Electronic Supplementary Material (ESI) for New Journal of Chemistry.
This journal is © The Royal Society of Chemistry and the Centre National de la Recherche Scientifique 2016

# Supplementary Material

# 2,4 and 2,5-bis(benzooxazol-2′-yl)hydroquinone (DHBO) and their borate complexes: Synthesis and Optical properties

Karima Benelhadj,[a] Julien Massue,*[a] and Gilles Ulrich*[a]

[a] *Institut de chimie et procédés pour l'énergie, l'environnement et la santé (ICPEES),Chimie Organique pour les Matériaux, la Biologie et l'Optique (COMBO), UMR CNRS 7515, Ecole Européenne de Chimie, Polymères et Matériaux (ECPM), 25 Rue Becquerel, 67087 Strasbourg Cedex 02, France.*

Contact: massue@unistra.fr, gulrich@unistra.fr

# S1 General information and equipements

All reactions were performed under a dry atmosphere of argon using standard Schlenck techniques. All chemicals were received from commercial sources (Aldrich, Alfa Aesar, Acros) and used without further purification. Dichloromethane were distilled over $P_2O_5$ under an argon atmosphere. Thin layer chromatography (TLC) was performed on silica gel coated with fluorescent indicator. Chromatographic purifications were conducted using 40-63 μm silica gel. All mixtures of solvents are given in v/v ratio.

$^1$H NMR (400.1 MHz) and $^{13}$C NMR (100.5 MHz) spectra were recorded on a Bruker Advance 400 MHz spectrometer, $^1$H NMR (300.1 MHz) and $^{13}$C NMR (75.5 MHz) or a Bruker Advance 300 MHz spectrometer with perdeuterated solvents with residual protonated solvent signals as internal references.

Absorption spectra were recorded using a dual-beam grating Schimadzu UV-3000 absorption spectrometer with a 1 cm quartz cell. The steady-state fluorescence emission and excitation spectra were obtained by using a Horiba S2 Jobin Yvon Fluoromax 4. All fluorescence spectra were corrected. Solvents for spectroscopy were spectroscopic grade and were used as received. All fluorescence spectra were corrected.

The fluorescence quantum yield ($\Phi_{exp}$) was calculated from eq (1).

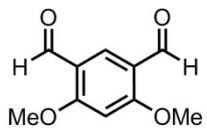
$$\Phi_{exp} = \Phi_{ref} \frac{I}{I_{ref}} \frac{OD_{ref}}{OD} \frac{\eta^2}{\eta^2_{ref}} \quad (eq\ 1)$$

I denotes the integral of the corrected emission spectrum, OD is the optical density at the excitation wavelength, and η is the refractive index of the medium. The reference systems used were: Quinine Φ= 55% in $H_2SO_4$ 1N, $\lambda_{exc}$ = 366 nm for dyes emitting below 480 nm, Rhodamine 6G, Φ= 88% in ethanol $\lambda_{exc}$ = 488 nm for dyes emitting between 480 and 570 nm and cresyl violet, Φ= 55% $\lambda_{exc}$ = 546 nm in ethanol for dyes emitting above 570 nm.

Luminescence lifetimes were measured on an Edimburgh Instruments spectrofluorimeter equipped with a R928photomultiplier and a PicoQuant PDL 800-D pulsed diode connected to a GwInstect GFG- 8015G delay generator. No filter was used for the excitation. Emission wavelengths were selected by a monochromator. Lifetimes were deconvoluted with FS-900 software using a light-scattering solution (LUDOX) for instrument response. The excitation source was a laser diode (λ 320 nm).

# S2 Synthetic protocols

**Compound 1**

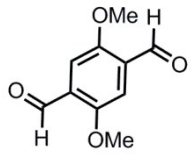


**1**

To a stirred solution of 1,3-dimethoxybenzene (1.5 g, 10.8 mmol), in $CH_2Cl_2$ (20 ml) was added dropwise a 1.0M solution of bromine in $CH_2Cl_2$ (2.30 mmol) at 0 °C under argon. The reaction was stirred for 30 min and progress was monitored by TLC. The product was then washed with saturated sodium thiosulfate and concentrated under vacuum to afford the brominated intermediate as a white solid which was used without further purification. 1.6N butyl-lithium in hexane (4.0 ml, 5.60 mmol) was syringed at room temperature to a stirred solution of the brominated intermediate in anhydrous ether (30 ml) under argon. The solution was stirred for 1 min. before anhydrous DMF (6.70 mmol) was added dropwise. The formed precipitate was stirred for 5 min before 10 ml of HCl (10%) was added. The stirring was continued for a further 15 min after which the precipitate was washed with water and extracted with ether. After solvent evaporation, the crude residue was purified by recrystallization in ethanol leading to compound **1** as a crystalline white powder (66% over 2 steps).

$^1$H NMR (300 MHz, $CDCl_3$) δ (ppm) = 10.27 (s, 2H, CHO), 8.34 (s, 1H, $H_a$), 6.45 (s, 1H), 4.02 (s, 6H, $CH_3$). $^{13}$C NMR (75 MHz, $CDCl_3$) δ (ppm) = 187.7, 167.5, 132.1, 119.0, 94.4, 56.3. ESI-HRMS calcd for $C_{10}H_{11}O_4$: 195.0652 (M+H) found 195.0643 (M+H).

**Compound 6**



**6**

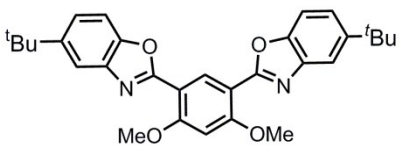
To a solution of *p*-dimethoxybenzene (1.40 g, 10 mmol) and N,N,N′,N′-tetramethylethylenediamine (7.5 ml, 50 mmol) in diethyl ether (40 ml) was added n-butyllithium (1.6M solution in hexane, 32 ml, 50 mmol) at 0 °C under argon. The mixture was then refluxed for 24h. After the mixture was cooled down to room temperature, N,N-dimethylformamide (5 ml, 55 mmol) was added to the mixture, which was stirred overnight at room temperature. After addition of water (25 ml), the mixture was extracted with chloroform. The organic layer was dried over anhydrous $MgSO_4$, filtered, and concentrated under vacuum to give a brown oil which was further purified by recrystallization from dichloromethane/pentane to afford compound **6** (46%).

$^1$H NMR (300 MHz, $CDCl_3$) δ (ppm) = 10.50 (s, 2H, CHO), 7.46 (s, 2H), 3.94 (s, 6H, $CH_3$). $^{13}$C NMR (75 MHz, $CDCl_3$) δ (ppm) = 189.4, 155.9, 129.3, 111.1, 56.4.

## General procedures for the synthesis of DHBO 2, 3 and 7

To a solution of 5-substituted-2-aminophenol in methanol was added 1 equiv. of the appropriate benzaldehyde **1** or **6**, 1 equiv. of phenylboronic acid and 3 equiv. of potassium cyanide. The mixture was stirred for 24 h at rt. After solvent evaporation, the crude residue was purified by silica gel chromatography eluting with $CH_2Cl_2$/Pet. Ether leading to the corresponding DHBO.

**DHBO 2**

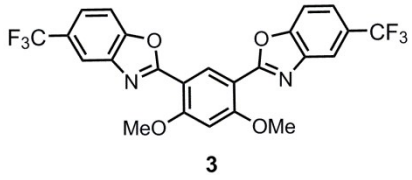


**2**

85%. $^1$H NMR (300 MHz, $CDCl_3$) δ (ppm) = 8.97 (s, 1H), 7.87 (d, 2H, $^4J_{3\text{-}1}$ = 1.8 Hz), 7.51 (d, 2H, $^3J_{2\text{-}1}$ = 8.5 Hz), 7.40 (d, 2H, $^3J_{1\text{-}2}$ = 8.5 Hz, $^4J_{1\text{-}3}$ = 1.8 Hz), 6.72 (s, 1H), 4.13 (s, 6H, $CH_3$), 1.39 (s, 18H, $^t$Bu). $^{13}$C NMR (75 MHz, $CDCl_3$) δ (ppm) = 162.0, 160.8, 148.3,

147.9, 142.3, 134.1, 122.6, 116.8, 109.6, 109.6, 96.3, 56.6, 35.1, 31.9. ESI-MS calcd $C_{30}H_{33}N_2O_4$: 485.2435 (M+H), found 485.2380 (M+H).

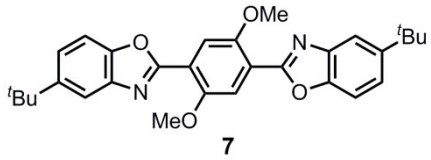
**DHBO 3**



**3**

94%. $^1$H NMR (300 MHz, $CDCl_3$) δ (ppm) = 9.02 (s, 1H), 8.01 (br s, 2H), 7.71 (d, 2H, $^3J_{2\text{-}1}$ = 8.4 Hz), 7.64 (d, 2H, $^3J_{1\text{-}2}$ = 8.4 Hz, $^4J_{1\text{-}3}$ = 1.2 Hz), 6.75 (s, 1H), 4.17 (s, 6H, $CH_3$). $^{13}$C NMR (75 MHz, $CDCl_3$) δ (ppm) = 162.9, 162.4, 152.1, 152.1, 142.5, 134.8, 129.8, 128.0, 127.6, 127.2, 126.8, 126.2, 124.9, 122.6, 122.4, 122.4, 122.3, 122.3, 118.0, 117.9, 117.9, 117.8, 111.0, 109.0, 96.4, 56.8. ESI-MS calcd $C_{24}H_{15}F_6N_2O_4$: 509.0931 (M+H), found 509.0925 (M+H).

**DHBO 7**



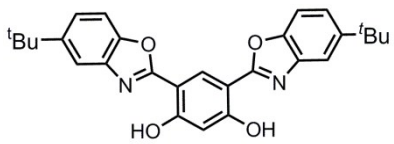
**7**

80%. $^1$H NMR (300 MHz, $CDCl_3$) δ (ppm) = 7.87 (br s, 4H), 7.51 (d, 2H, $^3J_{2\text{-}1}$ = 8.6 Hz), 7.42 (d, 2H, $^3J_{1\text{-}2}$ = 8.6 Hz, $^4J_{1\text{-}3}$ = 1.9 Hz), 4.08 (s, 6H, $CH_3$), 1.38 (s, 18H, $^t$Bu). $^{13}$C NMR (75 MHz, $CDCl_3$) δ (ppm) = 160.9, 152.3, 148.6, 148.2, 142.0, 123.3, 119.5, 117.0, 114.9, 109.8, 57.1, 35.0, 31.8.

## General procedures for the synthesis of DHBO 4, 5 and 8

$BBr_3$ 1M (4 equiv.) was added dropwise to a Schlenck tube containing a solution of DHBO **2**, **3** or **7** in $CH_2Cl_2$. The mixture was stirred at rt overnight in the dark. Water (20 ml) was then added and the reaction mixture was extracted several times with $CH_2Cl_2$. The combined organic phases were dried over $MgSO_4$, filtered, and concentrated under vacuum to afford DHBO **4**, **5** or **8** as grey solids.

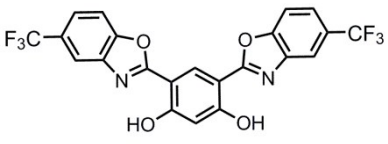
**DHBO 4**



**4**

73%. $^1$H NMR (300 MHz, $CDCl_3$) δ (ppm) = 12.02 (br s, 2H, OH), 8.68 (s, 1H), 7.73 (d, 2H, $^4J_{3\text{-}1}$ = 1.8 Hz), 7.54 (d, 2H, $^3J_{2\text{-}1}$ = 8.7 Hz), 7.44 (d, 2H, $^3J_{1\text{-}2}$ = 8.7 Hz, $^4J_{1\text{-}3}$ = 1.9 Hz), 6.80 (s, 1H), 1.41 (s, 18H, $^t$Bu). $^{13}$C NMR (75 MHz, $CDCl_3$) δ (ppm) = 163.1, 162.6, 148.9, 147.2, 140.0, 126.9, 123.1, 115.8, 109.8, 104.8, 104.7, 35.2, 31.9. ESI-MS calcd $C_{28}H_{28}N_2O_4$: 457.21 (M+H), found 457.27 (M+H).

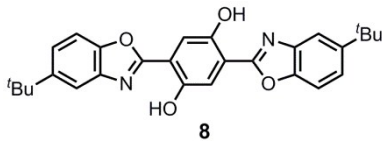
**DHBO 5**



**5**

69%. $^1$H NMR (300 MHz, $CDCl_3$) δ (ppm) = 11,70 (br s, 2H, OH), 8.72 (s, 1H), 8.01 (s, 2H), 7.74 (d, 2H, $^3J_{2\text{-}1}$ = 8.6 Hz), 7.68 (d, 2H, $^3J_{1\text{-}2}$ = 8.6 Hz), 6.83 (s, 1H). $^{13}$C NMR (75 MHz, $CDCl_3$) δ (ppm) = 163.9, 163.8, 150.9, 150.9, 140.3, 128.5, 128.1, 127.8, 125.9, 122.9, 122.9, 122.8, 122.8, 122.3, 117.0, 117.0, 116.9, 116.9, 111.2, 105.3, 104.2. ESI-MS calcd $C_{22}H_{11}F_6N_2O_4$: 481.0618 (M+H), found 481.0604 (M+H).

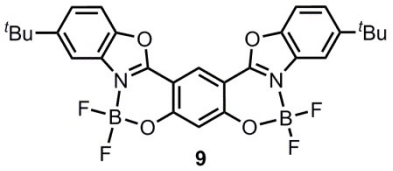
**DHBO 8**



**8**

88%. $^1$H NMR (300 MHz, $CDCl_3$) δ (ppm) = 12.45 (br s, 2H, OH), 7.62 (br s, 4H), 7.22 (d, 2H, $^3J_{2\text{-}1}$ = 8.7 Hz), 7.41 (d, 2H, $^3J_{1\text{-}2}$ = 8.7 Hz), 1.38 (s, 18H, $^t$Bu). $^{13}$C NMR (75 MHz, $CDCl_3$) δ (ppm) = 160.9, 152.3, 148.6, 148.2, 142.0, 123.3, 119.5, 117.0, 114.9, 109.8, 57.1, 35.0, 31.8. ESI-HRMS Calcd. for $C_{28}H_{28}N_2O_4$: 457.2122 (M+H), found 457.2136 (M+H).

**Borate complex 9**

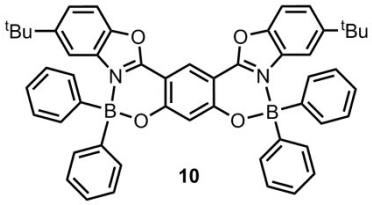


To a stirred solution of DHPO **4** in freshly distilled 1,2-dichloroethane, $BF_3.Et_2O$ (6 equiv.) was syringed under argon. After 5 min., N,N-Diisopropylethylamine (DIEA) (6 equiv.) was added and the resulting mixture stirred at 40 °C for 1 h. The crude solution was filtered through a column of basic $Al_2O_3$, eluting with $CH_2Cl_2$, to afford clean complex **9** as a white powder after evaporation of the solvents *in vacuo* (64%).$^1$H NMR (300 MHz, $CDCl_3$) δ (ppm) = 8.66 (s, 2H), 7.93 (s, 2H), 7.66 (s, 4H), 6.96 (s, 2H), 1.42 (s, 18H, $^t$Bu). $^{13}$C NMR (75 MHz, $CDCl_3$) δ (ppm) = 165.5, 160.4, 152.4, 147.0, 130.7, 125.9, 125.7, 113.7, 111.0, 109.2, 101.8, 35.7, 31.7. HRMS (ESI) Calcd. for $C_{28}H_{26}B_2F_4K_1N_2O_4$: 591.1656 (M + K), found: 591.1649 (M + K).

**General Procedure for the synthesis of borate complexes 10-12**

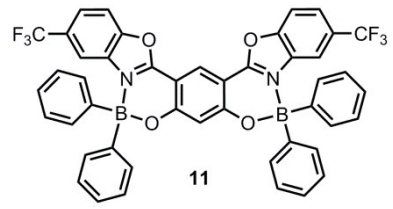
To a stirred solution of the corresponding DHBO in toluene (0.1 mL/mg), $BPh_3$ (6 equivalents) was added as a powder under argon. The resulting mixture was stirred at 60°C for 1 hour. The crude solution was then filtered through a column of basic $Al_2O_3$, eluting with $CH_2Cl_2$ and the solvents were evaporated *in vacuo*. Pure $BPh_2$ DHBO borate complexes **10-12** were obtained as white powders after recrystallisation in pentane or cyclohexane.

**Borate complex 10**



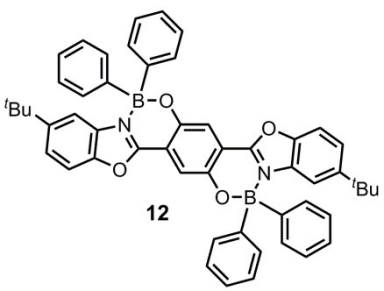
62%. $^1$H NMR (400 MHz, $CDCl_3$) δ (ppm) = 8.35 (s, 1H), 7.54 (d, 2H, $^3J_{2\text{-}1}$ = 8.8 Hz), 7.44 (d, 2H, $^3J_{1\text{-}2}$ = 8.8 Hz), 7.47-7.43 (m, 12H, CH Ar), 7.29-7.24 (m, 8H, CH Ar), 6.95 (s, 1H), 6.92 (d, 2H, $^4J_{3\text{-}1}$ = 1.8 Hz), 1.16 (s, 18H, $^t$Bu). $^{13}$C NMR (100 MHz, $CDCl_3$) δ (ppm) = 169.3, 160.2, 150.7, 147.1, 133.1, 133.0, 128.8, 127.4, 127.3, 127.2, 127.0, 126.1, 123.9, 114.4, 110.3, 109.6, 102.5, 35.1, 31.3. HRMS (ESI) Calcd. for $C_{52}H_{46}B_2K_1N_2O_4$: 823.3292 (M + K), found: 823.3286 (M + K).

**Borate complex 11**

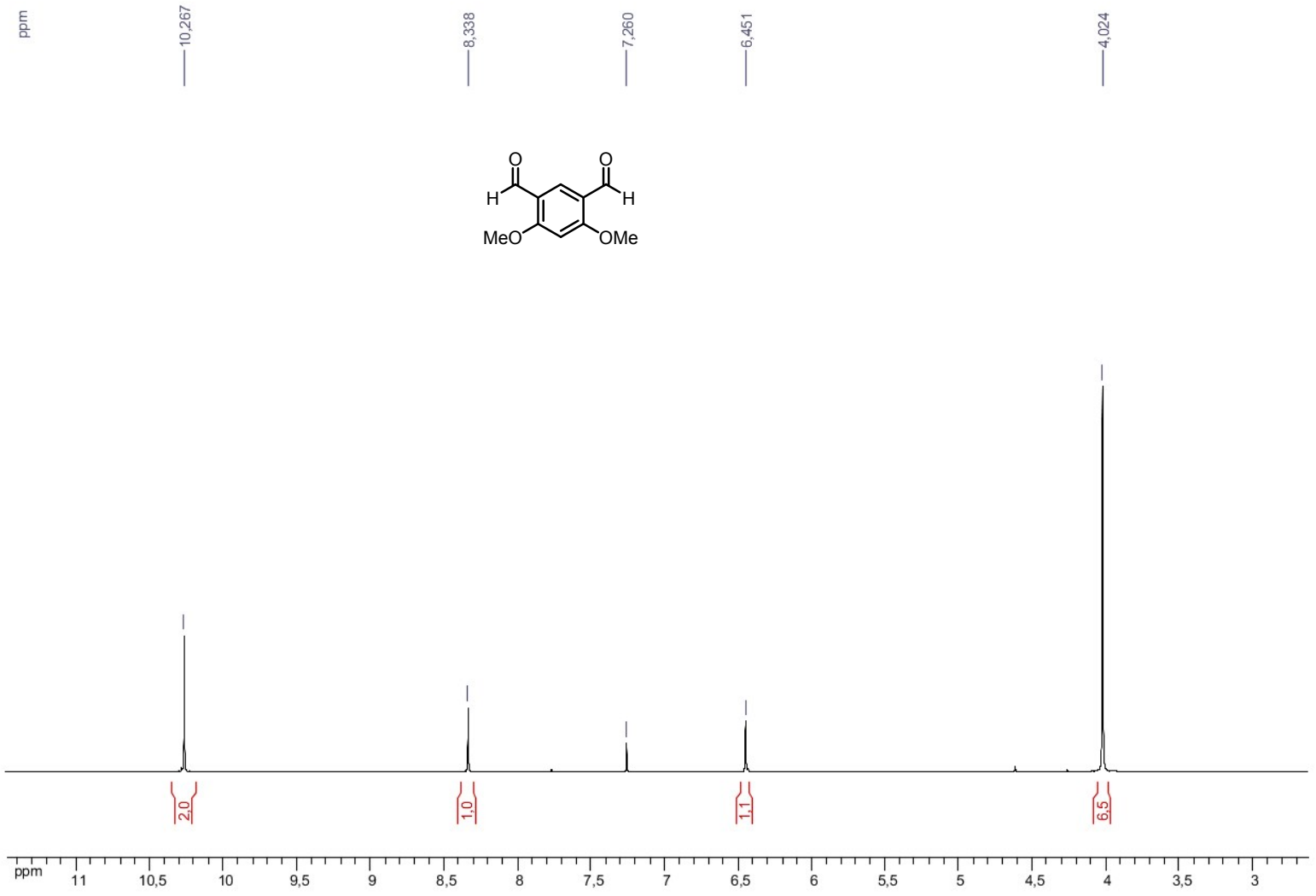


93%. $^1$H NMR (300 MHz, $CDCl_3$) δ (ppm) = 8.44 (s, 1H), 7.77 (d, 2H, $^3J_{2\text{-}1}$ = 8.6 Hz), 7.71 (d, 2H, $^3J_{1\text{-}2}$ = 8.6 Hz, $^4J_{1\text{-}3}$ = 1.2 Hz), 7.42-7.38 (m, 8H, CH Ar), 7.31-7.27 (m, 12H, CH Ar), 7.22 (br s, 2H), 6.95 (s, 1H). $^{13}$C NMR (100 MHz, $CDCl_3$) δ (ppm) = 170.3, 161.8, 150.6, 134.8, 133.6, 133.0, 131.2, 130.1, 129.8, 129.2, 128.4, 128.1, 127.8, 127.6, 127.5, 124.1, 115.3, 112.1, 109.9, 102.2. HRMS (ESI) Calcd. for $C_{46}H_{28}B_2F_6NaN_2O_4$: 831.2046 (M + Na), found: 831.1951 (M + Na).

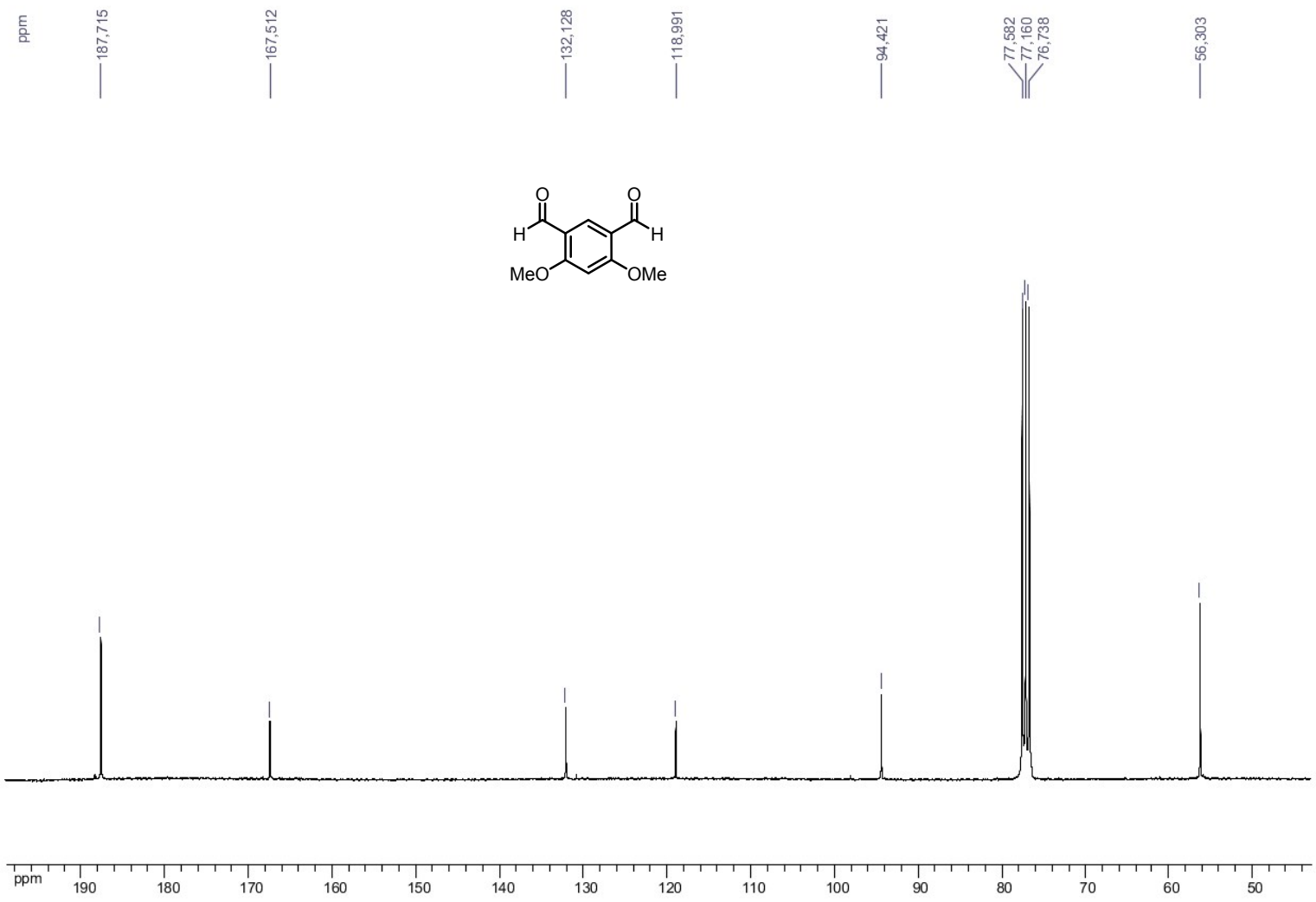
**Borate complex 12**



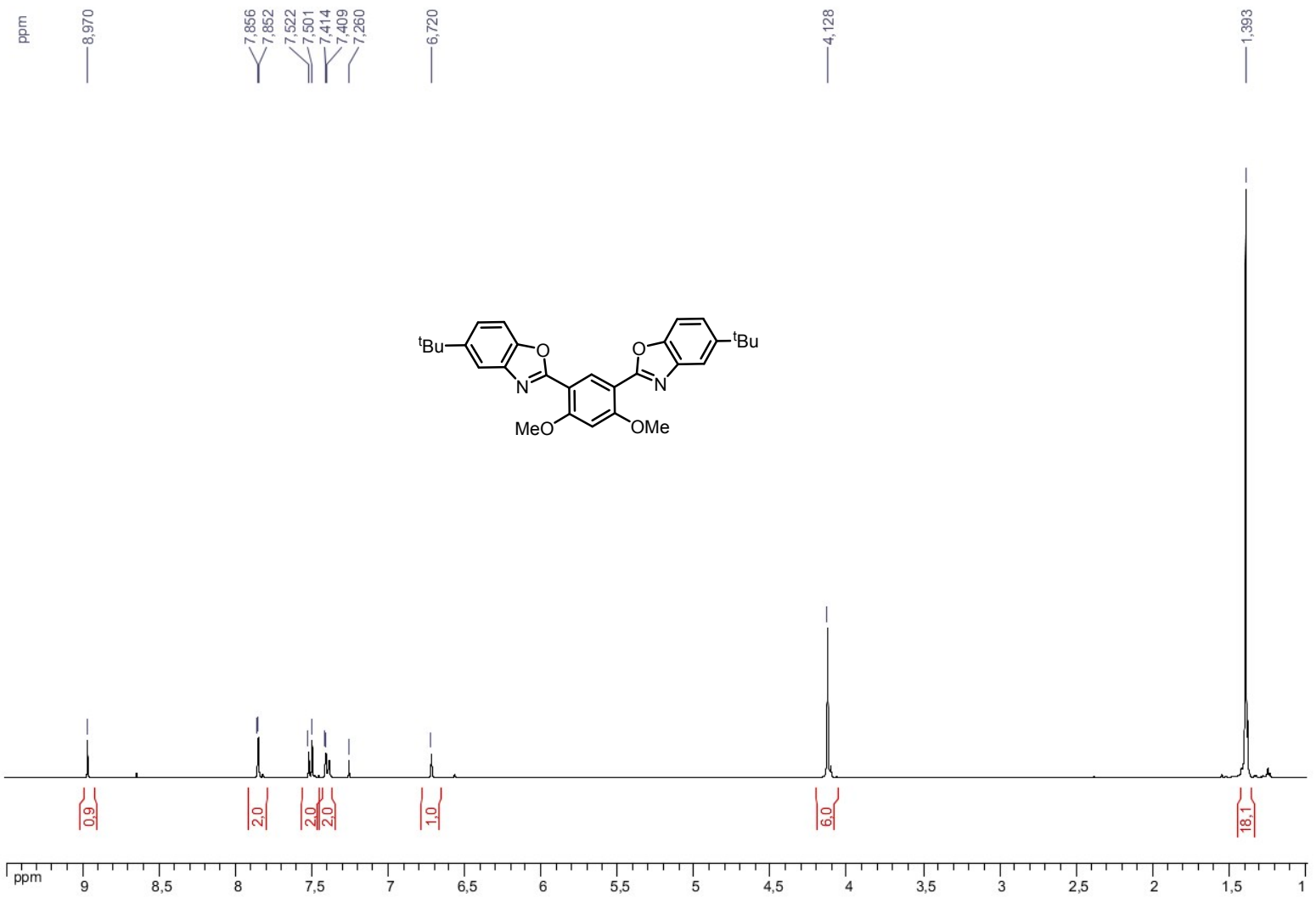
58%. $^1$H NMR (300 MHz, $CDCl_3$) δ (ppm) = 7.65 (s, 2H), 7.62 (d, 2H, $^3J_{2\text{-}1}$ = 8.9 Hz), 7.51 (d, 2H, $^3J_{1\text{-}2}$ = 8.7 Hz, $^4J_{1\text{-}3}$ = 1.8 Hz), 7.44-7.40 (m, 8H, CH Ar), 7.27-7.23 (m, 12H, CH Ar), 6.89 (d, 2H, $^4J_{3\text{-}1}$ = 1.8 Hz), 1.43 (s, 18H, $^t$Bu). $^{13}$C NMR (75 MHz, $CDCl_3$) δ (ppm) = 160.1, 154.3, 151.2, 147.8, 134.8, 133.3, 133.3, 128.1, 127.5, 127.0, 125.2, 116.4, 116.1, 114.9, 111.0, 35.3, 31.4, 27.1. HRMS (ESI) Calcd. for $C_{52}H_{46}B_2K_1N_2O_4$: 823.3292 (M + K), found: 823.3278 (M + K).



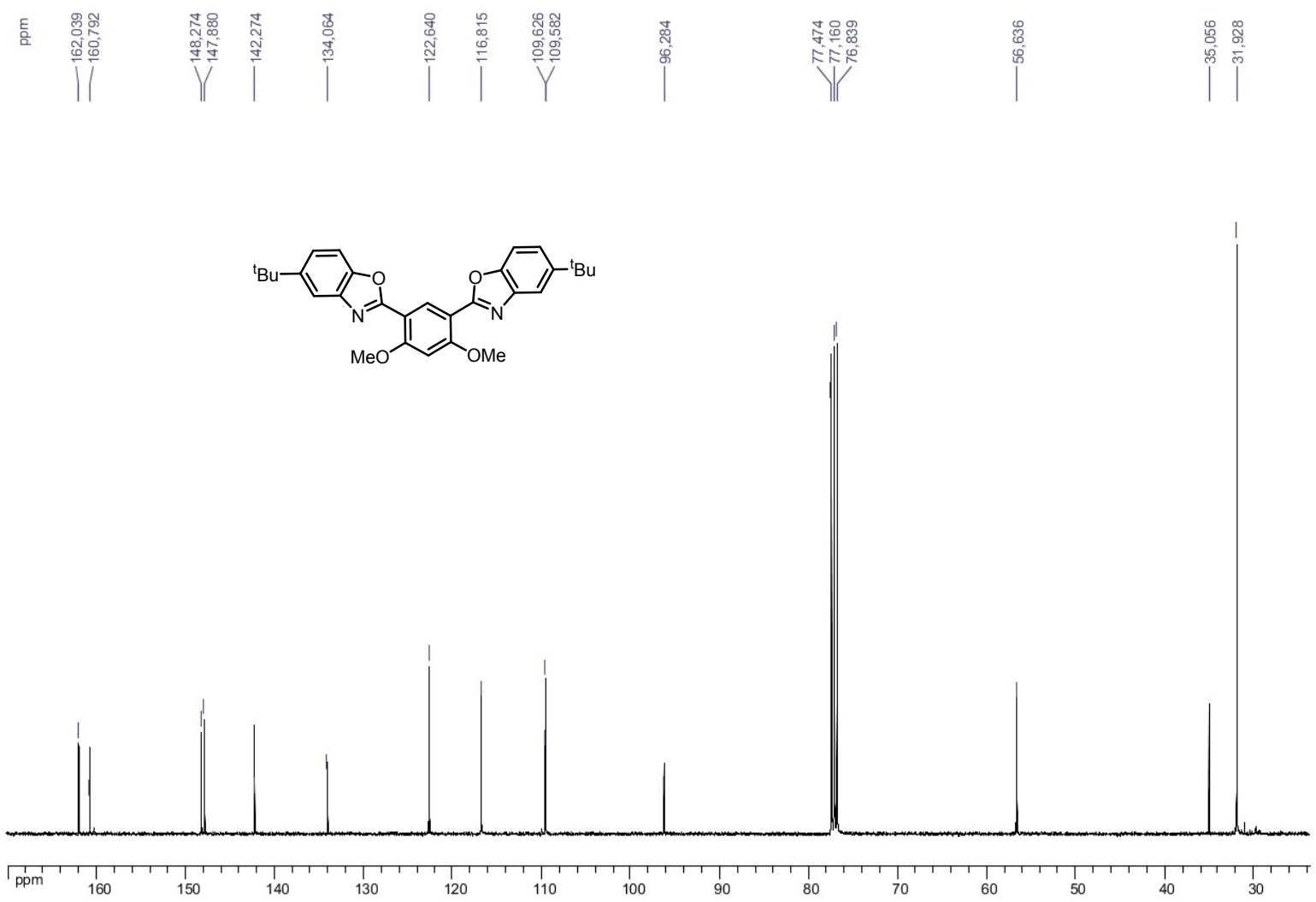

RMN $^{1}H$ ($CDCl_3$, 300MHz) **1**



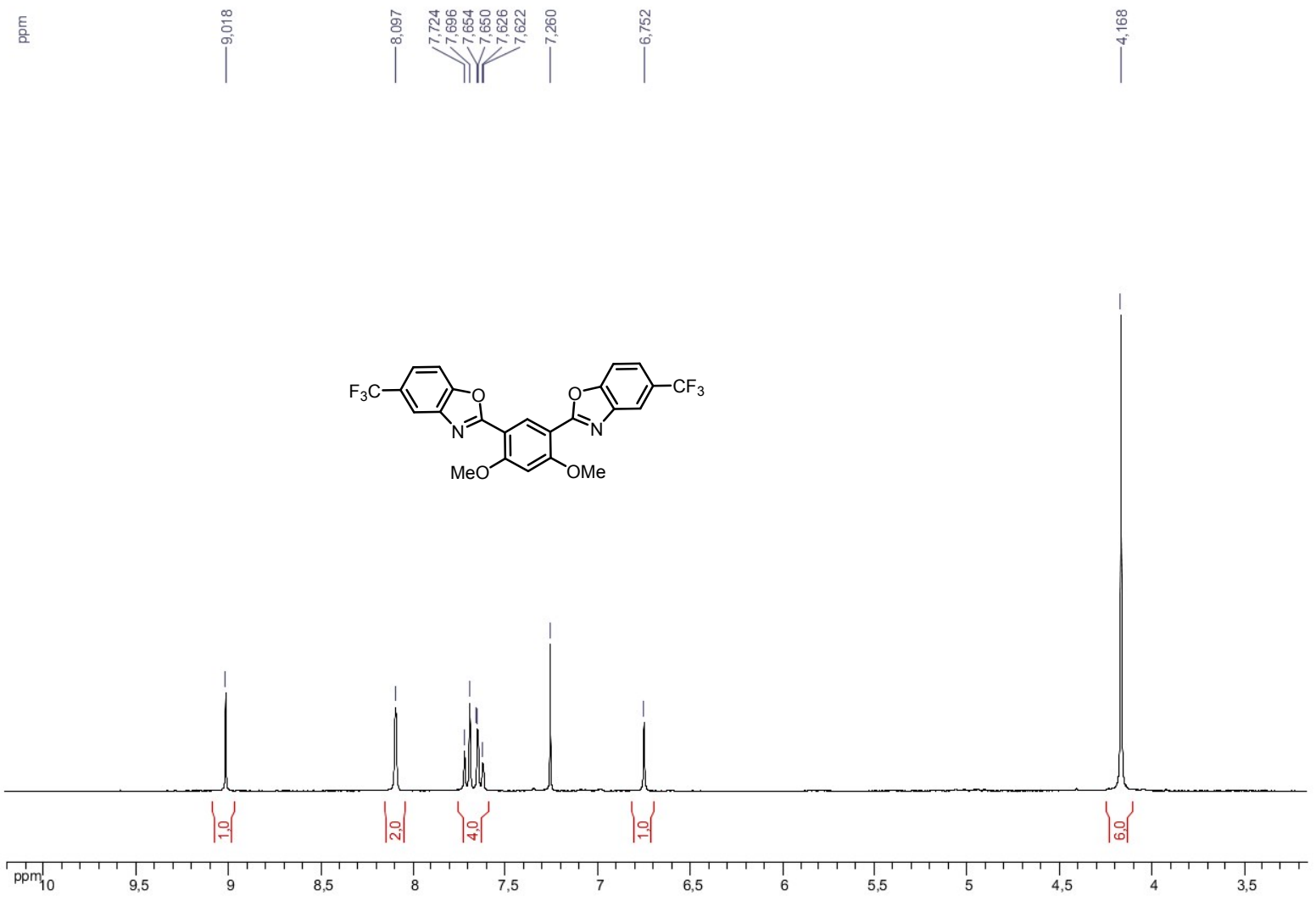

RMN $^{13}C$ ($CDCl_3$, 75MHz) **1**



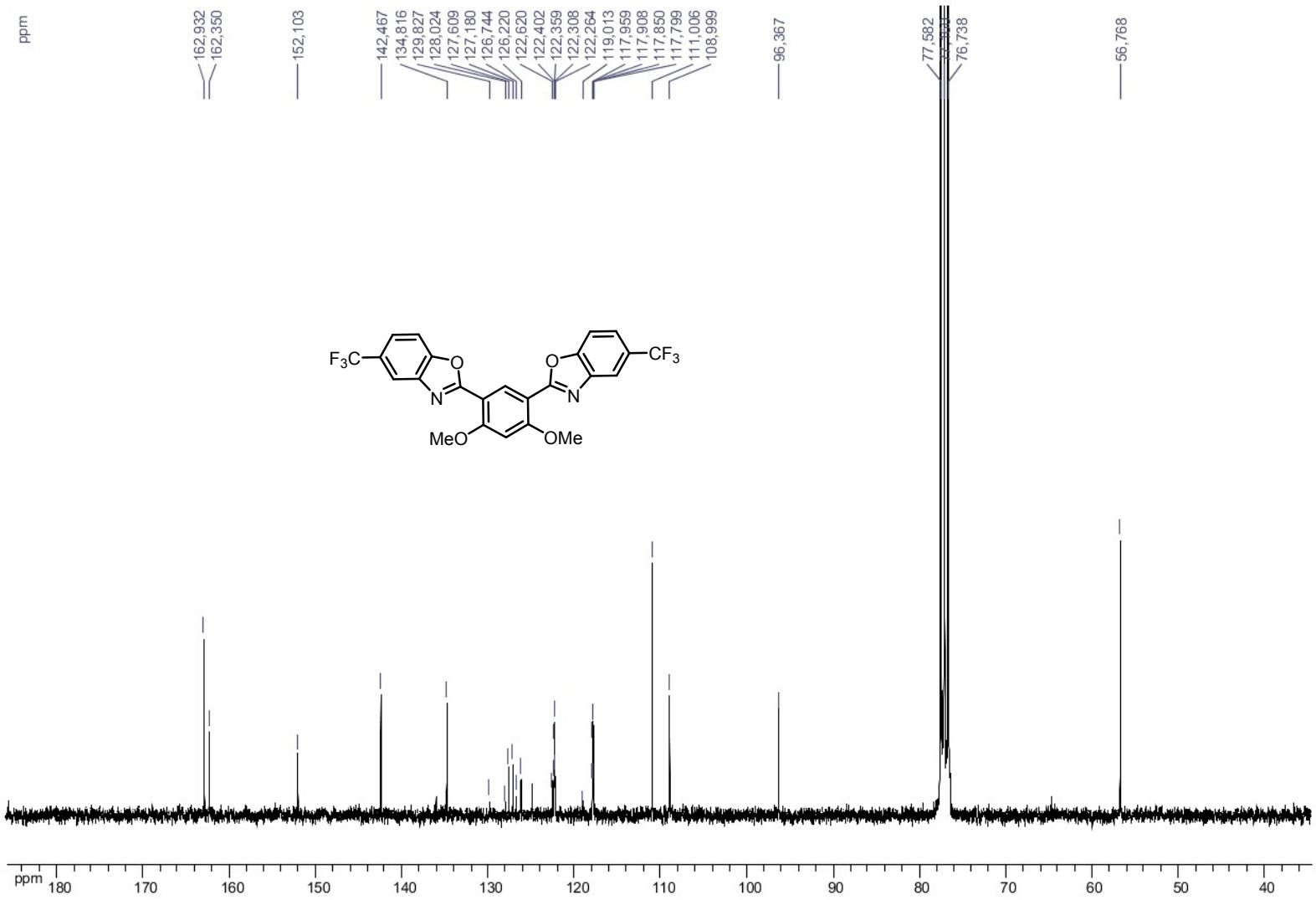

RMN $^{1}H$ ($CDCl_3$, 300MHz) **2**



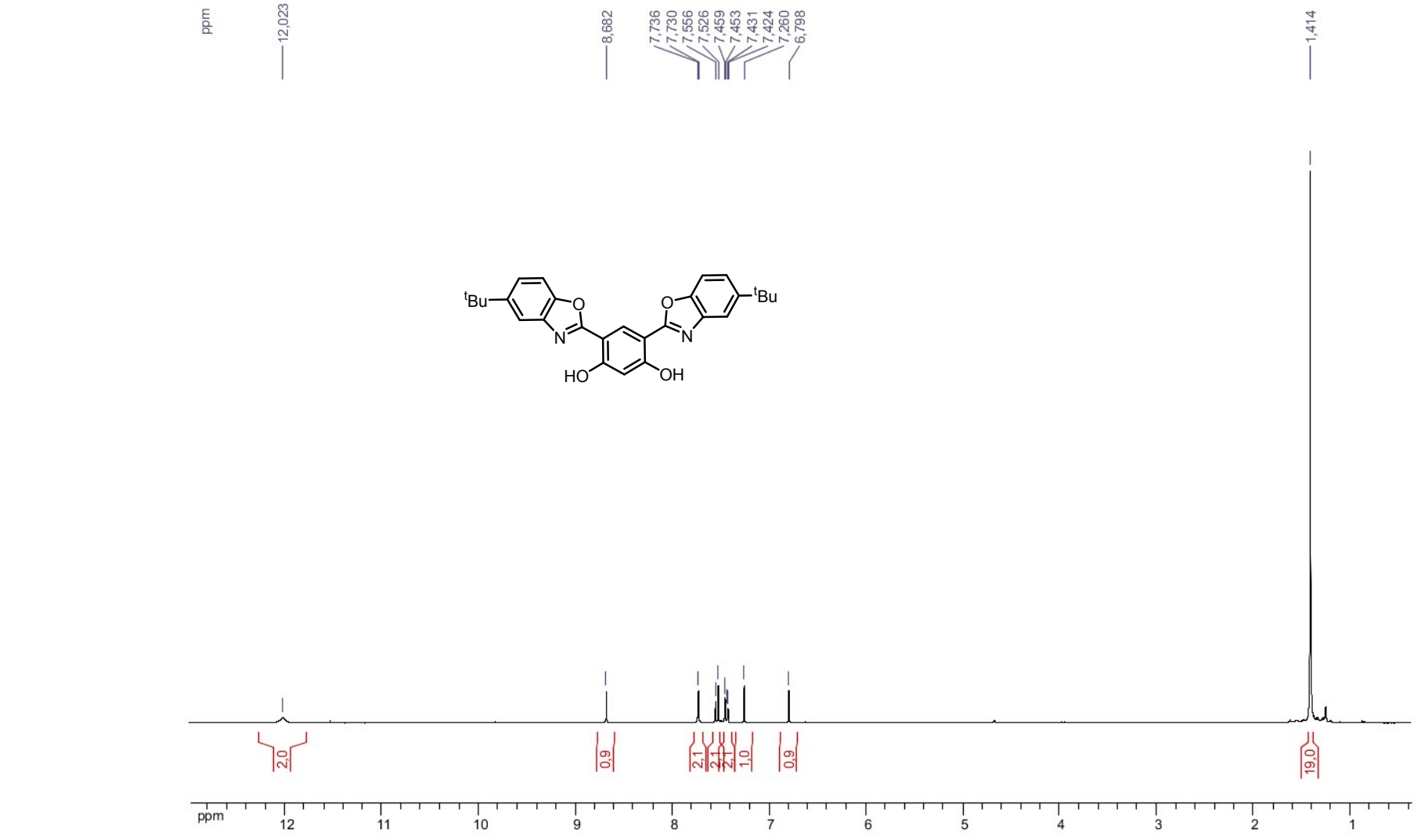

RMN $^{13}C$ ($CDCl_3$, 75MHz) **2**



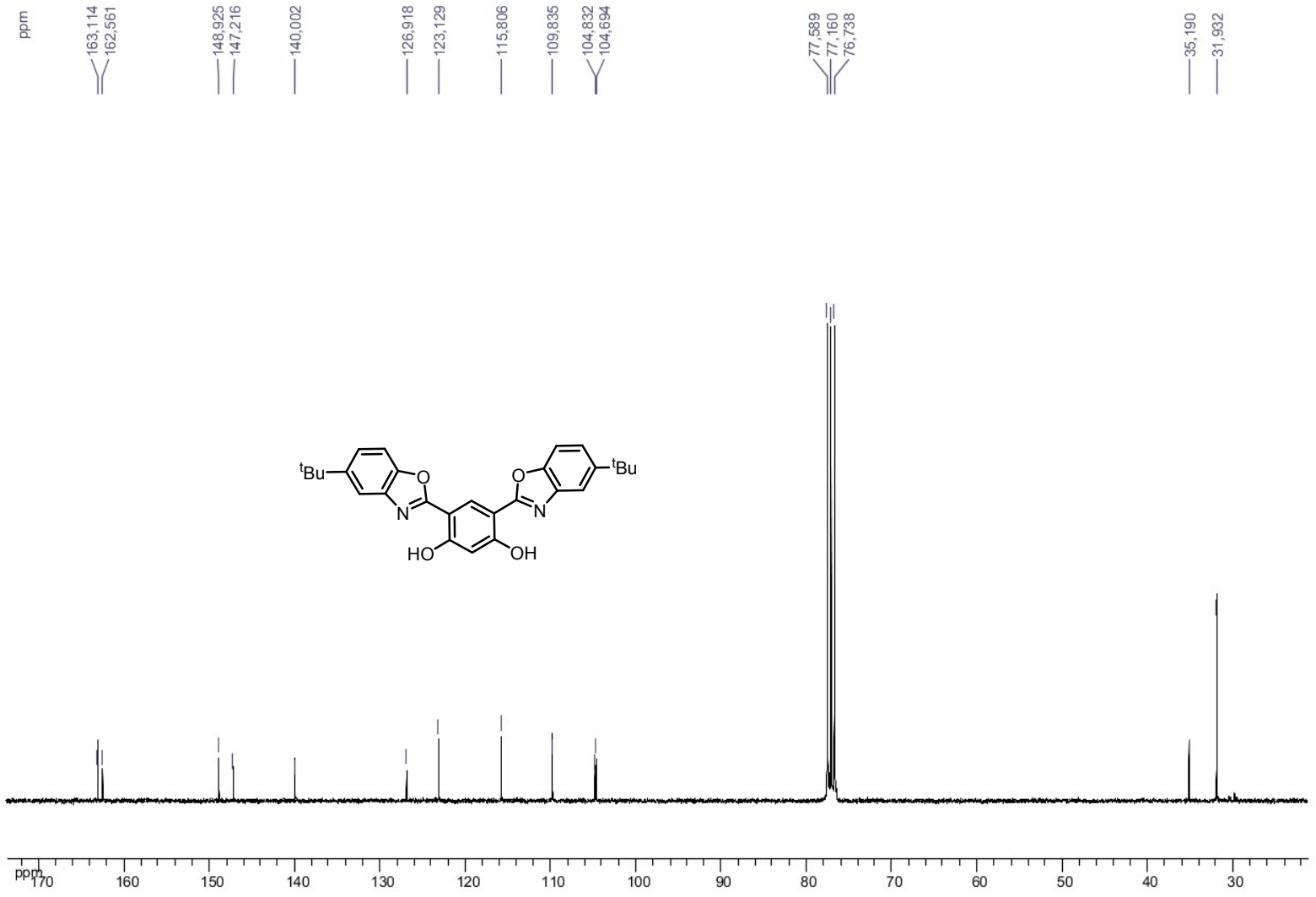

RMN $^{1}H$ ($CDCl_3$, 300MHz) **3**



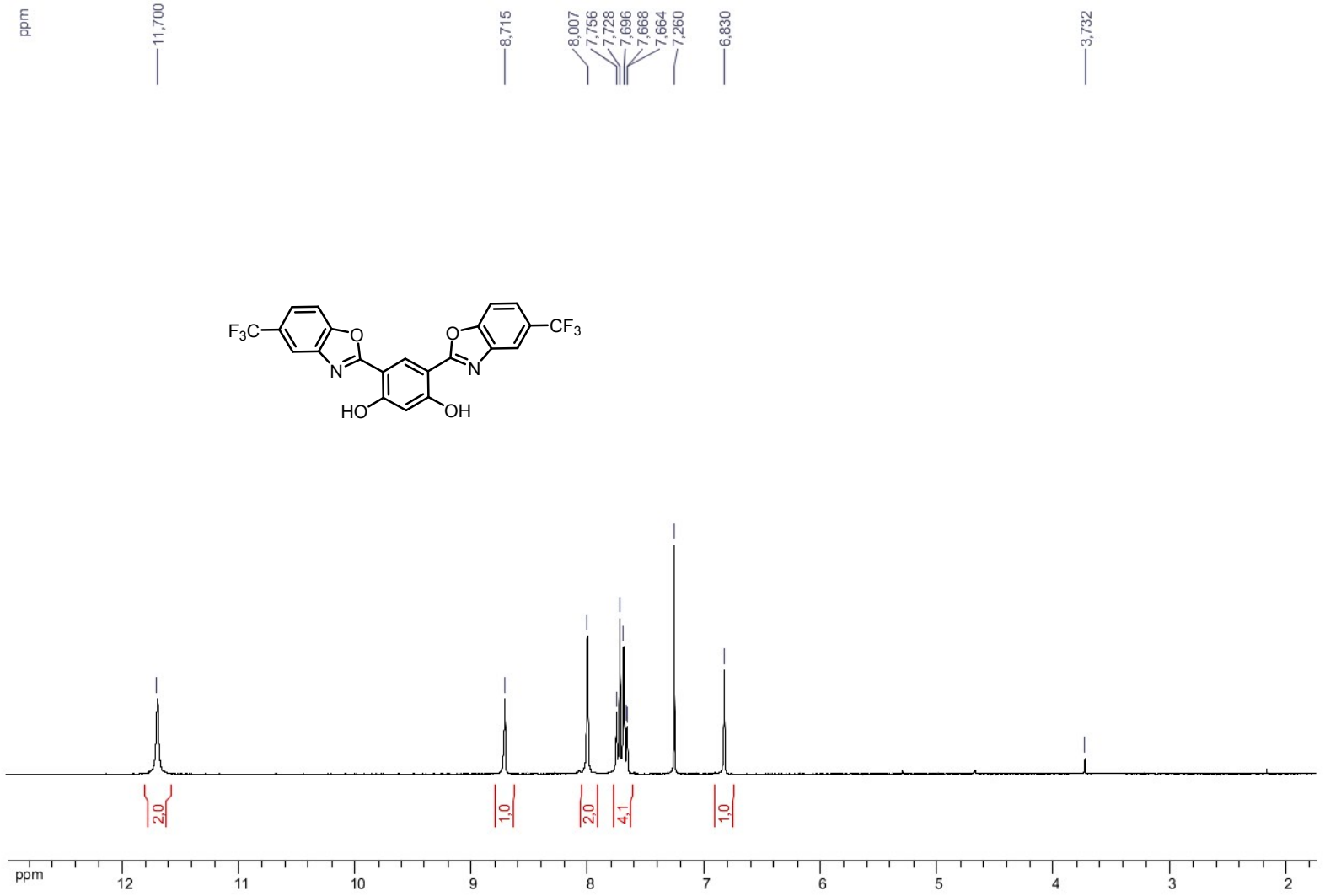

RMN $^{13}C$ ($CDCl_3$, 75MHz) **3**



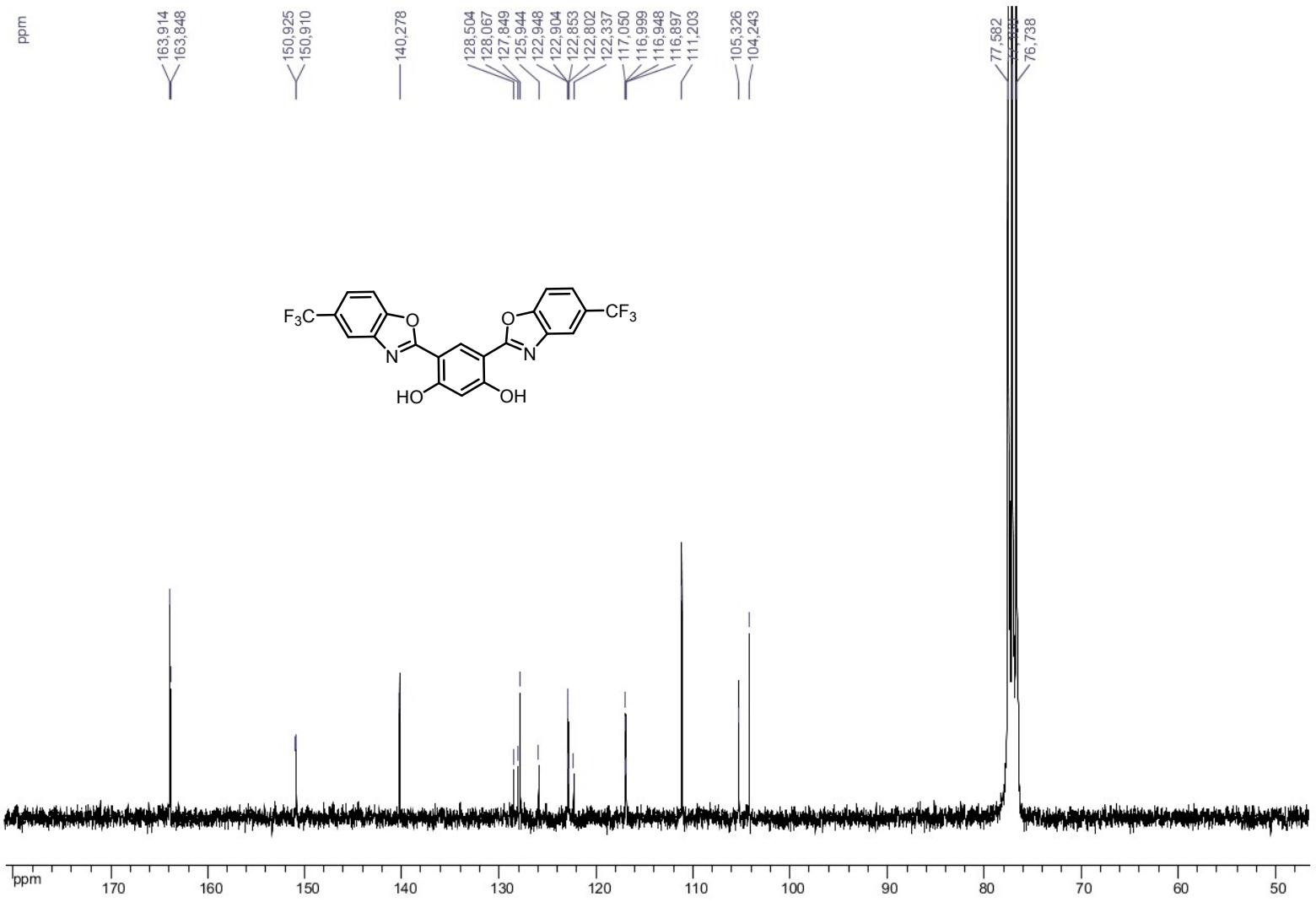

RMN $^{1}H$ ($CDCl_3$, 300MHz) **4**



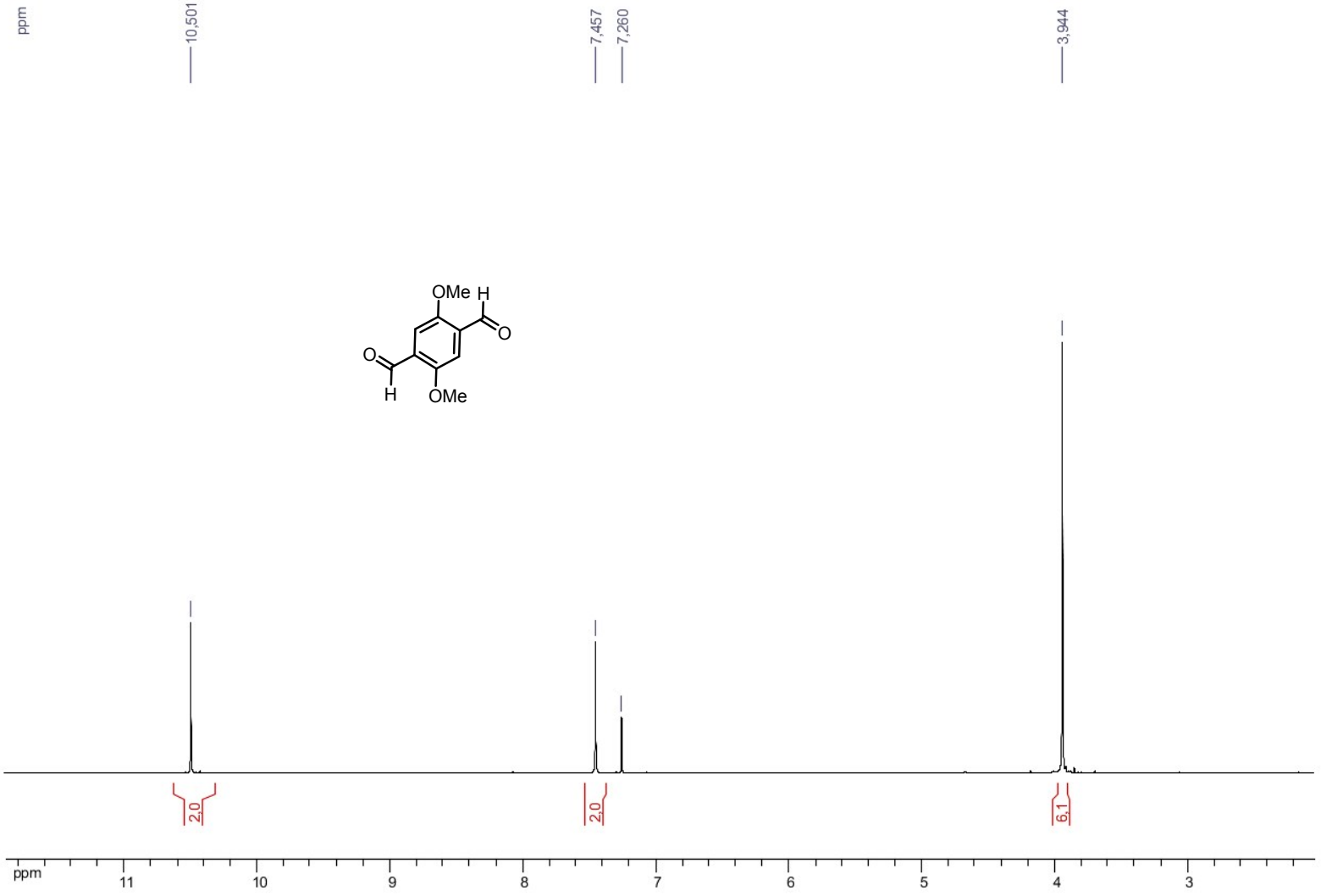

RMN $^{13}C$ ($CDCl_3$, 75MHz) **4**



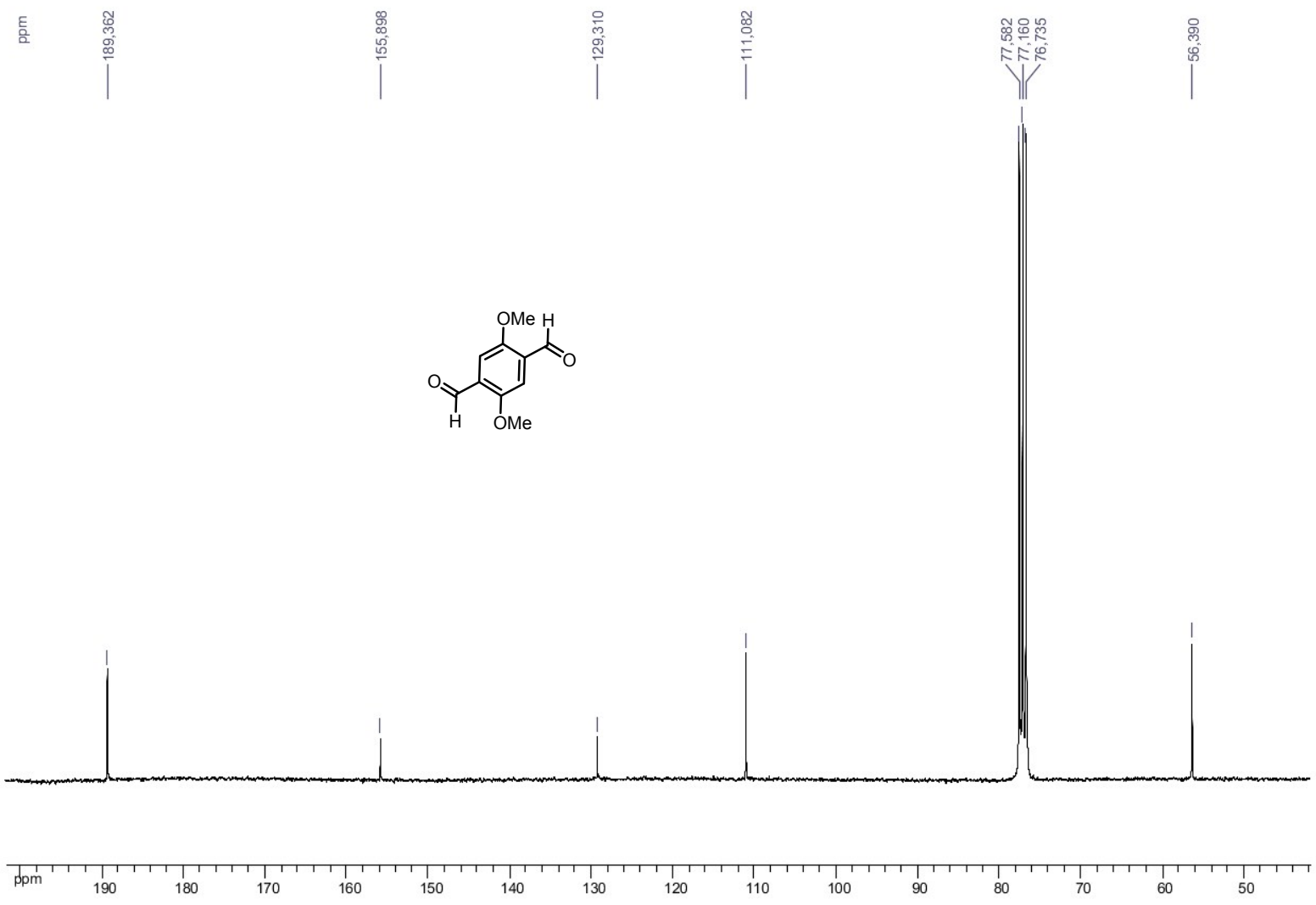

RMN $^{1}H$ ($CDCl_3$, 300MHz) **5**



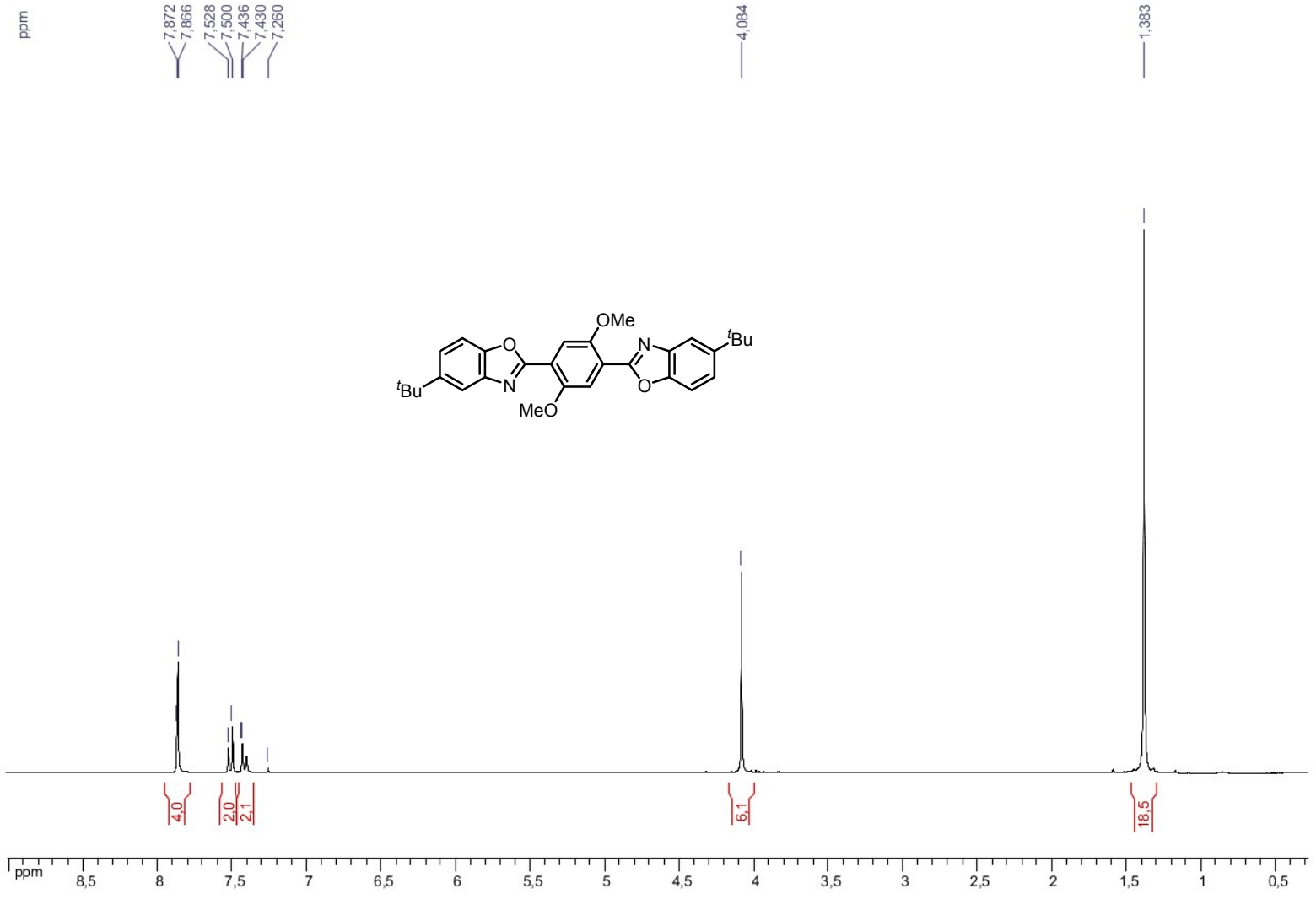

RMN $^{13}C$ ($CDCl_3$, 75MHz) **5**



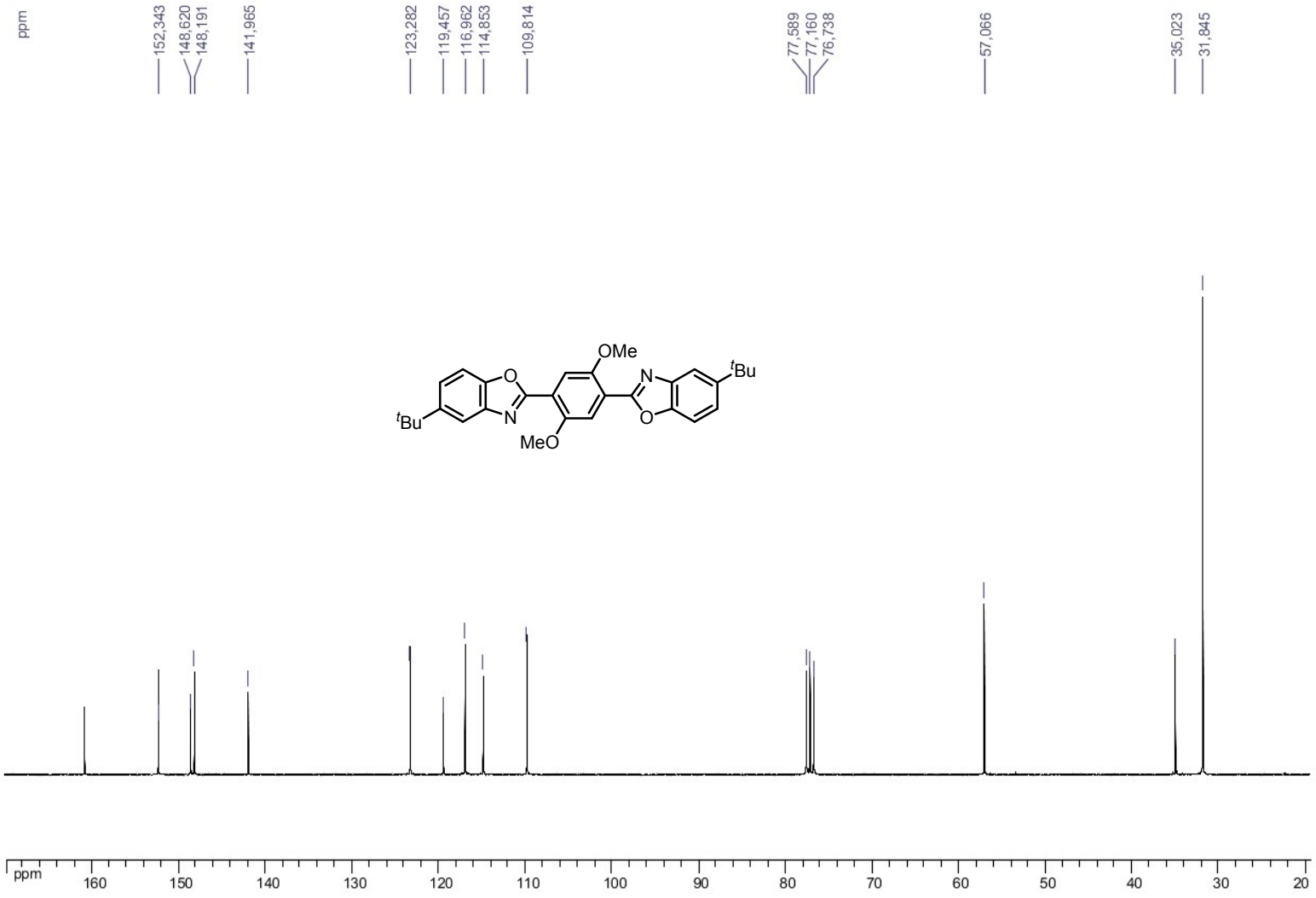

RMN $^{1}H$ ($CDCl_3$, 300MHz) **6**



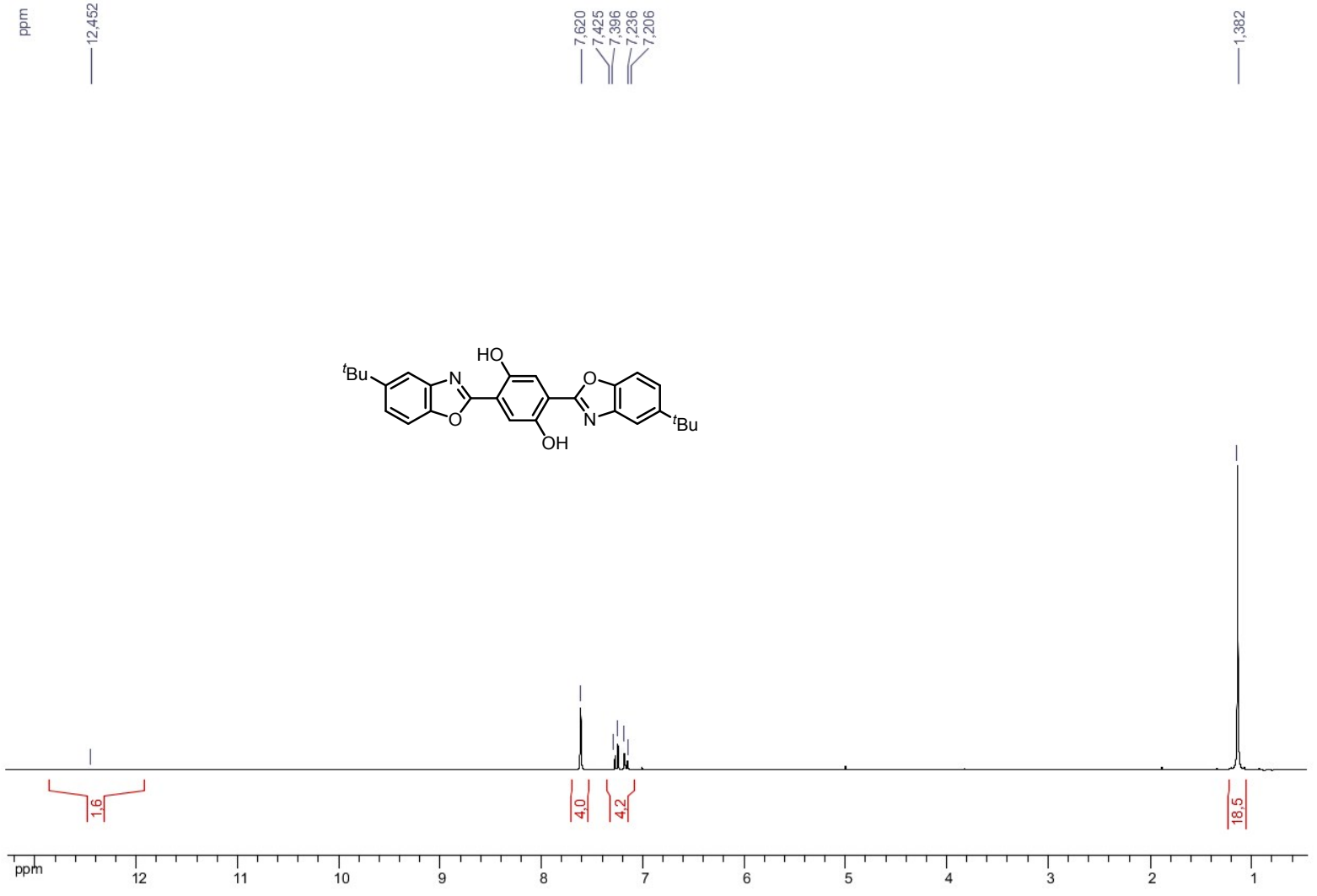

RMN $^{13}C$ ($CDCl_3$, 75MHz) **6**



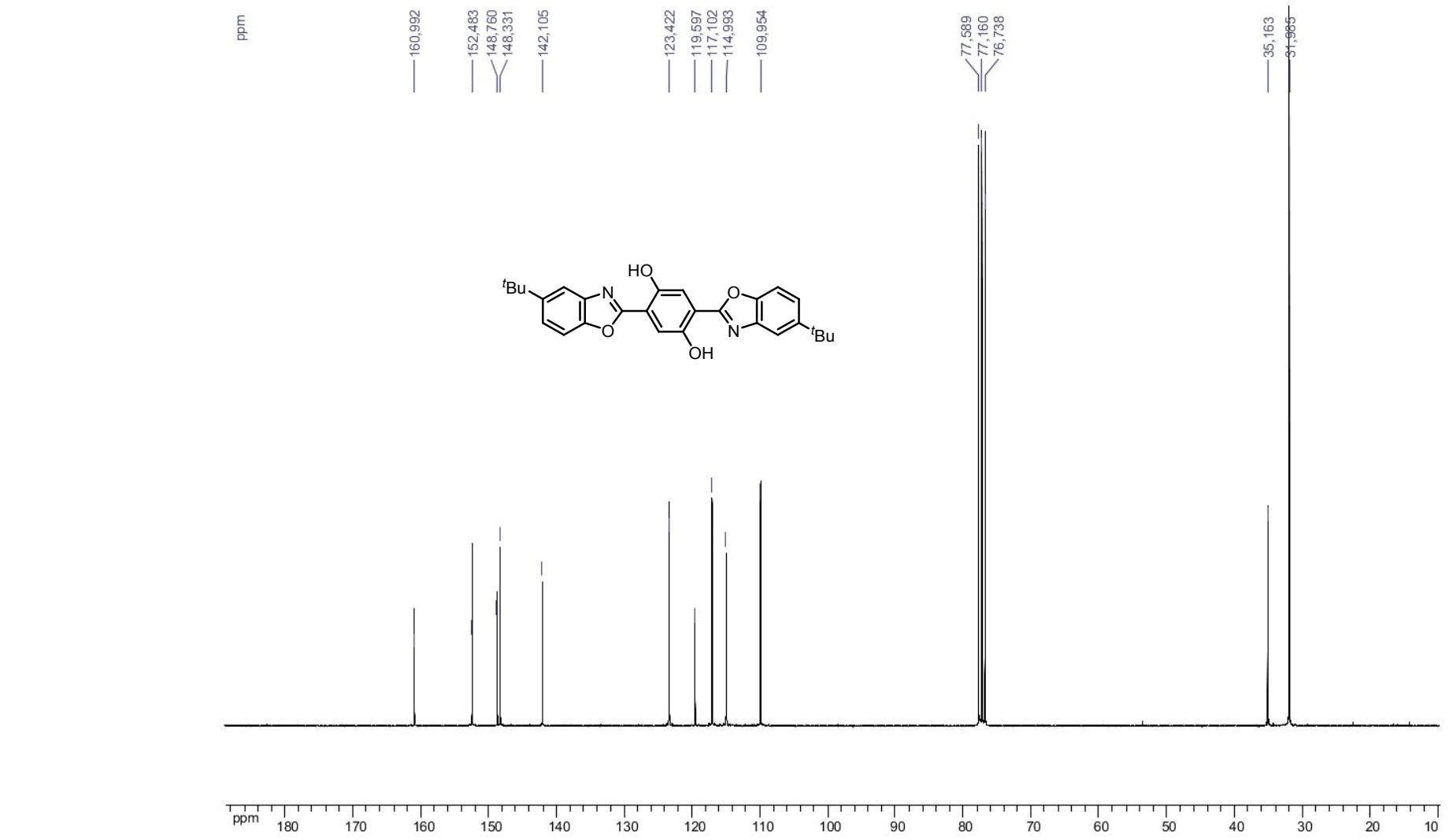

RMN $^{1}H$ ($CDCl_3$, 300MHz) **7**



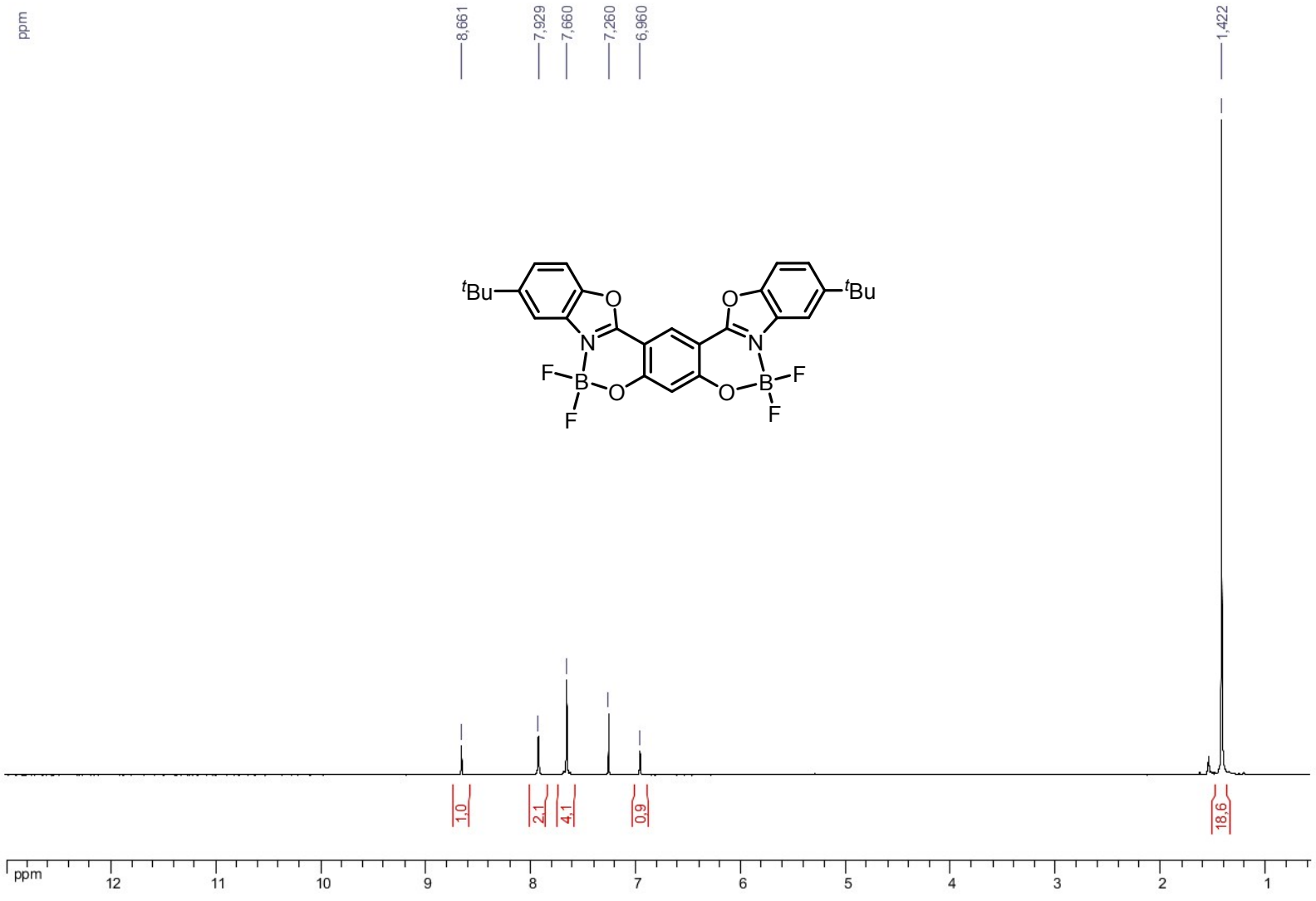

RMN $^{13}C$ ($CDCl_3$, 75MHz) **7**



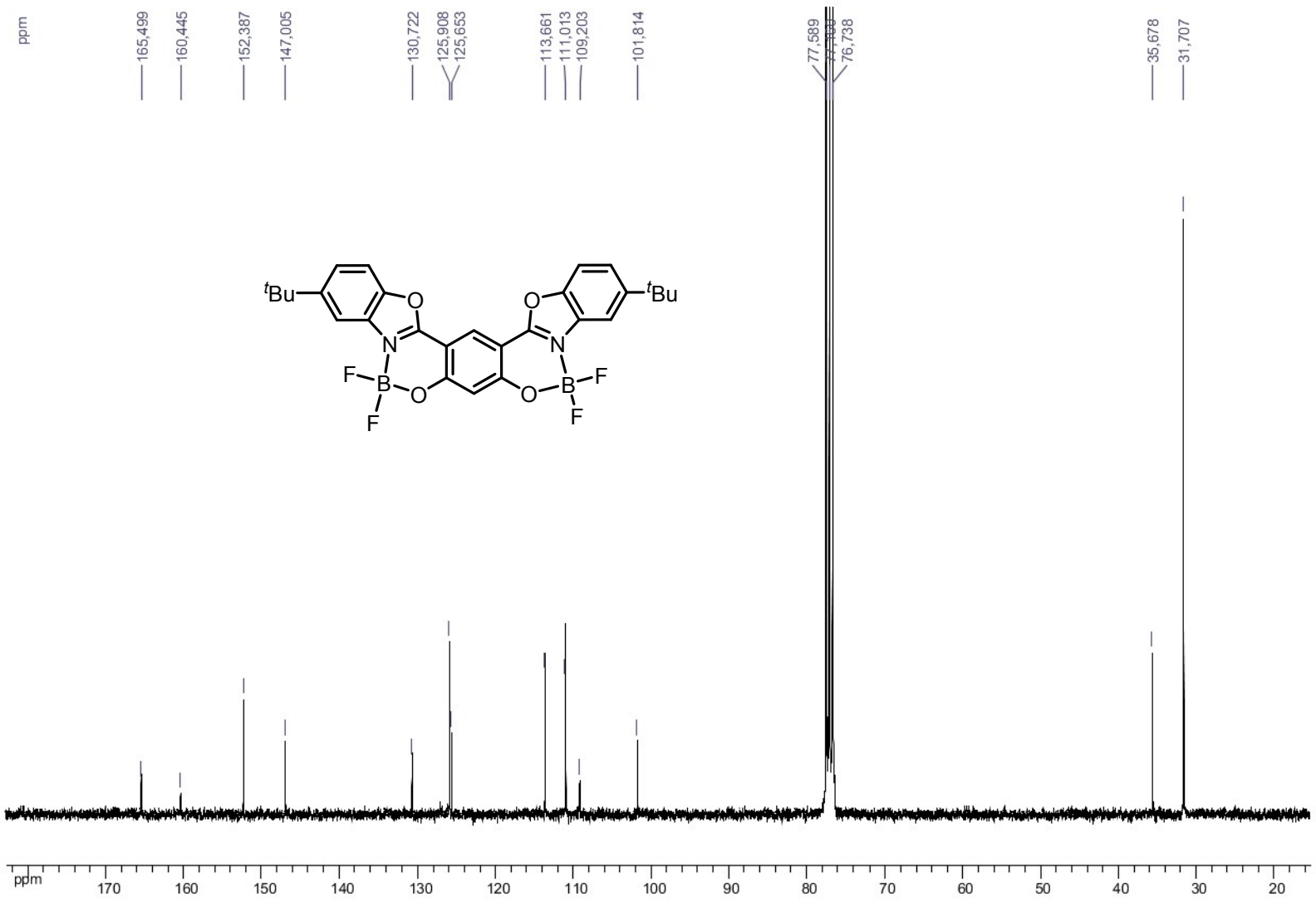

RMN $^{1}H$ ($CDCl_3$, 300MHz) **8**



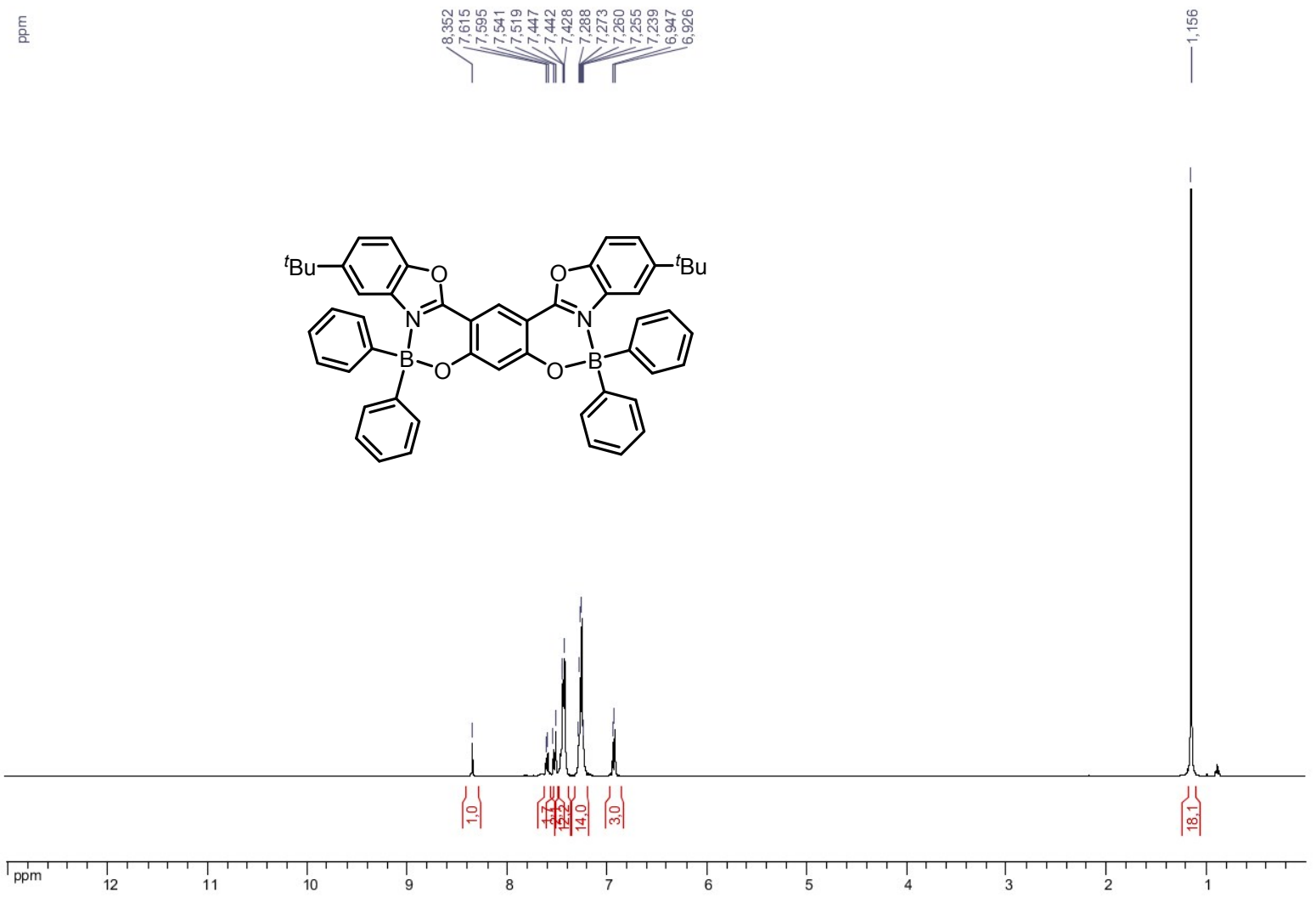

RMN $^{13}C$ ($CDCl_3$, 75MHz) **8**



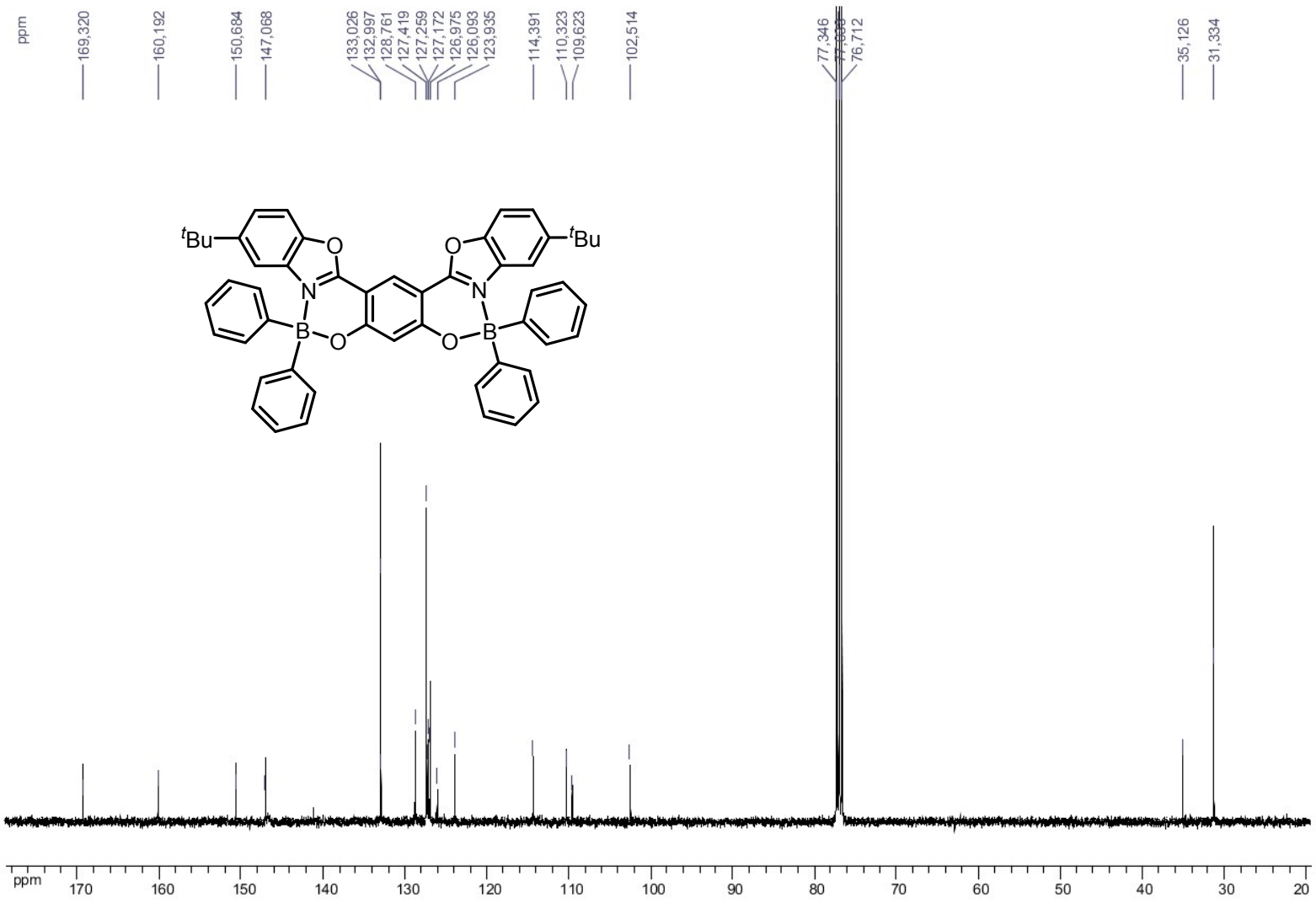

RMN $^{1}H$ ($CDCl_3$, 300MHz) **9**



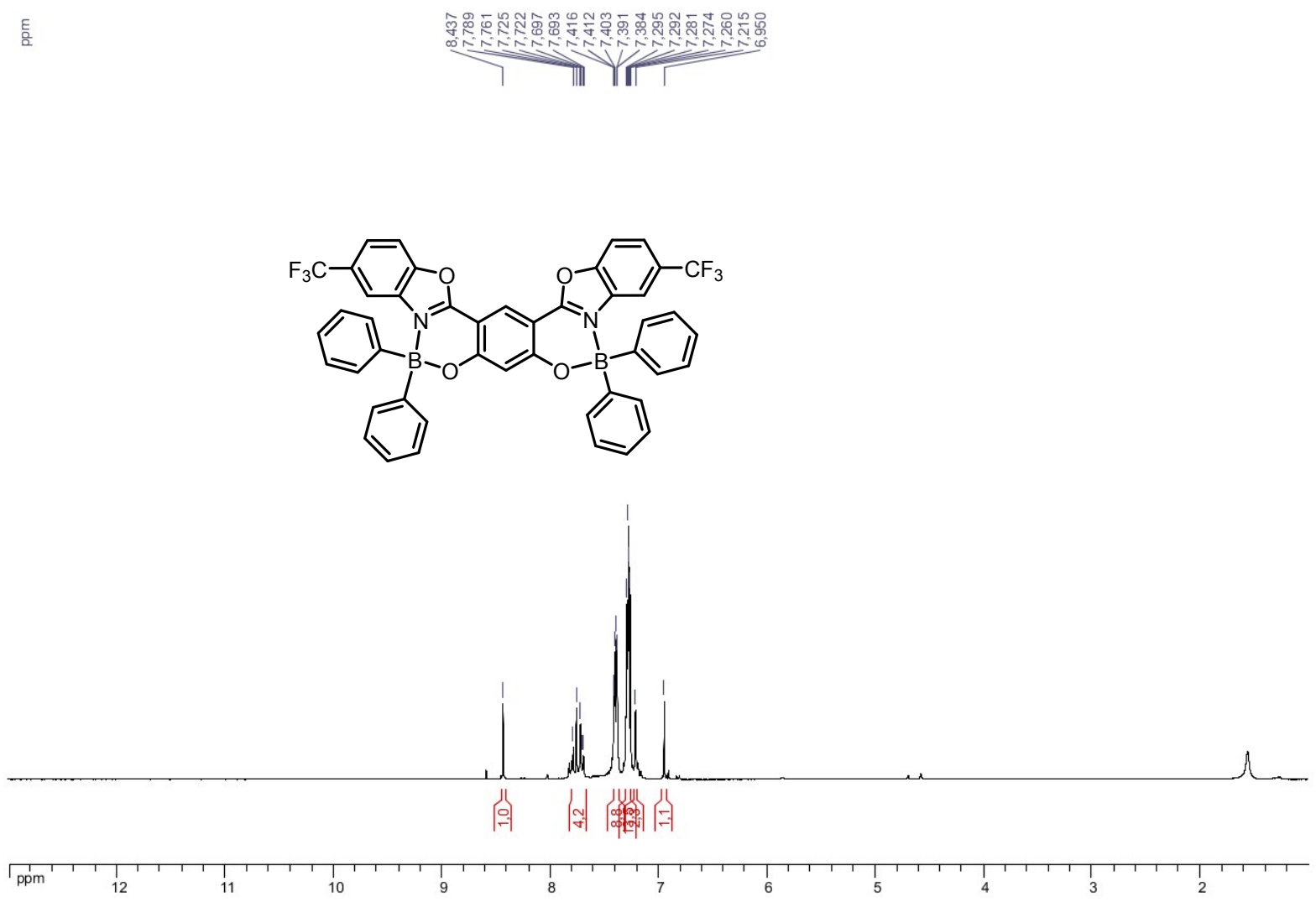

RMN $^{13}C$ ($CDCl_3$, 75MHz) **9**



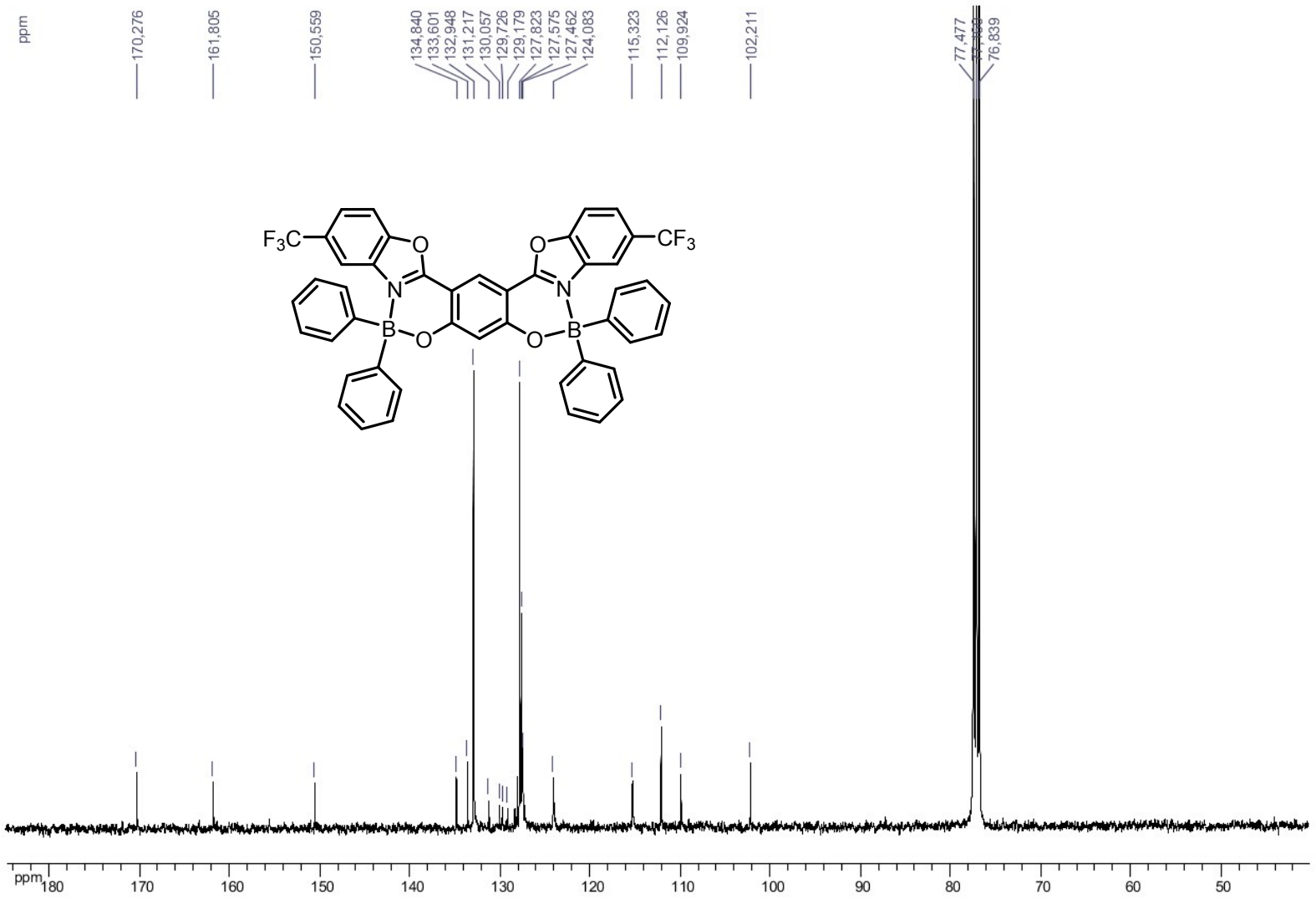

RMN $^{1}H$ ($CDCl_3$, 400MHz) **10**



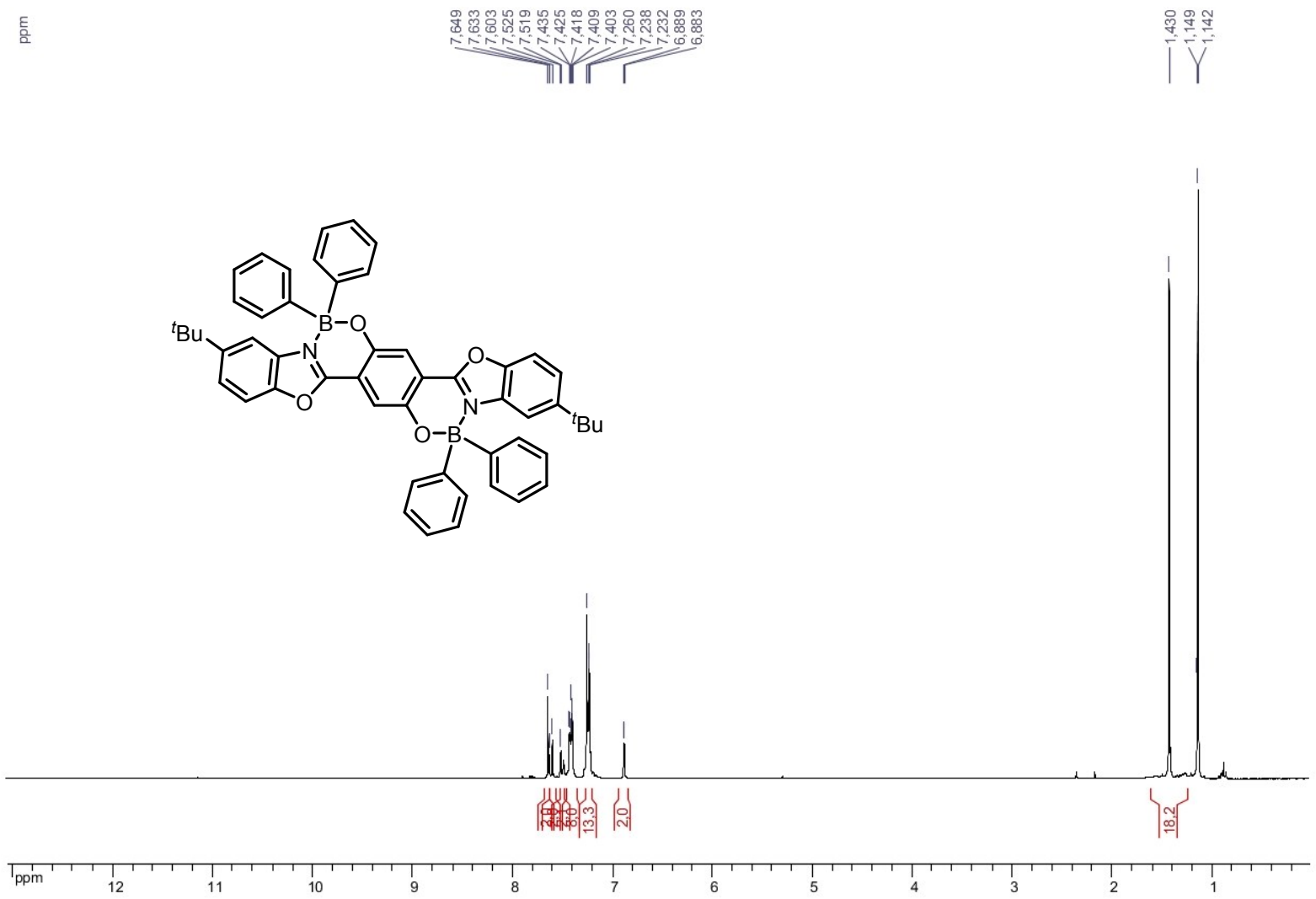

RMN $^{13}C$ ($CDCl_3$, 100MHz) **10**



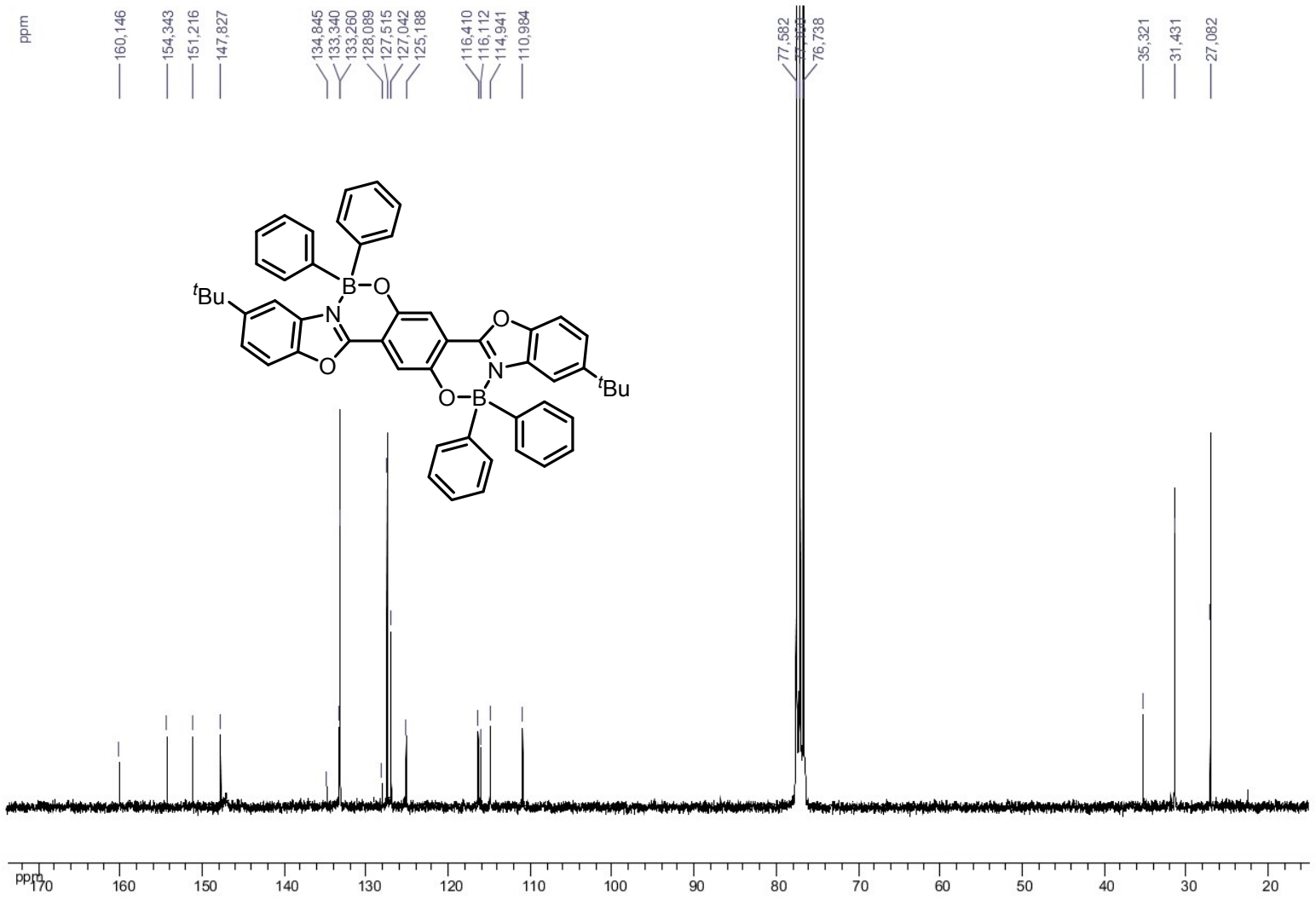

RMN $^{1}H$ ($CDCl_3$, 300MHz) **11**




RMN $^{13}C$ ($CDCl_3$, 100MHz) **11**




RMN $^{1}H$ ($CDCl_3$, 300MHz) **12**




RMN $^{13}C$ ($CDCl_3$, 100MHz) **12**

S4 Spectroscopic data

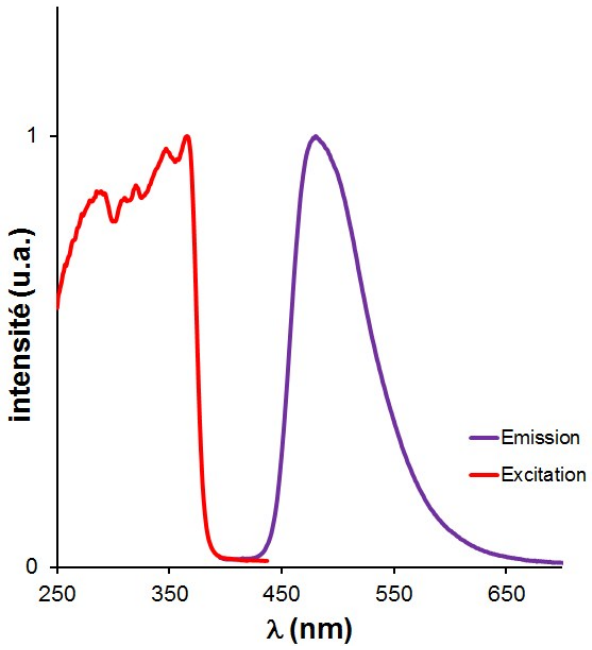



**Fig S4.1** Excitation (red) and emission (blue) of DHBO dye **4** in the solid-state (KBr pellet)

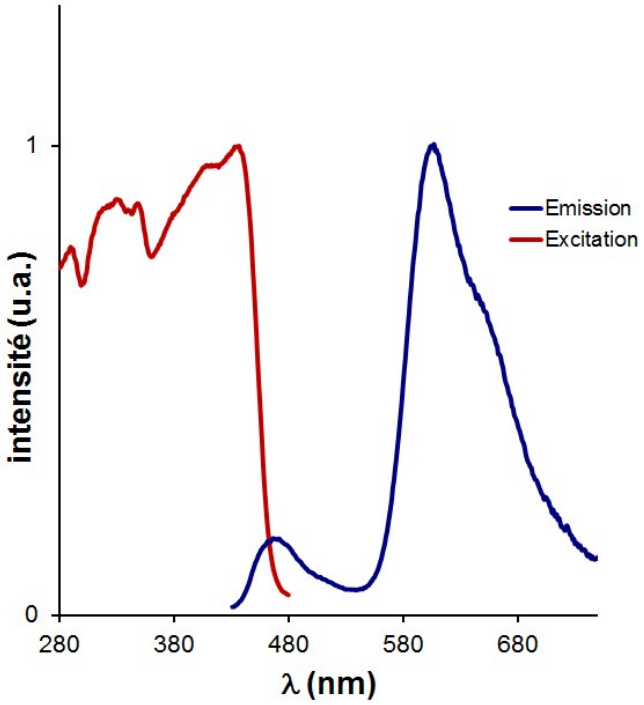



**Fig S4.2** Excitation (red) and emission (blue) of DHBO dye **8** in the solid-state (KBr pellet)

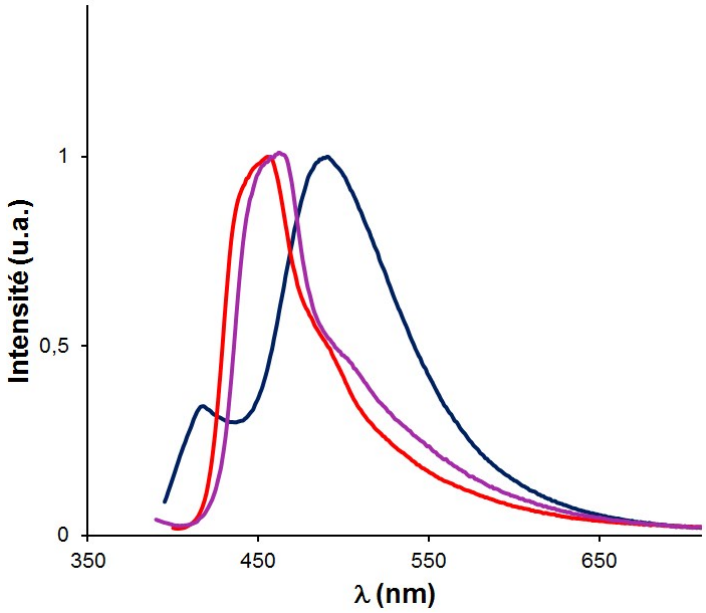
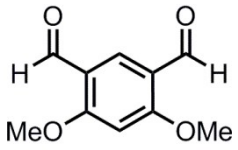



**Fig S4.3** Emission of DHBO dyes **9** (red) , **10** (purple) and **11** (blue) in the solid-state (KBr pellet)

# Mass Spectrum Molecular Formula Report

**Analysis Info**

| | |
|---|---|
| Analysis Name | D:\Data\Service masse 2015\O37735SK.d |
| Method | esi low pos.m |
| Sample Name | KB379 |
| Comment | |

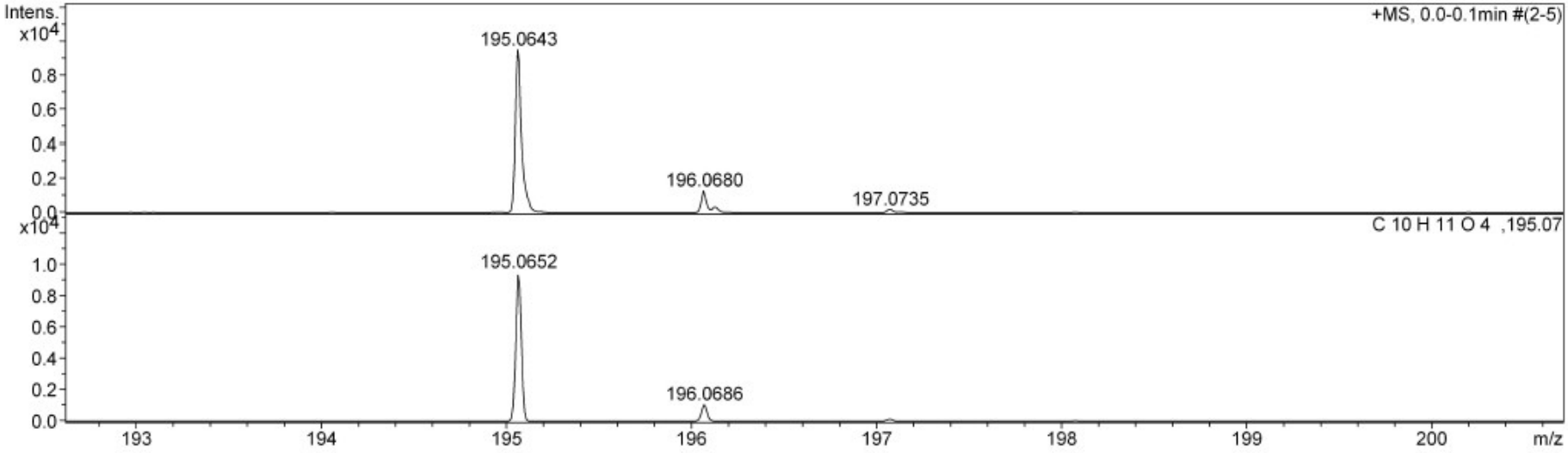



**1**

| | |
|---|---|
| Acquisition Date | 11/19/2015 9:07:26 AM |
| Operator | Administrator |
| Instrument | micrOTOF 66 |

**Acquisition Parameter**

| | | | | | |
|---|---|---|---|---|---|
| Source Type | ESI | Ion Polarity | Positive | Set Corrector Fill | 65 V |
| Scan Range | n/a | Capillary Exit | 80.0 V | Set Pulsar Pull | 817 V |
| Scan Begin | 50 m/z | Hexapole RF | 60.0 V | Set Pulsar Push | 817 V |
| Scan End | 3000 m/z | Skimmer 1 | 50.0 V | Set Reflector | 1700 V |
| | | Hexapole 1 | 24.3 V | Set Flight Tube | 8600 V |
| | | | | Set Detector TOF | 2275 V |

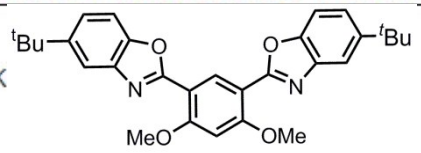



| Sum Formula | Sigma | m/z | Err [ppm] | Mean Err [ppm] | rdb | N Rule | e⁻ |
|---|---|---|---|---|---|---|---|
| C 10 H 11 O 4 | 0.01 | 195.0652 | 4.69 | 4.38 | 5.50 | ok | even |

# Mass Spectrum Molecular Formula Report

**Analysis Info**

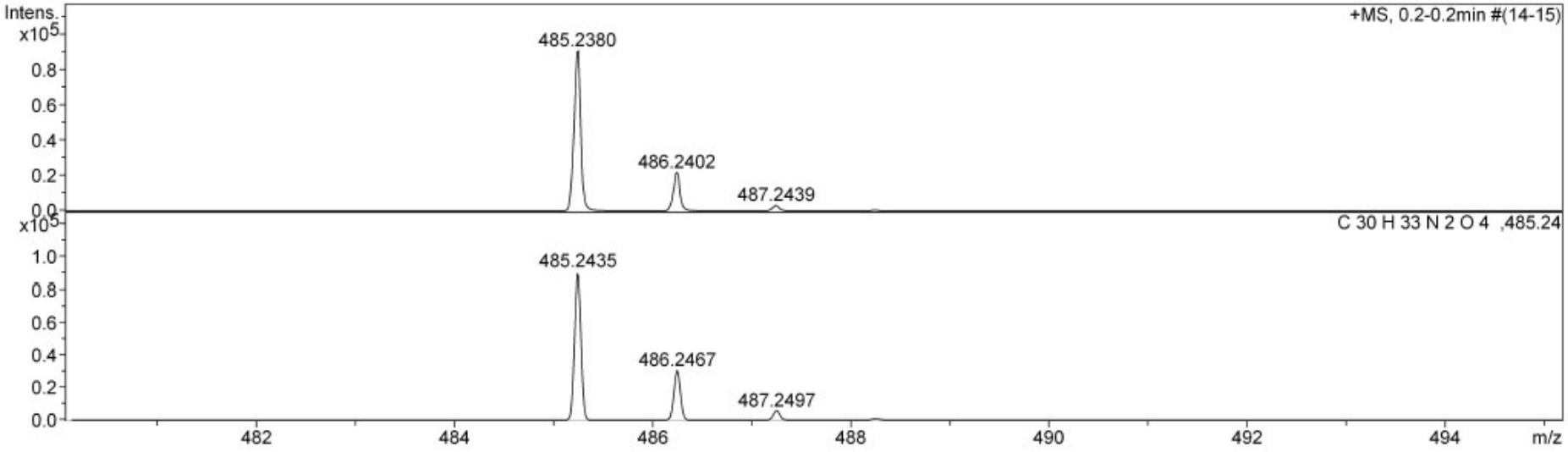
| | | | |
|---|---|---|---|
| Analysis Name | D:\Data\Service masse 2015\O37886SK | Acquisition Date | 11/27/2015 4:25:49 PM |
| Method | esi low pos.m | Operator | Administrator |
| Sample Name | KB377 | Instrument | micrOTOF 66 |
| Comment | | | |




**2**

**Acquisition Parameter**

| | | | | | |
|---|---|---|---|---|---|
| Source Type | ESI | Ion Polarity | Positive | Set Corrector Fill | 74 V |
| Scan Range | n/a | Capillary Exit | 80.0 V | Set Pulsar Pull | 817 V |
| Scan Begin | 50 m/z | Hexapole RF | 60.0 V | Set Pulsar Push | 810 V |
| Scan End | 3000 m/z | Skimmer 1 | 50.0 V | Set Reflector | 1700 V |
| | | Hexapole 1 | 24.3 V | Set Flight Tube | 8600 V |
| | | | | Set Detector TOF | 2275 V |

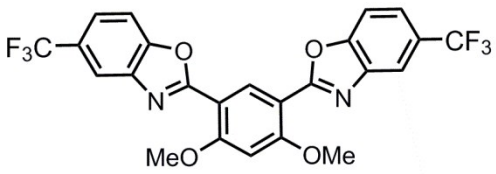



| Sum Formula | Sigma | m/z | Err [ppm] | Mean Err [ppm] | rdb | N Rule | e⁻ |
|---|---|---|---|---|---|---|---|
| C 30 H 33 N 2 O 4 | 0.05 | 485.2435 | 11.39 | 11.90 | 15.50 | ok | even |
| C 30 H 32 N 2 O 4 | 0.61 | 484.2357 | 1.96 | 2.27 | 16.00 | - | odd |
| C 30 H 31 N 2 O 4 | 0.71 | 483.2278 | -8.08 | -8.26 | 16.50 | ok | even |

# Mass Spectrum Molecular Formula Report

**Analysis Info**

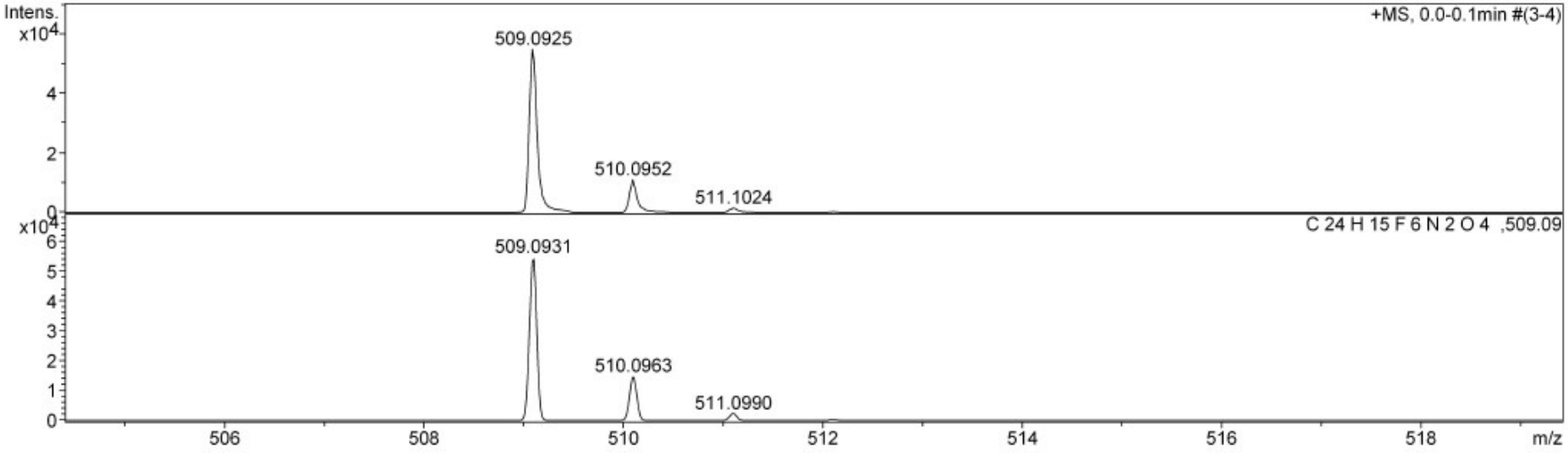
| | | | |
|---|---|---|---|
| Analysis Name | D:\Data\Service masse 2015\O | Acquisition Date | 11/19/2015 9:37:04 AM |
| Method | esi low pos.m | Operator | Administrator |
| Sample Name | KB383 | Instrument | micrOTOF 66 |
| Comment | | | |




**3**

**Acquisition Parameter**

| | | | | | |
|---|---|---|---|---|---|
| Source Type | ESI | Ion Polarity | Positive | Set Corrector Fill | 65 V |
| Scan Range | n/a | Capillary Exit | 80.0 V | Set Pulsar Pull | 817 V |
| Scan Begin | 50 m/z | Hexapole RF | 60.0 V | Set Pulsar Push | 817 V |
| Scan End | 3000 m/z | Skimmer 1 | 50.0 V | Set Reflector | 1700 V |
| | | Hexapole 1 | 24.3 V | Set Flight Tube | 8600 V |
| | | | | Set Detector TOF | 2275 V |

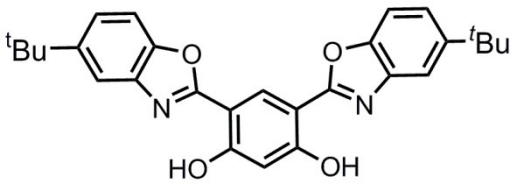



| Sum Formula | Sigma | m/z | Err [ppm] | Mean Err [ppm] | rdb | N Rule | e⁻ |
|---|---|---|---|---|---|---|---|
| C 24 H 15 F 6 N 2 O 4 | 0.04 | 509.0931 | 1.10 | 0.81 | 15.50 | ok | even |
| C 24 H 14 F 6 N 2 O 4 | 0.72 | 508.0852 | -7.97 | -8.14 | 16.00 | - | odd |

## Service de spectrometrie de masse - Institut de Chimie - Strasbourg - UMR 7177 CNRS / UDS

**Analysis Info**

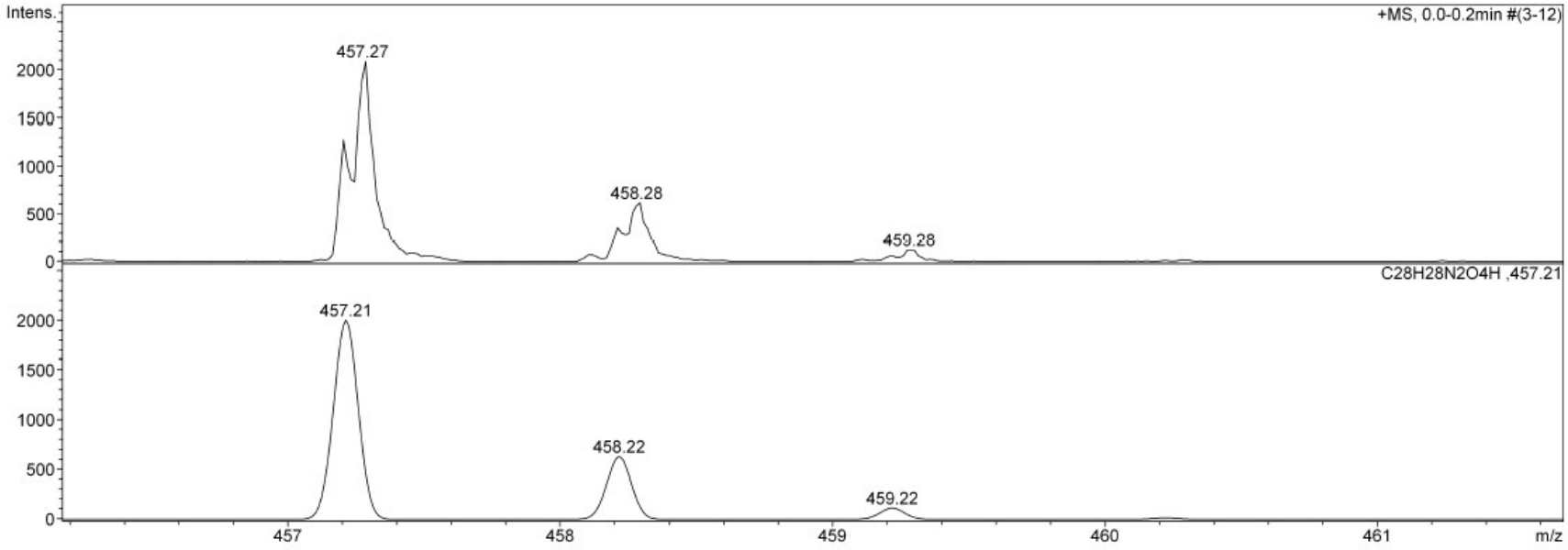
| | | | |
|---|---|---|---|
| Analysis Name | O37665SK.d | Acquisition Date | 10/29/2015 10:55:07 AM |
| Method | esi low pos.m | Operator | Administrator |
| Sample Name | KB382 | Instrument | micrOTOF |
| Comment | | | |




**4**

**Acquisition Parameter**

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| Source Type | ESI | Capillary | 4500 V | Nebulizer | 0.4 Bar | Corona | 219 nA |
| Ion Polarity | Positive | Set Capillary Exit | 80.0 V | Dry Gas | 4.0 l/min | Set Hexapole RF | 60.0 V |
| Scan Range | n/a | Set Skimmer 1 | 50.0 V | Dry Heater | 180 °C | APCI Heater | 514 °C |

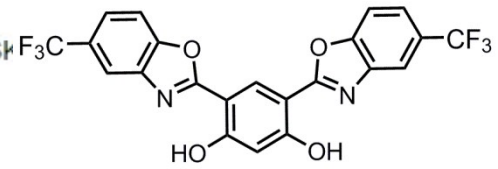



Bruker Daltonics DataAnalysis 3.1 printed: 11/16/2015 10:55:02 AM Page 1 of 1

# Mass Spectrum Molecular Formula Report

**Analysis Info**

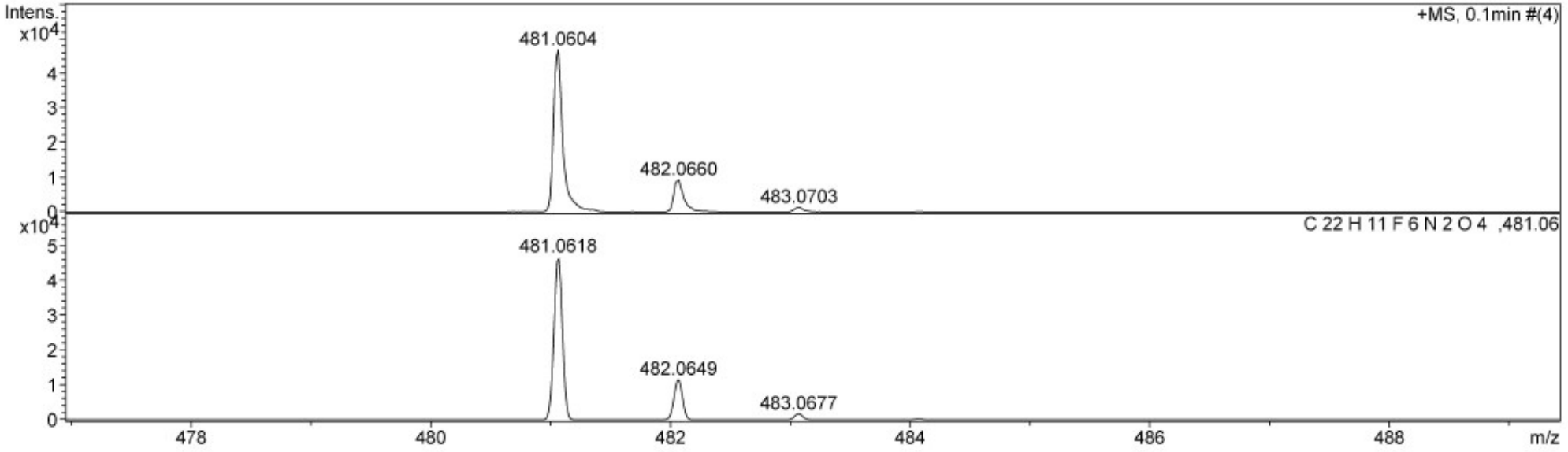
| | | | | | |
|---|---|---|---|---|---|
| Analysis Name | D:\Data\Service masse 2015\O37733SI | Acquisition Date | 11/19/2015 9:03:11 AM | | |
| Method | esi low pos.m | Operator | Administrator | | |
| Sample Name | KB393 | Instrument | micrOTOF | 66 | |
| Comment | | | | | |




**5**

**Acquisition Parameter**

| | | | | | |
|---|---|---|---|---|---|
| Source Type | ESI | Ion Polarity | Positive | Set Corrector Fill | 65 V |
| Scan Range | n/a | Capillary Exit | 80.0 V | Set Pulsar Pull | 817 V |
| Scan Begin | 50 m/z | Hexapole RF | 60.0 V | Set Pulsar Push | 817 V |
| Scan End | 3000 m/z | Skimmer 1 | 50.0 V | Set Reflector | 1700 V |
| | | Hexapole 1 | 24.3 V | Set Flight Tube | 8600 V |
| | | | | Set Detector TOF | 2275 V |

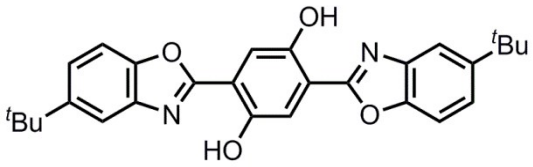



| Sum Formula | Sigma | m/z | Err [ppm] | Mean Err [ppm] | rdb | N Rule | e⁻ |
|---|---|---|---|---|---|---|---|
| C 22 H 11 F 6 N 2 O 4 | 0.03 | 481.0618 | 2.75 | 1.42 | 15.50 | ok | even |
| C 22 H 10 F 6 N 2 O 4 | 0.73 | 480.0539 | -6.89 | -8.05 | 16.00 | - | odd |

# Mass Spectrum Molecular Formula Report

**Analysis Info**

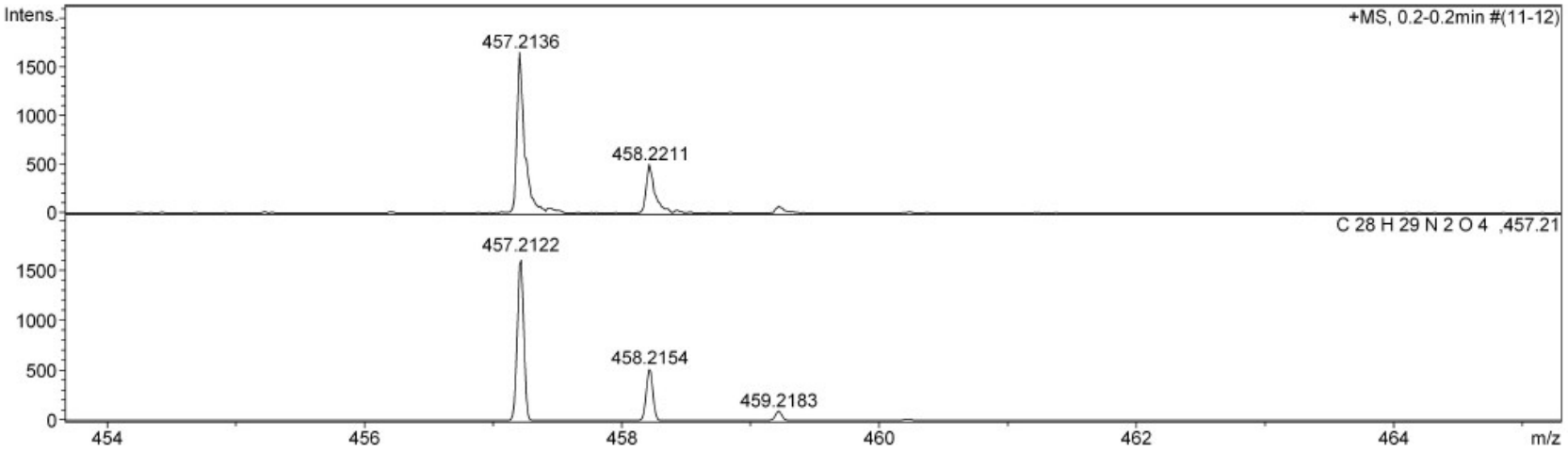
| | | | |
|---|---|---|---|
| Analysis Name | D:\Data\Service masse 2015\O37667SK.d | Acquisition Date | 10/29/2015 11:02:40 AM |
| Method | esi low pos.m | Operator | Administrator |
| Sample Name | KB336 | Instrument | micrOTOF 66 |
| Comment | | | |




**8**

**Acquisition Parameter**

| | | | | | |
|---|---|---|---|---|---|
| Source Type | ESI | Ion Polarity | Positive | Set Corrector Fill | 65 V |
| Scan Range | n/a | Capillary Exit | 80.0 V | Set Pulsar Pull | 817 V |
| Scan Begin | 50 m/z | Hexapole RF | 60.0 V | Set Pulsar Push | 817 V |
| Scan End | 3000 m/z | Skimmer 1 | 50.0 V | Set Reflector | 1700 V |
| | | Hexapole 1 | 24.3 V | Set Flight Tube | 8600 V |
| | | | | Set Detector TOF | 2275 V |

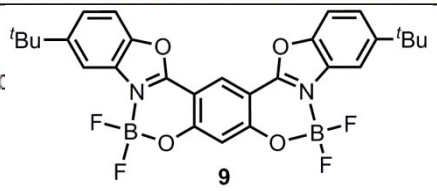



| Sum Formula | Sigma | m/z | Err [ppm] | Mean Err [ppm] | rdb | N Rule | e⁻ |
|---|---|---|---|---|---|---|---|
| C 28 H 29 N 2 O 4 | 0.03 | 457.2122 | -3.07 | -5.19 | 15.50 | ok | even |
| C 28 H 28 N 2 O 4 | 0.71 | 456.2044 | -13.10 | -16.08 | 16.00 | - | odd |

# Mass Spectrum Molecular Formula Report

**Analysis Info**

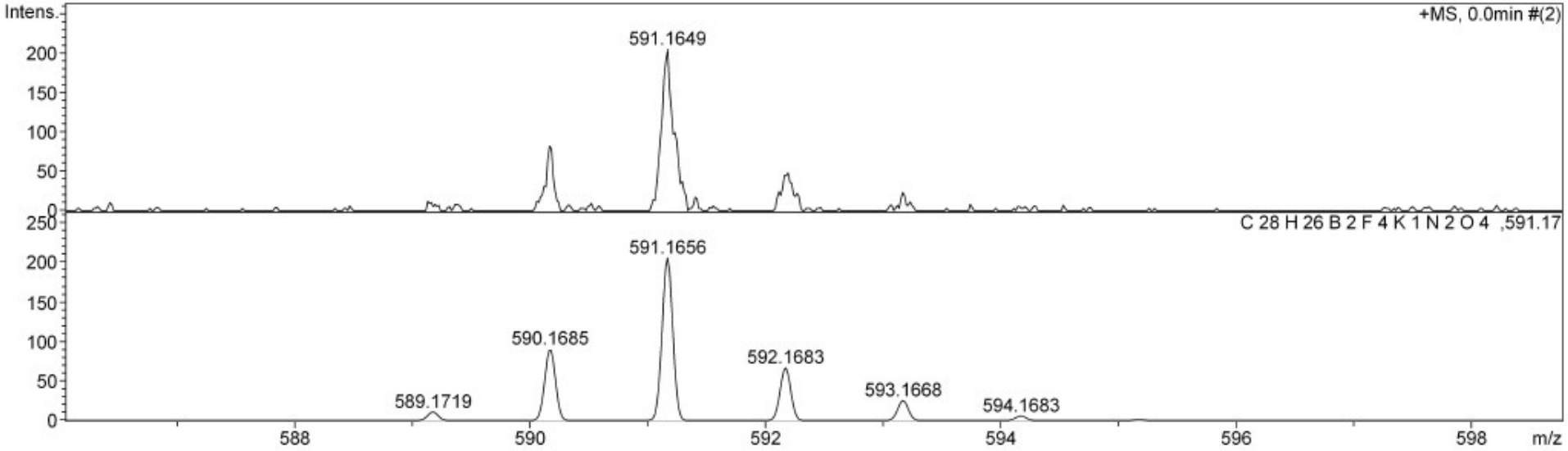
| | | | |
|---|---|---|---|
| Analysis Name | D:\Data\Service masse 2015\O37888SK.d | Acquisition Date | 11/30/2015 10:35:40 AM |
| Method | esi low pos.m | Operator | Administrator |
| Sample Name | KB385 | Instrument | micrOTOF 66 |
| Comment | | | |



9

**Acquisition Parameter**

| | | | | | |
|---|---|---|---|---|---|
| Source Type | ESI | Ion Polarity | Positive | Set Corrector Fill | 65 V |
| Scan Range | n/a | Capillary Exit | 80.0 V | Set Pulsar Pull | 817 V |
| Scan Begin | 50 m/z | Hexapole RF | 60.0 V | Set Pulsar Push | 817 V |
| Scan End | 3000 m/z | Skimmer 1 | 50.0 V | Set Reflector | 1700 V |
| | | Hexapole 1 | 24.3 V | Set Flight Tube | 8600 V |
| | | | | Set Detector TOF | 2275 V |

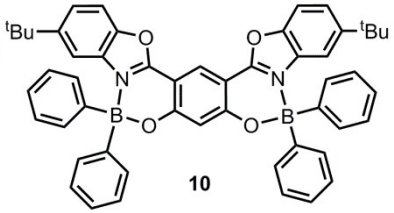



| Sum Formula | Sigma | m/z | Err [ppm] | Mean Err [ppm] | rdb | N Rule | e⁻ |
|---|---|---|---|---|---|---|---|
| C 28 H 26 B 2 F 4 K 1 N 2 O 4 | 0.23 | 591.1646 | -0.44 | 1.19 | 15.50 | ok | even |
| C 28 H 25 B 2 F 4 K 1 N 2 O 4 | 0.53 | 590.1568 | -7.57 | -7.35 | 16.00 | - | odd |

# Mass Spectrum Molecular Formula Report

**Analysis Info**

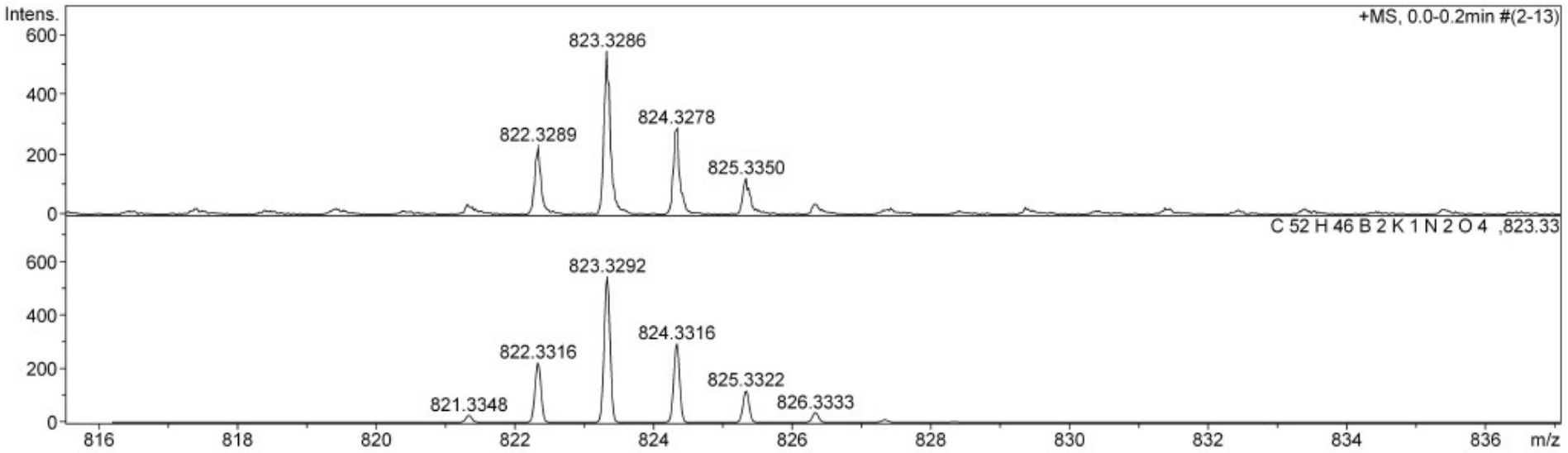
| | |
|---|---|
| Analysis Name | D:\Data\Service masse 2015\O37756SK.d |
| Method | esi wide pos.m |
| Sample Name | KB388 |
| Comment | |




| | |
|---|---|
| Acquisition Date | 11/19/2015 11:26:51 AM |
| Operator | Administrator |
| Instrument | micrOTOF 66 |

**Acquisition Parameter**

| | | | | | |
|---|---|---|---|---|---|
| Source Type | ESI | Ion Polarity | Positive | Set Corrector Fill | 65 V |
| Scan Range | n/a | Capillary Exit | 150.0 V | Set Pulsar Pull | 817 V |
| Scan Begin | 50 m/z | Hexapole RF | 220.0 V | Set Pulsar Push | 817 V |
| Scan End | 3000 m/z | Skimmer 1 | 50.0 V | Set Reflector | 1700 V |
| | | Hexapole 1 | 24.3 V | Set Flight Tube | 8600 V |
| | | | | Set Detector TOF | 2275 V |

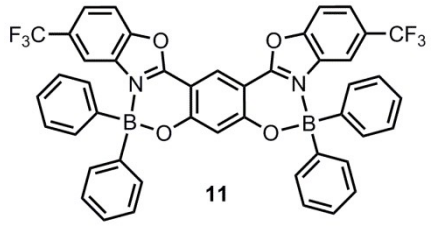



| Sum Formula | Sigma | m/z | Err [ppm] | Mean Err [ppm] | rdb | N Rule | e⁻ |
|---|---|---|---|---|---|---|---|
| C 52 H 46 B 2 K 1 N 2 O 4 | 0.03 | 823.3275 | -1.28 | 1.76 | 31.50 | ok | even |
| C 52 H 45 B 2 K 1 N 2 O 4 | 0.35 | 822.3197 | -5.79 | -5.96 | 32.00 | - | odd |
| C 52 H 47 B 2 K 1 N 2 O 4 | 0.35 | 824.3354 | 13.20 | 12.54 | 31.00 | - | odd |
| C 52 H 44 B 2 K 1 N 2 O 4 | 0.54 | 821.3119 | -14.60 | -14.64 | 32.50 | ok | even |

# Mass Spectrum Molecular Formula Report

**Analysis Info**

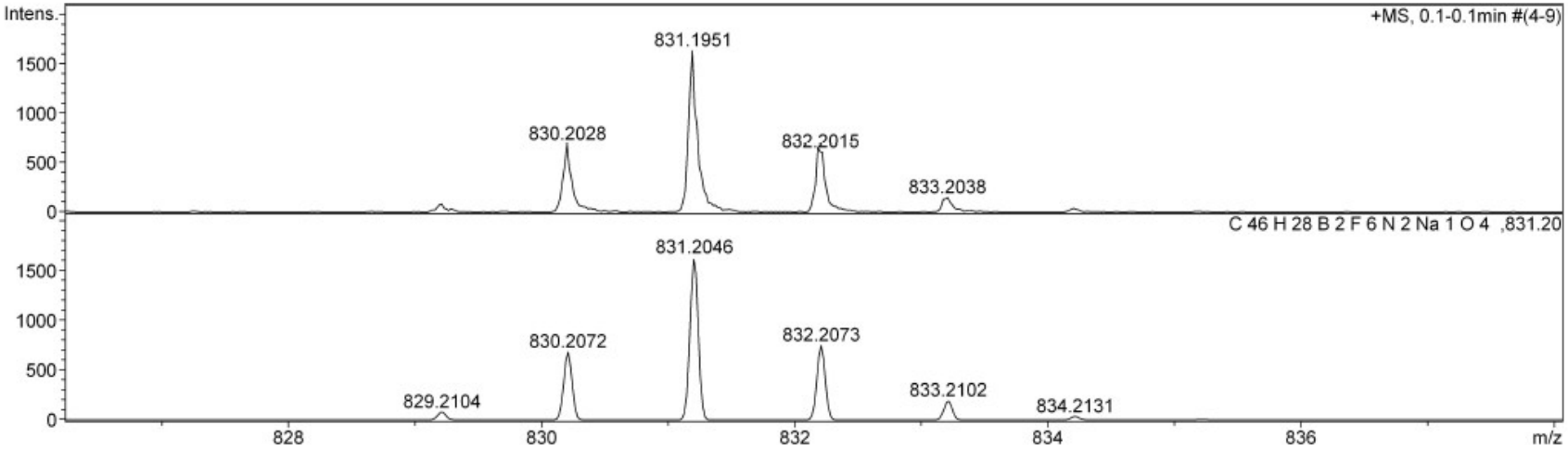
| | | | |
|---|---|---|---|
| Analysis Name | D:\Data\Service masse 2015\O37659SK.d | Acquisition Date | 10/29/2015 10:07:56 AM |
| Method | esi wide pos.m | Operator | Administrator |
| Sample Name | KB294 | Instrument | micrOTOF 66 |
| Comment | | | |




11

**Acquisition Parameter**

| | | | | | |
|---|---|---|---|---|---|
| Source Type | ESI | Ion Polarity | Positive | Set Corrector Fill | 65 V |
| Scan Range | n/a | Capillary Exit | 150.0 V | Set Pulsar Pull | 817 V |
| Scan Begin | 50 m/z | Hexapole RF | 220.0 V | Set Pulsar Push | 817 V |
| Scan End | 3000 m/z | Skimmer 1 | 50.0 V | Set Reflector | 1700 V |
| | | Hexapole 1 | 24.3 V | Set Flight Tube | 8600 V |
| | | | | Set Detector TOF | 2275 V |

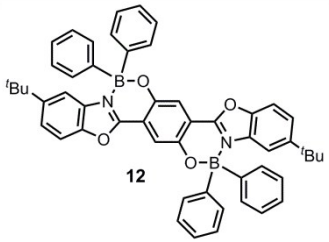



| Sum Formula | Sigma | m/z | Err [ppm] | Mean Err [ppm] | rdb | N Rule | e⁻ |
|---|---|---|---|---|---|---|---|
| C 46 H 28 B 2 F 6 N 2 Na 1 O 4 | 0.04 | 831.2032 | 9.71 | 8.77 | 31.50 | ok | even |
| C 46 H 27 B 2 F 6 N 2 Na 1 O 4 | 0.38 | 830.1953 | 5.24 | 1.44 | 32.00 | - | odd |
| C 46 H 26 B 2 F 6 N 2 Na 1 O 4 | 0.59 | 829.1875 | -0.70 | -4.56 | 32.50 | ok | even |
| C 46 H 25 B 2 F 6 N 2 Na 1 O 4 | 0.64 | 828.1797 | -6.62 | -10.50 | 33.00 | - | odd |

# Mass Spectrum Molecular Formula Report

**Analysis Info**

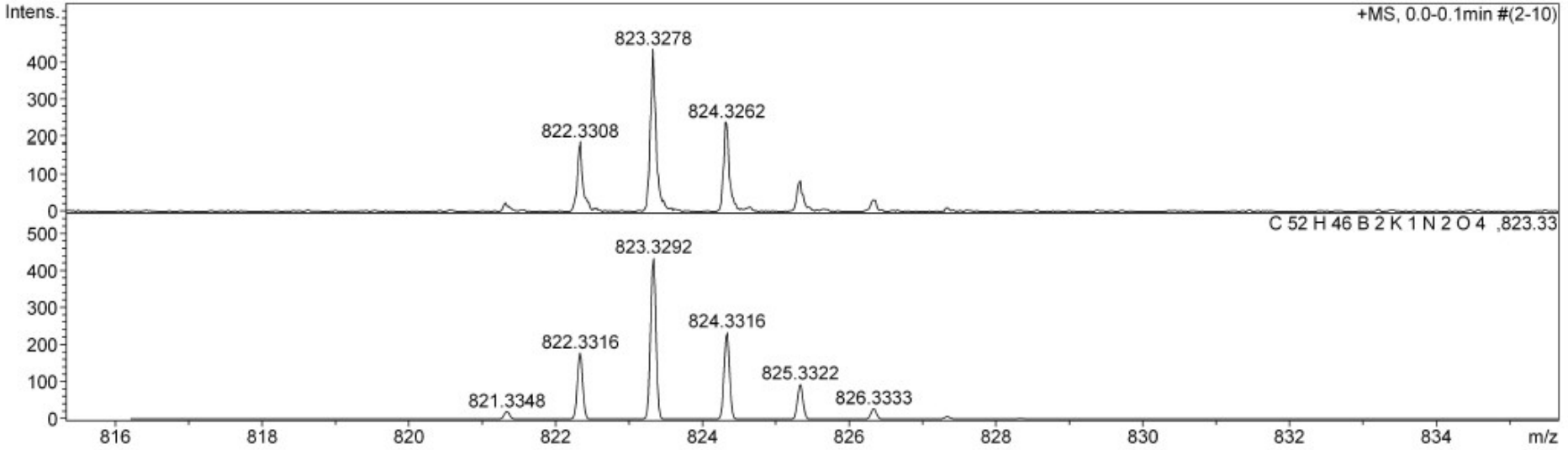
| | | | |
|---|---|---|---|
| Analysis Name | D:\Data\Service masse 2015\O37739SK.d | Acquisition Date | 11/19/2015 9:40:08 AM |
| Method | esi wide pos.m | Operator | Administrator |
| Sample Name | KB369 | Instrument | micrOTOF 66 |
| Comment | | | |



12

**Acquisition Parameter**

| | | | | | |
|---|---|---|---|---|---|
| Source Type | ESI | Ion Polarity | Positive | Set Corrector Fill | 65 V |
| Scan Range | n/a | Capillary Exit | 150.0 V | Set Pulsar Pull | 817 V |
| Scan Begin | 50 m/z | Hexapole RF | 220.0 V | Set Pulsar Push | 817 V |
| Scan End | 3000 m/z | Skimmer 1 | 50.0 V | Set Reflector | 1700 V |
| | | Hexapole 1 | 24.3 V | Set Flight Tube | 8600 V |
| | | | | Set Detector TOF | 2275 V |




| Sum Formula | Sigma | m/z | Err [ppm] | Mean Err [ppm] | rdb | N Rule | e⁻ |
|---|---|---|---|---|---|---|---|
| C 52 H 46 B 2 K 1 N 2 O 4 | 0.09 | 823.3275 | -0.36 | 2.86 | 31.50 | ok | even |
| C 52 H 45 B 2 K 1 N 2 O 4 | 0.34 | 822.3197 | -4.87 | -4.69 | 32.00 | - | odd |
| C 52 H 47 B 2 K 1 N 2 O 4 | 0.39 | 824.3354 | 14.12 | 12.42 | 31.00 | - | odd |
| C 52 H 44 B 2 K 1 N 2 O 4 | 0.54 | 821.3119 | -13.67 | -13.64 | 32.50 | ok | even |