Electronic Supplementary Material (ESI) for Green Chemistry.

Supporting Information

Protection of COOH and OH Groups in Acid, Base and Salt Free Reactions

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Materials and methods

All reactions were carried out under an atmosphere of air in glassware with magnetic stirring unless otherwise indicated. Commercially purchased reagents were used as received. Solvents were dried by Innovative Technology Solvent Purification System. Liquids and solutions were transferred via syringe. All reactions were monitored by thin-layer chromatography. GC data were recorded on Thermo TRACE 1300. GC-MS data were recorded on Thermo ISQ QD. ^{1}H and ^{13}C NMR spectra were recorded on Bruker-BioSpin AVANCE III HD. Data for ^{1}H NMR spectra are reported relative to chloroform as an internal standard (7.26 ppm) and are reported as follows: chemical shift (ppm), multiplicity (m), coupling constant (Hz), and integration. Data for ^{13}C NMR spectra are reported relative to chloroform as an internal standard (77.23 ppm) and are reported in terms of chemical shift (ppm). HRMS data were recorded on Thermo Finnigan Impact II UHR-TOF. Melting point was obtained from Shanghai Shengguang SGW X-4.

General procedure

General procedure A for Table 1: Catalyst, benzoic acid (0.4 mmol, 1.0 equiv.), and MTBE (1.0 mL) were added into the Schlenk tube with a stirring bar, and then the reaction mixture was heated at 90 ^{o}C for 8 hours. The mixture was filtered by a short silica gel column (about 3 g) or a short activated carbon column (about 2 g), which was washed by EA (10 mL). After added the 1,4-dimethoxybenzene into the solvent as the internal standard, the yield of product **3a** could be detected by GC analysis.

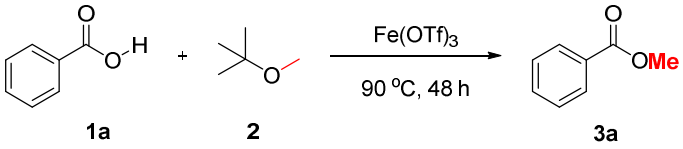
General procedure B for Table 2: $Fe(OTf)_3$ (0.05 mmol, 1 mol%), carboxylic acid **1** (5.0 mmol, 1.0 equiv.), and MTBE **2** (2.5 mL) were added into the Schlenk tube with a stirring bar, and then the reaction mixture was heated at 90 ^{o}C for 48 hours. The mixture was filtered by a short silica gel column (about 5 g) or a short activated carbon column (about 3 g), which was washed by EA (30 mL). The solvent was removed by rotary evaporation under vacuum and products **3** were attained directly without further purification.

General procedure C for Table 2: $Fe(OTf)_3$ (0.01 mmol, 0.1 mol%), phenol **4** (10 mmol, 1.0 equiv.) and IPA 5 (2.5 mL) were added into the Schlenk tube with a stirring bar, and then the reaction mixture was stirred at room temperature for 5 hours. The mixture was filtered by a short silica gel column (about 5 g) or a short activated carbon column (about 2 g), which was washed by EA (30 mL). The solvent was removed by rotary evaporation under vacuum and products **6** were attained directly without further purification.

General procedure D for Table 3: $Fe(OTf)_3$ (0.025 mmol, 0.5 mol%), alcohol **4** (5 mmol, 1.0 equiv.) and IPA **5** (2.5 mL) were added into the Schlenk tube with a stirring bar, and then the reaction mixture was stirred at room temperature for 5 hours. The solvent was removed by rotary evaporation under vacuum and the residue was chromatographed on silica gel to give the product **6**.

Efficiency of catalyst

Figure S1:



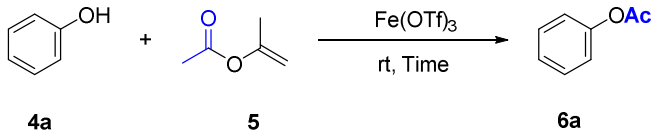
1a 2 3a

Entry	$Fe(OTf)_3$ (mol%)	MTBE (mL)	Yield (%)[b]	TON
1	1	10	90	90
2	0.5	10	87	174
3	0.1	10	53	265
4	1	3.5	81	81
5	1	2.2	72	72
6	0.5	3.5	73	146
7	0.1	3.5	49	490
8	0.05	3.5	44	880
9	0.01	3.5	23	2300

[a] Reaction conditions: benzoic acid **1a** (20 mmol, 1 equiv), MTBE, 48 h. [b] Yields of product **3a** were determined by GC analysis with 1,4-dimethoxybenzene as the internal standard.

General procedure for Figure S1: $Fe(OTf)_3$, benzoic acid **1a** (20.0 mmol, 1.0 equiv.), and MTBE **2** were added into the Schlenk tube with a stirring bar, and then the reaction mixture was heated at 90 °C for 48 hours. The mixture was filtered by a short silica gel column, which was washed by EA (30 mL). After added the 1,4-dimethoxybenzene into the solvent as the internal standard, the yield of product methyl benzoate **3a** could be detected by GC analysis.

Figure S2:



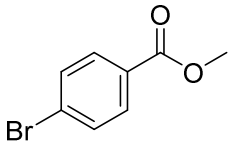
4a **5** **6a**

Entry	$Fe(OTf)_3$ (mol%)	IPA (mL)	Time (h)	Yield (%)[b]	TON
1	1	8	5	89	89
2	0.5	8	5	93	186
3	0.1	8	5	90	900
4	0.1	5	5	92	920
5	0.05	5	5	83	1660
6	0.01	5	24	67	6700
7[c]	10	2.5	24	NR	/

[a] Reaction conditions: phenol **4a** (20 mmol, 1 equiv), IPA **5**, room temperature. [b] Yields of product **6a** were determined by ^{1}H NMR analysis with 1,4-dimethoxybenzene as the internal standard. [c] Phenol **4a** (1 mmol, 1 equiv), IPA **5** (2.5 mL), room temperature, 24 h.

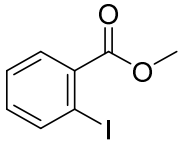
General procedure for Figure S2: $Fe(OTf)_3$, phenol **4a** (20 mmol, 1.0 equiv) and IPA **5** were added into the Schlenk tube with a stirring bar, and then the reaction mixture was stirred at room temperature. The mixture was filtered by a short silica gel column, which was washed by EA (30 mL). After added the 1,4-dimethoxybenzene into the solvent as the internal standard, the yield of product methyl benzoate **6a** could be detected by ^{1}H NMR.

Characterization data for the products



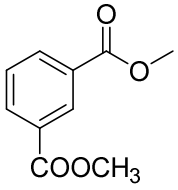
3b[1]

Following the general procedure B (967.5 mg, 90% yield, a pale yellow solid (m.p.: 75.1-75.6 ^{o}C)). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.90 (d, *J* = 7.7 Hz, 2H), 7.58 (d, *J* = 6.8 Hz, 2H), 3.91 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 166.36, 131.71, 131.11, 129.03, 128.03, 52.30.



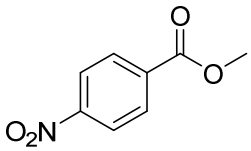
3c[1]

Following the general procedure B (2.0 mmol, $Fe(OTf)_3$ (5 mol %), MTBE (2.0 mL), 445.4 mg, 85% yield, product **3c** was chromatographed on silica gel as a clear oil). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.99 (d, *J* = 7.9 Hz, 1H), 7.80 (d, *J* = 7.7 Hz, 1H), 7.40 (t, *J* = 7.5 Hz, 1H), 7.15 (t, *J* = 8.4 Hz, 1H), 3.93 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 166.96, 141.32, 135.07, 132.66, 130.95, 127.90, 94.10, 52.52.



3d[2]

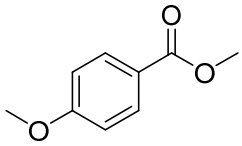
Following the general procedure B (853.6 mg, 88% yield, a white solid (m.p.: 64.0-64.6 ^{o}C)). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.68 (t, *J* = 1.8 Hz, 1H), 8.22 (dd, *J* = 7.8, 1.8 Hz, 2H), 7.53 (t, *J* = 7.8 Hz, 1H), 3.95 (s, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 166.18, 133.76, 130.67, 130.56, 128.59, 52.33.



3e[1]

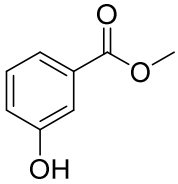
Following the general procedure B (2.0 mmol, $Fe(OTf)_3$ (5 mol %), MTBE (2.0 mL), 333.1 mg, 92% yield, , product **3e** was chromatographed on silica gel as a white solid (m.p.: 91.5-92.2 ^{o}C)). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.29 (d, *J* = 6.2 Hz, 2H), 8.22 (d,

J = 6.3 Hz, 2H), 3.99 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 165.15, 150.51, 135.47, 130.70, 123.53, 52.83.



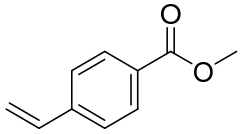
3f[1]

Following the general procedure B (2.0 mmol, $Fe(OTf)_3$ (5 mol %), MTBE (2.0 mL), 288.8 mg, 87% yield, , product **3f** was chromatographed on silica gel as a white solid (m.p.: 44.0-44.8 ^{o}C)). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.99 (d, *J* = 8.8 Hz, 2H), 6.92 (d, *J* = 8.8 Hz, 2H), 3.88 (s, 3H), 3.86 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 166.87, 163.31, 131.58, 122.58, 113.59, 55.42, 51.88.



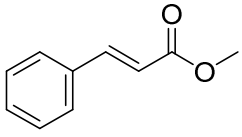
3g

Following the general procedure B (676.4 mg, 89% yield, a white solid (m.p.: 66.9-68.0 ^{o}C)). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.70 – 7.55 (m, 2H), 7.31 (t, *J* = 7.8 Hz, 1H), 7.13 – 7.04 (m, 1H), 6.44 (br, 1H), 3.92 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 167.49, 155.96, 131.25, 129.76, 121.86, 120.41, 116.40, 52.43. Compound **3g** is commercially available.



3h[3]

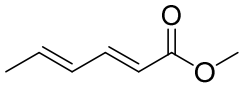
Following the general procedure B (2.0 mmol, $Fe(OTf)_3$ (5 mol %), MTBE (2.0 mL), 275.4 mg, 85% yield, product **3h** was chromatographed on silica gel as a clear oil). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.99 (d, *J* = 8.1 Hz, 2H), 7.46 (d, *J* = 8.1 Hz, 2H), 6.75 (dd, *J* = 17.6, 10.9 Hz, 1H), 5.86 (d, *J* = 17.6 Hz, 1H), 5.38 (d, *J* = 10.9 Hz, 1H), 3.91 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 166.87, 141.91, 136.01, 129.89, 129.26, 126.11, 116.49, 52.10.



3i[4]

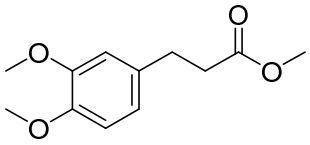
Following the general procedure B (729.0 mg, 90% yield, a clear oil). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.69 (d, *J* = 16.0 Hz, 1H), 7.55 – 7.45 (m, 2H), 7.37 (t, *J* = 3.8 Hz,

3H), 6.44 (d, *J* = 16.0 Hz, 1H), 3.80 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 167.41, 144.87, 134.38, 130.30, 128.89, 128.07, 117.80, 51.70.



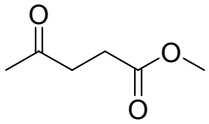
3j[5]

Following the general procedure B (541.8 mg, 86% yield, a clear oil). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.26 (dd, *J* = 15.3, 9.8 Hz, 1H), 6.30 – 6.06 (m, 2H), 5.78 (d, *J* = 15.4 Hz, 1H), 3.73 (s, 3H), 1.85 (d, *J* = 5.5 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 167.64, 145.12, 139.37, 129.72, 118.50, 51.34, 18.58.



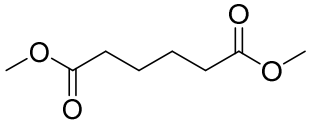
3k

Following the general procedure B (1097.5 mg, 98% yield, a white solid (m.p.: 34.7-35.4 °C)). ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.82 – 6.77 (m, 1H), 6.77 – 6.70 (m, 2H), 3.87 (s, 3H), 3.85 (s, 3H), 3.67 (s, 3H), 2.90 (t, *J* = 7.8 Hz, 2H), 2.66 – 2.57 (t, *J* = 7.8 Hz, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 173.39, 148.83, 147.45, 133.11, 120.06, 111.57, 111.22, 55.89, 55.80, 51.63, 36.01, 30.60. HRMS (ESI) m/z calcd. for ($C_{12}H_{16}O_4$) $[M+ Na]^+$: 247.0941, found: 247.0942.



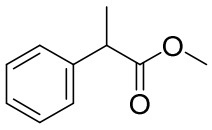
3l[6]

Following the general procedure B (598.0 mg, 92% yield, a clear oil). ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.60 (s, 3H), 2.70 (m, 2H), 2.51 (t, *J* = 6.1 Hz, 2H), 2.12 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 206.62, 173.12, 51.65, 37.81, 29.70, 27.62.



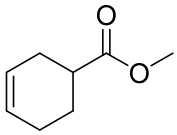
3m[7]

Following the general procedure B (809.1 mg, 93% yield, a clear oil). ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.67 (s, 6H), 2.40 – 2.28 (m, 4H), 1.72 – 1.59 (m, 4H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 173.61, 51.39, 33.52, 24.25.



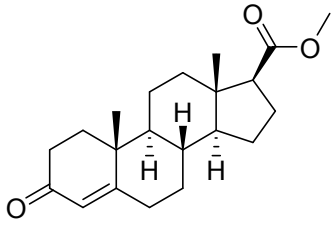
3n[8]

Following the general procedure B (762.6 mg, 93% yield, a clear oil). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.34 – 7.26 (m, 4H), 7.26 – 7.19 (m, 1H), 3.71 (q, *J* = 7.2 Hz, 1H), 3.63 (s, 3H), 1.49 (d, *J* = 7.2 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 174.99, 140.60, 128.68, 127.50, 127.18, 52.02, 45.44, 18.65.



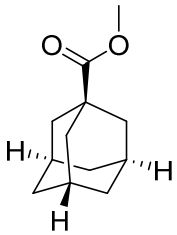
3o

Following the general procedure B (644.0 mg, 92% yield, a clear oil). ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.75 – 5.58 (m, 2H), 3.69 (s, 3H), 2.62 – 2.51 (m, 1H), 2.30 – 2.21 (m, 2H), 2.15 – 2.05 (m, 2H), 2.05 – 1.95 (m, 1H), 1.75 – 1.61 (m, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 176.24, 126.61, 125.14, 51.57, 39.18, 27.42, 25.05, 24.41. Compound **3o** is commercially available.



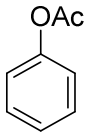
3p[9]

Following the general procedure B (1303.5 mg, 79% yield, product **3p** was chromatographed on silica gel as a white solid (m.p.: 116.5-117.2 ^{o}C)). ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.73 (s, 1H), 3.68 (s, 3H), 2.48 – 2.24 (m, 5H), 2.21 – 2.10 (m, 1H), 2.08 – 1.98 (m, 2H), 1.91 – 1.67 (m, 4H), 1.64 – 1.50 (m, 2H), 1.48 – 1.38 (m, 1H), 1.35 – 1.23 (m, 2H), 1.19 (s, 3H), 1.16 – 1.02 (m, 2H), δ 1.02 – 0.93 (m, 1H), 0.71 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 199.40, 174.31, 170.99, 123.88, 55.24, 55.06, 53.69, 51.27, 43.87, 38.59, 38.02, 35.70, 35.68, 33.93, 32.78, 31.91, 24.42, 23.57, 20.85, 17.35, 13.43.



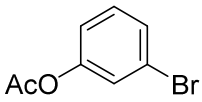
3q[10]

Following the general procedure B (911.8 mg, 94% yield, a clear oil). ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.65 (s, 3H), 2.05 – 1.97 (m, 3H), 1.93 – 1.84 (m, 6H), 1.77 – 1.65 (m, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 178.18, 51.52, 40.68, 38.84, 36.48, 27.93.



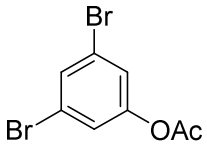
6a[11]

Following the general procedure C (10 mmol, 1361.5 mg, 99% yield, a clear oil). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38 – 7.31 (m, 2H), 7.22 – 7.16 (m, 1H), 7.10 – 7.03 (m, 2H), 2.25 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 169.52, 150.74, 129.48, 125.87, 121.64, 21.14.



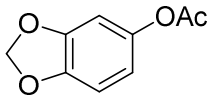
6b

Following the general procedure C (10 mmol, 2150.5 mg, 99% yield, a clear oil). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.30 – 7.25 (m, 1H), 7.20 (t, *J* = 2.1 Hz, 1H), 7.15 (t, *J* = 8.1 Hz, 1H), 6.98 – 6.92 (m, 1H), 2.19 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 168.98, 151.18, 130.49, 129.01, 125.12, 122.35, 120.50, 21.03. Compound **6b** is commercially available.



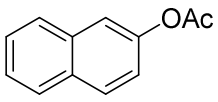
6c

Following the general procedure C (10 mmol, 2939.4 mg, 99% yield, a white solid (m.p.: 48.7-49.2 °C)). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.45 (t, *J* = 1.7 Hz, 1H), 7.16 (d, *J* = 1.7 Hz, 2H), 2.20 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 168.52, 151.38, 131.65, 124.13, 122.75, 20.96. Compound **6c** is commercially available.



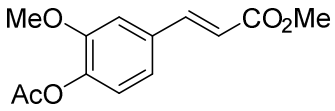
6d[12]

Following the general procedure C (1801.6 mg, 99% yield, a clear oil). ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.76 (d, *J* = 8.3 Hz, 1H), 6.60 (d, *J* = 2.3 Hz, 1H), 6.51 (dd, *J* = 8.4, 2.3 Hz, 1H), 5.95 (s, 2H), 2.25 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 169.79, 147.99, 145.35, 144.99, 113.91, 107.96, 103.73, 101.71, 20.98.



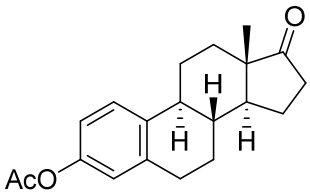
6e[12]

Following the general procedure C (5 mmol, $Fe(OTf)_3$ (0.2 mol %), IPA (2.5 mL), 931.1 mg, 99% yield, a white solid (m.p.: 62.3-63.5 ^oC)). ^1H NMR (400 MHz, $CDCl_3$) δ 7.88 – 7.74 (m, 3H), 7.55 (d, *J* = 2.4 Hz, 1H), 7.52 – 7.40 (m, 2H), 7.22 (dd, *J* = 8.9, 2.3 Hz, 1H), 2.34 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 169.68, 148.34, 133.77, 131.49, 129.44, 127.79, 127.67, 126.58, 125.74, 121.15, 118.56, 21.23.



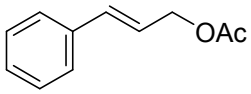
6f[13]

Following the general procedure C (5 mmol, $Fe(OTf)_3$ (0.2 mol %), IPA (2.5 mL), DCM (1.0 mL) 1251.3 mg, 99% yield, a white solid (m.p.: 118.4-119.2 ^oC)). ^1H NMR (400 MHz, $CDCl_3$) δ 7.64 (d, *J* = 15.9 Hz, 1H), 7.14 – 7.08 (m, 2H), 7.04 (d, *J* = 8.3 Hz, 1H), 6.39 (d, *J* = 15.9 Hz, 1H), 3.84 (s, 3H), 3.80 (s, 3H), 2.32 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 168.77, 167.23, 151.36, 144.13, 141.40, 133.31, 123.23, 121.18, 117.99, 111.24, 55.86, 51.74, 20.63.



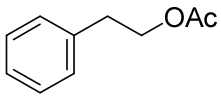
6g[14]

Following the general procedure C (5 mmol, $Fe(OTf)_3$ (0.2 mol %), IPA (2.5 mL), 1562.0 mg, 99% yield, a white solid (m.p.: 142.5-143.7 ^oC)). ^1H NMR (400 MHz, Chloroform-*d*) δ 7.31 – 7.27 (m, 1H), 6.85 (dd, *J* = 8.4, 2.7 Hz, 1H), 6.81 (d, *J* = 2.6 Hz, 1H), 2.95 – 2.87 (m, 2H), 2.51 (dd, *J* = 18.8, 8.4 Hz, 1H), 2.45 – 2.37 (m, 1H), 2.33 – 2.24 (m, 4H), 2.20 – 1.94 (m, 4H), 1.69 – 1.41 (m, 6H), 0.91 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 220.75, 169.84, 148.56, 138.02, 137.41, 126.42, 121.60, 118.76, 50.44, 47.95, 44.16, 38.00, 35.87, 31.56, 29.41, 26.35, 25.75, 21.60, 21.14, 13.84.



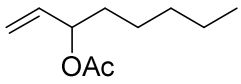
6h[15]

Following the general procedure D (5 mmol, $Fe(OTf)_3$ (0.5 mol %), IPA (2.5 mL), 0.83 g, 94% yield, a clear oil). ^1H NMR (400 MHz, $CDCl_3$) δ 7.40 – 7.35 (m, 2H), 7.34 – 7.28 (m, 2H), 7.27 – 7.21 (m, 1H), 6.64 (dt, *J* = 15.8, 1.3 Hz, 1H), 6.27 (dt, *J* = 15.9, 6.4 Hz, 1H), 4.72 (dd, *J* = 6.4, 1.4 Hz, 2H), 2.08 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 170.81, 136.22, 134.20, 128.62, 128.08, 126.62, 123.19, 65.08, 20.99.



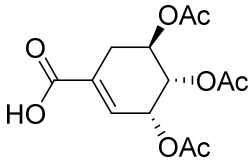
6i[16]

Following the general procedure D (5 mmol, $Fe(OTf)_3$ (0.5 mol %), IPA (2.5 mL), 0.78 g, 95% yield, a clear oil). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.31 – 7.24 (m, 2H), 7.23 – 7.16 (m, 3H), 4.26 (t, *J* = 7.1 Hz, 2H), 2.91 (t, *J* = 7.1 Hz, 2H), 1.99 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 170.98, 137.86, 128.93, 128.54, 126.60, 64.96, 35.12, 20.96.



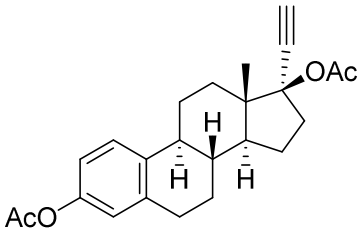
6j[17]

Following the general procedure D (5 mmol, $Fe(OTf)_3$ (0.5 mol %), IPA (2.5 mL), 0.78 g, 92% yield, a clear oil). ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.77 – 5.62 (m, 1H), 5.20 – 5.11 (m, 2H), 5.08 (d, *J* = 10.5 Hz, 1H), 1.99 (s, 3H), 1.61 – 1.46 (m, 2H), δ 1.29 – 1.19 (m, 6H), 0.80 (t, *J* = 6.8 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 170.30, 136.63, 116.43, 74.83, 34.12, 31.52, 24.69, 22.48, 21.19, 13.94.



6k[18]

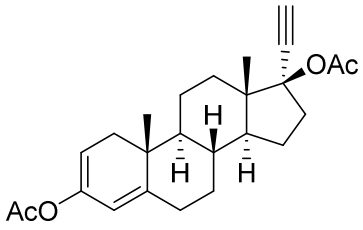
Following the general procedure D (2.5 mmol, $Fe(OTf)_3$ (1.0 mol %), IPA (2.5 mL), 0.50 g, 66% yield, a clear oil). ^{1}H NMR (400 MHz, $CDCl_3$) ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.84 (br, 1H), 6.82 (s, 1H), 5.71 (s, 1H), 5.34 – 5.14 (m, 2H), 2.86 (d, *J* = 18.9 Hz, 1H), 2.39 (d, *J* = 18.8 Hz, 1H), 2.10 – 1.99 (m, 9H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 177.00, 170.14, 170.07, 169.84, 134.66, 130.75, 67.54, 66.77, 66.03, 28.07, 20.95, 20.72, 20.70.



6l[19]

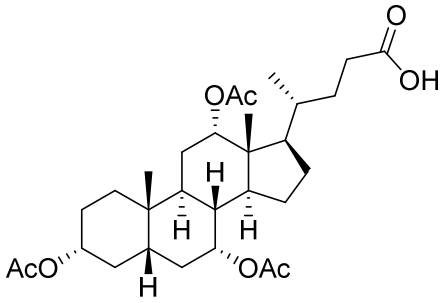
Following the general procedure D (2.5 mmol, $Fe(OTf)_3$ (1.0 mol %), IPA (2.5 mL), 0.86 g, 90% yield, a white solid (m.p.: 142.2-143.1 ^{o}C)). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.33 – 7.26 (m, 1H), 6.84 (dd, *J* = 8.4, 2.7 Hz, 1H), 6.79 (d, *J* = 2.6 Hz, 1H), 2.91 – 2.82 (m, 2H), 2.85 – 2.73 (m, 1H), 2.63 (s, 1H), 2.43 – 2.32 (m, 1H), 2.33 – 2.22 (m, 4H), 2.13 – 1.97 (m, 5H), 1.94 – 1.78 (m, 3H), 1.80 – 1.67 (m, 1H), 1.59 – 1.34 (m,

4H), 0.90 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 169.86, 169.60, 148.45, 138.17, 137.78, 126.45, 121.52, 118.62, 84.45, 83.37, 74.95, 47.87, 47.84, 43.63, 38.78, 37.37, 33.12, 29.54, 27.11, 26.18, 23.32, 21.47, 21.15, 13.41.



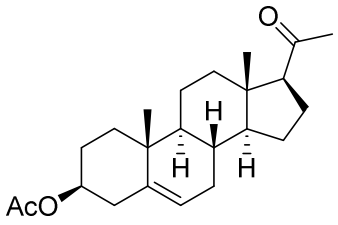
6m

Following the general procedure D (2.5 mmol, $Fe(OTf)_3$ (1.0 mol %), IPA (2.5 mL), 0.86 g, 87% yield, a white solid). ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.70 (s, 1H), 5.39 (t, *J* = 5.2, 1H), 2.79 – 2.70 (m, 1H), 2.60 (s, 1H), 2.52 – 2.41 (m, 1H), 2.24 – 2.11 (m, 5H), 2.07 – 2.02 (m, 4H), 1.92 – 1.82 (m, 2H), 1.78 – 1.66 (m, 5H), 1.64 – 1.50 (m, 2H), 1.39 – 1.31 (m, 2H), 1.12 – 1.01 (m, 4H), 0.92 – 0.88 (m, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 169.61, 169.37, 147.07, 139.39, 123.44, 116.91, 84.50, 83.36, 74.85, 49.20, 47.55, 47.52, 37.40, 34.91, 33.76, 32.91, 32.16, 31.42, 24.80, 23.62, 21.46, 21.10, 20.84, 18.87, 13.43. MS (EI): 396 [M^+].



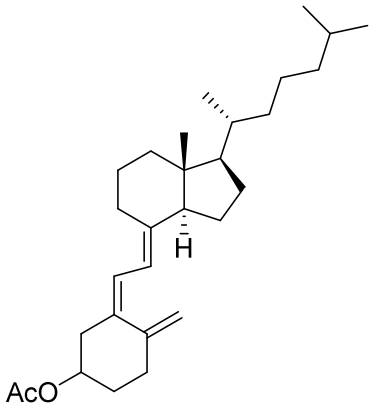
6n

Following the general procedure D (2.5 mmol, $Fe(OTf)_3$ (1.0 mol %), IPA (2.5 mL), 0.93 g, 70% yield, a clear oil). ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.10 (d, *J* = 2.9 Hz, 1H), 4.91 (q, *J* = 3.1 Hz, 1H), 4.58 (tt, *J* = 11.3, 4.3 Hz, 1H), 2.44 – 2.34 (m, 1H), 2.29 – 2.20 (m, 1H), 2.14 (s, 3H), 2.10 (s, 3H), 2.06 (s, 3H), 2.02 – 1.75 (m, 7H), 1.74 – 1.29 (m, 13H), 1.17 – 1.03 (m, 2H), 0.92 (s, 3H), 0.82 (d, *J* = 6.3 Hz, 3H), 0.73 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 179.68, 170.68, 170.63, 170.52, 75.41, 74.13, 70.74, 47.32, 45.05, 43.39, 40.90, 37.71, 34.67, 34.59, 34.54, 34.32, 31.23, 30.83, 30.53, 28.88, 27.16, 26.88, 25.57, 22.79, 22.57, 21.65, 21.52, 21.46, 17.48, 12.24. HRMS (ESI) m/z calcd. for ($C_{30}H_{46}O_6Na$) $[M+Na]^+$: 557.3085, found: 557.3081.



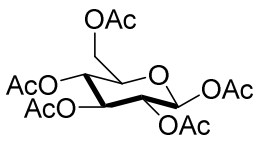
6o[20]

Following the general procedure D (2.5 mmol, $Fe(OTf)_3$ (1.0 mol %), IPA (2.5 mL), 0.81 g, 90% yield, a white solid (m.p.: 144.0-144.9 ^oC)). ^1H NMR (400 MHz, $CDCl_3$) δ 5.35 (d, *J* = 3.8 Hz, 1H), 4.64 – 4.52 (m, 1H), 2.51 (t, *J* = 8.8 Hz, 1H), 2.35 – 2.25 (m, 2H), 2.23 – 2.13 (m, 1H), 2.10 (s, 3H), 2.05 – 1.93 (m, 5H), 1.85 (d, *J* = 11.3 Hz, 2H), 1.72 – 1.54 (m, 5H), 1.52 – 1.42 (m, 3H), 1.24 – 1.11 (m, 3H), 1.04 – 0.94 (m, 4H), 0.61 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 209.49, 170.51, 139.65, 122.32, 73.83, 63.67, 56.83, 49.89, 43.97, 38.79, 38.07, 37.00, 36.60, 31.82, 31.76, 31.54, 27.73, 24.48, 22.83, 21.42, 21.03, 19.30, 13.22.



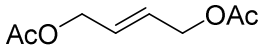
6p

Following the general procedure D (2.5 mmol, $Fe(OTf)_3$ (1.0 mol %), IPA (2.5 mL), 0.93 g, 87% yield, a clear oil). ^1H NMR (400 MHz, $CDCl_3$) δ 6.15 (d, *J* = 11.2 Hz, 1H), 5.96 (d, *J* = 11.4 Hz, 1H), 4.99 (d, *J* = 2.4 Hz, 1H), 4.87 (tt, *J* = 8.0, 3.9 Hz, 1H), 4.77 (d, *J* = 2.4 Hz, 1H), 2.79 – 2.70 (m, 1H), 2.50 (dd, *J* = 13.5, 4.1 Hz, 1H), 2.37 – 2.25 (m, 2H), 2.18 – 2.12 (m, 1H), 1.97 (s, 3H), 1.91 – 1.77 (m, 3H), 1.71 – 1.60 (m, 2H), 1.50 – 1.37 (m, 4H), 1.32 – 1.16 (m, 9H), 1.10 – 1.02 (m, 3H), 0.85 (d, *J* = 6.4 Hz, 3H), 0.80 (d, *J* = 1.9 Hz, 3H), 0.79 (d, *J* = 1.9 Hz, 3H), 0.47 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 170.65, 144.62, 142.50, 134.30, 122.46, 117.46, 112.74, 71.81, 56.59, 56.38, 45.93, 42.15, 40.55, 39.51, 36.15, 32.20, 31.98, 29.73, 29.08, 28.04, 27.69, 23.88, 23.59, 22.85, 22.59, 22.24, 21.44, 18.86, 12.00.



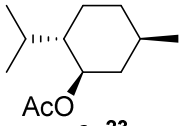
6q[21]

Following the general procedure D (1.0 mmol, $Fe(OTf)_3$ (10 mol %), IPA (2.5 mL), 0.5 h, 160 mg, 41% yield, a white solid (m.p.: 97.6-99.2 ^oC)). ^1H NMR (400 MHz, $CDCl_3$) δ 6.33 (d, *J* = 3.7 Hz, 1H), 5.51 – 5.44 (m, 1H), 5.18 – 5.07 (m, 2H), 4.30 – 4.24 (m, 1H), 4.16 – 4.07 (m, 2H), 2.19 (s, 3H), 2.10 (s, 3H), 2.05 (s, 3H), 2.03 (s, 3H), 2.02 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 170.59, 170.18, 169.63, 169.37, 168.73, 89.02, 69.79, 69.16, 67.85, 61.43, 20.83, 20.65, 20.62, 20.52, 20.41.



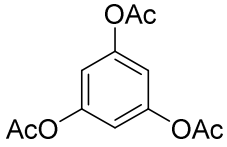
6r[22]

Following the general procedure D (1.0 mmol, $Fe(OTf)_3$ (10 mol %), IPA (2.5 mL), 0.5 h, 156.5 mg, 91% yield, a clear oil). ^1H NMR (400 MHz, $CDCl_3$) δ 5.78 – 5.73 (m, 2H), 4.68 (d, *J* = 5.2 Hz, 4H), 2.07 (s, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 170.62, 127.99, 59.92, 20.80.



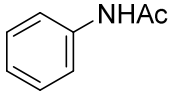
6s[23]

Following the general procedure D (1.0 mmol, $Fe(OTf)_3$ (10 mol %), IPA (2.5 mL), 0.5 h, 178.4 mg, 90% yield, a clear oil). ^1H NMR (400 MHz, $CDCl_3$) δ 4.76 – 4.58 (m, 1H), 2.03 (s, 3H), 2.01 – 1.94 (m, 1H), 1.91 – 1.82 (m, 1H), 1.73 – 1.62 (m, 2H), 1.54 – 1.42 (m, 1H), 1.40 – 1.30 (m, 1H), 1.26 (d, *J* = 4.2 Hz, 1H), 1.13 – 1.02 (m, 1H), 1.01 – 0.94 (m, 1H), 0.91 (d, *J* = 2.4 Hz, 3H), 0.89 (d, *J* = 2.9 Hz, 3H), 0.77 (d, *J* = 7.0 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 170.56, 74.07, 46.97, 40.90, 34.23, 31.33, 26.28, 23.46, 21.96, 21.23, 20.68, 16.33.



6t[24]

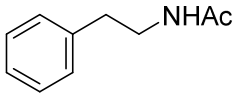
Following the general procedure D (1.0 mmol, $Fe(OTf)_3$ (10 mol %), IPA (2.5 mL), 0.5 h, 146.2 mg, 58% yield, a white solid (m.p.: 104.5-101.9 ^oC)). ^1H NMR (400 MHz, $CDCl_3$) δ 6.84 (s, 3H), 2.27 (s, 9H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 168.59, 151.09, 112.78, 21.07.



6u

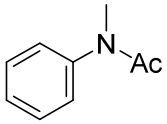
Following the general procedure D (1.0 mmol, $Fe(OTf)_3$ (10 mol %), IPA (2.5 mL), 24 h, 114.8 mg, 85% yield, a pale yellow solid (m.p.: 114.8-145.7 ^oC)). ^1H NMR (400 MHz, $CDCl_3$) δ 7.60 (s, 1H), 7.53 – 7.46 (m, 2H), 7.35 – 7.27 (m, 2H), 7.14 – 7.05 (m,

1H), 2.16 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 168.59, 137.94, 128.97, 124.31, 119.98, 24.55. Compound **6q** is commercially available.



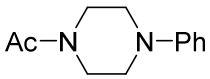
6v

Following the general procedure D (1.0 mmol, $Fe(OTf)_3$ (10 mol %), IPA (2.5 mL), 24 h, 119.0 mg, 73% yield, a pale yellow solid (m.p.: 49.5-50.5 ^{o}C)). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.34 – 7.28 (m, 2H), 7.27 – 7.22 (m, 1H), 7.21 – 7.17 (m, 2H), 5.66 (s, 1H), 3.51 (td, *J* = 7.0, 5.7 Hz, 2H), 2.81 (t, *J* = 7.0 Hz, 2H), 1.93 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 170.15, 138.89, 128.74, 128.64, 126.52, 40.69, 35.63, 23.30. Compound **6r** is commercially available.



6w

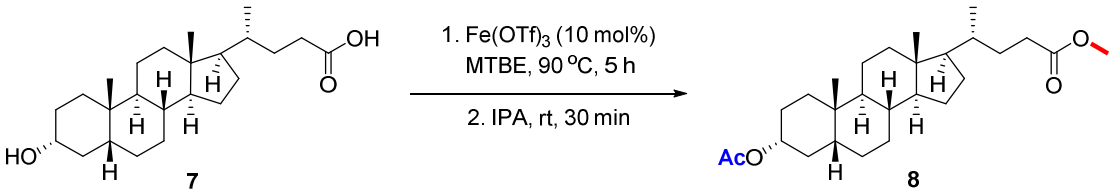
Following the general procedure D (1.0 mmol, $Fe(OTf)_3$ (10 mol %), IPA (2.5 mL), 24 h, 82.0 mg, 55% yield, a pale yellow solid (m.p.: 99.3-100.2 ^{o}C)). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.46 – 7.39 (m, 2H), 7.37 – 7.30 (m, 1H), 7.23 – 7.16 (m, 2H), 3.27 (s, 3H), 1.87 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 170.58, 144.62, 129.73, 127.71, 127.08, 37.17, 22.42. Compound **6s** is commercially available.



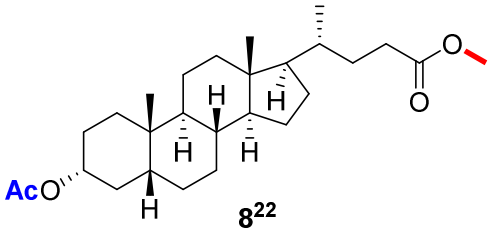
6x

Following the general procedure D (1.0 mmol, $Fe(OTf)_3$ (10 mol %), IPA (2.5 mL), 24 h, 151.0 mg, 74% yield, a yellow solid (m.p.: 94.1-94.9 ^{o}C)). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.33 – 7.25 (m, 2H), 6.97 – 6.88 (m, 3H), 3.77 (t, *J* = 5.2 Hz, 2H), 3.61 (t, *J* = 5.2 Hz, 2H), 3.16 (dt, *J* = 13.1, 5.3 Hz, 4H), 2.14 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 169.02, 150.92, 129.25, 120.56, 116.67, 49.70, 49.37, 46.23, 41.35, 21.36. Compound **6t** is commercially available.

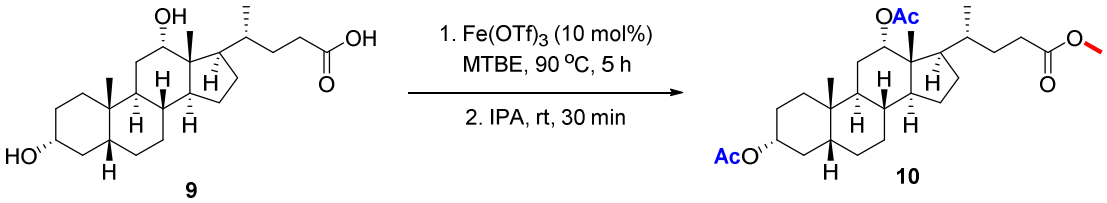
Sequential protection of COOH and OH in a one-pot reaction



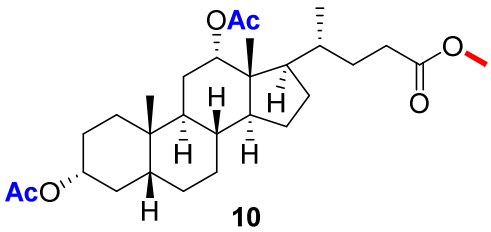
$Fe(OTf)_3$ (0.05 mmol, 10 mol%), lithocholic acid **7** (0.5 mmol, 1.0 equiv.), and MTBE (1 mL) were added into the Schlenk tube with a stirring bar. The reaction mixture was heated for 5 hours, and then cooled to room temperature. After remove the solvent under vacuum, IPA (1 mL) were added into the Schlenk tube. The reaction mixture was stirred at room temperature for 30 minutes. The mixture was filtered by a short silica gel column, which was washed by EA (30 mL). The solvent was removed by rotary evaporation under vacuum and the residue was chromatographed on silica gel to give the product **8** (164.4 mg, 76% yield, a white solid (m.p.: 126.5-126.9 °C)).



^{1}H NMR (400 MHz, $CDCl_3$) δ 4.71 (td, *J* = 11.3, 5.6 Hz, 1H), 3.66 (s, 3H), 2.41 – 2.30 (m, 1H), 2.27 – 2.17 (m, 1H), 2.03 (s, 3H), 1.99 – 1.93 (m, 1H), 1.91 – 1.75 (m, 5H), 1.72 – 1.65 (m, 1H), 1.61 – 1.50 (m, 2H), 1.49 – 1.21 (m, 11H), 1.19 – 0.98 (m, 6H), 0.96 – 0.88 (m, 6H), 0.64 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 174.75, 170.64, 74.38, 56.49, 55.98, 51.48, 42.72, 41.88, 40.40, 40.13, 35.77, 35.36, 35.03, 34.57, 32.23, 31.04, 30.99, 28.19, 27.01, 26.62, 26.32, 24.18, 23.34, 21.48, 20.83, 18.27, 12.03.



$Fe(OTf)_3$ (0.05 mmol, 10 mol%), deoxycholic acid **9** (0.5 mmol, 1.0 equiv.), and MTBE (1 mL) were added into the Schlenk tube with a stirring bar. The reaction mixture was heated for 5 hours, and then cooled to room temperature. After remove the solvent under vacuum, IPA (1 mL) were added into the Schlenk tube. The reaction mixture was stirred at room temperature for 30 minutes. The mixture was filtered by a short silica gel column, which was washed by EA (30 mL). The solvent was removed by rotary evaporation under vacuum and the residue was chromatographed on silica gel to give the product **10** (168.7 mg, 69% yield, a clear oil).

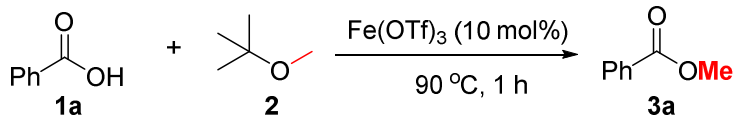


10

^{1}H NMR (400 MHz, $CDCl_3$) δ 5.11 – 5.05 (m, 1H), 4.76 – 4.64 (m, 1H), 3.66 (s, 3H), 2.39 – 2.28 (m, 1H), 2.25 – 2.15 (m, 1H), 2.10 (s, 3H), 2.03 (s, 3H), 1.93 – 1.76 (m, 4H), 1.74 – 1.53 (m, 8H), 1.51 – 1.23 (m, 9H), 1.22 – 1.01 (m, 3H), 0.91 (s, 3H), 0.81 (d, *J* = 6.4 Hz, 3H), 0.73 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 174.56, 170.53, 170.44, 75.88, 74.17, 51.48, 49.43, 47.56, 44.99, 41.81, 35.66, 34.71, 34.69, 34.38, 34.02, 32.24, 30.95, 30.82, 27.33, 26.87, 26.61, 25.85, 25.63, 23.42, 23.06, 21.44, 21.35, 17.49, 12.39. HRMS (ESI) m/z calcd. for ($C_{29}H_{46}O_6Na$) $[M+Na]^+$: 513.3187, found: 513.3185.

Mechanistic study

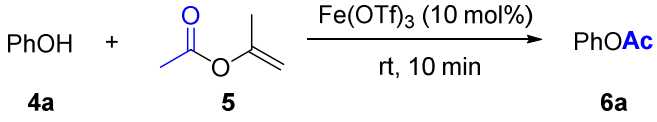
(a)



GC/MS:  H_2O

$Fe(OTf)_3$ (0.1 mmol, 10 mol%), benzoic acid (1.0 mmol, 1.0 equiv.), and MTBE (2.5 mL) were added into the Schlenk tube with a stirring bar, and then the reaction mixture was heated at 90 °C for 1 hour. The mixture was filtered by a short silica gel column, which was washed by EA (30 mL). After added the 1,4-dimethoxybenzene into the solvent as the internal standard, the yield of product **3a** could be detected by GC-MS. Isobutene (MS (Ion trap, EI): m/z (%) = 56.07 [M^+] (100.00)) and H_2O (MS (Ion trap, EI): m/z (%) = 18.07 [M^+] (100.00)) could be detected by GC-MS.

(b)



GC/MS: 

$Fe(OTf)_3$ (0.1 mmol, 10 mol%), phenol (1.0 mmol, 1.0 equiv.) and IPA (2.5 mL) were added into the Schlenk tube with a stirring bar, and then the reaction mixture was stirred at room temperature for 10 minutes. The reaction mixture was stirred at room temperature for 10 minutes. The mixture was filtered by a short silica gel column, which was washed by EA (30 mL). After added the 1,4-dimethoxybenzene into the solvent as the internal standard, the yield of product **3a** could be detected by GC-MS. Acetone (MS (Ion trap, EI): m/z (%) = 58.04 [M^+] (100.00)) could be detected by GC-MS.

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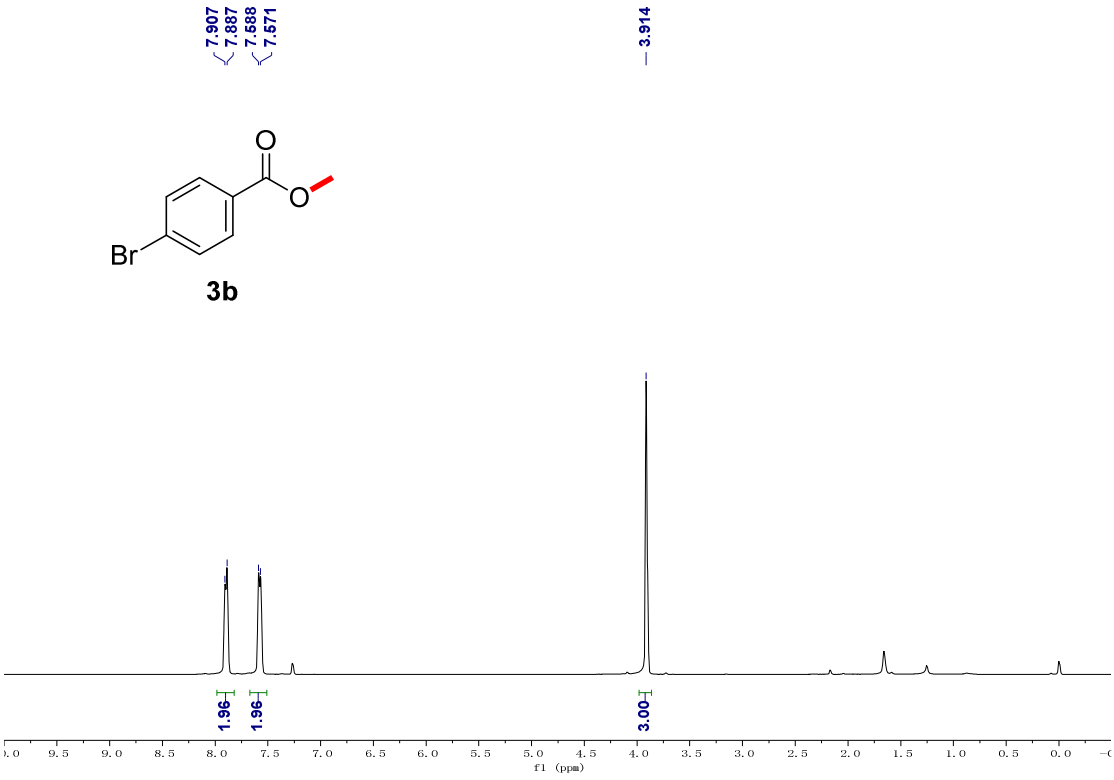
NMR spectra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Br
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1.96
3.00
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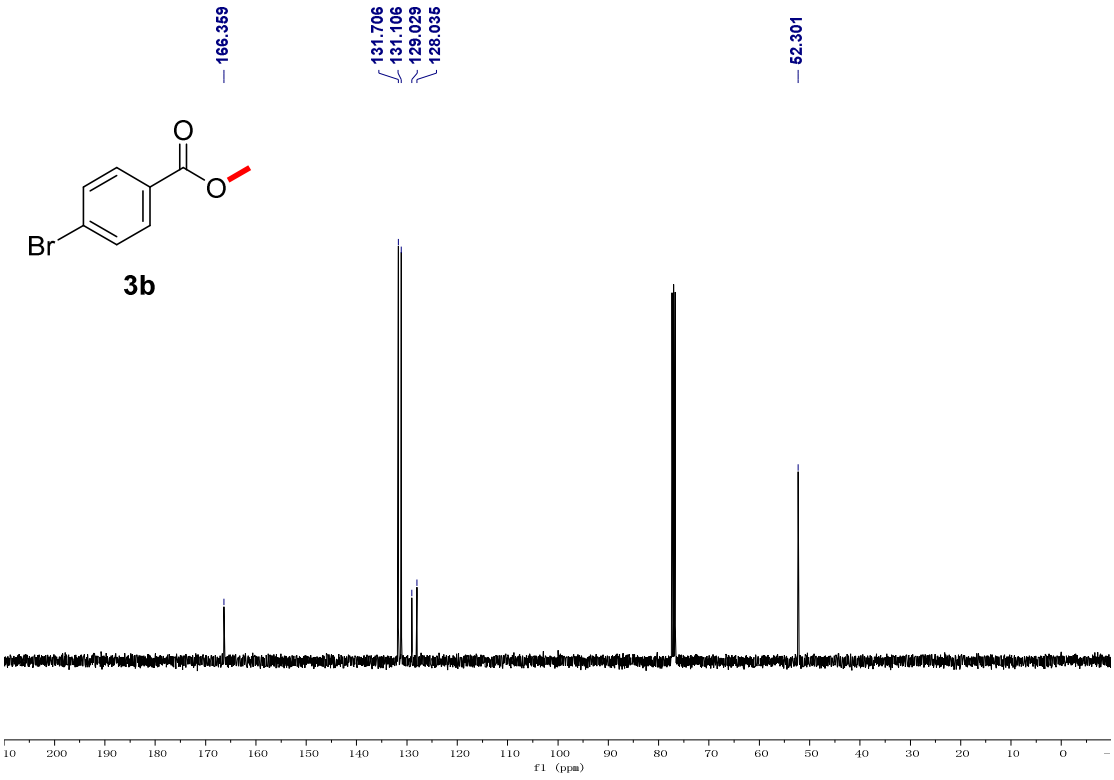
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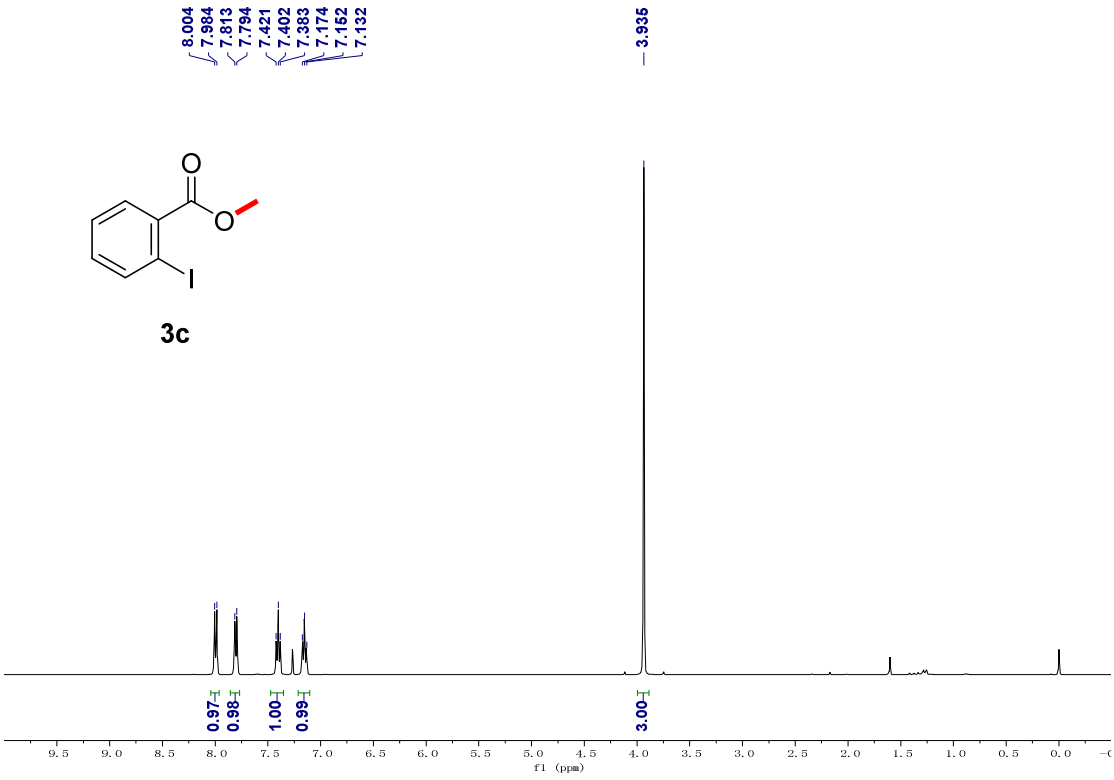
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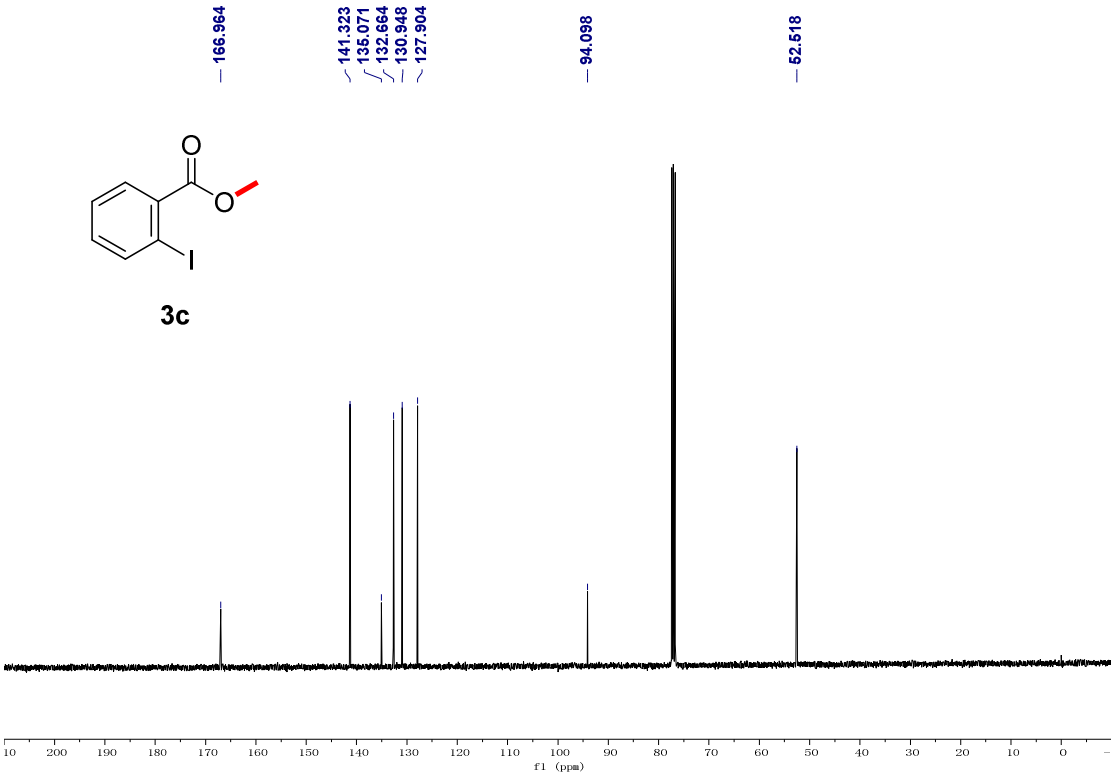
1.00
0.99
3.00
f1 (ppm)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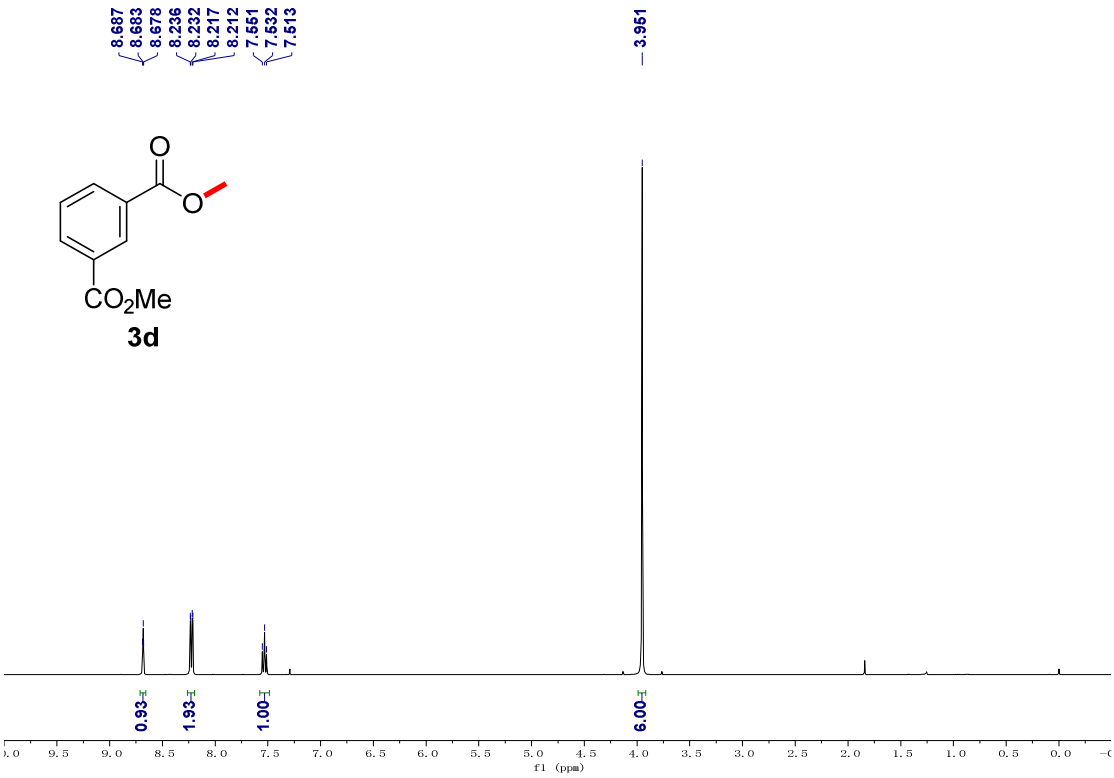
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3d
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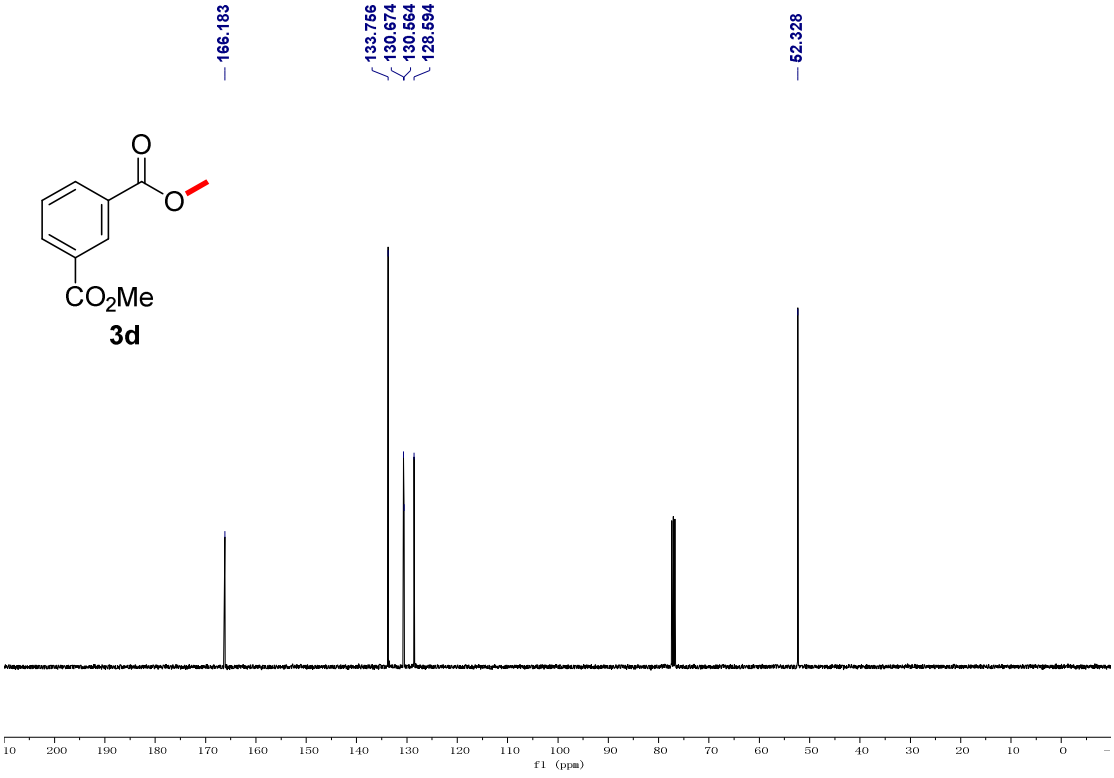
6.00
f1 (ppm)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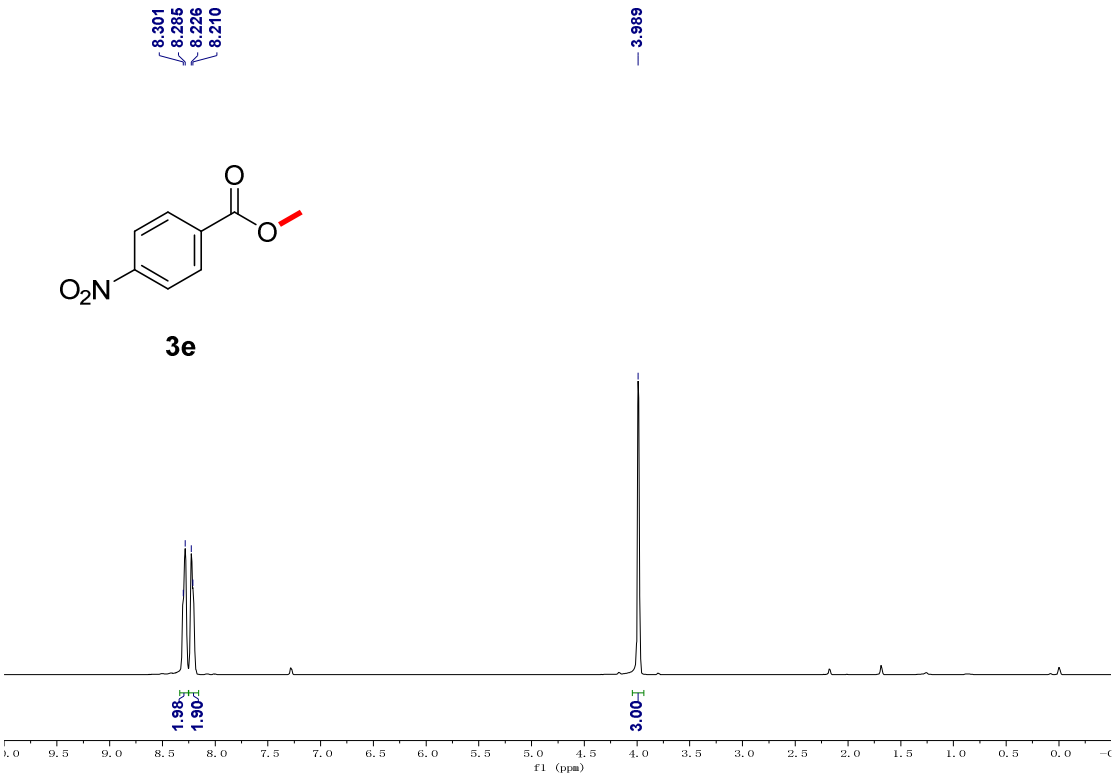
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3e
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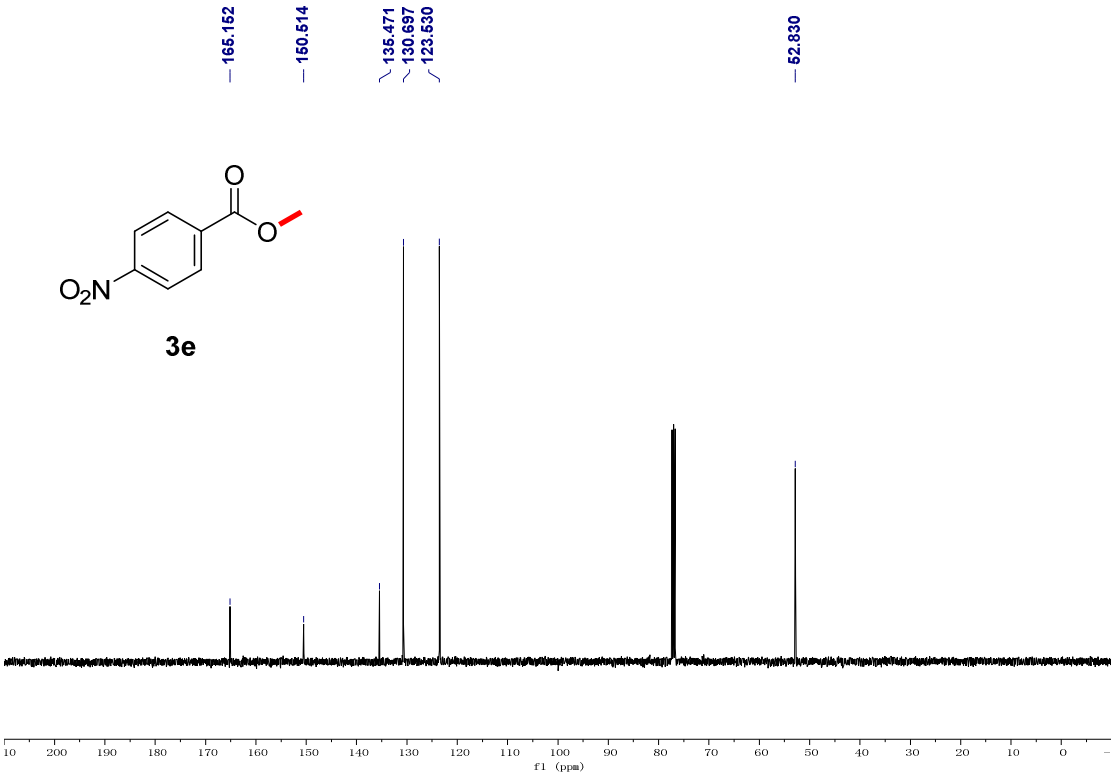
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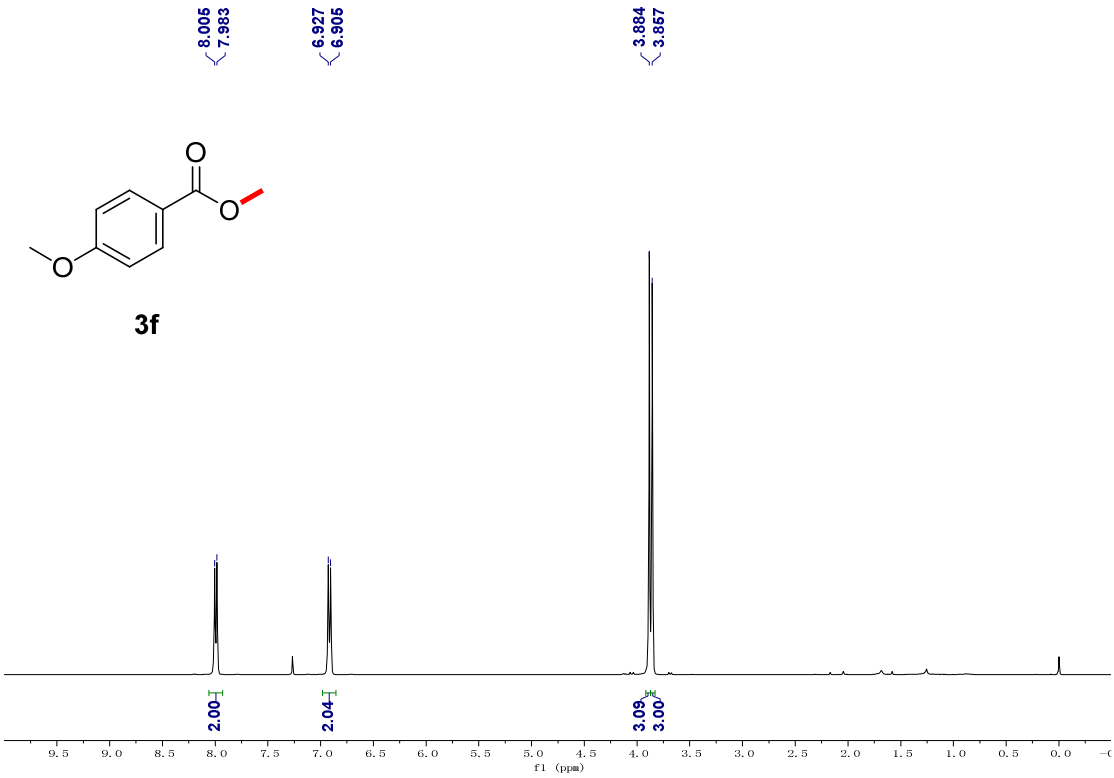
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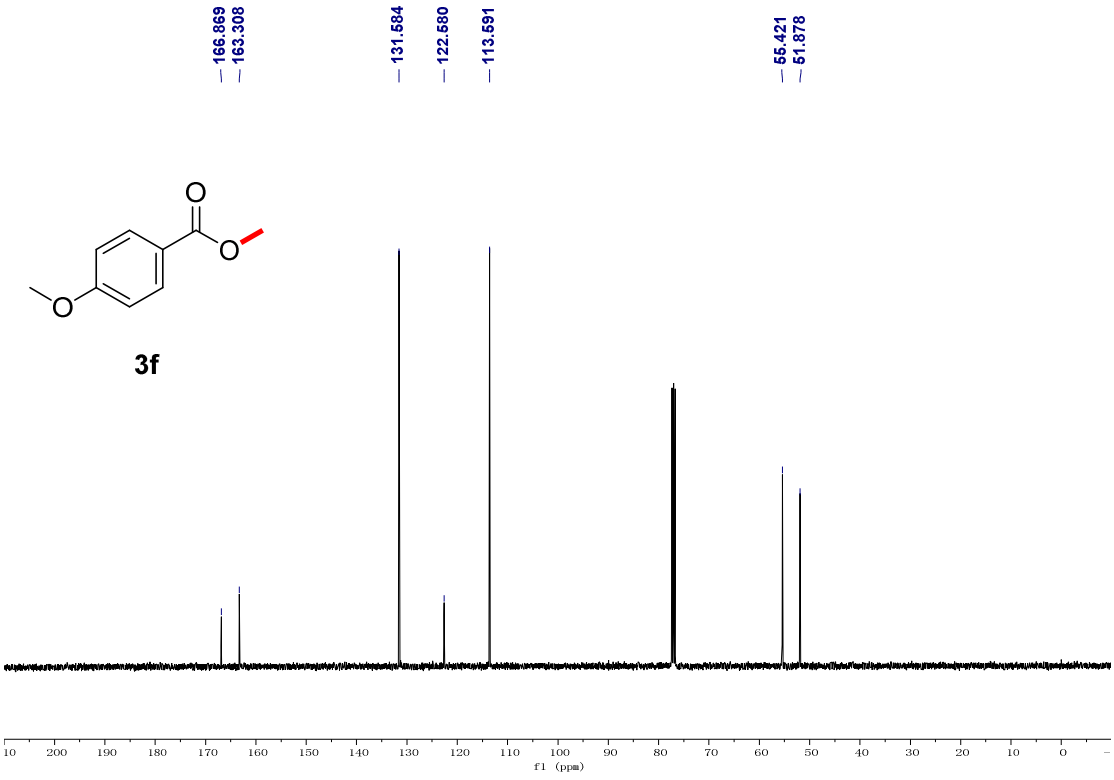
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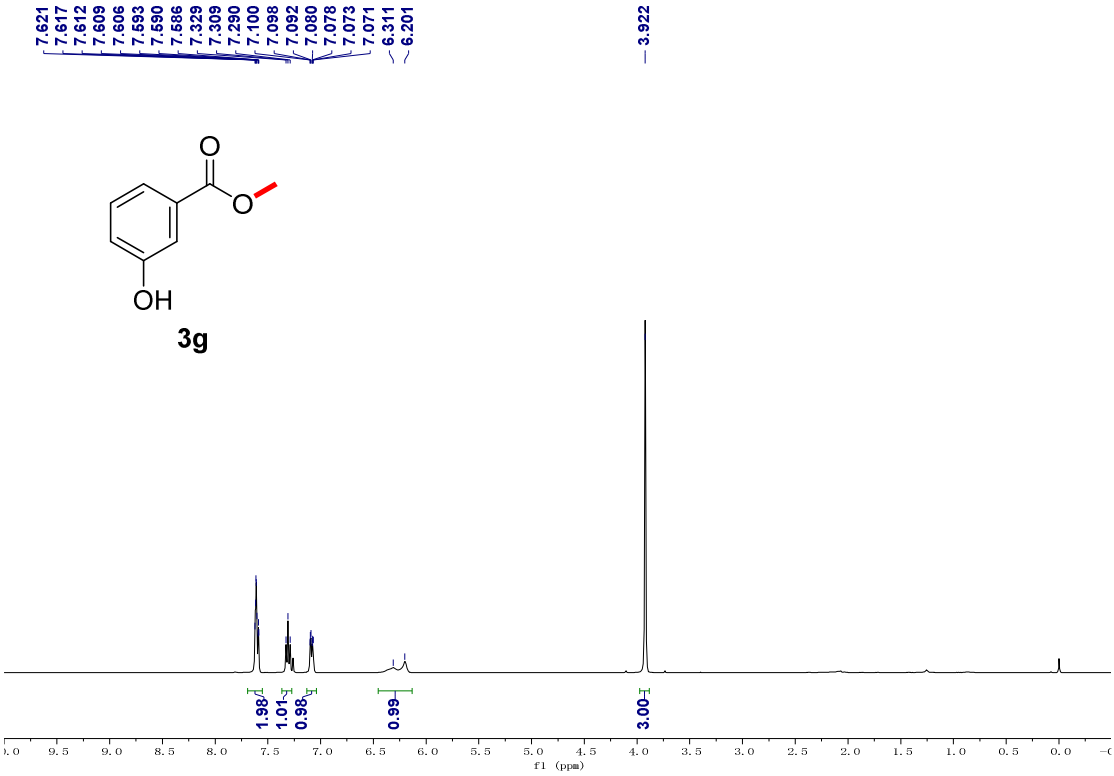
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7.098
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7.080
7.078
7.073
7.071
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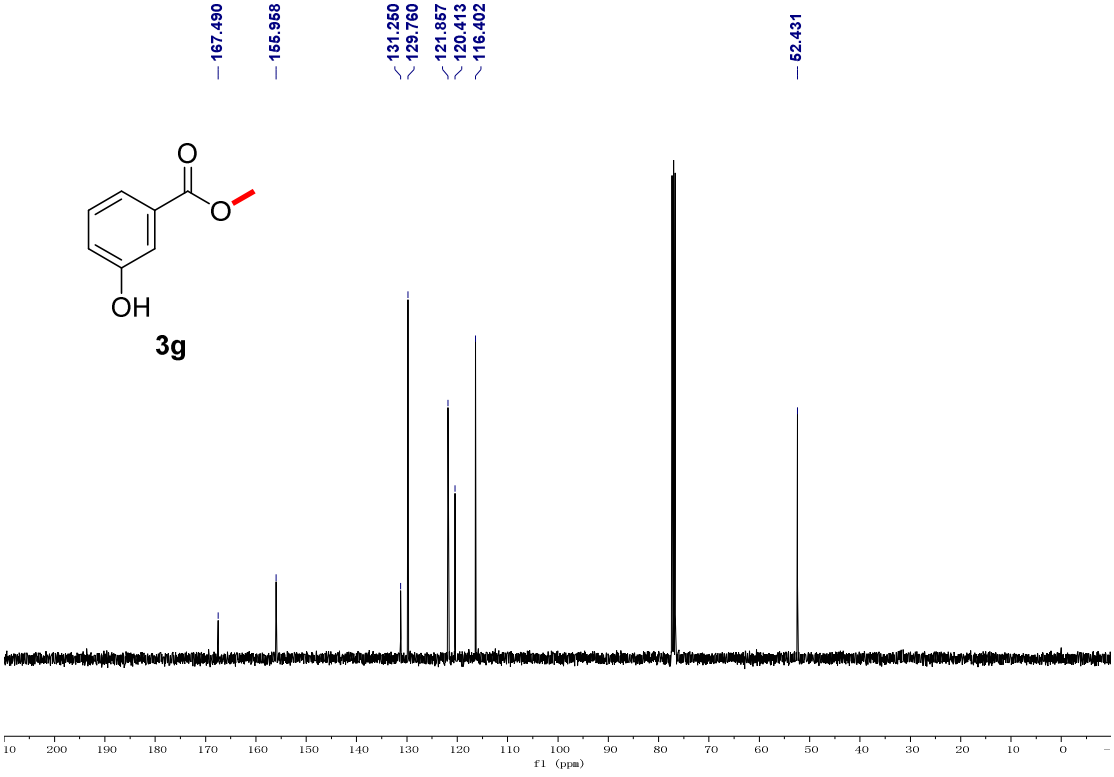
f1 (ppm)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OH
3g
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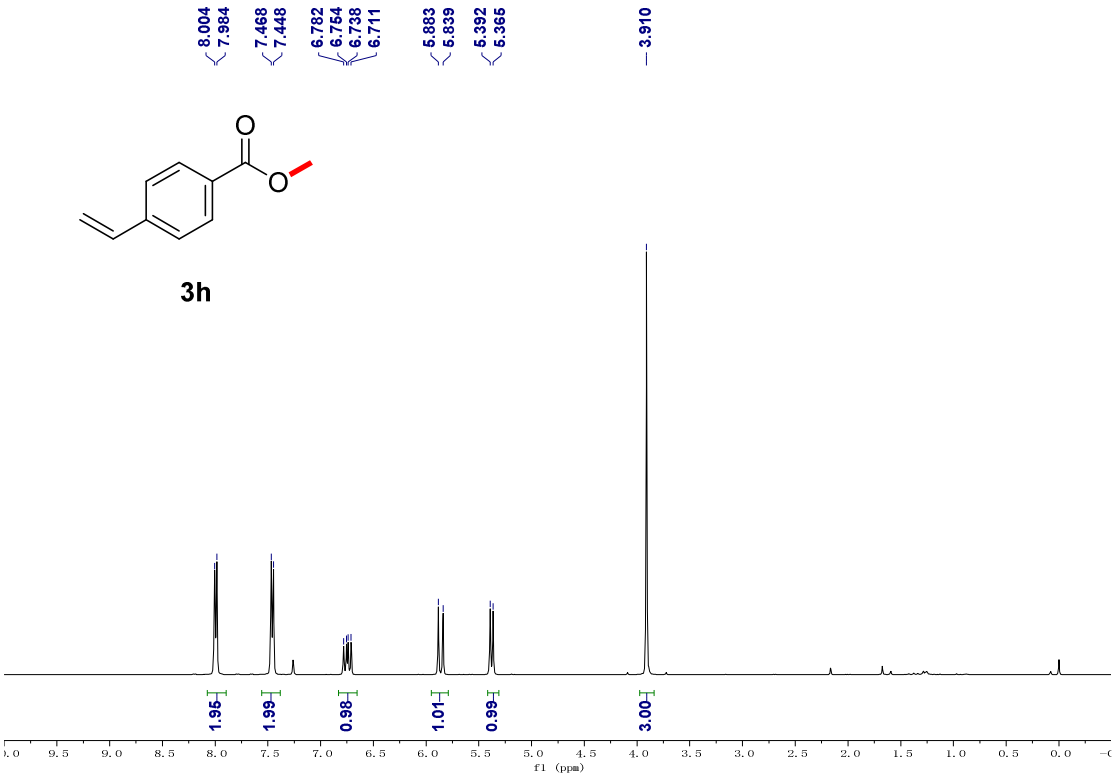
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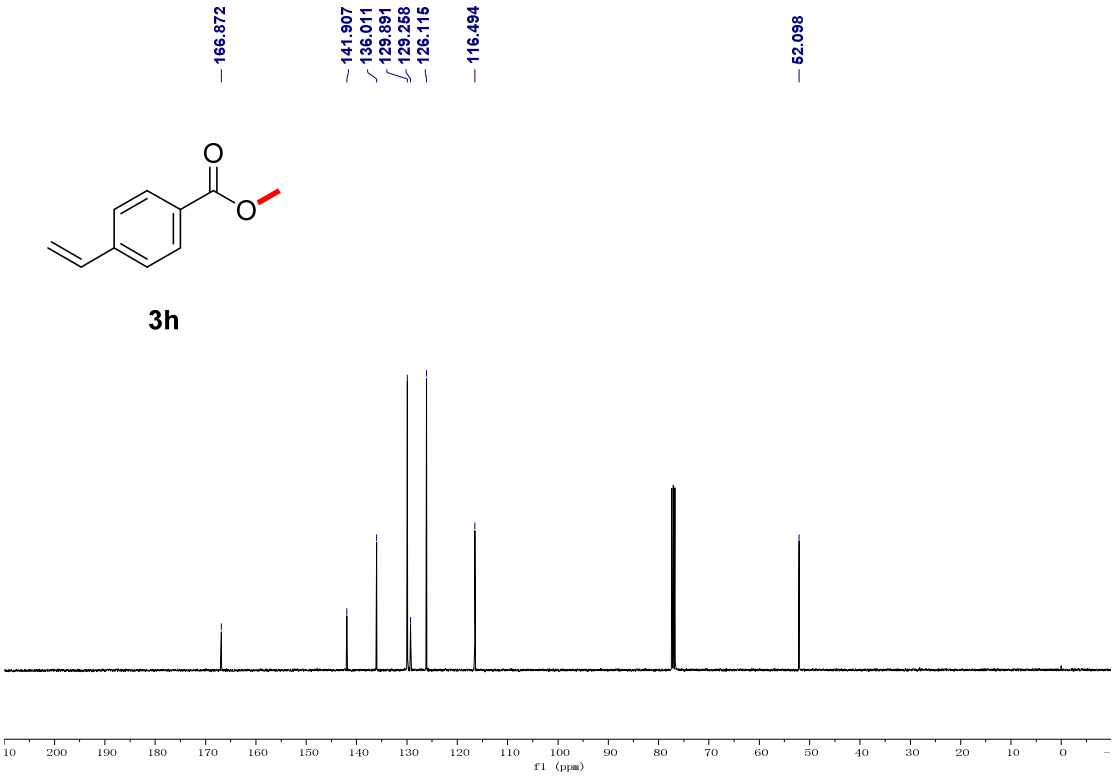
f1 (ppm)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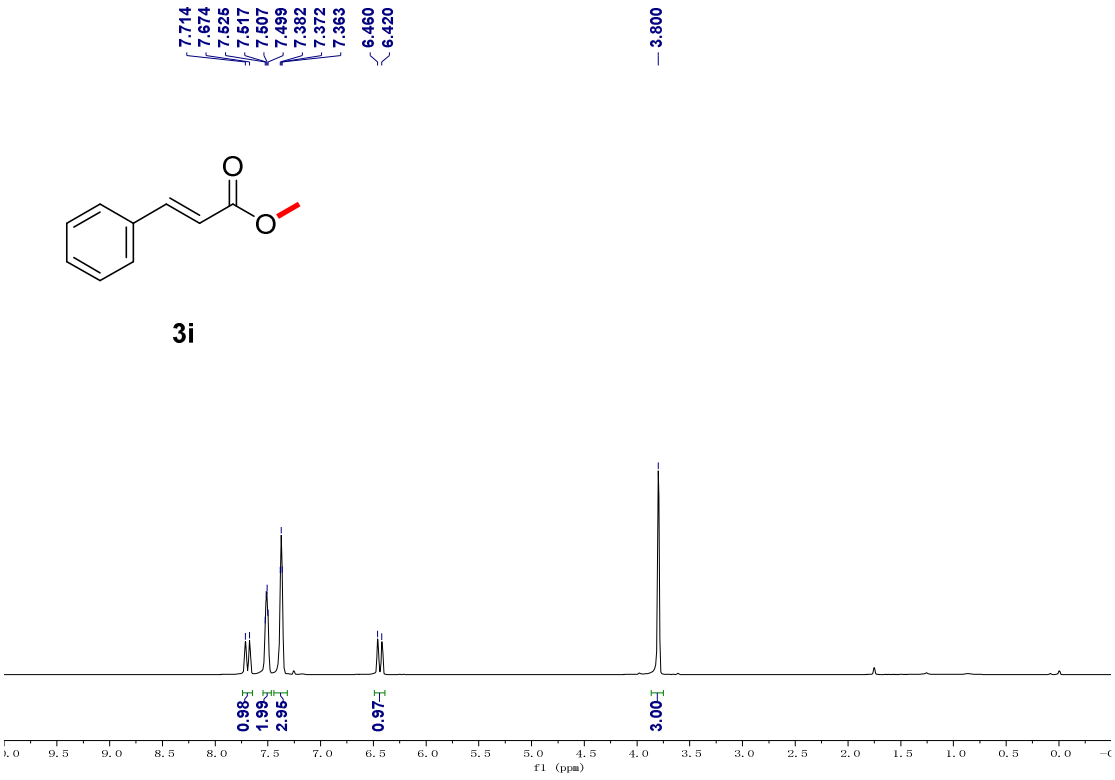
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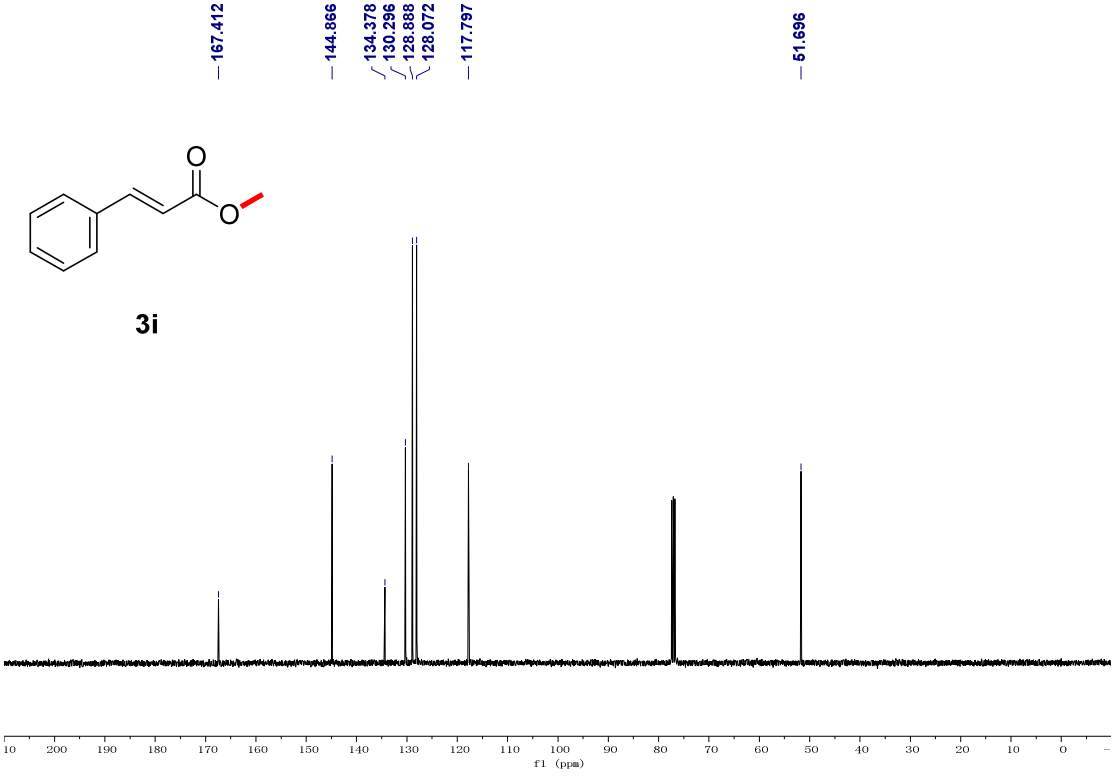
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3i


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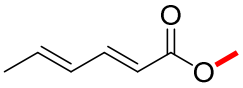

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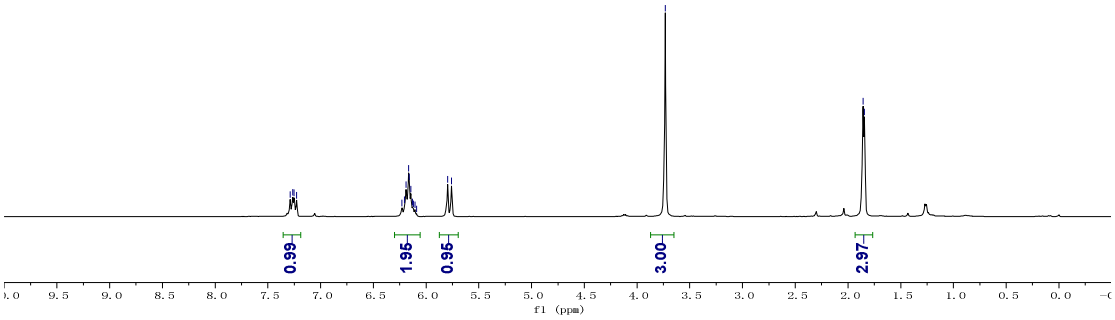
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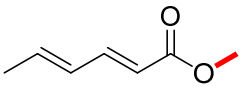

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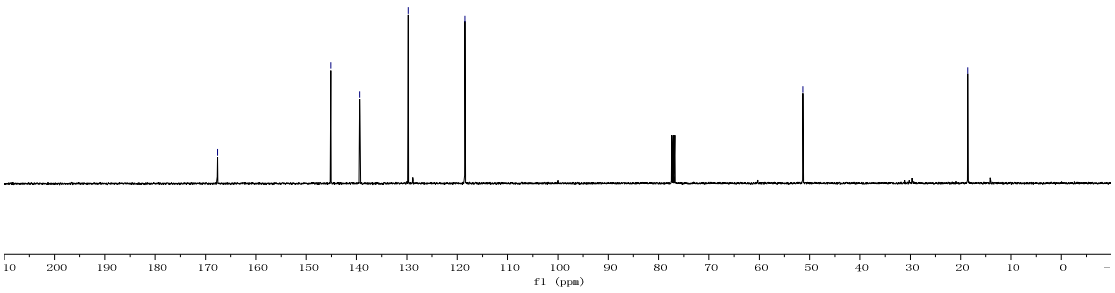
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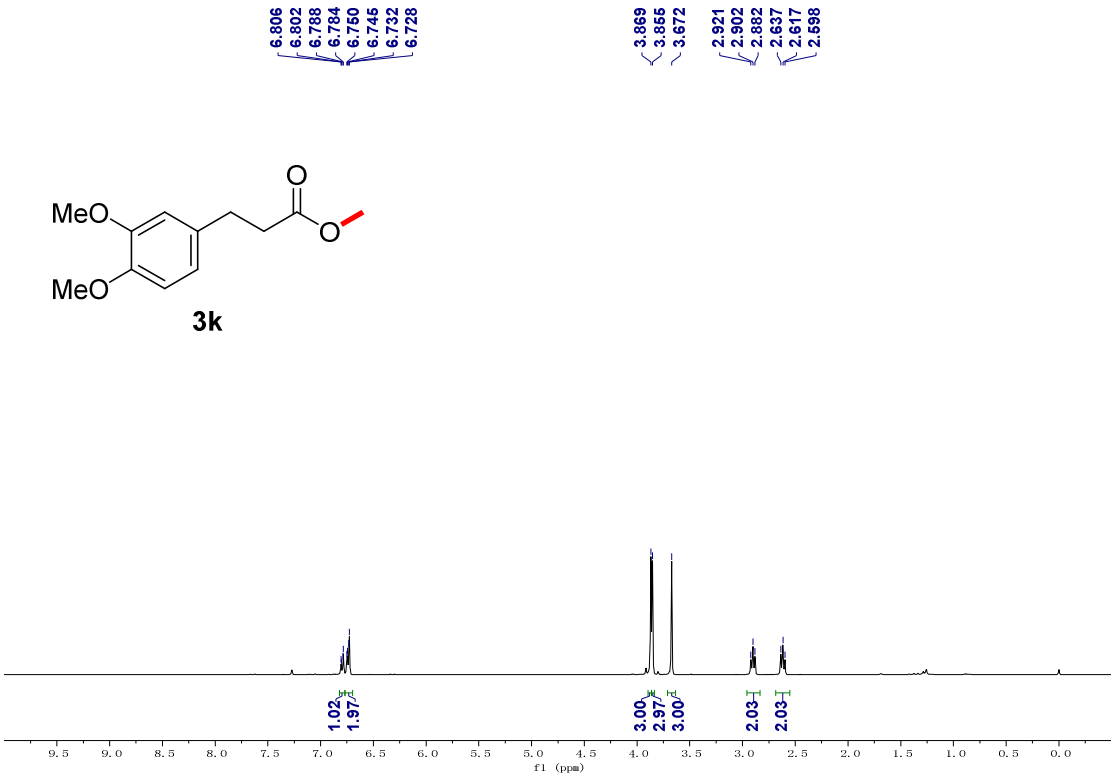
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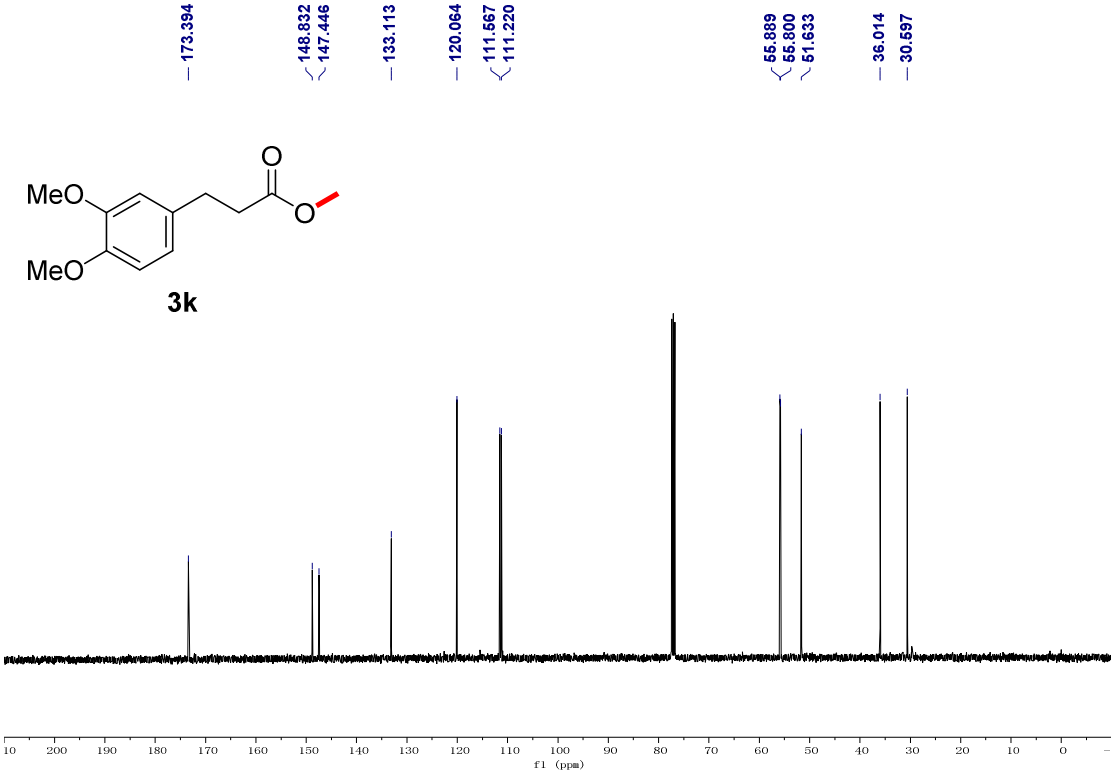
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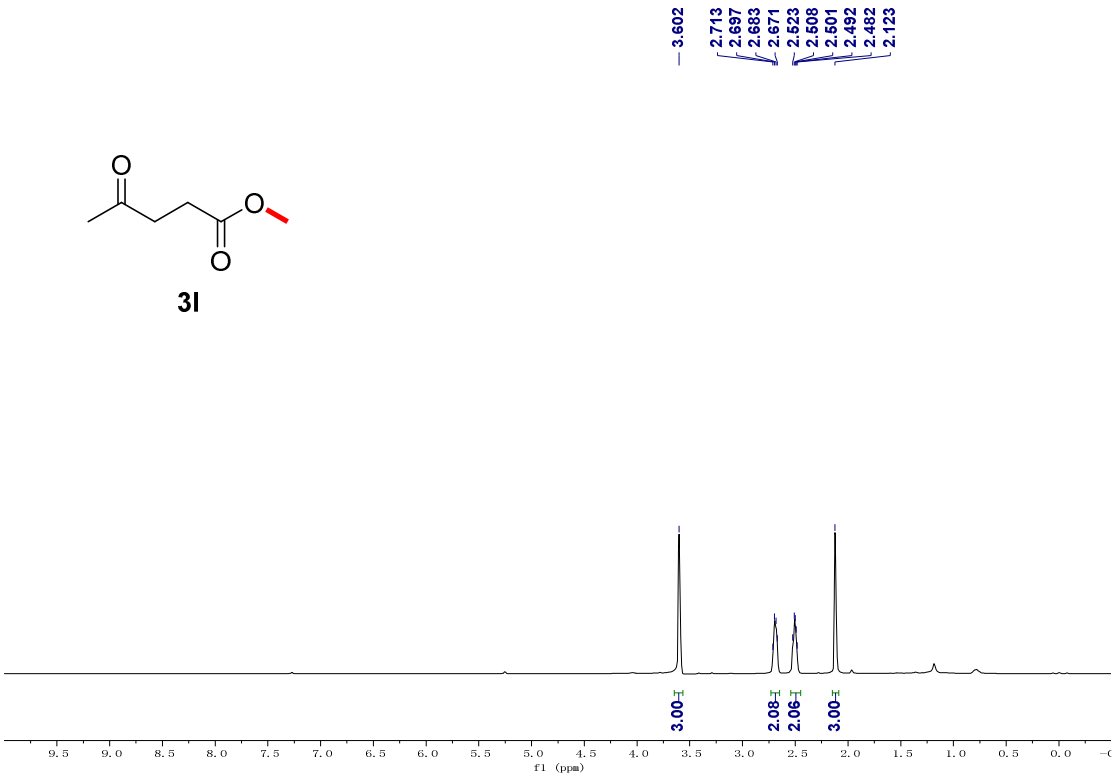
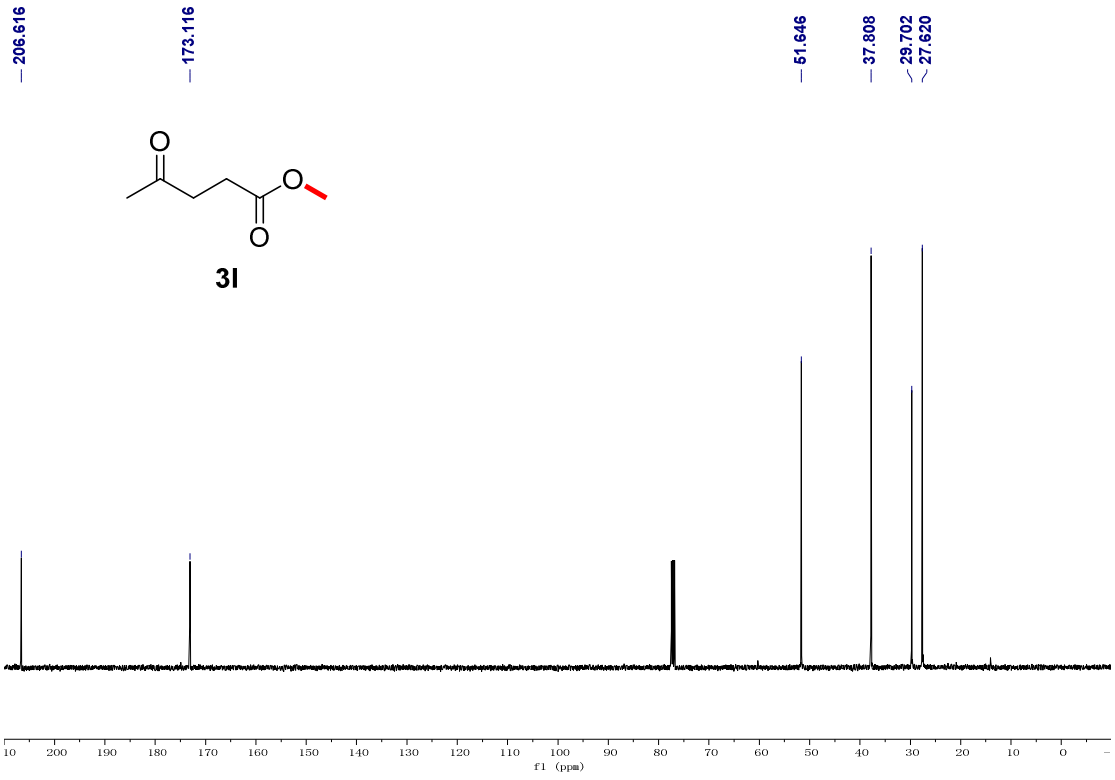
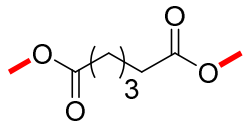
147.446
133.113
120.064
111.567
111.220
55.889
55.800
51.633
36.014
30.597
MeO
MeO
O
O
3k
f1 (ppm)

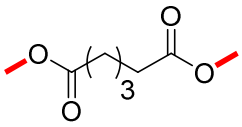

3.602
2.713
2.697
2.683
2.671
2.623
2.508
2.501
2.492
2.482
2.123
3l
3.00
2.08
2.06
3.00
f1 (ppm)


206.616
173.116
51.646
37.808
29.702
27.620
3l
f1 (ppm)



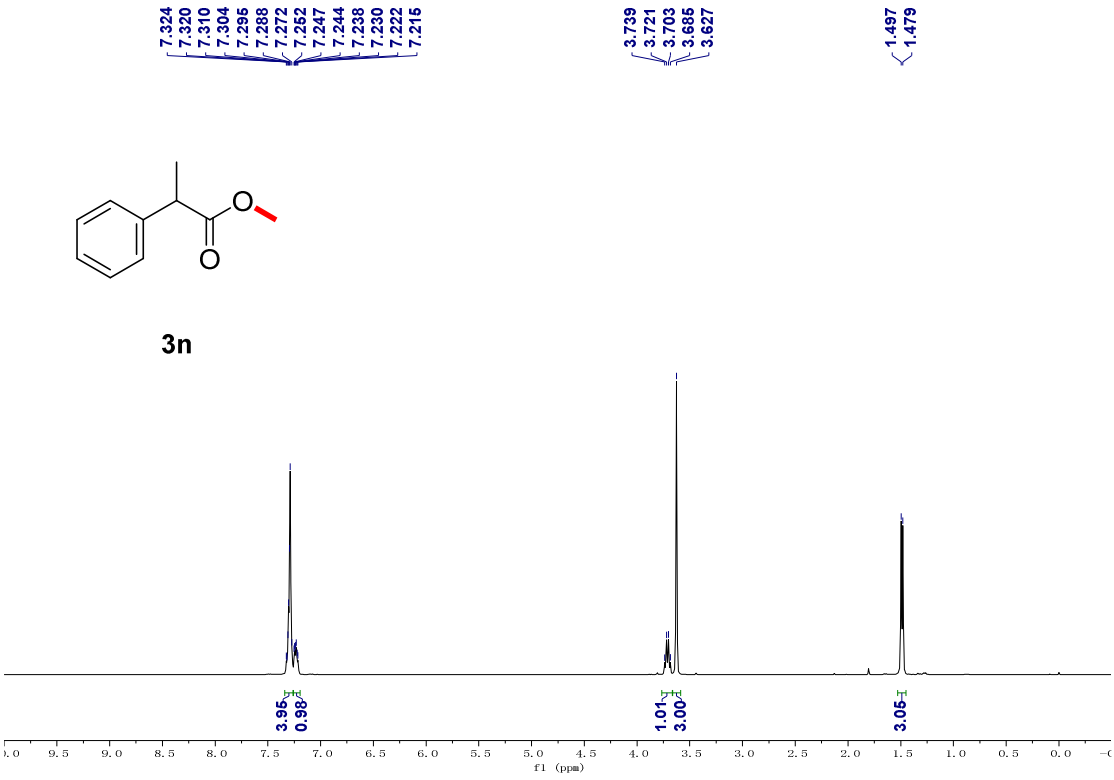
3m

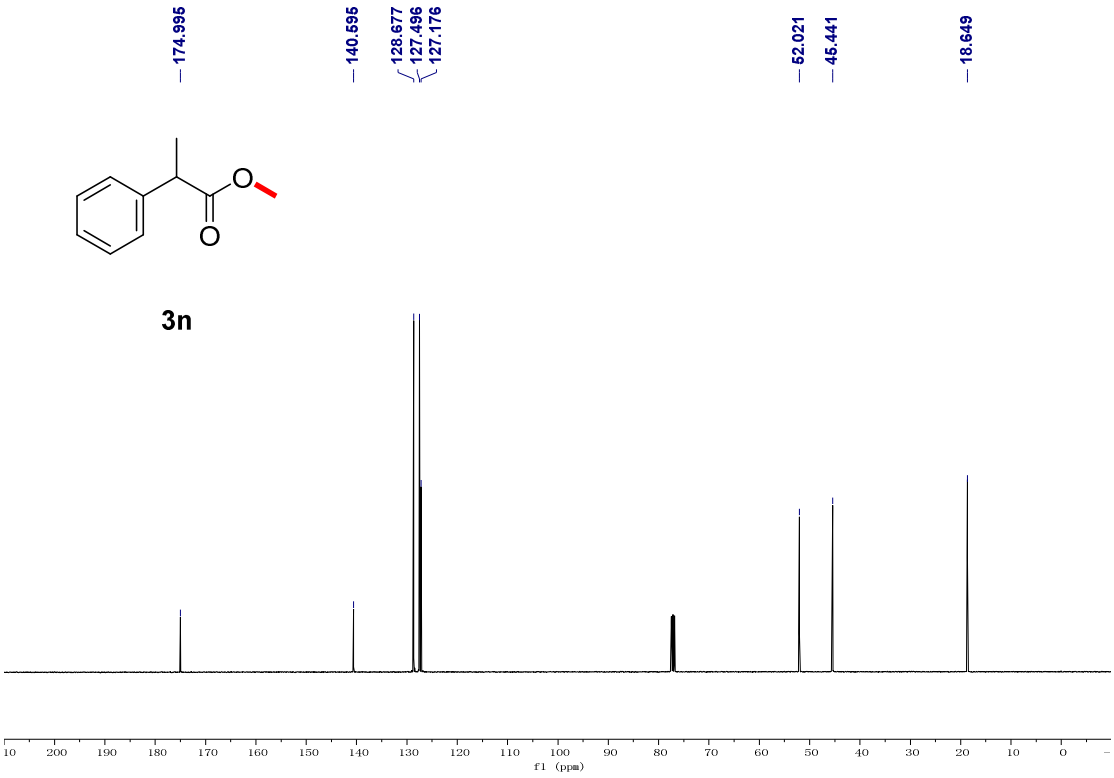
3.672
2.359
2.357
2.349
2.341
2.332
2.324
1.683
1.675
1.666
1.657
1.648
6.00
4.08
4.06
f1 (ppm)

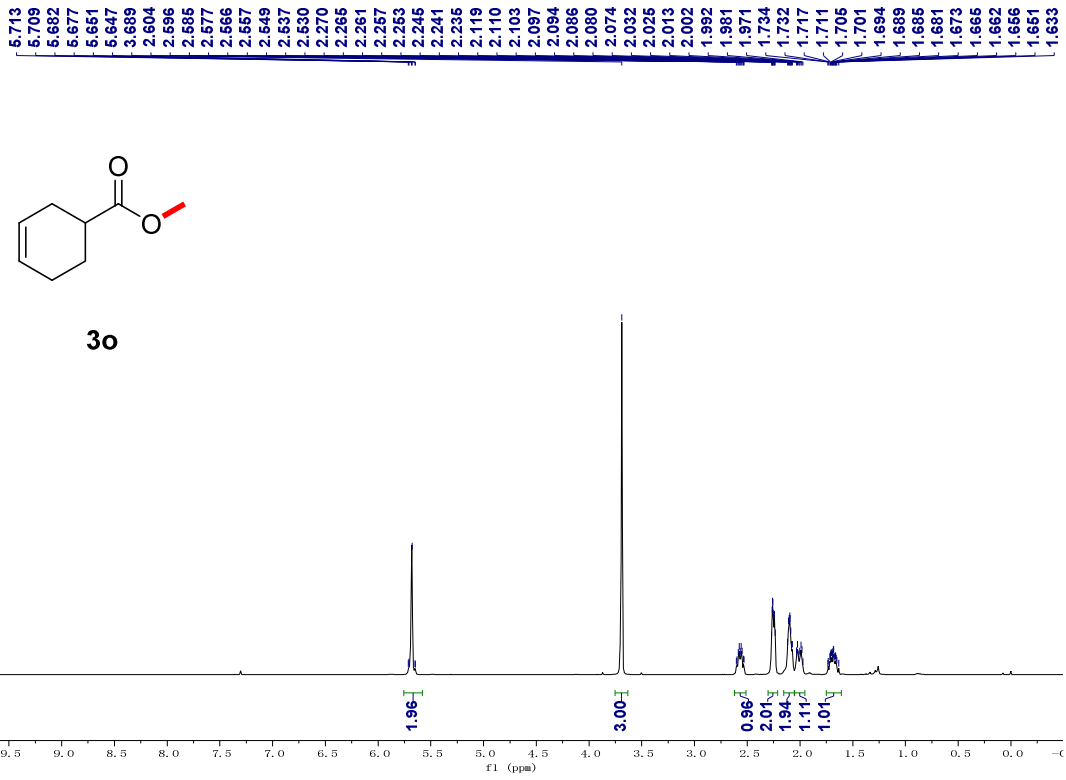


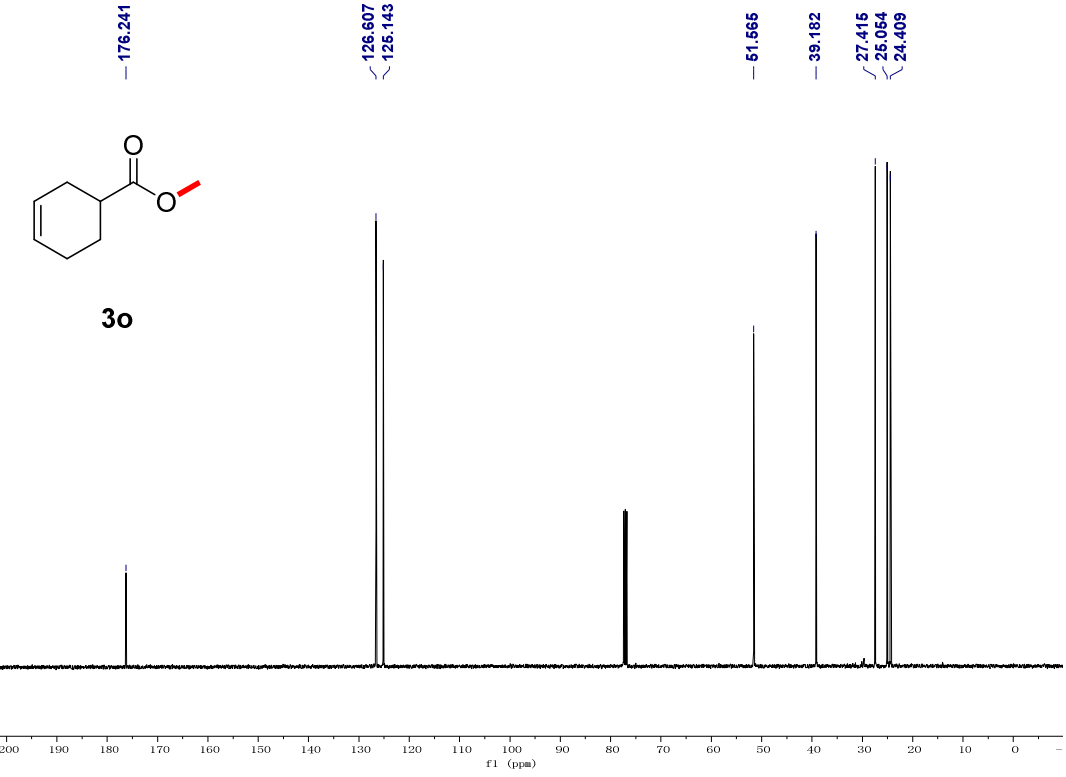
3m

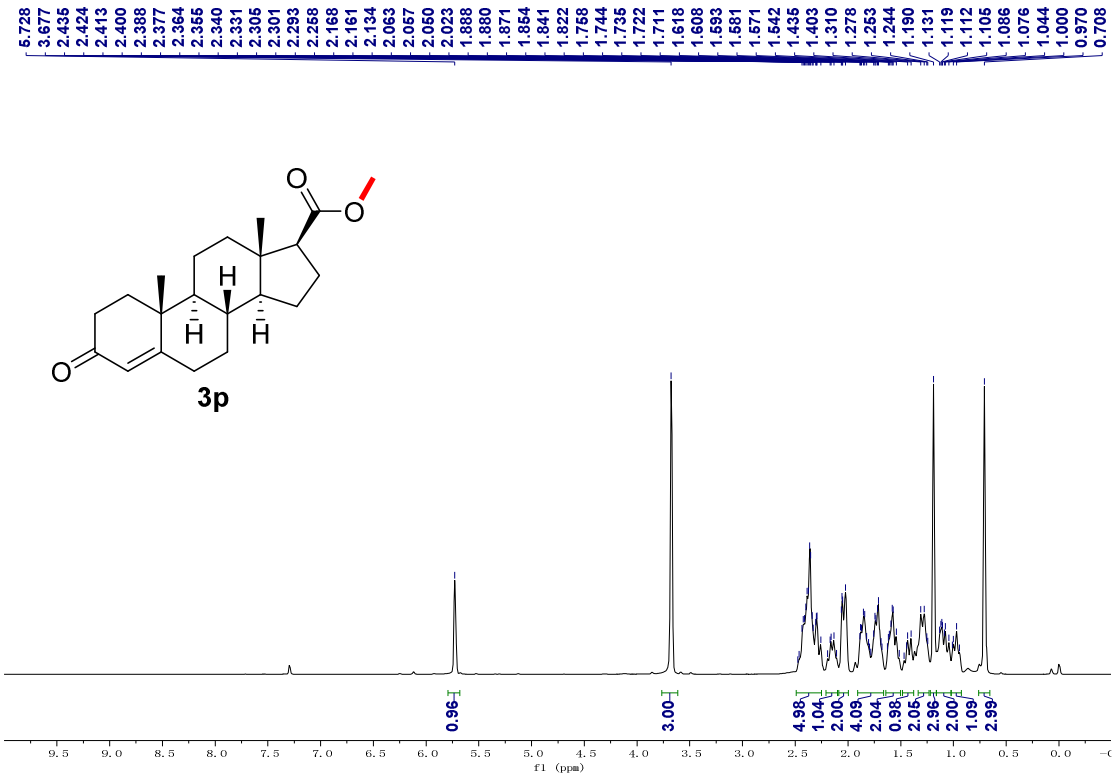
173.606
61.391
33.617
24.248
f1 (ppm)

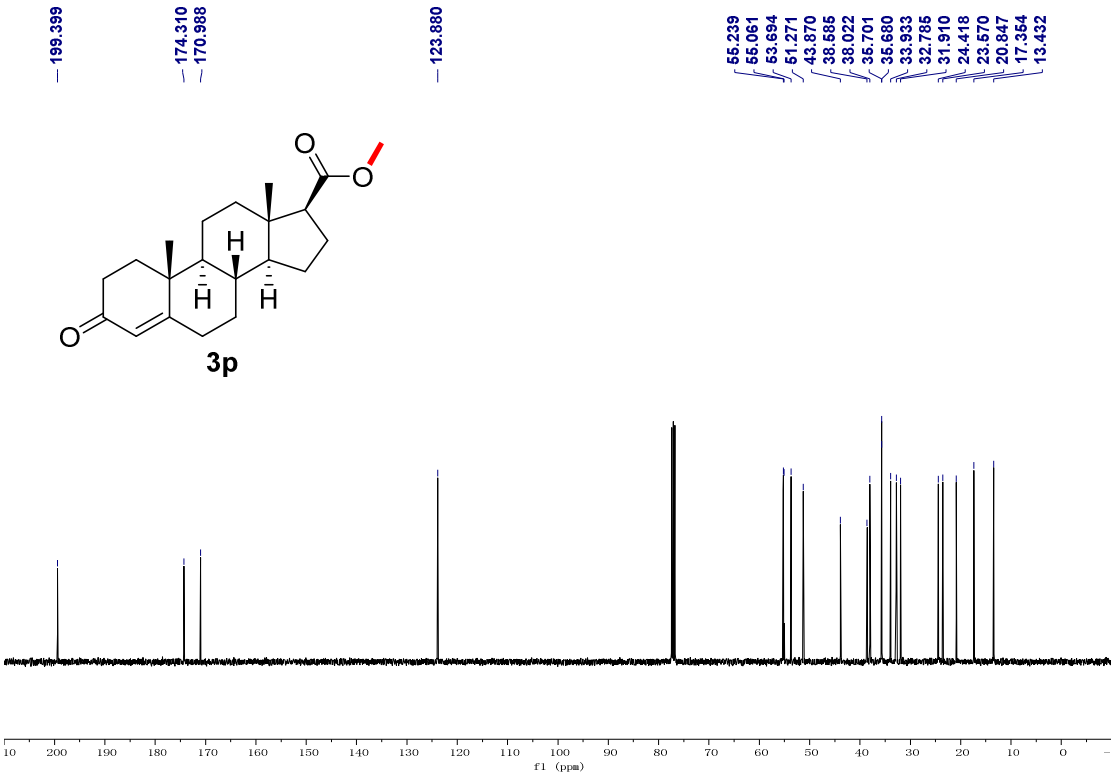

7.324
7.320
7.310
7.304
7.295
7.288
7.272
7.262
7.247
7.244
7.238
7.230
7.222
7.215
3.739
3.721
3.703
3.685
3.627
1.497
1.479
O
O
3n
3.95
0.98
1.01
3.00
3.05
f1 (ppm)

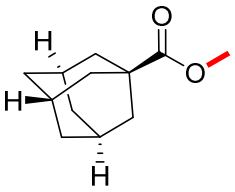

174.995
140.595
128.677
127.496
127.176
52.021
45.441
18.649
O
O
3n
f1 (ppm)


5.713
5.709
5.682
5.677
5.651
5.647
3.689
2.604
2.596
2.585
2.577
2.566
2.557
2.549
2.537
2.530
2.270
2.265
2.261
2.257
2.253
2.245
2.241
2.235
2.119
2.110
2.103
2.097
2.094
2.086
2.080
2.074
2.032
2.025
2.013
2.002
1.992
1.981
1.971
1.734
1.732
1.717
1.711
1.705
1.701
1.694
1.689
1.685
1.681
1.673
1.665
1.662
1.656
1.651
1.633
O
O
3o
1.96
3.00
0.96
2.01
1.94
1.11
1.01
f1 (ppm)


176.241
126.607
125.143
51.565
39.182
27.415
25.054
24.409
O
O
3o
f1 (ppm)

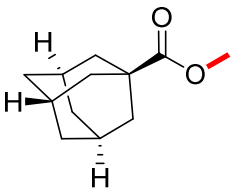

5.728
3.677
2.435
2.424
2.413
2.400
2.388
2.377
2.364
2.355
2.340
2.331
2.305
2.301
2.293
2.258
2.168
2.161
2.134
2.063
2.057
2.050
2.023
1.888
1.880
1.871
1.854
1.841
1.822
1.758
1.744
1.735
1.722
1.711
1.618
1.608
1.593
1.581
1.571
1.542
1.435
1.403
1.310
1.278
1.253
1.244
1.190
1.131
1.119
1.112
1.105
1.086
1.076
1.044
1.000
0.970
0.708
O
O
H
H
H
O
3p
0.96
3.00
4.98
1.04
2.00
4.09
2.04
0.98
2.05
2.96
2.00
1.09
2.99
f1 (ppm)


199.399
174.310
170.988
123.880
55.239
55.061
53.694
51.271
43.870
38.585
38.022
35.701
35.680
33.933
32.785
31.910
24.418
23.570
20.847
17.354
13.432
O
O
H
H
H
O
3p
f1 (ppm)



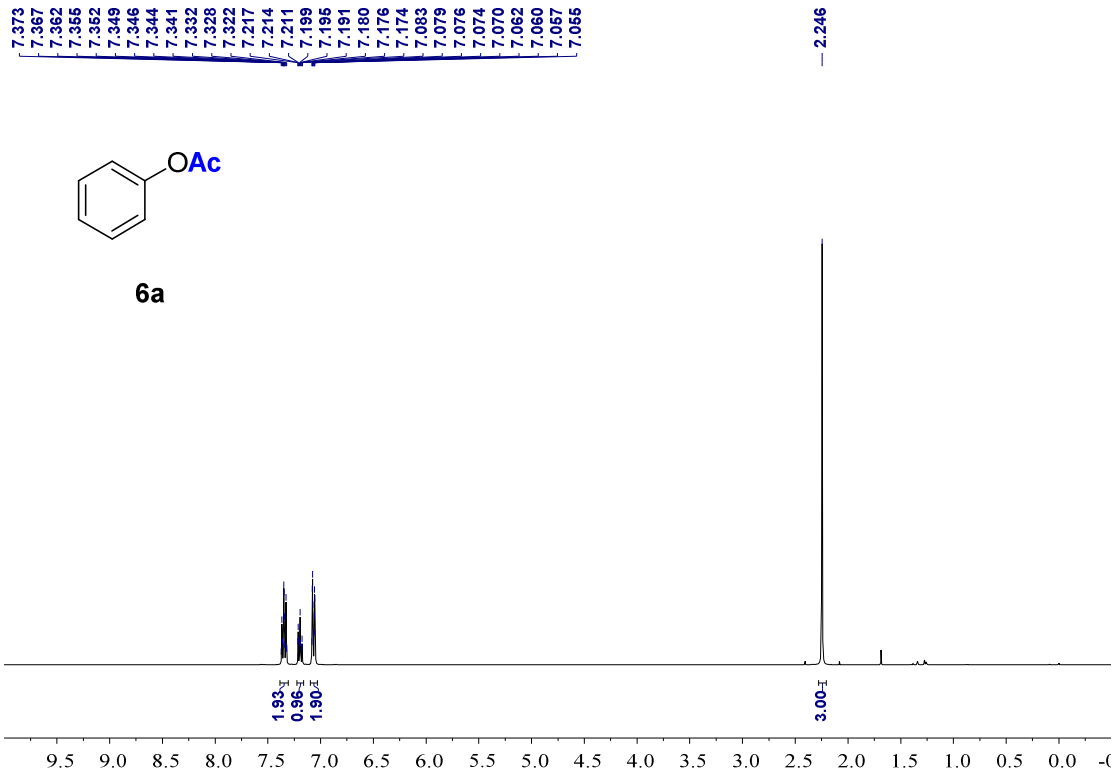
3q

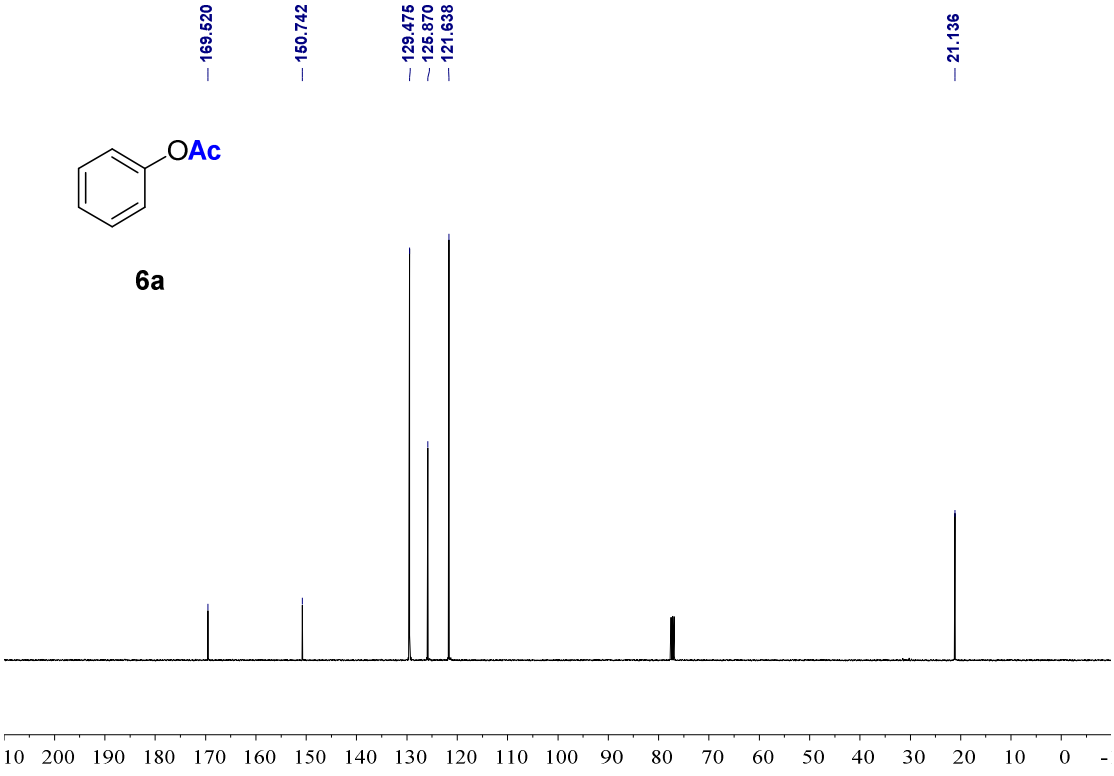
3.649
2.045
2.042
2.011
1.926
1.889
1.761
1.717
1.714
1.710
1.677
1.673
3.00
3.08
6.14
6.14
f1 (ppm)

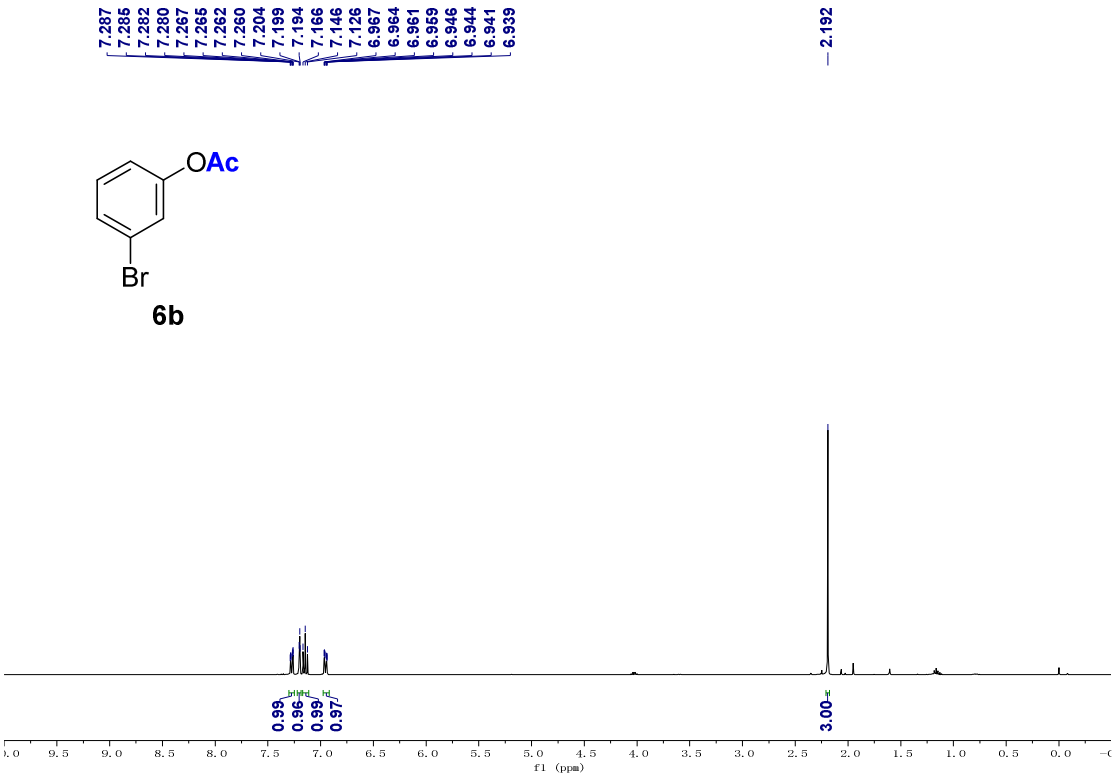


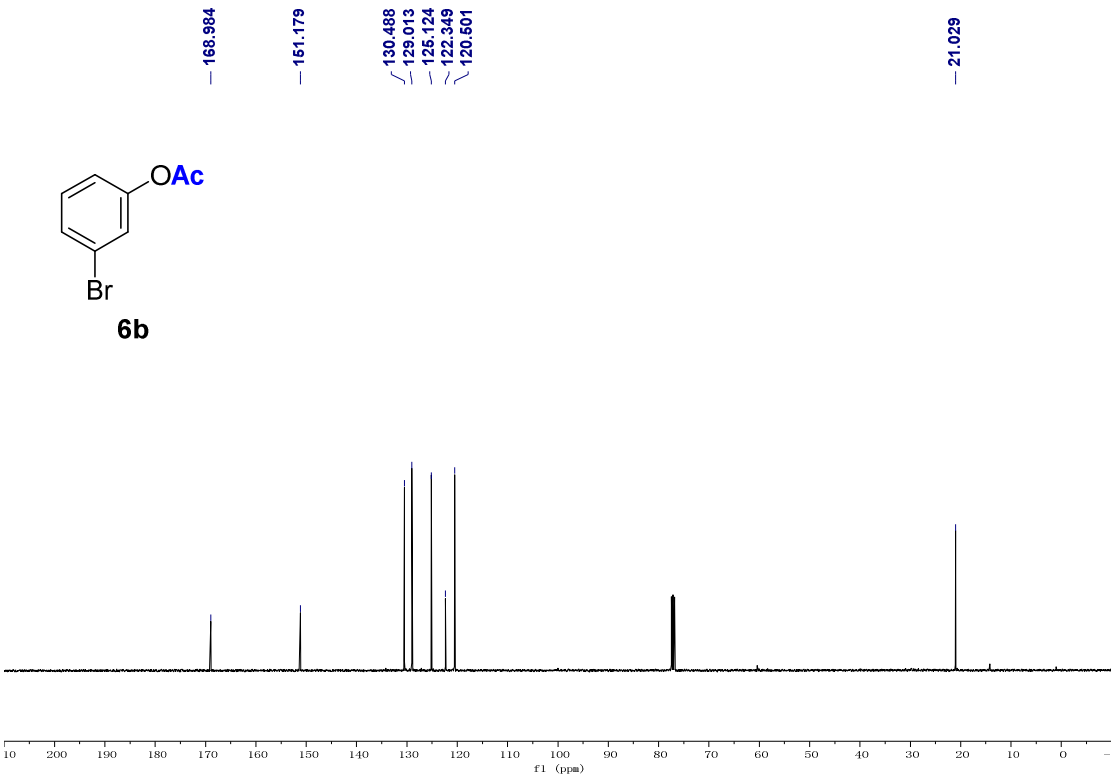
3q

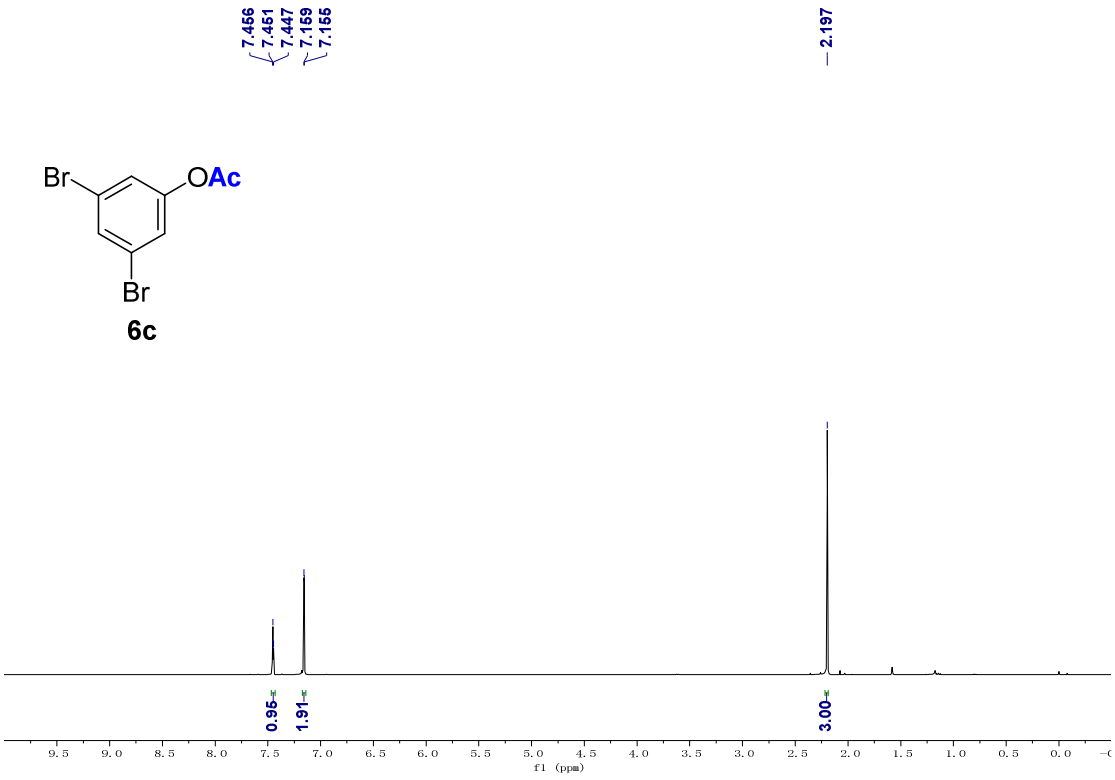
178.186
51.516
40.677
38.836
36.485
27.927
f1 (ppm)

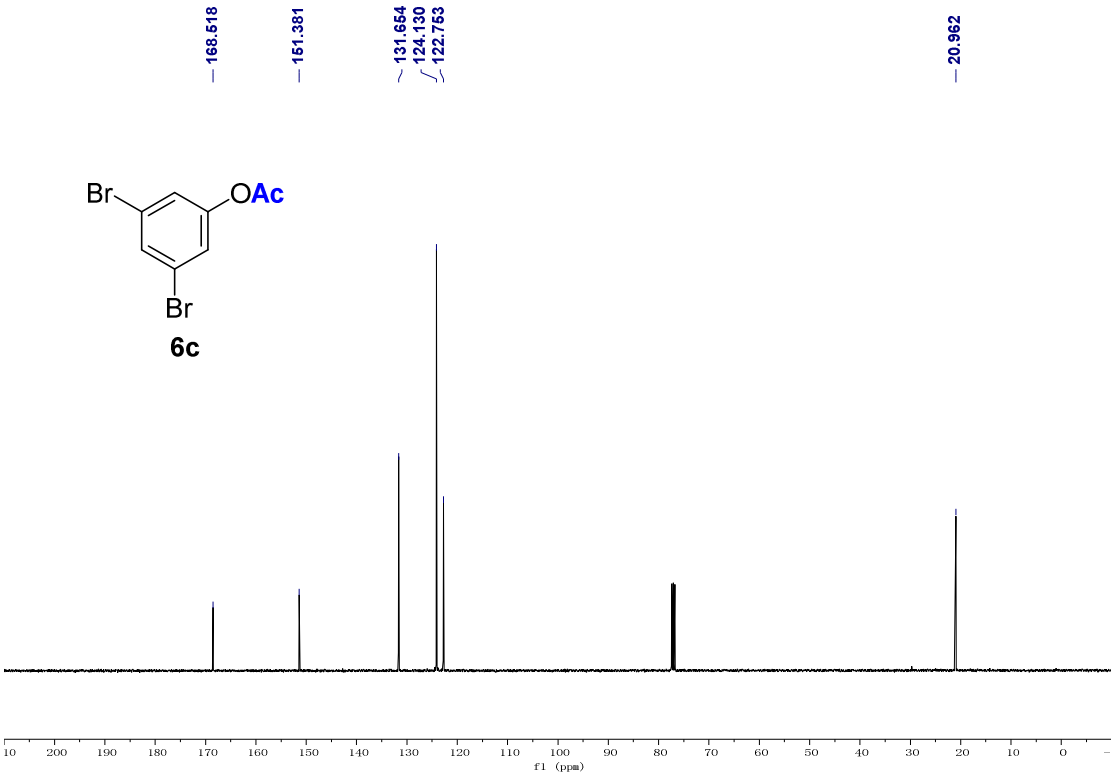

7.373
7.367
7.362
7.355
7.352
7.349
7.346
7.344
7.341
7.332
7.328
7.322
7.217
7.214
7.211
7.199
7.195
7.191
7.180
7.176
7.174
7.083
7.079
7.076
7.074
7.070
7.062
7.060
7.057
7.055
2.246
OAc
6a
1.93
0.96
1.90
3.00
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0

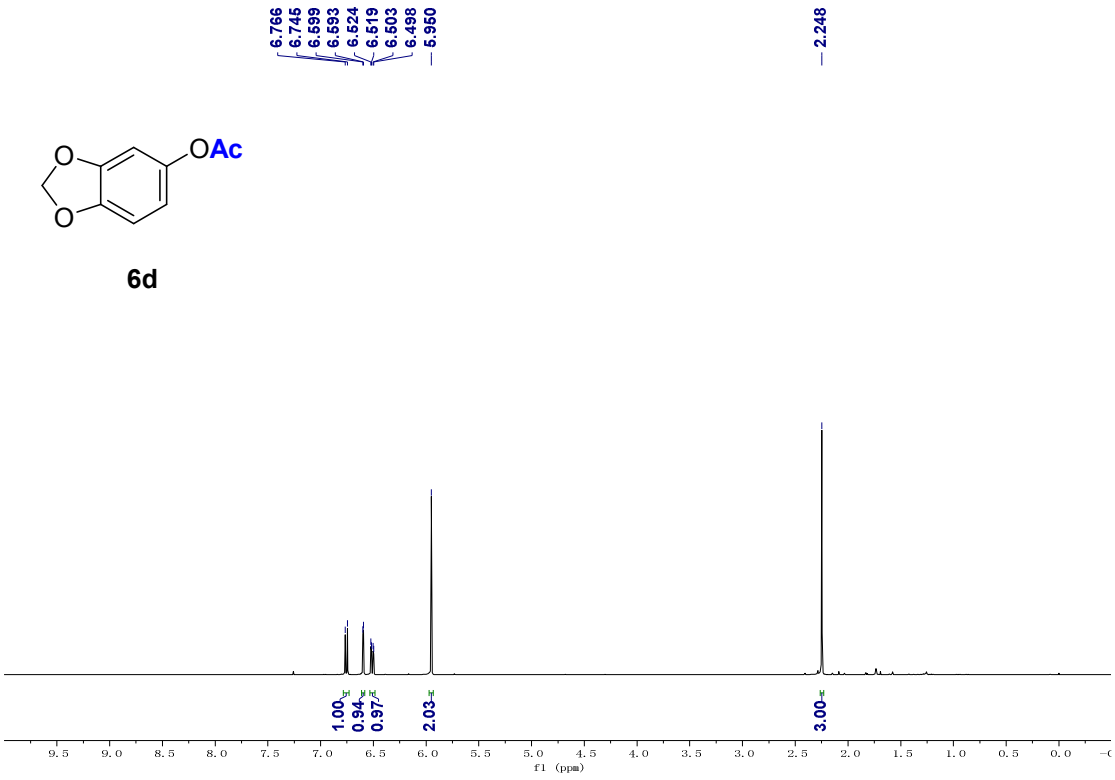

169.520
160.742
129.475
126.870
121.638
21.136
OAc
6a
10 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0

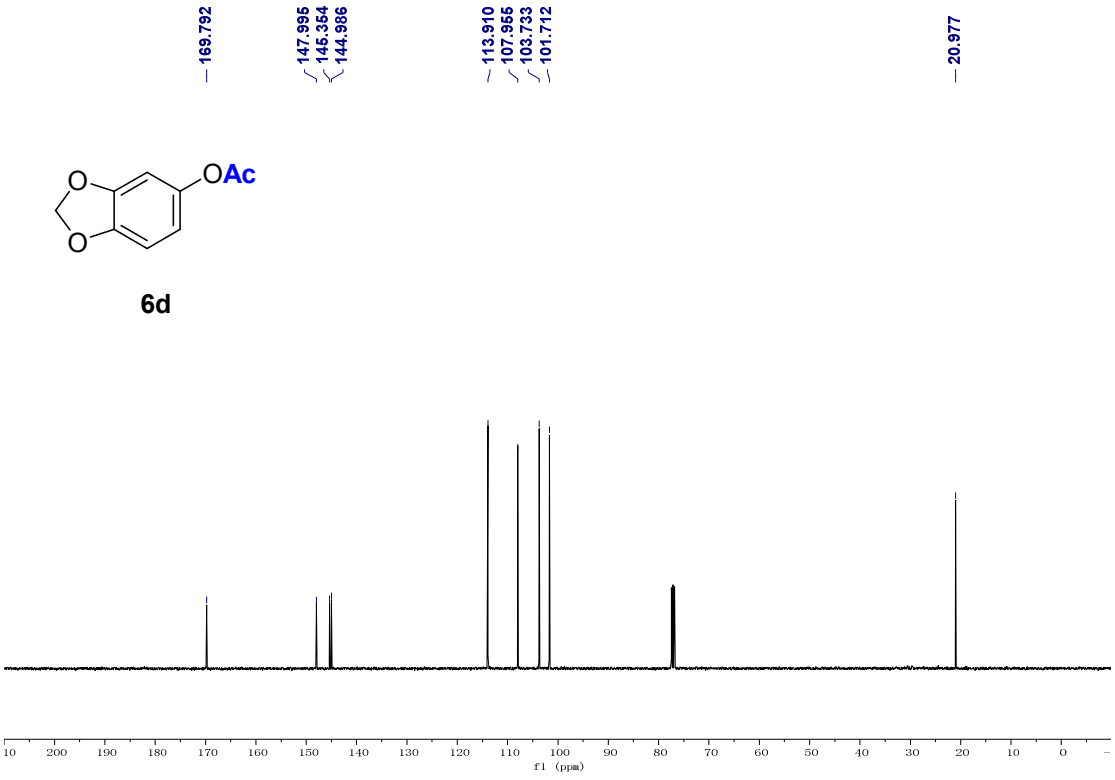

7.287
7.285
7.282
7.280
7.267
7.265
7.262
7.260
7.204
7.199
7.194
7.166
7.146
7.126
6.967
6.964
6.961
6.959
6.946
6.944
6.941
6.939
2.192
OAc
Br
6b
0.99
0.96
0.99
0.97
3.00
f1 (ppm)


168.984
161.179
130.488
129.013
125.124
122.349
120.501
21.029
OAc
Br
6b
f1 (ppm)


7.456
7.451
7.447
7.159
7.155
2.197
Br
OAc
Br
6c
0.95
1.91
3.00
f1 (ppm)


168.518
151.381
131.654
124.130
122.753
20.962
Br
OAc
Br
6c
f1 (ppm)


6.766
6.745
6.599
6.593
6.524
6.519
6.503
6.498
5.950
2.248
OAc
6d
1.00
0.94
0.97
2.03
3.00
f1 (ppm)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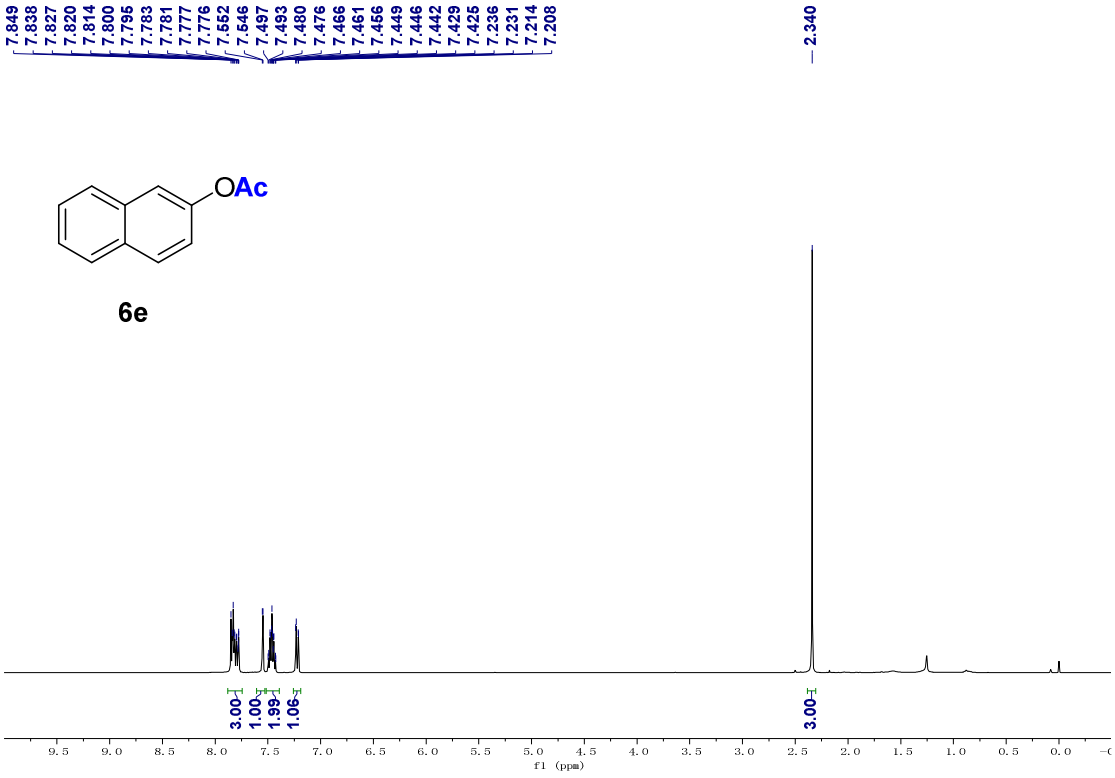
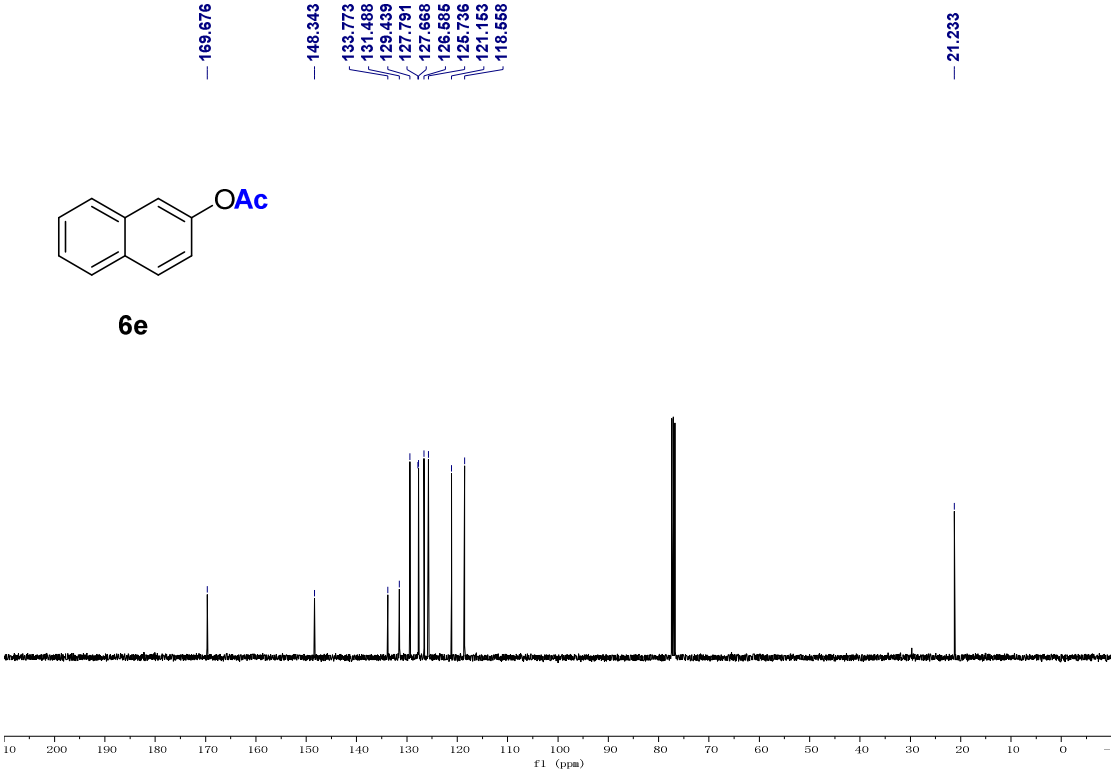
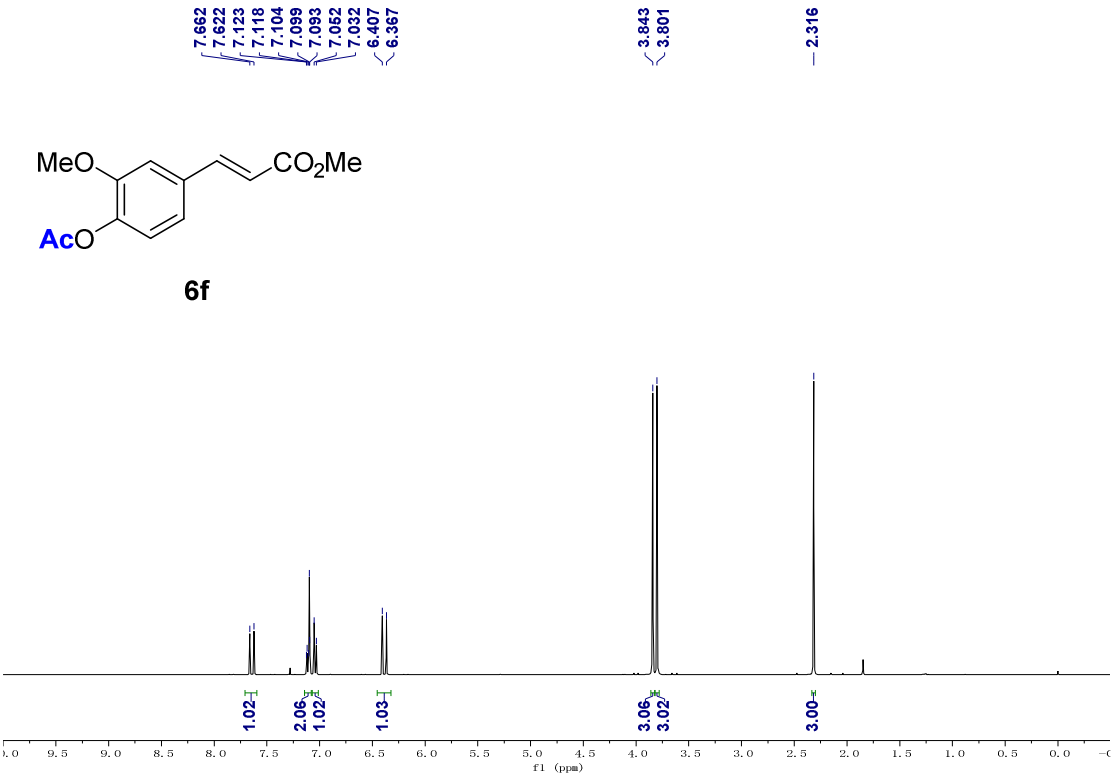
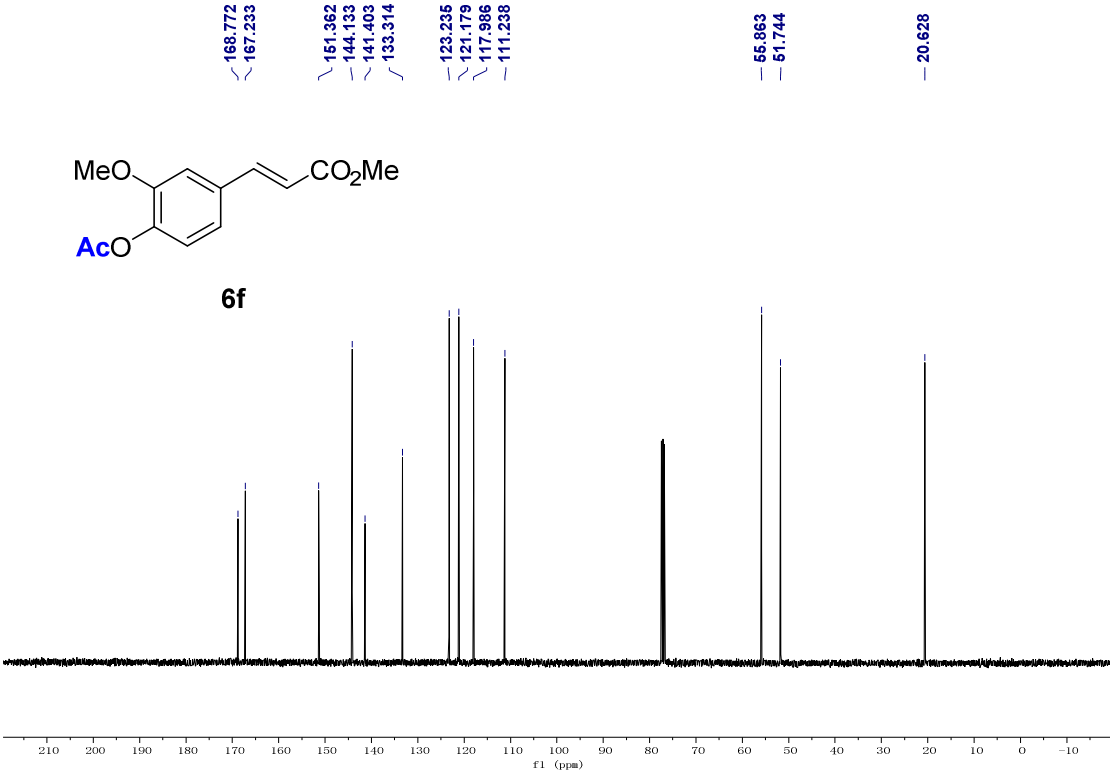
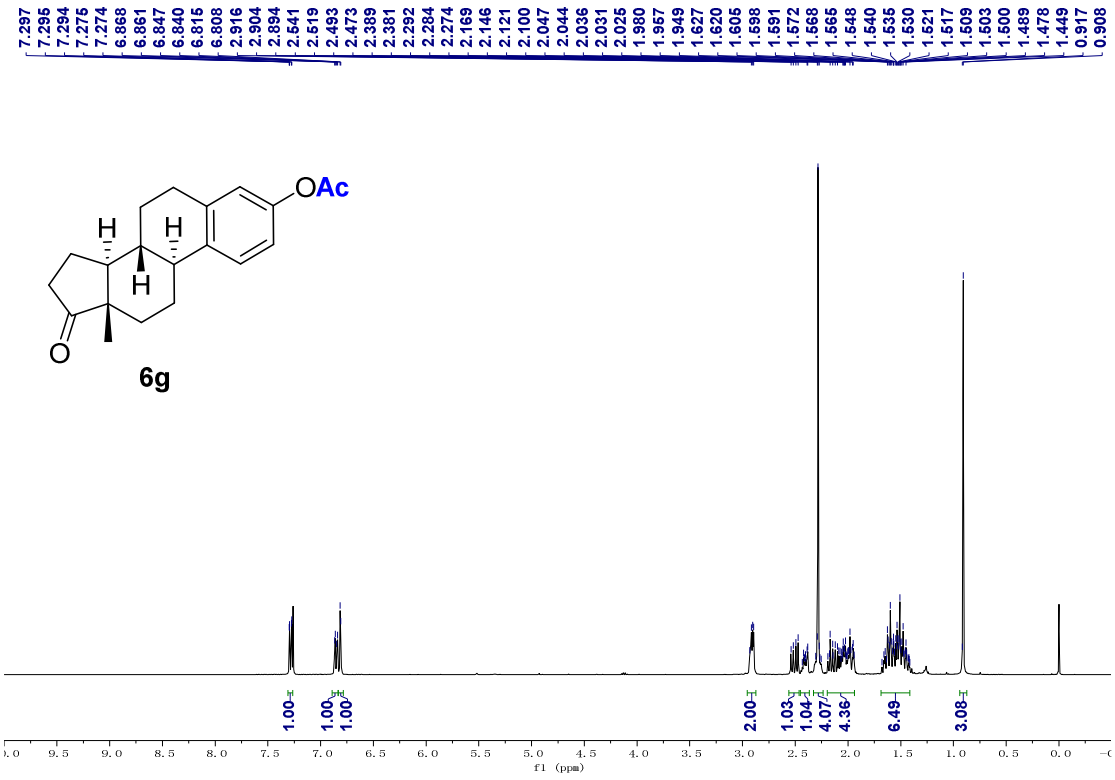
147.995
145.354
144.986
113.910
107.955
103.733
101.712
20.977
OAc
6d
f1 (ppm)

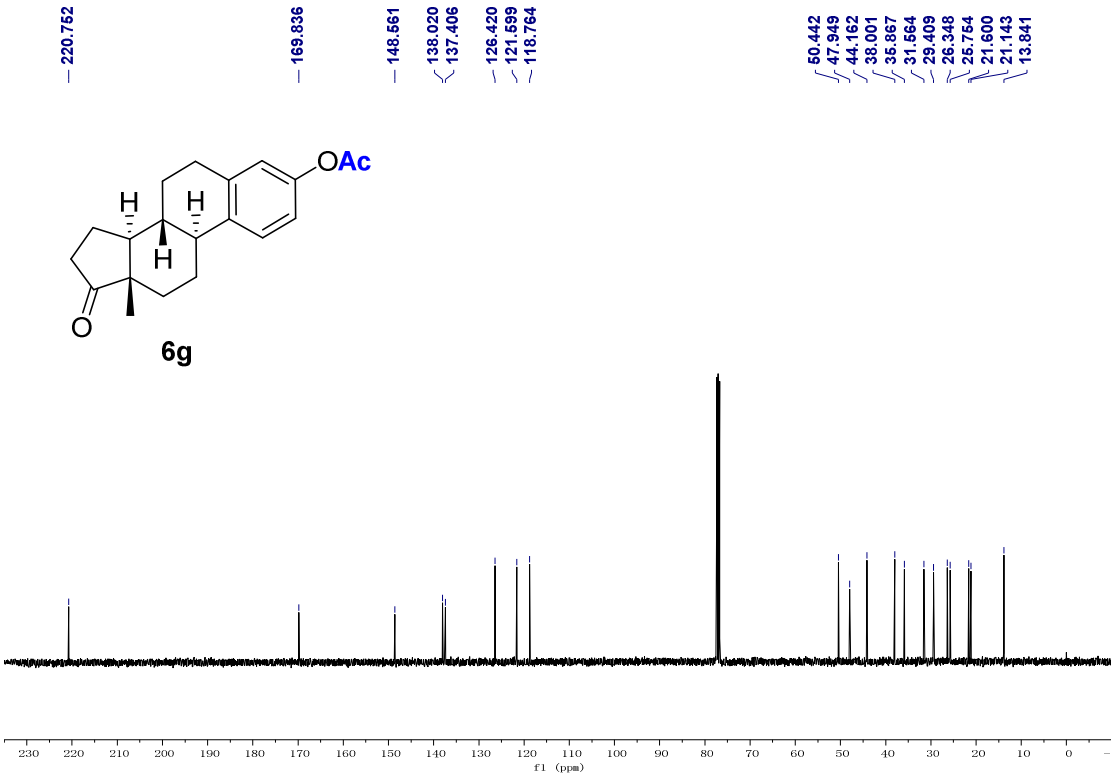

7.849
7.838
7.827
7.820
7.814
7.800
7.795
7.783
7.781
7.777
7.776
7.552
7.546
7.497
7.493
7.480
7.476
7.466
7.461
7.456
7.449
7.446
7.442
7.429
7.425
7.236
7.231
7.214
7.208
2.340
OAc
6e
3.00
1.00
1.99
1.06
3.00
f1 (ppm)


169.676
148.343
133.773
131.488
129.439
127.791
127.668
126.585
125.736
121.153
118.558
21.233
OAc
6e
f1 (ppm)


7.662
7.622
7.123
7.118
7.104
7.099
7.093
7.052
7.032
6.407
6.367
3.843
3.801
2.316
MeO
CO2Me
AcO
6f
1.02
2.06
1.02
1.03
3.06
3.02
3.00
f1 (ppm)


168.772
167.233
151.362
144.133
141.403
133.314
123.235
121.179
117.986
111.238
55.863
51.744
20.628
MeO
CO2Me
AcO
6f
f1 (ppm)


7.297
7.295
7.294
7.275
7.274
6.868
6.861
6.847
6.840
6.815
6.808
2.916
2.904
2.894
2.541
2.519
2.493
2.473
2.389
2.381
2.292
2.284
2.274
2.169
2.146
2.121
2.100
2.047
2.044
2.036
2.031
2.025
1.980
1.957
1.949
1.627
1.620
1.605
1.598
1.591
1.672
1.568
1.565
1.548
1.540
1.535
1.530
1.521
1.617
1.509
1.503
1.500
1.489
1.478
1.449
0.917
0.908
OAc
H
H
H
O
6g
1.00
1.00
1.00
2.00
1.03
1.04
4.07
4.36
6.49
3.08
f1 (ppm)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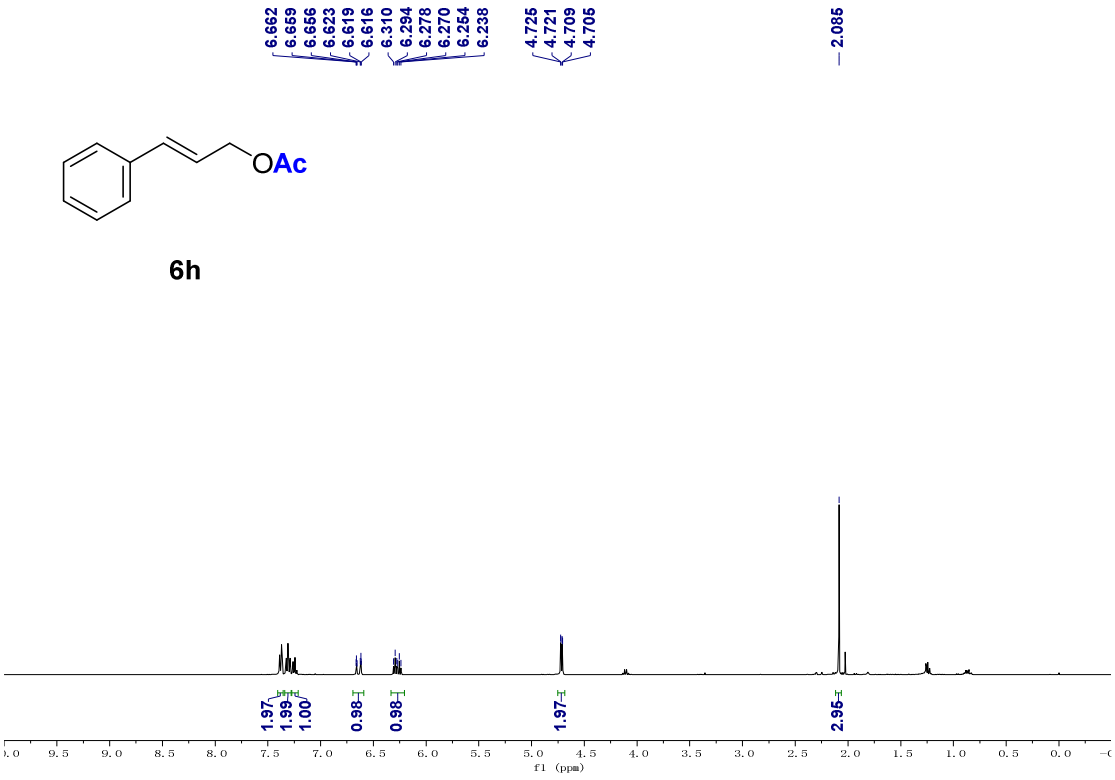
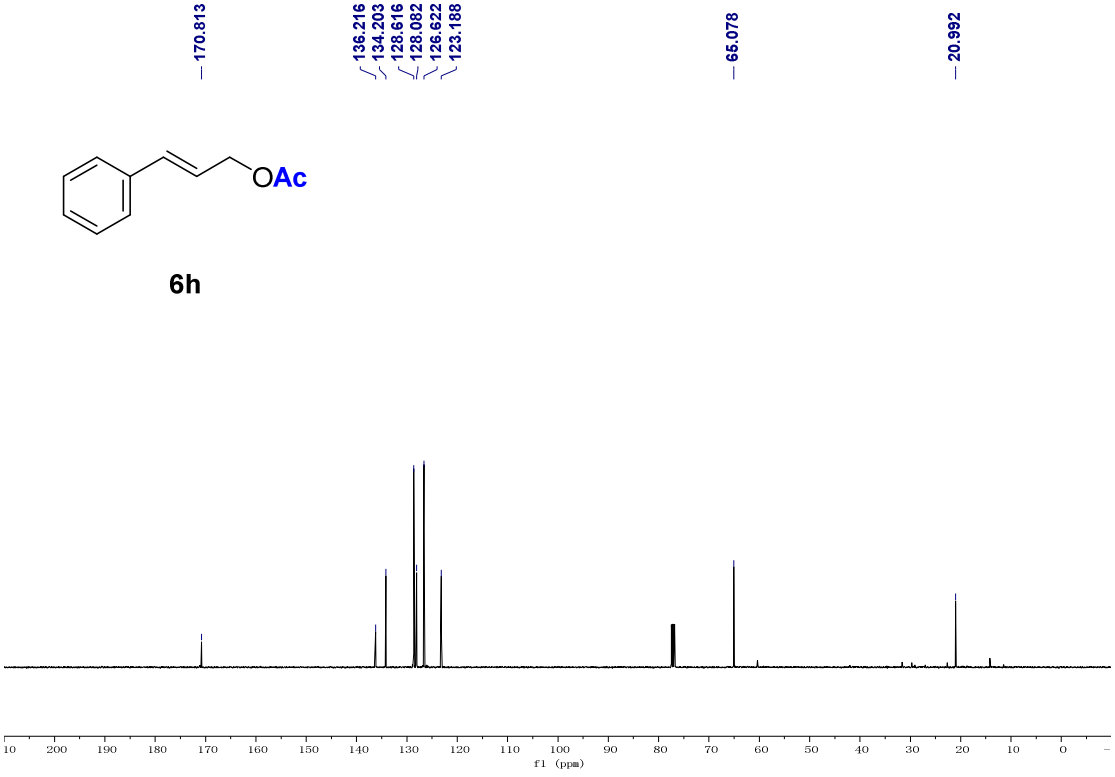
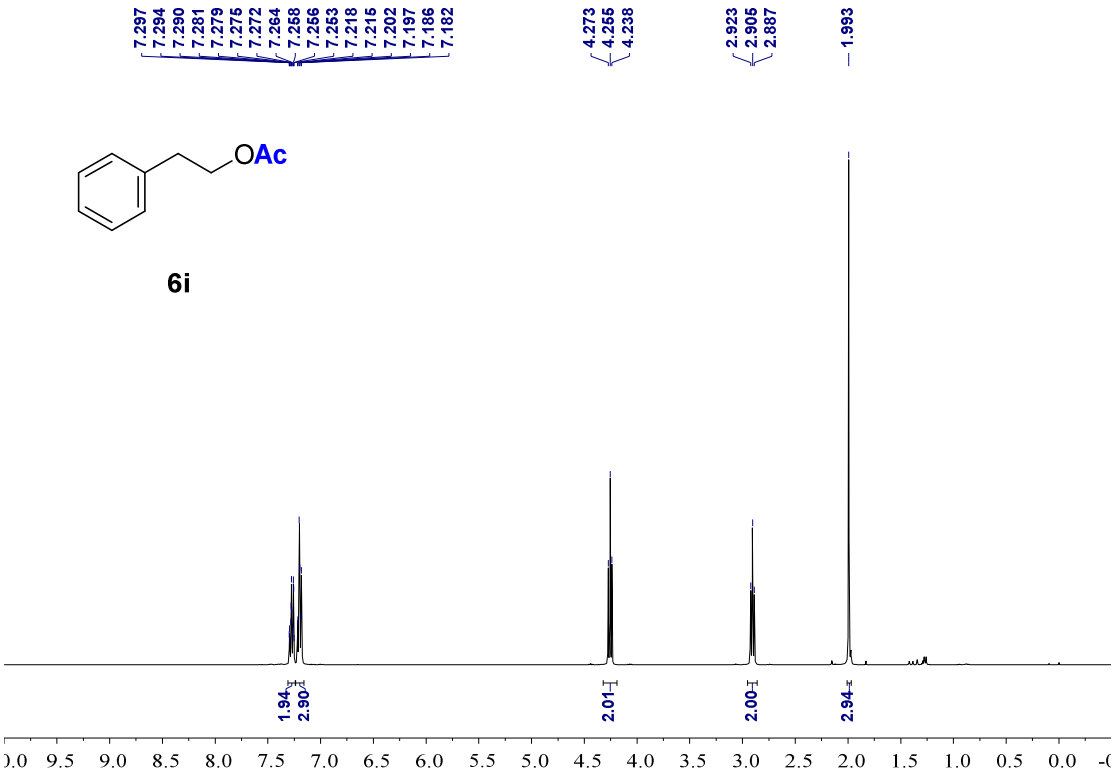
169.836
148.561
138.020
137.406
126.420
121.599
118.764
50.442
47.949
44.162
38.001
35.867
31.564
29.409
26.348
25.754
21.600
21.143
13.841
OAc
H
H
H
O
6g
f1 (ppm)

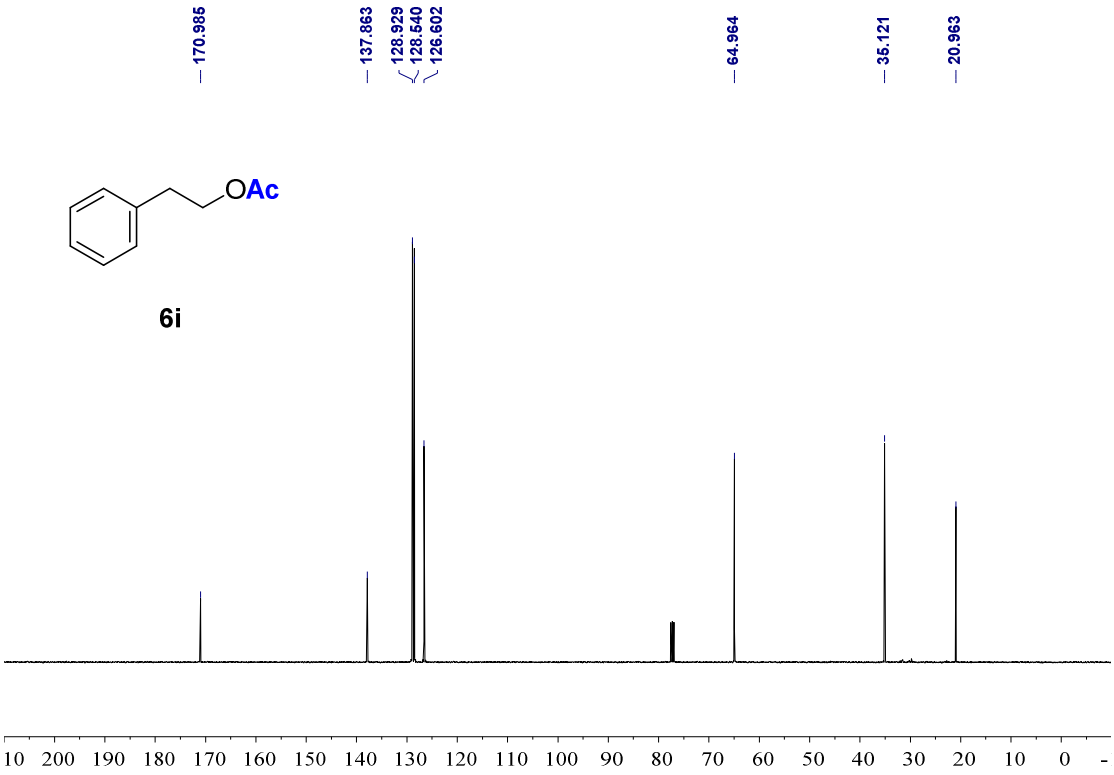

6.662
6.659
6.656
6.623
6.619
6.616
6.310
6.294
6.278
6.270
6.254
6.238
4.725
4.721
4.709
4.705
2.085
OAc
1.97
1.99
1.00
0.98
0.98
1.97
2.95
f1 (ppm)

6h


170.813
136.216
134.203
128.616
128.082
126.622
123.188
65.078
20.992
OAc
f1 (ppm)

6h


7.297
7.294
7.290
7.281
7.279
7.275
7.272
7.264
7.258
7.256
7.253
7.218
7.215
7.202
7.197
7.186
7.182
4.273
4.255
4.238
2.923
2.905
2.887
1.993
OAc
6i
1.94
2.90
2.01
2.00
2.94


170.985
137.863
128.929
128.540
126.602
64.964
35.121
20.963
OAc
6i


5.741
5.725
5.715
5.698
5.682
5.671
5.656
5.175
5.161
5.144
5.130
5.092
5.066
1.986
1.608
1.595
1.589
1.586
1.575
1.571
1.569
1.562
1.558
1.552
1.543
1.537
1.534
1.520
1.505
1.499
1.492
1.487
1.483
1.471
1.465
1.283
1.274
1.268
1.254
1.246
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1.220
1.215
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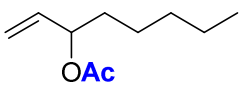
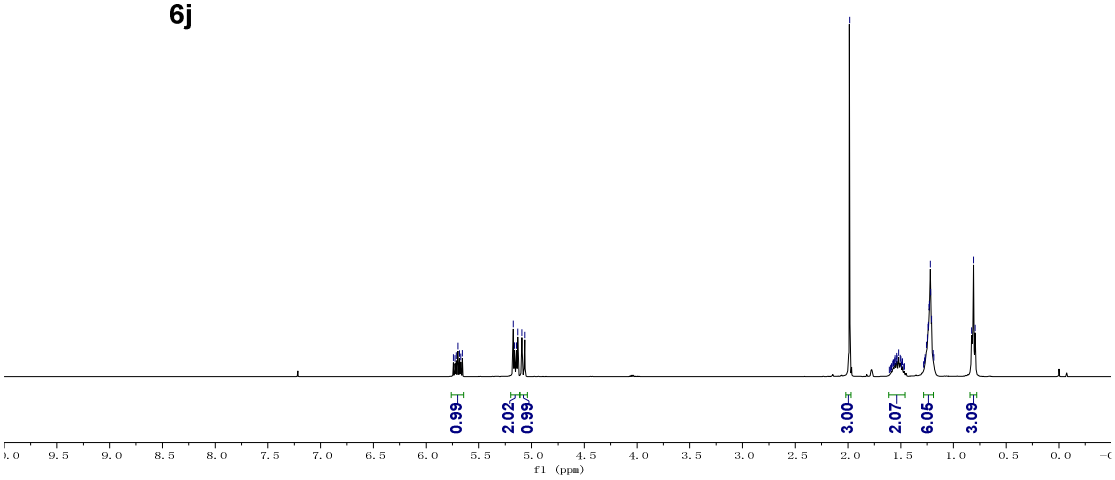
0.794


OAc

6j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0.99
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2.07
6.05
3.09
f1 (ppm)


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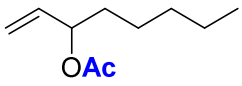
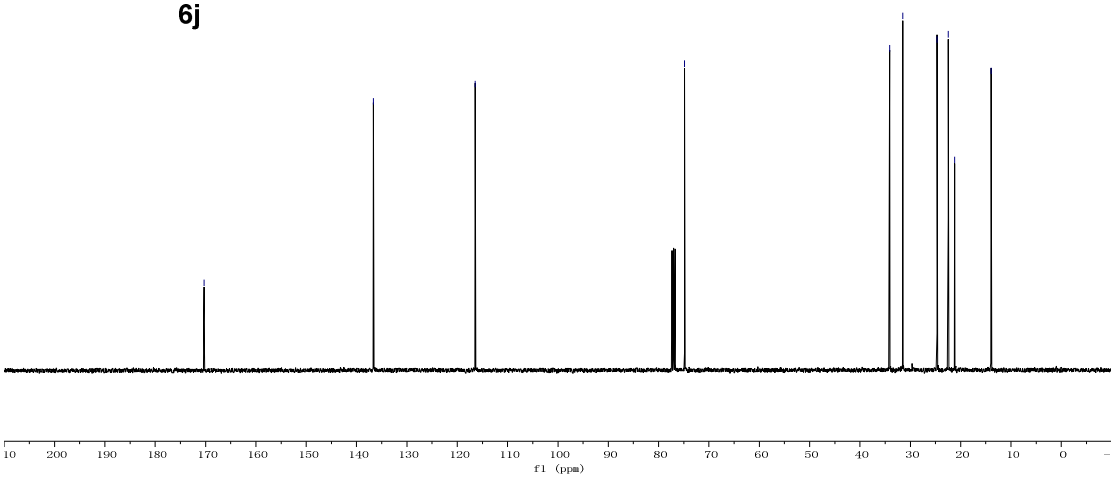
136.631
116.434
74.829
34.117
31.520
24.690
22.479
21.189
13.936


OAc

6j


f1 (ppm)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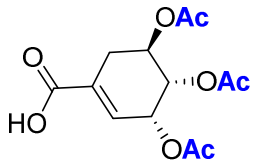
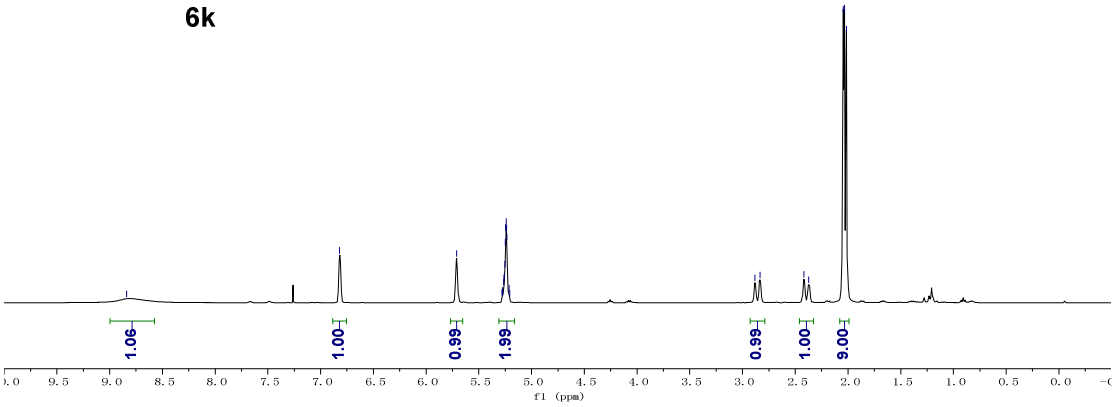
6.821
5.710
5.280
5.277
5.272
5.265
5.260
5.258
5.253
5.248
5.246
5.240
5.237
5.234
5.214
5.208
2.881
2.834
2.418
2.371
2.045
2.034
2.016


OAc
O
OAc
HO
OAc

6k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1.00
0.99
1.99
0.99
1.00
9.00
f1 (ppm)


176.999
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170.066
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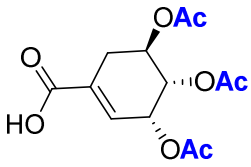
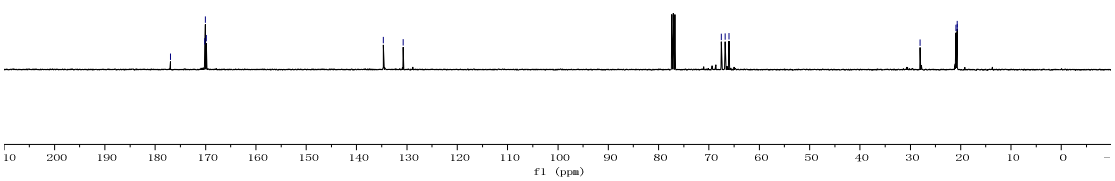
134.655
130.748
67.542
66.770
66.026
28.071
20.952
20.715
20.697


OAc
O
OAc
HO
OAc

6k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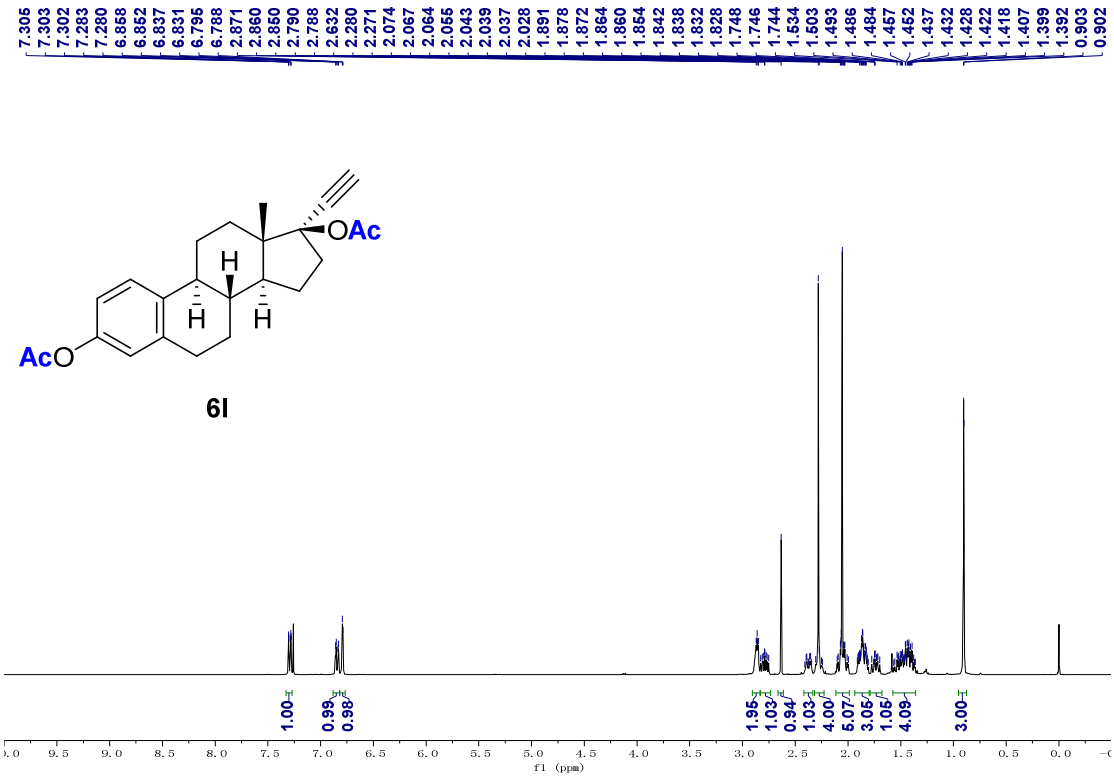
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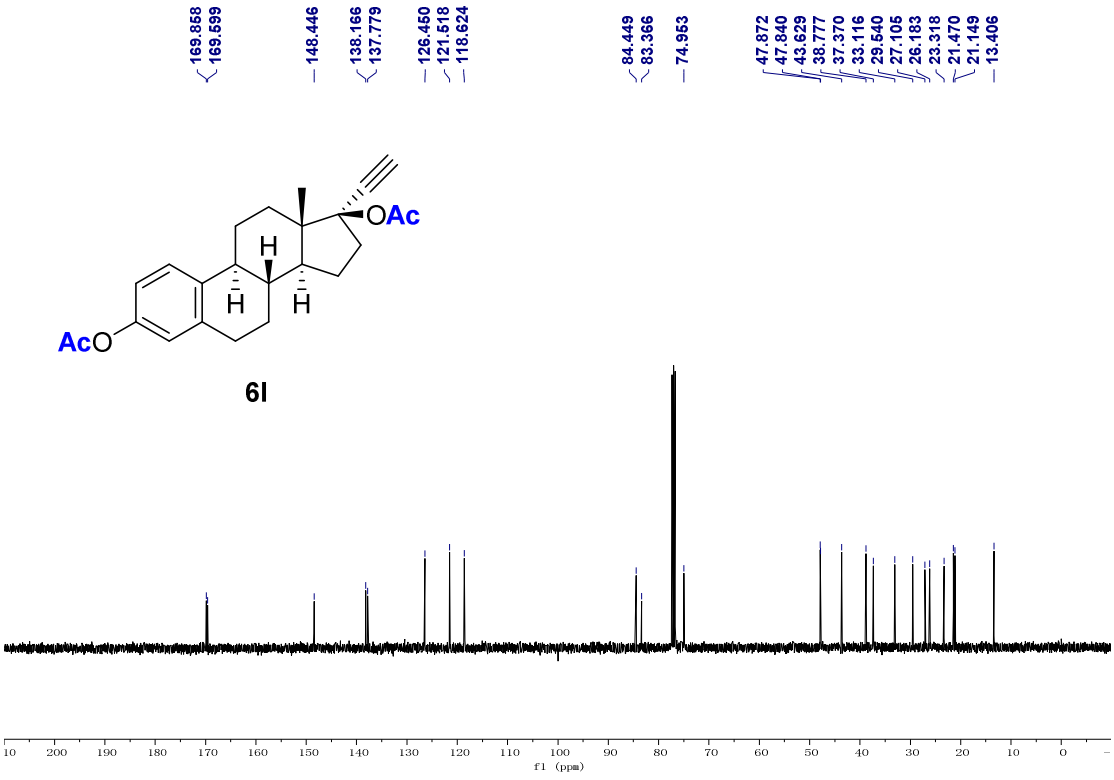
7.303
7.302
7.283
7.280
6.868
6.852
6.837
6.831
6.795
6.788
2.871
2.860
2.850
2.790
2.788
2.632
2.280
2.271
2.074
2.067
2.064
2.055
2.043
2.039
2.037
2.028
1.891
1.878
1.872
1.864
1.860
1.854
1.842
1.838
1.832
1.828
1.748
1.746
1.744
1.534
1.503
1.493
1.486
1.484
1.457
1.452
1.437
1.432
1.428
1.422
1.418
1.407
1.399
1.392
0.903
0.902
OAc
AcO
H
H
H
6l
1.00
0.99
0.98
1.95
1.03
0.94
1.03
4.00
5.07
3.05
1.05
4.09
3.00
f1 (ppm)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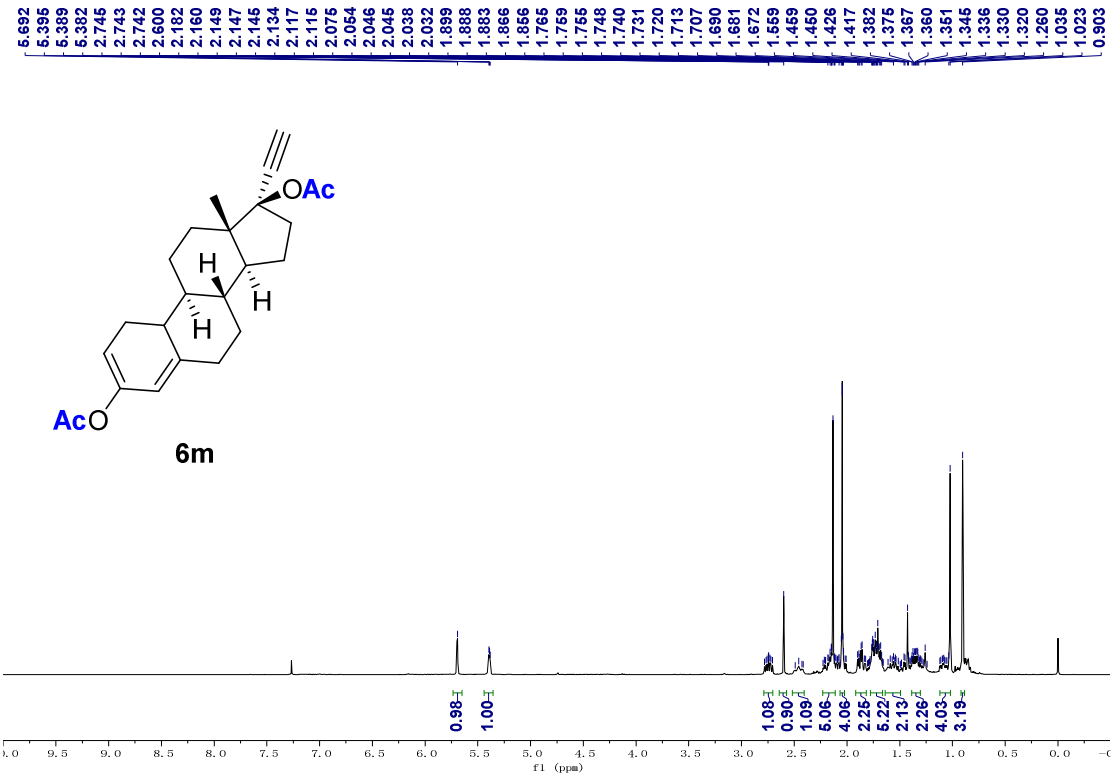
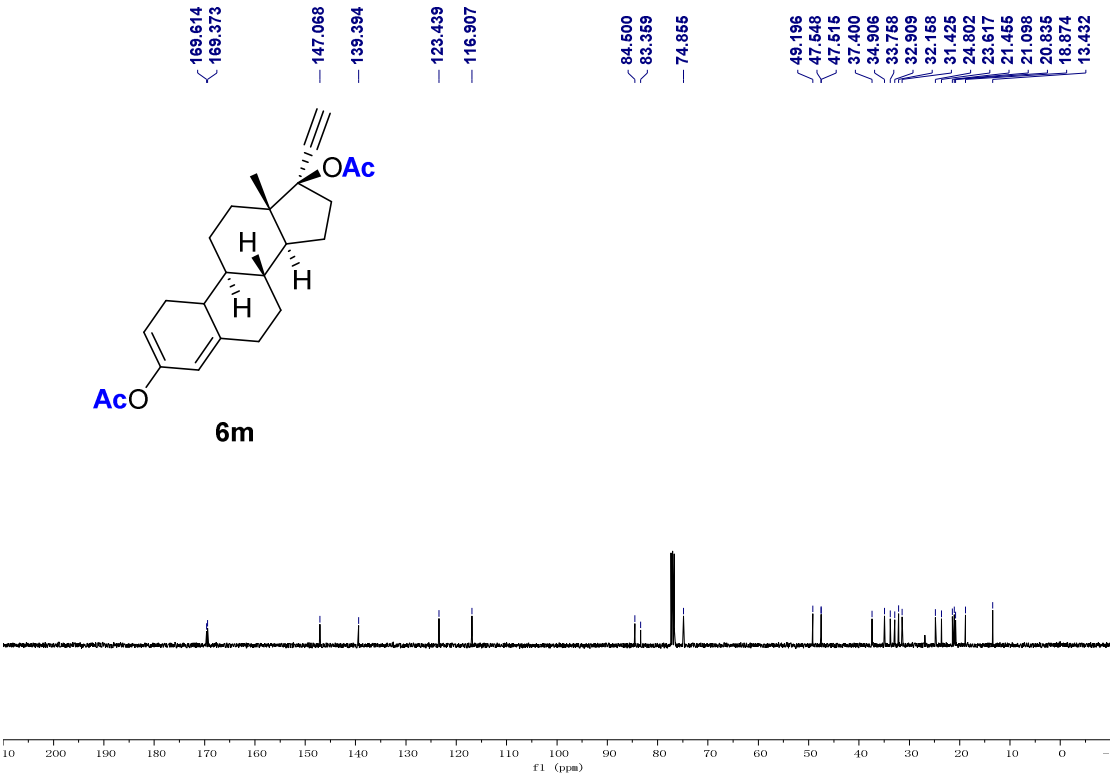
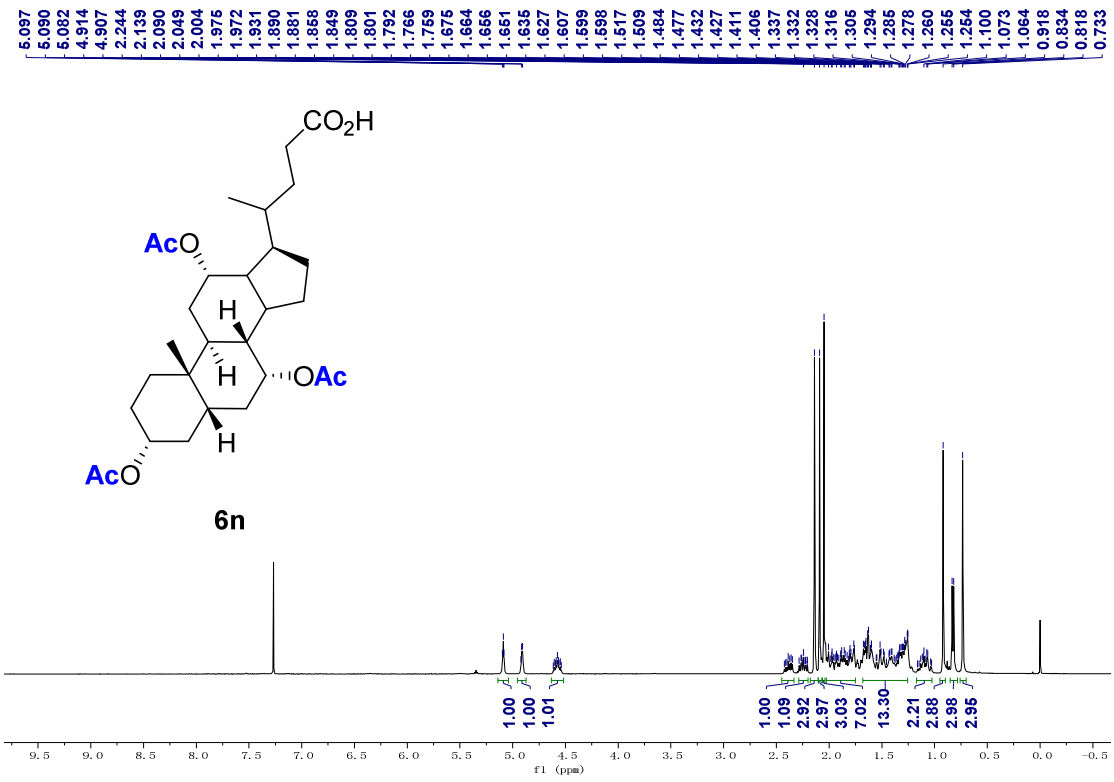
169.599
148.446
138.166
137.779
126.450
121.518
118.624
84.449
83.366
74.953
47.872
47.840
43.629
38.777
37.370
33.116
29.540
27.105
26.183
23.318
21.470
21.149
13.406
OAc
AcO
H
H
H
6l
f1 (ppm)


5.692
5.395
5.389
5.382
2.745
2.743
2.742
2.600
2.182
2.160
2.149
2.147
2.145
2.134
2.117
2.116
2.075
2.054
2.046
2.045
2.038
2.032
1.899
1.888
1.883
1.866
1.856
1.765
1.759
1.755
1.748
1.740
1.731
1.720
1.713
1.707
1.690
1.681
1.672
1.559
1.459
1.450
1.426
1.417
1.382
1.375
1.367
1.360
1.351
1.345
1.336
1.330
1.320
1.260
1.035
1.023
0.903
OAc
AcO
H
H
H
6m
0.98
1.00
1.08
0.90
1.09
5.06
4.06
2.25
5.22
2.13
2.26
4.03
3.19
f1 (ppm)


169.614
169.373
147.068
139.394
123.439
116.907
84.500
83.359
74.855
49.196
47.548
47.615
37.400
34.906
33.758
32.909
32.158
31.425
24.802
23.617
21.455
21.098
20.835
18.874
13.432
OAc
AcO
H
H
H
6m
f1 (ppm)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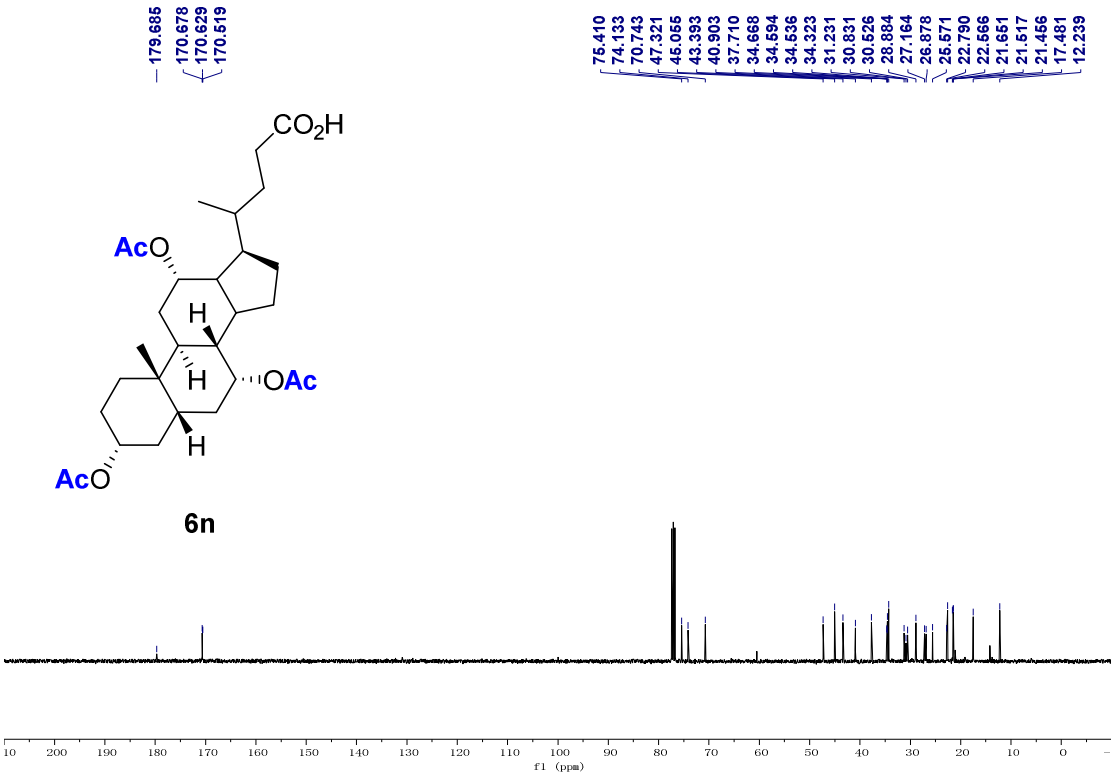
5.090
5.082
4.914
4.907
2.244
2.139
2.090
2.049
2.004
1.975
1.972
1.931
1.890
1.881
1.868
1.849
1.809
1.801
1.792
1.766
1.759
1.675
1.664
1.656
1.651
1.635
1.627
1.607
1.599
1.598
1.517
1.509
1.484
1.477
1.432
1.427
1.411
1.406
1.337
1.332
1.328
1.316
1.306
1.294
1.285
1.278
1.260
1.255
1.254
1.100
1.073
1.064
0.918
0.834
0.818
0.733
CO2H
AcO
H
H
OAc
H
AcO
6n
1.00
1.00
1.01
1.00
1.09
2.92
2.97
3.03
7.02
13.30
2.21
2.88
2.98
2.95
f1 (ppm)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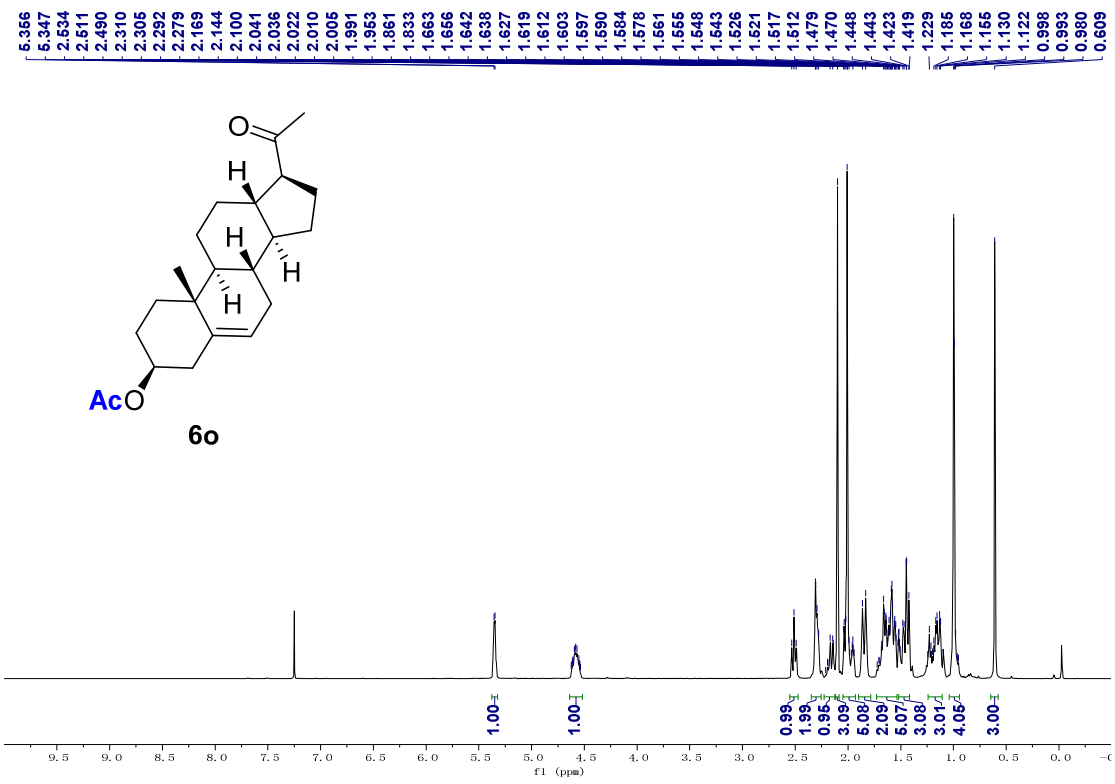
170.629
170.519
75.410
74.133
70.743
47.321
46.065
43.393
40.903
37.710
34.668
34.594
34.536
34.323
31.231
30.831
30.526
28.884
27.164
26.878
25.571
22.790
22.666
21.651
21.617
21.456
17.481
12.239
CO2H
AcO
H
H
OAc
H
AcO
6n
f1 (ppm)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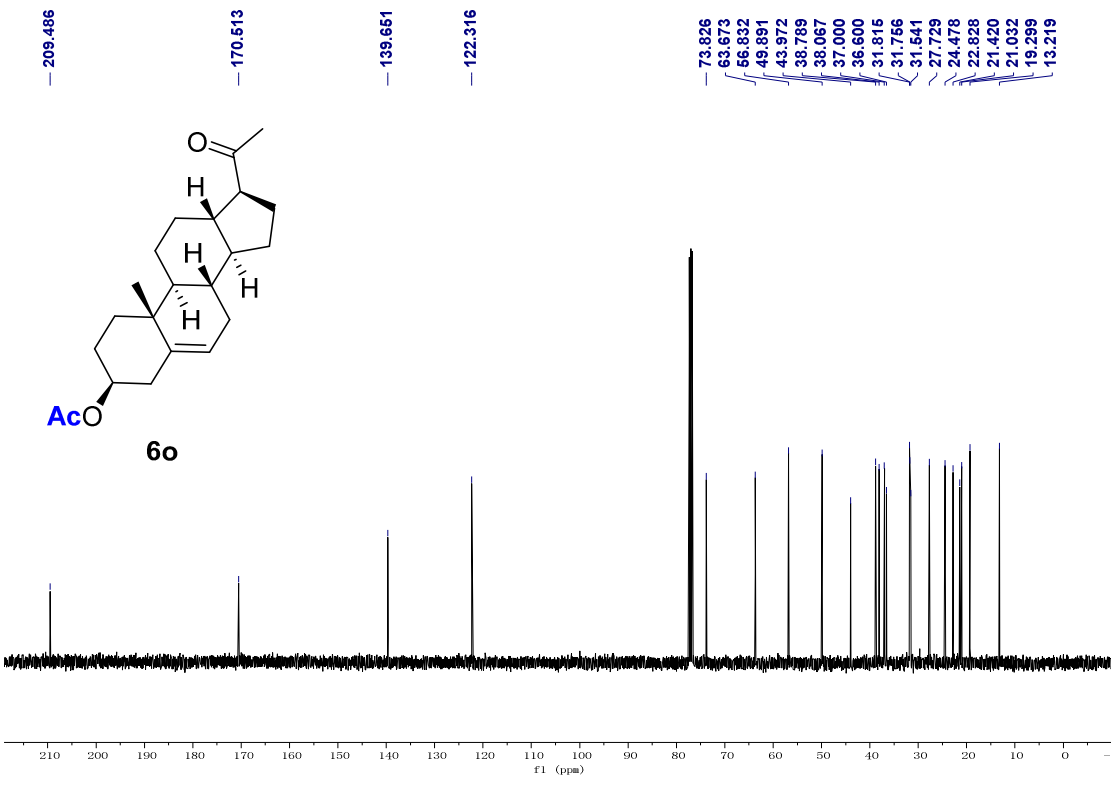
2.534
2.511
2.490
2.310
2.305
2.292
2.279
2.169
2.144
2.100
2.041
2.036
2.022
2.010
2.005
1.991
1.963
1.861
1.833
1.663
1.656
1.642
1.638
1.627
1.619
1.612
1.603
1.597
1.590
1.584
1.578
1.561
1.555
1.548
1.543
1.526
1.521
1.517
1.512
1.479
1.470
1.448
1.443
1.423
1.419
1.229
1.185
1.168
1.155
1.130
1.122
0.998
0.993
0.980
0.609
O
H
H
H
H
AcO
6o
1.00
1.00
0.99
1.99
0.95
3.09
5.08
2.09
5.07
3.08
3.01
4.06
3.00
f1 (ppm)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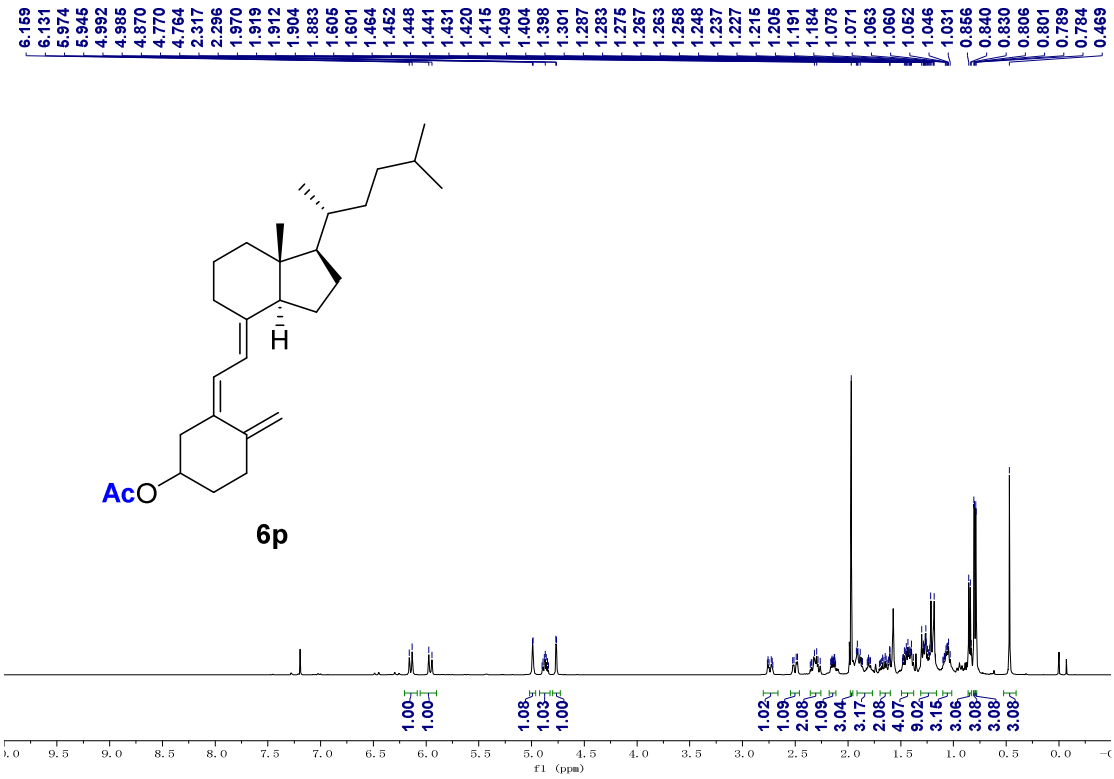
139.651
122.316
73.826
63.673
56.832
49.891
43.972
38.789
38.067
37.000
36.600
31.815
31.756
31.541
27.729
24.478
22.828
21.420
21.032
19.299
13.219
O
H
H
H
H
AcO
6o
f1 (ppm)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6.131
5.974
5.945
4.992
4.986
4.870
4.770
4.764
2.317
2.296
1.970
1.919
1.912
1.904
1.883
1.605
1.601
1.464
1.452
1.448
1.441
1.431
1.420
1.415
1.409
1.404
1.398
1.301
1.287
1.283
1.275
1.267
1.263
1.258
1.248
1.237
1.227
1.215
1.205
1.191
1.184
1.078
1.071
1.063
1.060
1.052
1.046
1.031
0.856
0.840
0.830
0.806
0.801
0.789
0.784
0.469
AcO
H
6p
1.00
1.00
1.08
1.03
1.00
1.02
1.09
2.08
1.09
3.04
3.17
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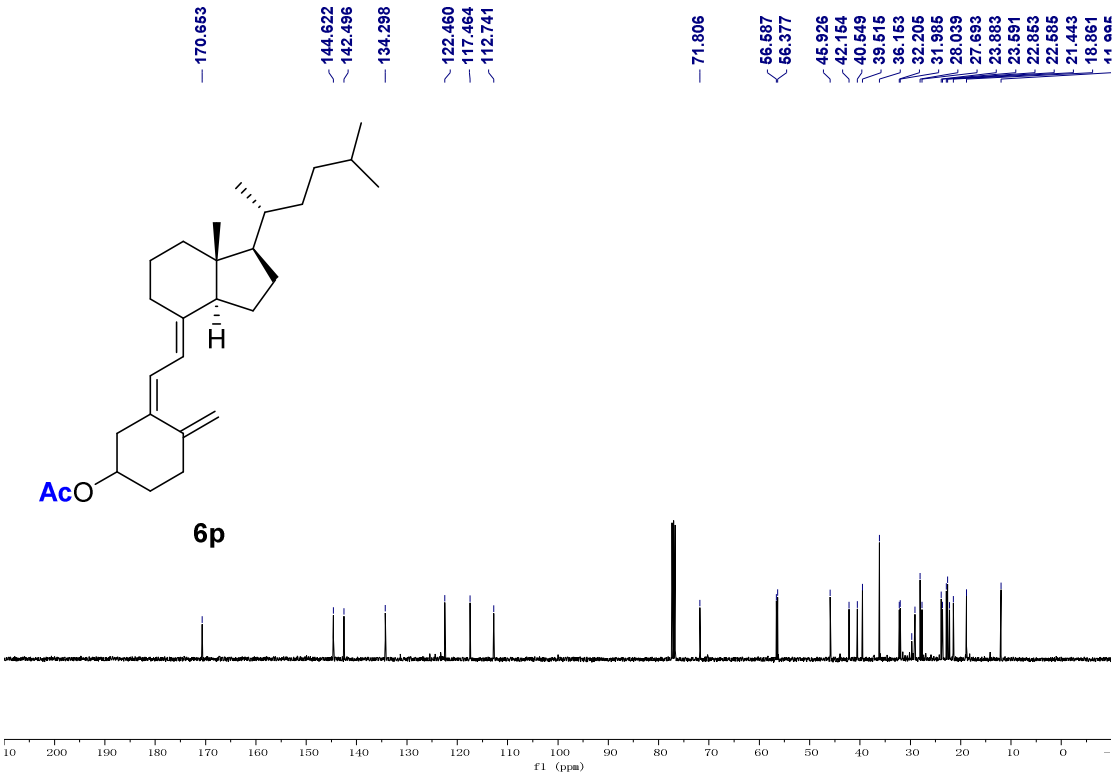
3.06
3.08
3.08
3.08
f1 (ppm)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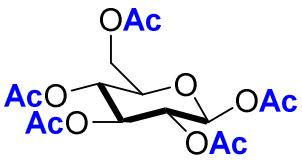
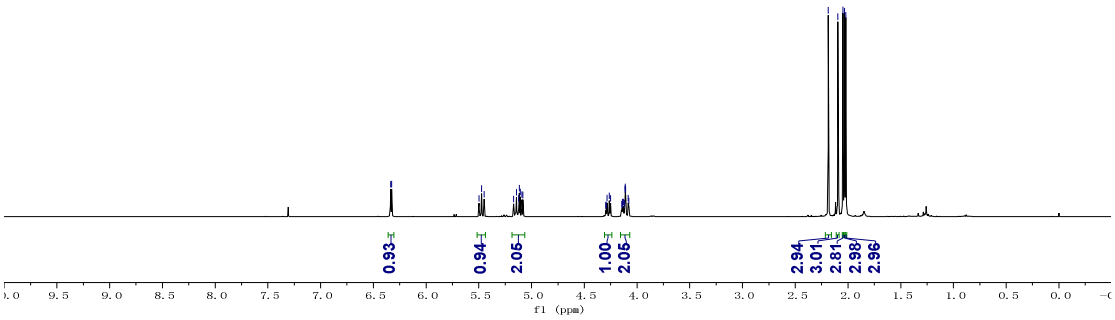
142.496
134.298
122.460
117.464
112.741
71.806
56.587
56.377
45.926
42.154
40.549
39.515
36.153
32.205
31.985
28.039
27.693
23.883
23.591
22.853
22.585
21.443
18.861
AcO
H
6p
f1 (ppm)

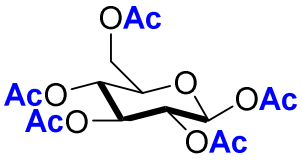

6.335
6.326
5.499
5.474
5.460
5.170
5.144
5.120
5.117
5.108
5.091
5.082
4.296
4.293
4.284
4.263
4.252
4.146
4.140
4.136
4.130
4.120
4.114
4.111
4.108
4.084
4.078
2.186
2.095
2.047
2.032
2.021


OAc
AcO
AcO
O
OAc
OAc

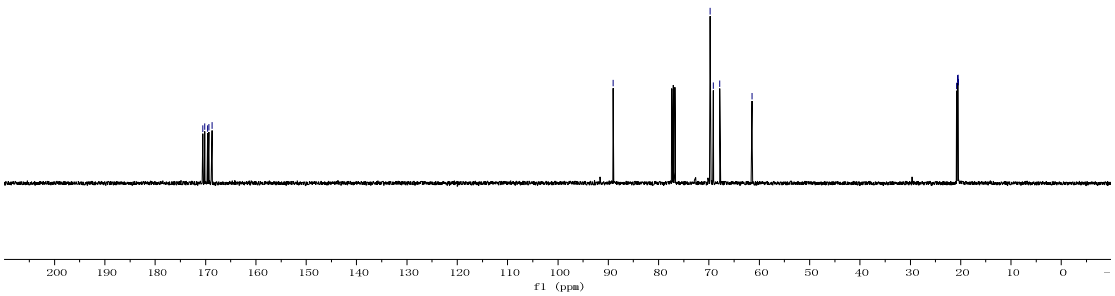
6q

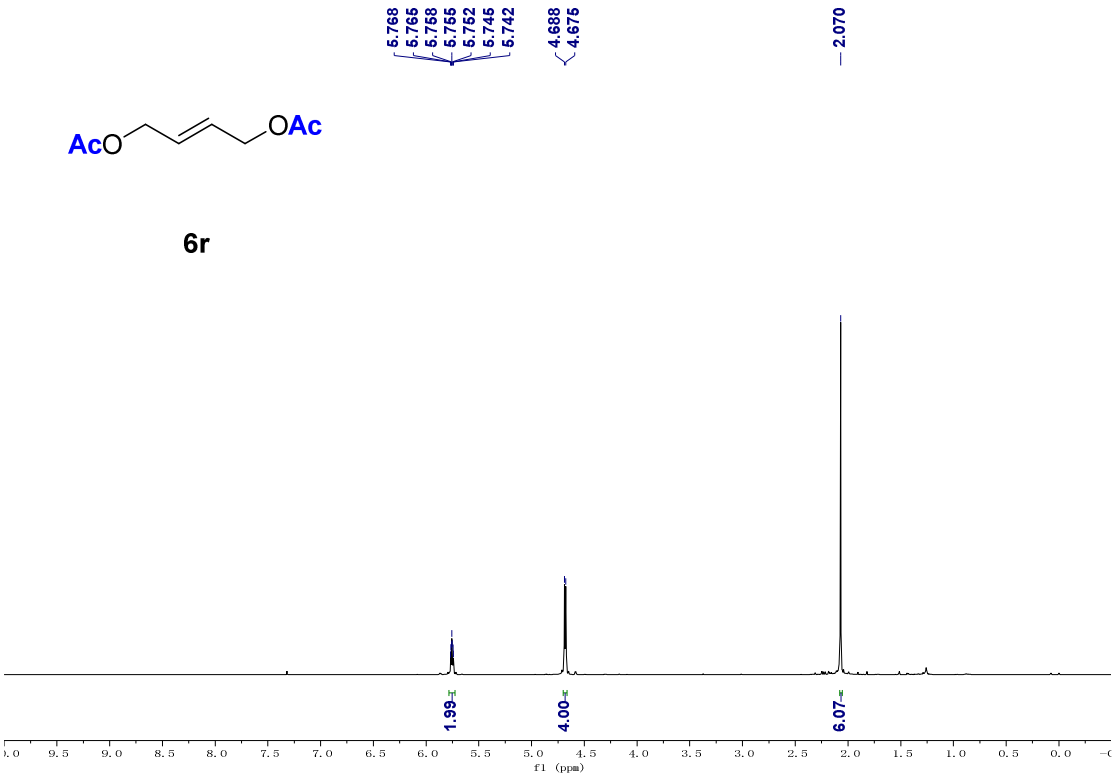

0.93
0.94
2.05
1.00
2.05
2.94
3.01
2.81
2.98
2.96
f1 (ppm)


170.566
170.165
169.610
169.351
168.709
89.015
69.780
69.153
67.846
61.418
20.832
20.650
20.617
20.524
20.403

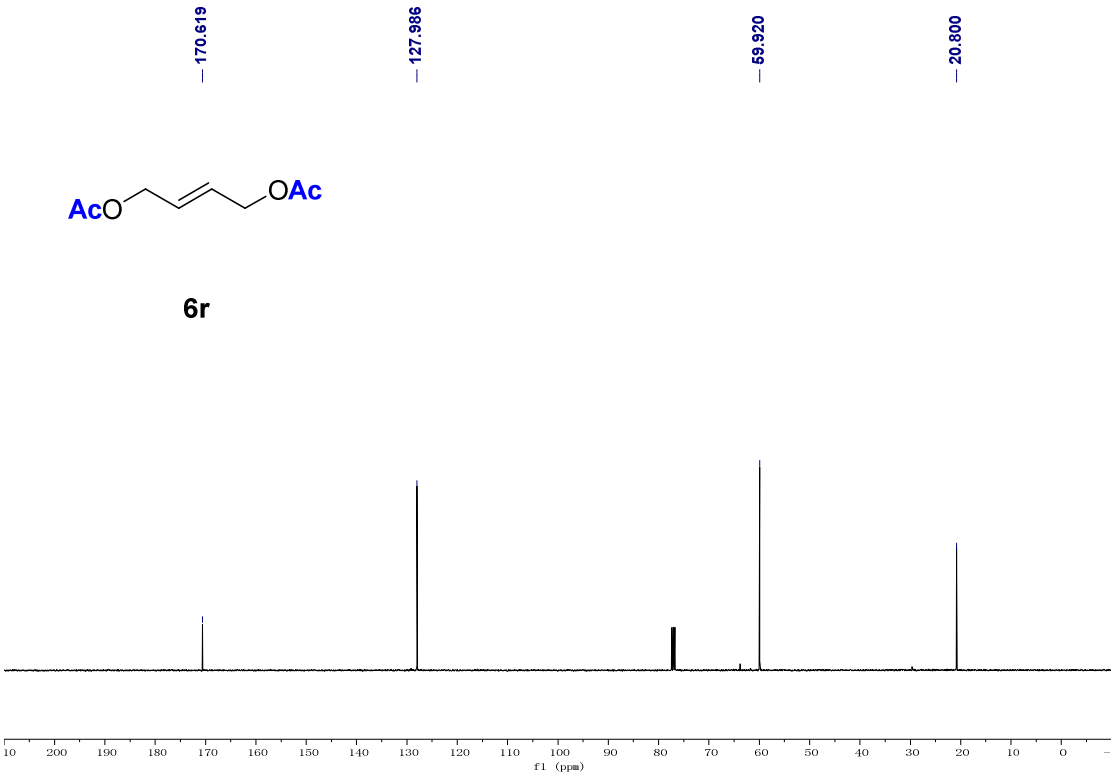

OAc
AcO
AcO
O
OAc
OAc

6q

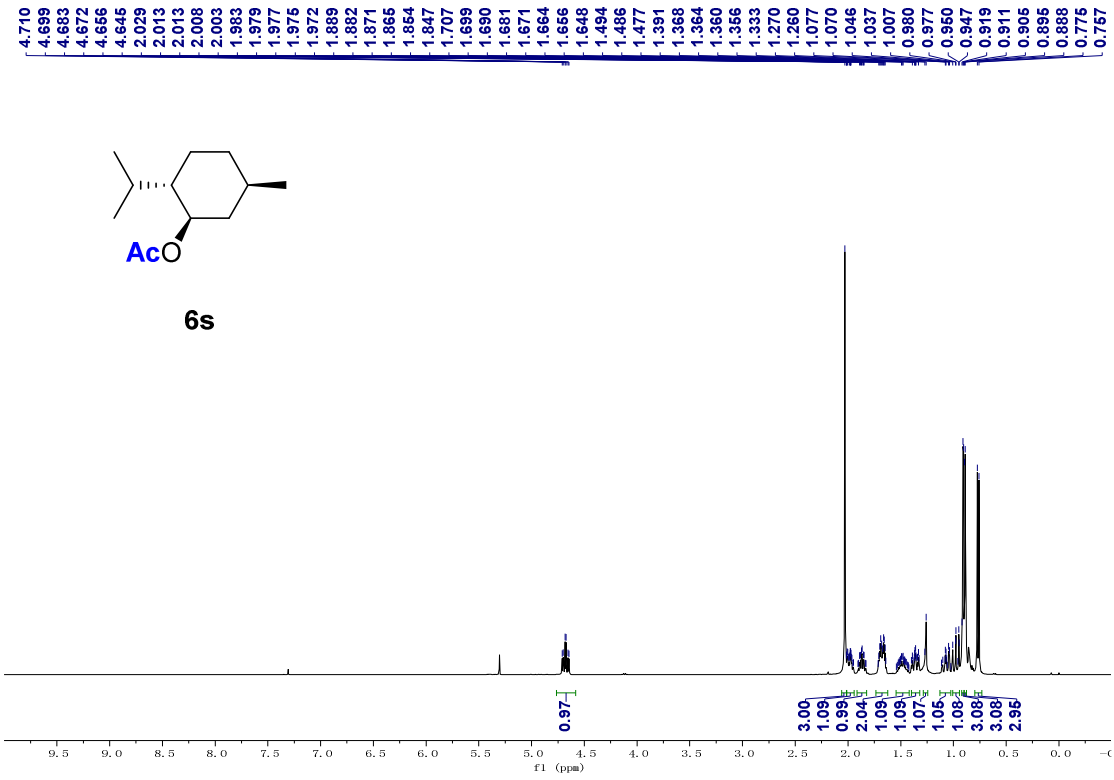

f1 (ppm)

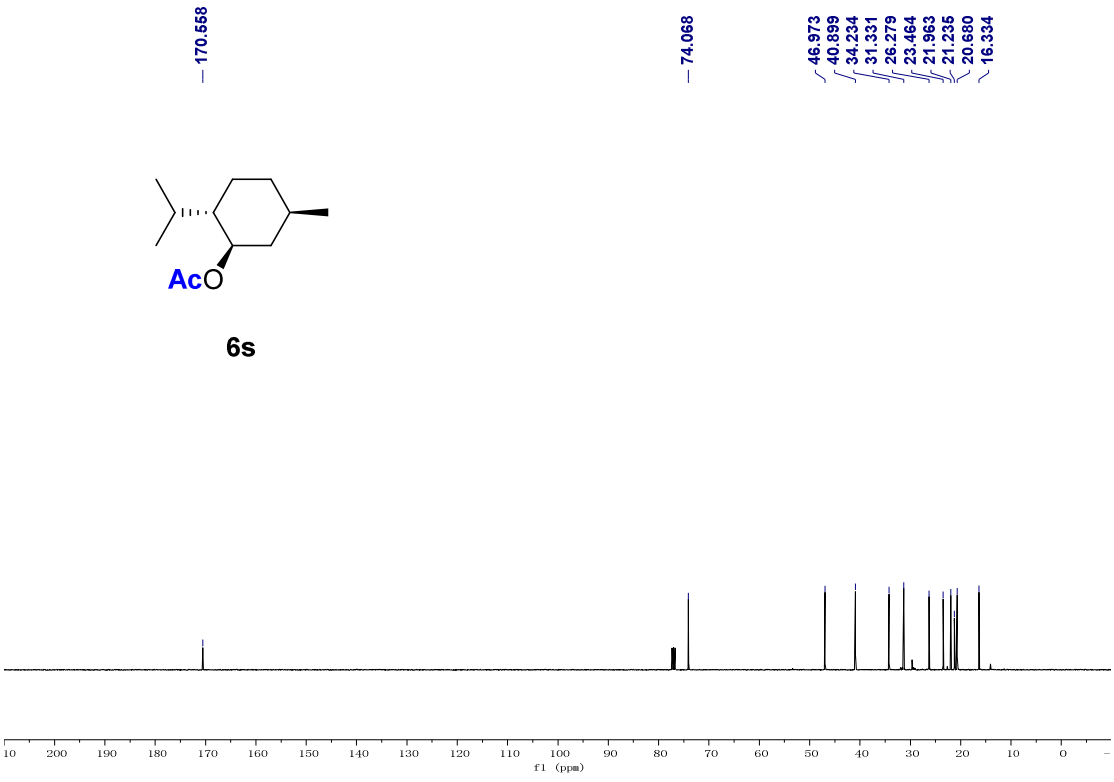

5.768
5.765
5.758
5.755
5.752
5.745
5.742
4.688
4.675
2.070
AcO
OAc
1.99
4.00
6.07
f1 (ppm)

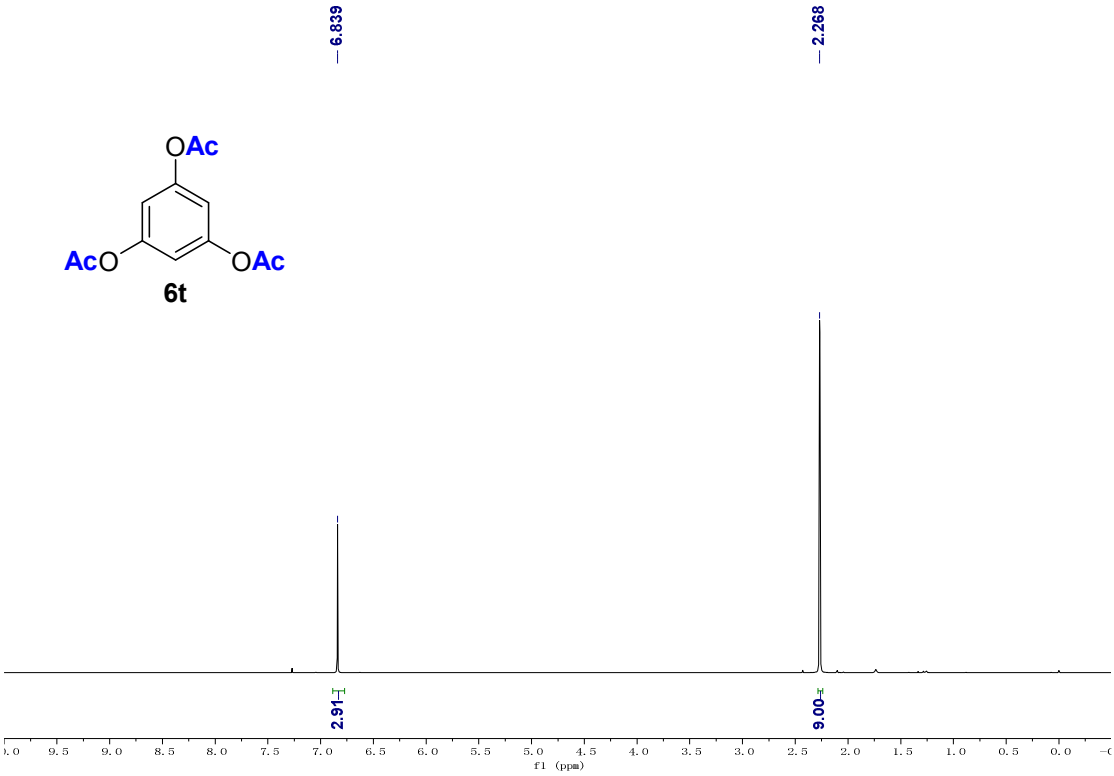
6r

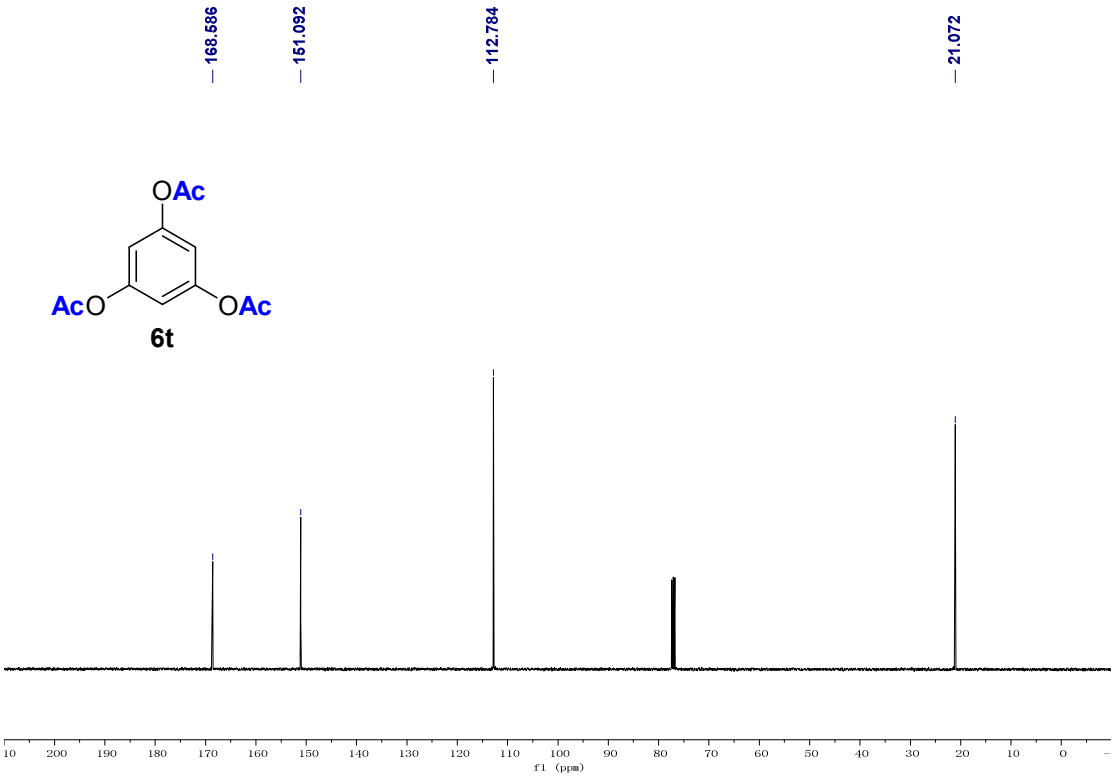

170.619
127.986
59.920
20.800
AcO
OAc
f1 (ppm)

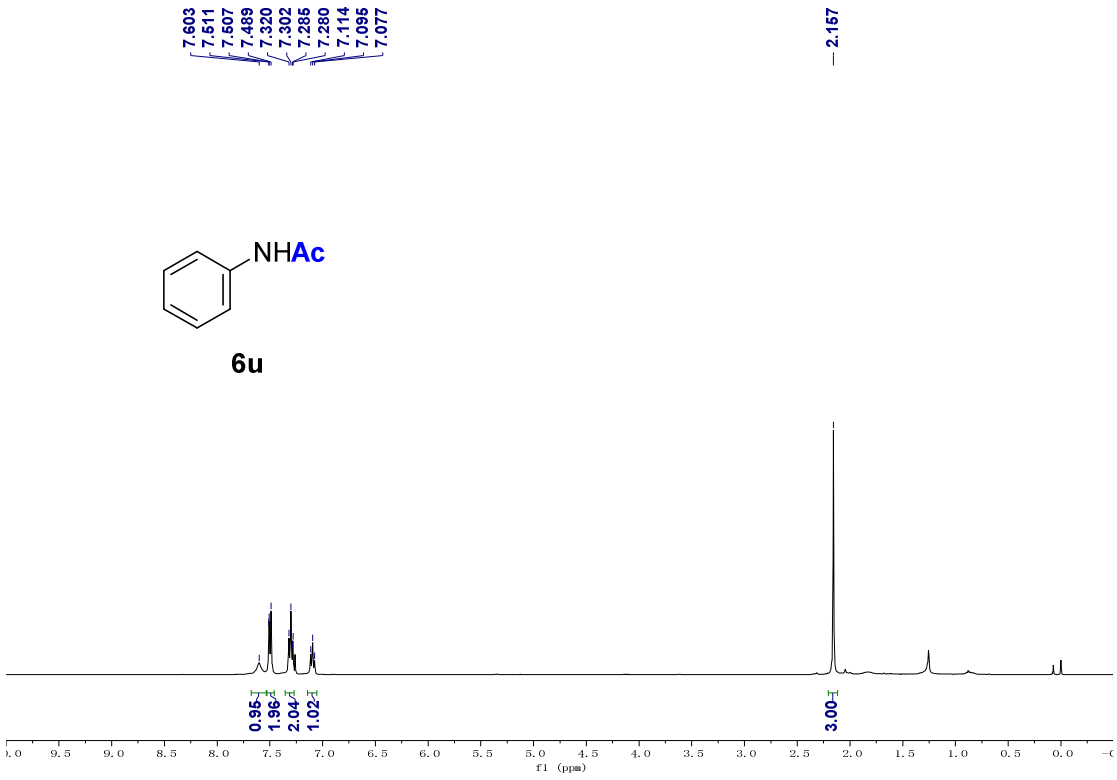
6r

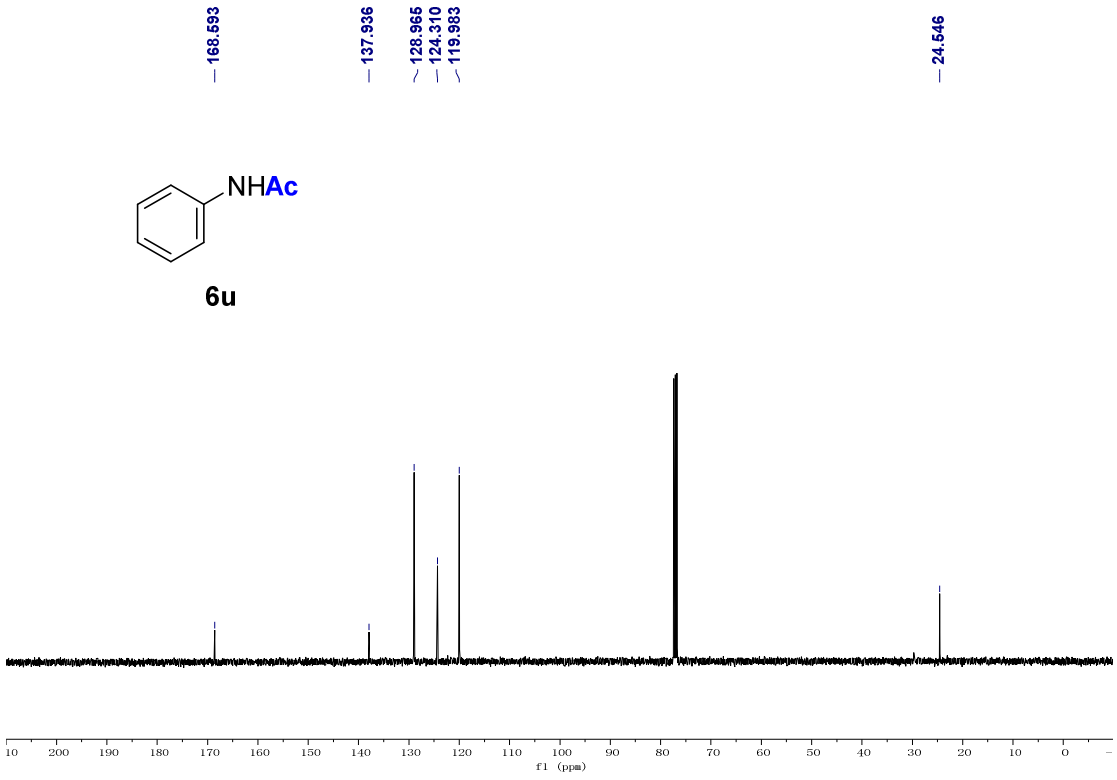

4.710 4.699 4.683 4.672 4.656 4.645 2.029 2.013 2.013 2.008 2.003 1.983 1.979 1.977 1.975 1.972 1.889 1.882 1.871 1.865 1.854 1.847 1.707 1.699 1.690 1.681 1.671 1.664 1.656 1.648 1.494 1.486 1.477 1.391 1.368 1.364 1.360 1.356 1.333 1.270 1.260 1.077 1.070 1.046 1.037 1.007 0.980 0.977 0.960 0.947 0.919 0.911 0.905 0.895 0.888 0.775 0.767
AcO
6s
0.97 3.00 1.09 0.99 2.04 1.09 1.09 1.07 1.05 1.08 3.08 3.08 2.96
f1 (ppm)


170.568 74.068 46.973 40.899 34.234 31.331 26.279 23.464 21.963 21.235 20.680 16.334
AcO
6s
f1 (ppm)


6.839
2.268
OAc
AcO
OAc
6t
2.91
9.00
f1 (ppm)


168.586
151.092
112.784
21.072
OAc
AcO
OAc
6t
f1 (ppm)


7.603
7.611
7.507
7.489
7.320
7.302
7.285
7.280
7.114
7.095
7.077
2.157
NHAc
6u
0.95
1.96
2.04
1.02
3.00
f1 (ppm)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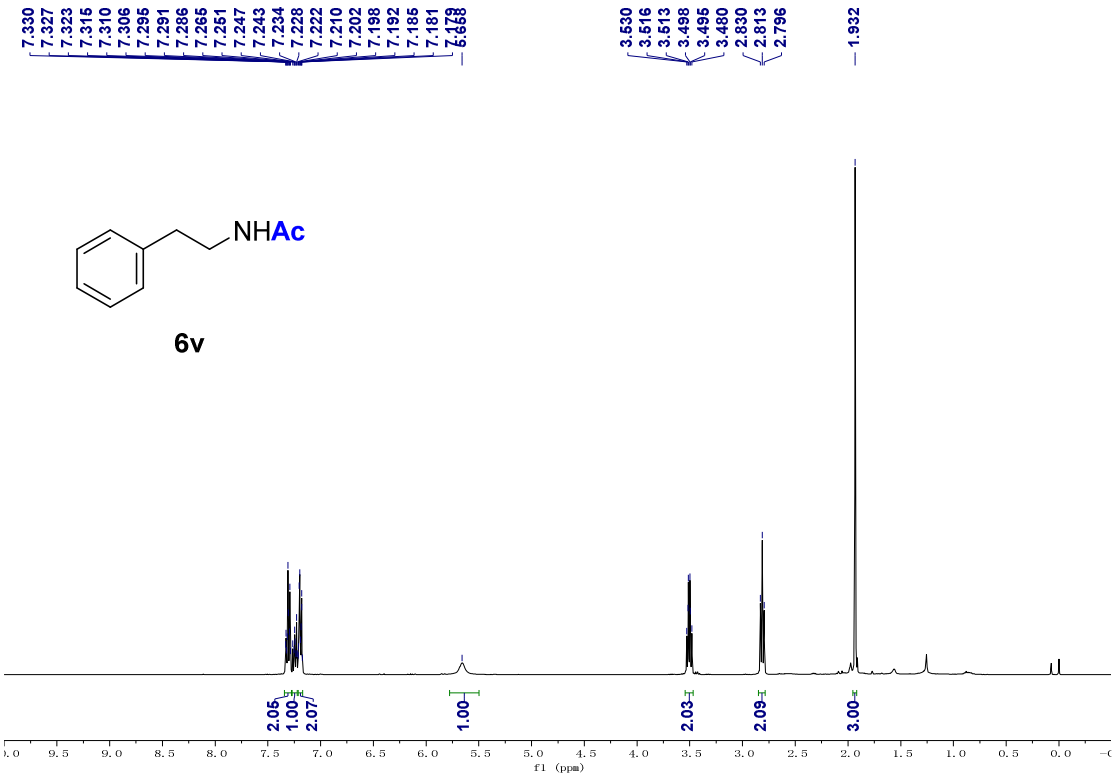
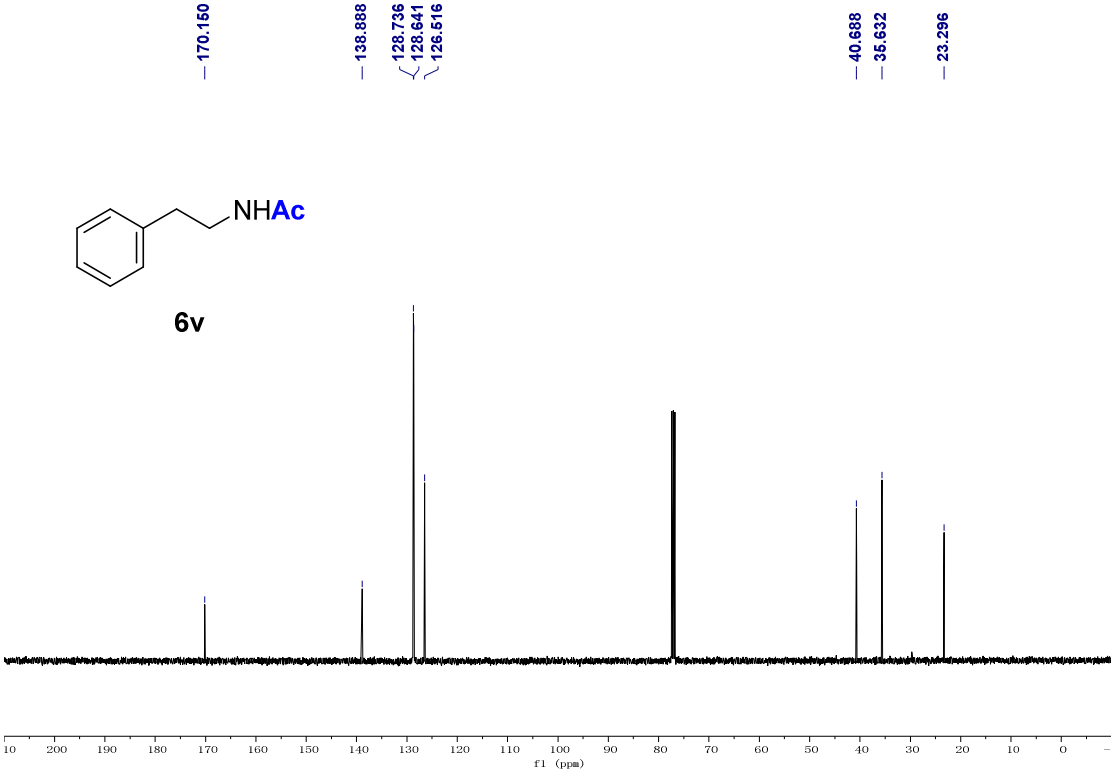
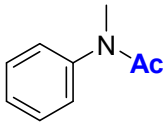
137.936
128.965
124.310
119.983
24.646
NHAc
6u
f1 (ppm)

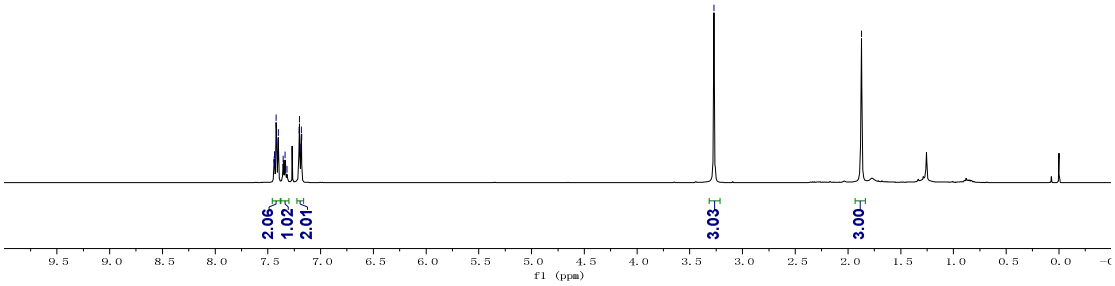

7.330
7.327
7.323
7.315
7.310
7.306
7.295
7.291
7.286
7.265
7.251
7.247
7.243
7.234
7.228
7.222
7.210
7.202
7.198
7.192
7.185
7.181
3.530
3.516
3.513
3.498
3.495
3.480
2.830
2.813
2.796
1.932
NHAc
6v
2.05
1.00
2.07
1.00
2.03
2.09
3.00
f1 (ppm)


170.150
138.888
128.736
128.641
126.516
40.688
35.632
23.296
NHAc
6v
f1 (ppm)

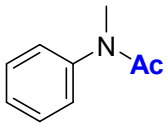

7.441
7.439
7.434
7.421
7.417
7.406
7.401
7.356
7.352
7.337
7.331
7.319
7.205
7.201
7.187
7.184
7.181
3.270
1.873


N
Ac

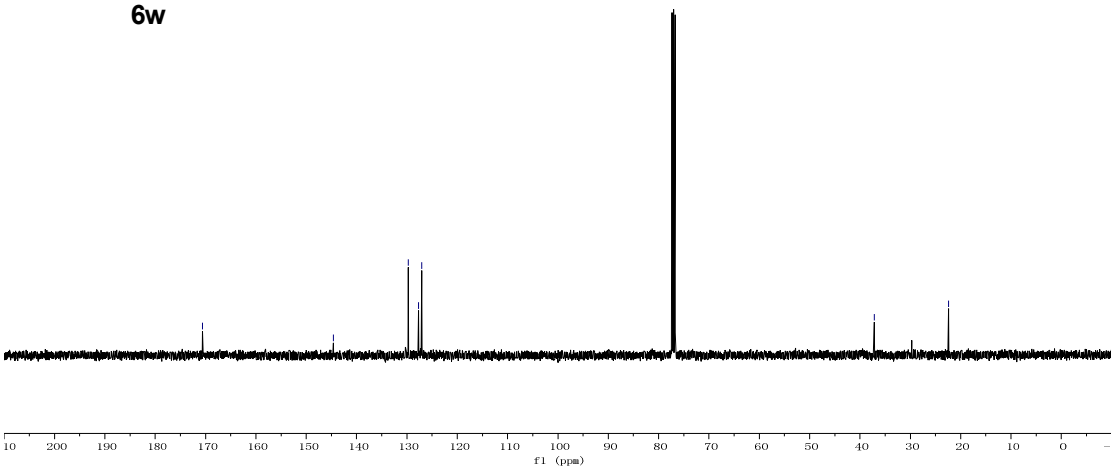
6w


2.06
1.02
2.01
3.03
3.00
f1 (ppm)


170.583
144.618
129.727
127.708
127.084
37.166
22.421

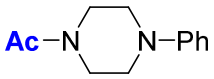

N
Ac

6w

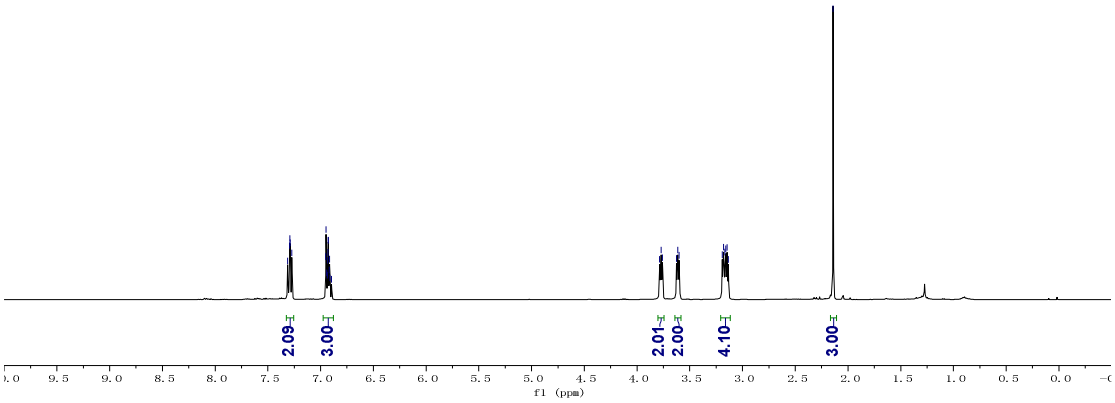

f1 (ppm)


7.312
7.294
7.290
7.289
7.272
6.951
6.948
6.942
6.937
6.934
6.932
6.929
6.926
6.918
6.915
6.912
6.897

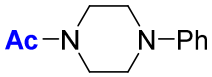

3.786
3.773
3.760
3.626
3.613
3.600
3.192
3.179
3.166
3.160
3.147
3.133
2.142


Ac
N
N
Ph

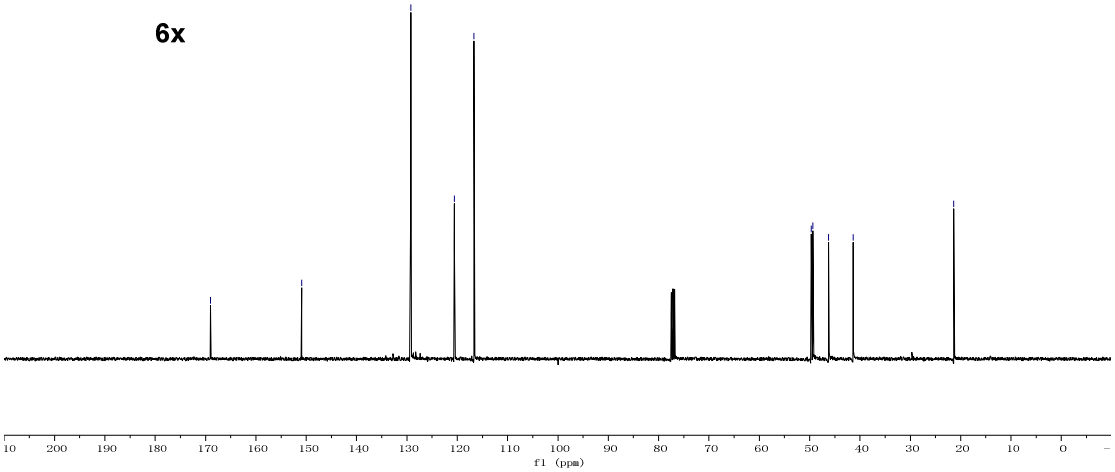
6x

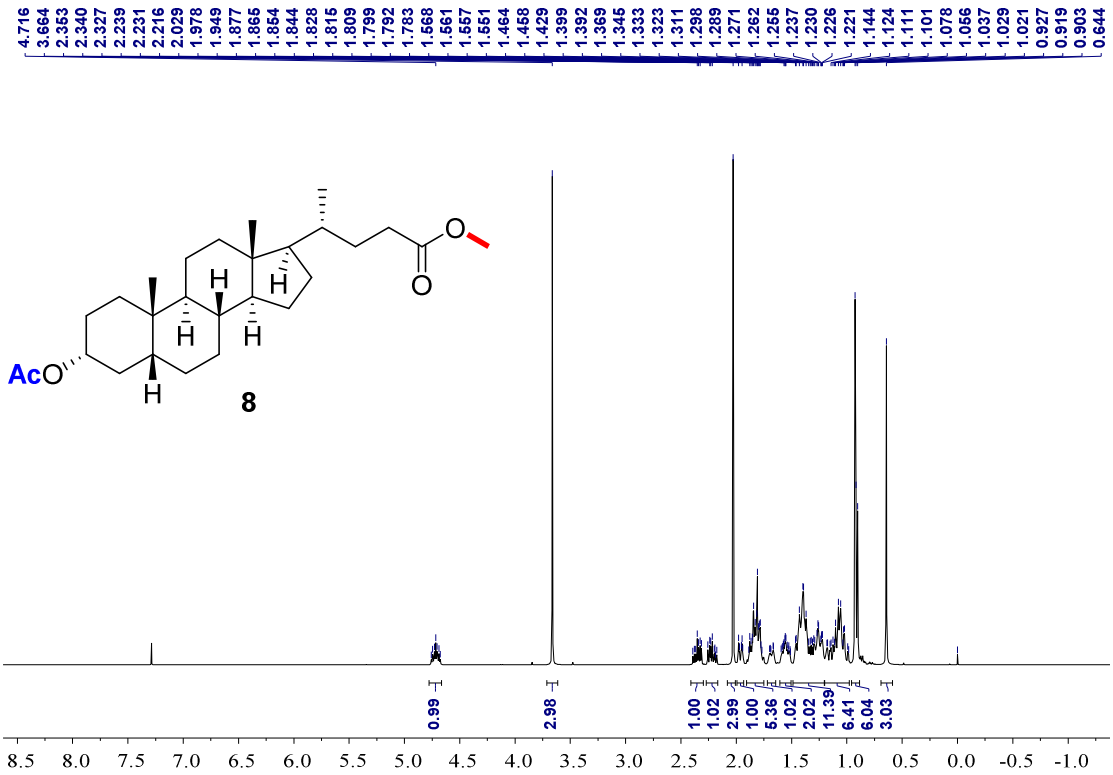

2.09
3.00
2.01
2.00
4.10
3.00
f1 (ppm)

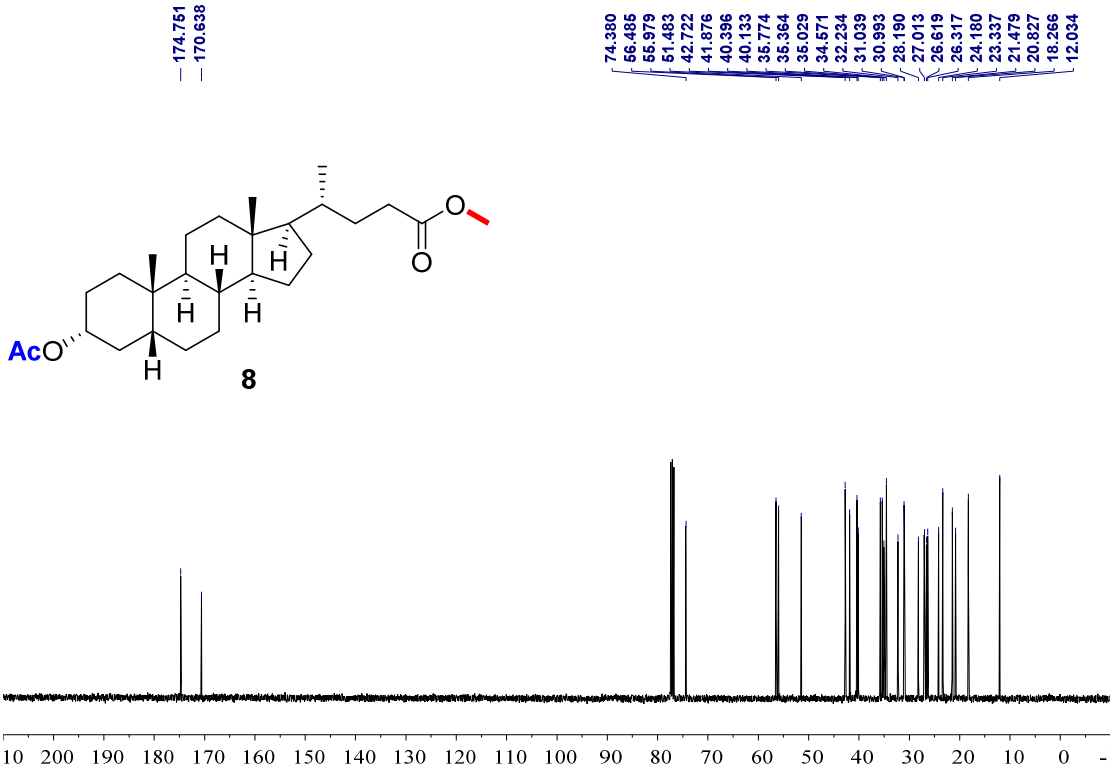

169.019
150.917
129.246
120.556
116.666
49.702
49.367
46.228
41.355
21.360

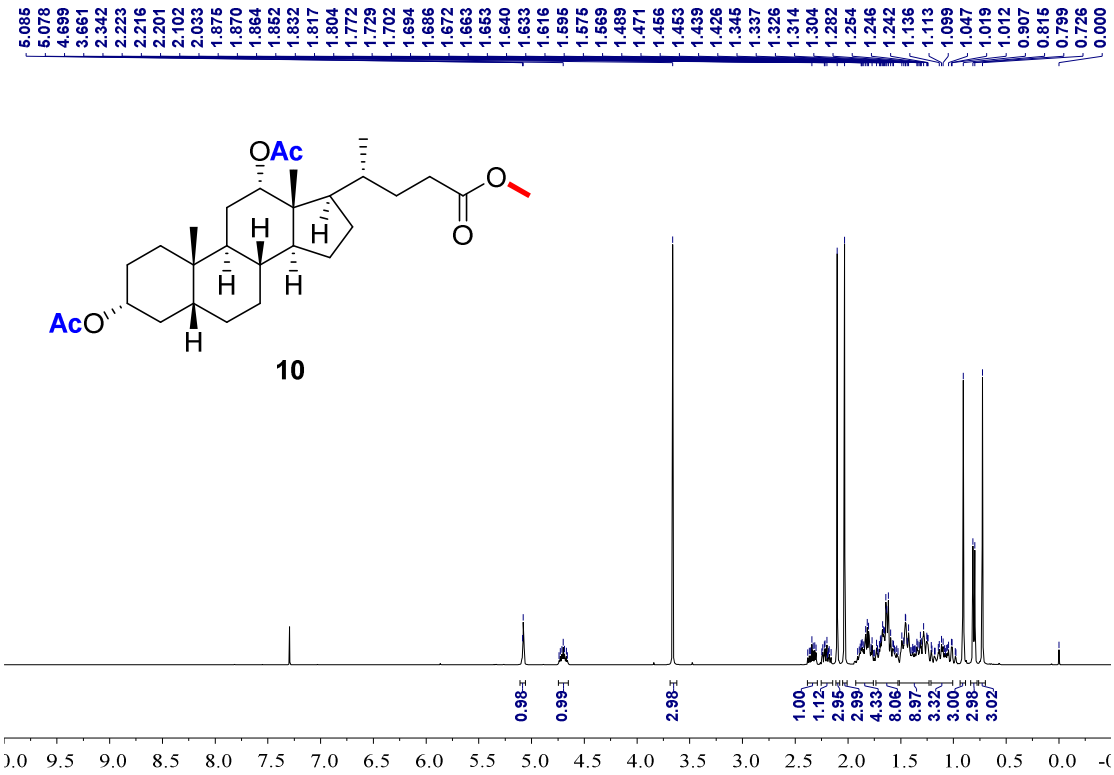

Ac
N
N
Ph

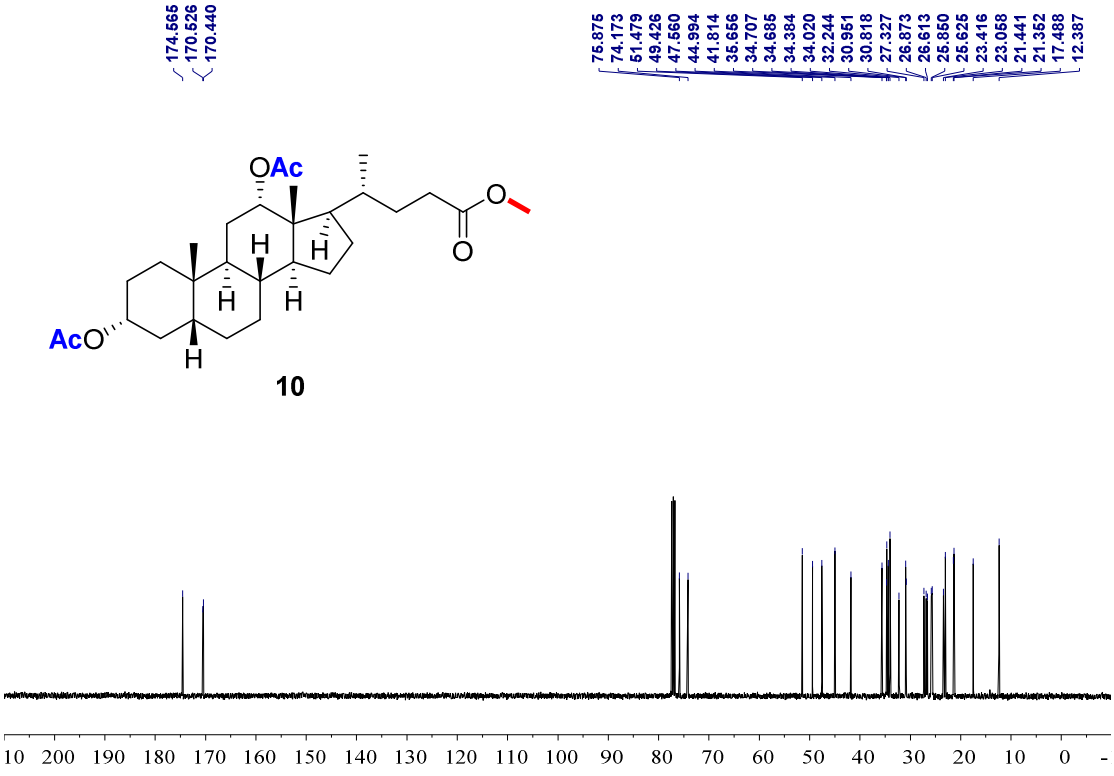
6x


f1 (ppm)


4.716
3.664
2.363
2.340
2.327
2.239
2.231
2.216
2.029
1.978
1.949
1.877
1.865
1.854
1.844
1.828
1.815
1.809
1.799
1.792
1.783
1.568
1.561
1.557
1.551
1.464
1.458
1.429
1.399
1.392
1.369
1.345
1.333
1.323
1.311
1.298
1.289
1.271
1.262
1.255
1.237
1.230
1.226
1.221
1.144
1.124
1.111
1.101
1.078
1.056
1.037
1.029
1.021
0.927
0.919
0.903
0.644
AcO
H
O
8
0.99
2.98
1.00
1.02
2.99
1.00
5.36
1.02
2.02
11.39
6.41
6.04
3.03
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0


174.751
170.638
74.380
56.485
55.979
51.483
42.722
41.876
40.396
40.133
35.774
35.364
35.029
34.571
32.234
31.039
30.993
28.190
27.013
26.619
26.317
24.180
23.337
21.479
20.827
18.266
12.034
AcO
H
O
8
10 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -


5.086 5.078 4.699 3.661 2.342 2.223 2.216 2.201 2.102 2.033 1.875 1.870 1.864 1.852 1.832 1.817 1.804 1.772 1.729 1.702 1.694 1.686 1.672 1.663 1.653 1.640 1.633 1.616 1.595 1.575 1.569 1.489 1.471 1.456 1.463 1.439 1.426 1.345 1.337 1.326 1.314 1.304 1.282 1.254 1.246 1.242 1.136 1.113 1.099 1.047 1.019 1.012 0.907 0.815 0.799 0.726 0.000
OAc
O
O
H
H
H
H
AcO
H
10
0.98 0.99 2.98 1.00 1.12 2.95 2.99 4.33 8.06 8.97 3.32 3.00 2.98 3.02
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


174.565 170.526 170.440
76.876 74.173 61.479 49.426 47.560 44.994 41.814 35.656 34.707 34.685 34.384 34.020 32.244 30.951 30.818 27.327 26.873 26.613 25.880 25.625 23.416 23.058 21.441 21.352 17.488 12.387
OAc
O
O
H
H
H
H
AcO
H
10
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0