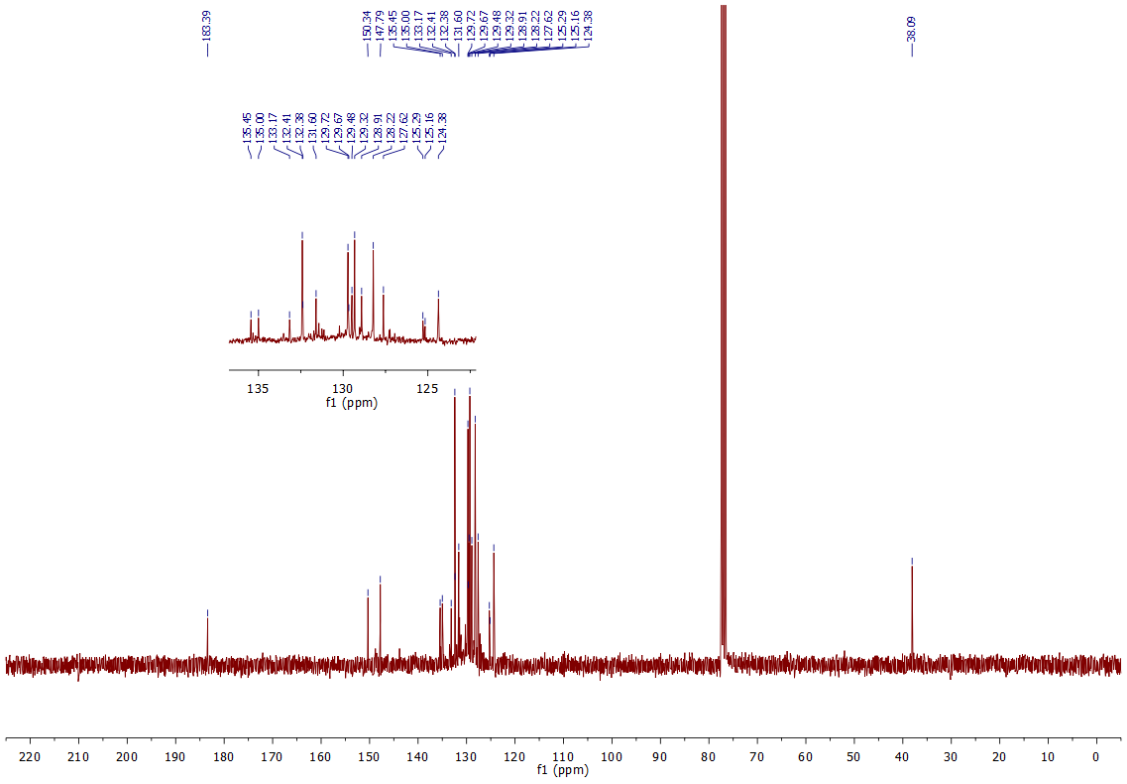
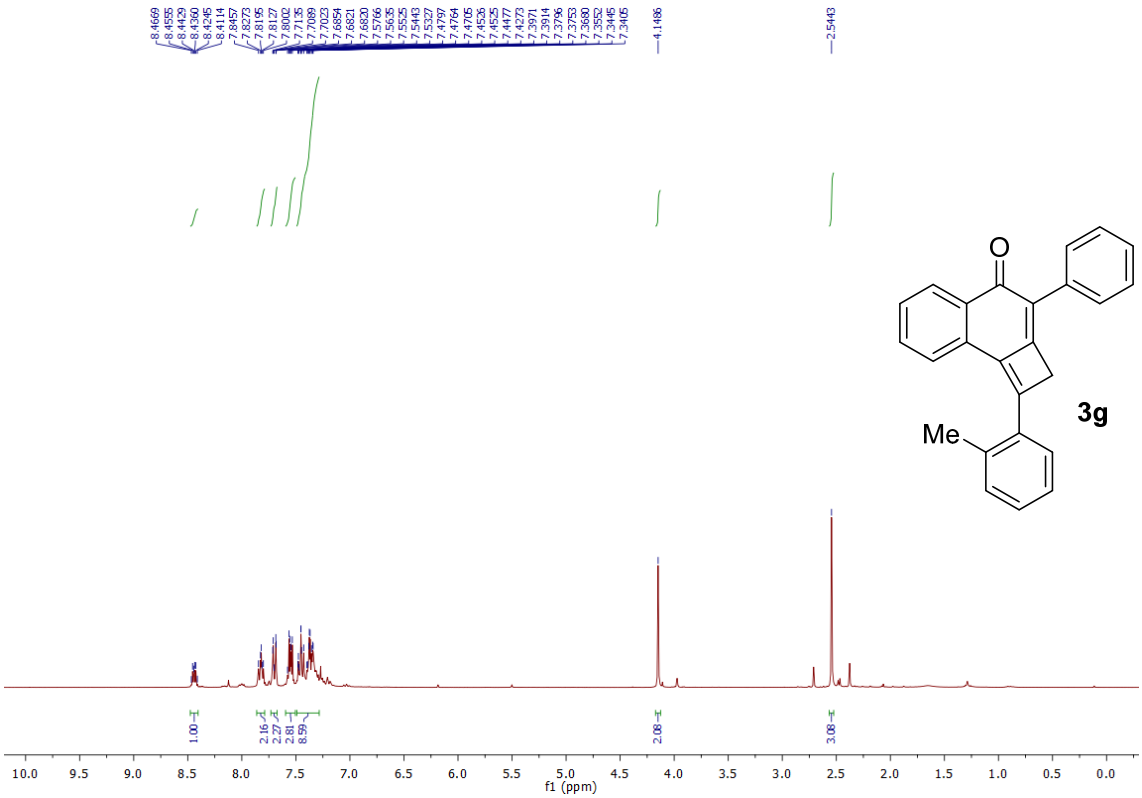
8.0538
8.0318
8.0272
7.5729
7.5479
7.2460
7.2427
7.2344
7.2140
7.2085
7.1965
7.1923
7.1706
7.1675
7.1498
7.0542
7.0307
7.0053
6.9707
6.9659
6.9614
6.9418
6.8574
3.5616
O
Br
3f
0.97
1.19
2.92
0.99
1.15
3.32
1.65
0.88
2.00
f1 (ppm)


180.39
150.34
147.79
135.45
135.00
133.17
132.41
132.38
131.60
129.72
129.67
129.48
129.32
128.91
128.22
127.62
125.29
125.16
124.38
38.09
f1 (ppm)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8.4360
8.4245
8.4114
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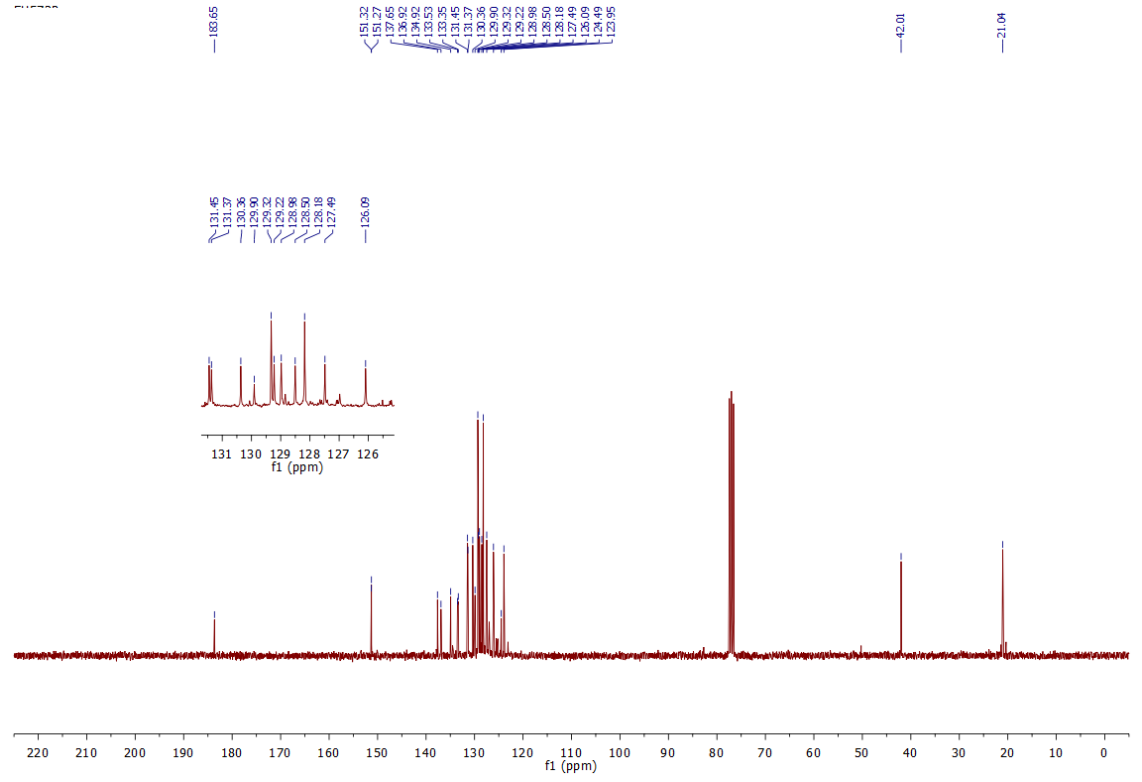
7.8195
7.8137
7.8002
7.7135
7.7089
7.7023
7.6854
7.6821
7.6820
7.5766
7.5635
7.5525
7.5443
7.5327
7.4797
7.4764
7.4705
7.4535
7.4525
7.4477
7.4273
7.3971
7.3914
7.3796
7.3753
7.3680
7.3552
7.3445
7.3405
4.1486
2.5443
O
Me
3g
1.00
2.16
2.27
2.81
8.59
2.08
3.08
f1 (ppm)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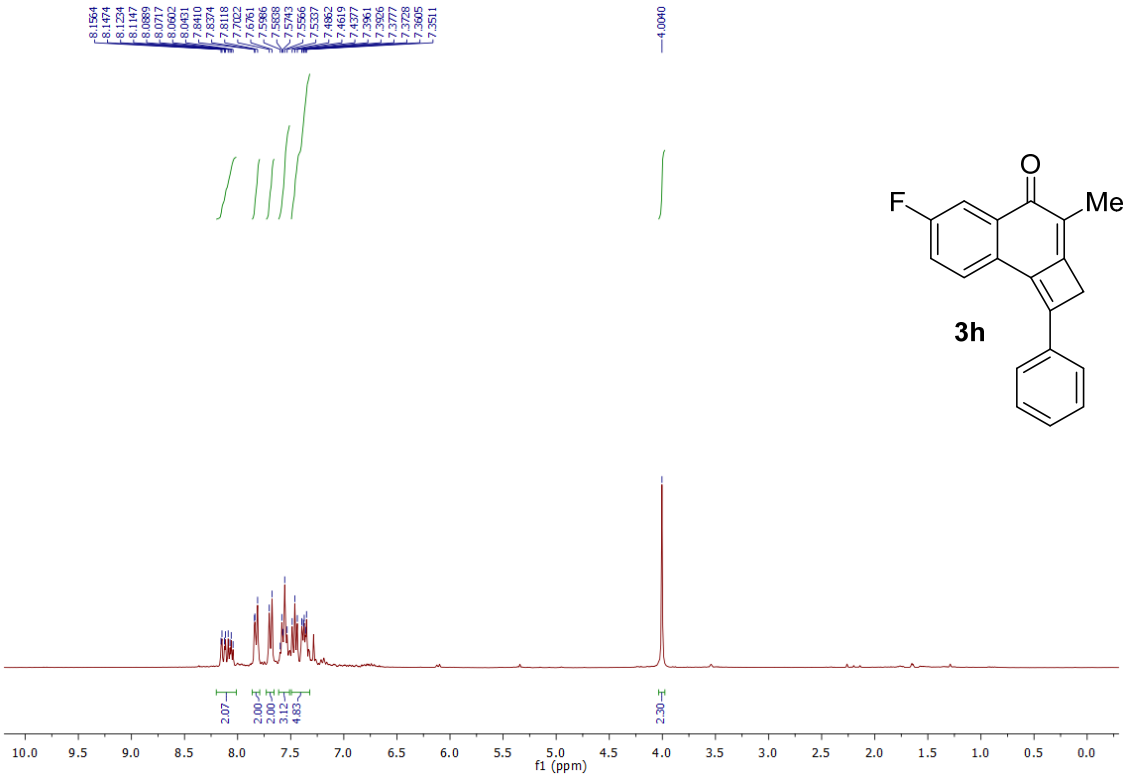
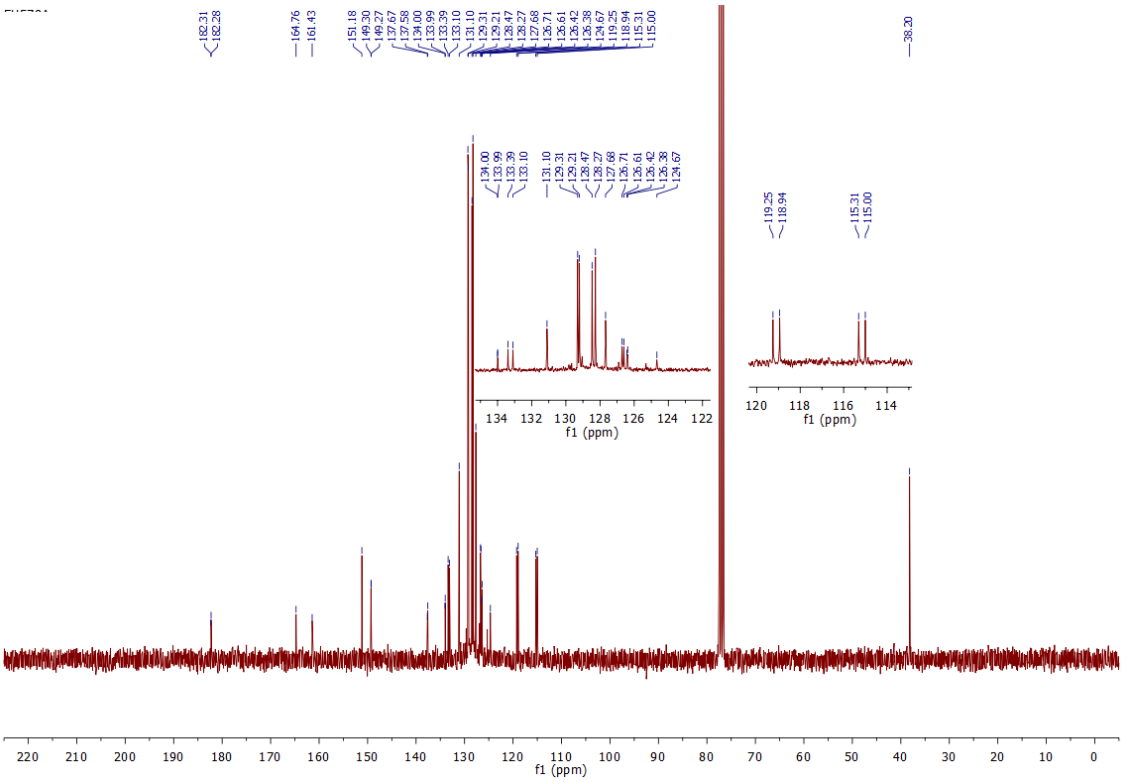
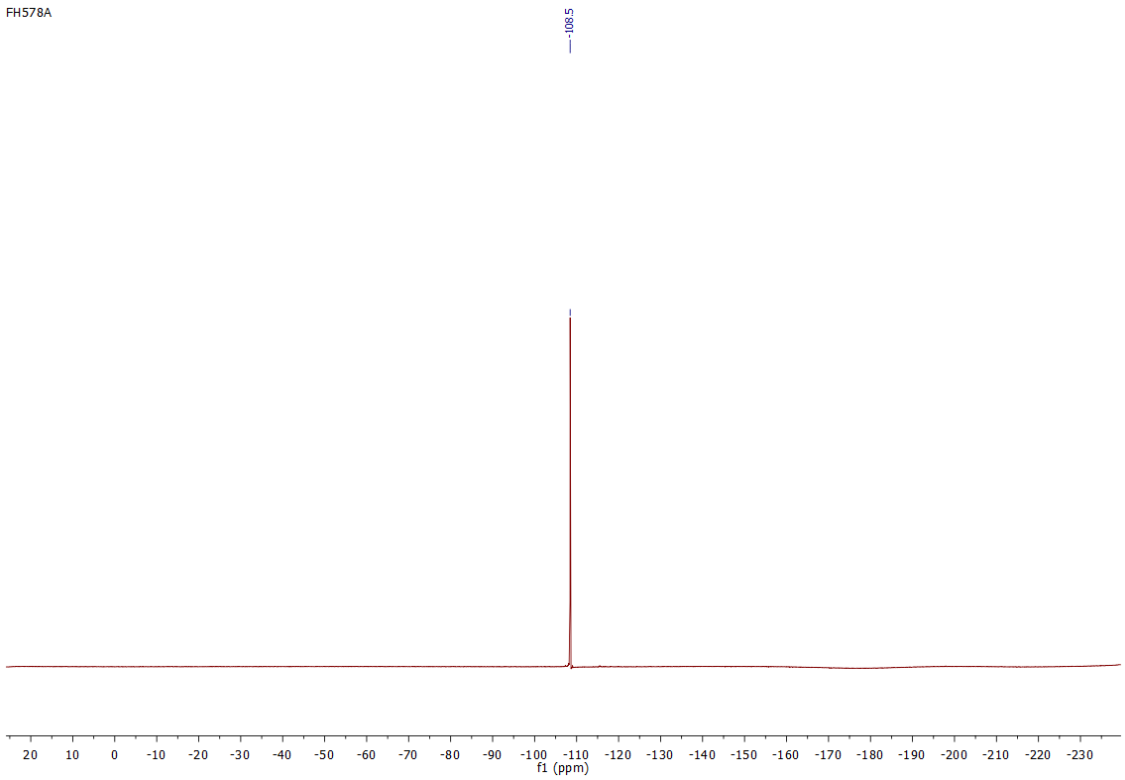
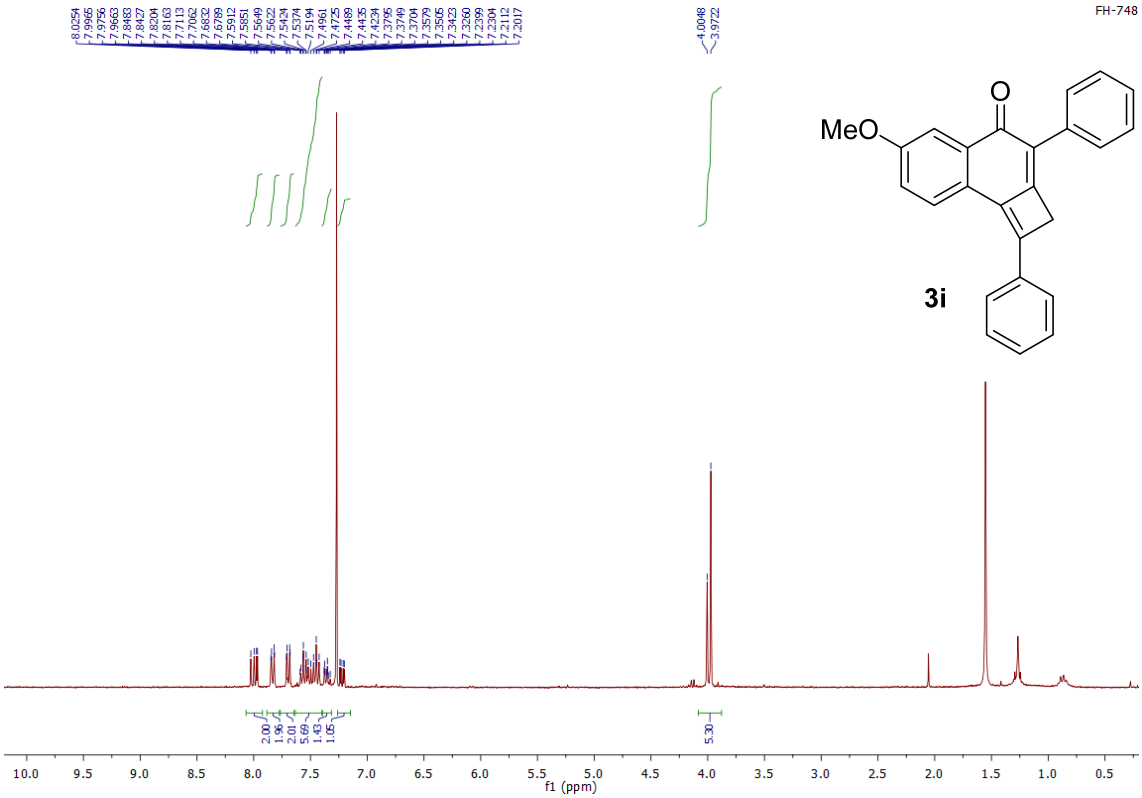
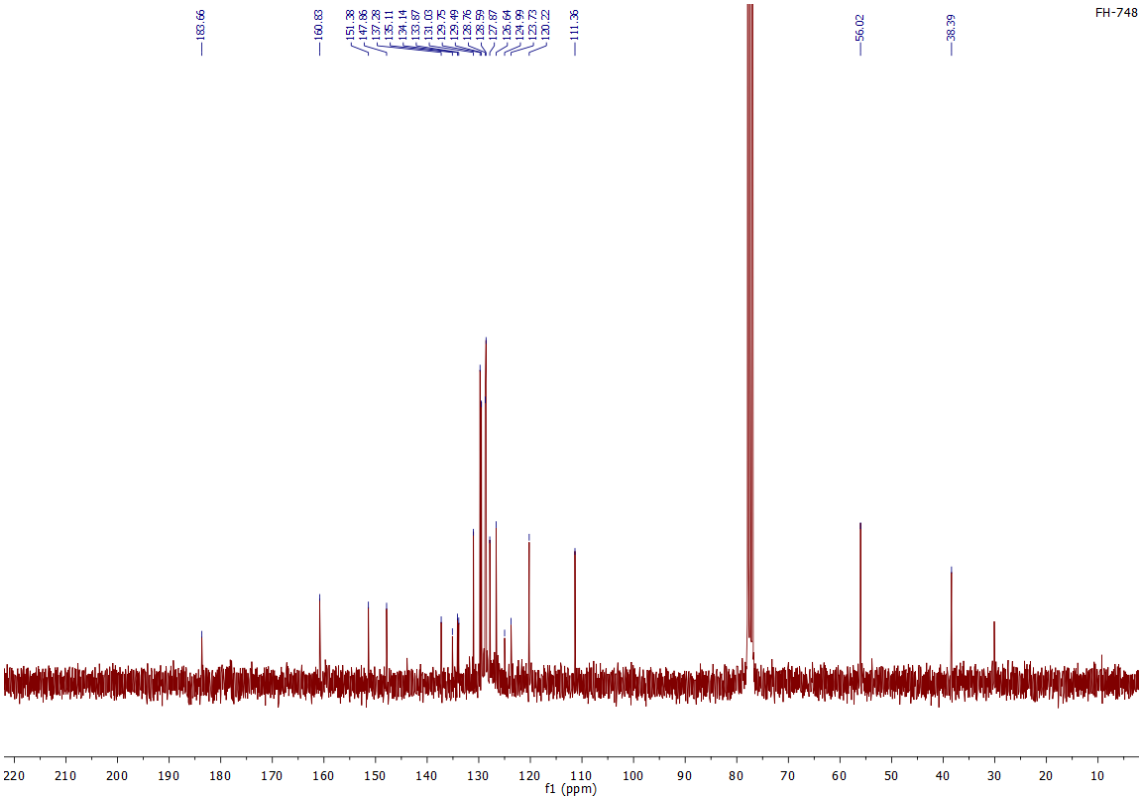
151.27
137.65
136.92
134.92
133.53
133.35
131.45
131.37
130.36
129.90
129.32
129.22
128.98
128.50
128.18
127.49
126.09
124.49
123.95
42.01
21.04
131 130 129 128 127 126
f1 (ppm)
f1 (ppm)

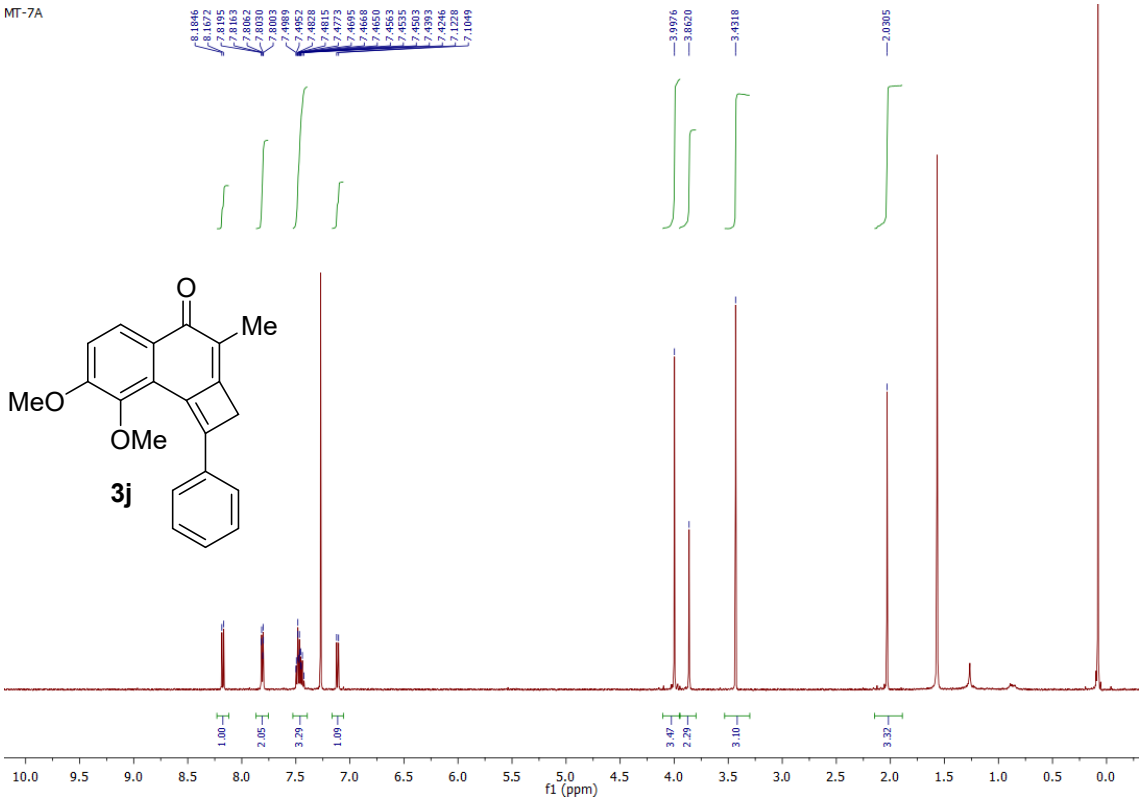

F
O
Me
3h
f1 (ppm)


f1 (ppm)


FH578A
-108.5
20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210 -220 -230
f1 (ppm)


FH-748
MeO
O
3i
f1 (ppm)


FH-748
f1 (ppm)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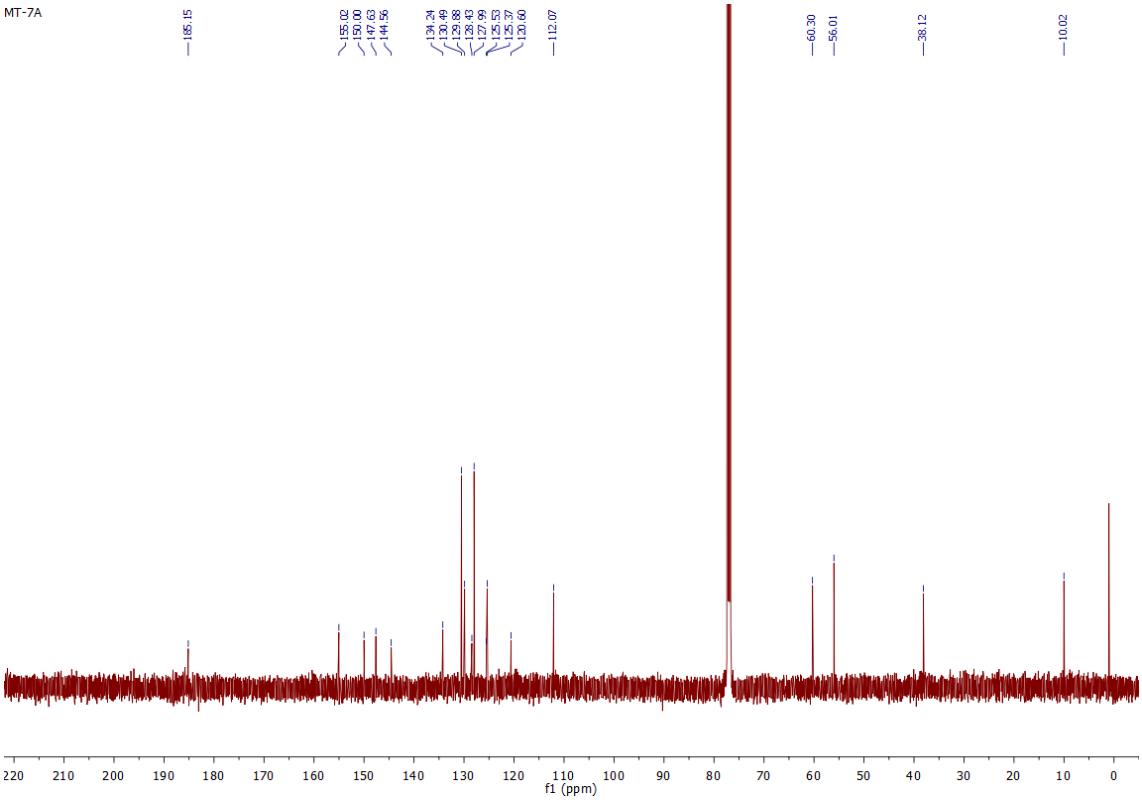
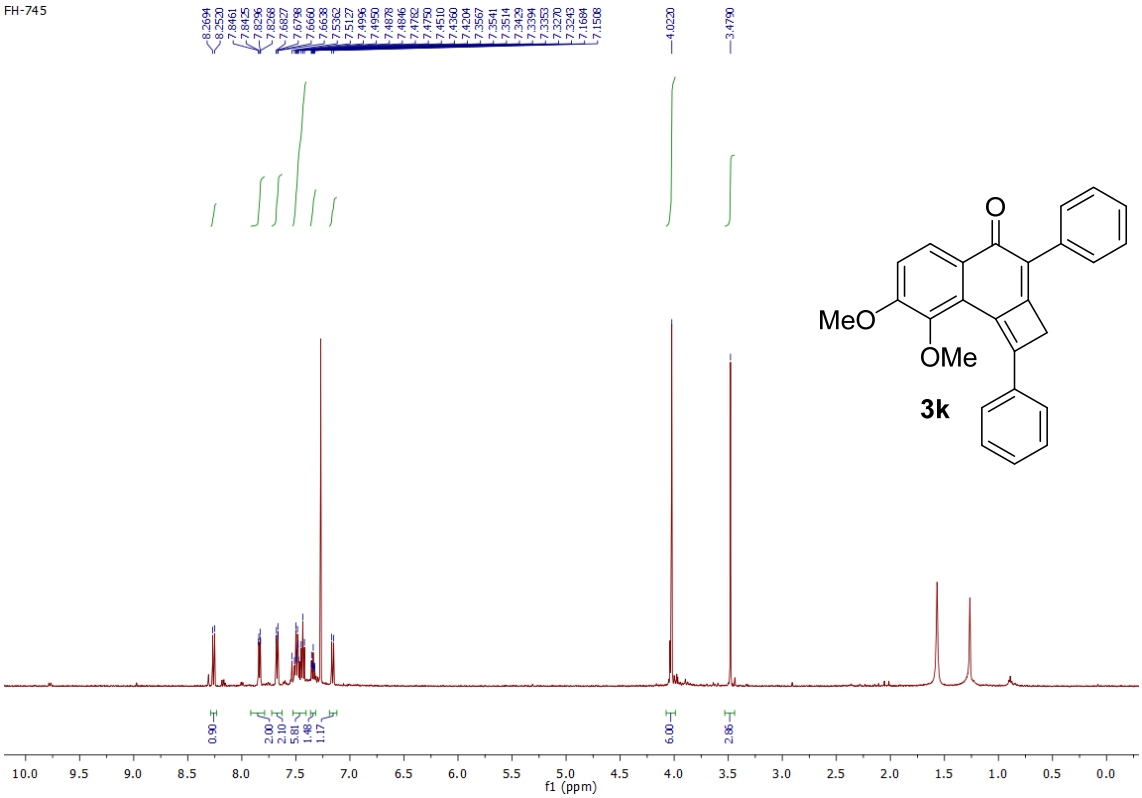
7.8030
7.8003
7.4989
7.4952
7.4828
7.4815
7.4773
7.4695
7.4668
7.4650
7.4563
7.4535
7.4503
7.4393
7.4246
7.2728
7.1049
3.9976
3.8620
3.4318
2.0305
O
Me
MeO
OMe
3j
1.00
2.05
3.29
1.09
3.47
2.29
3.10
3.32
f1 (ppm)


MT-7A
185.15
155.02
150.00
147.63
144.56
134.24
130.49
129.88
128.63
127.89
125.53
125.37
120.60
112.07
60.30
56.01
38.12
10.02
f1 (ppm)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7.8425
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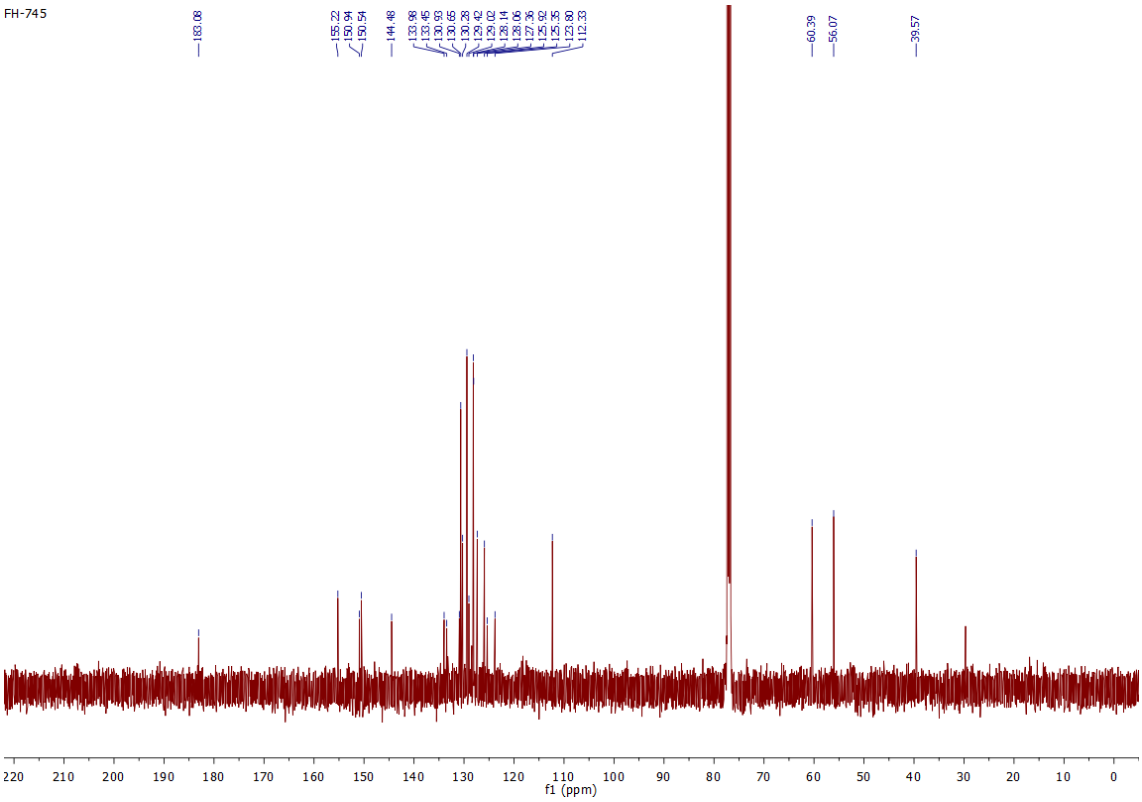
7.8268
7.6827
7.6798
7.6660
7.6638
7.5362
7.5127
7.4996
7.4950
7.4878
7.4846
7.4782
7.4750
7.4510
7.4380
7.4204
7.3567
7.3541
7.3514
7.3429
7.3394
7.3353
7.3270
7.3243
7.1694
7.1508
4.0220
3.4790
0.90
2.00
2.10
5.81
1.48
1.17
6.00
2.86
f1 (ppm)
MeO
OMe
O
3k


FH-745
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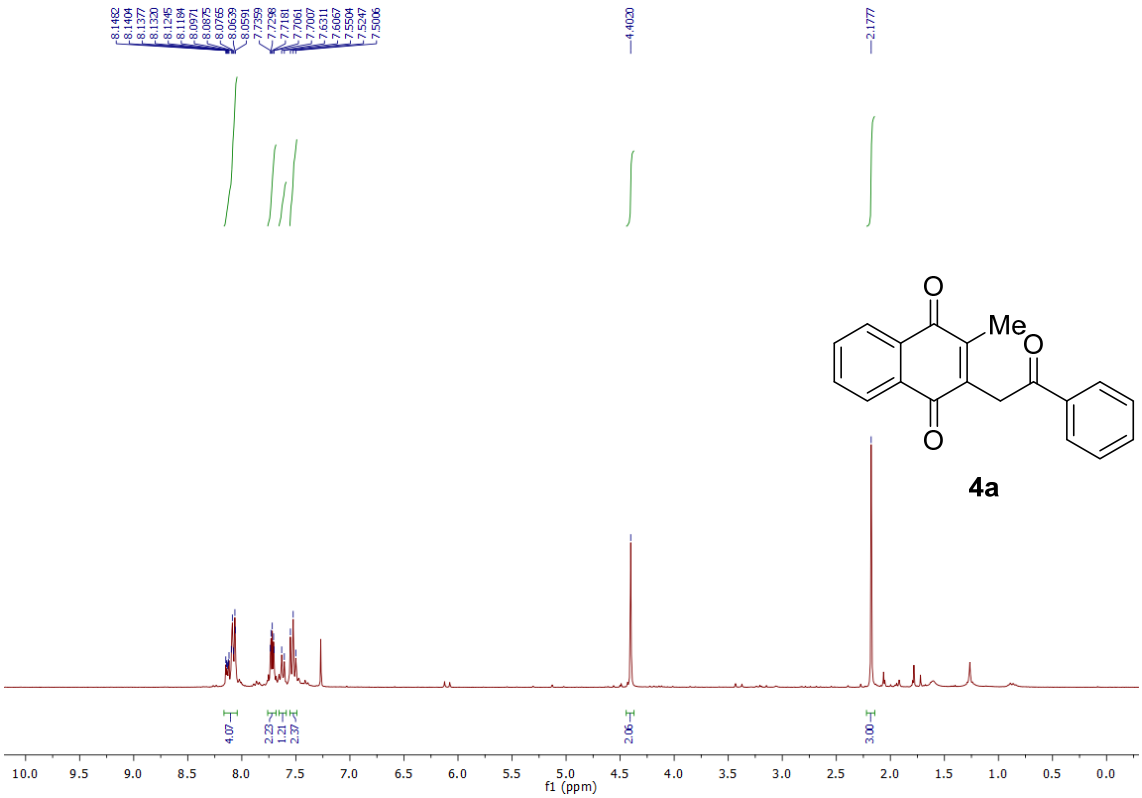
150.54
144.48
133.98
133.45
130.93
130.65
130.28
129.42
129.02
128.14
128.06
127.36
125.92
125.35
123.80
112.33
60.39
56.07
39.57
f1 (ppm)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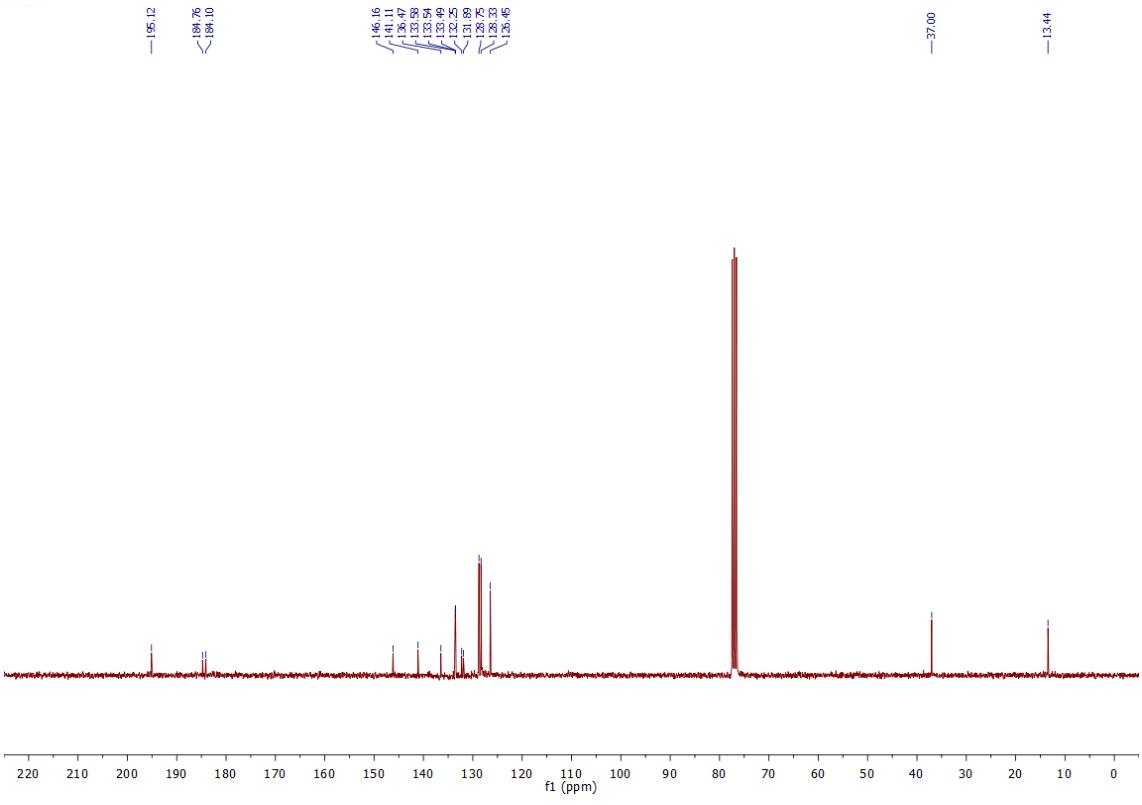
8.1184
8.0971
8.0875
8.0785
8.0659
8.0591
7.7298
7.7181
7.7061
7.7007
7.6311
7.6067
7.5504
7.5247
7.5006
4.4020
2.1777
Me
O
O
O
4a
4.07
2.23
1.21
2.37
2.06
3.00
f1 (ppm)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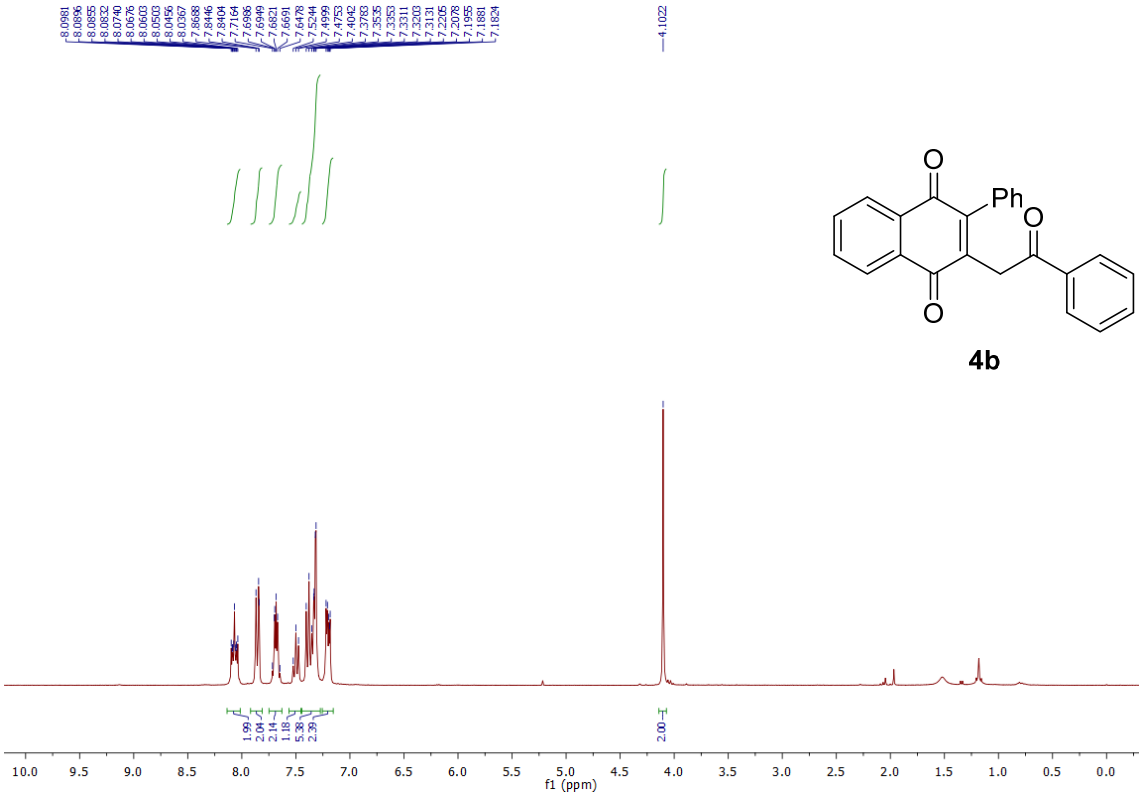
189.76
189.10
146.16
141.11
136.47
133.98
133.54
133.49
132.25
131.89
128.75
128.33
126.45
37.00
13.44
f1 (ppm)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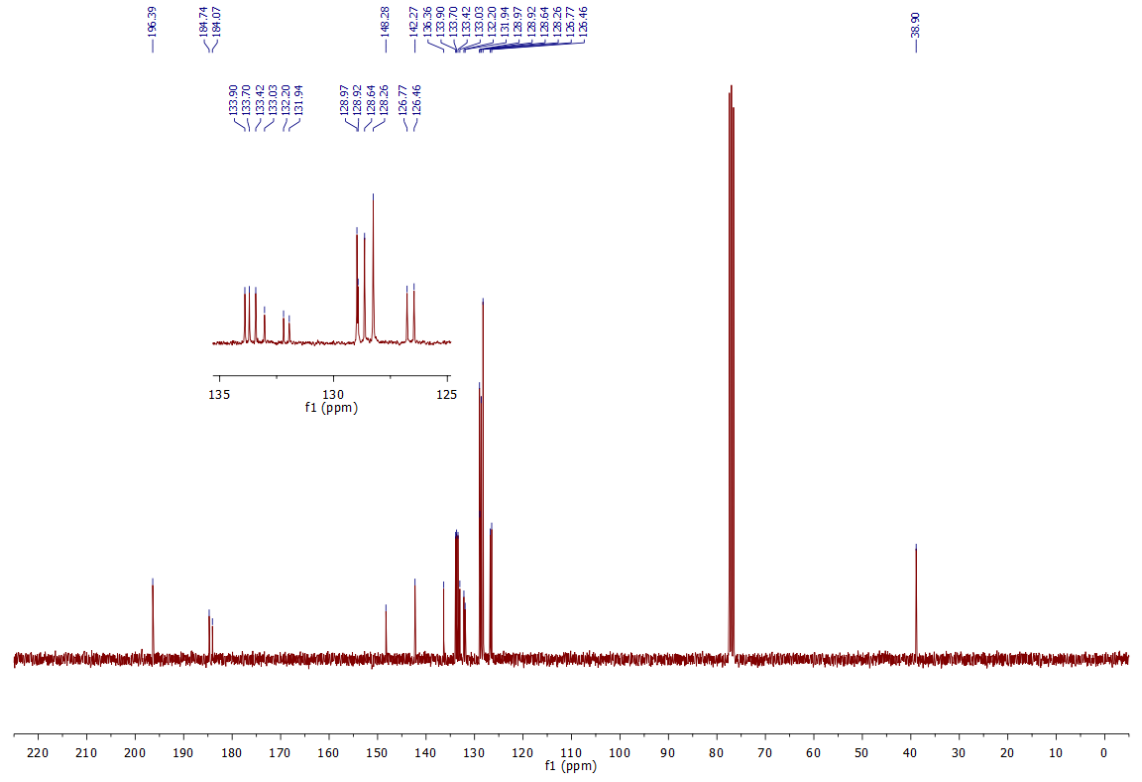
8.0693
8.0740
8.0676
8.0603
8.0503
8.0456
8.0367
7.8688
7.8446
7.8404
7.7164
7.6996
7.6949
7.6691
7.6478
7.5244
7.4999
7.4753
7.4042
7.3783
7.3535
7.3353
7.3311
7.3203
7.3131
7.2205
7.2078
7.1955
7.1881
7.1824
4.1022
O
Ph
O
O
4b
1.99
2.04
2.14
1.18
5.38
2.39
2.00
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)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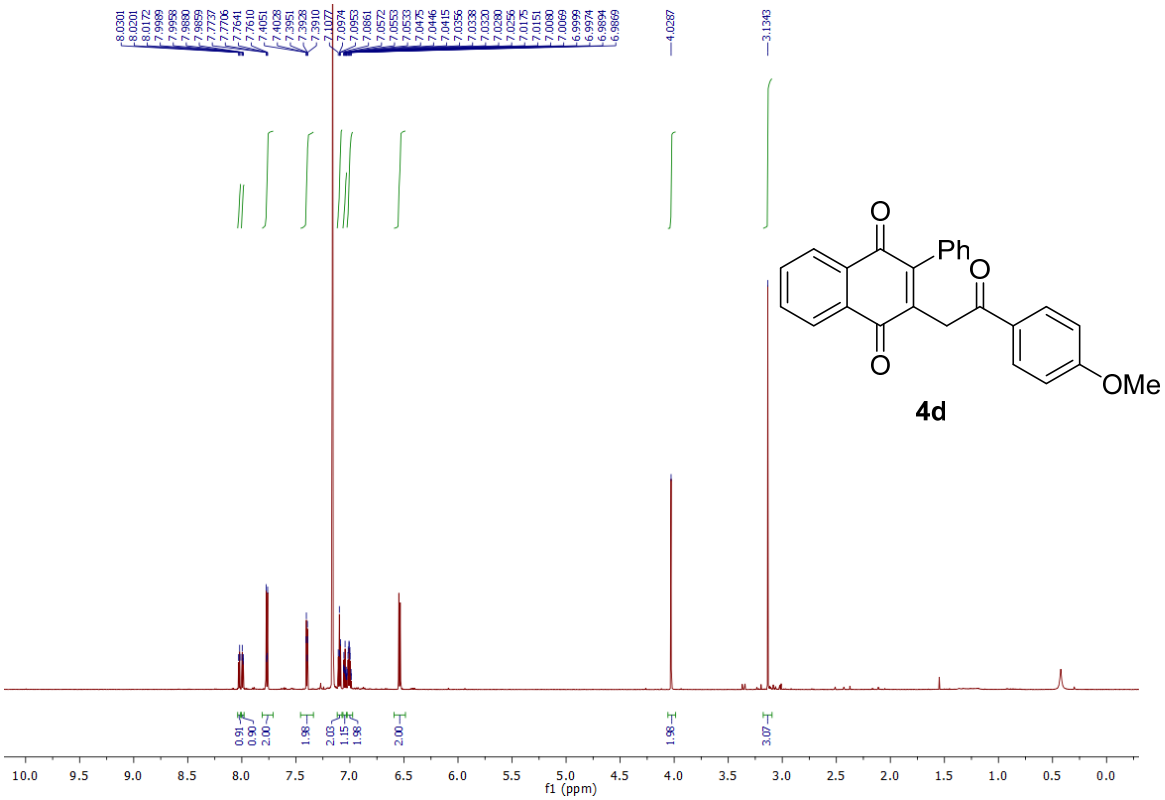
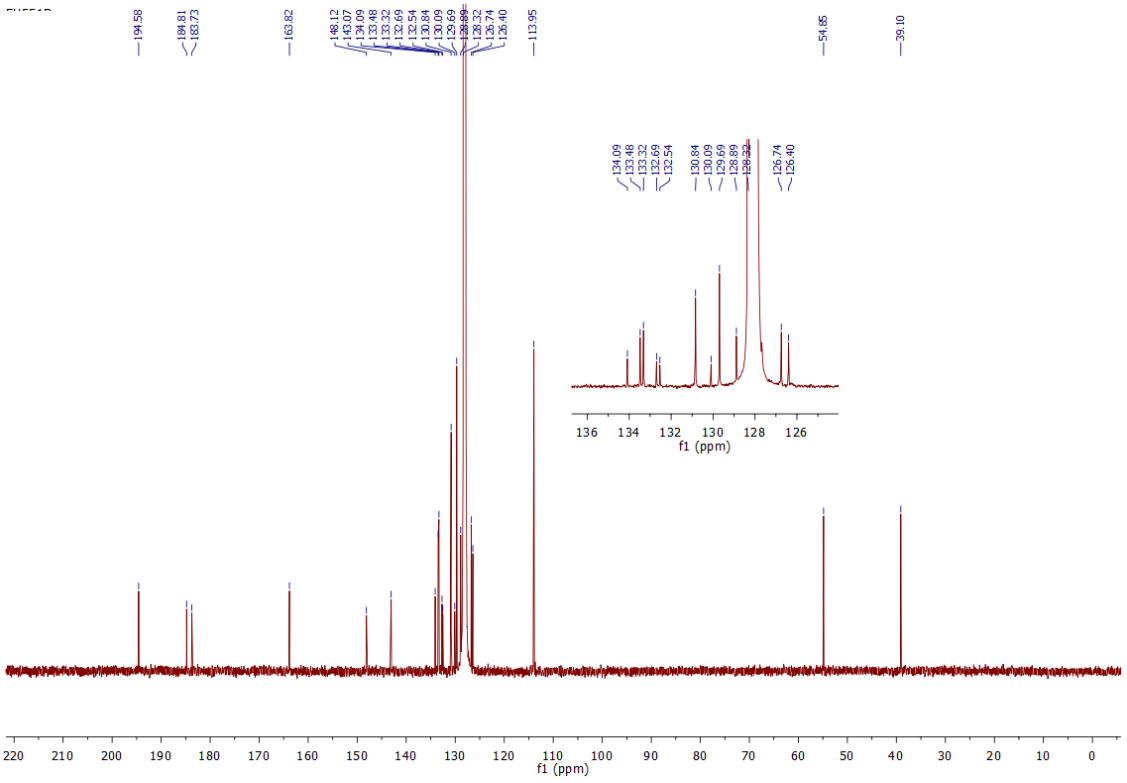
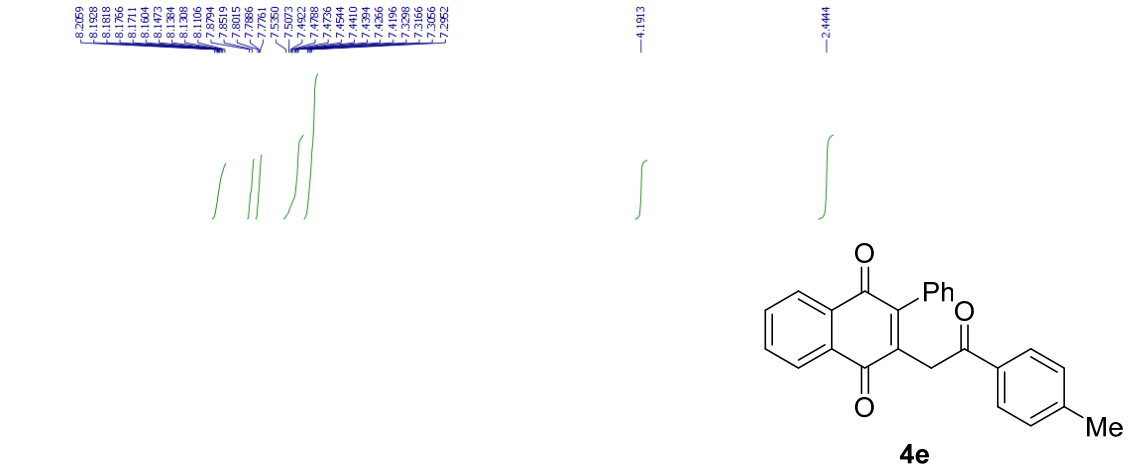
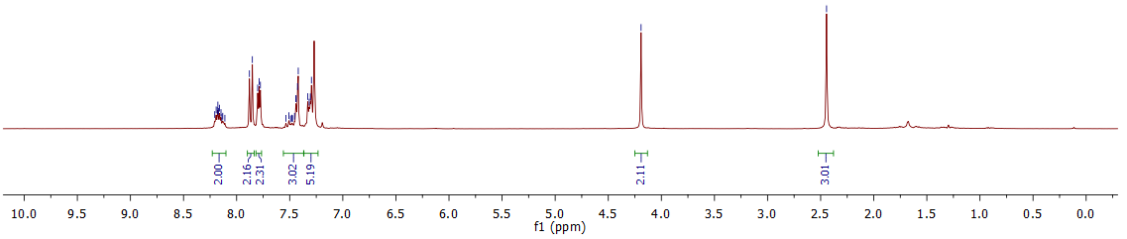
142.27
136.36
133.90
133.70
133.42
133.03
132.20
131.94
128.97
128.92
128.64
128.26
126.77
126.46
38.90
133.90
133.70
133.42
133.03
132.20
131.94
128.97
128.92
128.64
128.26
126.77
126.46
135
130
125
f1 (ppm)
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

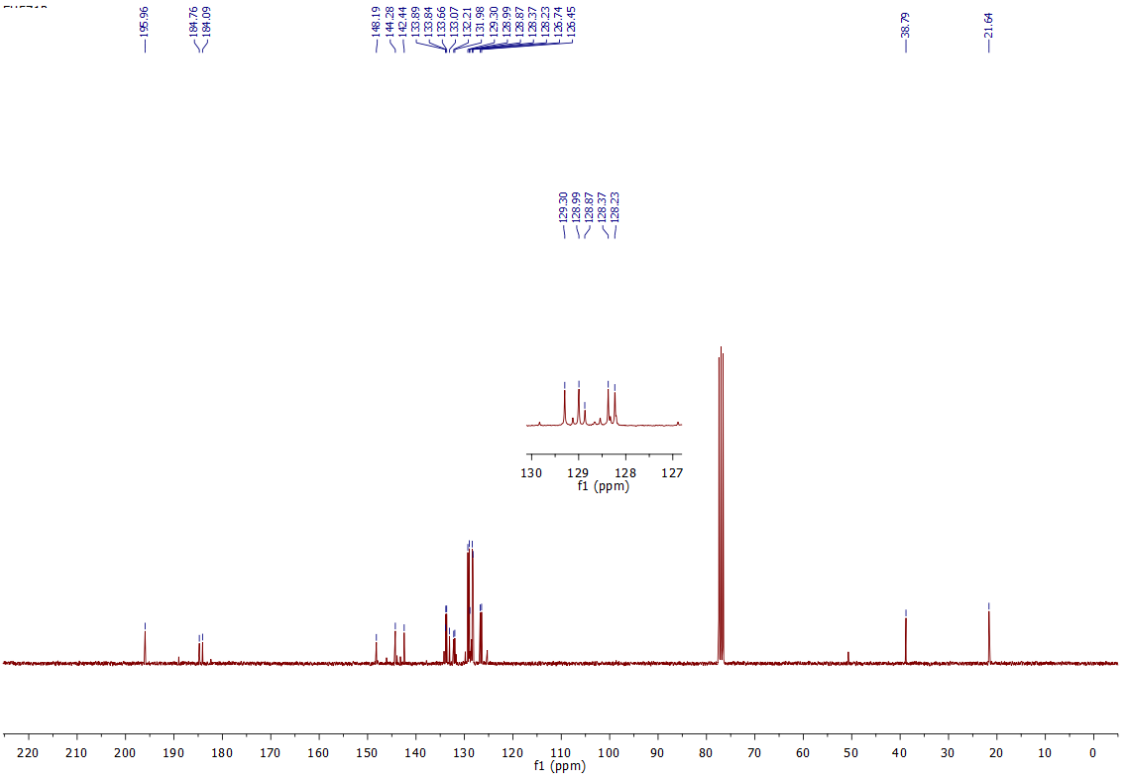

8.0301
8.0291
8.0172
7.9989
7.9958
7.9880
7.9859
7.7737
7.7706
7.7641
7.7610
7.4051
7.4028
7.3951
7.3928
7.3910
7.1077
7.0974
7.0953
7.0861
7.0572
7.0553
7.0533
7.0475
7.0446
7.0415
7.0356
7.0338
7.0320
7.0280
7.0256
7.0175
7.0151
7.0080
7.0069
6.9999
6.9974
6.9894
6.9869
4.0287
3.1343
0.91
0.90
2.00
1.98
2.03
1.15
1.98
2.00
1.98
3.07
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)
O
Ph
O
O
O
OMe
4d

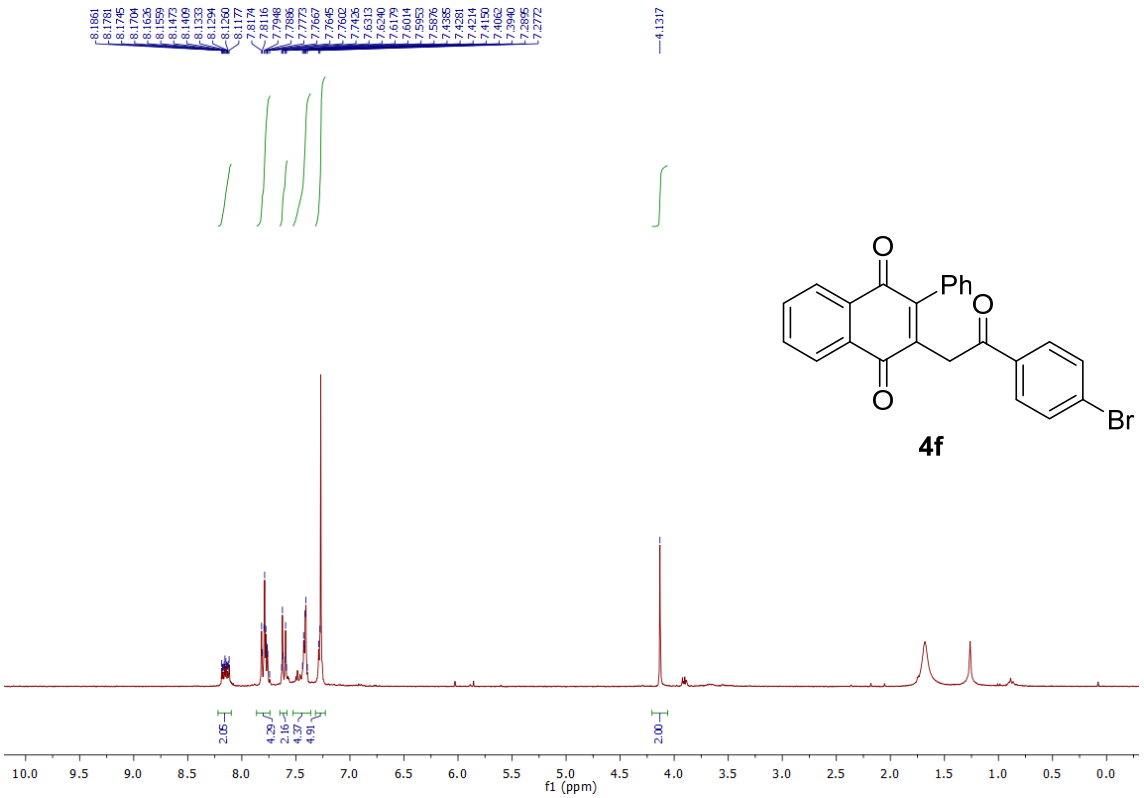

194.58
184.81
183.73
163.82
148.12
143.07
134.09
133.48
133.32
132.69
132.54
130.84
130.09
129.69
128.89
128.32
126.74
126.40
113.95
54.85
39.10
134.09
133.48
133.32
132.69
132.54
130.84
130.09
129.69
128.89
128.32
126.74
126.40
136 134 132 130 128 126
f1 (ppm)
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


8.2059
8.1928
8.1818
8.1766
8.1711
8.1604
8.1473
8.1384
8.1308
8.1106
7.8794
7.8519
7.8015
7.7886
7.7761
7.5350
7.5073
7.4922
7.4788
7.4736
7.4544
7.4410
7.4394
7.4366
7.4196
7.3298
7.3166
7.3056
7.2952
4.1913
2.4444
O
Ph
O
O
Me

4e


2.00
2.16
2.31
3.02
5.19
2.11
3.01
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


195.96
194.76
194.09
146.19
144.28
142.44
137.89
133.84
133.66
133.07
132.21
131.98
129.30
128.99
128.87
128.37
128.23
126.74
126.45
38.79
21.64
129.30
128.99
128.87
128.37
128.23
130 129 128 127
f1 (ppm)
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)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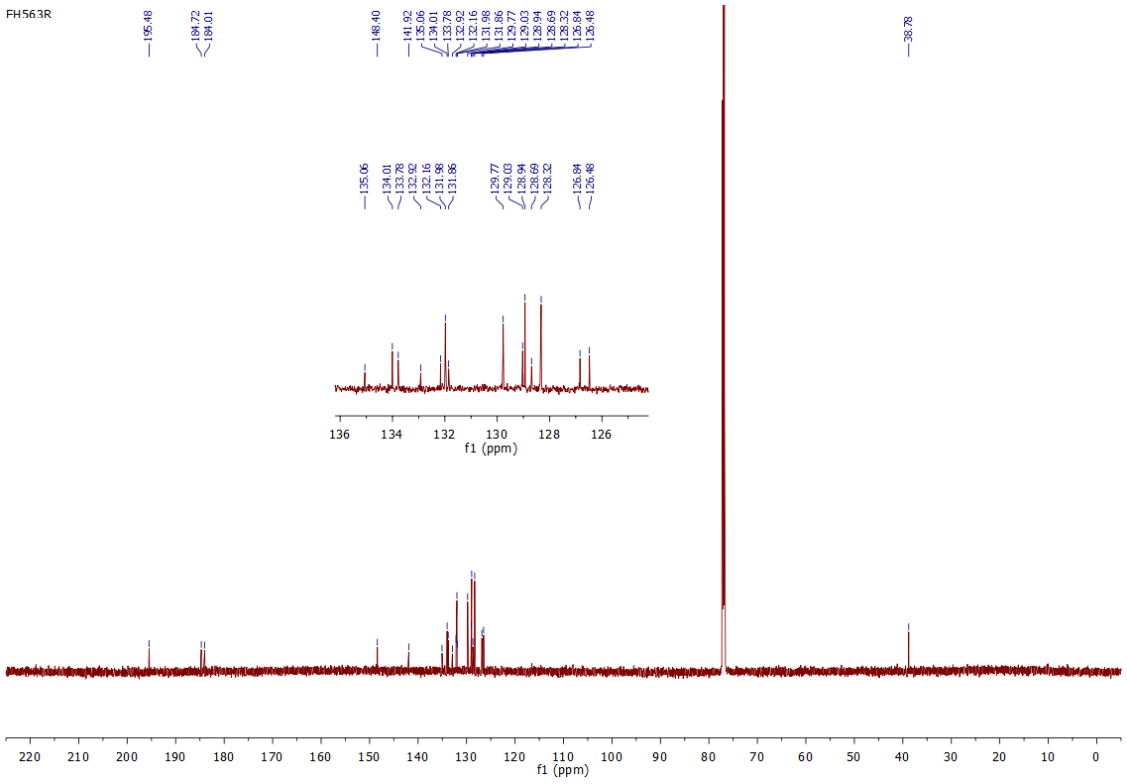
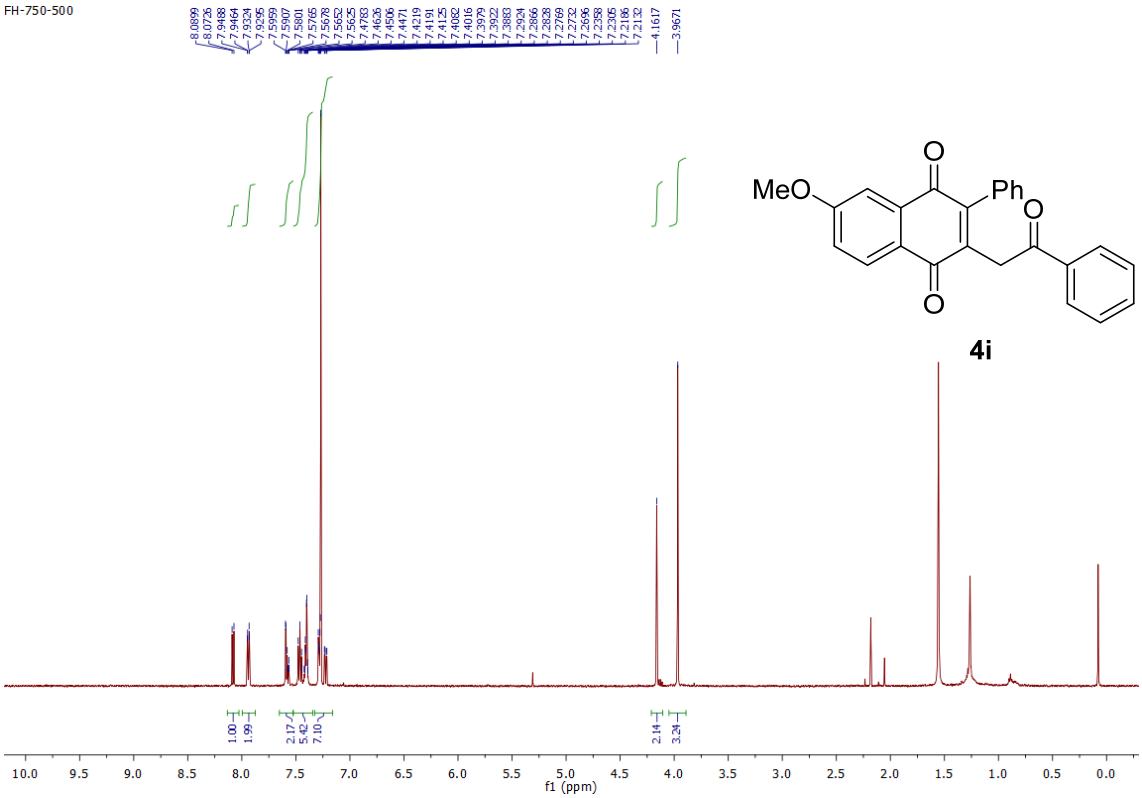
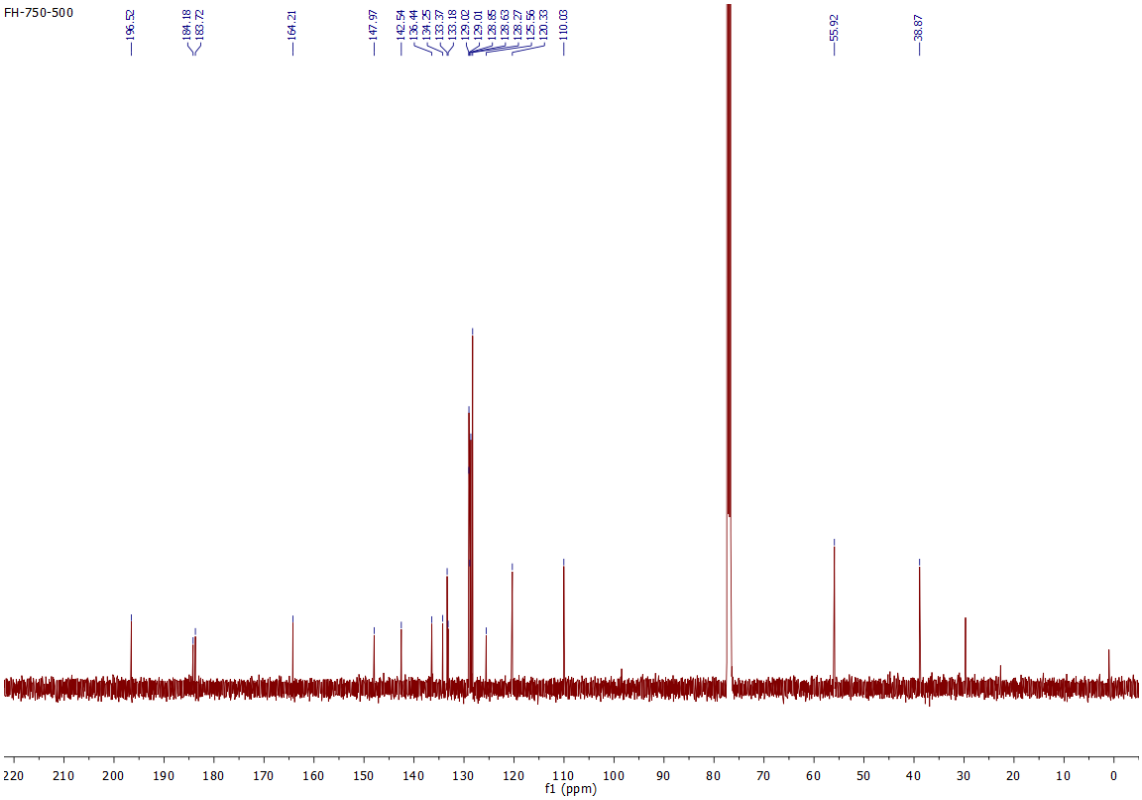
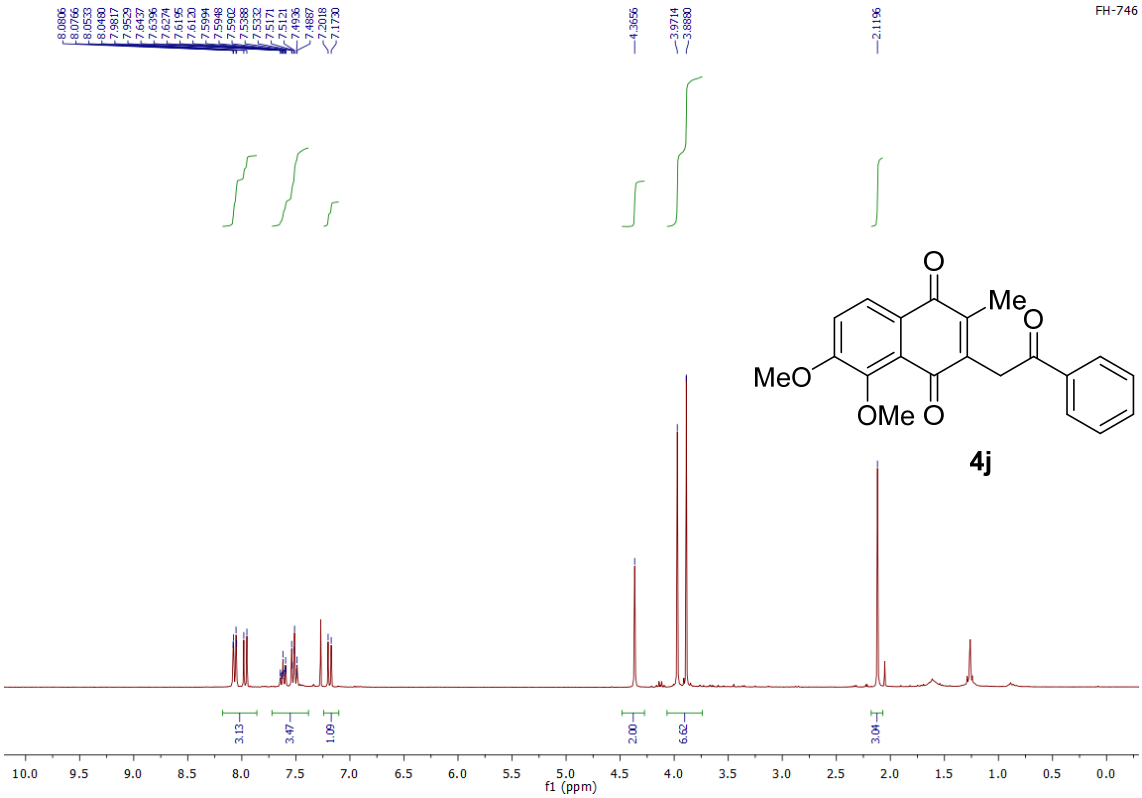
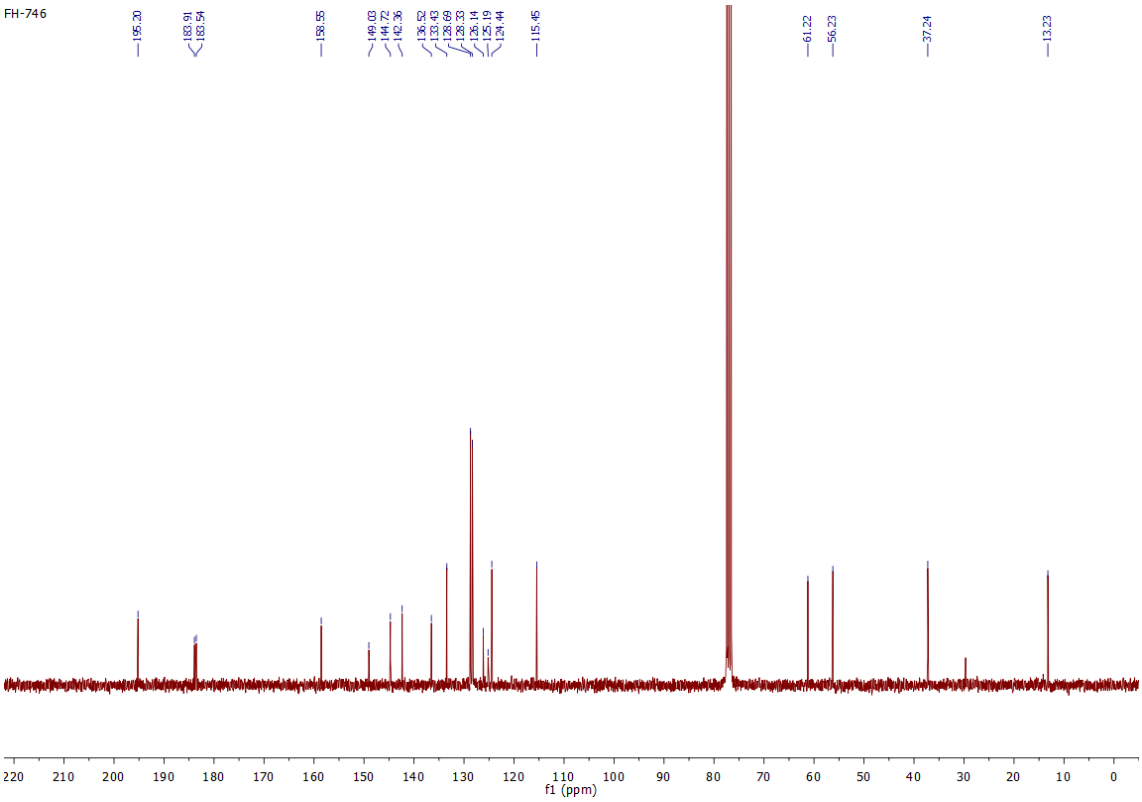
8.1781
8.1745
8.1704
8.1655
8.1595
8.1473
8.1409
8.1333
8.1294
8.1260
8.1177
7.8174
7.8116
7.7948
7.7886
7.7773
7.7667
7.7645
7.7602
7.7435
7.6313
7.6240
7.6179
7.6014
7.5953
7.5876
7.4385
7.4281
7.4214
7.4150
7.4062
7.3940
7.3905
7.2772
4.1317
2.05
4.29
2.16
4.37
4.91
2.00
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)
O
Ph
O
O
Br
4f

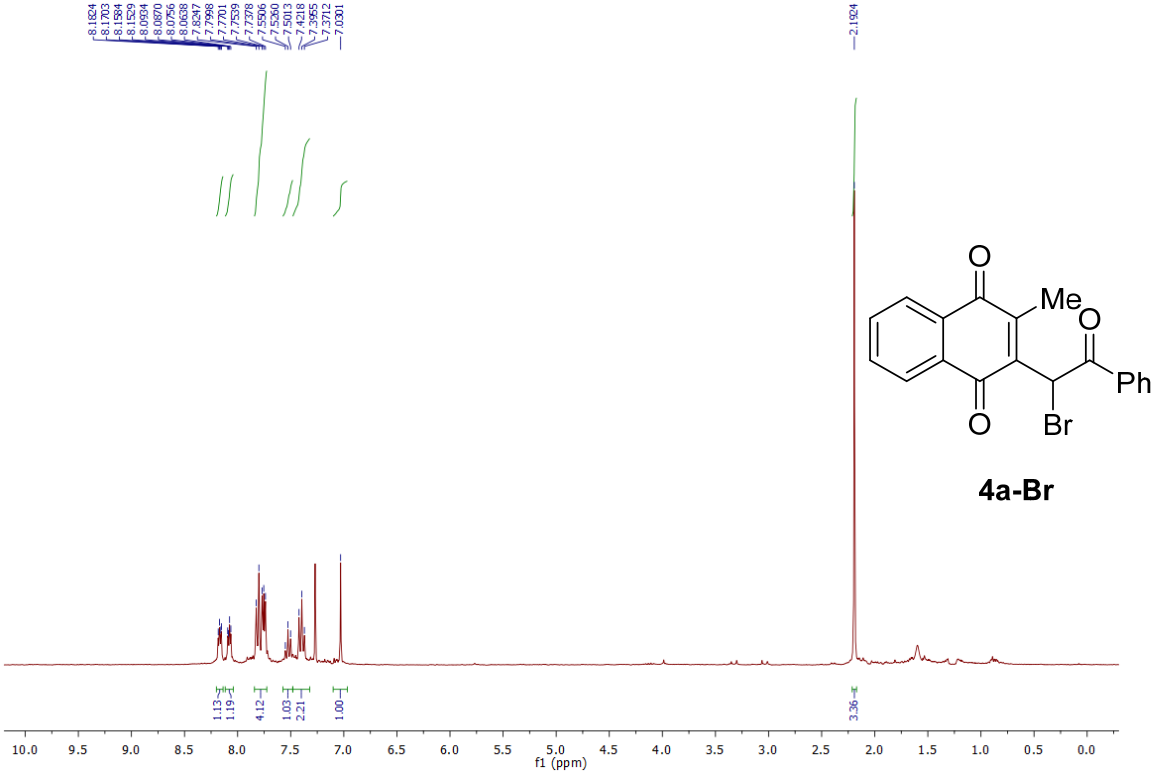

FH563R
195.48
184.72
184.01
148.40
141.92
135.06
134.01
133.78
132.92
132.16
131.98
131.86
129.77
129.03
128.94
128.69
128.32
126.84
126.48
38.78
136 134 132 130 128 126
f1 (ppm)
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


FH-750-500
MeO
Ph
O
O
O
4i
f1 (ppm)

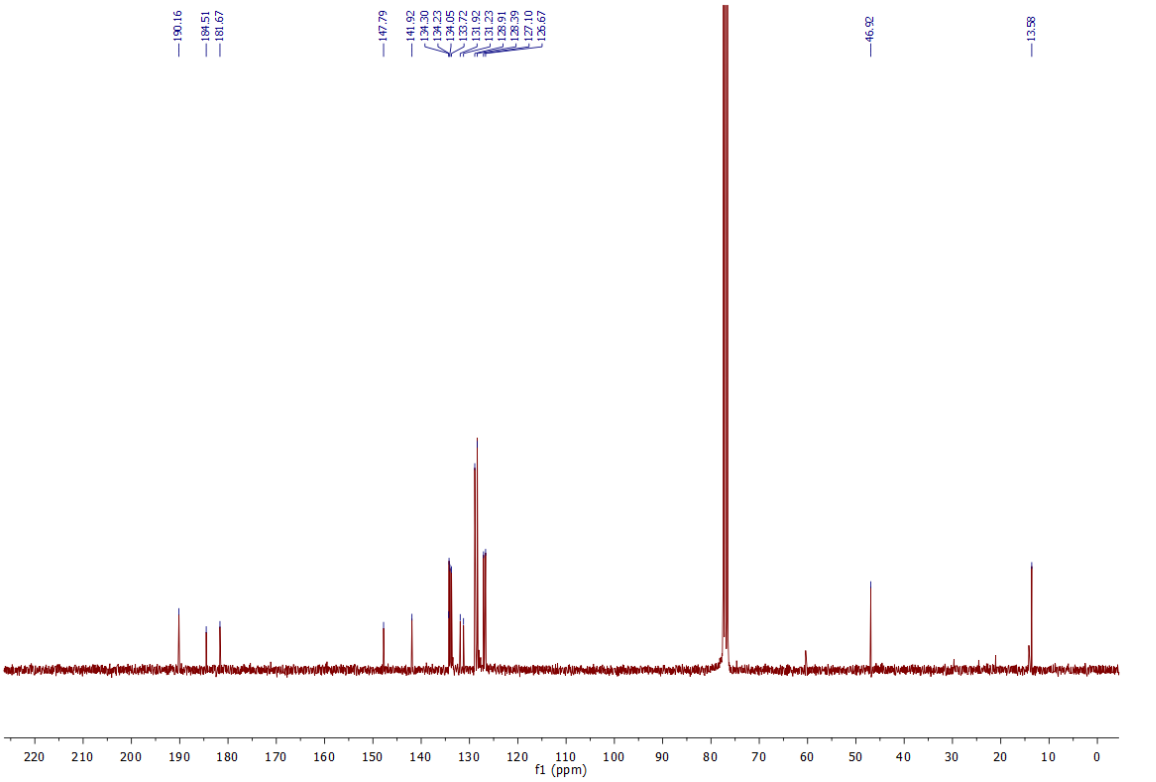

FH-750-500
f1 (ppm)

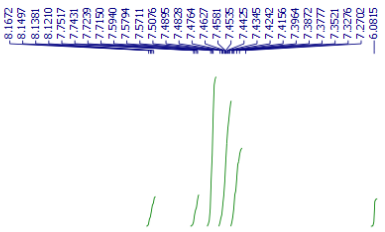

FH-746
8.0806
8.0766
8.0533
8.0480
7.9817
7.9529
7.6437
7.6396
7.6274
7.6195
7.6120
7.5994
7.5948
7.5902
7.5368
7.5332
7.5171
7.5121
7.4936
7.4887
7.2018
7.1730
4.3656
3.9714
3.8880
2.1196
O
Me
O
MeO
OMe
O
4j
3.13
3.47
1.09
2.00
6.62
3.04
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

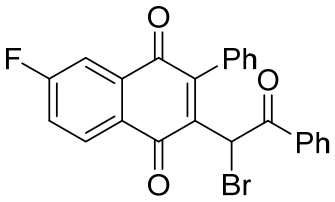

FH-746
195.20
183.91
183.54
158.55
149.03
144.72
142.36
136.52
133.43
128.69
128.33
126.14
125.19
124.44
115.45
61.22
56.23
37.24
13.23
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


8.1824
8.1703
8.1584
8.1529
8.0934
8.0870
8.0756
8.0638
7.8247
7.7998
7.7701
7.7559
7.7378
7.5506
7.5360
7.5013
7.4218
7.3955
7.3712
7.0301
2.1924
Me
O
Ph
O
Br
1.13
1.19
4.12
1.03
2.21
1.00
3.36
f1 (ppm)

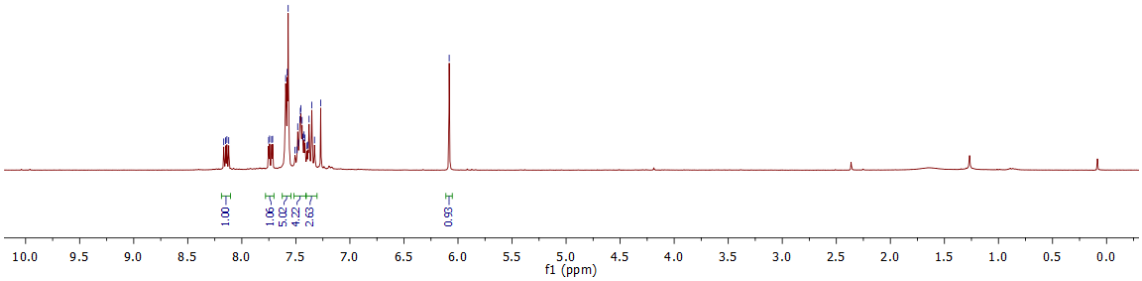
4a-Br

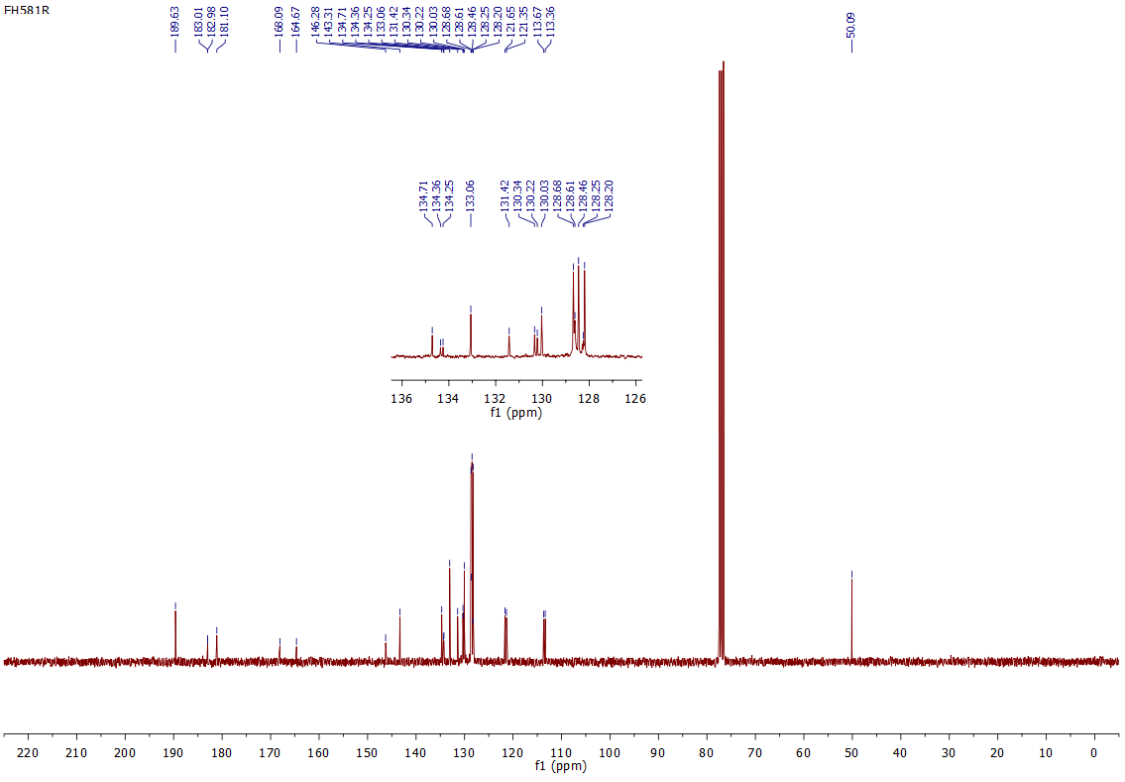

190.16
194.51
181.67
147.79
141.92
134.30
134.23
134.05
133.72
131.92
131.23
128.91
128.39
127.10
126.67
46.92
13.58
f1 (ppm)

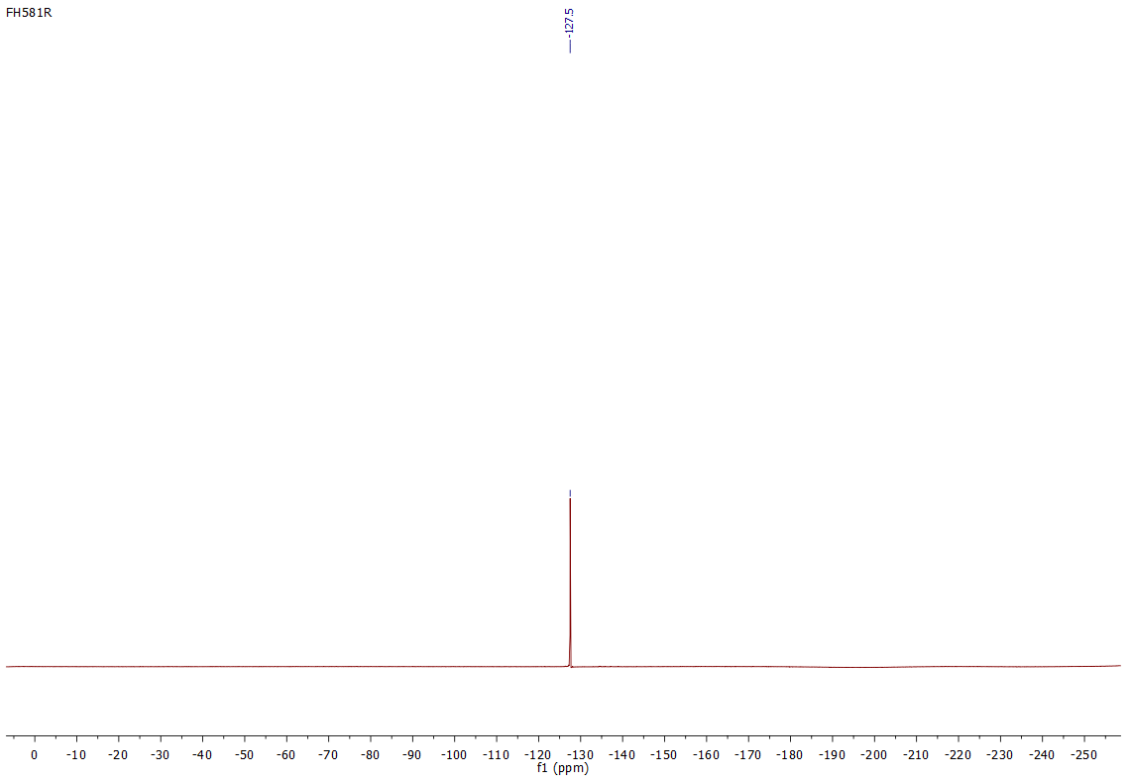

8.1672
8.1497
8.1381
8.1210
7.7517
7.7431
7.7239
7.7190
7.5940
7.5794
7.5711
7.5076
7.4895
7.4828
7.4764
7.4627
7.4581
7.4535
7.4425
7.4345
7.4242
7.3455
7.3964
7.3872
7.3777
7.3521
7.3276
7.2702
6.0815

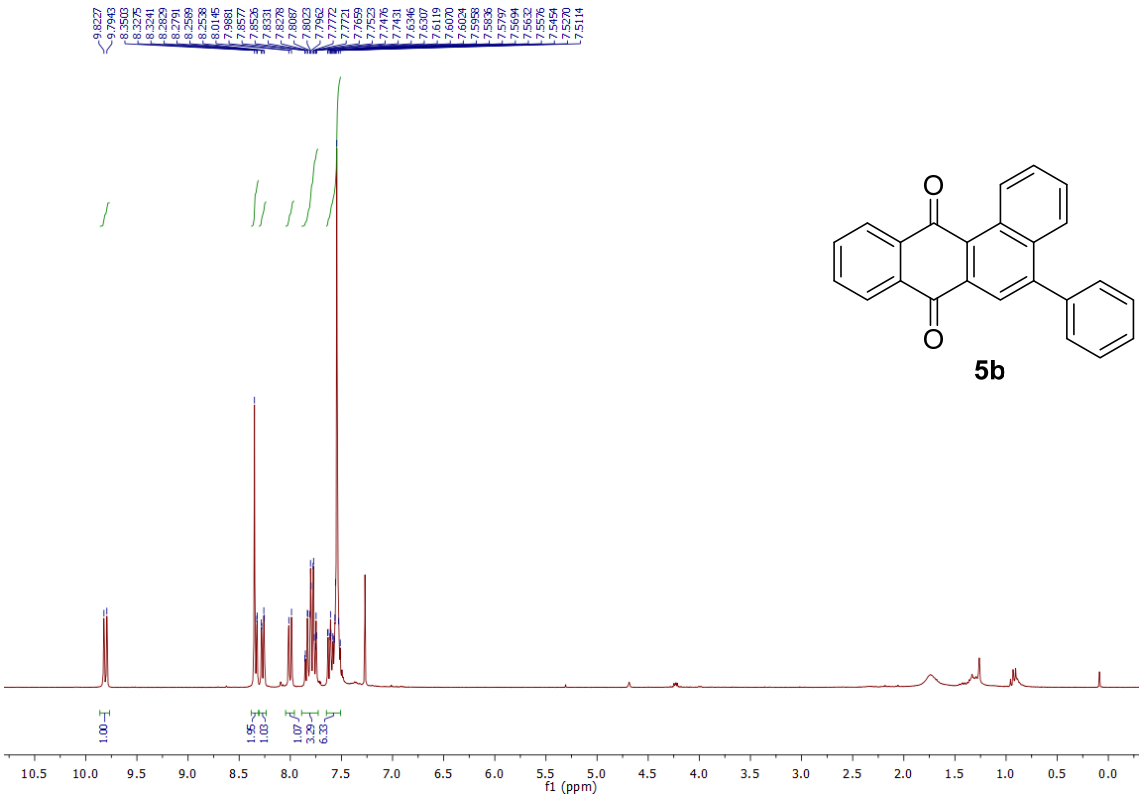

O
F
Ph
O
Ph
O
Br

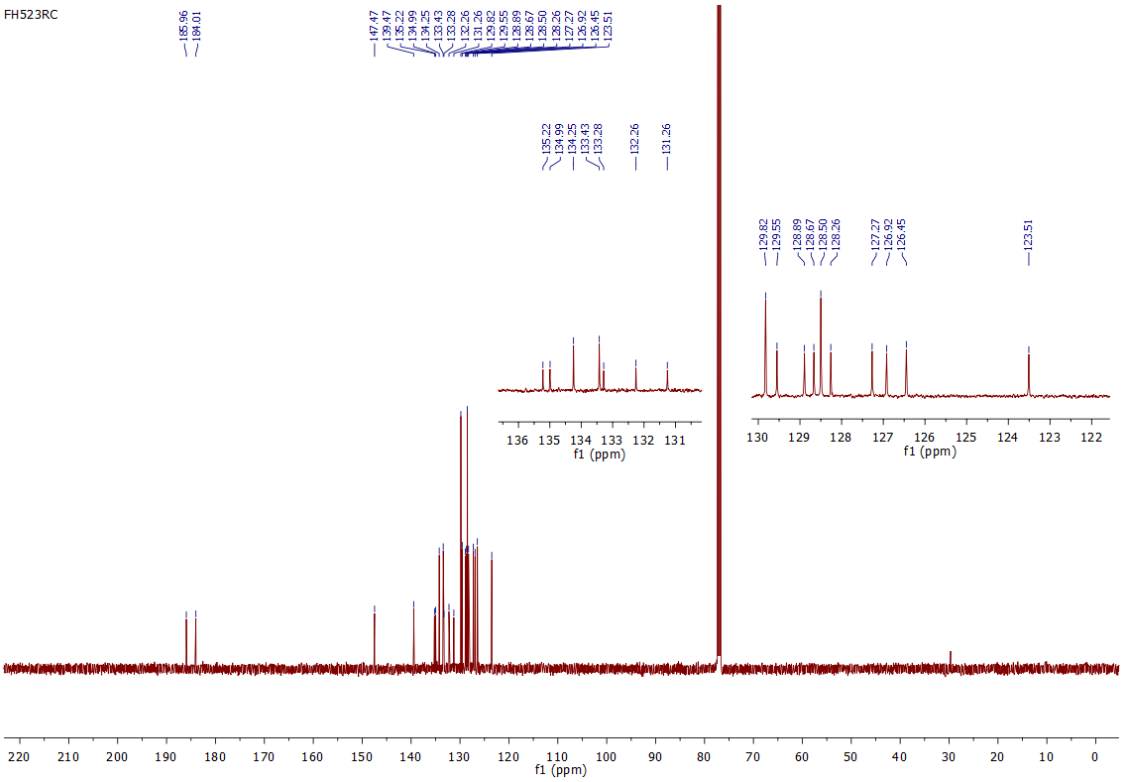
4h-Br


1.00
1.06
5.02
4.22
2.63
0.93
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


FH581R
189.63
183.01
182.98
181.10
160.09
164.67
146.28
143.31
134.71
134.36
134.25
133.06
131.42
130.34
130.22
130.03
128.68
128.61
128.46
128.25
128.20
121.65
121.35
113.67
113.36
50.09
136
134
132
130
128
126
f1 (ppm)
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


FH581R
-127.5
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-200
-210
-220
-230
-240
-250
f1 (ppm)


9.8227
9.7943
8.3503
8.3275
8.3241
8.2829
8.2791
8.2599
8.2558
8.0145
7.9891
7.8577
7.8526
7.8331
7.8278
7.8087
7.8023
7.7962
7.7772
7.7721
7.7659
7.7523
7.7476
7.7431
7.6346
7.6307
7.6119
7.6070
7.6024
7.5998
7.5836
7.5797
7.5694
7.5632
7.5576
7.5494
7.5370
7.5114
1.00
1.95
1.03
1.07
3.29
6.33
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)
O
O
5b


FH523RC
185.96
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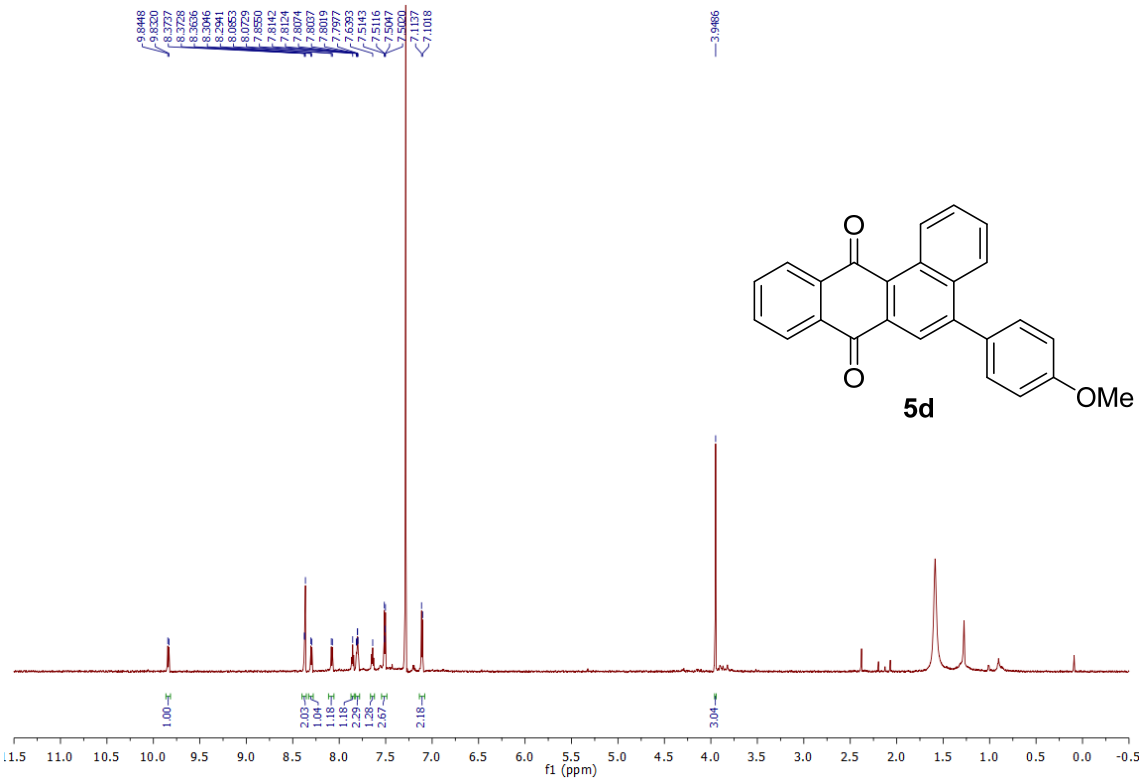
147.47
139.47
135.22
134.99
134.25
133.43
133.28
132.26
131.26
129.82
129.55
128.89
128.67
128.50
128.26
127.27
126.92
126.45
123.51
136 135 134 133 132 131
f1 (ppm)
130 129 128 127 126 125 124 123 122
f1 (ppm)
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)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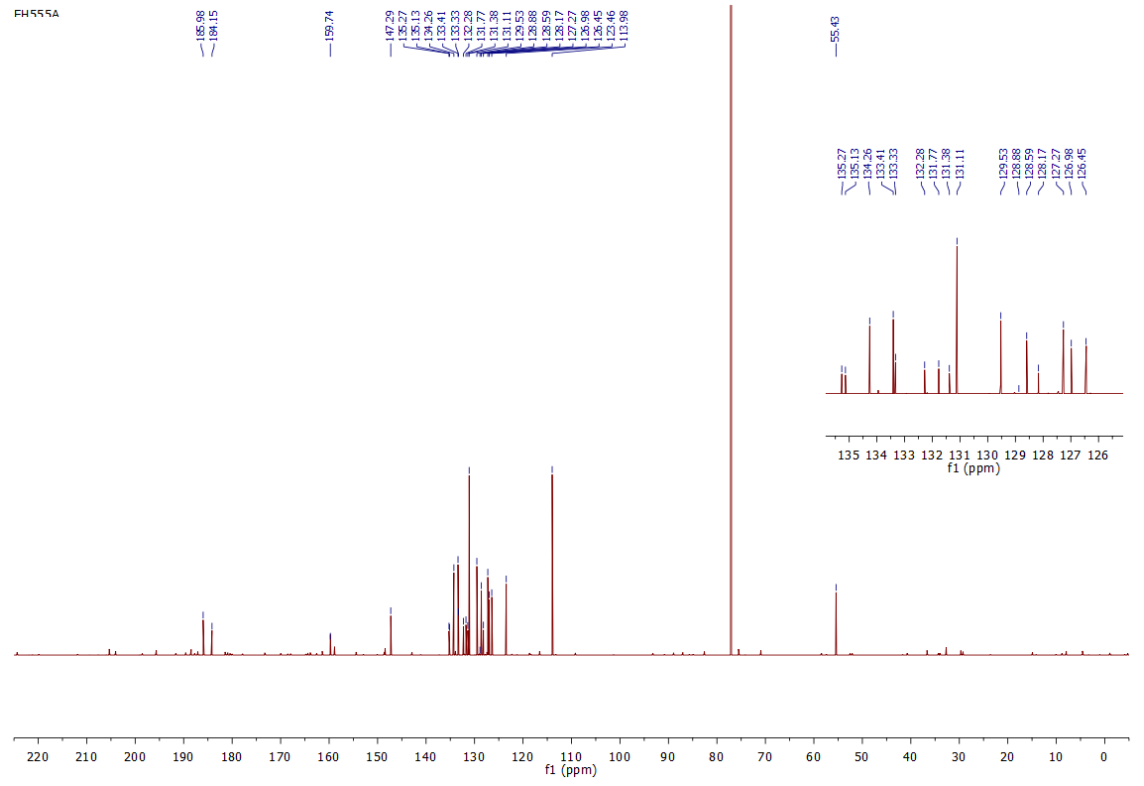
8.3737
8.3728
8.3636
8.3046
8.2941
8.0853
8.0729
7.8559
7.8142
7.8124
7.8074
7.8037
7.8019
7.7977
7.6393
7.5143
7.5116
7.5047
7.5001
7.1137
7.1018
3.9486
1.00
2.03
1.04
1.18
1.18
1.29
1.28
2.67
2.18
3.04
f1 (ppm)
O
O
OMe
5d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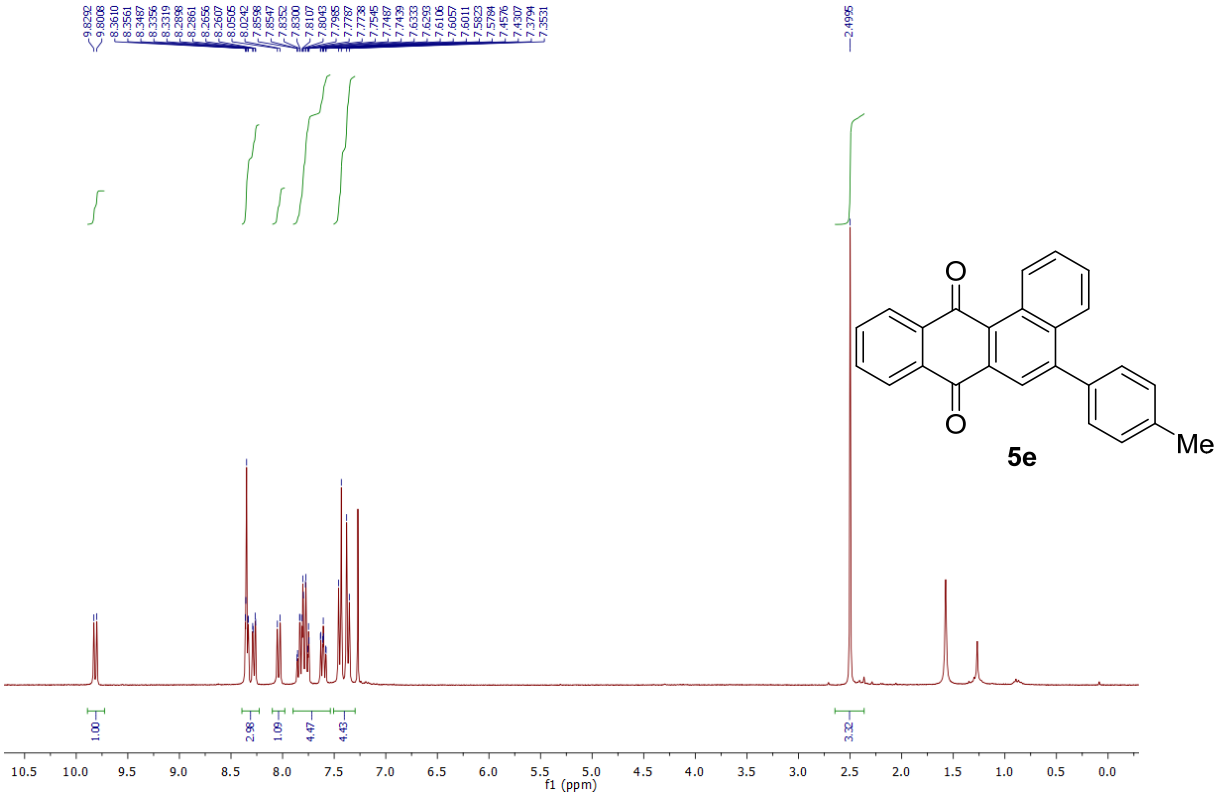
184.15
159.74
147.29
135.27
135.13
134.26
133.41
133.33
132.28
131.77
131.38
131.11
129.53
128.88
128.59
128.17
127.27
126.98
126.45
125.46
113.98
55.43
f1 (ppm)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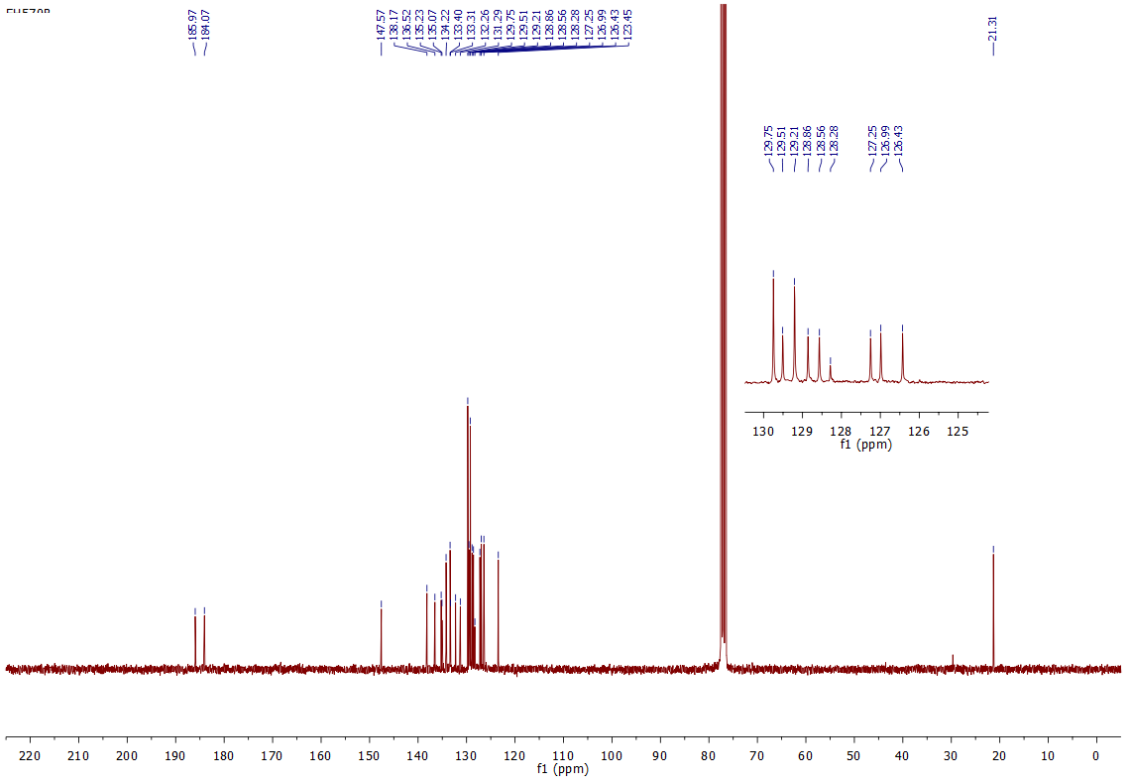
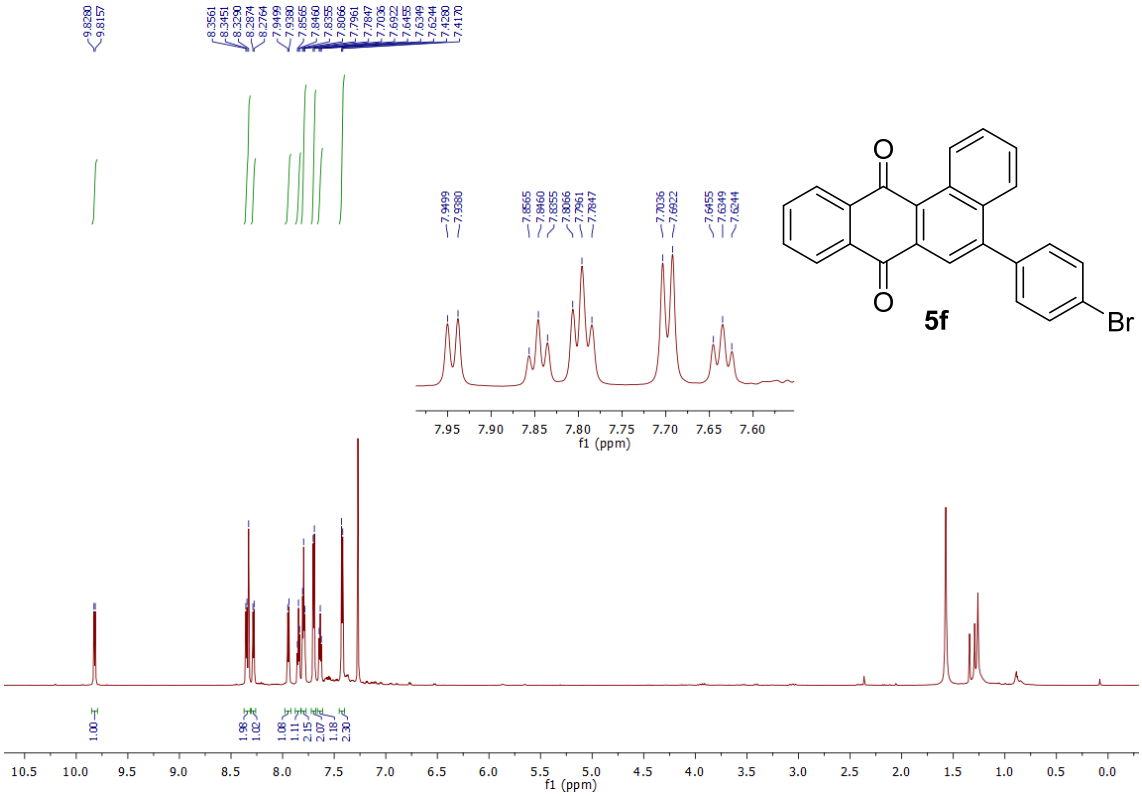
9.8008
8.3610
8.3561
8.3487
8.3356
8.3319
8.2898
8.2861
8.2656
8.2607
8.0595
8.0552
7.8598
7.8547
7.8352
7.8300
7.8107
7.8043
7.7985
7.7787
7.7738
7.7545
7.7487
7.7439
7.6333
7.6295
7.6106
7.6057
7.6011
7.5823
7.5784
7.4576
7.4307
7.3794
7.3531
2.4995
O
O
Me
5e
1.00
2.98
1.09
4.47
4.43
3.32
f1 (ppm)


185.97
184.07
147.57
138.17
136.52
135.23
135.07
134.22
133.40
133.31
132.26
131.29
129.75
129.51
129.21
128.86
128.56
128.28
127.25
126.99
126.43
125.45
21.31
129.75
129.51
129.21
128.86
128.56
128.28
127.25
126.99
126.43
130
129
128
127
126
125
f1 (ppm)
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)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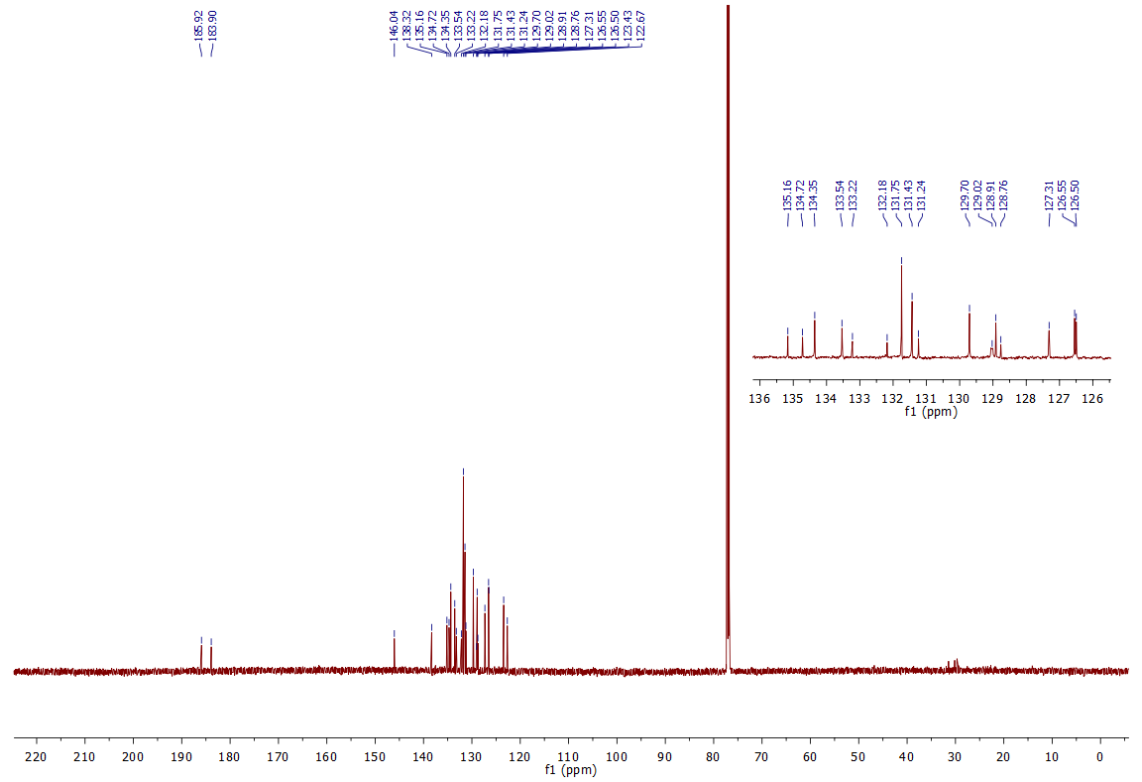
9.8157
8.3561
8.3451
8.3290
8.2874
8.2764
7.9499
7.9380
7.8665
7.8660
7.8655
7.8066
7.7961
7.7847
7.7036
7.6922
7.6455
7.6349
7.6244
7.4280
7.4170
O
O
Br
5f
f1 (ppm)


185.92
183.90
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138.32
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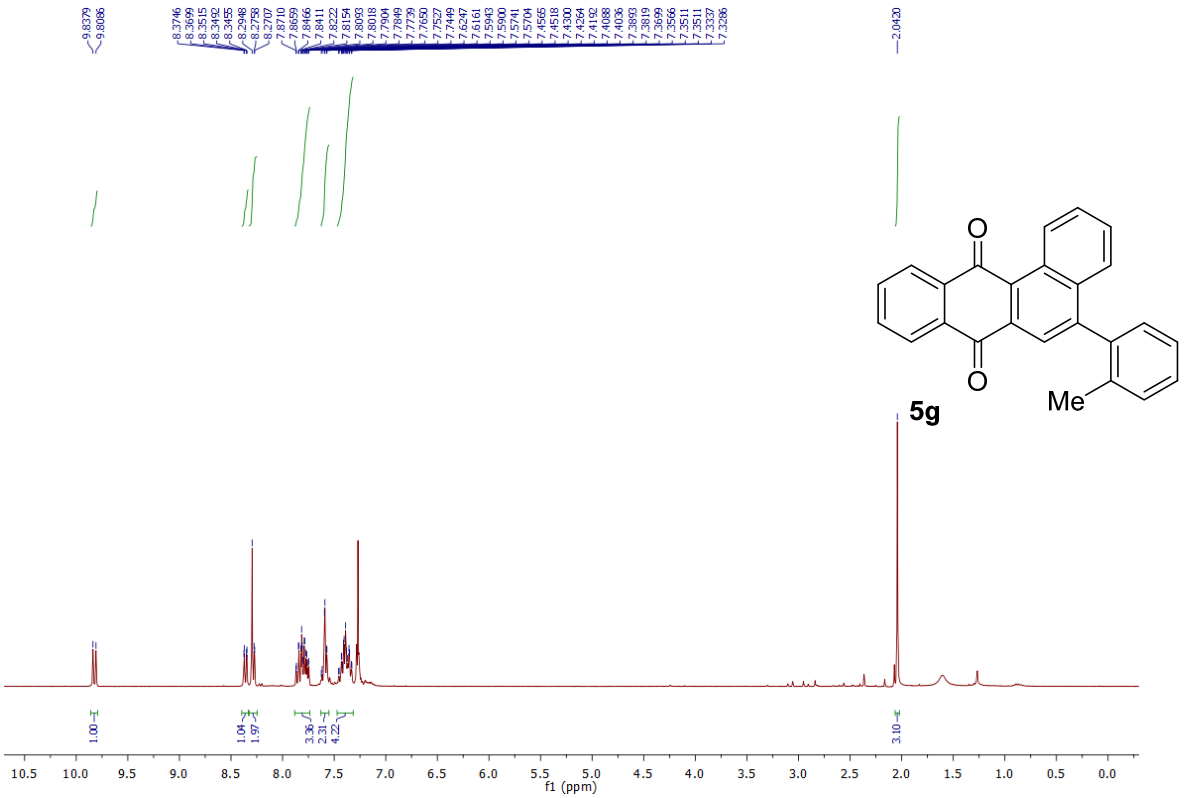
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1.04
1.97
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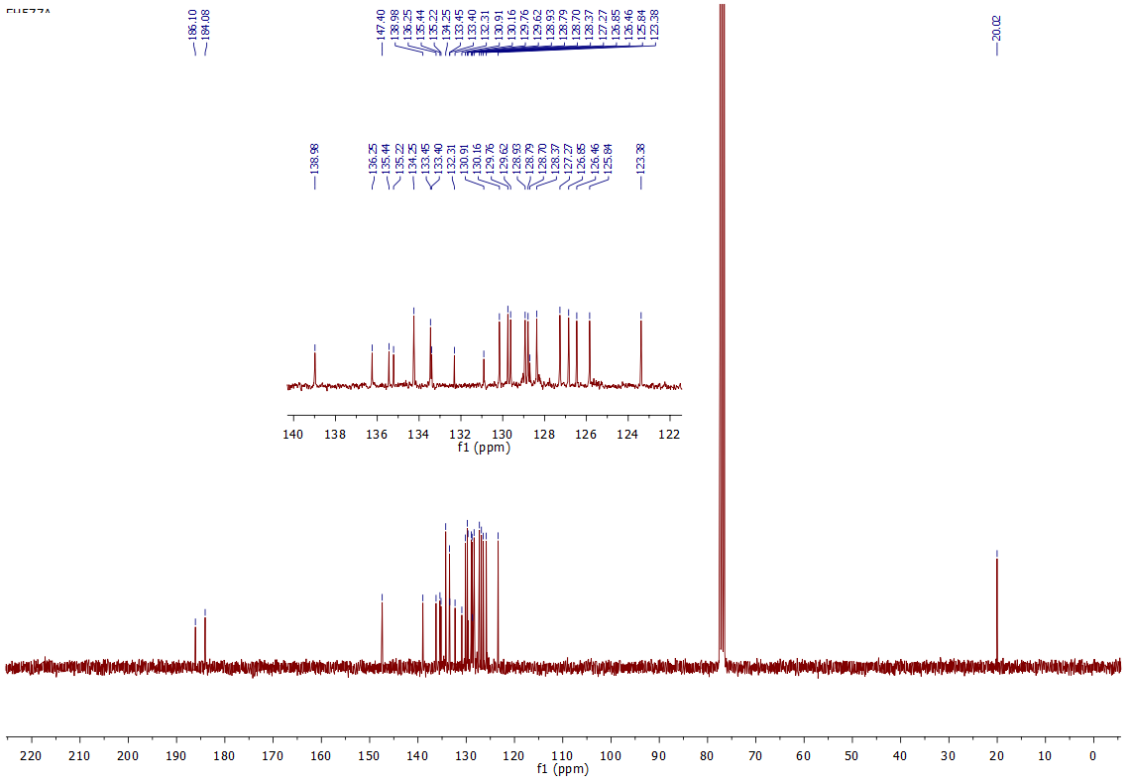
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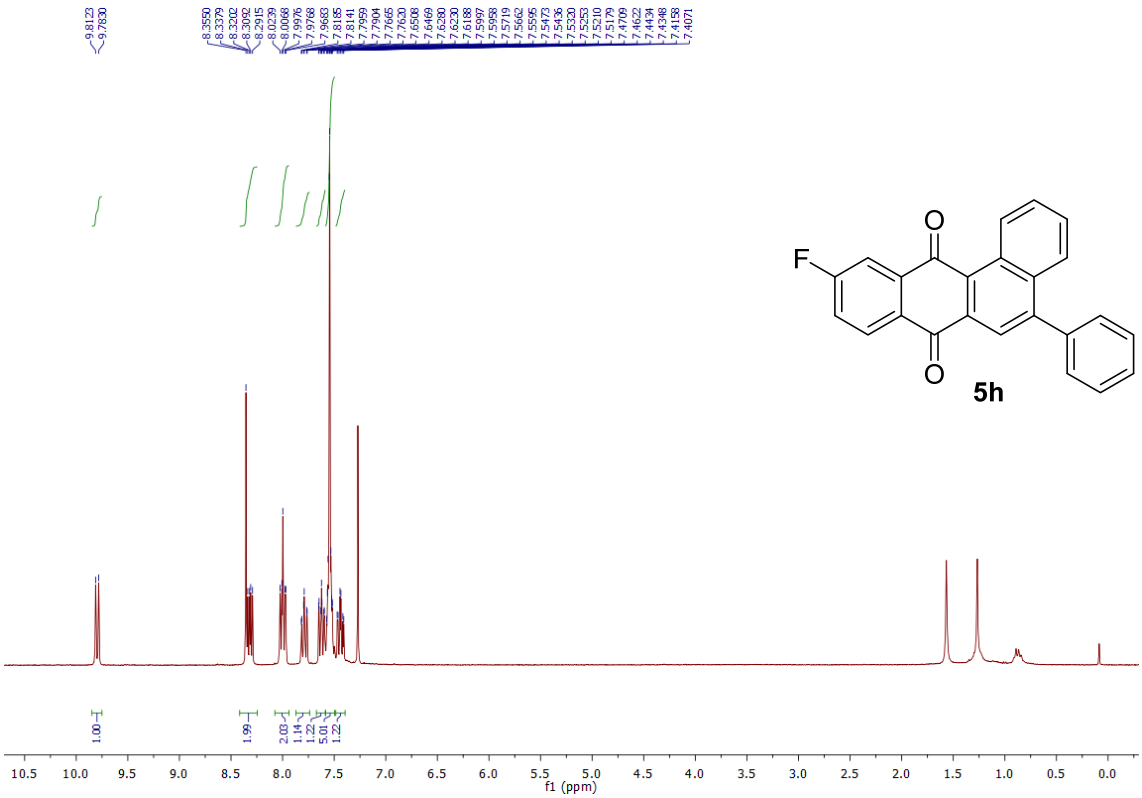
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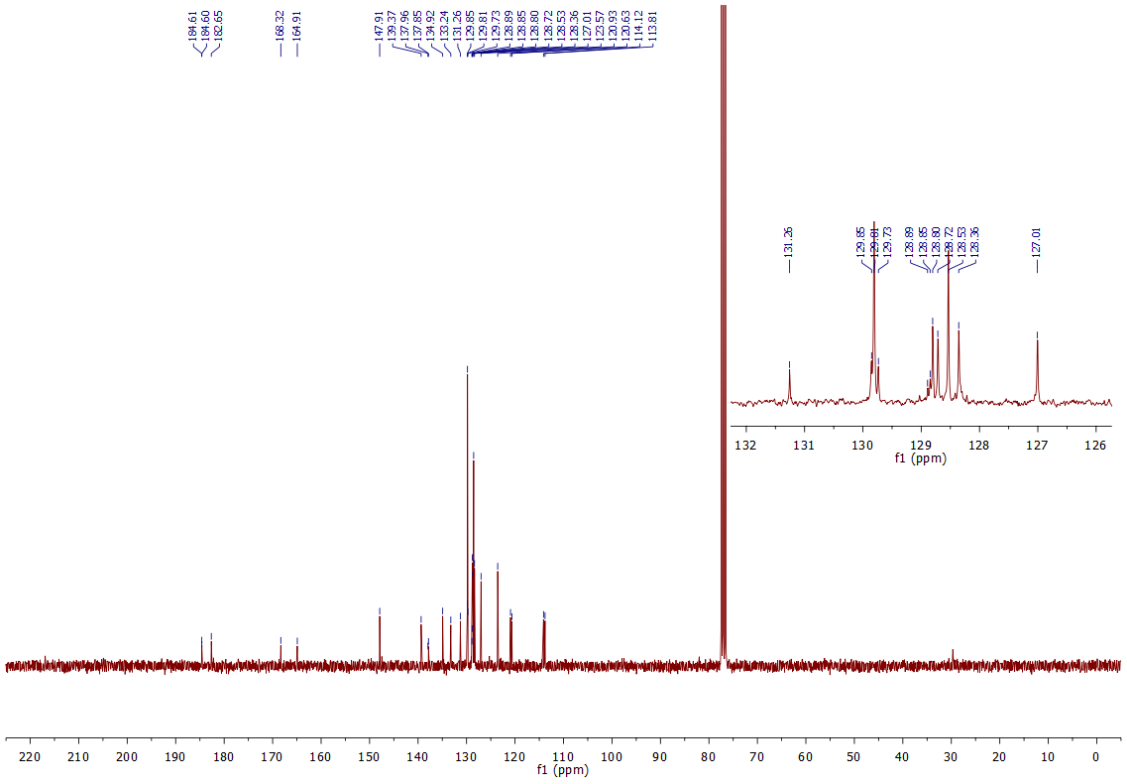
F
O
O
5h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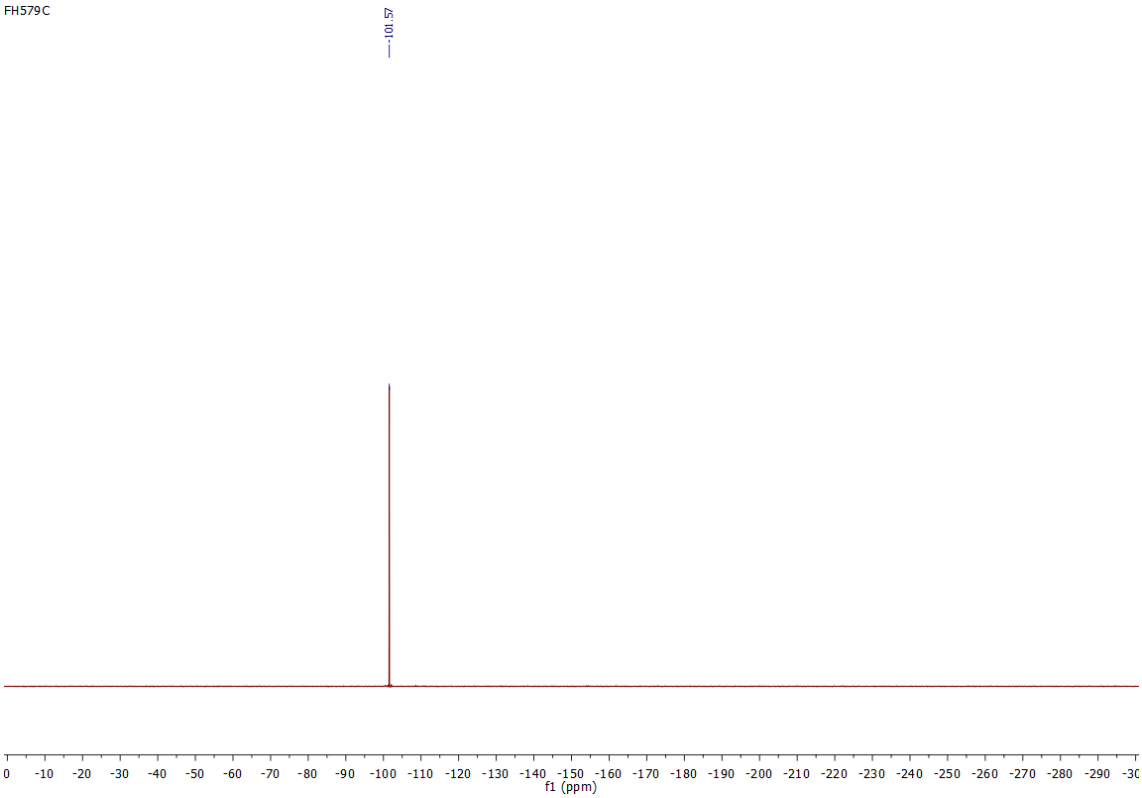
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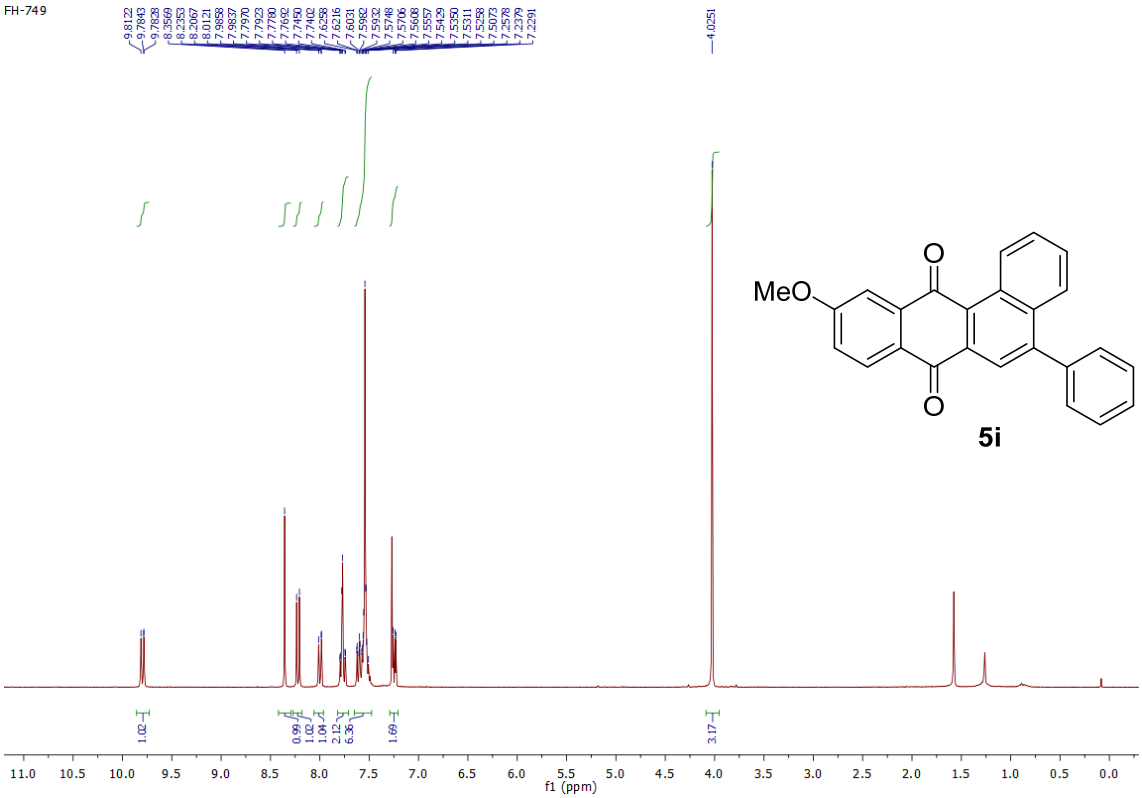
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O
O
5i
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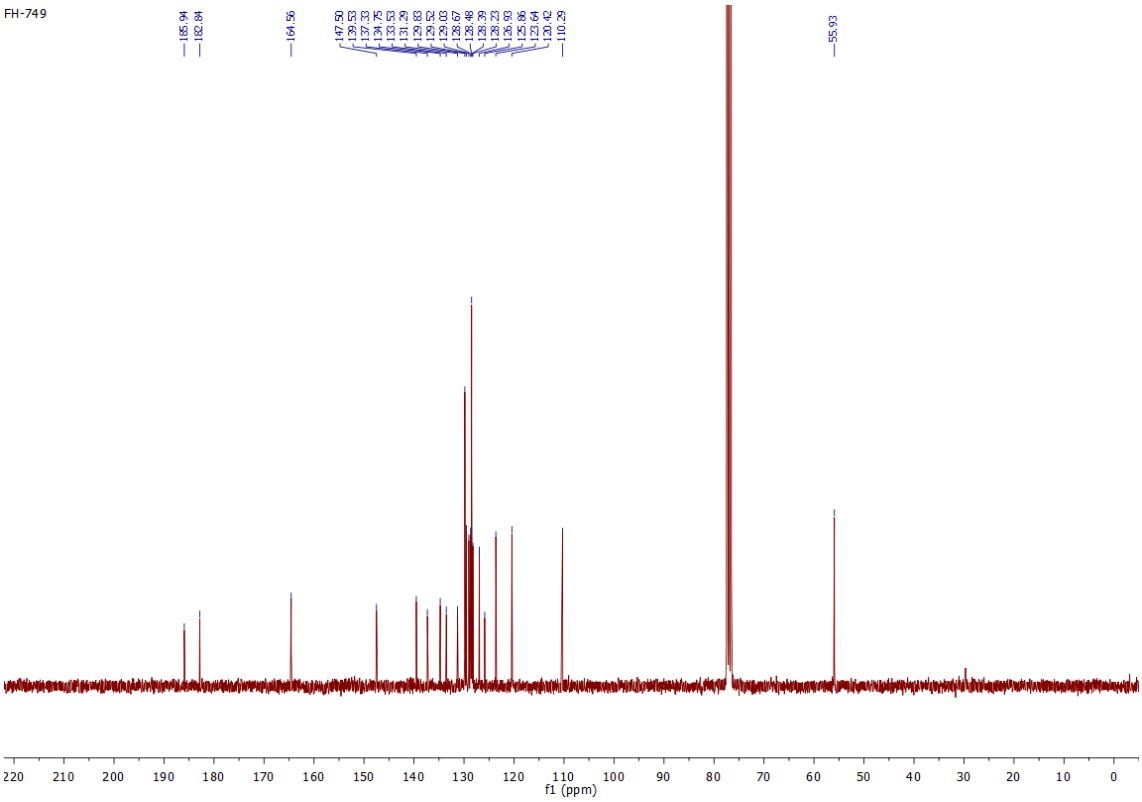
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f1 (ppm)

Additional Computational Results

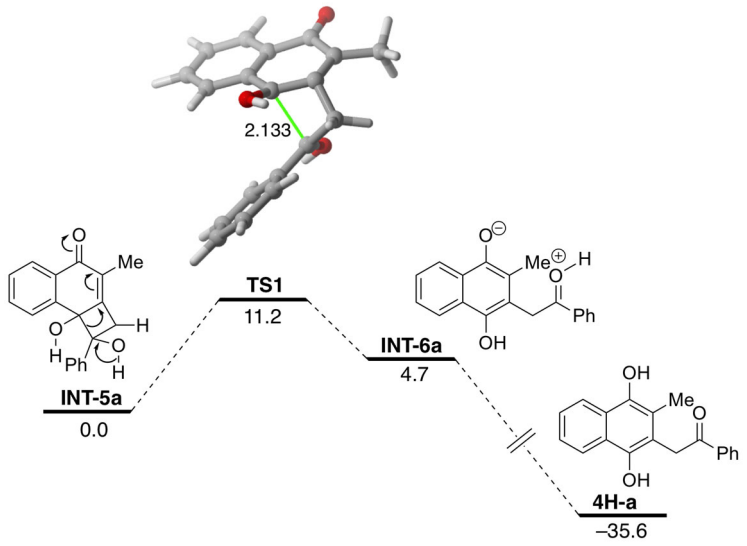

Figure S1. Computed reaction profile for the formation of **4H-a**. Relative free energies (ΔG, at 298 K) and bond distances are given in kcal/mol and angstroms, respectively. All data have been computed at the PCM(MeCN)-B3LYP-D3/def2-SVP level.

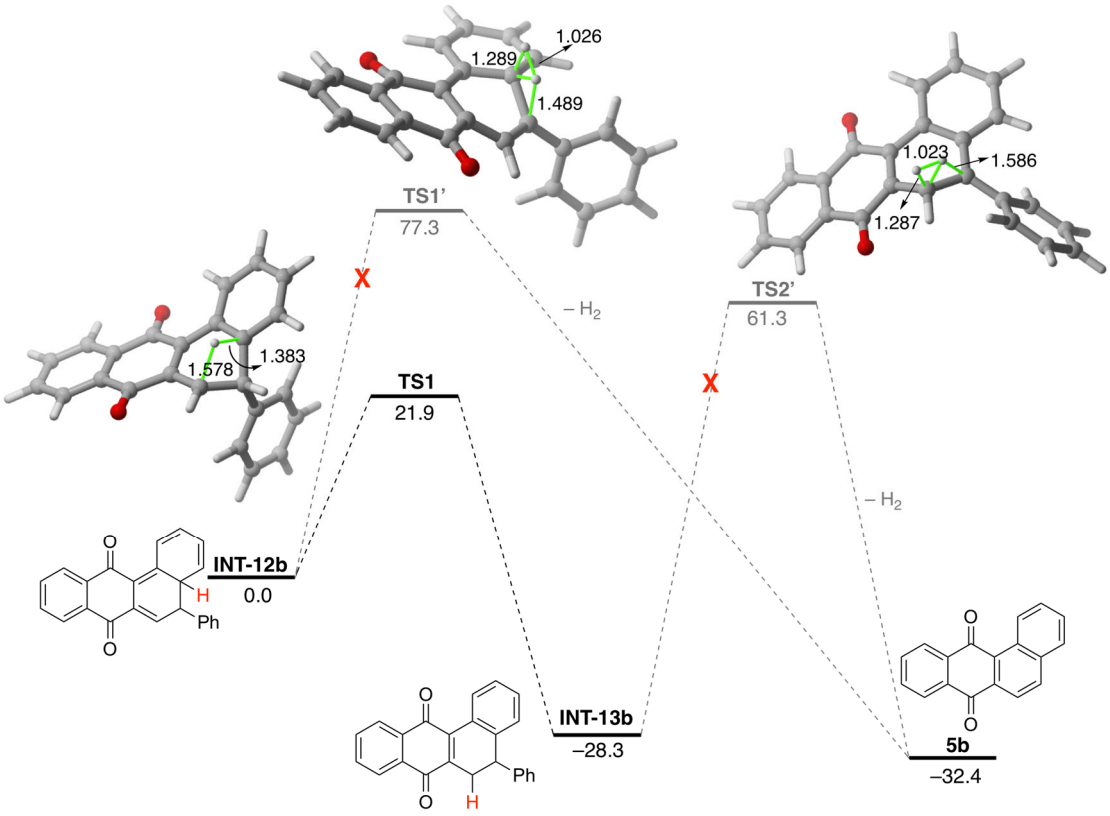

Figure S2. Computed reaction profile for the formation of **5b**. Relative free energies (ΔG, at 298 K) and bond distances are given in kcal/mol and angstroms, respectively. All data have been computed at the PCM(MeCN)-B3LYP-D3/def2-SVP level.

Computational Details

All the calculations reported in this paper were performed with the Gaussian 09 suite of programs.[1] Electron correlation was partially taken into account using the hybrid functional usually denoted as B3LYP[2] in conjunction with the D3 dispersion correction suggested by Grimme et al.[3] using the double-ζ quality plus polarization def2-SVP[4] basis set for all atoms. Reactants and products were characterized by frequency calculations,[5] and have positive definite Hessian matrices. Transition structures (TS's) show only one negative eigenvalue in their diagonalized force constant matrices, and their associated eigenvectors were confirmed to correspond to the motion along the reaction coordinate under consideration using the Intrinsic Reaction Coordinate (IRC) method.[6] Solvents effects were taken into account using the Polarizable Continuum Model (PCM)[7] during the geometry optimizations. This level is denoted PCM(MeCN)-B3LYP-D3/def2-SVP.

[1] Gaussian 09, Revision D.01, M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J. M. Millam, M. Klene, J. E. Knox, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, Ö. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski, and D. J. Fox, Gaussian, Inc., Wallingford CT, 2009.
[2] a) A. D. Becke, *J. Chem. Phys*. **1993**, *98*, 5648; b) C. Lee, W. Yang, R. G. Parr, *Phys. Rev. B* **1998**, *37*, 785; c) S. H. Vosko, L. Wilk, M. Nusair, *Can. J. Phys*. **1980**, *58*, 1200.
[3] S. Grimme, J. Antony, S. Ehrlich, H. Krieg, *J. Chem. Phys*. **2010**, *132*, 154104.
[4] F. Weigend, R. Alhrichs, *Phys. Chem. Chem. Phys*. **2005**, *7*, 3297.
[5] J. W. McIver, A. K. Komornicki, *J. Am. Chem. Soc.* **1972**, *94*, 2625.
[6] C. González, H. B. Schlegel, *J. Phys. Chem*. **1990**, *94*, 5523.
[7] a) S. Miertuš, E. Scrocco, J. Tomasi, *Chem. Phys*. **1981**, *55*, 117; b) J. L. Pascual-Ahuir, E. Silla, I. Tuñón, *J. Comp. Chem*. **1994**, *15*, 1127; c) Barone, V.; Cossi, M. *J. Phys. Chem. A*, **1998**, *102*, 1995.

Cartesian Coordinates

Cartesian coordinates (in Å) and free energies (in a. u.) of all the stationary points discussed in the text. All calculations have been performed at the PCM(MeCN)-B3LYP-D3/def2-SVP.

INT-5a: E = -958.387913

O	4.220093000	-1.038174000	0.370641000
C	3.022390000	-0.801523000	0.267743000
C	2.021885000	-1.904038000	0.196935000
C	0.730812000	-1.553148000	0.296735000
C	0.189278000	-0.154404000	0.492652000
C	1.150017000	0.926595000	0.080215000
C	2.524770000	0.606951000	0.062751000
C	3.465642000	1.613995000	-0.202759000
C	3.050373000	2.919525000	-0.467168000
C	1.685408000	3.230924000	-0.460606000
C	0.741400000	2.239310000	-0.174035000
H	-0.320302000	2.493058000	-0.149129000
H	1.354229000	4.250055000	-0.674396000
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H	4.524282000	1.347212000	-0.207271000
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C	-0.605539000	-2.097652000	-0.136582000
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C	-2.436201000	-0.195036000	-0.139337000
C	-2.755042000	0.978038000	0.561704000
C	-3.482973000	-0.987631000	-0.642779000
C	-4.091461000	1.349050000	0.754958000
C	-4.815374000	-0.618237000	-0.451671000
C	-5.123832000	0.554745000	0.249563000
H	-1.959951000	1.591091000	0.984329000
H	-3.246158000	-1.900203000	-1.196088000
H	-4.322799000	2.263739000	1.306724000
H	-5.616806000	-1.245716000	-0.850028000
H	-6.166375000	0.845034000	0.402428000
O	-0.191979000	0.127475000	1.834958000
H	-0.833033000	-0.533351000	2.136512000
H	-0.605485000	-2.781546000	-0.997476000
C	2.530651000	-3.288164000	-0.078644000
H	3.105437000	-3.317930000	-1.019084000
H	3.221600000	-3.605013000	0.719315000
H	1.707896000	-4.014062000	-0.141953000
O	-0.694736000	-0.383661000	-1.812664000
H	-0.810380000	0.560933000	-1.994071000

TS1·: E = -958.370084

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C	2.906828000	0.536507000	0.041964000
C	2.053013000	1.697418000	-0.227095000
C	0.789354000	1.526549000	-0.734266000
C	0.218851000	0.207932000	-0.975338000
C	0.962889000	-0.969875000	-0.585638000
C	2.271095000	-0.808087000	-0.062473000
C	2.990348000	-1.945370000	0.348835000
C	2.433823000	-3.215659000	0.244374000
C	1.141472000	-3.374802000	-0.291268000

C	0.417040000	-2.266650000	-0.714384000
H	-0.582598000	-2.379658000	-1.136355000
H	0.706358000	-4.373781000	-0.377069000
H	3.000063000	-4.091357000	0.571308000
H	3.996256000	-1.796848000	0.746230000
C	-0.879715000	1.211153000	0.553824000
C	-0.401844000	2.371499000	-0.308933000
H	-1.104211000	2.655149000	-1.102434000
C	-2.187661000	0.552574000	0.451177000
C	-2.455281000	-0.607357000	1.214585000
C	-3.174686000	0.993786000	-0.452750000
C	-3.666063000	-1.283875000	1.089257000
C	-4.388805000	0.313880000	-0.575029000
C	-4.641717000	-0.825993000	0.192988000
H	-1.703305000	-1.011637000	1.898143000
H	-3.012270000	1.893054000	-1.048548000
H	-3.848007000	-2.179403000	1.688136000
H	-5.142580000	0.681958000	-1.275232000
H	-5.590601000	-1.358279000	0.094037000
O	-0.722329000	-0.020253000	-1.944780000
H	-1.082680000	0.808713000	-2.286977000
H	-0.150821000	3.266929000	0.273389000
C	2.560054000	3.031895000	0.250620000
H	3.645405000	3.096144000	0.086018000
H	2.074315000	3.873626000	-0.262179000
H	2.395356000	3.152928000	1.337160000
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H	-0.460363000	0.401643000	2.255014000

INT-6a: E = -958.380455

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C	1.520258000	-1.800328000	0.284153000
C	0.461671000	-1.086365000	0.882050000
C	0.484813000	0.320478000	0.995493000
C	1.580139000	1.071732000	0.457705000
C	2.635420000	0.371396000	-0.194731000
C	3.699545000	1.110495000	-0.748507000
C	3.730380000	2.497029000	-0.669743000
C	2.685055000	3.189116000	-0.021299000
C	1.627948000	2.488262000	0.537797000
H	0.817489000	3.017057000	1.041522000
H	2.710215000	4.280034000	0.043242000
H	4.564279000	3.053738000	-1.105462000
H	4.498532000	0.549667000	-1.237225000
C	-1.618199000	-1.469328000	-0.073095000
C	-0.865075000	-1.783823000	1.178666000
H	-1.372369000	-1.418069000	2.079384000
C	-2.607315000	-0.437889000	-0.229897000
C	-2.965041000	0.042635000	-1.521106000
C	-3.256814000	0.136345000	0.894498000
C	-3.914610000	1.043405000	-1.671045000
C	-4.213076000	1.135313000	0.733430000
C	-4.544901000	1.597367000	-0.544791000
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H	-4.708106000	1.552115000	1.613124000
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H	-1.026395000	0.490252000	2.187001000
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H	1.468240000	-3.758808000	1.250350000
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C	1.381564000	1.746245000	-0.226900000
C	0.366280000	0.865998000	-0.729855000
C	0.562329000	-0.510885000	-0.716739000
C	1.799748000	-1.068565000	-0.270372000
C	2.840125000	-0.191595000	0.174964000
C	4.086670000	-0.759520000	0.562292000
C	4.283769000	-2.126495000	0.548080000
C	3.240566000	-2.992696000	0.138489000
C	2.027256000	-2.472436000	-0.266335000
H	1.220116000	-3.129049000	-0.592724000
H	3.401116000	-4.073633000	0.136942000
H	5.249658000	-2.540195000	0.848025000
H	4.915881000	-0.112075000	0.858340000
C	-1.965988000	1.532145000	-0.134361000
C	-0.941450000	1.433640000	-1.267288000
H	-1.301511000	0.797629000	-2.086298000
C	-2.909903000	0.386659000	0.089748000
C	-3.342411000	0.132119000	1.404563000
C	-3.391028000	-0.421059000	-0.958952000
C	-4.206347000	-0.928937000	1.670870000
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H	-2.977732000	0.774273000	2.208512000
H	-3.111839000	-0.214059000	-1.994222000
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H	-1.265104000	-1.150249000	-0.930804000
H	-0.791164000	2.442234000	-1.669701000
C	1.160073000	3.239837000	-0.196540000
H	1.942794000	3.739425000	0.386568000
H	1.182229000	3.665431000	-1.215717000
H	0.180332000	3.484370000	0.236073000
O	-1.959934000	2.479838000	0.632226000
H	4.169425000	1.628217000	1.238538000

Profile from INT-12b

INT-12b: E= -1073.610846

C	-0.572904000	1.456683000	-0.398403000
C	0.604257000	0.724648000	-0.257026000
C	1.768993000	1.214215000	0.509482000
C	0.680307000	-0.605762000	-0.895409000
C	1.968067000	-1.362811000	-0.988300000
C	3.148838000	-0.781497000	-0.299264000

C	3.046079000	0.426515000	0.419583000
C	-1.621989000	0.921606000	-1.363645000
C	-0.430165000	-1.244114000	-1.341504000
C	4.375902000	-1.463405000	-0.356938000
C	4.183453000	0.929848000	1.073361000
C	5.397918000	0.249506000	1.010231000
C	5.496699000	-0.952118000	0.291937000
H	4.422974000	-2.397667000	-0.918884000
H	4.089936000	1.864980000	1.627011000
H	6.275052000	0.653438000	1.521640000
H	6.449194000	-1.485070000	0.243190000
C	-1.791358000	-0.618668000	-1.298568000
C	-2.935072000	1.641372000	-1.380754000
H	-0.335179000	-2.273649000	-1.693264000
C	-0.854174000	2.714691000	0.246308000
H	-0.091840000	3.139142000	0.892382000
C	-2.057834000	3.343982000	0.093374000
H	-2.232614000	4.285898000	0.620514000
C	-3.127679000	2.797218000	-0.714457000
H	-4.083302000	3.324109000	-0.764354000
C	-2.622781000	-1.108740000	-0.113181000
C	-2.084970000	-1.161295000	1.183859000
C	-3.961538000	-1.485731000	-0.301035000
C	-2.870647000	-1.569410000	2.265557000
C	-4.748989000	-1.897907000	0.778974000
C	-4.205945000	-1.938455000	2.067280000
H	-1.042955000	-0.880840000	1.349192000
H	-4.393834000	-1.456438000	-1.305199000
H	-2.436245000	-1.601763000	3.268062000
H	-5.789135000	-2.189478000	0.612045000
H	-4.819128000	-2.260095000	2.912915000
H	-3.729629000	1.202352000	-1.990020000
H	-1.173868000	1.102411000	-2.368618000
H	-2.331510000	-0.910150000	-2.212664000
O	1.764251000	2.236416000	1.197877000
O	2.050158000	-2.423842000	-1.595715000

TS1: E = -1073.575869

C	-0.995897000	1.486528000	-0.014457000
C	0.246108000	0.781015000	-0.018956000
C	1.326893000	1.028423000	0.961709000
C	0.477255000	-0.058400000	-1.137076000
C	1.850061000	-0.502351000	-1.515545000
C	2.939903000	-0.248359000	-0.533283000
C	2.683132000	0.463255000	0.655929000
C	-1.998458000	1.065661000	-0.999993000
C	-0.591802000	-0.396382000	-1.989432000
C	4.228678000	-0.735010000	-0.794332000
C	3.724710000	0.672605000	1.570536000
C	5.005085000	0.183267000	1.306675000
C	5.258846000	-0.521337000	0.121870000
H	4.400318000	-1.283382000	-1.722241000
H	3.510072000	1.227527000	2.485180000
H	5.810701000	0.351339000	2.025381000
H	6.261184000	-0.904356000	-0.083555000
C	-1.980497000	-0.420129000	-1.362592000
C	-3.201017000	1.852476000	-1.151569000
H	-0.366267000	-0.970187000	-2.892013000
C	-1.255428000	2.675590000	0.731499000
H	-0.525848000	2.996698000	1.470770000

C	-2.393012000	3.420009000	0.506368000
H	-2.551225000	4.340590000	1.073680000
C	-3.370461000	3.016416000	-0.449672000
H	-4.270379000	3.620048000	-0.590164000
C	-2.225135000	-1.420022000	-0.244743000
C	-1.625900000	-2.688636000	-0.281891000
C	-3.075505000	-1.107055000	0.827013000
C	-1.874430000	-3.625874000	0.725573000
C	-3.324737000	-2.042197000	1.837051000
C	-2.724835000	-3.305050000	1.789647000
H	-0.952118000	-2.945837000	-1.103469000
H	-3.543456000	-0.120755000	0.877029000
H	-1.398361000	-4.608930000	0.681558000
H	-3.986798000	-1.780380000	2.666535000
H	-2.916236000	-4.035052000	2.580243000
H	-3.968262000	1.494334000	-1.842305000
H	-1.168467000	1.068081000	-2.106536000
H	-2.723753000	-0.578553000	-2.159934000
O	1.154232000	1.655420000	2.003124000
O	2.066712000	-1.070151000	-2.578389000

INT-13b: E = -1073.655886

C	-1.057675000	1.658235000	-0.175571000
C	0.250945000	0.970187000	-0.239783000
C	1.348164000	1.307550000	0.725821000
C	0.435523000	-0.019653000	-1.165162000
C	1.728465000	-0.734650000	-1.326183000
C	2.871907000	-0.309221000	-0.475409000
C	2.685679000	0.675670000	0.512575000
C	-2.193113000	0.994015000	-0.710337000
C	-0.703695000	-0.421943000	-2.061329000
C	4.128313000	-0.904974000	-0.642615000
C	3.761519000	1.053730000	1.326368000
C	5.015201000	0.464017000	1.149312000
C	5.199162000	-0.515827000	0.164714000
H	4.246081000	-1.672415000	-1.409554000
H	3.597621000	1.812104000	2.093686000
H	5.852771000	0.766463000	1.782158000
H	6.179880000	-0.977826000	0.029787000
C	-2.021473000	-0.406865000	-1.279920000
C	-3.434229000	1.636154000	-0.711146000
H	-0.498369000	-1.392922000	-2.526624000
C	-1.214243000	2.962503000	0.336345000
H	-0.350868000	3.491972000	0.732946000
C	-2.461631000	3.589241000	0.329421000
H	-2.558883000	4.603058000	0.725167000
C	-3.576604000	2.926871000	-0.191052000
H	-4.553829000	3.415847000	-0.203427000
C	-2.117508000	-1.487626000	-0.190897000
C	-1.207627000	-2.554625000	-0.104621000
C	-3.166304000	-1.440999000	0.745051000
C	-1.338836000	-3.536357000	0.885423000
C	-3.303303000	-2.421545000	1.730527000
C	-2.385903000	-3.475588000	1.807896000
H	-0.378346000	-2.639048000	-0.808079000
H	-3.887213000	-0.621651000	0.708414000
H	-0.612529000	-4.352084000	0.932034000
H	-4.129669000	-2.359541000	2.443532000
H	-2.487085000	-4.241339000	2.581156000
H	-4.301224000	1.121272000	-1.133356000

H	-0.778029000	0.308274000	-2.887979000
H	-2.844983000	-0.586590000	-1.990141000
O	1.165419000	2.055859000	1.675306000
O	1.840614000	-1.646529000	-2.138590000

TS1′: E = -1073.487510

C	-0.105884000	1.615907000	-0.074301000
C	0.957458000	0.710858000	0.041668000
C	2.342882000	1.147328000	0.414256000
C	0.727986000	-0.688667000	-0.182446000
C	1.790947000	-1.680305000	-0.254431000
C	3.193249000	-1.177640000	-0.142887000
C	3.450445000	0.168533000	0.183608000
C	-1.372690000	1.104611000	-0.744052000
C	-0.610158000	-1.169173000	-0.103824000
C	4.263581000	-2.063269000	-0.330872000
C	4.777609000	0.608232000	0.317472000
C	5.837019000	-0.275711000	0.115942000
C	5.579203000	-1.615618000	-0.208548000
H	4.036907000	-3.103414000	-0.571194000
H	4.957212000	1.652299000	0.579175000
H	6.867005000	0.075769000	0.213026000
H	6.408999000	-2.309745000	-0.363082000
C	-1.719355000	-0.373115000	-0.267428000
C	-2.546728000	2.022748000	-0.784193000
H	-0.746806000	-2.228006000	0.129851000
C	-0.087963000	3.004054000	0.283736000
H	0.837699000	3.390301000	0.702396000
C	-1.174585000	3.822135000	0.134690000
H	-1.114441000	4.870024000	0.434771000
C	-2.421478000	3.303804000	-0.370156000
H	-3.297865000	3.956806000	-0.397794000
C	-3.106590000	-0.824749000	0.000944000
C	-3.434086000	-1.294467000	1.286309000
C	-4.097677000	-0.861328000	-0.999596000
C	-4.714254000	-1.782301000	1.565749000
C	-5.379628000	-1.337878000	-0.717307000
C	-5.692701000	-1.799602000	0.566815000
H	-2.674624000	-1.267131000	2.071343000
H	-3.860492000	-0.532069000	-2.014444000
H	-4.949182000	-2.142608000	2.570470000
H	-6.134373000	-1.359847000	-1.507304000
H	-6.695653000	-2.174307000	0.785635000
H	-3.493654000	1.634496000	-1.151924000
H	-0.986871000	1.053711000	-1.972743000
H	-1.299233000	0.151477000	-1.596105000
O	2.605246000	2.256590000	0.866776000
O	1.570473000	-2.888350000	-0.404145000

TS2′: E = -1073.512571

C	-0.117262000	-1.816824000	0.381403000
C	0.946206000	-0.841357000	0.362141000
C	2.339046000	-1.189524000	-0.076000000
C	0.661272000	0.491824000	0.642173000
C	1.594791000	1.601781000	0.502312000
C	2.968766000	1.267405000	0.041057000
C	3.322861000	-0.070647000	-0.221116000
C	-1.483593000	-1.323960000	0.256296000

C	-0.687033000	0.866484000	1.137178000
C	3.914687000	2.287982000	-0.125848000
C	4.628197000	-0.367895000	-0.642657000
C	5.566522000	0.651625000	-0.804929000
C	5.209301000	1.982756000	-0.547207000
H	3.613212000	3.315493000	0.084774000
H	4.887433000	-1.408855000	-0.841895000
H	6.580267000	0.411404000	-1.134124000
H	5.944796000	2.780817000	-0.673891000
C	-1.775153000	0.062897000	0.413261000
C	-2.513428000	-2.286066000	0.007456000
H	-0.889716000	1.942114000	1.154702000
C	0.102388000	-3.224902000	0.376933000
H	1.114526000	-3.592231000	0.520337000
C	-0.931333000	-4.118800000	0.185481000
H	-0.736322000	-5.193564000	0.200029000
C	-2.247688000	-3.637641000	-0.021197000
H	-3.069105000	-4.344298000	-0.167335000
C	-2.993967000	0.766283000	0.001884000
C	-3.526325000	1.834974000	0.760909000
C	-3.656882000	0.431321000	-1.203450000
C	-4.667821000	2.522766000	0.343885000
C	-4.800928000	1.115389000	-1.612787000
C	-5.317187000	2.165579000	-0.842391000
H	-3.056748000	2.125921000	1.703991000
H	-3.248564000	-0.358569000	-1.836577000
H	-5.056323000	3.340075000	0.957039000
H	-5.285531000	0.836756000	-2.552313000
H	-6.211040000	2.703128000	-1.167747000
H	-3.542717000	-1.939880000	-0.090611000
H	-0.634529000	0.757608000	2.418583000
H	-1.323696000	0.182632000	1.928566000
O	2.690554000	-2.336572000	-0.326607000
O	1.272126000	2.763164000	0.777574000

5b: E = -1072.486930

C	-0.141824000	1.699750000	0.056718000
C	0.951628000	0.755030000	-0.012765000
C	2.386426000	1.179828000	-0.099804000
C	0.655393000	-0.615491000	-0.005736000
C	1.709797000	-1.682190000	-0.025294000
C	3.128319000	-1.250740000	-0.029239000
C	3.446162000	0.118750000	-0.061569000
C	-1.501078000	1.208488000	0.095364000
C	-0.679525000	-1.072546000	0.009689000
C	4.148790000	-2.212015000	-0.006510000
C	4.792850000	0.510925000	-0.070210000
C	5.805969000	-0.448503000	-0.042017000
C	5.485064000	-1.812841000	-0.010853000
H	3.871853000	-3.267314000	0.014672000
H	5.027178000	1.575865000	-0.099060000
H	6.852173000	-0.133680000	-0.045512000
H	6.279767000	-2.562109000	0.009285000
C	-1.754219000	-0.205096000	0.030744000
C	-2.571126000	2.138240000	0.235128000
H	-0.844408000	-2.149596000	-0.023203000
C	0.048308000	3.113938000	0.117344000
H	1.060012000	3.502696000	0.078146000
C	-1.017515000	3.983644000	0.229923000
H	-0.830983000	5.059346000	0.278631000

C	-2.341090000	3.495695000	0.299945000
H	-3.177998000	4.188795000	0.413598000
C	-3.128523000	-0.777367000	-0.014453000
C	-3.513192000	-1.757775000	0.918229000
C	-4.043921000	-0.403468000	-1.016526000
C	-4.782977000	-2.338834000	0.859793000
C	-5.310335000	-0.990009000	-1.078233000
C	-5.685562000	-1.956655000	-0.138339000
H	-2.812595000	-2.055461000	1.702083000
H	-3.753060000	0.340996000	-1.761075000
H	-5.068193000	-3.092112000	1.598441000
H	-6.005603000	-0.693890000	-1.867709000
H	-6.677762000	-2.412287000	-0.185576000
H	-3.591135000	1.762277000	0.307800000
O	2.737839000	2.348638000	-0.206307000
O	1.405140000	-2.867147000	-0.027255000