Supporting Information

Exploring Morita-Baylis-Hillman Reactions of *p*-Quinols

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General Considerations: Melting points were obtained in open capillary tubes and are uncorrected. ^{1}H- and ^{13}C-NMR spectra were generally recorded in a AV-300 Bruker at 300 and 75 MHz respectively using $CDCl_3$ or acetone-d_6 as solvent. A DRX-500 Bruker was used in the specific cases for ^{1}H-NMR (500 MHz), ^{13}C-NMR (125 MHz) and double resonance experiments. Chemical shifts are reported in ppm relative to $CDCl_3$ (δ 7.27 ppm) and acetone-d_6 (δ 2.09 ppm). HRMS were measured at 70 eV. All reactions were monitored by thin-layer chromatography that was performed on precoated sheets of silica gel 60, and flash column chromatography was done with silica gel 60 (230-400 mesh) of Merck. Eluting solvents are indicated in the text. Synthesis of 4-hydroxy-4-methylcyclohexa-2,5-dienone (*p*-quinol) **1** has been previously described.[1]

(1) Carreño, M. C.; González-López, M.; Urbano, A. *Angew. Chem. Int. Ed*. **2006**, *45*, 2737-2741.

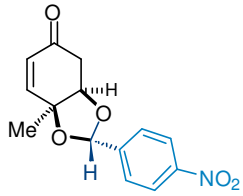
EXPERIMENTAL PROCEDURES

General procedure A: Synthesis of fusionated ketal derivatives 3a-d:

To a mixture of *p*-quinol (1.00 mmol) and the corresponding aldehyde (1.20 mmol) in CH_2Cl_2 (0.5 ml) was added DMAP (0.15 mmol, 15 mol %) at rt. After 3 days, the mixture was acidified with hydrochloric acid 10 % and then extracted with AcOEt (2 x 5 ml). The organic layer was dried over anhydrous $MgSO_4$, filtered and concentrated *in vacuo*. The crude product was purified by flash column chromatography (eluent indicated in each case).

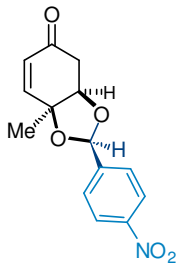
3a,4-Dihydro-7a-methyl-2-(4-nitrophenyl)[*d*][1,3]dioxol-5(7a*H*)-one (**3a**).

Following general procedure A, the reaction of **1** (52 mg, 0.42 mmol) with *p*-nitrobenzaldehyde (75.5 mg, 0.50 mmol) and DMAP (7.6 mg, 0.063 mmol) gave compound **3a**, as a 90:10 mixture of diastereoisomers, separated after flash chromatography (eluent Hex:AcOEt 3:1): major diastereoisomer (less polar) (78 mg, 67%) and minor diastereoisomer (most polar) (4 mg, 3%).



Major diastereoisomer: **(2*S**,3a*R**,7a*S**)-(3a)**: White solid. M.p.: 128-130 ºC. ^{1}H-NMR (300 MHz, $CDCl_3$): δ = 8.25 (d, *J* = 8.8 Hz, 2H), 7.64 (d, *J* = 8.8 Hz, 2H), 6.62 (dd, *J* = 10.4 and 2.1 Hz, 1H), 6.18 (dd, *J* = 10.3 and 0.8 Hz, 1H), 5.90 (s, 1H), 4.32 (q, *J* = 2.7 Hz, 1H), 3.02 (ddd, *J* = 17.3, 2.5 and 0.9 Hz, 1H), 2.67 (dd, *J* = 17.1 and 2.9 Hz, 1H), 1.63 (s, 3H). ^{13}C-NMR (75 MHz, $CDCl_3$): δ= 194.8, 148.4, 146.6, 145.0, 130.1, 127.2 (2C), 123.7 (2C), 101.1, 79.3, 78.5, 38.5, 21.2. MS (EI) *m/z* (%): 275 (0.4), 274 (2.2) [M-1]$^+$, 108 (84), 107 (100) HRMS Calcd for $C_{14}H_{13}NO_5$ 298.0685, found 298.0680[M+Na] $^+$.

Minor diastereoisomer: **(2*R**,3a*R**,7a*S**)-(3a)**: Colorless oil .^{1}H-NMR (300 MHz, $CDCl_3$): δ = 8.21 (d, *J* = 9.1 Hz, 2H), 7.56 (d, *J* = 9.1 Hz, 2H), 6.50 (dd, *J* = 10.3 and 2.4 Hz, 1H),

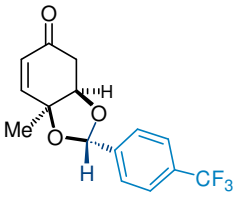


6.08 (s, 1H), 5.90 (dd, *J* = 10.3 and 0.7 Hz, 1H), 4.47 (dt, *J* = 3.6 and 2.4 Hz, 1H), 3.07 (ddd, *J* = 17.7, 2.5 and 0.9 Hz, 1H), 2.74 (dd, *J* = 17.8, 3.8 Hz, 1H), 1.60 (s, 3H). ^{13}C-NMR (75 MHz, $CDCl_3$): δ = 194.2, 149.3 (2C), 144.3, 127.6 (2C), 126.7, 123.6 (2C), 101.7, 81.4 (2C), 37.9, 21.9. MS (ES) *m/z* (%): 298 [M+Na] $^+$ (100). HRMS Calcd for $C_{14}H_{13}NO_5$ 298.0685, found 298.0682 [M+Na]$^+$.

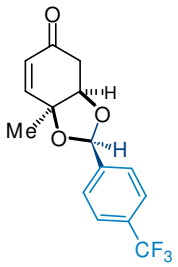
2-(4-Trifluoromethyl)phenyl-3a,4-dihydro-7a-methylbenzo[*d*] [1,3]dioxol-5(7a*H*)-one (3b).

Following general procedure A, the reaction of **1** (50 mg, 0.40 mmol) with *p*-(trifluoromethyl)benzaldehyde (65 µl, 0.48 mmol) and DMAP (7.2 mg, 0.060 mmol) gave compound **3b** as a 80:20 mixture of diastereoisomers, separated after flash chromatography (eluent Hex:AcOEt 3:1): major diastereoisomer (less polar) (53 mg, 44%) and minor diastereoisomer (most polar) (17 mg, 14 %).

Major diastereoisomer: **(2*S**,3a*R**,7a*S**)-3b**: White solid. M.p.: 58-60 ºC .^{1}H-NMR (300 MHz, $CDCl_3$): δ = 7.66 (d, *J* = 8.2 Hz, 2H), 7.58 (d, *J* = 8.2 Hz, 2H), 6.63 (dd, *J* = 10.3, 2.1 Hz, 1H), 6.17 (d, *J* = 10.4 Hz, 1H), 5.88 (s, 1H), 4.32 (q, *J* = 2.6 Hz, 1H), 3.00 (dd, *J* = 17.5 and 0.9 Hz, 1H), 2.65 (dd, *J* = 17.6 and 3.1 Hz, 1H), 1.62 (s, 3H). ^{13}C-NMR (75 MHz, $CDCl_3$): δ = 194.9, 146.8, 142.1, 131.4, 130.0 (q, *J* = 32.6 Hz), 126.6 (2C), 125.4 (q, *J* = 3.6 Hz, 2C), 123.9 (q, *J* = 272.6 Hz), 101.7, 79.2, 78.3, 38.5, 21.2. MS (ES) *m/z* (%): 299 (27) $[M+1]^+$, 321 (100) $[M+Na]^+$. HRMS Calcd for $C_{15}H_{13}F_3O_3$ 321.0706, found 321.0709 $[M+Na]^+$.



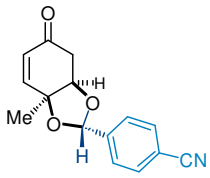
Minor diastereoisomer: **(2*R**,3a*R**,7a*S**)-3b**: White solid. M.p.: 52-54 ºC .^{1}H-NMR (300 MHz, $CDCl_3$): δ = 7.62 (d, *J* = 8.2 Hz, 2H), 7.50 (d, *J* = 8.1 Hz, 2H), 6.53 (dd, *J* = 10.4 and 2.3 Hz, 1H), 6.06 (s, 1H), 5.93 (d, *J* = 10.4 Hz, 1H), 4.46 (dt, *J* = 3.7 and 2.4 Hz, 1H), 3.07 (ddd, *J* = 17.8, 2.3 and 0.9 Hz, 1H), 2.74 (dd, *J* = 17.8 and 3.8 Hz, 1H), 1.60 (s, 3H). ^{13}C-NMR (75 MHz, $CDCl_3$): δ = 194.3, 149.5, 141.2, 131.4 (*J* = 32.3 Hz), 130.0, 127.0 (2C), 126.5, 125.3 (*J* = 3.8 Hz, 2C), 123.9 (*J* = 272.9 Hz), 102.2, 81.3, 76.8, 37.9, 21.9. MS (ES) *m/z* (%):321 (100) $[M+Na]^+$, 205 (14.3). HRMS Calcd for $C_{15}H_{13}F_3O_3$ 321.0706, found 321.0709 $[M+Na]^+$.



4-(3a,6,7,7a-Tetrahydro-3a-methyl-6-oxobenzo[*d*][1,3]dioxol-2-yl)benzonitrile (3c).

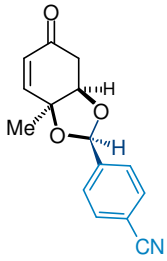
Following general procedure A, the reaction of **1** (50 mg, 0.40 mmol) with *p*-cianobenzaldehyde (65 µl, 0.48 mmol) and DMAP (7.2 mg, 0.060 mmol) gave compound **3c** as a 80:20 mixture of diastereoisomers, separated after flash chromatography (eluent Hex:AcOEt 3:1): major diastereoisomer (less polar) (43 mg, 42%) and minor diastereoisomer (most polar) (18 mg, 18 %).

Major diastereoisomer: **4-(2*S**,3a*S**,7a*R**)-3c** White solid. M.p.: 112-114 ºC .^{1}H-NMR



(300 MHz, $CDCl_3$): δ = 7.68 (d, *J* = 8.2 Hz, 2H), 7.56 (d, *J* = 8.2 Hz, 2H), 6.61 (dd, *J* = 10.5 and 2.3 Hz, 1H), 6.17 (d, *J* = 10.5 Hz, 1H), 5.85 (s, 1H), 4.29 (q, *J* = 2.4 Hz, 1H), 2.99 (ddd, *J* = 17.5, 2.6 and 1.1 Hz, 1H), 2.66 (dd, *J* = 17.4 and 3.1 Hz, 1H), 1.61 (s, 3H). ^{13}C-NMR (75 MHz, $CDCl_3$): δ= 194.8, 146.6, 143.2, 132.3 (2C), 130.1, 127.0 (2C), 118.5, 113.1, 101.4, 79.3, 78.5, 38.5, 21.2. MS (ES) m/z (%): 256 (100) $[M+1]^+$. HRMS Calcd for $C_{15}H_{13}NO_3$ 256.0961, found 256.0968 $[M+1]^+$.

Minor diastereoisomer: **4-(2*R**,3a*S**,7a*R**)-3c**: Yellow pale solid. M.p.: 98-100 ºC .^{1}H-

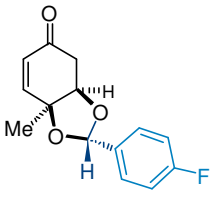


NMR (300 MHz, $CDCl_3$): δ = 7.65 (d, *J* = 8.2 Hz, 2H), 7.49 (d, *J* = 8.1 Hz, 2H), 6.50 (dd, *J* = 10.3 and 2.8 Hz, 1H), 6.04 (s, 1H), 5.91 (d, *J* = 10.3 Hz, 1H), 4.46 (dt, *J* = 3.7 and 2.3 Hz, 1H), 3.06 (ddd, *J* = 17.8, 2.4 and 1.0 Hz, 1H), 2.74 (dd, *J* = 17.8, 3.8 Hz, 1H), 1.59 (s, 3H).^{13}C-NMR (75 MHz, $CDCl_3$): δ= 194.1, 149.3, 142.4, 132.0 (2C), 127.4 (2C), 118.4, 113.1, 101.9, 81.3, 77.2, 37.9, 21. MS (ES) *m/z* (%): 279 (17.4) 278 (100) $[M+Na]^+$, 205 (12). HRMS Calcd for $C_{15}H_{13}NO_5$ 278.0780, found 278.0787 $[M+Na]^+$.

2-(4-Fluorophenyl)-3a,4-dihydro-7a-methylbenzo[*d*][1,3]dioxol-5(7a*H*)-one (3d).

Following general procedure A, the reaction of **1** (20 mg, 0.16 mmol) with *p*-fluorobenzaldehyde (20 µl, 0.19 mmol) and DMAP (2.9 mg, 0.024 mmol) gave compound **3d** as a 85:15 mixture of diastereoisomers, separated after flash chromatography (eluent Hex:AcOEt 3:1): major diastereoisomer (less polar) (21 mg, 53%) and minor diastereoisomer (most polar) (5 mg, 10 %).

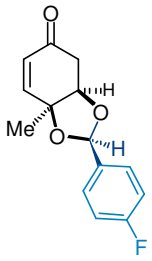
Major diastereoisomer: **(2*S**,3a*R**,7a*S**)-(3d)**: White solid. M.p.: 70-72 ºC .^{1}H-NMR



(300 MHz, $CDCl_3$): δ = 8.43 (m, 2H), 7.07 (m, 2H), 6.62 (dd, *J* = 10.3 and 2.1 Hz, 1H), 6.17 (dd, *J* = 10.4 and 1.0 Hz, 1H), 5.81 (s, 1H), 4.34 (q, *J* = 2.7 Hz, 1H), 3.00 (ddd, *J* = 17.5, 2.7 and 1.0 Hz, 1H), 2.65 (dd, *J* = 17.4, 3.2 Hz, 1H), 1.62 (s, 3H). ^{13}C-NMR (75 MHz, $CDCl_3$): δ= 195.1,

163.3 (d, *J* = 246 Hz), 146.9, 134.0, 130.1, 128.2 (d, *J* = 8.Hz, 2C), 115.3 (d, *J* = 21.7 Hz, 2C), 102.1, 79.1, 78.0, 38.6, 21.2. MS (ES) *m/z* (%): 271 (100) $[M+Na]^+$. HRMS Calcd for $C_{14}H_{13}FO_3$ 271.0740, found 271.0745 $[M+Na]^+$.

Minor diastereoisomer: **(2*R**,3a*R**,7a*S**)-(3d)**: White solid. M.p.: 50-52 ºC .^{1}H-NMR



(300 MHz, $CDCl_3$): δ = 7.36 (m, 2H), 7.04 (m, 2H), 6.57 (dd, *J* = 10.3 and 2.3 Hz, 1H), 5.99 (s, 1H), 5.97 (dd, *J* = 10.3 and 0.8 Hz, 1H), 4.43 (dt, *J* = 3.8 and 2.3 Hz, 1H), 3.06 (ddd, *J* = 17.7, 2.2 and 0.9 Hz, 1H), 2.74 (dd, *J* = 17.7 and 3.9 Hz, 1H), 1.58 (s, 3H). ^{13}C-NMR (75 MHz, $CDCl_3$): δ = 193.4, 158.9 (d, *J* = 272 Hz), 148.8, 132.1 (d, *J* = 3.4 Hz), 127.8 (d, *J* = 8.7 Hz, 2C), 125.3, 114.3 (d, *J* = 22.3 Hz, 2C), 101.7, 80.2, 76.2, 36.9, 21.1. MS (ES) *m/z* (%): 271 (100) $[M+Na]^+$, 249 (4), 203 (21). HRMS Calcd for $C_{14}H_{13}FO_3$ 271.0736, found 271.0740$[M+Na]^+$.

General procedure B: Synthesis of mono Morita-Baylis-Hillman adducts.

To a mixture of *p*-quinol (1.00 mmol) and the corresponding aromatic aldehyde (1.20 mmol) in MeOH (0.5 ml) was added DMAP (0.15 mmol, 15 mol %). The mixture was stirred at rt the time indicated in each case. Then, the mixture was acidified with hydrochloric acid 10 % and the organic solvent was eliminated. The resulting mixture was extracted with AcOEt (2 x 5 ml). The organic layer was dried over anhydrous $MgSO_4$, filtered and concentrated *in vacuo*. The crude product was purified by flash chromatography (eluent indicated in each case).

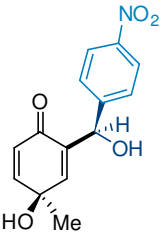
General procedure C: Synthesis of double Morita-Baylis-Hillman adducts.

To a mixture of *p*-quinol derivative (1.00 mmol), the corresponding aromatic aldehyde (2.00 mmol) and $LiClO_4$ (0.70 mmol, 70 mol%) in THF (0.5 ml) was added DABCO (0.15 mmol, 15 mol%). The mixture was stirred at rt and under argon during the time indicated in each case. Then, the mixture was acidified with hydrochloric acid 10 % and then extracted with AcOEt (2 x 5 ml). The organic layer was dried over anhydrous $MgSO_4$, filtered and concentrated *in vacuo*. The crude product was purified by flash chromatography (eluent indicated in each case).

2-(Hydroxy-(4-nitrophenyl)methyl)-4-methyl-*p*-quinol (4a).

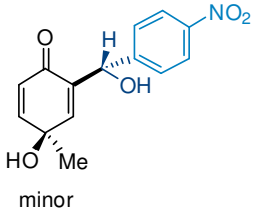
Following general procedure B, the reaction of **1** (23 mg, 0.18 mmol) with *p*-nitrobenzaldehyde (33 mg, 0.50 mmol) and DMAP (3.2 mg, 0.027 mmol) gave compound **4a** as a 60:40 mixture of diastereoisomers, separated after flash chromatography (eluent Hex:AcOEt 3:1): major diastereoisomer (less polar) (22 mg, 40%) and minor diastereoisomer (most polar) (12 mg, 24 %). Time reaction: 3 days.

Major diastereoisomer **(4a)**: **(4*S**)-2-((*R**)-Hydroxy-(4-nitrophenyl)methyl-4-methyl-p-quinol**: White solid. M.p.: 152-154 ºC .^{1}H-NMR (300 MHz, $CDCl_3$): δ = 8.21 (d, *J* = 8.9 Hz, 2H), 7.58 (d, *J* = 8.9 Hz, 2H), 6.94 (dd, *J* = 10.0 and 3.0 Hz, 1H), 6.72 (dd, *J* = 3.0 and 1.0 Hz, 1H), 6.13 (d, J = 10.1 Hz, 1H), 5.73 (brs, 1H), 3.38 (brs, 1H), 1.43 (s, 3H). ^{13}C-NMR (75 MHz, $CDCl_3$): δ= 185.1, 152.3, 148.2, 148.1, 147.5, 137.7, 127.3 (2C), 127.1, 123.7 (2C), 71.0, 67.7, 26.8. MS (ES) m/z (%): 298 (100) [M+Na]+, 258 (49). HRMS Calcd for $C_{14}H_{13}NO_5$ 298.0688, found 298.0685[M+Na]$^{+}$.



major

Minor diastereoisomer (**4a**): **(4*S**)-2-((*S**)-Hydroxy-(4-nitrophenyl)methyl-4-methyl-*p*-quinol**: White solid. M.p.:138-140 ºC .^{1}H-NMR (300 MHz, $CDCl_3$): δ = 8.19 (d, *J* = 8.9 Hz, 2H), 7.57 (d, *J* = 8.9 Hz, 2H), 6.91 (dd, *J* = 10.6 and 3.2 Hz, 1H), 6.78 (dd, *J* = 3.0 and 1.0 Hz, 1H), 6.11 (d, *J* = 10.5 Hz, 1H), 5.72 (brs, 1H), 3.37 (brs, 1H), 1.42 (brs, 1H). ^{13}C-NMR (75 MHz, $CDCl_3$): δ= 185.3, 152.4, 148.2, 148.4, 147.5, 137.6, 127.3 (2C), 127.1, 123.7 (2C), 71.3, 67.7, 26.7. MS (ES) *m/z* (%): 298 (23) [M+Na]$^{+}$, 111 (35), 61(100). HRMS Calcd for $C_{14}H_{13}NO_5$ 275.0794, found 211.0672[M+Na]$^{+}$.



minor

2-(Hydroxy-(4-(Trifluoromethyl)phenyl)methyl)-4-methyl-*p*-quinol (4b).

Following general procedure B, the reaction of **1** (50 mg, 0.40 mmol) with *p*-(trifluoromethyl)benzaldehyde (65 µl, 0.48 mmol) and DMAP (7.2 mg, 0.060 mmol) gave compound **4b** as a 60:40 mixture of diastereoisomers, separated after flash chromatography (eluent Hex:AcOEt 3:1): major diastereoisomer (less polar) (50 mg, 42%) and minor diastereoisomer (most polar) (33 mg, 28 %). Time reaction: 3 days.

Major diastereoisomer **(4b)**: **(4*S**)-2-((*R**)-Hydroxy-(4-(trifluoromethyl)phenyl)methyl)-4-methyl-*p*-quinol**. White solid. M.p.: 100-102 ºC .^{1}H-NMR (300 MHz, $CDCl_3$): δ = 7.62 (d, *J* = 8.0 Hz, 2H), 7.52 (d, *J* = 8.0 Hz, 2H), 6.90 (dd, *J* = 10.1 and 3.3 Hz, 1H), 6.69 (brs, 1H), 6.12 (d, *J* = 9.8 Hz, 1H), 5.69 (brs, 1H), 3.32 (brs, 1H), 1.50 (s, 3H). ^{13}C-NMR (75 MHz, $CDCl_3$): δ= 185.4, 152.3, 148.0, 144.9, 137.9, 130.0 (q, *J* = 32.4 Hz, 2C), 127.2, 126.8 (2C), 125.4 (q, *J* = 4.0 Hz), 124.1 (q, *J* = 271.9 Hz), 71.3, 67.7, 26.8. MS (FAB+) *m/z* (%): 299 (100) $[M+1]^+$, 298 (20) $[M]^+$, 297 (49). HRMS Calcd for $C_{15}H_{13}F_3O_3$ 298.0817, found 299.0899 $[M+1]^+$.

major

(S)-4-hydroxy-2-((S)-hydroxy(4-(trifluoromethyl)phenyl)methyl)-4-methylcyclohexa-2,5-dienone

Minor diastereoisomer (**4b)**:

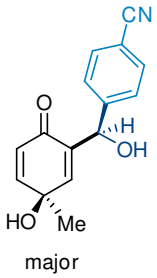
(4*S)-2-((*S**)-Hydroxy-(4-(trifluoromethyl)phenyl)methyl)-4-methyl-*p*-quinol**. White solid. M.p.:78-80 ºC .^{1}H-NMR (300 MHz, $CDCl_3$): δ = 7.62 (d, *J* = 8.1 Hz, 2H), 7.52 (d, *J* = 8.1 Hz, 2H), 6.90 (dd, *J* = 10.0 and 3.1 Hz, 1H), 6.72 (dd, *J* = 2.9 and 1.1 Hz, 1H), 6.13 (d, *J* = 10.5 Hz, 1H), 5.70 (d, *J* = 2.7 Hz 1H), 3.38 (d, *J* = 2.9 Hz, 1H), 1.47 (s, 3H). ^{13}C-NMR (75 MHz, $CDCl_3$): δ = 185.4, 152.2, 147.9, 144.9, 137.9, 130.0 (q, *J* = 32.7 Hz, 2C), 127.3, 126.8 (2C), 125.4 (q, *J* = 3.8 Hz), 124.0 (q, *J* = 272.6 Hz), 71.5, 67.6, 26.7. MS (ES+) *m/z* (%): 321 (49) $[M+Na]^+$, 281 (100). HRMS Calcd for $C_{15}H_{13}F_3O_3$ 321.0709 $[M+Na]^+$, found 321.0712 $[M+Na]^+$.

minor

2-Hydroxy-(4-cianophenyl)methyl-4-methyl-*p*-quinol (4c).

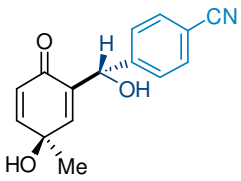
Following general procedure B, the reaction of **1** (50 mg, 0.40 mmol) with *p*-cianobenzaldehyde (65 μl, 0.48 mmol) and DMAP (7.2 mg, 0.060 mmol) gave compound **4c** as a 60:40 mixture of diastereoisomers, separated after flash chromatography (eluent Hex:AcOEt 3:1): major diastereoisomer (less polar) (33 mg, 28 %) and minor diastereoisomer (most polar) (24 mg, 24 %). Time reaction: 3 days.

Major diastereoisomer**(4c)**: **(4*S**)-2-((*R**)-Hydroxy-(4-cianophenyl)methyl)-4-methyl-*p*-quinol**: Colorless oil. ^{1}H-NMR (300 MHz, $CDCl_3$): δ = 7.63 (d, *J* = 8.2 Hz, 2H), 7.52 (d, *J* = 8.2 Hz, 2H), 6.91 (dd, *J* = 9.9 and 2.9 Hz, 1H), 6.72 (dd, *J* = 2.9 and 0.9 Hz, 1H), 6.12 (d, *J* = 9.9 Hz, 1H), 5.68 (brs, 1H), 3.40 (brs, 1H), 1.50 (s, 3H). ^{13}C-NMR (75 MHz, $CDCl_3$): δ = 185.2, 152.5, 148.2, 146.4, 137.7, 132.3 (2C), 127.2 (2C), 127.1, 118.6, 111.6, 71.1, 67.6, 26.8. MS (ES) *m/z* (%): 278 (77) $[M+Na]^+$, 239 (18.9), 238 (100). HRMS Calcd for $C_{15}H_{13}NO_3$ 278.0791, found 278.0787 $[M+Na]^+$.



major

Minor diastereoisomer **(4c)**: **(4*S**)-2-((*S**)-Hydroxy-(4-cianophenyl)methyl)-4-methyl-*p*-quinol**: Colorless oil. ^{1}H-NMR (300 MHz, $CDCl_3$): δ = 7.63 (d, *J* = 8.1 Hz, 2H), 7.51 (d, *J* = 8.3 Hz, 2H), 6.91 (dd, *J* = 9.8 and 3.0 Hz, 1H), 6.75 (d, *J* = 2.9 Hz, 1H), 6.12 (d, *J* = 9.9 Hz, 1H), 5.66 (s, 1H), 3.40 (s, 1H), 1.47 (s, 3H). ^{13}C-NMR (75 MHz, $CDCl_3$): δ = 185.3, 152.5, 148.3, 146.5, 137.5, 132.3 (2C), 127.2 (2C), 127.1, 118.8, 111.5, 71.3, 67.6, 26.7. MS (FAB+) m/z (%): 256 (16) $[M+1]^+$, 255 (2) $[M]^+$, 57 (100). HRMS Calcd for $C_{15}H_{13}NO_3$ 278.0787, found 278.0787 $[M+Na]^+$.

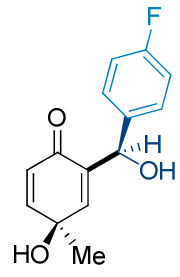


minor

2-Hydroxy-(4-Fluorophenyl)methyl)-4-methyl-*p*-quinol (4d).

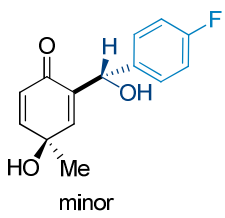
Following general procedure B, the reaction of **1** (40 mg, 0.32 mmol) with *p*-fluorobenzaldehyde (40 µl, 0.38 mmol) and DMAP (5.8 mg, 0.048 mmol) gave compound **4b** as a 60:40 mixture of diastereoisomers, separated after flash chromatography (eluent Hex:AcOEt 3:1): major diastereoisomer (less polar) (35 mg, 44%) and minor diastereoisomer (most polar) (22 mg, 28%). Time reaction: 4 days.

Major diastereoisomer **(4d)**: **(4*S**)-2-((*R**)-Hydroxy-(4-fluorophenyl)methyl)-4-methyl-*p*-quinol**. White solid. M.p.:128-130 ºC. ^{1}H-NMR (300 MHz, $CDCl_3$): δ = 7.38-7.34 (m, 2H), 7.07-7.02 (m, 2H), 6.89 (dd, *J* = 10.2 and 3.0 Hz, 1H), 6.67 (dd, *J* = 2.9 and 0.9 Hz, 1H), 6.12 (d, *J* = 10.0 Hz, 1H), 5.64 (brs, 1H), 3.23 (brs, 1H), 1.49 (s, 3H). ^{13}C-NMR (75 MHz, $CDCl_3$): δ = 185.6, 165.5 (d, *J* = 245 Hz), 152.1, 147.6, 138.4, 128.3 (d, *J* = 8.0 Hz, 2C), 127.3, 115.3 (d, *J* = 21.7 Hz, 2C), 71.1, 67.6, 26.8. MS (ES) m/z (%): 271 (100) $[M+Na]^+$, 231 (16). HRMS Calcd for $C_{14}H_{13}FO_3$ 271.0740, found 278.0747 $[M+Na]^+$.



major

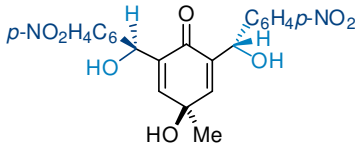
Minor diastereoisomer **(4d)**:



(4*S)-2-((*S**)-Hydroxy-(4-fluorophenyl)methyl)-4-methyl-*p*-quinol**. White solid. M.p.: 140-142 ºC. ^{1}H-NMR (300 MHz, $CDCl_3$): δ = 7.38-7.34 (m, 2H), 7.07-7.02 (m, 2H), 6.90 (dd, *J* = 10.0, 3.2 Hz, 1H), 6.70 (dd, *J* = 3.0, 1.2 Hz, 1H), 6.13 (d, *J* = 10.0 Hz, 1H), 5.64 (s, 1H), 3.43 (s, 1H), 1.47 (s, 3H). ^{13}C-NMR (75 MHz, $CDCl_3$): δ = 185.5, 162.3 (d, *J* = 242.5 Hz), 152.1, 147.5, 138.4, 128.3 (d, *J* = 8.0 Hz, 2C), 127.3, 115.4 (d, *J* = 21.5 Hz, 2C), 71.2, 67.6, 26.7. MS (ES) m/z (%): 271 (51) $[M+Na]^+$, 231 (100). HRMS Calcd for $C_{14}H_{13}FO_3$ 271.0740, found 278.0753 $[M+Na]^+$.

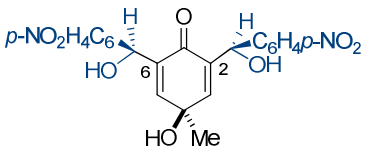
2,6-Bis(hydroxy(4-nitrophenyl)methyl)-4-methyl-*p*-quinol (5a), (6a) and (7a)

Following general procedure C, the reaction of **1** (70 mg, 0.56 mmol) with *p*-nitrobenzaldehyde (170 mg, 1.12 mmol), DABCO (9.4 mg, 0.084 mmol) and $LiClO_4$ (41.7 mg, 0.70 mmol) gave a 50:10:40 mixture of three diastereoisomers **5a**, **6a** and **7a**, separated after flash chromatography (eluent Hex:AcOEt 3:1): **5a** (less polar) (79 mg, 33%), **6a** (14 mg, 6%) and **7a** (most polar) (62 mg, 26%). Time reaction: 3 days.

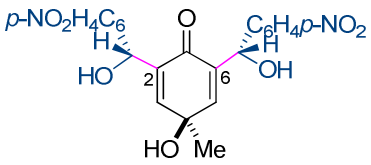


2,6-Bis-((*S)-hydroxy(4-nitrophenyl)methyl)-4-methyl-*p*-quinol (5a)**: Yellow solid. M.p.: 200-202 ºC .^{1}H-NMR (300 MHz, Acetone-d_6): δ = 8.15 (dd, *J* = 8.7 and 3.5 Hz, 4H), 7.65 (d, *J* = 8.7 Hz, 4H), 7.19 (m, 2H), 5.74 (brs, 1H), 5.69 (brs, 1H), 5.06 (brs, 1H), 1.47 (s, 3H). ^{13}C-NMR (75 MHz, Acetone-d_6): δ= 184.2, 152.1, 151.9, 149.7, 149.4, 148.0 (2C), 139.1, 138.9, 128.8 (2C), 123.9 (2C), 69.4, 69.1, 67.6, 27.8. MS (ES+) *m/z* (%): 449 (100) $[M+Na]^+$, 450 (23.5). HRMS Calcd for $C_{21}H_{18}N_2O_8$ 449.0940$[M+Na]^+$, found 449.0955 $[M+Na]^+$.

(4*s)-2-((*R**)-Hydroxy-(4-nitrophenyl)methyl)-6-((*S**)-hydroxy(4-nitrophenyl) methyl)-4-methyl-*p*-quinol (6a):** ^{1}H-NMR (300 MHz, Acetone-d_6): δ = 8.07 (d, *J* = 8.8 Hz, 4H), 7.57 (d, *J* = 8.8 Hz, 4H), 7.13 (brs, 2H), 5.80 (brs, 2H), 5.01 (brs, 2H), 1.49 (s, 3H). ^{13}C-NMR (75 MHz, Acetone-d_6): δ= 183.0, 150.5 (2C), 148.0 (2C), 146.5 (2C), 137.6 (2C), 127.1 (4C), 122.4 (4C), 67.9 (2C), 66.1, 26.5. MS (ES+) *m/z* (%): 449 (100) $[M+Na]^+$, 450 (24). HRMS Calcd for $C_{21}H_{18}N_2O_8$ 449.0940$[M+Na]^+$, found 449.0955 $[M+Na]^+$.



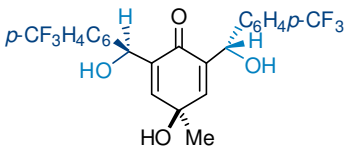
(4*r)-2-((*R**)-Hydroxy-(4-nitrophenyl)methyl)-6-((*S**)-hydroxy(4-nitrophenyl) methyl)-4-methyl-*p*-quinol (7a):** ^{1}H-NMR (300 MHz, Acetone-d_6): δ = 8.10 (d, *J* = 8.6 Hz, 4H), 7.62 (d, *J* = 8.6 Hz, 4H), 7.13 (brs, 2H), 5.75 (m, 2H), 5.02 (brs, 2H), 5.00 (brs, 2H), 1.43 (s, 3H). ^{13}C-NMR (75 MHz, Acetone-d_6): δ= 183.6, 150.0 (2C), 149.0 (2C), 147.0 (2C), 138.0 (2C), 127.7 (4C), 123.0 (4C), 68.7 (2C), 66.9, 26.8. MS (ES+) *m/z* (%): 449 (100) $[M+Na]^+$, 450 (24.3), 301 (48.7). HRMS Calcd for $C_{21}H_{18}N_2O_8$ 449.0946$[M+Na]^+$, found 449.0955 $[M+Na]^+$.



2,6-Bis(4-(trifluoromethyl)phenyl)(hydroxyl)methyl)-4-methyl-*p*-quinol (5b), (6b) and (7b).

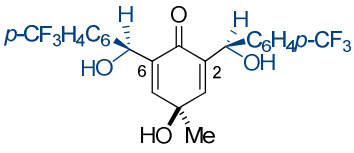
Following general procedure C, the reaction of **1** (70 mg, 0.56 mmol) with *p*-(trifluoromethyl) benzaldehyde (170 mg, 1.12 mmol), DABCO (9.4 mg, 0.084 mmol) and $LiClO_4$ (41.5 mg, 0.39 mmol) gave a 50:10:40 mixture of three diastereoisomers **5b**, **6b** and **7b**, separated after flash chromatography (eluent Hex:AcOEt 3:1): **5b** (less polar) (89 mg, 34%), **6b** (16 mg, 6%) and **7b** (most polar) (63 mg, 24 %). Time reaction: 2 days.

2,6-Bis((*R)-(4-(trifluoromethyl)phenyl)(hydroxyl)methyl)-4-methyl-*p*-quinol (5b).**



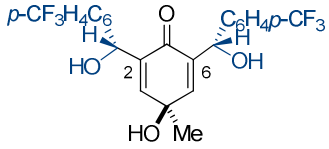
Yellow pale solid. M.p.: 170-172 ºC .^{1}H-NMR (300 MHz, $CDCl_3$): δ = 7.60 (d, *J* = 7.5 Hz, 4H), 7.47 (d, *J* = 7.5 Hz, 4H), 6.79 (dd, *J* = 15.0 and 2.4 Hz, 2H), 5.69 (s, 2H), 3.08 (brs, 2H), 1.48 (s, 3H). ^{13}C-NMR (75 MHz, $CDCl_3$): δ = 185.2, 148.5, 148.4, 144.8 (2C), 138.1 (2C), 130.2 (q, *J* = 32.3 Hz, 2C), 124.0 (q, *J* = 272.5 Hz, 2C), 125.5 (q, *J* = 3.6 Hz, 4C), 126.8 (4C), 70.7, 70.6, 67.6, 26.8. MS (FAB+) *m/z* (%): 473 (10.5) $[M+1]^+$, 437 (100), 173 (98). HRMS Calcd for $C_{23}H_{18}F_6O_4$ 495.1007 $[M+Na]^+$, found 495.1005 $[M+Na]^+$.

(4*s)-6-((*R**)-(4-(Trifluoromethyl)phenyl)(hydroxyl)methyl)-2-((*S**)-(4-(trifluoro methyl)phenyl)(hydroxyl)methyl)-4-methyl-*p*-quinol (6b).** ^{1}H-NMR (300 MHz, $CDCl_3$):



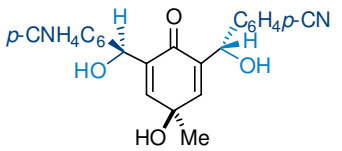
δ = 7.61 (d, *J* = 8.8 Hz, 4H), 7.48 (d, *J* = 8.8 Hz, 4H), 6.75 (s, 2H), 5.69 (s, 2H), 3.08 (brs, 2H), 1.52 (s, 3H). ^{13}C-NMR (75 MHz, $CDCl_3$): δ= 185.4, 148.4 (2C), 144.7 (2C), 138.1 (2C), 130.2 (q, *J* = 33.2 Hz, 2C), 126.8 (4C), 125.5 (q, *J* = 3.8 Hz, 4C), 124.0 (q, *J* = 273.2 Hz, 2C), 70.8 (2C), 67.7, 27.0. MS (FAB+) *m/z* (%): 473 (6) $[M+1]^+$, 421 (100), 437 (84). HRMS Calcd for $C_{23}H_{18}F_6O_4$ 495.0999, found 498.1001 $[M+Na]^+$.

(4*r)-2-((*R**)-(4-(Trifluoromethyl)phenyl)(hydroxyl)methyl)-6-((*S**)-(4-(trifluoro methyl)phenyl)(hydroxyl)methyl)-4-methyl-*p*-quinol (7b).** Yellow pale solid. M.p.: 120-122 ºC .^{1}H-NMR (300 MHz, $CDCl_3$): δ = 7.62 (d, *J* = 8.2 Hz, 4H), 7.47 (d, *J* = 8.1 Hz, 4H), 6.77 (s, 2H), 5.70 (s, 2H), 3.38 (brs, 2H), 1.43 (s, 3H). ^{13}C-NMR (75 MHz, $CDCl_3$): δ = 184.4, 148.8 (2C), 144.7 (2C), 138.0 (2C), 130.1 (q, J = 32.1 Hz, 2C), 126.8 (4C), 125.5 (q, J = 3.5 Hz, 4C), 124.0 (q, J = 271.8 Hz, 2C), 70.7 (2C), 67.4, 26.6. MS (FAB+) *m/z* (%): 473 (19) $[M+1]^+$, 455 (85), 173 (100). HRMS Calcd for $C_{23}H_{18}F_6O_4$ 495.0986, found 495.1001$[M+Na]^+$. r_t = 85.5 min, T = 25ºC

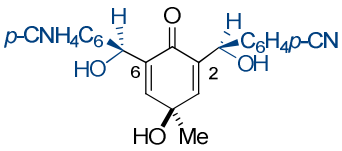


2,6-Bis(4-(cianophenyl)(hydroxyl)methyl)-4-methyl-*p*-quinol (5c), (6c) and (7c). Following general procedure C, the reaction of **1** (70 mg, 0.56 mmol) with *p*-cianobenzaldehyde (152 µl, 1.12 mmol), DABCO (9.4 mg, 0.084 mmol) and $LiClO_4$ (41.5 mg, 0.39 mmol) gave a 46:12:42 mixture of three diastereoisomers **5c**, **6c** and **7c**, separated after flash chromatography (eluent Hex:AcOEt 3:1): **5c** (less polar) (64 mg, 28%), **6c** (15 mg, 7%) and **7c** (most polar) (57 mg, 25%). Time reaction: 4 days.

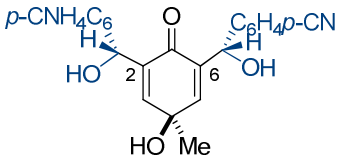
2,6-Bis((*R)-(4-(cianophenyl)(hydroxyl)methyl)-4-methyl-*p*-quinol (5c)**. Yellow pale solid. M.p.: 180-182 ºC .^{1}H-NMR (300 MHz, acetone-d_6): δ = 7.66-7.54 (m, 4H), 7.49 (d, *J* = 8.5 Hz, 4H), 6.84 (dd, *J* = 3.0, 1.0 Hz, 1H), 6.82 (dd, *J* = 3.0 and 0.9 Hz, 1H), 5.70 (d, *J* = 4.3 Hz, 1H), 5.67 (d, *J* = 5.0 Hz, 1H), 3.00 (d, *J* = 5.0 Hz, 1H), 2.94 (d, *J* = 4.7 Hz, 1H), 1.49 (s, 3H). ^{13}C-NMR (75 MHz, acetone-d_6): δ = 184.2, 150.0, 149.9, 149.5, 149.3, 139.1, 138.9, 132.8 (2C), 132.7 (2C), 128.7 (4C), 119.4 (2C), 111.6 (2C), 69.3, 69.6, 67.6, 27.8. . MS (ES+) *m/z* (%): 409 (100) $[M+Na]^+$. HRMS Calcd for $C_{23}H_{18}N_2O_4$ 409.1158$[M+Na]^+$, found 409.1136 $[M+Na]^+$.



(4*s)-6-((*R**)-(4-(Cianophenyl)(hydroxyl)methyl)-2-((*S**)-(4-(cianophenyl)-(hydroxyl) methyl)-4-methyl-*p*-quinol (6c).** ^{1}H-NMR (300 MHz, acetone-d_6): δ = 7.56 (d, *J* = 8.4 Hz, 4H), 7.49 (d, *J* = 8.5 Hz, 4H), 6.81 (s, 2H), 5.67 (d, *J* = 4.9 Hz, 2H), 3.04 (d, *J* = 4.8 Hz, 2H), 1.52 (s, 3H). ^{13}C-NMR (75 MHz, acetone-d_6): δ = 183.5,



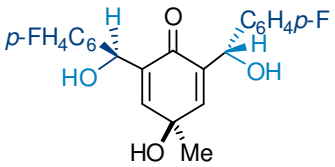
148.9 (2C), 148.4 (2C), 138.1 (2C), 131.7 (4C), 127.5 (4C), 118.4 (2C), 110.6 (2C), 68.5 (2C), 66.5, 27.0. MS (ES+) *m/z* (%): 409 (100) $[M+Na]^+$. HRMS Calcd for $C_{23}H_{18}N_2O_4$ 409.1158$[M+Na]^+$, found 409.1140 $[M+Na]^+$.

(4*r)-2-((*R**)-(4-(Cianophenyl)(hydroxyl)methyl-6-((*S**)-(4-(cianophenyl)(hydroxyl)methyl)-4-methyl-*p*-quinol (7c).** 

Yellow pale solid. M.p.: 181-183 ºC .^{1}H-NMR (300 MHz, acetone-d_6): δ = 7.60 (d, *J* = 8.3 Hz, 4H), 7.48 (d, *J* = 8.3 Hz, 4H), 6.82 (s, 2H), 5.65 (d, *J* = 5.2 Hz, 2H), 3.33 (d, *J* = 5.3 Hz, 2H), 1.45 (s, 3H). ^{13}C-NMR (75 MHz, acetone d_6): δ = 184.5, 149.9 (2C), 149.8 (2C), 138.9 (2C), 132.7 (4C), 128.5 (4C), 119.3 (2C), 111.5 (2C), 69.8 (2C), 67.8, 27.7. MS (ES+) *m/z* (%): 409 (100) $[M+Na]^+$, 410 (26.3), 301 (21.5). HRMS Calcd for $C_{23}H_{18}N_2O_4$ 409.1158$[M+Na]^+$, found 409.1147 $[M+Na]^+$.

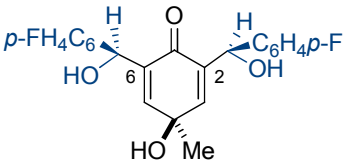
2,6-Bis(4-fluorophenyl)(hydroxyl)methyl)-4-hydroxy-4-methyl-*p*-quinol (5d), (6d) and (7d).

Following general procedure C, the reaction of **1** (70 mg, 0.56 mmol) with *p*-fluorobenzaldehyde (66 μl, 1.12 mmol), DABCO (9.4 mg, 0.084 mmol) and $LiClO_4$ (41.5 mg, 0.39 mmol) gave a 53:13:34 mixture of three diastereoisomers **5d**, **6d** and **7d**, separated after flash chromatography (eluent Hex:AcOEt 3:1): **5d** (less polar) (79 mg, 38%), **6d** (19 mg, 9%) and **7d** (most polar) (52 mg, 25 %). Time reaction: 4 days.

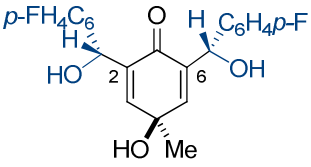
2,6-Bis((*R)-(4-fluorophenyl)(hydroxyl)methyl)-4-methyl-*p*-quinol (5d)**. White solid. M.p.: 154-156 ºC .^{1}H-NMR (300 MHz, $CDCl_3$): δ = 7.35-7.30 (m, 4H), 7.07-7.01 (m, 4H), 

6.79 (dd, *J* = 3.1 and 1.2 Hz, 1H), 6.75 (dd, *J* = 3.0 and 1.2 Hz, 1H), 5.64 (brs, 1H), 2.93 (brs, 2H), 1.47 (s, 3H). ^{13}C-NMR (75 MHz, $CDCl_3$): δ = 185.5, 162.4 (d, *J* = 247 Hz, 2C), 147.8 (2C), 138.6, 138.5, 136.6, 136.5, 128.3 (d, *J* = 8.4 Hz, 4C), 115.4 (d, *J* = 21.9 Hz, 4C), 70.5, 70.6, 67.7, 26.9. MS (ES) *m/z* (%): 395 (100) $[M+Na]^+$, 396 (26), 309 (49). HRMS Calcd for $C_{21}H_{18}F_2O_4$ 395.1061, found 395.1065 $[M+Na]^+$.

(4*s)-2-((*R**)-(4-Fluorophenyl)(hydroxyl)methyl)-6-((*S**)-(4-hydroxy-4-fluoro phenyl)(hydroxyl)methyl)-4-methyl-*p*-quinol (6d).** ^{1}H-NMR (300 MHz, $CDCl_3$): δ = 7.35-7.30 (m, 4H), 7.06-7.01 (m, 4H), 6.72 (s, 2H), 5.63 (brs, 2H), 3.03 (brs, 2H), 1.50 (s, 3H). ^{13}C-NMR (75 MHz, $CDCl_3$): δ = 185.7, 162.4 (d, *J* = 247 Hz, 2C), 148.0 (2C), 138.5 (2C), 136.0 (d, *J* = 2.9 Hz, 2C), 128.3 (d, *J* = 8.7 Hz, 4C), 115.4 (d, *J* = 21.3 Hz, 4C), 70.8 (2C), 67.5, 27.2. MS (ES+) *m/z* (%): 395 (30.9) $[M+Na]^+$, 393 (23.1). HRMS Calcd for $C_{21}H_{18}F_2O_4$ 395.1070, found 395.1065 $[M+Na]^+$.

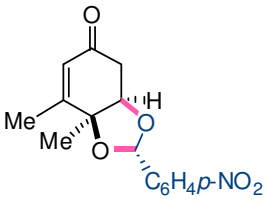


(4*r)-2-((*R**)-(4-Fluorophenyl)(hydroxyl)methyl)-6-((*S**)-(4-hydroxy-4-fluorophenyl) (hydroxyl)methyl)-4-methyl-*p*-quinol (7d)**. Yellow pale solid. M.p.: 138-140 ºC .^{1}H-NMR (300 MHz, $CDCl_3$): δ = 7.35-7.30 (m, 4H), 7.07-7.01 (m, 4H), 6.76 (s, 2H), 5.62 (s, 2H), 3.08 (brs, 2H), 1.44 (s, 3H). ^{13}C-NMR (75 MHz, $CDCl_3$): δ = 185.0, 162.7 (d, *J* = 242 Hz, 2C), 148.9 (2C), 140.5 (2C), 139.6 (2C), 129.5 (d, *J* = 8.3 Hz, 4C), 115.3 (d, *J* = 21.9 Hz, 4C), 69.6 (2C), 67.7, 27.9. MS (ES+) *m/z* (%): 395 (100) $[M+Na]^+$, 355 (37.6), 309 (43.8). HRMS Calcd for $C_{21}H_{18}F_2O_4$ 395.1069, found 395.1065 $[M+Na]^+$.

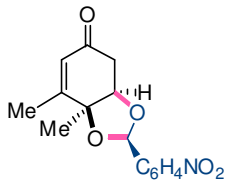


3a,4-Dihydro-7,7a-dimethyl-2-(4-nitrophenyl)benzo[*d*][1,3] dioxol-5(7aH)-one (9). Following general procedure A, the reaction of 3-methyl-*p*-quinol **8** (20 mg, 0.14 mmol) with *p*-nitrobenzaldehyde (25.3 mg, 0.50 mmol) and DMAP (3.4 mg, 0.028 mmol) gave compound **9** as a 90:10 mixture of diastereoisomers, separated after flash chromatography (eluent Hex:AcOEt 3:1): major diastereoisomer (less polar) (27 mg, 67%) and minor diastereoisomer (most polar) (3 mg, 7 %). Time reaction: 3 days.

Major diastereoisomer **(9)**: **(2*S**,3a*R**,7a*S**)-3a,4-Dihydro-7,7a-dimethyl-2-(4-nitrophenyl)benzo[*d*][1,3] dioxol-5(7aH)-one.** White solid. M.p.: 82-84 ºC . ^{1}H-NMR (300 MHz, $CDCl_3$): δ = 8.24 (d, *J* = 8.6 Hz, 2H), 6.63 (d, *J* = 8.6 Hz, 2H), 6.04 (m, 1H), 5.81 (s, 1H), 4.27 (t, *J* = 2.9 Hz, 1H), 2.98 (ddd, *J* = 17.7, 2.5 and 0.9 Hz, 1H), 2.64 (dd, *J* = 17.1 and 3.3 Hz, 1H), 2.09 (d, *J* = 1.4 Hz, 3H), 1.62 (s, 3H). ^{13}C-NMR (75 MHz, $CDCl_3$): δ= 194.3, 156.9, 148.5, 145.1, 128.3, 127.2 (2C), 123.6 (2C), 100.8, 80.7, 79.9, 38.1, 20.0, 17.6. MS (FAB) *m/z* (%): 283 (100), 290 $[M+H]^+$. HRMS Calcd for $C_{15}H_{15}NO_5$ 290.1028, found 290.1024 $[M+H]^+$.



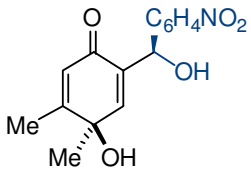
Minor diastereoisomer **(9)**: **(2*R**,3a*R**,7a*S**)-3a,4-Dihydro-7,7a-dimethyl-2-(4-nitrophenyl)benzo[*d*][1,3] dioxol-5(7aH)-one.** Colorless oil. ^{1}H-NMR (300 MHz, $CDCl_3$): δ = 8.20 (d, *J* = 8.3 Hz, 2H), 7.53 (d, *J* = 8.3 Hz, 2H), 6.07 (s, 1H), 5.80 (s, 1H), 4.44 (dd, *J* = 3.5 and 2.3 Hz, 1H), 3.07 (d, *J* = 17.7 Hz, 1H), 2.74 (dd, *J* = 17.7 and 3.8 Hz, 1H), 1.85 (s, 3H), 1.58 (s, 3H). ^{13}C-NMR (75 MHz, $CDCl_3$): δ= 193.8, 159.8, 152.6, 144.4, 127.4 (2C), 125.6, 123.6 (2C), 101.7, 82.1, 79.0, 37.6, 20.7, 18.2. MS (FAB) *m/z* (%): 290 $[M+H]^+$. HRMS Calcd for $C_{15}H_{15}NO_5$ 290.1028, found 290.1033 $[M+H]^+$.



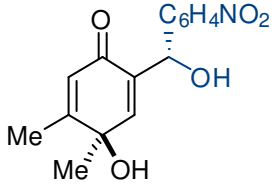
2-(Hydroxy(4-nitrophenyl)methyl)-4,5-dimethyl-*p*-quinol (10).

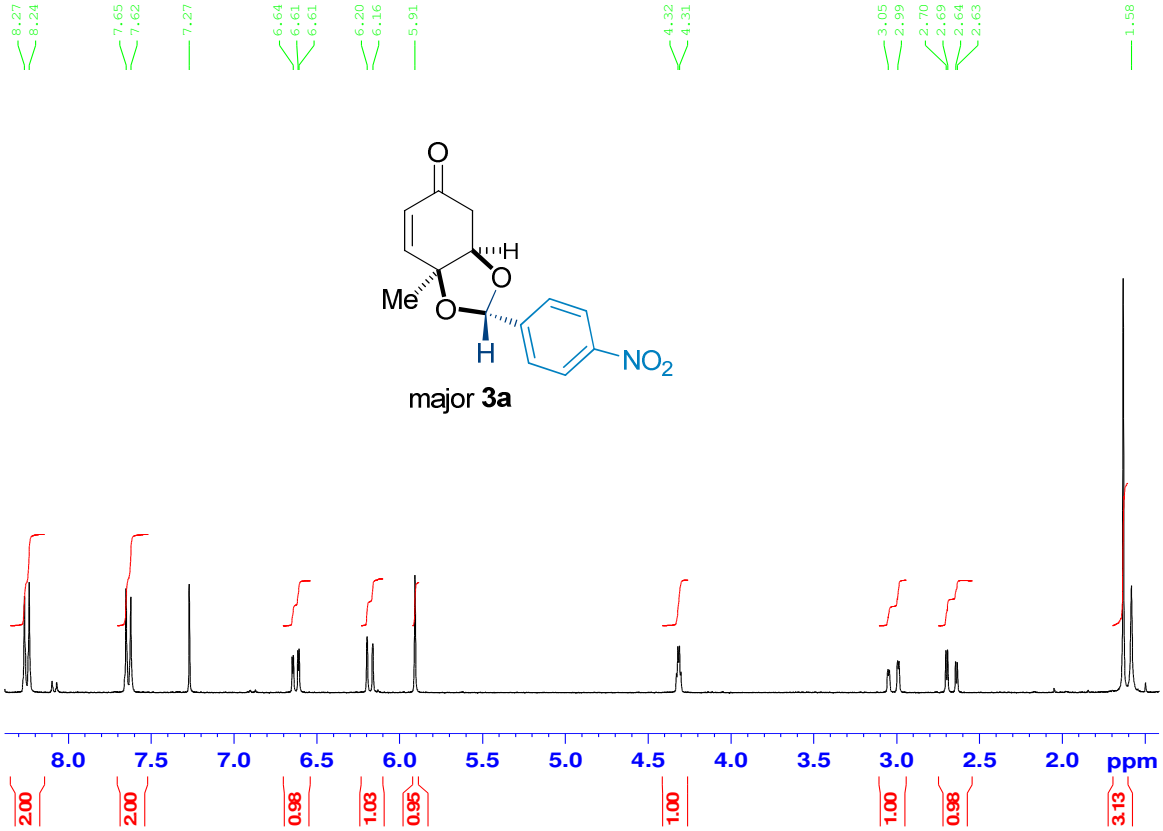
Following general procedure C, the reaction of **8** (40 mg, 0.29 mmol) with *p*-nitrobenzaldehyde (88 mg, 0.58 mmol), DABCO (6.5 mg, 0.058 mmol) and $LiClO_4$ (12.1 mg, 0.20 mmol) gave compound **10** as a 77:23 mixture of diastereoisomers, separated after flash chromatography (eluent Hex:AcOEt 3:1): minor diastereoisomer (less polar) (12 mg, 13%), major diastereoisomer (most polar) (43 mg, 48%). Time reaction: 3 days.

Major diastereoisomer: **(4*R**)-2-((*R**)-Hydroxy-(4-nitrophenyl)methyl)-4,5-dimethyl-*p*-quinol (10)**. White solid. M.p.: 132-134 ºC .^{1}H-NMR (300 MHz, $CDCl_3$): δ = 8.21 (d, *J* = 8.7 Hz, 2H), 7.58 (d, *J* = 8.7 Hz, 2H), 6.69 (d, *J* = 0.9 Hz, 1H), 6.01 (q, *J* = 1.5 Hz, 1H), 5.70 (s, 1H), 3.63 (s, 1H), 2.10 (d, *J* = 1.3 Hz, 3H), 1.45 (s, 3H). ^{13}C-NMR (75 MHz, $CDCl_3$): δ = 185.7, 162.9, 149.1, 148.5, 147.4, 137.1, 127.3 (2C), 125.8, 123.7 (2C), 71.5, 69.6, 26.1, 17.8. MS (ES) *m/z* (%): 312 (100) $[M+Na]^+$. HRMS Calcd for $C_{14}H_{15}NO_5$ 312.0848, found 312.0836 $[M+Na]^+$.



Minor diastereoisomer: **(4*R**)-2-((*S**)-Hydroxy-(4-nitrophenyl)methyl)-4,5-dimethyl-*p*-quinol (10)**. Pale yellow solid. M.p.: 152-154 ºC. ^{1}H-NMR (300 MHz, $CDCl_3$): δ = 8.21 (d, *J* = 8.4 Hz, 2H), 7.58 (d, *J* = 8.9 Hz, 2H), 6.66 (d, *J* = 1.0 Hz, 1H), 6.02 (q, *J* = 1.5 Hz, 1H), 5.72 (d, *J* = 3.3 Hz, 1H), 3.55 (d, *J* = 5.3 Hz, 1H), 2.10 (d, *J* = 1.2 Hz, 3H), 1.47 (s, 3H). ^{13}C-NMR (75 MHz, $CDCl_3$): δ = 185.6, 162.8, 148.9, 148.4, 147.4, 137.2, 127.3 (2C), 125.7, 123.6 (2C), 71.2, 69.6, 26.2, 17.8. MS (ES) *m/z* (%): 312 (100) $[M+Na]^+$. HRMS Calcd for $C_{14}H_{15}NO_5$ 312.0842, found 312.08273 $[M+Na]^+$.

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2.69
2.64
2.63
1.58
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O
Me
O
H
NO2
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5.5
5.0
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0.95
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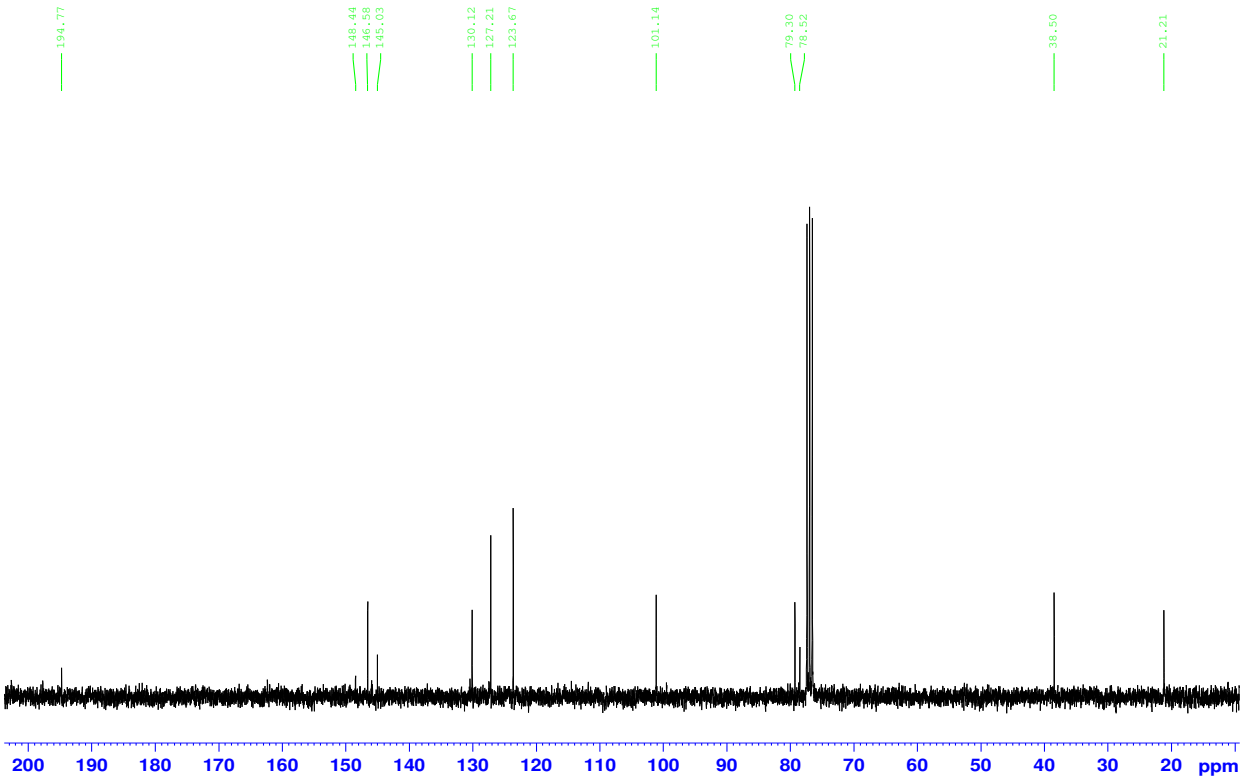
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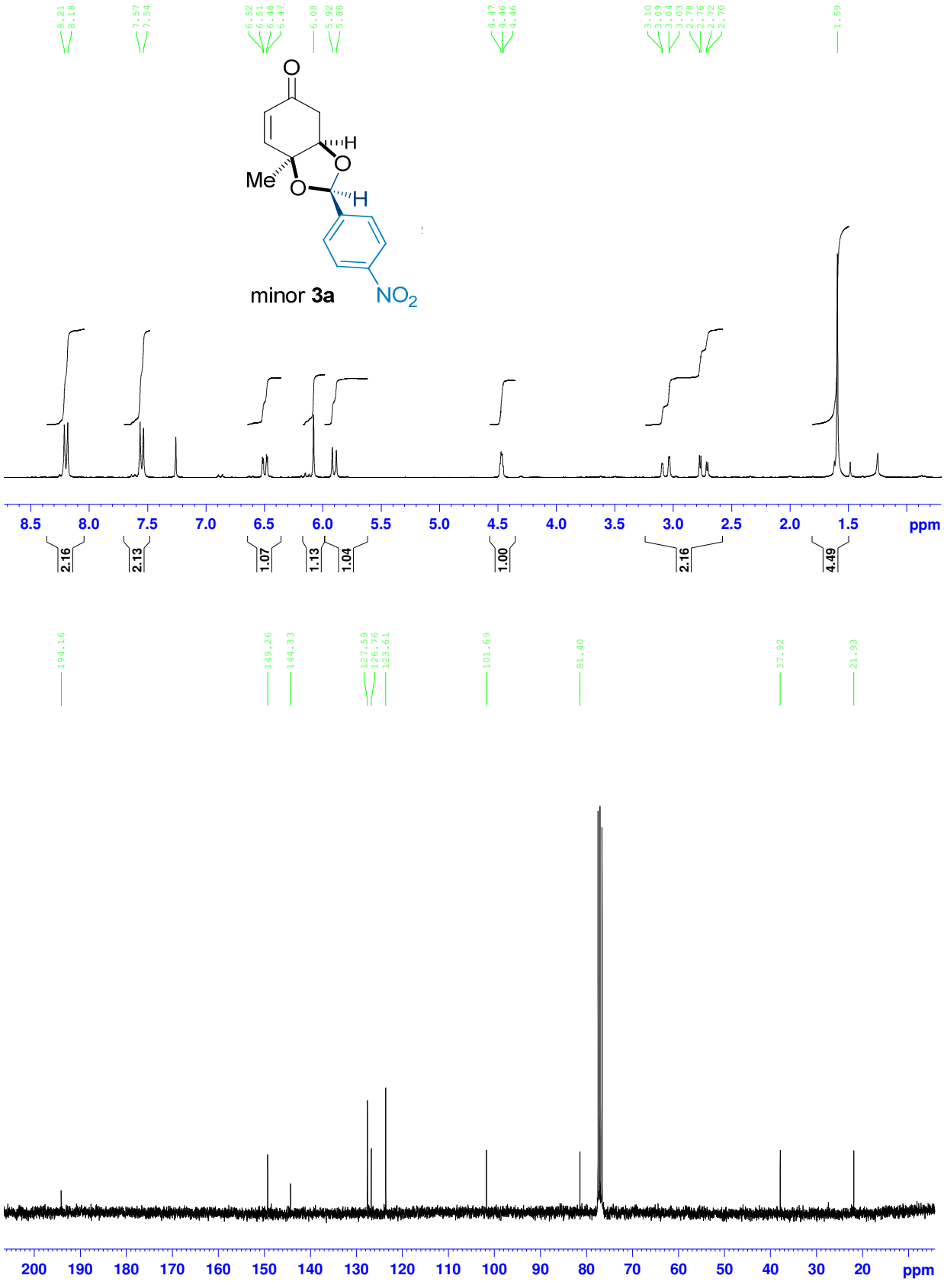
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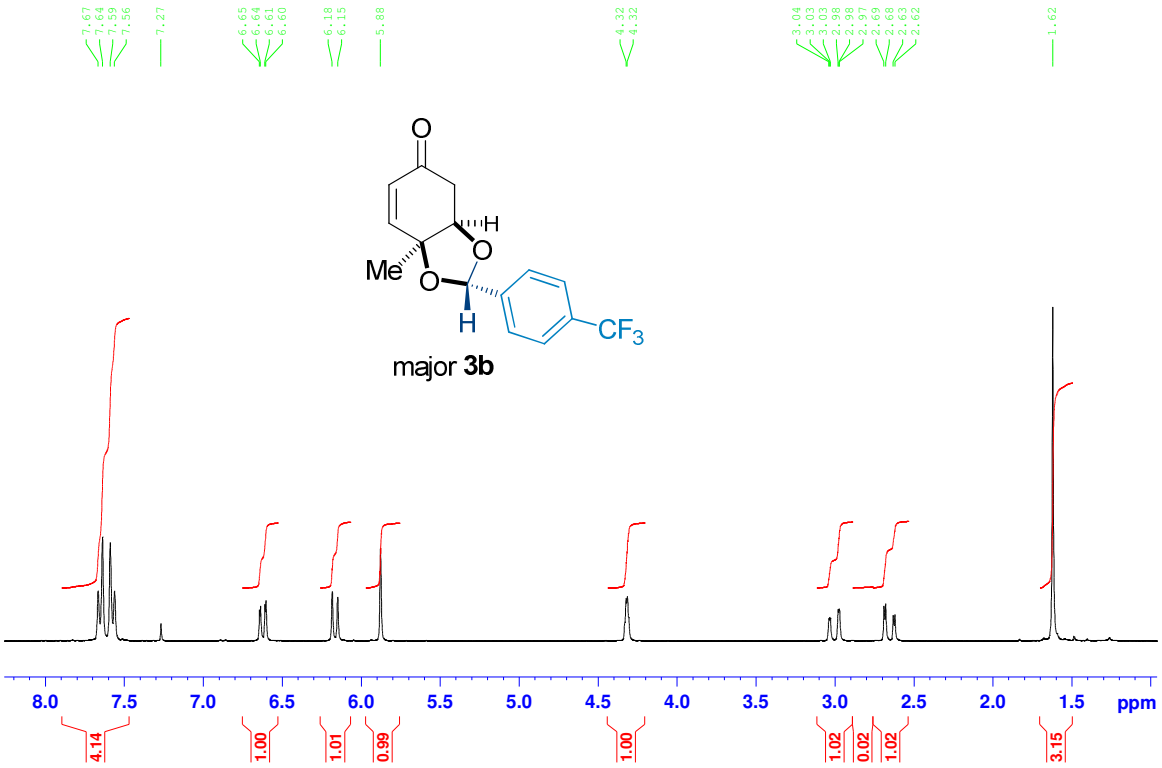
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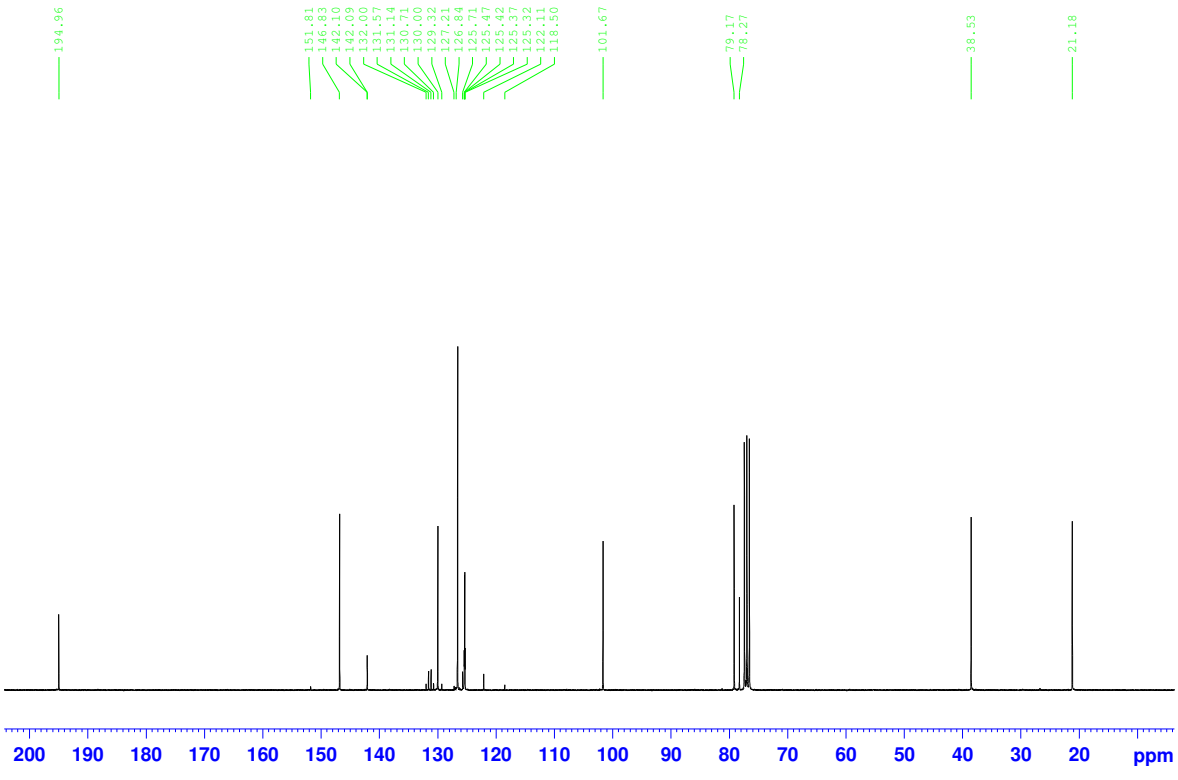
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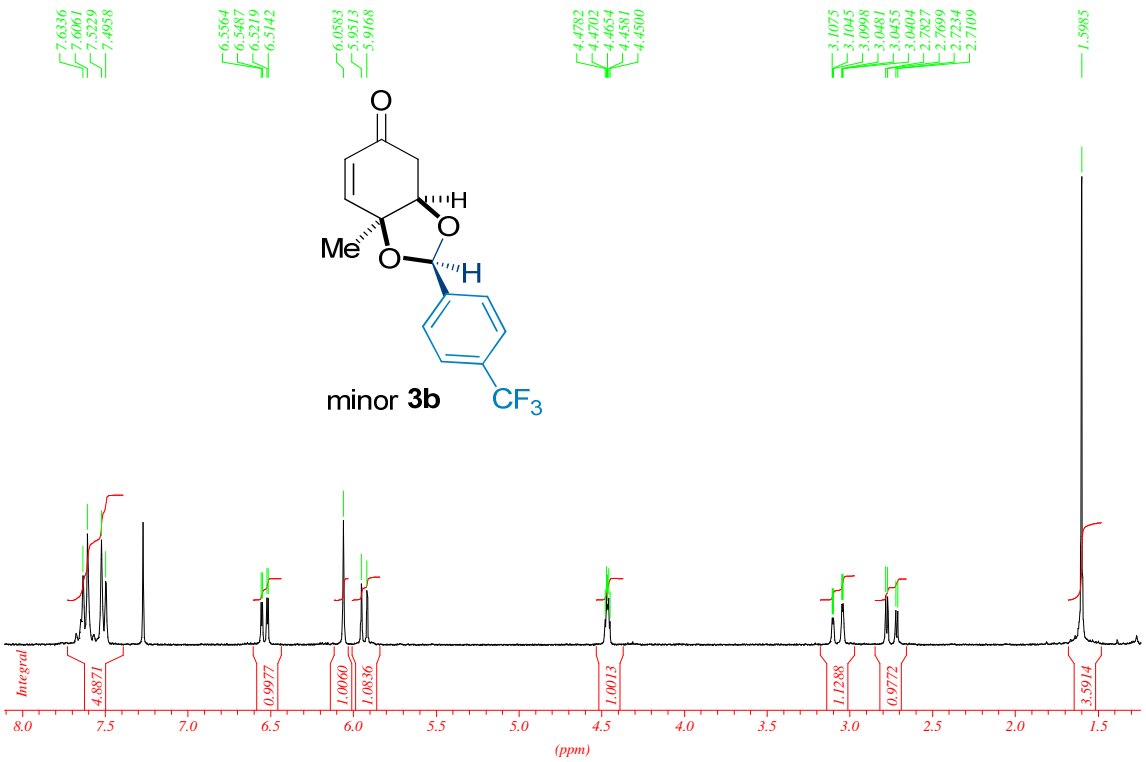
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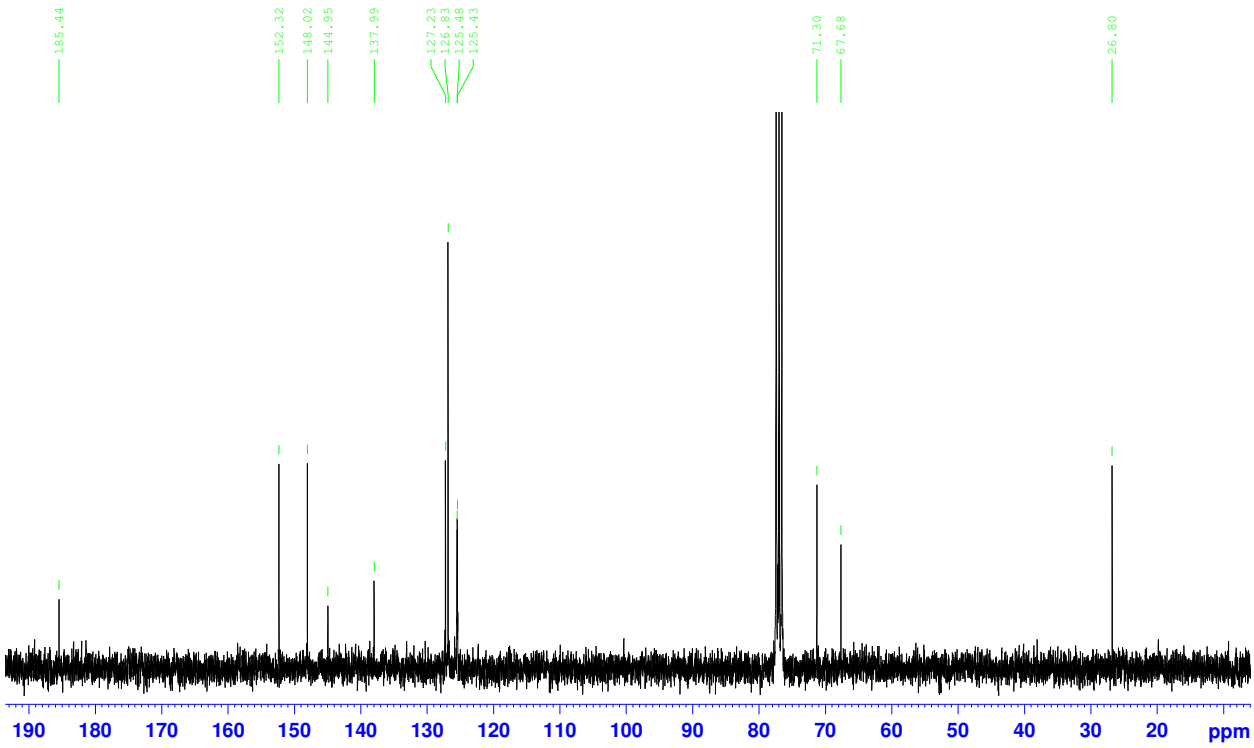
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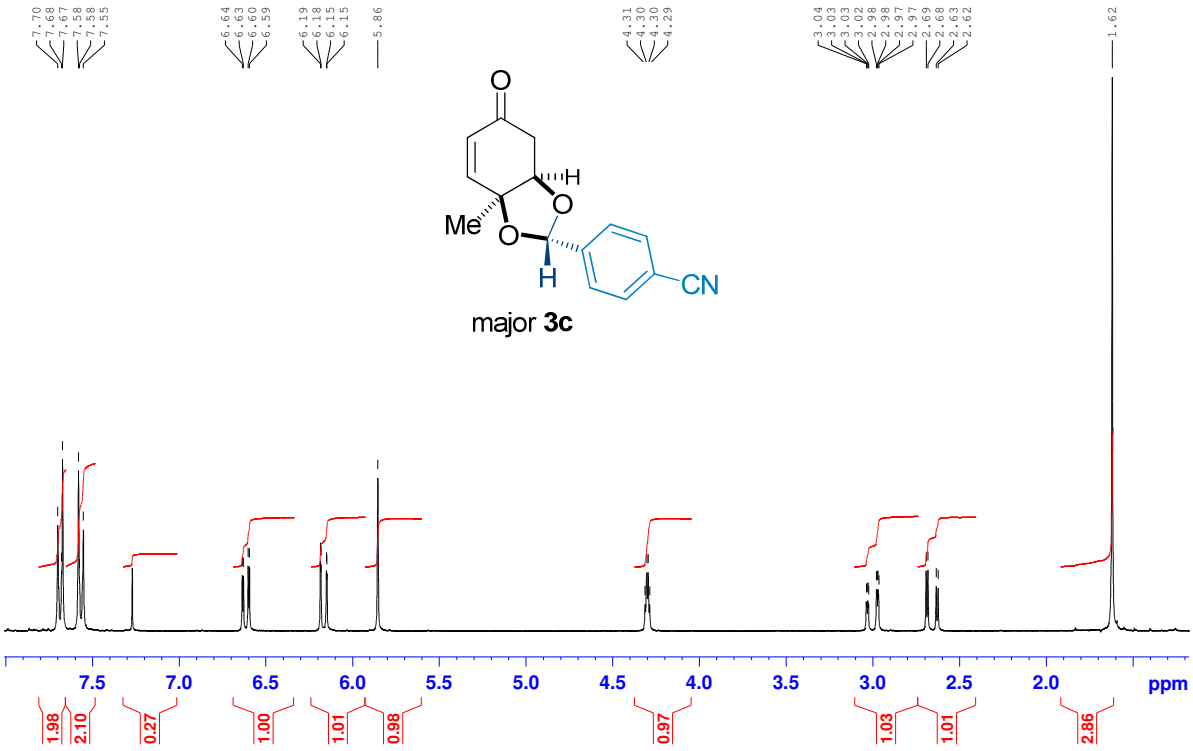
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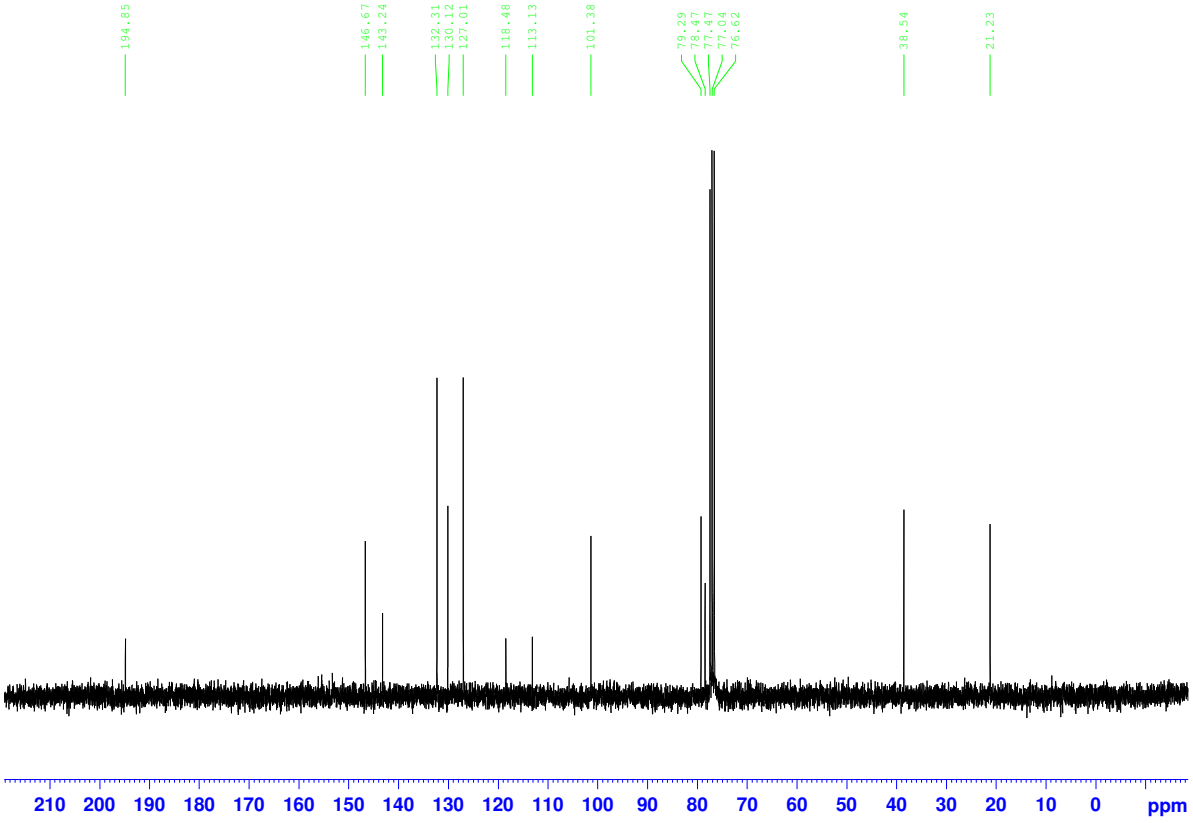
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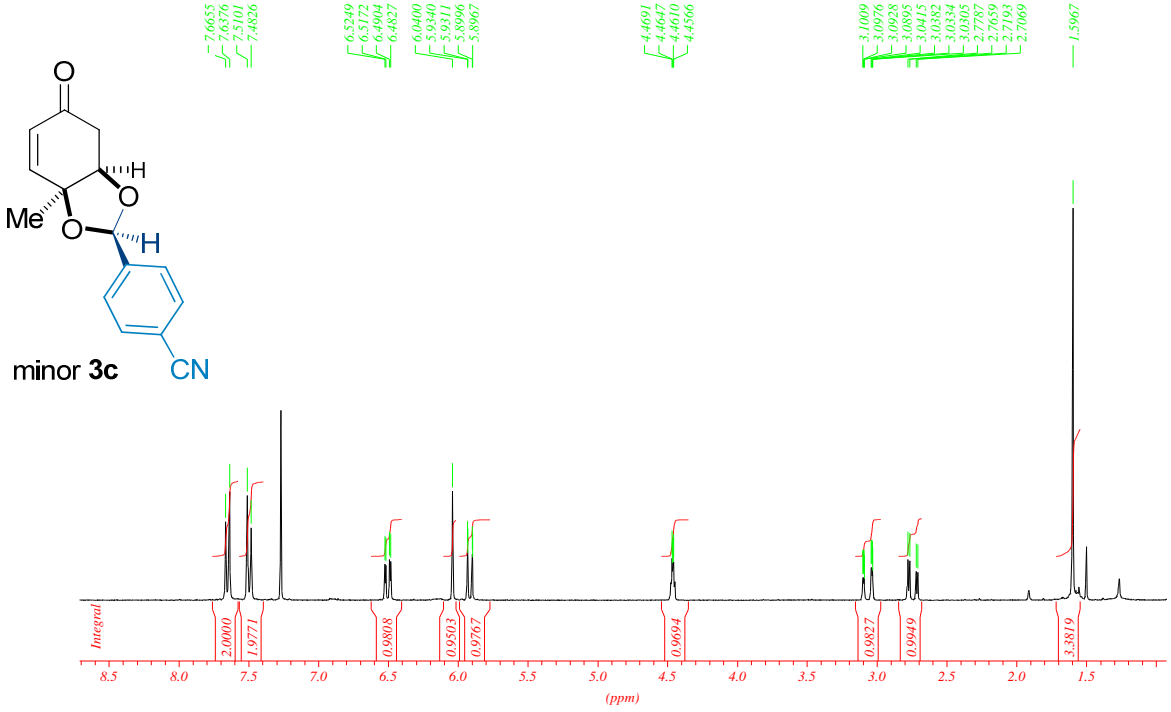
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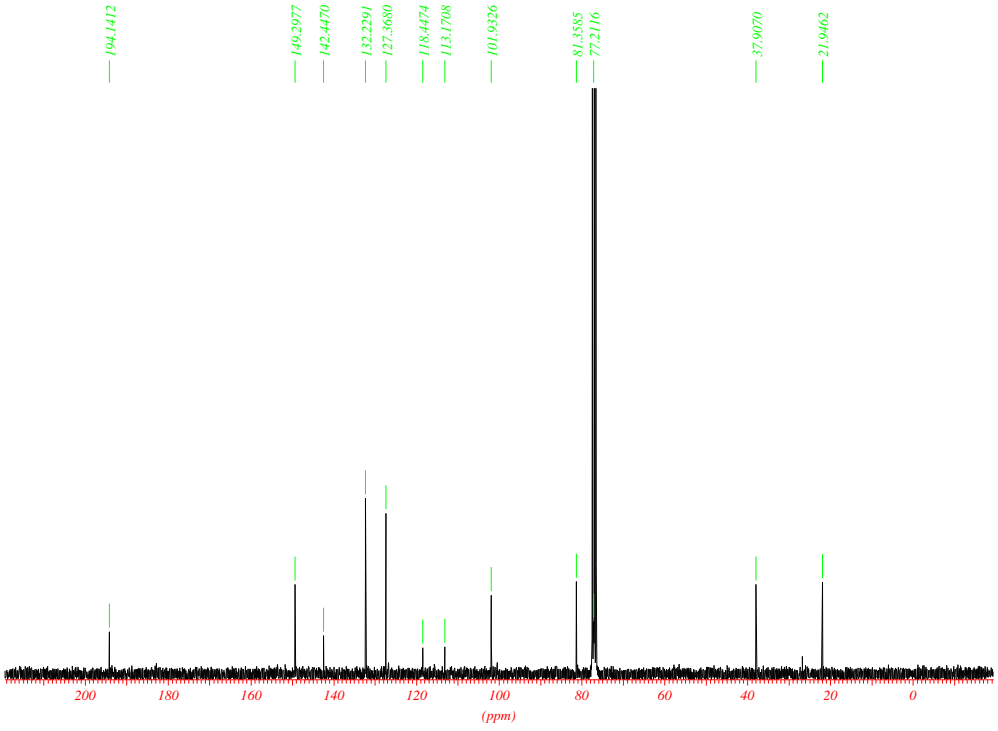
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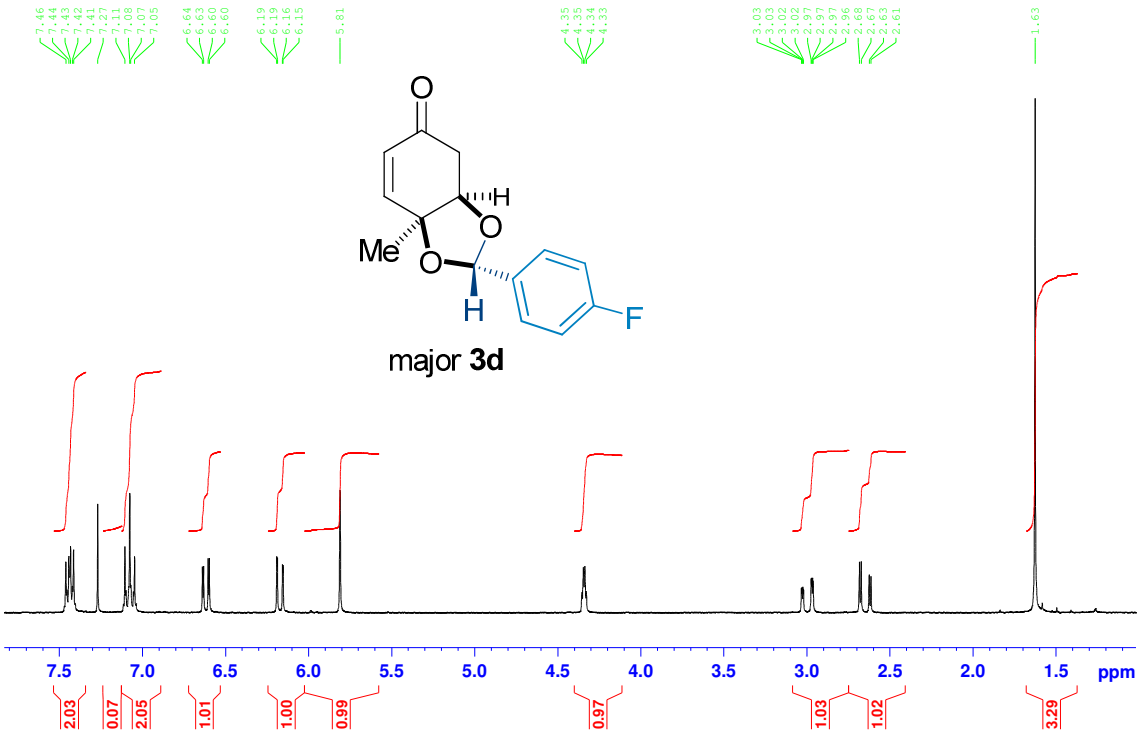
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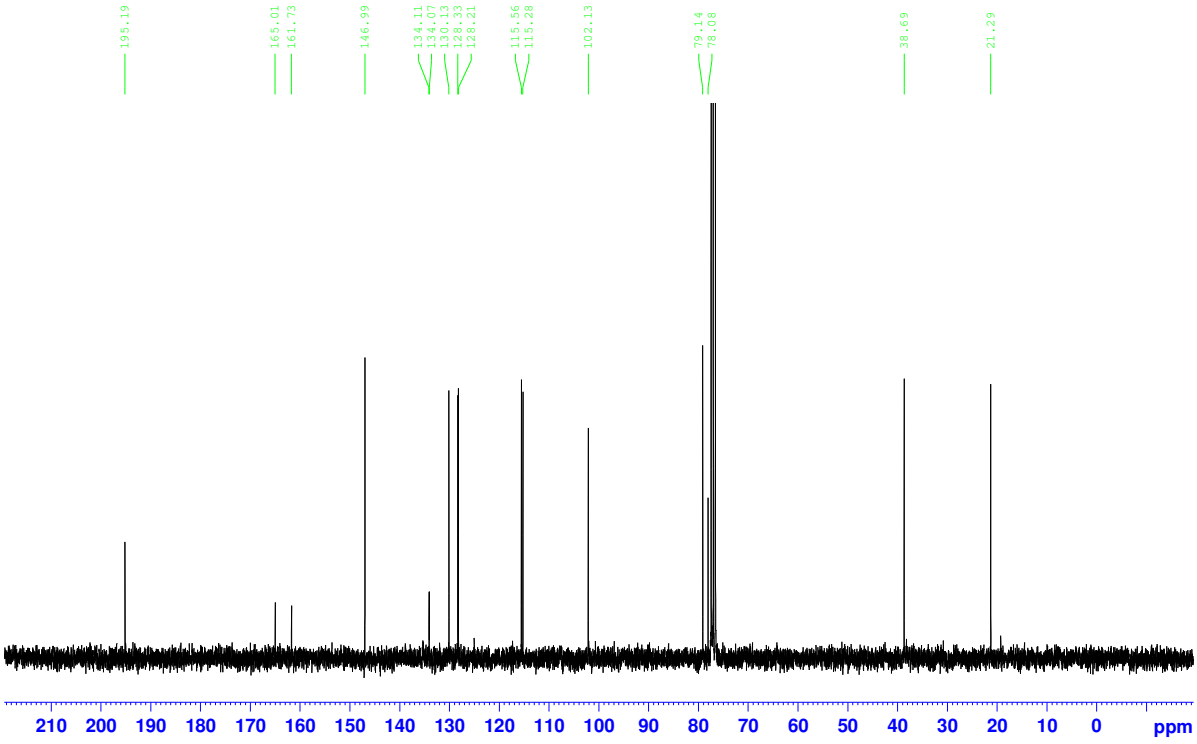
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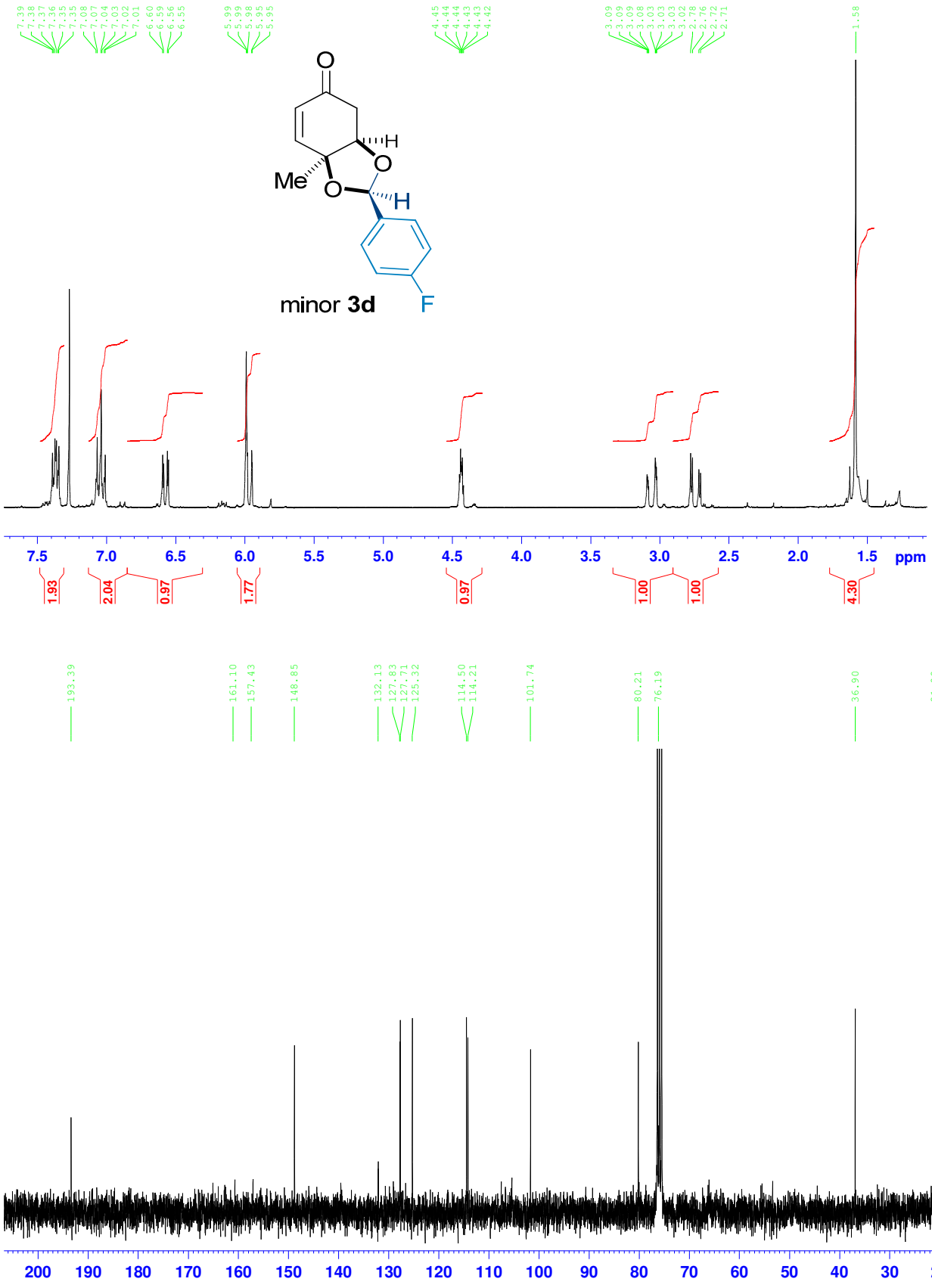
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7.07
7.04
7.03
7.02
7.01
6.60
6.59
6.56
6.55
5.99
5.99
5.98
5.95
5.95
4.45
4.44
4.44
4.43
4.43
4.42
3.09
3.09
3.09
3.08
3.03
3.03
3.03
3.02
2.78
2.76
2.72
2.71
1.58
O
H
O
Me
O
H
F
minor 3d
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
ppm
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2.04
0.97
1.77
0.97
1.00
1.00
4.30
193.39
161.10
157.43
148.85
132.13
127.83
127.71
125.32
114.50
114.21
101.74
80.21
76.19
36.90
21.08
200
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160
150
140
130
120
110
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80
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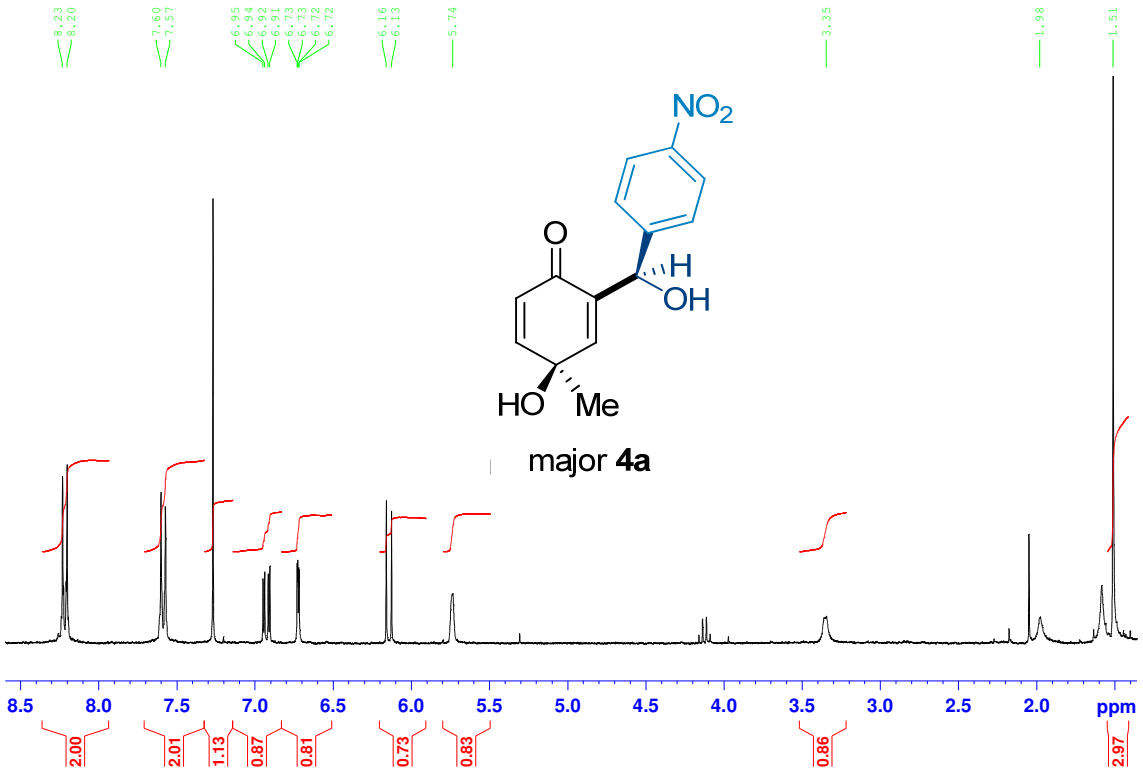
50
40
30
20
ppm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6.91
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6.73
6.72
6.72
6.16
6.13
5.74
3.35
1.98
1.51
NO2
O
H
OH
HO
Me
major 4a
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
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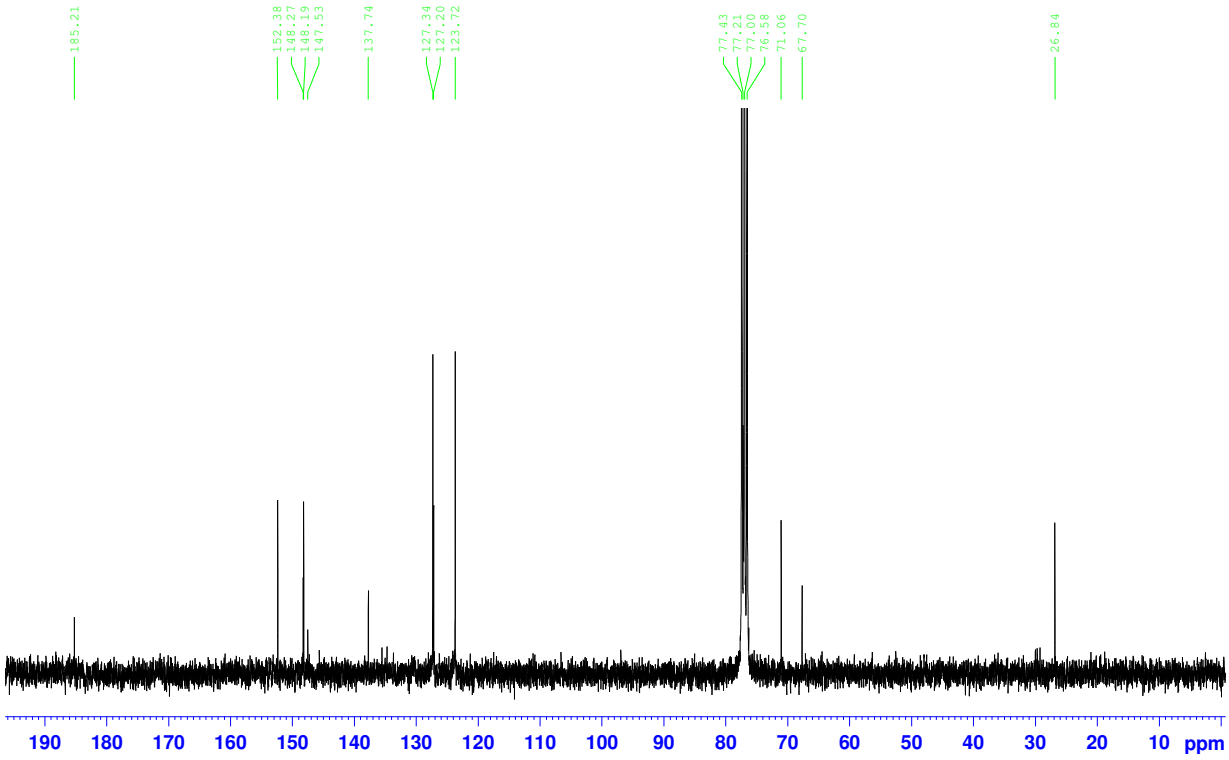
2.97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127.20
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77.21
77.00
76.58
71.06
67.70
26.84
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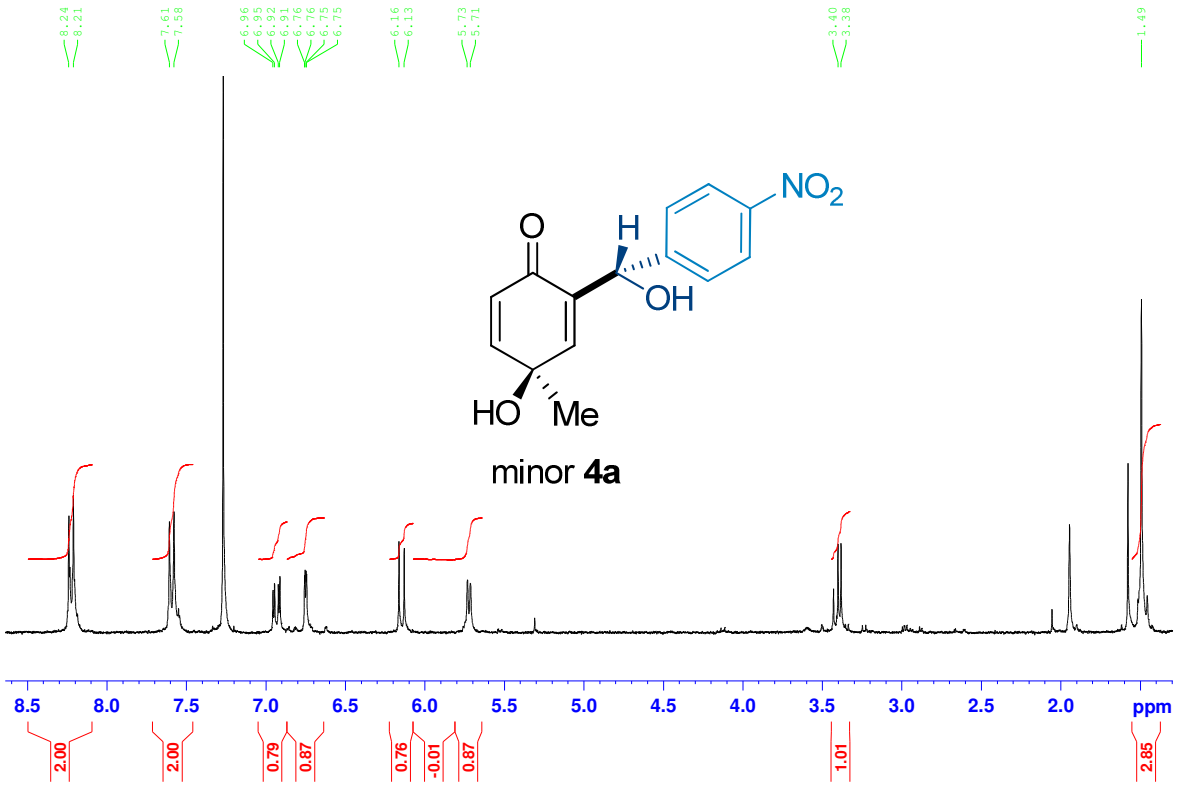
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm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8.21
7.61
7.58
6.96
6.95
6.92
6.91
6.76
6.76
6.75
6.75
6.16
6.13
5.73
5.71
3.40
3.38
1.49
NO2
O
H
OH
HO
Me
minor 4a
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
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ppm
2.00
2.00
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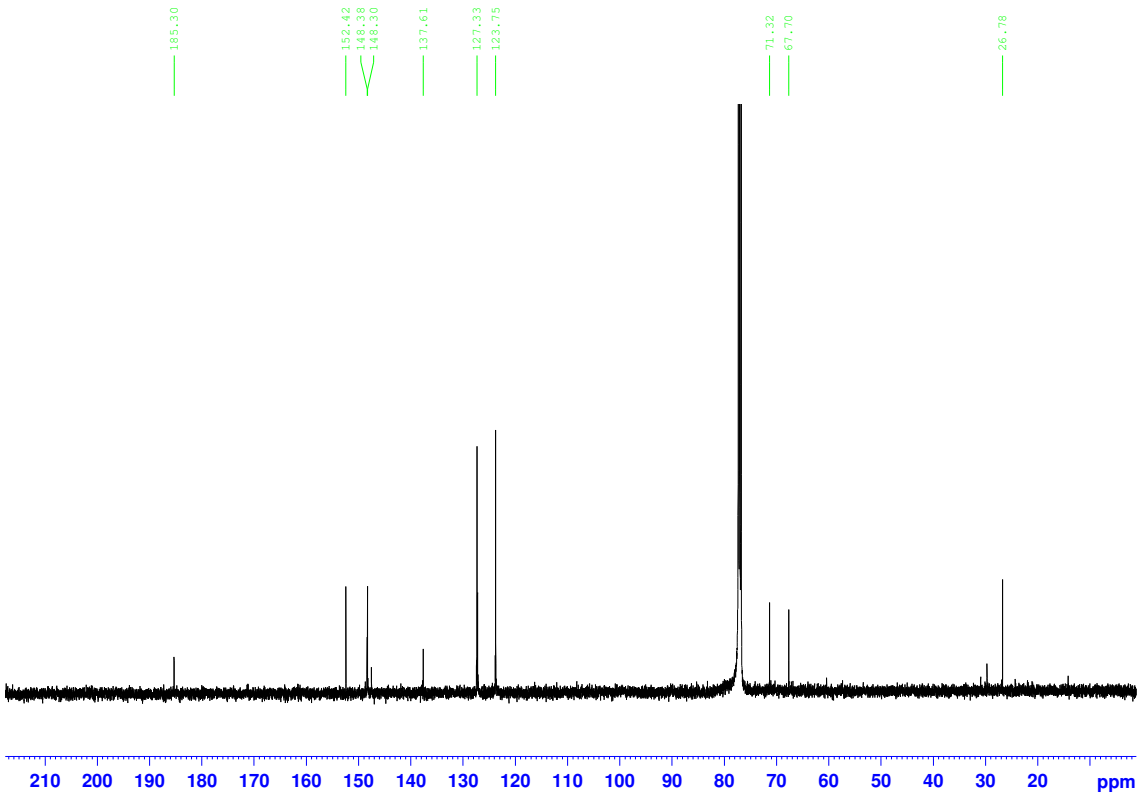
0.76
-0.01
0.87
1.01
2.85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148.30
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127.33
123.75
71.32
67.70
26.78
210
200
190
180
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160
150
140
130
120
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90
80
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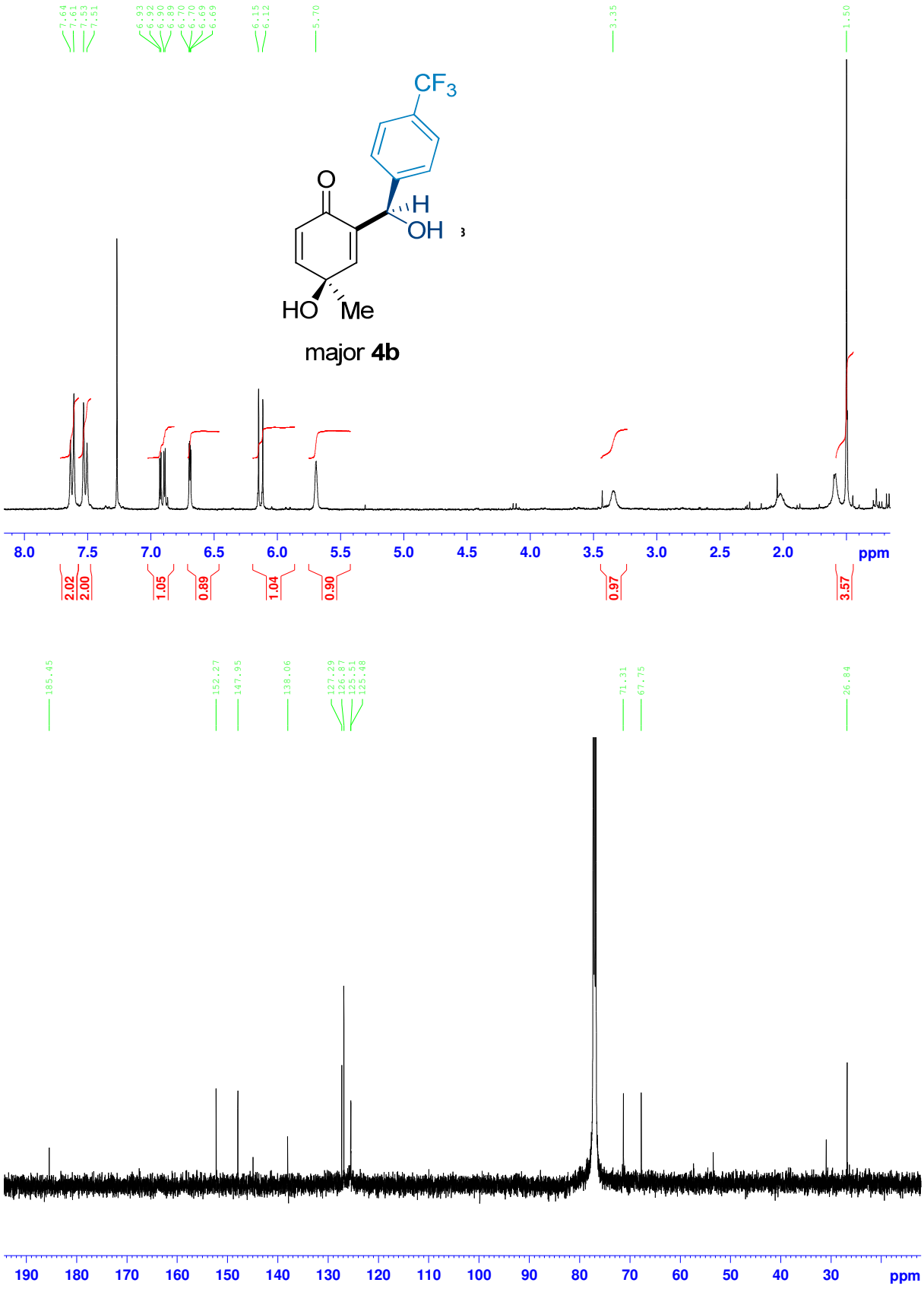
60
50
40
30
20
ppm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7.61
7.53
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6.92
6.90
6.89
6.70
6.70
6.69
6.69
6.15
6.12
5.70
3.35
1.50
CF3
O
H
OH
HO
Me
major 4b
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
ppm
2.02
2.00
1.05
0.89
1.04
0.90
0.97
3.57
185.45
152.27
147.95
138.06
127.29
126.87
125.51
125.48
71.31
67.75
26.84
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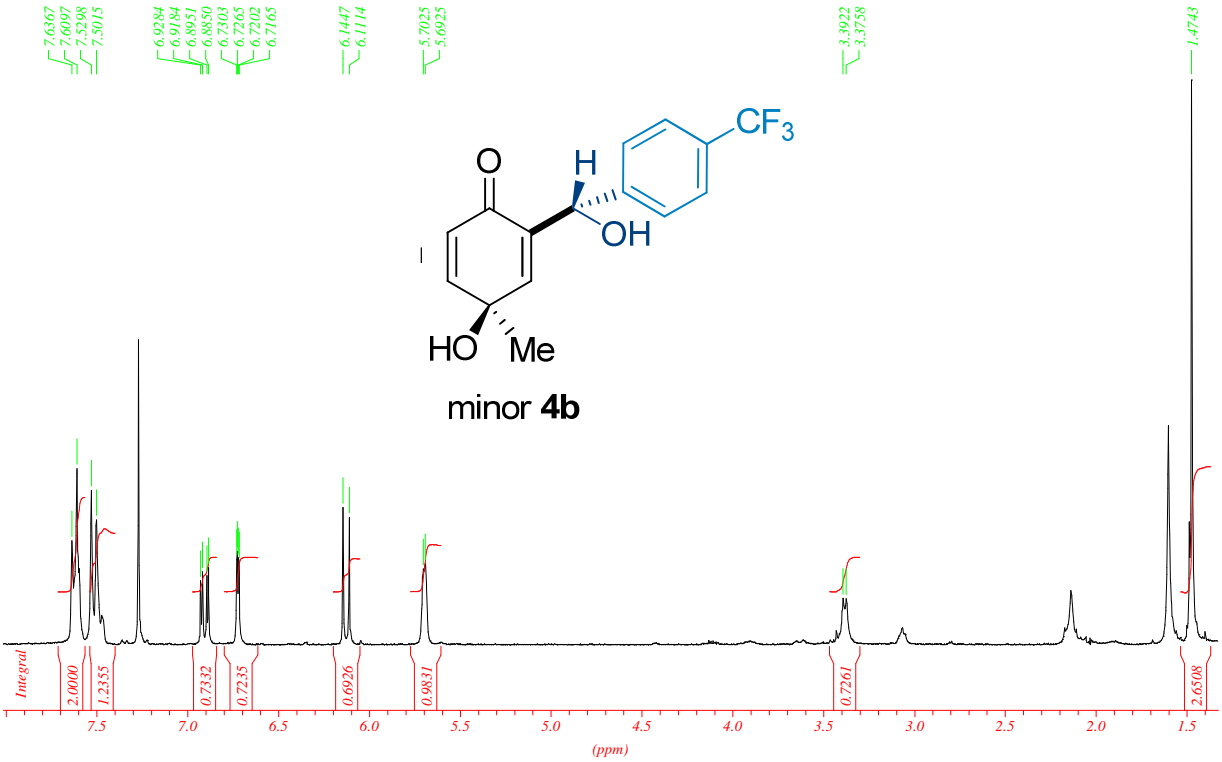
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
ppm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6.9284
6.9184
6.8951
6.8850
6.7303
6.7265
6.7202
6.7165
6.1447
6.1114
5.7025
5.6925
3.3922
3.3758
1.4743
CF3
O
H
OH
HO
Me
minor 4b
Integral
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1.2355
0.7332
0.7235
0.6926
0.9831
0.7261
2.6508
7.5
7.0
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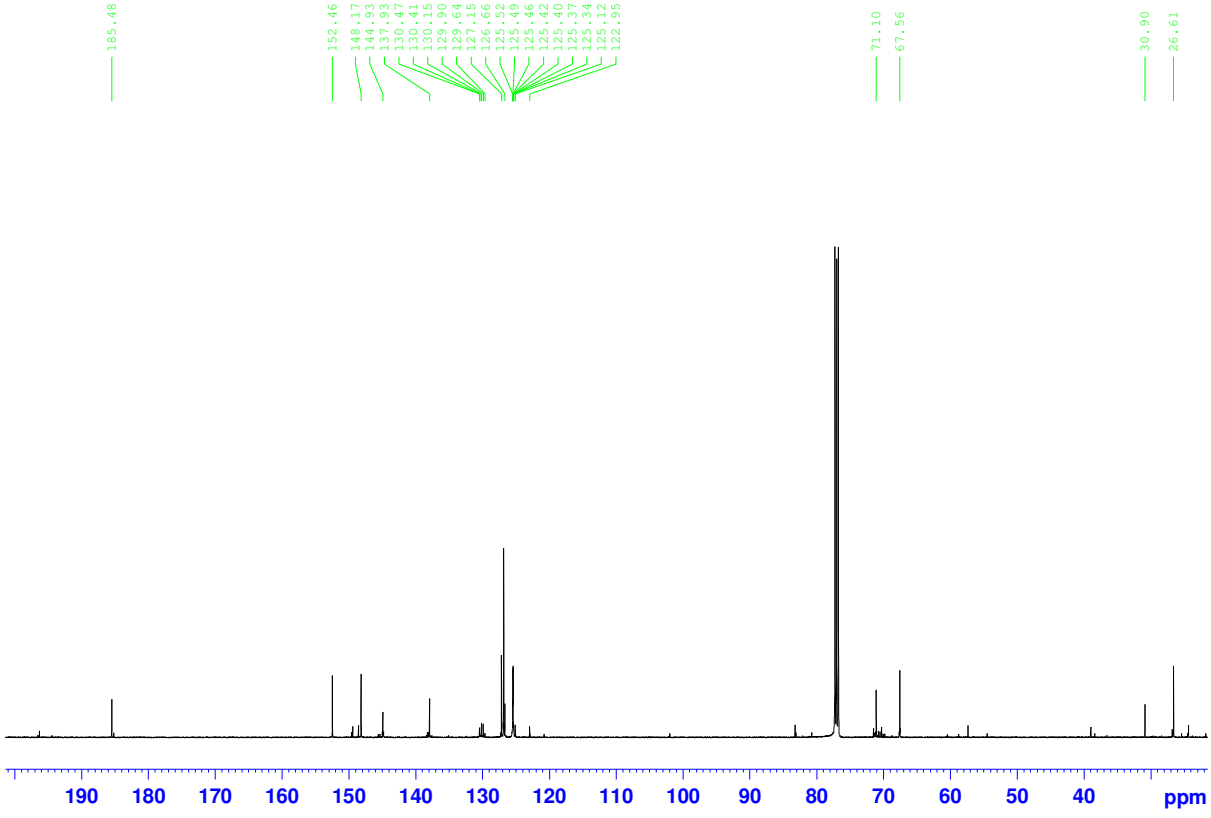
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
(ppm)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144.93
137.93
130.47
130.41
130.15
129.90
129.64
127.15
126.66
125.52
125.49
125.46
125.42
125.40
125.37
125.34
125.12
122.95
71.10
67.56
30.90
26.61
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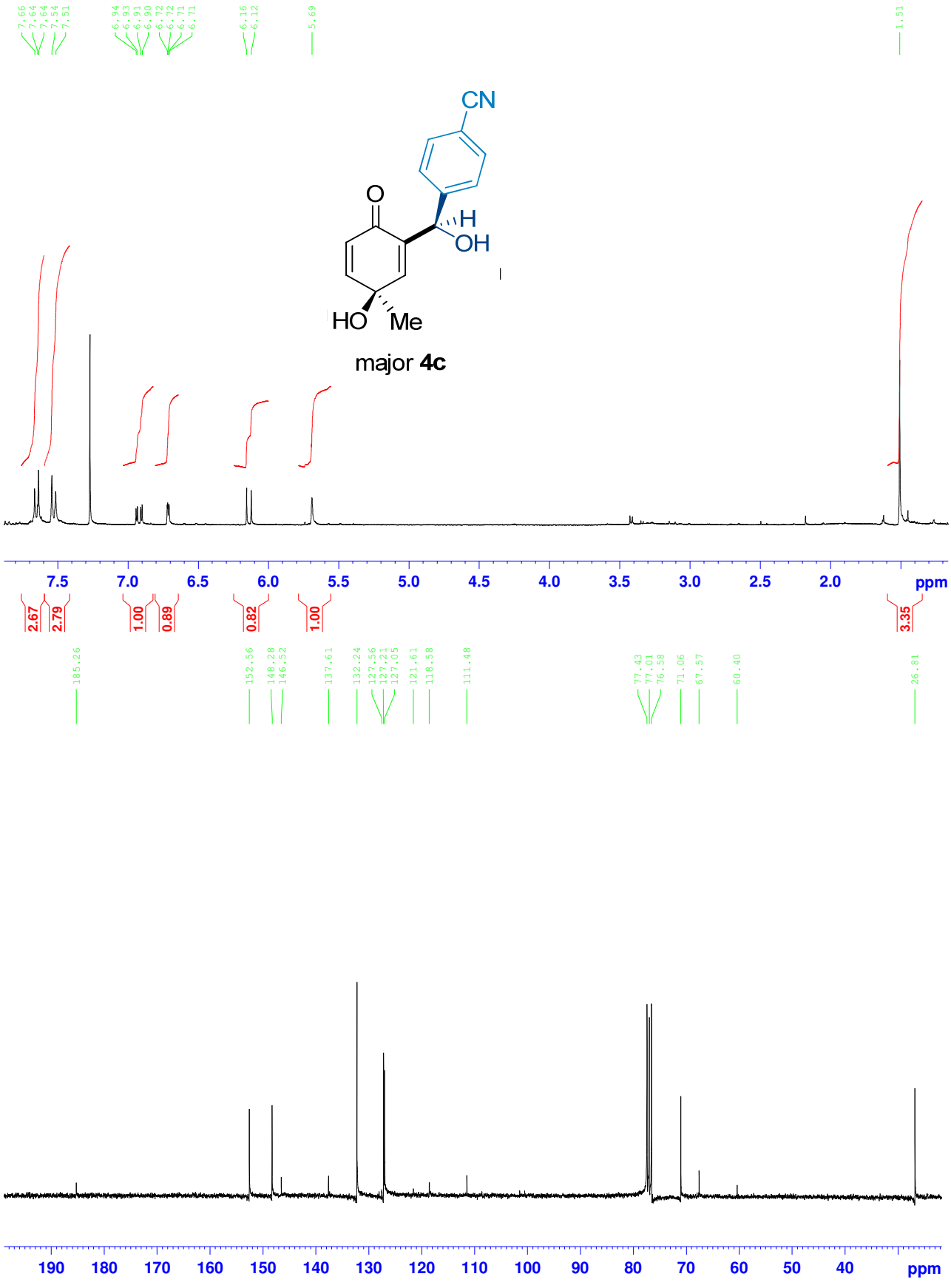
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
ppm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7.64
7.54
7.51
6.94
6.93
6.91
6.90
6.72
6.72
6.71
6.71
6.16
6.12
5.69
1.51
CN
O
H
OH
HO
Me
major 4c
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
ppm
2.67
2.79
1.00
0.89
0.82
1.00
3.35
185.26
152.56
148.28
146.52
137.61
132.24
127.56
127.21
127.05
121.61
118.58
111.48
77.43
77.01
76.58
71.06
67.57
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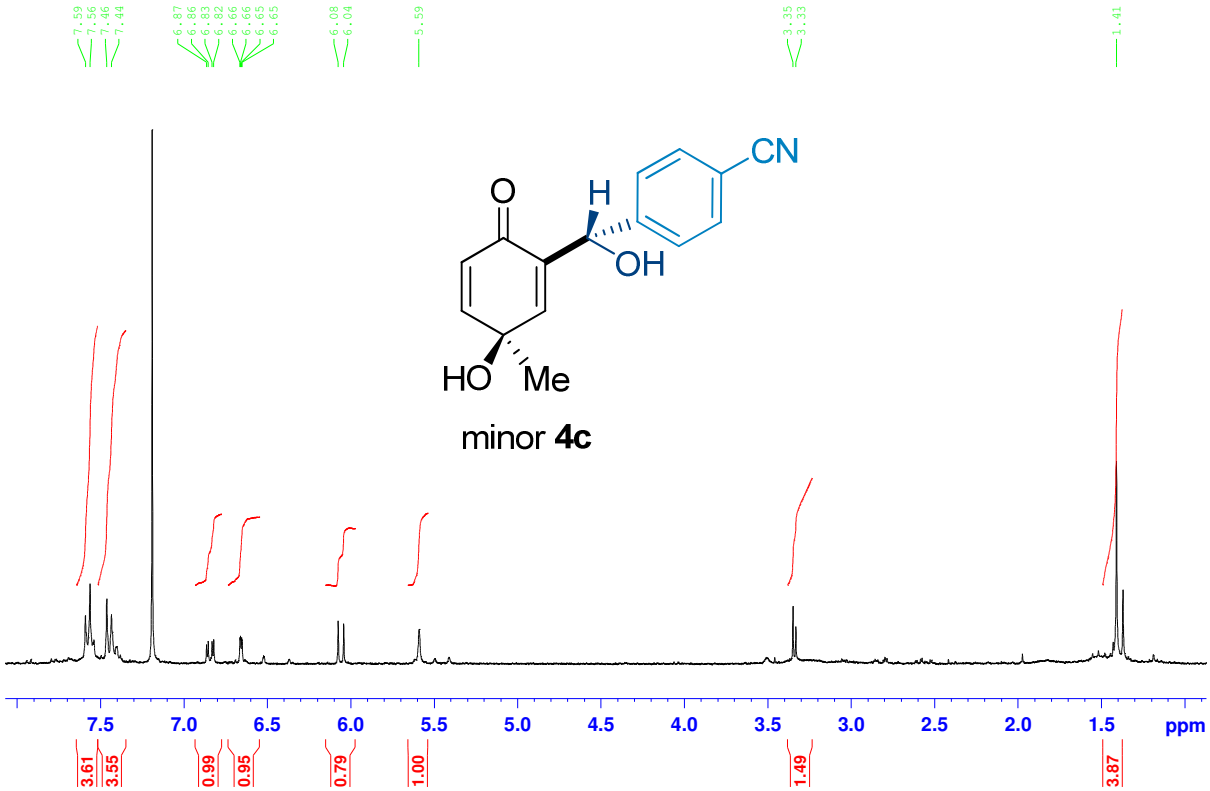
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
ppm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7.56
7.46
7.44
6.87
6.86
6.83
6.82
6.66
6.66
6.65
6.65
6.08
6.04
5.59
3.35
3.33
1.41
CN
O
H
OH
HO
Me
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
ppm
3.61
3.55
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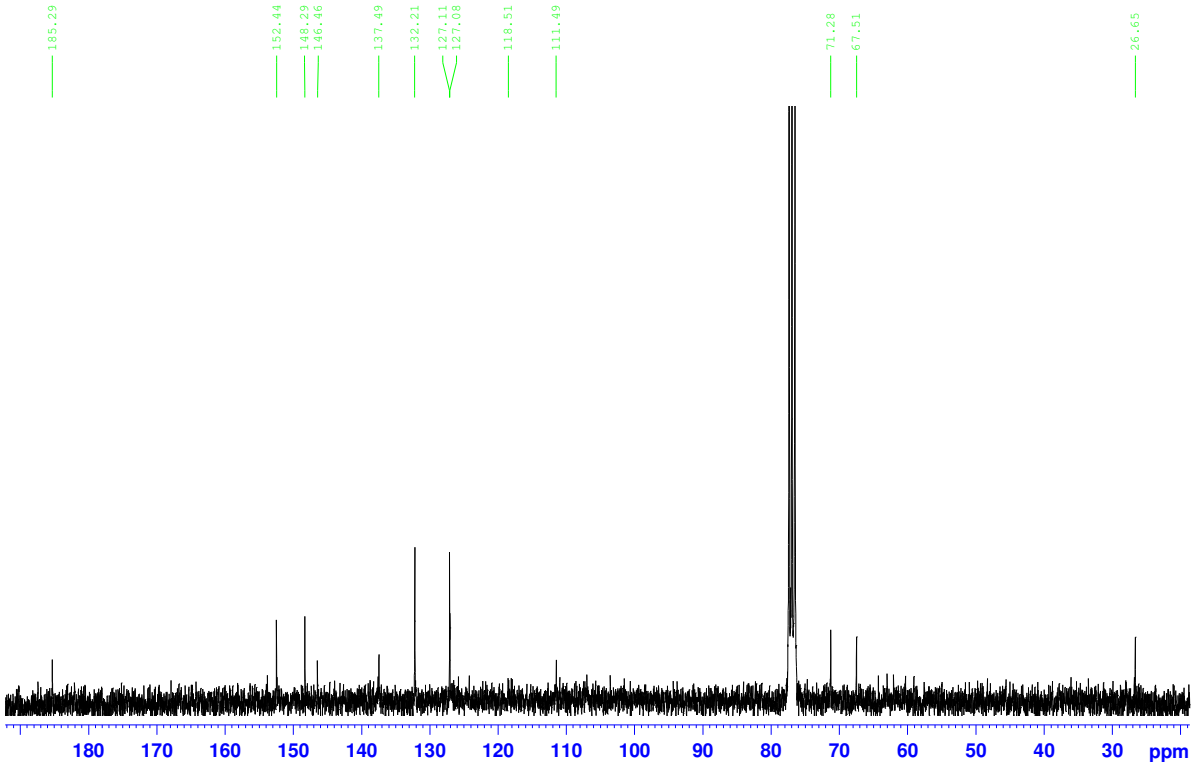
0.95
0.79
1.00
1.49
3.87

minor **4c**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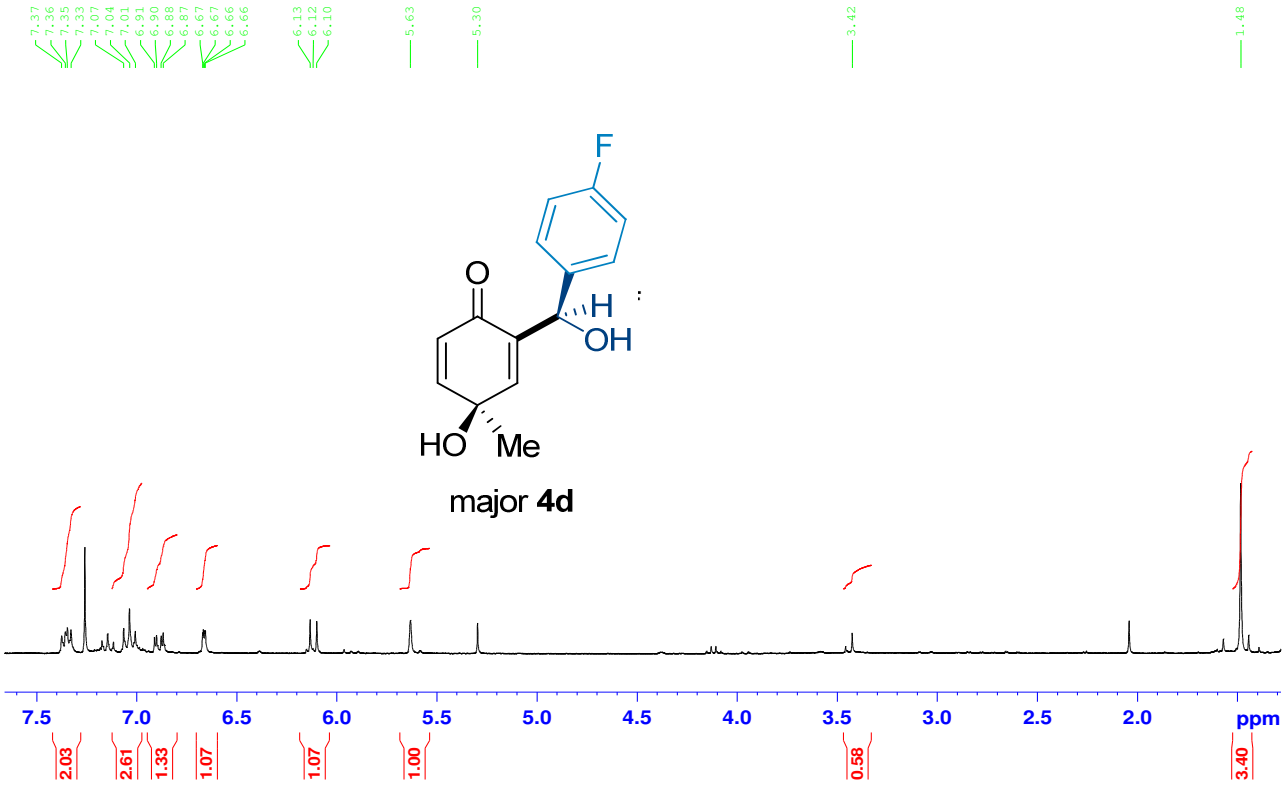
148.29
146.46
137.49
132.21
127.11
127.08
118.51
111.49
71.28
67.51
26.65
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
ppm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7.33
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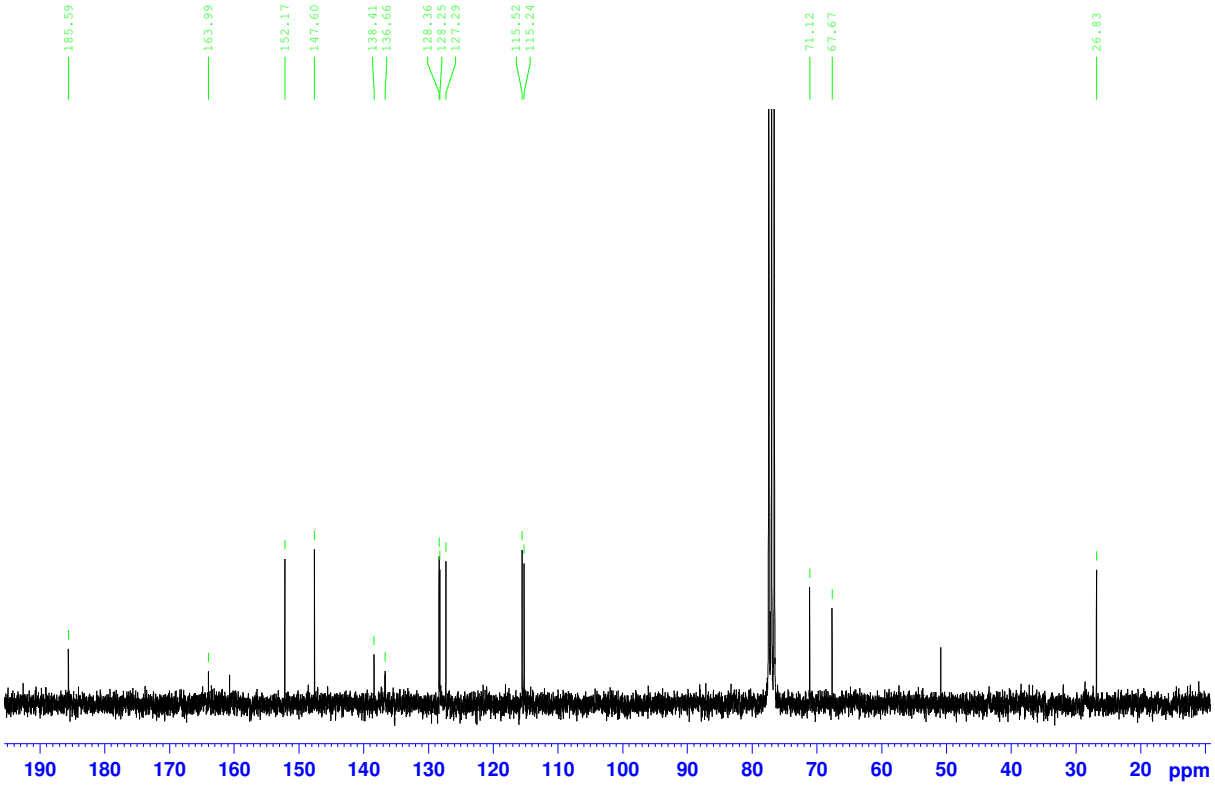
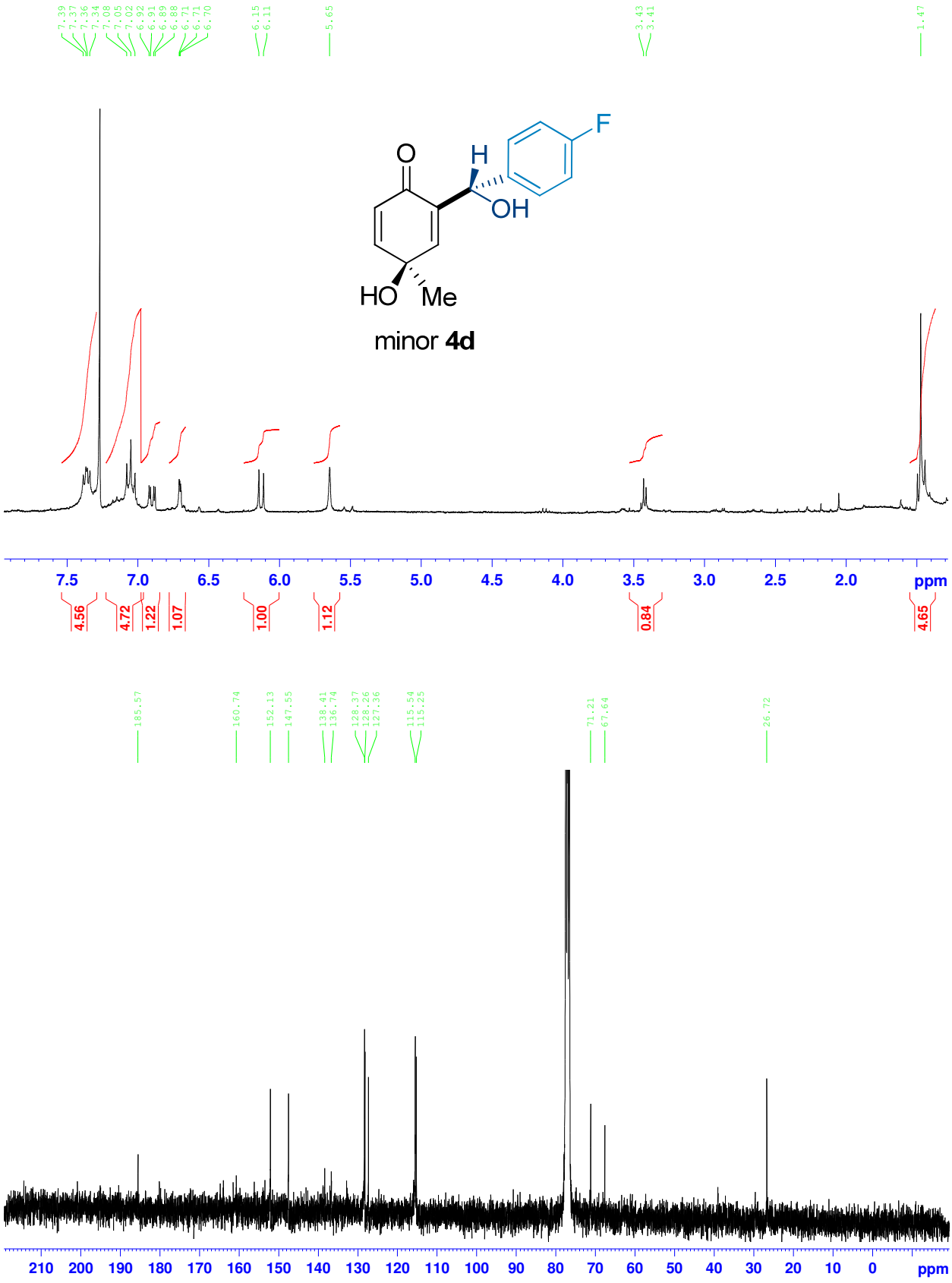
7.04
7.01
6.91
6.90
6.88
6.87
6.67
6.67
6.66
6.66
6.13
6.12
6.10
5.63
5.30
3.42
1.48
F
O
H
OH
HO
Me
major 4d
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
ppm
2.03
2.61
1.33
1.07
1.07
1.00
0.58
3.40


185.59
163.99
152.17
147.60
138.41
136.66
128.36
128.25
127.29
115.52
115.24
71.12
67.67
26.83
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
ppm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7.37
7.36
7.34
7.08
7.05
7.02
6.92
6.91
6.89
6.88
6.71
6.71
6.70
6.15
6.11
5.65
3.43
3.41
1.47
O
H
F
OH
HO
Me
minor 4d
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
ppm
4.56
4.72
1.22
1.07
1.00
1.12
0.84
4.65
185.57
160.74
152.13
147.55
138.41
136.74
128.37
128.26
127.36
115.54
115.25
71.21
67.64
26.72
210
200
190
180
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160
150
140
130
120
110
100
90
80
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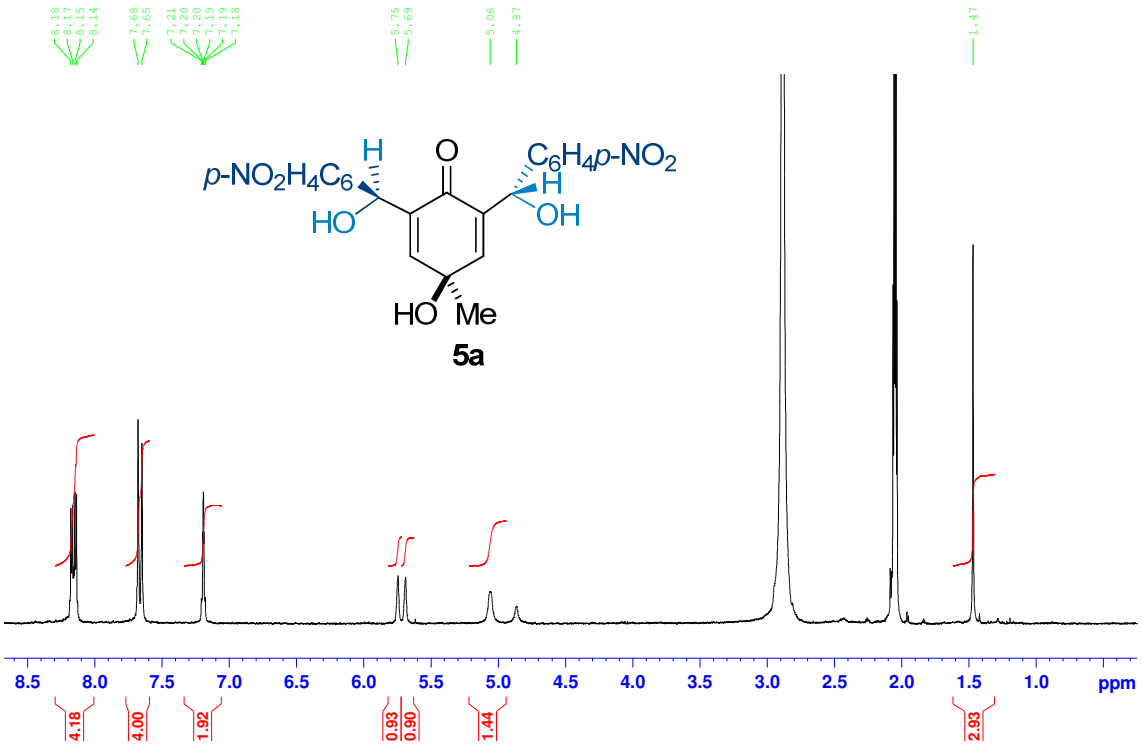
60
50
40
30
20
10
0
ppm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8.17
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7.65
7.21
7.20
7.20
7.19
7.19
7.18
5.75
5.69
5.06
4.87
1.47
p-NO2H4C6
H
O
C6H4p-NO2
H
HO
OH
HO
Me
5a
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
ppm
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1.92
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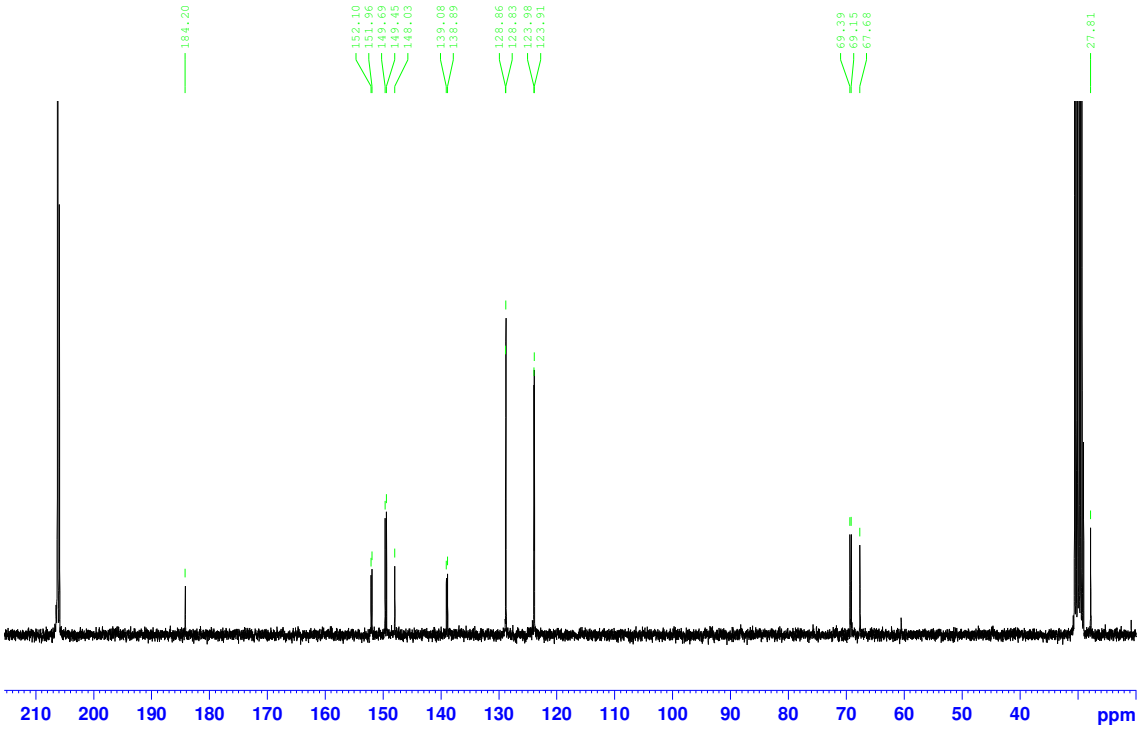
1.44
2.93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138.89
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128.83
123.98
123.91
69.39
69.15
67.68
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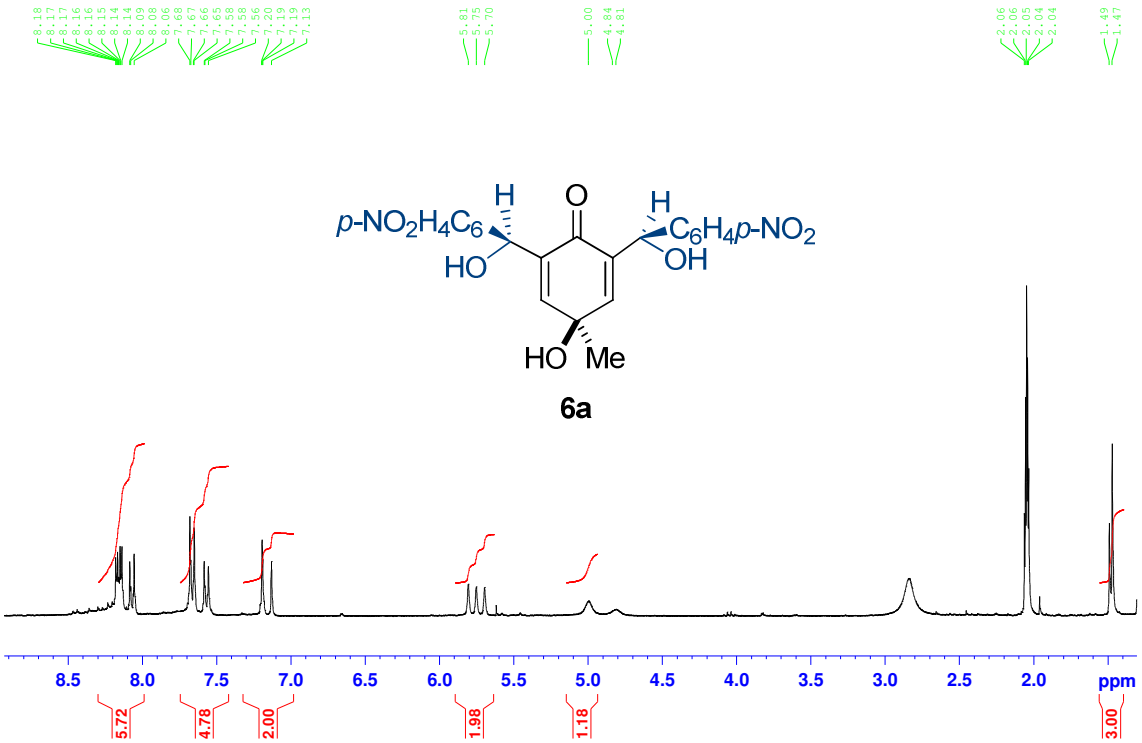
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
ppm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8.17
8.17
8.16
8.16
8.15
8.14
8.14
8.09
8.08
8.06
7.68
7.67
7.66
7.65
7.58
7.56
7.20
7.19
7.13
5.81
5.75
5.70
5.00
4.84
4.81
2.06
2.06
2.05
2.04
2.04
1.49
1.47
H
O
H
p-NO2H4C6
C6H4p-NO2
HO
OH
HO
Me
6a
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
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ppm
5.72
4.78
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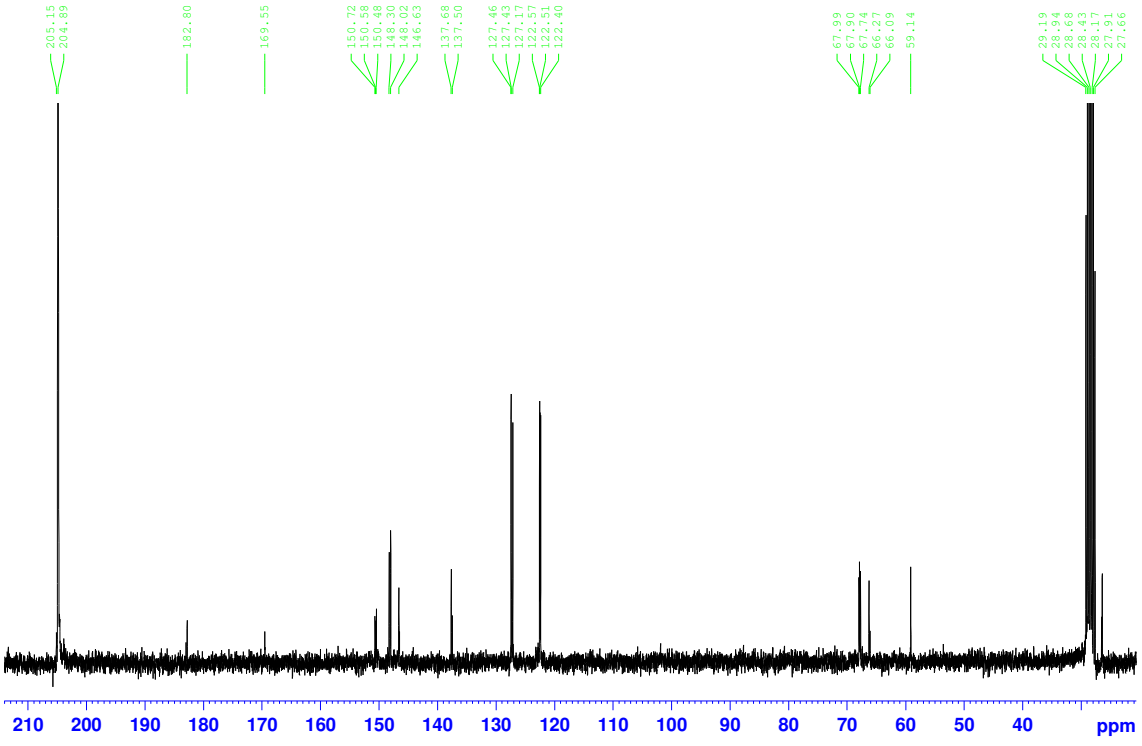
1.18
3.00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150.58
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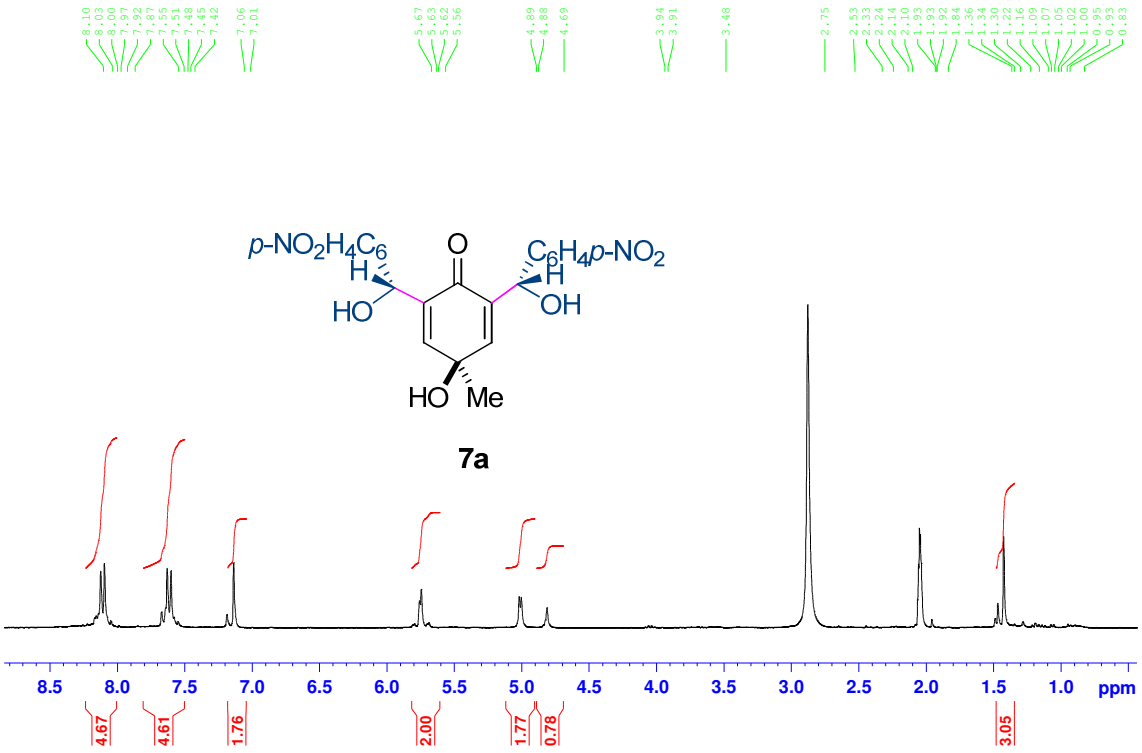
148.30
148.02
146.63
137.68
137.50
127.46
127.43
122.17
122.07
122.51
122.40
67.99
67.90
67.74
66.27
66.09
59.14
29.19
28.94
28.68
28.43
28.17
27.91
27.66
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
ppm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8.03
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7.87
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7.51
7.48
7.45
7.42
7.06
7.01
5.67
5.63
5.62
5.56
4.89
4.88
4.69
3.94
3.91
3.48
2.75
2.53
2.33
2.24
2.14
2.10
1.93
1.93
1.92
1.84
1.36
1.34
1.30
1.22
1.16
1.09
1.07
1.05
1.02
1.00
0.95
0.93
0.83
p-NO2H4C6
H
HO
O
C6H4p-NO2
H
OH
HO
Me
7a
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
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1.5
1.0
ppm
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4.61
1.76
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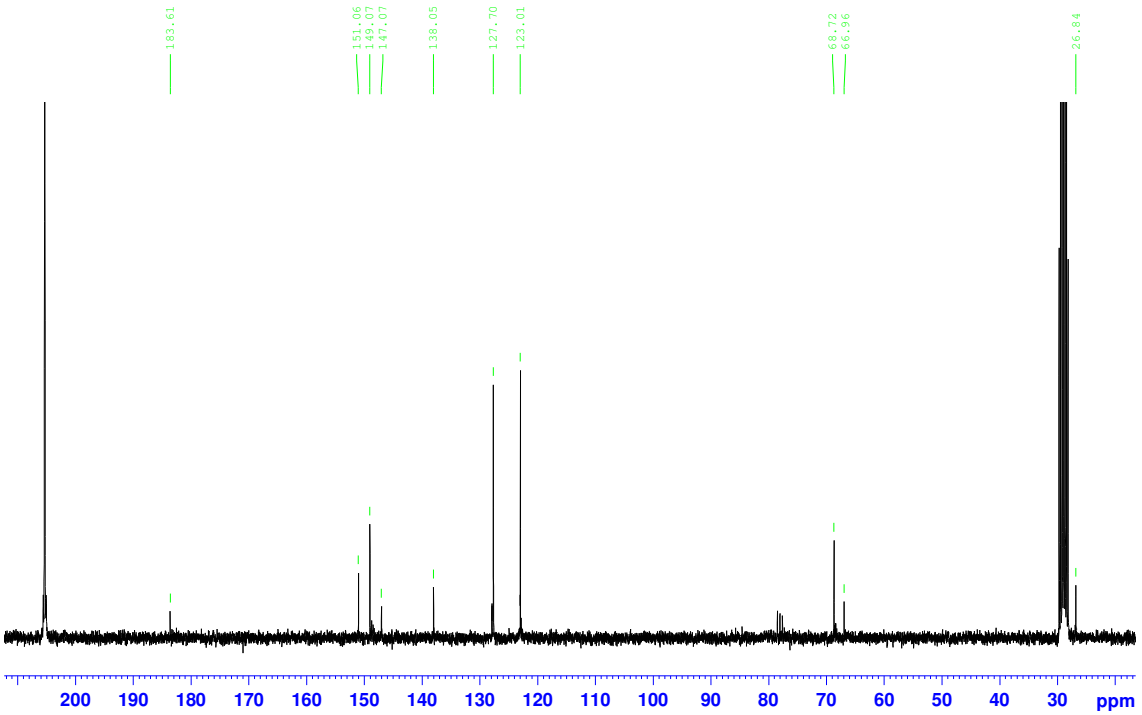
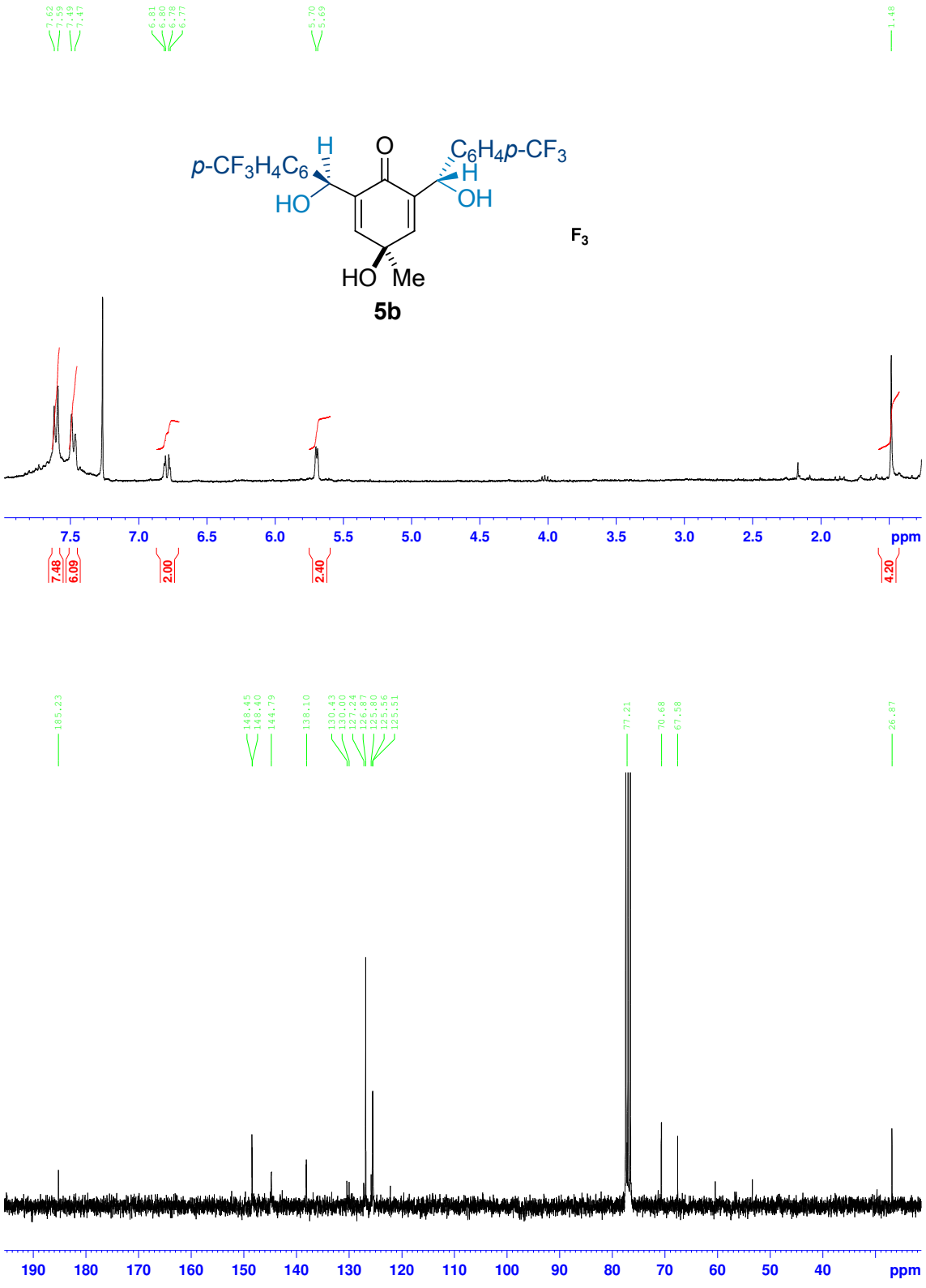
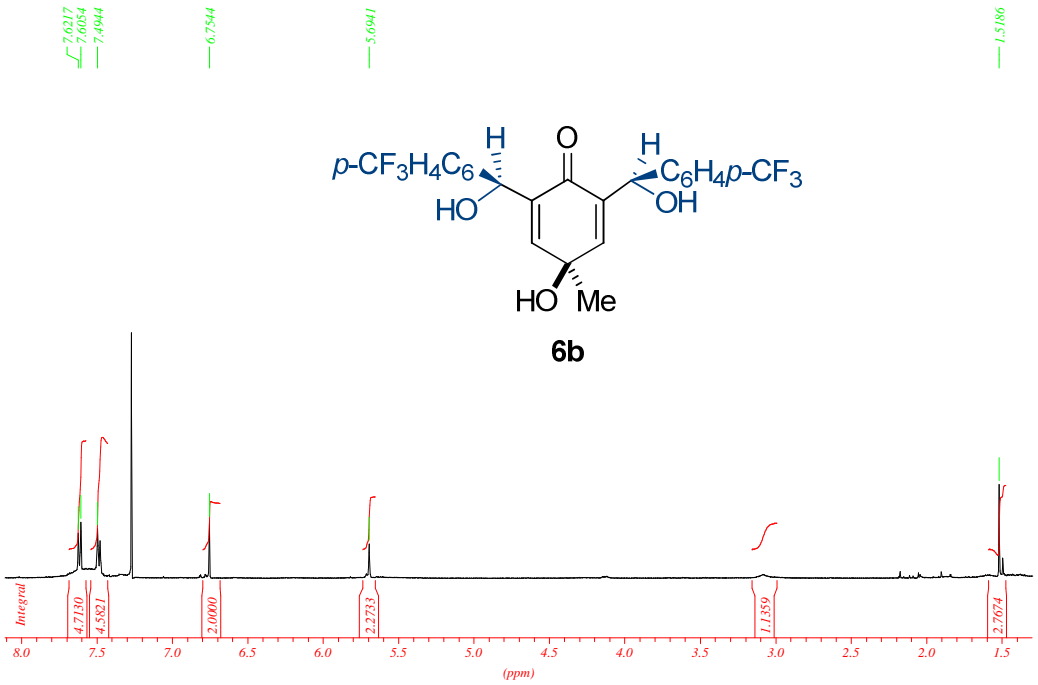
0.78
3.05


183.61
151.06
149.07
147.07
138.05
127.70
123.01
68.72
66.96
26.84
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
ppm


7.62
7.59
7.49
7.47
6.81
6.80
6.78
6.77
5.70
5.69
1.48
p-CF3H4C6
H
O
C6H4p-CF3
H
HO
OH
F3
HO
Me
5b
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
ppm
7.48
6.09
2.00
2.40
4.20
185.23
148.45
148.40
144.79
138.10
130.43
130.00
127.24
126.87
125.80
125.56
125.51
77.21
70.68
67.58
26.87
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
ppm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5.6941
1.5186
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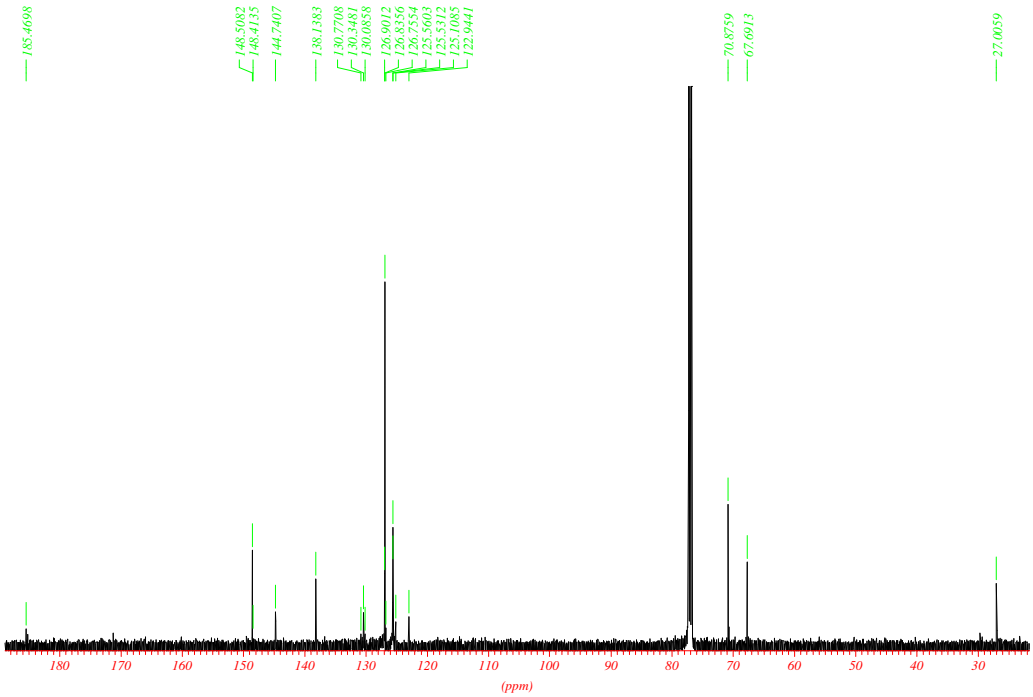
H
O
H
C6H4p-CF3
HO
OH
HO
Me
Integral
4.7130
4.5821
2.0000
2.2733
1.1359
2.7674
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
(ppm)

6b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126.9012
126.8356
126.7554
125.5603
125.5312
125.1085
122.9441
70.8759
67.6913
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160
150
140
130
120
110
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90
80
70
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50
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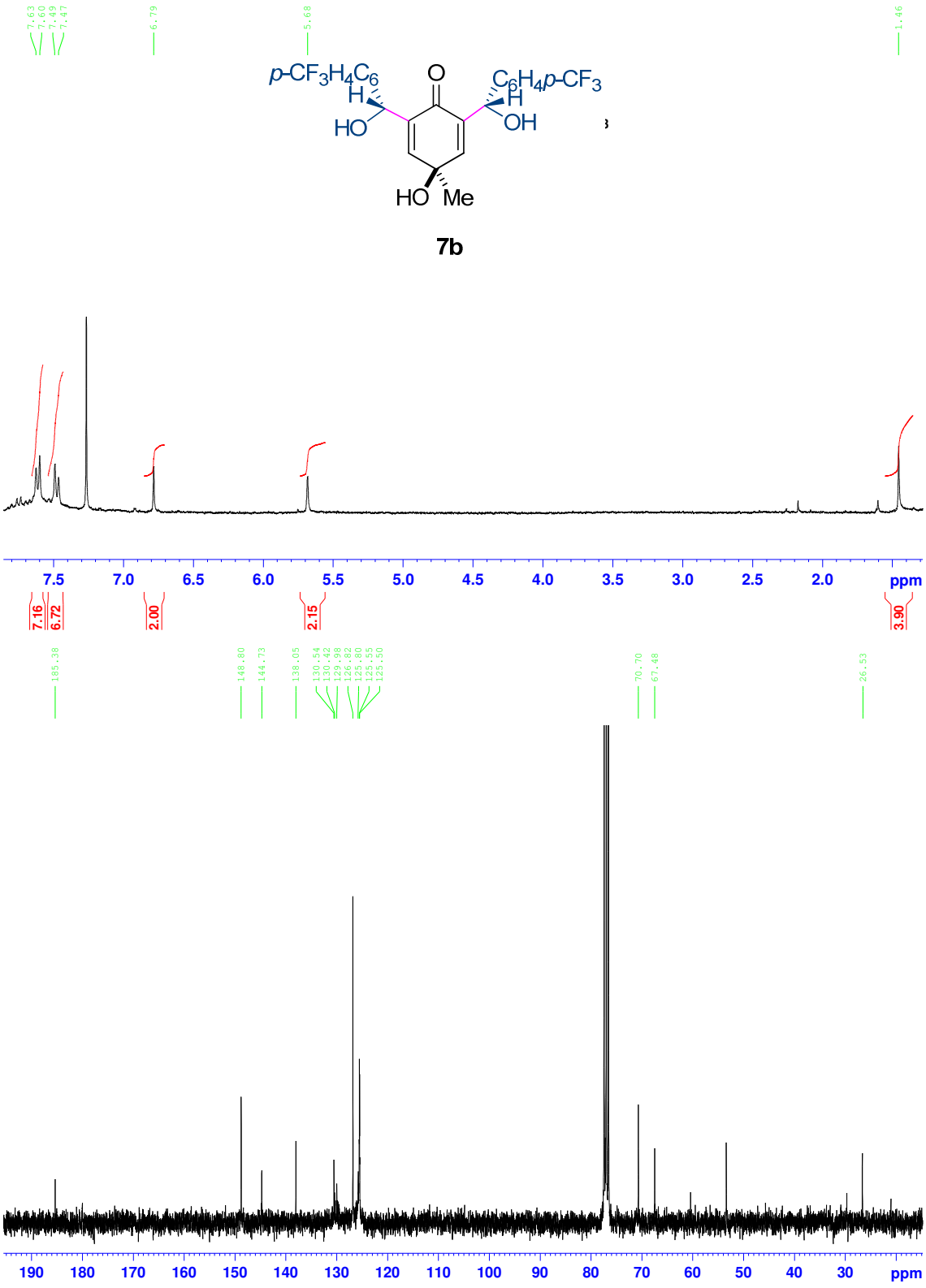
(ppm)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7.60
7.49
7.47
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5.68
1.46
p-CF3H4C6
H
HO
O
C6H4p-CF3
H
OH
HO
Me
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
ppm
7.16
6.72
2.00
2.15
3.90
185.38
148.80
144.73
138.05
130.54
130.42
129.98
126.82
125.80
125.55
125.50
70.70
67.48
26.53
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160
150
140
130
120
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100
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80
70
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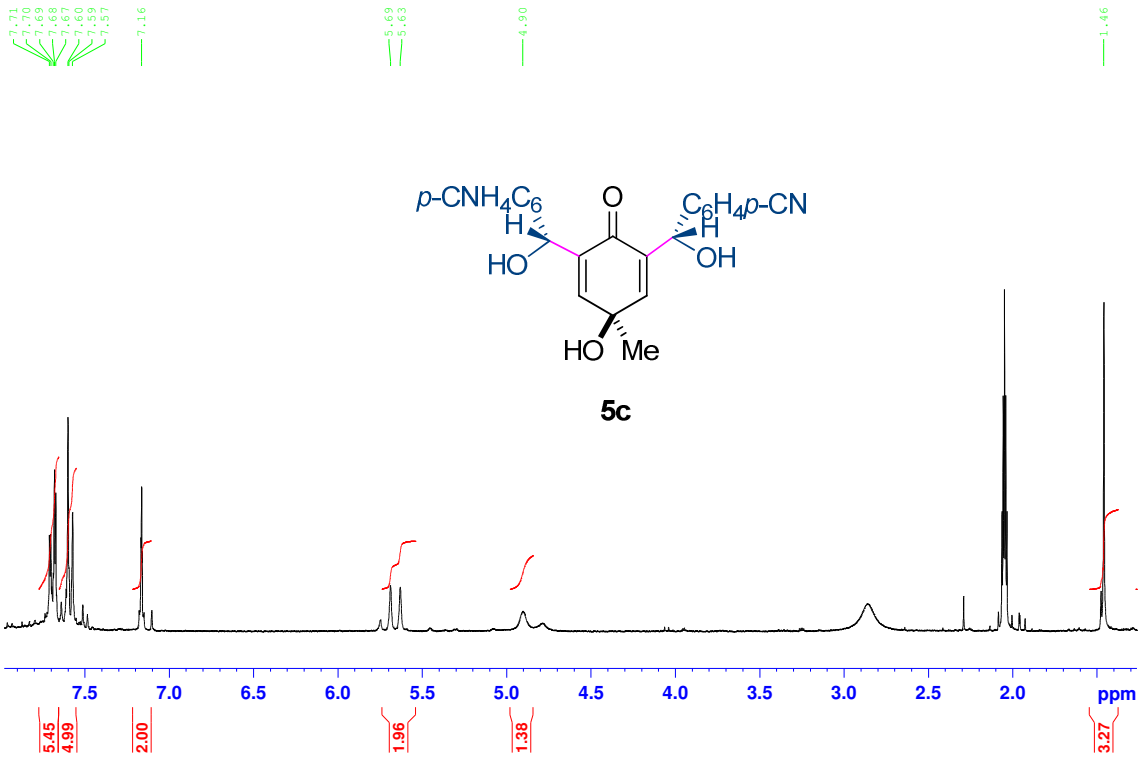
50
40
30
ppm

7b


7.71
7.70
7.69
7.68
7.67
7.60
7.59
7.57
7.16
5.69
5.63
4.90
1.46
p-CNH4C6
H
HO
O
C6H4p-CN
H
OH
HO
Me
5c
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
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3.0
2.5
2.0
ppm
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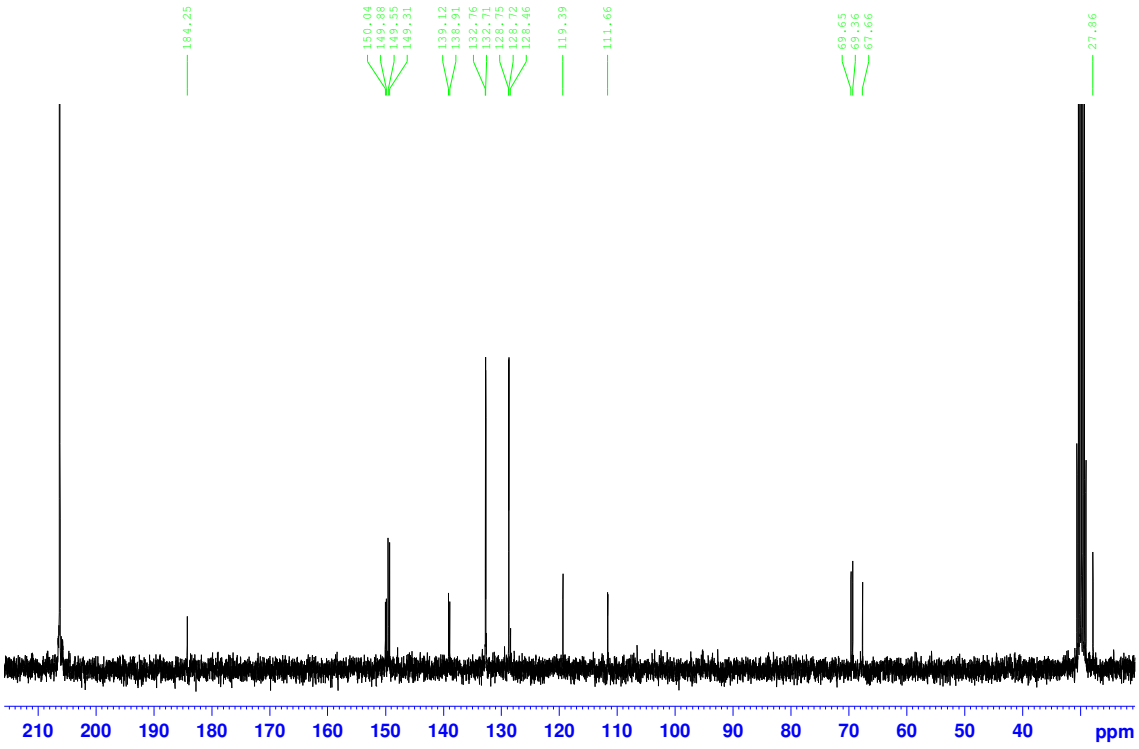
4.99
2.00
1.96
1.38
3.27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149.88
149.55
149.31
139.12
138.91
132.76
132.71
128.75
128.72
128.46
119.39
111.66
69.65
69.56
67.86
27.86
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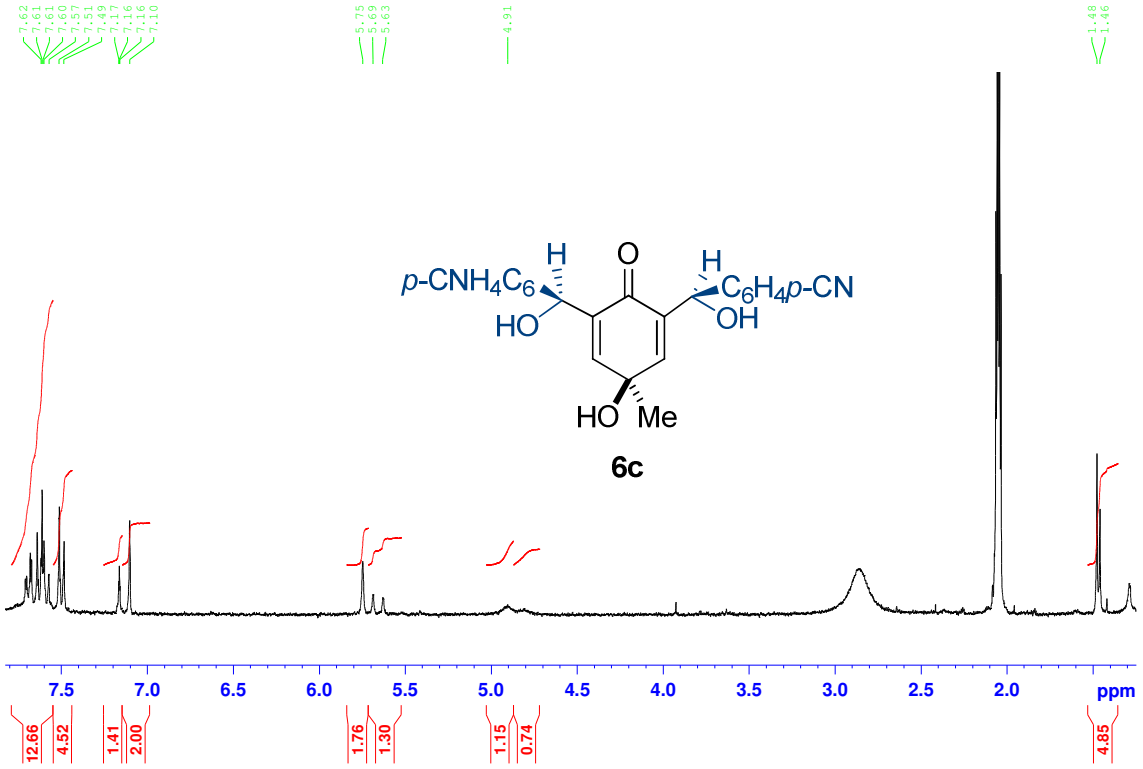
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
ppm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7.61
7.61
7.60
7.57
7.51
7.49
7.17
7.16
7.16
7.10
5.75
5.69
5.63
4.91
1.48
1.46
p-CNH4C6
H
O
H
C6H4p-CN
HO
OH
HO
Me
6c
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
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ppm
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2.00
1.76
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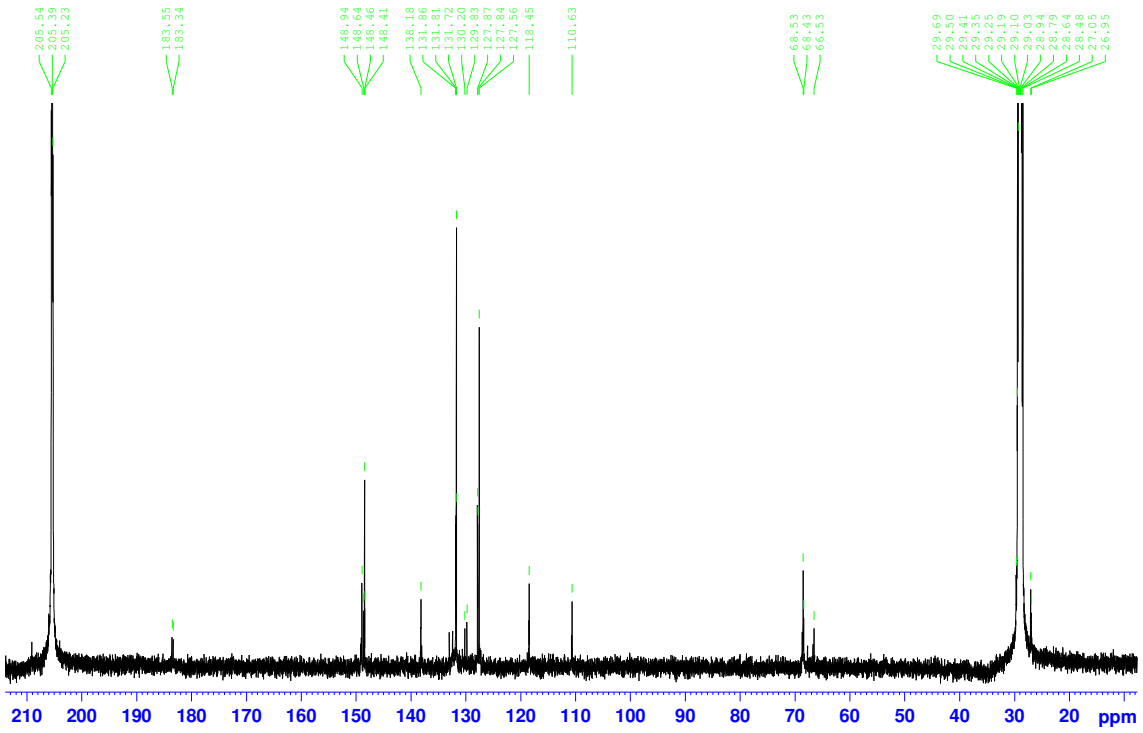
1.15
0.74
4.85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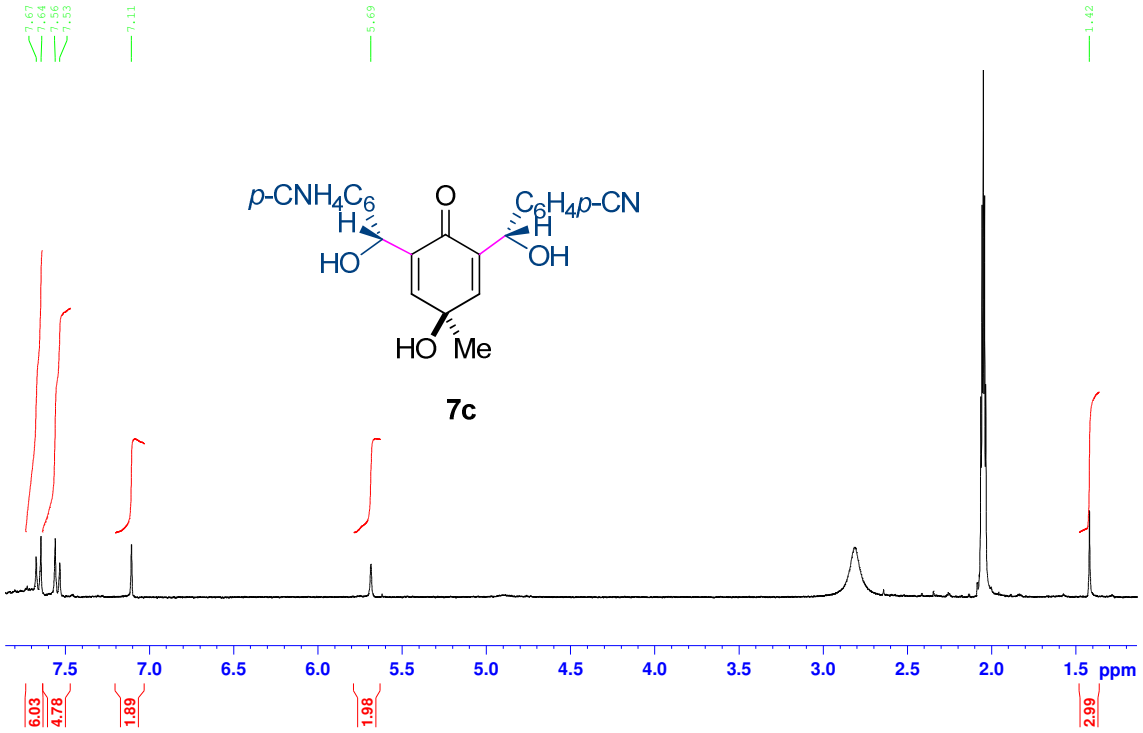
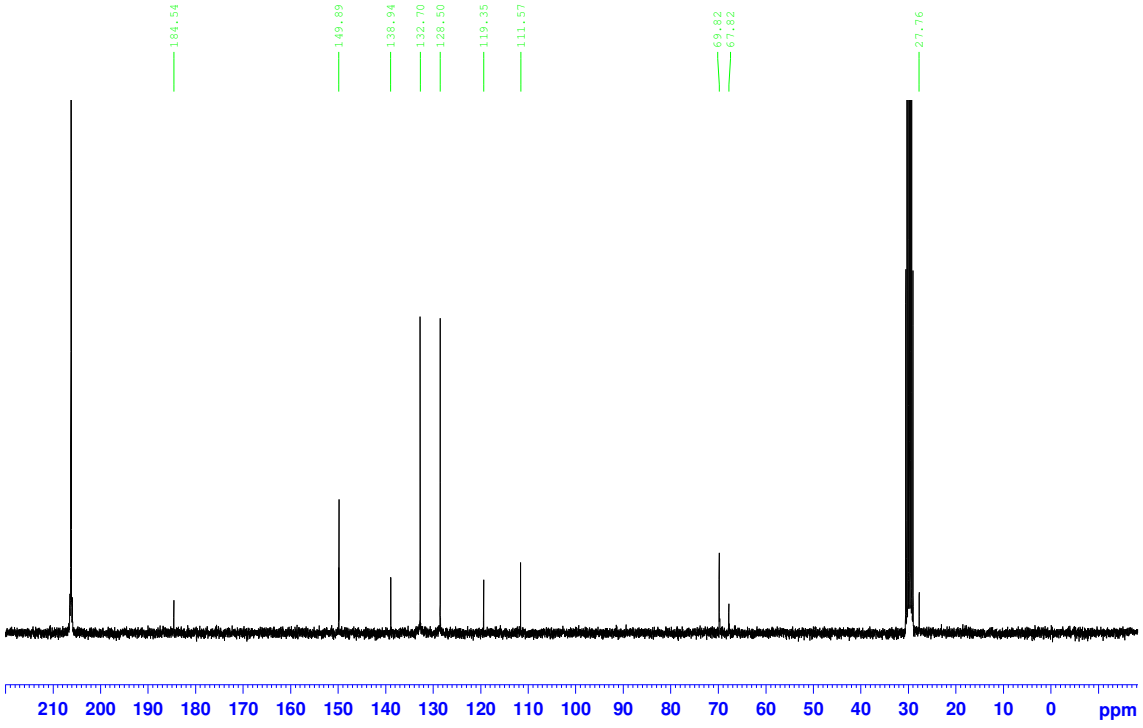
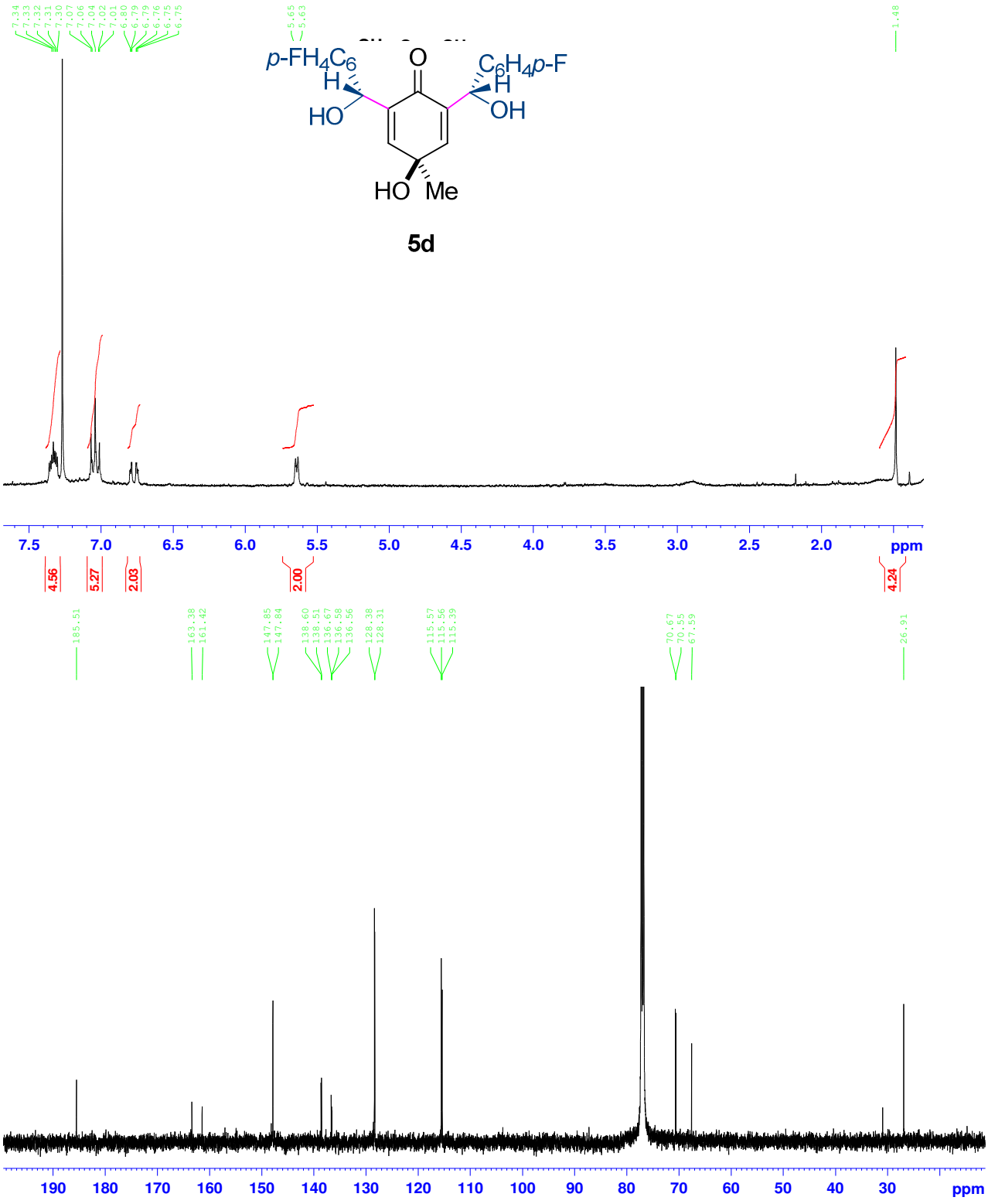
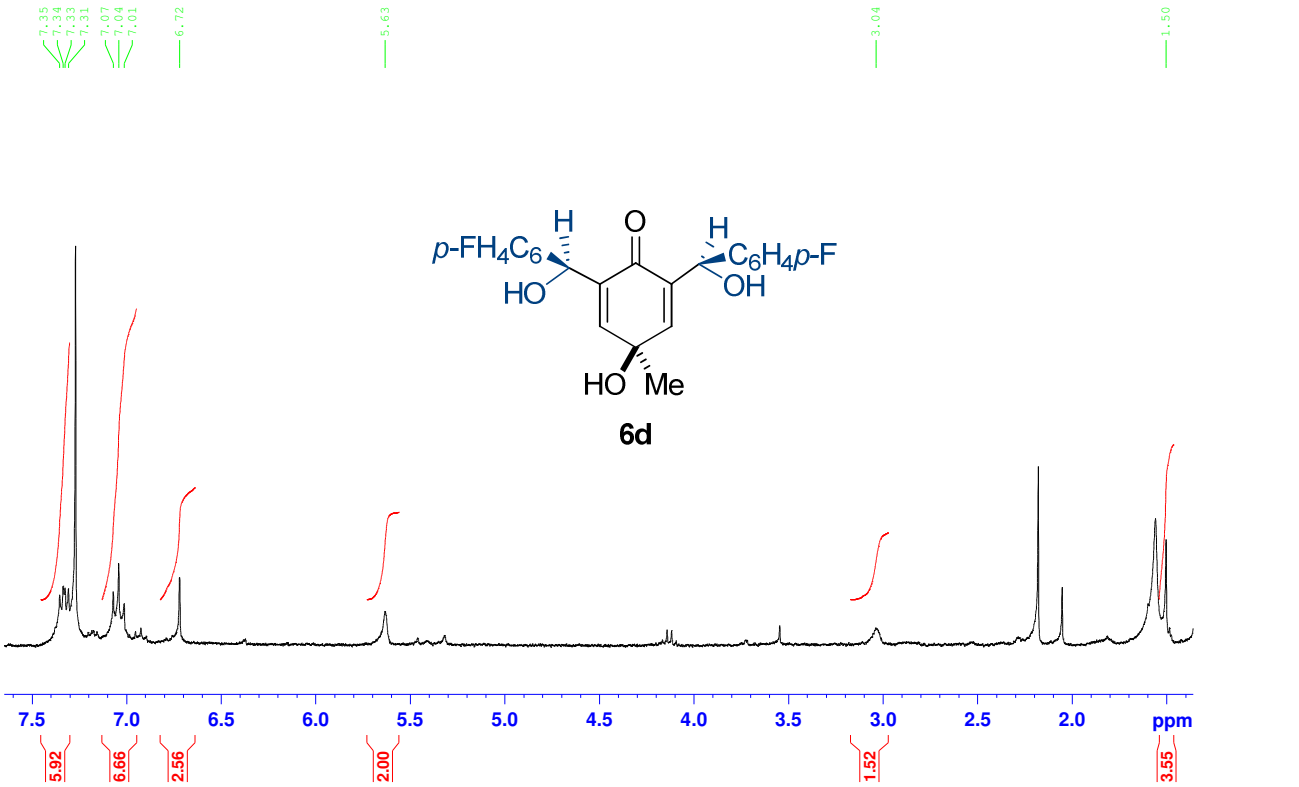
205.39
205.23
183.55
183.34
148.94
148.64
148.46
148.41
138.18
131.86
131.72
131.71
130.20
129.83
127.87
127.84
127.56
118.45
110.63
68.53
68.43
66.53
29.69
29.50
29.41
29.35
29.25
29.19
29.10
29.03
28.94
28.79
28.64
28.48
27.05
26.95
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
ppm

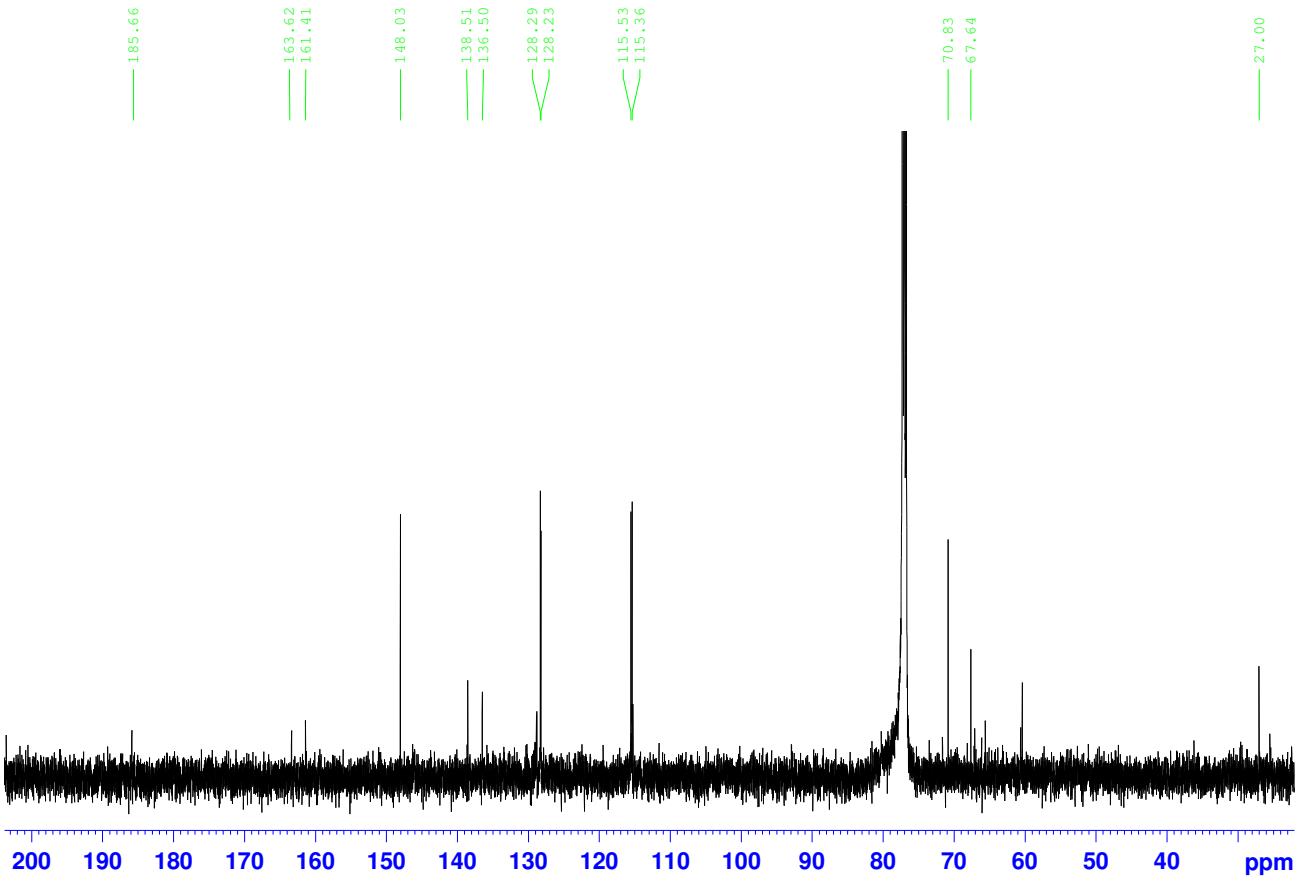

7.67
7.64
7.56
7.53
7.11
5.69
1.42
p-CNH4C6
H
HO
O
C6H4p-CN
H
OH
HO
Me
7c
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
ppm
6.03
4.78
1.89
1.98
2.99

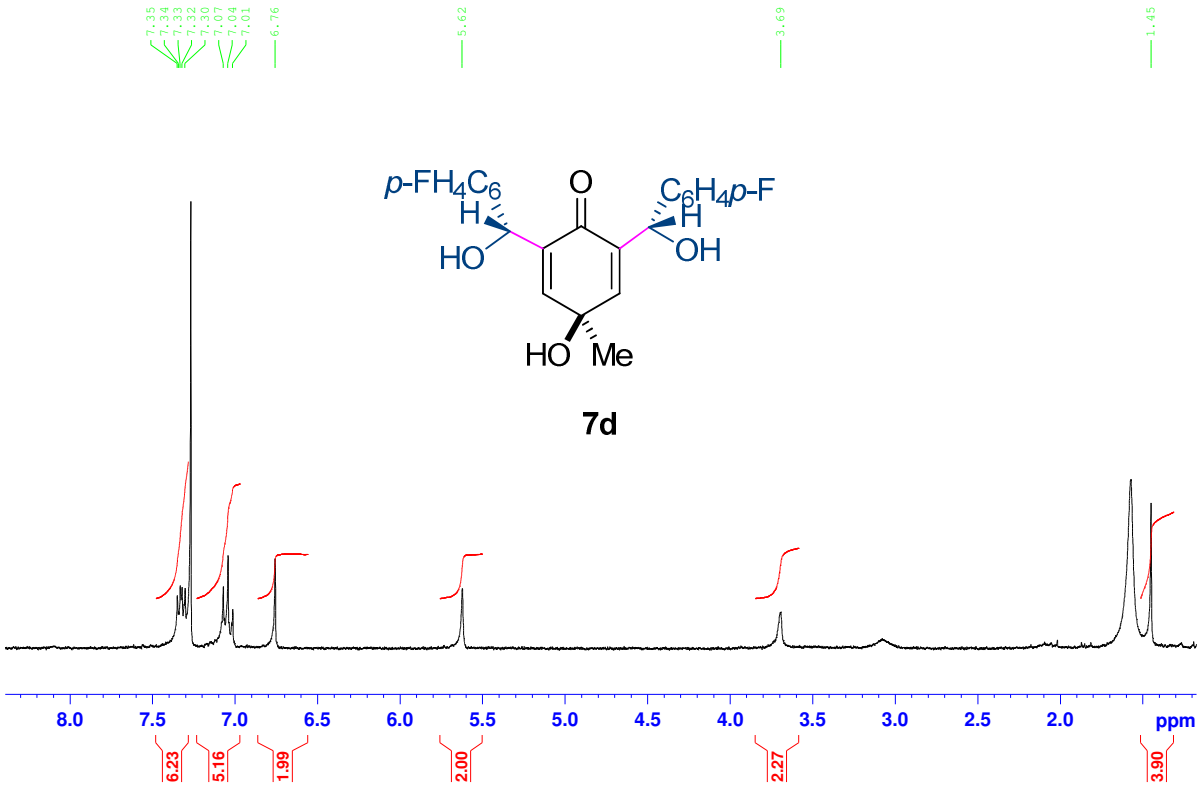

184.54
149.89
138.94
132.70
128.50
119.35
111.57
69.82
67.82
27.76
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm


p-FH4C6
H
HO
O
C6H4p-F
H
OH
HO
Me
5d
ppm
ppm

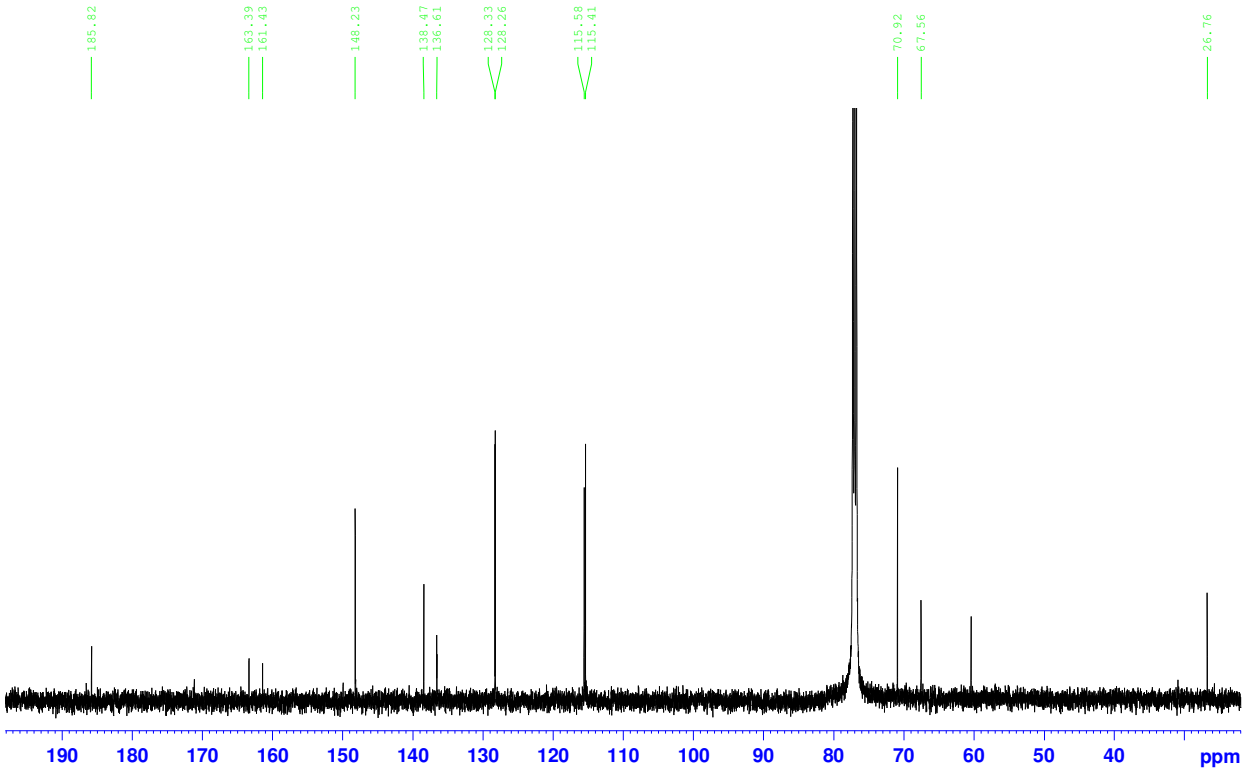

7.35
7.34
7.33
7.31
7.07
7.04
7.01
6.72
5.63
3.04
1.50
H
O
H
p-FH4C6
C6H4p-F
HO
OH
HO
Me
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
ppm
5.92
6.66
2.56
2.00
1.52
3.55

6d


185.66
163.62
161.41
148.03
138.51
136.50
128.29
128.23
115.53
115.36
70.83
67.64
27.00
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
ppm


7.35
7.34
7.33
7.32
7.30
7.07
7.04
7.01
6.76
5.62
3.69
1.45
p-FH4C6
H
HO
O
C6H4p-F
H
OH
HO
Me
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
ppm
6.23
5.16
1.99
2.00
2.27
3.90

7d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161.43
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138.47
136.61
128.33
128.26
115.58
115.41
70.92
67.56
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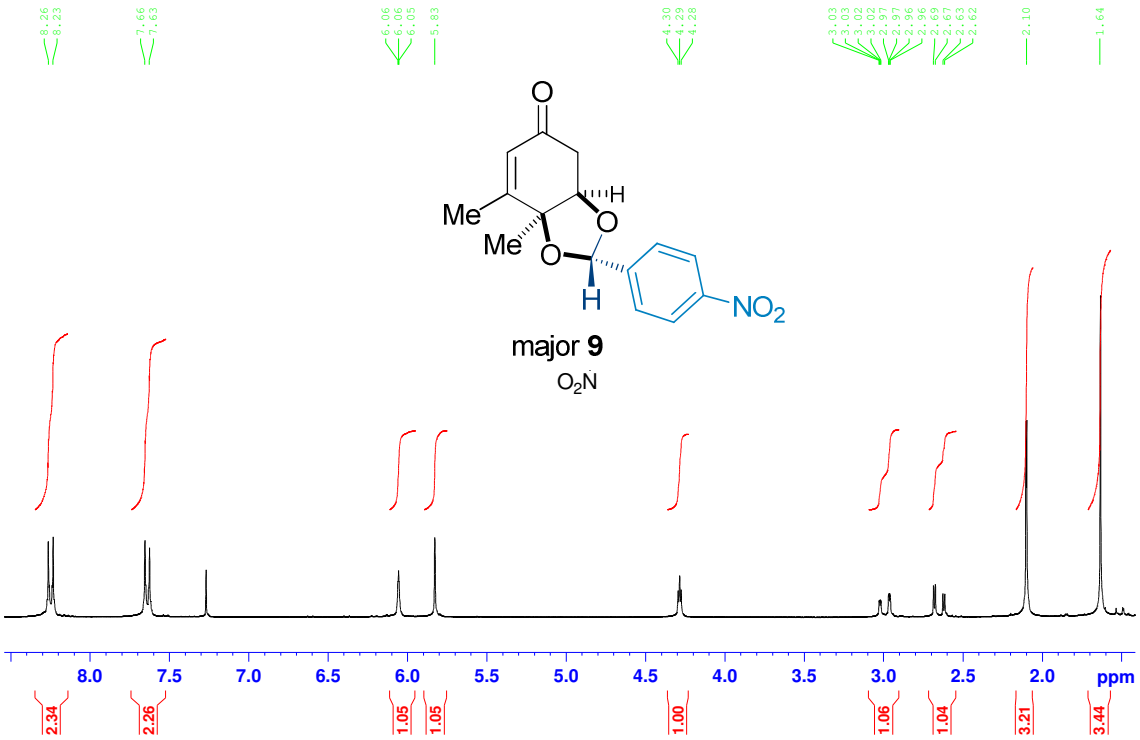
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
ppm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8.23
7.66
7.63
6.06
6.06
6.05
5.83
4.30
4.29
4.28
3.03
3.03
3.02
3.02
2.97
2.96
2.96
2.69
2.67
2.63
2.62
2.10
1.64
O
Me
Me
O
O
H
H
NO2
major 9
O2N
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
ppm
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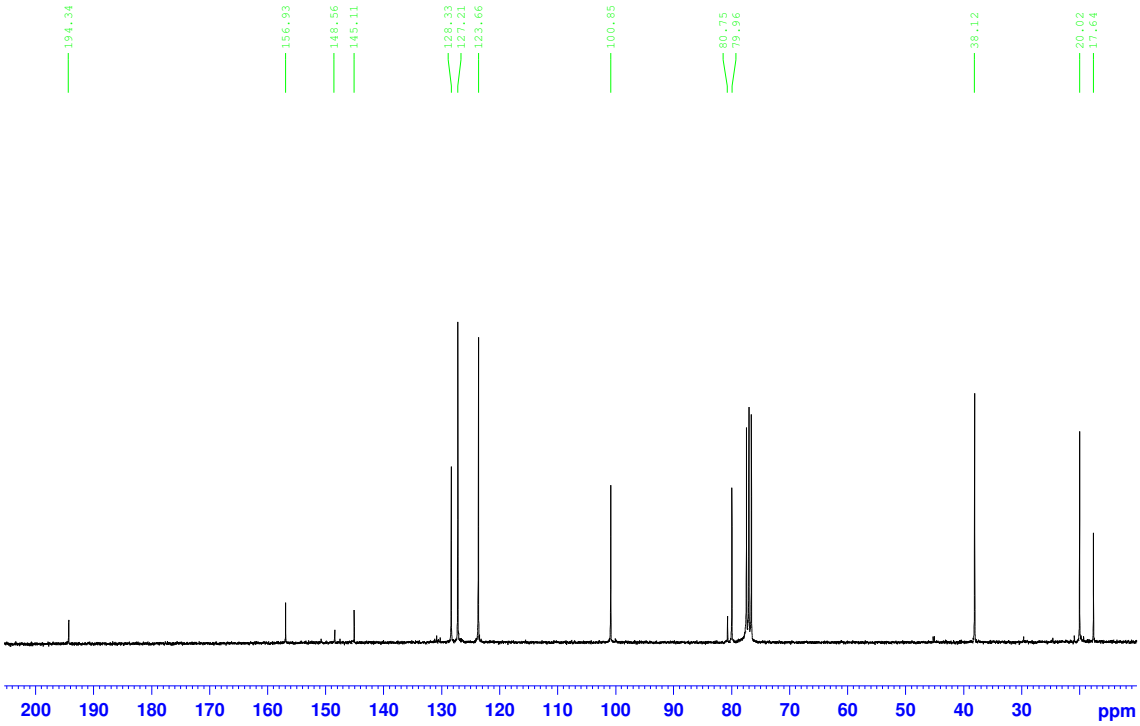
2.26
1.05
1.05
1.00
1.06
1.04
3.21
3.44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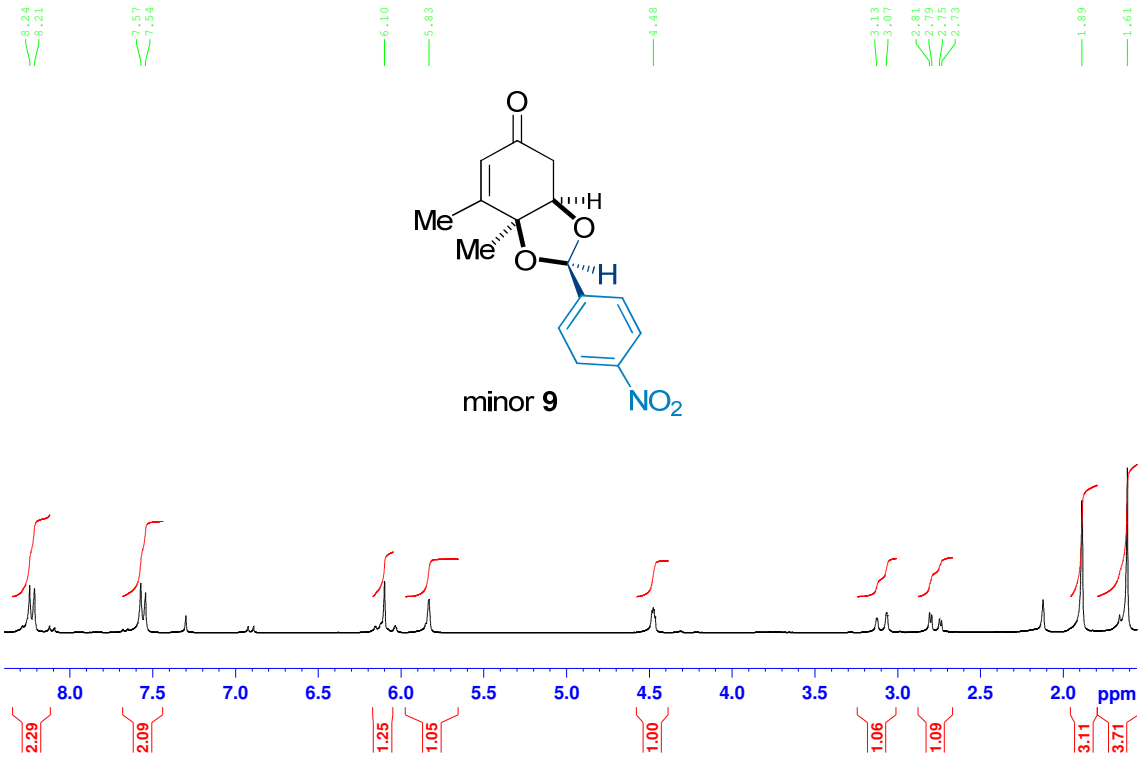
156.93
148.56
145.11
128.33
127.21
123.66
100.85
80.75
79.96
38.12
20.02
17.64
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
ppm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8.21
7.57
7.54
6.10
5.83
4.48
3.13
3.07
2.81
2.79
2.75
2.73
1.89
1.61
O
Me
Me
O
O
H
H
minor 9
NO2
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
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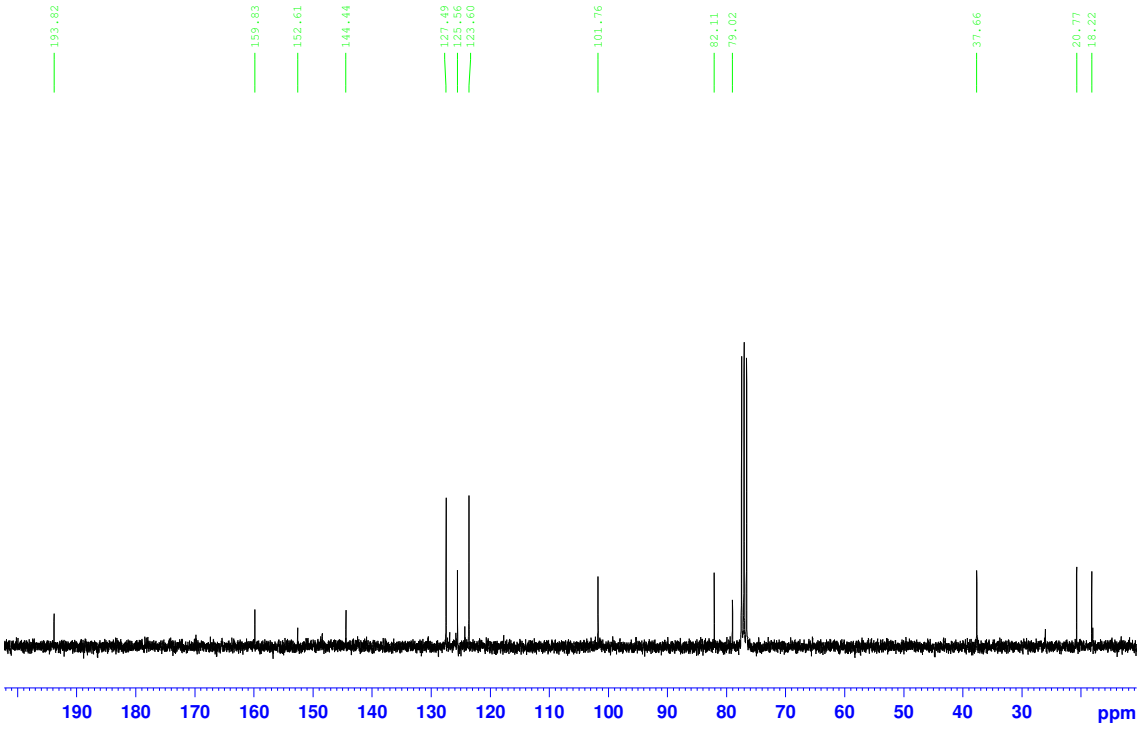
ppm
2.29
2.09
1.25
1.05
1.00
1.06
1.09
3.11
3.71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159.83
152.61
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127.49
125.56
123.60
101.76
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79.02
37.66
20.77
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150
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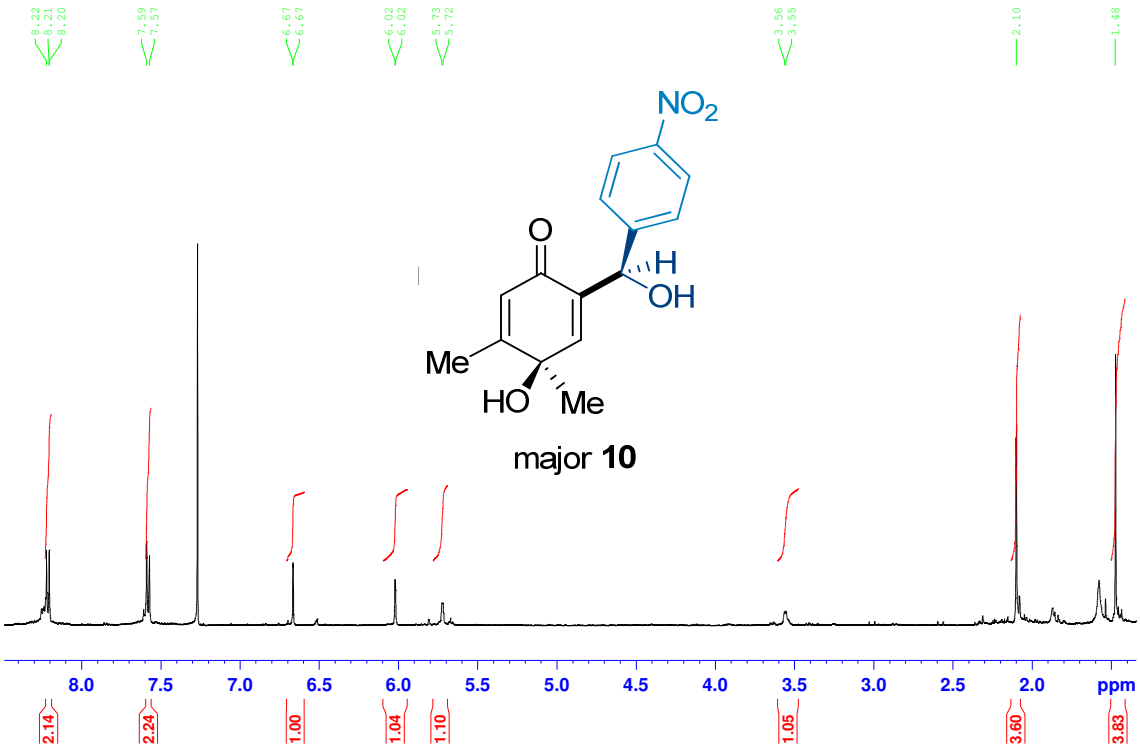
30
ppm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6.67
6.02
6.02
5.73
5.72
3.56
3.55
2.10
1.48
NO2
O
H
OH
Me
HO
Me
major 10
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
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2.0
ppm
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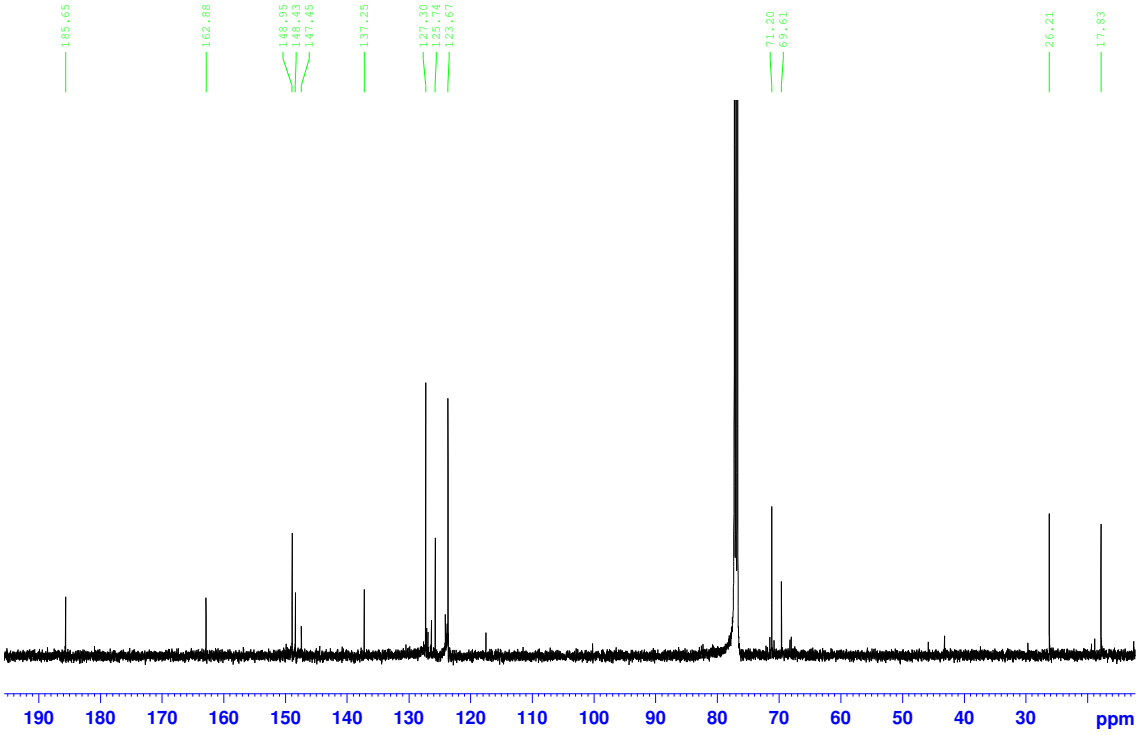
2.24
1.00
1.04
1.10
1.05
3.60
3.83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125.74
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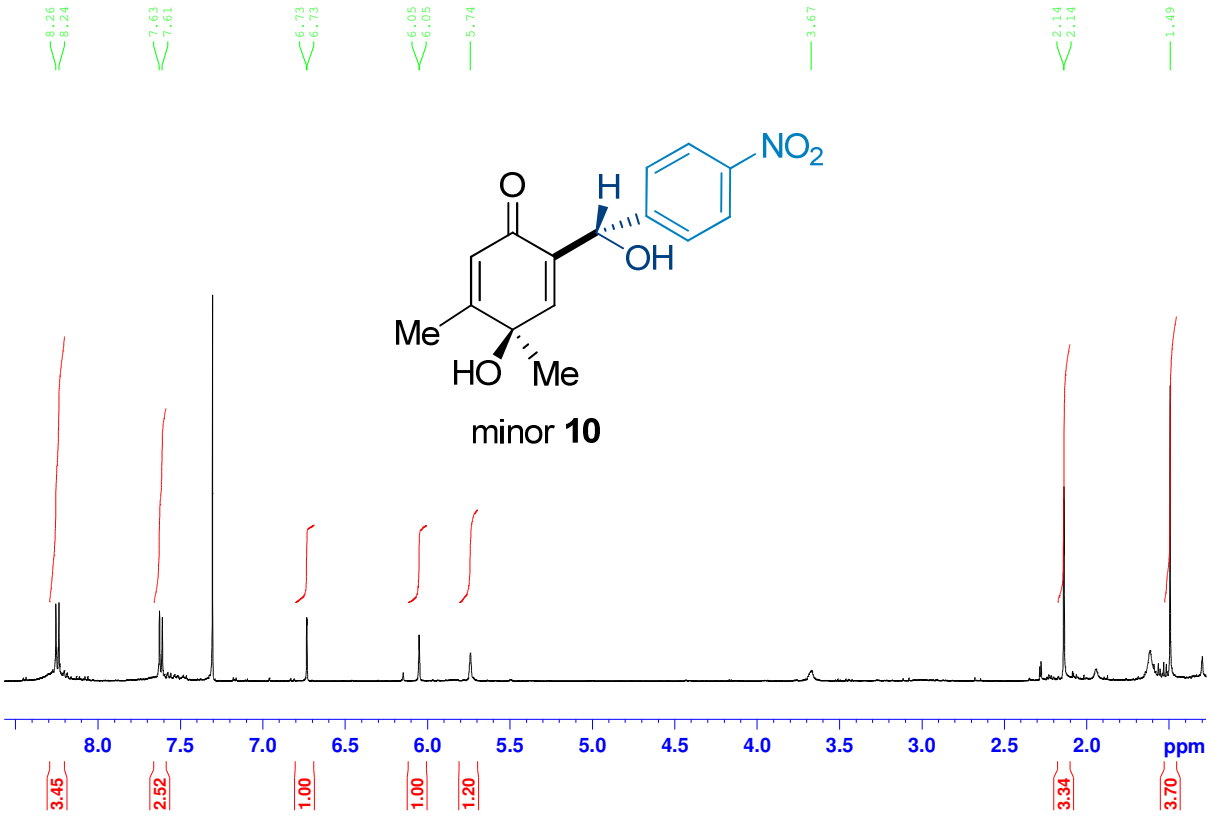
71.20
69.61
26.21
17.83
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
ppm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8.24
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7.61
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6.73
6.05
6.05
5.74
3.67
2.14
2.14
1.49
O
H
NO2
OH
Me
HO
Me
minor 10
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
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2.5
2.0
ppm
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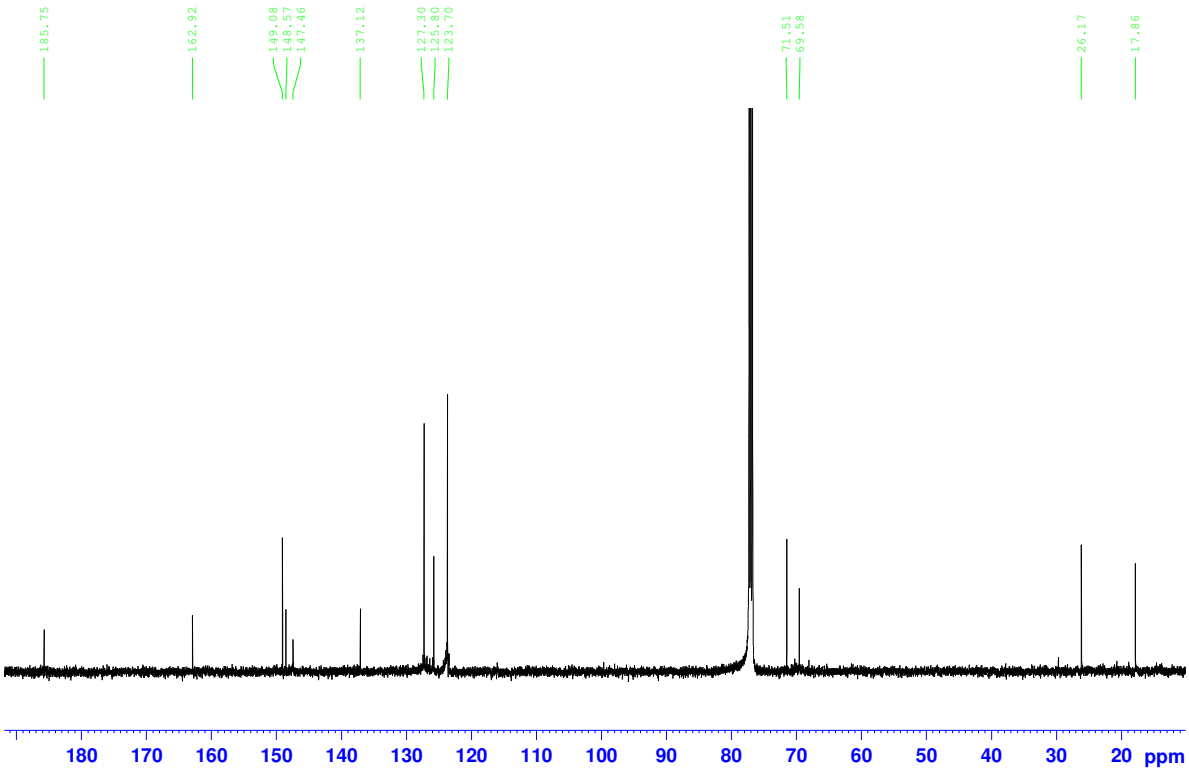
1.00
1.00
1.20
3.34
3.70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69.58
26.17
17.86
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
ppm