Electronic Supplementary Material (ESI) for Organic Chemistry Frontiers.

Supporting Information:

Rh(III)-catalyzed regioselective intermolecular Oxa-Pauson-Khand reaction of alkynes, arylboronic acids and CO to form butenolides

Mi-Na Zhao,[‡,a,b] Ying Zhang,[‡,a] Ning Ge,[‡,a] Le Yu,[‡,a] Shun Wang,[a] Zhi-Hui Ren[a] and Zheng-Hui Guan*[,a]

[a] Key Laboratory of Synthetic and Nature Molecule Chemistry of Ministry of Education, Department of Chemistry & Materials Science, Northwest University, Xi'an 710127, P. R. China

[b] Shaanxi Key Laboratory of Phytochemistry, College of Chemistry and Chemical Engineering, Baoji University of Arts and Sciences, Baoji, 721013, P. R. China

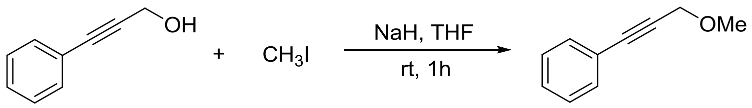
E-mail: guanzhh@nwu.edu.cn

CONTENTS

1. General information

^{1}H and ^{13}C NMR spectra were recorded on Bruker instrument (400 MHz) and (100 MHz) or Bruker instrument (600 MHz) and (151 MHz). The following abbreviations (or combinations thereof) were used to explain multiplicities: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, b = broad. Coupling constants, *J* were reported in Hertz unit (Hz). Preparative TLC was performed on TLC plates, analytical thin layer chromatography was performed on 10-25um silica gel GF254, visualization was carried out with UV light. Flash column chromatography was performed with SiO_2 (Silicycle Silica Gel 60 (200-300 mesh)). Unless otherwise stated, all reagents and solvents were purchased from commercial suppliers and used without further purification.

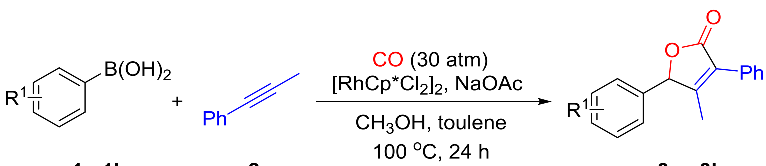
2. Typical procedure for preparation of alkyne 2e



2e

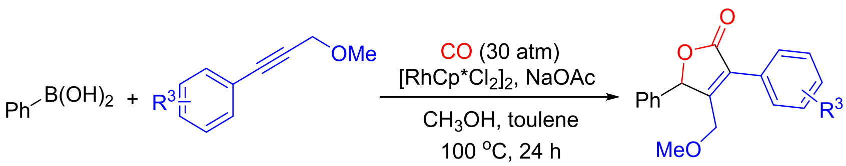
In a mixture of 3-phenylprop-2-yn-1-ol (10 mmol) and 30 mL of anhydrous THF, 0.48 g (20 mmol) of NaH was added slowly. Methyl iodide (12 mmol) was added dropwise at rt within 10 min. The mixture was stirred at ambient temperature for 1 h. After this period of time, the reaction mixture was quenched with H_2O (20 mL), extracted with ethyl acetate (3 × 20 mL) and washed with brine (30 mL). The organic layer was dried over by anhydrous Na_2SO_4 and evaporated in vacuo. The desired material **2e** was obtained after purification by flash chromatography on silica gel with hexanes/ethyl acetate as the eluent (20:1).

3. Typical procedure for the synthesis of asymmetric butenolides



1a-1l **2a** **3aa-3la**

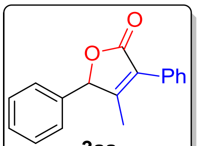
Arylboronic acid **1a-1l** (0.2 mmol), 1-phenyl-1-propyne **2a** (0.4 mmol, 46.4 mg), $[RhCp^*Cl_2]_2$ (0.5 mmol%, 0.6 mg), NaOAc (1.5 equiv, 24.6 mg) and methanol (1.0 equiv, 6.4 mg), toulene (2 mL) were charged in 5 mL round ampoule bottle and the bottle was placed in a autoclave. Then, the autoclave was evacuated and back-filled with CO (3-times, balloon), filled with 30 atm CO, and stirred at 100 °C for 24 hours. After this period of time, the autoclave was cooled to room temperature, and discharge the CO carefully. Then the reaction mixture was quenched with H_2O (10 mL), extracted with ethyl acetate (3 × 10 mL) and washed with brine (20 mL). The organic layer was dried over by anhydrous Na_2SO_4 and evaporated in vacuo. The desired butenolides **3aa-3la** were obtained after purification by flash chromatography on silica gel with hexanes/ethyl acetate (v/v = 10:1) as the eluent.



1a **2e-2m** **3ae-3am**

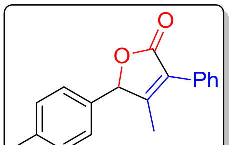
Phenylboronic acid **1a** (0.2 mmol, 24.4 mg), alkynes **2e-2m** (0.4 mmol), $[RhCp^*Cl_2]_2$ (2.5 mmol%, 3.1 mg), NaOAc (1.5 equiv, 24.6 mg) and methanol (1.0 eq, 6.4 mg), toulene (2 mL) were charged in a 5 mL round ampoule bottle and the bottle was placed in a autoclave. Then, the autoclave was evacuated and back-filled with CO (3-times, balloon), filled with 30 atm CO and stirred at 100 °C for 24 hours. After this period of time, the autoclave was cooled to room temperature, and discharge the CO carefully. Then the reaction mixture was quenched with H_2O (10 mL), extracted with ethyl acetate (3 × 10 mL) and washed with brine (20 mL). The organic layer was dried over by anhydrous Na_2SO_4 and evaporated in vacuo. The desired butenolides **3ae-3am** were obtained after purification by flash chromatography on silica gel with hexanes/ethyl acetate (v/v = 5:1) as the eluent.

4. Spectroscopic data of the products



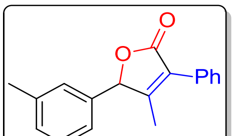
3aa

3aa[1]**:** Brown oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.56-7.54 (m, 2H), 7.48-7.44 (m, 2H), 7.42-7.39 (m, 4H), 7.30-7.27 (m, 2H), 5.74 (s, 1H), 2.00 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 172.8, 160.4, 134.8, 129.8, 129.5, 129.1, 129.0, 128.6, 128.6, 127.0, 126.5, 84.9, 13.4. HRMS Calcd (ESI) m/z for $C_{17}H_{15}O_2$: $[M+H]^+$ 251.1067. Found: 251.1064.



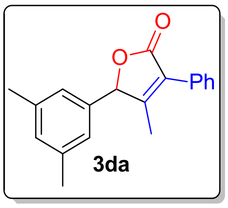
3ba

3ba: Yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.55 (m, 2H), 7.45 (t, J = 7.6 Hz, 2H), 7.40-7.36 (m, 1H), 7.22 (d, J = 8.0 Hz, 2H), 7.17 (d, J = 8.4 Hz, 2H), 5.71 (s, 1H), 2.37 (s, 3H), 2.00 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 172.8, 160.4, 139.4, 131.6, 129.7, 128.9, 128.5, 128.5, 126.9, 126.3, 84.8, 21.2, 13.3. HRMS Calcd (ESI) m/z for $C_{18}H_{17}O_2$: $[M+H]^+$ 265.1223. Found: 265.1230.

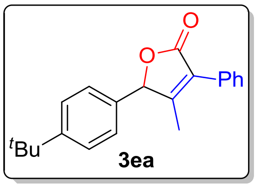


3ca

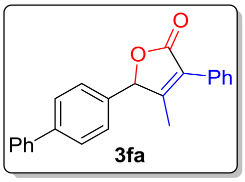
3ca: Yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.57-7.55 (m, 2H), 7.46 (t, J = 7.6 Hz, 2H), 7.39 (d, J = 7.6 Hz, 1H), 7.30 (t, J = 8.0 Hz, 1H), 7.20 (d, J = 8.0 Hz, 1H), 7.09 (d, J = 7.2 Hz, 2H), 5.71 (s, 1H), 2.36 (s, 3H), 2.00 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 172.9, 160.6, 139.0, 134.6, 130.2, 129.9, 129.0, 129.0, 128.6, 128.6, 127.5, 126.3, 124.2, 85.0, 21.4, 13.5. HRMS Calcd (ESI) m/z for $C_{18}H_{17}O_2$: $[M+H]^+$ 265.1223. Found: 265.1229.



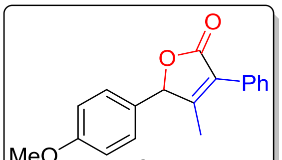
3da: Brown oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.58-7.56 (m, 2H), 7.48-7.44 (m, 2H), 7.41-7.39 (m, 1H), 5.67 (s, 1H), 2.33 (s, 6H), 2.01 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 172.9, 160.6, 138.7, 134.5, 131.0, 129.9, 129.0, 128.5, 128.5, 126.2, 124.6, 85.0, 21.2, 13.4. HRMS Calcd (ESI) m/z for $C_{19}H_{19}O_2$: $[M+H]^+$ 279.1380. Found: 279.1384.



3ea: White solid, mp 111-113 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.56-7.54 (m, 2H), 7.48-7.37 (m, 5H), 7.22 (d, *J* = 8.4 Hz, 2H), 5.74 (s, 1H), 2.02 (s, 3H), 1.33 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 172.8, 160.5, 152.6, 131.6, 129.9, 129.0, 128.5, 126.8, 126.4, 126.0, 85.0, 34.7, 31.3, 13.5. HRMS Calcd (ESI) m/z for $C_{21}H_{23}O_2$: $[M+H]^+$ 307.1693. Found: 307.1696.

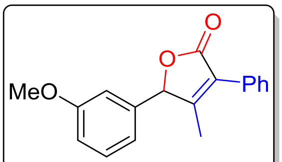


3fa: Orange solid, mp 115-116 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.64 (d, *J* = 8.0 Hz, 2H), 7.58 (t, *J* = 8.4 Hz, 4H), 7.48-7.44 (m, 4H), 7.37 (t, *J* = 8.0 Hz, 4H), 5.80 (s, 1H), 2.05 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 172.8, 160.3, 142.4, 140.2, 133.6, 129.7, 129.0, 128.9, 128.6, 128.5, 127.8, 127.7, 127.4, 127.1, 115.6, 84.6, 13.4. HRMS Calcd (ESI) m/z for $C_{23}H_{19}O_2$: $[M+H]^+$ 327.1380. Found: 327.1375.



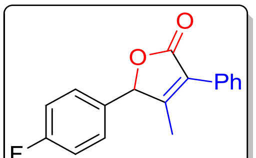
3ga

3ga: White oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.56-7.54 (m, 2H), 7.46 (t, *J* = 7.6 Hz, 2H), 7.40-7.37 (m, 1H), 7.21 (d, *J* = 8.8 Hz, 2H), 6.93 (d, *J* = 8.8 Hz, 2H), 5.71 (s, 1H), 3.82 (s, 3H), 2.00 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 172.8, 160.5, 160.5, 129.9, 129.0, 128.6, 128.6, 128.6, 126.6, 126.5, 114.5, 84.7, 55.4, 13.5. HRMS Calcd (ESI) m/z for $C_{18}H_{17}O_3$: $[M+H]^+$ 281.1172. Found: 281.1177.



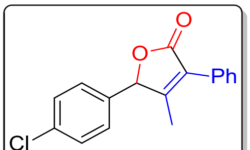
3ha

3ha: Brown oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.54 (d, *J* = 7.2 Hz, 2H), 7.46 (t, *J* = 7.6 Hz, 2H), 7.39 (t, *J* = 7.2 Hz, 1H), 6.93 (d, *J* = 8.0 Hz, 1H), 6.89 (d, *J* = 7.6 Hz, 1H), 6.80 (s, 1H), 5.72 (s, 1H), 3.81 (s, 3H), 2.02 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 172.8, 160.4, 160.1, 136.2, 130.1, 129.7, 128.9, 128.6, 128.5, 126.3, 119.2, 114.7, 112.4, 84.7, 55.3, 13.4. HRMS Calcd (ESI) m/z for $C_{18}H_{17}O_3$: $[M+H]^+$ 281.1172. Found: 281.1179.



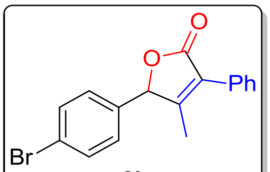
3ia

3ia: Brown oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.56-7.54 (m, 2H), 7.46 (t, *J* = 7.6 Hz, 2H), 7.41 (d, *J* = 7.2 Hz, 1H), 7.30-7.26 (m, 2H), 7.11 (t, *J* = 8.4 Hz, 2H), 5.74 (s, 1H), 2.00 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 172.6, 163.3 (d, J_{CF} = 247.2 Hz), 130.6 (d, J_{CF} = 3.2 Hz), 129.6, 129.0, 129.0, 128.9, 128.7, 128.6, 126.7, 116.2 (d, J_{CF} = 21.8 Hz), 84.1, 13.4. HRMS Calcd (ESI) m/z for $C_{17}H_{14}FO_2$: $[M+H]^+$ 269.0972. Found: 269.0974.



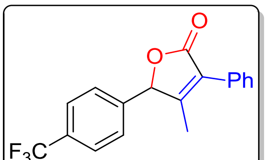
3ja

3ja: Yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.55-7.53 (m, 2H), 7.46 (t, J = 7.6 Hz, 2H), 7.41-7.38 (m, 3H), 7.25-7.22 (m, 2H), 5.73 (s, 1H), 2.00 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 172.5, 159.9, 135.3, 133.3, 129.8, 129.3, 128.9, 128.7, 128.5, 128.3, 126.6, 84.0, 13.3. HRMS Calcd (ESI) m/z for $C_{17}H_{14}ClO_2$: $[M+H]^+$ 285.0677. Found: 285.0677.



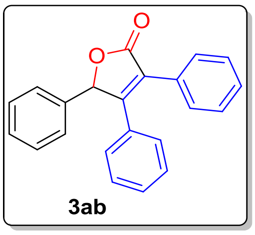
3ka

3ka: Brown oi; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.56-7.52 (m, 4H), 7.46 (t, J = 7.6 Hz, 2H), 7.40 (d, J = 7.6 Hz, 1H), 7.17 (d, J = 8.4 Hz, 2H), 5.71 (s, 3H), 2.00 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 172.6, 159.9, 133.8, 132.3, 129.0, 128.8, 128.6, 128.6, 123.6, 117.3, 84.1, 13.4. HRMS Calcd (ESI) m/z for $C_{17}H_{14}BrO_2$: $[M+H]^+$ 329.0172. Found: 329.0164.

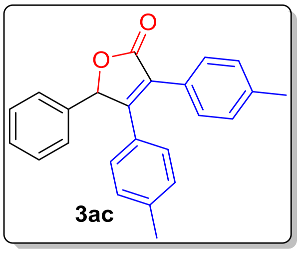


3la

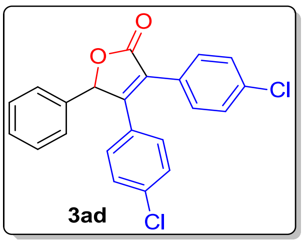
3la: White oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.69 (d, J = 8.0 Hz, 2H), 7.55-7.53 (m, 2H), 7.49-7.38 (m, 5H), 5.81 (s, 1H), 2.03 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 172.4, 159.6, 138.9, 131.6 (d, J_{CF} = 32.4 Hz), 129.4, 128.9, 128.8, 128.6, 127.9, 127.7, 127.2, 126.1 (q, J_{CF} = 3.7 Hz). HRMS Calcd (ESI) m/z for $C_{18}H_{14}F_3O_2$: $[M+H]^+$ 319.0940. Found: 319.0946.



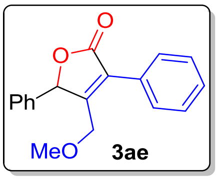
3ab[2]**:** Yellow oil; ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.48 (dd, *J* = 6.6, 3.0 Hz, 2H), 7.34 (dd, *J* = 5.0, 1.7 Hz, 3H), 7.31-7.28 (m, 5H), 7.24 (m, 1H), 7.19 (t, *J* = 7.6 Hz, 2H), 7.12-7.08 (m, 2H), 6.25 (s, 1H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 172.50, 159.42, 134.83, 131.18, 129.92, 129.90, 129.46, 129.40, 128.97, 128.88, 128.74, 128.60, 128.38, 127.67, 126.90, 83.73. HRMS Calcd (ESI) m/z for $C_{22}H_{17}O_2$: $[M+H]^+$ 313.1223. Found: 313.1230.



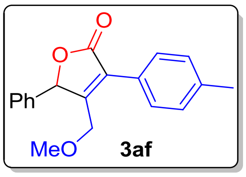
3ac: Brown oil; ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.38 (d, *J* = 8.1 Hz, 2H), 7.31-7.27 (m, 5H), 7.16 (d, *J* = 8.0 Hz, 2H), 7.02 (d, *J* = 8.3 Hz, 2H), 6.98 (d, *J* = 8.2 Hz, 2H), 6.22 (s, 1H), 2.35 (s, 3H), 2.24 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 172.81, 158.67, 140.17, 138.74, 135.22, 129.43, 129.32, 129.30, 128.92, 128.31, 127.76, 127.20, 126.25, 83.59, 21.42, 21.39. HRMS Calcd (ESI) m/z for $C_{24}H_{21}O_2$: $[M+H]^+$ 341.1536. Found: 341.1528.



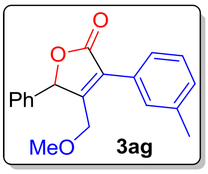
3ad: Yellow oil; ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.41 (d, *J* = 8.5 Hz, 2H), 7.35-7.30 (m, 5H), 7.26 (t, *J* = 4.7 Hz, 2H), 7.20 (d, *J* = 8.6 Hz, 2H), 7.02 (d, *J* = 8.6 Hz, 2H), 6.21 (s, 1H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 171.83, 158.43, 136.31, 135.24, 134.21, 130.75, 129.68, 129.60, 129.30, 129.14, 129.04, 127.94, 127.60, 126.25, 83.68. HRMS Calcd (ESI) m/z for $C_{22}H_{15}Cl_2O_2$: $[M+H]^+$ 381.0444. Found: 381.0453.



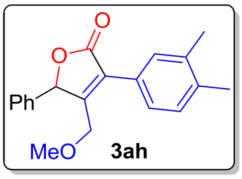
3ae: Brown oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.47-7.46 (m, 4H), 7.43-7.39 (m, 4H), 7.35-7.33 (m, 2H), 6.09 (s, 1H), 4.41 (d, *J* = 12.8 Hz, 1H), 3.96 (d, *J* = 12.8 Hz, 1H), 3.28 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 172.4, 159.9, 134.9, 129.2, 129.2, 129.2, 129.0, 128.6, 127.5, 126.7, 115.3, 82.6, 66.3, 59.1. HRMS Calcd (ESI) m/z for $C_{18}H_{17}O_3$: $[M+H]^+$ 281.1172. Found: 281.1168.



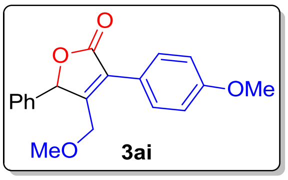
3af: Brown oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.41-7.32 (m, 7H), 7.26 (d, *J* = 8.0 Hz, 2H), 6.01 (s, 1H), 4.40 (d, *J* = 12.8 Hz, 1H), 3.97 (d, *J* = 13.2 Hz, 1H), 3.28 (s, 3H), 2.40 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 172.5, 159.1, 139.2, 135.0, 129.3, 129.1, 129.0, 128.9, 127.4, 126.7, 126.3, 82.5, 66.3, 59.0, 21.4. HRMS Calcd (ESI) m/z for $C_{19}H_{19}O_3$: $[M+H]^+$ 295.1329. Found: 295.1325.



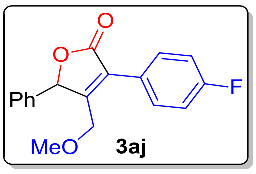
3ag: Yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.44-7.38 (m, 3H), 7.36-7.32 (m, 3H), 7.29 (s, 1H), 7.22 (d, *J* = 7.2 Hz, 2H), 6.08 (s, 1H), 4.40 (d, *J* = 13.2 Hz, 1H), 3.95 (d, *J* = 13.2 Hz, 1H), 3.28 (s, 3H), 2.40 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 172.4, 159.7, 138.3, 134.9, 129.9, 129.7, 129.2, 128.9, 128.5, 127.7, 126.7, 126.2, 82.5, 66.3, 59.0, 21.5. HRMS Calcd (ESI) m/z for $C_{19}H_{19}O_3$: $[M+H]^+$ 295.1329. Found: 295.1334.



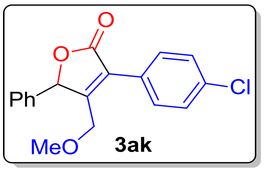
3ah: Yellow oil; ^{1}H NMR (400 MHz, CDCl$_3$) δ 7.42-7.37 (m, 3H), 7.34-7.32 (m, 2H), 7.25 (s, 1H), 7.22-7.15 (m, 2H), 6.02 (s, 1H), 4.40 (d, J = 12.8 Hz, 1H), 3.94 (d, J = 13.2 Hz, 1H), 3.27 (s, 3H), 2.30 (s, 3H), 2.30 (s, 3H). ^{13}C NMR (100 MHz, CDCl$_3$) δ 172.6, 159.0, 137.9, 136.9, 135.1, 130.1, 129.8, 129.1, 129.0, 127.6, 126.7, 126.7, 126.6, 82.5, 66.3, 59.0, 19.9, 19.7. HRMS Calcd (ESI) m/z for $C_{20}H_{21}O_3$: $[M+H]^+$ 309.1485. Found: 309.1480.



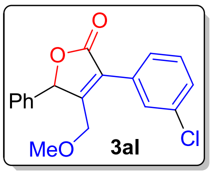
3ai: Brown oil; ^{1}H NMR (400 MHz, CDCl$_3$) δ 7.45-7.38 (m, 5H), 7.34-7.32 (m, 2H), 6.98 (d, J = 8.8 Hz, 2H), 6.06 (s, 1H), 4.40 (d, J = 12.8 Hz, 1H), 3.95 (d, J = 13.2 Hz, 1H), 3.85 (s, 3H), 3.28 (s, 3H) . ^{13}C NMR (100 MHz, CDCl$_3$) δ 172.6, 160.2, 158.1, 135.0, 130.5, 129.1, 128.9, 127.0, 126.7, 121.6, 114.1, 82.5, 66.3, 59.0, 55.4. HRMS Calcd (ESI) m/z for $C_{19}H_{19}O_4$: $[M+H]^+$ 311.1278. Found: 311.1279.



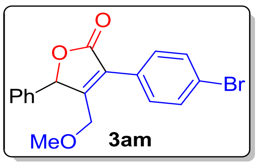
3aj: Brown oil; ^{1}H NMR (400 MHz, CDCl$_3$) δ 7.50-7.46 (m, 2H), 7.42-7.39 (m, 3H), 7.34-7.32 (m, 2H), 7.17-7.13 (m, 2H), 6.08 (s, 1H), 4.36 (d, J = 12.8 Hz, 1H), 3.95 (d, J = 13.2 Hz, 1H), 3.28 (s, 3H). ^{13}C NMR (100 MHz, CDCl$_3$) δ 172.3, 163.1 (d, J_{CF} = 248.3 Hz), 159.6, 134.7, 131.1 (d, J_{CF} = 8.2 Hz), 129.3, 129.0, 126.7, 126.6, 115.8 (d, J_{CF} = 21.6 Hz), 82.7, 66.2, 59.1. HRMS Calcd (ESI) m/z for $C_{18}H_{16}FO_3$: $[M+H]^+$ 299.1078. Found: 299.1075.



3ak: Yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.43-7.40 (m, 7H), 7.34-7.31 (m, 2H), 6.08 (s, 1H), 4.36 (d, J = 13.2 Hz, 1H), 3.95 (d, J = 12.8 Hz, 1H), 3.28 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 172.0, 160.2, 135.3, 134.6, 130.5, 129.3, 129.0, 128.9, 127.6, 126.7, 126.5, 82.7, 66.2, 59.1. HRMS Calcd (ESI) m/z for $C_{18}H_{16}ClO_3$: $[M+H]^+$ 315.0782. Found: 315.0778.



3al: Yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.47-7.46 (m, 1H), 7.43-7.37 (m, 6H), 7.34-7.32 (m, 2H), 6.09 (s, 1H), 4.37 (d, J = 13.2 Hz, 1H), 3.96 (d, J = 13.2 Hz, 1H), 3.29 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.8, 159.9, 133.5, 133.5, 129.9, 128.8, 128.3, 128.2, 128.1, 128.0, 126.3, 125.7, 125.3, 81.7, 65.1, 58.1. HRMS Calcd (ESI) m/z for $C_{18}H_{16}ClO_3$: $[M+H]^+$ 337.0602. Found: 337.0591.



3am: Brown oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.60-7.58 (m, 2H), 7.42-7.39 (m, 3H), 7.38-7.37 (m, 1H), 7.36-7.34 (m, 1H), 7.34-7.31 (m, 2H), 6.07 (s, 1H), 4.35 (d, J = 13.2 Hz, 1H), 3.94 (d, J = 13.2 Hz, 1H), 3.28 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 171.9, 160.2, 134.5, 131.8, 130.7, 129.3, 129.0, 128.1, 126.7, 126.6, 123.6, 82.7, 66.2, 59.1. HRMS Calcd (ESI) m/z for $C_{18}H_{16}BrO_3$: $[M+H]^+$ 359.0277. Found: 359.0268.

5. References

1. L. Artok, M. Kus, Ö. Aksın-Artok, F. N. Dege and F. Y. Özkılınc, *Tetrahedron*, 2009, **65**, 9125.

2. M. A. Ganiek, M. R. Becker, M. Ketels and P. Knochel, *Org. Lett.*, 2016, **18**, 828.

6. Data of Density functional theory (DFT) calculations

All calculations were performed with the Gaussian 09 package (1). The equilibrium geometries and transition states (TS) were fully optimized by the dispersion-corrected density functional method B3LYP-D3 (2-4) with the LanL2DZ basis set for Rh and 6-31G(d) basis set for other atoms (5-8). Normal vibrational mode analysis at the same level of theory confirmed that the optimized structures are minima (zero imaginary frequency) or saddle points (one imaginary frequency). Single-point corrected energies with solvent effects in Toluene were computed by the dispersion-corrected density functional method M06L-D3 (4, 9) with the SDD basis set for Rh (10-11) and 6-311++G (d,p) basis set for other atoms (12-14) using the SMD solvation model (15). The relative energies and free energies (at 373.15K) are in kcal/mol.

References:

1. Gaussian 09, rev. D.01 (Gaussian Inc., 2013).
2. A. D. Becke, Density - functional thermochemistry. III. The role of exact exchange. *J. Chem. Phys.* **98**, 5648-5652 (1993). DOI:10.1063/1.464913
3. C. Lee, W. Yang, R. G. Parr, Development of the Colle-Salvetti correlation-energy formula into a functional of the electron density. *Phys. Rev. B* **37**, 785-789 (1988). DOI: 10.1103/PhysRevB.37.785
4. S. Grimme, J. Antony, S. Ehrlich, H. Krieg, A consistent and accurate *ab initio* parametrization of density functional dispersion correction (DFT-D) for the 94 elements H-Pu. *J. Chem. Phys.* **132**, 154104 (2010). DOI: 10.1063/1.3382344
5. P. J. Hay and W. R. Wadt, Ab initio effective core potentials for molecular calculations-potentials for K to Au including the outermost core orbitals, *J. Chem. Phys.*, **82**, 299-310 (1985). DOI: 10.1063/1.448975
6. R. Ditchfield, W. J. Hehre, J. A. Pople, Self - consistent molecular - orbital methods. IX. An extended Gaussian - type basis for molecular - orbital studies of organic molecules. *J. Chem. Phys.* **54**, 724-728 (1971). DOI: 10.1063/1.1674902
7. W. J. Hehre, R. Ditchfield, J. A. Pople, Self-consistent molecular orbital methods. XII. Further extensions of Gaussian-type basis sets for use in molecular orbital studies of organic molecules. *J. Chem. Phys.* **54**, 2257-2261 (1971). DOI: 10.1007/BF00533485
8. P. C. Hariharan, J. A. Pople, The influence of polarization functions on molecular orbital hydrogenation energies. *Theor. Chim. Acta* **28**, 213-222 (1973). DOI: 10.1007/BF00533485
9. Y. Zhao and D. G. Truhlar, The M06 suite of density functionals for main group thermochemistry, thermochemical kinetics, noncovalent interactions, excited states, and transition elements: two new functionals and systematic testing of four M06-class functionals and 12 other functionals, *Theor. Chem. Acc.*, **120**, 215-241 (2008). DOI: 10.1007/s00214-007-0310-x
10. T. H. Dunning Jr. and P. J. Hay, in *Modern Theoretical Chemistry*, Ed. H. F. Schaefer III, Vol. 3 (Plenum, New York, 1977) 1-28.

11. D. Andrae, U. Haeussermann, M. Dolg, H. Stoll, and H. Preuss, Energy-adjusted ab initio pseudopotentials for the 2nd and 3rd row transition-elements, *Theor. Chem. Acc.*, **77**, 123-141(1990). DOI: 10.1007/BF01114537
12. A. D. McLean and G. S. Chandler, Contracted Gaussian-basis sets for molecular calculations. 1. 2nd row atoms, Z=11-18, *J. Chem. Phys.*, **72**, 5639-5648 (1980). DOI: 10.1063/1.438980
13. K. Raghavachari, J. S. Binkley, R. Seeger, and J. A. Pople, Self-Consistent Molecular Orbital Methods. 20. Basis set for correlated wave-functions, *J. Chem. Phys.*, **72**, 650-654 (1980). DOI: 10.1063/1.438955
14. A. J. H. Wachters, Gaussian basis set for molecular wavefunctions containing third-row atoms, *J. Chem. Phys.*, **52**, 1033 (1970). DOI: 10.1063/1.1673095
15. A. V. Marenich, C. J. Cramer, D. G. Truhlar, Universal solvation model based on solute electron density and on a continuum model of the solvent defined by the bulk dielectric constant and atomic surface tensions. *J. Phys. Chem. B* **113**, 6378-6396 (2009). DOI: 10.1021/jp810292n

Cartesian coordinates for optimized geometry

Im C

6	1.392639000	0.895503000	1.701497000
6	0.003145000	0.530344000	2.000716000
6	-0.840597000	1.576046000	1.517852000
6	-0.023855000	2.434753000	0.703287000
6	1.381492000	2.038089000	0.906153000
17	0.671093000	1.426095000	-2.462328000
6	-2.017577000	0.431683000	-0.846683000
8	-2.498830000	1.328356000	-1.503419000
6	-2.924882000	-0.642009000	-0.272274000
6	-4.307797000	-0.504076000	-0.477490000
6	-2.453106000	-1.730961000	0.473234000
6	-5.198273000	-1.431940000	0.057605000
1	-4.660420000	0.342989000	-1.056801000
6	-3.344908000	-2.661801000	1.007283000
1	-1.386520000	-1.850251000	0.622372000
6	-4.718949000	-2.513184000	0.803746000
1	-6.266362000	-1.313431000	-0.104724000
1	-2.966305000	-3.503369000	1.581425000
1	-5.413167000	-3.237088000	1.222372000
6	-0.383105000	-0.564559000	2.950042000
1	-0.150858000	-0.279589000	3.985899000
1	-1.450539000	-0.790166000	2.894571000
1	0.168350000	-1.486570000	2.735921000
6	-2.282670000	1.798704000	1.864327000
1	-2.810946000	2.319219000	1.062319000
1	-2.806563000	0.859863000	2.058681000

1	-2.348881000	2.417180000	2.769438000
6	2.575089000	0.157896000	2.241462000
1	3.495096000	0.412730000	1.712850000
1	2.713997000	0.396812000	3.305158000
1	2.445850000	-0.925162000	2.166791000
6	2.542561000	2.758100000	0.296609000
1	2.405098000	2.835840000	-0.788215000
1	2.627591000	3.775587000	0.699951000
1	3.484335000	2.236257000	0.485794000
6	-0.468667000	3.684050000	0.006520000
1	-1.481840000	3.567952000	-0.386320000
1	-0.449661000	4.542877000	0.692149000
1	0.182938000	3.895994000	-0.844041000
45	-0.057869000	0.511345000	-0.320130000
6	0.001476000	-1.552573000	-1.633188000
6	1.043272000	-1.500589000	-0.980461000
6	-0.987802000	-1.803764000	-2.684364000
1	-1.132140000	-0.884316000	-3.261684000
1	-0.610117000	-2.586208000	-3.353543000
1	-1.951446000	-2.124400000	-2.280024000
6	2.399657000	-1.657930000	-0.532750000
6	3.373992000	-0.734993000	-0.960881000
6	2.774819000	-2.740146000	0.281121000
6	4.701532000	-0.904461000	-0.577591000
1	3.060821000	0.098432000	-1.583401000
6	4.108469000	-2.898239000	0.660628000
1	2.019718000	-3.451022000	0.604083000
6	5.072905000	-1.982532000	0.234530000
1	5.451249000	-0.193448000	-0.914194000
1	4.393271000	-3.737723000	1.288933000
1	6.110480000	-2.108424000	0.531436000

TS-1

6	0.836526000	1.345277000	1.641724000
6	-0.524351000	0.963152000	1.875572000
6	-1.386786000	1.798062000	1.049466000
6	-0.563957000	2.611665000	0.250281000
6	0.835533000	2.309187000	0.590319000
17	0.889900000	1.148646000	-2.508664000
6	-1.469848000	-0.859012000	-1.426724000
8	-1.599651000	-0.760334000	-2.620262000
6	-2.628880000	-1.175557000	-0.528701000
6	-3.916142000	-0.864220000	-0.994326000
6	-2.474771000	-1.775237000	0.725985000

6	-5.030138000	-1.129311000	-0.201636000
1	-4.018454000	-0.411781000	-1.975444000
6	-3.593601000	-2.064582000	1.507998000
1	-1.477624000	-2.010495000	1.082837000
6	-4.871772000	-1.733287000	1.050357000
1	-6.023166000	-0.871615000	-0.559453000
1	-3.467009000	-2.541637000	2.476103000
1	-5.741696000	-1.947606000	1.665189000
6	-0.966519000	0.073519000	2.999389000
1	-0.864199000	0.600721000	3.957900000
1	-2.009367000	-0.228319000	2.894981000
1	-0.353180000	-0.831779000	3.060479000
6	-2.885338000	1.806375000	1.092316000
1	-3.311582000	2.088195000	0.126095000
1	-3.289318000	0.826745000	1.355572000
1	-3.243403000	2.527026000	1.840315000
6	2.032540000	0.828940000	2.382589000
1	2.936157000	0.879094000	1.770616000
1	2.204193000	1.418042000	3.293712000
1	1.901228000	-0.215901000	2.678343000
6	2.020406000	3.057379000	0.064237000
1	1.901277000	3.269046000	-1.000260000
1	2.138009000	4.007275000	0.604406000
1	2.939819000	2.478654000	0.187153000
6	-0.975073000	3.643352000	-0.753362000
1	-2.050586000	3.609547000	-0.946304000
1	-0.724654000	4.651173000	-0.395837000
1	-0.452994000	3.476043000	-1.701386000
45	0.047795000	0.465431000	-0.316066000
6	0.179392000	-1.805360000	-0.893484000
6	1.231674000	-1.176213000	-0.496142000
6	-0.186695000	-3.185975000	-1.344820000
1	-0.457974000	-3.179617000	-2.406087000
1	0.684885000	-3.835001000	-1.202226000
1	-1.030595000	-3.602507000	-0.784606000
6	2.627407000	-1.343536000	-0.144500000
6	3.595607000	-0.460386000	-0.658281000
6	3.021702000	-2.350431000	0.754289000
6	4.930934000	-0.597142000	-0.285303000
1	3.273318000	0.314345000	-1.347620000
6	4.360306000	-2.476548000	1.126764000
1	2.270754000	-3.022178000	1.161536000
6	5.317859000	-1.600819000	0.609720000
1	5.674024000	0.083323000	-0.692833000

1	4.654533000	-3.256810000	1.823895000
1	6.359665000	-1.698429000	0.902938000

Im D

6	2.308395000	0.776476000	1.217422000
6	1.232326000	1.544321000	1.782337000
6	1.038767000	2.733523000	0.946703000
6	1.892981000	2.635377000	-0.157918000
6	2.634449000	1.372480000	-0.042871000
17	0.325980000	0.642518000	-2.547560000
6	-2.124665000	-0.335747000	0.036543000
8	-1.567149000	0.806371000	0.055147000
6	-3.608836000	-0.327546000	0.000429000
6	-4.244161000	0.674941000	-0.752706000
6	-4.390386000	-1.243191000	0.721978000
6	-5.633995000	0.741463000	-0.802582000
1	-3.630318000	1.382395000	-1.300494000
6	-5.782341000	-1.159677000	0.686719000
1	-3.913376000	-2.002263000	1.332167000
6	-6.406371000	-0.174448000	-0.081607000
1	-6.116553000	1.508884000	-1.401472000
1	-6.378910000	-1.864601000	1.259220000
1	-7.491102000	-0.118768000	-0.117045000
6	0.574753000	1.324537000	3.111806000
1	1.078462000	1.898848000	3.901691000
1	-0.472363000	1.640962000	3.084719000
1	0.598789000	0.268715000	3.395633000
6	0.004564000	3.780734000	1.229622000
1	-0.024061000	4.541512000	0.446081000
1	-0.991532000	3.326398000	1.291504000
1	0.204153000	4.279899000	2.186279000
6	2.982709000	-0.403113000	1.845776000
1	3.381202000	-1.089118000	1.095403000
1	3.816255000	-0.062631000	2.474580000
1	2.295740000	-0.972377000	2.476888000
6	3.694880000	0.937625000	-1.006973000
1	3.339164000	1.054561000	-2.035122000
1	4.603736000	1.542559000	-0.884656000
1	3.959659000	-0.111999000	-0.859985000
6	2.019700000	3.562140000	-1.326233000
1	1.374652000	4.438068000	-1.220365000
1	3.055137000	3.910254000	-1.431347000
1	1.739207000	3.042457000	-2.249969000
45	0.518855000	0.727665000	-0.127385000

6	-1.292573000	-1.513951000	0.000730000
6	0.053186000	-1.214747000	-0.063574000
6	-1.854413000	-2.917269000	-0.114172000
1	-2.771453000	-2.925988000	-0.711813000
1	-1.129782000	-3.578348000	-0.596171000
1	-2.096334000	-3.360501000	0.861095000
6	1.109119000	-2.232303000	-0.124787000
6	2.065562000	-2.216850000	-1.158533000
6	1.223523000	-3.204245000	0.886501000
6	3.100640000	-3.149820000	-1.174027000
1	1.972034000	-1.470194000	-1.940643000
6	2.274817000	-4.121467000	0.878542000
1	0.491969000	-3.219647000	1.689873000
6	3.217069000	-4.098362000	-0.151900000
1	3.824003000	-3.133463000	-1.985266000
1	2.356325000	-4.854885000	1.676633000
1	4.034143000	-4.814746000	-0.161112000

Im C’

6	0.407507000	-2.486226000	1.248278000
6	-0.836050000	-1.914654000	1.498652000
6	-0.626665000	-0.492947000	1.814690000
6	0.782678000	-0.252179000	1.874958000
6	1.426783000	-1.435698000	1.415212000
17	1.627853000	-1.791404000	-1.924250000
6	0.773373000	1.067521000	-1.184986000
6	-2.185308000	-2.559771000	1.433459000
1	-2.835133000	-2.028313000	0.729988000
1	-2.119074000	-3.601134000	1.108468000
1	-2.676619000	-2.539341000	2.414678000
6	-1.673079000	0.414261000	2.386661000
1	-2.673363000	0.159475000	2.032473000
1	-1.671762000	0.333372000	3.482942000
1	-1.488660000	1.459828000	2.127644000
6	0.735311000	-3.887385000	0.838997000
1	1.273473000	-3.883477000	-0.116294000
1	1.380017000	-4.369978000	1.585115000
1	-0.164376000	-4.497882000	0.724145000
6	2.895178000	-1.721941000	1.379181000
1	3.489700000	-0.812755000	1.481688000
1	3.160740000	-2.401131000	2.200813000
1	3.165642000	-2.209343000	0.437070000
6	1.428012000	0.985803000	2.418348000
1	1.455032000	0.939742000	3.515929000

1	2.450775000	1.107363000	2.057848000
1	0.872514000	1.884254000	2.137062000
45	0.147983000	-0.670297000	-0.322869000
6	-1.958043000	-0.133350000	-1.135922000
6	-1.510029000	-1.082431000	-1.799323000
6	-2.878495000	0.834204000	-0.600899000
6	-2.530018000	2.181841000	-0.398027000
6	-4.180092000	0.409142000	-0.266163000
6	-3.457370000	3.070638000	0.140743000
1	-1.539275000	2.515452000	-0.676833000
6	-5.101141000	1.305759000	0.272795000
1	-4.457931000	-0.627400000	-0.432907000
6	-4.741715000	2.638882000	0.484522000
1	-3.175718000	4.109429000	0.291199000
1	-6.099780000	0.961497000	0.527851000
1	-5.458176000	3.336862000	0.908676000
6	-1.423558000	-2.084274000	-2.870948000
1	-1.115780000	-3.058926000	-2.481063000
1	-2.400413000	-2.178785000	-3.361168000
1	-0.673063000	-1.783213000	-3.606620000
8	0.118619000	1.667508000	-2.009833000
6	2.062716000	1.671040000	-0.689332000
6	2.029667000	3.021866000	-0.311232000
6	3.261090000	0.955181000	-0.596995000
6	3.171994000	3.636752000	0.199621000
1	1.102419000	3.577628000	-0.416773000
6	4.410630000	1.583663000	-0.114731000
1	3.283262000	-0.078293000	-0.920521000
6	4.366137000	2.917510000	0.300656000
1	3.133805000	4.677631000	0.510224000
1	5.343311000	1.027854000	-0.061927000
1	5.259663000	3.397517000	0.691031000

TS-1’

6	3.114391000	-0.407649000	0.584302000
6	2.262421000	-0.567999000	1.708017000
6	1.454541000	0.617371000	1.810671000
6	1.912764000	1.579257000	0.822257000
6	2.901705000	0.946866000	0.045281000
17	1.821365000	-1.138262000	-2.411869000
6	-0.828032000	0.394203000	-1.340364000
6	2.187662000	-1.738484000	2.642204000
1	1.148866000	-2.019605000	2.847757000
1	2.697603000	-2.613257000	2.230736000

1	2.659488000	-1.500803000	3.605139000
6	0.520858000	0.893441000	2.951988000
1	-0.132200000	0.037650000	3.153830000
1	1.097237000	1.086697000	3.867370000
1	-0.107207000	1.764791000	2.762883000
6	4.179447000	-1.342178000	0.102101000
1	4.156803000	-1.413055000	-0.988565000
1	5.170937000	-0.982422000	0.409526000
1	4.044041000	-2.349284000	0.505937000
6	3.693961000	1.525938000	-1.084492000
1	3.289133000	2.489022000	-1.405901000
1	4.738264000	1.679164000	-0.780441000
1	3.681500000	0.846863000	-1.942972000
6	1.443032000	2.996963000	0.691099000
1	2.060311000	3.665818000	1.306611000
1	1.504686000	3.343154000	-0.343774000
1	0.406093000	3.112640000	1.011363000
45	1.028901000	-0.354697000	-0.234325000
6	-1.078923000	-1.314517000	-0.410481000
6	-0.037546000	-2.064086000	-0.234016000
6	-2.515675000	-1.429010000	-0.131282000
6	-3.500175000	-0.993409000	-1.034577000
6	-2.920440000	-2.034059000	1.074578000
6	-4.851059000	-1.168887000	-0.739964000
1	-3.200556000	-0.527472000	-1.966993000
6	-4.272414000	-2.207816000	1.363708000
1	-2.159794000	-2.360024000	1.778739000
6	-5.243068000	-1.772357000	0.457734000
1	-5.601212000	-0.832485000	-1.450428000
1	-4.568116000	-2.678873000	2.297479000
1	-6.297890000	-1.901138000	0.684574000
6	0.380494000	-3.474304000	-0.101727000
1	0.974691000	-3.632546000	0.805024000
1	-0.489188000	-4.143543000	-0.081365000
1	1.010603000	-3.730255000	-0.961871000
8	-0.930939000	0.269921000	-2.536535000
6	-1.385096000	1.593753000	-0.628824000
6	-1.826546000	1.576137000	0.698938000
6	-1.463916000	2.786376000	-1.365427000
6	-2.346957000	2.731568000	1.281670000
1	-1.778940000	0.656586000	1.268215000
6	-1.957046000	3.947067000	-0.772774000
1	-1.130086000	2.782708000	-2.397966000
6	-2.405199000	3.921908000	0.551257000

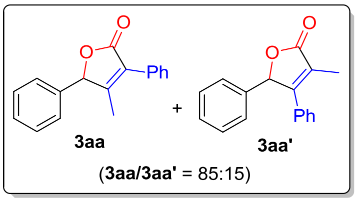
1	-2.706059000	2.701879000	2.306954000
1	-1.999374000	4.869922000	-1.344826000
1	-2.800987000	4.823759000	1.010396000

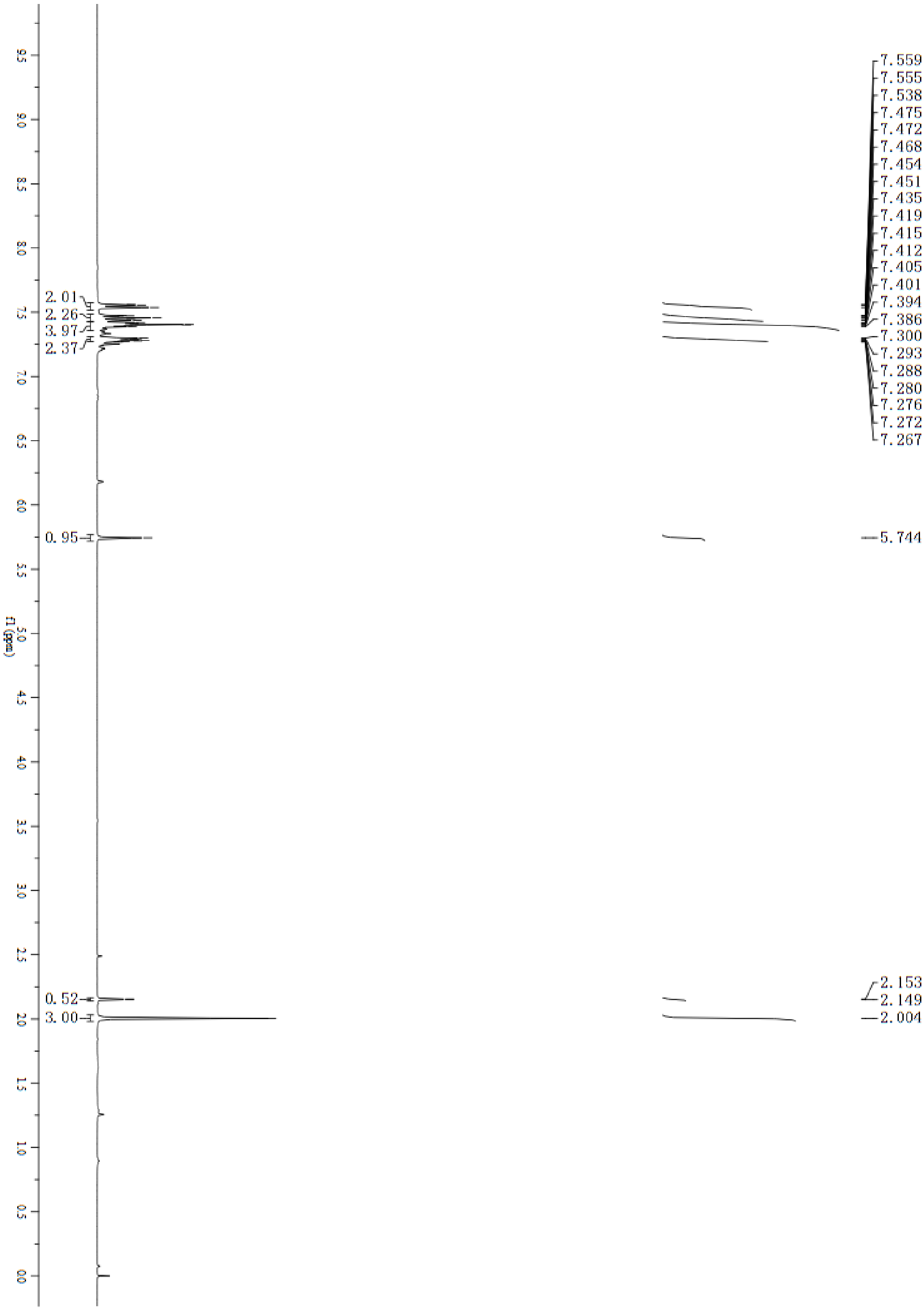
Im D’

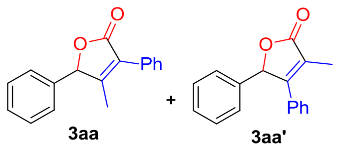
6	3.487737000	-0.803005000	-0.002048000
6	2.869656000	-0.896163000	1.288213000
6	2.520329000	0.437544000	1.688180000
6	3.113339000	1.370140000	0.724628000
6	3.707796000	0.620521000	-0.296384000
17	1.203081000	-0.174211000	-2.582967000
6	-1.304280000	0.752584000	0.037492000
6	2.659548000	-2.135332000	2.104152000
1	1.682697000	-2.136039000	2.597259000
1	2.733649000	-3.038160000	1.493330000
1	3.427658000	-2.203278000	2.885837000
6	1.869403000	0.846053000	2.975403000
1	1.254857000	0.038556000	3.383260000
1	2.621483000	1.113613000	3.730519000
1	1.222829000	1.715790000	2.824369000
6	4.025455000	-1.920683000	-0.842583000
1	3.801903000	-1.737130000	-1.897753000
1	5.114353000	-2.011855000	-0.729576000
1	3.574725000	-2.878689000	-0.569240000
6	4.380720000	1.108845000	-1.540810000
1	4.427045000	2.200209000	-1.574066000
1	5.405204000	0.720255000	-1.601884000
1	3.831215000	0.764887000	-2.424817000
6	2.973165000	2.859046000	0.824712000
1	3.475579000	3.241443000	1.722444000
1	3.398611000	3.363423000	-0.046034000
1	1.915282000	3.139681000	0.889964000
45	1.443135000	0.001026000	-0.176298000
6	-1.336083000	-0.691334000	0.035173000
6	-0.087682000	-1.271229000	-0.076449000
6	-2.607161000	-1.471106000	-0.003043000
6	-3.479871000	-1.359980000	-1.097052000
6	-2.953225000	-2.335108000	1.047083000
6	-4.670791000	-2.084626000	-1.133560000
1	-3.216375000	-0.697748000	-1.916818000
6	-4.142661000	-3.065658000	1.009595000
1	-2.282401000	-2.425441000	1.897915000
6	-5.007062000	-2.938909000	-0.079843000
1	-5.335431000	-1.985566000	-1.987738000

1	-4.395284000	-3.729575000	1.832384000
1	-5.935013000	-3.503749000	-0.109314000
6	0.128866000	-2.730684000	-0.314577000
1	0.779798000	-3.165024000	0.451936000
1	-0.800998000	-3.308438000	-0.347892000
1	0.648900000	-2.837216000	-1.275347000
8	-0.174635000	1.329207000	-0.031150000
6	-2.491306000	1.643608000	0.076739000
6	-3.647358000	1.334424000	0.812349000
6	-2.421868000	2.865972000	-0.613826000
6	-4.712219000	2.233188000	0.852408000
1	-3.709977000	0.400549000	1.358404000
6	-3.496548000	3.750955000	-0.587520000
1	-1.521851000	3.098160000	-1.173512000
6	-4.643745000	3.437249000	0.147357000
1	-5.598409000	1.989755000	1.431914000
1	-3.440103000	4.685938000	-1.138137000
1	-5.481243000	4.129540000	0.170935000

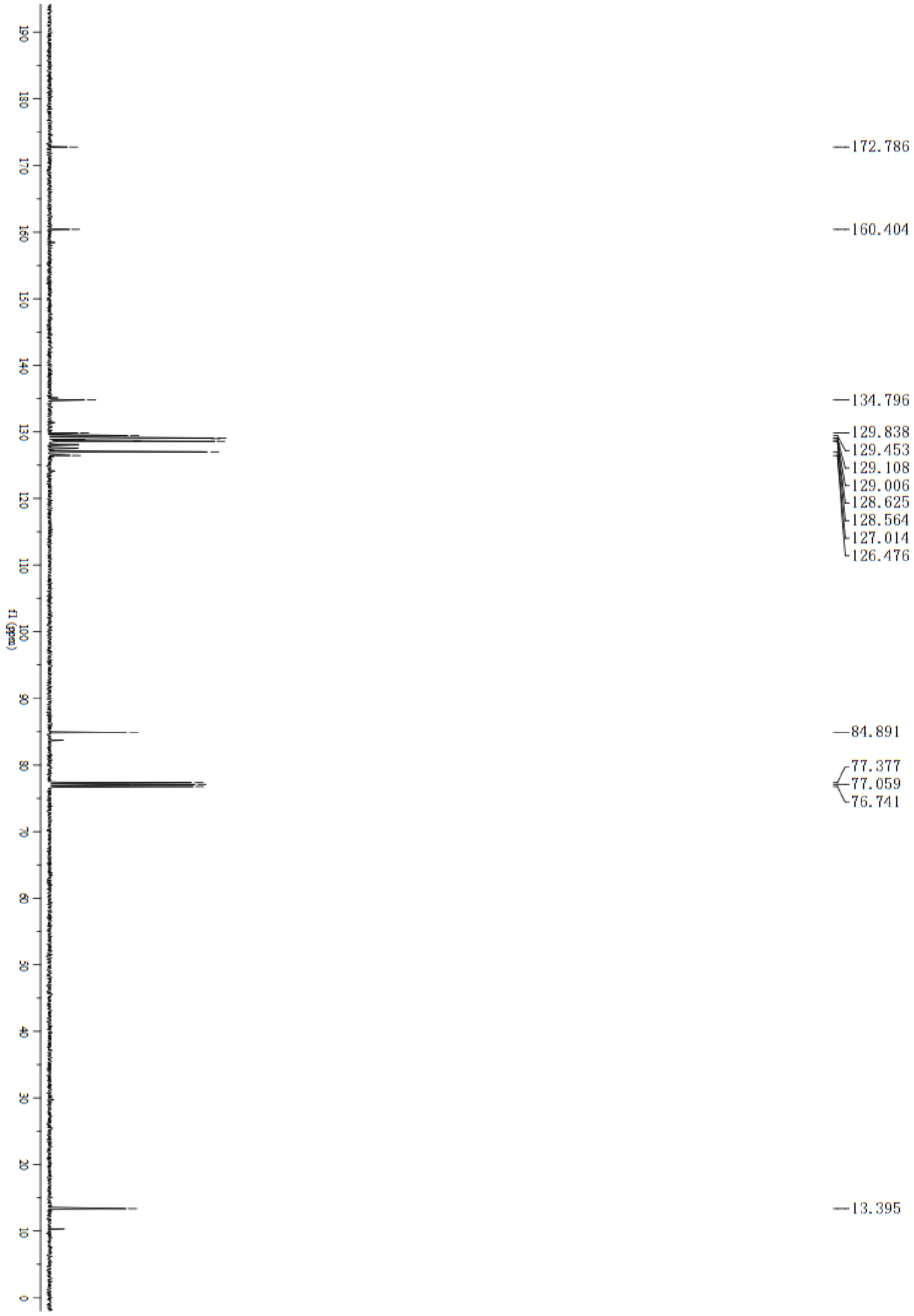
7. Appendix (copies of ^{1}H and ^{13}C NMR spectra)

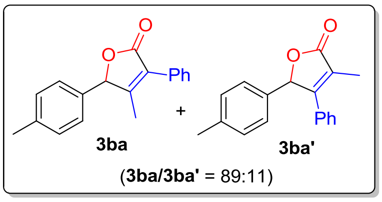


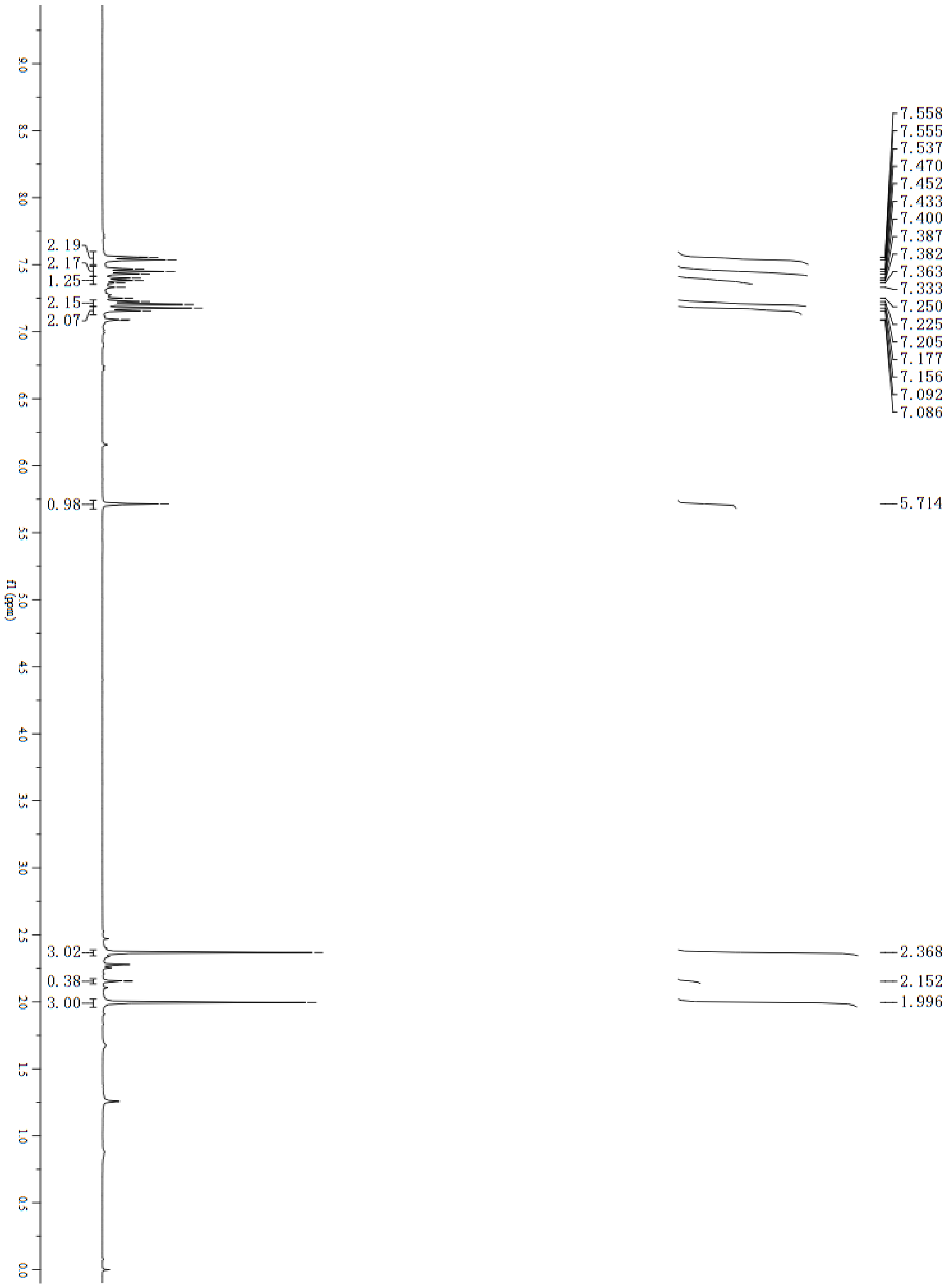


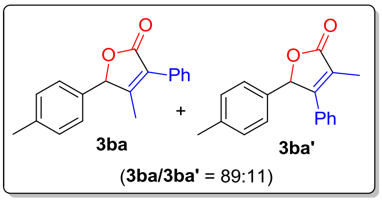

Ph
3aa
+
Ph
3aa'

(**3aa**/**3aa'** = 85:15)

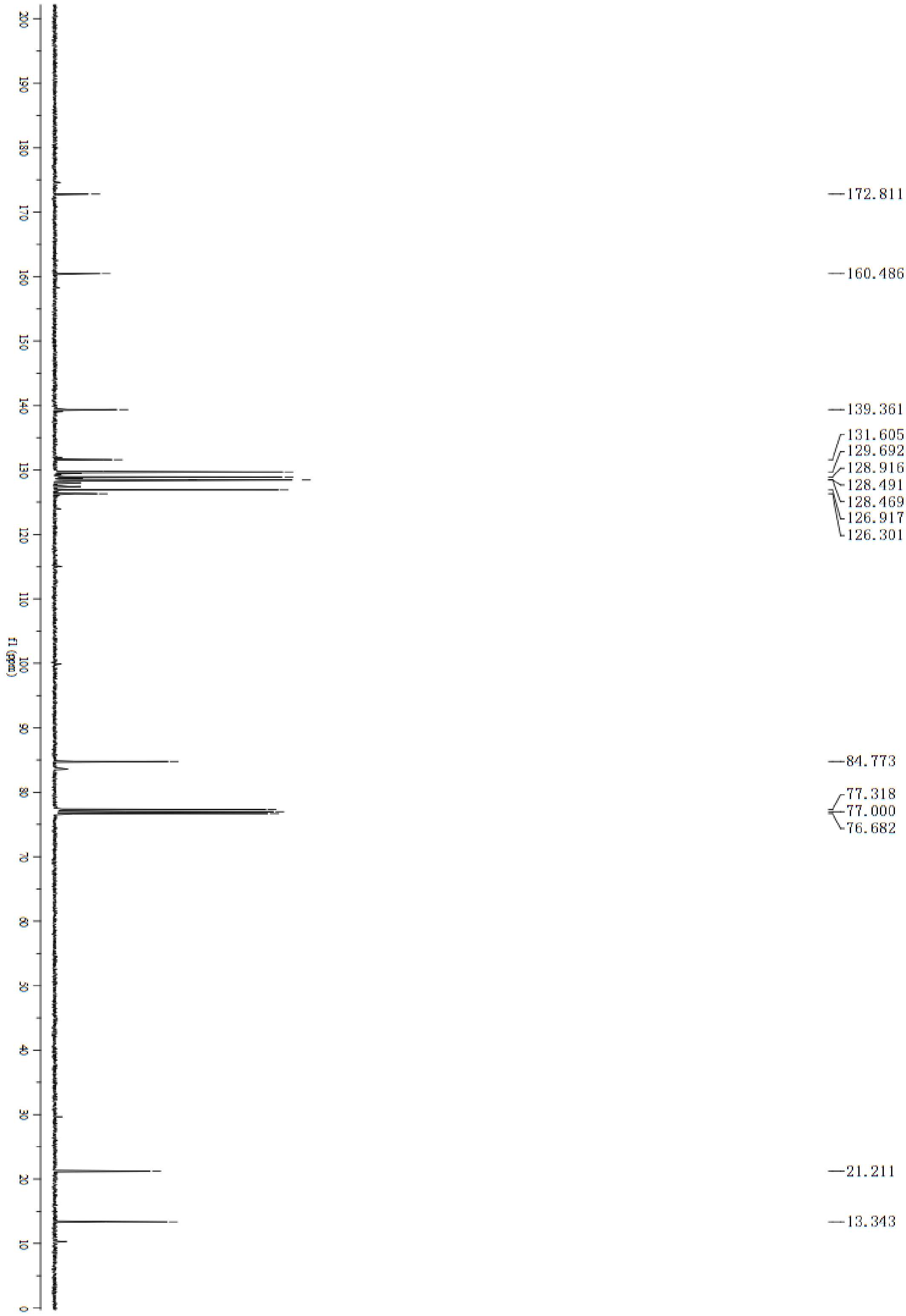

172.786
160.404
134.796
129.838
129.453
129.108
129.006
128.625
128.564
127.014
126.476
84.891
77.377
77.059
76.741
13.395

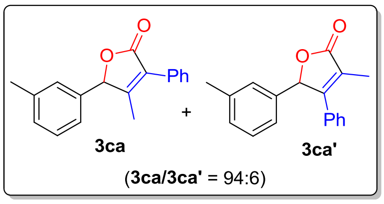

O
O
Ph
+
O
O
Ph
3ba
3ba'
(3ba/3ba' = 89:11)

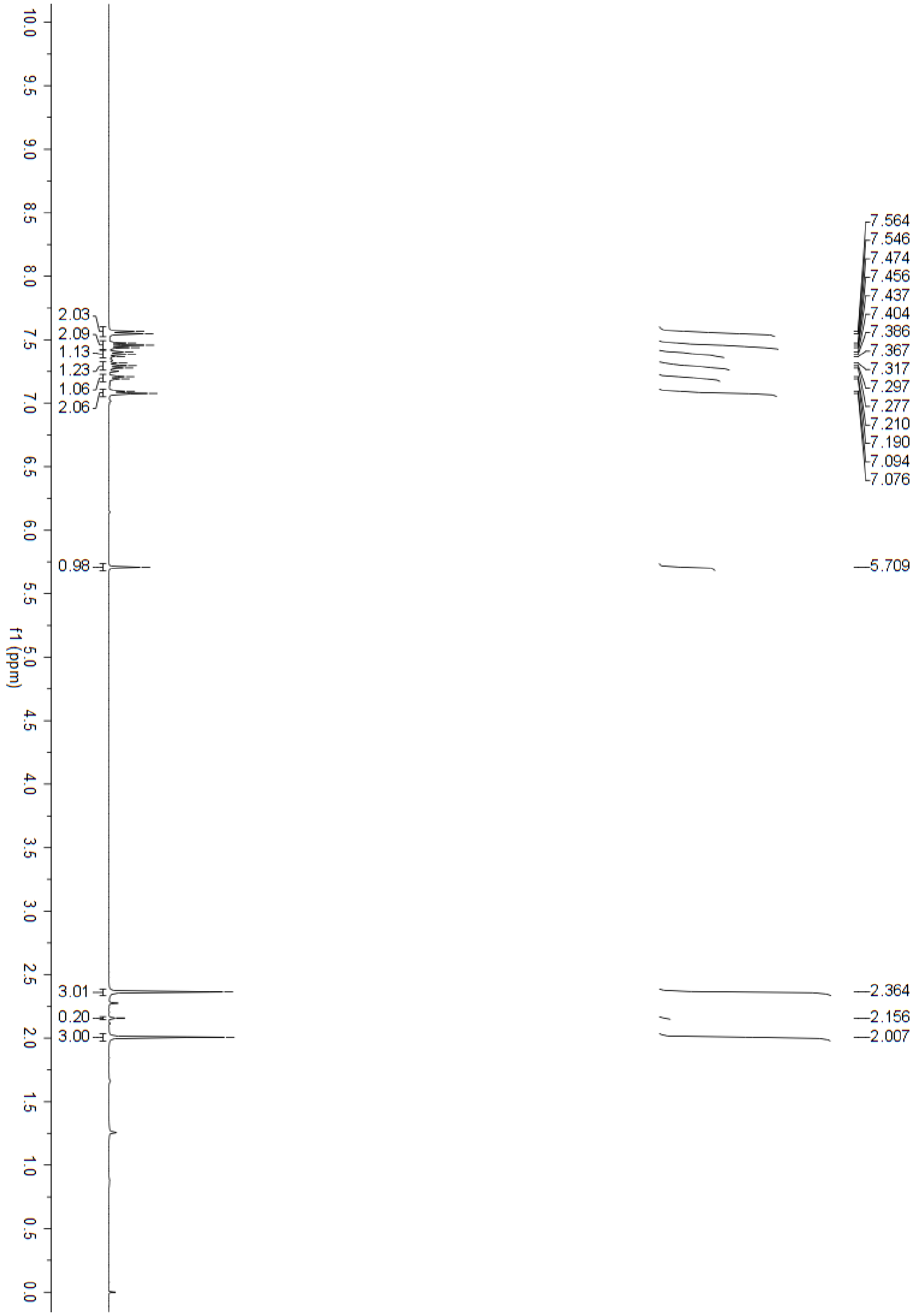

7.558
7.555
7.537
7.470
7.452
7.433
7.400
7.387
7.382
7.363
7.333
7.250
7.225
7.205
7.177
7.156
7.092
7.086
5.714
2.368
2.152
1.996
2.19
2.17
1.25
2.15
2.07
0.98
3.02
0.38
3.00
f1 (ppm)

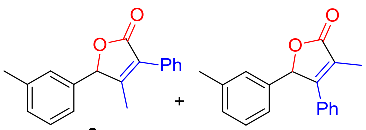

Ph
Ph
3ba
3ba'

(3ba/3ba' = 89:11)


172.811
160.486
139.361
131.605
129.692
128.916
128.491
128.469
126.917
126.301
84.773
77.318
77.000
76.682
21.211
13.343
f1 (ppm)

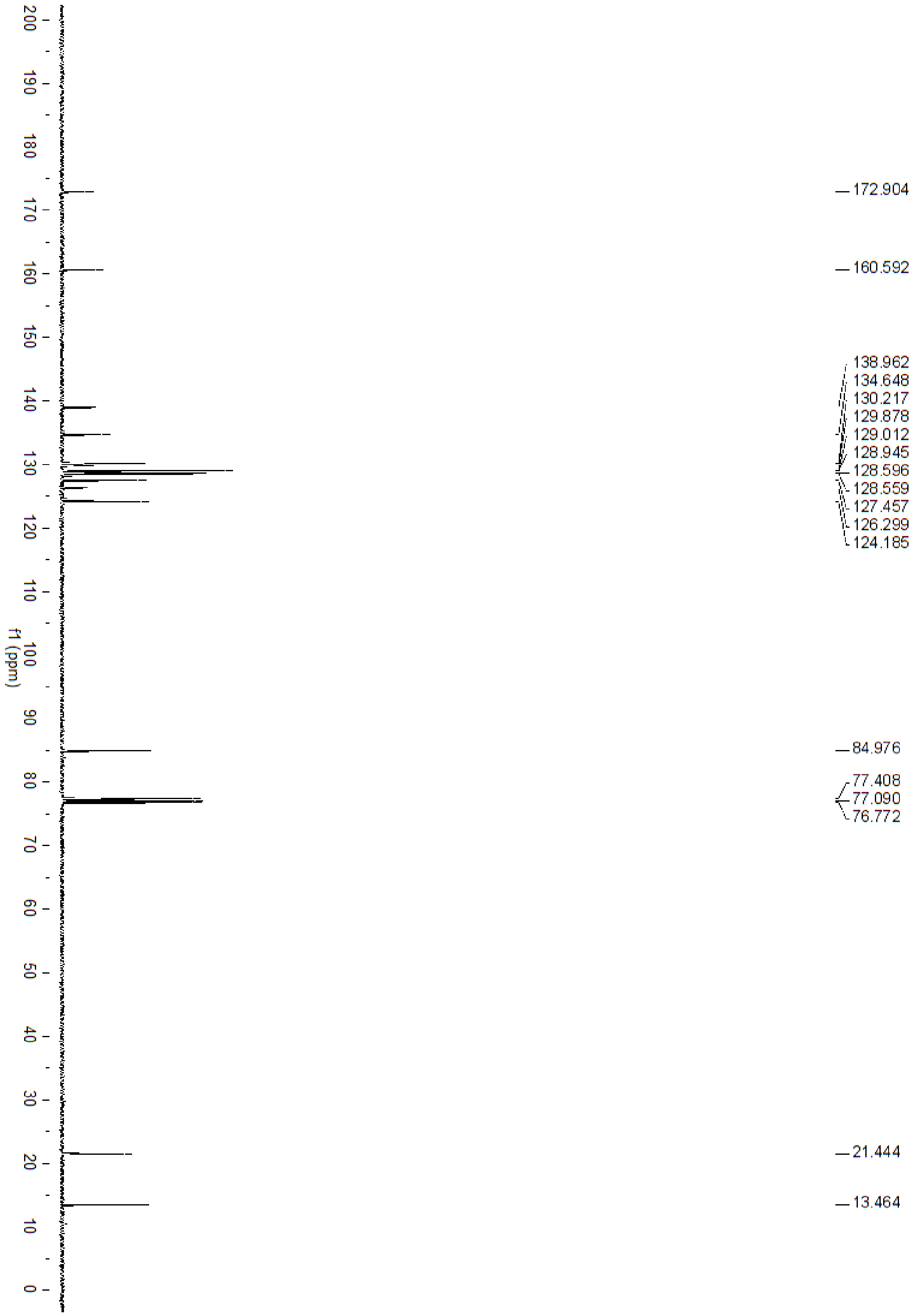

O
O
Ph
3ca
+
O
O
Ph
3ca'
(3ca/3ca' = 94:6)

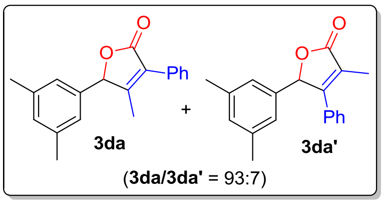

7.564
7.546
7.474
7.456
7.437
7.404
7.386
7.367
7.317
7.297
7.277
7.210
7.190
7.094
7.076
5.709
2.364
2.156
2.007
2.03
2.09
1.13
1.23
1.06
2.06
0.98
3.01
0.20
3.00
f1 (ppm)



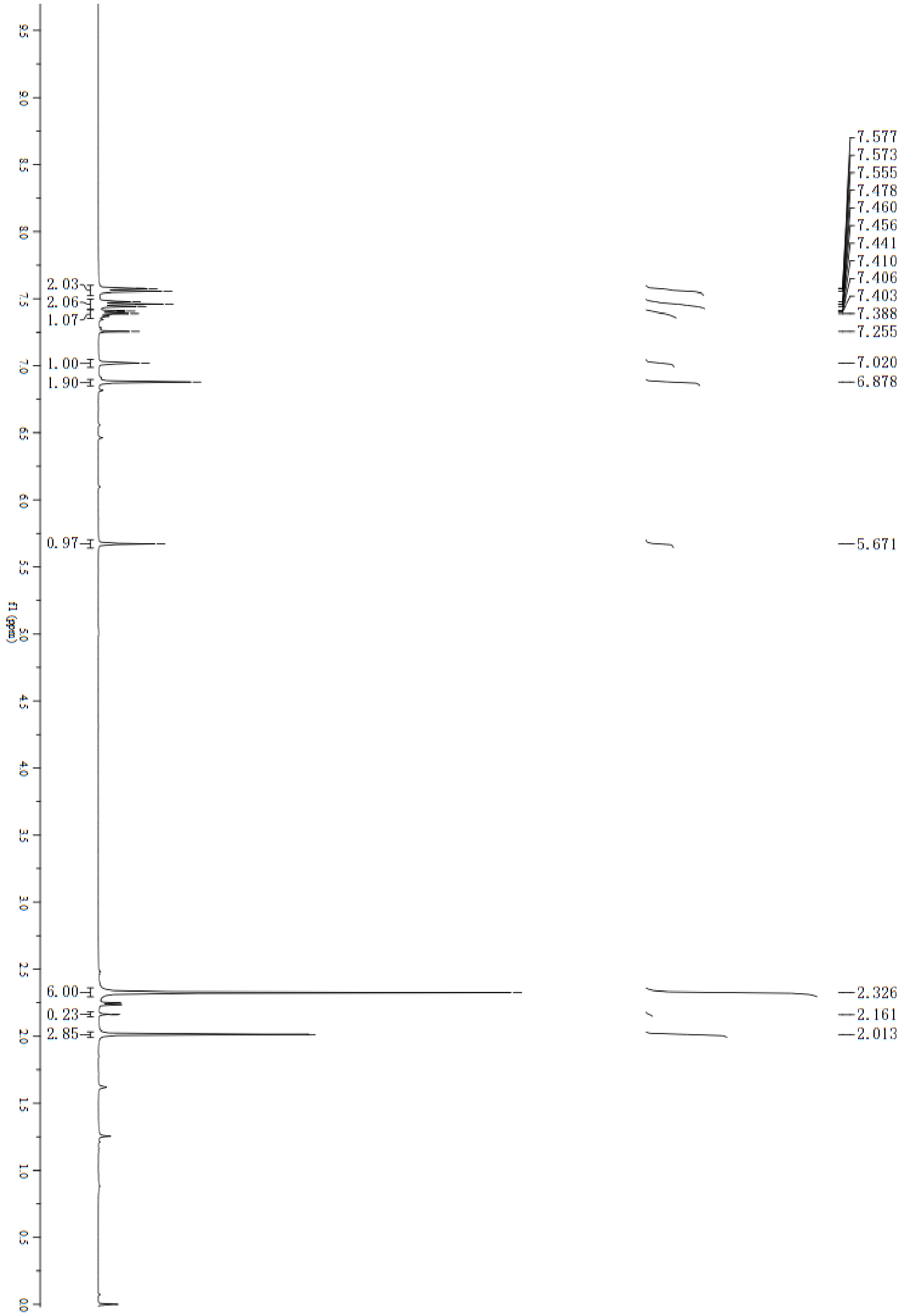
3ca **3ca'**

(**3ca**/**3ca'** = 94:6)

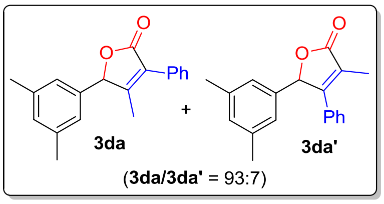


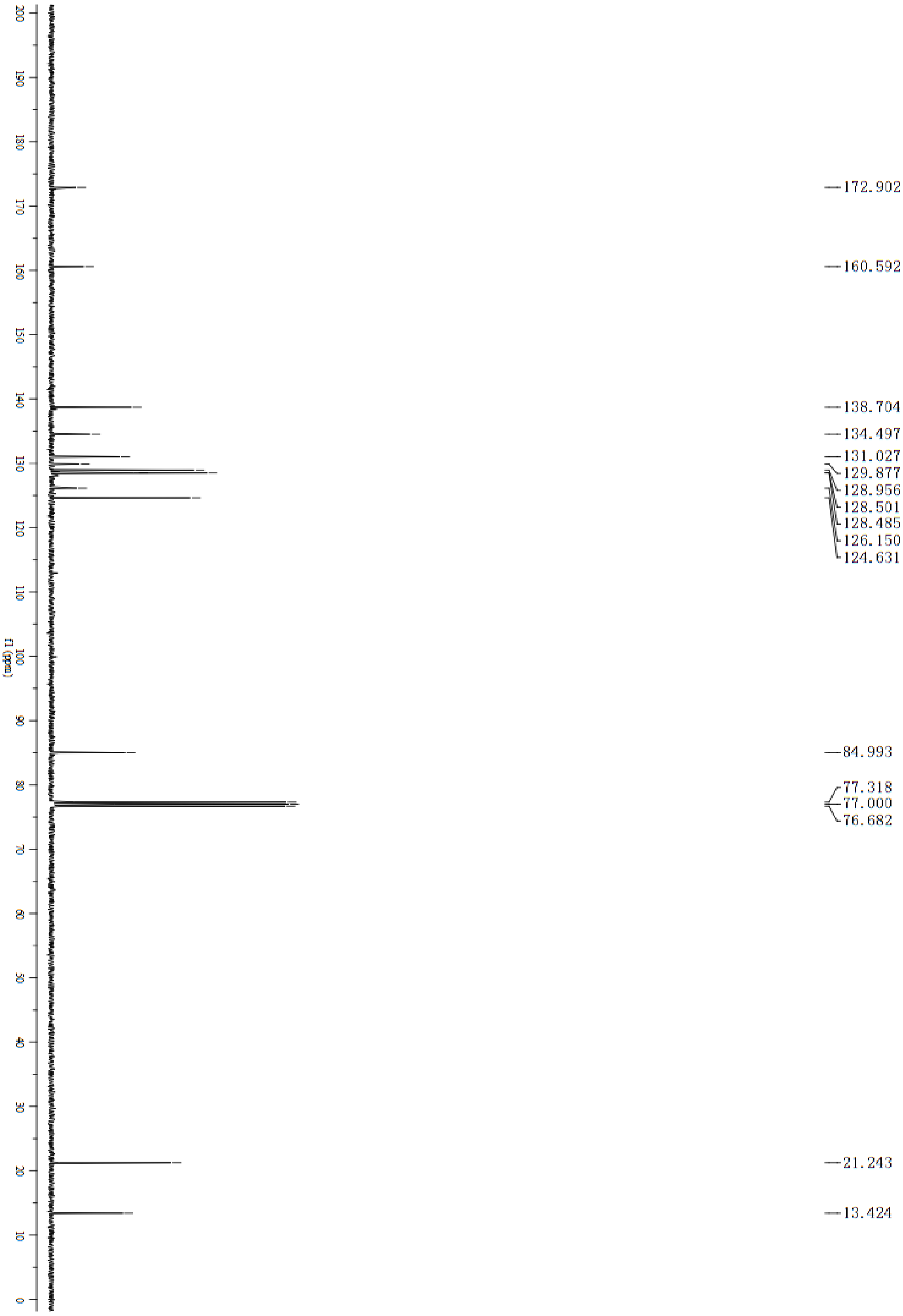


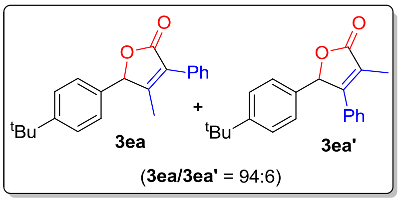
O
Ph
3da
+
3da'
(3da/3da' = 93:7)



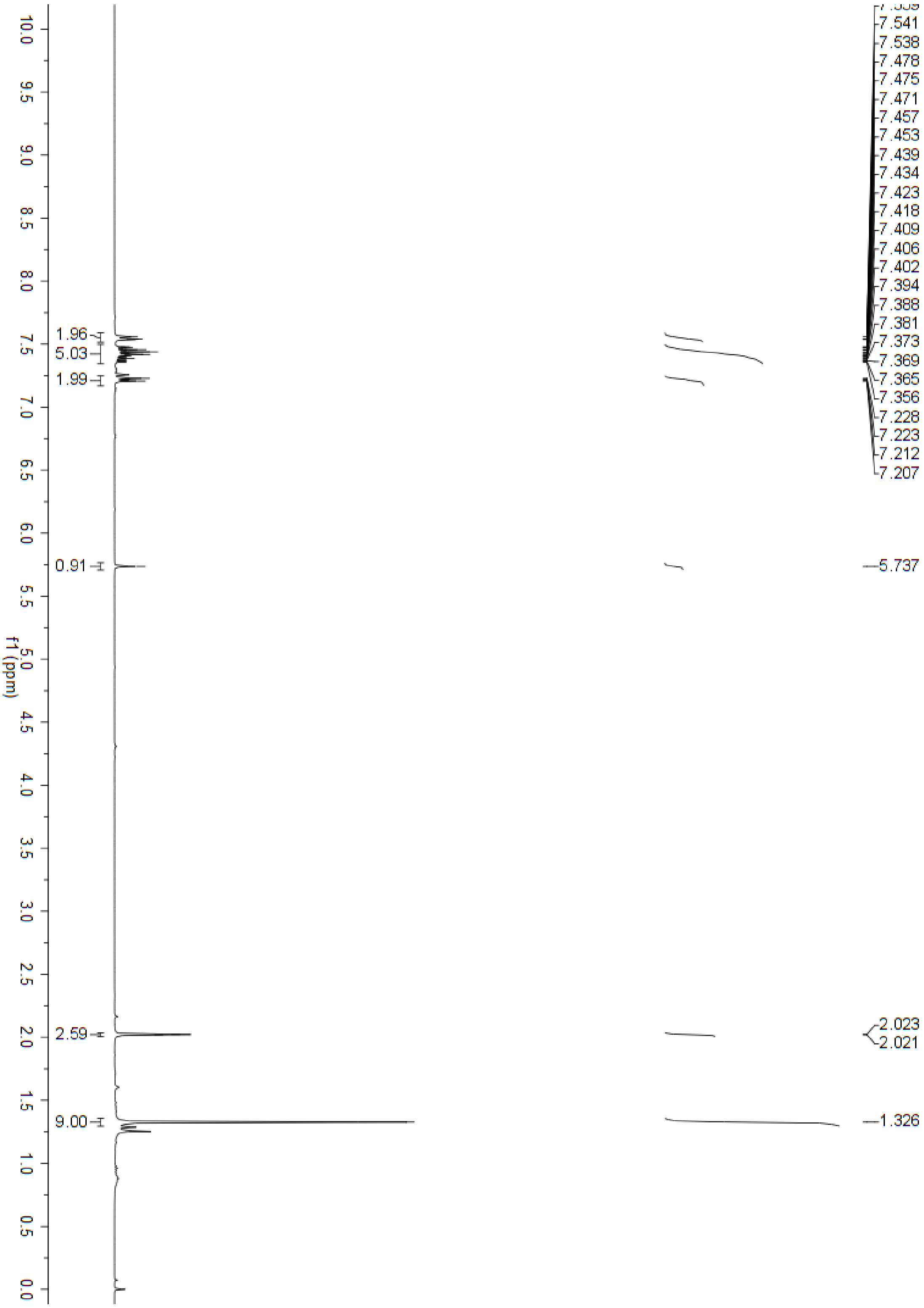
7.577
7.573
7.555
7.478
7.460
7.456
7.441
7.410
7.406
7.403
7.388
7.255
7.020
6.878
5.671
2.326
2.161
2.013
2.03
2.06
1.07
1.00
1.90
0.97
6.00
0.23
2.85
f1 (ppm)


O
O
Ph
3da
+
O
O
Ph
3da'
(3da/3da' = 93:7)

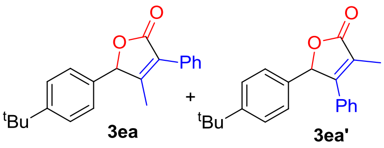

172.902
160.592
138.704
134.497
131.027
129.877
128.956
128.501
128.485
126.150
124.631
84.993
77.318
77.000
76.682
21.243
13.424
f1 (ppm)



Ph
tBu
3ea
+
Ph
3ea'
(3ea/3ea' = 94:6)

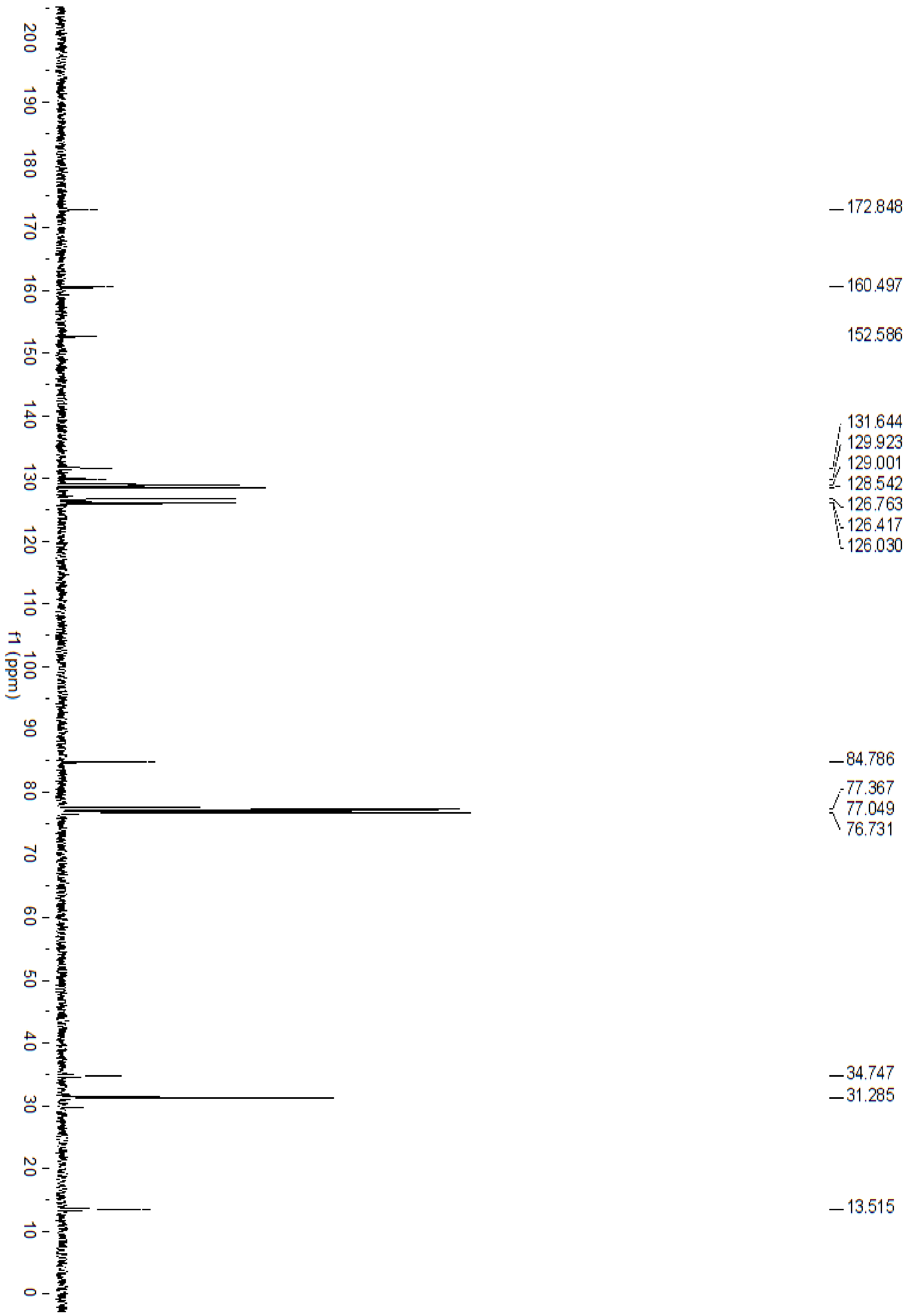


7.541
7.538
7.478
7.475
7.471
7.457
7.453
7.439
7.434
7.423
7.418
7.409
7.406
7.402
7.394
7.388
7.381
7.373
7.369
7.365
7.356
7.228
7.223
7.212
7.207
5.737
2.023
2.021
1.326
1.96
5.03
1.99
0.91
2.59
9.00
f1 (ppm)

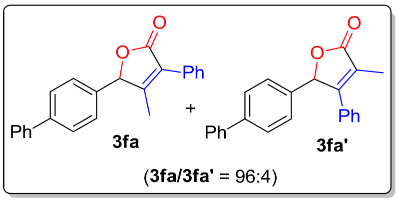


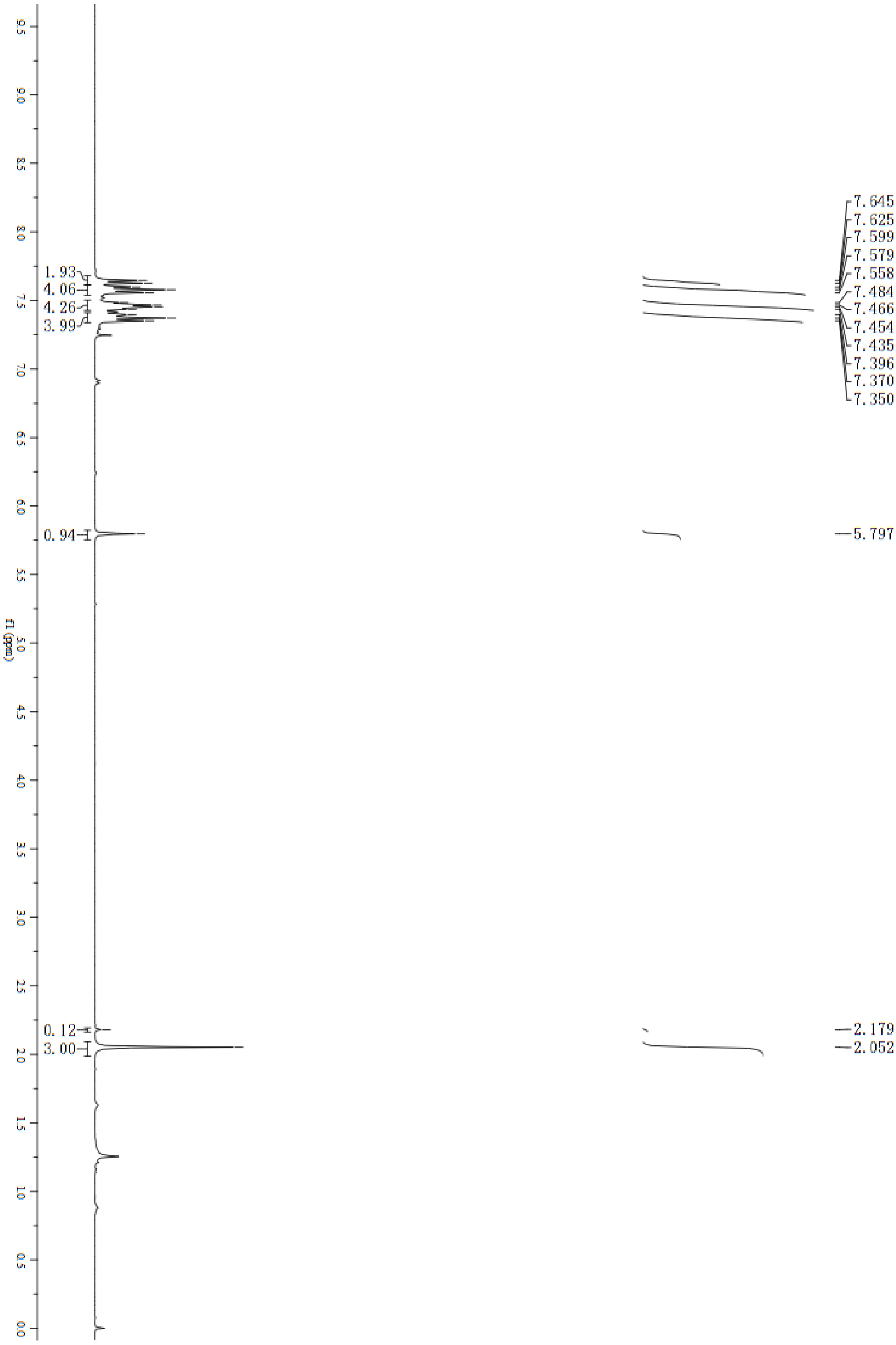
O
Ph
+
tBu
3ea
3ea'

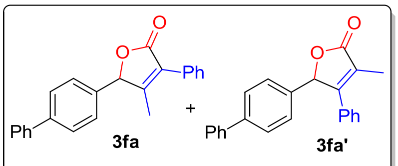
(**3ea**/**3ea'** = 94:6)

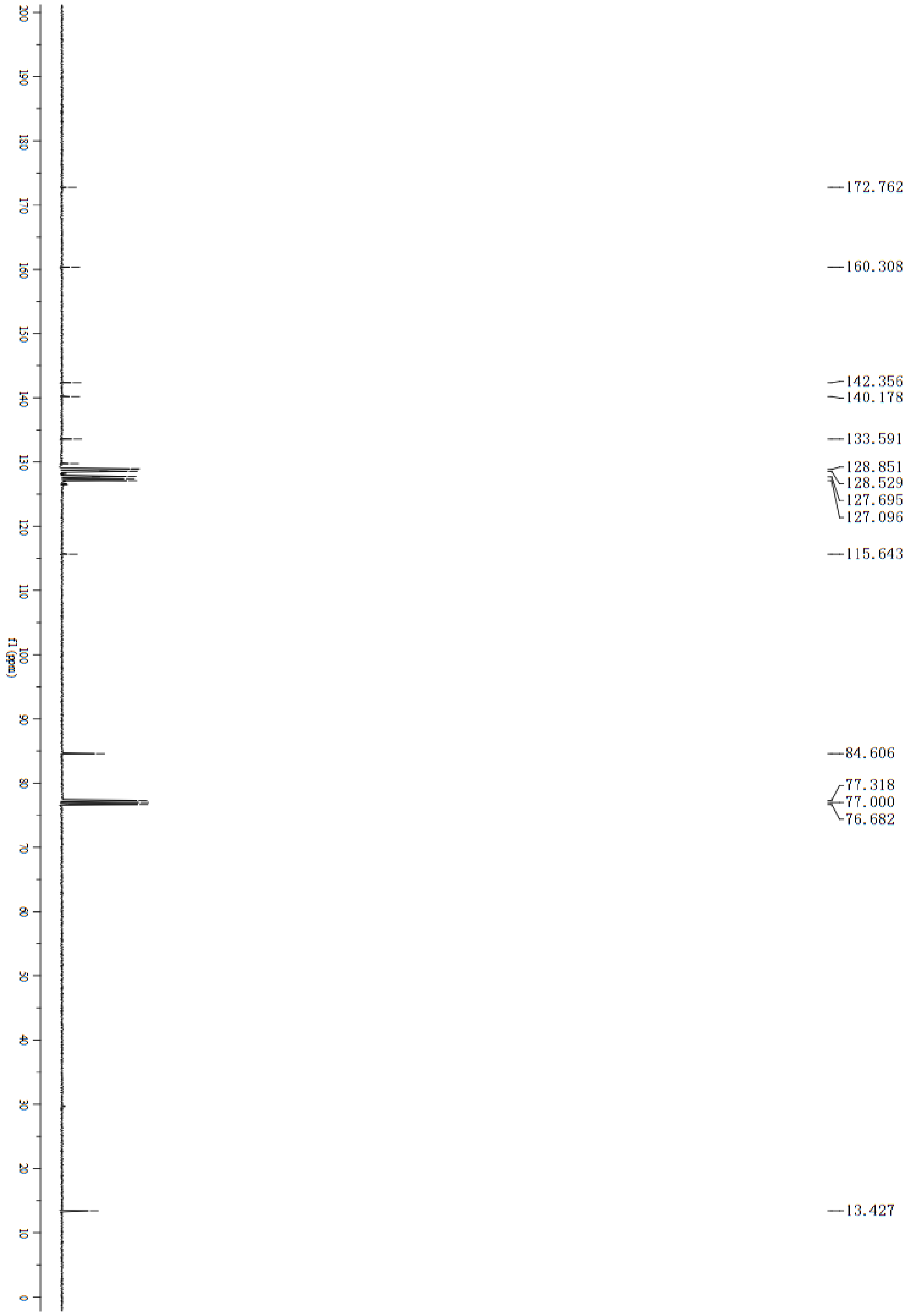


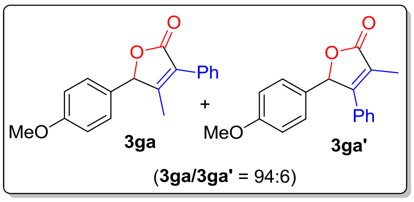
172.848
160.497
152.586
131.644
129.923
129.001
128.542
126.763
126.417
126.030
84.786
77.367
77.049
76.731
34.747
31.285
13.515
f1 (ppm)


O
O
Ph
Ph
3fa
+
O
O
Ph
Ph
3fa'
(3fa/3fa' = 96:4)

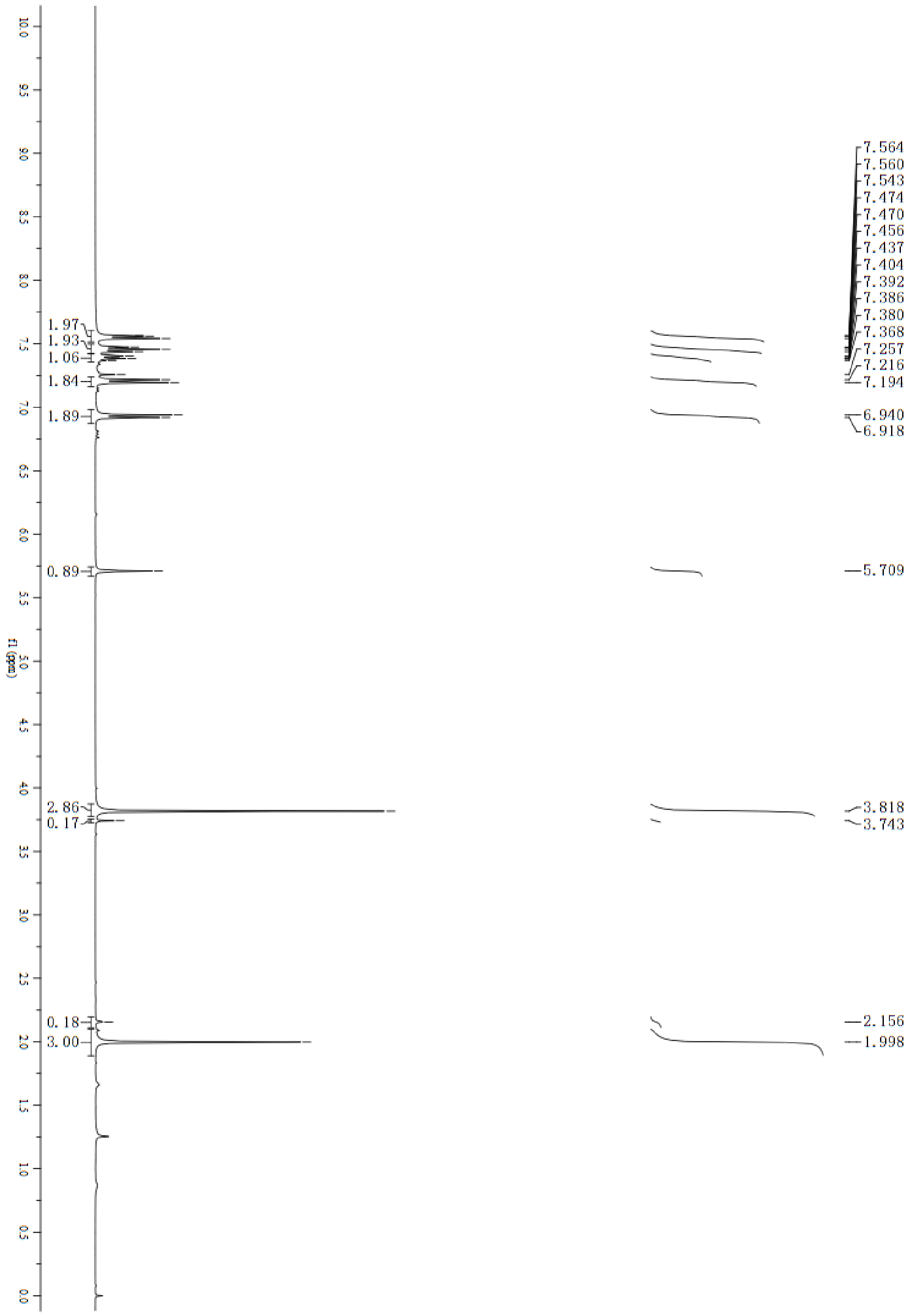

7.645
7.625
7.599
7.579
7.558
7.484
7.466
7.454
7.435
7.396
7.370
7.350
5.797
2.179
2.052
1.93
4.06
4.26
3.99
0.94
0.12
3.00
f1 (ppm)


Ph
Ph
3fa
+
Ph
Ph
3fa'
(**3fa**/**3fa'** = 96:4)

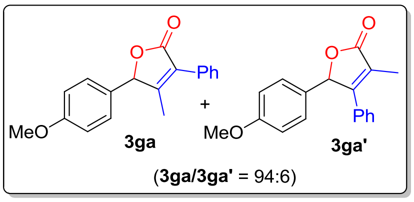

172.762
160.308
142.356
140.178
133.591
128.851
128.529
127.695
127.096
115.643
84.606
77.318
77.000
76.682
13.427
f1 (ppm)



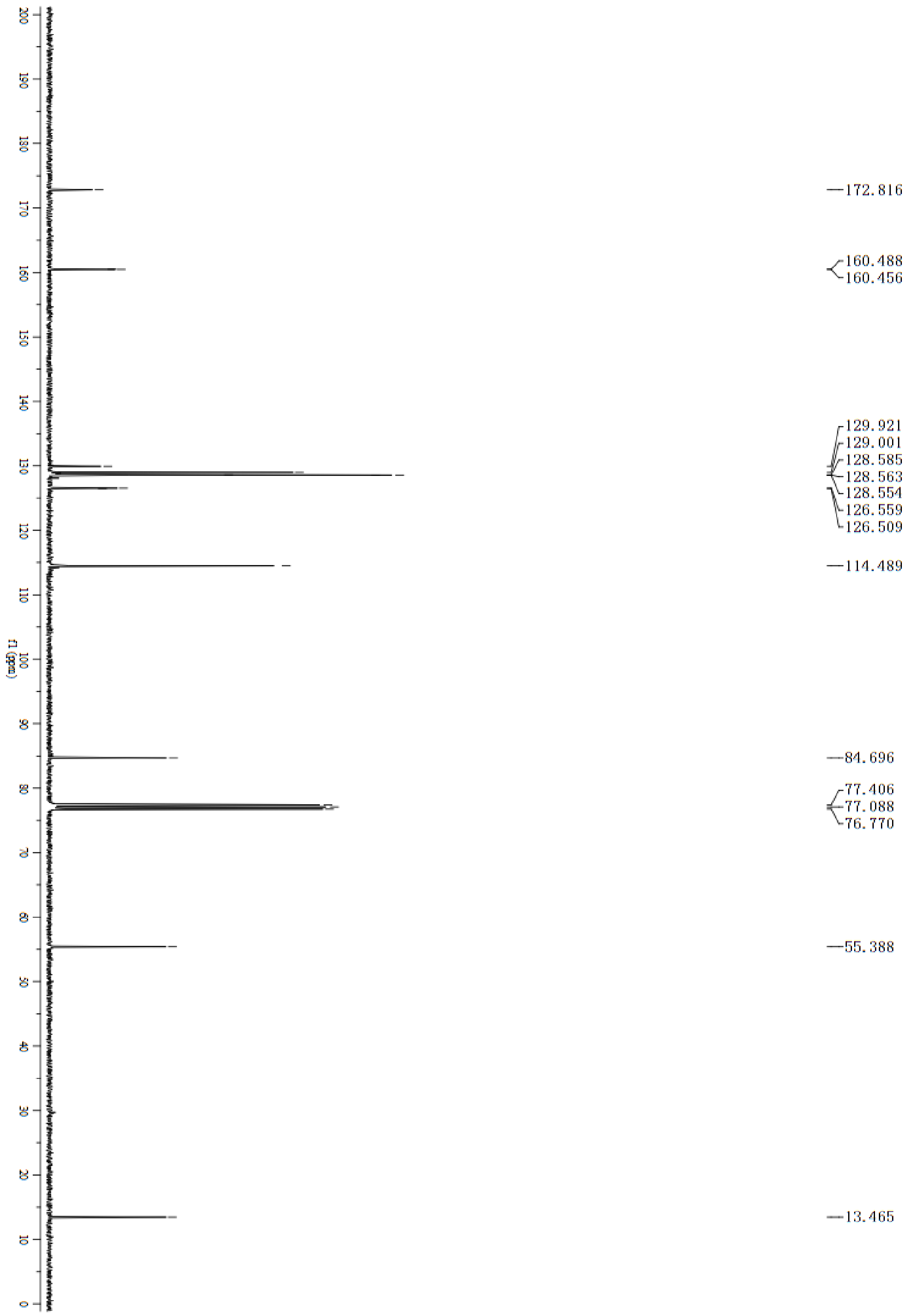
MeO
3ga
MeO
3ga'
Ph
Ph
(3ga/3ga' = 94:6)



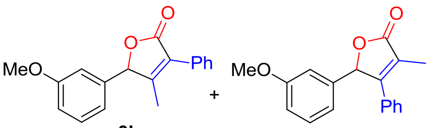
7.564
7.560
7.543
7.474
7.470
7.456
7.437
7.404
7.392
7.386
7.380
7.368
7.257
7.216
7.194
6.940
6.918
5.709
3.818
3.743
2.156
1.998
1.97
1.93
1.06
1.84
1.89
0.89
2.86
0.17
0.18
3.00
f1 (ppm)



MeO
3ga
MeO
3ga'
(3ga/3ga' = 94:6)

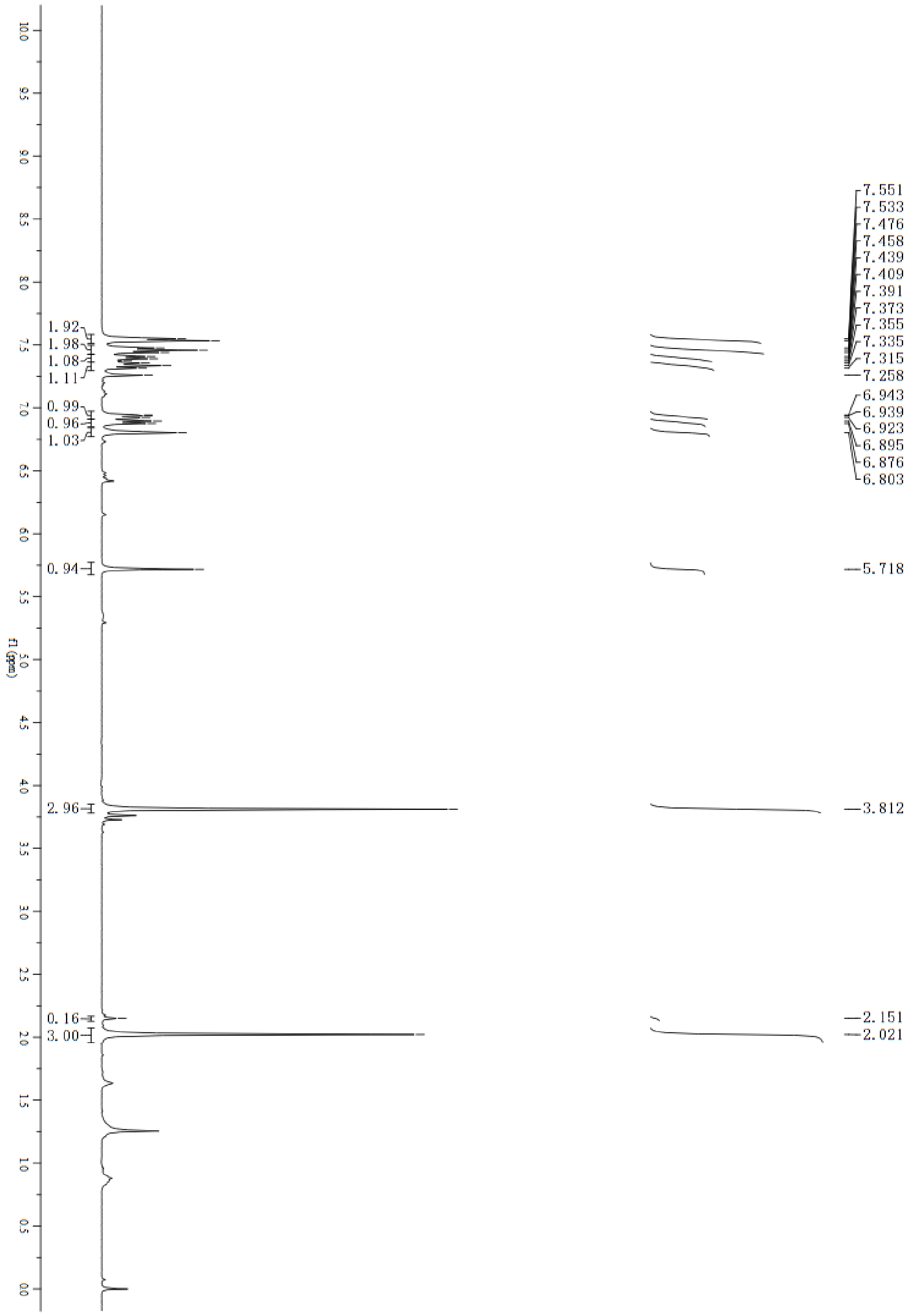


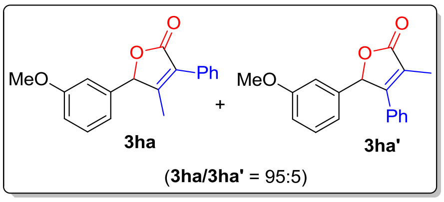
172.816
160.488
160.456
129.921
129.001
128.585
128.563
128.554
126.559
126.509
114.489
84.696
77.406
77.088
76.770
55.388
13.465
f1 (ppm)

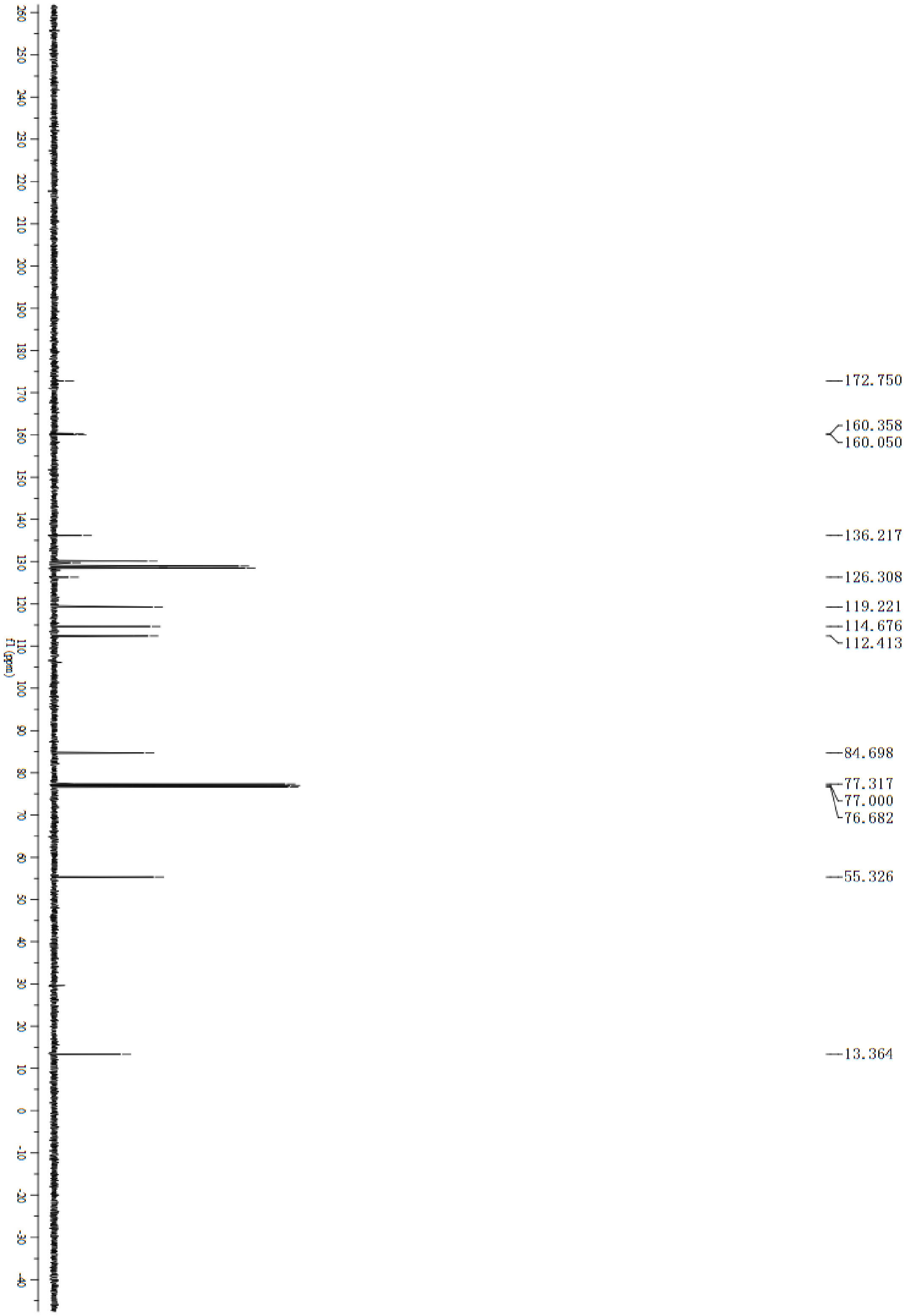


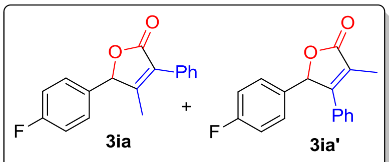
3ha **3ha'**

(**3ha**/**3ha'** = 95:5)

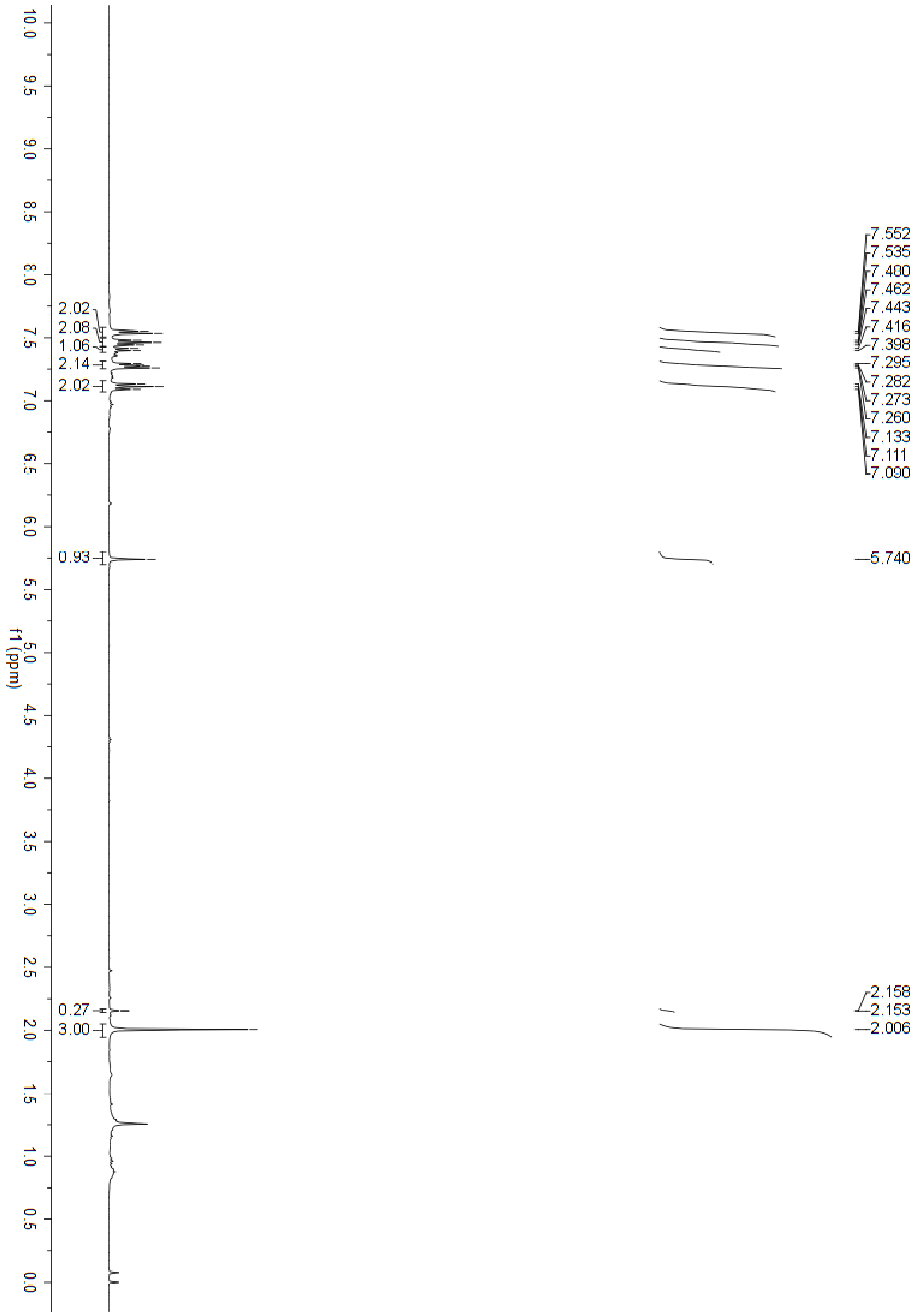


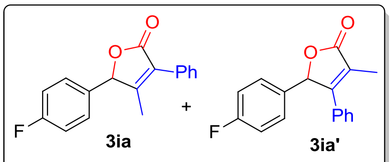

MeO
O
O
Ph
3ha
+
MeO
O
O
Ph
3ha'
(3ha/3ha' = 95:5)


172.750
160.358
160.050
136.217
126.308
119.221
114.676
112.413
84.698
77.317
77.000
76.682
55.326
13.364
f1 (ppm)

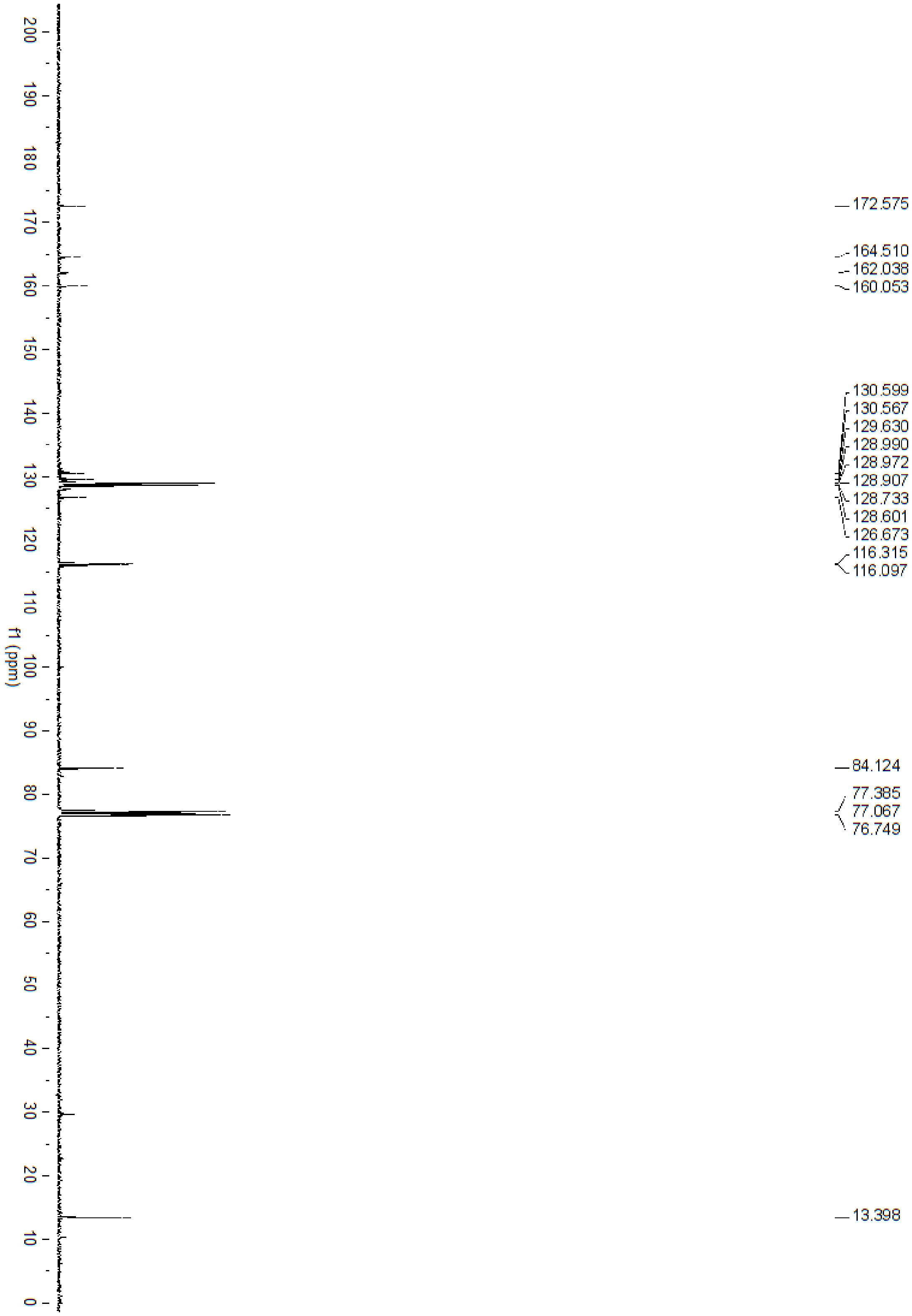

O
O
Ph
F
3ia
+
O
O
Ph
F
3ia'

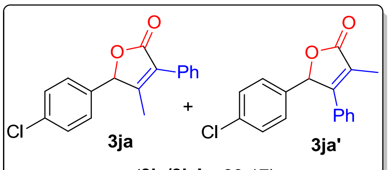
(**3ia**/**3ia'** = 92:8)


7.552
7.535
7.480
7.462
7.443
7.416
7.398
7.295
7.282
7.273
7.260
7.133
7.111
7.090
5.740
2.158
2.153
2.006
2.02
2.08
1.06
2.14
2.02
0.93
0.27
3.00
f1 (ppm)


O
O
Ph
F
3ia
+
O
O
Ph
F
3ia'

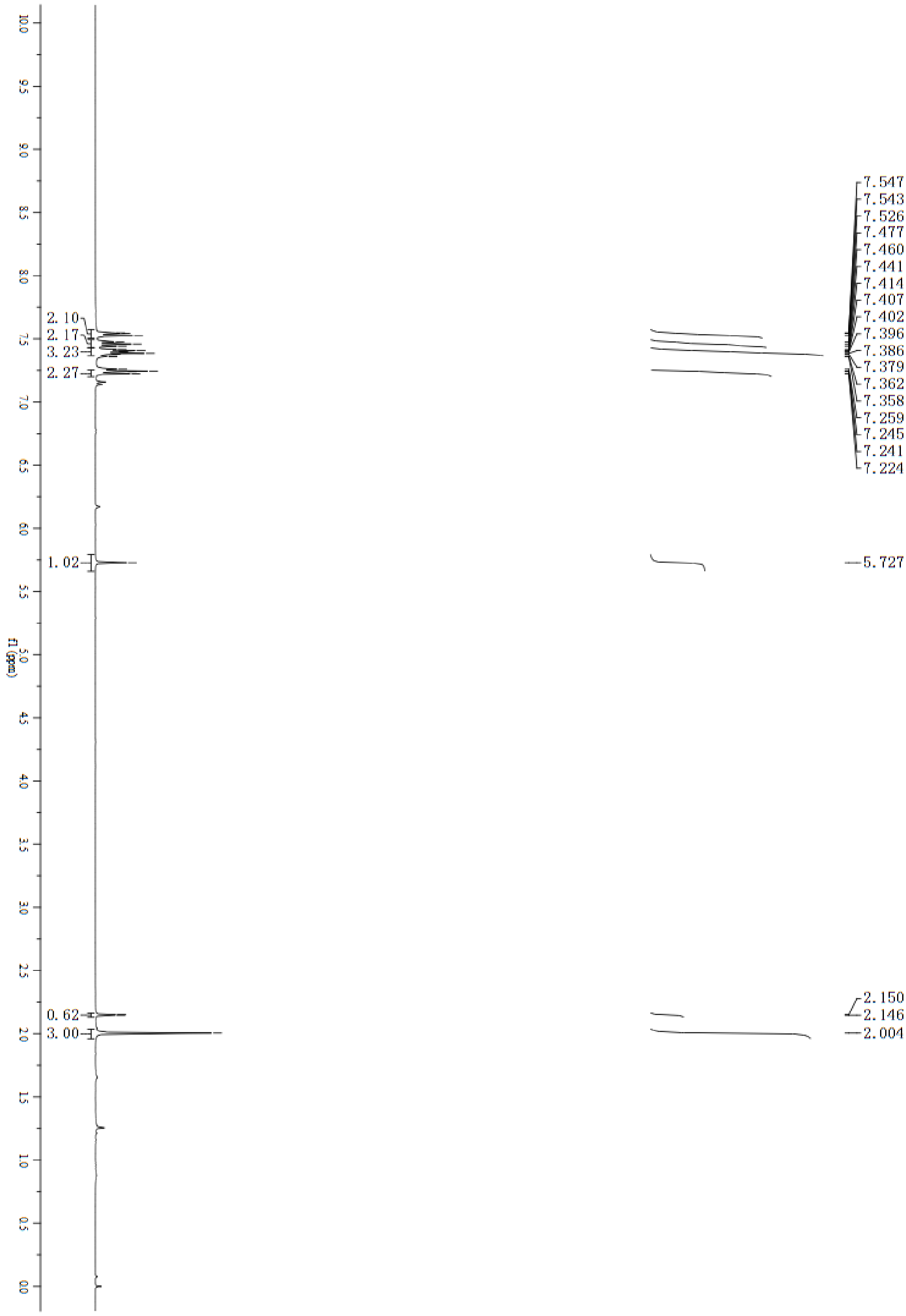
(**3ia**/**3ia'** = 92:8)

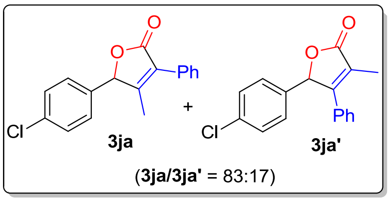

172.575
164.510
162.038
160.053
130.599
130.567
129.630
128.990
128.972
128.907
128.733
128.601
126.673
116.315
116.097
84.124
77.385
77.067
76.749
13.398
f1 (ppm)
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0

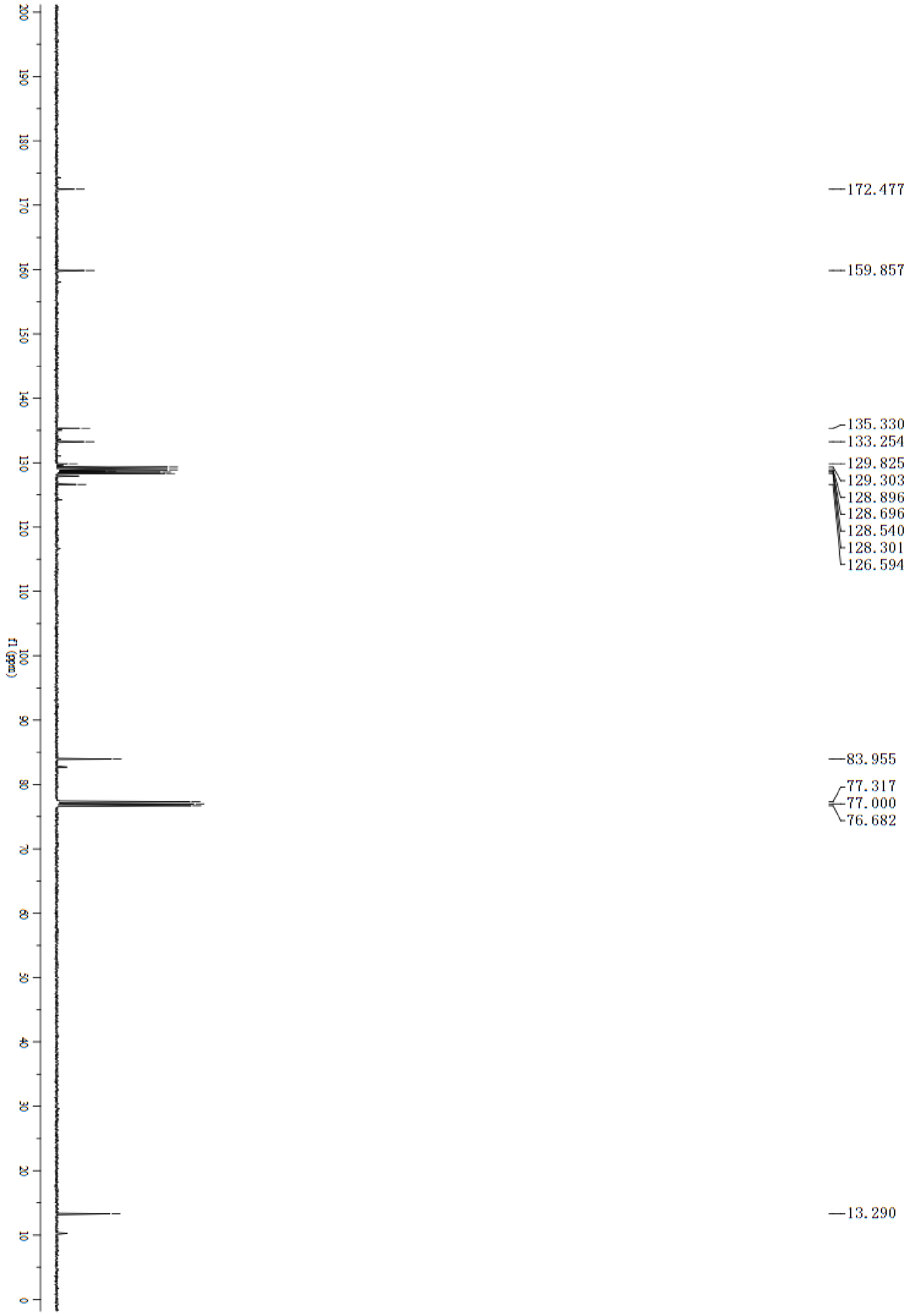


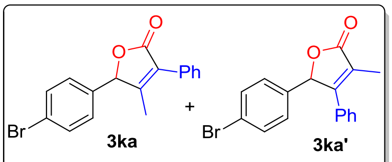
3ja **3ja'**

(**3ja/3ja'** = 83:17)



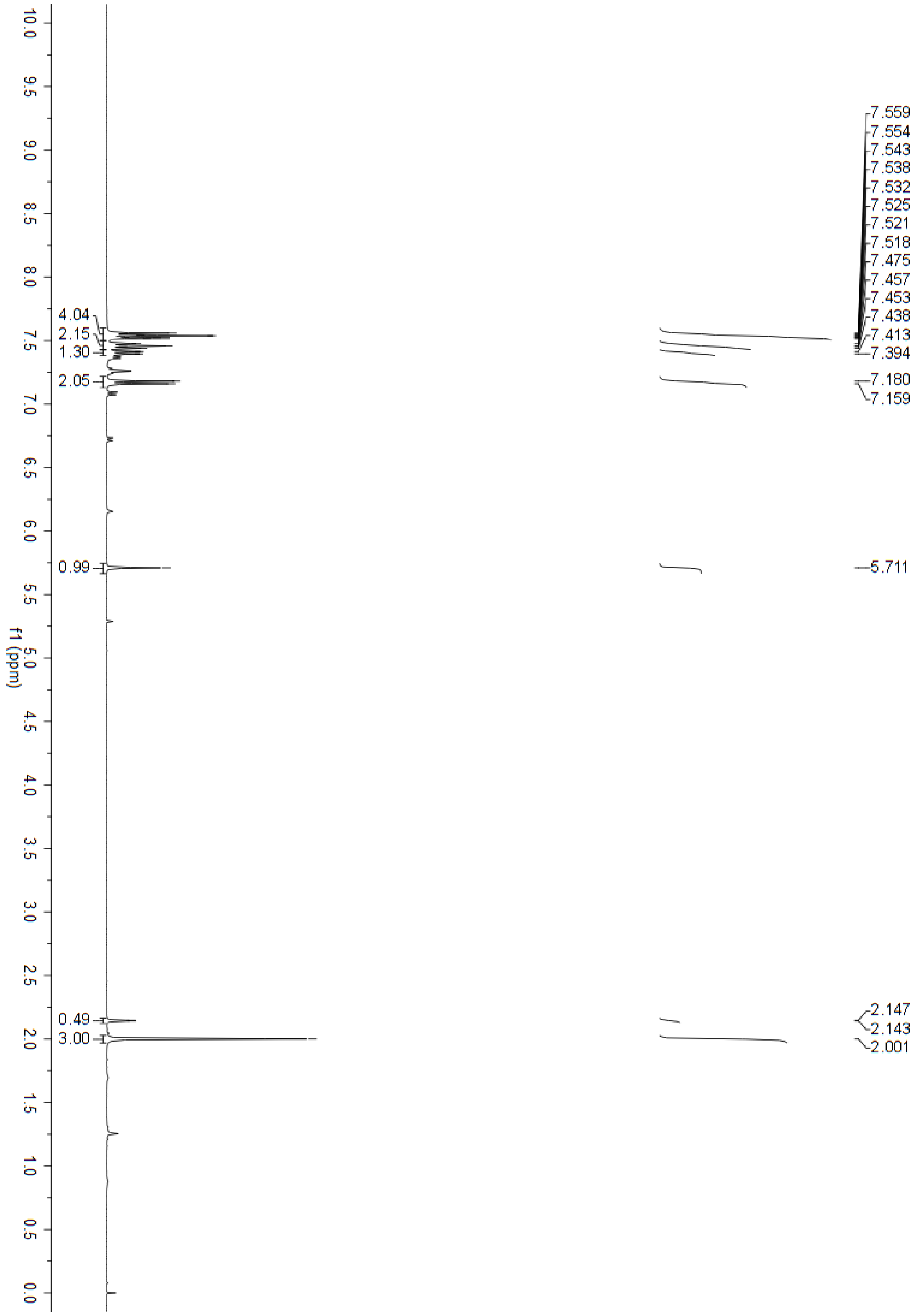

Ph
Cl
3ja
+
Ph
Cl
3ja'
(3ja/3ja' = 83:17)

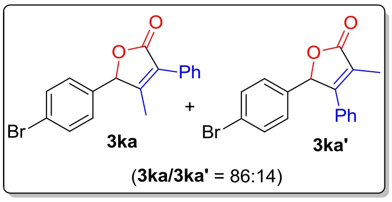

172.477
159.857
135.330
133.254
129.825
129.303
128.896
128.696
128.540
128.301
126.594
83.955
77.317
77.000
76.682
13.290
f1 (ppm)

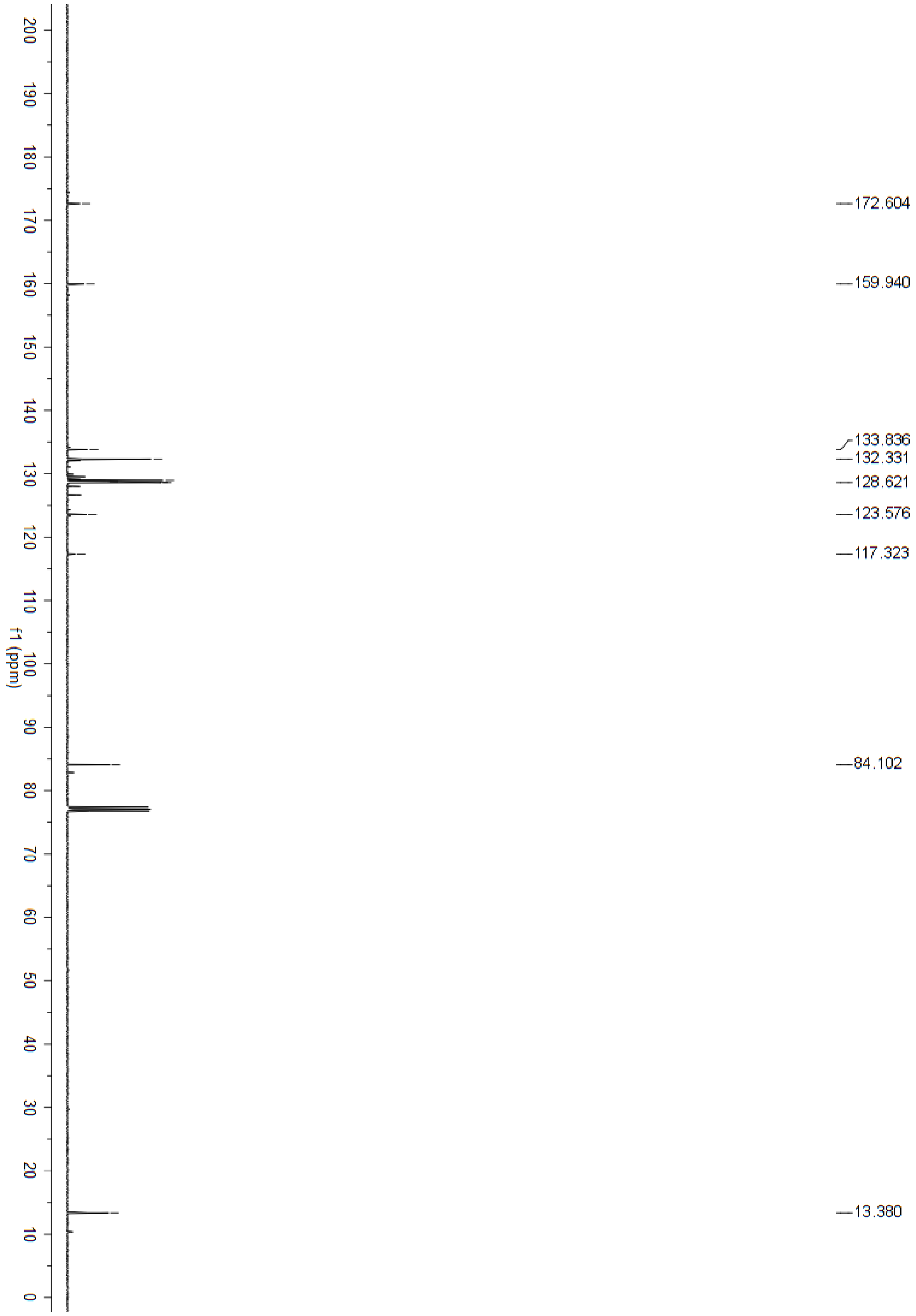


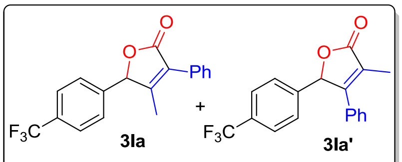
3ka **3ka'**

(**3ka/3ka'** = 86:14)

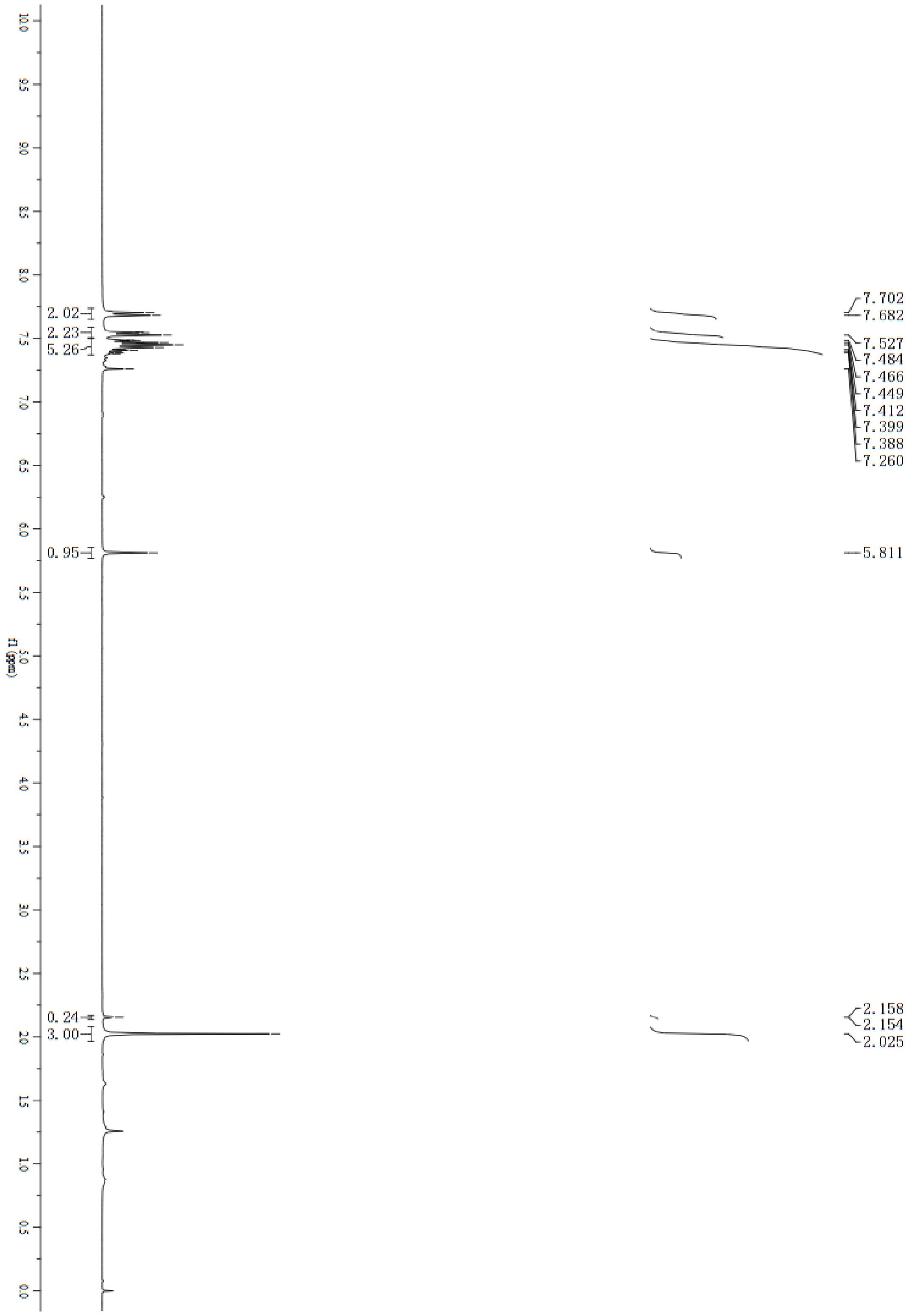


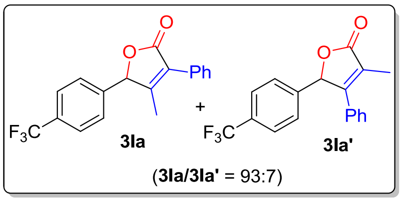

O
O
Ph
Br
3ka
+
O
O
Ph
Br
3ka'
(3ka/3ka' = 86:14)

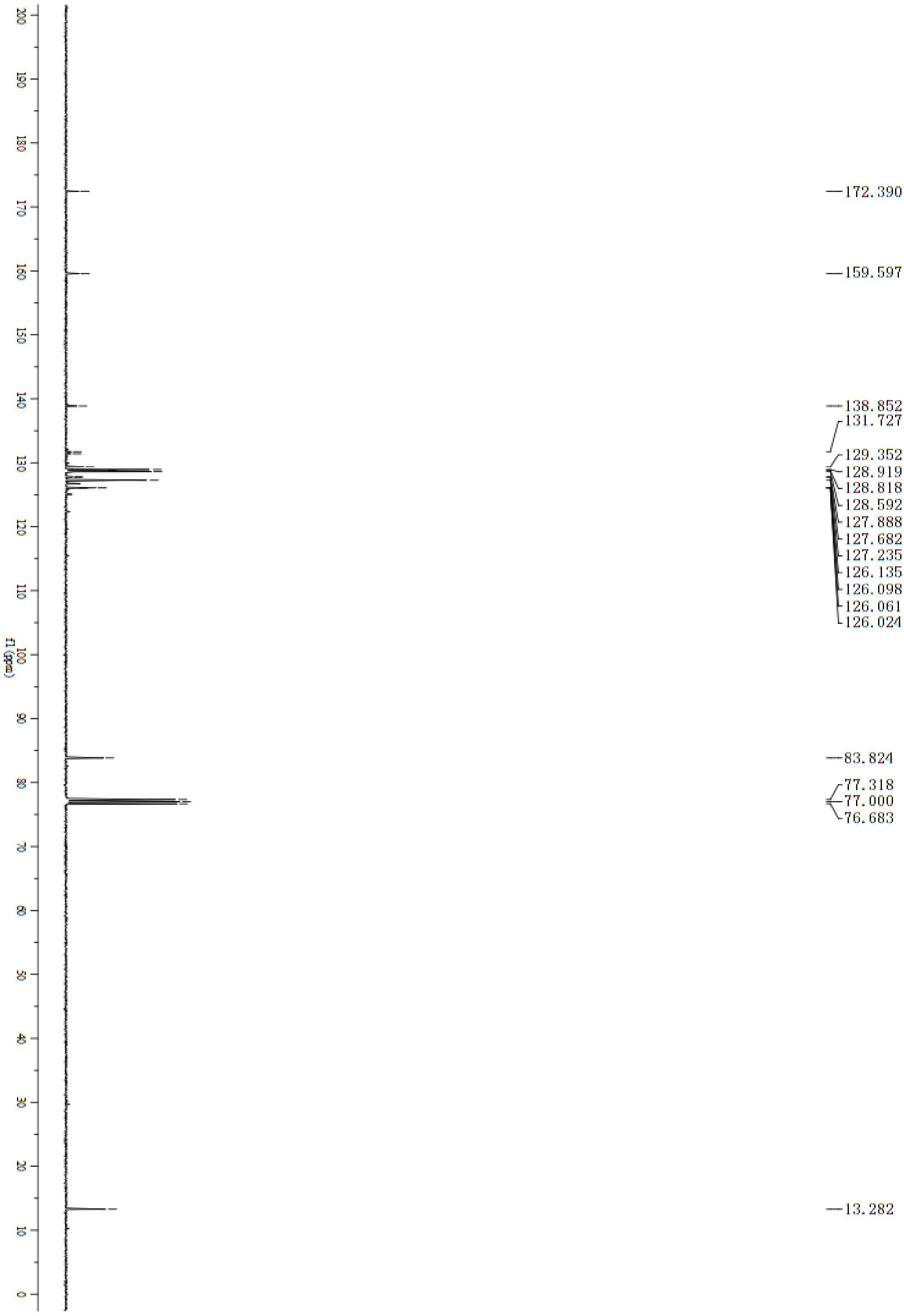

172.604
159.940
133.836
132.331
128.621
123.576
117.323
84.102
13.380
f1 (ppm)

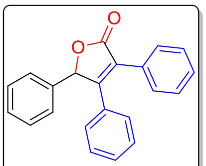

O
O
Ph
F_3C
3la
+
O
O
Ph
F_3C
3la'

(**3la**/**3la'** = 93:7)

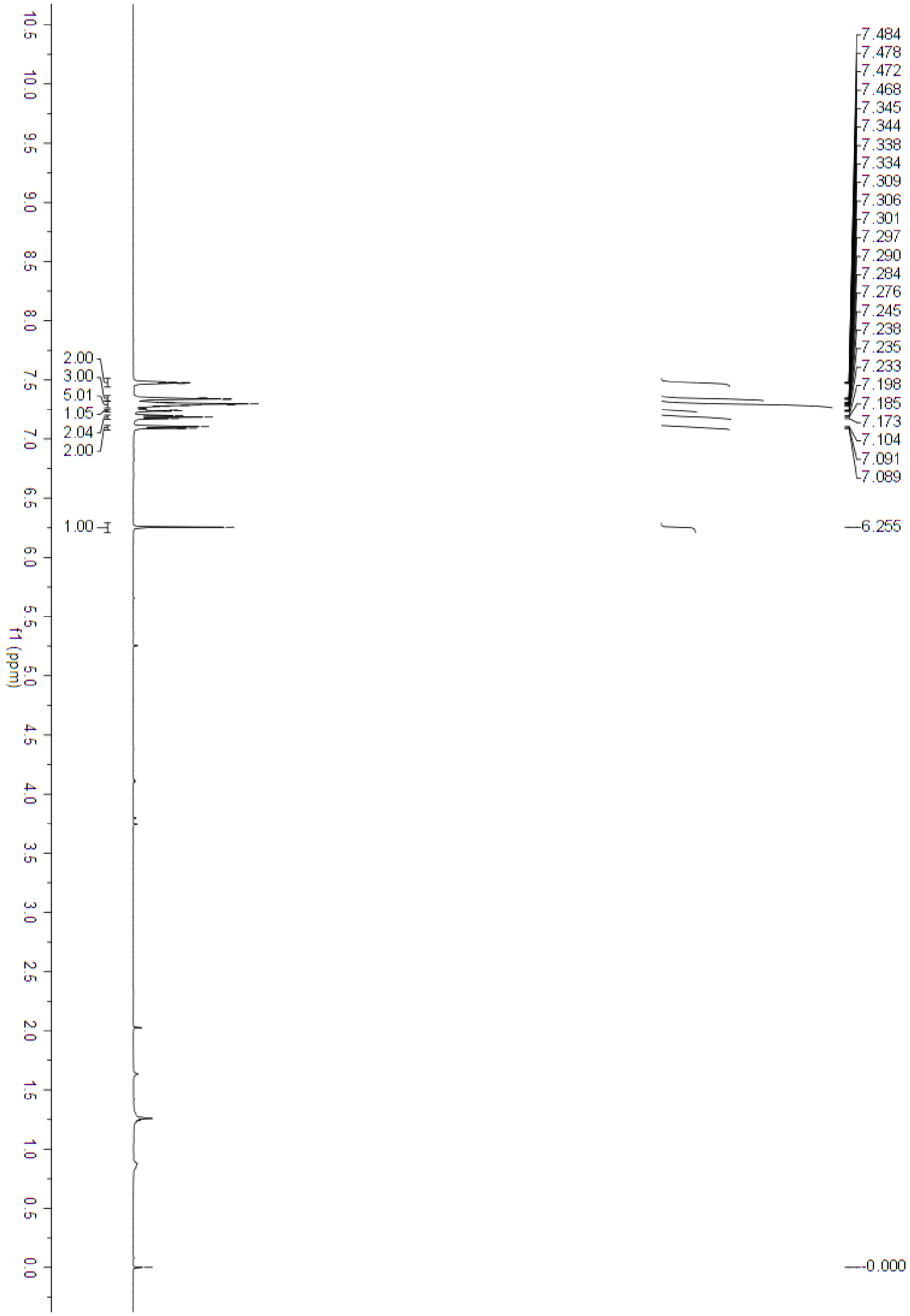

7.702
7.682
7.527
7.484
7.466
7.449
7.412
7.399
7.388
7.260
5.811
2.158
2.154
2.025
2.02
2.23
5.26
0.95
0.24
3.00
f1 (ppm)

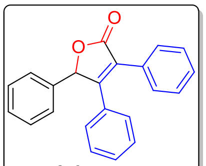

F3C
3la
+
F3C
3la'
Ph
Ph
(3la/3la' = 93:7)


172.390
159.597
138.852
131.727
129.352
128.919
128.818
128.592
127.888
127.682
127.235
126.135
126.098
126.061
126.024
83.824
77.318
77.000
76.683
13.282
f1 (ppm)

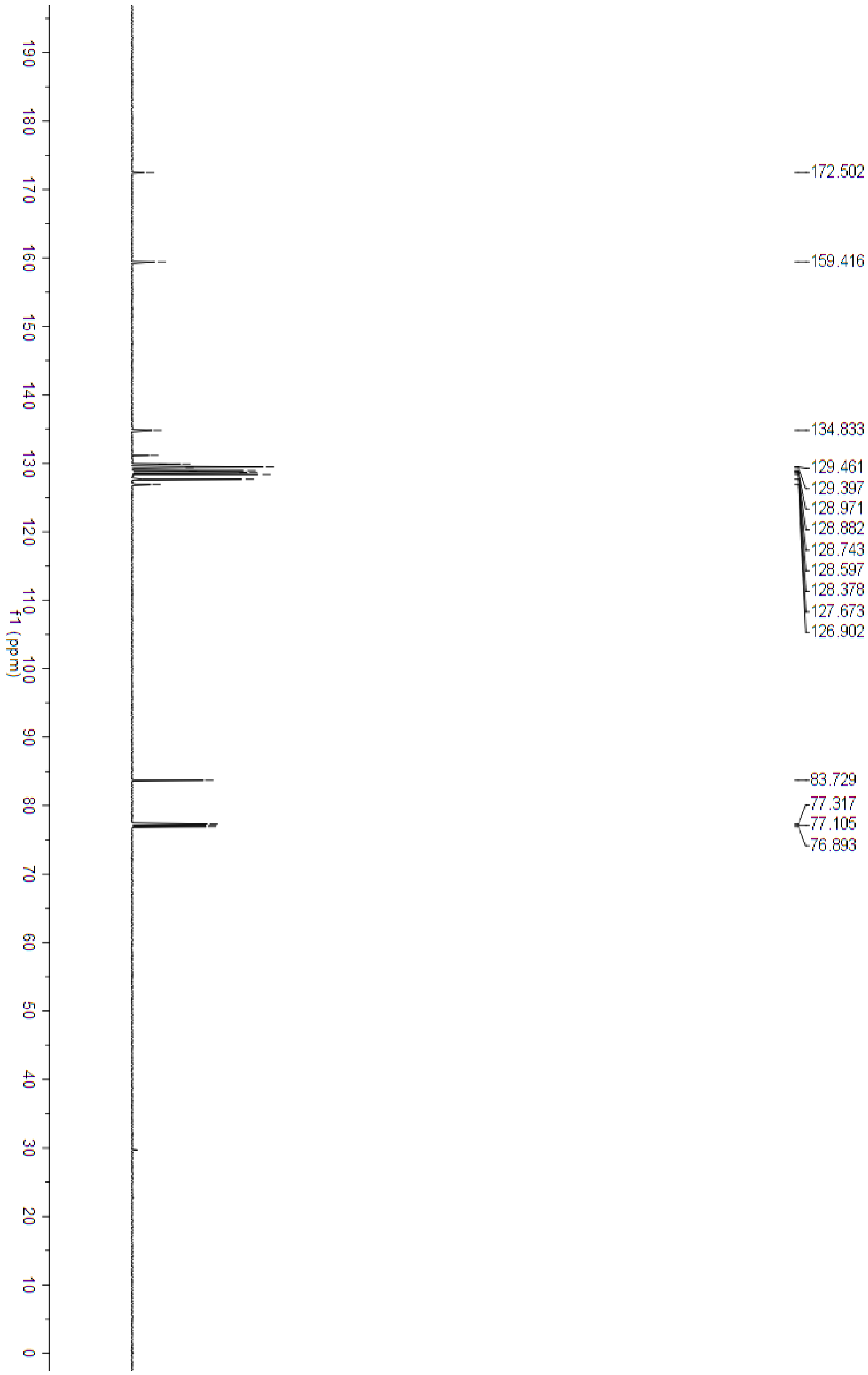


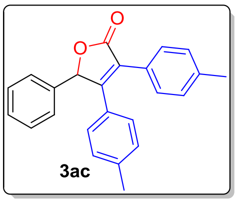
3ab

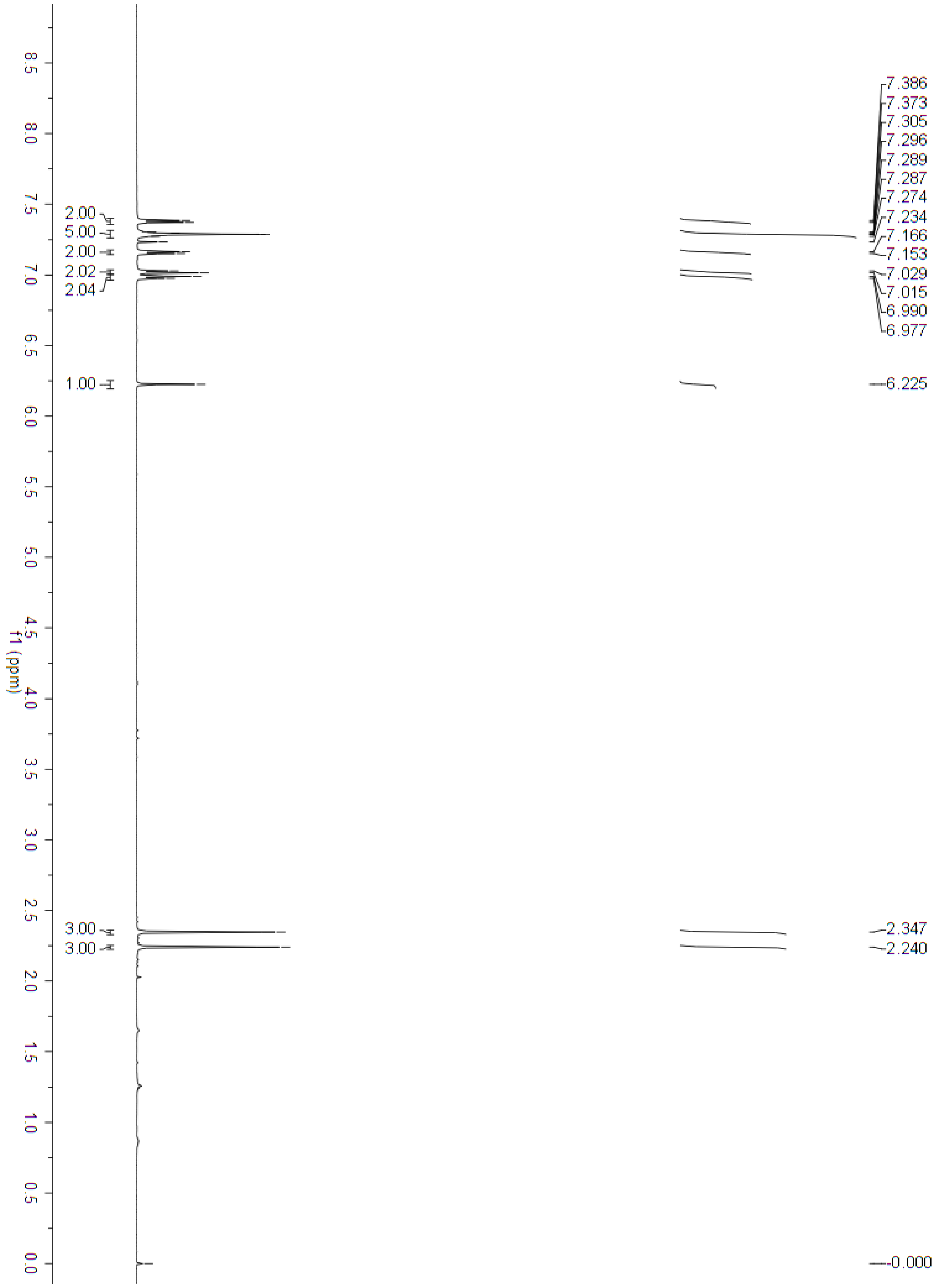

7.484
7.478
7.472
7.468
7.345
7.344
7.338
7.334
7.309
7.306
7.301
7.297
7.290
7.284
7.276
7.245
7.238
7.235
7.233
7.198
7.185
7.173
7.104
7.091
7.089
6.255
0.000
2.00
3.00
5.01
1.05
2.04
2.00
1.00
f1 (ppm)

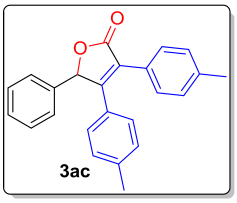


3ab

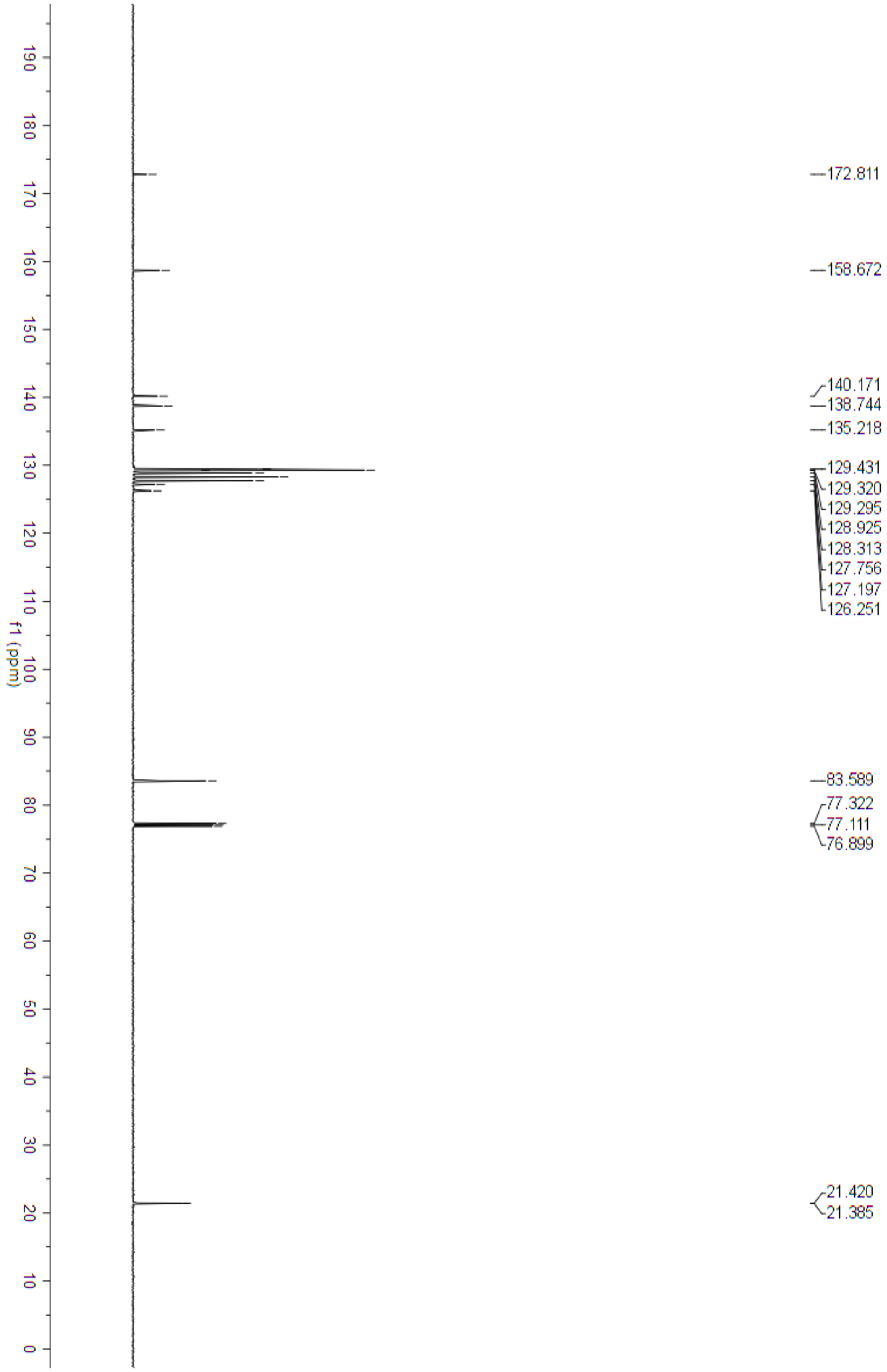

f1 (ppm)
172.502
159.416
134.833
129.461
129.397
128.971
128.882
128.743
128.597
128.378
127.673
126.902
83.729
77.317
77.105
76.893


O
O
3ac

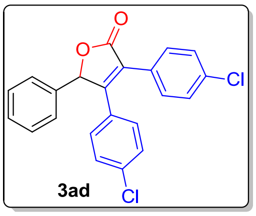

7.386
7.373
7.305
7.296
7.289
7.287
7.274
7.234
7.166
7.153
7.029
7.015
6.990
6.977
6.225
2.347
2.240
-0.000
2.00
5.00
2.00
2.02
2.04
1.00
3.00
3.00
f1 (ppm)

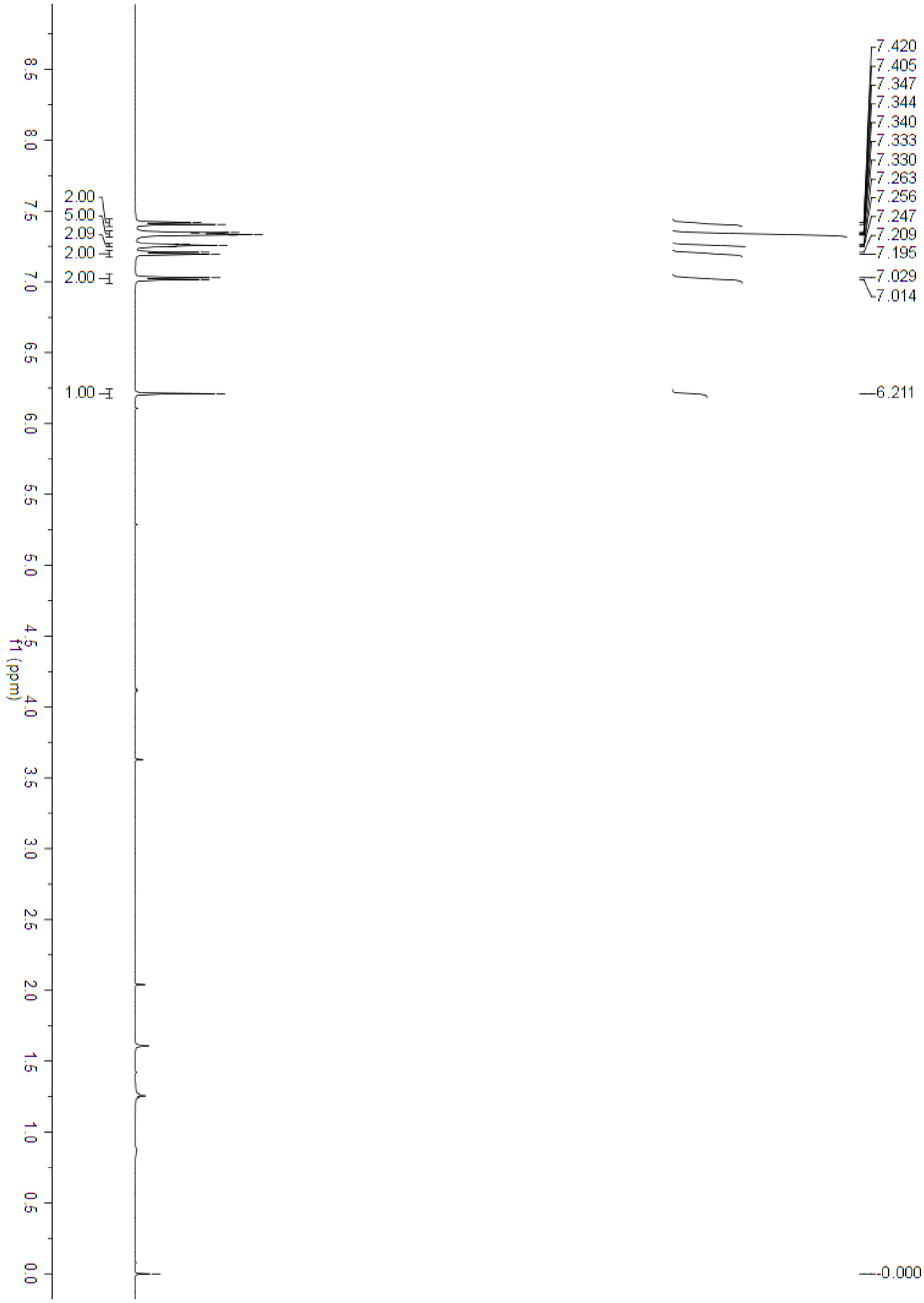


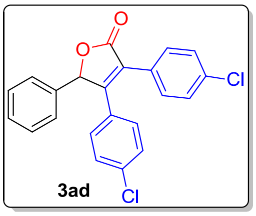
3ac

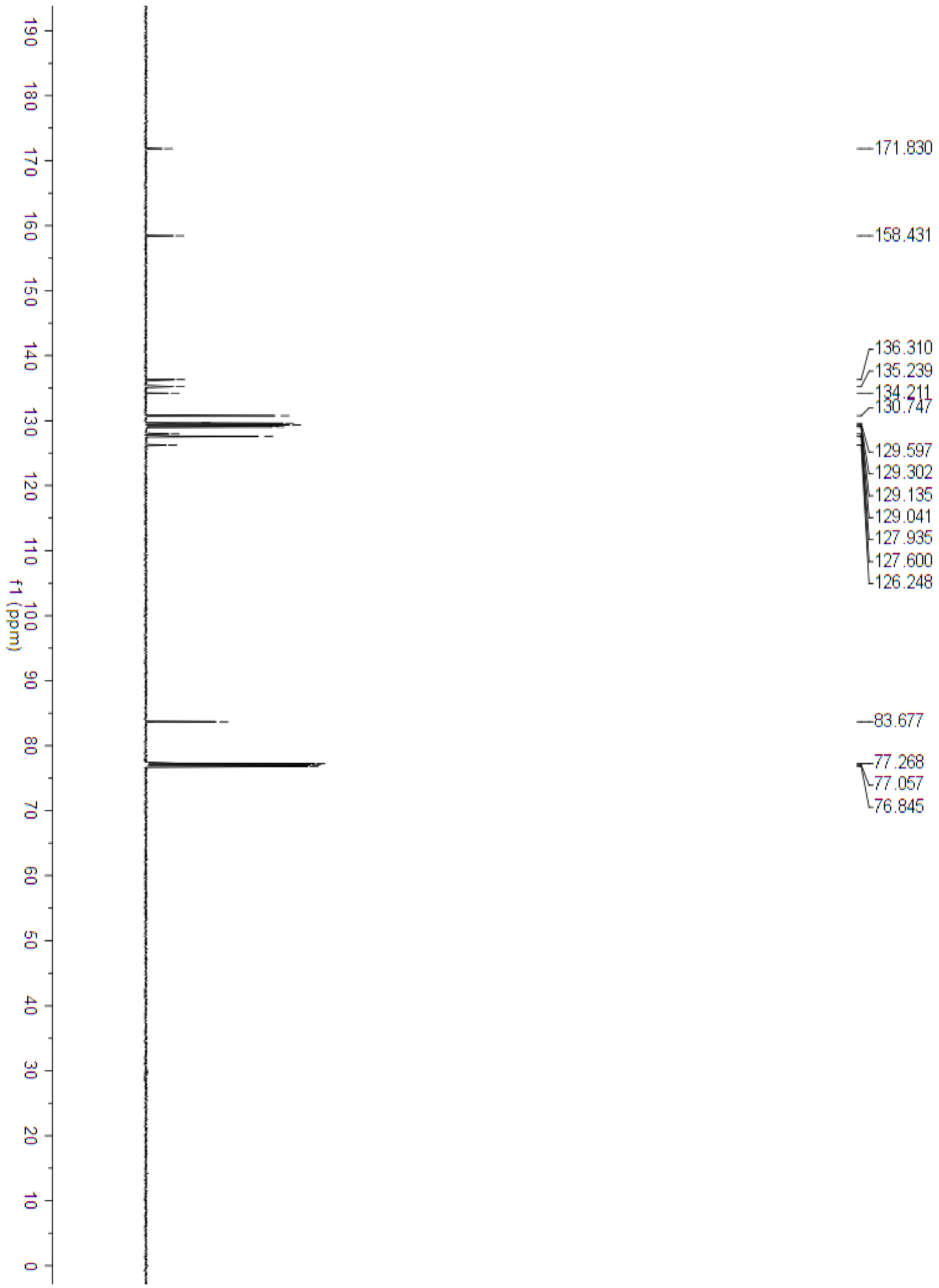


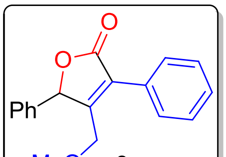
172.811
158.672
140.171
138.744
135.218
129.431
129.320
129.295
128.925
128.313
127.756
127.197
126.251
83.589
77.322
77.111
76.899
21.420
21.385
f1 (ppm)


O
Cl
Cl
3ad

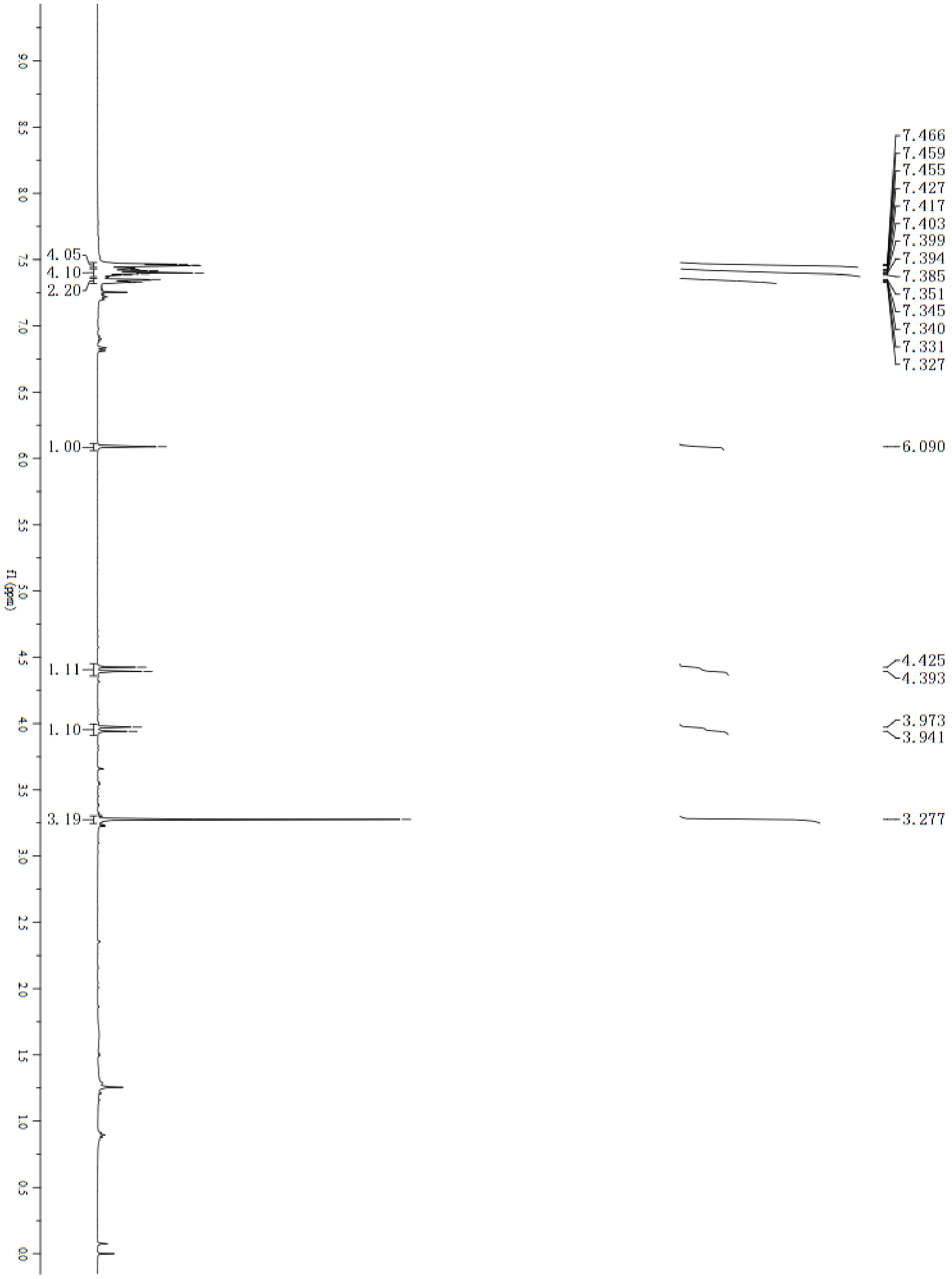

7.420
7.405
7.347
7.344
7.340
7.333
7.330
7.263
7.256
7.247
7.209
7.195
7.029
7.014
6.211
-0.000
2.00
5.00
2.09
2.00
2.00
1.00
f1 (ppm)

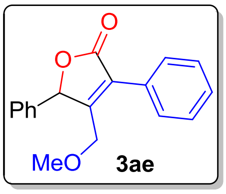

O
Cl
Cl
3ad

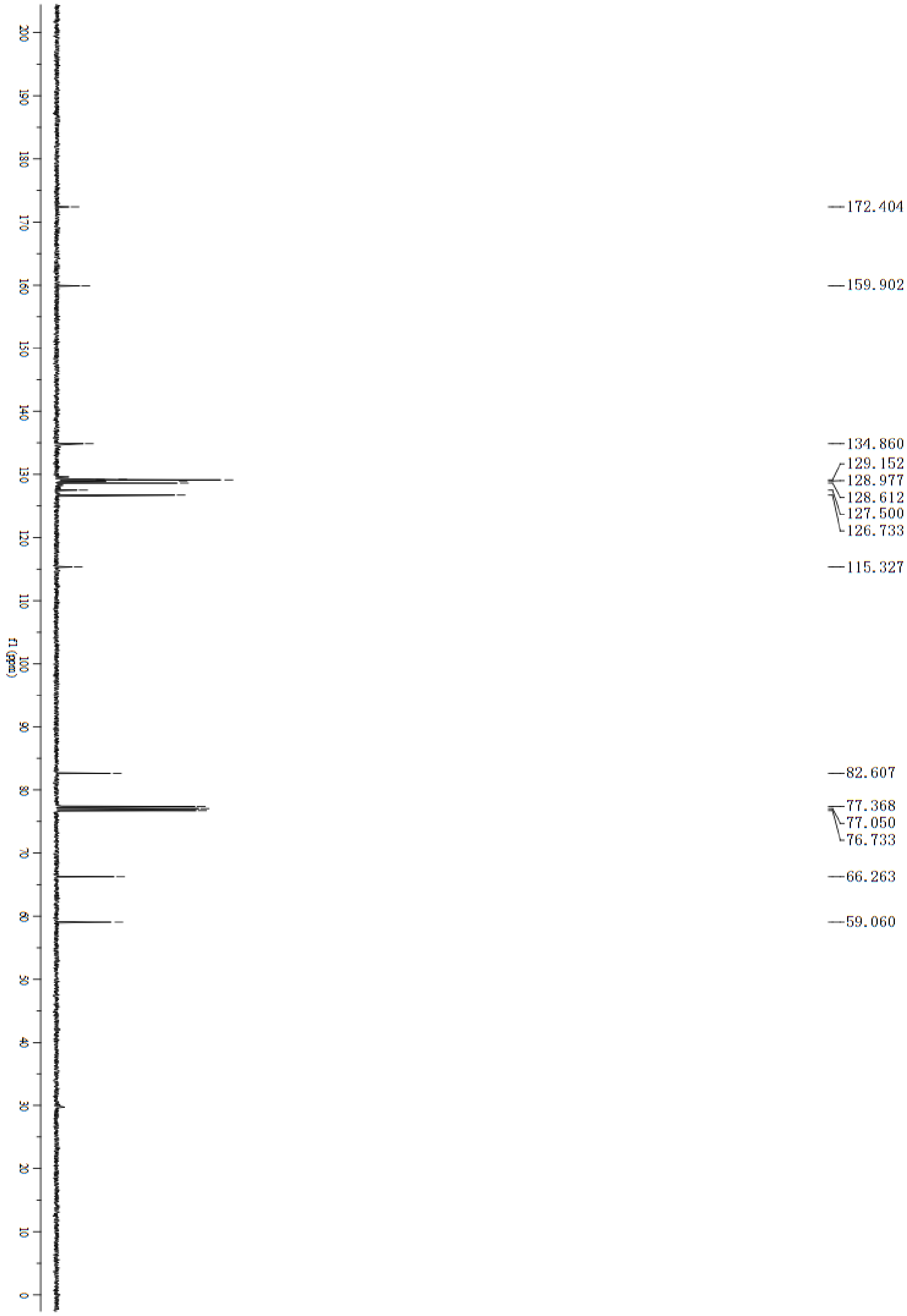

171.830
158.431
136.310
135.239
134.211
130.747
129.597
129.302
129.135
129.041
127.935
127.600
126.248
83.677
77.268
77.057
76.845
f1 (ppm)

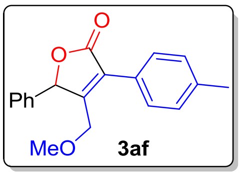

O
O
Ph
MeO

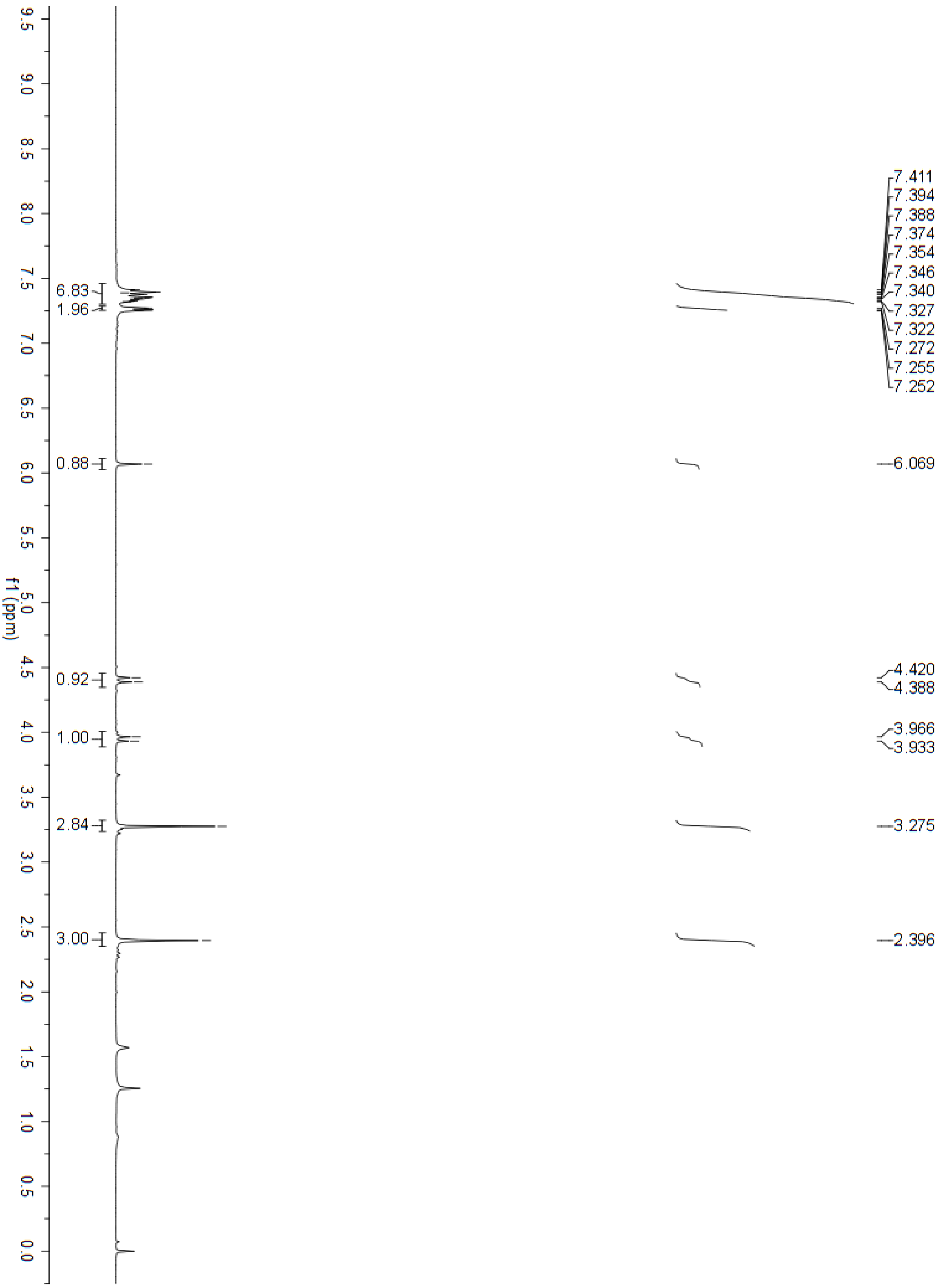
3ae

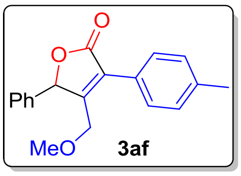

7.466
7.459
7.455
7.427
7.417
7.403
7.399
7.394
7.385
7.351
7.345
7.340
7.331
7.327
6.090
4.425
4.393
3.973
3.941
3.277
4.05
4.10
2.20
1.00
1.11
1.10
3.19
f1 (ppm)

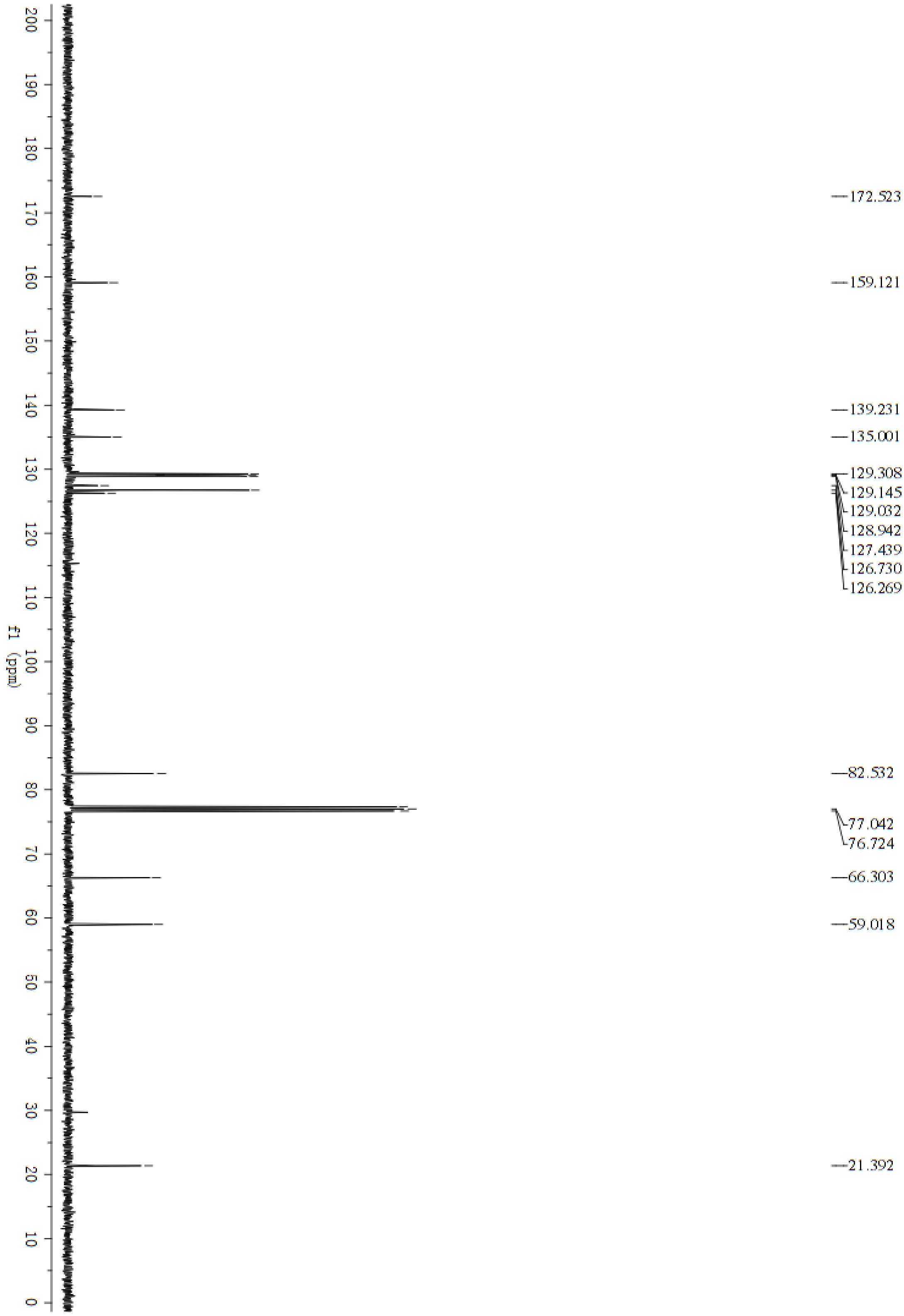

Ph
MeO
3ae

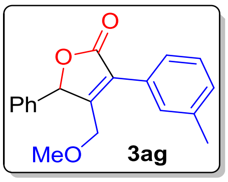

172.404
159.902
134.860
129.152
128.977
128.612
127.500
126.733
115.327
82.607
77.368
77.050
76.733
66.263
59.060
f1 (ppm)

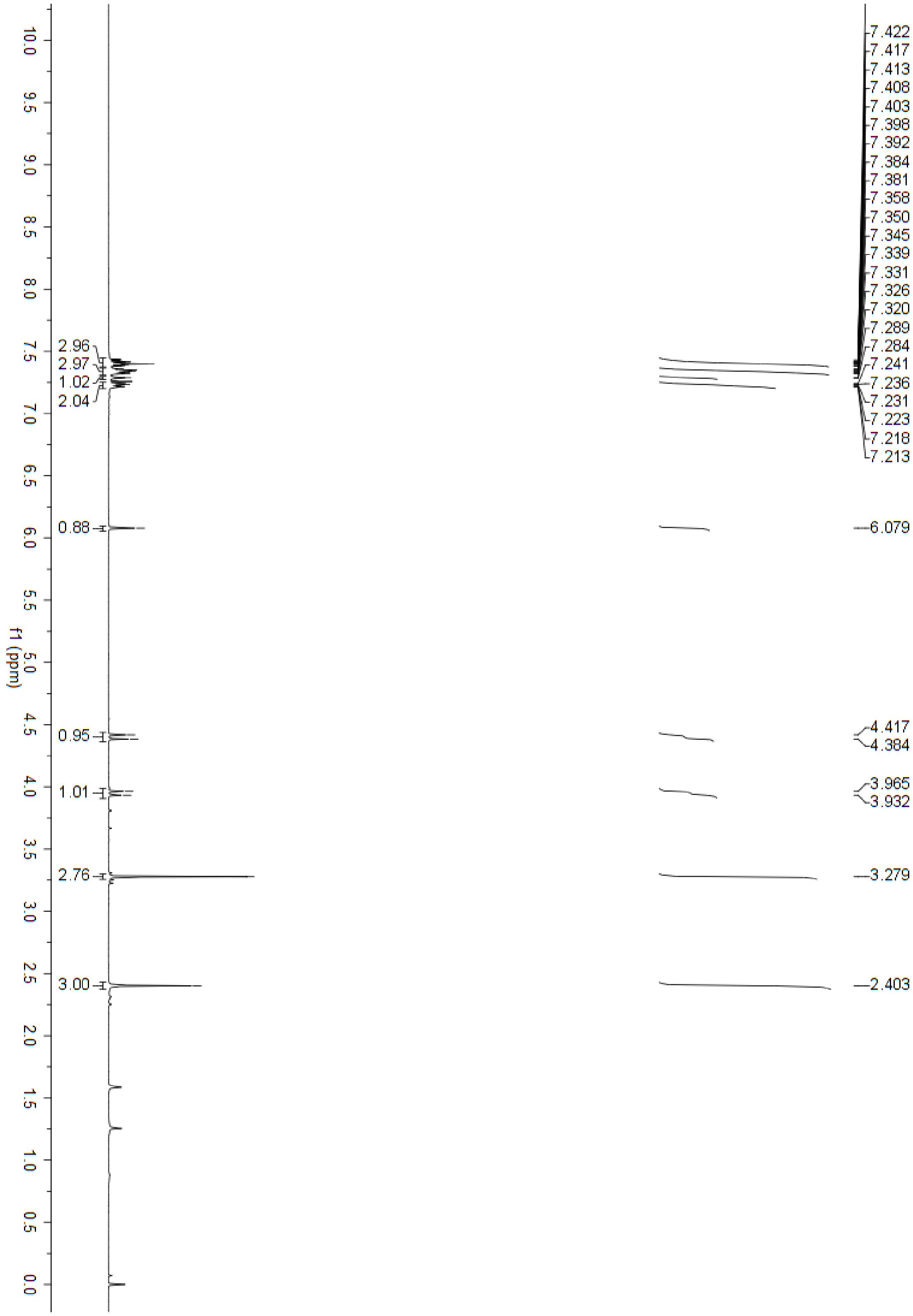

O
O
Ph
MeO
3af

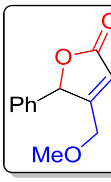

7.411
7.394
7.388
7.374
7.354
7.346
7.340
7.327
7.322
7.272
7.255
7.252
6.069
4.420
4.388
3.966
3.933
3.275
2.396
6.83
1.96
0.88
0.92
1.00
2.84
3.00
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

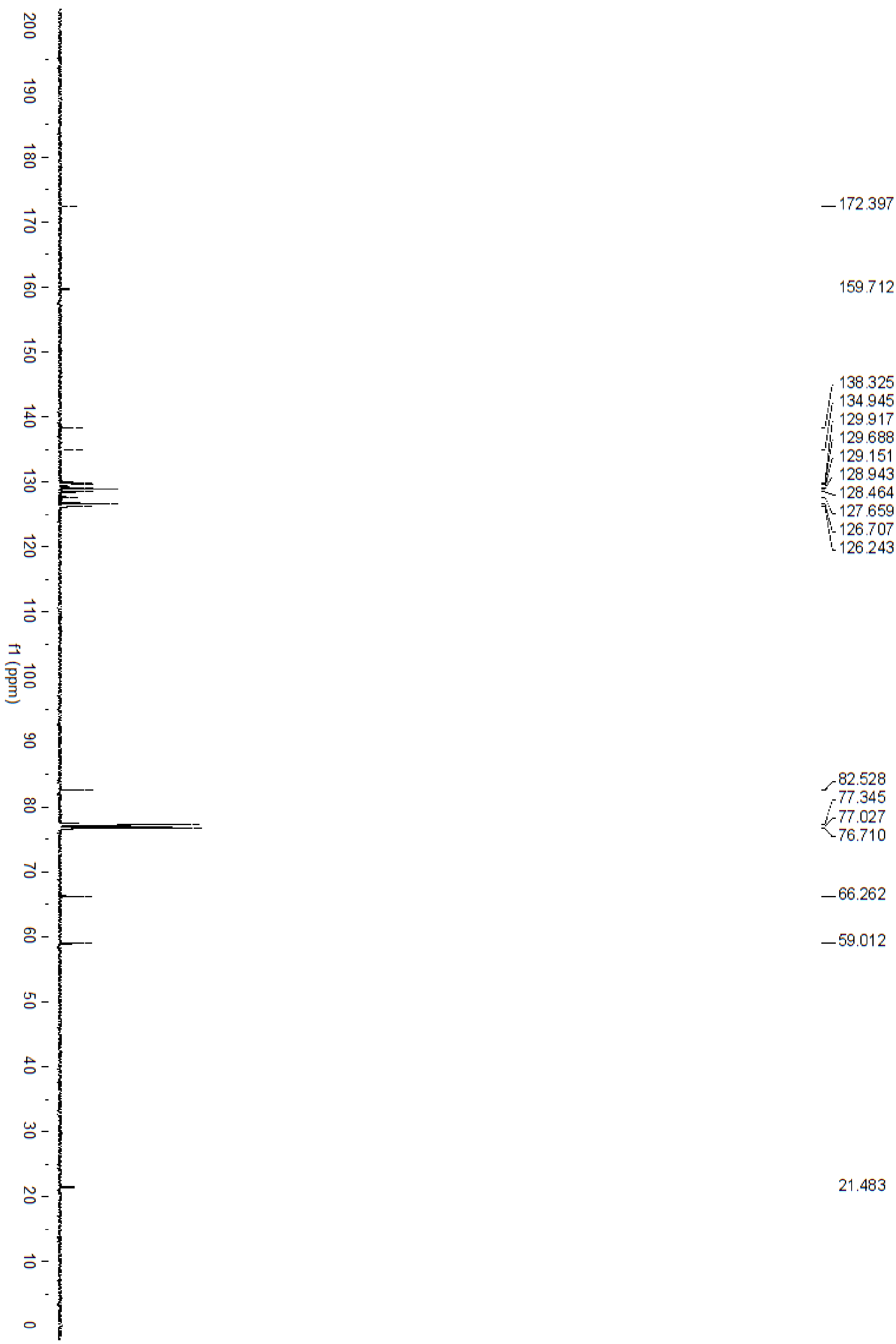

O
O
Ph
MeO
3af

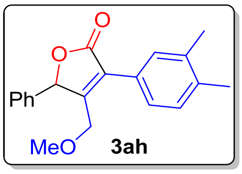

172.523
159.121
139.231
135.001
129.308
129.145
129.032
128.942
127.439
126.730
126.269
82.532
77.042
76.724
66.303
59.018
21.392
f1 (ppm)


O
O
Ph
MeO
3ag

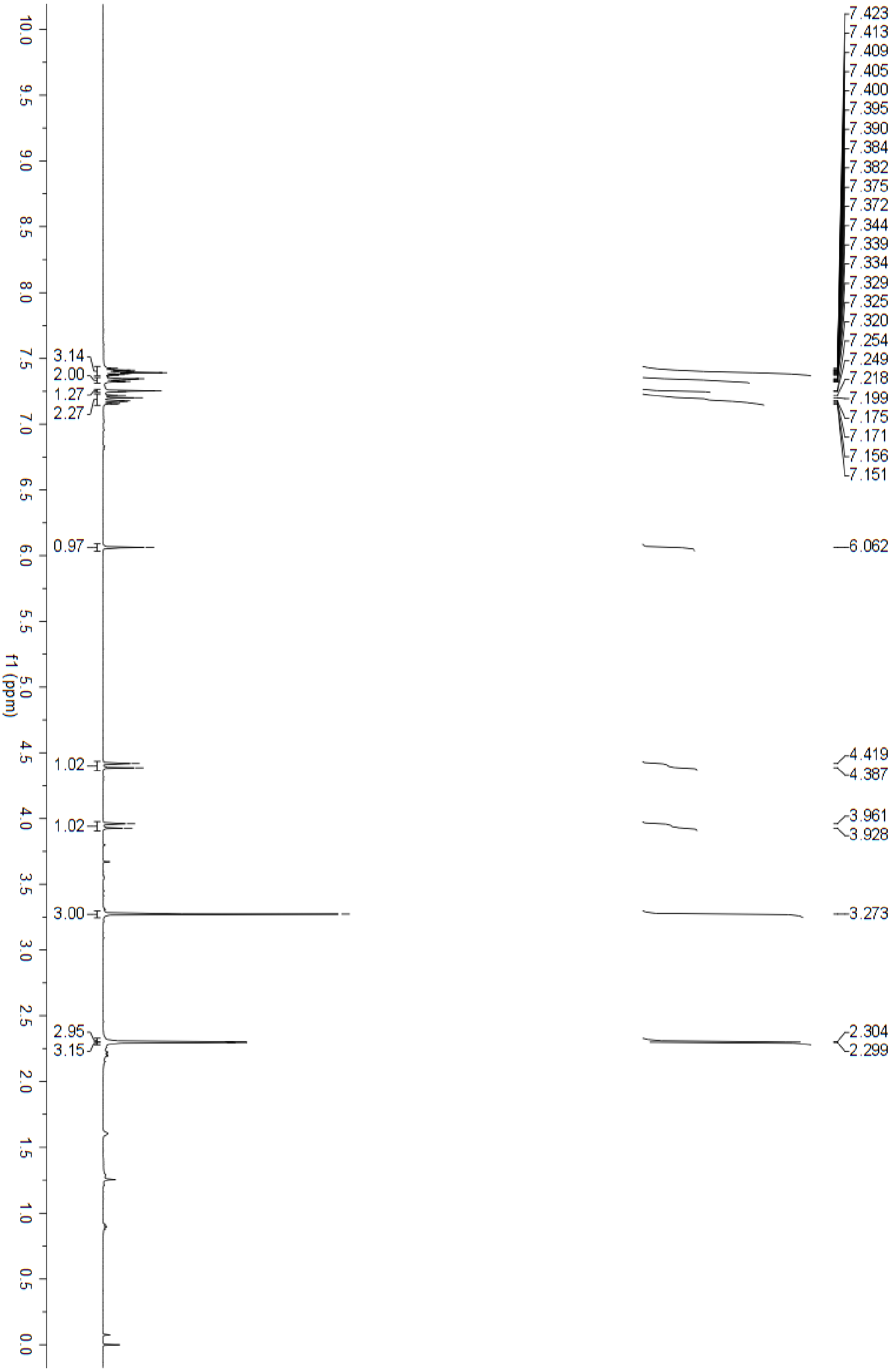

7.422
7.417
7.413
7.408
7.403
7.398
7.392
7.384
7.381
7.358
7.350
7.345
7.339
7.331
7.326
7.320
7.289
7.284
7.241
7.236
7.231
7.223
7.218
7.213
6.079
4.417
4.384
3.965
3.932
3.279
2.403
2.96
2.97
1.02
2.04
0.88
0.95
1.01
2.76
3.00
f1 (ppm)
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0

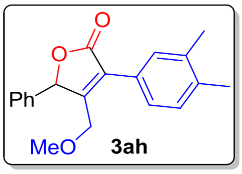

O
O
Ph
MeO
3ag


200
190
180
170
160
150
140
130
120
110
100
f1 (ppm)
90
80
70
60
50
40
30
20
10
0
172.397
159.712
138.325
134.945
129.917
129.688
129.151
128.943
128.464
127.659
126.707
126.243
82.528
77.345
77.027
76.710
66.262
59.012
21.483

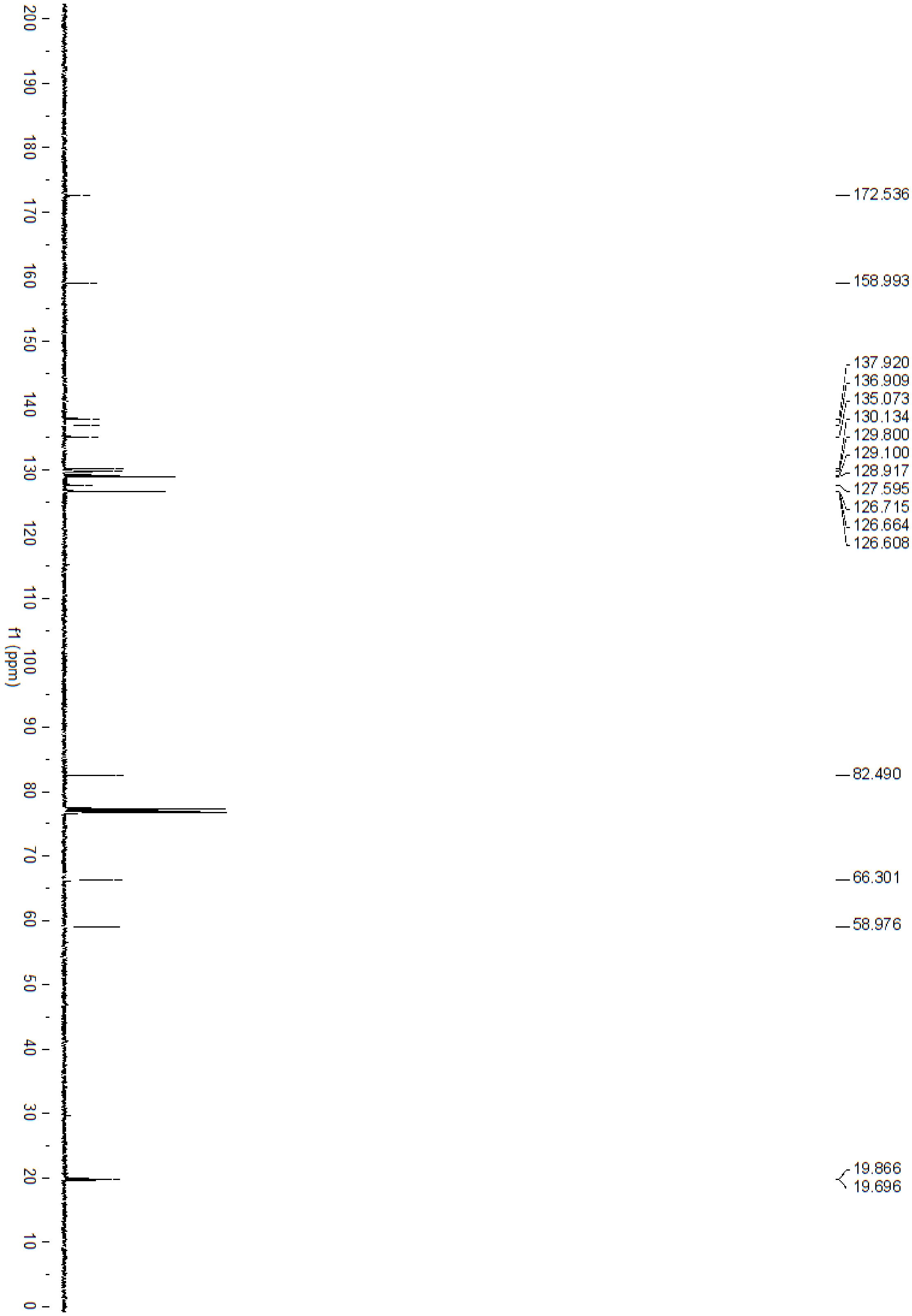

O
O
Ph
MeO

3ah

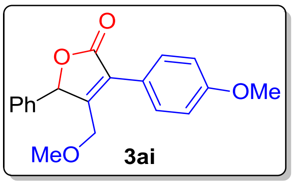

f1 (ppm)
7.423
7.413
7.409
7.405
7.400
7.395
7.390
7.384
7.382
7.375
7.372
7.344
7.339
7.334
7.329
7.325
7.320
7.254
7.249
7.218
7.199
7.175
7.171
7.156
7.151
6.062
4.419
4.387
3.961
3.928
3.273
2.304
2.299
3.14
2.00
1.27
2.27
0.97
1.02
1.02
3.00
2.95
3.15

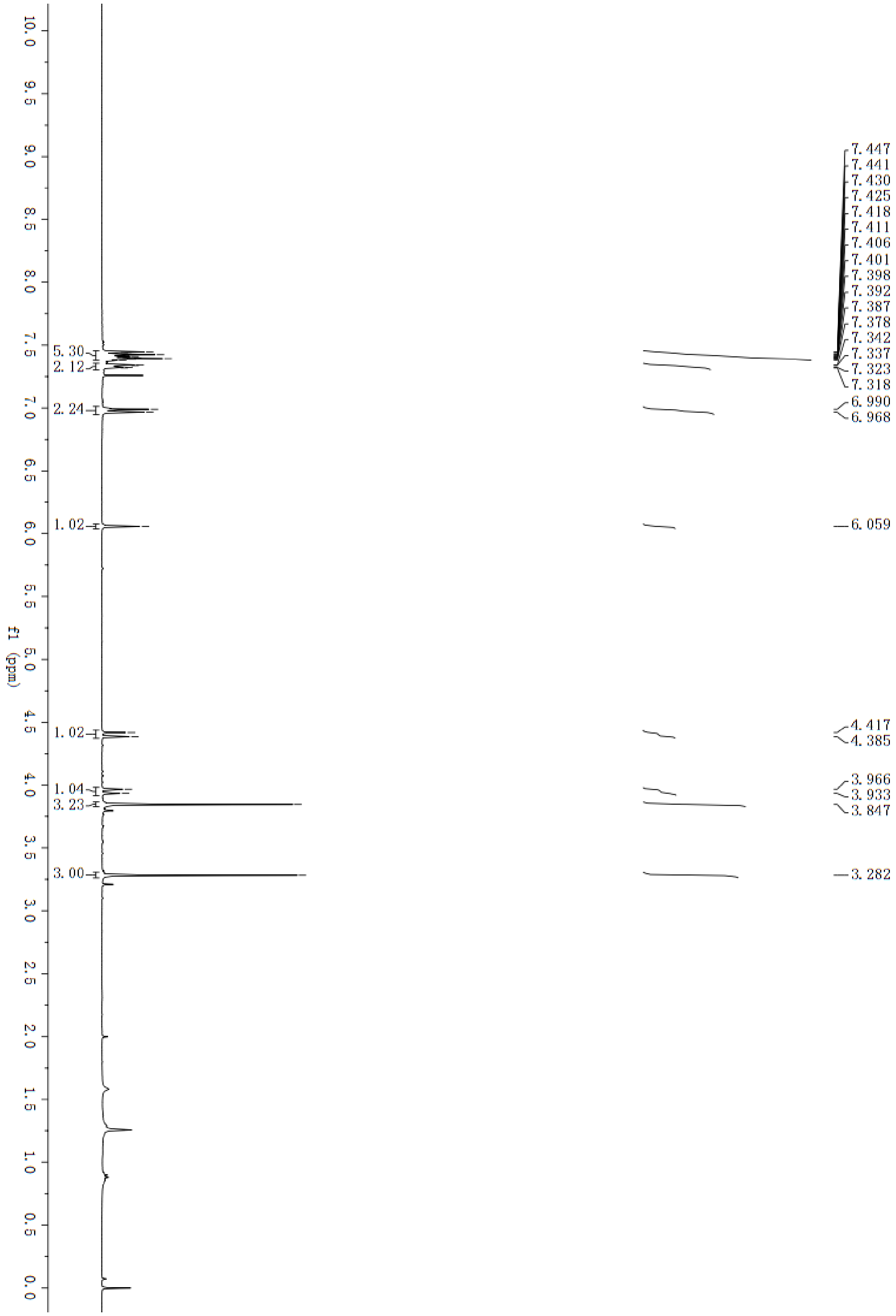


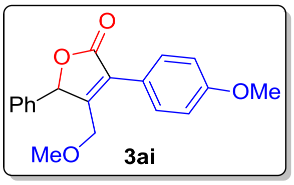
O
O
Ph
MeO
3ah



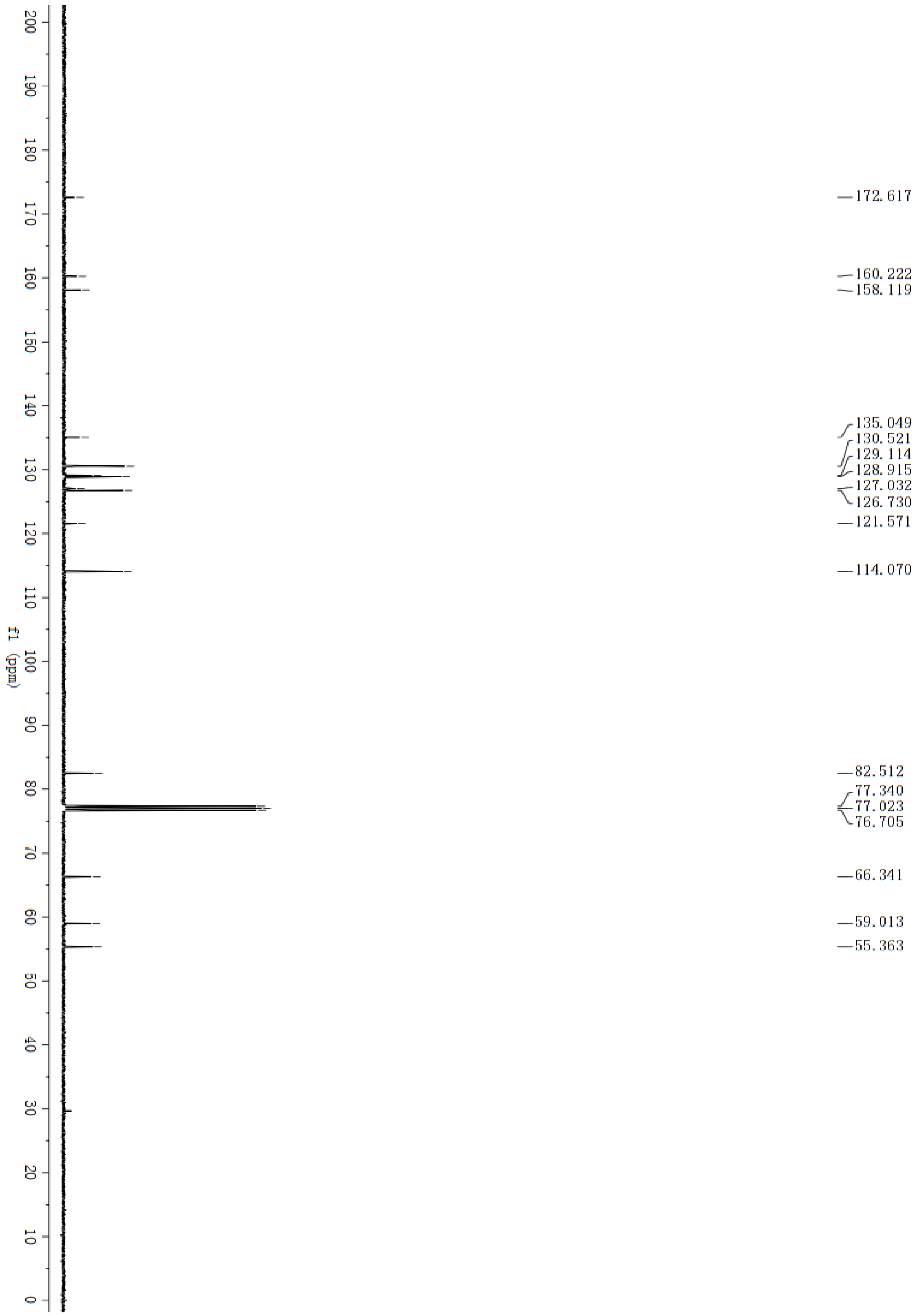
172.536
158.993
137.920
136.909
135.073
130.134
129.800
129.100
128.917
127.595
126.715
126.664
126.608
82.490
66.301
58.976
19.866
19.696
f1 (ppm)
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0

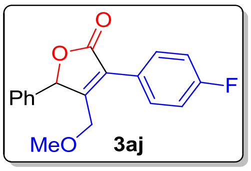

O
O
Ph
OMe
MeO
3ai



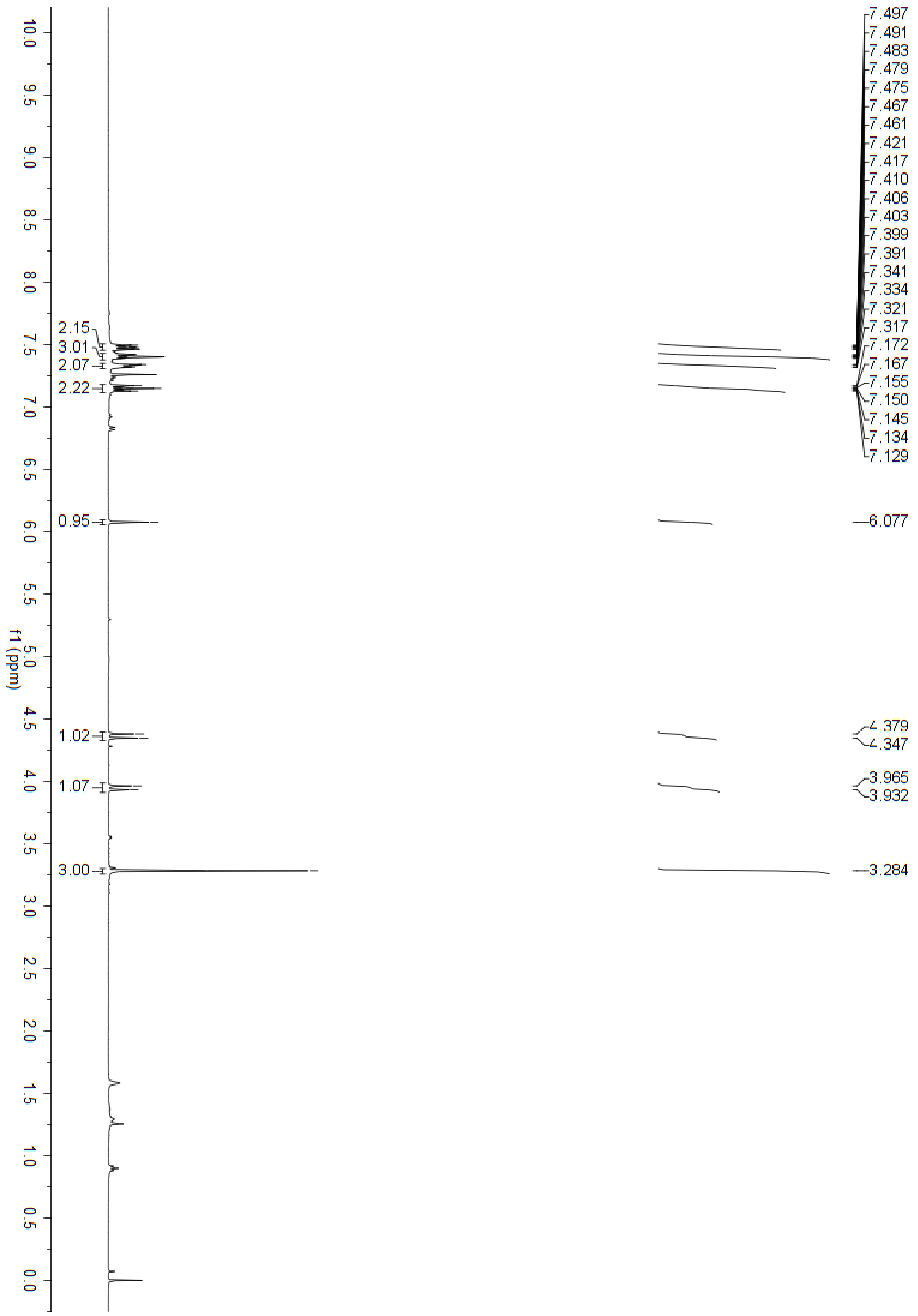

O
O
OMe
Ph
MeO

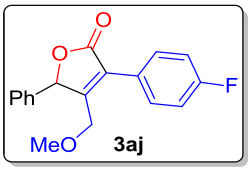
3ai

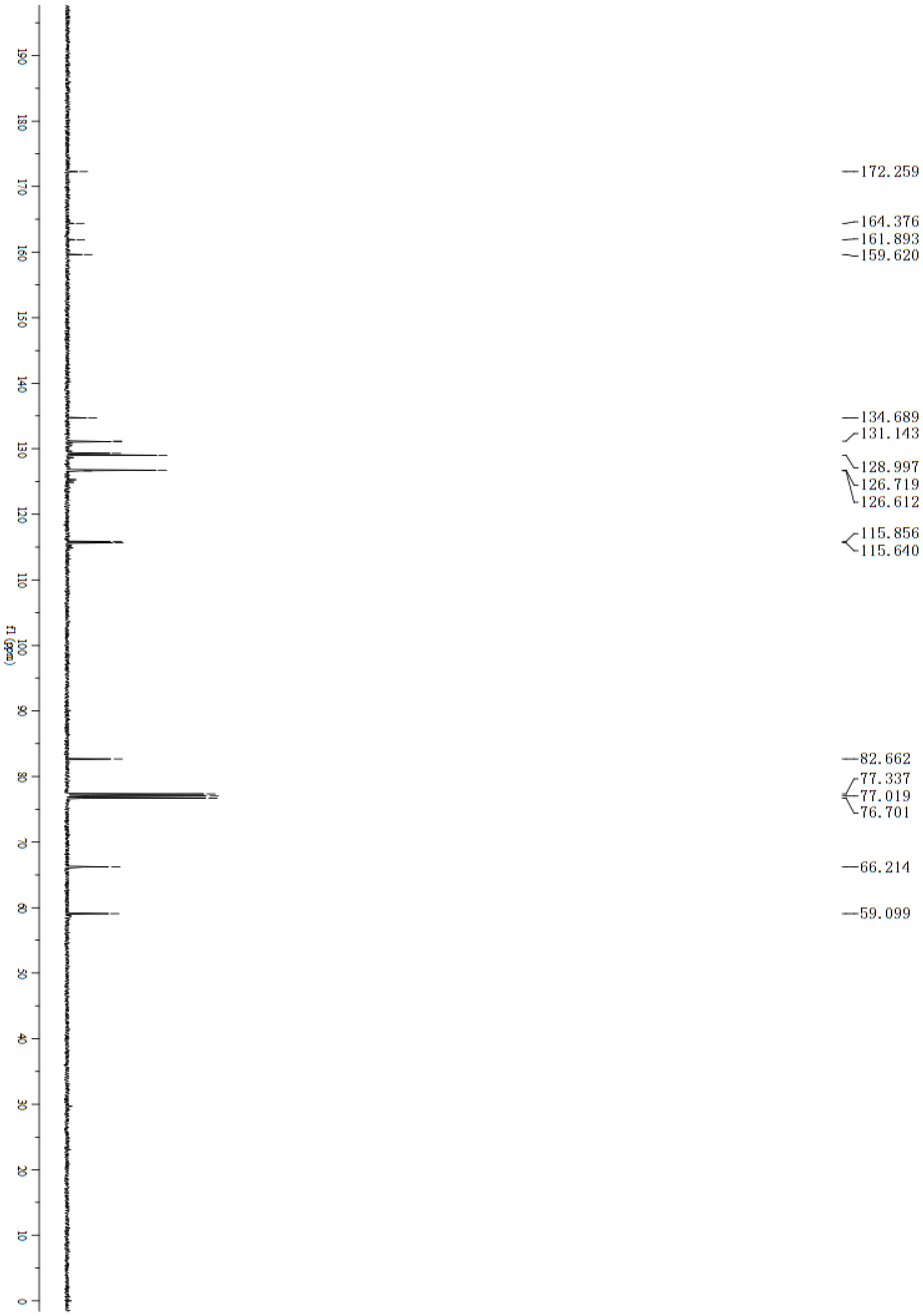

172.617
160.222
158.119
135.049
130.521
129.114
128.915
127.032
126.730
121.571
114.070
82.512
77.340
77.023
76.705
66.341
59.013
55.363
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

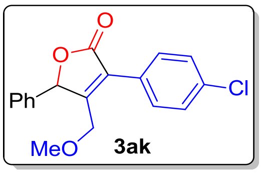

O
O
Ph
F
MeO

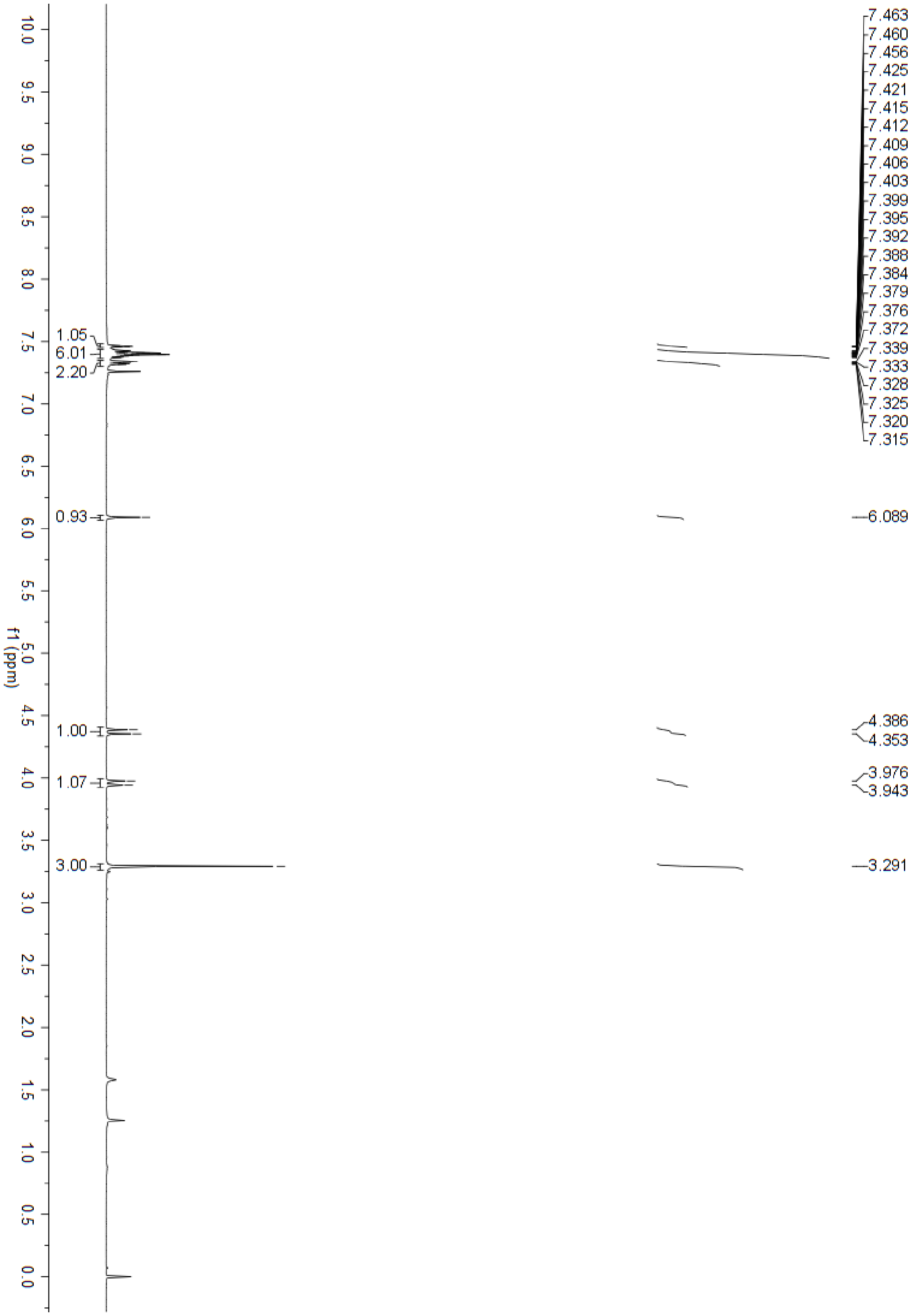
3aj

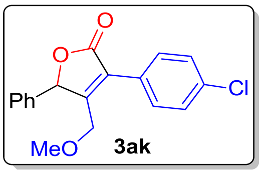

7.497
7.491
7.483
7.479
7.475
7.467
7.461
7.421
7.417
7.410
7.406
7.403
7.399
7.391
7.341
7.334
7.321
7.317
7.172
7.167
7.155
7.150
7.145
7.134
7.129
6.077
4.379
4.347
3.965
3.932
3.284
2.15
3.01
2.07
2.22
0.95
1.02
1.07
3.00
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

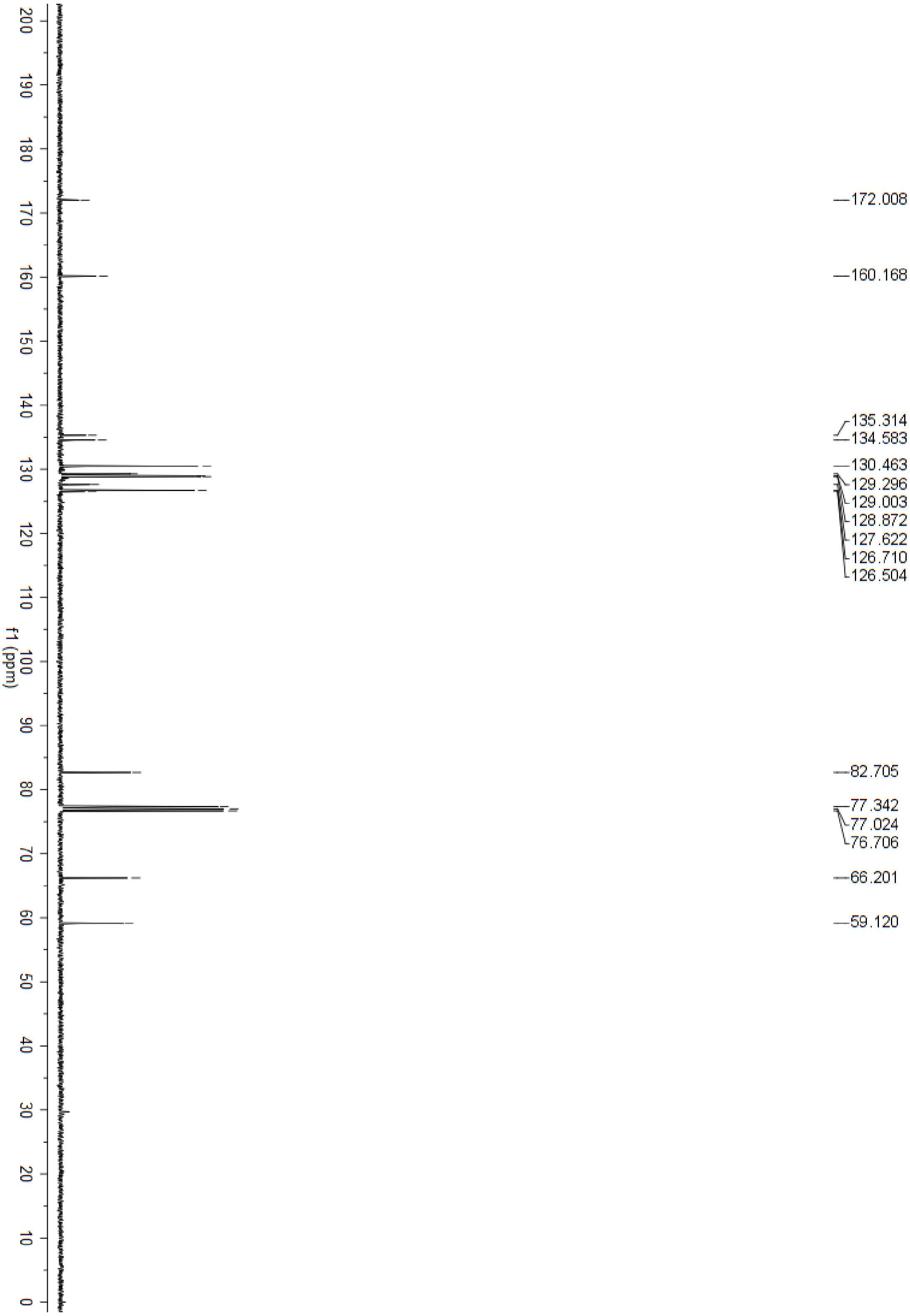

O
O
Ph
F
MeO
3aj

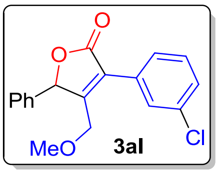

172.259
164.376
161.893
159.620
134.689
131.143
128.997
126.719
126.612
115.856
115.640
82.662
77.337
77.019
76.701
66.214
59.099
f1 (ppm)
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0

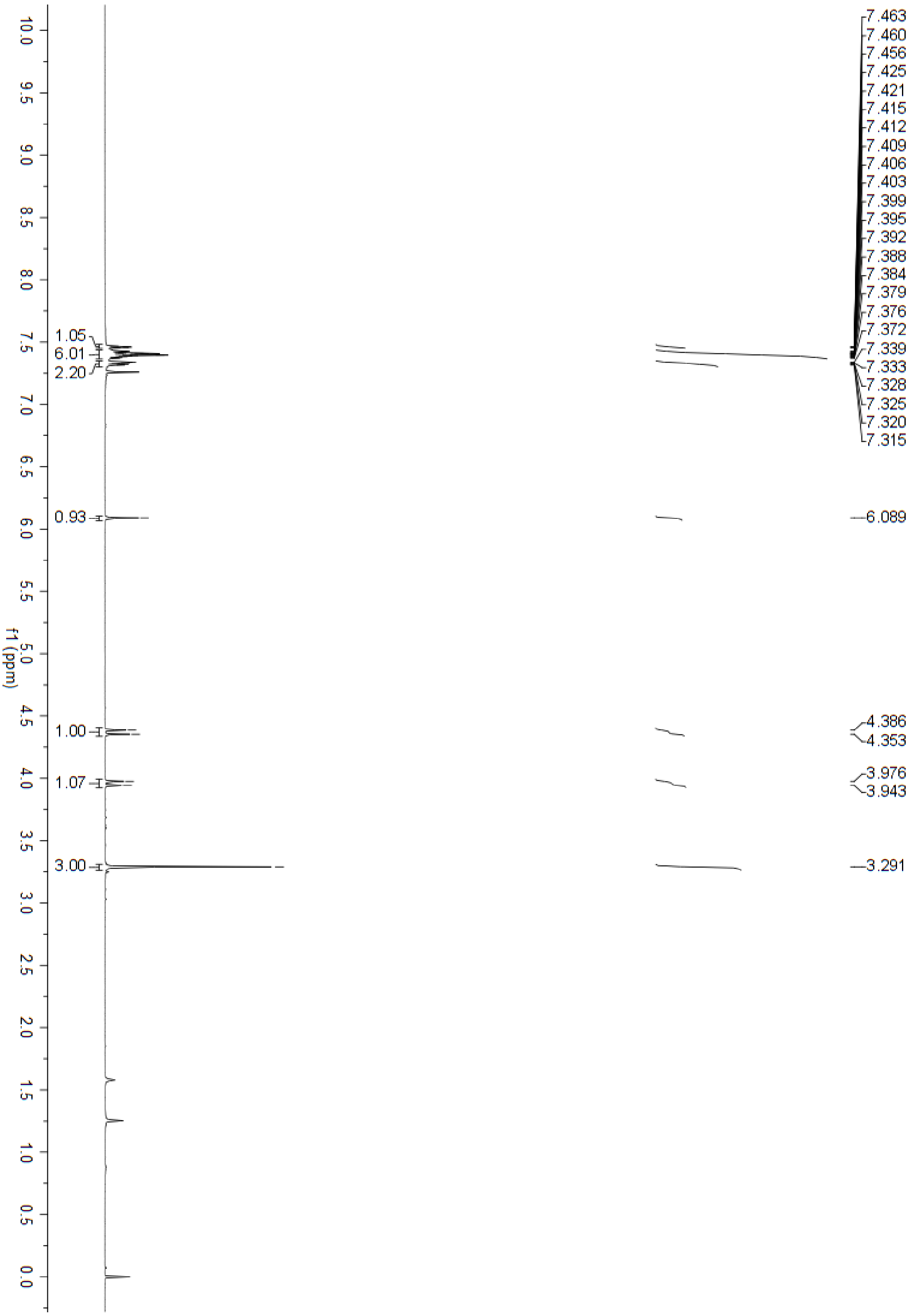

O
O
Ph
Cl
MeO
3ak

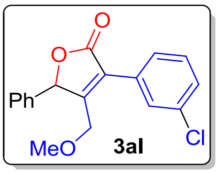

7.463
7.460
7.456
7.425
7.421
7.415
7.412
7.409
7.406
7.403
7.399
7.395
7.392
7.388
7.384
7.379
7.376
7.372
7.339
7.333
7.328
7.325
7.320
7.315
6.089
4.386
4.353
3.976
3.943
3.291
1.05
6.01
2.20
0.93
1.00
1.07
3.00
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

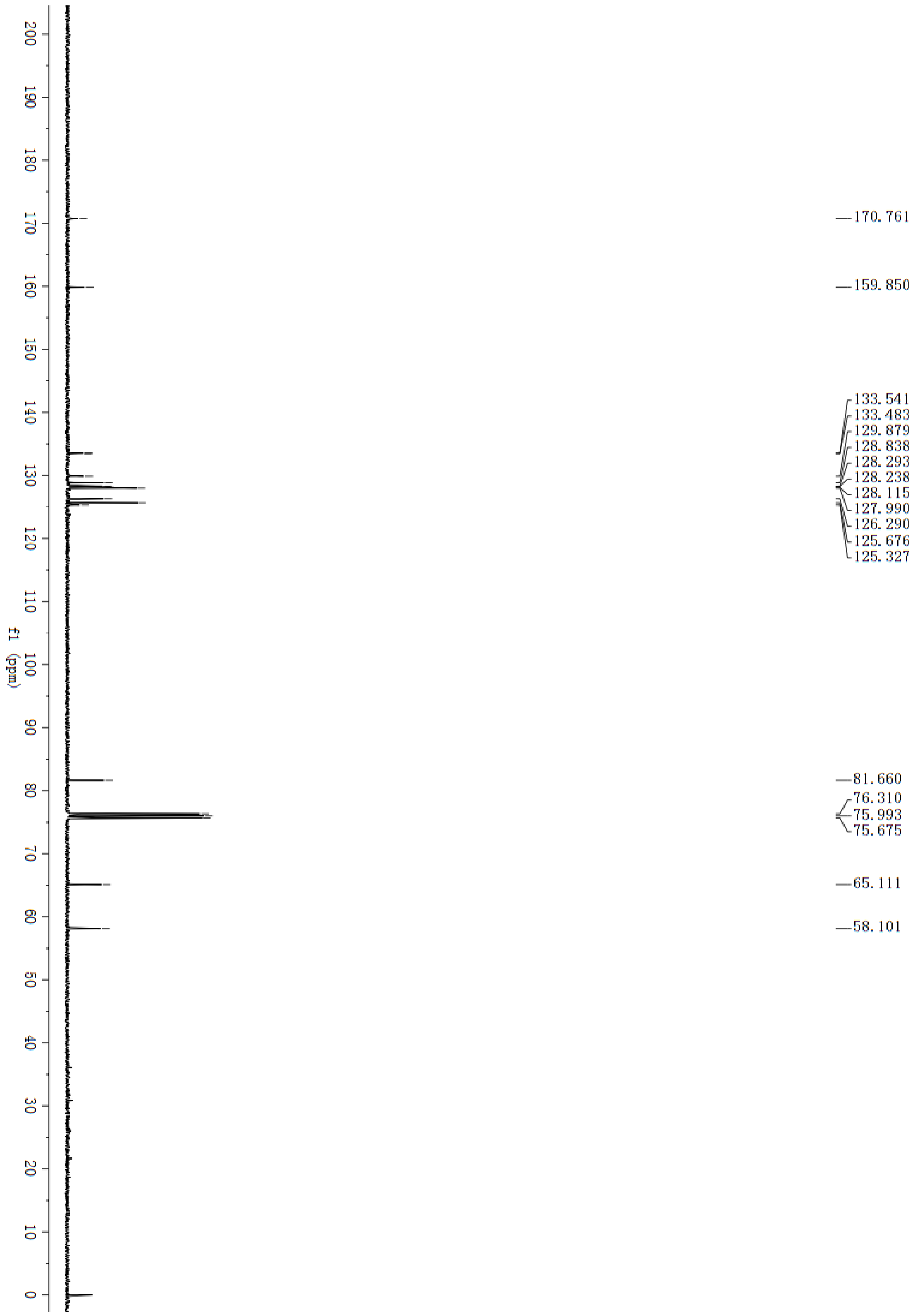

O
O
Ph
Cl
MeO
3ak

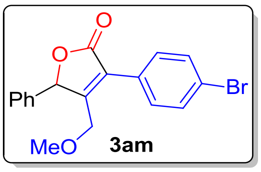

172.008
160.168
135.314
134.583
130.463
129.296
129.003
128.872
127.622
126.710
126.504
82.705
77.342
77.024
76.706
66.201
59.120
f1 (ppm)
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0

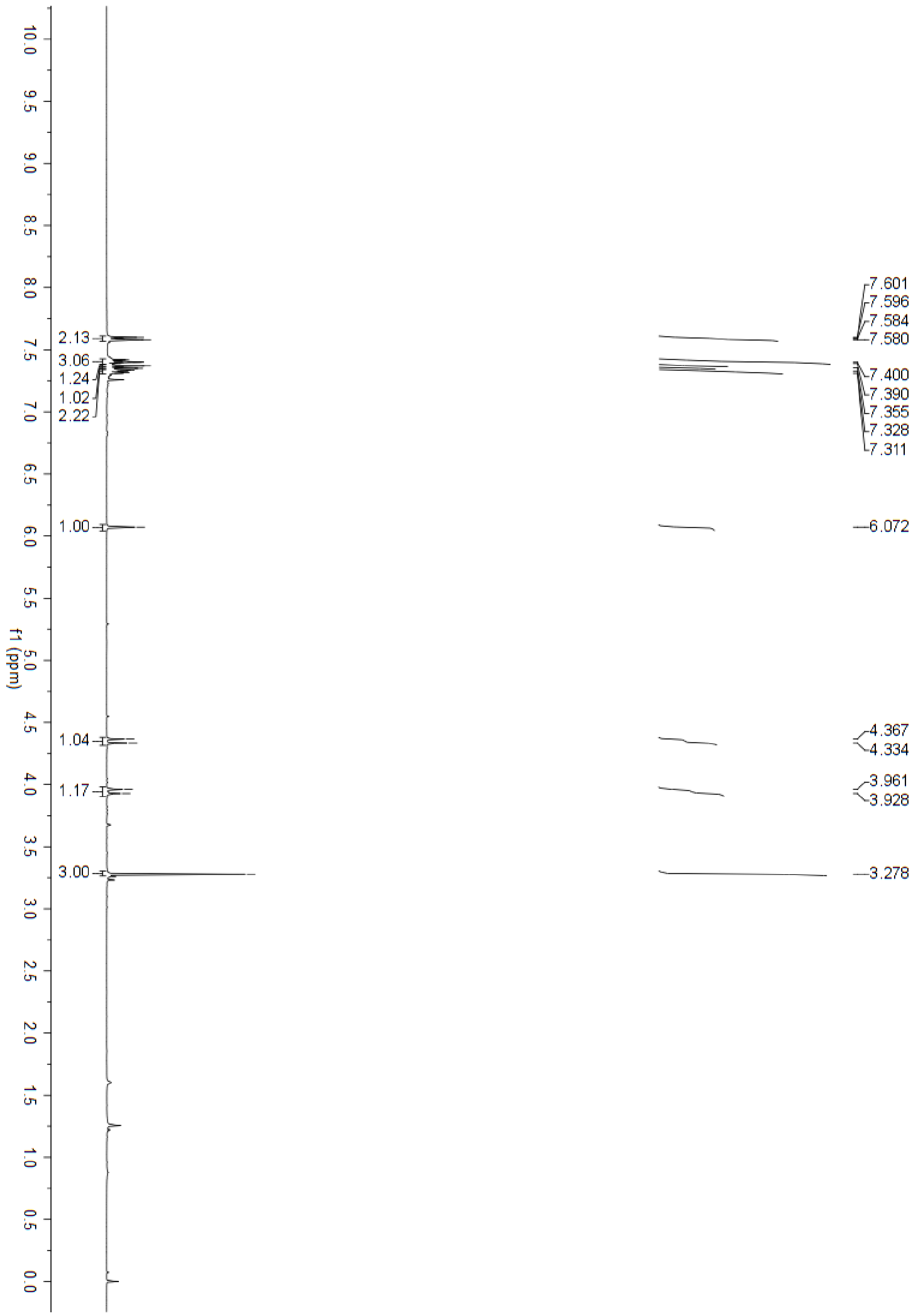

O
O
Ph
MeO
3al
Cl

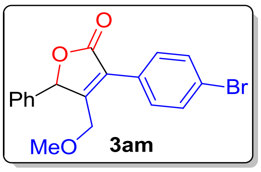

7.463
7.460
7.456
7.425
7.421
7.415
7.412
7.409
7.406
7.403
7.399
7.395
7.392
7.388
7.384
7.379
7.376
7.372
7.339
7.333
7.328
7.325
7.320
7.315
6.089
4.386
4.353
3.976
3.943
3.291
1.05
6.01
2.20
0.93
1.00
1.07
3.00
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

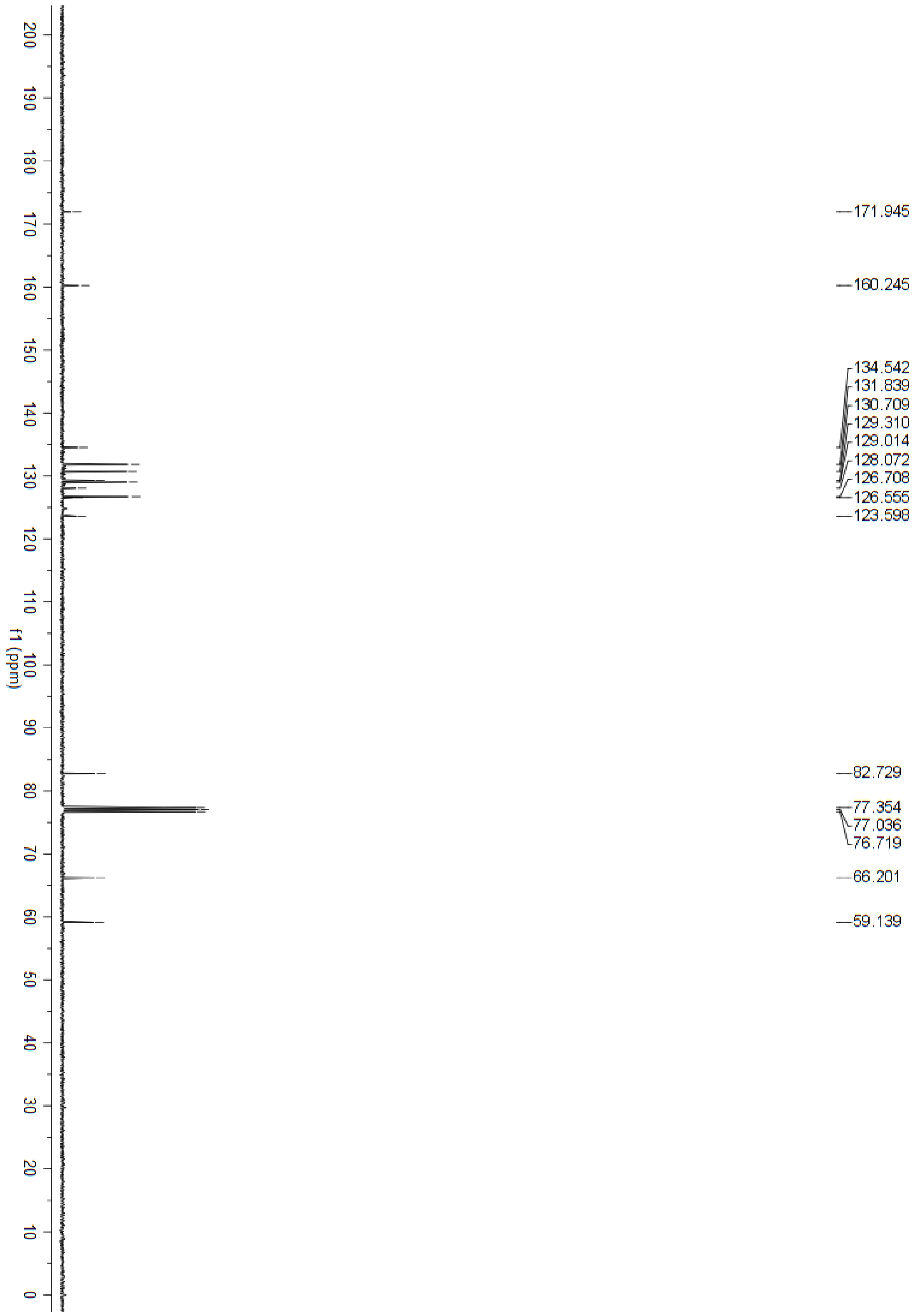

O
O
Ph
MeO
3al
Cl


170.761
159.850
133.541
133.483
129.879
128.838
128.293
128.238
128.115
127.990
126.290
125.676
125.327
81.660
76.310
75.993
75.675
65.111
58.101
f1 (ppm)
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0


O
O
Ph
Br
MeO
3am


f1 (ppm)
7.601
7.596
7.584
7.580
7.400
7.390
7.355
7.328
7.311
6.072
4.367
4.334
3.961
3.928
3.278
2.13
3.06
1.24
1.02
2.22
1.00
1.04
1.17
3.00


Ph
MeO
Br
O
O
3am


171.945
160.245
134.542
131.839
130.709
129.310
129.014
128.072
126.708
126.555
123.598
82.729
77.354
77.036
76.719
66.201
59.139
f1 (ppm)
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0