Synthesis of Catechols from Phenols via Pd-Catalyzed Silanol-Directed C–H Oxygenation

Chunhui Huang, Nugzar Ghavtadze, Buddhadeb Chattopadhyay, and Vladimir Gevorgyan*

Department of Chemistry, University of Illinois at Chicago,
845 West Taylor Street, 4500 SES, M/C 111, Chicago, Illinois 60607-7061

E-mail: vlad@uic.edu

Supporting Information

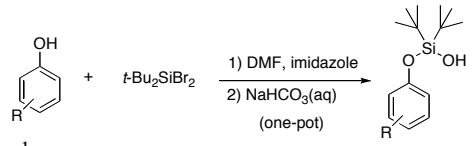
Content

General Information

NMR spectra were recorded on Bruker Avance DRX-500 (500 MHz) or DPX-400 (400 MHz) instrument. LRMS and HRMS analyses were performed on Micromass 70 VSE mass spectrometer.GC/MS analysis was performed on a Hewlett Packard Model 6890 GC interfaced to a Hewlett Packard Model 5973 mass selective detector (15 m x 0.25 mm capillary column, HP-5MS). Column chromatography was carried out employing Silicycle Silica-P flash silica gel (40-63 μm). Precoated silica gel plates F-254 were used for thin-layer analytical chromatography. All manipulations with transition metal catalysts were conducted in oven-dried glassware under inert atmosphere using a combination of glovebox and standard Schlenk techniques. Anhydrous solvents purchased from Aldrich were additionally purified on PureSolv PS-400-4 by Innovative Technology, Inc. purification system and/or stored over calcium hydride. All other starting materials were purchased from Strem Chemicals, Aldrich, Gelest Inc., or Alfa Aesar.

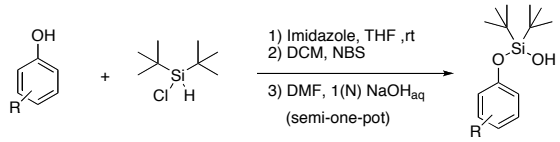
Part I. Preparation of Silanols.

Method A: One-pot procedure.



To a solution of *t*-Bu_2SiBr_2[1] (665mg, 2.2 mmol) in dry DMF (3 ml) imidazole (300 mg, 4.4 mmol) in dry DMF (2 ml) was added at 0 °C under argon atmosphere and stirred for 30 min at room temperature. The reaction mixture then was cooled down to 0 °C and solution of phenol (2.0 mmol) in dry DMF (2 ml) was added slowly. The reaction mixture was warmed up to RT and stirred overnight, then diluted with ether (20 ml) and treated with saturated aqueous solution of sodium bicarbonate (3 ml). The reaction mixture was stirred for additional 30 min at RT. The aqueous layer was extracted with ether and the organic phase was washed with brine and water. The combined organic extracts dried over Na_2SO_4 and evaporated under reduced pressure. The residue was purified by silica gel column chromatography (eluent: hexanes/AcOEt or hexanes/Et_2O) to give silanols.

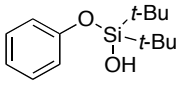
Method B: Semi-one-pot procedure.



To a stirred mixture of imidazole (749 mg, 11 mmol) and THF (40 ml), di-*t*-butylchlorosilane (938.6 mg, 5.25 mmol) was added at rt under argon atmosphere. To this mixture, phenol (5 mmol) in 10 mL of THF was added. The mixture was stirred until completion of the reaction by GC/MS. To this mixture, hexane (50 ml) was added and filtered. The filtrate was then evaporated by rotary evaporator under reduced pressure. To this crude mixture, 50 ml hexane was added filtered again, and evaporated to give the pure compound. To this compound, 25 ml DCM was added and NBS (981 mg, 1.1 equiv.) was added slowly. After monitoring by GC/MS, DMF (1.25 ml) and 1(N) aqueous NaOH (1.25 ml) was added and stirred at rt. Upon completion (judged by GC/MS), the mixture was evaporated by rotary evaporator under reduced pressure. Water (50 ml) was added and extracted with ether, dried over Na_2SO_4 and evaporated. The residue was purified by silica gel column chromatography to give the silanols.

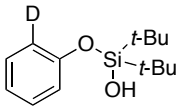
---

[1] This compound was prepared according to a known procedure: Gnanadesikan, V.; Corey, E. J. *J. Am. Chem. Soc.* **2008**, *130*, 8089–8093. To a solution of *t*-Bu_2SiH_2 (3.60 g, 25.0 mmol) in dry CH_2Cl_2 (150 ml) was added Br_2 (8.00 g, 50.0 mmol) at 0 °C under argon atmosphere. After stirring overnight at room temperature, the reaction mixture was evaporated to dryness. The crude product was purified by sublimation at 90 °C (~1.3 Torr). 6.76 g (22.4 mmol, 90%) *t*-Bu_2SiBr_2 was obtained as a waxy white solid. ^{1}H NMR (500 MHz, $CDCl_3$) δ ppm 1.20 (s, 18H). ^{13}C NMR (126 MHz, $CDCl_3$) δ ppm 26.0, 27.2.



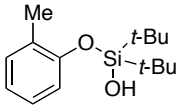
1a: (Method B, 86%, eluent: 3% EtOAc in hexanes)

^{1}H NMR (500 MHz, $CHCl_3$): δ ppm 7.24 (dd, *J* = 8.6, 7.4 Hz, 2H), 7.02-7.00 (m, 2H), 6.95 (t, *J* = 7.3 Hz, 1H), 2.26 (s, 1H), 1.09 (s, 18H).
^{13}C NMR (101 MHz, $CHCl_3$): δ ppm 155.7, 129.4, 121.2, 119.8, 27.4, 20.6.
HRMS (EI) calcd. for $C_{14}H_{24}O_2Si$ $[M]^+$: 252.15456. Found: 252.15375.



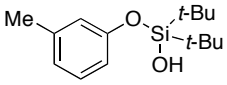
1a-*d*$_1$: (Method B, 86%, eluent: 3% EtOAc in hexanes)

^{1}H NMR (500 MHz, $CHCl_3$): δ ppm 7.17-7.32 (m, 2 H), 7.02 (d, *J*=7.70 Hz, 1 H), 6.88-6.98 (m, 1 H), 2.29 (s, 1 H), 1.10 (s, 18 H);
^{13}C NMR (126 MHz, $CHCl_3$): δ ppm 155.7, 134.3, 129.4, 129.3, 121.2, 119.8, 27.4, 20.6



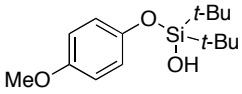
1b: (Method B, 83%, eluent: 2% Et_2O in hexanes)

^{1}H NMR (400 MHz, $CHCl_3$): δ ppm 7.16-7.14 (m, 2H), 7.09-7.05 (m, 1H), 6.87 (td, *J* = 7.37, 1.24 Hz, 1H), 2.41 (s, 1H), 2.29 (s, 3H), 1.11 (s, 18H).
^{13}C NMR (101 MHz, $CHCl_3$): δ ppm 154.2, 130.9, 127.8, 126.6, 120.9, 118.4, 27.5, 20.7, 16.9.
HRMS (EI) calcd. for $C_{15}H_{26}O_2Si$ $[M]^+$: 266.17021. Found: 266.16983.



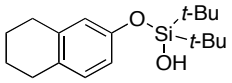
1c: (Method A, 95%; Method B, 67%, eluent: 3% Et_2O in hexanes)

^{1}H NMR (500 MHz, $CHCl_3$): δ ppm 7.12 (t, *J*=7.52 Hz, 1 H), 6.80 - 6.86 (m, 2 H), 6.77 (d, *J*=6.97 Hz, 1 H), 2.31 (s, 3 H), 2.24 (s, 1 H), 1.09 (s, 18 H);
^{13}C NMR (126 MHz, $CHCl_3$): δ ppm 155.6, 139.4, 129.1, 122.1, 120.5, 116.7, 27.4, 26.0, 20.6.
HRMS (EI) calcd. for $C_{15}H_{26}O_2Si$ $[M]^+$: 266.17021. Found: 266.17120.



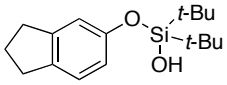
1d: (Method B, 82%, eluent: 2% Et_2O in hexanes)

^{1}H NMR (500 MHz, $CHCl_3$): δ ppm 6.92 (d, *J*=9.17 Hz, 2 H), 6.77 (d, *J*=9.17 Hz, 2 H), 3.76 (s, 3 H), 2.27 (s, 1 H), 1.07 (s, 18 H);
^{13}C NMR (126 MHz, $CHCl_3$): δ ppm 154.0, 149.5, 120.2, 114.5, 55.7, 27.4, 20.6.
HRMS (EI) calcd. for $C_{15}H_{26}O_3Si$ $[M]^+$: 282.16513. Found: 282.16617.



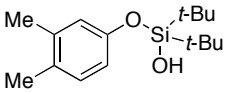
1e: (Method B, 65%, eluent: 2% Et_2O in hexanes)

^{1}H NMR (500 MHz, $CHCl_3$): δ ppm 6.93 (d, *J*=8.44 Hz, 1 H), 6.76 (dd, *J*=8.07, 2.57 Hz, 1 H), 6.72 (d, *J*=2.20 Hz, 1 H), 2.63 - 2.81 (m, 4 H), 2.28 (s, 1 H), 1.70 - 1.87 (m, 4 H), 1.10 (s, 18 H);
^{13}C NMR (126 MHz, $CHCl_3$) δ ppm 153.2, 138.1, 129.8, 119.7, 117.1, 29.6, 28.7, 27.4, 23.5, 23.2, 20.6.
HRMS (EI) calcd. for $C_{18}H_{30}O_2Si$ $[M]^+$: 306.20151. Found: 306.20234.



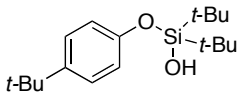
1f: (Method B, 68%, eluent: 2% Et_2O in hexanes)

^{1}H NMR (500 MHz, $CHCl_3$): δ ppm 7.07 (d, *J*=8.07 Hz, 1 H), 6.88 (d, *J*=1.83 Hz, 1 H), 6.78 (dd, *J*=8.07, 2.57 Hz, 1 H), 2.74 - 2.94 (m, 4 H), 2.25 (s, 1 H), 1.94 - 2.13 (m, 2 H), 1.10 (s, 18 H);
^{13}C NMR (126 MHz, $CHCl_3$): δ ppm 154.2, 145.6, 136.6, 124.6, 117.4, 115.7, 32.1, 27.4, 26.0, 25.8, 20.6.
HRMS (EI) calcd. for $C_{17}H_{28}O_2Si$ $[M]^+$: 292.18586. Found: 292.18685.



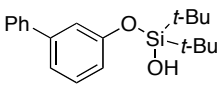
1g: (Method B, 76%, eluent: 2% Et_2O in hexanes)

^{1}H NMR (500 MHz, $CHCl_3$): δ ppm 6.98 (d, *J*=8.07 Hz, 1 H), 6.79 (d, *J*=2.20 Hz, 1 H), 6.74 (dd, *J*=8.44, 2.57 Hz, 1 H), 2.21 - 2.23 (m, 4 H), 2.19 (s, 3 H), 1.09 (s, 18 H);
^{13}C NMR (126 MHz, $CHCl_3$): δ ppm 153.6, 137.6, 130.2, 129.1, 120.9, 116.8, 27.4, 20.6, 19.9, 18.8.
HRMS (EI) calcd. for $C_{16}H_{28}O_2Si$ $[M]^+$: 280.18586. Found: 280.18684.



1h: (Method B, 81%, eluent: 2% Et_2O in hexanes)

^{1}H NMR (500 MHz, $CHCl_3$): δ ppm 7.24 (d, *J*=8.80 Hz, 2 H), 6.92 (d, *J*=8.80 Hz, 2 H), 2.23 (s, 1 H), 1.30 (s, 9 H), 1.09 (s, 18 H);
^{13}C NMR (126 MHz, $CHCl_3$): δ ppm 153.2, 143.8, 126.1, 119.1, 34.1, 31.6, 27.4, 20.6.
HRMS (EI) calcd. for $C_{18}H_{32}O_2Si$ $[M]^+$: 308.21716. Found: 308.21783.

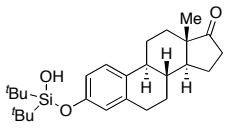


1i: (Method B, 74%, eluent: 2% Et_2O in hexanes)

^{1}H NMR (500 MHz, $CHCl_3$): δ ppm 7.63 (dd, *J* = 8.3, 1.2, 2H), 7.47 (*t*, J = 7.6, 2H), 7.38 (tt, *J* = 7.4, 1.6, 1H), 7.34 (t, *J* = 7.9, 1H), 7.30 (t, *J* = 2.0, 1H), 7.23 (ddd, *J* = 7.7, 1.7, 1.0, 1H), 7.05 (ddd, *J* = 8.1, 2.4, 1.0, 1H), 2.41 (s, 1H), 1.16 (s, 18H);

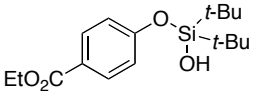
^{13}C NMR (126 MHz, $CHCl_3$): δ ppm 156.1, 142.7, 141.0, 129.7, 128.7, 127.3, 127.2, 126.8, 120.2, 118.7, 27.5, 20.7.

HRMS (EI) calcd. for $C_{20}H_{28}O_2Si$ $[M]^+$: 328.18586. Found: 328.18650.



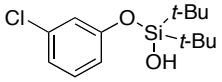
1j: (Method B, 99%, eluent: 15% Et_2O in hexanes)

^{1}H NMR (500 MHz, $CHCl_3$): δ ppm 7.13 (d, *J*=8.80 Hz, 1 H), 6.80 (dd, *J*=8.44, 2.20 Hz, 1 H), 6.73 (d, *J*=2.20 Hz, 1 H), 2.78 - 2.94 (m, 2 H), 2.50 (dd, *J*=18.89, 8.62 Hz, 1 H), 2.32 - 2.42 (m, 1 H), 2.20 - 2.30 (m, 1 H), 1.84 - 2.19 (m, 4 H), 1.32 - 1.71 (m, 6 H), 1.08 (s, 18 H), 0.91 (s, 3 H);
^{13}C NMR (126 MHz, $CHCl_3$): δ ppm 221.0, 153.6, 137.6, 132.5, 126.2, 119.7, 117.2, 50.5, 48.0, 44.1, 38.4, 35.9, 31.6, 29.5, 27.4, 26.6, 25.9, 21.6, 20.6, 13.9.
HRMS (EI) calcd. for $C_{26}H_{40}O_3Si$ $[M]^+$: 428.27468. Found: 428.27393.



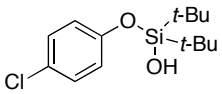
1k: (Method B, 86%, eluent: 4% Et_2O in hexanes)

^{1}H NMR (500 MHz, $CHCl_3$): δ ppm 7.92 (d, *J* = 8.91, 2H), 7.03 (d, *J* = 8.83, 2H), 4.33 (q, *J* = 7.12, 2H), 2.85 (s, 1H), 1.37 (t, *J* = 7.14, 3H), 1.07 (s, 18H);
^{13}C NMR (126 MHz, $CHCl_3$): δ ppm 166.6, 160.1, 131.5, 123.3, 119.5, 60.7, 27.3, 20.6, 14.3.
HRMS (EI) calcd. for $C_{17}H_{28}O_4Si$ $[M]^+$: 324.17569. Found: 324.17490.



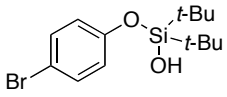
1l: (Method B, 59%, eluent: 1% Et_2O in hexanes)

^{1}H NMR (500 MHz, $CHCl_3$): δ ppm 7.14 (t, *J*=8.07 Hz, 1 H), 7.03 (t, *J*=2.20 Hz, 1 H), 6.94 (d, *J*=8.07 Hz, 1 H), 6.91 (dd, *J*=8.80, 1.83 Hz, 1 H), 2.37 (s, 1 H), 1.08 (s, 18 H);
^{13}C NMR (126 MHz, $CHCl_3$) δ ppm 156.5, 134.5, 130.1, 121.5, 120.2, 118.1, 27.3, 20.6.
HRMS (EI) calcd. for $C_{14}H_{23}O_2SiCl$ $[M]^+$: 286.11559. Found: 286.11535.



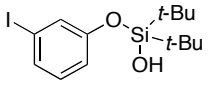
1m: (Method B, 77%, eluent: 2% Et_2O in hexanes)

^{1}H NMR (400 MHz, $CHCl_3$): δ ppm 7.18 (d, *J* = 8.96 Hz, 2H), 6.94 (d, *J* = 8.96 Hz, 2H), 2.33 (s, 1H), 1.07 (s, 18H).
^{13}C NMR (101 MHz, $CHCl_3$): δ ppm 154.4, 129.3, 126.1, 121.0, 27.3, 20.6.
HRMS (EI) calcd. for $C_{14}H_{23}O_2SiCl$ $[M]^+$: 286.11559. Found: 286.11510.



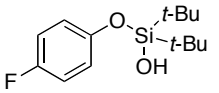
1n: (Method B, 79%, eluent: 3% Et_2O in hexanes)

^{1}H NMR (500 MHz, $CHCl_3$): δ ppm 7.32 (d, *J* = 8.95, 2H), 6.89 (d, *J* = 8.95, 2H), 2.27 (s, 1H), 1.07 (s, 18H);
^{13}C NMR (126 MHz, $CHCl_3$): δ ppm 154.9, 132.2, 121.5, 113.5, 27.3, 20.6.
HRMS (EI) calcd. for $C_{14}H_{23}O_2SiBr$ $[M]^+$: 330.06507. Found: 330.06637.



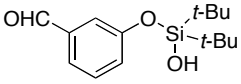
1o: (Method B, 74%, eluent: 2% Et_2O in hexanes)

^{1}H NMR (500 MHz, $CHCl_3$): δ ppm 7.39 (t, *J* = 1.87, 1H), 7.30-7.27 (m, 1H), 6.99 (dddd, *J* = 8.24, 2.26, 1.18, 0.54, 1H), 6.95 (d, *J* = 7.73, 1H), 2.31 (s, 1H), 1.07 (s, 18H);
^{13}C NMR (126 MHz, $CHCl_3$): δ ppm 156.3, 130.6, 130.4, 128.9, 119.2, 94.1, 27.3, 20.6.
HRMS (EI) calcd. for $C_{14}H_{23}O_2ISi$ $[M]^+$: 378.05124. Found: 378.05026.



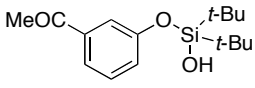
1p: (Method B, 66%, eluent: 2% Et_2O in hexanes)

^{1}H NMR (500 MHz, $CHCl_3$): δ ppm 6.57 - 7.16 (m, 4 H), 2.30 (s, 1 H), 1.08 (s, 18 H);
^{13}C NMR (126 MHz, $CHCl_3$): δ ppm 157.4 (d, *J*=238.6 Hz), 151.7, 120.7, 115.7 (d, *J*=22.2 Hz),, 27.4, 20.6.
HRMS (EI) calcd. for $C_{14}H_{23}O_2SiF$ $[M]^+$: 270.14514. Found: 270.14621.



1q: (Method B, 89%, eluent: 10% EtOAc in hexanes)

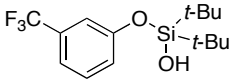
^{1}H NMR (500 MHz, $CHCl_3$): δ ppm 9.93 (s, 1H), 7.51-7.50 (m, 1H), 7.46 (dt, *J* = 7.5, 1.3 Hz, 1H), 7.39 (dd, *J* = 7.9, 7.6 Hz, 1H), 7.29 (ddd, *J* = 8.1, 2.5, 1.1 Hz, 1H), 2.77 (br. s, 1H), 1.08 (s, 18H);
^{13}C NMR (126 MHz, $CHCl_3$): δ ppm 192.4, 156.5, 137.8, 130.0, 126.3, 123.3, 119.8, 27.3, 20.6.
HRMS (EI) calcd. for $C_{15}H_{24}O_3Si$ $[M]^+$: 280.14948. Found: 280.15054.



1r: (Method B, 93%, eluent: 10% EtOAc in hexanes)

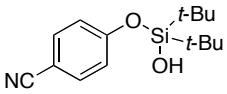
^{1}H NMR (400 MHz, $CHCl_3$): δ ppm 7.58 (t, *J* = 1.91 Hz, 1H), 7.51 (dt, *J* = 7.54, 1.38 Hz, 1H), 7.29 (t, *J* = 7.81 Hz, 1H), 7.23 (ddd, *J* = 8.12, 2.39, 1.17 Hz, 1H), 3.25 (s, 1H), 2.55 (s, 3H), 1.08 (s, 18H);
^{13}C NMR (101 MHz, $CHCl_3$): δ ppm 198.6, 156.2, 138.4, 129.5,

124.9, 121.4, 119.2, 27.3, 26.7, 20.7.
HRMS (EI) calcd. for $C_{16}H_{26}O_3Si$ $[M]^+$: 294.16513. Found: 294.16595.



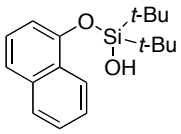
1s: (Method B, 57%, eluent: 2% Et_2O in hexanes)

^{1}H NMR (400 MHz, $CHCl_3$): δ ppm 7.33 (t, *J* = 7.95 Hz, 1H), 7.25-7.26 (m, 1H), 7.18-7.21 (m, 2H), 2.36 (s, 1H), 1.08 (s, 18H).
^{13}C NMR (101 MHz, $CHCl_3$): δ ppm 156.0, 131.8 (q, *J* = 31.44 Hz), 129.9, 123.9 (q, *J* = 272.81 Hz), 123.1, 117.9 (d, *J* = 3.70 Hz), 116.6 (d, *J* = 3.70 Hz), 27.3, 20.6.
HRMS (EI) calcd. for $C_{15}H_{23}O_2SiF_3$ $[M]^+$: 320.14195. Found: 320.14012.



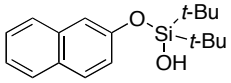
1t: (Method B, 96%, eluent: 10% EtOAc in hexanes)

^{1}H NMR (400 MHz, $CHCl_3$): δ ppm 7.50 (d, *J* = 8.89 Hz, 2H), 7.09 (d, *J* = 8.85 Hz, 2H), 2.91 (s, 1H), 1.07 (s, 18H);
^{13}C NMR (101 MHz, $CHCl_3$): δ ppm 160.0, 133.9, 120.7, 119.3, 104.1, 27.2, 20.6.
HRMS (EI) calcd. for $C_{15}H_{23}O_2NSi$ $[M]^+$: 277.14981. Found: 277.14879.



1u: (Method A, 94%, eluent: 5% EtOAc in hexanes)

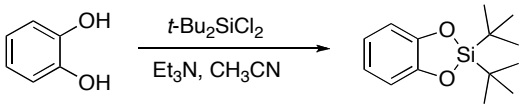
^{1}H NMR (500 MHz, $CHCl_3$): δ ppm 8.29 (m, 1H), 7.83 (m, 1H), 7.47-7.52 (m, 3H), 7.34 (t, *J* = 7.9 Hz, 1H), 7.27 (dd, *J* = 7.5, 0.6 Hz, 1H), 2.58 (s, 1H), 1.17 (s, 18H);
^{13}C NMR (126 MHz, $CHCl_3$): δ ppm 151.9, 135.0, 127.7, 127.1, 126.1, 126.0, 125.1, 122.5, 120.8, 112.6, 27.5, 20.9.



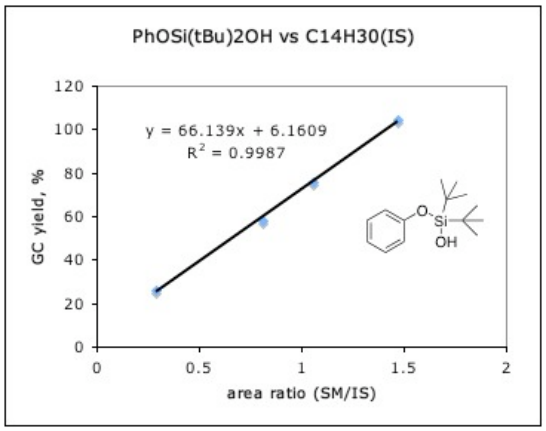
1v: (Method A, 96%; Method B, 72%, eluent: 2% Et_2O in hexanes)

^{1}H NMR (500 MHz, $CHCl_3$): δ ppm 7.78 (d, *J* = 8.15 Hz, 1H), 7.74 (d, *J* = 8.85 Hz, 1H), 7.72 (d, *J* = 8.23 Hz, 1H), 7.43 (td, *J* = 7.53, 1.26 Hz, 1H), 7.40 (d, *J* = 2.25 Hz, 1H), 7.34 (ddd, *J* = 8.12, 6.87, 1.23 Hz, 1H), 7.25 (dd, *J* = 8.81, 2.40 Hz, 1H), 2.38 (s, 1H), 1.13 (s, 18H);
^{13}C NMR (126 MHz, $CHCl_3$): δ ppm 153.5, 134.7, 129.3, 129.2, 127.6, 126.7, 126.1, 123.7, 121.7, 114.5, 27.4, 20.7.
HRMS (EI) calcd. for $C_{18}H_{26}O_2Si$ $[M]^+$: 302.17021. Found: 302.17005.

Calibration of GC:



The synthesis of 2,2-di-*tert*-butylbenzo[*d*][1,3,2]dioxasilole is based on a known procedure.[2] A two-neck flask equipped with a condenser was loaded with pyrocatechol (330 mg, 3 mmol) and flushed with argon. Anhydrous CH_3CN (20 ml) was added and followed by addition of dry Et_3N (0.8 mL, 5.74 mmol). Di-*tert*-butyldichlorosilane (0.7 ml, 3.3 mmol) was added via syringe and the reaction temperature was increased to 80 °C for 16 h. The volatile solvents were removed under reduced pressure and the residue was re-dissolved in chloroform (50 ml). The organic layer was washed with aqueous sodium bicarbonate solution and brine, dried over potassium carbonate, and concentrated. The pure product was obtained by Kugelrohr distillation as white solids (328.6 mg, 44%). ^{1}H NMR (500 MHz, $CDCl_3$) δ ppm 6.91 (dd, J = 5.76, 3.48 Hz, 2H), 6.79 (dd, J = 5.81, 3.44 Hz, 2H), 1.11 (s, 18H); ^{13}C NMR (126 MHz, $CDCl_3$) δ ppm 149.8, 120.8, 113.0, 26.1, 21.6. HRMS (EI) calcd. for $C_{14}H_{22}O_2Si$ $[M]^+$: 250.13891. Found: 250.13848.



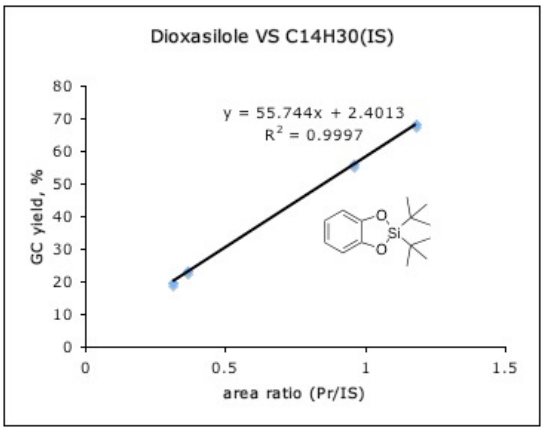
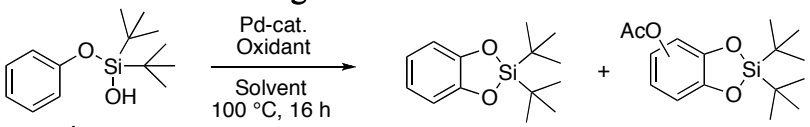


Table S1. Screening of reaction conditions.



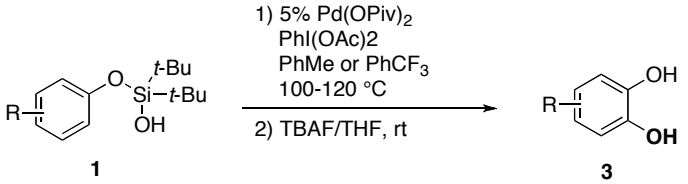
1a **2a** **2a'**

Entry	Pd-cat	Oxidant	Solvent	GC yield	
				of **2a**	**2a'**
1	$Pd(OAc)_2$ (5%)	$PhI(OAc)_2$ (1.5 eq)	PhMe	40 (67)	3
2	$[(Allyl)PdCl]_2$ (5%)	$PhI(OAc)_2$ (1.5 eq)	PhMe	13 (81)	0
3	$Pd(OTf)_2$ (5%)	$PhI(OAc)_2$ (1.5 eq)	PhMe	40 (78)	2
4	$PdCl_2$ (15%)	$PhI(OAc)_2$ (1.5 eq)	PhMe	45 (80)	3
5	$Pd(CH_3CN)_4(BF_4)_2$ (5%)	$PhI(OAc)_2$ (1.5 eq)	PhMe	29 (72)	0
6	$Pd(acac)_2$ (5%)	$PhI(OAc)_2$ (1.5 eq)	PhMe	10 (77)	0
7	$Pd(OPiv)_2$ (5%)	$PhI(OAc)_2$ (1.5 eq)	PhMe	50 (65)	3
8	$Pd(OPiv)_2$ (5%)	$PhI(OAc)_2$ (1.5 eq)	*p*-xylene	44 (68)	4

[2] Cren-Olive, C.; Lebrun, S.; Rolando, C. *J. Chem. Soc., Perkin Trans. 1*, **2002**, 821.

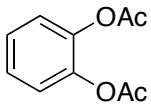
9	$Pd(OPiv)_2$ (5%)	$PhI(OAc)_2$ (1.5 eq)	*o*-xylene	35 (47)	2
10	$Pd(OPiv)_2$ (5%)	$PhI(OAc)_2$ (1.5 eq)	mesitylene	43 (64)	3
11	$Pd(OPiv)_2$ (5%)	$PhI(OAc)_2$ (1.5 eq)	DCE	19 (21)	10
12	$Pd(OPiv)_2$ (5%)	$PhI(OAc)_2$ (1.5 eq)	C_6F_6	37 (45)	3
13	$Pd(OPiv)_2$ (10%)	$PhI(OAc)_2$ (1.5 eq)	PhMe	46 (72)	4
14	$Pd(OPiv)_2$ (5%)	$PhI(OAc)_2$ (1.5 eq) + Li_2CO_3 (1.0 eq)	PhMe	43 (74)	2
15	**$Pd(OPiv)_2$ (5%)**	**$PhI(OAc)_2$ (2.0 eq)**	**PhMe**	**58 (79)**	**6**
16	$Pd(OPiv)_2$ (5%)	$PhI(OAc)_2$ (3.0 eq)	PhMe	47 (52)	6
17	$Pd(OPiv)_2$ (5%)	$PhI(OAc)_2$ (4.0 eq)	PhMe	39 (41)	4
18	$Pd(OPiv)_2$ (5%)	$PhI(OAc)_2$ (1.5 eq)	$PhCF_3$	47 (53)	14
19	$Pd(OPiv)_2$ (5%)	$PhI(OAc)_2$ (2.0 eq) + H_2O (5.0 eq)	PhMe	7 (18)	0
20	none	$PhI(OAc)_2$ (2.0 eq)	PhMe	NR	0
21	none	IBX (1.0 eq)	$CDCl_3$	NR (rt)	0

Part II: Preparation of catechols from phenol-derived silanols.



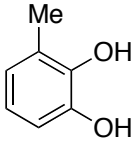
1 **3**

General procedure: An oven dried 2.5 ml Wheaton V-vial, containing a stirring bar, was charged with phenol-derived silanols (0.2 mmol), $Pd(OPiv)_2$ (3.1 mg, 0.01 mmol), and $PhI(OAc)_2$ (0.4 mmol for **3b**-**j**; 0.3 mmol for **3k**-**v**) under N_2 atmosphere. 2 ml of dry toluene (**3b**-**j**) or α,α,α-trifluorotoluene (**3k**-**v**) was added via syringes and the reaction vessel was capped with pressure screw cap. The reaction mixture was heated at 100 – 120 °C for 15 - 20 h. The resulting mixture was cooled down to room temperature and filtered through a short layer of silica gel over celite plug with the aid of EtOAc. The filtrate was concentrated under a reduced pressure. To the residue THF (1 ml) and TBAF (0.4 ml, 2 equiv) was added. The reaction mixture was stirred at room temperature for 1 - 2 h. After completion of the reaction, the mixture was washed with water, extracted with diethyl ether, dried over Na_2SO_4, and concentrated. The residue was purified by column chromatography on a silica gel (eluent: hexanes/EtOAc = 3/1 – 1/1) affording the corresponding catechol products. In case of **3d** and **3l**-**v**, upon completion of desilylation, Ac_2O (189 μl) and pyridine (160 μl) were added into the same pot. The reaction mixture was stirred overnight. The volatile was removed under reduced pressure. The residue was purified by column chromatography on a silica gel (eluent: hexanes/EtOAc = 10/1 – 5/1) affording the corresponding bis-acetated catechols.



4a: 1,2-phenylene diacetate[3]

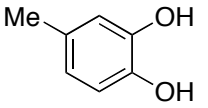
^{1}H NMR (500 MHz, CD_3OD) δ ppm 7.24-7.26 (m, 2H), 7.18-7.21 (m, 2H), 2.24 (s, 6H).
^{13}C NMR (126 MHz, CD_3OD) δ ppm 168.6, 142.4, 126.2, 123.2, 19.1.



3b: 3-Methylcatechol[4]

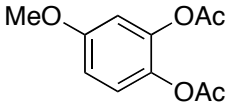
^{1}H NMR (500 MHz, $CDCl_3$) δ ppm 6.72 (s, 3 H), 5.13 (br. s., 2 H), 2.26 (s, 3 H).
^{13}C NMR (126 MHz, $CDCl_3$) δ ppm 143.0, 142.1, 124.5, 123.0, 120.2, 113.0, 15.4.

[3] Chakraborti, A. K.; Shivani, *J. Org. Chem.* **2006**, *71*, 5785.
[4] Lamande, L.; Boyer, D.; Munoz, A. *J. Organomet.Chem.* **1987**, *329*, 1.



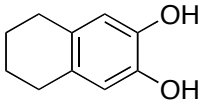
3c: 3,4-Dihydroxytoluene[5]

^{1}H NMR (500 MHz, $CDCl_3$) δ ppm 6.76 (d, *J*=8.07 Hz, 1 H), 6.70 (d, *J*=1.47 Hz, 1 H), 6.61 (dd, *J*=8.07, 1.28 Hz, 1 H), 5.03 (br. s., 2 H), 2.25 (s, 3 H).
^{13}C NMR (126 MHz, $CDCl_3$) δ ppm 143.3, 141.0, 131.0, 121.4, 116.2, 115.3, 20.7.



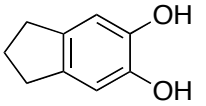
3d: 4-Methoxy-1,2-phenylene diacetate[6]

^{1}H NMR (500 MHz, $CDCl_3$) δ ppm 7.08 (d, *J*=8.99 Hz, 1 H), 6.78 (dd, *J*=8.99, 2.93 Hz, 1 H), 6.73 (d, *J*=2.75 Hz, 1 H), 3.78 (s, 3 H), 2.28 (s, 3 H), 2.27 (s, 3 H).
^{13}C NMR (126 MHz, $CDCl_3$) δ ppm 168.7, 168.2, 157.7, 142.5, 135.6, 123.6, 111.9, 109.1, 55.7, 20.63, 20.58.



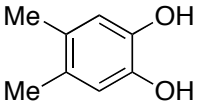
3e: 2,3-Dihydroxy-5,6,7,8-tetrahydronaphthalene[7]

^{1}H NMR (500 MHz, $CDCl_3$) δ ppm 6.57 (s, 2 H), 5.00 (br. s., 2 H), 2.59 - 2.69 (m, 4 H), 1.69 - 1.79 (m, 4 H).
^{13}C NMR (126 MHz, $CDCl_3$) δ ppm 141.2, 129.6, 115.6, 28.7, 23.3.



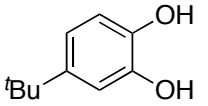
3f: 5,6-Dihydroxyindan[7]

^{1}H NMR (500 MHz, CD_3OD) δ ppm 6.62 (s, 2 H), 2.73 (t, *J*=7.24 Hz, 4 H), 1.99 (s, 2 H)
^{13}C NMR (126 MHz, CD_3OD) δ ppm 143.3, 134.6, 110.7, 32.0, 25.6.



3g: 4,5-Dimethylcatechol[8]

^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 6.66 (s, 2 H), 4.95 (br. s., 2 H), 2.14 (s, 6 H).
^{13}C NMR (101 MHz, $CDCl_3$) δ ppm 141.0, 129.0, 116.9, 19.0.

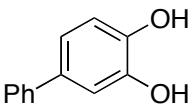


3h: 4-*tert*-Butylpyrocatechol[9]

^{1}H NMR (500 MHz, $CDCl_3$) δ ppm 6.92 (d, *J*=2.02 Hz, 1 H), 6.76 - 6.85 (m, 2 H), 5.21 (s, 1 H), 5.10 (s, 1 H), 1.27 (s, 9 H).
^{13}C NMR (126 MHz, $CDCl_3$) δ ppm 144.8, 143.0, 140.9, 117.7, 114.9, 113.0, 34.2, 31.5.

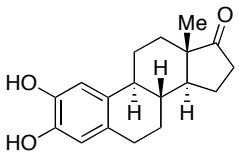
---

[5] Chernyak, N.; Dudnik, A. S.; Huang, C.; Gevorgyan, V. *J. Am. Chem. Soc.* **2010**, *132*, 8270.
[6] Magdziak, D.; Rodriguez, A. A.; Van De Water, R. W.; Pettus, T. R. R. *Org. Lett.* **2002**, *4*, 285.
[7] Ozaki, Y.; Oshio, I.; Ohsuga, Y.; Kaburagi, S.; Sung, Z.-Z.; Kim, S.-W. *Chem. Pharm. Bull.* **1991**, *39*, 1132.
[8] Scharf, H.-D.; Kuesters, W. *Chem. Ber.* **1972**, *105*, 564.



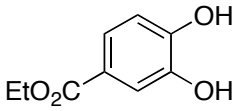
3i: 4-Phenylcatechol[7]

^{1}H NMR (400 MHz, CD_3CN) δ ppm 7.53 - 7.61 (m, 2 H), 7.41 (t, *J*=7.67 Hz, 2 H), 7.26 - 7.33 (m, 1 H), 7.12 (d, *J*=2.19 Hz, 1 H), 7.03 (dd, *J*=8.26, 2.27 Hz, 1 H), 6.90 (d, *J*=8.18 Hz, 1 H), 6.80 (br. s., 2 H).
^{13}C NMR (101 MHz, CD_3CN) δ ppm 144.8, 144.3, 140.7, 133.4, 128.8, 126.7, 126.4, 118.8, 115.6, 113.9.



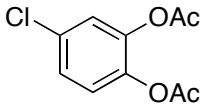
3j: 2-Hydroxyestrone[10]

^{1}H NMR (500 MHz, $CDCl_3$) δ ppm 6.81 (s, 1 H), 6.61 (s, 1 H), 5.31 (br. s., 2 H), 2.75 - 2.83 (m, 2 H), 2.51 (dd, *J*=19.35, 8.16 Hz, 1 H), 2.25 - 2.32 (m, 1 H), 2.11 - 2.25 (m, 2 H), 2.01 - 2.08 (m, 1 H), 1.91 - 2.01 (m, 2 H), 1.35 - 1.66 (m, 6 H), 0.91 (s, 3 H).
^{13}C NMR (126 MHz, $CDCl_3$) δ ppm 221.6, 141.6, 141.5, 132.3, 129.0, 115.5, 112.5, 50.4, 48.1, 44.0, 38.3, 35.9, 31.6, 28.8, 26.6, 26.0, 21.6, 13.9.



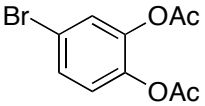
3k: Ethyl 3,4-dihydroxybenzoate[11]

^{1}H NMR (500 MHz, CD_3CN) δ ppm 7.44 (s, 1 H), 7.45 (s, 1 H), 7.14 (br. s., 2 H), 6.88 (d, *J*=7.89 Hz, 1 H), 4.27 (q, *J*=7.15 Hz, 2 H), 1.33 (t, *J*=7.06 Hz, 3 H).
^{13}C NMR (126 MHz, $CDCl_3$) δ ppm 167.2, 148.8, 143.1, 123.8, 122.7, 116.7, 114.8, 61.2, 14.3.
HRMS (EI) calcd. for $C_9H_9O_4$ $[M-H]^+$: 181.05009. Found: 181.04980.



3l(**3m**): 4-Chlorocatechol diacetate[12]

^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 7.22 - 7.27 (m, 1 H), 7.22 (s, 1 H), 7.11 - 7.15 (m, 1 H), 2.291 (s, 3 H), 2.287 (s, 3 H).
^{13}C NMR (126 MHz, $CDCl_3$) δ ppm 168.0, 167.8, 142.5, 140.9, 131.5, 126.7, 124.3, 124.0, 20.6.
HRMS (EI) calcd. for $C_{10}H_9O_4Cl$ $[M]^+$: 228.01894. Found: 228.01841.



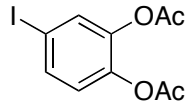
3n: 4-Bromocatechol diacetate[13]

^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 7.34 - 7.42 (m, 2 H), 7.04 -

---

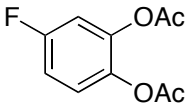
[9] Kamitori, Y.; Hojo, M.; Masuda, R.; Izumi, T.; Tsukamoto, S. *J. Org. Chem.* **1984**, *49*, 4161.
[10] (a) Fishman, J.; Liang, J. S. *Tetrahedron* **1968**, *24*, 2199. (b) Gelbke, H. P.; Haupt, O.; Knuppen, R. *Steroids* **1973**, *21*, 205.
[11] (a) Yamabuki, K.; Isobe, Y.; Onimura, K.; Oishi, T. *Chem. Lett.* **2007**, *36*, 1196. (b) Sawai, Y.; Moon, J.-H.; Sakata, K.; Watanabe, N. *J. Agric. Food Chem.* **2005**, *53*, 3598.
[12] Willstätter, R.; Müller, F. *Chem. Ber.* **1911**, *44*, 2171.
[13] Ziegler Jr., C. B.; Heck, R. F. *J. Org. Chem.* **1978**, *43*, 2949.

7.10 (m, 1 H), 2.29 (d, *J*=0.73 Hz, 6 H).
^{13}C NMR (126 MHz, $CDCl_3$) δ ppm 167.9, 167.8, 142.7, 141.5, 129.7, 126.8, 124.7, 118.7, 20.62, 20.58.
HRMS (EI) calcd. for $C_{10}H_9O_4Br$ $[M]^+$: 271.96842. Found: 271.96904.



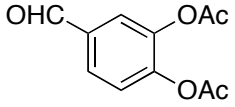
3o: 4-Iodocatechol diacetate

^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 7.57 (dd, *J*=8.48, 2.05 Hz, 1 H), 7.53 (d, *J*=2.05 Hz, 1 H), 6.94 (d, *J*=8.48 Hz, 1 H), 2.28 (s, 6 H).
^{13}C NMR (126 MHz, $CDCl_3$) δ ppm 167.9, 167.8, 142.7, 142.3, 135.7, 132.6, 125.1, 89.2, 20.64, 20.57.
HRMS (EI) calcd. for $C_{10}H_9O_4I$ $[M]^+$: 319.95459. Found: 319.95631.



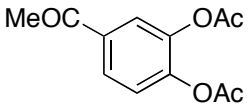
3p: 4-Fluorocatechol diacetate

^{1}H NMR (500 MHz, $CDCl_3$) δ ppm 7.12 - 7.17 (m, 1 H), 6.94 - 6.99 (m, 2 H), 2.29 (s, 3 H), 2.28 (s, 3 H).
^{13}C NMR (126 MHz, $CDCl_3$) δ ppm 168.2, 167.8, 159.9 (d, *J*=246.9 Hz), 142.6 (d, *J*=11.1 Hz), 138.3, 124.0 (d, *J*=9.2 Hz), 113.3 (d, *J*=23.1 Hz), 111.3 (d, *J*=25.9 Hz), 20.6, 20.5.



3q: 3,4-Diacetoxybenzaldehyde[14]

^{1}H NMR (500 MHz, $CDCl_3$) δ ppm 9.96 (s, 1 H), 7.79 (dd, *J*=8.25, 2.02 Hz, 1 H), 7.74 (d, *J*=1.83 Hz, 1 H), 7.39 (d, *J*=8.25 Hz, 1 H), 2.33 (s, 6 H).
^{13}C NMR (126 MHz, $CDCl_3$) δ ppm 190.0, 167.9, 167.5, 147.0, 142.8, 134.8, 128.2, 124.4, 124.3, 20.7, 20.6.
HRMS (EI) calcd. for $C_{11}H_{10}O_5$ $[M]^+$: 222.05282. Found: 222.05347.

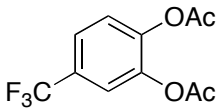


3r: 3,4-Diacetoxyacetophenone[15]

^{1}H NMR (500 MHz, $CDCl_3$) δ ppm 7.85 (dd, *J*=8.44, 2.02 Hz, 1 H), 7.78 (d, *J*=2.02 Hz, 1 H), 7.30 (d, *J*=8.44 Hz, 1 H), 2.58 (s, 3 H), 2.31 (d, *J*=2.02 Hz, 6 H).
^{13}C NMR (126 MHz, $CDCl_3$) δ ppm 196.0, 168.1, 167.7, 146.1, 142.3, 135.6, 126.9, 123.7, 123.7, 26.6, 20.7, 20.6.
HRMS (EI) calcd. for $C_{12}H_{12}O_5$ $[M]^+$: 236.06847. Found: 236.06881.

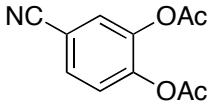
---

[14] Corda, L.; Fadda, A. M.; Maccioni, A.; Maccioni, A. M.; Podda, G. *J. Heterocycl. Chem.* **1988**, *25*, 311.
[15] Birnbaum, L. S.; Powell, G. *J. Org. Chem.* **1939**, *4*, 139.



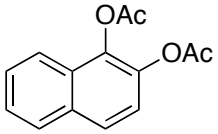
3s: 4-(Trifluoromethyl)-1,2-phenylene diacetate

^{1}H NMR (500 MHz, $CDCl_3$) δ ppm 7.53 (dd, *J*=8.44, 1.47 Hz, 1 H), 7.49 (d, *J*=2.02 Hz, 1 H), 7.34 (d, *J*=8.44 Hz, 1 H), 2.32 (s, 6 H).
^{13}C NMR (126 MHz, $CDCl_3$) δ ppm 167.7, 167.6, 144.9, 142.3, 129.0 (q, *J*=33.29 Hz), 124.1, 123.7 (d, *J*=3.7 Hz), 123.2 (q, *J*=271.88 Hz), 121.2 (d, *J*=3.7 Hz), 20.6, 20.5.
HRMS (EI) calcd. for $C_{11}H_9O_4F_3$ $[M]^+$: 262.04530. Found: 262.04627.



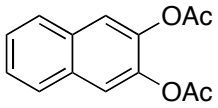
3t: 3,4-Diacetoxy-benzonitrile[16]

^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 7.56 (dd, *J*=8.33, 1.90 Hz, 1 H), 7.53 (d, *J*=1.75 Hz, 1 H), 7.33 (d, *J*=8.33 Hz, 1 H), 2.32 (s, 6 H).
^{13}C NMR (126 MHz, $CDCl_3$) δ ppm 167.6, 167.4, 146.1, 142.6, 130.7, 127.6, 124.8, 117.4, 110.5, 20.65, 20.55.
HRMS (EI) calcd. for $C_{11}H_9O_4N$ $[M]^+$: 219.05316. Found: 219.05379.



3u: 1,2-Diacetoxy-naphthalene[17]

^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 7.86 (t, *J*=8.62 Hz, 2 H), 7.78 (d, *J*=8.99 Hz, 1 H), 7.48 - 7.58 (m, 2 H), 7.35 (d, *J*=8.99 Hz, 1 H), 2.47 (s, 3 H), 2.35 (s, 3 H).
^{13}C NMR (126 MHz, $CDCl_3$) δ ppm 168.5, 168.2, 139.2, 137.0, 132.3, 128.0, 127.7, 127.0, 126.7, 126.2, 121.7, 121.2, 20.8, 20.5.



3v: 2,3-Diacetoxy-naphthalene[18]

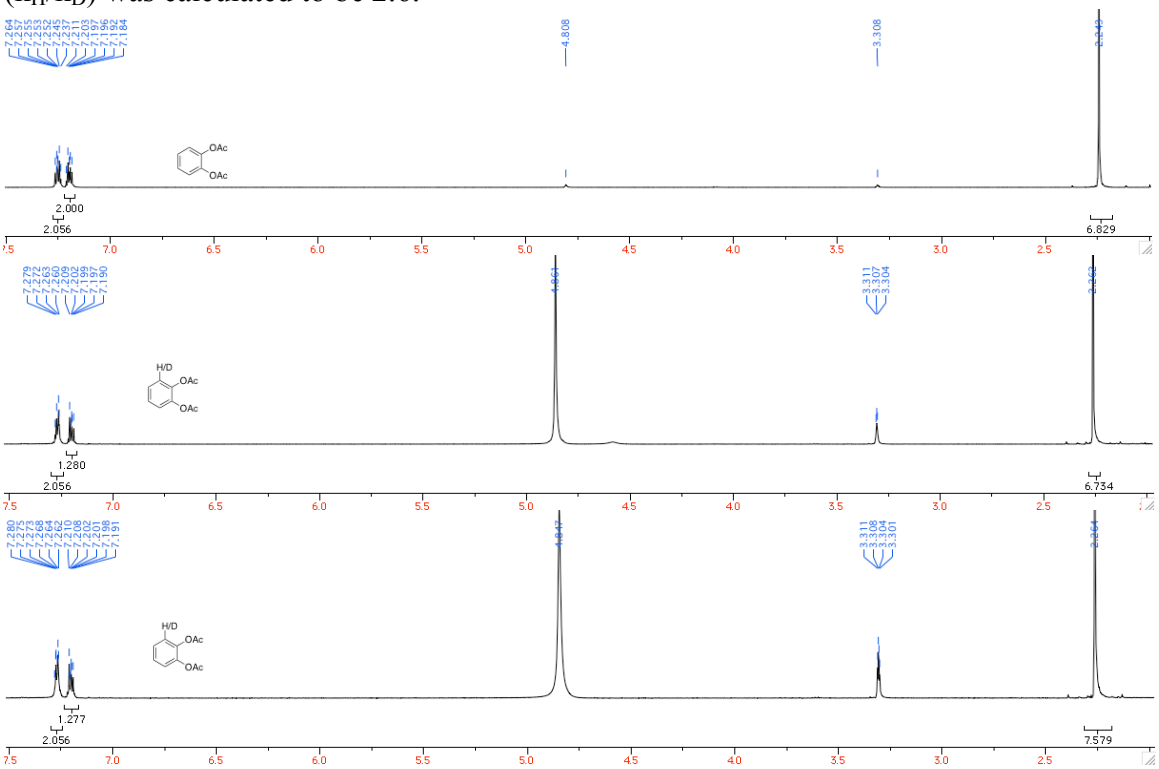
^{1}H NMR (500 MHz, $CDCl_3$) δ ppm 7.80 (dd, *J*=6.24, 3.30 Hz, 2 H), 7.67 (s, 2 H), 7.48 (dd, *J*=6.24, 3.30 Hz, 2 H), 2.35 (s, 6 H).
^{13}C NMR (126 MHz, $CDCl_3$) δ ppm 168.5, 141.0, 131.6, 127.5, 126.4, 120.9, 20.7.

[16] Hoesch, K.; v. Zarzecki, T. *Chem. Ber.* **1917**, *50*, 462.
[17] Smith, J. G.; Chu, N. G. *J. Org. Chem.* **1981**, *46*, 4083.
[18] Chen, C.-L.; Hosterttler, F. D. *Tetrahedron* **1969**, *25*, 3223.

Part III: Mechanistic Studies

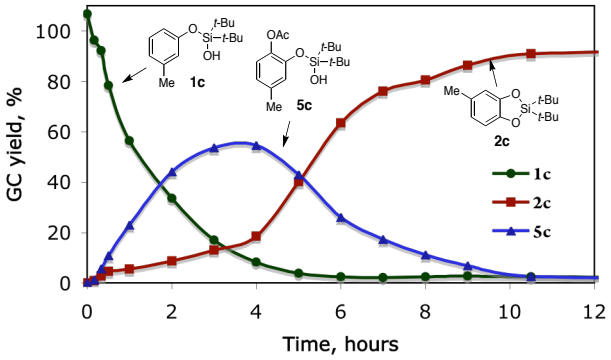
Determination of Intramolecular Kinetic Isotope Effect:

The KIE measurements were done as following. Two oven dried 2.5 ml Wheaton V-vial, containing a stirring bar, were charged with silanol **1a-*d*$_1$** (0.2 mmol), Pd(OPiv)$_2$ (3.1 mg, 0.01 mmol), and PhI(OAc)$_2$ (0.4 mmol) under N_2 atmosphere. 2 ml of dry toluene was added via syringes and the reaction vessel was capped with pressure screw cap. The reaction mixture was heated at 100 °C for 16 h. The resulting mixture was cooled down to room temperature and filtered through a celite plug with the aid of EtOAc. To the residue THF (1 ml) and TBAF (0.4 ml, 2 equiv) was added. The reaction mixture was stirred at room temperature for 2 h. Upon completion of desilylation, Ac_2O (189 µl) and pyridine (160 µl) were added into the same pot. The reaction mixture was stirred overnight. The volatile was removed under reduced pressure. The residues were purified by column chromatography on a silica gel. ^{1}H NMR (500 MHz, CD_3OD) analyses of the isolated mixtures of **4a** and **4a-*d*$_1$** showed an average of 28% hydrogen content at 7.18 – 7.21 ppm (72% ^{2}H-incorporation). Based on these results, the kinetic isotope effect (k_H/k_D) was calculated to be 2.6.



Reaction monitoring:

An oven dried 2.5 ml Wheaton V-vial, containing a stirring bar, was charged with silanol **1c** (53.2 mg, 0.2 mmol), $Pd(OPiv)_2$ (3.1 mg, 5 mol%), tetradecane (26 µl, 0.1 mmol, internal standard), and $PhI(OAc)_2$ (129 mg, 0.4 mmol) under N_2 atmosphere. 2 ml of dry toluene was added via syringes and the reaction vessel was capped with pressure screw cap. The reaction mixture was heated at 100 °C. Aliquots (~10 µl) were removed from the reaction mixture periodically and analyzed by GC/MS. Both starting material and products were calibrated with internal standard.



Synthesis of acetoxylated product 5c

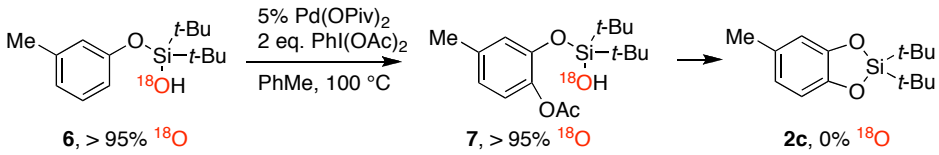
An oven dried 10 ml Wheaton V-vial, containing a stirring bar, was charged with silanol **1c** (266 mg, 1.0 mmol), $Pd(OPiv)_2$ (15.5 mg, 5 mol%), and $PhI(OAc)_2$ (645 mg, 2.0 mmol) under N_2 atmosphere. 10 ml of dry toluene was added via syringes and the reaction vessel was capped with pressure screw cap. The reaction mixture was heated at 100 °C for 3 h. The reaction mixture was cooled down to rt, filtered through a celite plug, and concentrated to dryness. The residue was purified by silica gel column chromatography to afford the product **5c** 142.4 mg (44%) along with the recovery of starting material **1c** 74.4 mg (28%).

5c: ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 7.02 (d, *J*=1.32 Hz, 1 H), 6.89 (d, *J*=8.18 Hz, 1 H), 6.73 (dd, *J*=8.04, 1.32 Hz, 1 H), 2.44 (br. s., 1 H), 2.28 (s, 3 H), 2.28 (s, 3 H), 1.06 (s, 18 H); ^{13}C NMR (126 MHz, $CDCl_3$) δ ppm 169.1, 147.0, 138.5, 136.7, 122.7, 122.0, 121.2, 27.2, 21.1, 20.8, 20.6.

Preparation of ^{18}O-Labeled Silanol 6

To a solution of *t*-Bu_2SiBr_2 (333mg, 1.1 mmol) in dry DMF (3 mL) imidazole (150 mg, 2.2 mmol) in dry DMF (1 mL) was added at 0 °C under argon atmosphere and stirred for 30 min at room temperature. The reaction mixture was then cooled down to 0°C and a solution of *m*-cresol (1.0 mmol) in dry DMF (1 mL) was added slowly. The reaction mixture was warmed up to RT and stirred overnight, then treated with $H_2{}^{18}O$ (36 μL). The reaction mixture was stirred for additional 1 h at room temperature. The solvent was evaporated under reduced pressure. The residue was purified by kugelrohr distillation (~1.3 Torr, 145-150°C) to give 160 mg pure product (60%). ^{1}H NMR (500 MHz, $CDCl_3$) δ ppm 7.11 (td, *J* = 7.4, 1.6 Hz, 1H), 6.79-6.81 (m, 2H), 6.76 (d, *J* = 7.7 Hz, 1H), 2.30 (s, 3H), 2.28 (s, 1H), 1.08 (s, 18H).

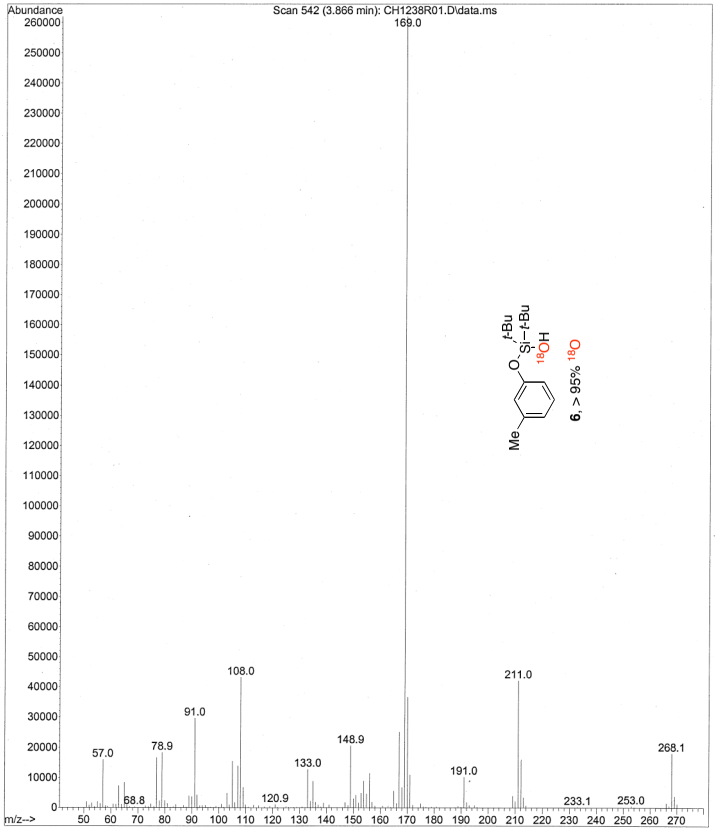
GC/MS trace of oxygenation of ^{18}O-labeled silanol 6



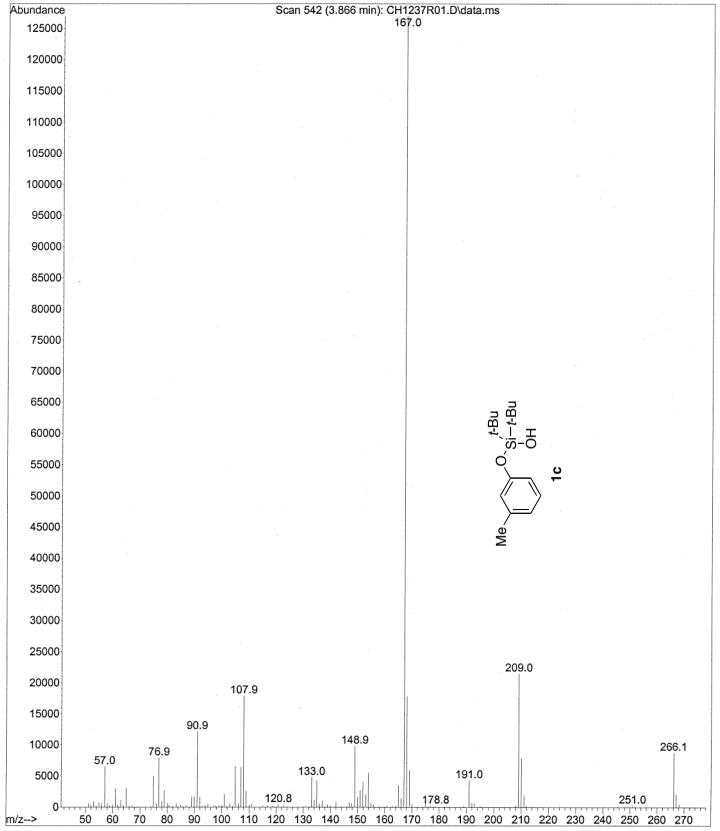
6, > 95% ^{18}O **7**, > 95% ^{18}O **2c**, 0% ^{18}O

An oven dried 2.5 ml Wheaton V-vial, containing a stirring bar, was charged with ^{18}O-labeled silanol **6** (26.8 mg, 0.1 mmol), $Pd(OPiv)_2$ (1.6 mg, 5 mol%), and $PhI(OAc)_2$ (65 mg, 0.2 mmol) under N_2 atmosphere. 1 ml of dry toluene was added via syringes and the reaction vessel was capped with pressure screw cap. The reaction mixture was heated at 100 °C. The reaction was monitored by GC/MS periodically. During the reaction, the acetoxylated product with ^{18}O isotope was formed and gradually declined. The abundance of ^{18}O in both starting material **6** and acetoxylated product **7** remained constant during the reaction. Cyclization product **2c** was formed with no ^{18}O incorporation. The following three pages are the comparison of GC/MS spectra between ^{18}O-labeled and normal starting materials and products.

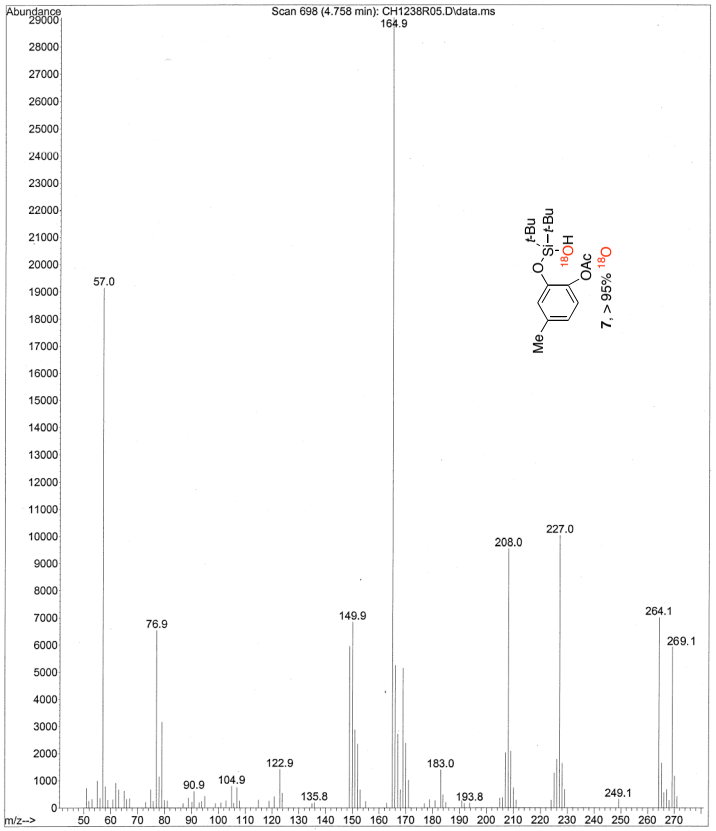
```
File       :C:\msdchem\1\data\Common\CH1238R01.D
Operator   : BG
Acquired   : 24 Aug 2011  17:35     using AcqMethod F100.M
Instrument :   GCMS1
Sample Name:
Misc Info  : 2min@rt
Vial Number: 27
```



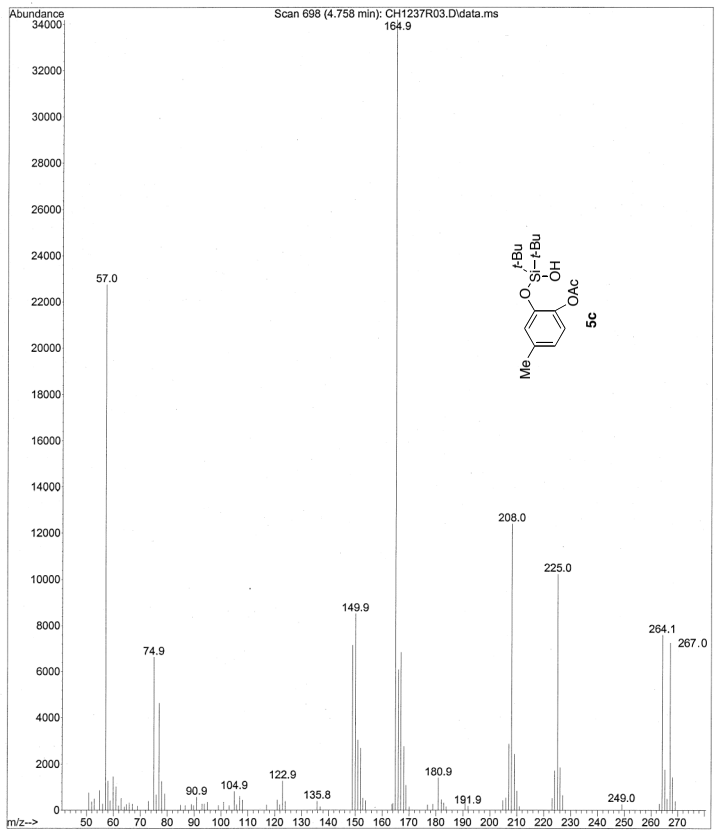

```
File       :C:\msdchem\1\data\Common\CH1237R01.D
Operator   : BG
Acquired   : 24 Aug 2011  12:17     using AcqMethod F100.M
Instrument :   GCMS1
Sample Name:
Misc Info  : 1h5min
Vial Number: 9
```



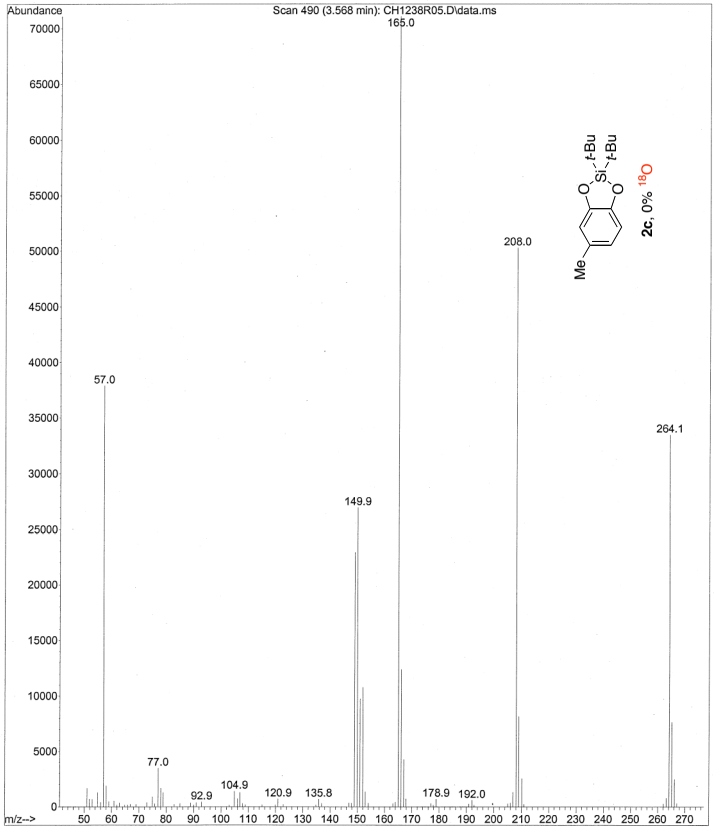
```
File       :C:\msdchem\1\data\Common\CH1238R05.D
Operator   : BG
Acquired   : 24 Aug 2011  21:28     using AcqMethod F100.M
Instrument :   GCMS1
Sample Name:
Misc Info  : 3.5h@100C
Vial Number: 39
```



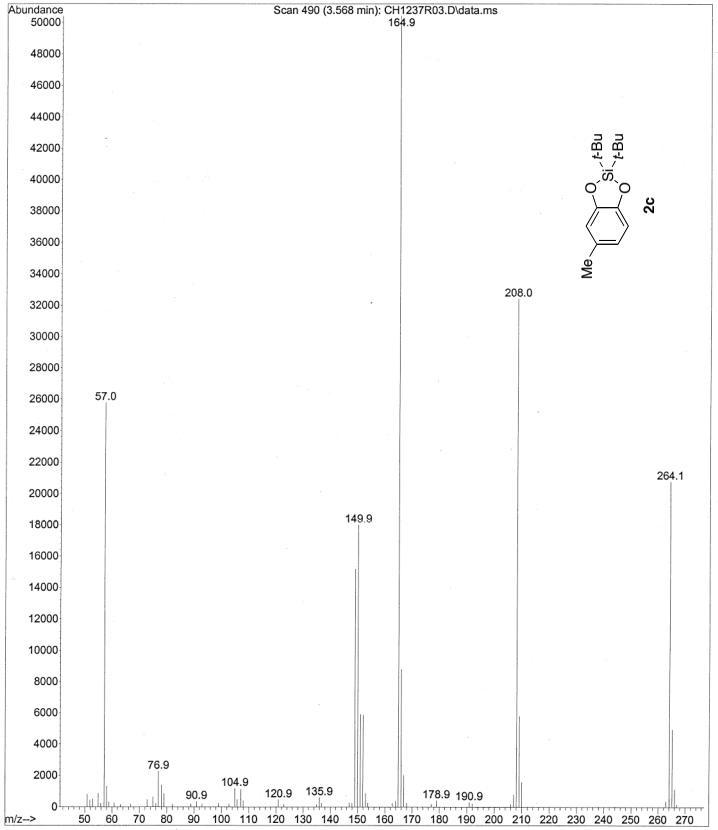

```
File       :C:\msdchem\1\data\Common\CH1237R03.D
Operator   : BG
Acquired   : 24 Aug 2011  14:38     using AcqMethod F100.M
Instrument :   GCMS1
Sample Name:
Misc Info  : 3h
Vial Number: 1
```



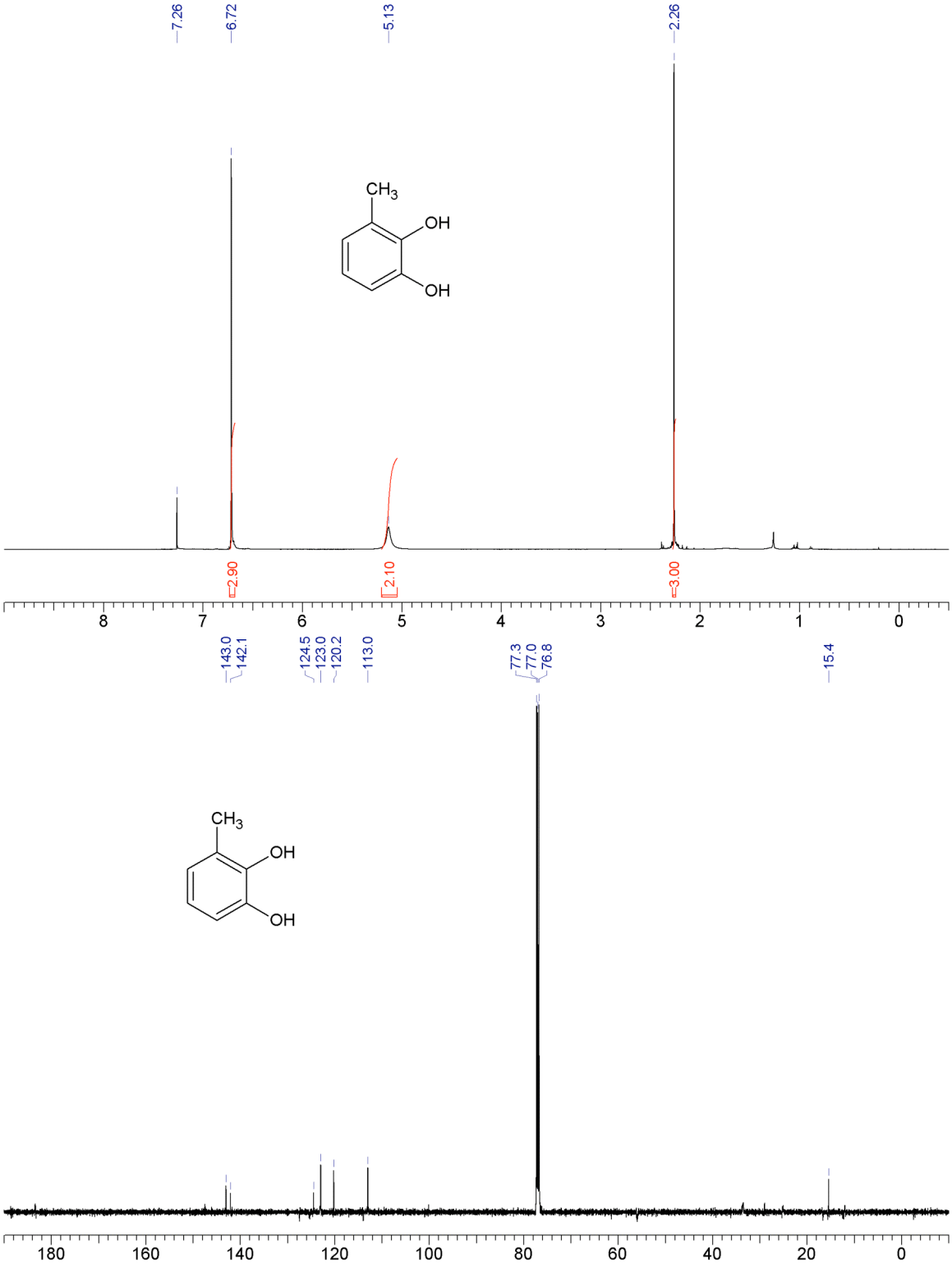
```
File       :C:\msdchem\1\data\Common\CH1238R05.D
Operator   : BG
Acquired   : 24 Aug 2011  21:28     using AcqMethod F100.M
Instrument :   GCMS1
Sample Name:
Misc Info  : 3.5h@100C
Vial Number: 39
```



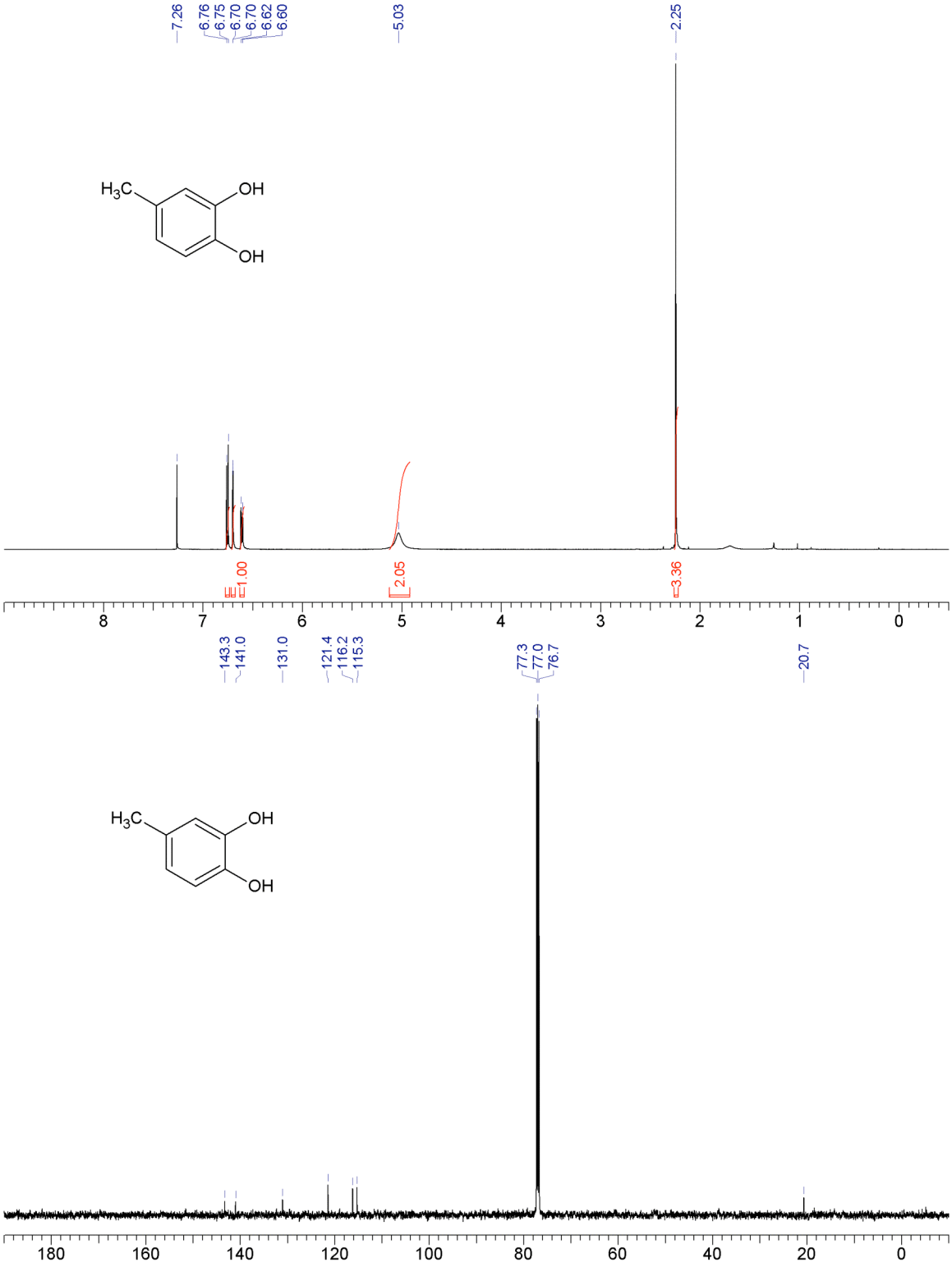

```
File       :C:\msdchem\1\data\Common\CH1237R03.D
Operator   : BG
Acquired   : 24 Aug 2011  14:38     using AcqMethod F100.M
Instrument :   GCMS1
Sample Name:
Misc Info  : 3h
Vial Number: 1
```



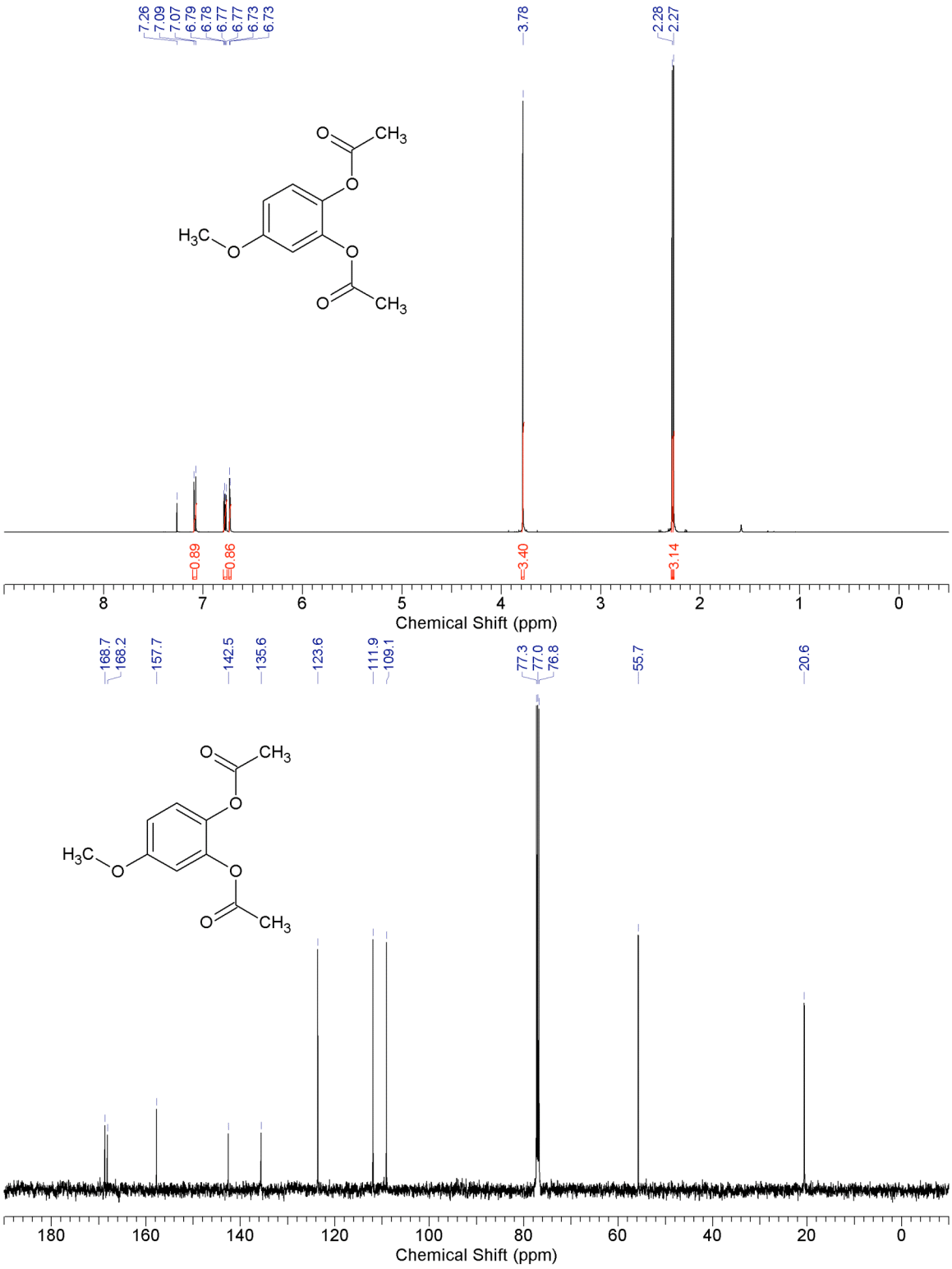
3b:


7.26
6.72
5.13
2.26
CH3
OH
OH
2.90
2.10
3.00
8
7
6
5
4
3
2
1
0
143.0
142.1
124.5
123.0
120.2
113.0
77.3
77.0
76.8
15.4
CH3
OH
OH
180
160
140
120
100
80
60
40
20
0

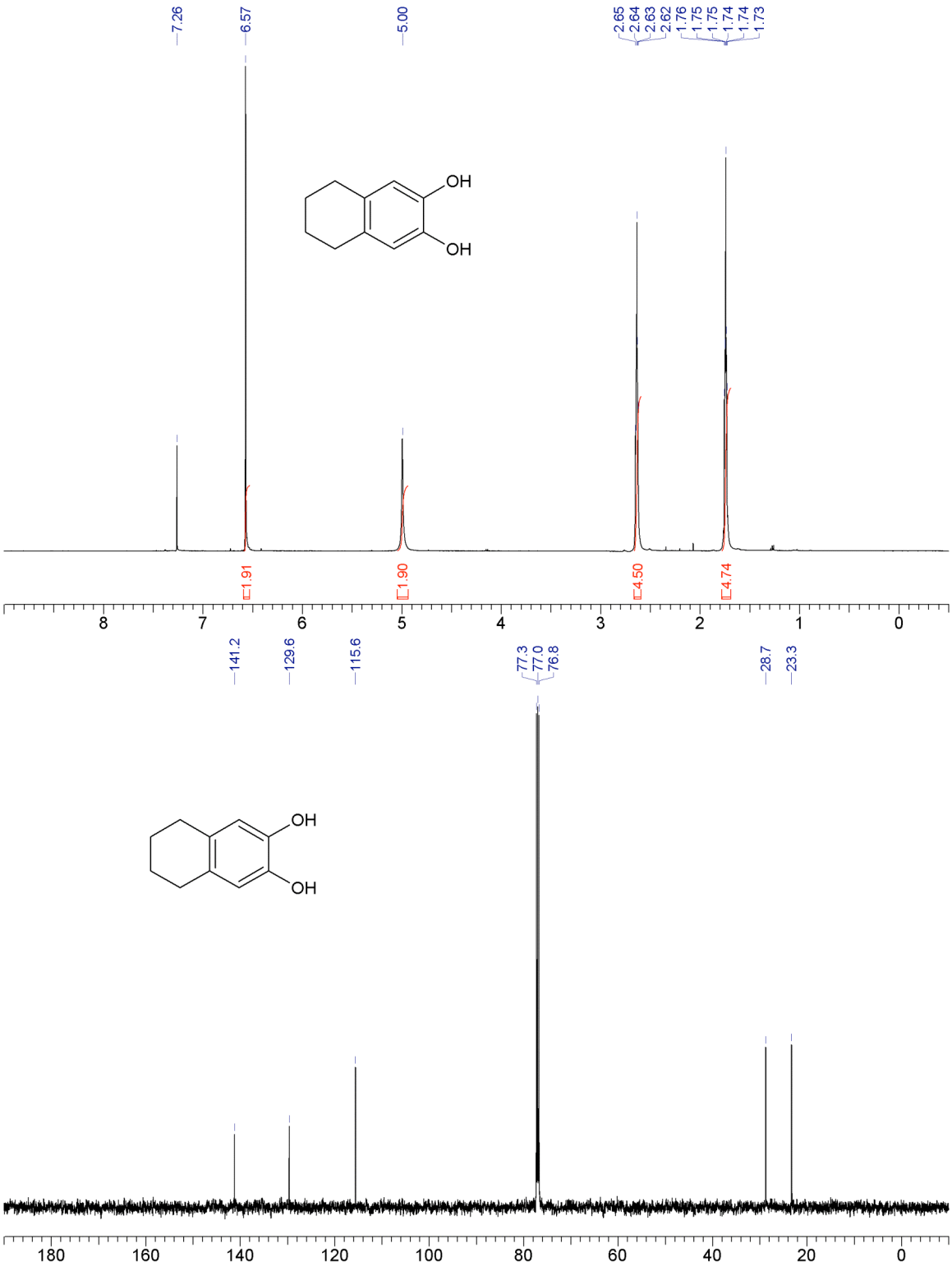
3c:


7.26
6.76
6.75
6.70
6.70
6.62
6.60
5.03
2.25
H3C
OH
OH
1.00
2.05
3.36
8
7
6
5
4
3
2
1
0
143.3
141.0
131.0
121.4
116.2
115.3
77.3
77.0
76.7
20.7
H3C
OH
OH
180
160
140
120
100
80
60
40
20
0

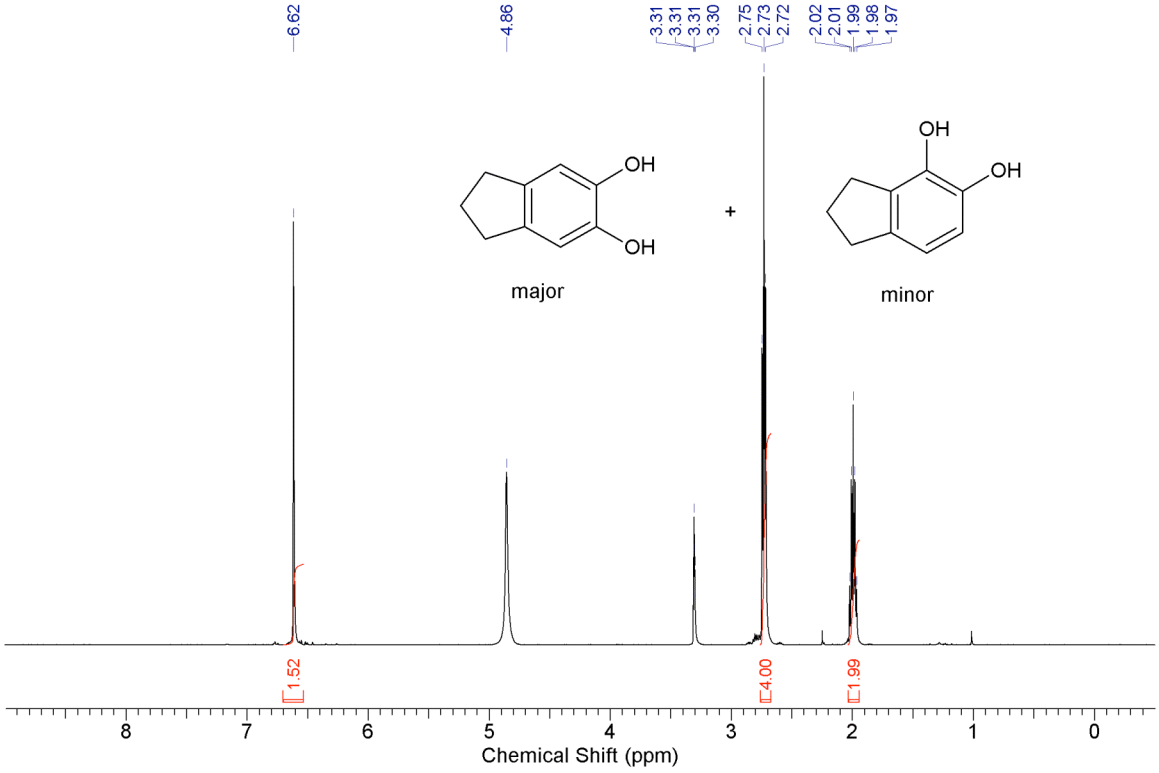
3d:

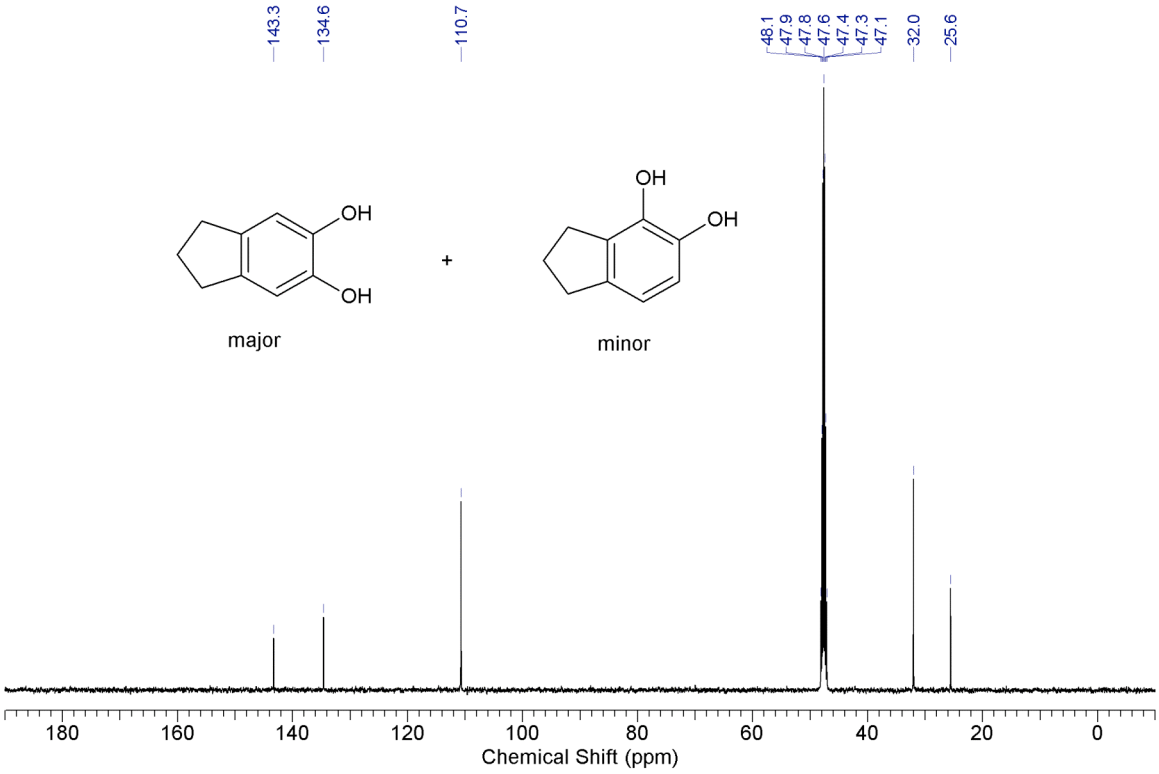

7.26
7.09
7.07
6.79
6.78
6.77
6.77
6.73
6.73
3.78
2.28
2.27
0.89
0.86
3.40
3.14
Chemical Shift (ppm)
168.7
168.2
157.7
142.5
135.6
123.6
111.9
109.1
77.3
77.0
76.8
55.7
20.6
Chemical Shift (ppm)

3e:

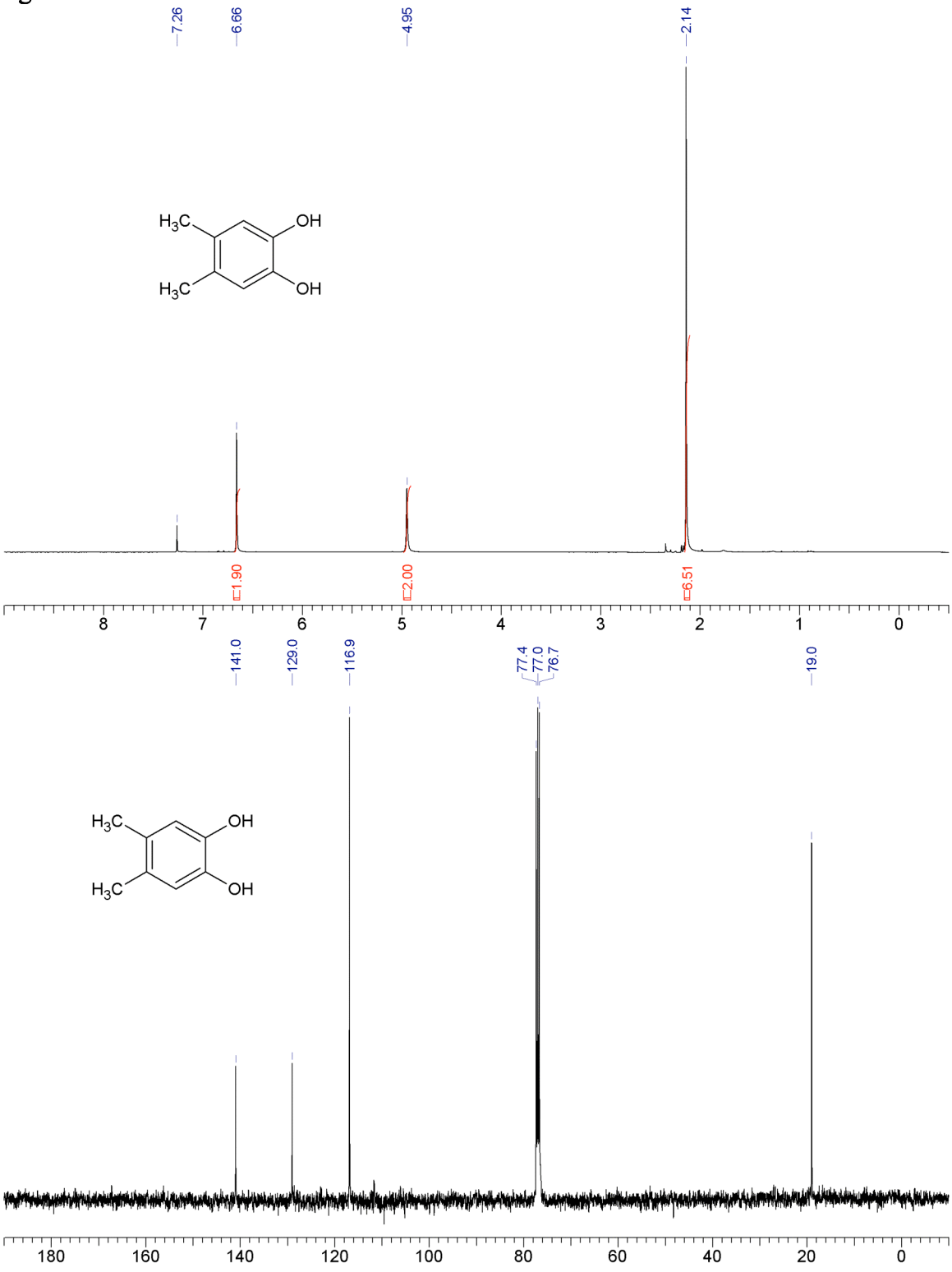

7.26
6.57
5.00
2.65
2.64
2.63
2.62
1.76
1.75
1.75
1.74
1.74
1.73
OH
OH
1.91
1.90
4.50
4.74
8
7
6
5
4
3
2
1
0
141.2
129.6
115.6
77.3
77.0
76.8
28.7
23.3
OH
OH
180
160
140
120
100
80
60
40
20
0

3f:

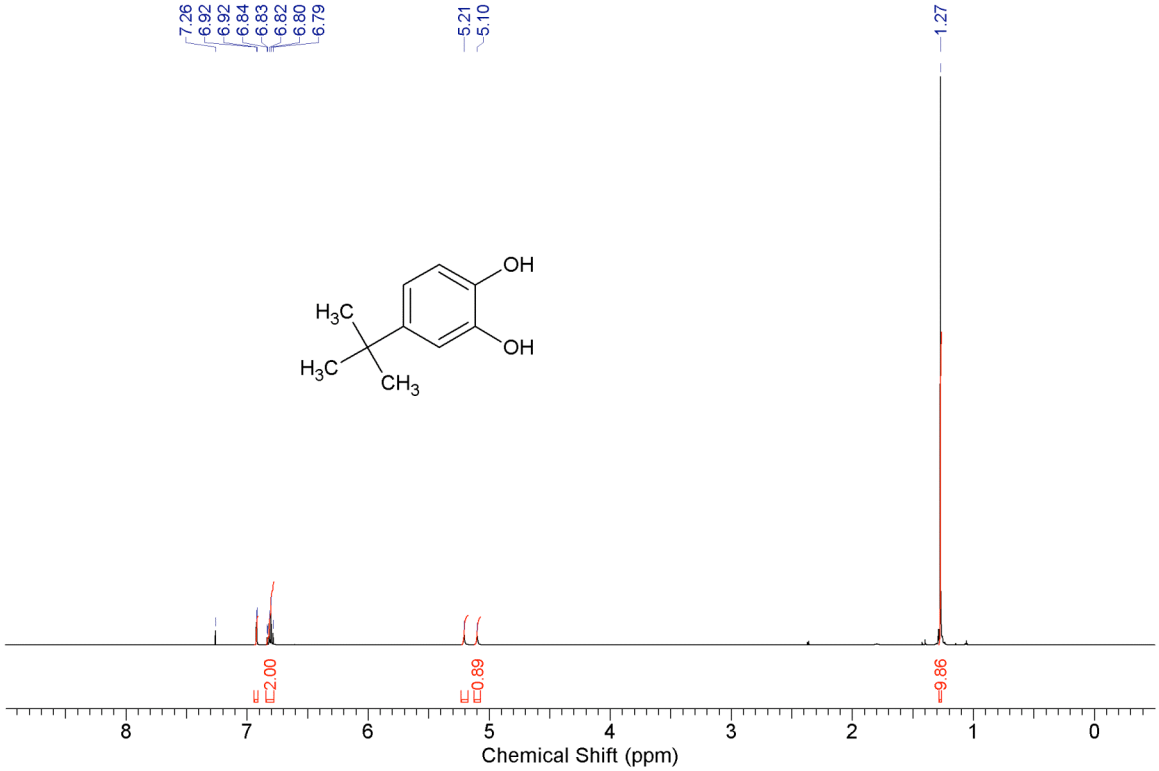

6.62
4.86
3.31
3.31
3.31
3.30
2.75
2.73
2.72
2.02
2.01
1.99
1.98
1.97
OH
OH
major
+
OH
OH
minor
1.52
4.00
1.99
8
7
6
5
4
3
2
1
0
Chemical Shift (ppm)

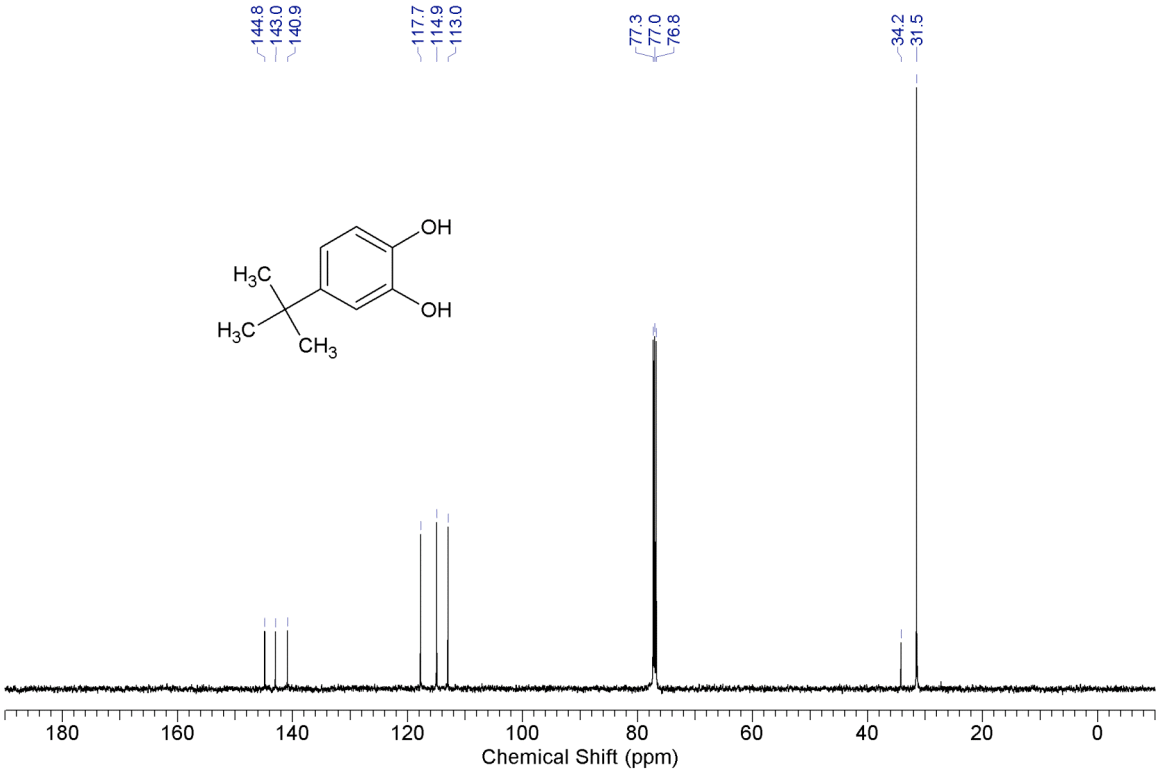

143.3
134.6
110.7
48.1
47.9
47.8
47.6
47.4
47.3
47.1
32.0
25.6
OH
OH
major
+
OH
OH
minor
180
160
140
120
100
80
60
40
20
0
Chemical Shift (ppm)

3g:

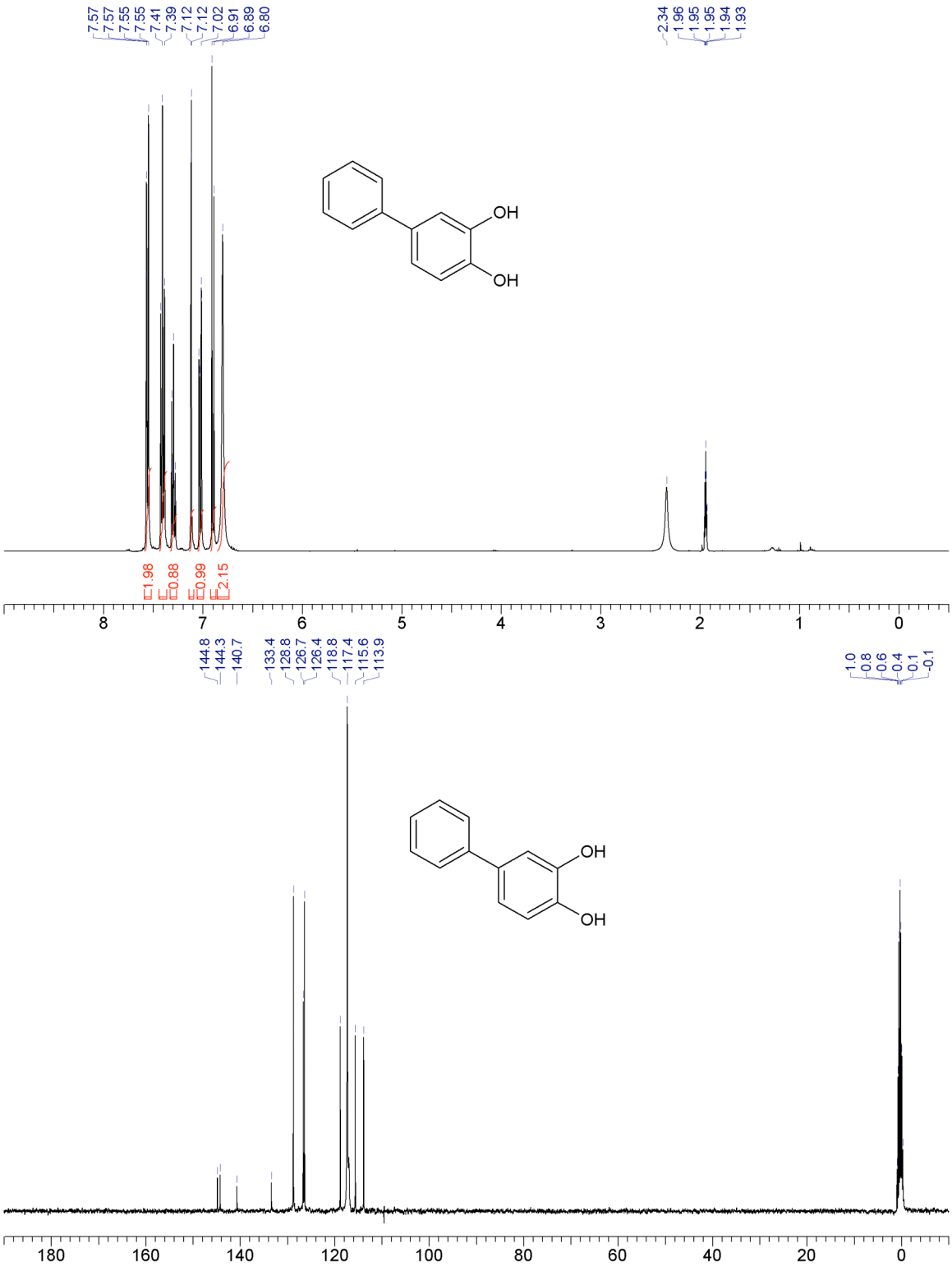

7.26
6.66
4.95
2.14
H3C
OH
H3C
OH
1.90
2.00
6.51
8
7
6
5
4
3
2
1
0
141.0
129.0
116.9
77.4
77.0
76.7
19.0
H3C
OH
H3C
OH
180
160
140
120
100
80
60
40
20
0

3h:

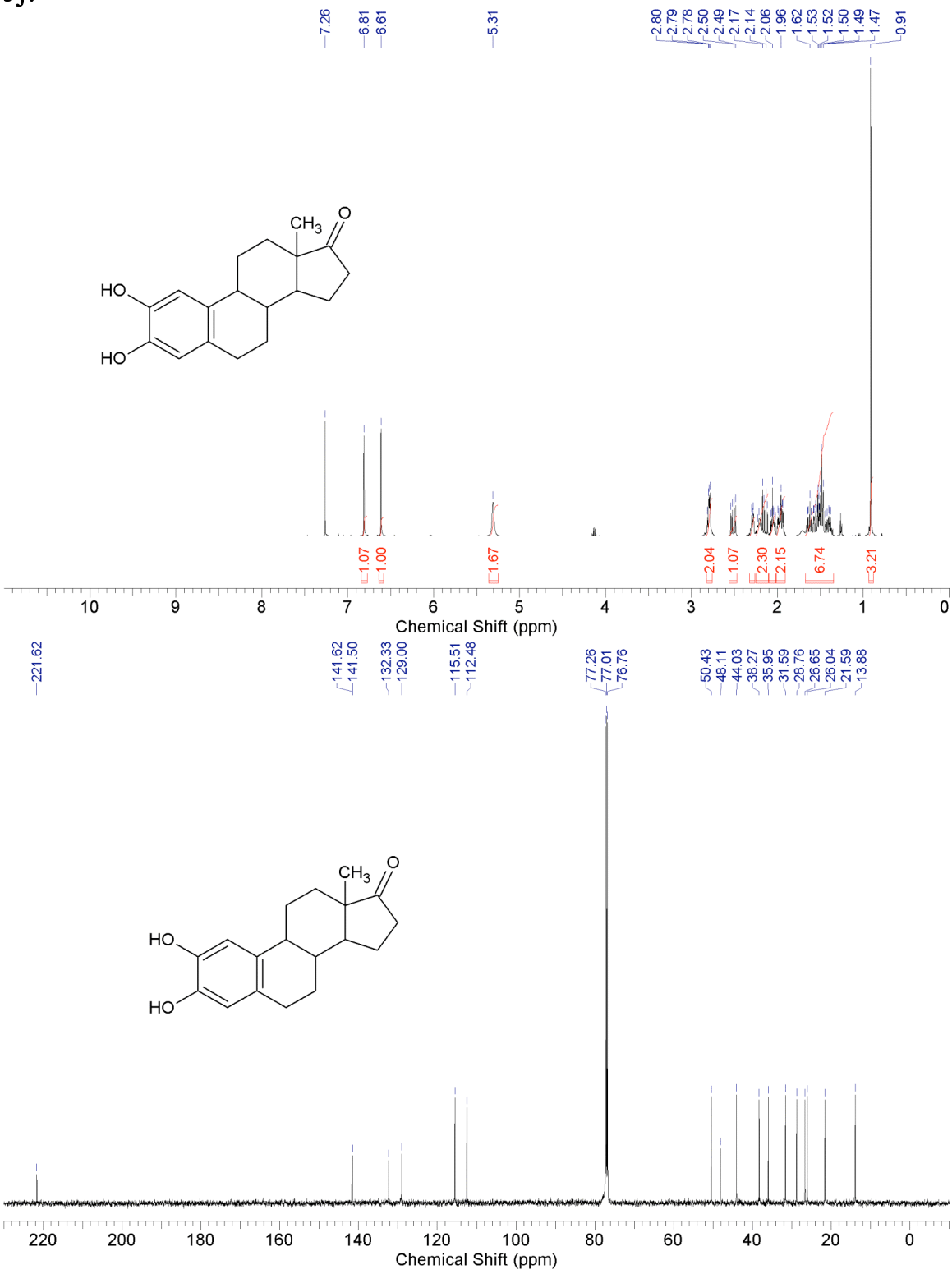

7.26
6.92
6.92
6.84
6.83
6.82
6.80
6.79
5.21
5.10
1.27
OH
OH
H3C
H3C
CH3
2.00
0.89
9.86
Chemical Shift (ppm)


144.8
143.0
140.9
117.7
114.9
113.0
77.3
77.0
76.8
34.2
31.5
OH
OH
H3C
H3C
CH3
Chemical Shift (ppm)

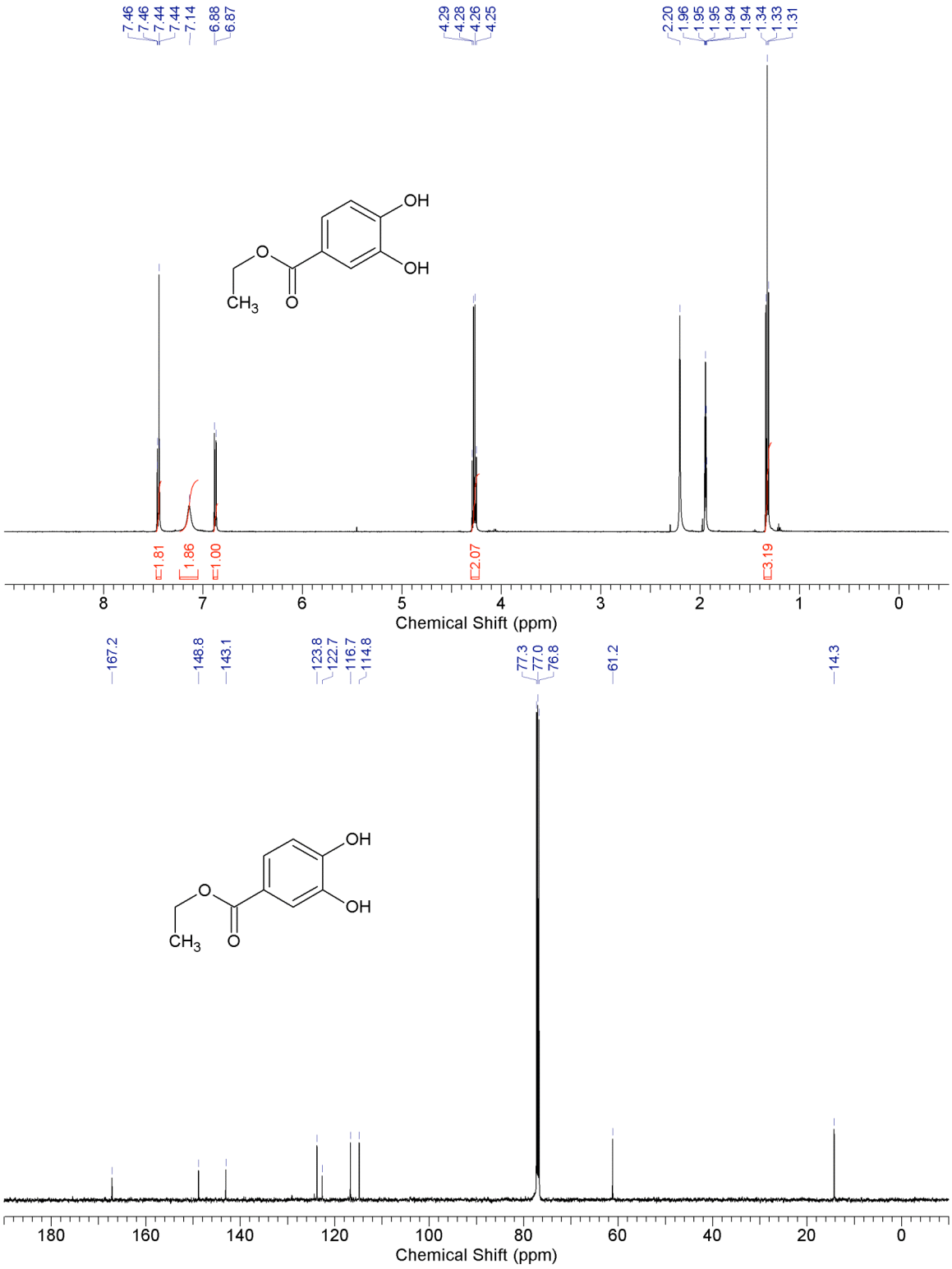
3i:


7.57
7.57
7.55
7.55
7.41
7.39
7.12
7.12
7.02
6.91
6.89
6.80
2.34
1.96
1.95
1.95
1.94
1.93
OH
OH
1.98
0.88
0.99
2.15
8
7
6
5
4
3
2
1
0
144.8
144.3
140.7
133.4
128.8
126.7
126.4
118.8
117.4
115.6
113.9
1.0
0.8
0.6
0.4
0.1
-0.1
OH
OH
180
160
140
120
100
80
60
40
20
0

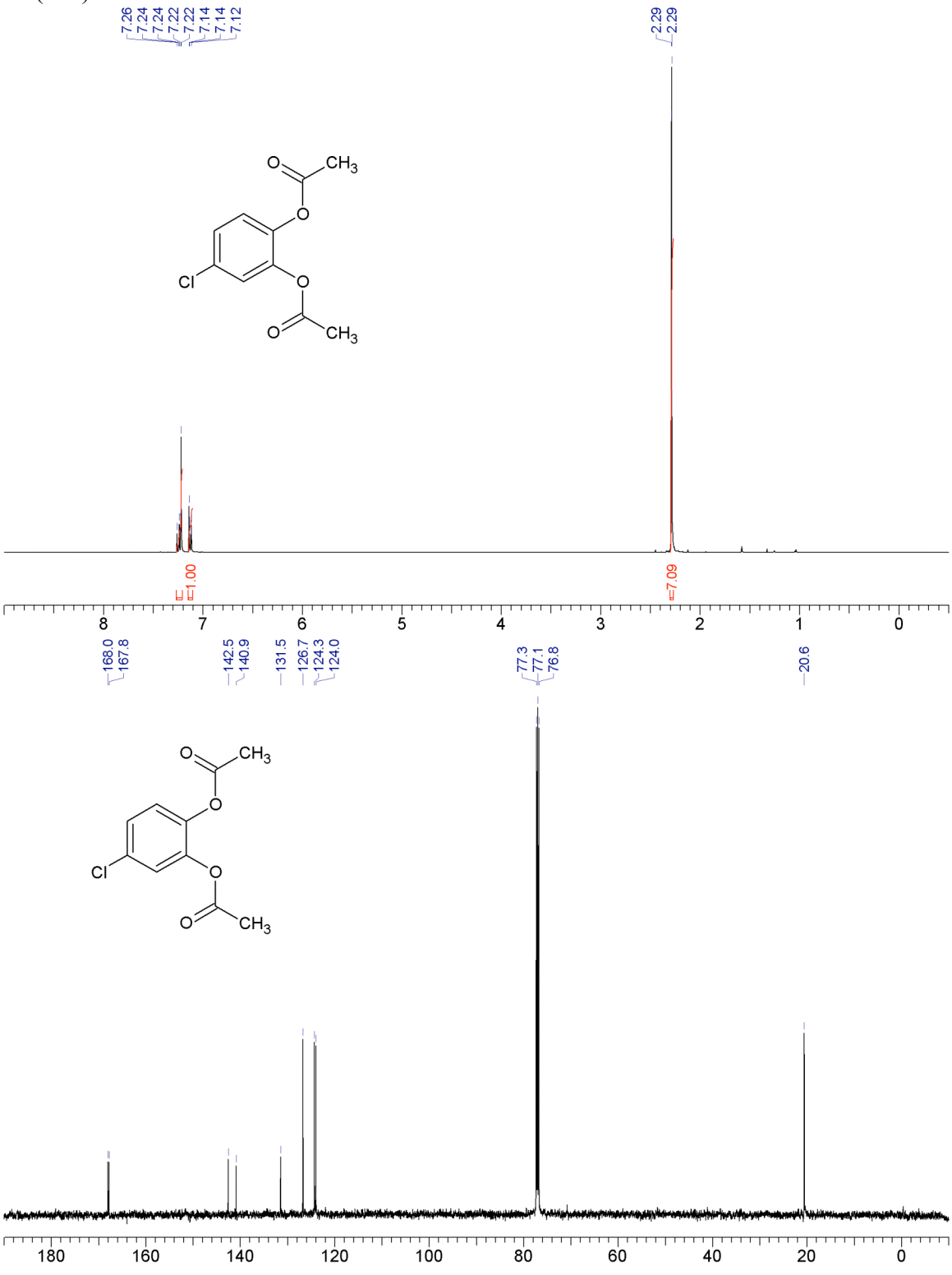
3j:


7.26
6.81
6.61
5.31
2.80
2.79
2.78
2.50
2.49
2.17
2.14
2.06
1.96
1.62
1.53
1.52
1.50
1.49
1.47
0.91
CH3
O
HO
HO
1.07
1.00
1.67
2.04
1.07
2.30
2.15
6.74
3.21
Chemical Shift (ppm)
221.62
141.62
141.50
132.33
129.00
115.51
112.48
77.26
77.01
76.76
50.43
48.11
44.03
38.27
35.95
31.59
28.76
26.65
26.04
21.59
13.88
Chemical Shift (ppm)

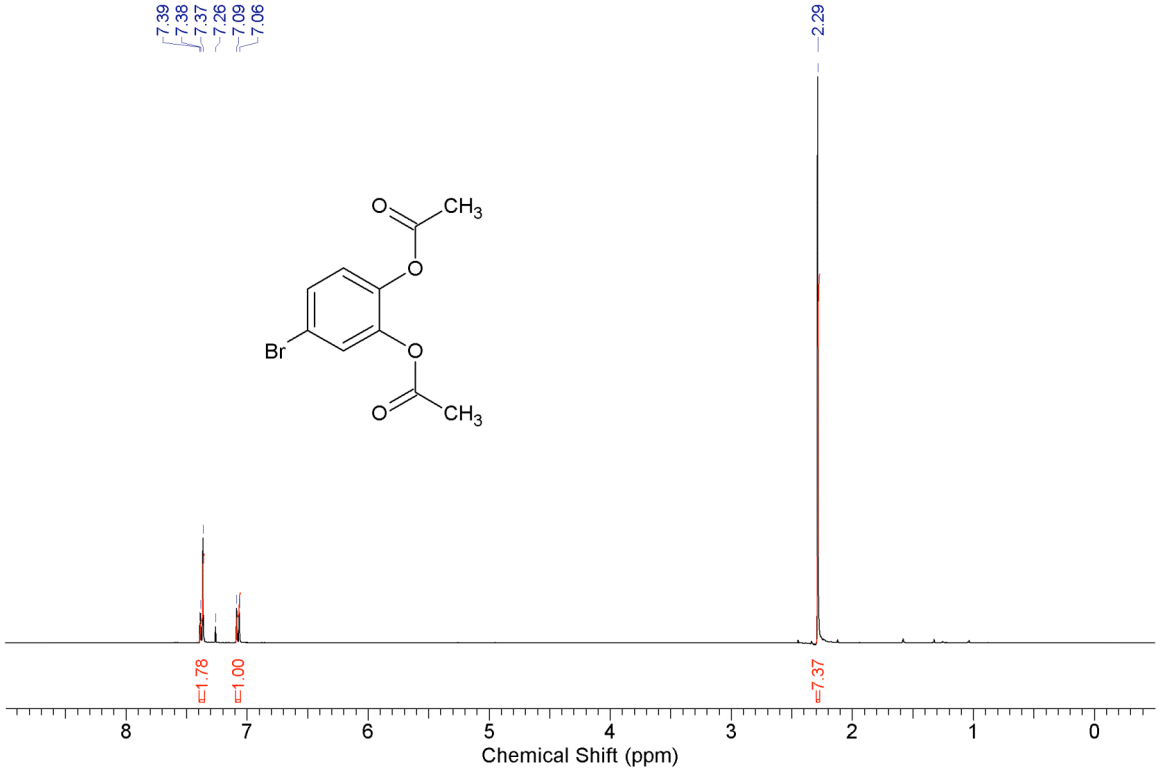
3k:

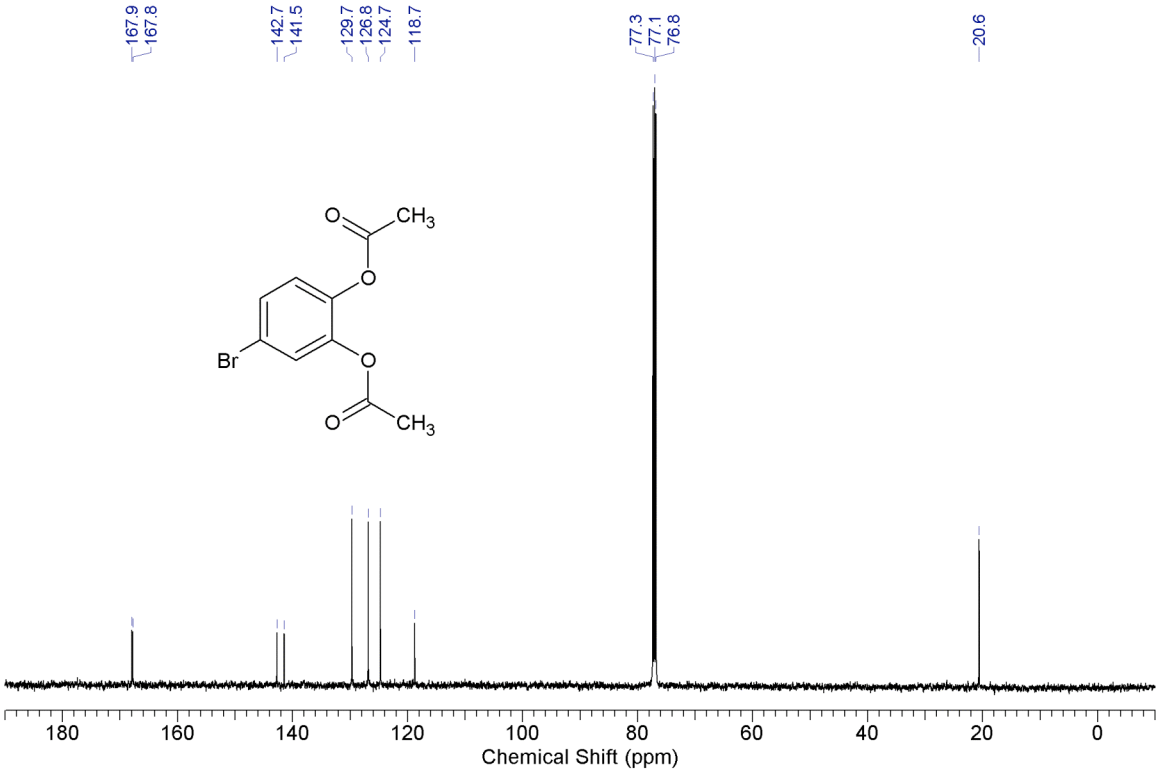

7.46
7.46
7.44
7.44
7.14
6.88
6.87
4.29
4.28
4.26
4.25
2.20
1.96
1.95
1.95
1.94
1.94
1.34
1.33
1.31
OH
OH
O
O
CH3
1.81
1.86
1.00
2.07
3.19
Chemical Shift (ppm)
167.2
148.8
143.1
123.8
122.7
116.7
114.8
77.3
77.0
76.8
61.2
14.3
OH
OH
O
O
CH3
Chemical Shift (ppm)

31 (3m):

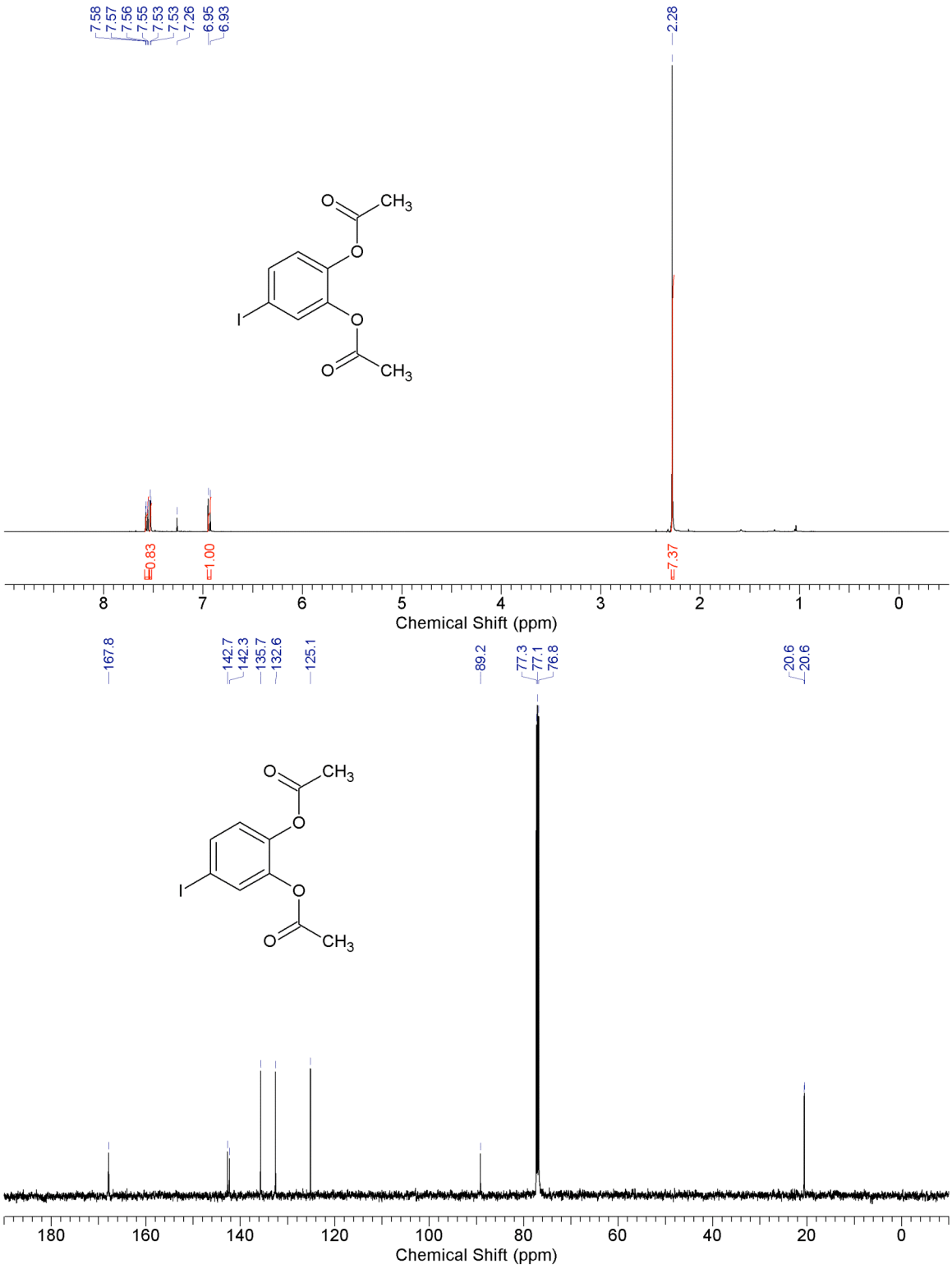

7.26
7.24
7.24
7.22
7.22
7.14
7.14
7.12
2.29
2.29
O
CH3
O
Cl
O
O
CH3
1.00
7.09
8
7
6
5
4
3
2
1
0
168.0
167.8
142.5
140.9
131.5
126.7
124.3
124.0
77.3
77.1
76.8
20.6
O
CH3
O
Cl
O
O
CH3
180
160
140
120
100
80
60
40
20
0

3n:

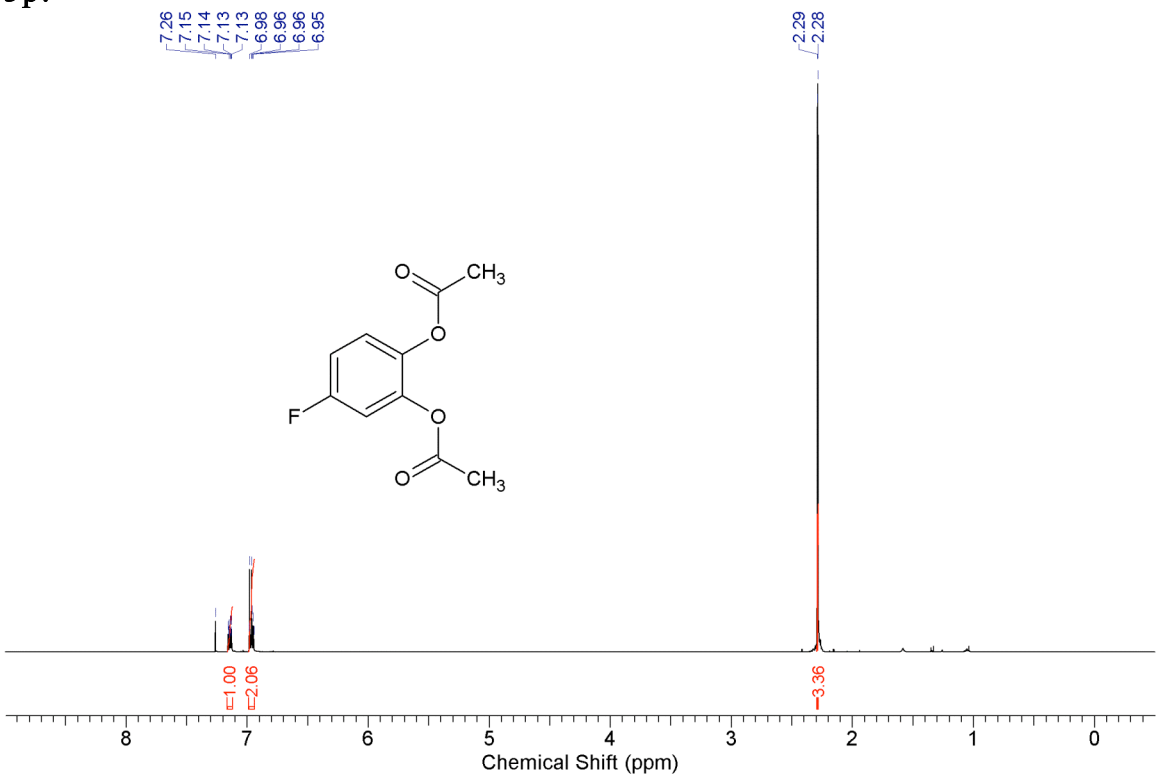

7.39
7.38
7.37
7.26
7.09
7.06
2.29
O
CH3
O
Br
O
O
CH3
1.78
1.00
7.37
8
7
6
5
4
3
2
1
0
Chemical Shift (ppm)

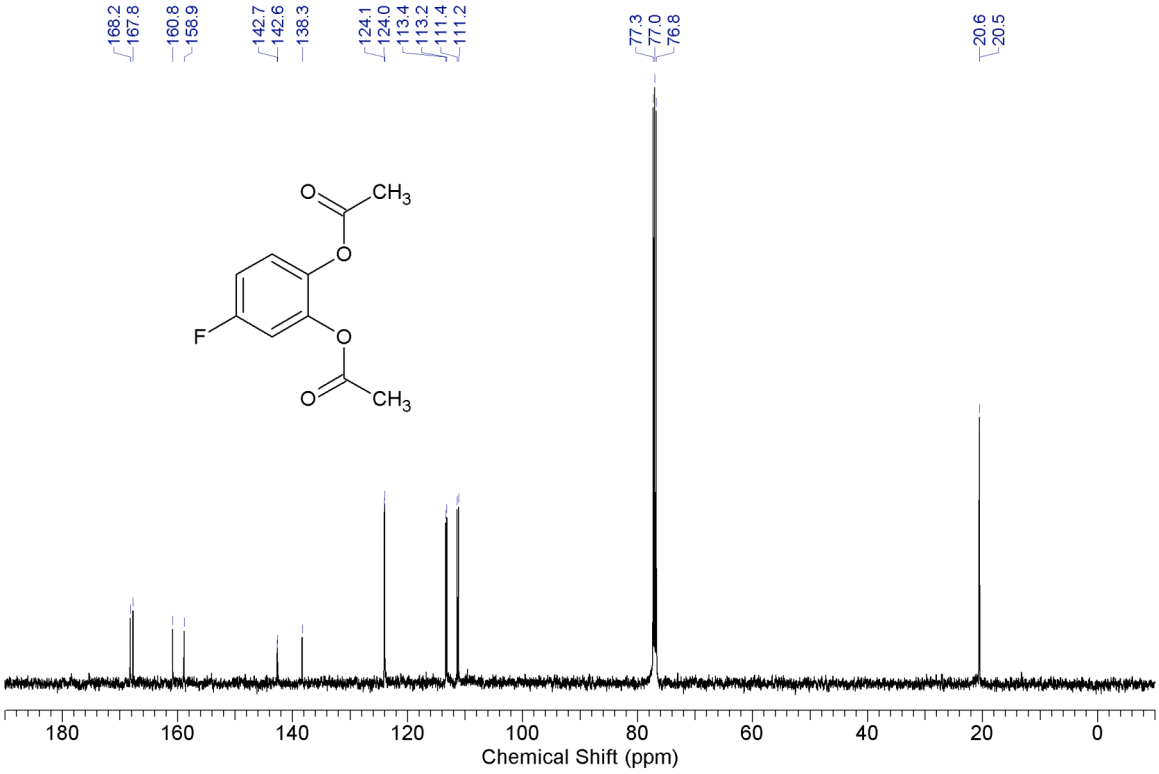

167.9
167.8
142.7
141.5
129.7
126.8
124.7
118.7
77.3
77.1
76.8
20.6
O
CH3
O
Br
O
O
CH3
180
160
140
120
100
80
60
40
20
0
Chemical Shift (ppm)

3o:

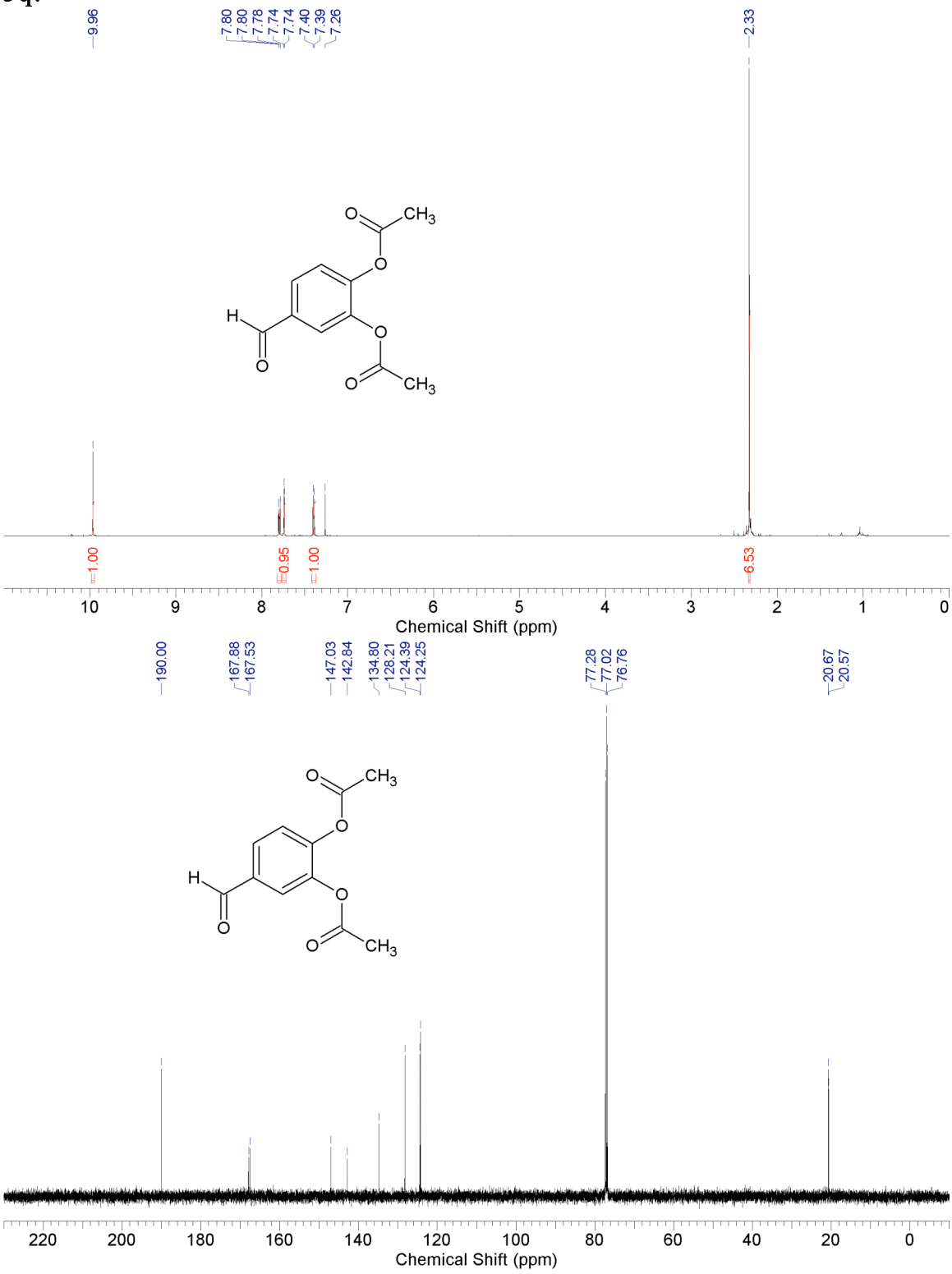

7.58
7.57
7.56
7.55
7.53
7.53
7.26
6.95
6.93
2.28
0.83
1.00
7.37
Chemical Shift (ppm)
167.8
142.7
142.3
135.7
132.6
125.1
89.2
77.3
77.1
76.8
20.6
20.6
Chemical Shift (ppm)

3p:

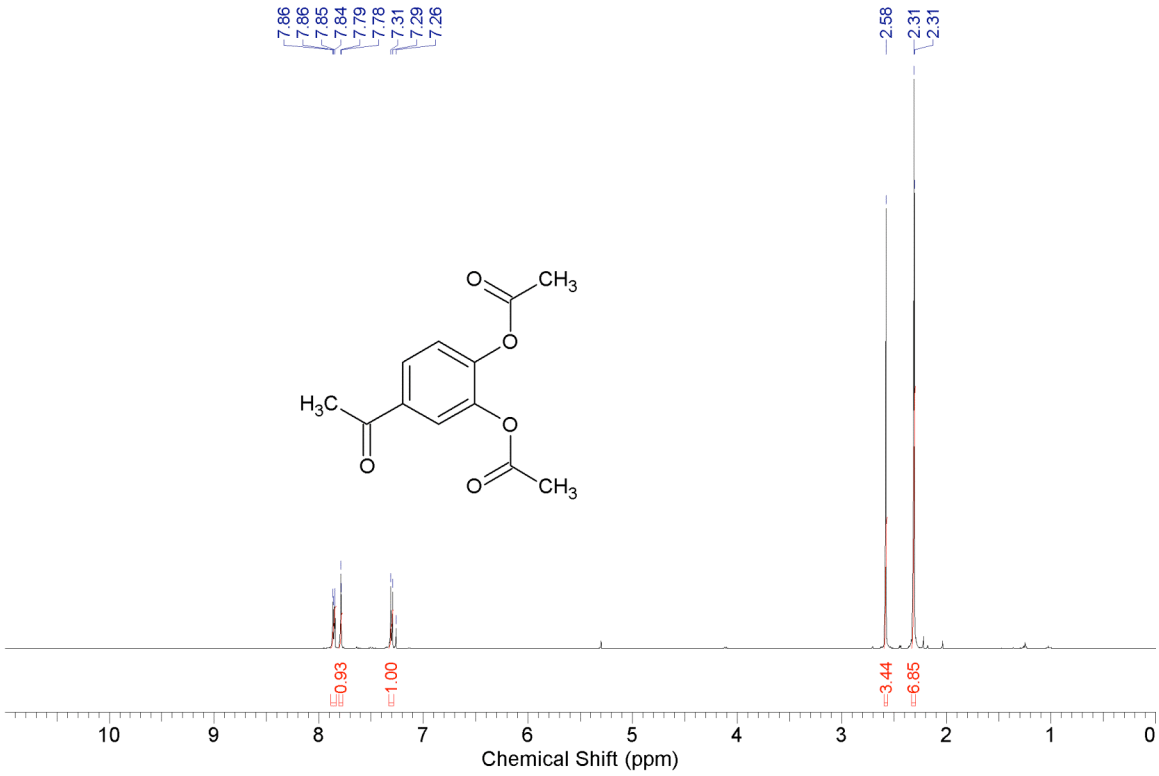

7.26
7.15
7.14
7.13
7.13
6.98
6.96
6.96
6.95
2.29
2.28
O
CH3
O
F
O
O
CH3
1.00
2.06
3.36
8
7
6
5
4
3
2
1
0
Chemical Shift (ppm)

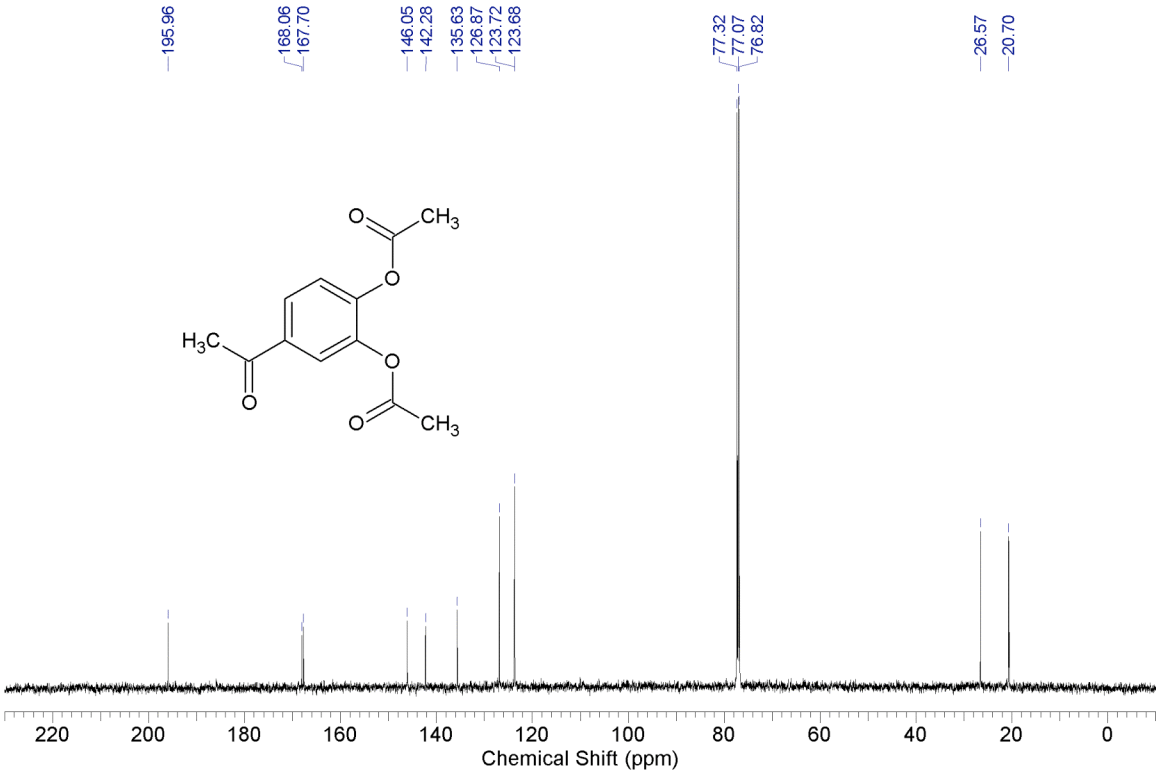

168.2
167.8
160.8
158.9
142.7
142.6
138.3
124.1
124.0
113.4
113.2
111.4
111.2
77.3
77.0
76.8
20.6
20.5
O
CH3
O
F
O
O
CH3
180
160
140
120
100
80
60
40
20
0
Chemical Shift (ppm)

3q:

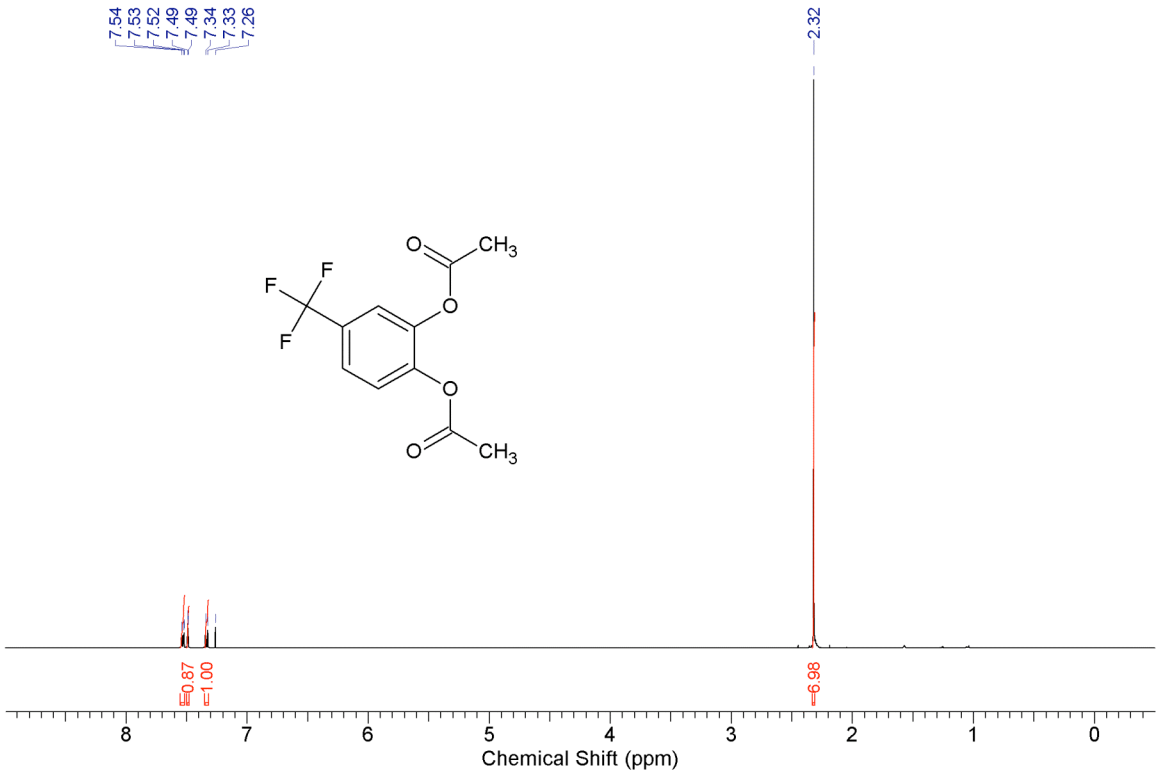

9.96
7.80
7.80
7.78
7.74
7.74
7.40
7.39
7.26
2.33
1.00
0.95
1.00
6.53
Chemical Shift (ppm)
190.00
167.88
167.53
147.03
142.84
134.80
128.21
124.39
124.25
77.28
77.02
76.76
20.67
20.57
Chemical Shift (ppm)

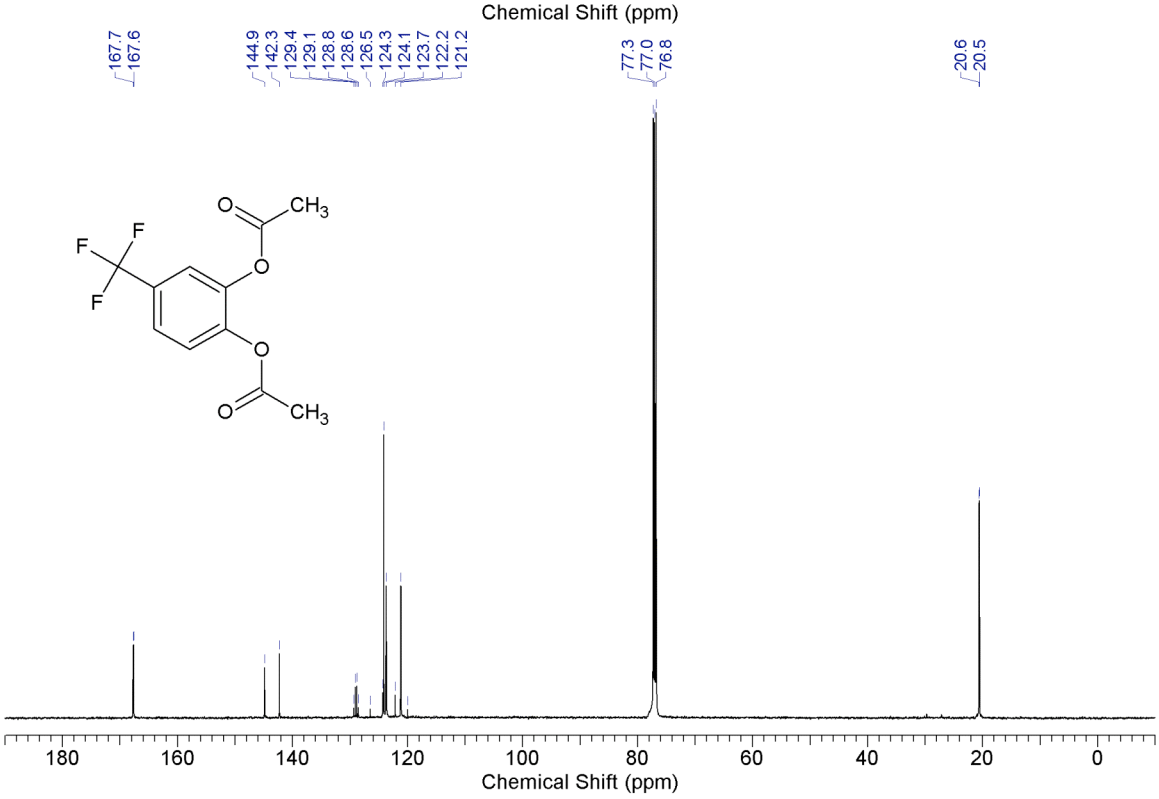
3r:


7.86
7.86
7.85
7.84
7.79
7.78
7.31
7.29
7.26
2.58
2.31
2.31
O
CH3
O
H3C
O
O
CH3
0.93
1.00
3.44
6.85
10
9
8
7
6
5
4
3
2
1
0
Chemical Shift (ppm)

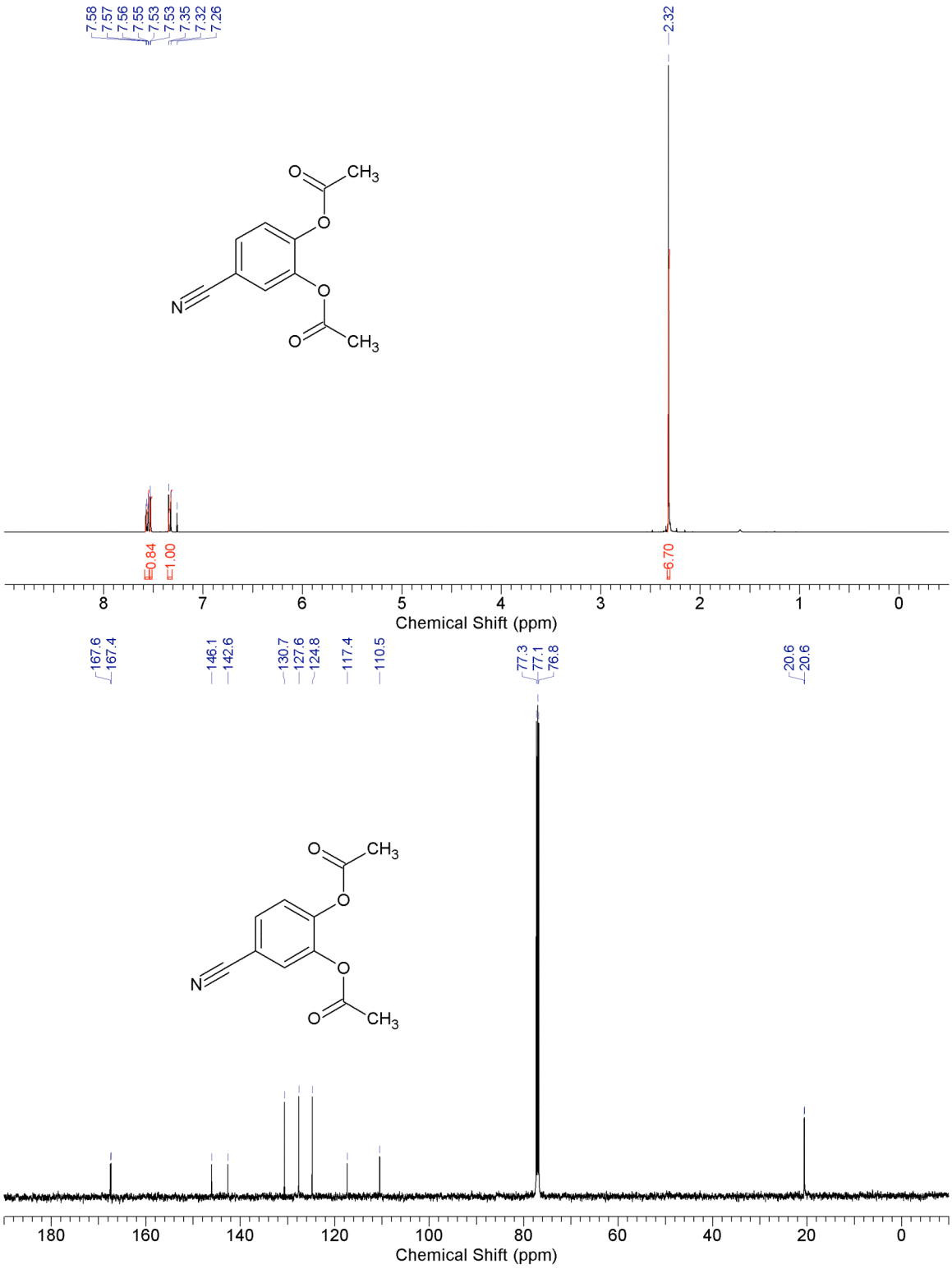

195.96
168.06
167.70
146.05
142.28
135.63
126.87
123.72
123.68
77.32
77.07
76.82
26.57
20.70
O
CH3
O
H3C
O
O
CH3
220
200
180
160
140
120
100
80
60
40
20
0
Chemical Shift (ppm)

3s:

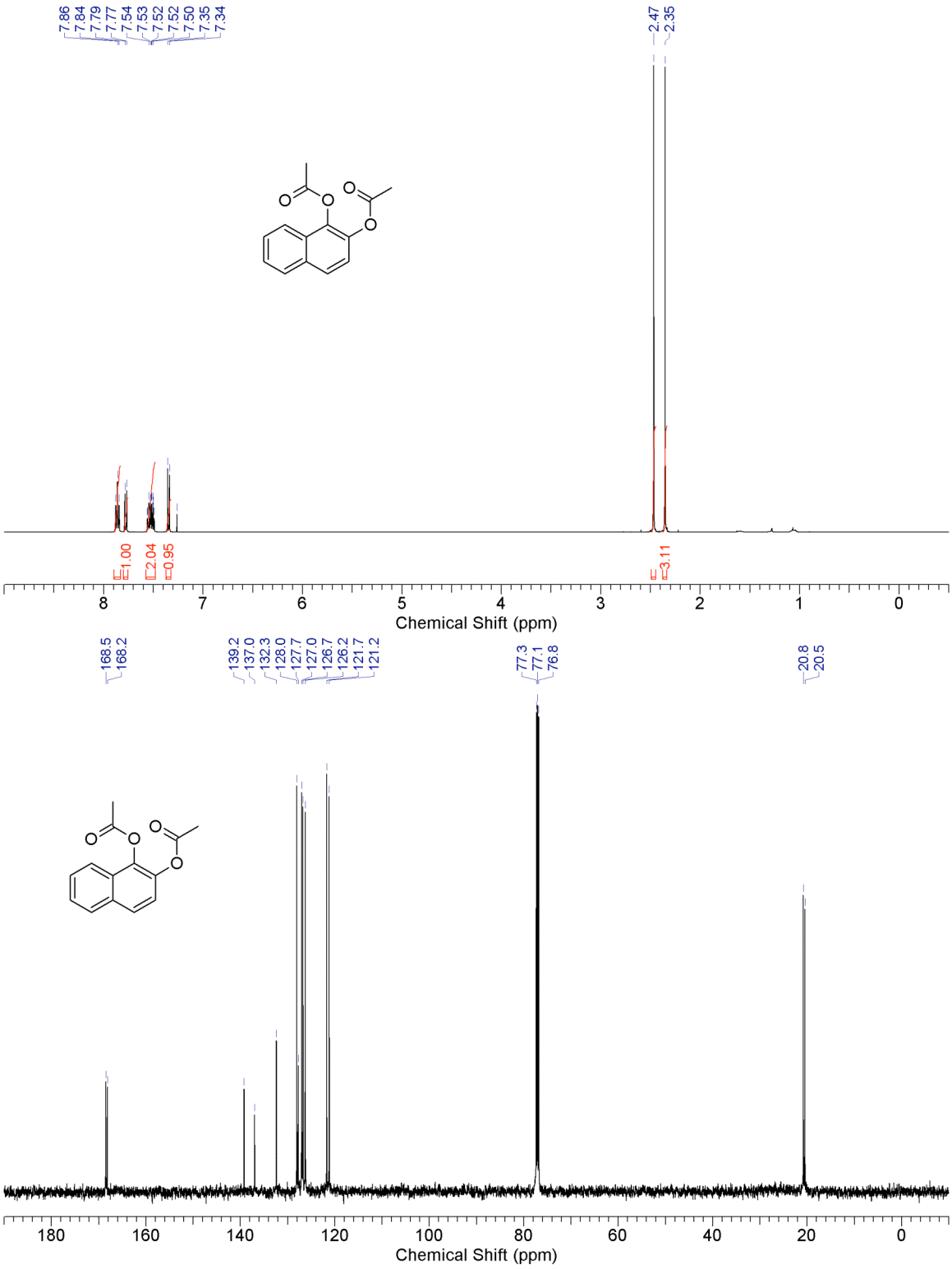

7.54
7.53
7.52
7.49
7.49
7.34
7.33
7.26
2.32
0.87
1.00
6.98
Chemical Shift (ppm)


167.7
167.6
144.9
142.3
129.4
129.1
128.8
128.6
126.5
124.3
124.1
123.7
122.2
121.2
77.3
77.0
76.8
20.6
20.5
Chemical Shift (ppm)

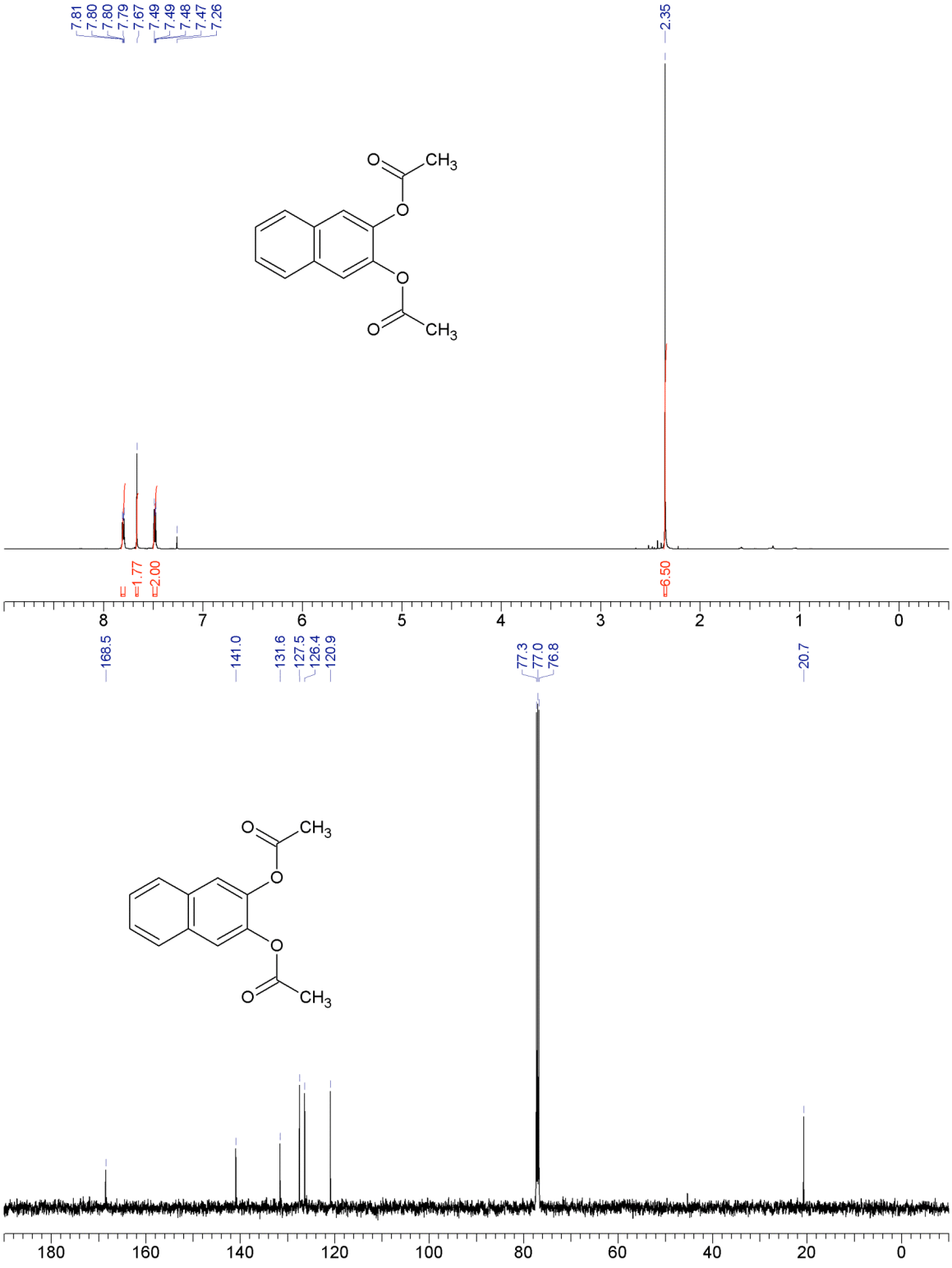
3t:


7.58
7.57
7.56
7.55
7.53
7.53
7.35
7.32
7.26
2.32
O
CH3
O
O
N
O
CH3
0.84
1.00
6.70
Chemical Shift (ppm)
167.6
167.4
146.1
142.6
130.7
127.6
124.8
117.4
110.5
77.3
77.1
76.8
20.6
20.6
Chemical Shift (ppm)

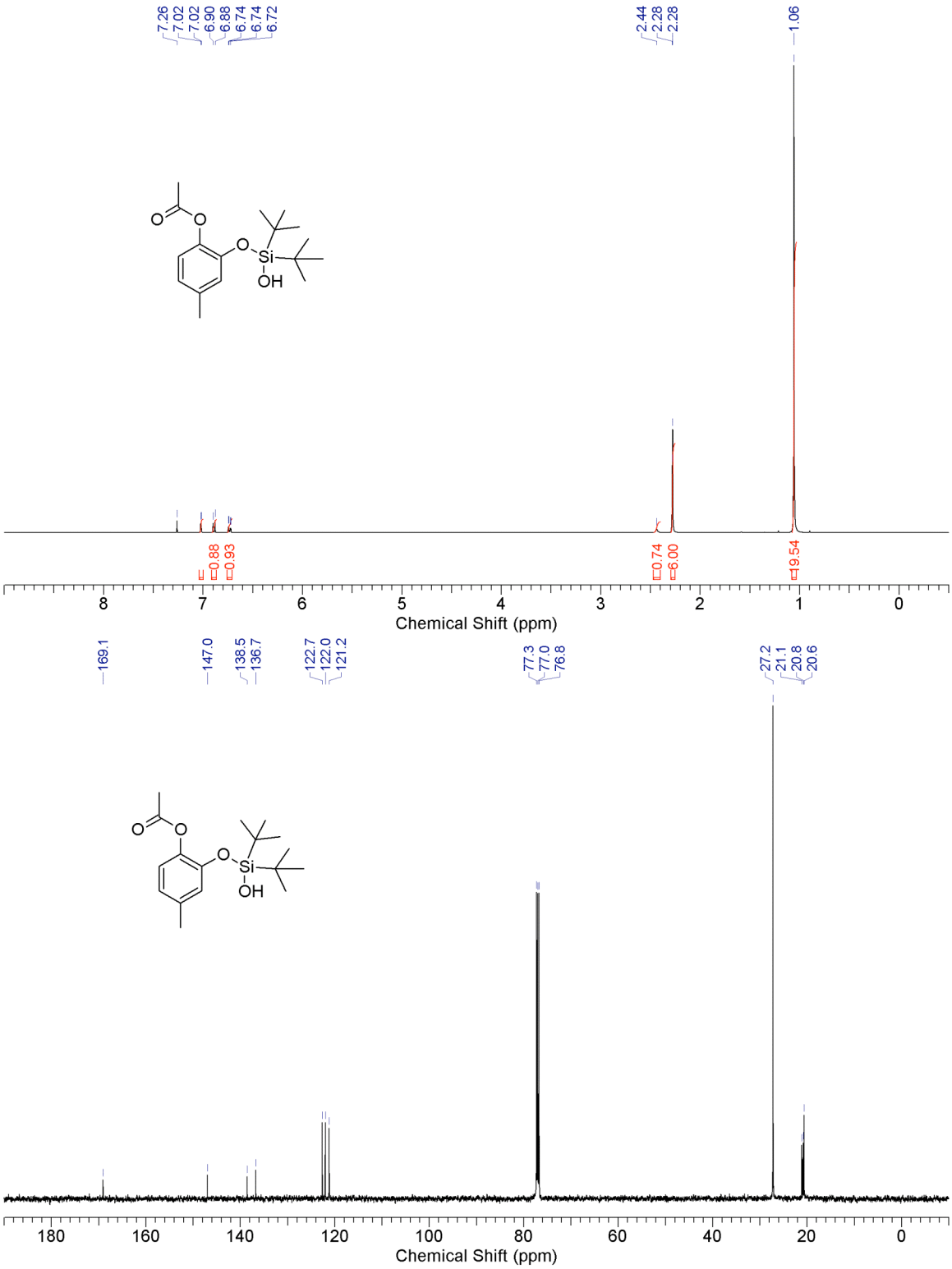
3u:


7.86
7.84
7.79
7.77
7.54
7.53
7.52
7.52
7.50
7.35
7.34
2.47
2.35
1.00
2.04
0.95
3.11
Chemical Shift (ppm)
168.5
168.2
139.2
137.0
132.3
128.0
127.7
127.0
126.7
126.2
121.7
121.2
77.3
77.1
76.8
20.8
20.5
Chemical Shift (ppm)

3v:


7.81
7.80
7.80
7.79
7.67
7.49
7.49
7.48
7.47
7.26
2.35
O
CH3
O
O
O
CH3
1.77
2.00
6.50
8
7
6
5
4
3
2
1
0
168.5
141.0
131.6
127.5
126.4
120.9
77.3
77.0
76.8
20.7
O
CH3
O
O
O
CH3
180
160
140
120
100
80
60
40
20
0

5c:


7.26
7.02
7.02
6.90
6.88
6.74
6.74
6.72
2.44
2.28
2.28
1.06
O
O
Si
OH
0.88
0.93
0.74
6.00
19.54
Chemical Shift (ppm)
169.1
147.0
138.5
136.7
122.7
122.0
121.2
77.3
77.0
76.8
27.2
21.1
20.8
20.6
Chemical Shift (ppm)