Experimental Evidence for the Formation of Phenoxenium Ions During Iodine(III)-Mediated Oxidative Dearomatization of Phenols

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SUPPORTING INFORMATION

Materials and Methods

Tetrahydrofuran (THF) was dried by passage through a column of activated molecular sieves. Methanol was purchased from Fisher Scientific and used without further purification. 4-phenylphenol (**5a**), 4'-bromo-(1,1'-biphenyl)-4-ol (**5e**), 4'-hydroxy-4-biphenylcarbonitrile were purchased from Sigma-Aldrich. All other chemicals were purchased from commercial sources and used as received.

Unless otherwise stated, reactions were monitored using thin-layer chromatography (TLC) using glass plates precoated with silica gel XHL w/ UV254 (250 mm) purchased from *SILICYCLE*® and visualized by UV light. Silica gel (particle size 32–63 mm) purchased from *SILICYCLE*® was used for flash column chromatography. Analytical achiral HPLC was performed with an Agilent ZORBAX XDB-CN, 4.6 X 150 mm, 3.5 μm at 254.4 mm.

^{1}H and ^{13}C NMR spectra are reported relative to the residual solvent peak (δ 7.26 and δ 77.00 for ^{1}H and ^{13}C in $CDCl_3$; δ 3.31 and δ 49.00 for ^{1}H and ^{13}C in CD_3OD), or tetramethylsilane (δ 0.00 for ^{1}H) when the residual solvent peak is obscured. Data for ^{1}H NMR spectra are reported as follows: (instrument field strength, solvent) chemical shift (δ ppm) (multiplicity, coupling constant (Hz), integration). Multiplicity is described using the following abbreviations: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet. Data for ^{13}C NMR spectra are reported in terms of chemical shift (δ ppm). Some reported spectra include minor solvent impurities of water (δ 1.56 ppm) and/or silicon grease (δ 0.07 ppm), which do not impact product assignments.

General computational details and references

Calculations were performed using the *Gaussian 09* suite[1] of electronic structure programs. All geometries were fully optimized at the M06-2X level[2] of density functional theory.[3] The 6–31+G(d) basis set[4] was used for C, H, O, F and Br. For iodine, the LANL2DZdp basis set[5] was used. An ultrafine grid density was used for numerical integration.[6] Unless otherwise noted, optimizations were performed with no frozen coordinates. Energy minima and transition states were identified though frequency analysis. In order to account for solvation effects, the SMD solvation model[7] for CH_3OH was employed during geometry optimizations. Graphics were generated using CYLview, 1.0b.[8]

(1) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Scalmani, G.; Barone, V.; Mennucci, B.; Petersson, G. A.; Nakatsuji, H.; Caricato, M.; Li, X.; Hratchian, H. P.; Izmaylov, A. F.; Bloino, J.; Zheng, G.; Sonnenberg, J. L.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Vreven, T.; Montgomery, J. A., Jr.; Peralta, J. E.; Ogliaro, F.; Bearpark, M.; Heyd, J. J.; Brothers, E.; Kudin, K. N.; Staroverov, V. N.; Keith, T.; Kobayashi, R.; Normand, J.; Raghavachari, K.; Rendell, A.; Burant, J. C.; Iyengar, S. S.; Tomasi, J.; Cossi, M.; Rega, N.; Millam, J. M.; Klene, M.; Knox, J. E.; Cross, J. B.; Bakken, V.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Martin, R. L.; Morokuma, K.; Zakrzewski, V. G.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Dapprich, S.; Daniels, A. D.; Farkas, O.; Foresman, J. B.; Ortiz, J. V.; Cioslowski, J.; Fox, D. J. *Gaussian 09*, Revision D.01; Gaussian, Inc.: Wallingford, CT, 2013.

(2) Zhao, Y.; Truhlar, D. G. *Theor. Chem. Acc.* **2008**, *120*, 215.

(3) Cramer, C. J. Essentials of Computational Chemistry: Theories and Models, 2nd ed.; Wiley: West Sussex, 2004.

(4) Hehre, W. J.; Radom, L.; Schleyer, P. v. R.; Pople, J. A. *Ab Initio Molecular Orbital Theory*; Wiley: New York, 1986.

(5) Check, C. E.; Faust, T.O.; Bailey, J.M.; Wright, B.J.; Gilbert, T.M.; Sunderlin, L.S. *J. Phys. Chem. A* **2001**, *105*, 8111.

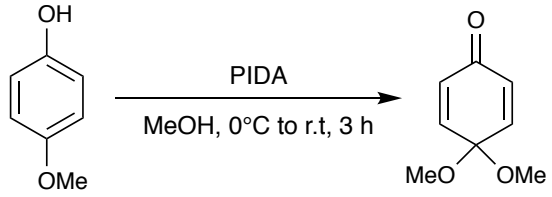
(6) Wheeler, S. E.; Houk, K. N. *J. Chem. Theory Comput.* **2010**, *6*, 395.

(7) Marenich, A. V.; Cramer, C. J.; Truhlar, D. G. *J. Phys. Chem. B* **2009**, *113*, 6378.

(8) Legault, C. Y., Université de Sherbrooke, 2009 (http://www.cylview.org).

1.0 Experimental Procedures–Preparative Reactions

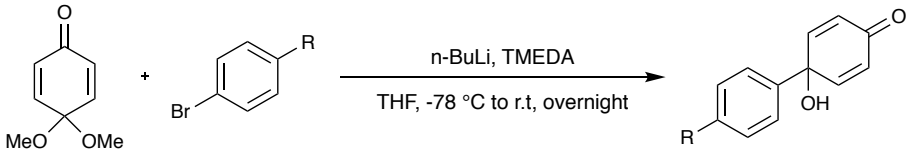
1.1 Synthesis of 4,4-dimethoxycyclohexa-2,5-dien-1-one



(Diacetoxyiodo)benzene (5.708g, 17.72 mmol, 1.1 eq.) was added in the solution of 4-methoxyphenol (2g, 16.11 mmol, 1 eq.) in methanol (80 mL) at 0 °C in an ice bath. The reaction was allowed to warm to room temperature and stirred for 3 hours. The reaction mixture was then quenched by 10% sodium thiosulfate solution, extracted with EtOAc (3X) and dried over Na_2SO_4. After concentration in vacuo, the crude residue was purified by flash column chromatography to afford yellow oil (2.46g, 99% yield). [9]

^{1}H NMR (400 MHz, $CDCl_3$) δ 6.82 (not first order doublet, *J* = 10.4 Hz, 2H), 6.28 (not first order doublet, *J* = 10.4 Hz, 2H), 3.38 (s, 6H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 184.97, 143.16, 129.83, 92.33, 50.24.

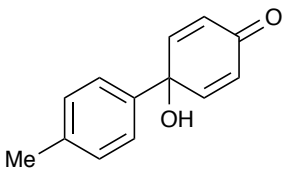
1.2 General procedure for the preparation of 4'-substituted-4-aryl-*para*-quinols



The 4-substituted-bromobenzene (3.89 mmol, 1.2 eq.) was loaded into a flame dried round bottom flask under argon and dissolved in dry THF (4 mL) at -78 °C. To this solution was added dropwise dry TMEDA (0.73 mL, 4.86 mmol, 1.5 eq.) followed by n-BuLi (3.04 mL, 4.86 mmol, 1.5 eq.) at –78°C and the reaction was stirred at that temperature for 1 hour. 4,4-dimethoxycyclohexa-2,5-dien-1-one (500 mg, 3.24 mmol, 1 eq.) was then added dropwise to the solution and stirred at –78°C for 2 hours. The reaction was allowed to warm up to room temperature and stirred for overnight. The reaction was then quenched by saturated NH_4Cl solution and the aqueous phase was extracted with EtOAc (3X). The combined organic layers were dried (Na_2SO_4) and concentrated in vacuo. The crude residue was purified by flash column chromatography to afford the desired product.

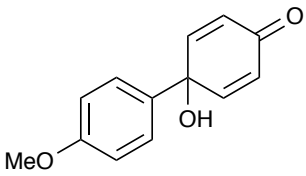
(9) Hammill, J. T.; Contreras-Garcia, J.; Virshup, A. M.; Beratan, D.; Yang, W.; Wipf, P. *Tetrahedron* **2010**, *66*, 5852–5862.

1-hydroxy-4'-methyl-[1,1'-biphenyl]-4(1*H*)-one [10]



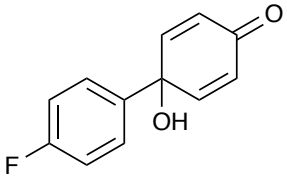
White solid (605.4 mg, 93.2% yield)
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.36 (d, *J* = 8.0 Hz, 2H), 7.19 (d, *J* = 7.9 Hz, 2H), 6.89 (d, *J* = 10 Hz, 2H), 6.22 (d, *J* = 10 Hz, 2H), 2.35 (s, 3H), 2.33 (s, 1H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 185.94, 151.15, 138.32, 135.67, 129.61, 126.63, 125.17, 70.87, 21.05.

1-hydroxy-4'-methoxy-[1,1'-biphenyl]-4(1*H*)-one [11]



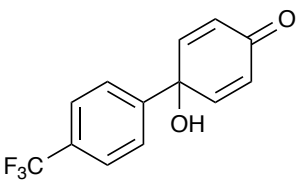
White solid (544 mg, 77.6% yield).
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39 (not first order doublet, *J* = 8.92 Hz, 2H), 6.92-6.87 (m, 4H), 6.20 (not first order doublet, *J* = 10.04 Hz, 2H), 3.81 (s, 3H), 2.56 (s, 1H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 186.01, 159.57, 151.36, 130.51, 126.57, 126.41, 114.26, 70.59, 55.31.

4'-fluoro-1-hydroxy-[1,1'-biphenyl]-4(1*H*)-one



White solid (580.1 mg, 87.6% yield).
^{1}H NMR (400 MHz, $CDCl_3$) δ δ 7.50 – 7.42 (m, 2H), 7.11 – 7.02 (m, 2H), 6.87 (not first order doublet, *J* = 10.08 Hz, 2H), 6.24 (not first order doublet, *J* = 10.08 Hz, 2H), 2.47 (s, 1H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 185.66, 162.63 (d, J_{CF} = 247.7 Hz), 150.75, 134.35 (d, J_{CF} = 3.2 Hz), 127.19 (d, J_{CF} = 8.4 Hz), 126.85, 115.81 (d, J_{CF} = 21.7 Hz), 70.57.
^{19}F NMR (376 MHz, $CDCl_3$) δ -113.42 (tt, *J* = 5.4, 8.9 Hz).
HRMS (ESI-) 203.0508 calc'd for $C_{12}H_8FO_2^-$, 203.0508 found

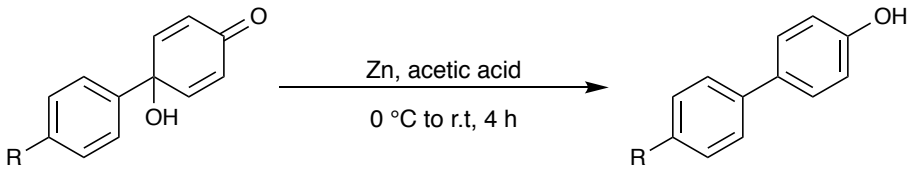
1-hydroxy-4'-(trifluoromethyl)-[1,1'-biphenyl]-4(1*H*)-one



Light yellow solid (704.8 mg, 85.5% yield).
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.65 (d, *J* = 8.6 Hz, 2H), 7.61 (d, *J* = 8.6 Hz, 2H), 6.88 (not first order doublet, *J* = 10.08 Hz, 2H), 6.28 (not first order doublet, *J* = 10.08 Hz, 2H) 2.48 (s, 1H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 185.57, 150.27, 142.59, 130.61 (q, J_{CF} = 32.6 Hz), 128.16, 125.88 (q, J_{CF} = 3.78 Hz), 125.84, 123.86 (d, J_{CF} = 272.2 Hz), 70.78
^{19}F NMR (376 MHz, $CDCl_3$) δ –62.55.
HRMS (ESI+) 277.0452 calc'd for $C_{13}H_9F_3O_2Na^+$, 277.0451 found

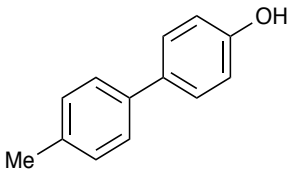
(10) Yakura, T.; Omoto, M.; Yamauchi, Y.; Tian, Y.; Ozono. A. *Tetrahedron* **2010**, *66*, 5833–5840.
(11) Capparelli, M. P.; DeSchepper, R. E.; Swenton, J. S. *J. Org. Chem.* **1987**, *52*, 4953–4961.

1.3 General procedure for the synthesis of 4'-subsituted-[1,1'-biphenyl]-4-ol



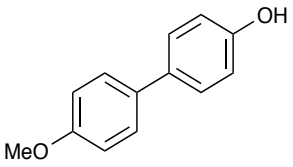
Zinc (326.9 mg, 5 mmol, 5 eq.) was added to a solution of the corresponding *para*-quinol (1 mmol, 1 eq.) in acetic acid (5 mL) at 0 °C in an ice bath. The reaction was allowed to warm to room temperature and stirred for 4 hours. The reaction mixture was then filtered through a pad of celite and wached with EtOAc. After concentration in vacuo, the residue was washed by saturated $NaHCO_3$ solution to neutralize the acetic acid. The aqueous layer was then extracted with EtOAc (3X) and dried over Na_2SO_4. After concentration in vacuo, the residue was purified by flash column chromatography to afford the desired product.

4'-methyl-[1,1'-biphenyl]-4-ol (5a) [12]



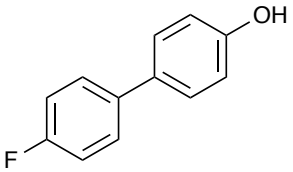
White solid (quantitative yield).
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.48 – 7.41 (m, 4H), 7.23 (d, *J* = 7.7 Hz, 3H), 6.91 (not first order doublet, *J* = 8.6 Hz, 2H), 4.74 (s, 1H), 2.39 (s, 3H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 154.72, 137.84, 136.41, 134.00, 129.43, 128.18, 126.54, 115.57, 21.02.

4'-methoxy-[1,1'-biphenyl]-4-ol (5b) [12]



White solid (180.5 mg, 90.1% yield).
^{1}H NMR (400 MHz, CD_3OD) δ 7.45 (not first order doublet, *J* = 8.88 Hz, 2H), 7.38 (not first order doublet, *J* = 8.68 Hz, 2H), 6.94 (not first order doublet, *J* = 8.88 Hz, 2H), 6.82 (not first order doublet, *J* = 8.56 Hz, 2H), 3.81 (s, 3H).
^{13}C NMR (101 MHz, CD_3OD) δ 160.02, 157.57, 134.99, 133.62, 128.57, 128.39, 116.52, 115.10, 55.67.

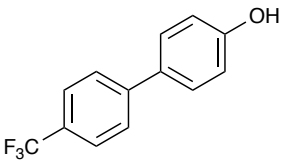
4'-fluoro-[1,1'-biphenyl]-4-ol (5d) [13]



White solid (174.7 mg, 92.8 % yield).
^{1}H NMR (400 MHz, CD_3OD) δ 7.52 (m, 2H), 7.41 (d, *J* = 8.36 Hz, 2H), 7.10 (not first order doublet, *J* = 8.7 Hz, 2H), 6.84 (not first order doublet, *J* = 8.72, 2H).
^{13}C NMR (100 MHz, CD_3OD) δ 163.30 (d, J_{CF} = 243.7 Hz), 158.16, 138.76 (d, J_{CF} = 3.2 Hz), 132.8, 129.09 (d, J_{CF} = 7.9 Hz), 128.96, 116.63, 116.28 (d, J_{CF} = 21.6 Hz).
^{19}F NMR (376 MHz, CD_3OD) δ –119.3 (tt, *J* = 5.3, 9.3 Hz).

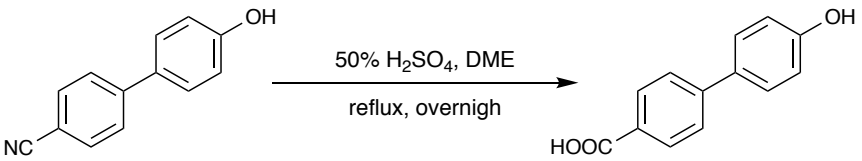
(12) Edwards, G. A.; Trafford, M. A.; Hamilton, A. E.; Buxton, A. M.; Bardeaux, M. C.; Chalker, J. M. *J. Org. Chem.* **2014**, *79*, 2094–2104.
(13) Sandgren, V.; Back, M.; Kvarnstrom, I.; Dahlgren, A. The Open Medicinal Chemistry Journal. **2013**, *7*, 1–15.

4'-(trifluoromethyl)-[1,1'-biphenyl]-4-ol (5g) [14]



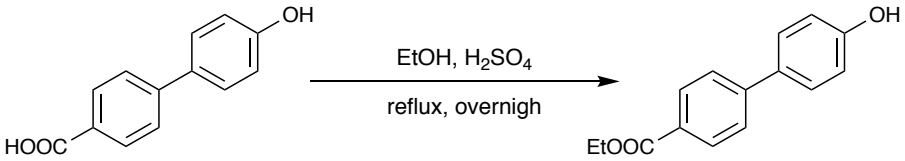
White solid (220.7 mg, 92.6 % yield).
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.67 (d, *J* = 8.96 Hz, 2H), 7.65 (d, *J* = 8.68 Hz, 2H), 7.51 (not first order doublet, *J* = 8.68 Hz, 2H), 6.94 (not first order doublet, *J* = 8.72 Hz, 2H), 4.80 (s, 1H).
^{13}C NMR (101 MHz, $CDCl_3$,) δ 155.69, 144.14, 132.51, 128.68(q, J_{CF} = 32.16 Hz), 128.61, 126.85, 125.67 (q, J_{CF} = 3.5Hz), 125.68 (q, J_{CF} = 271.83) 115.87.
^{19}F NMR (376 MHz, $CDCl_3$) δ –62.17.

1.4 Synthesis of 4'-hydroxy-[1,1'-biphenyl]-4-carboxylic acid



Dimethoxyethane (7 ml) was added to a solution of the 4'-hydroxy-4-biphenylcarbonitrile (300 mg, 1.54 mmol) in 50% of H_2SO_4 (5 mL) and refluxed overnight. The reaction was allowed to cool to room temperature and concentrated in vacuo. The reaction mixture was carefully quenched with 10% NaOH solution while in an ice bath and when bubbling ceased it was washed with saturated $NaHCO_3$ solution and extracted with EtOAc (3x). The remaining aqueous layer was then acidified with 10% HCl solution and extracted with EtOAc (3x). The organic layer drained, dried over Na_2SO_4 and concentrated in vacuo. The extracted product was used in next step without further purification.

1.5 Synthesis of ethyl 4'-hydroxy-[1,1'-biphenyl]-4-carboxylate (5f)

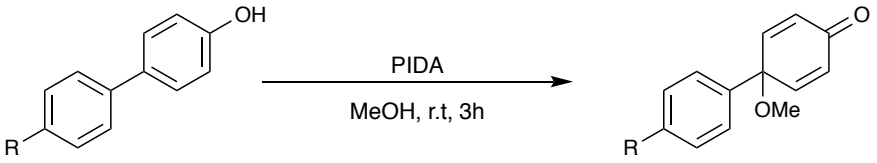


Concentrated H_2SO_4 (0.5 mL) was added to a solution of the crude 4'-hydroxy-[1,1'-biphenyl]-4-carboxylic acid dissolved in EtOH (10 mL). The mixture was then refluxed overnight. The reaction was cooled to room temperature and concentrated in vacuo. Saturated $NaHCO_3$ solution was added slowly to the mixture and extracted with EtOAc (3x). The combined organic layers were dried over Na_2SO_4 and concentrated in vacuo. The residue was purified by flash column chromatography to afford a white solid. (215.1 mg, 57.8% yield over 2 steps).[15]

(14) Chadwick, J.; Amewu, R. K.; Marti, F.; Garah, F. B. E.; Sharma, R.; Berry, N. G.; Stocks, P. A; Saward, H. B.; Wittlin, S.; Ward, S. A.; O'Neill, P. M. *ChemMedChem*, **2011**, *6*, 1357–1361.
(15) Kang, S. H,; Jang, K. S.; Theato, P.; Zentel, R.; Chang, J. Y. *Macromolecules* **2007**, *40*, 8349–8354.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.09 (not first order doublet, *J* = 8.64 Hz, 2H), 7.61 (not first order doublet, *J* = 8.64 Hz, 2H), 7.53 (not first order doublet, *J* = 8.72 Hz,2H), 6.94 (not first order doublet, *J* = 8.72 Hz, 2H), 5.11 (s, 1H), 4.40 (q, *J* = 7.1 Hz, 2H), 1.42 (t, *J* = 7.1 Hz, 3H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 167.08, 156.14, 145.26, 132.36, 130.08, 128.56, 128.30, 126.42, 115.86, 61.16, 14.30.

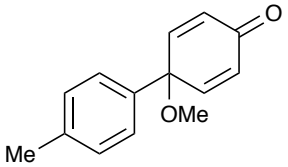
1.6 General procedure for the preparative oxidative dearomatization of 4'-subsituted-[1,1'-biphenyl]-4-ols



4'-Subsituted-[1,1'-biphenyl]-4-ol (0.2 mmol, 1 eq.) and (diacetoxyiodo)benzene (70.9 mg, 0.22 mmol, 1.1 eq.) was dissolved in methanol (2 mL) and stirred for 3 hours at room temperature. The reaction mixture was then quenched with 10% sodium thiosulfate solution, extracted with EtOAc (3X) and dried over Na_2SO_4. After concentration in vacuo, the residue was purified by flash column chromatography to afford the desired product.

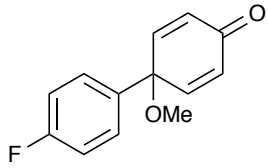
The preparation of compounds 1-methoxy-[1,1'-biphenyl]-4(1*H*)-one (**6a**), 4'-bromo-1-methoxy-[1,1'-biphenyl]-4(1*H*)-one (**6e**), and 1,4'-dimethoxy-[1,1'-biphenyl]-4(1*H*)-one (**6b**) using a similar procedure has been reported in the literature.[16]

1-methoxy-4'-methyl-[1,1'-biphenyl]-4(1*H*)-one (6a)



Incomplete reaction after 3 hrs. Light yellow solid (22 mg, 51.4% yield).
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.33 (not first order doublet, *J* = 8.28 Hz, 2H), 7.17 (d, *J* = 8.12 Hz, 2H), 6.79 (not first order doublet, *J* = 10.16 Hz, 2H), 6.39 (not first order doublet, *J* = 10.16 Hz, 2H), 3.42 (s, 3H), 2.34 (s, 3H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 185.66, 150.70, 138.21, 135.19, 129.88, 129.46, 125.57, 76.43, 52.83, 21.05.
HRMS (ESI+) 237.0892 calc'd for $C_{14}H_{14}O_2Na^+$, 237.0892 found.

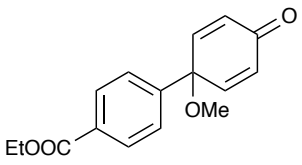
4'-fluoro-1-methoxy-[1,1'-biphenyl]-4(1*H*)-one (6d)



Incomplete reaction after 3 hrs. Light yellow solid (21.4 mg, 49.1% yield).
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.47 – 7.40 (m, 2H), 7.09 – 7.01 (m, 2H), 6.76 (not first order doublet, *J* = 10.2 Hz, 2H), 6.41 (not first order doublet, *J* = 10.2 Hz, 2H), 3.42 (s, 3H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 185.38, 162.55 (d, J_{CF} = 247.5 Hz), 150.26, 134.04 (d, J_{CF} = 3.1 Hz), 130.15, 127.54 (d, J_{CF} = 8.4 Hz), 115.65 (d, J_{CF} = 21.6 Hz), 76.09, 52.91.
^{19}F NMR (376 MHz, $CDCl_3$) δ –113.52 (tt, *J* = 5.2, 8.4 Hz).
HRMS (ESI+) 241.0641 calc'd for $C_{13}H_{11}FO_2Na^+$, 241.0641 found.

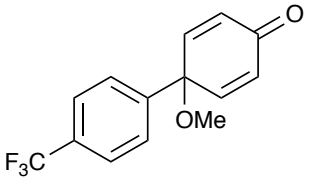
(16) Sawama, Y.; Masude, M.; Nakatani, R.; Yokoyama, H.; Monguchi, Y.; Dohi, T.; Kita, Y.; Sajiki, H. *Adv. Synth. Catal.* **2016**, *358*, 3683–3687.

ethyl 1'-methoxy-4'-oxo-1',4'-dihydro-[1,1'-biphenyl]-4-carboxylate (6f)



Light yellow solid (40.6 mg, 74.6% yield).
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.02 (not first order doublet, *J* = 8.48 Hz, 2H), 7.52 (not first order doublet, *J* = 8.48 Hz, 2H), 6.76 (not first order doublet, *J* = 10.2 Hz, 2H), 6.44 (not first order doublet, *J* = 10.16 Hz, 2H), 4.37 (q, *J* = 7.1 Hz, 2H), 3.44 (s, 3H), 1.38 (t, *J* = 7.1 Hz, 3H)
^{13}C NMR (101 MHz, $CDCl_3$) δ 185.24, 166.03, 149.71, 143.06, 130.49, 130.40, 129.93, 125.69, 76.44, 61.04, 52.88, 14.25.
HRMS (ESI+) 295.0946 calc'd for $C_{16}H_{16}O_4Na^+$, 295.0948 found.

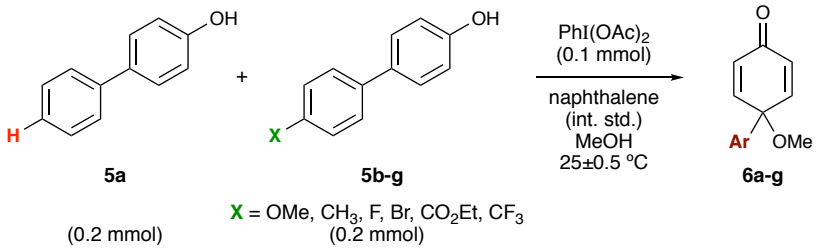
1-methoxy-4'-(trifluoromethyl)-[1,1'-biphenyl]-4(1*H*)-one (6g)



Incomplete reaction after 3 hrs. Light yellow solid (27.1 mg, 50.6% yield).
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.62 (d, *J* = 8.8 Hz, 2H), 7.58 (d, *J* = 8.7 Hz, 2H) 6.75 (not first order doublet, *J* = 10.2 Hz, 2H), 6.4 (not first order doublet, *J* = 10.2 Hz, 2H), 3.44 (s, 3H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 185.17, 149.63, 142.36, 130.64, 130.18 (d, J_{CF} = 32.7 Hz), 126.20, 125.64 (q, J_{CF} = 3.8 Hz), 123.87 (d, J_{CF} = 272.2 Hz), 76.30, 52.93.
^{19}F NMR (376 MHz, $CDCl_3$) δ –62.55
HRMS (ESI+) 291.0609 calc'd for $C_{14}H_{11}F_3O_2Na^+$, 291.0609 found.

2.0 Experimental Procedures–Competition Experiments

2.1.1 General procedure for each of the competition experiments



For each of the competition experiments (except 4-phenylphenol versus itself), naphthalene (12.8 mg, 0.1 mmol, 0.5 eq.), 4-phenylphenol (**5a**, 34 mg, 0.2 mmol, 1 eq.) and a substituted 4-phenylphenol (**5b-g**, 0.2 mmol, 1 eq.) were dissolved in methanol (2 mL) at 25±0.5 °C. A 20 μL aliquot was transferred to an HPLC vial and diluted to 2 mL with an isopropyl/hexane mixture to determine the ratios of starting materials. (Diacetoxyiodo)benzene (32.2 mg, 0.1 mmol, 0.5 eq.) was then added to the remaining reaction mixture and stirred at 25±0.5 °C. After 2 hours, a 20 μL aliquot was transferred to an HPLC vial and diluted to 2 mL with an isopropyl/hexane mixture to determine the ratios of starting materials after the (diacetoxyiodo)benzene was consumed. Each experiment was run in triplicate.

2.1.2 Procedure for the competition experiment of 4-phenylphenol

Naphthalene (12.8 mg, 0.1 mmol, 0.25 eq.) and 4-phenylphenol (**5a**, 68.1 mg, 0.4 mmol, 1 eq.) were dissolved in methanol (2 mL) at 25±0.5 °C. A 20 μL aliquot was transferred to an HPLC vial and diluted to 2 mL with an isopropyl/hexane mixture to determine the ratios of starting materials. (Diacetoxyiodo)benzene (32.2 mg, 0.1 mmol, 0.25 eq.) was added to the remaining reaction mixture and stirred at 25±0.5 °C. After 2 hours, a 20 μL aliquot was transferred to an HPLC vial and diluted to 2 mL with an isopropyl/hexane mixture to determine the ratios of starting materials after the (diacetoxyiodo)benzene was consumed. This experiment was run in triplicate.

2.2 HPLC data for analyzing the relative ratios of starting materials

The following tables contain the HPLC data (peak areas) used to measure the relative rates. Equation 1 from the main text was used to calculate k_X/k_H. IS = internal standard (naphthalene)

4-phenylphenol (**5a**)							
Species		Peak Area		Relative Ratios			
run 1	mmol	start	2 hrs	start (cmpd/IS)	2hrs (cmpd/IS)	2hrs/start	k_H/k_H
napthalene	0.1006	3476.8	3527.3	1	1	0	1
5a	0.4001	75942.7	55450.1	21.84270018	15.72026763	0.719703493	

run2	mmol	start	2 hrs	start (cmpd/IS)	2hrs (cmpd/IS)	2hrs/start	k_H/k_H
napthalene	0.0999	1540.5	1751.6	1	1	0	1
5a	0.4001	36618.6	29505.6	23.77059396	16.84494177	0.708646229	

run3	mmol	start	2 hrs	start (cmpd/IS)	2hrs (cmpd/IS)	2hrs/start	k_H/k_H
napthalene	0.0999	1577.8	1829.7	1	1	1	1
5a	0.4001	36470.7	29745.3	23.11490683	16.25692737	0.703309232	

4-phenylphenol (**5a**) vs 4'-methoxy-[1,1'-biphenyl]-4-ol (**5b**)							
Species		Peak Area		Relative Ratios			
run1	mmol	start	2 hrs	start (cmpd/IS)	2hrs (cmpd/IS)	2hrs/start	k_{OCH3}/k_H
napthalene	0.1006	3149.6	1534.2	1	1	0	1.840096547
5a	0.2003	53784.1	15735.3	17.0764859	10.2563551	0.600612747	
5b	0.1998	60132	11463.7	19.09194818	7.472102725	0.391374555	

run2	mmol	start	2 hrs	start (cmpd/IS)	2hrs (cmpd/IS)	2hrs/start	k_{OCH3}/k_H
napthalene	0.0999	1478.2	1271.4	1	1	0	2.325964578
5a	0.2003	19332.6	13154.4	13.07847382	10.34638981	0.791100701	
5b	0.1998	20621.6	10284	13.95048031	8.088721095	0.579816674	

run3	mmol	start	2 hrs	start (cmpd/IS)	2hrs (cmpd/IS)	2hrs/start	k_{OCH3}/k_H
napthalene	0.0999	1619	1819.7	1	1	0	2.634426399
5a	0.2003	19211.5	17505.1	11.86627548	9.61977249	0.810681709	
5b	0.1998	20158.2	13034	12.45101915	7.16271913	0.575271714	

4-phenylphenol (**5a**) vs 4'-fluoro-[1,1'-biphenyl]-4-ol (**5d**)							
Species		Peak Area		Relative Ratios			
run 1	mmol	start	2 hrs	start (cmpd/IS)	2hrs (cmpd/IS)	2hrs/start	k_F/k_H
napthalene	0.0999	1680.6	1709.3	1	1	0	0.944843818
5a	0.2003	26698.4	13663.7	15.88623111	7.993740128	0.503186695	
5d	0.1998	28746	15279.6	17.1046055	8.939097876	0.522613508	

run2	mmol	start	2 hrs	start (cmpd/IS)	2hrs (cmpd/IS)	2hrs/start	k_F/k_H
napthalene	0.0999	1441.5	1847.1	1	1	0	0.869380723
5a	0.1998	17229.8	14762.2	11.95268817	7.992095718	0.668644208	
5d	0.1998	17087.3	15430.4	11.85383281	8.353851984	0.704738469	

run3	mmol	start	2 hrs	start (cmpd/IS)	2hrs (cmpd/IS)	2hrs/start	k_F/k_H
napthalene	0.1006	1774.6	1742.5	1	1	0	0.852365254
5a	0.1998	20231.6	13467.6	11.40065367	7.728895265	0.677934397	
5d	0.2009	20854.5	14702.2	11.75166235	8.437417504	0.717976509	

4-phenylphenol (**5a**) vs 4'-bromo-[1,1'-biphenyl]-4-ol (**5e**)							
Species		Peak Area		Relative Ratios			
run 1	mmol	start	2 hrs	start (cmpd/IS)	2hrs (cmpd/IS)	2hrs/start	k_{Br}/k_H
napthalene	0.0999	1417.2	1512.6	1	1	0	
5a	0.2003	17318.1	11794.4	12.21994073	7.79743488	0.638091056	0.654694731
5e	0.2003	15686.2	12475.8	11.06844482	8.247917493	0.745174017	

run2	mmol	start	2 hrs	start (cmpd/IS)	2hrs (cmpd/IS)	2hrs/start	k_{Br}/k_H
napthalene	0.0999	1316.4	1375	1	1	0	
5a	0.1998	16280.1	11213.1	12.36713765	8.154981818	0.659407379	0.587520536
5e	0.1999	15010.3	12275.9	11.40253722	8.927927273	0.782977253	

run3	mmol	start	2 hrs	start (cmpd/IS)	2hrs (cmpd/IS)	2hrs/start	k_{Br}/k_H
napthalene	0.0999	1562.3	1711.3	1	1	0	
5a	0.2003	20184.9	13885	12.91998976	8.11371472	0.627996993	0.636241699
5e	0.1999	18679.8	15219	11.95660245	8.893239058	0.743793155	

4-phenylphenol (**5a**) vs ethyl 4'-hydroxy-[1,1'-biphenyl]-4-carboxylate (**5f**)							
Species		Peak Area		Relative Ratios			
run 1	mmol	start	2 hrs	start (cmpd/IS)	2hrs (cmpd/IS)	2hrs/start	k_{CO2Et}/k_H
napthalene	0.0999	1083.3	1451.8	1	1	0	
5a	0.1998	12466.3	8438.8	11.50770793	5.81264637	0.505108959	0.493536276
5f	0.2002	1622.9	1552.6	1.498107634	1.069431051	0.713854617	

run2	mmol	start	2 hsr	start (cmpd/IS)	2hrs (cmpd/IS)	2hrs/start	k_{CO2Et}/k_H
napthalene	0.0999	1071	1359.5	1	1	0	
5a	0.1998	12279.2	8113.8	11.46517274	5.968223612	0.520552437	0.492539725
5f	0.2002	1655.3	1523.4	1.545564893	1.120559029	0.72501584	

run3	mmol	start	2 hrs	start (cmpd/IS)	2hrs (cmpd/IS)	2hrs/start	k_{CO2Et}/k_H
napthalene	0.0999	1106.9	1214.3	1	1	0	
5a	0.1998	12530.3	7141.8	11.32017346	5.88141316	0.519551505	0.486662724
5f	0.2002	1624.1	1295.5	1.467250881	1.066869802	0.727121596	

4-phenylphenol (**5a**) vs 4'-(trifluoromethyl)-[1,1'-biphenyl]-4-ol (**5g**)							
Species		Peak Area		Relative Ratios			
run 1	mmol	start	2 hrs	start (cmpd/IS)	2hrs (cmpd/IS)	2hrs/start	k_{CF3}/k_H
napthalene	0.0999	1622.5	1505.4	1	1	0	
5a	0.1998	19210.3	10292.2	11.83993837	6.836853992	0.577439998	0.218556803
5g	0.1998	12396.4	10200.9	7.640308166	6.77620566	0.88690214	

run2	mmol	start	2 hrs	start (cmpd/IS)	2hrs (cmpd/IS)	2hrs/start	k_{CF3}/k_H
napthalene	0.0999	1532.5	1121.7	1	1	0	
5a	0.1998	19787.9	6839.8	12.91216966	6.097708835	0.472245099	0.418774486
5g	0.1998	12521.6	6694	8.170701468	5.967727556	0.7303813	

run3	mmol	start	2 hrs	start (cmpd/IS)	2hrs (cmpd/IS)	2hrs/start	k_{CF3}/k_H
napthalene	0.0991	1539.5	1671.4	1	1	0	
5a	0.1998	19124.9	11521.9	12.42279961	6.893562283	0.554912137	0.263917042
5g	0.1998	12192	11331.1	7.919454368	6.779406486	0.856044643	

4-Phenylphenol (**5a**) and 4'-methyl-[1,1'-biphenyl]-4-ol (**5c**) had the same retention time on the HPLC. Because of this, k_{CH3}/k_H was determined using a modified procedure. First procedure 2.1.1 was used to carry out a competition experiment between phenol **5c** and phenol **5e**. The relative rate constant obtained from this set of experiments was then multiplied by k_{Br}/k_H, according to the following relationship:

$$\frac{k_{\mathrm{CH3}}}{k_{\mathrm{H}}} = \frac{k_{\mathrm{CH3}}}{k_{\mathrm{Br}}} \times \frac{k_{\mathrm{Br}}}{k_{\mathrm{H}}}$$

4'-bromo-[1,1'-biphenyl]-4-ol (**5e**) vs 4'-methyl-[1,1'-biphenyl]-4-ol (**5c**)							
Species		Peak Area		Relative Ratios			
run 1	mmol	start	2 hrs	start (cmpd/IS)	2hrs (cmpd/IS)	2hrs/start	k_{CH3}/k_{Br}
napthalene	0.0999	1227.8	363.1	1	1	0	1.989359213
5e	0.1999	13033.8	2798.5	10.61557257	7.707243184	0.726031793	
5c	0.1997	15349.8	2401	12.50187327	6.612503443	0.52892101	

run2	mmol	start	2 hrs	start (cmpd/IS)	2hrs (cmpd/IS)	2hrs/start	k_{CH3}/k_{Br}
napthalene	0.0999	1282.8	1488	1	1	0	2.296218502
5e	0.1999	13842.6	12722.9	10.7909261	8.550336022	0.792363505	
5c	0.1997	14992.9	10191.5	11.68763642	6.849126344	0.586014665	

run3	mmol	start	2 hrs	start (cmpd/IS)	2hrs (cmpd/IS)	2hrs/start	k_{CH3}/k_{Br}
napthalene	0.0999	1120.5	1758	1	1	0	1.794946315
5e	0.1999	14921	15288.3	13.31637662	8.696416382	0.653061762	
5c	0.1997	17505.3	12782.9	15.6227577	7.271274175	0.46542834	

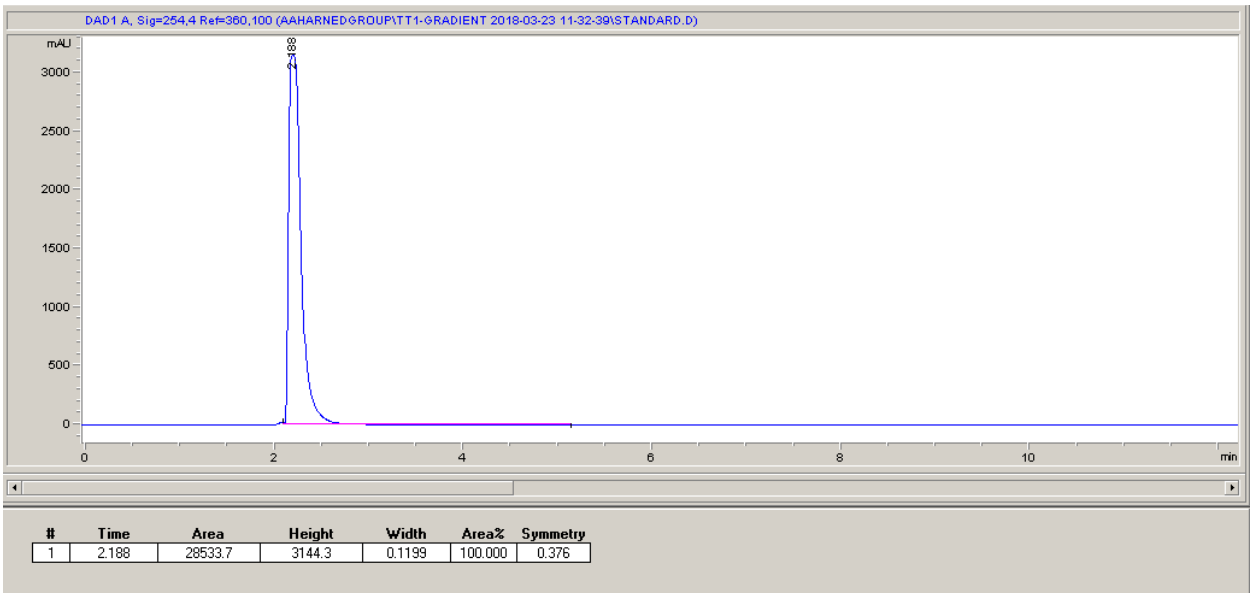
After averaging the three runs for the different competition experiments, the following values were used to generate the different Hammett plots:

compound	X	k_X/k_H	log (k_X/k_H)
5a	H	1.000	0.000
5b	OCH_3	2.267	0.355
5c	CH_3	1.265	0.102
5d	F	0.889	-0.051
5e	Br	0.626	-0.203
5f	CO_2Et	0.491	-0.309
5g	CF_3	0.300	-0.522

2.3 Representative HPLC traces

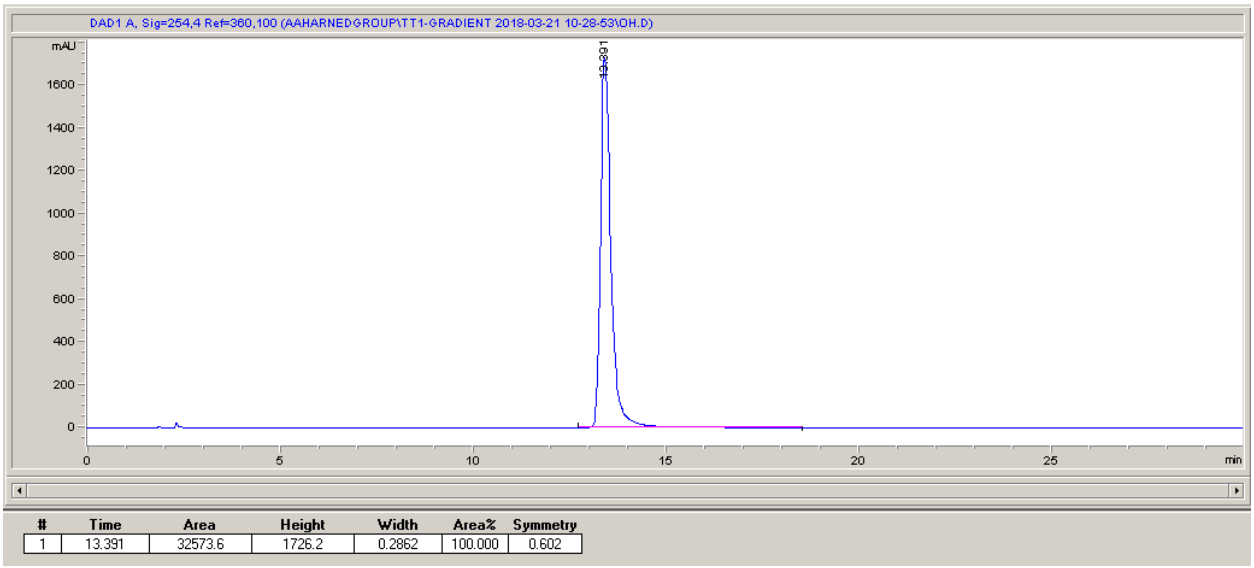
2.3.1 HPLC Chromatogram of 4-phenylphenol (5a) versus itself (hexane/isopropanol = 99:1, 1.0 mL/ min)

Naphthalene:



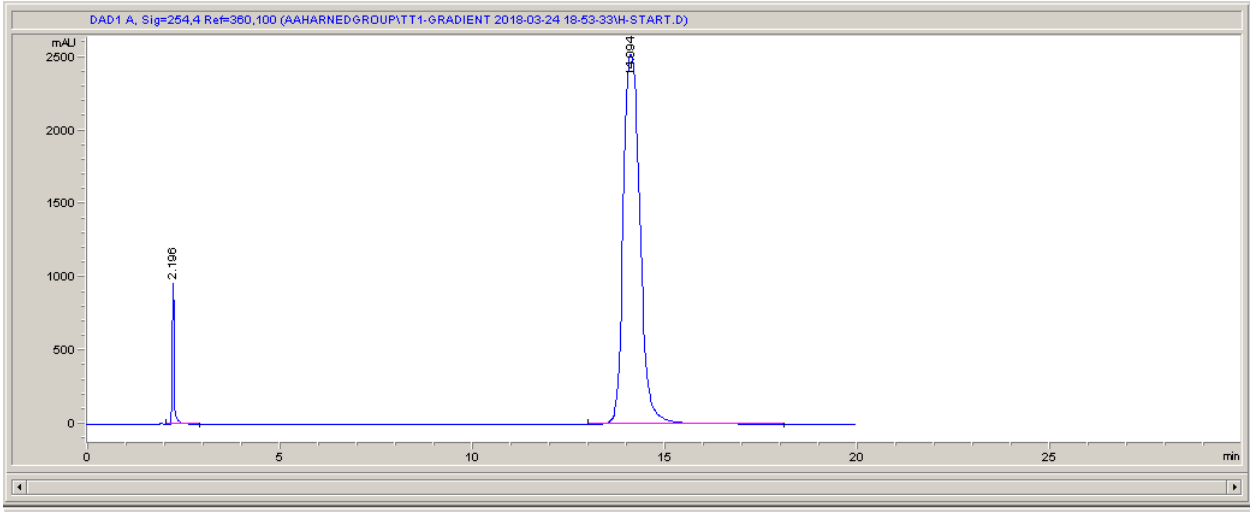
#	Time	Area	Height	Width	Area%	Symmetry
1	2.188	28533.7	3144.3	0.1199	100.000	0.376

4-phenylphenol (**5a**):



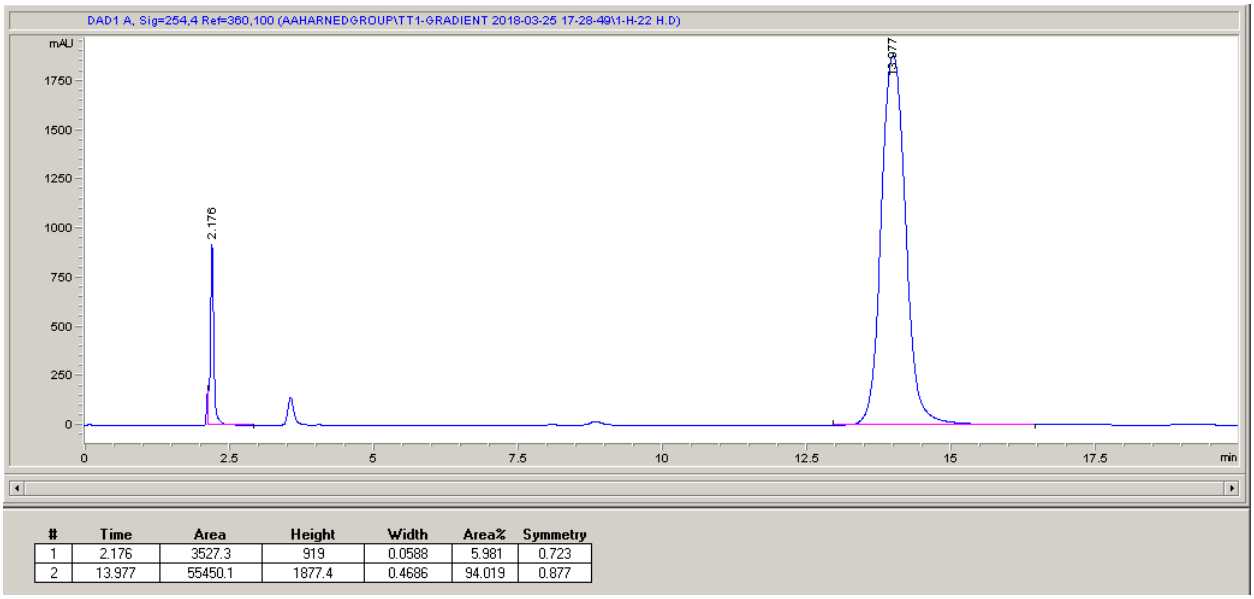
#	Time	Area	Height	Width	Area%	Symmetry
1	13.391	32573.6	1726.2	0.2862	100.000	0.602

experiment start:



#	Time	Area	Height	Width	Area%	Symmetry
1	2.196	3476.8	957.4	0.0544	4.378	0.676
2	14.094	75942.7	2514.5	0.4804	95.622	0.743

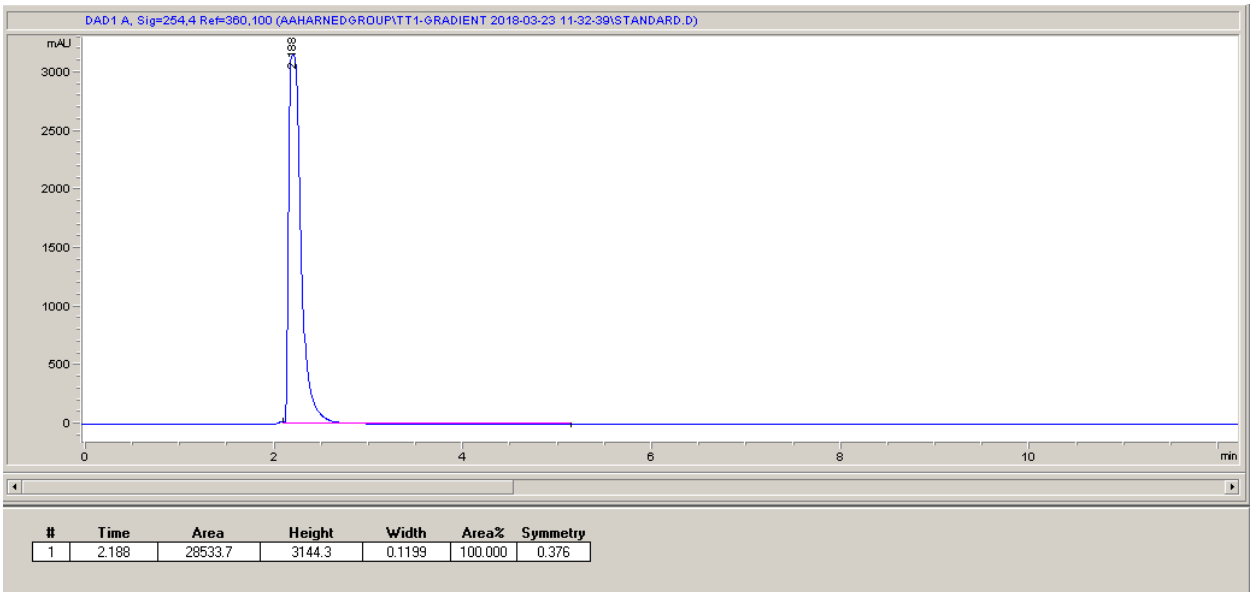
after 2 hrs:



#	Time	Area	Height	Width	Area%	Symmetry
1	2.176	3527.3	919	0.0588	5.981	0.723
2	13.977	55450.1	1877.4	0.4686	94.019	0.877

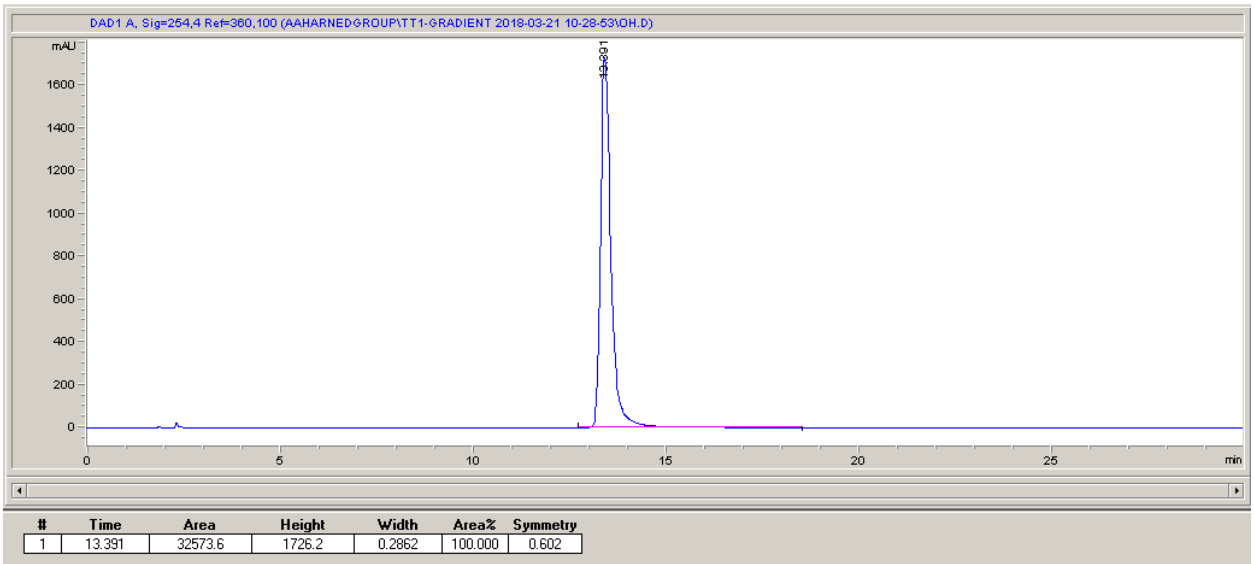
2.3.2 HPLC Chromatogram of 4-phenylphenol (5a) vs 4'-methoy-[1,1'-biphenyl]-4-ol (5b) (hexane/isopropanol = 99:1, 1.0 mL/ min)

Naphthalene:



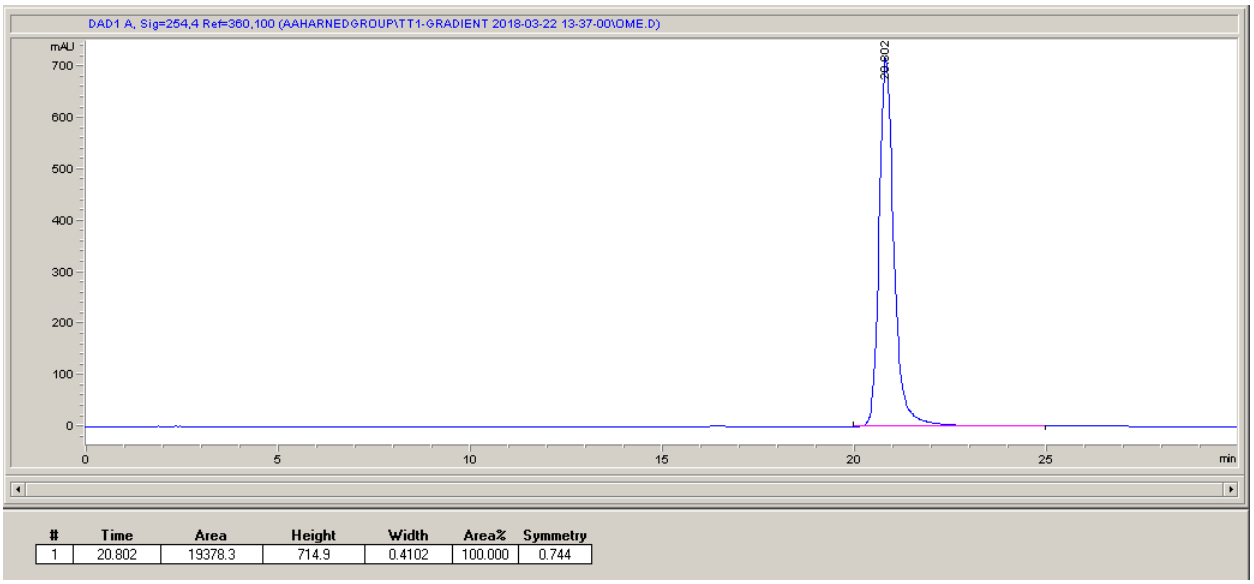
#	Time	Area	Height	Width	Area%	Symmetry
1	2.188	28533.7	3144.3	0.1199	100.000	0.376

4-phenylphenol (**5a**):



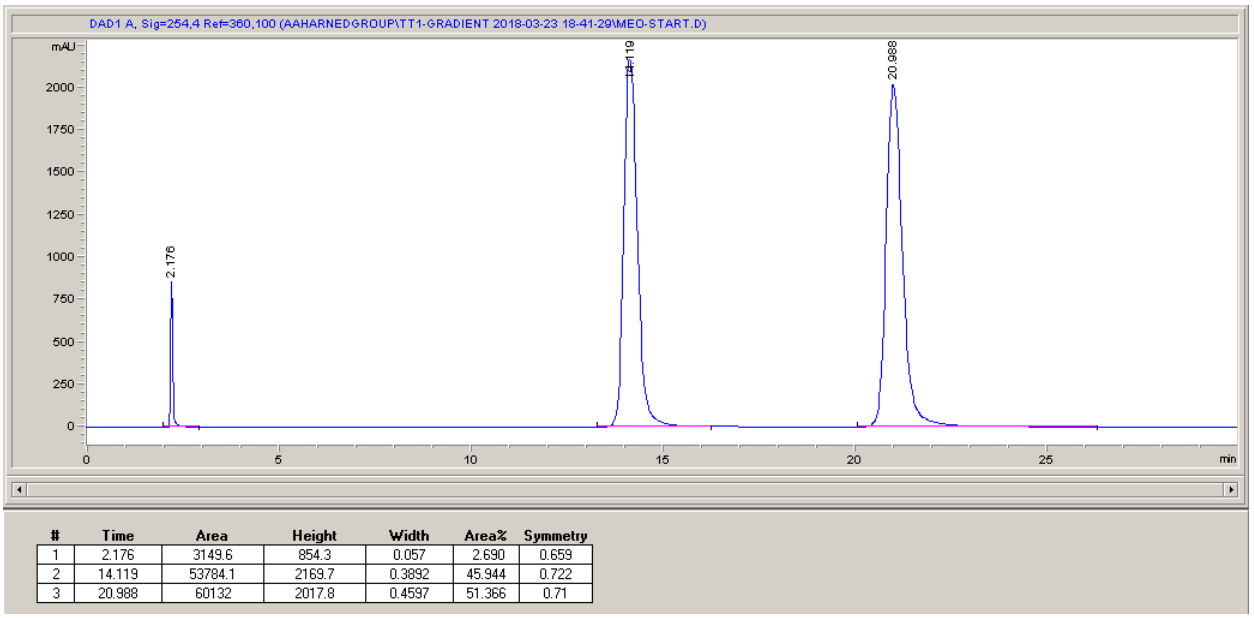
#	Time	Area	Height	Width	Area%	Symmetry
1	13.391	32573.6	1726.2	0.2862	100.000	0.602

4’-methoy-[1,1’-biphenyl]-4-ol (**5b**):



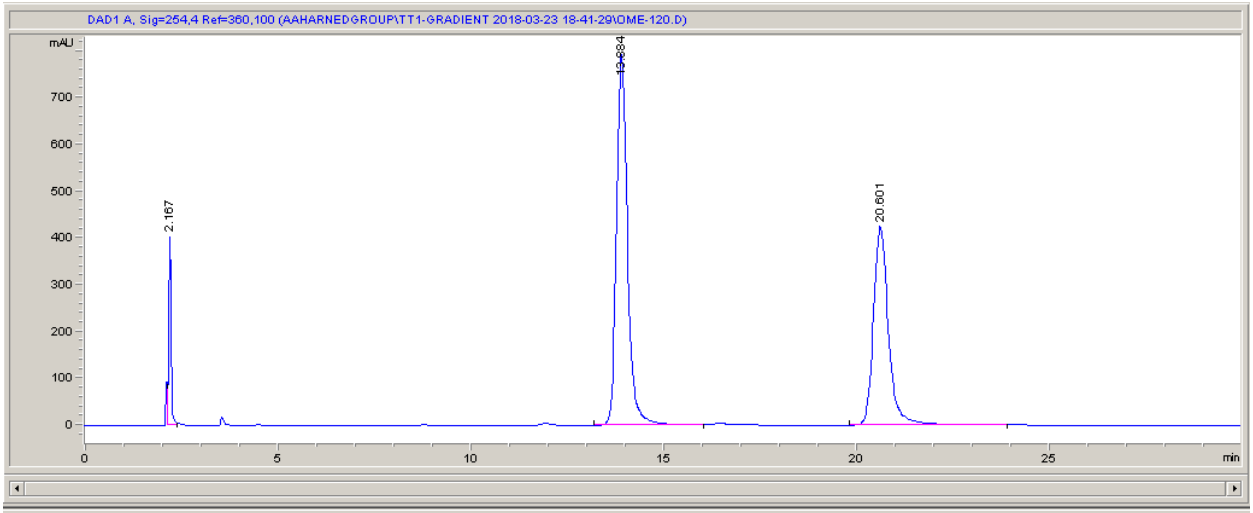
#	Time	Area	Height	Width	Area%	Symmetry
1	20.802	19378.3	714.9	0.4102	100.000	0.744

experiment start:



#	Time	Area	Height	Width	Area%	Symmetry
1	2.176	3149.6	854.3	0.057	2.690	0.659
2	14.119	53784.1	2169.7	0.3892	45.944	0.722
3	20.988	60132	2017.8	0.4597	51.366	0.71

after 2 hrs:

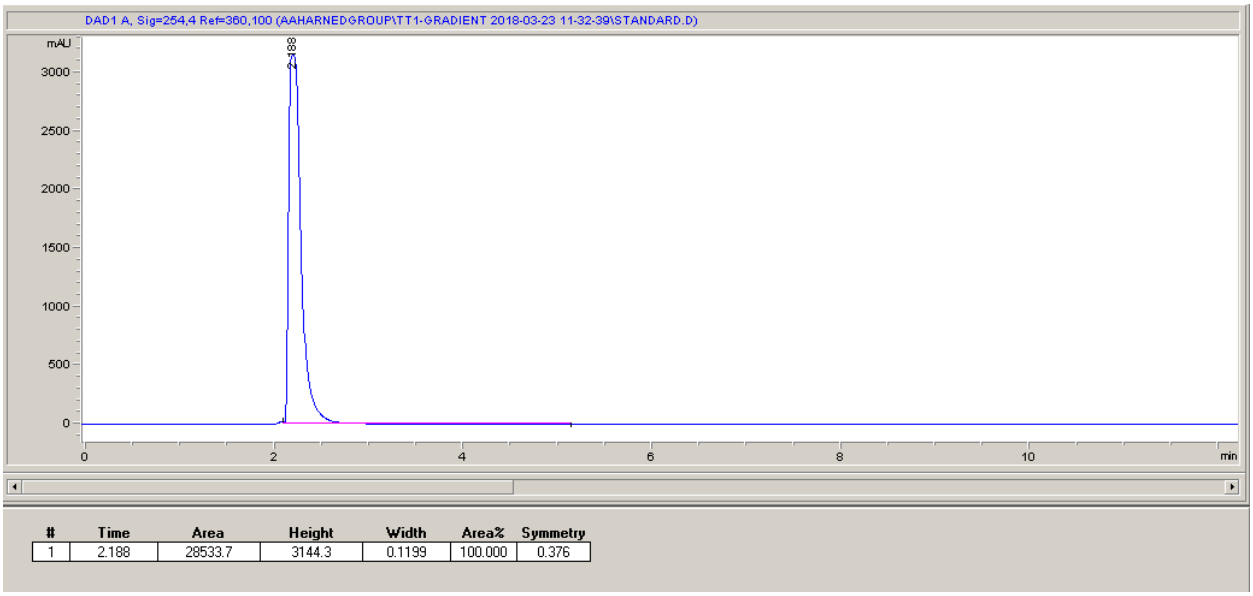


#	Time	Area	Height	Width	Area%	Symmetry
1	2.167	1534.2	402.4	0.0565	5.339	0.742
2	13.884	15735.3	791.4	0.304	54.763	0.753
3	20.601	11463.7	424.1	0.4094	39.897	0.77

2.3.3 HPLC Chromatogram of 4-phenylphenol (5a) vs 4'-fluoro-[1,1'-biphenyl]-4-ol (5d)

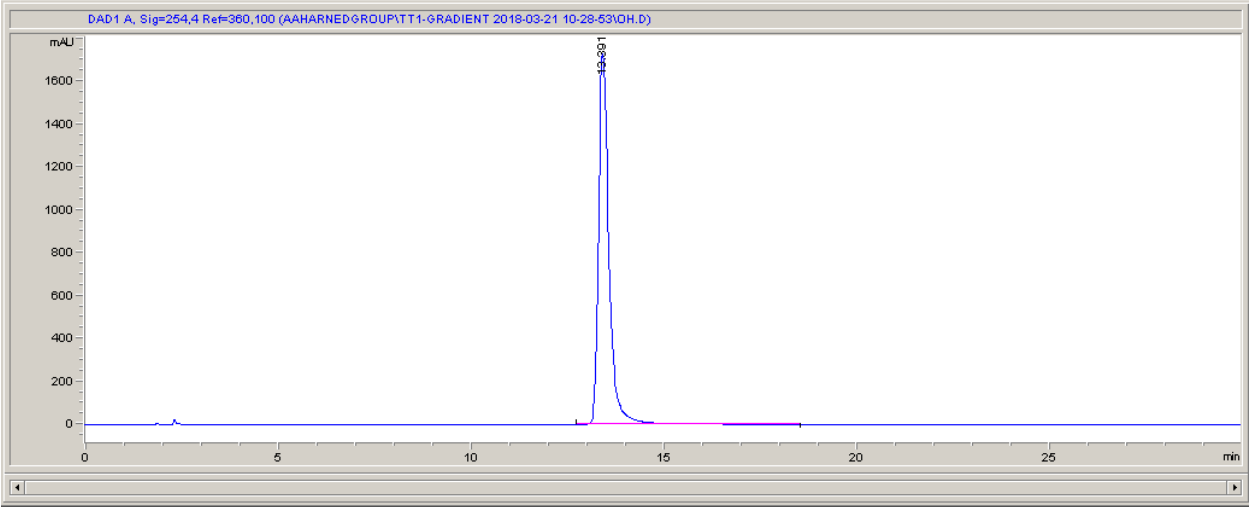
(hexane/isopropanol = 99:1, 1.0 mL/ min)

Naphthalene:



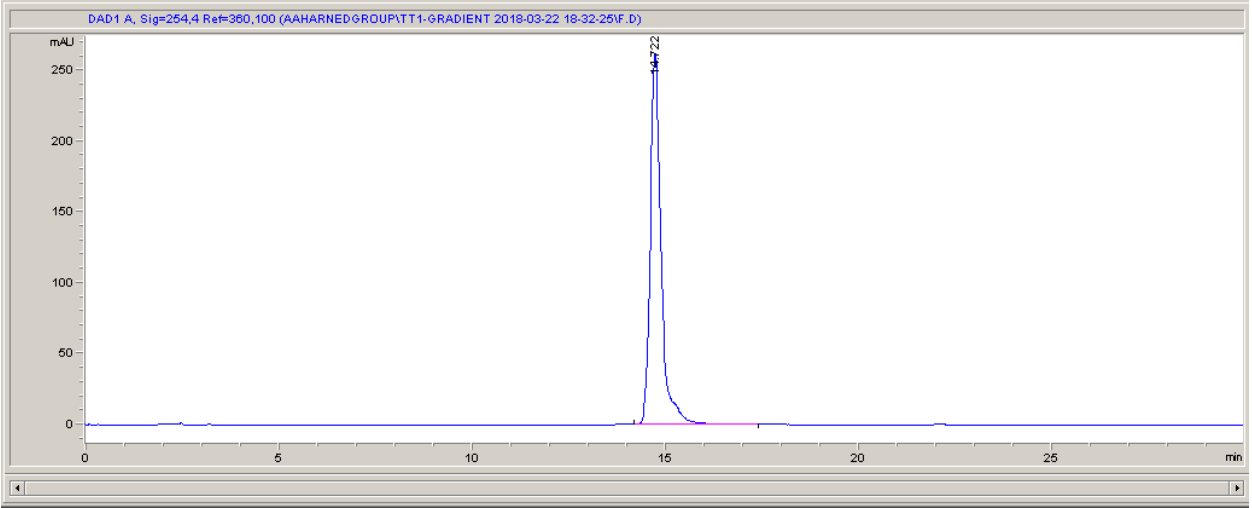
#	Time	Area	Height	Width	Area%	Symmetry
1	2.188	28533.7	3144.3	0.1199	100.000	0.376

4-phenylphenol (**5a**):



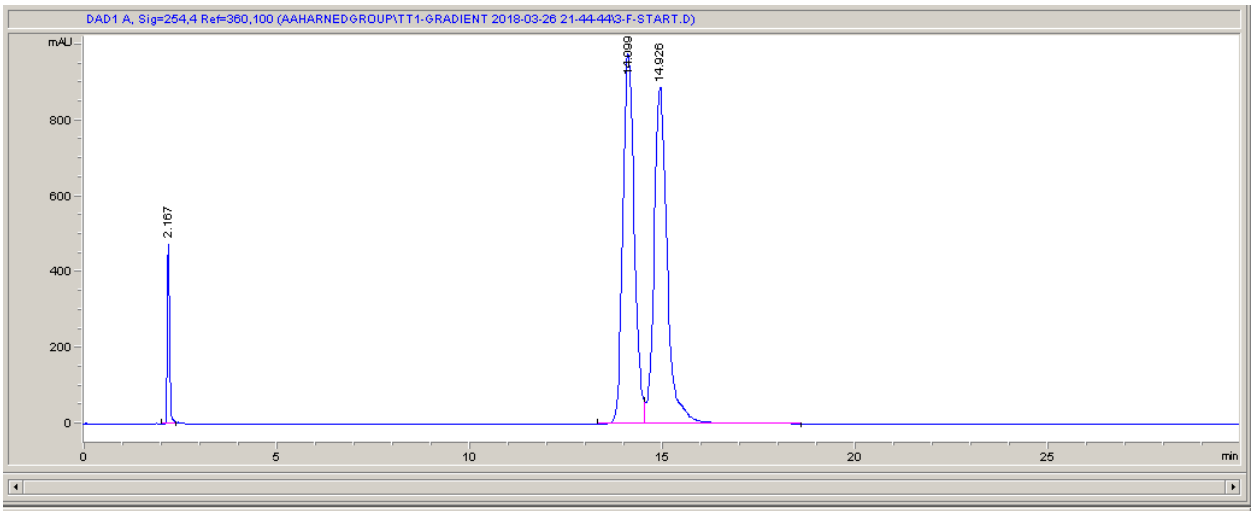
#	Time	Area	Height	Width	Area%	Symmetry
1	13.391	32573.6	1726.2	0.2862	100.000	0.602

4’-fluoro-[1,1’-biphenyl]-4-ol (**5d**):



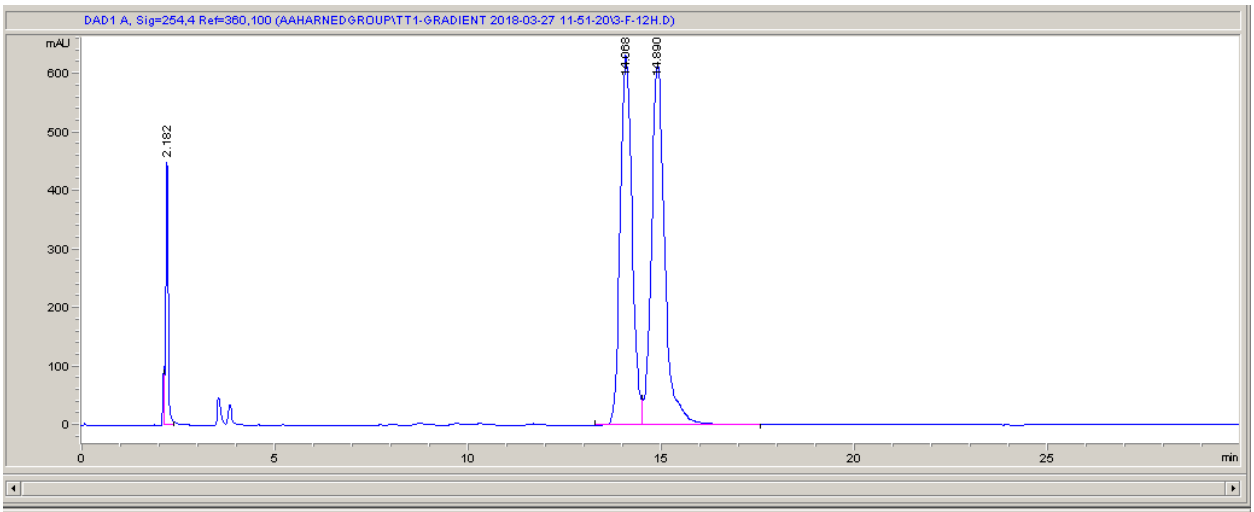
#	Time	Area	Height	Width	Area%	Symmetry
1	14.722	5184	261.5	0.2993	100.000	0.726

experiment start:



#	Time	Area	Height	Width	Area%	Symmetry
1	2.167	1774.6	476.5	0.0554	4.140	0.683
2	14.099	20231.6	975	0.3241	47.203	0.817
3	14.926	20854.5	887.1	0.3583	48.657	0.736

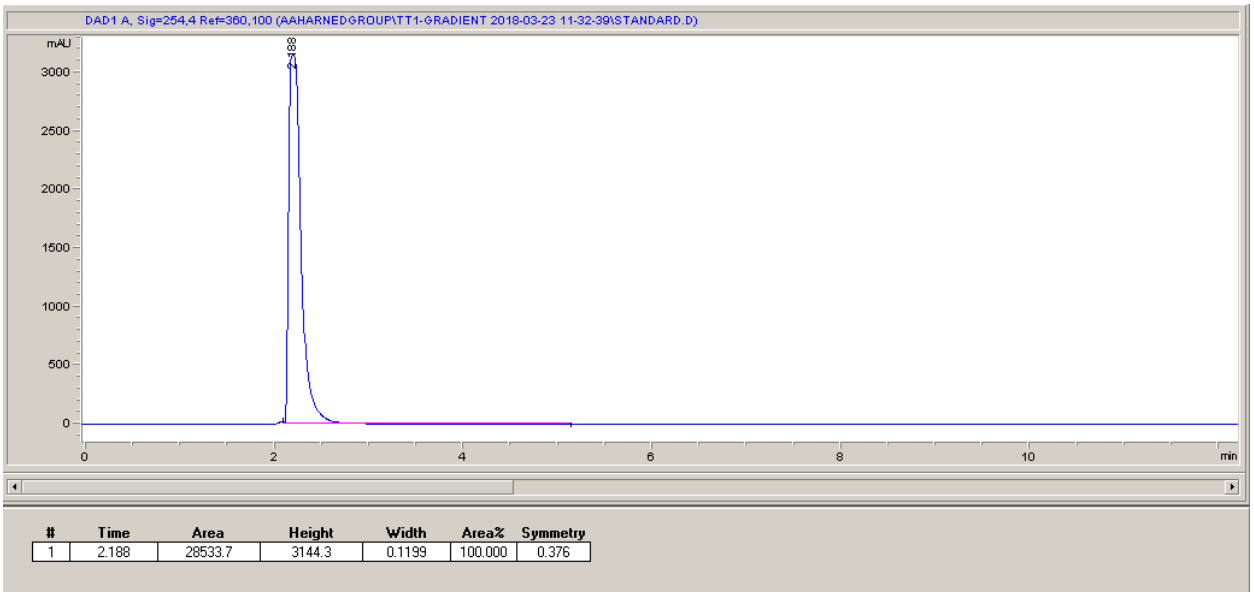
after 2 hrs:



#	Time	Area	Height	Width	Area%	Symmetry
1	2.182	1742.5	450.6	0.0571	5.825	0.731
2	14.068	13467.6	631.2	0.3329	45.024	0.855
3	14.89	14702.2	614	0.3653	49.151	0.767

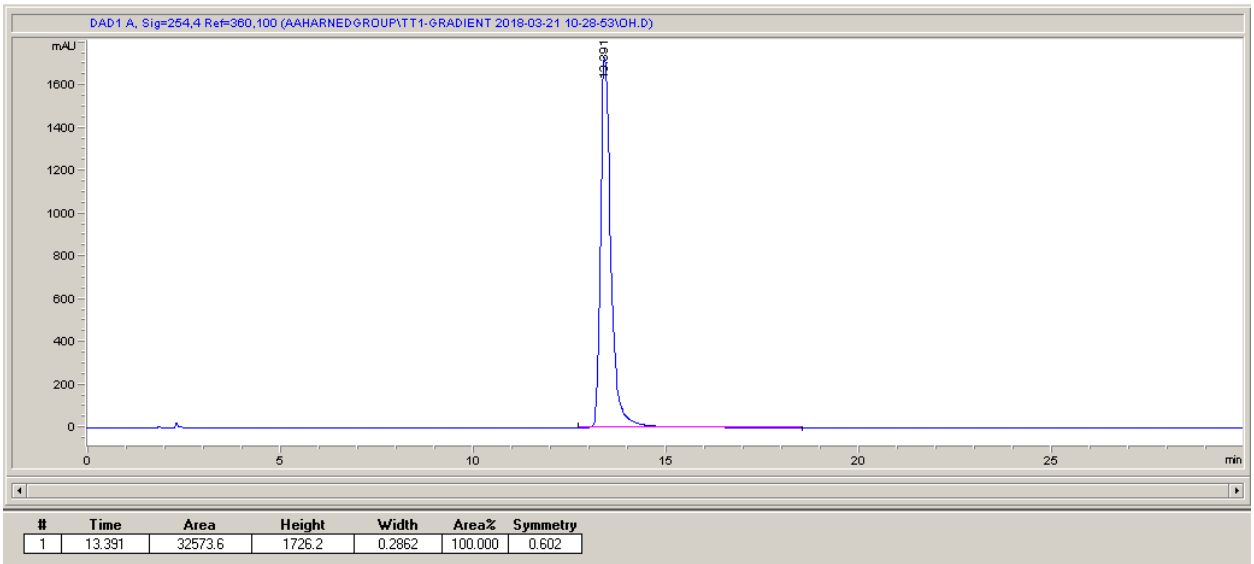
2.3.4 HPLC Chromatogram of 4-phenylphenol (5a) vs 4'-bromo-[1,1'-biphenyl]-4-ol (5e)
(Condition: hexane/isopropanol = 99:1, 1.0 mL/ min)

Naphthalene:



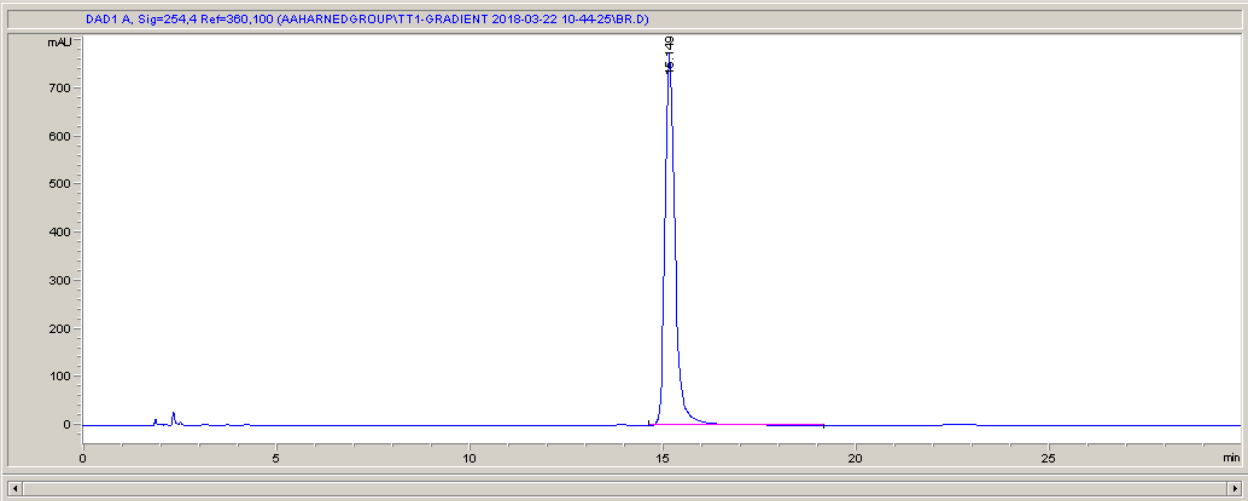
#	Time	Area	Height	Width	Area%	Symmetry
1	2.188	28533.7	3144.3	0.1199	100.000	0.376

4-phenylphenol (**5a**):



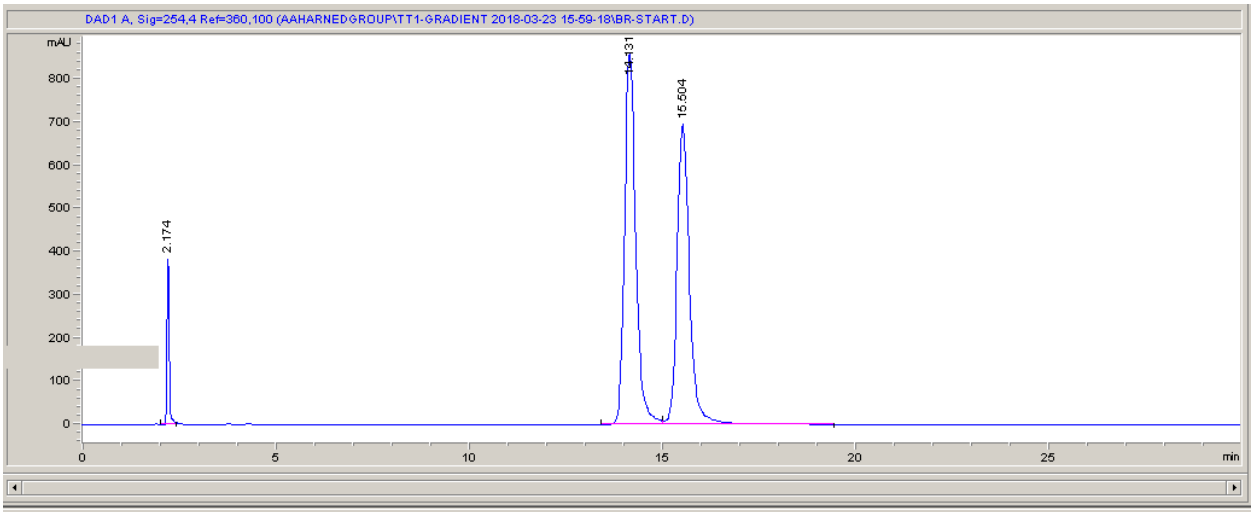
#	Time	Area	Height	Width	Area%	Symmetry
1	13.391	32573.6	1726.2	0.2862	100.000	0.602

4’-bromo-[1,1’-biphenyl]-4-ol (**5e**):



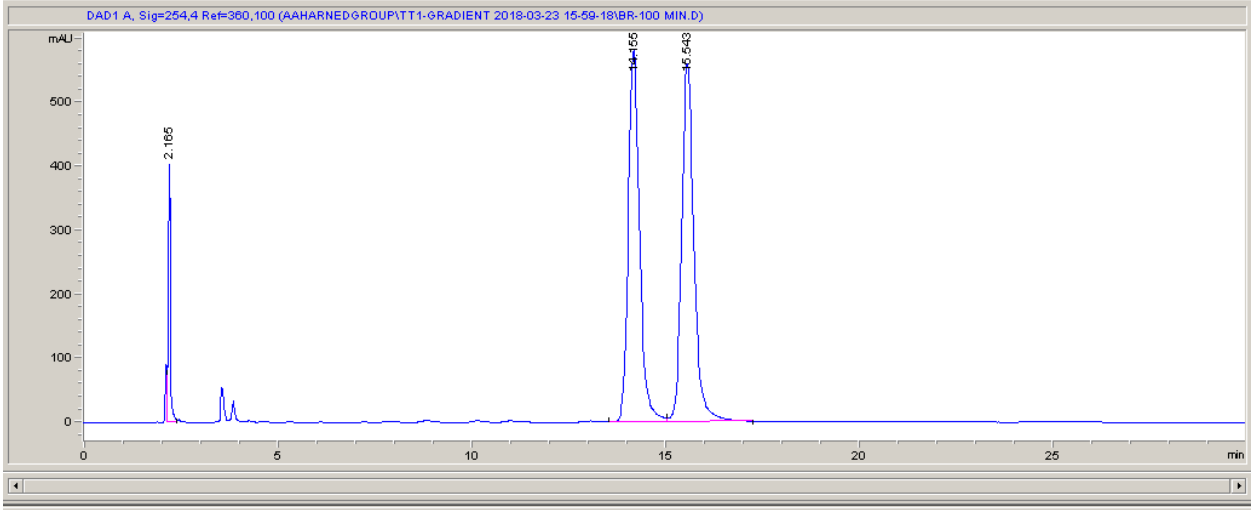
#	Time	Area	Height	Width	Area%	Symmetry
1	15.149	14089.5	771.1	0.2772	100.000	0.702

experiment start:



#	Time	Area	Height	Width	Area%	Symmetry
1	2.174	1417.2	385.3	0.0549	4.117	0.681
2	14.131	17318.1	856.5	0.3119	50.312	0.76
3	15.504	15686.2	696.2	0.3429	45.571	0.745

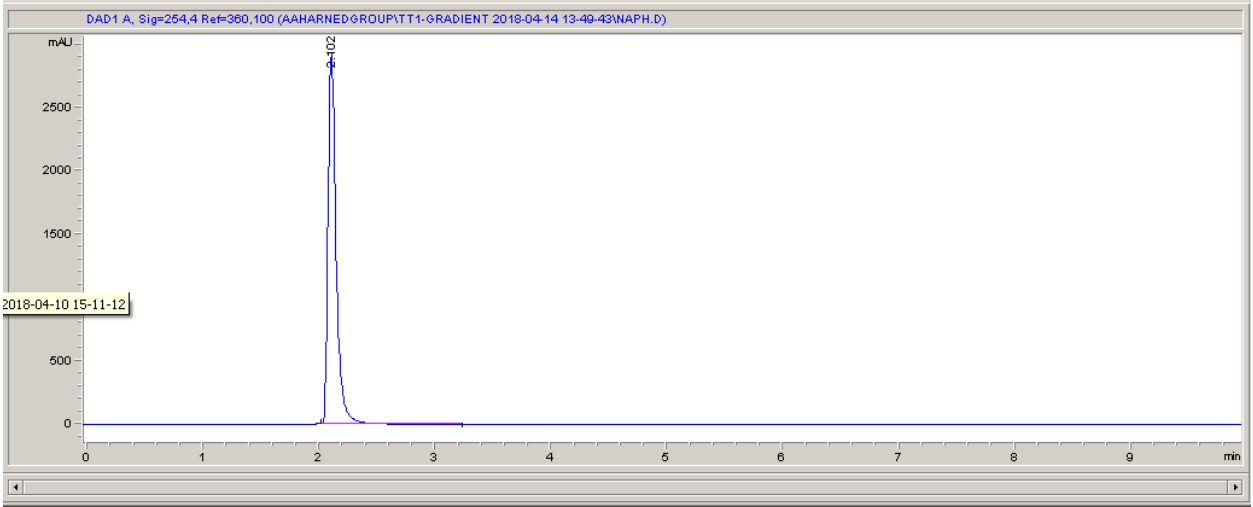
after 2 hrs:



#	Time	Area	Height	Width	Area%	Symmetry
1	2.165	1512.6	404	0.0557	5.867	0.753
2	14.155	11794.4	580.2	0.3112	45.745	0.792
3	15.543	12475.8	559	0.3404	48.388	0.783

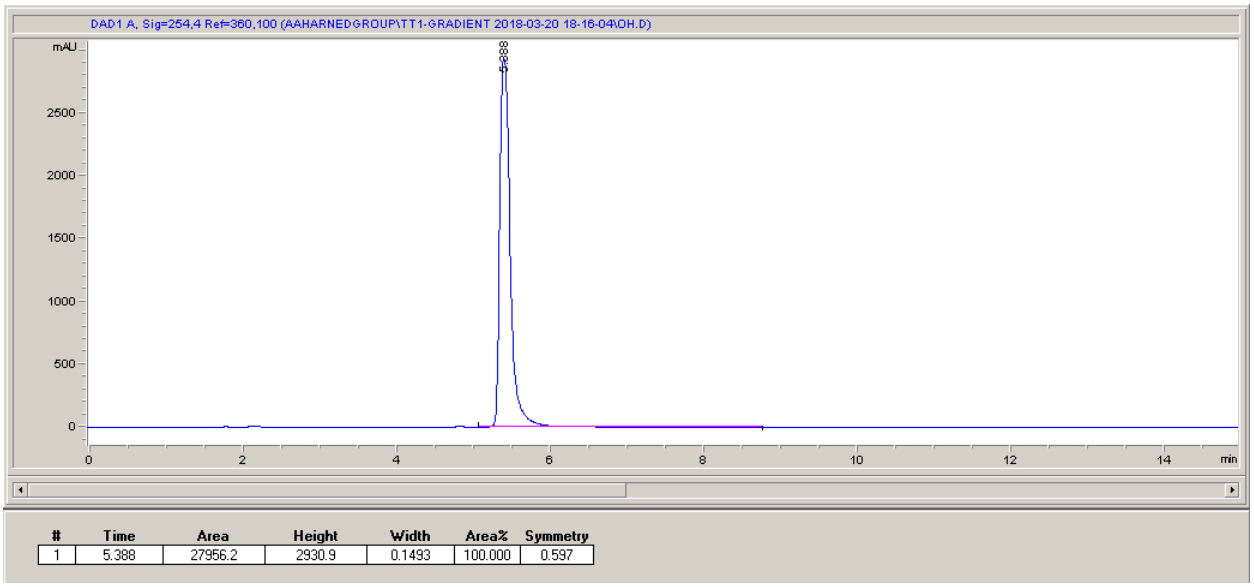
2.3.5 HPLC Chromatogram of 4-phenylphenol (5a) vs ethyl 4'-hydroxy-[1,1'-biphenyl]-4-carboxylate (5f) (hexane/isopropanol = 95:5, 1.0 mL/ min)

Naphthalene:



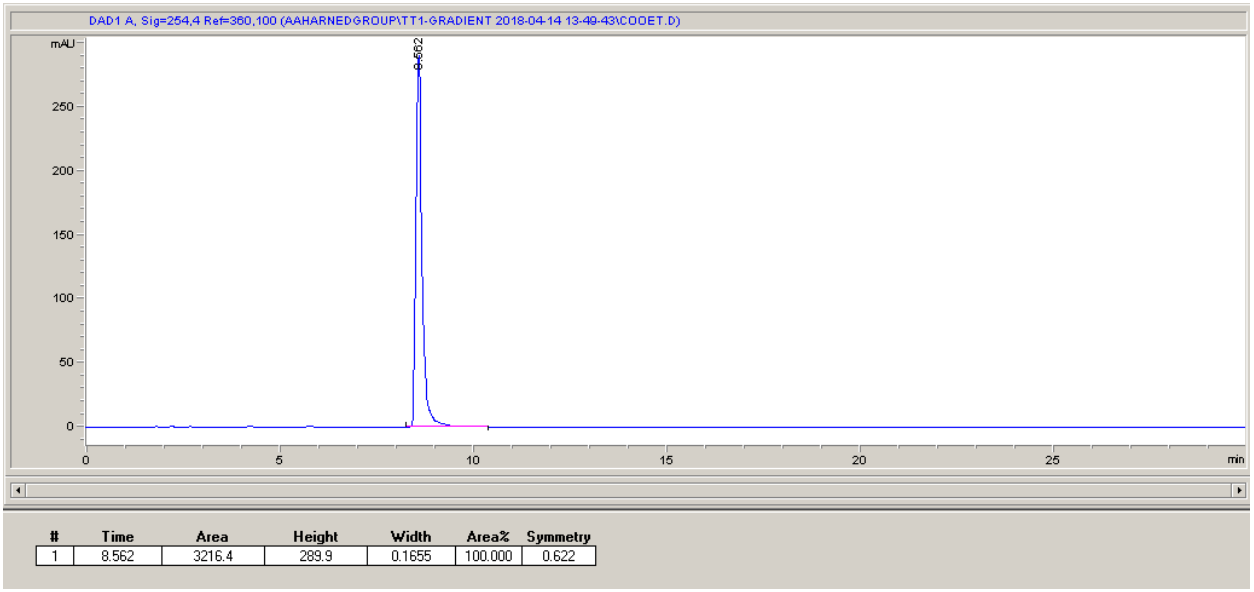
#	Time	Area	Height	Width	Area%	Symmetry
1	2.102	14193.7	2923	0.0747	100.000	0.587

4-phenylphenol (**5a**):



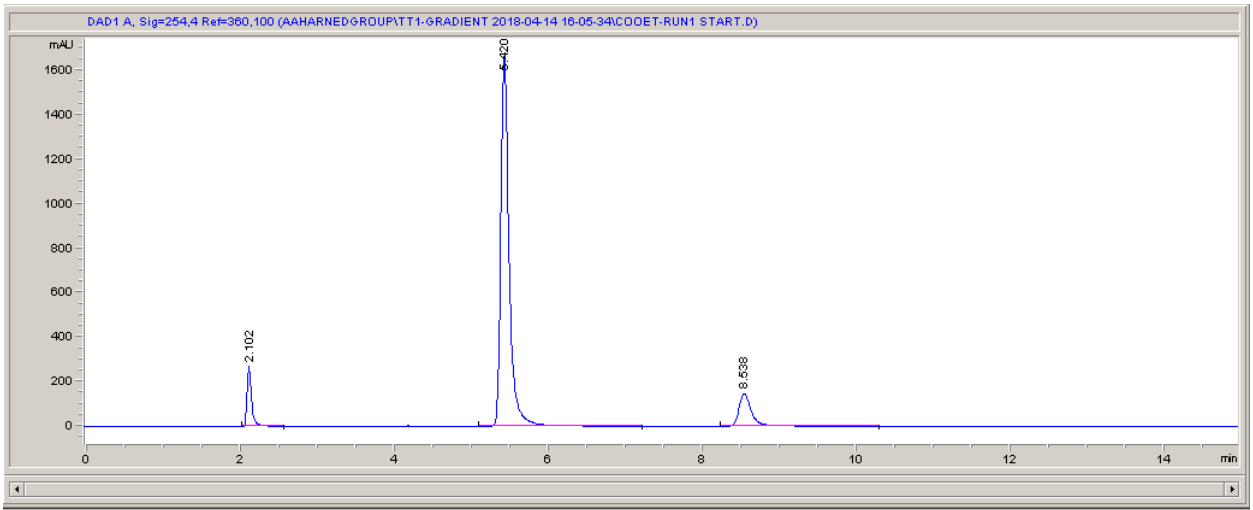
#	Time	Area	Height	Width	Area%	Symmetry
1	5.388	27956.2	2930.9	0.1493	100.000	0.597

ethyl 4’-hydroxy-[1,1’-biphenyl]-4-carboxylat (**5f**):



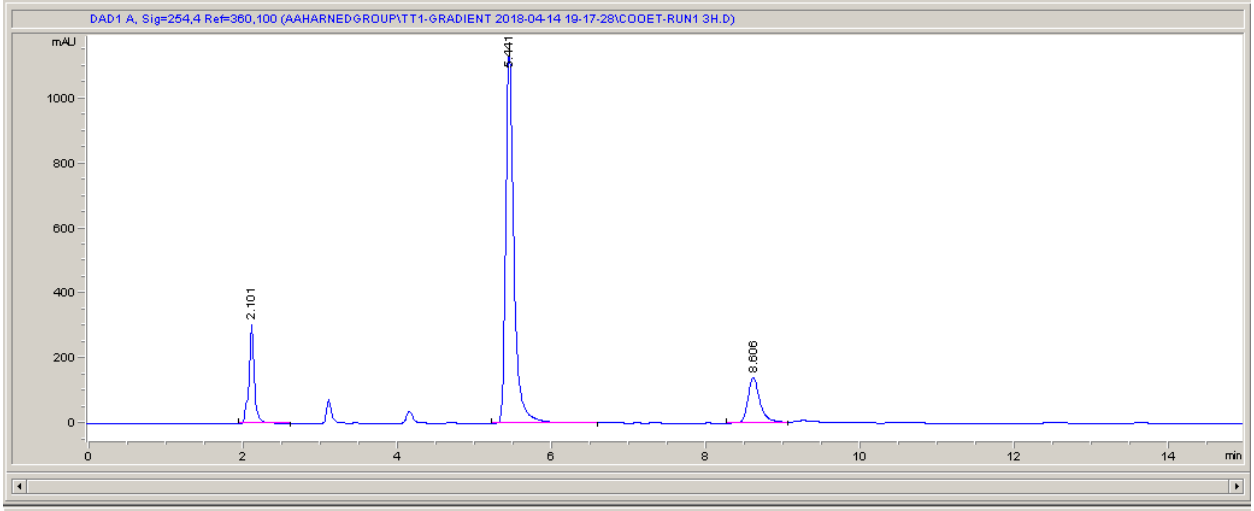
#	Time	Area	Height	Width	Area%	Symmetry
1	8.562	3216.4	289.9	0.1655	100.000	0.622

experiment start:



#	Time	Area	Height	Width	Area%	Symmetry
1	2.102	1083.3	267.8	0.0612	7.140	0.638
2	5.42	12466.3	1659.8	0.1116	82.164	0.637
3	8.538	1622.9	146.2	0.1655	10.696	0.656

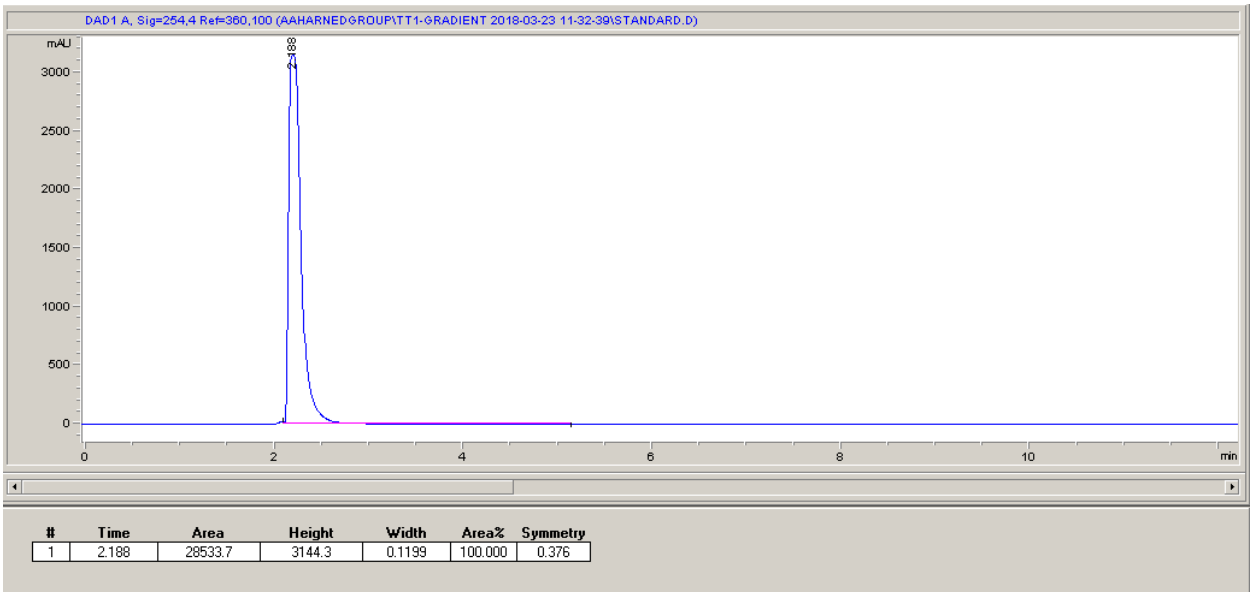
after 2 hrs:



#	Time	Area	Height	Width	Area%	Symmetry
1	2.101	1451.8	303.3	0.0698	12.687	0.952
2	5.441	8438.8	1136.8	0.1126	73.745	0.646
3	8.606	1552.6	140.7	0.1647	13.568	0.693

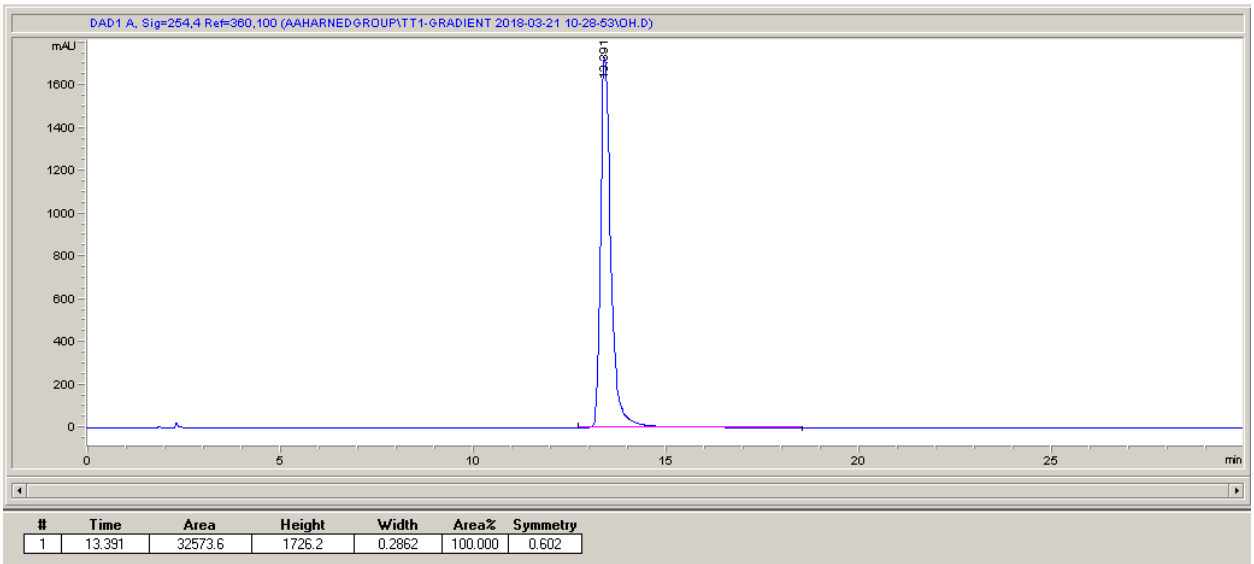
2.3.6 HPLC Chromatogram of 4-phenylphenol (5a) vs 4'-(trifluoromethyl)-[1,1'-biphenyl]-4-ol (5g) (hexane/isopropanol = 99:1, 1.0 mL/ min)

Naphthalene:



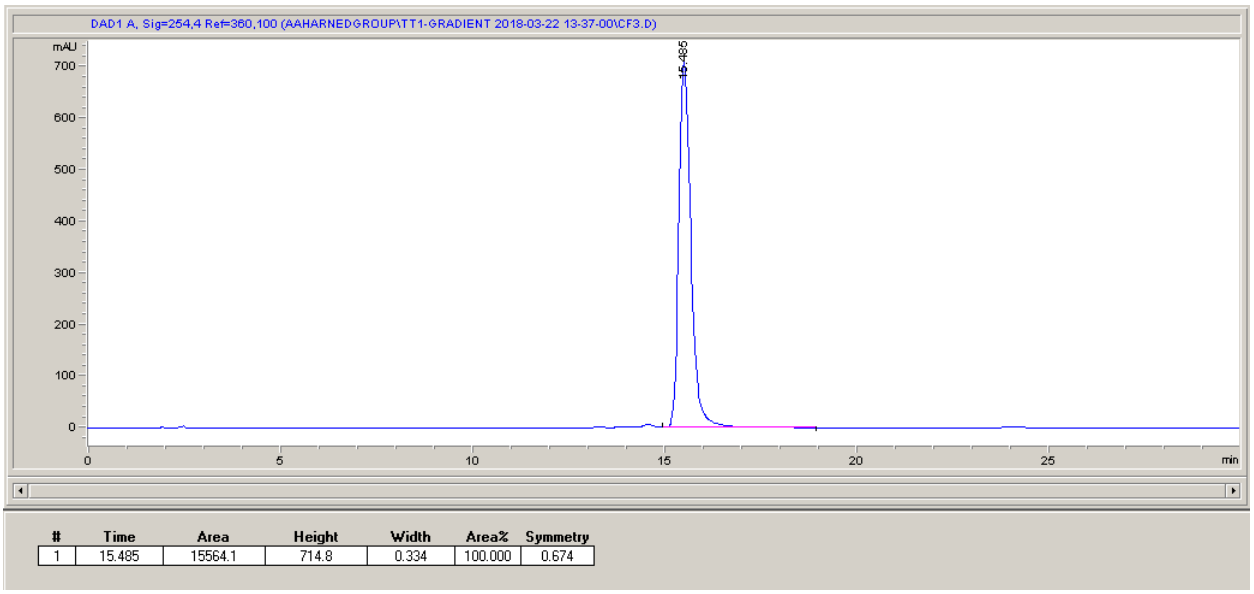
#	Time	Area	Height	Width	Area%	Symmetry
1	2.188	28533.7	3144.3	0.1199	100.000	0.376

4-phenylphenol (**5a**):



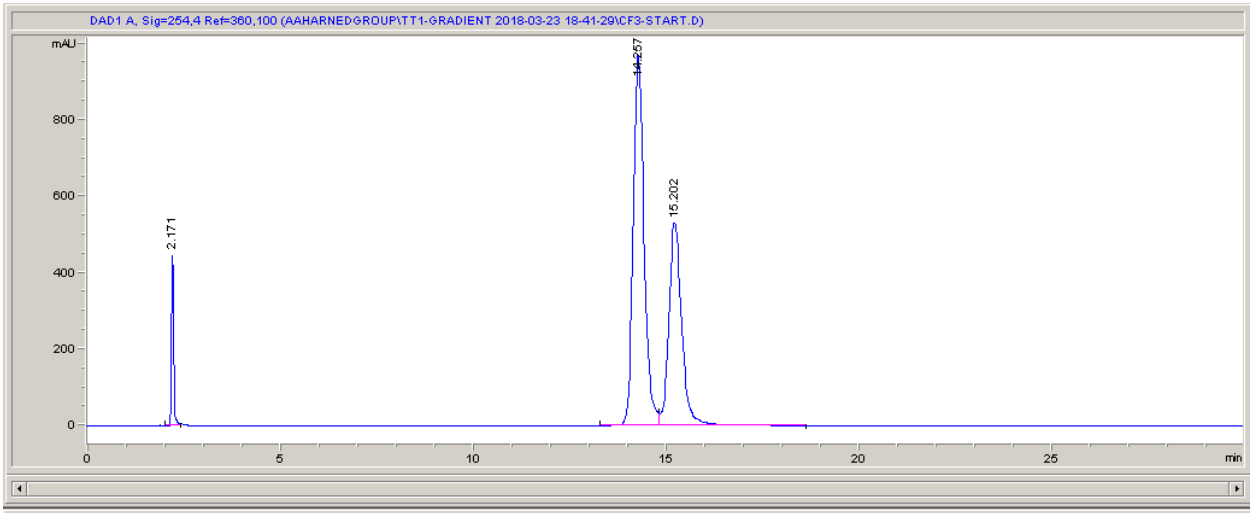
#	Time	Area	Height	Width	Area%	Symmetry
1	13.391	32573.6	1726.2	0.2862	100.000	0.602

4’-(trifluoromethyl)-[1,1’-biphenyl]-4-ol (**5g**):



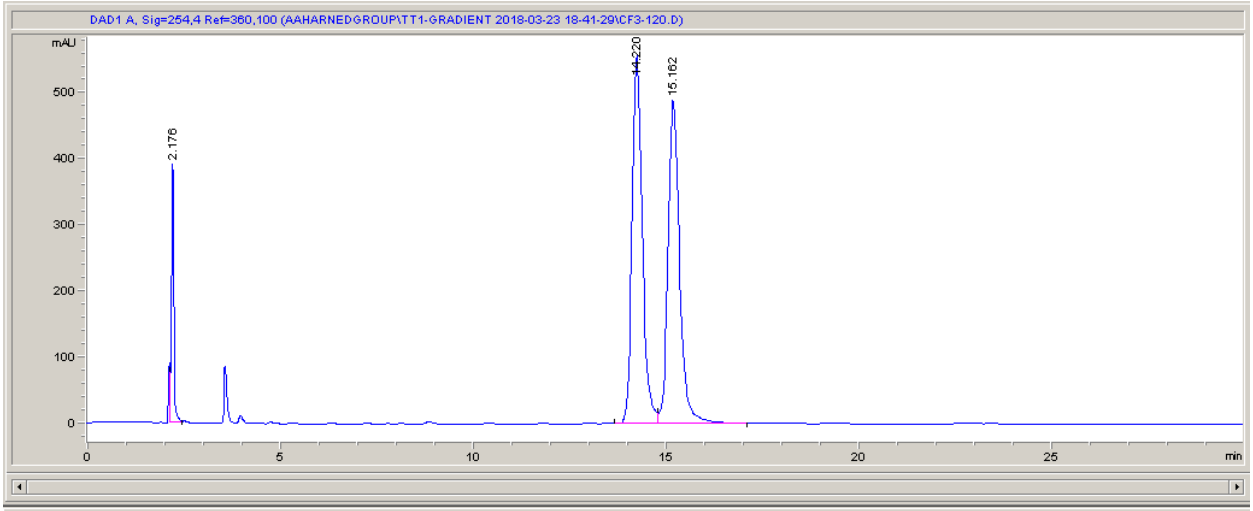
#	Time	Area	Height	Width	Area%	Symmetry
1	15.485	15564.1	714.8	0.334	100.000	0.674

experiment start:



#	Time	Area	Height	Width	Area%	Symmetry
1	2.171	1622.5	448.7	0.0542	4.883	0.692
2	14.257	19210.3	967.5	0.3056	57.812	0.792
3	15.202	12396.4	530.4	0.3586	37.306	0.744

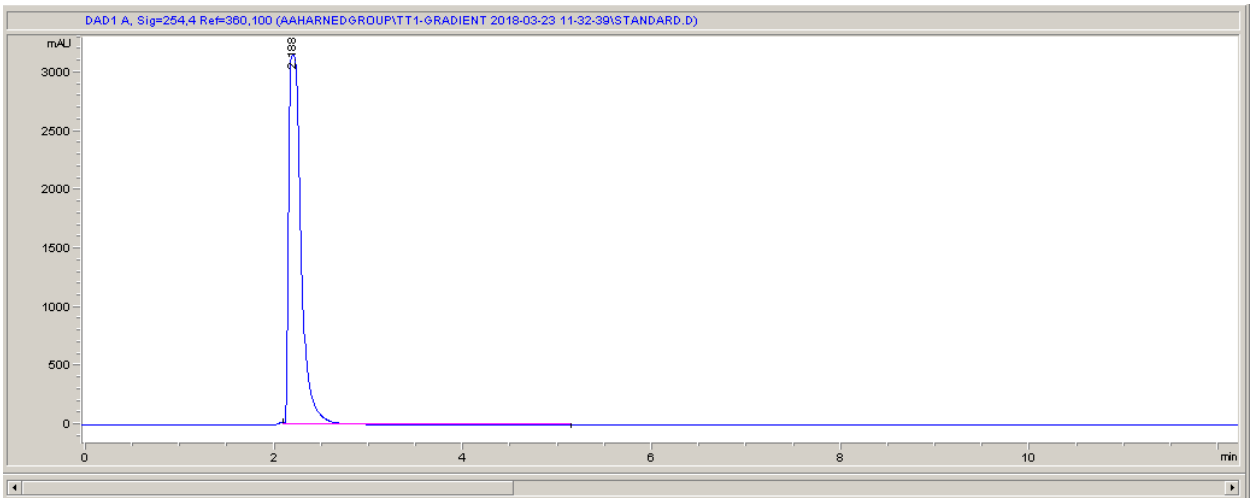
after 2 hrs:



#	Time	Area	Height	Width	Area%	Symmetry
1	2.176	1505.4	390.2	0.059	6.843	0.714
2	14.22	10292.2	556.9	0.2836	46.786	0.784
3	15.162	10200.9	487.4	0.3202	46.371	0.737

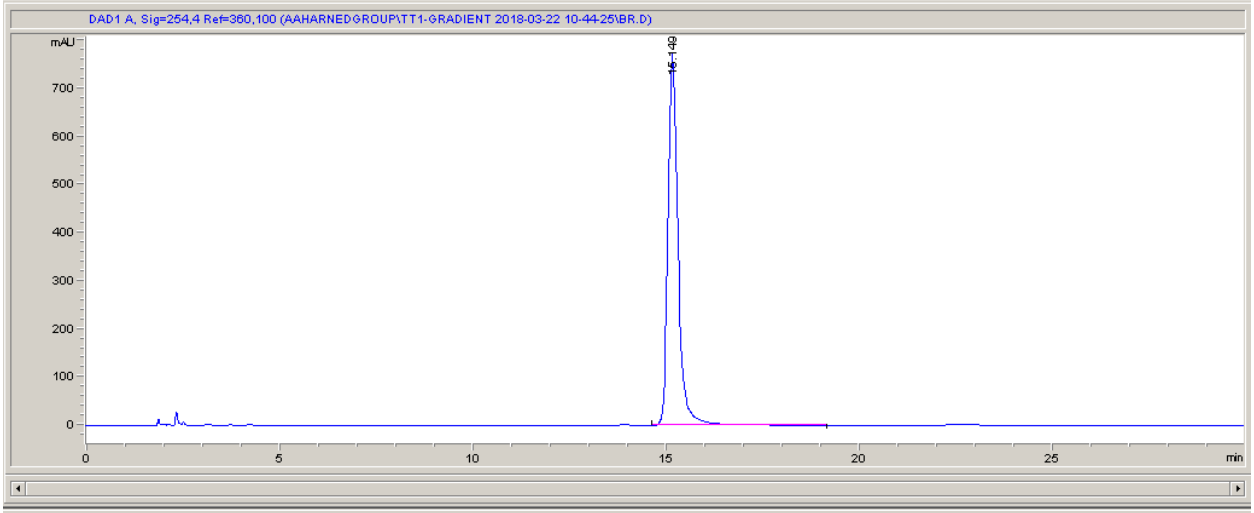
2.3.7 HPLC Chromatogram of 4'-bromo-[1,1'-biphenyl]-4-ol (5e) vs 4'-methyl-[1,1'-biphenyl]-4-ol (5c) (hexane/isopropanol = 99:1, 1.0 mL/ min)

Naphthalene:



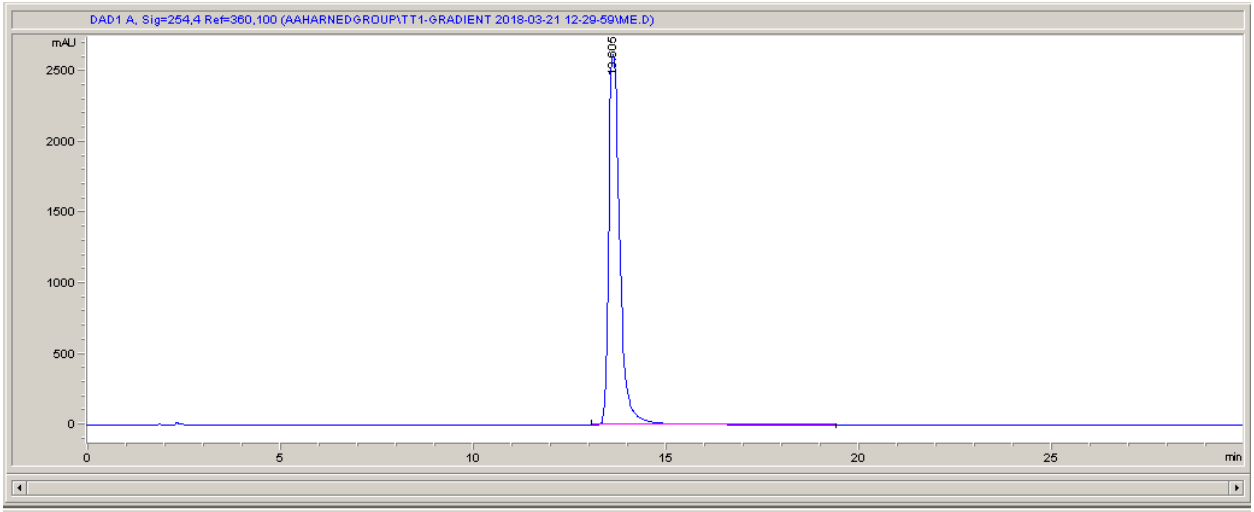
#	Time	Area	Height	Width	Area%	Symmetry
1	2.188	28533.7	3144.3	0.1199	100.000	0.376

4’-bromo-[1,1’-biphenyl]-4-ol (**5e**):



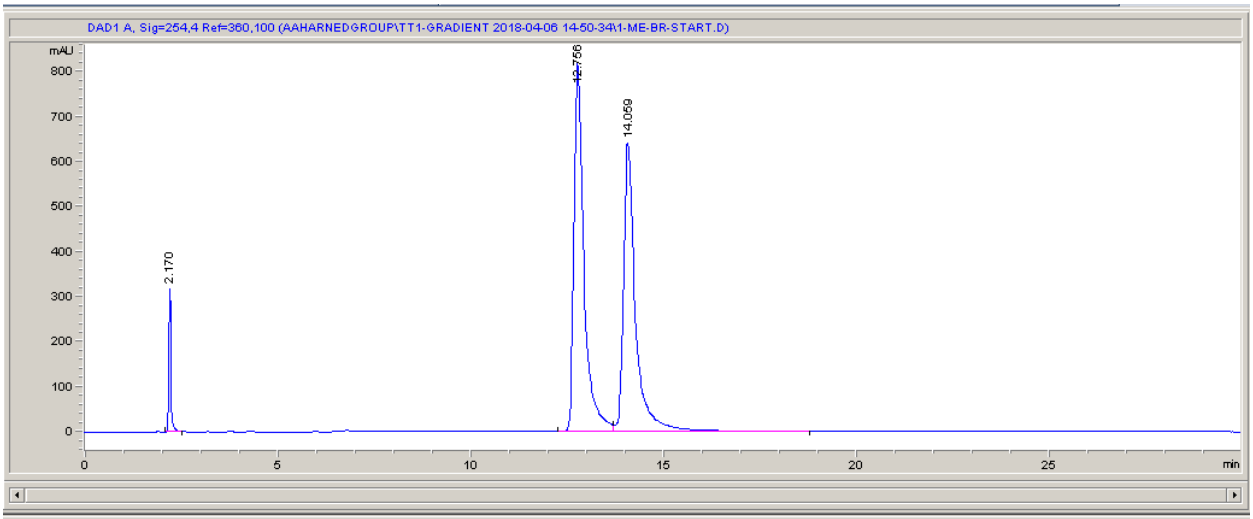
#	Time	Area	Height	Width	Area%	Symmetry
1	15.149	14089.5	771.1	0.2772	100.000	0.702

4’-methyl-[1,1’-biphenyl]-4-ol (**5c**):



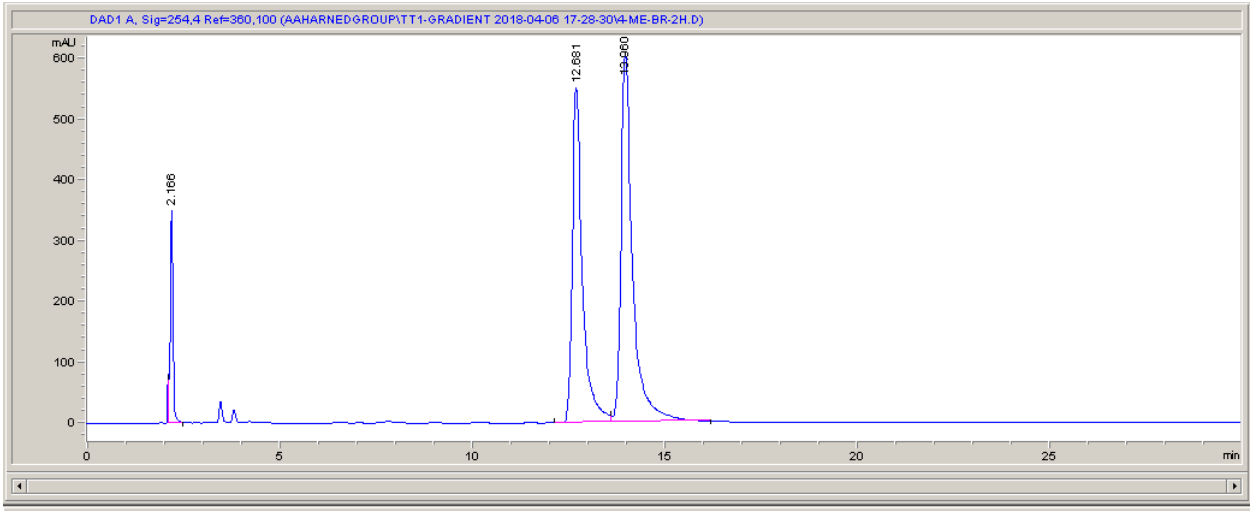
#	Time	Area	Height	Width	Area%	Symmetry
1	13.605	52959.4	2614.3	0.3123	100.000	0.561

experiment start:



#	Time	Area	Height	Width	Area%	Symmetry
1	2.17	1282.8	318.5	0.061	4.259	0.665
2	12.756	14992.9	819.4	0.2695	49.780	0.543
3	14.059	13842.6	642	0.3135	45.961	0.509

after 2 hrs:



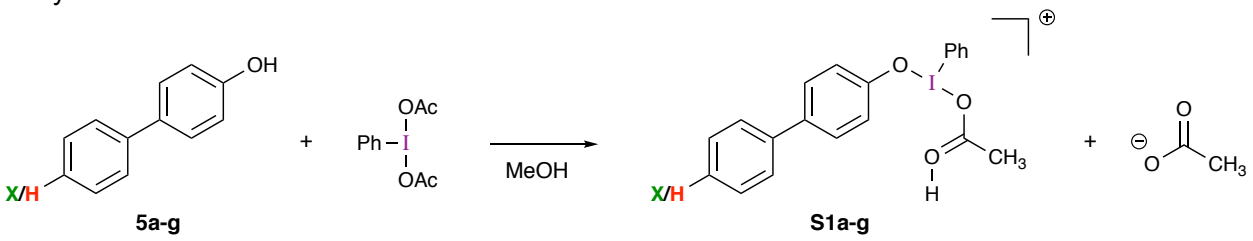
#	Time	Area	Height	Width	Area%	Symmetry
1	2.166	1488	351.6	0.0614	6.098	0.735
2	12.681	10191.5	551.4	0.2716	41.764	0.551
3	13.96	12722.9	604.9	0.3054	52.138	0.519

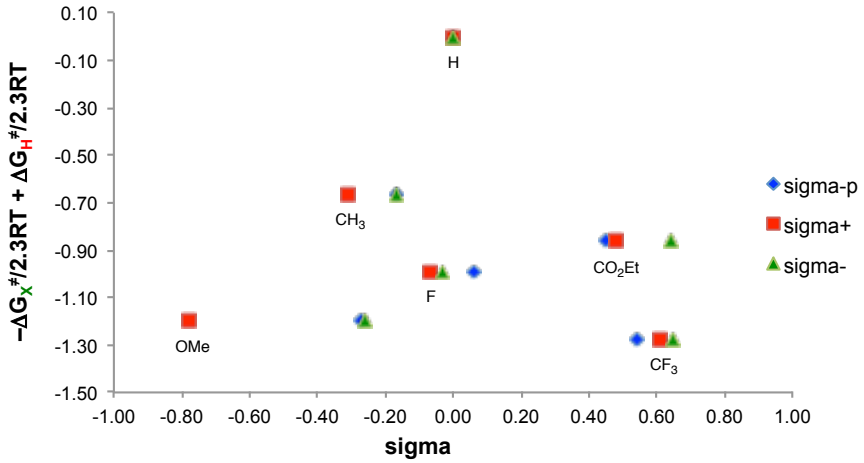
3.0 Additional Information for Hammett Plots

The following sigma values from the literature[17] were used for all Hammett plots.

	σ_p	σ^+	σ^-	σ_R	σ_I
H	0.00	0.00	0.00	0.00	0.00
CF_3	0.54	0.61	0.65	0.11	0.40
OCH_3	-0.27	-0.78	-0.26	-0.58	0.30
Br	0.23	0.15	0.25	-0.25	0.47
F	0.06	-0.07	-0.03	-0.48	0.54
CH_3	-0.17	-0.31	-0.17	-0.16	-0.01
CO_2Et	0.45	0.48	0.64	0.11	0.32

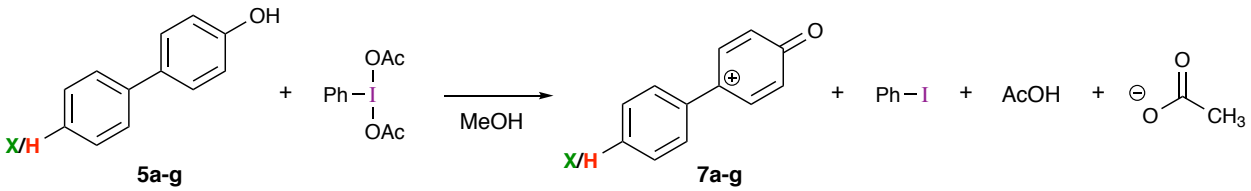
(1) A Hammett plot was constructed using the calculated free energy change for the formation of aryl-λ^3-iodane **S1** from the different substituted 4-phenylphenols (**5a-g**) and $PhI(OAc)_2$. In this case, a nonlinear plot was observed with all sigma values. The free energy changes were also relatively small (< 2 kcal/mol) suggesting that the initial ligand exchange process is rapid and likely reversible.

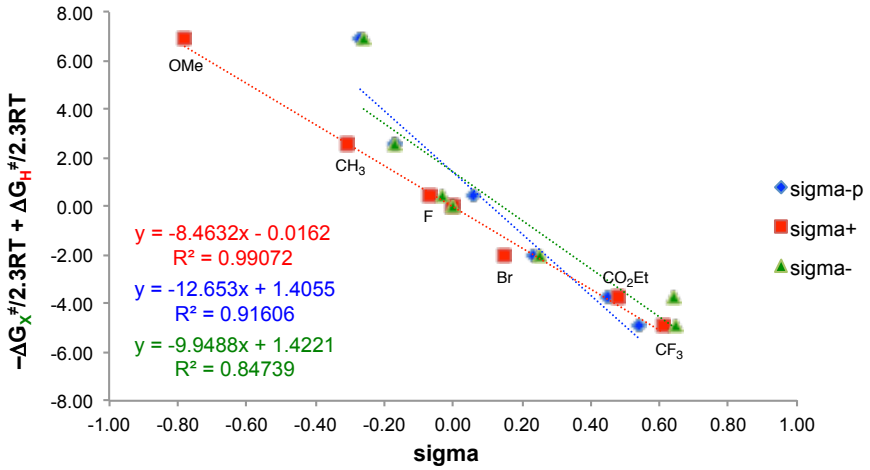




(17) Values for σ_p, σ^+, and σ^- were obtained from Hansch, C.; Leo, A.; Taft, R. W. *Chem. Rev.* **1991**, *91*, 165. Values for σ_I and σ_R were obtained from Charton, M. *Prog. Phys. Org. Chem.* **1981**, *13*, 119.

(2) As mentioned in the main text, a Hammett plot was constructed using the calculated free energy change for the formation of phenoxenium ion **7a-g** from the different substituted 4-phenylphenols (**5a-g**) and $PhI(OAc)_2$. In this case, the use of σ^+ values gave a linear plot with very good correlation. Notably, the plots using σ^- and σ_p values resulted in plots with a curvature that was quite similar to that observed for the Hammett plot of the experimental data (see Figure 2B in main text).

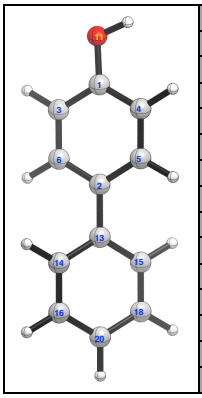




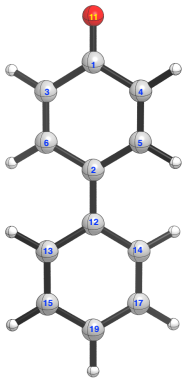
4.0 Additional Computational Experiments Concerning the Mechanism

1. General methods: Two alternative computational methods were employed: (1) M06-2X/DGDZVP with IEFPCM=methanol and (2) B97D3/DGDZVP with IEFPCM=methanol. An ultrafine integration grid was used in all cases. The DGDVP basis set was suggested by the reviewer in order to avoid effects of basis set mixing. The alternative solvation model was suggested by the reviewer as well. The M06-2X fucntionals were previously used in our calculations. The B97D3 functionals were chosen as a suitable alternative as they include Grimme's dispersion correction. M06-2X also contains dispersion corrections.

The originally calculated Mulliken charges for the neutral phenol and phenoxenium ion ar given below for comparison.



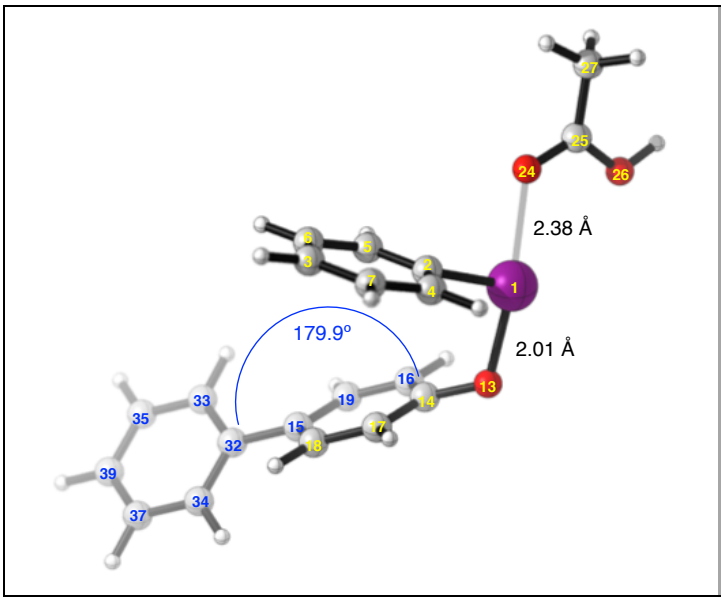
atom	charge
C1	0.136395
C2	0.495426
C3	-0.157656
C4	0.032744
C5	-0.133693
C6	-0.164721
O11	-0.202718
C13	0.297091
C14	0.124131
C15	0.125480
C16	-0.300477
C18	-0.302315
C20	0.050313
sum	*0.0*



atom	charge
C1	-0.027648
C2	1.159182
C3	0.062465
C4	0.062227
C5	-0.141503
C6	-0.142271
O11	-0.457011
C12	0.741443
C13	0.241214
C14	0.242795
C15	-0.466372
C17	-0.466620
C19	0.192100
sum	*1.000001*

2. Evaluation of structure and partial charges in neutral and protonated iodine-bound phenol complexes:

(a) The calculated (M06-2X/6-31+G(d) and LANL2DZdp with SMD=methanol) structure of the protonated iodine-bound phenol complex used in our original work is shown below along with the calculated partial charges (Mulliken with charges summed into heavy atoms).

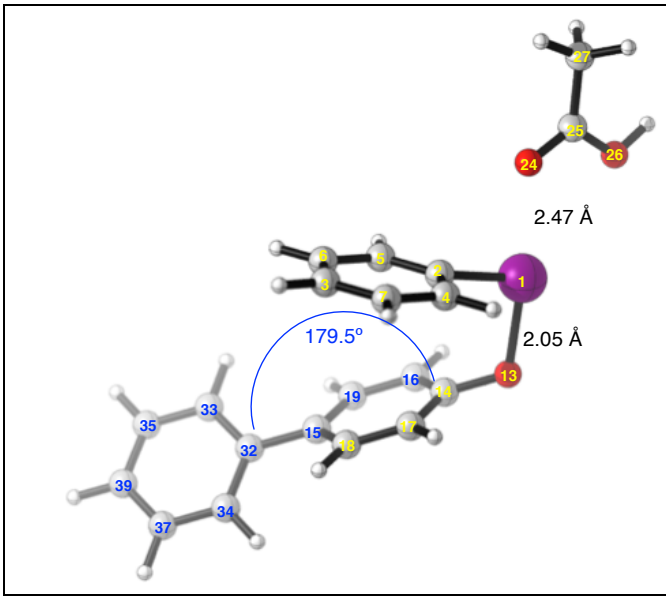


atom	charge
I1	0.952142
C2	1.119326
C3	0.008243
C4	-0.308939
C5	-0.656779
C6	0.032802
C7	0.082810
sum	*1.229605*
O24	-0.484900
C25	0.852907
O26	-0.012709
C27	-0.209631
sum	*0.145667*
O13	-0.502790
C14	0.057569
C15	0.320261
C16	0.063425
C17	-0.296040
C18	0.196073
C19	-0.220764
sum	*-0.382266*

atom	charge
C32	0.222547
C33	0.137771
C34	-0.016215
C35	-0.194303
C37	-0.100815
C39	-0.041992
sum	*0.006993*

Notes: No imaginary frequencies.

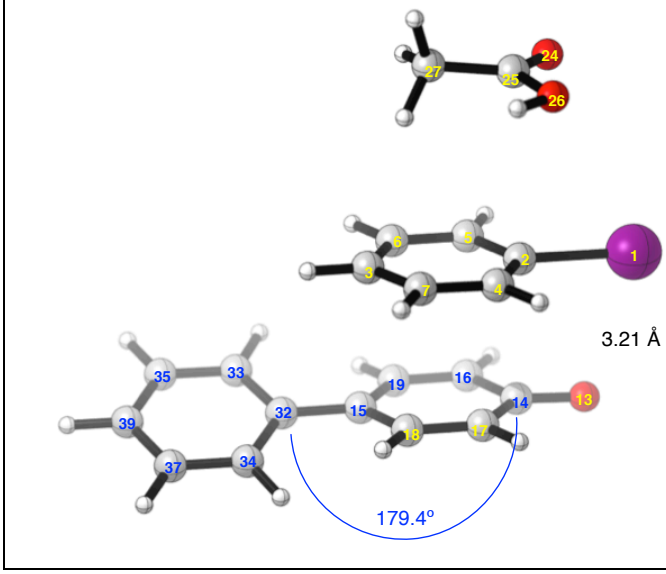
(b) The calculated structure (M06-2X/DGDZVP with IEFPCM=methanol) of the protonated iodine-bound phenol complex is shown below along with the calculated partial charges (Mulliken with charges summed into heavy atoms).



atom	charge	atom	charge
I1	0.820242	C32	0.185901
C2	-0.010669	C33	-0.082005
C3	0.054081	C34	-0.082542
C4	0.047513	C35	-0.003984
C5	0.074832	C37	-0.003670
C6	0.051689	C39	-0.003087
C7	0.048789	*sum*	*0.010613*
sum	*1.086477*		
O24	-0.457390		
C25	0.515274		
O26	-0.008779		
C27	0.127401		
sum	*0.176506*		
O13	-0.586055		
C14	0.410563		
C15	0.208753		
C16	-0.106752		
C17	-0.078024		
C18	-0.058339		
C19	-0.063740		
sum	*-0.273594*		

Notes: No imaginary frequencies.

(c) The calculated structure (B97D3/DGDZVP with IEFPCM=methanol) of the protonated iodine-bound phenol complex is shown below along with the calculated partial charges (Mulliken with charges summed into heavy atoms).

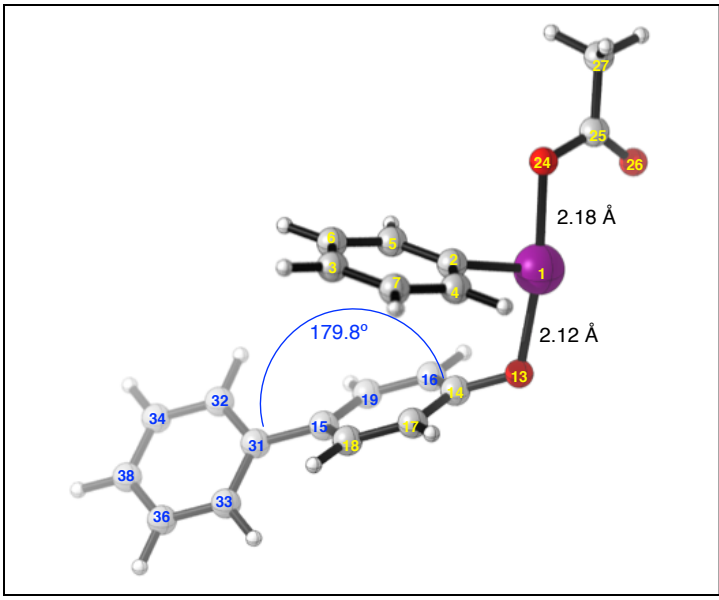


atom	charge	atom	charge
I1	0.037274	C32	0.268616
C2	0.078807	C33	-0.021931
C3	0.045149	C34	-0.032470
C4	0.017451	C35	0.028679
C5	0.019824	C37	0.033357
C6	0.067121	C39	0.074398
C7	0.050799	*sum*	*0.350649*
sum	*0.316425*		
O24	-0.381146		
C25	0.395417		
O26	-0.037922		
C27	0.042169		
sum	*0.018518*		
O13	-0.360913		
C14	0.433642		
C15	0.324511		
C16	-0.040124		
C17	-0.046695		
C18	0.005379		
C19	-0.001391		
sum	*0.314409*		

Notes: Two imaginary frequencies (–21.32 and –10.10) corresponding to rocking motions involving all fragments. There is clearly no I–O bonding. Partial charge analysis reveals the

phenolic portion is probably best thought of as a phenoxenium ion. This calculation started with a geometry very similar to that found in Parts 2.a and 2.b shown above.

(d) The calculated structure (M06-2X/DGDZVP with IEFPCM=methanol) of the neutral iodine-bound phenol complex is shown below along with the calculated partial charges (Mulliken with charges summed into heavy atoms).

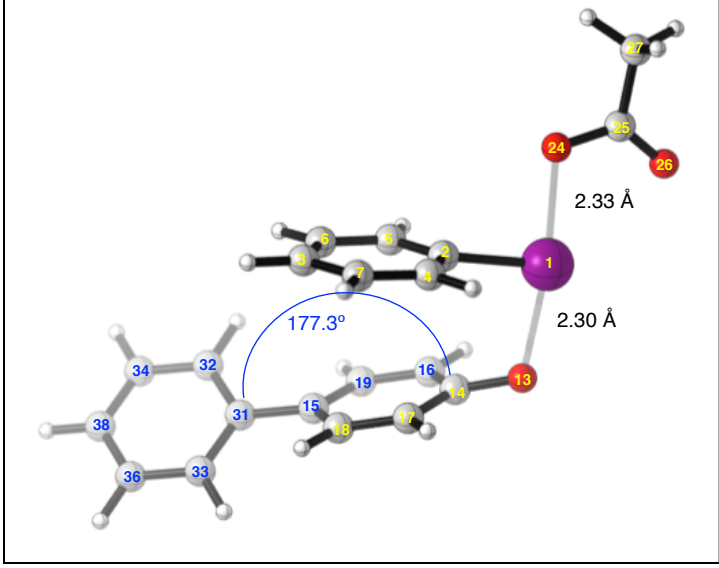


atom	charge
I1	0.765584
C2	0.016783
C3	0.035750
C4	0.022723
C5	0.056351
C6	0.035845
C7	0.034522
sum	*0.967558*
O24	-0.553151
C25	0.488926
O26	-0.498011
C27	0.048250
sum	*-0.513986*
O13	-0.648933
C14	0.416471
C15	0.197447
C16	-0.142965
C17	-0.106276
C18	-0.075284
C19	-0.079471
sum	*-0.439011*

atom	charge
C31	0.183734
C32	-0.086554
C33	-0.087921
C34	-0.007367
C36	-0.007044
C38	-0.009408
sum	*-0.01456*

Notes: No imaginary frequencies.

(e) The calculated structure (B97D3/DGDZVP with IEFPCM=methanol) of the neutral iodine-bound phenol complex is shown below along with the calculated partial charges (Mulliken with charges summed into heavy atoms).



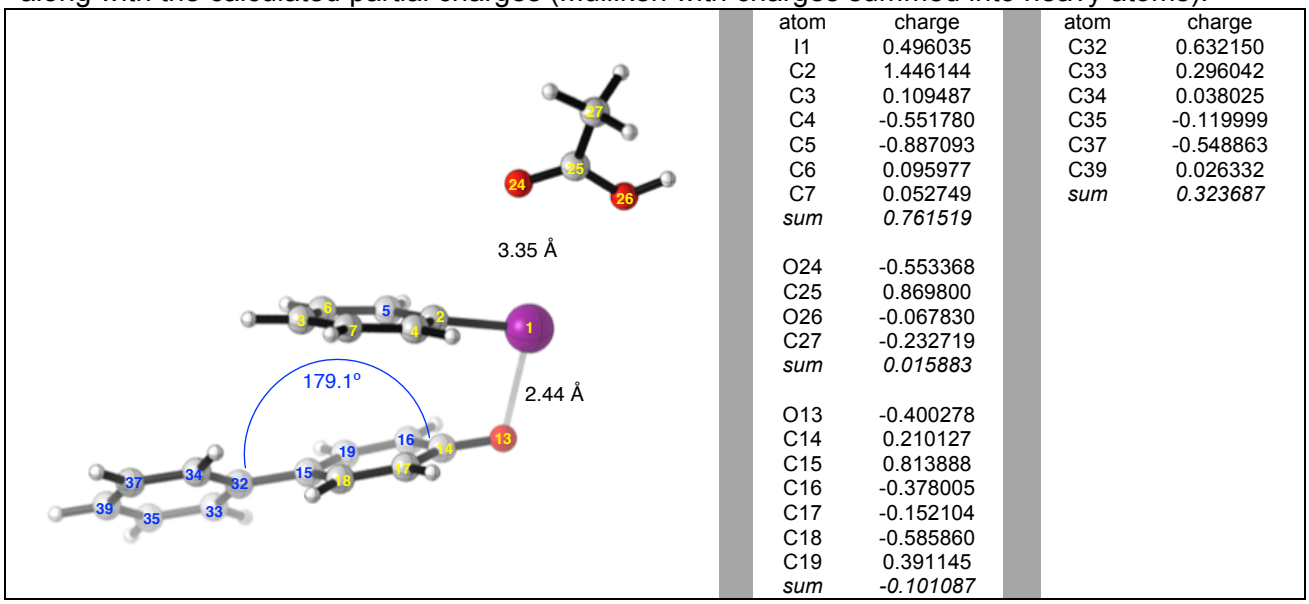
atom	charge
I1	0.535259
C2	0.132194
C3	0.027733
C4	-0.016152
C5	0.024731
C6	0.053172
C7	0.036491
sum	*0.793428*
O24	-0.450766
C25	0.430530
O26	-0.457445
C27	0.032671
sum	*-0.44501*
O13	-0.558412
C14	0.417157
C15	0.259112
C16	-0.142556
C17	-0.112136
C18	-0.091996
C19	-0.105288
sum	*-0.334119*

atom	charge
C31	0.229686
C32	-0.102321
C33	-0.110341
C34	-0.010785
C36	-0.008543
C38	-0.011993
sum	*-0.014297*

Notes: Two imaginary frequencies (–22.96 and –9.78) corresponding to twisting of the acetate C–C bond and a rocking motion involving all fragments. Several attempts were made to reoptimize the structure in order to remove these frequencies, but all gave the same result.

3. Evaluation of structure and partial charges in protonated unimolecular decomposition transition states:

(a) The calculated (M06-2X/6-31+G(d) and LANL2DZdp with SMD=methanol) structure of the protonated unimolecular decomposition transition state used in our original work is shown below along with the calculated partial charges (Mulliken with charges summed into heavy atoms).

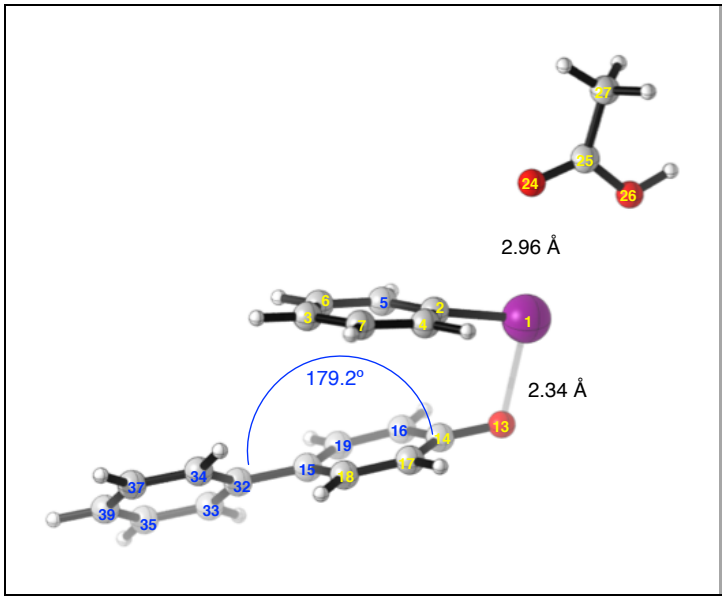


atom	charge
I1	0.496035
C2	1.446144
C3	0.109487
C4	-0.551780
C5	-0.887093
C6	0.095977
C7	0.052749
sum	*0.761519*
O24	-0.553368
C25	0.869800
O26	-0.067830
C27	-0.232719
sum	*0.015883*
O13	-0.400278
C14	0.210127
C15	0.813888
C16	-0.378005
C17	-0.152104
C18	-0.585860
C19	0.391145
sum	*-0.101087*

atom	charge
C32	0.632150
C33	0.296042
C34	0.038025
C35	-0.119999
C37	-0.548863
C39	0.026332
sum	*0.323687*

Notes: One imaginary frequency (–177.45) corresponding to stretching of the I–O13 bond. Note that the sum of the partial charges for O13 to C19 has become less negative (more positive) than in the starting structure (Part 2.a above).

(b) The calculated (M06-2X/DGDZVP with IEFPCM=methanol) structure of the protonated unimolecular decomposition transition state is shown below along with the calculated partial charges (Mulliken with charges summed into heavy atoms).

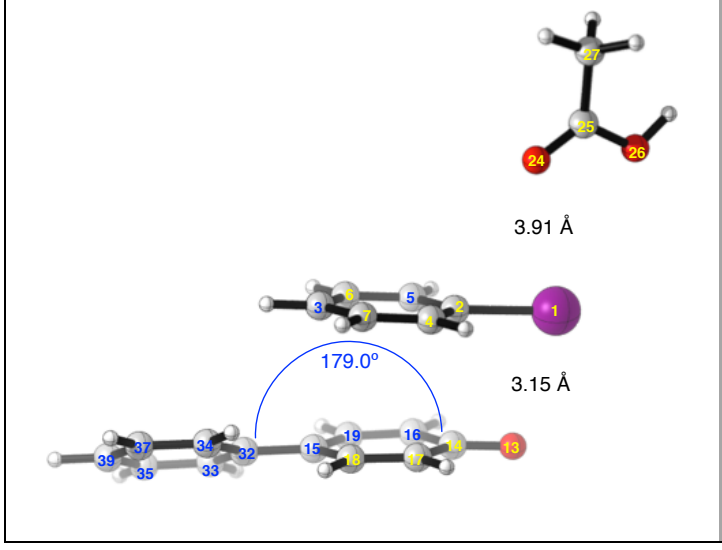


atom	charge
I1	0.539317
C2	-0.038307
C3	0.060468
C4	0.064972
C5	0.061262
C6	0.069920
C7	0.050992
sum	*0.808624*
O24	-0.429732
C25	0.463658
O26	-0.053216
C27	0.083187
sum	*0.063897*
O13	-0.475080
C14	0.403548
C15	0.245457
C16	-0.036480
C17	-0.043379
C18	-0.024908
C19	-0.036528
sum	*0.03263*

atom	charge
C32	0.208019
C33	-0.070318
C34	-0.063094
C35	0.002651
C37	-0.002222
C39	0.019813
sum	*0.094849*

Notes: One imaginary frequency (–181.75) corresponding to stretching of the I–O13 bond.

(c) The calculated (B97D3/DGDZVP with IEFPCM=methanol) structure of the protonated unimolecular decomposition transition state is shown below along with the calculated partial charges (Mulliken with charges summed into heavy atoms).



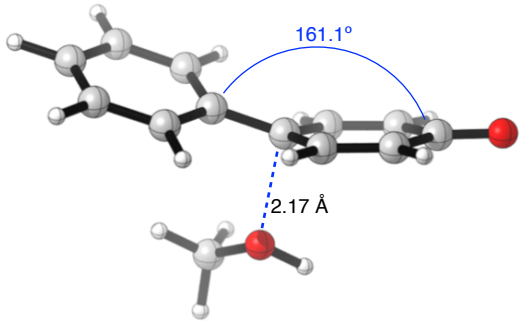
atom	charge
I1	0.051855
C2	0.095650
C3	0.044761
C4	0.018816
C5	0.016733
C6	0.068929
C7	0.057548
sum	*0.354292*
O24	-0.375322
C25	0.380154
O26	-0.031695
C27	0.043107
sum	*0.016244*
O13	-0.366450
C14	0.431503
C15	0.314944
C16	-0.045794
C17	-0.046478
C18	0.008563
C19	-0.005752
sum	*0.290536*

atom	charge
C32	0.270137
C33	-0.032369
C34	-0.021647
C35	0.030419
C37	0.020641
C39	0.071747
sum	*0.338928*

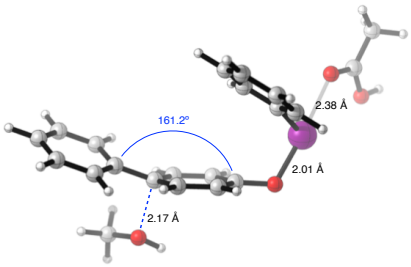
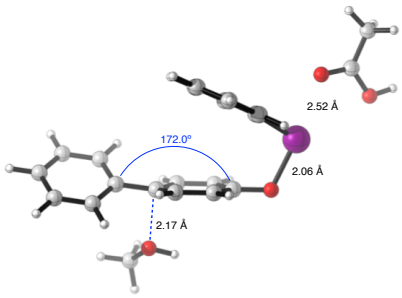
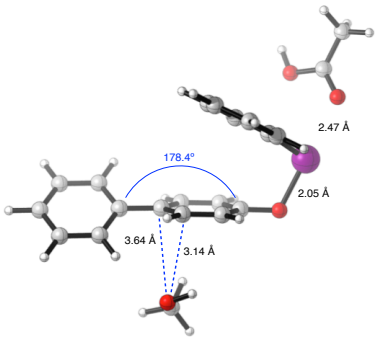
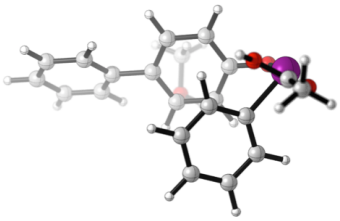
Notes: Three imaginary frequencies (–29.37, –21.60 and –13.09) corresponding to rocking of the acetic acid, and rocking motions involving all fragments. This structure was obtained after two rounds of optimization to a transition state. The starting structure was similar to that used for

Part 3.a and 3.b above. These optimizations were also run with a step size of 1 in order to ensure account for a flat potential energy surface. Further rounds of optimization just caused the acetic acid to move further away from the iodobenzene.

4. Attempts at locating bimolecular decomposition transition state:
Attempts were made at locating the biomolecular decomposition transition state using a "forcing" methodology reported in our previous paper (*Org. Biomol. Chem.* **2018**, *16*, 2324). Briefly, this involved generating an initial guess structure in which the incoming methanol molecule and the 4-arylphenol moiety of the protonated (or neutral) iodine-bound phenol complex are positioned close to what was observed in the transition state that was located for the trapping of the phenoxenium ion. This initial guess was then minimized with the C–O bond distance between the methanol and para carbon of the phenol frozen. This minimized structure was then used (with the frozen distance removed) as the initial structure for a transition state calculation. This method was used after a simple relaxed scan of the C–O bond distance failed to locate a transition state. For each set of calculations shown below we provide the initial starting structure, initially minimized structure with frozen C–O distance, and final structure returned by the transition state calculation. For comparison, our originally calculated transition state for the reaction between the phenoxenum ion and methanol is given below along with important measurements.

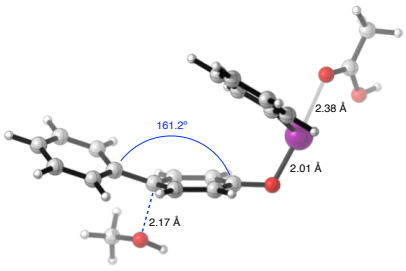
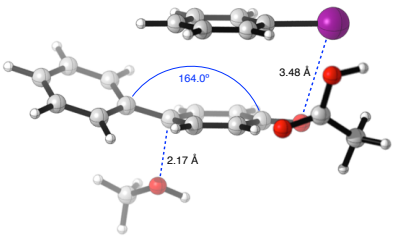
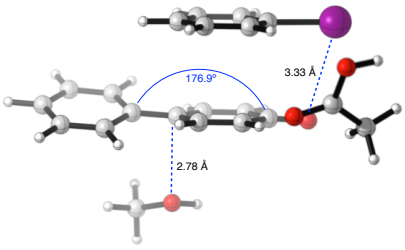


(a) Method = M06-2X/DGDZVP with IEFPCM=methanol

Starting structure	Minimized structure with frozen C–O distance	Final structure from transition state calculation
		 (side view)  (top view)

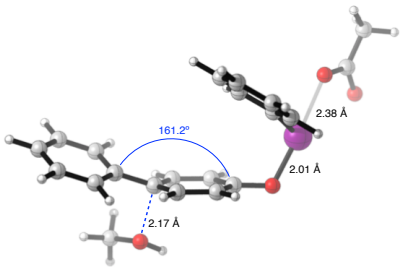
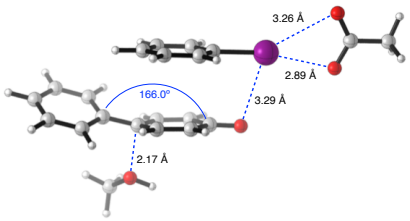
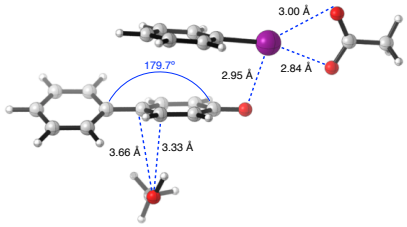
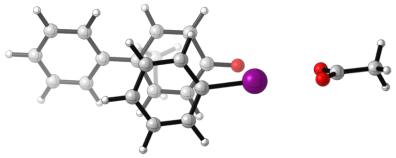
Notes: Just like our originally reported calculations (*Org. Biomol. Chem.* **2018**, *16*, 2324) The methanol moves away from the phenolic portion during the transition state optimization. In fact it actually moves in such a way that it is under the meta carbon atom. The biaryl linkage also flattens out during the two optimization steps.

(b) Method = B97D3/DGDZVP with IEFPCM=methanol

Starting structure	Minimized structure with frozen C–O distance	Final structure from transition state calculation
		

Notes: During the first optimization the acetic acid has been lost and the I–O13 bond has completely broken. But, once the frozen C–O distance is removed, the methanol once again moves away from the para carbon and the biaryl linkage flattens out.

(c) Method = B97D3/DGDZVP with IEFPCM=methanol – These calculations were run starting with the neutral iodine-bound phenol complex

Starting structure	Minimized structure with frozen C–O distance	Final structure from transition state calculation
		 (side view)  (top view)

Notes: Given the problems associated with these functionals with the protonated species, an attempt was made to locate the bimolecular fragmentation using the neutral complex as the starting structure. The movement of the acetate seen during the first optimization is very similar to what was seen when modeling the neutral unimolecular fragmentation during our reported work (*Org. Biomol. Chem.* **2018**, *16*, 2324). Again, when the C–O restriction is removed, the methanol moves away from the para carbon and becomes located under the meta carbon. The methanol adopts a conformation in which the lone pairs of the oxygen are pointed away from the phenolic aromatic ring. The biaryl linkage also flattens out during the transition state optimization.

5. Conclusions:

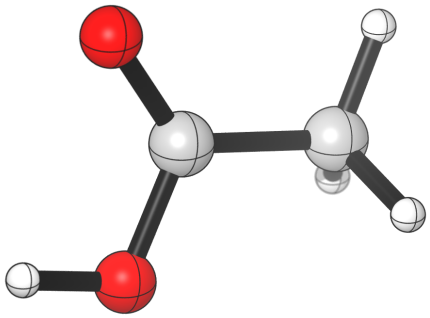
The above work demonstrates that our original basis sets give, qualitatively, similar results to the DGDZVP basis set suggested by the reviewer. In addition, the difficulties experienced when using the B97D3 funcationals suggests that M06-2X is better able to handle the weak interactions between the acetic acid and the iodine. Not only that, but the B97D3 functionals displayed poor performance in modeling the neutral complex (Part 2.e). More importantly, none of the methods were able to locate a transition state for the bimolecular decomposition. All attempts at forcing the methanol to add to the para carbon resulted in the methanol moving away.

5.0 Final Coordinates and Energies for Fully Optimized Structures

The final optimized geometry of each species is given below, along with the following:
(i) Number of imaginary frequencies (frequency if present)
(ii) Returned energies (in Hartrees) at 298.15 K and 1 atm using SMD^{Methanol} solvation.

CH_3CO_2H

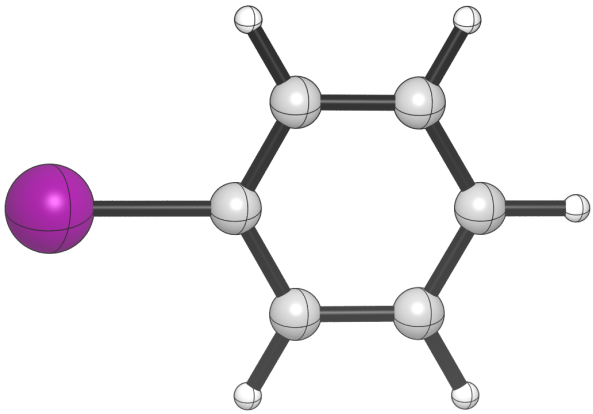
C	0.086000	0.116000	-0.001000
O	0.626000	1.207000	0.000000
O	0.789000	-1.025000	-0.000000
H	1.745000	-0.819000	0.004000
C	-1.390000	-0.124000	-0.000000
H	-1.661000	-0.745000	-0.859000
H	-1.667000	-0.669000	0.907000
H	-1.921000	0.827000	-0.041000



*** 0 imaginary frequencies ***
Sum of electronic and zero-point Energies= -228.943330
Sum of electronic and thermal Energies= -228.938781
Sum of electronic and thermal Enthalpies= -228.937836
Sum of electronic and thermal Free Energies= -228.970548

iodobenzene

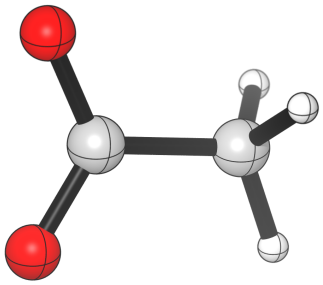
C	0.000000	0.000000	-0.555000
C	0.000000	0.000000	-3.337000
C	0.000000	1.215000	-1.241000
C	0.000000	-1.215000	-1.241000
C	0.000000	-1.207000	-2.637000
C	0.000000	1.207000	-2.637000
H	0.000000	2.156000	-0.699000
H	0.000000	-2.156000	-0.699000
H	0.000000	-2.151000	-3.175000
H	0.000000	2.151000	-3.175000
H	0.000000	0.000000	-4.423000
I	0.000000	0.000000	1.548000



*** 0 imaginary frequencies ***
Sum of electronic and zero-point Energies= -242.799995
Sum of electronic and thermal Energies= -242.794157
Sum of electronic and thermal Enthalpies= -242.793212
Sum of electronic and thermal Free Energies= -242.831025

$CH_3CO_2^-$ (acetate anion)

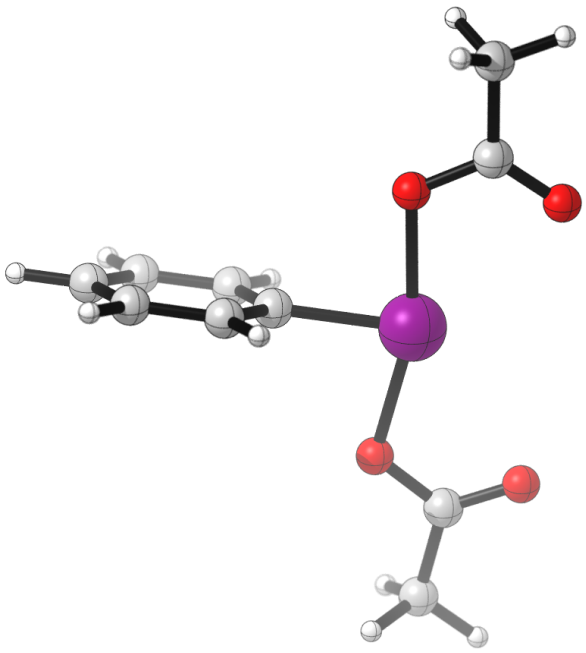
C	0.176000	-0.001000	0.000000
O	0.721000	1.140000	-0.000000
C	-1.348000	-0.040000	-0.000000
H	-1.727000	0.483000	0.884000
H	-1.727000	-1.064000	-0.004000
H	-1.727000	0.489000	-0.881000
O	0.805000	-1.097000	0.000000



*** 0 imaginary frequencies ***
Sum of electronic and zero-point Energies= -228.499134
Sum of electronic and thermal Energies= -228.494858
Sum of electronic and thermal Enthalpies= -228.493914
Sum of electronic and thermal Free Energies= -228.526108

Iodobenzene diacetate

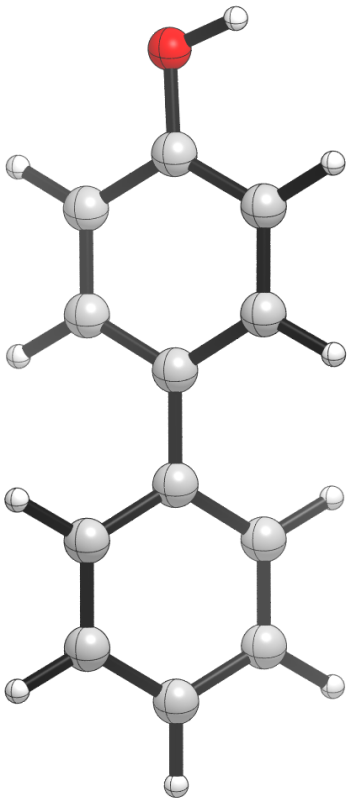
I	-0.000000	-0.621000	-0.000000
C	0.000000	1.469000	0.000000
C	0.000000	4.228000	-0.000000
C	-0.228000	2.139000	-1.199000
C	0.229000	2.139000	1.199000
C	0.229000	3.534000	1.189000
C	-0.228000	3.534000	-1.189000
H	-0.403000	1.591000	-2.120000
H	0.403000	1.592000	2.120000
H	0.405000	4.075000	2.114000
H	-0.405000	4.075000	-2.114000
H	0.000000	5.314000	-0.000000
O	2.122000	-0.329000	-0.040000
O	-2.122000	-0.329000	0.040000
C	2.801000	-1.452000	-0.054000
C	-2.801000	-1.452000	0.054000
O	2.248000	-2.551000	-0.054000
O	-2.248000	-2.551000	0.054000
C	4.293000	-1.268000	-0.062000
H	4.581000	-0.629000	-0.901000
H	4.792000	-2.235000	-0.139000
H	4.598000	-0.766000	0.862000
C	-4.293000	-1.268000	0.062000
H	-4.581000	-0.629000	0.901000
H	-4.792000	-2.235000	0.139000
H	-4.598000	-0.766000	-0.862000



*** 0 imaginary frequencies ***
Sum of electronic and zero-point Energies= -699.446469
Sum of electronic and thermal Energies= -699.429749
Sum of electronic and thermal Enthalpies= -699.428805
Sum of electronic and thermal Free Energies= -699.494192

4-phenylphenol

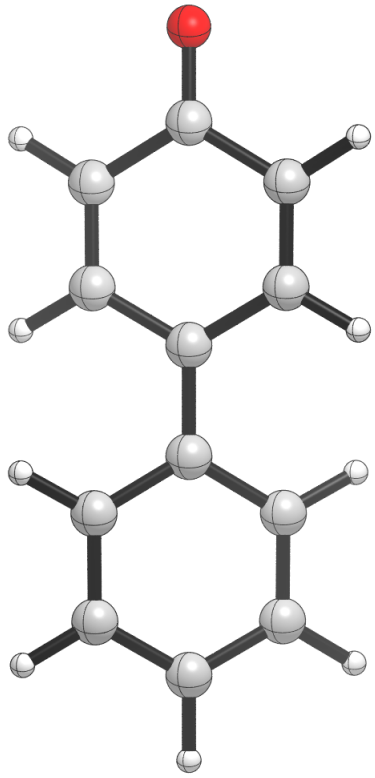
C	-3.109000	-0.014000	-0.004000
C	-0.297000	-0.004000	-0.000000
C	-2.407000	-1.163000	-0.371000
C	-2.417000	1.140000	0.365000
C	-1.024000	1.137000	0.365000
C	-1.017000	-1.152000	-0.367000
H	-2.958000	-2.053000	-0.666000
H	-2.968000	2.030000	0.659000
H	-0.499000	2.037000	0.674000
H	-0.483000	-2.048000	-0.675000
O	-4.474000	-0.075000	-0.025000
H	-4.854000	0.780000	0.240000
C	1.189000	0.000000	0.001000
C	1.911000	-1.143000	0.374000
C	1.904000	1.148000	-0.372000
C	3.305000	-1.140000	0.372000
H	1.378000	-2.038000	0.687000
C	3.298000	1.153000	-0.371000
H	1.366000	2.040000	-0.685000
C	4.005000	0.008000	0.001000
H	3.844000	-2.035000	0.670000
H	3.833000	2.051000	-0.669000
H	5.092000	0.011000	0.001000



*** 0 imaginary frequencies ***
Sum of electronic and zero-point Energies= -538.142434
Sum of electronic and thermal Energies= -538.132359
Sum of electronic and thermal Enthalpies= -538.131415
Sum of electronic and thermal Free Energies= -538.178435

4-phenylphenoxenium cation

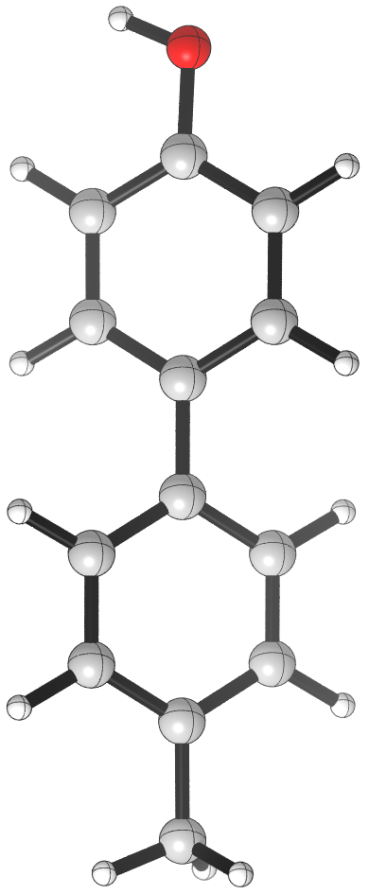
C	-3.183000	0.000000	0.000000
C	-0.332000	-0.000000	-0.000000
C	-2.414000	-1.249000	-0.213000
C	-2.414000	1.249000	0.213000
C	-1.069000	1.239000	0.197000
C	-1.069000	-1.239000	-0.198000
H	-2.984000	-2.157000	-0.392000
H	-2.983000	2.157000	0.391000
H	-0.525000	2.156000	0.388000
H	-0.526000	-2.156000	-0.389000
O	-4.402000	0.000000	0.000000
C	1.090000	-0.000000	-0.000000
C	1.818000	-1.211000	0.202000
C	1.818000	1.210000	-0.202000
C	3.198000	-1.199000	0.219000
H	1.298000	-2.141000	0.398000
C	3.197000	1.200000	-0.219000
H	1.297000	2.141000	-0.398000
C	3.888000	0.000000	0.000000
H	3.746000	-2.117000	0.401000
H	3.746000	2.118000	-0.401000
H	4.974000	0.000000	0.000000



*** 0 imaginary frequencies ***
Sum of electronic and zero-point Energies= -537.300665
Sum of electronic and thermal Energies= -537.290618
Sum of electronic and thermal Enthalpies= -537.289674
Sum of electronic and thermal Free Energies= -537.336962

4-(4-methylphenyl)phenol

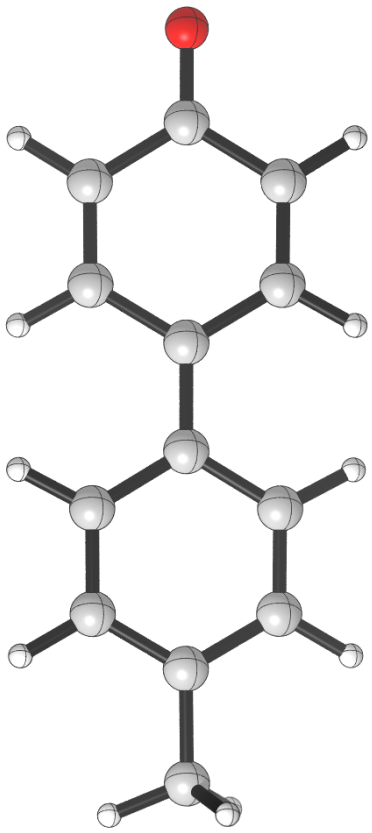
C	3.580000	-0.015000	0.003000
C	0.768000	-0.003000	0.000000
C	2.878000	-1.166000	0.363000
C	2.889000	1.142000	-0.357000
C	1.496000	1.139000	-0.358000
C	1.488000	-1.153000	0.360000
H	3.428000	-2.058000	0.651000
H	3.440000	2.034000	-0.645000
H	0.971000	2.042000	-0.661000
H	0.954000	-2.051000	0.662000
O	4.946000	-0.076000	0.023000
H	5.327000	0.782000	-0.232000
C	-0.718000	0.002000	0.001000
C	-1.445000	-1.141000	-0.367000
C	-1.438000	1.146000	0.367000
C	-2.837000	-1.135000	-0.365000
H	-0.917000	-2.040000	-0.677000
C	-2.833000	1.148000	0.363000
H	-0.906000	2.043000	0.676000
C	-3.557000	0.010000	-0.000000
H	-3.375000	-2.034000	-0.660000
H	-3.366000	2.050000	0.657000
C	-5.064000	0.001000	-0.001000
H	-5.456000	-0.277000	-0.986000
H	-5.454000	-0.726000	0.720000
H	-5.465000	0.985000	0.260000



*** 0 imaginary frequencies ***
Sum of electronic and zero-point Energies= -577.412258
Sum of electronic and thermal Energies= -577.400407
Sum of electronic and thermal Enthalpies= -577.399463
Sum of electronic and thermal Free Energies= -577.450579

4-(4-methylphenyl)phenoxenium cation

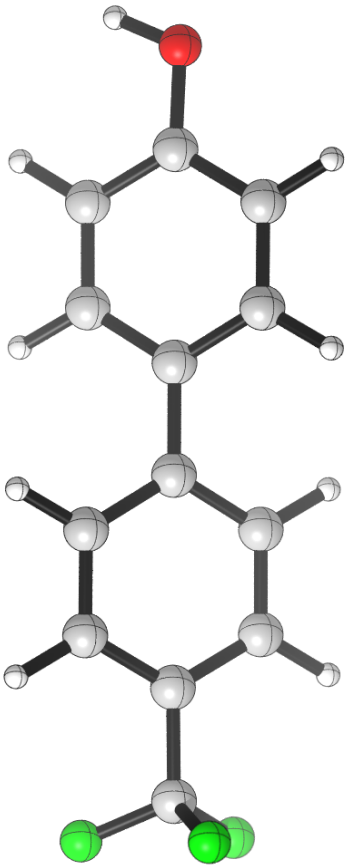
C	3.657000	-0.003000	-0.000000
C	0.790000	0.002000	0.001000
C	2.888000	1.258000	-0.082000
C	2.884000	-1.261000	0.083000
C	1.540000	-1.248000	0.078000
C	1.543000	1.249000	-0.075000
H	3.456000	2.181000	-0.152000
H	3.449000	-2.186000	0.153000
H	1.010000	-2.189000	0.153000
H	1.018000	2.192000	-0.149000
O	4.878000	-0.005000	-0.001000
C	-0.623000	0.003000	-0.001000
C	-1.366000	1.225000	0.077000
C	-1.370000	-1.219000	-0.079000
C	-2.740000	1.219000	0.083000
H	-0.861000	2.179000	0.154000
C	-2.742000	-1.207000	-0.086000
H	-0.867000	-2.174000	-0.156000
C	-3.458000	0.008000	-0.003000
H	-3.285000	2.155000	0.155000
H	-3.290000	-2.142000	-0.159000
C	-4.948000	-0.006000	0.002000
H	-5.321000	-0.568000	-0.862000
H	-5.307000	-0.529000	0.897000
H	-5.364000	1.002000	-0.012000



*** 0 imaginary frequencies ***
Sum of electronic and zero-point Energies= -576.575956
Sum of electronic and thermal Energies= -576.564148
Sum of electronic and thermal Enthalpies= -576.563204
Sum of electronic and thermal Free Energies= -576.614735

4-(4-trifluoromethylphenyl)phenol

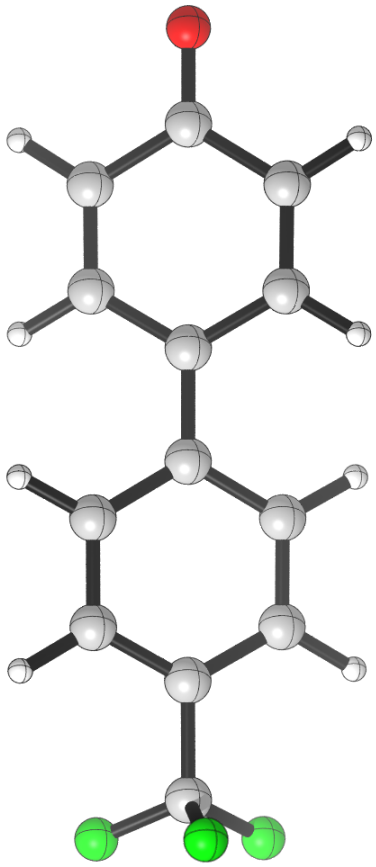
C	4.661000	-0.016000	0.012000
C	1.852000	-0.003000	-0.006000
C	3.957000	-1.167000	0.370000
C	3.972000	1.141000	-0.355000
C	2.580000	1.141000	-0.360000
C	2.567000	-1.155000	0.357000
H	4.506000	-2.058000	0.662000
H	4.526000	2.032000	-0.641000
H	2.058000	2.043000	-0.666000
H	2.032000	-2.052000	0.657000
O	6.024000	-0.079000	0.039000
H	6.408000	0.778000	-0.215000
C	0.368000	0.003000	-0.013000
C	-0.353000	-1.143000	-0.381000
C	-0.346000	1.155000	0.348000
C	-1.743000	-1.142000	-0.388000
H	0.177000	-2.041000	-0.686000
C	-1.737000	1.167000	0.339000
H	0.188000	2.049000	0.657000
C	-2.433000	0.017000	-0.031000
H	-2.285000	-2.037000	-0.680000
H	-2.273000	2.068000	0.627000
C	-3.930000	0.003000	0.003000
F	-4.464000	1.227000	-0.166000
F	-4.412000	-0.457000	1.182000
F	-4.460000	-0.789000	-0.949000



*** 0 imaginary frequencies ***
Sum of electronic and zero-point Energies= -875.095495
Sum of electronic and thermal Energies= -875.081813
Sum of electronic and thermal Enthalpies= -875.080868
Sum of electronic and thermal Free Energies= -875.138109

4-(4-trifluoromethylphenyl)phenoxenium cation

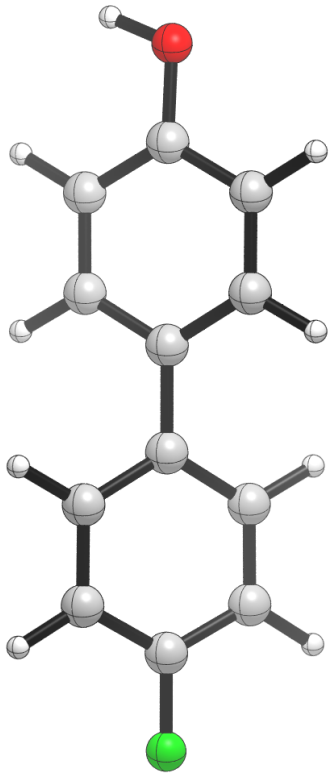
C	4.718000	-0.002000	0.016000
C	1.878000	0.000000	-0.014000
C	3.954000	1.247000	-0.230000
C	3.947000	-1.250000	0.243000
C	2.601000	-1.236000	0.212000
C	2.607000	1.235000	-0.229000
H	4.527000	2.150000	-0.418000
H	4.515000	-2.154000	0.442000
H	2.049000	-2.147000	0.409000
H	2.060000	2.146000	-0.440000
O	5.936000	-0.002000	0.030000
C	0.444000	0.002000	-0.022000
C	-0.275000	1.205000	0.202000
C	-0.276000	-1.199000	-0.251000
C	-1.658000	1.201000	0.213000
H	0.244000	2.132000	0.415000
C	-1.659000	-1.191000	-0.274000
H	0.243000	-2.127000	-0.460000
C	-2.338000	0.006000	-0.034000
H	-2.203000	2.118000	0.410000
H	-2.205000	-2.107000	-0.475000
C	-3.847000	-0.001000	0.007000
F	-4.293000	-0.220000	1.258000
F	-4.370000	-0.959000	-0.770000
F	-4.367000	1.168000	-0.395000



*** 0 imaginary frequencies ***
Sum of electronic and zero-point Energies= -874.244019
Sum of electronic and thermal Energies= -874.230527
Sum of electronic and thermal Enthalpies= -874.229583
Sum of electronic and thermal Free Energies= -874.286014

4-(4-fluorophenyl)phenol

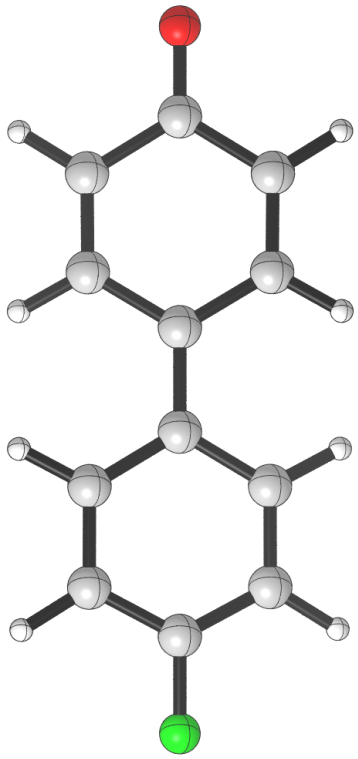
C	-3.543000	0.013000	0.004000
C	-0.732000	0.005000	0.000000
C	-2.842000	1.161000	0.376000
C	-2.850000	-1.139000	-0.370000
C	-1.458000	-1.135000	-0.370000
C	-1.452000	1.150000	0.373000
H	-3.393000	2.049000	0.674000
H	-3.401000	-2.028000	-0.667000
H	-0.932000	-2.034000	-0.683000
H	-0.919000	2.045000	0.685000
O	-4.908000	0.073000	0.025000
H	-5.288000	-0.781000	-0.244000
C	0.753000	0.001000	-0.001000
C	1.475000	1.144000	-0.377000
C	1.470000	-1.145000	0.376000
C	2.868000	1.152000	-0.379000
H	0.945000	2.039000	-0.692000
C	2.863000	-1.159000	0.377000
H	0.936000	-2.037000	0.692000
C	3.530000	-0.005000	-0.001000
H	3.432000	2.031000	-0.675000
H	3.423000	-2.041000	0.673000
F	4.886000	-0.008000	-0.001000



*** 0 imaginary frequencies ***
Sum of electronic and zero-point Energies= -637.363710
Sum of electronic and thermal Energies= -637.352783
Sum of electronic and thermal Enthalpies= -637.351839
Sum of electronic and thermal Free Energies= -637.401005

4-(4-fluorophenyl)phenoxenium cation

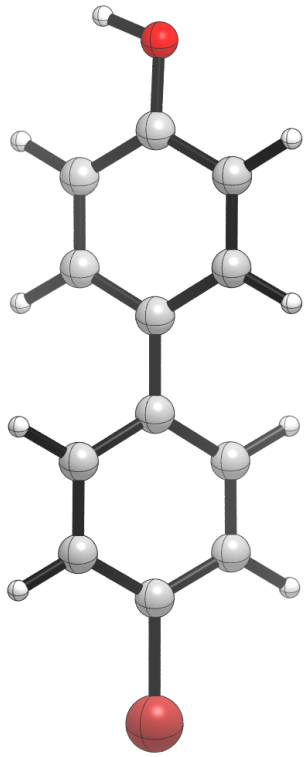
C	3.619000	-0.000000	0.000000
C	0.756000	-0.000000	-0.000000
C	2.848000	1.259000	-0.112000
C	2.848000	-1.259000	0.112000
C	1.503000	-1.248000	0.103000
C	1.503000	1.248000	-0.103000
H	3.415000	2.180000	-0.207000
H	3.415000	-2.180000	0.207000
H	0.975000	-2.186000	0.202000
H	0.975000	2.186000	-0.202000
O	4.839000	0.000000	0.000000
C	-0.662000	-0.000000	-0.000000
C	-1.399000	1.223000	0.105000
C	-1.399000	-1.223000	-0.105000
C	-2.774000	1.226000	0.115000
H	-0.893000	2.174000	0.206000
C	-2.774000	-1.226000	-0.116000
H	-0.893000	-2.174000	-0.206000
C	-3.433000	0.000000	-0.000000
H	-3.346000	2.142000	0.210000
H	-3.346000	-2.142000	-0.210000
F	-4.759000	0.000000	-0.000000



*** 0 imaginary frequencies ***
Sum of electronic and zero-point Energies= -636.522581
Sum of electronic and thermal Energies= -636.511664
Sum of electronic and thermal Enthalpies= -636.510720
Sum of electronic and thermal Free Energies= -636.560436

4-(4-bromophenyl)phenol

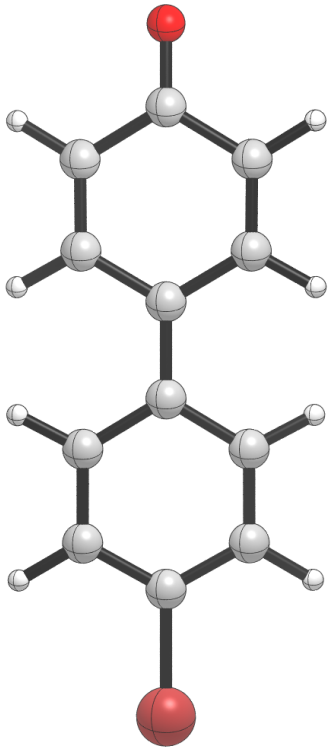
C	-4.723000	0.012000	0.004000
C	-1.913000	0.005000	0.001000
C	-4.023000	1.161000	0.374000
C	-4.029000	-1.141000	-0.368000
C	-2.637000	-1.137000	-0.366000
C	-2.633000	1.152000	0.369000
H	-4.575000	2.049000	0.670000
H	-4.580000	-2.031000	-0.663000
H	-2.110000	-2.036000	-0.676000
H	-2.100000	2.048000	0.678000
O	-6.088000	0.070000	0.024000
H	-6.467000	-0.784000	-0.243000
C	-0.430000	0.002000	-0.001000
C	0.291000	1.145000	-0.375000
C	0.287000	-1.142000	0.374000
C	1.683000	1.153000	-0.374000
H	-0.238000	2.041000	-0.690000
C	1.680000	-1.154000	0.372000
H	-0.244000	-2.036000	0.689000
C	2.363000	-0.001000	-0.001000
H	2.224000	2.046000	-0.671000
H	2.219000	-2.048000	0.669000
Br	4.259000	-0.004000	-0.000000



*** 0 imaginary frequencies ***
Sum of electronic and zero-point Energies= -3109.361303
Sum of electronic and thermal Energies= -3109.349920
Sum of electronic and thermal Enthalpies= -3109.348976
Sum of electronic and thermal Free Energies= -3109.400270

4-(4-bromophenyl)phenoxenium cation

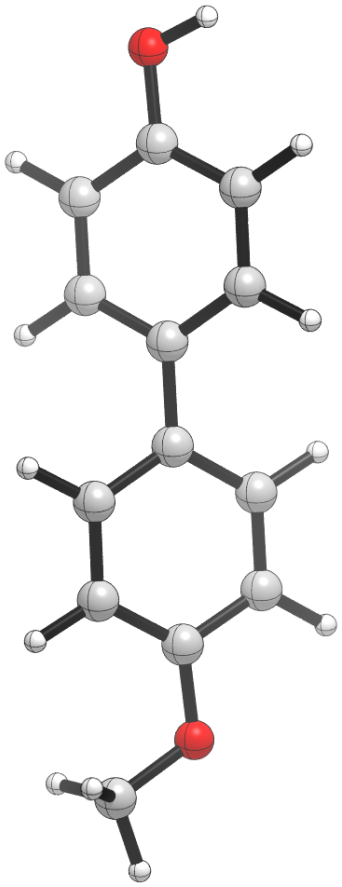
C	-4.788000	0.000000	0.001000
C	-1.928000	-0.000000	0.000000
C	-4.018000	-1.262000	-0.079000
C	-4.017000	1.262000	0.079000
C	-2.672000	1.249000	0.066000
C	-2.672000	-1.249000	-0.066000
H	-4.584000	-2.186000	-0.145000
H	-4.584000	2.186000	0.145000
H	-2.144000	2.191000	0.132000
H	-2.144000	-2.191000	-0.132000
O	-6.008000	0.000000	-0.000000
C	-0.504000	-0.000000	0.000000
C	0.233000	-1.220000	0.072000
C	0.233000	1.220000	-0.072000
C	1.610000	-1.222000	0.076000
H	-0.267000	-2.177000	0.145000
C	1.610000	1.222000	-0.076000
H	-0.267000	2.176000	-0.144000
C	2.289000	-0.000000	-0.000000
H	2.155000	-2.158000	0.139000
H	2.155000	2.157000	-0.139000
Br	4.157000	0.000000	-0.000000



*** 0 imaginary frequencies ***
Sum of electronic and zero-point Energies= -3108.515395
Sum of electronic and thermal Energies= -3108.504207
Sum of electronic and thermal Enthalpies= -3108.503263
Sum of electronic and thermal Free Energies= -3108.554349

4-(4-methoxyphenyl)phenol

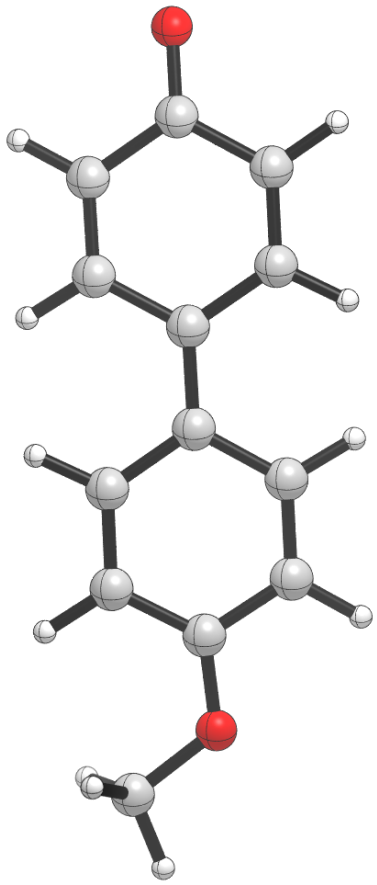
C	-3.993000	-0.117000	0.024000
C	-1.184000	0.028000	-0.012000
C	-3.243000	-1.220000	-0.385000
C	-3.351000	1.058000	0.416000
C	-1.959000	1.122000	0.396000
C	-1.855000	-1.141000	-0.402000
H	-3.756000	-2.126000	-0.697000
H	-3.938000	1.913000	0.743000
H	-1.473000	2.037000	0.724000
H	-1.284000	-2.001000	-0.744000
O	-5.355000	-0.243000	0.019000
H	-5.773000	0.585000	0.310000
C	0.299000	0.104000	-0.032000
C	1.086000	-1.004000	0.297000
C	0.961000	1.293000	-0.383000
C	2.481000	-0.949000	0.281000
H	0.608000	-1.935000	0.593000
C	2.346000	1.368000	-0.401000
H	0.383000	2.170000	-0.664000
C	3.114000	0.245000	-0.069000
H	3.051000	-1.831000	0.551000
H	2.853000	2.288000	-0.680000
O	4.468000	0.411000	-0.116000
C	5.282000	-0.705000	0.224000
H	6.312000	-0.362000	0.129000
H	5.095000	-1.026000	1.255000
H	5.108000	-1.540000	-0.464000



*** 0 imaginary frequencies ***
Sum of electronic and zero-point Energies= -652.592089
Sum of electronic and thermal Energies= -652.579534
Sum of electronic and thermal Enthalpies= -652.578590
Sum of electronic and thermal Free Energies= -652.631413

4-(4-methoxyphenyl)phenoxenium cation

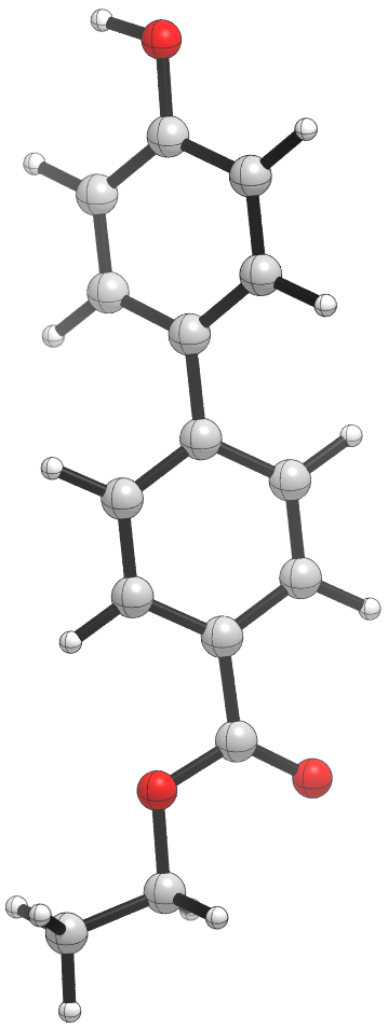
C	-4.063000	-0.125000	-0.012000
C	-1.193000	0.031000	0.018000
C	-3.362000	1.171000	0.077000
C	-3.225000	-1.338000	-0.075000
C	-1.884000	-1.257000	-0.054000
C	-2.020000	1.235000	0.087000
H	-3.977000	2.065000	0.138000
H	-3.740000	-2.292000	-0.145000
H	-1.310000	-2.172000	-0.116000
H	-1.548000	2.206000	0.166000
O	-5.286000	-0.190000	-0.031000
C	0.203000	0.110000	0.015000
C	0.892000	1.378000	-0.059000
C	1.024000	-1.074000	0.079000
C	2.250000	1.448000	-0.075000
H	0.338000	2.305000	-0.126000
C	2.388000	-1.014000	0.075000
H	0.570000	-2.053000	0.156000
C	3.024000	0.254000	-0.010000
H	2.772000	2.397000	-0.145000
H	2.971000	-1.925000	0.138000
C	5.198000	-0.723000	0.005000
H	5.007000	-1.364000	-0.859000
H	6.202000	-0.308000	-0.045000
H	5.055000	-1.267000	0.941000
O	4.320000	0.418000	-0.035000



*** 0 imaginary frequencies ***
Sum of electronic and zero-point Energies= -651.764950
Sum of electronic and thermal Energies= -651.752371
Sum of electronic and thermal Enthalpies= -651.751427
Sum of electronic and thermal Free Energies= -651.804877

4-(4-ethoxycarbonylphenyl)phenol

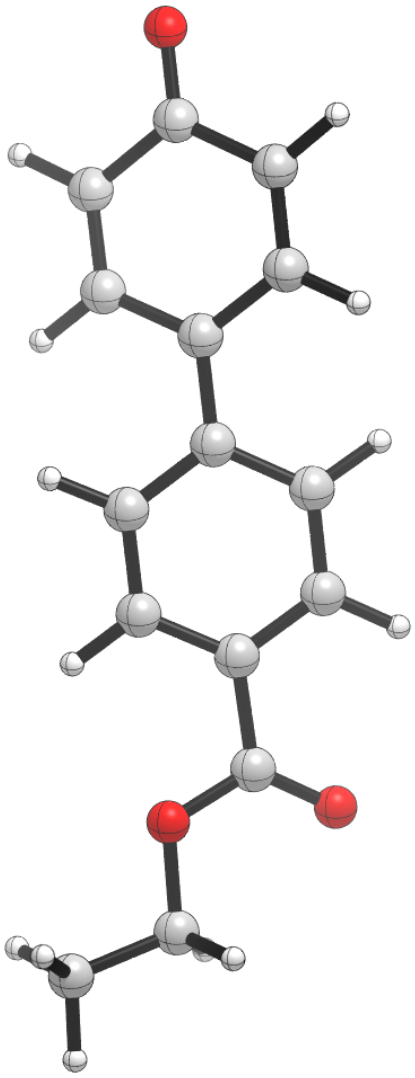
C	-5.114000	-0.286000	0.050000
C	-2.322000	0.017000	-0.001000
C	-4.529000	0.869000	0.573000
C	-4.315000	-1.290000	-0.498000
C	-2.932000	-1.134000	-0.518000
C	-3.147000	1.014000	0.542000
H	-5.162000	1.638000	1.005000
H	-4.776000	-2.183000	-0.913000
H	-2.323000	-1.916000	-0.964000
H	-2.704000	1.909000	0.970000
O	-6.475000	-0.379000	0.103000
H	-6.775000	-1.220000	-0.283000
C	-0.848000	0.176000	-0.029000
C	-0.265000	1.435000	-0.244000
C	-0.002000	-0.929000	0.157000
C	1.116000	1.585000	-0.272000
H	-0.897000	2.302000	-0.413000
C	1.380000	-0.785000	0.129000
H	-0.430000	-1.910000	0.346000
C	1.947000	0.476000	-0.086000
H	1.555000	2.562000	-0.447000
H	2.015000	-1.651000	0.281000
C	3.420000	0.677000	-0.127000
O	3.953000	1.753000	-0.346000
C	5.551000	-0.333000	0.060000
H	5.841000	0.034000	-0.929000
H	5.862000	0.397000	0.813000
C	6.111000	-1.707000	0.340000
H	7.204000	-1.662000	0.320000
H	5.799000	-2.062000	1.327000
H	5.781000	-2.425000	-0.416000
O	4.110000	-0.439000	0.099000



*** 0 imaginary frequencies ***
Sum of electronic and zero-point Energies= -805.175470
Sum of electronic and thermal Energies= -805.159748
Sum of electronic and thermal Enthalpies= -805.158803
Sum of electronic and thermal Free Energies= -805.219881

4-(4-ethoxycarbonylphenyl)phenoxenium cation

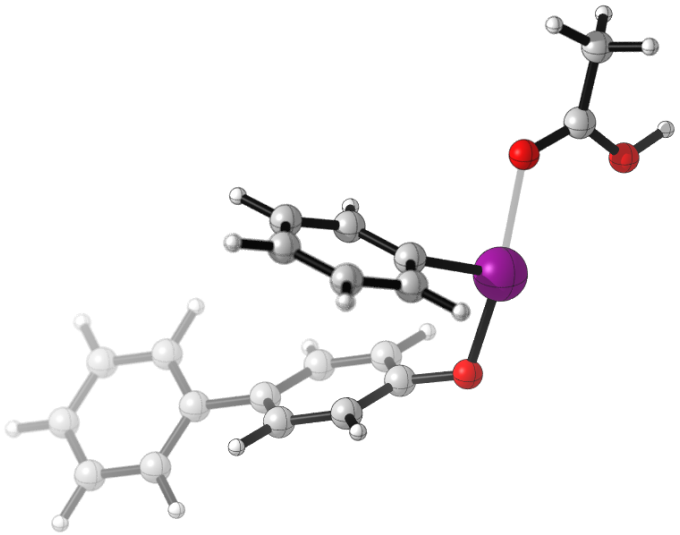
C	-5.173000	-0.322000	0.037000
C	-2.347000	-0.001000	0.010000
C	-4.542000	0.966000	0.417000
C	-4.277000	-1.440000	-0.349000
C	-2.940000	-1.277000	-0.344000
C	-3.204000	1.109000	0.387000
H	-5.205000	1.770000	0.724000
H	-4.748000	-2.374000	-0.641000
H	-2.300000	-2.092000	-0.659000
H	-2.758000	2.046000	0.698000
O	-6.383000	-0.458000	0.043000
C	-0.925000	0.162000	-0.016000
C	-0.346000	1.456000	-0.110000
C	-0.068000	-0.970000	0.046000
C	1.026000	1.603000	-0.162000
H	-0.969000	2.339000	-0.195000
C	1.305000	-0.809000	0.036000
H	-0.474000	-1.968000	0.153000
C	1.851000	0.475000	-0.080000
H	1.468000	2.589000	-0.262000
H	1.952000	-1.676000	0.110000
C	3.337000	0.688000	-0.130000
O	3.840000	1.771000	-0.353000
C	5.467000	-0.313000	0.050000
H	5.748000	0.053000	-0.942000
H	5.772000	0.420000	0.800000
C	6.028000	-1.686000	0.332000
H	7.121000	-1.637000	0.310000
H	5.718000	-2.038000	1.321000
H	5.698000	-2.406000	-0.422000
O	4.022000	-0.422000	0.092000



*** 0 imaginary frequencies ***
Sum of electronic and zero-point Energies= -804.325666
Sum of electronic and thermal Energies= -804.309954
Sum of electronic and thermal Enthalpies= -804.309009
Sum of electronic and thermal Free Energies= -804.370294

Protonated iodane from 4-phenylphenol

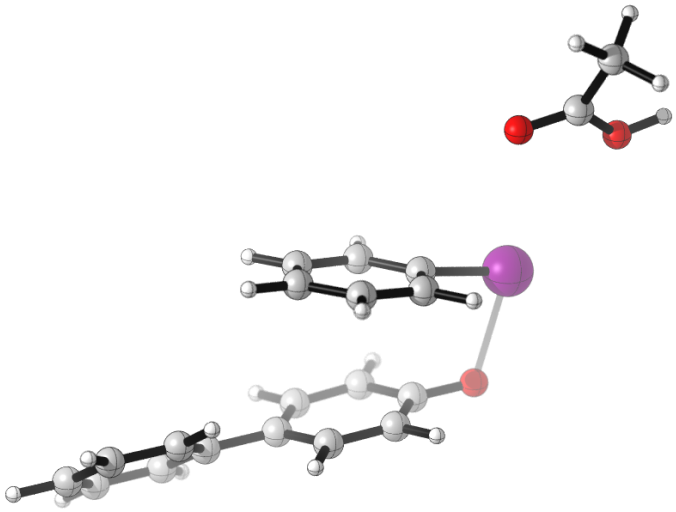
I	-2.218000	-0.652000	-0.547000
C	-1.475000	1.243000	-0.108000
C	-0.333000	3.703000	0.366000
C	-1.750000	2.287000	-0.989000
C	-0.646000	1.391000	1.002000
C	-0.074000	2.642000	1.234000
C	-1.167000	3.529000	-0.739000
H	-2.395000	2.138000	-1.850000
H	-0.444000	0.556000	1.666000
H	0.578000	2.781000	2.091000
H	-1.367000	4.358000	-1.412000
H	0.121000	4.673000	0.551000
O	-0.688000	-0.990000	-1.810000
C	0.586000	-0.863000	-1.295000
C	3.198000	-0.578000	-0.319000
C	1.088000	-1.791000	-0.382000
C	1.370000	0.210000	-1.718000
C	2.670000	0.342000	-1.236000
C	2.386000	-1.645000	0.098000
H	0.465000	-2.622000	-0.061000
H	0.954000	0.935000	-2.412000
H	3.269000	1.189000	-1.558000
H	2.779000	-2.383000	0.792000
O	-3.891000	0.107000	0.959000
C	-4.874000	-0.599000	1.218000
O	-4.955000	-1.772000	0.629000
C	-5.949000	-0.170000	2.156000
H	-6.900000	-0.139000	1.614000
H	-5.716000	0.812000	2.564000
H	-6.038000	-0.906000	2.961000
H	-5.754000	-2.271000	0.887000
C	4.582000	-0.430000	0.199000
C	4.884000	-0.731000	1.535000
C	5.615000	0.015000	-0.638000
C	6.183000	-0.591000	2.020000
H	4.094000	-1.059000	2.206000
C	6.915000	0.156000	-0.152000
H	5.406000	0.233000	-1.682000
C	7.204000	-0.147000	1.179000
H	6.396000	-0.822000	3.061000
H	7.704000	0.495000	-0.818000
H	8.216000	-0.038000	1.557000



*** 0 imaginary frequencies ***
Sum of electronic and zero-point Energies= -1009.054132
Sum of electronic and thermal Energies= -1009.031249
Sum of electronic and thermal Enthalpies= -1009.030305
Sum of electronic and thermal Free Energies= -1009.111270

Transition state to form 4-phenylphenoxenium cation

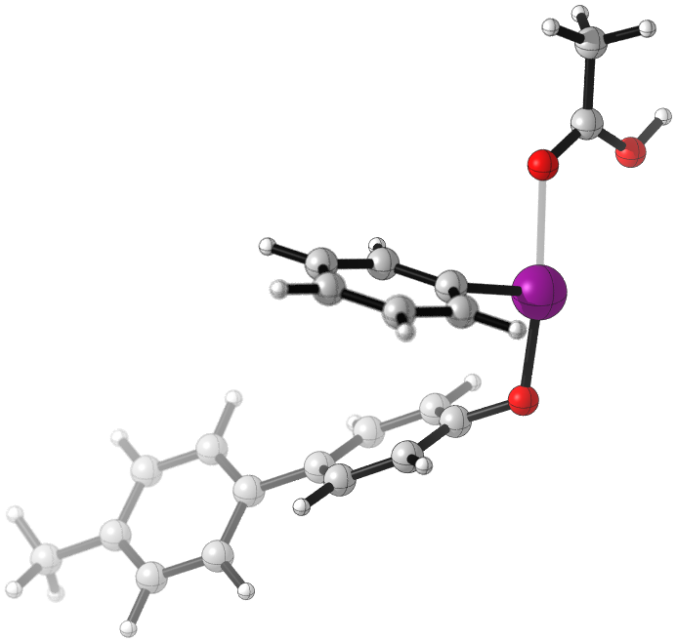
I	2.385000	-1.099000	-0.007000
C	1.054000	0.449000	-0.079000
C	-0.911000	2.400000	-0.082000
C	0.970000	1.342000	1.005000
C	0.174000	0.534000	-1.168000
C	-0.820000	1.510000	-1.152000
C	-0.009000	2.326000	0.986000
H	1.660000	1.259000	1.839000
H	0.269000	-0.147000	-2.008000
H	-1.520000	1.575000	-1.980000
H	-0.082000	3.027000	1.813000
H	-1.683000	3.165000	-0.082000
O	0.517000	-2.490000	0.718000
C	-0.617000	-1.908000	0.550000
C	-3.129000	-0.673000	0.212000
C	-1.395000	-2.145000	-0.633000
C	-1.123000	-1.003000	1.538000
C	-2.351000	-0.410000	1.367000
C	-2.633000	-1.571000	-0.770000
H	-0.978000	-2.791000	-1.402000
H	-0.523000	-0.824000	2.426000
H	-2.736000	0.253000	2.135000
H	-3.211000	-1.757000	-1.669000
C	-4.429000	-0.012000	0.024000
C	-5.460000	-0.646000	-0.694000
C	-4.663000	1.268000	0.557000
C	-6.690000	-0.018000	-0.865000
H	-5.313000	-1.646000	-1.092000
C	-5.889000	1.898000	0.371000
H	-3.874000	1.787000	1.094000
C	-6.907000	1.256000	-0.338000
H	-7.482000	-0.527000	-1.407000
H	-6.049000	2.893000	0.775000
H	-7.866000	1.747000	-0.478000
O	4.232000	1.639000	-0.579000
C	5.387000	1.330000	-0.355000
O	5.699000	0.025000	-0.317000
C	6.504000	2.301000	-0.119000
H	6.963000	2.106000	0.856000
H	6.121000	3.320000	-0.153000
H	7.272000	2.166000	-0.887000
H	6.644000	-0.121000	-0.129000



*** 1 imaginary frequency (-177.4491) ***
Sum of electronic and zero-point Energies= -1009.037077
Sum of electronic and thermal Energies= -1009.014037
Sum of electronic and thermal Enthalpies= -1009.013093
Sum of electronic and thermal Free Energies= -1009.095789

Protonated iodane from 4-(4-methylphenyl)phenol

I	-2.550000	-0.611000	-0.586000
C	-1.838000	1.272000	-0.055000
C	-0.747000	3.725000	0.552000
C	-2.110000	2.349000	-0.897000
C	-1.037000	1.383000	1.079000
C	-0.492000	2.631000	1.380000
C	-1.552000	3.587000	-0.580000
H	-2.732000	2.227000	-1.778000
H	-0.836000	0.522000	1.709000
H	0.136000	2.743000	2.258000
H	-1.749000	4.441000	-1.221000
H	-0.315000	4.693000	0.790000
O	-1.069000	-0.833000	-1.927000
C	0.223000	-0.744000	-1.446000
C	2.867000	-0.537000	-0.540000
C	0.779000	-1.778000	-0.693000
C	0.971000	0.394000	-1.748000
C	2.286000	0.488000	-1.300000
C	2.092000	-1.670000	-0.248000
H	0.184000	-2.660000	-0.469000
H	0.515000	1.197000	-2.321000
H	2.856000	1.387000	-1.524000
H	2.527000	-2.490000	0.318000
O	-4.170000	0.016000	1.042000
C	-5.066000	-0.763000	1.385000
O	-5.097000	-1.949000	0.816000
C	-6.094000	-0.412000	2.404000
H	-7.089000	-0.495000	1.954000
H	-5.928000	0.601000	2.768000
H	-6.034000	-1.128000	3.231000
H	-5.837000	-2.502000	1.135000
C	4.267000	-0.425000	-0.055000
C	4.631000	-0.907000	1.209000
C	5.260000	0.170000	-0.845000
C	5.944000	-0.797000	1.665000
H	3.878000	-1.351000	1.856000
C	6.571000	0.277000	-0.385000
H	5.012000	0.538000	-1.838000
C	6.937000	-0.207000	0.876000
H	6.198000	-1.168000	2.656000
H	7.324000	0.738000	-1.021000
C	8.362000	-0.118000	1.356000
H	8.947000	-0.973000	0.995000
H	8.850000	0.790000	0.989000
H	8.414000	-0.122000	2.449000

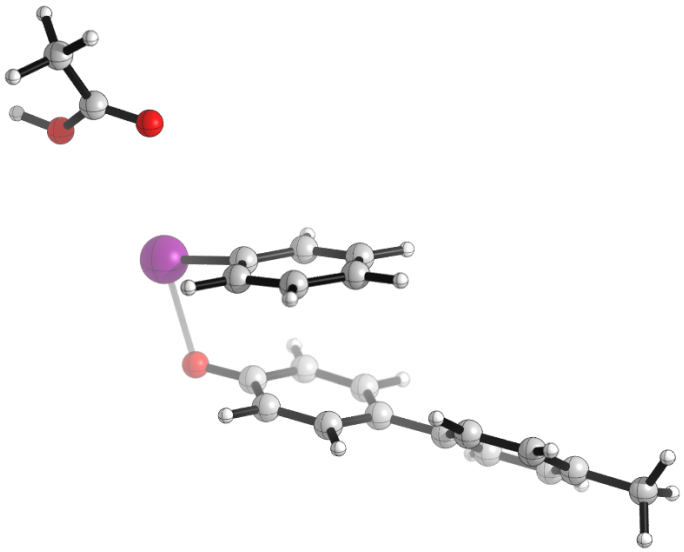


*** 0 imaginary frequencies ***
Sum of electronic and zero-point Energies= -1048.323671
Sum of electronic and thermal Energies= -1048.299155

Sum of electronic and thermal Enthalpies=	-1048.298211
Sum of electronic and thermal Free Energies=	-1048.381972

Transition state to form 4-(4-methylphenyl)phenoxenium cation

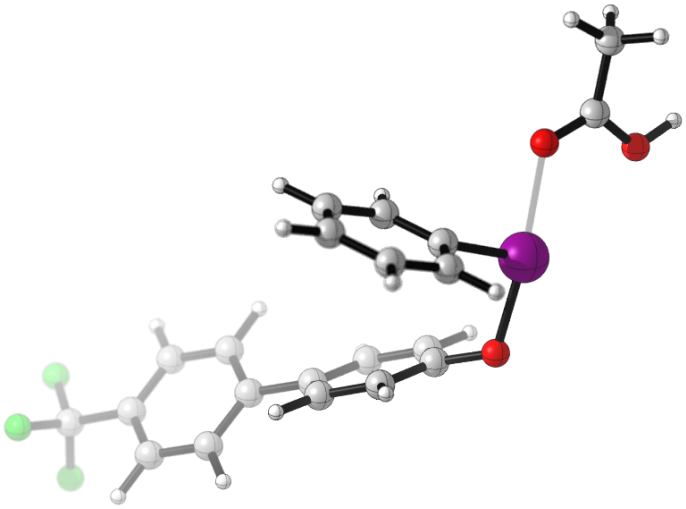
I	2.736000	-0.998000	-0.001000
C	1.346000	0.499000	-0.029000
C	-0.705000	2.358000	0.029000
C	1.224000	1.352000	1.082000
C	0.462000	0.578000	-1.115000
C	-0.574000	1.508000	-1.069000
C	0.202000	2.292000	1.094000
H	1.918000	1.274000	1.913000
H	0.585000	-0.073000	-1.975000
H	-1.278000	1.568000	-1.895000
H	0.098000	2.962000	1.942000
H	-1.510000	3.087000	0.053000
O	0.949000	-2.476000	0.691000
C	-0.218000	-1.953000	0.534000
C	-2.800000	-0.860000	0.224000
C	-0.979000	-2.206000	-0.653000
C	-0.775000	-1.102000	1.541000
C	-2.035000	-0.577000	1.383000
C	-2.249000	-1.703000	-0.779000
H	-0.526000	-2.807000	-1.437000
H	-0.187000	-0.910000	2.434000
H	-2.456000	0.042000	2.168000
H	-2.815000	-1.902000	-1.683000
C	-4.140000	-0.284000	0.055000
C	-5.125000	-0.951000	-0.694000
C	-4.472000	0.952000	0.641000
C	-6.396000	-0.406000	-0.838000
H	-4.912000	-1.918000	-1.139000
C	-5.738000	1.496000	0.478000
H	-3.725000	1.507000	1.202000
C	-6.726000	0.825000	-0.259000
H	-7.147000	-0.947000	-1.407000
H	-5.968000	2.461000	0.924000
C	-8.105000	1.409000	-0.397000
H	-8.654000	1.319000	0.548000
H	-8.058000	2.474000	-0.645000
H	-8.679000	0.895000	-1.172000
O	4.533000	1.687000	-0.641000
C	5.691000	1.384000	-0.428000
O	6.009000	0.080000	-0.388000
C	6.806000	2.360000	-0.206000
H	7.274000	2.174000	0.766000
H	6.419000	3.378000	-0.244000
H	7.569000	2.224000	-0.979000
H	6.956000	-0.061000	-0.208000



*** 1 imaginary frequency (-191.3515) ***
Sum of electronic and zero-point Energies= -1048.307660
Sum of electronic and thermal Energies= -1048.282944
Sum of electronic and thermal Enthalpies= -1048.281999
Sum of electronic and thermal Free Energies= -1048.367353

Protonated iodane from 4-(4-trifluoromethylphenyl)phenol

I	-3.388000	-0.581000	-0.541000
C	-2.802000	1.321000	0.072000
C	-1.883000	3.820000	0.773000
C	-3.252000	2.424000	-0.651000
C	-1.904000	1.428000	1.132000
C	-1.447000	2.699000	1.481000
C	-2.780000	3.684000	-0.288000
H	-3.948000	2.307000	-1.476000
H	-1.564000	0.548000	1.669000
H	-0.746000	2.808000	2.303000
H	-3.116000	4.559000	-0.836000
H	-1.520000	4.806000	1.049000
O	-2.003000	-0.570000	-2.000000
C	-0.682000	-0.531000	-1.600000
C	2.010000	-0.419000	-0.843000
C	-0.059000	-1.672000	-1.094000
C	0.023000	0.666000	-1.729000
C	1.364000	0.713000	-1.358000
C	1.279000	-1.611000	-0.720000
H	-0.622000	-2.597000	-1.004000
H	-0.484000	1.549000	-2.109000
H	1.904000	1.653000	-1.443000
H	1.766000	-2.509000	-0.347000
O	-4.935000	-0.249000	1.235000
C	-5.808000	-1.092000	1.475000
O	-5.855000	-2.160000	0.708000
C	-6.787000	-0.943000	2.588000
H	-7.802000	-0.979000	2.179000
H	-6.621000	0.001000	3.105000
H	-6.669000	-1.781000	3.282000
H	-6.576000	-2.773000	0.951000
C	3.434000	-0.358000	-0.430000
C	3.880000	-1.050000	0.703000
C	4.360000	0.399000	-1.166000
C	5.214000	-0.991000	1.099000
H	3.177000	-1.625000	1.299000
C	5.692000	0.463000	-0.779000
H	4.040000	0.926000	-2.061000
C	6.115000	-0.233000	0.356000
H	5.541000	-1.527000	1.984000
H	6.402000	1.046000	-1.361000
C	7.560000	-0.152000	0.743000

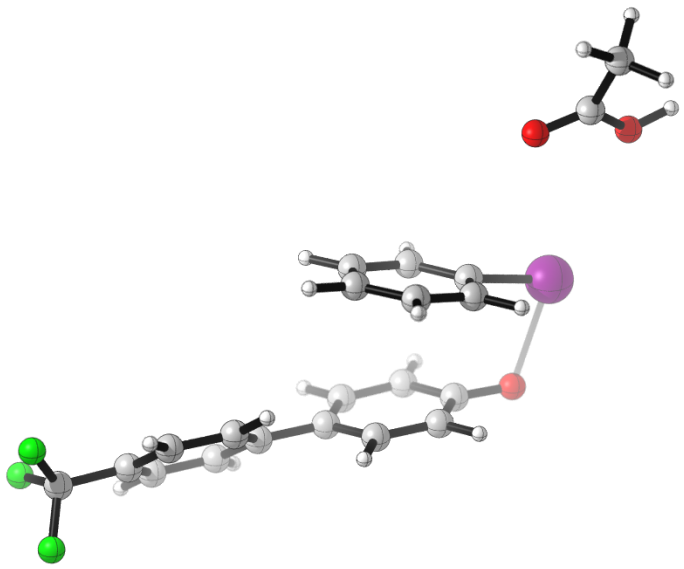


F	7.830000	-0.780000	1.900000
F	7.978000	1.125000	0.888000
F	8.369000	-0.699000	-0.192000

*** 0 imaginary frequencies ***
Sum of electronic and zero-point Energies= -1346.004758
Sum of electronic and thermal Energies= -1345.978179
Sum of electronic and thermal Enthalpies= -1345.977235
Sum of electronic and thermal Free Energies= -1346.068175

Transition state to form 4-(4-trifluoromethylphenyl)phenoxenium cation

I	3.679000	-1.096000	-0.030000
C	2.195000	0.302000	0.096000
C	0.070000	2.065000	0.321000
C	2.032000	1.037000	1.286000
C	1.313000	0.456000	-0.985000
C	0.239000	1.333000	-0.855000
C	0.973000	1.928000	1.383000
H	2.727000	0.904000	2.110000
H	1.470000	-0.097000	-1.906000
H	-0.462000	1.449000	-1.677000
H	0.838000	2.505000	2.293000
H	-0.762000	2.757000	0.410000
O	1.917000	-2.750000	0.529000
C	0.750000	-2.241000	0.416000
C	-1.853000	-1.192000	0.199000
C	-0.001000	-2.390000	-0.803000
C	0.166000	-1.504000	1.501000
C	-1.106000	-1.000000	1.386000
C	-1.281000	-1.910000	-0.885000
H	0.474000	-2.898000	-1.638000
H	0.745000	-1.390000	2.414000
H	-1.552000	-0.472000	2.224000
H	-1.842000	-2.029000	-1.807000
C	-3.217000	-0.648000	0.085000
C	-4.186000	-1.316000	-0.682000
C	-3.568000	0.542000	0.744000
C	-5.478000	-0.812000	-0.782000
H	-3.943000	-2.250000	-1.179000
C	-4.854000	1.057000	0.634000
H	-2.828000	1.086000	1.323000
C	-5.802000	0.376000	-0.129000
H	-6.223000	-1.345000	-1.364000
H	-5.110000	1.985000	1.136000
C	-7.207000	0.902000	-0.203000
F	-7.258000	2.244000	-0.125000
F	-7.972000	0.432000	0.806000
F	-7.827000	0.552000	-1.344000
O	4.832000	2.223000	-0.638000

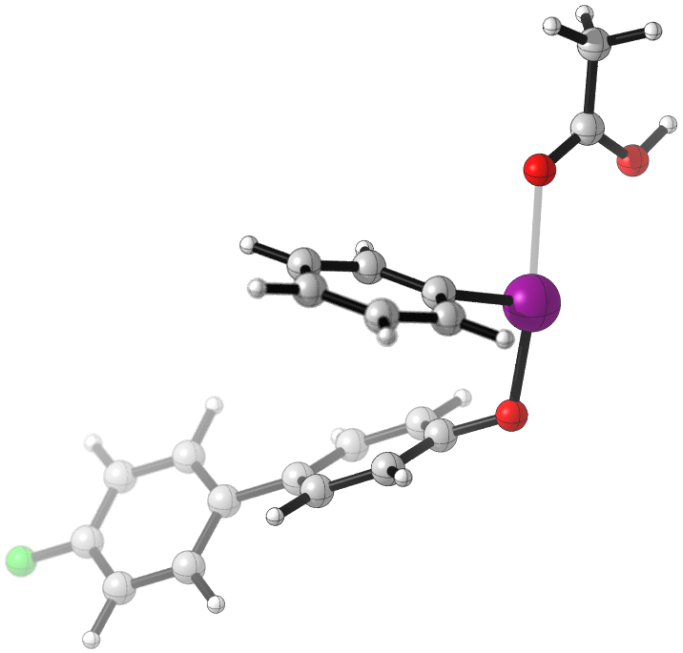


C	6.037000	2.123000	-0.506000
O	6.596000	0.912000	-0.660000
C	6.962000	3.257000	-0.185000
H	7.520000	3.034000	0.730000
H	6.390000	4.176000	-0.057000
H	7.684000	3.380000	-0.999000
H	7.562000	0.941000	-0.533000

*** 1 imaginary frequency (-164.0430) ***
Sum of electronic and zero-point Energies= -1345.985267
Sum of electronic and thermal Energies= -1345.958764
Sum of electronic and thermal Enthalpies= -1345.957820
Sum of electronic and thermal Free Energies= -1346.048406

Protonated iodane from 4-(4-fluorophenyl)phenol

I	-2.531000	-0.608000	-0.592000
C	-1.825000	1.275000	-0.055000
C	-0.740000	3.729000	0.562000
C	-2.098000	2.353000	-0.893000
C	-1.024000	1.384000	1.081000
C	-0.483000	2.633000	1.387000
C	-1.543000	3.592000	-0.571000
H	-2.719000	2.233000	-1.775000
H	-0.821000	0.521000	1.708000
H	0.144000	2.743000	2.266000
H	-1.742000	4.448000	-1.209000
H	-0.311000	4.697000	0.804000
O	-1.046000	-0.822000	-1.931000
C	0.245000	-0.737000	-1.447000
C	2.885000	-0.537000	-0.530000
C	0.802000	-1.783000	-0.712000
C	0.989000	0.409000	-1.725000
C	2.302000	0.501000	-1.272000
C	2.114000	-1.679000	-0.261000
H	0.210000	-2.670000	-0.505000
H	0.532000	1.221000	-2.285000
H	2.868000	1.406000	-1.476000
H	2.551000	-2.508000	0.290000
O	-4.156000	0.009000	1.031000
C	-5.052000	-0.773000	1.370000
O	-5.079000	-1.958000	0.799000
C	-6.083000	-0.425000	2.387000
H	-7.076000	-0.508000	1.933000
H	-5.919000	0.586000	2.755000
H	-6.025000	-1.143000	3.212000
H	-5.819000	-2.512000	1.114000
C	4.281000	-0.427000	-0.037000
C	4.637000	-0.930000	1.224000
C	5.272000	0.185000	-0.818000
C	5.943000	-0.829000	1.697000

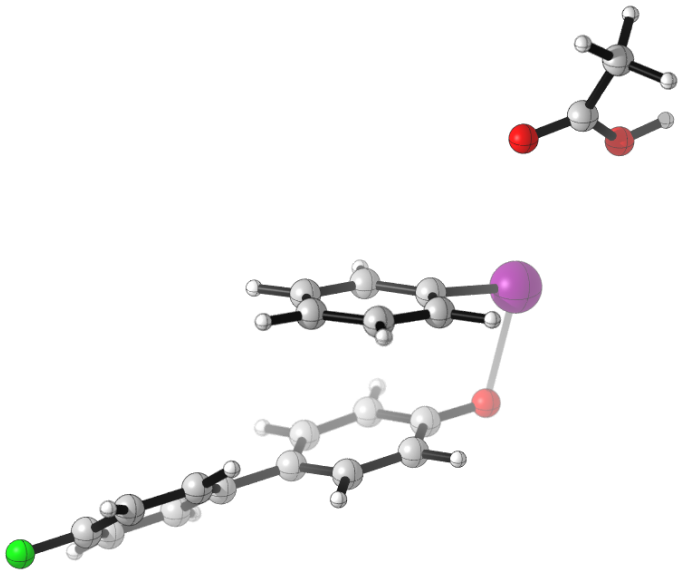


H	3.883000	-1.389000	1.856000
C	6.584000	0.297000	-0.361000
H	5.026000	0.564000	-1.806000
C	6.887000	-0.215000	0.890000
H	6.225000	-1.207000	2.675000
H	7.358000	0.763000	-0.962000
F	8.160000	-0.111000	1.344000

*** 0 imaginary frequencies ***
Sum of electronic and zero-point Energies= -1108.274514
Sum of electronic and thermal Energies= -1108.250968
Sum of electronic and thermal Enthalpies= -1108.250024
Sum of electronic and thermal Free Energies= -1108.331683

Transition state to form 4-(4-fluorophenyl)phenoxenium cation

I	2.722000	-1.029000	-0.003000
C	1.329000	0.466000	-0.026000
C	-0.714000	2.334000	0.030000
C	1.205000	1.316000	1.088000
C	0.450000	0.553000	-1.116000
C	-0.582000	1.487000	-1.071000
C	0.187000	2.259000	1.099000
H	1.896000	1.231000	1.922000
H	0.576000	-0.094000	-1.979000
H	-1.281000	1.554000	-1.900000
H	0.083000	2.926000	1.949000
H	-1.515000	3.067000	0.052000
O	0.903000	-2.515000	0.677000
C	-0.251000	-1.974000	0.524000
C	-2.815000	-0.841000	0.220000
C	-1.016000	-2.206000	-0.669000
C	-0.797000	-1.121000	1.537000
C	-2.048000	-0.575000	1.382000
C	-2.278000	-1.683000	-0.790000
H	-0.571000	-2.807000	-1.456000
H	-0.207000	-0.945000	2.432000
H	-2.462000	0.045000	2.170000
H	-2.847000	-1.865000	-1.696000
C	-4.148000	-0.245000	0.054000
C	-5.145000	-0.913000	-0.679000
C	-4.450000	1.003000	0.629000
C	-6.411000	-0.360000	-0.830000
H	-4.948000	-1.890000	-1.109000
C	-5.705000	1.576000	0.474000
H	-3.689000	1.550000	1.179000
C	-6.659000	0.876000	-0.252000
H	-7.195000	-0.873000	-1.377000
H	-5.946000	2.546000	0.897000
F	-7.883000	1.422000	-0.400000
O	4.503000	1.724000	-0.626000

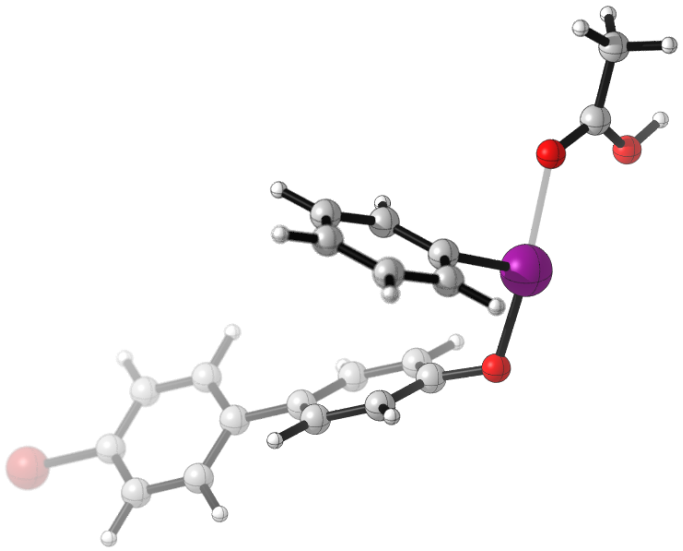


C	5.663000	1.426000	-0.417000
O	5.988000	0.124000	-0.381000
C	6.775000	2.406000	-0.196000
H	7.250000	2.217000	0.772000
H	6.383000	3.423000	-0.226000
H	7.534000	2.279000	-0.975000
H	6.937000	-0.012000	-0.203000

*** 1 imaginary frequency (-177.0673) ***
Sum of electronic and zero-point Energies= -1108.257547
Sum of electronic and thermal Energies= -1108.233740
Sum of electronic and thermal Enthalpies= -1108.232796
Sum of electronic and thermal Free Energies= -1108.316301

Protonated iodane from 4-(4-bromophenyl)phenol

I	-3.505000	-0.591000	-0.559000
C	-2.834000	1.291000	0.020000
C	-1.808000	3.754000	0.701000
C	-3.162000	2.391000	-0.770000
C	-2.006000	1.383000	1.137000
C	-1.494000	2.636000	1.475000
C	-2.637000	3.634000	-0.416000
H	-3.805000	2.286000	-1.638000
H	-1.762000	0.505000	1.726000
H	-0.846000	2.733000	2.341000
H	-2.879000	4.507000	-1.014000
H	-1.404000	4.725000	0.969000
O	-2.051000	-0.737000	-1.938000
C	-0.745000	-0.647000	-1.504000
C	1.947000	-0.460000	-0.759000
C	-0.138000	-1.710000	-0.834000
C	-0.029000	0.517000	-1.784000
C	1.311000	0.602000	-1.417000
C	1.201000	-1.612000	-0.469000
H	-0.711000	-2.609000	-0.621000
H	-0.526000	1.342000	-2.287000
H	1.860000	1.515000	-1.629000
H	1.677000	-2.457000	0.023000
O	-5.151000	-0.072000	1.081000
C	-5.949000	-0.930000	1.477000
O	-5.845000	-2.143000	0.976000
C	-7.014000	-0.639000	2.477000
H	-7.990000	-0.791000	2.005000
H	-6.923000	0.388000	2.829000
H	-6.926000	-1.339000	3.313000
H	-6.512000	-2.758000	1.338000
C	3.382000	-0.368000	-0.387000
C	3.853000	-0.922000	0.811000
C	4.299000	0.272000	-1.231000
C	5.198000	-0.843000	1.161000

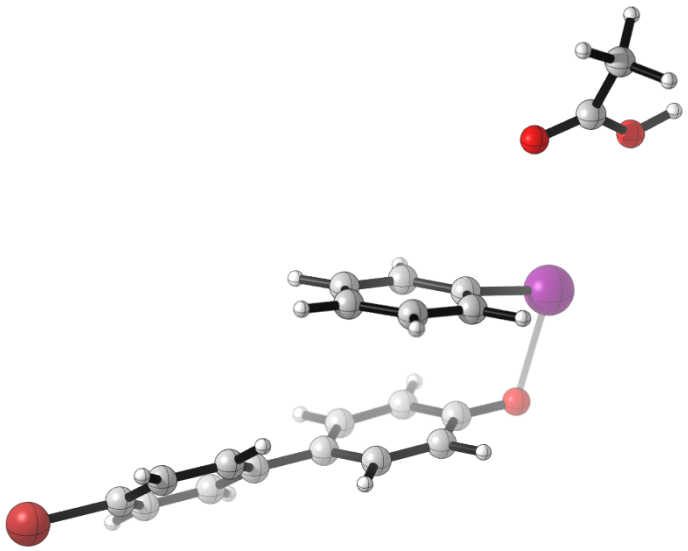


H	3.161000	-1.406000	1.495000
C	5.648000	0.360000	-0.895000
H	3.968000	0.691000	-2.178000
C	6.083000	-0.201000	0.301000
H	5.546000	-1.272000	2.096000
H	6.346000	0.851000	-1.565000
Br	7.922000	-0.086000	0.768000

*** 0 imaginary frequencies ***
Sum of electronic and zero-point Energies= -3579.949408
Sum of electronic and thermal Energies= -3579.925167
Sum of electronic and thermal Enthalpies= -3579.924222
Sum of electronic and thermal Free Energies= -3580.009511

Transition state to form 4-(4-bromophenyl)phenoxenium cation

I	3.720000	-1.054000	-0.049000
C	2.236000	0.343000	0.095000
C	0.095000	2.078000	0.359000
C	2.088000	1.074000	1.288000
C	1.334000	0.485000	-0.970000
C	0.252000	1.350000	-0.821000
C	1.019000	1.952000	1.404000
H	2.798000	0.949000	2.099000
H	1.481000	-0.066000	-1.894000
H	-0.465000	1.457000	-1.630000
H	0.892000	2.527000	2.317000
H	-0.745000	2.759000	0.464000
O	2.018000	-2.703000	0.529000
C	0.831000	-2.225000	0.427000
C	-1.798000	-1.231000	0.228000
C	0.073000	-2.400000	-0.779000
C	0.241000	-1.500000	1.514000
C	-1.043000	-1.023000	1.408000
C	-1.220000	-1.947000	-0.853000
H	0.550000	-2.902000	-1.617000
H	0.824000	-1.369000	2.421000
H	-1.491000	-0.502000	2.249000
H	-1.783000	-2.084000	-1.771000
C	-3.164000	-0.700000	0.116000
C	-4.130000	-1.361000	-0.661000
C	-3.528000	0.482000	0.784000
C	-5.424000	-0.864000	-0.764000
H	-3.886000	-2.290000	-1.166000
C	-4.814000	0.996000	0.675000
H	-2.795000	1.027000	1.372000
C	-5.752000	0.314000	-0.098000
H	-6.166000	-1.394000	-1.353000
H	-5.077000	1.918000	1.182000
Br	-7.508000	1.008000	-0.248000
O	4.928000	2.179000	-0.649000

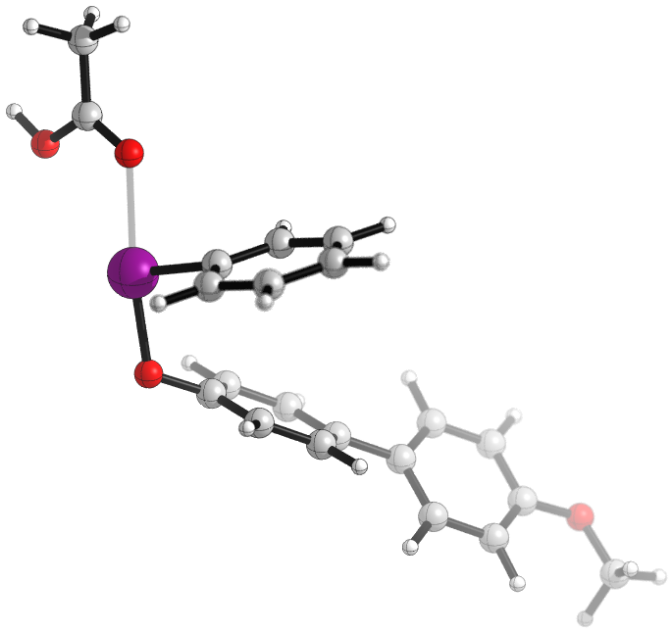


C	6.131000	2.071000	-0.517000
O	6.683000	0.857000	-0.672000
C	7.063000	3.201000	-0.196000
H	7.618000	2.975000	0.721000
H	6.496000	4.123000	-0.069000
H	7.787000	3.319000	-1.008000
H	7.649000	0.881000	-0.545000

*** 1 imaginary frequencies (-176.3363) ***
Sum of electronic and zero-point Energies= -3579.931411
Sum of electronic and thermal Energies= -3579.907078
Sum of electronic and thermal Enthalpies= -3579.906134
Sum of electronic and thermal Free Energies= -3579.991940

Protonated iodane from 4-(4-methoxyphenyl)phenol

I	-2.870000	-0.600000	-0.578000
C	-2.159000	1.284000	-0.052000
C	-1.071000	3.740000	0.549000
C	-2.437000	2.359000	-0.893000
C	-1.353000	1.397000	1.079000
C	-0.810000	2.647000	1.377000
C	-1.880000	3.599000	-0.580000
H	-3.063000	2.236000	-1.771000
H	-1.147000	0.537000	1.708000
H	-0.178000	2.761000	2.252000
H	-2.082000	4.452000	-1.220000
H	-0.640000	4.709000	0.785000
O	-1.399000	-0.820000	-1.930000
C	-0.103000	-0.747000	-1.457000
C	2.552000	-0.580000	-0.572000
C	0.458000	-1.810000	-0.750000
C	0.642000	0.402000	-1.718000
C	1.961000	0.478000	-1.279000
C	1.778000	-1.723000	-0.318000
H	-0.136000	-2.700000	-0.554000
H	0.182000	1.228000	-2.254000
H	2.527000	1.386000	-1.469000
H	2.218000	-2.568000	0.205000
O	-4.481000	0.030000	1.060000
C	-5.374000	-0.749000	1.412000
O	-5.409000	-1.936000	0.845000
C	-6.394000	-0.398000	2.440000
H	-7.392000	-0.481000	1.998000
H	-6.224000	0.615000	2.802000
H	-6.326000	-1.112000	3.267000
H	-6.147000	-2.488000	1.170000
C	3.958000	-0.491000	-0.104000
C	4.353000	-1.058000	1.120000
C	4.934000	0.161000	-0.865000
C	5.666000	-0.976000	1.559000

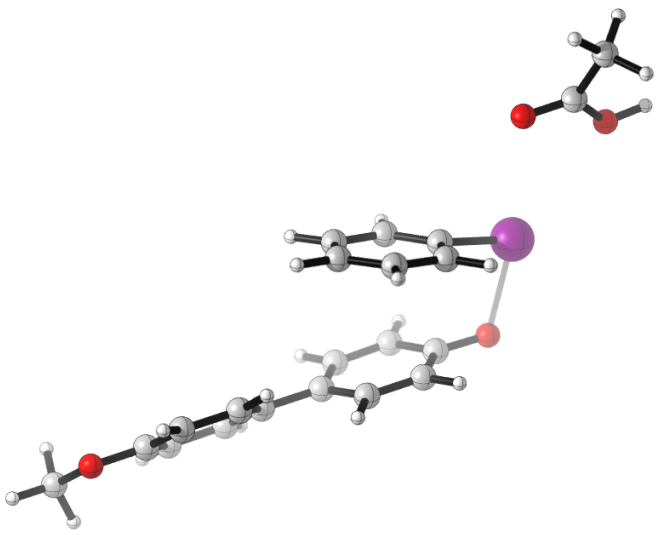


H	3.619000	-1.553000	1.750000
C	6.260000	0.255000	-0.437000
H	4.669000	0.594000	-1.826000
C	6.628000	-0.319000	0.782000
H	5.964000	-1.408000	2.511000
H	6.985000	0.763000	-1.063000
C	8.890000	0.403000	0.553000
H	9.806000	0.316000	1.137000
H	9.038000	-0.055000	-0.431000
H	8.627000	1.460000	0.436000
O	7.891000	-0.288000	1.293000

*** 0 imaginary frequencies ***
Sum of electronic and zero-point Energies= -1123.503027
Sum of electronic and thermal Energies= -1123.477906
Sum of electronic and thermal Enthalpies= -1123.476961
Sum of electronic and thermal Free Energies= -1123.561647

Transition state to form 4-(4-methoxyphenyl)phenoxenium cation

I	3.045000	-0.970000	-0.032000
C	1.666000	0.539000	-0.033000
C	-0.376000	2.403000	0.076000
C	1.575000	1.391000	1.081000
C	0.756000	0.619000	-1.096000
C	-0.276000	1.552000	-1.025000
C	0.556000	2.334000	1.118000
H	2.289000	1.310000	1.895000
H	0.855000	-0.035000	-1.957000
H	-1.000000	1.613000	-1.833000
H	0.475000	3.004000	1.968000
H	-1.179000	3.133000	0.120000
O	1.302000	-2.426000	0.711000
C	0.120000	-1.920000	0.573000
C	-2.491000	-0.880000	0.309000
C	-0.659000	-2.196000	-0.595000
C	-0.430000	-1.073000	1.582000
C	-1.704000	-0.573000	1.448000
C	-1.941000	-1.718000	-0.699000
H	-0.212000	-2.794000	-1.385000
H	0.171000	-0.861000	2.462000
H	-2.120000	0.042000	2.240000
H	-2.520000	-1.935000	-1.591000
C	-3.844000	-0.338000	0.169000
C	-4.829000	-1.026000	-0.559000
C	-4.202000	0.889000	0.768000
C	-6.124000	-0.533000	-0.681000
H	-4.601000	-1.986000	-1.013000
C	-5.479000	1.399000	0.641000
H	-3.460000	1.463000	1.315000
C	-6.453000	0.688000	-0.080000

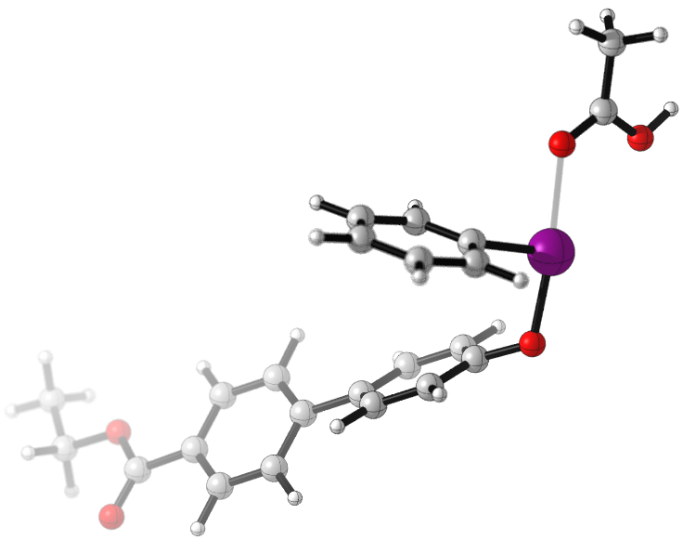


H	-6.861000	-1.105000	-1.232000
H	-5.748000	2.352000	1.088000
C	-8.707000	0.568000	-0.843000
H	-8.894000	-0.413000	-0.396000
H	-9.597000	1.190000	-0.748000
H	-8.446000	0.457000	-1.901000
O	-7.677000	1.257000	-0.138000
O	4.848000	1.632000	-0.718000
C	6.005000	1.328000	-0.495000
O	6.323000	0.026000	-0.453000
C	7.118000	2.305000	-0.264000
H	7.577000	2.119000	0.712000
H	6.730000	3.323000	-0.305000
H	7.887000	2.170000	-1.031000
H	7.269000	-0.116000	-0.266000

*** 1 imaginary frequency (–220.3853) ***
Sum of electronic and zero-point Energies= -1123.488454
Sum of electronic and thermal Energies= -1123.463002
Sum of electronic and thermal Enthalpies= -1123.462058
Sum of electronic and thermal Free Energies= -1123.549361

Protonated iodane from 4-(4-ethoxycarbonylphenyl)phenol

I	-3.755000	-0.305000	-0.703000
C	-3.057000	1.029000	0.735000
C	-1.980000	2.827000	2.521000
C	-3.478000	2.356000	0.679000
C	-2.112000	0.574000	1.653000
C	-1.575000	1.492000	2.555000
C	-2.926000	3.258000	1.589000
H	-4.210000	2.682000	-0.053000
H	-1.797000	-0.466000	1.663000
H	-0.837000	1.161000	3.279000
H	-3.239000	4.298000	1.567000
H	-1.555000	3.537000	3.224000
O	-2.415000	0.390000	-2.033000
C	-1.081000	0.317000	-1.692000
C	1.651000	0.242000	-1.089000
C	-0.405000	-0.903000	-1.704000
C	-0.412000	1.497000	-1.366000
C	0.949000	1.455000	-1.076000
C	0.953000	-0.935000	-1.403000
H	-0.942000	-1.813000	-1.960000
H	-0.962000	2.434000	-1.342000
H	1.462000	2.376000	-0.811000
H	1.481000	-1.884000	-1.441000
O	-5.264000	-0.805000	1.056000
C	-6.078000	-1.732000	0.957000
O	-6.080000	-2.432000	-0.157000
C	-7.040000	-2.077000	2.040000

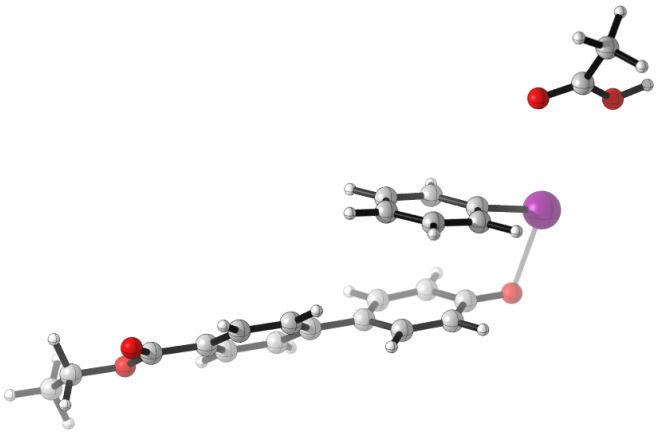


H	-8.060000	-1.978000	1.655000
H	-6.892000	-1.416000	2.893000
H	-6.887000	-3.120000	2.336000
H	-6.750000	-3.143000	-0.151000
C	3.103000	0.204000	-0.786000
C	3.661000	-0.867000	-0.070000
C	3.949000	1.238000	-1.215000
C	5.022000	-0.905000	0.210000
H	3.022000	-1.668000	0.289000
C	5.309000	1.204000	-0.938000
H	3.542000	2.066000	-1.790000
C	5.854000	0.133000	-0.224000
H	5.433000	-1.737000	0.771000
H	5.956000	2.006000	-1.282000
C	7.316000	0.135000	0.052000
O	8.075000	1.017000	-0.316000
O	7.722000	-0.925000	0.746000
C	9.130000	-0.996000	1.065000
H	9.398000	-0.103000	1.637000
H	9.695000	-0.998000	0.128000
C	9.346000	-2.261000	1.859000
H	9.061000	-3.143000	1.277000
H	10.406000	-2.347000	2.118000
H	8.766000	-2.246000	2.787000

*** 0 imaginary frequencies ***
Sum of electronic and zero-point Energies= -1276.084850
Sum of electronic and thermal Energies= -1276.056297
Sum of electronic and thermal Enthalpies= -1276.055353
Sum of electronic and thermal Free Energies= -1276.150854

Transition state to form 4-(4-ethoxycarbonylphenyl)phenoxenium cation

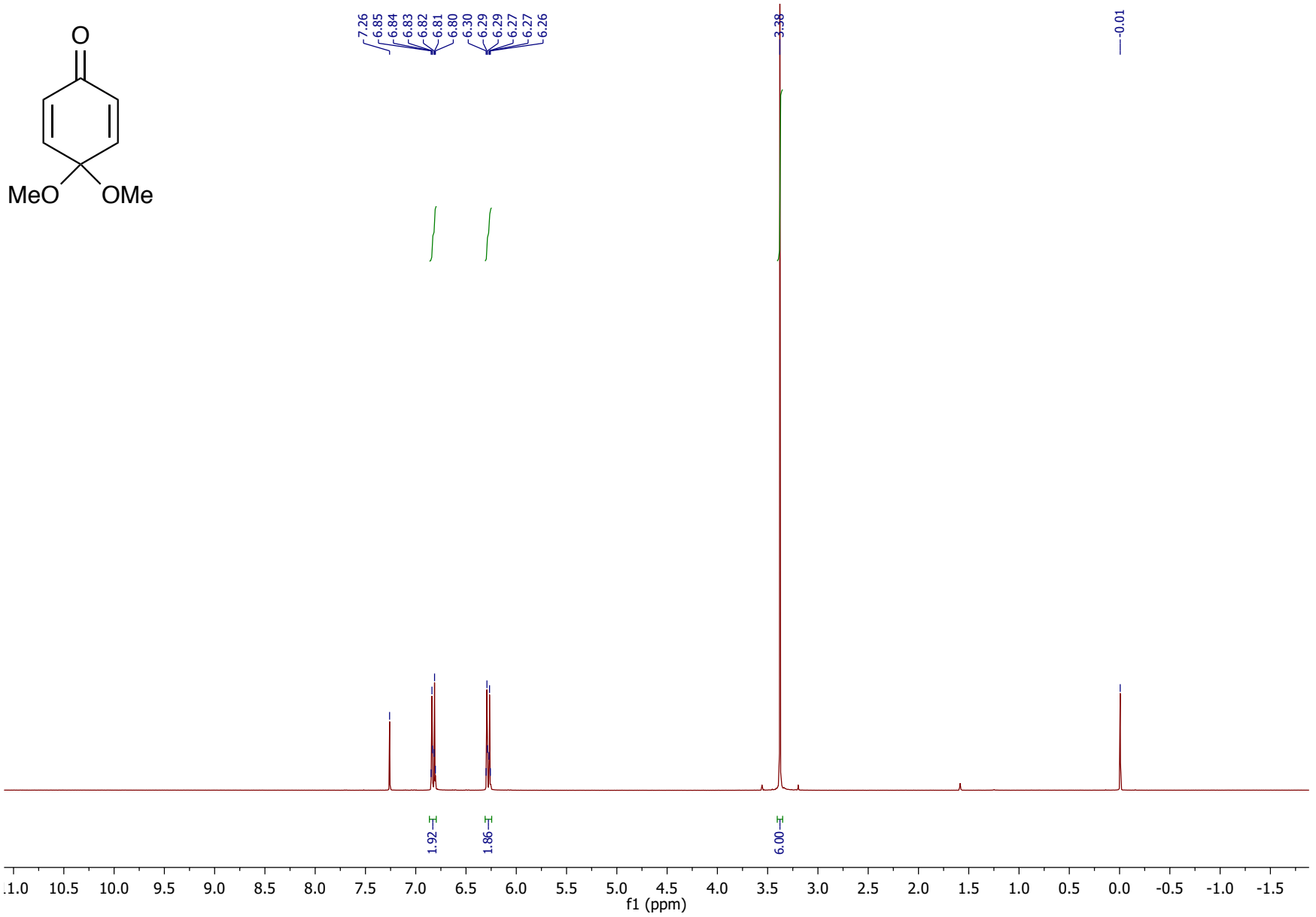
I	3.983000	-1.061000	-0.129000
C	2.496000	0.331000	0.029000
C	0.363000	2.073000	0.316000
C	2.395000	1.108000	1.198000
C	1.548000	0.431000	-1.002000
C	0.471000	1.298000	-0.840000
C	1.330000	1.989000	1.325000
H	3.140000	1.017000	1.983000
H	1.658000	-0.157000	-1.909000
H	-0.280000	1.373000	-1.622000
H	1.241000	2.599000	2.219000
H	-0.474000	2.756000	0.429000
O	2.285000	-2.712000	0.584000
C	1.104000	-2.223000	0.529000
C	-1.514000	-1.189000	0.429000
C	0.277000	-2.433000	-0.629000
C	0.582000	-1.447000	1.618000

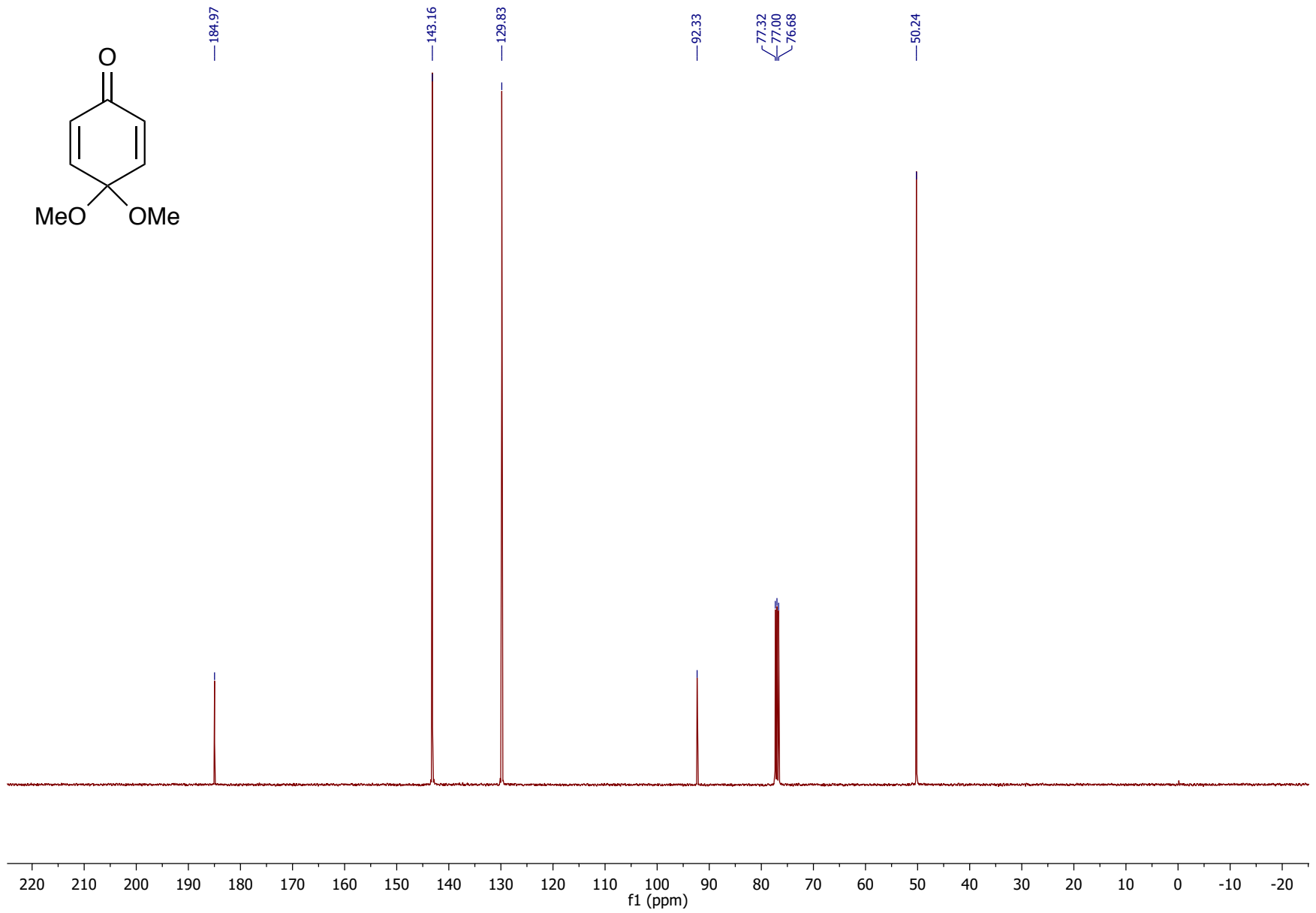


C	-0.697000	-0.949000	1.561000
C	-1.010000	-1.962000	-0.651000
H	0.700000	-2.978000	-1.469000
H	1.216000	-1.291000	2.487000
H	-1.092000	-0.384000	2.399000
H	-1.628000	-2.126000	-1.528000
C	-2.873000	-0.628000	0.362000
C	-3.893000	-1.308000	-0.325000
C	-3.168000	0.600000	0.980000
C	-5.176000	-0.779000	-0.388000
H	-3.693000	-2.270000	-0.787000
C	-4.446000	1.136000	0.904000
H	-2.389000	1.153000	1.496000
C	-5.454000	0.448000	0.221000
H	-5.958000	-1.322000	-0.909000
H	-4.666000	2.091000	1.370000
C	-6.812000	1.063000	0.160000
O	-7.090000	2.136000	0.668000
O	-7.691000	0.322000	-0.507000
C	-9.033000	0.849000	-0.624000
H	-9.430000	1.001000	0.384000
H	-8.975000	1.816000	-1.132000
C	-9.842000	-0.158000	-1.406000
H	-9.880000	-1.119000	-0.884000
H	-10.865000	0.214000	-1.519000
H	-9.418000	-0.311000	-2.403000
O	5.182000	2.166000	-0.787000
C	6.386000	2.055000	-0.660000
O	6.935000	0.840000	-0.815000
C	7.321000	3.183000	-0.343000
H	7.877000	2.958000	0.573000
H	6.757000	4.107000	-0.219000
H	8.045000	3.296000	-1.157000
H	7.902000	0.862000	-0.692000

*** 1 imaginary frequency (-168.0200) ***
Sum of electronic and zero-point Energies= -1276.065452
Sum of electronic and thermal Energies= -1276.036863
Sum of electronic and thermal Enthalpies= -1276.035919
Sum of electronic and thermal Free Energies= -1276.130229

6.0 Copies of NMR spectra

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MeO
OMe
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77.00
76.68
50.24
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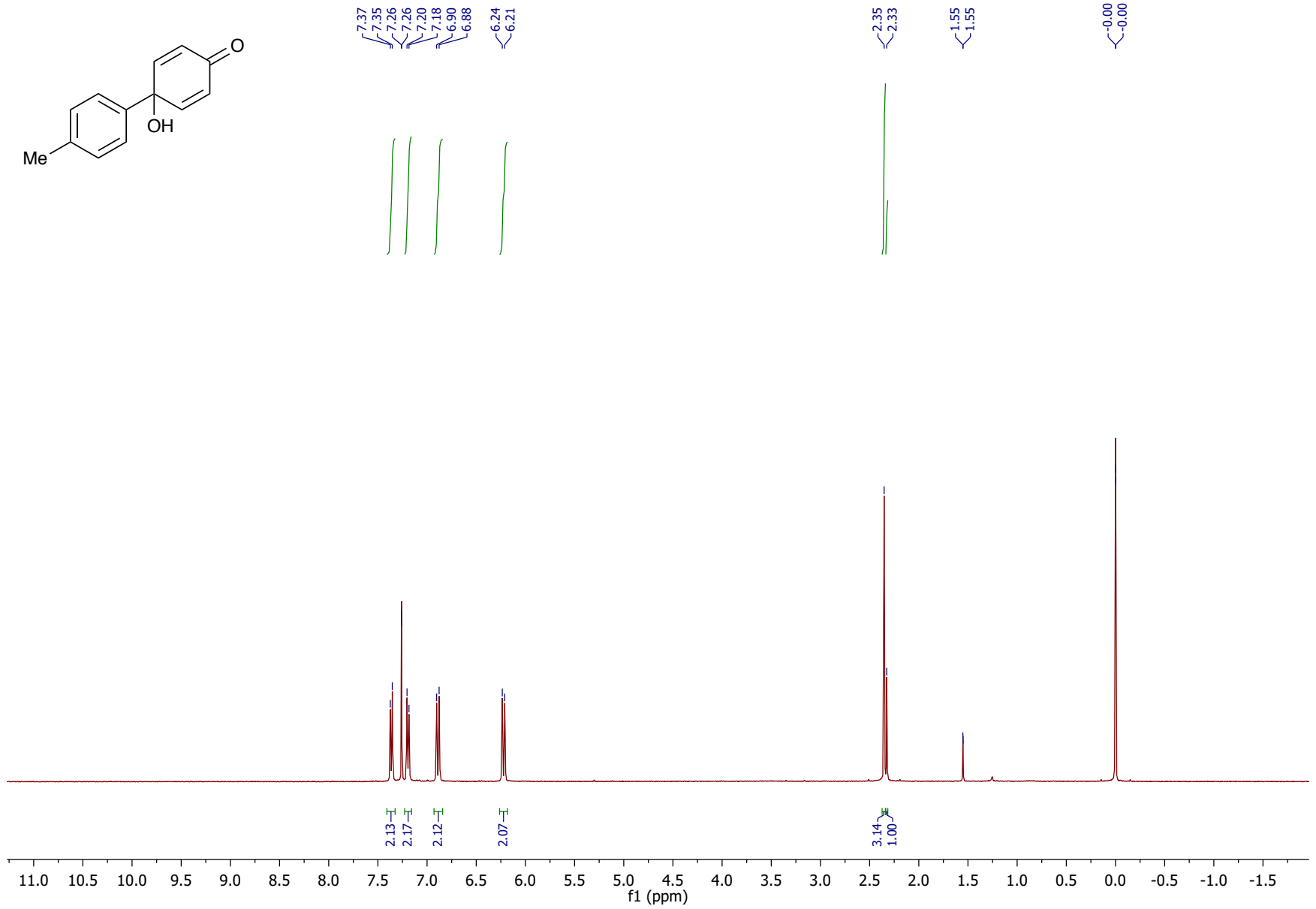
f1 (ppm)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OH
Me
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7.26
7.26
7.20
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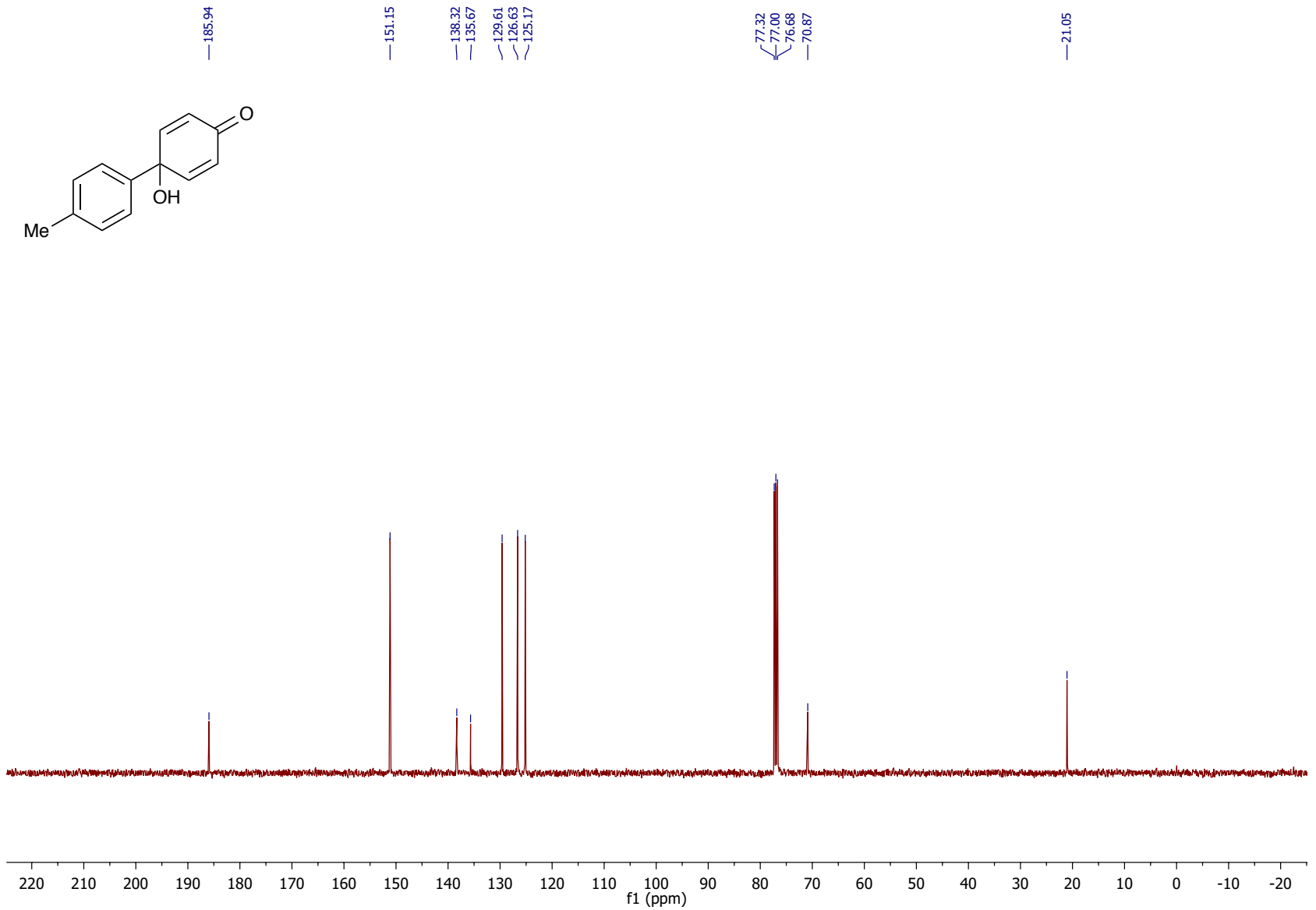
6.88
6.24
6.21
2.35
2.33
1.55
1.55
-0.00
-0.00
2.13
2.17
2.12
2.07
3.14
1.00
11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0 -1.5
f1 (ppm)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77.00
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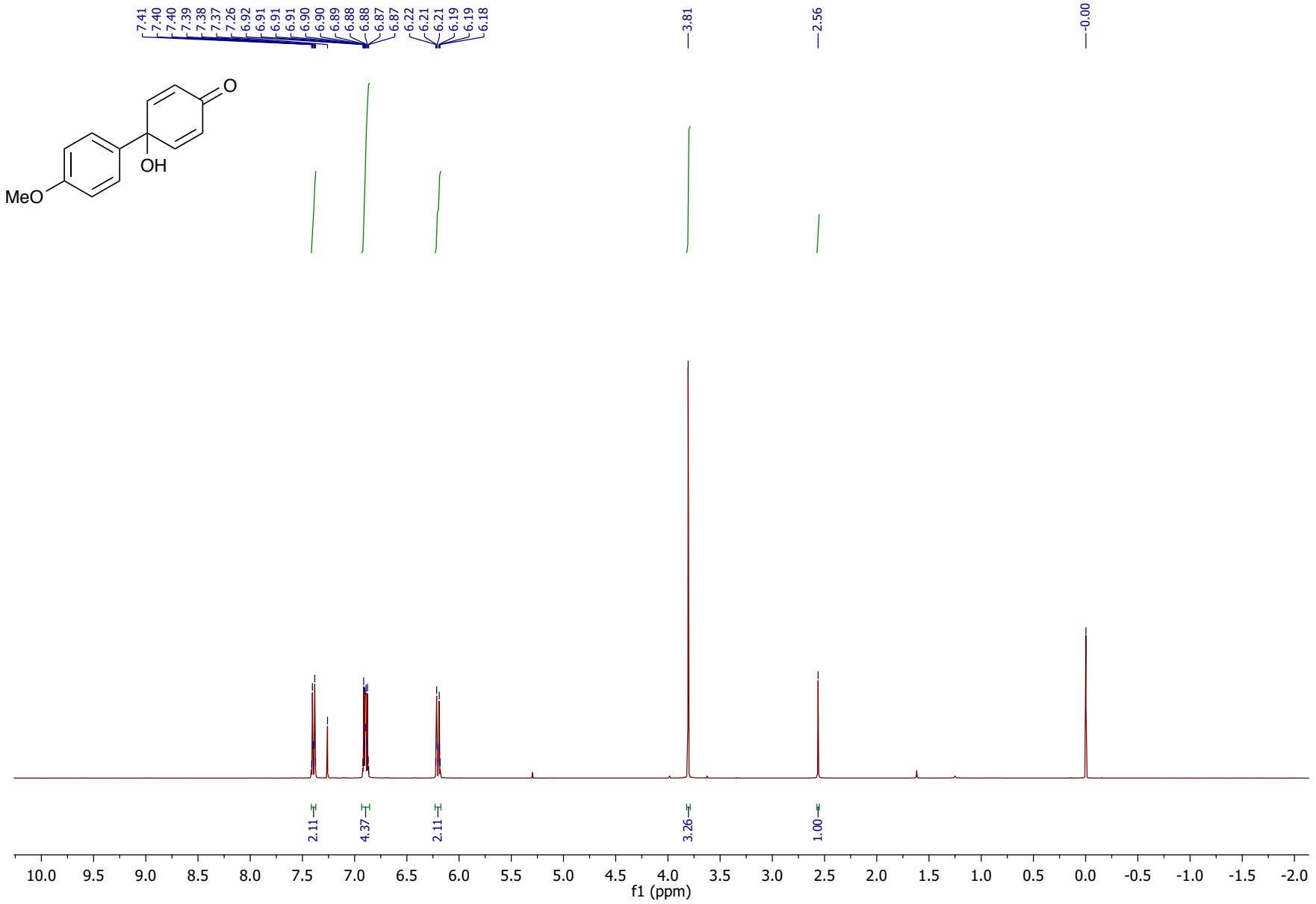
O
OH
Me
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20
f1 (ppm)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6.91
6.91
6.90
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6.89
6.88
6.88
6.87
6.87
6.22
6.21
6.21
6.19
6.19
6.18
3.81
2.56
0.00
O
OH
MeO
2.11
4.37
2.11
3.26
1.00
10.0
9.5
9.0
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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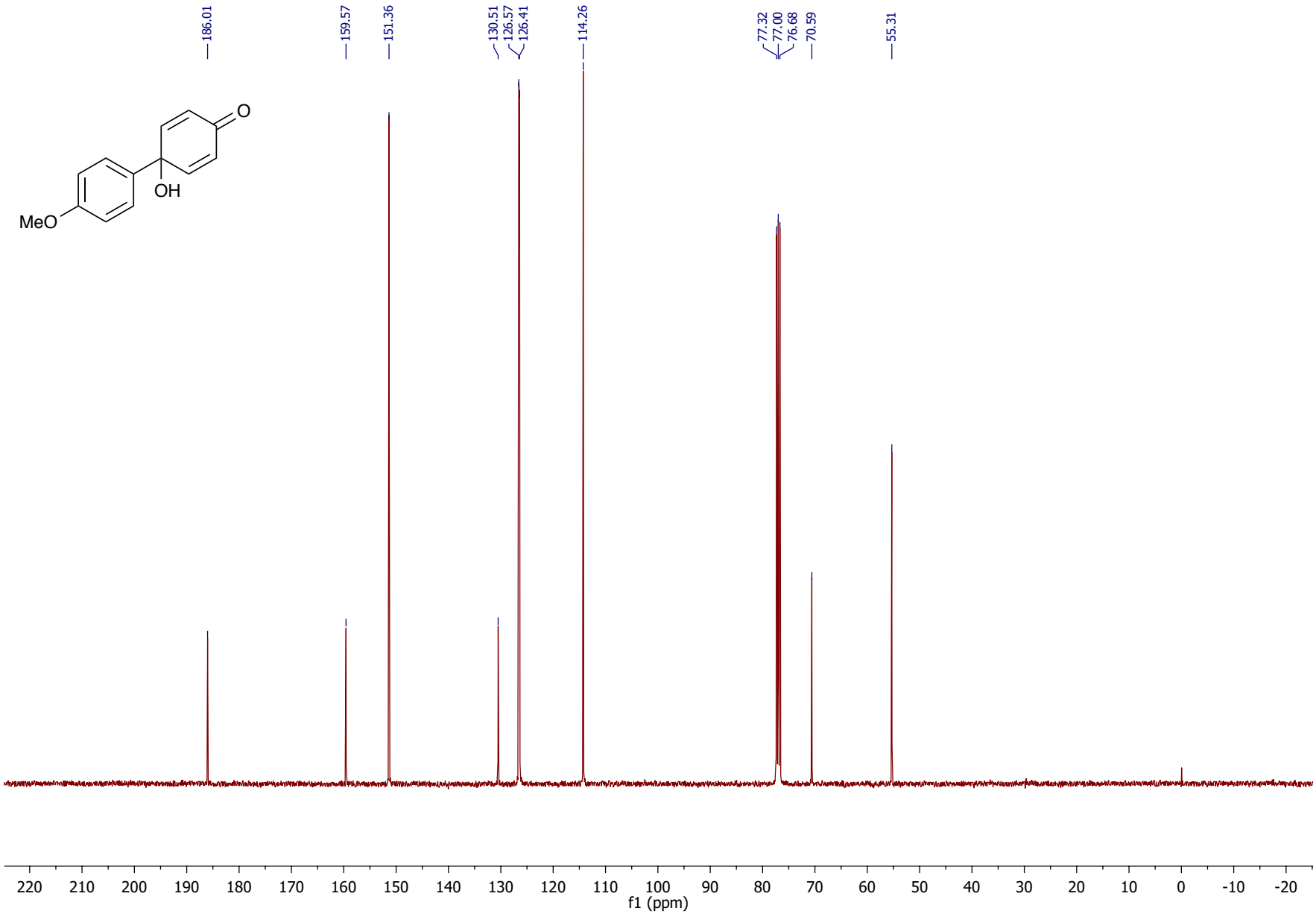
f1 (ppm)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77.32
77.00
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55.31
O
OH
MeO
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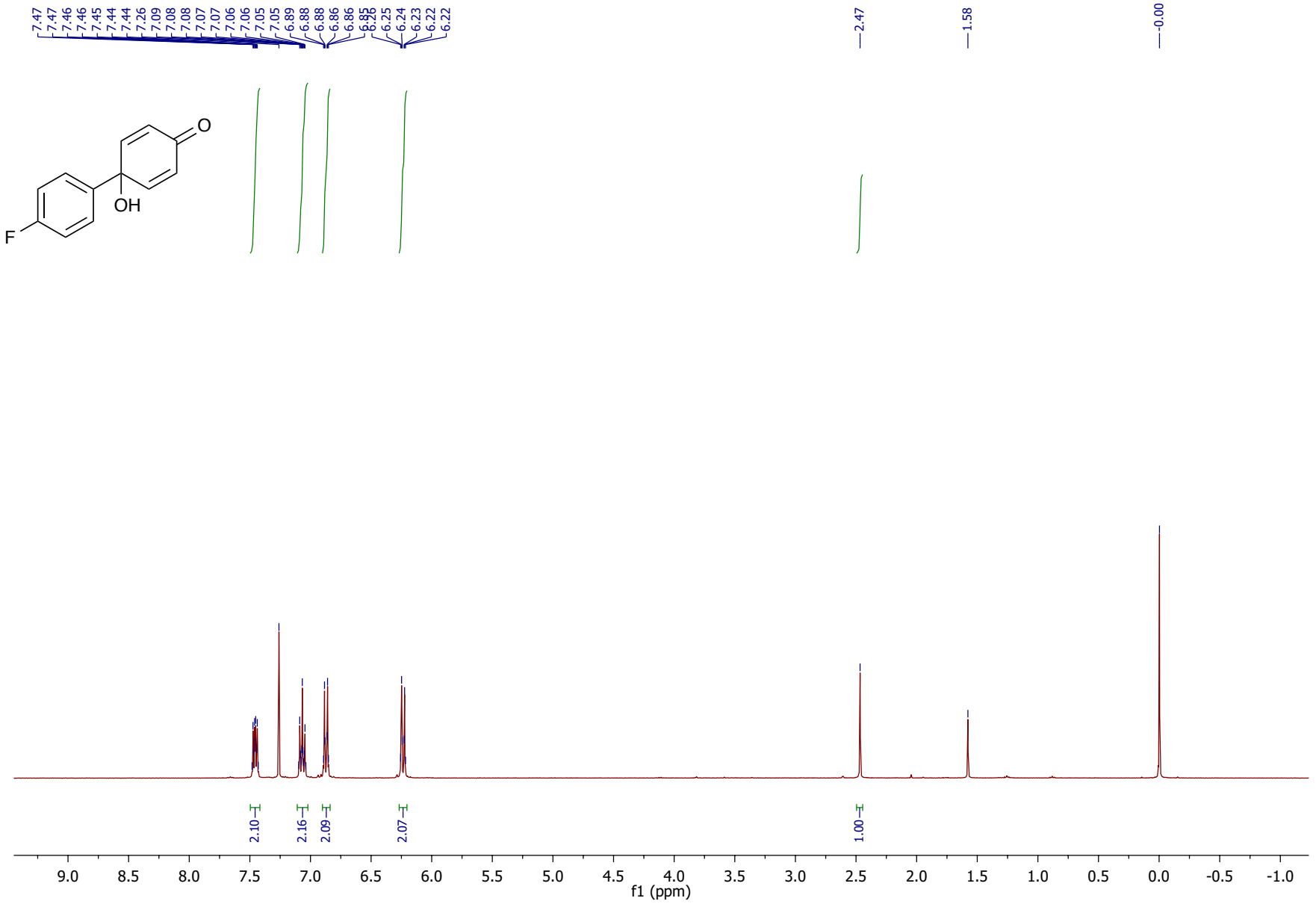
f1 (ppm)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7.44
7.44
7.26
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7.08
7.08
7.07
7.07
7.06
7.06
7.05
7.05
6.89
6.88
6.88
6.86
6.86
6.25
6.24
6.23
6.22
6.22
2.47
1.58
-0.00
O
OH
F
2.10
2.16
2.09
2.07
1.00
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
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2.0
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1.0
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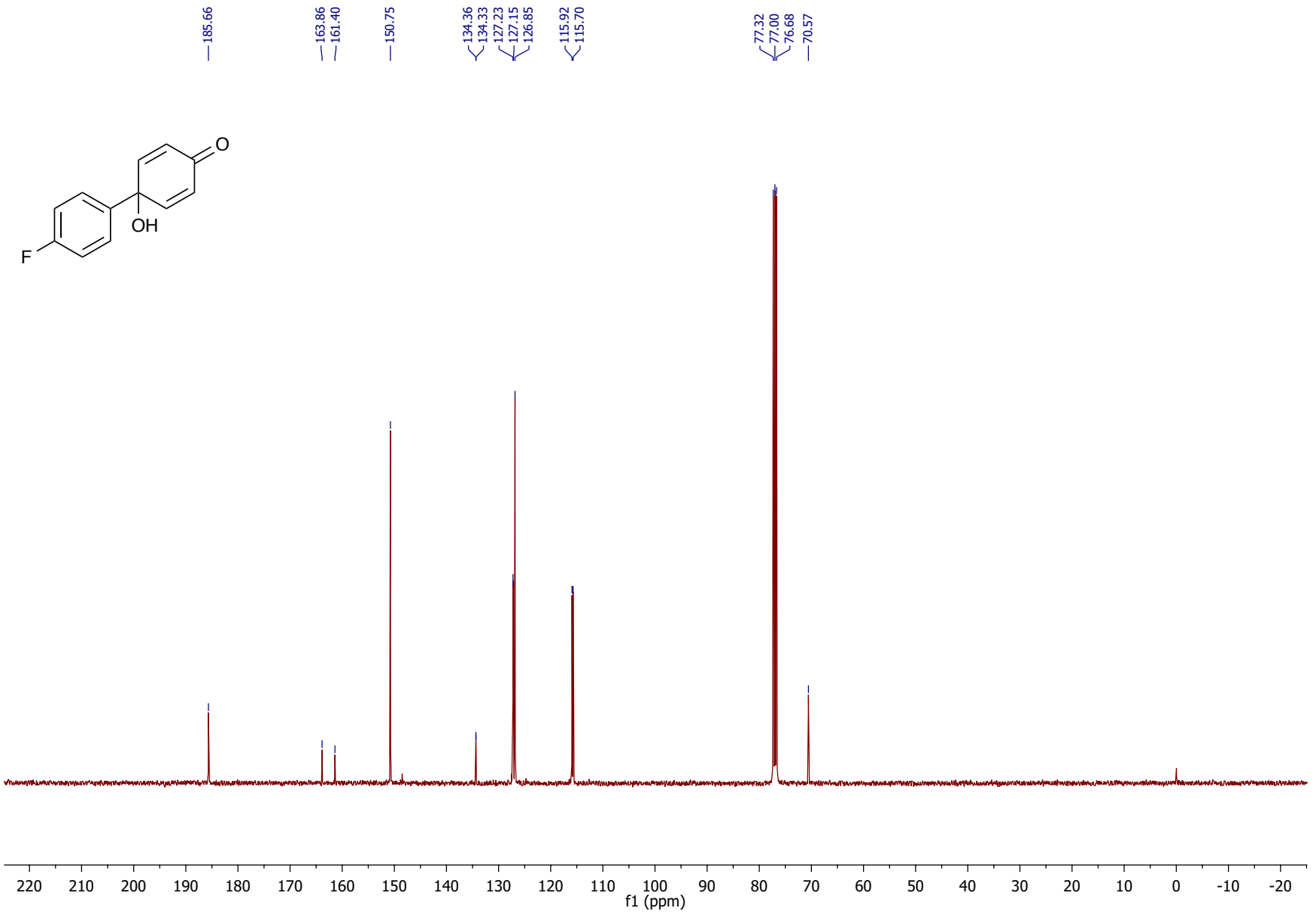
f1 (ppm)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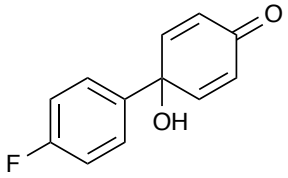
150.75
134.36
134.33
127.23
127.15
126.85
115.92
115.70
77.32
77.00
76.68
70.57
O
OH
F
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20
f1 (ppm)


O
OH
F

-113.39
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-113.28
-113.32
-113.36
-113.40
-113.44
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-113.56
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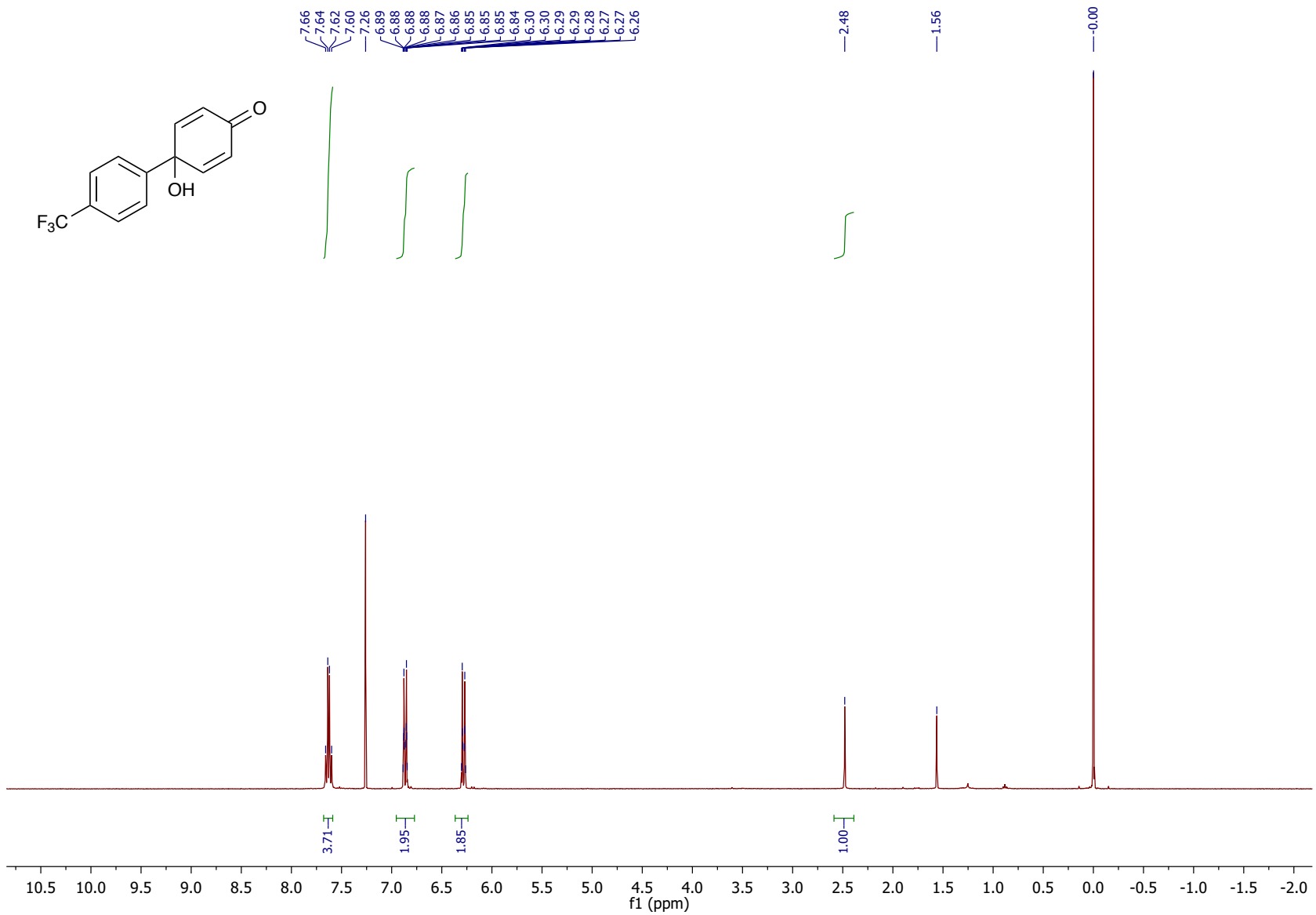
-113.72
-113.76
-113.80
f1 (ppm)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6.85
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6.85
6.84
6.30
6.30
6.29
6.29
6.28
6.27
6.27
6.26
2.48
1.56
-0.00
O
OH
F3C
3.71
1.95
1.85
1.00
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0 -1.5 -2.0
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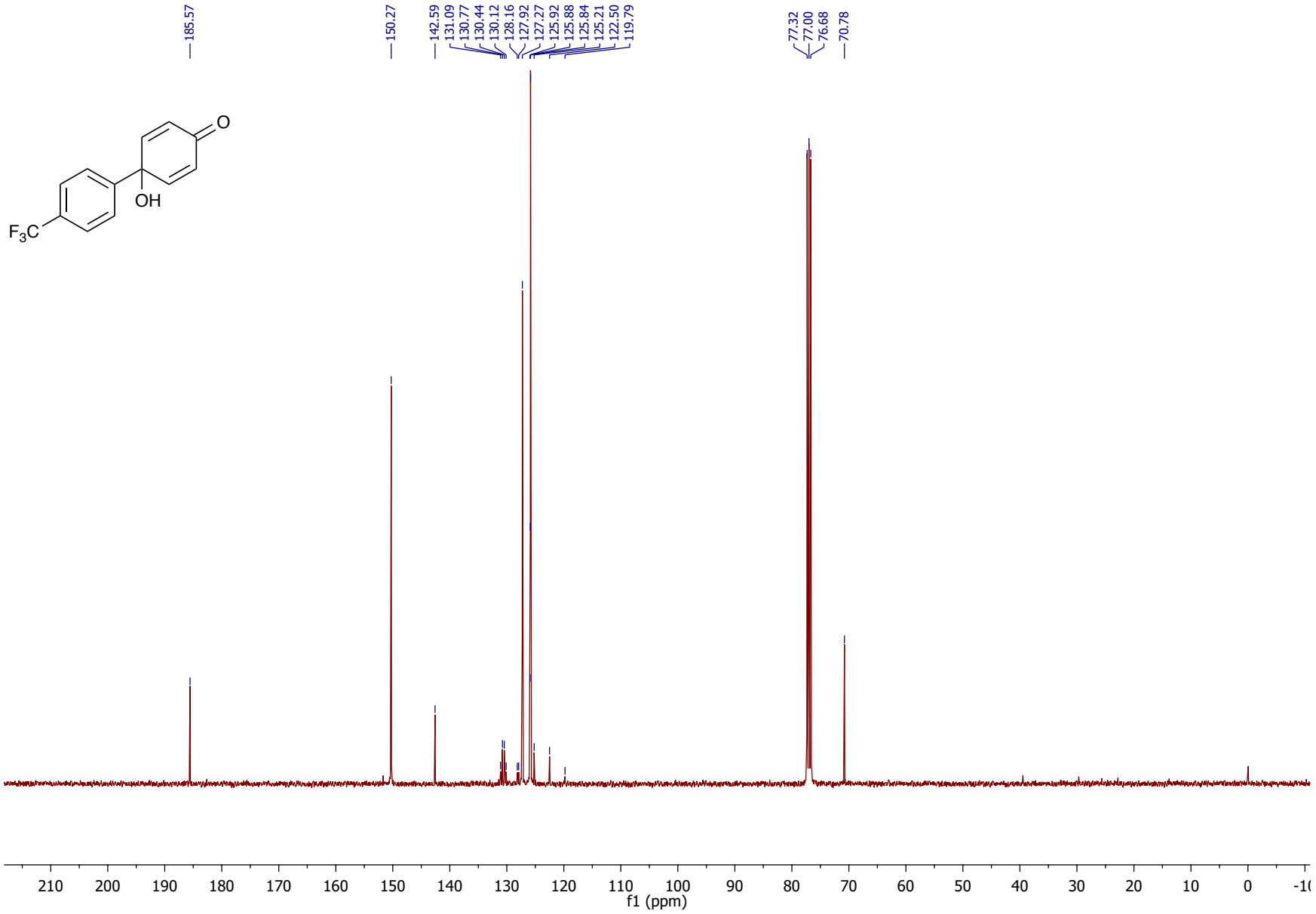
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130.12
128.16
127.92
127.27
125.92
125.88
125.84
125.21
122.50
119.79
77.32
77.00
76.68
70.78
O
OH
F3C
210
200
190
180
170
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150
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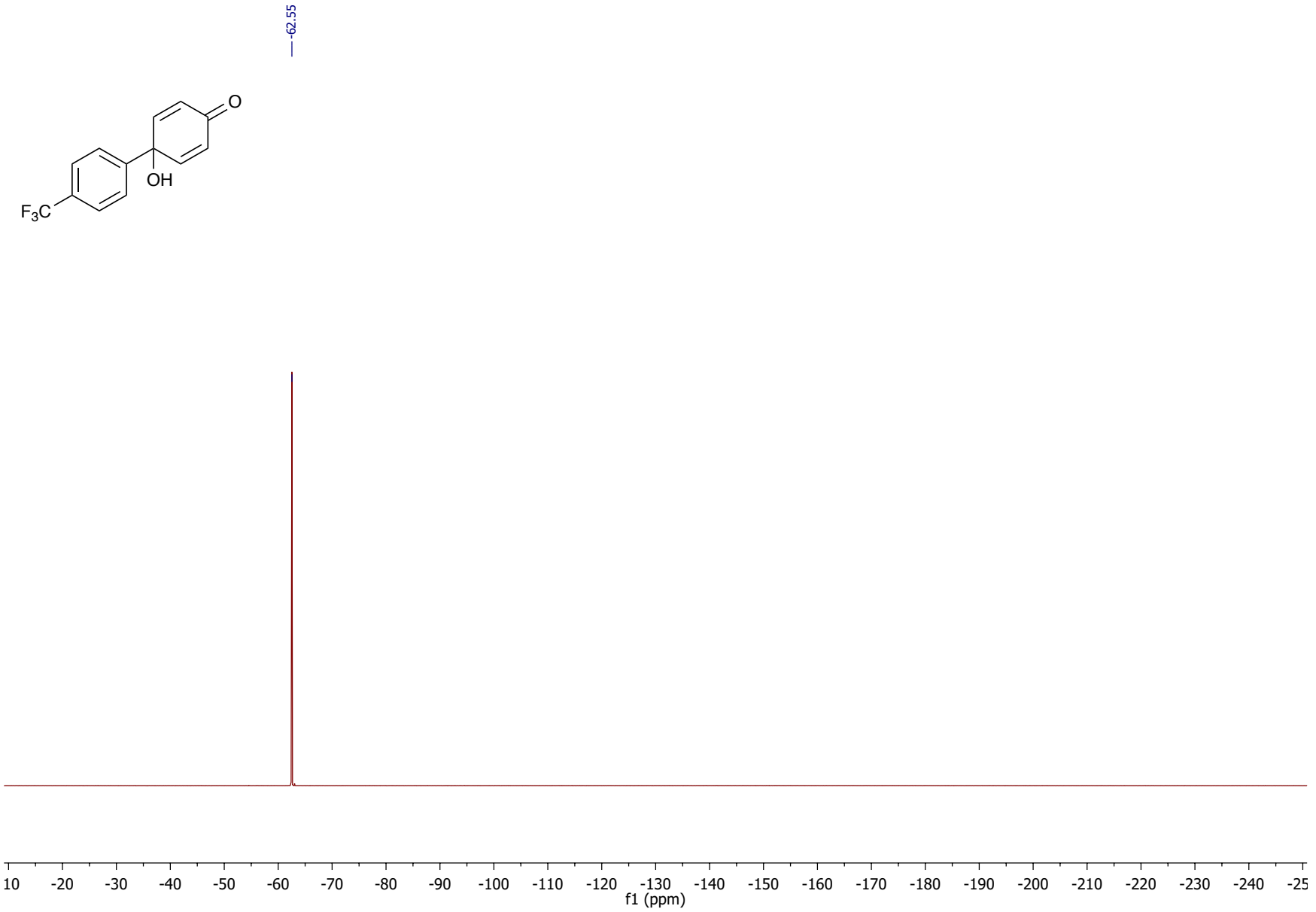
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)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O
OH
F3C
10
-20
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-40
-50
-60
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-80
-90
-100
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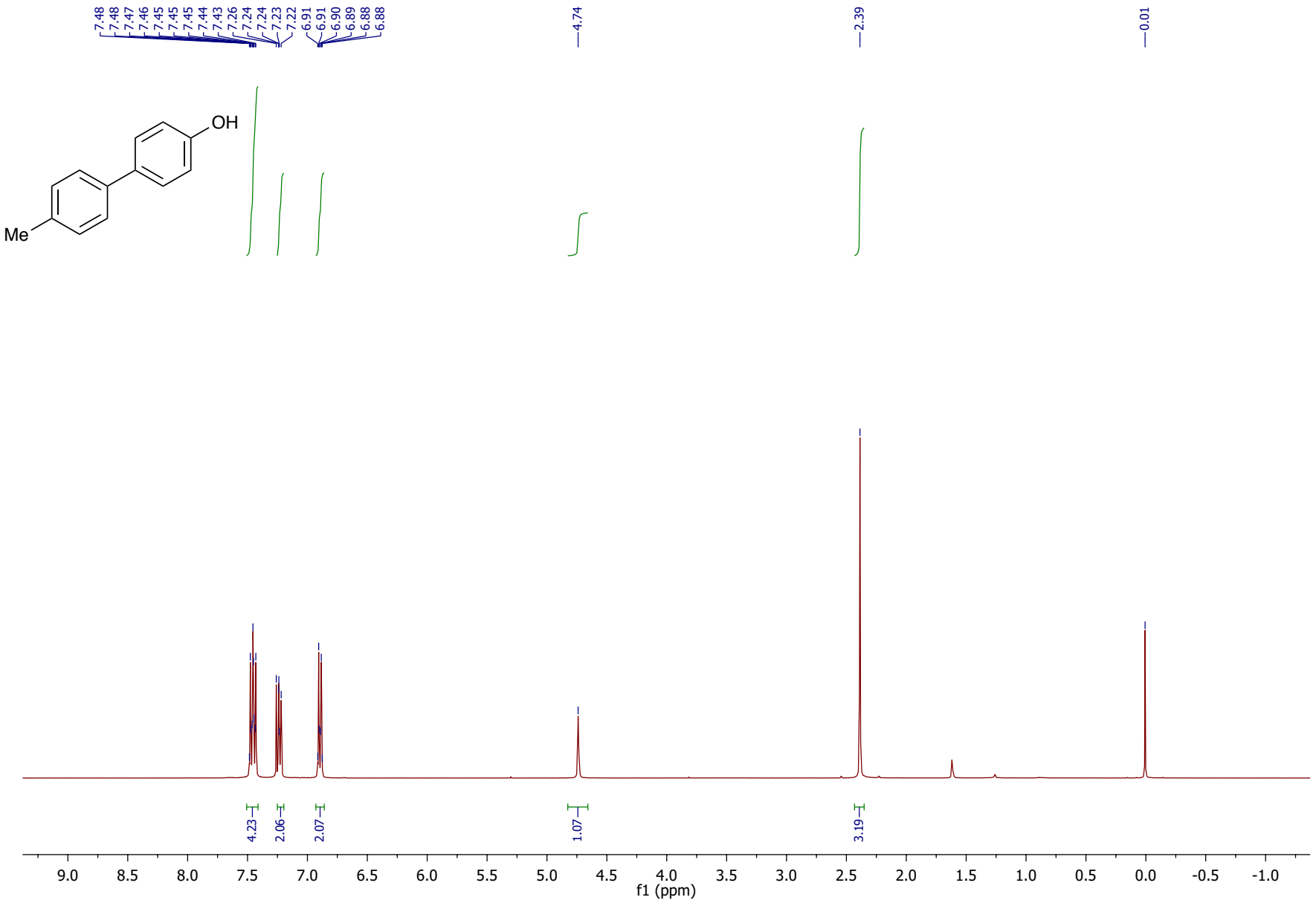
f1 (ppm)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6.91
6.90
6.89
6.88
6.88
4.74
2.39
0.01
OH
Me
4.23
2.06
2.07
1.07
3.19
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
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2.0
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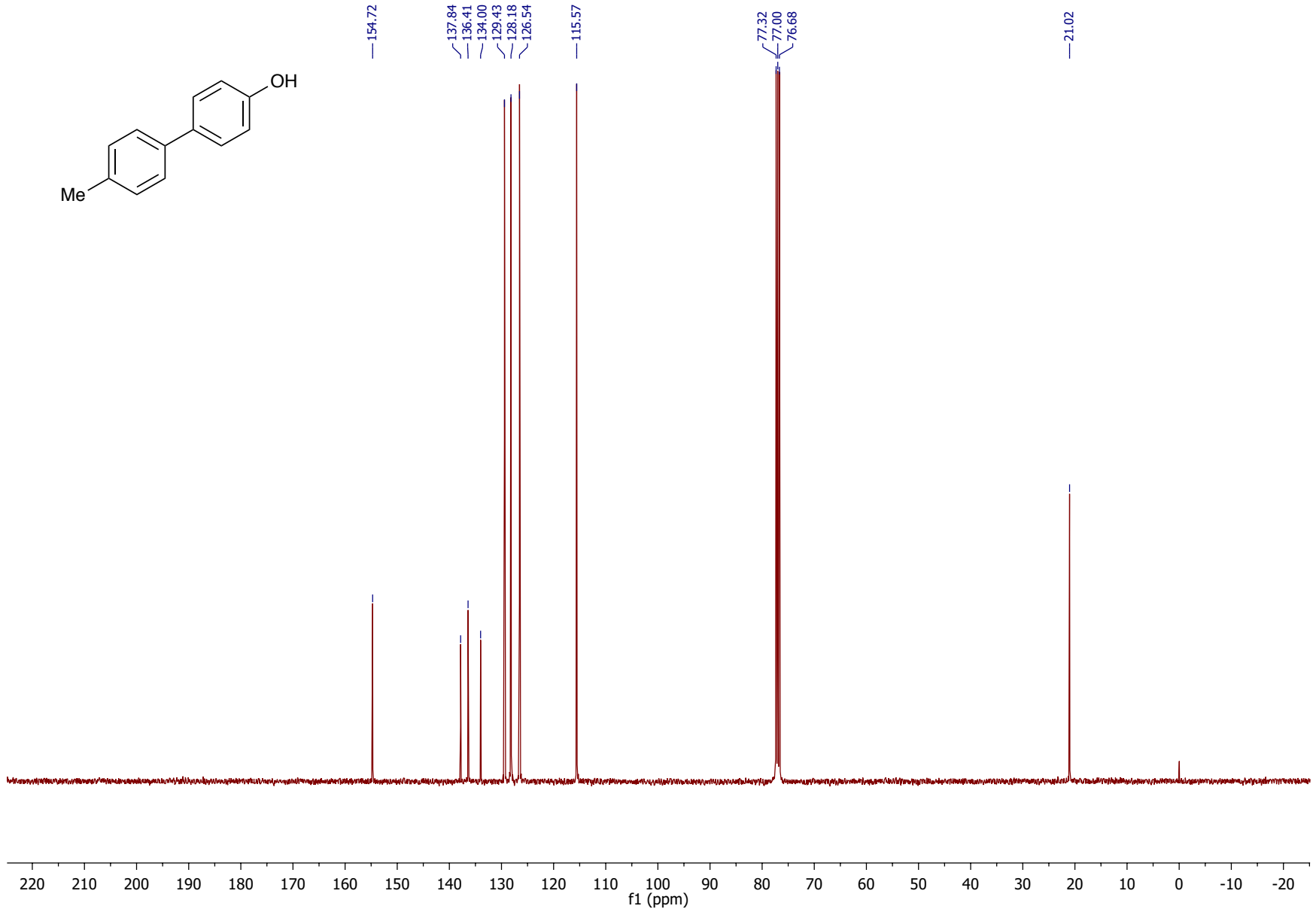
f1 (ppm)


OH
Me
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128.18
126.54
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77.00
76.68
21.02
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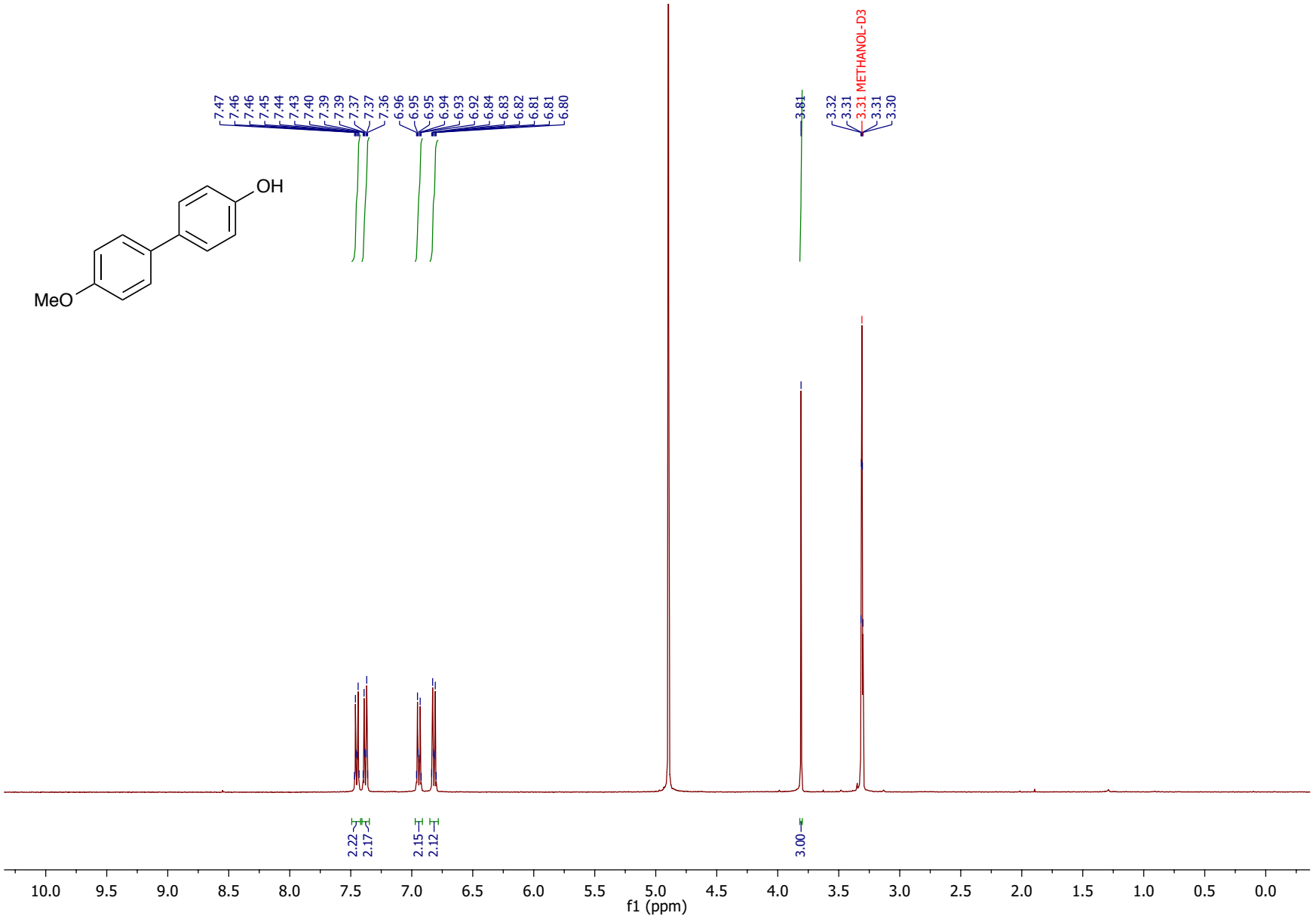
f1 (ppm)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6.95
6.94
6.93
6.92
6.84
6.83
6.82
6.81
6.81
6.80
3.81
3.32
3.31
3.31 METHANOL-D3
3.31
3.30
OH
MeO
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2.17
2.15
2.12
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9.0
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8.0
7.5
7.0
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5.5
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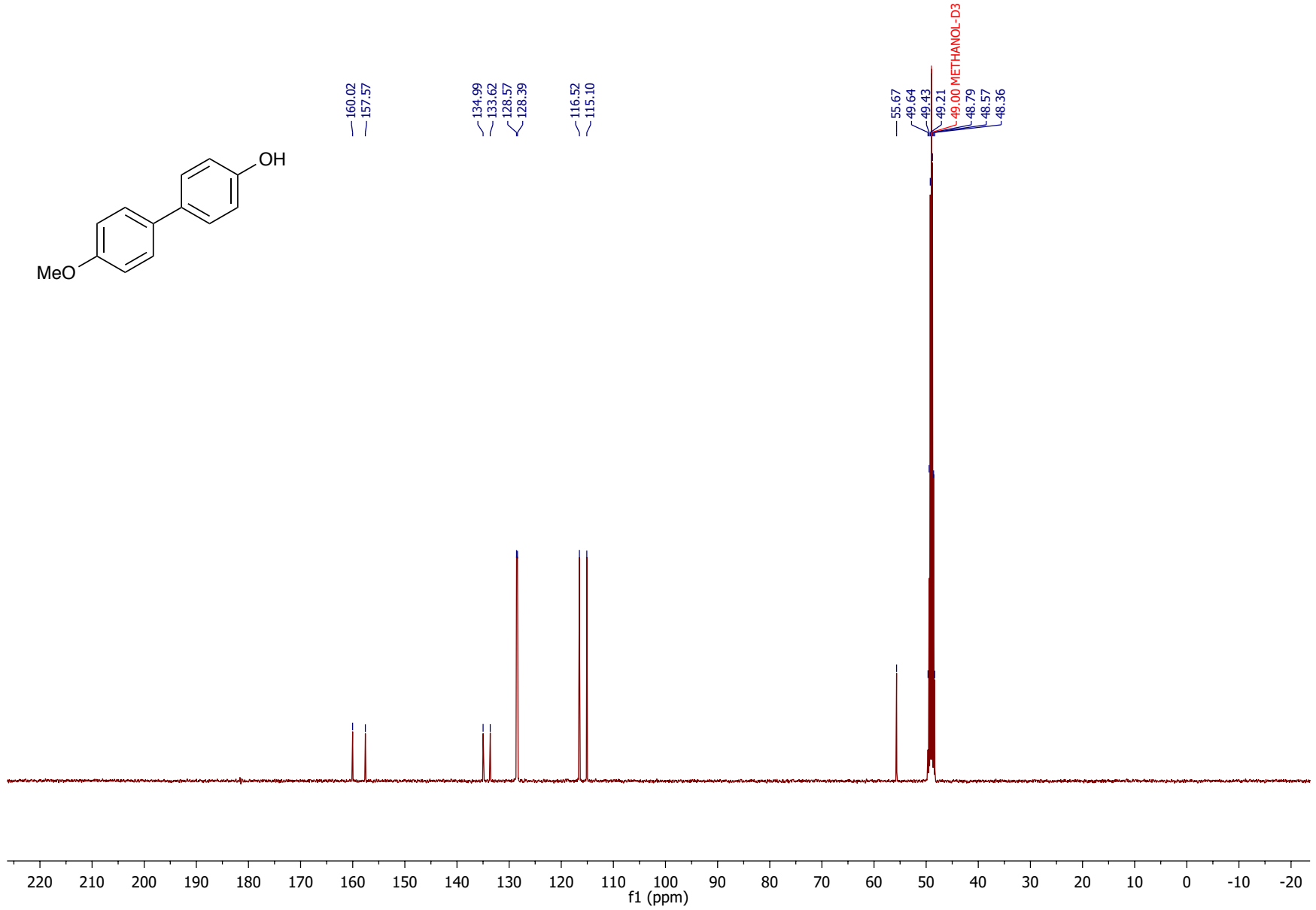
f1 (ppm)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MeO
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49.21
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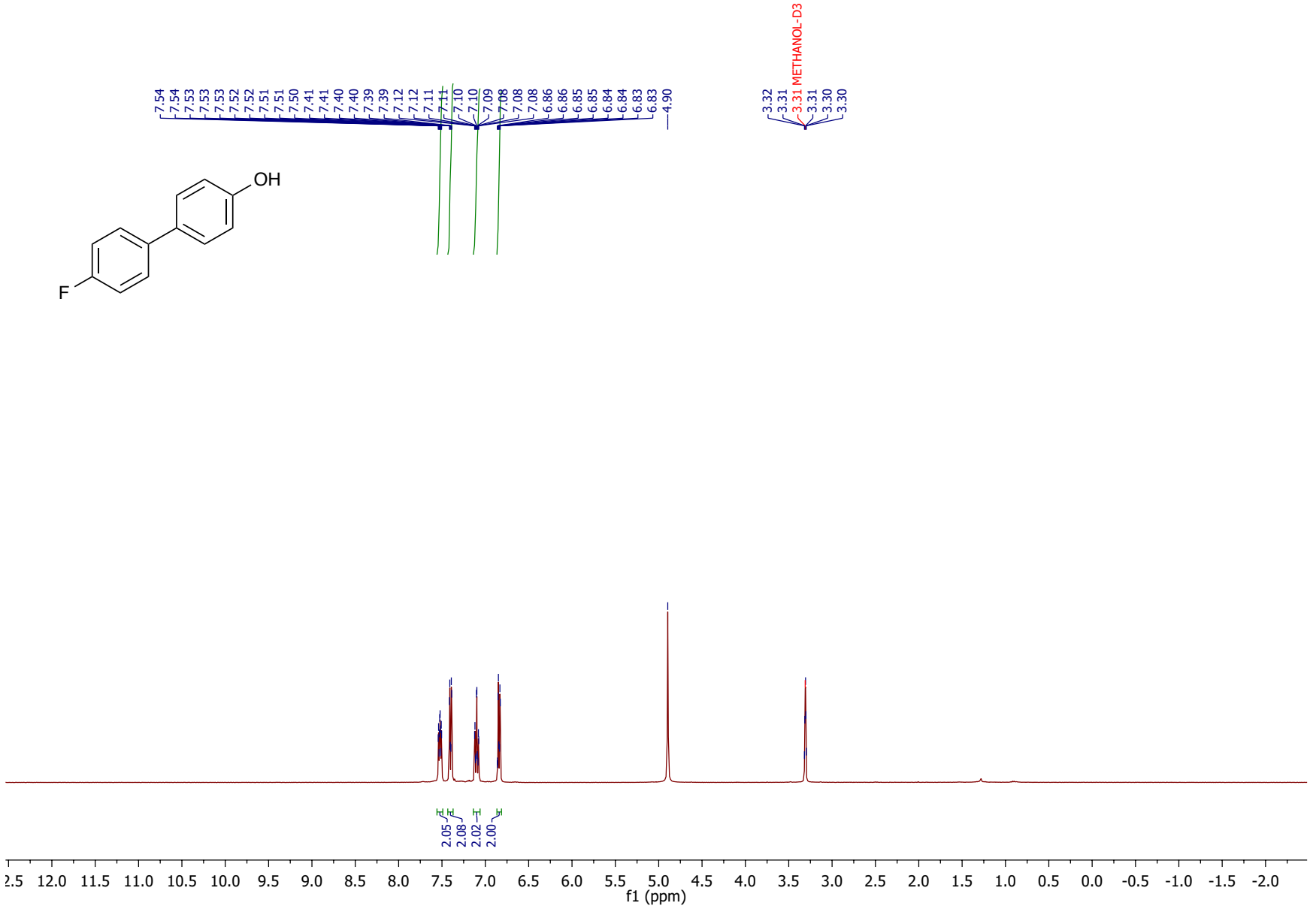
f1 (ppm)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3.31 METHANOL-D3
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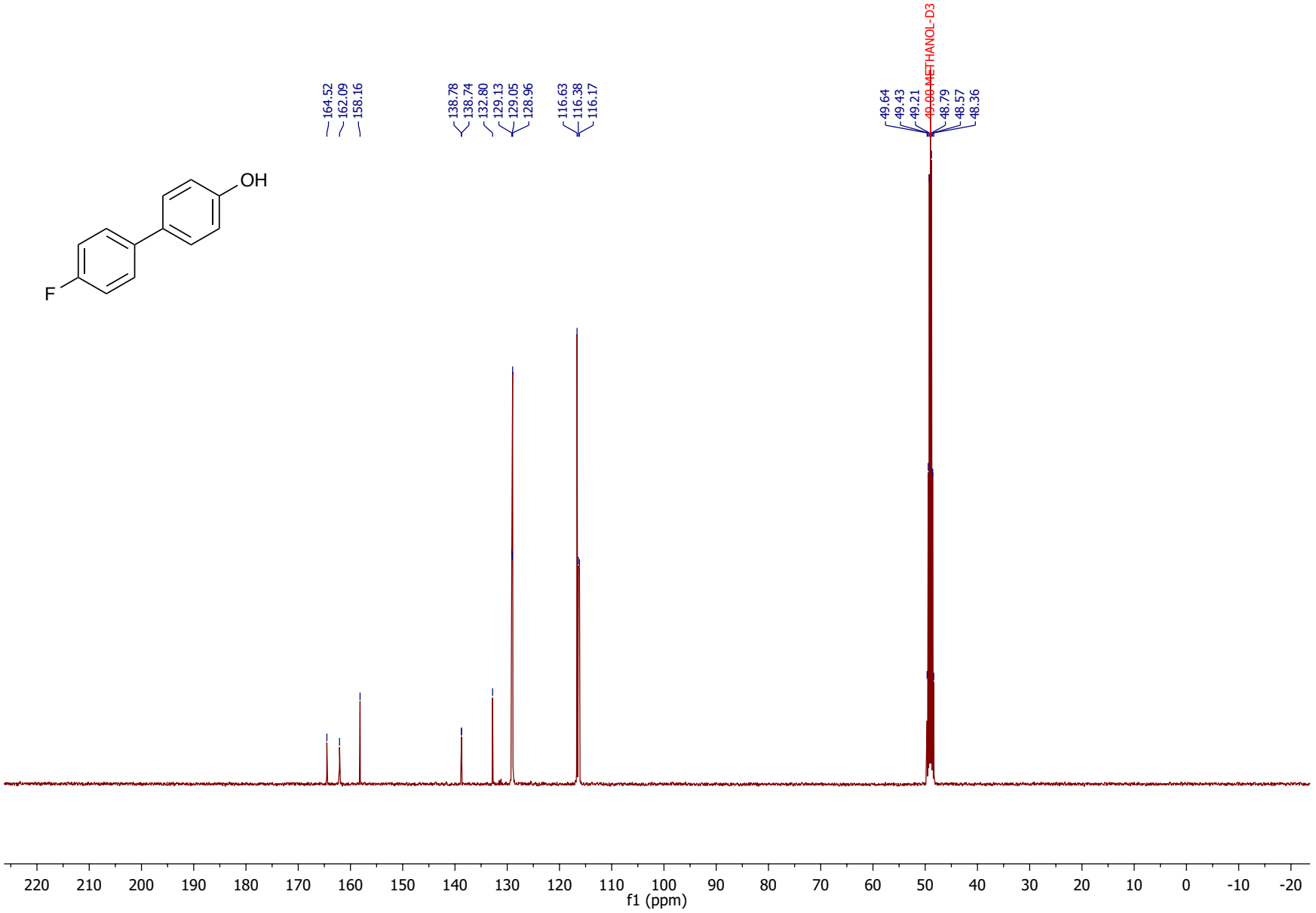
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129.05
128.96
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116.38
116.17
49.64
49.43
49.21
49.00 METHANOL-D3
48.79
48.57
48.36
OH
F
220
210
200
190
180
170
160
150
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130
120
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100
90
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70
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40
30
20
10
0
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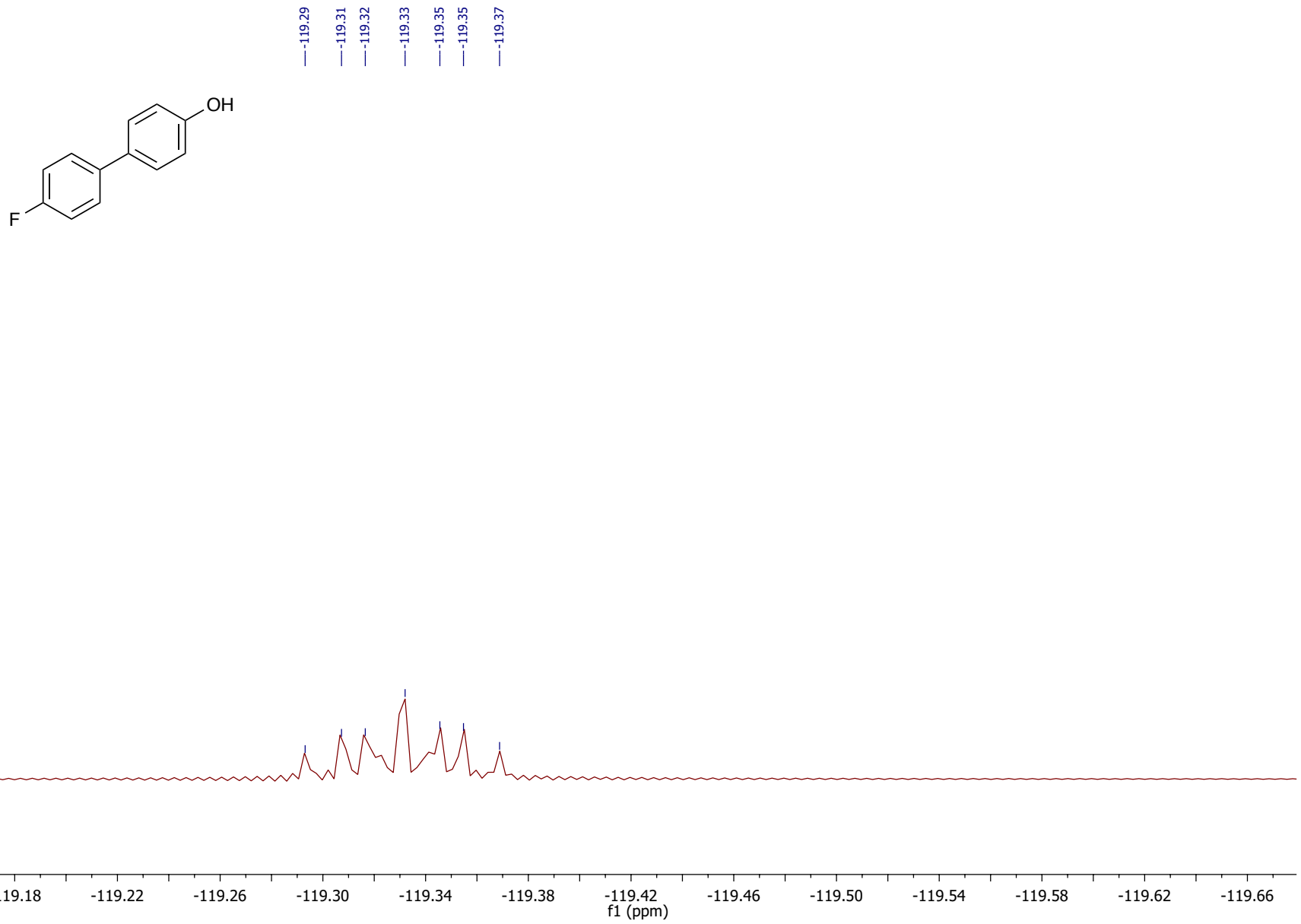
-20
f1 (ppm)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-119.37
OH
F
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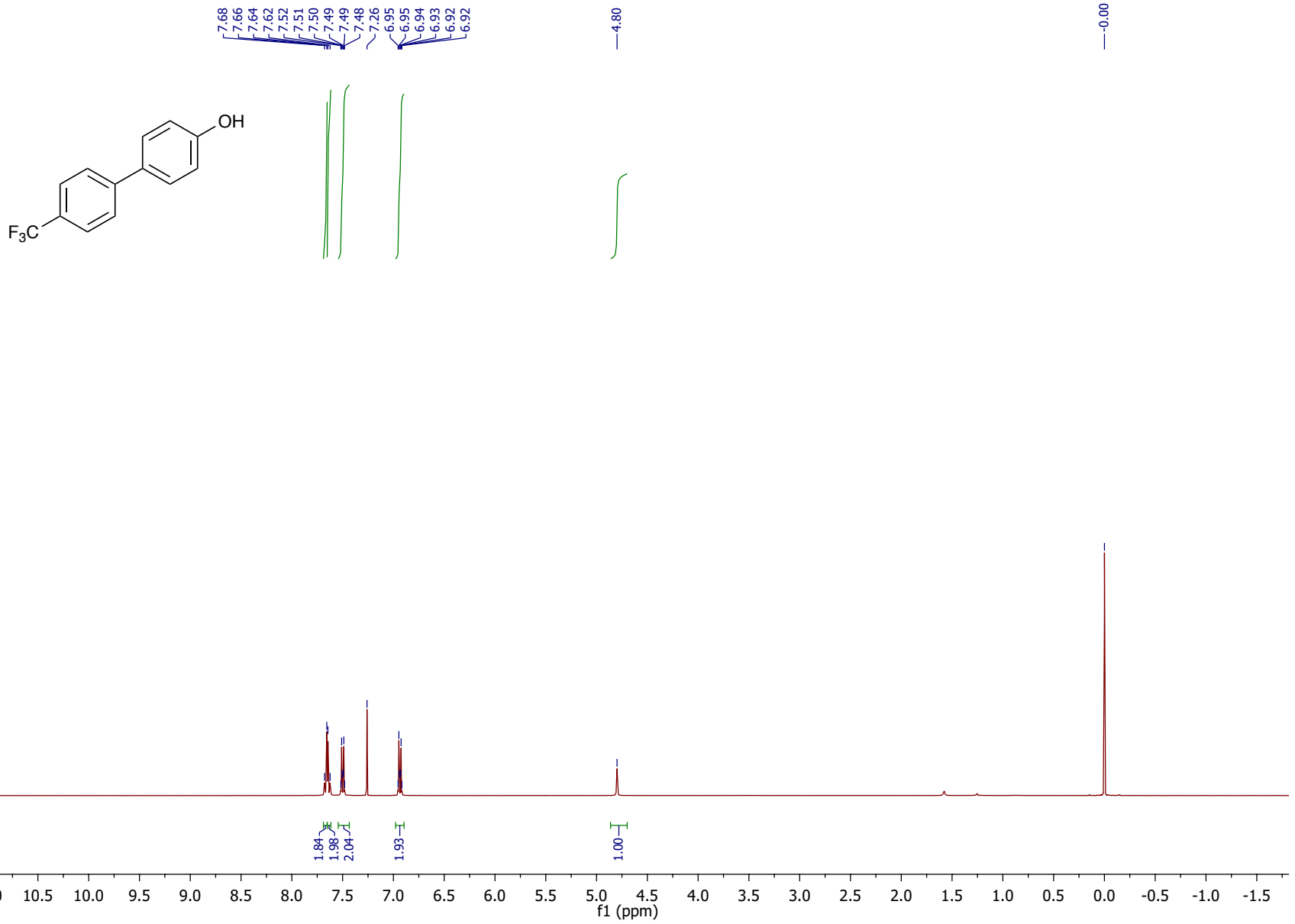
f1 (ppm)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6.93
6.92
6.92
4.80
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F3C
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2.04
1.93
1.00
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
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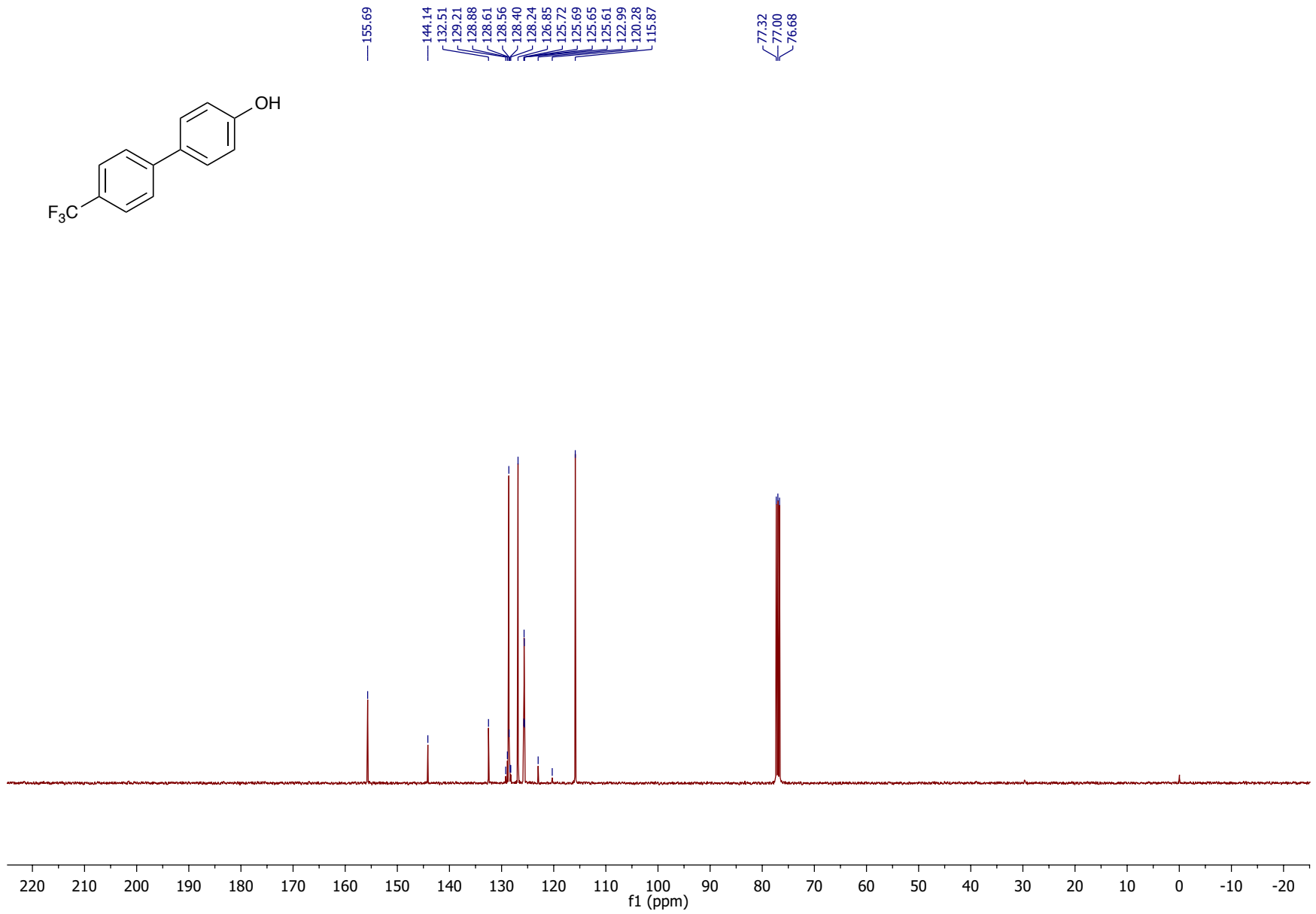
-1.5
f1 (ppm)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122.99
120.28
115.87
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77.00
76.68
OH
F3C
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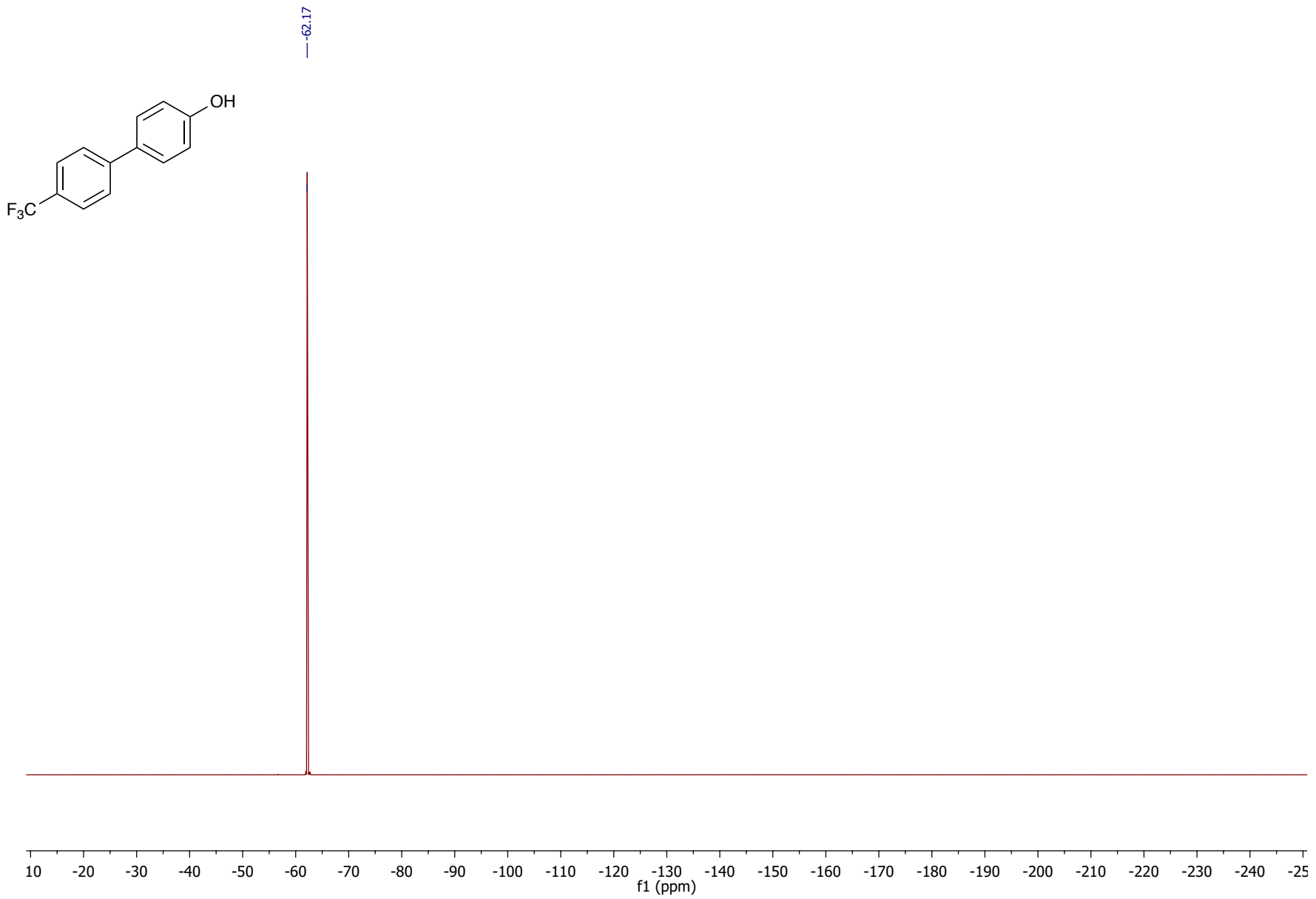
f1 (ppm)


-62.17
OH
F3C
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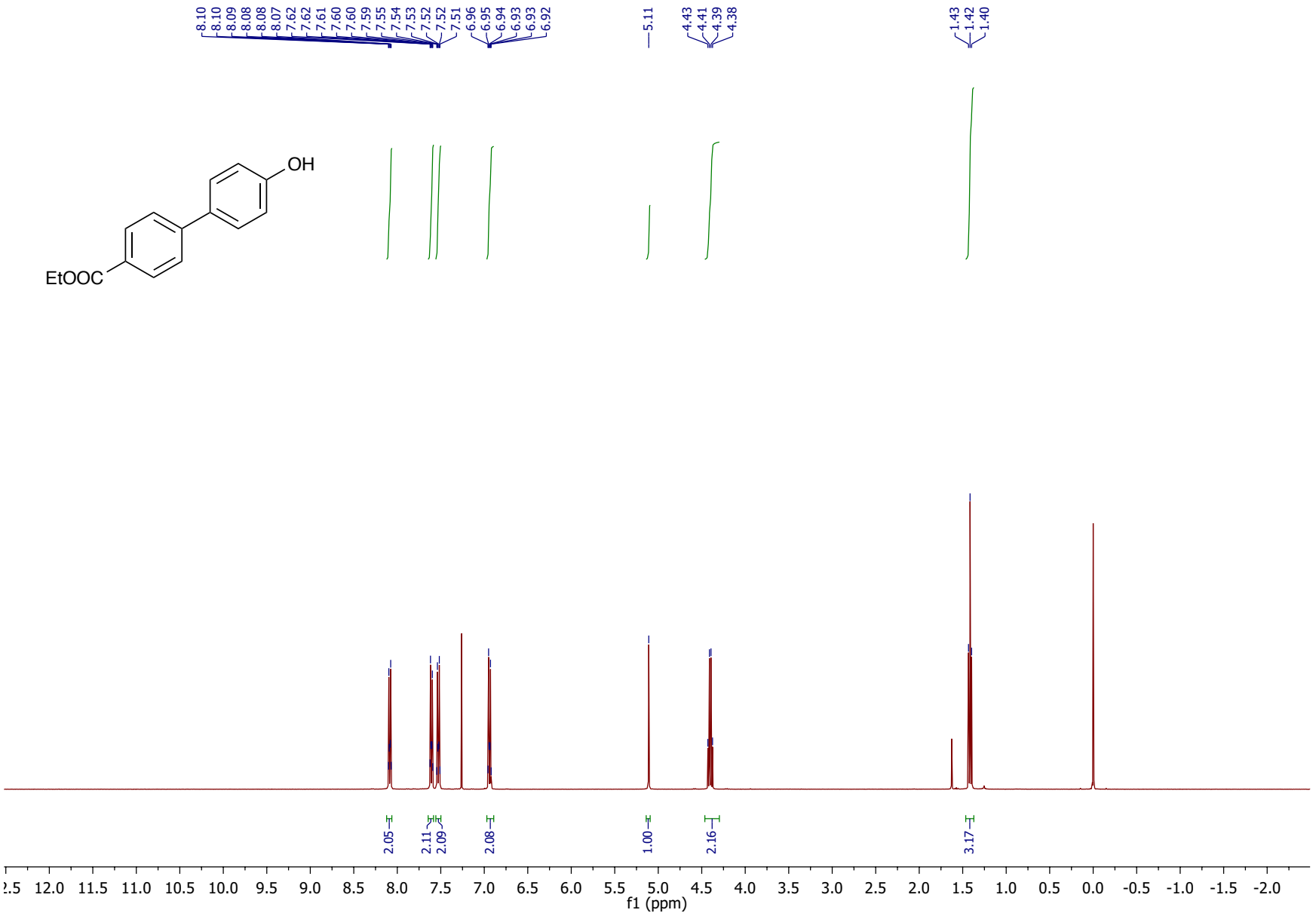
f1 (ppm)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4.38
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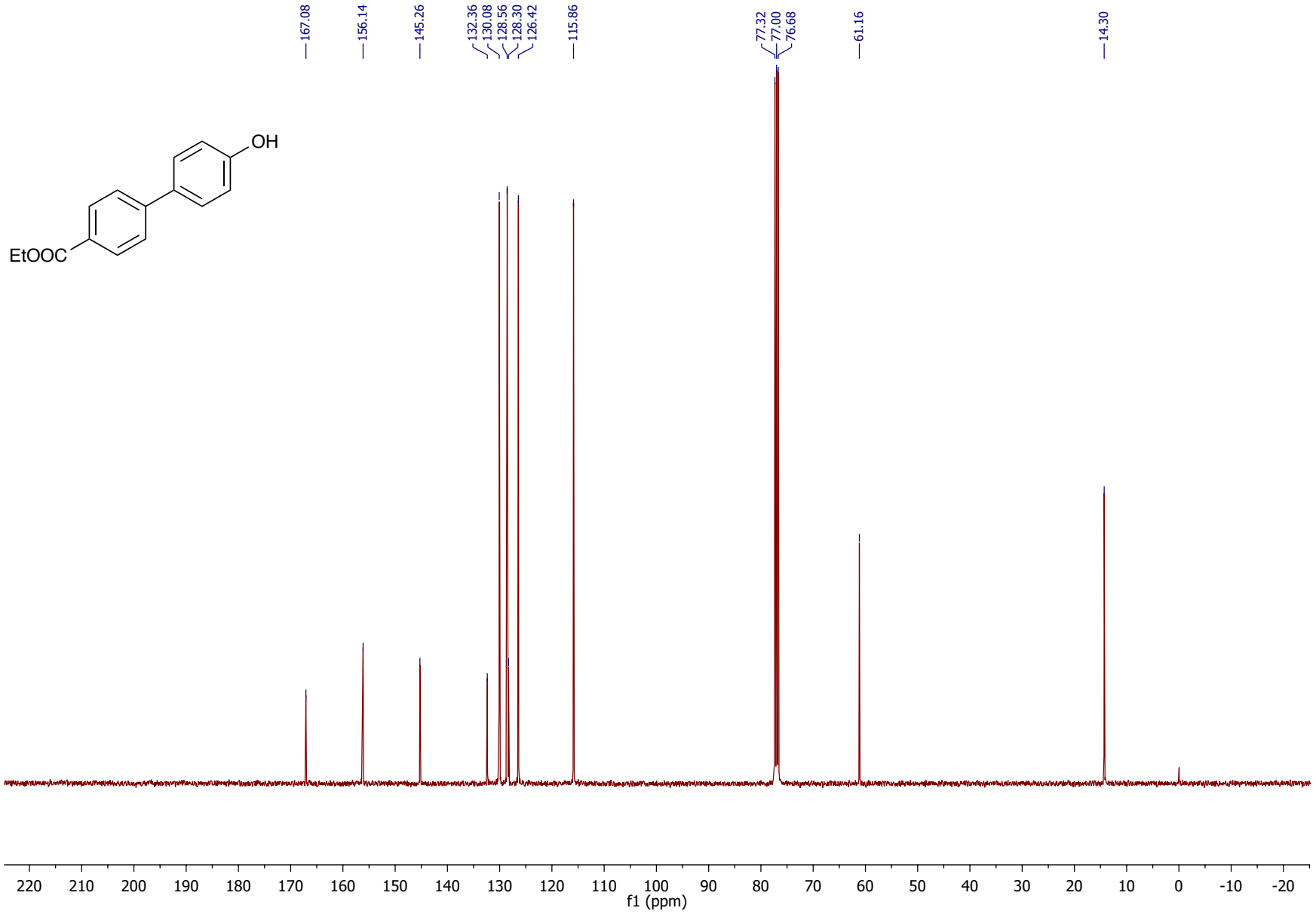
f1 (ppm)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77.00
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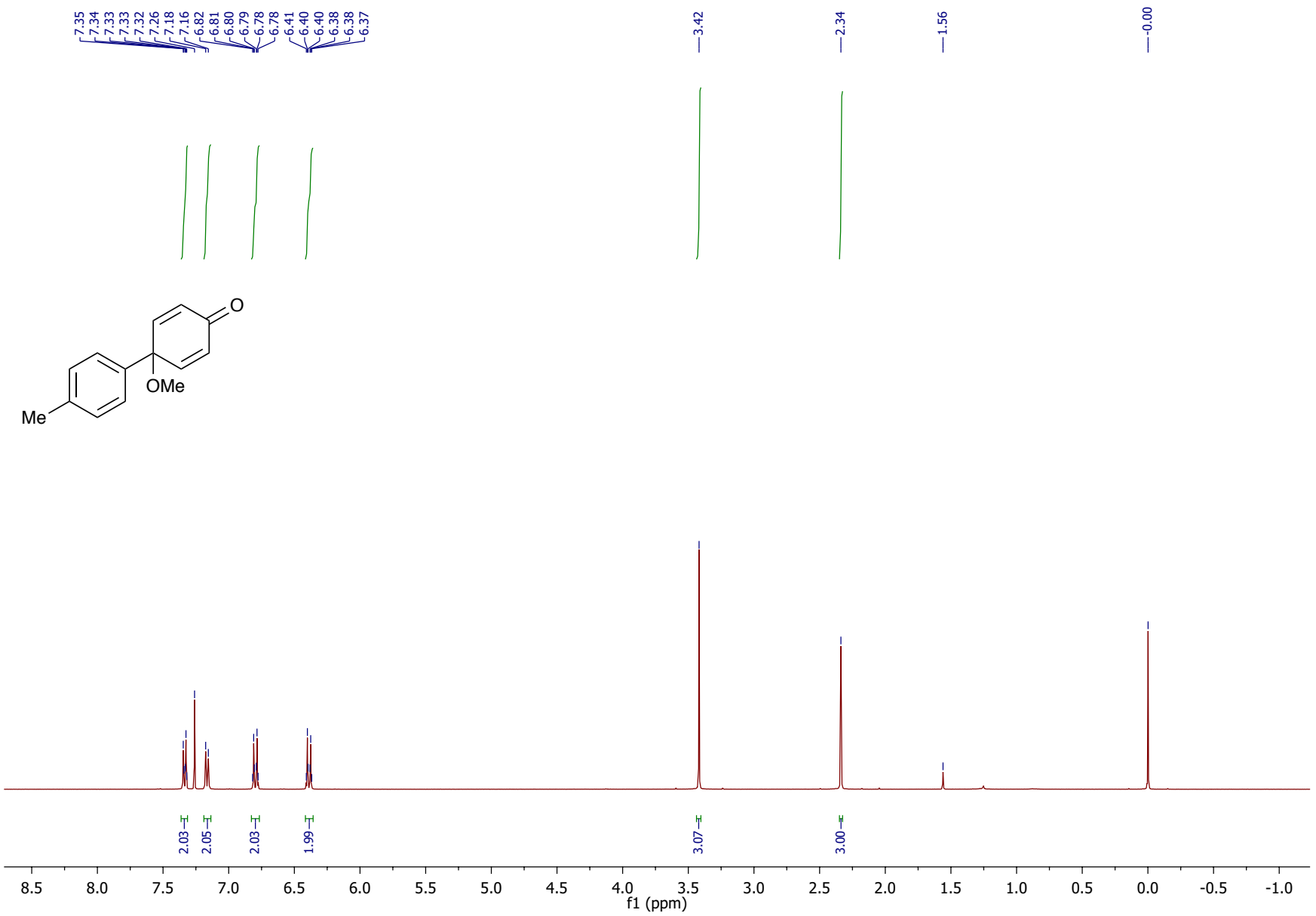
14.30
OH
EtOOC
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20
f1 (ppm)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6.38
6.37
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O
OMe
Me
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2.05
2.03
1.99
3.07
3.00
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
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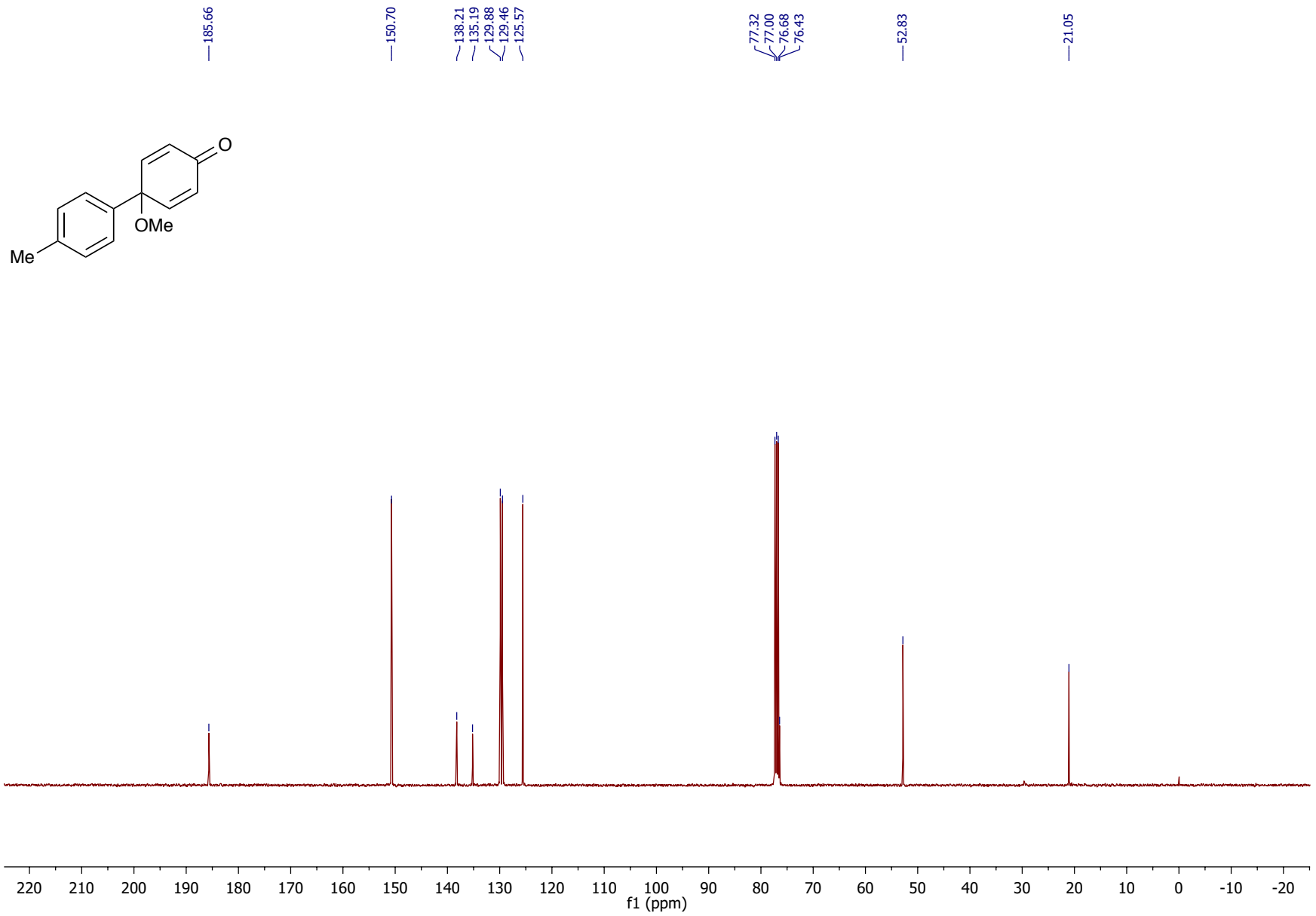
f1 (ppm)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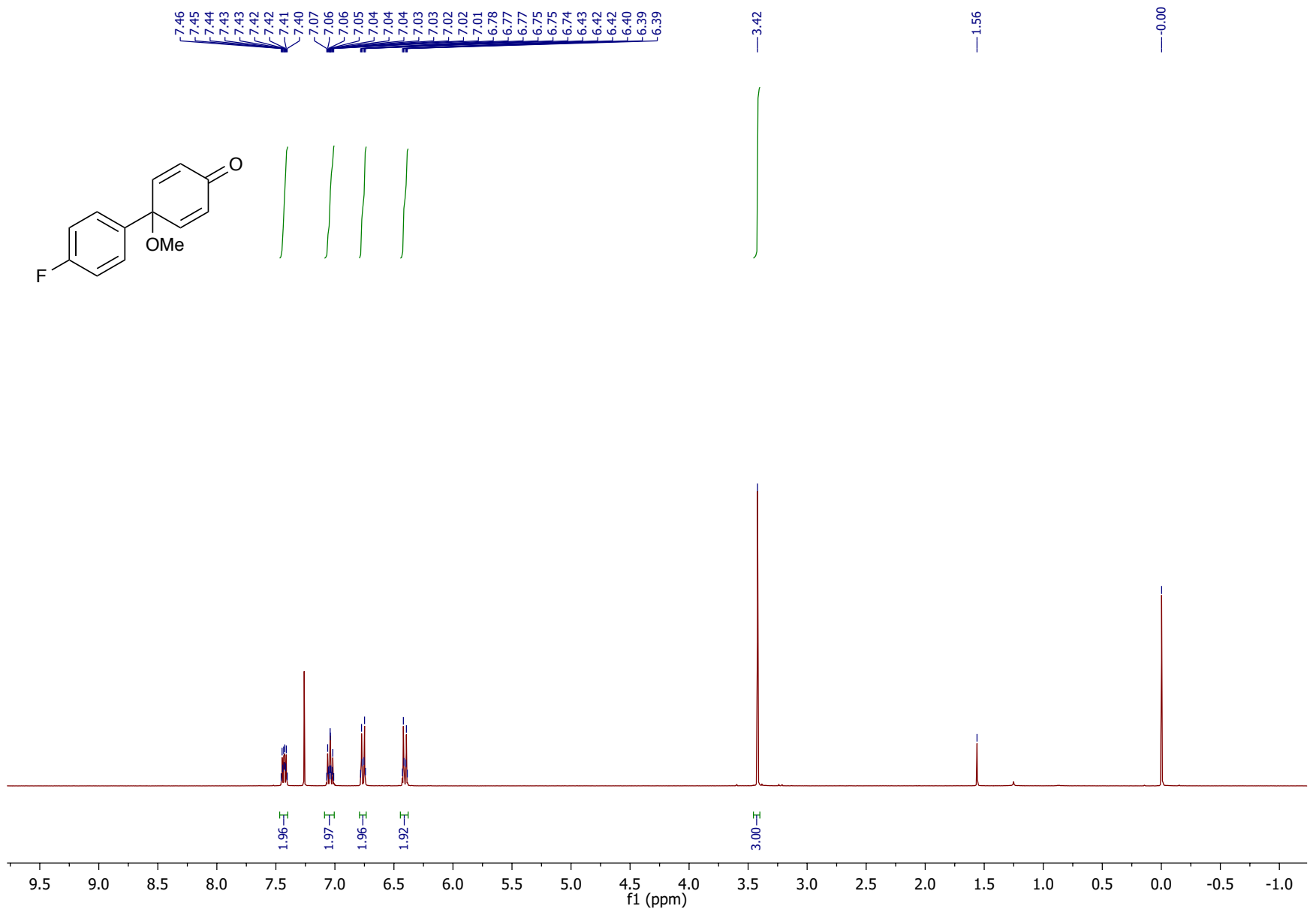
129.88
129.46
125.57
77.32
77.00
76.68
76.43
52.83
21.05
O
OMe
Me
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20
f1 (ppm)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7.07
7.06
7.06
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7.04
7.04
7.04
7.03
7.03
7.02
7.02
7.01
6.78
6.77
6.77
6.75
6.75
6.74
6.43
6.42
6.42
6.40
6.39
6.39
3.42
1.56
0.00
O
OMe
F
1.96
1.97
1.96
1.92
3.00
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
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2.0
1.5
1.0
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0.0
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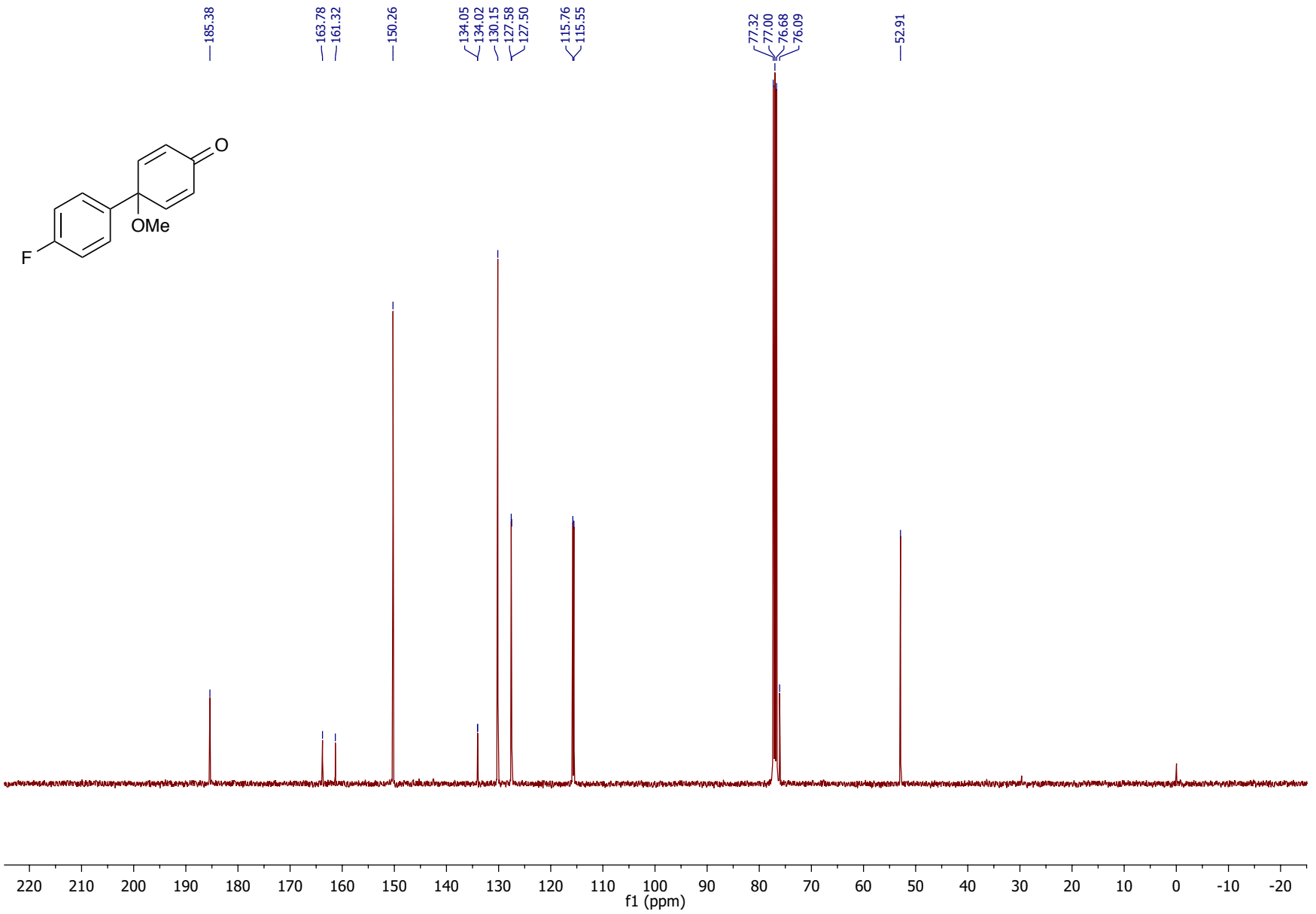
-1.0
f1 (ppm)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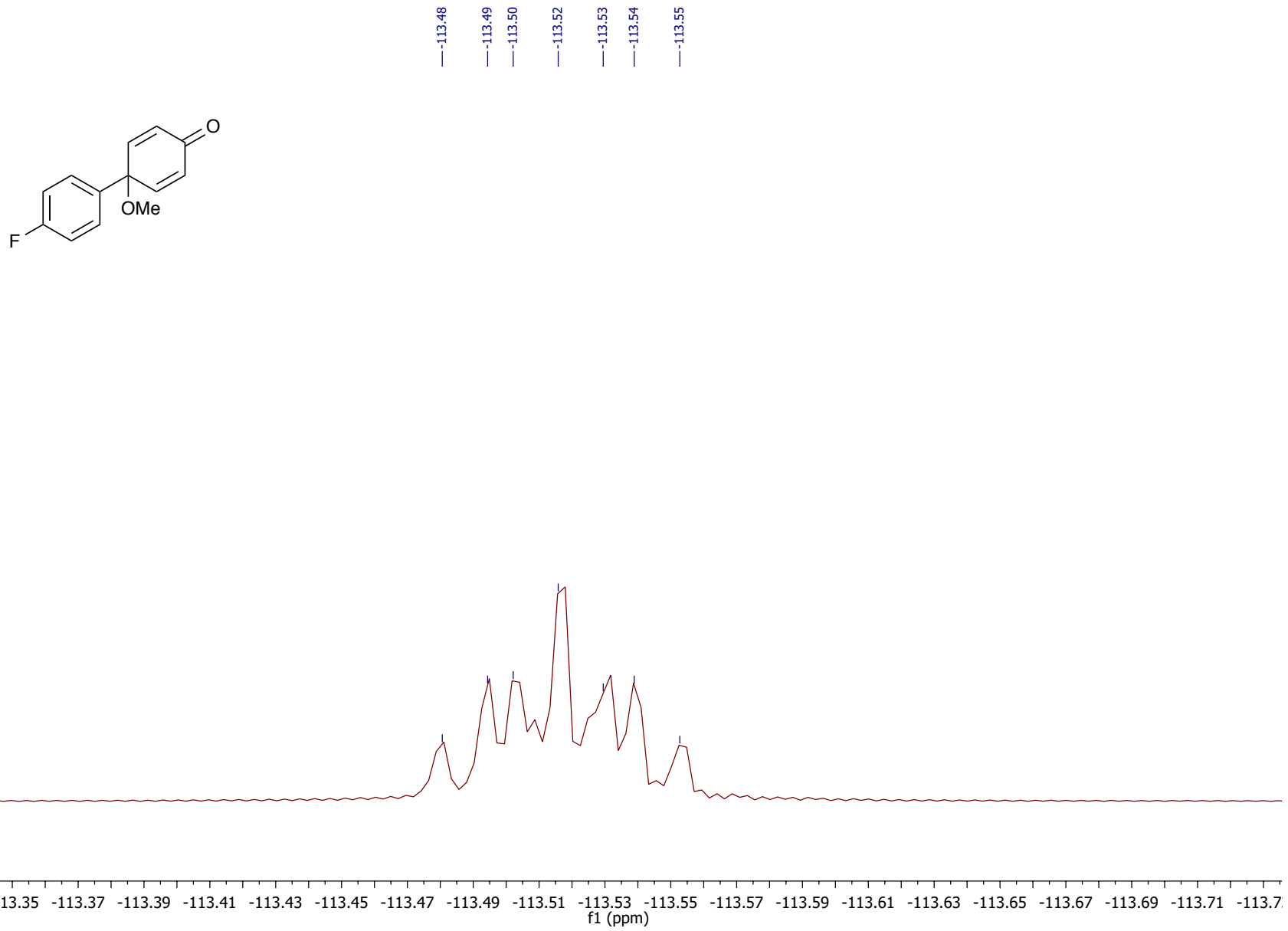
134.05
134.02
130.15
127.58
127.50
115.76
115.55
77.32
77.00
76.68
76.09
52.91
O
OMe
F
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20
f1 (ppm)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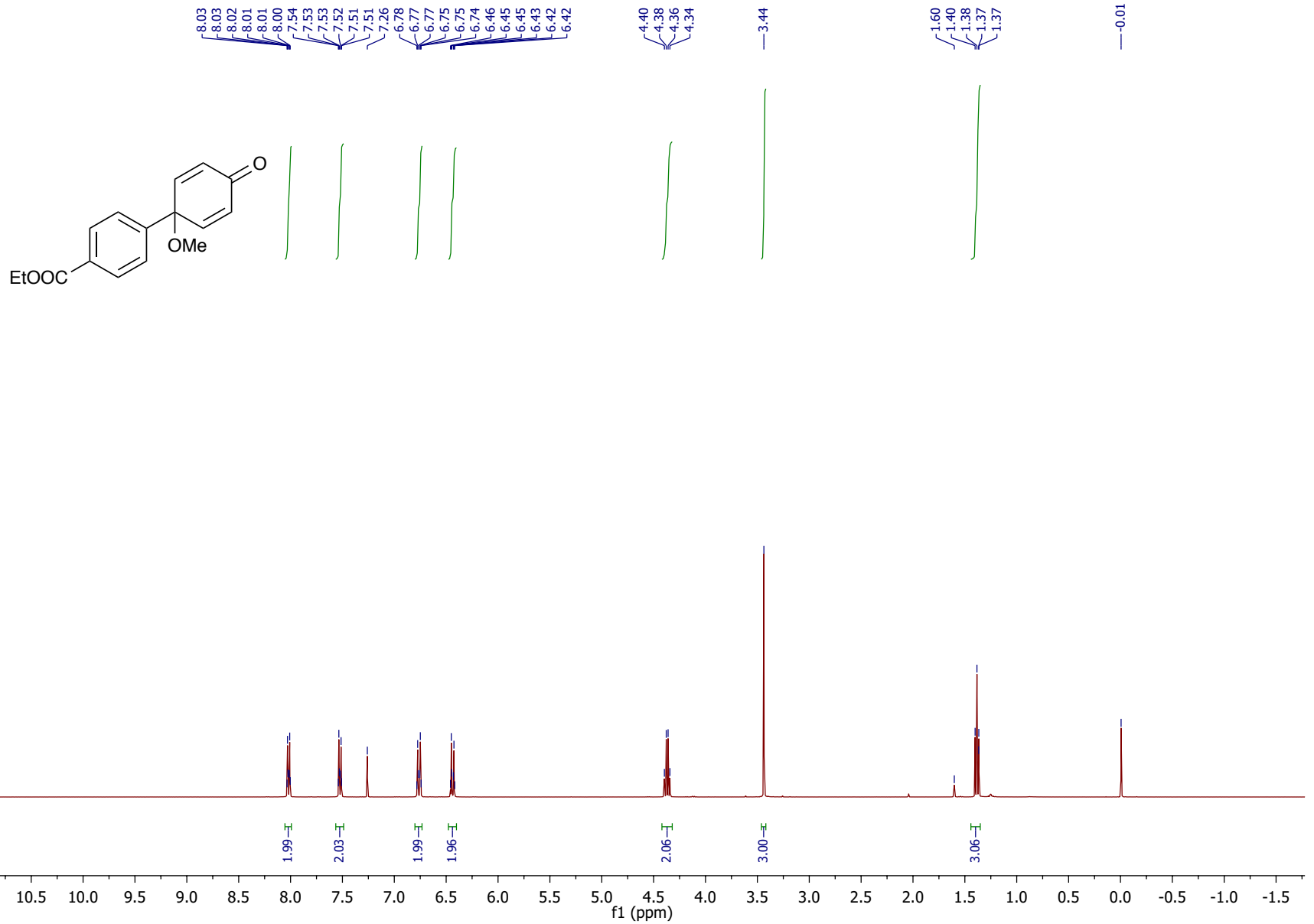
-113.50
-113.52
-113.53
-113.54
-113.55
O
OMe
F
-113.35 -113.37 -113.39 -113.41 -113.43 -113.45 -113.47 -113.49 -113.51 -113.53 -113.55 -113.57 -113.59 -113.61 -113.63 -113.65 -113.67 -113.69 -113.71
f1 (ppm)


8.03
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8.02
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8.01
8.00
7.54
7.53
7.53
7.52
7.51
7.51
7.26
6.78
6.77
6.77
6.75
6.75
6.74
6.46
6.45
6.45
6.43
6.42
6.42
4.40
4.38
4.36
4.34
3.44
1.60
1.40
1.38
1.37
1.37
-0.01
O
OMe
EtOOC
1.99
2.03
1.99
1.96
2.06
3.00
3.06
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
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1.5
1.0
0.5
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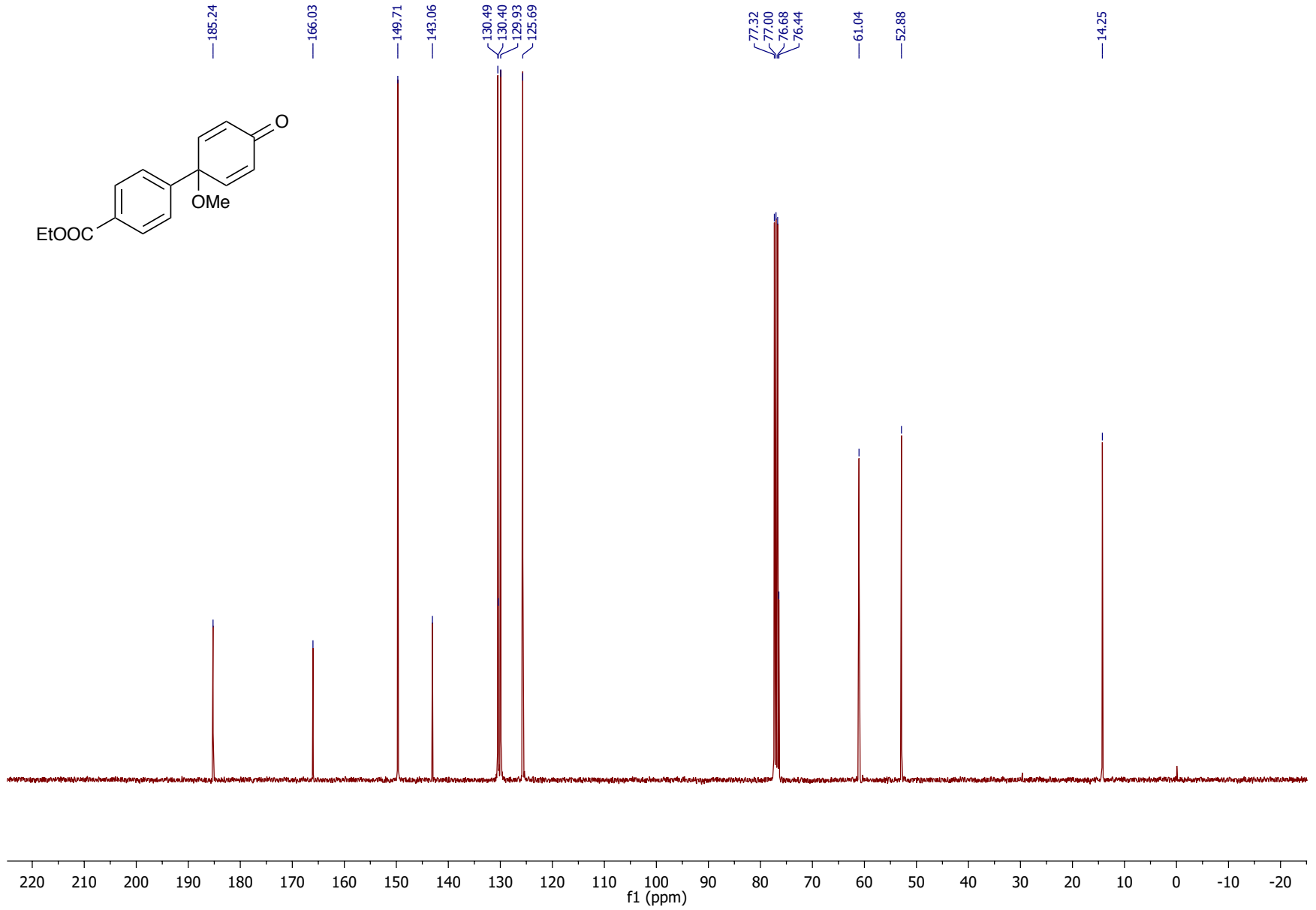
-0.5
-1.0
-1.5
f1 (ppm)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166.03
149.71
143.06
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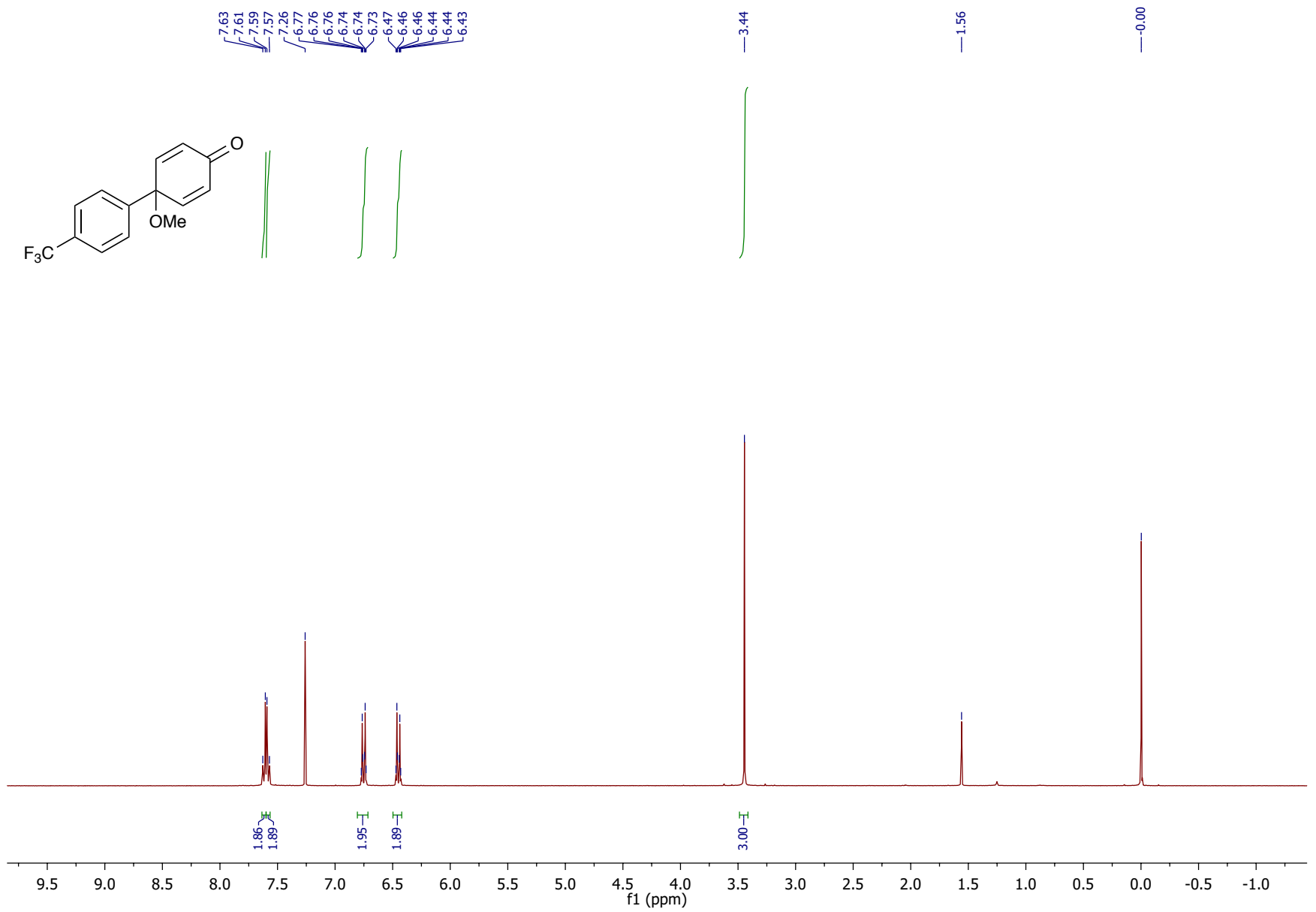
130.40
129.93
125.69
77.32
77.00
76.68
76.44
61.04
52.88
14.25
O
OMe
EtOOC
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20
f1 (ppm)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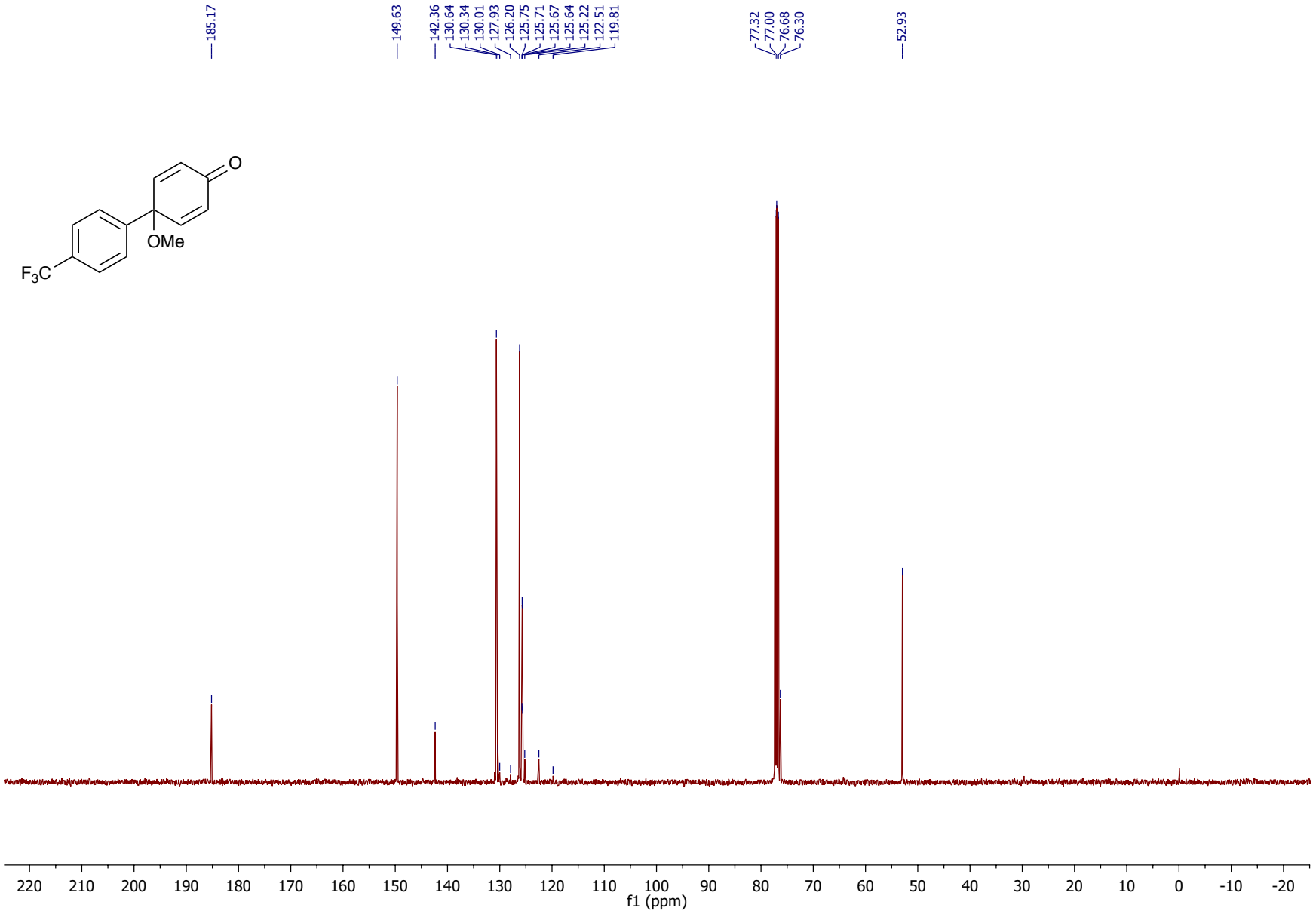
7.61
7.59
7.57
7.26
6.77
6.76
6.76
6.74
6.74
6.73
6.47
6.46
6.46
6.44
6.44
6.43
3.44
1.56
0.00
O
OMe
F3C
1.86
1.89
1.95
1.89
3.00
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1.0
f1 (ppm)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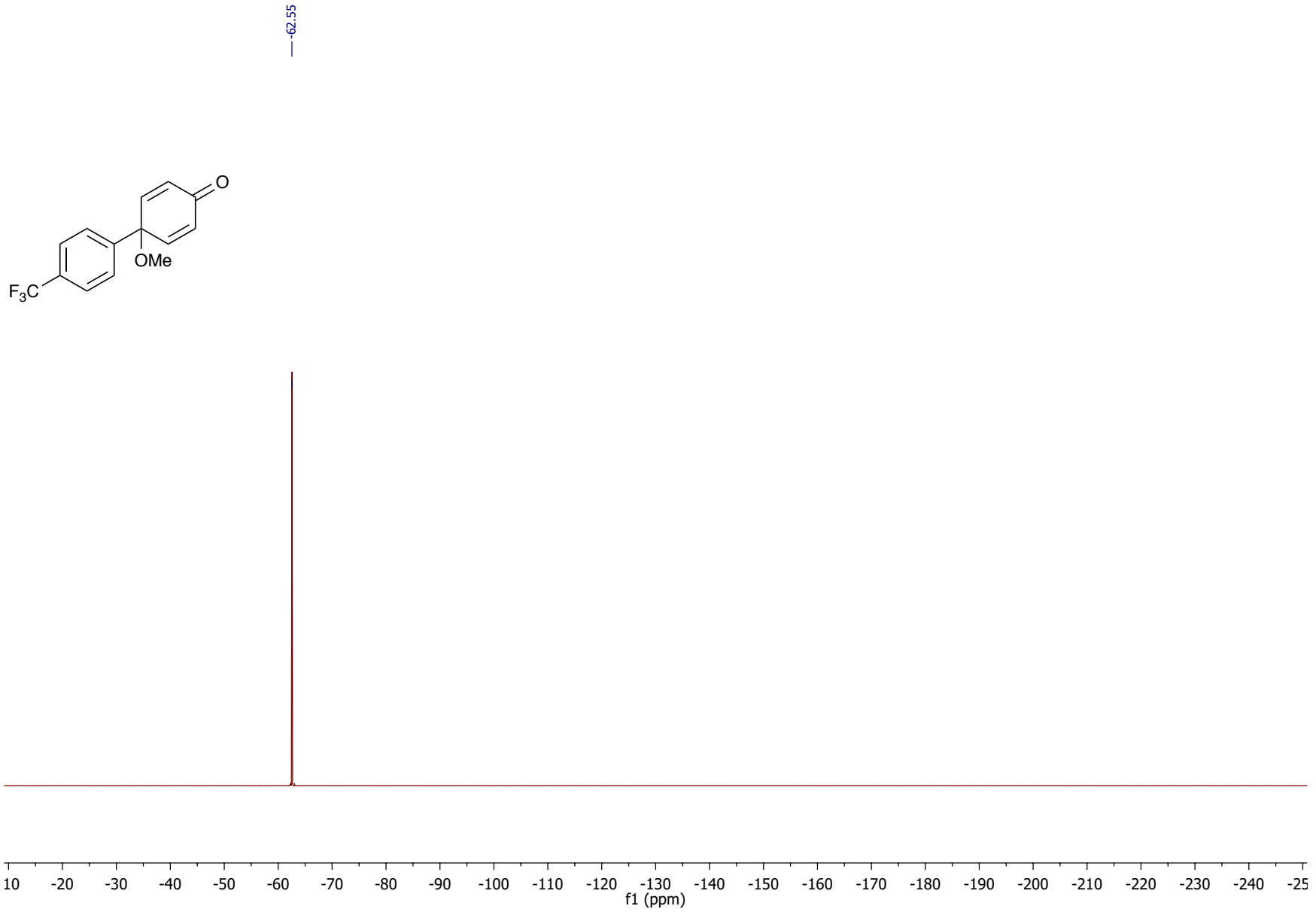
142.36
130.64
130.34
130.01
127.93
126.20
125.75
125.71
125.67
125.64
125.22
122.51
119.81
77.32
77.00
76.68
76.30
52.93
O
OMe
F3C
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20
f1 (ppm)


-62.55
O
OMe
F3C
10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210 -220 -230 -240 -25
f1 (ppm)