Electronic Supplementary Material (ESI) for Organic & Biomolecular Chemistry.

Supporting Information

Trichloroacetonitrile as an efficient activating agent for *ipso*-hydroxylation of arylboronic acids to phenolic compounds

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1. General information

All reagents were purchased from Energy, Sigma-Aldrich, Alfa Aesar, or TCI, and used without further purification. Acetonitrile was freshly distilled from calcium hydride before use. Reactions were monitored by thin layer chromatography (TLC) and visualized by UV lamp (254 nm) or by staining with a solution of phosphomolybdic acid in EtOH followed by heating. Flash column chromatography was performed using 230-400 mesh silica gel. Yields refer to purified compounds unless otherwise noted.

^{1}H NMR (400 MHz), ^{13}C NMR (100 MHz) spectra were obtained on Bruker 400M nuclear resonance spectrometers. ^{1}H NMR and ^{13}C NMR chemical shifts are referenced with respect to $CDCl_3$ (^{1}H NMR: residual $CHCl_3$ at δ 7.26, ^{13}C NMR: $CDCl_3$ triplet at δ 77.16). Data for ^{1}H NMR spectra were reported as chemical shifts (δ ppm), broad peak (b), multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, p = pentet, h = hextet, m = multiplet), coupling constant (Hz) and integration; data for ^{13}C NMR were reported in terms of chemical shift (δ ppm) and no special nomenclature is used for equivalent carbons. HR-ESI-MS spectra were recorded on a Bruker Esquire LC mass spectrometer and Thermo Scientific LTQ Orbitrap XL using electrospray ionization.

2. Optimization of reaction conditions[a] and the reaction device

Table S1 Screening the amount of TBHP and Cl_3CCN

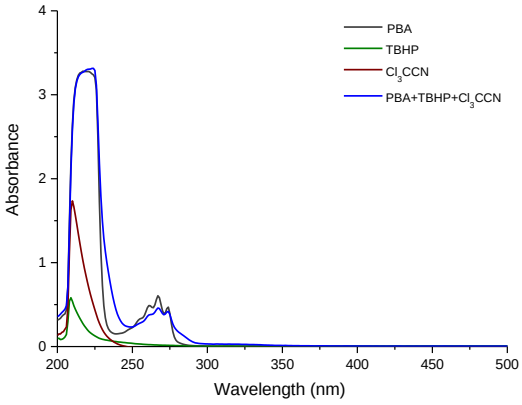
Entry	TBHP	Cl_3CCN	Yield[b][%]
1	1.0 eq.	0.5 eq.	40%
2	1.0 eq.	1.0 eq.	60%
3	1.0 eq.	1.2 eq.	72%
4	1.0 eq.	1.5 eq.	78%
5	1.0 eq.	2.0 eq.	47%
6	1.0 eq.	3.0 eq.	40%
7	0.5 eq.	1.5 eq.	32%
8	0.8 eq.	1.5 eq.	93%
9	1.0 eq.	1.5 eq.	96%
10	1.5 eq.	1.5 eq.	96%
11	2.0 eq.	1.5 eq.	96%

[a] Unless otherwise noted, all reactions were performed on 0.6 mmol scale.

[b] Isolated yields.

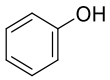
Scheme S1: Reaction device photo

3. UV-vis absorption spectra experiment

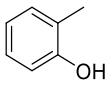


Scheme S2: UV-vis absorption spectra of phenylboronic acid (PBA) (0.001 M), TBHP (0.001 M), Cl_3CCN (0.001 M), and the mixture of PBA, TBHP and Cl_3CCN (0.001 M, PBA; PBA: TBHP: Cl_3CCN =1:1:1.5) in THF

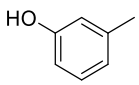
4. Characterization of products



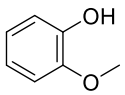
2a[1]: Colorless solid, 54 mg (96% yield); **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.27 (dd, *J* = 8.6, 7.4 Hz, 2H; H_{Ar}), 6.97 (tt, *J* = 7.4, 1.1 Hz, 1H; H_{Ar}), 6.87 (dd, *J* = 8.6, 1.1 Hz, 2H; H_{Ar}), 5.18 (s, 1H; OH); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 155.4 (C_{Ar}), 129.8 (C_{Ar}), 121.0 (C_{Ar}), 115.5 (C_{Ar}); **GC-MS (EI)**: *m/z* (%): 94 (100), 66, 50, 39, 28.



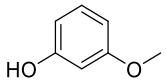
2b[2]: Colorless liquid, 25 mg (38% yield); **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.18-7.10 (m, 1H; H_{Ar}), 7.08 (dd, *J* = 7.7, 1.7 Hz, 1H; H_{Ar}), 6.85 (td, *J* = 7.4, 1.1 Hz, 1H; H_{Ar}), 6.78 (dd, *J* = 7.9, 1.1 Hz, 1H; H_{Ar}), 4.73 (s, 1H; OH), 2.26 (s, 3H; CH_3); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 153.9 (C_{Ar}), 131.2 (C_{Ar}), 127.3 (C_{Ar}), 123.8 (C_{Ar}), 120.9 (C_{Ar}), 115.0 (C_{Ar}), 15.8 (CH_3); **GC-MS (EI)**: *m/z* (%): 108, 90, 77, 51, 39, 28 (100).



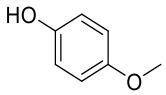
2c[3]: Colorless liquid, 63 mg (97% yield); **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.14 (t, *J* = 7.7 Hz, 1H; H_{Ar}), 6.77 (d, *J* = 7.5 Hz, 1H; H_{Ar}), 6.72-6.60 (m, 2H; H_{Ar}), 4.51 (s, 1H; OH), 2.23 (s, 3H; CH_3); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 155.5 (C_{Ar}), 134.0 (C_{Ar}), 130.0 (C_{Ar}), 121.7 (C_{Ar}), 116.2 (C_{Ar}), 112.5 (C_{Ar}), 21.4 (CH_3); **GC-MS (EI)**: *m/z* (%): 108 (100), 79, 53, 39, 26.



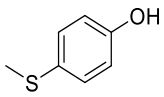
2d[4]: Colorless liquid, 33 mg (45% yield); **^{1}H NMR** (400 MHz, $CDCl_3$): δ 6.69-6.90 (m, 1H; H_{Ar}), 6.86 (q, *J* = 3.5 Hz, 3H; H_{Ar}), 5.60 (s, 1H; OH), 3.89 (s, 3H; CH_3); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 146.7 (C_{Ar}), 145.8 (C_{Ar}), 121.6 (C_{Ar}), 120.3 (C_{Ar}), 114.7 (C_{Ar}), 110.9 (C_{Ar}), 56.0 (CH_3); **GC-MS (EI)**: *m/z* (%): 124, 88, 74 (100), 63, 51, 38, 28.



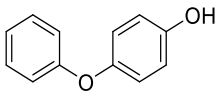
2e[5]: Yellow oil, 71 mg (95% yield); **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.21-7.08 (m, 1H; H_{Ar}), 6.55-6.49 (m, 1H; H_{Ar}), 6.48-6.39 (m, 2H; H_{Ar}), 5.58 (s, 1H; OH), 3.78 (s, 3H; CH_3); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 161.0 (C_{Ar}), 156.9 (C_{Ar}), 130.3 (C_{Ar}), 108.1 (C_{Ar}), 106.6 (C_{Ar}), 101.7 (C_{Ar}), 55.4 (CH_3); **GC-MS (EI)**: *m/z* (%): 124 (100), 94, 81, 66, 53, 28.



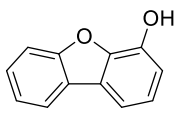
2f[6]: Colorless oil, 73 mg (98% yield); **^{1}H NMR** (400 MHz, $CDCl_3$): δ 6.93-6.59 (m, 4H; H_{Ar}), 4.71 (s, 1H; OH), 3.77 (s, 3H; CH_3); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 153.8 (C_{Ar}), 149.7 (C_{Ar}), 116.2 (C_{Ar}), 115.1 (C_{Ar}), 56.0 (CH_3); **GC-MS (EI)**: *m/z* (%): 124, 95, 81 (100), 66, 50, 39, 27.



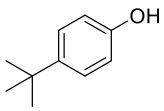
2g[7]: White solid, 51 mg (61% yield); **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.25-7.19 (m, 2H; H_{Ar}), 6.81-6.75 (m, 2H; H_{Ar}), 4.74 (s, 1H; OH), 2.44 (s, 3H; CH_3); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 154.2 (C_{Ar}), 130.5 (C_{Ar}), 128.9 (C_{Ar}), 116.2 (C_{Ar}), 18.2 (CH_3); **GC-MS (EI)**: *m/z* (%): 140 (100), 125, 97, 69, 45, 28.



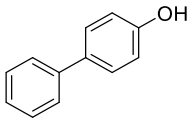
2h[4]: White solid, 64 mg (57% yield); **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.34-7.24 (m, 2H; H_{Ar}), 7.05 (td, *J* = 7.3, 1.2 Hz, 1H; H_{Ar}), 6.98-6.89 (m, 4H; H_{Ar}), 6.85-6.78 (m, 2H; H_{Ar}), 4.73 (s, 1H; OH); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 153.5 (C_{Ar}), 151.8 (C_{Ar}), 150.3 (C_{Ar}), 129.8 (C_{Ar}), 122.6 (C_{Ar}), 121.1 (C_{Ar}), 117.1 (C_{Ar}), 116.5 (C_{Ar}); **GC-MS (EI)**: *m/z* (%): 188, 157, 129, 109, 77 (100), 51, 39, 28.



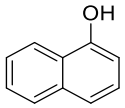
2i[8]: Yellow solid, 91 mg (82% yield); **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.94 (dd, *J* = 7.8 ,1.3 Hz, 1H; H_{Ar}), 7.63-7.41 (m, 3H; H_{Ar}), 7.36 (td, *J* = 7.6, 1.0 Hz, 1H; H_{Ar}), 7.23 (t, *J* = 7.8 Hz, 1H; H_{Ar}), 7.05 (dd, *J* = 7.9, 1.0 Hz, 1H; H_{Ar}),5.56 (s, 1H; OH); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 156.2 (C_{Ar}), 144.2 (C_{Ar}), 141.2 (C_{Ar}), 127.4 (C_{Ar}), 125.9 (C_{Ar}), 124.7 (C_{Ar}), 123.8 (C_{Ar}), 123.8 (C_{Ar}), 121.1 (C_{Ar}), 113.8 (C_{Ar}), 112.9 (C_{Ar}), 111.9 (C_{Ar}); **GC-MS (EI)**: *m/z* (%): 184 (100), 155, 128, 102, 28.



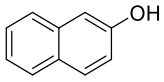
2j[7]: White solid, 88 mg (98% yield); **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.33-7.26 (m, 2H; H_{Ar}), 6.88-6.74 (m, 2H; H_{Ar}), 5.13 (s, 1H; OH), 1.32 (s, 9H; CH_3); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 153.2 (C_{Ar}), 143.7 (C_{Ar}), 126.6 (C_{Ar}), 114.9 (C_{Ar}), 34.2 (C), 31.7 (CH_3); **GC-MS (EI)**: *m/z* (%): 150 (100), 135, 107, 91, 77, 41, 28.



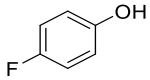
2k[9]: White solid, 91 mg (89% yield); **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.55 (dd, *J* = 7.6, 1.6 Hz, 2H; H_{Ar}), 7.49 (t, *J* = 7.6 Hz, 2H; H_{Ar}), 7.42 (t, *J* = 7.6 Hz, 2H; H_{Ar}), 7.36-7.28 (m, 1H; H_{Ar}), 6.92 (d, *J* = 8.7 Hz, 2H; H_{Ar}), 4.72 (s, 1H; OH); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 155.2 (C_{Ar}), 140.9 (C_{Ar}), 134.2 (C_{Ar}), 128.9 (C_{Ar}), 128.5 (C_{Ar}), 126.9 (C_{Ar}), 126.9 (C_{Ar}), 115.8 (C_{Ar}); **GC-MS (EI)**: *m/z* (%): 170 (100), 141, 155, 63, 28.



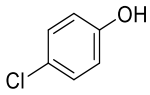
2i[1]: Brown solid, 76 mg (88% yield); **^{1}H NMR** (400 MHz, $CDCl_3$): δ 8.28-8.90 (m, 1H; H_{Ar}), 7.96-7.73 (m, 1H; H_{Ar}), 7.68-7.39 (m, 3H; H_{Ar}), 7.33 (t, *J* = 7.8 Hz, 1H; H_{Ar}), 6.82 (dd, *J* = 7.5, 1.0 Hz, 1H; H_{Ar}), 5.45-5.28 (m, 1H; OH); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 151.5 (C_{Ar}), 134.9 (C_{Ar}), 127.8 (C_{Ar}), 126.6 (C_{Ar}), 126.0 (C_{Ar}), 125.4 (C_{Ar}), 124.5 (C_{Ar}), 121.7 (C_{Ar}), 120.9 (C_{Ar}), 108.1 (C_{Ar}); **GC-MS (EI)**: *m/z* (%): 144, 115 (100), 89, 63, 50, 28.



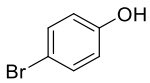
2m[7]: Brown solid, 48 mg (55% yield); **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.78 (t, *J* = 9.0 Hz, 2H; H_{Ar}), 7.69 (d, *J* = 8.2 Hz, 1H; H_{Ar}), 7.45 (ddd, *J* = 8.2, 6.7, 1.3 Hz, 1H; H_{Ar}), 7.36 (ddd, *J* = 8.1, 6.8, 1.2 Hz; 1H; H_{Ar}), 7.20-7.07 (m, 2H; H_{Ar}), 5.29 (s, 1H; OH); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 153.4 (C_{Ar}), 134.8 (C_{Ar}), 130.1 (C_{Ar}), 129.2 (C_{Ar}), 128.0 (C_{Ar}), 126.7 (C_{Ar}), 126.6 (C_{Ar}), 123.8 (C_{Ar}), 117.9 (C_{Ar}), 109.7 (C_{Ar}); **GC-MS (EI)**: *m/z* (%): 144, 115 (100), 104, 86, 75, 62, 39, 29.



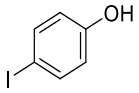
2n[8]: Yellow solid, 66 mg (98% yield); **^{1}H NMR** (400 MHz, $CDCl_3$): δ 6.92 (t, *J* = 8.6 Hz, 2H; H_{Ar}), 6.63-6.66 (m, 2H; H_{Ar}), 4.99 (s, 1H; OH); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 157.4 (d, *J* = 237.7 Hz; C_{Ar}), 151.7 (d, *J* = 2.2 Hz; C_{Ar}), 116.4 (d, *J* = 8.0 Hz; C_{Ar}), 116.1 (d, *J* = 23.4 Hz; C_{Ar}); **GC-MS (EI)**: *m/z* (%): 112, 83, 57, 28 (100).



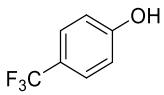
2o[10]: White solid, 68 mg (88% yield); **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.19 (d, *J* = 9.0 Hz, 2H; H_{Ar}), 6.77 (d, *J* = 8.8 Hz, 2H; H_{Ar}), 5.08 (s, 1H; OH); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 154.3 (C_{Ar}), 129.7 (C_{Ar}), 125.7 (C_{Ar}), 116.8 (C_{Ar}); **GC-MS (EI)**: *m/z* (%): 128 (100), 99, 72, 65, 62, 37, 28.



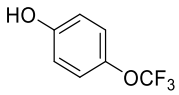
2p[11]: Brown solid, 87 mg (85% yield); **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.38-7.27 (m, 2H; H_{Ar}), 6.78-6.67 (m, 2H; H_{Ar}), 5.28 (m, 1H; OH); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 154.8 (C_{Ar}), 132.6 (C_{Ar}), 117.4 (C_{Ar}), 113.0 (C_{Ar}); **GC-MS (EI)**: *m/z* (%): 172, 93, 81, 65 (100), 39.



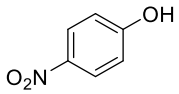
2q[7]: White solid, 45 mg (34% yield); **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.51 (d, *J* = 8.7 Hz, 2H; H_{Ar}), 6.33 (d, *J* = 8.7 Hz, 2H; H_{Ar}), 4.94 (s, 1H; OH); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 155.5 (C_{Ar}), 138.6 (C_{Ar}), 117.9 (C_{Ar}), 82.8 (C_{Ar}); **GC-MS (EI)**: *m/z* (%): 220, 178, 127, 93, 65 (100), 39, 27.



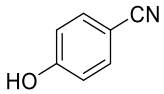
2r[7]: Yellow solid, 63 mg (65% yield); **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.56-7.42 (m, 2H; H_{Ar}), 6.98-6.83 (m, 2H; H_{Ar}); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 158.5 (C_{Ar}), 127.3 (q, *J* = 3.7 Hz; C_{Ar}), 124.5 (q, *J* = 271.0 Hz; CF_3), 123.3 (q, *J* = 32.8 Hz; C_{Ar}), 115.6 (C_{Ar}); **GC-MS (EI)**: *m/z* (%): 162, 152 (100), 28.



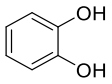
2s[12]: Colorless oil, 51 mg (48% yield); **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.10 (d, *J* = 8.6 Hz, 2H; H_{Ar}), 6.82 (d, *J* = 8.9 Hz, 2H; H_{Ar}); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 154.3 (C_{Ar}), 142.9 (C_{Ar}), 122.8 (C_{Ar}), 116.3 (C_{Ar}), 119.6 (d, *J* = 658.4 Hz; CF_3); **GC-MS (EI)**: *m/z* (%): 178, 109, 64, 69 (100), 53, 28.



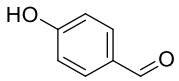
2t[7]: Colorless solid, 66 mg (79% yield); **^{1}H NMR** (400 MHz, $CDCl_3$): δ 8.18 (d, *J* = 8.6 Hz, 2H; H_{Ar}), 6.93 (d, *J* = 8.7 Hz, 2H; H_{Ar}), 6.23 (s, 1H; OH); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 161.8 (C_{Ar}), 141.7 (C_{Ar}), 126.5 (C_{Ar}), 115.9 (C_{Ar}); **GC-MS (EI)**: *m/z* (%): 139, 135, 109, 78, 75, 64, 45, 30 (100), 26.



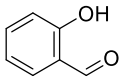
2u[7]: White solid, 61 mg (85% yield); **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.49 (d, *J* = 8.7 Hz, 2H; H_{Ar}), 6.87 (d, *J* = 8.7 Hz, 2H; H_{Ar}), 6.55 (s, 1H; OH); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 160.3 (C_{Ar}), 134.5 (C_{Ar}), 119.4 (CN), 116.6 (C_{Ar}), 103.2 (C_{Ar}); **GC-MS (EI)**: *m/z* (%): 119 (100), 91, 75, 64, 50, 39, 29.



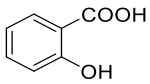
2v[13]: White solid, 44 mg (66% yield); **^{1}H NMR** (400 MHz, $CDCl_3$): δ 6.91-6.85 (m, 2H; H_{Ar}), 6.84-6.79 (m, 2H; H_{Ar}), 5.35 (d, *J* = 4.5 Hz, 2H; OH); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 143.7 (C_{Ar}), 121.4 (C_{Ar}), 115.7 (C_{Ar}); **GC-MS (EI)**: *m/z* (%): 110, 64, 51, 28 (100).



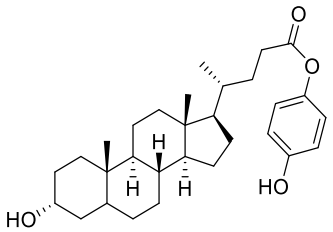
2w[4]: Colorless solid, 55 mg (75% yield); **^{1}H NMR** (400 MHz, $CDCl_3$): δ 9.86 (s, 1H, COH), δ 7.82 (d, *J* = 8.2 Hz, 2H, H_{Ar}), 6.98 (d, *J* = 8.2 Hz, 2H, H_{Ar}), 6.36 (s, 1H, OH); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 191.4 (C=O), 161.8 (C_{Ar}), 132.7 (C_{Ar}), 130.0 (C_{Ar}), 116.2 (C_{Ar}); **GC-MS (EI)**: *m/z* (%): 121 (100), 93, 65, 50, 39, 29.



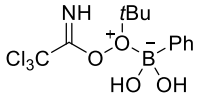
2x[1]: Yellow liquid, 23 mg (31% yield); **^{1}H NMR** (400 MHz, $CDCl_3$): δ 11.02 (s, 1H; OH), 9.91 (s, 1H; COH), 7.55 (ddd, *J* = 17.1, 8.2, 1.7 Hz, 2H; H_{Ar}), 7.13-6.82 (m, 2H; H_{Ar}); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 196.8 (C=O), 161.8 (C_{Ar}), 137.2 (C_{Ar}), 133.9 (C_{Ar}), 120.8 (C_{Ar}), 120.0 (C_{Ar}), 117.8 (C_{Ar}); **GC-MS (EI)**: *m/z* (%): 121, 80, 64 (100), 45, 38, 28.



2y[2]: White solid, 47 mg (57% yield); **^{1}H NMR** (400 MHz, $CDCl_3$): δ 10.38 (s, 1H; COOH), 7.94 (dd, *J* = 8.0, 1.7 Hz, 1H; H_{Ar}), 7.53 (ddd, *J* = 8.7, 7.2, 1.7 Hz, 1H; H_{Ar}), 7.02 (dd, *J* = 8.5, 1.0 Hz, 1H; H_{Ar}), 6.99-6.90 (m, 1H; H_{Ar}); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 175.0 (C=O), 162.3 (C_{Ar}), 137.1 (C_{Ar}), 131.1 (C_{Ar}), 119.8 (C_{Ar}), 118.0 (C_{Ar}), 111.4 (C_{Ar}); **GC-MS (EI)**: *m/z* (%): 138, 123, 95, 81, 67, 43, 28 (100).



2z: White solid, 79 mg (28% yield); **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.02-6.84 (m, 2H; H_{Ar}), 6.84-6.73 (m, 2H; H_{Ar}), 3.64 (tt, *J* = 11.0, 4.6 Hz, 1H; CH), 2.58 (ddd, *J* = 14.9, 9.8, 4.9 Hz, 1H; CH_2), 2.44 (ddd, *J* = 15.7, 9.1, 6.8 Hz, 1H; CH_2), 2.01-1.82 (m, 4H; CH_2), 1.83-1.63 (m, 4H; CH_2), 1.62-1.45 (m, 4H; CH_2), 1.44-1.31 (m, 7H; CH_2, CH), 1.26 (ddq, *J* = 11.2, 6.7, 2.8 Hz, 3H; CH), 1.17-1.03 (m, 4H; CH_2), 1.10-0.95 (d, *J* = 6.2 Hz, 3H; CH_3), 0.92 (s, 3H; CH_3), 0.66 (s, 3H; CH_3); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 172.5 (C=O), 153.5 (C_{Ar}), 144.4 (C_{Ar}), 122.6 (C_{Ar}), 166.1 (C_{Ar}), 72.3 (CH), 56.7 (CH), 56.1 (CH), 42.9 (CH), 42.2 (CH), 40.6 (CH_2), 40.3 (C), 36.6 (CH_2), 36.0 (CH_2), 35.5 (CH), 35.5 (C), 34.7 (CH), 31.5 (CH_2), 31.2 (CH_2), 30.7 (CH_2), 28.4 (CH_2), 27.3 (CH_2), 26.6 (CH_2), 24.4 (CH_2), 23.5 (CH_2), 21.0 (CH_3), 18.5 (CH_3), 12.2 (CH_3); **HRMS** (ES+) exact mass calculated for $[M+K]^+$ ($C_{30}H_{44}O_4$) requires m/z 507.2871, found m/z 507.2883.



Lewis adduct intermediate (III): **GC-MS (EI)**: *m/z* (%): 355, 331, 311, 281, 267, 253, 237, 207(100), 133, 119, 104, 91, 73, 28.

5. References

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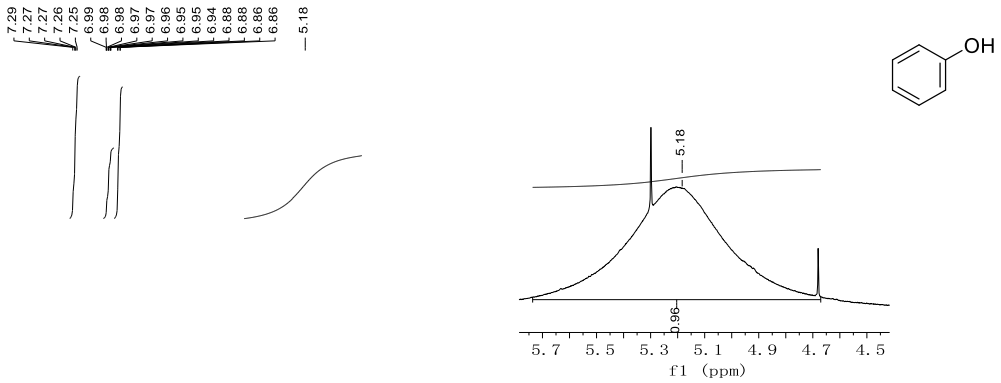
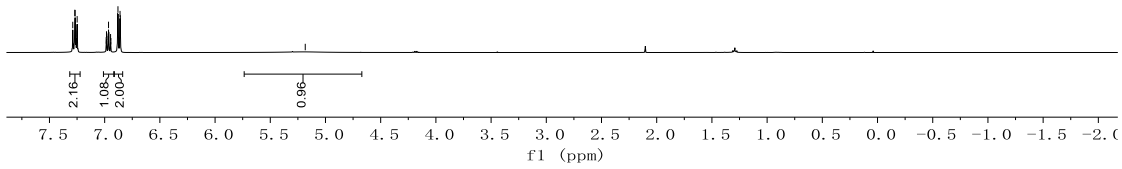
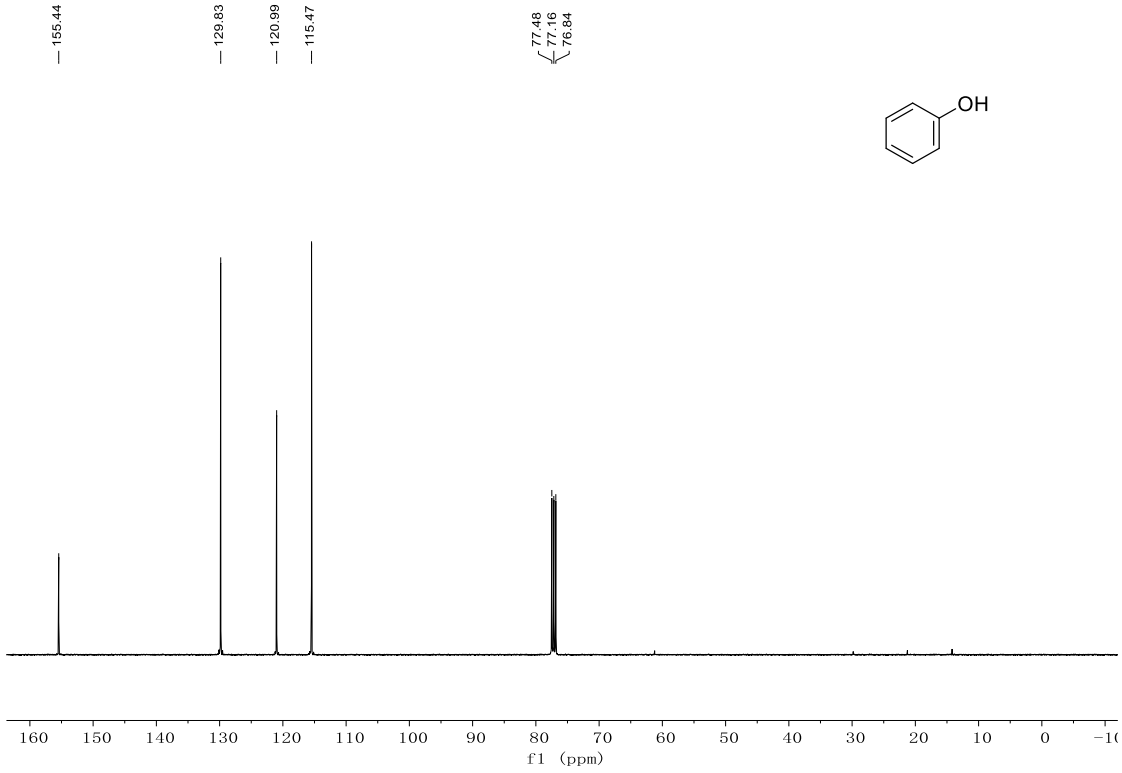
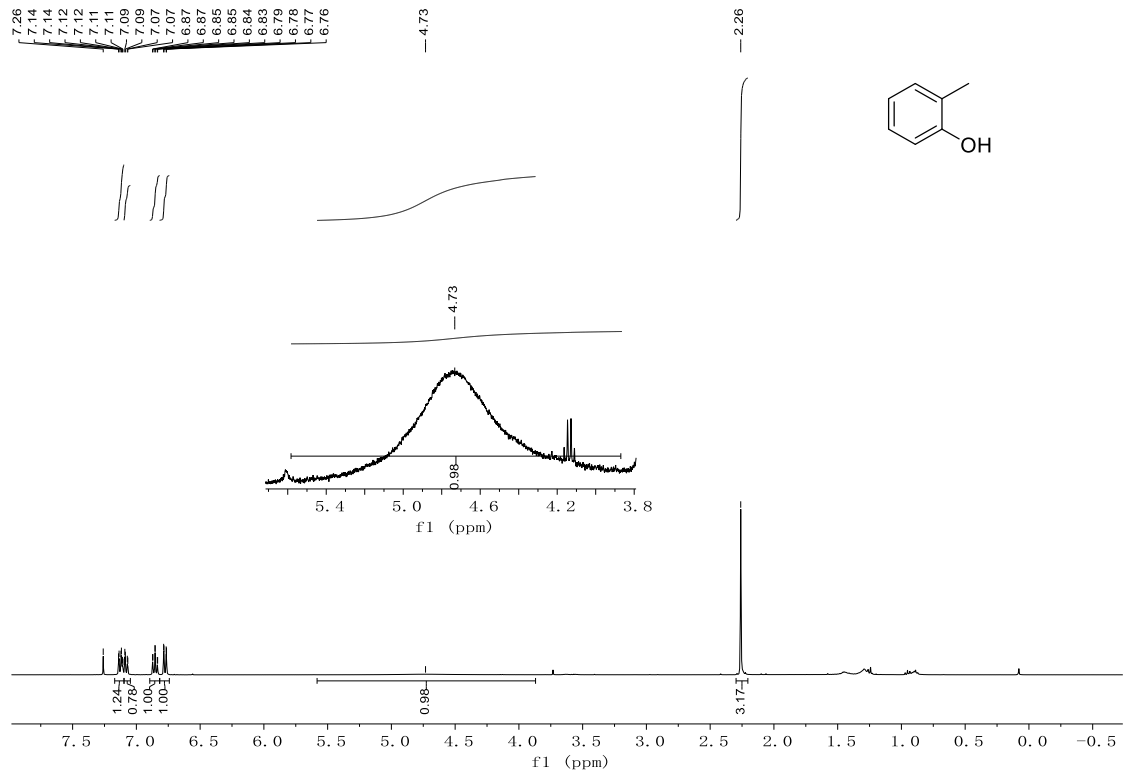
6. ^{1}H, ^{13}C NMR spectra of products





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6.85
6.85
6.84
6.83
6.79
6.78
6.77
6.76
4.73
2.26
OH
4.73
0.98
5.4
5.0
4.6
4.2
3.8
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0.78
1.00
1.00
0.98
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7.5
7.0
6.5
6.0
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5.0
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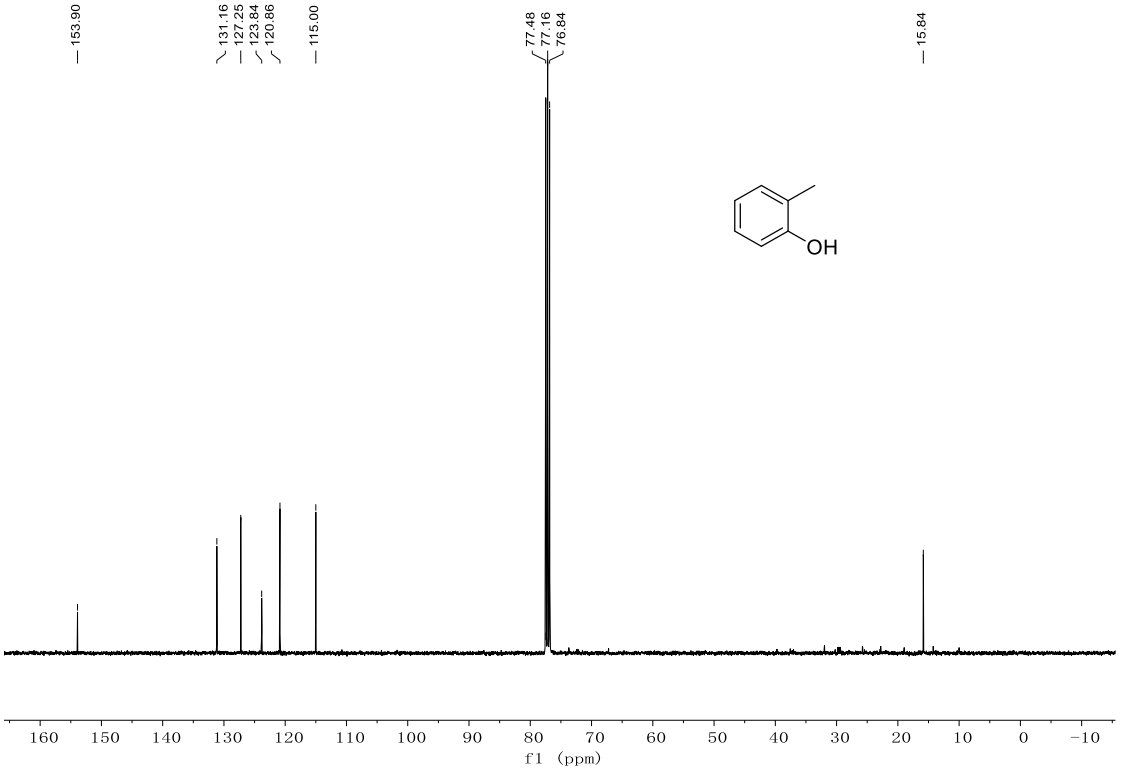
f1 (ppm)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100
90
80
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60
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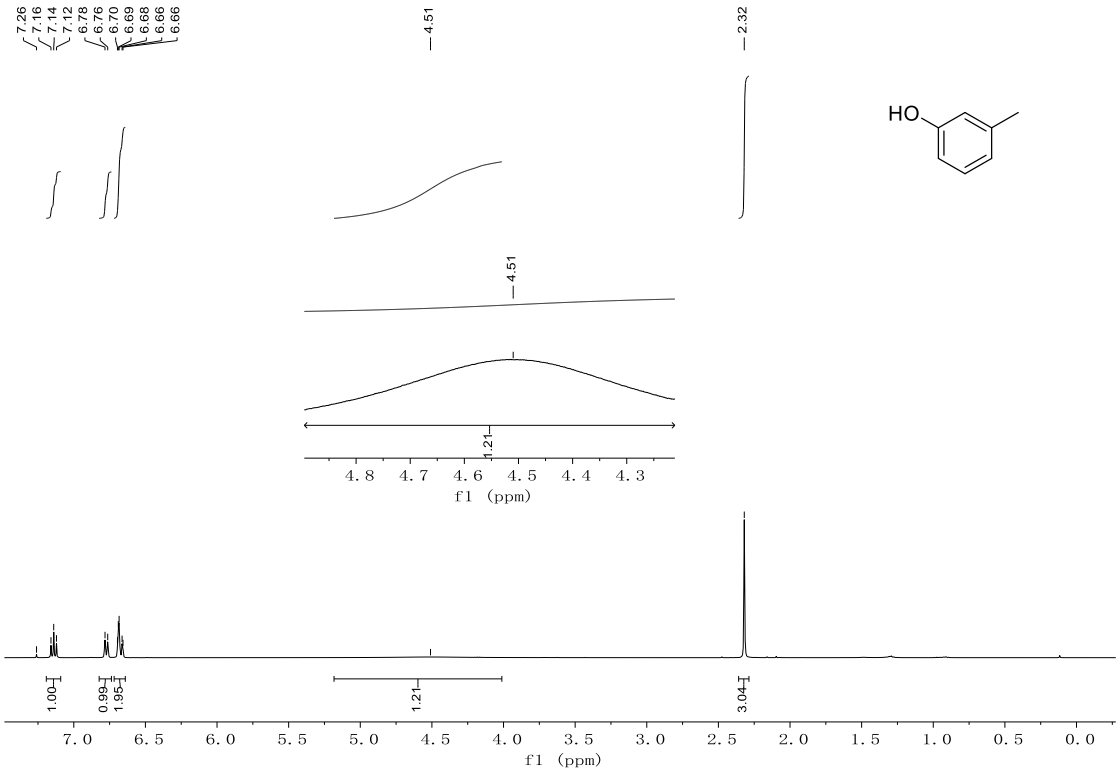
40
30
20
10
0
−10
f1 (ppm)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HO
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1.95
1.21
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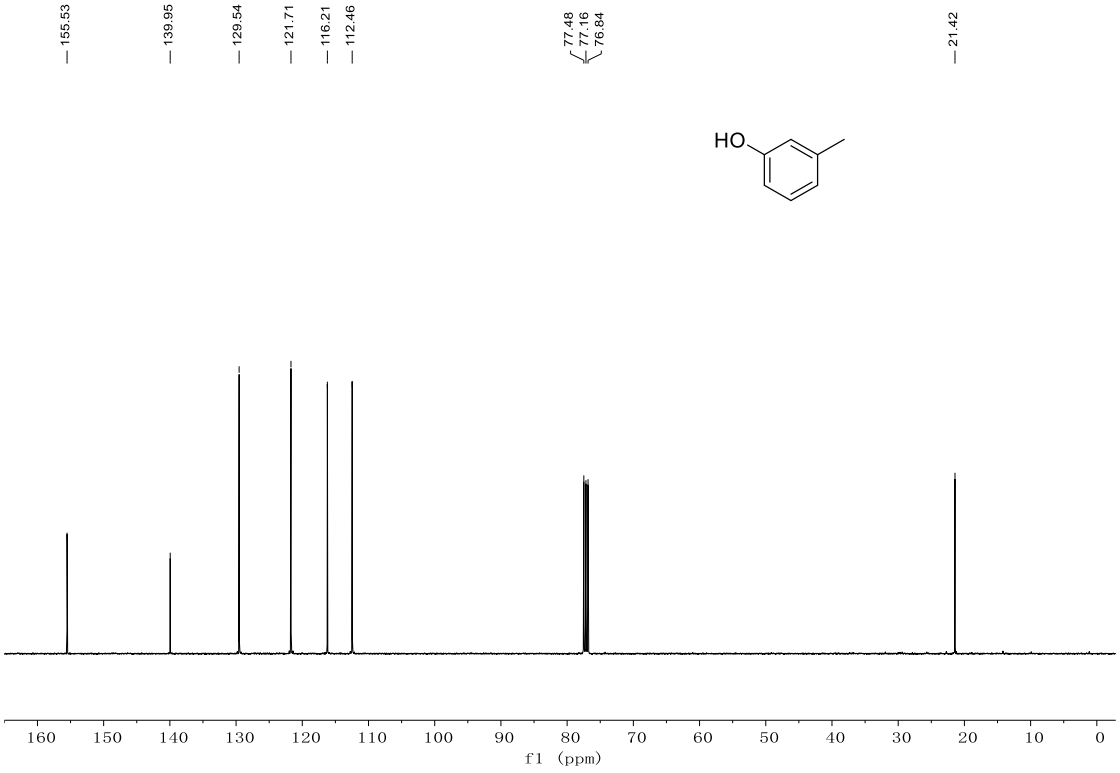
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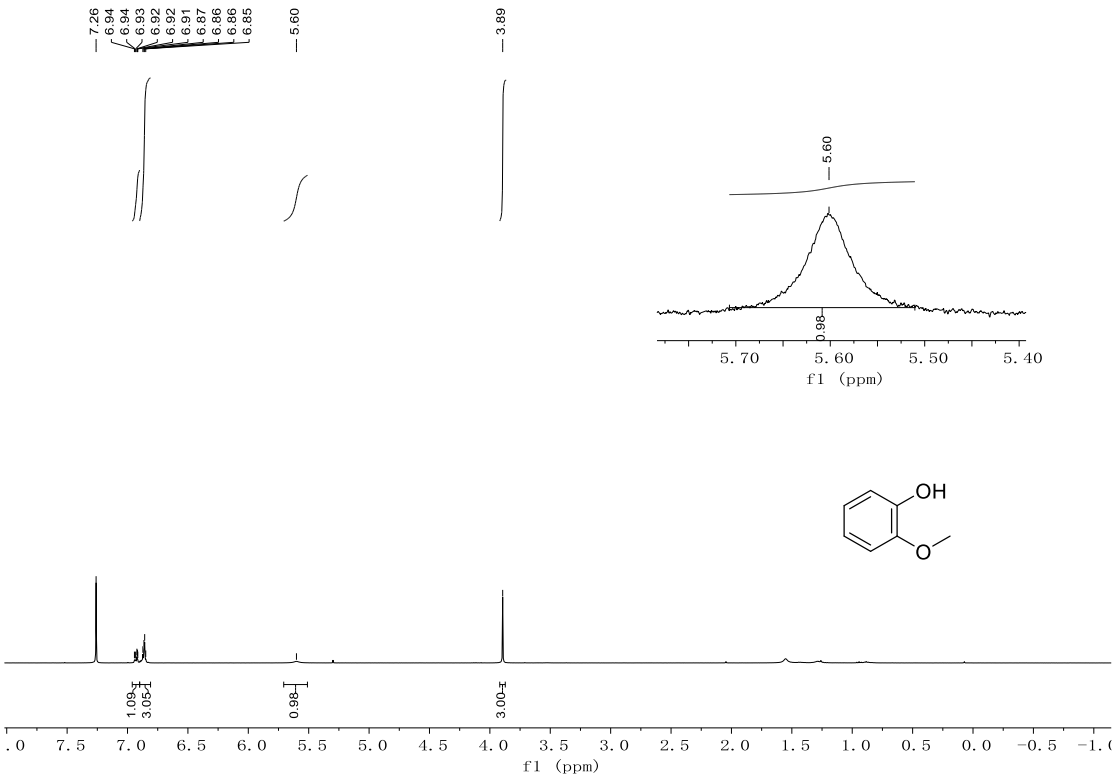
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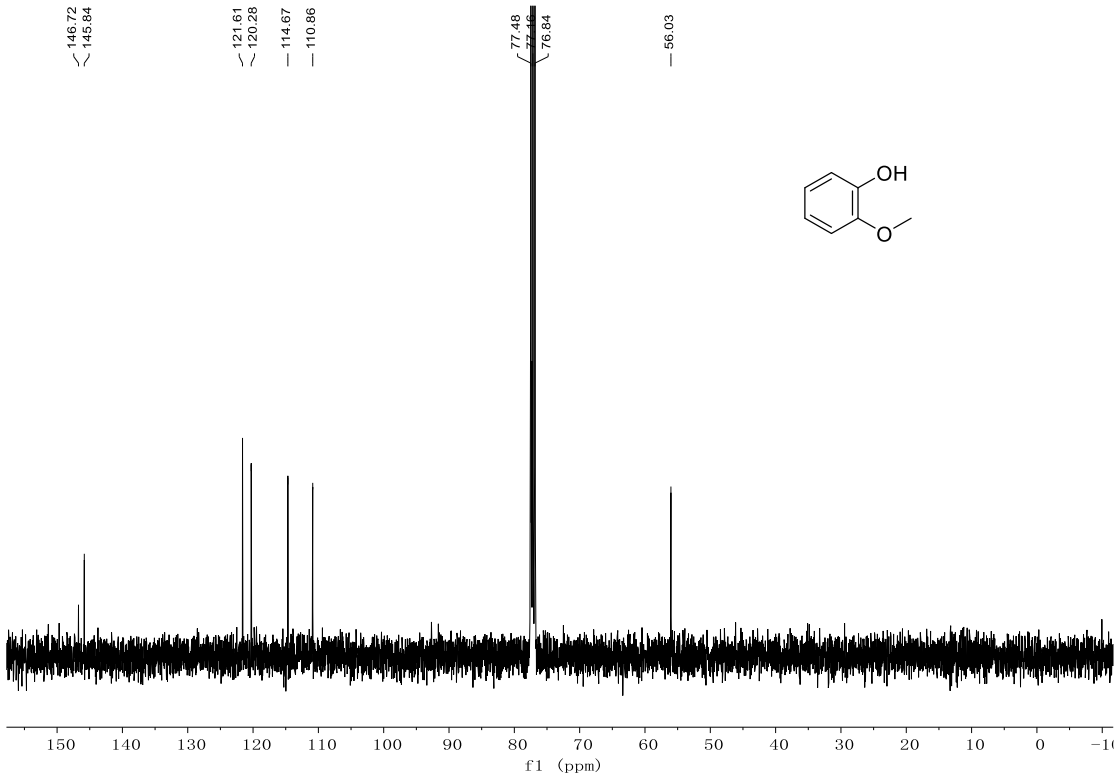
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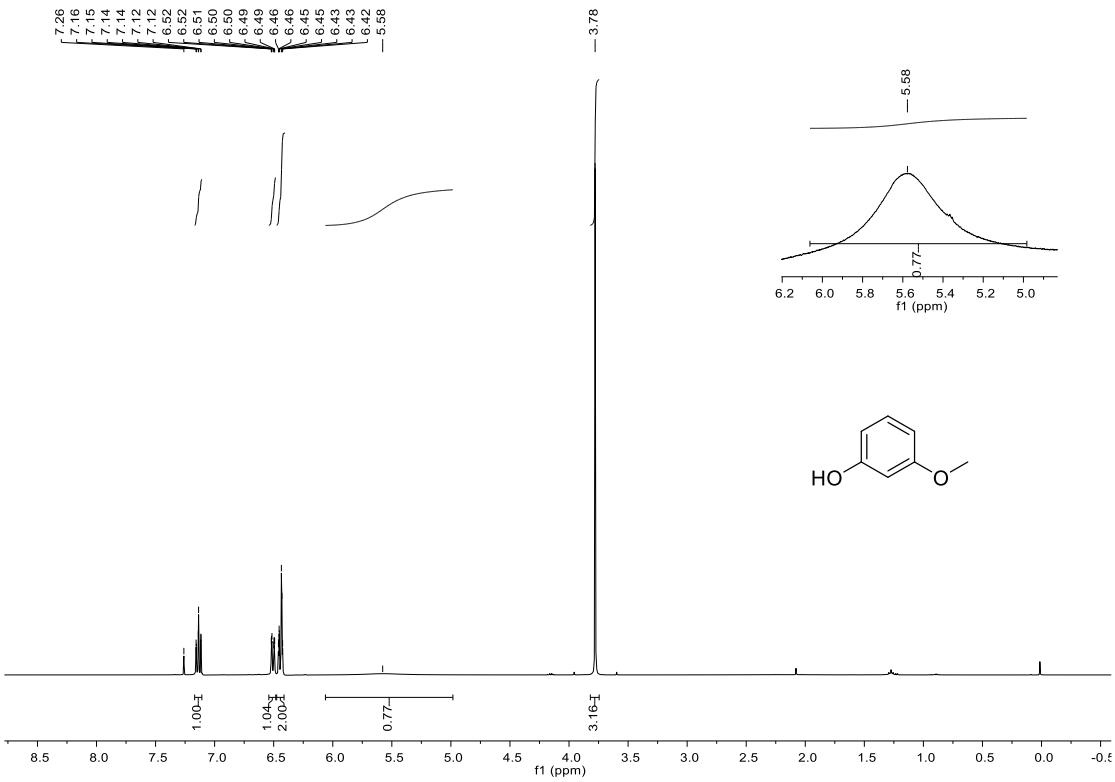
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6.49
6.46
6.46
6.45
6.45
6.43
6.43
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3.78
5.58
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O
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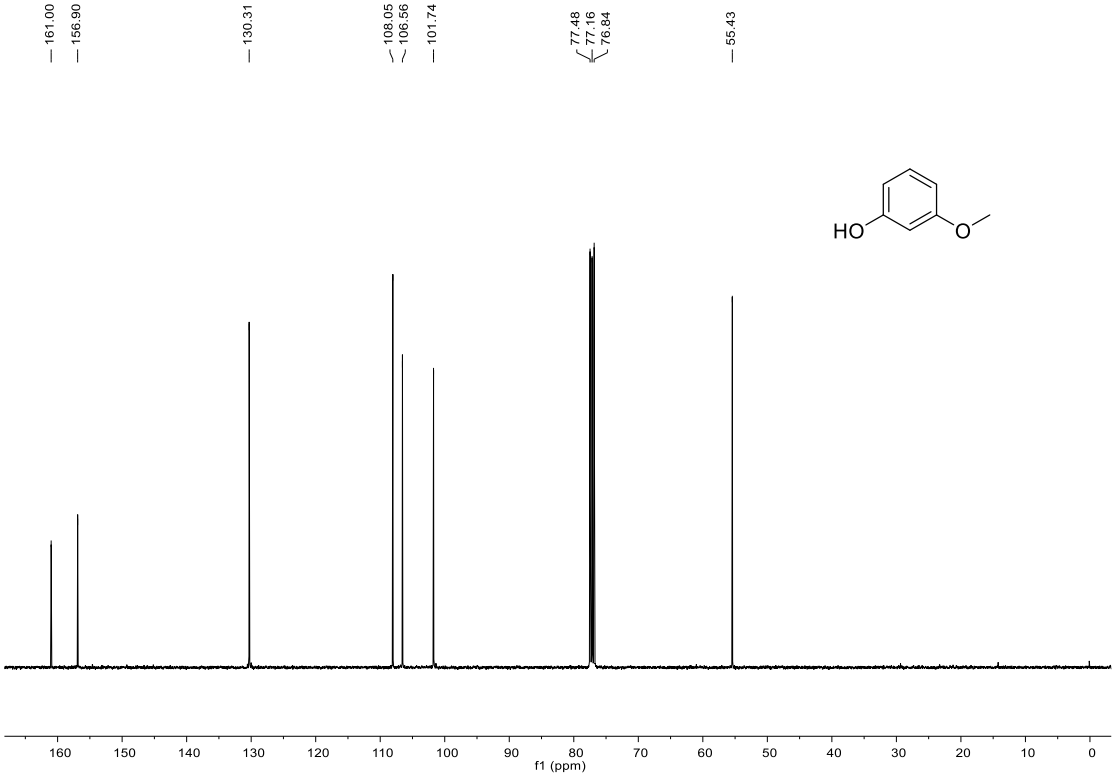
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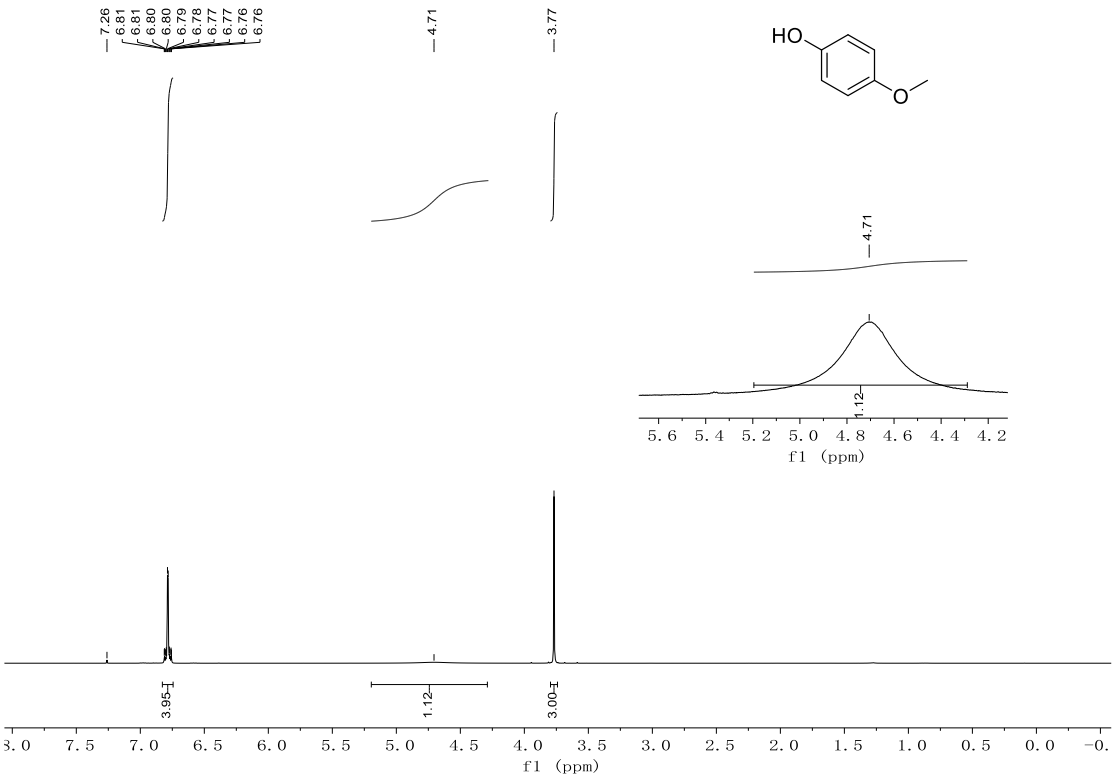
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3.00
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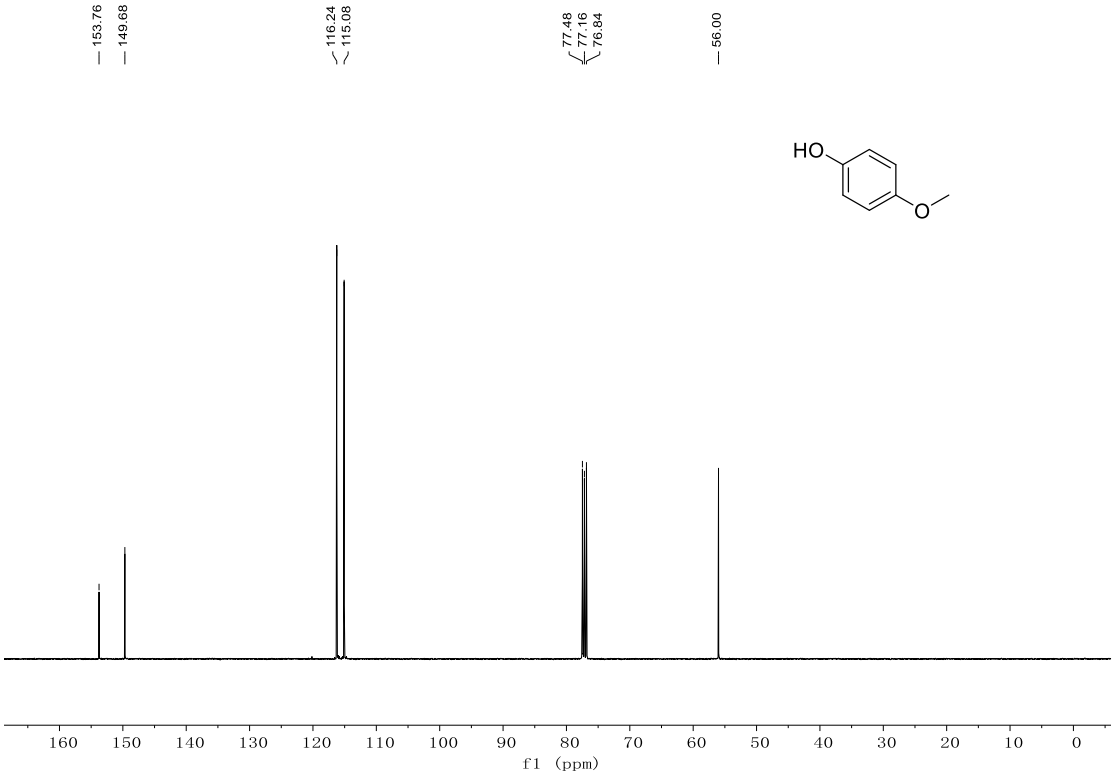
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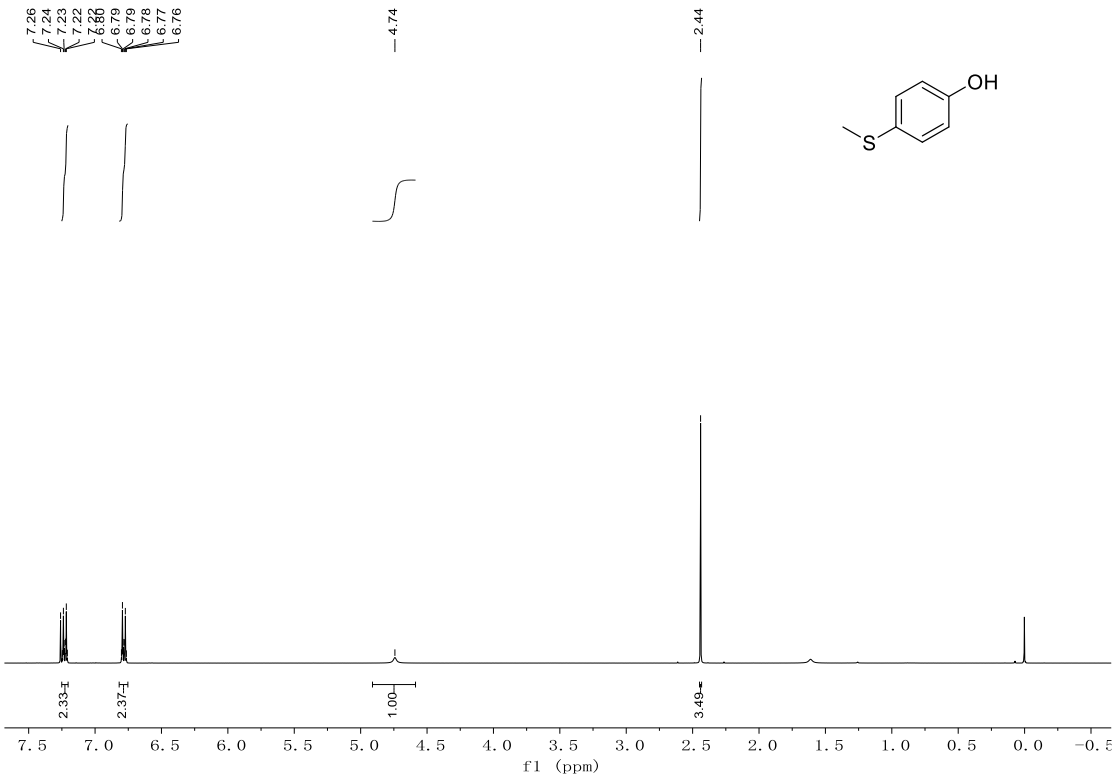
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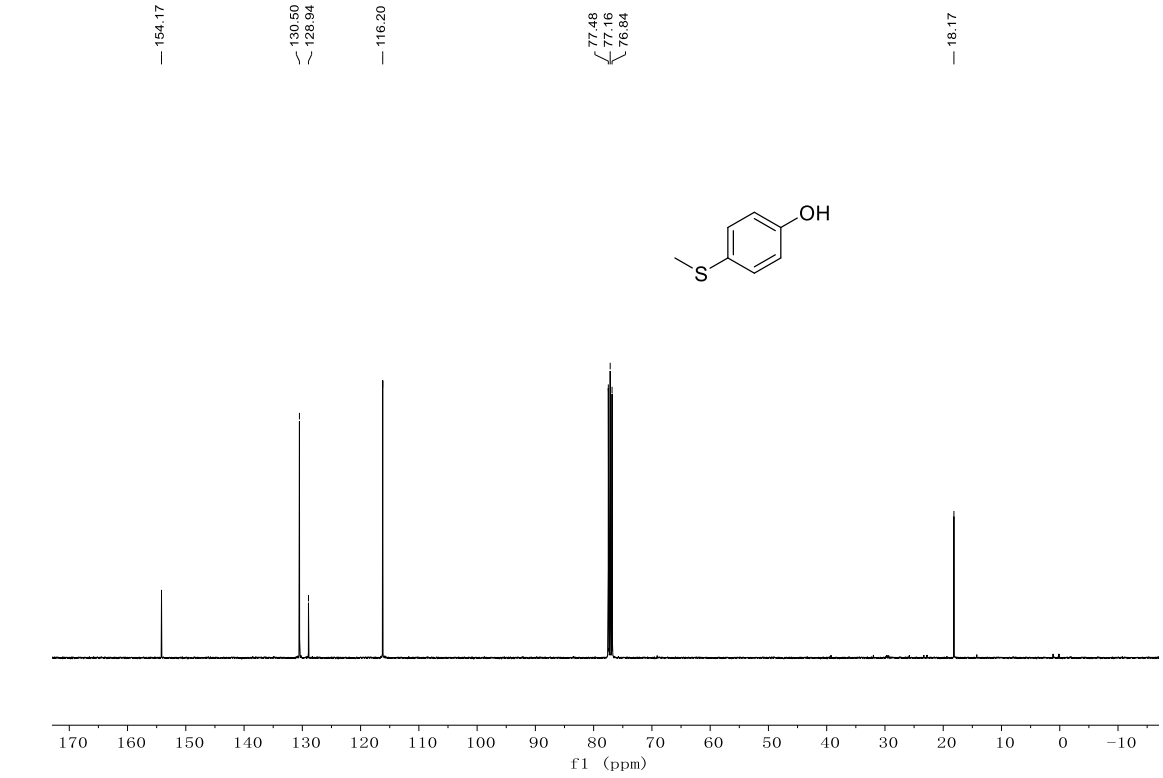
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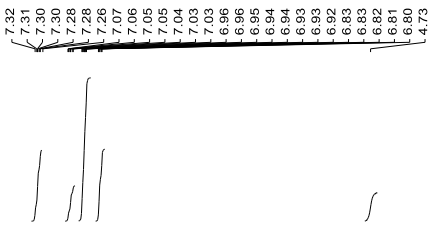
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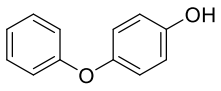
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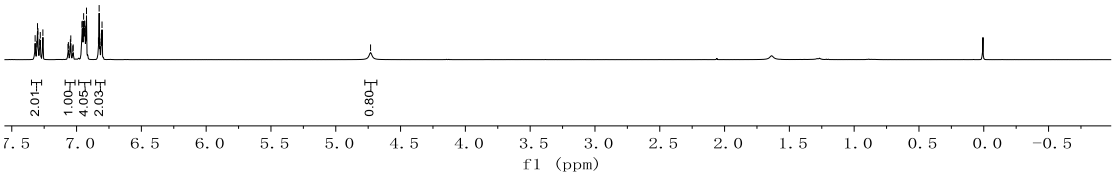
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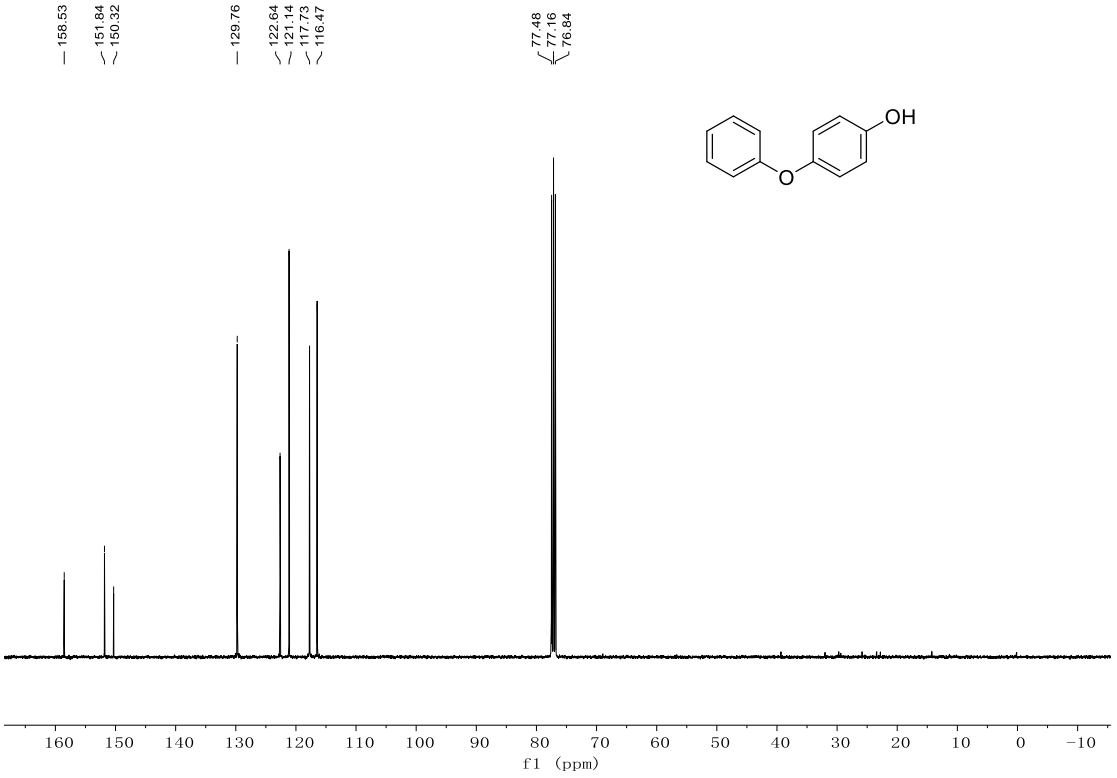
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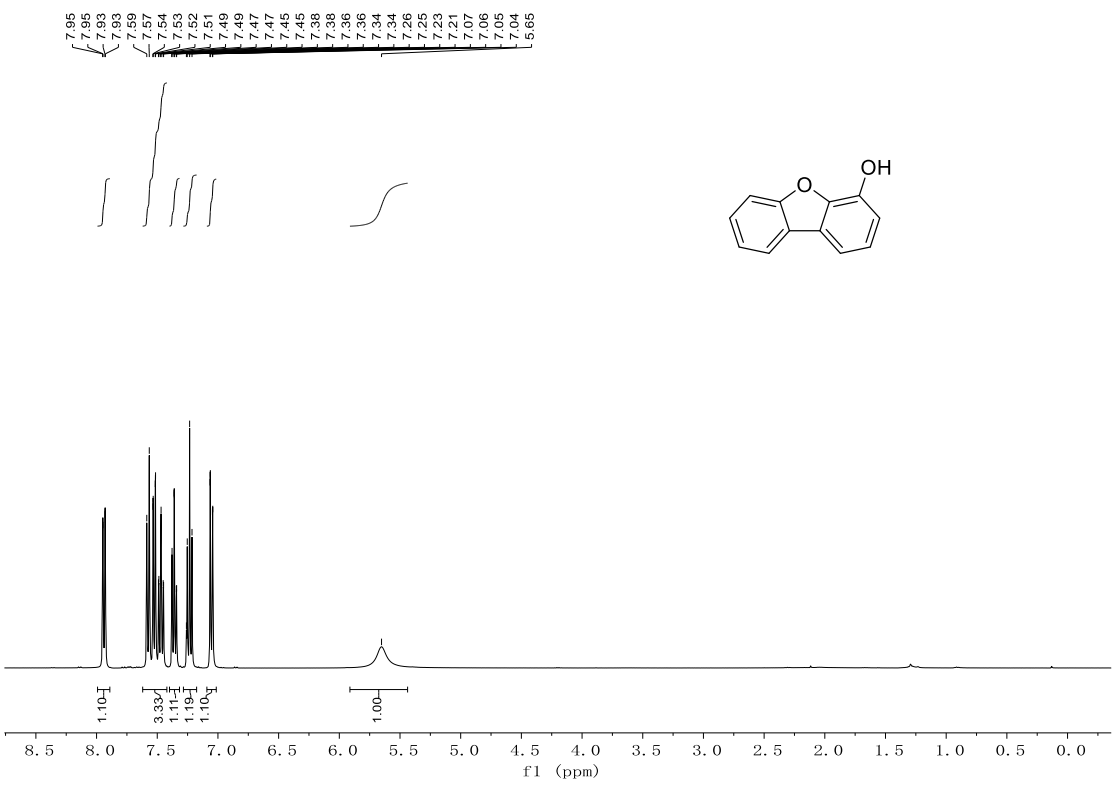
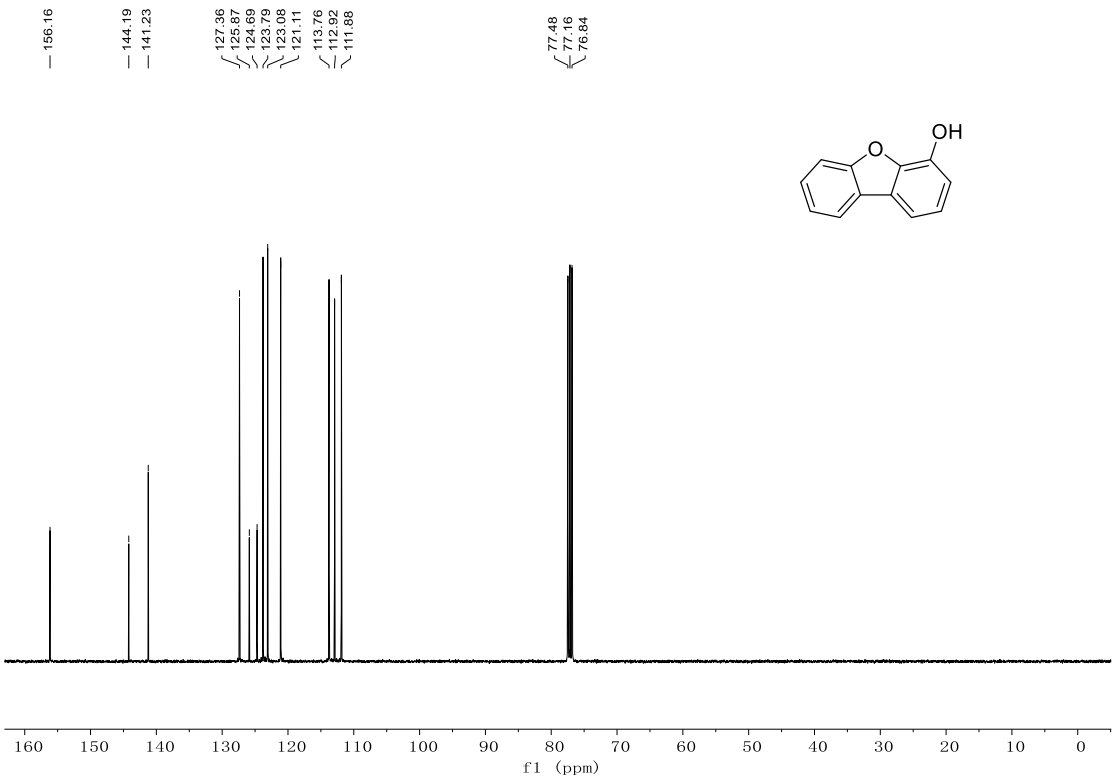

7.95
7.95
7.93
7.93
7.59
7.57
7.54
7.53
7.52
7.51
7.49
7.49
7.47
7.47
7.45
7.45
7.38
7.38
7.36
7.36
7.34
7.34
7.26
7.25
7.23
7.21
7.07
7.06
7.05
7.04
5.65
O
OH
1.10
3.33
1.11
1.19
1.10
1.00
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)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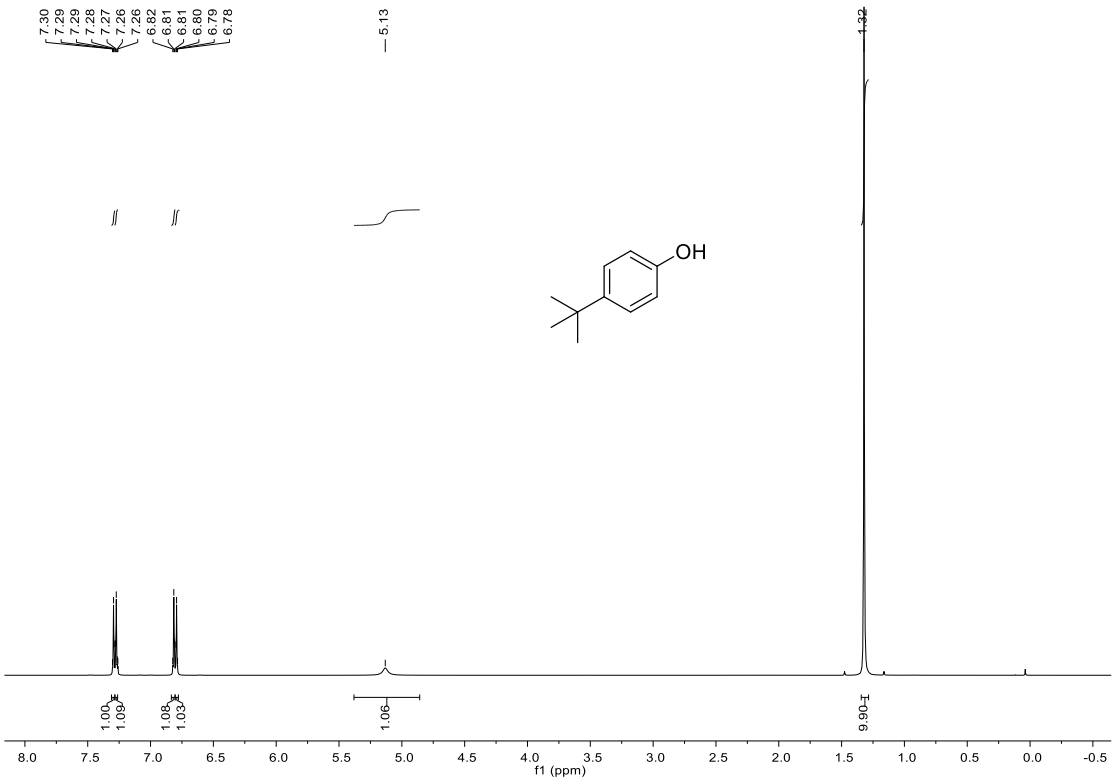
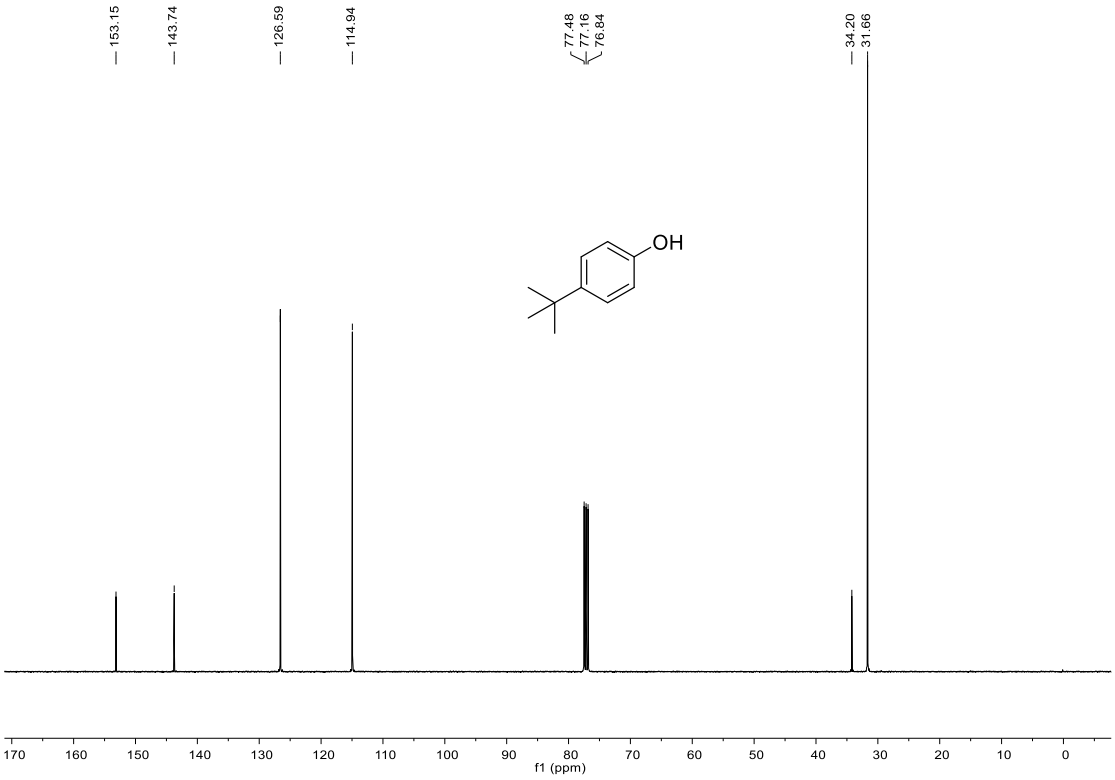
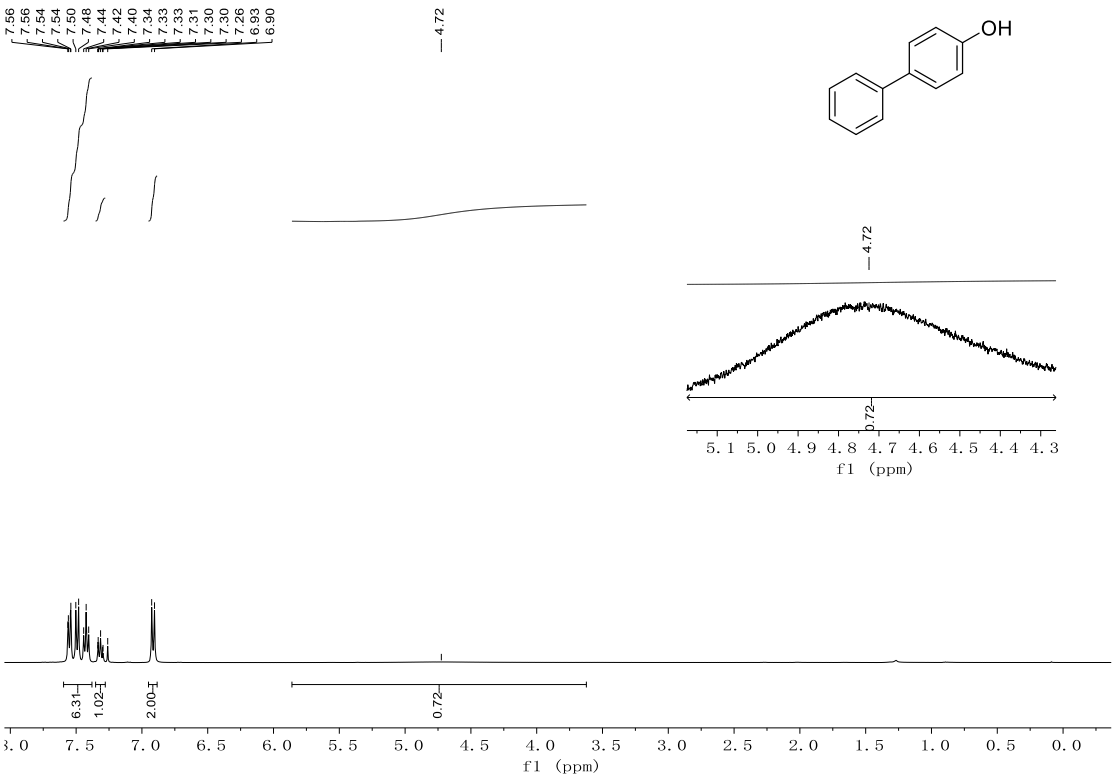
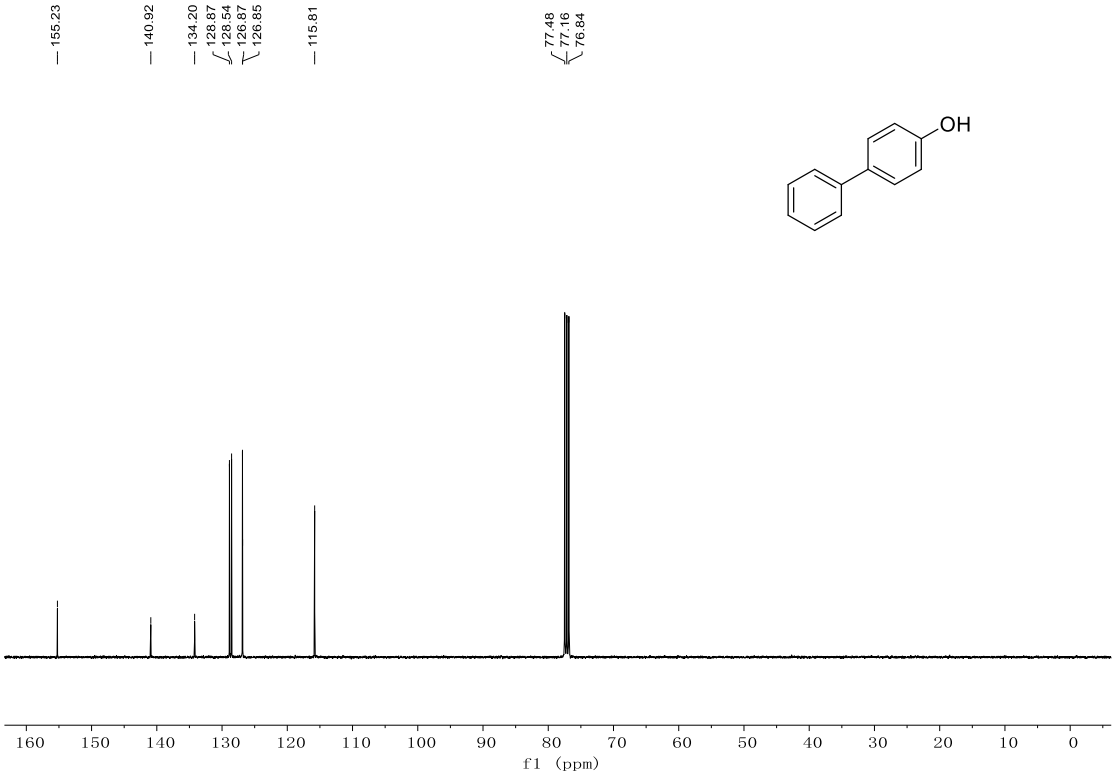
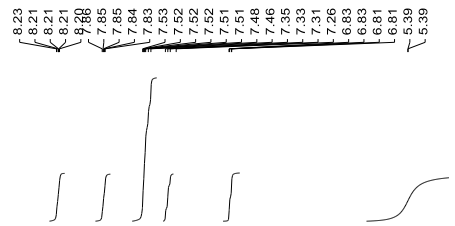
144.19
141.23
127.36
125.87
124.69
123.79
123.08
121.11
113.76
112.92
111.88
77.48
77.16
76.84
O
OH
160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

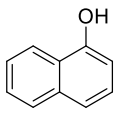

7.30
7.29
7.29
7.28
7.27
7.26
7.26
6.82
6.81
6.81
6.80
6.79
6.78
5.13
1.32
OH
1.00
1.09
1.08
1.03
1.06
9.90
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)

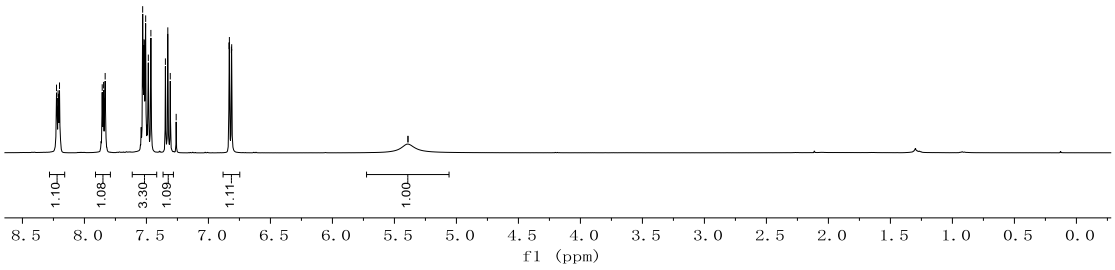

153.15
143.74
126.59
114.94
77.48
77.16
76.84
34.20
31.66
OH
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

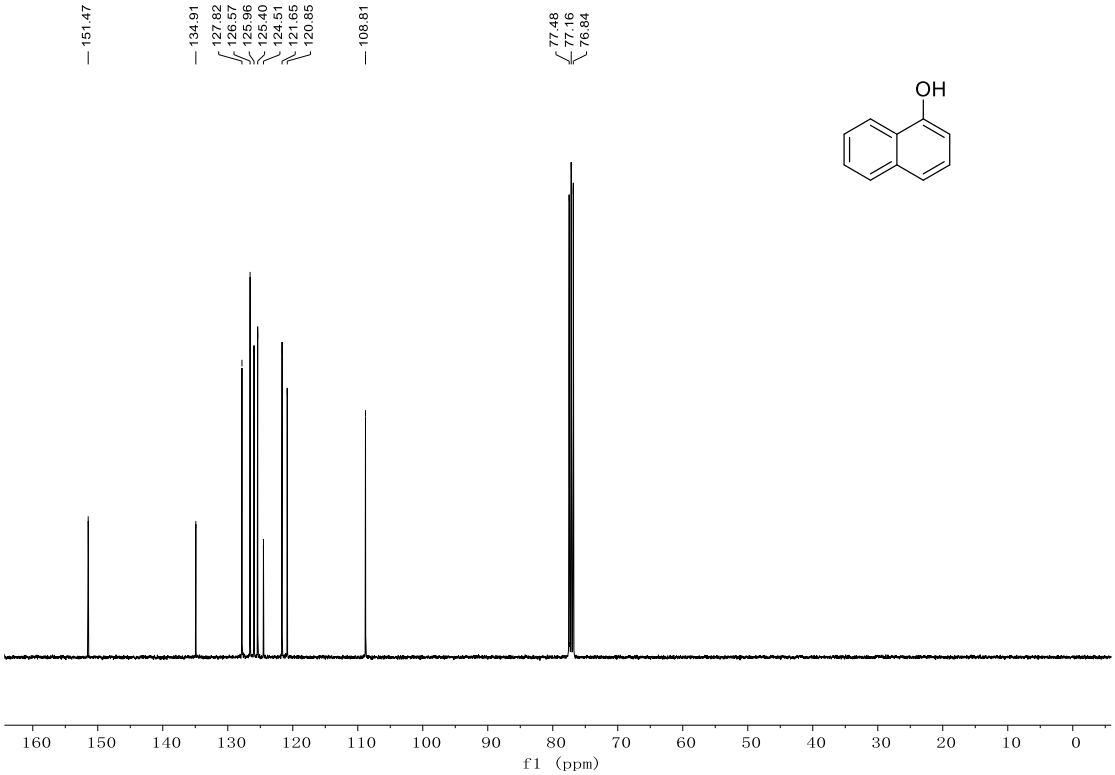

7.56
7.56
7.54
7.54
7.50
7.48
7.44
7.42
7.40
7.34
7.33
7.31
7.30
7.30
7.26
6.93
6.90
4.72
OH
4.72
0.72
5.1 5.0 4.9 4.8 4.7 4.6 4.5 4.4 4.3
f1 (ppm)
6.31
1.02
2.00
0.72
7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


155.23
140.92
134.20
128.87
128.54
126.87
126.85
115.81
77.48
77.16
76.84
OH
160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

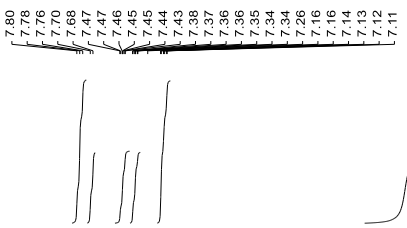

8.23
8.21
8.21
8.21
7.88
7.85
7.85
7.84
7.83
7.53
7.52
7.52
7.52
7.51
7.51
7.48
7.46
7.35
7.33
7.31
7.26
6.83
6.83
6.81
6.81
5.39
5.39

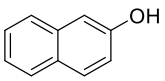

OH

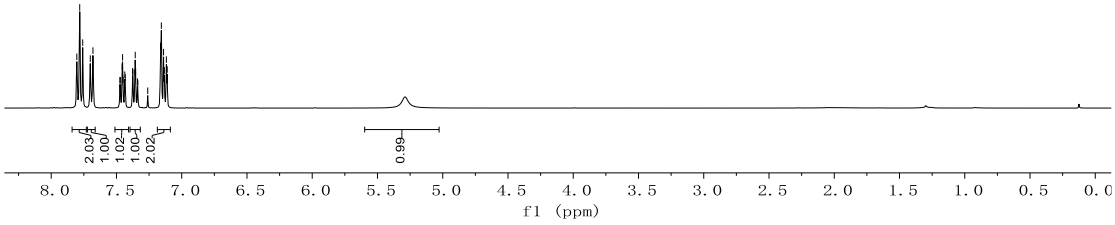

1.10
1.08
3.30
1.09
1.11
1.00
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

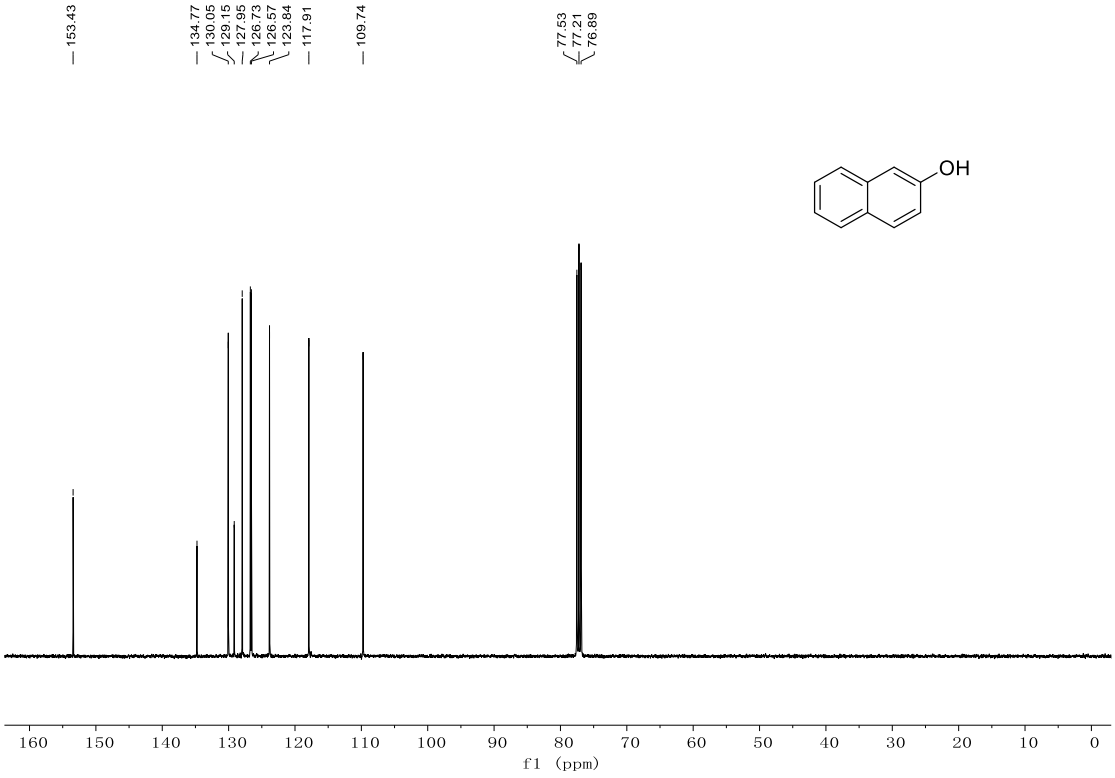

151.47
134.91
127.82
126.57
125.96
125.40
124.51
121.65
120.85
108.81
77.48
77.16
76.84
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

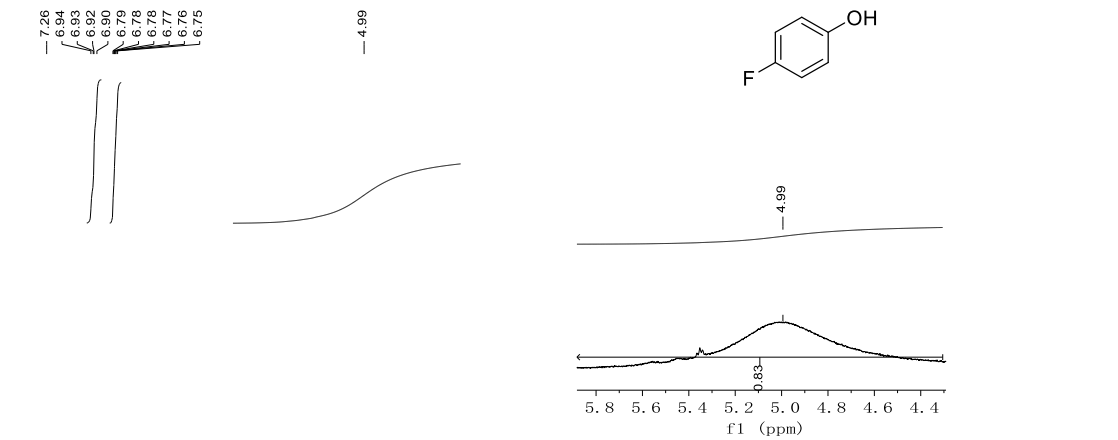
OH

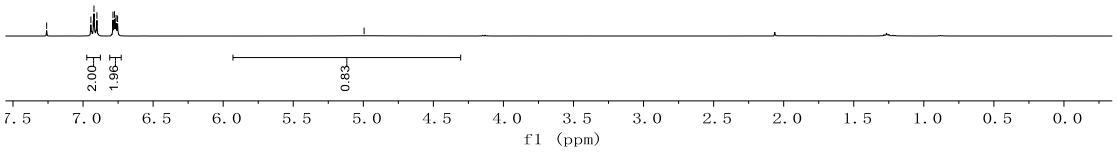

7.80
7.78
7.76
7.70
7.68
7.47
7.47
7.46
7.45
7.45
7.44
7.43
7.38
7.37
7.36
7.36
7.35
7.34
7.34
7.26
7.16
7.16
7.14
7.13
7.12
7.11

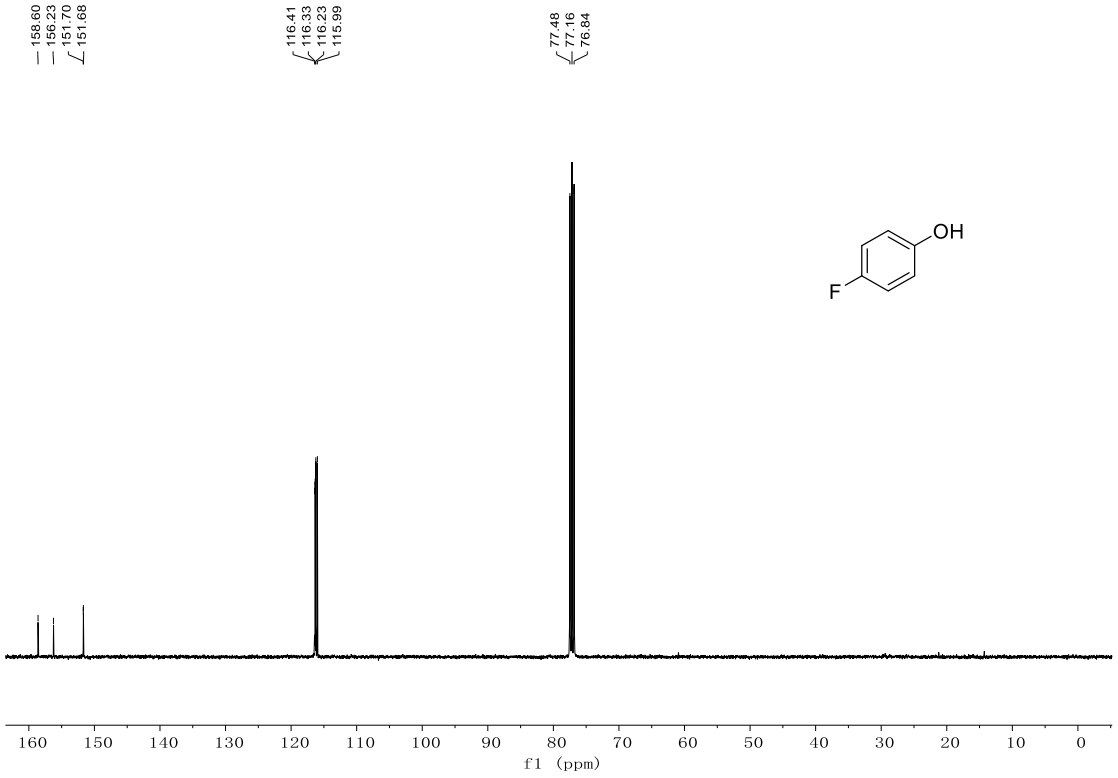

OH

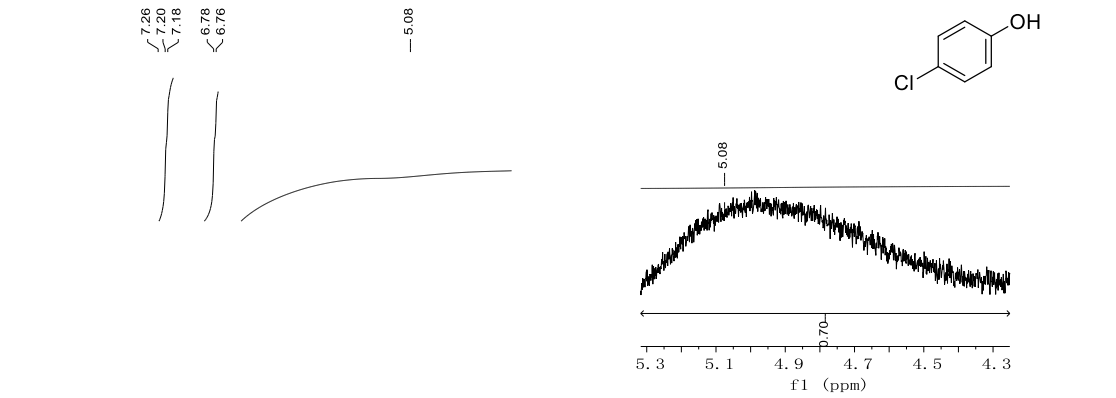

2.03
1.00
1.02
1.00
2.02
0.99
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

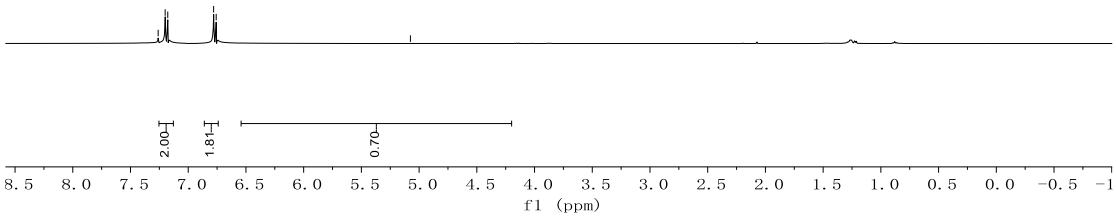

153.43
134.77
130.05
129.15
127.95
126.73
126.57
123.84
117.91
109.74
77.53
77.21
76.89
OH
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

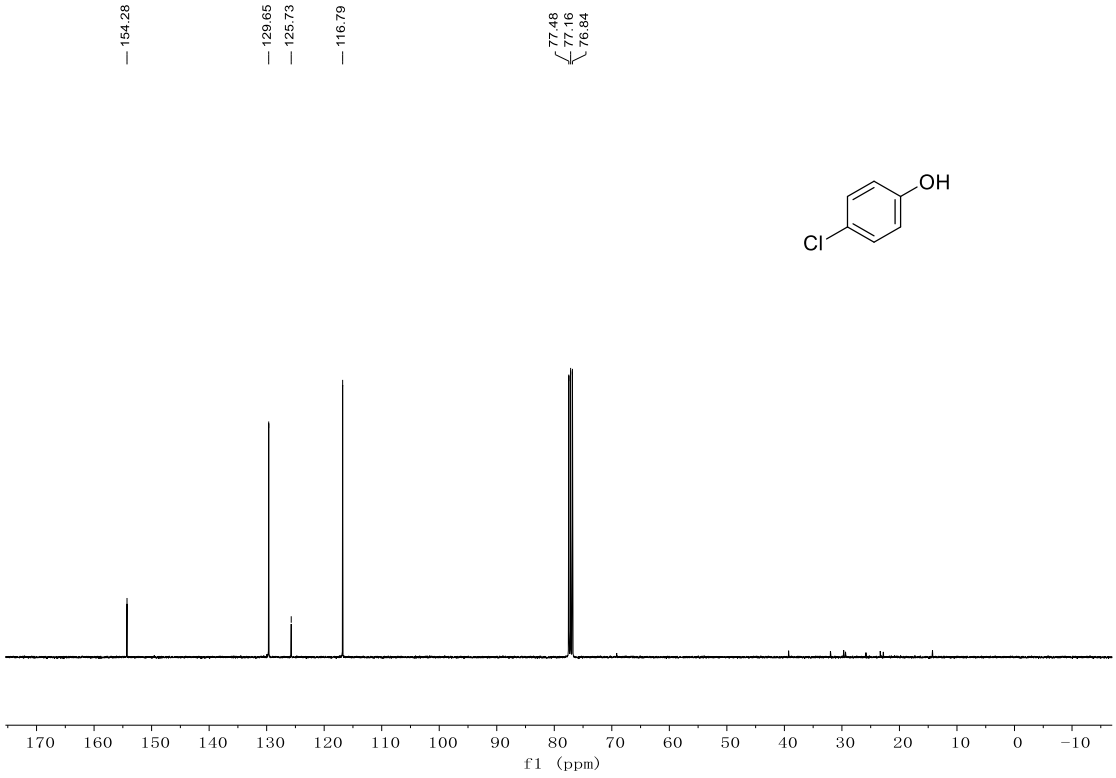

7.26
6.94
6.93
6.92
6.90
6.79
6.78
6.78
6.77
6.76
6.75
4.99
OH
F
4.99
0.83
5.8 5.6 5.4 5.2 5.0 4.8 4.6 4.4
f1 (ppm)

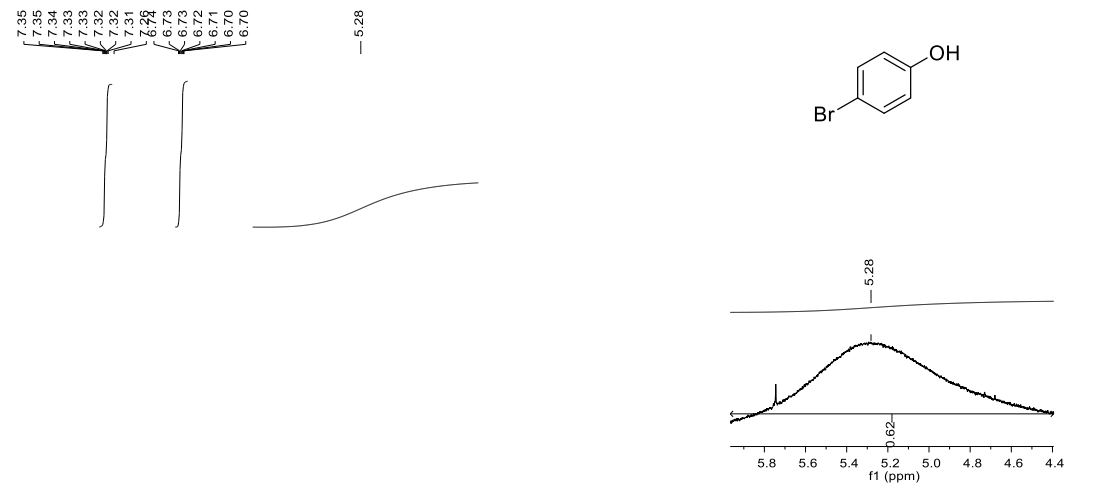

2.00
1.96
0.83
7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

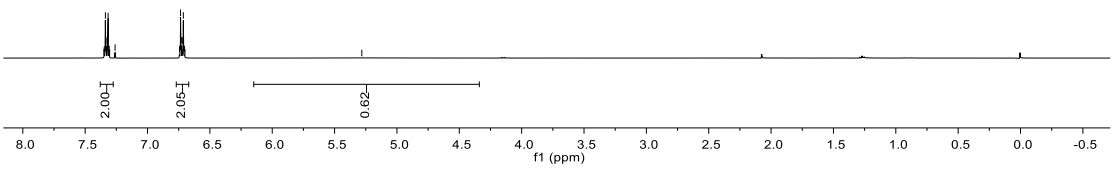

158.60
156.23
151.70
151.68
116.41
116.33
116.23
115.99
77.48
77.16
76.84
OH
F
160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

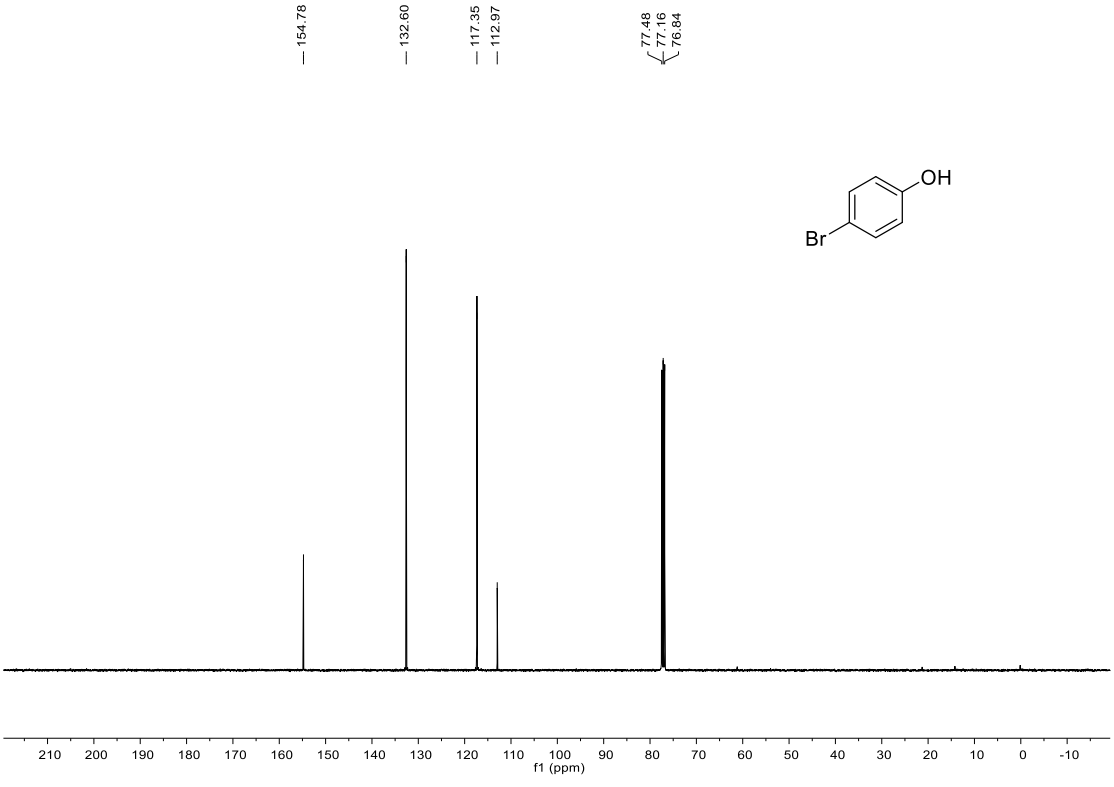

7.26
7.20
7.18
6.78
6.76
5.08
OH
Cl
5.08
0.70
5.3
5.1
4.9
4.7
4.5
4.3
f1 (ppm)

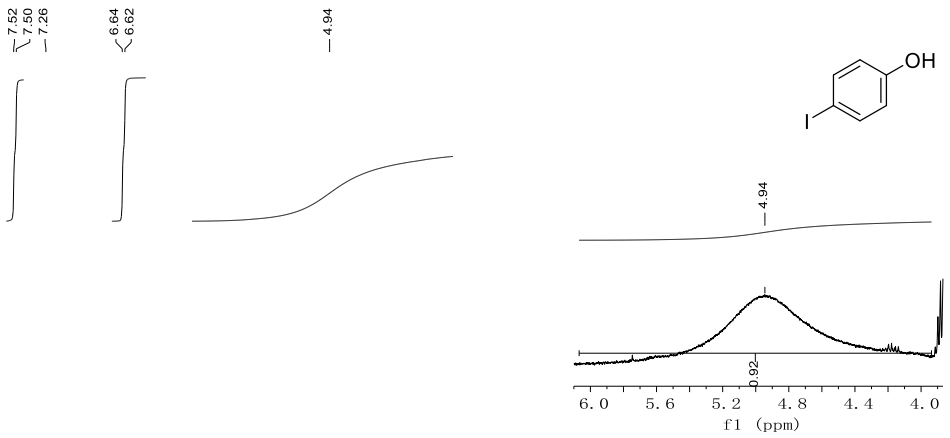

2.00
1.81
0.70
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
−0.5
−1
f1 (ppm)

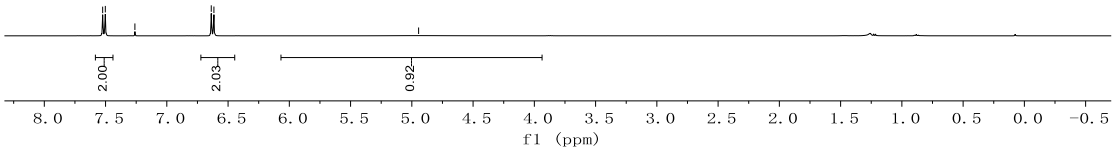

154.28
129.65
125.73
116.79
77.48
77.16
76.84
OH
Cl
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
−10
f1 (ppm)

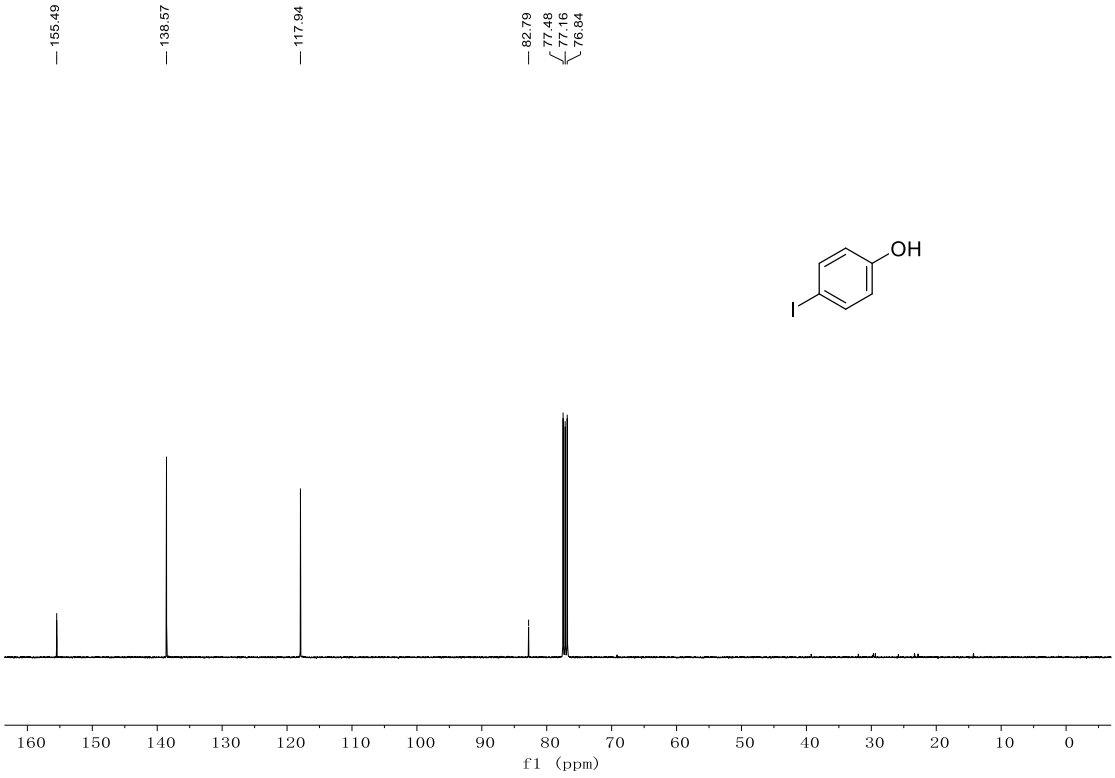

7.35
7.35
7.34
7.33
7.33
7.32
7.32
7.31
6.73
6.73
6.72
6.71
6.70
6.70
5.28
OH
Br
5.28
0.62
5.8
5.6
5.4
5.2
5.0
4.8
4.6
4.4
f1 (ppm)

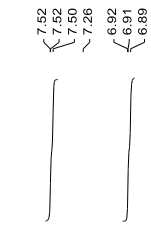

2.00
2.05
0.62
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)


154.78
132.60
117.35
112.97
77.48
77.16
76.84
OH
Br
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)


7.52
7.50
7.26
6.64
6.62
4.94
OH
I
4.94
0.92
6.0
5.6
5.2
4.8
4.4
4.0
f1 (ppm)


2.00
2.03
0.92
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
f1 (ppm)


155.49
138.57
117.94
82.79
77.48
77.16
76.84
OH
I
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)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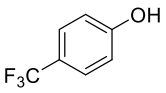
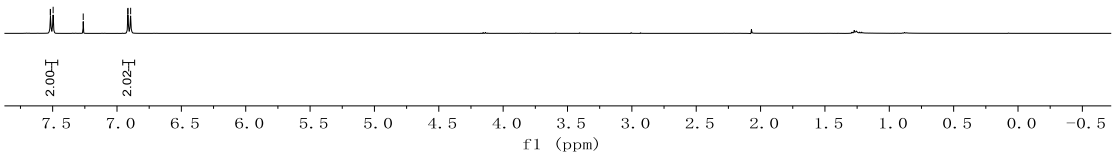
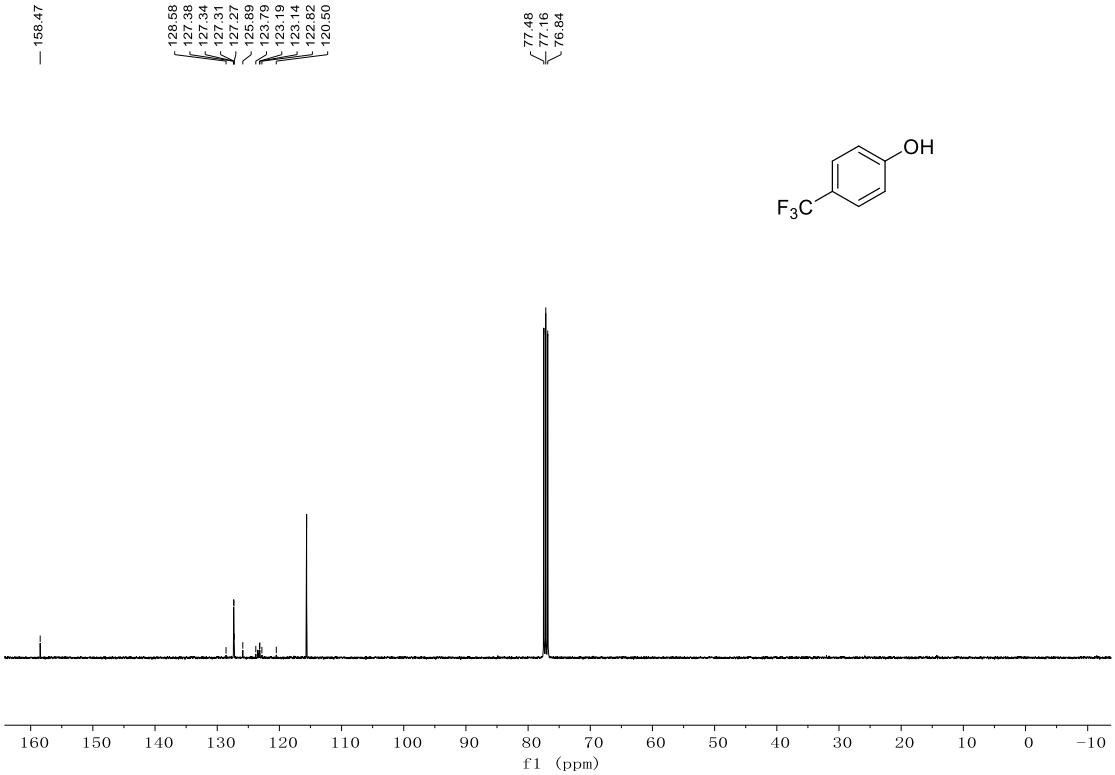
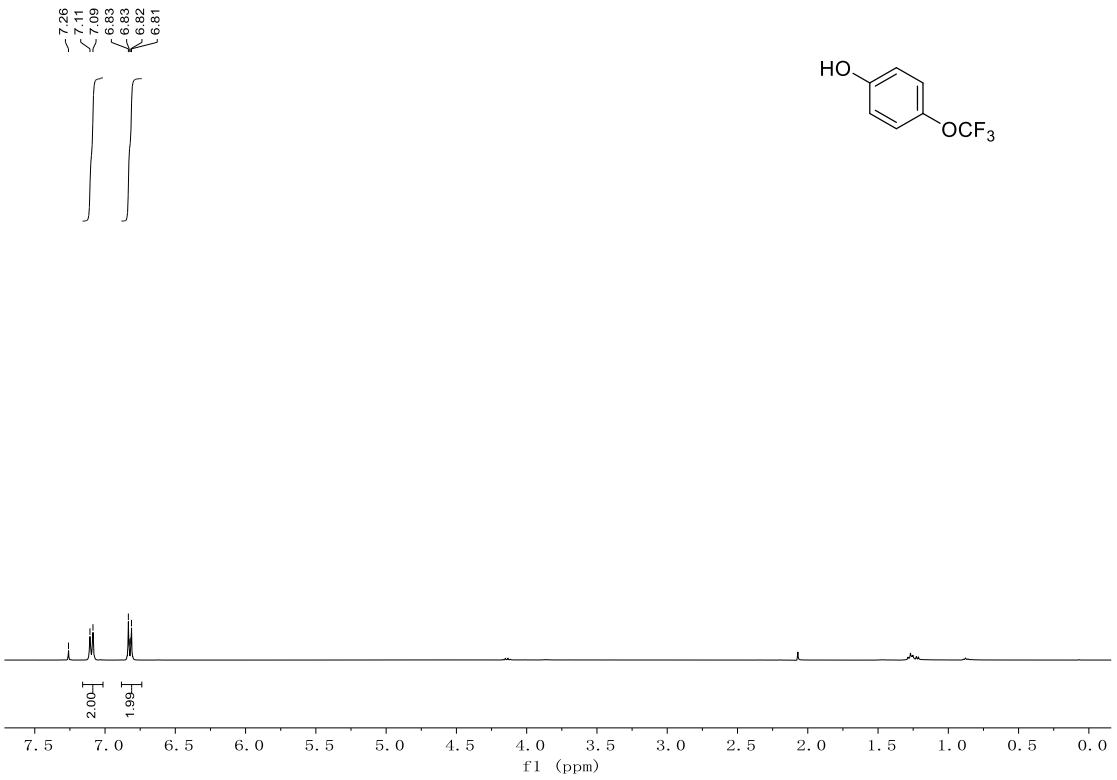
7.52
7.50
7.26
6.92
6.91
6.89

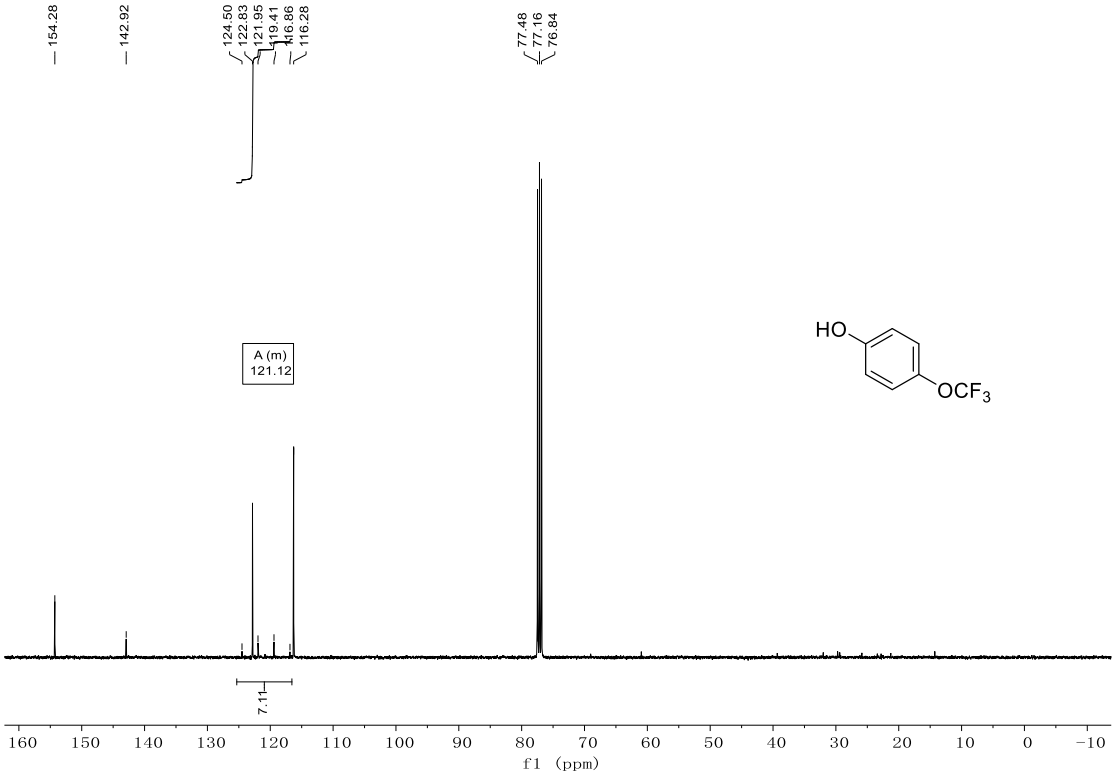

OH
F3C

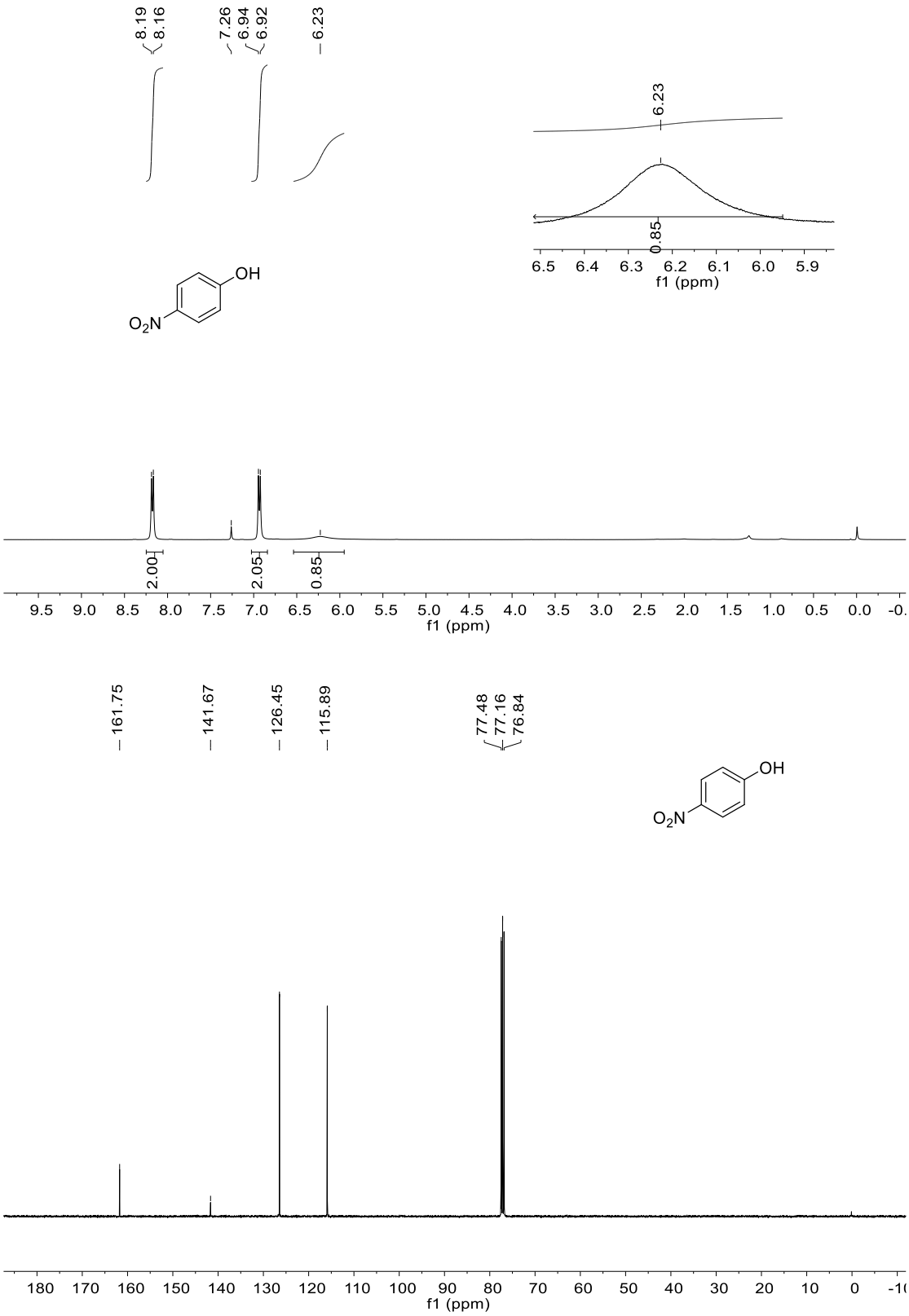

2.00
2.02
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
−0.5
f1 (ppm)

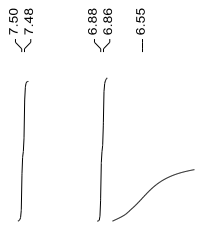

158.47
128.58
127.38
127.34
127.31
127.27
125.89
123.79
123.19
123.14
122.82
120.50
77.48
77.16
76.84
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
−10
f1 (ppm)

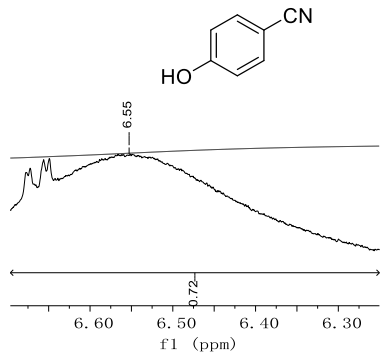
OH
F3C

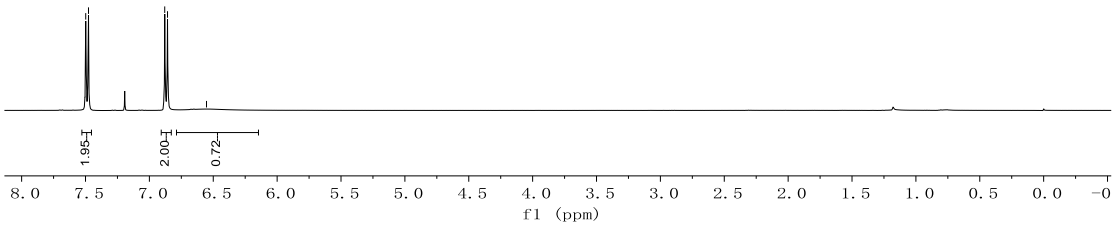

7.26
7.11
7.09
6.83
6.83
6.82
6.81
HO
OCF3
2.00
1.99
7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

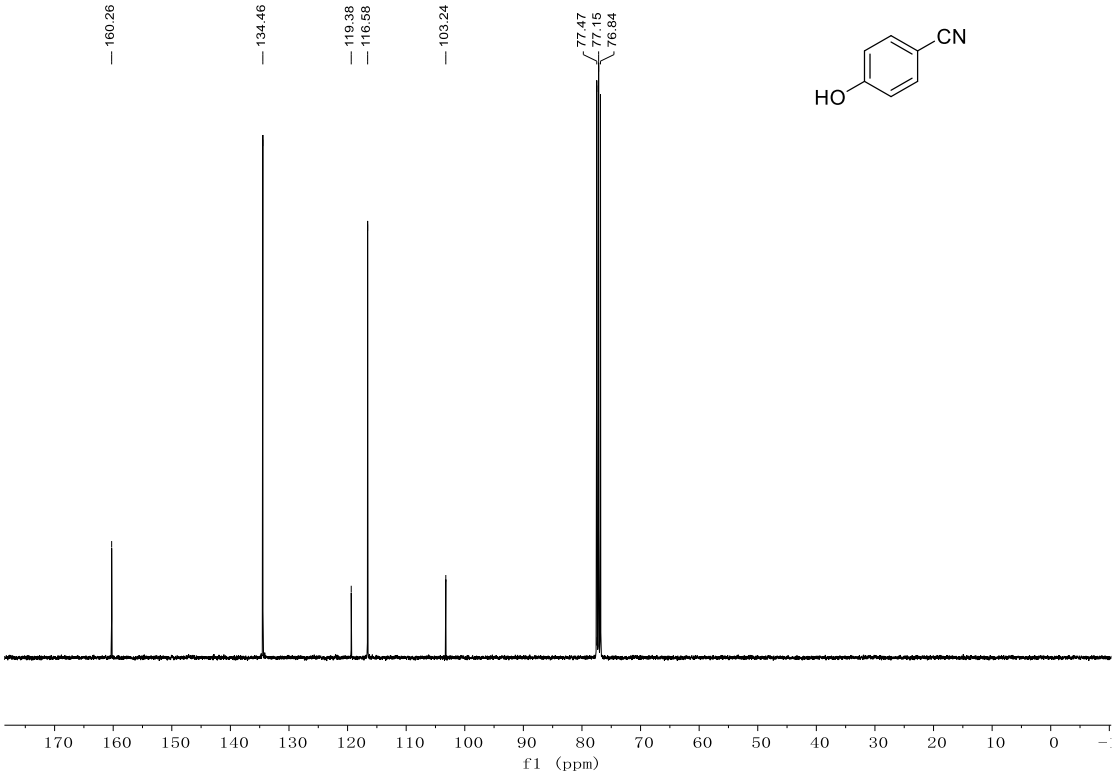

154.28
142.92
124.50
122.83
121.95
119.41
116.86
116.28
77.48
77.16
76.84
A (m)
121.12
HO
OCF3
7.11
160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 −10
f1 (ppm)

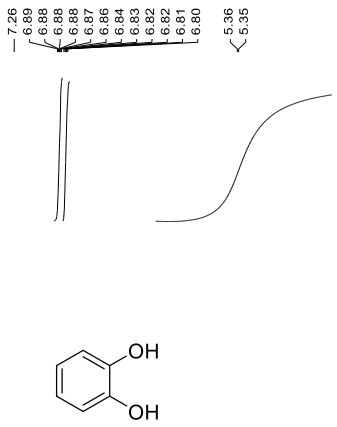

8.19
8.16
7.26
6.94
6.92
6.23
OH
O2N
6.23
0.85
6.5 6.4 6.3 6.2 6.1 6.0 5.9
f1 (ppm)
2.00
2.05
0.85
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)
161.75
141.67
126.45
115.89
77.48
77.16
76.84
OH
O2N
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

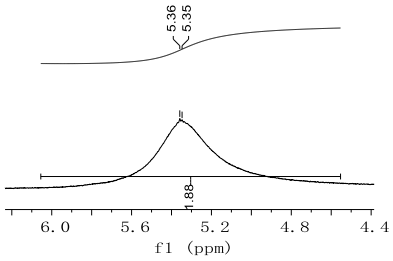

7.50
7.48
6.88
6.86
6.55

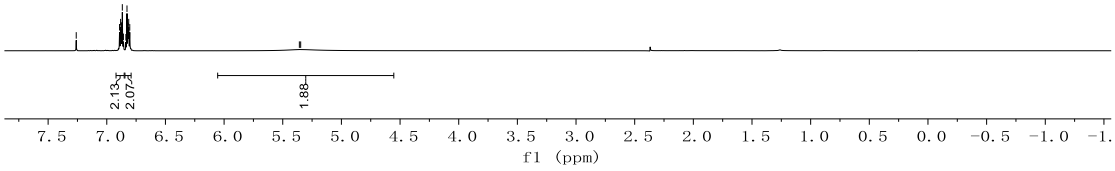

CN
HO
6.55
0.72
6.60
6.50
6.40
6.30
f1 (ppm)

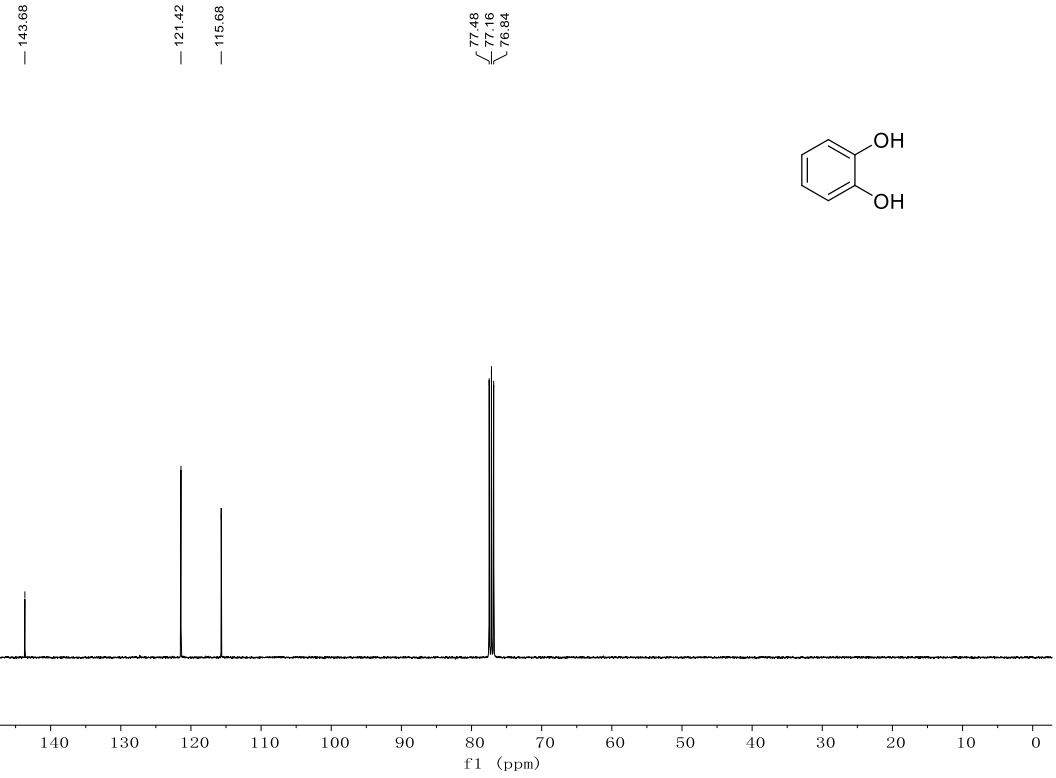

1.95
2.00
0.72
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

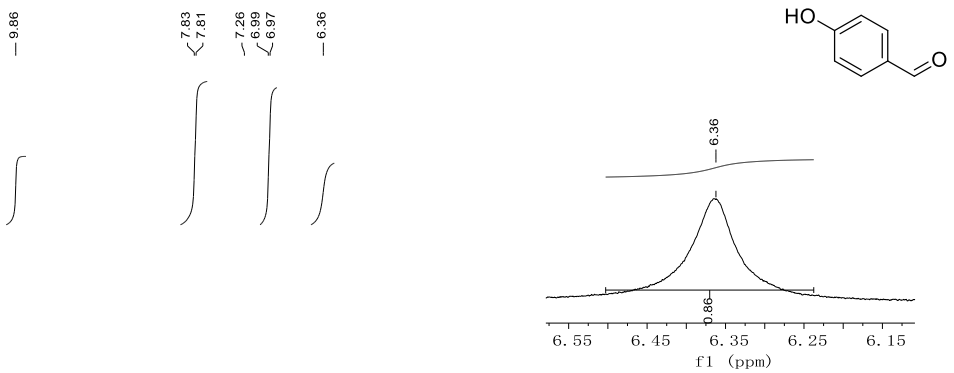

160.26
134.46
119.38
116.58
103.24
77.47
77.15
76.84
CN
HO
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

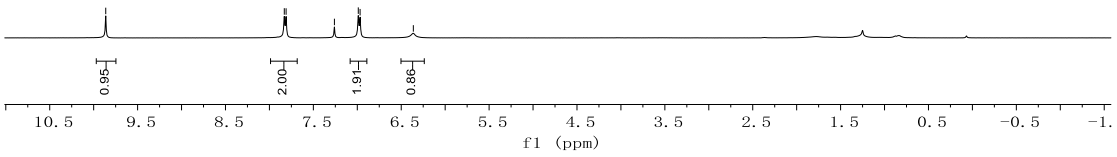

7.26
6.89
6.88
6.88
6.88
6.87
6.86
6.84
6.83
6.82
6.82
6.81
6.80
5.36
5.35
OH
OH

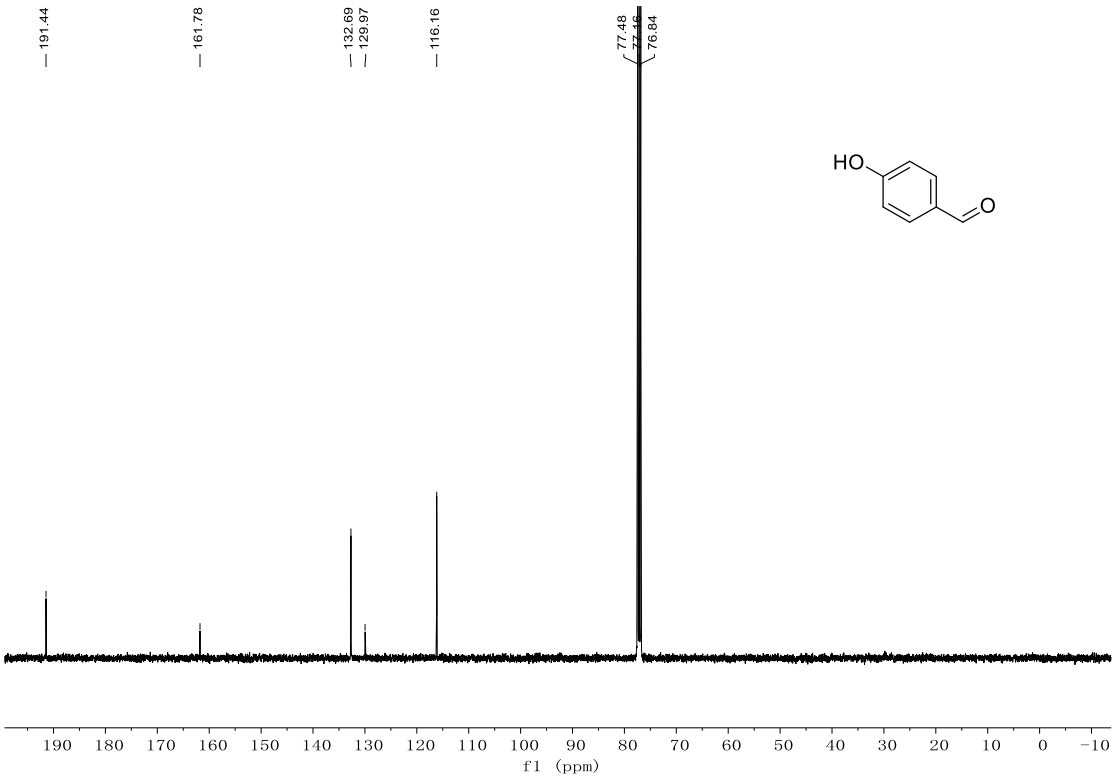

5.36
5.35
1.88
6.0
5.6
5.2
4.8
4.4
f1 (ppm)

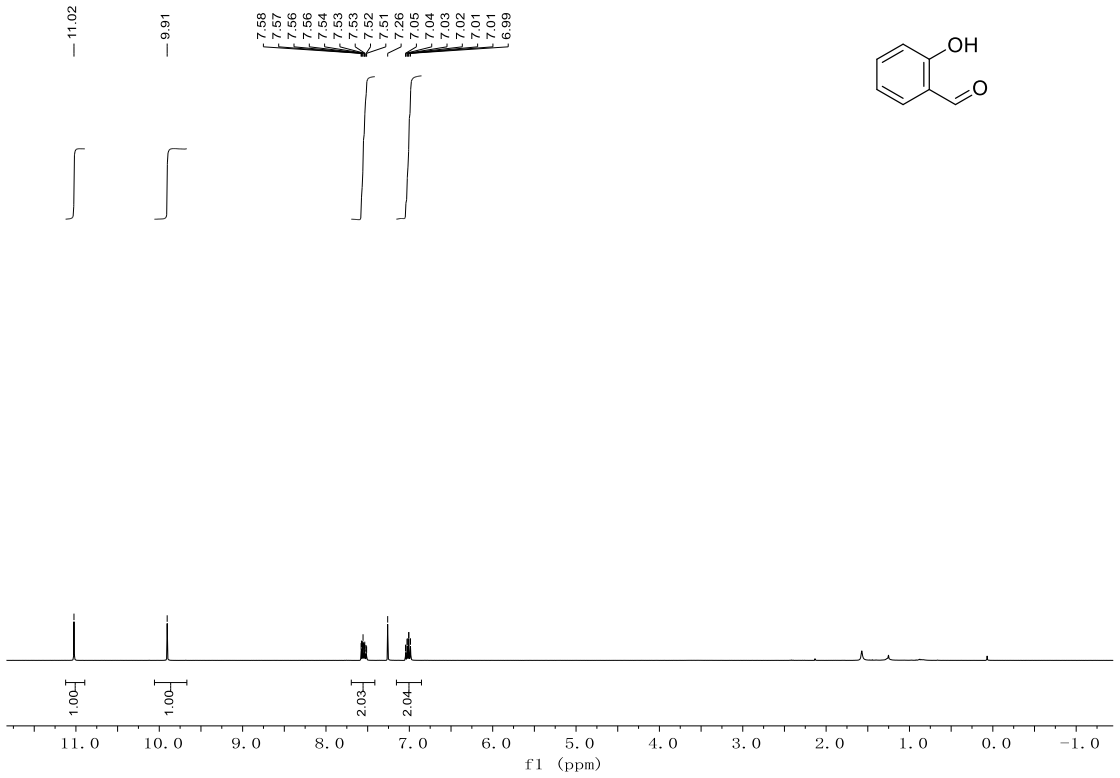

2.13
2.07
1.88
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1.0
f1 (ppm)

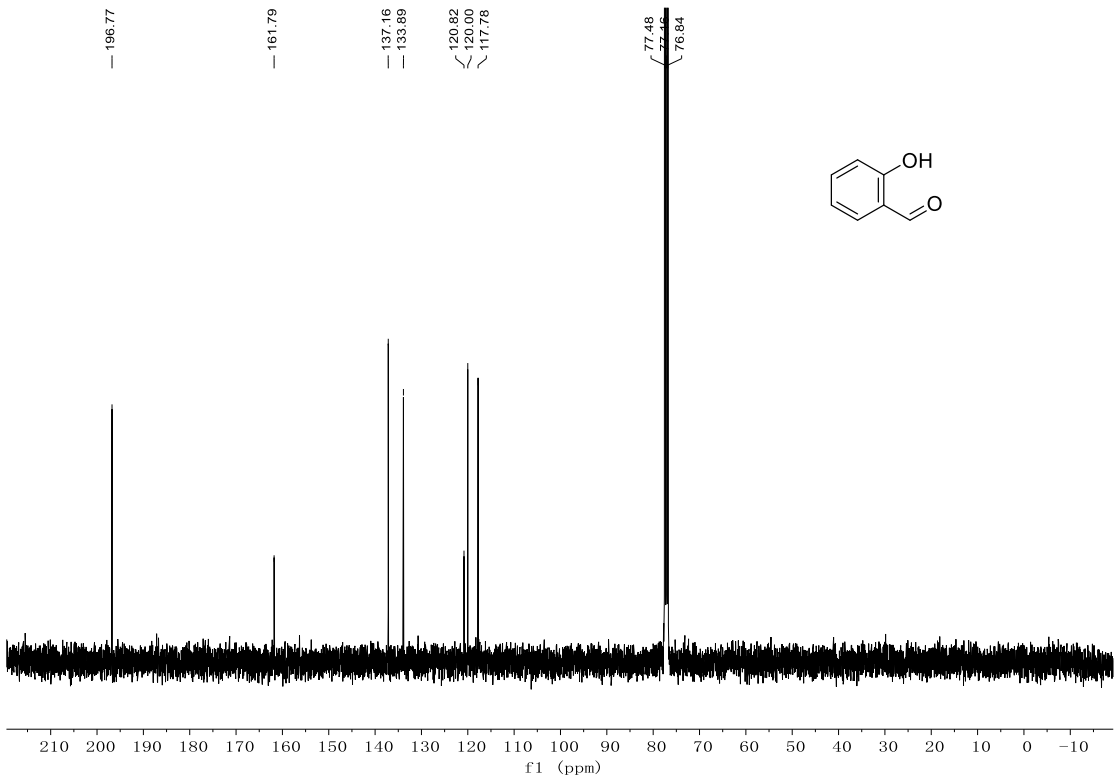

143.68
121.42
115.68
77.48
77.16
76.84
OH
OH
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

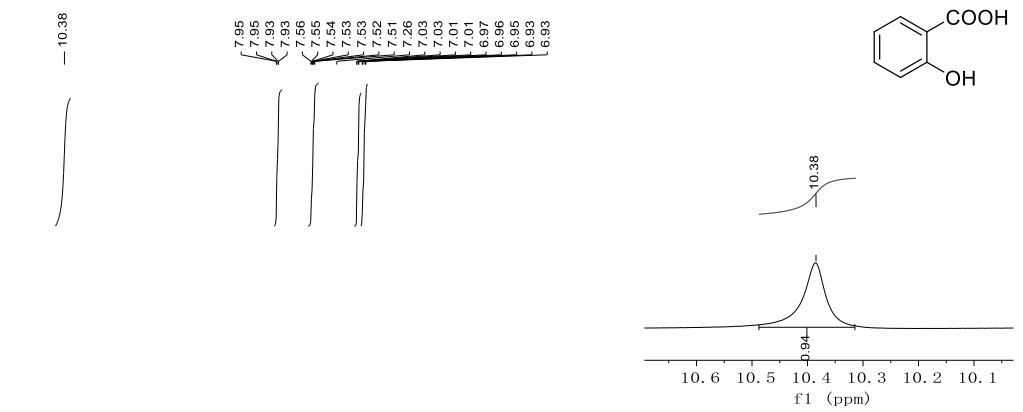

9.86
7.83
7.81
7.26
6.99
6.97
6.36
HO
O
6.36
0.86
6.55
6.45
6.35
6.25
6.15
f1 (ppm)

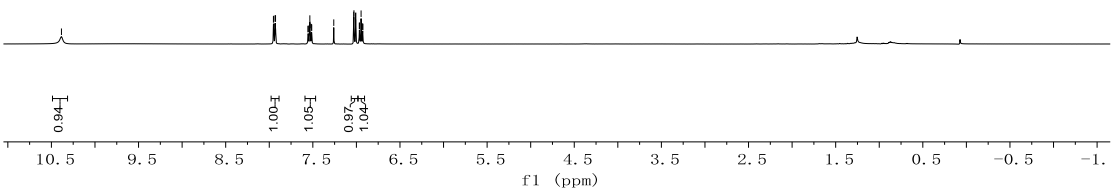

0.95
2.00
1.91
0.86
10.5
9.5
8.5
7.5
6.5
5.5
4.5
3.5
2.5
1.5
0.5
−0.5
−1.
f1 (ppm)

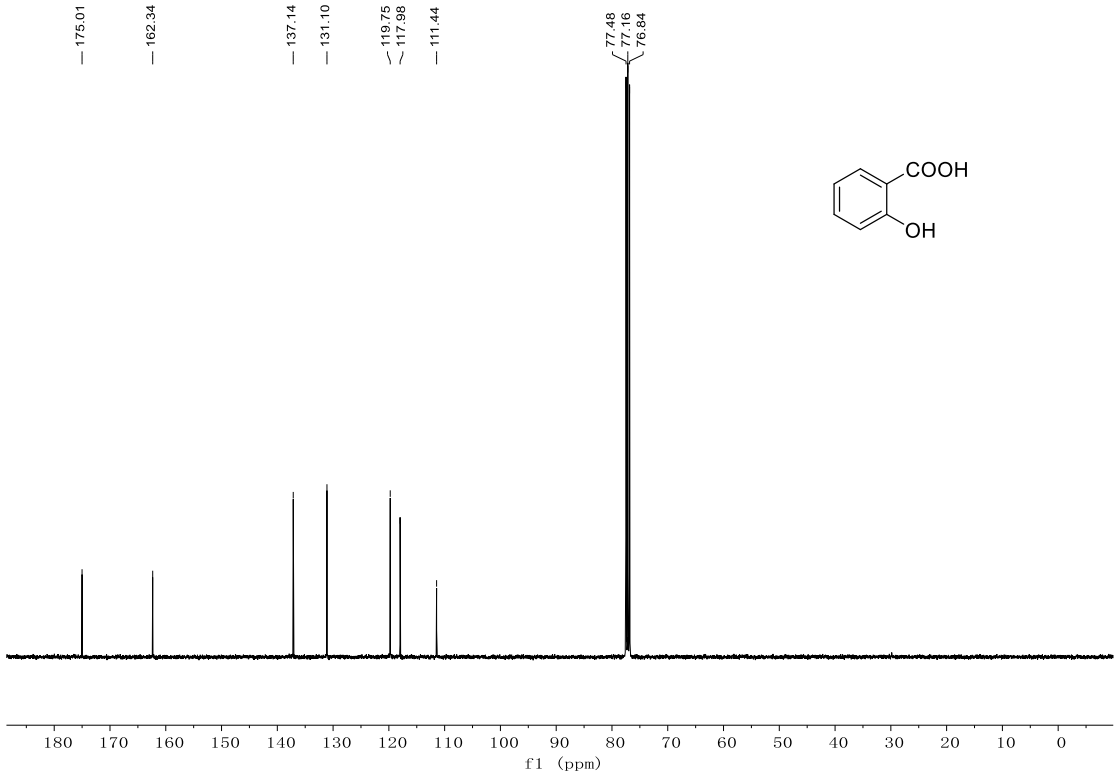

191.44
161.78
132.69
129.97
116.16
77.48
77.16
76.84
HO
O
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
−10
f1 (ppm)

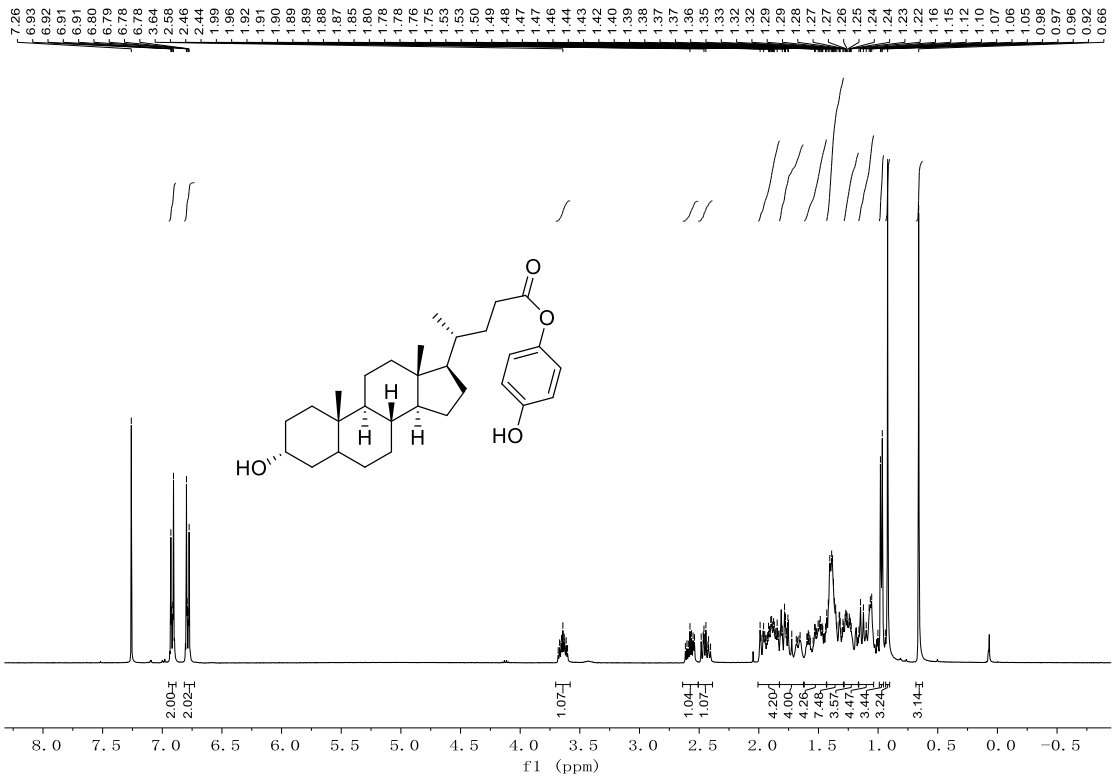

11.02
9.91
7.58
7.57
7.56
7.56
7.54
7.53
7.53
7.52
7.51
7.26
7.05
7.04
7.03
7.02
7.01
7.01
6.99
OH
O
1.00
1.00
2.03
2.04
11.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
-1.0
f1 (ppm)

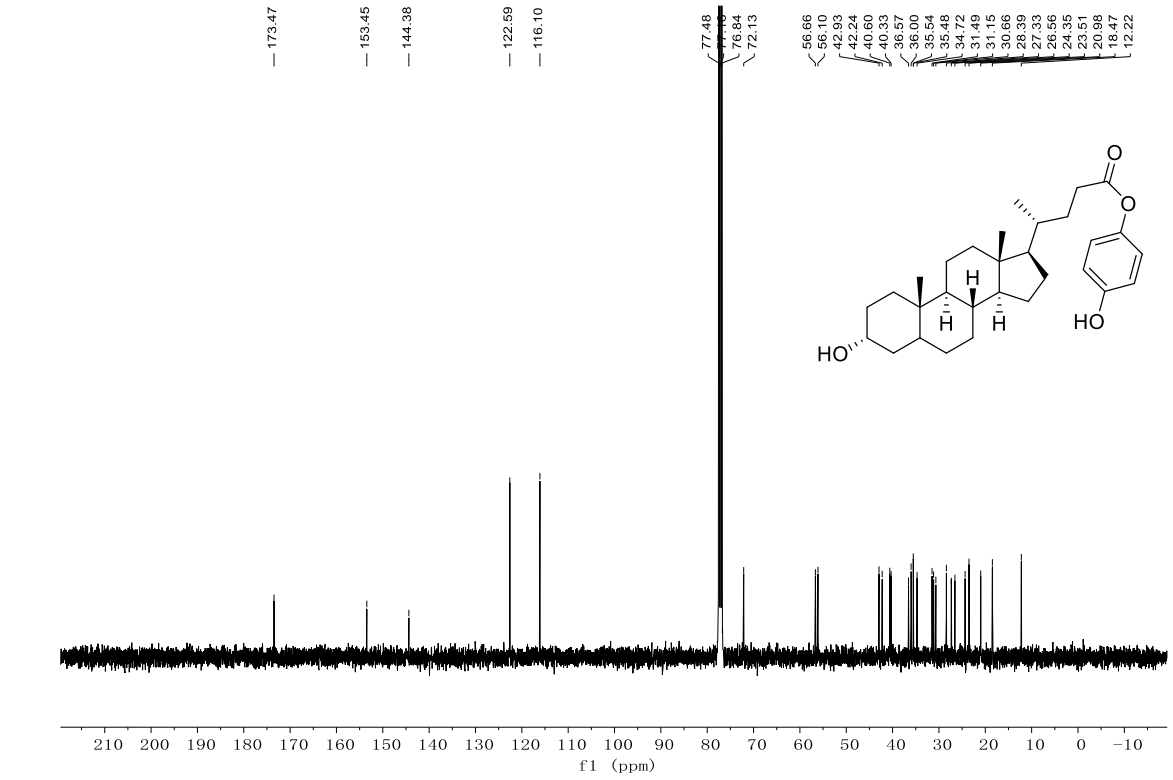

196.77
161.79
137.16
133.89
120.82
120.00
117.78
77.48
77.16
76.84
OH
O
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)


10.38
7.95
7.95
7.93
7.93
7.56
7.55
7.54
7.53
7.53
7.52
7.51
7.26
7.03
7.03
7.01
7.01
6.97
6.96
6.95
6.93
6.93
COOH
OH
10.38
0.94
10.6 10.5 10.4 10.3 10.2 10.1
f1 (ppm)


0.94
1.00
1.05
0.97
1.04
10.5 9.5 8.5 7.5 6.5 5.5 4.5 3.5 2.5 1.5 0.5 -0.5 -1.
f1 (ppm)


175.01
162.34
137.14
131.10
119.75
117.98
111.44
77.48
77.16
76.84
COOH
OH
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


7.26 6.93 6.92 6.91 6.91 6.80 6.79 6.78 6.78 3.64 2.58 2.46 2.44 1.99 1.96 1.92 1.91 1.90 1.89 1.89 1.88 1.87 1.85 1.80 1.78 1.78 1.76 1.75 1.53 1.53 1.50 1.49 1.48 1.47 1.47 1.46 1.44 1.43 1.42 1.40 1.39 1.38 1.37 1.37 1.36 1.35 1.33 1.32 1.29 1.29 1.28 1.27 1.27 1.26 1.25 1.24 1.24 1.23 1.22 1.16 1.15 1.12 1.10 1.07 1.06 1.05 0.98 0.97 0.96 0.92 0.66
O
O
H
H
H
HO
HO
2.00 2.02 1.07 1.04 1.07 4.20 4.00 4.26 7.48 3.57 4.47 3.44 3.24 3.14
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
f1 (ppm)


173.47 153.45 144.38 122.59 116.10 77.48 76.84 72.13 56.66 56.10 42.93 42.24 40.60 40.33 36.57 36.00 35.54 35.48 34.72 31.49 31.15 30.66 28.39 27.33 26.56 24.35 23.51 20.98 18.47 12.22
O
O
H
H
H
HO
HO
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 −10
f1 (ppm)