Supporting information for:

Facile synthesis of biarylmethanes and tetrasubstituted arenes *via* base-mediated [3+3] benzannulation reaction of Morita-Baylis-Hillman adducts and unsaturated sulfones

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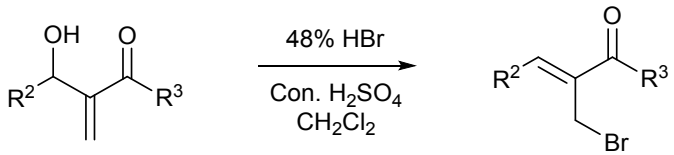
General Information: All ^{1}H NMR (400 MHz) and ^{13}C NMR (100 MHz) spectra were recorded in $CDCl_3$ solvent at ambient temperature, chemical shift δ are given in ppm on a scale downfield from TMS, and the coupling constant *J* are in Hz. The signal patterns are indicated as follows: s, singlet; d, doublet; t, triplet; dd, doublet of doublet; m, multiplet. FTIR spectra were recorded as neat. Melting points were recorded on an electrothermal apparatus and are uncorrected. All the reagents and solvents were used without further purification unless specified otherwise. Technical grade ethyl acetate and petroleum ether used for column chromatography were distilled prior to use. Column chromatography was carried out using silica gel (60-120 mesh and 100- 200 mesh) packed in glass columns. All reactions were performed in oven-dried glassware with magnetic stirring. TLC analysis was performed on commercially prepared 60 F_{254} silica gel plates. Visualization of spots on TLC plate was accomplished with UV light (254 nm) and staining by $KMnO_4$. High-resolution mass spectra were recorded with q-TOF electrospray mass spectrometer. All purchased chemicals were used as received. The Morita-Baylis-Hillman (MBH) bromides **4a-p** were prepared from methyl vinyl ketone and various aldehydes as previously reported.[1] 1,3-*Bis*-toluenesulfonylpropene **3a** and 1,3-*bis*-phenylsulfonylprpopene **3b** were also prepared by following the reported protocol.[2]

General procedure for the preparation of MBH bromides 4a-p[1]



R^2 = aryl, heteroaryl, alkyl; R^3 = Me, Et **4a-p**

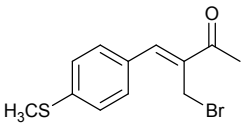
To a solution of the MBH adduct in CH_2Cl_2 (3 mL/mmol of MBH adduct) kept at 0 °C, 48% HBr solution (0.4 mL/mmol of the MBH adduct) was added dropwise. Then, con. H_2SO_4 (0.3 mL/mmol of MBH

[1] R. Buchholtz and H. M. R. Hoffmann, *Helv. Chim. Acta*., 1991, **74**, 1213.

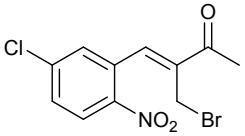
[2] (a) E. T. Gallagher and D. H. Grayson, *Org. Biomol. Chem*. 2003, **1**, 1374. (b) A. Padwa, Y. Gareau, B. Harrison, N. Brian and H. Bryan, *J. Org. Chem*., 1991, **56**, 2713.

adduct) was added and stirred overnight at room temperature. The reaction mixture was diluted with water (10 mL) and extracted with CH_2Cl_2 (3 X10 mL). The combined extracts were dried with anhydrous sodium sulfate and solvent was evaporated on a rotavapor. Column chromatography of the resulting residue on silica gel using ethyl acetate-petroleum ether as eluent afforded analytically pure samples of the MBH bromide **4a-p**.

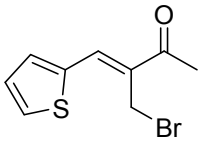
Spectroscopic data for novel MBH bromides



4f, (Z)-3-(bromomethyl)-4-[4-(methylthio)phenyl]but-3-en-2-one
Colorless crystal, 558 mg, 87% (from 500 mg of MBH adduct)
R_f = 0.8 (20% ethyl acetate in hexanes)
Melting point: 93-94 °C
IR (KBr) υ_{max}: 2922, 2852, 1657, 1614, 1587, 1489 cm^{-1}
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.58 (s, 1H), 7.55(d, *J* = 8.4Hz, 2H), 7.32(d, *J* = 8.4Hz, 2H), 4.38 (s, 2H), 2.53 (s, 3H), 2.50 (s, 3H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 197.1, 142.6, 142.5, 142.0, 136.3, 130.4, 125.8, 25.9, 25.4, 15.0.
HRMS calcd for $C_{12}H_{14}BrOS$ (M+H) 284.9949; found 284.9949.

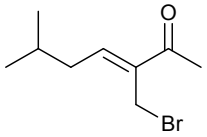


4h, (Z)-3-(bromomethyl)-4-(5-chloro-2-nitrophenyl)but-3-en-2-one
Pale yellow solid, 553 mg, 89% (from 500 mg of MBH adduct)
R_f = 0.6 (20% ethyl acetate in hexanes)
Melting point: 108-109 °C
IR (KBr) υ_{max}: 1676, 1599, 1560, 1523, 1464, 1427, 1338, 906, 813, 679, 526 cm^{-1}
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.21 (d, *J* = 8.8 Hz, 1H), 7.88 (s, 1H), 7.75 (d, *J* = 2.2Hz, 1H), 7.57 (dd, *J* = 8.8, 2.2Hz, 1H), 4.06 (s, 2H), 2.53 (s, 3H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 196.4, 145.3, 140.9, 138.6, 138.2, 132.2, 130.3, 129.9, 127.0, 26.2, 23.6
HRMS calcd for $C_{11}H_{10}BrClNO_3$ (M+H) 317.9533; found 317.9544



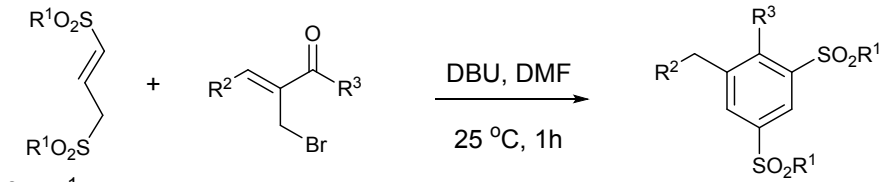
4k, (Z)-3-(bromomethyl)-4-(thiophen-2-yl)but-3-en-2-one
Yellow solid, 531mg, 79% (from 500 mg of MBH adduct)
R_f = 0.7 (20% ethyl acetate in hexanes)
Melting point: 129-131 °C
IR (KBr) υ_{max}: 2922, 1659, 1603, 1414, 1203, 700 cm^{-1}

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.75 (s, 1H), 7.68 (dd, *J* = 5.2, 0.4 Hz, 1H), 7.51 (dd, *J* = 3.6, 0.4 Hz, 1H), 7.20 (dd, *J* = 5.2, 3.6 Hz, 1H), 4.55 (s, 2H), 2.48 (s, 3H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 196.6, 137.1, 135.5, 134.1, 133.6, 132.6, 128.3, 25.8, 25.0
HRMS calcd for $C_9H_{10}BrOS$ (M+H) 244.9636; found 244.9636.



4n, (Z)-3-(bromomethyl)-6-methylhept-3-en-2-one
Pale Yellow oil, 505 mg, 72% (from 500 mg of MBH adduct)
R_f = 0.7 (20% ethyl acetate in hexanes)
IR (KBr) υ_{max}: 2957, 1670, 1462, 412 cm^{-1}
^{1}H NMR (400 MHz, $CDCl_3$) δ 6.81 (t, *J* = 7.5Hz, 1H), 4.16 (s, 2H), 2.33 (s, 3H), 2.25-2.21 (m, 2H), 1.87-1.79 (m, 1H), 0.96 (d, *J* = 6.7Hz, 6H)
^{13}C NMR (100 MHz, $CDCl_3$) δ 196.7, 147.7, 139.0, 38.3, 28.3, 25.6, 22.8, 22.7
HRMS calcd for $C_9H_{16}BrO$ (M+H) 219.0385; found 219.0379.

General procedure for the DBU-mediated benzannulation reaction



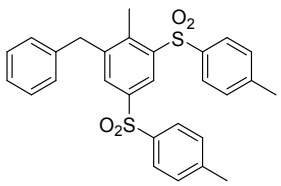
3a, R^1 = *p*-tolyl
3b, R^1 = phenyl

4a-p

5aa-pa

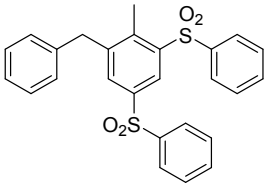
DBU (0.07 mL, 0.45 mmol) was added to a solution of MBH bromide **4a-p** (0.30 mmol) and 1,3-bissulfonylpropene **3a-b** (0.33 mmol) in DMF (5 mL). The reaction mixture was stirred at 25 °C for 1h. After completion of the reaction, 10 mL deionized water was added and the solution was extracted with ethylacetate (3×10 mL). The combined organic layers were washed with brine, dried over sodium sulfate and the solvent was evaporated off on a rotavpor under reduced pressure. The residue was subjected to column charomatography on silica gel using petroleum ether-ethyl acetate as eluent to afford analytically pure sample of the product.

Spectroscopic data for the products 5aa-5na

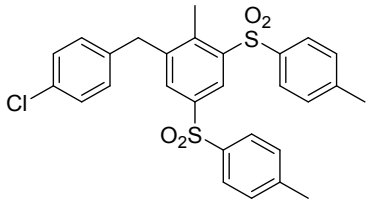


5aa, 4,4'-(5-benzyl-4-methyl-1,3-phenylenedisulfonyl)bis(methylbenzene)
White solid, 110 mg, 75%

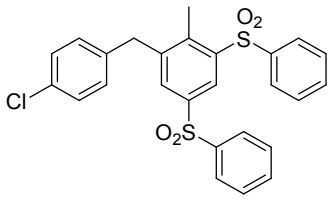
R_f = 0.6 (20% ethyl acetate in hexanes)
Melting point: 189-191 °C
IR (KBr) υ_{max}: 3082, 2926, 1591, 1492, 1442, 1319, 1294, 1147, 540 cm^{-1}
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.63 (d, *J* = 2.0 Hz, 1H), 7.87 (d, *J* = 2.0, 1H), 7.79 (d, *J* = 8.4 Hz, 2H), 7.71 (d, *J* = 8.4 Hz, 2H), 7.33-7.29 (m, 4H), 7.27-7.20 (m, 3H), 6.94 (d, *J* = 6.5Hz, 2H), 4.00 (s, 2H), 2.43 (s, 6H), 2.35 (s, 3H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 144.8, 143.7, 142.3, 141.9, 140.3, 137.9, 137.7, 137.4, 133.2, 130.2, 130.0, 128.9, 128.6, 128.0, 127.9, 126.9, 39.7, 21.7, 16.3
HRMS calcd for $C_{28}H_{27}O_4S_2$ (M+H) 491.1351; found 491.1346.



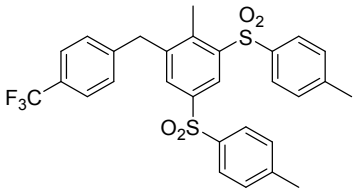
5ab, (5-benzyl-4-methyl-1, 3-phenylenedisulfonyl)dibenzene
White solid, 108 mg, 75%
R_f = 0.6 (20% ethyl acetate in hexanes)
Melting point: 160-162 °C
IR (KBr) υ_{max}: 3086, 3059, 1583, 1496, 1446, 1315, 1147, 835, 567 cm^{-1}
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.68 (d, *J* = 2.0 Hz, 1H), 7.92 (dd, *J* = 7.2, 1.6 Hz, 2H), 7.89 (d, *J* = 2.0, 1H), 7.82 (dd, *J* = 7.2, 1.6 Hz, 2H), 7.61 (t, *J* = 7.2, 2H), 7.65-7.48 (m, 4H), 7.28-7.17 (m, 3H), 6.94 (d, *J* = 6.8Hz, 2H), 4.00 (s, 2H), 2.35 (s, 3H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 143.9, 142.7, 141.6, 140.9, 140.3, 140.0, 137.6, 133.8, 133.5, 129.6, 129.4, 129.0, 128.5, 127.9, 127.1, 126.9, 39.7, 16.4.
HRMS calcd for $C_{26}H_{23}O_4S_2$ (M+H) 463.1038; found 463.1049.



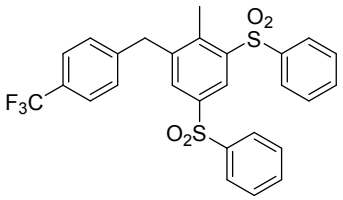
5ba, 4,4'-[5-(4-chlorobenzyl)-4-methyl-1,3-phenylenedisulfonyl]bis(methylbenzene)
White solid, 112 mg, 71%
R_f = 0.6 (20% ethyl acetate in hexanes)
Melting point: 192-194 °C
IR (KBr) υ_{max}: 3066, 2920, 1595, 1492, 1435, 1404, 1303, 1143, 817, 711, 667 cm^{-1}
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.62 (d, *J* = 2.0 Hz, 1H), 7.83 (d, *J* = 2.0, 1H), 7.79 (d, *J* = 8.4 Hz, 2H), 7.70 (d, *J* = 8.4, 2H), 7.33-7.29 (m, 4H), 7.20 (d, *J* = 8.4 Hz, 2H), 6.86 (d, *J* = 8.4, 2H), 3.95 (s, 2H), 2.42 (s, 6H), 2.32 (s, 3H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 144.9 (2), 143.1, 142.2, 142.1, 140.5, 137.8, 137.3, 136.3, 133.1, 132.7, 130.3, 130.0, 129.9, 129.0, 128.0, 127.9, 127.0, 39.0, 21.74, 16.3.
HRMS calcd for $C_{28}H_{26}ClO_4S_2$ (M+H) 525.0961; found 525.0978.



5bb, (5-(4-chlorobenzyl)-4-methyl-1, 3-phenylenedisulfonyl)dibenzene
White solid, 112 mg, 74%
R_f = 0.4 (20% ethyl acetate in hexanes)
Melting point: 147-149 °C
IR (KBr) υ_{max}: 3082, 1581, 1489, 1442, 1315, 1149, 559 cm^{-1}
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.68 (d, *J* = 2.0 Hz, 1H), 7.92 (dd, *J* = 8.0, 1.6 Hz, 2H), 7.85 (d, *J* = 2.0 Hz, 1H), 7.82 (dd, *J* = 8.0, 1.6 Hz, 2H), 7.64-7.59 (m, 2H), 7.55(d, *J* = 7.6 Hz, 2H), 7.52 (d, *J* = 7.6 Hz, 2H), 7.21 (d, *J* = 8.4 Hz, 2H), 6.86 (d, *J* = 8.4 Hz, 2H), 3.97 (s, 2H), 2.33 (s, 3H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 144.3, 142.5, 141.8, 140.7, 140.2, 136.1, 133.8, 133.4, 132.8, 129.9, 129.7, 129.4, 129.1, 127.9, 127.3, 39.0, 16.4.
HRMS calcd for $C_{26}H_{22}ClO_4S_2$ (M+H) 497.0648; found 497.0631.

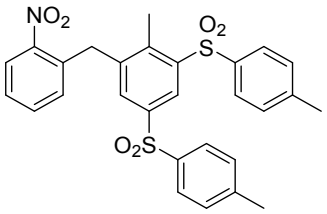


5ca, 4,4'-{4-methyl-5-[4-(trifluromethyl)benzyl]-1,3-phenylenedisulfonyl}bis(methylbenzene)
White solid, 110 mg, 66%
R_f = 0.6 (20% ethyl acetate in hexanes)
Melting point: 187-189 °C
IR (KBr) υ_{max}: 3082, 2925, 1593, 1419, 1323, 1149, 1112, 812, 709, 659 cm^{-1}
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.64 (d, *J* = 2.0 Hz, 1H), 7.85 (d, *J* = 2.0, 1H), 7.79 (d, *J* = 8.4 Hz, 2H), 7.70 (d, *J* = 8.4, 2H), 7.49 (d, *J* = 8.1, 2H), 7.33-7.28 (m, 4H), 7.05 (d, *J* = 8.1, 2H), 4.05 (s, 2H), 2.42 (s, 6H), 2.32 (s, 3H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 144.9, 144.8, 142.4, 142.1(2), 140.5, 137.6, 137.1, 133.1, 130.2, 129.9, 128.7, 127.9, 127.8, 127.1, 125.7 (q, *J* = 3.8Hz), 39.3, 21.6(2), 16.3.
HRMS calcd for $C_{29}H_{26}F_3O_4S_2$ (M+H) 559.1225; found 559.1206.

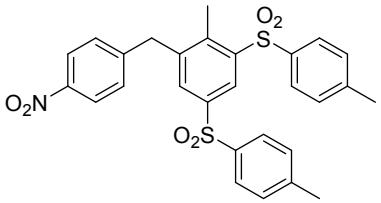


5cb, {4-methyl-5-[4-(trifluromethyl)benzyl]-1,3-phenylenedisulfonyl}dibenzene
White solid, 110 mg, 69%
R_f = 0.5 (20% ethyl acetate in hexanes)
Melting point: 156-157 °C
IR (KBr) υ_{max}: 3066, 1583, 1448, 1325, 1298, 1142, 1112, 1070, 690, 549 cm^{-1}

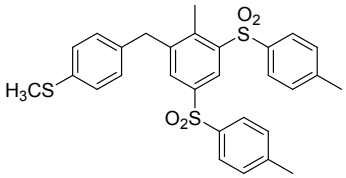
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.69 (d, *J* = 2.0 Hz, 1H), 7.90 (dd, *J* = 8.0, 1.6 Hz, 2H), 7.87 (d, *J* = 2.0 Hz, 1H), 7.82 (dd, *J* = 8.8, 1.6 Hz, 2H), 7.63-7.54 (m, 2H), 7.53-7.49 (m, 6H), 7.05 (d, *J* = 8.0 Hz, 2H), 4.07 (s, 2H), 2.34 (s, 3H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 142.6, 142.4, 141.9, 141.7, 140.5, 140.2, 140.0, 133.8, 133.7, 133.4, 129.6, 129.3, 128.7, 127.8(2), 127.3, 125.8 (q, *J* = 3.6 Hz), 39.3, 16.3.
HRMS calcd for $C_{27}H_{22}F_3O_4S_2$ (M+H) 531.0912; found 531.0930.



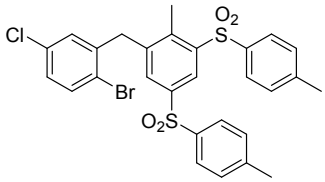
5da, 4,4'-[4-methyl-5-(2-nitrobenzyl)-1,3-phenylenedisulfonyl]bis(methylbenzene)
White solid, 93 mg, 58%
R_f = 0.4 (20% ethyl acetate in hexanes)
Melting point: 170-172 °C
IR (KBr) υ_{max}: 3059, 2922, 1593, 1523, 1435, 1348, 1315, 1143, 837, 659 cm^{-1}
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.63 (d, *J* = 1.6 Hz, 1H), 8.01 (dd, *J* = 8.0, 1.4 Hz, 1H), 7.73 (d, *J* = 8.4Hz, 2H), 7.71 (d, *J* = 8.4 Hz, 2H), 7.63 (d, *J* = 1.6 Hz, 1H), 7.53-7.40 (m, 2H), 7.32-7.28 (m ,4H), 6.92 (d, *J* = 7.6Hz, 1H), 4.28 (s, 2H), 2.41 (s, 6H), 2.34 (s, 3H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 149.0, 144.9, 142.1(2), 141.8, 140.6, 137.7, 137.2, 133.8, 132.8, 132.3, 131.6, 130.2, 130.0, 128.5, 128.0, 127.9, 127.1, 125.5, 36.6, 21.8, 16.3.
HRMS calcd for $C_{28}H_{26}NO_6S_2$ (M+H) 536.1202; found 536.1243.



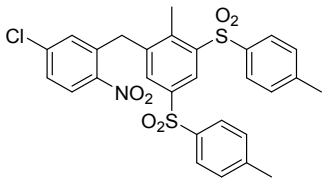
5ea, 4,4'-[4-methyl-5-(4-nitrobenzyl)-1,3-phenylenedisulfonyl]bis(methylbenzene)
White solid, 90 mg, 56%
R_f = 0.4 (20% ethyl acetate in hexanes)
Melting point: 122-124 °C
IR (KBr) υ_{max}: 3072, 2924, 1597, 1519, 1492, 1438, 1348, 1309, 1145, 837, 812, 705, 661 cm^{-1}
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.65 (d, *J* = 1.6 Hz, 1H), 8.08 (d, *J* = 8.5 Hz, 2H), 7.87 (d, *J* = 1.6 Hz, 1H), 7.80 (d, *J* = 8.3 Hz, 2H), 7.70 (d, *J* = 8.3 Hz, 2H), 7.33-7.29 (m, 4H), 7.10 (d, *J* = 8.5Hz, 2H), 4.10 (s, 2H), 2.42 (s, 6H), 2.31 (s, 3H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 146.9, 145.5, 145.1(2), 142.4, 142.2, 141.8, 140.8, 137.6, 137.0, 133.2, 130.4, 130.1, 129.3, 128.0, 127.9, 127.4, 124.1, 39.5, 21.8, 16.4
HRMS calcd for $C_{28}H_{26}NO_6S_2$ (M+H) 536.1202; found 536.1225.



5fa, 4,4'-[4-methyl-5-(4-methylthiobenzyl)-1,3-phenylenedisulfonyl]bis(methylbenzene)
White solid, 126 mg, 78%
R_f = 0.5 (20% ethyl acetate in hexanes)
Melting point: 145-147 °C
IR (KBr) υ_{max}: 3062, 2924, 1593, 1492, 1436, 1319, 1147, 1085, 707, 671, 545 cm^{-1}
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.62 (d, *J* = 1.5 Hz, 1H), 7.86 (d, *J* = 1.5 Hz, 1H), 7.78 (d, *J* = 8.2 Hz, 2H), 7.70 (d, *J* = 8.2 Hz, 2H), 7.32-7.28 (m, 4H), 7.12 (d, *J* = 8.2Hz, 2H), 6.85 (d, *J* = 8.2Hz, 2H), 3.94 (s, 2H), 2.45 (s, 3H), 2.42 (s, 6H), 2.33 (s, 3H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 144.7, 143.4, 142.1, 141.8, 140.2, 137.7, 137.2, 136.8, 134.4, 133.0, 130.1, 130.1, 129.9, 129.8, 128.9, 127.8, 126.9, 126.7, 39.0, 21.6, 21.6, 16.2, 15.8.
HRMS calcd for $C_{29}H_{29}O_4S_3$ (M+H) 537.1228; found 537.1247.

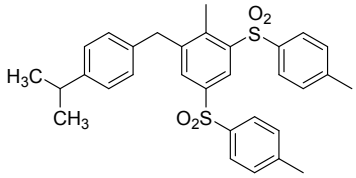


5ga, 4,4'-[5-(2-bromo-5-chlorobenzyl)-4-methyl-1,3-phenylenedisulfonyl]bis(methylbenzene)
White solid, 121 mg, 67%
R_f = 0.5 (20% ethyl acetate in hexanes)
Melting point: 189-191 °C
IR (KBr) υ_{max}: 3062, 2924, 1593, 1448, 1317, 1143, 1087,812, 711, 549 cm^{-1}
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.67 (d, *J* = 1.8 Hz, 1H), 7.77 (d, *J* = 8.3 Hz, 2H), 7.71 (d, *J* = 8.3Hz, 2H), 7.68 (d, *J* = 1.8 Hz, 1H), 7.50(d, *J* = 8.5, 1H), 7.31 (d, *J* = 8.4 Hz, 4H), 7.11 (dd, *J* = 8.5, 2.4 Hz, 1H), 6.62 (d, *J* = 2.4 Hz, 1H), 4.00 (s, 2H), 2.42 (s, 6H), 2.32 (s, 3H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 144.9, 142.2, 142.0, 141.5, 140.6, 139.0, 137.7, 137.2, 134.3, 134.2, 134.0, 132.7, 130.3(2), 130.1, 130.0, 129.0, 127.9, 127.1, 122.7, 39.7, 21.8, 21.73, 16.3.
HRMS calcd for $C_{28}H_{25}BrClO_4S_2$ (M+H) 603.0066; found 603.0076.

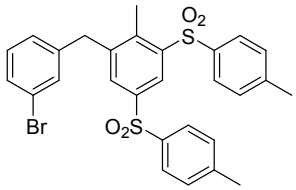


5ha, 4,4'-[5-(5-chloro-2-nitrobenzyl)-4-methyl-1,3-phenylenedisulfonyl]bis(methylbenzene)
White solid, 106 mg, 62%
R_f = 0.5 (20% ethyl acetate in hexanes)
Melting point: 182-184 °C
IR (KBr) υ_{max}: 3067, 2927, 1525, 1440, 1313, 1296, 1145,813, 549 cm^{-1}

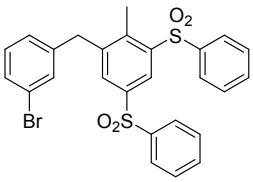
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.66 (d, *J* = 1.6 Hz, 1H), 8.01 (d, *J* = 8.6 Hz, 1H), 7.75 (d, *J* = 8.2 Hz, 2H), 7.70 (d, *J* = 8.3 Hz, 2H), 7.65 (d, *J* = 1.6, 1H), 7.42 (dd, *J* = 8.6, 2.0 Hz, 1H), 7.32 (d, *J* = 8.0, 4H), 6.81 (d, *J* = 2.0, 1H), 4.28 (s, 2H), 2.42 (s, 6H), 2.34 (s, 3H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 147.3, 145.0(2), 142.3, 142.0, 140.8(2), 140.3, 137.6, 137.2, 135.0, 132.3, 131.4, 130.3, 130.1, 128.7, 128.0, 127.9, 127.4, 127.0, 36.5, 21.7, 16.3.
HRMS calcd for $C_{28}H_{25}ClNO_6S_2$ (M+H) 570.0812; found 570.0832.



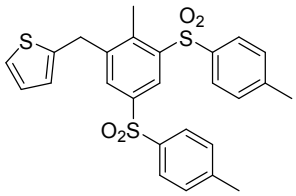
5ia, 4,4'-[5-(4-isopropylbenzyl)-4-methyl-1,3-phenylenedisulfonyl]bis(methylbenzene)
White solid, 120 mg, 75%
R_f = 0.7 (20% ethyl acetate in hexanes)
Melting point: 167-168 °C
IR (KBr) υ_{max}: 3078, 2964, 1593, 1425, 1319, 1139, 1083, 808, 705, 671, 565 cm^{-1}
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.61 (d, *J* = 1.8 Hz, 1H), 7.87 (d, *J* = 1.9 Hz, 1H), 7.79 (d, *J* = 8.2 Hz, 2H), 7.70 (d, *J* = 8.2Hz, 2H), 7.32-7.28 (m, 4H), 7.09 (d, *J* = 8.0 Hz, 2H), 6.85 (d, *J* = 8.0 Hz, 2H), 3.95 (s, 2H), 2.89-2.80 (m, 1H), 2.42 (s, 6H), 2.35 (s, 3H), 1.21 (d, J = 6.8 Hz, 6H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 147.5, 144.8(2), 144.0, 142.3, 141.8, 140.2, 138.0, 137.4, 135.0, 133.2, 130.2, 130.0, 128.4, 128.0, 127.9, 126.9, 126.8, 39.2, 33.7, 24.0, 21.7, 16.4
HRMS calcd for $C_{31}H_{33}O_4S_2$ (M+H) 533.1820; found 533.1829.



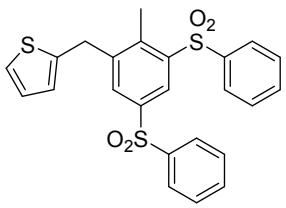
5ja, 4,4'-[5-(3-bromobenzyl)-4-methyl-1,3-phenylenedisulfonyl]bis(methylbenzene)
White solid, 125 mg, 73%
R_f = 0.6 (20% ethyl acetate in hexanes)
Melting point: 204-206 °C
IR (KBr) υ_{max}: 3072, 2924, 1591, 1566, 1446, 1294, 1141, 840, 812, 709, 661, 545 cm^{-1}
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.65 (d, *J* = 1.6 Hz, 1H), 7.84 (d, *J* = 1.6Hz, 1H), 7.79 (d, *J* = 8.3Hz, 2H), 7.70 (d, *J* = 8.3Hz, 2H), 7.35-7.29 (m, 5H), 7.14-7.10 (m, 1H), 7.05 (s, 1H), 6.87 (d, *J* = 7.7Hz, 1H), 3.96 (s, 2H), 2.42 (s, 6H), 2.33 (s, 3H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 144.8, 144.7, 142.6, 142.1, 141.9, 140.4, 139.9, 137.6, 137.1, 133.0, 131.4, 131.3, 130.3, 130.2, 129.9, 127.8, 127.8, 127.1, 126.9, 122.8, 39.0, 21.6(2), 16.2.
HRMS calcd for $C_{28}H_{26}BrO_4S_2$ (M+H) 569.0456; found 569.0444.



5jb, [5-(3-bromobenzyl)-4-methyl-1,3-phenylenedisulfonyl]dibenzene
White solid, 124 mg, 76%
$\mathbf{R_f}$ = 0.5 (20% ethyl acetate in hexanes)
Melting point: 156-157 °C
IR (KBr) υ_{max}: 3064, 1568, 1446, 1309, 1143, 1978, 684, 567 cm^{-1}
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.68 (d, *J* = 1.6 Hz, 1H), 7.92 (d, *J* = 7.6 Hz, 2H), 7.87 (d, *J* = 1.6 Hz, 1H), 7.82 (d, *J* = 7.2 Hz, 2H), 7.62-7.60 (m, 2H), 7.56-7.50 (m, 4H), 7.34 (d, *J* = 7.4 Hz, 1H), 7.14-7.01 (m, 1H), 7.07 (s, 1H), 6.86 (d, *J* = 7.4 Hz, 1H), 3.97 (s, 2H), 2.33 (s, 3H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 143.0, 142.6, 141.8, 140.7, 140.2, 139.9, 133.9, 133.8, 133.5, 131.5, 130.5, 130.2, 129.7, 129.5, 127.9, 127.3, 127.2, 123.0, 39.2, 16.4.
HRMS calcd for $C_{26}H_{22}BrO_4S_2$ (M+H) 541.0143; found 541.0122.

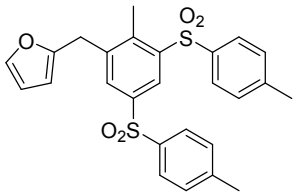


5ka, 2-(2-methyl-3,5ditosylbenzyl)thiophene
White solid, 107 mg, 72%
$\mathbf{R_f}$ = 0.6 (20% ethyl acetate in hexanes)
Melting point: 199-201 °C
IR (KBr) υ_{max}: 2924, 1591, 1498, 1436, 1315, 1294, 1143, 1083,812, 542 cm^{-1}
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.63 (d, *J* = 2.0 Hz, 1H), 7.95 (d, *J* = 2.0 Hz, 1H), 7.80 (d, *J* = 8.0 Hz, 2H), 7.70 (d, *J* = 8.0 Hz, 2H), 7.32-7.29 (m, 4H), 7.14 (d, *J* = 5.1 Hz, 1H), 6.88 (dd, *J* = 5.1, 3.5 Hz, 1H), 6.58 (d, *J* = 3.5 Hz, 1H), 4.14 (s, 2H), 2.41 (s, 6H), 2.40 (s, 3H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 144.9, 143.2, 142.0, 141.9, 140.5, 140.4, 137.9, 137.3, 132.8, 130.2, 130.0, 128.0, 127.9, 127.2, 125.9, 124.8, 124.7, 34.0, 21.8, 16.2.
HRMS calcd for $C_{26}H_{25}O_4S_3$ (M+H) 497.0915; found 497.0933.

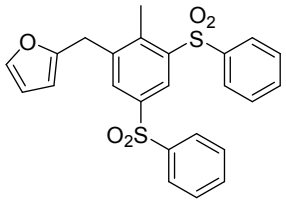


5kb, 2-[2-methyl-3,5bis(phenylsulfonyl)benzyl]thiophene
White solid, 104 mg, 74%
$\mathbf{R_f}$ = 0.5 (20% ethyl acetate in hexanes)
Melting point: 187-189 °C
IR (KBr) υ_{max}: 3082, 2362, 1581, 1444, 1311, 1147, 1089, 725, 686, 570 cm^{-1}

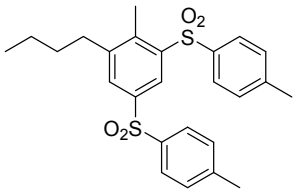
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.69 (d, *J* = 2.0 Hz, 1H), 7.98 (d, *J* = 2.0 Hz, 1H), 7.94 (d, *J* = 7.8Hz, 2H), 7.83 (dd, *J* = 7.8Hz, 2H), 7.62-7.60 (m, 2H), 7.56- 7.52 (m, 4H), 7.14 (dd, *J* = 5.2, 1.2 Hz, 1H), 6.88 (dd, *J* = 5.2, 3.6Hz, 1H), 6.59 (dd, *J* = 3.6, 1.2Hz, 1H), 4.16 (s, 2H), 2.41 (s, 3H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 143.4, 142.3, 141.7, 140.8, 140.3, 140.2(2), 133.8, 133.1, 129.7, 126.4, 127.9, 127.4, 127.2, 126.0, 124.8, 34.0, 16.2.
HRMS calcd for $C_{24}H_{21}O_4S_3$ (M+H) 469.0602; found 469.0590.



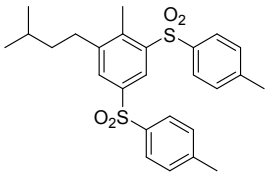
5la, 2-(2-methyl-3,5-ditosylbenzyl)furan
White solid, 100 mg, 70%
R_f = 0.5 (20% ethyl acetate in hexanes)
Melting point: 203-204 °C
IR (KBr) υ_{max}: 2926, 1593, 1498, 1440, 1315, 1294, 1143, 1083,810, 707, 553 cm^{-1}
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.63 (d, *J* = 1.9 Hz, 1H), 7.90 (d, *J* = 1.9 Hz, 1H), 7.81 (d, *J* = 8.3Hz, 2H), 7.71 (d, *J* = 8.3Hz, 2H), 7.32-7.30 (m, 4H), 7.28 (dd, *J* = 1.9, 0.8 Hz, 1H), 6.25 (dd, *J* = 3.2, 1.9 Hz, 1H), 5.88 (dd, *J* = 3.2Hz, 1H), 3.96 (s, 2H), 2.41 (s, 9H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 151.2, 144.8, 142.1, 142.0, 141.8, 141.2, 140.4, 137.9, 137.3, 133.0, 130.3, 130.0, 128.0, 127.9, 127.2, 110.6, 110.5, 107.5, 107.4, 32.5, 21.7, 16.1.
HRMS calcd for $C_{26}H_{25}O_5S_2$ (M+H) 481.1143; found 481.1166.



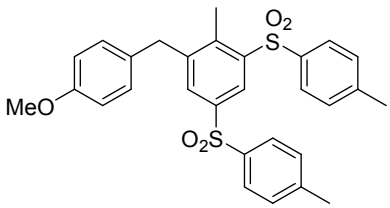
5lb, 2-[2-methyl-3,5bis(phenylsulfonyl)benzyl]furan
White solid, 97 mg, 71%
R_f = 0.5 (20% ethyl acetate in hexanes)
Melting point: 175-177 °C
IR (KBr) υ_{max}: 2922, 2855, 2306, 1585, 1444,1307, 1145, 725, 535 cm^{-1}
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.67 (d, *J* = 2.0 Hz, 1H), 7.97-7.88 (m, 3H), 7.83 (dd, *J* = 8.4, 1.2 Hz, 2H), 7.64-7.55 (m, 2H), 7.57-7.50 (m, 4H), 7.28 (dd, *J* = 2.0, 0.8Hz, 1H), 6.26 (dd, *J* = 3.2, 2.0 Hz, 1H), 5.88 (dd, *J* = 3.2, 0.8 Hz, 1H), 3.97 (s, 2H), 2.42 (s, 3H).).
^{13}C NMR (100 MHz, $CDCl_3$) δ 151.1, 141.6, 141.4, 140.3, 140.1, 133.8, 133.3, 129.6, 129.4, 127.9, 110.6(2), 107.5(2), 32.5, 16.2.
HRMS calcd for $C_{24}H_{21}O_5S_2$ (M+H) 453.0830; found 453.0840



5ma, 4, 4'-(5-butyl-4-methyl-1,3-phenylenedisulfonyl)bis(methylbenzene)
White solid, 99 mg, 72%
R_f = 0.7 (20% ethyl acetate in hexanes)
Melting point: 146-148 °C
IR (KBr) υ_{max}: 3068, 2953, 2924, 2864, 1593, 1442, 1309, 1296, 1145, 1085, 813, 565, 549 cm^{-1}
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.56 (d, *J* = 2.0 Hz, 1H), 7.91 (d, *J* = 2.0Hz, 1H), 7.82 (d, *J* = 8.4 Hz, 2H), 7.70 (d, *J* = 8.4 Hz, 2H), 7.32-7.25 (m, 4H), 2.60 (t, *J* = 8.0 Hz, 2H), 2.40 (s, 6H), 2.38 (s, 3H), 1.48-1.44 (m, 2H), 1.35-1.29 (m, 2H), 0.89 (t, *J* = 7.3 Hz, 3H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 145.8, 144.8, 144.7, 141.5, 141.4, 140.0, 138.1, 137.5, 132.2, 130.2, 130.0, 128.0, 127.9, 126.3, 33.5, 31.9, 22.6, 21.7, 15.8, 13.9.
HRMS calcd for $C_{25}H_{29}O_4S_2$ (M+H) 457.1507; found 457.1499.

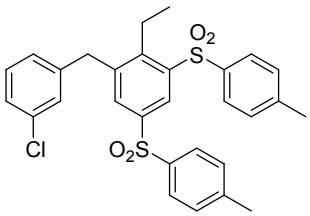


5na, 4, 4'-(5-isopentyl-4-methyl-1,3-phenylenedisulfonyl)bis(methylbenzene)
White solid, 103 mg, 73%
R_f = 0.7 (20% ethyl acetate in hexanes)
Melting point: 165-167 °C
IR (KBr) υ_{max}: 3072, 2958, 2908, 1593, 1442, 1313, 1296, 1145, 1083, 812, 549 cm^{-1}
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.56 (d, *J* = 2.0 Hz, 1H), 7.92 (d, *J* = 2.0 Hz, 1H), 7.85 (d, *J* = 8.4 Hz, 2H), 7.71 (d, *J* = 8.4 Hz, 2H), 7.33-7.26 (m, 4H), 2.60 (t, *J* = 8Hz, 2H), 2.42 (s, 6H),2.39 (s, 3H), 1.59-1.56 (m, 1H), 1.38-1.32 (m, 2H), 0.91 (d, *J* = 6.7 Hz, 6H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 146.0, 144.7(2), 141.5, 141.3, 140.1, 138.1, 137.5, 132.1, 130.2, 130.0, 128.0, 127.9, 126.3, 39.0, 31.7, 28.3, 22.4, 21.7, 15.7.
HRMS calcd for $C_{26}H_{31}O_4S_2$ (M+H) 471.1664; found 471.1657.



5oa, 4,4'-(5-(4-methoxybenzyl)-4-methyl-1,3-phenylenedisulfonyl)bis(methylbenzene)
White solid, 128 mg, 82%
Rf = 0.5 (20% ethyl acetate in hexanes)
Melting point: 167-169 °C
IR (KBr) υ_{max}: 2926, 1591, 1510, 1444, 1315, 1246, 1150, 567, 545 cm^{-1}

1H NMR (400 MHz, $CDCl_3$) δ 8.61 (d, J = 1.8 Hz, 1H), 7.84 (d, J = 1.8Hz, 1H), 7.78 (d, J = 8.2Hz, 2H), 7.69 (d, J = 8.2Hz, 2H), 7.29(dd, J= 7.9, 5.9Hz, 4H), 6.85 (d, J = 8.5Hz, 2H), 6.77 (d, J = 8.5Hz, 2H), 3.91 (s, 2H), 3.76 (s, 3H), 2.40(s, 6H), 2.34 (s, 3H).
13C NMR (100 MHz, $CDCl_3$) δ 158.4, 144.8, 144.7, 144.2, 142.2, 141.8, 140.2, 137.9, 137.4, 133.0, 130.2, 129.9, 129.6, 128.0, 127.9, 126.7, 114.3, 55.3, 38.8, 21.7, 16.2.
HRMS calcd for $C_{29}H_{28}O_5S_2$ (M+H) 521.1456; found 521.1479.

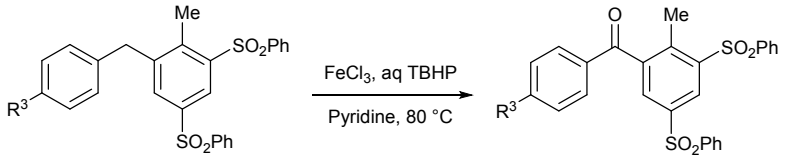


5pa, 4,4'-(5-(3-chlorobenzyl)-4-ethyl-1,3-phenylenedisulfonyl)bis(methylbenzene)
White solid, 102 mg, 63 %
Rf = 0.6 (20% ethyl acetate in hexanes)
Melting point: 146-148 °C
IR (KBr) υ_{max}: 2976, 1591, 1475, 1429, 1317, 1294, 1147, 669, 559 cm^{-1}
1H NMR (400 MHz, $CDCl_3$) δ 8.59 (d, J = 1.6 Hz, 1H), 7.74-7.69 (m, 5H), 7.31 (dd, J = 8.4, 2.0Hz, 4H), 7.20-7.18 (m, 2H), 6.89(s, 1H), 6.84 (dd, J = 8.4, 1.6Hz, 1H), 3.99 (s, 2H), 2.89 (q, J = 7.4Hz 2H), 2.41(s, 6H), 0.88 (t, J = 7.4Hz, 3H).
13C NMR (100 MHz, $CDCl_3$) δ 147.7, 144.9, 144.8, 142.7, 141.9, 140.5, 140.4, 137.9, 137.7, 134.8, 133.7, 130.3, 130.2, 130.1, 128.7, 128.0, 127.9, 127.3, 127.2, 126.9, 37.6, 22.9, 21.7, 14.1
HRMS calcd for $C_{29}H_{27}ClO_4S_2$ (M+H) 539.1118; found 539.1121

Procedure for the gram scale benzannulation reaction

DBU (0.88 mL, 5.88 mmol) was added to a solution of MBH bromide **5j** (1g, 3.92 mmol) and 1,3-bis-tolylsulfonylpropene **3a** (1.51 g, 4.31 mmol) in DMF (15 mL). The reaction mixture was stirred at 25 °C for 1h. After completion of the reaction, 50 mL deionized water was added and the solution was extracted with ethylacetate (3×30 mL). Work-up and column chromatography as described above afforded a white solid (1.58 g, 71%) which was identical to the product **5ja** obtained in the low-scale reaction.

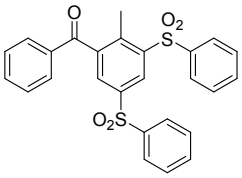
General procedure for $FeCl_3$-TBHP mediated benzylic oxidation



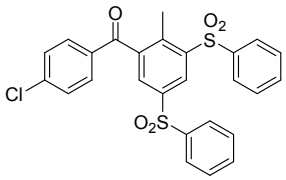
R^3 = H, **5ab**
R^3 = Cl, **5bb**

R^3 = H, **10a**, 92%
R^3 = Cl, **10b**, 93%

To a solution of $FeCl_3.6H_2O$ (2.2 mg, 0.008 mmol) in pyridine (0.5 mL), the bis-sulfonyl arene **5ab** or **5bb** (0.22 mmol) was added. To this, *tert*-butyl hydroperoxide (0.05 mL, 0.33 mmol) was added and the reation mixture heated at 80 °C for 24 h. Then the reaction mixture was poured into a separating funnel containing 10 mL 1N HCl. It was then extracted with dichloromethane (3 X 10 mL). The combined organic layers was dried with anhydrous sodium sulphate, filtered and evaporated to dryness on a rotavapor. The residue was subjected to column chromatography on silica gel using petroleum ether-ethyl acetate as eluent to afford the benzphenones **10a-b** in analytically pure form.

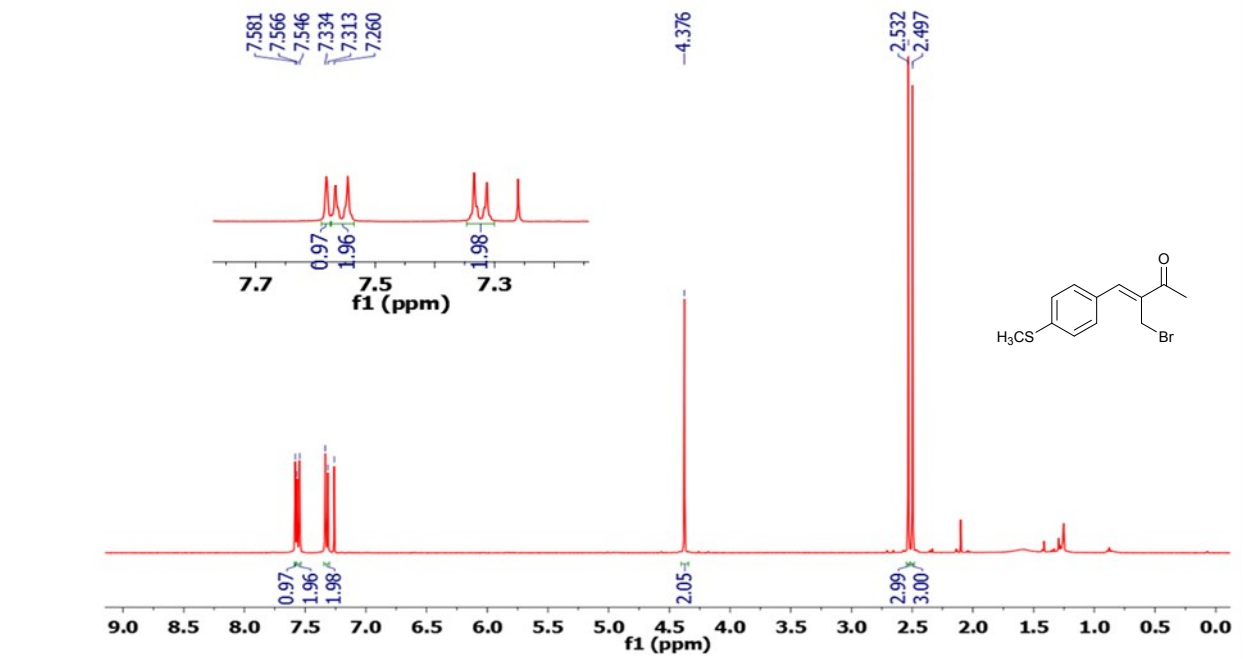


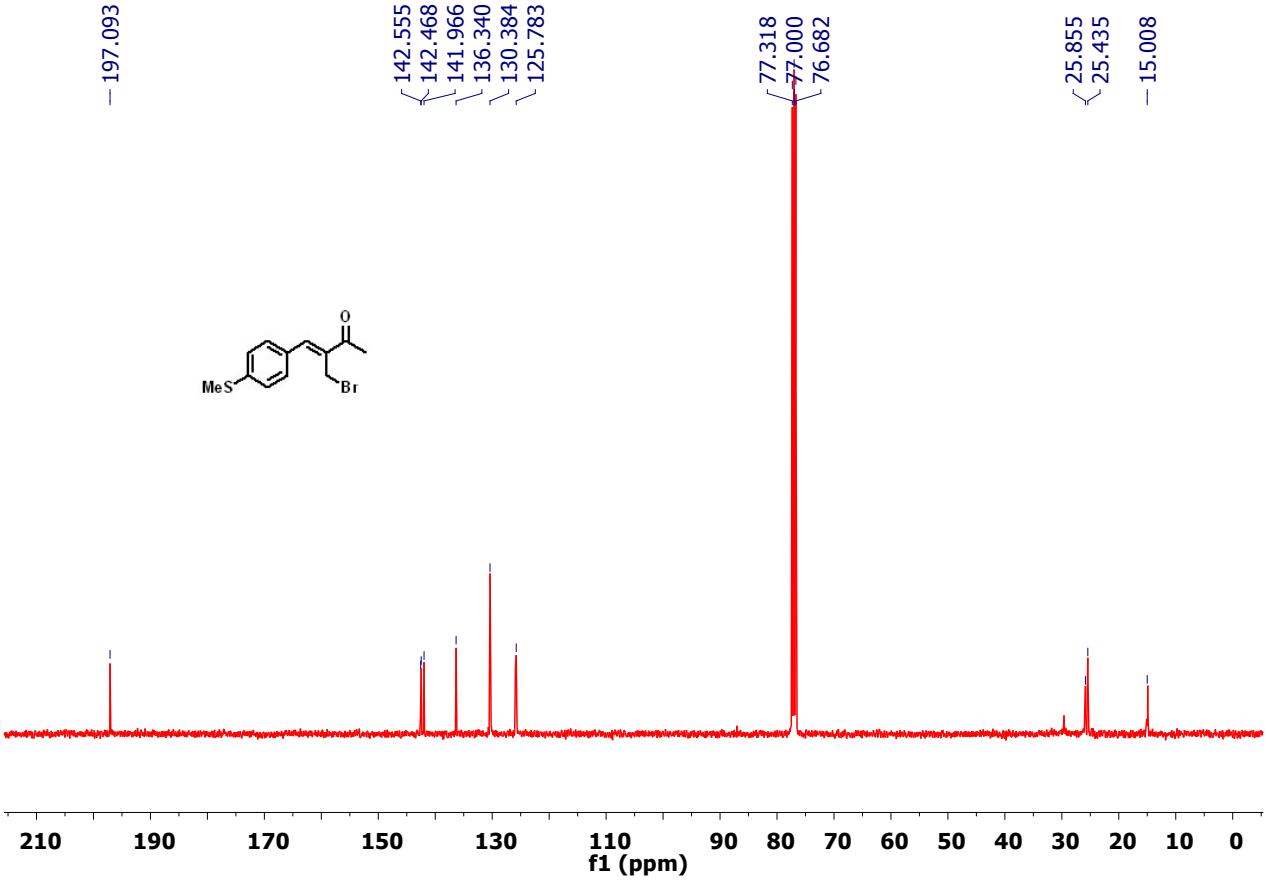
10a, [2-methyl-3,5-bis(phenylsulfonyl)phenyl](phenyl)methanone
White solid, 96 mg, 92%
R_f = 0.5 (20% ethyl acetate in hexanes)
Melting point: 168-170 °C
IR (KBr) υ_{max}: 3066, 1664, 1583, 1442, 1296, 1145, 1078, 727, 684, 559 cm^{-1}
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.88 (d, *J* = 1.9 Hz, 1H), 8.03 (d, *J* = 1.9 Hz, 1H), 7.96 (d, *J* = 7.6 Hz, 2H), 7.86 (d, *J* = 7.6 Hz, 2H), 7.67-7.63 (m, 5H), 7.58- 7.53 (m, 4H), 7.46 (t, *J* = 8.0 Hz, 2H), 2.36 (s, 3H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 195.3, 143.4, 142.3, 141.6, 140.5, 140.3, 139.6, 135.7, 134.8, 134.1, 130.8, 130.2, 129.8, 129.6, 129.1, 128.1, 128.0, 17.4.
HRMS calcd for $C_{26}H_{21}O_5S_2$ (M+H) 477.0830; found 477.0852.

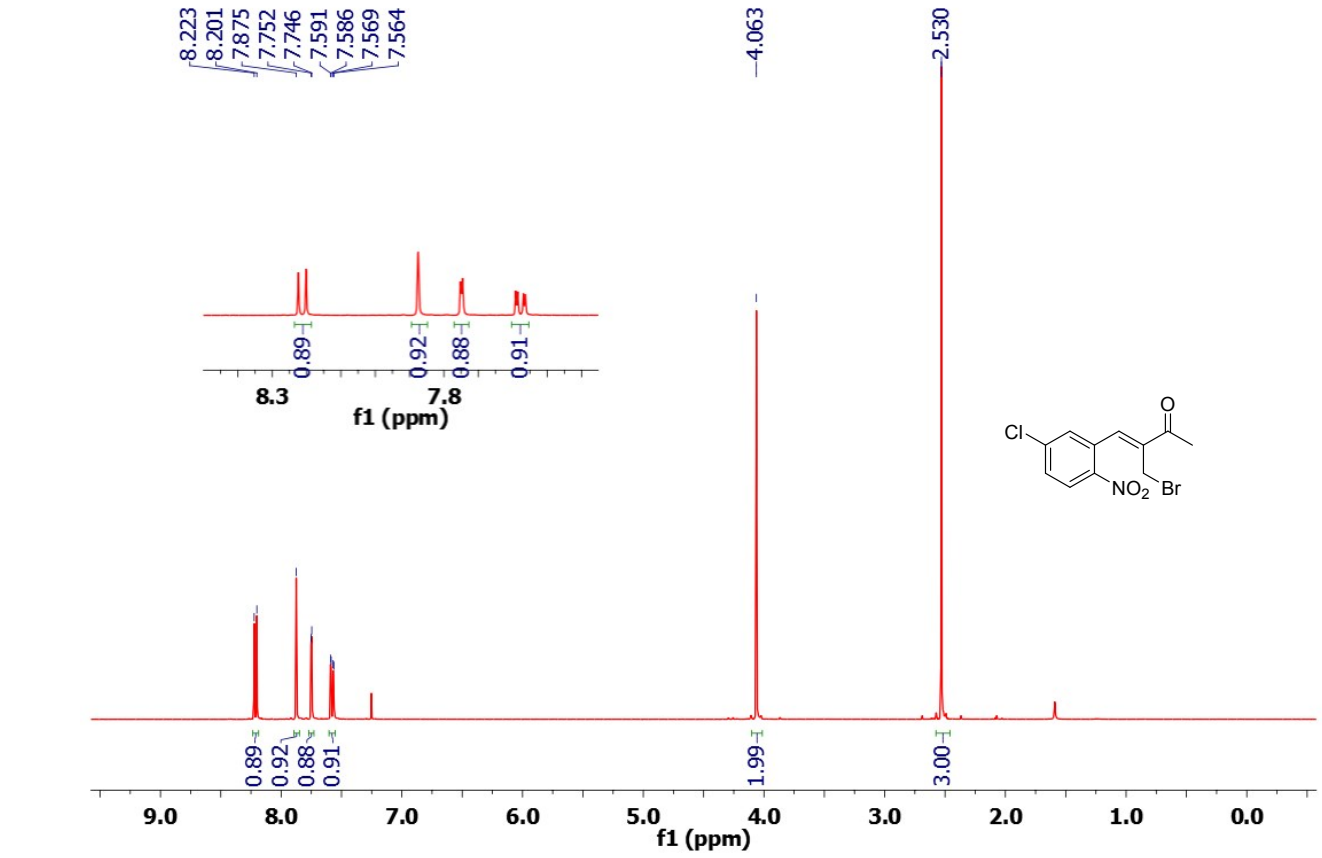


10b, (4-chlorophenyl)[2-methyl-3,5-bis(phenylsulfonyl)phenyl]methanone
White solid, 102 mg, 91%
R_f = 0.6 (20% ethyl acetate in hexanes)
Melting point: 153-155 °C
IR (KBr) υ_{max}: 3068, 2974, 1672, 1585, 1444, 1317, 1143, 1085, 723, 688, 559 cm^{-1}
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.87 (d, *J* = 1.9 Hz, 1H), 8.00 (d, *J* = 1.9 Hz, 1H), 7.95 (d, *J* = 7.6 Hz, 2H), 7.85 (d, *J* = 7.6, 2H), 7.67- 7.53(m, 8H), 7.43 (d, *J* = 8.5, 2H), 2.35 (s, 3H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 194.1, 142.8, 142.5, 141.6, 141.5, 140.7, 140.3, 139.6, 134.2, 134.1, 131.5, 130.7, 129.8, 129.6, 128.2, 128.0, 17.4.
HRMS calcd for $C_{26}H_{20}ClO_5S_2$ (M+H) 511.0441; found 511.0461.

NMR Spectra of new compounds



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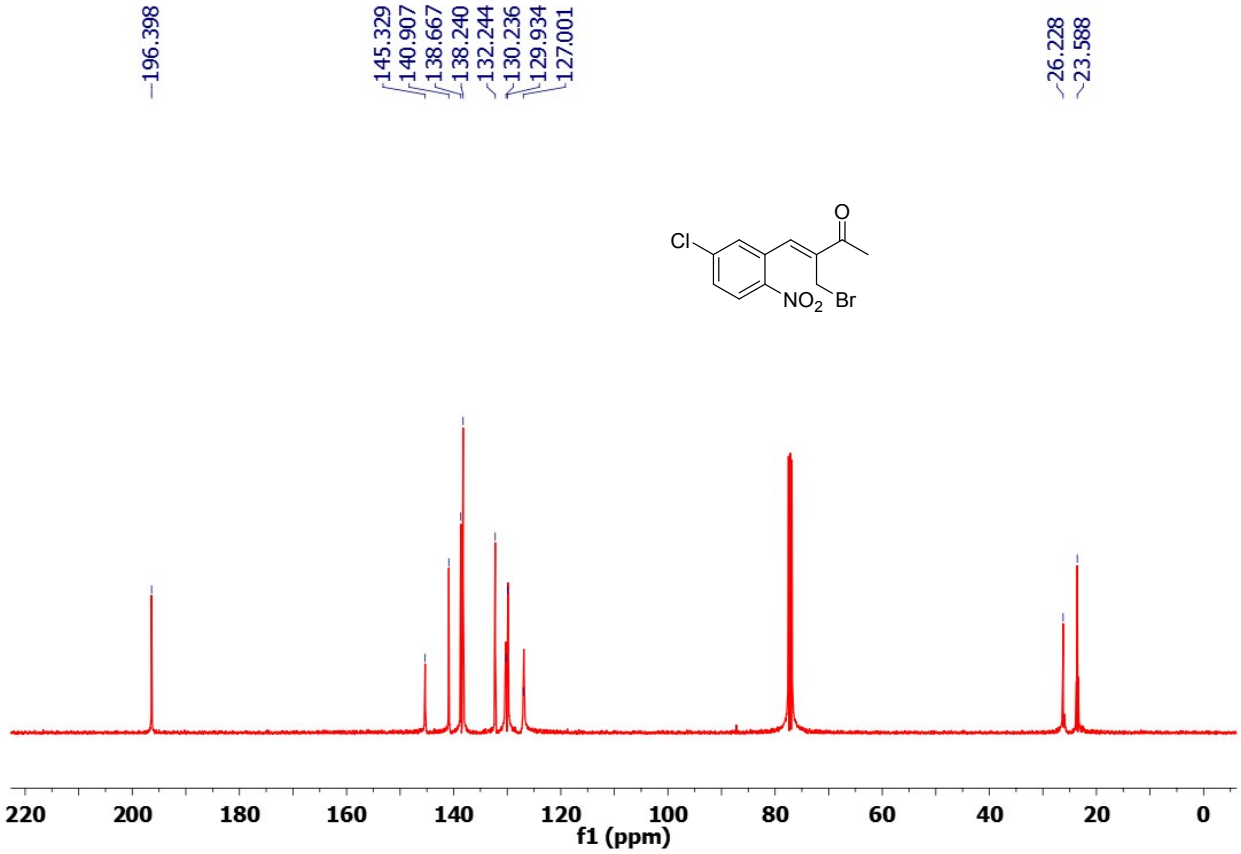
7.875
7.752
7.746
7.591
7.586
7.569
7.564
4.063
2.530
0.89
0.92
0.88
0.91
8.3
7.8
f1 (ppm)
Cl
O
NO2
Br
1.99
3.00
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0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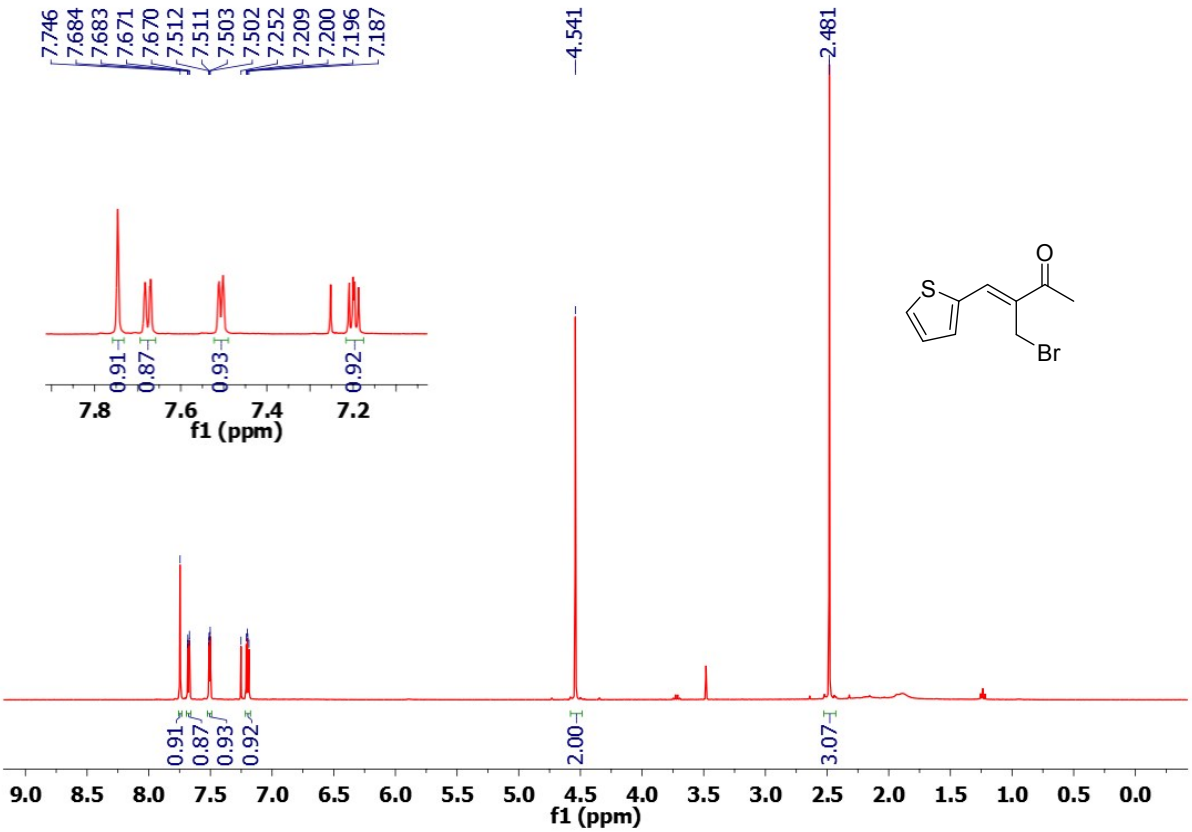
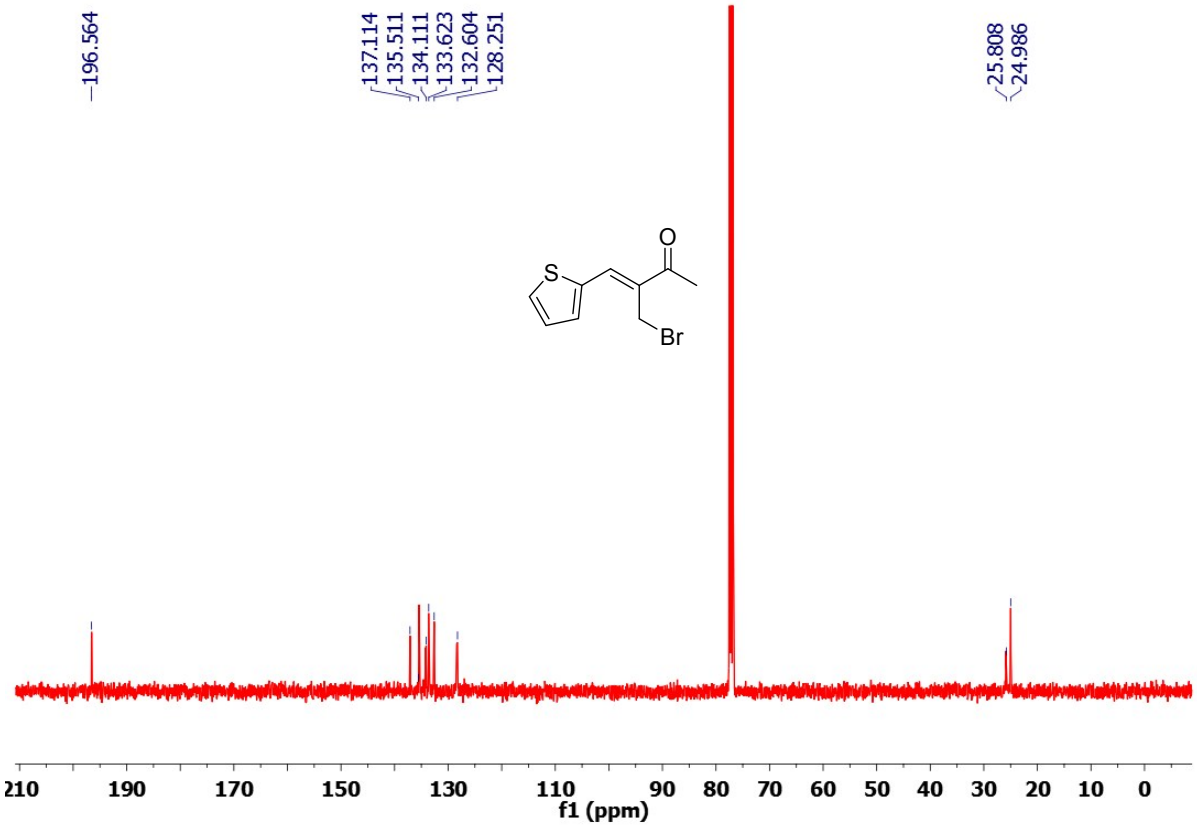
145.329
140.907
138.667
138.240
132.244
130.236
129.934
127.001
26.228
23.588
Cl
O
NO2
Br
220
200
180
160
140
120
100
80
60
40
20
0
f1 (ppm)


7.746
7.684
7.683
7.671
7.670
7.512
7.511
7.503
7.502
7.252
7.209
7.200
7.196
7.187
4.541
2.481
0.91
0.87
0.93
0.92
2.00
3.07
f1 (ppm)
O
S
Br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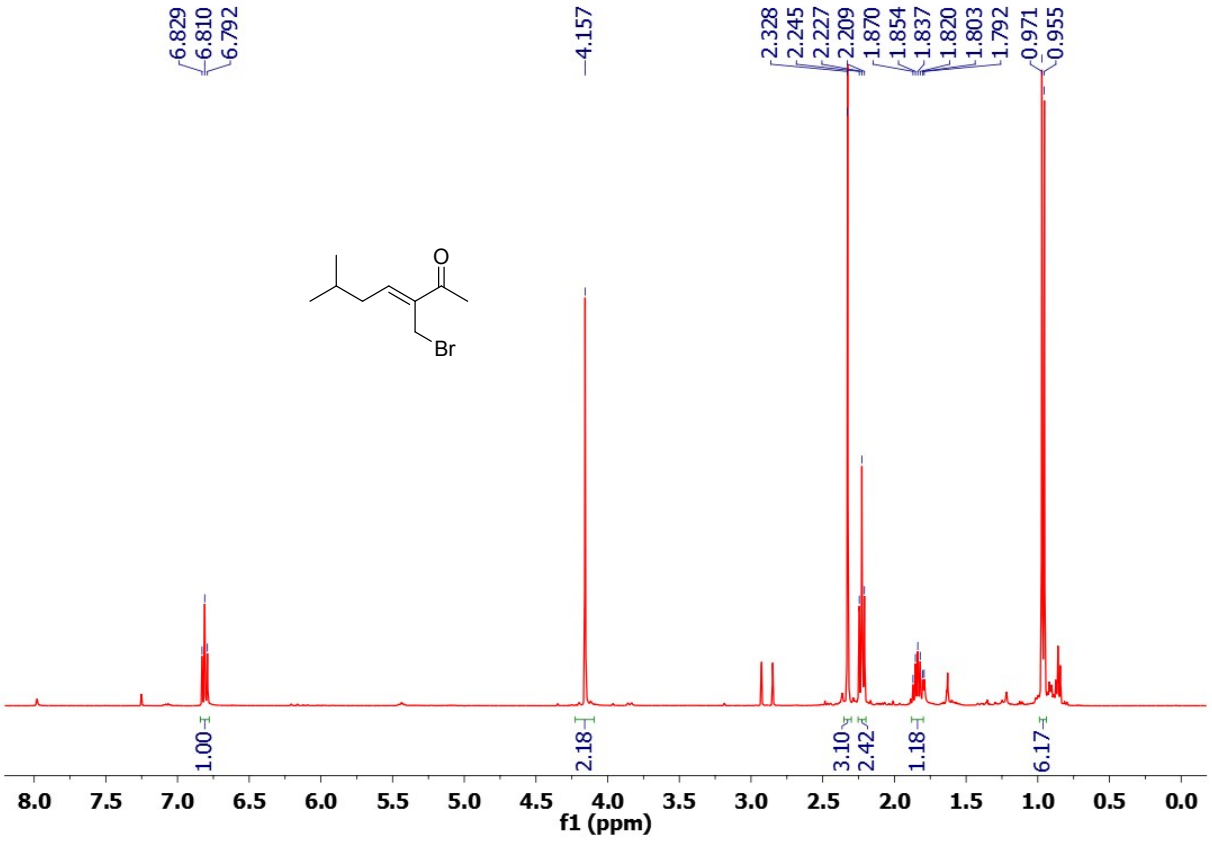
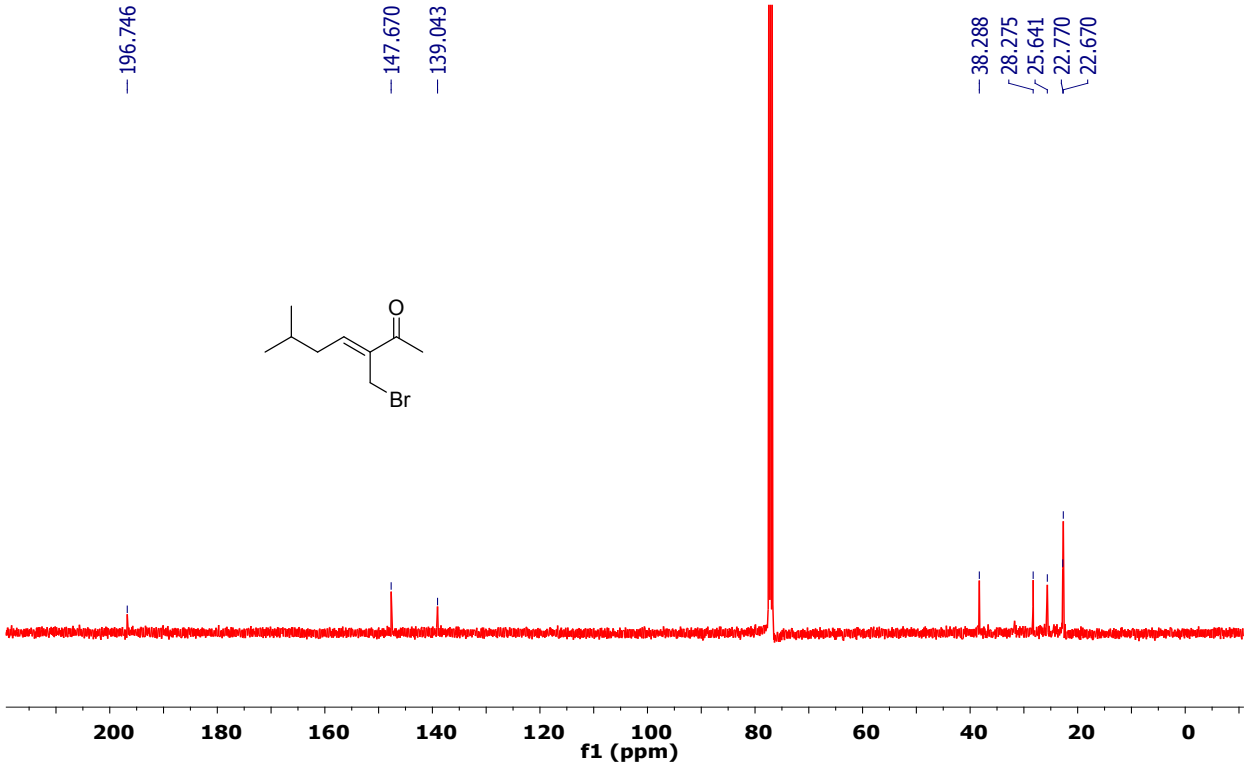
137.114
135.511
134.111
133.623
132.604
128.251
25.808
24.986
f1 (ppm)
O
S
Br


6.829
6.810
6.792
4.157
2.328
2.245
2.227
2.209
1.870
1.854
1.837
1.820
1.803
1.792
0.971
0.955
O
Br
1.00
2.18
3.10
2.42
1.18
6.17
8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


196.746
147.670
139.043
38.288
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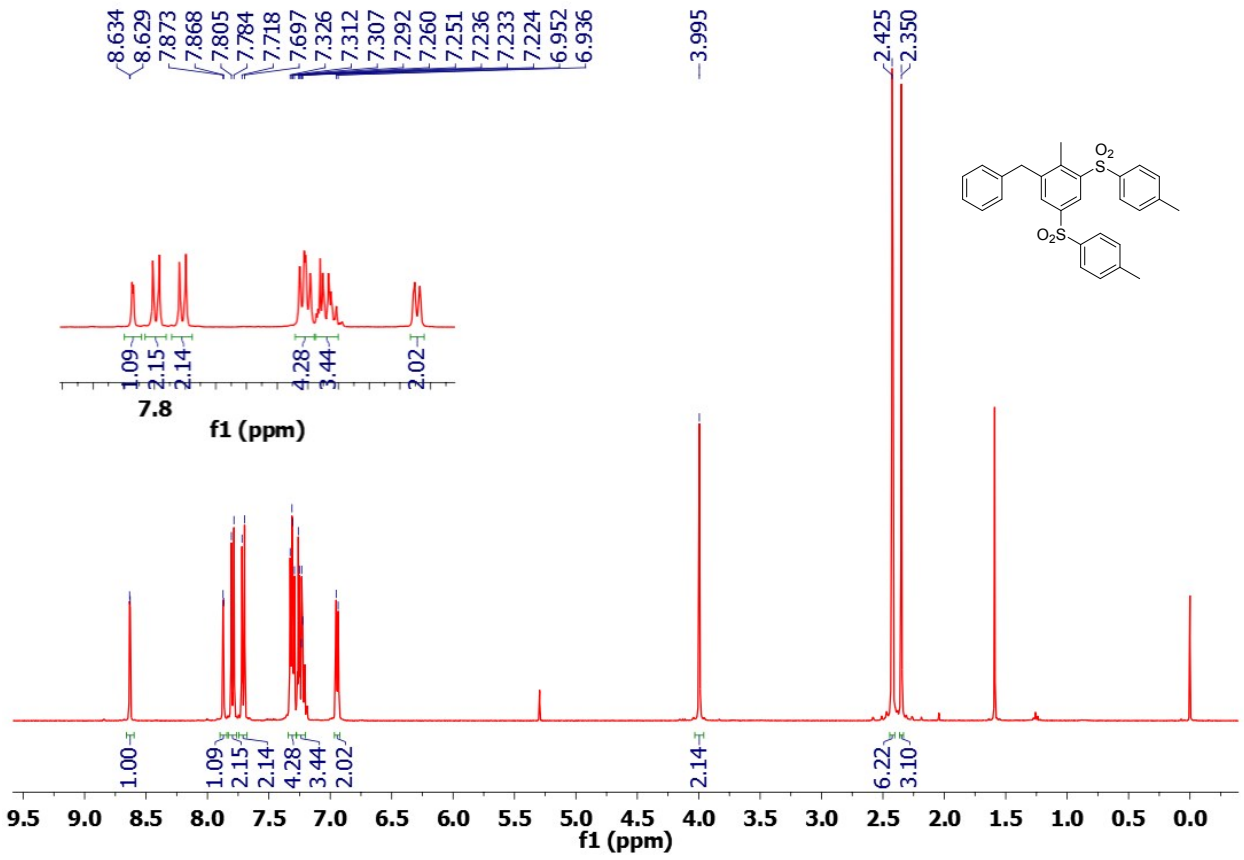
25.641
22.770
22.670
O
Br
200 180 160 140 120 100 80 60 40 20 0
f1 (ppm)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8.629
7.873
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7.805
7.784
7.718
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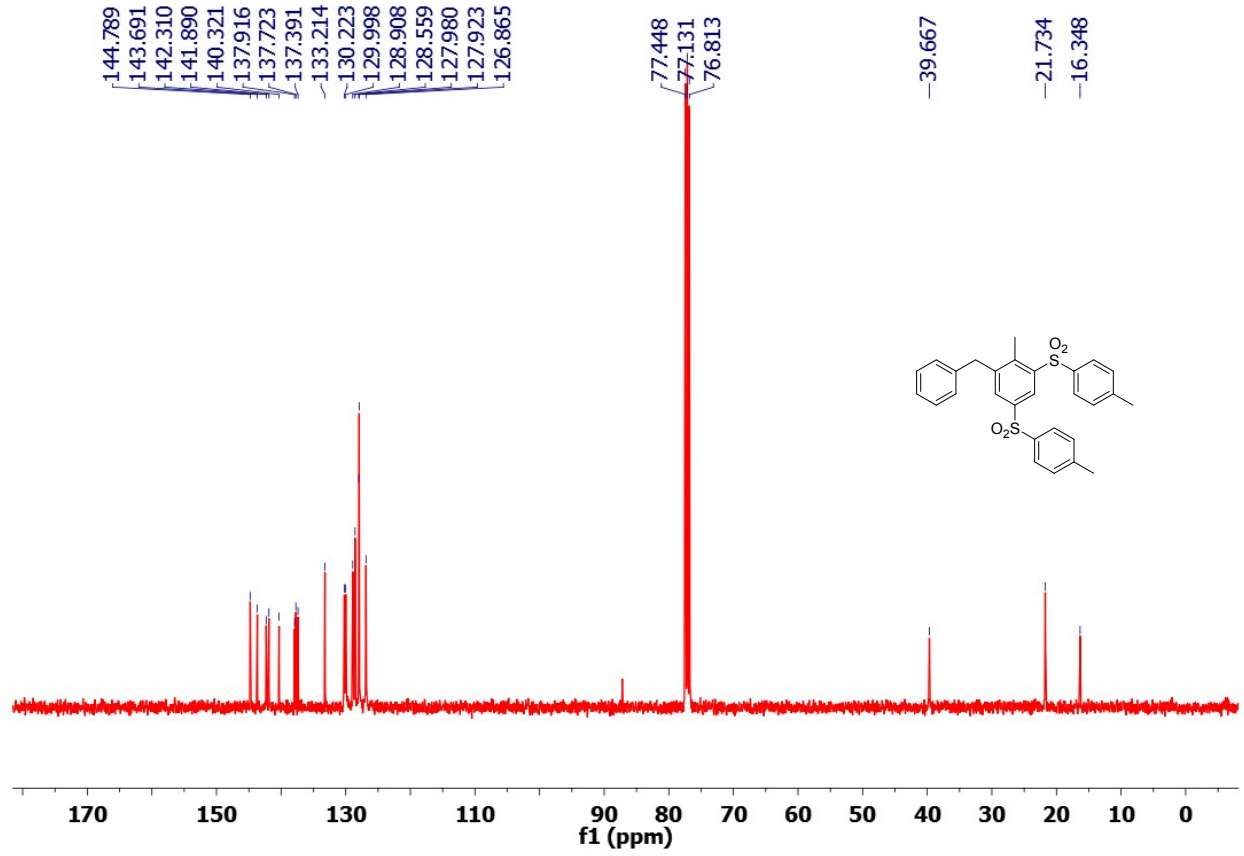
7.326
7.312
7.307
7.292
7.260
7.251
7.236
7.233
7.224
6.952
6.936
3.995
2.425
2.350
1.09
2.15
2.14
4.28
3.44
2.02
7.8
f1 (ppm)
1.00
1.09
2.15
2.14
4.28
3.44
2.02
2.14
6.22
3.10
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)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141.890
140.321
137.916
137.723
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133.214
130.223
129.998
128.908
128.559
127.980
127.923
126.865
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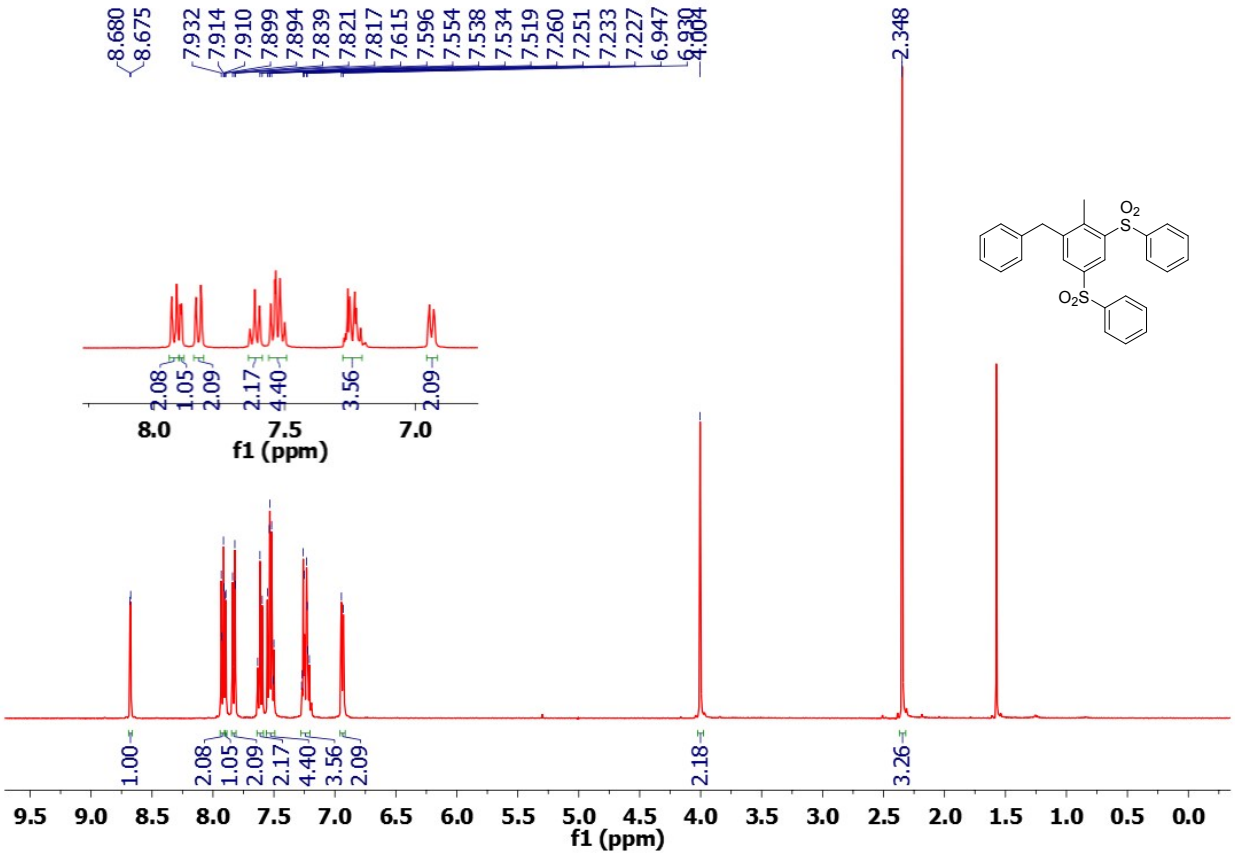
77.131
76.813
39.667
21.734
16.348
170 150 130 110 90 80 70 60 50 40 30 20 10 0
f1 (ppm)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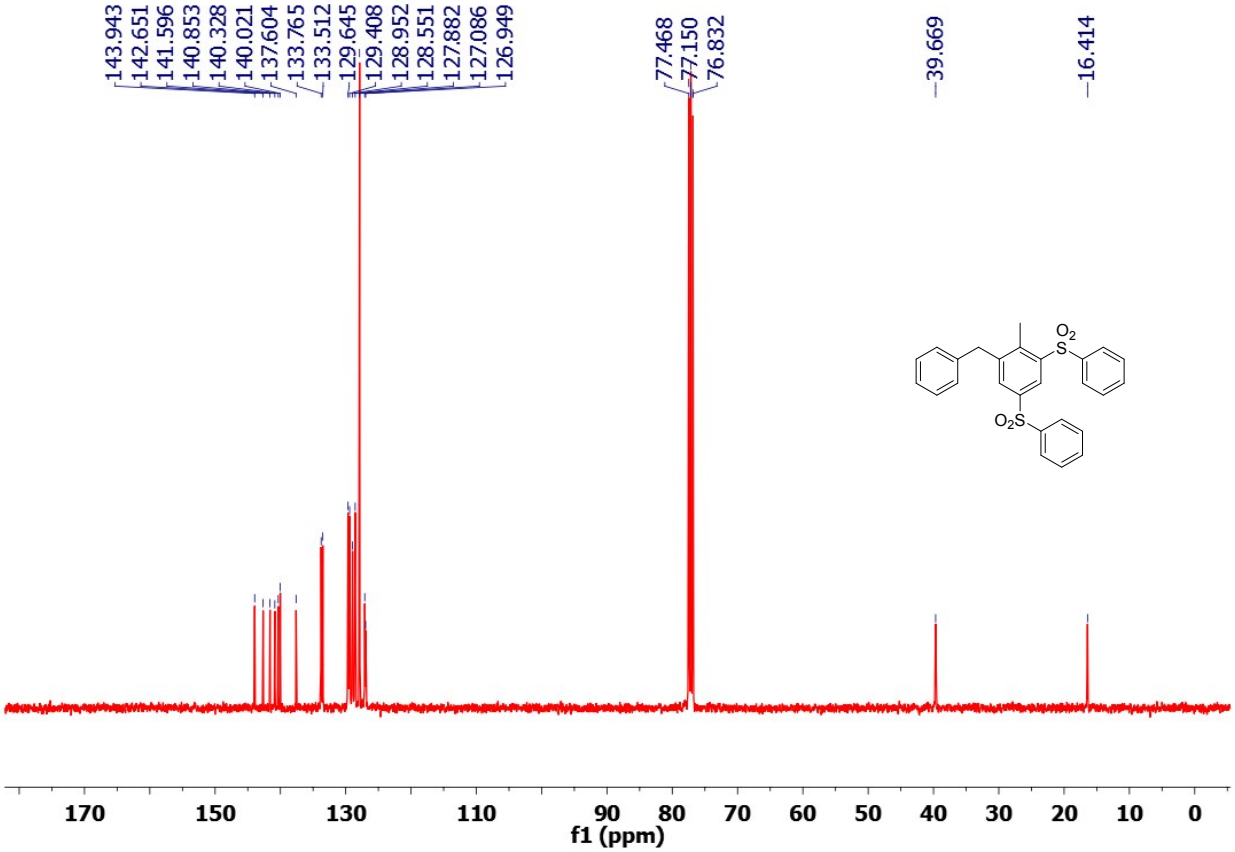
7.894
7.839
7.821
7.817
7.615
7.596
7.554
7.538
7.534
7.519
7.260
7.251
7.233
7.227
6.947
6.930
4.004
2.348
O2
S
O2S
2.08
1.05
2.09
2.17
4.40
3.56
2.09
8.0
7.5
7.0
f1 (ppm)
1.00
2.08
1.05
2.09
2.17
4.40
3.56
2.09
2.18
3.26
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)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141.596
140.853
140.328
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137.604
133.765
133.512
129.645
129.408
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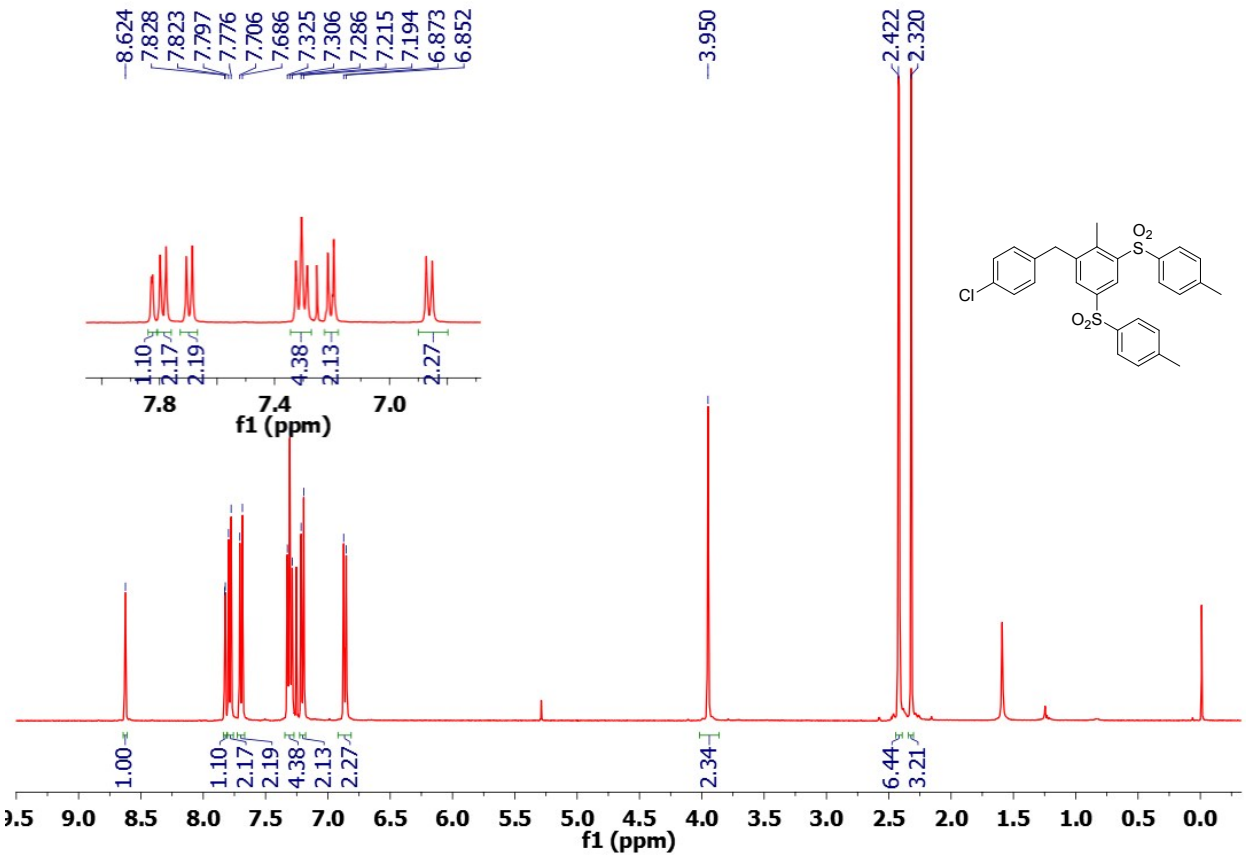
128.551
127.882
127.086
126.949
77.468
77.150
76.832
39.669
16.414
O2
S
O2S
170 150 130 110 90 80 70 60 50 40 30 20 10 0
f1 (ppm)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7.776
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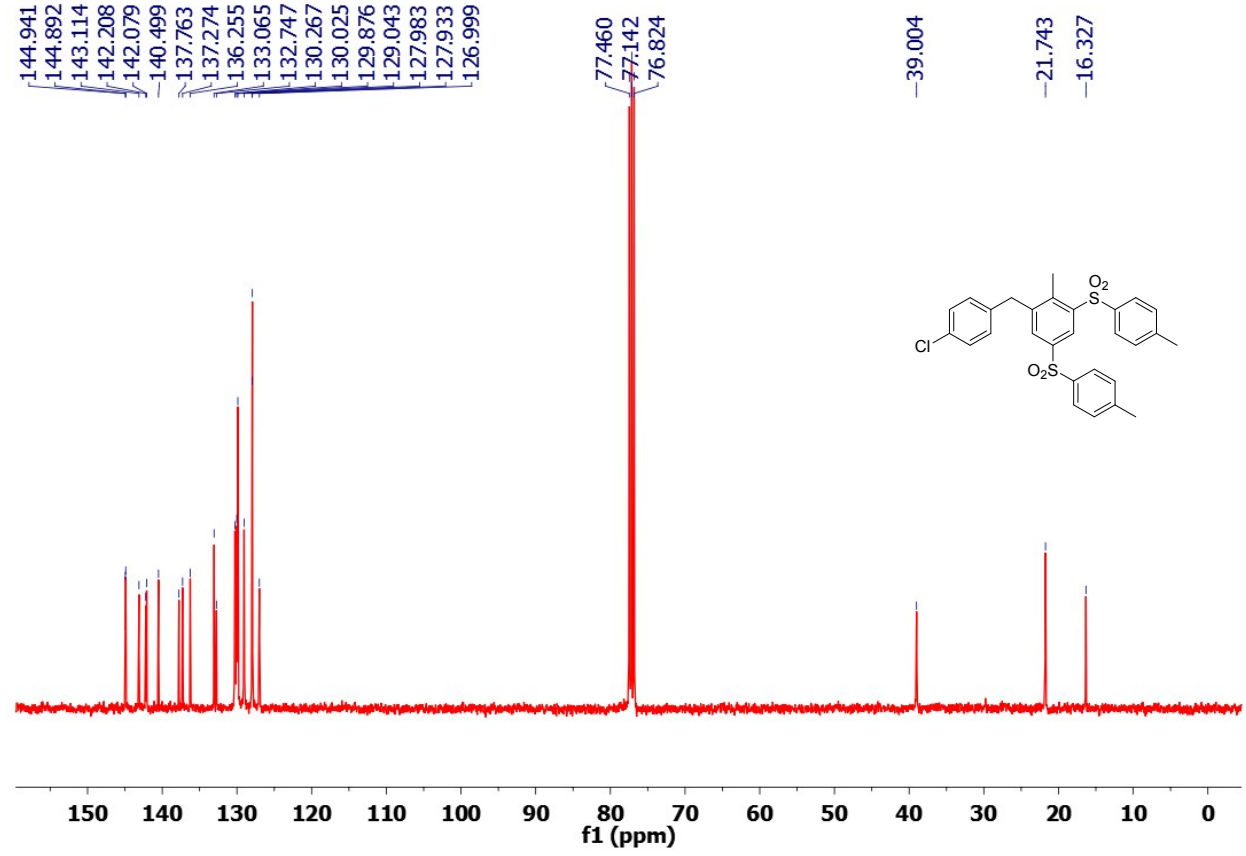
7.686
7.325
7.306
7.286
7.215
7.194
6.873
6.852
3.950
2.422
2.320
1.10
2.17
2.19
4.38
2.13
2.27
7.8
7.4
7.0
f1 (ppm)
1.00
2.34
6.44
3.21
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)
Cl
O2S
O2S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137.274
136.255
133.065
132.747
130.267
130.025
129.876
129.043
127.983
127.933
126.999
77.460
77.142
76.824
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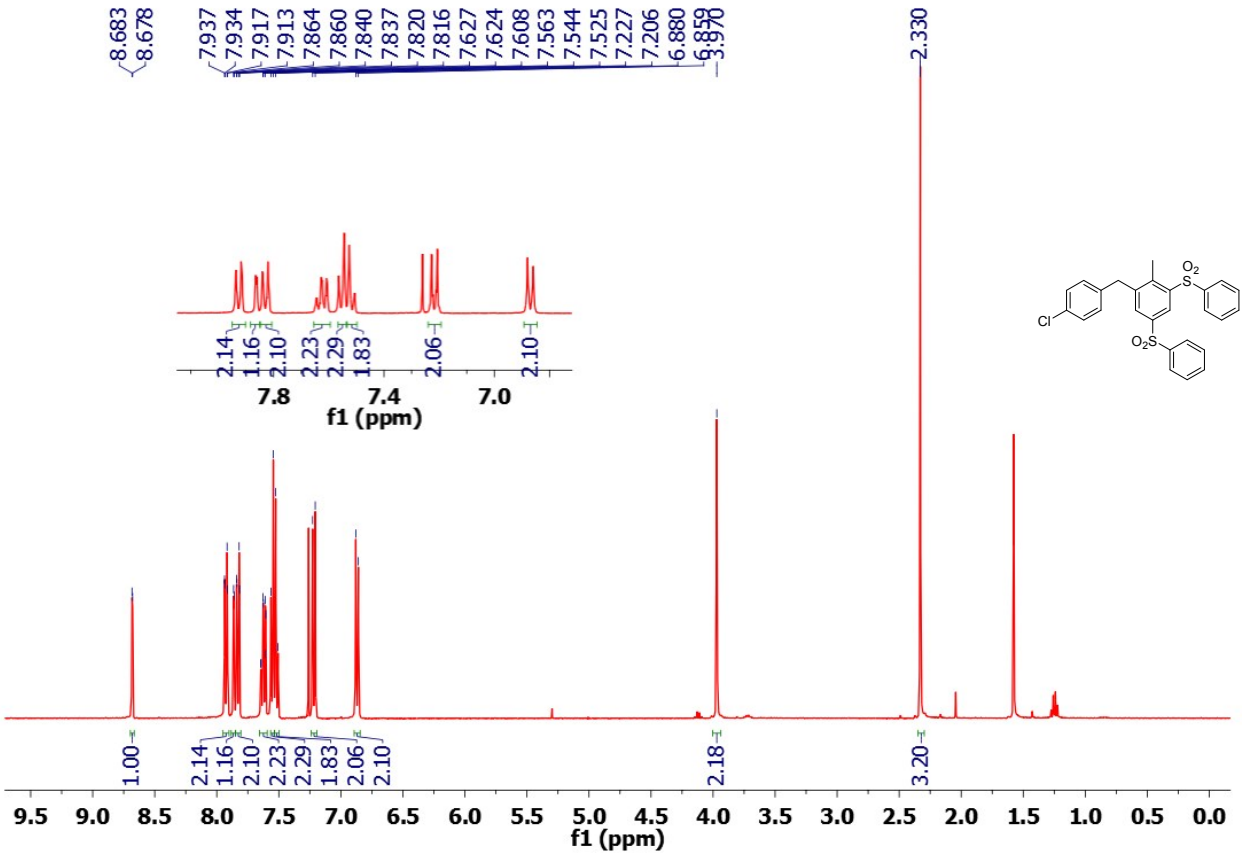
21.743
16.327
150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)
Cl
O2S
O2S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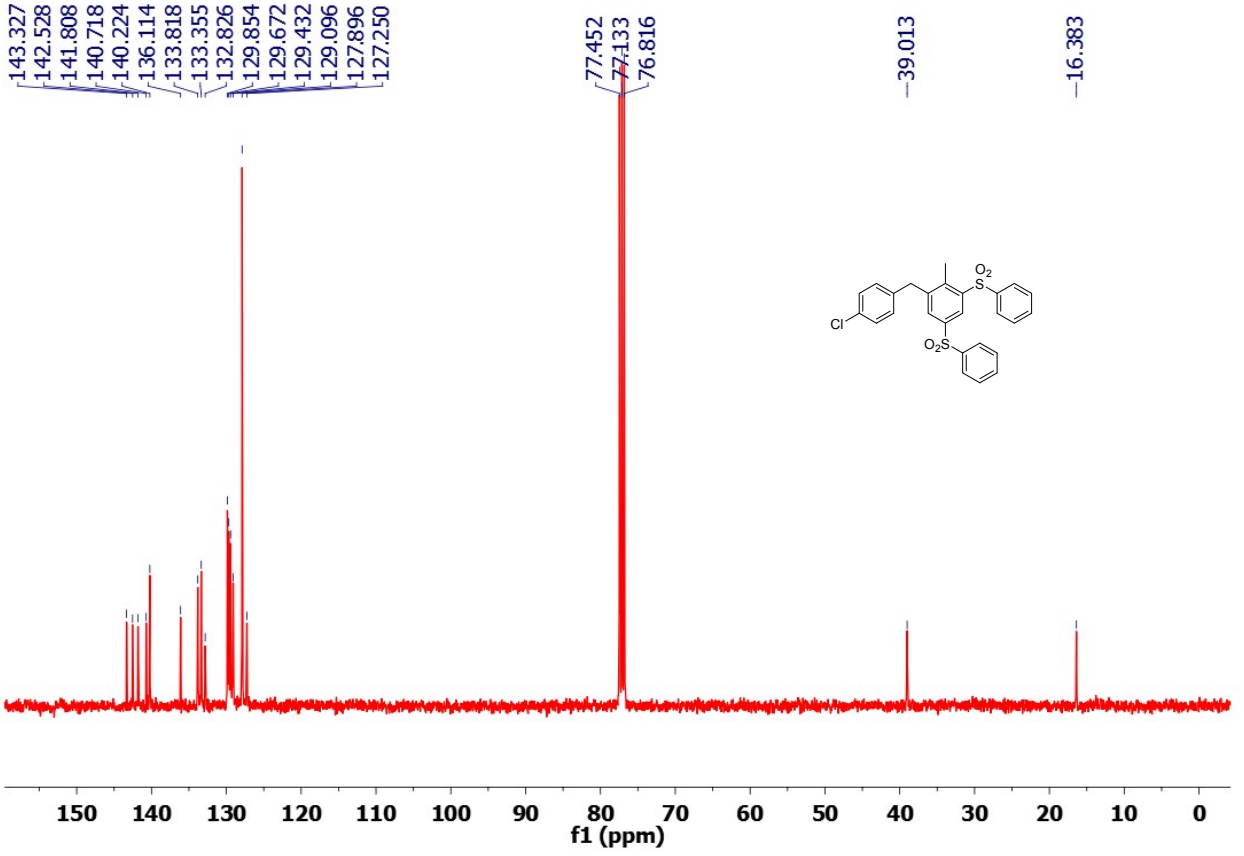
7.816
7.627
7.624
7.608
7.563
7.544
7.525
7.227
7.206
6.880
6.859
3.970
2.330
2.14
1.16
2.10
2.23
2.29
1.83
2.06
2.10
7.8
7.4
7.0
f1 (ppm)
Cl
O2
S
O2S
1.00
2.14
1.16
2.10
2.23
2.29
1.83
2.06
2.10
2.18
3.20
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)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127.896
127.250
77.452
77.133
76.816
39.013
16.383
Cl
O2
S
O2S
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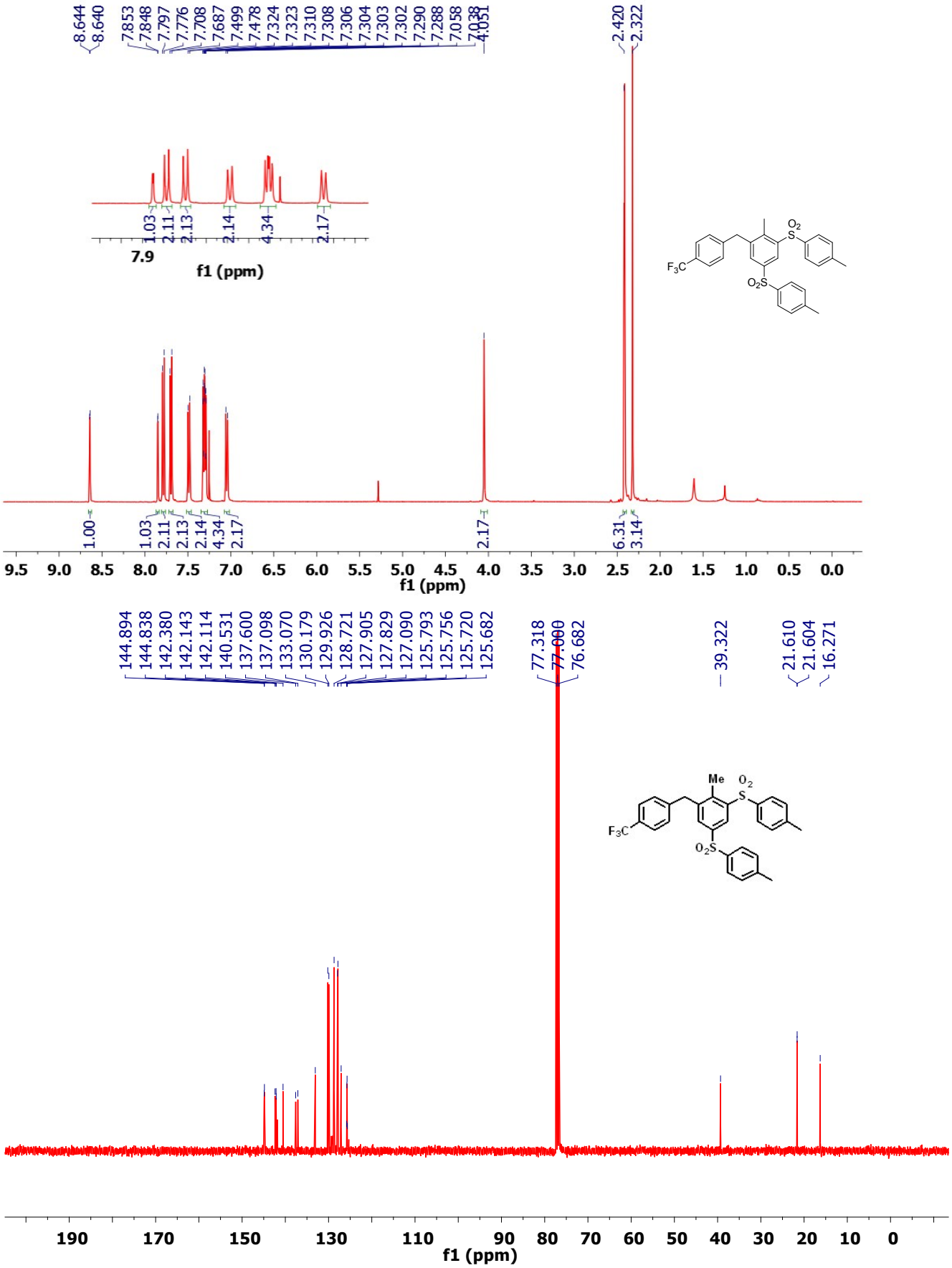
f1 (ppm)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7.304
7.303
7.302
7.290
7.288
7.058
7.038
4.051
2.420
2.322
1.03
2.11
2.13
2.14
4.34
2.17
7.9
f1 (ppm)
1.00
1.03
2.11
2.13
2.14
4.34
2.17
2.17
6.31
3.14
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)
144.894
144.838
142.380
142.143
142.114
140.531
137.600
137.098
133.070
130.179
129.926
128.721
127.905
127.829
127.090
125.793
125.756
125.720
125.682
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76.682
39.322
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21.604
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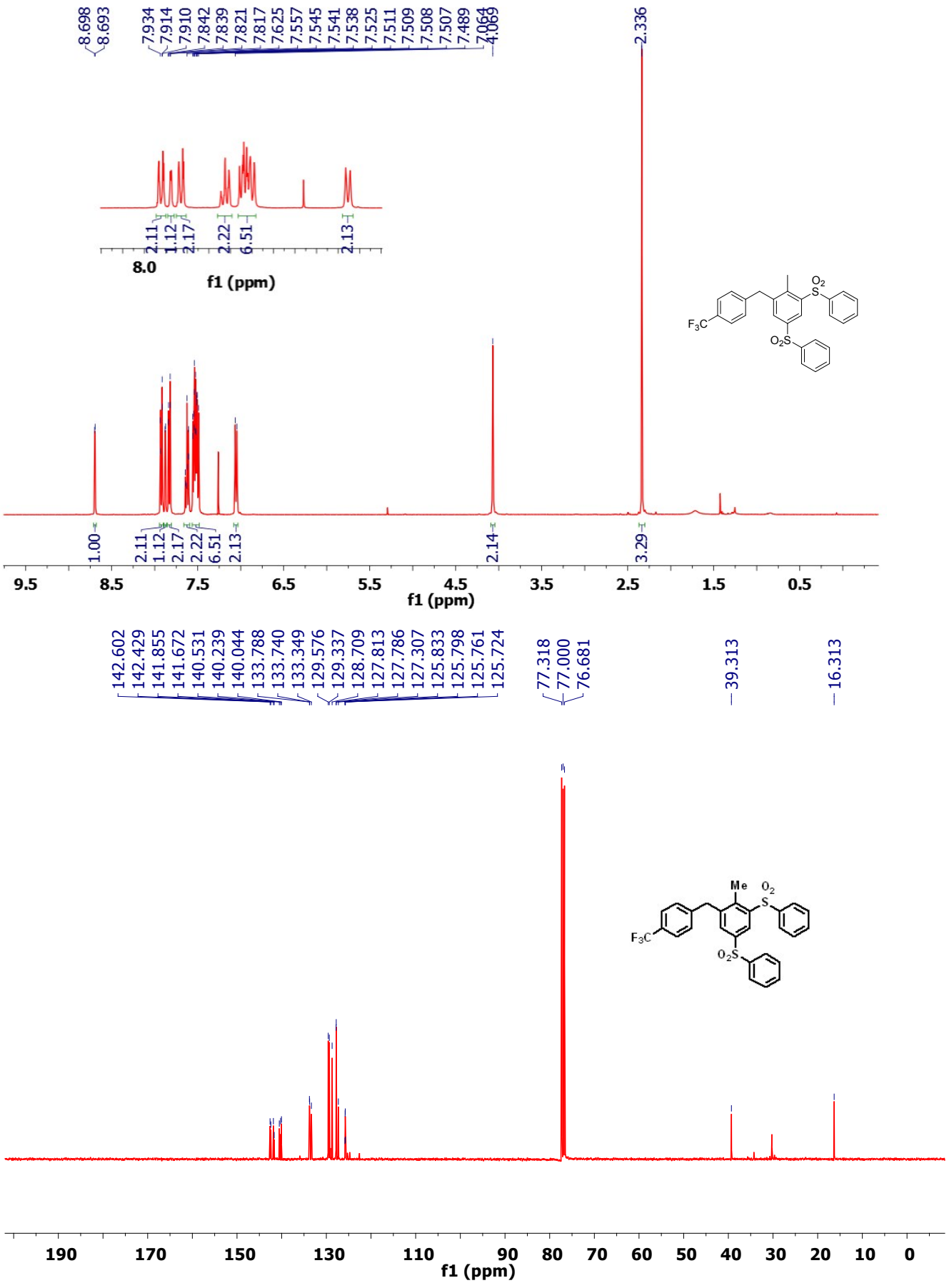
f1 (ppm)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7.508
7.507
7.489
7.064
4.069
2.336
2.11
1.12
2.17
2.22
6.51
2.13
8.0
f1 (ppm)
1.00
2.11
1.12
2.17
2.22
6.51
2.13
2.14
3.29
9.5
8.5
7.5
6.5
5.5
4.5
3.5
2.5
1.5
0.5
f1 (ppm)
142.602
142.429
141.855
141.672
140.531
140.239
140.044
133.788
133.740
133.349
129.576
129.337
128.709
127.813
127.786
127.307
125.833
125.798
125.761
125.724
77.318
77.000
76.681
39.313
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Me
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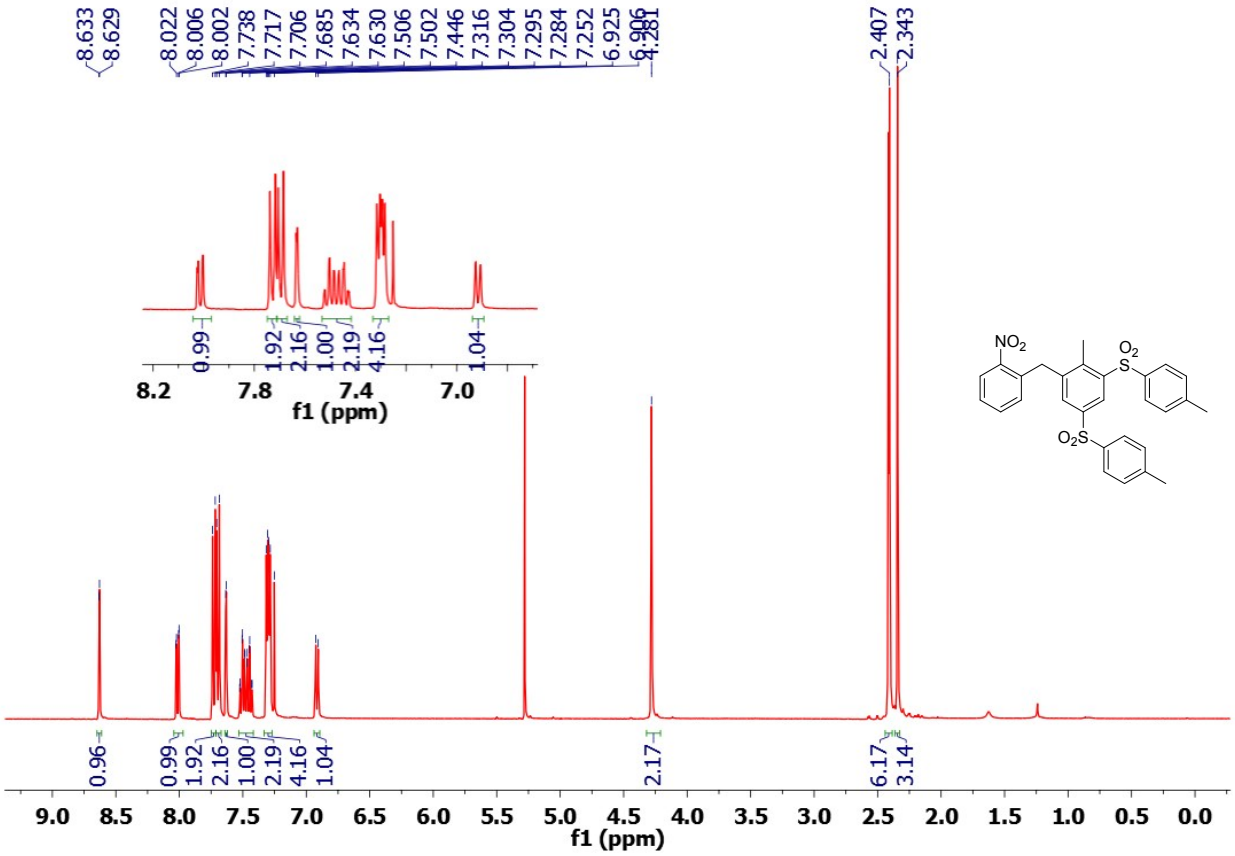
170
150
130
110
90
80
70
60
50
40
30
20
10
0
f1 (ppm)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8.002
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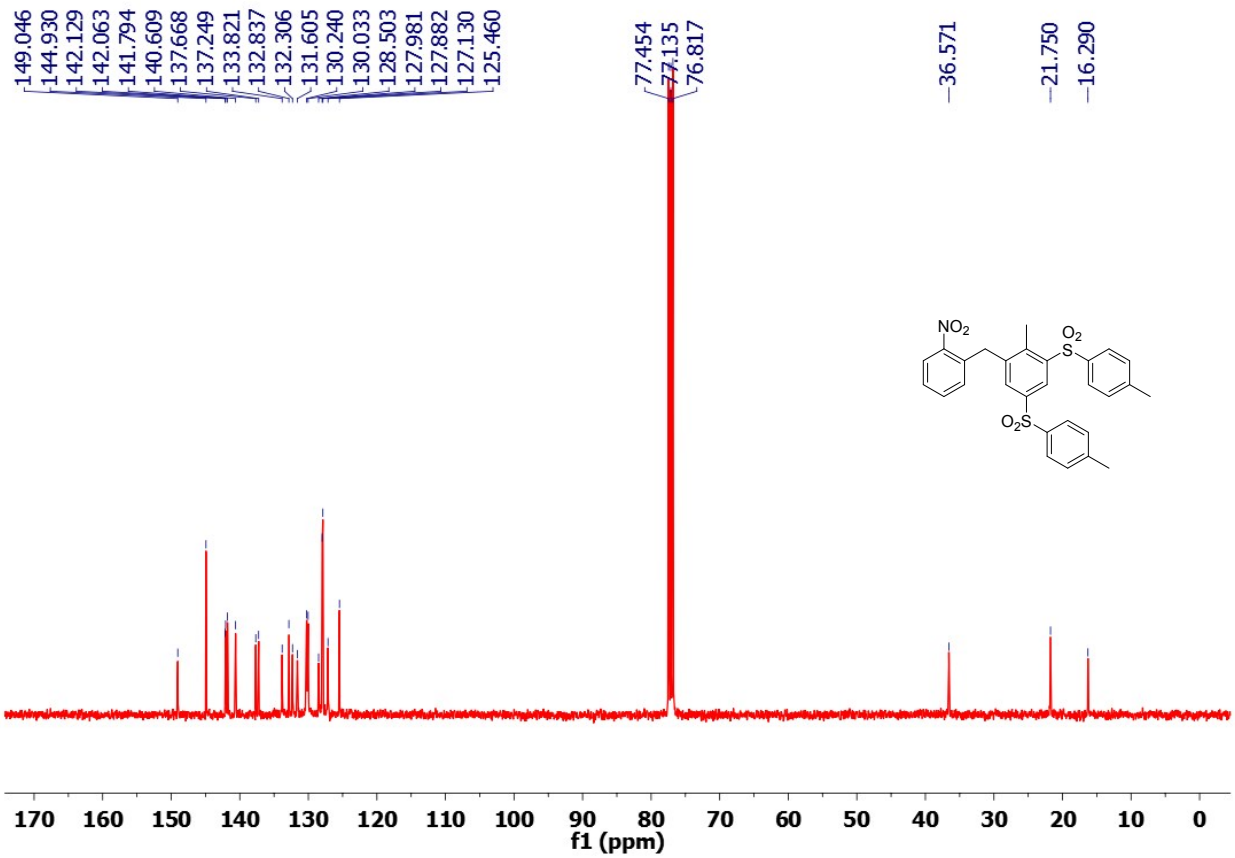
7.706
7.685
7.634
7.630
7.506
7.502
7.446
7.316
7.304
7.295
7.284
7.252
6.925
2.407
2.343
0.96
0.99
1.92
2.16
1.00
2.19
4.16
1.04
2.17
6.17
3.14
f1 (ppm)
NO2
O2
S
O2S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137.249
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130.033
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127.882
127.130
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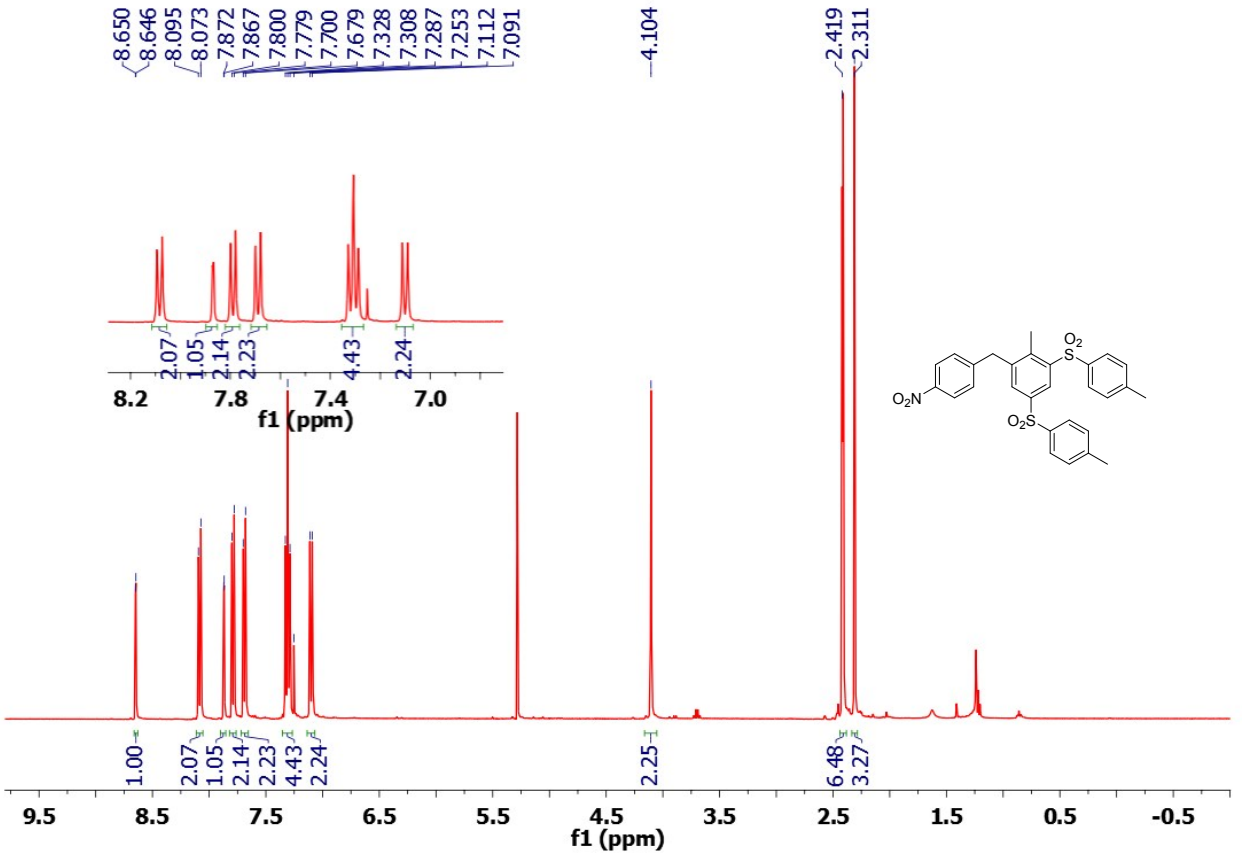
77.135
76.817
36.571
21.750
16.290
f1 (ppm)
NO2
O2
S
O2S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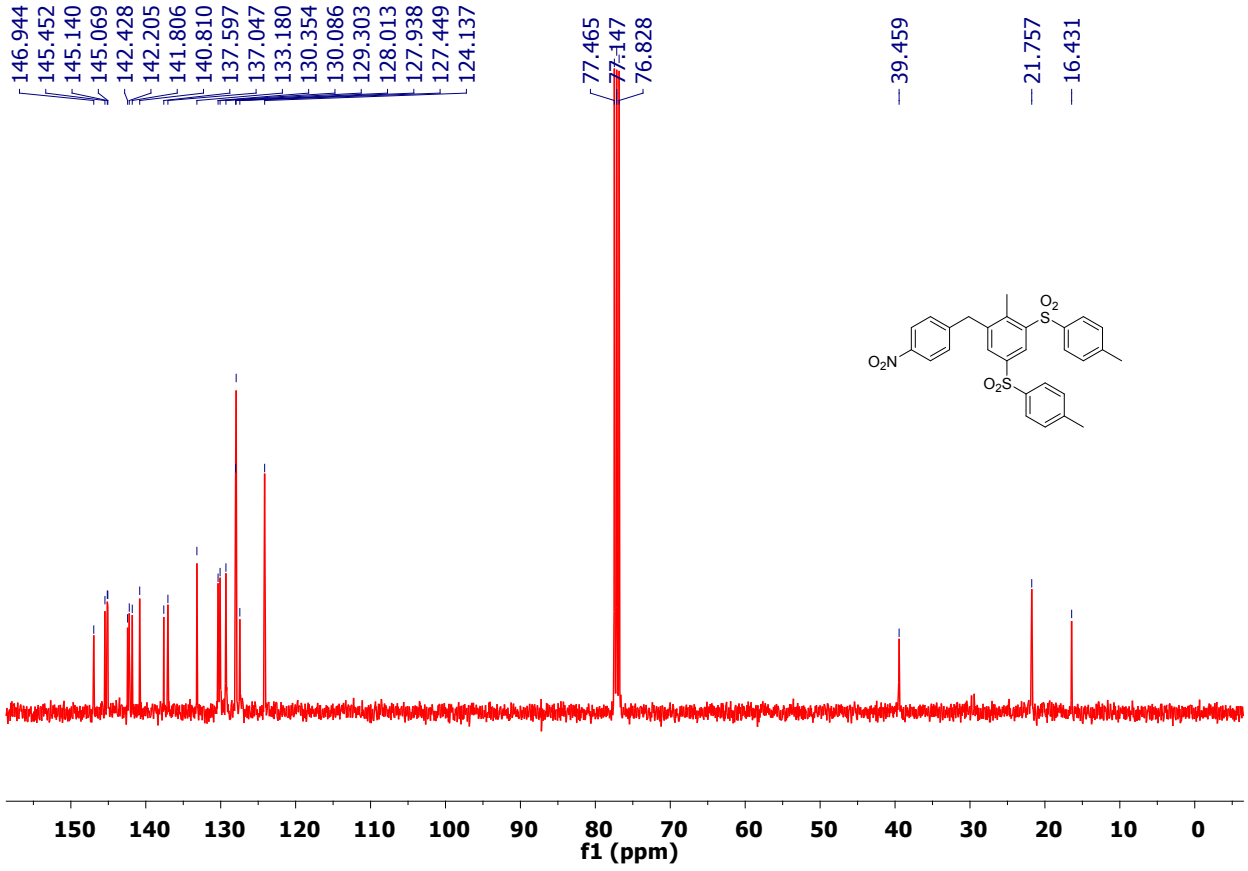
7.779
7.700
7.679
7.328
7.308
7.287
7.253
7.112
7.091
4.104
2.419
2.311
2.07
1.05
2.14
2.23
4.43
2.24
8.2
7.8
7.4
7.0
f1 (ppm)
1.00
2.07
1.05
2.14
2.23
4.43
2.24
2.25
6.48
3.27
9.5
8.5
7.5
6.5
5.5
4.5
3.5
2.5
1.5
0.5
-0.5
f1 (ppm)
O2N
O2S
O2S
O2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142.205
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137.047
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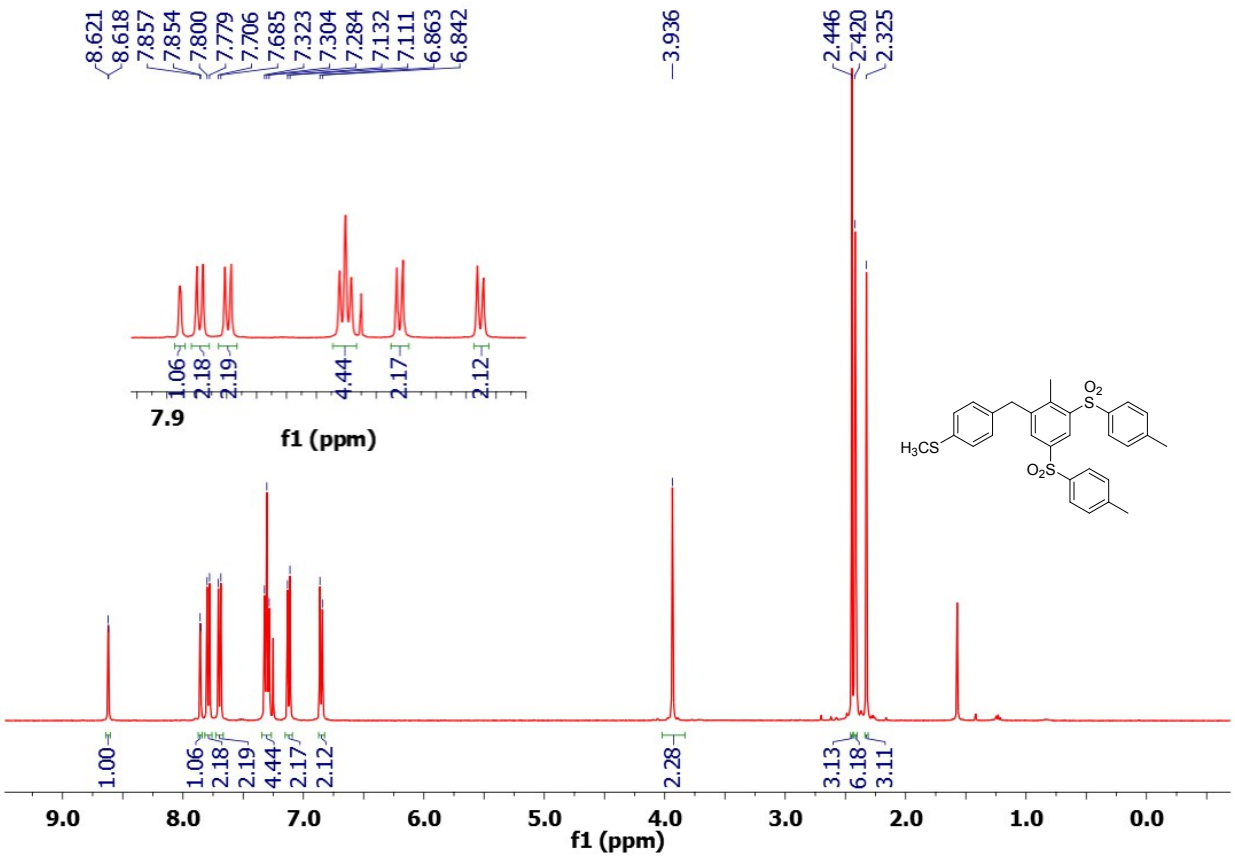
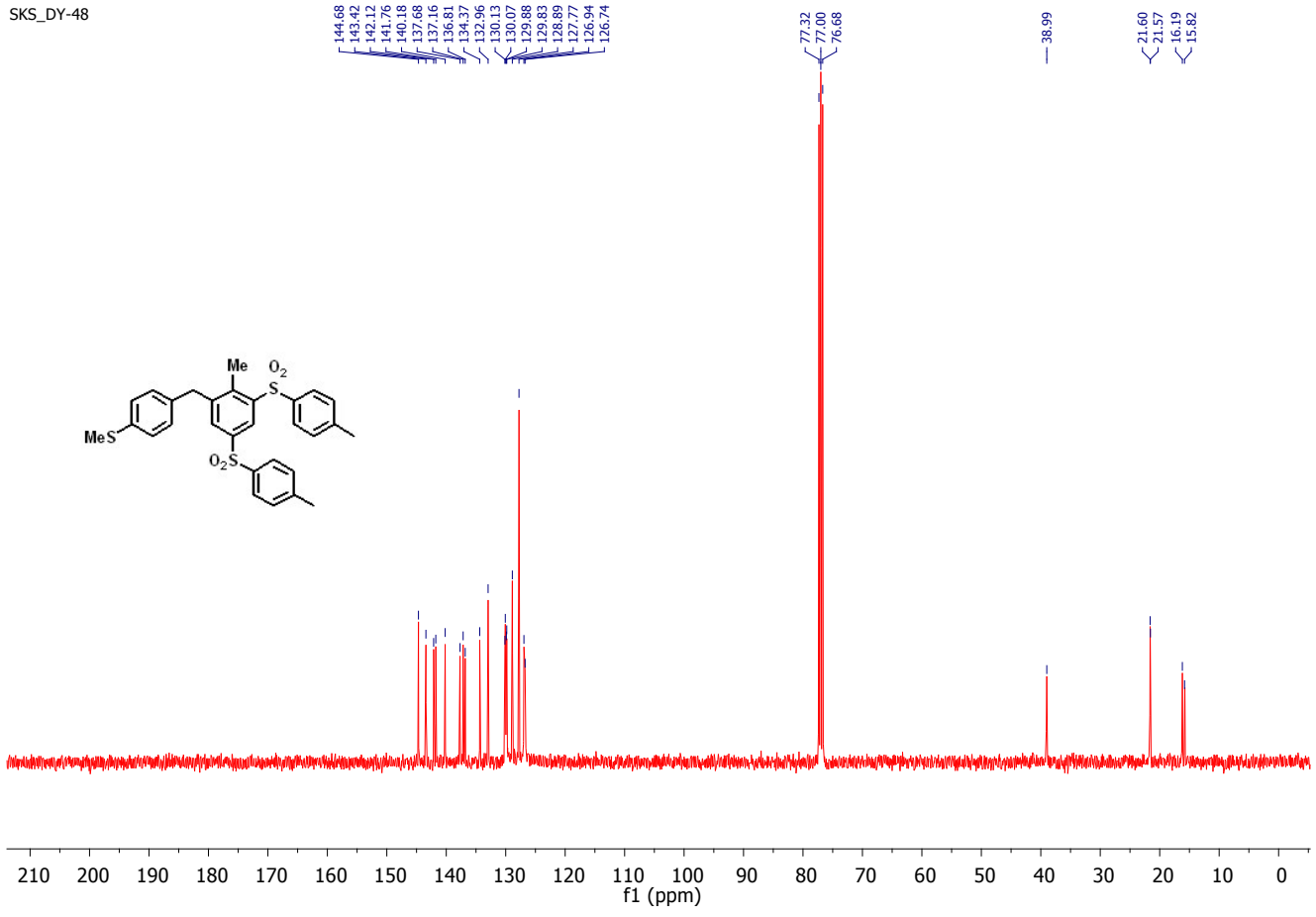
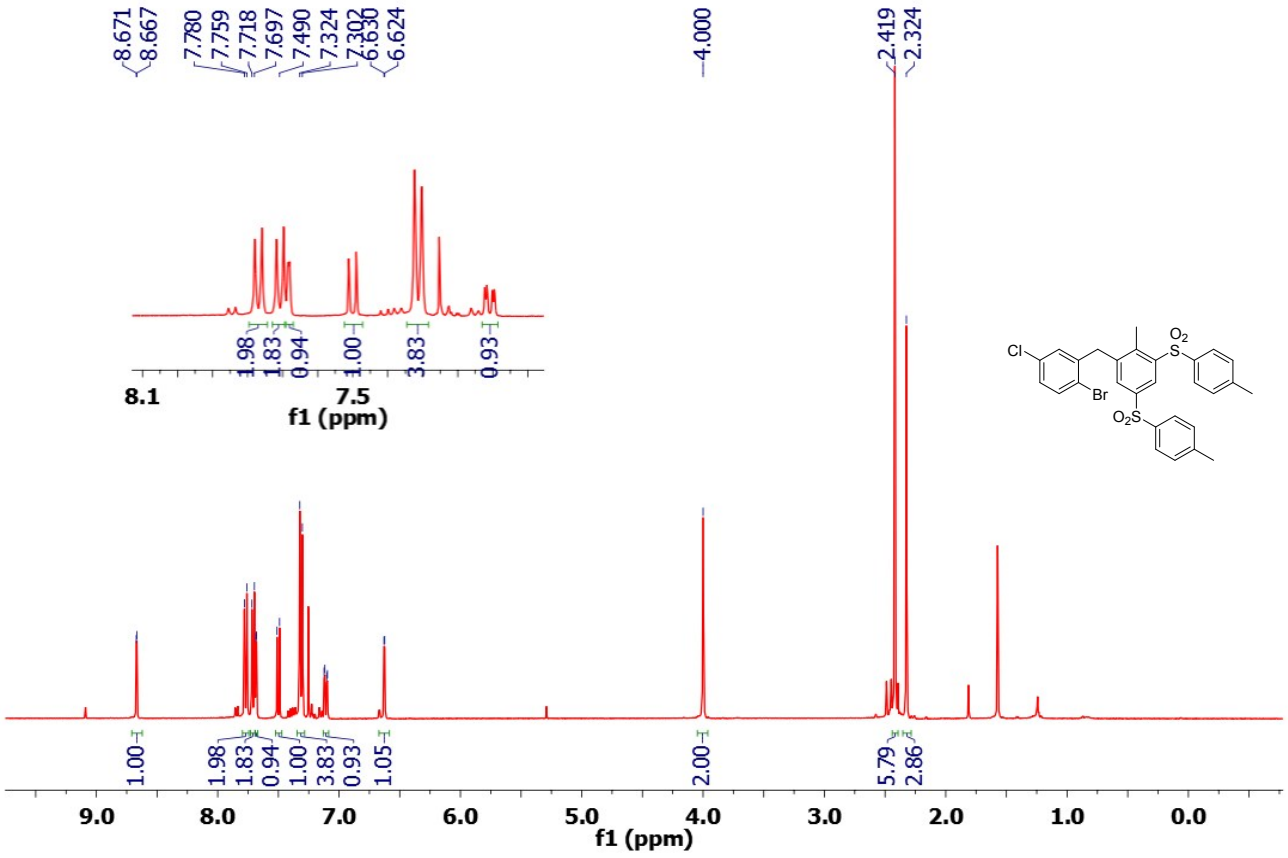
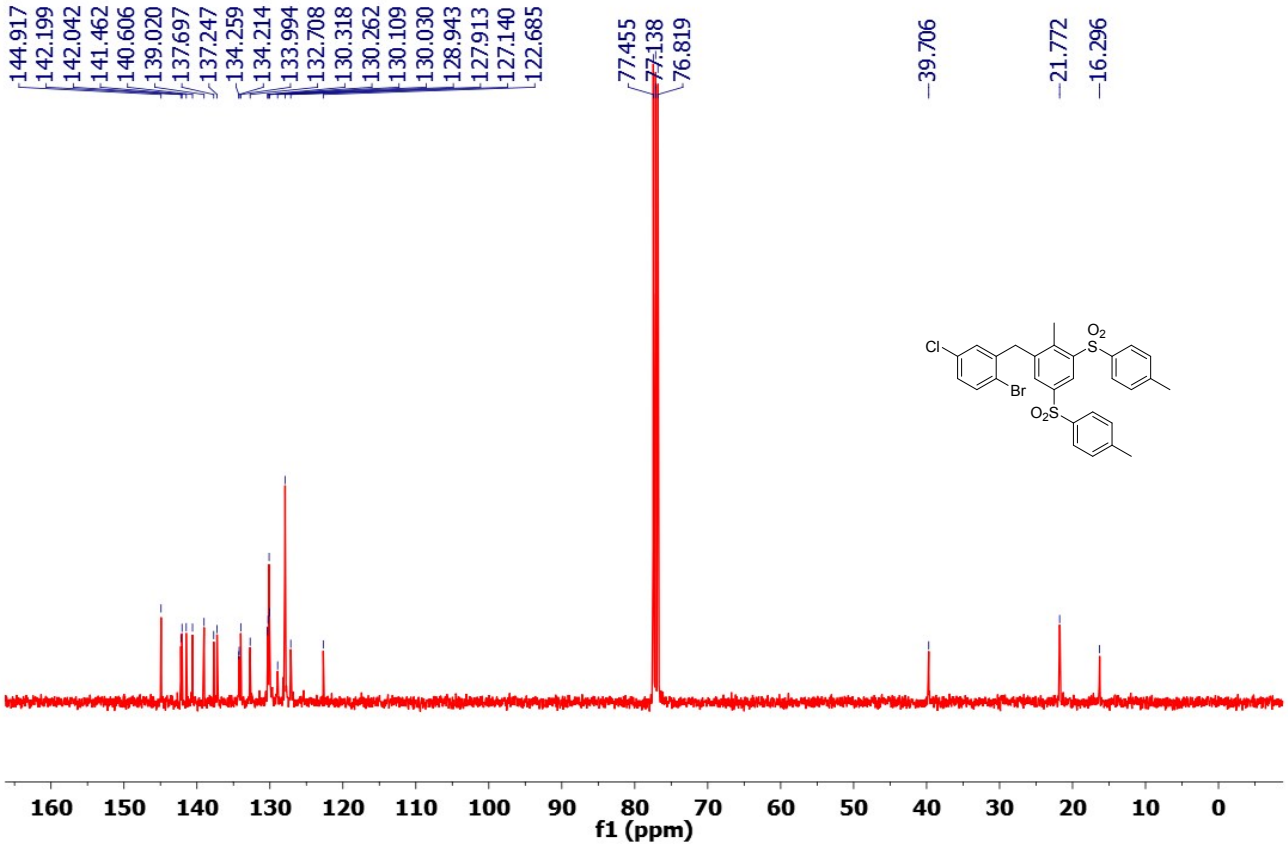
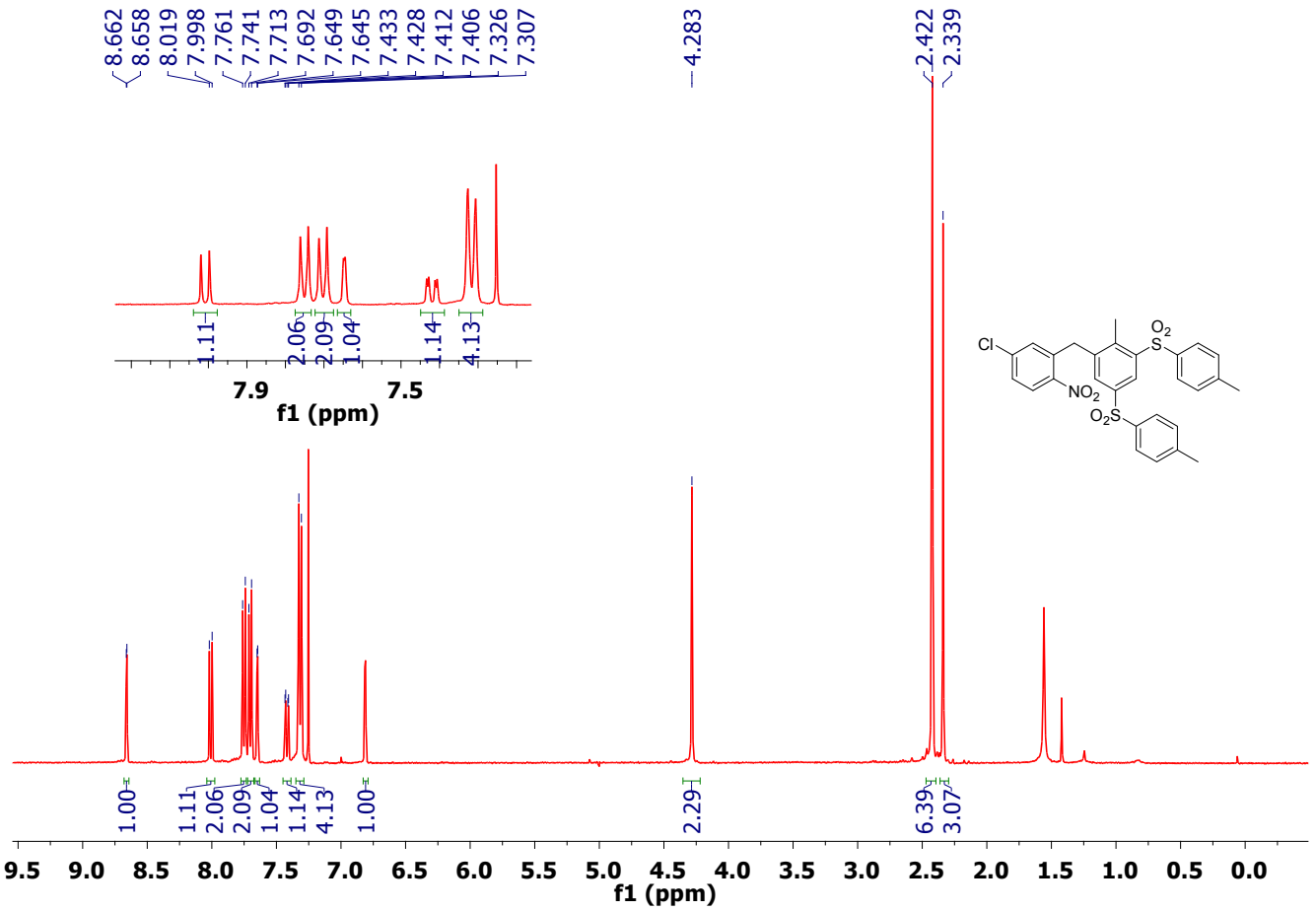
130.086
129.303
128.013
127.938
127.449
124.137
77.465
77.147
76.828
39.459
21.757
16.431
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)
O2N
O2S
O2S
O2

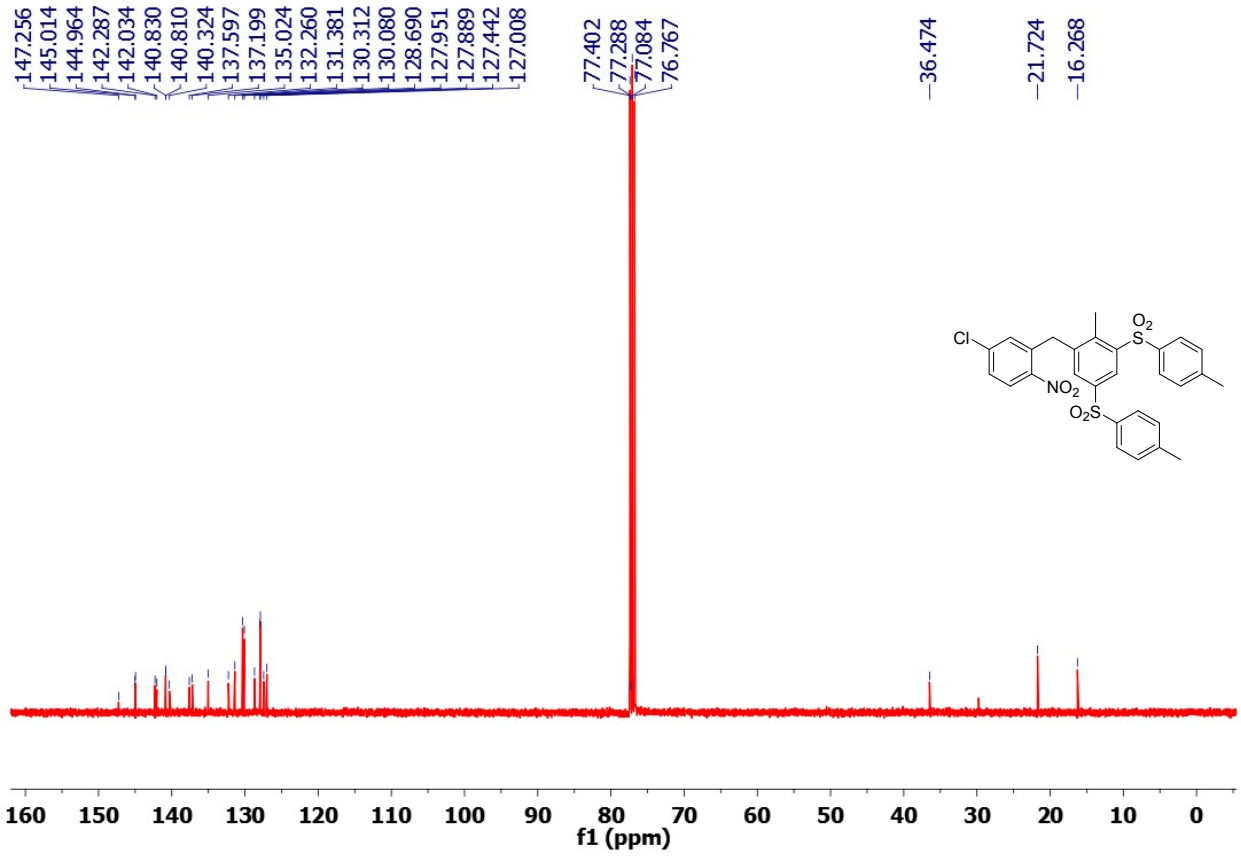

8.621
8.618
7.857
7.854
7.800
7.779
7.706
7.685
7.323
7.304
7.284
7.132
7.111
6.863
6.842
3.936
2.446
2.420
2.325
1.06
2.18
2.19
4.44
2.17
2.12
7.9
f1 (ppm)
1.00
1.06
2.18
2.19
4.44
2.17
2.12
2.28
3.13
6.18
3.11
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
f1 (ppm)
H3CS
O2S
O2S

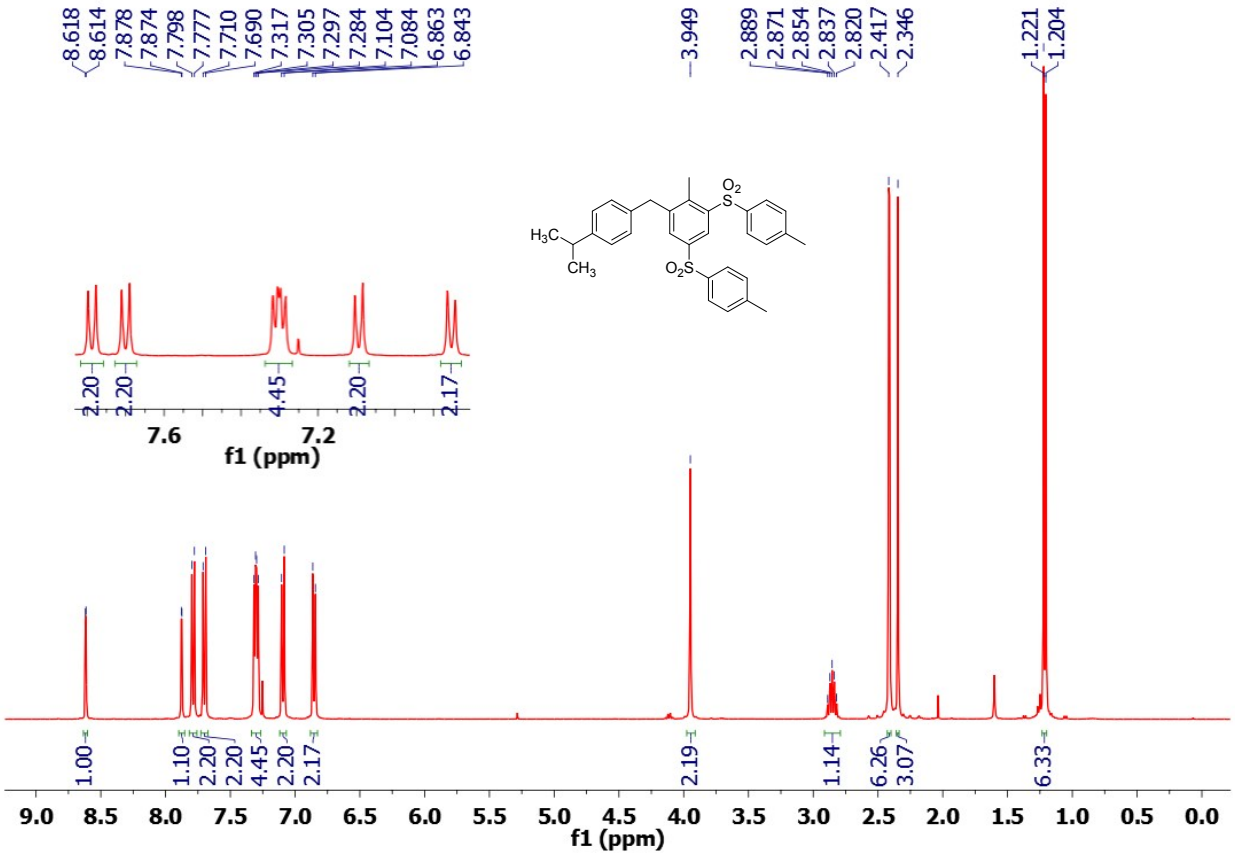

SKS_DY-48
144.68
143.42
142.12
141.76
140.18
137.68
137.16
136.81
134.37
132.96
130.13
130.07
129.88
129.83
128.89
127.77
126.94
126.74
77.32
77.00
76.68
38.99
21.60
21.57
16.19
15.82
Me
O2S
MeS
O2S
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

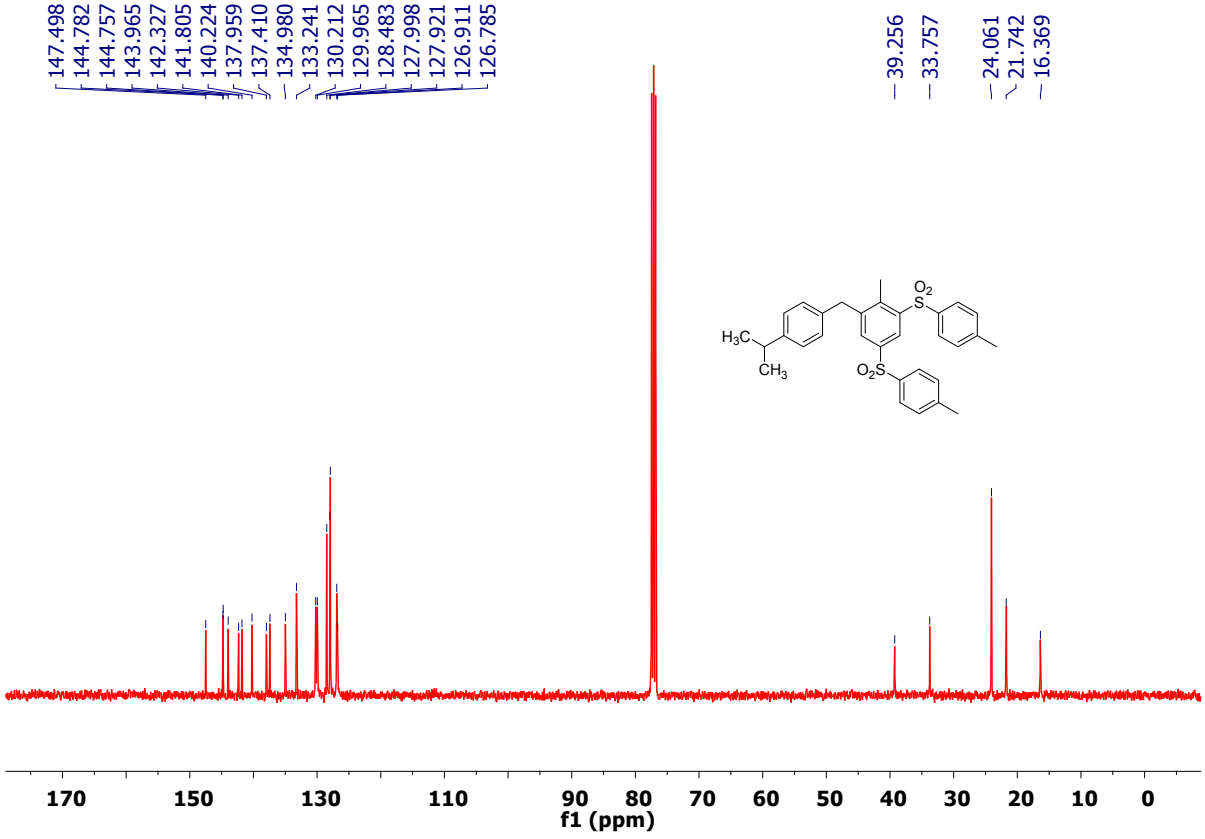

8.671
8.667
7.780
7.759
7.718
7.697
7.490
7.324
7.302
6.630
6.624
4.000
2.419
2.324
1.98
1.83
0.94
1.00
3.83
0.93
8.1
7.5
f1 (ppm)
Cl
Br
O2S
O2S
1.00
1.98
1.83
0.94
1.00
3.83
0.93
1.05
2.00
5.79
2.86
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
f1 (ppm)

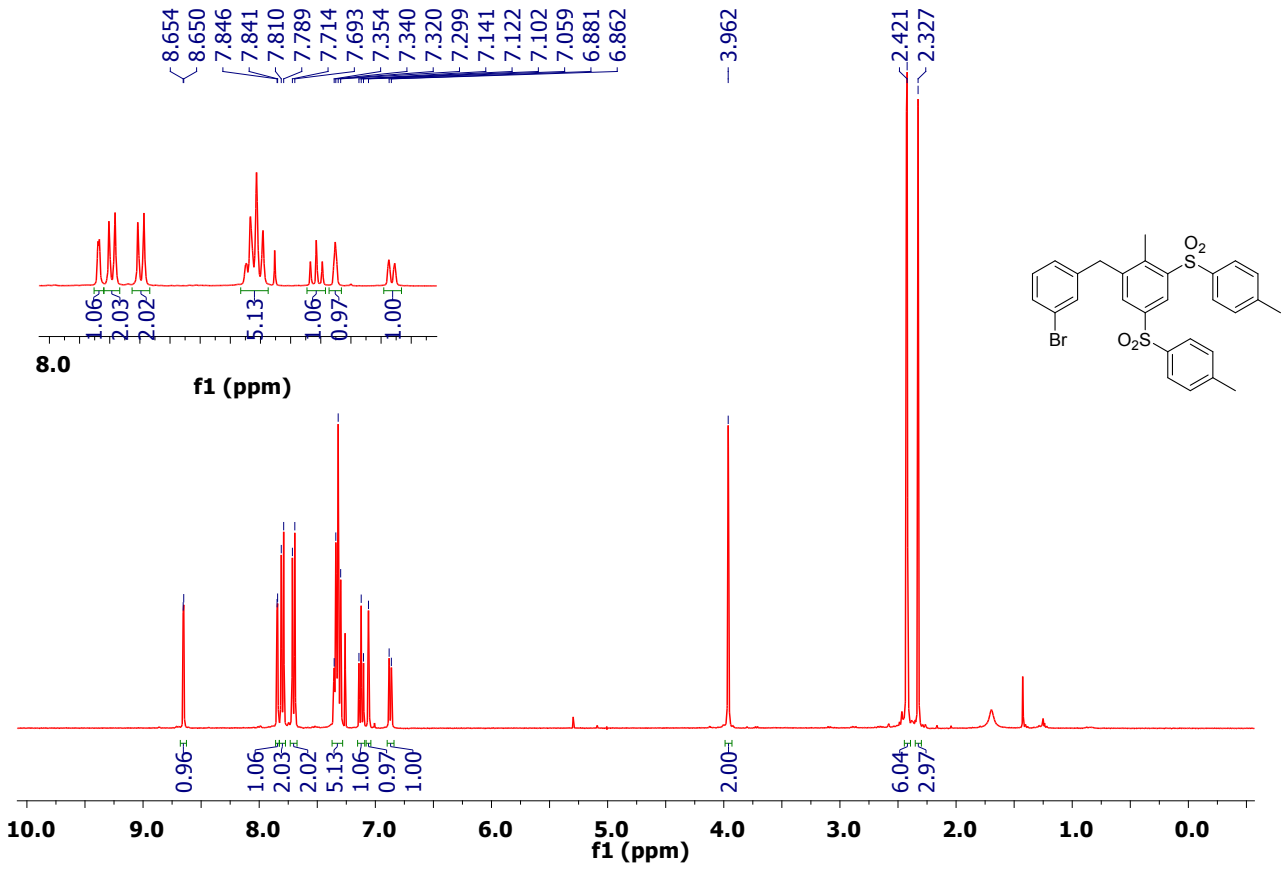

144.917
142.199
142.042
141.462
140.606
139.020
137.697
137.247
134.259
134.214
133.994
132.708
130.318
130.262
130.109
130.030
128.943
127.913
127.140
122.685
77.455
77.138
76.819
39.706
21.772
16.296
Cl
Br
O2S
O2S
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

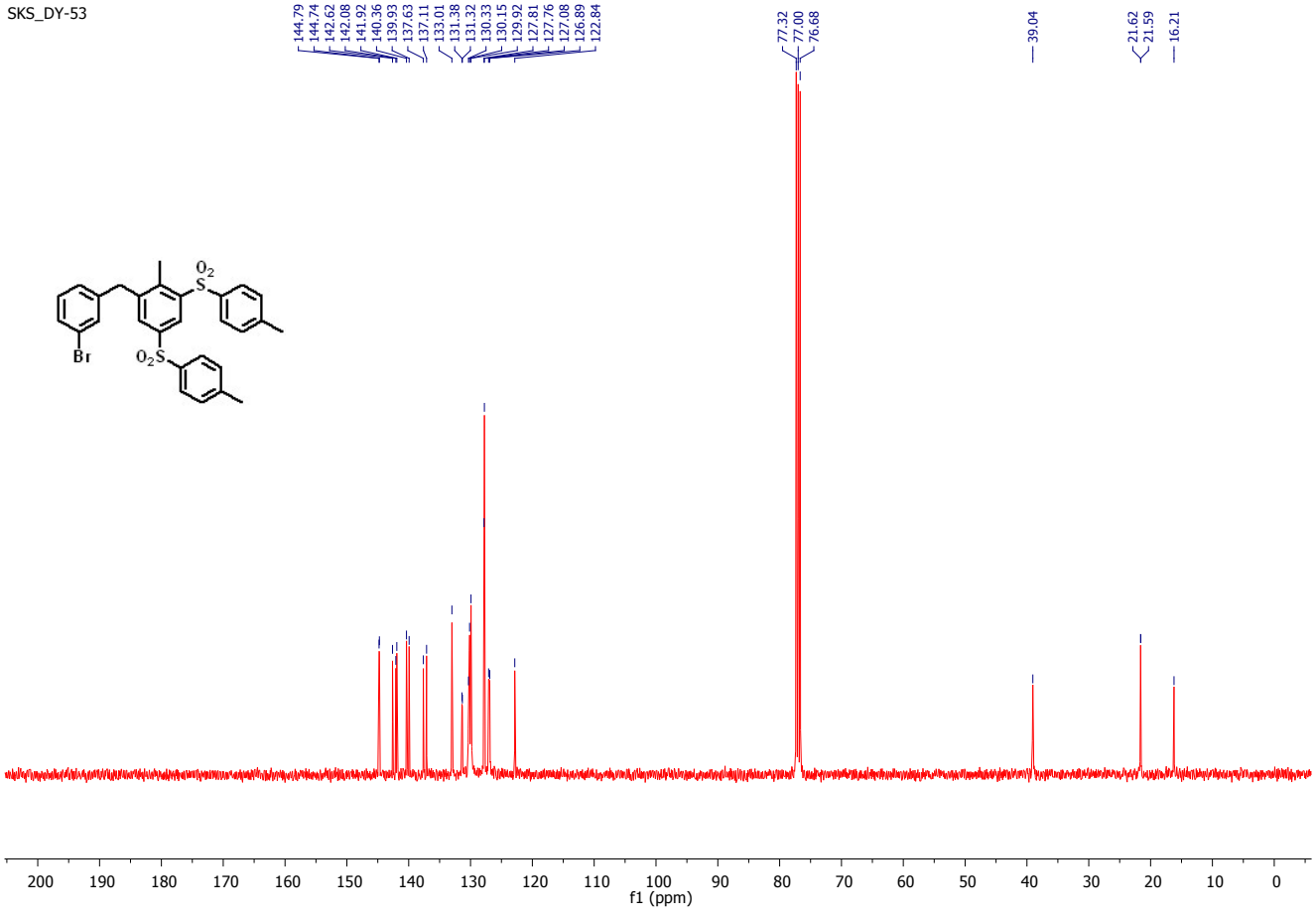

8.662
8.658
8.019
7.998
7.761
7.741
7.713
7.692
7.649
7.645
7.433
7.428
7.412
7.406
7.326
7.307
4.283
2.422
2.339
1.11
2.06
2.09
1.04
1.14
4.13
7.9
7.5
f1 (ppm)
1.00
1.11
2.06
2.09
1.04
1.14
4.13
1.00
2.29
6.39
3.07
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)
Cl
NO2
O2S
O2S

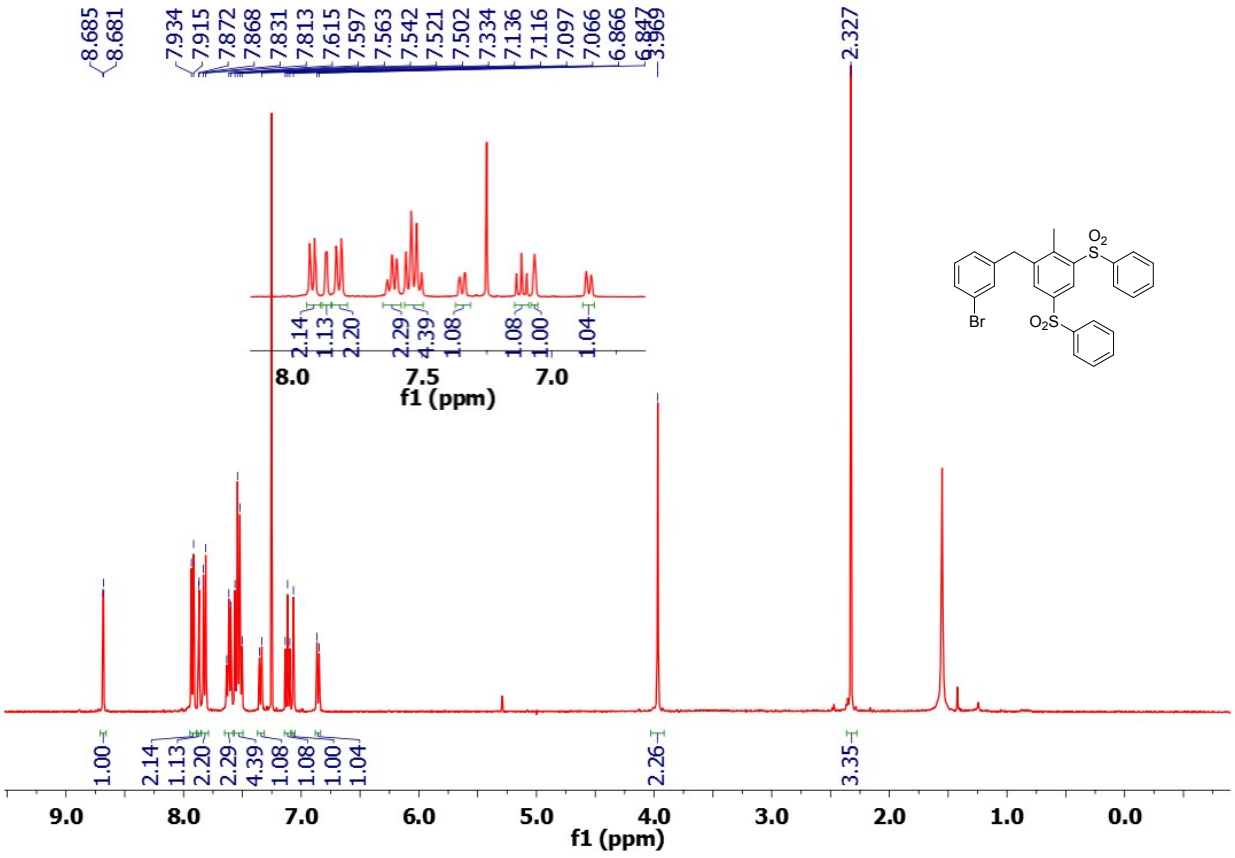

147.256
145.014
144.964
142.287
142.034
140.830
140.810
140.324
137.597
137.199
135.024
132.260
131.381
130.312
130.080
128.690
127.951
127.889
127.442
127.008
77.402
77.288
77.084
76.767
36.474
21.724
16.268
160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)
Cl
NO2
O2S
O2S

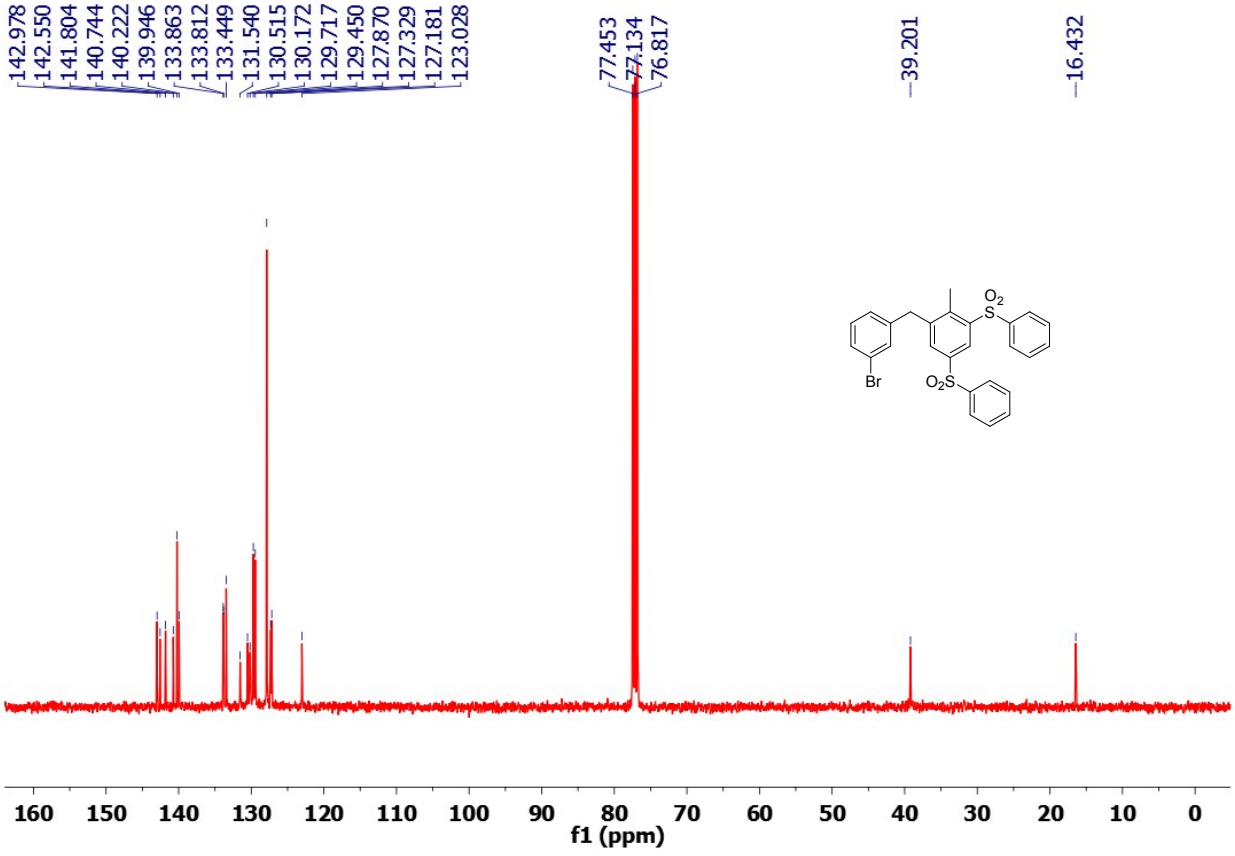

8.618
8.614
7.878
7.874
7.798
7.777
7.710
7.690
7.317
7.305
7.297
7.284
7.104
7.084
6.863
6.843
3.949
2.889
2.871
2.854
2.837
2.820
2.417
2.346
1.221
1.204
O2
S
H3C
CH3
O2S
2.20
2.20
4.45
2.20
2.17
7.6
7.2
f1 (ppm)
1.00
1.10
2.20
2.20
4.45
2.20
2.17
2.19
1.14
6.26
3.07
6.33
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

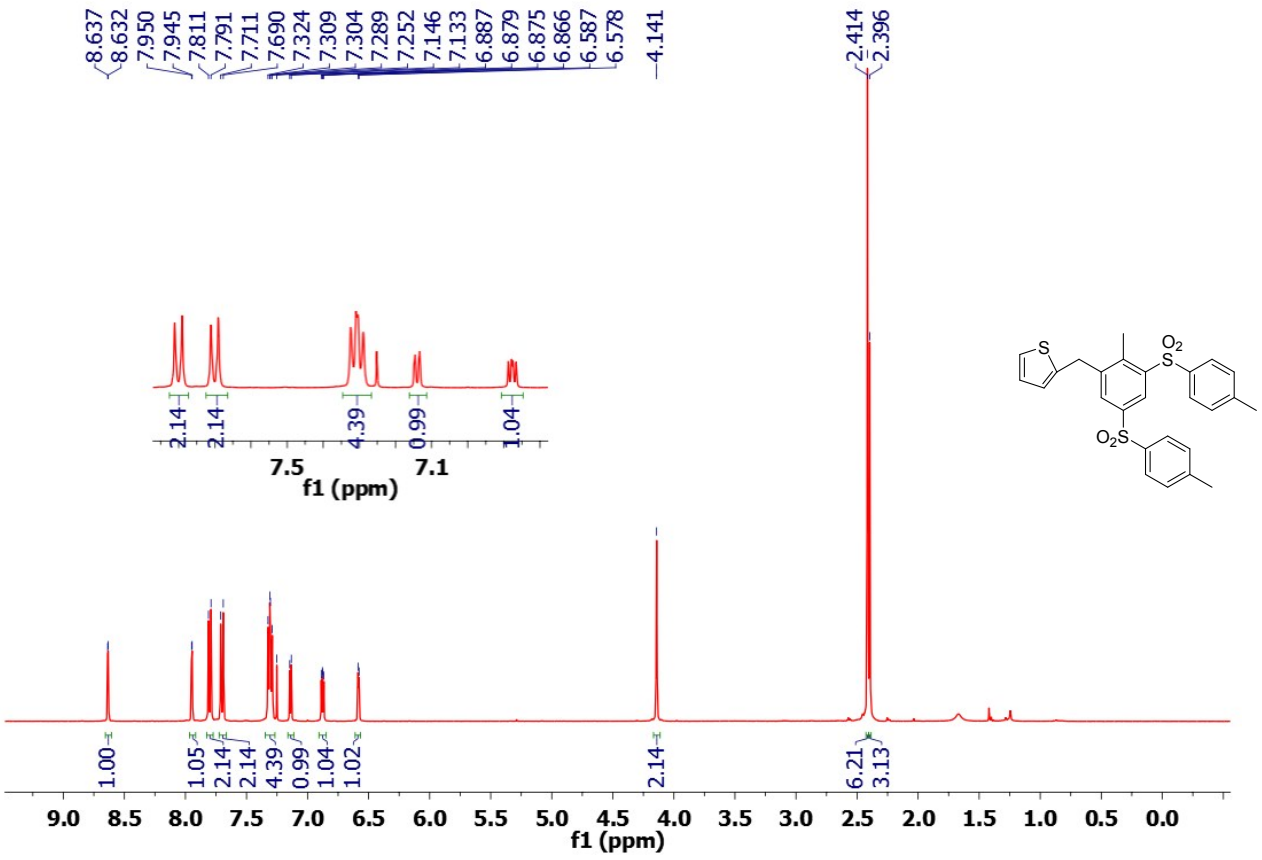

147.498
144.782
144.757
143.965
142.327
141.805
140.224
137.959
137.410
134.980
133.241
130.212
129.965
128.483
127.998
127.921
126.911
126.785
39.256
33.757
24.061
21.742
16.369
O2
S
H3C
CH3
O2S
170
150
130
110
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

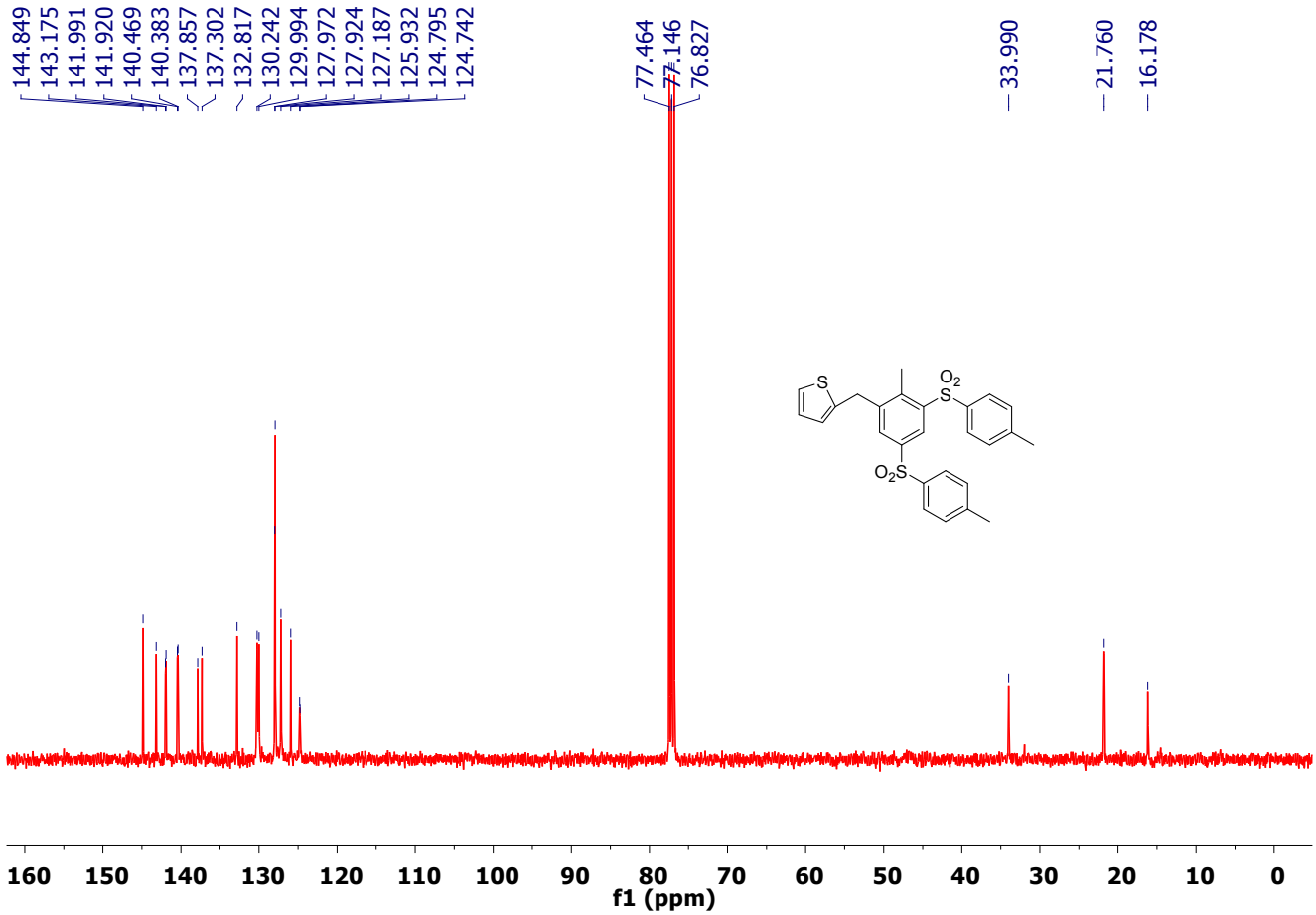

8.654
8.650
7.846
7.841
7.810
7.789
7.714
7.693
7.354
7.340
7.320
7.299
7.141
7.122
7.102
7.059
6.881
6.862
3.962
2.421
2.327
1.06
2.03
2.02
5.13
1.06
0.97
1.00
8.0
f1 (ppm)
Br
0.96
1.06
2.03
2.02
5.13
1.06
0.97
1.00
2.00
6.04
2.97
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
f1 (ppm)

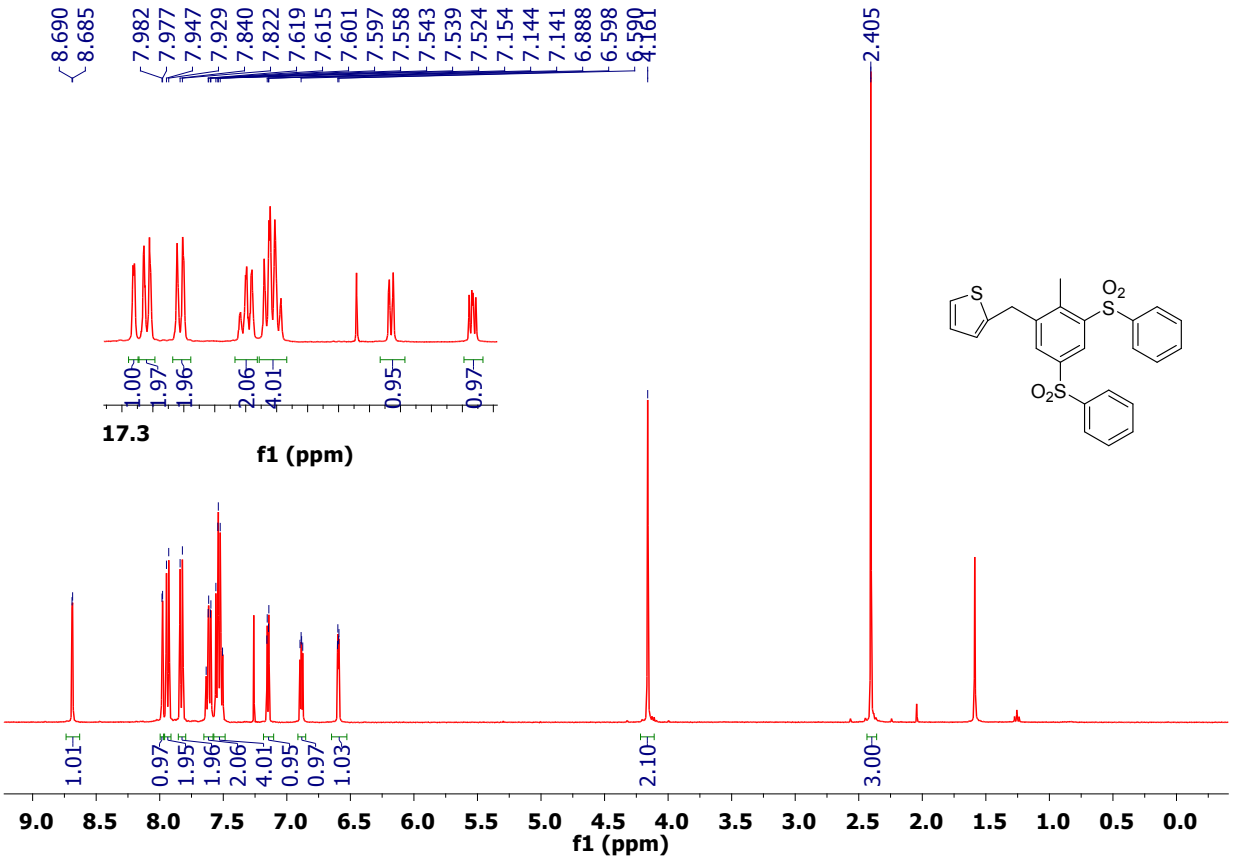

SKS_DY-53
144.79
144.74
142.62
142.08
141.92
140.36
139.93
137.63
137.11
133.01
131.38
131.32
130.33
130.15
129.92
127.81
127.76
127.08
126.89
122.84
77.32
77.00
76.68
39.04
21.62
21.59
16.21
Br
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

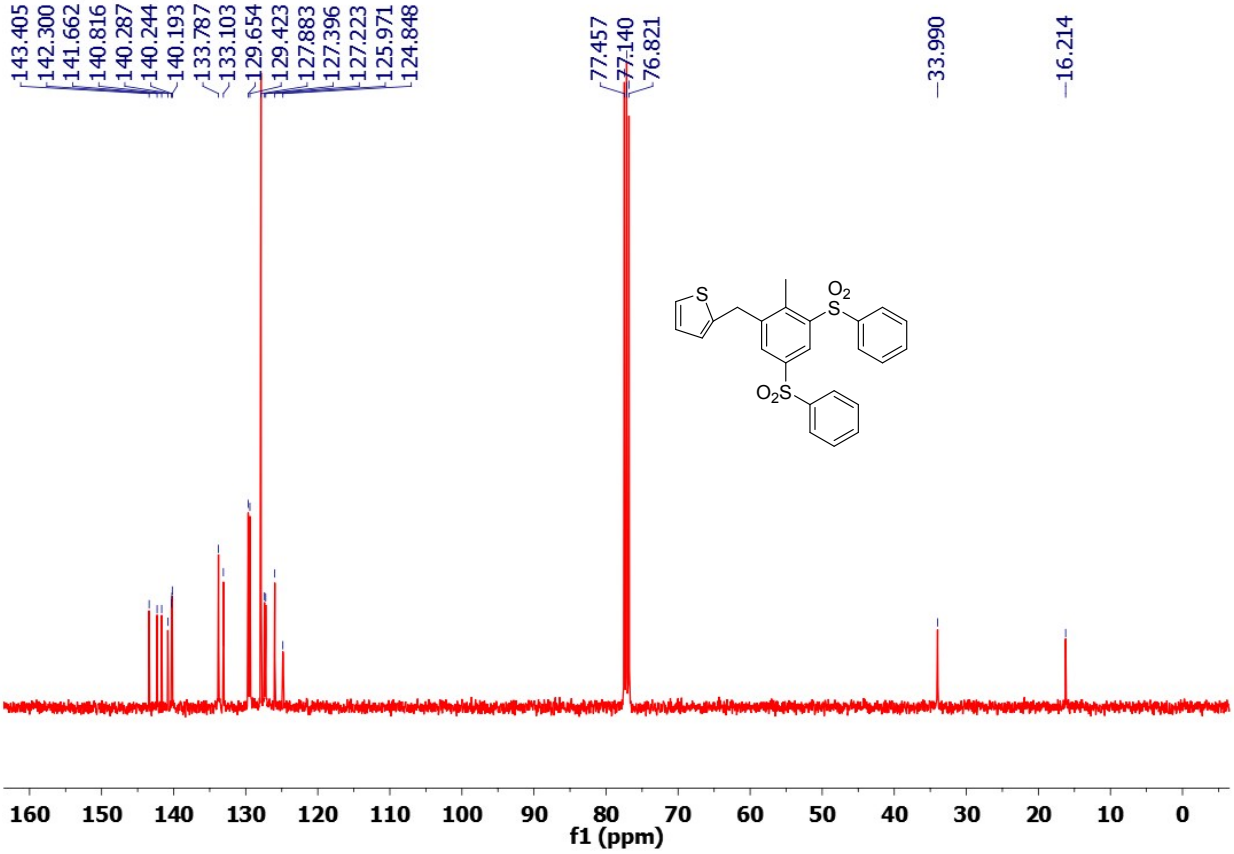

8.685
8.681
7.934
7.915
7.872
7.868
7.831
7.813
7.615
7.597
7.563
7.542
7.521
7.502
7.334
7.136
7.116
7.097
7.066
6.866
2.327
2.14
1.13
2.20
2.29
4.39
1.08
1.08
1.00
1.04
8.0
7.5
7.0
f1 (ppm)
Br
O2S
O2
1.00
2.14
1.13
2.20
2.29
4.39
1.08
1.08
1.00
1.04
2.26
3.35
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
f1 (ppm)

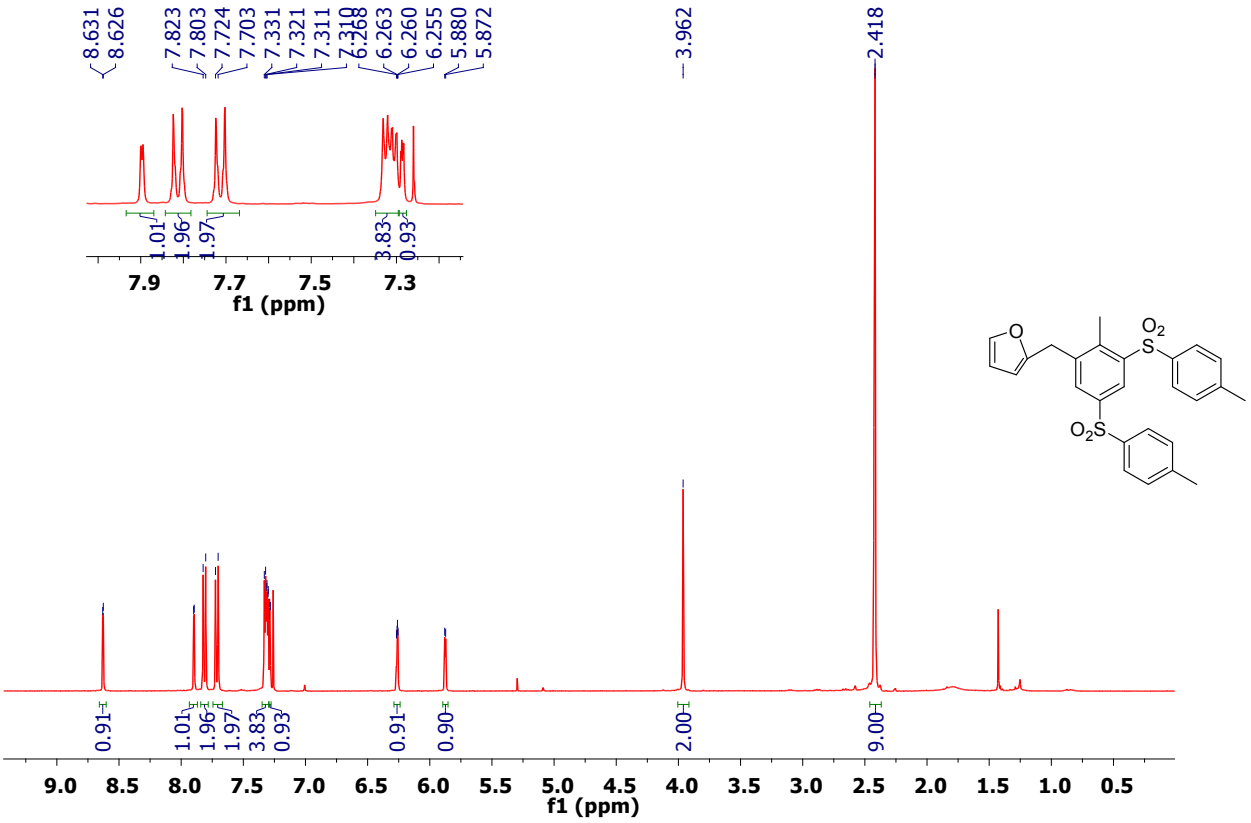

142.978
142.550
141.804
140.744
140.222
139.946
133.863
133.812
133.449
131.540
130.515
130.172
129.717
129.450
127.870
127.329
127.181
123.028
77.453
77.134
76.817
39.201
16.432
Br
O2S
O2
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

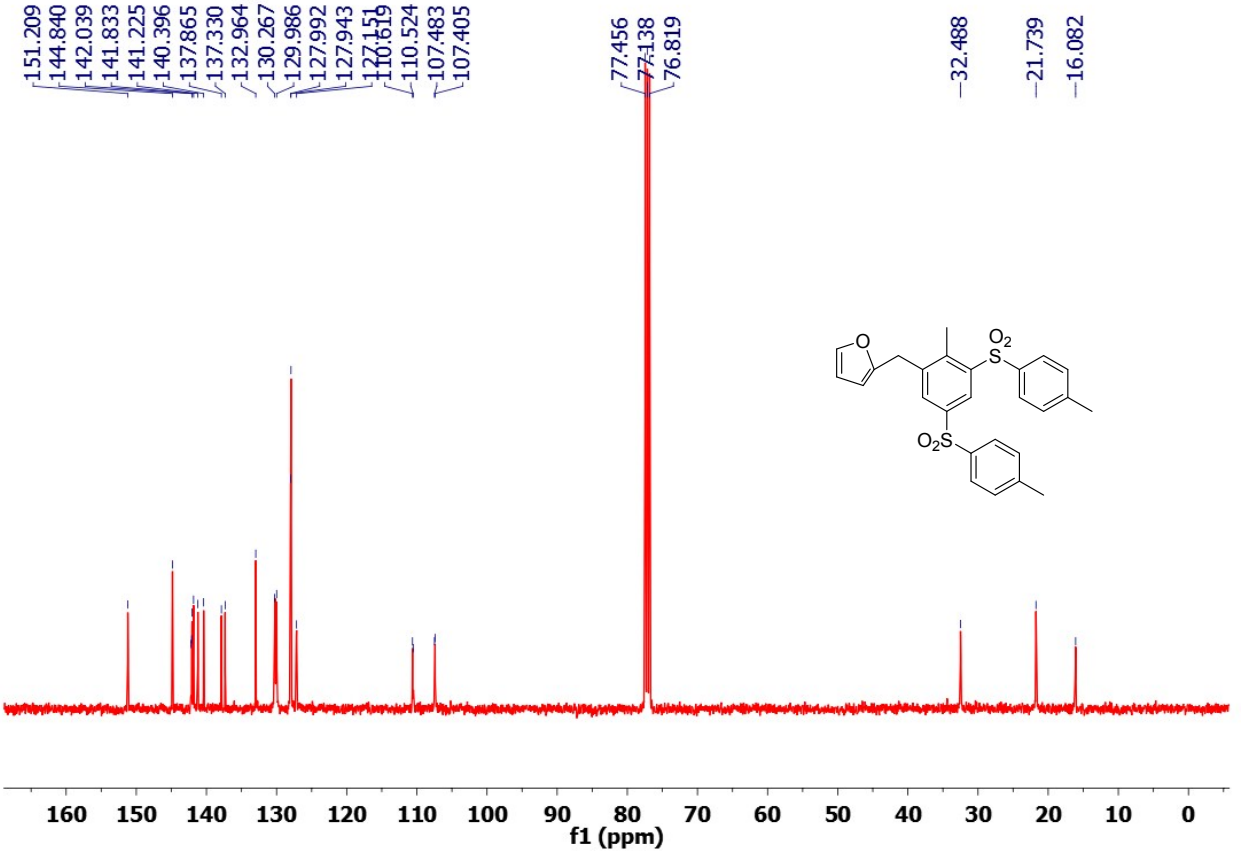

8.637
8.632
7.950
7.945
7.811
7.791
7.711
7.690
7.324
7.309
7.304
7.289
7.252
7.146
7.133
6.887
6.879
6.875
6.866
6.587
6.578
4.141
2.414
2.396
2.14
2.14
4.39
0.99
1.04
7.5
7.1
f1 (ppm)
1.00
1.05
2.14
2.14
4.39
0.99
1.04
1.02
2.14
6.21
3.13
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

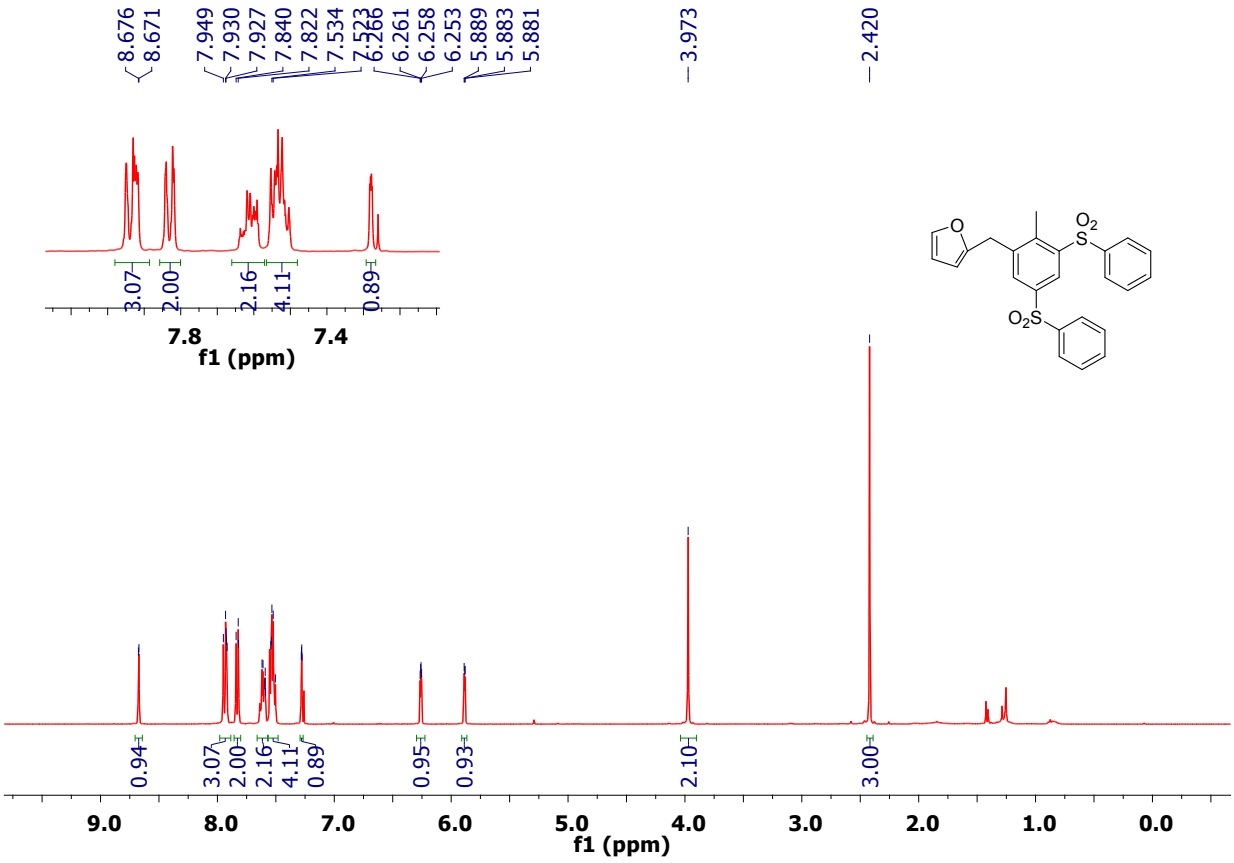

144.849
143.175
141.991
141.920
140.469
140.383
137.857
137.302
132.817
130.242
129.994
127.972
127.924
127.187
125.932
124.795
124.742
77.464
77.146
76.827
33.990
21.760
16.178
160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

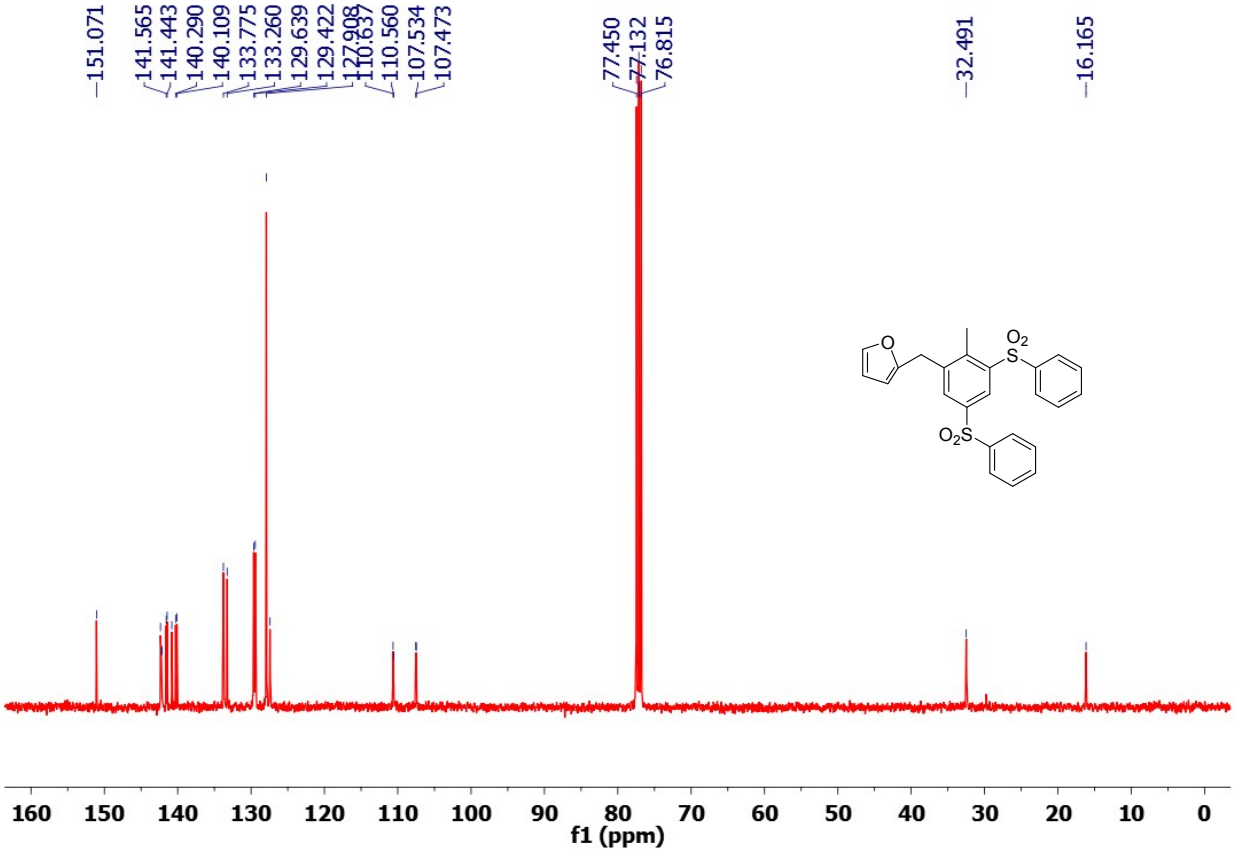

8.690
8.685
7.982
7.977
7.947
7.929
7.840
7.822
7.619
7.615
7.601
7.597
7.558
7.543
7.539
7.524
7.154
7.144
7.141
6.888
6.598
6.590
4.161
2.405
1.00
1.97
1.96
2.06
4.01
0.95
0.97
17.3
f1 (ppm)
1.01
0.97
1.95
1.96
2.06
4.01
0.95
0.97
1.03
2.10
3.00
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)
S
O2
S
O2S

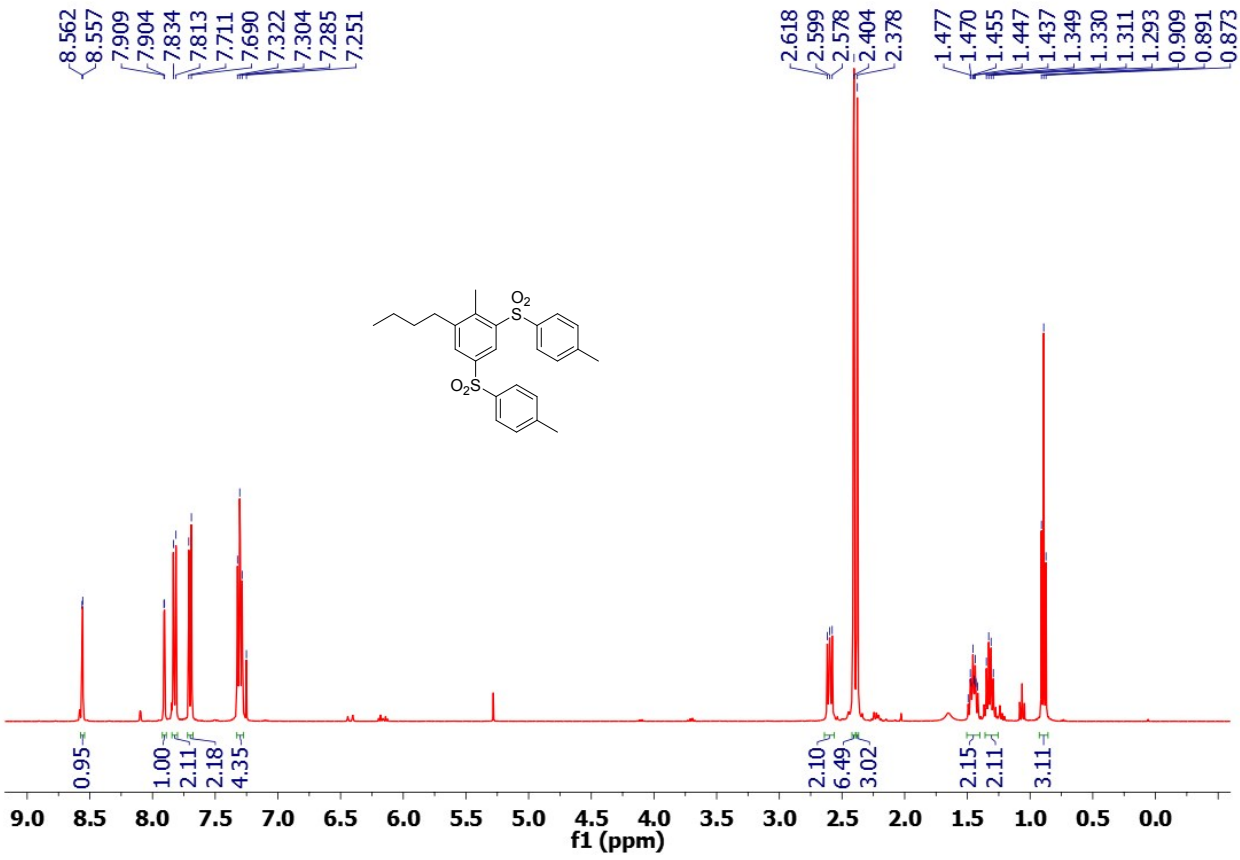

143.405
142.300
141.662
140.816
140.287
140.244
140.193
133.787
133.103
129.654
129.423
127.883
127.396
127.223
125.971
124.848
77.457
77.140
76.821
33.990
16.214
160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)
S
O2
S
O2S


8.631
8.626
7.823
7.803
7.724
7.703
7.331
7.321
7.311
6.263
6.260
6.255
5.880
5.872
3.962
2.418
1.01
1.96
1.97
3.83
0.93
7.9
7.7
7.5
7.3
f1 (ppm)
O
O2
S
O2S
0.91
1.01
1.96
1.97
3.83
0.93
0.91
0.90
2.00
9.00
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)


151.209
144.840
142.039
141.833
141.225
140.396
137.865
137.330
132.964
130.267
129.986
127.992
127.943
110.524
107.483
107.405
77.456
77.138
76.819
32.488
21.739
16.082
O
O2
S
O2S
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


8.676
8.671
7.949
7.930
7.927
7.840
7.822
7.534
7.523
6.266
6.261
6.258
6.253
5.889
5.883
5.881
3.973
2.420
3.07
2.00
2.16
4.11
0.89
7.8
7.4
f1 (ppm)
O
O2S
O2S
0.94
3.07
2.00
2.16
4.11
0.89
0.95
0.93
2.10
3.00
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
f1 (ppm)


151.071
141.565
141.443
140.290
140.109
133.775
133.260
129.639
129.422
127.908
110.637
110.560
107.534
107.473
77.450
77.132
76.815
32.491
16.165
O
O2S
O2S
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


8.562
8.557
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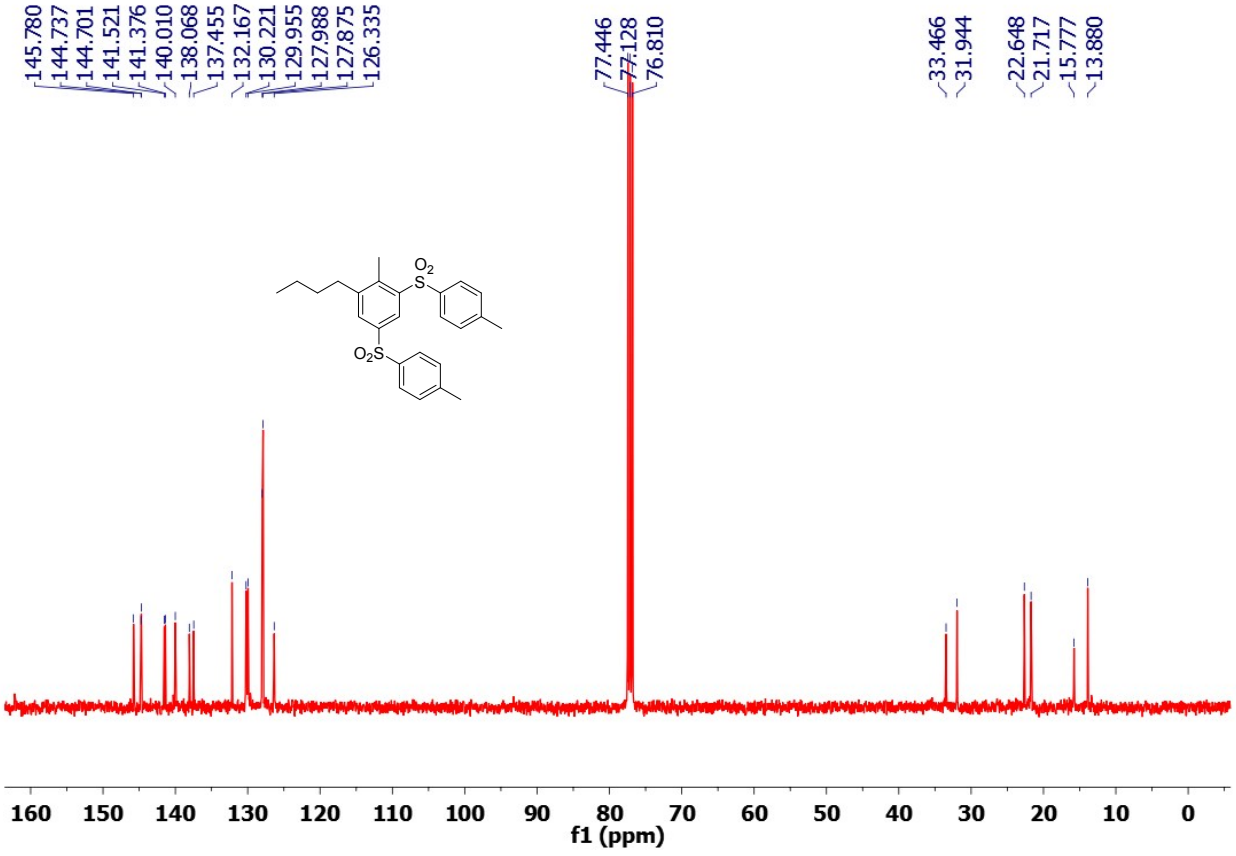
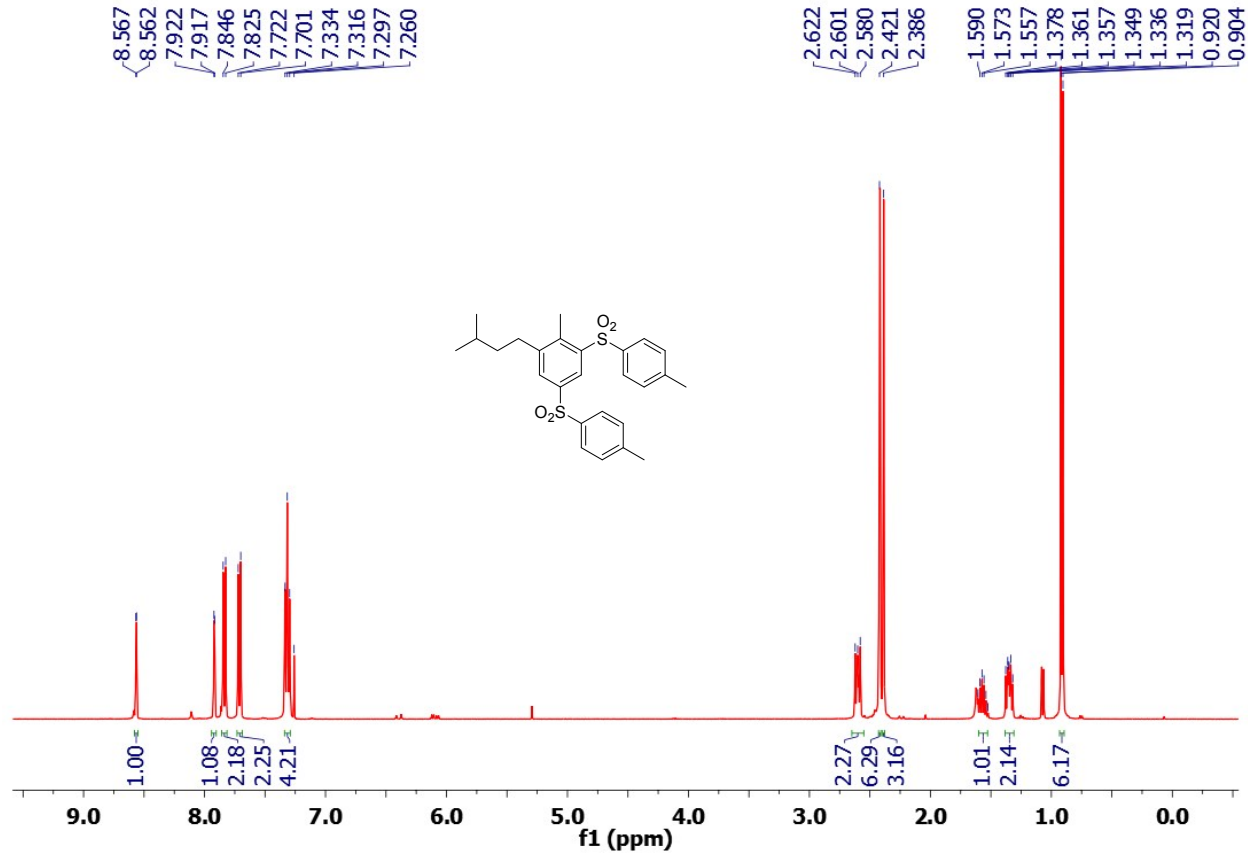
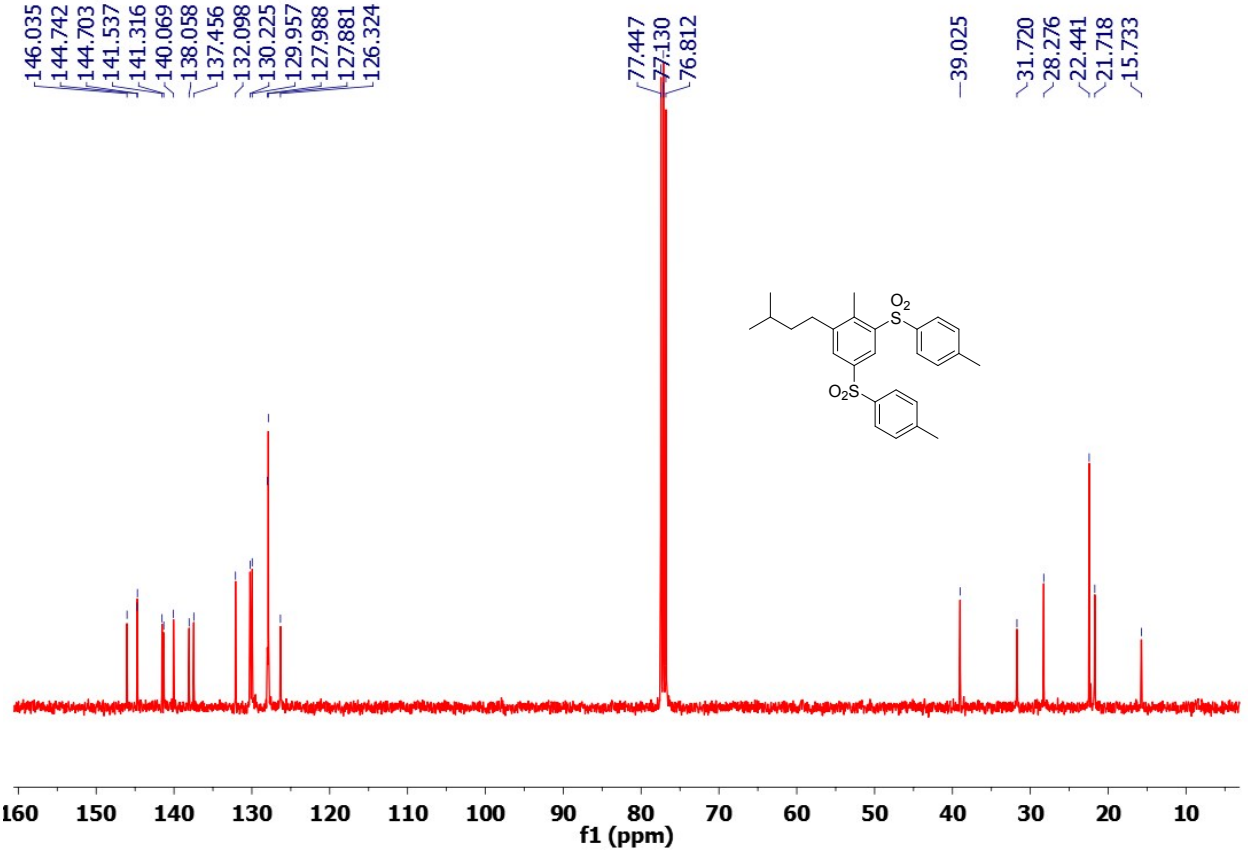
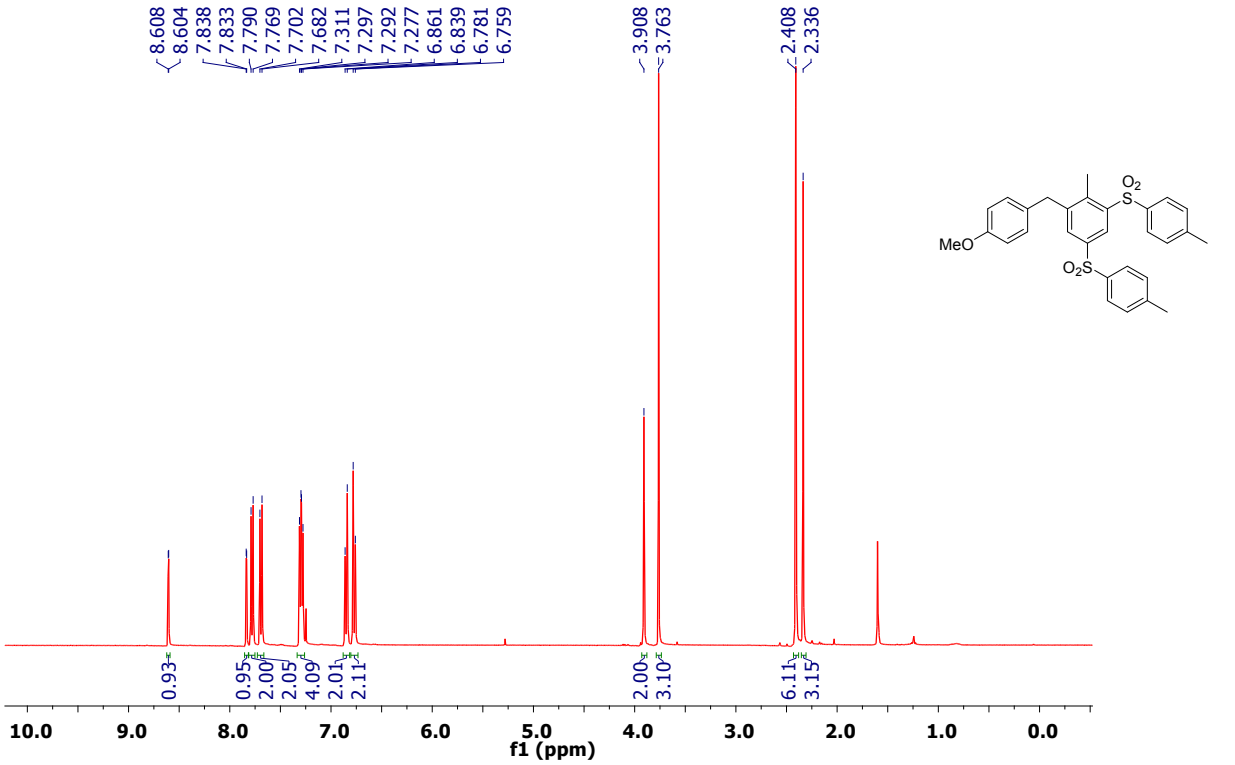
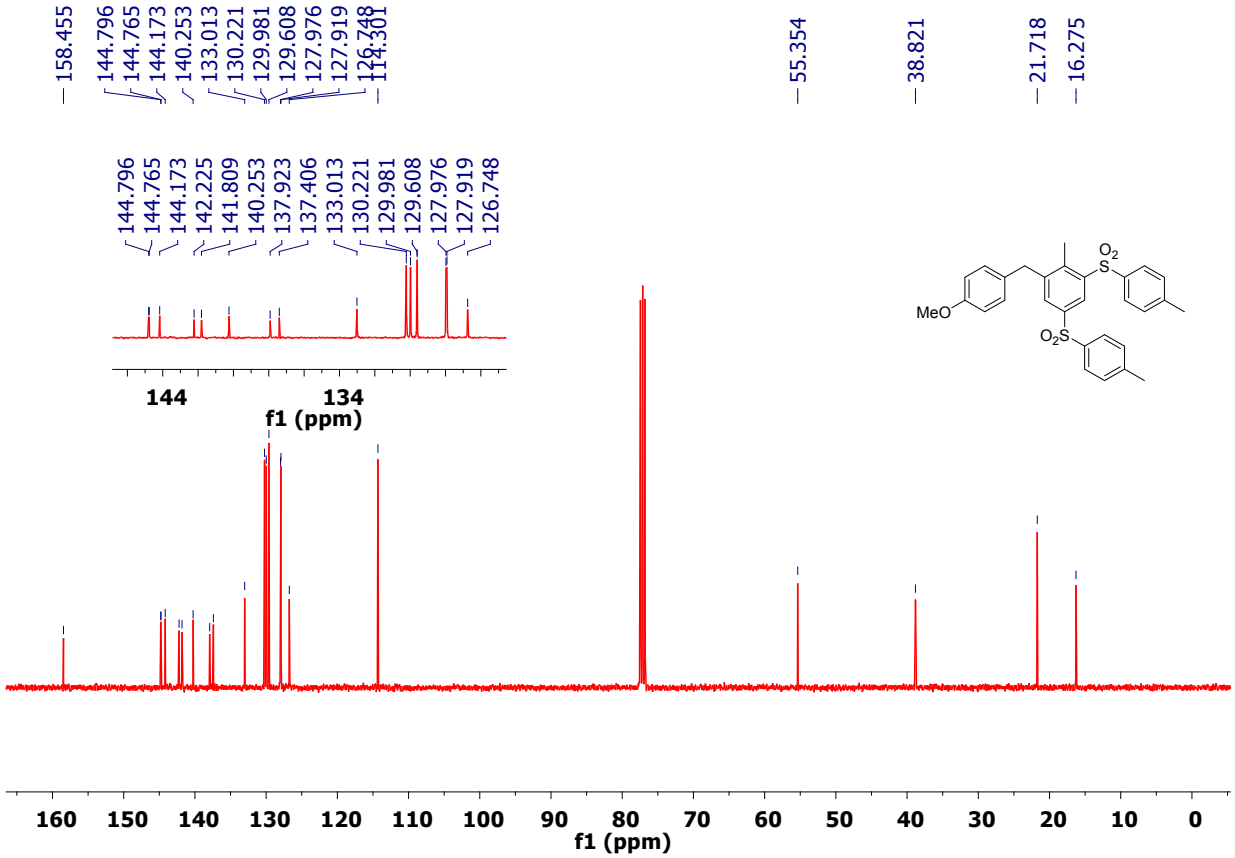
7.904
7.834
7.813
7.711
7.690
7.322
7.304
7.285
7.251
2.618
2.599
2.578
2.404
2.378
1.477
1.470
1.455
1.447
1.437
1.349
1.330
1.311
1.293
0.909
0.891
0.873
O2
S
O2S
0.95
1.00
2.11
2.18
4.35
2.10
6.49
3.02
2.15
2.11
3.11
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

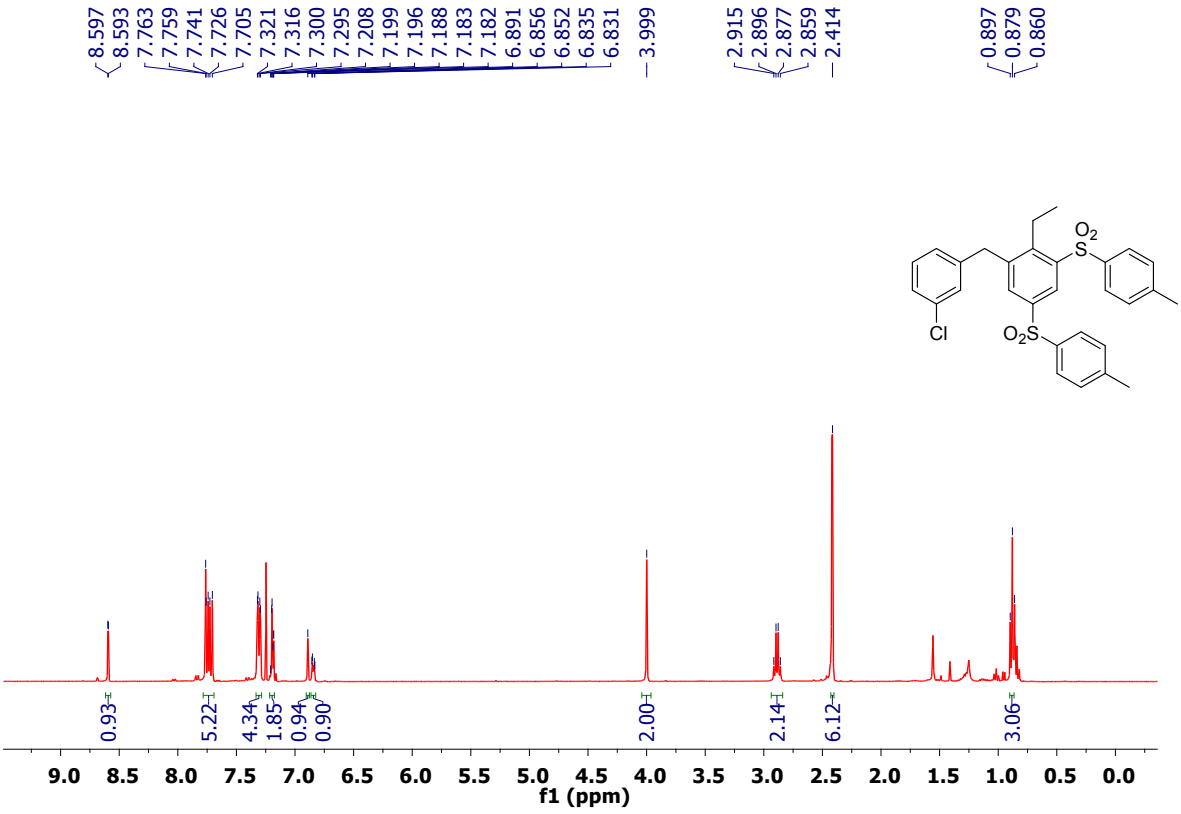

145.780
144.737
144.701
141.521
141.376
140.010
138.068
137.455
132.167
130.221
129.955
127.988
127.875
126.335
77.446
77.128
76.810
33.466
31.944
22.648
21.717
15.777
13.880
O2
S
O2S
160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

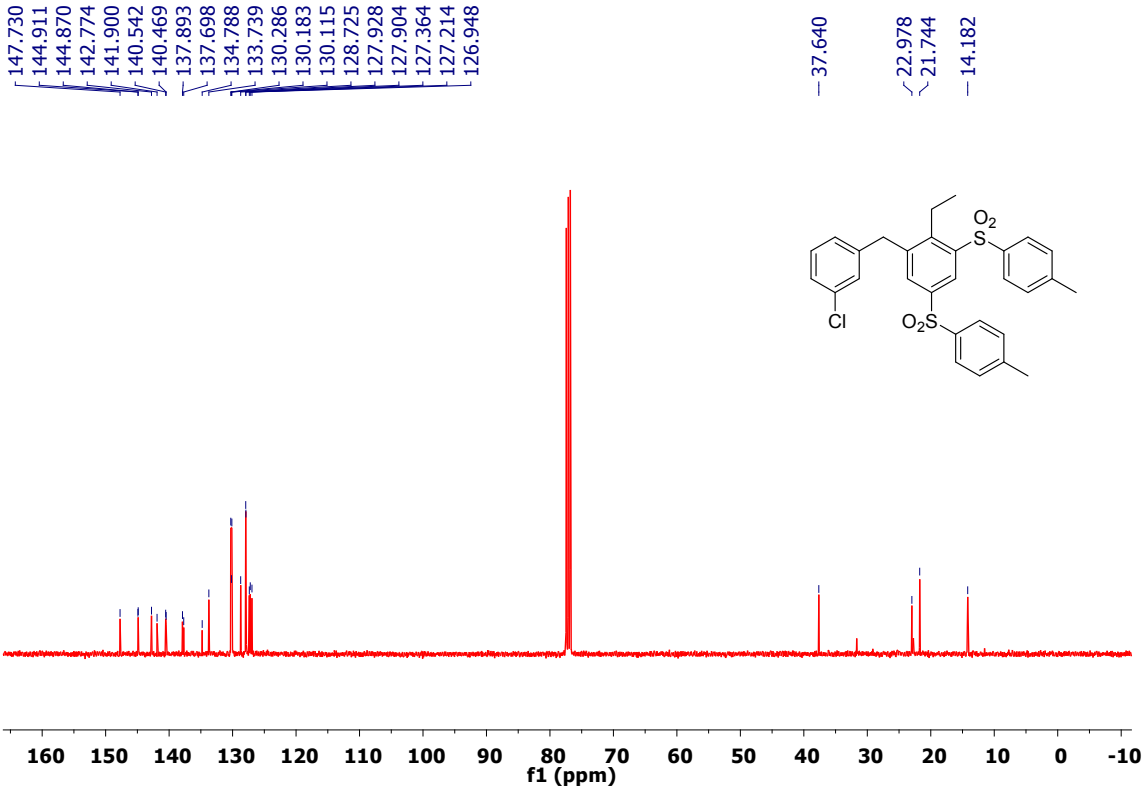

8.567
8.562
7.922
7.917
7.846
7.825
7.722
7.701
7.334
7.316
7.297
7.260
2.622
2.601
2.580
2.421
2.386
1.590
1.573
1.557
1.378
1.361
1.357
1.349
1.336
1.319
0.920
0.904
O2S
O2S
1.00
1.08
2.18
2.25
4.21
2.27
6.29
3.16
1.01
2.14
6.17
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
f1 (ppm)

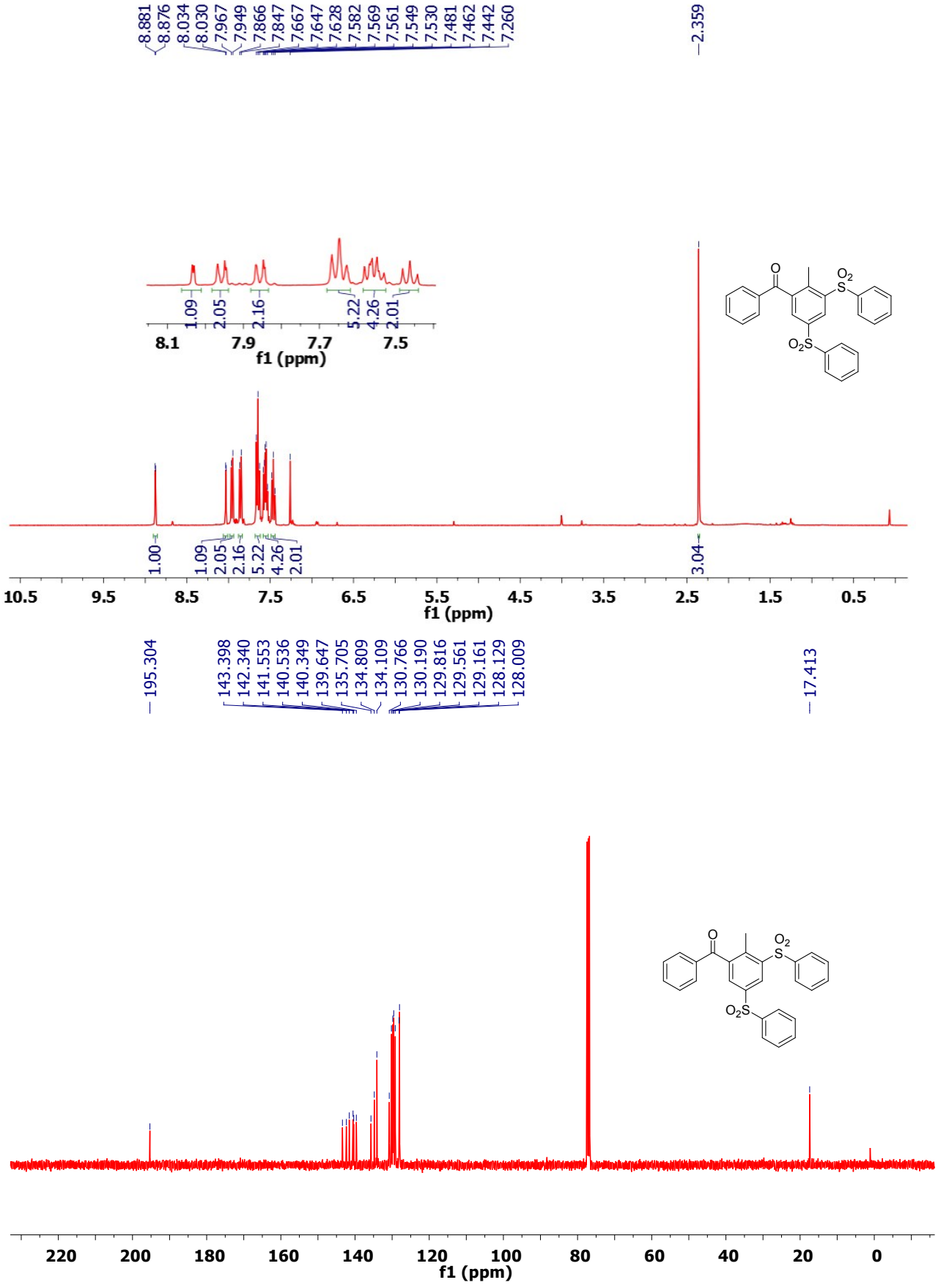

146.035
144.742
144.703
141.537
141.316
140.069
138.058
137.456
132.098
130.225
129.957
127.988
127.881
126.324
77.447
77.130
76.812
39.025
31.720
28.276
22.441
21.718
15.733
O2S
O2S
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

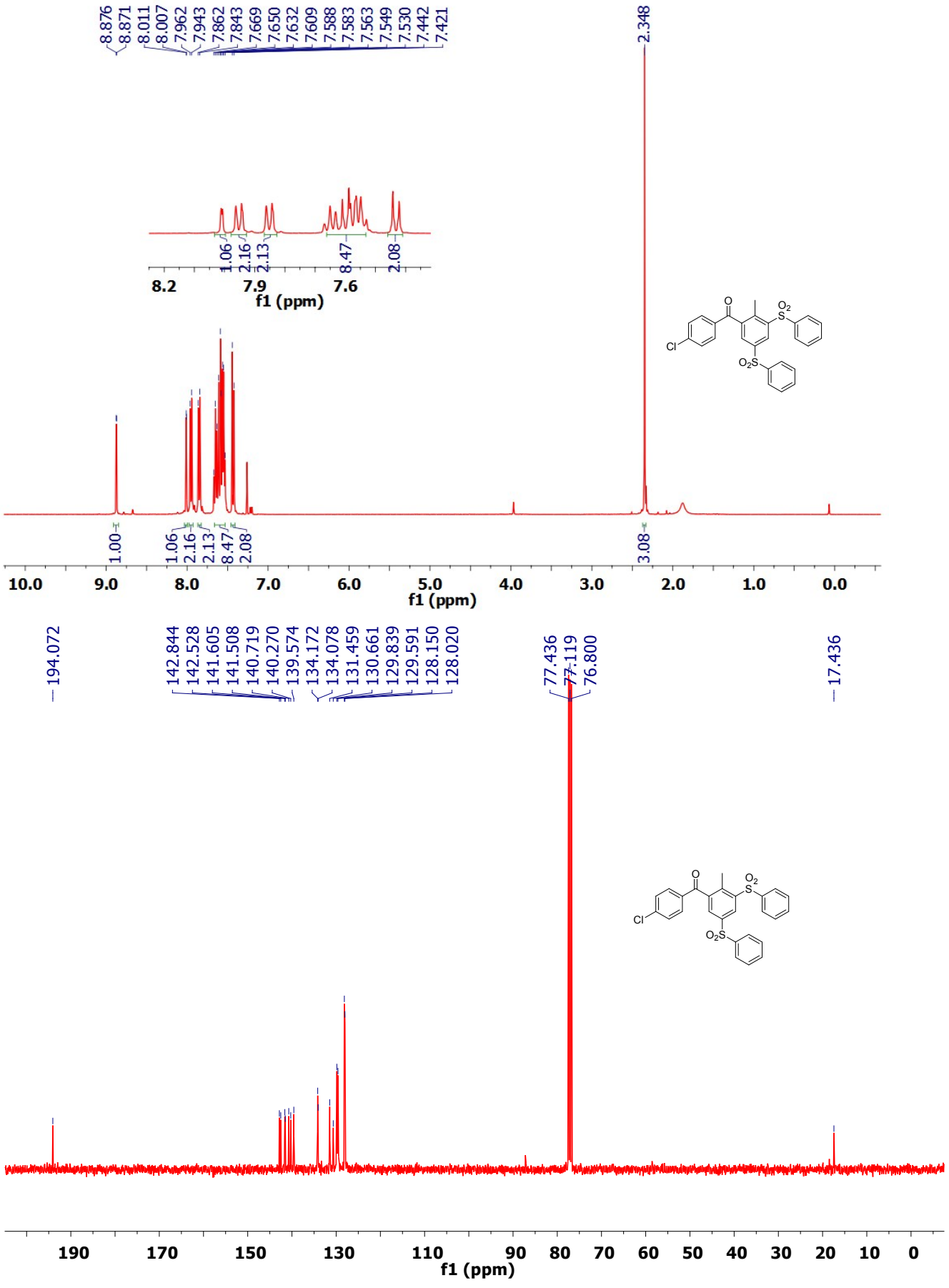

8.608
8.604
7.838
7.833
7.790
7.769
7.702
7.682
7.311
7.297
7.292
7.277
6.861
6.839
6.781
6.759
3.908
3.763
2.408
2.336
0.93
0.95
2.00
2.05
4.09
2.01
2.11
2.00
3.10
6.11
3.15
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
f1 (ppm)
MeO
O2
S
O2S


158.455
144.796
144.765
144.173
140.253
133.013
130.221
129.981
129.608
127.976
127.919
126.748
114.301
55.354
38.821
21.718
16.275
144.796
144.765
144.173
142.225
141.809
140.253
137.923
137.406
133.013
130.221
129.981
129.608
127.976
127.919
126.748
144
134
f1 (ppm)
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)
MeO
O2
S
O2S


8.597
8.593
7.763
7.759
7.741
7.726
7.705
7.321
7.316
7.300
7.295
7.208
7.199
7.196
7.188
7.183
7.182
6.891
6.856
6.852
6.835
6.831
3.999
2.915
2.896
2.877
2.859
2.414
0.897
0.879
0.860
O2
S
Cl
O2S
0.93
5.22
4.34
1.85
0.94
0.90
2.00
2.14
6.12
3.06
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


147.730
144.911
144.870
142.774
141.900
140.542
140.469
137.893
137.698
134.788
133.739
130.286
130.183
130.115
128.725
127.928
127.904
127.364
127.214
126.948
37.640
22.978
21.744
14.182
O2
S
Cl
O2S
160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


8.881
8.876
8.034
8.030
7.967
7.949
7.866
7.847
7.667
7.647
7.628
7.582
7.569
7.561
7.549
7.530
7.481
7.462
7.442
7.260
2.359
1.09
2.05
2.16
5.22
4.26
2.01
8.1
7.9
7.7
7.5
f1 (ppm)
O
O2
S
O2S
1.00
1.09
2.05
2.16
5.22
4.26
2.01
3.04
10.5
9.5
8.5
7.5
6.5
5.5
4.5
3.5
2.5
1.5
0.5
f1 (ppm)
195.304
143.398
142.340
141.553
140.536
140.349
139.647
135.705
134.809
134.109
130.766
130.190
129.816
129.561
129.161
128.129
128.009
17.413
220
200
180
160
140
120
100
80
60
40
20
0
f1 (ppm)


8.876
8.871
8.011
8.007
7.962
7.943
7.862
7.843
7.669
7.650
7.632
7.609
7.588
7.583
7.563
7.549
7.530
7.442
7.421
2.348
1.06
2.16
2.13
8.47
2.08
8.2
7.9
7.6
f1 (ppm)
1.00
1.06
2.16
2.13
8.47
2.08
3.08
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
f1 (ppm)
194.072
142.844
142.528
141.605
141.508
140.719
140.270
139.574
134.172
134.078
131.459
130.661
129.839
129.591
128.150
128.020
77.436
77.119
76.800
17.436
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
f1 (ppm)