Supplementary Material (ESI) for Organic & Biomolecular Chemistry

An Efficient Synthesis of (±)-Frondosin B using a Stille-Heck Reaction Sequence.

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Experimental Section

General:

Tetrahydrofuran (THF) was dried by distillation from sodium wire and benzophenone (sodium benzophenone ketyl) under nitrogen gas ($N_{2(g)}$). Dichloromethane (DCM) and dichloroethane (DCE) were dried by refluxing over CaH_2 under $N_{2(g)}$. *N*-methylpyrrolidinone (NMP) and ethanol were used as commercially supplied (anhydrous/reagent grade). Petroleum spirit (PS, 40-60°C fraction), *n*-hexane and water (H_2O) were purified by distillation. Additional solvent abbreviations used are as follows: ethyl acetate as EtOAc, diethyl ether as Et_2O. Brine herein refers to saturated aqueous NaCl.

Degas procedure: A typical degassing procedure is as follows: The solvent was stirred vigorously and a high vacuum [<5 mBar] was applied for 0.1 h, resulting in some effervescence. The flask was then backfilled with $N_{2(g)}$, and the procedure repeated (x 3) in order to remove all dissolved gases. For volatile solvents (*e.g.* THF) the procedure was performed at -78 °C.

Thin Layer Chromatography (TLC) was performed with 0.25 mm silica gel 60F plates with 254 nm fluorescent indicator (Merck). TLC plates were visualised with both ultraviolet light and vanillin or anisaldehyde development dip and heating. Products were isolated using silica gel 60, 230-400 mesh (Merck) or alumina (neutral, Brockmann grades I or II) column chromatography or plates where appropriate.

Microwave reactions were performed using a CEM Discover unit. Reactions were performed in sealed 10 mL vials with infrared temperature detection, the standard 300 W maximum power and (without ramp-time).

Nuclear Magnetic Resonance (NMR) spectra were recorded at 300.1 MHz for ^1H and 75.5 MHz for ^{13}C, referenced to the solvent. ^1H-NMR spectra are reported in terms of chemical shift (δ, reported in ppm), multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, dd = doublet of doublets, dt = doublet of triplets, ddd = doublet of doublet of doublets, td = triplet of doublets, tt = triplet of triplets, m = multiplet, m_c = centered multiplet), coupling constant (*J*, reported in Hz) and integration (number of hydrogens = H). ^{13}C-NMR spectra are reported in terms of chemical shift (δ, reported in ppm), and the number of attached protons (C) = quaternary, (CH) = methine, (CH_2) = methylene, (CH_3) = methyl; (C=O) = carbonyl, this assignment was made on the basis of a *J*-modulated spin echo (J-MOD) experiment.

Low Resolution Mass Spectrometry (LRMS) data was obtained mass spectrometer equipped with an atmospheric pressure (ESI/APCI) ion source. High Resolution Mass Spectrometry (HRMS) data was obtained with an EI, ESI or APCI ion source, and reported in atomic mass units. Calculated values and names were taken from Chemdraw Ultra version 10.0 (2006) and were corrected where necessary. Melting points were determined with an electrothermal melting point apparatus and not corrected.

2-Bromo-5-methoxybenzofuran-3(2*H*)-one (10). To a stirred suspension of $CuBr_2$ (670 mg, 3.0 mmol) in EtOAc (1.8 mL) was added a solution of 5-methoxybenzo[*b*]furanone **9** (300 mg, 1.5 mmol) in $CHCl_3$ (2.5 mL) in one portion and the reaction mixture stirred while an exothermic reaction took place, then for a further 1 h at RT. After this time the reaction was lowered into a 90°C oil bath and stirred at mild reflux for a further 1 h, then cooled and filtered. The pad of CuBr and product was washed with Et_2O (10 mL) and the volatiles removed under reduced pressure. Column chromatography of the resultant black oil on silica gel with Et_2O-PS (3:47) delivered ketone **10** as a pale yellow solid (87 mg, 0.36 mmol, 24%), mp = 64-65°C. ^{1}H-NMR (300 MHz, $CDCl_3$): δ 7.27 (dd, *J* = 9.0, 2.7 Hz, 1H), 7.12 (d, *J* = 2.7 Hz, 1H), 7.06 (d, *J* = 9.0 Hz, 1H), 6.48 (s, 1H), 3.81 (s, 3H). ^{13}C-NMR (75.5 MHz, $CDCl_3$): δ 194.8 (C=O), 165.3 (C), 156.4 (C), 128.2 (CH), 118.1 (C), 114.8 (CH), 105.7 (CH), 76.6 (CH), 56.1 (CH_3). HRMS (+ESI) Calculated $[C_9H_8BrO_3]^+$ ($M+H^+$): 242.9657, found: 242.9648.

2-Chloro-5-methoxybenzofuran-3(2*H*)-one (11). To a stirred solution of 5-methoxybenzo[*b*]furanone **9** (0.473 g, 2.88 mmol) in $CHCl_3$ (10 mL) at -10°C was added in one portion and as rapidly as possible SO_2Cl_2 (290 μL, 486 mg, 3.60 mmol). The reaction mixture was stirred 1 h, poured into brine (10 mL), the organic layer separated and aqueous layer extracted with DCM (3 x 50 mL). The combined organics were dried over $MgSO_4$ and the volatiles removed under reduced pressure to yield the crude product (0.807 g). Column chromatography on silica gel with Et_2O-PS (7:93) delivered ketone **11** as a pale-yellow solid (0.477 mg, 2.39 mmol, 83%), mp = 43-45°C. ^{1}H-NMR (300 MHz, $CDCl_3$): δ 7.30 (dd, *J* = 9.0, 3.0 Hz, 1H), 7.12 (d, *J* = 3.0 Hz, 1H), 7.09 (d, *J* = 9.0 Hz, 1H), 6.06 (s, 1H), 3.82 (s, 3H). ^{13}C-NMR (75.5 MHz, $CDCl_3$): δ 194.3 (C=O), 166.0 (C), 156.2 (C), 128.6 (CH), 118.1 (C), 114.6 (CH), 105.6 (CH), 85.6 (CH), 56.1 (CH_3). HRMS (+ESI) Calculated $[C_9H_8ClO_3]^+$ ($M+H^+$): 199.0162, found 199.0160.

2-Bromo-5-methoxybenzofuran-3-yl trifluoromethanesulfonate (12)

To a stirred solution of 2-bromoketone **10** (71 mg, 0.29 mmol) in DCM (2 mL) at -78°C was added dropwise NEt_3 (140 μL, 1.00 mmol) by syringe, then dropwise Tf_2O [59 μL, 98 mg, 0.35 mmol, solution in DCM (1 mL)] by syringe. The reaction was allowed to return to RT while stirred for 20 h, then the volatiles were removed under reduced pressure. Column chromatography of the crude product on alumina (neutral, Brockmann Grade II) with Et_2O-PS (1:99) delivered triflate **12** as a colourless crystalline solid (80 mg, 0.213 mmol, 73%), mp = 46-47°C. ^{1}H-NMR (300 MHz, $CDCl_3$): δ 7.36 (d, *J* = 9.6, 2.1 Hz, 1H), 6.96 (m, 2H), 3.86 (s, 3H). ^{13}C-NMR (75.5 MHz, $CDCl_3$): δ 157.2 (C) 146.1 (C), 138.8 (C), 127.6 (C), 121.8 (C), 118.6 (CF_3, J = 321 Hz), 115.2 (CH), 112.7 (CH), 100.0 (CH), 55.9 (CH_3). HRMS (+ESI) Calculated $[C_{10}H_7BrF_3O_5]^+$ (M+H$^+$): 374.9150, found: 374.9146.

3-Trimethylstannyl-2-(but-3′-enyl)cyclohex-2-enone (14). Was prepared according to the previously published procedure.[5a] ^{1}H NMR (300 MHz, $CDCl_3$): δ 5.87 (m$_c$, 1H), 4.95 (m, 2H), 2.48 (t, J = 5.7 Hz, 2H), 2.38 (t, J = 6.6 Hz, 2H), 2.30 (m$_c$, *2*H), 2.10 (m$_c$, 2H), 1.94 (m$_c$, 2H), 0.24 (s, 9H).

2-Chloro-5-methoxybenzofuran-3-yl trifluoromethanesulfonate (13). To a stirred solution of 2-chloroketone **11** (330 mg, 1.66 mmol) in DCM (12 mL) at -78°C under $N_{2(g)}$ was added dry NEt_3 (771 μL, 560 mg, 5.53 mmol). The pale yellow reaction mixture became an vivid green colour immediately and there was added Tf_2O (338 μL, 564 mg, 1.99 mmol, solution in DCM [4 mL], dropwise over the course of 0.1 h), during which time the colour dissipated. The reaction mixture was allowed to return to RT while stirred for 14 h. After this time the volatiles were removed under reduced pressure. Chromatography of the brown crude oil on alumina (short column, neutral, Brockmann grade II) with EtOAc-PS (1:67) delivered triflate **13** as a pale yellow oil (548 mg, 1.66 mmol, 100%), mp = 47-48.5°C. ^{1}H-NMR (300 MHz, $CDCl_3$): δ 7.35 (dd, J = 8.7, 0.9 Hz, 1H), 6.98 (dd, J = 8.7, 2.4 Hz, 1H), 6.96 (s$_{br}$, 1H), 3.87 (s, 3H). ^{13}C-NMR (75.5 MHz, $CDCl_3$): δ 157.3 (C) 146.1 (C), 138.8 (C), 127.6 (C), 121.8 (C), 118.6 (CF_3, J = 321 Hz), 115.2 (CH), 112.7 (CH), 100.0 (CH), 55.9 (CH_3). HRMS (+ESI) Calculated $[C_{10}H_7ClF_3O_5]^+$ (M+H$^+$): 330.9655, found: 330.9652.

11-Methoxy-7-methylene-1,2,3,5,6,7-hexahydro-8-oxa-dibenzo[*a,h*]azulen-4-one (17a), 11-Methoxy-7-methyl-1,2,3,5-tetrahydro-8-oxa-dibenzo[*a,h*]azulen-4-one (17b), 9-Methoxy-7-methylene-1,2,3,5,6,7-hexahydro-12-oxa-dibenzo[*a,e*]azulen-4-one (18a), 9-Methoxy-7-methyl-1,2,3,5-tetrahydro-12-oxa-dibenzo[*a,e*]azulen-4-one (18b) and 6-Ethyl-10-methoxy-2,3-dihydrobenzo[*b*]naphtho[1,2-*d*]furan-4(1*H*)-one (20).

17a,b and 18a,b from 12: Zinc chloride ($ZnCl_2$, 42 mg, 0.31 mmol) was flame dried carefully in a Schlenk tube under vacuum and cooled under $N_{2(g)}$, NMP (2 mL) was added and the solution degassed (for a description of degas procedure see General). 2-Bromobenzo[*b*]furan-3-yl triflate **12** (58 mg, 0.154 mmol), $Pd(dba)_2$ (8.7 mg, 0.015 mmol) and TFP (8.1 mg, 0.035 mmol) were then added and the degas procedure repeated once. Stannane **14** (72 mg, 0.22 mmol) was added, the reaction mixture heated to 65°C for 0.2 h, then CuTC (3 mg, 0.016 mmol) was added and the reaction monitored by TLC, which showed a complete consumption of starting materials after 4 h. After a further 1.5 h the reaction was cooled, passed through a plug of alumina (neutral, Brockmann grade II) and the organics washed through with Et_2O (30 mL). The organics were then washed with H_2O (2 x 30 mL), the combined aqueous washings extracted with Et_2O (30 mL), the combined organics washed with H_2O (2 x 10 mL), dried over $MgSO_4$ and the volatiles removed under reduced pressure. Planar chromatography of the yellow crude on silica gel with EtOAc-PS (3:17) delivered a mixture of **17a** and **17b** (low R_f, **a:b** 1:1 ratio, 23.3 mg, 0.079 mmol, 51%) as a pale yellow viscous gum and a separate fraction was isolated which contained a mixture of **18a** and **18b** (high R_f, **a:b** 2:1, 13.1 mg, 0.044 mmol, 29%).

This mixture of isomers **17a,b** was dissolved in ethanol (2 mL) and $RhCl_3$ (1.6 mg, 0.05 eq.) added. The brown reaction mixture was heated to 75°C and stirred for 5h, then cooled, poured into H_2O (10 mL) and extracted with Et_2O (3 x 5 mL). The combined extracts were dried over $MgSO_4$, and concentrated under reduced pressure to deliver the ketone **17b** (23.2 mg, 0.079 mmol, 100%) as a thick colourless gum which solidified upon standing at -20°C. The mixture of isomers **18a,b** isomerised to **18b** upon standing in $CDCl_3$ for 24h.

17b: mp = 111-112°C. ^{1}H-NMR (300 MHz, $CDCl_3$): δ 7.51 (d, J = 9.0 Hz, 1H), 7.27 (d, J = 2.7 Hz, 1H), 7.04 (dd, J = 9.0, 2.7 Hz, 1H), 5.81 (td, J = 6.9, 1.2 Hz, 1H), 3.95 (s, 3H), 3.12 (t, 6.0 Hz, 2H), 2.81 (m_{br}, 2H), 2.63 (t, 6.9 Hz, 2H), 2.24 (d, J = 1.2 Hz, 3H), 2.16 (m_c, 2H). ^{13}C-NMR (75.5 MHz, $CDCl_3$): δ197.2 (C=O), 159.0 (C), 156.1 (C), 148.9 (C), 146.2 (C), 128.2 (C), 127.5 (C), 126.9 (CH), 126.3 (C), 120.8 (C), 113.3 (CH), 112.1 (CH), 105.2 (CH), 56.2 (CH_3), 38.2 (CH_2), 29.2 (CH_2), 23.6 (CH_2), 23.5 (CH_2), 18.0 (CH_3). HRMS (+APCI) Calculated $[C_{19}H_{19}O_3]^+$ ($M+H^+$): 295.1332, found: 295.1323. Previously reported.[3e]

18b: mp = 126-128°C. ^{1}H-NMR (300 MHz, $CDCl_3$): δ 7.45 (d, J = 9.0 Hz, 1H), 7.28 (d, J = 2.4 Hz, 1H), 7.03 (dd, J = 9.0, 2.4 Hz, 1H), 5.46 (t, J = 7.2 Hz, 1H), 3.89 (s, 3H), 2.94 (t, J = 6.0 Hz, 2H), 2.74 (d, J = 6.9 Hz, 2H), 2.51 (t, J = 6.3 Hz, 2H), 2.34 (s, 3H), 2.13 (tt, 6.9, 6.0 Hz, 2H). ^{13}C-NMR (75.5 MHz, $CDCl_3$): δ193.9 (C=O), 155.9 (C), 154.1 (C), 149.7 (C), 141.1 (C), 130.0 (C), 127.9 (C), 127.0 (C), 125.9 (C), 120.6 (CH), 115.0 (CH), 112.1 (CH), 105.4 (CH), 56.1 (CH_3), 38.3 (CH_2), 26.4 (CH_2), 23.4 (CH_2), 22.3 (CH_2), 20.9 (CH_3). HRMS (+APCI) Calculated $[C_{19}H_{19}O_3]^+$ ($M+H^+$): 295.1332, found: 295.1325.

17a,b and 20 from 19 using Method A (see main text): To a microwave tube (2 mL capacity) under a stream of $N_{2(g)}$ was added caesium carbonate Cs_2CO_3 (freshly flame-dried under vacuum, 92 mg, 0.28 mmol). Chloroalkene **19** (see below) (47 mg, 0.14 mmol) was then added under $N_{2(g)}$ along with NMP (1.5 mL) and a tight septum cap fitted. The suspension was degassed (see General section) and the septum removed under a stream of $N_{2(g)}$, Pd(t-$Bu_3P)_2$ (14.5 mg, 0.028 mmol) added and a new septum cap fitted. The reaction mixture was stirred at 85°C under microwave irradiation for 1 h, after which time TLC analysis revealed complete conversion of the chloroalkene **19** to two lower R_f products. The reaction mixture was poured onto brine-H_2O (1:3, 20 mL), extracted with Et_2O (2 x 10 mL), the combined organics washed with H_2O (3 x 10 mL), brine (10 mL), then dried over $MgSO_4$ and the volatiles removed under reduced pressure to deliver the crude as an orange oil (60 mg). Planar chromatography on silica gel with Et_2O-DCM-PS (4:23:23) gave **17a,b** as a yellow resin (**a:b** 1:1, 18.5 mg, 0.063 mmol, 41%) and **20** as a colourless amorphic solid (23.5 mg, 0.083 mmol, 59%).

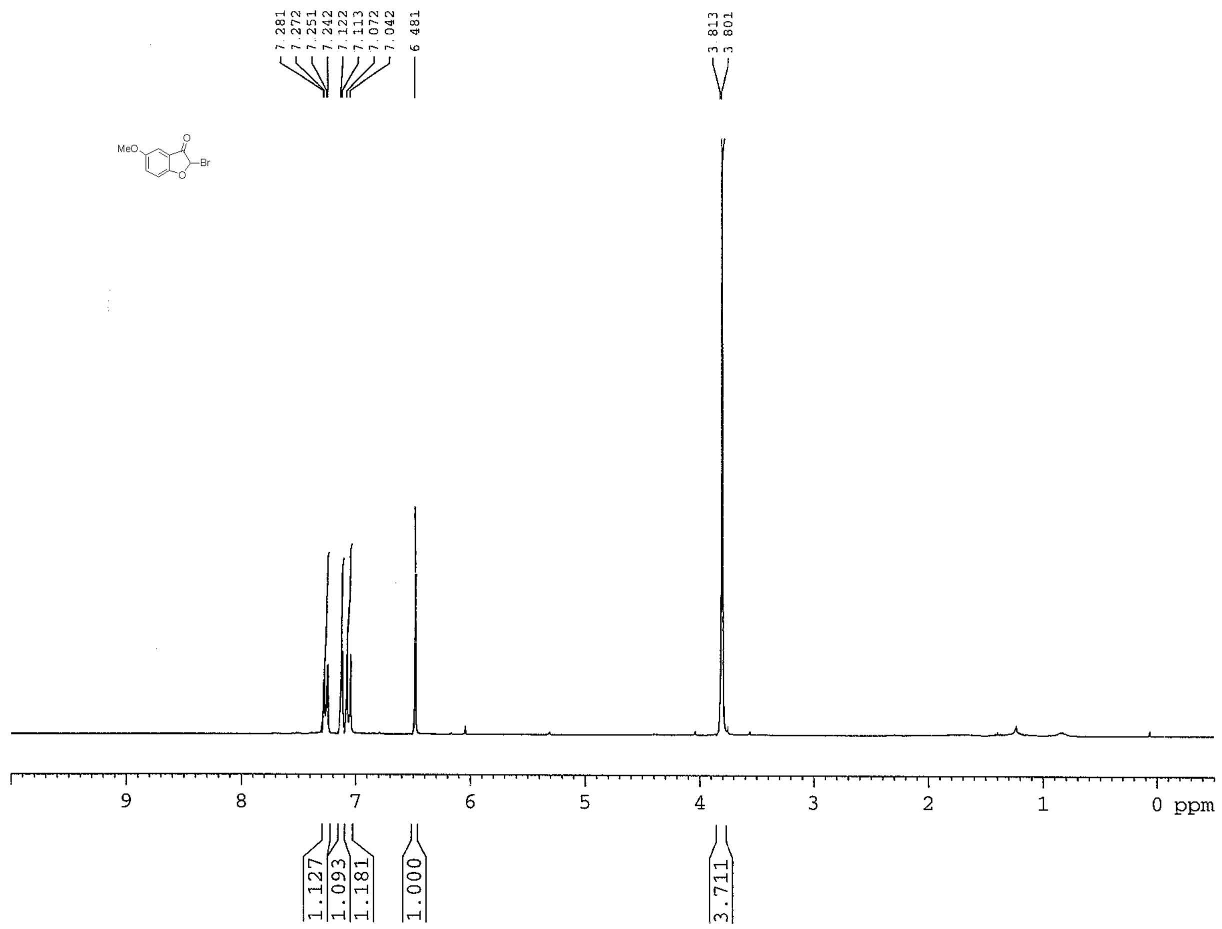
20: mp = 112.5-113.5°C. ^{1}H-NMR (300 MHz, $CDCl_3$): δ 8.06 (s, 1H), 7.53 (d, *J* = 9.0 Hz, 1H), 7.51 (d, *J* = 2.7 Hz, 1H), 7.08 (dd, *J* = 9.0, 2.7 Hz, 1H), 3.94 (s, 3H), 3.44 (t, *J* = 6.0 Hz, 2H), 2.99 (q, *J* = 7.5 Hz, 2H), 2.74 (t, *J* = 6.6 Hz, 2H), 2.32 (tt, *J* = 6.6, 6.3 Hz, 2H) 1.39 (t, *J* = 7.5 Hz, 3H). ^{13}C-NMR (75.5 MHz, $CDCl_3$): δ 197.7 (C=O), 156.1 (C), 151.3 (C), 138.6 (C), 128.4 (C), 126.9 [2 x inequivalent (C) signals], 125.9 (CH), 125.3 (C), 121.9 (C), 114.2 (CH), 112.2 (CH), 106.5 (CH), 56.2 (CH_3), 38.7 (CH_2), 26.9 (CH_2), 23.0 (CH_2), 22.7 (CH_2), 14.0 (CH_3). HRMS (+APCI) Calculated $[C_{19}H_{19}O_3]^+$ (M+H$^+$): 295.1332, found: 295.1327.

17a,b from 19 using Method D (see main text): To a microwave tube (10 mL capacity) under a stream of $Ar_{(g)}$ was added potasssium carbonate K_2CO_3 (freshly flame-dried under vacuum, 32.0 mg, 0.23 mmol). Chloroalkene **19** (se below) (25.4 mg, 0.077 mmol) was then added under $Ar_{(g)}$ along with DMA (1.00 mL) and a septum cap fitted. The suspension was degassed (description: General) and the septum removed under a stream of $Ar_{(g)}$, $Pd(OAc)_2$ (1.7 mg, 0.008 mmol) and XPhos (7.5 mg, 0.016 mmol) added and a microwave septum cap fitted. The reaction mixture was stirred at 100 °C under microwave irradiation for 0.5 h (CEM Discover, 300 watts/200 psi max, infrared temperature detector, typical power usage 5-6 watts), after which time TLC analysis (silica, heptane/EtOAc 4:1) revealed complete conversion of the **19** to a lower R_f spot [TLC eluent: heptane-EtOAc (1:5)]. The reaction mixture was poured onto brine-H_2O (1:3, 20 mL), extracted with Et_2O (2 x 10 mL), the combined organics washed with H_2O (3 x 10 mL), brine (10 mL), then dried over $MgSO_4$ and the volatiles removed under reduced pressure to deliver the crude as a brown solid (31 mg). Column chromatography of the crude on silica gel with heptane-EtOAc (1:7) followed and ketones **17a**,**b** were delivered as a pale yellow solid (**a:b** 9:1, 18.7 mg, 0.064 mmol, 83%). This mixture was fully isomerised to **17b** using $RhCl_3$ prior to characterisation (as described above).

2-(But-3-enyl)-3-(2-chloro-5-methoxybenzofuran-3-yl)cyclohex-2-enone (19). $ZnCl_2$ (341 mg, 2.50 mmol) was flame dried carefully in a round-bottomed flask under vacuum then cooled under $N_{2(g)}$, and NMP (4 mL) added and the stirred solution degassed (see General). 2-Chloroalkenyl triflate **13** (276 mg, 0.83 mmol), $Pd(dba)_2$ (47 mg, 0.083 mmol) and TFP (58 mg, 0.25 mmol) were then added. The reaction mixture became dark brown then pale yellow in colour and the degas procedure was repeated. Stannane **14** (389 mg, 1.24 mmol) was added and the reaction mixture heated to 65°C in an oil bath under $N_{2(g)}$ for 0.2 h. After this time CuTC (16 mg, 0.083 mmol) was added. TLC revealed a total absence of coupled product prior to copper salt addition but significant amounts within 0.1 h of its addition.

After a further 5 h heating the starting materials were consumed as indicated by TLC, the reaction was cooled and passed through a plug of alumina (neutral, Brockmann grade II) and the organics flushed through with Et_2O (60 mL). The organics were washed with H_2O (2 x 100 mL), the combined aqueous washings extracted with Et_2O (30 mL), the combined organics washed with H_2O (2 x 30 mL), dried over $MgSO_4$ and the volatiles removed under reduced pressure. Column chromatography of the yellow crude product on silica gel with EtOAc-PS (1:19 then 7:93) delivered chloride **19** as a colourless viscous gum which became yellow when stored (258 mg, 0.78 mmol, 94%). ^{1}H-NMR (300 MHz, $CDCl_3$): δ 7.37 (d, *J* = 9.0 Hz, 1H), 6.93 (dd, *J* = 9.0, 2.7 Hz, 1H), 6.72 (d, *J* = 2.7 Hz, 1H), 5.56 (m_c, 1H), 4.84 (m, 2H), 3.84 (s, 3H), 2.74-2.59 (m, 4H), 2.43 (m, 1H), 2.29 (m, 1H), 2.18 (m, 2H), 2.10 (m, 2H). ^{13}C-NMR (75.5 MHz, $CDCl_3$): δ 198.6 (C=O), 156.7 (C), 148.5 (C), 145.6 (C), 139.8 (C), 138.0 (CH), 137.7 (C), 127.8 (C), 116.2 (C), 114.8 (CH_2), 113.3 (CH), 111.8 (CH), 102.2 (CH), 56.0 (CH_3), 38.3 (CH_2), 33.2 (CH_2), 31.0 (CH_2), 26.7 (CH_2), 22.7 (CH_2). HRMS (+ESI) Calculated $[C_{19}H_{20}ClO_3]^+$ ($M+H^+$): 331.1101, found: 331.1100.

Bromide **10** (300 MHz, $CDCl_3$)



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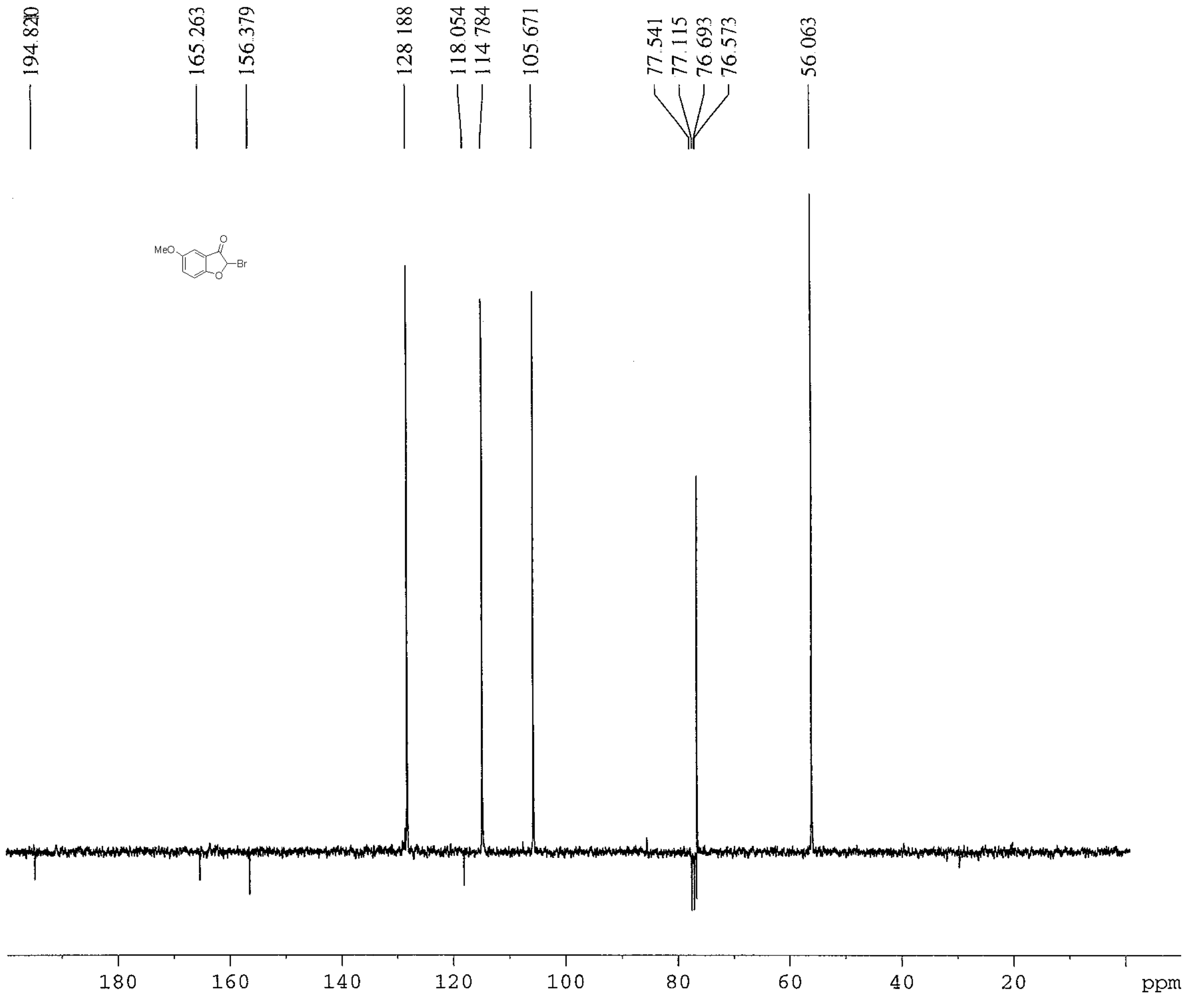
Bromide **10** (75.5 MHz, $CDCl_3$)



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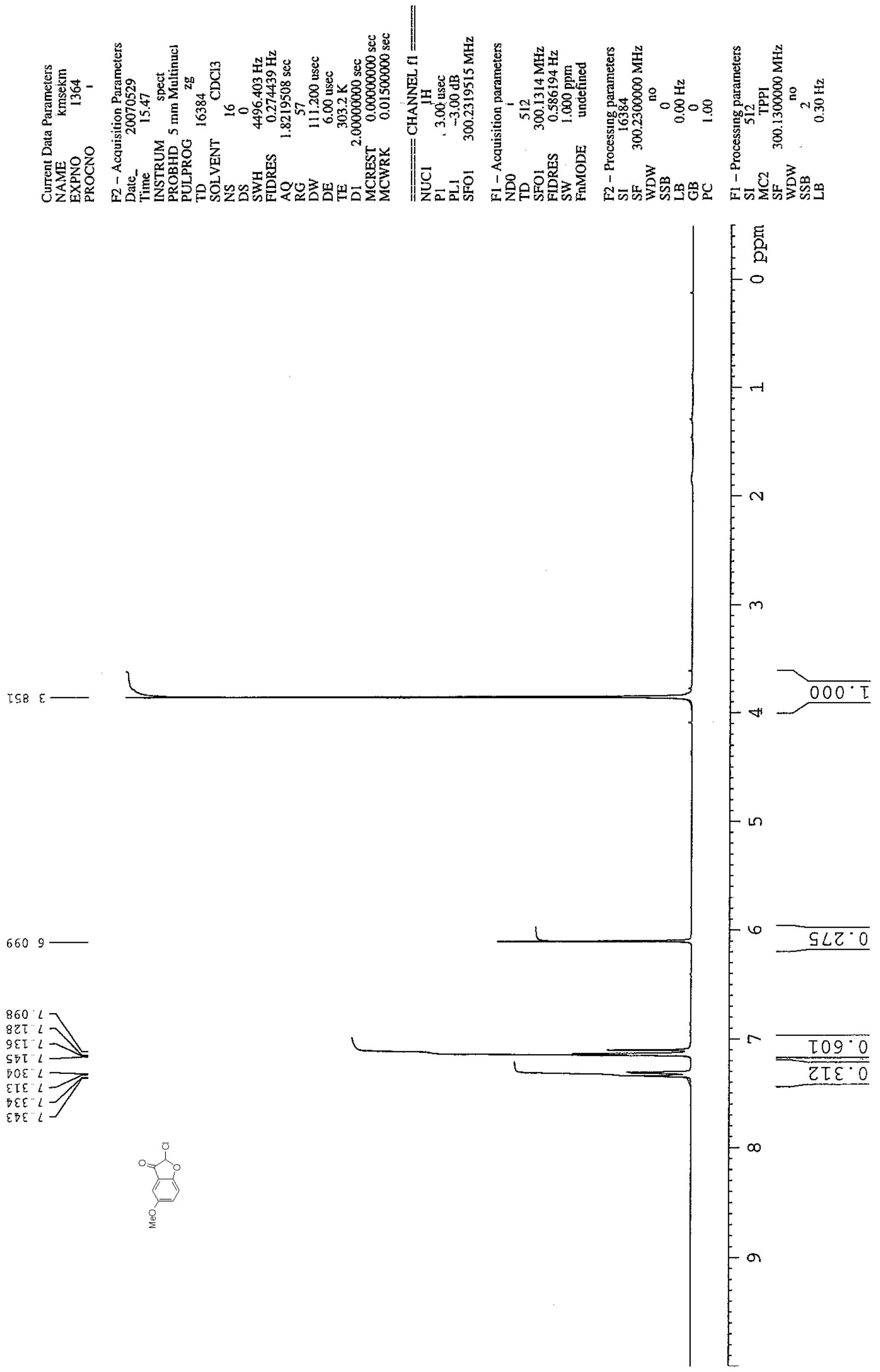
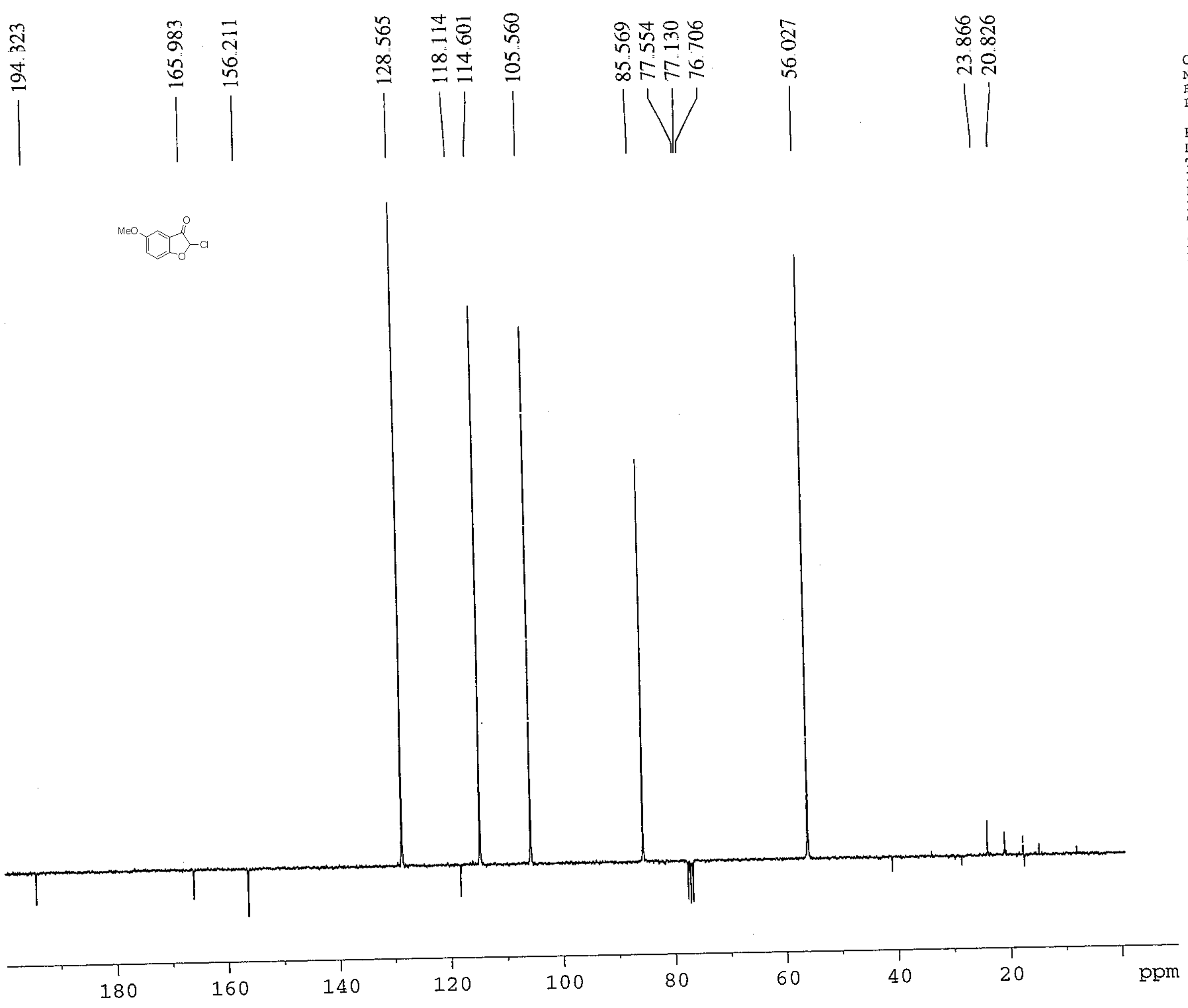
Chloride 11 (300 MHz, $CDCl_3$)



Chloride **11** (75.5 MHz, $CDCl_3$)



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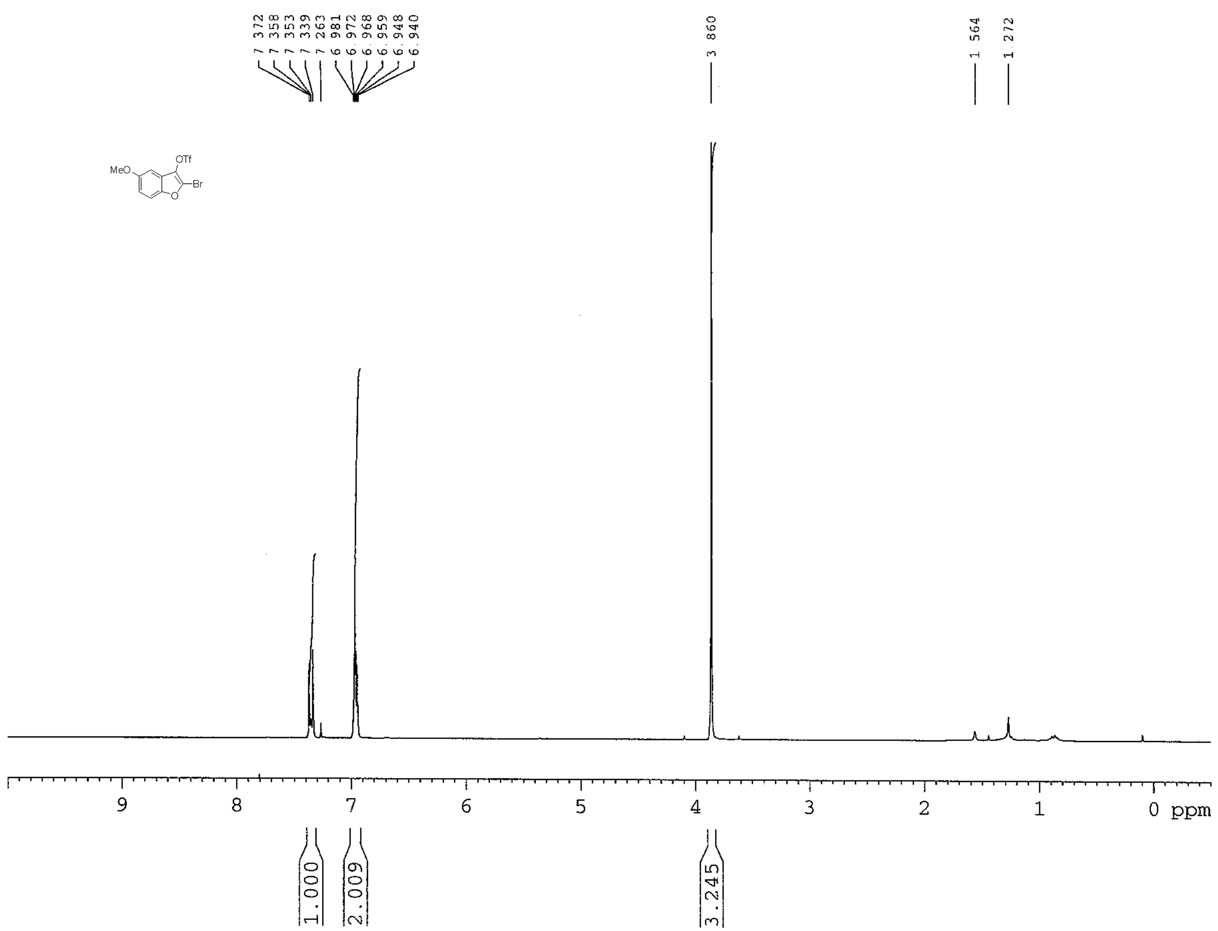
F2 - Processing parameters
SI                 32768
SF            75.4928940 MHz
WDW                   EM
SSB                    0
LB                  3.00 Hz
GB                     0
PC                  1.00

F1 - Processing parameters
```

Triflate **12** (300 MHz, CDCl$_3$)



```
Current Data Parameters
NAME          kmsekm
EXPNO           1345
PROCNO             1

F2 - Acquisition Parameters
Date_       20070519
Time           18.06
INSTRUM        spect
PROBHD  5 mm Multinucl
PULPROG           zg
TD             16384
SOLVENT        CDCl3
NS                16
DS                 0
SWH       4496.403 Hz
FIDRES    0.274439 Hz
AQ      1.8219508 sec
RG             101.6
DW        111.200 usec
DE           6.00 usec
TE           303.2 K
D1     2.00000000 sec
MCREST 0.00000000 sec
MCWRK  0.01500000 sec

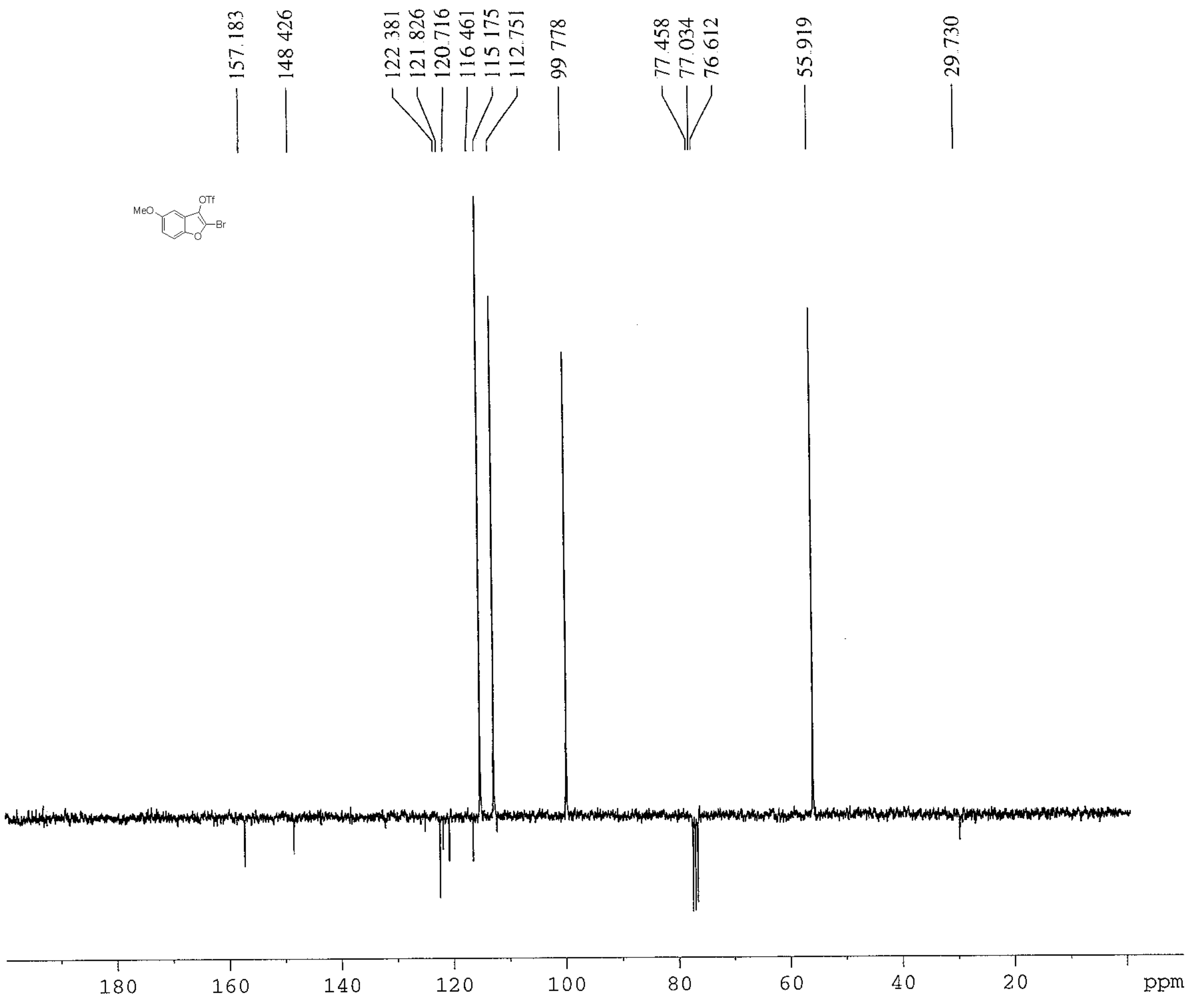
======== CHANNEL f1 ======
NUC1              1H
P1           3.00 usec
PL1          -3.00 dB
SFO1   300.2319515 MHz

F1 - Acquisition parameters
ND0                1
TD               512
SFO1     300.1314 MHz
FIDRES    0.586194 Hz
SW         1.000 ppm
FnMODE     undefined

F2 - Processing parameters
SI             16384
SF     300.2300171 MHz
WDW               no
SSB                0
LB           0.00 Hz
GB                 0
PC              1.00

F1 - Processing parameters
SI               512
MC2             TPPI
SF     300.1300000 MHz
WDW               no
SSB                2
LB           0.30 Hz
```

Triflate **12** (75.5 MHz, CDCl$_3$)



```
Current Data Parameters
NAME            kmsekm
EXPNO             1346
PROCNO               1

F2 - Acquisition Parameters
Date_         20070519
Time             18.10
INSTRUM          spect
PROBHD   5 mm Multinucl
PULPROG           jmod
TD               32768
SOLVENT          CDCl3
NS                2426
DS                   4
SWH          18115.941 Hz
FIDRES        0.552855 Hz
AQ           0.9044468 sec
RG              1149.4
DW              27.600 usec
DE                6.00 usec
TE               303.2 K
CNST2      145.0000000
CNST11       1.0000000
D1          2.00000000 sec
d20         0.00689655 sec
DELTA       0.00001426 sec
MCREST      0.00000000 sec
MCWRK       0.01500000 sec

======== CHANNEL f1 ========
NUC1               13C
P1               11.20 usec
p2               22.40 usec
PL1               0.00 dB
SFO1        75.5018965 MHz

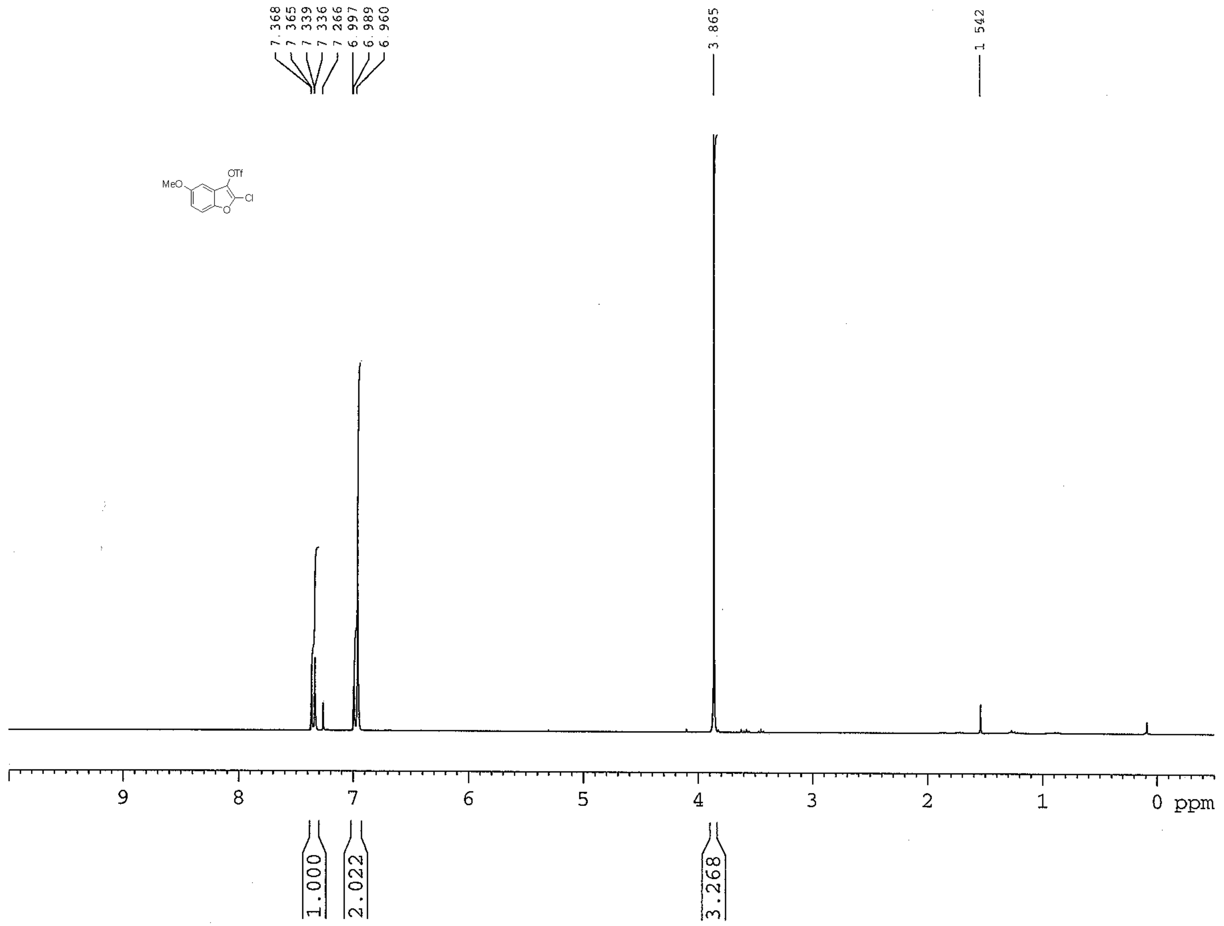
======== CHANNEL f2 ========
CPDPRG2        waltz16
NUC2                1H
PCPD2           100.00 usec
PL2              -3.00 dB
PL12             19.40 dB
SFO2       300.2320007 MHz

F1 - Acquisition parameters
ND0                  3
TD                 512
SFO1          300.1314 MHz
FIDRES        0.586194 Hz
SW               1.000 ppm
FnMODE       undefined

F2 - Processing parameters
SI               32768
SF          75.4928940 MHz
WDW                 EM
SSB                  0
LB                3.00 Hz
GB                   0
PC                1.00

F1 - Processing parameters
```

Triflate **13** (300 MHz, CDCl$_3$)



Current Data Parameters
NAME kmsekm
EXPNO 1250
PROCNO 1

F2 – Acquisition Parameters
Date_ 20070404
Time 18.55
INSTRUM spect
PROBHD 5 mm Multinucl
PULPROG zg
TD 16384
SOLVENT CDCl3
NS 16
DS 0
SWH 4496.403 Hz
FIDRES 0.274439 Hz
AQ 1.8219508 sec
RG 256
DW 111.200 usec
DE 6.00 usec
TE 303.2 K
D1 2.00000000 sec
MCREST 0.00000000 sec
MCWRK 0.01500000 sec

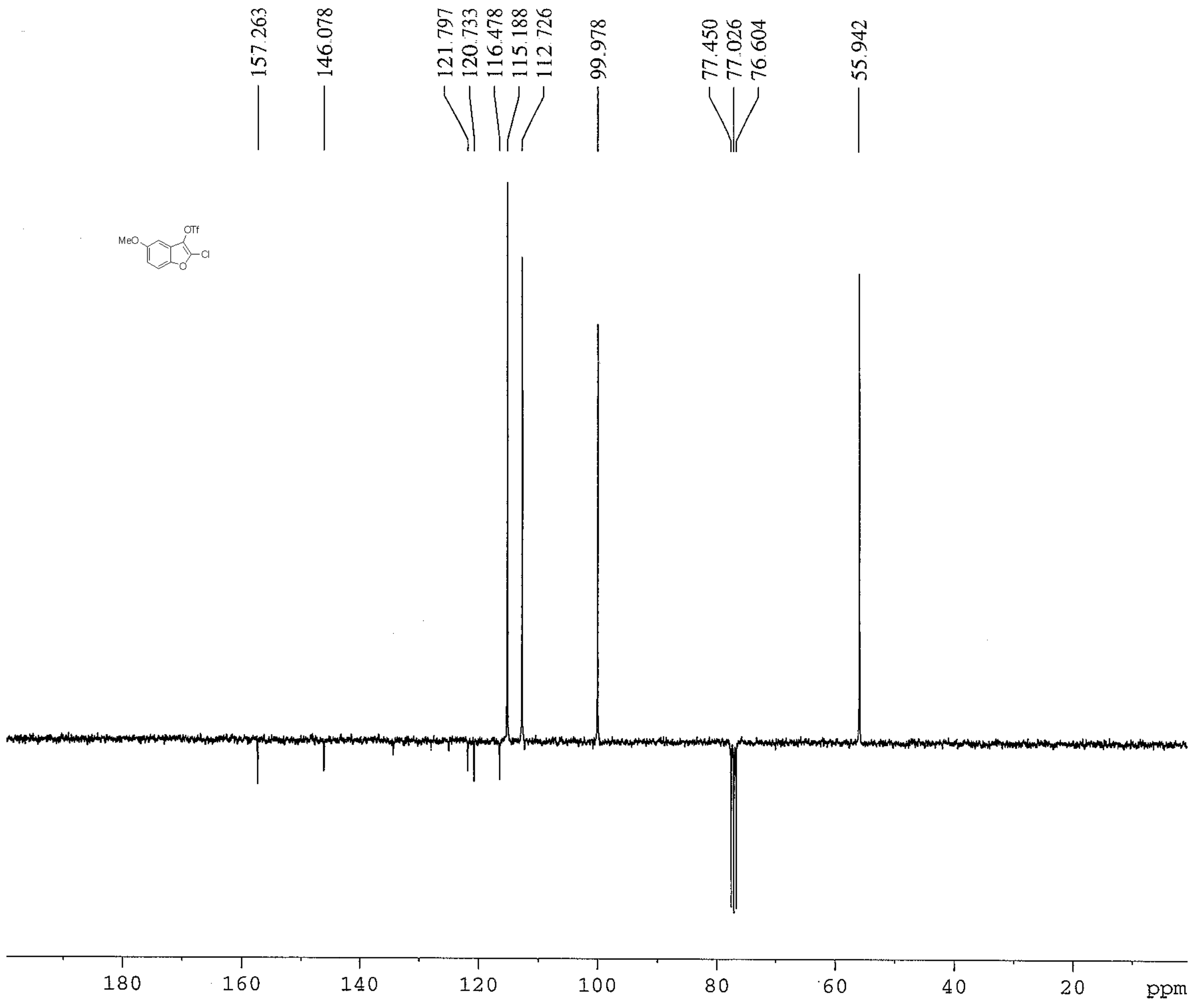
======== CHANNEL f1 ========
NUC1 1H
P1 3.00 usec
PL1 -3.00 dB
SFO1 300.2319515 MHz

F1 – Acquisition parameters
ND0 1
TD 512
SFO1 300.1314 MHz
FIDRES 0.586194 Hz
SW 1.000 ppm
FnMODE undefined

F2 – Processing parameters
SI 16384
SF 300.2300165 MHz
WDW no
SSB 0
LB 0.00 Hz
GB 0
PC 1.00

F1 – Processing parameters
SI 512
MC2 TPPI
SF 300.1300000 MHz
WDW no
SSB 2
LB 0.30 Hz

Triflate **13** (75.5 MHz, $CDCl_3$)



```
Current Data Parameters
NAME             kmsekm
EXPNO              1251
PROCNO                1

F2 - Acquisition Parameters
Date_          20070404
Time              19.00
INSTRUM           spect
PROBHD   5 mm Multinucl
PULPROG            jmod
TD                32768
SOLVENT           CDCl3
NS                15003
DS                    4
SWH           18115.941 Hz
FIDRES         0.552855 Hz
AQ            0.9044468 sec
RG               1149.4
DW               27.600 usec
DE                 6.00 usec
TE                303.2 K
CNST2       145.0000000
CNST11        1.0000000
D1           2.00000000 sec
d20          0.00689655 sec
DELTA        0.00001426 sec
MCREST       0.00000000 sec
MCWRK        0.01500000 sec

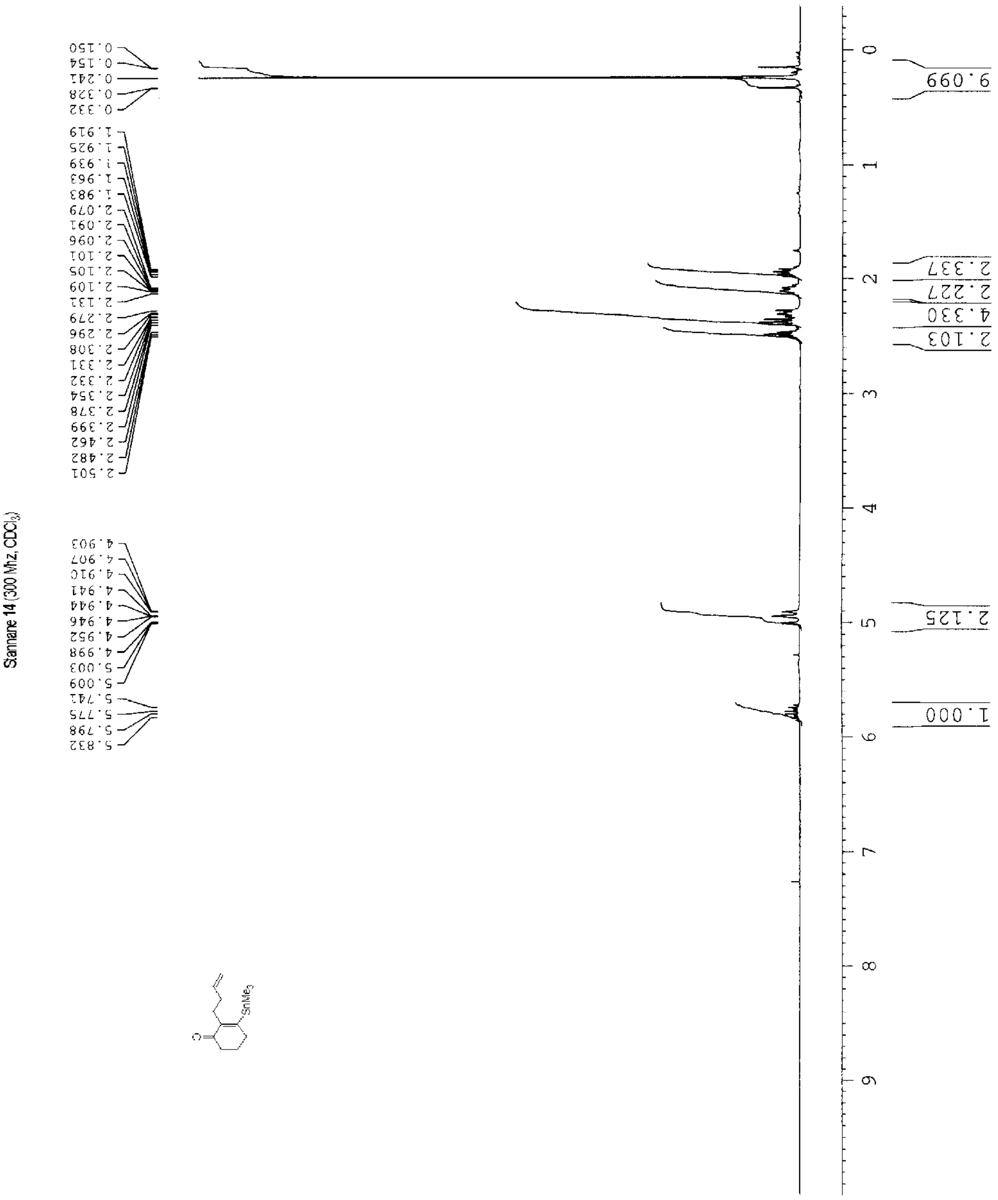
======== CHANNEL f1 ========
NUC1                13C
P1                11.20 usec
p2                22.40 usec
PL1                0.00 dB
SFO1         75.5018965 MHz

======== CHANNEL f2 ========
CPDPRG2         waltz16
NUC2                 1H
PCPD2            100.00 usec
PL2               -3.00 dB
PL12              19.40 dB
SFO2        300.2320007 MHz

F1 - Acquisition parameters
ND0                   3
TD                  512
SFO1           300.1314 MHz
FIDRES         0.586194 Hz
SW                1.000 ppm
FnMODE        undefined

F2 - Processing parameters
SI                32768
SF           75.4928940 MHz
WDW                  EM
SSB                   0
LB                 3.00 Hz
GB                    0
PC                 1.00

F1 - Processing parameters
```


Stannane 14 (300 Mhz, CDCl$_3$)
0.150
0.154
0.241
0.328
0.332
1.919
1.925
1.939
1.963
1.983
2.079
2.091
2.096
2.101
2.105
2.109
2.131
2.279
2.296
2.308
2.331
2.332
2.354
2.378
2.399
2.462
2.482
2.501
4.903
4.907
4.910
4.941
4.944
4.946
4.952
4.998
5.003
5.009
5.741
5.775
5.798
5.832
9.099
2.337
2.227
4.330
2.103
2.125
1.000
0
1
2
3
4
5
6
7
8
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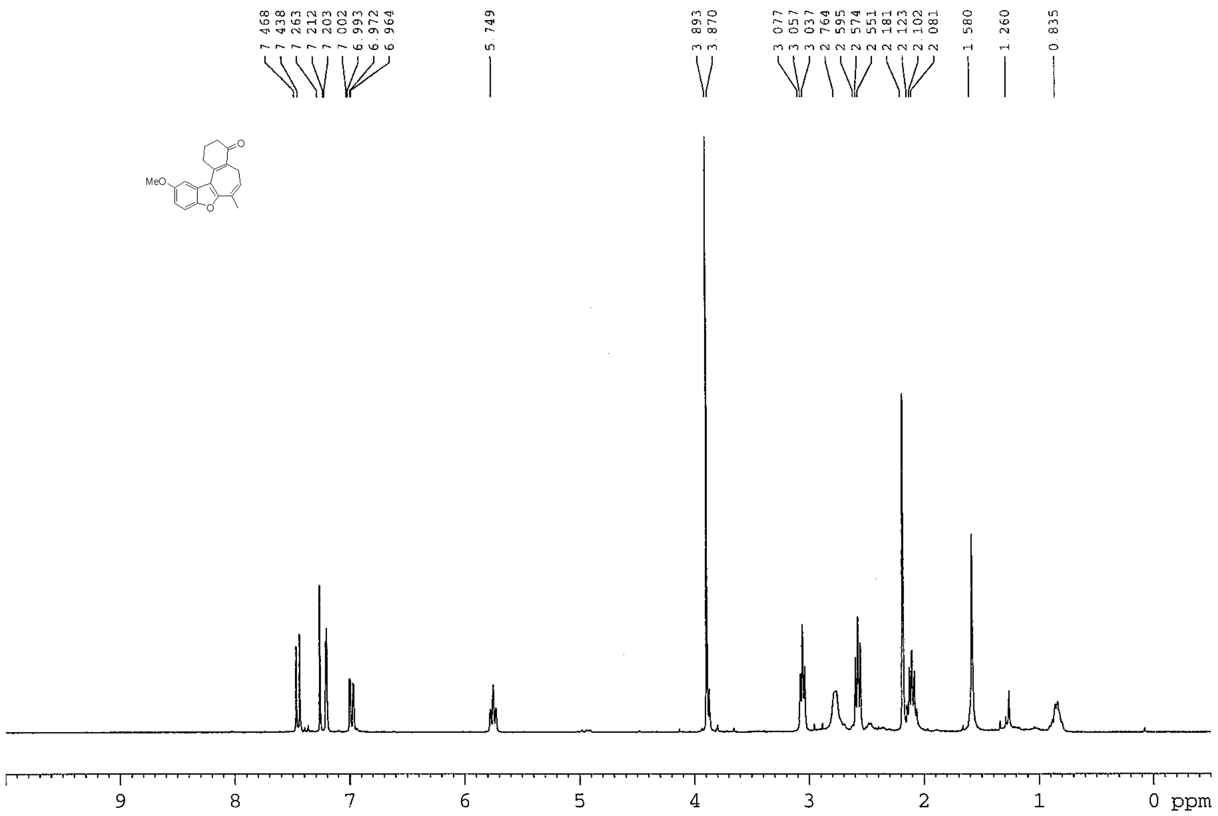
O
SnMe3

Tetracycle **17b** (300 MHz, CDCl$_3$)



```
Current Data Parameters
NAME          kmsekm
EXPNO           1418
PROCNO             1

F2 - Acquisition Parameters
Date_       20070816
Time            9.23
INSTRUM        spect
PROBHD  5 mm Multinucl
PULPROG           zg
TD             16384
SOLVENT        CDCl3
NS                16
DS                 0
SWH       4496.403 Hz
FIDRES    0.274439 Hz
AQ      1.8219508 sec
RG             287.4
DW        111.200 usec
DE          6.00 usec
TE           303.2 K
D1     2.00000000 sec
MCREST 0.00000000 sec
MCWRK  0.01500000 sec

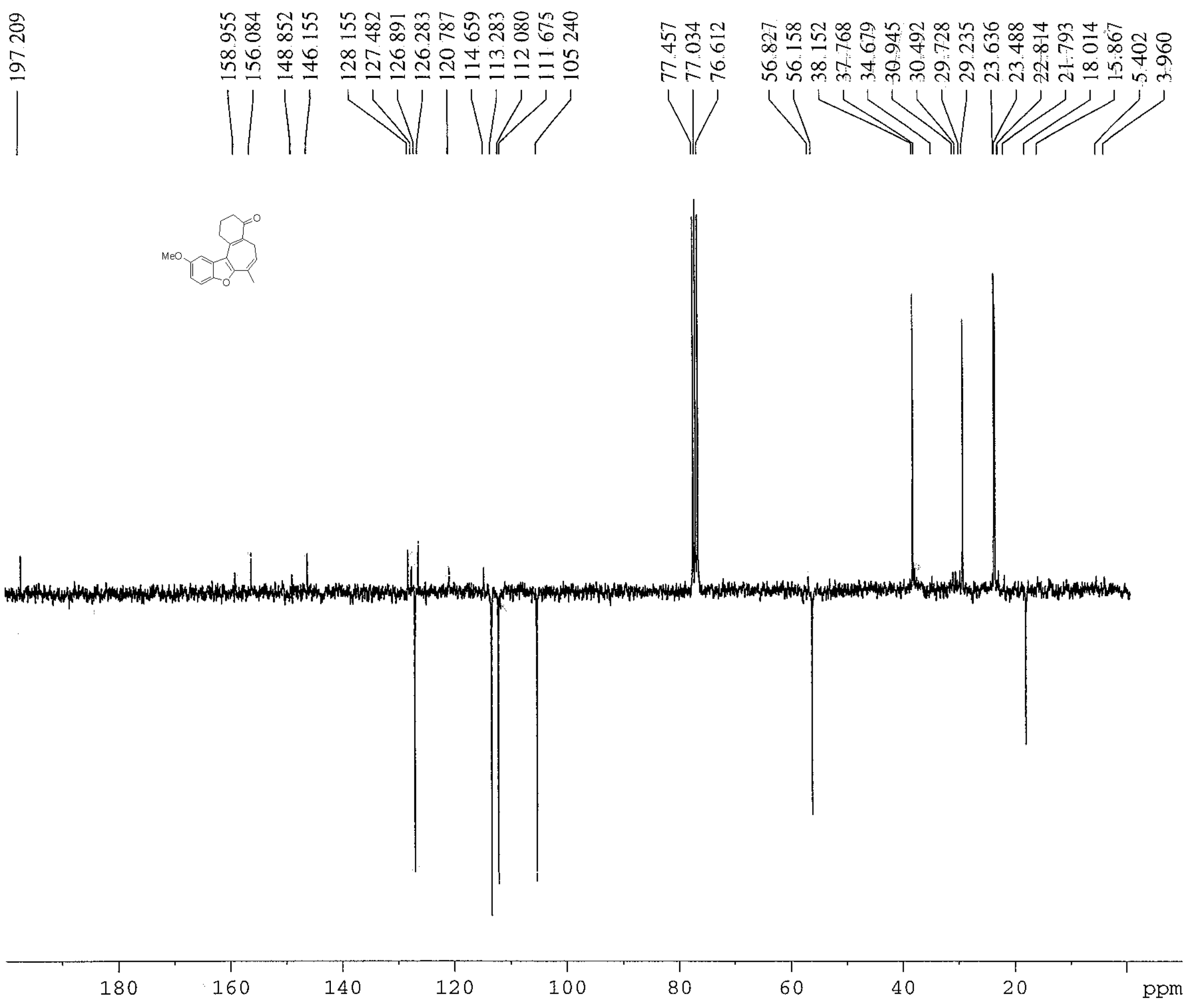
======== CHANNEL f1 =====
NUC1              1H
P1         3.00 usec
PL1         -3.00 dB
SFO1  300.2319515 MHz

F1 - Acquisition parameters
ND0                1
TD               512
SFO1    300.1314 MHz
FIDRES   0.586194 Hz
SW         1.000 ppm
FnMODE     undefined

F2 - Processing parameters
SI             16384
SF    300.2300174 MHz
WDW               no
SSB                0
LB           0.00 Hz
GB                 0
PC              1.00

F1 - Processing parameters
SI               512
MC2             TPPI
SF    300.1300000 MHz
WDW               no
SSB                2
LB           0.30 Hz
```

Tetracycle **17b** (75.5 MHz, $CDCl_3$)



```
Current Data Parameters
NAME       copy_of_kmsekm
EXPNO                1420
PROCNO                  1

F2 - Acquisition Parameters
Date_            20070818
Time                16.32
INSTRUM             spect
PROBHD   5 mm Multinucl
PULPROG              jmod
TD                  32768
SOLVENT             CDCl3
NS                  22134
DS                      4
SWH             18115.941 Hz
FIDRES           0.552855 Hz
AQ              0.9044468 sec
RG                 1149.4
DW                 27.600 usec
DE                   6.00 usec
TE                  303.2 K
CNST2         145.0000000
CNST11          1.0000000
D1             2.00000000 sec
d20            0.00689655 sec
DELTA          0.00001426 sec
MCREST         0.00000000 sec
MCWRK          0.01500000 sec

======== CHANNEL f1 ========
NUC1                  13C
P1                  11.20 usec
p2                  22.40 usec
PL1                  0.00 dB
SFO1          75.5018965 MHz

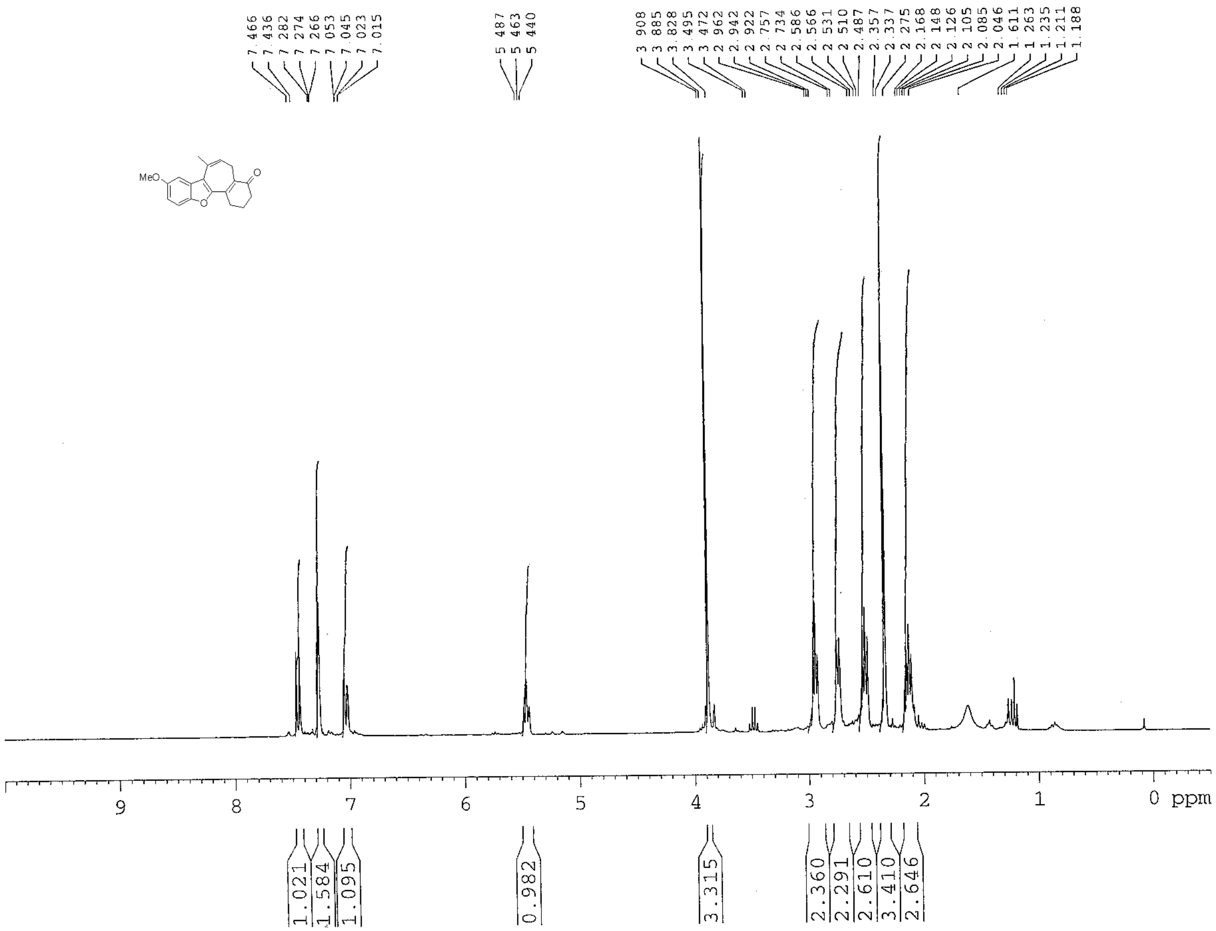
======== CHANNEL f2 ========
CPDPRG2           waltz16
NUC2                   1H
PCPD2              100.00 usec
PL2                 -3.00 dB
PL12                19.40 dB
SFO2         300.2320007 MHz

F1 - Acquisition parameters
ND0                     3
TD                    512
SFO1             300.1314 MHz
FIDRES           0.586194 Hz
SW                  1.000 ppm
FnMODE          undefined

F2 - Processing parameters
SI                  32768
SF             75.4928940 MHz
WDW                    EM
SSB                     0
LB                   3.00 Hz
GB                      0
PC                   1.00

F1 - Processing parameters
```

Tetracycle **18b** (300 MHz, CDCl$_3$)



Current Data Parameters
NAME kmsekm
EXPNO 1382
PROCNO 202

F2 – Acquisition Parameters
Date_ 20070608
Time 12.47
INSTRUM spect
PROBHD 5 mm Multinucl
PULPROG zg
TD 16384
SOLVENT CDCl3
NS 16
DS 0
SWH 4496.403 Hz
FIDRES 0.274439 Hz
AQ 1.8219508 sec
RG 181
DW 111.200 usec
DE 6.00 usec
TE 303.2 K
D1 2.00000000 sec
MCREST 0.00000000 sec
MCWRK 0.01500000 sec

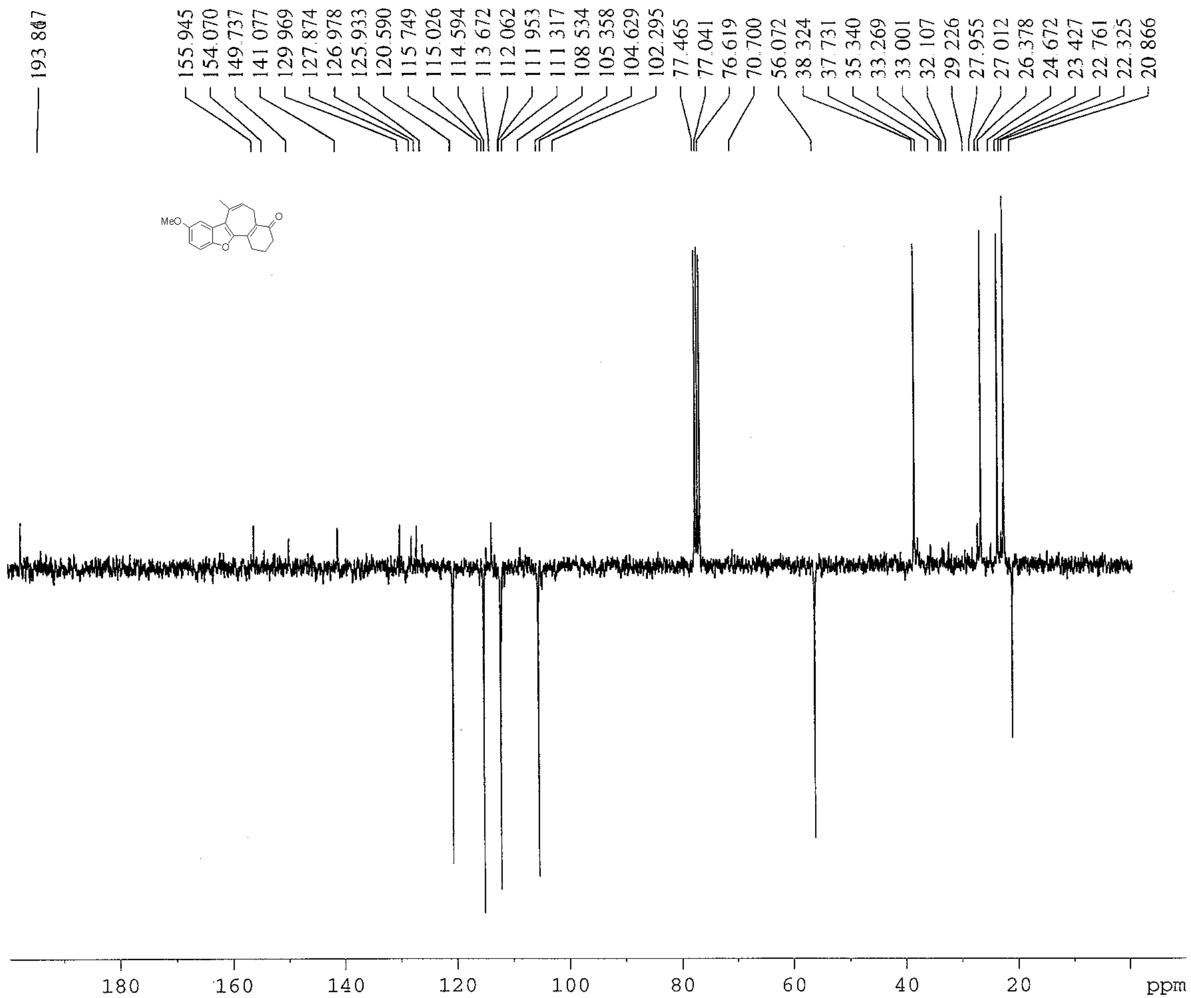
======= CHANNEL f1 =====
NUC1 1H
P1 3.00 usec
PL1 -3.00 dB
SFO1 300.2319515 MHz

F1 – Acquisition parameters
ND0 1
TD 512
SFO1 300.1314 MHz
FIDRES 0.586194 Hz
SW 1.000 ppm
FnMODE undefined

F2 – Processing parameters
SI 16384
SF 300.2300165 MHz
WDW no
SSB 0
LB 0.00 Hz
GB 0
PC 1.00

F1 – Processing parameters
SI 512
MC2 TPPI
SF 300.1300000 MHz
WDW no
SSB 2
LB 0.30 Hz

Tetracycle **18b** (75.5 MHz, $CDCl_3$)



```
Current Data Parameters
NAME               kmsekm
EXPNO                1380
PROCNO                  1

F2 - Acquisition Parameters
Date_            20070607
Time                18.47
INSTRUM             spect
PROBHD   5 mm Multinucl
PULPROG              jmod
TD                  32768
SOLVENT             CDCl3
NS                  15975
DS                      4
SWH             18115.941 Hz
FIDRES           0.552855 Hz
AQ              0.9044468 sec
RG                 1149.4
DW                 27.600 usec
DE                   6.00 usec
TE                  303.2 K
CNST2         145.0000000
CNST11          1.0000000
D1             2.00000000 sec
d20            0.00689655 sec
DELTA          0.00001426 sec
MCREST         0.00000000 sec
MCWRK          0.01500000 sec

======== CHANNEL f1 ========
NUC1                  13C
P1                  11.20 usec
p2                  22.40 usec
PL1                  0.00 dB
SFO1           75.5018965 MHz

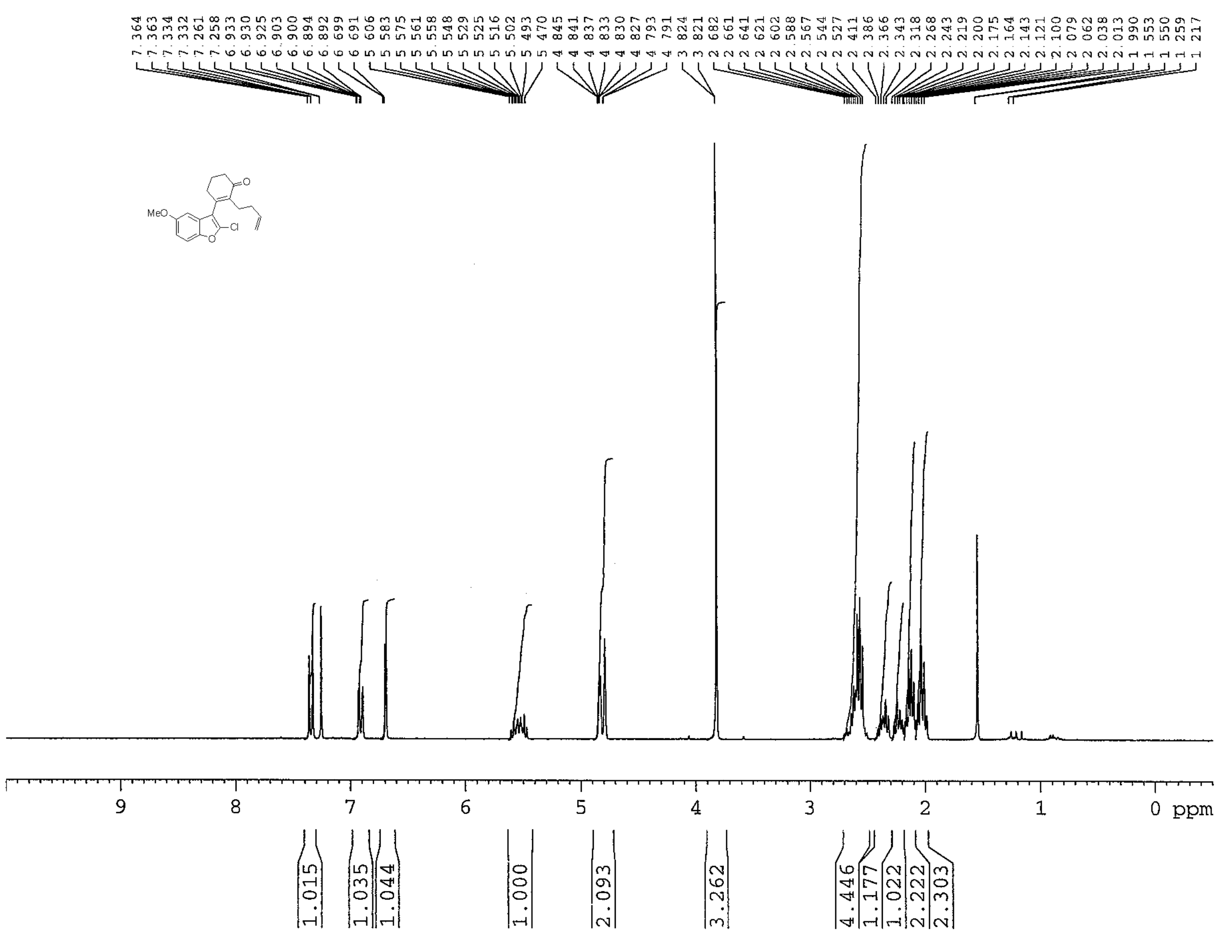
======== CHANNEL f2 ========
CPDPRG2           waltz16
NUC2                   1H
PCPD2              100.00 usec
PL2                 -3.00 dB
PL12                19.40 dB
SFO2          300.2320007 MHz

F1 - Acquisition parameters
ND0                     3
TD                    512
SFO1             300.1314 MHz
FIDRES           0.586194 Hz
SW                  1.000 ppm
FnMODE          undefined

F2 - Processing parameters
SI                  32768
SF             75.4928940 MHz
WDW                    EM
SSB                     0
LB                   3.00 Hz
GB                      0
PC                   1.00

F1 - Processing parameters
```

Chloride **19** (300 MHz, $CDCl_3$)



Current Data Parameters
NAME kmsekm
EXPNO 1253
PROCNO 1

F2 – Acquisition Parameters
Date_ 20070410
Time 12.19
INSTRUM spect
PROBHD 5 mm Multinucl
PULPROG zg
TD 16384
SOLVENT CDCl3
NS 16
DS 0
SWH 4496.403 Hz
FIDRES 0.274439 Hz
AQ 1.8219508 sec
RG 256
DW 111.200 usec
DE 6.00 usec
TE 303.2 K
D1 2.00000000 sec
MCREST 0.00000000 sec
MCWRK 0.01500000 sec

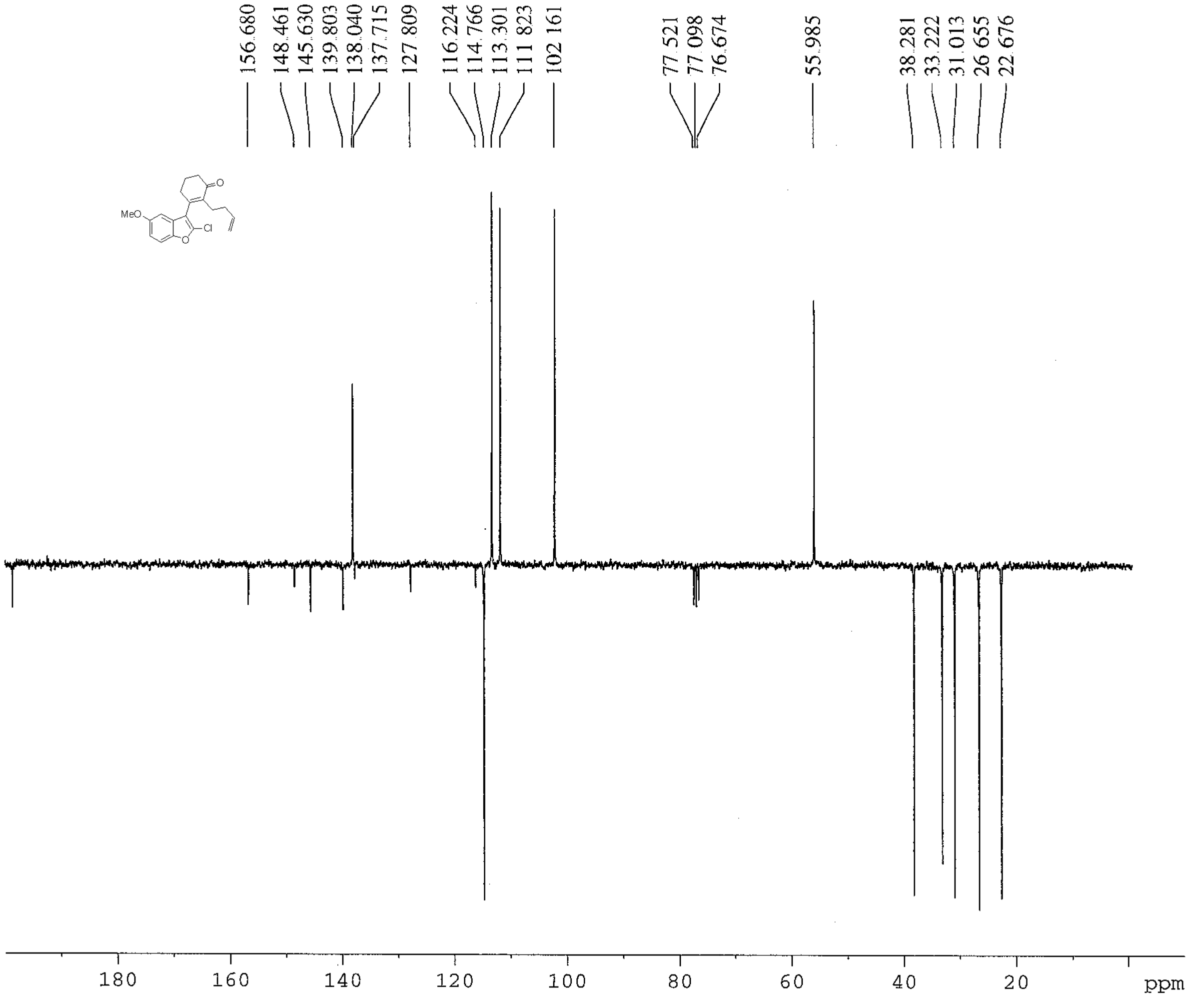
======= CHANNEL f1 =====
NUC1 1H
P1 3.00 usec
PL1 -3.00 dB
SFO1 300.2319515 MHz

F1 – Acquisition parameters
ND0 1
TD 512
SFO1 300.1314 MHz
FIDRES 0.586194 Hz
SW 1.000 ppm
FnMODE undefined

F2 – Processing parameters
SI 16384
SF 300.2300185 MHz
WDW no
SSB 0
LB 0.00 Hz
GB 0
PC 1.00

F1 – Processing parameters
SI 512
MC2 TPPI
SF 300.1300000 MHz
WDW no
SSB 2
LB 0.30 Hz

Chloride **19** (75.5 MHz, CDCl$_3$)



```
Current Data Parameters
NAME              kmsekm
EXPNO               1266
PROCNO                 1

F2 - Acquisition Parameters
Date_           20070417
Time                8.14
INSTRUM            spect
PROBHD   5 mm Multinucl
PULPROG             jmod
TD                 32768
SOLVENT            CDCl3
NS                  1141
DS                     4
SWH            18115.941 Hz
FIDRES          0.552855 Hz
AQ             0.9044468 sec
RG                1149.4
DW                27.600 usec
DE                  6.00 usec
TE                 303.2 K
CNST2        145.0000000
CNST11         1.0000000
D1            2.00000000 sec
d20           0.00689655 sec
DELTA         0.00001426 sec
MCREST        0.00000000 sec
MCWRK         0.01500000 sec

======== CHANNEL f1 ========
NUC1                 13C
P1                 11.20 usec
p2                 22.40 usec
PL1                 0.00 dB
SFO1          75.5018965 MHz

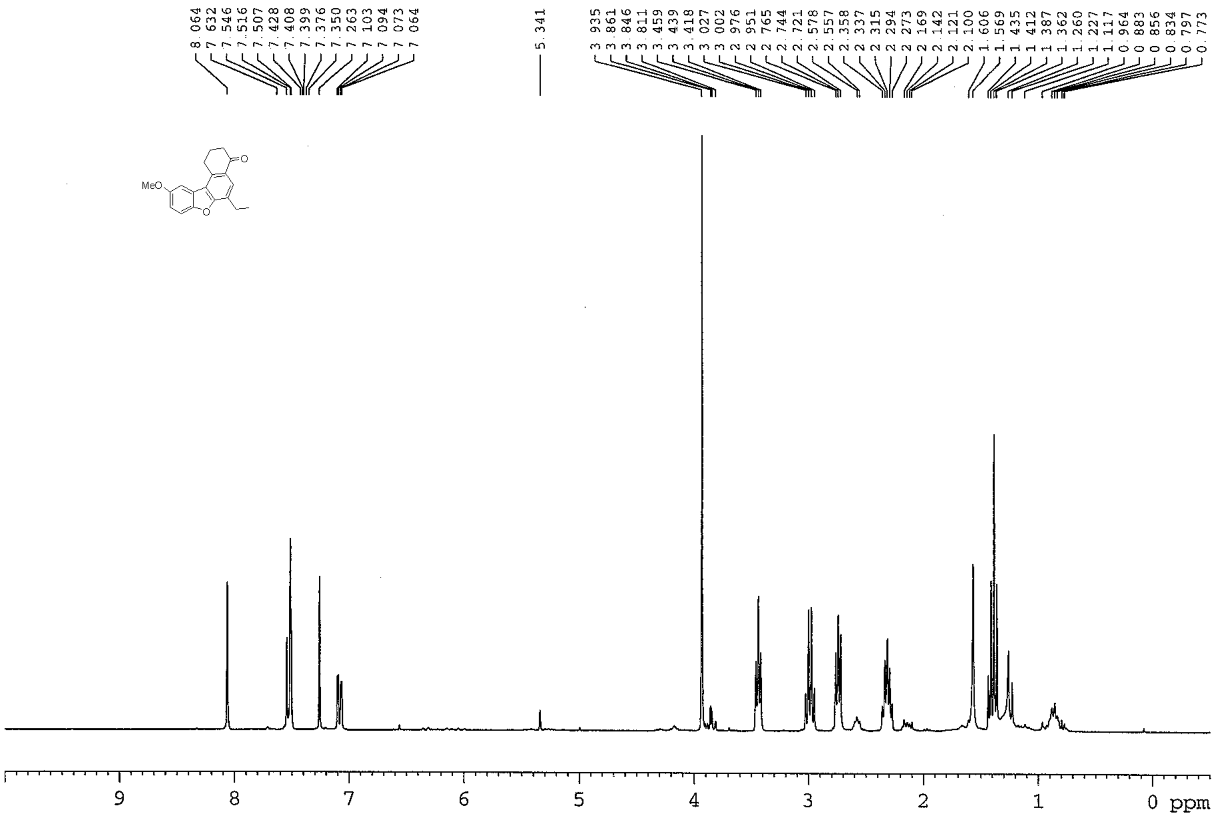
======== CHANNEL f2 ========
CPDPRG2          waltz16
NUC2                  1H
PCPD2             100.00 usec
PL2                -3.00 dB
PL12               19.40 dB
SFO2         300.2320007 MHz

F1 - Acquisition parameters
ND0                    3
TD                   512
SFO1            300.1314 MHz
FIDRES          0.586194 Hz
SW                 1.000 ppm
FnMODE         undefined

F2 - Processing parameters
SI                 32768
SF            75.4928940 MHz
WDW                   EM
SSB                    0
LB                  3.00 Hz
GB                     0
PC                  1.00

F1 - Processing parameters
```

Tetracycle **20** (300 MHz, $CDCl_3$)



```
Current Data Parameters
NAME          kmsekm
EXPNO           1376
PROCNO             1

F2 - Acquisition Parameters
Date_       20070613
Time           18.42
INSTRUM        spect
PROBHD  5 mm Multinucl
PULPROG           zg
TD             16384
SOLVENT        CDCl3
NS                16
DS                 0
SWH        4496.403 Hz
FIDRES     0.274439 Hz
AQ        1.8219508 sec
RG               256
DW          111.200 usec
DE            6.00 usec
TE             303.2 K
D1      2.00000000 sec
MCREST  0.00000000 sec
MCWRK   0.01500000 sec

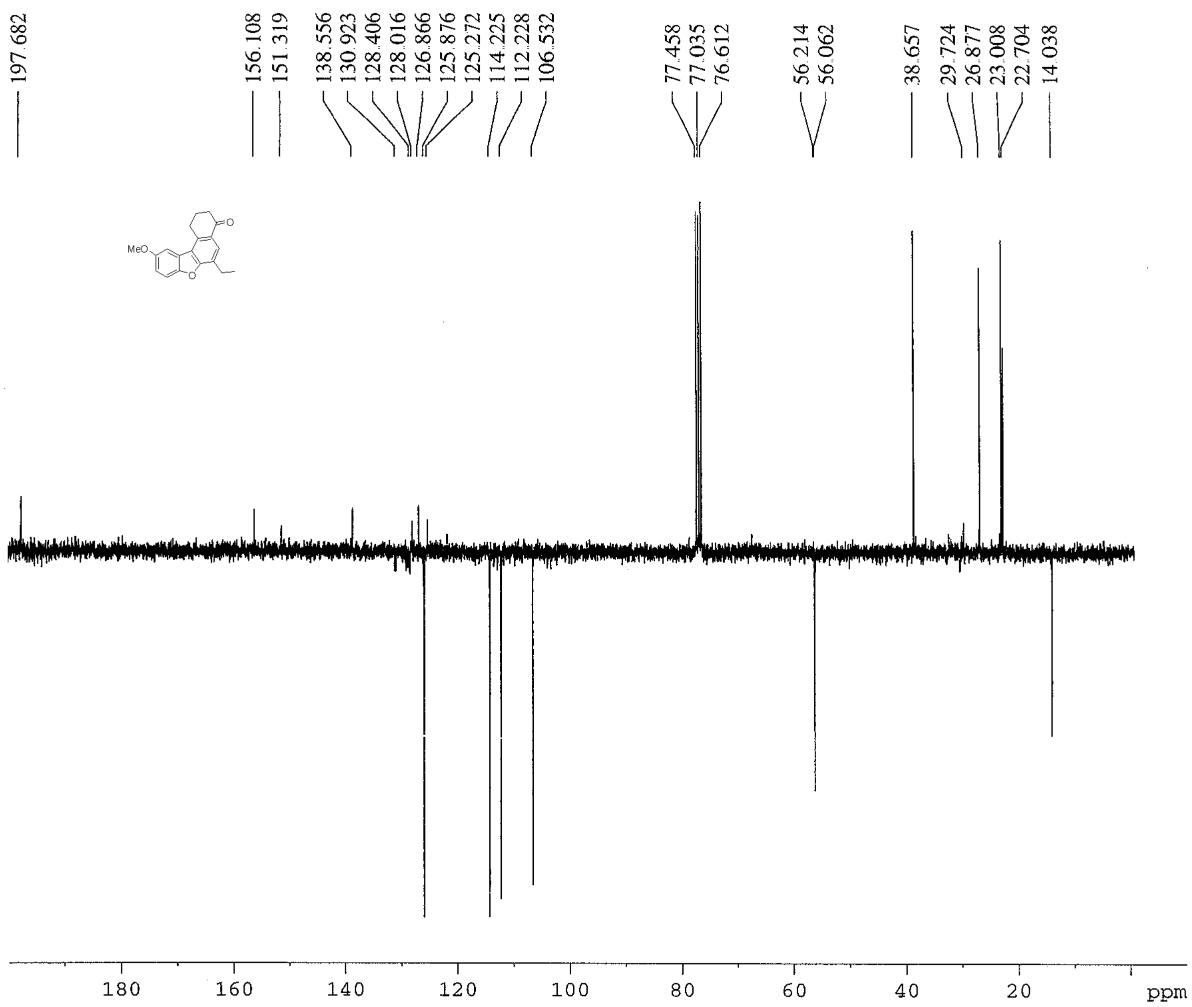
======== CHANNEL f1 ========
NUC1              1H
P1           3.00 usec
PL1          -3.00 dB
SFO1   300.2319515 MHz

F1 - Acquisition parameters
ND0                1
TD               512
SFO1     300.1314 MHz
FIDRES   0.586194 Hz
SW         1.000 ppm
FnMODE     undefined

F2 - Processing parameters
SI             16384
SF    300.2300176 MHz
WDW               no
SSB                0
LB           0.00 Hz
GB                 0
PC              1.00

F1 - Processing parameters
SI               512
MC2             TPPI
SF    300.1300000 MHz
WDW            QSINE
SSB                2
LB           0.30 Hz
```

Tetracycle **20** (75.5 MHz, $CDCl_3$)



```
Current Data Parameters
NAME               kmsekm
EXPNO                1387
PROCNO                  1

F2 - Acquisition Parameters
Date_            20070620
Time                17.41
INSTRUM             spect
PROBHD   5 mm Multinucl
PULPROG              jmod
TD                  32768
SOLVENT             CDCl3
NS                  18067
DS                      4
SWH             18115.941 Hz
FIDRES           0.552855 Hz
AQ              0.9044468 sec
RG                 1625.5
DW                 27.600 usec
DE                   6.00 usec
TE                  303.2 K
CNST2         145.0000000
CNST11          1.0000000
D1             2.00000000 sec
d20            0.00689655 sec
DELTA          0.00001426 sec
MCREST         0.00000000 sec
MCWRK          0.01500000 sec

======== CHANNEL f1 ========
NUC1                  13C
P1                  11.20 usec
p2                  22.40 usec
PL1                  0.00 dB
SFO1          75.5018965 MHz

======== CHANNEL f2 ========
CPDPRG2           waltz16
NUC2                   1H
PCPD2              100.00 usec
PL2                 -3.00 dB
PL12                19.40 dB
SFO2         300.2320007 MHz

F1 - Acquisition parameters
ND0                     3
TD                    512
SFO1             300.1314 MHz
FIDRES           0.586194 Hz
SW                  1.000 ppm
FnMODE          undefined

F2 - Processing parameters
SI                  32768
SF             75.4928940 MHz
WDW                    EM
SSB                     0
LB                   1.00 Hz
GB                      0
PC                   1.00

F1 - Processing parameters
```