Supporting Information for

Gold-Catalyzed Cascade Cycloisomerizations of 1,7-Diyn-3,6-bis(propargyl carbonate)s: Stereoselective Synthesis of Naphtho[*b*]cyclobutenes

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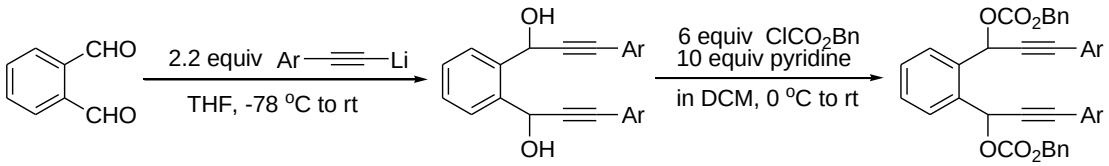
General Methods. All reactions were carried out under argon. THF and toluene were distilled from sodium and benzophenone. Unless noted, all commercial reagents were used without further purification. Ph_3PAuCl[1] and PPh_3AuNTf_2[2] were prepared according to the published methods. (Acetonitrile)[(2-biphenyl)di-*tert*-butylphosphine]gold(I) hexafluoroantimonate was purchased from Aldrich Chemical Company. $AgSbF_6$ was purchased from Stream or Aldrich Chemical Company. AgOTf and $AgBF_4$ were purchased from Acros Company. 1,2-Phenylenebis(3-phenylprop-2-yne-1,1-diyl) dimethyl dicarbonate **1a-1** was prepared according to published method.[3]

^1H NMR spectra was recorded at 300 or 400 MHz, ^{13}C NMR spectra was recorded at 75 or 100 MHz, in $CDCl_3$ (containing 0.03% TMS) solutions. ^1H NMR spectra was recorded with tetramethylsilane (δ= 0.00 ppm) as internal reference; ^{13}C

NMR spectra was recorded with $CDCl_3$ (δ = 77.00 ppm) as internal reference. High-resolution mass spectra was obtained by using Waters Micromass GCT, Bruker Daltonics, Inc. APEXIII 7.0 TESLA FTMS, IonSpec 4.7 Tesla FTMS or Agilent Technologies 6224 TOF LC/MS mass spectrometer. Single crystal X-ray diffraction data was collected on a Bruker SMART diffractometer at 293(2) K with graphite-monochromated Mo-Kα radiation (λ=0.71073 Å).

Synthesis of 1,7-diyn-3,6-bis(propargyl carbonate)s 1a-2, 1a-3, 1h, 1n and 1o.

Typical procedure for the synthesis of 1,2-phenylenebis(3-phenylprop-2-yne-1,1-diyl) dibenzyl dicarbonate (1a-2).

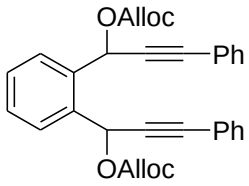


1a-2, Ar = Ph

To a solution of ethynylbenzene (13.2 mL, 120.0 mmol) in THF (120.0 mL) was added n-BuLi (44.0 mL, 110.0 mmol, 2.5 M in hexanes) at -78 °C. After stirring at the same temperature for 0.5 h, dry-ice/ acetone bath was withdrawed, then after ca. 10-15 min, phthalaldehyde (6.71 g, 50.0 mmol) was added. The resulting solution was stirred at room temperature for 1.5 h. Then the mixture was quenched with saturated ammonium chloride solution. The reaction mixture was extracted with ethyl acetate, and dried over anhydrous Na_2SO_4. The solvent was evaporated and the residue was purified by chromatography on silica gel (eluent: petroleum ether: acetone = 3:1) to afford 1,1'-(1,2-phenylene)bis(3-phenylprop-2-yn-1-ol) as a sticky yellow oil.

To a solution of above alcohol (1.69 g, 5.0 mmol) in DCM (20 mL) was added pyridine (4.0 mL, 50.0 mmol) at 0 °C. After stirring for several minutes, a DCM solution of benzyl chloroformate (4.3 mL, 30.0 mmol) was added dropwise (in some cases, the benzyl chloroformate was added directly, however, we found that the use of a DCM solution of benzyl chloroformate afforded better yields). The resulting solution was warmed up to room temperature and stirred for 4 h. Then the mixture was quenched with saturated ammonium chloride solution. The reaction mixture was

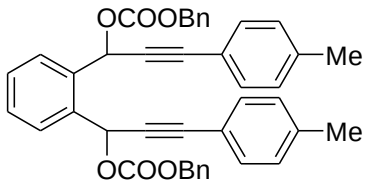
extracted with dichloromethane and dried over anhydrous Na_2SO_4 (in some cases, ethyl acetate was used to extract the recation mixture). The solvent was evaporated and the residue was purified by chromatography on silica gel (eluent: petroleum ether / ethyl acetate = 10:1) to afford compound **1a-2** as a mixture of two diastereomers with a ratio of 1 : 1.20 (2.75 g, 91% isolated yield) as a yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) two isomers: δ 7.80 (dd, *J* = 5.8, 3.2 Hz), 7.76 (dd, *J* = 5.8, 3.2 Hz), 7.46-7.38 (m), 7.32-7.20 (m), 7.01 (s, 1H), 6.99 (s, 1H), 5.18 and 5.03 (ABq, *J* = 12.0 Hz, 2H), 5.16 and 5.01 (ABq, *J* = 12.0 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) two isomers: δ 153.83, 153.81, 134.78, 134.72, 134.67, 134.49, 131.82, 131.78, 129.67, 129.56, 129.38, 128.77, 128.70, 128.38, 128.36, 128.32, 128.15, 128.10, 128.07, 128.02, 121.66, 88.63, 88.20, 84.77, 84.69, 69.88, 67.50, 67.17. IR (film): 3064, 3034, 1750, 1490, 1455, 1443, 1382, 1239, 1030, 925, 906, 756, 691 cm^{-1}; HRMS (ESI) calcd for $C_{40}H_{30}O_6Na$ $[M+Na]^+$: 629.1935, found 629.1946.



1a-3

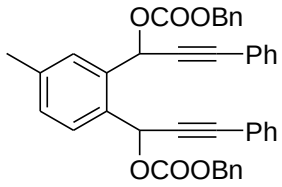
1,2-Phenylenebis(3-phenylprop-2-yne-1,1-diyl) diallyl dicarbonate (1a-3). To a solution of 1,1'-(1,2-phenylene)bis(3-phenylprop-2-yn-1-ol) (1.0 g, 3.0 mmol) in DCM (20 mL) were added pyridine (2.4 mL, 30.0 mmol) and DMAP (0.3 mmol, 36.6 mg) at 0 ^{o}C. After stirring for several minutes, allyl chloromate (1.9 mL, 18.0 mmol) was added dropwise. The resulting solution was warmed up to room temperature and stirred for 2 h. Then the mixture was quenched with saturated ammonium chloride solution. The reaction mixture was extracted with dichloromethane and dried over anhydrous Na_2SO_4. The solvent was evaporated and the residue was purified by chromatography on silica gel (eluent: petroleum ether / ethyl acetate = 10:1) to afford compound (**1a-3**) as a mixture of two diastereomers with a ratio of 1 : 1.18 (1.52 g, 100% isolated yield) as a yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) two isomers: δ 7.80 (dd, *J* = 5.8, 3.6 Hz), 7.77 (dd, *J* = 5.6, 3.6 Hz), 7.46-7.40 (m), 7.32-7.22 (m), 7.00 (s),

6.98 (s), 5.94-5.81 (m), 5.35-5.28 (m), 5.23-5.19 (m), 4.69-4.48 (m). ^{13}C NMR (100 MHz, $CDCl_3$) two isomers: δ 153.74, 153.70, 134.74, 134.56, 131.89, 131.86, 131.28, 131.23, 129.72, 129.60, 129.44, 128.85, 128.81, 128.75, 128.13, 128.08, 121.77, 118.95, 118.89, 88.62, 88.17, 84.78, 84.70, 68.83, 67.45, 67.12. IR (film): 3082, 3063, 2985, 2950, 2229, 1751, 1644, 1593, 1491, 1455, 1444, 1384, 1369, 1318, 1233, 1071, 1031, 906, 787, 757, 691 cm^{-1}. HRMS (ESI) calcd for $C_{32}H_{26}O_6$ $[M+Na]^+$: 529.1627, found 529.1612.



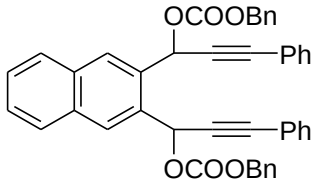
1h

1,2-Phenylenebis(3-(*p*-tolyl)prop-2-yne-1,1-diyl) dibenzyl dicarbonate (1h). Column chromatography on silica gel (eluent: petroleum ether: ethyl acetate =5:1) afforded the title product as a mixture of two diastereomers with a ratio of 1 : 1.27 in ca. 57% yield over two steps as a yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) two isomers: δ 7.79 (dd, *J* = 6.0, 3.2 Hz), 7.75 (dd, *J* = 5.8, 3.2 Hz), 7.43-7.40 (m), 7.32-7.26 (m), 7.05-7.00 (m), 5.16 and 5.01 (ABq, *J* = 12.0 Hz, 2H), 5.15 and 5.00 (ABq, *J* = 12.0 Hz, 2H), 2.30 (s), 2.29 (s). ^{13}C NMR (100 MHz, $CDCl_3$) two isomers: δ 153.90, 153.89, 138.96, 138.88, 134.90, 134.86, 134.83, 134.65, 131.83, 131.78, 129.64, 129.53, 129.40, 128.86, 128.82, 128.42, 128.41, 128.37, 128.34, 128.20, 128.17, 118.75, 118.73, 88.86, 88.45, 84.15, 84.07, 69.89, 67.64, 67.31, 21.42, 21.41. IR (film): 3064, 3032, 2956, 1751, 1509, 1498, 1455, 1382, 1319, 1241, 1022, 1007, 924, 906, 817, 785, 754, 697 cm^{-1}. HRMS (ESI) calcd for $C_{42}H_{34}O_6Na$ $[M+Na]^+$: 657.22476, found 657.22694.



1n

Dibenzyl ((4-methyl-1,2-phenylene)bis(3-phenylprop-2-yne-1,1-diyl)) dicarbonate (1n). Column chromatography on silica gel (eluent: petroleum ether: ethyl acetate =10:1) afforded the title product as a mixture of two diastereomers with a ratio of 1 : 1 in 34% yield over two steps as a yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) two isomers: δ 7.67 (d, *J* = 8.0 Hz), 7.64 (d, *J* = 8.0 Hz), 7.58 (s), 7.55 (s), 7.42-7.37 (m), 7.29-7.19 (m), 7.01 (s), 7.00 (s), 6.96 (s), 5.17 and 5.02 (ABq, *J* = 12.4 Hz), 5.16 and 5.01 (ABq, *J* = 12.4 Hz), 5.14 and 4.99 (ABq, *J* = 12.4 Hz), 2.36 (s). ^{13}C NMR (100 MHz, $CDCl_3$) two isomers: δ153.91, 153.89, 153.88, 153.85, 139.85, 139.73, 134.89, 134.86, 134.82, 134.80, 134.58, 134.37, 131.87, 131.83, 131.82, 131.79, 131.58, 130.37, 130.28, 129.99, 129.50, 129.33, 128.96, 128.75, 128.74, 128.69, 128.42, 128.41, 128.40, 128.36, 128.33, 128.23, 128.20, 128.17, 128.15, 128.10, 128.05, 121.82, 121.80, 88.49, 88.47, 88.06, 88.02, 84.94, 84.90, 84.86, 69.90, 69.86, 69.85, 67.58, 67.52, 67.22, 21.16. IR (film): 3063, 3034, 2957, 1751, 1490, 1456, 1443, 1382, 1319, 1234, 1030, 923, 904, 787, 756, 692 cm^{-1}. HRMS (ESI) calcd for $C_{41}H_{32}O_6Na$ $[M+Na]^+$: 643.20911, found 643.20697.



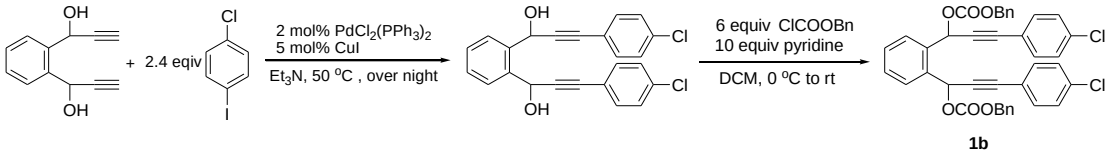
1o

Dibenzyl (naphthalene-2,3-diylbis(3-phenylprop-2-yne-1,1-diyl)) dicarbonate (1o). Column chromatography on silica gel (eluent: petroleum ether: ethyl acetate =20:1 to 10:1) afforded the title product as a mixture of two diastereomers with a ratio of 1 : 1.4 in 53% yield over two steps as a yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) two isomers: δ 8.27 (s), 8.24 (s), 7.82-7.79 (m), 7.47-7.38 (m), 7.29-7.15 (m), 5.17 and 5.00 (ABq, *J* = 12.0 Hz, 2H), 5.15 and 4.98 (ABq, *J* = 12.0 Hz, 2H). ^{13}C NMR

(100 MHz, $CDCl_3$) two isomers: δ 153.88, 153.84, 134.76, 134.68, 133.01, 132.99, 131.82, 131.79, 131.77, 131.76, 129.55, 128.81, 128.76, 128.68, 128.34, 128.32, 128.27, 128.11, 128.06, 128.05, 128.00, 127.99, 127.89, 127.85, 127.24, 127.15, 121.65, 88.78, 88.35, 84.91, 84.82, 69.86, 69.84, 67.92, 67.62. IR (film): 3062, 3034, 2958, 1755, 1598, 1491, 1456, 1443, 1383, 1226, 1180, 1098, 1071, 1030, 1008, 994, 895, 788, 755, 691 cm^{-1}. HRMS (ESI) calcd for $C_{44}H_{32}O_6Na$ $[M+Na]^+$: 679.2091, found 679.2063.

Synthesis of 1,7-diyn-3,6-bis(propargyl carbonate)s 1b-1g, 1i and 1j.

Typical procedure for the synthesis of 1,2-phenylenebis(3-(4-chlorophenyl)prop-2-yne-1,1-diyl) dibenzyl dicarbonate (1b).

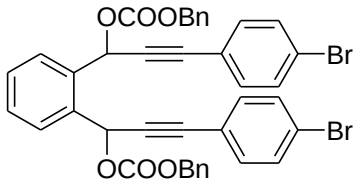


1b

To a solutin of 1,1'-(1,2-phenylene)bis(prop-2-yn-1-ol) (558.6 mg, 3.0 mmol) in triethylamine (20 mL) were added 1-chloro-4-iodobenzene (1.72 g, 7.2 mmol), $PdCl_2(PPh_3)_2$ (42.1 mg, 0.06 mmol) and CuI (28.6 mg, 0.15 mmol) at room temperature, then the mixture was heated overnight at 50 ^oC. After the starting material was consumed, the reaction mixture was quenched with saturated NH_4Cl solution, extracted with ethyl acetate, and dried over anhydrous Na_2SO_4. The solvent was evaporated and the residue was used directly for the next step.

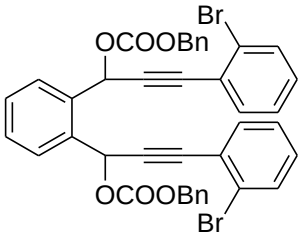
To a solution of above diol in DCM (20 mL) were added pyridine (2.4 mL, 30 mmol) at 0 ^oC. After stirring for several minutes, a DCM solution of benzyl chloroformate (2.6 mL, 18.0 mmol) was added dropwise. The resulting solution was warmed up to room temperature and stirred for 2.5 h. Then the mixture was quenched with saturated ammonium chloride solution. The reaction mixture was extracted with dichloromethane and dried over anhydrous Na_2SO_4. The solvent was evaporated and

the residue was purified by chromatography on silica gel (eluent: petroleum ether / ethyl acetate = 5:1) to afford compound (**1b**) as a mixture of two diastereomers with a ratio of 1 : 1.58 in 80% isolated yield (1.62 g) over two steps as a yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) two isomers: δ 7.77 (dd, *J* = 5.8, 3.2 Hz), 7.72 (dd, *J* =5.8, 3.2 Hz), 7.41-7.37 (m), 7.25-7.23 (m), 7.16-7.11 (m), 7.043 (s), 7.037 (s), 5.15 and 5.01 (ABq, *J* = 12.0 Hz, 2H), 5.13 and 5.00 (ABq, *J* = 12.0 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) two isomers: δ 153.81, 153.80, 134.93, 134.84, 134.71, 134.63, 134.48, 134.34, 133.04, 129.80, 129.68, 129.32, 128.81, 128.47, 128.45, 128.42, 128.41, 128.21, 128.18, 120.12, 87.47, 87.00, 85.68, 85.60, 70.01, 70.00, 67.33, 67.15. IR (film): 3036, 2950, 1751, 1489, 1382, 1242, 1091, 1016, 927, 907, 828, 755, 696 cm^{-1}.HRMS (ESI) calcd for $C_{40}H_{28}Cl_2O_6Na$ $[M+Na]^+$: 697.1155, found 697.1162.



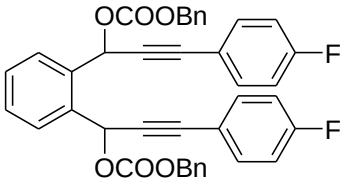
1c

1,2-Phenylenebis(3-(4-bromophenyl)prop-2-yne-1,1-diyl) dibenzyl dicarbonate (1c). Column chromatography on silica gel (eluent: petroleum ether: ethyl acetate =10:1) afforded the title product as a mixture of two diastereomers with a ratio of 1 : 1 in 72% yield over two steps as a yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) two isomers: δ 7.77 (dd, *J* = 5.6, 3.2 Hz), 7.72 (dd, *J* = 5.6, 3.2 Hz), 7.40-7.36 (m), 7.30-7.21 (m), 7.18-7.14 (m), 7.05 (s), 7.04 (s), 5.14 and 5.00 (ABq, *J* = 12.0 Hz, 2H), 5.12 and 4.98 (ABq, *J* = 12.0 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) two isomers: δ 153.65, 153.62, 134.54, 134.45, 134.30, 134.17, 133.03, 133.01, 131.21, 131.15, 129.67, 129.56, 129.18, 128.73, 128.26, 128.24, 128.00, 127.97, 123.08, 123.00, 120.34, 120.31, 87.40, 86.92, 85.81, 85.73, 69.81, 69.79, 67.17, 67.03. IR (film): 3065, 3033, 2957, 1751, 1487, 1383, 1318, 1242, 1096, 1071, 1012, 927, 907, 825, 786, 754, 697 cm^{-1}. HRMS (ESI) calcd for $C_{40}H_{28}O_6Br_2Na$ $[M+Na]^+$: 785.0145, found 785.0133.



1d

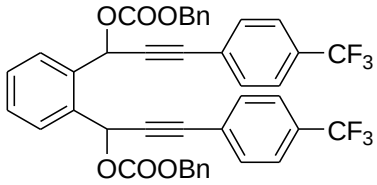
1,2-Phenylenebis(3-(2-bromophenyl)prop-2-yne-1,1-diyl) dibenzyl dicarbonate (1d). Column chromatography on silica gel (eluent: petroleum ether: ethyl acetate =10:1) afforded the title product as a mixture of two diastereomers with a ratio of 1 : 1.63 in 63% yield over two steps as a yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) two isomers: δ 7.90-7.85 (m), 7.52-7.38 (m), 7.33-7.26 (m), 7.18-7.08 (m), 7.07 (s), 7.03 (s), 5.18 and 5.03 (ABq, *J* = 12.0 Hz, 2H), 5.17 and 5.00 (ABq, *J* = 12.4 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) two isomers: δ 153.83, 134.85, 134.77, 134.36, 134.02, 133.77, 133.65, 132.25, 132.23, 130.01, 129.95, 129.85, 129.71, 129.07, 128.44, 128.41, 128.37, 128.23, 128.18, 126.80, 126.77, 125.80, 125.77, 123.98, 123.93, 89.08, 89.05, 87.06, 86.79, 69.99, 69.94, 67.70, 66.95. IR (film): 3060, 3030, 2964, 1751, 1470, 1382, 1315, 1248, 1007, 907, 785, 754, 697 cm^{-1}. HRMS (ESI) calcd for $C_{40}H_{28}O_6Br_2Na$ $[M+Na]^+$: 785.0145, found 785.0143.



1e

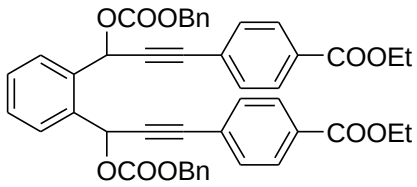
1,2-Phenylenebis(3-(4-fluorophenyl)prop-2-yne-1,1-diyl) dibenzyl dicarbonate (1e). Column chromatography on silica gel (eluent: petroleum ether: ethyl acetate =10:1) afforded the title product as a mixture of two diastereomers with a ratio of 1 : 1.54 in 85% yield over two steps as a yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) two isomers: δ 7.78 (dd, *J* = 5.8, 3.6 Hz), 7.73 (dd, *J* =5.4, 4.0 Hz), 7.44-7.41 (m), 7.38-7.26 (m), 7.01 (s), 7.00 (s), 6.94-6.86 (m), 5.17 and 5.03 (ABq, *J* = 12.0 Hz, 2H), 5.16 and 5.02 (ABq, *J* = 12.0 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) two isomers: δ 162.72 (d, $^{1}J_{C\text{-}F}$ = 250.5 Hz), 162.66 (d, $^{1}J_{C\text{-}F}$ = 250.5 Hz), 153.86, 153.84, 134.77,

134.71, 134.60, 134.44, 133.84 (d, $^{3}J_{C\text{-}F}$ = 8.3 Hz), 133.83 (d, $^{3}J_{C\text{-}F}$ = 8.6 Hz), 129.75, 129.63, 129.32, 128.77, 128.44, 128.41, 128.40, 128.19, 128.16, 117.77 (d, $^{4}J_{C\text{-}F}$ = 3.2 Hz), 115.44 (d, $^{2}J_{C\text{-}F}$ = 22.0 Hz), 115.37 (d, $^{2}J_{C\text{-}F}$ = 22.1 Hz), 87.58, 87.12, 84.51 (d, $^{5}J_{C\text{-}F}$ = 1.5 Hz), 84.45 (d, $^{5}J_{C\text{-}F}$ = 1.1 Hz), 69.97, 69.96, 67.41, 67.19. IR (film): 3066, 3034, 2958, 1751, 1600, 1507, 1455, 1382, 1319, 1236, 1156, 1093, 1014, 926, 907, 837, 755, 697 cm^{-1}. HRMS (ESI) calcd for $C_{40}H_{28}O_6F_2Na$ [M+Na]$^{+}$: 665.1746, found 665.1740.



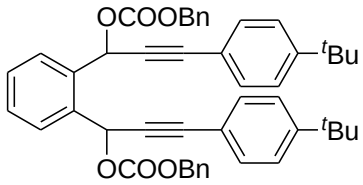
1f

1,2-phenylenebis(3-(4-(trifluoromethyl)phenyl)prop-2-yne-1,1-diyl) dibenzyl dicarbonate (1f). Column chromatography on silica gel (eluent: petroleum ether: ethyl acetate =10:1) afforded the title product as a mixture of two diastereomers with a ratio of 1 : 1.69 in 50% yield over two steps as a yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) two isomers: δ 7.78 (dd, *J* = 5.4, 3.2 Hz), 7.74 (dd, *J* =5.8, 3.2 Hz), 7.48-7.42 (m), 7.32-7.27 (m), 7.03 (s), 7.02 (s), 5.19 and 5.06 (ABq, *J* = 11.6 Hz, 2H), 5.16 and 5.03 (ABq, *J* = 11.6 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) two isomers: δ 153.87, 153.86, 134.72, 134.62, 134.39, 134.26, 132.11, 132.07, 130.57 (q, $^{2}J_{C\text{-}F}$ = 32.8 Hz), 130.49 (q, $^{2}J_{C\text{-}F}$ = 33.0 Hz), 129.98, 129.86, 129.37, 128.94, 128.60, 128.55, 128.53, 128.51, 128.27, 128.26, 125.48, 125.47, 125.14 (q, $^{3}J_{C\text{-}F}$ = 3.7 Hz), 125.03 (q, $^{3}J_{C\text{-}F}$ = 3.9 Hz), 123.70 (q, $^{1}J_{C\text{-}F}$ = 272.2 Hz), 123.68 (q, $^{1}J_{C\text{-}F}$ = 272.4 Hz), 87.21, 87.06, 86.98, 86.72, 70.18, 67.24, 67.13. IR (film): 3067, 3035, 2959, 1752, 1615, 1498, 1456, 1406, 1383, 1325, 1242, 1170, 1126, 1106, 1068, 1018, 929, 908, 843, 784, 754, 697 cm^{-1}. HRMS (ESI) calcd for $C_{42}H_{28}O_6F_6Na$ [M+Na]$^{+}$: 765.1682, found 765.1673.



1g

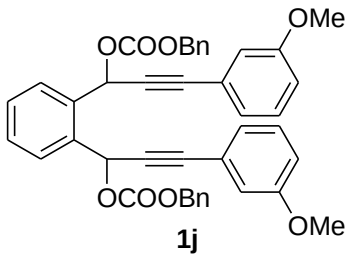
Diethyl 4,4'-(1,2-phenylenebis(3-(((benzyloxy)carbonyl)oxy)prop-1-yne-3,1-diyl))-dibenzoate (1g). Column chromatography on silica gel (eluent: petroleum ether: ethyl acetate =10:1) afforded the title product as a mixture of two diastereomers with a ratio of 1 : 1.6 in 79% yield over two steps as a yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) two isomers: δ 7.93-7.88 (m), 7.80 (dd, *J* = 5.6, 3.6 Hz), 7.76 (dd, *J* =5.4, 3.6 Hz), 7.46-7.42 (m), 7.28-7.25 (m), 7.08 (s), 5.18 and 5.05 (ABq, *J* = 11.6 Hz, 2H), 5.15 and 5.02 (ABq, *J* = 12.0 Hz, 2H), 4.32 (q, *J* = 6.8, 4H), 1.34 (t, *J* = 6.8, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) two isomers: δ 165.39, 165.38, 153.63, 153.61, 134.56, 134.47, 134.25, 134.11, 131.48, 130.23, 130.15, 129.72, 129.59, 129.22, 129.02, 128.97, 128.77, 128.26, 128.24, 128.22, 128.00, 127.96, 125.92, 125.89, 87.61, 87.35, 87.26, 87.13, 69.84, 67.11, 66.97, 60.84, 13.97. IR (film): 2981, 1752, 1717, 1606, 1456, 1405, 1272, 1243, 1176, 1106, 1021, 928, 908, 754, 769, 696 cm^{-1}. HRMS (ESI) calcd for $C_{46}H_{38}O_{10}Na$ $[M+Na]^+$: 773.2357, found 773.2342.



1i

1,2-Phenylenebis(3-(4-(*tert*-butyl)phenyl)prop-2-yne-1,1-diyl) dibenzyl dicarbonate (1i). Column chromatography on silica gel (eluent: petroleum ether: ethyl acetate =5:1) afforded the title product as a mixture of two diastereomers with a ratio of 1 : 1.52 in 29% yield over two steps as a yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) two isomers: δ 7.79 (dd, *J* = 5.8, 3.2 Hz), 7.76 (dd, *J* =5.6, 3.2 Hz), 7.40-7.33 (m), 7.28-7.21 (m), 7.06 (s), 7.04 (s), 5.15 and 5.01 (ABq, *J* = 12.0 Hz), 5.13 and 4.98 (ABq, *J* = 12.4 Hz, 2H), 1.25 (s), 1.24 (s). ^{13}C NMR (100 MHz, $CDCl_3$) two isomers: δ 153.83, 153.80, 151.94, 151.87, 134.79, 134.77, 134.74, 134.58, 131.61, 131.56,

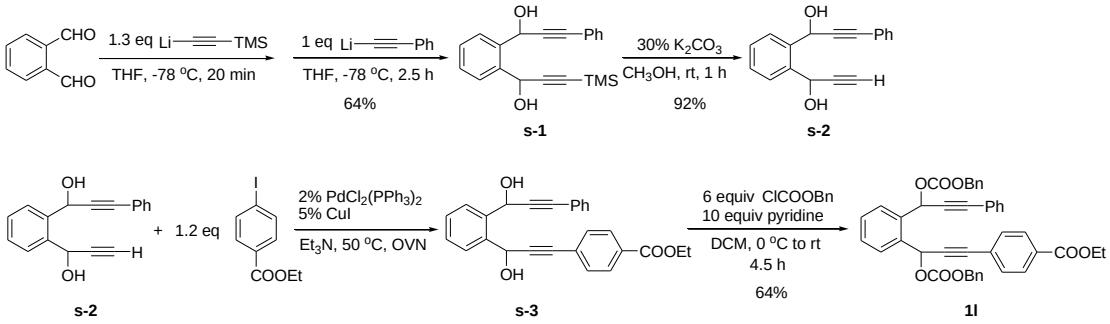
129.57, 129.46, 129.33, 128.78, 128.34, 128.33, 128.29, 128.26, 128.12, 128.09, 125.03, 124.99, 118.71, 88.77, 88.33, 84.20, 84.14, 69.78, 67.58, 67.26, 34.57, 34.56, 30.95. IR (film): 3033, 2962, 2863, 1751, 1505, 1456, 1383, 1243, 1021, 926, 907, 836, 696 cm^{-1}. HRMS (ESI) calcd for $C_{48}H_{46}O_6Na$ $[M+Na]^+$: 741.3187, found 741.3178.



1j

1,2-Phenylenebis(3-(3-methoxyphenyl)prop-2-yne-1,1-diyl) dibenzyl dicarbonate (1j). Column chromatography on silica gel (eluent: petroleum ether: ethyl acetate =5:1) afforded the title product as a mixture of two diastereomers with a ratio of 1 : 1.30 in 33% yield over two steps as a yellow oil. ^1H NMR (400 MHz, $CDCl_3$) two isomers: δ 7.79 (dd, *J* = 5.8, 3.6 Hz), 7.75 (dd, *J* = 5.8, 3.6 Hz), 7.42-7.39 (m), 7.28-7.23 (m), 7.14-6.93 (m), 6.83-6.79 (m), 5.15 and 5.00 (ABq, *J* = 12.0 Hz, 2H), 5.13 and 4.98 (ABq, *J* = 12.0 Hz, 2H), 3.62 (s). ^{13}C NMR (100 MHz, $CDCl_3$) two isomers: δ 158.97, 158.94, 153.77, 153.75, 134.68, 134.61, 134.58, 134.39, 129.66, 129.56, 129.30, 129.13, 129.09, 128.80, 128.32, 128.31, 128.28, 128.08, 128.04, 124.26, 124.22, 122.52, 116.35, 116.31, 115.50, 115.44, 88.49, 88.05, 84.48, 84.39, 69.83, 67.38, 67.09, 54.92. IR (film): 3066, 3033, 2959, 2835, 1751, 1596, 1574, 1489, 1456, 1382, 1320, 1249, 1206, 1175, 1165, 1045, 928, 908, 785, 755, 698, 687 cm^{-1}. HRMS (ESI) calcd for $C_{42}H_{34}O_8Na$ $[M+Na]^+$: 689.2146, found 689.2174.

Synthesis of 1,7-diyn-3,6-bis(propargyl carbonate)s 1k, 1l and 1m. Typical procedure for the synthesis of ethyl 4-(3-(((benzyloxy)carbonyl)oxy)-3-(2-(1-(((benzyloxy)carbonyl)oxy)-3-phenylprop-2-yn-1-yl)phenyl)prop-1-yn-1-yl)benzoate (1l).



A THF solution of ethynyltrimethylsilane (1.84 mL, 13.0 mmol in 20 mL THF) and phenylacetylene (1.1 mL, 10 mmol in 20 mL THF) were placed in two 100 mL round bottom flasks respectively. n-BuLi (2.5 M in hexane, 5.2 mL, 13.0 mmol) was added to the ethynyltrimethylsilane solution, and n-BuLi (2.5 M in hexane, 4.0 mL, 10.0 mmol) was added to the phenylacetylene solution at -78 °C. This deprotonation reaction was stirred for 10 min. (deprotonation of phenylacetylene was also accomplished accordingly). To the solution of lithium trimethylsilylacetylide was then added a THF solution of phthaldehyde (1.34 g, 10.0 mmol in 20 mL). The mixture was stirred for 10 minuets at -78 °C before a solution of lithium phenylacetylide was added. The reaction mixture was warmed up to room temperature and stirred for 2.5 h. Then the mixture was quenched with saturated ammonium chloride solution. The reaction mixture was extracted with ethyl acetate and dried over anhydrous Na_2SO_4. The solvent was evaporated and the residue was purified by chromatography on silica gel (eluent: petroleum ether / ethyl acetate = 3:1) to afford the diol **s-1** as a colorless oil .

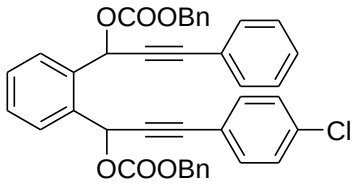
To a solution of above diol **s-1** (2.96 g, 8.8 mmol) were added MeOH (30 mL) and K_2CO_3 (364 mg, 2.64 mmol), after stirring for 1 h at room temperature. The mixture was quenched with H_2O, extracted with ethyl acetate and dried over anhydrous Na_2SO_4. The solvent was evaporated and the residue was purified by chromatography on silica gel (eluent: petroleum ether: acetone = 3:1) to afford diol **s-2** as a mixture of two diastereomers with a ratio of 1 : 4.8 in 92% isolated yield (2.12 g) as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) two isomers: δ 7.91-7.82 (m), 7.69-7.60 (m), 7.50-7.45 (m), 7.40-7.27 (m), 6.16 (s), 6.04 (s), 5.98 (s), 5.85 (d), 4.38 (s), 4.27 (s), 3.93 (s), 3.86 (s), 2.70-2.67 (m). ^{13}C NMR (100 MHz, $CDCl_3$) two

isomers: δ 137.98, 137.72, 137.56, 137.22, 131.72, 129.13, 129.10, 128.64, 128.60, 128.26, 128.25, 127.98, 127.89, 122.18, 122.15, 87.75, 87.65, 87.47, 82.69, 82.34, 75.90, 75.56, 63.75, 62.92, 62.16, 61.43. IR (film): 3360, 3289, 1597, 1489, 1453, 1442, 1323, 1300, 1199, 1176, 1098, 1046, 1027, 1014, 997, 965, 939, 811, 773, 758, 736, 694, 664 cm^{-1}. HRMS (MALDI/DHB) calcd for $C_{18}H_{14}O_2Na$ $[M+Na]^+$: 285.0886, found 285.0883.

To a solutin of diol **s-2** (524.6 mg, 2.0 mmol) in triethylamine (20 mL) were added ethyl 4-iodobenzoate (662.57 mg, 2.4 mmol), $PdCl_2(PPh_3)_2$ (28.0 mg, 0.04 mmol) and CuI (19.0 mg, 0.10 mmol) at room temperature, then the mixture was heated overnight at 50 ^oC. After the starting material was consumed, the mixture was quenched with saturated ammonium chloride solution, extracted with ethyl acetate, and dried over anhydrous Na_2SO_4. The solvent was evaporated, and the residue was purified by chromatography on silica gel (petroleum: acetone = 3:1) to afford diol **s-3** as a yellow oil.

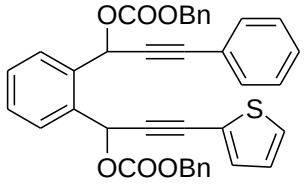
To a solution of above diol **s-3** (646.8 mg, 1.57 mmol) in DCM (20 mL) was added pyridine (1.3 mL, 15.7 mmol) at 0 ^oC. After stirring for several minutes, benzyl chloroformate (1.3 mL, 9.4 mmol) was added. The resulting solution was warmed up to room temperature and stirred for 1 h. Then the mixture was quenched with saturated ammonium chloride solution. The reaction mixture was extracted with dichloromethane and dried over anhydrous Na_2SO_4. The solvent was evaporated and the residue was purified by chromatography on silica gel (eluent: petroleum ether / ethyl acetate = 10:1) to afford the title product (**1l**) as a mixture of two diastereomers (dr = ca. 4.5:1) in 64% yield (0.87 g) over two steps as a yellow oil. ^1H NMR (400 MHz, $CDCl_3$) two isomers: δ 7.92-7.88 (m), 7.76-7.74 (m), 7.46-7.38 (m), 7.31-7.20 (m), 7.05 (s), 7.03 (s), 6.98 (s), 5.18-5.15 (m), 5.05-4.99 (m), 4.35 (q, *J* = 7.2 Hz), 1.38 (t, *J* = 7.2, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) major isomer: δ 165.84, 153.89, 153.83, 134.74, 134.58, 134.26, 131.87, 131.73, 130.30, 129.72, 129.67, 129.22, 129.18, 128.88, 128.83, 128.48, 128.28, 128.25, 128.11, 126.28, 121.72, 88.34, 87.59, 87.28, 84.67, 84.59, 70.06, 70.03, 67.33, 67.01, 61.11, 14.23. Minor isomer: 134.82,

134.80, 134.78, 131.76, 130.38, 129.81, 128.20, 128.16, 88.41, 87.50，84.59, 67.64, 67.10, 61.22. Other peaks are overlapped with the signal of the major isomer. IR (film): 3024, 2964, 1747, 1715, 1490, 1455, 1382, 1231, 1176, 1105, 1020, 924, 905, 785, 769, 754, 736, 692 cm^{-1}. HRMS (ESI) calcd for $C_{43}H_{34}O_8Na$ $[M+Na]^+$: 701.2146, found 701.2120.



1k

(**1k**). Column chromatography on silica gel (eluent: petroleum ether: ethyl acetate =10:1) afforded the title product as a mixture of two diastereomers (dr = ca. 1:7.1) in 78% yield over two steps from **s-2** as a yellow oil. ^1H NMR (400 MHz, $CDCl_3$) two isomers: δ 7.77-7.71 (m), 7.44-7.36 (m), 7.29-7.14 (m), 7.01(s), 7.00 (s), 5.16 and 5.02 (ABq, *J* = 12.4 Hz), 5.15 and 5.02 (ABq, *J* = 11.6 Hz), 5.14 and 4.99 (ABq, *J* = 12.0 Hz). ^{13}C NMR (100 MHz, $CDCl_3$) major isomer: δ 153.86, 153.81, 134.79, 134.72, 134.53, 134.36, 133.06, 131.82, 129.64, 129.61, 128.84, 128.77, 128.70, 128.43, 128.40, 128.23, 128.18, 128.07, 121.68, 120.20, 88.25, 86.99, 85.79, 84.72, 69.97, 67.24, 67.06. Minor isomer: 134.86, 134.69, 134.56, 133.08, 129.76, 129.74, 129.44, 129.31, 128.15, 128.13, 88.72, 87.44, 85.72, 84.66, 67.53, 67.38. Other peaks are overlapped with the signal of the major isomer. IR (film): 3057, 3028, 1746, 1489, 1455, 1381, 1317, 1232, 1180, 1090, 1015, 996, 924, 905, 828, 785, 754, 736, 692 cm^{-1}. HRMS (ESI) calcd for $C_{40}H_{29}O_6ClNa$ $[M+Na]^+$: 663.1545, found 663.1530.



1m

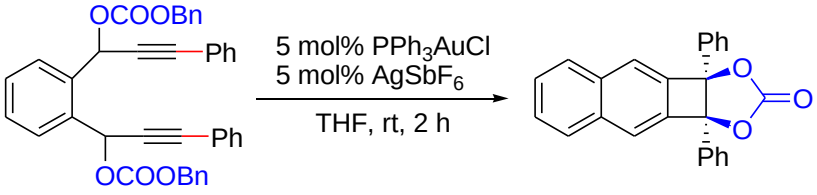
(**1m**). Column chromatography on silica gel (eluent: petroleum ether: ethyl acetate =10:1) afforded the title product as a mixture of two diastereomers (dr = ca. 1:4.14) in

70% yield over two steps from **s-2** as a brown oil. ^{1}H NMR (400 MHz, $CDCl_3$) two isomers: δ 7.75-7.72 (m), 7.44-7.37 (m), 7.32-7.16 (m), 7.08 (s), 7.02 (s), 6.97 (s), 6.95 (s), 6.89-6.86 (m), 5.17 and 5.05 (ABq, *J* = 12.0 Hz), 5.14 and 4.98 (ABq, *J* = 12.0 Hz). Some peaks of minor isomer are overlapped with the signal of the major isomer. ^{13}C NMR (100 MHz, $CDCl_3$) major isomers: δ 153.85, 153.81, 134.81, 134.74, 134.53, 134.24, 133.24, 131.83, 129.66, 129.63, 128.93, 128.74, 128.44, 128.43, 128.42, 128.25, 128.22, 128.07, 127.98, 126.86, 126.82, 121.72, 121.55, 88.56, 88.32, 84.67, 81.64, 69.99, 69.97, 67.25, 67.18. Minor isomer: 134.84, 134.67, 134.46, 133.31, 131.91, 129.78, 129.76, 129.49, 129.41, 128.83, 128.38, 128.18, 128.17, 128.13, 128.02, 126.86, 88.79, 84.59, 67.64, 67.45. Other peaks are overlapped with the signal of the major isomer. IR (film): 3073, 3028, 1745, 1490, 1455, 1381, 1314, 1231, 1192, 1178, 923, 904, 784, 754, 692 cm^{-1}. HRMS (ESI) calcd for $C_{38}H_{28}O_6SNa$ $[M+Na]^+$: 635.1499, found 635.1489.

Typical procedure for the synthesis of *cis*-dihydrocyclobuta[*b*]naphthalene 2a.

(All reactions were carried out on 0.2 mmol scale).

Condition **A**:

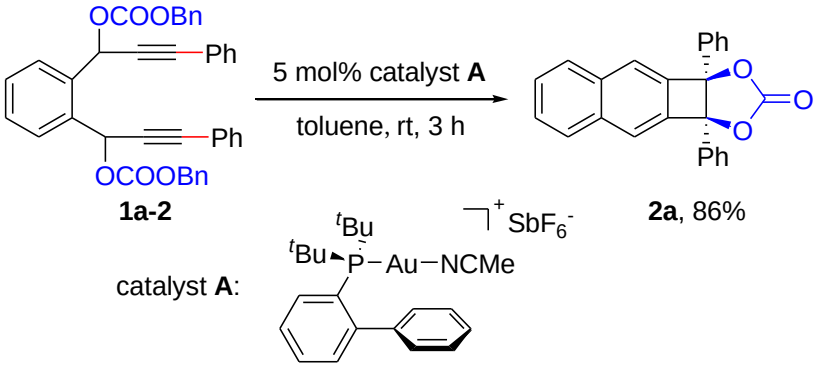


1a-2 **2a**, 87%

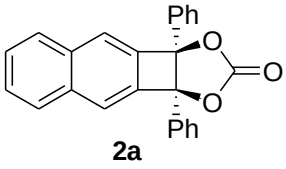
Condition A: In a glovebox, to a Schlenk tube was added $AgSbF_6$ (3.4 mg, 0.01 mmol). Then the Schlenk tube was removed from the glovebox, PPh_3AuCl (5 mg, 0.01 mmol) and THF (0.5 mL) were successively added and the mixture was stirred at room temperature for 15-20 min. Then a THF solution of **1a-2** (121.3 mg, 0.2 mmol in 1.5 mL THF) was added. After the reaction mixture was stirred at room temperature for 2 h, the solvent was evaporated under the reduced pressure and the residue was purified by chromatography on silica gel (petroleum: ethyl acetate = 20:1) to afford **2a** (63.4 mg, 87%) as a white solid. In a separate experiment, we also isolated a byproduct of benzyl alcohol in 23% yield. It is noted that under condition A,

the reaction mixture became viscous as the reaction progressed. It was found that partial polymerization of THF solvent occurred under the conditions as evidenced by the NMR spectra of the crude reaction mixture.

Condition **B**:

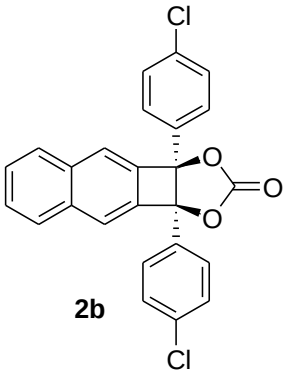


Condition B: To a solution of 1,2-phenylenebis(3-phenylprop-2-yne-1,1-diyl) dibenzyl dicarbonate **1a-2** (121.3 mg, 0.2 mmol) in toulene (2 mL) was added [Johnphos(MeCN)Au]SbF_6 (7.7 mg, 0.01 mmol). After the reaction mixture was stirred at room temperature for 3 h, the solvent was evaporated under the reduced pressure and the residue was purified by chromatography on silica gel (petroleum: ethyl acetate = 20:1) to afford **2a** (62.7 mg, 86%) as a white solid.



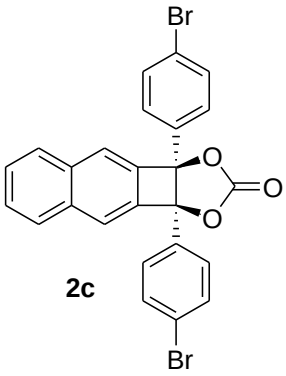
2a

(3aR*,9bS*)-3a,9b-Diphenyl-3a,9b-dihydronaphtho[2',3':3,4]cyclobuta[1,2-*d*][1,3]dioxol-2-one (2a). M.p. 206-207 ^{o}C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.04 (s, 2H), 7.98 (dd, *J* = 6.0, 3.6 Hz, 2H), 7.59 (dd, *J* = 6.4, 3.2 Hz, 2H), 7.23-7.21 (m, 4H), 7.16-7.15 (m, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 154.51, 141.54, 135.74, 132.39, 129.15, 129.04, 128.12, 127.19, 126.78, 123.95, 95.24. IR (film): 3064, 1803, 1594, 1499, 1450, 1268, 1221, 1207, 1139, 1039, 1029, 1006, 881, 753, 729, 696 cm^{-1}. HRMS (EI) calcd for $C_{25}H_{16}O_3$: 364.1099, found 364.1101.



2b

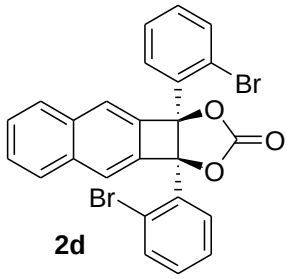
(3aR*,9bS*)-3a,9b-Bis(4-chlorophenyl)-3a,9b-dihydronaphtho[2',3':3,4]cyclobut a[1,2-*d*][1,3]dioxol-2-one (2b). Condition A was used. Column chromatography on silica gel (petroleum ether: ethyl acetate =20:1) afforded the title product in 76% (65.6 mg) yield as a white solid. M.p. 239-240 ^{o}C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.07 (s, 2H), 8.01 (dd, *J* = 6.2, 3.2 Hz, 2H), 7.64 (dd, *J* = 6.4, 3.2 Hz, 2H), 7.21-7.14 (m, 8H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 154.02, 140.94, 135.88, 135.48, 130.88, 129.25, 128.69, 128.14, 127.52, 124.09, 94.67. IR (film): 3060, 2920, 2849, 1799, 1597, 1505, 1494, 1410, 1399, 1310, 1228, 1206, 1149, 1138, 1094, 1036, 1018, 1004, 885, 839, 797, 767, 754 cm^{-1}. HRMS (ESI) calcd for $C_{25}H_{14}Cl_2O_3Na$ $[M+Na]^+$: 455.0214, found 455.0212.



2c

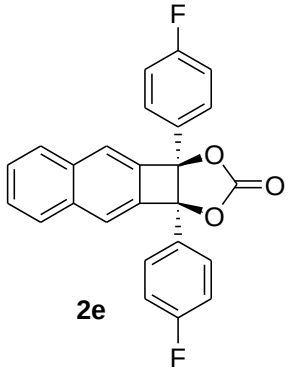
(3aR*,9bS*)-3a,9b-Bis(4-bromophenyl)-3a,9b-dihydronaphtho[2',3':3,4]cyclobut a[1,2-*d*][1,3]dioxol-2-one (2c). Condition A: Column chromatography on silica gel (petroleum ether: ethyl acetate =20:1) and recrystallization afforded the title product in 75% yield (77.5 mg) as a white solid. Condition B: Column chromatography on silica gel (petroleum ether: ethyl acetate =20:1) afforded the title product in 62% yield (65.2 mg) as a white solid. M.p. 238-240 ^{o}C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.07 (s,

2H), 8.01 (dd, *J* = 6.2, 3.2 Hz, 2H), 7.65 (dd, *J* = 6.0, 3.2 Hz, 2H), 7.37-7.34 (m, 4H), 7.11-7.08 (m, 4H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 153.96, 140.85, 135.84, 131.63, 131.36, 129.23, 128.39, 127.51, 124.06, 123.81, 94.63. IR (film): 3060, 2920, 2846, 1809, 1755, 1597, 1505, 1489, 1410, 1396, 1265, 1220, 1206, 1150, 1140, 1074, 1039, 1012, 920, 882, 841, 820, 765, 753, 737, 699 cm^{-1}. HRMS (ESI) calcd for $C_{25}H_{14}Br_2O_3Na$ $[M+Na]^+$: 542.9202, found 542.9208.



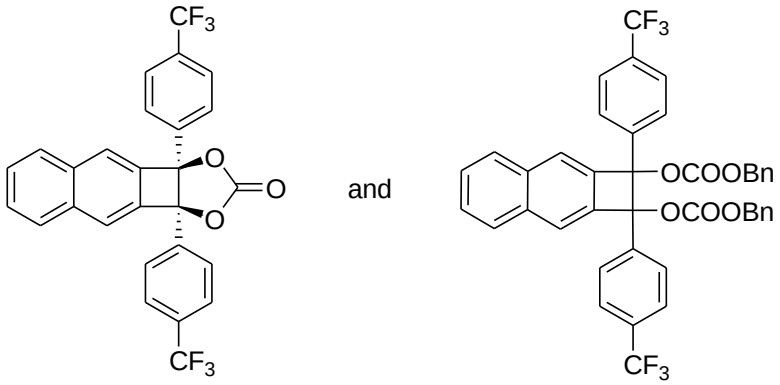
2d

(3aR*,9bS*)-3a,9b-Bis(2-bromophenyl)-3a,9b-dihydronaphtho[2',3':3,4]cyclobuta[1,2-d][1,3]dioxol-2-one (2d). Condition A was used. Column chromatography on silica gel (petroleum ether: ethyl acetate =20:1) afforded the title product in 72% yield (74.9 mg) as a white solid. M.p. 229-230 ^{o}C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.12 (dd, *J* = 8.0, 1.2 Hz, 2H), 8.05 (s, 2H), 7.98 (dd, *J* = 6.2, 3.2 Hz, 2H), 7.61 (dd, *J* = 6.4, 3.2 Hz, 2H), 7.38-7.35 (m, 4H), 7.21-7.17 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 153.53, 141.65, 135.42, 134.52, 132.25, 131.60, 131.00, 129.26, 127.19, 126.83, 123.37, 121.73, 95.39. IR (film): 3054, 1809, 1590, 1563, 1506, 1471, 1436, 1296, 1282, 1222, 1061, 1032, 1021, 882, 756, 743, 695 cm^{-1}. HRMS (EI) calcd for $C_{25}H_{14}O_3Br_2$:519.9310, found 519.9314.



2e

(3aR*,9bS*)-3a,9b-Bis(4-fluorophenyl)-3a,9b-dihydronaphtho[2',3':3,4]cyclobuta[1,2-*d*][1,3]dioxol-2-one (2e). Condition A was used. Column chromatography on silica gel (petroleum ether: ethyl acetate =20:1) afforded the title product in 85% yield (68.5 mg) as a white solid. M.p. 203-204 ^{o}C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.08 (s, 2H), 8.00 (dd, *J* = 6.2, 3.6 Hz, 2H), 7.63 (dd, *J* = 6.4, 3.6 Hz, 2H), 7.22-7.18 (m, 4H), 6.91-6.86 (m, 4H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 162.97 (d, $^{1}J_{C\text{-}F}$ = 249.9 Hz), 154.12, 141.11, 135.83, 129.20, 128.75 (d, $^{3}J_{C\text{-}F}$ = 8.6 Hz), 128.31 (d, $^{4}J_{C\text{-}F}$ = 3.2 Hz), 127.41, 124.06, 115.43 (d, $^{2}J_{C\text{-}F}$ = 21.6 Hz), 94.72 (d, $^{5}J_{C\text{-}F}$ = 1.0 Hz). IR (film): 3057, 2923, 1805, 1603, 1511, 1415, 1304, 1270, 1226, 1161, 1139, 1038, 1015, 883, 846, 766, 756 cm^{-1}. HRMS (EI) calcd for $C_{25}H_{14}O_3F_2$: 400.0911, found 400.0918.



2f **3**

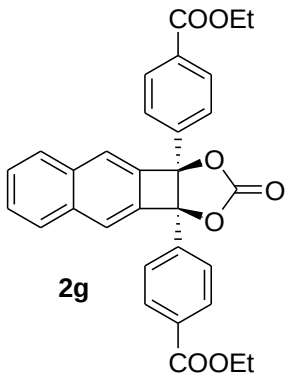
(3aR*,9bS*)-3a,9b-Bis(4-(trifluoromethyl)phenyl)-3a,9b-dihydronaphtho[2',3':3,4]cyclobuta[1,2-*d*][1,3]dioxol-2-one (2f). Condition A was used. In this case, column chromatography on silica gel (petroleum ether: ethyl acetate =20:1) afforded the product **2f** in 74% yield (73.8 mg) as a white solid (M.p. 185-186 ^{o}C), and the product **3** in 12% yield (17.3 mg) as a mixture of two diastereomers in a ratio of 1:1.25 (determined by HPLC).

Characterization data for **2f**:

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.11 (s, 2H), 8.04 (dd, *J* = 6.2, 3.2 Hz, 2H), 7.68 (dd, *J* = 6.4, 3.2 Hz, 2H), 7.48 (m, 4H), 7.38-7.35 (m, 4H). ^{13}C NMR (100 MHz, $CDCl_3$)**:** δ 153.80, 140.57, 136.13 (q, $^{5}J_{C\text{-}F}$ = 1.6 Hz), 135.99, 131.52 (q, $^{2}J_{C\text{-}F}$ = 32.8 Hz), 129.32, 127.74, 127.20, 125.46 (q, $^{3}J_{C\text{-}F}$ = 4.0 Hz), 124.24, 123.47 (q, $^{1}J_{C\text{-}F}$ = 272.8 Hz), 94.55.

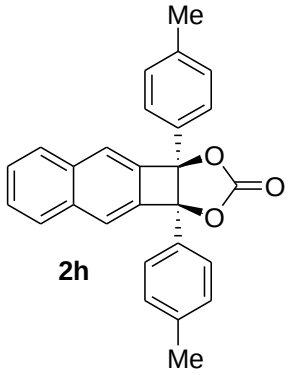
IR (film): 3069, 2926, 2849, 1816, 1620, 1504, 1416, 1328, 1220, 1205, 1169, 1127, 1070, 1041, 1018, 853, 754 cm^{-1}. HRMS (EI) calcd for $C_{27}H_{14}O_3F_6$: 500.0847, found 500.0848.

Characterization data for **3**: ^1H NMR (400 MHz, $CDCl_3$) two isomers: δ 8.26 (s, 2H), 8.01 (dd, *J* = 5.8, 2.8, 2H), 7.63-7.61 (m, 6H), 7.46-7.44 (m, 4H), 7.27-7.26 (m, 6H), 7.12-7.11 (m, 4H), 4.96 and 4.87 (ABq, *J* =12.0 Hz, 4H). ^{13}C NMR (100 MHz, $CDCl_3$) two isomers: δ 152.78, 141.22, 139.37, 135.88, 134.64, 130.50 (q, $^2J_{C-F}$ = 32.8 Hz), 129.24, 128.54, 128.49, 128.08, 127.96, 127.59, 127.02, 126.82, 125.30 (q, $^3J_{C-F}$ = 3.7 Hz), 124.01 (q, $^1J_{C-F}$ = 271.7 Hz), 91.92, 69.68. IR (film): 3063, 3030, 2950, 2923, 1751, 1620, 1505, 1456, 1413, 1377, 1326, 1242, 1166, 1114, 1066, 1030, 1018, 946, 889, 850, 802, 787, 752, 706, 696 cm^{-1}. HRMS (ESI) calcd for $C_{42}H_{28}F_6O_6Na$ $[M+Na]^+$: 765.1713, found 765.1682.



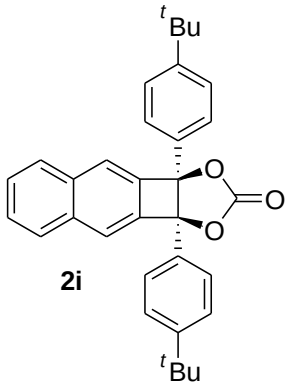
2g

Diethyl 4,4'-((3aR*,9bS*)-2-oxo-3a,9b-dihydronaphtho[2',3':3,4]cyclobuta-[1,2-*d*][1,3]dioxole-3a,9b-diyl)dibenzoate (2g). Condition A was used. Column chromatography on silica gel (petroleum ether: ethyl acetate =20:1) afforded the title product in 74% yield (75.2 mg) as a white solid. M.p. 157-159 ^oC. ^1H NMR (400 MHz, $CDCl_3$) δ 8.11 (s, 2H), 8.04 (dd, *J* = 6.0, 3.6 Hz, 2H), 7.88-7.86 (m, 4H), 7.66 (dd, *J* = 6.2, 3.6 Hz, 2H), 7.31-7.29 (m, 4H), 4.32 (q, *J* = 7.2, 4H), 1.35 (t, *J* = 7.2, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.68, 154.01, 140.80, 136.80, 135.90, 131.22, 129.51, 129.27, 127.56, 126.71, 124.17, 94.81, 61.21, 14.15. IR (film): 3057, 2982, 2959, 2926, 1813, 1718, 1413, 1367, 1276, 1219, 1205, 1108, 1041, 1020, 854, 763, 737 cm^{-1}. HRMS (ESI) calcd for $C_{31}H_{24}O_7Na$ $[M+Na]^+$: 531.1414, found 531.1438.



2h

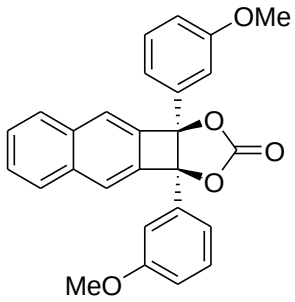
(3aR*,9bS*)-3a,9b-Di-*p*-tolyl-3a,9b-dihydronaphtho[2',3':3,4]cyclobuta[1,2-*d*][1,3]dioxol-2-one (2h). Condition A was used. Column chromatography on silica gel (petroleum ether: ethyl acetate =10:1) afforded the title product in 82% yield (64.3 mg) as a white solid. M.p. 199-201 ^{o}C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.04 (s, 2H), 7.98 (dd, *J* = 6.4, 3.2 Hz, 2H), 7.60 (dd, *J* = 6.4, 3.2 Hz, 2H), 7.13-7.11 (m, 4H), 7.00-6.98 (m, 4H), 2.22 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 154.65, 142.01, 138.95, 135.76, 129.57, 129.18, 128.91, 127.12, 126.83, 123.85, 95.38, 21.09. IR (film): 3051, 3024, 2917, 2858, 1801, 1506, 1453, 1415, 1270, 1223, 1186, 1148, 1139, 1038, 1022, 882, 836, 795, 767, 753, 737 cm^{-1}. HRMS (EI) calcd for $C_{27}H_{20}O_3$: 392.1412, found 392.1406.



2i

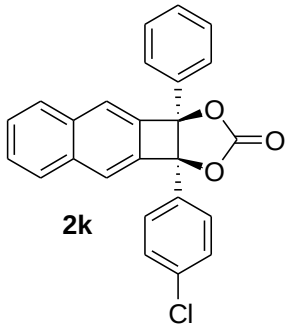
(3aR*,9bS*)-3a,9b-Bis(4-*tert*-butylphenyl)-3a,9b-dihydronaphtho[2',3':3,4]cyclobuta[1,2-*d*][1,3]dioxol-2-one (2i). Condition A was used. Column chromatography on silica gel (petroleum ether: ethyl acetate =20:1) afforded the title product in 70% yield (66.7 mg) as a white solid. M.p. 179-180 ^{o}C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.08 (s, 2H), 8.01 (dd, *J* = 6.2, 3.2 Hz, 2H), 7.63 (dd, *J* = 6.6, 3.2 Hz, 2H), 7.17-7.15 (m, 4H),

7.11-7.09 (m, 4H), 1.18 (s, 18H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 154.85, 152.09, 141.87, 135.76, 129.54, 129.20, 127.10, 126.57, 124.89, 123.97, 95.33, 34.43, 31.02. IR (film): 3057, 2962, 2868, 1812, 1617, 1590, 1510, 1459, 1413, 1272, 1221, 1040, 1020, 1005, 881, 845, 767, 748 cm^{-1}. HRMS (EI) calcd for $C_{33}H_{32}O_3$: 476.2351, found 476.2348.



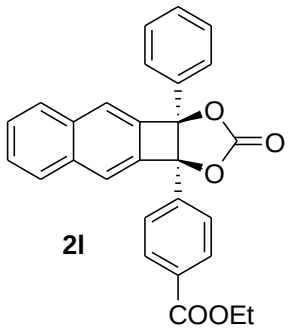
2j

(3aR*,9bS*)-3a,9b-Bis(3-methoxyphenyl)-3a,9b-dihydronaphtho[2',3':3,4]cyclobuta[1,2-*d*][1,3]dioxol-2-one (2j). Condition B was used. Column chromatography on silica gel (petroleum ether: ethyl acetate =10:1) afforded the title product in 45% yield (38.2 mg) as a white solid. M.p. 208-210 ^{o}C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.08 (s, 2H), 8.01 (dd, *J* = 6.2, 3.6 Hz, 2H), 7.63 (dd, *J* = 6.4, 3.2 Hz, 2H), 7.13-7.09 (m, 2H), 6.83-6.81 (m, 2H), 6.76-6.75 (m, 4H), 3.65 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.32, 154.51, 141.65, 135.82, 133.99, 129.29, 129.25, 127.25, 123.94, 119.42, 114.81, 112.42, 95.18, 55.24. IR (film): 3072, 3000, 2959, 2911, 2840, 1794, 1748, 1600, 1491, 1465, 1432, 1291, 1226, 1161, 1147, 1136, 1032, 1013, 951, 889, 873, 832, 809, 756, 696 cm^{-1}. HRMS (MALDI/DHB) calcd for $C_{27}H_{21}O_5$ $[M+H]^+$: 425.1384, found 425.1383.

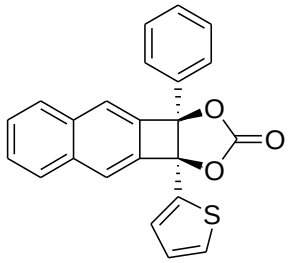


2k

(3aR*,9bS*)-3a-(4-Chlorophenyl)-9b-phenyl-3a,9b-dihydronaphtho[2',3':3,4]cyclobuta[1,2-*d*][1,3]dioxol-2-one (2k). Condition A was used. Column chromatography on silica gel (petroleum ether: ethyl acetate =20:1) afforded the title product in 76% yield (61.2 mg) as a white solid. M.p. 181-183 ^{o}C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.09 (s, 1H), 8.06 (s, 1H), 8.02-8.00 (m, 2H), 7.64 (dd, *J* = 6.2, 3.2 Hz, 2H), 7.22 (s, 5H), 7.15 (s, 4H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 154.29, 141.39, 141.24, 135.88, 135.84, 135.21, 132.19, 131.20, 129.36, 129.25, 129.24, 128.47, 128.39, 128.21, 127.40, 127.38, 126.80, 124.18, 123.94, 95.30, 94.68. IR (film): 1797, 1595, 1507, 1495, 1452, 1404, 1268, 1230, 1198, 1089, 1043, 1033, 1005, 886, 836, 811, 757, 734, 693, 678 cm^{-1}. HRMS (ESI) calcd for $C_{25}H_{15}O_3ClNa$ $[M+Na]^+$: 421.0602, found 421.0598.

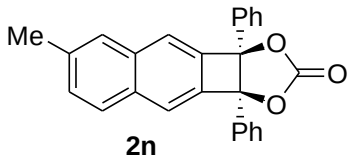


Ethyl 4-((3aR*,9bS*)-2-Oxo-9b-phenyl-3a,9b-dihydronaphtho[2',3':3,4]-cyclobuta[1,2-*d*][1,3]dioxol-3a-yl)benzoate (2l). Condition A was used. Column chromatography on silica gel (petroleum ether: ethyl acetate =20:1) afforded the title product in 82% yield (71.9 mg) as a white solid. M.p. 199-200 ^{o}C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.11 (s, 1H), 8.07 (s, 1H), 8.03-8.00 (m, 2H), 7.87-7.85 (m, 2H), 7.65-7.62 (m, 2H), 7.31-7.28 (m, 2H), 7.25-7.18 (m, 5H), 4.30 (q, *J* = 7.2 Hz, 2H), 1.34 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.78, 154.26, 141.30, 141.12, 137.28, 135.84, 132.00, 130.97, 129.35, 129.33, 129.23, 128.35, 127.40, 127.37, 126.80, 126.73, 124.18, 123.96, 95.39, 94.70, 61.12, 14.15. IR (film): 3063, 2956, 2925, 2852, 1811, 1716, 1614, 1593, 1450, 1411, 1277, 1221, 1206, 1140, 1108, 1040, 883, 761, 732, 696 cm^{-1}. HRMS (MALDI/DHB) calcd for $C_{28}H_{21}O_5$ $[M+H]^+$: 437.1384, found 437.1383.



2m

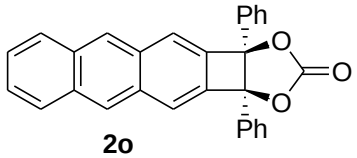
(3aR*,9bS*)-3a-Phenyl-9b-(thien-2-yl)-3a,9b-dihydronaphtho[2',3':3,4]cyclobuta [1,2-*d*][1,3]dioxol-2-one (2m). Condition B was used. Column chromatography on silica gel (petroleum ether: ethyl acetate =20:1) afforded the title product in 55% yield (40.5 mg) as a little yellow solid. M.p. 191-192 ^{o}C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.15 (s, 1H), 8.05 (s, 1H), 8.03 -7.99 (m, 2H), 7.64 (dd, *J* = 6.2, 3.6 Hz, 2H), 7.30-7.20 (m, 6H), 6.91-6.90 (m, 1H), 6.84-6.82 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 153.88, 141.91, 141.17, 136.05, 135.79, 135.43, 132.30, 129.32, 129.26, 128.36, 128.21, 128.03, 127.40, 127.32, 126.98, 126.73, 124.02, 123.74, 95.45, 92.84. IR (film): 3101, 3069, 2917, 1805, 1593, 1510, 1451, 1358, 1262, 1240, 1206, 1136, 1028, 875, 848, 764, 738, 711, 698 cm^{-1}. HRMS (MALDI/DHB) calcd for $C_{23}H_{15}O_3S$ $[M+H]^+$: 371.0736, found 371.0731.



2n

(3aR*,9bS*)-6-Methyl-3a,9b-diphenyl-3a,9b-dihydronaphtho[2',3':3,4]cyclobuta[1,2-*d*][1,3]dioxol-2-one (2n). Condition B was used. Column chromatography on silica gel (petroleum ether: ethyl acetate =20:1) afforded the title product in 79% yield (60.0 mg) as a white solid. M.p. 213-214 ^{o}C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.02 (s, 1H), 7.98 (s, 1H), 7.89 (d, *J* = 8.4, 1H), 7.76 (s, 1H), 7.46 (dd, *J* = 8.8, 2.0 Hz, 1H), 7.24-7.15 (m, 10H), 2.57 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 154.68, 141.63, 140.70, 137.24, 136.08, 134.09, 132.57, 132.56, 129.59, 129.03, 128.93, 128.14, 128.12, 126.86, 126.84, 123.71, 123.17, 95.33, 95.27, 21.73. IR (film): 3064, 2922, 1805, 1620, 1593, 1499, 1450, 1319, 1304, 1269, 1226, 1197, 1139, 1041, 1030, 1007,

891, 809, 784, 767, 730, 696, 676 cm^{-1}. HRMS (MALDI/DHB) calcd for $C_{26}H_{19}O_3$ $[M+H]^+$: 379.1329, found 379.1328.



2o

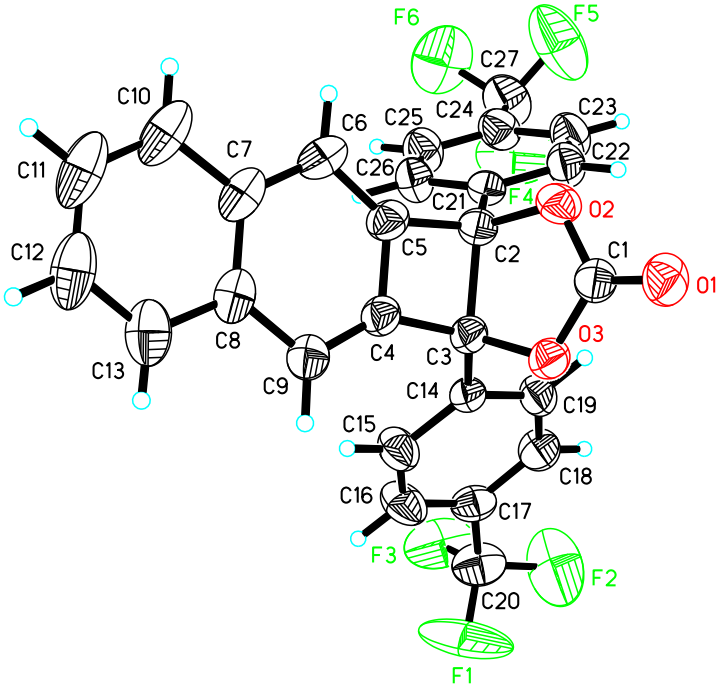
(3aR*,11bS*)-3a,11b-Diphenyl-3a,11b-dihydroanthra[2',3':3,4]cyclobuta[1,2-*d*][1,3]dioxol-2-one (2o). Condition A: Column chromatography on silica gel (petroleum ether: ethyl acetate =20:1) afforded the title product in 44% yield (36.5 mg) as a little yellow solid. Condition B: Column chromatography on silica gel (petroleum ether: ethyl acetate =20:1) afforded the title product in 77% yield (63.9 mg) as a little yellow solid. M.p. 236-237 ^oC. ^1H NMR (400 MHz, $CDCl_3$) δ 8.54 (s, 2H), 8.18 (s, 2H), 8.02 (dd, *J* = 6.4, 3.2 Hz, 2H), 7.53 (dd, *J* = 6.4, 3.2 Hz, 2H), 7.27-7.25 (m, 4H), 7.19-7.16 (m, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 154.67, 140.76, 133.05, 132.46, 132.04, 129.10, 128.18, 128.08, 128.06, 126.85, 126.44, 124.31, 95.48. IR (film): 3059, 1813, 1580, 1498, 1450, 1421, 1301, 1220, 1149, 1041, 1005, 901, 781, 740, 718, 696 cm^{-1}. HRMS (ESI) calcd for $C_{29}H_{18}O_3Na$ $[M+Na]^+$: 437.1148, found 437.1131.

Reference:

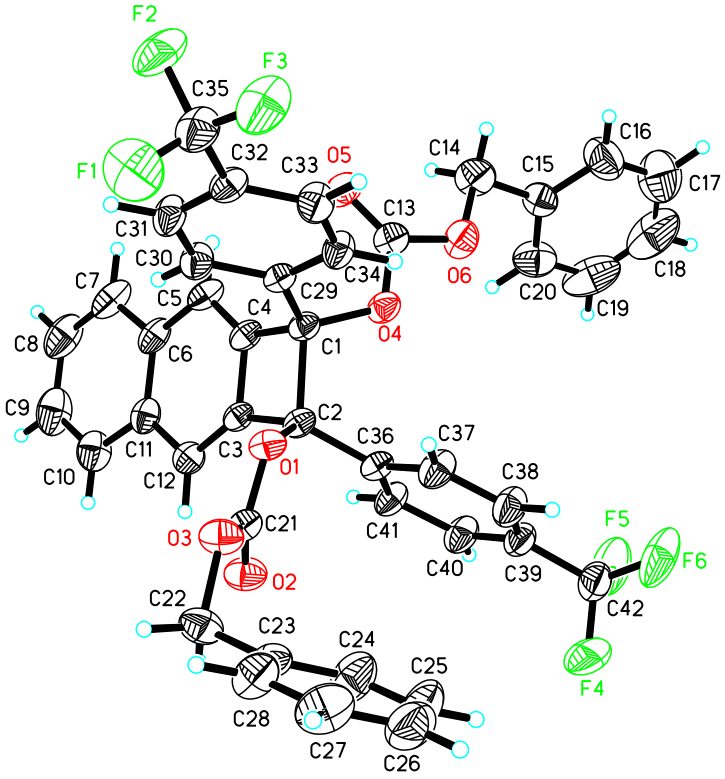
(1) P. Braunstein, H. Lehner and D. Matt, *Inorg. Synth.* **1990**, *27*, 218.

(2) N. Mezailles, L. Ricard and F. Gagosz, *Org. Lett.* **2005**, *7*, 4133.

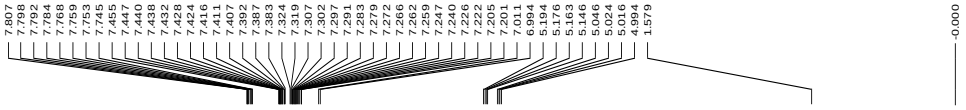
(3) M. Chen, Y. Chen and Y. Liu, *Chem. Commun.*, **2012**, *48*, 12189.



X-ray crystal structure of compound **2f** (fluoro atoms on CF_3 groups are disordered)



X-ray crystal structure of the *trans*-isomer of **3** (fluoro atoms on one of the CF_3 groups are disordered)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7.432
7.428
7.424
7.416
7.411
7.407
7.392
7.387
7.383
7.324
7.319
7.307
7.302
7.297
7.291
7.283
7.279
7.272
7.266
7.262
7.259
7.247
7.240
7.226
7.222
7.205
7.201
7.011
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5.024
5.016
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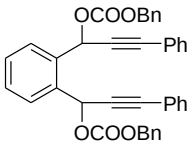
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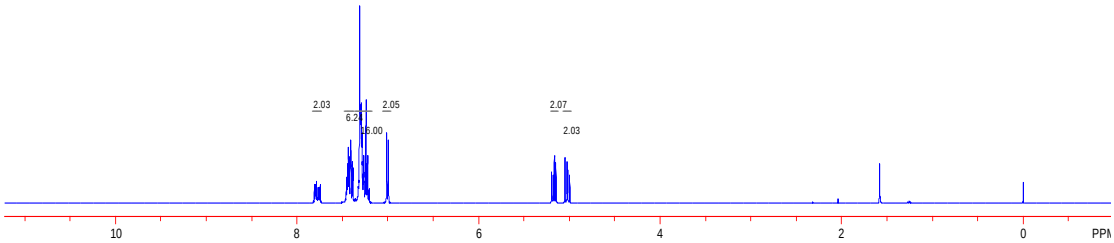
Ph
Ph
OCOOBn

1a-2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2.05
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2.07
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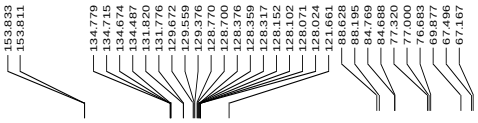
10
8
6
4
2
0
PPM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128.359
128.317
128.152
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128.071
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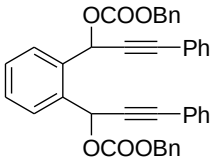
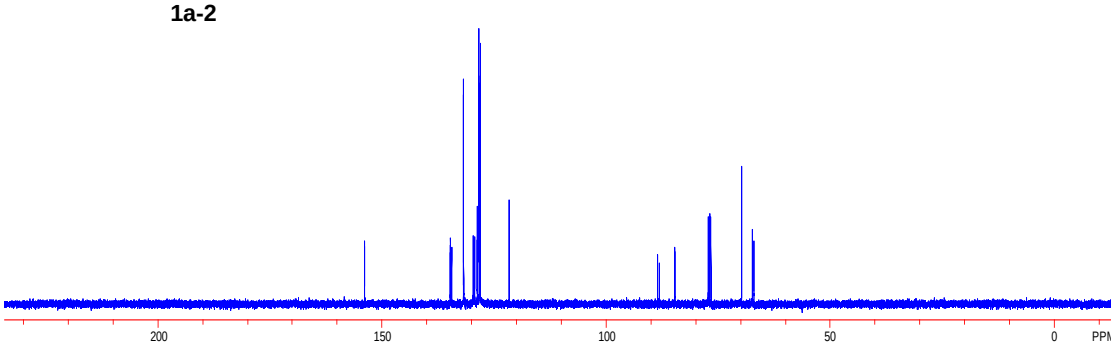
69.877
67.496
67.167


OCOOBn
Ph
Ph
OCOOBn

1a-2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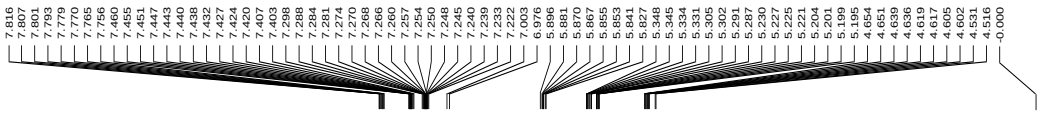
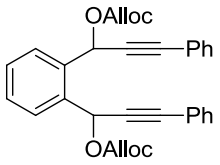
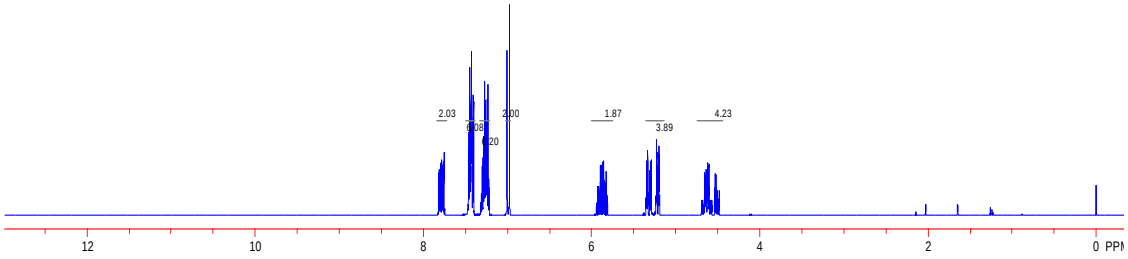



OAlloc
Ph
Ph
OAlloc

1a-3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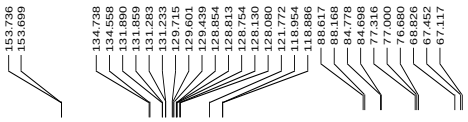
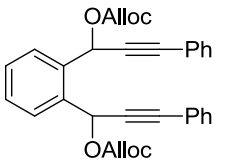
4.23
12
10
8
6
4
2
0 PPM

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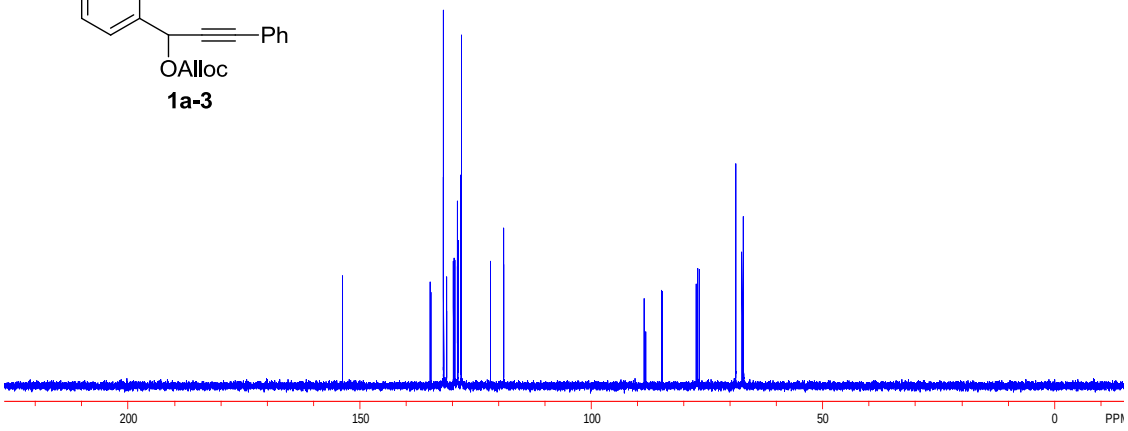
Ph
Ph
OAlloc

1a-3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50
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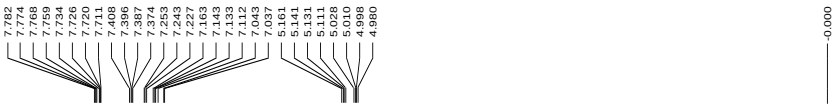
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7.711
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7.253
7.243
7.227
7.163
7.143
7.133
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5.131
5.111
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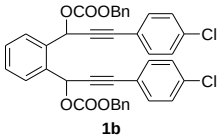
4.980
0.000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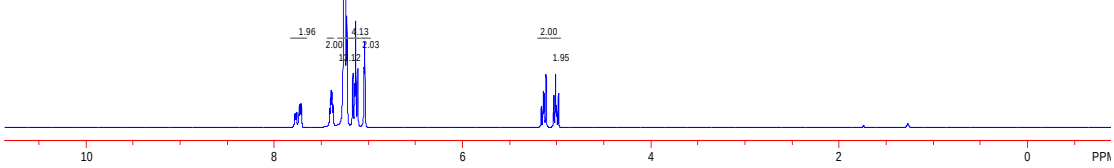
Cl
Cl
OCOOBn

1b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10
8
6
4
2
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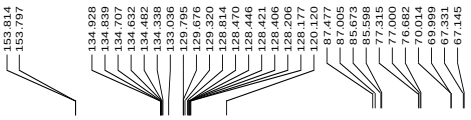
PPM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69.999
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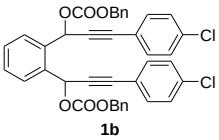
67.145


OCOOBn
Cl
Cl
OCOOBn

1b

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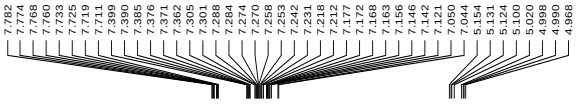
150
100
50
0
PPM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7.172
7.168
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7.156
7.146
7.142
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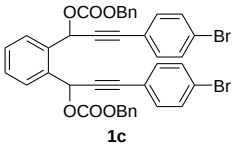
OCOOBn
Br
Br
OCOOBn

1c

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10
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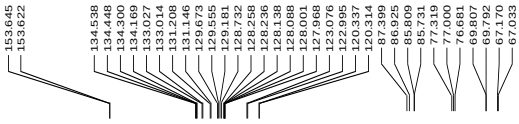
6
4
2
0
PPM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128.258
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128.138
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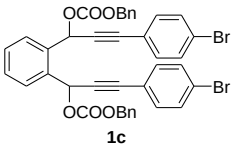
67.033


OCOOBn
Br
Br
OCOOBn

1c

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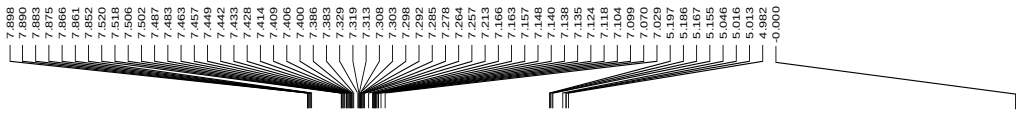
PPM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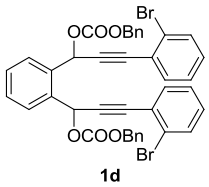
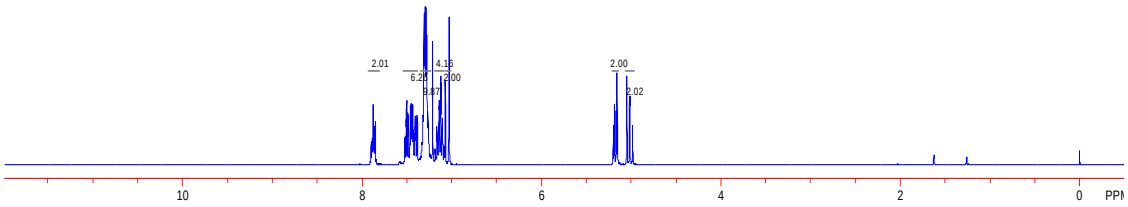

Br
OCOOBn
OCOOBn
Br

1d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4
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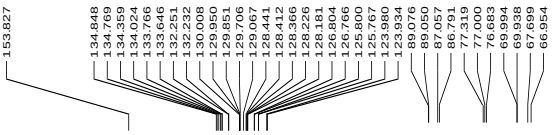
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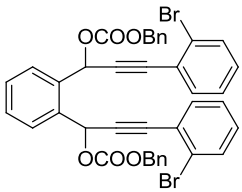
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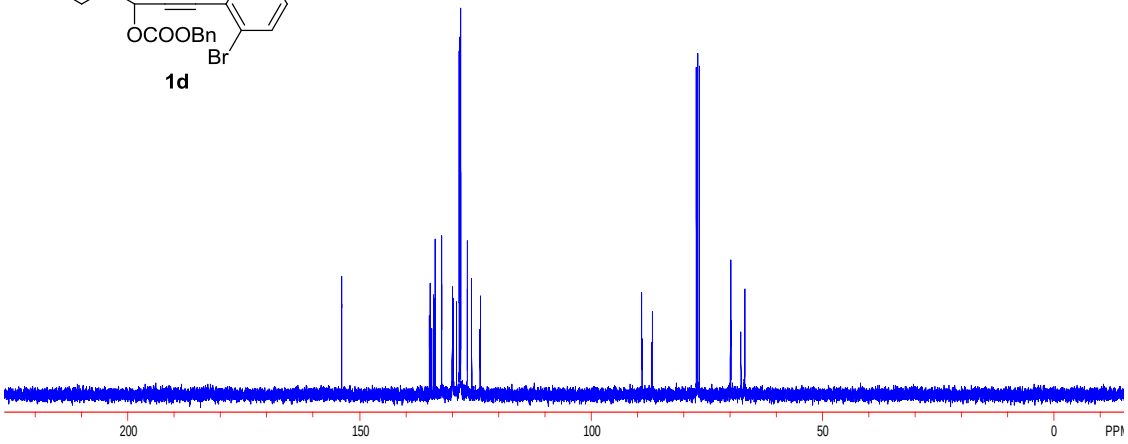
OCOOBn
OCOOBn
Br

1d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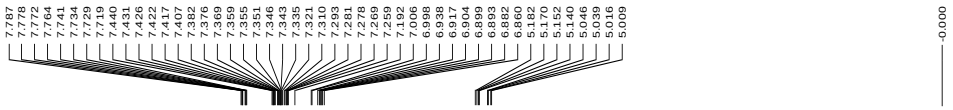
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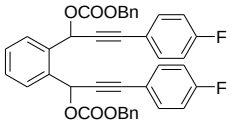
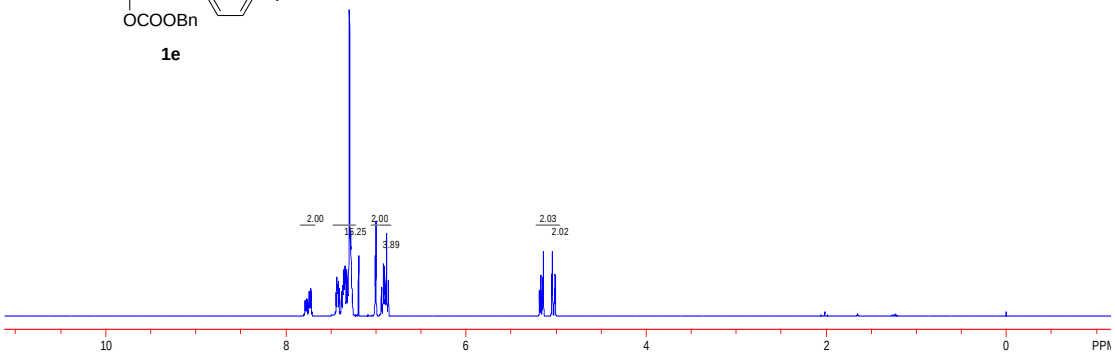

OCOOBn
F
F
OCOOBn

1e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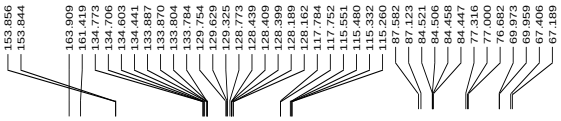
2.02
10
8
6
4
2
0
PPM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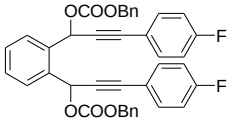
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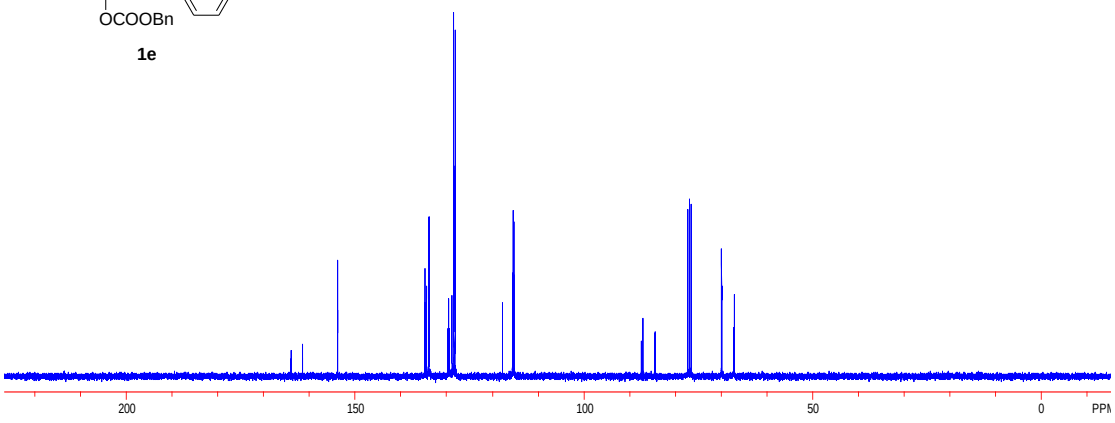
F
OCOOBn

1e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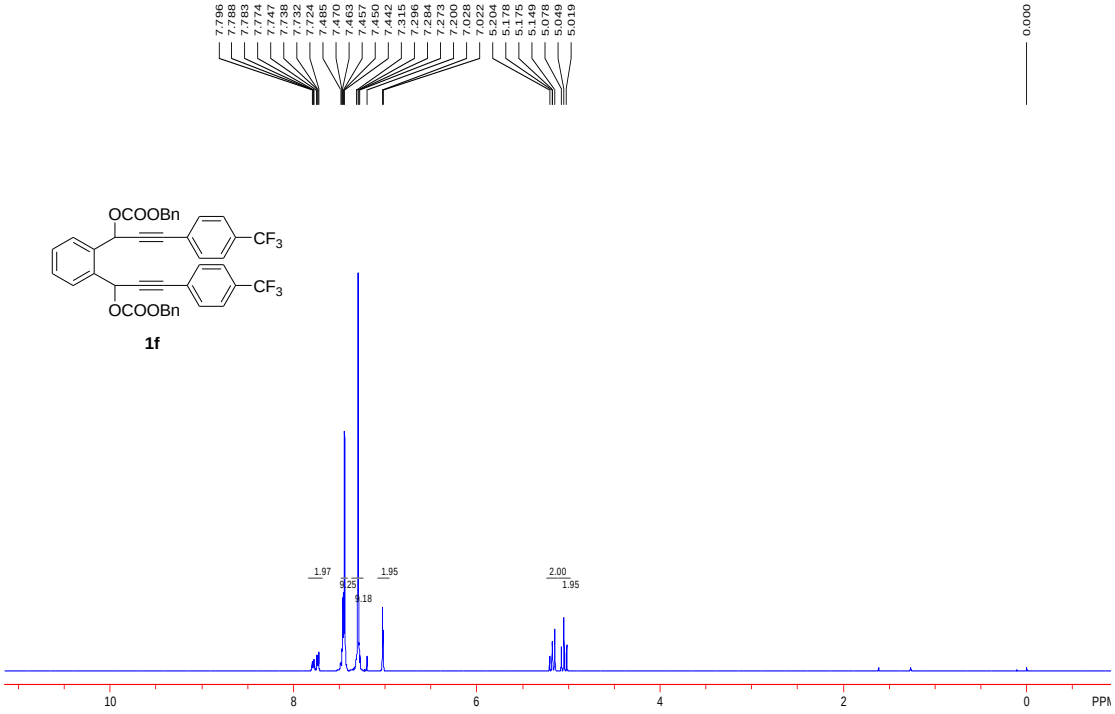
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7.200
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5.204
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5.175
5.149
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OCOOBn
CF3
CF3
OCOOBn
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10
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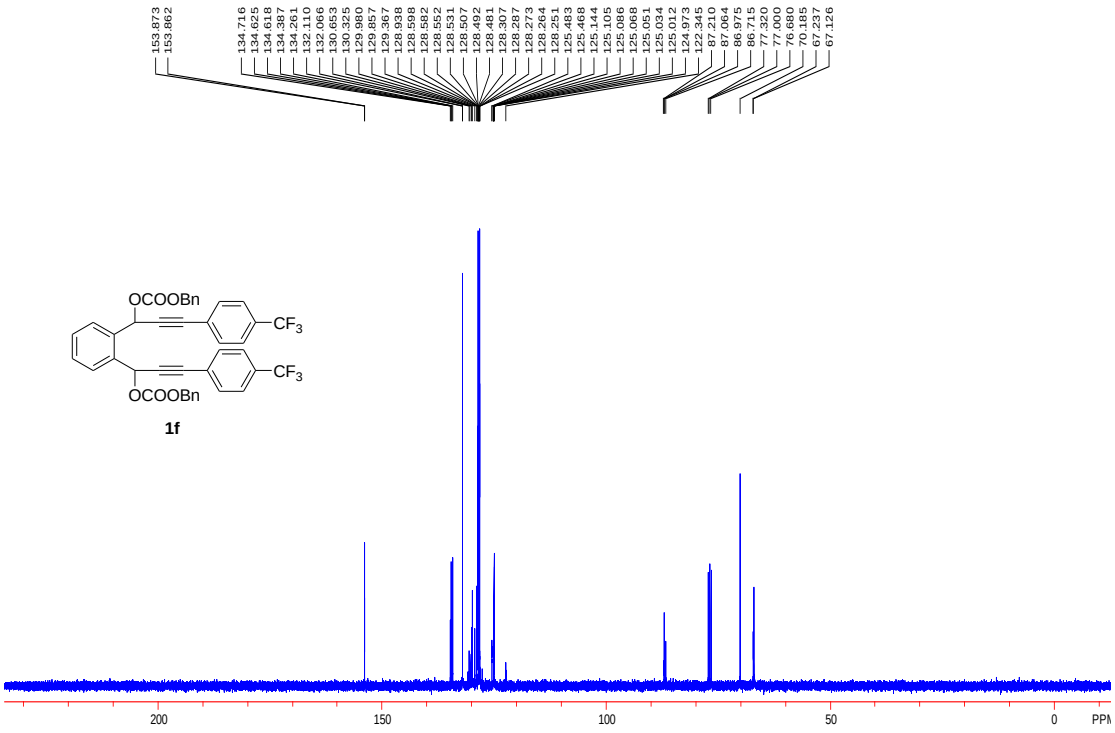
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OCOOBn
CF3
CF3
OCOOBn
1f
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150
100
50
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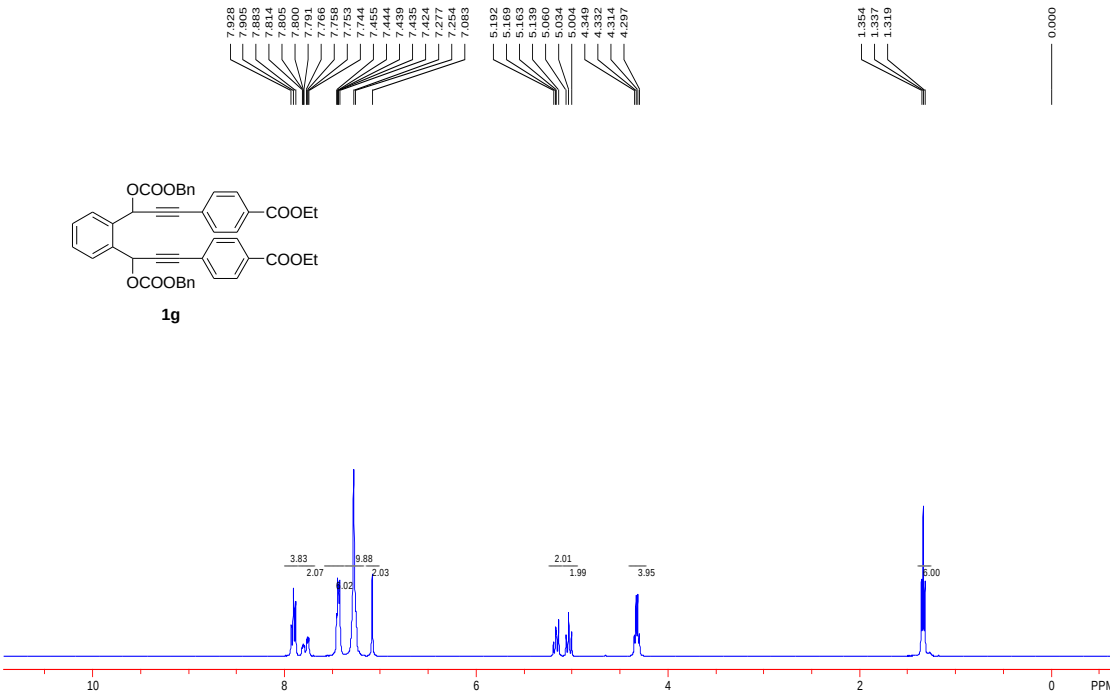
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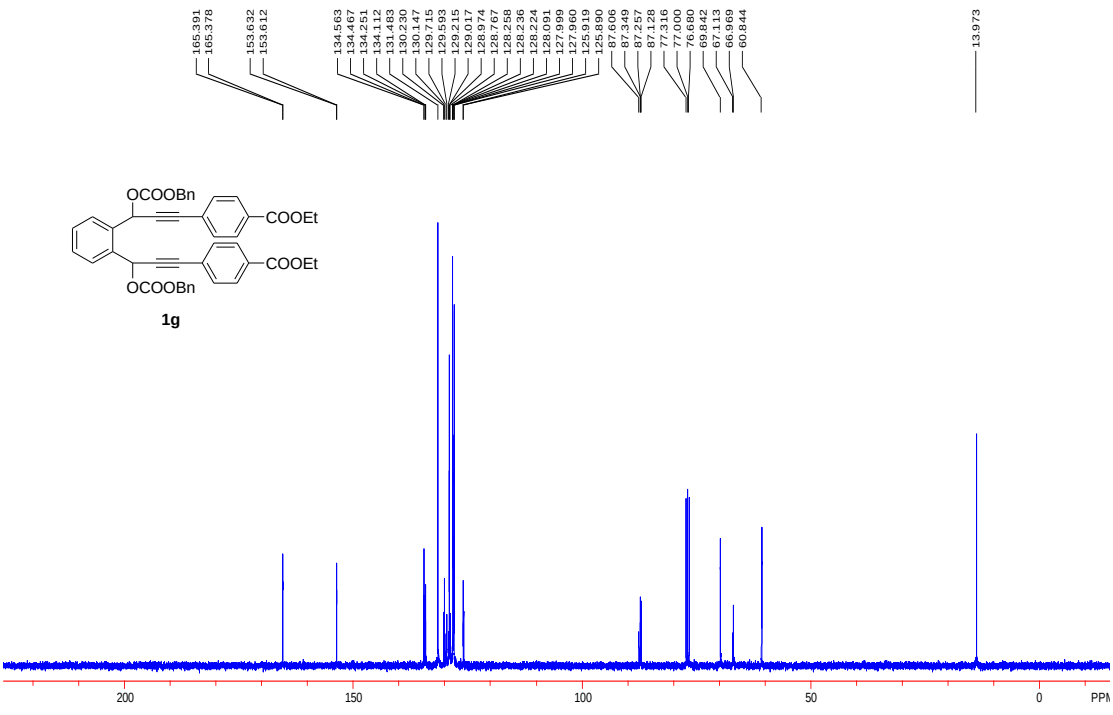
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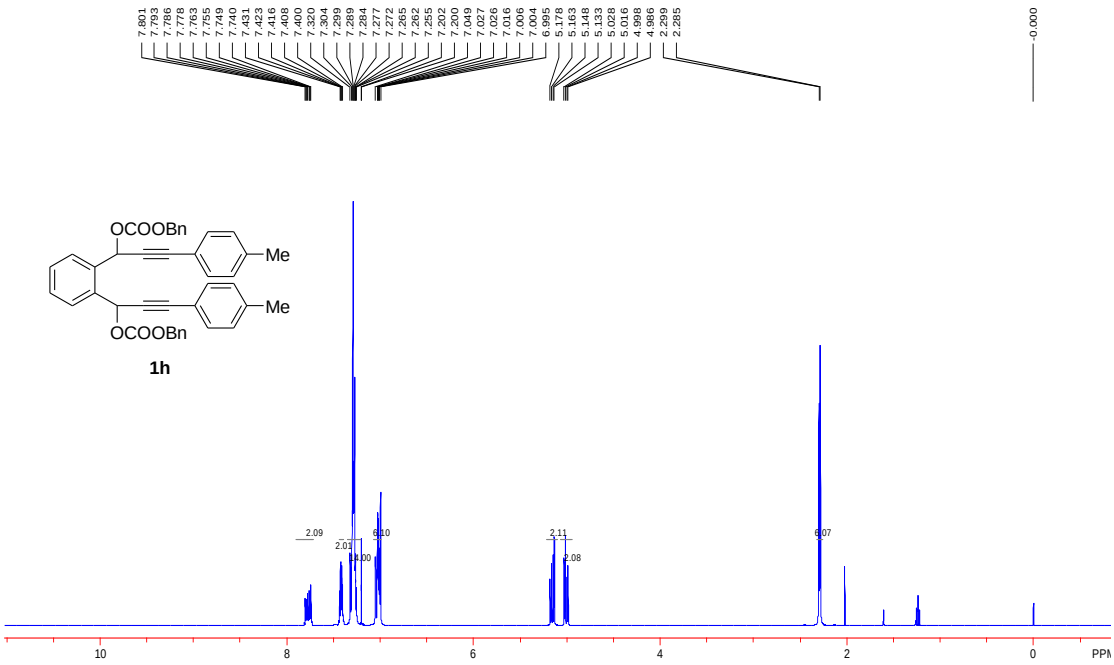
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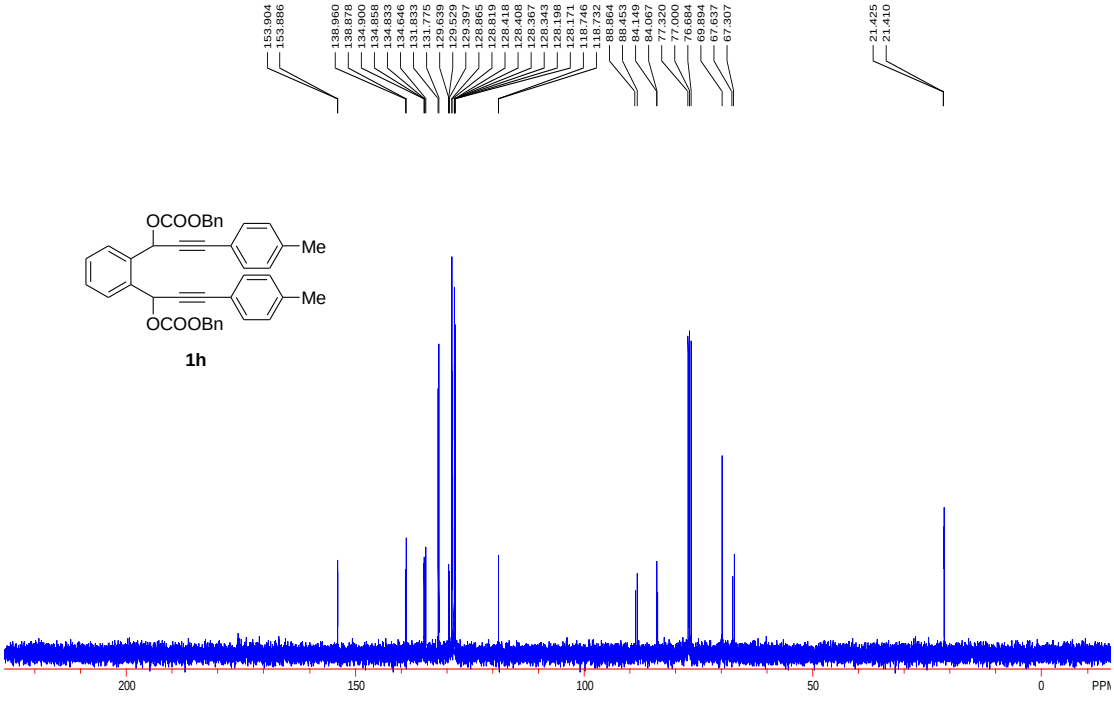
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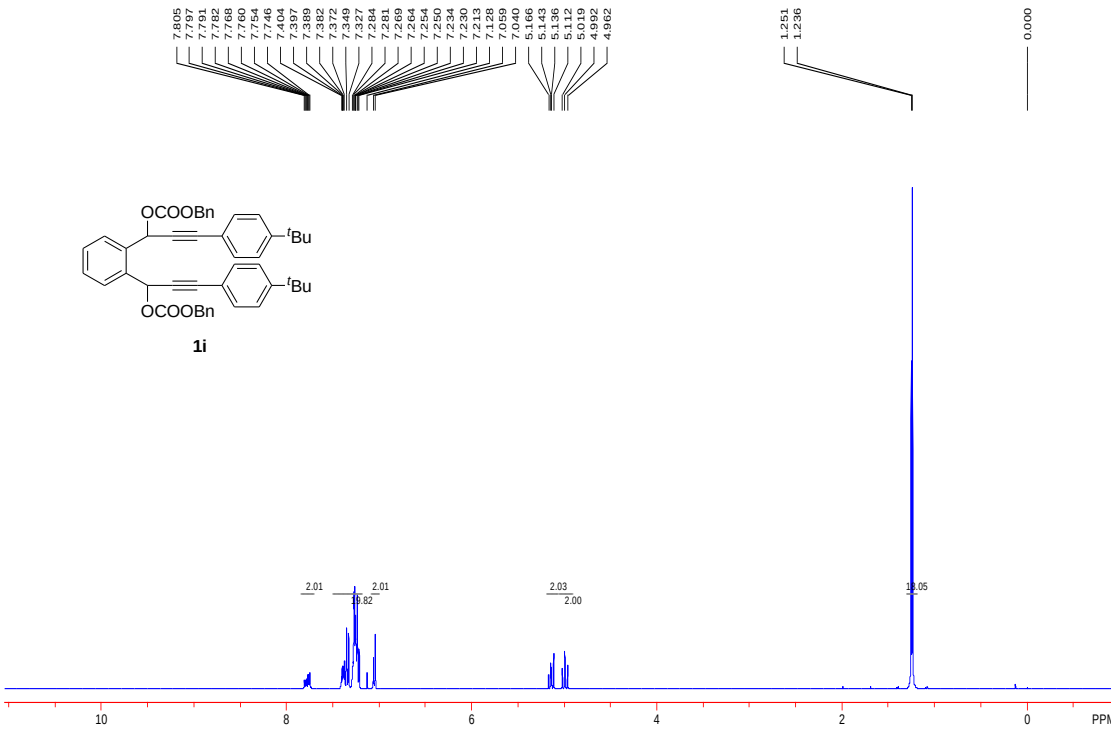
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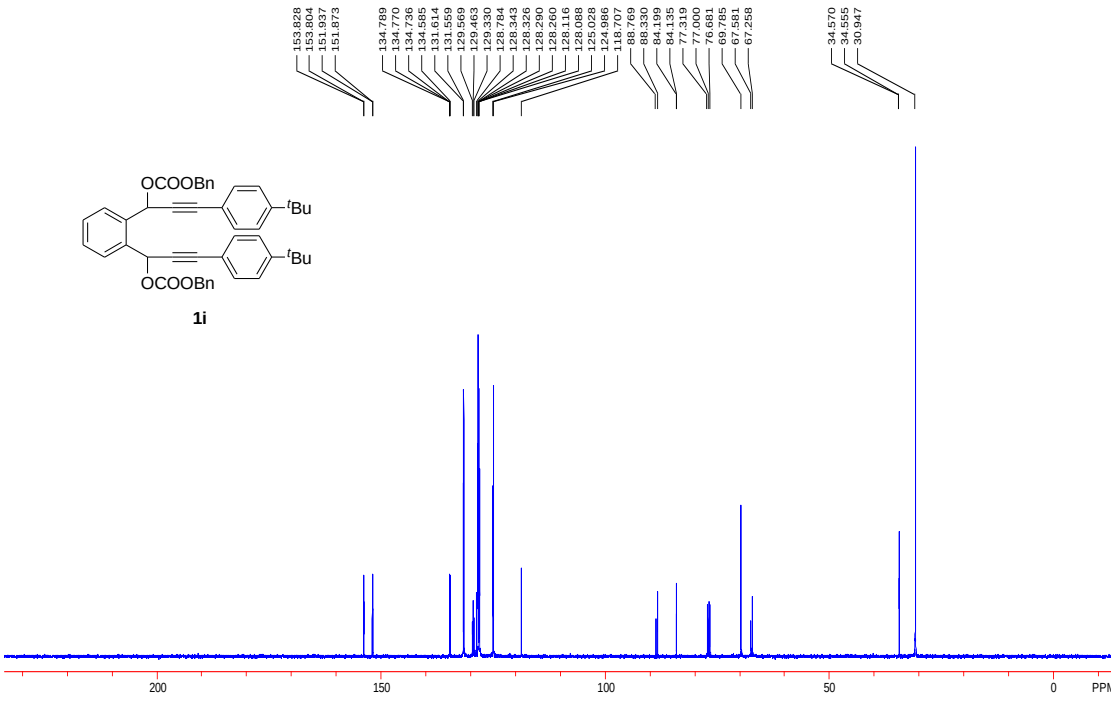
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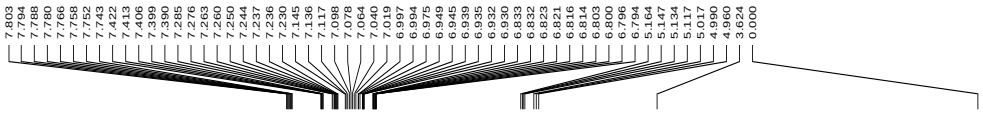
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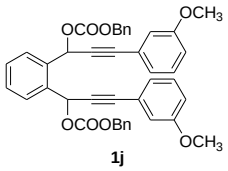
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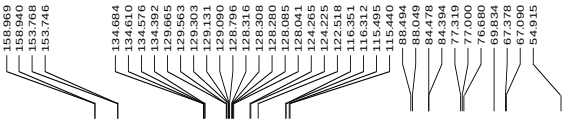
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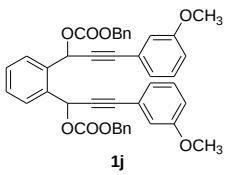
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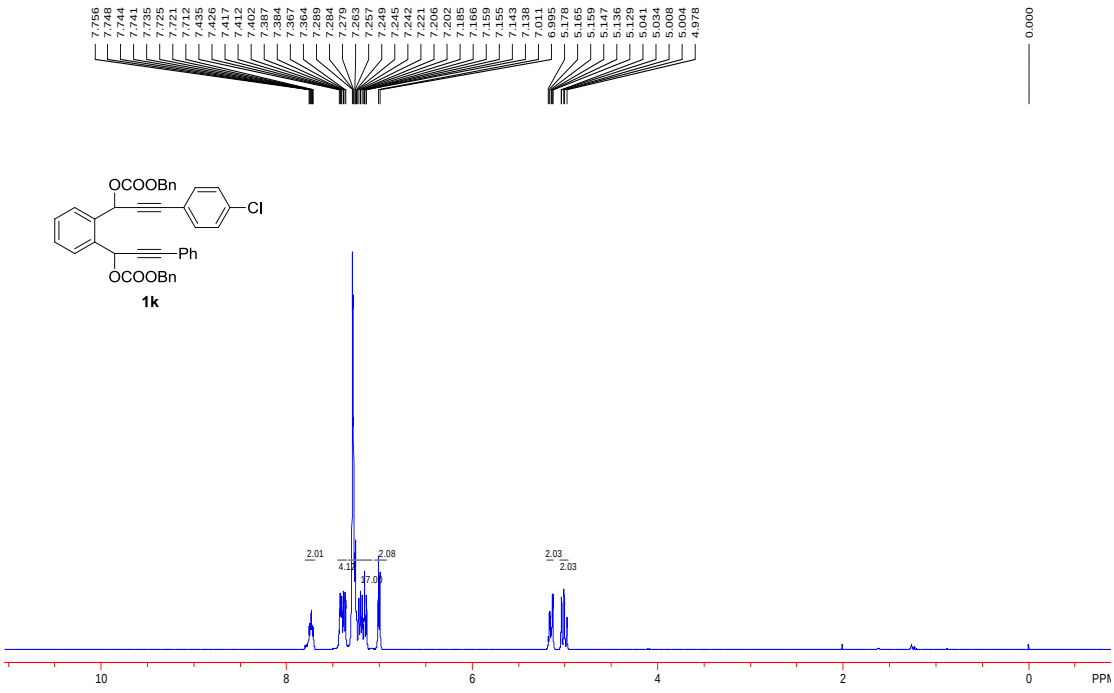
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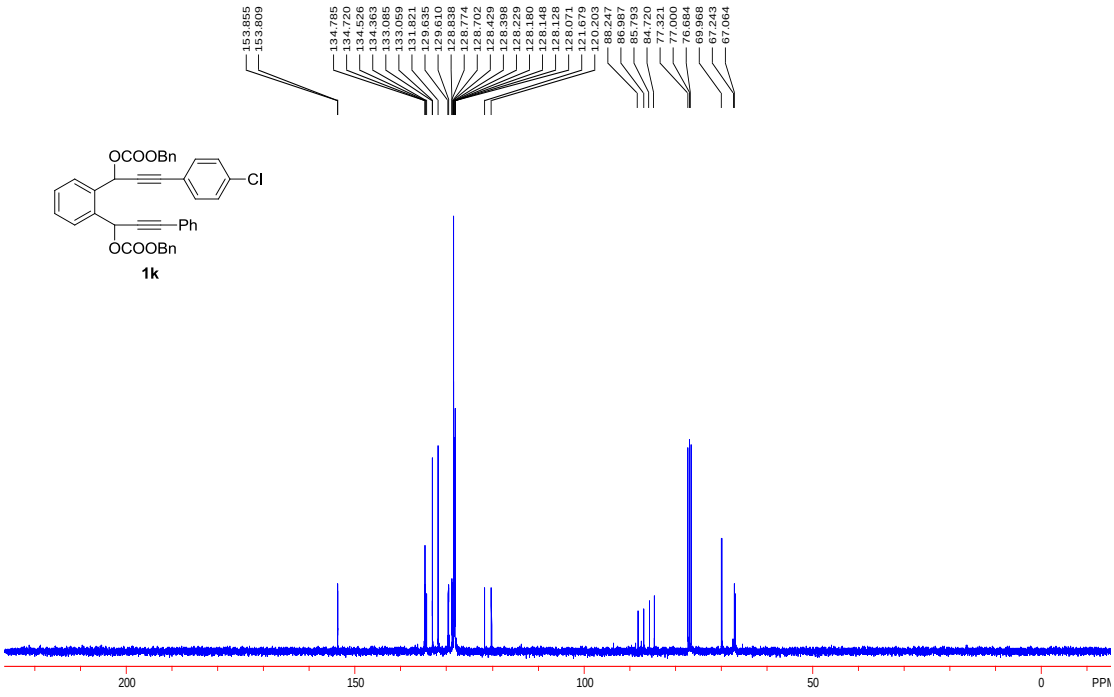
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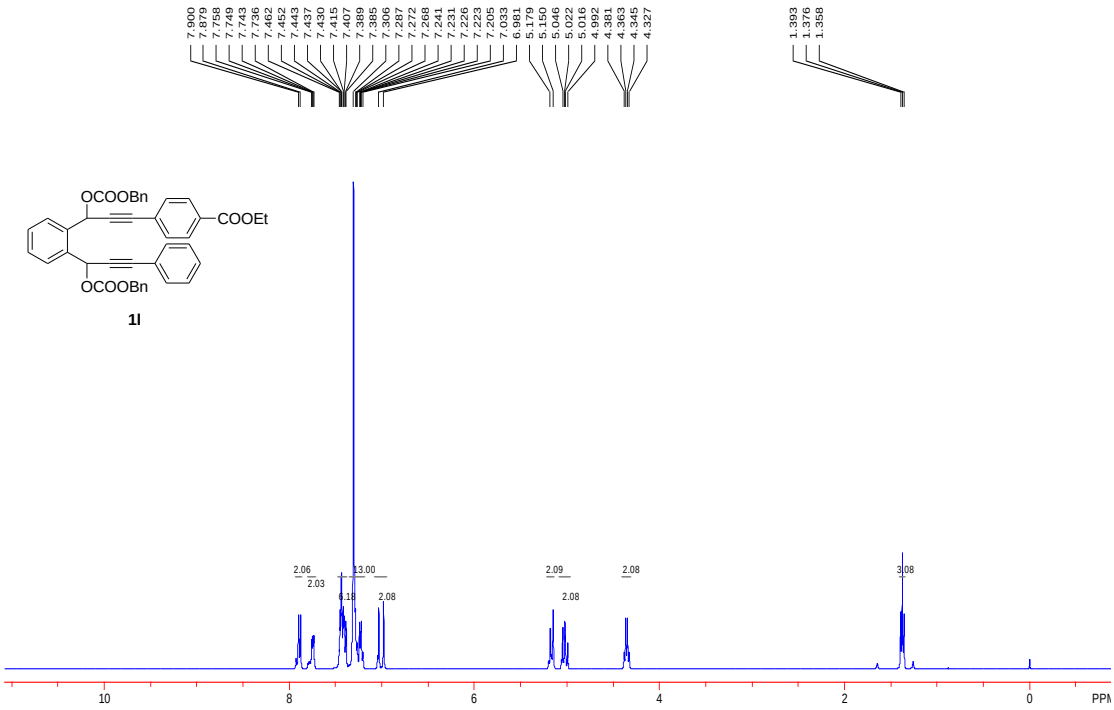
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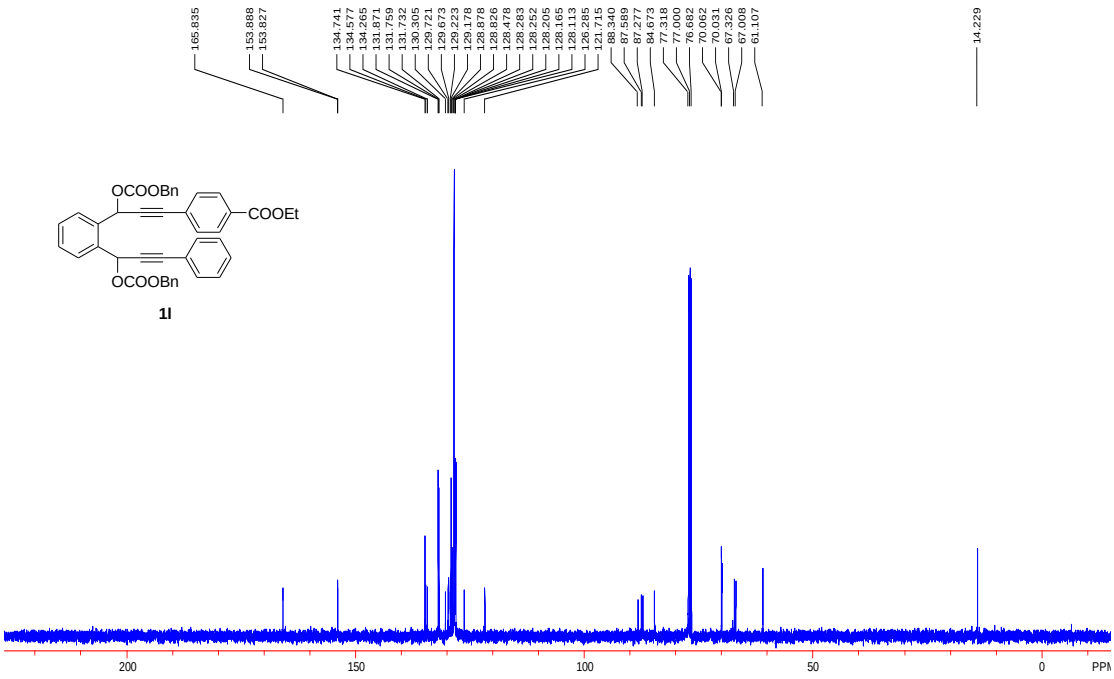
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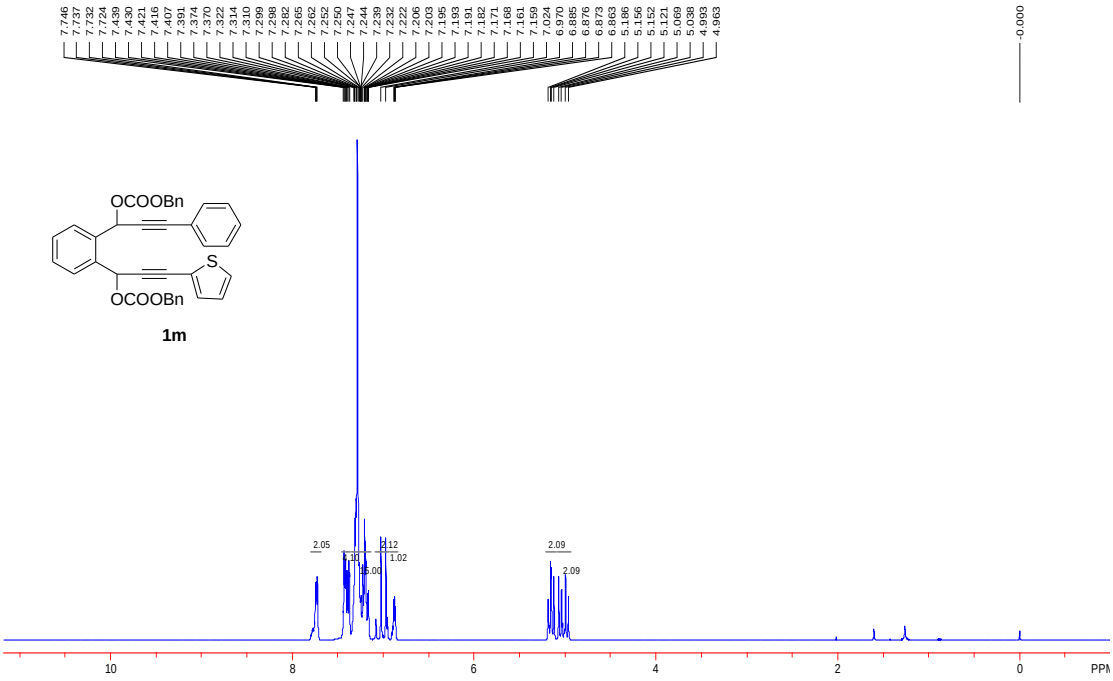
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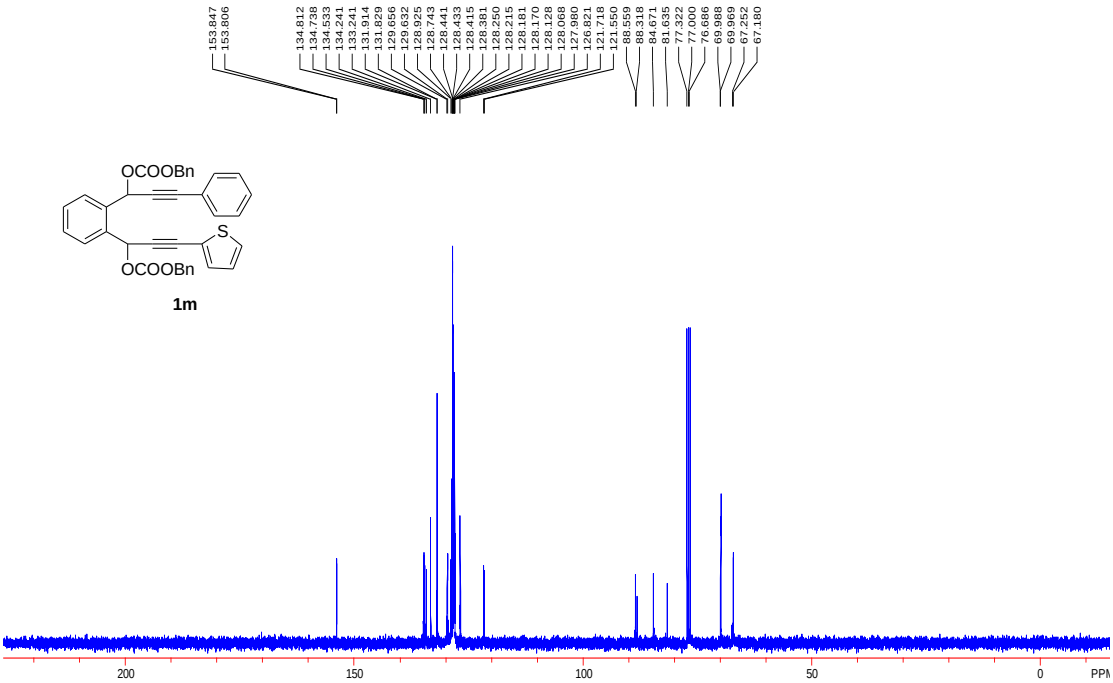
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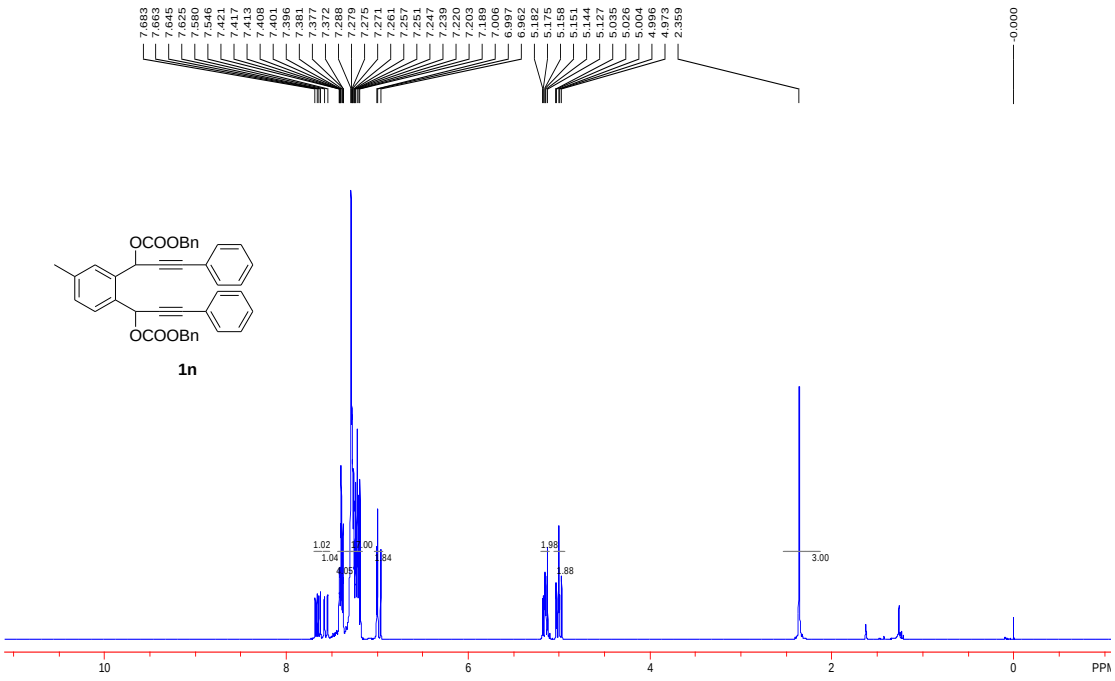
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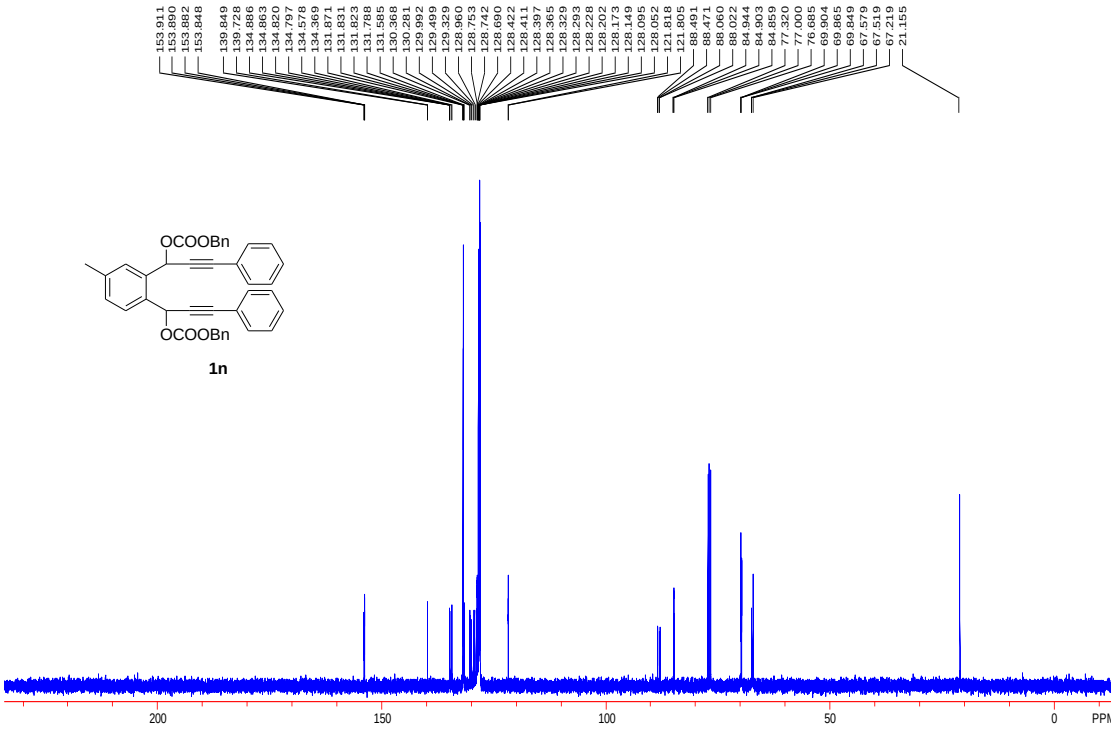
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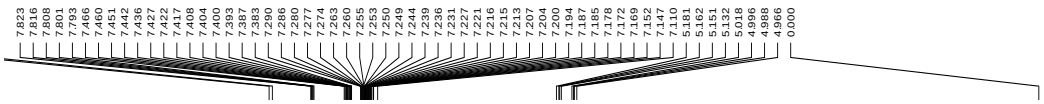
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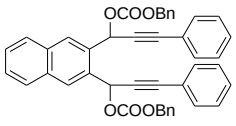
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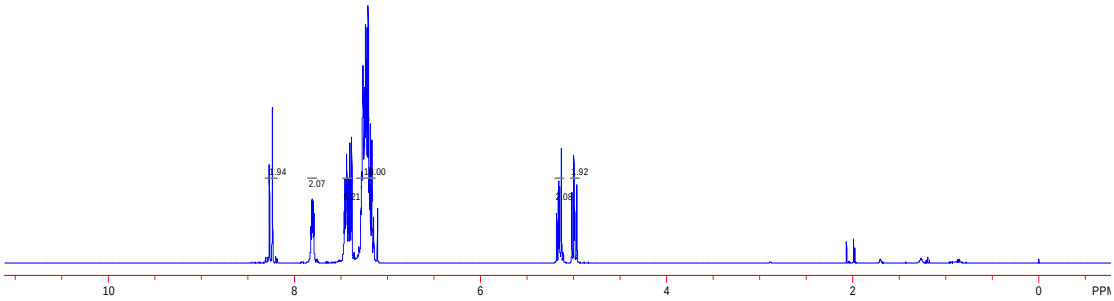
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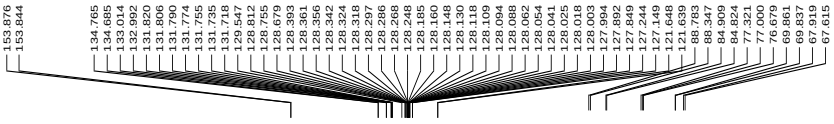
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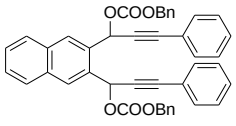
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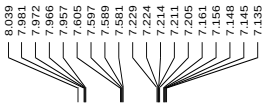
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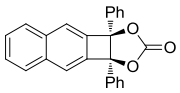
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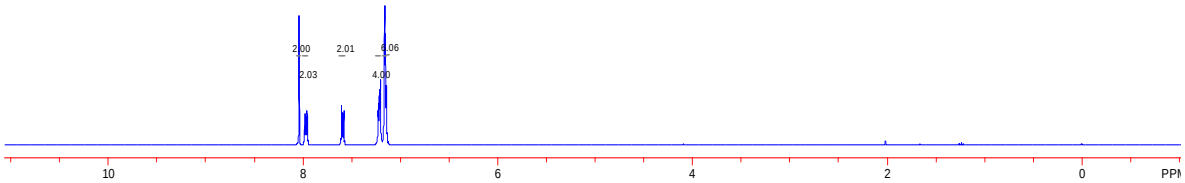
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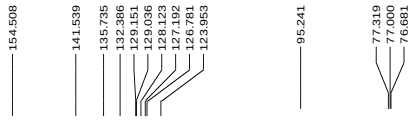
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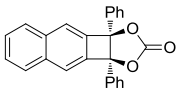
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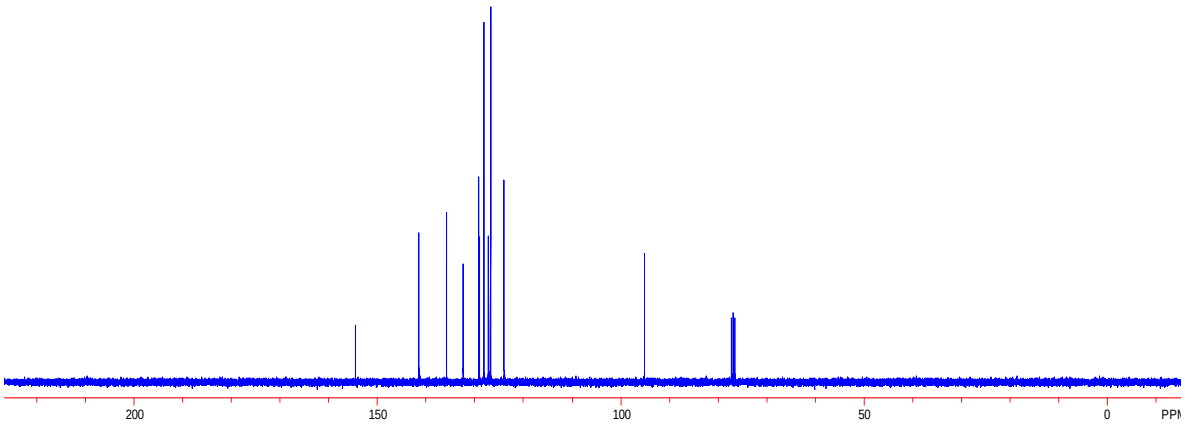
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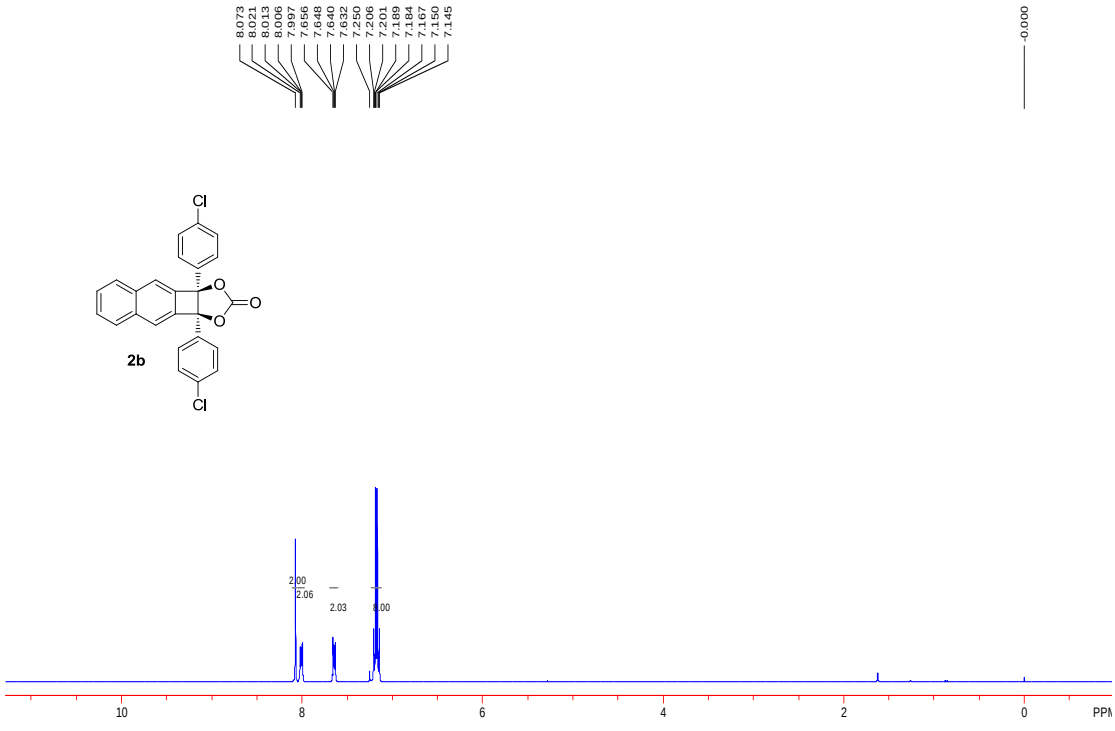
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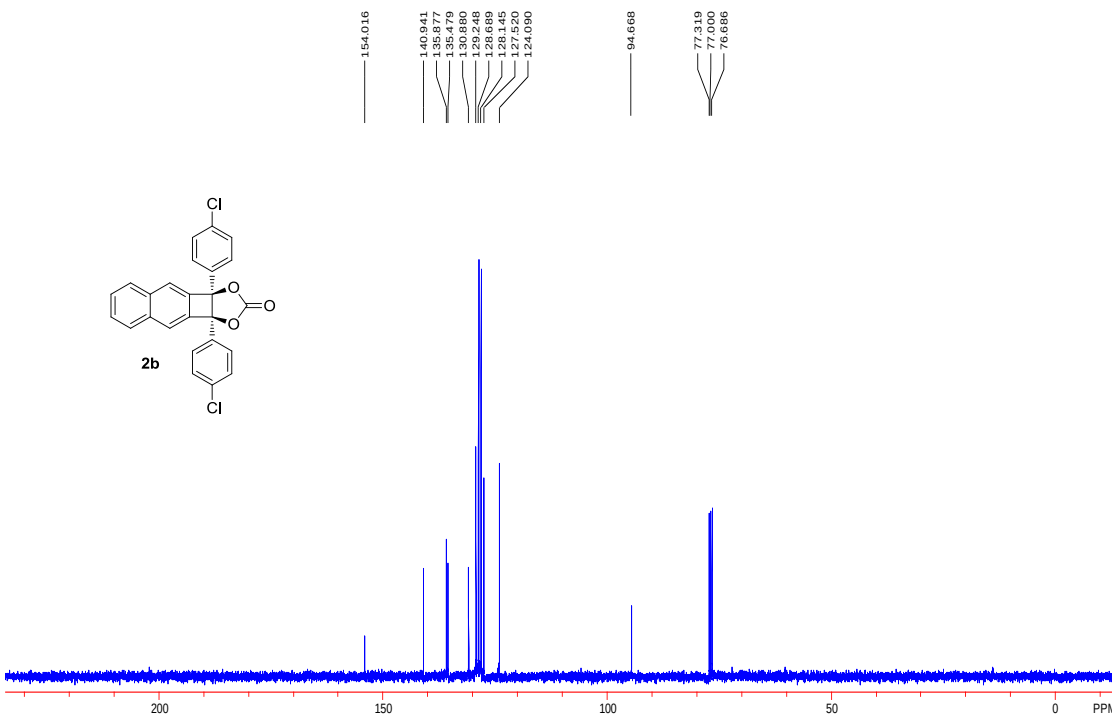
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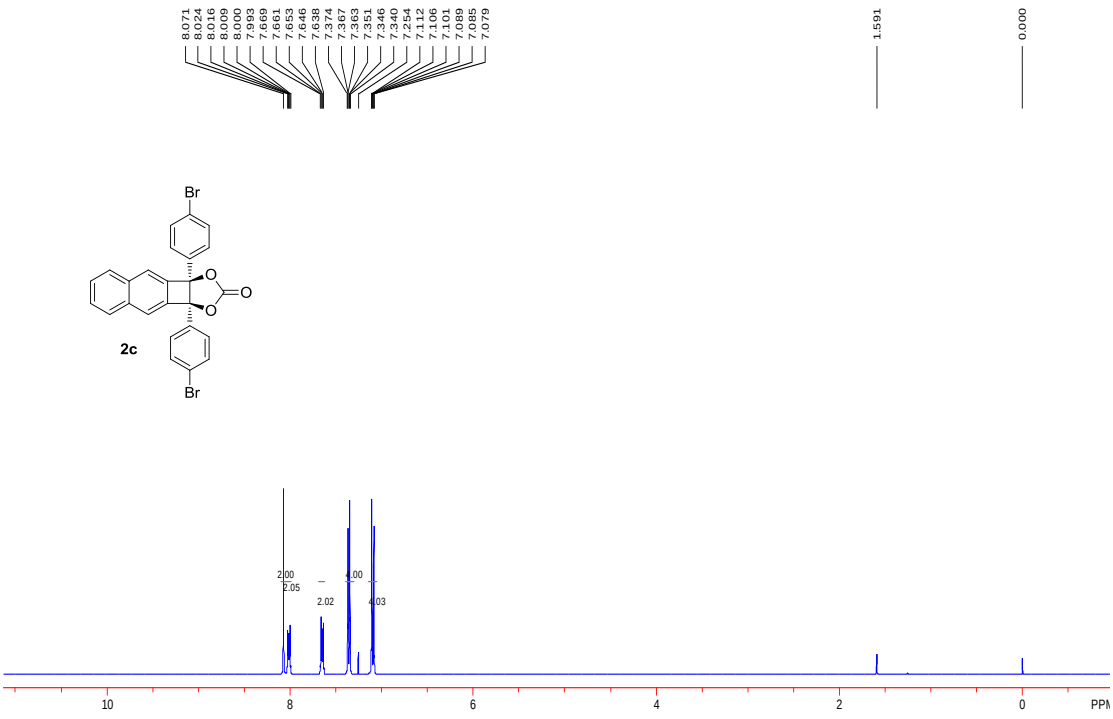
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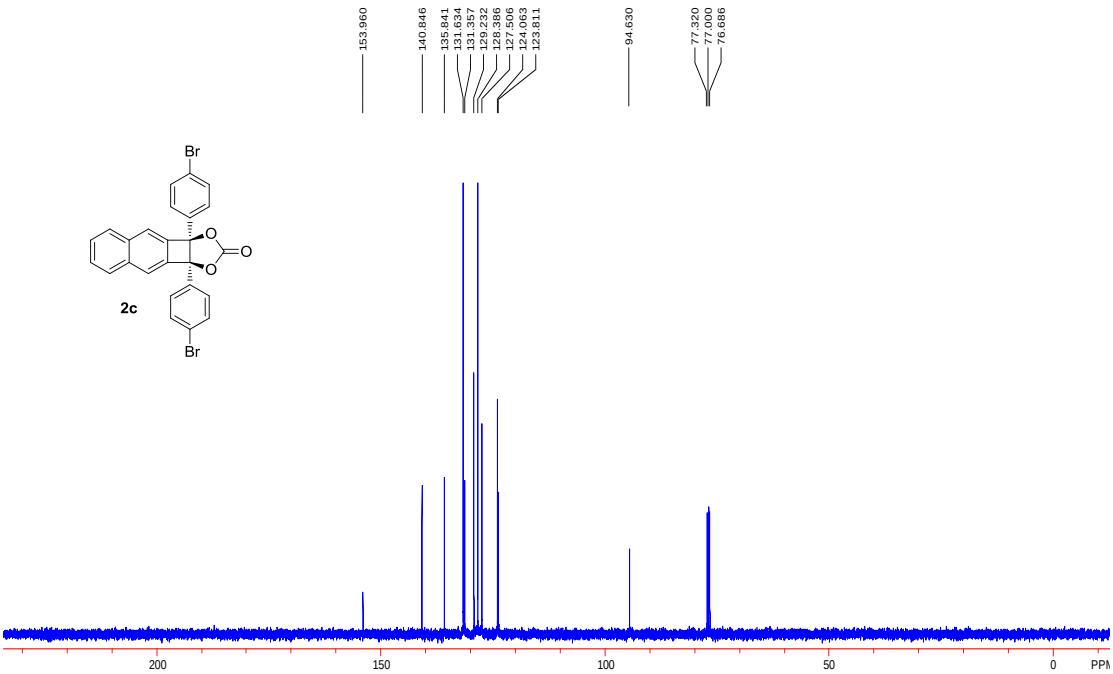
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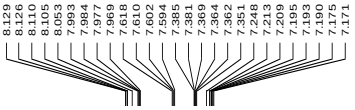
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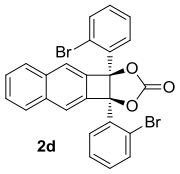
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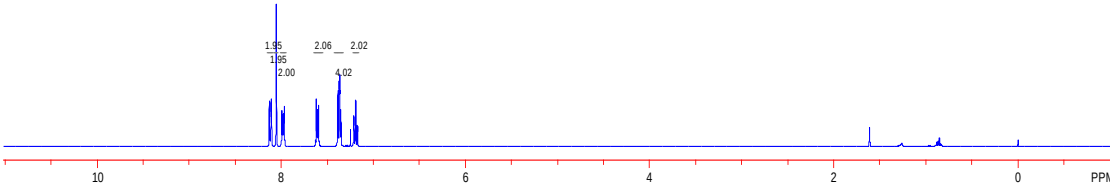
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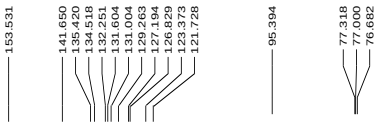
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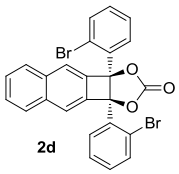
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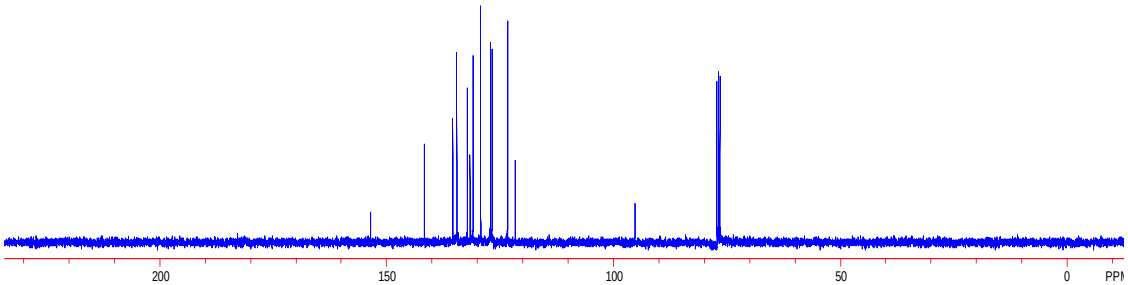
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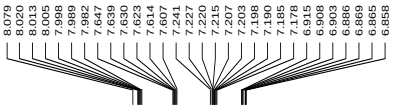
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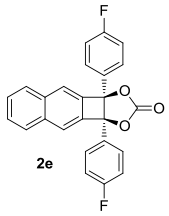
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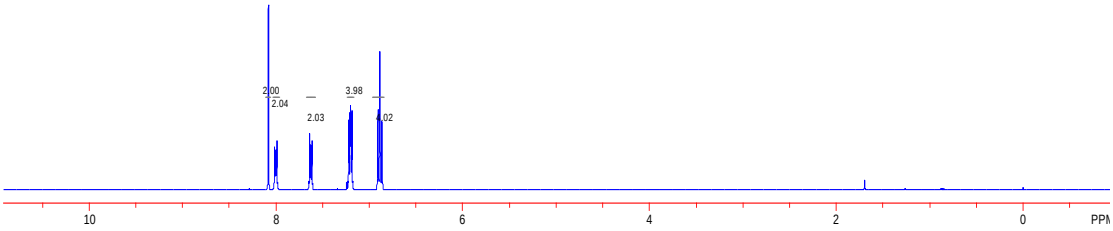
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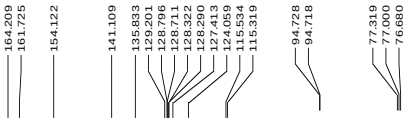
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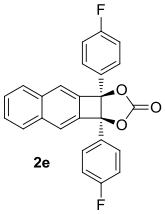
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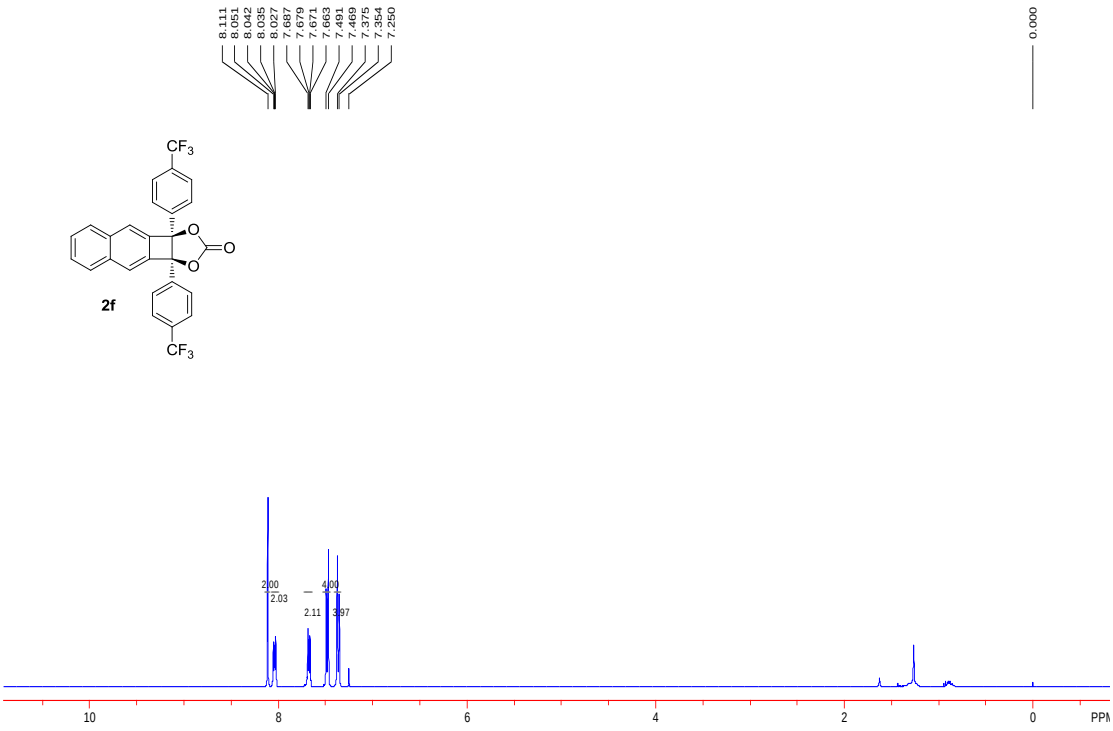
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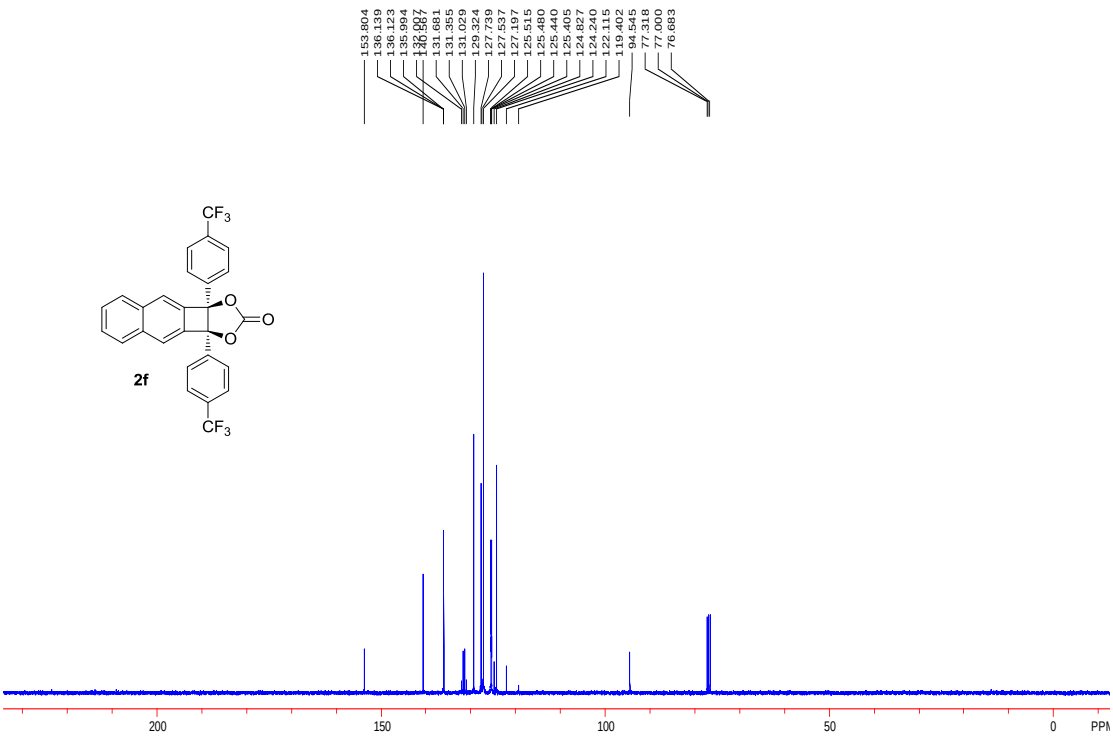
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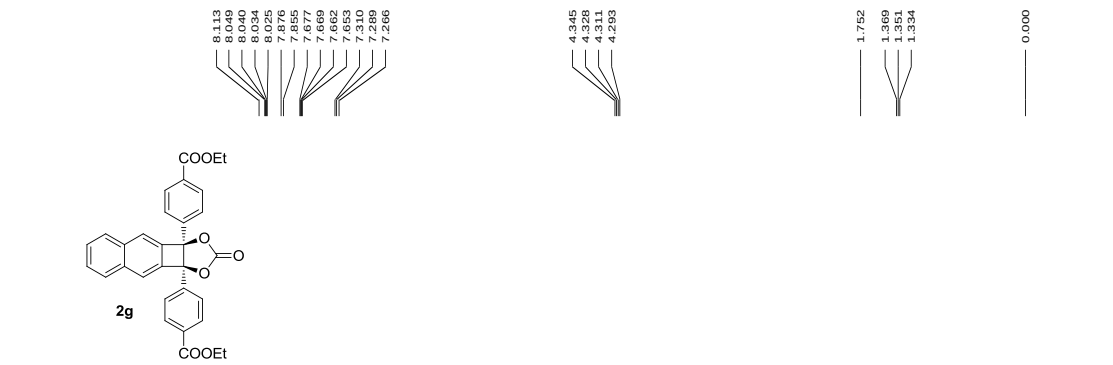
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O
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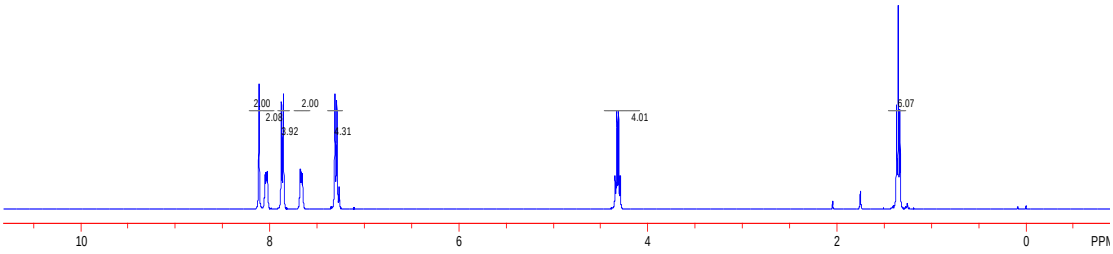
COOEt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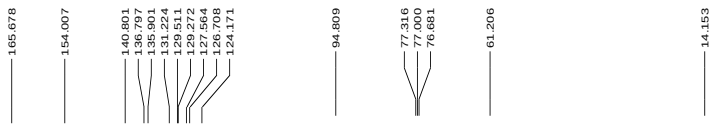
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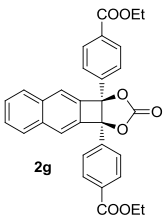
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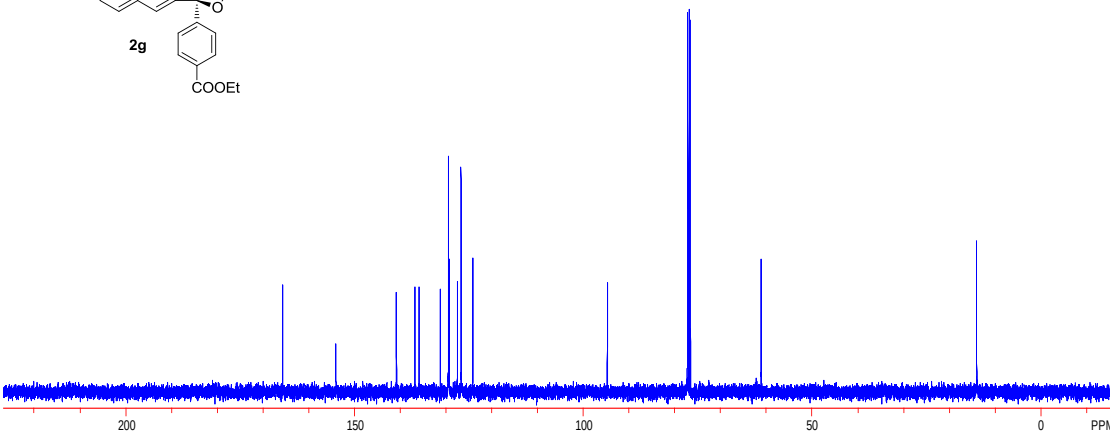
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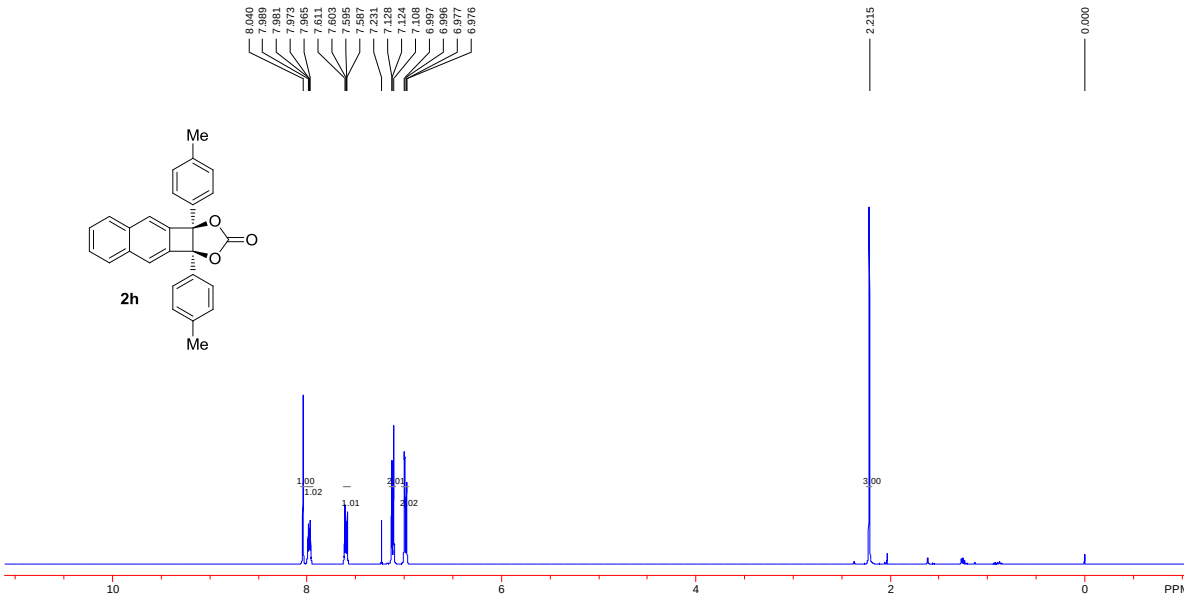
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O
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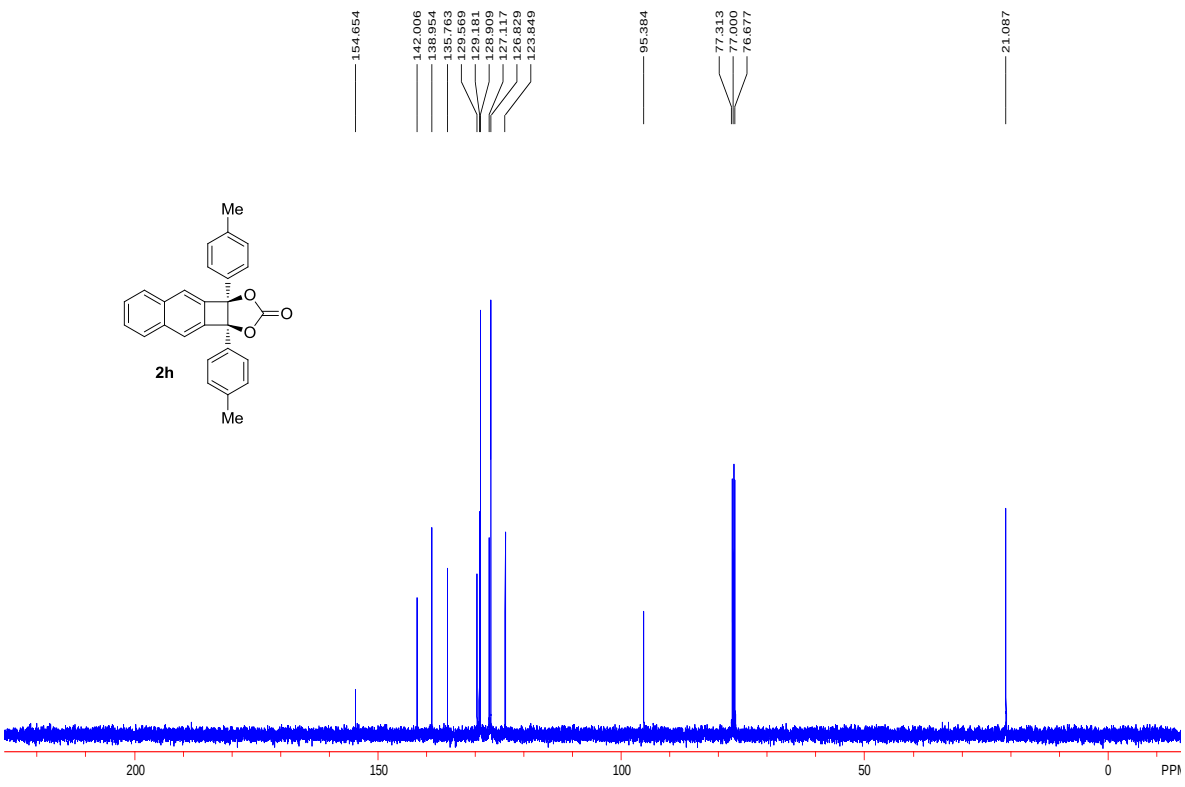
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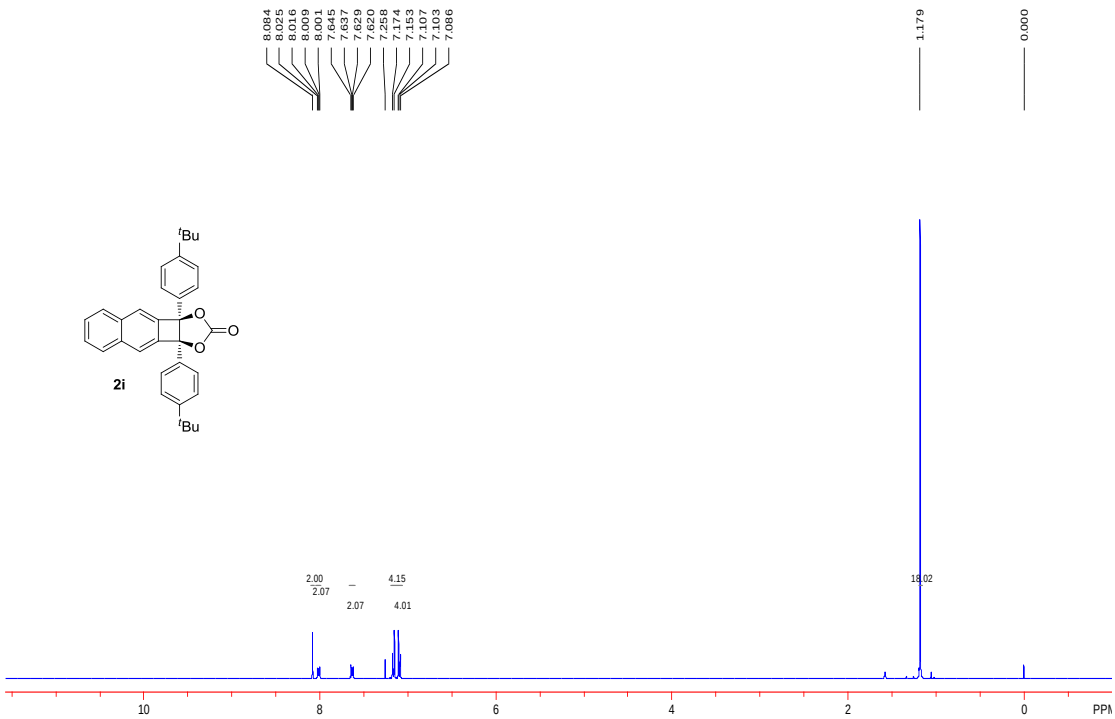
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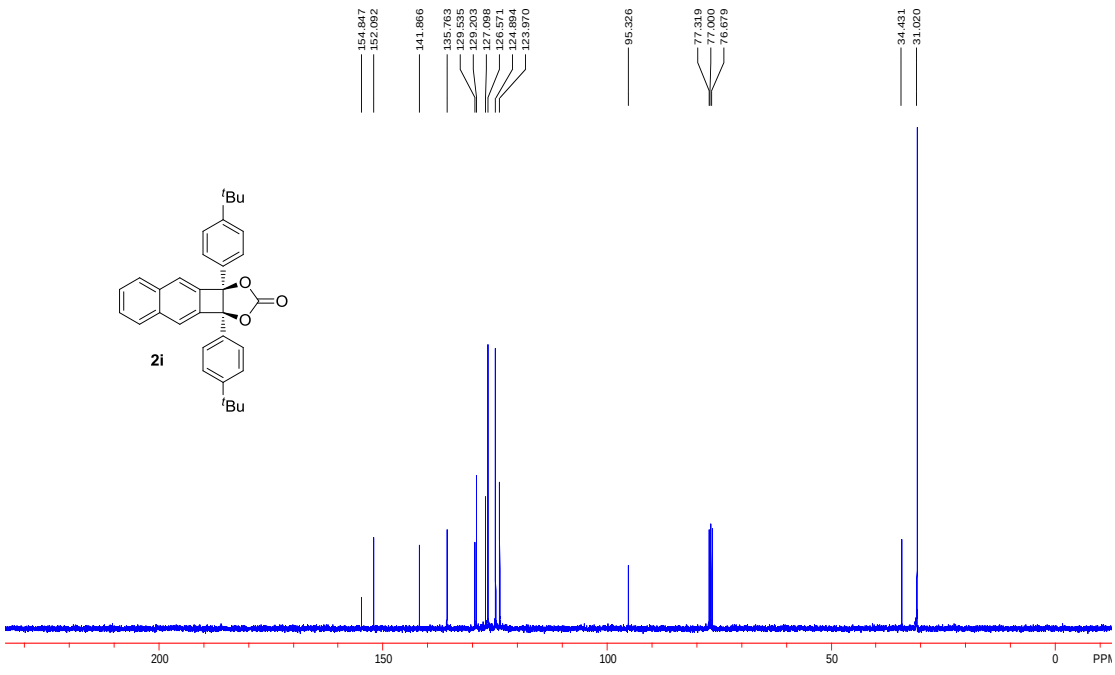
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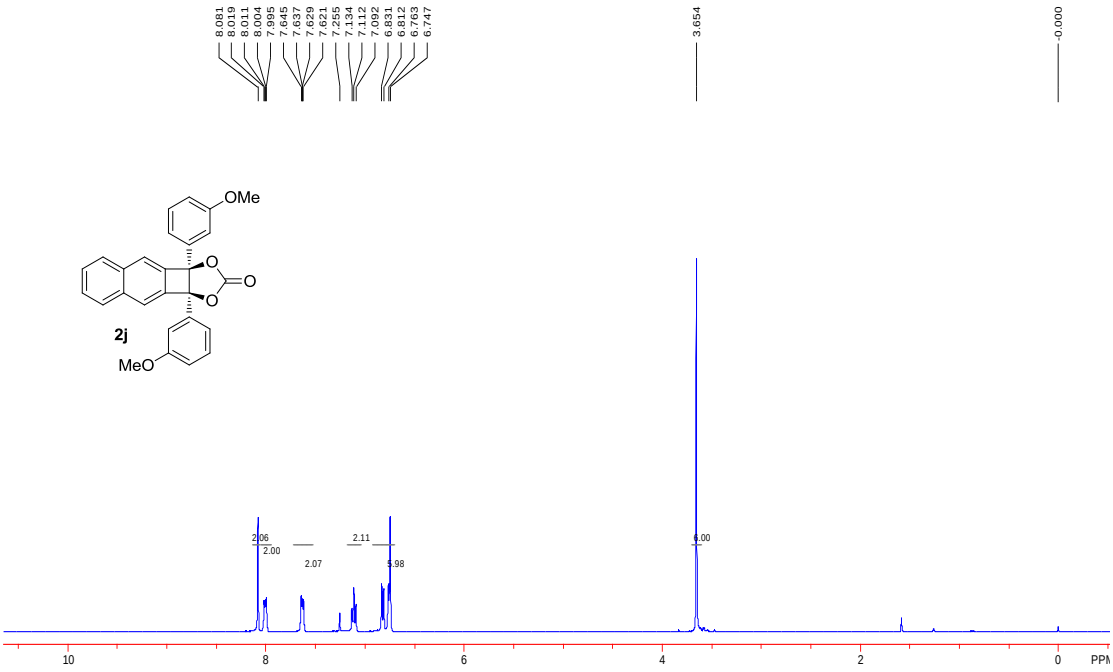
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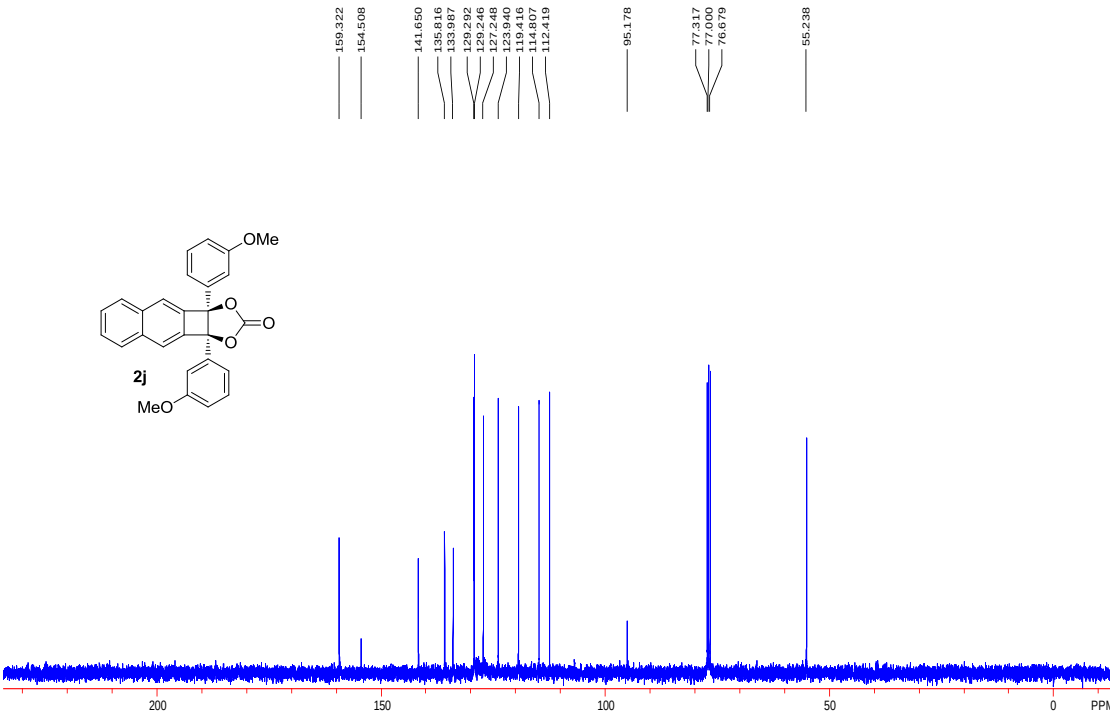
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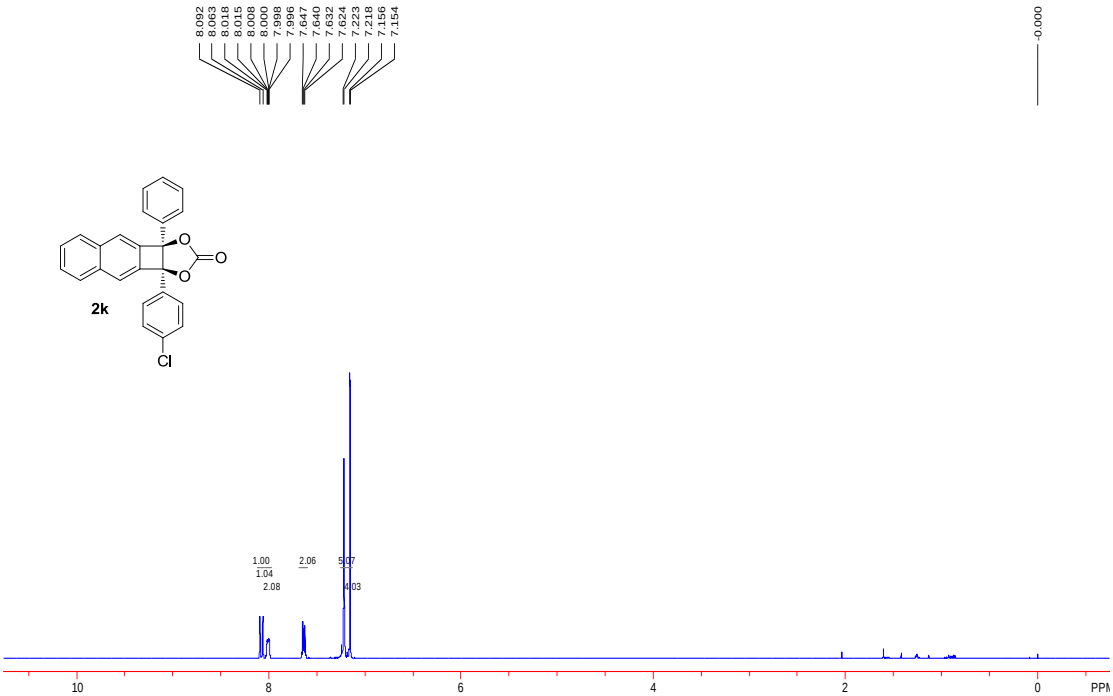
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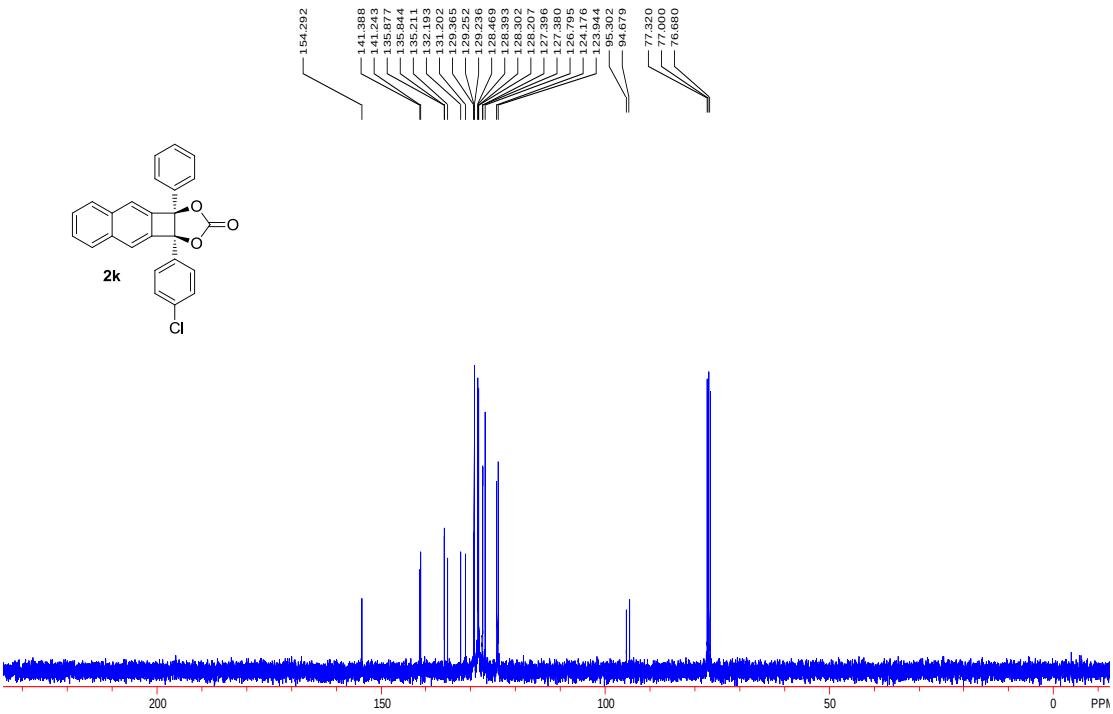
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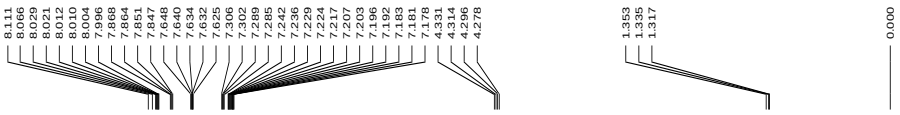
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7.625
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7.285
7.242
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7.229
7.224
7.217
7.207
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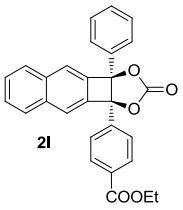
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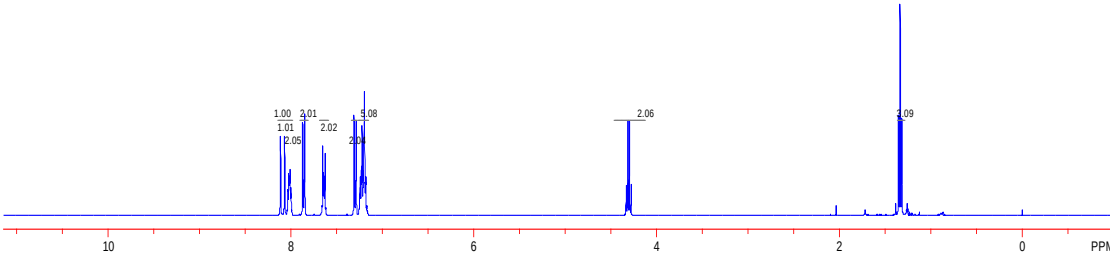
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2.06
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10
8
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4
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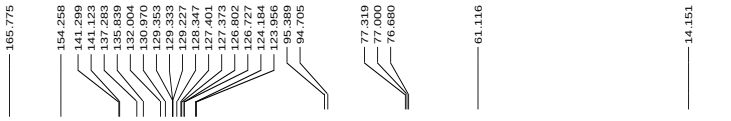
0
PPM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127.401
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123.956
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94.705
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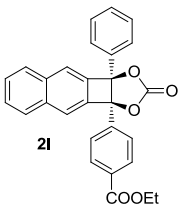
77.000
76.680
61.116
14.151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O
2l
COOEt

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100
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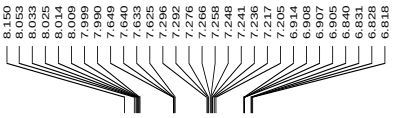
0
PPM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7.633
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7.296
7.292
7.276
7.266
7.258
7.248
7.241
7.236
7.217
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6.818

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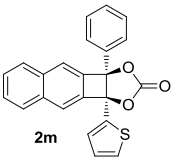
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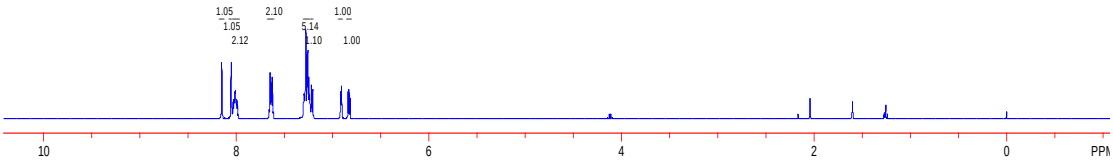
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4
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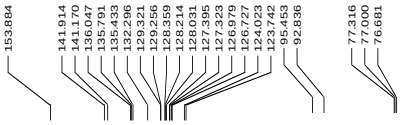
PPM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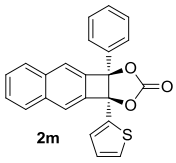
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O
O
S
2m

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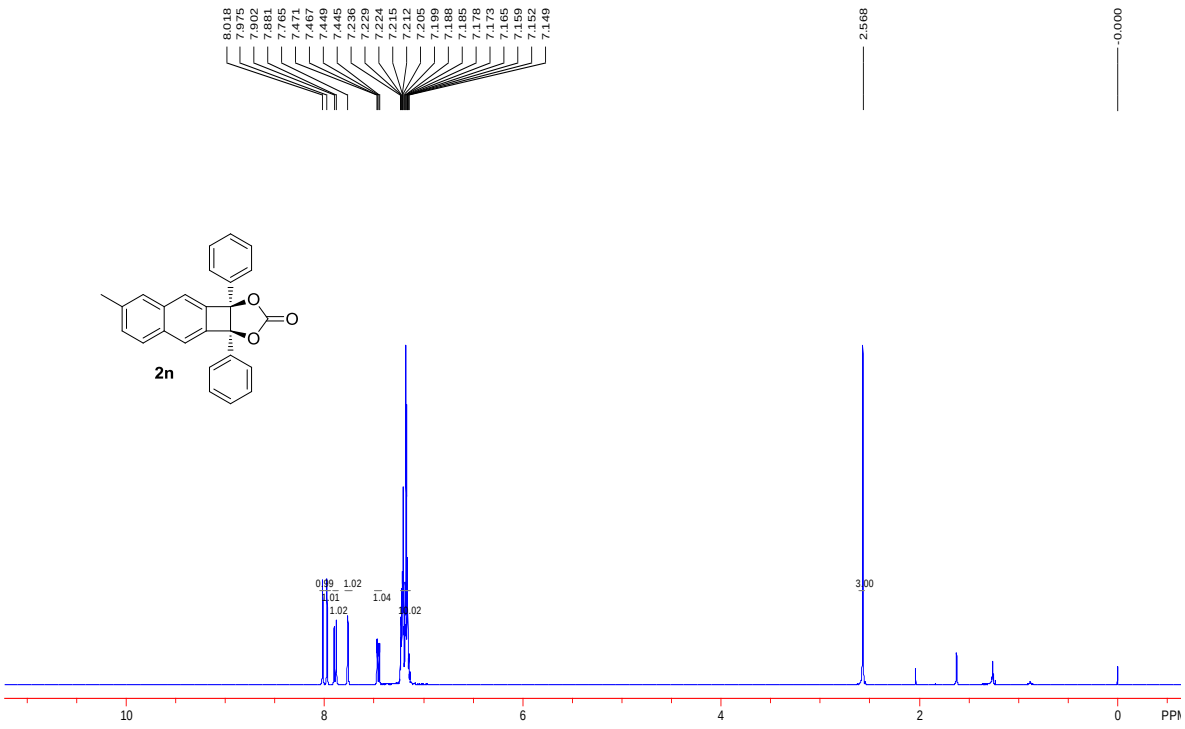
0
PPM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7.215
7.212
7.205
7.199
7.188
7.185
7.178
7.173
7.165
7.159
7.152
7.149
2.568
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1.02
1.02
1.04
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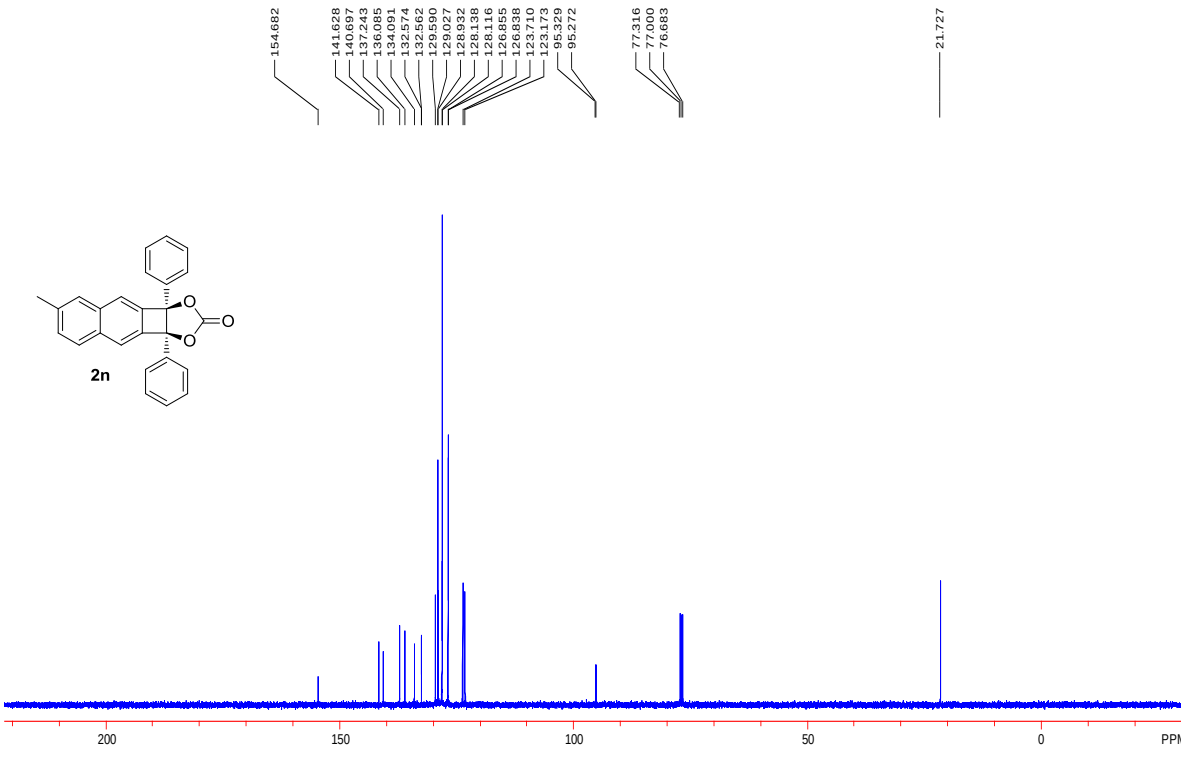
10
8
6
4
2
0
PPM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128.116
126.855
126.838
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76.683
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2n
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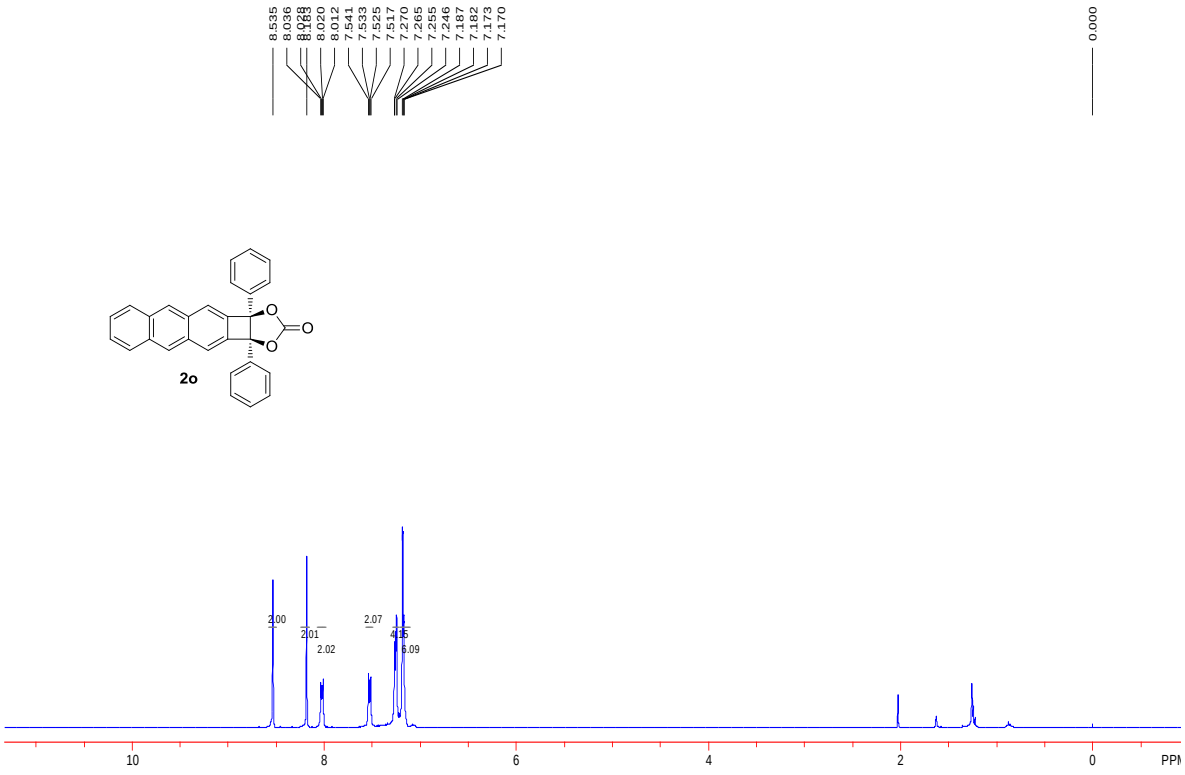
150
100
50
0
PPM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7.265
7.255
7.246
7.187
7.182
7.173
7.170
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2o
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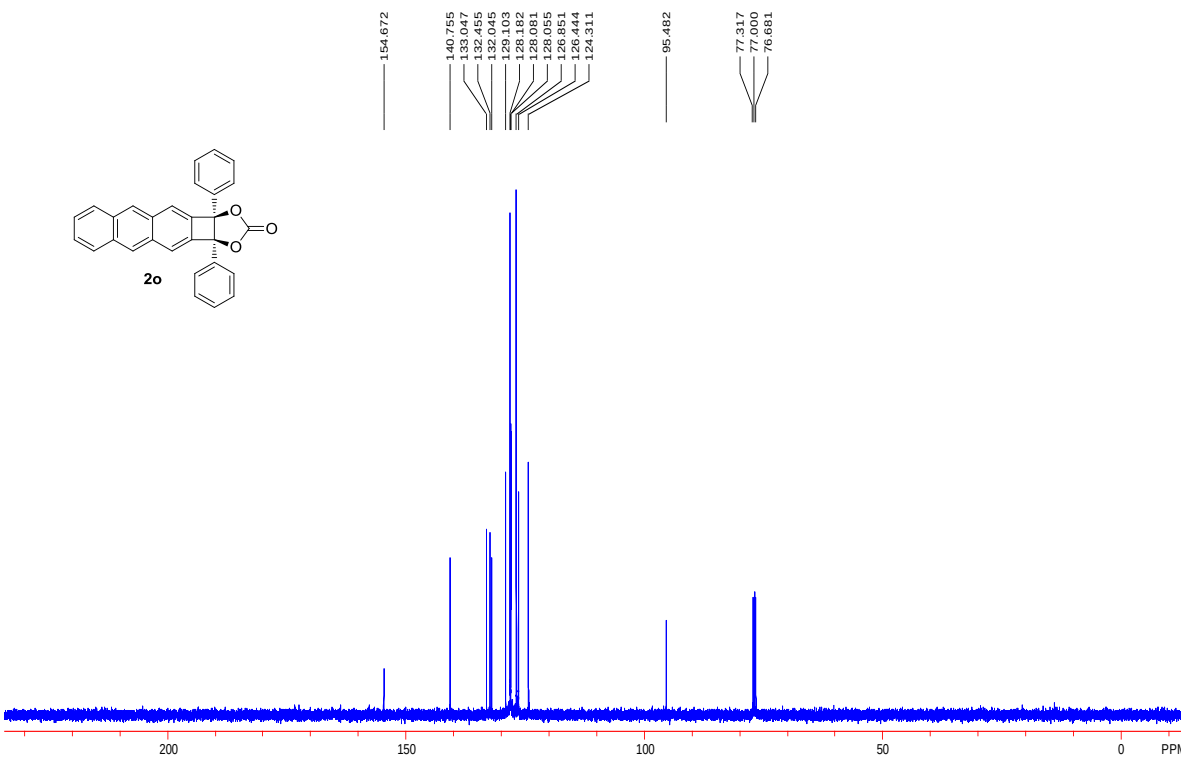
2.01
2.02
2.07
4.15
6.09
10
8
6
4
2
0
PPM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2o
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100
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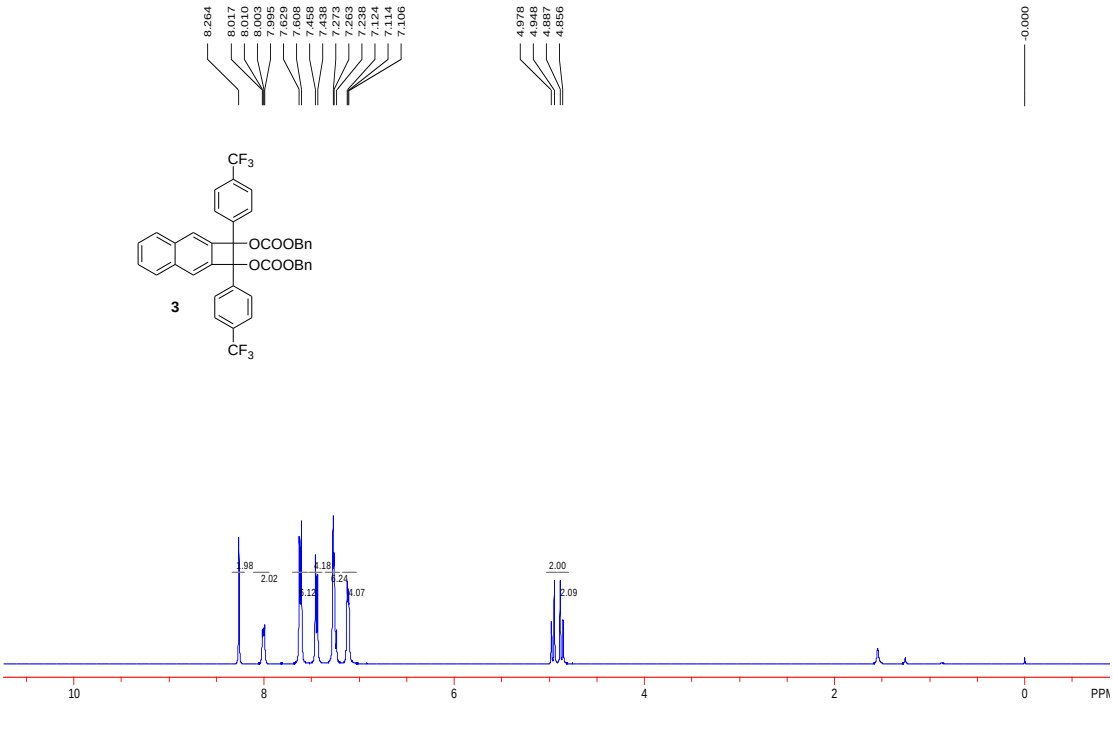
0
PPM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7.124
7.114
7.106
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4.887
4.856
-0.000
CF3
OCOOBn
OCOOBn
3
CF3
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4
2
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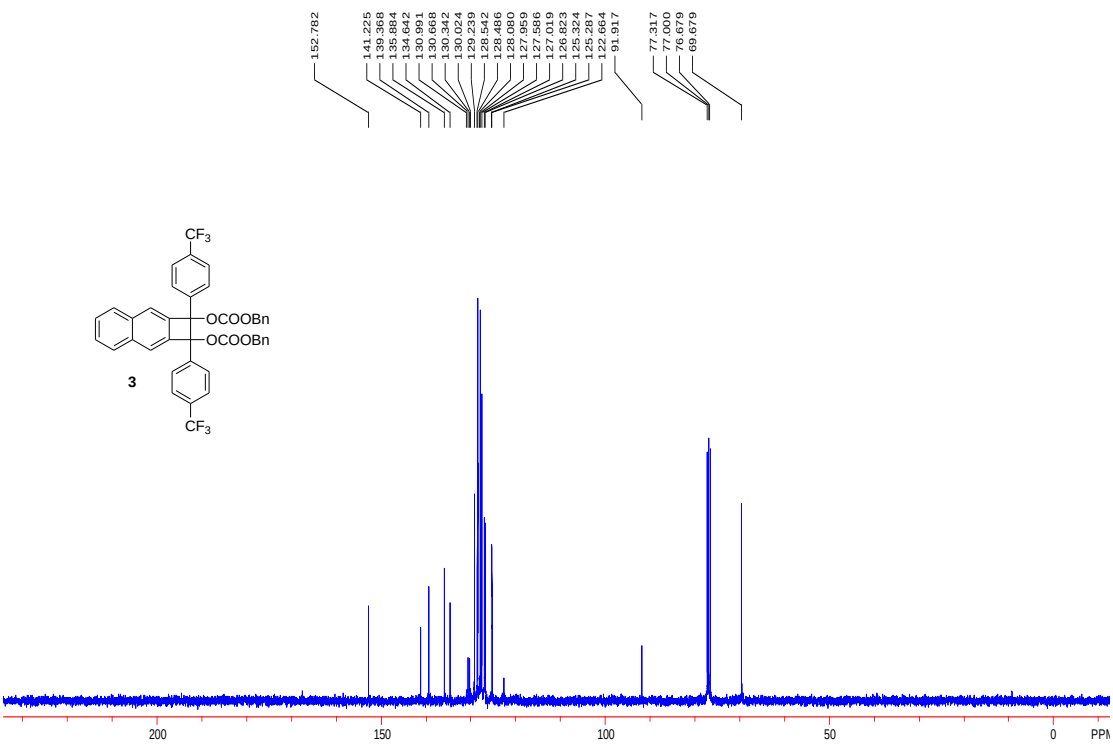
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127.586
127.019
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125.287
122.664
91.917
77.317
77.000
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69.679
CF3
OCOOBn
OCOOBn
3
CF3
200
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100
50
0
PPM