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Copper-catalyzed, silver-mediated formal [3+2] cycloaddition of simple alkynes with β-ketoesters though propargylic C(sp^3)-H functionalization

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Supporting Information

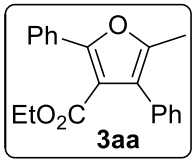
General Information

All reactions were carried out under a nitrogen atmosphere. Solvents were purified by standard procedure before use. Commercial reagents were used without further purification. Flash chromatography was performed on silica gel 60 (40-63μm, 60Å). Thin layer chromatography (TLC) was performed on glass plates coated with silica gel 60 with F254 indicator. Proton nuclear magnetic resonance (^{1}H NMR) spectra were recorded on a Bruker 400 MHz spectrometer. Chemical shifts for protons are reported in parts per million downfield from tetramethylsilane and are referenced to residual protium in the NMR solvent ($CDCl_3$ = δ 7.26). Carbon nuclear magnetic resonance (^{13}C NMR) spectra were recorded on a Bruker 100 MHz spectrometer. Chemical shifts for carbon are reported in parts per million downfield from tetramethylsilane and are referenced to the carbon resonances of the solvent ($CDCl_3$ = δ 77.07). Data are represented as follows: chemical shift, multiplicity (br = broad, s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet), coupling constants in Hertz (Hz), integration. Only the most important and relevant frequencies are reported. ESI HRMS spectra were recorded on BioTOF Q. Aryl aryl propyne derivatives **1**[1] and β-ketoesters **2**[2] were prepared following the procedure described in the literature. **1k** was purchased from commercial sources (CAS: 1823-14-9).

General procedure for Copper-Catalyzed Formal [3+2] Cycloaddition

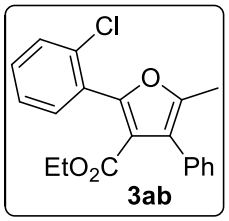
A solution of CuI (1.9 mg, 0.01 mmol) and 1,10-Phenanthroline hydrate (2.2 mg, 0.011 mmol) in 1 mL of anhydrous ethanol placed in an oven-dried Schlenk flask was stirred at room temperature under a nitrogen atmosphere for 1 h. A solution of propynyl arenes **1** (0.44 mmol), β-ketoesters **2** (0.2 mmol) and Ag_2CO_3 (66.2 mg, 0.24 mmol) in 2 mL of anhydrous ethanol was added. The reaction mixture was allowed to stir for 24 h at 80 °C. Then the reaction mixture was cooled to room temperature, DBU (36.5 mg, 0.24 mmol) was added directly to the resulting reaction mixture without further purification and continued stirring at 80 °C being monitored by TLC. The reaction mixture was then filtered, washed with dichloromethane (10 mL) and concentrated under vacuum. The residue was purified by silica gel chromatography to afford highly functionalized furans **3**.

Ethyl 5-methyl-2,4-diphenylfuran-3-carboxylate (3aa). Pale yellow oil was obtained in 93% yield after purification with column chromatography on silica gel (petroleum ether/ethyl acetate, 100/1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.85–7.82 (m, 2H), 7.43–7.29 (m, 8H), 4.09 (q, *J* = 7.1 Hz, 2H), 2.32 (s, 3H), 0.97 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (101



MHz, $CDCl_3$) δ 164.7, 154.0, 148.5, 133.0, 130.1, 129.6, 128.8, 128.2, 128.0, 127.6, 127.0, 123.0, 114.8, 60.5, 13.7, 12.1.The spectrum is in accordance with the literature[3].

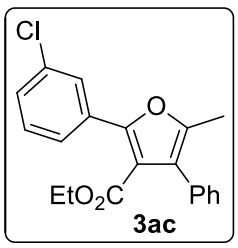
Ethyl 2-(2-chlorophenyl)-5-methyl-4-phenylfuran-3-carboxylate (3ab). Pale yellow oil was



3ab

obtained in 53% yield after purification with column chromatography on silica gel (petroleum ether/ethyl acetate, 100/1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.55–7.53 (m, 1H), 7.48–7.46 (m, 1H), 7.42–7.31 (m, 7H), 4.02 (q, *J* = 7.1 Hz, 2H), 2.32 (s, 3H), 0.92 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 163.4, 152.8, 149.4, 134.1, 132.5, 131.9, 130.4, 130.3, 130.1, 129.7, 127.9, 127.1, 126.3, 122.2, 116.8, 60.2, 13.6, 12.1. HRMS calc. for $C_{20}H_{17}ClO_3$ $[M+Na]^+$: 363.0764, found: 363.0764.

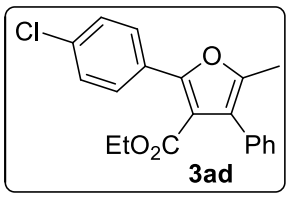
Ethyl 2-(3-chlorophenyl)-5-methyl-4-phenylfuran-3-carboxylate (3ac). Pale yellow oil was



3ac

obtained in 91% yield after purification with column chromatography on silica gel (petroleum ether/ethyl acetate, 100/1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.86–7.85 (m, 1H), 7.77–7.74 (m, 1H), 7.41–7.24 (m, 8H), 4.11 (q, *J* = 7.1 Hz, 2H), 2.32 (s, 3H), 1.00 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 164.4, 152.2, 149.0, 134.2, 132.7, 131.7, 129.6, 129.5, 128.7, 128.1, 127.5, 127.2, 125.6, 123.3, 115.7, 60.7, 13.6, 12.1. HRMS calc. for $C_{20}H_{17}ClO_3$ $[M+Na]^+$: 363.0764, found: 363.0768.

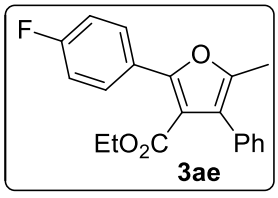
Ethyl 2-(4-chlorophenyl)-5-methyl-4-phenylfuran-3-carboxylate (3ad). Pale yellow solid was



3ad

obtained in 90% yield after purification with column chromatography on silica gel (petroleum ether/ethyl acetate, 100/1). M.p.: 66–68 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.82–7.80 (m, 2H), 7.41–7.36 (m, 4H), 7.34–7.24 (m, 3H), 4.08 (q, *J* = 7.1 Hz, 2H), 2.31 (s, 3H), 0.97 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 164.5, 152.9, 148.8, 134.7, 132.9, 129.6, 128.9, 128.6, 128.4, 128.0, 127.1, 123.2, 115.2, 60.6, 13.6, 12.1. HRMS calc. for $C_{20}H_{17}ClO_3$ $[M+Na]^+$: 363.0764, found: 363.0766.

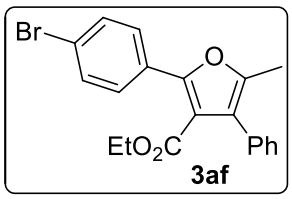
Ethyl 2-(4-fluorophenyl)-5-methyl-4-phenylfuran-3-carboxylate (3ae). Pale yellow solid was



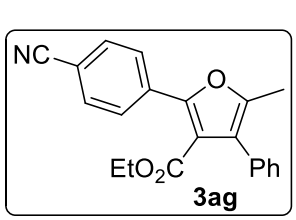
3ae

obtained in 89% yield after purification with column chromatography on silica gel (petroleum ether/ethyl acetate, 100/1). M.p.: 66–68 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.88–7.84 (m, 2H), 7.41–7.36 (m, 2H), 7.34–7.28 (m, 3H), 7.13–7.08 (m, 2H), 4.07 (q, *J* = 7.1 Hz, 2H), 2.31 (s, 3H), 0.96 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 164.5, 163.0 (d, *J* = 249.2 Hz), 153.5, 148.5, 133.0, 129.8 (d, *J* = 8.3 Hz),129.6, 128.0, 127.1, 126.4 (d, *J* = 3.4 Hz), 123.0, 115.2 (d, *J* = 21.7 Hz), 114.6, 60.5, 13.6, 12.0. HRMS calc. for $C_{20}H_{17}FO_3$ $[M+Na]^+$: 347.1059, found: 347.1054.

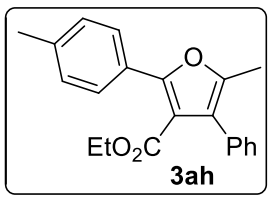
Ethyl 2-(4-bromophenyl)-5-methyl-4-phenylfuran-3-carboxylate (3af). Pale yellow solid was obtained in 82% yield after purification with column chromatography on silica gel (petroleum ether/ethyl acetate, 100/1). M.p.: 56–58 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.67–7.64 (m, 2H), 7.46–7.43 (m, 2H), 7.31–7.27 (m, 2H), 7.25–7.18 (m, 3H), 3.99 (q, *J* = 7.1 Hz, 2H), 2.22 (s, 3H), 0.88 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 164.5, 152.9, 148.8, 132.9, 131.4, 129.6, 129.1, 129.0, 128.0, 127.1, 123.2, 123.0, 115.3, 60.6, 13.6, 12.1. HRMS calc. for $C_{20}H_{17}BrO_3$ $[M+Na]^+$: 407.0259, found: 407.0265.



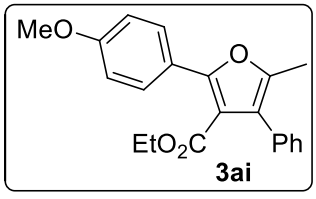
Ethyl 2-(4-cyanophenyl)-5-methyl-4-phenylfuran-3-carboxylate (3ag). Pale yellow solid was obtained in 60% yield after purification with column chromatography on silica gel (petroleum ether/ethyl acetate, 20/1). M.p.: 113–115 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.00 (d, *J* = 8.5 Hz, 2H), 7.69 (d, *J* = 8.5 Hz, 2H), 7.42–7.32 (m, 3H), 7.29–7.26 (m, 2H), 4.10 (q, *J* = 7.1 Hz, 2H), 2.35 (s, 3H), 0.97 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 164.3, 151.1, 150.0, 134.0, 132.4, 132.0, 129.5, 128.1, 127.5, 127.3, 123.8, 118.8, 117.3, 111.7, 60.9, 13.6, 12.2. HRMS calc. for $C_{21}H_{17}NO_3$ $[M+H]^+$: 332.1287, found: 332.1282.



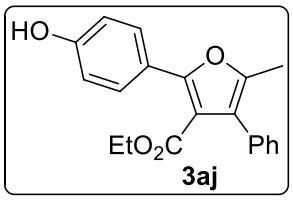
Ethyl 5-methyl-4-phenyl-2-(p-tolyl)furan-3-carboxylate (3ah). Pale yellow oil was obtained in 94% yield after purification with column chromatography on silica gel (petroleum ether/ethyl acetate, 100/1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.74–7.72 (m, 2H), 7.40–7.36 (m, 2H), 7.3 –7.28 (m, 3H), 7.23–7.21 (m, 2H), 4.08 (q, J = 7.1 Hz, 2H), 2.38 (s, 3H), 2.31 (s, 3H), 0.98 (t, J = 7.1 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 164.7, 154.4, 148.1, 138.8, 133.2, 129.6, 128.9, 128.0, 127.6, 127.4, 127.0, 122.9, 114.3, 60.4, 21.4, 13.7, 12.1. HRMS calc. for $C_{21}H_{20}O_3$ $[M+Na]^+$: 343.1310, found: 343.1308.



Ethyl 2-(4-methoxyphenyl)-5-methyl-4-phenylfuran-3-carboxylate (3ai). White solid was obtained in 88% yield after purification with column chromatography on silica gel (petroleum ether/ethyl acetate, 50/1). M.p.: 54–56 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.82–7.80 (m, 2H), 7.40–7.36 (m, 2H), 7.33–7.28 (m, 3H), 6.96–6.94 (m, 2H), 4.07 (q, *J* = 7.1 Hz, 2H), 3.84 (s, 3H), 2.30 (s, 3H), 0.97 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 164.7, 160.1, 154.6, 147.8, 133.3, 129.7, 129.3, 127.9, 126.9, 122.9, 122.8, 113.6, 60.3, 55.3, 13.7, 12.0. HRMS calc. for $C_{21}H_{20}O_4$ $[M+Na]^+$: 359.1259, found: 359.1251.



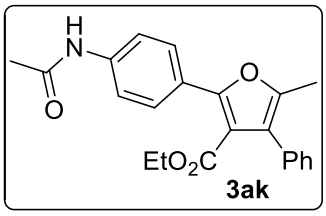
Ethyl 2-(4-hydroxyphenyl)-5-methyl-4-phenylfuran-3-carboxylate (3aj). White solid was



3aj

obtained in 31% yield after purification with column chromatography on silica gel (petroleum ether/ethyl acetate, 5/1). M.p.: 140–142 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.74 (d, *J* = 8.7 Hz, 2H), 7.50–7.15 (m, 6H), 6.85 (d, *J* = 8.7 Hz, 1H), 5.70 (s, 1H), 4.07 (q, *J* = 7.1 Hz, 2H), 2.30 (s, 3H), 0.95 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 165.1, 156.5, 155.0, 147.8, 141.5, 133.3, 129.6, 129.6, 127.9, 126.9, 122.7, 115.2, 113.4, 60.5, 13.6, 12.0. HRMS calc. for $C_{20}H_{18}O_4$ $[M+H]^+$: 323.1283, found: 323.1286.

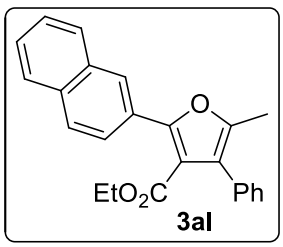
Ethyl 2-(4-acetamidophenyl)-5-methyl-4-phenylfuran-3-carboxylate (3ak). Pale yellow solid was



3ak

obtained in 89% yield after purification with column chromatography on silica gel (petroleum ether/ethyl acetate, 1/1). M.p.: 144–146 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.17 (s, 1H), 7.78 (d, *J* = 8.4 Hz, 2H), 7.56 (d, *J* = 8.5 Hz, 2H), 7.39–7.35 (m, 2H), 7.32–7.25 (m, 3H), 4.09 (q, *J* = 7.1 Hz, 2H), 2.30 (s, 3H), 2.12 (s, 3H), 0.98 (t, J = 7.2 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 168.9, 165.0, 154.0, 148.3, 138.7, 133.0, 129.6, 128.3, 128.0, 127.0, 125.7, 122.9, 119.3, 114.2, 60.6, 24.5, 13.6, 12.0.HRMS calc. for $C_{22}H_{21}NO_4$ $[M+H]^+$: 364.1549, found: 364.1544.

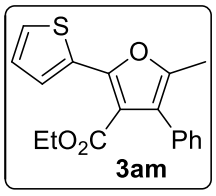
Ethyl 5-methyl-2-(naphthalen-2-yl)-4-phenylfuran-3-carboxylate (3al). Pale yellow solid was



3al

obtained in 89% yield after purification with column chromatography on silica gel (petroleum ether/ethyl acetate, 100/1). M.p.: 106–108 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.37 (s, 1H), 7.94–7.82 (m, 4H), 7.50 –7.46 (m, 2H), 7.42–7.38 (m, 2H), 7.34–7.30 (m, 3H), 4.12 (q, *J* = 7.1 Hz, 2H), 2.36 (s, 3H), 0.99 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 164.8, 154.0, 148.7, 133.3, 133.1, 133.0, 129.6, 128.6, 128.0, 127.8, 127.7, 127.5, 127.1, 127.1, 126.7, 126.4, 125.1, 123.2, 115.2, 60.6, 13.7, 12.2. HRMS calc. for $C_{24}H_{20}O_3$ $[M+Na]^+$: 379.1310, found: 379.1305.

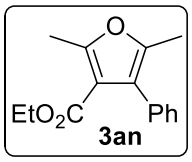
Ethyl 5-methyl-4-phenyl-2-(thiophen-2-yl)furan-3-carboxylate (3am). Pale yellow oil was



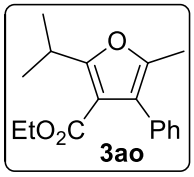
3am

obtained in 94% yield after purification with column chromatography on silica gel (petroleum ether/ethyl acetate, 100/1).^{1}H NMR (400 MHz, $CDCl_3$) δ 7.89–7.88 (m, 1H), 7.29–7.25 (m, 6H), 7.10–7.08 (m, 1H), 4.11 (q, *J* = 7.1 Hz, 2H), 2.28 (s, 3H), 0.99 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 164.1, 150.6, 148.1, 133.1, 131.8, 129.8, 127.8, 127.8, 127.3, 127.2, 127.0, 123.0, 113.2, 60.4, 13.7, 12.0. HRMS calc. for $C_{18}H_{16}O_3S$ $[M+Na]^+$: 335.0718, found: 335.0711.

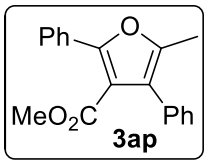
Ethyl 2,5-dimethyl-4-phenylfuran-3-carboxylate (3an). Pale yellow oil was obtained in 92% yield after purification with column chromatography on silica gel (petroleum ether/ethyl acetate, 100/1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37–7.33 (m, 2H), 7.31–7.23 (m, 3H), 4.11 (q, *J* = 7.1 Hz, 2H), 2.57 (s, 3H), 2.19 (s, 3H), 1.09 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 164.3, 157.4, 147.1, 133.3, 130.0, 127.6, 126.8, 121.4, 113.5, 59.8, 14.1, 14.0, 11.8. HRMS calc. for $C_{15}H_{16}O_3$ $[M+H]^+$: 245.1178, found: 245.1140.



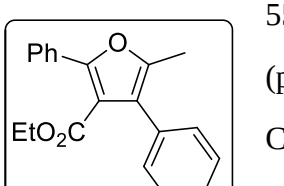
Ethyl 2-isopropyl-5-methyl-4-phenylfuran-3-carboxylate(3ao). Pale yellow oil was obtained in 81% yield after purification with column chromatography on silica gel (petroleum ether/ethyl acetate, 100/1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37–7.32 (m, 2H), 7.30–7.23 (m, 3H), 4.09 (q, *J* = 7.1 Hz, 2H), 3.72 (p, *J* = 7.0 Hz, 1H), 2.20 (s, 3H), 1.30 (d, *J* = 7.0 Hz, 6H), 1.05 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 165.2, 164.3, 146.9, 133.5, 130.0, 127.6, 126.7, 121.1, 111.7, 59.7, 27.3, 21.0, 13.8, 11.8. HRMS calc. for $C_{17}H_{20}O_3$ $[M+Na]^+$: 295.1310, found: 295.1312.



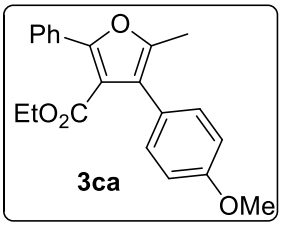
Methyl 5-methyl-2,4-diphenylfuran-3-carboxylate(3ap). White solid was obtained in 91% yield after purification with column chromatography on silica gel (petroleum ether/ethyl acetate, 100/1). M.p.: 94–96 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.73–7.71 (m, 2H), 7.36–7.29 (m, 5H), 7.27–7.21 (m, 3H), 3.52 (s, 3H), 2.25 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 165.2, 154.1, 148.6, 132.8, 130.1, 129.5, 128.8, 128.3, 128.1, 127.6, 127.1, 122.9, 114.5, 51.5, 12.1.HRMS calc. for $C_{19}H_{16}O_3$ $[M+H]^+$: 293.1178, found: 293.1176.



Ethyl 5-methyl-2-phenyl-4-(p-tolyl)furan-3-carboxylate (3ba). Pale yellow solid was obtained in 55% yield after purification with column chromatography on silica gel (petroleum ether/ethyl acetate, 100/1). M.p.: 66–68 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.82–7.79 (m, 2H), 7.43–7.32 (m, 3H), 7.23–7.18 (m, 4H), 4.11 (q, *J* = 7.1 Hz, 2H), 2.38 (s, 3H), 2.31 (s, 3H), 1.02 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 164.8, 153.8, 148.4, 136.6, 130.2, 129.9, 129.5, 128.7, 128.7, 128.2, 127.6, 122.9, 114.9, 60.5, 21.3, 13.7, 12.1. HRMS calc. for $C_{21}H_{20}O_3$ $[M+Na]^+$: 343.1310, found: 343.1305.

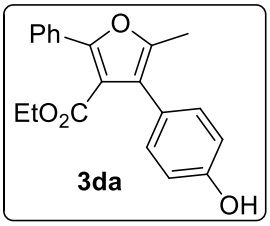


Ethyl 4-(4-methoxyphenyl)-5-methyl-2-phenylfuran-3-carboxylate (3ca). Pale yellow oil was obtained in 72% yield after purification with column chromatography on silica gel (petroleum ether/ethyl acetate, 100/1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.82–7.80 (m, 2H), 7.42–7.32 (m, 3H), 7.25–7.21 (m, 2H), 6.95–6.91 (m, 2H), 4.11 (q, *J* = 7.1 Hz, 2H), 3.82 (s, 3H), 2.30 (s, 3H), 1.03 (t, *J* = 7.1 Hz,



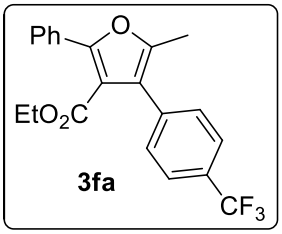
3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 164.8, 158.7, 153.8, 148.4, 130.8, 130.2, 128.7, 128.2, 127.6, 125.2, 122.5, 114.9, 113.5, 60.5, 55.3, 13.8, 12.1. HRMS calc. for $C_{21}H_{20}O_4$ $[M+Na]^+$: 359.1259, found: 329.1251.

Ethyl 4-(4-hydroxyphenyl)-5-methyl-2-phenylfuran-3-carboxylate (3da). White solid was



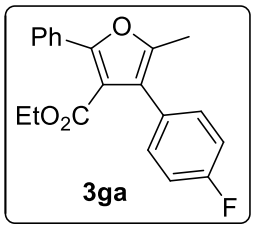
obtained in 59% yield after purification with column chromatography on silica gel (petroleum ether/ethyl acetate, 5/1). M.p.: 115–117 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.79–7.76 (m, 2H), 7.43–7.33 (m, 3H), 7.15–7.13 (m, 2H), 6.80– 6.78 (m, 2H), 5.84 (s, 1H), 4.14 (q, *J* = 7.1 Hz, 2H), 2.30 (s, 3H), 1.05 (t, *J* = 7.1 Hz, 3H).; ^{13}C NMR (101 MHz, $CDCl_3$) δ 165.3, 155.0, 154.1, 148.5, 130.8, 130.2, 129.0, 128.8, 128.2, 127.7, 124.8, 122.6, 115.1, 60.8, 13.7, 12.0. HRMS calc. for $C_{20}H_{18}O_4$ $[M+H]^+$: 323.1283, found: 323.1279.

Ethyl 5-methyl-2-phenyl-4-(4-(trifluoromethyl)phenyl)furan-3-carboxylate (3fa). Pale yellow oil



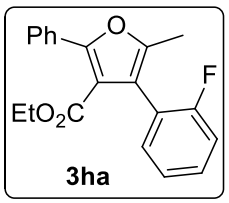
was obtained in 53% yield after purification with column chromatography on silica gel (petroleum ether/ethyl acetate, 100/1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.85–7.82 (m, 2H), 7.66–7.64 (m, 2H), δ 7.45–7.36 (m, 5H), 4.09 (q, *J* = 7.1 Hz, 2H), 2.32 (s, 3H), 0.98 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 164.1, 154.9, 148.9, 137.0, 130.0, 129.8, 129.1, 128.2, 127.9, 124.9 (q, *J* = 3.7 Hz) , 121.9, 114.3, 100.0, 60.6, 13.6, 12.1. ^{13}C NMR (101 MHz, $CDCl_3$) δ 164.1, 154.9, 149.0, 137.0, 130.0, 129.8, 129.2 (d, *J* = 32.4 Hz), 129.1, 128.2, 127.9, 124.90 (q, *J* = 3.8 Hz), 124.3 (d, *J* = 272.0 Hz), 121.9, 114.3, 60.6, 13.6, 12.0. HRMS calc. for $C_{21}H_{17}F_3O_3$ $[M+Na]^+$: 397.1027, found: 397.1029.

Ethyl 4-(4-fluorophenyl)-5-methyl-2-phenylfuran-3-carboxylate (3ga). Pale yellow solid was

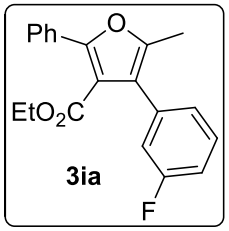


obtained in 96% yield after purification with column chromatography on silica gel (petroleum ether/ethyl acetate, 100/1). M.p.: 64–66 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.83–7.81 (m, 2H), 7.44–7.36 (m, 3H), 7.29–7.24 (m, 3H), 7.10–7.06 (m, 2H), 4.10 (q, *J* = 7.2 Hz, 2H), 2.29 (s, 3H), 1.01 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 164.4, 162.0 (d, *J* = 246.0 Hz), 154.4, 148.6, 131.3 (d, *J* = 8.0 Hz), 130.0, 129.0 (d, *J* = 3.4 Hz), 129.0, 128.2, 127.8, 122.0, 114.9 (d, *J* = 21.4 Hz), 114.6, 60.5, 13.7, 12.0. HRMS calc. for $C_{20}H_{17}FO_3$ $[M+Na]^+$: 347.1059, found: 347.1060.

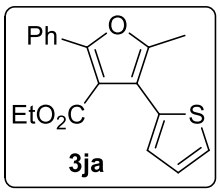
Ethyl 4-(2-fluorophenyl)-5-methyl-2-phenylfuran-3-carboxylate (3ha). Pale yellow oil was obtained in 86% yield after purification with column chromatography on silica gel (petroleum ether/ethyl acetate, 100/1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.89–7.87 (m, 2H), 7.44–7.35 (m, 3H), 7.34–7.24 (m, 3H), 7.19–7.09 (m, 2H), 4.08 (q, *J* = 7.1 Hz, 2H), 2.29 (s, 3H), 0.97 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 164.0, 160.4 (d, *J* = 246.4 Hz), 155.1, 149.3, 131.7 (d, *J* = 3.3 Hz), 130.0, 129.2 (d, *J* = 8.1 Hz), 129.0, 128.1, 128.1, 123.7 (d, *J* = 3.6 Hz), 121.1 (d, *J* = 15.8 Hz), 116.8, 115.3 (d, *J* = 22.1 Hz), 114.8, 60.4, 13.6, 12.1. HRMS calc. for $C_{20}H_{17}FO_3$ [M+Na]$^+$: 347.1059, found: 347.1058.



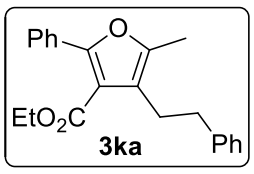
Ethyl 4-(3-fluorophenyl)-5-methyl-2-phenylfuran-3-carboxylate (3ia). Pale yellow oil was obtained in 94% yield after purification with column chromatography on silica gel (petroleum ether/ethyl acetate, 100/1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.85–7.82 (m, 2H), 7.44–7.32 (m, 4H), 7.09–7.00 (m, 3H), 4.11 (q, *J* = 7.1 Hz, 2H), 2.32 (s, 3H), 1.01 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 164.3, 162.5 (d, *J* = 245.2 Hz), 154.4, 148.7, 135.3 (d, *J* = 8.4 Hz), 129.9, 129.4 (d, *J* = 8.5 Hz), 129.0, 128.2, 127.7, 125.4 (d, *J* = 2.8 Hz), 122.0, 116.7(d, *J* = 21.7 Hz), 114.5, 113.9 (d, *J* = 21.0 Hz), 60.6, 13.6, 12.1. HRMS calc. for $C_{20}H_{17}FO_3$ [M+Na]$^+$: 347.1059, found: 347.1055.



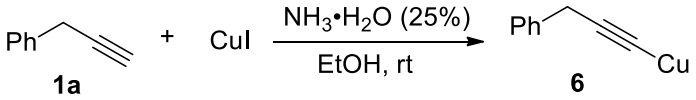
Ethyl 5-methyl-2-phenyl-4-(thiophen-2-yl)furan-3-carboxylate (3ja). Pale yellow oil was obtained in 40% yield after purification with column chromatography on silica gel (petroleum ether/ethyl acetate, 100/1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.80–7.78 (m, 2H), 7.43–7.33 (m, 4H), 7.08–7.02(m, 2H), 4.16 (q, *J* = 7.1 Hz, 2H), 2.39 (s, 3H), 1.09 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 164.4, 153.9, 149.9, 133.3, 129.9, 128.9, 128.2, 127.5, 127.4, 126.8, 125.5, 115.9, 115.1, 60.8, 13.7, 12.4. HRMS calc. for $C_{18}H_{16}O_3S$ [M+H]$^+$: 313.0898, found: 313.0896.



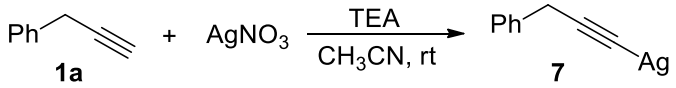
Ethyl 5-methyl-4-phenethyl-2-phenylfuran-3-carboxylate (3ka). Colorless oil was obtained in 60% yield after purification with column chromatography on silica gel (petroleum ether/ethyl acetate, 100/1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.76–7.74 (m, 2H), 7.42–7.33 (m, 3H), 7.29 –7.25 (m, 2H), 7.21–7.15 (m, 3H), 4.30 (q, *J* = 7.1 Hz, 2H), 2.85 (m, 4H), 1.99 (s, 3H), 1.30 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 164.6, 155.3, 148.5, 141.9, 130.6, 128.7, 128.7, 128.3, 128.3, 127.9, 125.9, 119.9, 113.9, 60.3, 36.8, 26.8, 14.2, 11.0. HRMS calc. for $C_{22}H_{22}O_3$ [M+H]$^+$: 335.1647, found: 335.1628.



Preparation of Cu-acetylide 6[4] and Ag-acetylide 7[5]

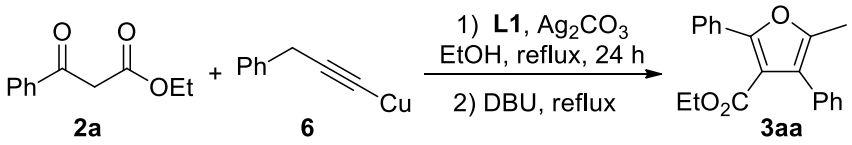


To a solution of copper iodide (3.81 g, 20.0 mmol) in a mixture of ammonium hydroxide (25% NH_3 solution, 55 mL) and ethanol (30 mL) was added prop-2-yn-1-ylbenzene **1a** (1.16g, 10.0 mmol) dropwise. The deep blue reaction mixture was stirred overnight at room temperature under nitrogen and the yellow precipitate was collected by filtration and successively washed with ammonium hydroxide (25% NH_3 solution, 3x50 mL), water (3x50 mL), ethanol (3x50 mL), and diethyl ether (3x50 mL). The bright yellow solid was then dried under high vacuum overnight to afford 1.01g (3-phenylprop-1-yn-1-yl)copper **6**[4] in 57% yield which was used without further purification.

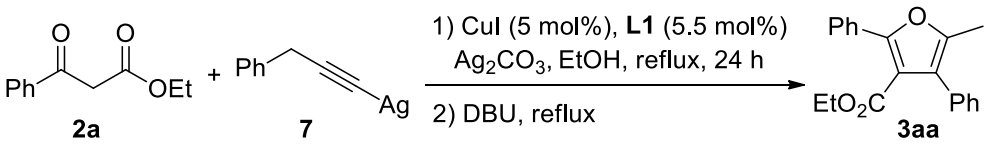


Silver nitrate (1.70 g, 10 mmol) was dissolved in acetonitrile (50 mL). Then prop-2-yn-1-ylbenzene **1a** (1.16 g, 10 mmol) and triethylamine (1.4 mL, 10 mmol) were added successively with vigorous stirring and the mixture was stirred overnight under a nitrogen atmosphere in darkness. The white precipitate formed was collected by filtration, washed thoroughly with acetonitrile (2 × 10 mL). The white solid was then dried in darkness under high vacuum to afford 1.78g (3-phenylprop-1-yn-1-yl)silver **7**[5] in 80% yield which was used immediately without further purification.

Experimental procedure for control experiments eq.3 and eq.4

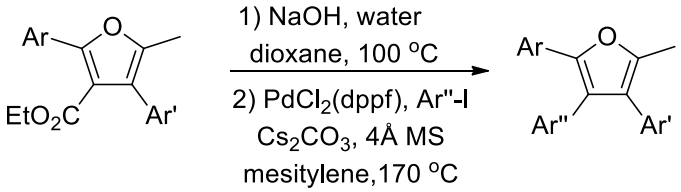


Ethyl 3-oxo-3-phenylpropanoate **2a** (38.4 mg, 0.2 mmol), (3-phenylprop-1-yn-1-yl)copper **6** (78.6 mg, 0.44 mmol), 1,10-phenanthroline hydrate **L1** (95.1 mg, 0.48 mmol), and Ag_2CO_3 (66.2 mg, 0.24 mmol) were added to 3 mL anhydrous ethanol in an oven-dried Schlenk flask under a nitrogen atmosphere, the reaction stirred at 80 ^oC for 24 h. Then the reaction mixture was cooled to room temperature, DBU (36.5 mg, 0.24 mmol) was added directly to the resulting reaction mixture without further purification and continued stirring at 80 ^oC being monitored by TLC. The reaction mixture was then filtered, washed with dichloromethane (10 mL) and concentrated under vacuum. The residue was purified by silica gel chromatography (petroleum ether/ethyl acetate, 100/1) to afford pale yellow oil **3aa** in 89% yield.



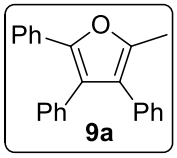
A solution of CuI (1.9 mg, 0.01 mmol) and 1,10-phenanthroline hydrate **L1** (2.2 mg, 0.011 mmol) in 1 mL of anhydrous ethanol placed in an oven-dried Schlenk flask was stirred at room temperature under a nitrogen atmosphere for 1 h. A solution of ethyl 3-oxo-3-phenylpropanoate **2a** (38.4 mg, 0.2 mmol), (3-phenylprop-1-yn-1-yl)silver **7** (98.1 mg, 0.44 mmol) and $^{i}Pr_2NEt$ (42 μL, 0.24 mmol) in 2 mL of anhydrous ethanol was added. The reaction mixture was allowed to stir for 24 h at 80 °C. Then the reaction mixture was cooled to room temperature, DBU (36.5 mg, 0.24 mmol) was added directly to the resulting reaction mixture without further purification and continued stirring at 80 °C being monitored by TLC. The reaction mixture was then filtered, washed with dichloromethane (10 mL) and concentrated under vacuum. The residue was purified by silica gel chromatography (petroleum ether/ethyl acetate, 100/1) to afford pale yellow oil **3aa** in 31% yield.

Transformation of cycloadduct via catalytic decarboxylative coupling



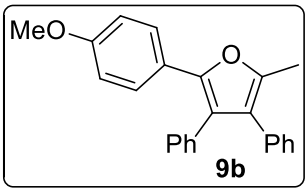
Transformation of cycloadduct proceeded according to the literature[6]. Cycloadduct **3** (0.25 mmol, 1 equiv) in 0.5 M aq. NaOH (2 equiv, 4 mL/mmol) and dioxane was stirred at 100 °C for 12 h. At this time, the mixture was acidified by concd aq HCl and extracted with EtOAc to afford the carboxylic acid without further purification. $PdCl_2$(dppf) (10 mol %), carboxylic acid **3'** (0.25 mmol, 1 equiv), iodide (2 equiv), Cs_2CO_3 (3 equiv), 4Å MS (300 mg/mmol) and 4 mL mesitylene were added to an oven-dried Schlenk flask equipped with a stir bar under nitrogen atmosphere. The reaction mixture was stirred at 170 °C for 12 h. After the reaction was complete, the flask were filtered through the plug of silica gel, and then concentrated by rotary evaporation. The residue was purified by flash chromatography, eluting with hexane/EtOAc to afford the product **9**.

2-Methyl-3,4,5-triphenylfuran (9a). White solid was obtained in 84% yield after purification with column chromatography on silica gel (petroleum ether/ethyl acetate, 100/1). M.p.: 130–132 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.44–7.41 (m, 2H), 7.24–7.18 (m, 8H), 7.17–7.12 (m, 3H), 7.06–7.03 (m, 2H), 2.42 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ

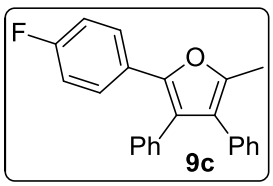


147.9, 146.9, 133.8, 133.1, 131.3, 130.4, 129.8, 128.5, 128.3, 128.1, 127.1, 127.0, 126.46, 125.7, 123.9, 123.0, 12.6. HRMS calc. for $C_{23}H_{18}O$ $[M+H]^+$: 311.1436, found: 311.1433.

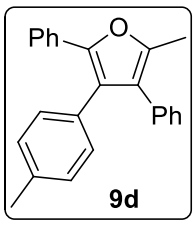
2-(4-Methoxyphenyl)-5-methyl-3,4-diphenylfuran (9b). White solid was obtained in 86% yield after purification with column chromatography on silica gel (petroleum ether/ethyl acetate, 20/1). M.p.: 128–130 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37–7.34 (m, 2H), 7.25–7.13 (m, 8H), 7.06–7.04 (m, 2H), 6.78–6.76 (m, 2H), 3.76 (s, 3H), 2.42 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 158.6, 147.2, 147.0, 133.9, 133.2, 130.4, 129.7, 128.4, 128.0, 127.2, 126.8, 126.3, 124.1, 123.6, 121.4, 113.8, 55.2, 12.6. HRMS calc. for $C_{24}H_{20}O_2$ $[M+H]^+$: 341.1542, found: 341.1544.



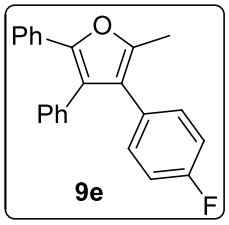
2-(4-Fluorophenyl)-5-methyl-3,4-diphenylfuran (9c). White solid was obtained in 87% yield after purification with column chromatography on silica gel (petroleum ether/ethyl acetate, 100/1). M.p.: 144–146 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.42–7.36 (m, 2H), 7.27–7.18 (m, 6H), 7.17–7.12 (m, 2H), 7.06–7.03 (m, 2H), 6.94–6.89 (m, 2H), 2.42 (s, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 161.78 (d, J = 246.9 Hz), 147.80, 146.10, 133.53, 132.94, 130.33, 129.71, 128.65, 128.52, 128.06, 127.41 (d, J = 7.9 Hz), 127.12, 126.45, 123.82, 122.59, 115.28 (d, J = 21.7 Hz), 12.56. HRMS calc. for $C_{23}H_{17}FO$ $[M+H]^+$: 329.1342, found: 329.1336.



2-Methyl-3,5-diphenyl-4-(p-tolyl)furan (9d). White solid was obtained in 83% yield after purification with column chromatography on silica gel (petroleum ether/ethyl acetate, 100/1). M.p.: 104–106 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.45–7.41 (m, 2H), 7.25–7.12 (m, 8H), 7.07–7.04 (m, 6H), 2.41 (s, 3H), 2.31 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 147.8, 146.8, 136.6, 133.2, 131.4, 130.6, 130.2, 129.8, 129.2, 128.3, 128.0, 126.8, 126.4,125.6, 123.9, 122.9, 21.4, 12.6. HRMS calc. for $C_{24}H_{20}O$ $[M+H]^+$: 325.1592, found: 325.1590.



3-(4-Fluorophenyl)-2-methyl-4,5-diphenylfuran (9e). White solid was obtained in 85% yield after purification with column chromatography on silica gel (petroleum ether/ethyl acetate, 100/1). M.p.: 138–140 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.43–7.41 (m, 2H), 7.27–7.12 (m, 8H), 7.02–6.98 (m, 2H), 6.95–6.90 (m, 2H), 2.41 (s, 3H); ^{13}C NMR (101 MHz, CDCl3) δ 161.6 (d, J = 245.5 Hz), 147.8, 146.9, 133.6, 131.2 (d, J = 7.9 Hz), 131.1, 130.3, 129.0 (d, J = 3.3 Hz), 128.5, 128.3, 127.1, 127.0, 125.6, 123.0, 122.8, 115.0 (d, J = 21.3 Hz), 12.5. HRMS calc. for $C_{23}H_{17}FO$ $[M+H]^+$: 329.1342, found: 329.1346.



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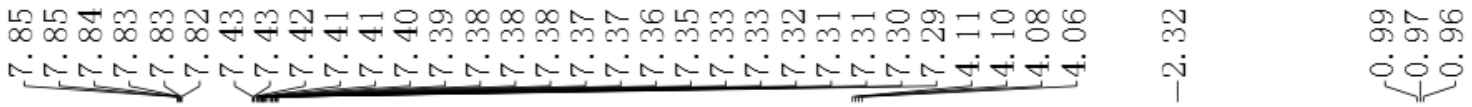
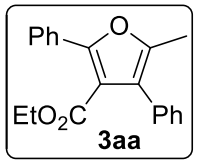
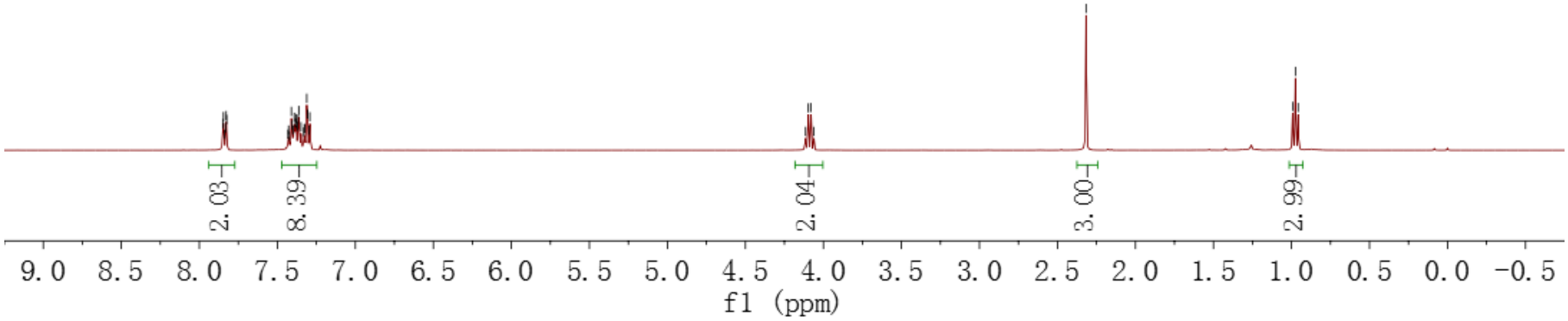
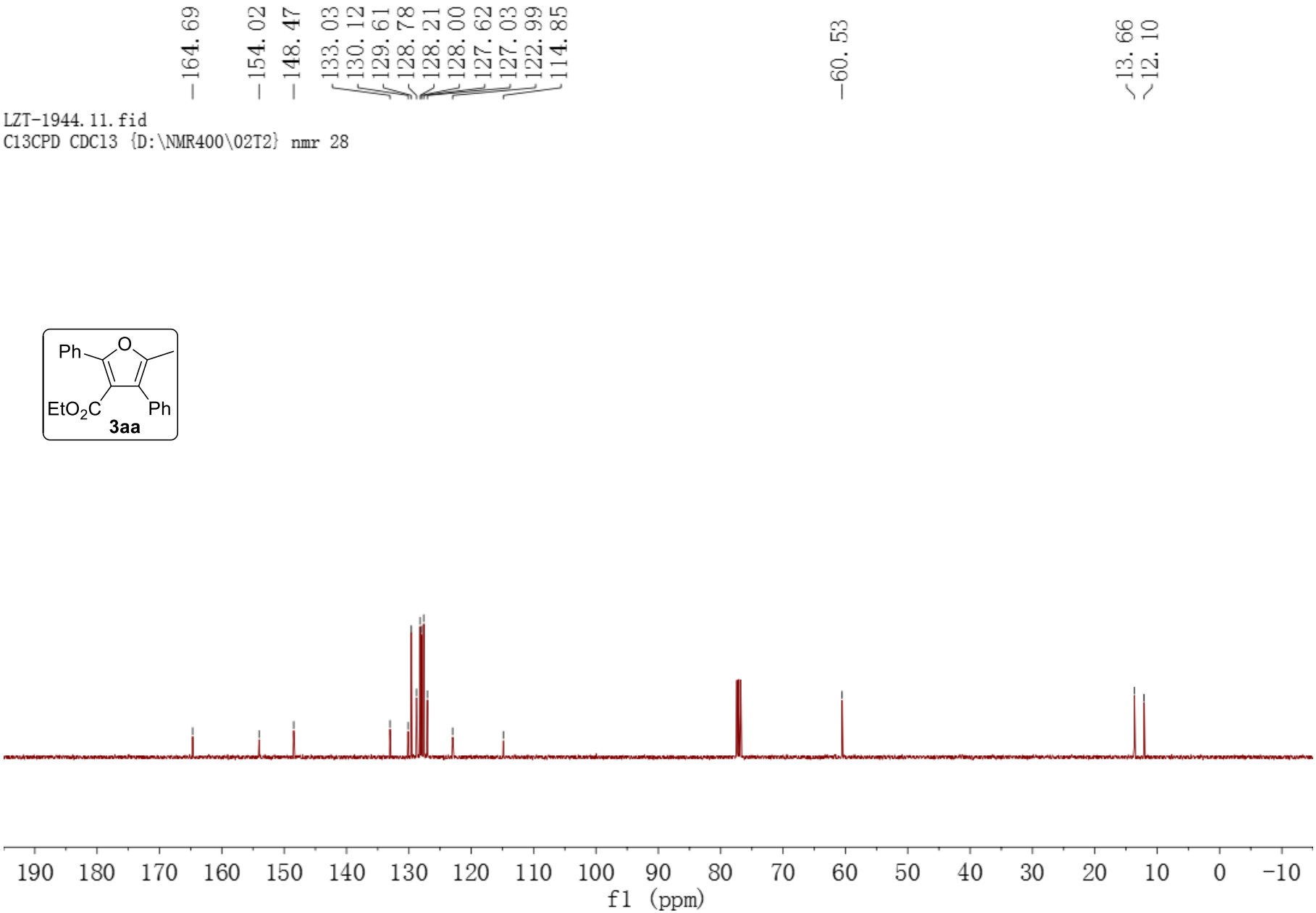


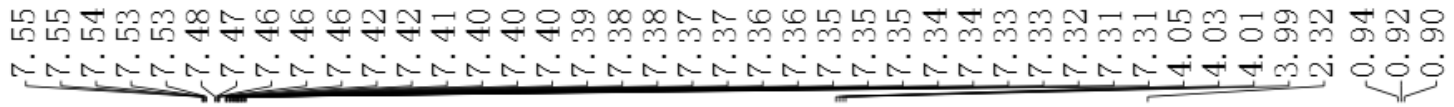
LZT-1944.10.fid
PROTON CDCl3 {D:\NMR400\02T2} nmr 28



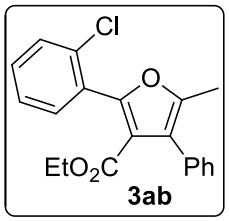
3aa

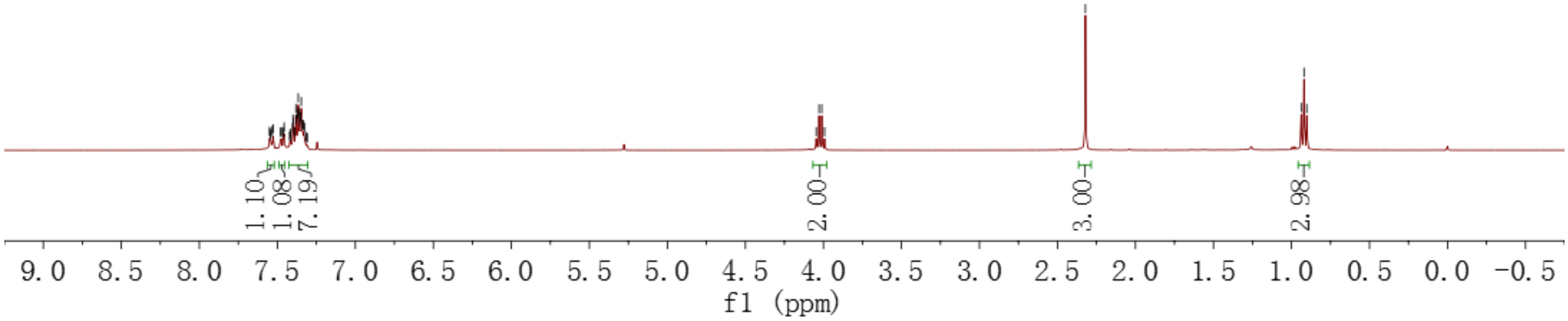


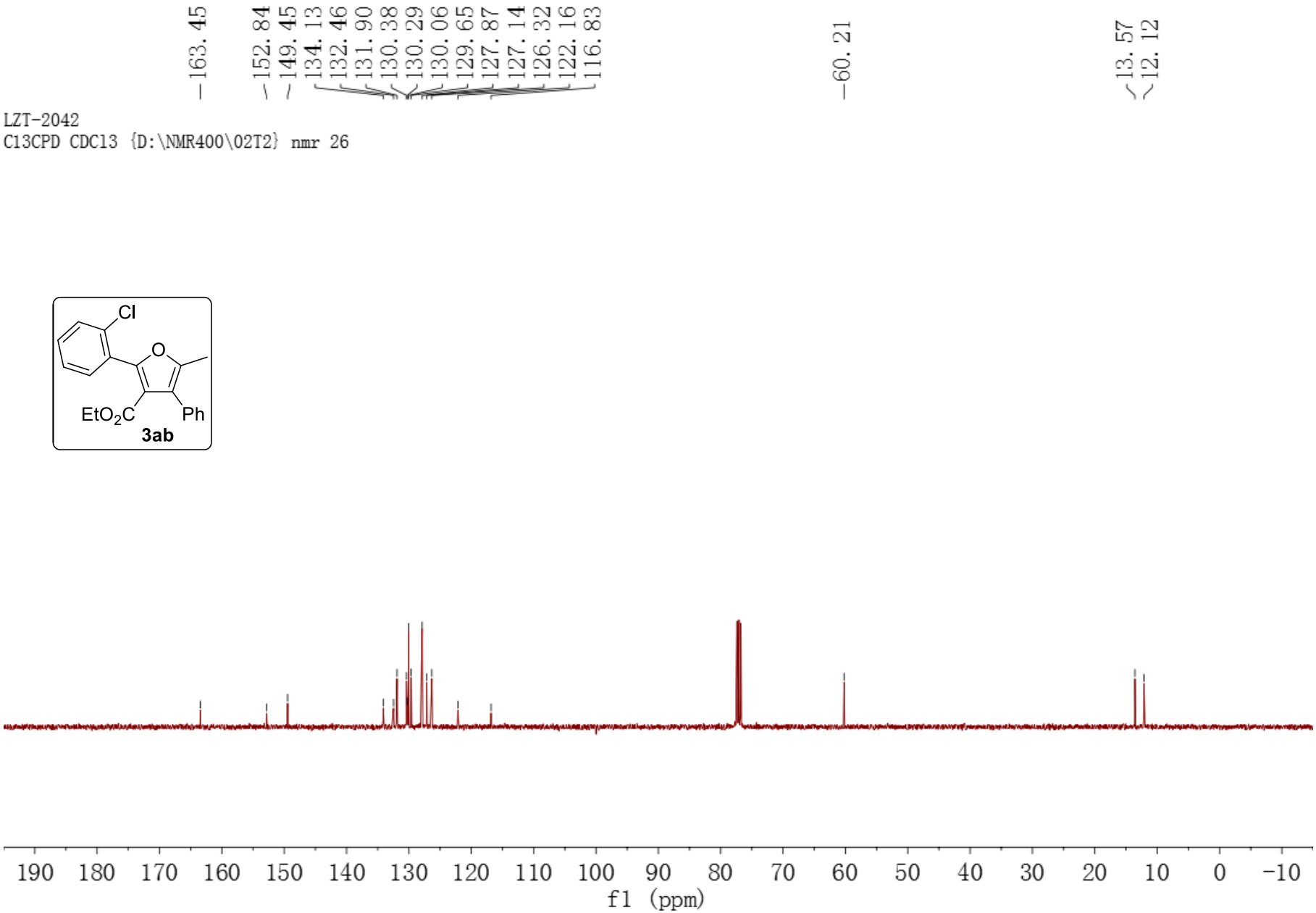

164.69
154.02
148.47
133.03
130.12
129.61
128.78
128.21
128.00
127.62
127.03
122.99
114.85
60.53
13.66
12.10
LZT-1944.11.fid
C13CPD CDCl3 {D:\NMR400\02T2} nmr 28
Ph
O
EtO2C
Ph
3aa
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

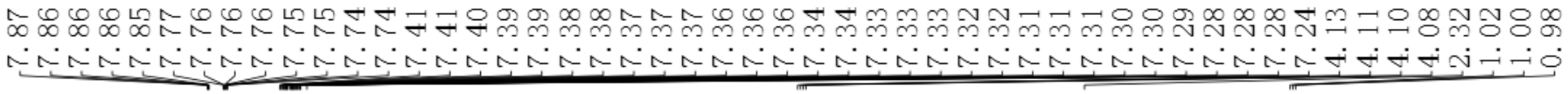


LZT-2042
PROTON CDCl3 {D:\NMR400\02T2} nmr 26

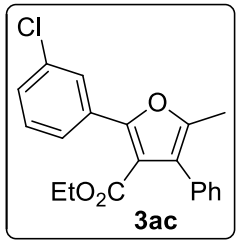




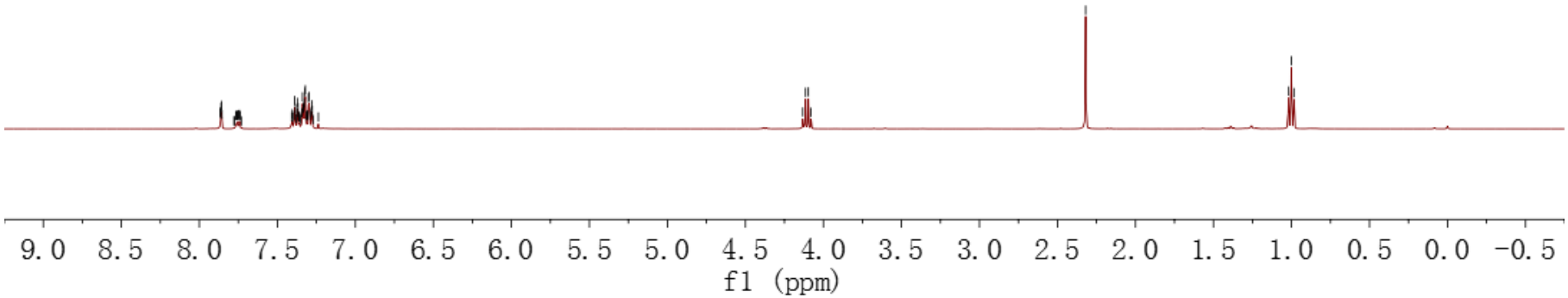

163.45
152.84
149.45
134.13
132.46
131.90
130.38
130.29
130.06
129.65
127.87
127.14
126.32
122.16
116.83
60.21
13.57
12.12
LZT-2042
C13CPD CDCl3 {D:\NMR400\02T2} nmr 26
Cl
O
EtO2C
Ph
3ab
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

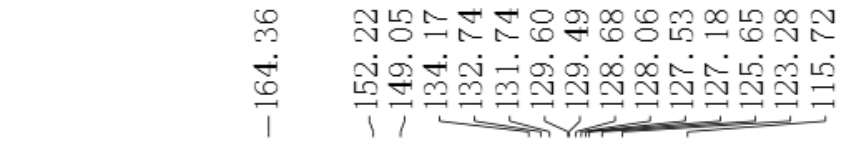


LZT-2053
PROTON CDC13 {D:\NMR400\02T2} nmr 48

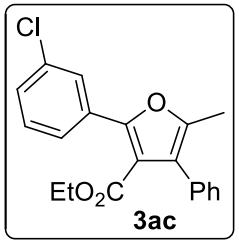


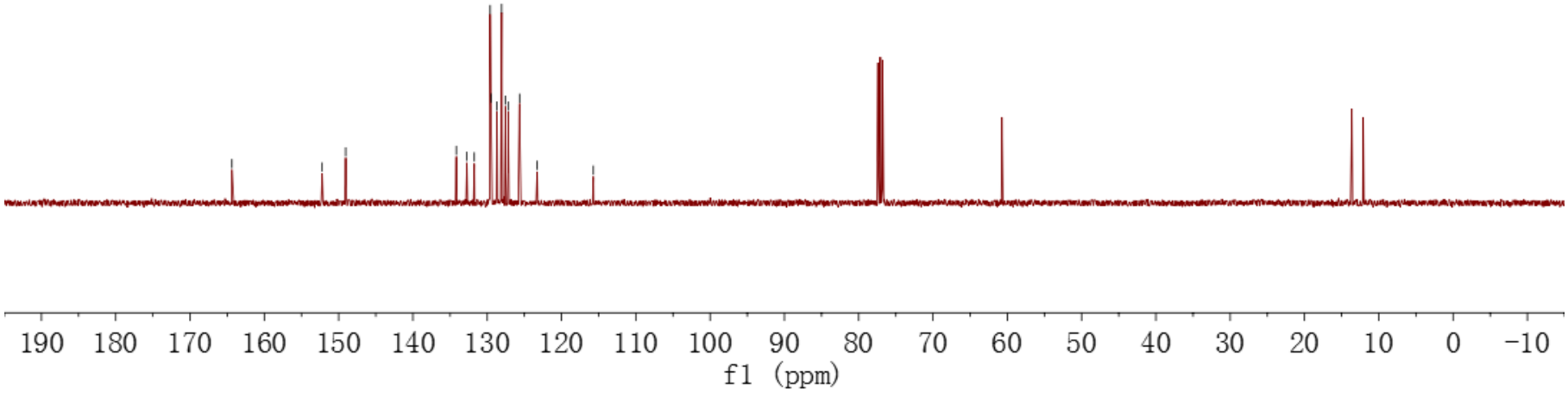
3ac

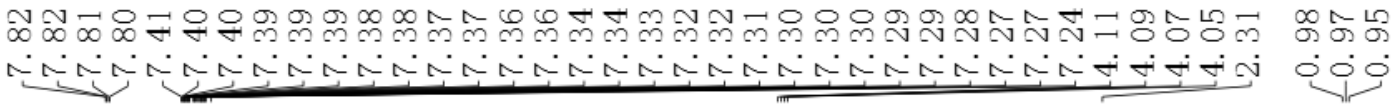




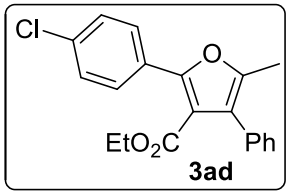
LZT-2053
C13CPD CDCl3 {D:\NMR400\02T2} nmr 48

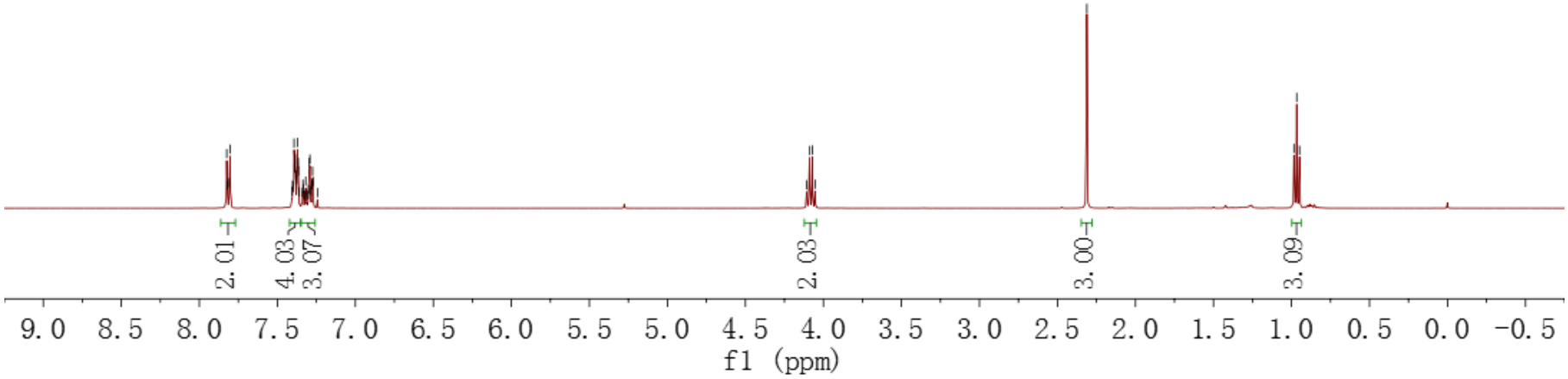


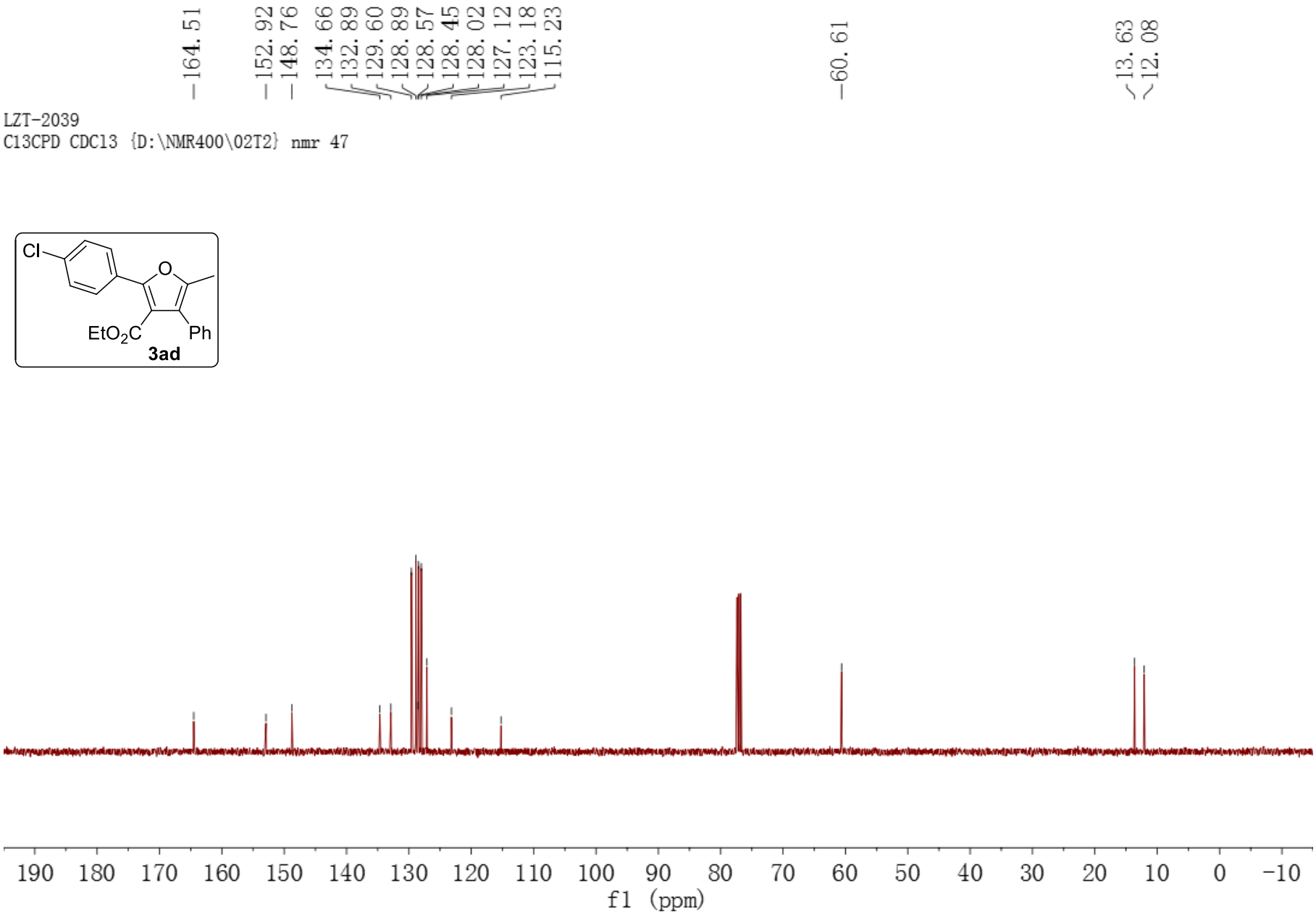


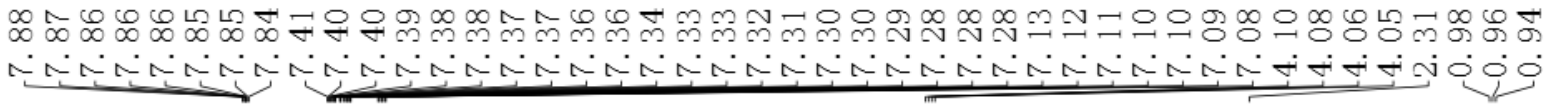


LZT-2039
PROTON CDC13 {D:\NMR400\02T2} nmr 47

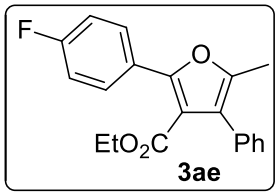


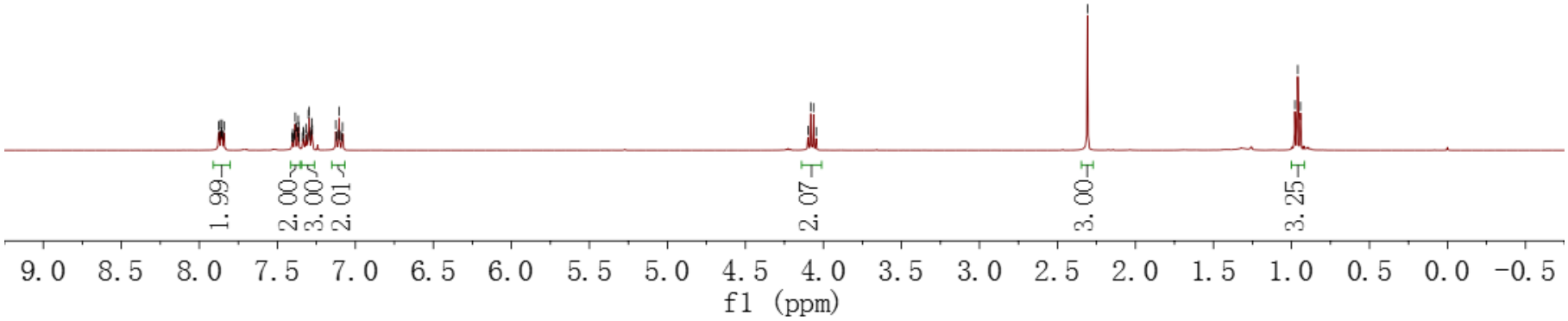



164.51
152.92
148.76
134.66
132.89
129.60
128.89
128.57
128.45
128.02
127.12
123.18
115.23
60.61
13.63
12.08
LZT-2039
C13CPD CDCl3 {D:\NMR400\02T2} nmr 47
Cl
O
EtO2C
Ph
3ad
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)



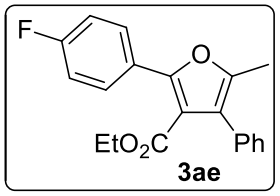
LZT-2038
PROTON CDC13 {D:\NMR400\02T2} nmr 45



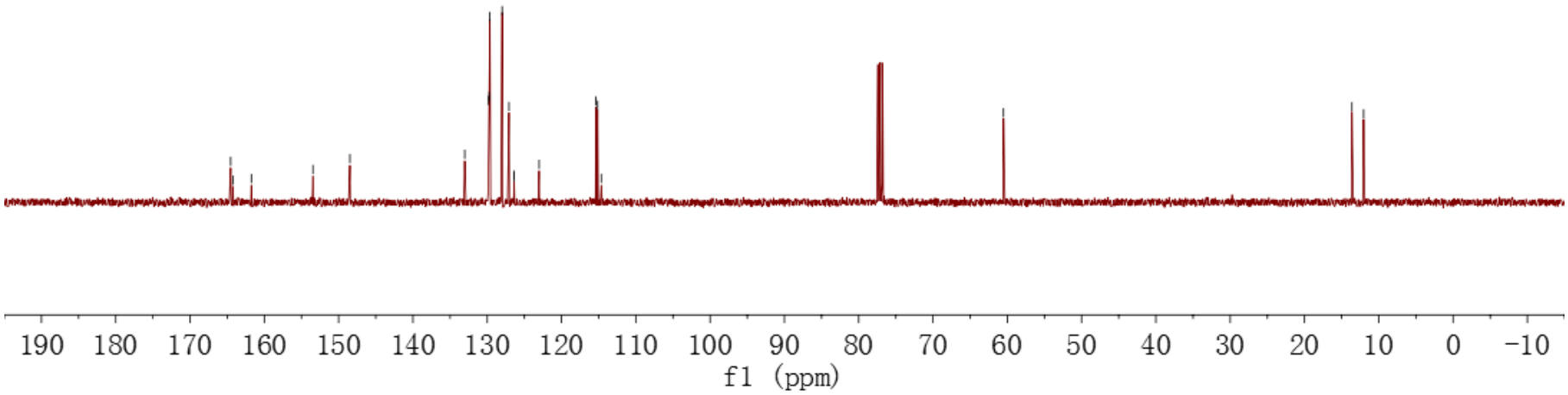


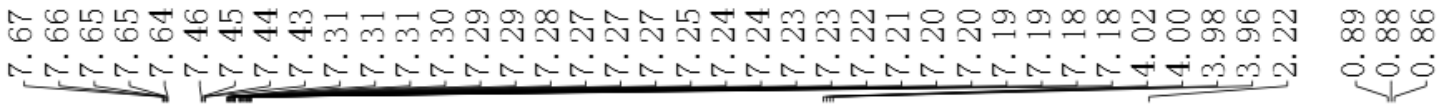
164.53
164.22
161.74
153.46
148.48
133.02
129.82
129.74
129.64
127.99
127.07
126.40
126.37
123.02
115.36
115.14
114.65
60.52
13.62
12.04

LZT-2038
C13CPD CDCl3 {D:\NMR400\02T2} nmr 15

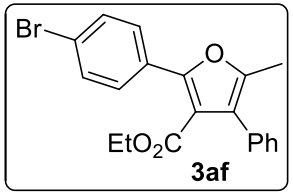


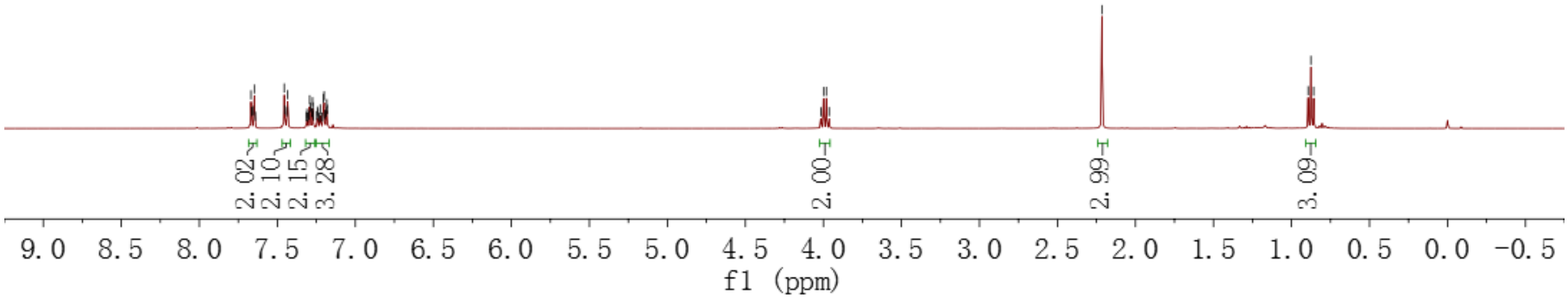
3ae

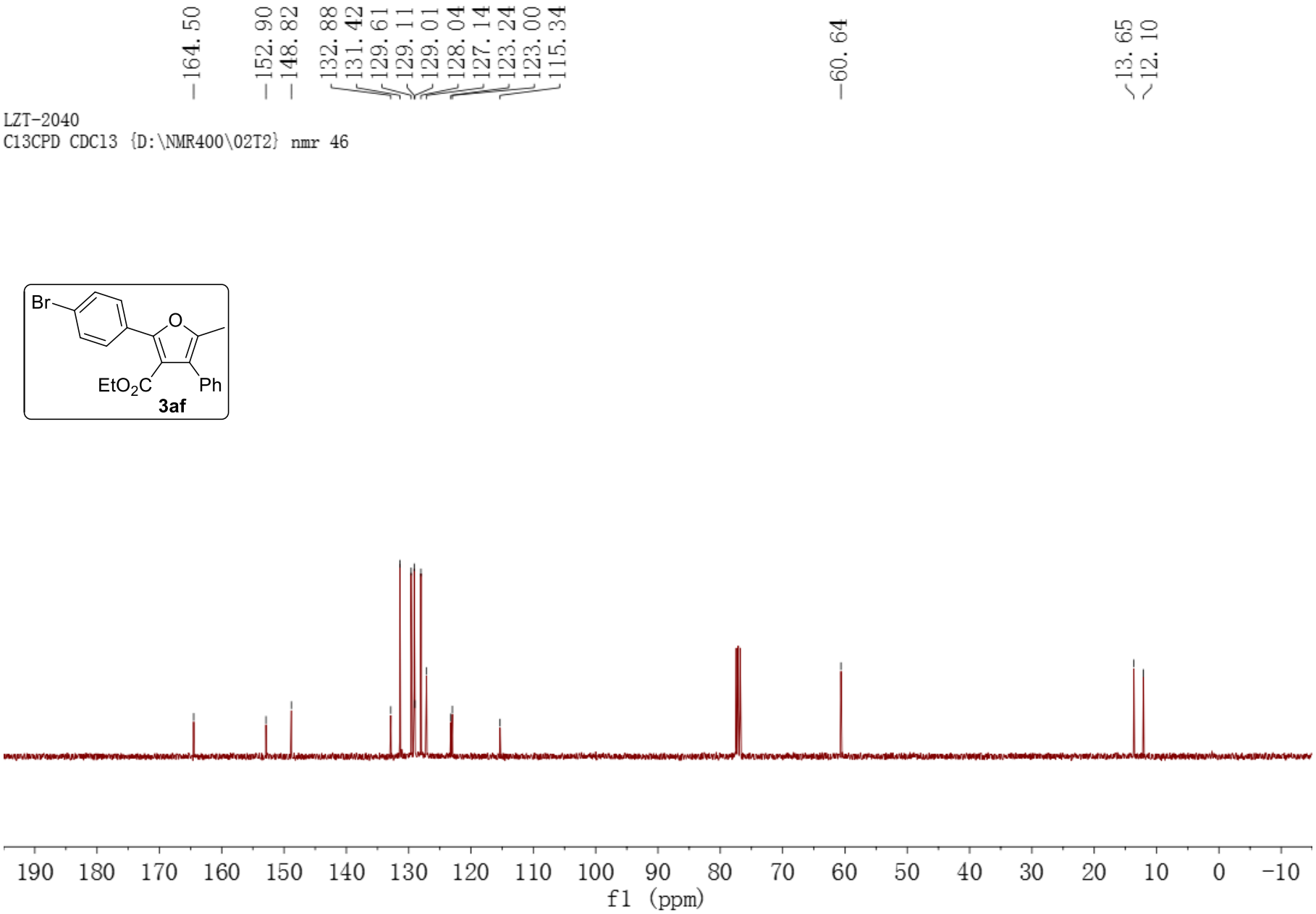


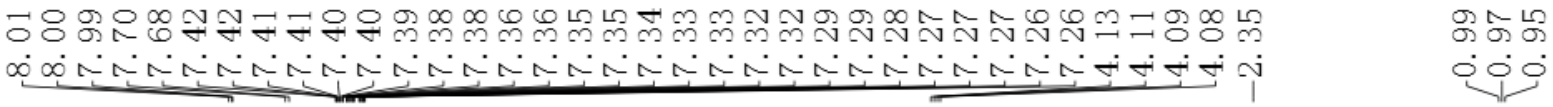


LZT-2040
PROTON CDC13 {D:\NMR400\02T2} nmr 46

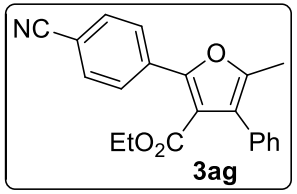


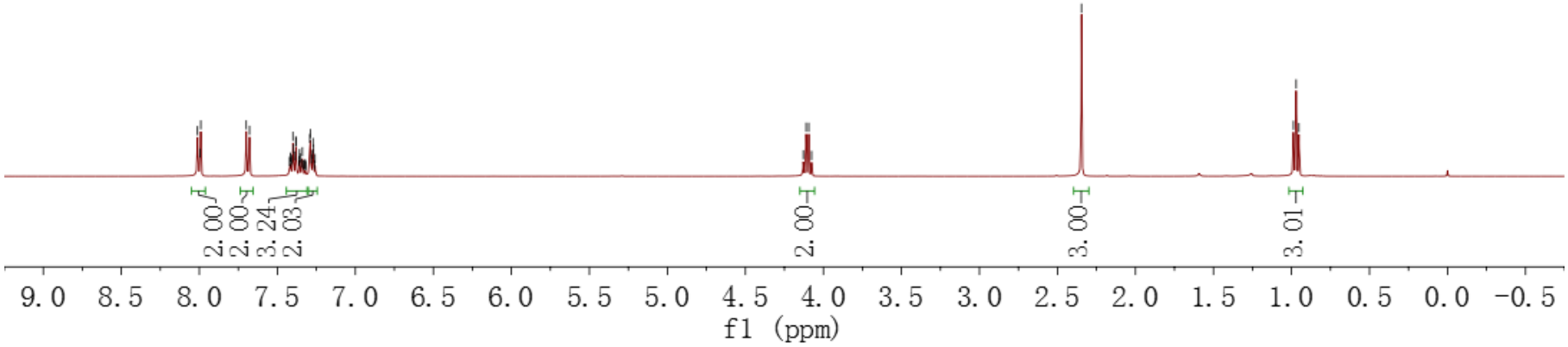


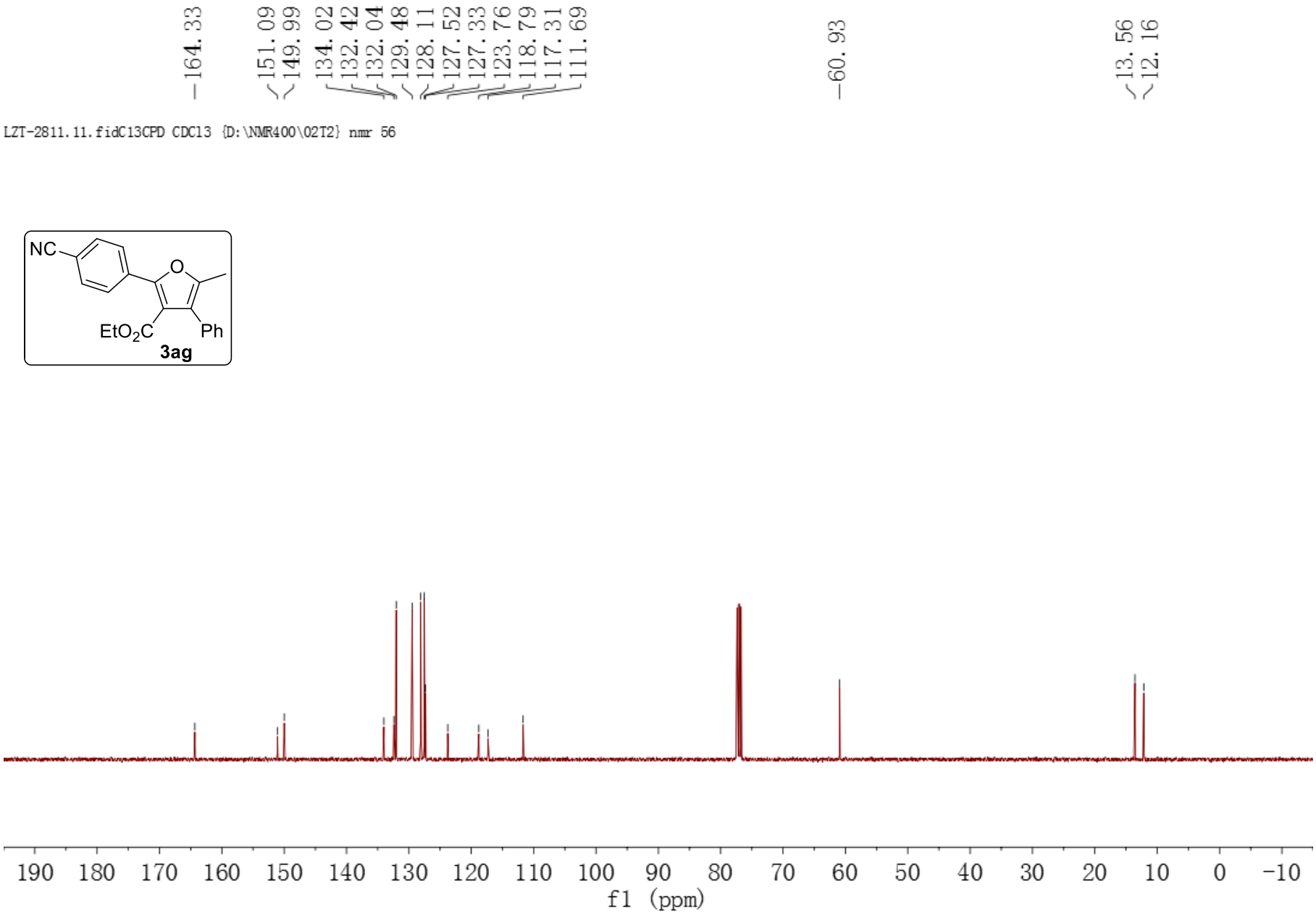

164.50
152.90
148.82
132.88
131.42
129.61
129.11
129.01
128.04
127.14
123.24
123.00
115.34
60.64
13.65
12.10
LZT-2040
C13CPD CDCl3 {D:\NMR400\02T2} nmr 46
Br
O
EtO2C
Ph
3af
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

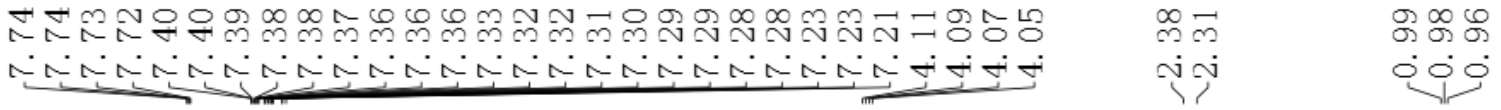


LZT-2811.10.fidPROTON CDCl3 {D:\NMR400\02T2} nmr 56

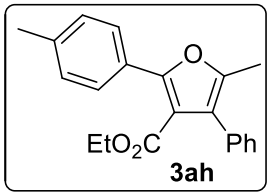


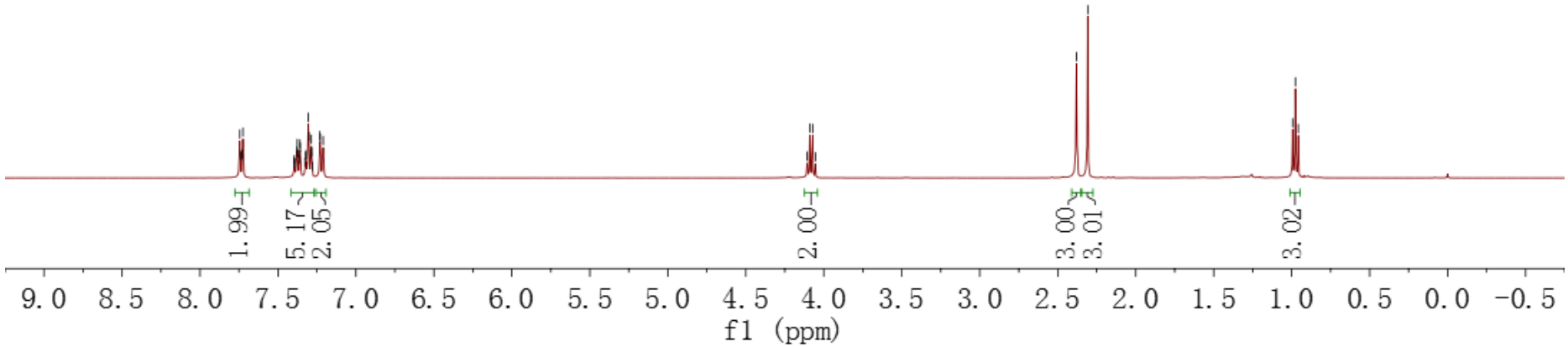


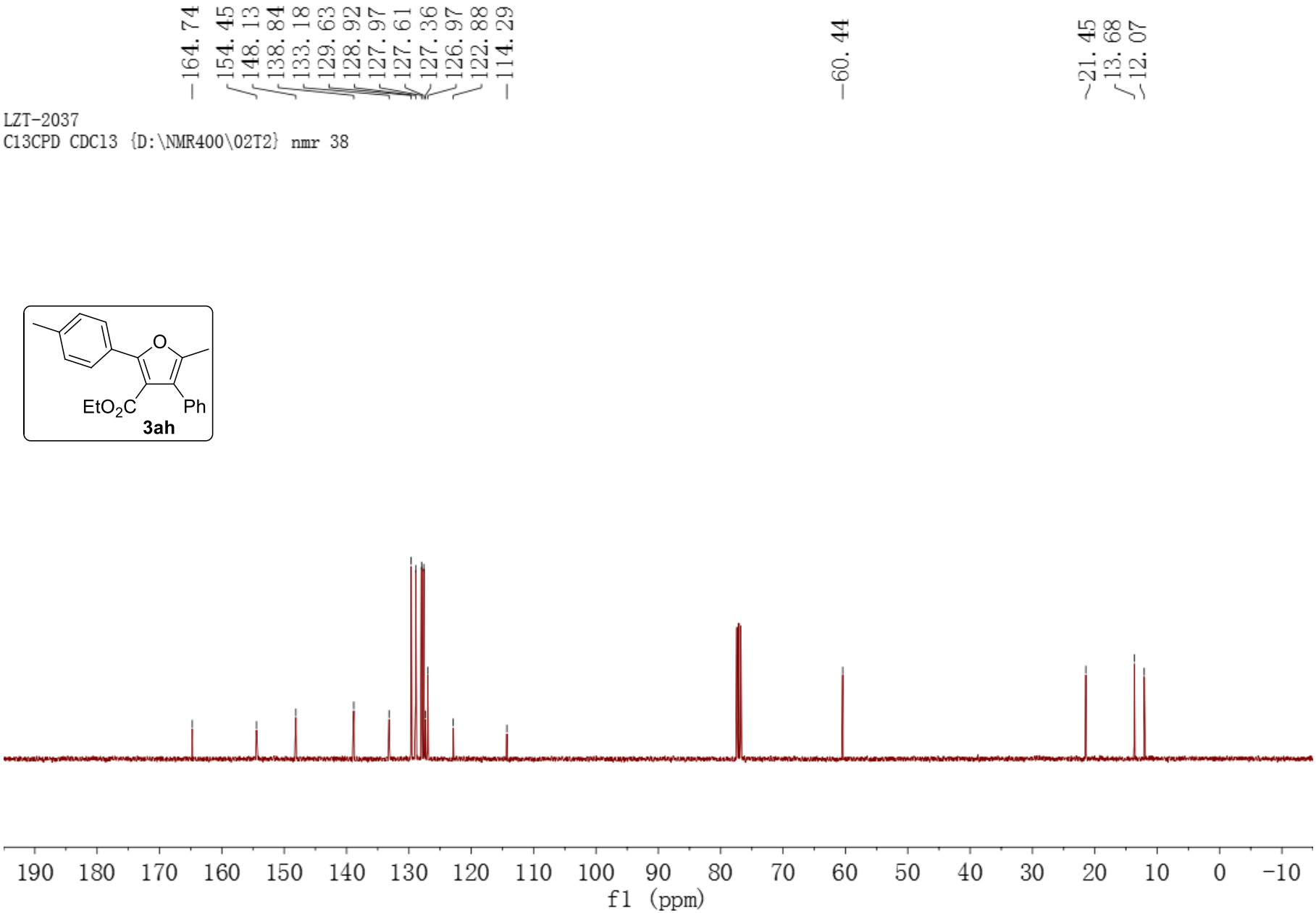

164.33
151.09
149.99
134.02
132.42
132.04
129.48
128.11
127.52
127.33
123.76
118.79
117.31
111.69
60.93
13.56
12.16
LZT-2811.11.fidC13CPD CDCl3 {D:\NMR400\02T2} nmr 56
NC
O
EtO2C
Ph
3ag
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

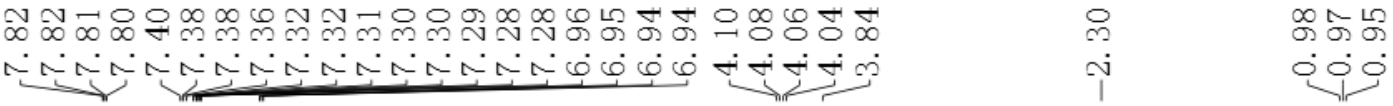


LZT-2037
PROTON CDC13 {D:\NMR400\02T2} nmr 38

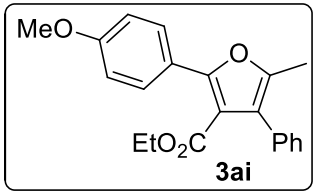


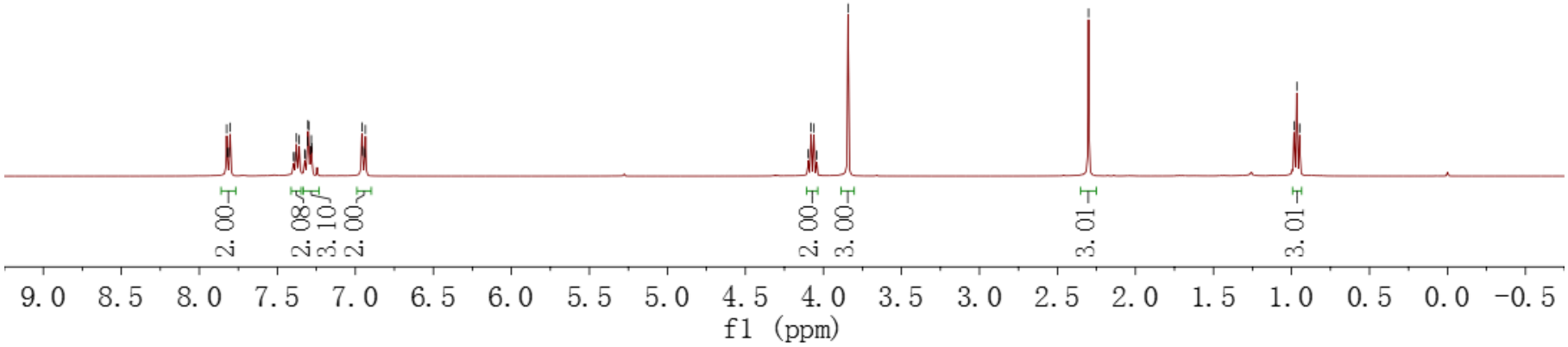


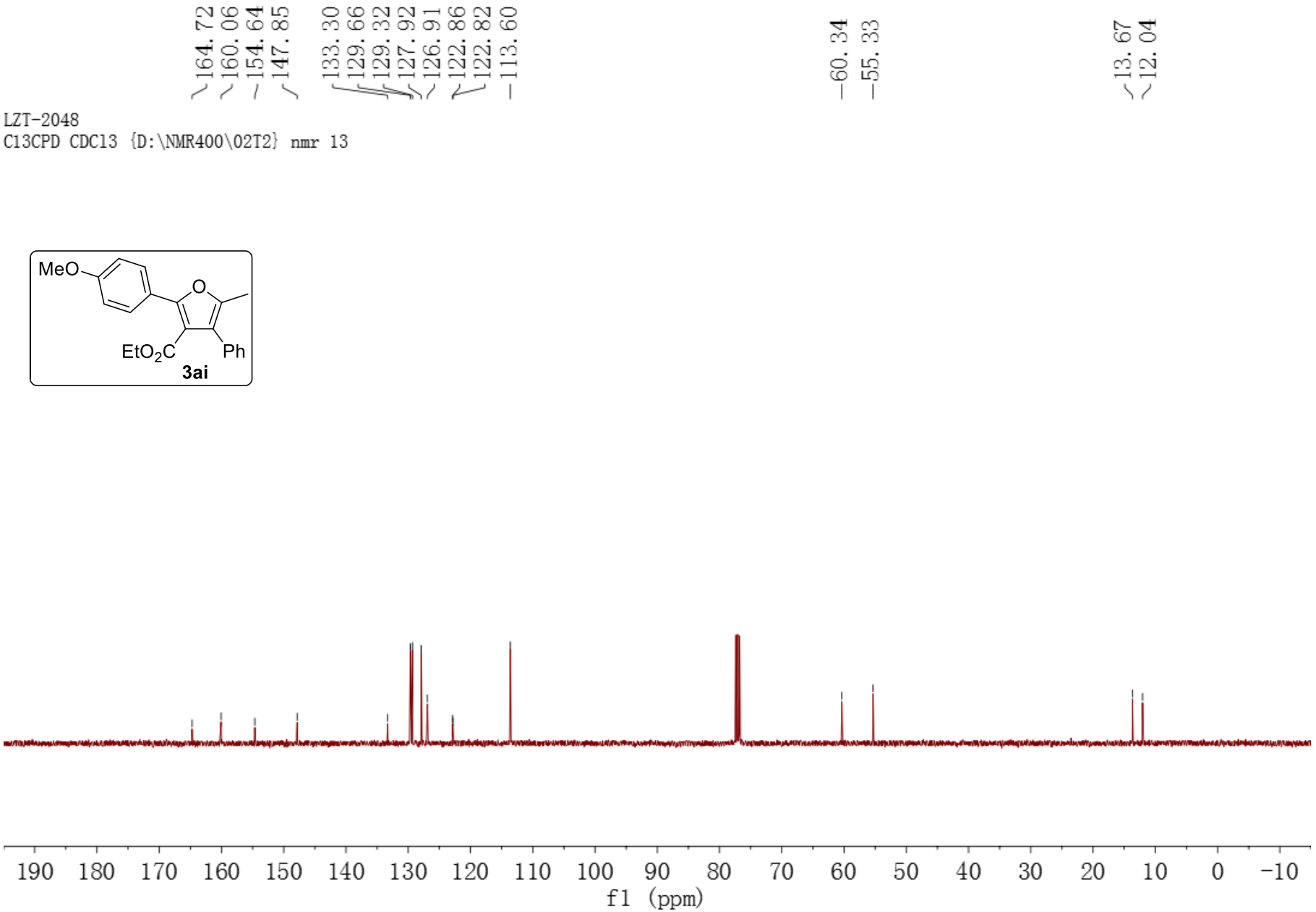

164.74
154.45
148.13
138.84
133.18
129.63
128.92
127.97
127.61
127.36
126.97
122.88
114.29
60.44
21.45
13.68
12.07
LZT-2037
C13CPD CDCl3 {D:\NMR400\02T2} nmr 38
EtO2C
Ph
3ah
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

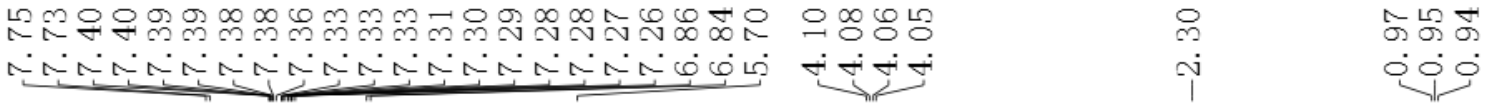


LZT-2048
PROTON CDC13 {D:\NMR400\02T2} nmr 13

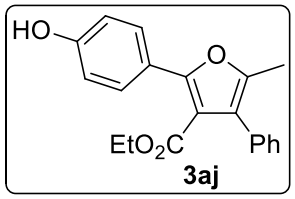




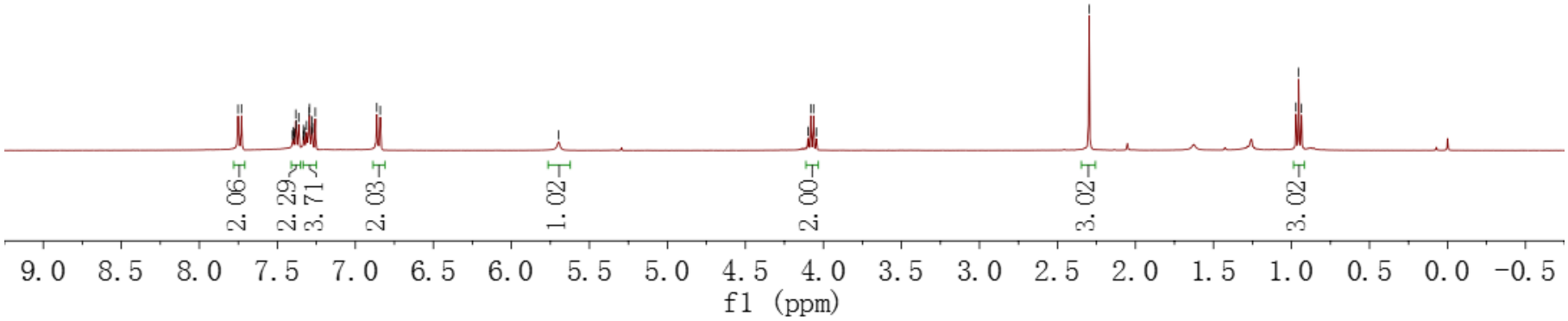

164.72
160.06
154.64
147.85
133.30
129.66
129.32
127.92
126.91
122.86
122.82
113.60
60.34
55.33
13.67
12.04
LZT-2048
C13CPD CDCl3 {D:\NMR400\02T2} nmr 13
MeO
O
EtO2C
Ph
3ai
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

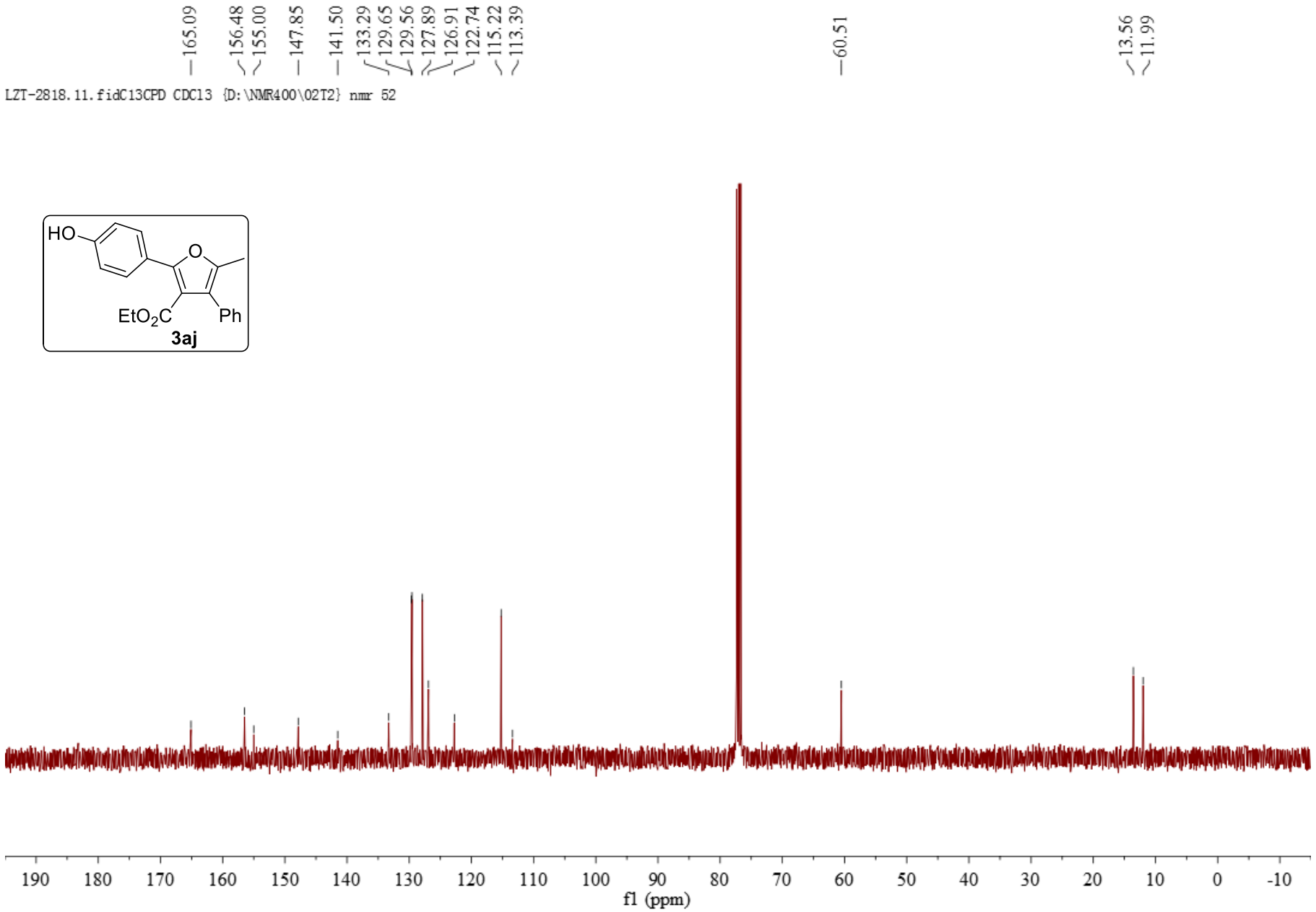


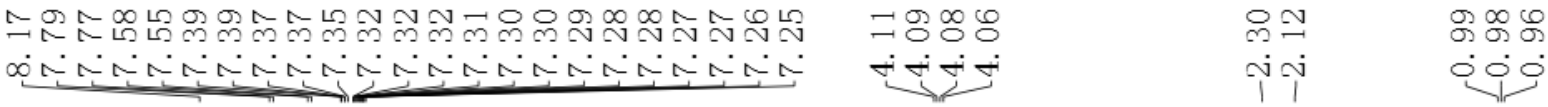
LZT-2818.10.fidPROTON CDCl3 {D:\NMR400\02T2} nmr 52



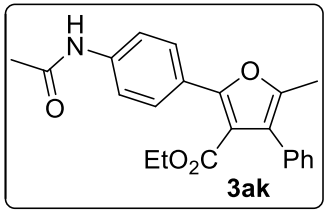
3aj

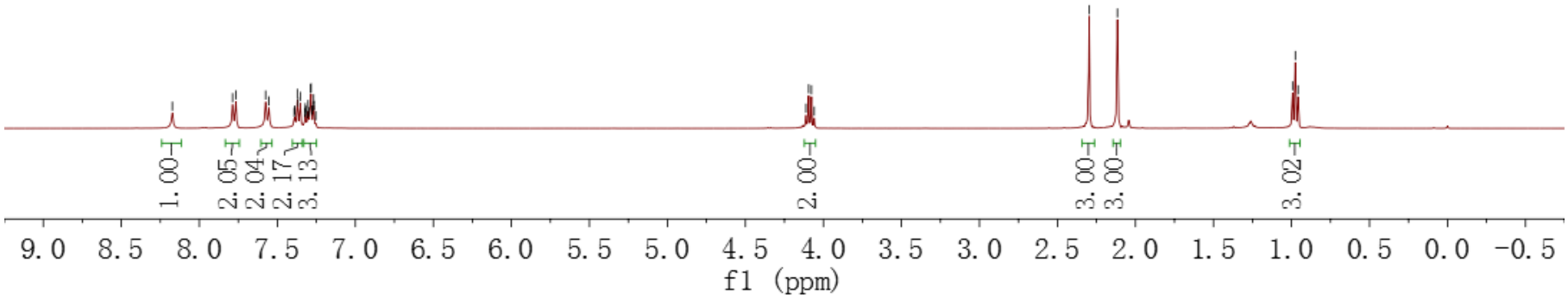



165.09
156.48
155.00
147.85
141.50
133.29
129.65
129.56
127.89
126.91
122.74
115.22
113.39
60.51
13.56
11.99
LZT-2818.11.fidC13CPD CDCl3 {D:\NMR400\02T2} nmr 52
HO
O
EtO2C
Ph
3aj
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)



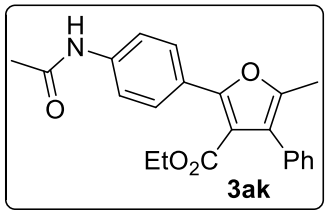
LZT-2819.10.fidPROTON CDCl3 {D:\NMR400\02T2} nmr 52



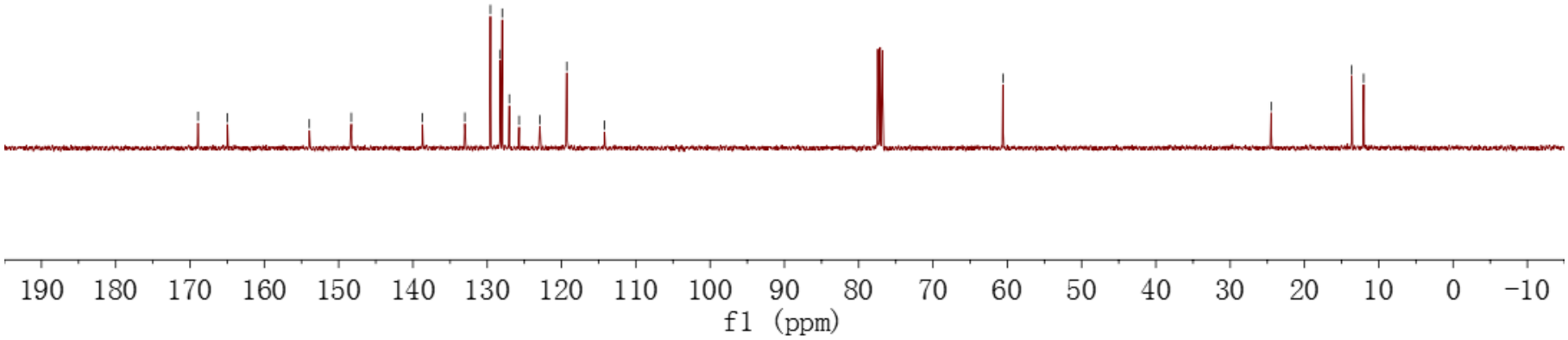


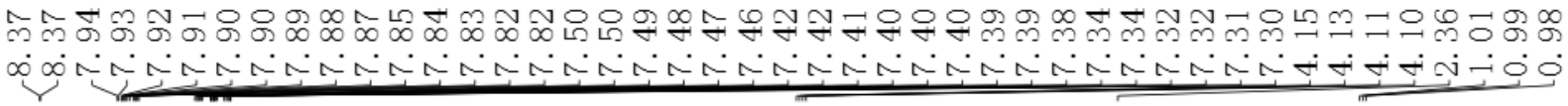
168.92
164.96
153.95
148.29
138.72
133.02
129.57
128.27
127.98
127.02
125.70
122.92
119.30
114.21
60.59
24.50
13.65
12.03

LZT-2819.11.fidC13CPD CDCl3 {D:\NMR400\02T2} nmr 52

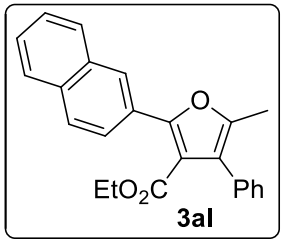


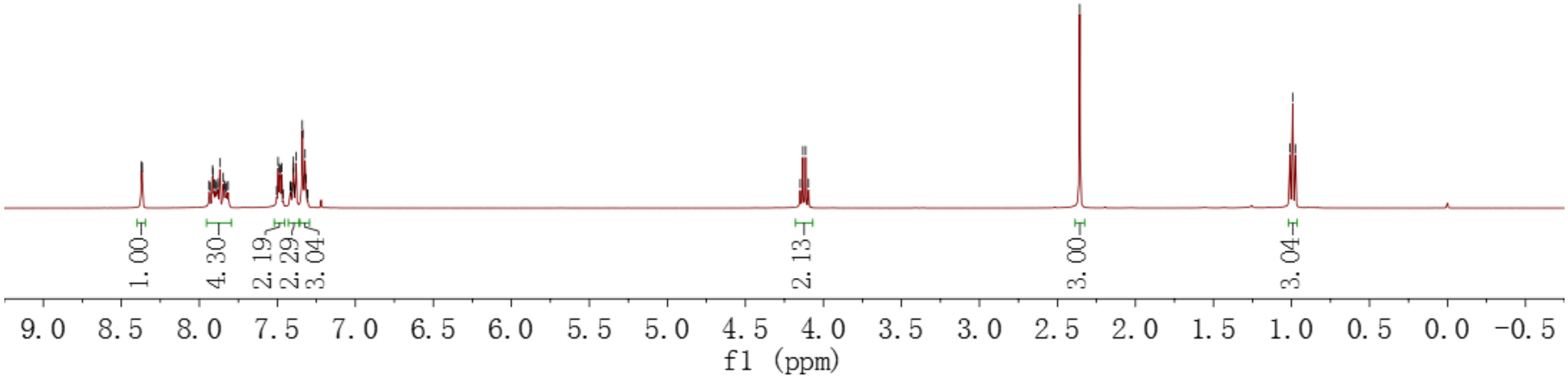
3ak

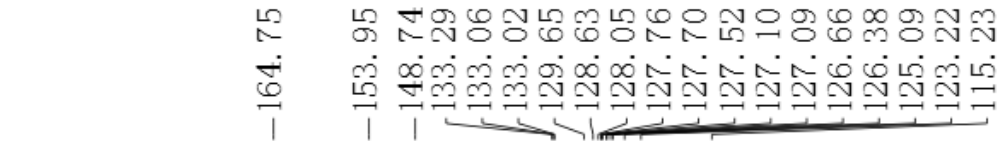




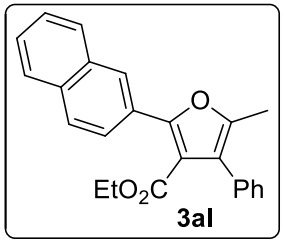
LZT-2043.10.fid
PROTON CDCl3 {D:\NMR400\02T2} nmr 47

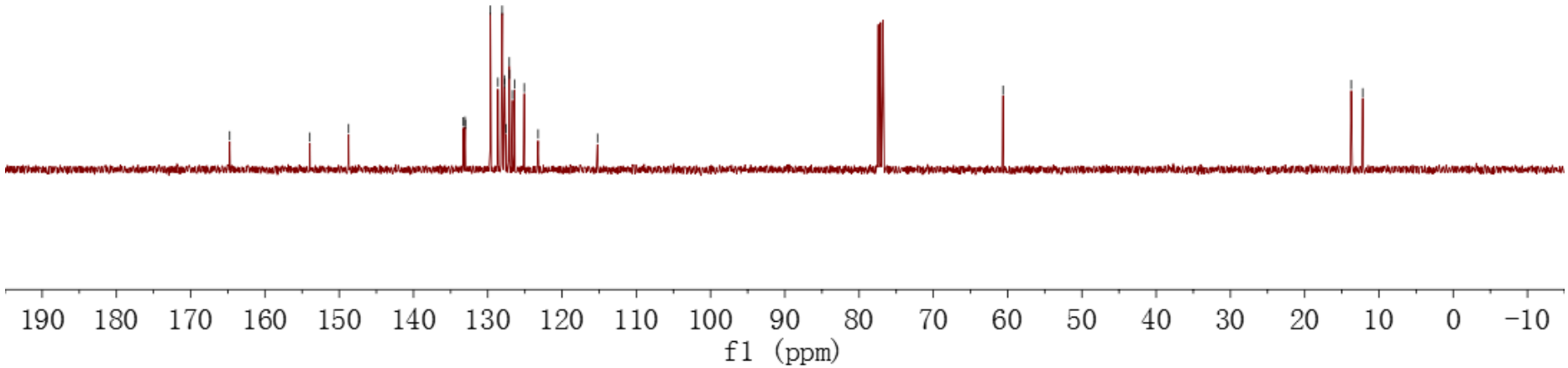


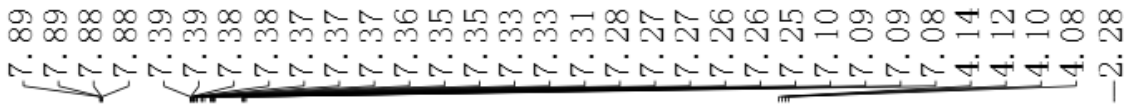




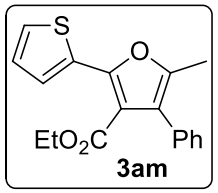
LZT-2043.11.fid
C13CPD CDC13 {D:\NMR400\02T2} nmr 47

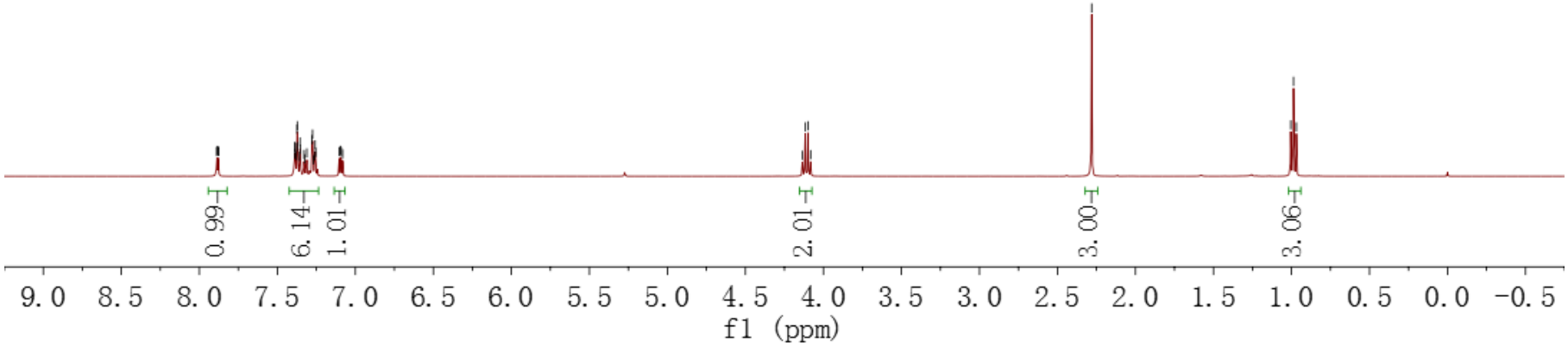


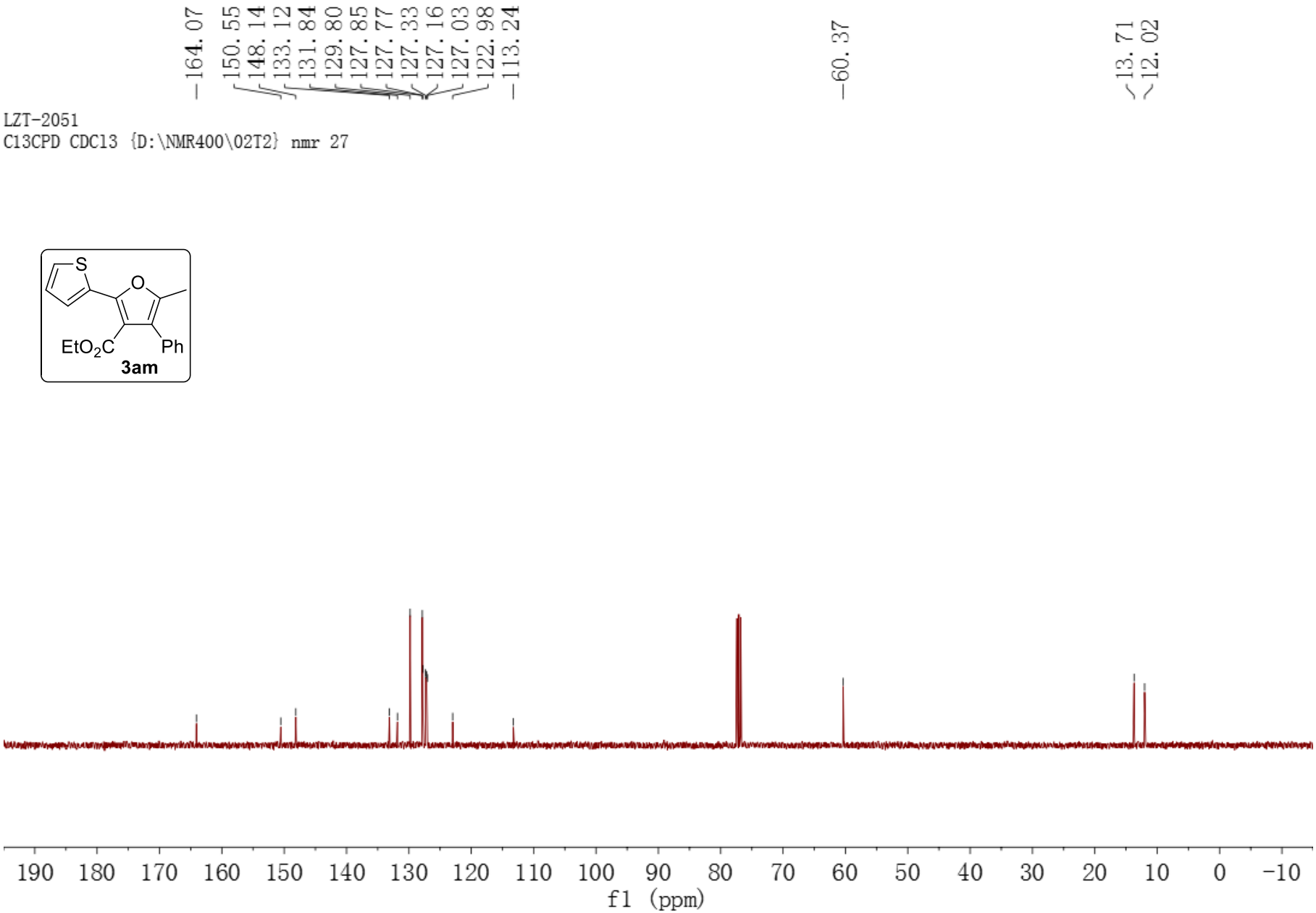




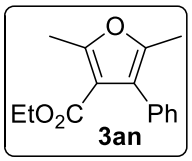
LZT-2051
PROTON CDC13 {D:\NMR400\02T2} nmr 27

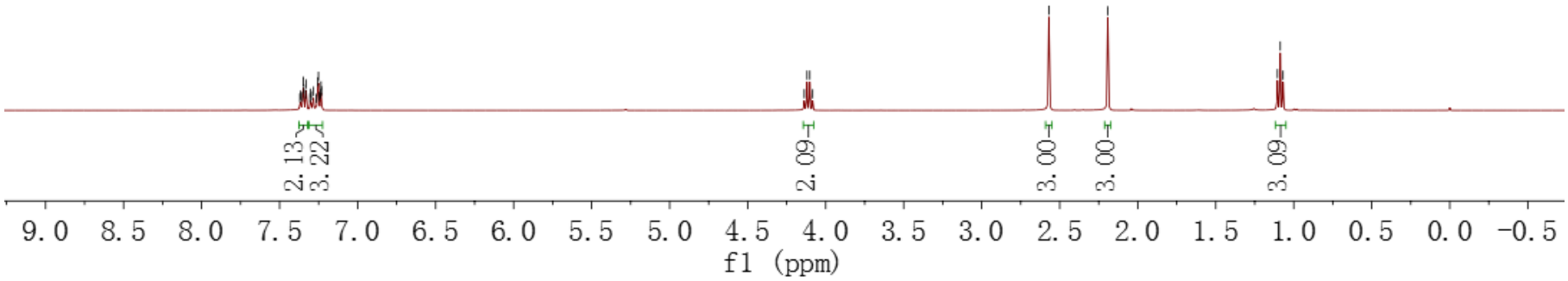


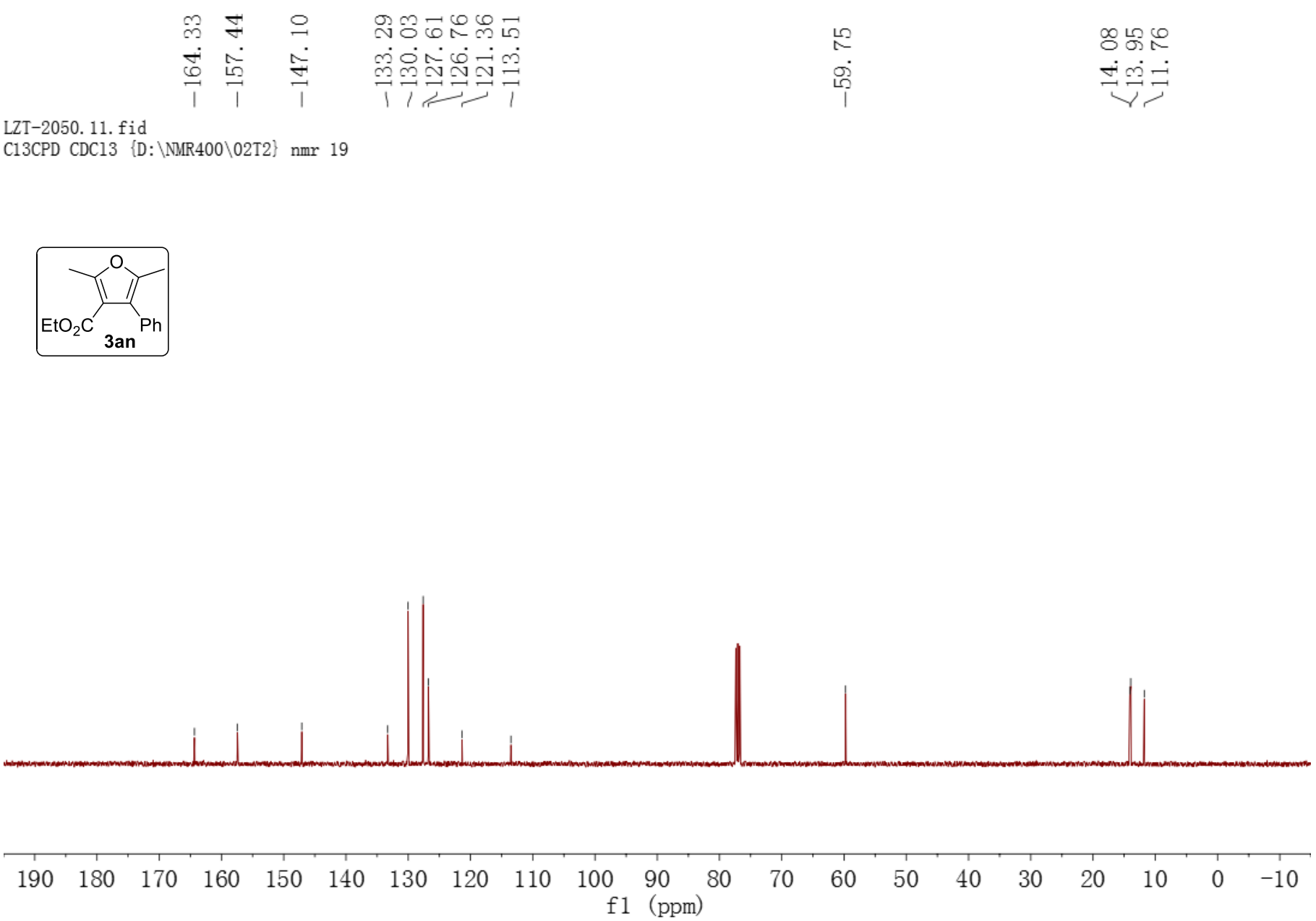


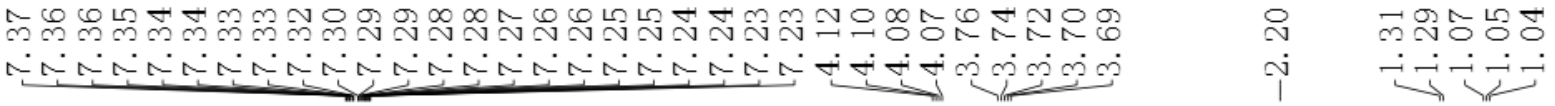

164.07
150.55
148.14
133.12
131.84
129.80
127.85
127.77
127.33
127.16
127.03
122.98
113.24
60.37
13.71
12.02
LZT-2051
C13CPD CDCl3 {D:\NMR400\02T2} nmr 27
S
O
EtO2C
Ph
3am
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

LZT-2050.10.fid
PROTON CDCl3 {D:\NMR400\02T2} nmr 19

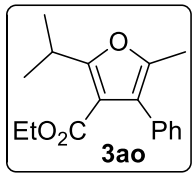


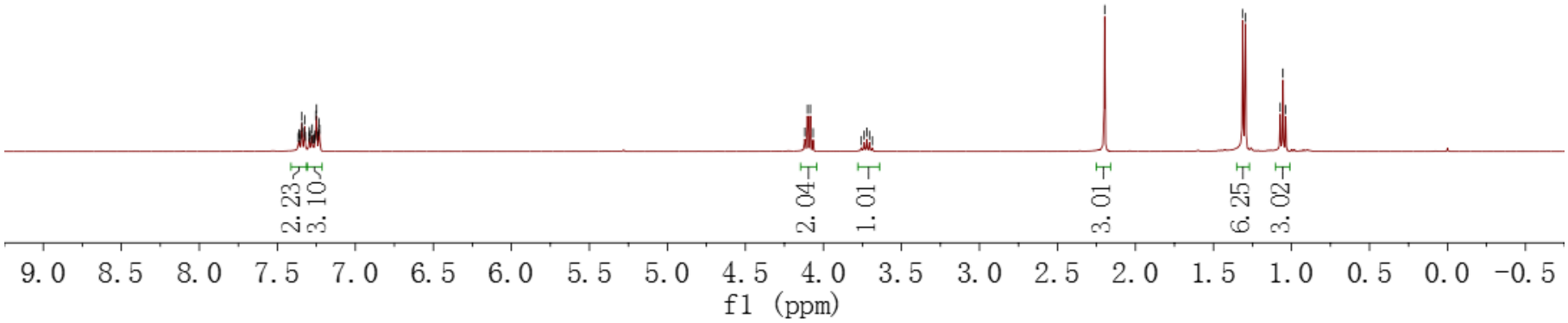


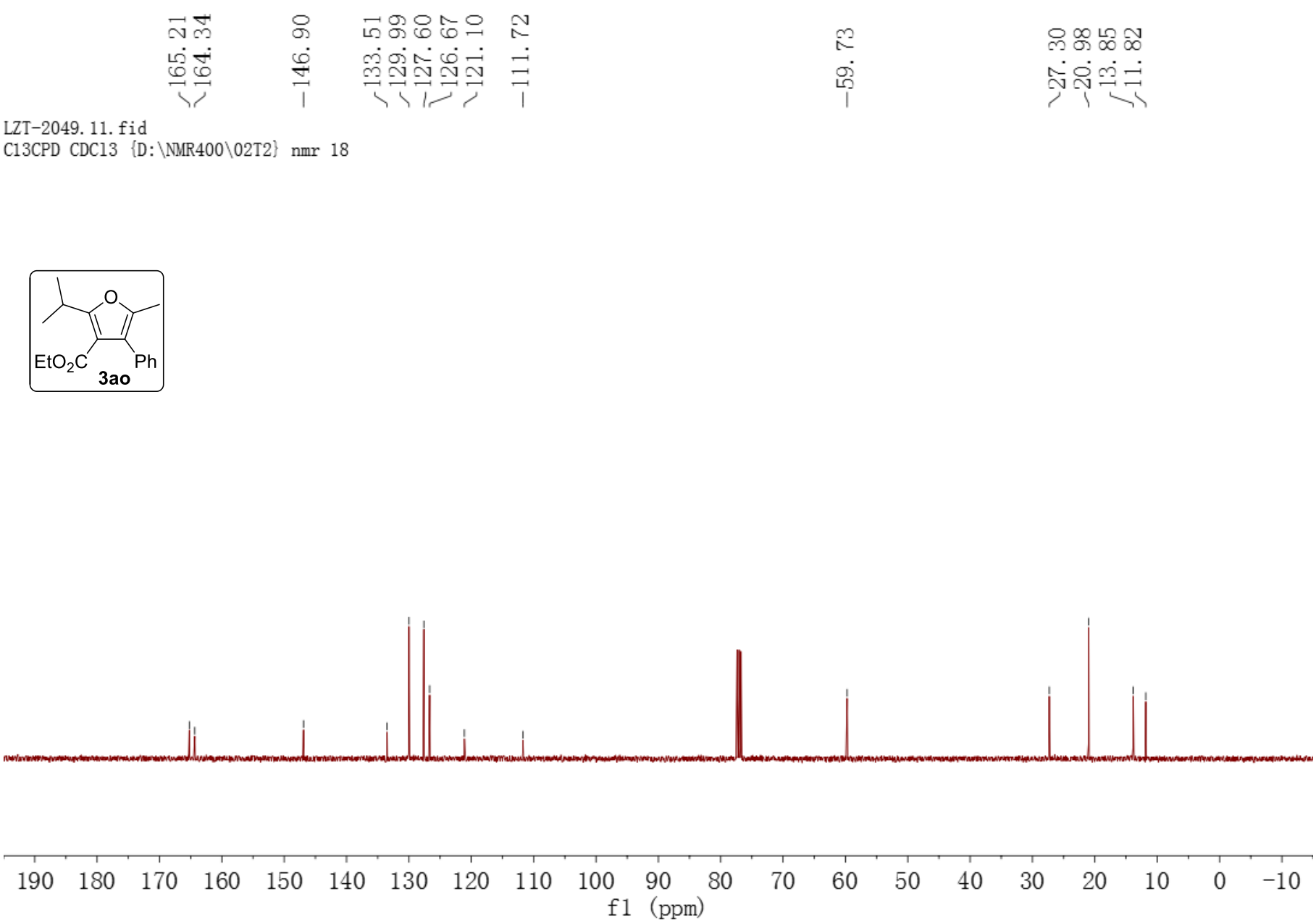

164.33
157.44
147.10
133.29
130.03
127.61
126.76
121.36
113.51
59.75
14.08
13.95
11.76
LZT-2050.11.fid
C13CPD CDCl3 {D:\NMR400\02T2} nmr 19
O
EtO2C
Ph
3an
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

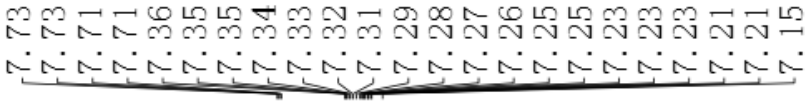


LZT-2049.10.fid
PROTON CDCl3 {D:\NMR400\02T2} nmr 18

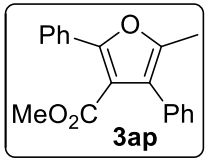


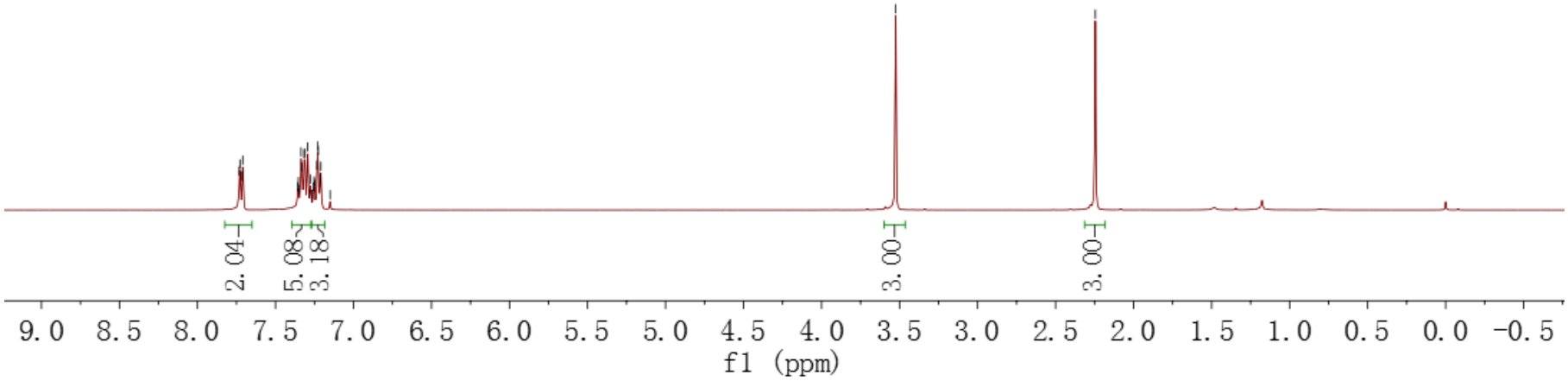



165.21
164.34
146.90
133.51
129.99
127.60
126.67
121.10
111.72
59.73
27.30
20.98
13.85
11.82
LZT-2049.11.fid
C13CPD CDCl3 {D:\NMR400\02T2} nmr 18
O
EtO2C
Ph
3ao
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)



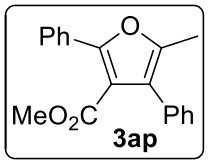
LZT-1400
PROTON CDCl3 {D:\NMR400\02T2} nmr 40



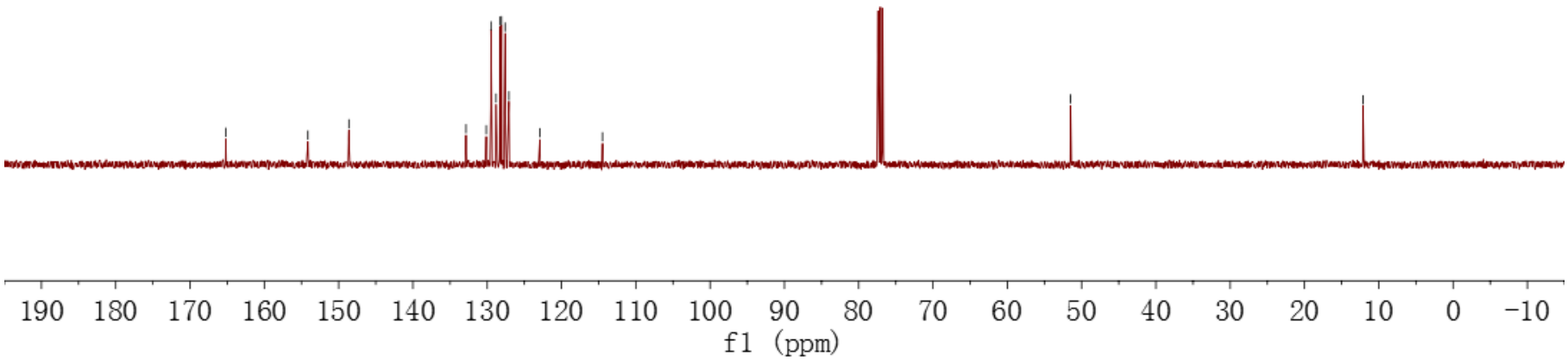


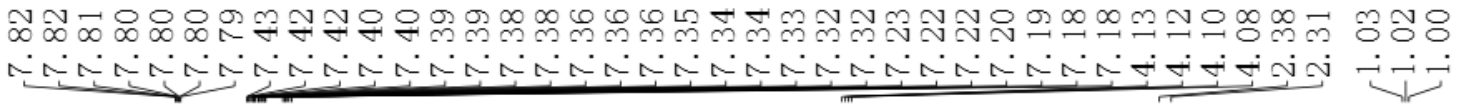
165.19
154.13
148.62
132.85
130.13
129.50
128.82
128.27
128.07
127.58
127.08
122.90
114.49
51.48
12.13

LZT-1400
C13CPD CDCl3 {D:\NMR400\02T2} nmr 40

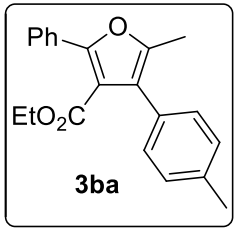


3ap

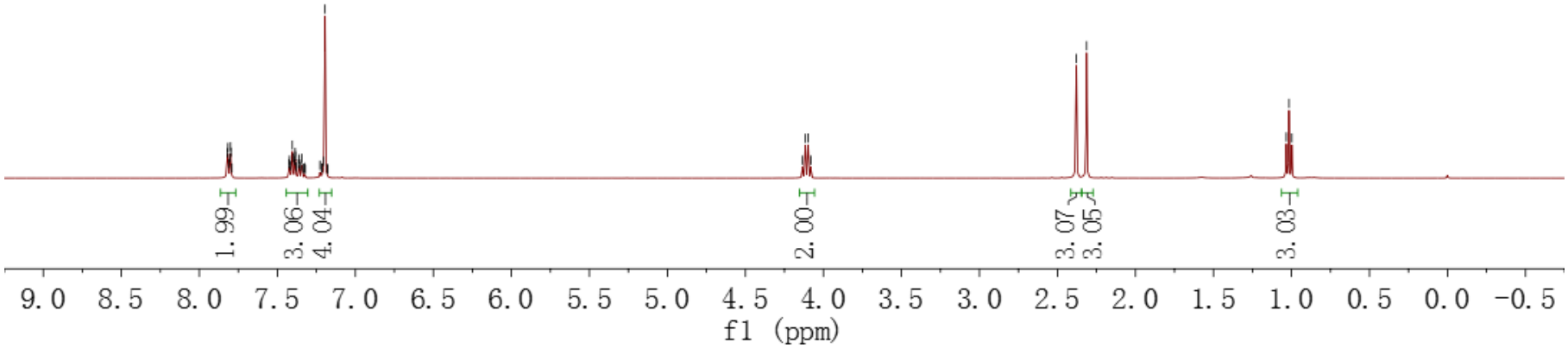


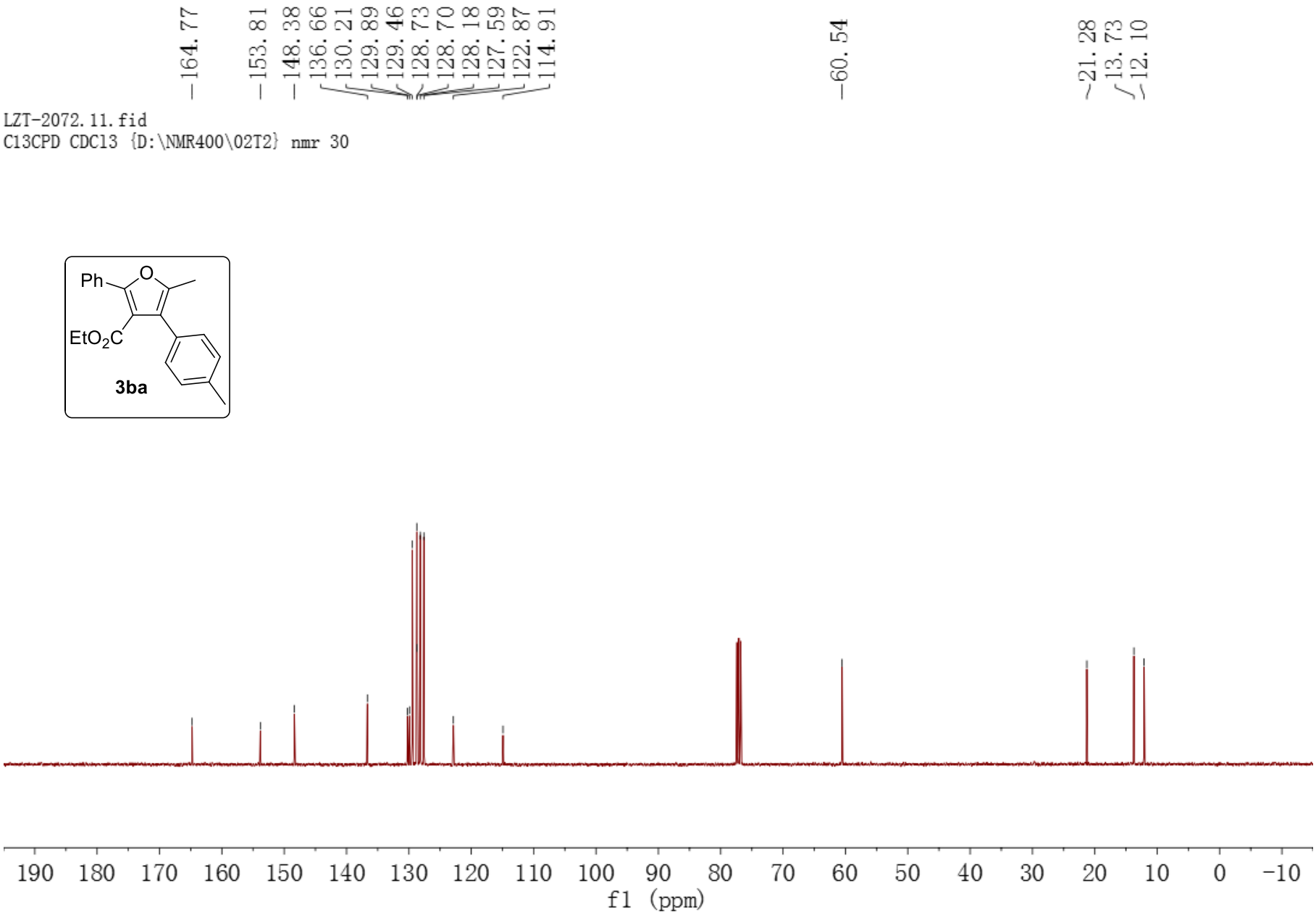


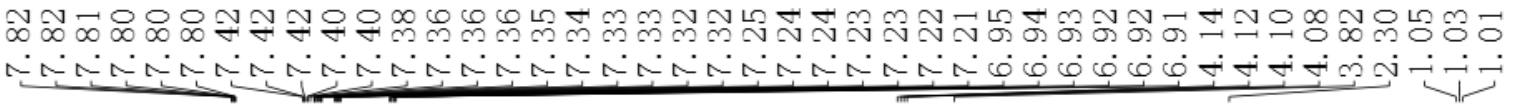
LZT-2072.10.fid
PROTON CDCl3 {D:\NMR400\02T2} nmr 30



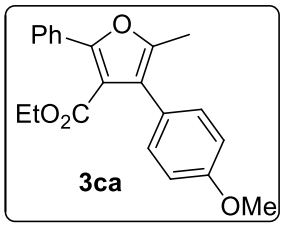
3ba

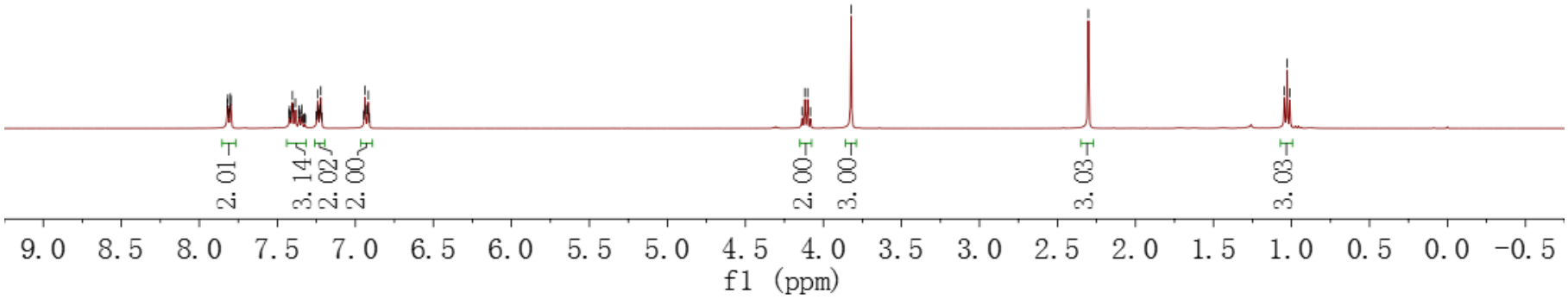



164.77
153.81
148.38
136.66
130.21
129.89
129.46
128.73
128.70
128.18
127.59
122.87
114.91
60.54
21.28
13.73
12.10
LZT-2072.11.fid
C13CPD CDCl3 {D:\NMR400\02T2} nmr 30
Ph
O
EtO2C
3ba
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)



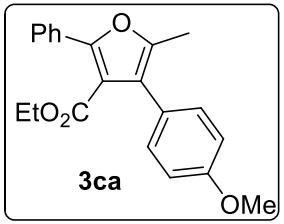
LZT-2073.10.fid
PROTON CDCl3 {D:\NMR400\02T2} nmr 27



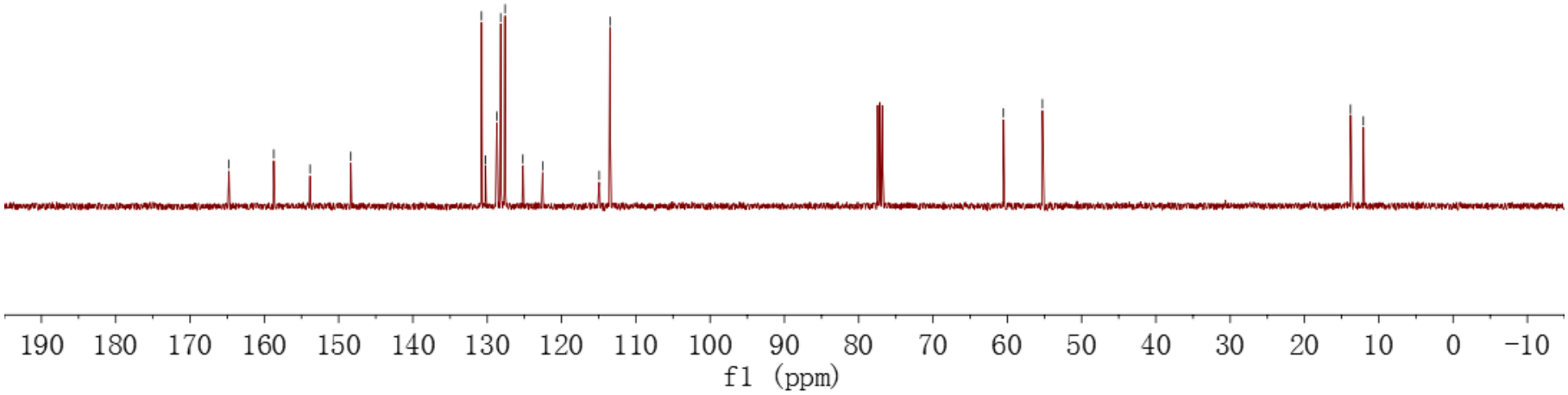


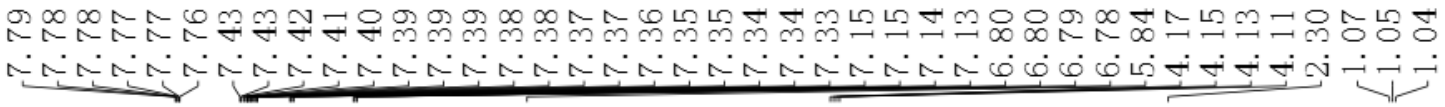
164.77
158.72
153.85
148.36
130.77
130.23
128.71
128.18
127.60
125.19
122.54
114.92
113.48
60.52
55.27
13.80
12.07

LZT-2073.11.fid
C13CPD CDCl3 {D:\NMR400\02T2} nmr 36

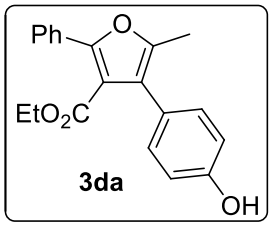


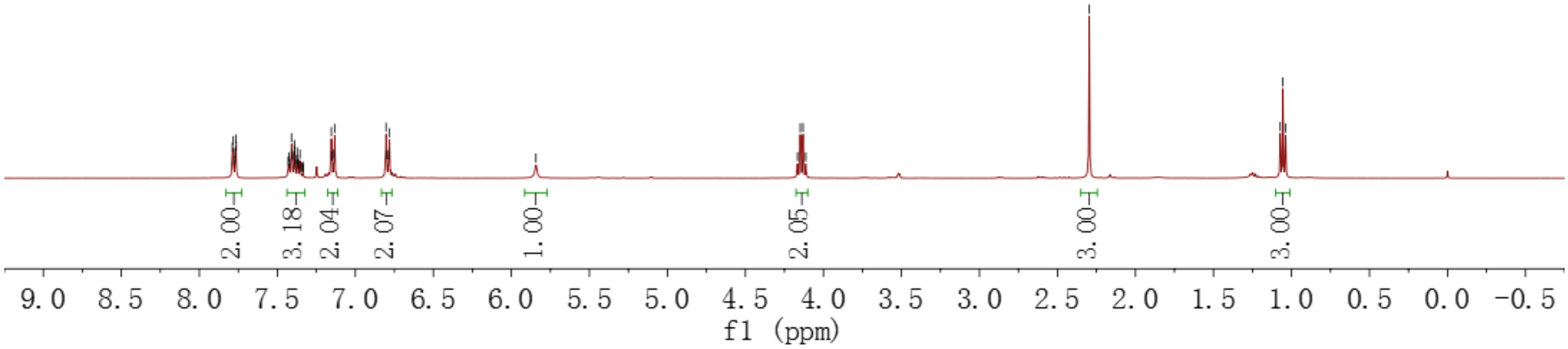
3ca

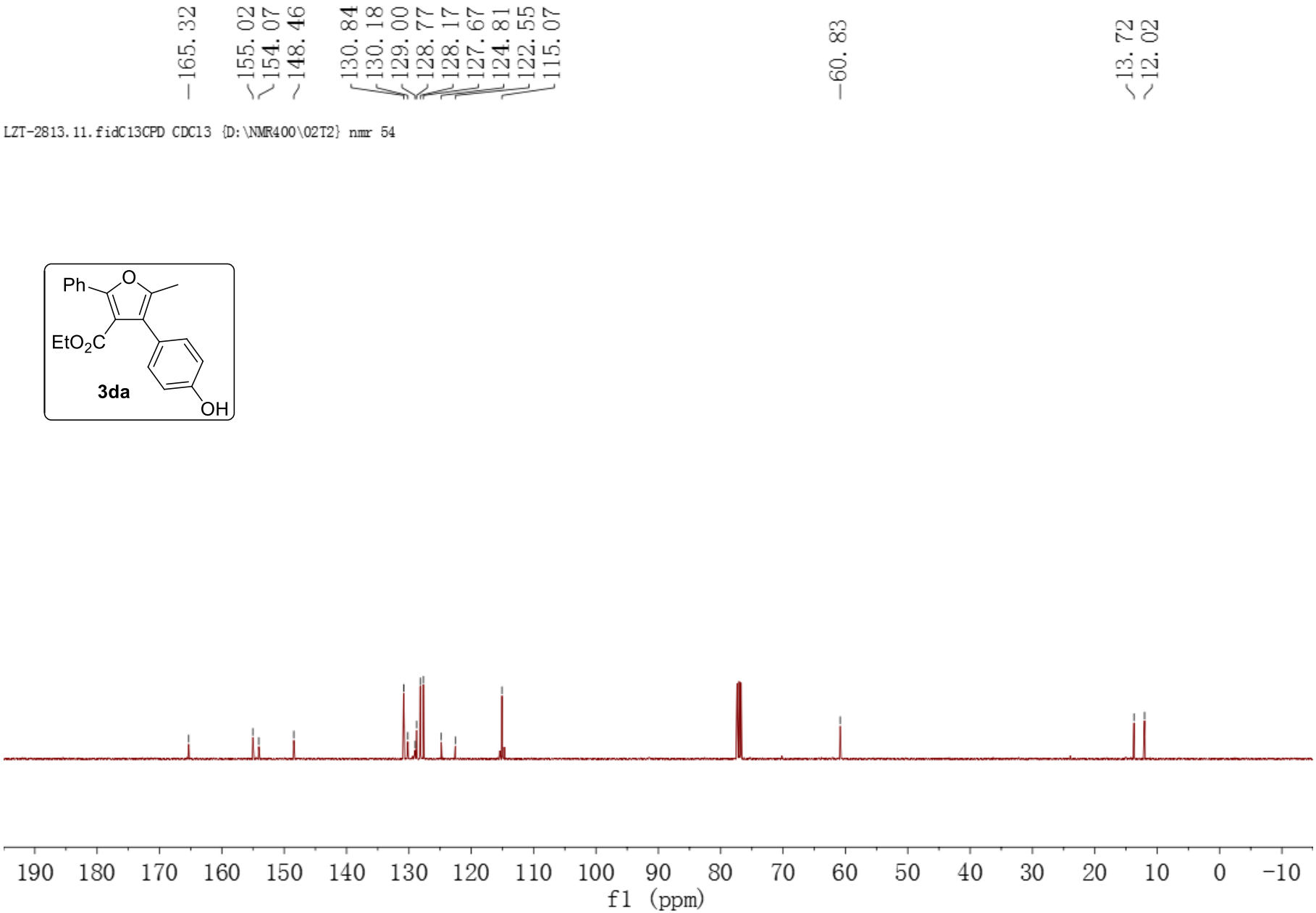


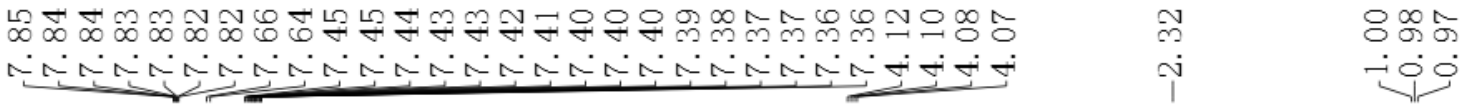


LZT-2813.10.fidPROTON CDCl3 {D:\NMR400\02T2} nmr 54

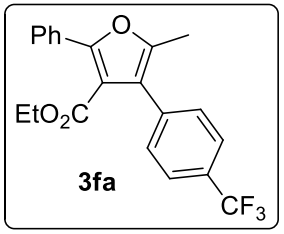


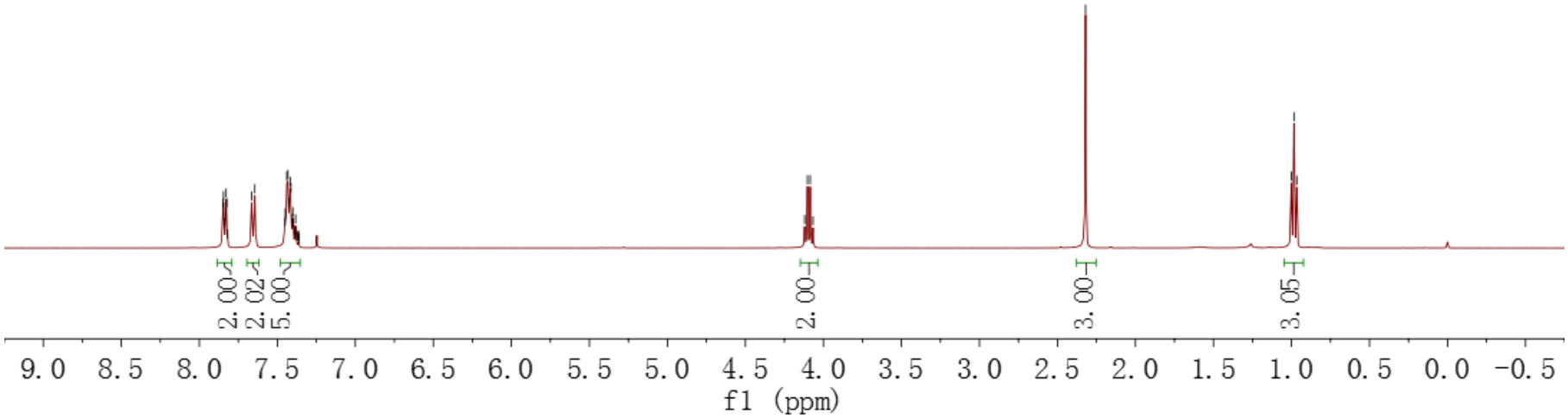


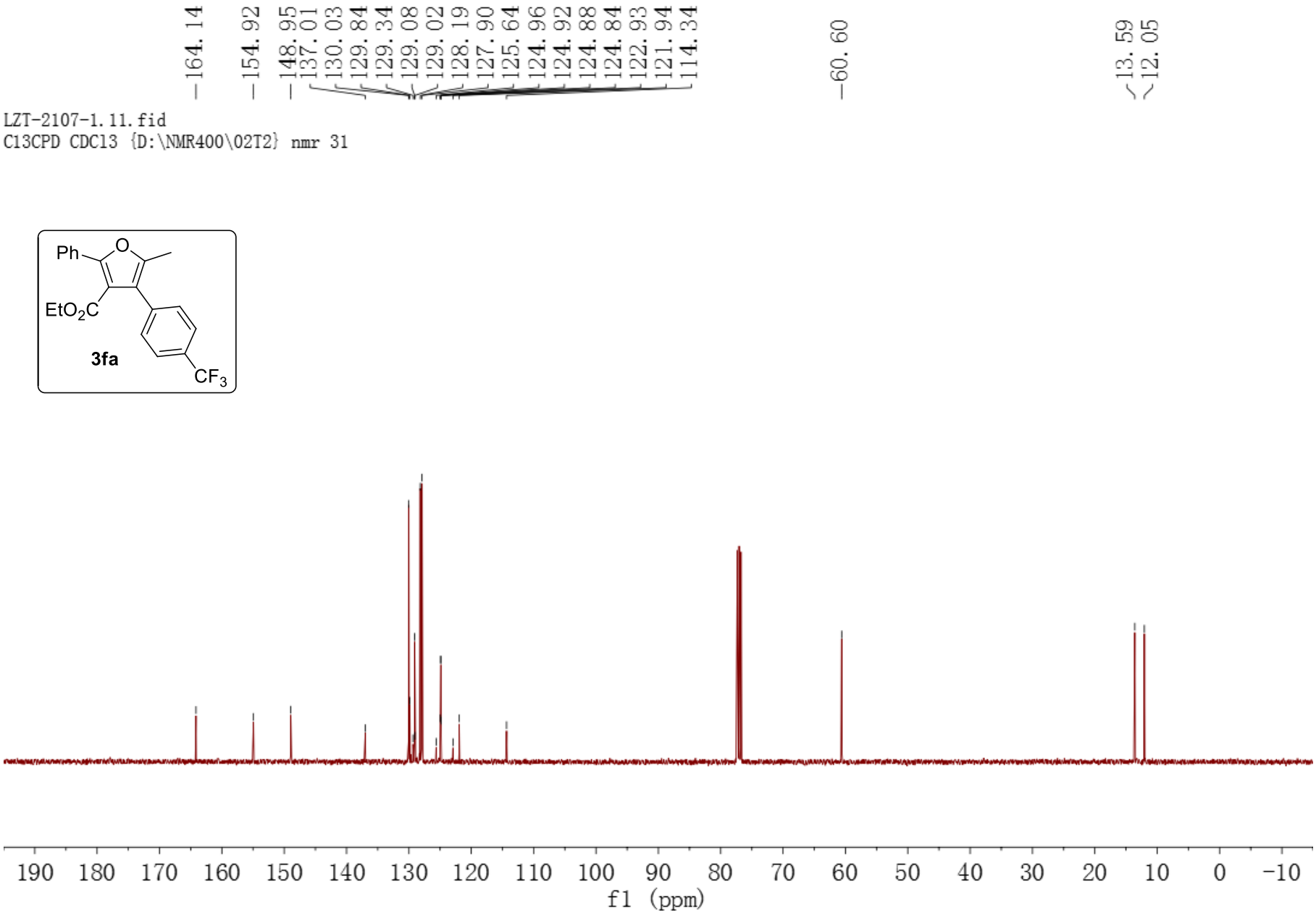

165.32
155.02
154.07
148.46
130.84
130.18
129.00
128.77
128.17
127.67
124.81
122.55
115.07
60.83
13.72
12.02
LZT-2813.11.fidC13CPD CDCl3 {D:\NMR400\02T2} nmr 54
Ph
O
EtO2C
3da
OH
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

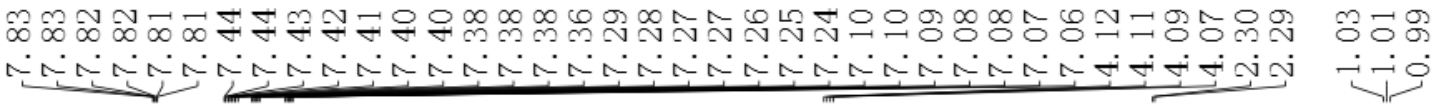


LZT-2107-1.10.fid
PROTON CDCl3 {D:\NMR400\02T2} nmr 31

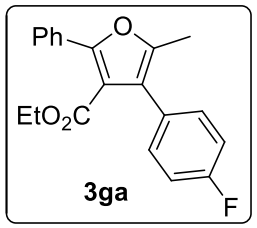




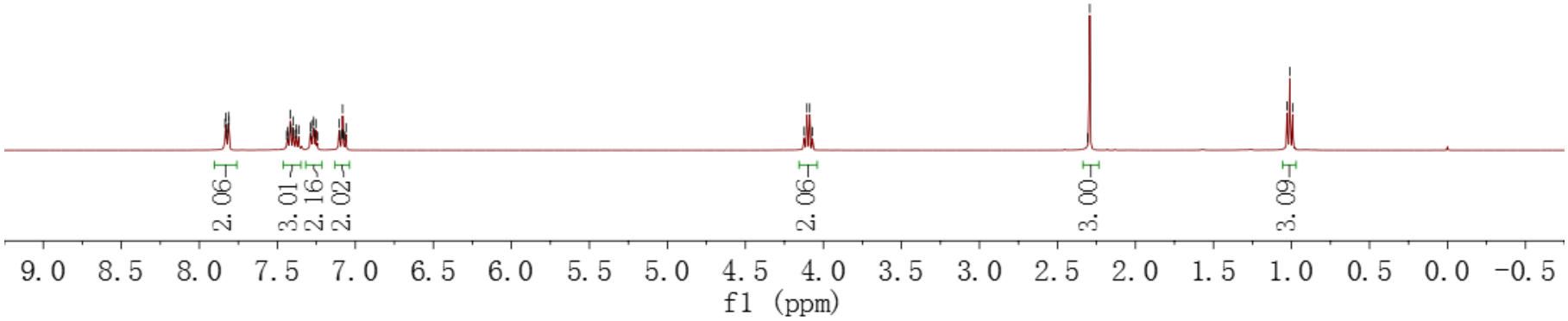

164.14
154.92
148.95
137.01
130.03
129.84
129.34
129.08
129.02
128.19
127.90
125.64
124.96
124.92
124.88
124.84
122.93
121.94
114.34
60.60
13.59
12.05
LZT-2107-1.11.fid
C13CPD CDCl3 {D:\NMR400\02T2} nmr 31
Ph
O
EtO2C
3fa
CF3
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

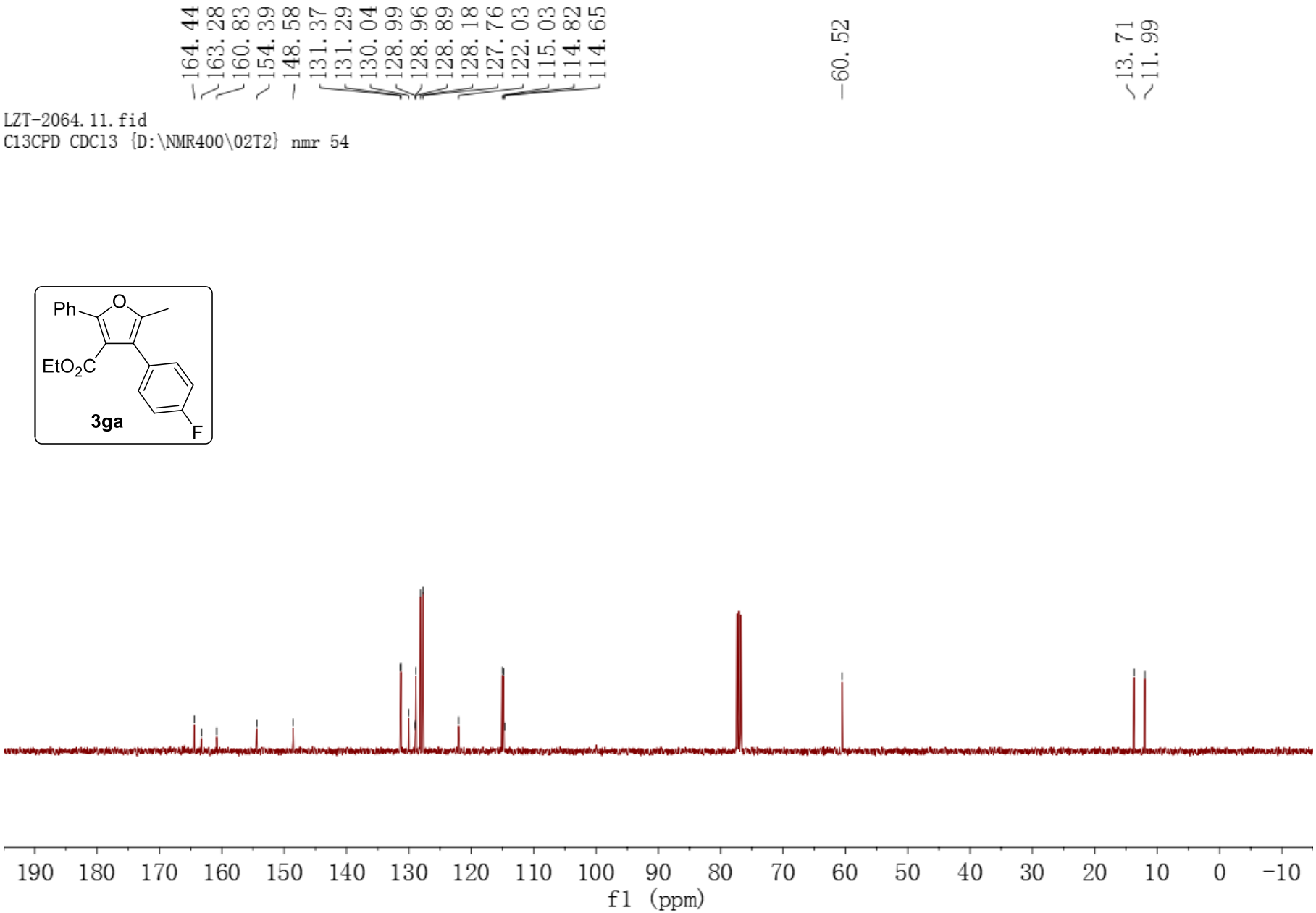


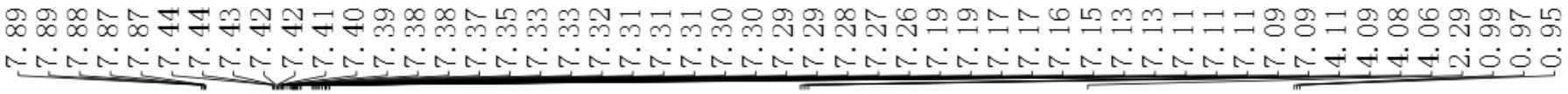
LZT-2064.10.fid
PROTON CDCl3 {D:\NMR400\02T2} nmr 54



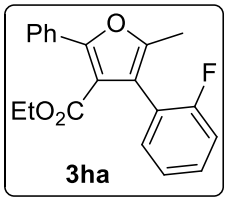
3ga

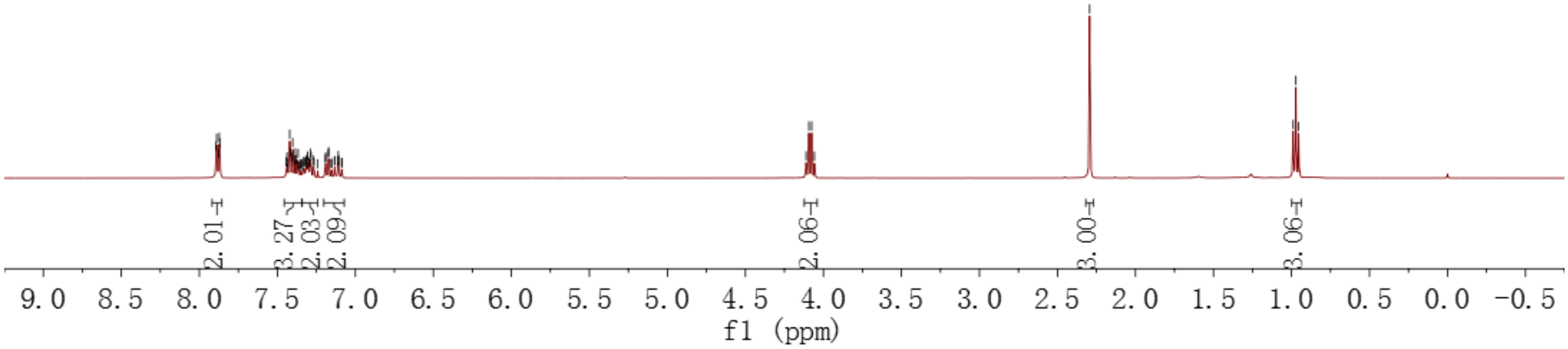


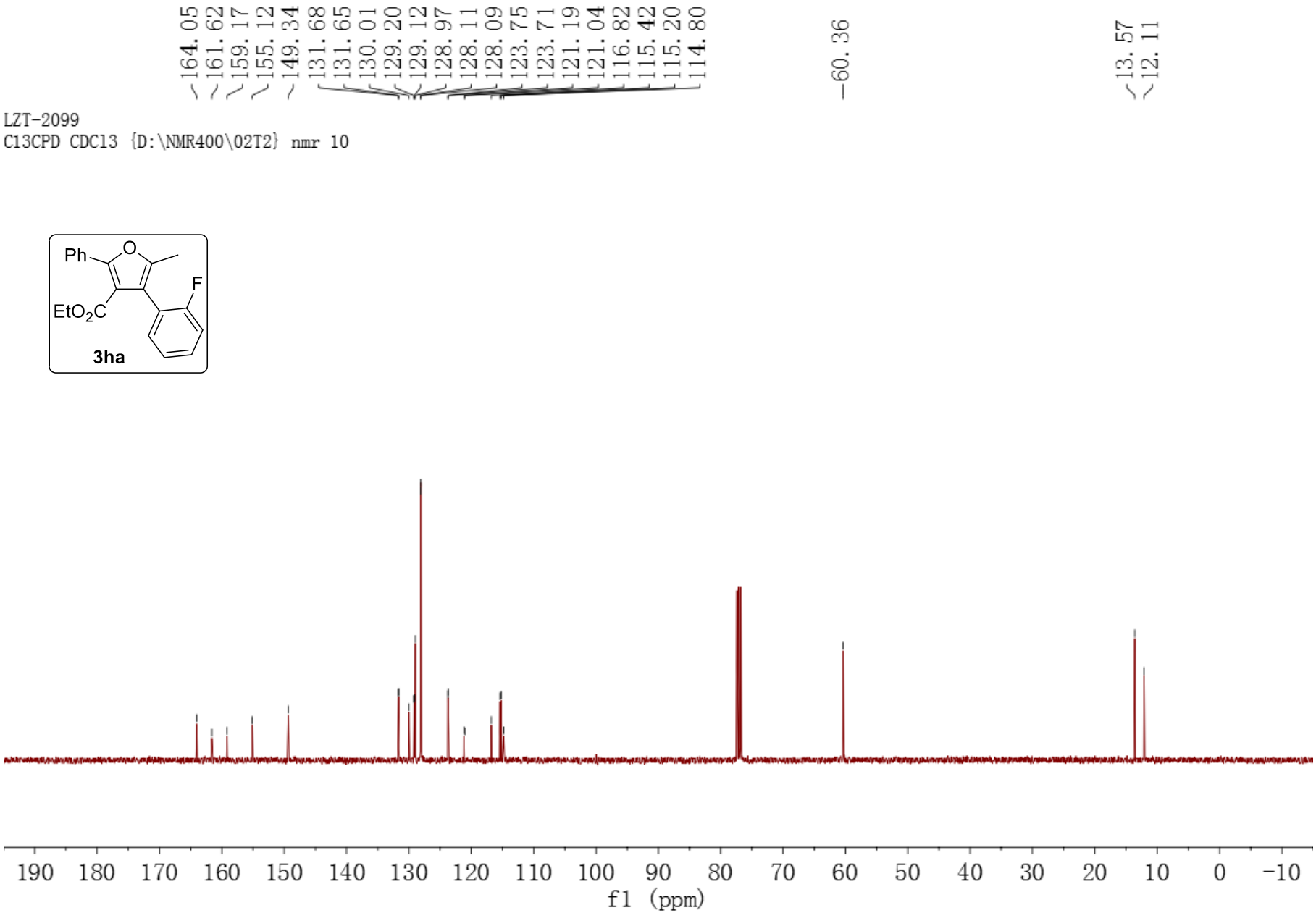

164.44
163.28
160.83
154.39
148.58
131.37
131.29
130.04
128.99
128.96
128.89
128.18
127.76
122.03
115.03
114.82
114.65
60.52
13.71
11.99
LZT-2064.11.fid
C13CPD CDCl3 {D:\NMR400\02T2} nmr 54
Ph
O
EtO2C
3ga
F
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

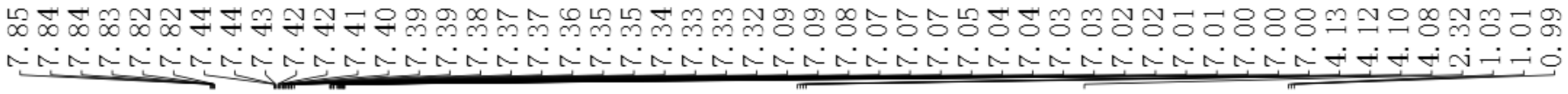


LZT-2099
PROTON CDC13 {D:\NMR400\02T2} nmr 10

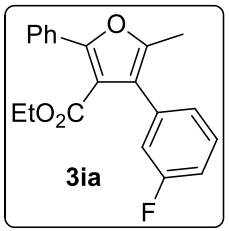


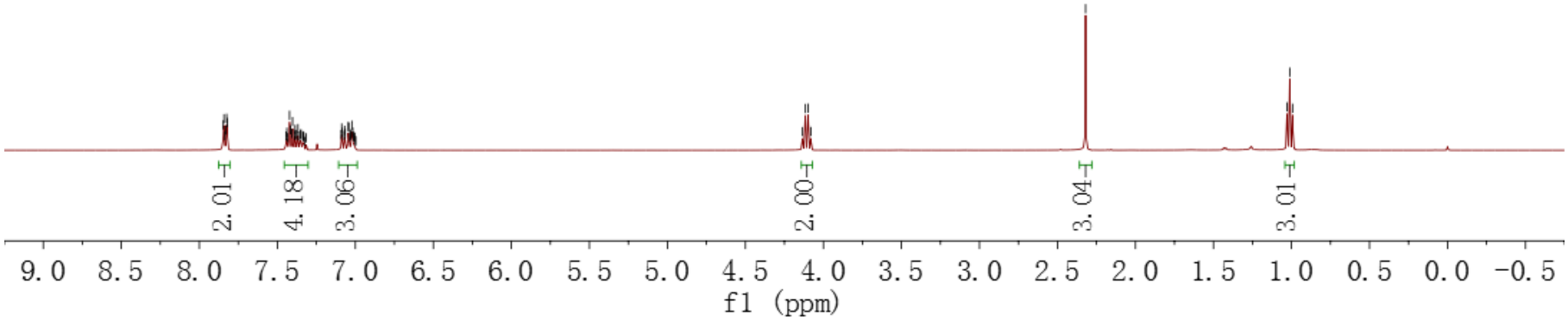


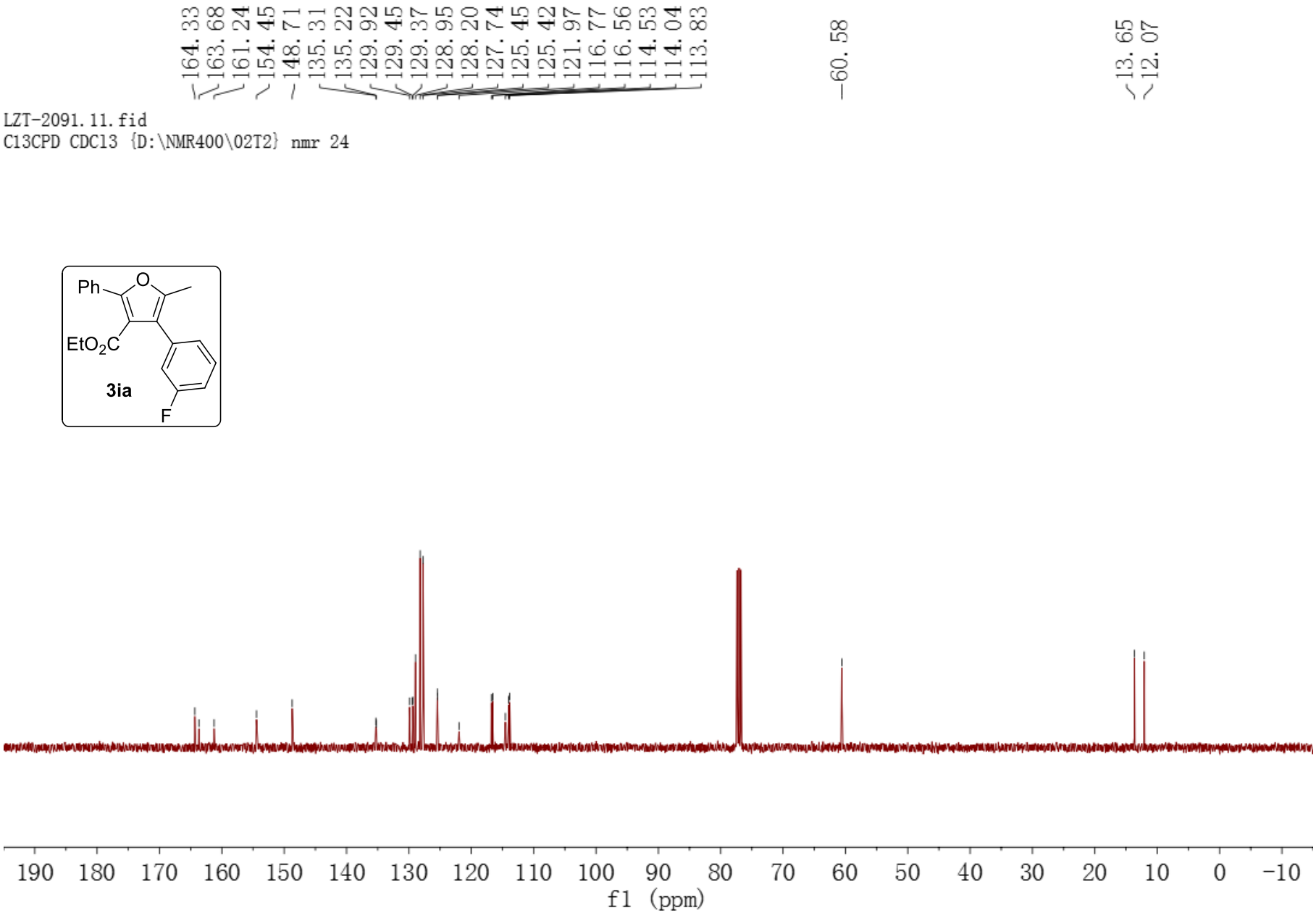

164.05
161.62
159.17
155.12
149.34
131.68
131.65
130.01
129.20
129.12
128.97
128.11
128.09
123.75
123.71
121.19
121.04
116.82
115.42
115.20
114.80
60.36
13.57
12.11
LZT-2099
C13CPD CDCl3 {D:\NMR400\02T2} nmr 10
Ph
O
F
EtO2C
3ha
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

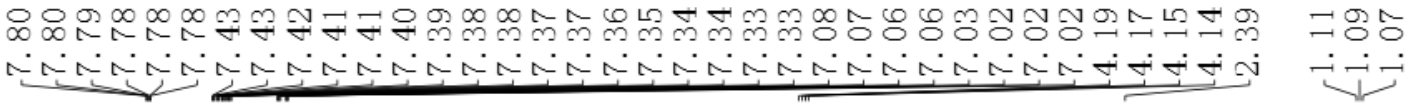


LZT-2091.10.fid
PROTON CDCl3 {D:\NMR400\02T2} nmr 24

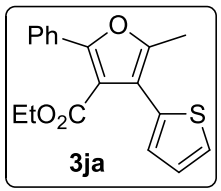


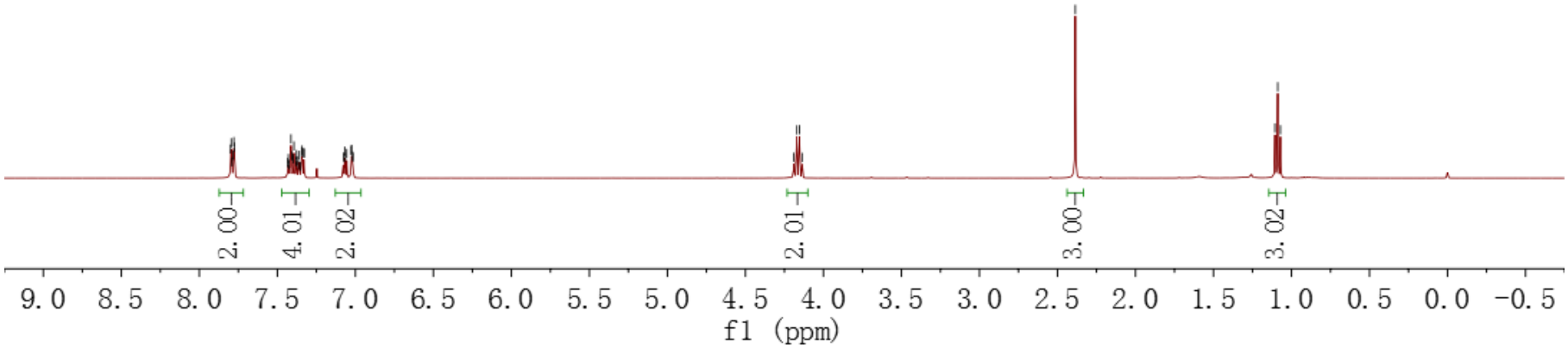


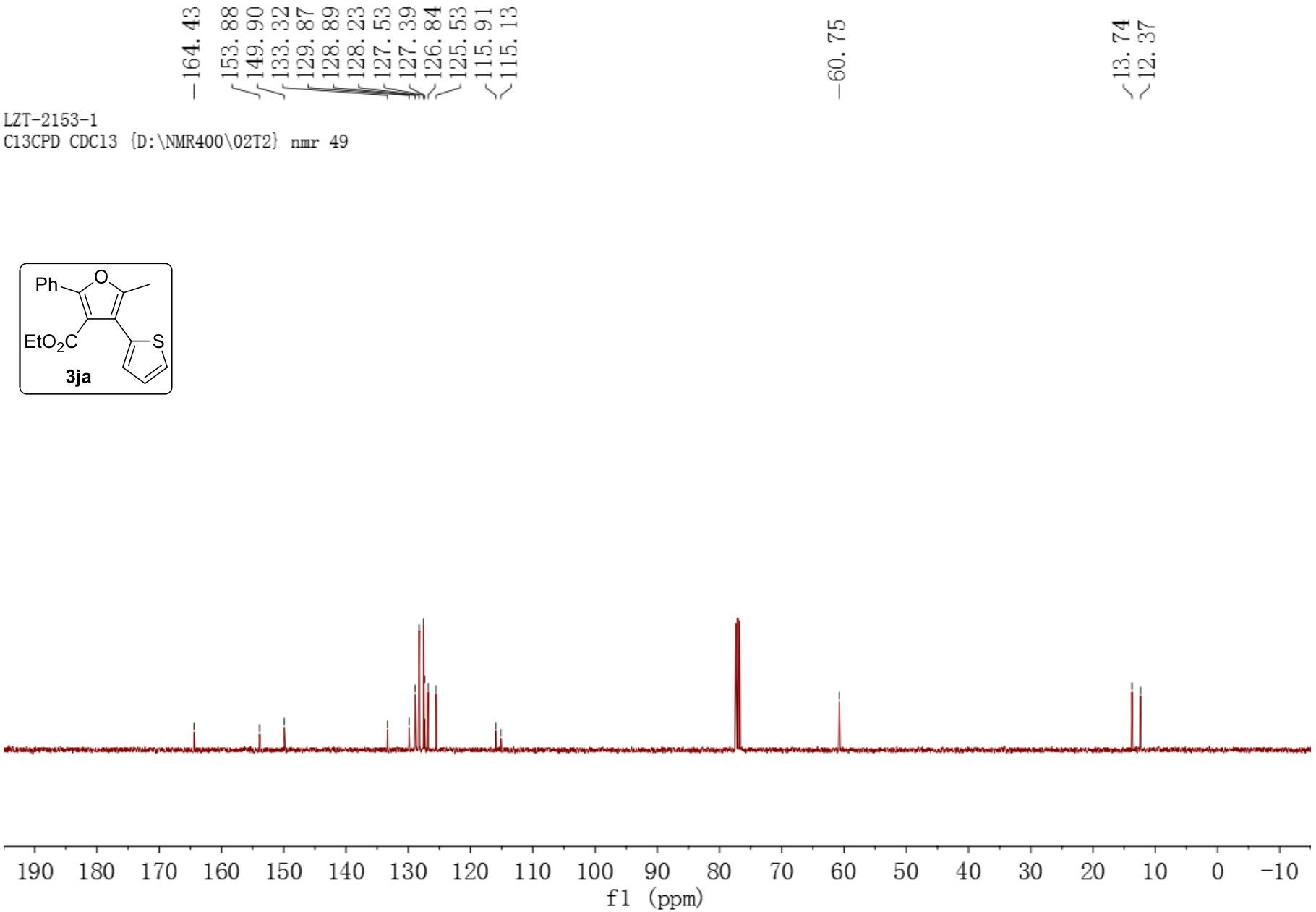

164.33
163.68
161.24
154.45
148.71
135.31
135.22
129.92
129.45
129.37
128.95
128.20
127.74
125.45
125.42
121.97
116.77
116.56
114.53
114.04
113.83
60.58
13.65
12.07
LZT-2091.11.fid
C13CPD CDCl3 {D:\NMR400\02T2} nmr 24
Ph
O
EtO2C
3ia
F
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

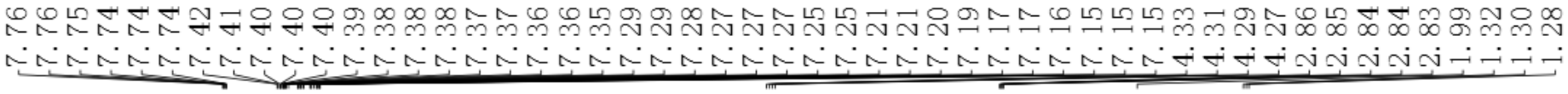


LZT-2153-1
PROTON CDC13 {D:\NMR400\02T2} nmr 49

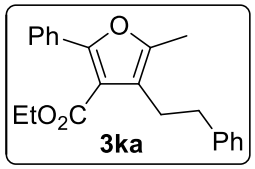




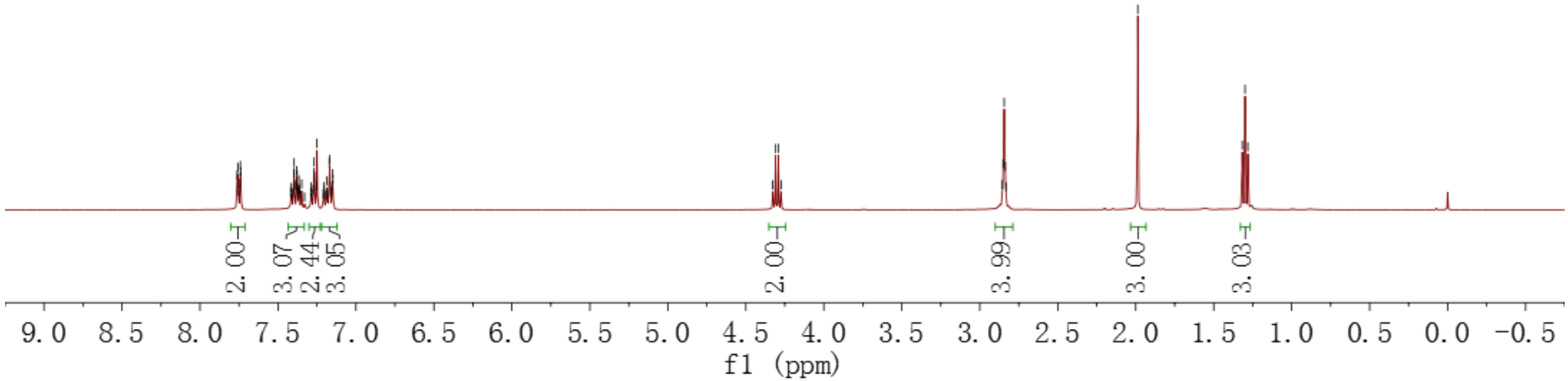

164.43
153.88
149.90
133.32
129.87
128.89
128.23
127.53
127.39
126.84
125.53
115.91
115.13
60.75
13.74
12.37
LZT-2153-1
C13CPD CDCl3 {D:\NMR400\02T2} nmr 49
Ph
O
EtO2C
S
3ja
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

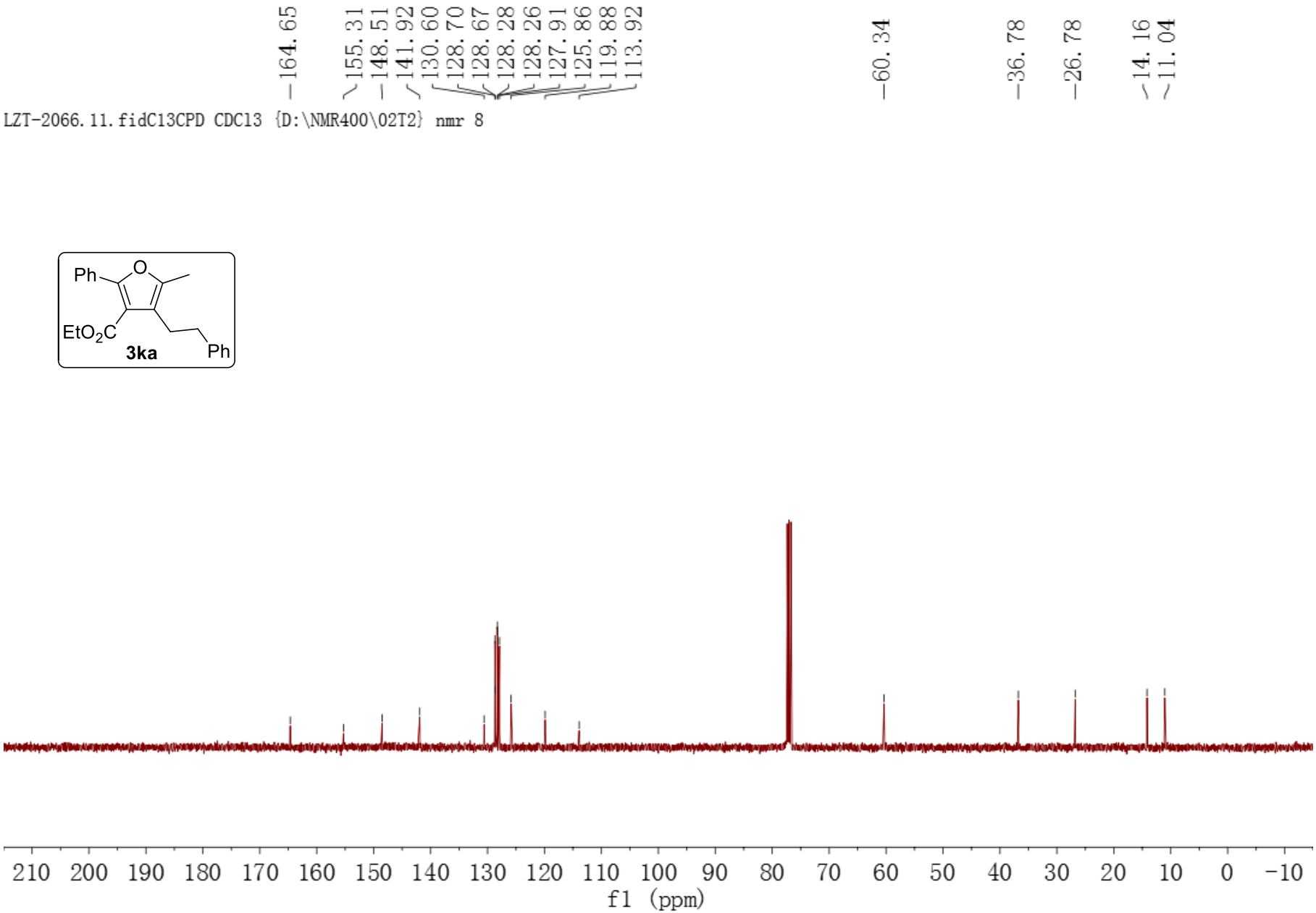


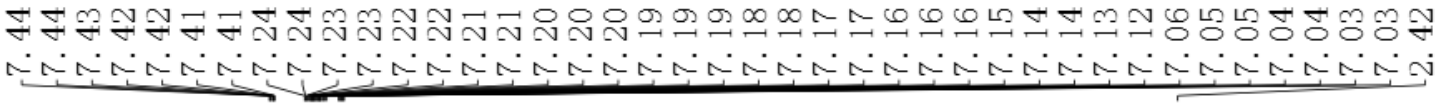
LZT-2066.10.fid
PROTON CDC13 {D:\NMR400\02T2} nmr 8



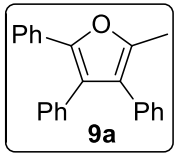
3ka

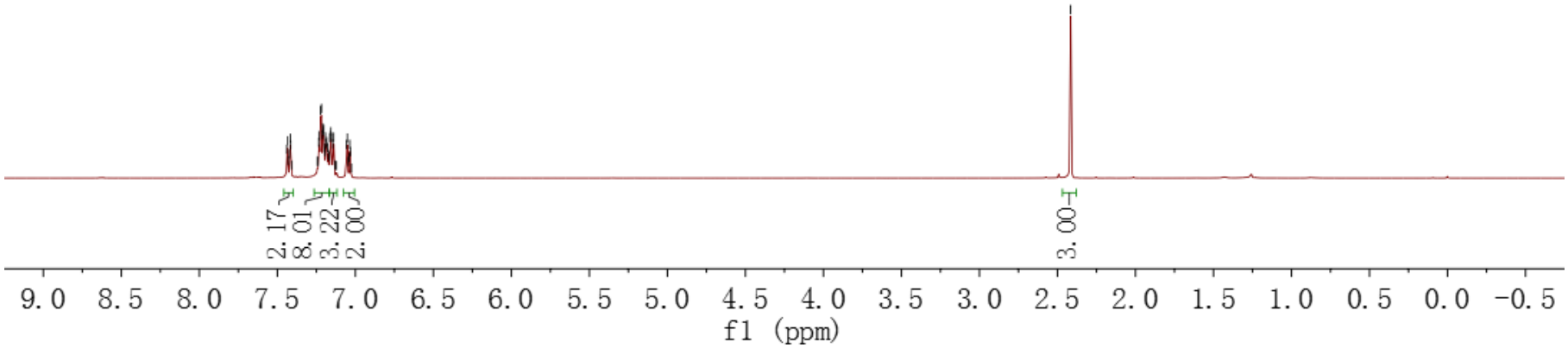



164.65
155.31
148.51
141.92
130.60
128.70
128.67
128.28
128.26
127.91
125.86
119.88
113.92
60.34
36.78
26.78
14.16
11.04
LZT-2066.11.fidC13CPD CDC13 {D:\NMR400\02T2} nmr 8
Ph
O
EtO2C
3ka
Ph
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)



LZT-2773.10.fidPROTON CDCl3 {D:\NMR400\02T2} nmr 13

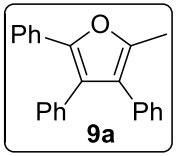




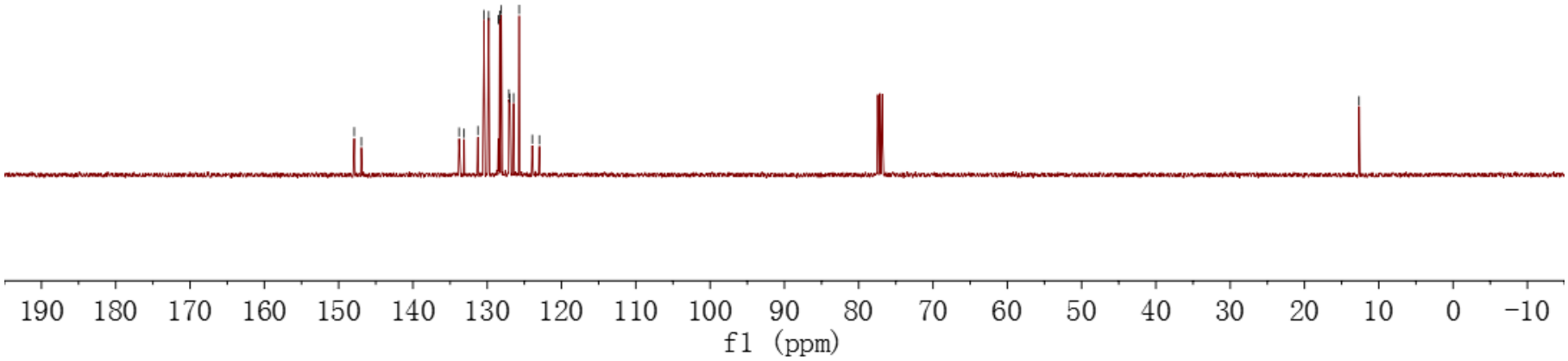
147.90
146.94
133.79
133.11
131.26
130.45
129.80
128.51
128.33
128.10
127.08
126.95
126.46
125.70
123.94
122.97

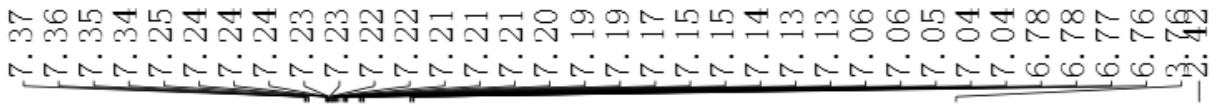
12.65

LZT-2773.11.fidC13CPD CDCl3 {D:\NMR400\02T2} nmr 13

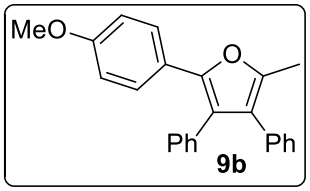


9a

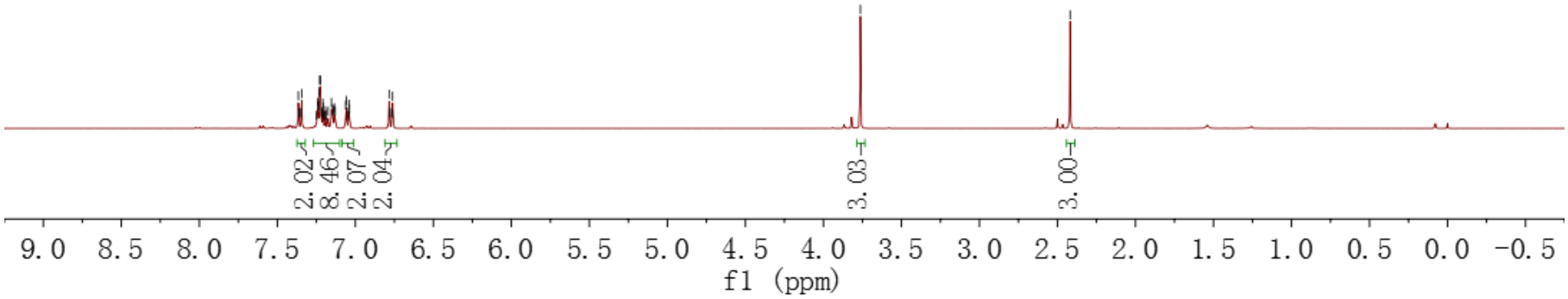




LZT-2783.10.fidPROTON CDC13 {D:\NMR400\02T2} nmr 57

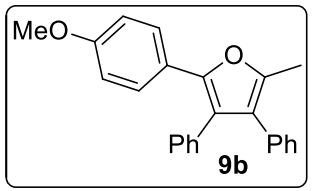


9b

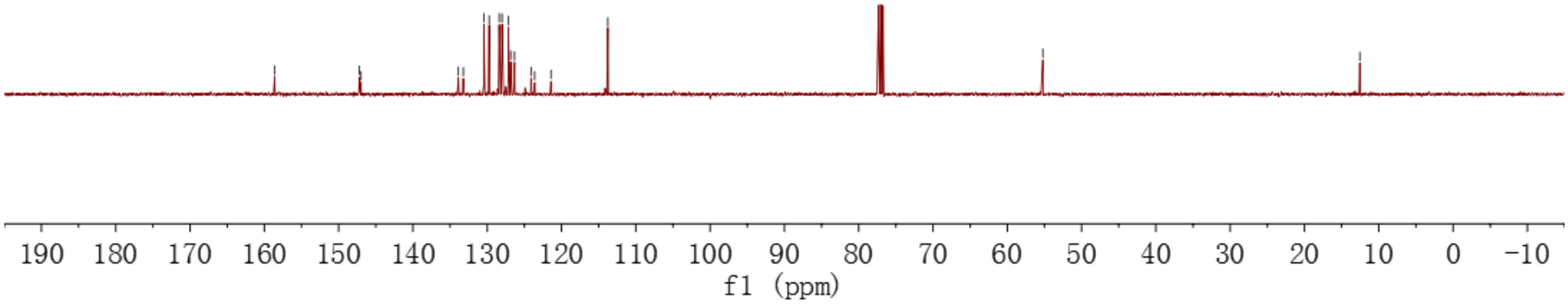


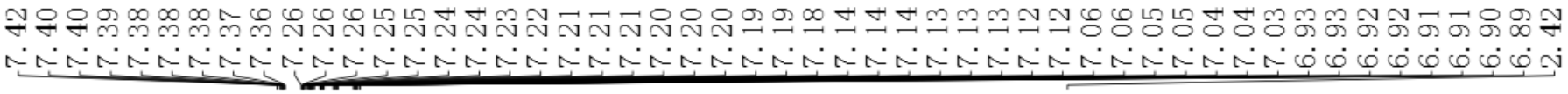
158.63
147.21
146.99
133.89
133.22
130.43
129.73
128.39
128.01
127.15
126.84
126.32
124.10
123.61
121.41
113.76
55.21
12.56

LZT-2783.11.fidC13CPD CDCl3 {D:\NMR400\02T2} nmr 57

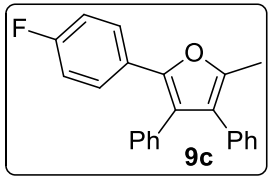


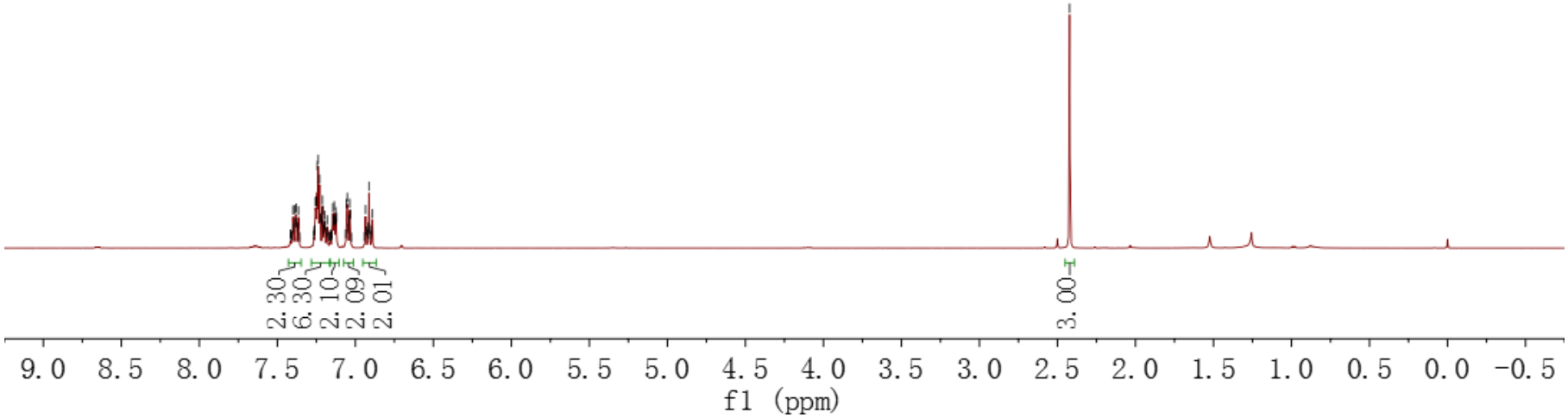
9b





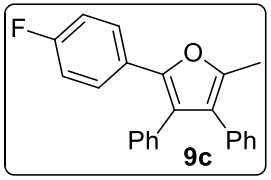
LZT-2782.10.fidPROTON CDCl3 {D:\NMR400\02T2} nmr 38



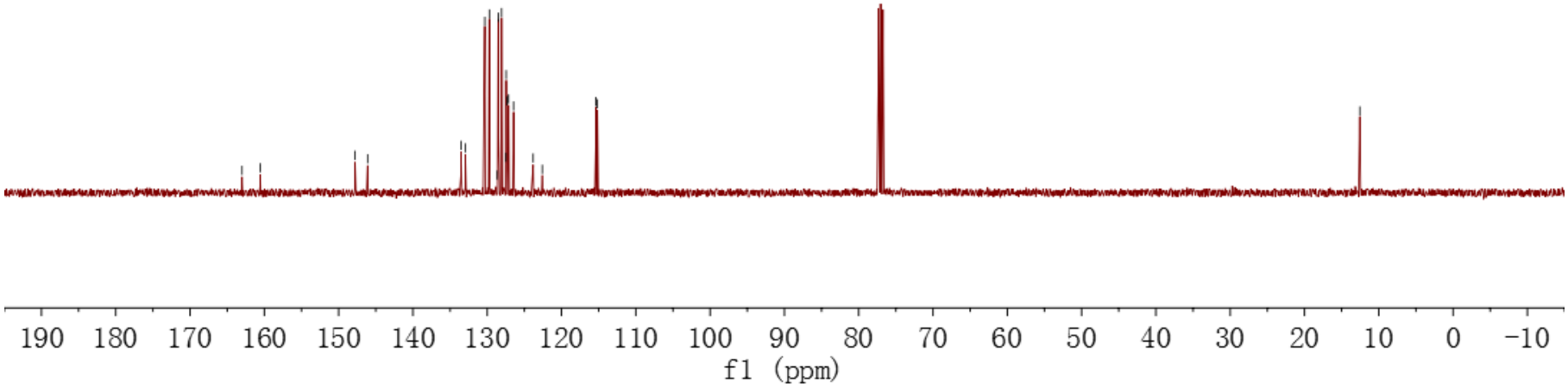


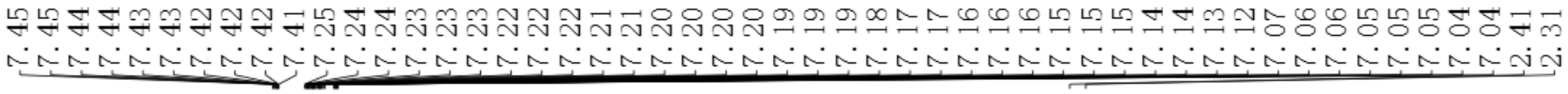
163.00
160.55
147.80
146.10
133.53
132.94
130.33
129.71
128.65
128.52
128.06
127.48
127.45
127.37
127.12
126.45
123.82
122.59
115.39
115.17
12.56

LZT-2782.11.fidC13CPD CDCl3 {D:\NMR400\02T2} nmr 38

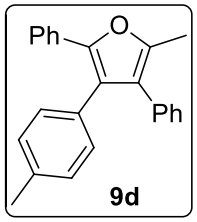


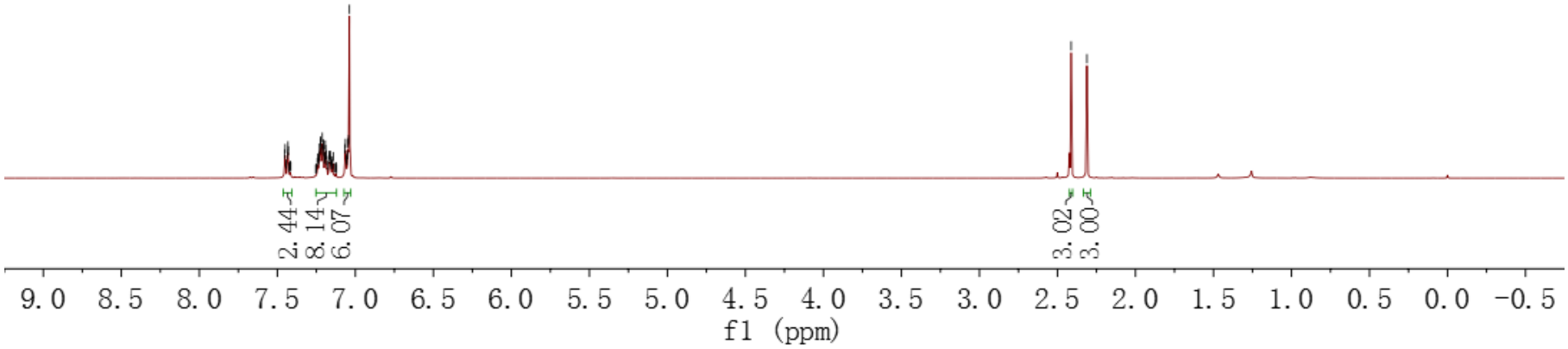
9c





LZT-2780.10.fidPROTON CDCl3 {D:\NMR400\02T2} nmr 36

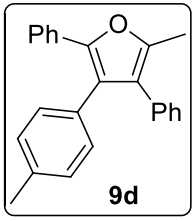




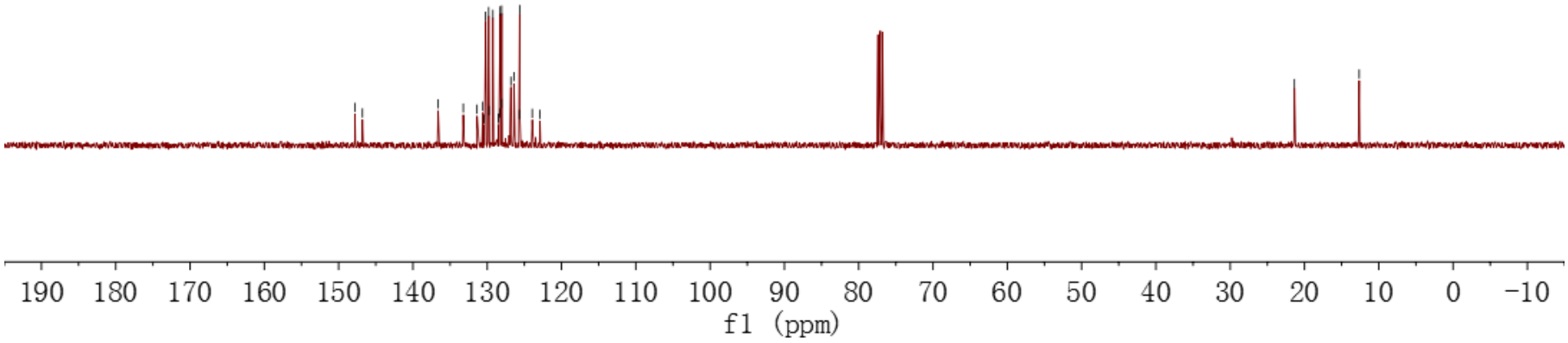
147.81
146.79
136.60
133.22
131.37
130.60
130.42
130.22
129.80
129.77
129.23
128.48
128.31
128.27
128.07
128.05
126.82
126.38
125.67
125.64
123.94
122.89

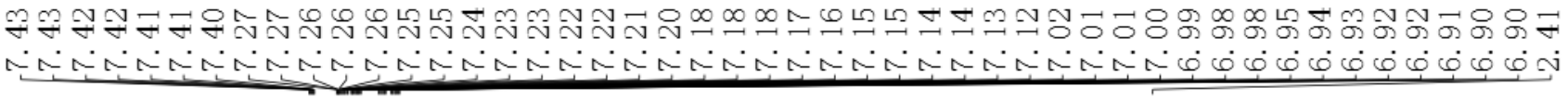
-21.35
-12.63

LZT-2780.11.fidC13CPD CDCl3 {D:\NMR400\02T2} nmr 36

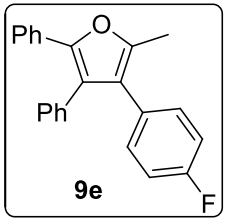


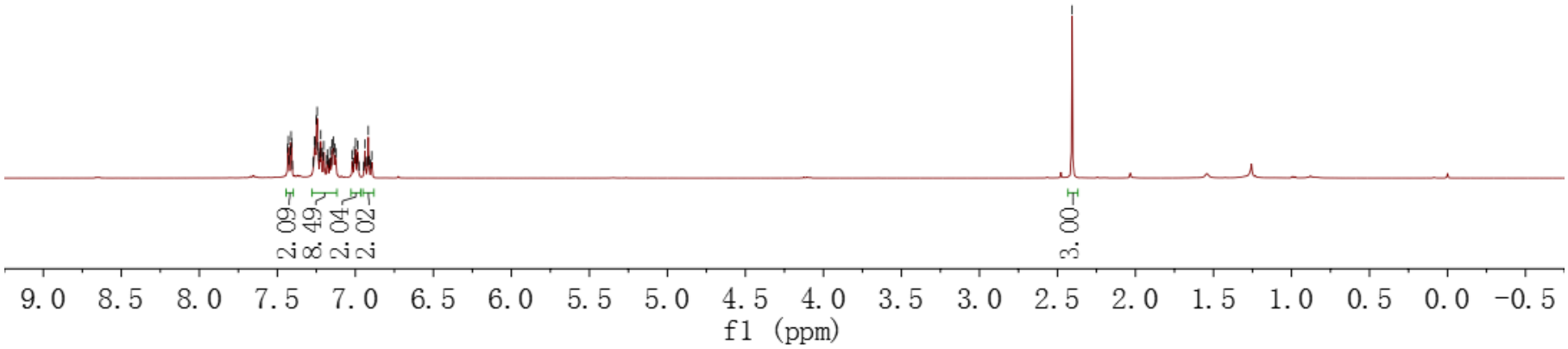
9d

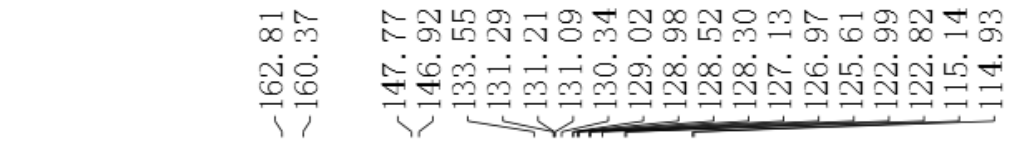




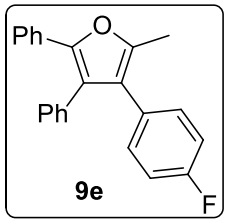
LZT-2781.10.fidPROTON CDCl3 {D:\NMR400\02T2} nmr 37







LZT-2781.11.fidC13CPD CDC13 {D:\NMR400\02T2} nmr 37



9e