Electronic Supplementary Information

Efficient Synthesis of Benzocyclotrimer Analogues by Negishi Cross-Coupling and Intramolecular Nucleophilic Substitution

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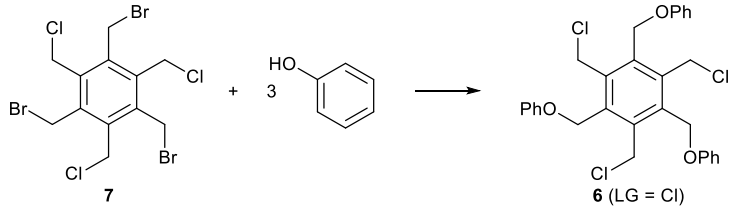
Table of Contents

Materials and general methods.

All reactions were performed under N_2 atmosphere in oven-dried glassware with magnetic stirring. Unless otherwise indicated, all reagents were purchased from commercial suppliers and used without any further purification. All solvents were purified by standard techniques.[1] Organic solutions were concentrated under reduced pressure on a rotary evaporator or an oil pump. Reactions were monitored through thin layer chromatography (TLC) on silica gel-precoated aluminum plates. Compounds were visualized by use of UV light, 2.5% phosphomolybdic acid in ethanol or vanillin with acetic and sulfuric acid in ethanol with heating. Anhydrous magnesium sulfate was used for drying solutions. Column chromatographies were performed on silica gel, 60 Å and 0.2-0.5 mm. ^{1}H NMR spectra were recorded at 400, 500 or 600 MHz, ^{13}C NMR spectra were recorded at 100, 125 or 150 MHz, and chemical shifts are reported in ppm and referenced to the solvent peak. Melting points were taken on a capillary melting point apparatus and are uncorrected. Low- and high-resolution mass spectra were recorded with TOF analyzer mass spectrometers by using electrospray ionization (ESI).

Experimental details for the preparation of BCT analogues



1,3,5-tris(bromomethyl)-2,4,6-tris(chloromethyl) benzene (**7**) was obtained in two synthetic steps from mesitylene according to the procedure described by Choi and coworkers.[2]

Preparation of (((2,4,6-tris(chloromethyl)benzene-1,3,5-triyl)tris(methylene))tris(oxy))tribenzene 6 (LG = Cl). 1,3,5-Tris(bromomethyl)-2,4,6-tris(chloromethyl) benzene (**7**) (4.0 g, 7.96 mmol) along with phenol (2.4 g, 25.48 mmol) were dissolved in dry THF (265 mL, 0.03 M) at 70 °C and anhydrous potassium carbonate (6.6 g, 47.78 mmol) was added. The reaction mixture was stirred at that temperature for 6 days. The reaction mixture was poured into water (400 mL) and extracted with ethyl ether (3 x 100 mL). The combined organic solutions were dried over Na_2SO_4, and the resulting solution was concentrated and purified by column chromatography, yielding the triphenyl ether **6** (LG = Cl) (3.49 g, 81% yield) as a white solid: mp 135-137 ºC; ^{1}H-NMR (δ, $CDCl_3$, 400 MHz) 4.76 (s, 6H), 5.28 (s, 6H), 7.06 (m, 9H), 7.38 (m, 6H); ^{13}C-NMR (δ, $CDCl_3$, 100 MHz) 39.0 (t), 62.8 (t), 114.6 (d), 121.8 (d), 129.8 (d), 136.5 (s), 139.8 (s), 158.4 (s); HRMS (ESI) *m/z* calcd. for $C_{30}H_{27}O_3Na^{35}Cl_2{}^{37}Cl$ $(M+Na)^+$ 565.0894, found 565.0904.

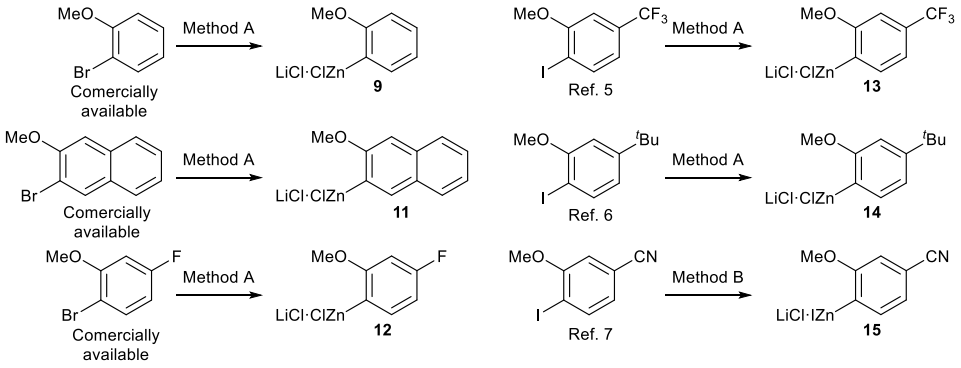
Preparation of the aryl organozinc.

General procedure for preparation of ArZnCl·LiCl. Method A: $ZnCl_2$ was placed in a previously weighted round bottom flask equipped with a stir bar and it was fused through drying with a heat gun under high vacuum for 20 minutes before use. Once the flask reached the room temperature, it was filled with dry nitrogen and weighted again to determinate the amount of anhydrous $ZnCl_2$. Dry THF was added to get a 1.50 M solution and the resulting mixture was stirred vigorously until the $ZnCl_2$

[1] W. L. F. Armarego and D. D. Perrin, Purification of Laboratory Chemicals, 4th ed.; Butterworth-Heinemann: Oxford, 1996.
[2] H.-J. Choi, Y. S. Park, S. H. Yun, H.-S. Kim, C. S. Cho, K. Ko and K. H. Ahn, *Org. Lett.* 2002, **4**, 795.

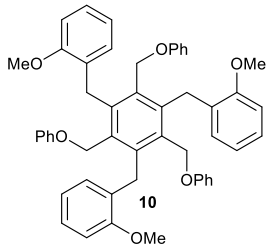
had completely dissolved. The aryl bromide or iodide (2.67 mmol) was placed in a round bottom flask equipped with a stir bar, and the flask was evacuated and back-filled with dry nitrogen (three cycles), and then dry THF (5.4 mL) was added. The aryl bromide solution was cooled to -78 °C and a solution of *n*-BuLi in hexanes (1.5 M, 1.78 mL, 2.67 mmol)[3] was added over 6 minutes. The resulting solution was stirred at -78 °C for 30 minutes. After this time, the solution of $ZnCl_2$ (1.50 M, 1.78 mL, 2.67 mmol) was added. The resulting mixture was allowed to warm to room temperature, and then it was stirred for 45 minutes. The solution of the aryzinc reagent was titrated using I_2, according to Knochel's method (the concentration was typically around 0.25 M).[4]

General procedure for preparation of ArZnI·LiCl. Method B: Anhydrous LiCl was placed in a previously weighted round bottom flask equipped with a stir bar and it was fused through drying with a heat gun under high vacuum for 20 minutes before use. Once the flask reached the room temperature, it was filled with dry nitrogen and weighted again to determinate the amount of anhydrous LiCl. Zinc dust (490 mg, 7.5 mmol, 3.0 equivalents respect to LiCl) was added under nitrogen and the flask was evacuated and back-filled with dry nitrogen (three cycles), and then dry THF (5 mL) and 1,2-dibromoethane (4.3 µL, 0.05 mmol) were added and the mixture was stirred at 70 °C for 10 minutes. Chlorotrimethylsilane (6.3 µL, 0.05 mmol) was then added and the resulting mixture was again stirred at 70 °C for 10 minutes. Then, the mixture was cooled to room temperature, aryl iodide (2.5 mmol) was added and the mixture was stirred at 70 °C for 24 hours. The mixture was cooled and diluted with dry THF (3 mL). Next, the unreacted zinc was allowed to settle down, and the resulting solution was used with a concentration around 0.3 M.
These solutions of aryl organozinc reagents were stored at -20 °C under an inert atmosphere for several weeks without deterioration.

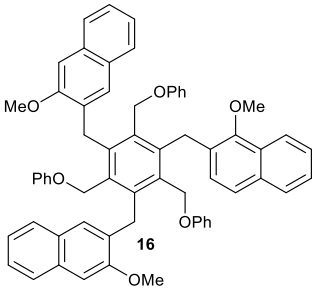


[3] *n*-BuLi (Aldrich, 1.6 M in hexanes) was titrated using anhydrous diphenylacetic acid.
[4] A. Krasovskiy and P. Knochel, *Synthesis* 2006, 890.
[5] K. Aikawa, Y. Miyazaki and K. Mikami, *Bull. Chem. Soc. Jpn.* 2012, **85**, 201.
[6] 3-(*Tert*-butyl)phenol was used as starting material and the iodination was performed according to the procedure described by N. Ortega, S. Urban, B. Beiring and F. Glorius, *Angew. Chem. Int. Ed.* 2012, **51**, 1710. Further methylation was performed using the conditions described by K. Aikawa, Y. Miyazaki and K. Mikami, *Bull. Chem. Soc. Jpn.* 2012, **85**, 201.
[7] 3-Hydroxybenzoic acid was used as starting material and the iodination provided the 3-hydroxy-4-iodobenzoic acid. See: A. Speicher, T. Backes, K. Hesidens and J. Kolz, *Beilstein J. Org. Chem.* 2009**, 5**, 71. Conversion of the carboxylic acid to the corresponding nitrile was accomplished by chlorination, amination and dehydration. See: S. T. Nguyen, J. D. Williams, M. M. Butler, X. Ding, D. M. Mills, T. F. Tashjian, R. G. Panchal, S. K. Weir, C. Moon, H.-O. Kim, J. A. Marsden, N. P. Peet, T. L. Bowlin, *Bioorg. Med. Chem. Lett.* 2014, **24**, 3366. Further etherification of the phenol group with iodomethane in acetone and potassium carbonate at 35 ºC, provided the 4-iodo-3-methoxybenzonitrile in good yield. ^{1}H-NMR (δ, $CDCl_3$, 400 MHz) 3.92 (s, 3H), 6.99 (dd, J = 6.5, 1.5 Hz, 1H), 7.00 (s, 1H), 7.89 (d, J = 8.4 Hz, 1H); ^{13}C-NMR (δ, $CDCl_3$, 100 MHz) 56.7 (q), 92.9 (s), 113.2 (s), 113.2 (d), 118.2 (s), 125.7 (d), 140.5 (d), 158.6 (s); HRMS (ESI) *m/z* calcd. for C_8H_6NONa $(M+Na)^+$ 281.9392, found 281.9390.

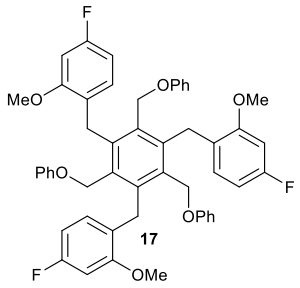
General procedure for Negishi cross-coupling reaction.
An oven-dried round bottom flask equipped with a stir bar was charged with the triphenyl ether **6** (LG = Cl) and with the corresponding catalyst (5 mol% respect to the triphenyl ether **6**). Then the flask was evacuated using a high vacuum pump for 15 minutes. Then, the flask was filled with dry nitrogen, dry THF (0.1 M) and with a THF solution of the suitable aryl organozinc (6.0 equivalents), and the mixture reaction was vigorously stirred a 70 °C until the TLC showed the end of the reaction. After the mixture was cooled to room temperature, the solved was evaporated under vacuum and the oil residue was purified by a chromatography column to obtain the tris(diarylmethane) compounds.



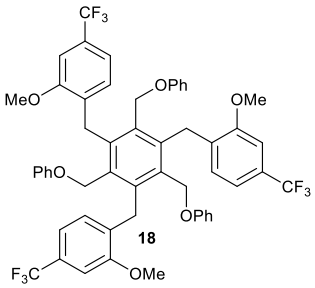
Preparation of 2,2',2''-((2,4,6-tris(phenoxymethyl)benzene-1,3,5-triyl)tris(methylene))tris(methoxybenzene) (10). The general procedure for the Negishi cross-coupling reaction was applied to the triphenyl ether **6** (100 mg, 0.184 mmol) and the organozinc **9** (0.25 M, 4.4 mL, 1.1 mmol) using the $PdCl_2[Amphos]_2$ as catalyst (6.5 mg, 0.0092 mmol) to obtain the tris(diarylmethane) **10** as a colorless oil (108 mg, 77% yield). ^{1}H-NMR (δ, $CDCl_3$, 500 MHz) 3.55 (s, 9H), 4.24 (s, 6H), 4.82 (s, 6H), 6.72 (m, 9H), 6.77 (dd, J = 7.4, 1.2 Hz, 3H), 6.85 (ddd, J = 7.4, 7.4, 0.8 Hz, 3H), 6.88 (dd, J = 7.3, 7.3 Hz, 3H), 7.17 (m, 9H); ^{13}C-NMR (δ, $CDCl_3$, 125 MHz) 28.5 (t), 55.0 (q), 65.0 (t), 109.7 (d), 114.8 (d), 120.4 (d), 120.6 (d), 127.0 (d), 128.7 (d), 129.1 (d), 129.2 (s), 134.5 (s), 142.3 (s), 156.6 (s), 159.0 (s); HRMS (ESI) *m/z* calcd. for $C_{51}H_{48}O_6Na$ $(M+Na)^+$ 779.3349, found 779.3352.



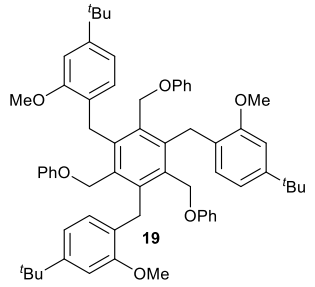
Preparation of 3,3',3''-((2,4,6-tris(phenoxymethyl)benzene-1,3,5-triyl)tris(methylene))tris(2-methoxynaphthalene) (16). The general procedure for the Negishi cross-coupling reaction was applied to the triphenyl ether **6** (100 mg, 0.184 mmol) and the organozinc **11** (0.25 M, 4.4 mL, 1.1 mmol) using the $PdCl_2[Amphos]_2$ as catalyst (6.5 mg, 0.0092 mmol) to obtain the tris(diarylmethane) **16** as a colorless oil (117 mg, 70% yield). ^{1}H-NMR (δ, $CDCl_3$, 400 MHz) 3.69 (s, 9H), 4.42 (s, 6H), 4.87 (s, 6H), 6.67 (d, J = 7.9 Hz, 6H), 6.86 (dd, J = 7.3, 7.3 Hz, 3H), 7.00 (s, 3H), 7.12 (d, J = 7.3 Hz, 3H), 7.14 (d, J = 7.3 Hz, 3H), 7.23 (s, 3H), 7.34 (m, 3H), 7.41 (m, 3H), 7.66 (d, J = 8.1 Hz, 3H), 7.69 (d, J = 8.1 Hz, 3H); ^{13}C-NMR (δ, $CDCl_3$, 100 MHz) 29.1 (t), 55.2 (q), 65.0 (t), 104.5 (d), 114.7 (d), 120.6 (d), 123.5 (d), 125.7 (d), 126.3 (d), 127.3 (d), 127.7 (d), 128.7 (s), 129.1 (d), 131.4 (s), 133.3 (s), 134.7 (s), 142.4 (s), 155.7 (s), 159.0 (s); HRMS (ESI) *m/z* calcd. for $C_{63}H_{54}O_6Na$ $(M+Na)^+$ 929.3818, found 929.3821.



Preparation of 4,4',4''-((2,4,6-tris(phenoxymethyl)benzene-1,3,5-triyl)tris(methylene))tris(1-fluoro-3-methoxybenzene) (17). The general procedure for the Negishi cross-coupling reaction was applied to the triphenyl ether **6** (100 mg, 0.184 mmol) and the organozinc **12** (0.25 M, 4.4 mL, 1.1 mmol) using the $PdCl_2[Amphos]_2$ as catalyst (6.5 mg, 0.0092 mmol) to obtain the tris(diarylmethane) **17** as a colorless oil (91 mg, 61% yield). ^{1}H-NMR (δ, $CDCl_3$, 400 MHz) 3.52 (s, 9H), 4.16 (s, 6H), 4.80 (s, 6H), 6.67 (dd, J = 10.9, 2.4 Hz, 3H), 6.86 (ddd, J = 8.3, 8.3, 2.5 Hz, 3H), 6.70 (m, 9H), 6.89 (dd, J = 7.3, 7.3 Hz, 3H), 7.19 (dd, J = 8.5, 7.4 Hz, 6H); ^{13}C-NMR (δ, $CDCl_3$, 100 MHz) 28.0 (t), 55.2 (q), 64.8 (t), 98.2 (d, $^2J_{(C,F)}$ = 26.1 Hz), 106.3 (d, $^2J_{(C,F)}$ = 21.2 Hz), 114.5 (d), 120.7 (d), 124.6 (d, $^4J_{(C,F)}$ = 3.3 Hz), 129.2 (d), 129.3 (d, $^3J_{(C,F)}$ = 9.9 Hz), 134.5 (s), 142.3 (s), 157.4 (d, $^3J_{(C,F)}$ = 9.8 Hz), 158.9 (s), 162.2 (d, $^1J_{(C,F)}$ = 243.8 Hz); HRMS (ESI) *m/z* calcd. for $C_{51}H_{45}O_6NaF_3$ $(M+Na)^+$ 833.3066, found 833.3076.

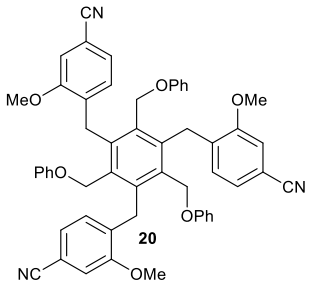


Preparation of 4,4',4''-((2,4,6-tris(phenoxymethyl)benzene-1,3,5-triyl)tris(methylene))tris(3-methoxy-1-(trifluoromethyl)benzene) (18). The general procedure for the Negishi cross-coupling reaction was applied to the triphenyl ether **6** (100 mg, 0.184 mmol) and the organozinc **13** (0.25 M, 10.3 mL, 2.58 mmol) using the $PdCl_2(PPh_3)_2$ as catalyst (13 mg, 0.0184 mmol) to obtain the tris(diarylmethane) **18** as a colorless oil (122 mg, 69% yield). ^{1}H-NMR (δ, $CDCl_3$, 400 MHz) 3.57 (s, 9H), 4.26 (s, 6H), 4.81 (s, 6H), 6.61 (d, J = 7.9 Hz, 6H), 6.88 (m, 9H), 7.15 (m, 9H); ^{13}C-NMR (δ, $CDCl_3$, 100 MHz) 28.6 (t), 55.3 (q), 64.7 (t), 106.5 (d), 114.4 (d), 117.2 (d), 120.9 (d), 129.0 (d), 129.2 (d), 129.4 (d, J = 32.2 Hz), 133.1 (s), 134.8 (s), 141.9 (s), 156.5 (s), 158.5 (s); HRMS (ESI) *m/z* calcd. for $C_{54}H_{45}O_6NaF_9$ $(M+Na)^+$ 983.2970, found 983.2961.



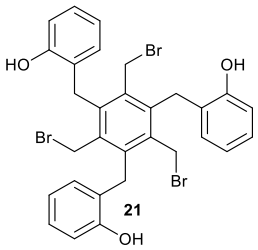
Preparation of 4,4',4''-((2,4,6-tris(phenoxymethyl)benzene-1,3,5-triyl)tris(methylene))tris(1-(*tert*-butyl)-3-methoxybenzene) (19). The general procedure for the Negishi cross-coupling reaction was applied to the triphenyl ether **6** (100 mg, 0.184 mmol) and the organozinc **14** (0.25 M, 6.6 mL,

1.7 mmol) using the $PdCl_2[Amphos]_2$ as catalyst (6.5 mg, 0.0092 mmol) to obtain the tris(diarylmethane) **19** as a colorless oil (107 mg, 63% yield). ^{1}H-NMR (δ, $CDCl_3$, 400 MHz) 1.35 (s, 27H), 3.57 (s, 9H), 4.24 (s, 6H), 4.90 (s, 6H), 6.75 (m, 12H), 6.90 (m, 6H), 7.00 (s, 3H), 7.19 (d, J = 7.4 Hz, 3H), 7.21 (d, J = 7.4 Hz, 3H); ^{13}C-NMR (δ, $CDCl_3$, 100 MHz) 28.1 (t), 31.5 (q), 34.7 (s), 54.9 (q), 65.2 (t), 107.3 (d), 114.9 (d), 117.2 (d), 120.4 (d), 126.3 (s), 128.2 (d), 129.0 (d), 134.3 (s), 142.5 (s), 150.1 (s), 156.3 (s), 159.1 (s); HRMS (ESI) *m/z* calcd. for $C_{63}H_{72}O_6Na$ $(M+Na)^+$ 947.5227, found 947.5232.



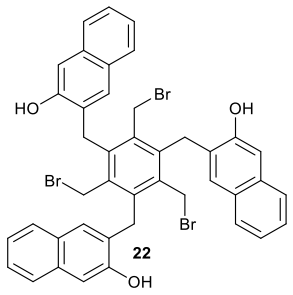
Preparation of 4,4',4''-((2,4,6-tris(phenoxymethyl)benzene-1,3,5-triyl)tris(methylene))tris(3-methoxybenzonitrile) (20). The general procedure for the Negishi cross-coupling reaction was applied to the triphenyl ether **6** (100 mg, 0.184 mmol) and the organozinc **15** (0.3 M, 3.7 mL, 1.1 mmol) using the $PdCl_2(PPh_3)_2$ as catalyst (13 mg, 0.0184 mmol) to obtain the tris(diarylmethane) **20** as a white solid (86 mg, 56% yield). ^{1}H-NMR (δ, $CDCl_3$, 400 MHz) 3.57 (s, 9H), 4.25 (s, 6H), 4.77 (s, 6H), 6.58 (dd, J = 7.9 Hz, 6H), 6.86 (d, J = 1.3 Hz, 3H), 6.87 (d, J = 7.8 Hz, 3H), 6.91 (dd, J = 7.3, 7.3 Hz, 3H), 7.17 (d, J = 7.7, 1.4 Hz, 3H), 7.18 (d, J = 7.4 Hz, 3H), 7.19 (d, J = 7.4, 3H); ^{13}C-NMR (δ, $CDCl_3$, 100 MHz) 28.9 (t), 55.4 (q), 64.6 (t), 110.8 (s), 112.7 (d), 114.2 (d), 118.9 (s), 121.1 (d), 124.6 (d), 129.3 (d), 129.5 (d), 134.9 (s), 135.0 (s), 141.5 (s), 156.5 (s), 158.3 (s); IR ($CHCl_3$) (cm^{-1}) 3019, 2232, 1598, 1587, 1573, 1493, 1218; HRMS (ESI) *m/z* calcd. for $C_{54}H_{45}N_3O_6Na$ $(M+Na)^+$ 854.3206, found 854.3213.

General procedure for deprotection of the methyl ethers.
To a solution of the tris(diarylmethane) in CH_2Cl_2 (0.02 M) at -78 °C was added 9 equivalents of a 1.0 M solution of BBr_3 in CH_2Cl_2, and the reaction was slowly warmed to room temperature overnight. The reaction mixture was diluted with CH_2Cl_2 and washed with a saturated aqueous solution of $NaHCO_3$. The organic phases were dried over anhydrous Na_2SO_4, filtered, concentrated under vacuum and purified by a chromatography column to obtain the triphenol derivative.

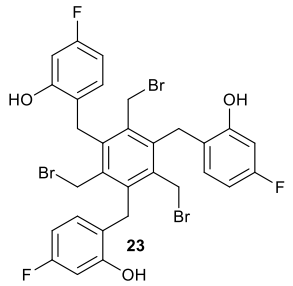


Preparation of 2,2',2''-((2,4,6-tris(bromomethyl)benzene-1,3,5-triyl)tris(methylene))triphenol 21. The general procedure for deprotection of the methyl ethers was applied to the tris(diarylmethane) **10** (111 mg, 0.147 mmol) to obtain the triphenol derivative **21** as a light brown oil (83 mg, 84% yield). ^{1}H-NMR (δ, $CDCl_3$, 500 MHz) 4.25 (s, 6H), 4.36 (s, 6H), 5.19 (s, 3H), 6.44 (d, J = 7.3 Hz, 3H), 6.79 (ddd, J = 7.5, 7.5, 0.8 Hz, 3H), 6.82 (d, J = 8.0 Hz, 3H), 7.10 (ddd, J = 8.0, 7.5, 1.2 Hz, 3H); ^{13}C-NMR (δ, $CDCl_3$, 125 MHz) 28.7 (t), 28.8 (t), 115.2 (d), 121.1 (d), 125.4 (s), 127.5 (d), 127.8 (d),

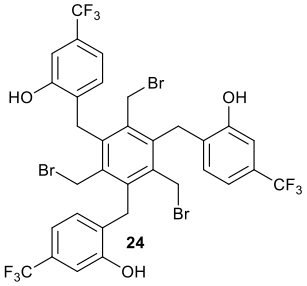
136.3 (s), 140.4 (s), 153.6 (s); HRMS (ESI) *m/z* calcd. for $C_{30}H_{27}O_3Na\ ^{79}Br_2{}^{81}Br\ (M+Na)^+$ 696.9388, found 696.9384.



Preparation of 3,3',3''-((2,4,6-tris(bromomethyl)benzene-1,3,5-triyl)tris(methylene))tris(naphthalen-2-ol) 22. The general procedure for deprotection of the methyl ethers was applied to the tris(diarylmethane) **16** (90 mg, 0.099 mmol) to obtain the triphenol derivative **22** as a light brown oil (50 mg, 61% yield). ^{1}H-NMR (δ, acetone-d_6, 400 MHz) 4.50 (s, 6H), 4.63 (s, 6H), 7.05 (s, 3H), 7.29 (ddd, J = 6.9, 6.9, 1.2 Hz, 3H), 7.31 (s, 3H), 7.35 (ddd, J = 6.9, 6.9, 1.2 Hz, 3H), 7.62 (d, J = 8.0 Hz, 3H), 7.65 (d, J = 8.2 Hz, 3H); ^{13}C-NMR (δ, acetone-d_6, 100 MHz) 30.0 (t), 30.2 (t), 109.8 (d), 124.1 (d), 126.8 (d), 126.9 (d), 127.4 (d), 128.2 (d), 129.5 (s), 130.0 (s), 135.0 (s), 137.7 (s), 141.9 (s), 154.8 (s); HRMS (ESI) *m/z* calcd. for $C_{42}H_{33}O_3Na^{79}Br^{81}Br_2$ $(M+Na)^+$ 848.9837, found 848.9844.

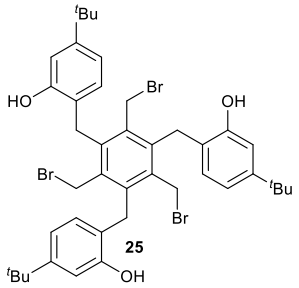


Preparation of 6,6',6''-((2,4,6-tris(bromomethyl)benzene-1,3,5-triyl)tris(methylene))tris(3-fluorophenol) 23. The general procedure for deprotection of the methyl ethers was applied to the tris(diarylmethane) **17** as a colorless oil (90 mg, 0.111 mmol) to obtain the triphenol derivative **23** (64 mg, 79% yield). ^{1}H-NMR (δ, $CDCl_3$, 400 MHz) 4.24 (s, 6H), 4.28 (s, 6H), 5.60 (br s, 3H), 6.36 (dd, J = 8.2, 6.6 Hz, 3H), 6.51 (ddd, J = 8.4, 8.4, 2.4 Hz, 3H), 6.59 (dd, J = 9.4, 2.4 Hz, 3H); ^{13}C-NMR (δ, $CDCl_3$, 125 MHz) 28.3 (t), 28.4 (t), 103.2 (d, $^2J_{(C,F)}$ = 24.6 Hz), 107.7 (d, $^2J_{(C,F)}$ = 21.4 Hz), 121.1 (d, $^4J_{(C,F)}$ = 3.3 Hz), 128.2 (d, $^3J_{(C,F)}$ = 9.4 Hz), 136.4 (s), 140.3 (s), 154.4 (d, $^3J_{(C,F)}$ = 10.5 Hz), 162.1 (d, $^1J_{(C,F)}$= 245.6 Hz); HRMS (ESI) *m/z* calcd. for $C_{30}H_{24}O_3F_3Na^{79}Br^{81}Br_2$ $(M+Na)^+$ 752.9084, found 752.9098.

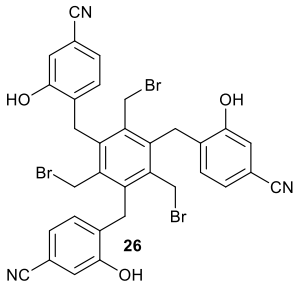


Preparation of 6,6',6''-((2,4,6-tris(bromomethyl)benzene-1,3,5-triyl)tris(methylene))tris(3-(trifluoromethyl)phenol) 24. The general procedure for deprotection of the methyl ethers was

applied to the tris(diarylmethane) **18** (105 mg, 0.109 mmol) to obtain the triphenol derivative **24** as a light brown oil (71 mg, 74% yield). ^{1}H-NMR (δ, $CDCl_3$, 500 MHz) 4.22 (s, 6H), 4.39 (s, 6H), 6.56 (d, J = 8.1 Hz, 3H), 7.08 (s, 3H), 7.09 (d, J = 8.1 Hz, 3H); ^{13}C-NMR (δ, $CDCl_3$, 125 MHz) 28.1 (t), 28.9 (t), 112.0 (d), 117.9 (d, J = 4.1 Hz), 123.7 (q, J = 272.0 Hz), 127.9 (d), 129.5 (s), 130.3 (q, J = 32.0 Hz), 136.7 (s), 139.8 (s), 153.7 (s); HRMS (ESI) *m/z* calcd. for $C_{33}H_{24}O_3F_9Na^{79}Br^{81}Br_2$ $(M-H)^+$ 878.9013, found 878.9023.



Preparation of 6,6',6''-((2,4,6-tris(bromomethyl)benzene-1,3,5-triyl)tris(methylene))tris(3-(*tert*-butyl)phenol) 25. The general procedure for deprotection of the methyl ethers was applied to the tris(diarylmethane) **19** (118 mg, 0.127 mmol) to obtain the triphenol derivative **25** as a colorless oil (86 mg, 80% yield). ^{1}H-NMR (δ, $CDCl_3$, 400 MHz) 1.28 (s, 27H), 4.26 (s, 6H), 4.32 (s, 6H), 5.13 (br s, 3H), 6.37 (d, J = 8.0 Hz, 3H), 6.82 (dd, J = 8.0, 1.8 Hz, 3H), 6.86 (d, J = 1.8 Hz, 3H); ^{13}C-NMR (δ, $CDCl_3$, 100 MHz) 28.4 (t), 29.2 (t), 31.3 (q), 34.4 (s), 112.7 (d), 118.0 (d), 122.2 (s), 127.0 (d), 136.2 (s), 140.4 (s), 151.4 (s), 153.2 (s); HRMS (ESI) *m/z* calcd. for $C_{42}H_{51}O_3Na^{79}Br^{81}Br_2$ $(M+Na)^+$ 867.1245, found 867.1234.

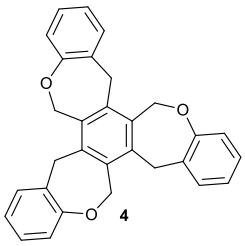


Preparation of 4,4',4''-((2,4,6-tris(bromomethyl)benzene-1,3,5-triyl)tris(methylene))tris(3-hydroxybenzonitrile) 26. The general procedure for deprotection of the methyl ethers was applied to the tris(diarylmethane) **20** (80 mg, 0.096 mmol) using 30.0 equivalents of BBr_3, to obtain the triphenol derivative **26** as a light brown oil (58 mg, 81% yield). ^{1}H-NMR (δ, acetone-d_6, 400 MHz) 4.43 (s, 6H), 4.47 (s, 6H), 6.73 (d, J = 7.8 Hz, 3H), 7.12 (dd, J = 7.8, 1.6 Hz, 3H), 7.26 (d, J = 1.6 Hz, 3H), 9.68 (s, 3H); ^{13}C-NMR (δ, acetone-d_6, 100 MHz) 29.6 (t), 29.9 (t), 111.9 (s), 118.2 (d), 119.2 (s), 124.7 (d), 129.7 (d), 132.7 (s), 137.8 (s), 141.0 (s), 156.4 (s); IR ($CHCl_3$) (cm^{-1}) 3232, 3024, 2229, 1711, 1605, 1582, 1418, 1287, 1263; HRMS (ESI) *m/z* calcd. for $C_{33}H_{24}N_3O_3Na^{79}Br^{81}Br_2$ $(M+Na)^+$ 773.9225, found 773.9233.

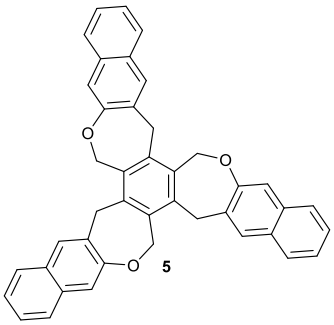
General procedure for cyclization.

To a solution of the triphenol derivative in dry DMF (0.02 M) was added 6 equivalents of anhydrous potassium carbonate, and the mixture was warmed to 50 °C and stirred vigorously overnight. After the mixture was cooled to room temperature, it was diluted with CH_2Cl_2 and washed with an HCl solution (0.1 M) and water. The organic phases were dried over Na_2SO_4, and the resulting solution

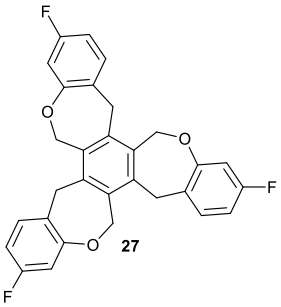
was concentrated and purified by column chromatography, yielding the corresponding BTC analogue.



Preparation of the BCT analogue 4. The general procedure for the cyclization was applied to the triphenol derivative **21** (52 mg, 0.077 mmol) to obtain the BCT analogue **4** (18.2 mg, 58% yield) as a white solid: mp 262 ºC (decomposition); ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.44 (s, 6H), 5.58 (s, 6H), 6.72 (d, *J* = 8.1 Hz, 3H), 6.81 (dd, *J* = 7.4, 7.4 Hz, 3H), 7.08 (m, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 34.2 (t), 65.0 (t), 119.1 (d), 121.0 (d), 123.2 (s), 128.6 (d), 131.0 (s), 131.0 (d), 140.7 (s), 156,3 (s); HRMS (ESI) *m/z* calcd for $C_{30}H_{24}O_3Na$ $[M+Na]^+$: 455.1623, found: 455.1627; Elemental analysis (%) calcd for $C_{30}H_{24}O_3$: C 83.31, H 5.59; found: C 83.11, H 5.71.

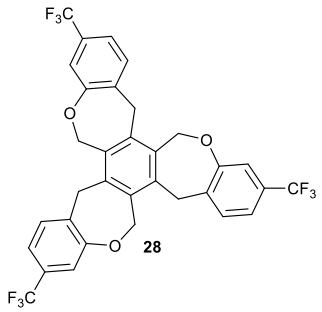


Preparation of the BCT analogue 5. The general procedure for the cyclization was applied to the triphenol derivative **22** (48 mg, 0.058 mmol) to obtain the BCT analogue **5** (17 mg, 50% yield) as a white solid: mp 294 ºC (decomposition); ^{1}H NMR (600 MHz, $CDCl_3$) δ 4.63 (s, 6H), 5.71 (s, 6H), 7.16 (s, 3H), 7.28 (dd, *J* = 7.6, 7.6 Hz, 3H), 7.33 (dd, *J* = 7.6, 7.6 Hz, 3H), 7.58 (d, *J* = 8.4 Hz, 3H), 7.63 (s, 3H), 7.71 (d, *J* = 7.8 Hz, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 34.7 (t), 65.7 (t), 114.2 (d), 123.9 (d), 126.0 (s), 126.0 (d), 126.1 (d), 127.0 (d), 129.1 (s), 129.2 (d), 131.4 (s), 134.1 (s), 139.9 (s), 154,6 (s); HRMS (ESI) *m/z* calcd for $C_{42}H_{30}O_3Na$ $[M+Na]^+$: 605.2093, found: 605.2086.

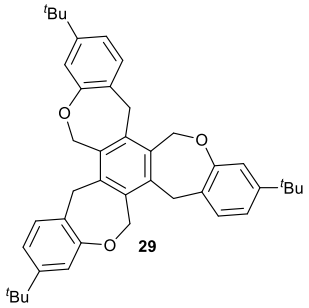


Preparation of the BCT analogue 27. The general procedure for the cyclization was applied to the triphenol derivative **23** (50 mg, 0.069 mmol) to obtain the BCT analogue **27** (18.7 mg, 56% yield) as a white solid: mp 256 ºC (decomposition); ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.39 (s, 6H), 5.56 (s, 6H), 6.43 (dd, *J* = 10.2, 2.6 Hz, 3H), 6.53 (ddd, *J* = 8.1, 8.1, 2.7 Hz, 3H), 7.03 (dd, *J* = 8.4, 6.7 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 33.6 (t), 64.8 (t), 106.2 (d, $^{2}J_{(C,F)}$ = 24.7 Hz), 107.9 (d, $^{2}J_{(C,F)}$ = 21.1

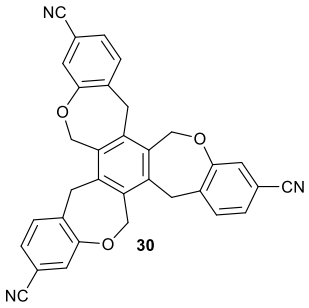
Hz), 118.8 (d, $^{4}J_{(C,F)}$ = 3.0 Hz), 130.7 (s), 131.8 (d, $^{3}J_{(C,F)}$ = 9.5 Hz), 141.0 (s), 157.1 (d, $^{3}J_{(C,F)}$ = 11.8 Hz), 162.7 (d, $^{1}J_{(C,F)}$ = 244.9 Hz); HRMS (ESI) *m/z* calcd for $C_{30}H_{20}O_3F_3$ $[M-H]^+$: 485.1365, found: 485.1368.



Preparation of the BCT analogue 28. The general procedure for the cyclization was applied to the triphenol derivative **24** (50 mg, 0.057 mmol) to obtain the BCT analogue **28** (14 mg, 38% yield) as a white solid: mp 239 ºC (decomposition); ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.50 (s, 6H), 5.62 (s, 6H), 6.97 (d, *J* = 1.2 Hz, 3H), 7.07 (dd, *J* = 7.9, 1.2 Hz, 3H), 7.22 (d, *J* = 8.0 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 34.1 (t), 65.0 (t), 116.4 (d), 117.6 (d), 125.0 (s), 126.4 (s), 131.0 (s), 131.5 (d), 140.5 (s), 156.2 (s); HRMS (ESI) *m/z* calcd for $C_{33}H_{20}O_3F_9$ $[M-H]^+$: 635.1269, found: 635.1266.

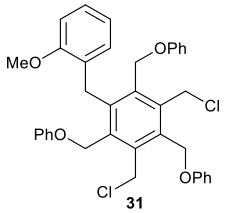


Preparation of the BCT analogue 29. The general procedure for the cyclization was applied to the triphenol derivative **25** (78 mg, 0.092 mmol) to obtain the BCT analogue **29** (33 mg, 59% yield) as a colorless sticky oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.24 (s, 27H), 4.43 (s, 6H), 5.57 (s, 6H), 6.76 (s, 3H), 6.86 (dd, *J* = 7.9, 1.4 Hz, 3H), 7.05 (d, *J* = 7.9 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 31.2 (q), 33.9 (t), 34.3 (s), 64.8 (t), 116.0 (d), 118.1 (d), 120.0 (s), 130.8 (d), 131.0 (s), 140.9 (s), 152.1 (s), 155.9 (s); HRMS (ESI) *m/z* calcd for $C_{42}H_{48}O_3Na$ $[M+Na]^+$: 623.3501, found: 623.3500.



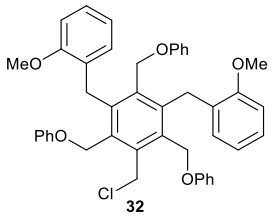
Preparation of the BCT analogue 30. The general procedure for the cyclization was applied to the triphenol derivative **26** (44 mg, 0.059 mmol). Once the reaction was complete, it was diluted with water and extracted with CH_2Cl_2, the organic phases were dried over anhydrous Na_2SO_4, filtered and concentrated. In this case, the solid crude was suspended in hot CH_2Cl_2 and filtered through a pad of celite and the organic solution was concentrated to obtain the BCT analogue **30** (19 mg, 65% yield)

as a white solid. ^{1}H NMR (500 MHz, DMSO-d_6) δ 4.65 (s, 6H), 5.78 (s, 6H), 7.08 (d, J = 1.6 Hz, 3H), 7.26 (dd, J = 7.9, 1.6 Hz, 3H), 7.57 (d, J = 8.1 Hz, 3H); ^{13}C NMR (125 MHz, DMSO-d_6) δ 32.8 (t), 64.5 (t), 110.9 (s), 118.3 (s), 121.6 (d), 124.1 (d), 129.4 (s), 131.4 (s), 132.6 (d), 140.4 (s), 156.3 (s); IR ($CHCl_3$) (cm^{-1}) 2976, 2930, 2875, 2233, 1562, 1558, 1582, 1494, 1410; HRMS (ESI) *m/z* calcd for $C_{33}H_{21}N_3O_3Na$ $[M+Na]^+$: 530.1481, found: 530.1484.



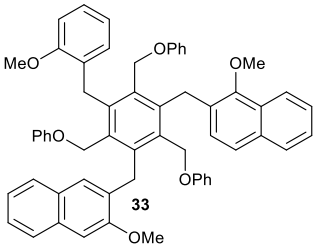
31

Preparation of (((2,4-bis(chloromethyl)-6-(2-methoxybenzyl)benzene-1,3,5-triyl)tris(methylene))tris(oxy))tribenzene (31). The general procedure for the Negishi cross-coupling reaction was applied to the triphenyl ether **6** (200 mg, 0.369 mmol) using one equivalent of the organozinc **9** (0.25 M, 1.5 mL, 0.369 mmol) and the $PdCl_2(PPh_3)_2$ as catalyst (13 mg, 0.018 mmol) to recover starting material (50 mg) and obtain the mono-coupling product **31** as a light brown oil (112 mg, 50% yield, 67% brsm). ^{1}H-NMR (δ, $CDCl_3$, 400 MHz) 3.59 (s, 3H), 4.21 (s, 2H), 4.81 (s, 4H), 5.05 (s, 4H), 5.32 (s, 2H), 6.68 (d, J = 7.4 Hz, 1H), 6.77 (d, J = 8.0 Hz, 1H), 6.85 (dd, J = 7.4, 7.4 Hz, 1H), 6.91 (d, J = 8.0 Hz, 4H), 6.98 (dd, J = 7.2, 7.2 Hz, 2H), 7.06 (dd, J = 7.3, 7.3 Hz, 1H), 7.11 (d, J = 8.0 Hz, 2H), 7.18 (ddd, J = 7.8, 7.8, 1.3 Hz, 1H), 7.28 (m, 4H), 7.39 (dd, J = 8.4, 7.6 Hz, 2H); ^{13}C-NMR (δ, $CDCl_3$, 100 MHz) 28.3 (t), 39.5 (t), 55.0 (q), 62.9 (t), 63.8 (t), 109.9 (d), 114.7 (d), 114.7 (d), 120.6 (d), 121.3 (d), 121.7 (d), 127.4 (d), 127.9 (s), 128.7 (d), 129.5 (d), 129.7 (d), 134.3 (s), 136.7 (s), 139.5 (s), 143.2 (s), 156.4 (s), 158.6 (s), 158.6 (s); HRMS (ESI) *m/z* calcd. for $C_{37}H_{34}O_4Na^{35}Cl_2$ $(M+Na)^+$ 635.1732, found 635.1751.

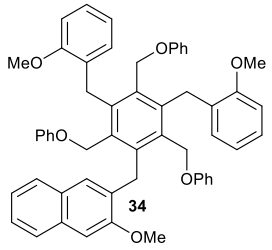


32

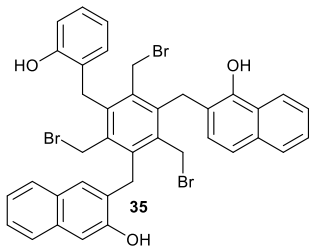
Preparation of (((2-(chloromethyl)-4,6-bis(2-methoxybenzyl)benzene-1,3,5-triyl)tris(methylene))tris(oxy))tribenzene (32). The general procedure for the Negishi cross-coupling reaction was applied to the triphenyl ether **6** (200 mg, 0.369 mmol) using two equivalents of the organozinc **9** (0.25 M, 3.0 mL, 0.738 mmol) and the $PdCl_2(PPh_3)_2$ as catalyst (13 mg, 0.018 mmol) to obtain the di-coupling product **32** as a light brown oil (126 mg, 50% yield), the mono-coupling product **31** (29 mg) and the tri-coupling product **10** (55 mg). ^{1}H-NMR (δ, $CDCl_3$, 400 MHz) 3.57 (s, 6H), 4.23 (s, 4H), 4.79 (s, 2H), 4.86 (s, 2H), 5.08 (s, 4H), 6.73 (m, 6H), 6.85 (ddd, J = 7.5, 7.5, 1.0 Hz, 2H), 6.88 (d, J = 7.6 Hz, 1H), 6.92 (d, J = 7.8 Hz, 4H), 6.97 (dd, J = 7.4, 7.3 Hz, 2H), 7.17 (m, 4H), 7.28 (dd, J = 8.7, 7.4, Hz, 4H); ^{13}C-NMR (δ, $CDCl_3$, 100 MHz) 28.3 (t), 40.1 (t), 55.0 (q), 64.0 (t), 64.8 (t), 109.8 (d), 114.7 (d), 114.7 (d), 120.5 (d), 120.7 (d), 121.1 (d), 127.2 (d), 128.6 (s), 128.7 (d), 129.1 (d), 129.4 (d), 134.4 (s), 136.9 (s), 139.2 (s), 142.7 (s), 156.5 (s), 158.8 (s), 158.9 (s); HRMS (ESI) *m/z* calcd. for $C_{44}H_{41}O_5Na^{35}Cl$ $(M+Na)^+$ 707.2540, found 7072549.



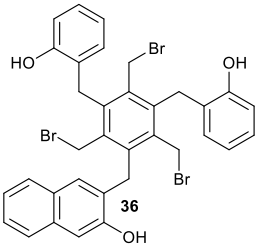
Preparation of 1-methoxy-2-(3-(2-methoxybenzyl)-5-((3-methoxynaphthalen-2-yl)methyl)-2,4,6-tris(phenoxymethyl)benzyl)naphthalene (33). The general procedure for the Negishi cross-coupling reaction was applied to the mono-coupling product **31** (111 mg, 0.18 mmol) using four equivalents of the organozinc **11** (0.25 M, 2.9 mL, 0.72 mmol) and the $PdCl_2[Amphos]_2$ as catalyst (6.3 mg, 0.09 mmol) to obtain the tris(diarylmethane) **33** as a colorless oil (99 mg, 64% yield). ^{1}H-NMR (δ, $CDCl_3$, 400 MHz) 3.54 (s, 3H), 3.69 (s, 6H), 4.30 (s, 2H), 4.39 (s, 4H), 4.83 (s, 2H), 4.86 (s, 4H), 6.62 (d, *J* = 7.9 Hz, 2H), 6.72 (m, 5H), 6.88 (m, 5H), 7.00 (s, 2H), 7.10 (dd, *J* = 8.6, 7.4 Hz, 3H), 7.16 (m, 6H), 7.33 (ddd, *J* = 8.0, 7.1, 1.1 Hz, 2H), 7.40 (ddd, *J* = 8.1, 7.0, 1.2 Hz, 2H), 7.64 (d, *J* = 7.9 Hz, 2H), 7.70 (d, *J* = 8.0 Hz, 2H); ^{13}C-NMR (δ, $CDCl_3$, 100 MHz) 28.5 (t), 29.1 (t), 55.0 (q), 55.2 (q), 65.0 (t), 65.0 (t), 104.5 (d), 109.8 (d), 114.6 (d), 114.7 (d), 120.4 (d), 120.5 (d), 120.6 (d), 123.5 (d), 125.7 (d), 126.2 (d), 127.0 (d), 127.3 (d), 127.7 (d), 128.6 (d), 128.7 (s), 129.1 (d), 129.1 (d), 129.2 (s), 131.4 (s), 133.3 (s), 134.6 (s), 134.7 (s), 142.2 (s), 142.7 (s), 155.8 (s), 156.6 (s), 159.0 (s), 159.0 (s); HRMS (ESI) *m/z* calcd. for $C_{59}H_{52}O_6Na$ $(M+Na)^+$ 879.3662, found 879.3663.



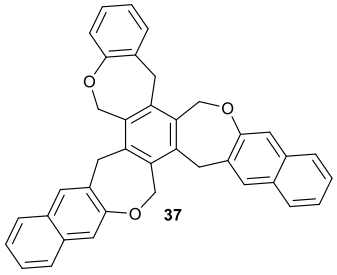
Preparation of 2-(3,5-bis(2-methoxybenzyl)-2,4,6-tris(phenoxymethyl)benzyl)-3-methoxynaphthalene (34). The general procedure for the Negishi cross-coupling reaction was applied to the di-coupling product **32** (126 mg, 0.18 mmol) using two equivalents of the organozinc **11** (0.25 M, 1.5 mL, 0.37 mmol) and the $PdCl_2[Amphos]_2$ as catalyst (6.5 mg, 0.09 mmol) to obtain the tris(diarylmethane) **34** as a colorless oil (99 mg, 67% yield). ^{1}H-NMR (δ, $CDCl_3$, 400 MHz) 3.55 (s, 6H), 3.70 (s, 3H), 4.28 (s, 4H), 4.37 (s, 2H), 4.83 (s, 4H), 4.87 (s, 2H), 6.68 (dd, *J* = 8.5, 0.8 Hz, 4H), 6.75 (dd, *J* = 7.7, 7.6 Hz, 4H), 6.87 (m, 7H), 7.00 (s, 1H), 7.17 (m, 9H), 7.34 (ddd, *J* = 8.0, 7.0, 1.1 Hz, 1H), 7.41 (ddd, *J* = 8.1, 7.0, 1.2 Hz, 1H), 7.63 (d, *J* = 7.9 Hz, 1H), 7.71 (d, *J* = 8.0 Hz, 1H); ^{13}C-NMR (δ, $CDCl_3$, 100 MHz) 28.5 (t), 29.1 (t), 55.0 (q), 55.2 (q), 65.0 (t), 65.1 (t), 104.5 (d), 109.7 (d), 114.7 (d), 114.8 (d), 120.4 (d), 120.5 (d), 120.6 (d), 123.5 (d), 125.7 (d), 126.2 (d), 127.0 (d), 127.3 (d), 127.7 (d), 128.6 (d), 128.7 (s), 129.1 (d), 129.1 (d), 129.2 (s), 131.4 (s), 133.3 (s), 134.5 (s), 134.6 (s), 142.0 (s), 142.5 (s), 155.8 (s), 156.6 (s), 159.0 (s), 159.0 (s); HRMS (ESI) *m/z* calcd. for $C_{55}H_{50}O_6Na$ $(M+Na)^+$ 829.3505, found 829.3503.



Preparation of 2-(2,4,6-tris(bromomethyl)-3-(2-hydroxybenzyl)-5-((3-hydroxynaphthalen-2-yl)methyl)benzyl)naphthalen-1-ol (35). The general procedure for deprotection of the methyl ethers was applied to the tris(diarylmethane) **33** (80 mg, 0.093 mmol) to obtain the triphenol derivative **35** as a light brown oil (65 mg, 89% yield). ^{1}H-NMR (δ, $CDCl_3$, 400 MHz) 4.27 (s, 2H), 4.30 (s, 4H), 4.42 (s, 2H), 4.53 (s, 4H), 5.32 (br s, 1H), 5.67 (br s, 2H), 6.58 (d, *J* = 6.8 Hz, 1H), 6.83 (dd, *J* = 8.3, 8.2 Hz, 2H), 6.87 (s, 2H), 7.10 (ddd, *J* = 7.8, 7.8, 1.2 Hz, 1H), 7.15 (s, 2H), 7.29 (ddd, *J* = 7.5, 7.5, 1.1 Hz, 2H), 7.37 (ddd, *J* = 7.5, 7.5, 1.1 Hz, 2H), 7.50 (d, *J* = 8.1 Hz, 2H), 7.64 (d, *J* = 8.1 Hz, 2H); ^{13}C-NMR (δ, $CDCl_3$, 100 MHz) 28.7 (t), 28.7 (t), 29.3 (t), 109.5 (d), 115.3 (d), 121.1 (d), 123.9 (d), 125.5 (s), 125.9 (d), 126.2 (d), 126.9 (d), 127.2 (d), 127.4 (d), 127.9 (d), 128.3 (s), 128.9 (s), 133.5 (s), 136.5 (s), 136.6 (s), 140.3 (s), 140.6 (s), 152.2 (s), 153.6 (s); HRMS (ESI) *m/z* calcd. for $C_{38}H_{30}O_3{}^{79}Br^{81}Br_2$ $(M\text{-}H)^+$ 774.9704, found 774.9722.

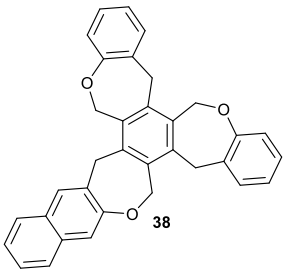


Preparation of 2,2'-((2,4,6-tris(bromomethyl)-5-((3-hydroxynaphthalen-2-yl)methyl)-1,3-phenylene)bis(methylene))diphenol (36). The general procedure for deprotection of the methyl ethers was applied to the tris(diarylmethane) **34** (120 mg, 0.149 mmol) to obtain the triphenol derivative **36** as a light brown oil (93 mg, 86% yield). ^{1}H-NMR (δ, $CDCl_3$, 400 MHz) 4.26 (s, 4H), 4.30 (s, 2H), 4.39 (s, 4H), 4.50 (s, 2H), 5.22 (br s, 2H), 5.56 (br s, 1H), 6.51 (dd, *J* = 7.8, 1.0 Hz, 2H), 6.82 (m, 5H), 7.10 (ddd, *J* = 7.6, 7.6, 1.2 Hz, 2H), 7.16 (s, 1H), 7.29 (ddd, *J* = 8.0, 6.9, 1.1 Hz, 1H), 7.38 (ddd, *J* = 8.1, 7.0, 1.2 Hz, 1H), 7.47 (d, *J* = 8.0 Hz, 1H), 7.65 (d, *J* = 8.2 Hz, 1H); ^{13}C-NMR (δ, $CDCl_3$, 100 MHz) 28.7 (t), 28.8 (t), 29.2 (t), 109.5 (d), 115.2 (d), 121.1 (d), 123.9 (d), 125.4 (s), 125.9 (d), 126.2 (d), 126.9 (d), 127.2 (d), 127.4 (d), 127.9 (d), 128.2 (s), 128.9 (s), 133.4 (s), 136.4 (s), 140.1 (s), 140.5 (s), 152.2 (s), 153.6 (s); HRMS (ESI) *m/z* calcd. for $C_{34}H_{28}O_3{}^{79}Br_2{}^{81}Br$ $(M\text{-}H)^+$ 722.9568, found 722.9565.



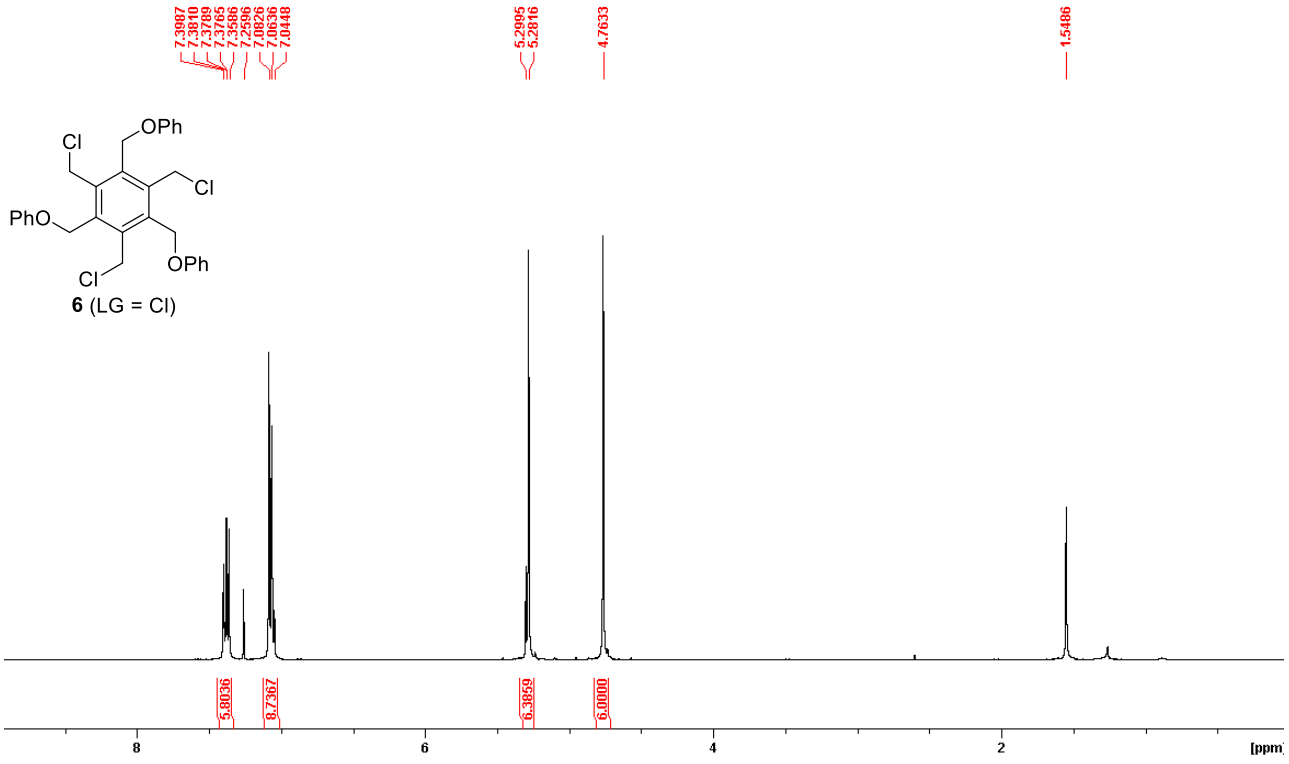
Preparation of the BCT analogue 37. The general procedure for the cyclization was applied to the triphenol derivative **35** (39 mg, 0.05 mmol) to obtain the BCT analogue **37** (9.4 mg, 35% yield) as a white solid: mp 205-209 ºC; ^{1}H-NMR (δ, $CDCl_3$, 400 MHz) 4.42 (s, 2H), 4.59 (s, 4H), 5.61 (s, 2H), 5.62 (s, 2H), 5.69 (s, 2H), 6.73 (dd, *J* = 8.1, 1.1 Hz, 1H), 6.82 (ddd, *J* = 7.4, 7.4, 1.2 Hz, 1H), 7.08 (m, 2H), 7.14 (s, 1H), 7.16 (s, 1H), 7.27 (m, 2H), 7.32 (m, 2H), 7.59 (dd, *J* = 8.8, 8.8 Hz, 4H), 7.67 (d, *J* = 7.5 Hz, 1H), 7.71 (d, *J* = 7.8 Hz, 1H); ^{13}C-NMR (δ, $CDCl_3$, 100 MHz) 34.1 (t), 34.6 (t), 34.7 (t), 64.9 (t), 65.7 (t), 65.8 (t), 114.2 (d), 119.1 (d), 121.0 (d), 123.1 (s), 123.9 (d), 126.0 (d), 126.1 (s), 126.1 (d), 127.0 (d), 128.6 (d), 129.1 (s), 129.1 (d), 131.1 (d), 131.1 (s), 131.3 (s), 131.3 (s), 134.1

(s), 139.8 (s), 140.0 (s), 140.7 (s), 154.6 (s), 156.3 (s); HRMS (ESI) *m/z* calcd. for $C_{38}H_{28}O_3Na$ $(M+Na)^+$ 555.1936, found 555.1941.



38

Preparation of the BCT analogue 38. The general procedure for the cyclization was applied to the triphenol derivative **36** (47 mg, 0.06 mmol) to obtain the BCT analogue **38** (15 mg, 50% yield) as a white solid: mp 260-263 ºC; ^{1}H-NMR (δ, $CDCl_3$, 400 MHz) 4.43 (s, 4H), 4.61 (s, 2H), 5.56 (s, 2H), 5.63 (s, 2H), 5.64 (s, 2H), 6.72 (ddd, *J* = 7.7, 6.4, 1.2 Hz, 2H), 6.81 (ddd, *J* = 7.4, 7.4, 1.2 Hz, 1H), 6.82 (ddd, *J* = 7.4, 7.4, 1.2 Hz, 1H), 7.08 (m, 4H), 7.14 (s, 1H), 7.27 (ddd, *J* = 8.1, 6.8, 1.2 Hz, 1H), 7.33 (ddd, *J* = 8.1, 6.8, 1.3 Hz, 1H), 7.58 (d, *J* = 8.1 Hz, 1H), 7.60 (s, 1H), 7.69 (d, *J* = 8.0 Hz, 1H); ^{13}C-NMR (δ, $CDCl_3$, 100 MHz) 34.1 (t), 34.2 (t), 34.7 (t), 64.9 (t), 65.0 (t), 65.7 (t), 114.2 (d), 119.1 (d), 121.0 (d), 123.1 (s), 123.2 (s), 123.9 (d), 126.0 (d), 126.1 (d), 126.1 (s), 127.0 (d), 128.6 (d), 128.6 (d), 129.1 (s), 129.1 (d), 131.0 (s), 131.1 (d), 131.1 (s), 131.2 (s), 134.1 (s), 139.9 (s), 140.6 (s), 140.8 (s), 154.6 (s), 156.3 (s); HRMS (ESI) *m/z* calcd. for $C_{34}H_{26}O_3Na$ $(M+Na)^+$ 505.1780, found 505.1779.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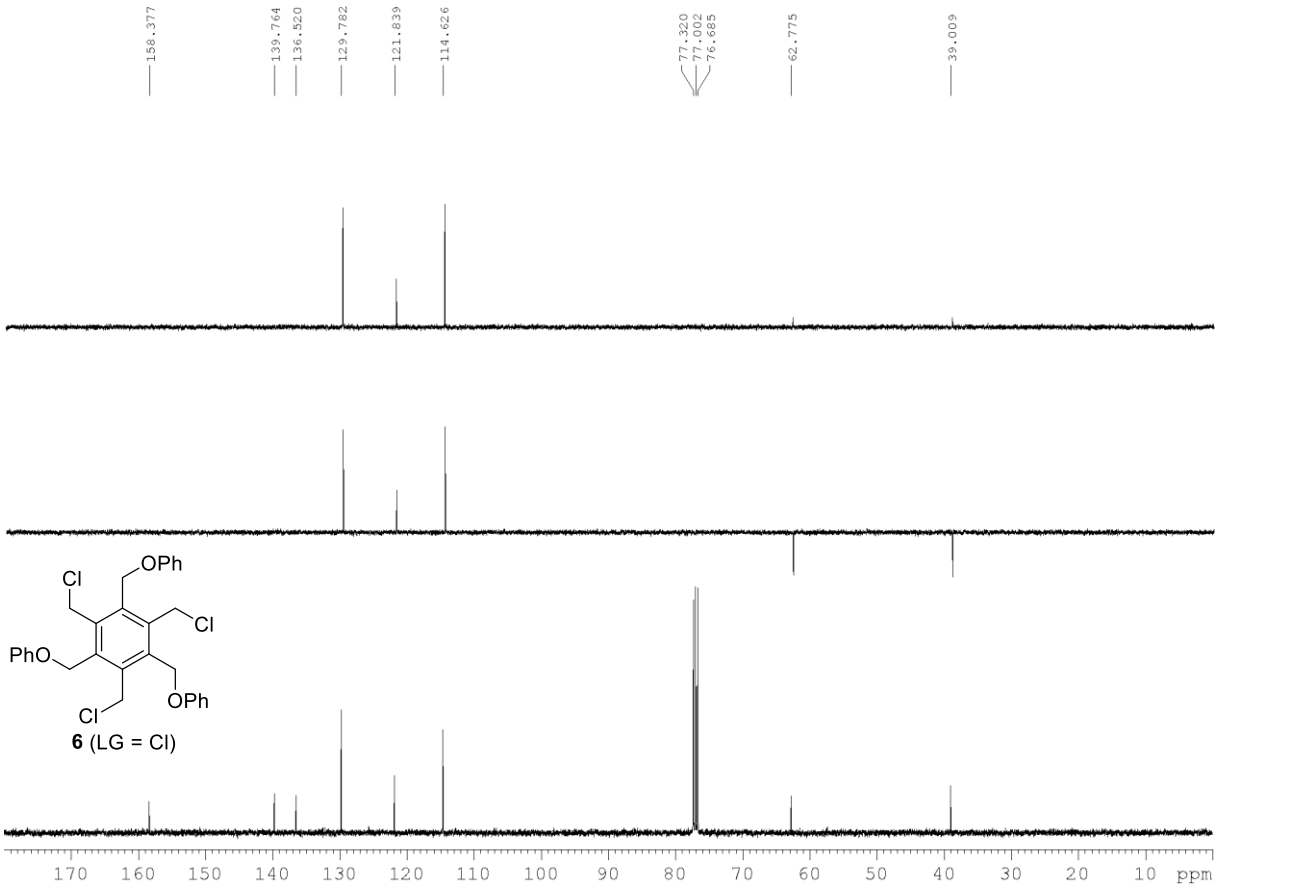
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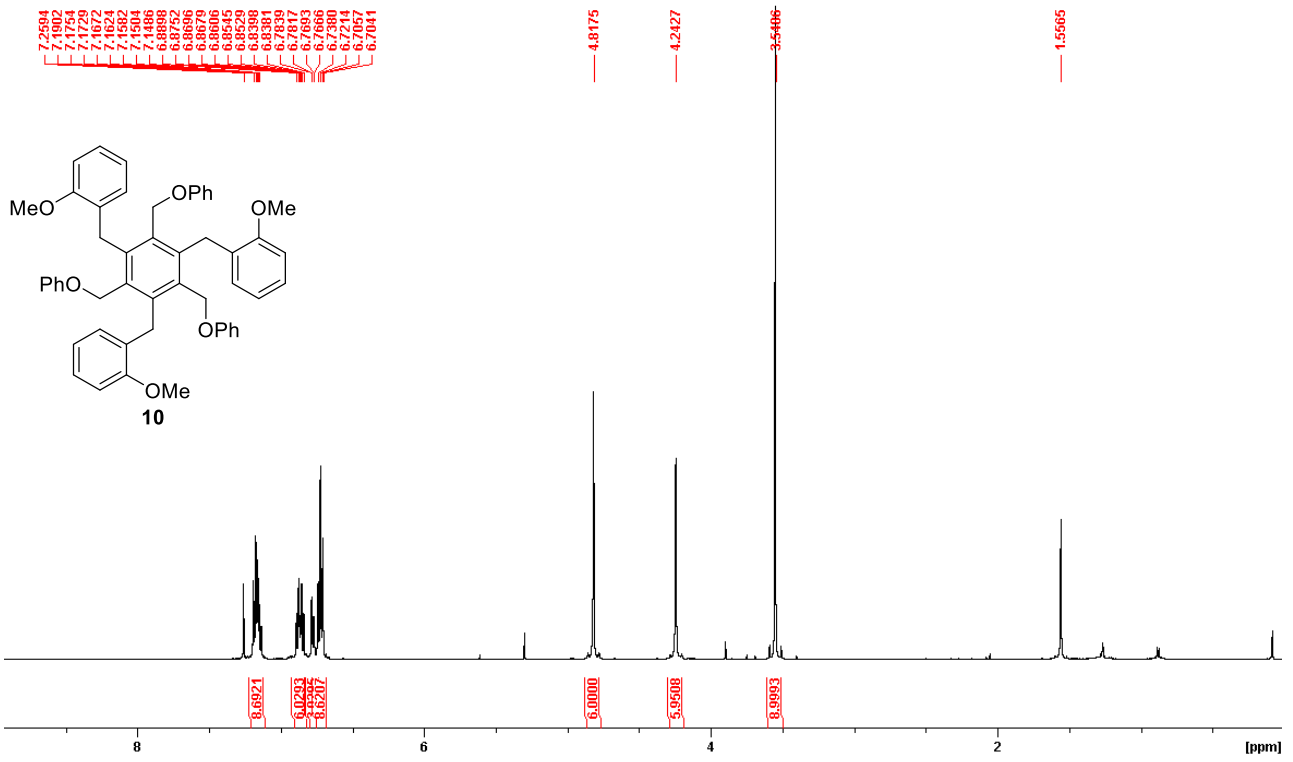
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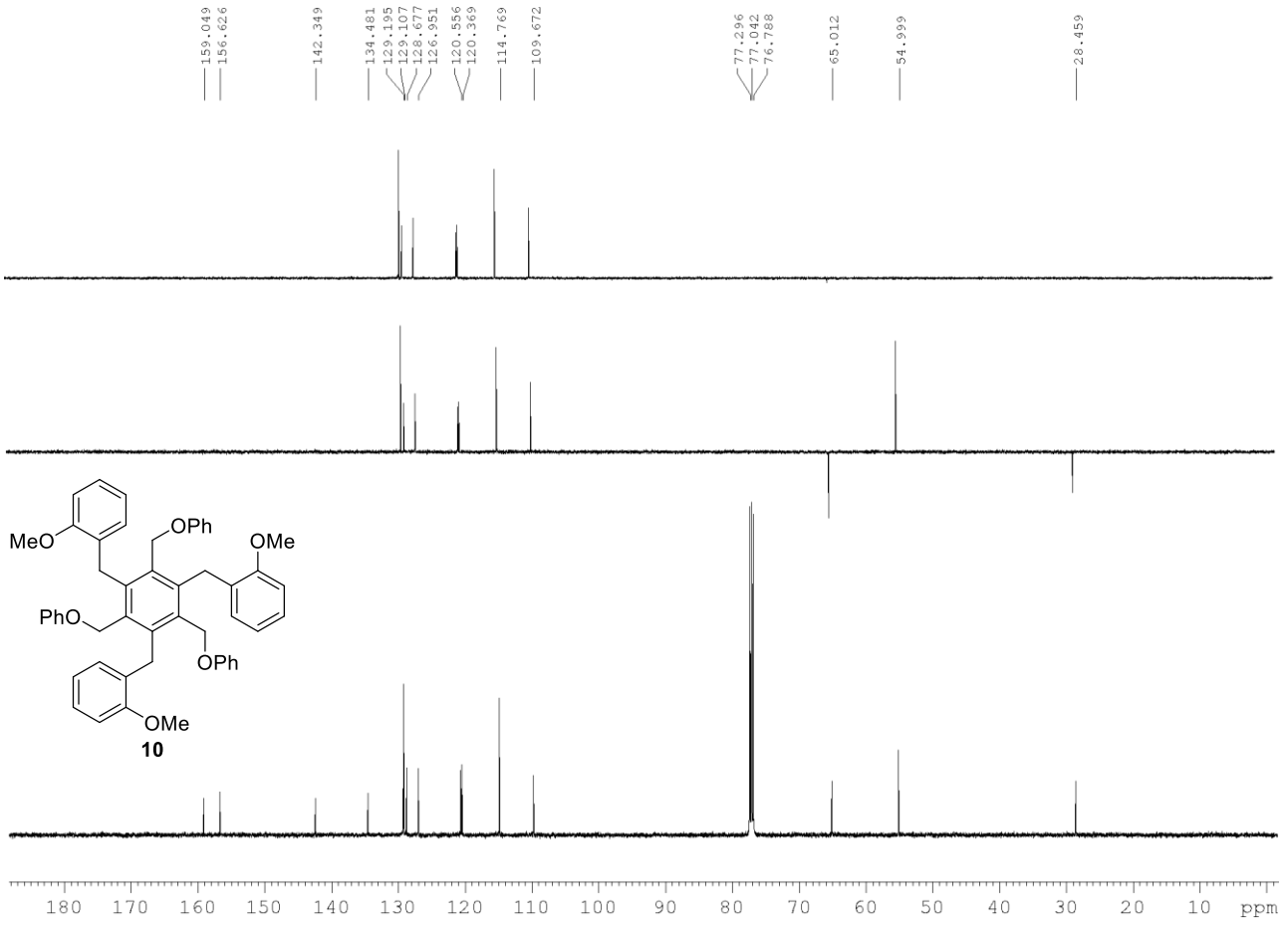
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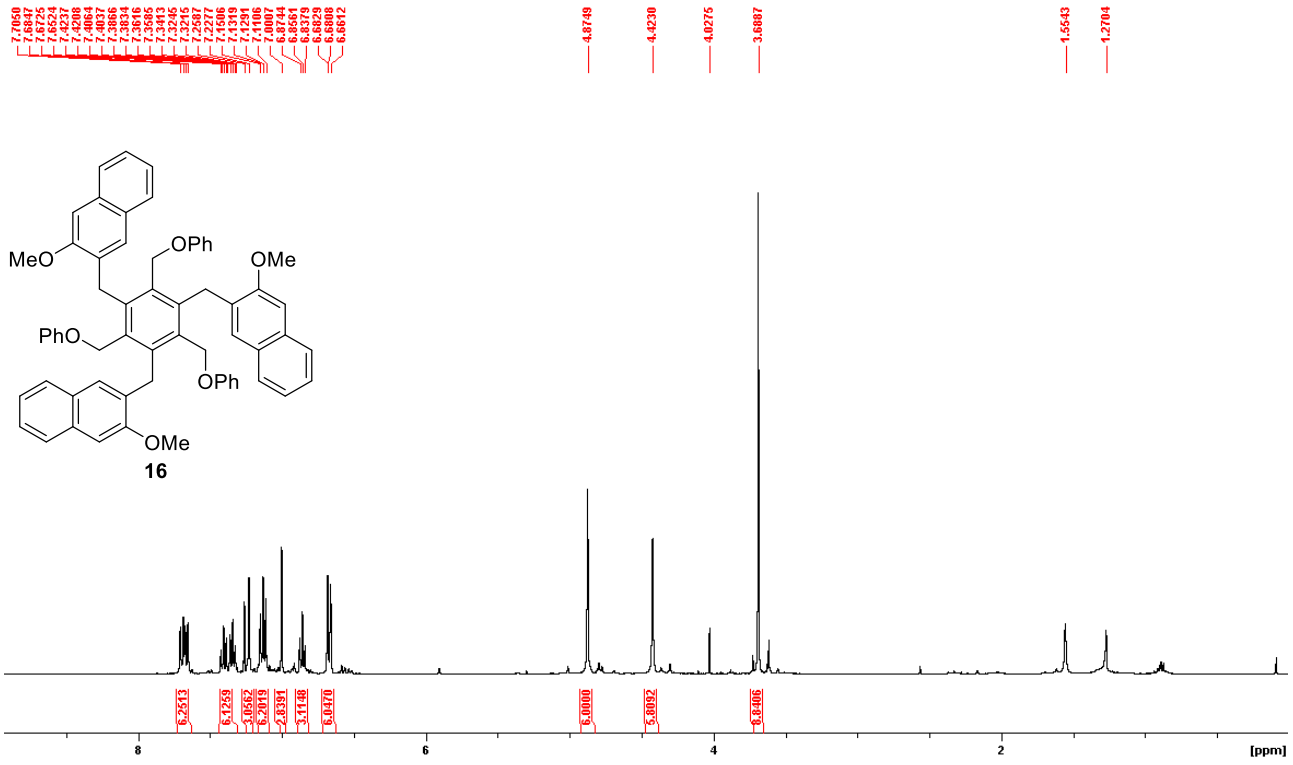
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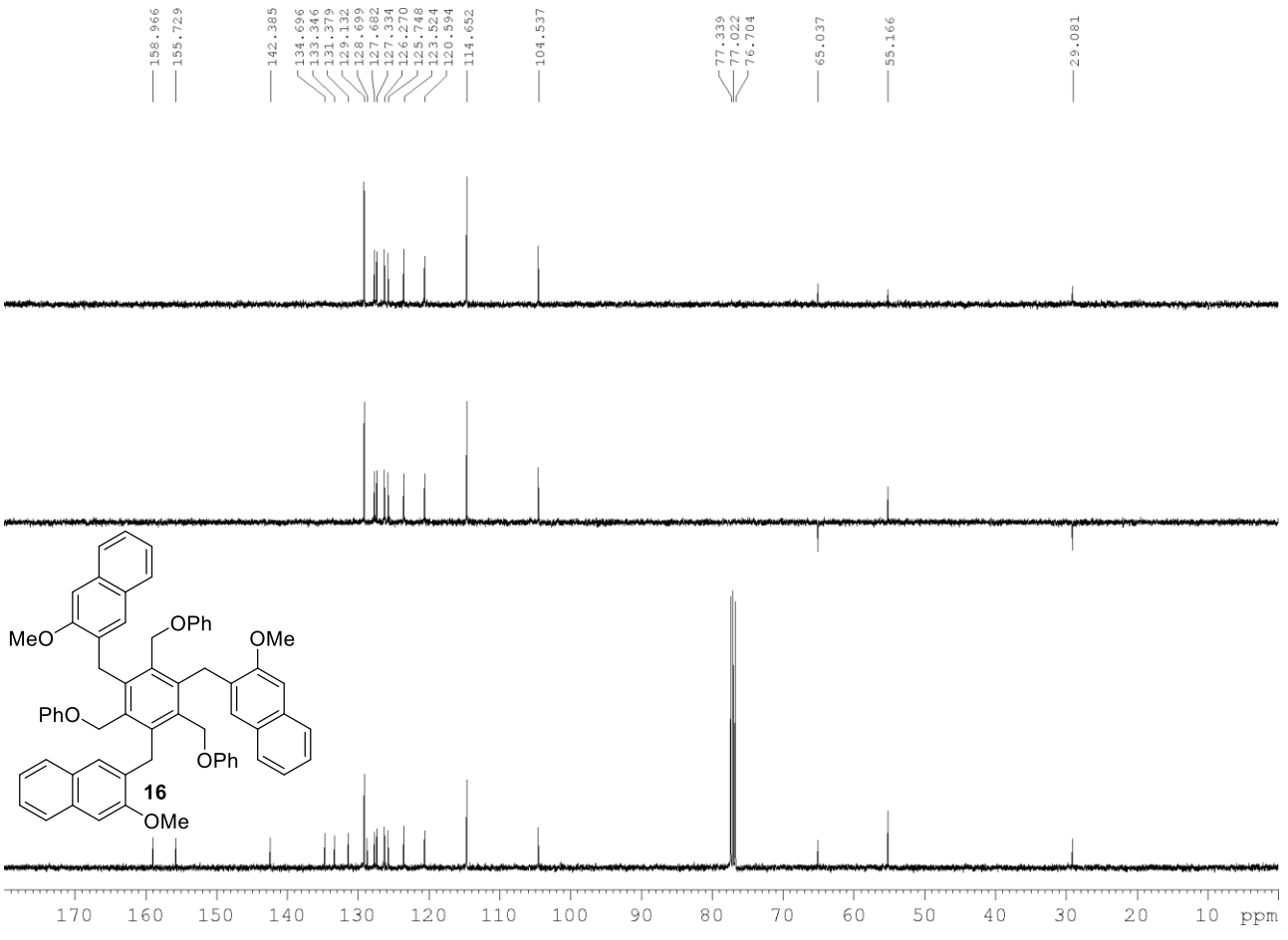
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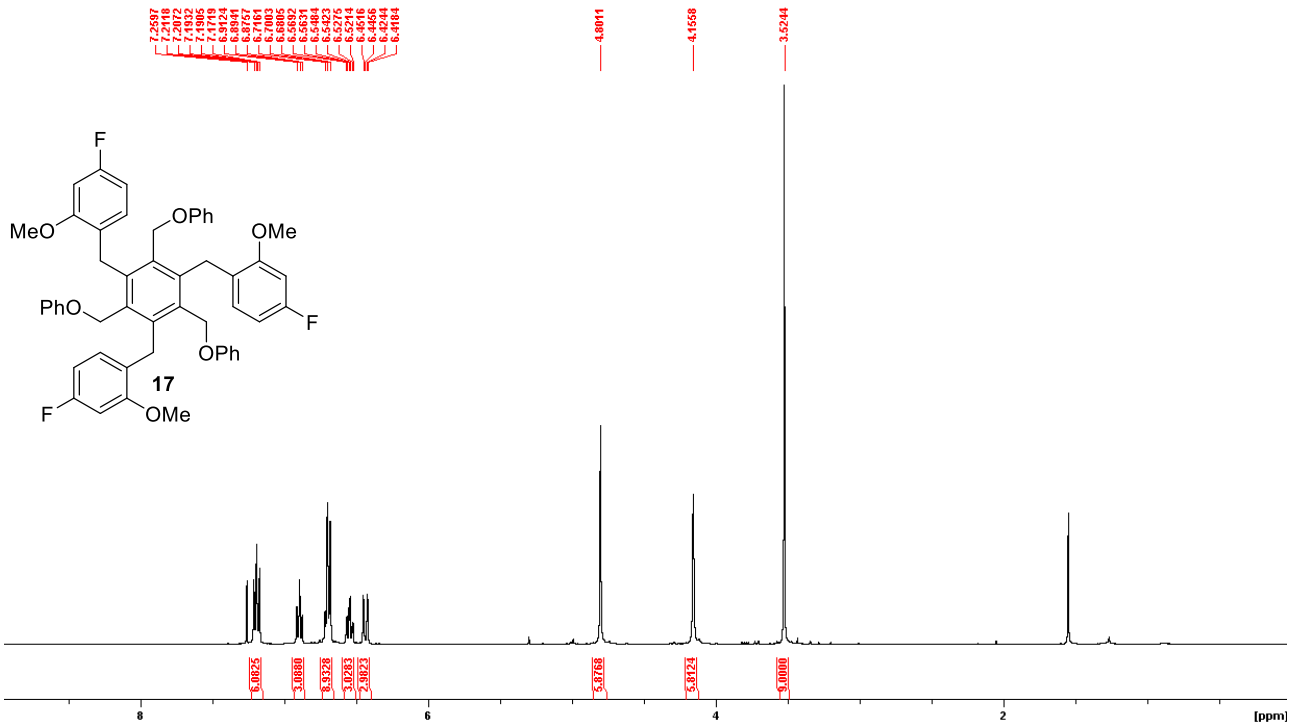
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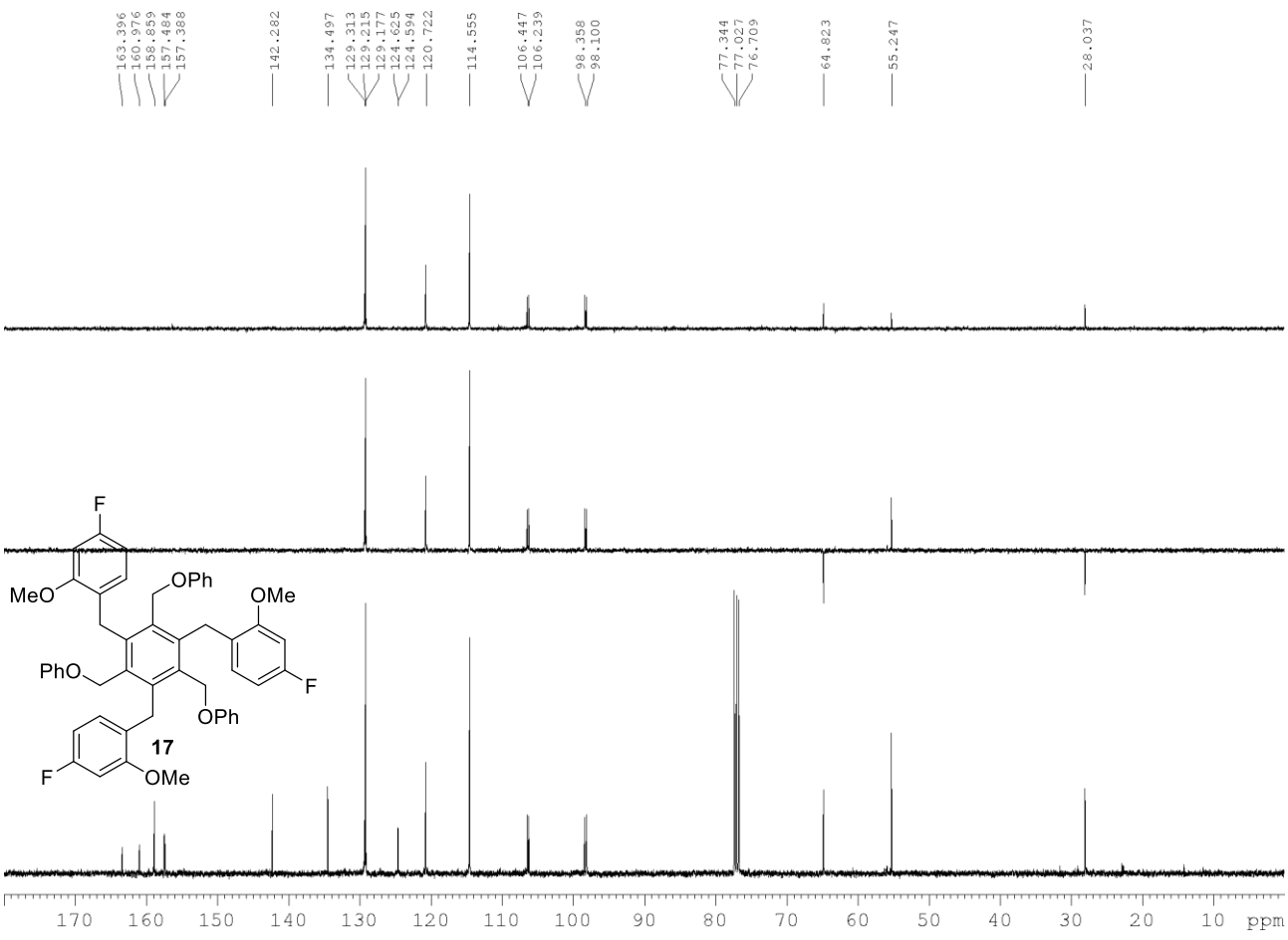
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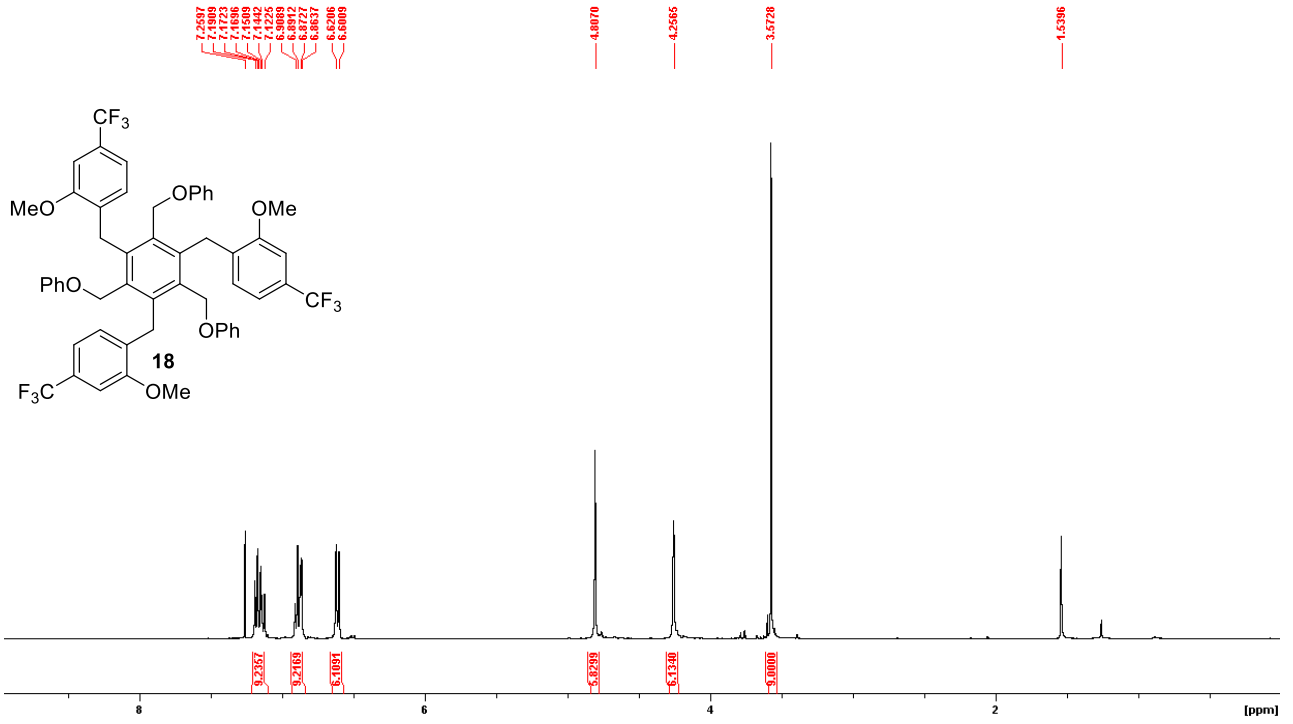
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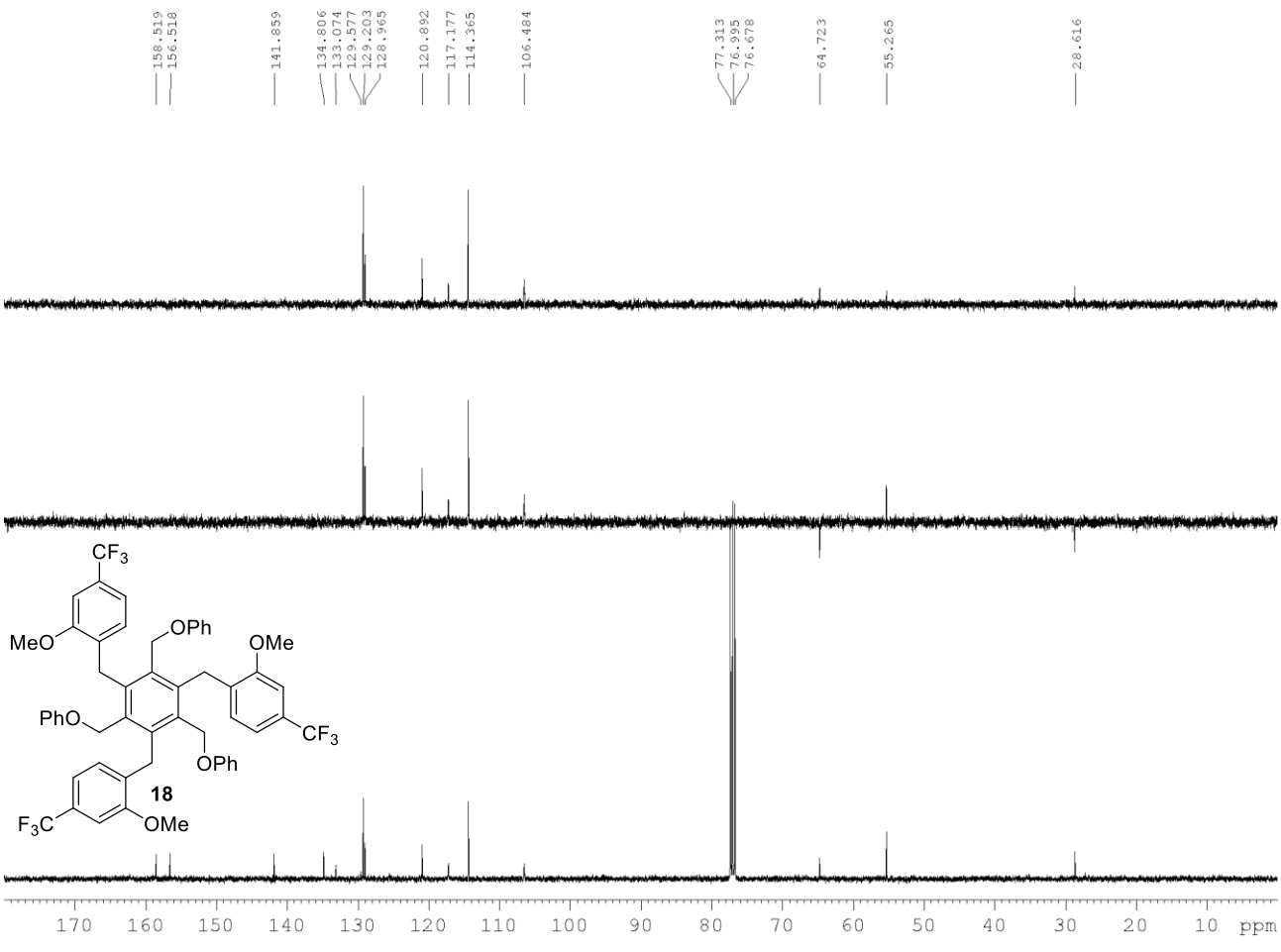
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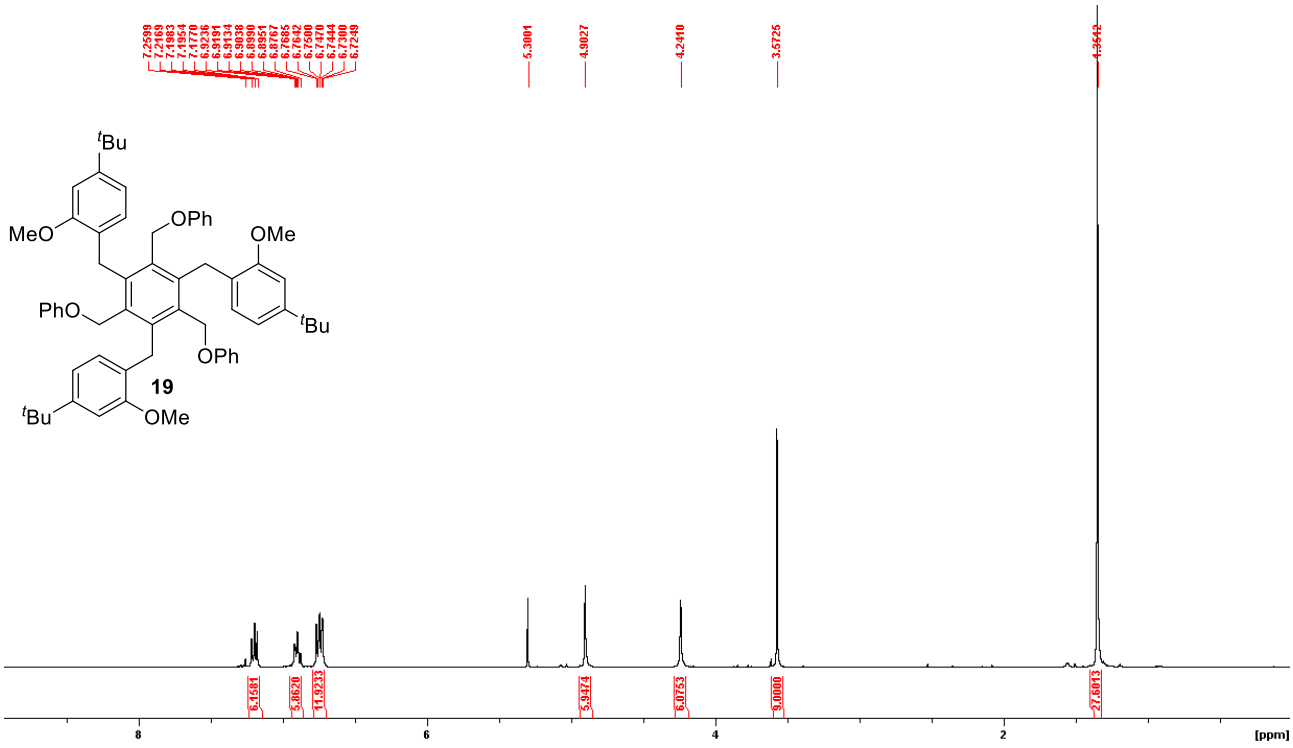
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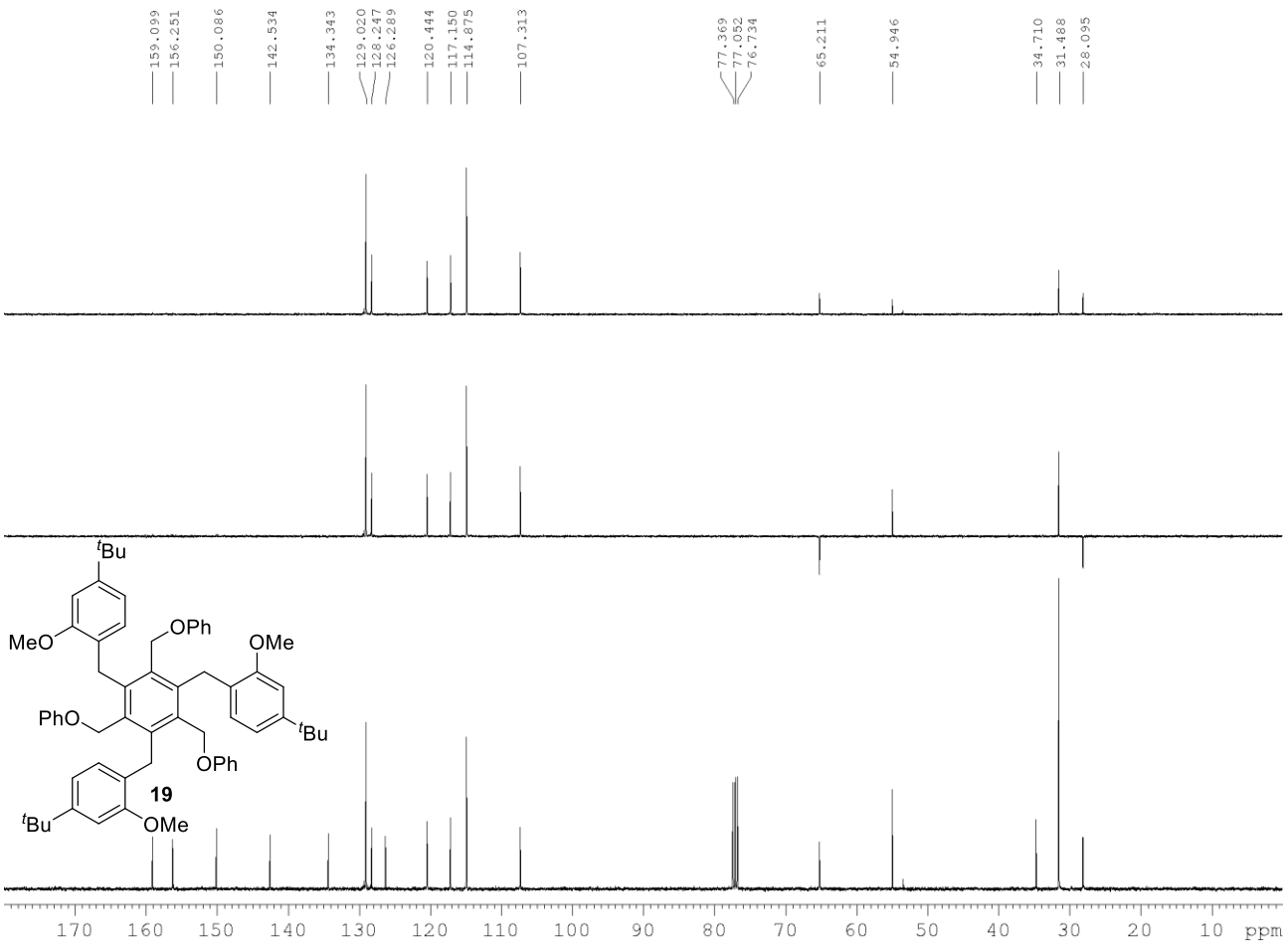
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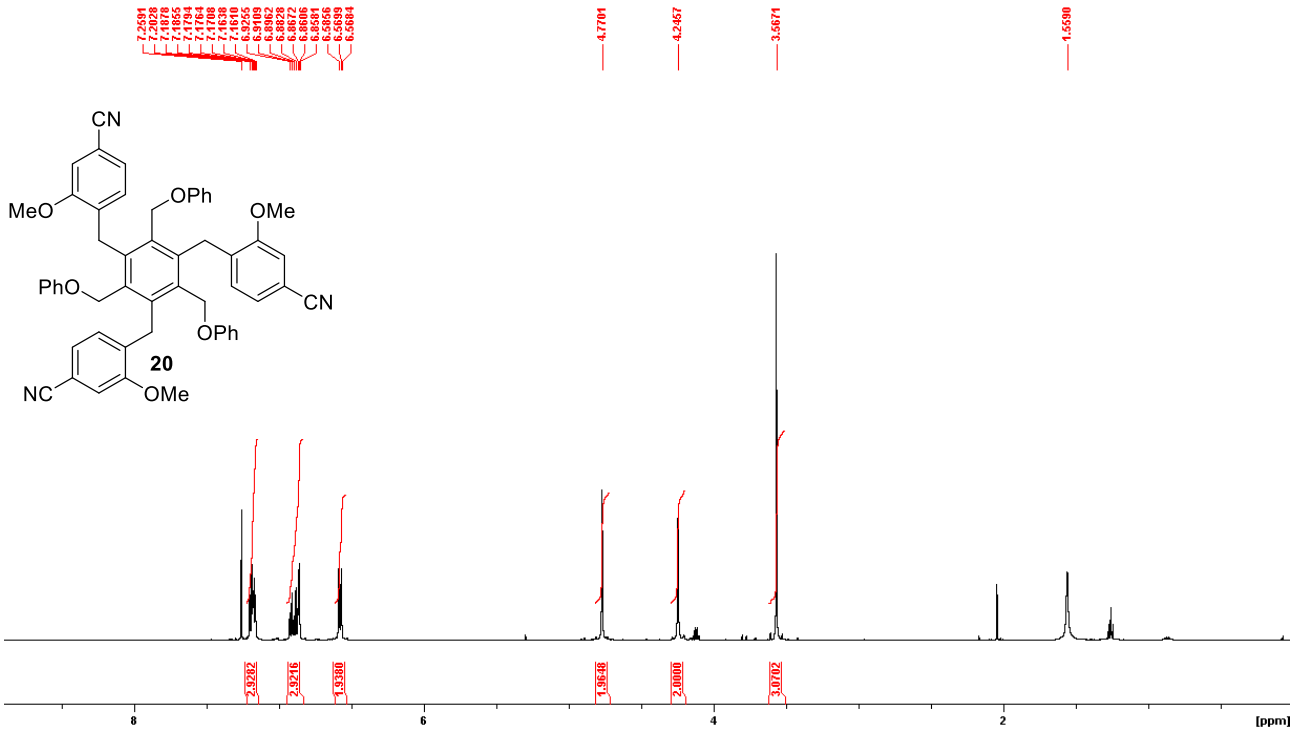
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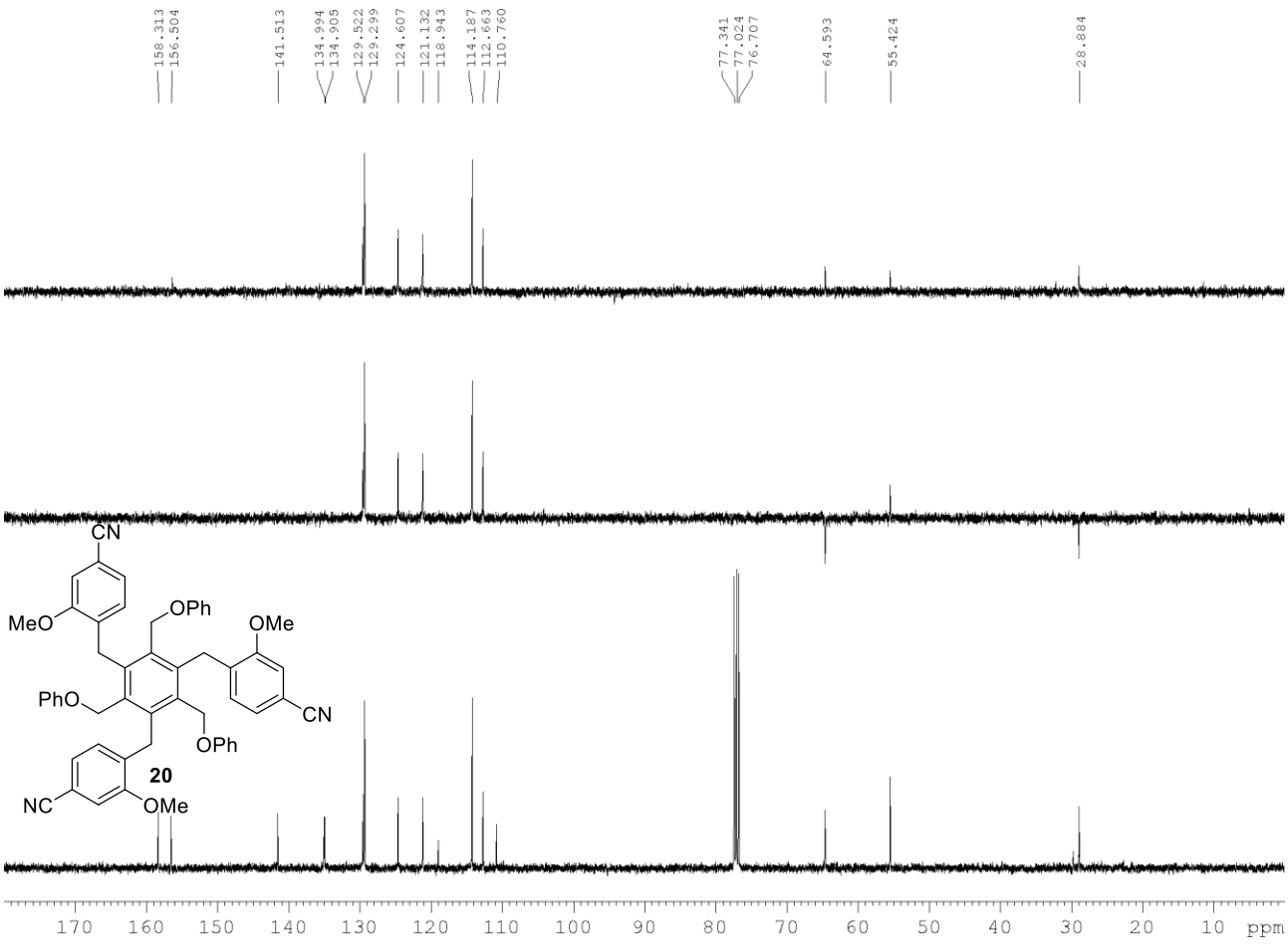
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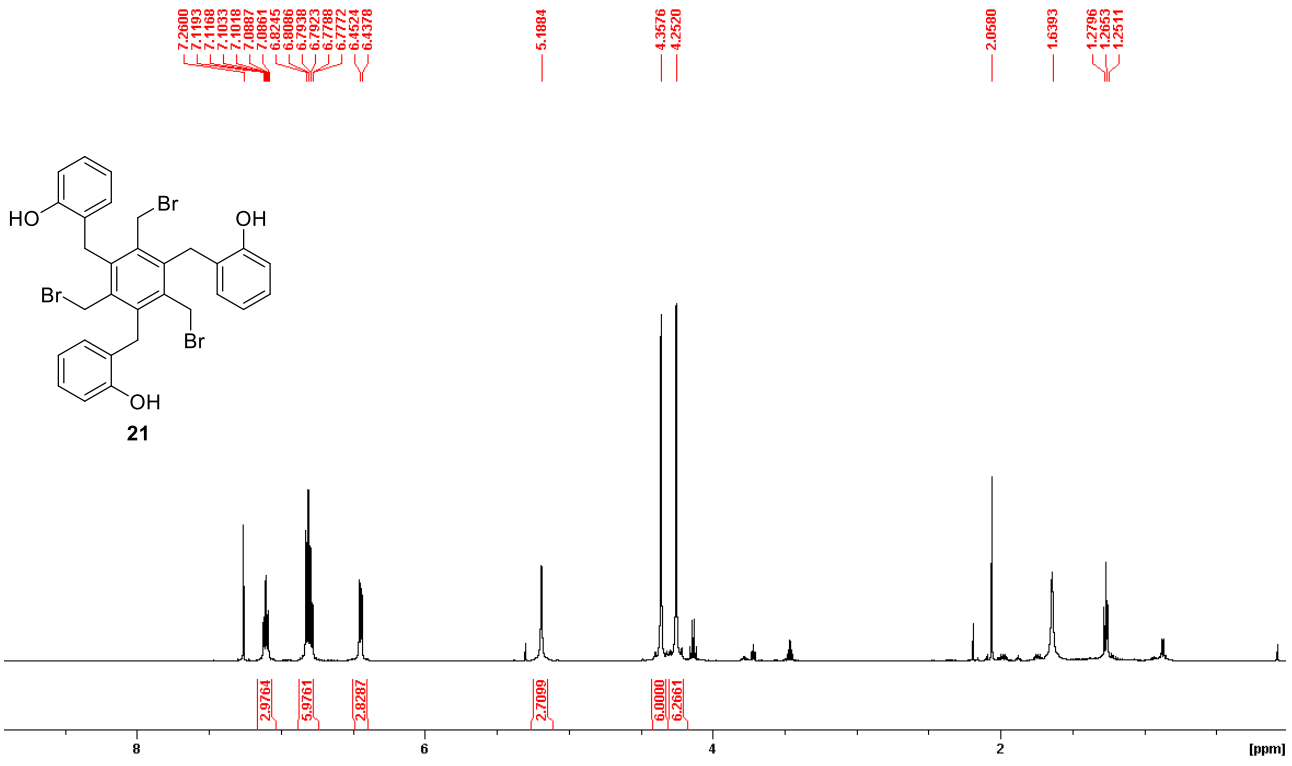
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7.0861
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6.7788
6.7772
6.4524
6.4378
5.1884
4.3576
4.2520
2.0580
1.6393
1.2796
1.2653
1.2511
HO
Br
OH
Br
Br
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6.2661
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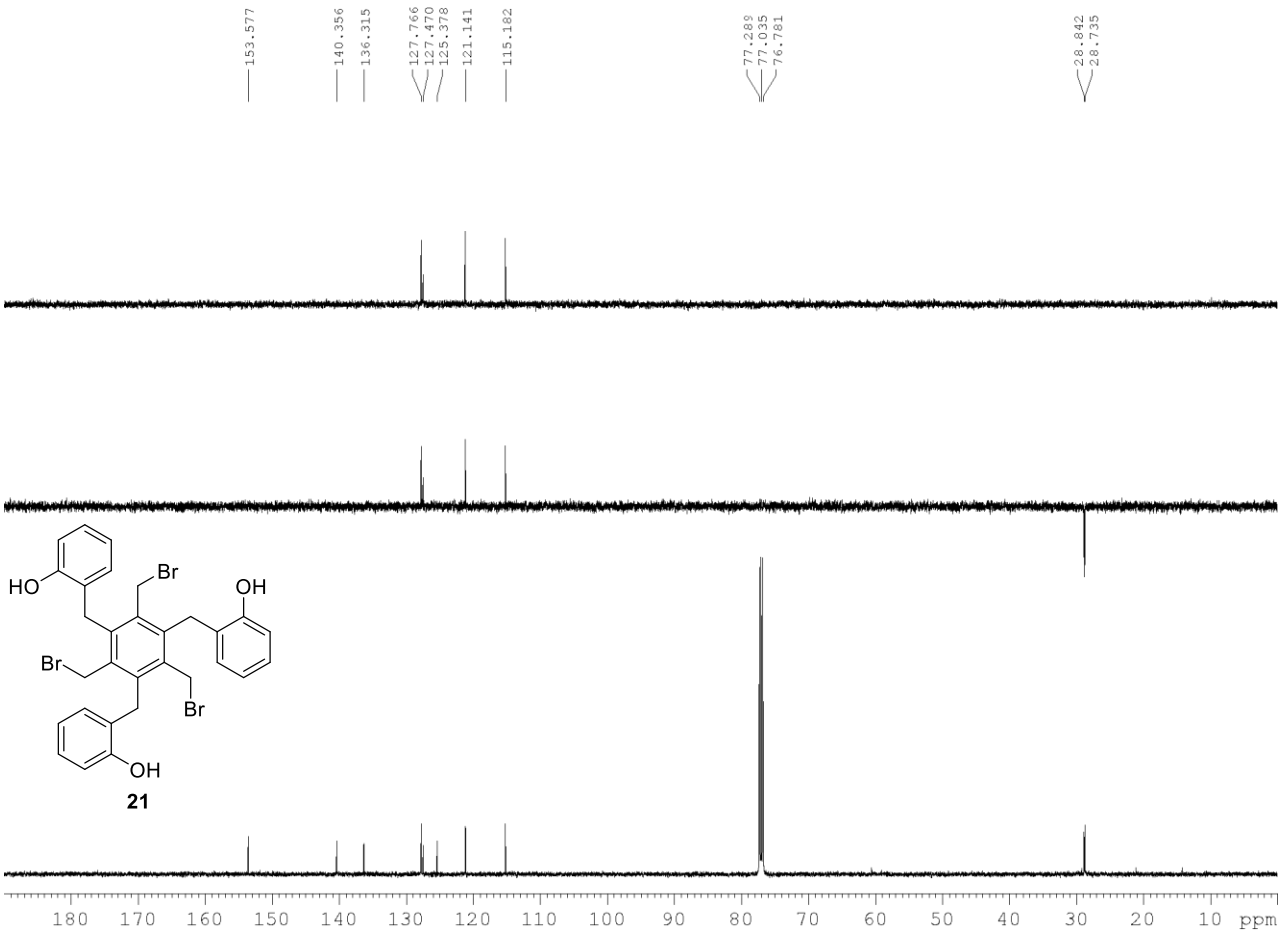
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136.315
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127.470
125.378
121.141
115.182
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76.781
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28.735
HO
Br
OH
Br
Br
OH
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150
140
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110
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70
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20
10
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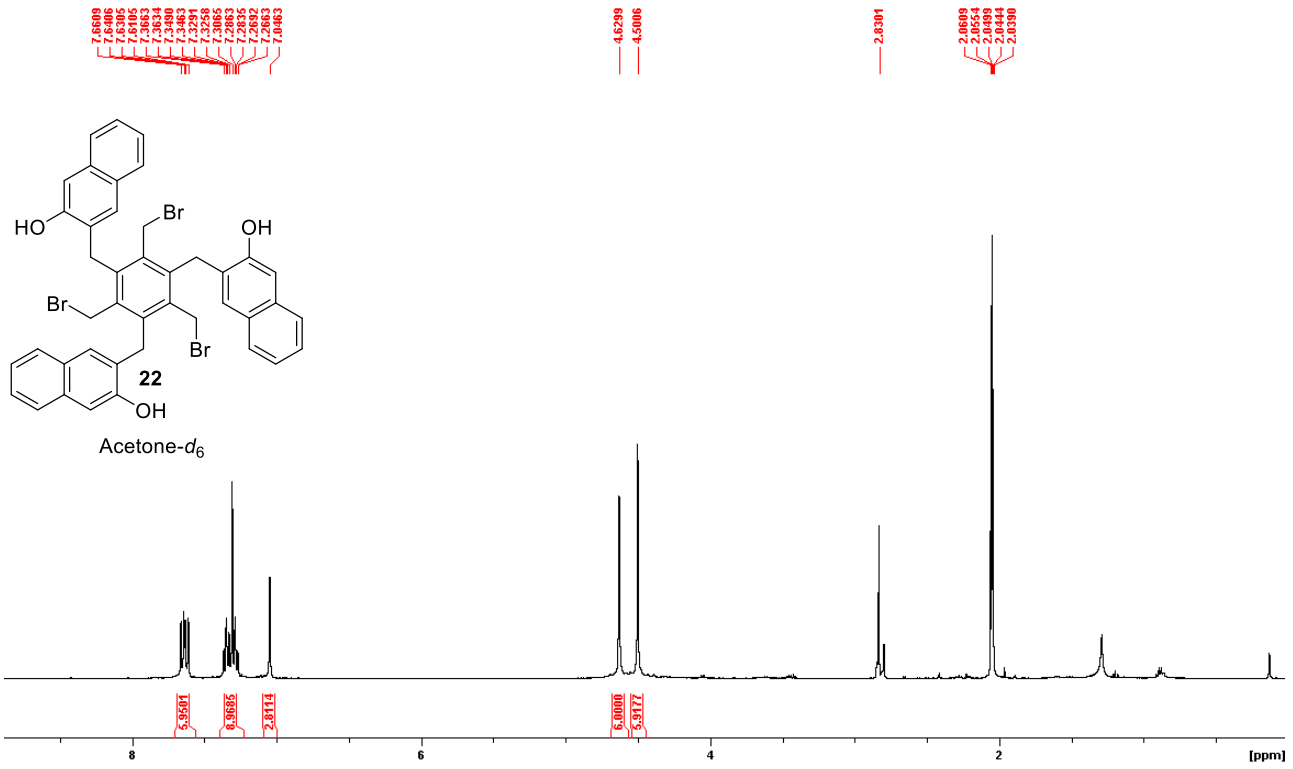
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7.3291
7.3258
7.2865
7.2853
7.2835
7.2692
7.2663
7.0463
4.6239
4.5806
2.8301
2.0609
2.0554
2.0439
2.0344
2.0290
HO
Br
OH
Br
Br
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OH
Acetone-d_6
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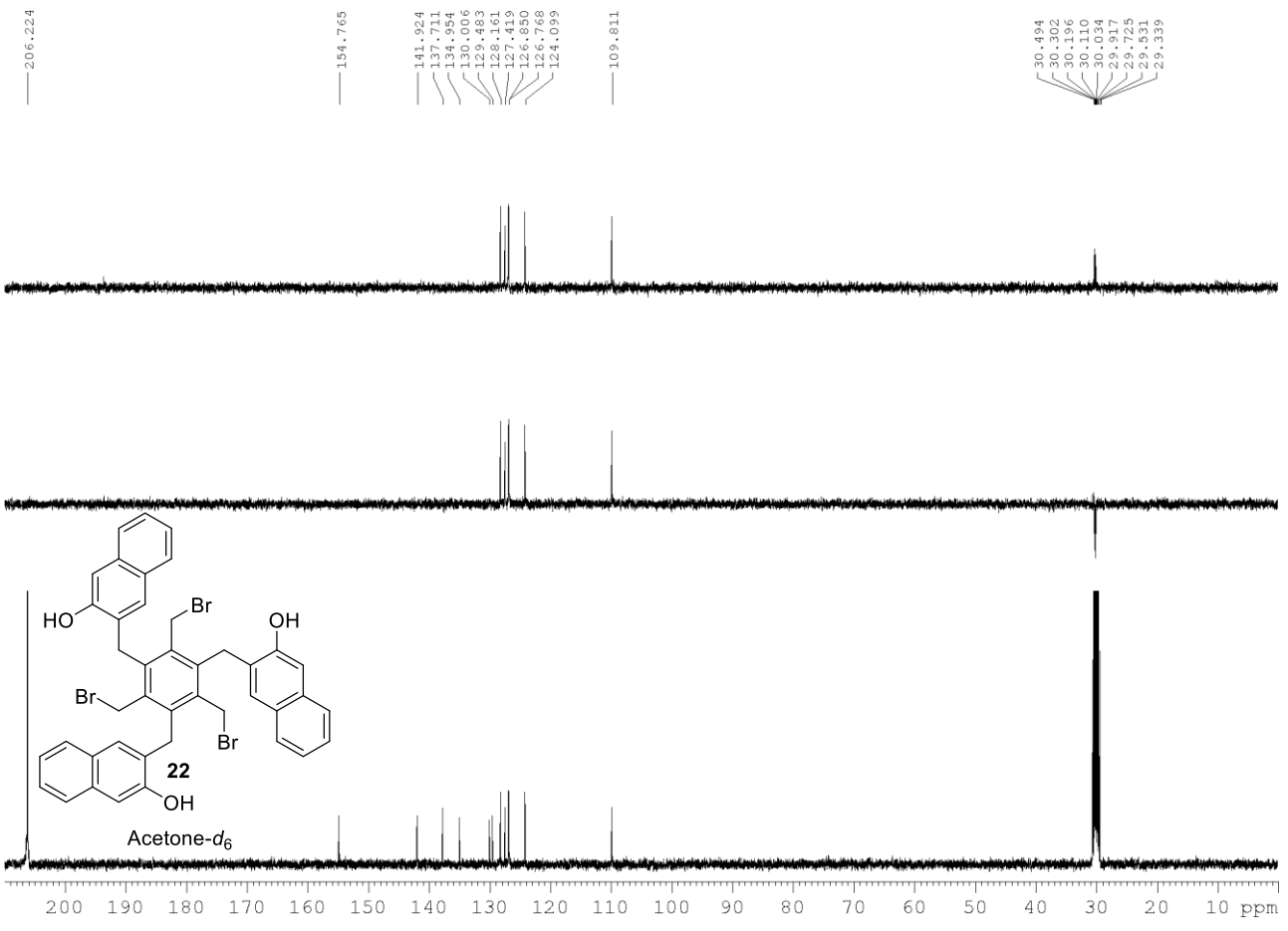
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124.099
109.811
30.494
30.302
30.196
30.110
30.034
29.917
29.725
29.531
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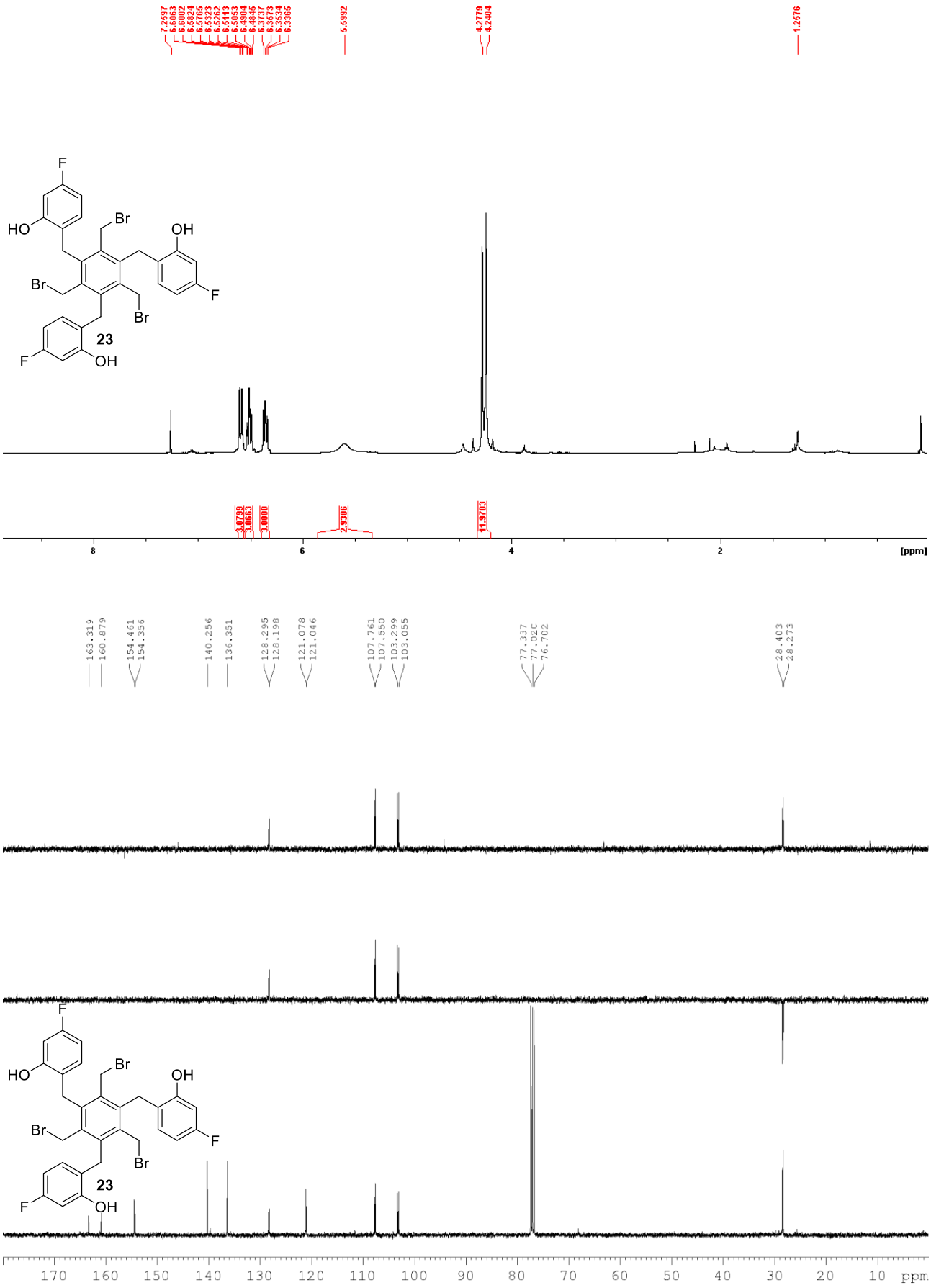
Br
OH
Br
Br
22
OH
Acetone-d_6
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm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6.5113
6.5053
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6.4845
6.3737
6.3573
6.3534
6.3365
5.5992
4.2779
4.2604
1.2576
F
HO
Br
OH
Br
F
Br
23
F
OH
3.0799
3.0663
3.0000
2.9306
11.9703
8
6
4
2
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154.356
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136.351
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103.055
77.337
77.022
76.702
28.403
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150
140
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70
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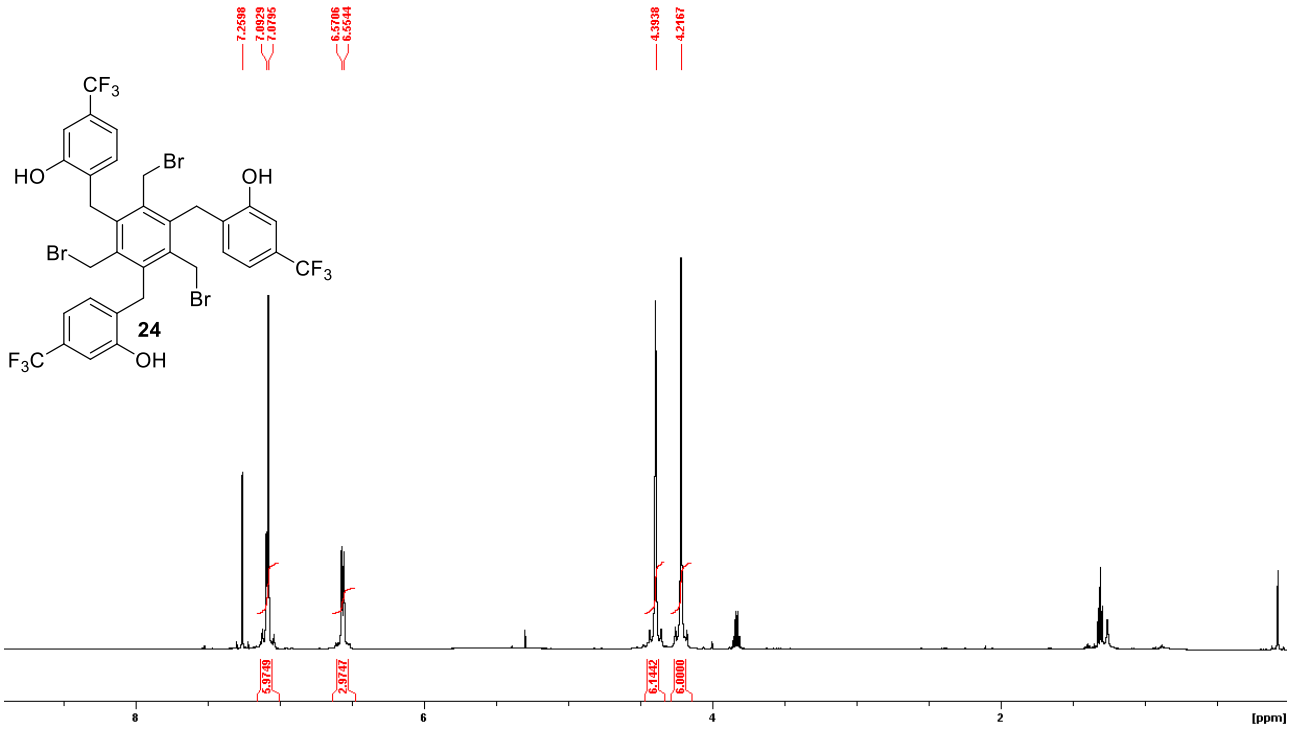
50
40
30
20
10
ppm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7.0795
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HO
Br
OH
Br
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F3C
OH
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4
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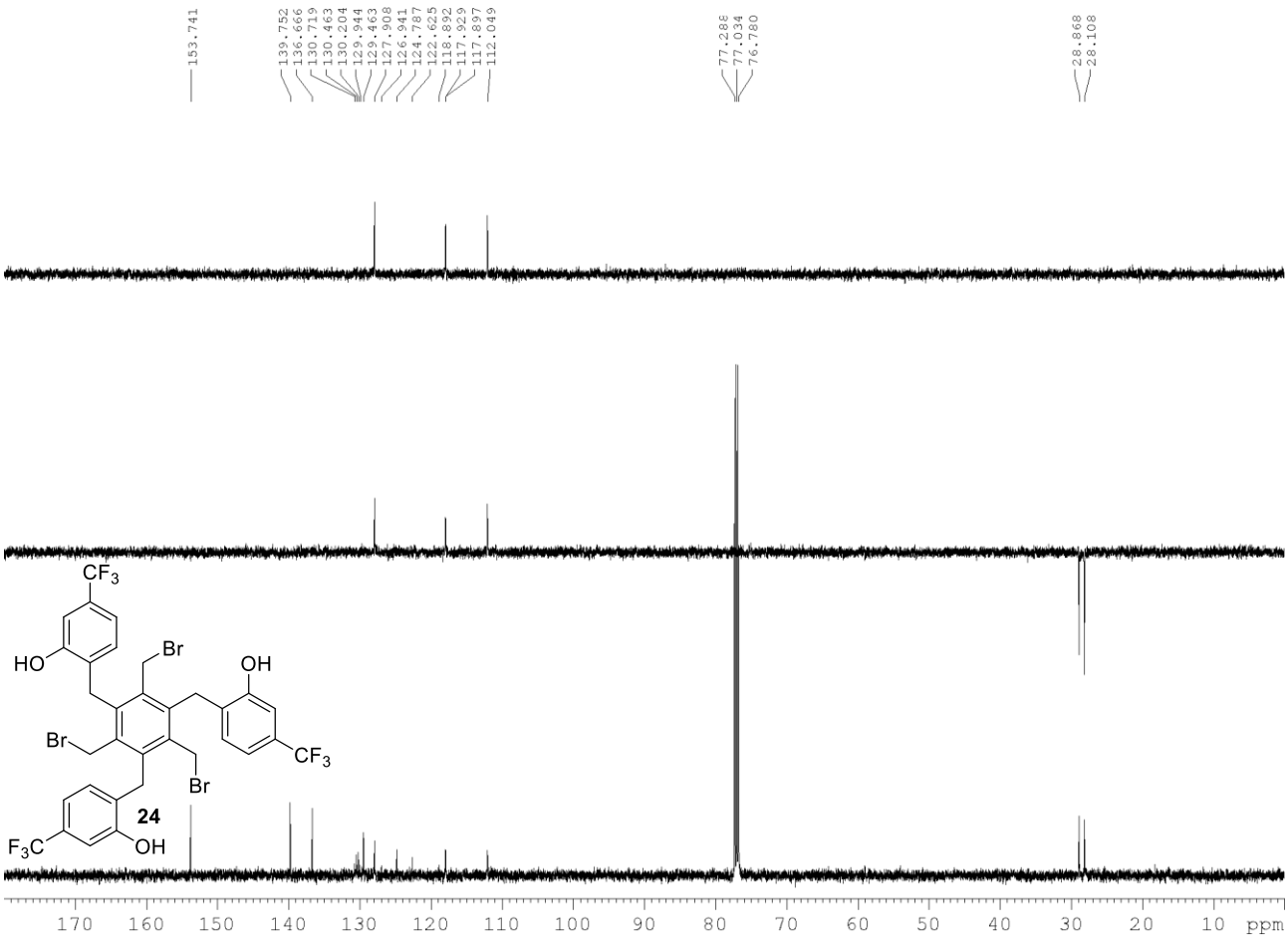
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130.463
130.204
129.944
129.463
127.908
126.941
124.787
122.625
118.892
117.929
117.897
112.049
77.288
77.034
76.780
28.868
28.108
CF3
HO
Br
OH
Br
CF3
Br
24
F3C
OH
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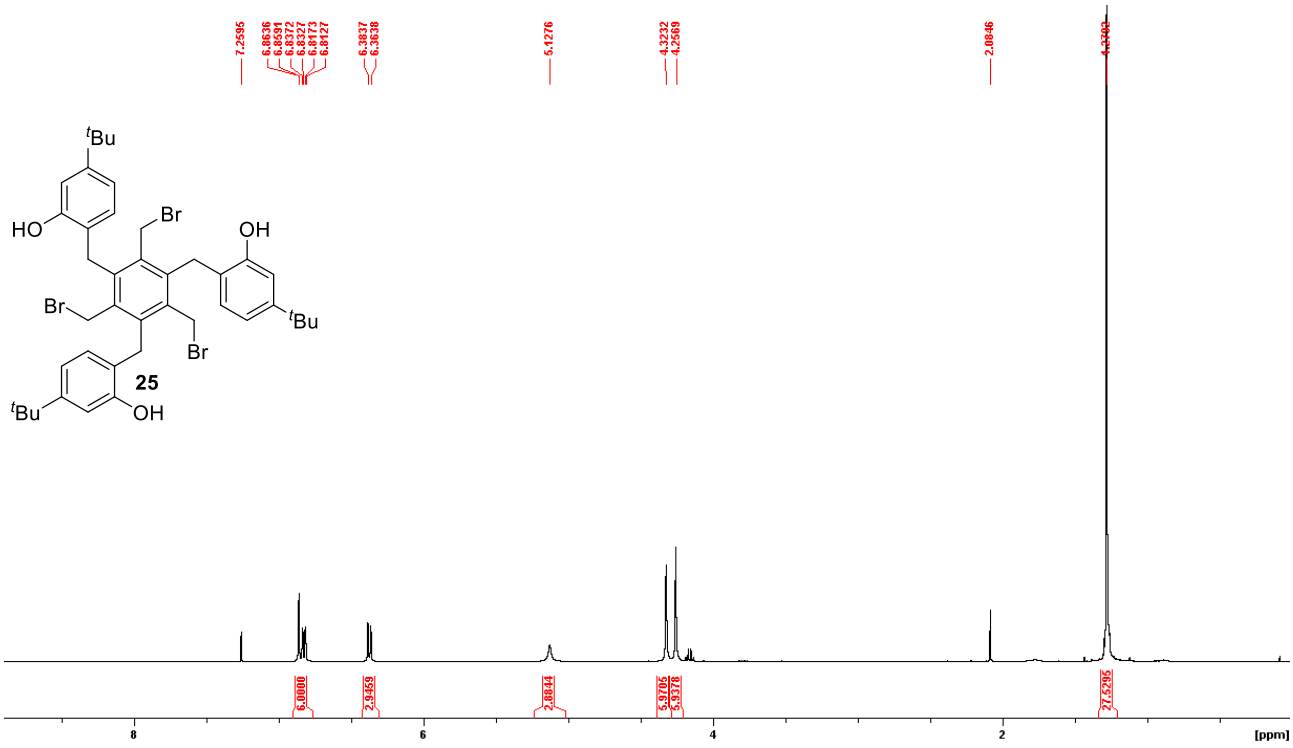
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm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6.8173
6.8127
6.3837
6.3638
5.1276
4.3232
4.2569
2.0846
1.3503
6.0000
2.9459
2.8844
5.9705
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6
4
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OH
Br
tBu
Br
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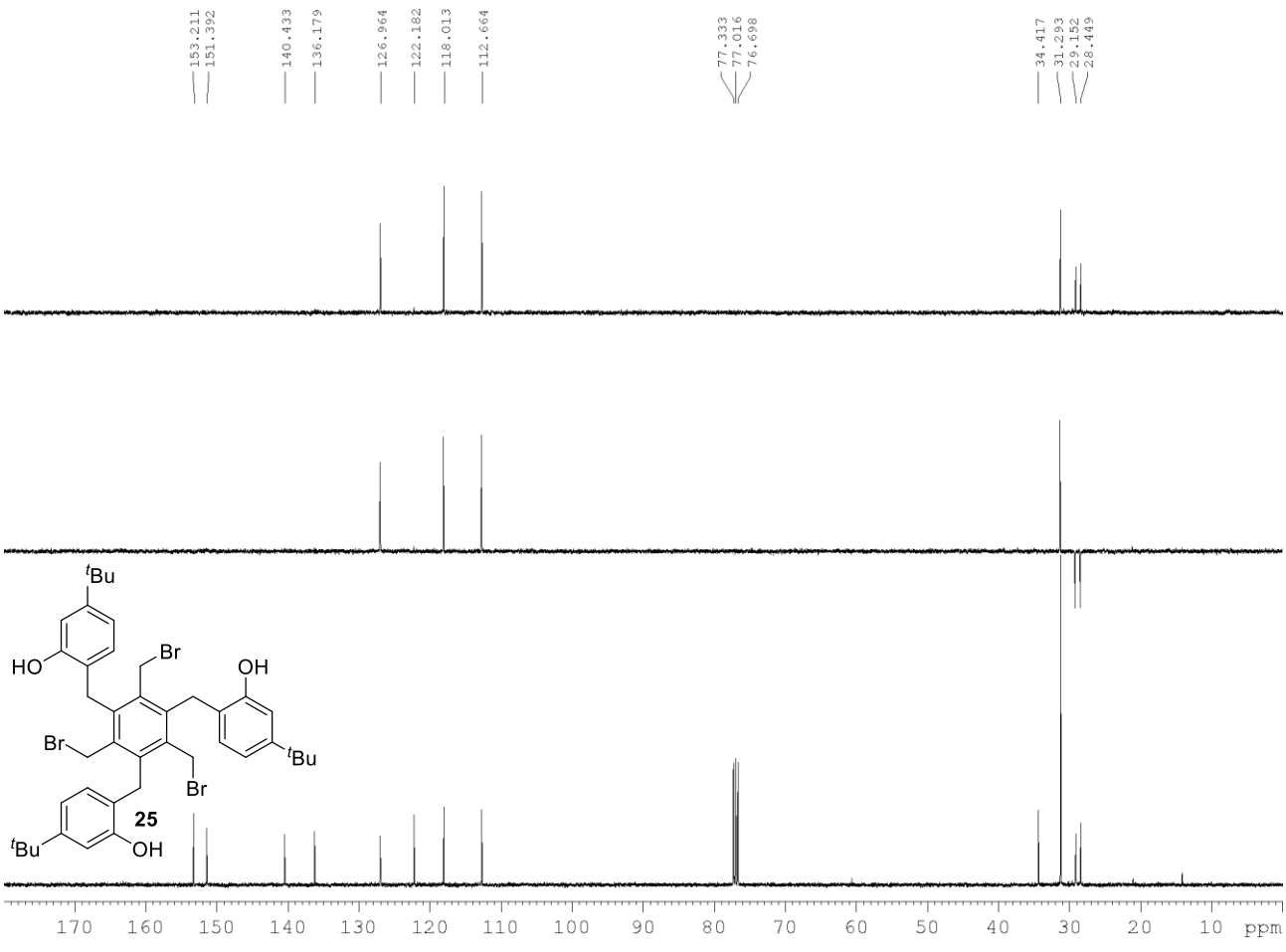
tBu
OH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77.016
76.698
34.417
31.293
29.152
28.449
tBu
HO
Br
OH
Br
tBu
Br
25
tBu
OH
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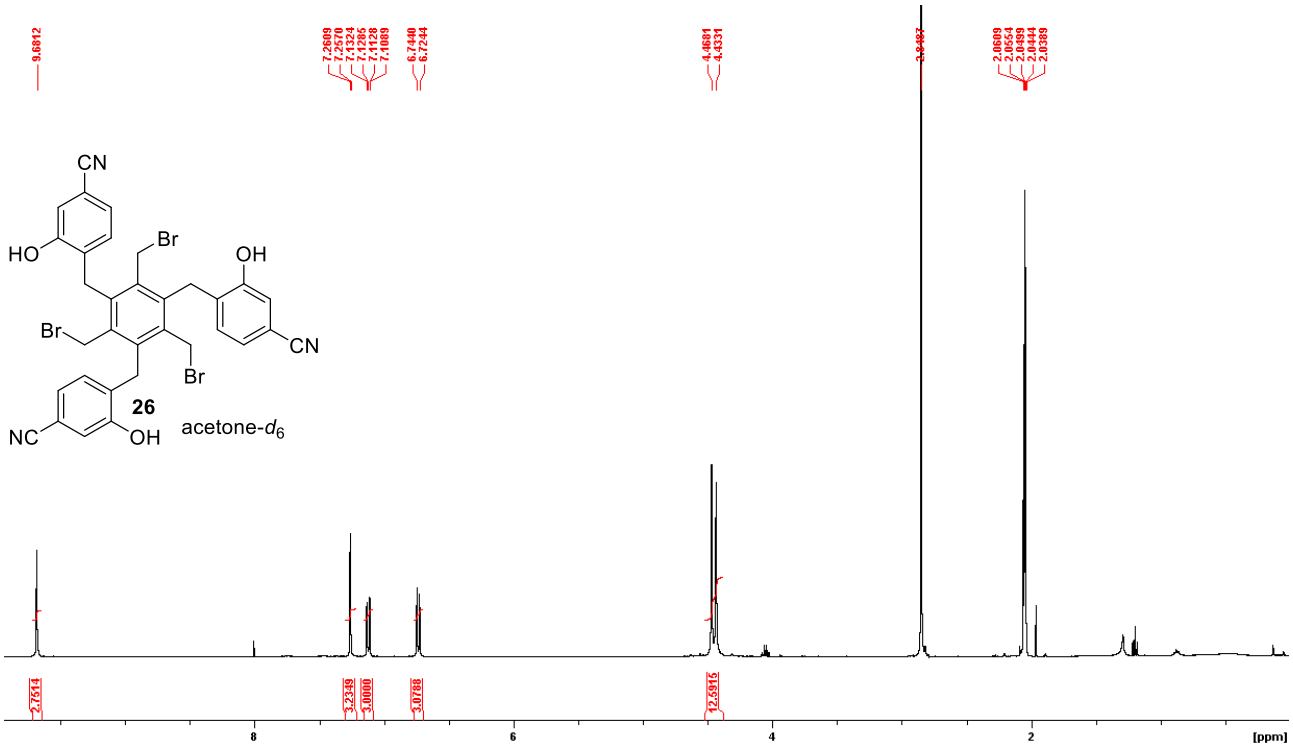
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm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7.1089
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6.7244
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4.4331
2.0689
2.0554
2.0499
2.0444
2.0389
CN
HO
Br
OH
Br
CN
Br
NC
OH
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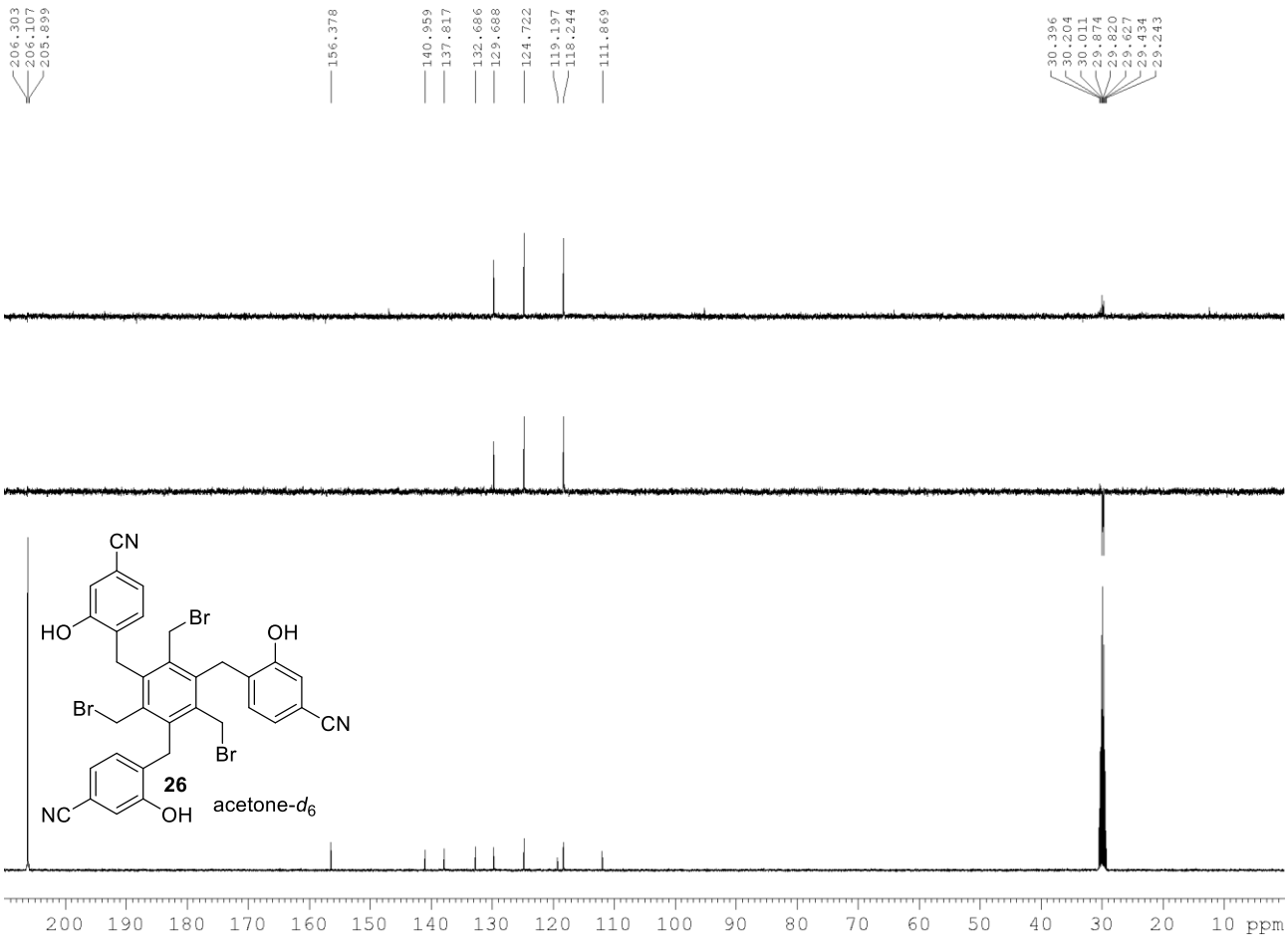
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129.688
124.722
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118.244
111.869
30.396
30.204
30.011
29.874
29.820
29.627
29.434
29.243
CN
HO
Br
OH
Br
CN
Br
NC
OH
26
acetone-d6
200
190
180
170
160
150
140
130
120
110
100
90
80
70
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30
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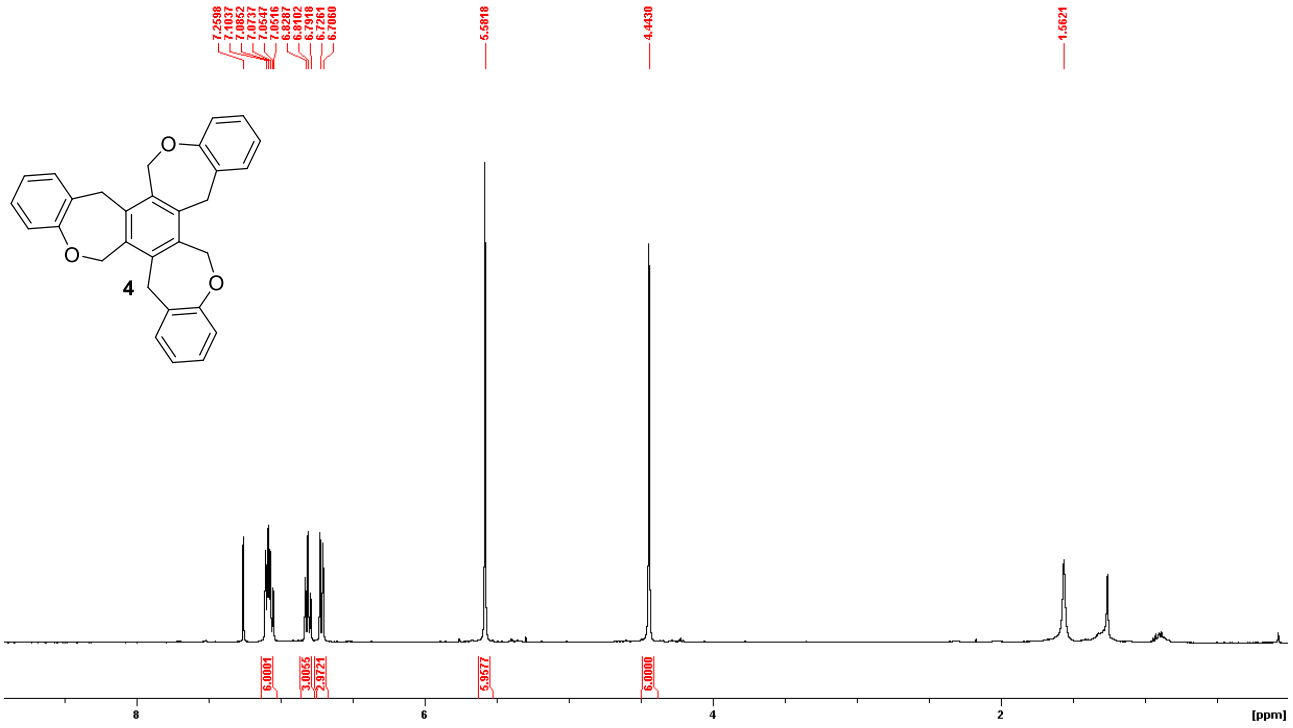
10
ppm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6.7060
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6.0000
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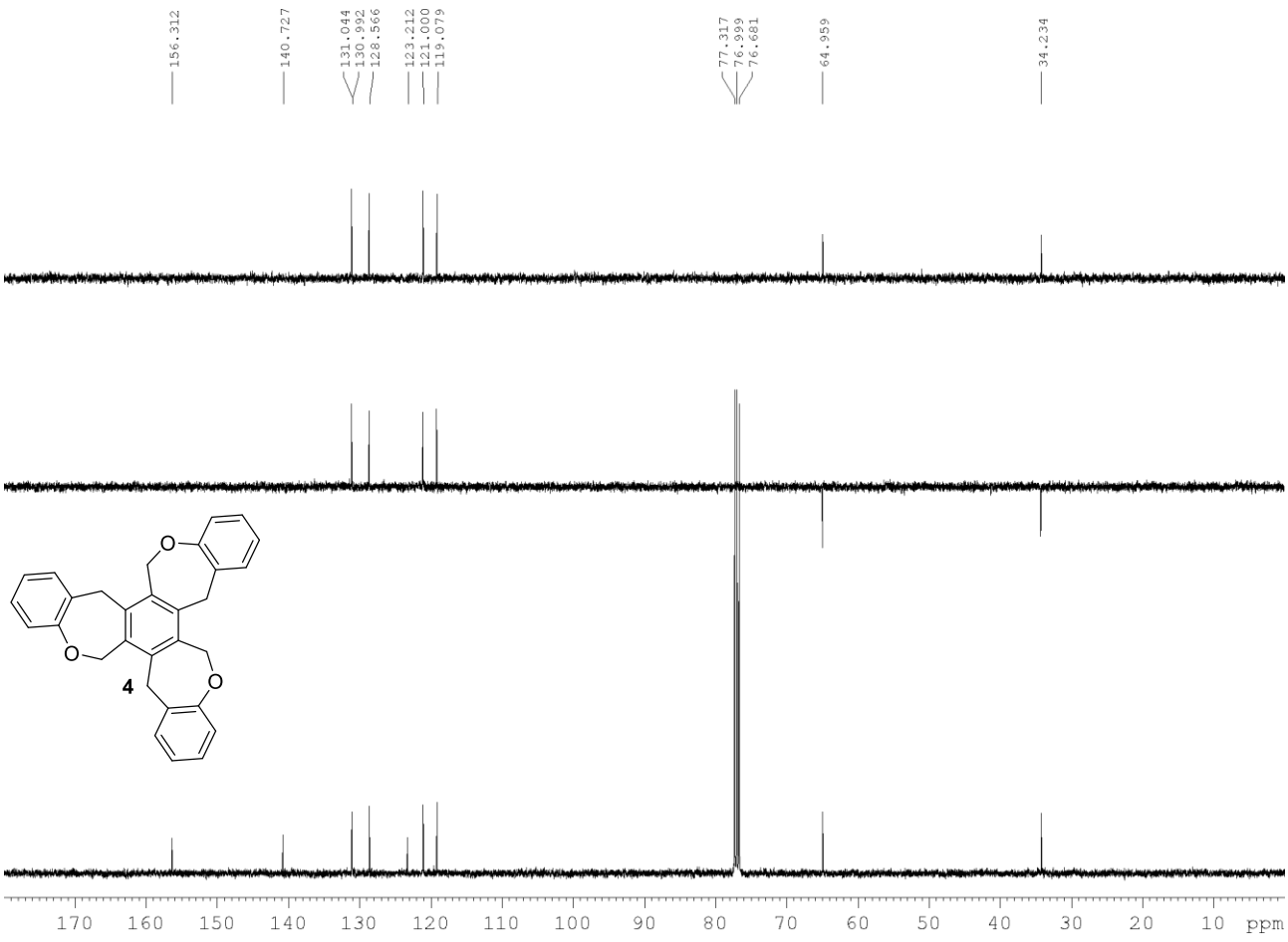
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121.090
119.079
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76.999
76.681
64.959
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150
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130
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110
100
90
80
70
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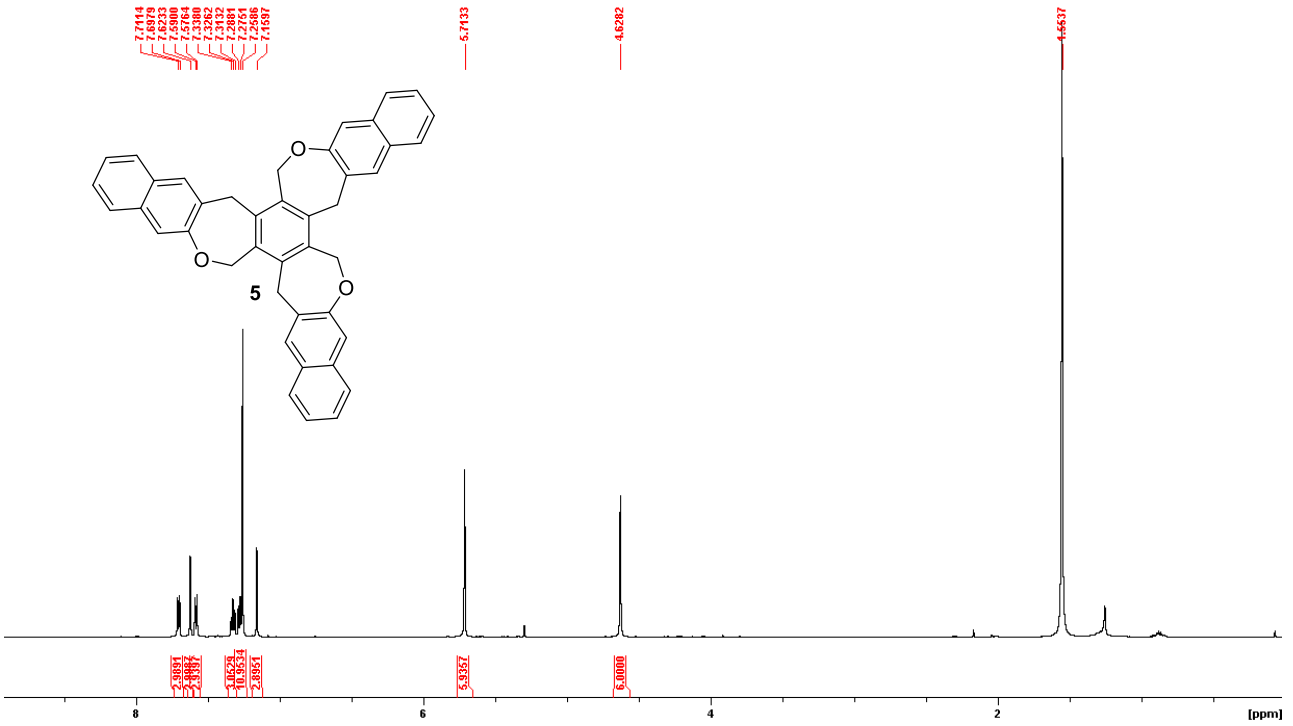
40
30
20
10
ppm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4.5537
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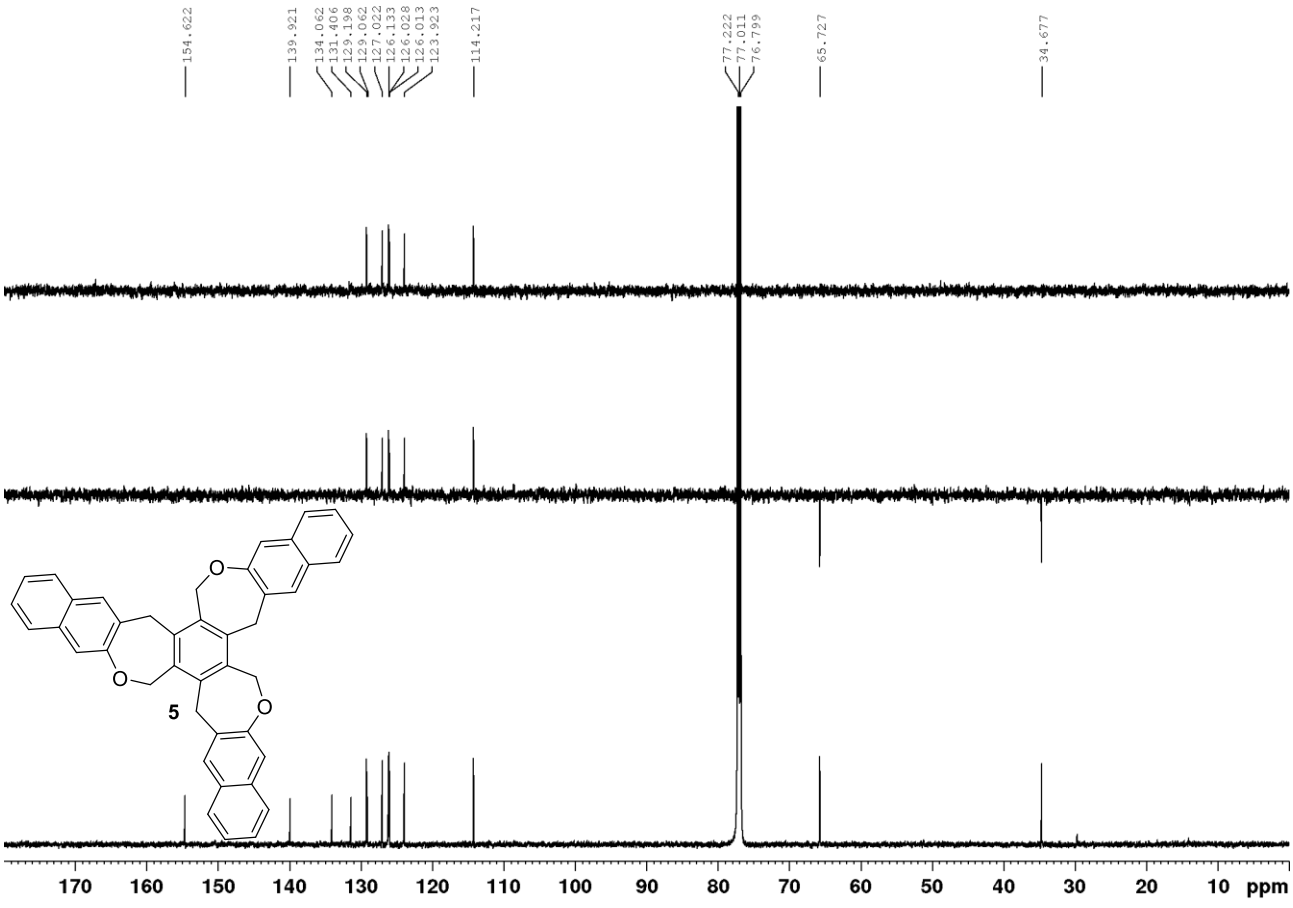
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127.022
126.133
126.028
126.013
123.923
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77.011
76.799
65.727
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40
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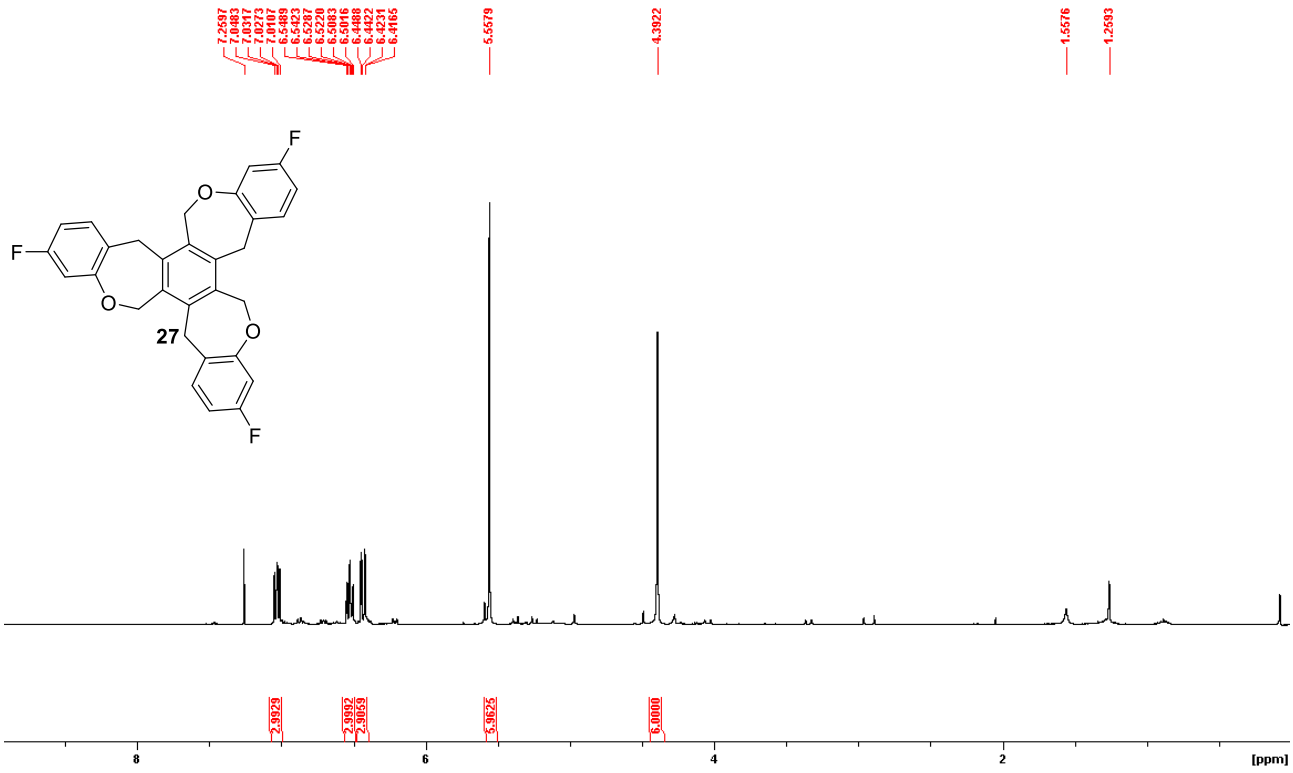
ppm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6.4888
6.4822
6.4231
6.4165
5.5579
4.3922
1.5576
1.2593
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O
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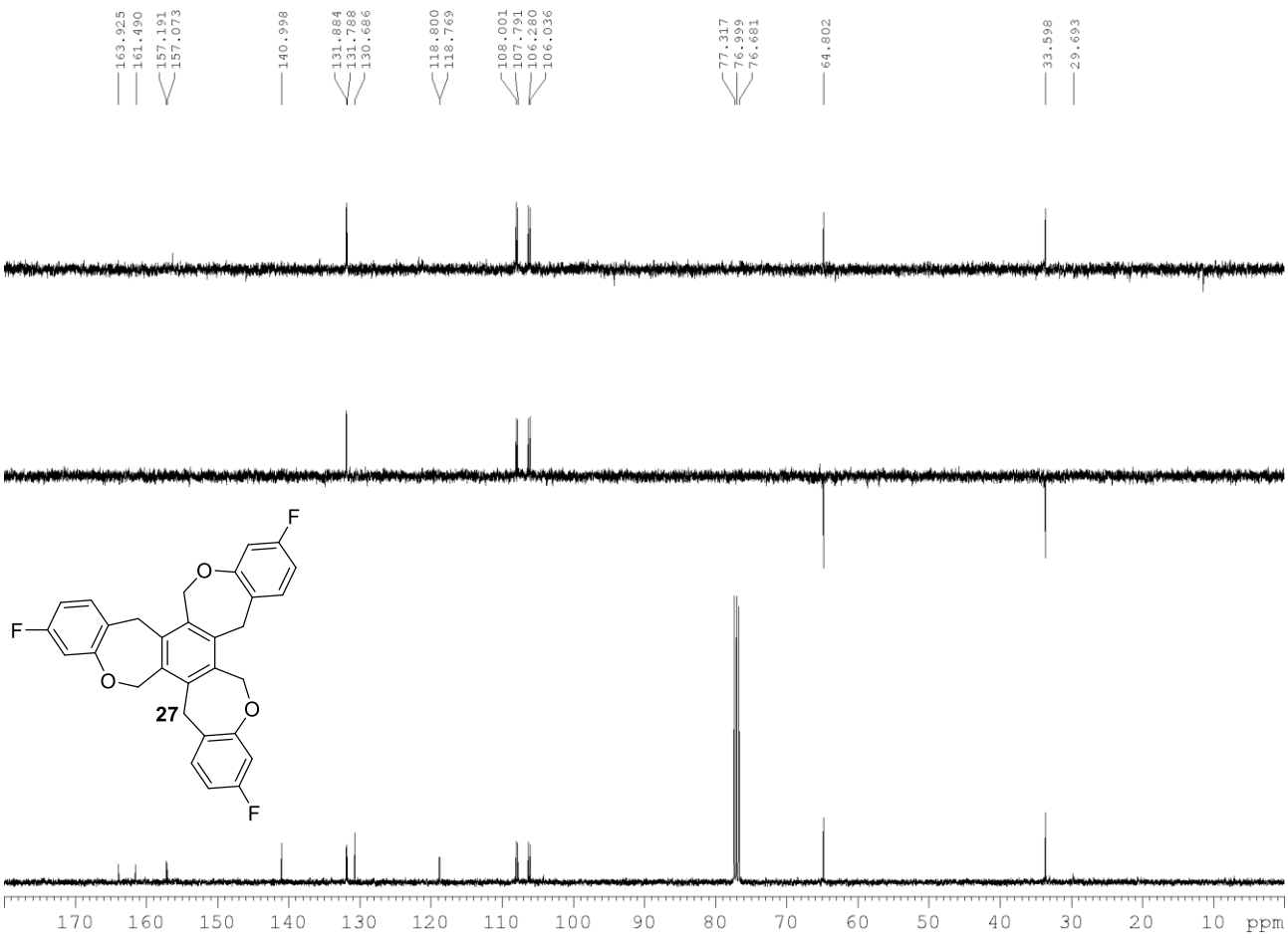
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106.280
106.036
77.317
76.999
76.681
64.802
33.598
29.693
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F
O
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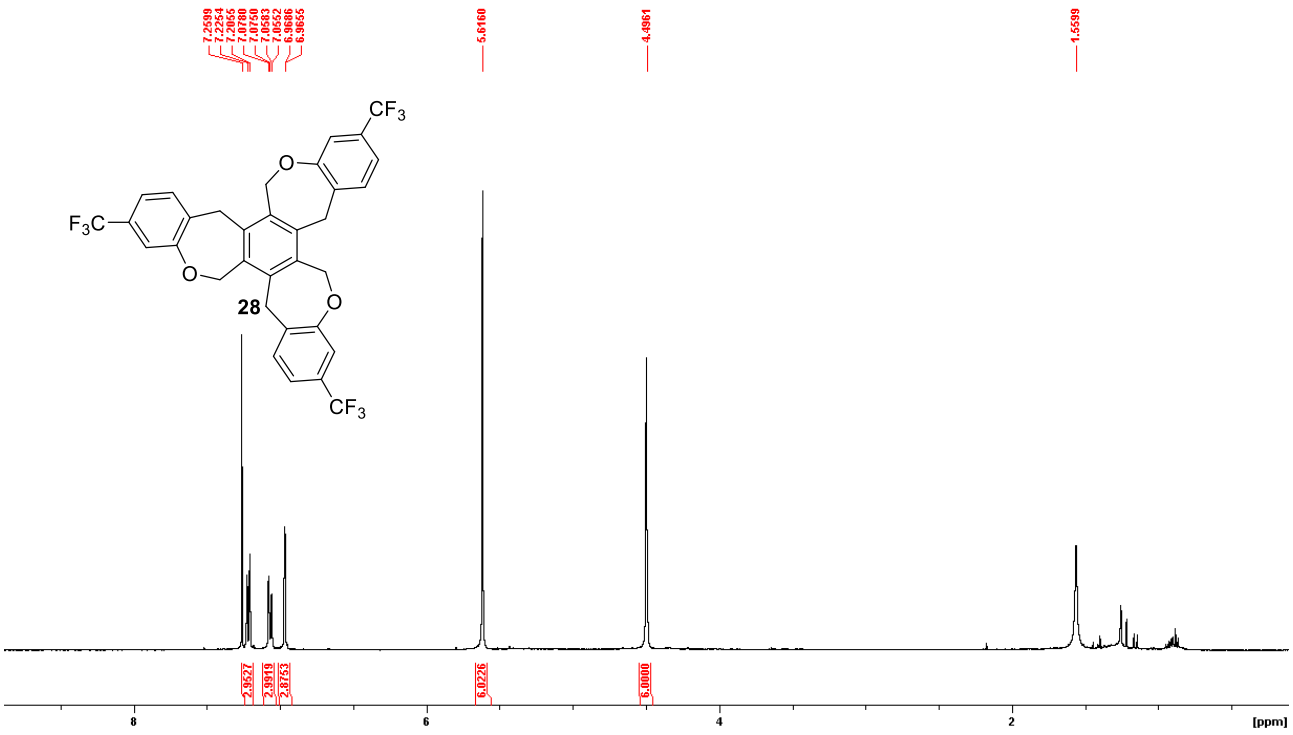
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7.0552
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2.9527
2.9919
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O
O
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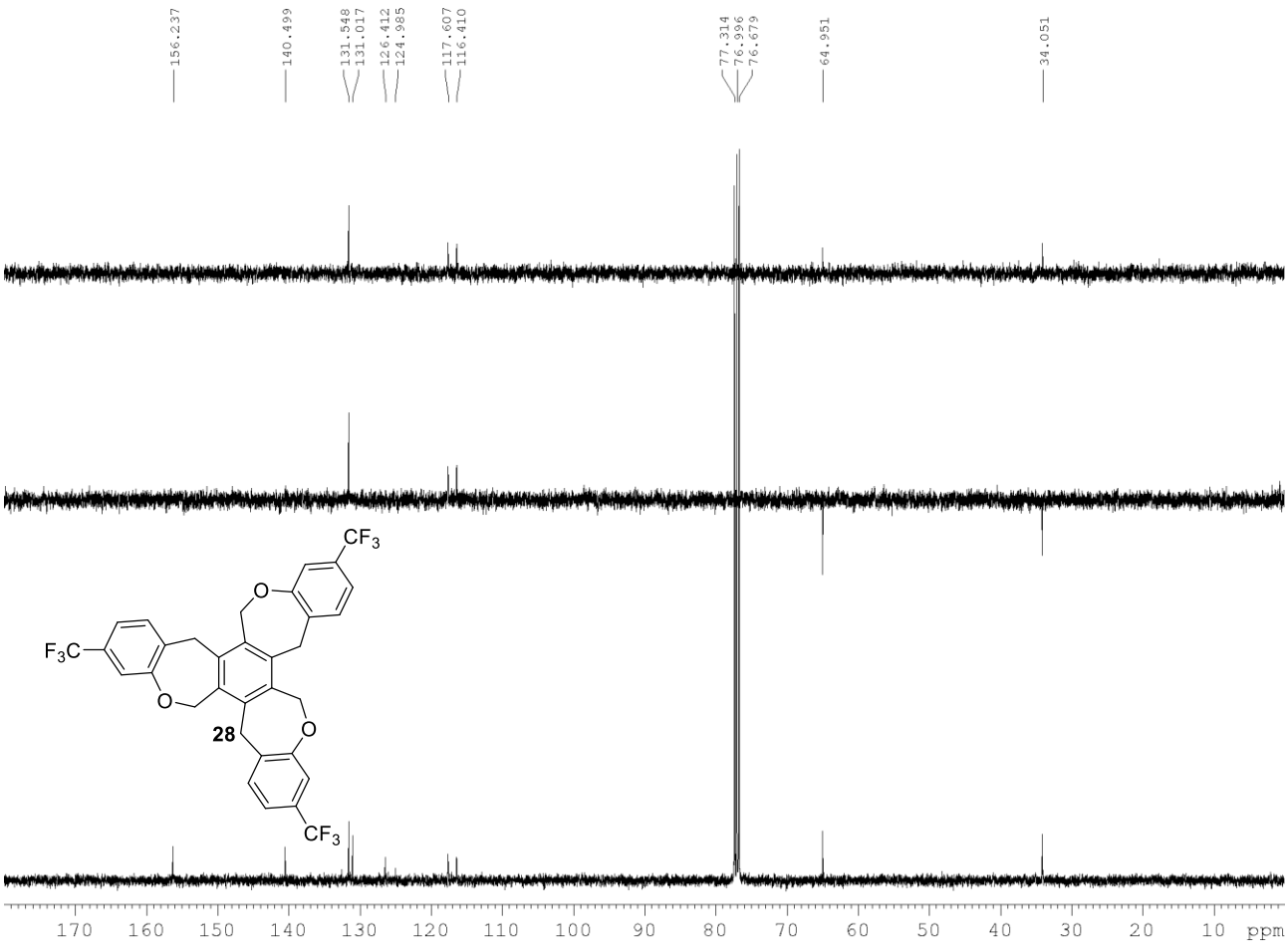
CF3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76.679
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34.051
CF3
F3C
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O
O
O
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150
140
130
120
110
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70
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30
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10
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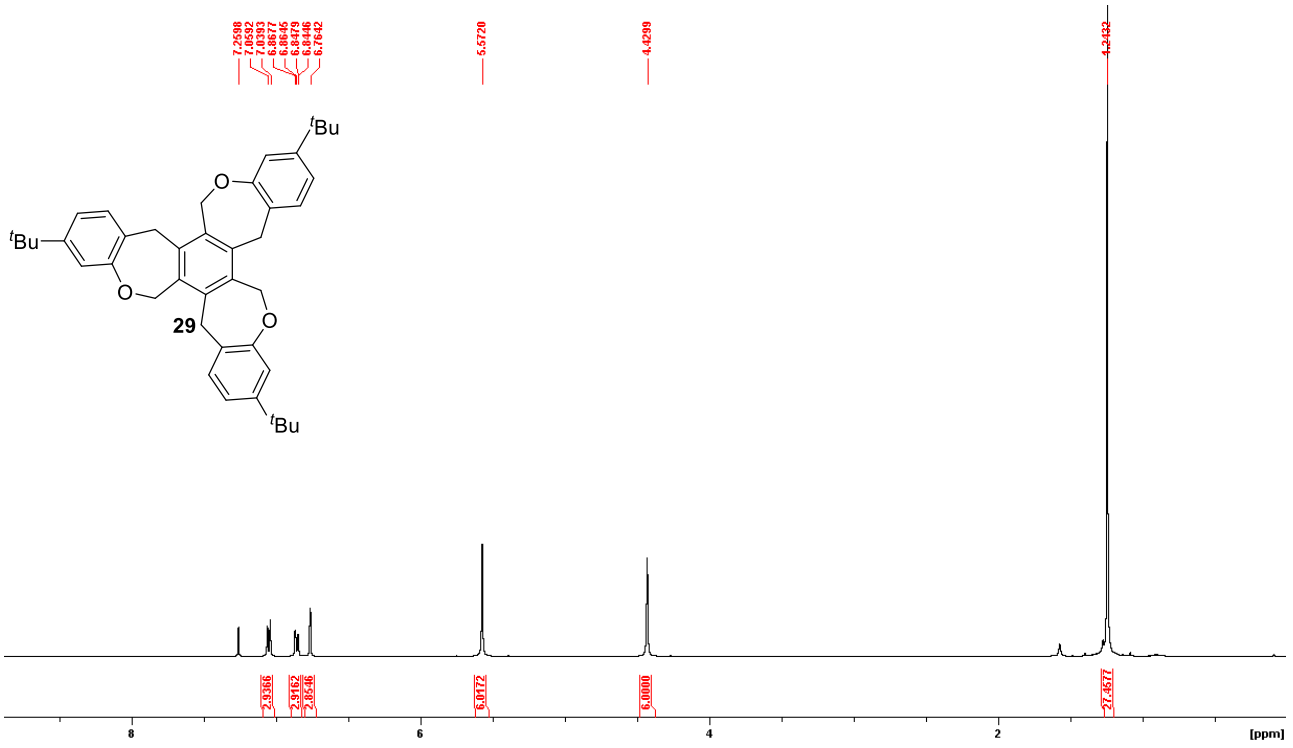
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6.8446
6.7842
5.5720
4.4299
1.2432
tBu
tBu
O
O
O
O
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4
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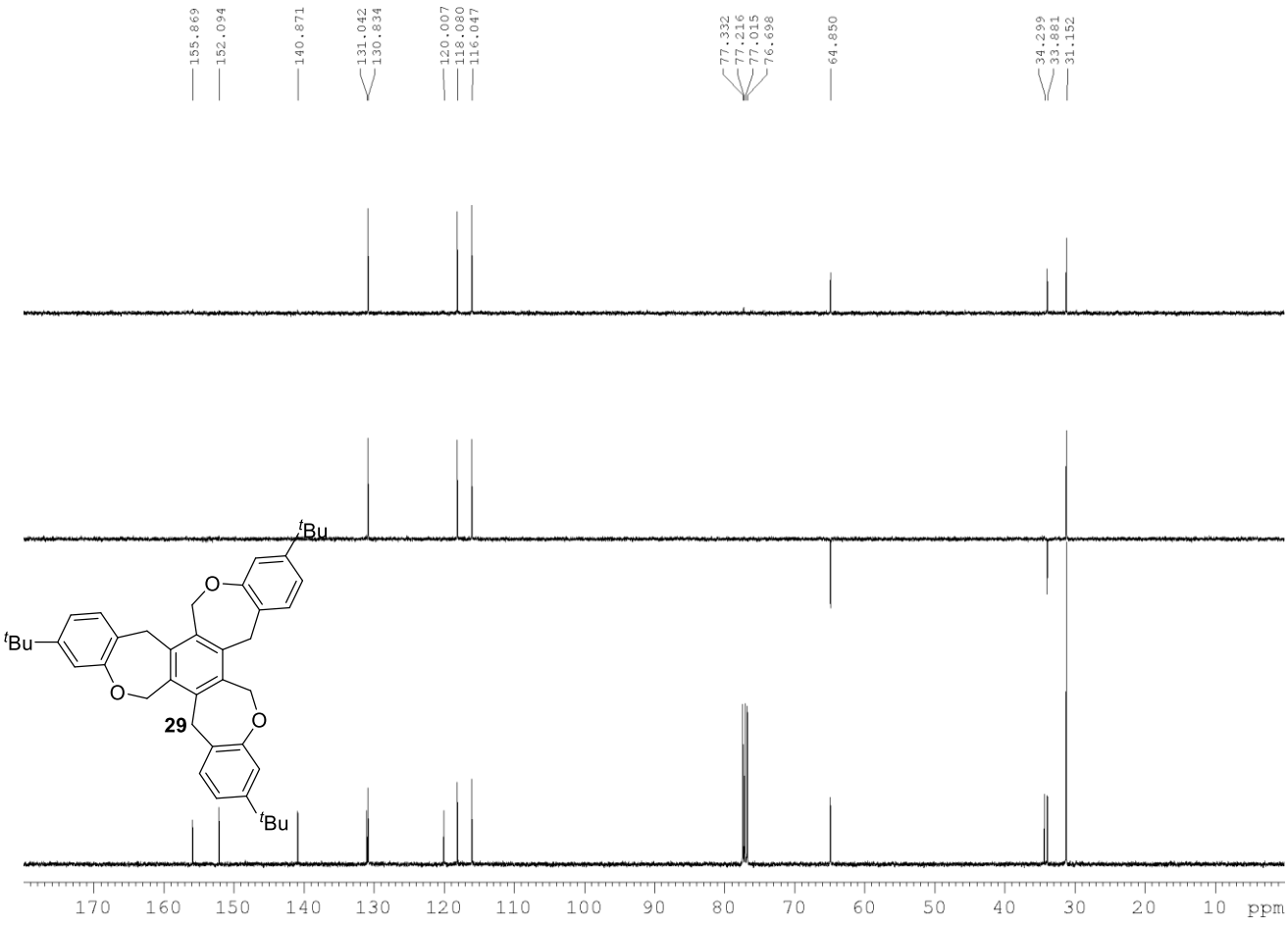
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31.152
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O
O
O
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70
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50
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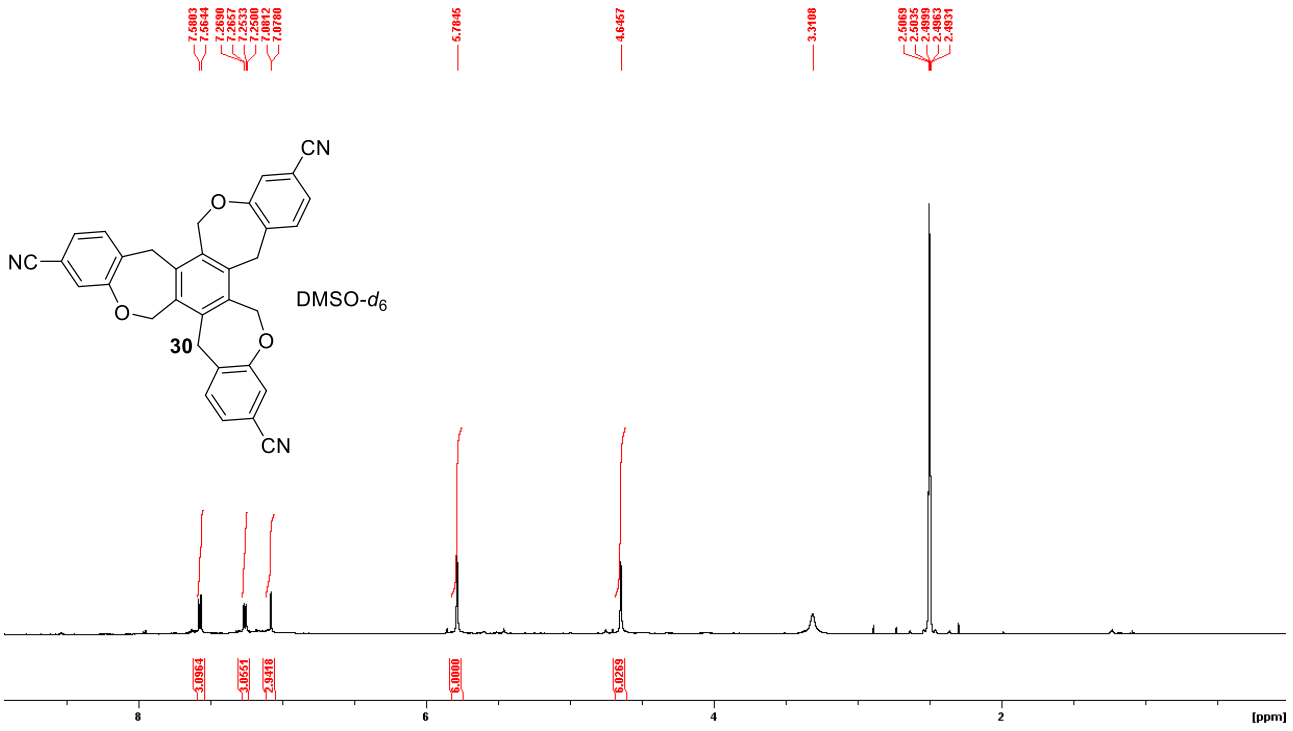
ppm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2.4931
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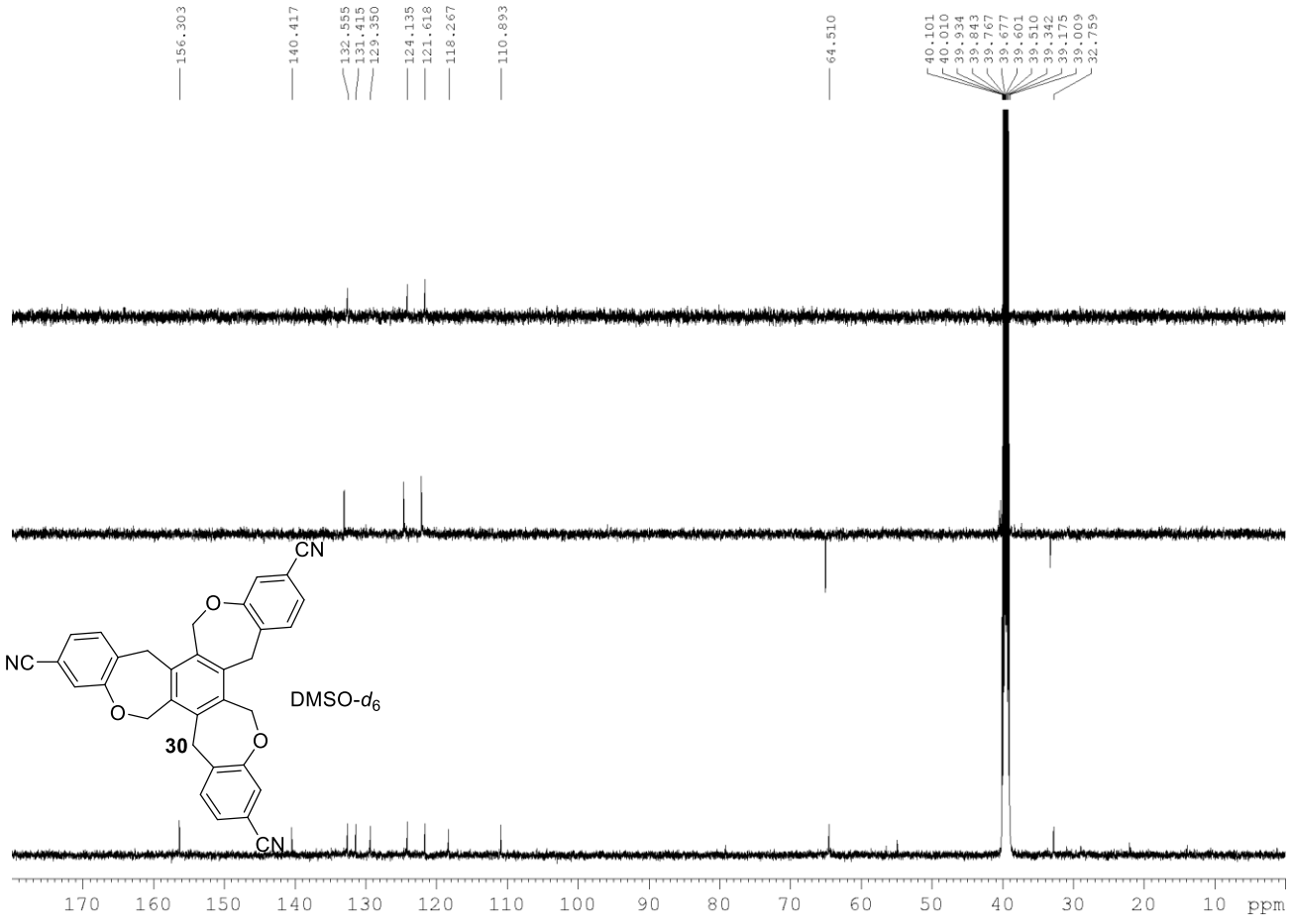
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39.510
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32.759
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NC
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O
O
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CN
DMSO-d_6
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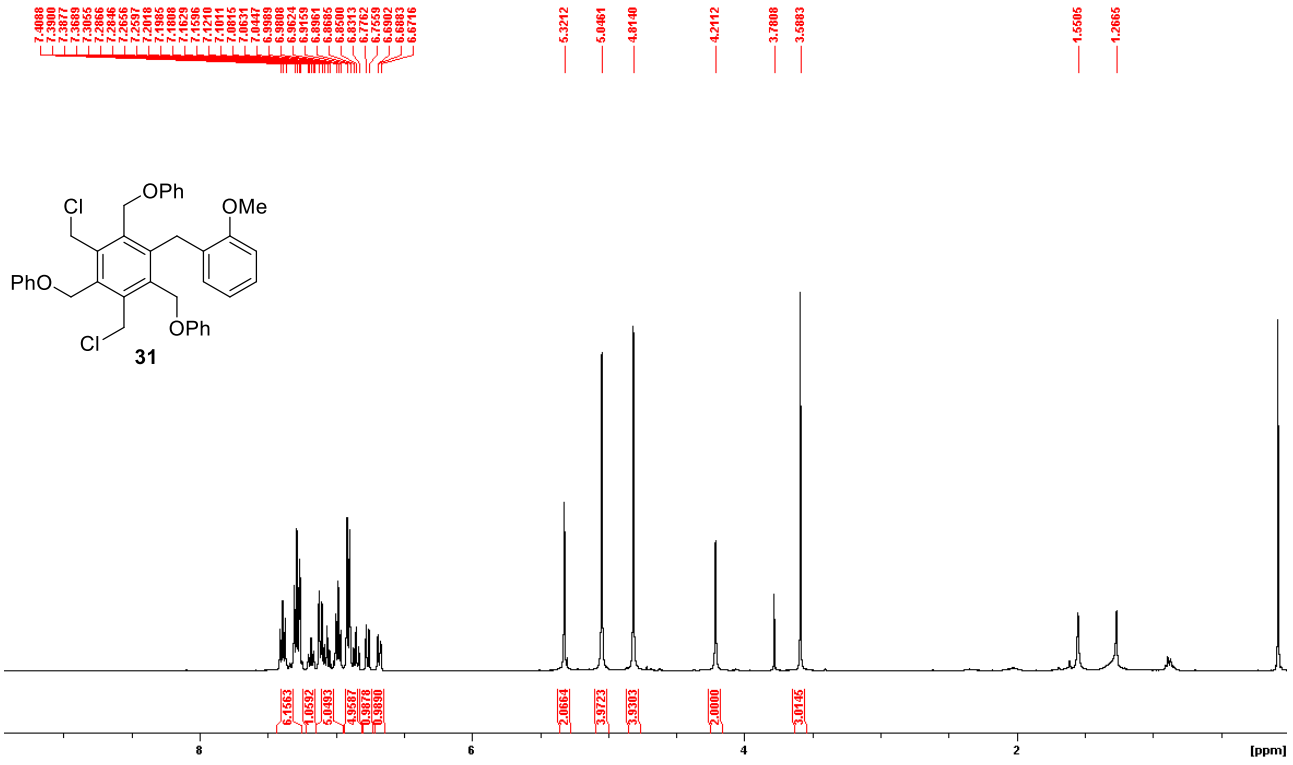
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7.1995
7.1888
7.1629
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7.1210
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7.0637
7.0447
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6.7559
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6.6883
6.6716
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Cl
OMe
PhO
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OPh
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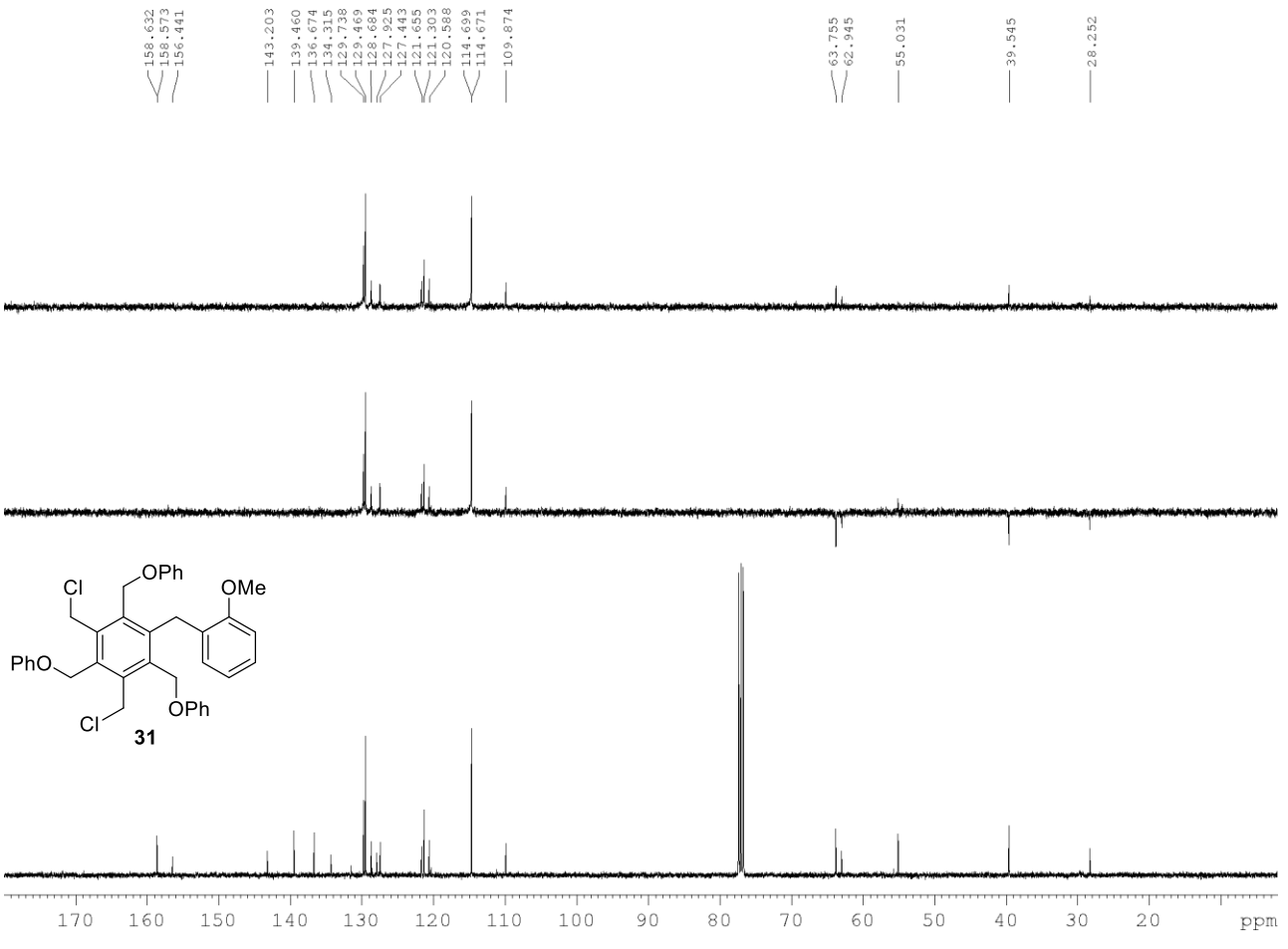
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121.303
120.588
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114.671
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63.755
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OPh
Cl
OMe
PhO
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150
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80
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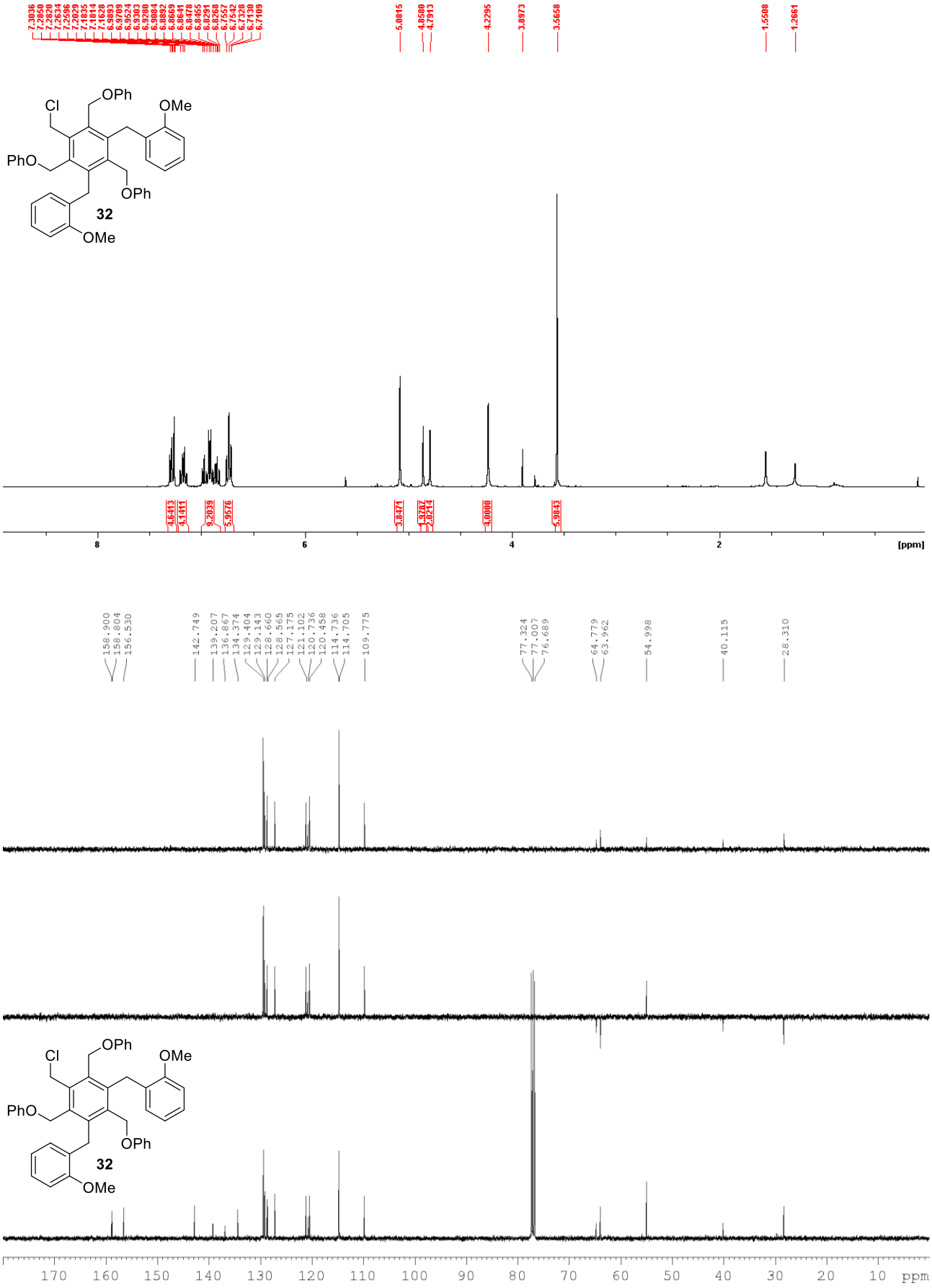
20
ppm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OPh
Cl
OMe
PhO
OPh
32
OMe
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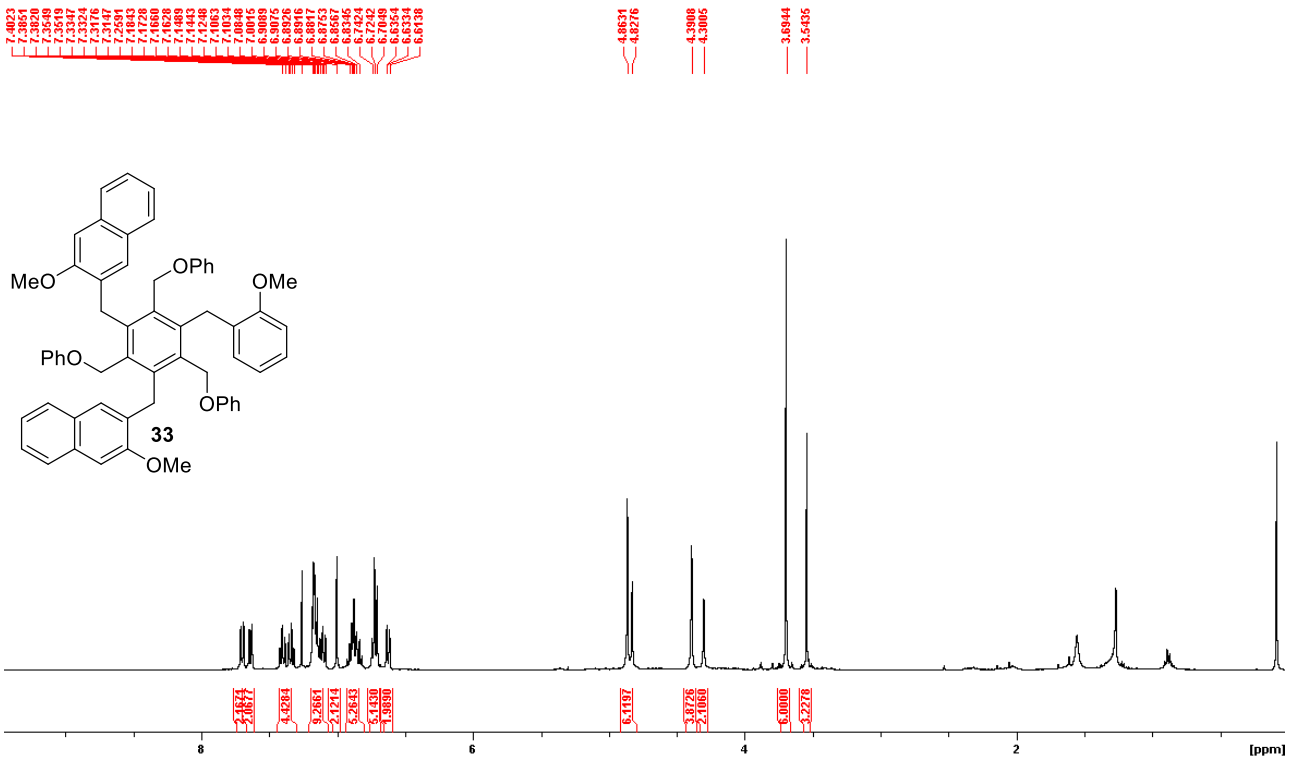
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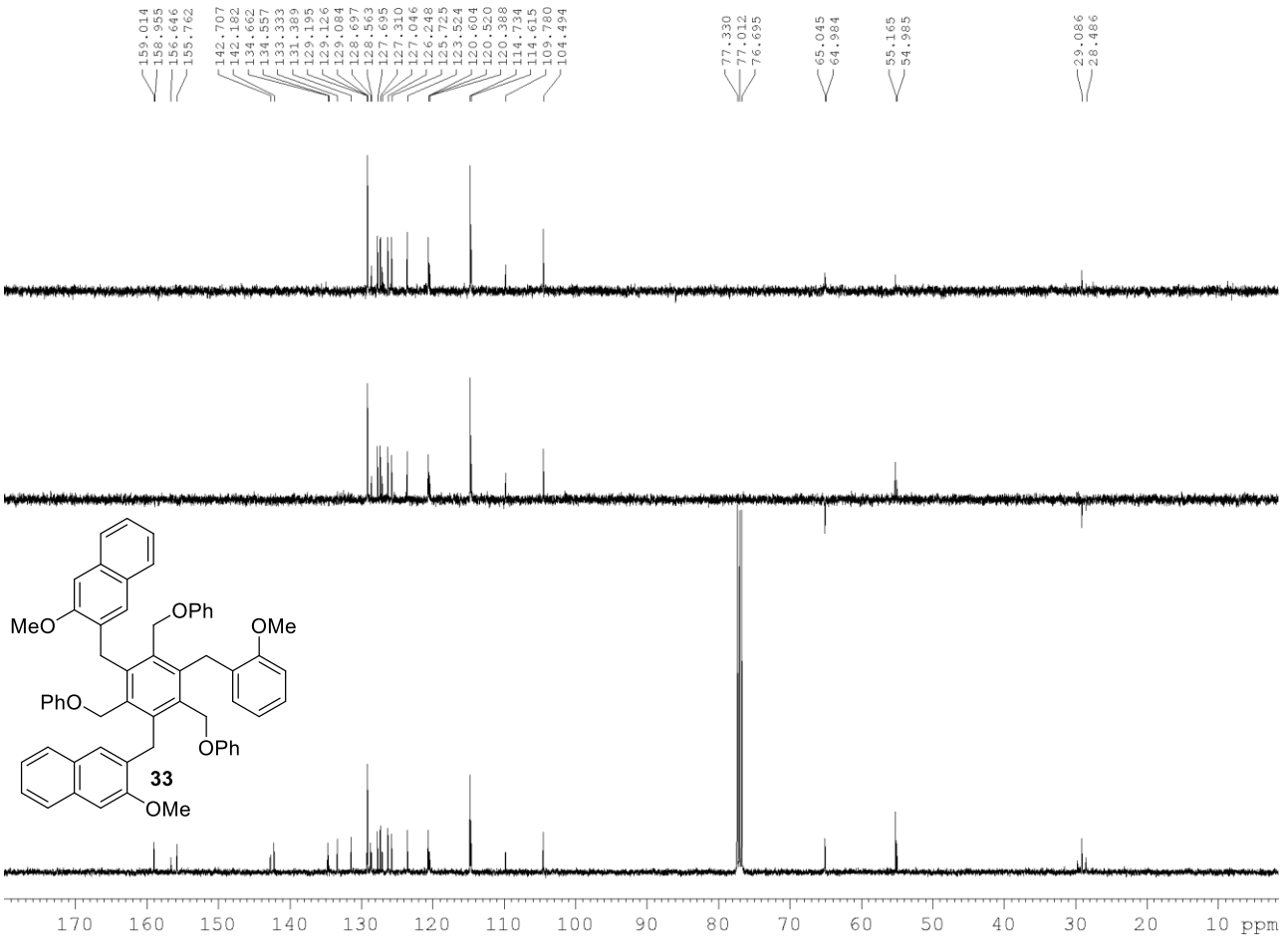
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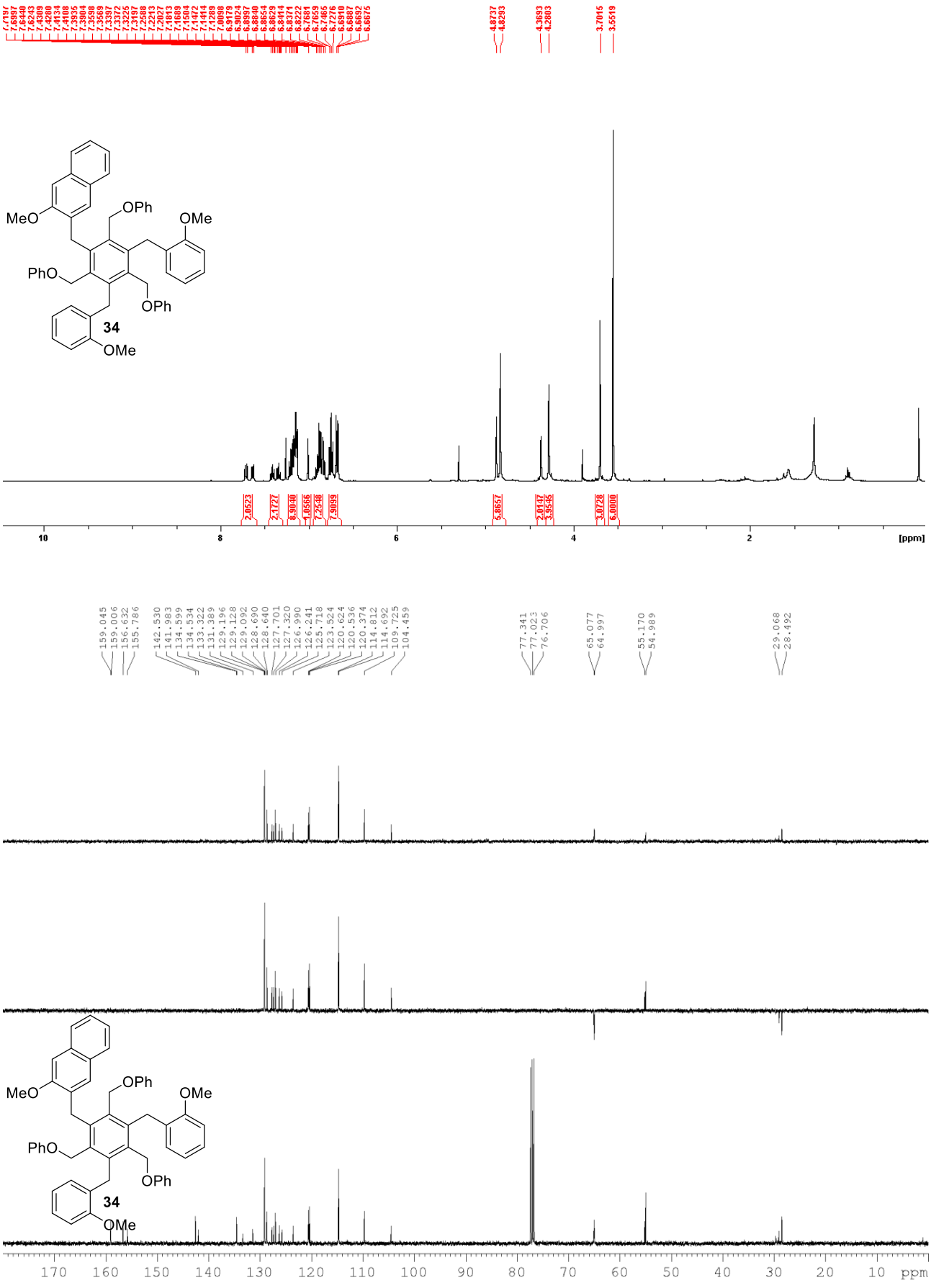
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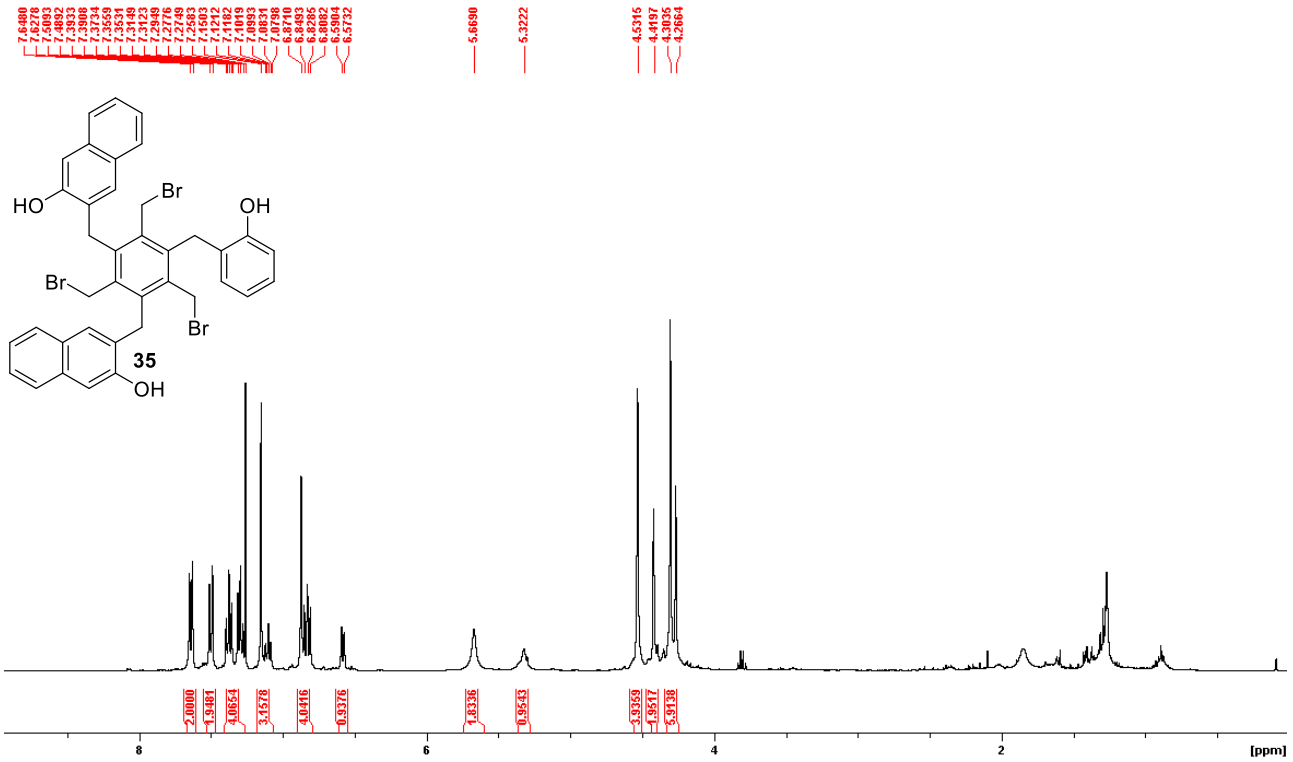
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7.2949
7.2776
7.2749
7.2583
7.2403
7.1912
7.1182
7.1019
7.0993
7.0831
7.0798
6.8710
6.8493
6.8285
6.8082
6.5904
6.5732
5.6690
5.3222
4.5315
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4.3035
4.2664
HO
Br
OH
Br
Br
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OH
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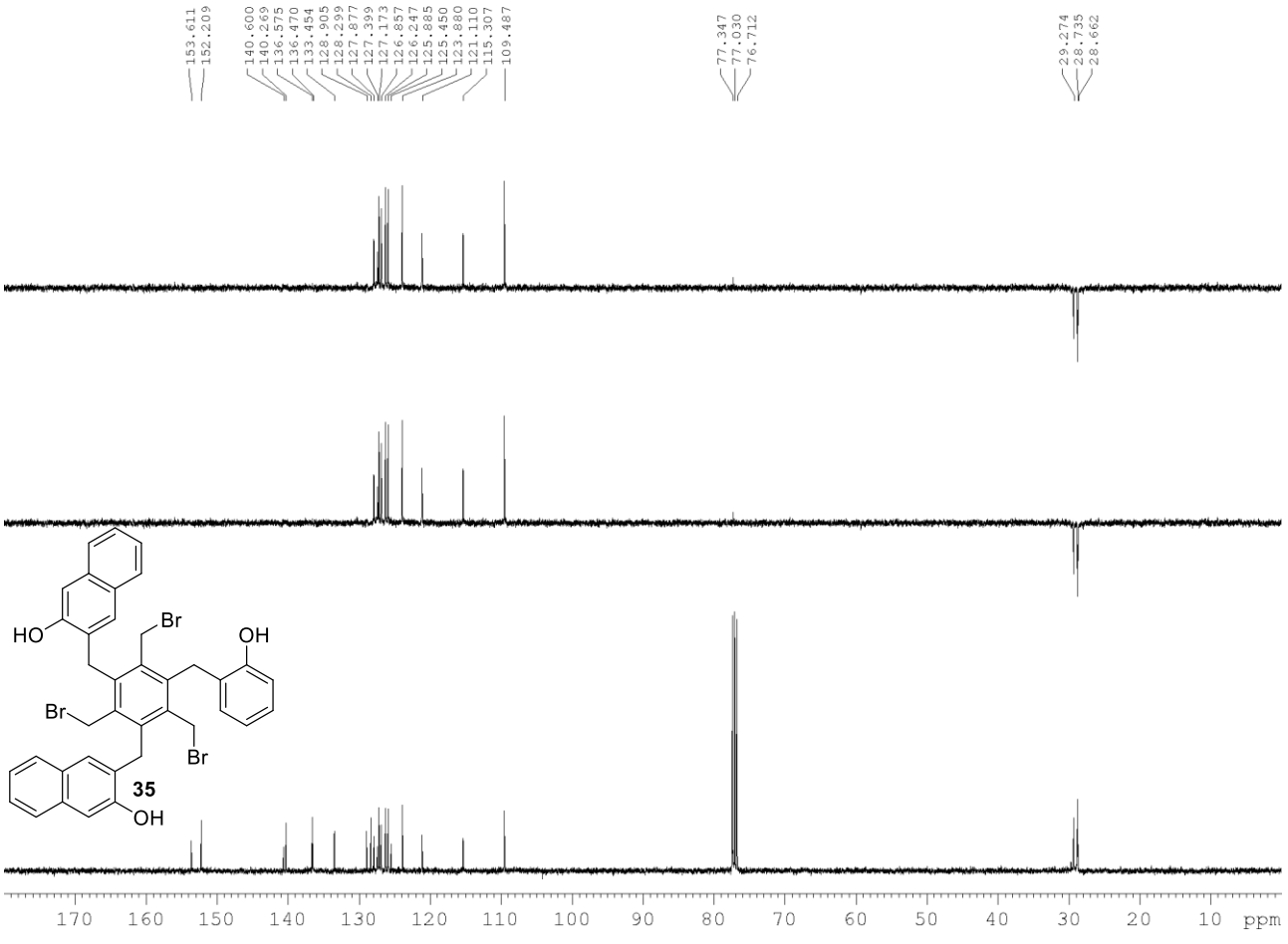
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125.450
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OH
Br
Br
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OH
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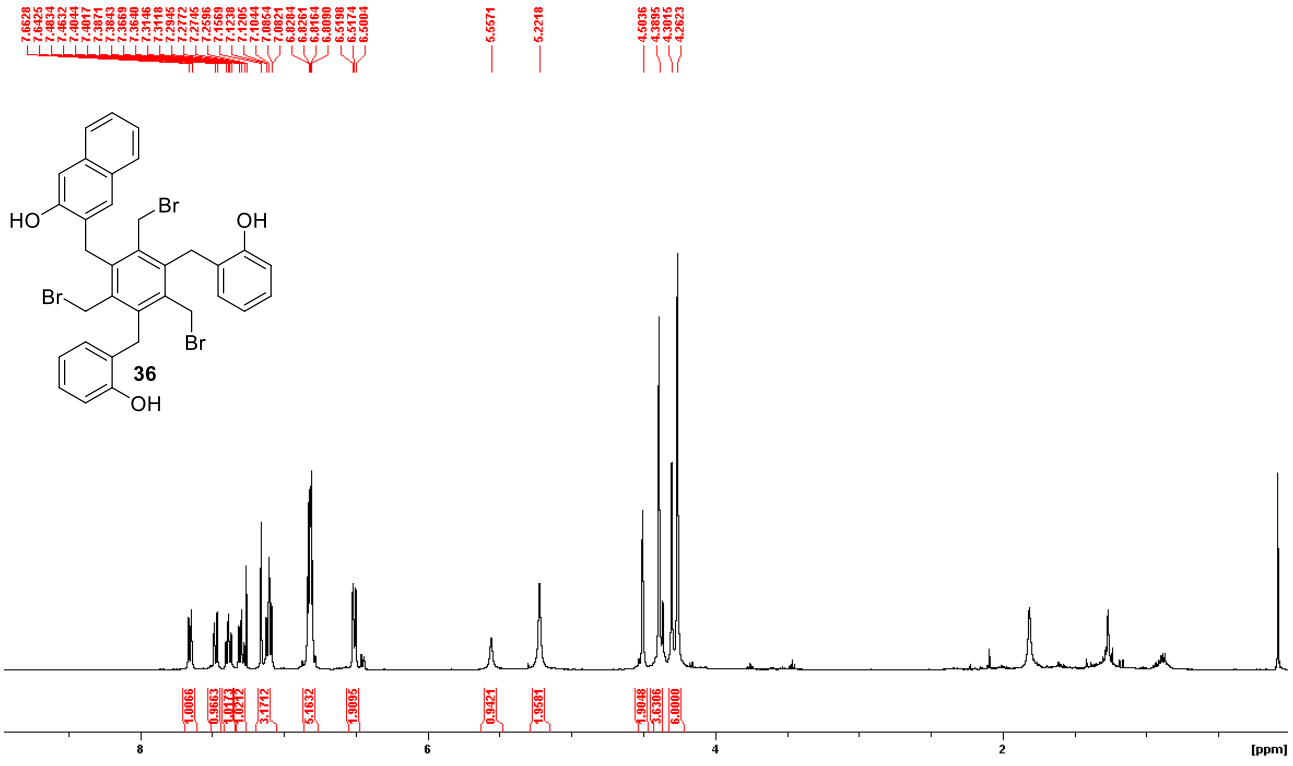
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7.3118
7.2945
7.2772
7.2745
7.2596
7.1583
7.1228
7.1205
7.1044
7.0854
7.0821
6.8284
6.8261
6.8064
6.8090
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5.2218
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4.2623
HO
Br
OH
Br
Br
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OH
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1.9048
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6.0000
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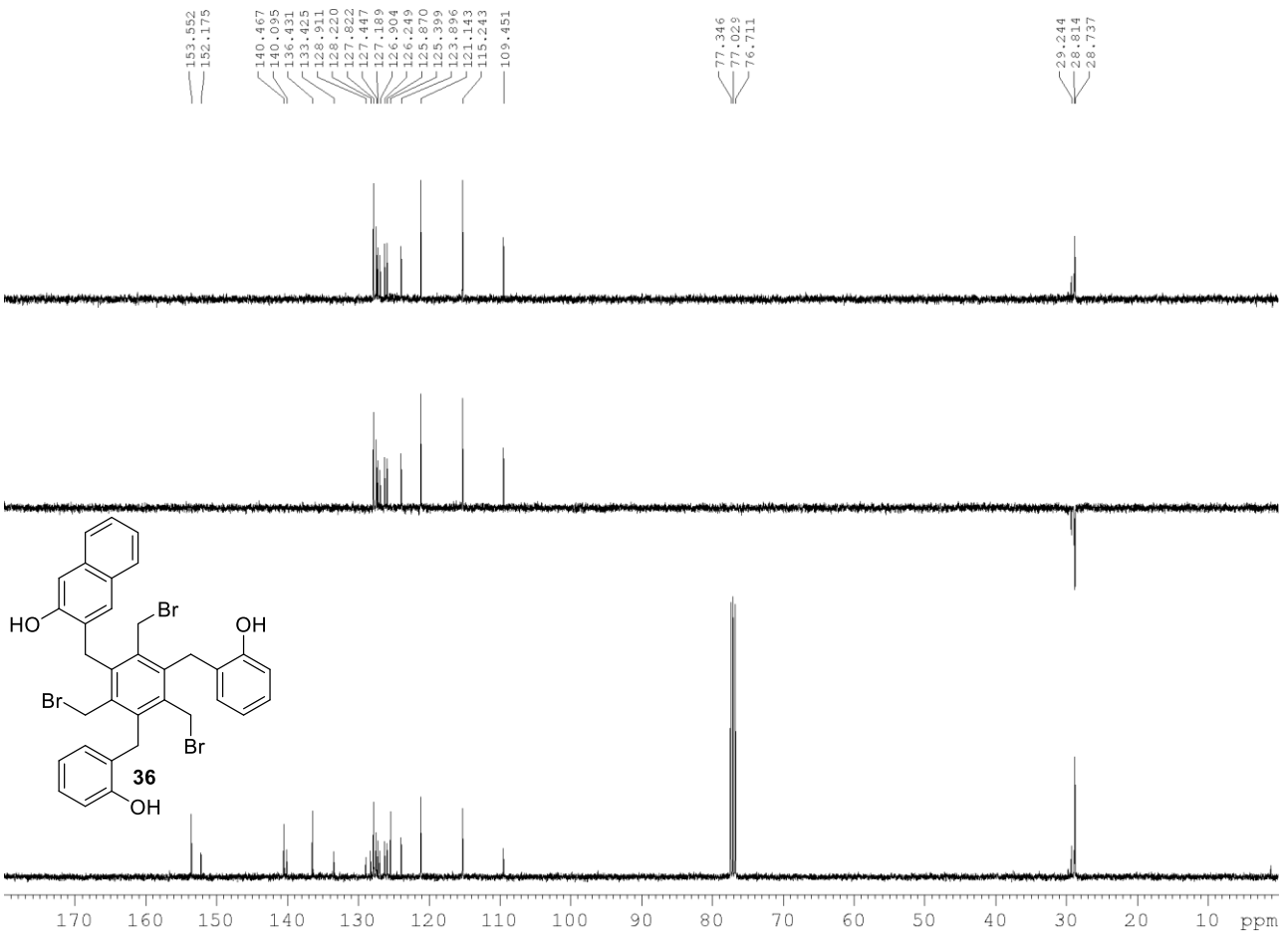
4
2
[ppm]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77.029
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29.244
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28.737
HO
Br
OH
Br
Br
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OH
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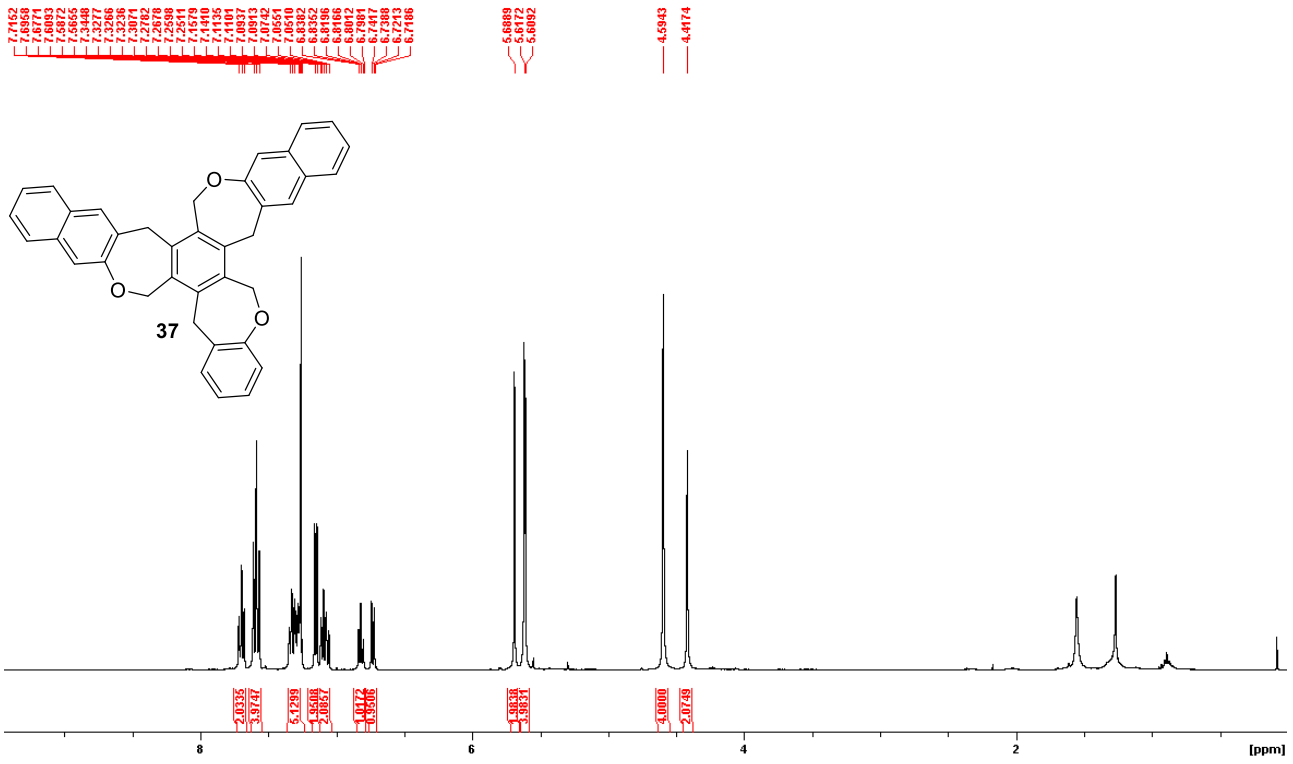
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7.3266
7.3236
7.2901
7.2782
7.2678
7.2598
7.2511
7.1579
7.1410
7.1405
7.1181
7.0937
7.0913
7.0742
7.0551
7.0510
6.8352
6.8322
6.8196
6.8166
6.8012
6.7981
6.7417
6.7388
6.7293
6.7166
5.6889
5.6172
5.6092
4.5943
4.4174
37
2.0335
3.9747
5.1299
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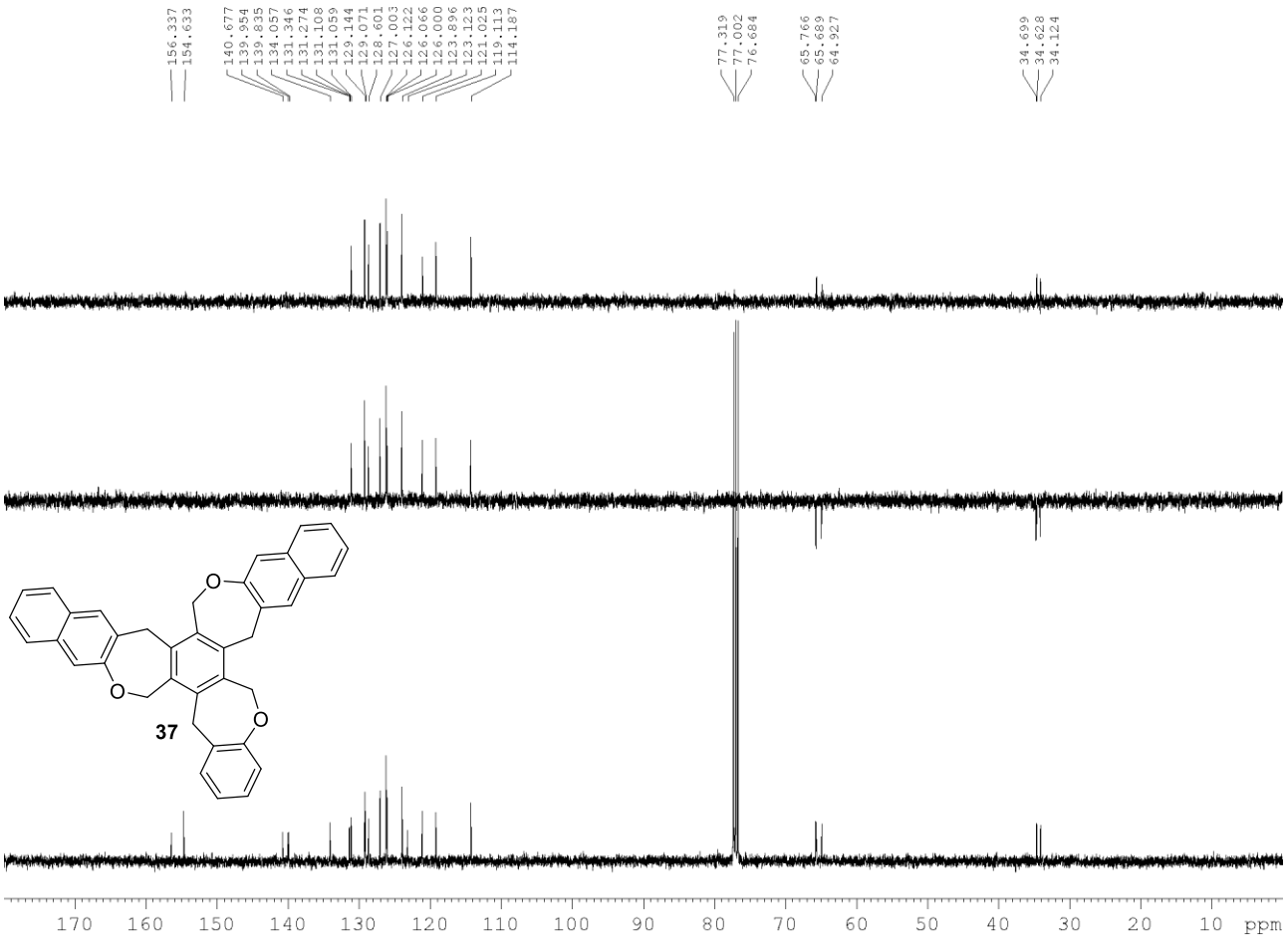
[ppm]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126.122
126.066
126.000
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123.123
121.025
119.113
114.187
77.319
77.002
76.684
65.766
65.689
64.927
34.699
34.628
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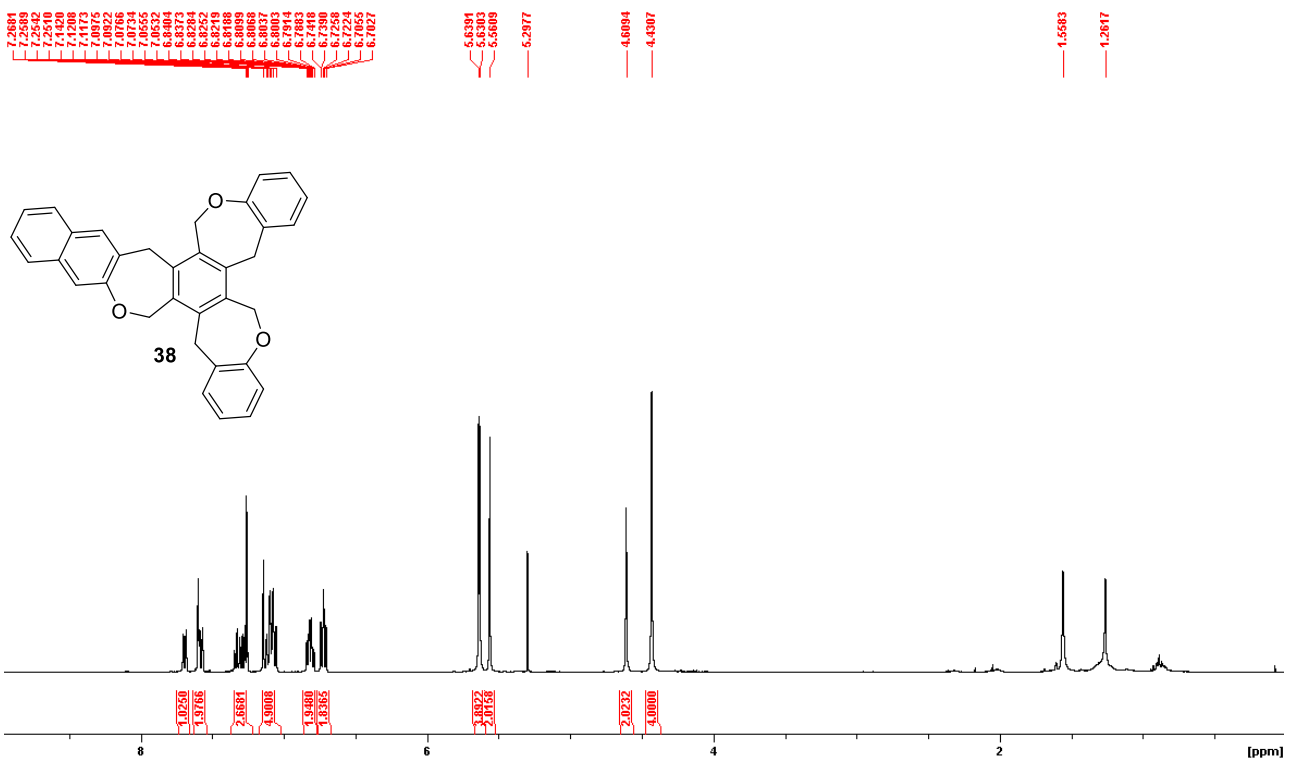
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7.1420
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7.1173
7.0975
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7.0706
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7.0555
7.0532
6.8404
6.8373
6.8284
6.8252
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6.8188
6.8099
6.8068
6.8037
6.8003
6.7944
6.7883
6.7418
6.7390
6.7258
6.7224
6.7055
6.7027
5.6391
5.6301
5.5609
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1.2617
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1.0250
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4
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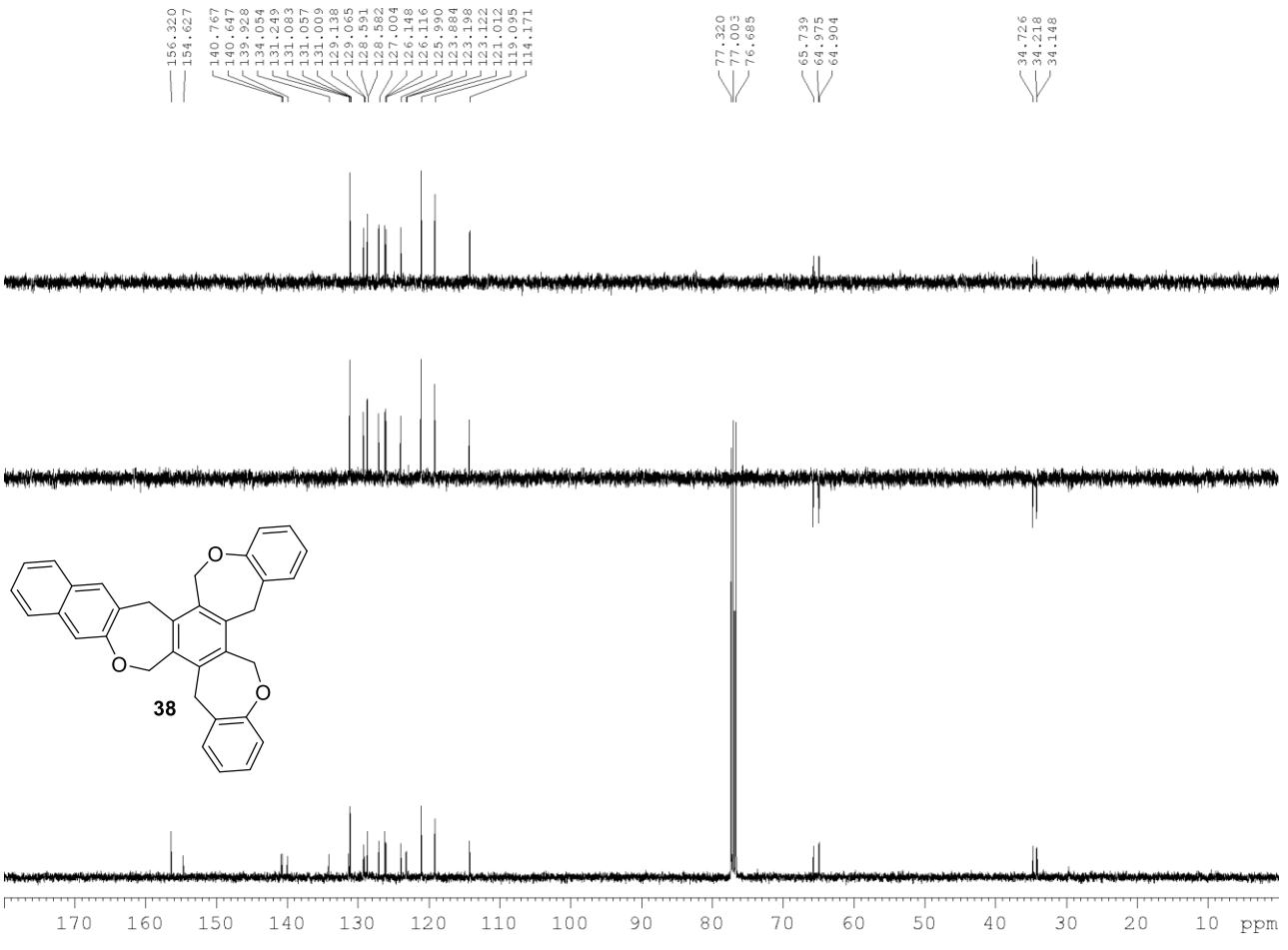
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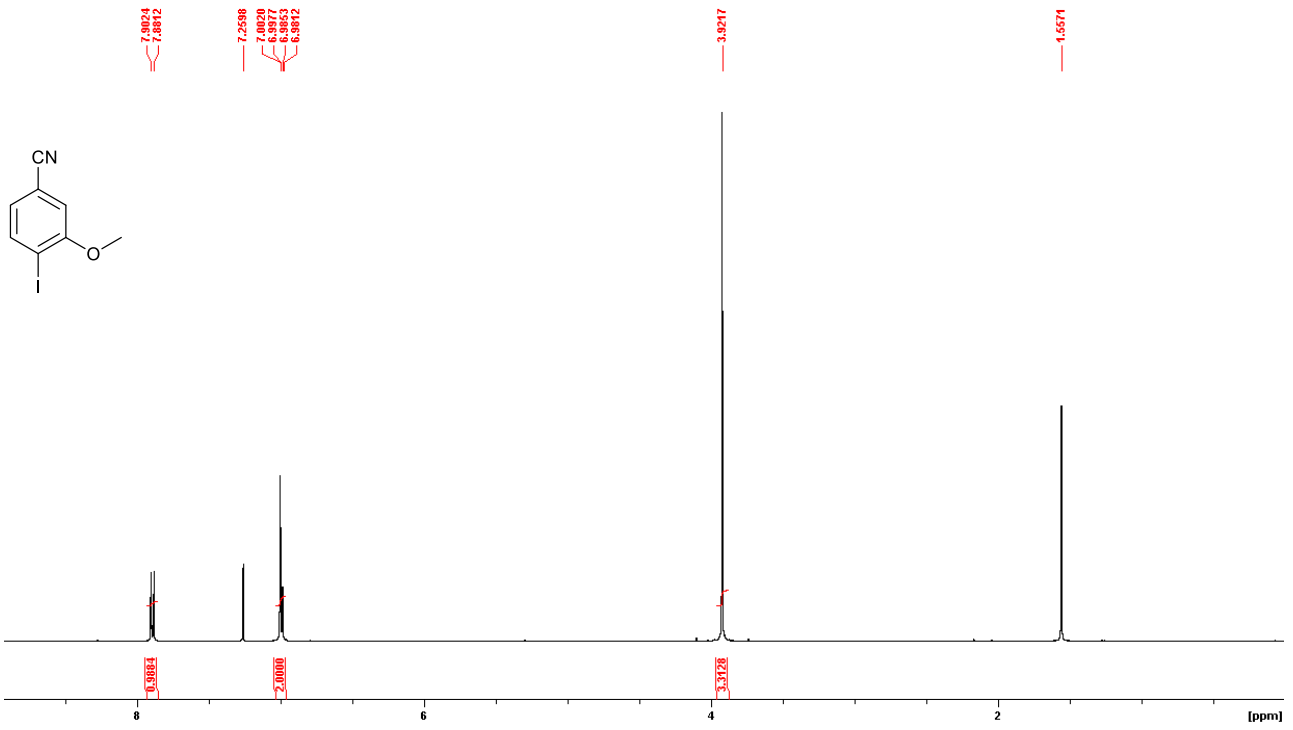
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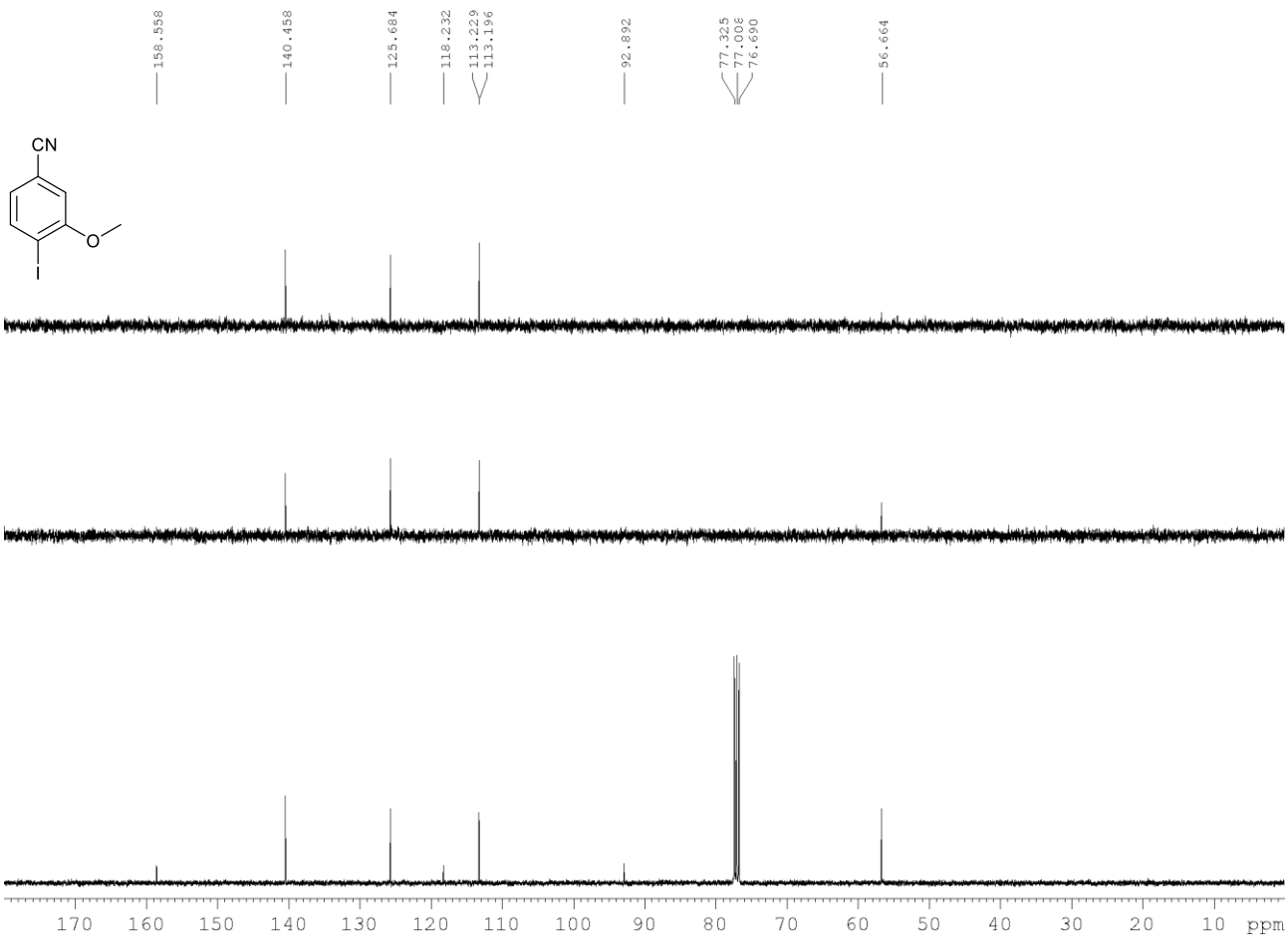
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CN
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I
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160
150
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120
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100
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80
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50
40
30
20
10
ppm