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Total Synthesis of (–)-Panduratin D

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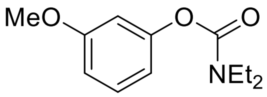
Supporting Information

General information

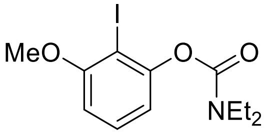
The reactions were performed in flame-dried glassware under positive nitrogen pressure unless stated otherwise. All the reactions were monitored by TLC using TLC glass plates precoated with silica gel 60 F_{254} (Merck). The visualization of TLC was done with UV, $KMnO_4$ stain, or ammonium molybdate stain. Column chromatography was performed on silica gel Geduran® Si 60 (230-400 mesh) (Merck). ^1H and ^{13}C NMR spectra were recorded in Bruker N 600 MHz, AV-400 MHz, AVIII-400 MHz, AV-500 MHz spectrometers, and chemical shifts were measured in δ (ppm) with residual solvent peaks as internal standards ($CDCl_3$, δ 7.26 ppm in ^1H NMR, δ 77.16 ppm in ^{13}C NMR). Abbreviations in the NMR data are m = multiplet, s = singlet, d = doublet, t = triplet, br = broad, dd = doublet of doublet, dm = doublet of multiplet, dt = doublet of triplet, td = triplet of doublet, q = quartet, p = pentet, h =heptet. Enantioselectivity of UV active Diels-Alder product was determined by Agilent HPLC using Daicel chiral columns Chiralpak AD-H. Specific rotation was recorded in Jassco 2020 polarimeter. The melting point was determined by the Buchi M-565 instrument. Cold-Spray Ionization Mass spectra were recorded in JMS-T100LP AccuTOF LC-plus 4G mass spectrometer.

3-methoxyphenyl diethylcarbamate **(3)**[1]



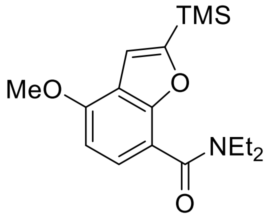
To a solution of 3-methoxyphenol (2.0 gm, 161 mmol) in CH_3CN (32.22 mL) was added oven-dried K_2CO_3 (3.340 gm, 24.16 mmol) under a nitrogen atmosphere and diethylcarbomyl chloride (3.063 mL, 24.16 mmol) respectively. The reaction mixture was heated to reflux for 3 hours. After completion of the conversion, the reaction mixture was quenched with H_2O and extracted with EtOAc. The organic extracts were washed with 1N aq. NaOH solution followed by water and brine. The organic extracts were dried over Na_2SO_4 and concentrated under vacuum to give the crude product, which was purified by column chromatography (6-7% EtOAc/Hexane) to afford 3-methoxyphenyl diethylcarbamate (3.413 gm, 95%) as a colorless oil. Spectral data for **3** was in accordance with literature report. ^{1}H NMR (600 MHz, $CDCl_3$) δ: 7.24 (t, 1H, *J* = 8.2 Hz), 6.74-6.71(m, 2H), 6.68 (t, 1H, *J* = 2.3 Hz), 3.79 (s, 3H), 3.43-3.38 (m, 4H), 1.24-1.19 (m 6H); ^{13}C NMR (150 MHz, $CDCl_3$) δ: 160.5, 154.2, 152.7, 129.6, 114.1, 111.2, 107.8, 55.5, 42.3, 42, 14.3, 13.5;)

2-iodo-3-methoxyphenyl diethylcarbamate **(4)**[1]



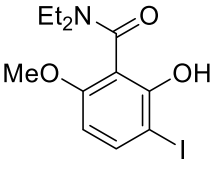
To a solution of 3-methoxyphenyl diethylcarbamate **3** (900 mg, 4.03 mmol) in dry THF (73 mL) was added *t*-BuLi (3.45 mL, 1.40 M, 4.84 mmol) in dropwise manner over 20 minutes at -78 °C. After stirring at -78 °C for 1hour, a solution of iodine (1.23 gm, 4.84 mmol) in THF (7.3 mL) was added to the reaction mixture in dropwise manner over 20 min at -78 °C. The reaction mixture was stirred at same temperature for 1 hour and gradually warm to room temperature and stir for 14 hours. The reaction was quenched slowly by using 10 mL of sat. NH_4Cl solution at 0 °C. and extracted by EtOAc. The combined organic layers were washed with brine, dried over Na_2SO_4 and concentrated under vacuum to give the crude product, which was purified by column chromatography (6-7% EtOAc/Hexane) to afford 2-iodo-3-methoxyphenyl diethylcarbamate **4** **(**1.12 gm, 80%) as white amorphous solid. Spectral data was in accordance with literature report.^{1}H NMR (600 MHz, $CDCl_3$) δ: 7.28 (t, 1H, *J* = 8.2 Hz), 6.82 (dd, 1H, *J* =0.9, 8.1 Hz), 6.66 (dd, 1H, *J* =0.9, 8.1 Hz), 3.88 (s, 3H), 3.59 (q, 2H, *J* = 7.1 Hz), 3.39 (q, 2H, *J* = 7.1 Hz), 1.32 (t, 3H, *J* = 7.1 Hz), 1.22 (t, 3H, *J* = 7.1 Hz); ^{13}C NMR (150 MHz, $CDCl_3$) δ: 159.6, 153.2, 153.1, 129.6, 116.1, 107.8, 83.93, 56.8, 42.4, 42.2, 14.5, 13.4

N, N-diethyl-4-methoxy-2-(trimethylsilyl)benzofuran-7-carboxamide **(6)**



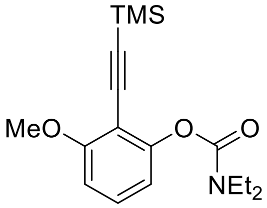
Solution of *N,N*-diethyl-2-hydroxy-4-methoxy-3-((trimethylsilyl)ethynyl)benzamide **9** (250 mg, 0.78 mmol), Et_3N (436 µL, 3.13 mmol), $Pd(PPh_3)_2Cl_2$ (5.5 mg, 7.8 µmol) and CuI (1.5 mg, 15.6 µmol) in 2.5 mL anhydrous CH_3CN in a pressure tube was degassed twice by using freeze-pump-thaw cycle, and then heated to 65 °C for 18 hours. After completion of conversion, the reaction mixture was passed through short celite plug and washed with EtOAc. Filtrate was concentrated under vacuum to give the crude product, which was purified by using column chromatography (8-9% EtOAc/Hexane) to afford *N, N*-diethyl-4-methoxy-2-(trimethylsilyl)benzofuran-7-carboxamide **6** (183 mg, 73%) as brown color gummy liquid. ^1H NMR (500 MHz, $CDCl_3$) δ: 7.23 (d, 1H, *J* = 5.5 Hz), 7.03 (s, 1H), 6.61 (d, 1H, *J* = 5.5 Hz), 3.91 (s, 3H), 3.61 (q, 2H, *J* = 6.1 Hz), 3.20 (q, 2H, *J* = 6.1 Hz), 1.26 (t, 3H, *J* = 6.1 Hz), 1.04 (t, 3H, *J* = 6.1 Hz) 0.28 (s, 9H); ^{13}C NMR (125 MHz, $CDCl_3$) δ: 167.8, 162.8, 155, 154.3, 125, 118.3, 115.2, 113.5, 103.1, 55.8, 43.1, 39.1, 14.3, 13, -1.7; IR (KBr film, ῡ): 3482, 2965, 2899, 2838, 1629, 1530, 1499, 1458, 1429, 1379, 1354, 1279, 1250, 1220, 1174, 1155, 1098, 913, 843, 758, 629 cm^{-1}. HRMS-ESI$^+$ (m/z): $[M+H]^+$ calcd. for $C_{17}H_{25}NO_3NaSi$ 342.1496, found 342.1493.

N,N-diethyl-2-hydroxy-3-iodo-6-methoxybenzamide (**7**)[2]



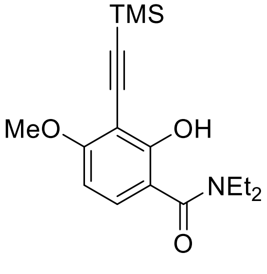
To a solution of 2-iodo-3-methoxyphenyl diethylcarbamate **3** (100 mg, 0.29 mmol) in dry THF (0.71 mL) in a flame dried Schlenk tube under nitrogen atmosphere, was added freshly prepared (By using distilled diisopropyl amine (84 µL, 0.6 mmol) in THF (0.29 mL) and *n*-BuLi (294 µL, 0.57 mmol, 1.95M solution in hexane) lithium diisopropylamide (LDA, 2 M in THF) solution at 0 °C. The reaction mixture was warmed to room temperature gradually and stir for 14 hours at room temperature. After completion of reaction, it was quenched by using 1N HCl (1 mL), and extracted by using Ethyl acetate, combined organic layers were washed with brine, dried over Na_2SO_4 and concentrated under vacuum to give the crude product, which was purified by column chromatography (10-15% EtOAc/Hexane) to afford N,N-diethyl-2-hydroxy-3-iodo-6-methoxybenzamide **7** (41 mg, 41%) as pale yellow solid . The spectral data was in accordance with the literature report.[2] ^1H NMR (400 MHz, Acetone d_6) δ: 7.65 (d, 1H, *J*= 8.8 Hz), 6.49 (d, 1H, *J*= 8.8 Hz), 3.82 (s, 3H), 3.52 (br s, 2H), 3.20 (br s, 2H), 1.18 (br s, 3H), 1.10 (br s, 3H). ^{13}C NMR (100 MHz, Acetone d$_6$) δ: 166.3, 158, 155, 140.1, 115.2, 106.4, 75.9, 56.4, 43.6, 39.6, 14.3, 13.1

3-methoxy-2-((trimethylsilyl)ethynyl)phenyl diethylcarbamate **(8)**



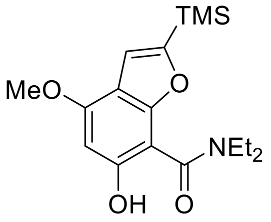
To a solution of 2-iodo-3-methoxyphenyl diethylcarbamate **4** (500 mg, 1.43 mmol), in anhydrous CH_3CN (7.2 mL) were added, diethylamine (592 µL, 5.72 mmol), $Pd(PPh_3)_2Cl_2$ (50.2 mg, 0.07 mmol), and CuI (27.2 mg, 0.14 mmol) in a flame dried pressure tube and reaction mixture was degassed twice by using freeze-pump-thaw cycle. To this, trimethylsilylacetylene (203 µL, 1.43 mmol) was added at room temperature and the resulting mixture was heated to 65 °C for 13 hours. The reaction mixture was cooled down and then added trimethylsilylacetylene 203 µL (1.43 mmol). This mixture was again heated for 13 hours at 65 °C. After completion of conversion, the reaction mixture was passed through short celite plug (washed with EtOAc and concentrated under vacuum to give the crude product, which was purified by column chromatography (4-5% EtOAc/Hexane) to afford 3-methoxy-2-((trimethylsilyl)ethynyl)phenyl diethylcarbamate as gummy liquid **8** (436 mg, 95%). ^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.23 (t, 1H, *J* = 8.2 Hz), 6.80 (dd, 1H, *J* =0.9, 8.1 Hz), 6.70 (dd, 1H, *J* =0.9, 8.1 Hz), 3.86 (s, 3H), 3.49 (q, 2H, *J* = 7.1 Hz), 3.38 (q, 2H, *J* = 7.1 Hz), 1.30 (t, 3H, *J* = 7.1 Hz), 1.20 (t, 3H, *J* = 7.1 Hz), 0.22 (s, 9H); ^{13}C NMR (125 MHz, $CDCl_3$) δ: 161.1, 154.1, 153.5, 129.5, 115.2, 107.7, 107.3, 103.2, 96.4, 56.3, 42.5, 42.2, 14.5, 13.6, 0.16; IR (KBr film, ῡ): 2973, 2934, 1720, 1599, 1576, 1468, 1437, 1416, 1380, 1365, 1315, 1283, 1239, 1220, 1153, 1119, 1091, 969, 913, 768, 726, 542 cm^{-1}. HRMS (MALDI) m/e : Calcd for $C_{17}H_{26}NO_3Si$ $[M+H]^+$: 320.1682 Found 320.1690.

N,N-diethyl-2-hydroxy-4-methoxy-3-((trimethylsilyl)ethynyl)benzamide **(9)**



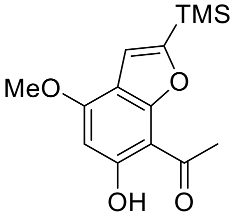
To a solution of 3-methoxy-2-((trimethylsilyl)ethynyl)phenyl diethylcarbamate **8** (400 mg, 1.25 mmol) in THF (3.75 mL) in a flame dried Schlenk tube at -78 °C, was added freshly prepared lithium diisopropylamide (LDA) solution (2.68 mL, 2 M in THF, 2.5 mmol). After stirring for 1 hour at -78 °C, the reaction mixture was warmed to room temperature gradually and stir for 14 hours. The reaction mixture then cooled down to -50 °C and freshly distilled TMSCl (160 µL, 1.25 mmol) was added. After stirring for 1 hour at -50 °C, the reaction mixture was quickly filtered through silica gel at the same temperature and subsequently washed with EtOAc. The filtrate was concentrated under vacuum to give crude product, which was purified by column chromatography (8-9% EtOAc/Hexane) to afford *N,N*-diethyl-2-hydroxy-4-methoxy-3-((trimethylsilyl)ethynyl)benzamide **9** (285 mg, 71%) as gummy liquid. ^{1}H NMR (600 MHz, CDCl$_3$) δ: 9.57 (s, 1H), 7.20 (d, 1H, *J* = 8.7 Hz), 6.39 (d, 1H, *J* = 8.7 Hz), 3.89 (s, 3H), 3.45 (q, 4H, *J* = 7.1 Hz), 1.22 (t, 6H, *J* = 7.1 Hz) 0.28 (s, 9H); ^{13}C NMR (100 MHz, CDCl$_3$) δ: 170.4, 162.8, 160.1, 128.9, 112.8, 105.1, 101.4, 101.2, 95.9, 56.2, 42, 13.5, 0.26; IR (KBr film, ῡ): 2966, 2899, 2840, 2154, 1618, 1499, 1459, 1378, 1351, 1277, 1247, 1171, 1128, 1096, 920, 858, 788, 759, 602 cm^{-1}. HRMS-ESI$^+$ (m/z): [M+H]$^+$ calcd. for $C_{17}H_{25}NO_3NaSi$ 342.1496, found 342.1496.

N, N-diethyl-6-hydroxy-4-methoxy-2-(trimethylsilyl)benzofuran-7-carboxamide **(10)**



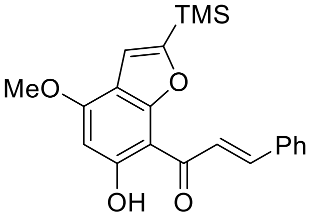
To a solution of N, N-diethyl-4-methoxy-2-(trimethylsilyl)benzofuran-7-carboxamide **6** (135 mg, 0.42 mmol) in 2.5 mL anhydrous THF at -78 °C was added *t*-BuLi (939 µL, 1.35 M in pentane, 1.27 mmol) in dropwise manner. The reaction mixture was stirred for 3 hours at same temperature and then it was added to pre-cooled solution of triisopropyl borate (290 µL, 1.27 mmol) in dry THF (3 mL) at -78 °C. The reaction mixture was warmed to 0 °C and kept stirring for another 1 hour. glacial acetic acid (72.5 µL, 1.27 mmol) and 30% H_2O_2 (143 µL, 1.27 mmol) were added to the reaction mixture respectively and stir for 14 hours at room temperature. After completion of conversion, the reaction was quenched by EtOAc and H_2O. Extracted by using EtOAc, organic layers were washed with brine and dried over Na_2SO_4, concentrated under vacuum to give the crude product, which was purified by column chromatography (10-12% EtOAc/Hexane) to afford *N, N*-diethyl-6-hydroxy-4-methoxy-2-(trimethylsilyl)benzofuran-7-carboxamide **10** (113 mg, 80%) as pink solid. mp: 130 °C. ^{1}H NMR (500 MHz, CDCl$_3$) δ: 9.94 (s, 1H), 6.97 (s, 1H), 6.34 (s, 1H), 3.90 (s, 3H), 3.53 (q, 4H, *J* = 7.1 Hz), 1.24 (t, 6H, *J* = 7.1 Hz) 0.30 (s, 9H); ^{13}C NMR (125 MHz, CDCl$_3$) δ: 168.7, 160.7, 160, 155.7, 155.6, 113.9, 111.2, 98.4, 94.9, 55.8, 41.4, 13.7, -1.5; IR (KBr film, ῡ): 2964, 1618, 1483, 1442, 1380, 1315, 1250, 1210, 1170, 1139, 1123, 911, 842, 755 cm^{-1}. HRMS-ESI$^+$ (m/z): [M+H]$^+$ calcd. for $C_{17}H_{26}NO_4Si$ 336.1626, found 336.1625.

1-(6-hydroxy-4-methoxy-2-(trimethylsilyl)benzofuran-7-yl)ethan-1-one **(11)**



A commercial solution of correspounding MeLi (0.42 mL, 0.83 M, 0.35 mmol) was cooled to 0 °C and *N*,*N*-diethyl-6-hydroxy-4-methoxy-2-(trimethylsilyl)benzofuran -7-carboxamide **10** (47 mg, 0.14 mmol), dissolved in dry THF (0.23 mL) at 0 °C, was slowly added dropwise. The solution was then stirred for 2 hours at room temperture, 1N HCl (2 mL) was added and extracted with EtOAc. The combined organic layers were washed with brine, dried ($MgSO_4$), filtered, and concentrated under vacuum to give the crude product, which was purified by column chromatography (4-5% EtOAc/Hexane) to give 1-(6-hydroxy-4-methoxy-2-(trimethylsilyl)benzofuran-7-yl)ethan-1-one **11** (20.3 mg, 52%) and starting material **10** (4.5 mg, 9.6%) as colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 6.98 (s, 1H), 6.23 (s, 1H), 3.93 (s, 3H), 2.82 (s, 3H), 0.32 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: = 200.8, 165.7, 160.9, 159.3, 158.7, 113.5, 111.6, 102.5, 94.2, 55.9, 30.7, -1.8; IR (film ῡ) 3447, 1628, 1607 cm^{-1}; HRMS (ESI) m/e : Calcd for $C_{14}H_{19}O_4Si$ [M+H]$^+$: 279.1053 Found 279.1049.

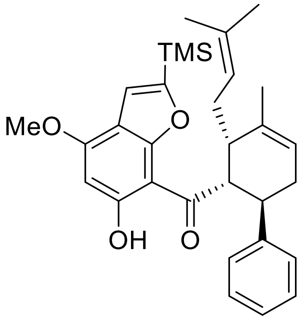
(E)-1-(6-hydroxy-4-methoxy-2-(trimethylsilyl)benzofuran-7-yl)-3-phenylprop-2-en-1-one **(12)**



To a solution of *N, N*-diethyl-6-hydroxy-4-methoxy-2-(trimethylsilyl)benzofuran-7-carboxamide **10** (50 mg, 0.15 mmol) in THF (0.3 mL) in a flame-dried Schlenk tube, was added freshly prepared lithium tetramethylpiperidine (LTMP) (4 equiv, 0.60 mmol, 2 M in THF) , at 0 °C and stirred for 10 min at the same temperature. TBDMSCl (26.9 mg, 0.18 mmol) was added quickly by relying on inert gas over-pressure at 0 °C and gradually warmed to room temperature and stirred for 2 hours. Methyl iodide (42.3mg, 0.3 mmol) was then added to the reaction mixture at 0 °C and stirred for 30 min at room temperature. After 30 min, benzaldehyde (20.5 mg, 0.19

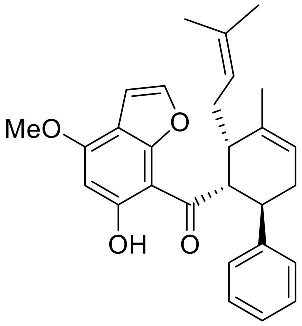
mmol) was added to the reaction mixture and stirred for 12 hours at room temperature. Upon completion of the reaction, it was then quenched with 1 N HCl (2.5 mL) at 0 °C. The resulting mixture was extracted with Ethyl acetate and washed with brine. The combined organic layers were dried over Na_2SO_4 and concentrated under vacuum to give the crude product, which was purified by column chromatography (2-3% EtOAc/Hexane) to afford the (*E*)-1-(6-hydroxy-4-methoxy-2-(trimethylsilyl)benzofuran-7-yl)-3-phenylprop-2-en-1-one **12** (29 mg, 53%) as saffron color solid. mp: 148 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ: 14.42 (s, 1H), 8.39 (d, 1H, *J* = 15.5 Hz), 7.97 (d, 1H, *J* = 15.5 Hz), 7.73-7.71 (m, 2H), 7.45-7.41 (m, 3H), 7.03 (s, 1H), 6.30 (s, 1H), 3.97 (s, 3H), 0.40 (s, 9H); ^{13}C NMR (125 MHz, $CDCl_3$) δ: 190.3, 167.8, 160.9, 159.8, 158.5, 143.9, 135.5, 130.6, 129.1, 128.7, 125.7, 113.9, 112, 103.1, 94.8, 56, -1.4; IR (KBr film, $\bar{\upsilon}$): 2952, 1637, 1616, 1597, 1571, 1527, 1499, 1463, 1444, 1401, 1370, 1330, 1300, 1245, 1219, 1173, 997, 974, 843, 813, 752, 721 cm^{-1}. HRMS-ESI$^+$ (m/z): $[M+H]^+$ calcd. for $C_{21}H_{22}O_4NaSi$ 389.1180, found 389.1189.

(6-hydroxy-4-methoxy-2-(trimethylsilyl)benzofuran-7-yl)((1*R*,2*R*,3*S*)-4-methyl-3-(3-methylbut-2-en-1-yl)-1,2,3,6-tetrahydro-[1,1'-biphenyl]-2-yl)methanone **(13)**



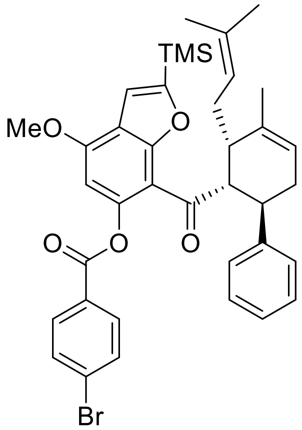
To a solution of (*S*)-3,3'-diphenyl-[1,1'-binaphthalene]-2,2'-diol **L3** (71.7 mg, 0.16 mmol) in 0.4 mL anhydrous THF, was added $BH_3\cdot THF$ (163 μL, 1 M solution in THF, 0.16 mmol) and glacial Acetic acid (9.3 μL, 0.16 mmol) respectively. The resulting mixture was stirred at rt for 30 minutes. Solvent was removed under high vacuum and further dried for 3 hours under nitrogen atmosphere. The residue was re-dissolved in THF (0.5 mL) and added the pre activated 5 Å molecular sieve (300 mg) and (*E*)-1-(6-hydroxy-4-methoxy-2-(trimethylsilyl)benzofuran-7-yl)-3-phenylprop-2-en-1-one **12** (30 mg, 0.08 mmol). The resulting mixture was stirred at rt for 4 hours and then ocimene (69.7 μL, 0.41 mmol) was added to the reaction mixture at same temperature. The reaction was stirred at rt for 96 hours and monitored by TLC. The mixture was filtered through the Celite, and further washed with Ethyl acetate, and concentrated under vacuum to give the crude product, which was purified by column chromatography (1-2% EtOAc/Hexane) to afford (6-hydroxy-4-methoxy-2-(trimethylsilyl)benzofuran-7-yl)((1*R*,2*R*,3*S*)-4-methyl-3-(3-methylbut-2-en-1-yl)-1,2,3,6-tetrahydro-[1,1'-biphenyl]-2-yl)methanone **13** (14.5 mg, 35%) as colorless oil, along with starting material **12** (11.8 mg, 39%). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 13.63 (s, 1H), 7.20-7.19 (m, 4H), 7.11-7.08 (m, 1H), 7.03 (s, 1H), 6.17 (s, 1H), 5.51 (bs, 1H), 4.82 (tt, 1H, *J*= 7, 1.6 Hz), 4.78 (dd, 1H, *J*= 7, 4.8 Hz), 3.91 (s, 3H), 3.51-3.45 (m, 1H), 2.60-2.57 (m, 1H), 2.47-2.42 (m, 1H), 2.36-2.30 (m, 1H), 2.14-2.08 (m, 2H), 1.77 (s, 3H), 1.50 (s, 3H), 1.47 (s, 3H), 0.36 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 204.2, 166.5, 160.7, 159, 158, 146.8, 136.9, 132, 128.5, 127.2, 125.8, 124.3, 121.4, 113.6, 111.6, 103.3, 94.7, 56, 53.7, 42.9, 36.9, 36.2, 29, 25.7, 22.9, 18.1, -1.7. *ee*$_{(endo)}$ = 95% [determined by HPLC, Chiralpak AD-H column, 1.5% IPA/Hexane, 0.3 mL/min, 254 nm, $t_{r(endo\ (\mathrm{minor}))}$ = 10.79, $t_{r(endo\ (\mathrm{major}))}$ = 11.39 min]. $[\alpha]_D^{21}$ = -6.58° (*c* 0.5 $CHCl_3$). IR (KBr film, ῡ): 2932, 2897, 2834, 1616, 1495, 1442, 1228, 842, 548, 528 cm^{-1}. HRMS-FAB$^+$ (m/z): $[M+H]^+$ calcd. for $C_{31}H_{39}O_4Si$ 503.2618, found 503.2618.

(–)-Panduratin D[3]



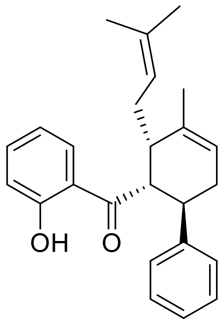
To solution of (6-hydroxy-4-methoxy-2-(trimethylsilyl)benzofuran-7-yl)((1*R*,2*R*,3*S*)-4-methyl-3-(3-methylbut-2-en-1-yl)-1,2,3,6-tetrahydro-[1,1'-biphenyl]-2-yl)methanone **13** (10 mg, 0.02 mmol) in anhydrous THF (0.3 mL) was added TBAF (20 µL, 1 M solution in THF, 0.02 mmol) dropwise at room temperature. Stir reaction mixture for 30 minutes and quench by H_2O. Extract by using EtOAc. Combined organic layers were washed with brine, dried over Na_2SO_4 and concentrated under vacuum to give crude product, which was purified by using column chromatography (3-4% EtOAc/Hexane) to give (–)-panduratin D (7.7 mg, 90%) as colorless oil. Spectral data was in accordance with the reported in literature.^{1}H NMR (500 MHz, $CDCl_3$) δ: 13.66 (s, 1H), 7.59 (d, 1H, *J*=2.2 Hz), 7.24-7.19 (m, 4H), 7.12-7.08 (m, 1H), 6.84 (d, 1H, *J*= 2.2 Hz), 6.22 (s, 1H), 5.50 (bs, 1H), 4.82-4.78 (m, 1H), 4.62 (dd, 1H, *J*= 4.8, 6.4 Hz), 3.92 (s, 3H), 3.52-3.47 (m, 1H), 2.58-2.55 (m, 1H), 2.49-2.43 (m, 1H), 2.34-2.28 (m, 1H), 2.17-2.10 (m, 2H), 1.80 (s, 3H), 1.49 (s, 3H), 1.46 (s, 3H). ^{13}C NMR (150 MHz, $CDCl_3$) δ: 204, 166.3, 159, 154.6, 146.8, 142.4, 137.2, 132.2, 128.5, 127.2, 125.8, 124.1, 121.3, 110.8, 104.5, 103.2, 95.1, 56, 53.4, 42.5, 37, 35.6, 29, 25.7, 22.9, 18. $[\alpha]_D^{21}$ = -3.07° (*c* 0.5 $CHCl_3$). IR (KBr film, ῡ): 3850, 3672, 3646, 3443, 3027, 2964, 2924, 2852, 1747, 1714, 1621, 1558, 1506, 1493, 1453, 1375, 1266, 1209, 1160, 1082, 983, 823, 767, 700 cm^{-1}. HRMS-ESI$^+$ (m/z): $[M+H]^+$ calcd. for $C_{28}H_{31}O_4$ 431.2217, found 431.2222.

4-methoxy-7-((1*R*,2*R*,3*S*)-4-methyl-3-(3-methylbut-2-en-1-yl)-1,2,3,6-tetrahydro-[1,1'-biphenyl]-2-carbonyl)-2-(trimethylsilyl)benzofuran-6-yl 4-bromobenzoate **(14)**



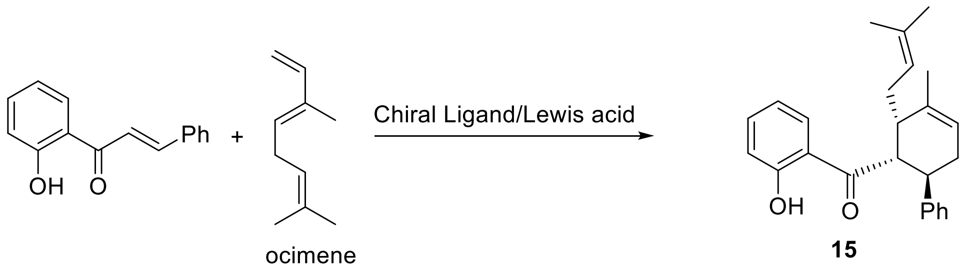
To solution of(6-hydroxy-4-methoxy-2-(trimethylsilyl)benzofuran-7-yl)((1*R*,2*R*,3*S*)-4-methyl-3-(3-methylbut-2-en-1-yl)-1,2,3,6-tetrahydro-[1,1'-biphenyl]-2-yl)methanone **13** (10 mg, 0.02 mmol) in anhydrous dichloromethane (0.4 mL) was added 4-bromo benzoyl chloride (6.55 mg, 0.03 mmol) and triethylamine (8.27 µL, 0.06 mmol) at 0 ºC and stir for 10 min. at same temperature. Reaction mixture was then brought to room temperature and stir for another 12 hours. After completion of reaction, it was quenched by H_2O and extracted by using dichloromethane. Combined organic layers were washed with brine, dried over Na_2SO_4 and concentrated under vacuum to give crude product, which was purified by using column chromatography (1-2% DCM/Hexane) to afford 4-methoxy-7-((1*R*,2*R*,3*S*)-4-methyl-3-(3-methylbut-2-en-1-yl)-1,2,3,6-tetrahydro-[1,1'-biphenyl]-2-carbonyl)-2-(trimethylsilyl)benzofuran-6-yl 4-bromobenzoate **14** (8.6 mg, 63%) as a white solid. mp 160 ºC. The single crystal for X-ray analysis was obtained from Hexane solvent at -20 ºC. ^{1}H NMR (400 MH$_Z$, $CDCl_3$) δ: 7.77 (d, 2H, *J*= 7.2 Hz), 7.51 (d, 2H, *J*= 7.2 Hz), 7.25-7.09 (m, 5H), 6.44 (s, 1H), 5.41 (bs, 1H), 5.05, (t, 1H, *J*= 7 Hz), 4.51 (dd, 1H, *J*= 8, 3 Hz), 3.93 (s, 3H), 3.38 (m, 1H), 2.61 (bs, 1H), 2.42-2.38 (m, 1H), 2.29-2.25 (m, 1H), 2.20-2.13 (m, 1H), 2.09-2.04 (m, 1H), 1.73 (s, 3H), 1.59 (s, 3H), 1.46 (s, 3H), 0.39 (s, 9H). ^{13}C NMR (100 MH$_Z$, $CDCl_3$) δ: 198, 165, 163.6, 157.2, 155.2, 149.2, 146.7, 137.6, 132.2, 131.8, 131.3, 128.6, 128.5, 128.4, 127.5, 125.7, 124.6, 120.9, 117.2, 113.4, 111.9, 100.8, 56.1, 55.9, 41.6, 37.8, 36.2, 29.2, 25.9, 23.4, 18, -1.7. $[\alpha]_D^{21}$ = -8.39° (*c* 0.5 $CHCl_3$). IR (KBr film, ῡ): 3440, 2958, 2920, 2851, 1747, 1676, 1607, 1583, 1463, 1261, 1139, 1102, 1021, 841 cm^{-1}. HRMS-ESI$^+$ (m/z): $[M+H]^+$ calcd. for $C_{38}H_{41}O_5NaSiBr$ 707.1799, found 707.1797

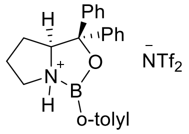
(2-hydroxyphenyl)((1R,2R,3S)-4-methyl-3-(3-methylbut-2-en-1-yl)-1,2,3,6-tetrahydro-[1,1'-biphenyl]-2-yl)methanone (**15**)

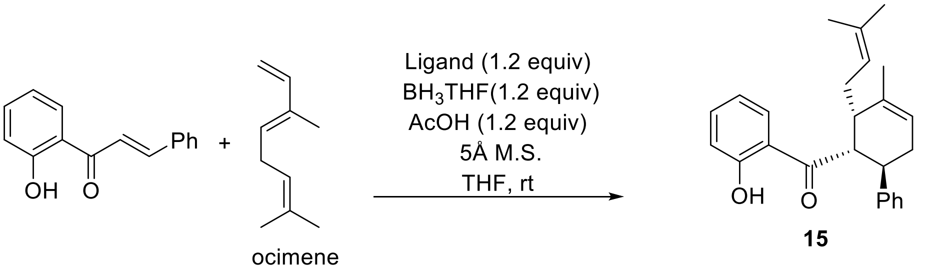


To a solution of *(R)*-3,3'-bis(3,5-bis(trifluoromethyl)phenyl)-[1,1'-binaphthalene]-2,2'-diol (152 mg, 0.21 mmol) in 0.2 mL anhydrous THF, was added $BH_3 \cdot THF$ (214 μL, 1 M solution in THF, 0.21 mmol) and glacial Acetic acid (12.2 μL, 0.21 mmol) respectively. The resulting mixture was stirred at rt for 30 minutes. Solvent was removed under high vacuum and further dried for 30 minutes under nitrogen atmosphere. The residue was dissolved in THF and added the pre-activated 5 Å molecular sieve (200 mg) and (*E*)-1-(2-hydroxyphenyl)-3-phenylprop-2-en-1-one (20 mg, 0.09 mmol). The resulting mixture was stirred at rt for 1.5 hours and then ocimene (75.9 μL, 0.44 mmol) was added to the reaction mixture at same temperature. The reaction was stirred at rt for 36 hours and monitored by TLC. The mixture was filtered through the Celite, and further washed with Ethyl acetate, and concentrated under vacuum to give the crude product, which was purified by column chromatography (1-2% EtOAc/Hexane) to afford (2-hydroxyphenyl)((1*R*,2*R*,3*S*)-4-methyl-3-(3-methylbut-2-en-1-yl)-1,2,3,6-tetrahydro-[1,1'-biphenyl]-2-yl)methanone **15** (27.3 mg, 85%) as colorless oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ: 12.28 (s, 1H), 7.88 (dd, 1H, *J*= 1.6, 8.7 Hz), 7.43 (td, 1H, *J*= 1.6, 7.3 Hz), 7.23-7.18 (m, 4H), 7.13-7.10 (m, 1H), 6.93-6.90 (m, 2H), 5.51 (bs, 1H), 4.73-4.70 (m, 1H), 4.19 (dd, 1H, *J*= 11.3, 5.1 Hz), 3.47-3.41 (m, 1H), 2.55-2.42 (m, 2H), 2.29-2.23 (m, 1H), 2.15-2.10 (m, 2H), 1.80 (s, 3H), 1.49 (s, 3H), 1.45 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 207.3, 162.9, 146.1, 136.4, 136, 132.8, 129.3, 128.6, 127.1, 126.1, 123.6, 121.7, 120.1, 118.9, 118.8, 49.9, 44.4, 36.9, 35.4, 28.9, 25.7, 22.7, 18.1 . $ee_{(endo)}$ = 96% [determined by HPLC, Chiralpak AD-H column, 2% IPA/Hexane, 1 mL/min, 254 nm, $t_{r(endo\ (major)}$ = 3.81, $t_{r(endo\ (minor))}$ = 4.37 min]. $[\alpha]_D^{21}$ = -33.09° (*c* 0.5 $CHCl_3$). IR (KBr film, ῡ): 3038, 3060, 3027, 2961, 2923, 2853, 1636, 1611, 1582, 1445, 1377, 1324, 1195, 1033, 803, 754, 699 cm^{-1}. HRMS-FAB$^+$ (m/z): $[M+H]^+$ calcd. for $C_{25}H_{29}O_2$ 361.2168, found 361.2159

Model Substrate study for Diels-Alder reaction



entry	Chiral ligand/Lewis acid	solvent	temp °C	yield%	*ee*
1		toluene	-78 °C - rt	0	--
2	$Ti(O^iPr)_4$/(+)-DIPT	DCM	-78 °C - rt	0	--
3	Et_2AlCl/BINOL	DCM	0 °C - rt	0	--
4	$AlMe_3$/BINOL	DCM	0 °C - rt	0	--



entry	Chiral ligand/Lewis acid	Time	yield%	*ee*
1	*S*-BINOL	44	28	33
2[a]	*S*-BINOL	66	50	30
3	THT-OH	44	10	0
4	L-2	24	60	95

5[a]	L-2	22	85	97
6	L-3	48	41	81

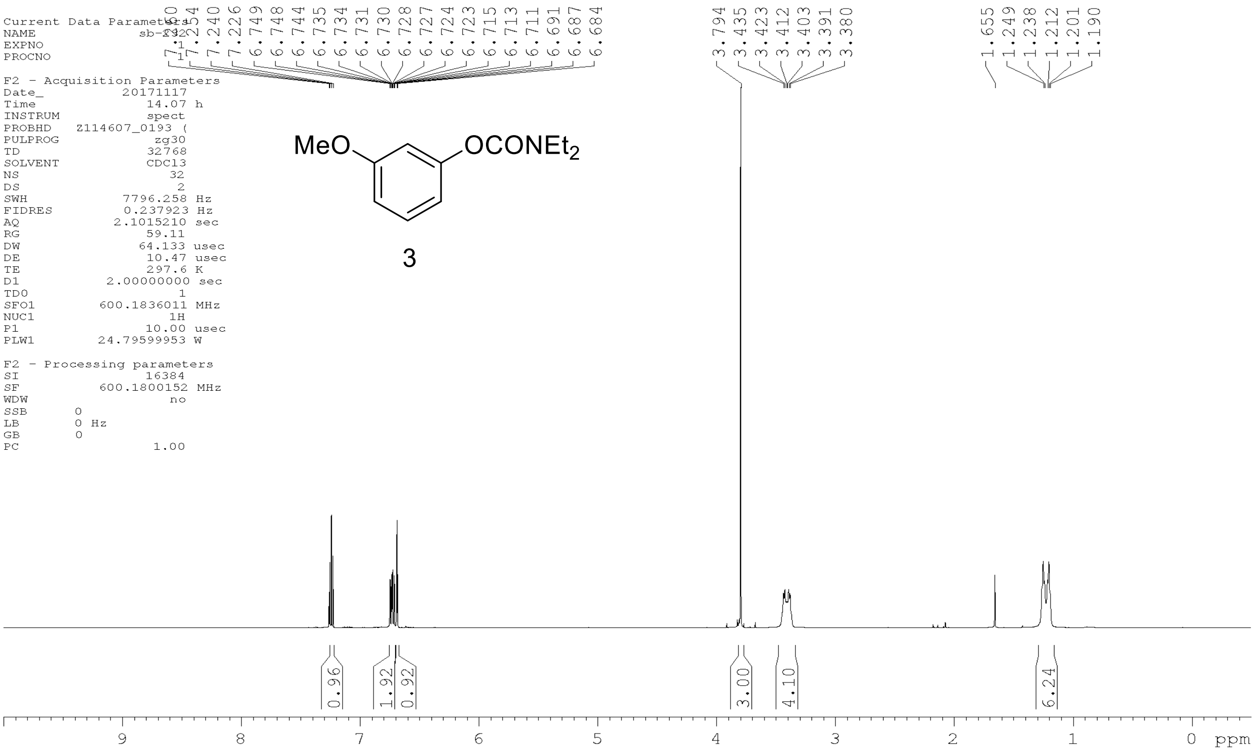
a= (2.4 equiv) ligand, (2.4 equiv) BH_3THF and (2.4 equiv) AcOH was used

References

1) Chauder, B. A.; Kalinin, A. V.; Snieckus, V. Directed *ortho* Metalation Reactions of Aryl *O*-Carbamates; A Regiospecific Synthesis of 2,2-Disubstituted 2*H*-1-Benzopyrans. *Synthesis* **2001,** 140-144.

2) Miller, R. E.; Rantanen, T.; Ogilvie, K. A.; Groth, U.; Snieckus, V., Combined directed ortho Metalation−Halogen Dance (HD) Synthetic Strategies. HD−Anionic ortho Fries Rearrangement and Double HD Sequences. *Org. Lett.* **2010,** *12*, 2198–2201.

3) Win, N. N.; Awale, S.; Esumi, H.; Tezuka, Y.; Kadota, S., Panduratins D-I, Novel Secondary Metabolites from Rhizomes of *Boesenbergia Pandurata. Chem. Pharm. Bull.* **2008,** *56*, 491–496.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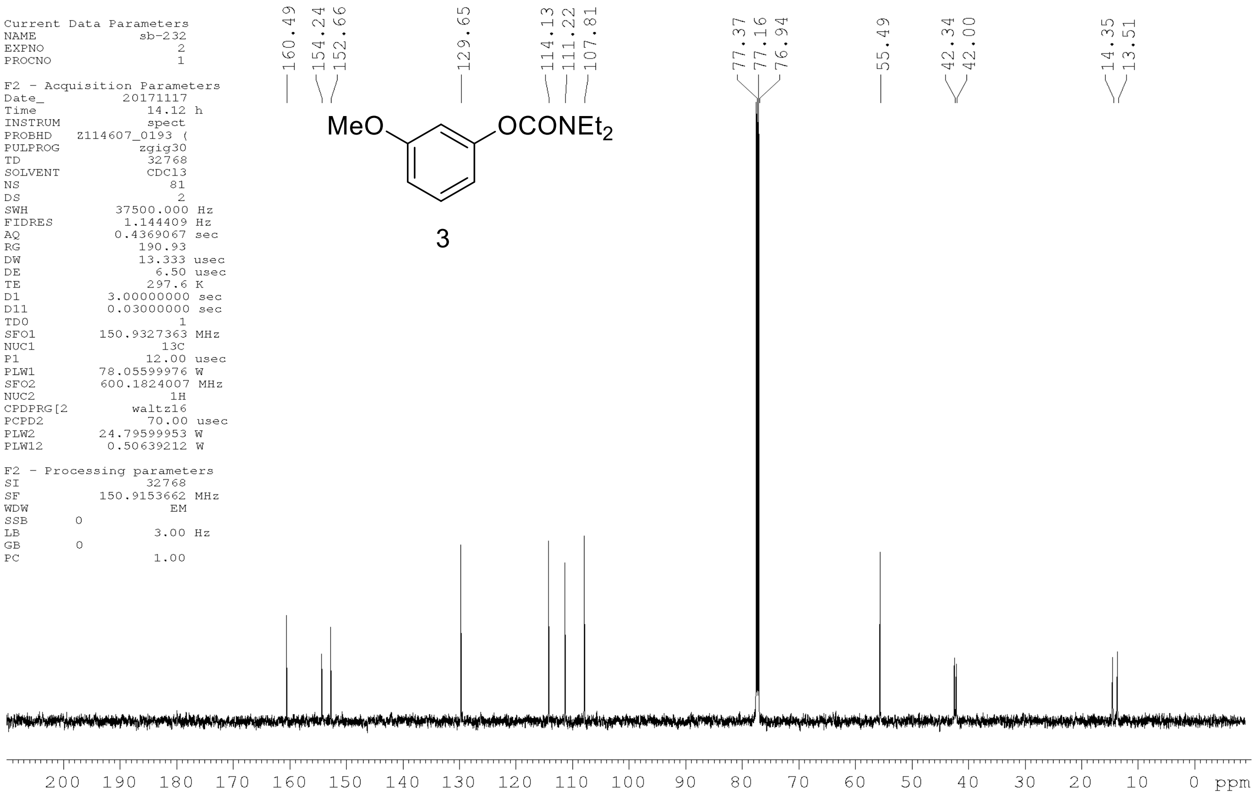
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42.34
42.00
14.35
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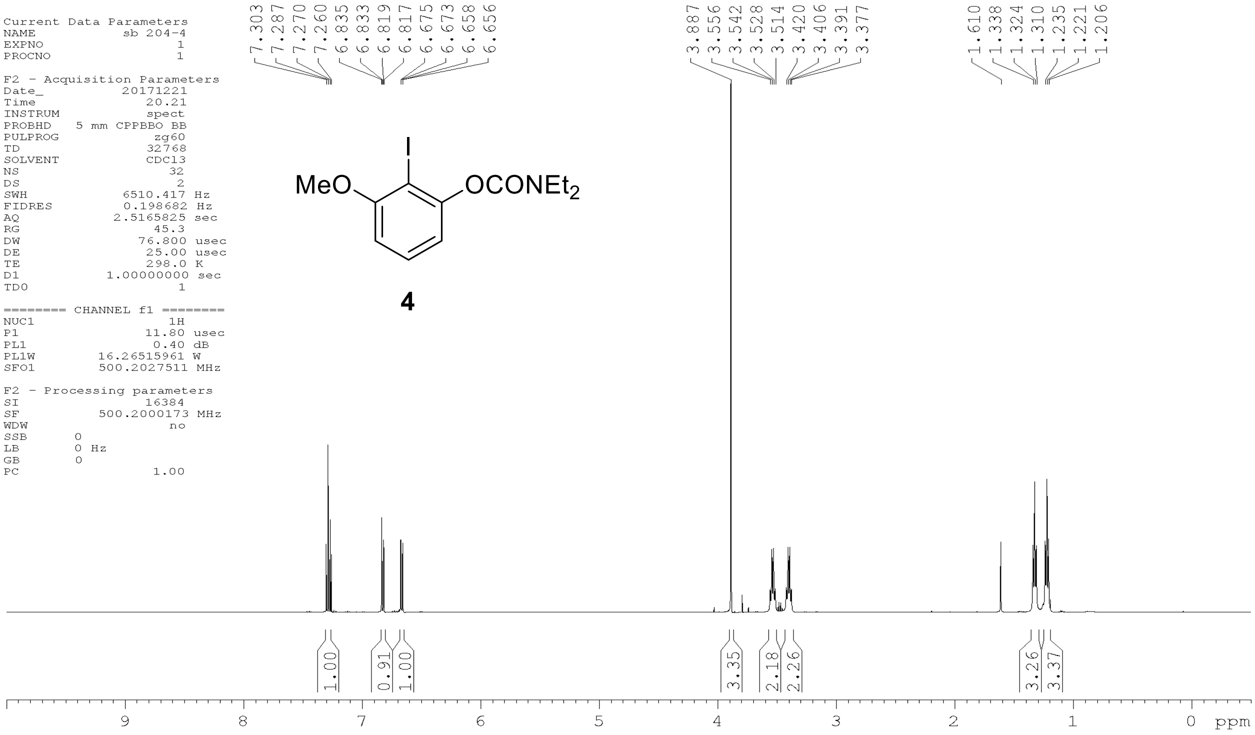

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FIDRES          0.198682 Hz
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RG                  45.3
DW                76.800 usec
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TE                 298.0 K
D1            1.00000000 sec
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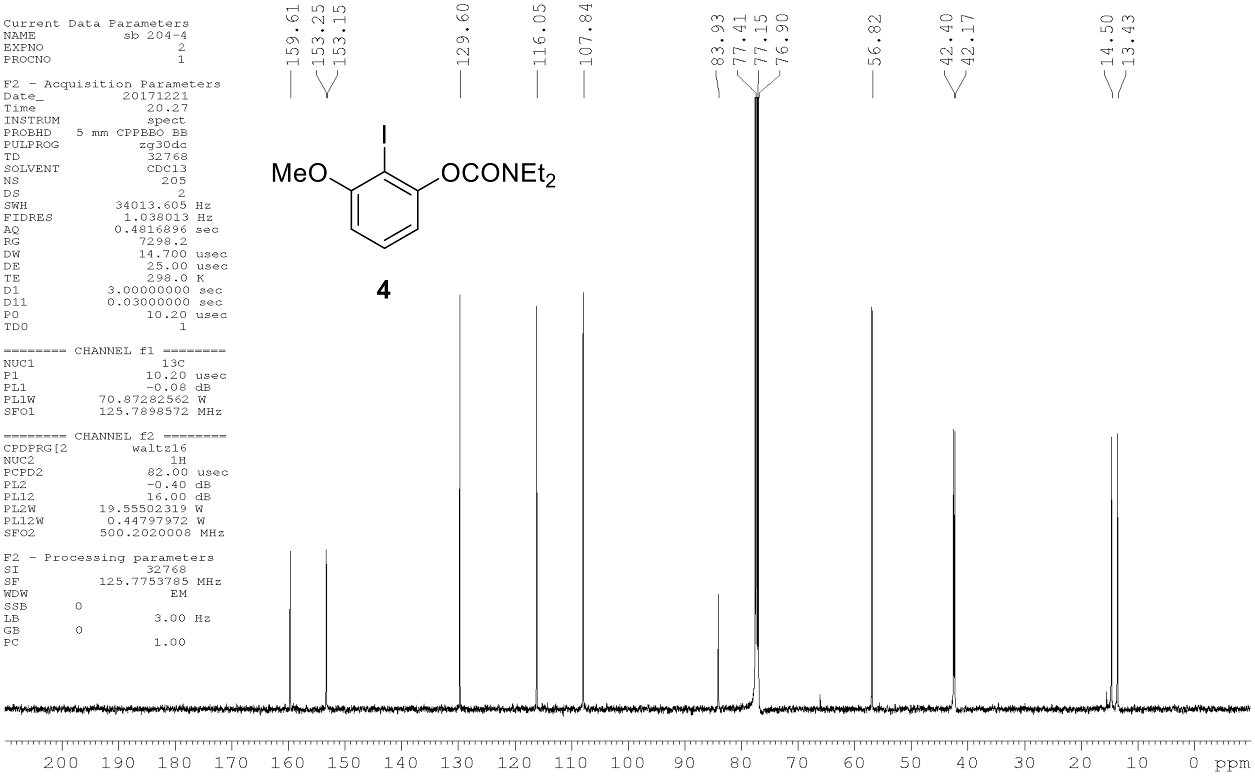

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TE                 298.0 K
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P1                 10.20 usec
PL1                -0.08 dB
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PL12               16.00 dB
PL2W         19.55502319 W
PL12W         0.44797972 W
SFO2         500.2020008 MHz

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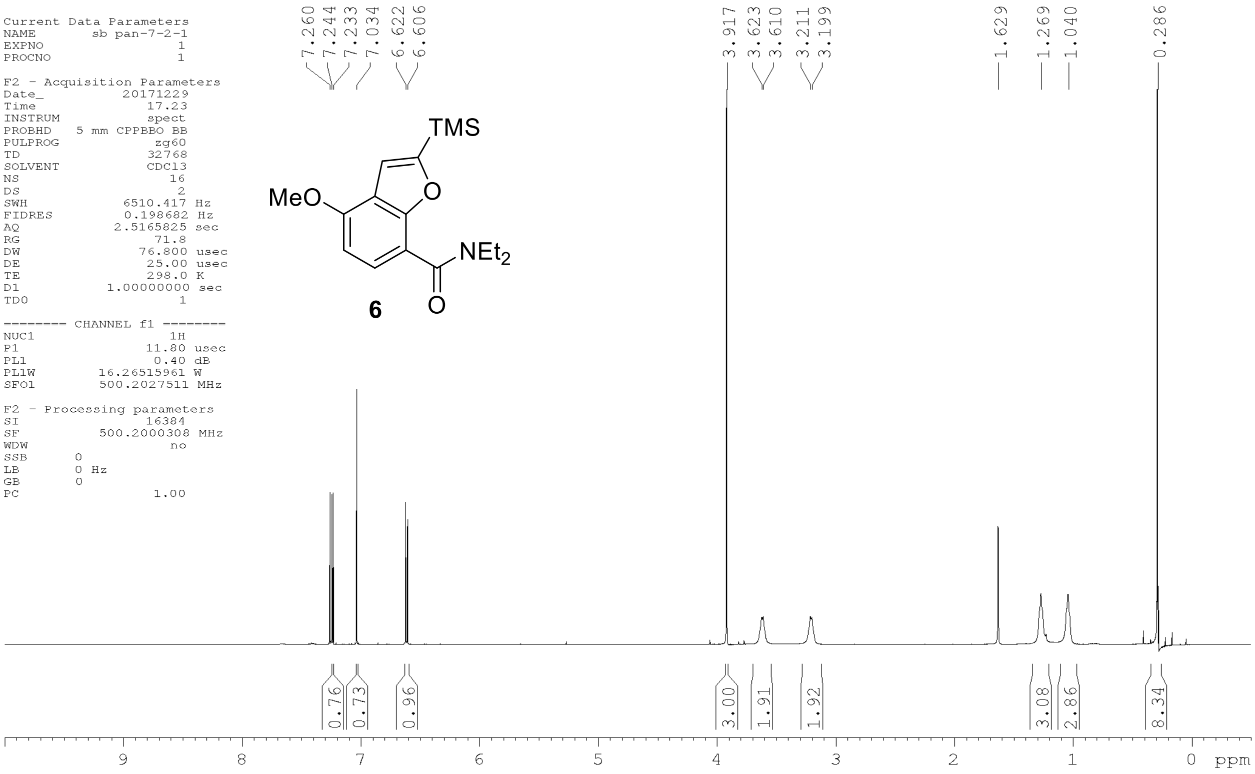

6

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TD                32768
SOLVENT           CDCl3
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FIDRES         0.198682 Hz
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TE                298.0 K
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======== CHANNEL f1 ========
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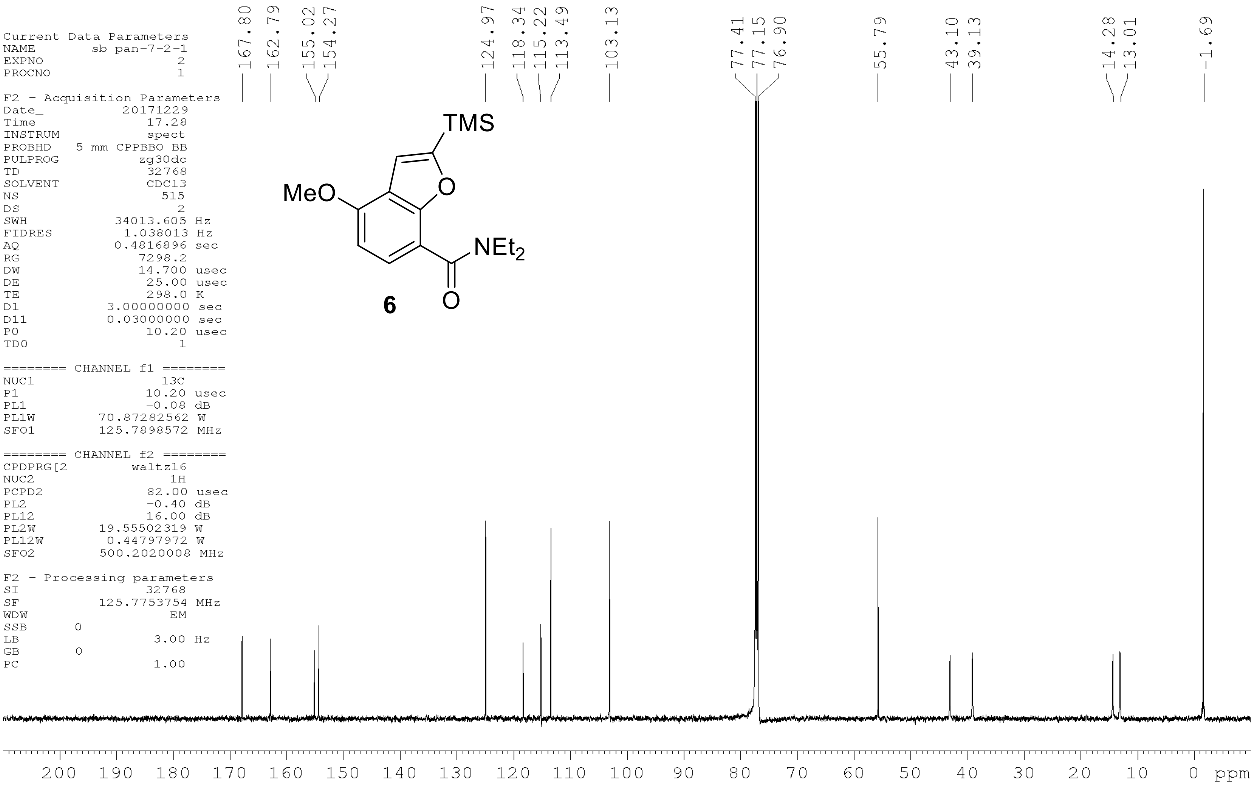

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DW               14.700 usec
DE                25.00 usec
TE                298.0 K
D1           3.00000000 sec
D11          0.03000000 sec
P0                10.20 usec
TD0                   1

======== CHANNEL f1 ========
NUC1                13C
P1                10.20 usec
PL1               -0.08 dB
PL1W        70.87282562 W
SFO1        125.7898572 MHz

======== CHANNEL f2 ========
CPDPRG[2        waltz16
NUC2                 1H
PCPD2             82.00 usec
PL2               -0.40 dB
PL12              16.00 dB
PL2W        19.55502319 W
PL12W        0.44797972 W
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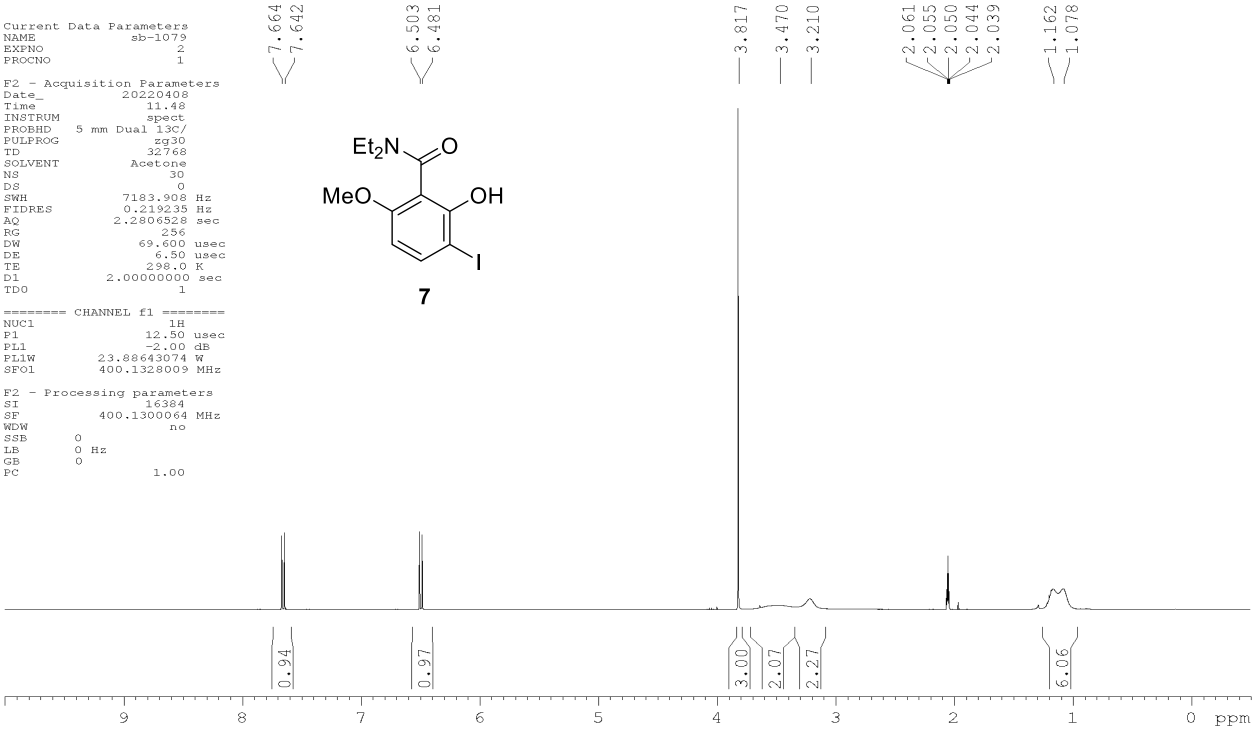

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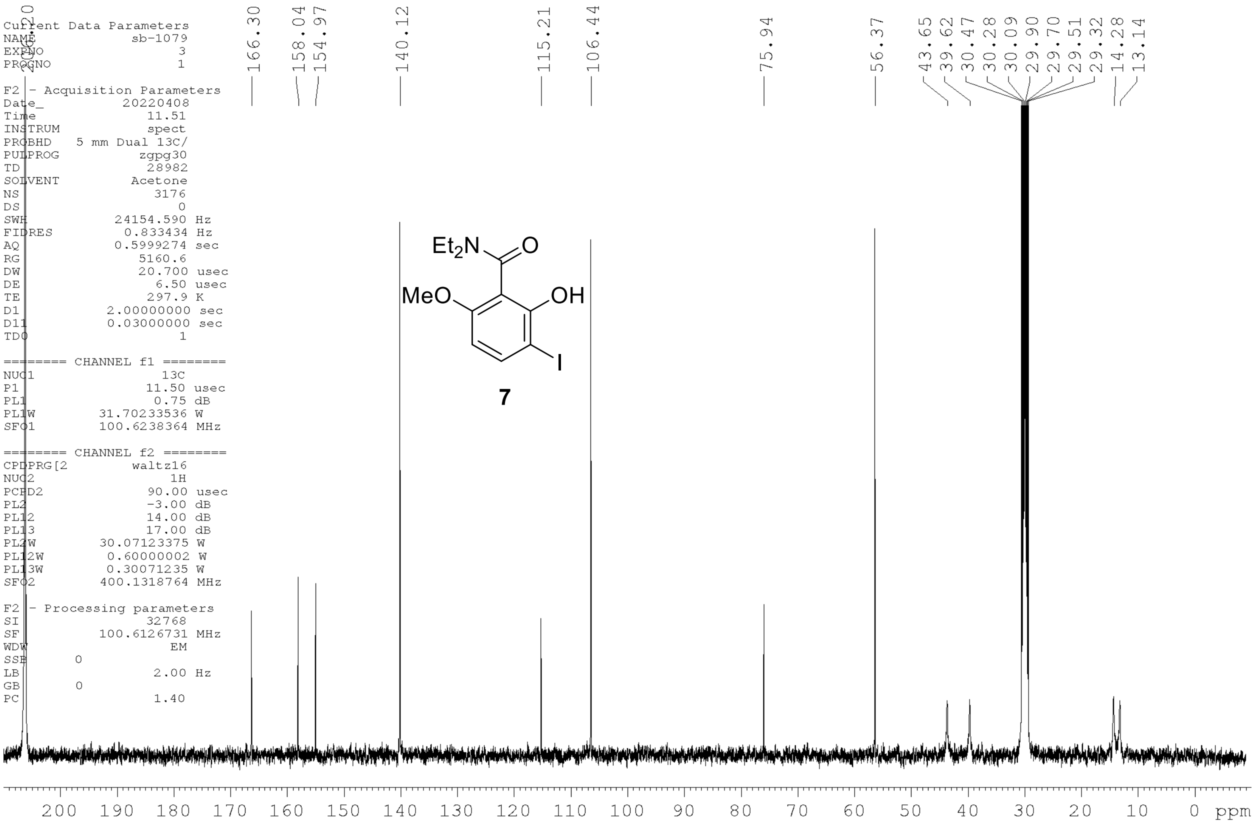
7



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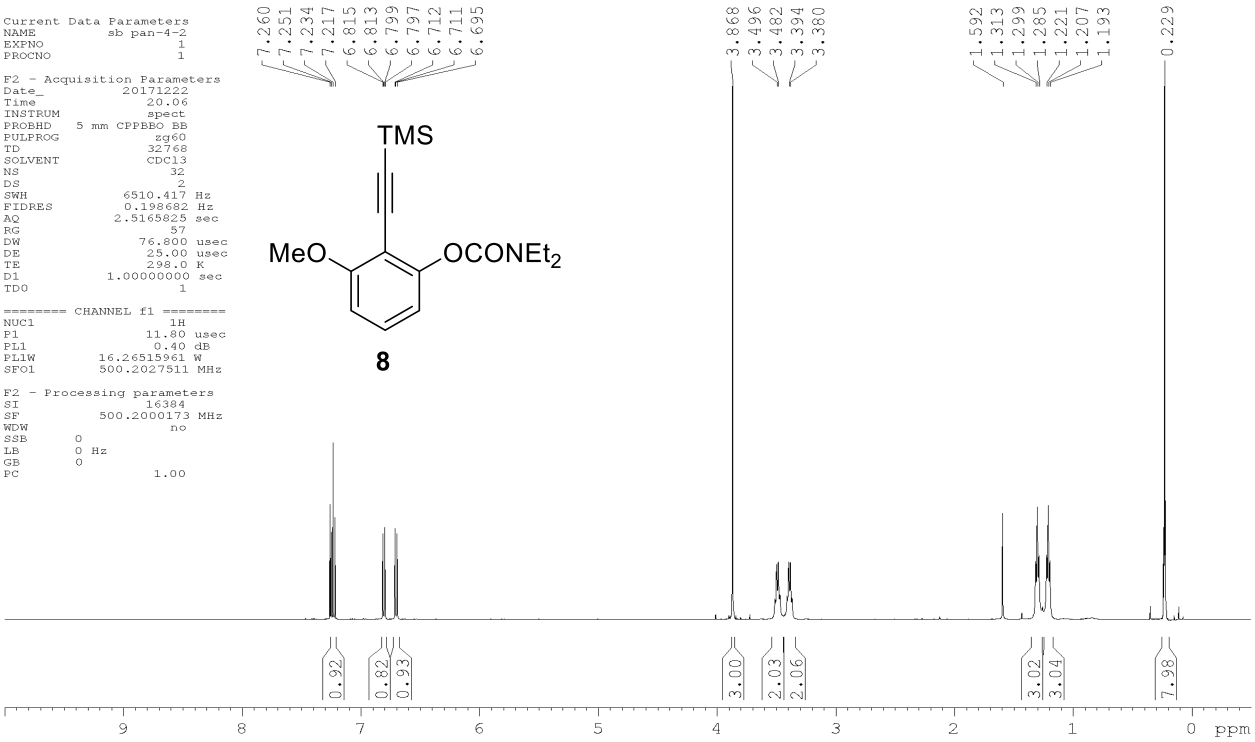
7



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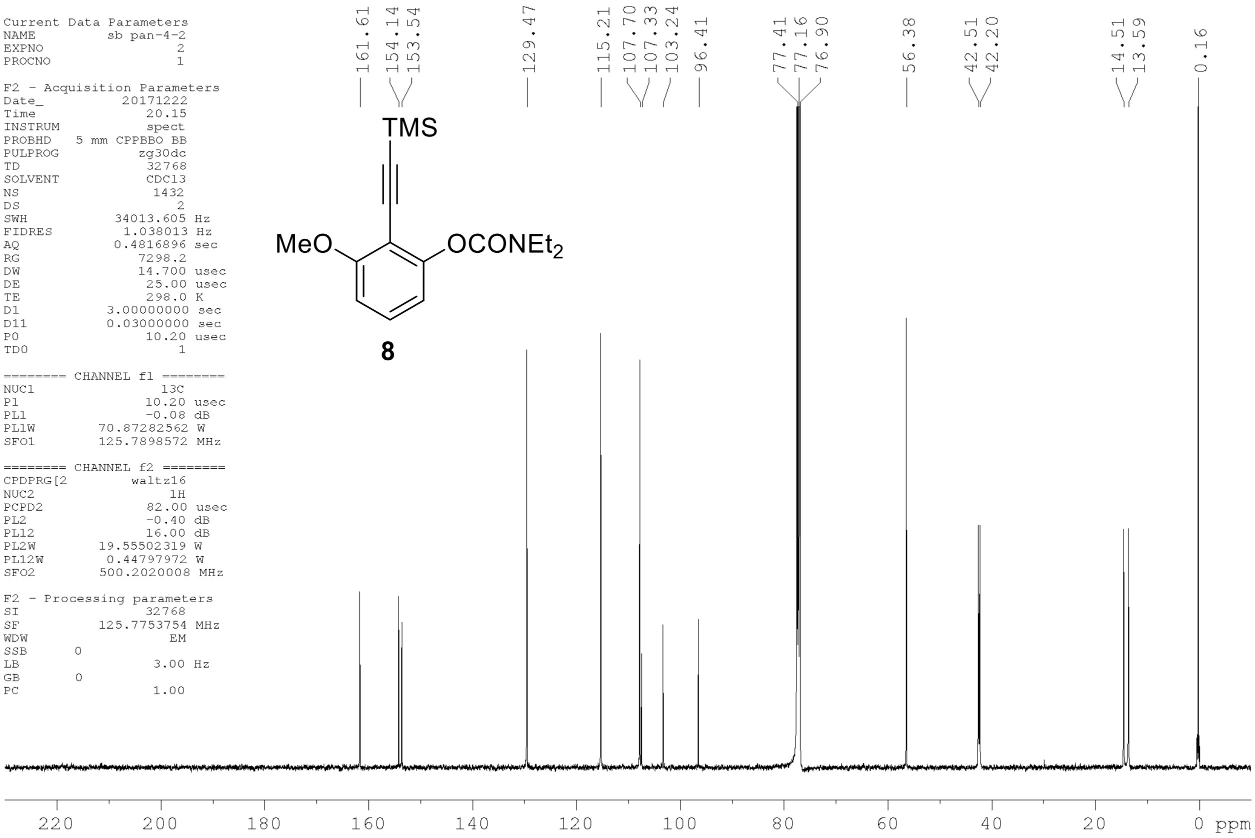
AQ             2.5165825 sec
RG                    57
DW                76.800 usec
DE                 25.00 usec
TE                 298.0 K
D1            1.00000000 sec
TD0                    1

======== CHANNEL f1 ========
NUC1                  1H
P1                 11.80 usec
PL1                 0.40 dB
PL1W         16.26515961 W
SFO1         500.2027511 MHz

F2 - Processing parameters
SI                 16384
SF           500.2000173 MHz
WDW                   no
SSB      0
LB       0 Hz
GB       0
PC                  1.00
```



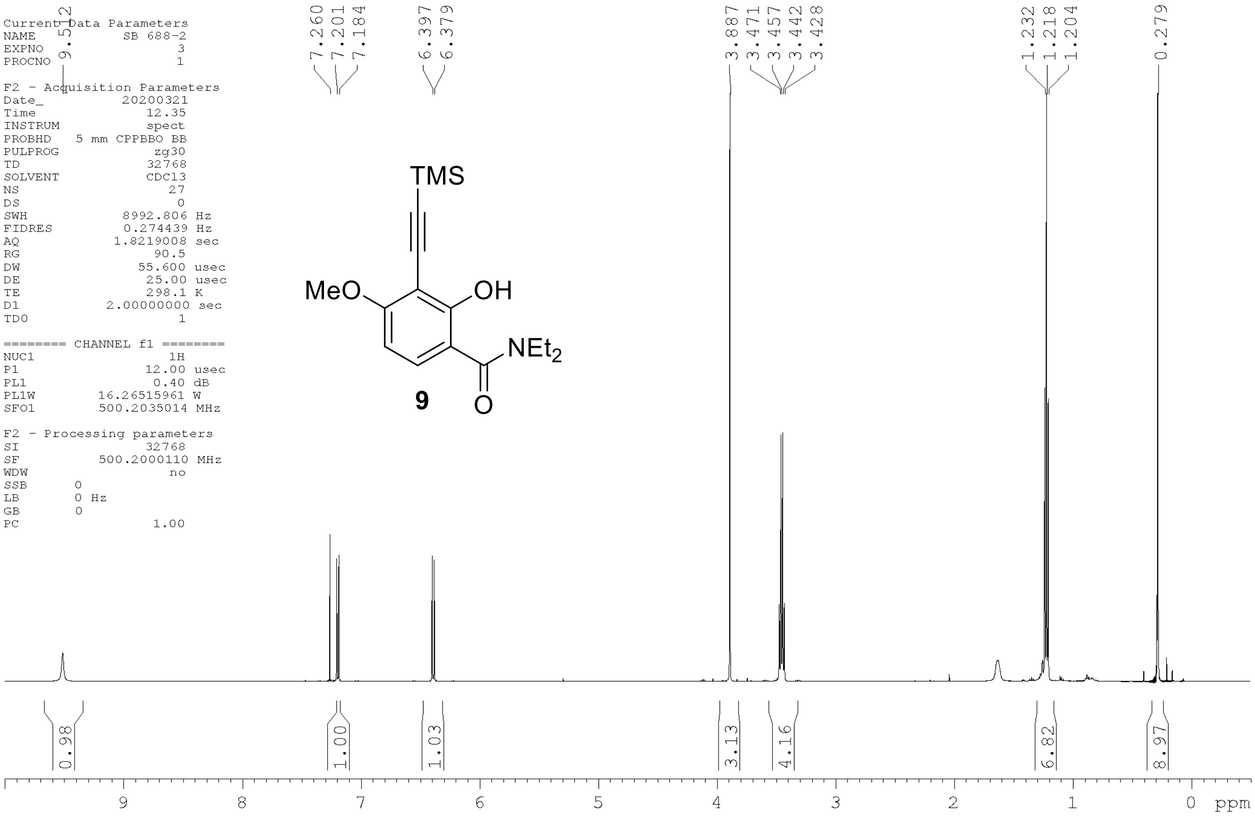
```
Current Data Parameters
NAME          sb pan-4-2
EXPNO                  2
PROCNO                 1

F2 - Acquisition Parameters
Date_           20171222
Time               20.15
INSTRUM            spect
PROBHD   5 mm CPPBBO BB
PULPROG           zg30dc
TD                 32768
SOLVENT            CDCl3
NS                  1432
DS                     2
SWH            34013.605 Hz
FIDRES          1.038013 Hz
AQ             0.4816896 sec
RG                7298.2
DW                14.700 usec
DE                 25.00 usec
TE                 298.0 K
D1            3.00000000 sec
D11           0.03000000 sec
P0                 10.20 usec
TD0                    1

======== CHANNEL f1 ========
NUC1                 13C
P1                 10.20 usec
PL1                -0.08 dB
PL1W         70.87282562 W
SFO1         125.7898572 MHz

======== CHANNEL f2 ========
CPDPRG[2         waltz16
NUC2                  1H
PCPD2              82.00 usec
PL2                -0.40 dB
PL12               16.00 dB
PL2W         19.55502319 W
PL12W         0.44797972 W
SFO2         500.2020008 MHz

F2 - Processing parameters
SI                 32768
SF           125.7753754 MHz
WDW                   EM
SSB      0
LB                  3.00 Hz
GB       0
PC                  1.00
```

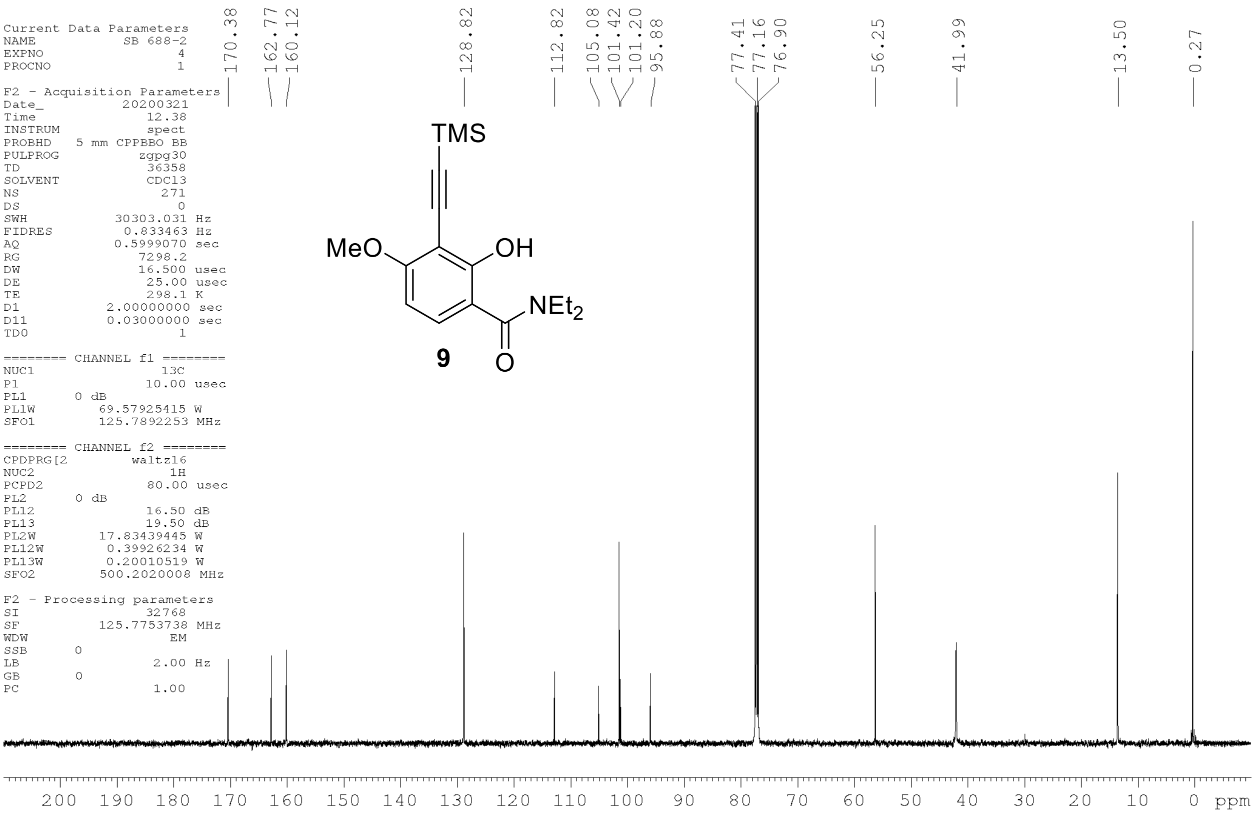


```
Current Data Parameters
NAME          SB 688-2
EXPNO                3
PROCNO               1

F2 - Acquisition Parameters
Date_         20200321
Time             12.35
INSTRUM          spect
PROBHD   5 mm CPPBBO BB
PULPROG           zg30
TD               32768
SOLVENT          CDCl3
NS                  27
DS                   0
SWH           8992.806 Hz
FIDRES        0.274439 Hz
AQ           1.8219008 sec
RG                90.5
DW              55.600 usec
DE               25.00 usec
TE               298.1 K
D1          2.00000000 sec
TD0                  1

======== CHANNEL f1 ========
NUC1                1H
P1               12.00 usec
PL1               0.40 dB
PL1W       16.26515961 W
SFO1       500.2035014 MHz

F2 - Processing parameters
SI               32768
SF         500.2000110 MHz
WDW                 no
SSB      0
LB       0 Hz
GB       0
PC                1.00
```



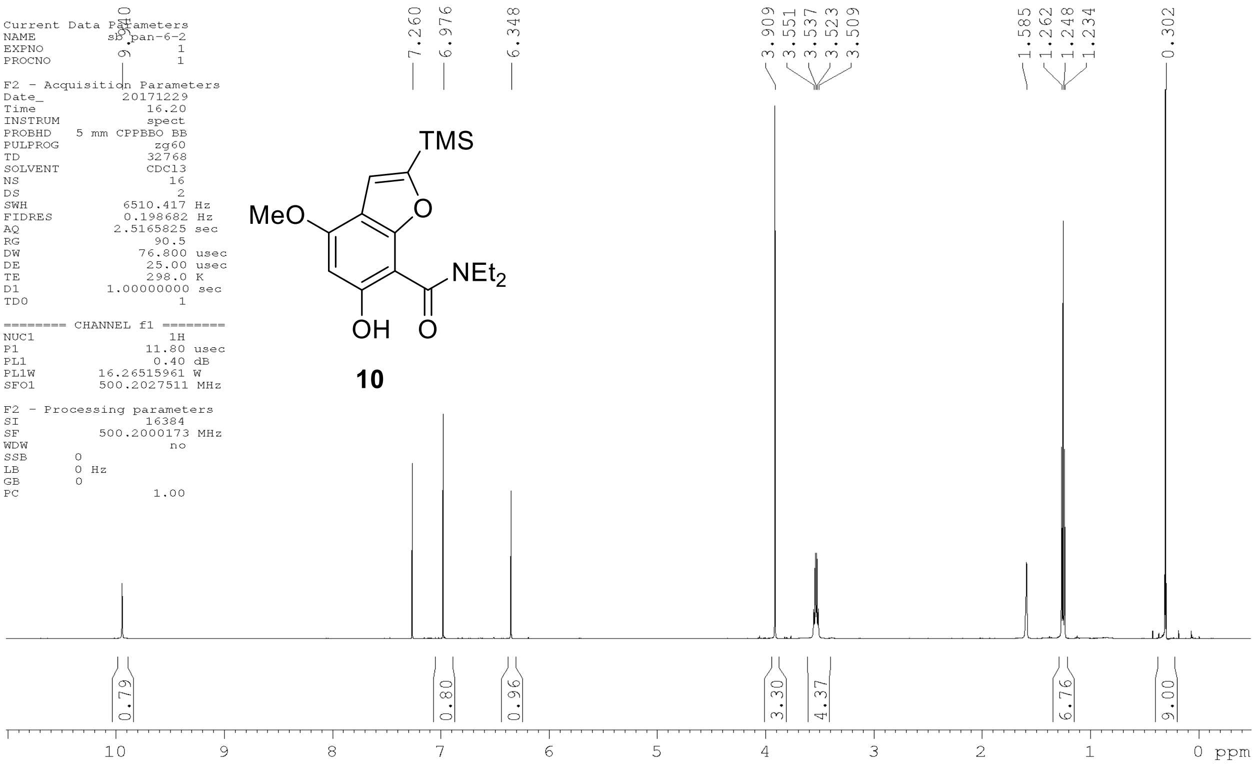
```
Current Data Parameters
NAME          SB 688-2
EXPNO                4
PROCNO               1

F2 - Acquisition Parameters
Date_         20200321
Time             12.38
INSTRUM          spect
PROBHD   5 mm CPPBBO BB
PULPROG         zgpg30
TD               36358
SOLVENT          CDCl3
NS                 271
DS                   0
SWH          30303.031 Hz
FIDRES        0.833463 Hz
AQ           0.5999070 sec
RG              7298.2
DW              16.500 usec
DE               25.00 usec
TE               298.1 K
D1          2.00000000 sec
D11         0.03000000 sec
TD0                  1

======== CHANNEL f1 ========
NUC1               13C
P1               10.00 usec
PL1      0 dB
PL1W       69.57925415 W
SFO1       125.7892253 MHz

======== CHANNEL f2 ========
CPDPRG[2         waltz16
NUC2                1H
PCPD2            80.00 usec
PL2      0 dB
PL12             16.50 dB
PL13             19.50 dB
PL2W       17.83439445 W
PL12W       0.39926234 W
PL13W       0.20010519 W
SFO2       500.2020008 MHz

F2 - Processing parameters
SI               32768
SF         125.7753738 MHz
WDW                 EM
SSB      0
LB                2.00 Hz
GB       0
PC                1.00
```



```
Current Data Parameters
NAME           sb pan-6-2
EXPNO                   1
PROCNO                  1

F2 - Acquisition Parameters
Date_            20171229
Time                16.20
INSTRUM             spect
PROBHD    5 mm CPPBBO BB
PULPROG              zg60
TD                  32768
SOLVENT             CDCl3
NS                     16
DS                      2
SWH              6510.417 Hz
FIDRES           0.198682 Hz
AQ              2.5165825 sec
RG                   90.5
DW                 76.800 usec
DE                  25.00 usec
TE                  298.0 K
D1             1.00000000 sec
TD0                     1

======== CHANNEL f1 ========
NUC1                   1H
P1                  11.80 usec
PL1                  0.40 dB
PL1W          16.26515961 W
SFO1          500.2027511 MHz

F2 - Processing parameters
SI                  16384
SF            500.2000173 MHz
WDW                    no
SSB      0
LB       0 Hz
GB       0
PC                   1.00
```

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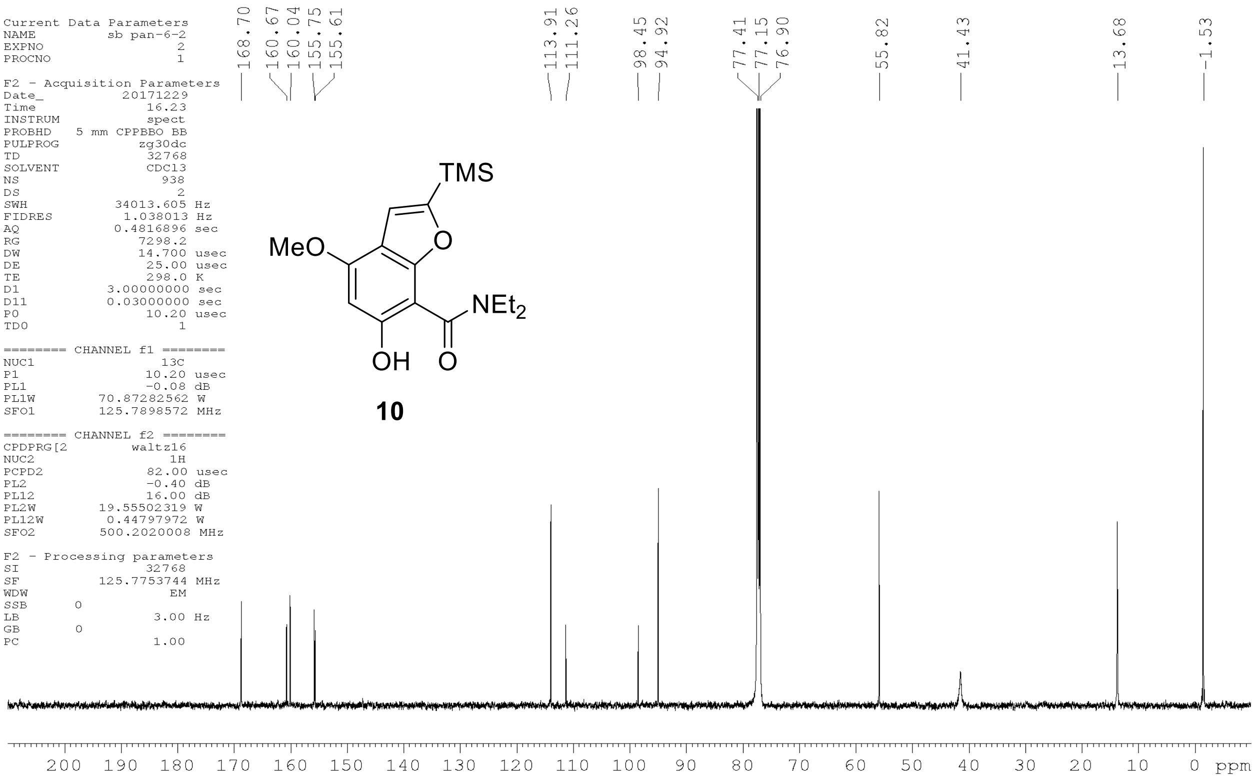

```
Current Data Parameters
NAME           sb pan-6-2
EXPNO                   2
PROCNO                  1

F2 - Acquisition Parameters
Date_            20171229
Time                16.23
INSTRUM             spect
PROBHD    5 mm CPPBBO BB
PULPROG            zg30dc
TD                  32768
SOLVENT             CDCl3
NS                    938
DS                      2
SWH             34013.605 Hz
FIDRES           1.038013 Hz
AQ              0.4816896 sec
RG                 7298.2
DW                 14.700 usec
DE                  25.00 usec
TE                  298.0 K
D1             3.00000000 sec
D11            0.03000000 sec
P0                  10.20 usec
TD0                     1

======== CHANNEL f1 ========
NUC1                  13C
P1                  10.20 usec
PL1                 -0.08 dB
PL1W          70.87282562 W
SFO1          125.7898572 MHz

======== CHANNEL f2 ========
CPDPRG[2          waltz16
NUC2                   1H
PCPD2               82.00 usec
PL2                 -0.40 dB
PL12                16.00 dB
PL2W          19.55502319 W
PL12W          0.44797972 W
SFO2          500.2020008 MHz

F2 - Processing parameters
SI                  32768
SF            125.7753744 MHz
WDW                    EM
SSB      0
LB                   3.00 Hz
GB       0
PC                   1.00
```

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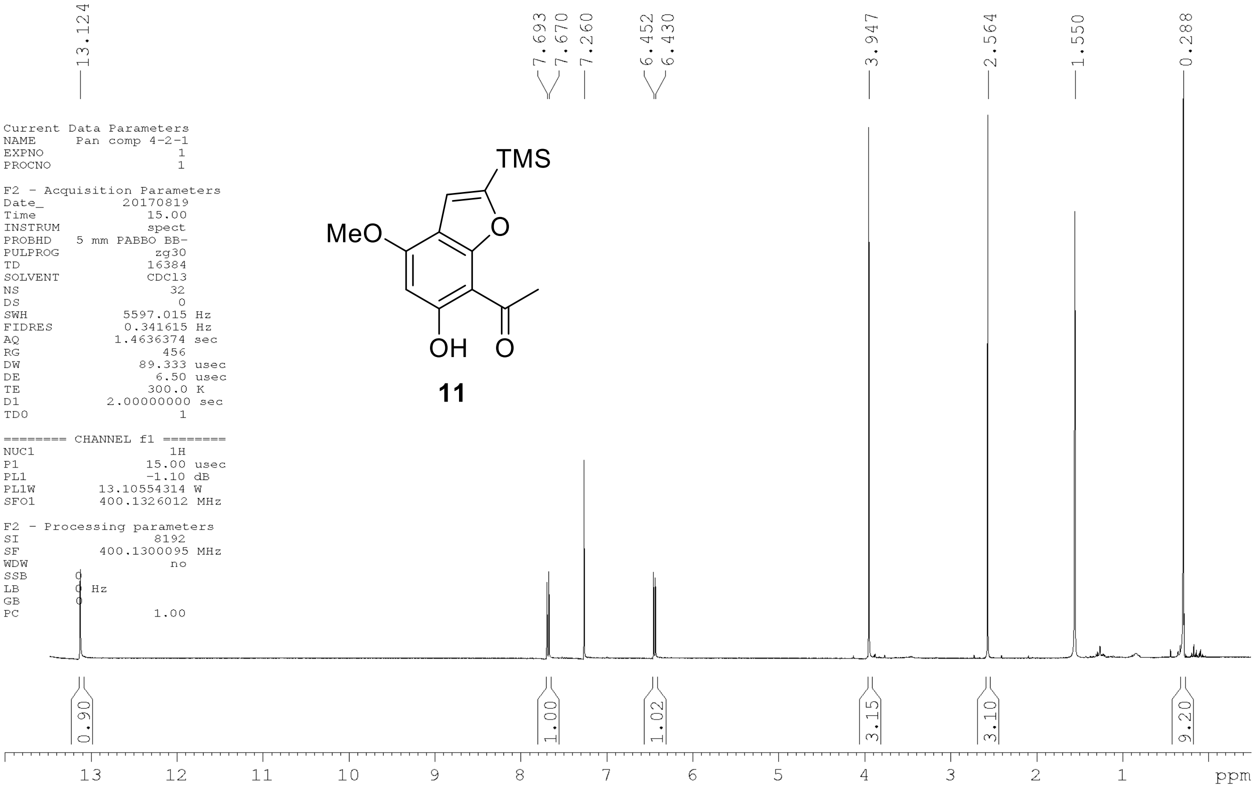


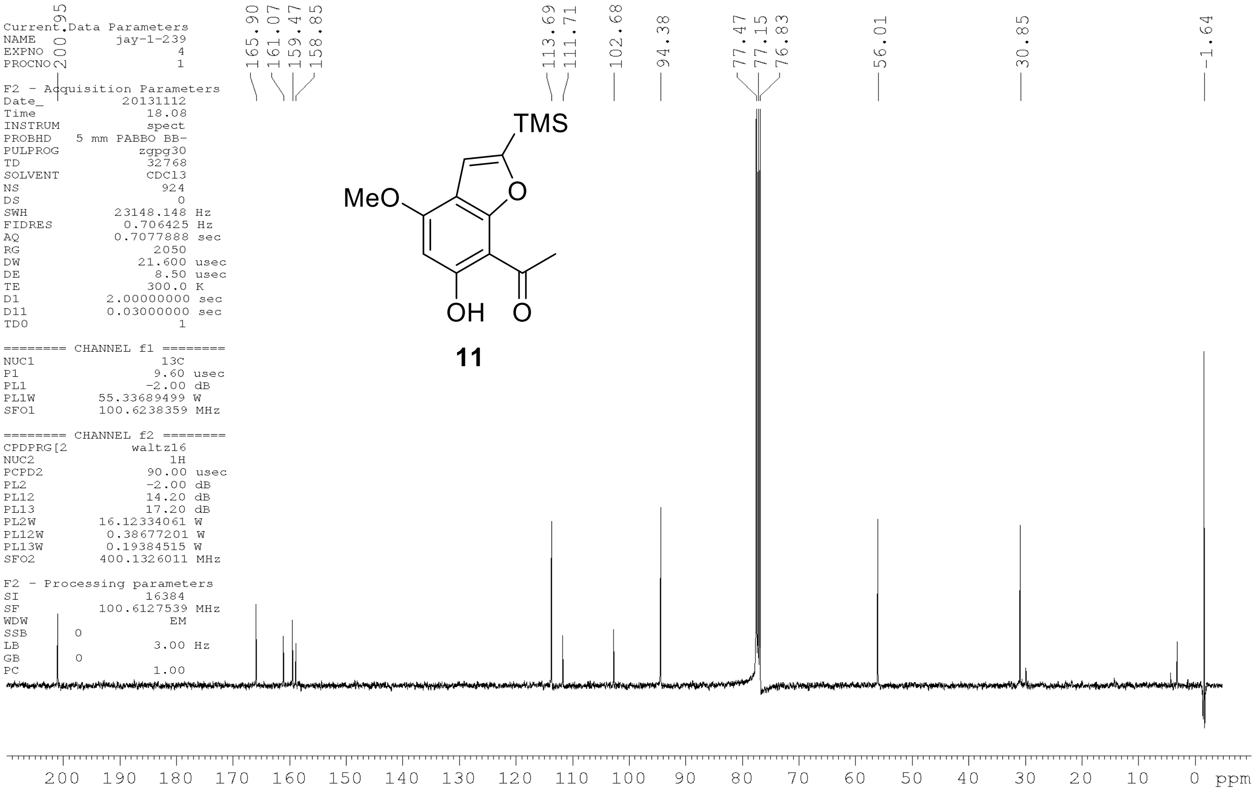
11

```
Current Data Parameters
NAME     Pan comp 4-2-1
EXPNO                 1
PROCNO                1

F2 - Acquisition Parameters
Date_          20170819
Time              15.00
INSTRUM           spect
PROBHD   5 mm PABBO BB-
PULPROG            zg30
TD                16384
SOLVENT           CDCl3
NS                   32
DS                    0
SWH            5597.015 Hz
FIDRES         0.341615 Hz
AQ            1.4636374 sec
RG                  456
DW               89.333 usec
DE                 6.50 usec
TE                300.0 K
D1           2.00000000 sec
TD0                   1

======== CHANNEL f1 ========
NUC1                 1H
P1                15.00 usec
PL1               -1.10 dB
PL1W        13.10554314 W
SFO1        400.1326012 MHz

F2 - Processing parameters
SI                 8192
SF          400.1300095 MHz
WDW                  no
SSB      0
LB       0 Hz
GB       0
PC                 1.00
```



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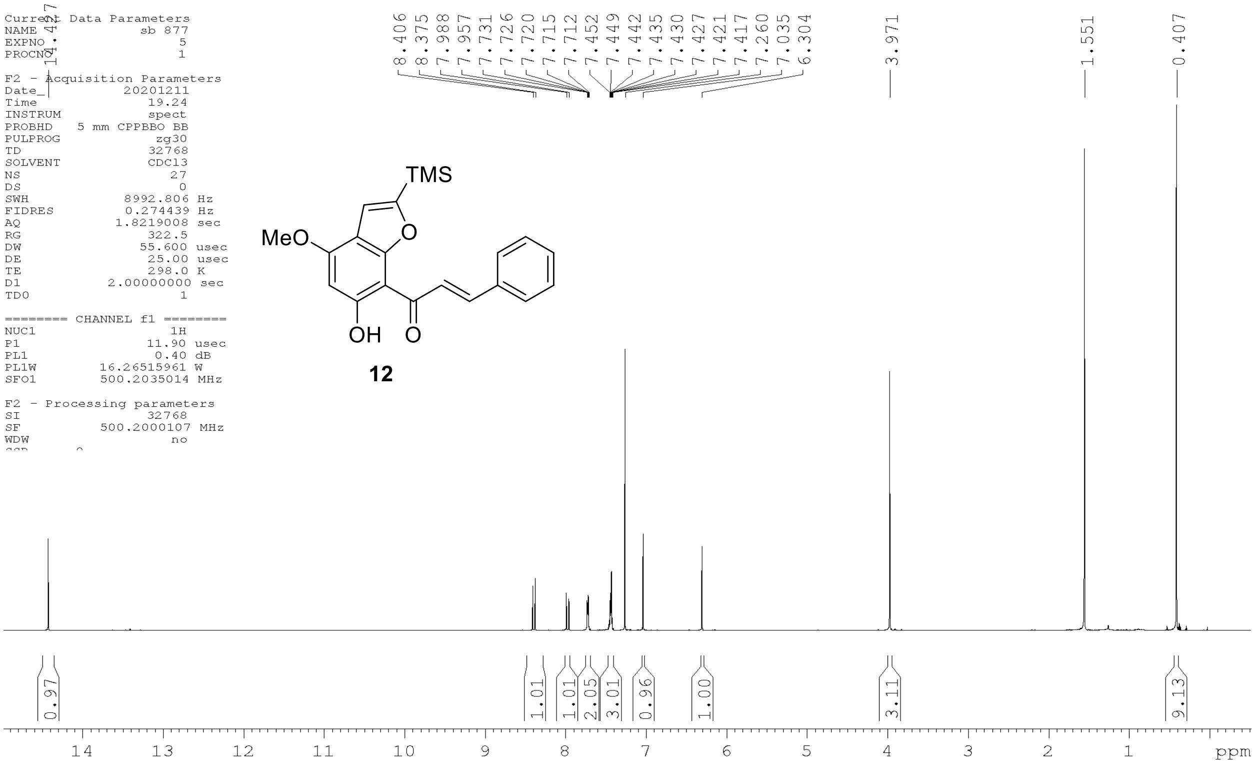
```
Current Data Parameters
NAME         jay-1-239
EXPNO                4
PROCNO               1

F2 - Acquisition Parameters
Date_         20131112
Time             18.08
INSTRUM          spect
PROBHD   5 mm PABBO BB-
PULPROG        zgpg30
TD               32768
SOLVENT          CDCl3
NS                 924
DS                   0
SWH          23148.148 Hz
FIDRES        0.706425 Hz
AQ           0.7077888 sec
RG                2050
DW              21.600 usec
DE                8.50 usec
TE               300.0 K
D1          2.00000000 sec
D11         0.03000000 sec
TD0                  1

======== CHANNEL f1 ========
NUC1               13C
P1                9.60 usec
PL1              -2.00 dB
PL1W       55.33689499 W
SFO1       100.6238359 MHz

======== CHANNEL f2 ========
CPDPRG[2       waltz16
NUC2                1H
PCPD2            90.00 usec
PL2              -2.00 dB
PL12             14.20 dB
PL13             17.20 dB
PL2W       16.12334061 W
PL12W       0.38677201 W
PL13W       0.19384515 W
SFO2       400.1326011 MHz

F2 - Processing parameters
SI               16384
SF         100.6127539 MHz
WDW                 EM
SSB      0
LB                3.00 Hz
GB       0
PC                1.00
```

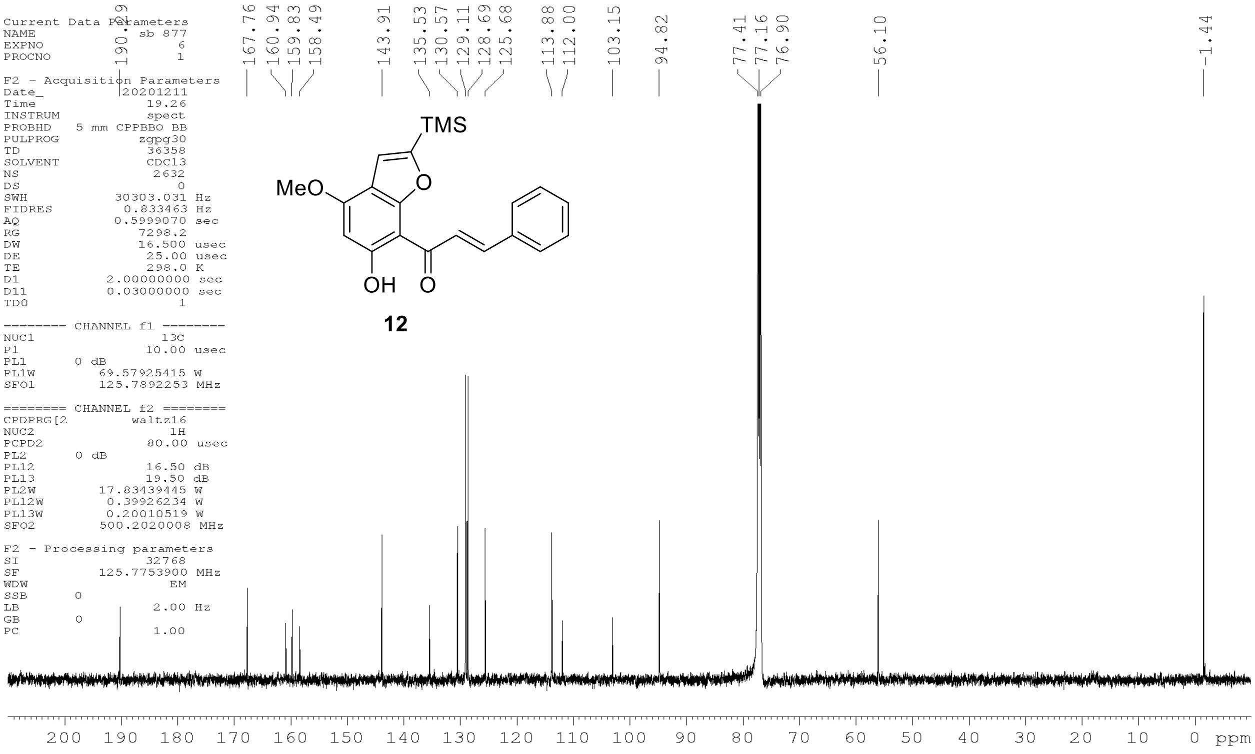


```
Current Data Parameters
NAME              sb 877
EXPNO                  5
PROCNO                 1

F2 - Acquisition Parameters
Date_           20201211
Time               19.24
INSTRUM            spect
PROBHD   5 mm CPPBBO BB
PULPROG             zg30
TD                 32768
SOLVENT            CDCl3
NS                    27
DS                     0
SWH             8992.806 Hz
FIDRES          0.274439 Hz
AQ             1.8219008 sec
RG                 322.5
DW                55.600 usec
DE                 25.00 usec
TE                 298.0 K
D1            2.00000000 sec
TD0                    1

======== CHANNEL f1 ========
NUC1                  1H
P1                 11.90 usec
PL1                 0.40 dB
PL1W         16.26515961 W
SFO1         500.2035014 MHz

F2 - Processing parameters
SI                 32768
SF           500.2000107 MHz
WDW                   no
```



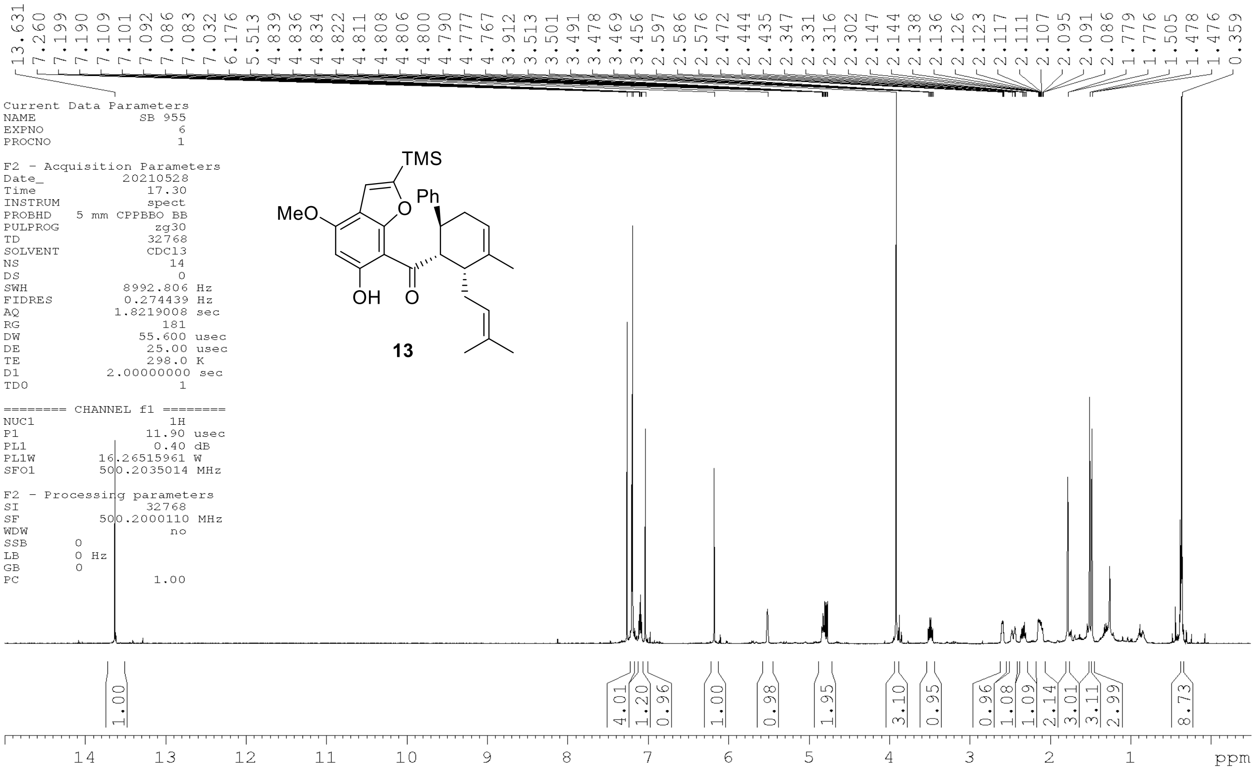
```
Current Data Parameters
NAME              sb 877
EXPNO                  6
PROCNO                 1

F2 - Acquisition Parameters
Date_           20201211
Time               19.26
INSTRUM            spect
PROBHD   5 mm CPPBBO BB
PULPROG          zgpg30
TD                 36358
SOLVENT            CDCl3
NS                  2632
DS                     0
SWH            30303.031 Hz
FIDRES          0.833463 Hz
AQ             0.5999070 sec
RG                7298.2
DW                16.500 usec
DE                 25.00 usec
TE                 298.0 K
D1            2.00000000 sec
D11           0.03000000 sec
TD0                    1

======== CHANNEL f1 ========
NUC1                 13C
P1                 10.00 usec
PL1        0 dB
PL1W         69.57925415 W
SFO1         125.7892253 MHz

======== CHANNEL f2 ========
CPDPRG[2         waltz16
NUC2                  1H
PCPD2              80.00 usec
PL2        0 dB
PL12               16.50 dB
PL13               19.50 dB
PL2W         17.83439445 W
PL12W         0.39926234 W
PL13W         0.20010519 W
SFO2         500.2020008 MHz

F2 - Processing parameters
SI                 32768
SF           125.7753900 MHz
WDW                   EM
SSB        0
LB                  2.00 Hz
GB         0
PC                  1.00
```

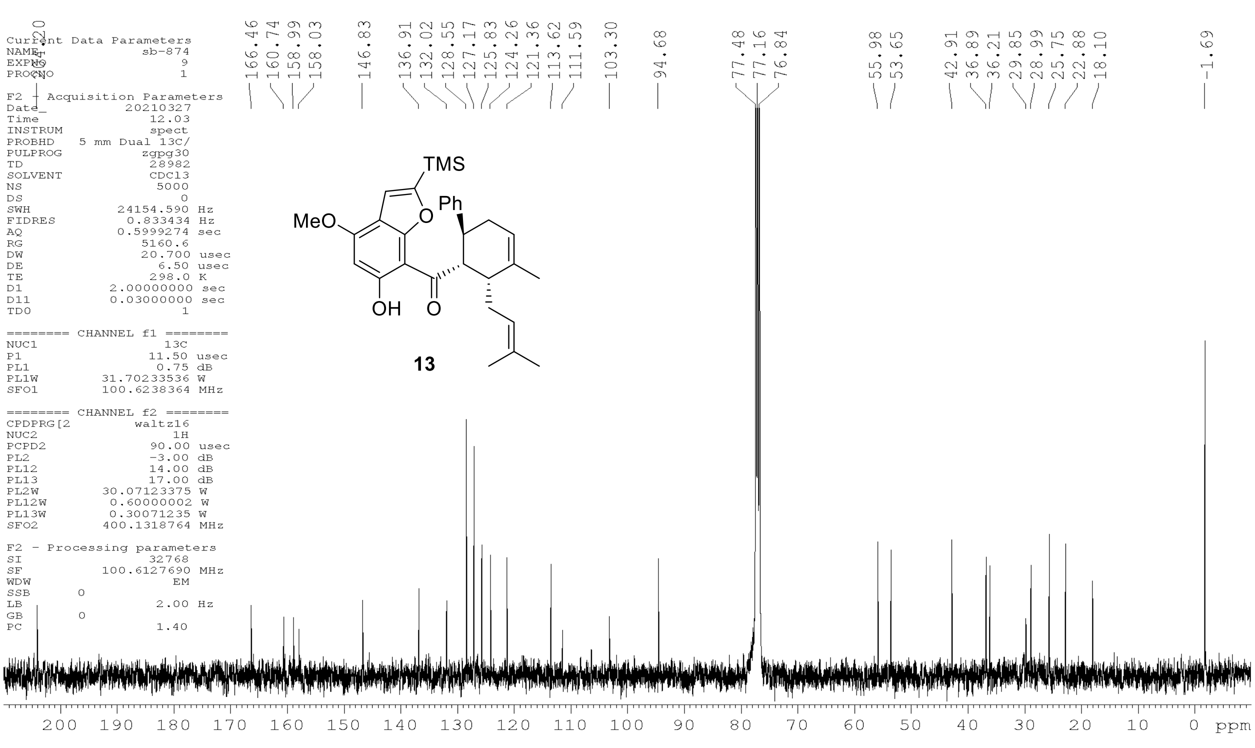


```
Current Data Parameters
NAME              SB 955
EXPNO                  6
PROCNO                 1

F2 - Acquisition Parameters
Date_           20210528
Time               17.30
INSTRUM            spect
PROBHD   5 mm CPPBBO BB
PULPROG             zg30
TD                 32768
SOLVENT            CDCl3
NS                    14
DS                     0
SWH             8992.806 Hz
FIDRES          0.274439 Hz
AQ             1.8219008 sec
RG                   181
DW                55.600 usec
DE                 25.00 usec
TE                 298.0 K
D1            2.00000000 sec
TD0                    1

======== CHANNEL f1 ========
NUC1                  1H
P1                 11.90 usec
PL1                 0.40 dB
PL1W         16.26515961 W
SFO1         500.2035014 MHz

F2 - Processing parameters
SI                 32768
SF           500.2000110 MHz
WDW                   no
SSB      0
LB       0 Hz
GB       0
PC                  1.00
```



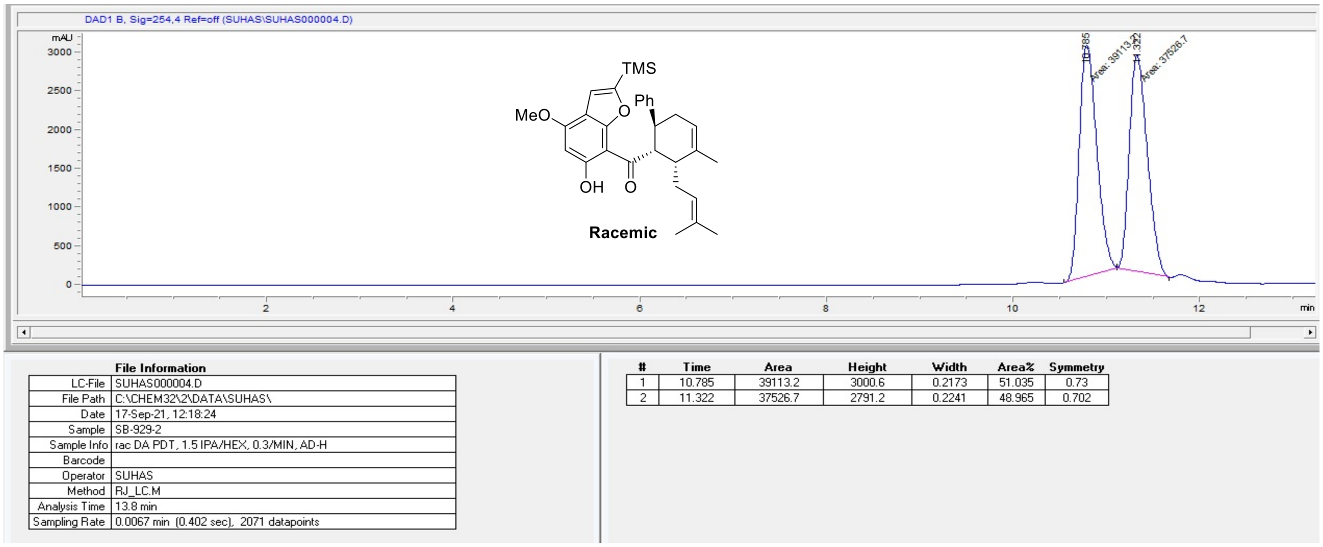
```
Current Data Parameters
NAME              sb-874
EXPNO                  9
PROCNO                 1

F2 - Acquisition Parameters
Date_           20210327
Time               12.03
INSTRUM            spect
PROBHD   5 mm Dual 13C/
PULPROG           zgpg30
TD                 28982
SOLVENT            CDCl3
NS                  5000
DS                     0
SWH            24154.590 Hz
FIDRES          0.833434 Hz
AQ             0.5999274 sec
RG                5160.6
DW                20.700 usec
DE                  6.50 usec
TE                 298.0 K
D1            2.00000000 sec
D11           0.03000000 sec
TD0                    1

======== CHANNEL f1 ========
NUC1                 13C
P1                 11.50 usec
PL1                 0.75 dB
PL1W         31.70233536 W
SFO1         100.6238364 MHz

======== CHANNEL f2 ========
CPDPRG[2         waltz16
NUC2                  1H
PCPD2              90.00 usec
PL2                -3.00 dB
PL12               14.00 dB
PL13               17.00 dB
PL2W         30.07123375 W
PL12W         0.60000002 W
PL13W         0.30071235 W
SFO2         400.1318764 MHz

F2 - Processing parameters
SI                 32768
SF           100.6127690 MHz
WDW                   EM
SSB      0
LB                  2.00 Hz
GB       0
PC                  1.40
```



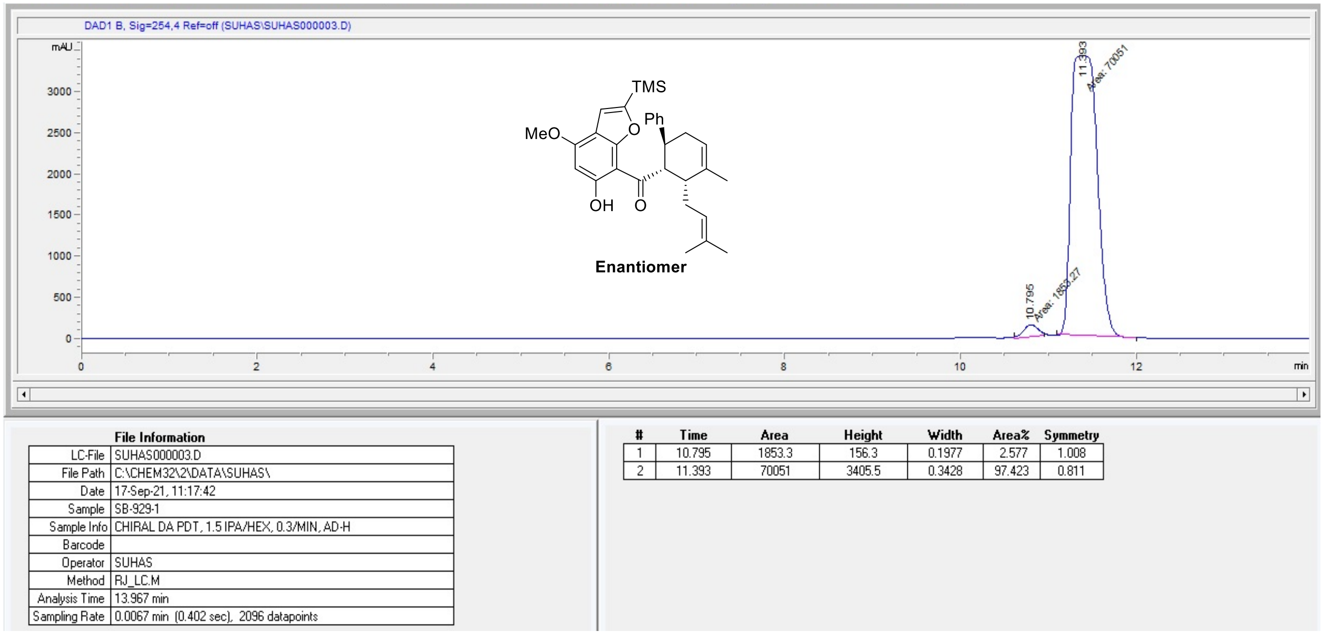
DAD1 B, Sig=254,4 Ref=off (SUHAS\SUHAS000004.D)

Racemic

File Information

LC-File	SUHAS000004.D
File Path	C:\CHEM32\2\DATA\SUHAS\
Date	17-Sep-21, 12:18:24
Sample	SB-929-2
Sample Info	rac DA PDT, 1.5 IPA/HEX, 0.3/MIN, AD-H
Barcode	
Operator	SUHAS
Method	RJ_LC.M
Analysis Time	13.8 min
Sampling Rate	0.0067 min (0.402 sec), 2071 datapoints

#	Time	Area	Height	Width	Area%	Symmetry
1	10.785	39113.2	3000.6	0.2173	51.035	0.73
2	11.322	37526.7	2791.2	0.2241	48.965	0.702



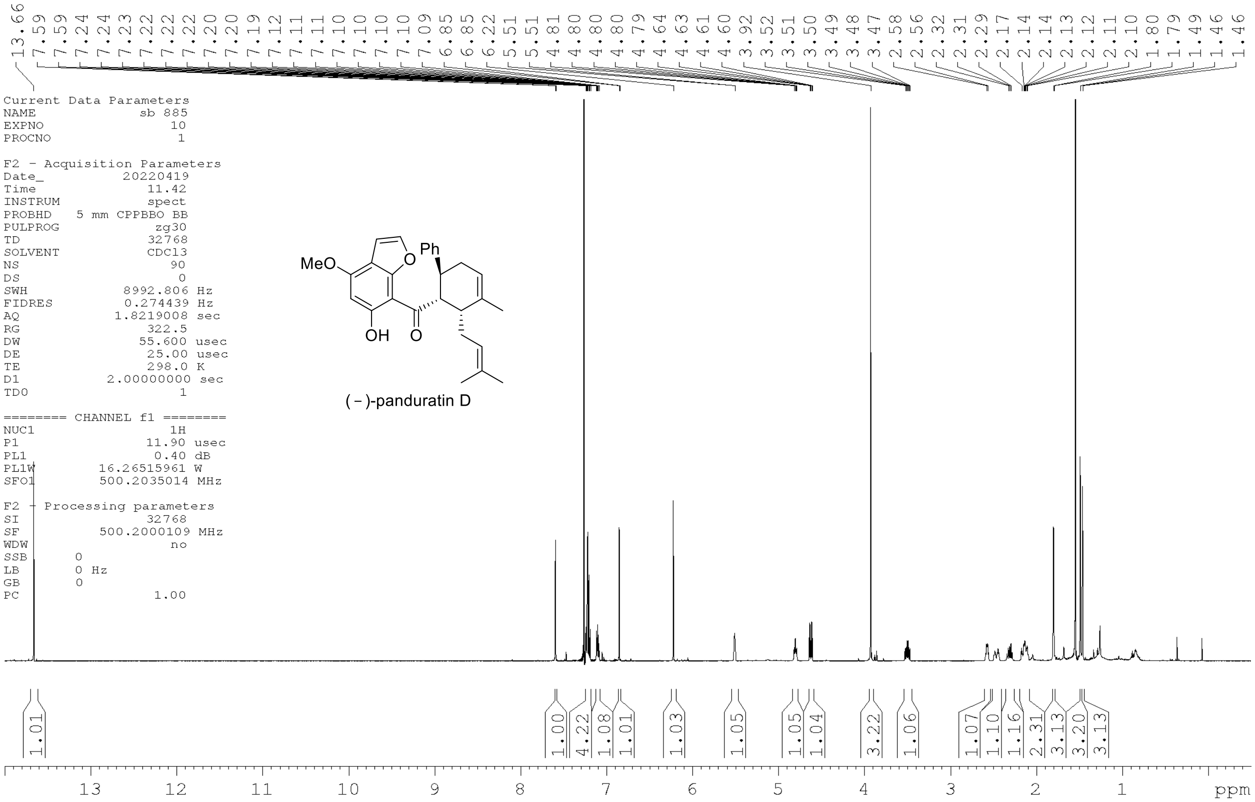
DAD1 B, Sig=254,4 Ref=off (SUHAS\SUHAS000003.D)

Enantiomer

File Information

LC-File	SUHAS000003.D
File Path	C:\CHEM32\2\DATA\SUHAS\
Date	17-Sep-21, 11:17:42
Sample	SB-929-1
Sample Info	CHIRAL DA PDT, 1.5 IPA/HEX, 0.3/MIN, AD-H
Barcode	
Operator	SUHAS
Method	RJ_LC.M
Analysis Time	13.967 min
Sampling Rate	0.0067 min (0.402 sec), 2096 datapoints

#	Time	Area	Height	Width	Area%	Symmetry
1	10.795	1853.3	156.3	0.1977	2.577	1.008
2	11.393	70051	3405.5	0.3428	97.423	0.811

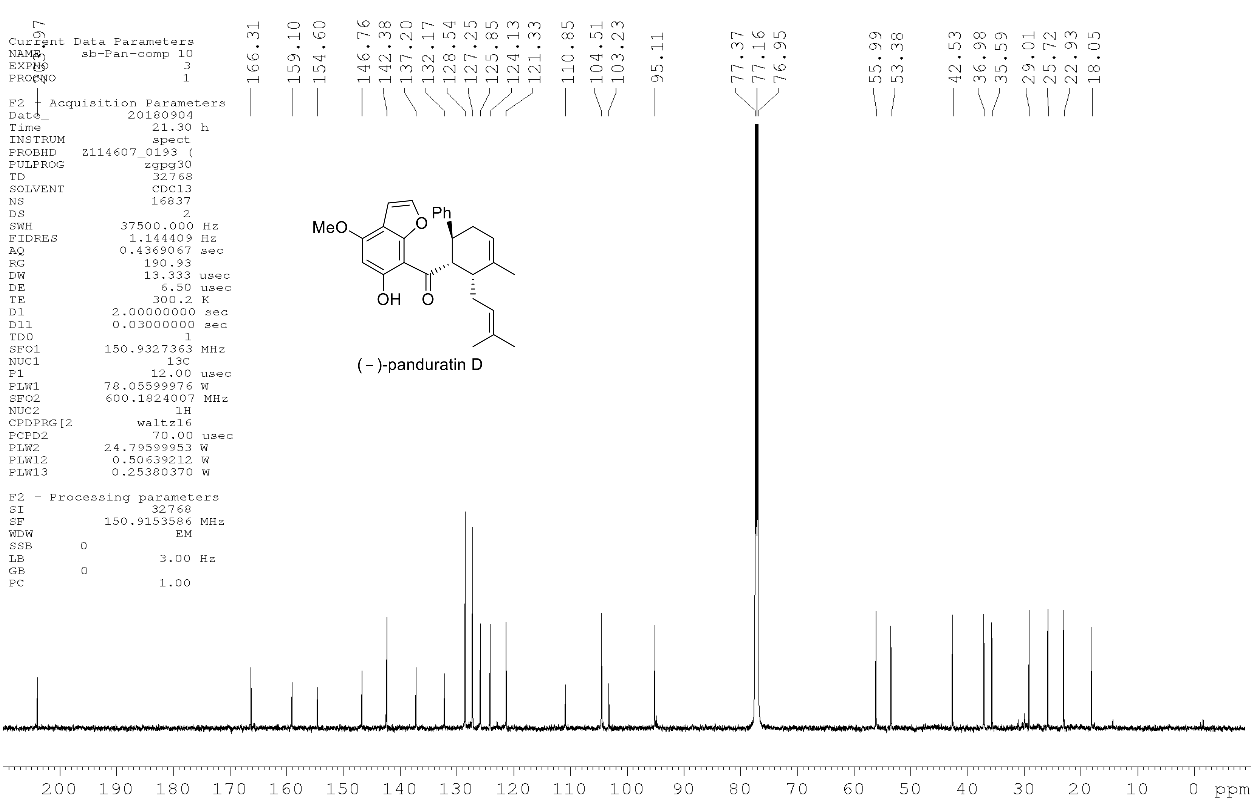


```
Current Data Parameters
NAME              sb 885
EXPNO                 10
PROCNO                 1

F2 - Acquisition Parameters
Date_           20220419
Time               11.42
INSTRUM            spect
PROBHD   5 mm CPPBBO BB
PULPROG             zg30
TD                 32768
SOLVENT            CDCl3
NS                    90
DS                     0
SWH             8992.806 Hz
FIDRES          0.274439 Hz
AQ             1.8219008 sec
RG                 322.5
DW                55.600 usec
DE                 25.00 usec
TE                 298.0 K
D1            2.00000000 sec
TD0                    1

======== CHANNEL f1 ========
NUC1                  1H
P1                 11.90 usec
PL1                 0.40 dB
PL1W         16.26515961 W
SFO1         500.2035014 MHz

F2 - Processing parameters
SI                 32768
SF           500.2000109 MHz
WDW                   no
SSB      0
LB       0 Hz
GB       0
PC                  1.00
```



```
Current Data Parameters
NAME        sb-Pan-comp 10
EXPNO                  3
PROCNO                 1

F2 - Acquisition Parameters
Date_           20180904
Time              21.30 h
INSTRUM            spect
PROBHD   Z114607_0193 (
PULPROG           zgpg30
TD                 32768
SOLVENT            CDCl3
NS                 16837
DS                     2
SWH            37500.000 Hz
FIDRES          1.144409 Hz
AQ             0.4369067 sec
RG                190.93
DW                13.333 usec
DE                  6.50 usec
TE                 300.2 K
D1            2.00000000 sec
D11           0.03000000 sec
TD0                    1
SFO1         150.9327363 MHz
NUC1                 13C
P1                 12.00 usec
PLW1         78.05599976 W
SFO2         600.1824007 MHz
NUC2                  1H
CPDPRG[2         waltz16
PCPD2              70.00 usec
PLW2         24.79599953 W
PLW12         0.50639212 W
PLW13         0.25380370 W

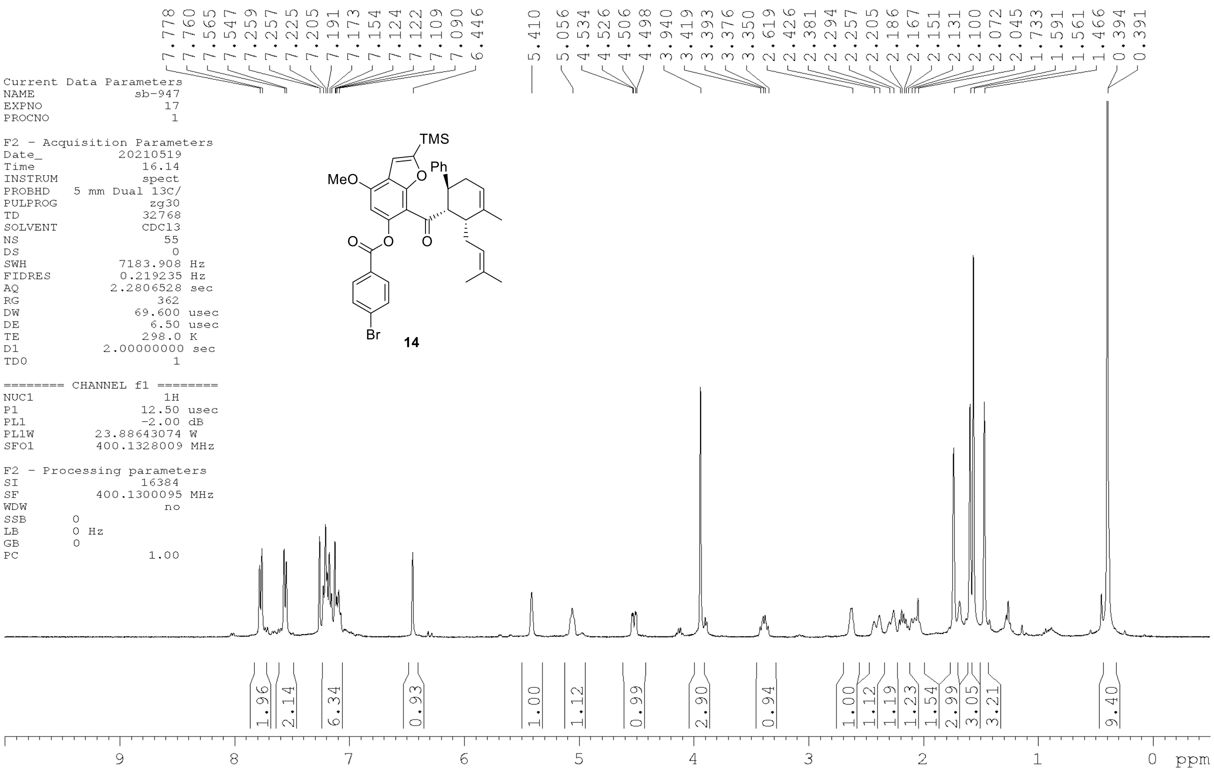
F2 - Processing parameters
SI                 32768
SF           150.9153586 MHz
WDW                   EM
SSB      0
LB                  3.00 Hz
GB       0
PC                  1.00
```

```
Current Data Parameters
NAME              sb-947
EXPNO                 17
PROCNO                 1

F2 - Acquisition Parameters
Date_           20210519
Time               16.14
INSTRUM            spect
PROBHD   5 mm Dual 13C/
PULPROG             zg30
TD                 32768
SOLVENT            CDCl3
NS                    55
DS                     0
SWH             7183.908 Hz
FIDRES          0.219235 Hz
AQ             2.2806528 sec
RG                   362
DW                69.600 usec
DE                  6.50 usec
TE                 298.0 K
D1            2.00000000 sec
TD0                    1

======== CHANNEL f1 ========
NUC1                  1H
P1                 12.50 usec
PL1                -2.00 dB
PL1W         23.88643074 W
SFO1         400.1328009 MHz

F2 - Processing parameters
SI                 16384
SF           400.1300095 MHz
WDW                   no
SSB      0
LB       0 Hz
GB       0
PC                  1.00
```



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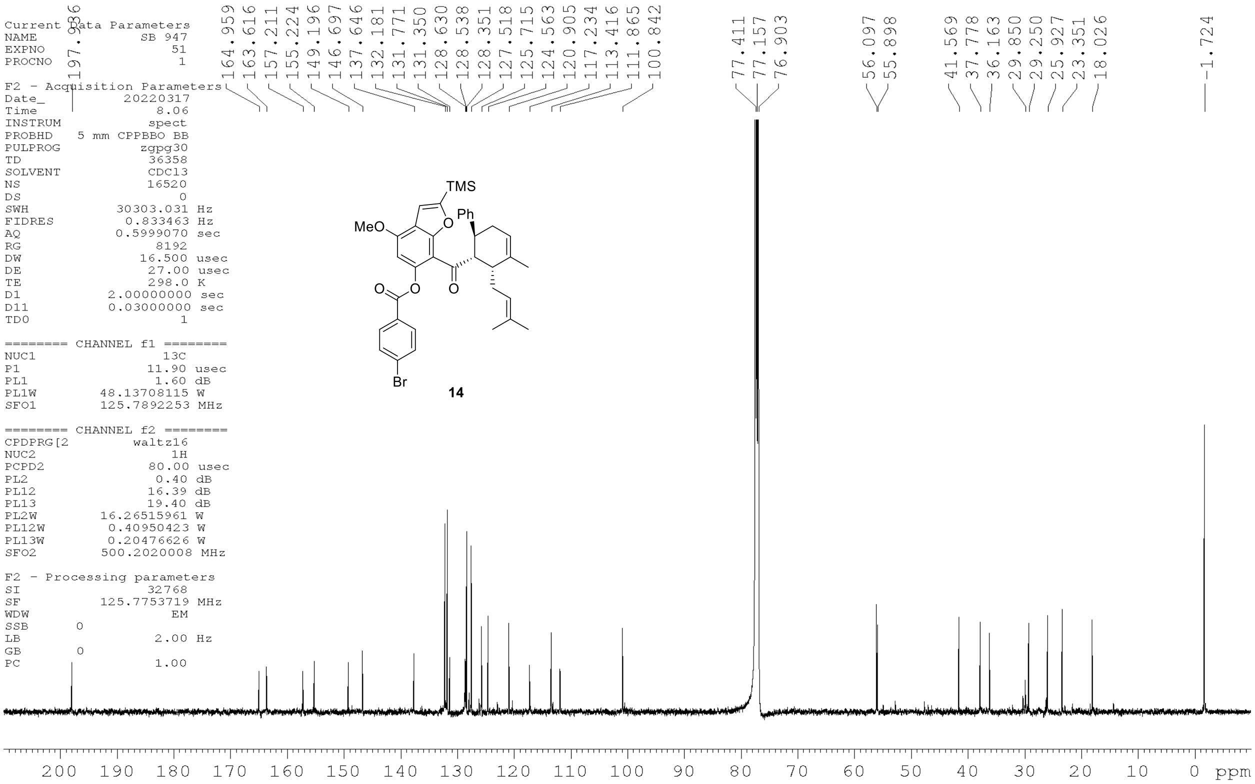
```
Current Data Parameters
NAME              SB 947
EXPNO                 51
PROCNO                 1

F2 - Acquisition Parameters
Date_           20220317
Time                8.06
INSTRUM            spect
PROBHD   5 mm CPPBBO BB
PULPROG           zgpg30
TD                 36358
SOLVENT            CDCl3
NS                 16520
DS                     0
SWH            30303.031 Hz
FIDRES          0.833463 Hz
AQ             0.5999070 sec
RG                  8192
DW                16.500 usec
DE                 27.00 usec
TE                 298.0 K
D1            2.00000000 sec
D11           0.03000000 sec
TD0                    1

======== CHANNEL f1 ========
NUC1                 13C
P1                 11.90 usec
PL1                 1.60 dB
PL1W         48.13708115 W
SFO1         125.7892253 MHz

======== CHANNEL f2 ========
CPDPRG[2         waltz16
NUC2                  1H
PCPD2              80.00 usec
PL2                 0.40 dB
PL12               16.39 dB
PL13               19.40 dB
PL2W         16.26515961 W
PL12W         0.40950423 W
PL13W         0.20476626 W
SFO2         500.2020008 MHz

F2 - Processing parameters
SI                 32768
SF           125.7753719 MHz
WDW                   EM
SSB      0
LB                  2.00 Hz
GB       0
PC                  1.00
```



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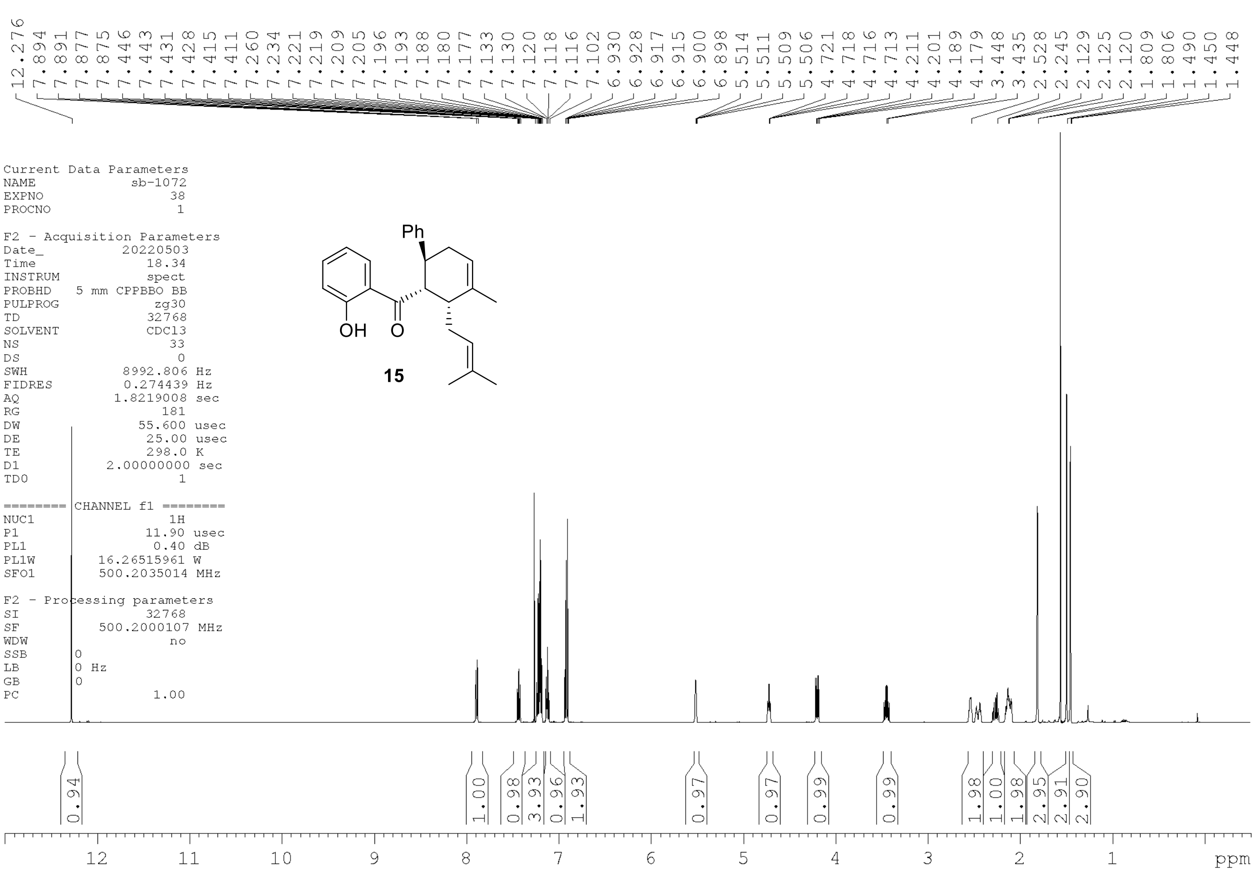

```
Current Data Parameters
NAME              sb-1072
EXPNO                  38
PROCNO                  1

F2 - Acquisition Parameters
Date_            20220503
Time                18.34
INSTRUM             spect
PROBHD   5 mm CPPBBO BB
PULPROG              zg30
TD                  32768
SOLVENT             CDCl3
NS                     33
DS                      0
SWH              8992.806 Hz
FIDRES           0.274439 Hz
AQ              1.8219008 sec
RG                    181
DW                 55.600 usec
DE                  25.00 usec
TE                  298.0 K
D1             2.00000000 sec
TD0                     1

======== CHANNEL f1 ========
NUC1                   1H
P1                  11.90 usec
PL1                  0.40 dB
PL1W          16.26515961 W
SFO1        500.2035014 MHz

F2 - Processing parameters
SI                  32768
SF          500.2000107 MHz
WDW                    no
SSB      0
LB       0 Hz
GB       0
PC                   1.00
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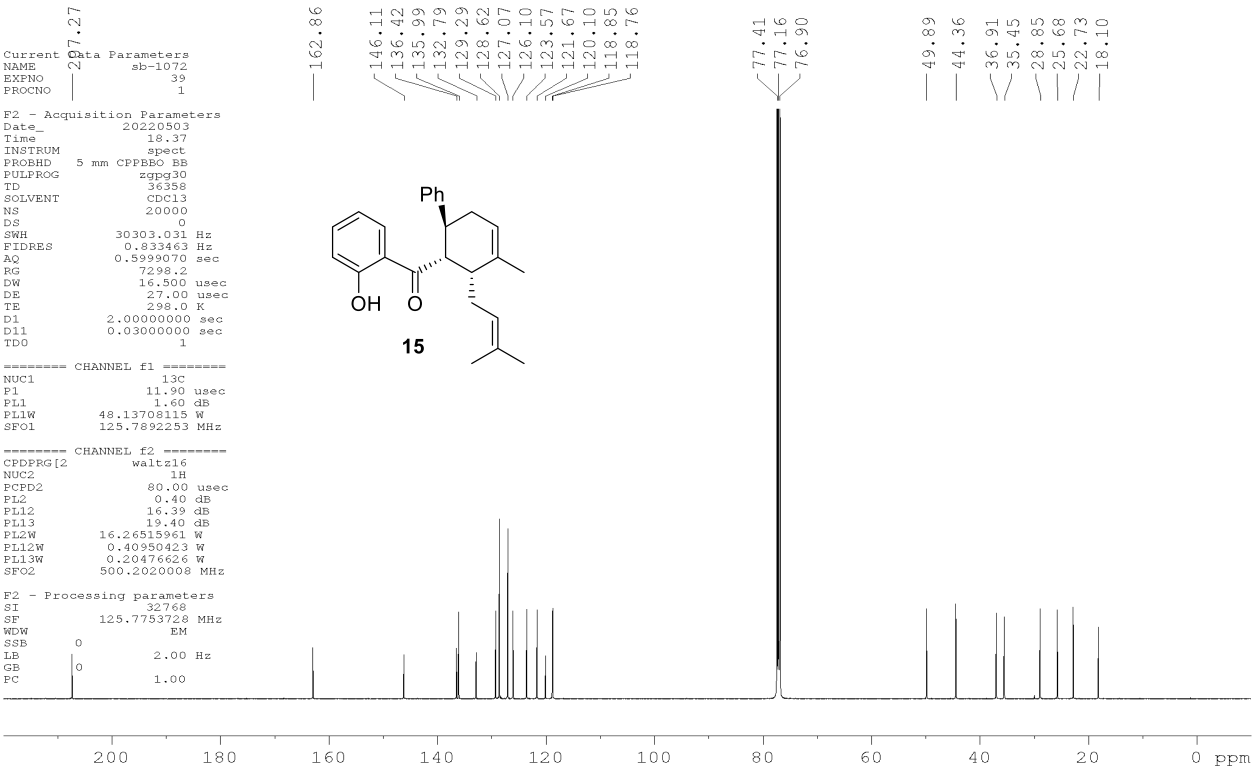

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Current Data Parameters
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EXPNO                  39
PROCNO                  1

F2 - Acquisition Parameters
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Time                18.37
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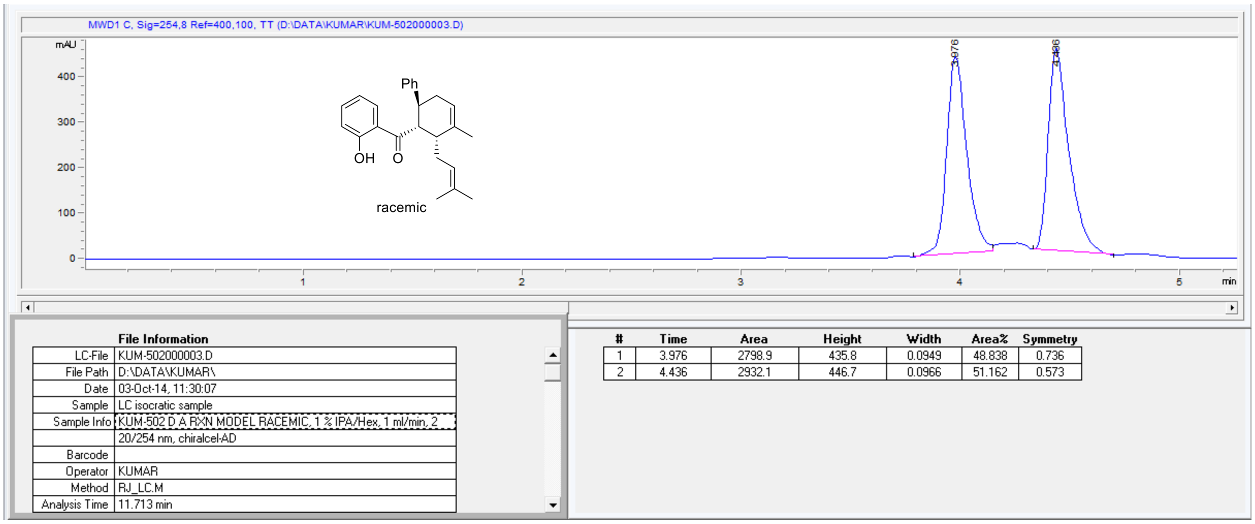
PROBHD   5 mm CPPBBO BB
PULPROG           zgpg30
TD                  36358
SOLVENT             CDCl3
NS                  20000
DS                      0
SWH             30303.031 Hz
FIDRES           0.833463 Hz
AQ              0.5999070 sec
RG                 7298.2
DW                 16.500 usec
DE                  27.00 usec
TE                  298.0 K
D1             2.00000000 sec
D11            0.03000000 sec
TD0                     1

======== CHANNEL f1 ========
NUC1                  13C
P1                  11.90 usec
PL1                  1.60 dB
PL1W          48.13708115 W
SFO1        125.7892253 MHz

======== CHANNEL f2 ========
CPDPRG[2          waltz16
NUC2                   1H
PCPD2               80.00 usec
PL2                  0.40 dB
PL12                16.39 dB
PL13                19.40 dB
PL2W          16.26515961 W
PL12W          0.40950423 W
PL13W          0.20476626 W
SFO2        500.2020008 MHz

F2 - Processing parameters
SI                  32768
SF          125.7753728 MHz
WDW                    EM
SSB      0
LB                   2.00 Hz
GB       0
PC                   1.00
```



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File Information

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Date	03-Oct-14, 11:30:07
Sample	LC isocratic sample
Sample Info	KUM-502 D A RXN MODEL RACEMIC, 1 % IPA/Hex, 1 ml/min, 2
	20/254 nm, chiralcel-AD
Barcode	
Operator	KUMAR
Method	RJ_LC.M
Analysis Time	11.713 min

#	Time	Area	Height	Width	Area%	Symmetry
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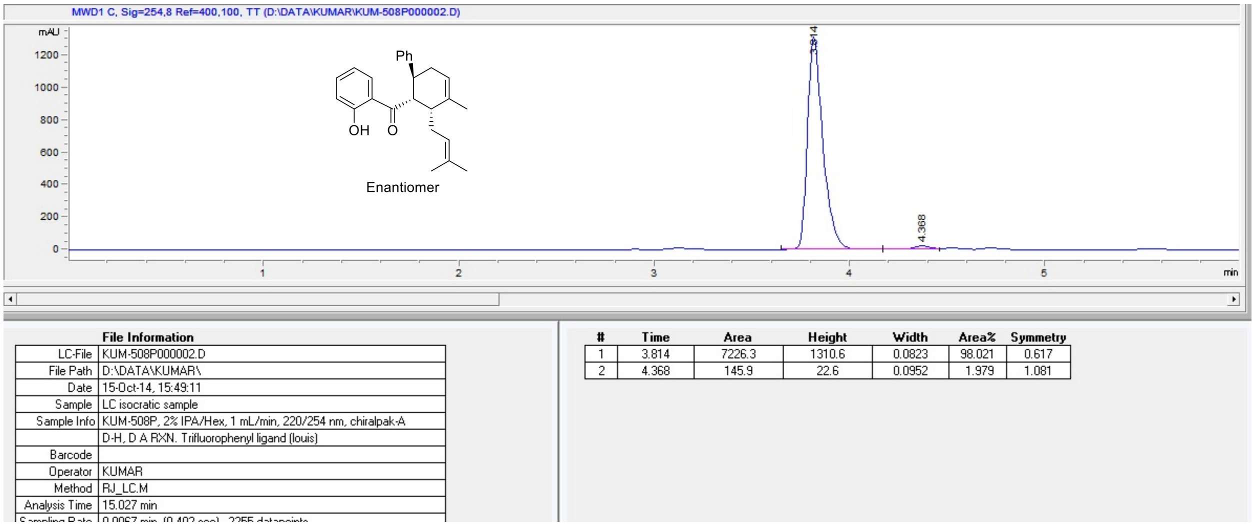
2	4.436	2932.1	446.7	0.0966	51.162	0.573



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File Information

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File Path	D:\DATA\KUMAR\
Date	15-Oct-14, 15:49:11
Sample	LC isocratic sample
Sample Info	KUM-508P, 2% IPA/Hex, 1 mL/min, 220/254 nm, chiralpak-A
	D-H, D A RXN. Trifluorophenyl ligand (louis)
Barcode	
Operator	KUMAR
Method	RJ_LC.M
Analysis Time	15.027 min

#	Time	Area	Height	Width	Area%	Symmetry
1	3.814	7226.3	1310.6	0.0823	98.021	0.617
2	4.368	145.9	22.6	0.0952	1.979	1.081

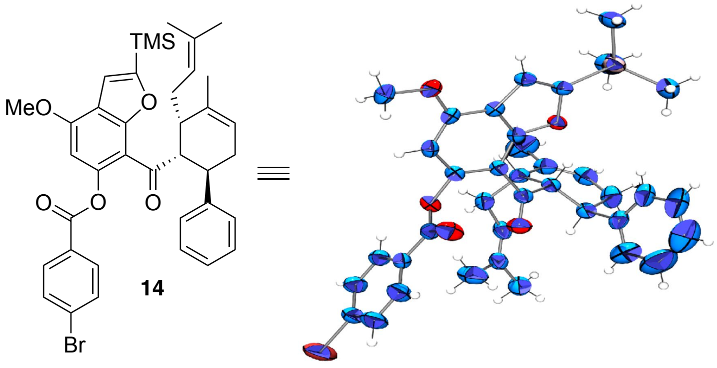

Figure S1. X-ray crystal structure establishing the absolute configuration of **14** derived from **13** (displacement ellipsoids are drawn at the 50% probability level CCDC-2154709).

Table S1. Crystal data and structure refinement for d23352.

Identification code	d23352	
Empirical formula	C38 H41 Br O5 Si	
Formula weight	685.71	
Temperature	200(2) K	
Wavelength	0.71073 Å	
Crystal system	Triclinic	
Space group	P -1	
Unit cell dimensions	a = 11.507(7) Å	α= 81.31(2)°.
	b = 11.622(7) Å	β= 69.658(19)°.
	c = 15.292(8) Å	γ = 70.312(14)°.
Volume	1804.2(18) Å^3	
Z	2	
Density (calculated)	1.262 Mg/m^3	
Absorption coefficient	1.212 mm^{-1}	
F(000)	716	
Crystal size	0.19 x 0.14 x 0.07 mm^3	

Theta range for data collection	1.98 to 25.46°.
Index ranges	-13<=h<=13, -14<=k<=14, -18<=l<=18
Reflections collected	42693
Independent reflections	6617 [R(int) = 0.0550]
Completeness to theta = 25.46°	98.9 %
Absorption correction	multi-scan
Max. and min. transmission	0.9199 and 0.8024
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	6617 / 0 / 413
Goodness-of-fit on F^2	1.004
Final R indices [I>2sigma(I)]	R1 = 0.0441, wR2 = 0.1111
R indices (all data)	R1 = 0.0686, wR2 = 0.1250
Largest diff. peak and hole	0.328 and -0.647 e.Å^{-3}

Table S2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) for d23352. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
C(1)	8825(3)	2175(3)	6158(2)	54(1)
C(2)	9407(3)	3033(3)	6190(2)	67(1)
C(3)	8882(3)	4231(3)	5927(2)	55(1)
C(4)	7784(2)	4567(2)	5634(2)	39(1)
C(5)	7215(3)	3684(2)	5620(2)	44(1)
C(6)	7730(3)	2490(2)	5884(2)	52(1)
C(7)	7268(2)	5867(2)	5349(2)	39(1)
C(8)	5613(2)	7227(2)	4764(2)	36(1)
C(9)	4656(2)	7968(2)	5476(2)	37(1)
C(10)	3928(2)	9115(2)	5249(2)	35(1)
C(11)	2758(3)	9635(3)	6836(2)	50(1)
C(12)	4138(2)	9474(2)	4300(2)	33(1)
C(13)	3567(2)	10544(2)	3811(2)	37(1)
C(14)	4158(2)	10375(2)	2887(2)	39(1)
C(15)	2666(3)	12766(3)	2222(2)	68(1)
C(16)	5551(3)	11592(3)	1103(2)	71(1)
C(17)	3484(4)	10432(3)	1137(2)	76(1)
C(18)	5085(2)	8683(2)	3620(2)	33(1)
C(19)	5902(2)	7535(2)	3807(2)	34(1)
C(20)	7005(2)	6738(2)	3076(2)	38(1)

C(21)	6825(2)	6704(2)	2140(2)	39(1)
C(22)	8116(3)	6263(2)	1347(2)	45(1)
C(23)	9020(3)	7018(3)	1230(2)	49(1)
C(24)	8624(3)	8276(3)	1065(2)	63(1)
C(25)	9425(5)	8984(4)	942(3)	88(1)
C(26)	10642(6)	8467(6)	968(3)	108(2)
C(27)	11092(5)	7226(7)	1132(4)	121(2)
C(28)	10264(4)	6493(4)	1261(3)	85(1)
C(29)	7823(3)	6299(3)	426(2)	62(1)
C(30)	6590(3)	6036(3)	531(2)	58(1)
C(31)	5706(3)	5881(3)	1334(2)	53(1)
C(32)	4480(4)	5597(5)	1391(3)	98(1)
C(33)	5879(3)	5951(2)	2260(2)	44(1)
C(34)	6229(3)	4660(2)	2742(2)	50(1)
C(35)	7374(3)	3724(2)	2132(2)	49(1)
C(36)	8456(3)	3046(2)	2303(2)	51(1)
C(37)	9533(3)	2194(3)	1596(2)	68(1)
C(38)	8730(4)	3058(3)	3197(3)	77(1)
O(1)	7678(2)	6676(2)	5392(1)	55(1)
O(2)	6234(2)	6032(1)	5042(1)	41(1)
O(3)	3003(2)	9946(2)	5860(1)	45(1)
O(4)	5119(2)	9217(1)	2747(1)	37(1)
O(5)	7996(2)	6112(2)	3248(1)	53(1)
Br(1)	9529(1)	513(1)	6505(1)	95(1)
Si(1)	3965(1)	11313(1)	1806(1)	48(1)

Table S3. Bond lengths [Å] and angles [°] for d23352.

C(1)-C(6)	1.380(4)
C(1)-C(2)	1.390(4)
C(1)-Br(1)	1.900(3)
C(2)-C(3)	1.378(4)
C(2)-H(2)	0.9500
C(3)-C(4)	1.399(4)
C(3)-H(3)	0.9500
C(4)-C(5)	1.396(4)
C(4)-C(7)	1.484(3)
C(5)-C(6)	1.372(4)
C(5)-H(5)	0.9500
C(6)-H(6)	0.9500
C(7)-O(1)	1.204(3)
C(7)-O(2)	1.371(3)
C(8)-C(9)	1.397(3)
C(8)-C(19)	1.400(3)
C(8)-O(2)	1.408(3)
C(9)-C(10)	1.382(3)
C(9)-H(9)	0.9500
C(10)-O(3)	1.352(3)
C(10)-C(12)	1.407(3)
C(11)-O(3)	1.432(3)
C(11)-H(11A)	0.9800

C(11)-H(11B)	0.9800
C(11)-H(11C)	0.9800
C(12)-C(18)	1.393(3)
C(12)-C(13)	1.431(3)
C(13)-C(14)	1.350(4)
C(13)-H(13)	0.9500
C(14)-O(4)	1.414(3)
C(14)-Si(1)	1.876(3)
C(15)-Si(1)	1.859(3)
C(15)-H(15A)	0.9800
C(15)-H(15B)	0.9800
C(15)-H(15C)	0.9800
C(16)-Si(1)	1.876(4)
C(16)-H(16A)	0.9800
C(16)-H(16B)	0.9800
C(16)-H(16C)	0.9800
C(17)-Si(1)	1.869(4)
C(17)-H(17A)	0.9800
C(17)-H(17B)	0.9800
C(17)-H(17C)	0.9800
C(18)-O(4)	1.378(3)
C(18)-C(19)	1.404(3)
C(19)-C(20)	1.501(3)
C(20)-O(5)	1.222(3)
C(20)-C(21)	1.523(4)

C(21)-C(22)	1.537(4)
C(21)-C(33)	1.562(4)
C(21)-H(21)	1.0000
C(22)-C(23)	1.524(4)
C(22)-C(29)	1.549(4)
C(22)-H(22)	1.0000
C(23)-C(28)	1.369(5)
C(23)-C(24)	1.389(4)
C(24)-C(25)	1.381(5)
C(24)-H(24)	0.9500
C(25)-C(26)	1.337(7)
C(25)-H(25)	0.9500
C(26)-C(27)	1.375(7)
C(26)-H(26)	0.9500
C(27)-C(28)	1.428(7)
C(27)-H(27)	0.9500
C(28)-H(28)	0.9500
C(29)-C(30)	1.501(5)
C(29)-H(29A)	0.9900
C(29)-H(29B)	0.9900
C(30)-C(31)	1.328(4)
C(30)-H(30)	0.9500
C(31)-C(33)	1.514(4)
C(31)-C(32)	1.526(5)
C(32)-H(32A)	0.9800

C(32)-H(32B)	0.9800
C(32)-H(32C)	0.9800
C(33)-C(34)	1.556(4)
C(33)-H(33)	1.0000
C(34)-C(35)	1.509(4)
C(34)-H(34A)	0.9900
C(34)-H(34B)	0.9900
C(35)-C(36)	1.320(4)
C(35)-H(35)	0.9500
C(36)-C(37)	1.500(4)
C(36)-C(38)	1.508(5)
C(37)-H(37A)	0.9800
C(37)-H(37B)	0.9800
C(37)-H(37C)	0.9800
C(38)-H(38A)	0.9800
C(38)-H(38B)	0.9800
C(38)-H(38C)	0.9800

C(6)-C(1)-C(2)	122.1(3)
C(6)-C(1)-Br(1)	118.0(2)
C(2)-C(1)-Br(1)	119.9(2)
C(3)-C(2)-C(1)	118.7(3)
C(3)-C(2)-H(2)	120.7
C(1)-C(2)-H(2)	120.7
C(2)-C(3)-C(4)	120.1(3)

C(2)-C(3)-H(3)	119.9
C(4)-C(3)-H(3)	119.9
C(5)-C(4)-C(3)	119.7(2)
C(5)-C(4)-C(7)	122.5(2)
C(3)-C(4)-C(7)	117.8(2)
C(6)-C(5)-C(4)	120.5(2)
C(6)-C(5)-H(5)	119.8
C(4)-C(5)-H(5)	119.8
C(5)-C(6)-C(1)	118.9(3)
C(5)-C(6)-H(6)	120.6
C(1)-C(6)-H(6)	120.6
O(1)-C(7)-O(2)	124.1(2)
O(1)-C(7)-C(4)	125.3(2)
O(2)-C(7)-C(4)	110.6(2)
C(9)-C(8)-C(19)	125.3(2)
C(9)-C(8)-O(2)	116.0(2)
C(19)-C(8)-O(2)	118.3(2)
C(10)-C(9)-C(8)	119.3(2)
C(10)-C(9)-H(9)	120.3
C(8)-C(9)-H(9)	120.3
O(3)-C(10)-C(9)	126.0(2)
O(3)-C(10)-C(12)	115.5(2)
C(9)-C(10)-C(12)	118.5(2)
O(3)-C(11)-H(11A)	109.5
O(3)-C(11)-H(11B)	109.5

H(11A)-C(11)-H(11B)	109.5
O(3)-C(11)-H(11C)	109.5
H(11A)-C(11)-H(11C)	109.5
H(11B)-C(11)-H(11C)	109.5
C(18)-C(12)-C(10)	119.5(2)
C(18)-C(12)-C(13)	106.2(2)
C(10)-C(12)-C(13)	134.2(2)
C(14)-C(13)-C(12)	108.0(2)
C(14)-C(13)-H(13)	126.0
C(12)-C(13)-H(13)	126.0
C(13)-C(14)-O(4)	109.5(2)
C(13)-C(14)-Si(1)	134.29(18)
O(4)-C(14)-Si(1)	116.17(17)
Si(1)-C(15)-H(15A)	109.5
Si(1)-C(15)-H(15B)	109.5
H(15A)-C(15)-H(15B)	109.5
Si(1)-C(15)-H(15C)	109.5
H(15A)-C(15)-H(15C)	109.5
H(15B)-C(15)-H(15C)	109.5
Si(1)-C(16)-H(16A)	109.5
Si(1)-C(16)-H(16B)	109.5
H(16A)-C(16)-H(16B)	109.5
Si(1)-C(16)-H(16C)	109.5
H(16A)-C(16)-H(16C)	109.5
H(16B)-C(16)-H(16C)	109.5

Si(1)-C(17)-H(17A)	109.5
Si(1)-C(17)-H(17B)	109.5
H(17A)-C(17)-H(17B)	109.5
Si(1)-C(17)-H(17C)	109.5
H(17A)-C(17)-H(17C)	109.5
H(17B)-C(17)-H(17C)	109.5
O(4)-C(18)-C(12)	109.6(2)
O(4)-C(18)-C(19)	125.7(2)
C(12)-C(18)-C(19)	124.6(2)
C(8)-C(19)-C(18)	112.6(2)
C(8)-C(19)-C(20)	123.0(2)
C(18)-C(19)-C(20)	124.4(2)
O(5)-C(20)-C(19)	120.1(2)
O(5)-C(20)-C(21)	121.7(2)
C(19)-C(20)-C(21)	118.2(2)
C(20)-C(21)-C(22)	113.5(2)
C(20)-C(21)-C(33)	109.4(2)
C(22)-C(21)-C(33)	113.1(2)
C(20)-C(21)-H(21)	106.8
C(22)-C(21)-H(21)	106.8
C(33)-C(21)-H(21)	106.8
C(23)-C(22)-C(21)	112.4(2)
C(23)-C(22)-C(29)	110.4(2)
C(21)-C(22)-C(29)	109.2(2)
C(23)-C(22)-H(22)	108.3

C(21)-C(22)-H(22)	108.3
C(29)-C(22)-H(22)	108.3
C(28)-C(23)-C(24)	116.8(3)
C(28)-C(23)-C(22)	122.0(3)
C(24)-C(23)-C(22)	121.2(3)
C(25)-C(24)-C(23)	122.6(4)
C(25)-C(24)-H(24)	118.7
C(23)-C(24)-H(24)	118.7
C(26)-C(25)-C(24)	120.4(4)
C(26)-C(25)-H(25)	119.8
C(24)-C(25)-H(25)	119.8
C(25)-C(26)-C(27)	119.8(4)
C(25)-C(26)-H(26)	120.1
C(27)-C(26)-H(26)	120.1
C(26)-C(27)-C(28)	119.8(4)
C(26)-C(27)-H(27)	120.1
C(28)-C(27)-H(27)	120.1
C(23)-C(28)-C(27)	120.5(4)
C(23)-C(28)-H(28)	119.8
C(27)-C(28)-H(28)	119.8
C(30)-C(29)-C(22)	115.3(2)
C(30)-C(29)-H(29A)	108.4
C(22)-C(29)-H(29A)	108.4
C(30)-C(29)-H(29B)	108.4
C(22)-C(29)-H(29B)	108.4

H(29A)-C(29)-H(29B)	107.5
C(31)-C(30)-C(29)	125.7(3)
C(31)-C(30)-H(30)	117.2
C(29)-C(30)-H(30)	117.2
C(30)-C(31)-C(33)	121.3(3)
C(30)-C(31)-C(32)	122.9(3)
C(33)-C(31)-C(32)	115.8(3)
C(31)-C(32)-H(32A)	109.5
C(31)-C(32)-H(32B)	109.5
H(32A)-C(32)-H(32B)	109.5
C(31)-C(32)-H(32C)	109.5
H(32A)-C(32)-H(32C)	109.5
H(32B)-C(32)-H(32C)	109.5
C(31)-C(33)-C(34)	111.1(2)
C(31)-C(33)-C(21)	110.4(2)
C(34)-C(33)-C(21)	115.6(2)
C(31)-C(33)-H(33)	106.4
C(34)-C(33)-H(33)	106.4
C(21)-C(33)-H(33)	106.4
C(35)-C(34)-C(33)	114.1(2)
C(35)-C(34)-H(34A)	108.7
C(33)-C(34)-H(34A)	108.7
C(35)-C(34)-H(34B)	108.7
C(33)-C(34)-H(34B)	108.7
H(34A)-C(34)-H(34B)	107.6

C(36)-C(35)-C(34)	128.2(3)
C(36)-C(35)-H(35)	115.9
C(34)-C(35)-H(35)	115.9
C(35)-C(36)-C(37)	121.3(3)
C(35)-C(36)-C(38)	124.2(3)
C(37)-C(36)-C(38)	114.5(3)
C(36)-C(37)-H(37A)	109.5
C(36)-C(37)-H(37B)	109.5
H(37A)-C(37)-H(37B)	109.5
C(36)-C(37)-H(37C)	109.5
H(37A)-C(37)-H(37C)	109.5
H(37B)-C(37)-H(37C)	109.5
C(36)-C(38)-H(38A)	109.5
C(36)-C(38)-H(38B)	109.5
H(38A)-C(38)-H(38B)	109.5
C(36)-C(38)-H(38C)	109.5
H(38A)-C(38)-H(38C)	109.5
H(38B)-C(38)-H(38C)	109.5
C(7)-O(2)-C(8)	117.62(19)
C(10)-O(3)-C(11)	117.9(2)
C(18)-O(4)-C(14)	106.60(17)
C(15)-Si(1)-C(17)	112.00(17)
C(15)-Si(1)-C(14)	105.64(13)
C(17)-Si(1)-C(14)	107.52(15)
C(15)-Si(1)-C(16)	111.36(17)

C(17)-Si(1)-C(16)	111.03(18)
C(14)-Si(1)-C(16)	109.03(14)

Symmetry transformations used to generate equivalent atoms:

Table S4. Anisotropic displacement parameters ($Å^2 x 10^3$)for d23352. The anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U^{11} + ... + 2 h k a^* b^* U^{12}]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
C(1)	48(2)	45(2)	67(2)	17(1)	-23(1)	-13(1)
C(2)	57(2)	66(2)	86(2)	23(2)	-43(2)	-21(2)
C(3)	58(2)	53(2)	66(2)	14(1)	-33(2)	-25(1)
C(4)	40(1)	40(1)	32(1)	3(1)	-9(1)	-12(1)
C(5)	41(1)	44(1)	47(2)	1(1)	-18(1)	-12(1)
C(6)	49(2)	41(2)	68(2)	5(1)	-21(1)	-15(1)
C(7)	41(1)	41(1)	33(1)	-2(1)	-9(1)	-13(1)
C(8)	41(1)	34(1)	35(1)	1(1)	-14(1)	-11(1)
C(9)	42(1)	44(1)	27(1)	2(1)	-10(1)	-18(1)
C(10)	33(1)	39(1)	32(1)	-6(1)	-5(1)	-14(1)
C(11)	50(2)	62(2)	32(2)	-8(1)	-2(1)	-18(1)
C(12)	32(1)	36(1)	33(1)	-4(1)	-9(1)	-12(1)
C(13)	37(1)	34(1)	39(1)	-6(1)	-13(1)	-5(1)
C(14)	39(1)	34(1)	40(2)	-3(1)	-16(1)	-4(1)
C(15)	72(2)	55(2)	54(2)	4(1)	-20(2)	8(2)
C(16)	67(2)	74(2)	57(2)	17(2)	-14(2)	-16(2)
C(17)	86(2)	85(2)	57(2)	-13(2)	-37(2)	-9(2)
C(18)	35(1)	34(1)	32(1)	-1(1)	-11(1)	-12(1)
C(19)	38(1)	34(1)	31(1)	-3(1)	-11(1)	-11(1)
C(20)	43(1)	31(1)	36(1)	-2(1)	-11(1)	-9(1)

C(21)	45(1)	31(1)	33(1)	-3(1)	-9(1)	-5(1)
C(22)	53(2)	35(1)	36(1)	-7(1)	-6(1)	-7(1)
C(23)	51(2)	53(2)	34(2)	-10(1)	1(1)	-16(1)
C(24)	74(2)	56(2)	49(2)	-9(1)	6(2)	-30(2)
C(25)	108(3)	86(3)	64(2)	-21(2)	13(2)	-58(3)
C(26)	117(4)	141(5)	91(3)	-26(3)	-12(3)	-83(4)
C(27)	66(3)	172(6)	132(5)	-11(4)	-33(3)	-43(3)
C(28)	62(2)	97(3)	91(3)	-13(2)	-19(2)	-20(2)
C(29)	84(2)	65(2)	36(2)	-7(1)	-9(2)	-30(2)
C(30)	77(2)	53(2)	45(2)	-8(1)	-27(2)	-13(2)
C(31)	54(2)	54(2)	49(2)	-8(1)	-21(1)	-8(1)
C(32)	76(3)	149(4)	86(3)	-27(3)	-37(2)	-34(3)
C(33)	42(1)	42(1)	41(2)	-6(1)	-11(1)	-5(1)
C(34)	57(2)	46(2)	45(2)	2(1)	-9(1)	-21(1)
C(35)	67(2)	35(1)	40(2)	0(1)	-11(1)	-16(1)
C(36)	58(2)	36(1)	48(2)	4(1)	-9(1)	-13(1)
C(37)	73(2)	47(2)	61(2)	-5(1)	-2(2)	-8(2)
C(38)	80(2)	67(2)	73(2)	-13(2)	-34(2)	4(2)
O(1)	62(1)	41(1)	70(1)	-1(1)	-30(1)	-17(1)
O(2)	49(1)	34(1)	41(1)	5(1)	-20(1)	-13(1)
O(3)	45(1)	50(1)	31(1)	-10(1)	-3(1)	-9(1)
O(4)	43(1)	35(1)	28(1)	-1(1)	-12(1)	-4(1)
O(5)	49(1)	54(1)	45(1)	-7(1)	-17(1)	2(1)
Br(1)	81(1)	56(1)	148(1)	38(1)	-61(1)	-15(1)
Si(1)	51(1)	47(1)	37(1)	2(1)	-18(1)	-2(1)

Table S5. Hydrogen coordinates (x 10^4) and isotropic displacement parameters (Å^{2}x 10^3) for d23352.

	x	y	z	U(eq)
H(2)	10153	2797	6389	80
H(3)	9266	4830	5944	66
H(5)	6466	3912	5425	52
H(6)	7340	1890	5879	63
H(9)	4507	7687	6110	45
H(11A)	2438	8923	6992	75
H(11B)	2101	10328	7198	75
H(11C)	3566	9440	6987	75
H(13)	2890	11249	4087	45
H(15A)	2440	13254	1690	103
H(15B)	2980	13228	2528	103
H(15C)	1894	12584	2667	103
H(16A)	6236	10806	950	107
H(16B)	5780	12058	1467	107
H(16C)	5467	12056	526	107
H(17A)	3427	10877	548	114
H(17B)	2635	10331	1507	114
H(17C)	4137	9626	1006	114
H(21)	6381	7564	1967	47

H(22)	8567	5395	1498	54
H(24)	7767	8665	1036	75
H(25)	9110	9843	839	105
H(26)	11194	8957	874	130
H(27)	11953	6857	1159	145
H(28)	10578	5634	1369	102
H(29A)	7778	7119	119	74
H(29B)	8561	5697	6	74
H(30)	6427	5975	-25	69
H(32A)	4454	5580	759	147
H(32B)	3709	6230	1738	147
H(32C)	4487	4799	1711	147
H(33)	5009	6428	2673	52
H(34A)	6424	4731	3310	60
H(34B)	5460	4363	2942	60
H(35)	7309	3609	1551	59
H(37A)	9277	2231	1042	102
H(37B)	9701	1357	1865	102
H(37C)	10324	2437	1419	102
H(38A)	9474	3362	3063	115
H(38B)	8930	2226	3473	115
H(38C)	7962	3593	3635	115