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

Exploitation of Donor-Acceptor Cyclopropanes and *N*-Sulfonyl 1-Azadienes Towards the Synthesis of Spiro-Cyclopentane Benzofuran Derivatives

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Experimental Section

All reactions were carried out under inert atmosphere using oven dried glassware. All solvents and reagents were obtained from commercial sources and were purified using standard procedure prior to use. The developed chromatogram was analyzed by UV lamp (254 nm), or *p*-Anisaldehyde solution. Products were purified by flash chromatography on silica gel (mesh size 230-400). The ^{1}H and ^{13}C-NMR spectra were recorded in $CDCl_3$. Chemical shifts of ^{1}H and ^{13}C-NMR spectra are expressed in parts per million (ppm). All coupling constants are given in absolute values and are expressed in Hz. The description of the signals includes: s = singlet, d = doublet, dd = doublet of doublet, t = triplet, dt = doublet of triplet, q = quartet, pent = pentet, br = broad and m = multiplet. The DACs[1] and azadienes[2c] were prepared according to the known methods.

(E)-N-((Z)-2-benzylidenebenzofuran-3(2H)-ylidene)-4-methylbenzenesulfonamide (**2a**)[2c]: **^{1}H NMR** (400 MHz, $CDCl_3$): δ 8.78 (d, *J* = 8.1 Hz, 1H), 8.00 (d, *J* = 8.2 Hz, 2H), 7.89 (d, *J* = 7.0 Hz, 2H), 7.69 (ddd, *J* = 8.5, 7.2, 1.4 Hz, 1H), 7.47–7.35 (m, 5H), 7.33 (d, *J* = 8.3 Hz, 1H), 7.29 (t, *J* = 7.7 Hz, 1H), 7.12 (s, 1H), 2.48 (s, 3H).

(E)-N-((Z)-2-benzylidenebenzofuran-3(2H)-ylidene)-4-nitrobenzenesulfonamide (2b)[2b]: **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.69 (d, *J* = 8.0 Hz, 1H), 8.46-8.37 (m, 2H), 8.34-8.24 (m, 2H), 7.91-7.88 (m, 2H), 7.76-7.70 (m, 1H), 7.49-7.39 (m, 3H), 7.36 (d, J = 8.4 Hz, 1H), 7.34-7.29 (m, 1H), 7.12 (s, 1H)

(E)-4-methyl-N-((Z)-2-(4-methylbenzylidene)benzofuran-3(2H)-ylidene)benzenesulfonamide (**2c**)[2c]: **^{1}H NMR** (400 MHz, $CDCl_3$): δ 8.78 (d, *J* = 8.1 Hz, 1H), 8.00 (d, *J* = 8.3 Hz, 2H), 7.79 (d, *J* = 7.9 Hz, 2H), 7.67 (ddd, *J* = 8.5, 7.2, 1.4 Hz, 1H), 7.37 (d, *J* = 8.1 Hz, 2H), 7.32 (d, *J* = 8.3 Hz, 1H), 7.28 (d, *J* = 7.8 Hz, 1H), 7.25 (d, *J* = 8.0 Hz, 2H), 7.12 (s, 1H), 2.47 (s, 3H), 2.40 (s, 3H).

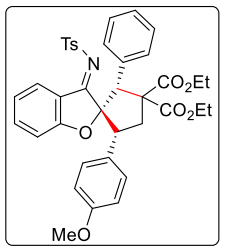
N-((Z)-2-((Z)-4-fluorobenzylidene)benzofuran-3(2H)-ylidene)-4-methylbenzenesulfonamide (2d)[2a]: **^{1}H NMR** (400 MHz, $CDCl_3$): δ 8.77 (d, *J* = 8.0 Hz, 1H), 7.99 (d, *J* = 8.2 Hz, 2H), 7.87 (dd, *J* = 8.7, 5.6 Hz, 2H), 7.71-7.63 (m, 1H), 7.37 (d, *J* = 8.1 Hz, 2H), 7.33 – 7.27 (m, 2H), 7.11 (t, *J* = 8.7 Hz, 2H), 7.05 (s, 1H), 2.47 (s, 3H).

(E)-N-((Z)-2-(4-chlorobenzylidene)benzofuran-3(2H)-ylidene)-4-methylbenzenesulfonamide (2e)[2c]:**^{1}H NMR** (400 MHz, $CDCl_3$): δ 8.77 (d, *J* = 8.1 Hz, 1H), 7.99 (d, *J* = 8.3 Hz, 2H), 7.81 (d, *J* = 8.6 Hz, 2H), 7.68 (ddd, *J* = 8.5, 7.3, 1.4 Hz, 1H), 7.43-7.35 (m, 4H), 7.32 (d, *J* = 3.9 Hz, 1H), 7.29 (d, *J* = 3.7 Hz, 1H), 7.03 (s, 1H), 2.47 (s, 3H).

General procedure of 3

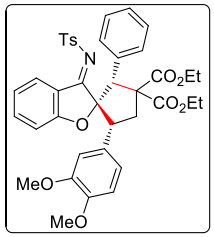
A two-necked round bottom flask was charged with DACs **1** (1.0 equiv.), *N*-sulfonyl 1-azadienes **2** (1.0 equiv.) and MgI_2 (0.2 equiv.) under nitrogen atmosphere. DCM was added to the reaction mixture and solution was stirred it at room temperature until the consumption of cyclopropane (as monitored by TLC). Reaction mixture was filtered through thin pad of celite and solvent was concentrated in rotary evaporator. The residue was purified by flash column chromatography on silica gel using ethyl acetate/hexane as eluent.

Diethyl(2R,2'R,5'R,E)-5'-(4-methoxyphenyl)-2'-phenyl-3-(tosylimino)-3H-spiro[benzofuran-2,1'-cyclopentane]-3',3'-dicarboxylate (3aa): Reaction time: 7 h, **1a** (62 mg, 0.21 mmol), **2a** (80 mg, 0.21 mmol), yield = 69%, 96 mg, nature = viscous liquid. R_f-value: 0.30 (Ethyl acetate/hexane) = 2:8. ^{1}H-NMR (400 MHz, $CDCl_3$) δ 8.22 (d, *J* = 8.0 Hz, 1H), 8.03 (d, *J* = 8.4 Hz, 2H), 7.41 (d, *J* = 8.3 Hz, 2H), 7.37-7.33 (m, 1H), 7.19-7.17 (m, 4H), 7.07-7.04 (m, 3H), 6.89 (d, *J* = 8.4 Hz, 1H), 6.78 (t, *J* = 8.3 Hz, 1H), 6.64 (d, *J* = 8.7 Hz, 2H), 4.90 (s, 1H), 4.31-4.23 (m, 1H), 4.20-4.12 (m, 1H), 3.95-3.87 (m, 1H), 3.83 (t, *J* = 14.1 Hz, 1H), 3.66 (s, 3H), 3.64-3.57 (m, 1H), 3.54-3.46 (m, 1H), 2.57 (dd, *J* = 6.9, 6.5 Hz, 1H), 2.50 (s, 3H), 1.20 (t, *J* = 6.9 Hz, 3H), 0.71 (t, *J* = 7.3 Hz, 3H). ^{13}C-NMR (100 MHz, $CDCl_3$) δ 180.2, 171.9, 170.2, 169.9, 158.9, 143.4, 138.9, 134.0, 130.4, 129.6, 128.1, 127.6, 127.0, 126.1, 121.9, 118.4, 113.6, 112.1, 101.2, 62.8, 62.1,



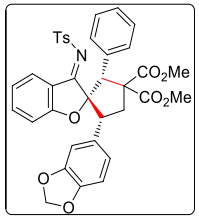
61.5, 60.0, 55.1, 53.9, 38.5, 21.7, 14.0, 13.3. IR ($\bar{\upsilon}$, cm^{-1}) 2981, 1720, 1576, 1515, 1464, 1302, 1248, 1181, 1147, 1088, 1018, 905, 877, 828, 747, 704. HRMS (ESI) calcd for $C_{38}H_{38}NO_8S^+$ $[M+H]^+$; 668.2318 found 668.2334.

Diethyl(2R,2'R,5'R,E)-5'-(3,4-dimethoxyphenyl)-2'-phenyl-3-(tosylimino)-3H-spiro[benzofuran-2,1'-cyclopentane]-3',3'-dicarb

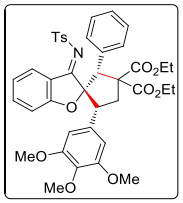


oxylate (3ba): Reaction time: 8 h, **1b** (46 mg, 0.14 mmol), **2a** (54 mg, 0.14 mmol), yield = 62%, 61 mg, Nature = yellow solid, Melting Point = 111 ^oC R_f-value: 0.25 (Ethyl acetate/hexane) = 2:8. ^{1}H-NMR (400 MHz, $CDCl_3$) δ 8.22 (d, *J* = 8.1 Hz, 1H), 8.02 (d, *J* = 8.2 Hz, 2H), 7.41 (d, *J* = 8.4 Hz, 2H), 7.37-7.33 (m, 1H), 7.20-7.18 (m, 2H), 7.07-7.06 (m, 3H), 6.87-6.79 (m, 3H), 6.75 (m, 1H), 6.63 (d, *J* = 8.3 Hz, 1H), 4.93 (s, 1H), 4.32-4.24 (m, 1H), 4.21-4.10 (m, 1H), 3.98-3.87 (m, 1H), 3.81 (d, *J* = 14.3 Hz, 1H), 3.78 (s, 3H), 3.74 (s, 3H), 3.63 (dd, *J* = 8.4, 6.7 Hz, 1H), 3.53-3.45 (m, 1H), 2.59 (dd, *J* = 7.3, 6.5 Hz, 1H), 2.50 (s, 3H), 1.20 (t, *J* = 7.1 Hz, 3H), 0.71 (t, *J* = 7.6 Hz, 3H). ^{13}C-NMR (100 MHz, $CDCl_3$) δ 180.3, 171.9, 170.2, 169.9, 148.3, 143.4, 138.9, 133.9, 130.3, 129.6, 128.0, 127.7, 126.9, 122.0, 120.3, 118.4, 112.0, 111.5, 110.4, 101.2, 62.8, 62.1, 61.5, 59.9, 55.9, 55.7, 54.2, 38.1, 21.7, 14.0, 13.3. IR ($\bar{\upsilon}$, cm^{-1}) 2936, 1718, 1601, 1459, 1145, 1087, 1015, 835, 751, 701. HRMS (ESI) calcd for $C_{39}H_{40}NO_9S^+$ $[M+H]^+$; 698.2424 found 698.2451.

Dimethyl(2R,2'R,5'R,E)-5'-(benzo[d][1,3]dioxol-5-yl)-2'-phenyl-3-(tosylimino)-3H-spiro[benzofuran-2,1'-cyclopentane]-3',3'-di carboxylate (3ca): Reaction time: 8 h, **1c** (52 mg, 0.18 mmol), **2a** (70 mg, 0.18 mmol), yield = 61%, 72 mg, Nature = viscous liquid.

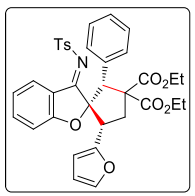


R_f-value: 0.25 (Ethyl acetate/hexane) = 2:8. ^{1}H-NMR (400 MHz, $CDCl_3$) δ 8.24 (d, *J* = 8.3 Hz, 1H), 8.01 (d, *J* = 8.4 Hz, 2H), 7.44-7.37 (m, 3H), 7.17-7.14 (m, 2H), 7.09-7.06 (m, 3H), 6.95 (d, *J* = 8.2 Hz, 1H), 6.84-6.80 (m, 2H), 6.68-6.66 (m, 1H), 6.54 (d, *J* = 8.7 Hz, 1H), 5.82-5.81 (m, 2H), 4.84 (s, 1H), 3.80-3.73 (m, 1H), 3.75 (s, 3H), 3.58 (dd, *J* = 7.3, 6.8 Hz, 1H), 326 (s, 3H), 2.57 (dd, *J* = 6.9, 6.8 Hz, 1H), 2.50 (s, 3H). ^{13}C-NMR (100 MHz, $CDCl_3$) δ 179.7, 172.3, 170.2, 170.1, 147.4, 147.0, 143.5, 138.9, 133.6, 130.5, 130.1, 129.6, 128.1, 127.8, 127.0, 122.2, 122.0, 112.2, 108.8, 107.9, 101.0, 100.9, 62.7, 60.3, 54.2, 53.3, 52.4, 38.7, 21.7. IR ($\bar{\upsilon}$, cm^{-1}) 2922, 1728, 1595, 1482, 1276, 1144, 1089, 1038, 934, 873, 805, 753, 733, 700. HRMS (ESI) calcd for $C_{36}H_{32}NO_9S^+$ $[M+H]^+$; 654.1798 found 654.1741.

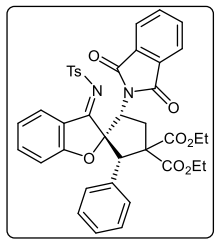
Diethyl(2R,2'R,5'R,E)-2'-phenyl-3-(tosylimino)-5'-(3,4,5-trimethoxyphenyl)-3H-spiro[benzofuran-2,1'-cyclopentane]-3',3'-dicarboxylate (3da): 

Reaction time: 6 h, **1d** (55 mg, 0.15 mmol), **2a** (59 mg, 0.15 mmol), yield = 59 %, 64 mg, Nature = viscous liquid. R_f-value: 0.22 (Ethyl acetate/hexane) = 2:8. ^{1}H-NMR (400 MHz, $CDCl_3$) δ 8.23 (d, *J* = 8.3 Hz, 1H), 8.01 (d, *J* = 8.2 Hz, 2H), 7.42-7.34 (m, 3H), 7.20-7.18 (m, 2H), 7.09-7.06 (m, 3H), 6.86-6.80 (m, 2H), 6.48 (s, 2H), 4.95 (s, 1H), 4.32-4.24 (m, 1H), 4.21-4.13 (m, 1H), 3.95-3.87 (m, 1H), 3.83 (t, *J* = 13.9 Hz, 1H), 3.78 (s, 6H), 3.68 (s, 3H), 3.64-3.59 (m, 1H), 3.53-3.45 (m, 1H), 2.62 (dd, *J* = 7.4, 6.0, 1H), 2.49 (s, 3H), 1.21 (t, *J* = 7.2 Hz, 3H), 0.71 (t, *J* = 7.2 Hz, 3H). ^{13}C-NMR (100 MHz, $CDCl_3$) δ 180.3, 171.8, 170.2, 169.9, 152.7, 143.5, 138.9, 137.3, 133.8, 130.3, 129.7, 129.6, 128.0, 127.8, 126.9, 122.1, 118.5, 112.0, 105.4, 101.1, 62.8, 62.2, 61.6, 60.8, 59.7, 56.2, 54.7, 37.9, 21.7, 14.0, 13.3. IR ($\bar{\upsilon}$, cm^{-1}) 2936, 1725, 1581, 1509, 1458, 1300, 1250, 1146, 1126, 1086, 1018, 905, 827, 734, 702. HRMS (ESI) calcd for $C_{40}H_{42}NO_{10}S^+$ $[M+H]^+$; 728.2529 found 728.2523.

Diethyl(2S,2'R,5'R,E)-5'-(furan-2-yl)-2'-phenyl-3-(tosylimino)-3H-spiro[benzofuran-2,1'-cyclopentane]-3',3'-dicarboxylate (3ea): Reaction time: 8 h, **1e** (39 mg, 0.15 mmol), **2a** (57 mg, 0.15 mmol), yield = 66%, 62 mg, Nature = viscous liquid. R_f-value: 0.28 (Ethyl acetate/hexane) = 2:8. ^{1}H-NMR (400 MHz, $CDCl_3$) δ 8.33 (d, *J* = 8.1 Hz, 1H), 8.00 (d, *J* = 8.5 Hz, 2H), 7.44-7.37 (m, 3H), 7.19-7.13 (m, 2H), 7.10-7.04 (m, 4H), 6.93 (d, *J* = 8.3 Hz, 1H), 6.90-6.86 (m, 1H), 6.10-6.07 (m, 2H), 4.84 (s, 1H), 4.30-4.22 (m, 1H), 4.20-4.12 (m, 1H), 3.94-3.86 (m, 1H), 3.81-3.70 (m, 2H), 3.53-3.45 (m, 1H), 2.71-2.61 (m, 1H), 2.48 (s, 3H), 1.20 (t, *J* = 7.0 Hz, 3H), 0.70 (t, *J* = 7.0 Hz, 3H). ^{13}C-NMR (100 MHz, $CDCl_3$) δ 179.7, 171.6, 170.1, 169.5, 149.2, 143.4, 142.0, 138.8, 133.5, 130.6, 130.3, 129.5, 128.0, 127.8, 127.0, 122.0, 118.2, 112.2, 110.0, 107.8, 100.3, 62.9, 62.2, 61.6, 59.7, 48.3, 36.8, 21.7, 14.0, 13.3. IR ($\bar{\upsilon}$, cm^{-1}) 2980, 1721, 1578, 1515, 1463, 1302, 1249, 1222, 1181, 1147, 1088, 905, 876, 827, 747, 705. HRMS (ESI) calcd for $C_{35}H_{34}NO_8S^+$ $[M+H]^+$; 628.2005 found 628.2000.

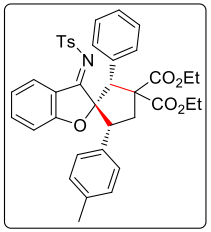


Diethyl(2S,2'S,5'R,E)-5'-(1,3-dioxoisoindolin-2-yl)-2'-phenyl-3-(tosylimino)-3H-spiro[benzofuran-2,1'-cyclopentane]-3',3'-dicarboxylate (**3fa**) : Reaction time: 6 h, **1f** (72 mg, 0.21 mmol), **2a** (80 mg, 0.21 mmol), yield = 55%, 81 mg, Nature = white solid, Melting Point = 98 ºC, R_f-value: 0.28 (Ethyl acetate/hexane) = 2:8. ^{1}H-NMR (400 MHz, $CDCl_3$) δ 8.31 (d, *J* =

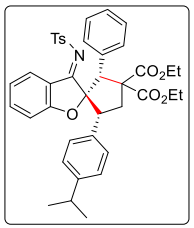


8.2 Hz, 1H), 8.15 (d, *J* = 8.2 Hz, 2H), 7.74-7.72 (m, 2H), 7.63-7.61 (m, 2H), 7.43 (d, *J* = 8.2 Hz, 2H), 7.37-7.33 (m, 1H), 7.25-7.22 (m, 2H), 7.10-7.07 (m, 3H), 7.00 (d, *J* = 8.4 Hz, 1H), 6.85-6.81 (m, 1H), 5.07-5.01 (m, 1H), 4.97-4.89 (m, 2H), 4.27-4.19 (m, 1H), 4.18-4.10 (m, 1H), 3.94-3.86 (m, 1H), 3.56-3.48 (m, 1H), 2.53 (dd, *J* = 6.8, 6.5 Hz, 1H), 2.50 (s, 3H), 1.18 (t, *J* = 6.9 Hz, 3H), 0.72 (t, *J* = 6.8 Hz, 3H). ^{13}C-NMR (100 MHz, $CDCl_3$) δ 177.6, 171.2, 169.7, 168.7, 167.3, 143.4, 138.9, 134.0, 133.2, 131.2, 130.6, 129.5, 128.0, 127.8, 127.3, 123.5, 122.3, 117.7, 112.3, 99.5, 62.3, 61.8, 61.7, 57.7, 33.2, 21.7, 13.9, 13.3. IR ($\bar{\upsilon}$, cm^{-1}) 2926, 1723, 1600, 1462, 1366, 1266, 1155, 1090, 877, 829, 703. HRMS (ESI) calcd for $C_{39}H_{35}N_2O_9S^+$ $[M+H]^+$; 707.2063 Found 707.2072.

Diethyl(2R,2'R,5'R,E)-2'-phenyl-5'-(p-tolyl)-3-(tosylimino)-3H-spiro[benzofuran-2,1'-cyclo pentane]-3',3'-dicarboxylate (3ga) : Reaction time: 10 h, **1g** (59 mg, 0.21 mmol), **2a** (80 mg, 0.21 mmol), yield = 57%, 78 mg, Nature = viscous liquid, R_f-value: 0.29 (Ethyl acetate/hexane) = 2:8. ^{1}H-NMR (400 MHz, $CDCl_3$) δ 8.22 (d, *J* = 8.0 Hz, 1H), 8.03 (d, *J* = 8.0 Hz, 2H), 7.41 (d, *J* = 8.2 Hz, 2H), 7.36-7.32 (m, 1H), 7.20-7.14 (m, 4H), 7.07-7.05 (m, 3H), 6.90 (t, *J* = 8.6 Hz, 3H), 6.80-6.76 (m, 1H), 4.90 (s, 1H), 4.31-6-4.23 (m, 1H), 4.20-4.11 (m, 1H), 3.96-3.89 (m, 1H), 3.85-3.82 (m, 1H), 3.61 (dd, *J* = 7.8, 6.2 Hz, 1H), 3.54-3.46 (m, 1H), 2.58 (dd, *J* = 7.0, 6.1 Hz, 1H), 2.50 (s, 3H), 2.15 (s, 3H), 1.20 (t, *J* = 7.0 Hz, 3H), 0.71 (t, *J* = 7.3 Hz, 3H). ^{13}C-NMR (100 MHz, $CDCl_3$) δ 180.1, 171.9, 170.1, 169.9, 143.4, 138.8, 137.3, 133.9, 131.0, 130.4, 130.3, 129.6, 128.8, 128.4, 127.9, 127.7, 127.0, 121.9, 118.4, 112.1, 101.2, 62.8, 62.1, 61.5, 60.2, 54.2, 38.5, 21.7, 21.0, 14.0, 13.3. IR ($\bar{\upsilon}$, cm^{-1}) 2977, 1718, 1577, 1463, 1303, 1273, 1208, 1183, 1147, 1117, 1088, 1017, 905, 877, 827, 705. HRMS (ESI) calcd for $C_{38}H_{38}NO_7S^+$ $[M+H]^+$; 652.2369 found 652.2322.

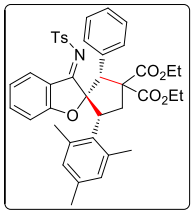


Diethyl(2R,2'S,5'S,E)-5'-(4-isopropylphenyl)-2'-phenyl-3-(tosylimino)-3H-spiro[benzofuran-2,1'-cyclopentane]-3',3'-dicarboxy late (3ha) : Reaction time: 12 h, **1h** (65 mg, 0.21 mmol), **2a** (80 mg, 0.21 mmol), yield = 56%, 80 mg, Nature = viscous liquid, R_f-value: 0.32 (Ethyl acetate/hexane) = 2:8. ^{1}H-NMR (400 MHz, $CDCl_3$) δ 8.21 (d, *J* = 8.2 Hz, 1H), 8.03 (d, *J* = 8.2 Hz, 2H), 7.41 (d, *J* = 8.2 Hz, 2H), 7.32 (t, *J* = 7.7 Hz, 1H), 7.21-7.16 (m, 4H), 7.08-7.03 (m, 3H), 6.95 (d, *J* = 8.2 Hz, 2H), 6.86 (d, *J* = 8.6 Hz, 1H), 6.76 (t, *J* = 8.2 Hz, 1H), 4.92 (s, 1H), 4.30-4.22 (m, 1H), 4.20-4.12 (m, 1H), 3.95-3.87 (m, 1H), 3.84 (d, *J* = 13.9 Hz, 1H), 3.62 (dd, *J* = 7.5, 6.6 Hz, 1H), 3.54-3.46 (m, 1H), 2.71 (septet, *J* =



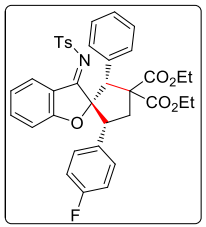
7.5, 6.9, 6.9, 1H), 2.59 (dd, *J* = 7.1, 6.5 Hz, 1H), 2.50 (s, 3H), 1.19 (t, *J* = 7.3 Hz, 3H), 1.08 (d, *J* = 6.9 Hz, 6H), 0.71 (t, *J* = 6.9 Hz, 3H). ^{13}C-NMR (100 MHz, $CDCl_3$) δ 180.2, 171.9, 170.1, 169.9, 148.2, 143.4, 139.0, 138.6, 134.0, 131.3, 130.3, 129.6, 128.5, 127.9, 127.7, 127.0, 126.1, 121.8, 118.4, 112.2, 101.3, 62.9, 62.1, 61.5, 60.0, 54.3, 38.4, 33.6, 23.8, 21.7, 14.0, 13.3. IR ($\bar{\upsilon}$, cm^{-1}) 2979, 1723, 1574, 1463, 1306, 1258, 1203, 1181, 1147, 1088, 1018, 852, 827, 748, 704. HRMS (ESI) calcd for $C_{40}H_{42}NO_7S^+$ $[M+H]^+$; 680.2682 found 680.2656.

Diethyl(2S,2'R,5'R,E)-5'-mesityl-2'-phenyl-3-(tosylimino)-3H-spiro[benzofuran-2,1'-cyclopentane]-3',3'-dicarboxylate (3ia): Reaction Time: 7 h, **1i** (52 mg, 0.17 mmol), **2a** (64 mg, 0.17 mmol), yield = 63%, 72 mg, Nature = viscous liquid, R_f-value: 0.27



(Ethyl acetate/hexane) = 2:8, ^{1}H-NMR (400 MHz, $CDCl_3$) δ 8.22 (d, *J* = 8.2 Hz, 1H), 7.98 (d, *J* = 8.2 Hz, 2H), 7.42-7.37 (m, 3H), 7.19-7.16 (m, 2H), 7.08-7.04 (m, 3H), 6.96 (d, *J* = 8.3 Hz, 1H), 6.84-6.80 (m, 1H), 6.65 (d, *J* = 8.1 Hz, 2H), 4.91 (s, 1H), 4.29-4.12 (m, 4H), 3.99-3.91 (m, 1H), 3.58-3.50 (m, 1H), 2.83 (s, 3H), 2.50 (s, 3H), 2.47 (m, 1H), 2.29 (s, 3H), 2.07 (s, 3H), 1.18 (t, *J* = 7.3 Hz, 3H), 0.74 (t, *J* = 7.3 Hz, 3H). ^{13}C-NMR (100 MHz, $CDCl_3$) δ 180.1, 172.1, 170.4, 169.5, 143.4, 138.8, 138.6, 136.6, 133.7, 131.8, 130.5, 129.8, 129.6, 127.9, 127.7, 127.6, 127.1, 121.9, 117.7, 111.6, 103.5, 63.2, 61.9, 61.5, 60.8, 49.1, 37.5, 23.0, 22.4, 21.7, 20.5, 14.0, 13.3. IR ($\bar{\upsilon}$, cm^{-1}) 2980, 1726, 1600, 1461, 1264, 1183, 1155, 1089, 908, 830, 732, 702. HRMS (ESI) calcd for $C_{40}H_{42}NO_7S^+$ $[M+H]^+$; 680.2682 found 680.2658.

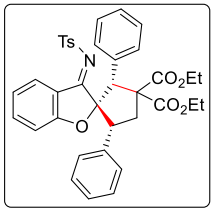
Diethy(2R,2'R,5'R,E)-5'-(4-fluorophenyl)-2'-phenyl-3-(tosylimino)-3H-spiro[benzofuran-2,1'-cyclopentane]-3',3'-dicarboxylate (3ja): Reaction time: 9 h, **1j** (45 mg, 0.16 mmol), **2a** (61 mg, 0.16 mmol), yield = 68%, 71 mg, Nature = viscous liquid, R_f-value: 0.30



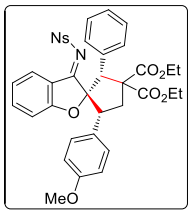
(Ethyl acetate/hexane) = 2:8. ^{1}H-NMR (400 MHz, $CDCl_3$) δ 8.22 (d, *J* = 8.2 Hz, 1H), 8.02 (d, *J* = 8.3 Hz, 2H), 7.41 (d, *J* = 8.1 Hz, 2H), 7.38-7.34 (m, 1H), 7.25-7.21 (m, 2H), 7.19-716 (m, 2H), 7.08-7.04 (m, 3H), 6.88 (d, *J* = 8.7 Hz, 1H), 6.83-6.77 (m, 3H), 4.90 (s, 1H), 4.32-4.24 (m, 1H), 4.20-4.12 (m, 1H), 3.96-3.88 (m, 1H), 3.82 (t, *J* = 13.6 Hz, 1H), 3.62 (dd, *J* = 7.7, 6.2 Hz, 1H), 3.54-3.46 (m, 1H), 2.59 (dd, *J* = 6.9, 6.8 Hz, 1H), 2.50 (s, 3H), 1.20 (t, *J* = 7.2 Hz, 3H), 0.71 (t, *J* = 7.0 Hz, 3H). ^{13}C-NMR (100 MHz, $CDCl_3$) δ 179.8, 171.8, 170.6, 169.8, 162.2 (d, *J* = 246.5 Hz), 143.5, 139.0, 133.7, 130.4, 130.3, 130.1 (d, *J* = 8.3 Hz), 129.8 (d, *J* = 2.8 Hz) 129.6, 127.9 (d, *J* = 22.7 Hz),

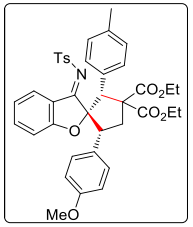
127.0, 122.1, 115.0 (d, J = 21.1 Hz), 112.1, 101.0, 62.8, 62.1, 61.6, 59.9, 53.9, 38.4, 21.7, 14.0, 13.3. IR ($\bar{\upsilon}$, cm^{-1}) 2924, 1727, 1601, 1532, 1462, 1308, 1254, 1158, 1089, 830, 703. HRMS (ESI) calcd for $C_{37}H_{35}FNO_7S^+$ $[M+H]^+$; 656.2118 found 656.2126.

Diethy(2S,2'R,5'R,E)-2',5'-diphenyl-3-(tosylimino)-3H-spiro[benzofuran-2,1'-cyclopentane]-3',3'-dicarboxylate (**3ka**) : Reaction time: 11 h, **1k** (56 mg, 0.21 mmol), **2a** (80 mg, 0.21 mmol), yield = 52%, 70 mg, Nature = viscous liquid, R_f-value: 0.39 (Ethyl acetate/hexane) = 2:8. ^{1}H-NMR (400 MHz, $CDCl_3$) δ 8.21 (d, J = 8.3 Hz, 1H), 8.03 (d, J = 8.4 Hz, 2H), 7.41 (d, J = 8.3 Hz, 2H), 7.35-7.31 (m, 1H), 7.28-7.25 (m, 1H), 7.20-7.18 (m, 2H), 7.13-7.04 (m, 7H), 6.87 (d, J = 8.3 Hz, 1H), 6.80-6.76 (m, 1H), 4.92 (s, 1H), 4.31-4.23 (m, 1H), 4.20-4.13 (m, 1H), 3.96-3.85 (m, 2H), 3.64 (dd, J = 8.2, 6.2 Hz, 1H), 3.54-3.46 (m, 1H), 2.61 (dd, J = 7.1, 6.5 Hz, 1H), 2.50 (s, 3H), 1.20 (t, J = 7.2 Hz, 3H), 0.71 (t, J = 7.4 Hz, 3H). ^{13}C-NMR (100 MHz, $CDCl_3$) δ 180.0, 171.9, 170.0, 169.9, 143.4, 138.8, 134.1, 133.9, 130.4, 130.3, 129.6, 128.6, 128.1, 128.0, 127.7, 127.0, 121.9, 118.3, 112.1, 101.2, 62.9, 62.1, 61.6, 60.0, 54.5, 38.2, 21.7, 14.0, 13.3. IR ($\bar{\upsilon}$, cm^{-1}) 2964, 1726, 1576, 1461, 1314, 1262, 1149, 1086, 1018, 876, 826, 750, 700. HRMS (ESI) calcd for $C_{37}H_{36}NO_7S^+$ $[M+H]^+$; 638.2212 found 638.2206.



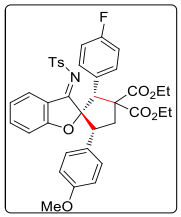
Diethyl(2R,2'R,5'R,E)-5'-(4-methoxyphenyl)-3-(((4-nitrophenyl)sulfonyl)imino)-2'-phenyl-3H-spiro[benzofuran-2,1'-cyclopentane]-3',3'-dicarboxylate (3ab): Reaction time: 10 h, **1a** (44 mg, 0.15 mmol), **2b** (62 mg, 0.15 mmol), yield = 66%, 69 mg, Nature = viscous liquid, R_f-value: 0.26 (Ethyl acetate/hexane) = 2:8. ^{1}H-NMR (400 MHz, $CDCl_3$) δ 8.49 (d, J = 9.1 Hz, 2H), 8.38 (d, J = 9.1 Hz, 2H), 8.15 (d, J = 8.0 Hz, 1H), 7.43-7.39 (m, 1H), 7.19-7.15 (m, 4H), 7.10-706 (m, 3H), 6.91 (d, J = 8.4 Hz, 1H), 6.86-6.83 (m, 1H), 6.65 (d, J = 8.7 Hz, 2H), 4.95 (s, 1H), 4.33-4.25 (m, 1H), 4.20-4.12 (m, 1H), 3.94-3.80 (m, 2H), 3.66 (s, 3H), 3.59 (dd, J = 8.0, 6.4 Hz, 1H), 3.52-3.44 (m, 1H), 2.58 (dd, J = 7.2, 6.3 Hz, 1H), 1.21 (t, J = 7.0 Hz, 3H), 0.70 (t, J = 7.2 Hz, 3H). ^{13}C-NMR (100 MHz, $CDCl_3$) δ 182.3, 171.9, 170.7, 169.6, 159.1, 150.1, 147.5, 139.9, 133.7, 130.2, 129.9, 129.4, 128.3, 128.1, 127.9, 125.7, 124.3, 122.3, 118.2, 113.6, 112.4, 101.5, 62.9, 62.3, 61.6, 60.1, 55.1, 54.2, 38.6, 14.0, 13.3. IR ($\bar{\upsilon}$, cm^{-1}) 2930, 1724, 1574, 1529, 1460, 1305, 1250, 1156, 1088, 1014, 903, 826, 701. HRMS (ESI) calcd for $C_{37}H_{35}N_2O_{10}S^+$ $[M+H]^+$; 699.2012 found 699.2010.

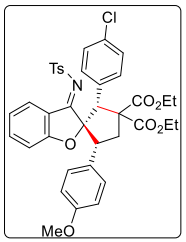




Diethyl(2R,2'R,5'R,E)-5'-(4-methoxyphenyl)-2'-(p-tolyl)-3-(tosylimino)-3H-spiro[benzofuran-2,1'-cyclopentane]-3',3'-dicarboxylate (3ac): Reaction time: 9 h, **1a** (60 mg, 0.20 mmol), **2c** (80 mg, 0.20 mmol), yield = 67%, 91 mg, Nature = viscous liquid. R_f-value: 0.29 (Ethyl acetate/hexane) = 2:8. ^{1}H-NMR (400 MHz, $CDCl_3$) δ 8.22 (d, *J* = 8.2 Hz, 1H), 8.02 (d, *J* = 8.2 Hz, 2H), 7.40 (d, *J* = 8.2 Hz, 2H), 7.34 (t, *J* = 8.0 Hz, 1H), 7.17 (d, *J* = 8.8 Hz, 2H), 7.06 (d, *J* = 8.2 Hz, 2H), 6.89-6.84 (m, 3H), 6.78 (t, *J* = 7.7 Hz, 1H), 6.63 (d, *J* = 8.7 Hz, 2H), 4.86 (s, 1H), 4.30-4.22 (m, 1H), 4.19-4.11 (m, 1H), 3.97-3.89 (m, 1H), 3.81 (t, *J* = 14.0 Hz, 1H), 3.65 (s, 3H), 3.61-3.49 (m, 2H), 2.55 (dd, *J* = 7.0, 6.5 Hz, 1H), 2.49 (s, 3H), 2.15 (s, 3H), 1.19 (t, *J* = 7.1 Hz, 3H), 0.74 (t, *J* = 7.3 Hz, 3H). ^{13}C-NMR (100 MHz, $CDCl_3$) δ 180.3, 171.9, 170.2, 170.0, 158.9, 143.4, 138.9, 137.2, 130.8, 130.3, 130.1, 129.6, 128.6, 127.0, 126.2, 121.8, 118.4, 113.4, 112.1, 101.4, 62.8, 62.0, 61.5, 59.7, 55.1, 54.0, 38.5, 21.7, 21.0, 14.0, 13.3. IR ($\bar{\upsilon}$, cm^{-1}) 2926, 1726, 1601, 1513, 1461, 1251, 1156, 1089, 1033, 826, 734. HRMS (ESI) calcd for $C_{39}H_{40}NO_8S^+$ $[M+H]^+$; 682.2475 found 682.2463.

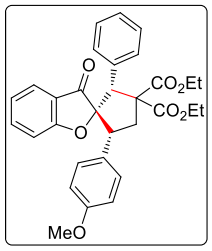
Diethyl(2R,2'R,5'R,E)-2'-(4-fluorophenyl)-5'-(4-methoxyphenyl)-3-(tosylimino)-3H-spiro[b enzofuran-2,1'-cyclopentane]-3',3'-dicarboxylate (3ad): Reaction time: 8 h, **1a** (52 mg, 0.17 mmol), **2d** (70 mg, 0.17 mmol), yield = 68%, 79 mg, Nature = viscous liquid. R_f-value: 0.31 (Ethyl acetate/hexane) = 2:8. ^{1}H-NMR (400 MHz, $CDCl_3$) δ 8.24 (d, *J* = 8.4 Hz, 1H), 8.02 (d, *J* = 8.4 Hz, 2H), 7.41 (d, *J* = 7.9 Hz, 2H), 7.39-7.35 (m, 1H), 7.18-7.14 (m, 4H), 6.88 (d, *J* = 8.3 Hz, 1H), 6.84-6.80 (m, 1H), 6.75 (t, *J* = 7.7 Hz, 2H), 6.64 (d, *J* = 8.9 Hz, 2H), 4.88 (s, 1H), 4.31-4.23 (m, 1H), 4.20-4.12 (m, 1H), 4.00-3.91 (m, 1H), 3.80 (t, *J* = 13.8 Hz, 1H), 3.66 (s, 3H), 3.61-3.51 (m, 2H), 2.57 (dd, *J* = 7.2, 6.5 Hz, 1H), 2.50 (s, 3H), 1.21 (t, *J* = 7.1 Hz, 3H), 0.74 (t, *J* = 7.3 Hz, 3H). ^{13}C-NMR (100 MHz, $CDCl_3$) δ 179.9, 171.8, 170.0, 169.8, 162.3 (d, *J* = 246.5 Hz), 159.0, 143.5, 139.0, 131.9 (d, *J* = 7.4 Hz), 130.4, 129.8 (d, *J* = 2.7 Hz, 129.6 (d, *J* = 6.0 Hz), 127.0, 126.2, 126.0, 122.1, 118.3, 114.9 (d, *J* = 20.8 Hz), 113.5, 112.1, 101.1, 62.7, 62.2, 61.6, 59.2, 55.1, 53.9, 38.4, 21.7, 14.0, 13.4. IR ($\bar{\upsilon}$, cm^{-1}) 2981, 1727, 1601, 1582, 1511, 1462, 1303, 1250, 1225, 1182, 1160, 1089, 1017, 880. HRMS (ESI) calcd for $C_{38}H_{37}NO_8FS^+$ $[M+H]^+$; 686.2224 found 686.2209.



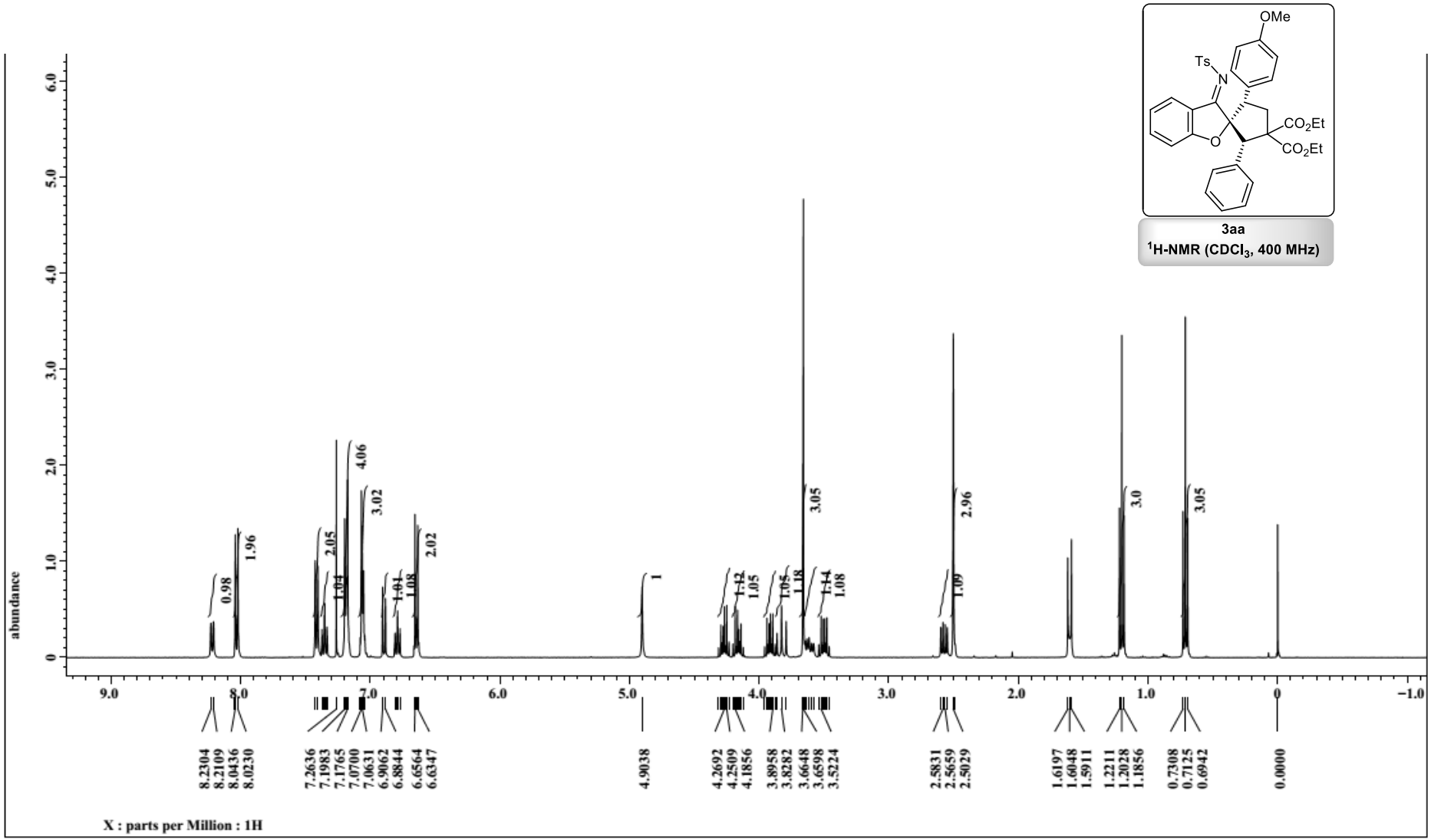


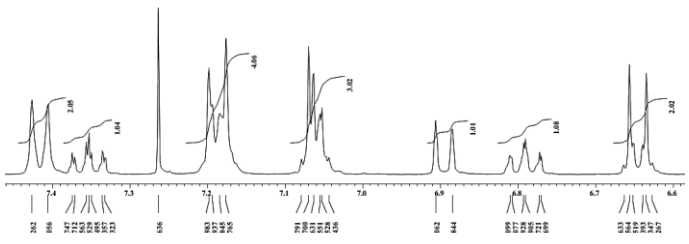
Diethyl(2R,2'R,5'R,E)-2'-(4-chlorophenyl)-5'-(4-methoxyphenyl)-3-(tosylimino)-3H-spiro[b enzofuran-2,1'-cyclopentane]-3',3'-dicarboxylate (3ae): Reaction time: 7 h, **1a** (50 mg, 0.17 mmol), **2e** (71 mg, 0.17 mmol), yield = 69%, 78 mg, Nature = viscous liquid, R_f-value: 0.30 (Ethyl acetate/hexane) = 2:8. ^{1}H-NMR (400 MHz, $CDCl_3$) δ 8.24 (d, *J* = 8.0 Hz, 1H), 8.01 (d, *J* = 8.2 Hz, 2H), 7.42-7.36 (m, 3H), 7.18-7.12 (m, 4H), 7.04 (d, *J* = 8.4 Hz, 2H), 6.89 (d, *J* = 8.5 Hz, 1H), 6.85-6.81 (m, 1H), 6.64 (d, *J* = 8.9 Hz, 2H), 4.86 (s, 1H), 4.31-4.23 (m, 1H), 4.20-4.12(m, 1H), 4.01-3.92 (m, 1H), 3.80 (t, *J* = 13.9, 1H), 3.66 (s, 3H), 3.62-3.52 (m, 2H), 2.57 (dd, *J* = 7.0, 6.7 Hz, 1H), 2.50 (s, 3H), 1.20 (t, *J* = 7.3 Hz, 3H), 0.79 (t, *J* = 7.2 Hz, 3H). ^{13}C-NMR (100 MHz, $CDCl_3$) δ 179.8, 171.7, 170.0, 169.7, 159.0, 143.5, 139.1, 133.7, 132.6, 131.6, 130.4, 129.6, 129.5, 128.1, 127.0, 125.8, 122.1, 118.3, 113.5, 112.1, 101.1, 62.7, 62.2, 61.7, 59.1, 55.1, 54.0, 38.4, 21.7, 14.0, 13.4. IR ($\bar{\upsilon}$, cm^{-1}) 2922, 1739, 1709, 1549, 1491, 1450, 1289, 1239, 1196, 1166, 1133, 969, 900, 805, 726. HRMS (ESI) calcd for $C_{38}H_{37}ClNNaO_8S^+$ $[M+Na]^+$; 724.1648 found 724.1681.

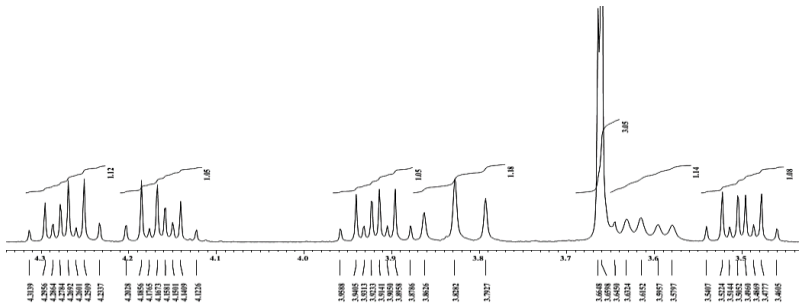
5.4.4 Procedure for the synthesis of (1'R,2'S,5'S)-diethyl 5'-(4-methoxyphenyl)-3-oxo-2'-phenyl-3H-spiro[benzofuran-2,1'-cyclopentane]-3',3'-dicarboxylate (4ab): 3ab (80 mg) was dissolved in toluene (2 mL) and basic alumina (Brockmann activity I, 1.5 g) was added. The reaction mixture was refluxed for overnight. The reaction mixture was purified by silica gel column chromatography.

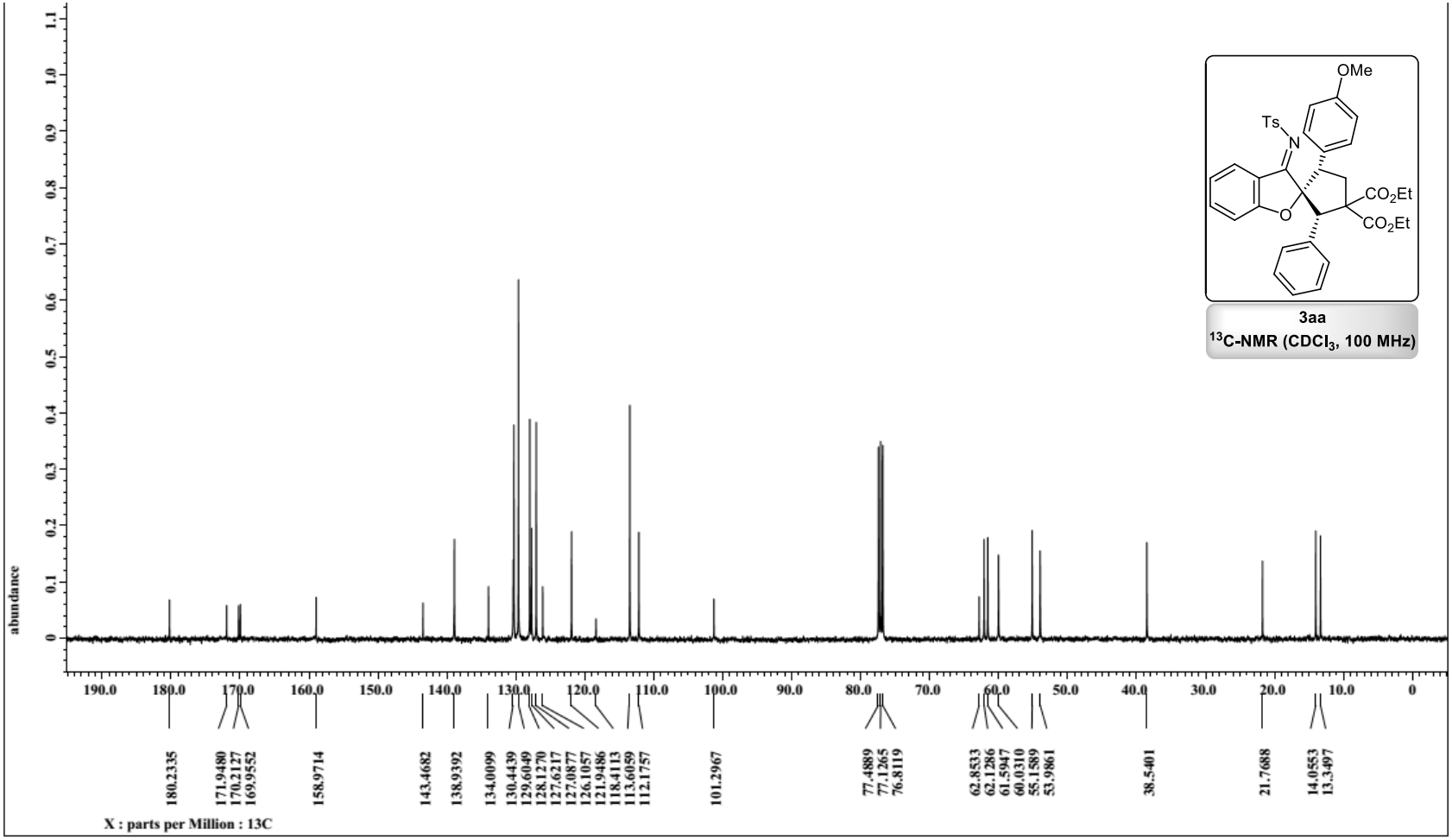


Reaction time: 14 h, **4ab** (80 mg, 0.11 mmol), yield = 80%, 47 mg, Nature = white solid , Melting point = 115 ^{o}C, R_f-value: 0.30 (Ethyl acetate/hexane) = 2:8. ^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.35-7.30 (m, 3H), 7.27-7.21 (m, 3H), 7.08-7.04 (m, 3H), 6.94 (d, *J* = 8.2 Hz, 1H), 6.73 (t, *J* = 7.6 Hz, 1H), 6.64 (d, *J* = 8.7 Hz, 2H), 4.92 (s, 1H), 4.34-4.19 (m, 2H), 3.95-3.87 (m, 1H), 3.80 (t, *J* = 14.4, 1H), 3.69-3.62 (m, 1H), 3.66 (s, 3H), 3.53-3.45 (m, 1H), 2.62 (dd, *J* = 7.0, 6.3 Hz, 1H), 1.25 (t, *J* = 7.2 Hz, 3H), 0.71 (t, *J* = 6.9 Hz, 3H). ^{13}C-NMR (100 MHz, $CDCl_3$) δ 200.5, 172.0, 171.3, 170.0, 158.8, 138.0, 134.3, 130.4, 129.7, 127.8, 127.5, 126.6, 123.8, 121.6, 121.4, 113.4, 112.8, 99.0, 63.2, 62.1, 61.5, 57.6, 55.1, 51.3, 38.9, 14.1, 13.3. IR ($\bar{\upsilon}$, cm^{-1}) 2923, 1724, 1611, 1514, 1461, 1245, 1218, 1178, 1098, 1030, 919, 870, 755, 702. HRMS (ESI) calcd for $C_{31}H_{31}O_7^+$ $[M+H]^+$; 515.2070 found 515.2065.


OMe
Ts
N
O
CO2Et
CO2Et
3aa
1H-NMR (CDCl3, 400 MHz)
abundance
X : parts per Million : 1H






OMe
Ts
N
O
CO2Et
CO2Et
3aa
13C-NMR (CDCl3, 100 MHz)
abundance
X : parts per Million : 13C
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171.9480
170.2127
169.9552
158.9714
143.4682
138.9392
134.0099
130.4439
129.6049
128.1270
127.6217
127.0877
126.1057
121.9486
118.4113
113.6059
112.1757
101.2967
77.4889
77.1265
76.8119
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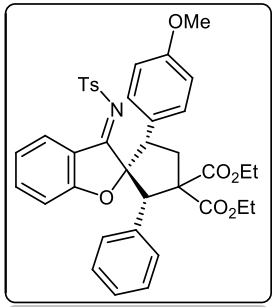
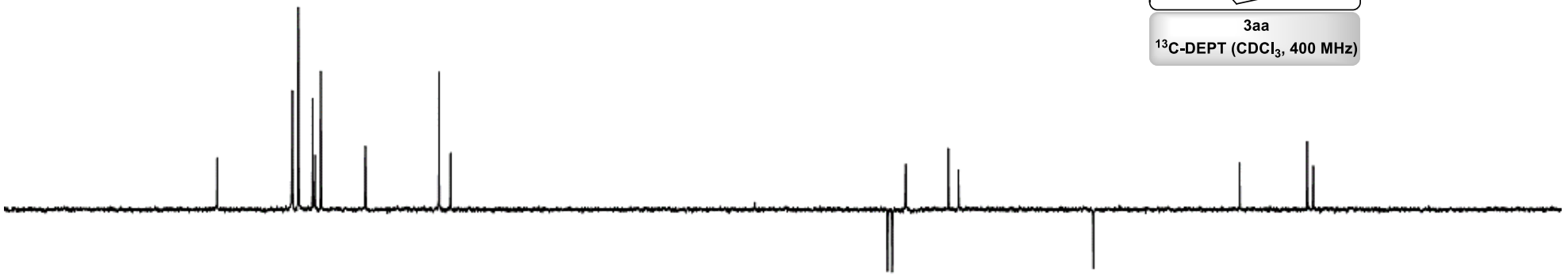
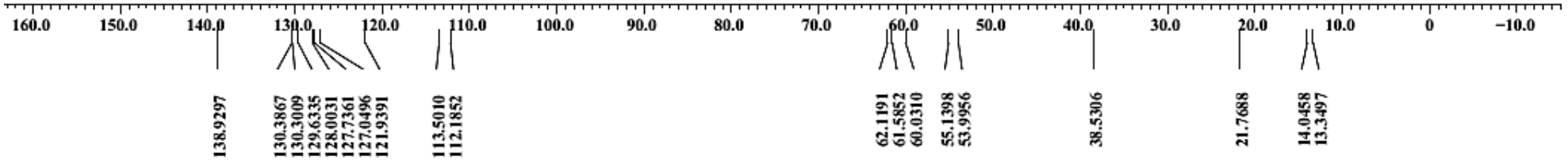
53.9861
38.5401
21.7688
14.0553
13.3497



3aa

^{13}C-DEPT ($CDCl_3$, 400 MHz)





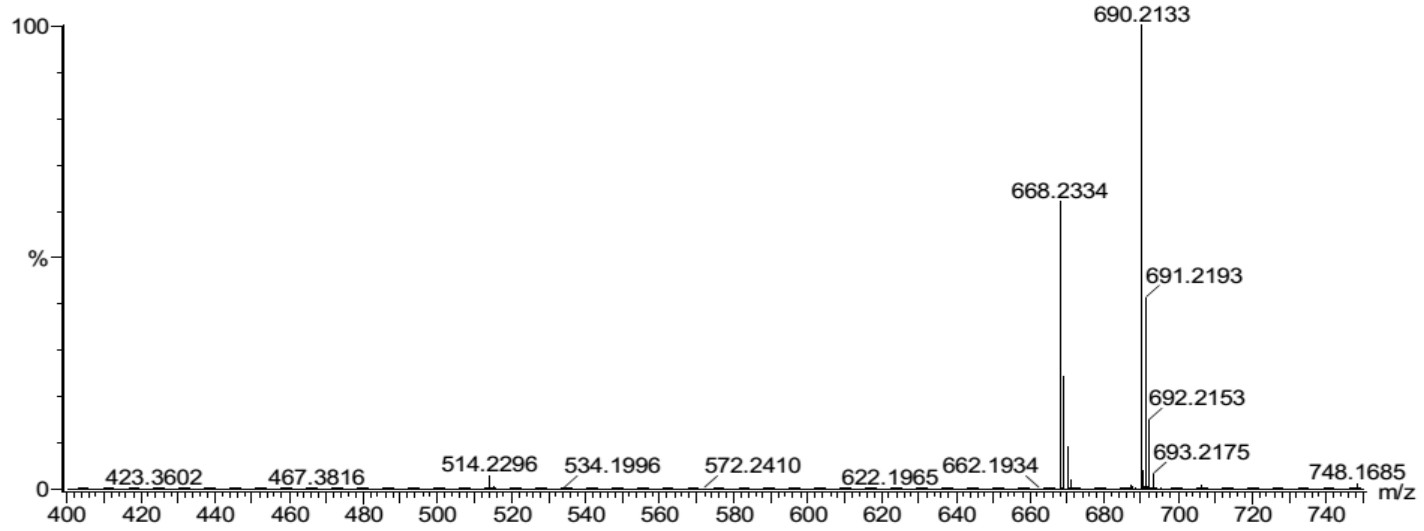
138.9297
130.3867
130.3009
129.6335
128.0031
127.7361
127.0496
121.9391
113.5010
112.1852
62.1191
61.5852
60.0310
55.1398
53.9956
38.5306
21.7688
14.0458
13.3497

HRMS Spectra of **3aa:**

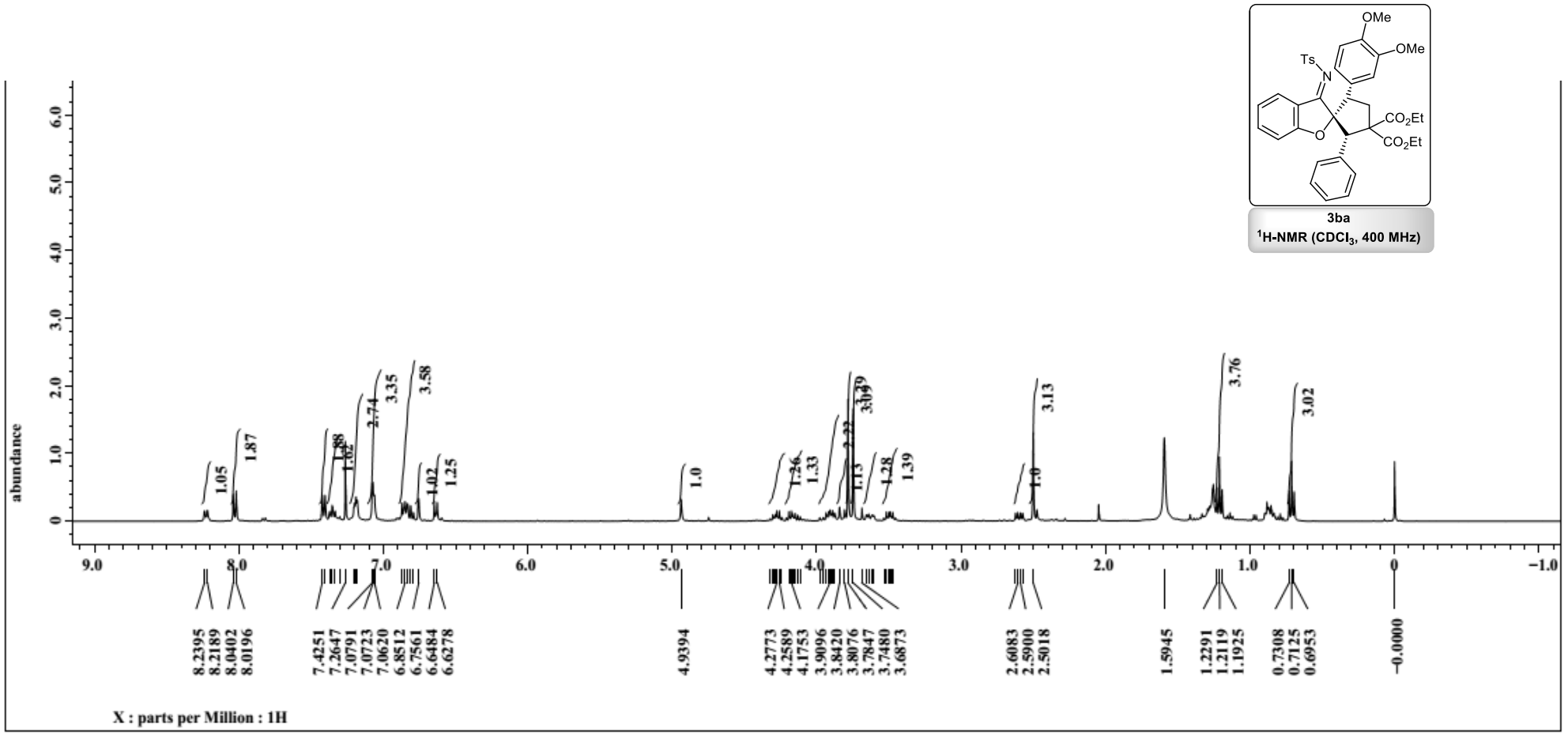
Single Mass Analysis
Tolerance = 100.0 PPM / DBE: min = -1.5, max = 50.0
Element prediction: Off
Number of isotope peaks used for i-FIT = 3

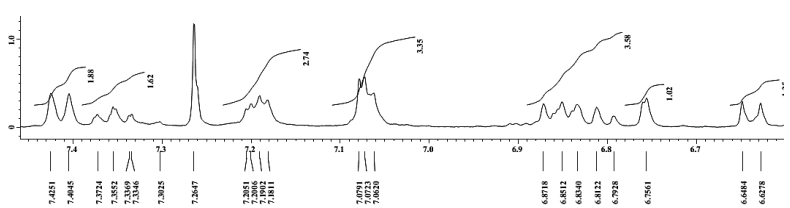
Monoisotopic Mass, Even Electron Ions
24 formula(e) evaluated with 1 results within limits (up to 50 closest results for each mass)
Elements Used:
C: 30-40 H: 31-40 N: 0-2 O: 0-8 S: 0-1

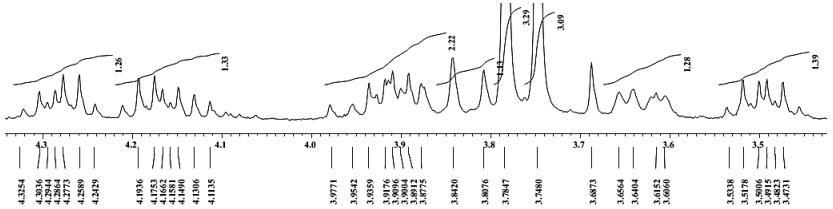
Sample Name : 07-04-030 INDIAN INSTITUTE OF TECHNOLOGY XEVO G2-XS QTOF
Test Name : HRMS-1 ROPAR
260218-07-04-030 11 (0.122) AM (Top,4, Ar,10000.0,0.00,0.00); Sm (Mn, 1x3.00); Cm (9:14) 1: TOF MS ES+
9.24e+007

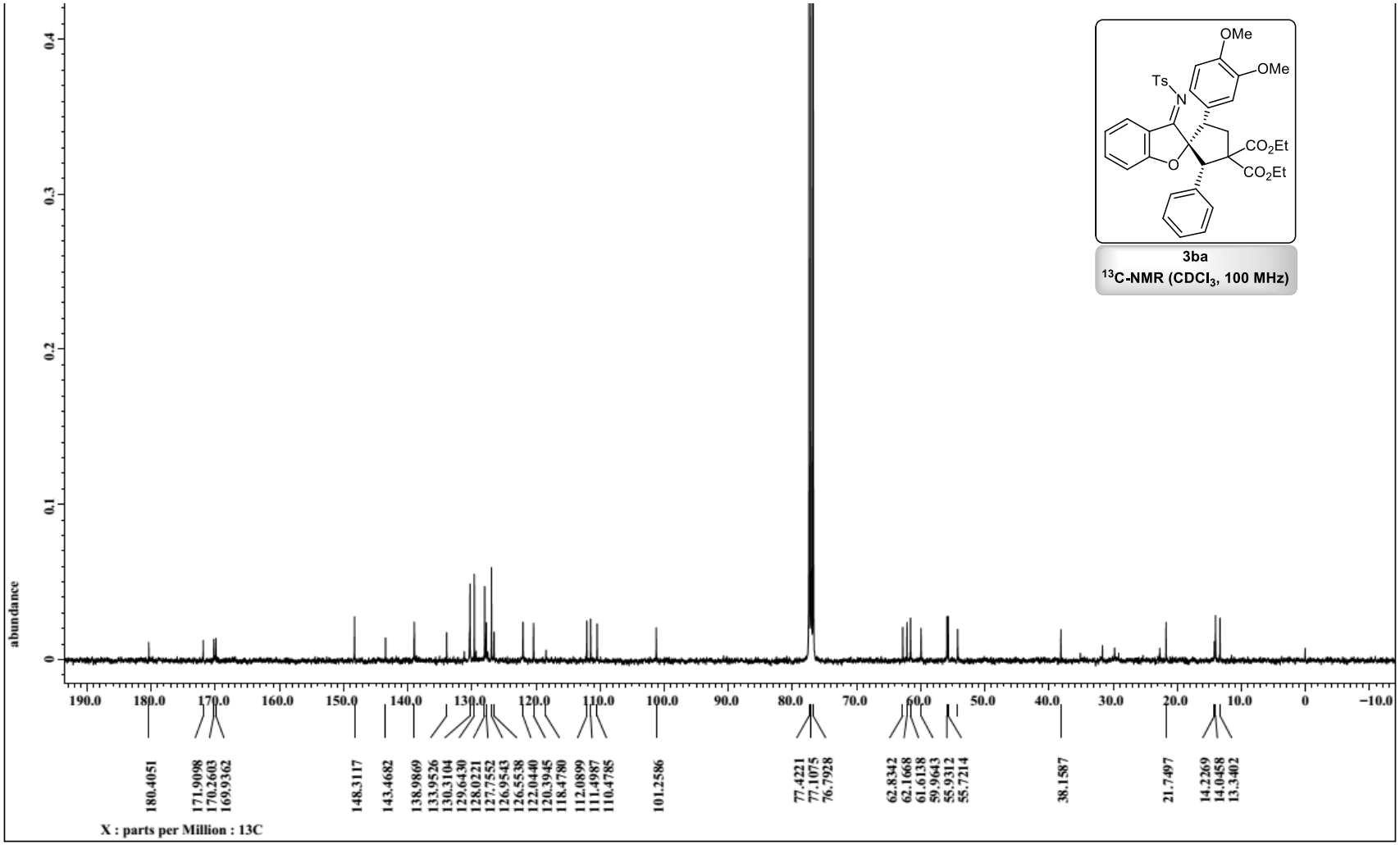


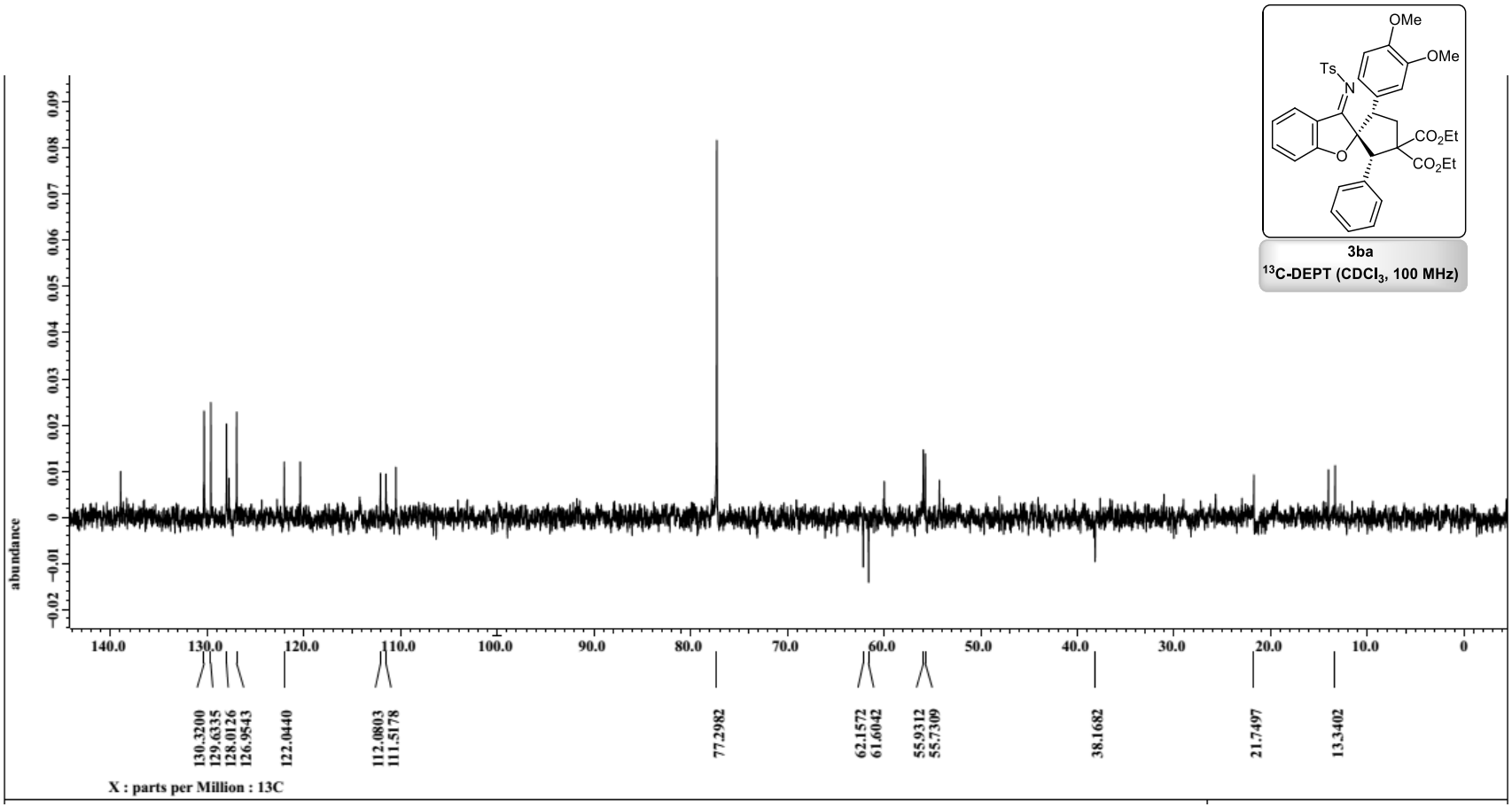
Minimum:				-1.5				
Maximum:		5.0	100.0	50.0				
Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	Norm	Conf(%)	Formula
668.2334	668.2318	1.6	2.4	20.5	405.1	n/a	n/a	C38 H38 N O8 S


OMe
OMe
Ts
N
O
CO2Et
CO2Et
3ba
1H-NMR (CDCl3, 400 MHz)
abundance
X : parts per Million : 1H






OMe
OMe
Ts
N
O
CO2Et
CO2Et
3ba
13C-NMR (CDCl3, 100 MHz)
abundance
0
0.1
0.2
0.3
0.4
190.0
180.0
170.0
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0
−10.0
180.4051
171.9098
170.2603
169.9362
148.3117
143.4682
138.9869
133.9526
130.3104
129.6430
128.0221
127.7552
126.9543
126.5538
122.0440
120.3945
118.4780
112.0899
111.4987
110.4785
101.2586
77.4221
77.1075
76.7928
62.8342
62.1668
61.6138
59.9643
55.9312
55.7214
38.1587
21.7497
14.2269
14.0458
13.3402
X : parts per Million : 13C


OMe
OMe
Ts
N
O
CO2Et
CO2Et
3ba
13C-DEPT (CDCl3, 100 MHz)
abundance
0.09
0.08
0.07
0.06
0.05
0.04
0.03
0.02
0.01
0
−0.01
−0.02
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0
130.3200
129.6335
128.0126
126.9543
122.0440
112.0803
111.5178
77.2982
62.1572
61.6042
55.9312
55.7309
38.1682
21.7497
13.3402
X : parts per Million : 13C

HRMS Spectra of **3ba:**

Single Mass Analysis

Tolerance = 100.0 PPM / DBE: min = -1.5, max = 50.0

Element prediction: Off

Number of isotope peaks used for i-FIT = 3

Monoisotopic Mass, Even Electron Ions

32 formula(e) evaluated with 1 results within limits (up to 50 closest results for each mass)

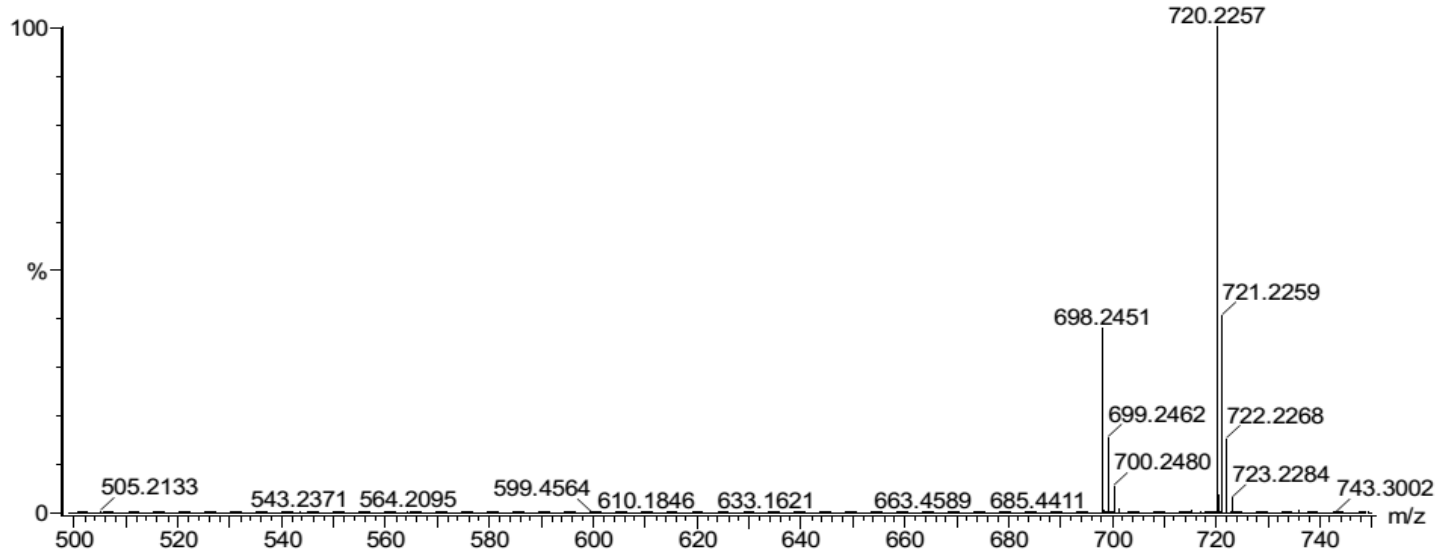
Elements Used:

C: 30-40 H: 31-40 N: 0-2 O: 0-9 S: 0-1

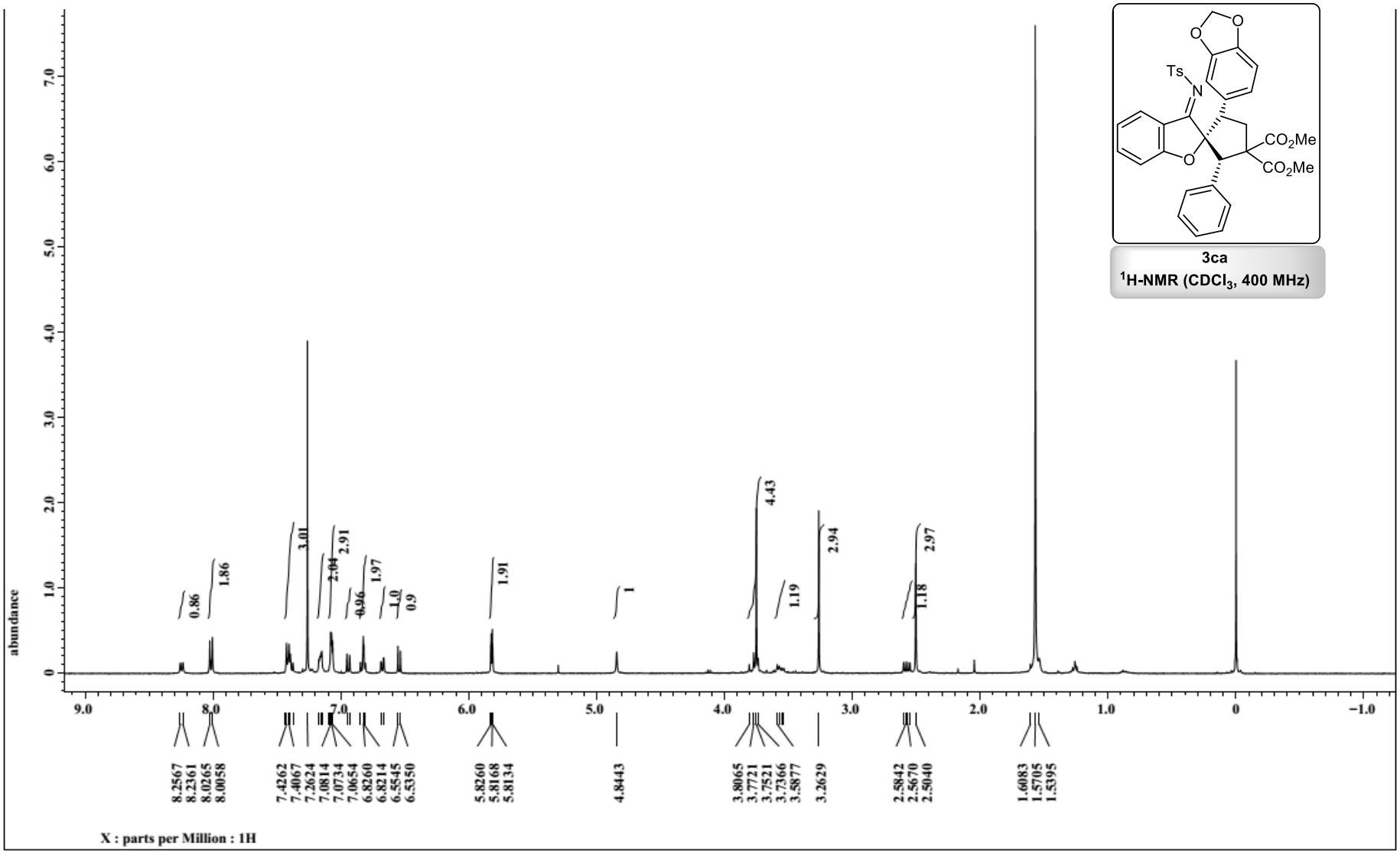
Sample Name : 07-02-320 INDIAN INSTITUTE OF TECHNOLOGY XEVO G2-XS QTOF

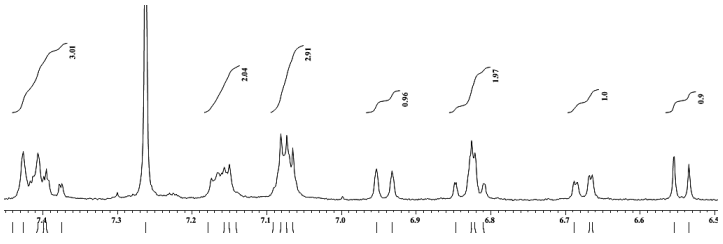
Test Name : HRMS-1 ROPAR

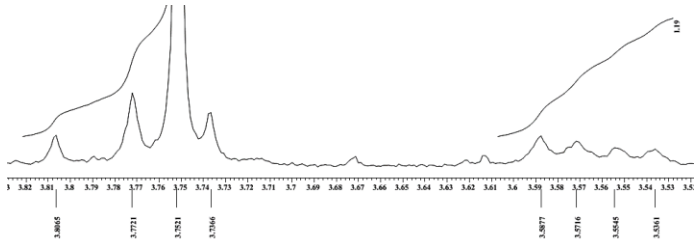
260218-07-02-320 11 (0.122) AM (Top,4, Ar,10000.0,0.00,0.00); Sm (Mn, 1x3.00); Cm (11:13) 1: TOF MS ES+ 2.83e+007

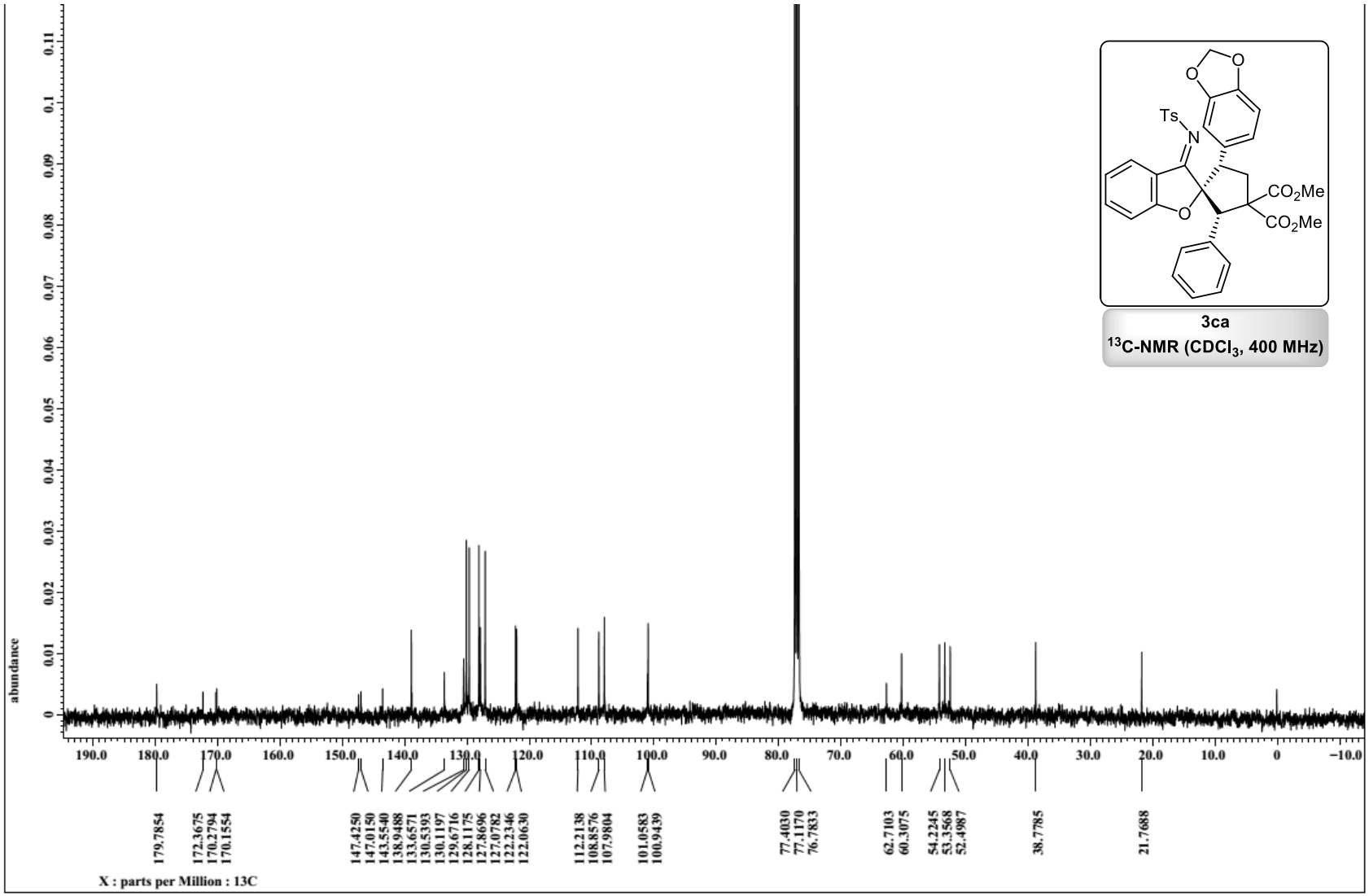


Minimum:				-1.5				
Maximum:		5.0	100.0	50.0				
Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	Norm	Conf(%)	Formula
698.2451	698.2424	2.7	3.9	20.5	345.4	n/a	n/a	C39 H40 N O9 S


Ts
N
O
O
O
O
CO2Me
CO2Me
3ca
1H-NMR (CDCl3, 400 MHz)
abundance
X : parts per Million : 1H

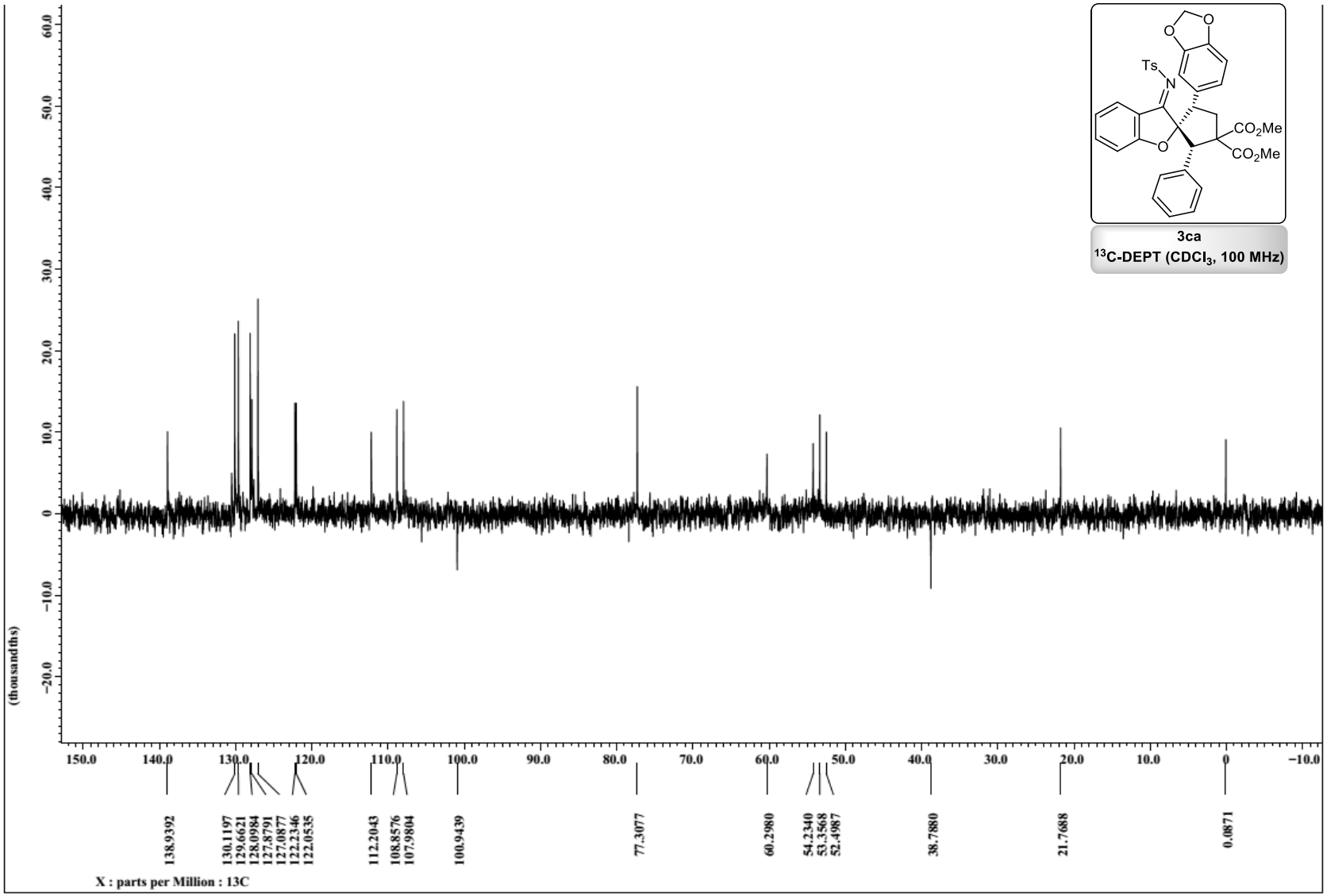






3ca

^{13}C-NMR ($CDCl_3$, 400 MHz)

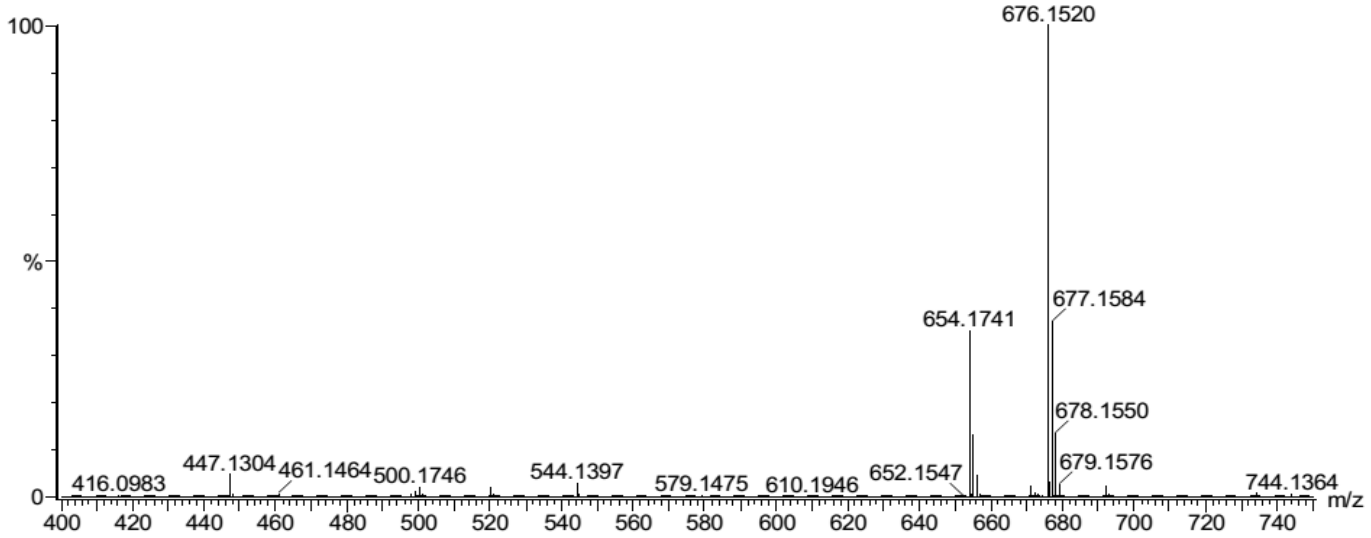

Ts
N
O
O
O
CO2Me
CO2Me
3ca
13C-DEPT (CDCl3, 100 MHz)
(thousandths)
60.0
50.0
40.0
30.0
20.0
10.0
0
−10.0
−20.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0
−10.0
138.9392
130.1197
129.6621
128.0984
127.8791
127.0877
122.2346
122.0535
112.2043
108.8576
107.9804
100.9439
77.3077
60.2980
54.2340
53.3568
52.4987
38.7880
21.7688
0.0871
X : parts per Million : 13C

HRMS Spectra of **3ca:**

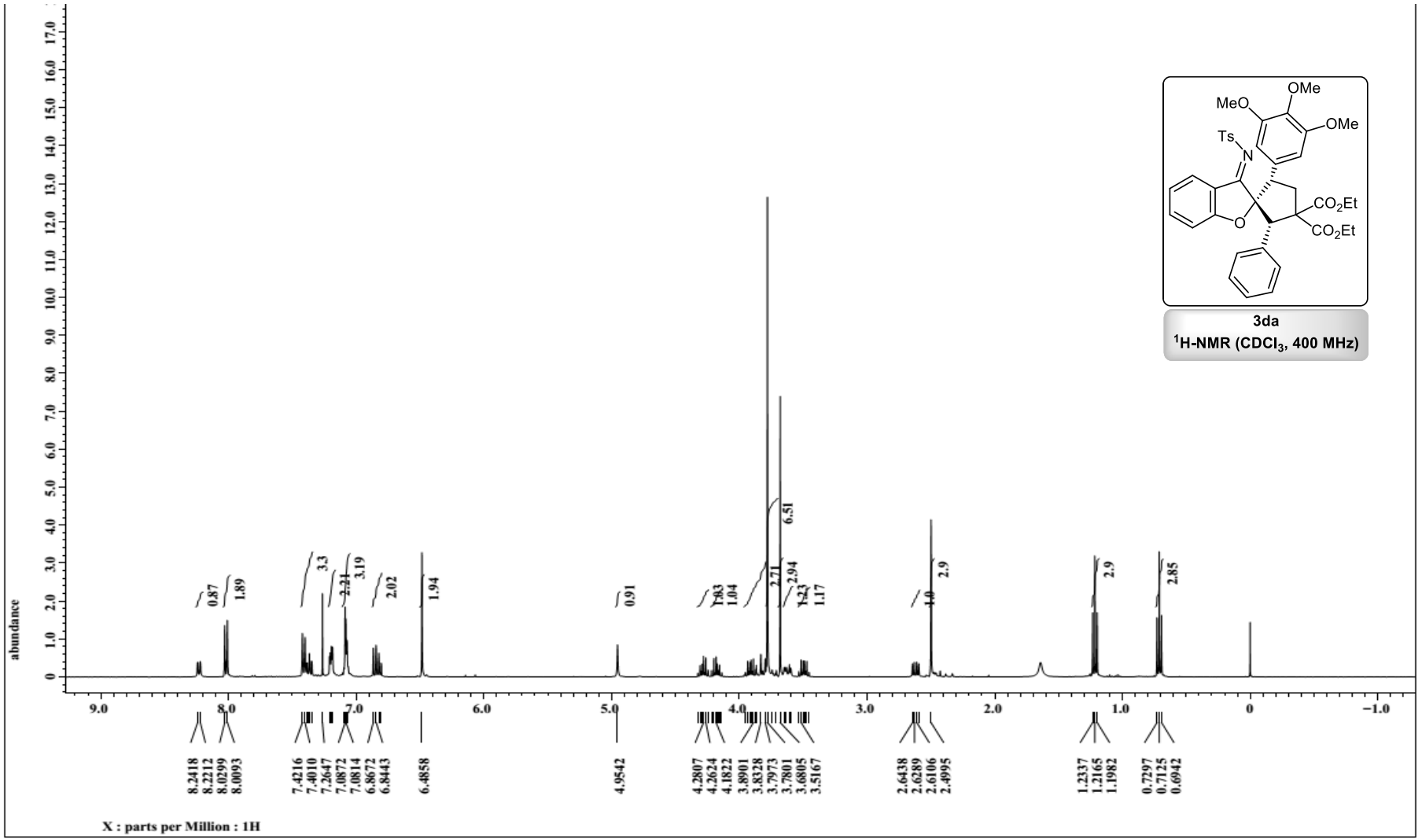
Single Mass Analysis
Tolerance = 10.0 PPM / DBE: min = -1.5, max = 50.0
Element prediction: Off
Number of isotope peaks used for i-FIT = 3

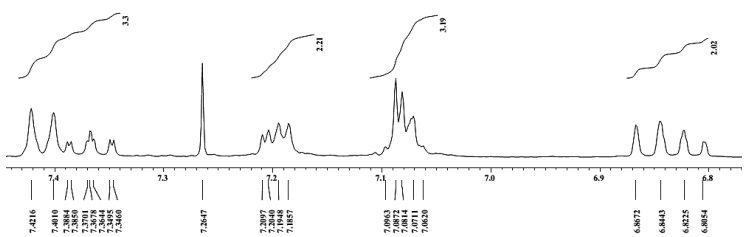
Monoisotopic Mass, Even Electron Ions
33 formula(e) evaluated with 1 results within limits (up to 50 closest results for each mass)
Elements Used:
C: 35-40 H: 31-42 N: 0-2 O: 0-10 S: 0-1

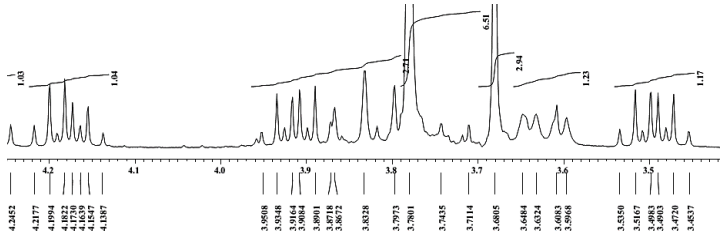
Sample Name : 07-04-029 INDIAN INSTITUTE OF TECHNOLOGY XEVO G2-XS QTOF
Test Name : HRMS-1 ROPAR
260218-07-04-029 11 (0.122) AM (Top,4, Ar,10000.0,0.00,0.00); Sm (Mn, 1x3.00); Cm (4:23) 1: TOF MS ES+
8.29e+007

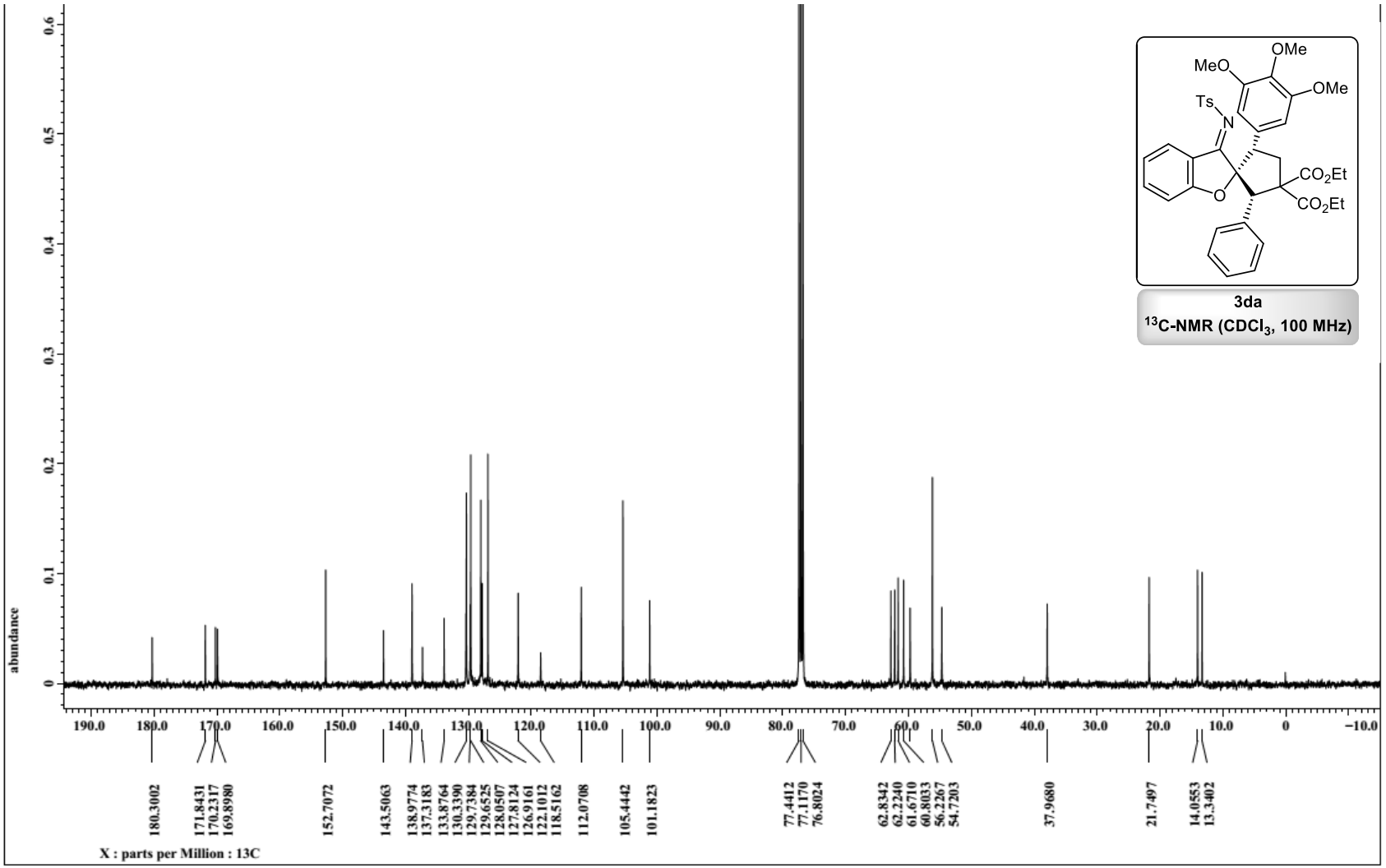


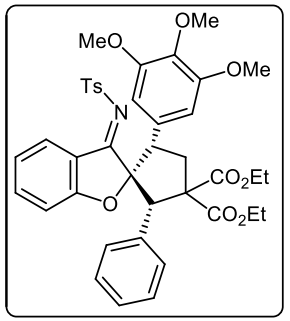
Minimum:				-1.5				
Maximum:		5.0	10.0	50.0				
Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	Norm	Conf(%)	Formula
654.1741	654.1798	-5.7	-8.7	21.5	456.0	n/a	n/a	C36 H32 N O9 S


abundance
X : parts per Million : 1H
3da
1H-NMR (CDCl3, 400 MHz)
OMe
MeO
OMe
Ts
N
O
CO2Et
CO2Et



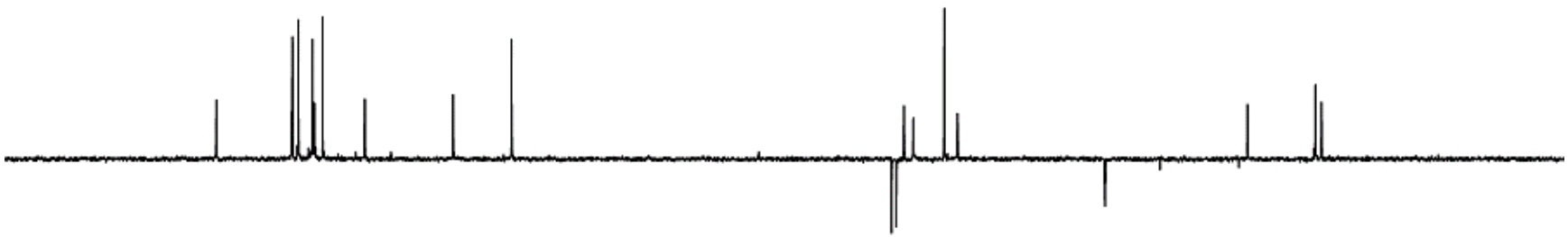


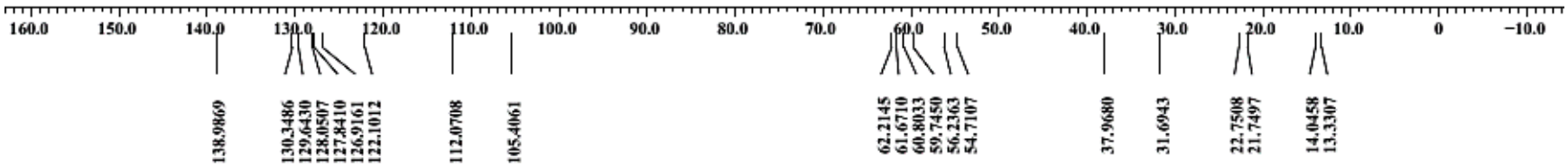

abundance
0
0.1
0.2
0.3
0.4
0.5
0.6
190.0
180.0
170.0
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0
−10.0
180.3002
171.8431
170.2317
169.8980
152.7072
143.5063
138.9774
137.3183
133.8764
130.3390
129.7384
129.6525
128.0507
127.8124
126.9161
122.1012
118.5162
112.0708
105.4442
101.1823
77.4412
77.1170
76.8024
62.8342
62.2240
61.6710
60.8033
56.2267
54.7203
37.9680
21.7497
14.0553
13.3402
X : parts per Million : 13C
OMe
MeO
OMe
Ts
N
O
CO2Et
CO2Et
3da
13C-NMR (CDCl3, 100 MHz)



3da

^{13}C-DEPT ($CDCl_3$, 100 MHz)





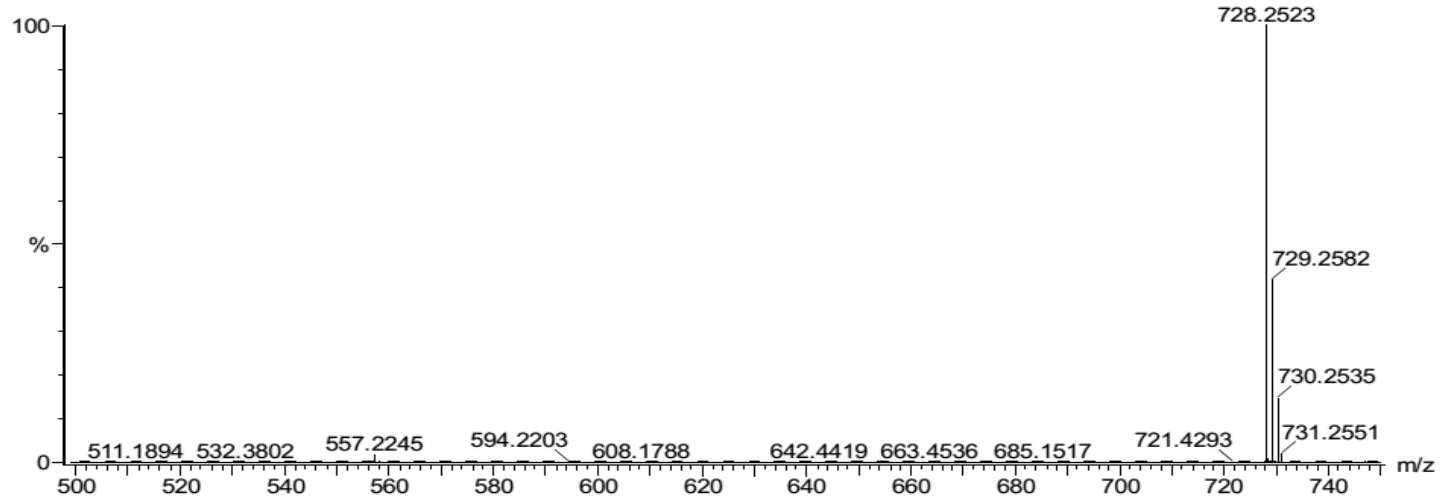
138.9869
130.3486
129.6430
128.0507
127.8410
126.9161
122.1012
112.0708
105.4061
62.2145
61.6710
60.8033
59.7450
56.2363
54.7107
37.9680
31.6943
22.7508
21.7497
14.0458
13.3307

HRMS Spectra of **3da**:

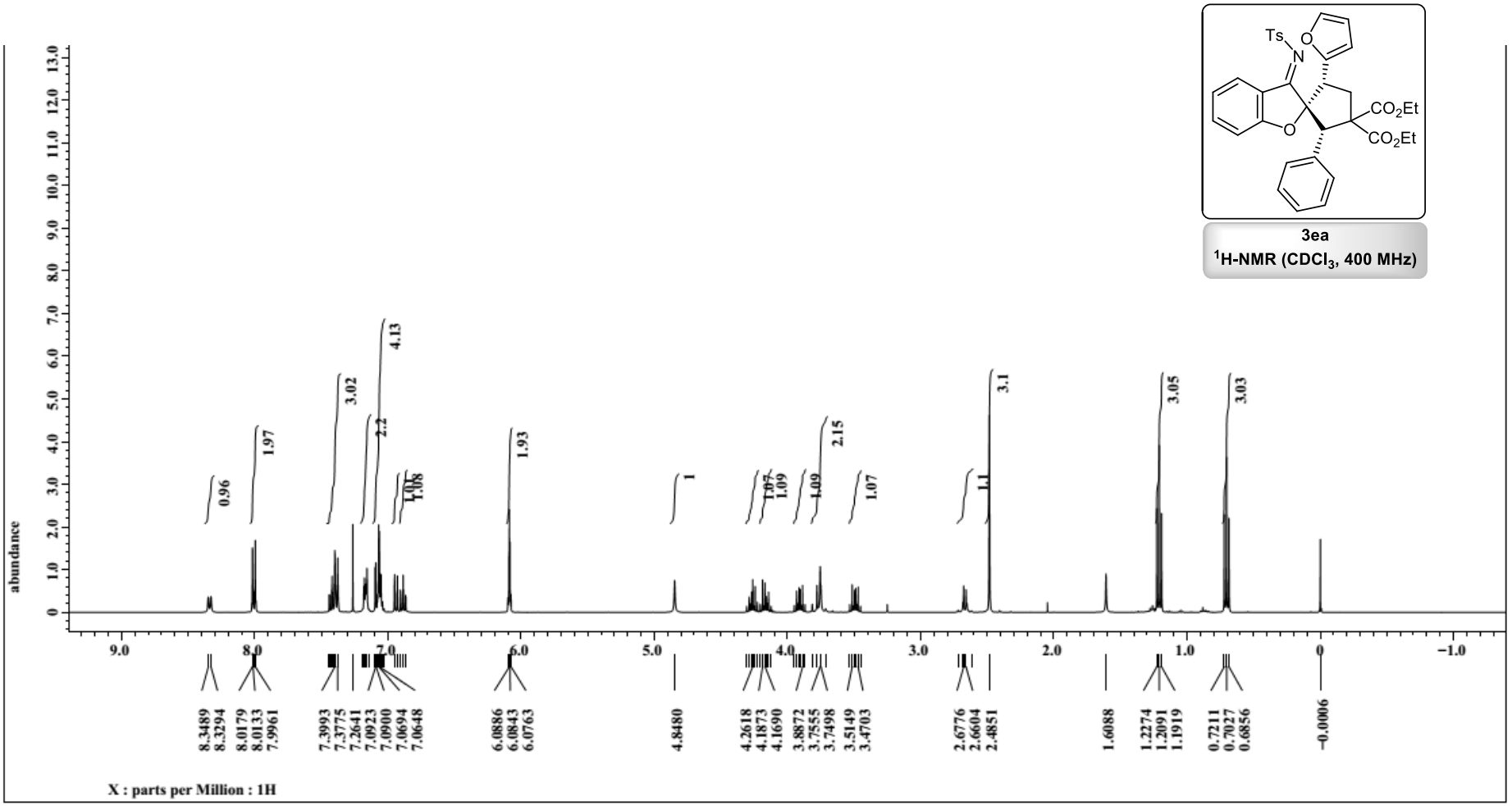
Single Mass Analysis
Tolerance = 100.0 PPM / DBE: min = -1.5, max = 50.0
Element prediction: Off
Number of isotope peaks used for i-FIT = 3

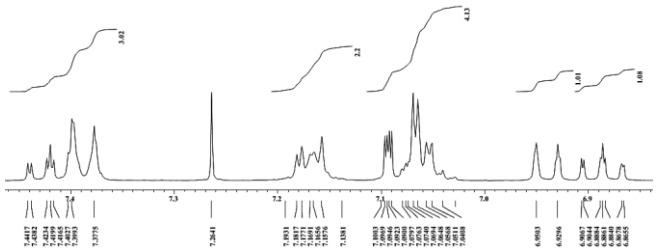
Monoisotopic Mass, Even Electron Ions
44 formula(e) evaluated with 1 results within limits (up to 50 closest results for each mass)
Elements Used:
C: 35-40 H: 31-42 N: 0-2 O: 0-10 S: 0-1

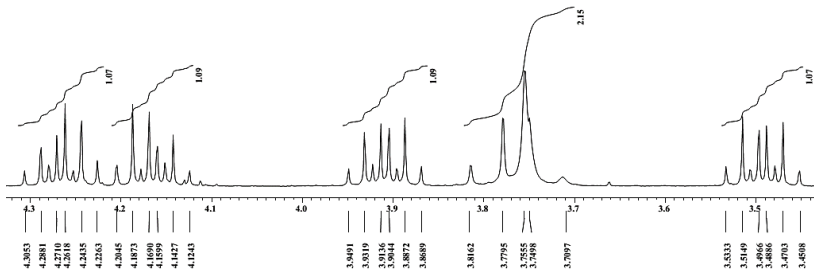
Sample Name : 15-01-026 INDIAN INSTITUTE OF TECHNOLOGY XEVO G2-XS QTOF
Test Name : HRMS-1 ROPAR
260218-15-01-026 13 (0.140) AM (Top,4, Ar,10000.0,0.00,0.00); Sm (Mn, 1x3.00); Cm (13:18) 1: TOF MS ES+
1.28e+007

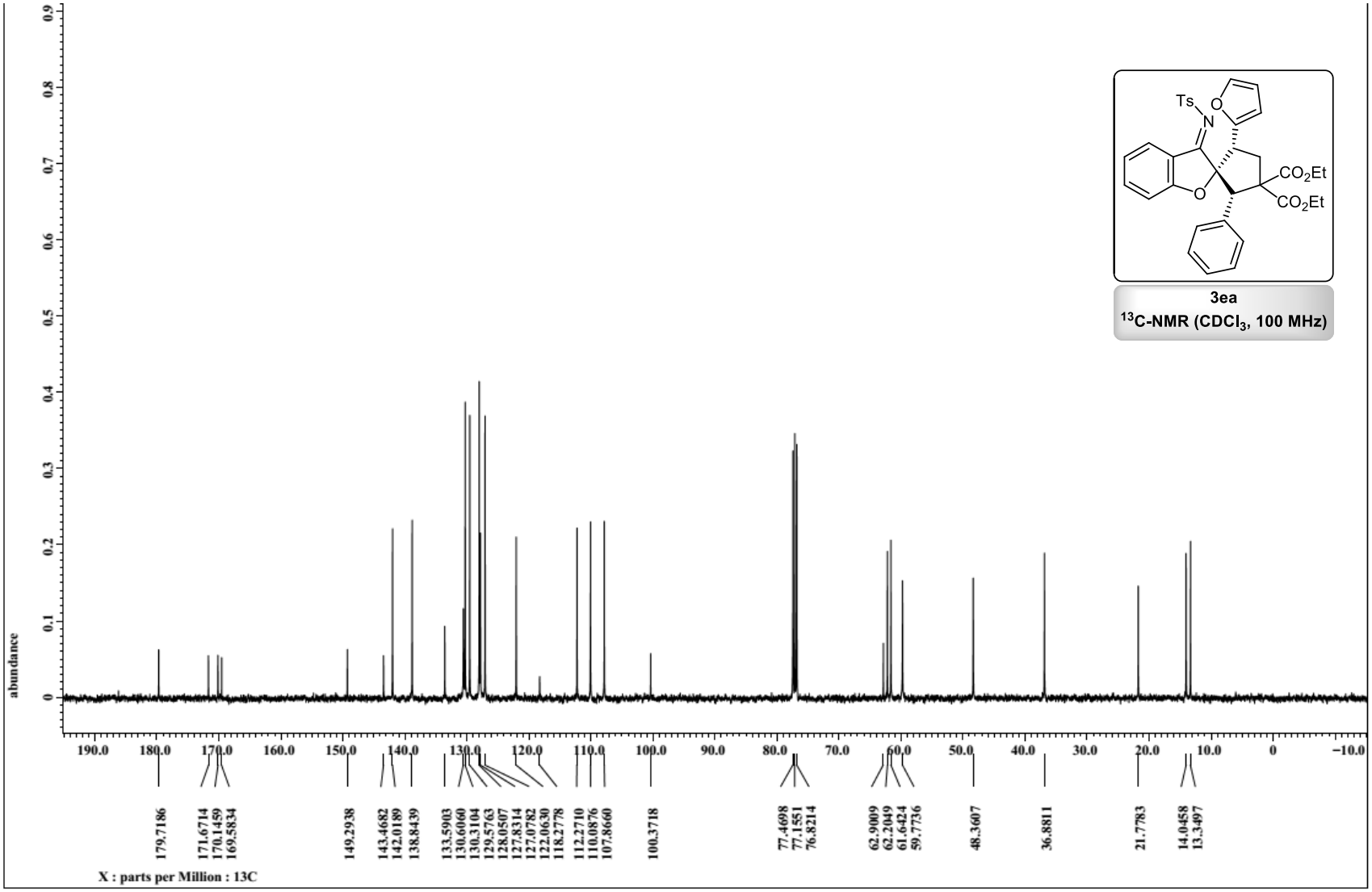


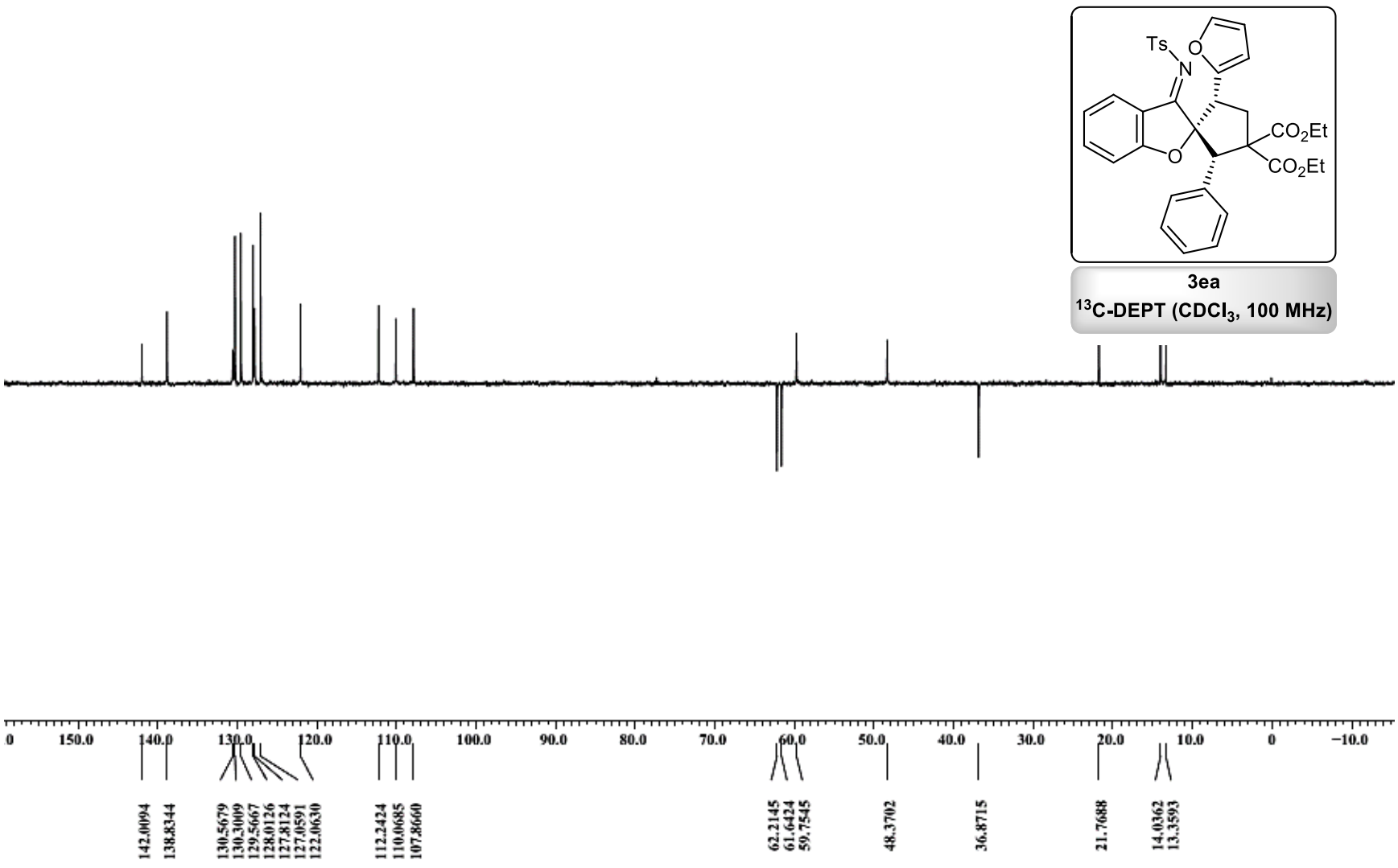
Minimum:				-1.5				
Maximum:		5.0	100.0	50.0				
Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	Norm	Conf(%)	Formula
728.2523	728.2529	-0.6	-0.8	20.5	348.2	n/a	n/a	C40 H42 N O10 S


Ts
N
O
O
CO2Et
CO2Et
3ea
1H-NMR (CDCl3, 400 MHz)
abundance
X : parts per Million : 1H






Ts
N
O
O
CO2Et
CO2Et
3ea
13C-NMR (CDCl3, 100 MHz)
abundance
0
0.1
0.2
0.3
0.4
0.5
0.6
0.7
0.8
0.9
190.0
180.0
170.0
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0
-10.0
179.7186
171.6714
170.1459
169.5834
149.2938
143.4682
142.0189
138.8439
133.5903
130.6060
130.3104
129.5763
128.0507
127.8314
127.0782
122.0630
118.2778
112.2710
110.0876
107.8660
100.3718
77.4698
77.1551
76.8214
62.9009
62.2049
61.6424
59.7736
48.3607
36.8811
21.7783
14.0458
13.3497
X : parts per Million : 13C

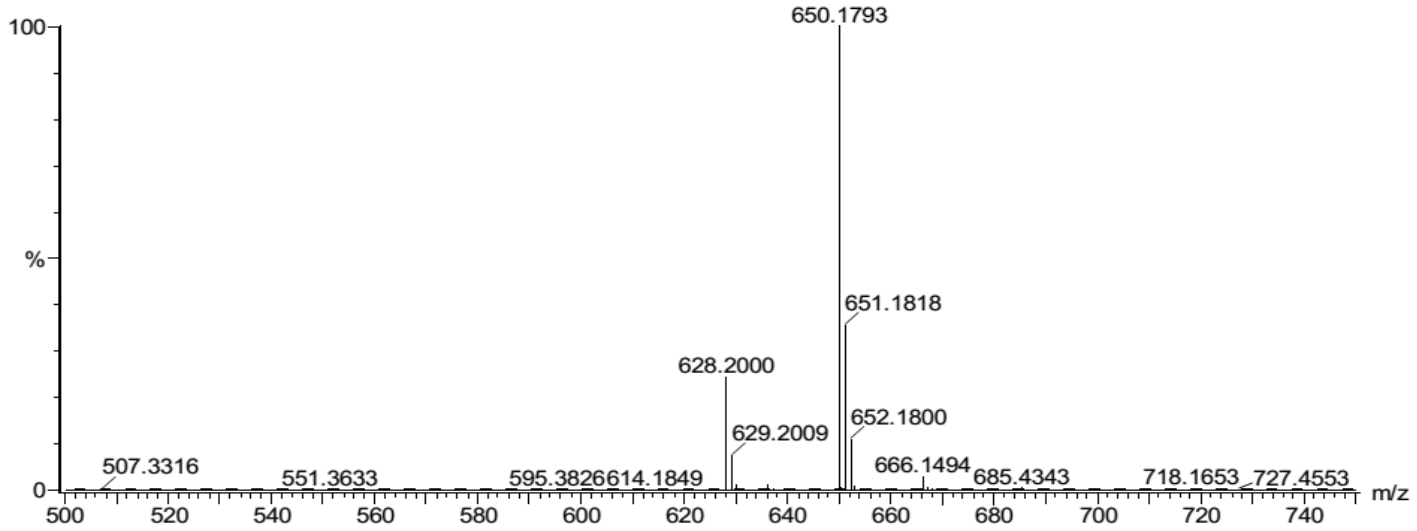

Ts
N
O
O
CO_2Et
CO_2Et
3ea
^{13}C-DEPT ($CDCl_3$, 100 MHz)
0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0
−10.0
142.0094
138.8344
130.5679
130.3009
129.5667
128.0126
127.8124
127.0591
122.0630
112.2424
110.0685
107.8660
62.2145
61.6424
59.7545
48.3702
36.8715
21.7688
14.0362
13.3593

HRMS Spectra of **3ea**:

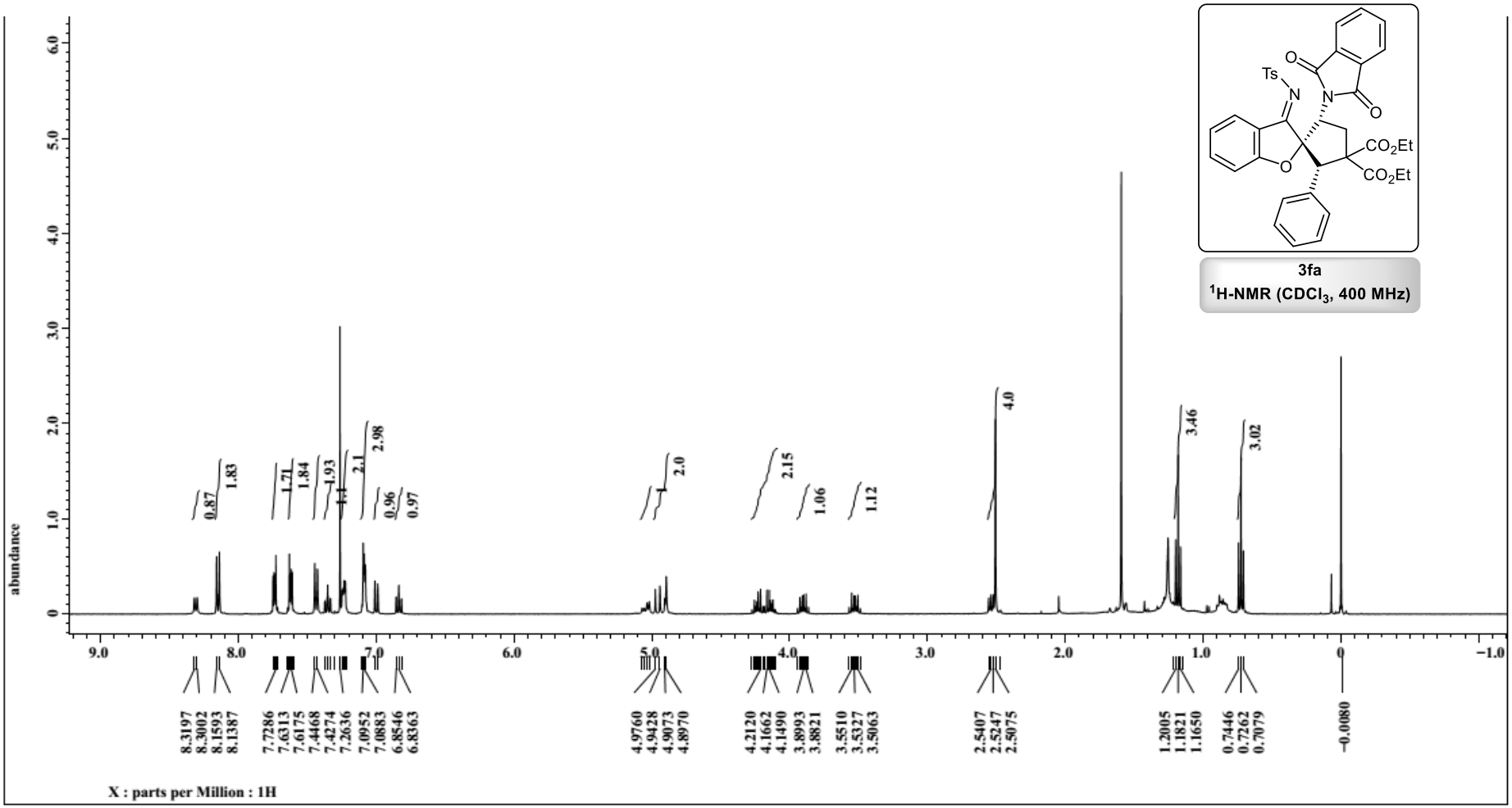
Single Mass Analysis
Tolerance = 10.0 PPM / DBE: min = -1.5, max = 50.0
Element prediction: Off
Number of isotope peaks used for i-FIT = 3

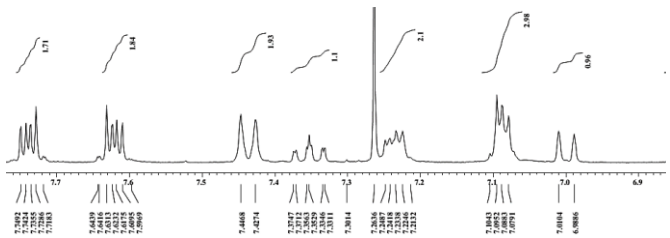
Monoisotopic Mass, Even Electron Ions
34 formula(e) evaluated with 1 results within limits (up to 50 closest results for each mass)
Elements Used:
C: 35-40 H: 31-42 N: 0-2 O: 0-10 S: 0-1

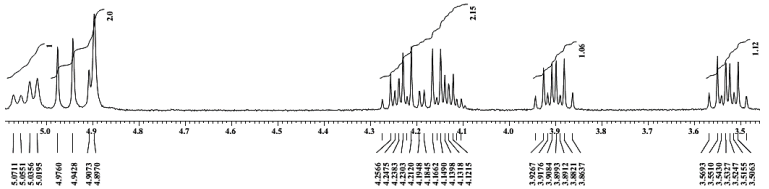
Sample Name : 07-04-033 INDIAN INSTITUTE OF TECHNOLOGY XEVO G2-XS QTOF
Test Name : HRMS-1 ROPAR
260218-07-04-033 11 (0.122) AM (Top,4, Ar,10000.0,0.00,0.00); Sm (Mn, 1x3.00); Cm (6:19) 1: TOF MS ES+
1.71e+007

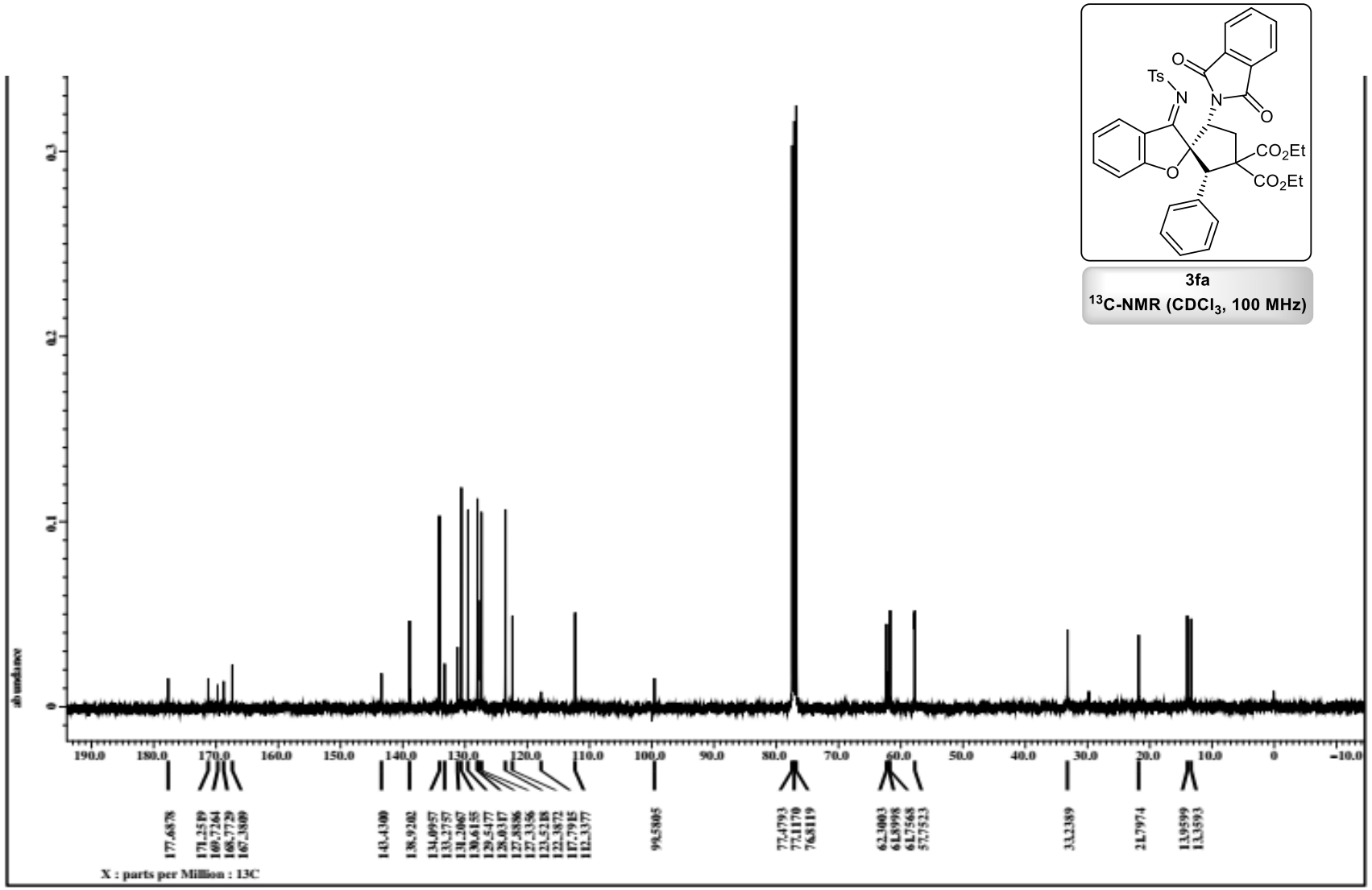


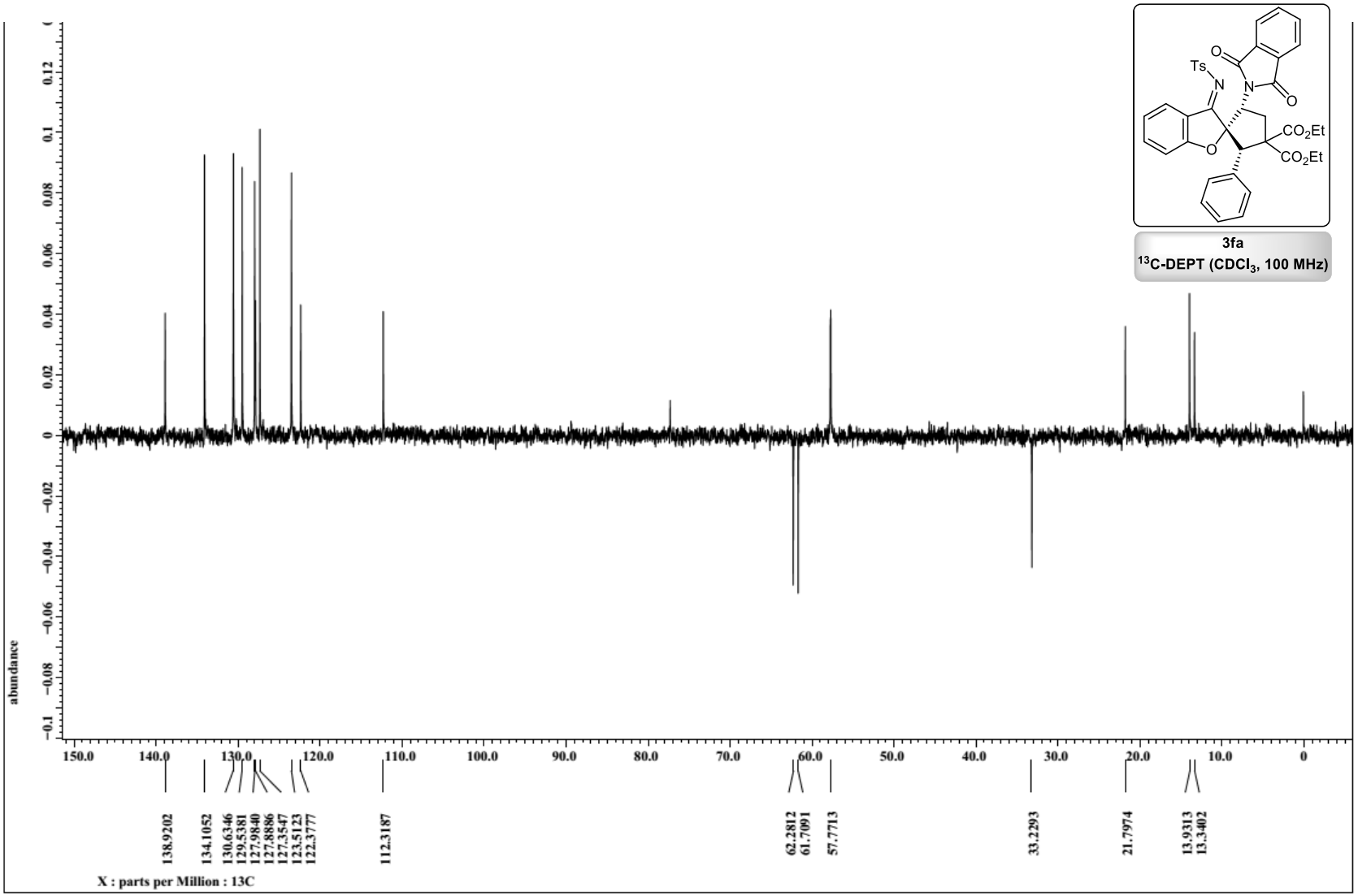
Minimum:				-1.5				
Maximum:		5.0	10.0	50.0				
Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	Norm	Conf(%)	Formula
628.2000	628.2005	-0.5	-0.8	19.5	439.6	n/a	n/a	C35 H34 N O8 S


Ts
N
O
N
O
O
O
CO2Et
CO2Et
3fa
1H-NMR (CDCl3, 400 MHz)
abundance
X : parts per Million : 1H






Ts
N
O
N
O
O
O
CO2Et
CO2Et
3fa
13C-NMR (CDCl3, 100 MHz)
abundance
0.3
0.2
0.1
0
190.0
180.0
170.0
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0
-10.0
177.6878
171.2519
169.7264
168.7729
167.3809
143.4300
138.9202
134.0957
133.2757
131.2067
130.6155
129.5477
128.0317
127.8886
127.3356
123.5218
122.3872
117.7915
112.3377
99.5805
77.4793
77.1170
76.8119
62.3003
61.8998
61.7568
57.7523
33.2389
21.7974
13.9599
13.3593
X : parts per Million : 13C

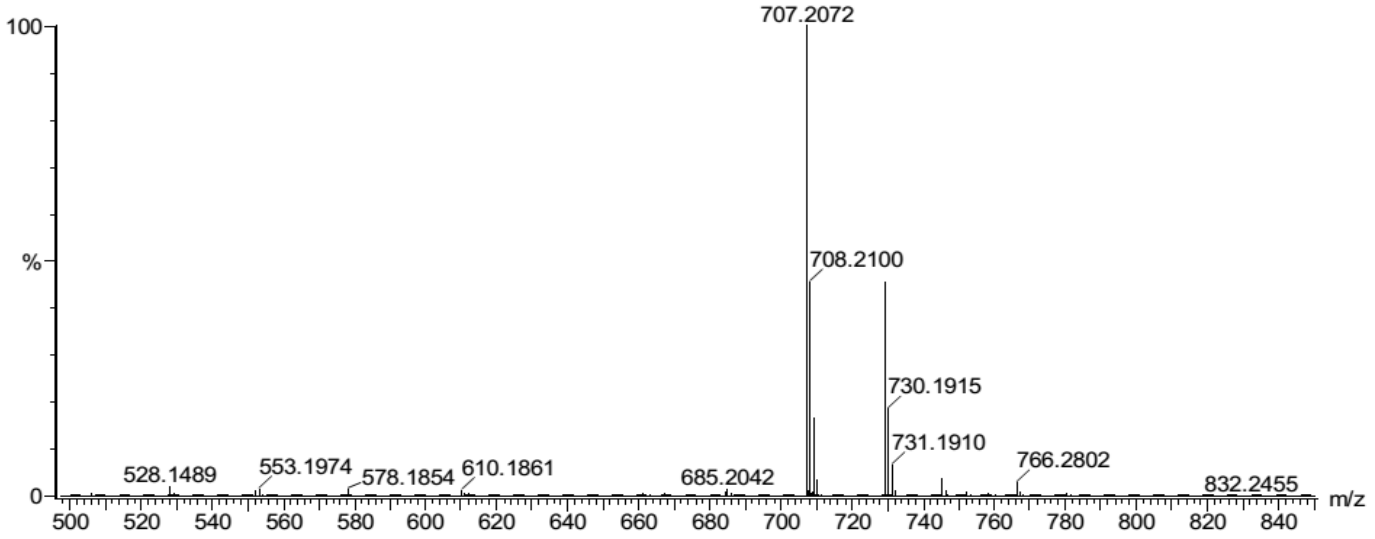

Ts
N
O
N
O
O
CO2Et
CO2Et
O
3fa
13C-DEPT (CDCl3, 100 MHz)
abundance
0.12
0.1
0.08
0.06
0.04
0.02
0
−0.02
−0.04
−0.06
−0.08
−0.1
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0
138.9202
134.1052
130.6346
129.5381
127.9840
127.8886
127.3547
123.5123
122.3777
112.3187
62.2812
61.7091
57.7713
33.2293
21.7974
13.9313
13.3402
X : parts per Million : 13C

HRMS Spectra of **3fa**:

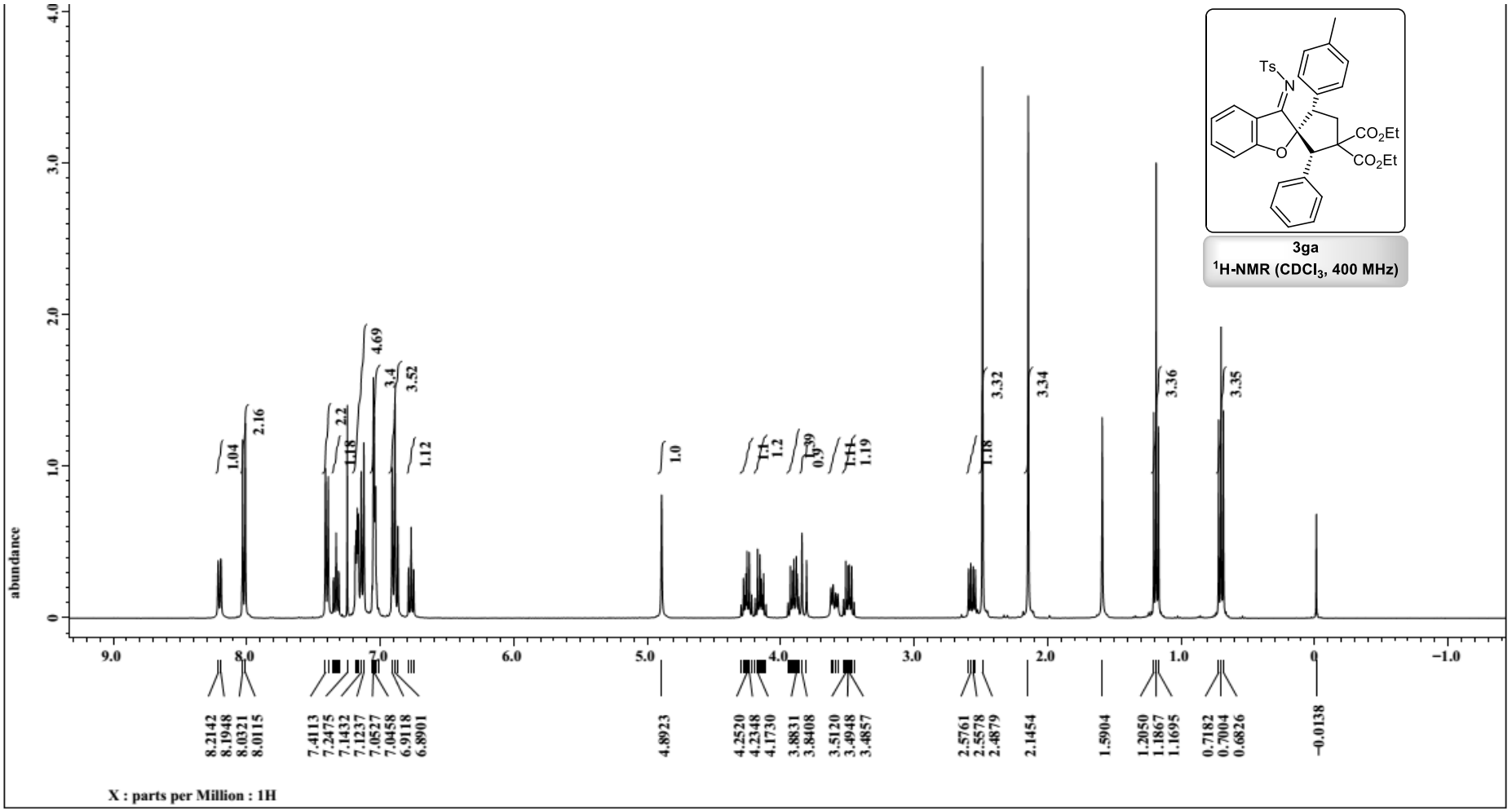
Single Mass Analysis
Tolerance = 50.0 PPM / DBE: min = -1.5, max = 50.0
Element prediction: Off
Number of isotope peaks used for i-FIT = 3

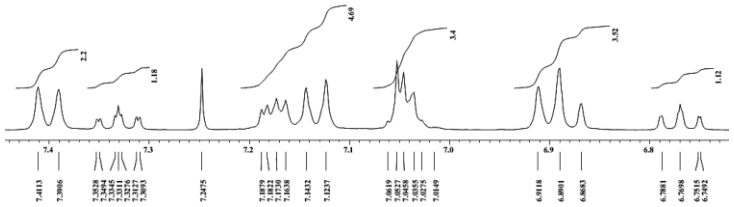
Monoisotopic Mass, Even Electron Ions
33 formula(e) evaluated with 1 results within limits (up to 50 best isotopic matches for each mass)
Elements Used:
C: 8-40 H: 30-35 N: 0-2 O: 0-9 S: 0-1

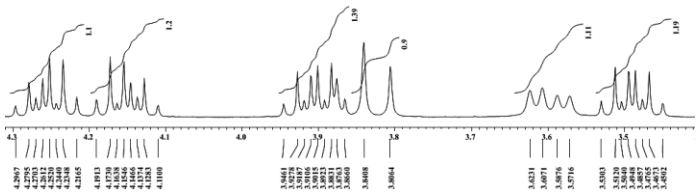
Sample Name : 07-04-120 I.I.T.ROPAR XEVO G2-XS QTOF
Test Name : HRMS-1
030119-07-04-120 14 (0.148) AM2 (Ar,19000.0,0.00,0.00); Cm (14:19) 1: TOF MS ES+
5.70e+007

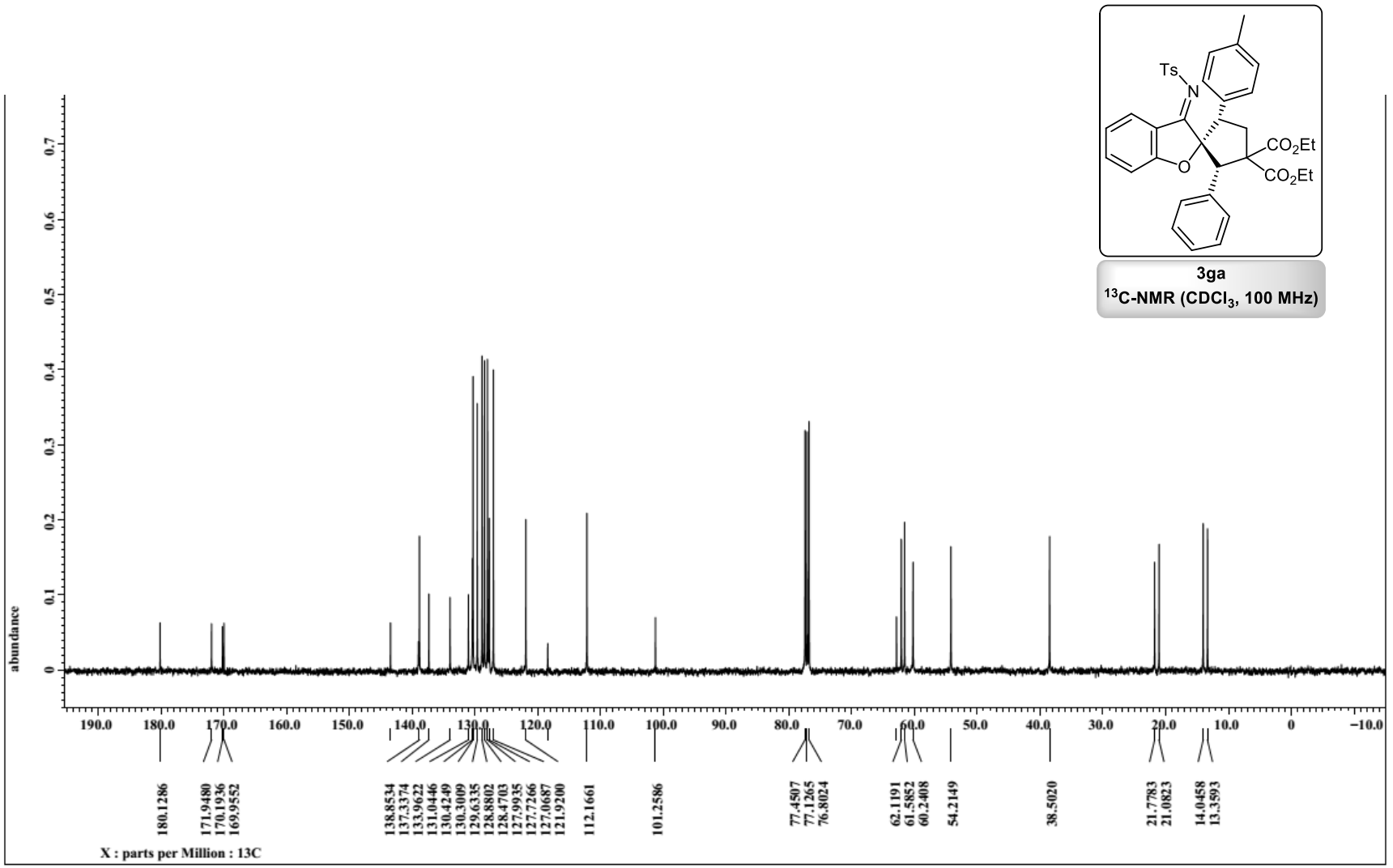


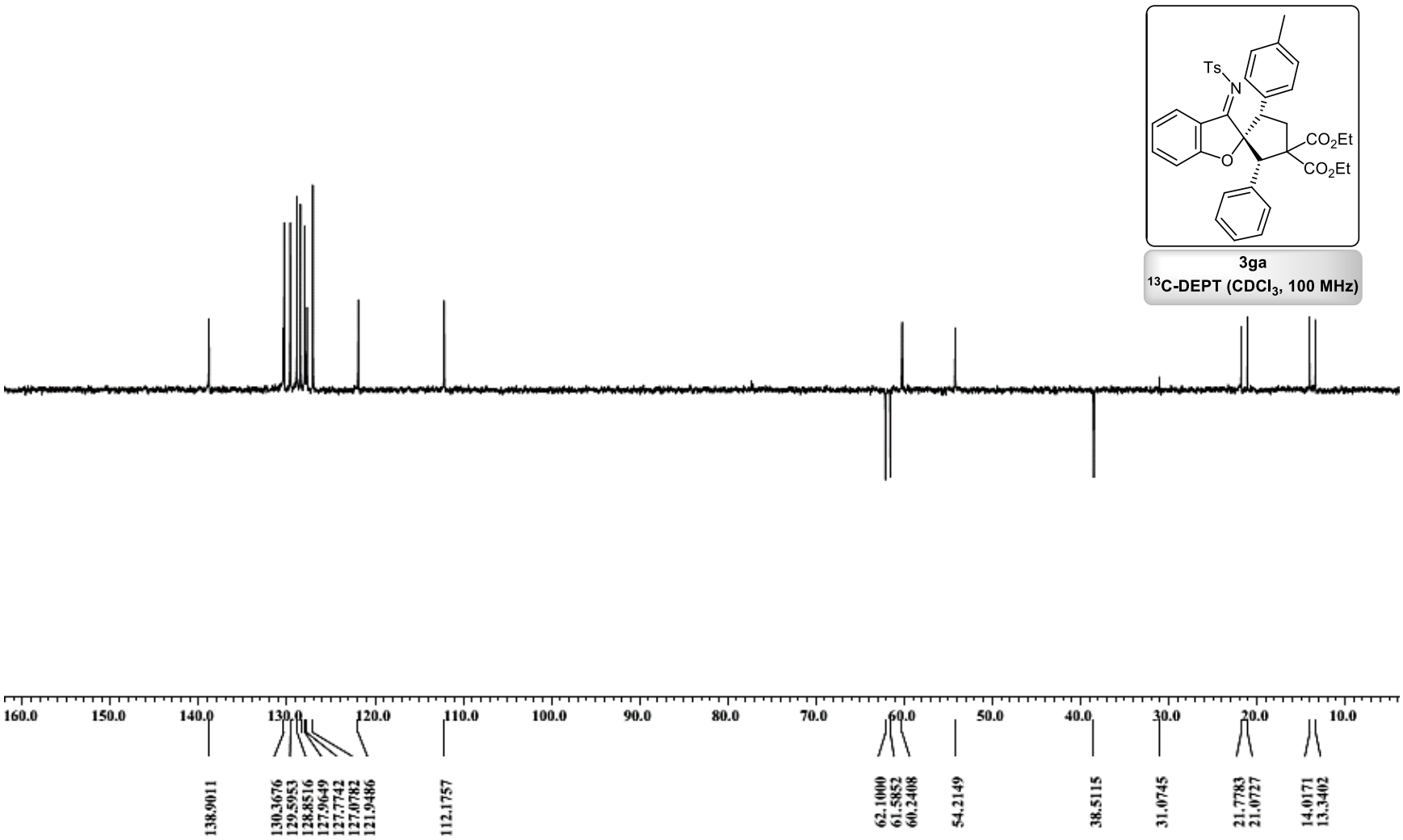
Minimum:				-1.5				
Maximum:		5.0	50.0	50.0				
Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	Norm	Conf(%)	Formula
707.2072	707.2063	0.9	1.3	23.5	364.6	n/a	n/a	C39 H35 N2 O9 S


Ts
N
O
CO2Et
CO2Et
3ga
1H-NMR (CDCl3, 400 MHz)
abundance
X : parts per Million : 1H






Ts
N
O
CO2Et
CO2Et
3ga
13C-NMR (CDCl3, 100 MHz)
abundance
0
0.1
0.2
0.3
0.4
0.5
0.6
0.7
190.0
180.0
170.0
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0
−10.0
180.1286
171.9480
170.1936
169.9552
138.8534
137.3374
133.9622
131.0446
130.4249
130.3009
129.6335
128.8802
128.4703
127.9935
127.7266
127.0687
121.9200
112.1661
101.2586
77.4507
77.1265
76.8024
62.1191
61.5852
60.2408
54.2149
38.5020
21.7783
21.0823
14.0458
13.3593
X : parts per Million : 13C



3ga

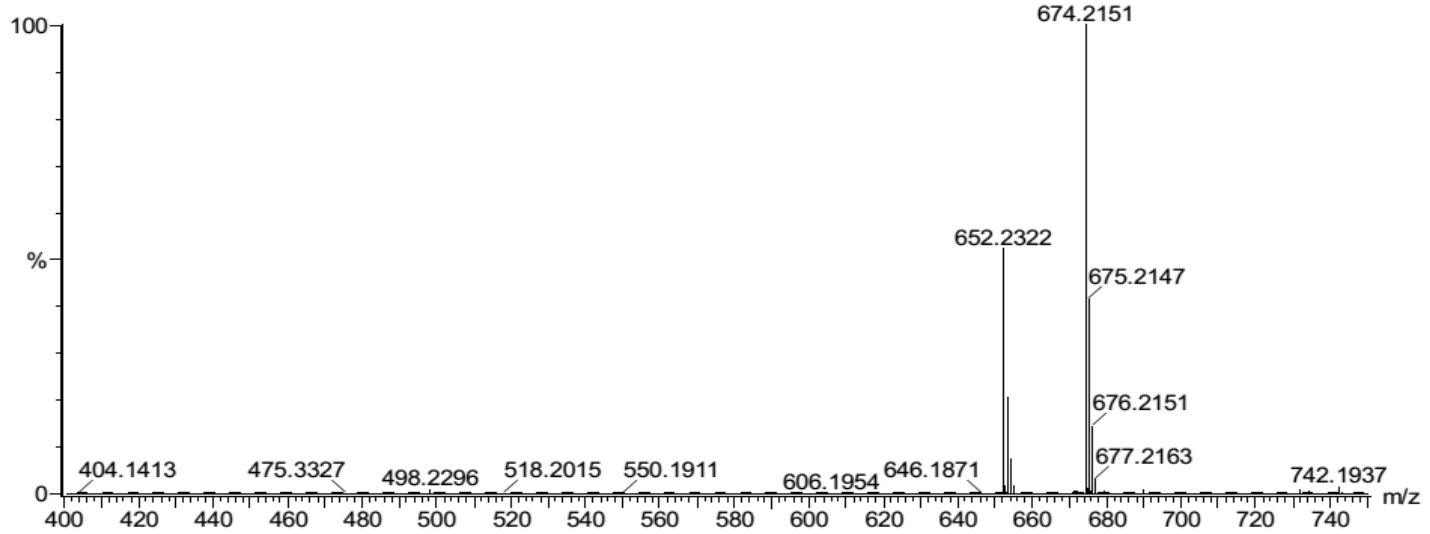
^{13}C-DEPT ($CDCl_3$, 100 MHz)

HRMS Spectra of **3ga:**

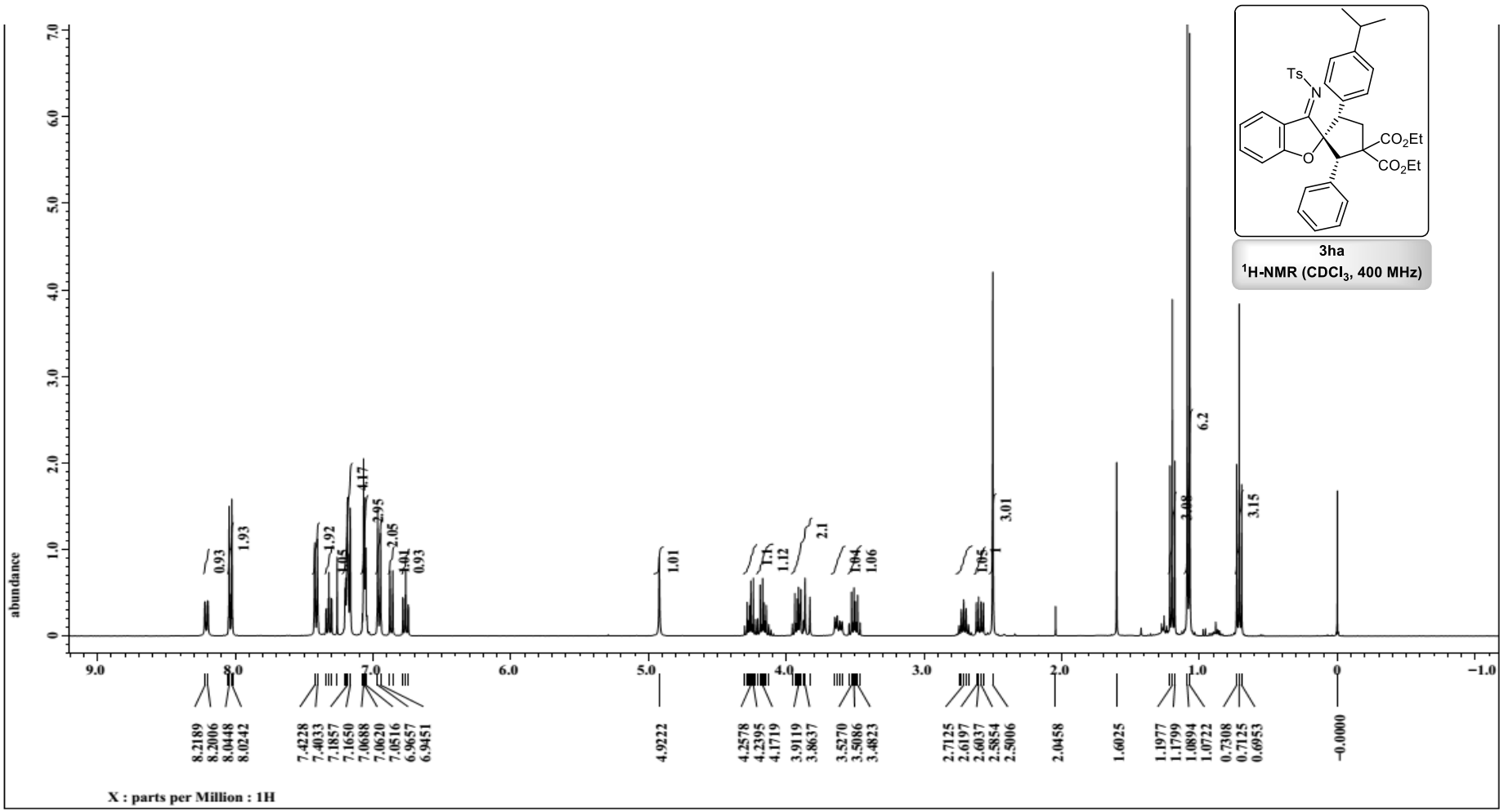
Single Mass Analysis
Tolerance = 10.0 PPM / DBE: min = -1.5, max = 50.0
Element prediction: Off
Number of isotope peaks used for i-FIT = 3

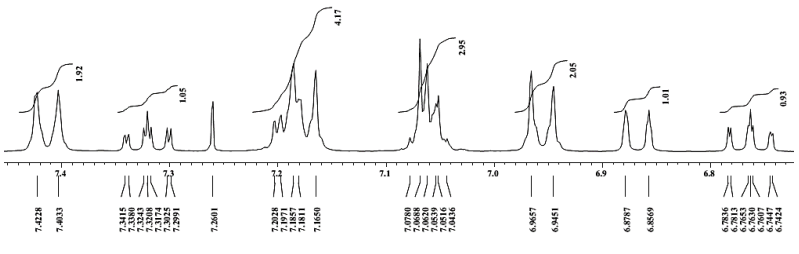
Monoisotopic Mass, Even Electron Ions
33 formula(e) evaluated with 1 results within limits (up to 50 closest results for each mass)
Elements Used:
C: 35-40 H: 31-42 N: 0-2 O: 0-10 S: 0-1

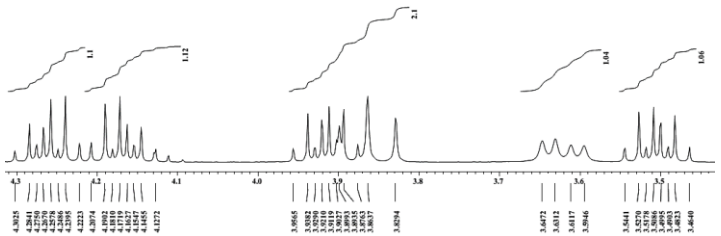
Sample Name : 15-01-027 INDIAN INSTITUTE OF TECHNOLOGY XEVO G2-XS QTOF
Test Name : HRMS-1 ROPAR
260218-15-01-027 11 (0.123) AM (Top,4, Ar,10000.0,0.00,0.00); Sm (Mn, 1x3.00); Cm (6:18) 1: TOF MS ES+
1.42e+008

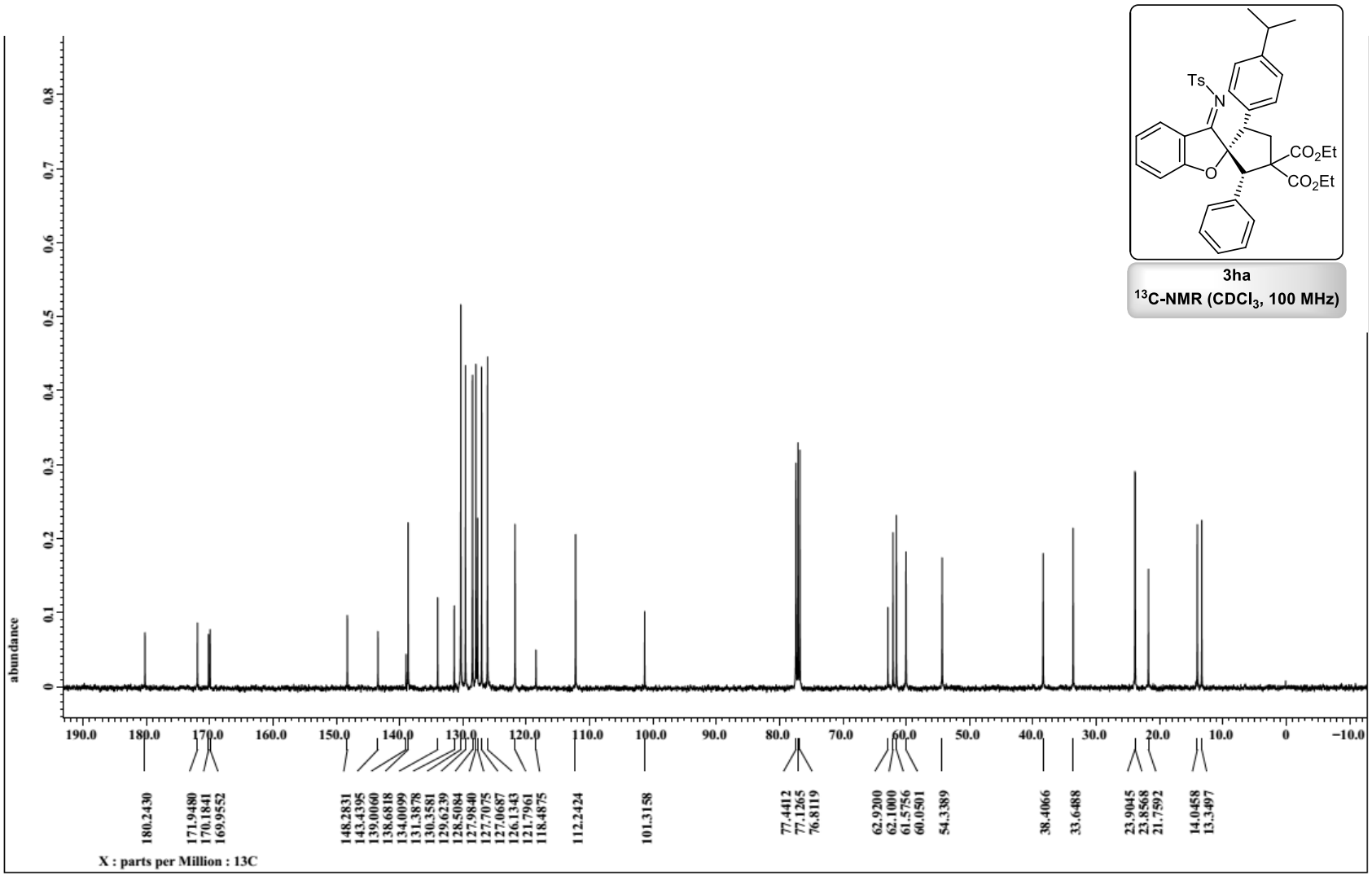


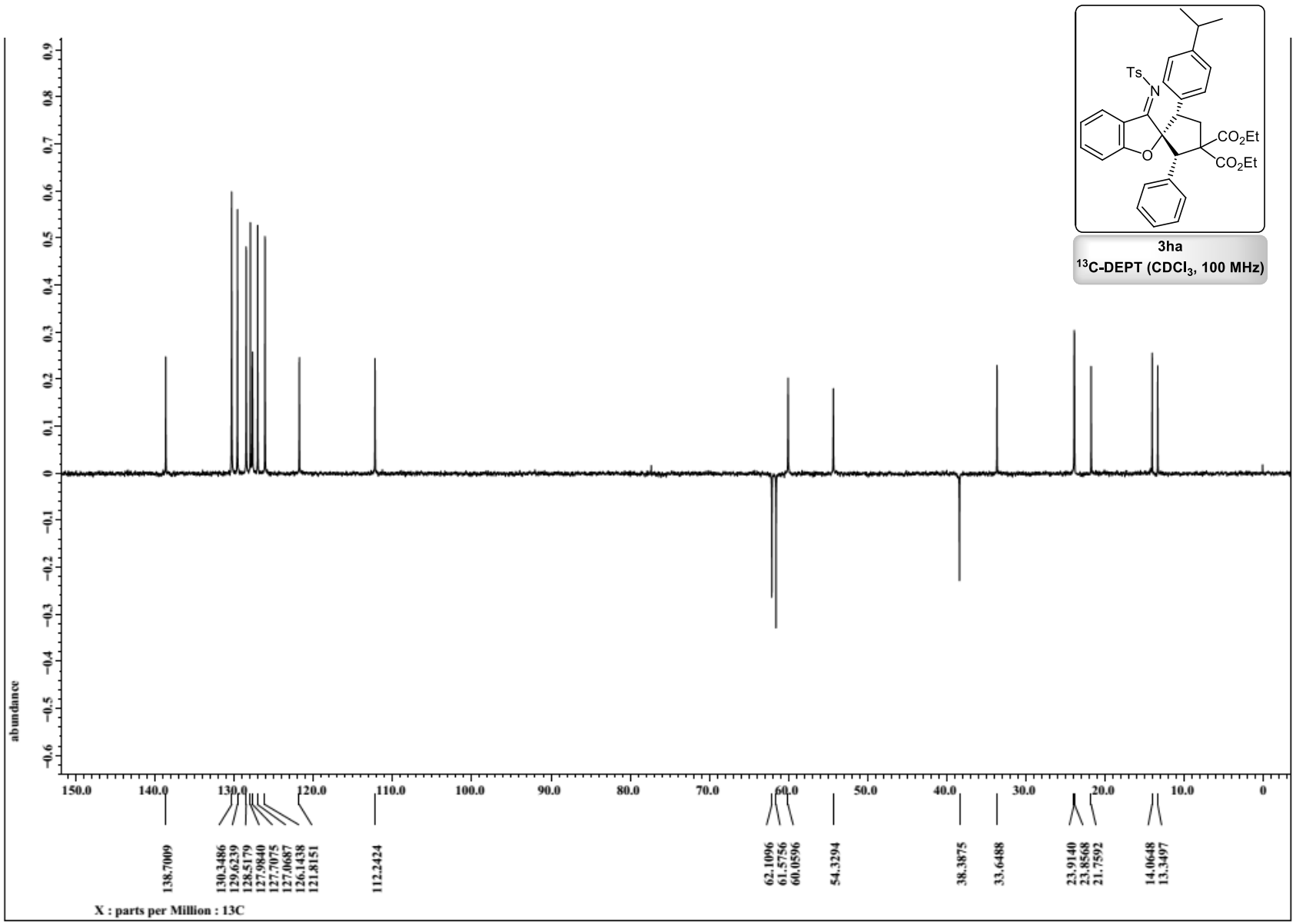
Minimum:				-1.5				
Maximum:		5.0	10.0	50.0				
Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	Norm	Conf(%)	Formula
652.2322	652.2369	-4.7	-7.2	20.5	418.2	n/a	n/a	C38 H38 N O7 S


Ts
N
O
CO2Et
CO2Et
3ha
1H-NMR (CDCl3, 400 MHz)
abundance
X : parts per Million : 1H






Ts
N
O
CO_2Et
CO_2Et
3ha
^{13}C-NMR ($CDCl_3$, 100 MHz)
abundance
0
0.1
0.2
0.3
0.4
0.5
0.6
0.7
0.8
190.0
180.0
170.0
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0
−10.0
180.2430
171.9480
170.1841
169.9552
148.2831
143.4395
139.0060
138.6818
134.0099
131.3878
130.3581
129.6239
128.5084
127.9840
127.7075
127.0687
126.1343
121.7961
118.4875
112.2424
101.3158
77.4412
77.1265
76.8119
62.9200
62.1000
61.5756
60.0501
54.3389
38.4066
33.6488
23.9045
23.8568
21.7592
14.0458
13.3497
X : parts per Million : 13C

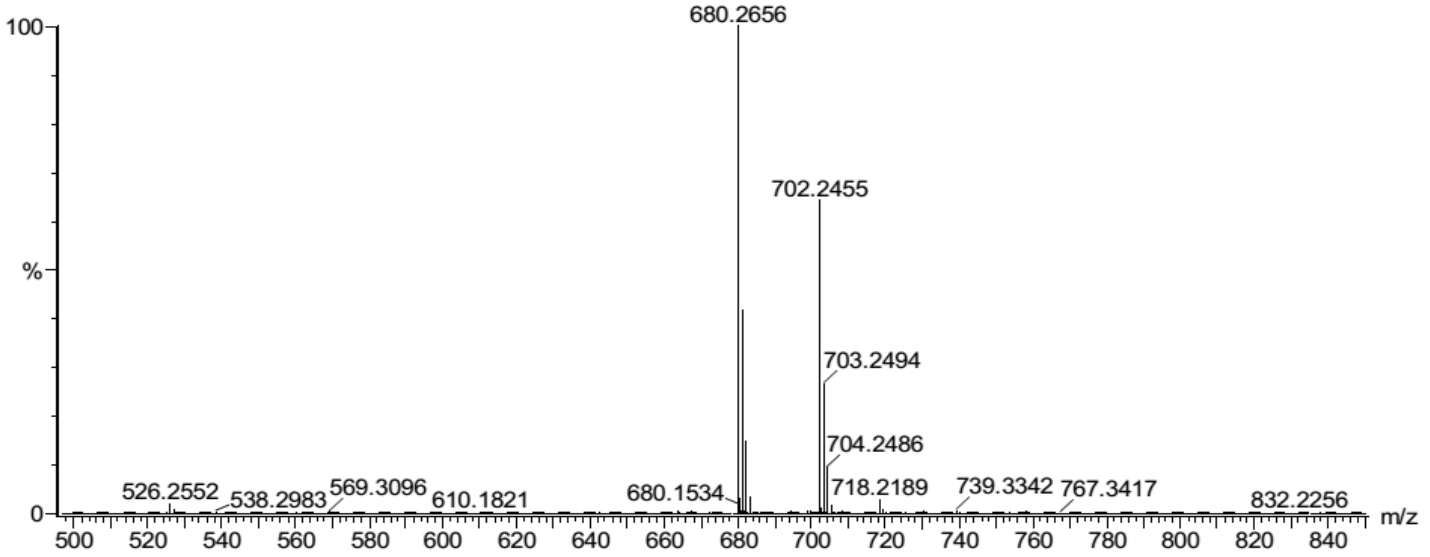

Ts
N
O
CO2Et
CO2Et
3ha
13C-DEPT (CDCl3, 100 MHz)
abundance
X : parts per Million : 13C
138.7009
130.3486
129.6239
128.5179
127.9840
127.7075
127.0687
126.1438
121.8151
112.2424
62.1096
61.5756
60.0596
54.3294
38.3875
33.6488
23.9140
23.8568
21.7592
14.0648
13.3497

HRMS Spectra of **3ha:**

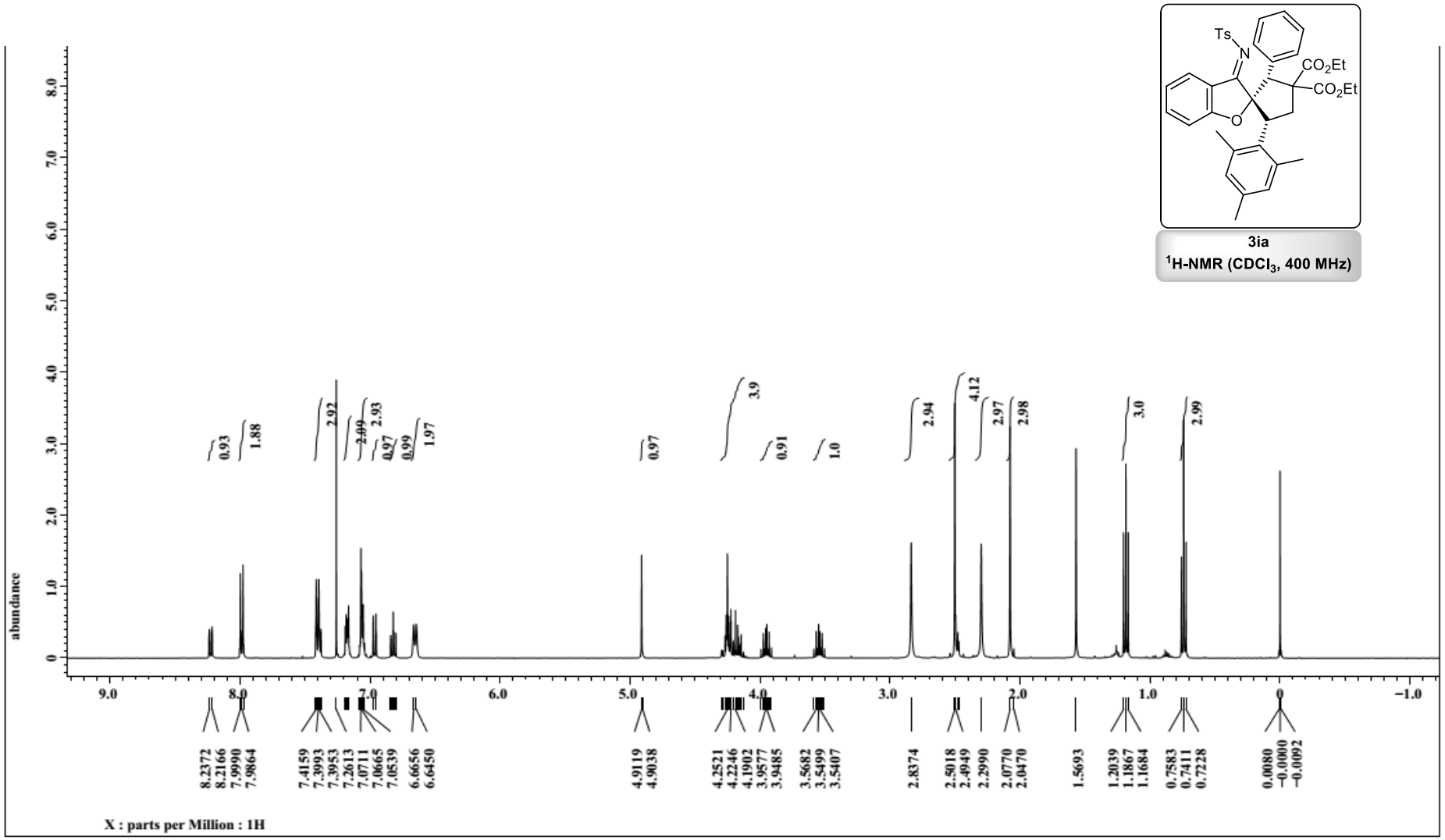
Single Mass Analysis
Tolerance = 10.0 PPM / DBE: min = -1.5, max = 50.0
Element prediction: Off
Number of isotope peaks used for i-FIT = 3

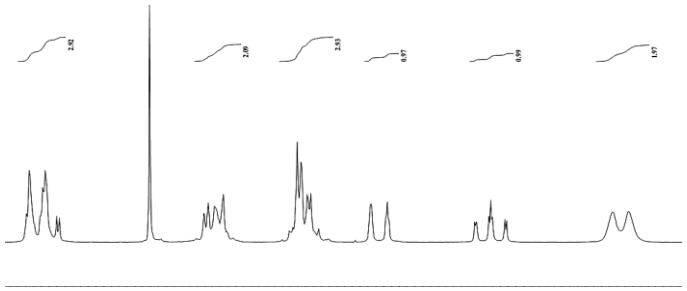
Monoisotopic Mass, Even Electron Ions
49 formula(e) evaluated with 1 results within limits (up to 50 best isotopic matches for each mass)
Elements Used:
C: 8-40 H: 10-45 N: 0-2 O: 1-7 S: 0-2

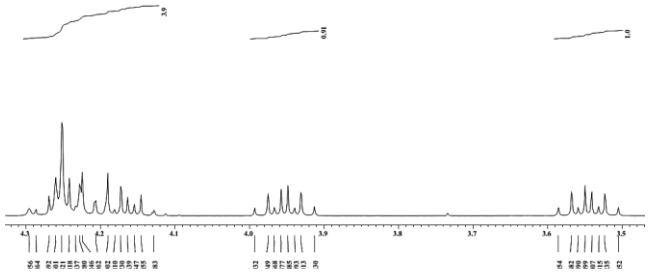
Sample Name : 07-04-136 I.I.T.ROPAR XEVO G2-XS QTOF
Test Name : HRMS-1
190219-07-04-136 16 (0.165) AM (Top,4, Ar,10000.0,0.00,0.00); Cm (16:23) 1: TOF MS ES+
2.83e+007

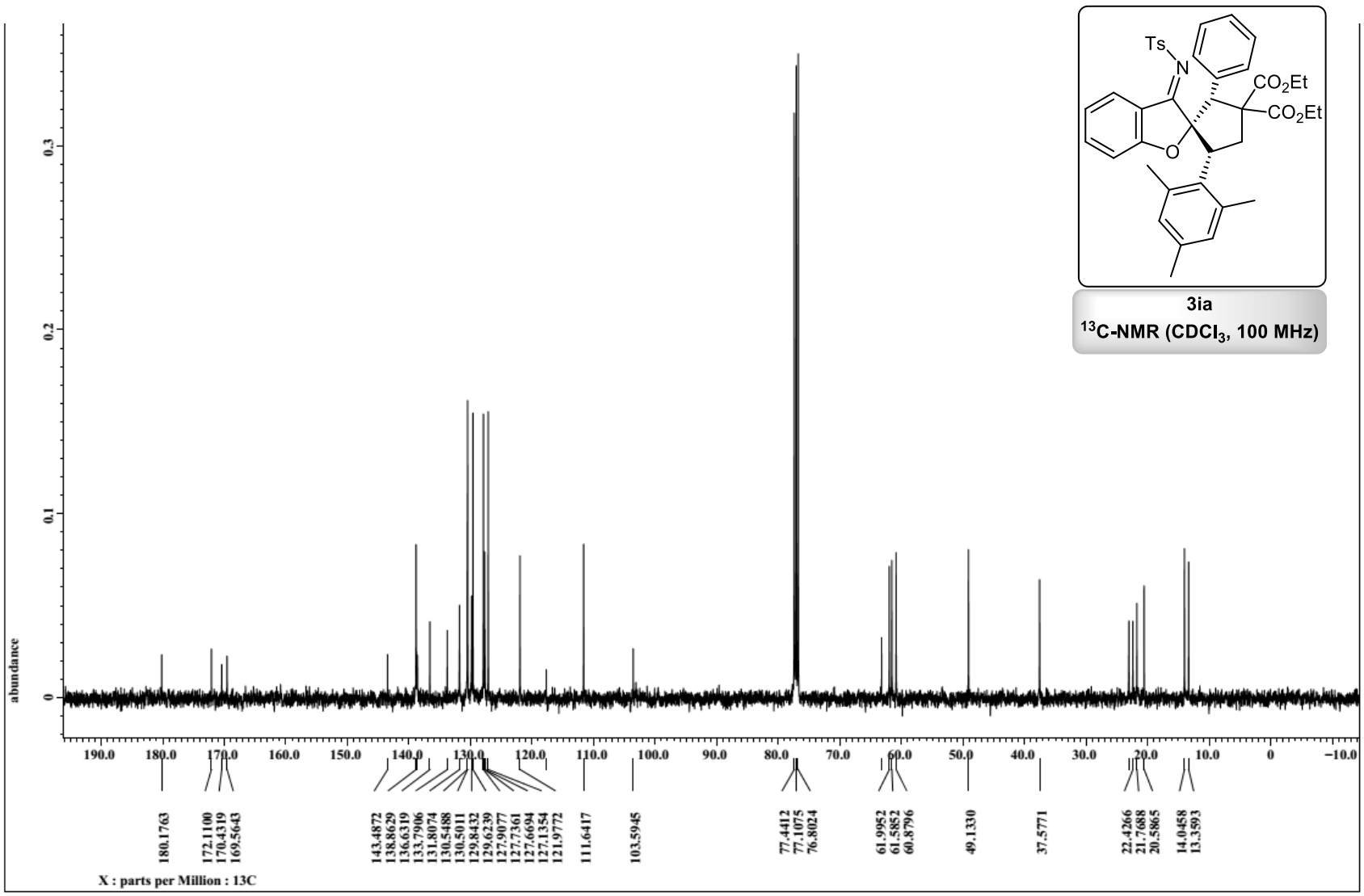


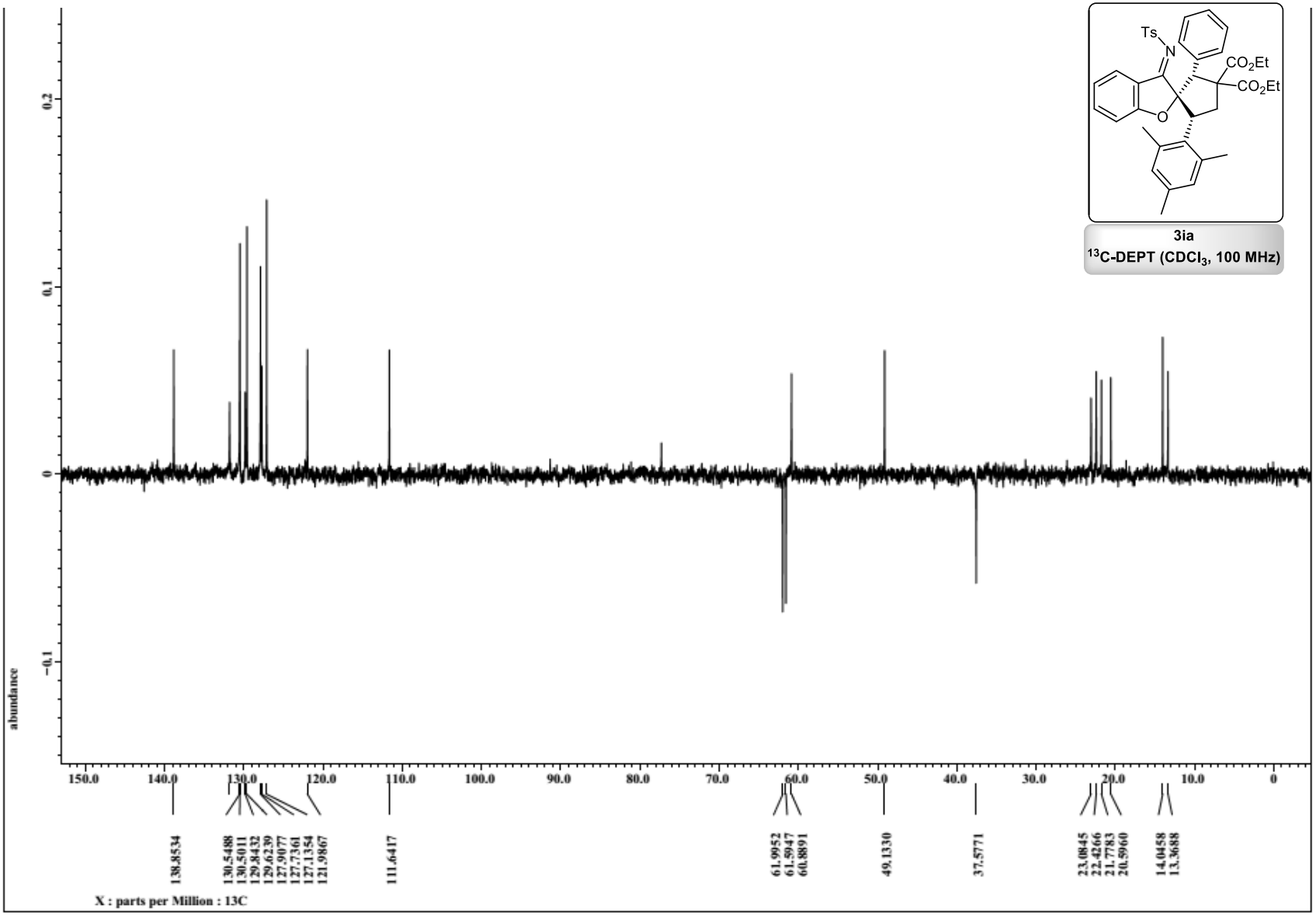
Minimum:				-1.5				
Maximum:		5.0	10.0	50.0				
Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	Norm	Conf(%)	Formula
680.2656	680.2682	-2.6	-3.8	20.5	599.5	n/a	n/a	C40 H42 N O7 S


Ts
N
O
CO2Et
CO2Et
3ia
1H-NMR (CDCl3, 400 MHz)
abundance
X : parts per Million : 1H






Ts
N
O
CO2Et
CO2Et
3ia
13C-NMR (CDCl3, 100 MHz)
abundance
0
0.1
0.2
0.3
190.0
180.0
170.0
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0
−10.0
180.1763
172.1100
170.4319
169.5643
143.4872
138.8629
136.6319
133.7906
131.8074
130.5488
130.5011
129.8432
129.6239
127.9077
127.7361
127.6694
127.1354
121.9772
111.6417
103.5945
77.4412
77.1075
76.8024
61.9952
61.5852
60.8796
49.1330
37.5771
22.4266
21.7688
20.5865
14.0458
13.3593
X : parts per Million : 13C

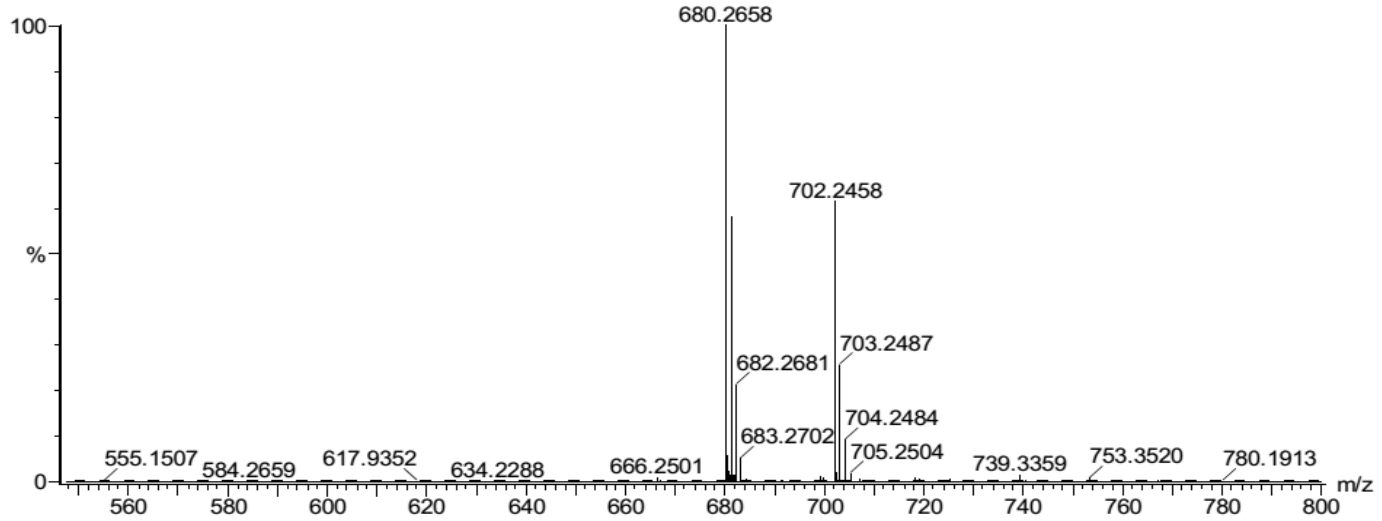

Ts
N
O
CO_2Et
CO_2Et
3ia
^{13}C-DEPT ($CDCl_3$, 100 MHz)
abundance
0.2
0.1
0
−0.1
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0
138.8534
130.5488
130.5011
129.8432
129.6239
127.9077
127.7361
127.1354
121.9867
111.6417
61.9952
61.5947
60.8891
49.1330
37.5771
23.0845
22.4266
21.7783
20.5960
14.0458
13.3688
X : parts per Million : 13C

HRMS Spectra of **3ia:**

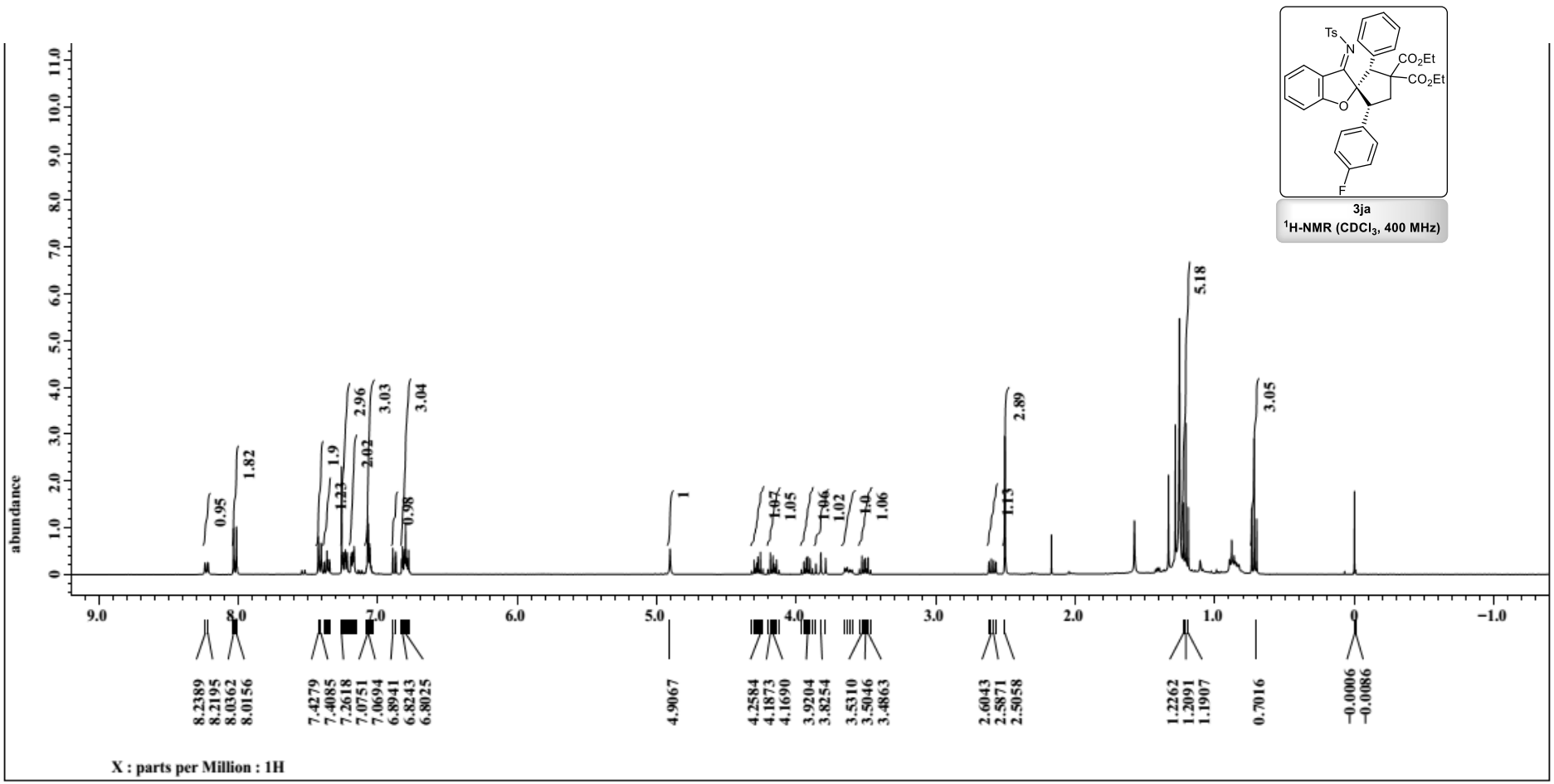
Single Mass Analysis
Tolerance = 10.0 PPM / DBE: min = -1.5, max = 50.0
Element prediction: Off
Number of isotope peaks used for i-FIT = 3

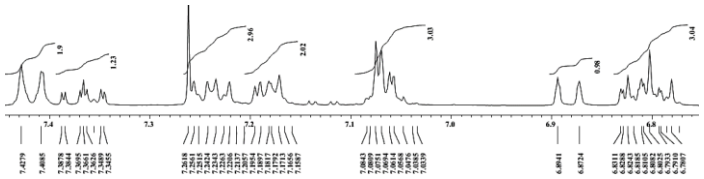
Monoisotopic Mass, Even Electron Ions
67 formula(e) evaluated with 1 results within limits (up to 50 best isotopic matches for each mass)
Elements Used:
C: 35-40 H: 35-42 N: 0-2 O: 0-7 Na: 0-1 S: 0-1 Cl: 0-1

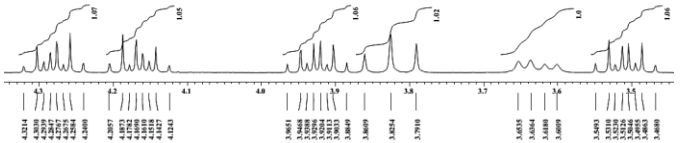
Sample Name : 07-04-068 I.I.T.ROPAR XEVO G2-XS QTOF
Test Name : HRMS-1
150518-07-04-068 16 (0.165) AM2 (Ar,16000.0,0.00,0.00); Cm (16:19) 1: TOF MS ES+
5.74e+007

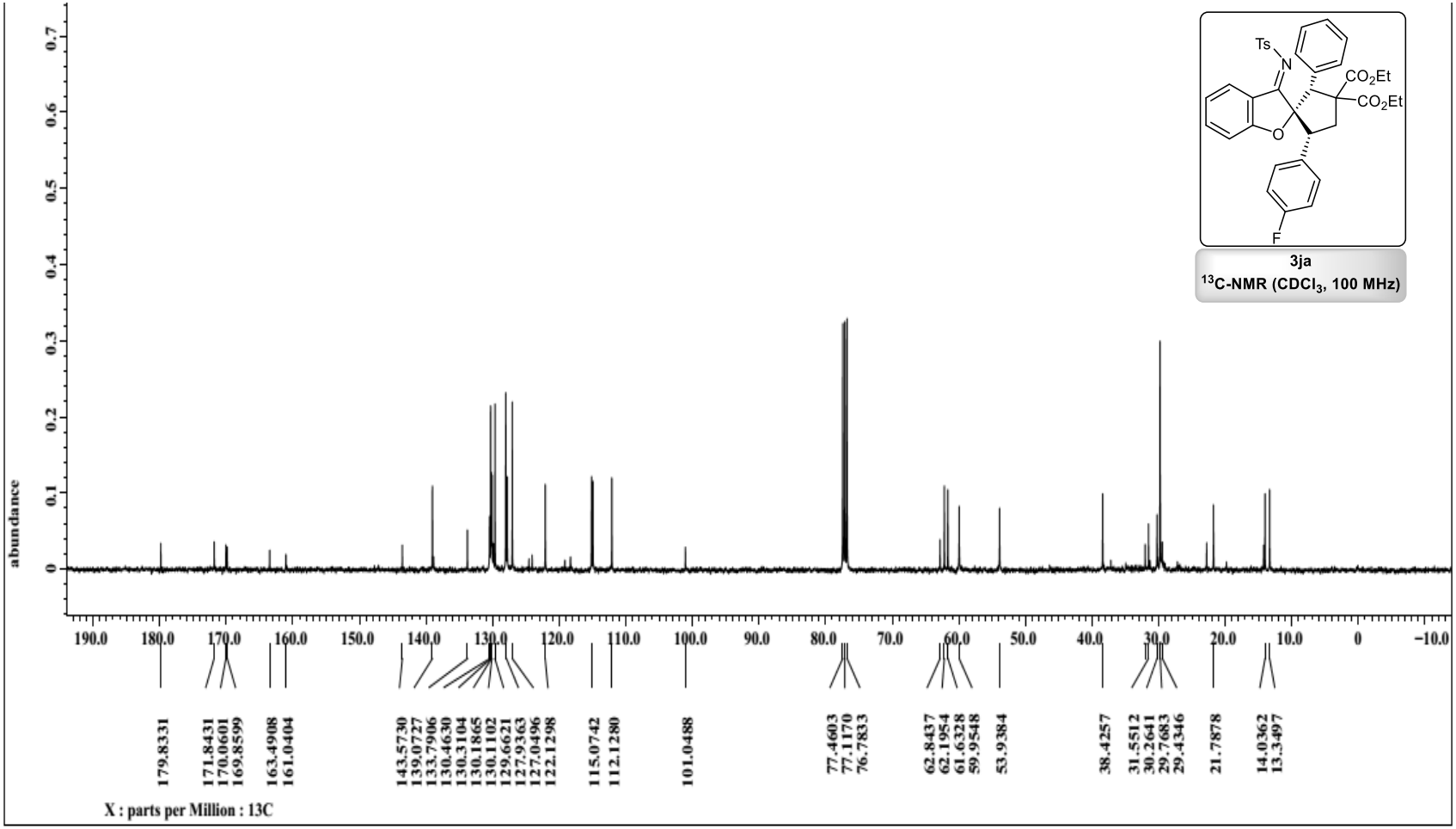


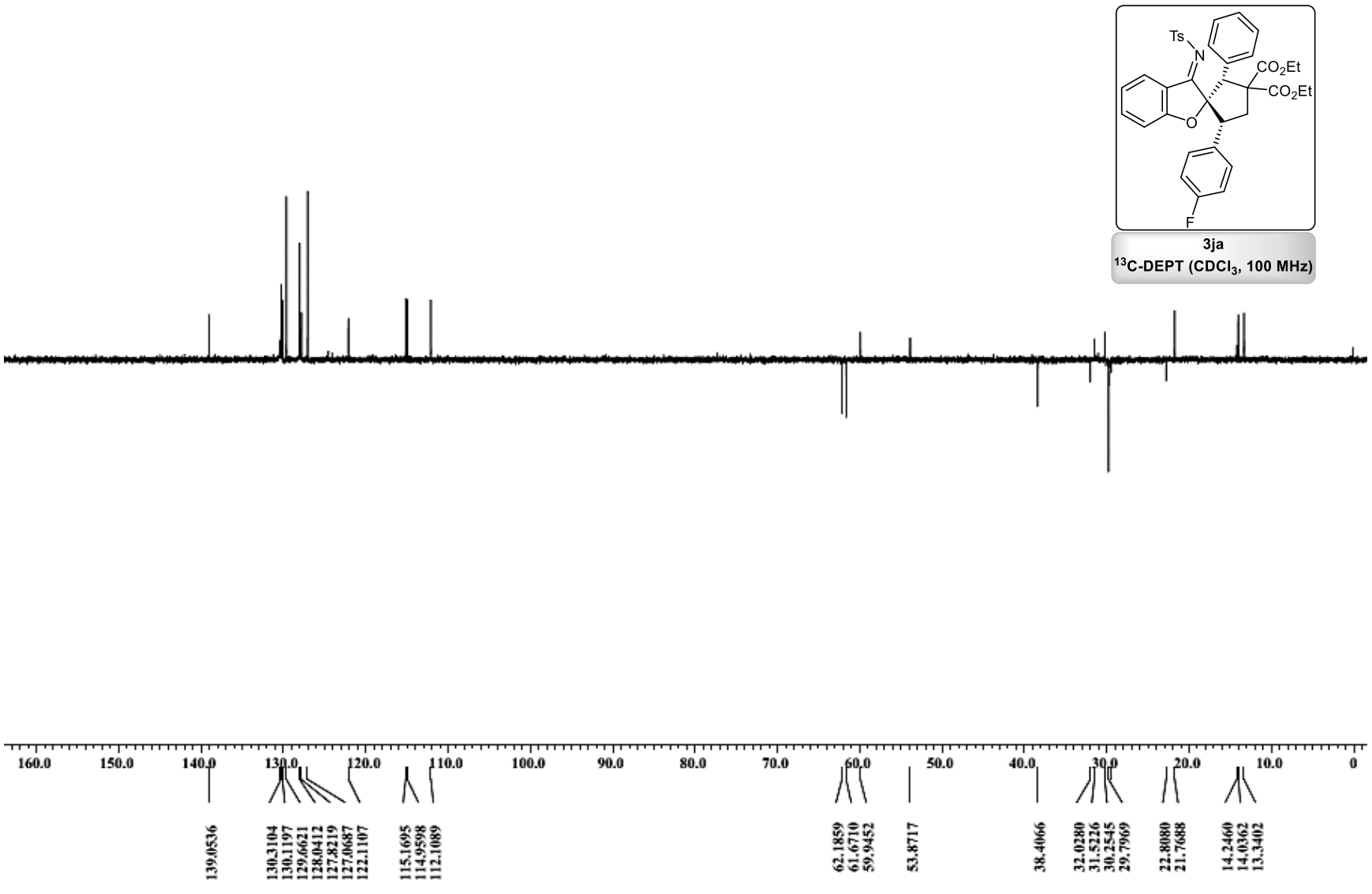
Minimum:				-1.5				
Maximum:		5.0	10.0	50.0				
Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	Norm	Conf(%)	Formula
680.2658	680.2682	-2.4	-3.5	20.5	421.6	n/a	n/a	C40 H42 N O7 S


Ts
N
O
CO2Et
CO2Et
F
3ja
1H-NMR (CDCl3, 400 MHz)
abundance
X : parts per Million : 1H






Ts
N
CO2Et
CO2Et
O
F
3ja
13C-NMR (CDCl3, 100 MHz)
abundance
0
0.1
0.2
0.3
0.4
0.5
0.6
0.7
190.0
180.0
170.0
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0
−10.0
179.8331
171.8431
170.0601
169.8599
163.4908
161.0404
143.5730
139.0727
133.7906
130.4630
130.3104
130.1865
130.1102
129.6621
127.9363
127.0496
122.1298
115.0742
112.1280
101.0488
77.4603
77.1170
76.7833
62.8437
62.1954
61.6328
59.9548
53.9384
38.4257
31.5512
30.2641
29.7683
29.4346
21.7878
14.0362
13.3497
X : parts per Million : 13C

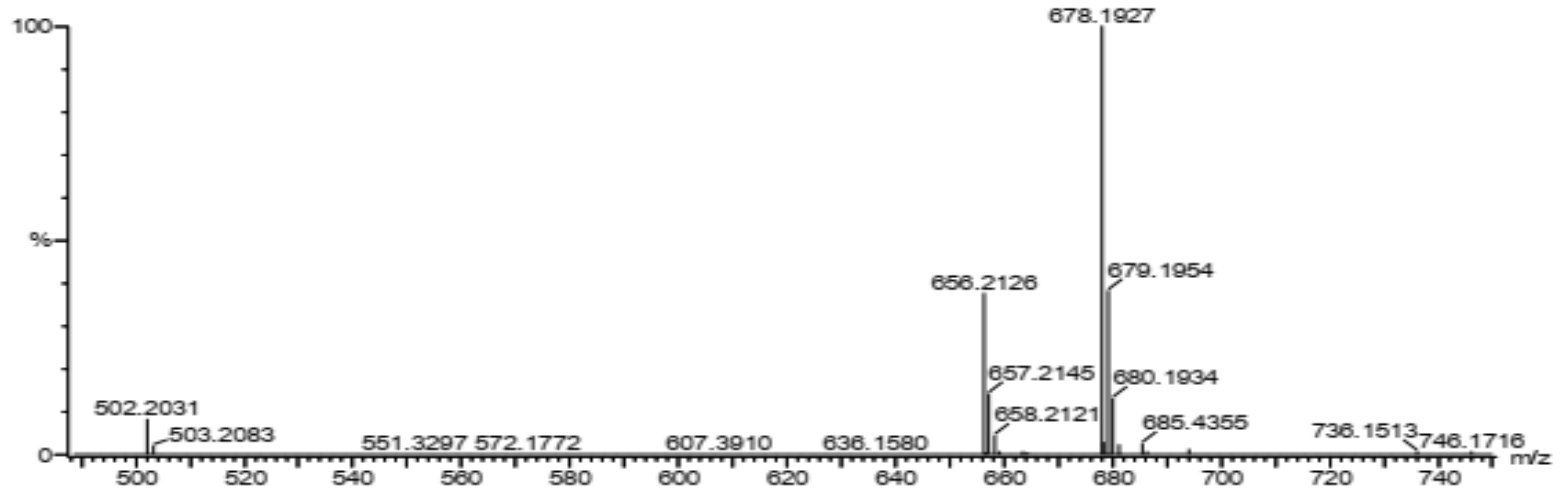

Ts
N
O
CO2Et
CO2Et
F
3ja
13C-DEPT (CDCl3, 100 MHz)
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0
139.0536
130.3104
130.1197
129.6621
128.0412
127.8219
127.0687
122.1107
115.1695
114.9598
112.1089
62.1859
61.6710
59.9452
53.8717
38.4066
32.0280
31.5226
30.2545
29.7969
22.8080
21.7688
14.2460
14.0362
13.3402

HRMS Spectra of **3ja:**

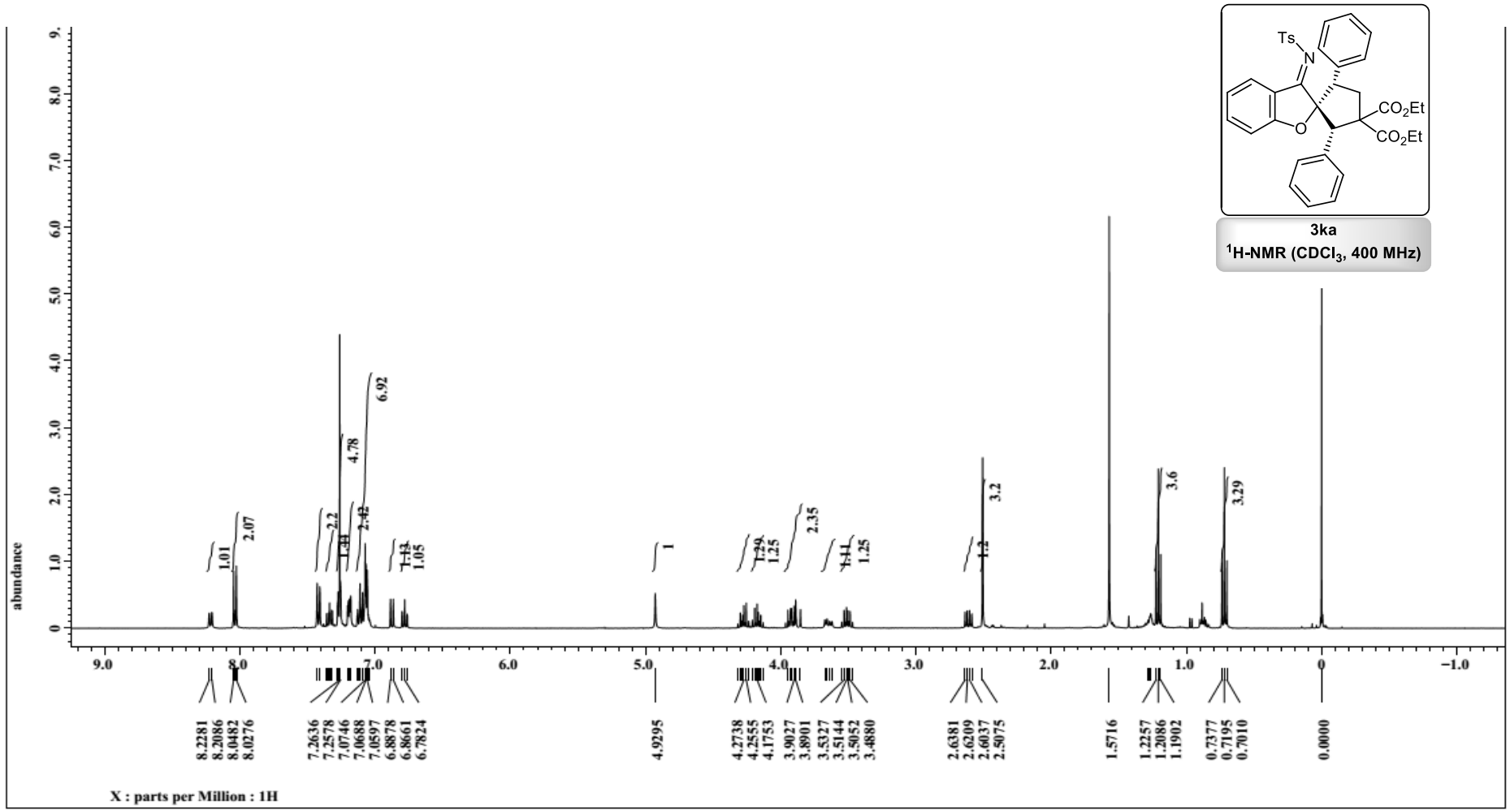
Single Mass Analysis
Tolerance = 5.0 PPM / DBE: min = -1.5, max = 50.0
Element prediction: Off
Number of isotope peaks used for i-FIT = 3

Monoisotopic Mass, Odd and Even Electron Ions
26 formula(e) evaluated with 1 results within limits (up to 50 closest results for each mass)
Elements Used:
C: 35-39 H: 30-35 N: 0-1 O: 0-7 F: 0-1 S: 0-1

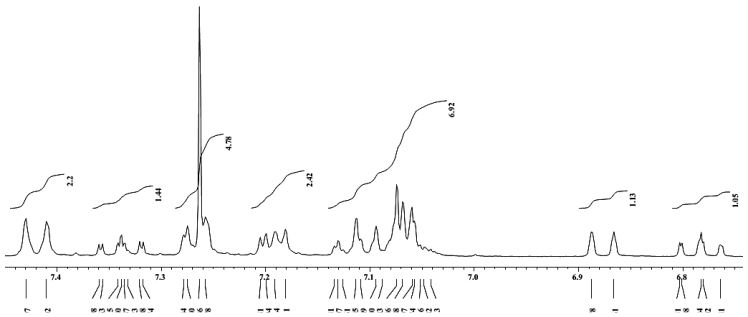
Sample Name : 07-04-040 INDIAN INSTITUTE OF TECHNOLOGY XEVO G2-XS QTOF
Test Name : HRMS-1 ROPAR
070318-07-04-040 11 (0.122) AM (Top,4, Ar,10000.0,0.00,0.00); Sm (Mn, 1x3.00); Cm (8:19) 1: TOF MS ES+ 5.09e+007

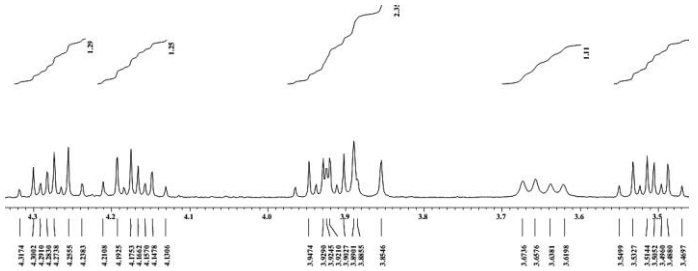


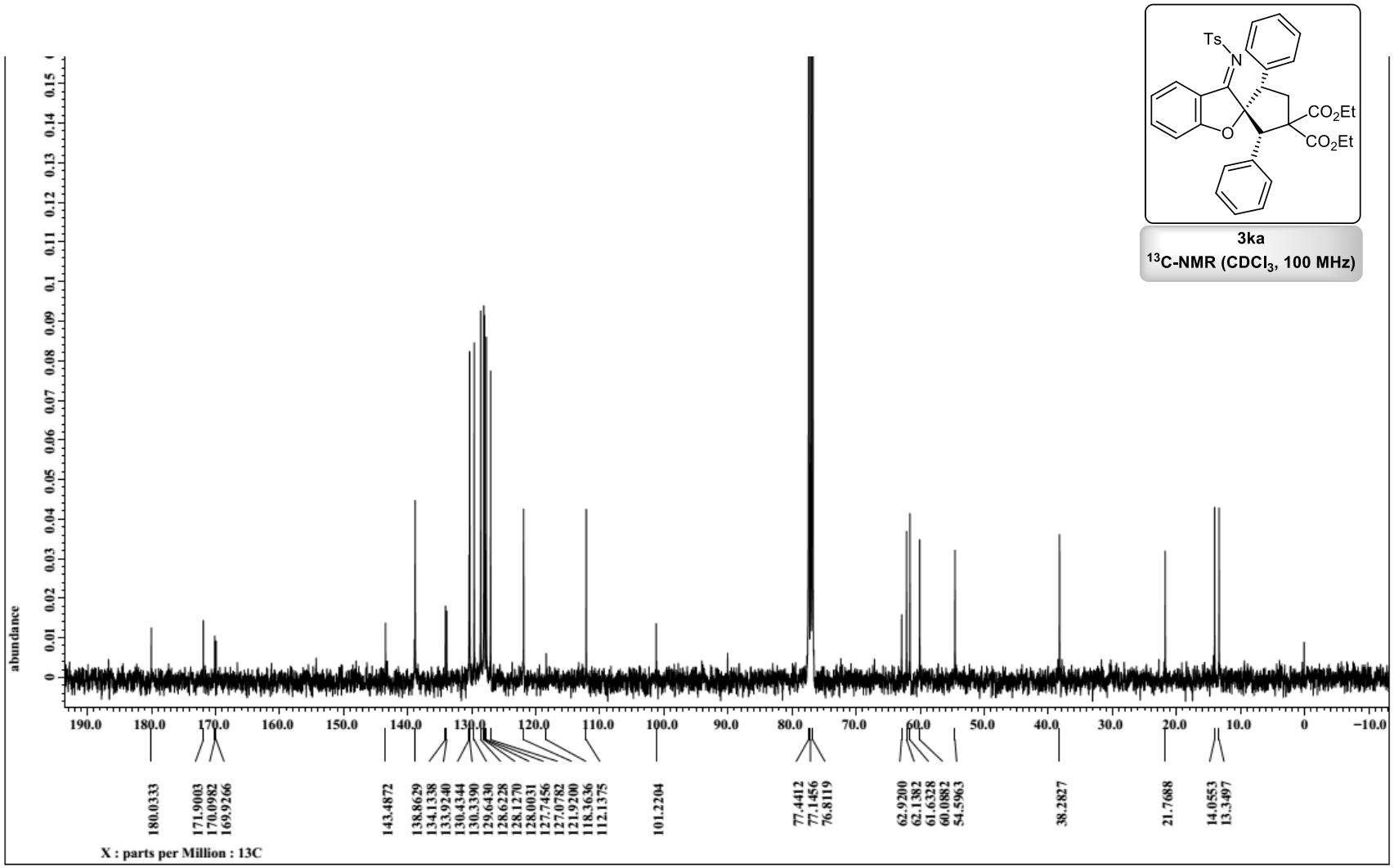
Minimum:				-1.5				
Maximum:		5.0	5.0	50.0				
Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	Norm	Conf(%)	Formula
656.2126	656.2118	0.8	1.2	20.5	372.9	n/a	n/a	C37 H35 N O7 F S

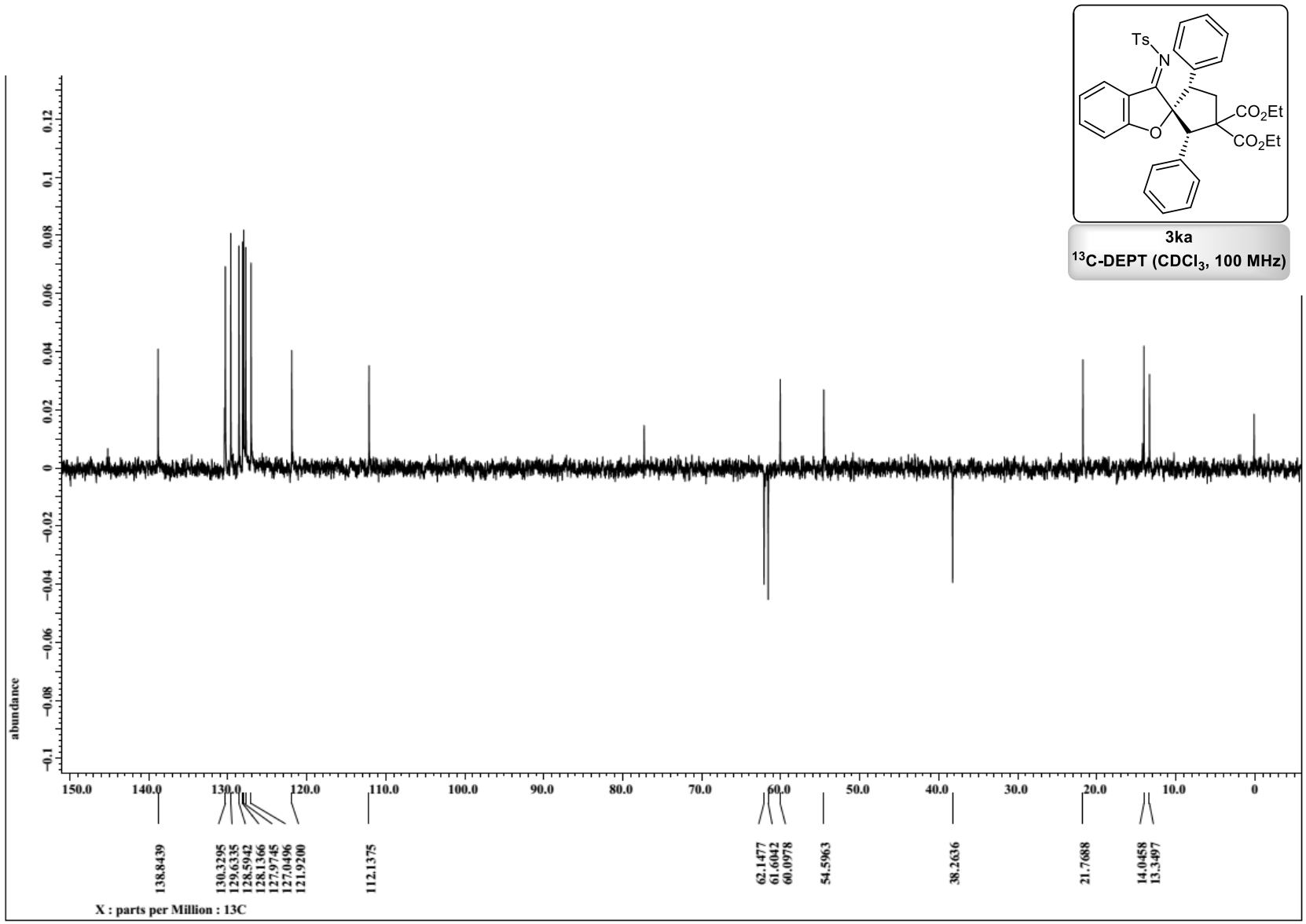

Ts
N
O
CO2Et
CO2Et
3ka
1H-NMR (CDCl3, 400 MHz)
abundance
X : parts per Million : 1H

-






Ts
N
O
CO2Et
CO2Et
3ka
13C-NMR (CDCl3, 100 MHz)
abundance
0 0.01 0.02 0.03 0.04 0.05 0.06 0.07 0.08 0.09 0.1 0.11 0.12 0.13 0.14 0.15
190.0 180.0 170.0 160.0 150.0 140.0 130.0 120.0 110.0 100.0 90.0 80.0 70.0 60.0 50.0 40.0 30.0 20.0 10.0 0 −10.0
180.0333
171.9003
170.0982
169.9266
143.4872
138.8629
134.1338
133.9240
130.4344
130.3390
129.6430
128.6228
128.1270
128.0031
127.7456
127.0782
121.9200
118.3636
112.1375
101.2204
77.4412
77.1456
76.8119
62.9200
62.1382
61.6328
60.0882
54.5963
38.2827
21.7688
14.0553
13.3497
X : parts per Million : 13C


Ts
N
O
CO2Et
CO2Et
3ka
13C-DEPT (CDCl3, 100 MHz)
abundance
0.12
0.1
0.08
0.06
0.04
0.02
0
−0.02
−0.04
−0.06
−0.08
−0.1
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0
138.8439
130.3295
129.6335
128.5942
128.1366
127.9745
127.0496
121.9200
112.1375
62.1477
61.6042
60.0978
54.5963
38.2636
21.7688
14.0458
13.3497
X : parts per Million : 13C

HRMS Spectra of **3ka:**

Single Mass Analysis

Tolerance = 5.0 PPM / DBE: min = -1.5, max = 50.0

Element prediction: Off

Number of isotope peaks used for i-FIT = 3

Monoisotopic Mass, Even Electron Ions

24 formula(e) evaluated with 1 results within limits (up to 50 best isotopic matches for each mass)

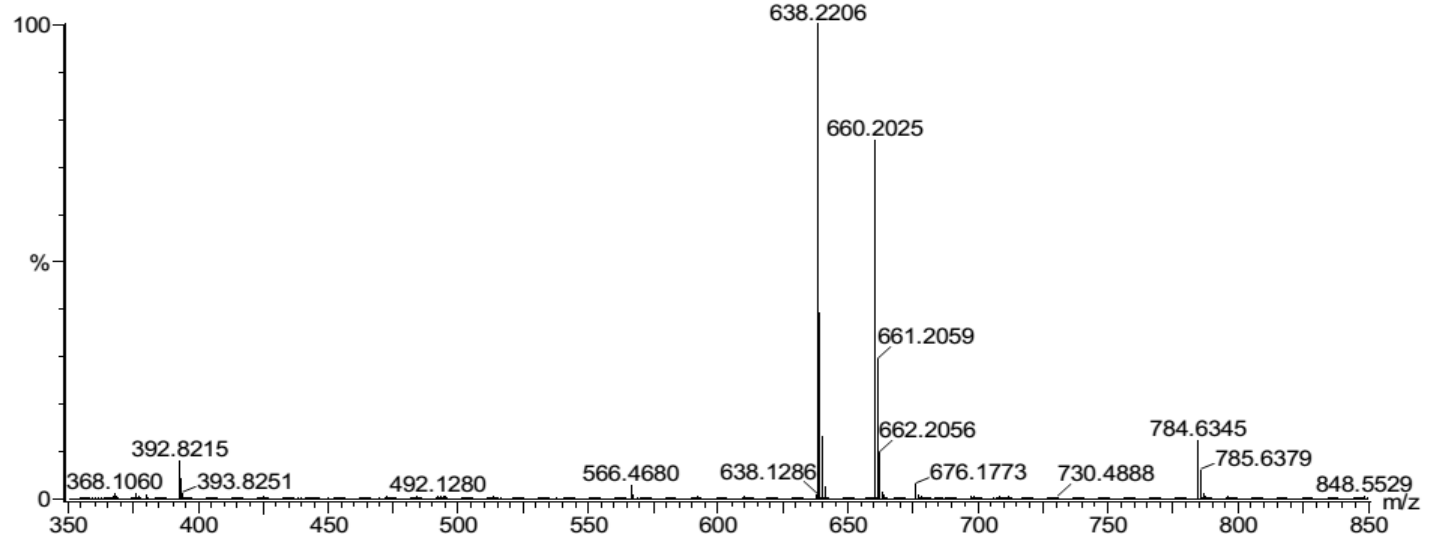
Elements Used:

C: 8-40 H: 35-45 N: 0-2 O: 1-7 S: 0-2

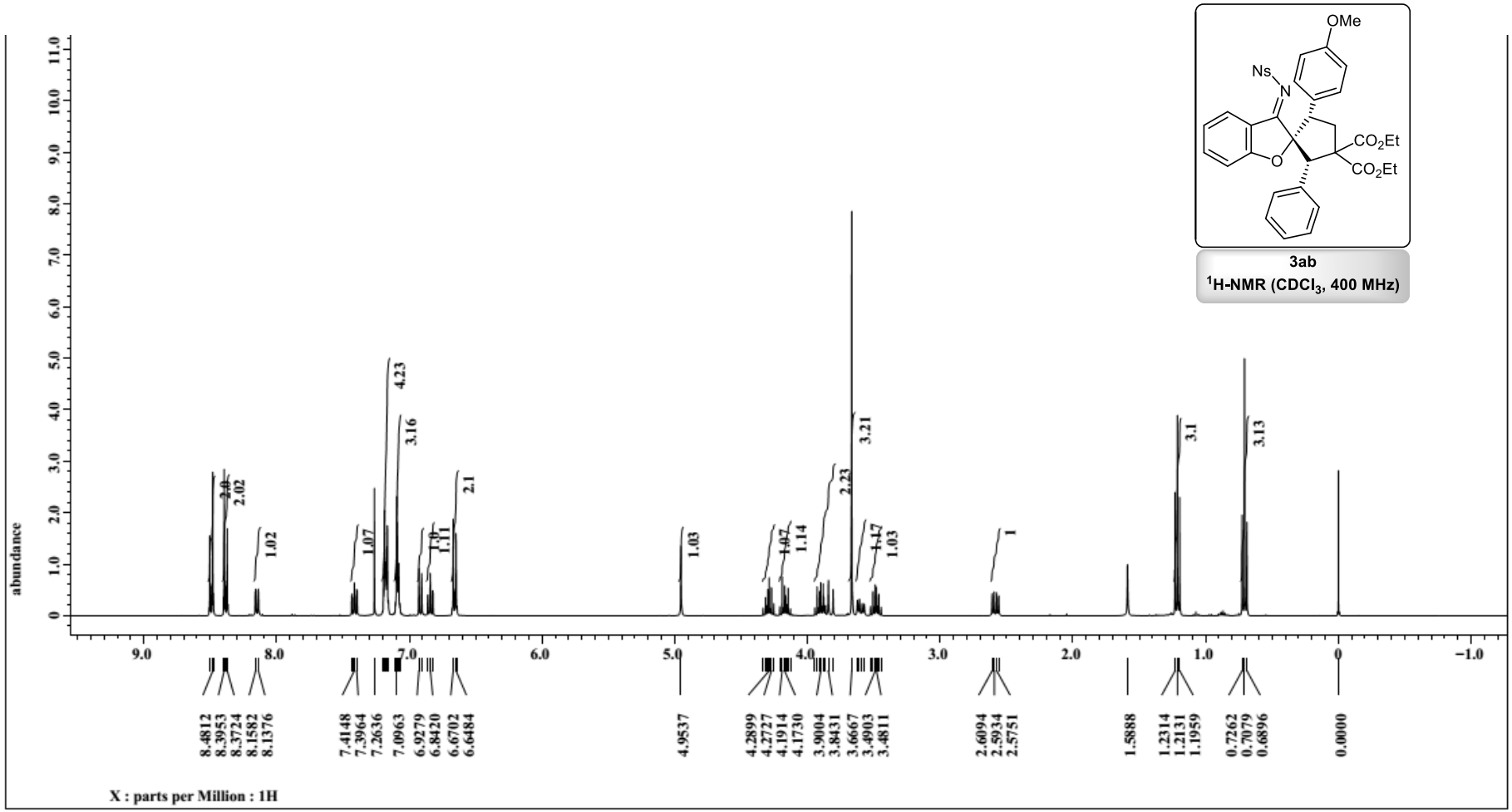
Sample Name : 07-04-137 I.I.T.ROPAR XEVO G2-XS QTOF

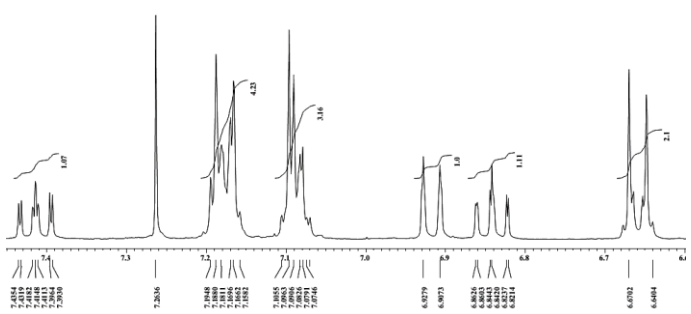
Test Name : HRMS-1

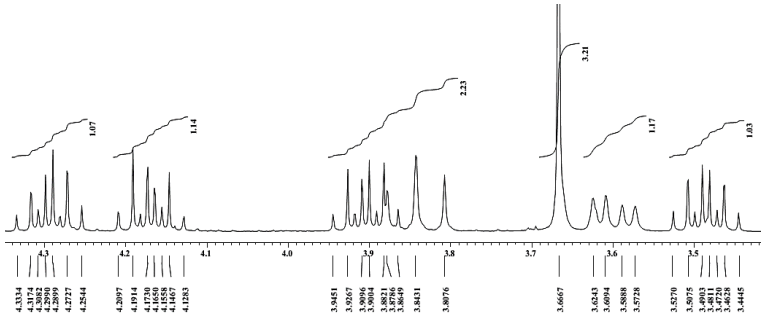
190219-07-04-137- 17 (0.174) AM2 (Ar,21000.0,0.00,0.00); Cm (17:19) 1: TOF MS ES+ 7.15e+006

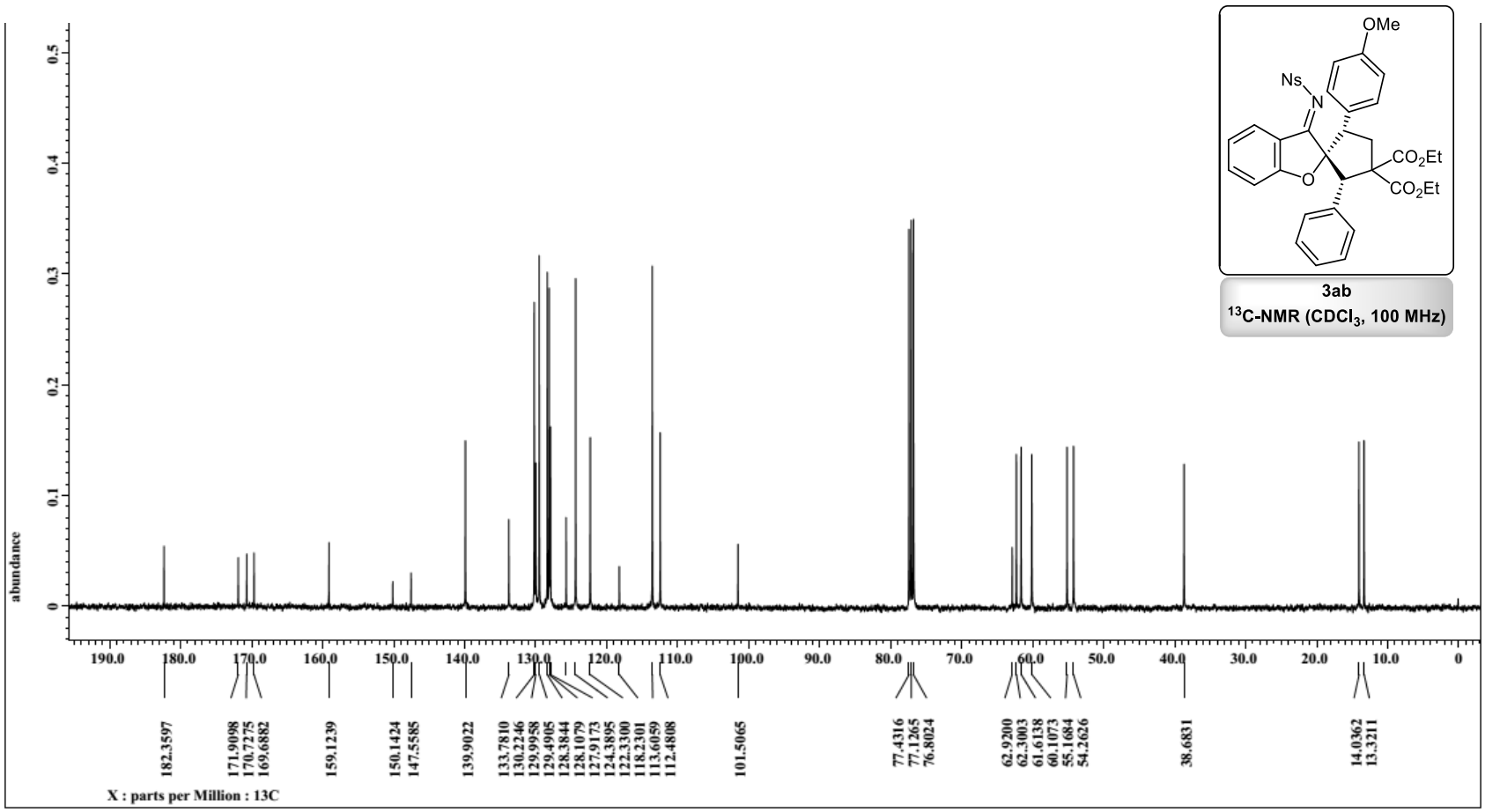


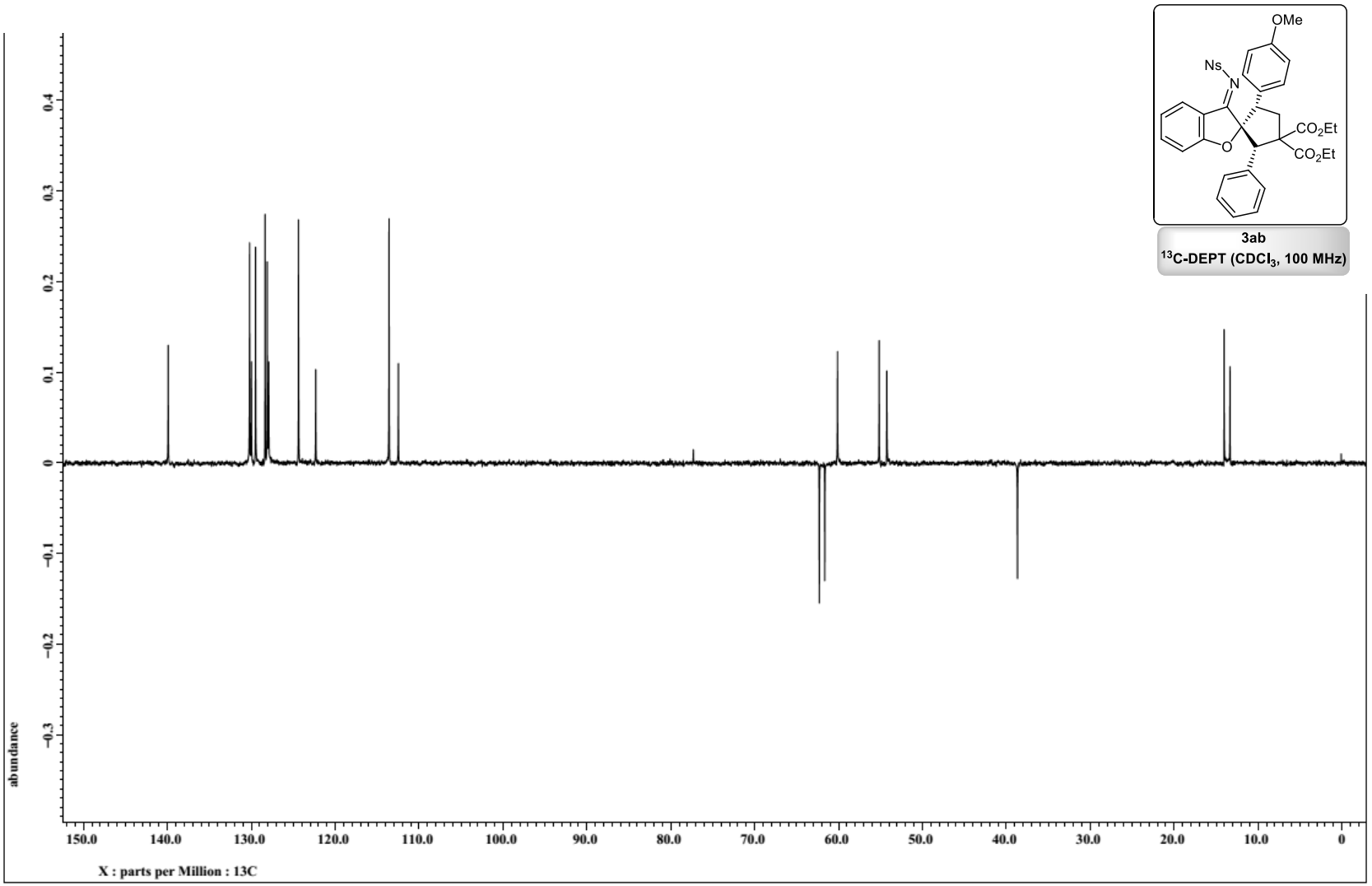
Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	Norm	Conf(%)	Formula
Minimum:				-1.5				
Maximum:		5.0	5.0	50.0				
638.2206	638.2212	-0.6	-0.9	20.5	446.8	n/a	n/a	C37 H36 N O7 S


OMe
Ns
N
O
CO2Et
CO2Et
3ab
1H-NMR (CDCl3, 400 MHz)
abundance
X : parts per Million : 1H






OMe
Ns
N
O
CO2Et
CO2Et
3ab
13C-NMR (CDCl3, 100 MHz)
abundance
0
0.1
0.2
0.3
0.4
0.5
190.0
180.0
170.0
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0
182.3597
171.9098
170.7275
169.6882
159.1239
150.1424
147.5585
139.9022
133.7810
130.2246
129.9958
129.4905
128.3844
128.1079
127.9173
124.3895
122.3300
118.2301
113.6059
112.4808
101.5065
77.4316
77.1265
76.8024
62.9200
62.3003
61.6138
60.1073
55.1684
54.2626
38.6831
14.0362
13.3211
X : parts per Million : 13C

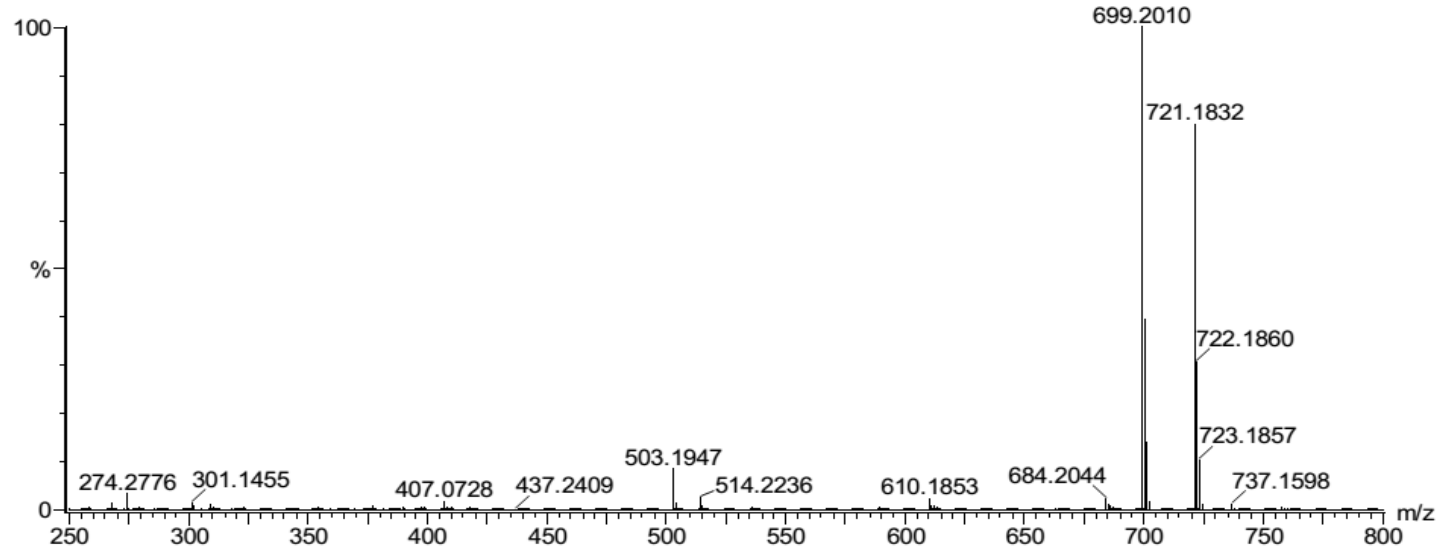

OMe
Ns
N
O
CO_2Et
CO_2Et
3ab
^{13}C-DEPT ($CDCl_3$, 100 MHz)
abundance
0.4
0.3
0.2
0.1
0
−0.1
−0.2
−0.3
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0
X : parts per Million : 13C

HRMS Spectra of **3ab:**

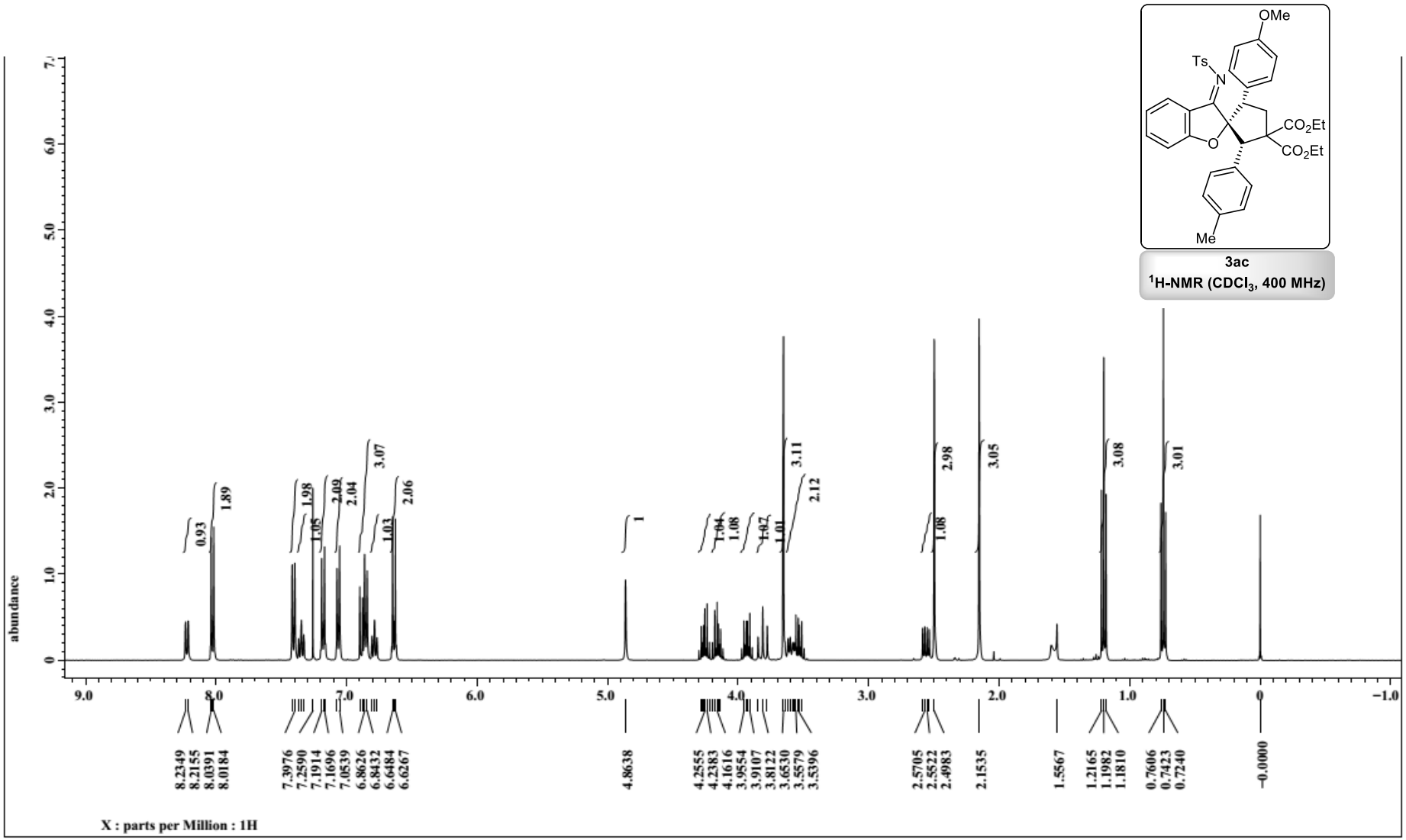
Single Mass Analysis
Tolerance = 15.0 PPM / DBE: min = -1.5, max = 50.0
Element prediction: Off
Number of isotope peaks used for i-FIT = 3

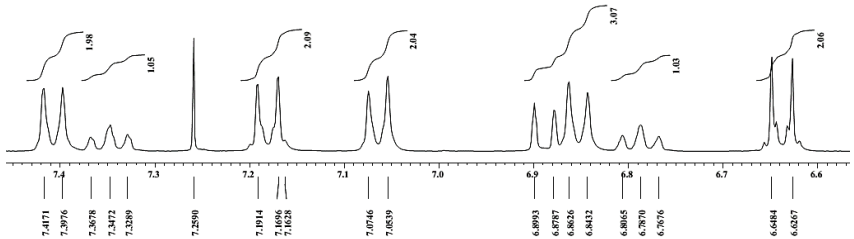
Monoisotopic Mass, Even Electron Ions
37 formula(e) evaluated with 1 results within limits (up to 50 best isotopic matches for each mass)
Elements Used:
C: 35-39 H: 30-35 N: 0-2 O: 0-10 S: 0-1

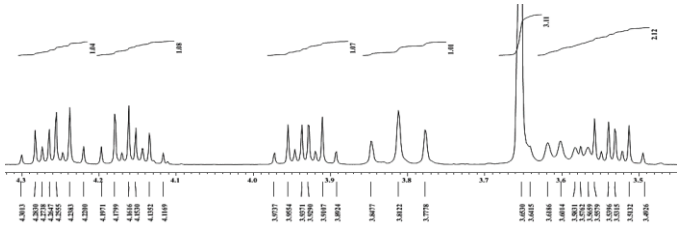
Sample Name : 07-04-079 I.I.T.ROPAR XEVO G2-XS QTOF
Test Name : HRMS-1
210518-07-04-079 19 (0.203) AM2 (Ar,16000.0,0.00,0.00); Cm (19) 1: TOF MS ES+
2.16e+006

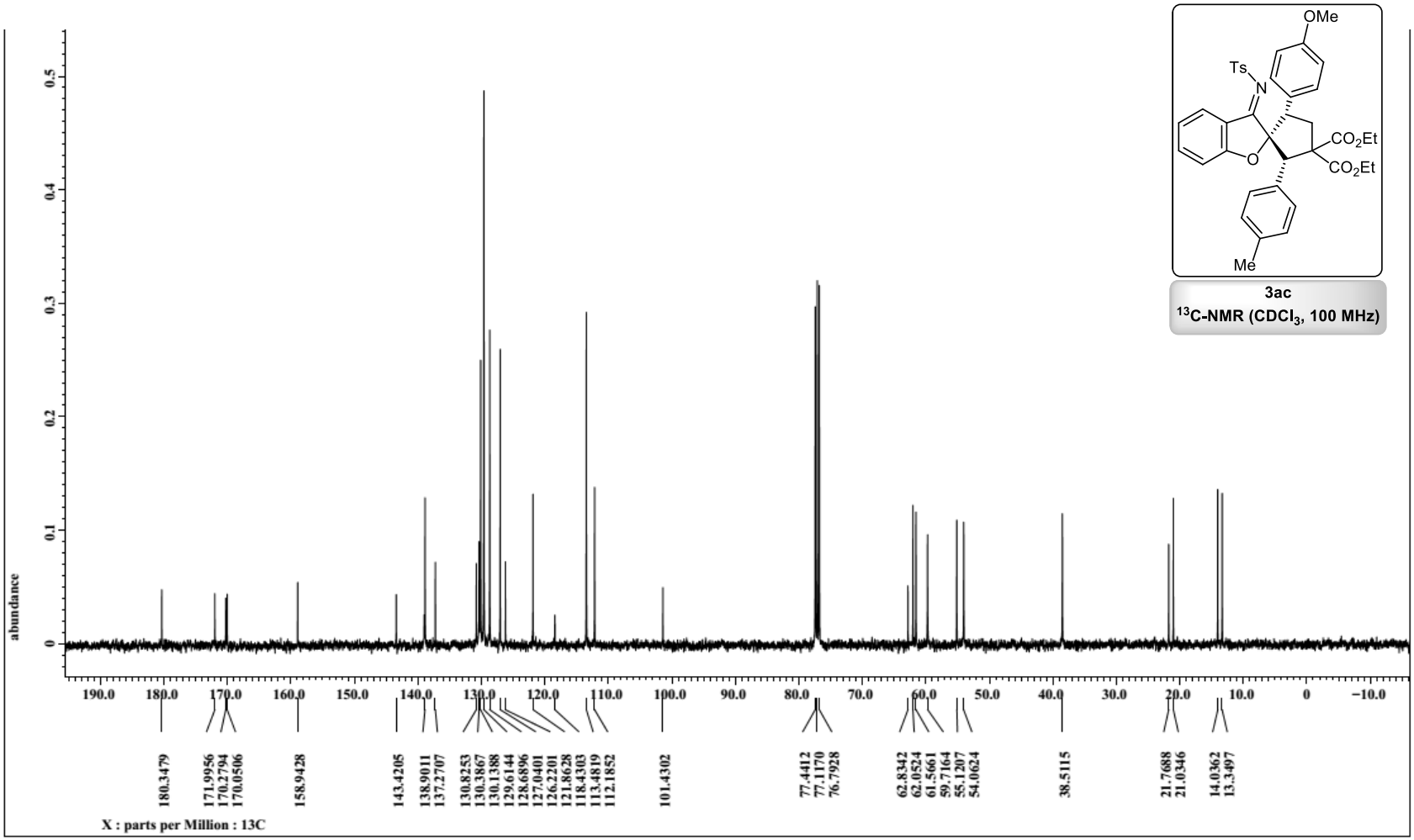


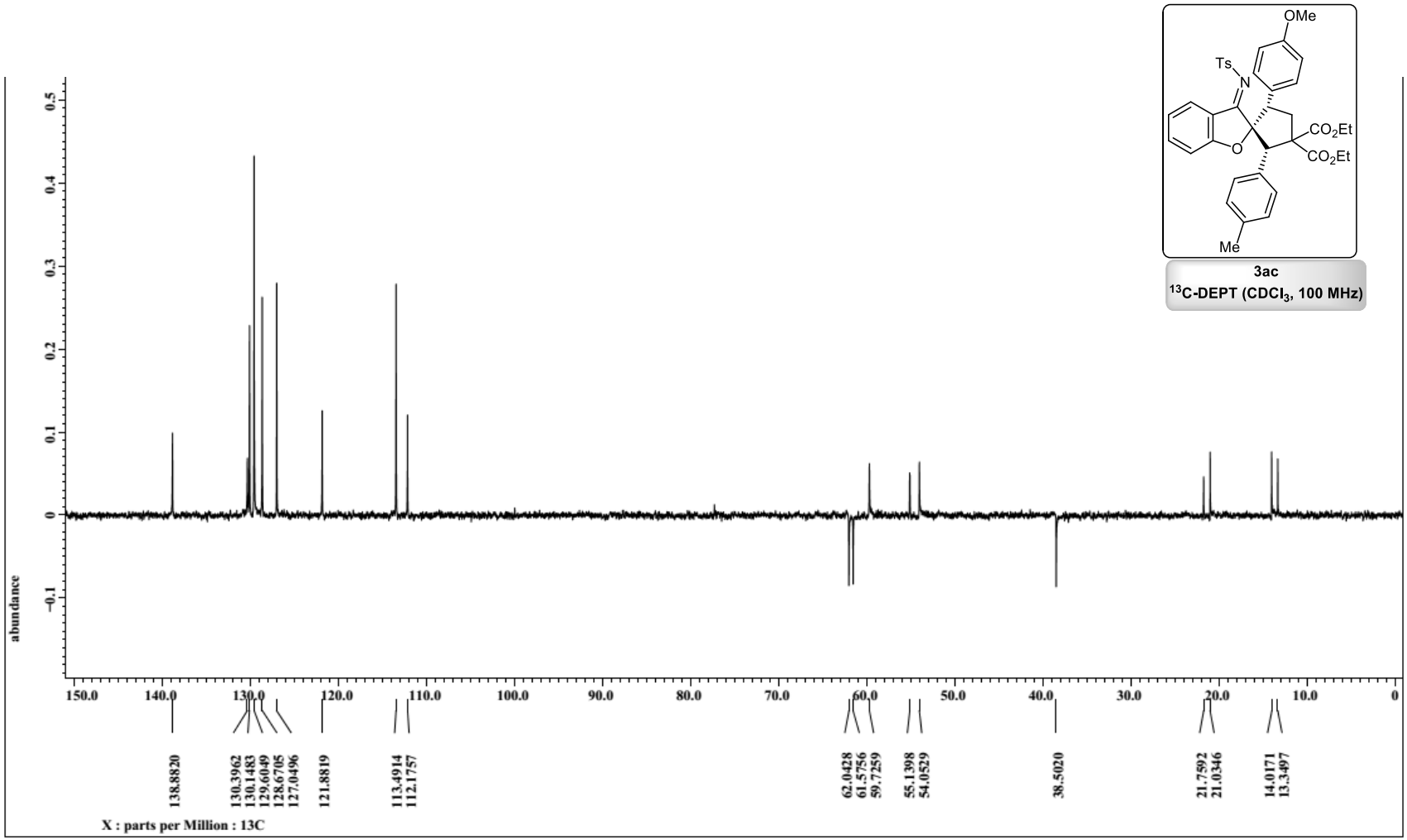
Minimum:				-1.5				
Maximum:		5.0	15.0	50.0				
Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	Norm	Conf(%)	Formula
699.2010	699.2012	-0.2	-0.3	21.5	205.2	n/a	n/a	C37 H35 N2 O10 S


OMe
Ts
N
O
CO2Et
CO2Et
Me
3ac
1H-NMR (CDCl3, 400 MHz)
abundance
X : parts per Million : 1H






OMe
Ts
N
O
CO2Et
CO2Et
Me
3ac
13C-NMR (CDCl3, 100 MHz)
abundance
0
0.1
0.2
0.3
0.4
0.5
190.0
180.0
170.0
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0
−10.0
180.3479
171.9956
170.2794
170.0506
158.9428
143.4205
138.9011
137.2707
130.8253
130.3867
130.1388
129.6144
128.6896
127.0401
126.2201
121.8628
118.4303
113.4819
112.1852
101.4302
77.4412
77.1170
76.7928
62.8342
62.0524
61.5661
59.7164
55.1207
54.0624
38.5115
21.7688
21.0346
14.0362
13.3497
X : parts per Million : 13C

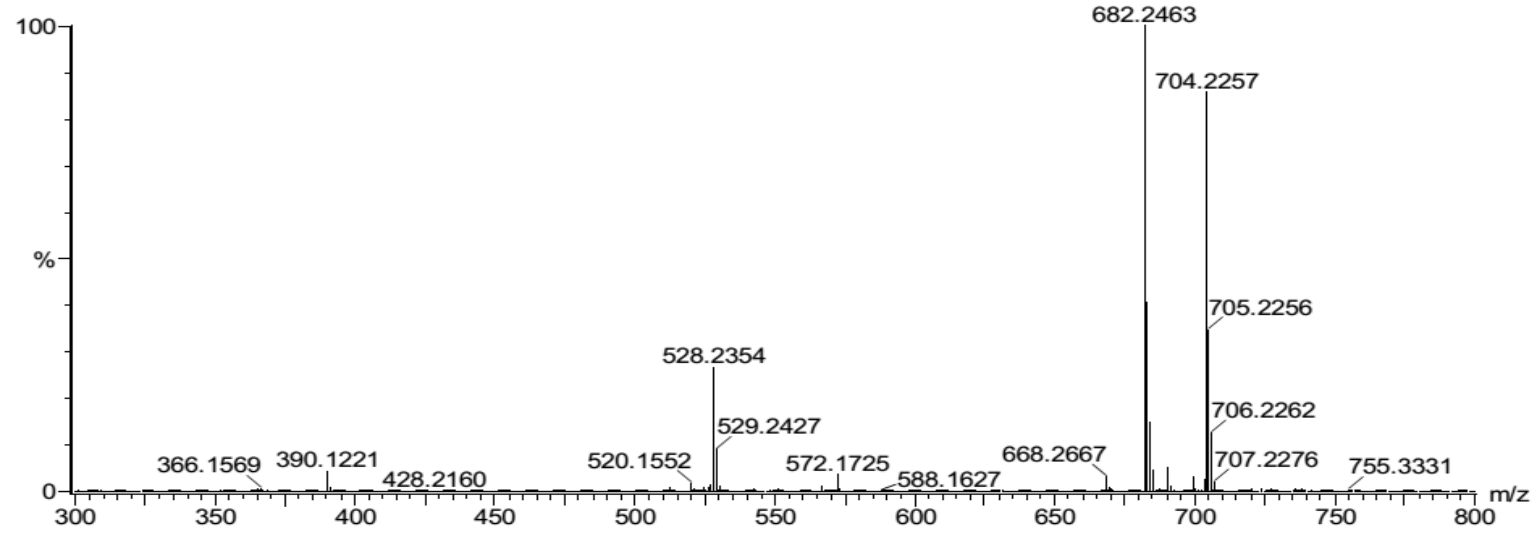

OMe
Ts
N
O
CO2Et
CO2Et
Me
3ac
13C-DEPT (CDCl3, 100 MHz)
abundance
0.5
0.4
0.3
0.2
0.1
0
−0.1
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0
138.8820
130.3962
130.1483
129.6049
128.6705
127.0496
121.8819
113.4914
112.1757
62.0428
61.5756
59.7259
55.1398
54.0529
38.5020
21.7592
21.0346
14.0171
13.3497
X : parts per Million : 13C

HRMS Spectra of **3ac:**

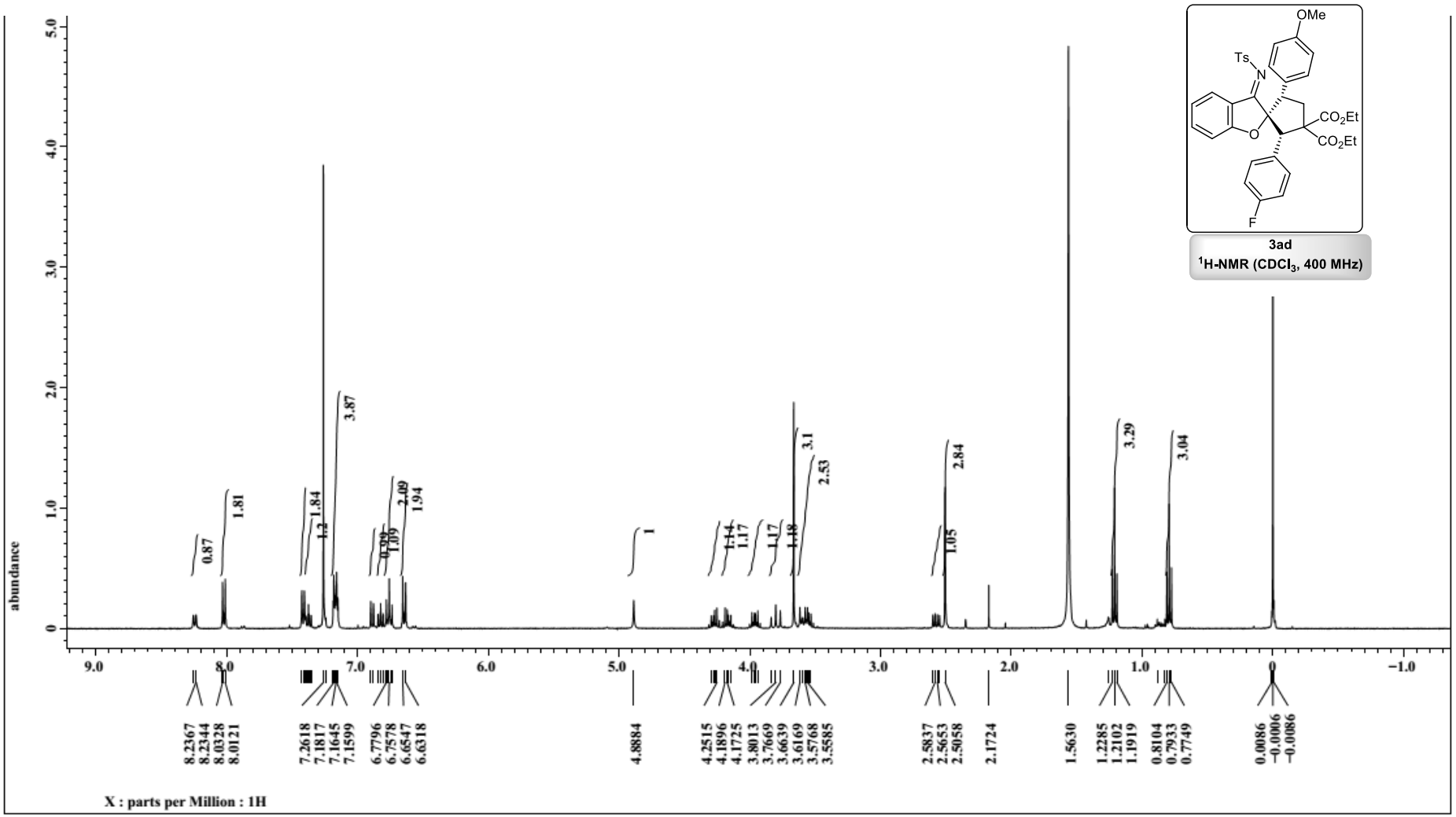
Single Mass Analysis
Tolerance = 25.0 PPM / DBE: min = -1.5, max = 50.0
Element prediction: Off
Number of isotope peaks used for i-FIT = 3

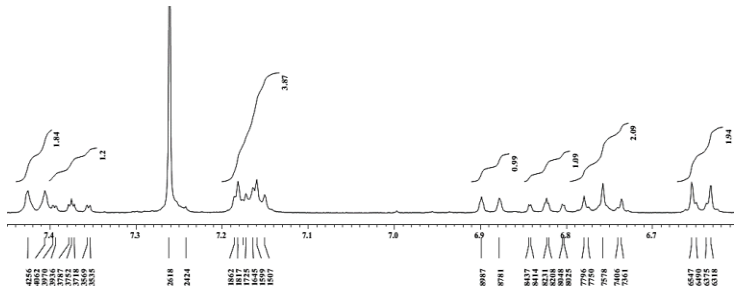
Monoisotopic Mass, Even Electron Ions
58 formula(e) evaluated with 1 results within limits (up to 50 best isotopic matches for each mass)
Elements Used:
C: 32-39 H: 32-40 N: 0-2 O: 0-8 F: 0-1 S: 0-1

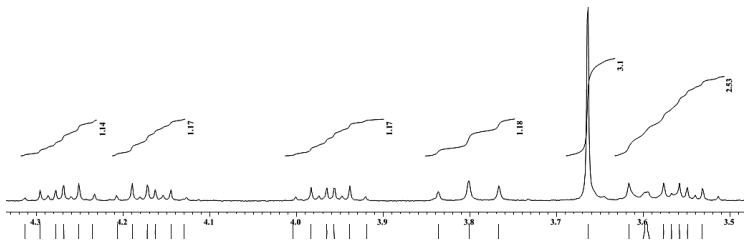
Sample Name : 07-04-055 I.I.T.ROPAR XEVO G2-XS QTOF
Test Name : HRMS-1
010518-07-04-055 17 (0.174) AM (Top,4, Ar,10000.0,0.00,0.00); Cm (17:18) 1: TOF MS ES+
1.13e+007

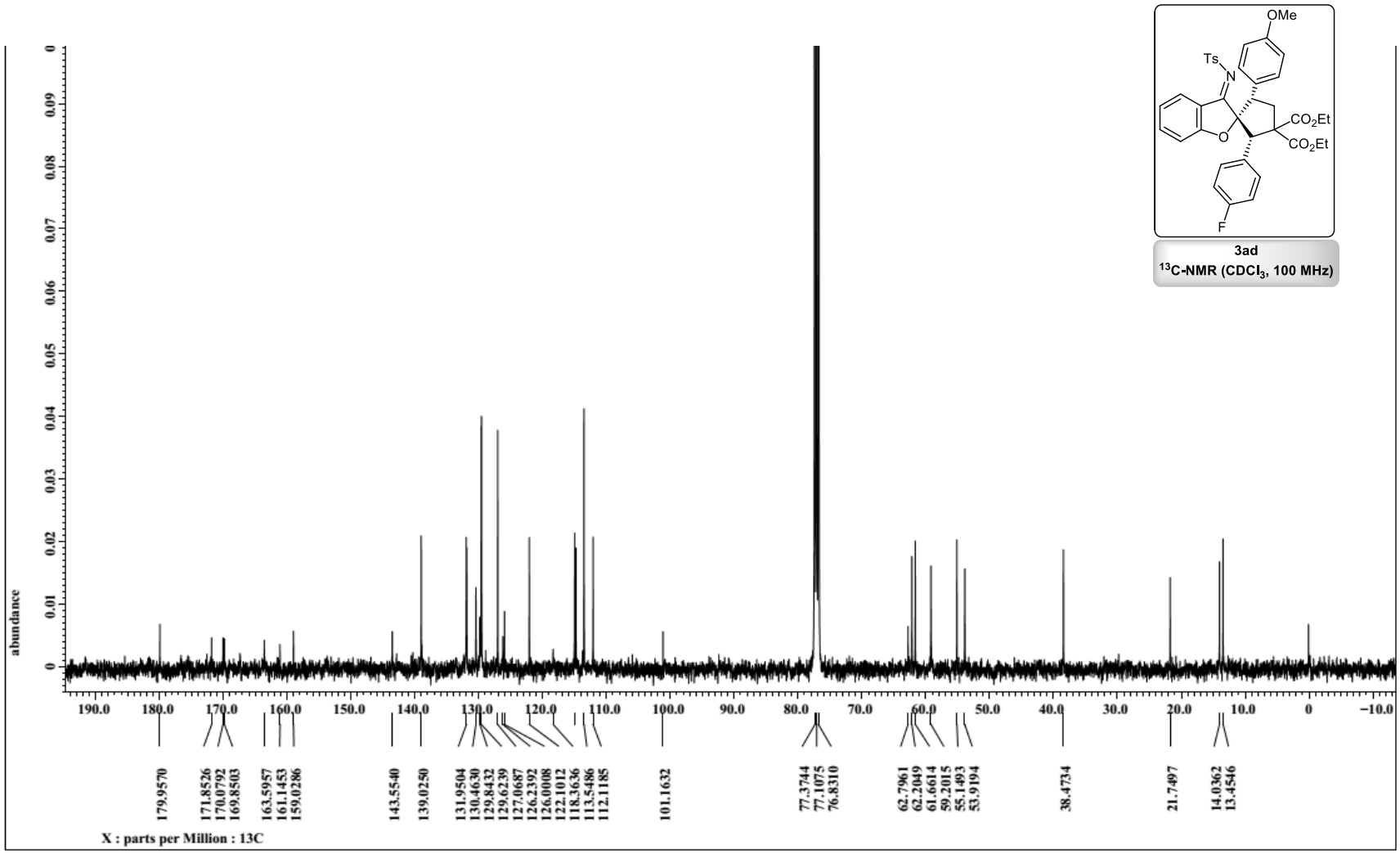


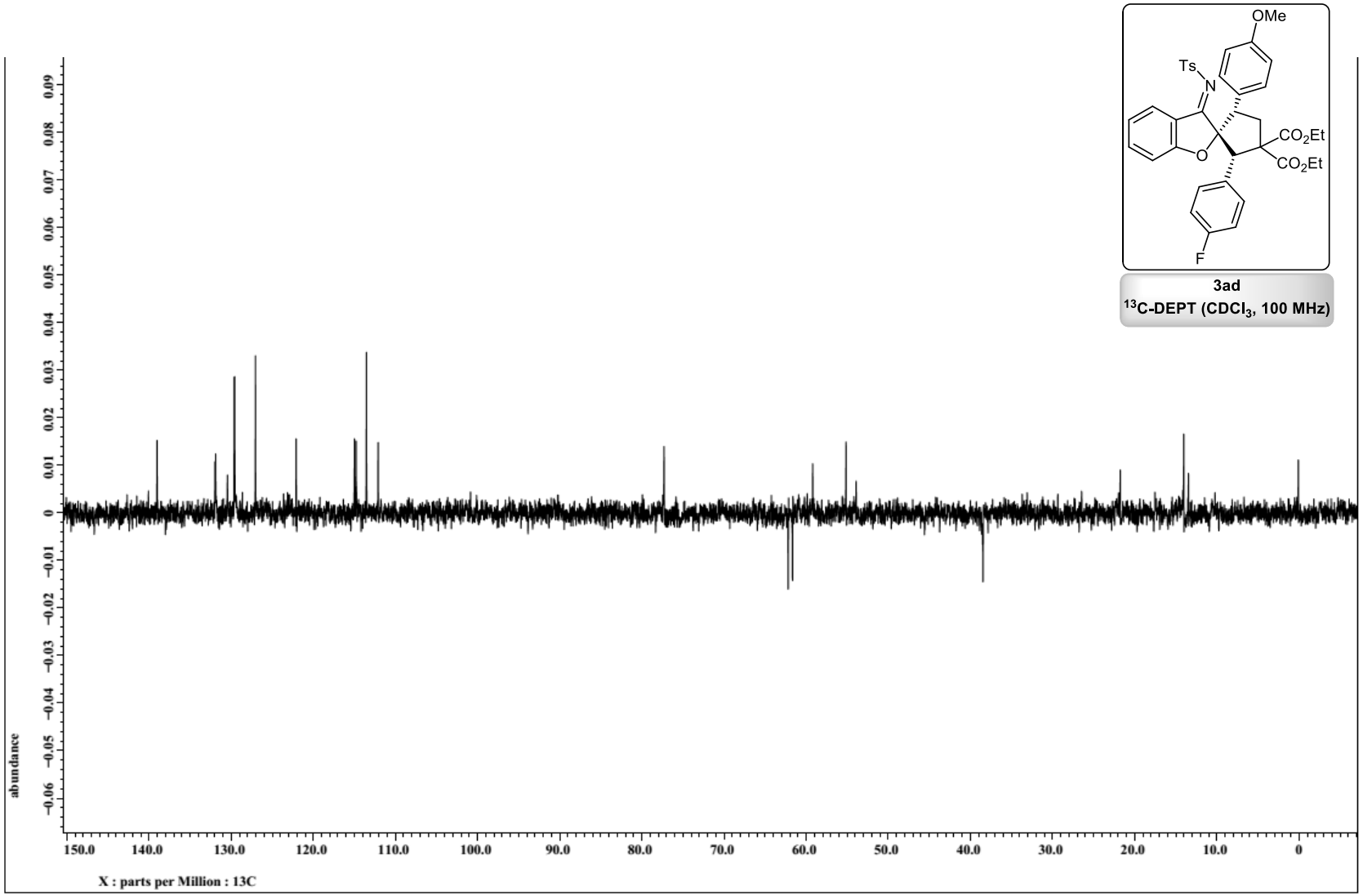
Minimum:				-1.5				
Maximum:		5.0	25.0	50.0				
Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	Norm	Conf(%)	Formula
682.2463	682.2475	-1.2	-1.8	20.5	441.9	n/a	n/a	C39 H40 N O8 S


OMe
Ts
N
O
CO2Et
CO2Et
F
3ad
1H-NMR (CDCl3, 400 MHz)
abundance
X : parts per Million : 1H






OMe
Ts
N
O
CO2Et
CO2Et
F
3ad
13C-NMR (CDCl3, 100 MHz)
abundance
X : parts per Million : 13C
179.9570
171.8526
170.0792
169.8503
163.5957
161.1453
159.0286
143.5540
139.0250
131.9504
130.4630
129.8432
129.6239
127.0687
126.2392
126.0008
122.1012
118.3636
113.5486
112.1185
101.1632
77.3744
77.1075
76.8310
62.7961
62.2049
61.6614
59.2015
55.1493
53.9194
38.4734
21.7497
14.0362
13.4546

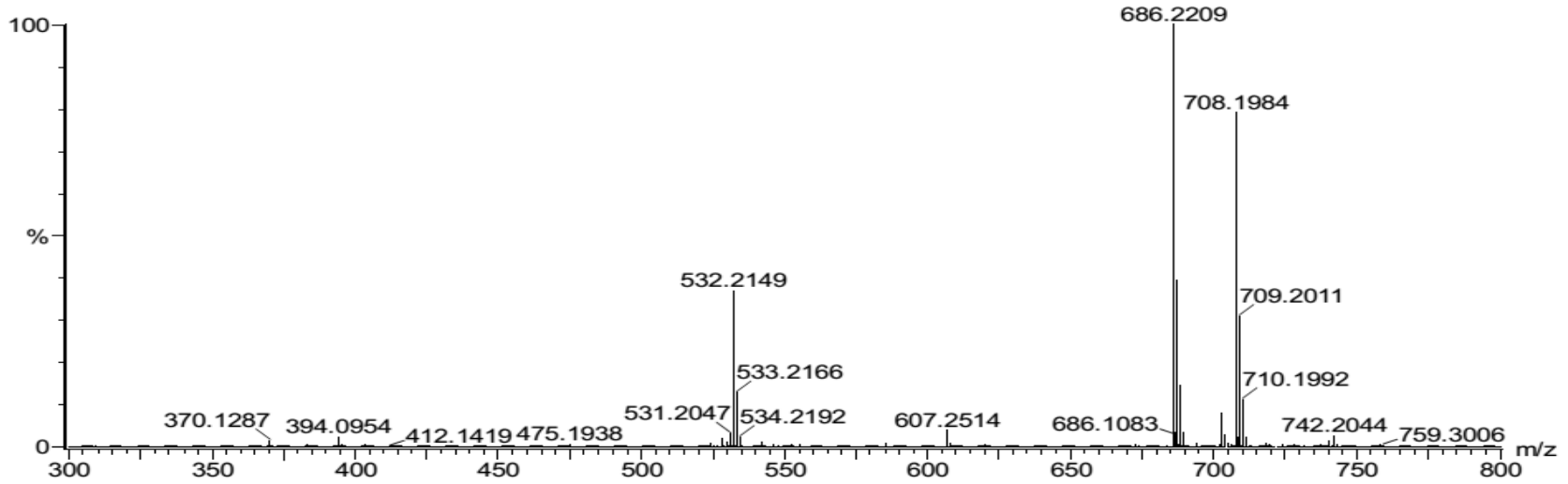

OMe
Ts
N
O
CO2Et
CO2Et
F
3ad
13C-DEPT (CDCl3, 100 MHz)
abundance
0.09
0.08
0.07
0.06
0.05
0.04
0.03
0.02
0.01
0
−0.01
−0.02
−0.03
−0.04
−0.05
−0.06
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0
X : parts per Million : 13C

HRMS Spectra of **3ad:**

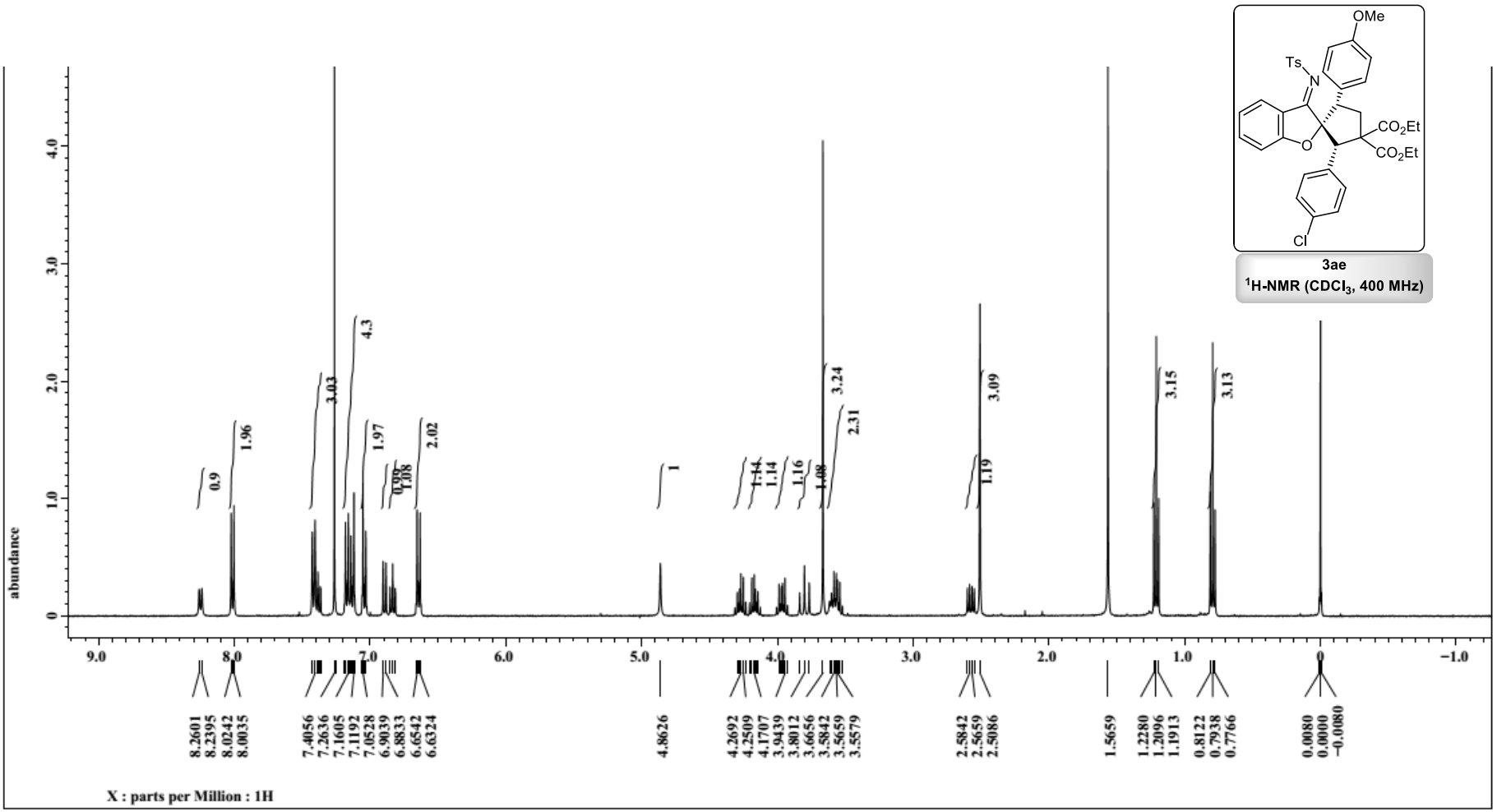
Single Mass Analysis
Tolerance = 25.0 PPM / DBE: min = -1.5, max = 50.0
Element prediction: Off
Number of isotope peaks used for i-FIT = 3

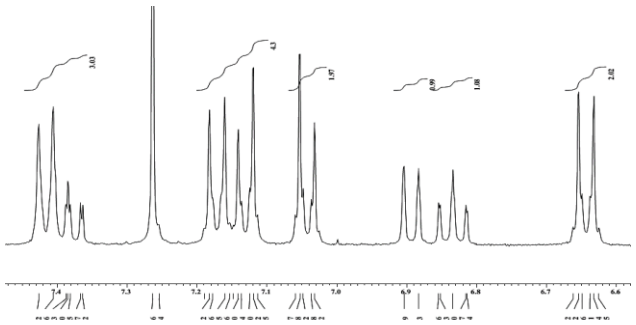
Monoisotopic Mass, Even Electron Ions
58 formula(e) evaluated with 1 results within limits (up to 50 best isotopic matches for each mass)
Elements Used:
C: 32-39 H: 32-40 N: 0-2 O: 0-8 F: 0-1 S: 0-1

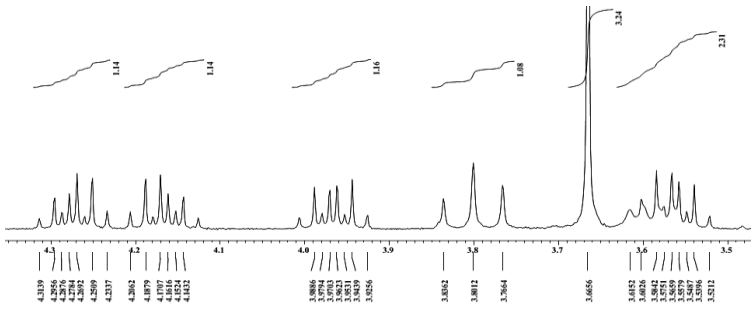
Sample Name : 07-04-050 I.I.T.ROPAR XEVO G2-XS QTOF
Test Name : HRMS-1
010518-07-04-050 15 (0.157) AM (Top,4, Ar,10000.0,0.00,0.00); Cm (15:18) 1: TOF MS ES+
2.58e+007

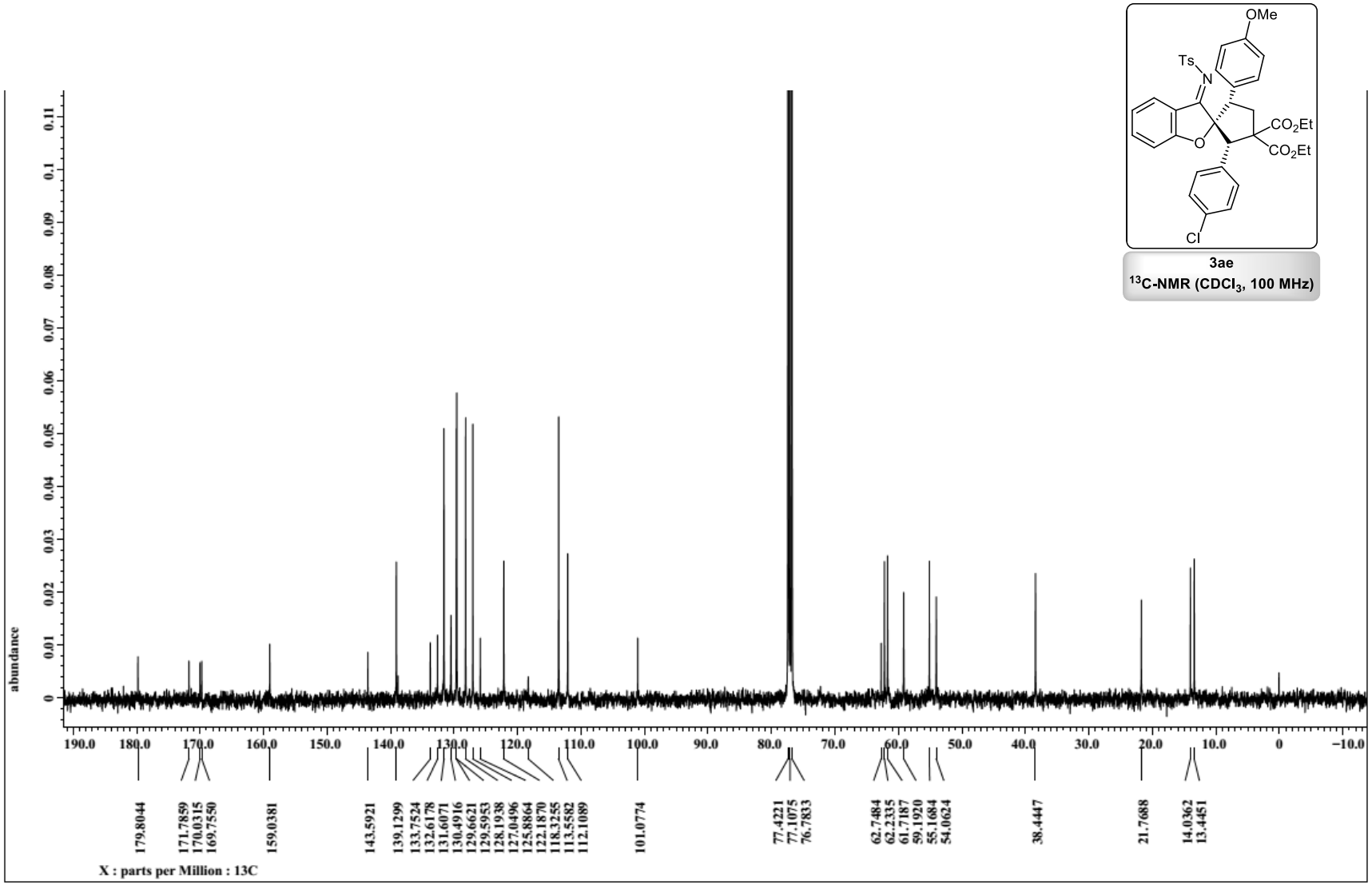


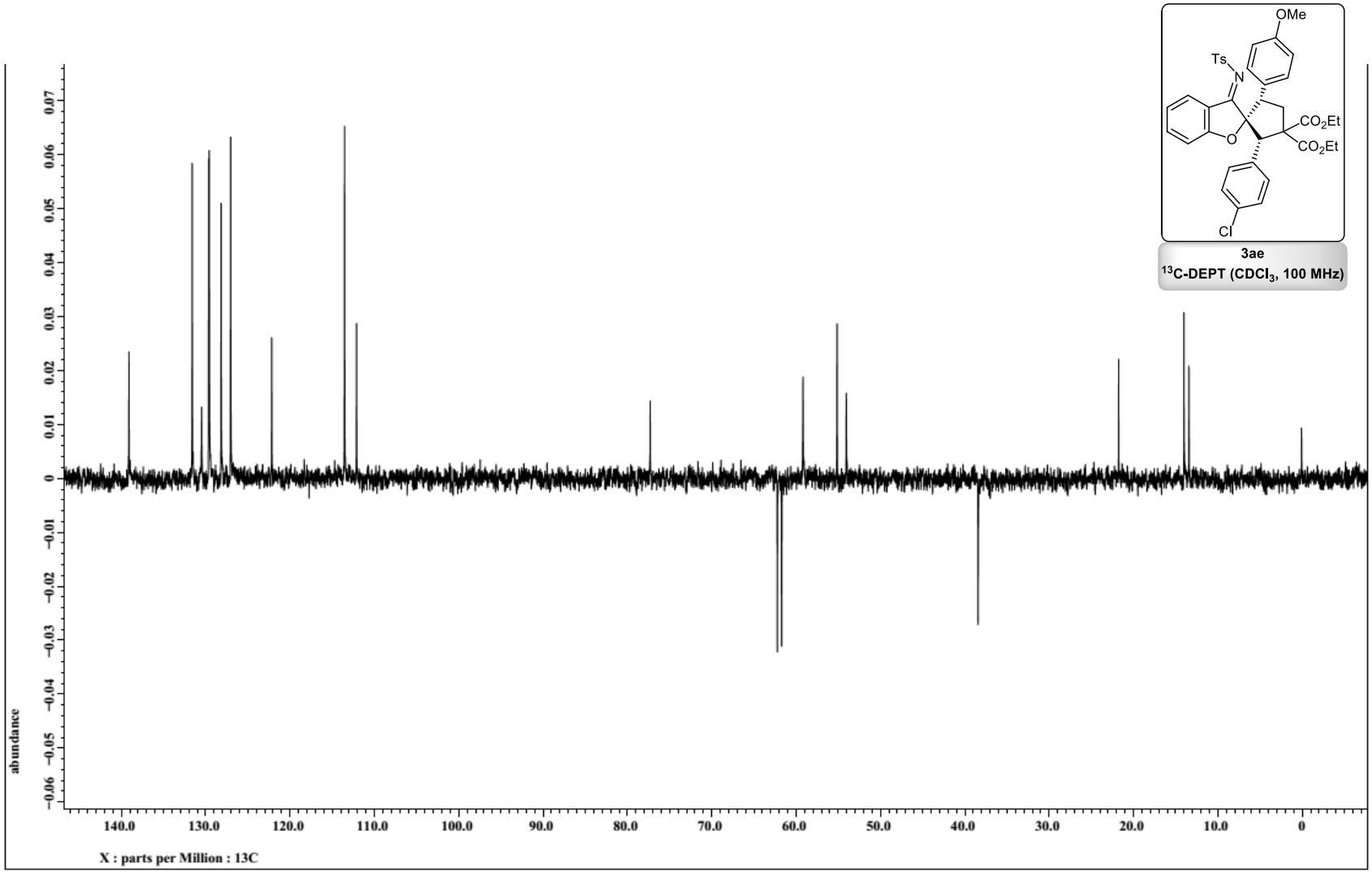
Minimum:				-1.5				
Maximum:		5.0	25.0	50.0				
Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	Norm	Conf(%)	Formula
686.2209	686.2224	-1.5	-2.2	20.5	562.0	n/a	n/a	C38 H37 N O8 F S


OMe
Ts
N
O
CO2Et
CO2Et
Cl
3ae
1H-NMR (CDCl3, 400 MHz)
abundance
X : parts per Million : 1H






OMe
Ts
N
O
CO2Et
CO2Et
Cl
3ae
13C-NMR (CDCl3, 100 MHz)
abundance
0
0.01
0.02
0.03
0.04
0.05
0.06
0.07
0.08
0.09
0.1
0.11
190.0
180.0
170.0
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0
−10.0
179.8044
171.7859
170.0315
169.7550
159.0381
143.5921
139.1299
133.7524
132.6178
131.6071
130.4916
129.6621
129.5953
128.1938
127.0496
125.8864
122.1870
118.3255
113.5582
112.1089
101.0774
77.4221
77.1075
76.7833
62.7484
62.2335
61.7187
59.1920
55.1684
54.0624
38.4447
21.7688
14.0362
13.4451
X : parts per Million : 13C


OMe
Ts
N
O
CO2Et
CO2Et
Cl
3ae
13C-DEPT (CDCl3, 100 MHz)
abundance
0.07
0.06
0.05
0.04
0.03
0.02
0.01
0
−0.01
−0.02
−0.03
−0.04
−0.05
−0.06
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0
X : parts per Million : 13C

HRMS Spectra of **3ae:**

Single Mass Analysis

Tolerance = 10.0 PPM / DBE: min = -1.5, max = 50.0

Element prediction: Off

Number of isotope peaks used for i-FIT = 3

Monoisotopic Mass, Even Electron Ions

112 formula(e) evaluated with 1 results within limits (up to 50 best isotopic matches for each mass)

Elements Used:

C: 35-40 H: 35-40 N: 0-2 O: 0-8 S: 0-1 Cl: 0-1 Na: 0-1

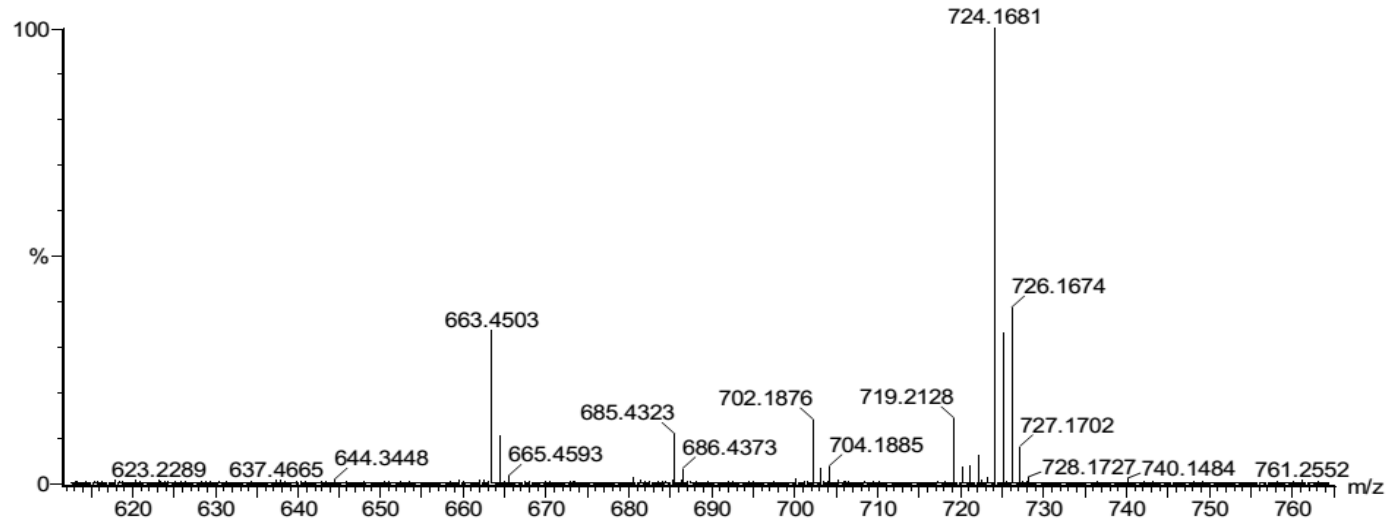
Sample Name : 07-04-067 I.I.T.ROPAR XEVO G2-XS QTOF

Test Name : HRMS-1

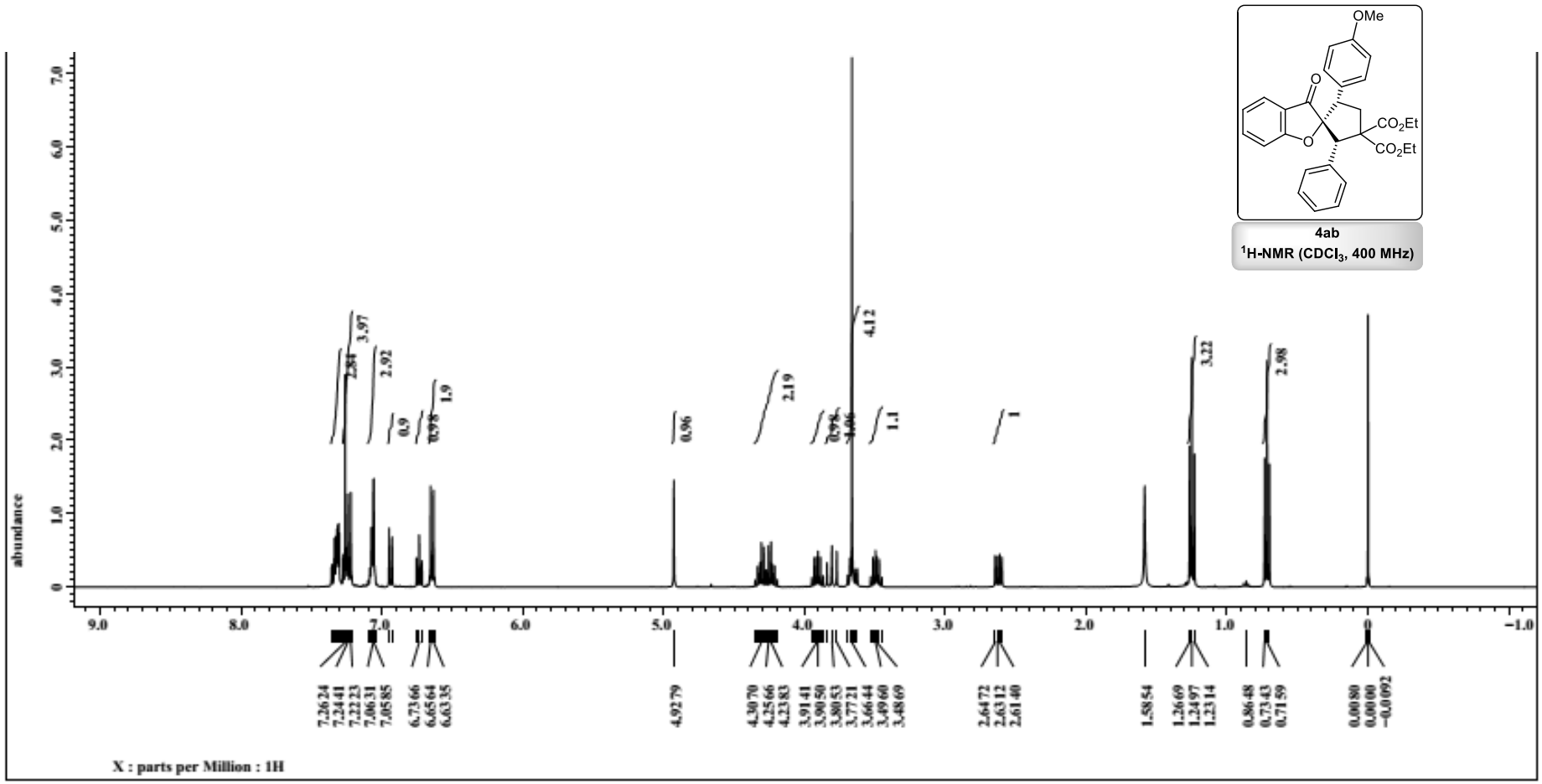
150518-07-04-067 13 (0.140) AM2 (Ar,16000.0,0.00,0.00); Cm (13:18)

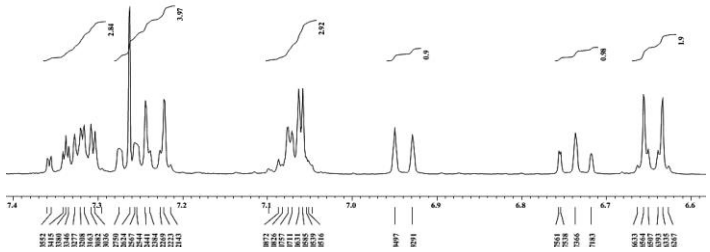
1: TOF MS ES+

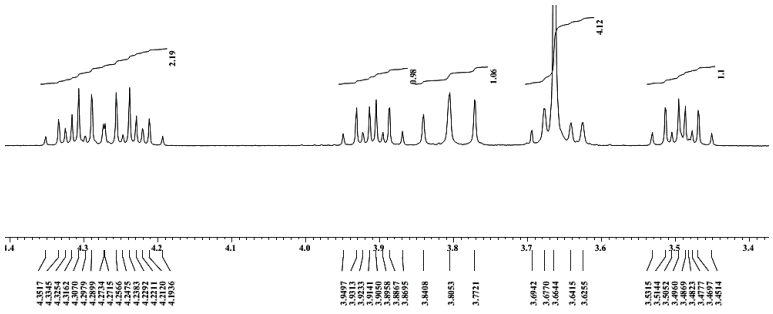
2.26e+006

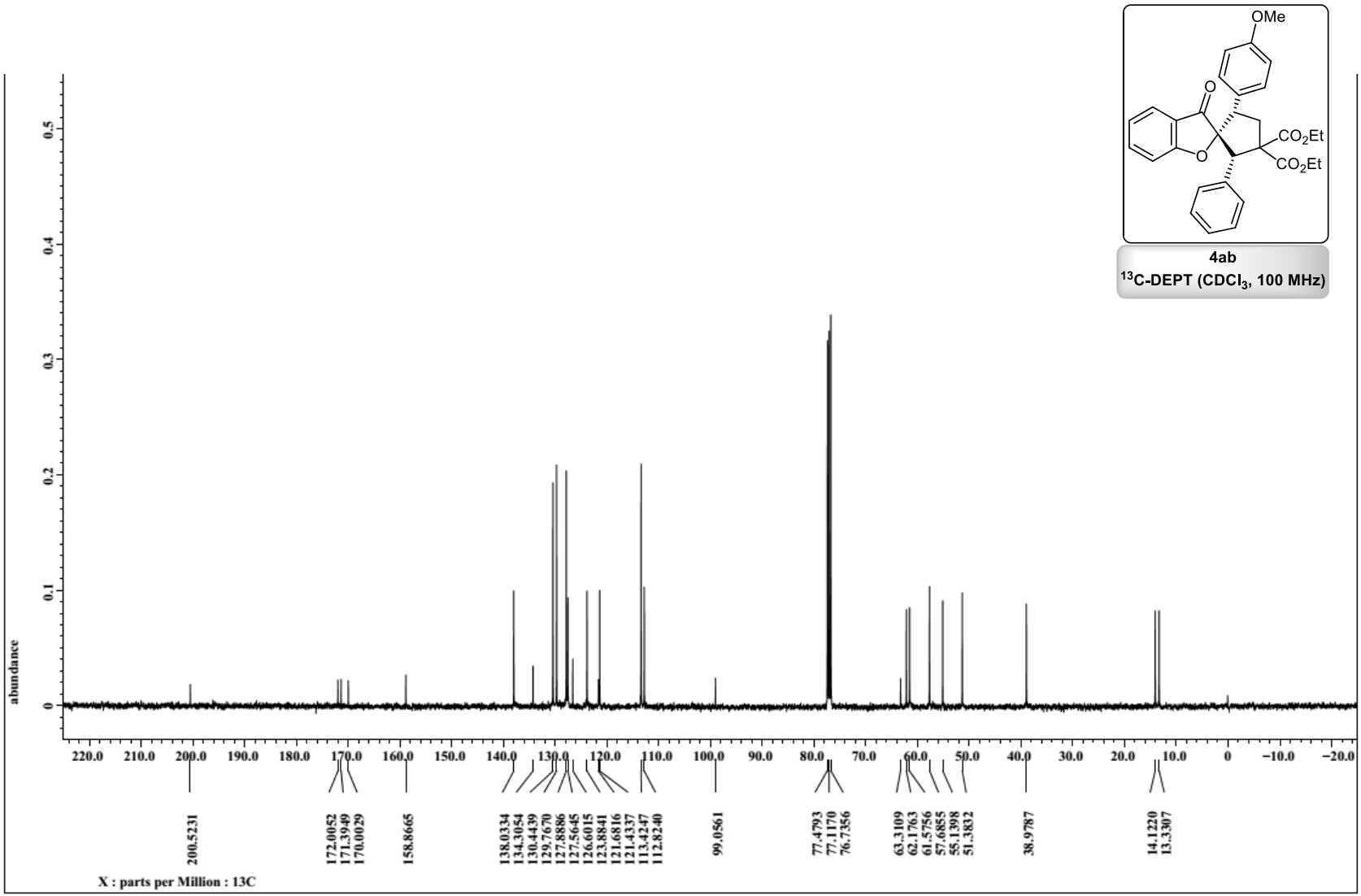


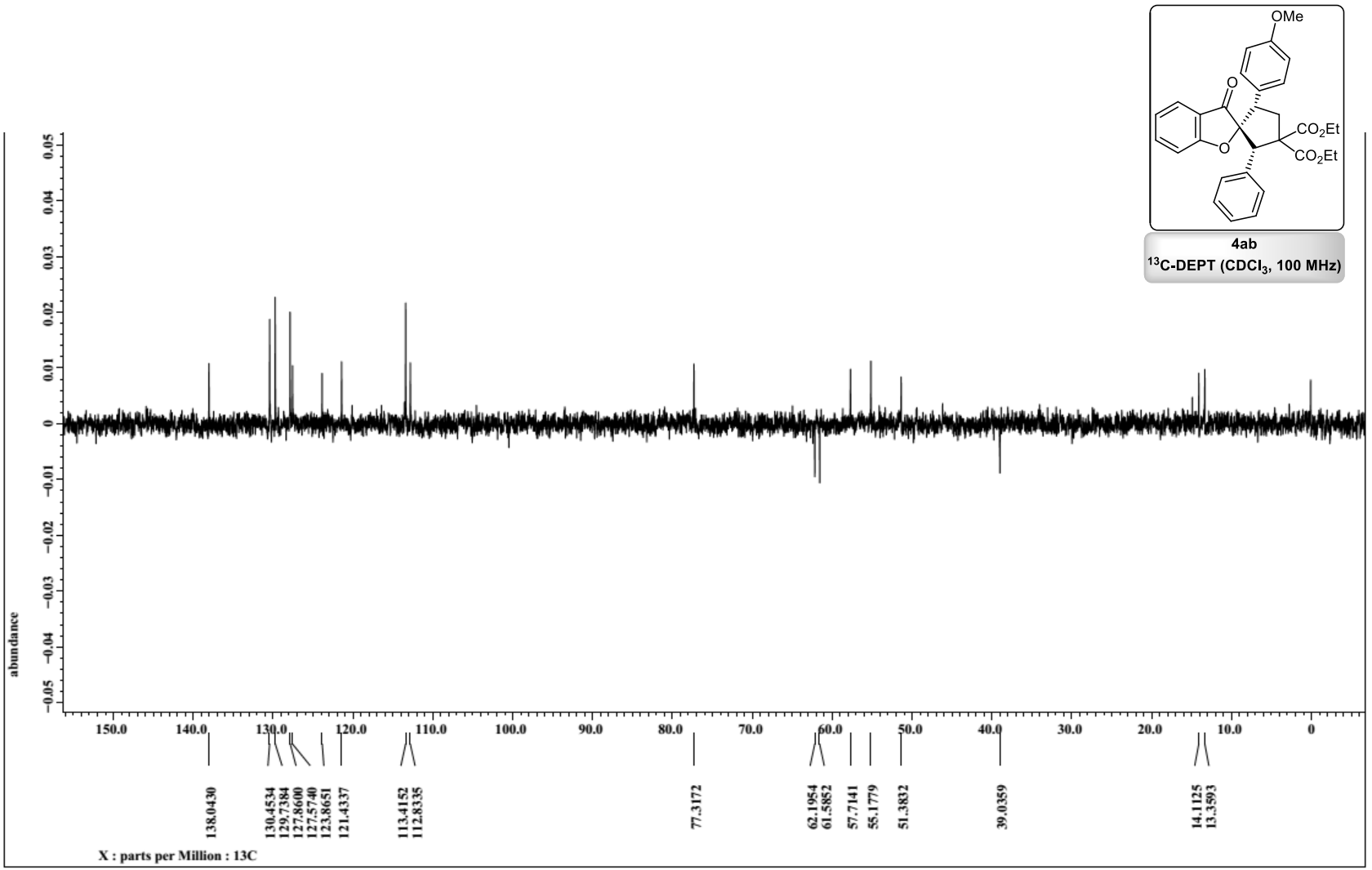
Minimum:				-1.5				
Maximum:		5.0	10.0	50.0				
Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	Norm	Conf(%)	Formula
724.1681	724.1748	-6.7	-9.3	20.5	255.6	n/a	n/a	C38 H36 N O8 S Cl Na


OMe
O
O
CO2Et
CO2Et
4ab
1H-NMR (CDCl3, 400 MHz)
abundance
X : parts per Million : 1H






OMe
O
O
CO2Et
CO2Et
4ab
13C-DEPT (CDCl3, 100 MHz)
abundance
0
0.1
0.2
0.3
0.4
0.5
220.0 210.0 200.0 190.0 180.0 170.0 160.0 150.0 140.0 130.0 120.0 110.0 100.0 90.0 80.0 70.0 60.0 50.0 40.0 30.0 20.0 10.0 0 −10.0 −20.0
200.5231
172.0052
171.3949
170.0029
158.8665
138.0334
134.3054
130.4439
129.7670
127.8886
127.5645
126.6015
123.8841
121.6816
121.4337
113.4247
112.8240
99.0561
77.4793
77.1170
76.7356
63.3109
62.1763
61.5756
57.6855
55.1398
51.3832
38.9787
14.1220
13.3307
X : parts per Million : 13C

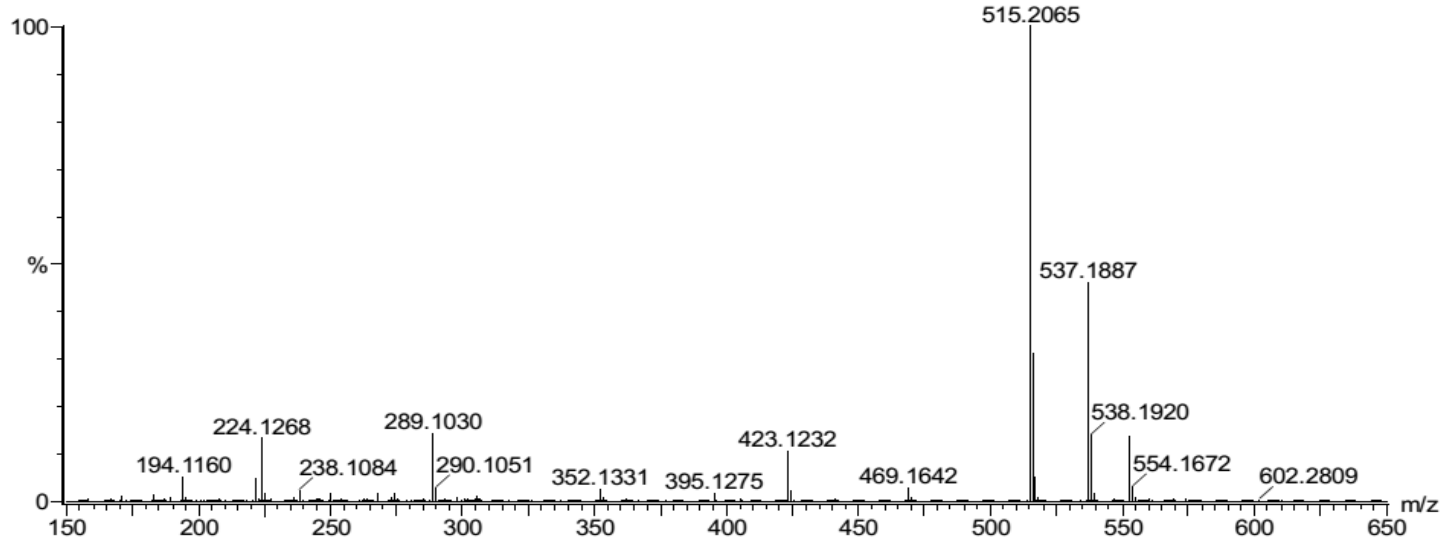

OMe
O
O
CO2Et
CO2Et
4ab
13C-DEPT (CDCl3, 100 MHz)
abundance
0.05
0.04
0.03
0.02
0.01
0
−0.01
−0.02
−0.03
−0.04
−0.05
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0
138.0430
130.4534
129.7384
127.8600
127.5740
123.8651
121.4337
113.4152
112.8335
77.3172
62.1954
61.5852
57.7141
55.1779
51.3832
39.0359
14.1125
13.3593
X : parts per Million : 13C

HRMS Spectra of **4ab:**

Single Mass Analysis
Tolerance = 10.0 PPM / DBE: min = -1.5, max = 50.0
Element prediction: Off
Number of isotope peaks used for i-FIT = 3

Monoisotopic Mass, Even Electron Ions
3 formula(e) evaluated with 1 results within limits (up to 50 closest results for each mass)
Elements Used:
C: 25-35 H: 31-35 O: 0-7

Sample Name : 15-01-129 I.I.T.ROPAR XEVO G2-XS QTOF
Test Name : HRMS-1
090818-15-01-129 19 (0.203) AM2 (Ar,19000.0,0.00,0.00); Cm (19) 1: TOF MS ES+
1.17e+006



Minimum:				-1.5				
Maximum:		5.0	10.0	50.0				
Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	Norm	Conf(%)	Formula
515.2065	515.2070	-0.5	-1.0	16.5	353.2	n/a	n/a	C31 H31 O7

2. X-Ray diffraction:

For the determination of X-ray crystal structures of **3ba** and **4ab** a single crystal was selected and mounted with paratone oil on a glass fiber using gum. The data was collected at 293K on a CMOS based Bruker D8 Venture PHOTON 100 diffractometer equipped with INCOATEC micro-focus source with graphite monochromatic Mo Kα radiation (λ = 0.71073 Å) operation at 50 kV and 30 mA. For the integration of diffraction profiles SAINT program[3] was used. Absorption correction was done applying SADABS program.[4] The crystal structure was solved by SIR 92[5] and refined by full matrix least square method using SHELXL-97[6] WinGX system, Ver 1.70.01.[7] All the non-hydrogen atoms in the structure were located the Fourier map and refined anisotropically. The hydrogen atoms were fixed by HFIX in their ideal positions and refined using riding model with isotropic thermal parameters.

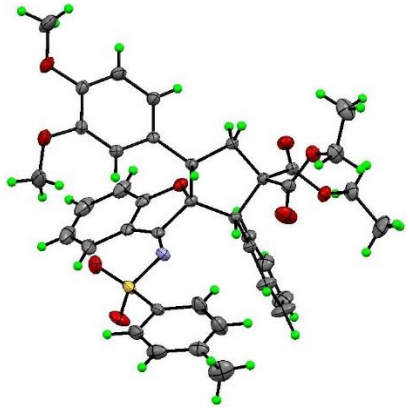


Figure 1: ORTEP structure of **3ba**

CCDC No.	CCDC 1860991
Formula	C39 H39 N O9 S
Formula weight	697.78
Crystal System	Monoclinic
Space group	P21/c
a, b, c (Å)	17.483(5), 8.483(5), 24.544(5)
α, β, γ (°)	90, 97.103(5), 90
V (Å^3)	3612(2)

Z	4
Calculated Density (g/cm^3)	1.283
Absorption coefficient (mm^{-1})	0.146
F(000)	1472
Theta range for data collection:	2.3 to 28.4
Data set	-23: 23; -10: 11; -32: 32
Reflection	178649
Independent refl.	9006, (R(int) = 0.178)
data [I > 2σ(I)]	4870
R indices (all data)	R = 0.1027, wR_2 = 0.1748
S	1.16
Min. and Max. Resd. Dens. (e/Å^3)	-0.31 and 0.19

Table 1 Selected bond lengths [Å] of **3ba.**

S1-O1	1.435(3)	C10-C11	1.373(7)
S1-O2	1.429(3)	C11-C12	1.379(7)
S1-N1	1.632(3)	C12-C13	1.362(6)
S1-C5	1.754(4)	C13-C14	1.382(5)
O3-C34	1.367(4)	C15-C16	1.542(4)
O3-C38	1.399(5)	C15-C19	1.531(4)
O4-C35	1.368(4)	C16-C17	1.525(4)
O4-C39	1.399(5)	C16-C32	1.516(4)
O5-C14	1.355(4)	C17-C18	1.541(4)
O5-C15	1.449(3)	C18-C19	1.573(4)
O6-C29	1.195(4)	C18-C26	1.523(4)
O7-C29	1.327(4)	C18-C29	1.524(4)
O7-C30	1.453(4)	C19-C20	1.508(4)
O8-C26	1.329(4)	C20-C21	1.389(5)
O8-C27	1.460(4)	C20-C25	1.382(5)
O9-C26	1.189(4)	C21-C22	1.374(5)
N1-C8	1.291(4)	C22-C23	1.364(6)

C1-C2	1.505(6)	C23-C24	1.359(7)
C2-C3	1.364(6)	C24-C25	1.381(6)
C2-C7	1.365(6)	C27-C28	1.484(6)
C3-C4	1.380(6)	C30-C31	1.496(6)
C4-C5	1.378(5)	C32-C33	1.402(4)
C5-C6	1.369(5)	C32-C37	1.371(4)
C6-C7	1.374(6)	C33-C34	1.373(4)
C8-C9	1.439(5)	C34-C35	1.395(5)
C8-C15	1.511(4)	C35-C36	1.371(5)
C9-C10	1.402(5)	C36-C37	1.390(5)
C9-C14	1.386(5)	C1-H1A	0.9600

Table 2 Selected bond angles [º] of **3ba**

O1-S1-O2	116.93(17)	C9-C10-C11	118.3(4)
O1-S1-N1	108.61(14)	C10-C11-C12	120.6(4)
O1-S1-C5	108.30(16)	C11-C12-C13	122.7(4)
O2-S1-N1	112.23(15)	C12-C13-C14	116.7(3)
O2-S1-C5	108.95(15)	O5-C14-C9	114.5(3)
N1-S1-C5	100.50(14)	O5-C14-C13	122.9(3)
C34-O3-C38	118.4(3)	C9-C14-C13	122.6(3)
C35-O4-C39	117.4(3)	O5-C15-C8	105.6(2)
C14-O5-C15	106.9(2)	O5-C15-C16	107.6(2)
C29-O7-C30	116.0(3)	O5-C15-C19	112.9(2)
C26-O8-C27	117.9(2)	C8-C15-C16	113.4(2)
S1-N1-C8	124.1(2)	C8-C15-C19	114.2(2)
C1-C2-C3	121.5(4)	C16-C15-C19	103.2(2)
C1-C2-C7	121.8(4)	C15-C16-C17	101.6(2)
C3-C2-C7	116.8(4)	C15-C16-C32	115.5(2)
C2-C3-C4	122.1(4)	C17-C16-C32	116.2(2)
C3-C4-C5	119.9(4)	C16-C17-C18	105.4(2)
S1-C5-C4	117.6(3)	C17-C18-C19	104.7(2)
S1-C5-C6	123.6(3)	C17-C18-C26	109.3(2)

C4-C5-C6	118.8(3)	C17-C18-C29	111.4(2)
C5-C6-C7	119.6(4)	C19-C18-C26	110.3(2)
C2-C7-C6	122.8(4)	C19-C18-C29	111.8(2)
N1-C8-C9	137.2(3)	C26-C18-C29	109.3(2)
N1-C8-C15	116.8(3)	C15-C19-C18	105.4(2)
C9-C8-C15	106.1(3)	C15-C19-C20	118.2(2)
C8-C9-C10	134.5(3)	C18-C19-C20	117.2(2)
C8-C9 -C14	106.4(3)	C19-C20-C21	123.5(3)
C10-C9-C14	119.1(3)	C19-C20-C25	118.5(3)
C2-C20-C25	117.9(3)	C2-C1-H1C	109.00
C20-C21-C22	120.7(3)	H1A-C1-H1B	109.00
C21-C22-C23	120.3(4)	H1A -C1-H1C	110.00
C22-C23-C24	120.2(4)	H1B-C1-H1C	109.00
C23-C24-C25	120.1(4)	C2-C3-H3	119.00
C20-C25-C24	120.8(4)	C4-C3-H3	119.00
O8-C26-O9	123.5(3)	C3-C4-H4	120.00
O8-C26-C18	110.7(3)	C5-C4-H4	120.00
O9-C26-C18	125.7(3)	C5-C6-H6	120.00
O8-C27-C28	106.9(3)	C7-C6-H6	120.00
O6-C29-O7	124.6(3)	C2-C7-H7	119.00
O6-C29-C18	124.9(3)	C6-C7-H7	119.00
O7-C29-C18	110.5(3)	C9-C10-H10	121.00
O7-C30-C31	106.8(3)	C11-C10-H10	121.00
C16-C32-C33	120.4(2)	C10-C11-H11	120.00
C16-C32-C37	122.1(3)	C12-C11-H11	120.00
C33-C32-C37	117.6(3)	C11-C12-H12	119.00
C32-C33-C34	121.5(3)	C13-C12-H12	119.00
O3-C34-C33	125.3(3)	C12-C13-H13	122.00
O3-C34-C35	114.7(3)	C14-C13-H13	122.00
C33-C34 -C35	120.0(3)	C15-C16-H16	108.00
O4 -C35-C34	116.1(3)	C17-C16-H16	108.00
O4-C35-C36	125.0(3)	C32-C16-H16	108.00
C34-C35-C36	118.9(3)	C16-C17-H17A	111.00

C35-C36-C37	120.7(3)	C16-C17-H17B	111.00
C32-C37-C36	121.3(3)	C18-C17-H17A	111.00
C2-C1-H1A	109.00	C18-C17-H17B	111.00
C2-C1-H1B	109.00	H17A-C17 -H17B	109.00

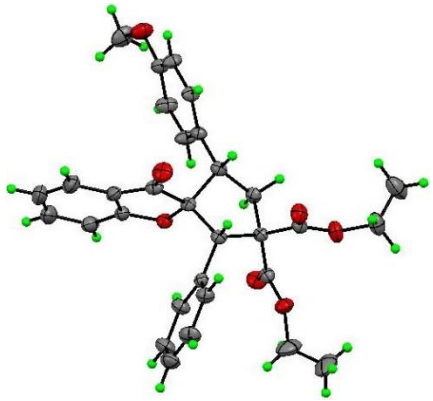


Figure 2: ORTEP structure of **4ab**

CCDC No.	CCDC 1862808
Formula	C31H30O7
Formula weight	514.55
Crystal System	Triclinic
Space group	P-1
a, b, c (Å)	9.539, 9.870, 15.022
α, β, γ (°)	95.6, 97.2, 99.2
V ($Å^3$)	1374.4(11)
Z	2
Calculated Density (g/cm^3)	1.243
Absorption coefficient (mm^{-1})	0.088
F(000)	544
Theta range for data collection:	2.2 to 28.3

Data set	-12: 12; -13:13; -20: 19
Reflection	24174
Independent refl.	6760, (R(int) = 0.077)
data [I > 2σ(I)]	3531
R indices (all data)	R = 0.0806, wR_2 = 0.0806
S	1.04
Min. and Max. Resd. Dens. (e/Å^3)	-0.24 and 0.31

Table 3 Selected bond lengths [Å] of **4ab**.

O1-C4	1.445(4)	C16-C17	1.404(6)
O1-C31	1.364(4)	C18-C19	1.389(4)
O2-C25	1.211(4)	C18-C23	1.378(5)
O3-C15	1.199(4)	C19-C20	1.365(5)
O4-C15	1.333(4)	C20-C21	1.366(5)
O4-C16	1.458(5)	C21-C22	1.387(5)
O5-C12	1.326(4)	C22-C23	1.382(6)
O5-C13	1.452(7)	C25-C26	1.440(5)
O6-C12	1.194(4)	C26-C27	1.403(5)
O7-C21	1.369(4)	C26-C31	1.386(5)
O7-C24	1.406(5)	C27-C28	1.355(7)
C1-C2	1.545(4)	C28-C29	1.384(8)
C1-C5	1.585(4)	C29-C30	1.379(7)
C1-C12	1.528(4)	C30-C31	1.377(5)
C1-C15	1.515(4)	C2-H2A	0.9700
C2-C3	1.525(4)	C2-H2B	0.9700
C3-C4	1.546(4)	C3-H3	0.9800
C3-C18	1.503(4)	C5-H5	0.9800
C4-C5	1.526(4)	C7-H7	0.9300
C4-C25	1.529(4)	C8-H8	0.9300
C5-C6	1.504(4)	C9-H9	0.9300
C6-C7	1.391(5)	C10-H10	0.9300

C6-C11	1.376(5)	C11-H11	0.9300
C7-C8	1.383(5)	C13-H13A	0.9700
C8-C9	1.366(7)	C13-H13B	0.9700
C9-C10	1.367(6)	C14-H14A	0.9600
C10-C11	1.390(6)	C14-H14B	0.9600
C13-C14	1.295(9)	C14-H14C	0.9600

Table 4 Selected bond angles [º] of **4ab**.

C4-O1-C31	108.2(2)	C8-C9-C10	119.2(4)
C15-O4-C16	119.0(3)	C9-C10-C11	120.3(4)
C12-O5-C13	116.7(3)	C6-C11-C10	121.5(3)
C21-O7-C24	118.9(3)	O5-C12-O6	124.5(3)
C2-C1-C5	104.6(2)	O5-C12-C1	110.7(3)
C2 -C1 -C12	111.8(2)	O6-C12-C1	124.8(3)
C2-C1-C15	108.3(2)	O5-C13-C14	115.4(6)
C5-C1-C12	111.5(2)	O3-C15-O4	123.3(3)
C5-C1-C15	110.5(2)	O3-C15-C1	125.4(3)
C12-C1-C15	110.0(2)	O4-C15-C1	111.2(2)
C1-C2-C3	105.4(2)	O4-C16-C17	110.3(3)
C2-C3-C4	101.1(2)	C3-C18-C19	120.3(3)
C2-C3-C18	117.3(2)	C3-C18-C23	123.3(3)
C4-C3-C18	116.0(2)	C19-C18-C23	116.4(3)
O1-C4-C3	109.2(2)	C18-C19-C20	122.0(3)
O1-C4-C5	112.8(2)	C19-C20-C21	120.6(3)
O1-C4-C25	105.0(2)	O7-C21-C20	116.7(3)
C3-C4-C5	103.0(2)	O7-C21-C22	123.9(3)
C3-C4-C25	112.7(2)	C20-C21-C22	119.4(3)
C5-C4-C25	114.2(2)	C21-C22-C23	118.9(4)
C1-C5-C4	104.7(2)	C18-C23-C22	122.7(4)
C1-C5-C6	118.2(2)	O2-C25-C4	123.7(3)
C4-C5-C6	117.9(2)	O2-C25-C26	130.3(3)
C5-C6-C7	123.8(3)	C4-C25-C26	106.1(2)

C5-C6-C11	119.2(3)	C25-C26-C27	133.9(3)
C7-C6-C11	117.1(3)	C25-C26-C31	107.1(3)
C6-C7-C8	121.2(4)	C27-C26-C31	119.0(3)
C7-C8-C9	120.6(4)	C26-C27-C28	118.7(4)
C27-C28-C29	121.0(5)	O5-C13-H13B	108.00
C28-C29-C30	122.0(5)	C14-C13-H13A	108.00
C29 -C30-C31	116.4(4)	C14-C13-H13B	108.00
O1-C31-C26	113.6(3)	H13A-C13-H13B	107.00
O1-C31-C30	123.5(3)	C13-C14-H14A	109.00
C26-C31-C30	122.8(3)	C13-C14-H14B	109.00

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