

**Regiospecific synthesis of polysubstituted furans with mono- to
tricarboxylates from various sulfonium acylmethylides and
acetylenic esters**

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Analytic data of furan products 3

Dimethyl 2-phenylfuran-3,4-dicarboxylate (3aa).¹ Colorless liquid, 25 mg, yield 79%, $R_f = 0.31$ (PE/EtOAc = 5/1, v/v). ^1H NMR (400 MHz, CDCl₃): δ 7.97 (s, 1H, ArH), 7.70 (d, $J = 7.8$ Hz, 2H, ArH), 7.44–7.38 (m, 3H, ArH), 3.91 (s, 3H), 3.85 (s, 3H). ^{13}C NMR (101 MHz, CDCl₃): δ 164.8, 162.2, 154.1, 146.2, 129.4, 128.7, 128.4, 126.4, 119.7, 113.5, 52.7, 51.9.

Dimethyl 2-(4-methylphenyl)furan-3,4-dicarboxylate (3ab).¹ White solid, m.p. 99–101 °C, 30 mg, yield 89%, $R_f = 0.56$ (PE/EtOAc = 5/1, v/v). ^1H NMR (400 MHz, CDCl₃): δ 7.94 (s, 1H, ArH), 7.60 (d, $J = 8.2$ Hz, 2H, ArH), 7.22 (d, $J = 8.3$ Hz, 2H, ArH), 3.90 (s, 3H), 3.85 (s, 3H), 2.38 (s, 3H). ^{13}C NMR (101 MHz, CDCl₃): δ 164.8, 162.3, 154.5, 145.9, 139.6, 129.3, 126.4, 125.9, 119.7, 112.8, 52.6, 51.9, 21.3.

Dimethyl 2-(4-methoxyphenyl)furan-3,4-dicarboxylate (3ac).¹ White solid, m.p. 54–55 °C, 21 mg, yield 59%, $R_f = 0.39$ (PE/EtOAc = 5/1, v/v). ^1H NMR (400 MHz, CDCl₃): δ 7.91 (s, 1H, ArH), 7.67 (d, $J = 8.9$ Hz, 2H, ArH), 6.94 (d, $J = 8.9$ Hz, 2H, ArH), 3.89 (s, 3H), 3.85 (s, 3H), 3.84 (s, 3H). ^{13}C NMR (101 MHz, CDCl₃): δ 164.9, 162.3, 160.5, 154.7, 145.7, 128.2, 121.4, 119.7, 114.1, 112.0, 55.3, 52.5, 51.9.

Dimethyl 2-(4-fluorophenyl)furan-3,4-dicarboxylate (3ad). White solid, m.p. 95–97 °C, 30 mg, yield 87%, $R_f = 0.56$ (PE/EtOAc = 5/1, v/v). IR (KBr): ν = 3154, 2955, 1730, 1601, 1506, 842 cm⁻¹. ^1H NMR (400 MHz, CDCl₃): δ 7.95 (s, 1H, ArH), 7.76–7.69 (m, 2H, ArH), 7.15–7.08 (m, 2H, ArH), 3.90 (s, 3H), 3.86 (s, 3H). ^{13}C NMR (101 MHz, CDCl₃): δ 164.6, 163.3 (d, $J_{F-C} = 250.5$ Hz), 162.0, 153.6, 146.1, 128.7 (d, $J_{F-C} = 8.6$ Hz), 125.0 (d, $J_{F-C} = 3.0$ Hz), 119.9, 115.8 (d, $J_{F-C} = 22.0$ Hz), 113.3, 52.7, 52.0. ^{19}F NMR (377 MHz, CDCl₃): δ -110.5. HR-MS (ESI) m/z [M+H]⁺ calcd for C₁₄H₁₂FO₅⁺: 279.0663, found: 279.0667.

Dimethyl 2-(4-chlorophenyl)furan-3,4-dicarboxylate (3ae).² White solid, m.p. 96–97 °C, 26 mg, yield 73%, $R_f = 0.56$ (PE/EtOAc = 5/1, v/v). ^1H NMR (400 MHz, CDCl₃): δ 7.96 (s, 1H, ArH), 7.66 (d, $J = 8.7$ Hz, 2H, ArH), 7.39 (d, $J = 8.9$ Hz, 2H, ArH), 3.91 (s, 3H), 3.86 (s, 3H). ^{13}C NMR (101 MHz, CDCl₃): δ 164.6, 162.1, 153.2, 146.3, 135.5, 129.0, 127.8, 127.1, 119.9, 113.9, 52.8, 52.0.

Dimethyl 2-(4-bromophenyl)furan-3,4-dicarboxylate (3af).¹ White solid, m.p. 80–82 °C, 33 mg, yield 79%, $R_f = 0.69$ (PE/EtOAc = 5/1, v/v). ^1H NMR (400 MHz, CDCl₃): δ 7.96 (s, 1H, ArH), 7.59 (d, $J = 9.0$ Hz, 2H, ArH), 7.55 (d, $J = 8.9$ Hz, 2H, ArH), 3.91 (s, 3H), 3.85 (s, 3H). ^{13}C NMR (101 MHz, CDCl₃): δ 164.5, 162.0, 153.1, 146.4, 131.9, 127.9, 127.6, 123.8, 119.9, 114.0, 52.8, 52.0.

Dimethyl 2-(4-trifluoromethylphenyl)furan-3,4-dicarboxylate (3ag). White solid, m.p. 82–84 °C, 35 mg, yield 86%, $R_f = 0.41$ (PE/EtOAc = 5/1, v/v). IR (KBr): ν = 3147, 2960, 1731, 1621, 1509, 841 cm⁻¹. ^1H NMR (400 MHz, CDCl₃): δ 8.00 (s, 1H, ArH), 7.84 (d, $J = 8.2$ Hz, 2H, ArH), 7.68 (d, $J = 8.3$ Hz, 2H, ArH), 3.93 (s, 3H), 3.87 (s, 3H). ^{13}C NMR (101 MHz, CDCl₃): δ 164.4, 161.9, 152.3, 146.8, 131.9, 131.05 (q, $J_{F-C} = 32.6$ Hz), 126.6, 125.69 (q, $J_{F-C} = 3.8$ Hz), 123.77 (q, $J_{F-C} = 272.3$ Hz), 120.1, 115.2, 52.9, 52.1. ^{19}F NMR (377 MHz, CDCl₃): δ -62.9. HR-MS (ESI) m/z [M+H]⁺ calcd for C₁₅H₁₂F₃O₅⁺: 329.0631, found: 329.0634.

Dimethyl 2-(4-cyanophenyl)furan-3,4-dicarboxylate (3ah). White yellow solid, m.p. 154–155 °C, 30 mg, yield 85%, $R_f = 0.31$ (PE/EtOAc = 5/1, v/v). IR (KBr): ν = 3160, 2961, 2230, 1748, 1609, 1503, 855 cm⁻¹. ^1H NMR (400 MHz, CDCl₃): δ 8.02 (s, 1H, ArH), 7.83 (d, $J = 8.5$ Hz, 2H, ArH), 7.70 (d, $J = 8.5$ Hz, 2H, ArH), 3.93 (s, 3H), 3.86 (s, 3H). ^{13}C NMR (101 MHz, CDCl₃): δ 164.3, 161.7, 151.5, 147.1, 132.6, 132.5, 126.6, 120.3, 118.3, 115.9, 112.7, 53.0, 52.1. HR-MS (ESI) m/z [M+H]⁺ calcd for C₁₅H₁₂NO₅⁺: 286.0710, found: 286.0707.

Dimethyl 2-(4-nitrophenyl)furan-3,4-dicarboxylate (3ai). Yellow white solid, m.p. 149–150 °C, 17 mg, yield 45%, $R_f = 0.46$ (PE/EtOAc = 5/1, v/v). IR (KBr): ν = 3143, 2958, 1729, 1518, 1491, 1339, 853 cm⁻¹. ^1H NMR (400 MHz, CDCl₃): δ 8.28 (d, $J = 8.9$ Hz, 2H, ArH), 8.05 (s, 1H, ArH), 7.90 (d, $J = 8.9$ Hz, 2H, ArH), 3.95 (s, 3H), 3.87 (s, 3H). ^{13}C NMR (101 MHz, CDCl₃): δ 164.2, 161.7, 151.2, 147.8, 147.4, 134.3, 126.9, 124.0, 120.4, 116.4, 53.0, 52.2. HR-MS (ESI) m/z [M+H]⁺ calcd for C₁₄H₁₂NO₇⁺: 306.0608, found: 306.0616.

Dimethyl 2-(3,4-dichlorophenyl)furan-3,4-dicarboxylate (3aj). White solid, m.p. 90–92 °C, 30 mg, yield 74%, $R_f = 0.57$ (PE/EtOAc = 5/1, v/v). IR (KBr): ν = 3153, 2953, 1731, 1560, 1384, 885, 814 cm⁻¹. ^1H NMR (400 MHz, CDCl₃): δ 7.97 (s, 1H, ArH), 7.84 (d, $J = 2.1$ Hz, 1H, ArH), 7.58 (dd, $J = 8.5$, 2.1 Hz, 1H, ArH), 7.49 (d, $J = 8.5$ Hz, 1H, ArH), 3.92 (s, 3H), 3.86 (s, 3H). ^{13}C NMR (101 MHz, CDCl₃): δ 164.2, 161.9, 151.8, 146.6, 133.7, 133.1, 130.7, 128.5, 128.3, 125.6, 120.1, 114.7, 52.9, 52.1. HR-MS (ESI) m/z [M+H]⁺ calcd for C₁₄H₁₁Cl₂O₅⁺: 328.9978, found: 328.9978.

Dimethyl 2-(naphthalen-1-yl)furan-3,4-dicarboxylate (3ak). Light green liquid, 33 mg, yield 85%, $R_f = 0.57$ (PE/EtOAc = 5/1, v/v). IR (KBr): ν = 3148, 2952, 1731, 1551 cm⁻¹. ^1H NMR (400 MHz, CDCl₃): δ 8.11 (s, 1H, ArH), 7.96 (d, $J = 8.3$ Hz, 1H, ArH), 7.92–7.88 (m, 1H, ArH), 7.84–7.79 (m, 1H, ArH), 7.67 (d, $J = 7.1$ Hz, 1H, ArH), 7.56–7.48 (m, 3H, ArH), 3.91 (s, 3H), 3.66 (s, 3H). ^{13}C NMR (101 MHz, CDCl₃): δ 163.5, 162.3, 156.0, 147.0, 133.5, 131.5, 130.6, 129.0, 128.4, 126.9, 126.2, 126.1, 125.1, 124.8, 119.3, 116.3, 52.2, 52.0. HR-MS (ESI) m/z [M+H]⁺ calcd for C₁₈H₁₅O₅⁺: 311.0914, found: 311.0914.

Dimethyl 2-(naphthalen-2-yl)furan-3,4-dicarboxylate (3al). Green white solid, m.p. 105–107 °C, 29 mg, yield 75%, $R_f = 0.39$ (PE/EtOAc = 10/1, v/v). IR (KBr): ν = 3150, 2952, 1731, 1551 cm⁻¹. ^1H NMR (400 MHz,

CDCl_3): δ 8.24–8.22 (m, 1H, ArH), 8.02 (s, 1H, ArH), 7.92–7.82 (m, 3H, ArH), 7.77 (dd, J = 8.7, 1.8 Hz, 1H, ArH), 7.56–7.48 (m, 2H, ArH), 3.95 (s, 3H), 3.88 (s, 3H). ^{13}C NMR (101 MHz, CDCl_3): δ 164.9, 162.2, 154.2, 146.4, 133.4, 133.0, 128.6, 128.4, 127.7, 127.1, 126.7, 126.2, 126.0, 123.4, 119.9, 113.8, 52.7, 52.0. HR-MS (ESI) m/z [M+H] $^+$ calcd for $\text{C}_{18}\text{H}_{15}\text{O}_5^+$: 311.0914, found: 311.0915.

Diethyl 2-phenylfuran-3,4-dicarboxylate (3ba). Colorless liquid, 20 mg, yield 56%, R_f = 0.64 (PE/EtOAc = 5/1, v/v). IR (KBr): ν = 3150, 2983, 2938, 1728, 1578, 1447, 772, 704 cm^{-1} . ^1H NMR (400 MHz, CDCl_3): δ 7.96 (s, 1H, ArH), 7.71 (dd, J = 8.2, 1.6 Hz, 2H, ArH), 7.45–7.35 (m, 3H, ArH), 4.39 (q, J = 7.1 Hz, 2H), 4.32 (q, J = 7.1 Hz, 2H), 1.35 (t, J = 7.1 Hz, 6H). ^{13}C NMR (101 MHz, CDCl_3): δ 164.4, 161.8, 153.7, 146.1, 129.3, 128.8, 128.6, 126.4, 120.1, 113.9, 61.8, 60.9, 14.2, 14.0. HR-MS (ESI) m/z [M+H] $^+$ calcd for $\text{C}_{16}\text{H}_{17}\text{O}_5^+$: 289.1071, found: 289.1072.

Diethyl 2-(4-methylphenyl)furan-3,4-dicarboxylate (3bb). Colorless liquid, 20 mg, yield 56%, R_f = 0.64 (PE/EtOAc = 5/1, v/v). IR (KBr): ν = 3151, 2984, 2938, 1729, 1608, 1508 cm^{-1} . ^1H NMR (400 MHz, CDCl_3): δ 7.94 (s, 1H, ArH), 7.61 (d, J = 8.2 Hz, 2H, ArH), 7.22 (d, J = 8.2 Hz, 2H, ArH), 4.37 (q, J = 7.1 Hz, 2H), 4.31 (q, J = 7.1 Hz, 2H), 2.38 (s, 3H), 1.35 (t, J = 7.1 Hz, 6H). ^{13}C NMR (101 MHz, CDCl_3): δ 164.5, 161.9, 154.1, 145.8, 139.5, 129.3, 126.4, 126.1, 120.1, 113.3, 61.7, 60.8, 21.4, 14.2, 14.0. HR-MS (ESI) m/z [M+H] $^+$ calcd for $\text{C}_{17}\text{H}_{19}\text{O}_5^+$: 303.1227, found: 303.1227.

Diethyl 2-(4-bromophenyl)furan-3,4-dicarboxylate (3bf). Emerald liquid, 31 mg, yield 68%, R_f = 0.64 (PE/EtOAc = 5/1, v/v). IR (KBr): ν = 3148, 2983, 2937, 1727, 1586, 1487, 829 cm^{-1} . ^1H NMR (400 MHz, CDCl_3): δ 7.96 (s, 1H, ArH), 7.61 (d, J = 8.8 Hz, 2H, ArH), 7.55 (d, J = 8.8 Hz, 2H, ArH), 4.38 (q, J = 7.1 Hz, 2H), 4.32 (q, J = 7.1 Hz, 2H), 1.35 (t, J = 7.1 Hz, 6H). ^{13}C NMR (101 MHz, CDCl_3): δ 164.2, 161.7, 152.8, 146.2, 131.9, 127.9, 127.7, 123.7, 120.3, 114.4, 61.9, 61.0, 14.2, 14.0. HR-MS (ESI) m/z [M+H] $^+$ calcd for $\text{C}_{16}\text{H}_{16}\text{BrO}_5^+$: 367.0176, found: 367.0177.

Ethyl 2-phenyl-4-(trifluoromethyl)furan-3-carboxylate (3ca). Colorless liquid, 22 mg, yield 57%, R_f = 0.79 (PE/EtOAc = 10/1, v/v). IR (KBr): ν = 3130, 2986, 2936, 1727, 1599, 1583, 1491, 765, 692 cm^{-1} . ^1H NMR (400 MHz, CDCl_3): δ 7.82–7.78 (m, 3H, ArH), 7.47–7.43 (m, 3H, ArH), 4.32 (q, J = 7.2 Hz, 2H), 1.31 (t, J = 7.1 Hz, 3H). ^{13}C NMR (101 MHz, CDCl_3): δ 161.9, 159.5, 142.5 (q, $J_{\text{F-C}} = 6.8$ Hz), 130.1, 128.6, 128.5, 128.2, 121.7 (q, $J_{\text{F-C}} = 267.4$ Hz), 118.8 (q, $J_{\text{F-C}} = 37.5$ Hz), 111.2, 61.3, 13.7. ^{19}F NMR (377 MHz, CDCl_3): δ -58.9. HR-MS (ESI) m/z [M+H] $^+$ calcd for $\text{C}_{14}\text{H}_{12}\text{F}_3\text{O}_3^+$: 285.0733, found: 285.0725.

Ethyl 2-(4-methylphenyl)-4-(trifluoromethyl)furan-3-carboxylate (3cb). Colorless liquid, 20 mg, yield 54%, R_f = 0.66 (PE/EtOAc = 10/1, v/v). IR (KBr): ν = 3129, 2986, 2928, 1726, 1615, 1578, 1505, 822 cm^{-1} . ^1H NMR (400 MHz, CDCl_3): δ 7.78 (q, J = 1.3 Hz, 1H, ArH), 7.72–7.69 (m, 2H, ArH), 7.25 (d, J = 8.0 Hz, 2H, ArH), 4.32 (q, J = 7.2 Hz, 2H), 2.40 (s, 3H), 1.32 (t, J = 7.1 Hz, 3H). ^{13}C NMR (101 MHz, CDCl_3): δ 162.0, 159.9, 142.2 (q, $J_{\text{F-C}} = 7.3$ Hz), 140.4, 128.9, 128.5, 125.8, 121.8 (q, $J_{\text{F-C}} = 267.5$ Hz), 118.8 (q, $J_{\text{F-C}} = 37.5$ Hz), 110.7, 61.2, 21.5, 13.7. ^{19}F NMR (377 MHz, CDCl_3): δ -58.9. HR-MS (ESI) m/z [M+H] $^+$ calcd for $\text{C}_{15}\text{H}_{14}\text{F}_3\text{O}_3^+$: 299.0890, found: 299.0889.

Ethyl 2-(4-bromophenyl)-4-(trifluoromethyl)furan-3-carboxylate (3cf). Light Green liquid, 20 mg, yield 44%, R_f = 0.66 (PE/EtOAc = 5/1, v/v). IR (KBr): ν = 2986, 2929, 1726, 1592, 1575, 1505, 822 cm^{-1} . ^1H NMR (400 MHz, CDCl_3): δ 7.84 (s, 1H, ArH), 7.75 (d, J = 8.6 Hz, 2H, ArH), 7.61 (d, J = 8.6 Hz, 2H, ArH), 4.35 (q, J = 7.1 Hz, 2H), 1.36 (t, J = 7.1 Hz, 3H). ^{13}C NMR (101 MHz, CDCl_3): δ 161.7, 158.4, 142.7 (q, $J_{\text{F-C}} = 6.8$ Hz), 131.5, 130.0, 127.4, 124.7, 121.6 (q, $J_{\text{F-C}} = 267.5$ Hz), 119.0 (q, $J_{\text{F-C}} = 37.7$ Hz), 111.7, 61.5, 13.7. ^{19}F NMR (377 MHz, CDCl_3): δ -58.9. HR-MS (ESI) m/z [M+H] $^+$ calcd for $\text{C}_{14}\text{H}_{11}\text{BrF}_3\text{O}_3^+$: 362.9838, found: 362.9832.

2-Ethyl 3,4-dimethyl 5-phenylfuran-2,3,4-tricarboxylate (3am). Golden yellow liquid, 17 mg, yield 52%, R_f = 0.18 (PE/EtOAc = 10/1, v/v). IR (KBr): ν = 2987, 2953, 1733, 1580, 1598, 1446, 774, 696 cm^{-1} . ^1H NMR (400 MHz, CDCl_3): δ 7.96–7.90 (m, 2H, ArH), 7.52–7.42 (m, 3H, ArH), 4.39 (q, J = 7.2 Hz, 2H), 3.97 (s, 3H), 3.82 (s, 3H), 1.38 (t, J = 7.1 Hz, 3H). ^{13}C NMR (101 MHz, CDCl_3): δ 163.5, 161.8, 159.6, 157.2, 139.9, 130.9, 129.1, 128.3, 127.9, 127.1, 113.6, 61.8, 53.0, 52.3, 14.1. HR-MS (ESI) m/z [M+H] $^+$ calcd for $\text{C}_{17}\text{H}_{17}\text{O}_7^+$: 333.0969, found: 333.0963.

Trimethyl 5-methylfuran-2,3,4-tricarboxylate (3an).³ Light yellow solid, m.p. 94–96 °C, 19 mg, yield 75%, R_f = 0.36 (PE/EtOAc = 3/1, v/v). ^1H NMR (400 MHz, CDCl_3): δ 3.95 (s, 3H), 3.90 (s, 3H), 3.84 (s, 3H), 2.66 (s, 3H). ^{13}C NMR (101 MHz, CDCl_3): δ 163.6, 162.3, 162.0, 157.6, 138.9, 126.1, 114.0, 53.0, 52.5, 52.1, 14.2.

Triethyl 5-phenylfuran-2,3,4-tricarboxylate (3bm). Light green liquid, 17 mg, yield 48%, R_f = 0.19 (PE/EtOAc = 10/1, v/v). IR (KBr): ν = 2984, 2937, 1732, 1580, 1597, 1490, 774, 694 cm^{-1} . ^1H NMR (400 MHz, CDCl_3): δ 7.97–7.92 (m, 2H, ArH), 7.51–7.41 (m, 3H, ArH), 4.43 (q, J = 7.1 Hz, 2H), 4.39 (q, J = 7.1 Hz, 2H), 4.29 (q, J = 7.1 Hz, 2H), 1.42 (t, J = 7.1 Hz, 3H), 1.38 (t, J = 7.1 Hz, 3H), 1.29 (t, J = 7.1 Hz, 3H). ^{13}C NMR (101 MHz, CDCl_3): δ 163.1, 161.4, 159.5, 157.3, 139.7, 130.8, 129.2, 128.2, 128.0, 127.4, 113.9, 62.1, 61.7, 61.3, 14.2, 14.0, 13.9. HR-MS (ESI) m/z [M+H] $^+$ calcd for $\text{C}_{19}\text{H}_{21}\text{O}_7^+$: 361.1282, found: 361.1284.

3,4-Diethyl 2-methyl 5-methylfuran-2,3,4-tricarboxylate (3bn). Colorless liquid, 17 mg, yield 61%, R_f = 0.21 (PE/EtOAc = 10/1, v/v). IR (KBr): ν = 2984, 1723, 1600, 1564, 1440, 1388 cm^{-1} . ^1H NMR (400 MHz,

CDCl_3): δ 4.41 (q, J = 7.1 Hz, 2H), 4.30 (q, J = 7.1 Hz, 2H), 3.89 (s, 3H), 2.66 (s, 3H), 1.39 (t, J = 7.1 Hz, 3H), 1.33 (t, J = 7.1 Hz, 3H). ^{13}C NMR (101 MHz, CDCl_3): δ 163.1, 162.2, 161.6, 157.6, 138.8, 126.4, 114.1, 62.1, 61.0, 52.4, 14.1, 14.0. HR-MS (ESI) m/z [M+H] $^+$ calcd for $\text{C}_{13}\text{H}_{17}\text{O}_7^+$: 285.0969, found: 285.0970.

Methyl 2-phenylfuran-3-carboxylate (3da).⁴ Colorless liquid, 8 mg, yield 15%, R_f = 0.54 (PE/EtOAc = 10/1, v/v). ^1H NMR (400 MHz, CDCl_3): δ 8.00–7.95 (m, 2H), 7.48–7.37 (m, 4H), 6.84 (d, J = 2.0 Hz, 1H), 3.83 (s, 3H). ^{13}C NMR (101 MHz, CDCl_3): δ 164.0, 157.6, 141.2, 129.7, 129.4, 128.3, 128.1, 113.5, 112.9, 51.61.

2-Ethyl 4-methyl 5-phenylfuran-2,4-dicarboxylate (3dm). White solid, m.p. 98–100 °C. 4 mg, yield 15%, R_f = 0.63 (PE/EtOAc = 3/1, v/v). IR (KBr): ν = 2983, 2954, 1726, 1594, 1577, 1490, 1447, 764, 692 cm^{-1} . ^1H NMR (400 MHz, CDCl_3): δ 8.11–8.02 (m, 2H, ArH), 7.57 (s, 1H, ArH), 7.48–7.45 (m, 3H, ArH), 4.40 (q, J = 7.1 Hz, 2H), 3.86 (s, 3H), 1.40 (t, J = 7.1 Hz, 3H). ^{13}C NMR (101 MHz, CDCl_3): δ 163.0, 160.2, 158.3, 142.9, 130.5, 128.9, 128.6, 128.2, 120.2, 115.1, 61.3, 51.9, 14.3. HR-MS (ESI) m/z [M+H] $^+$ calcd for $\text{C}_{15}\text{H}_{15}\text{O}_5^+$: 275.0914, found: 275.0917.

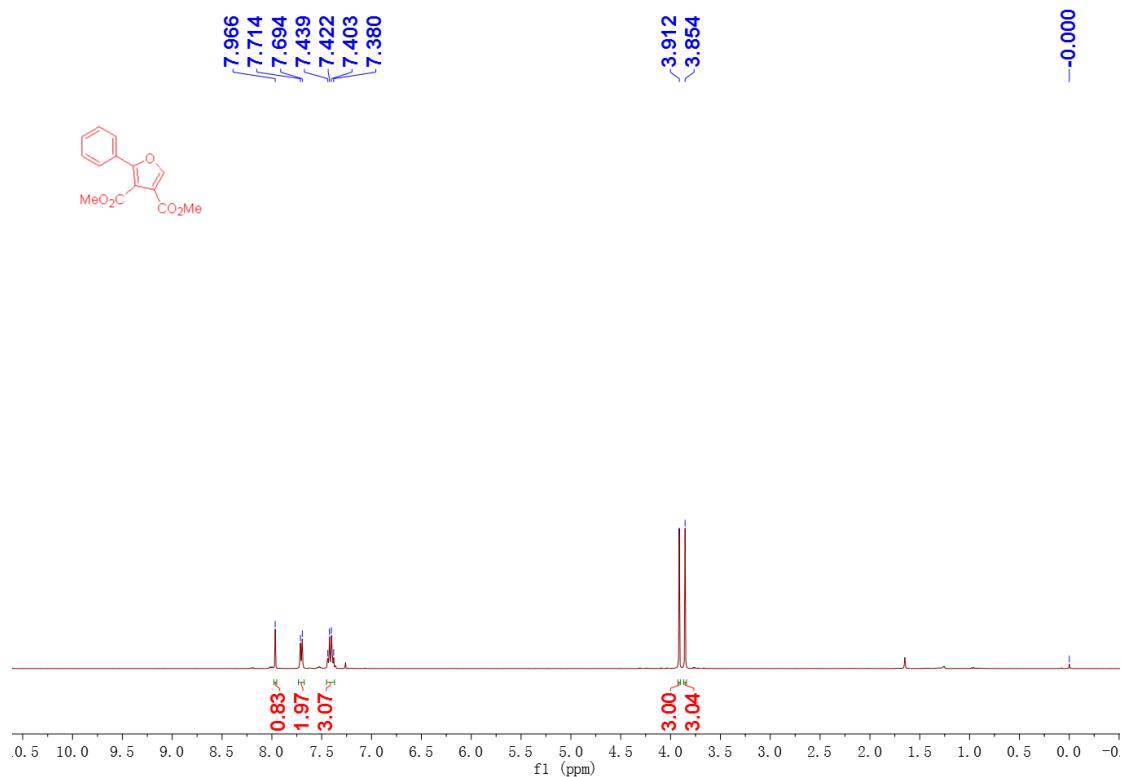
4-Ethyl 2-methyl 5-methylfuran-2,4-dicarboxylate (3en).⁵ Colorless liquid, 10 mg, yield 48%, R_f = 0.45 (PE/EtOAc = 10/1, v/v). IR (KBr): ν = 2956, 1720, 1604 cm^{-1} . ^1H NMR (400 MHz, CDCl_3): δ 7.41 (s, 1H), 4.31 (q, J = 7.1 Hz, 2H), 3.90 (s, 3H), 2.66 (s, 3H), 1.36 (t, J = 7.1 Hz, 3H). ^{13}C NMR (101 MHz, CDCl_3): δ 162.9, 162.7, 158.7, 142.1, 118.7, 115.78, 60.6, 52.1, 14.3, 14.2. HR-MS (ESI) m/z [M+H] $^+$ calcd for $\text{C}_{10}\text{H}_{13}\text{O}_5^+$: 213.0757, found: 285.0970.

References

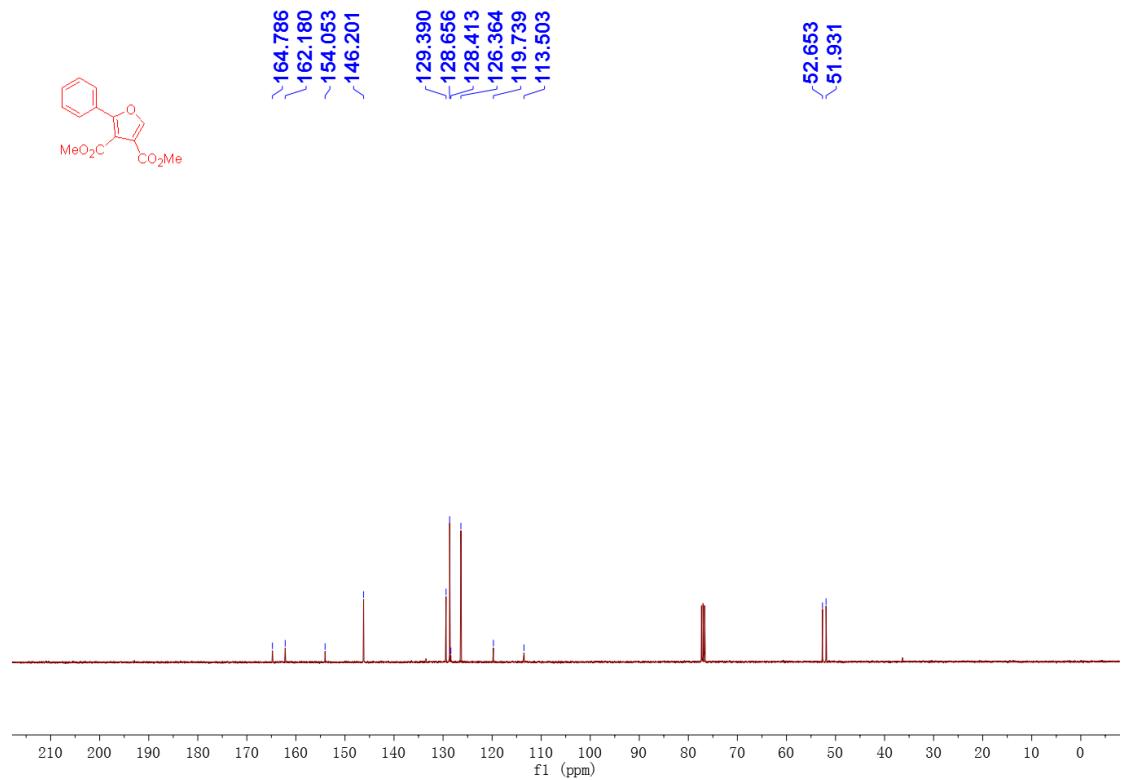
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Copies of ^1H and ^{13}C NMR spectra of furan products 3

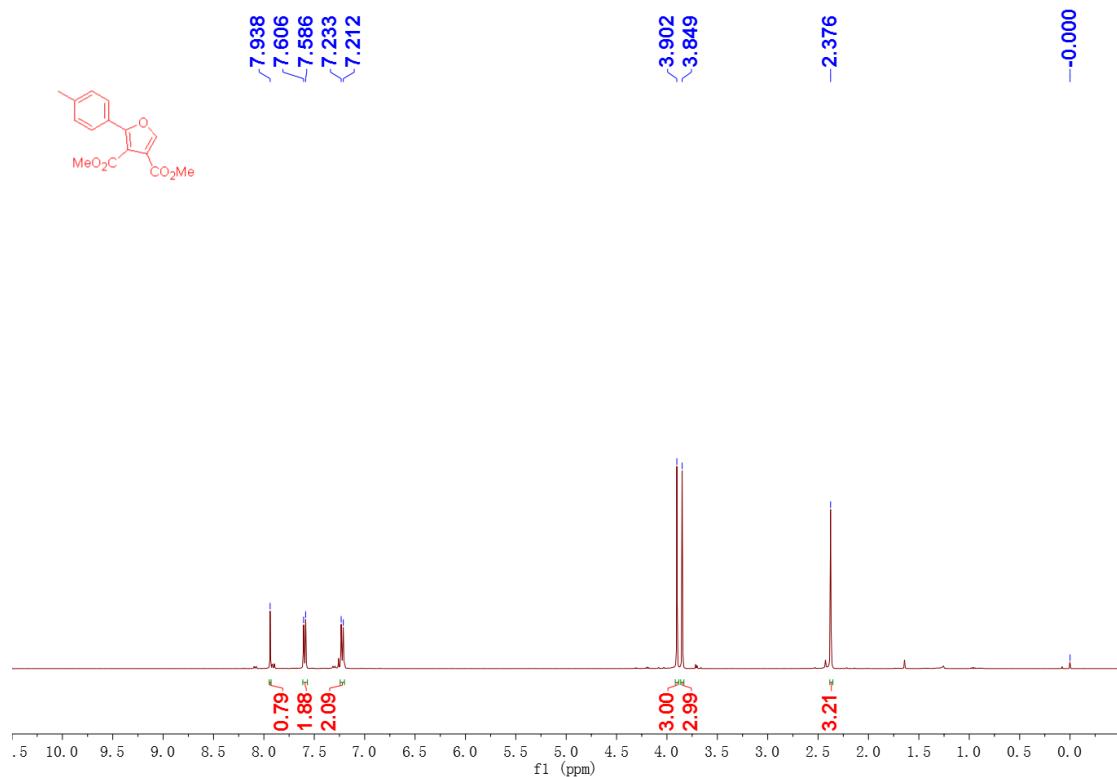
^1H NMR (400 MHz, CDCl_3) of compound 3aa



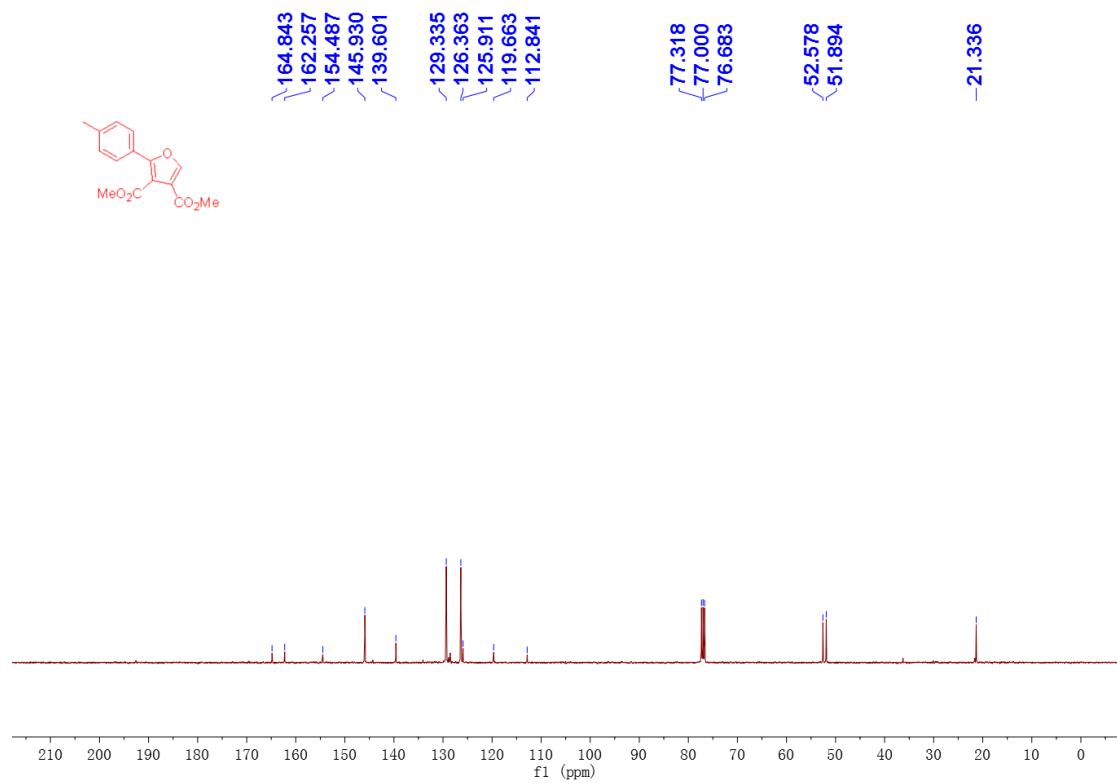
^{13}C NMR (101 MHz, CDCl_3)



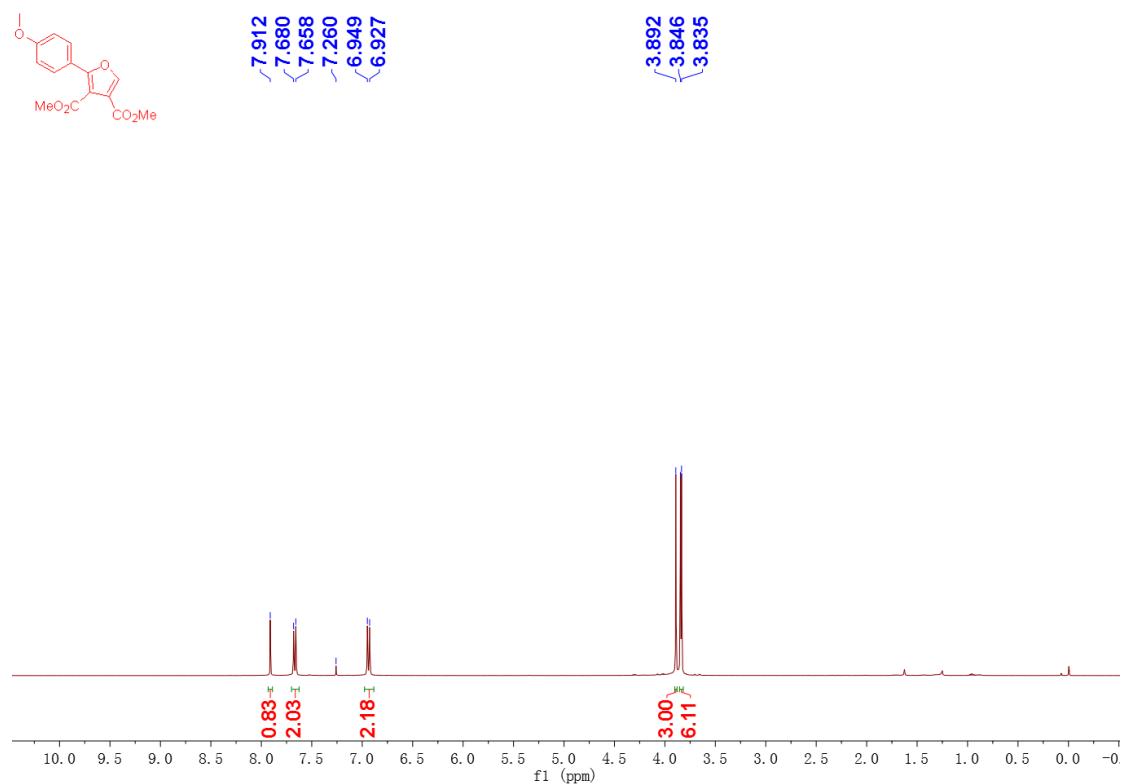
¹H NMR (400 MHz, CDCl₃) of compound **3ab**



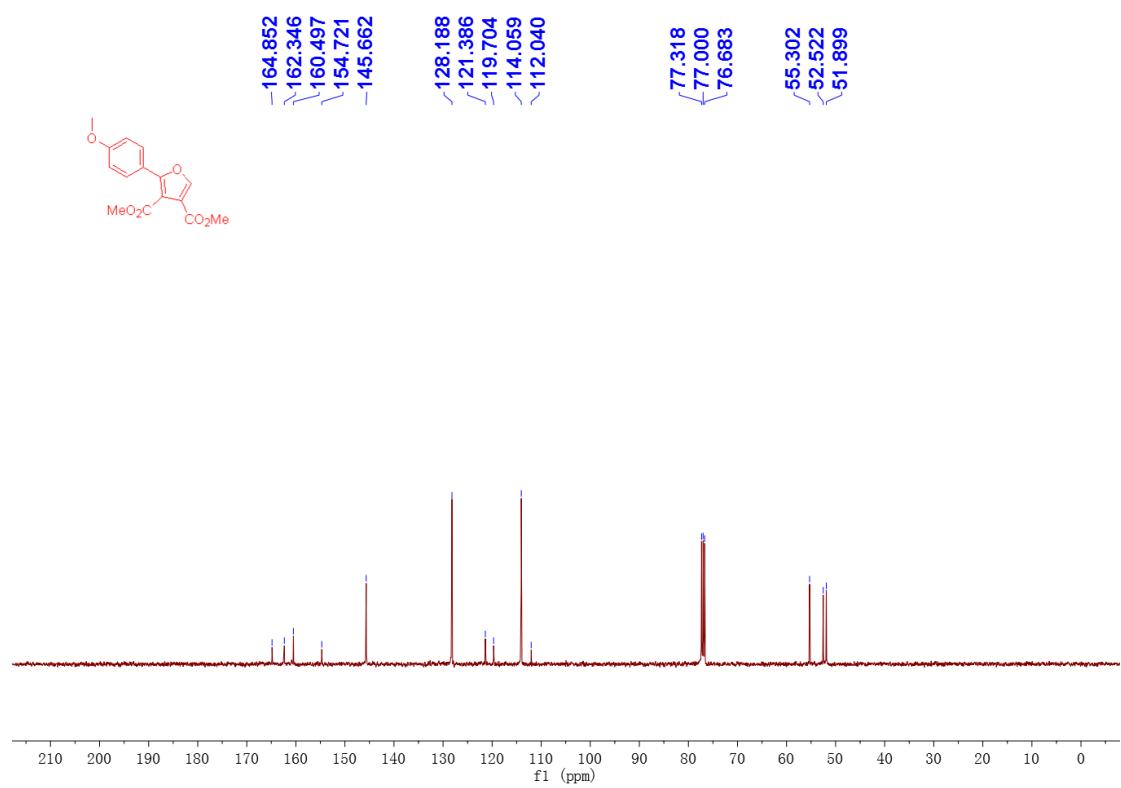
¹³C NMR (101 MHz, CDCl₃)



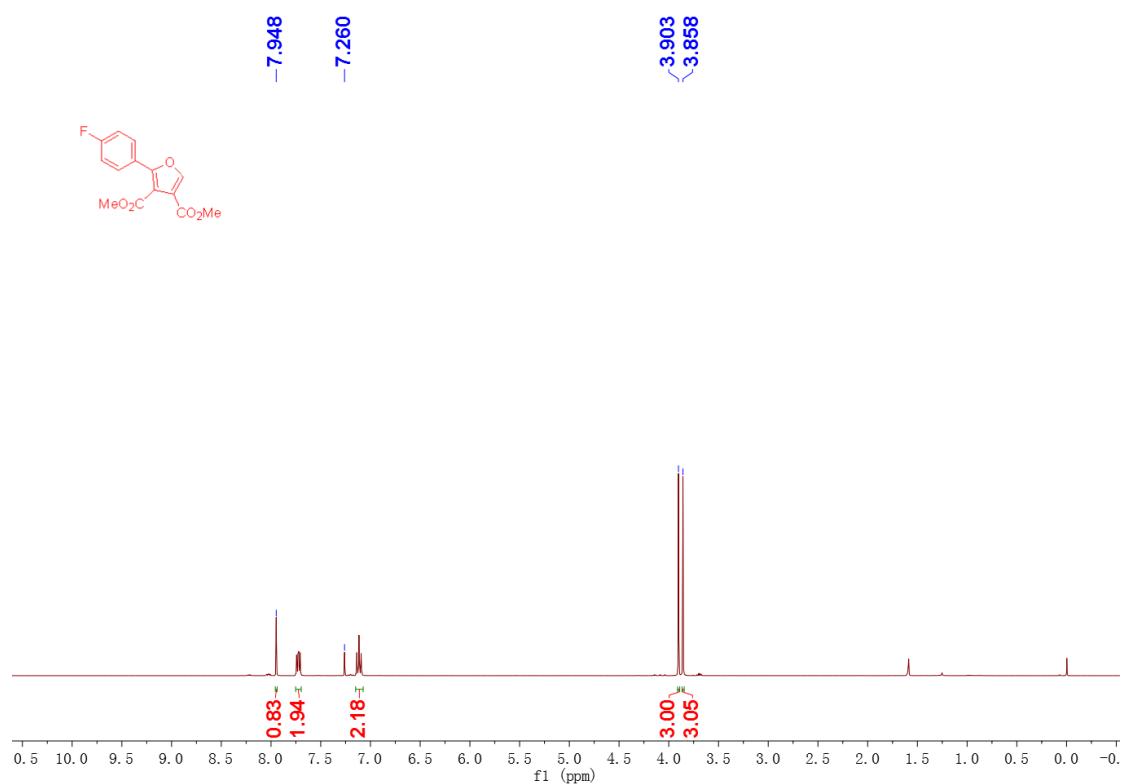
¹H NMR (400 MHz, CDCl₃) of compound 3ac



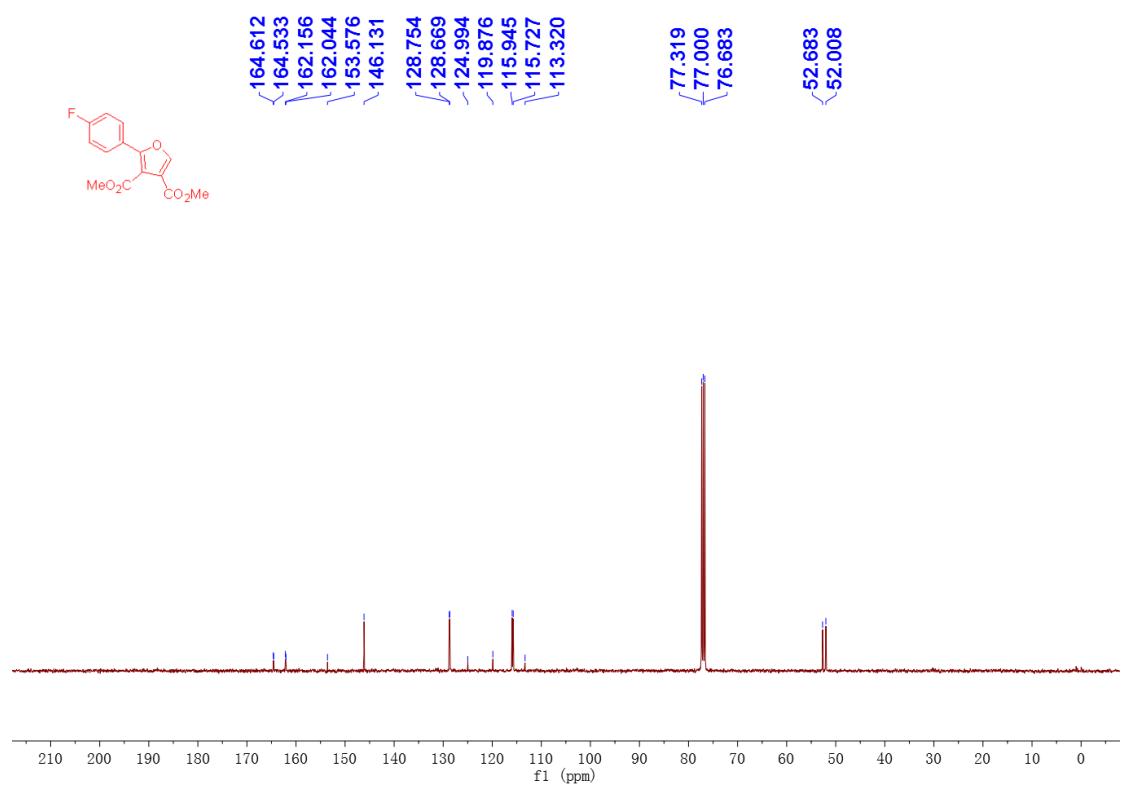
¹³C NMR (101 MHz, CDCl₃)



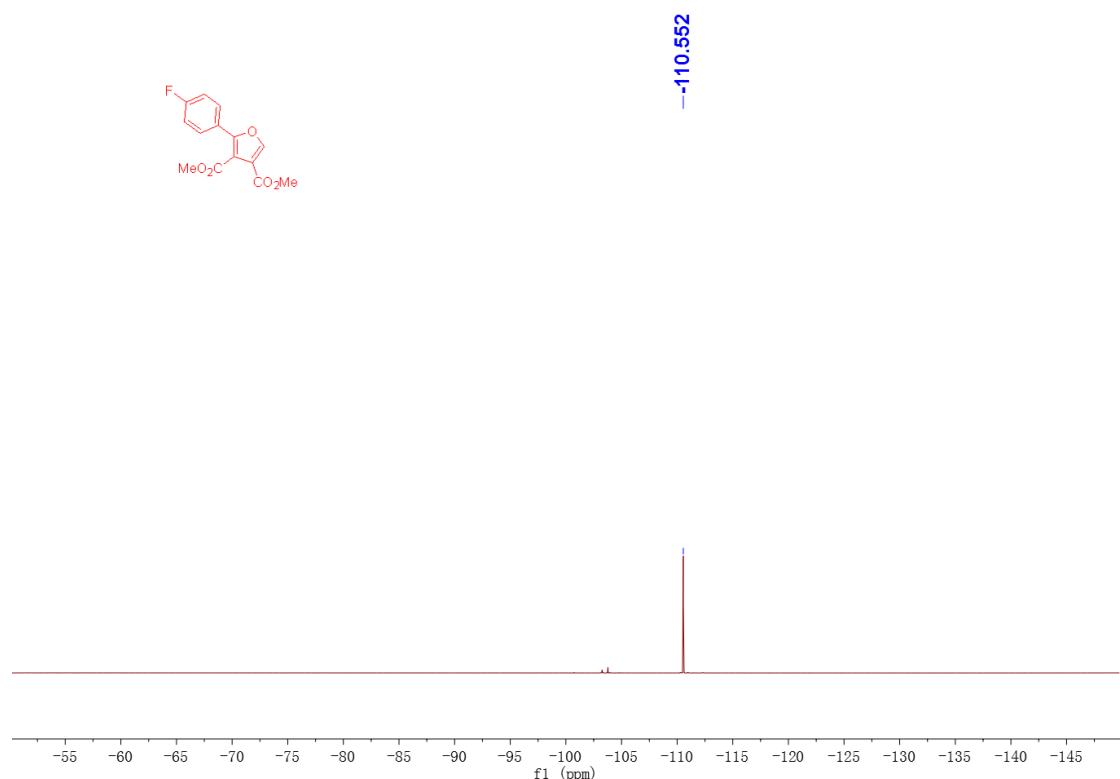
¹H NMR (400 MHz, CDCl₃) of compound **3ad**



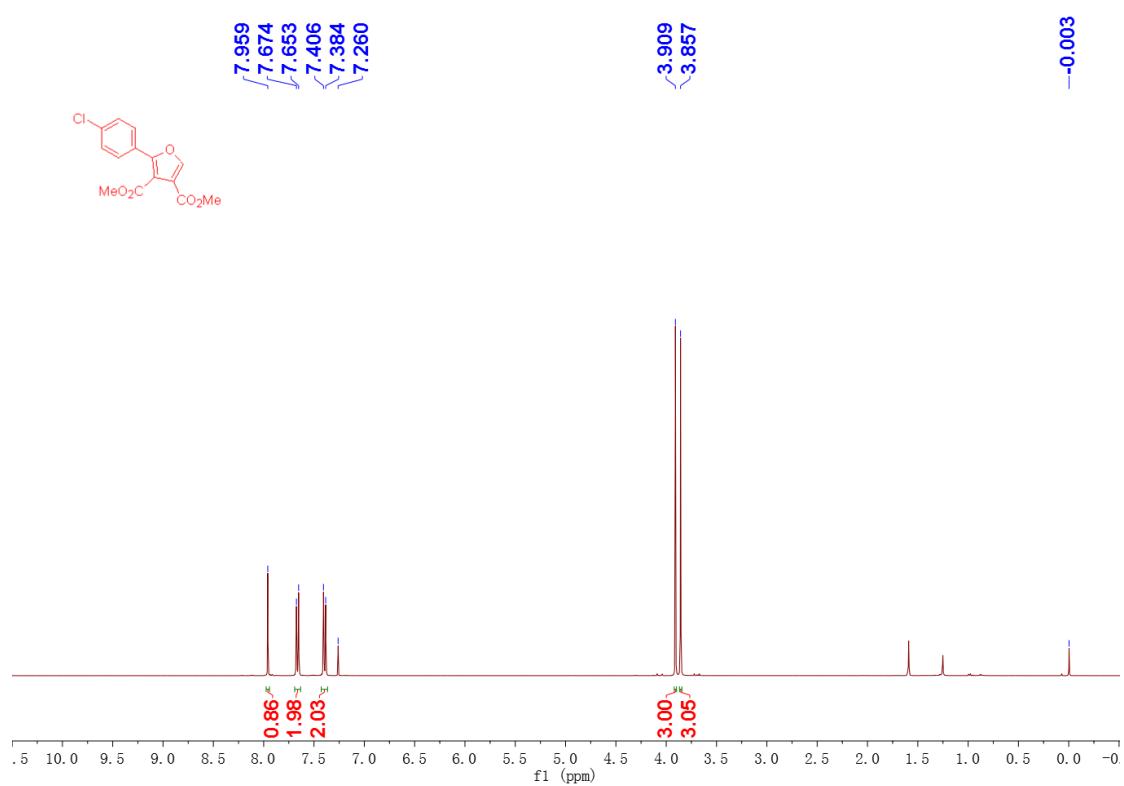
¹³C NMR (101 MHz, CDCl₃)



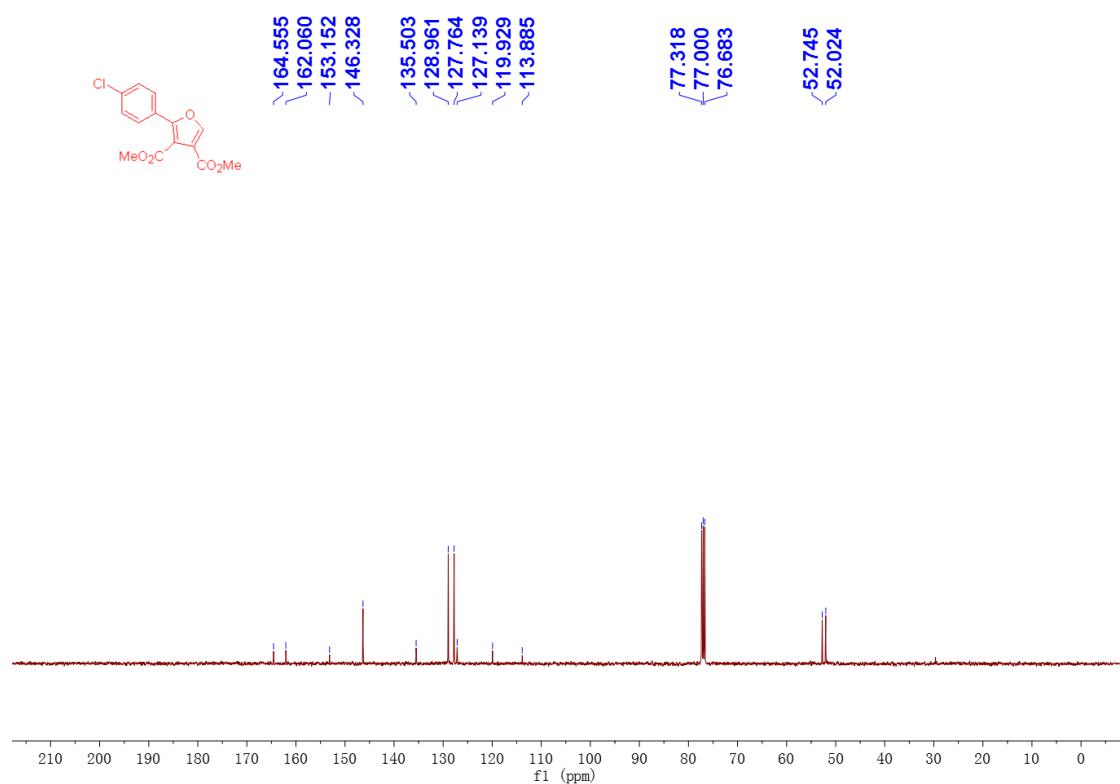
¹⁹F NMR (377 MHz, CDCl₃)



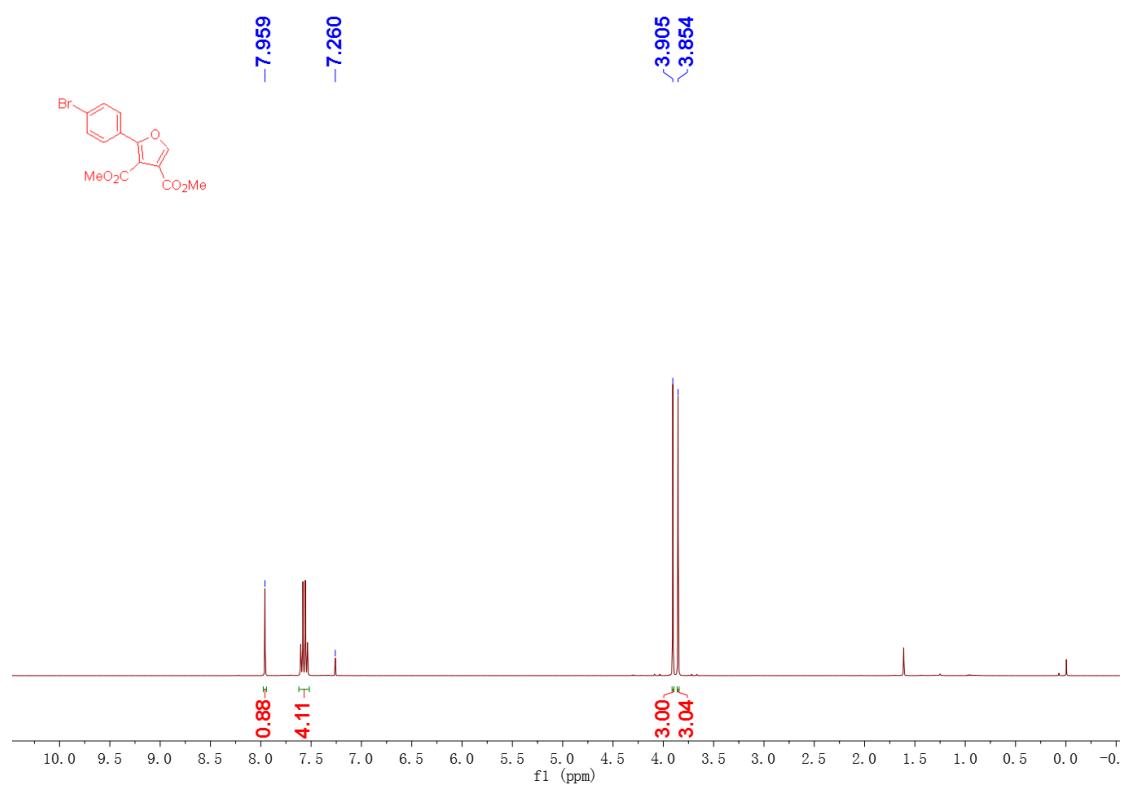
¹H NMR (400 MHz, CDCl₃) of compound 3ae



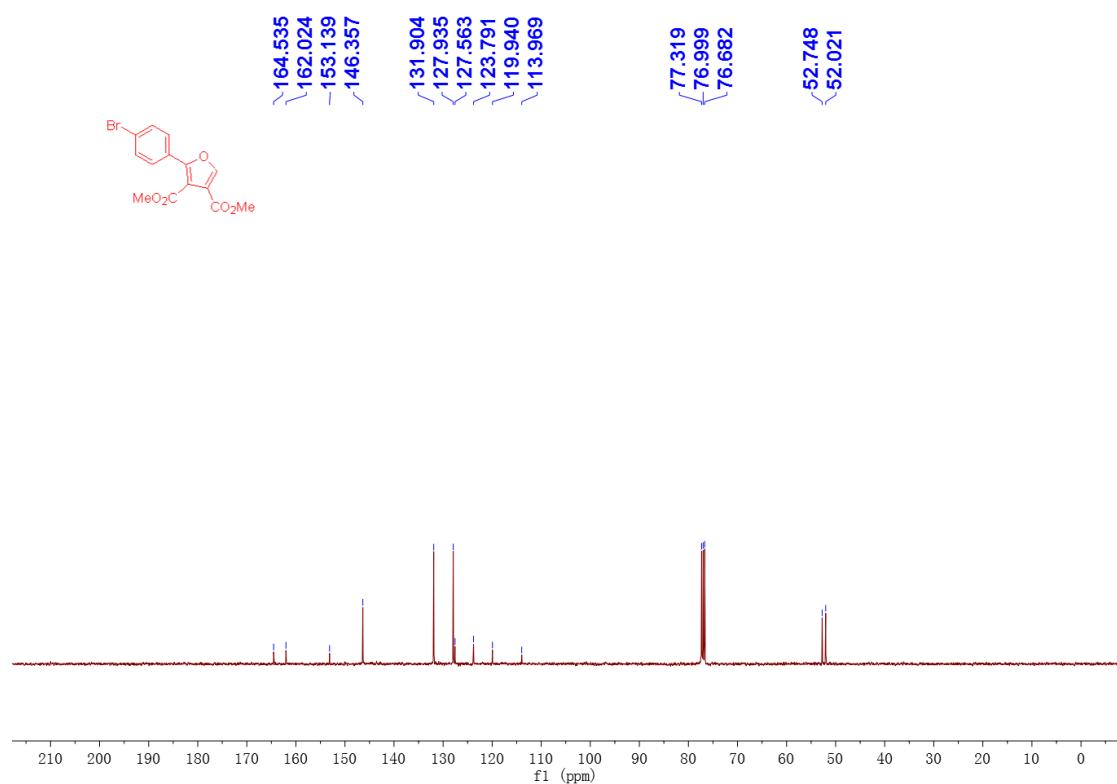
¹³C NMR (101 MHz, CDCl₃)



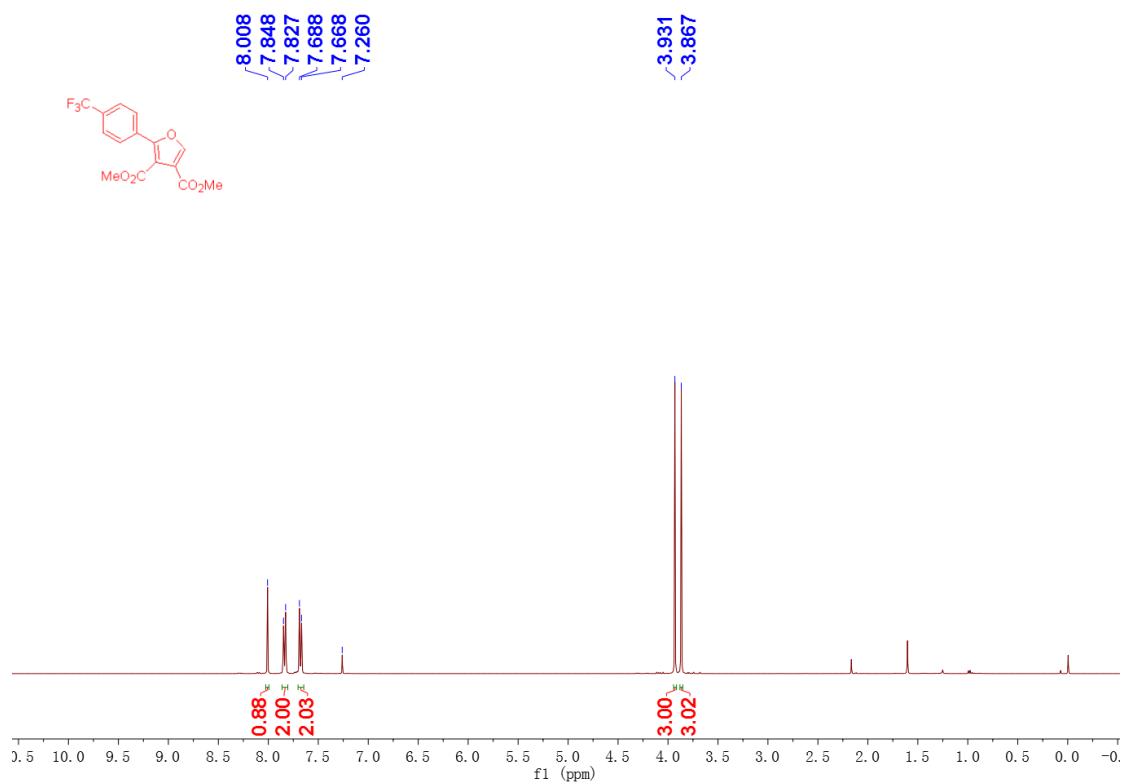
¹H NMR (400 MHz, CDCl₃) of compound 3af



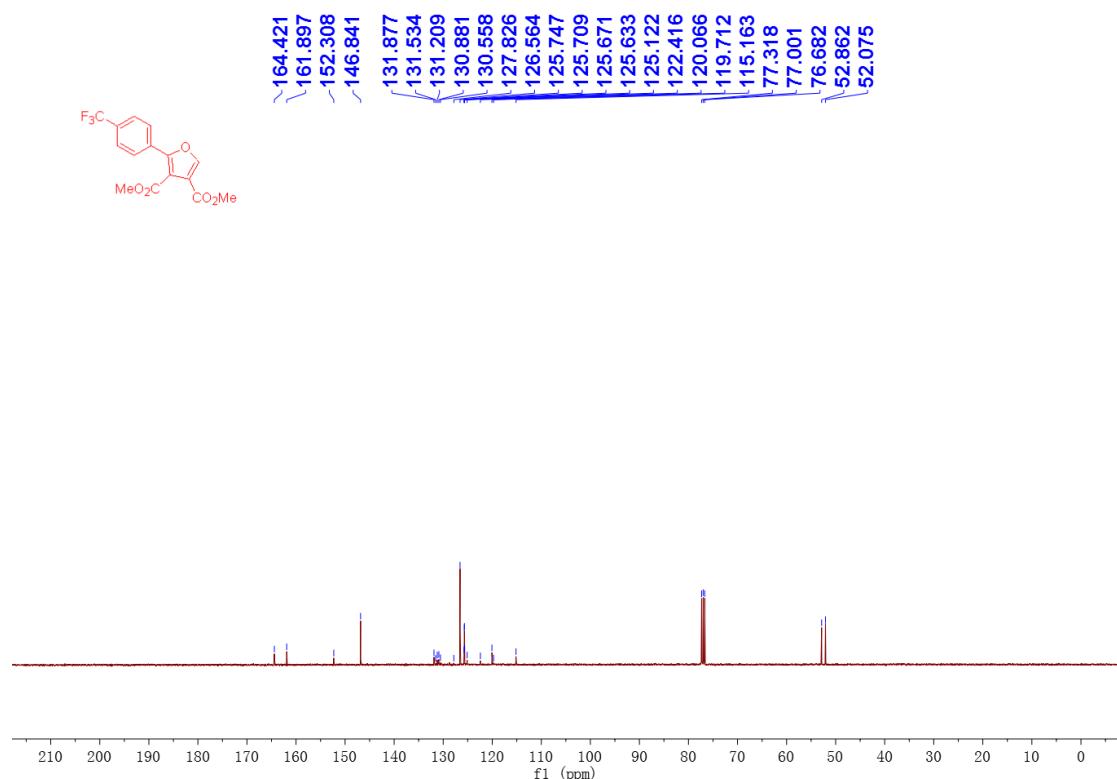
¹³C NMR (101 MHz, CDCl₃)



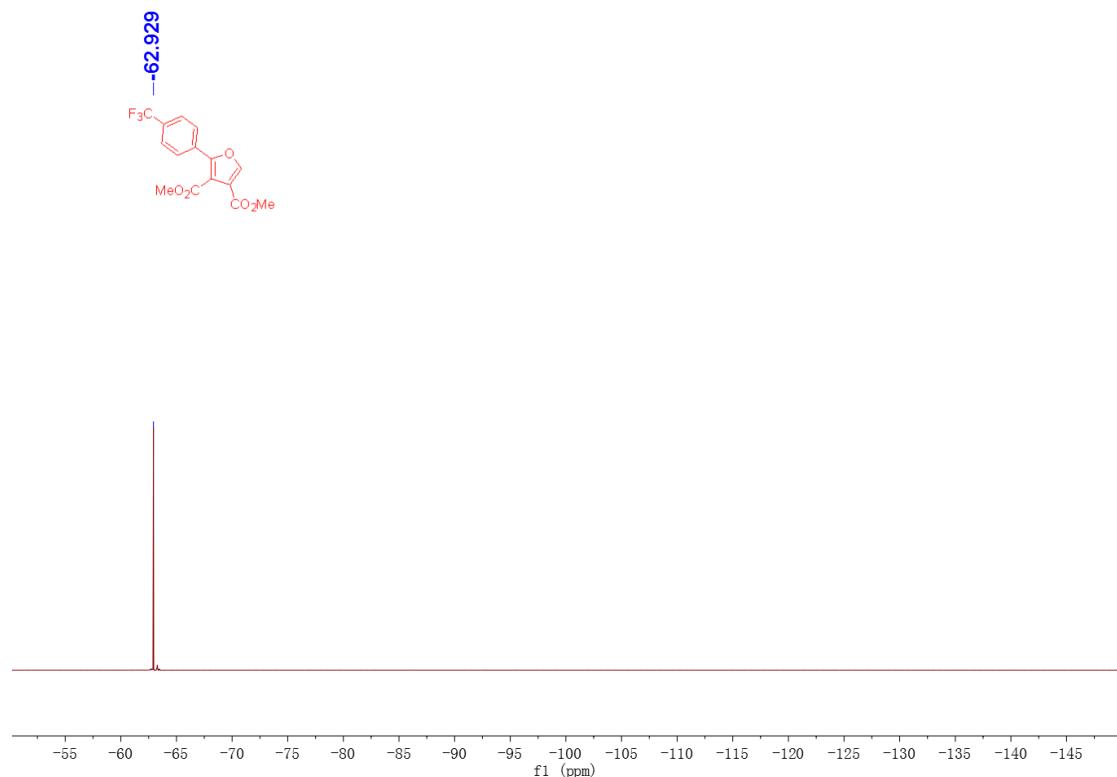
¹H NMR (400 MHz, CDCl₃) of compound 3ag



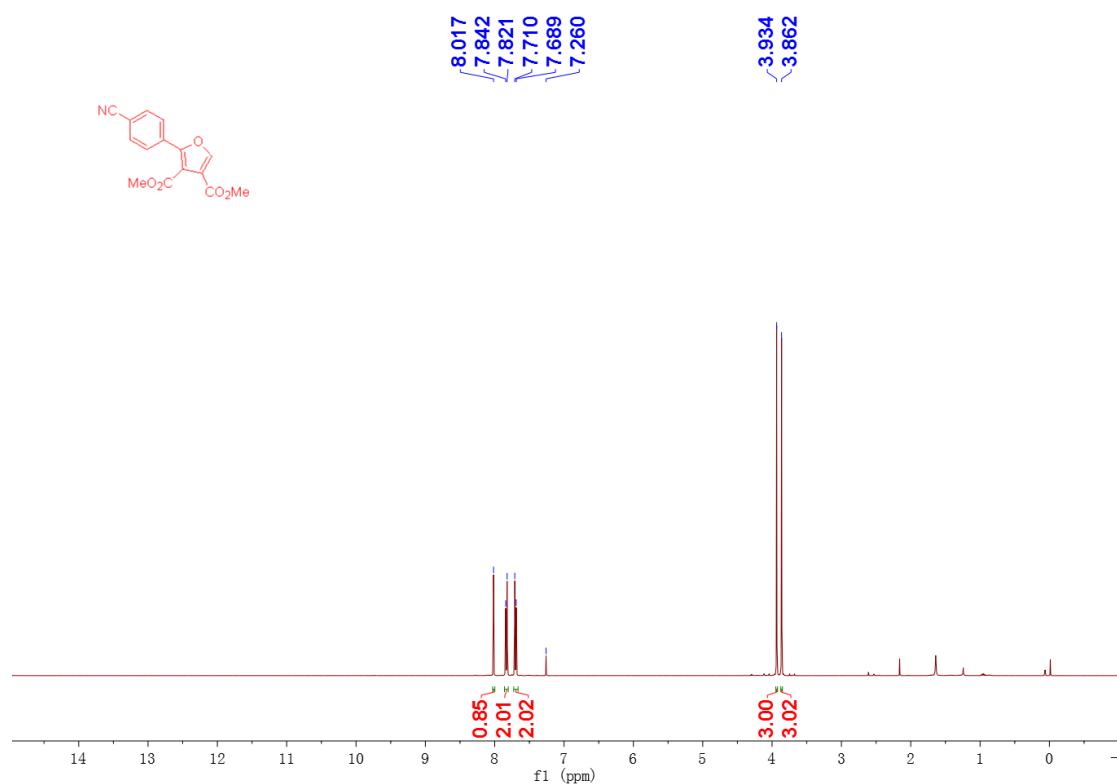
¹³C NMR (101 MHz, CDCl₃)



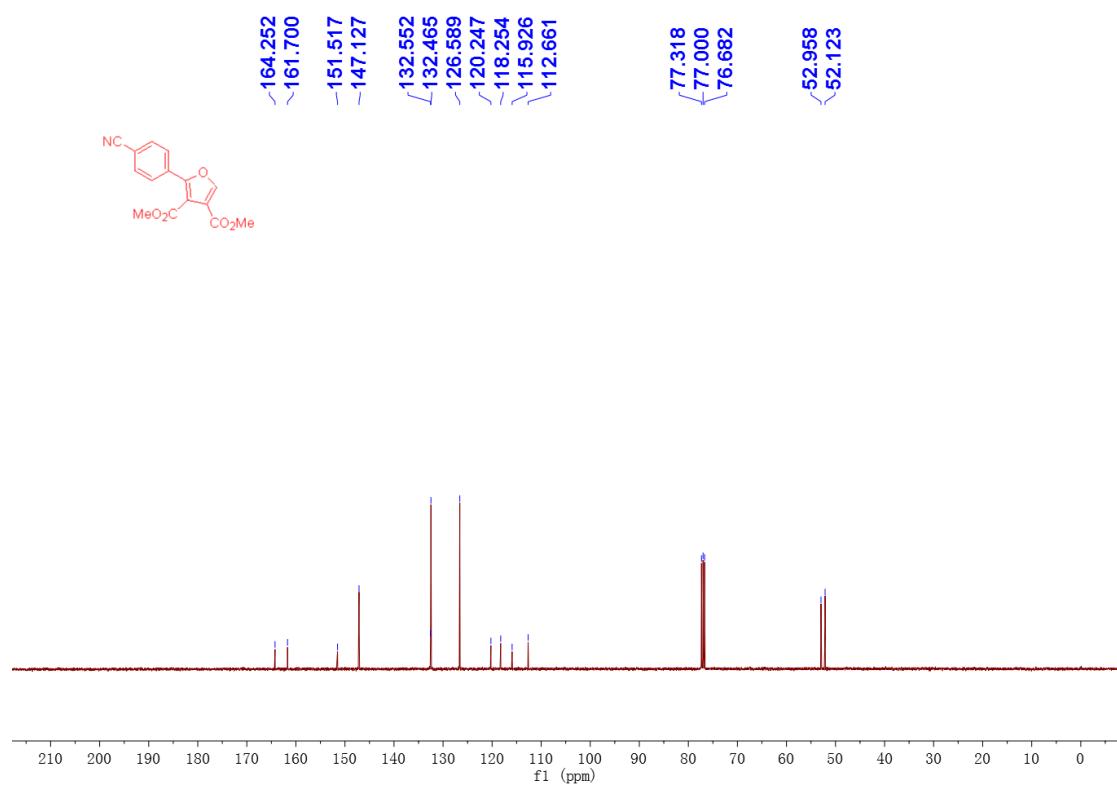
¹⁹F NMR (377 MHz, CDCl₃)



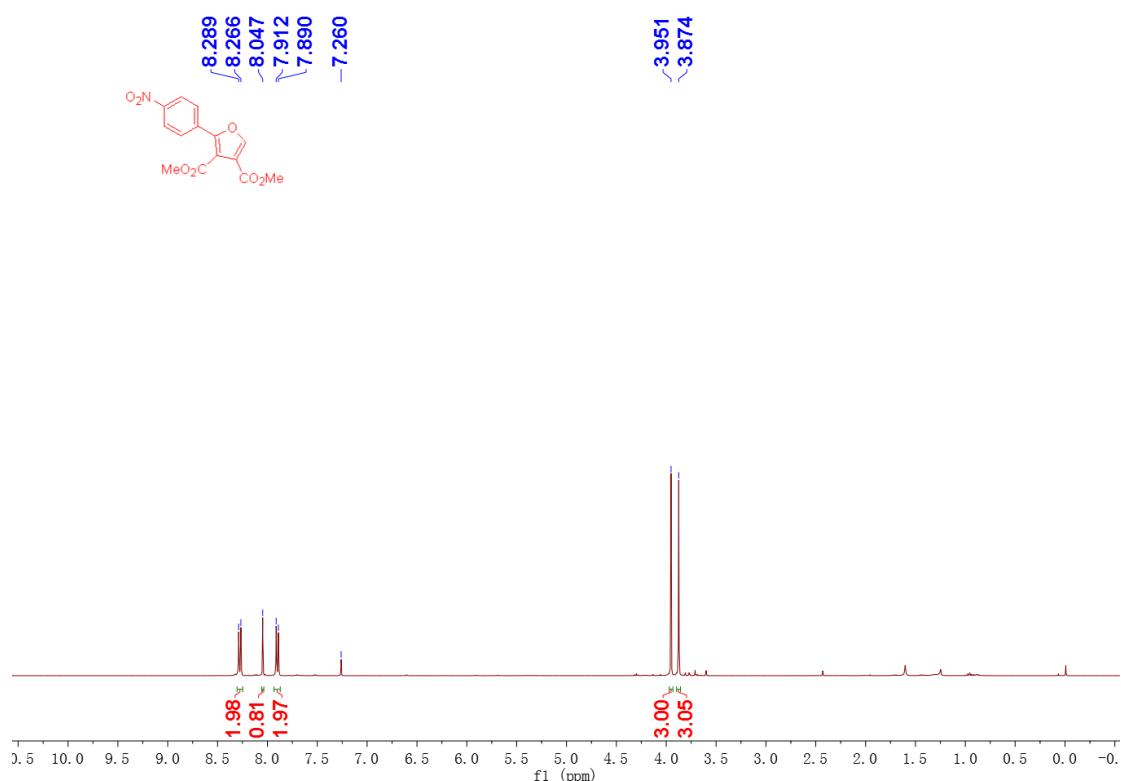
¹H NMR (400 MHz, CDCl₃) of compound **3ah**



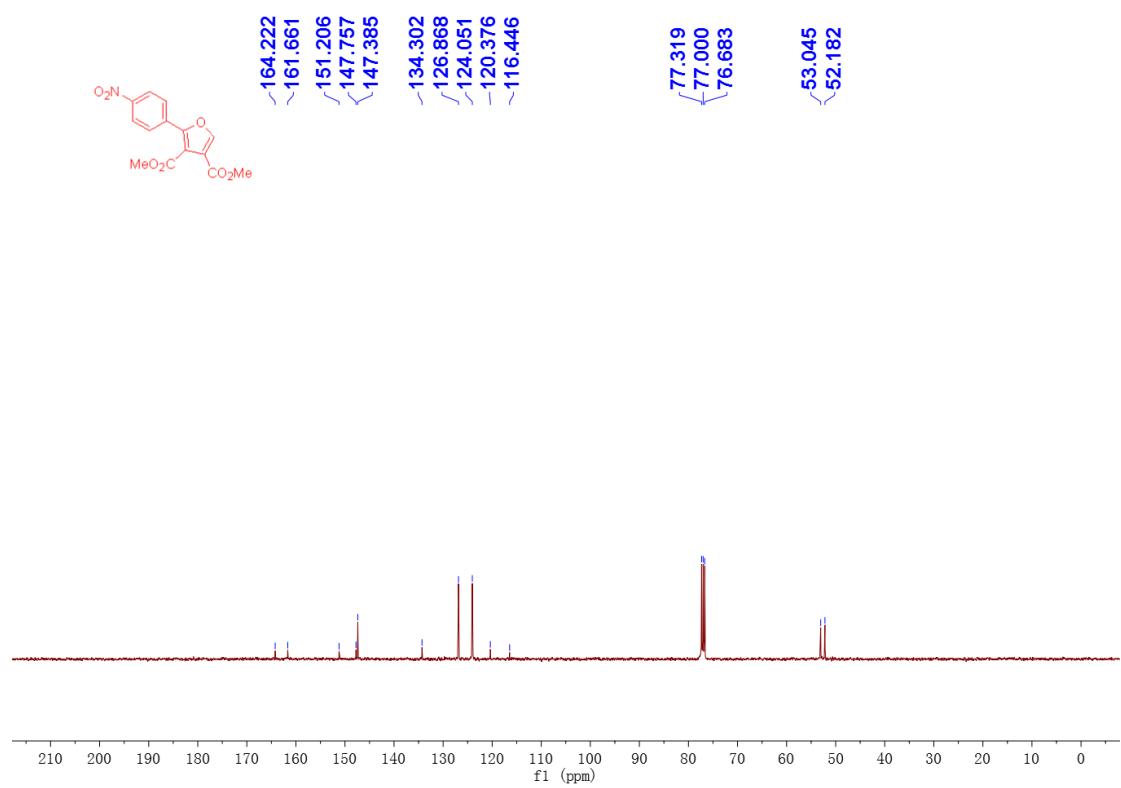
¹³C NMR (101 MHz, CDCl₃)



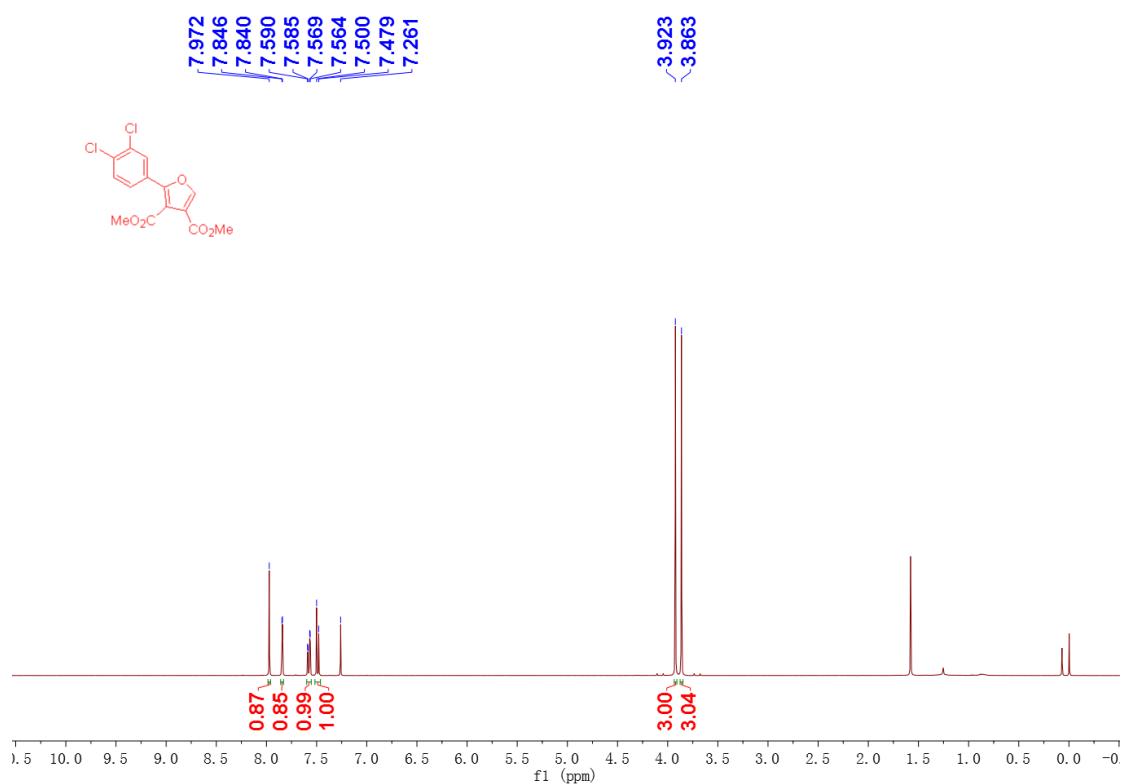
¹H NMR (400 MHz, CDCl₃) of compound 3ai



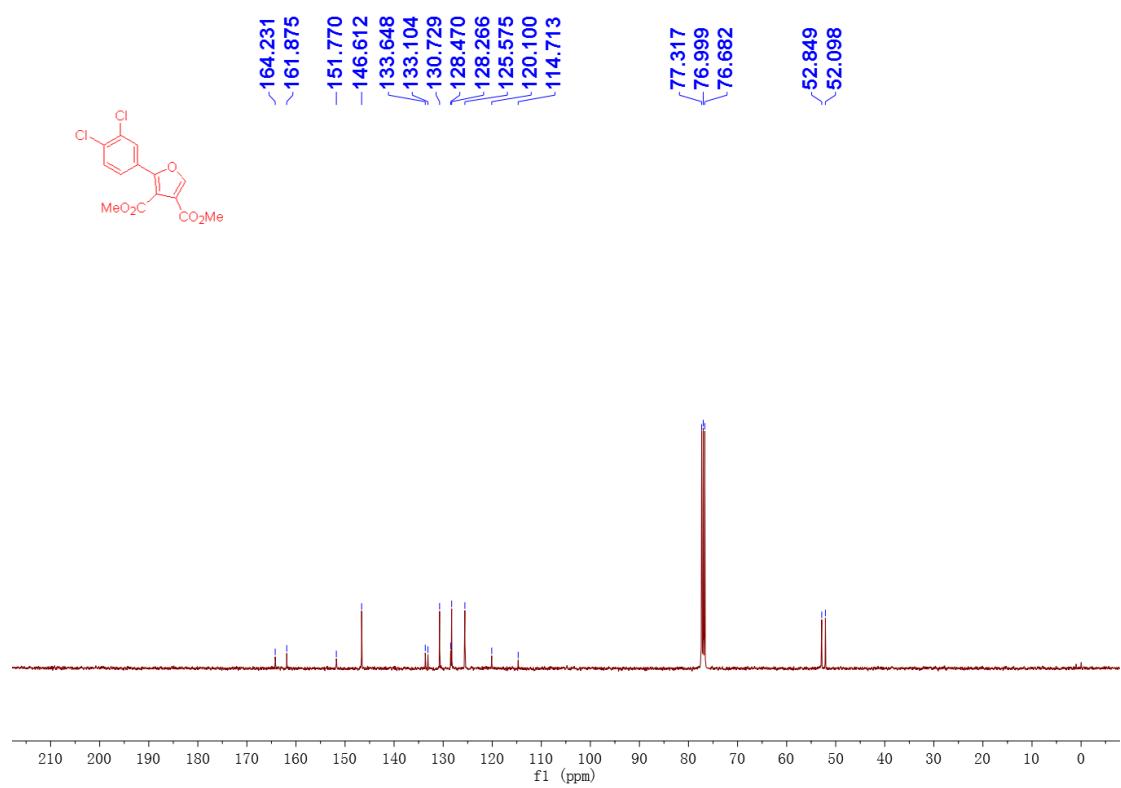
¹³C NMR (101 MHz, CDCl₃)



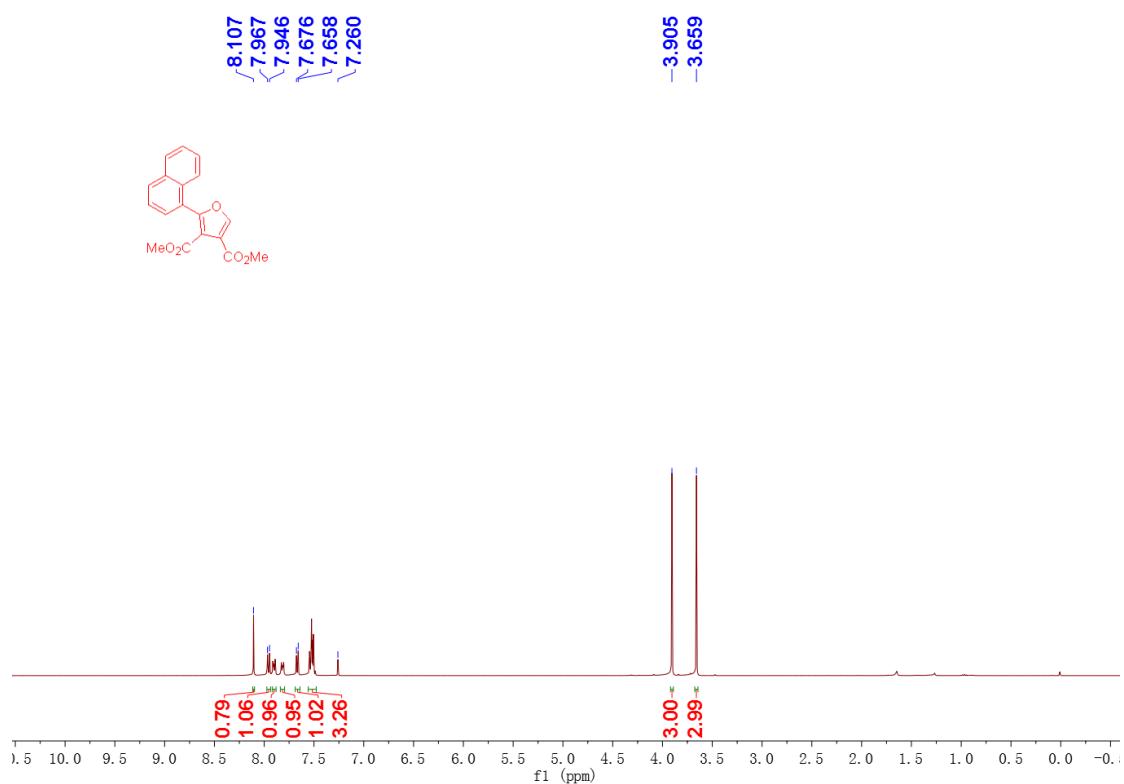
¹H NMR (400 MHz, CDCl₃) of compound 3aj



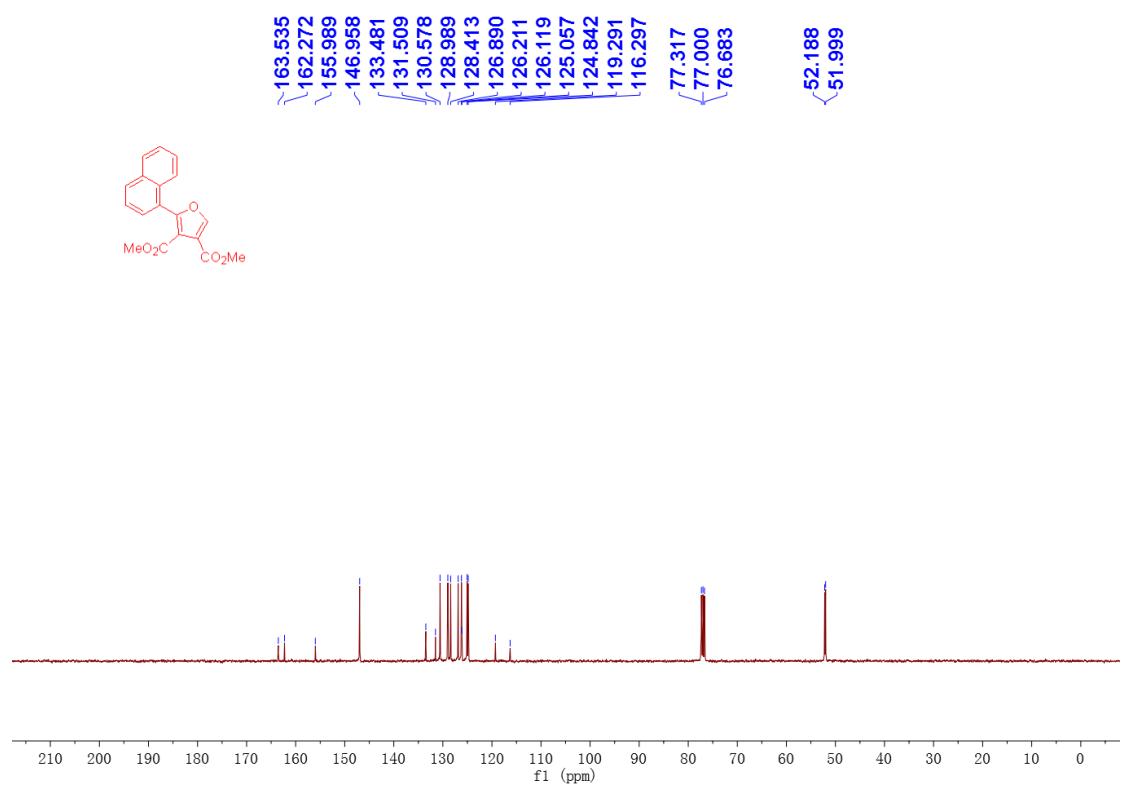
¹³C NMR (101 MHz, CDCl₃)



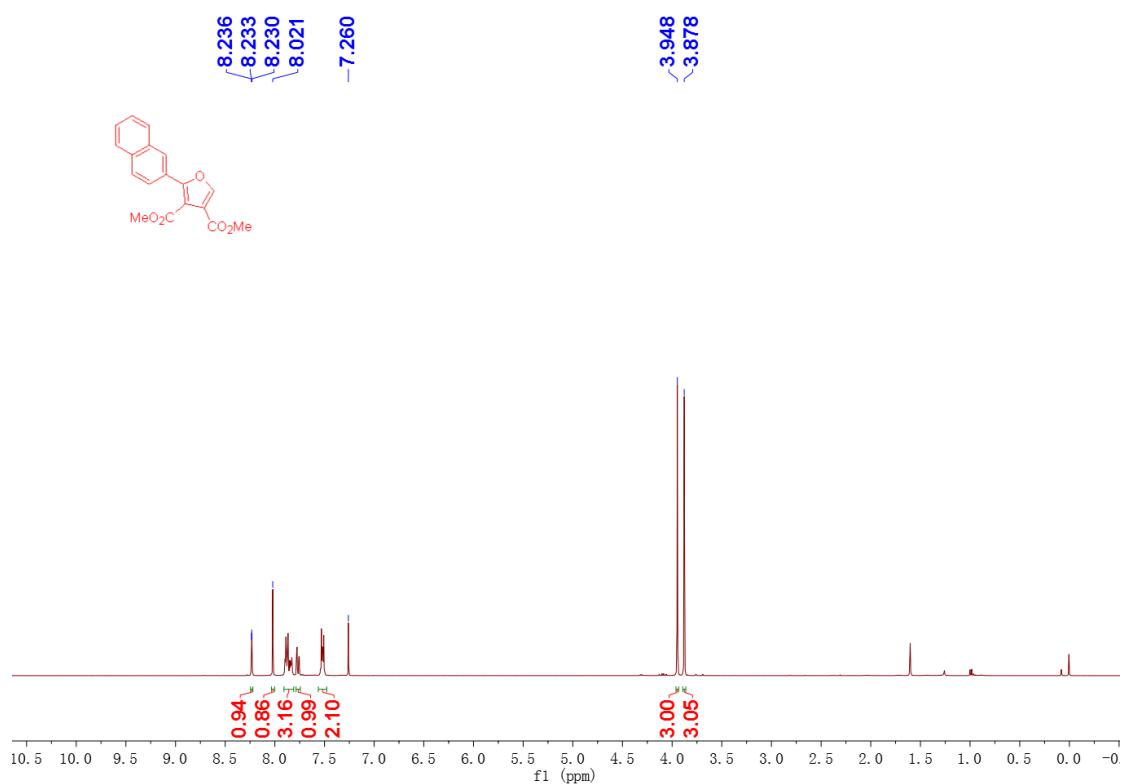
¹H NMR (400 MHz, CDCl₃) of compound 3ak



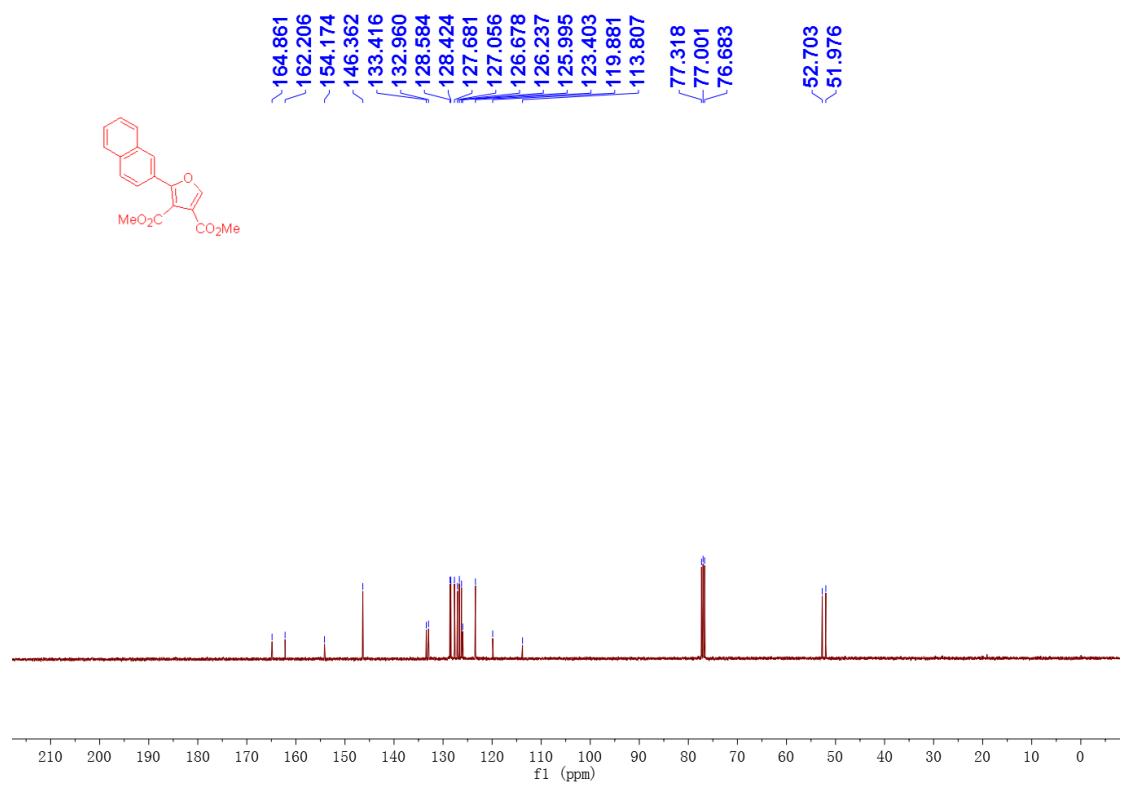
¹³C NMR (101 MHz, CDCl₃)



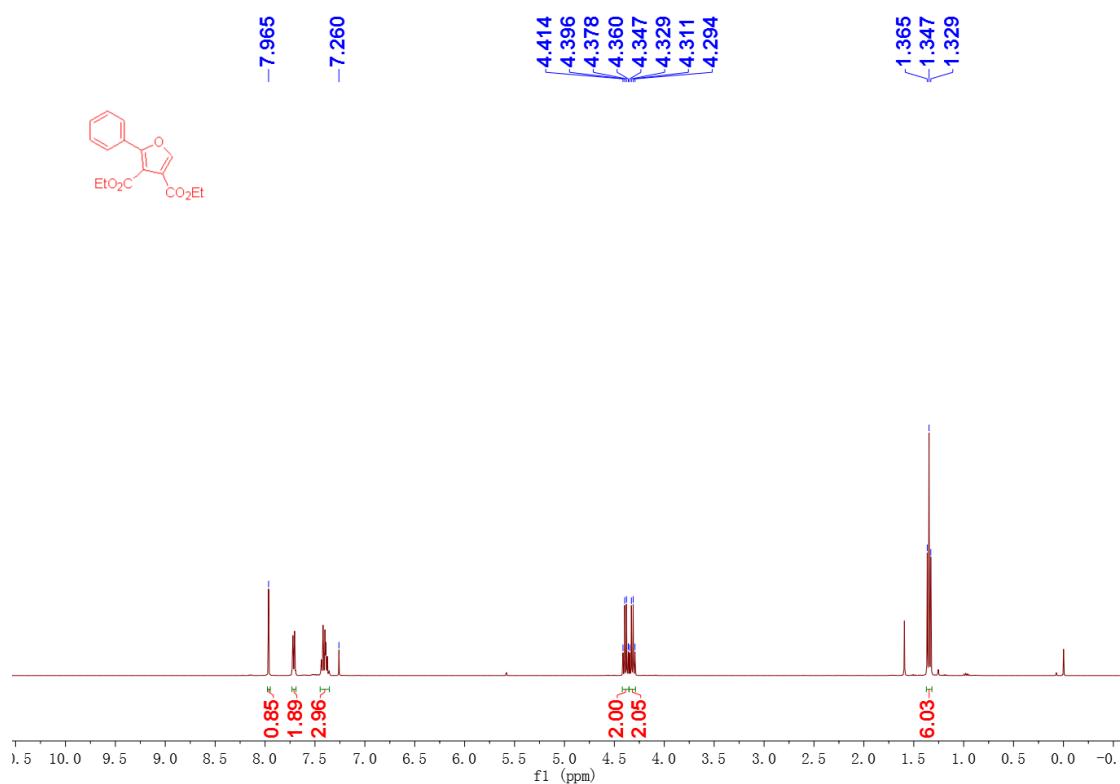
¹H NMR (400 MHz, CDCl₃) of compound 3al



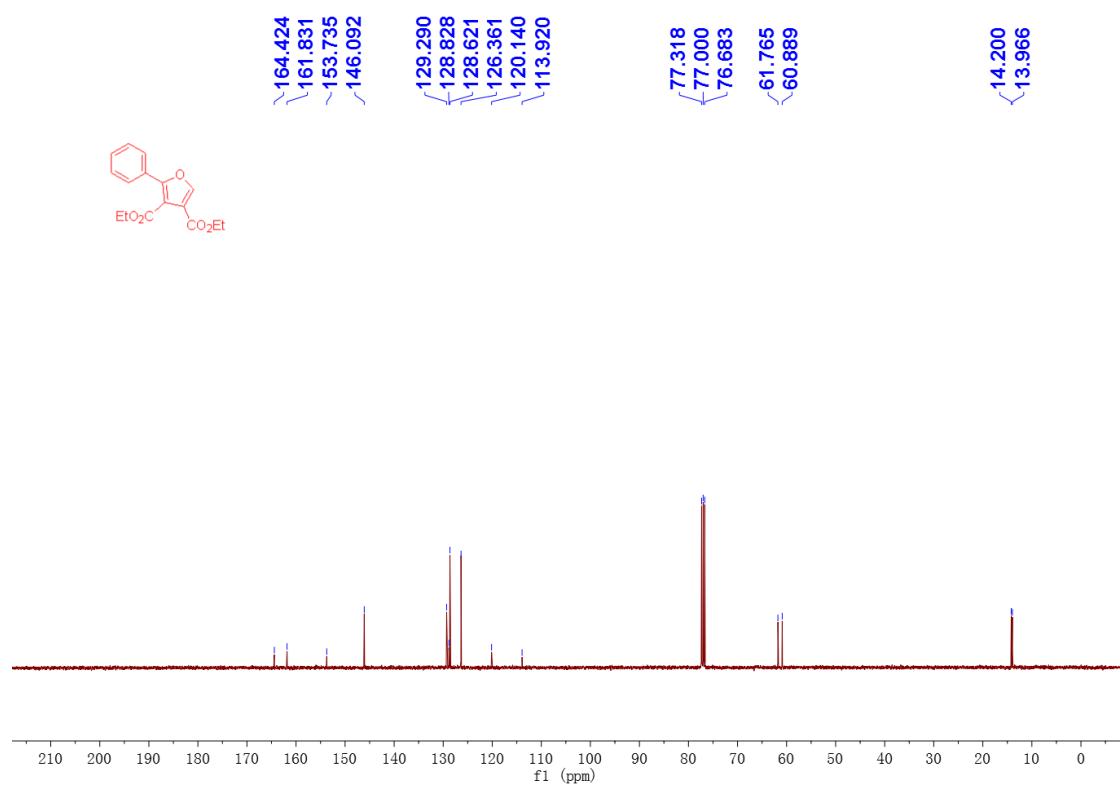
¹³C NMR (101 MHz, CDCl₃)



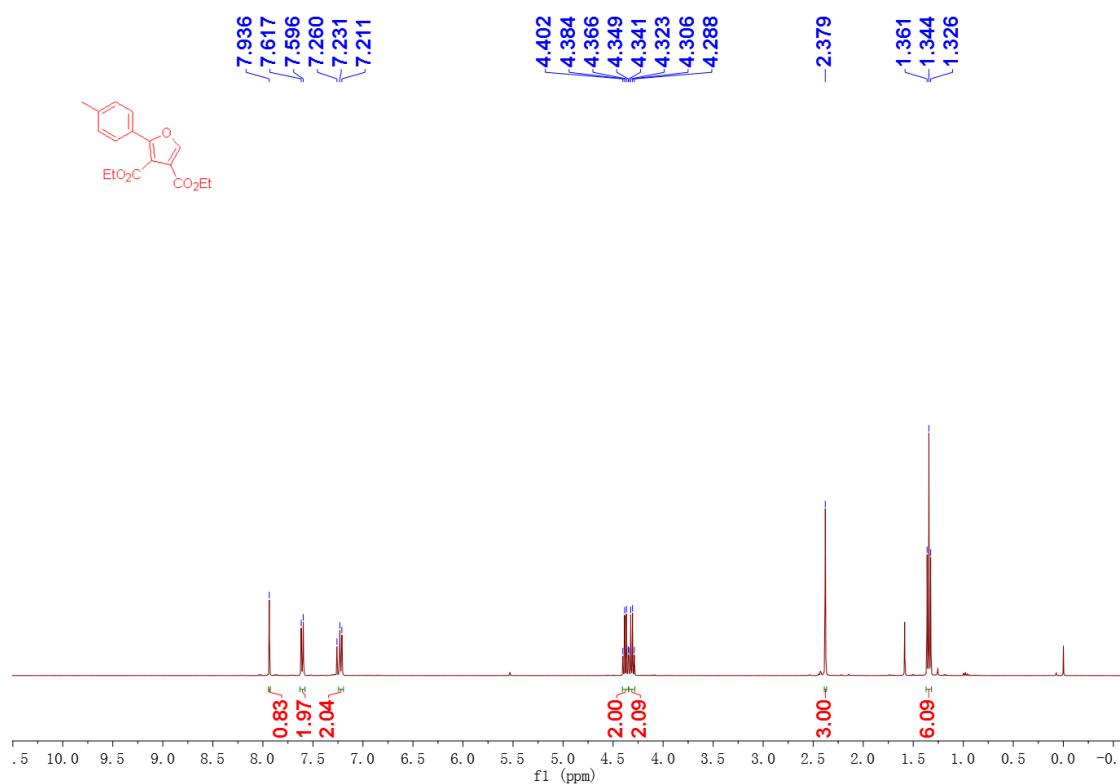
¹H NMR (400 MHz, CDCl₃) of compound **3ba**



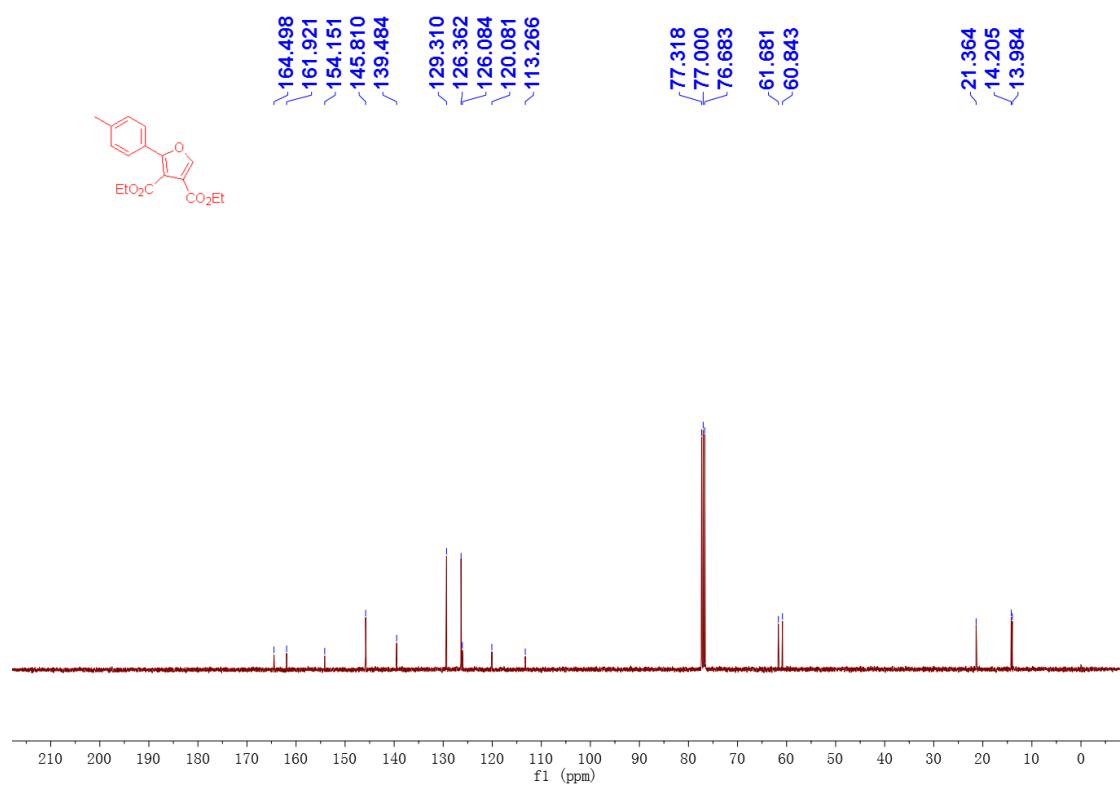
¹³C NMR (101 MHz, CDCl₃)



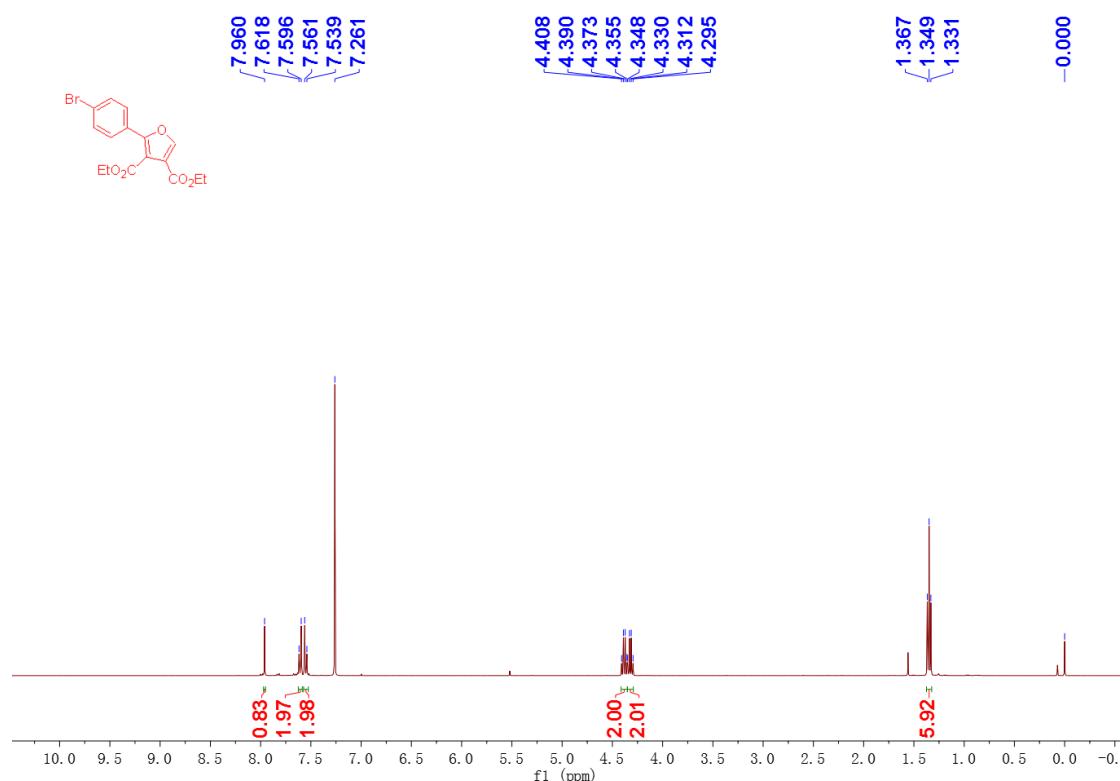
¹H NMR (400 MHz, CDCl₃) of compound **3bb**



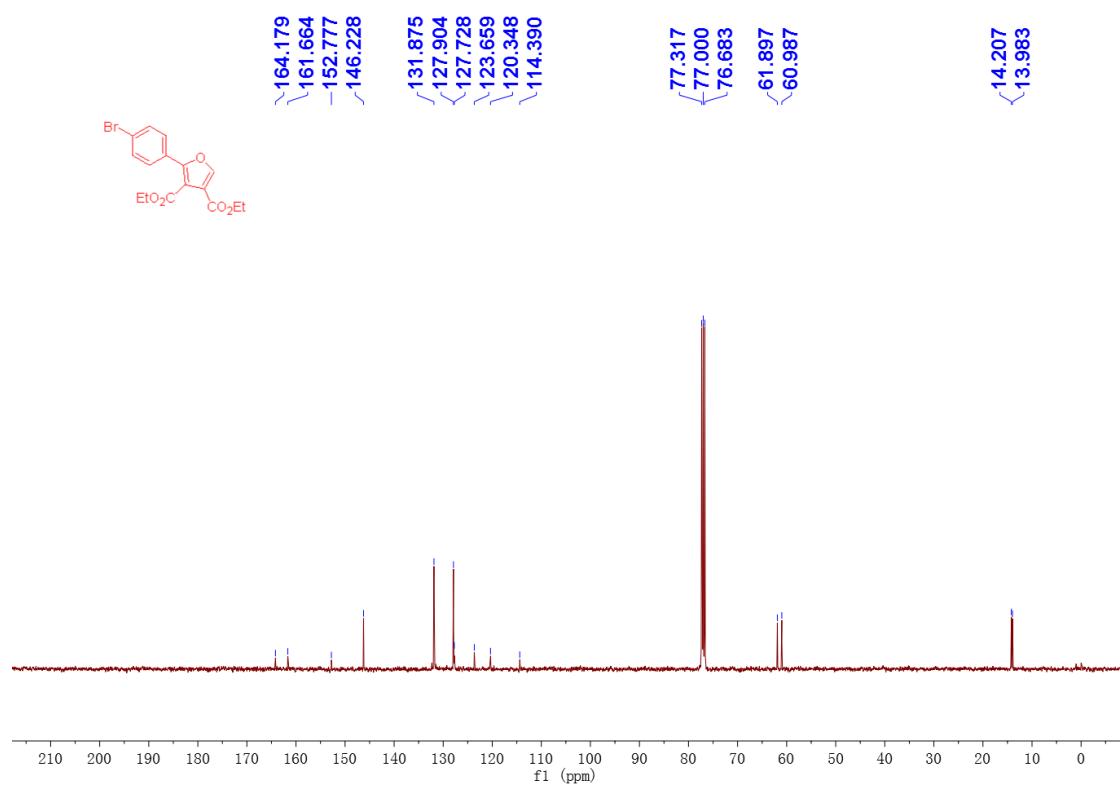
¹³C NMR (101 MHz, CDCl₃)



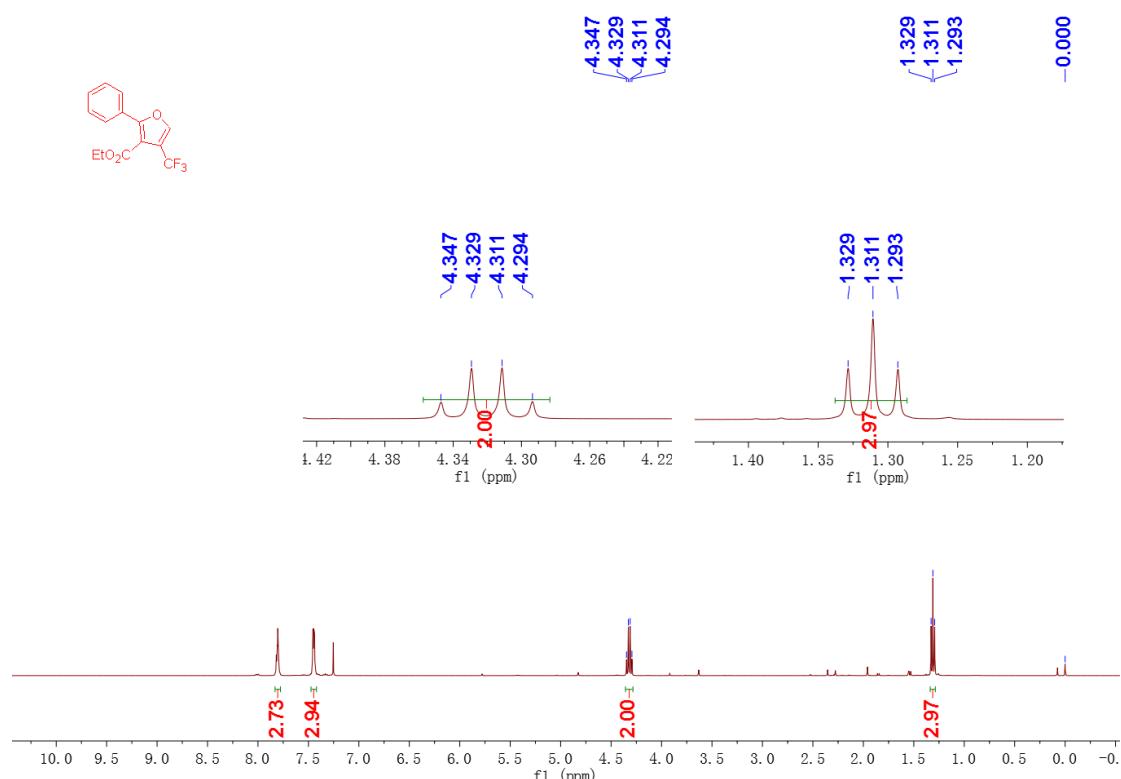
¹H NMR (400 MHz, CDCl₃) of compound **3bf**



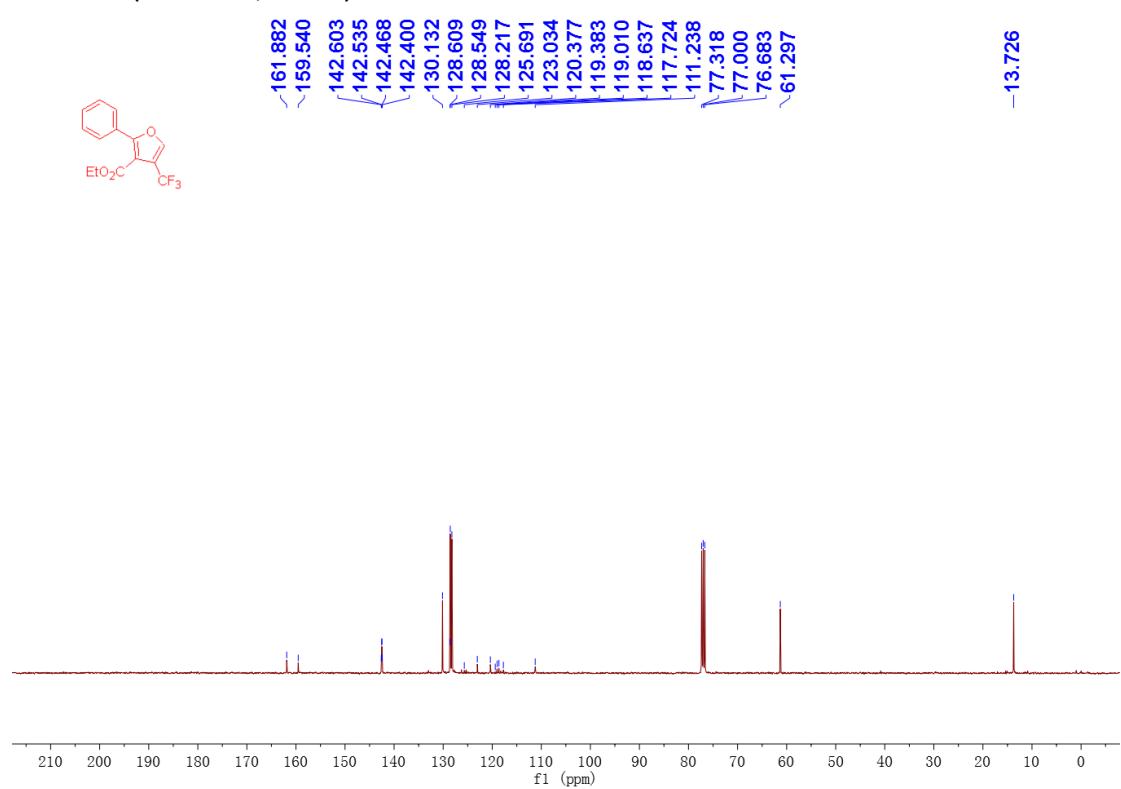
¹³C NMR (101 MHz, CDCl₃)



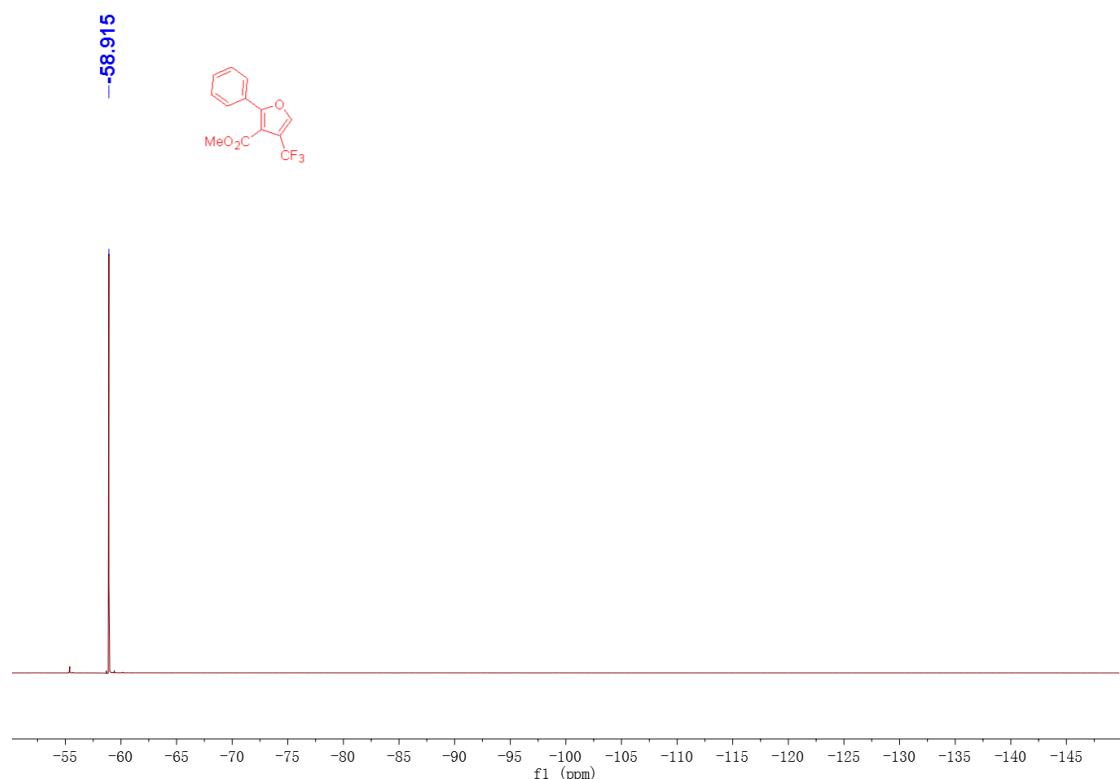
¹H NMR (400 MHz, CDCl₃) of compound 3ca



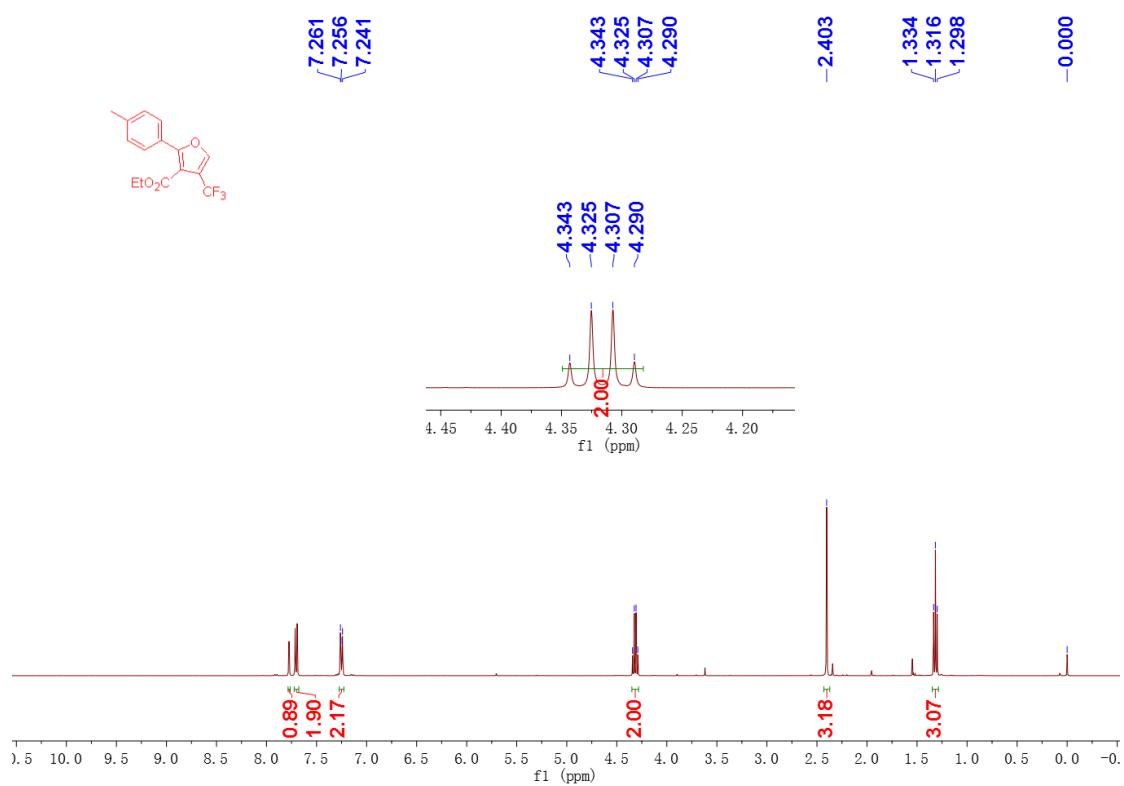
¹³C NMR (101 MHz, CDCl₃)



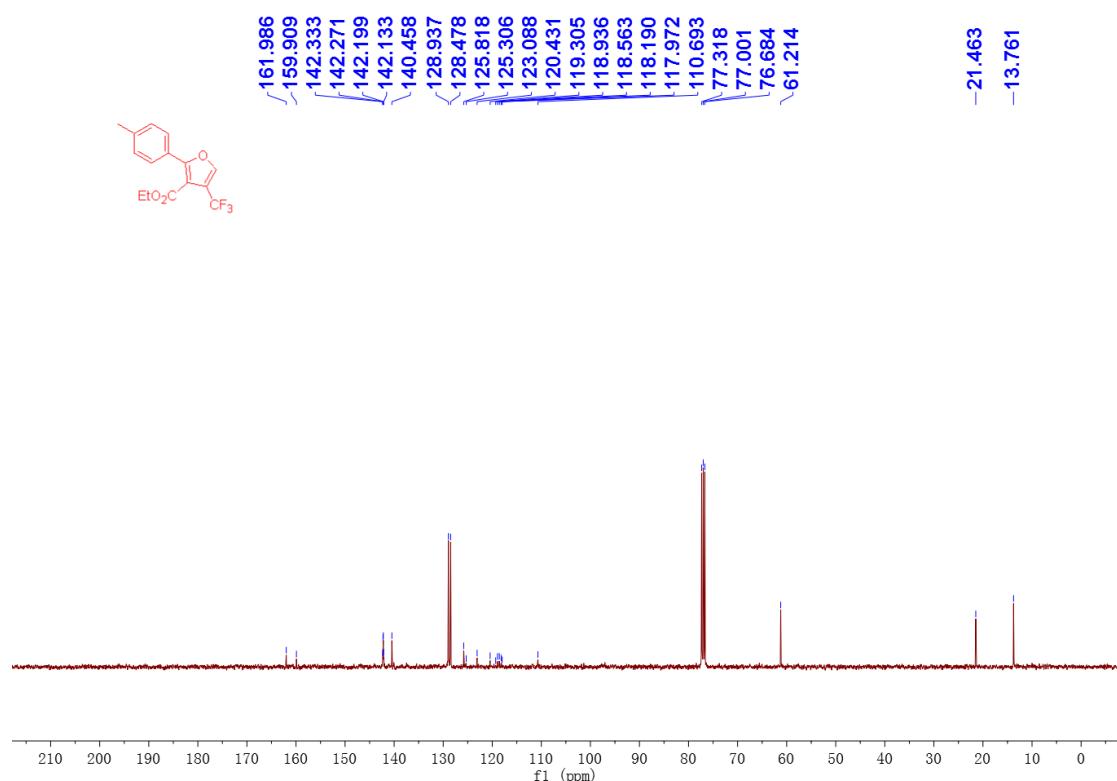
¹⁹F NMR (376 MHz, CDCl₃)



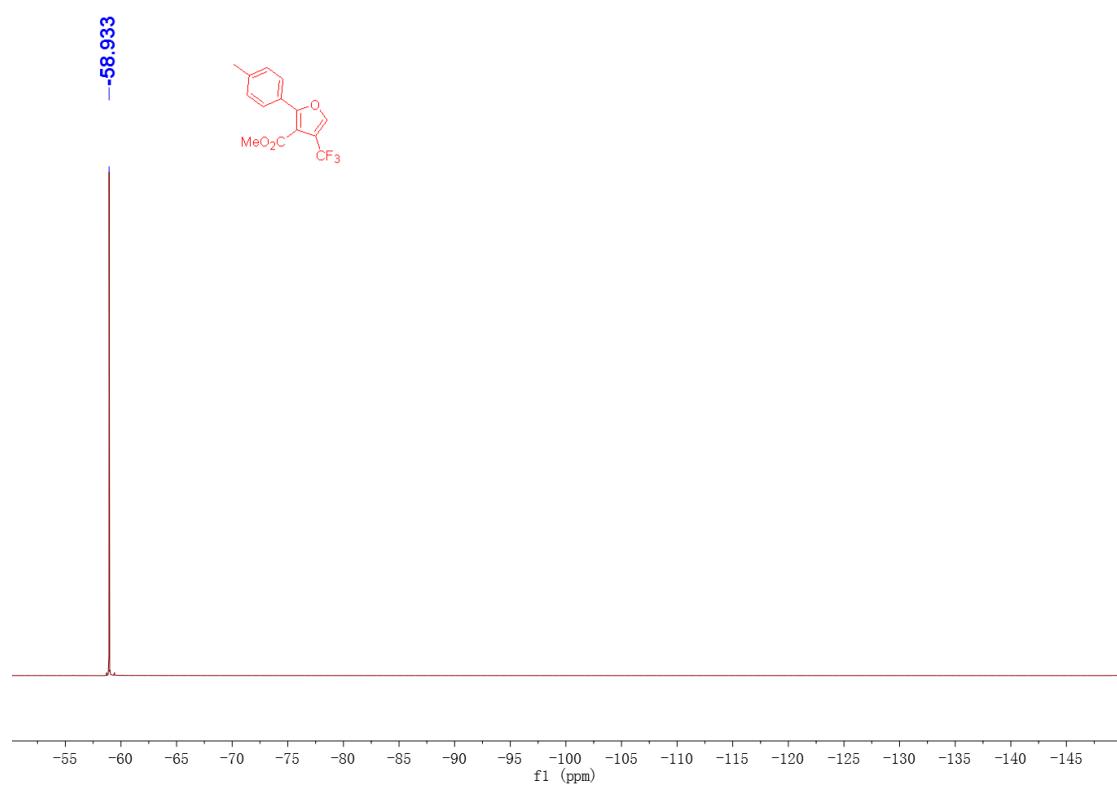
¹H NMR (400 MHz, CDCl₃) of compound 3cb



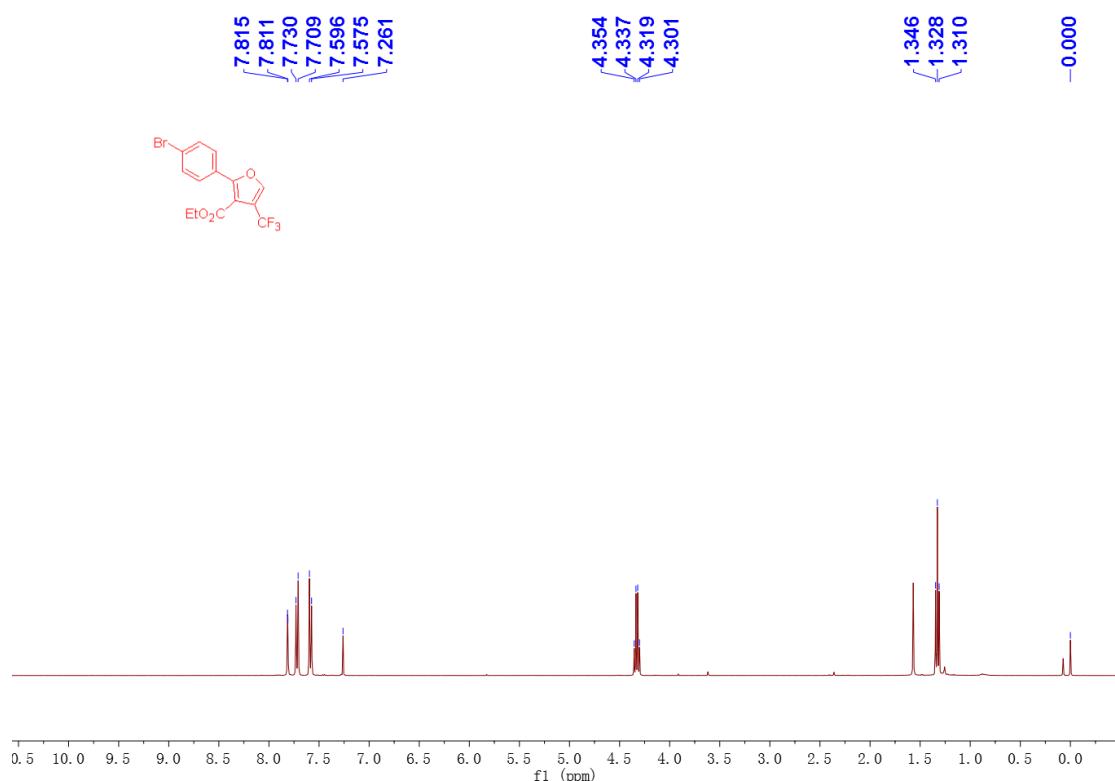
¹³C NMR (101 MHz, CDCl₃)



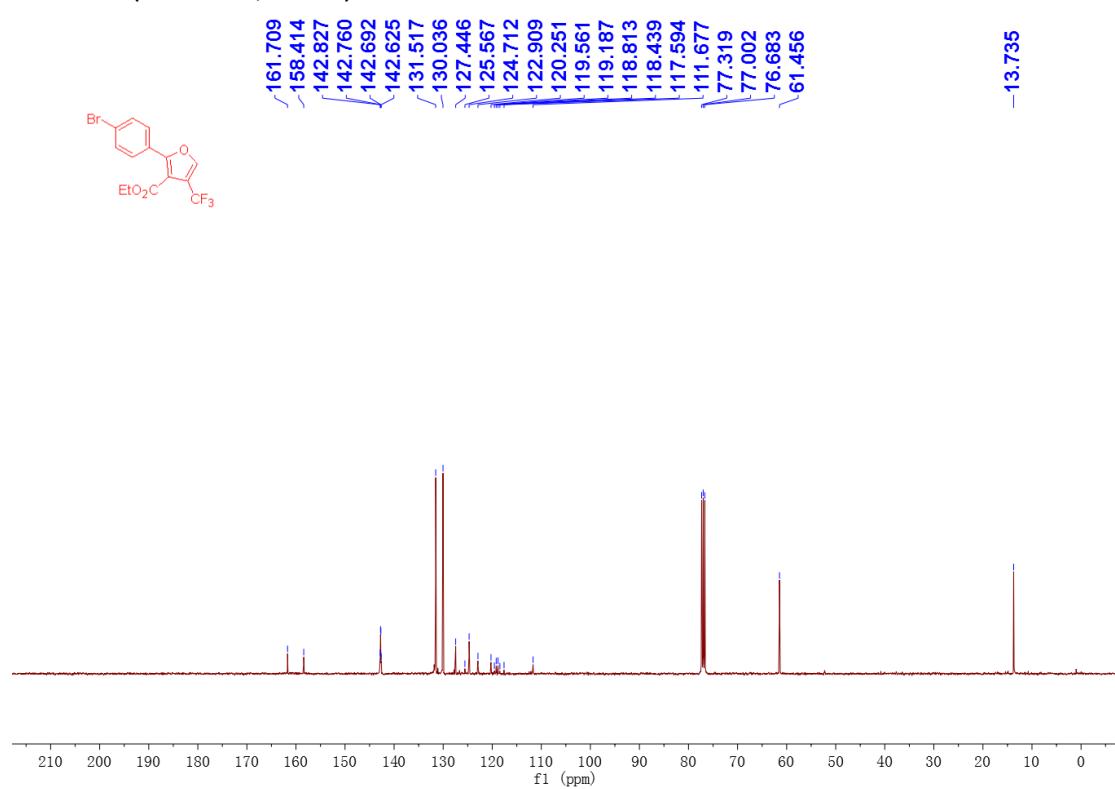
¹⁹F NMR (376 MHz, CDCl₃)



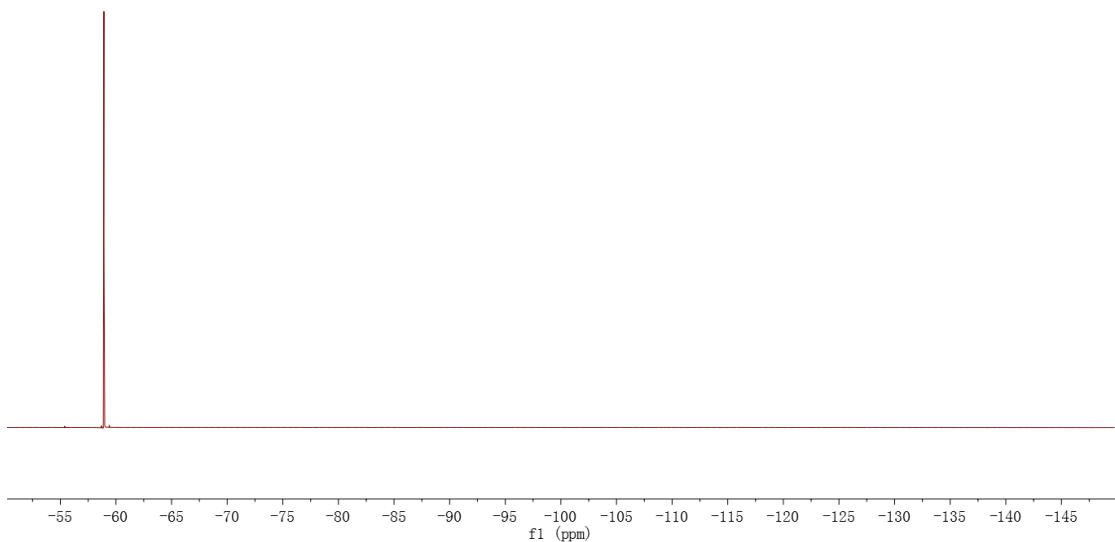
¹H NMR (400 MHz, CDCl₃) of compound 3cf



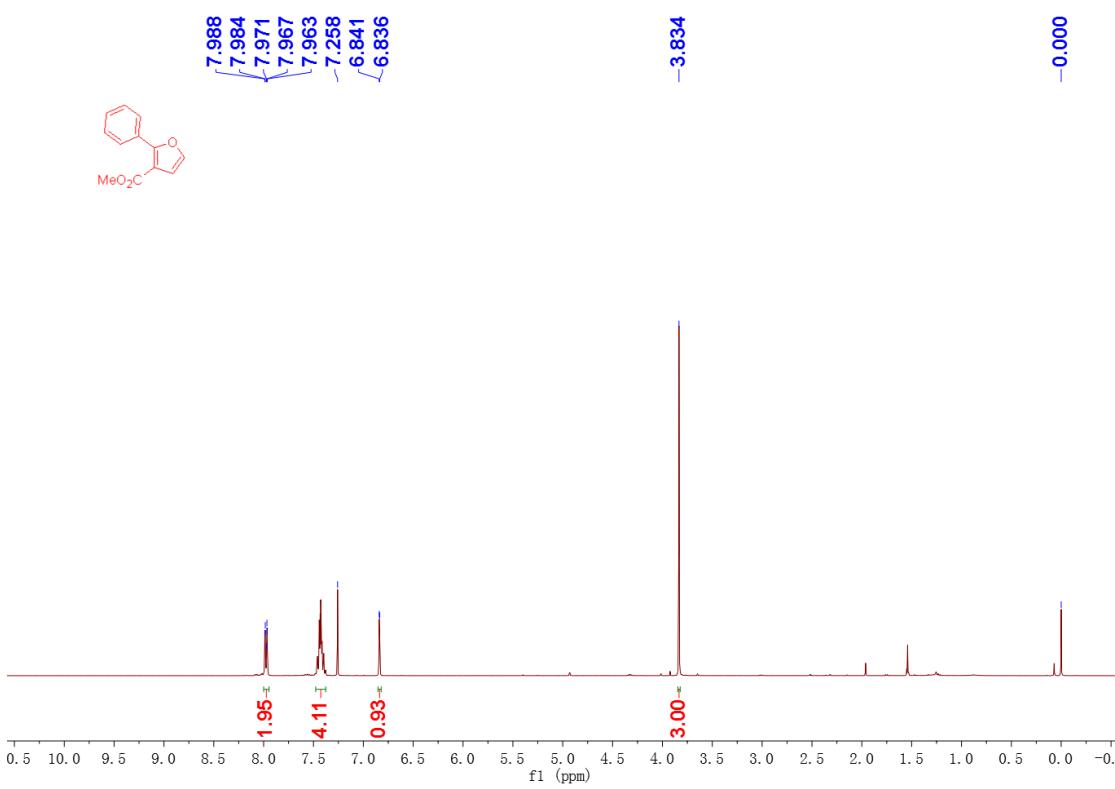
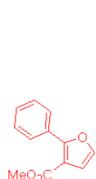
¹³C NMR (101 MHz, CDCl₃)



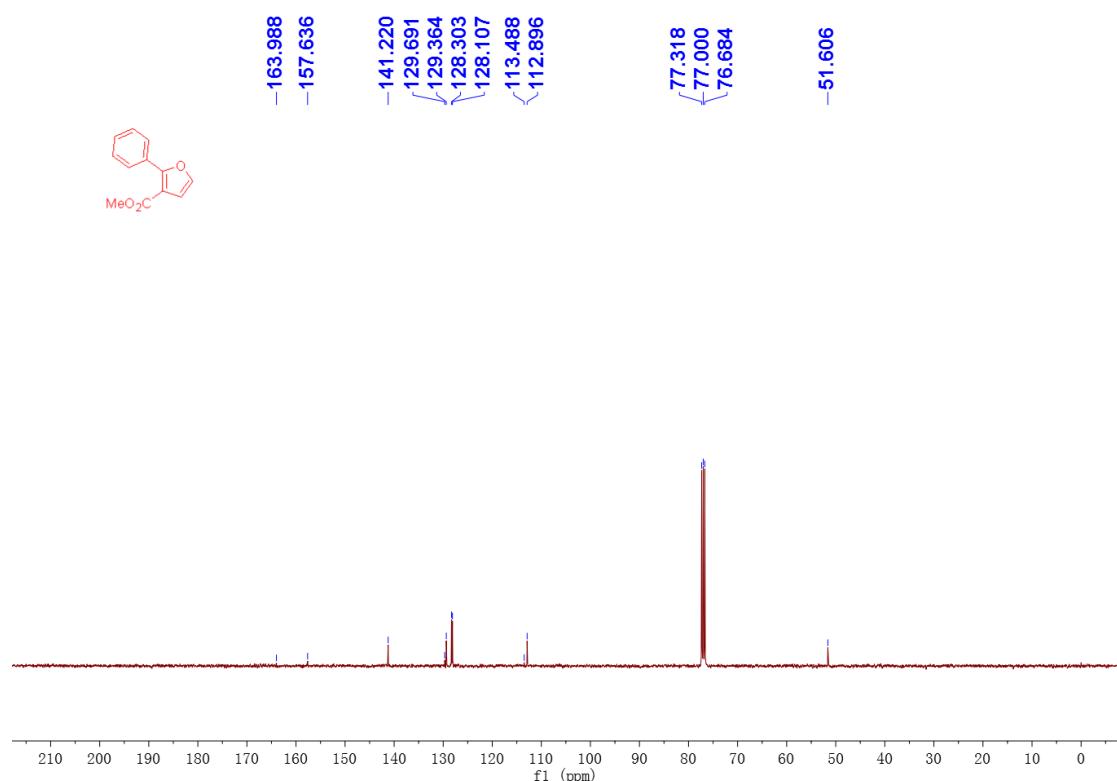
¹⁹F NMR (376 MHz, CDCl₃)



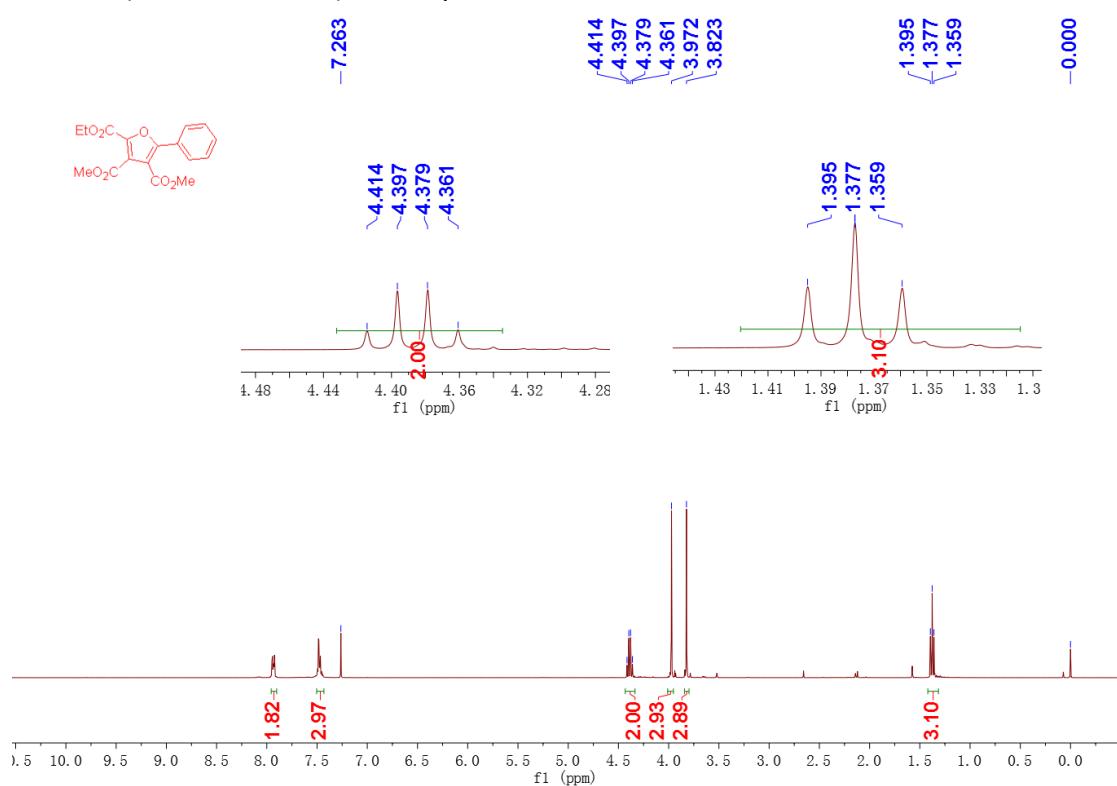
¹H NMR (400 MHz, CDCl₃) of compound **3da**



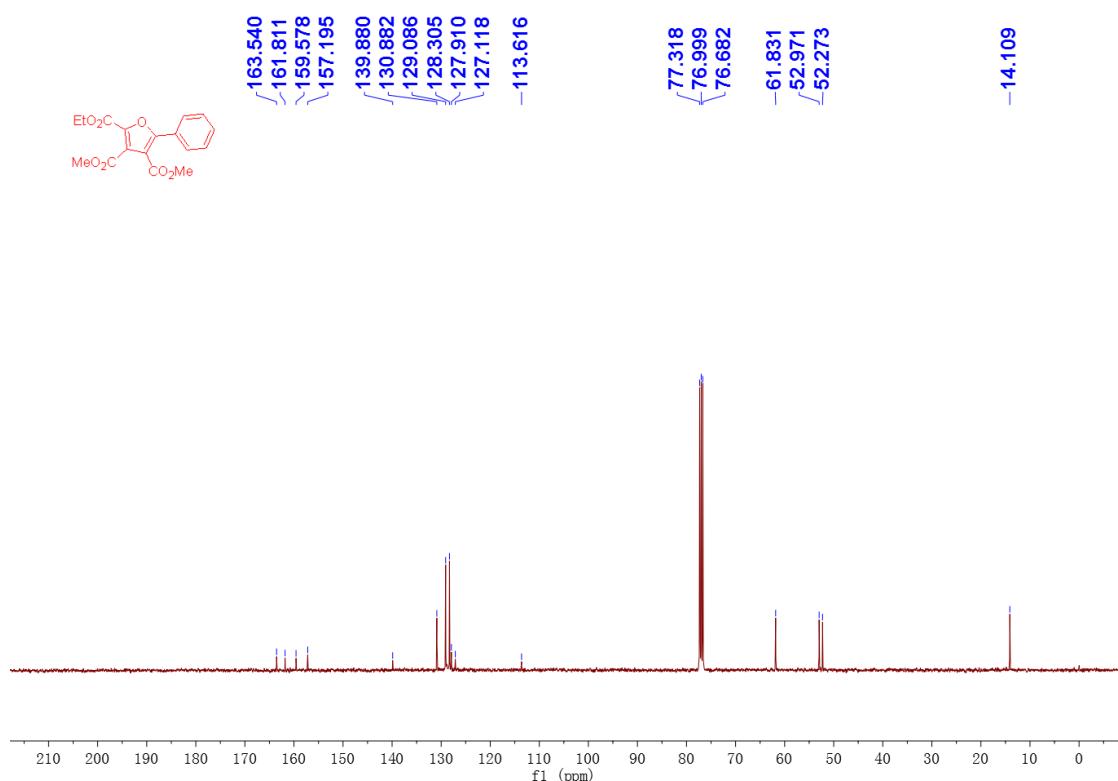
¹³C NMR (101 MHz, CDCl₃)



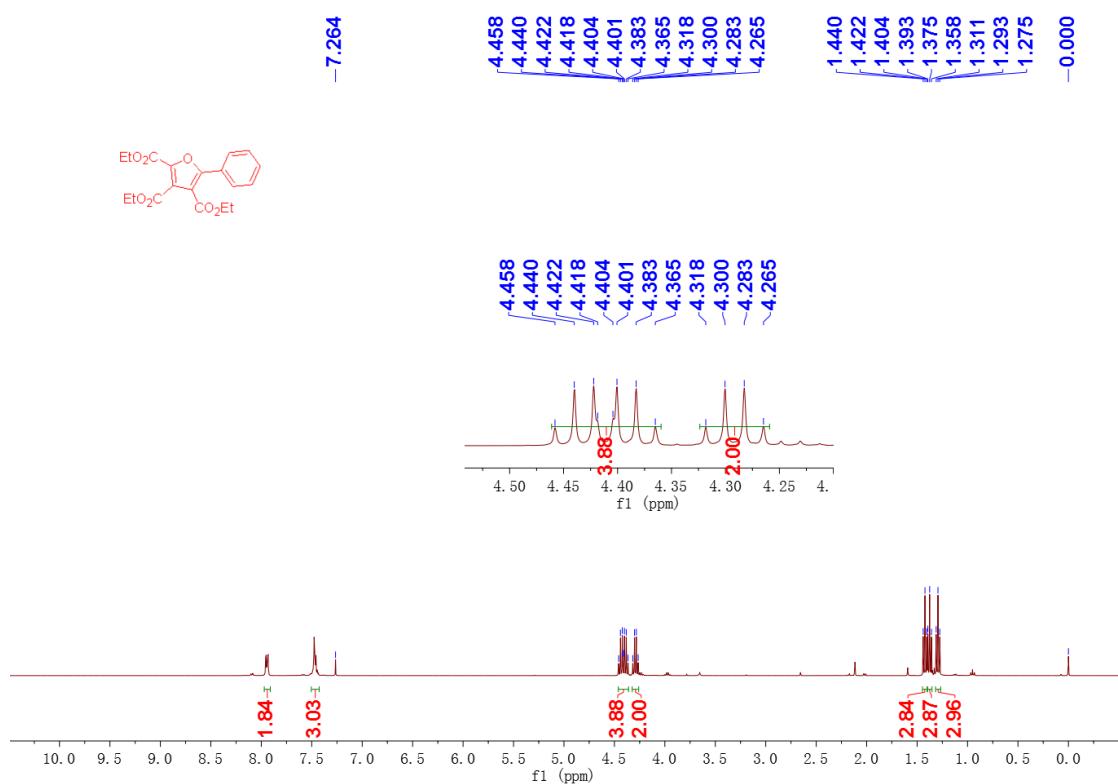
¹H NMR (400 MHz, CDCl₃) of compound 3am



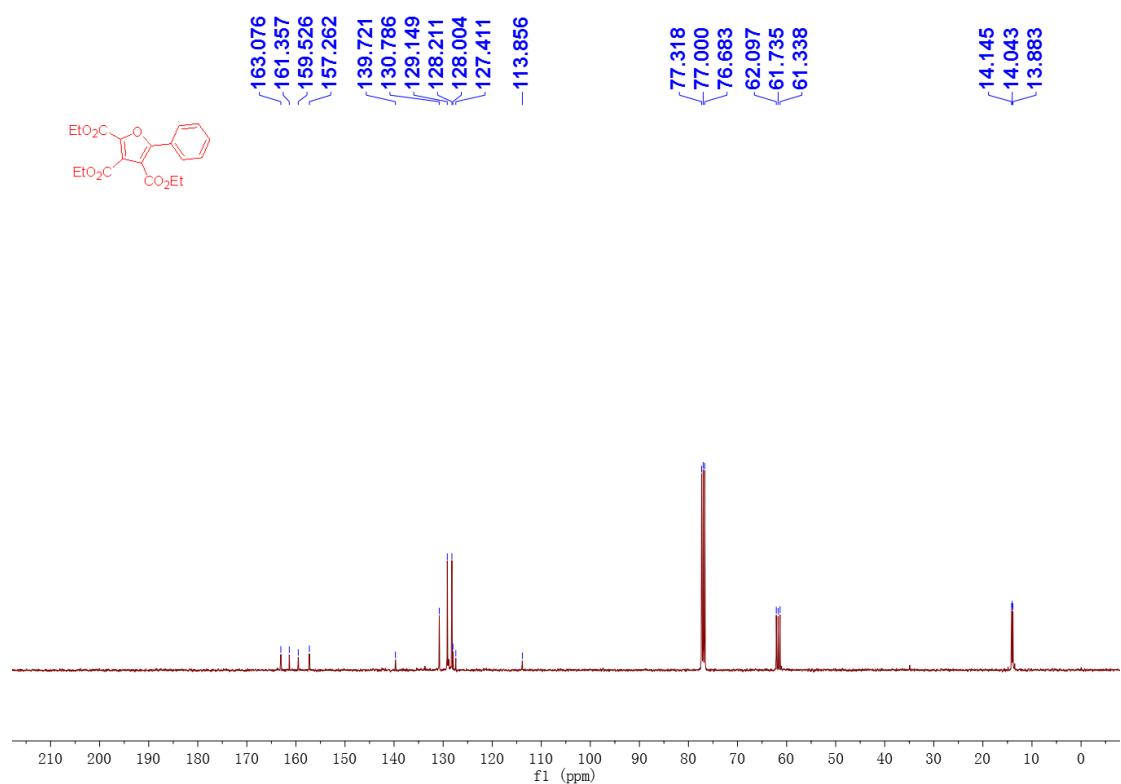
¹³C NMR (101 MHz, CDCl₃)



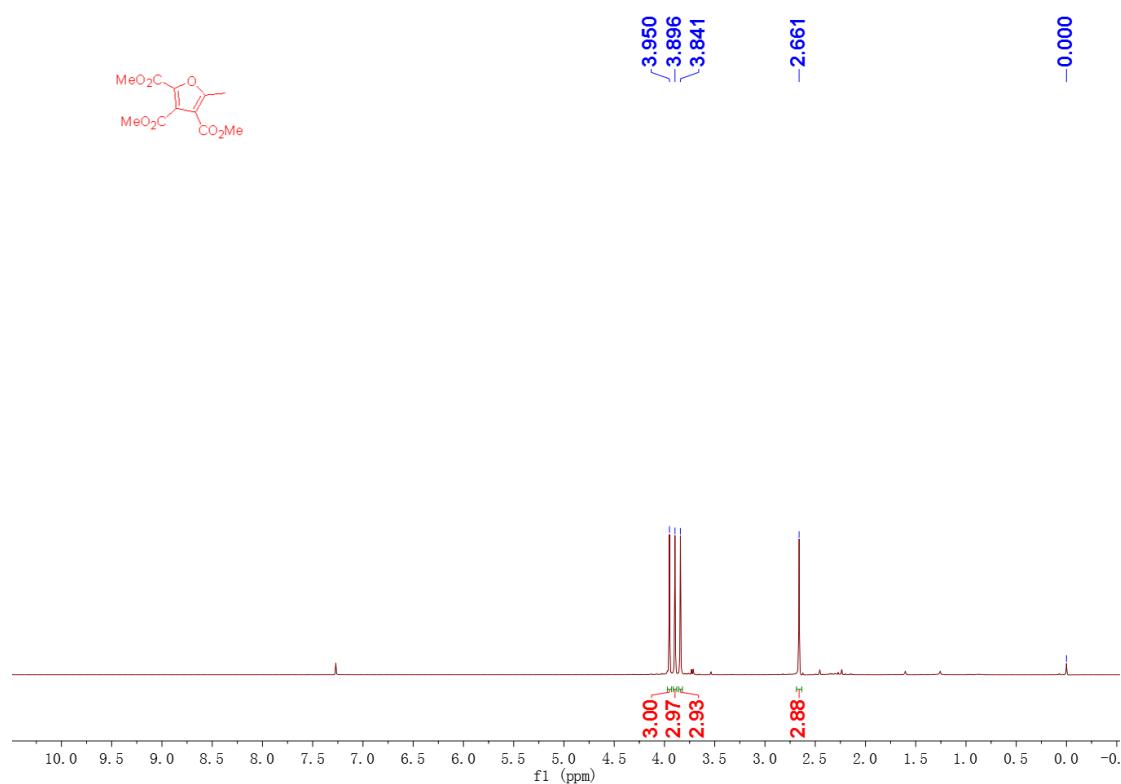
¹H NMR (400 MHz, CDCl₃) of compound 3bm



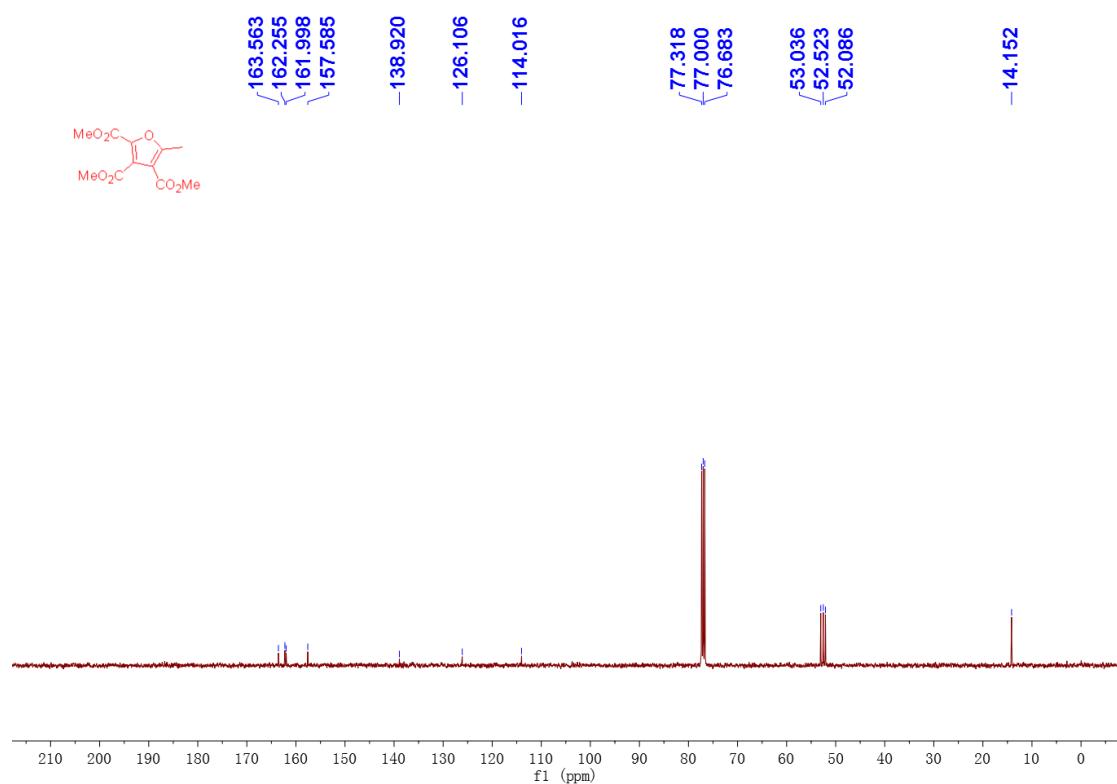
¹³C NMR (101 MHz, CDCl₃)



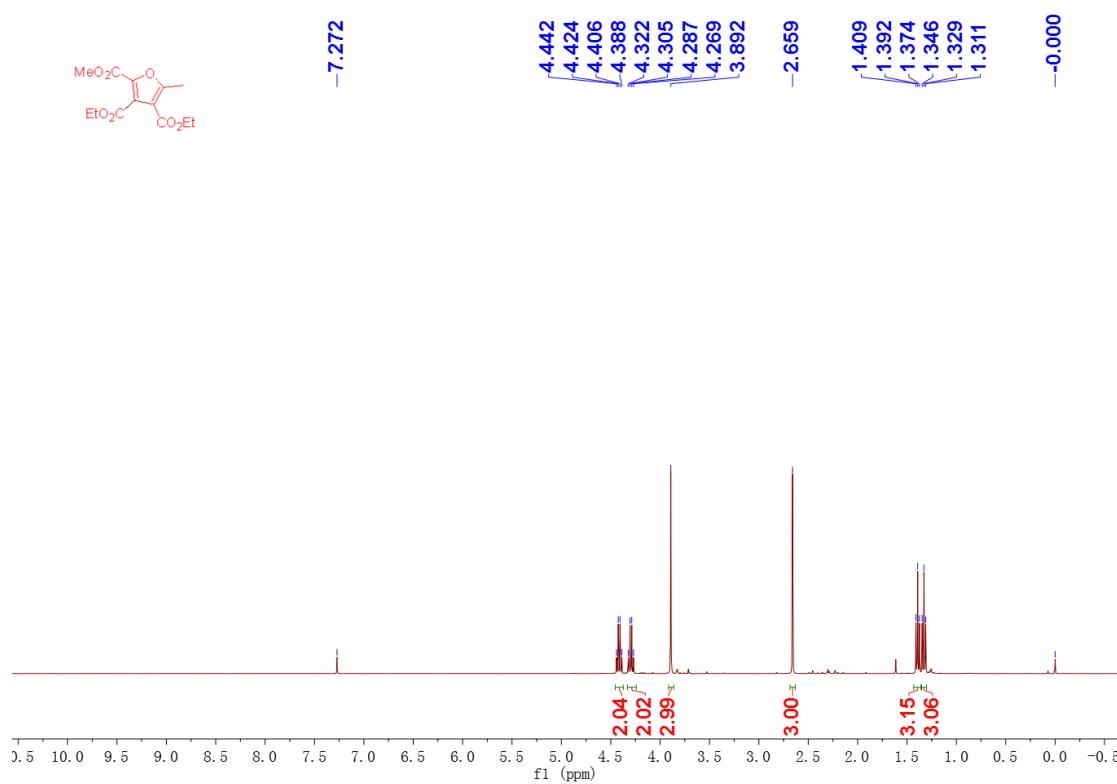
¹H NMR (400 MHz, CDCl₃) of compound 3an



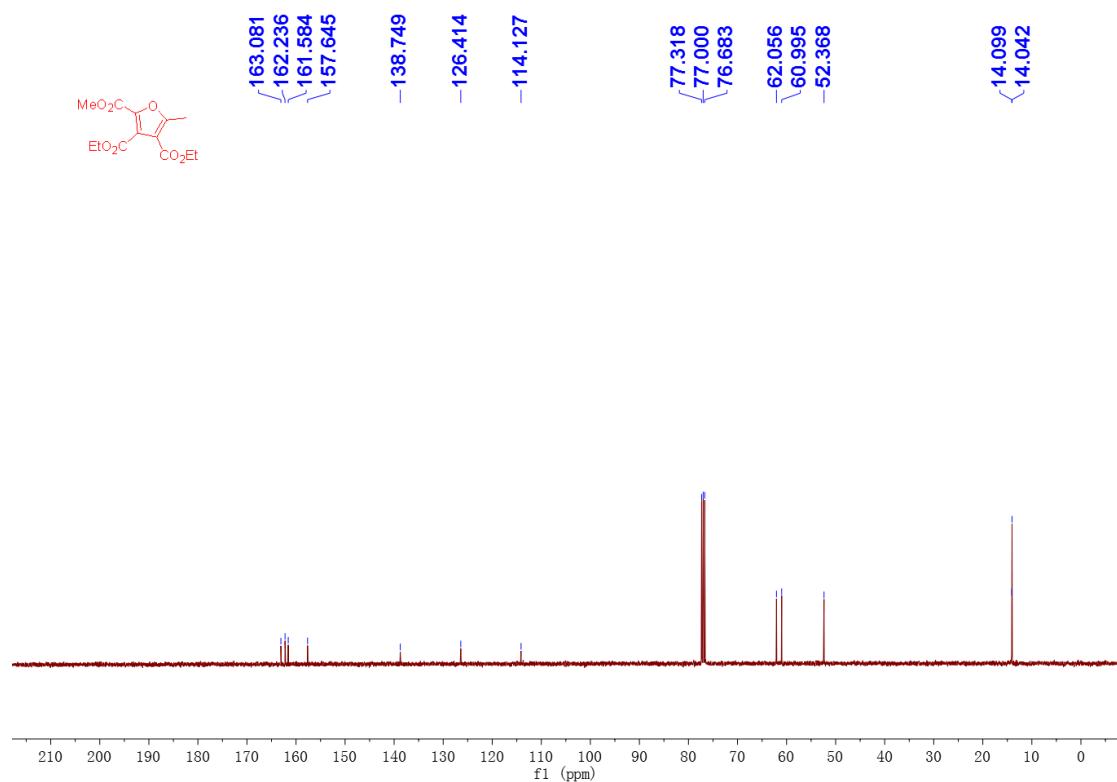
¹³C NMR (101 MHz, CDCl₃)



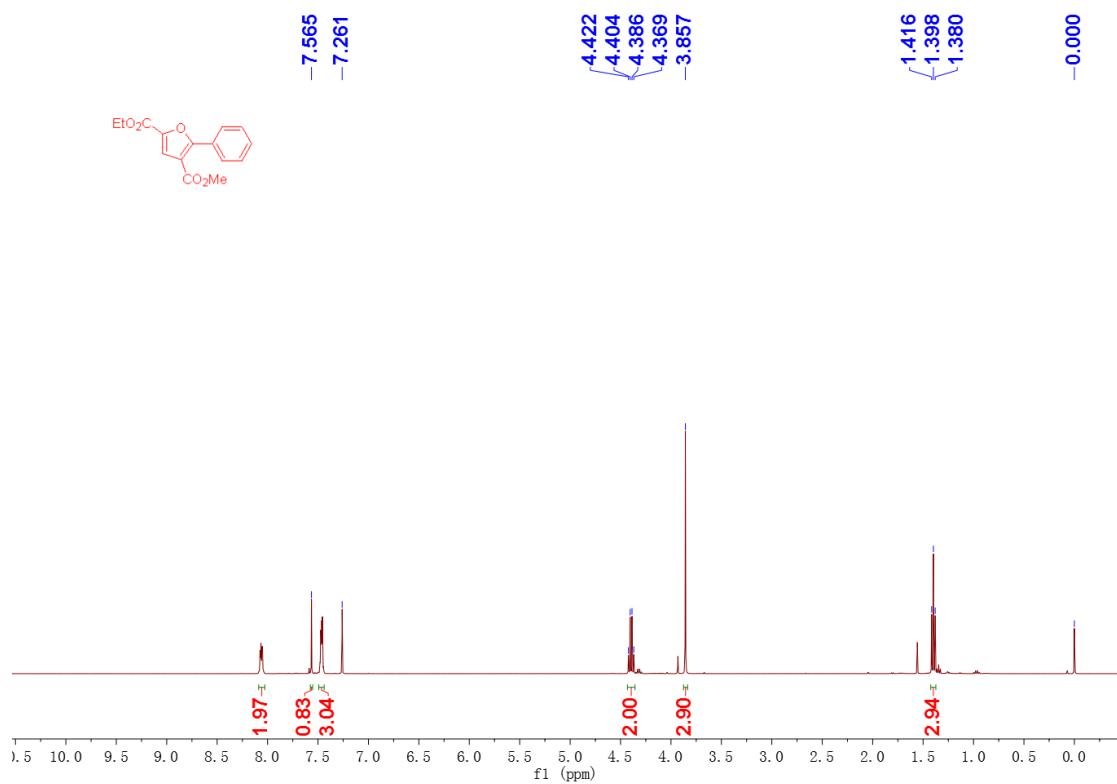
¹H NMR (400 MHz, CDCl₃) of compound 3bn



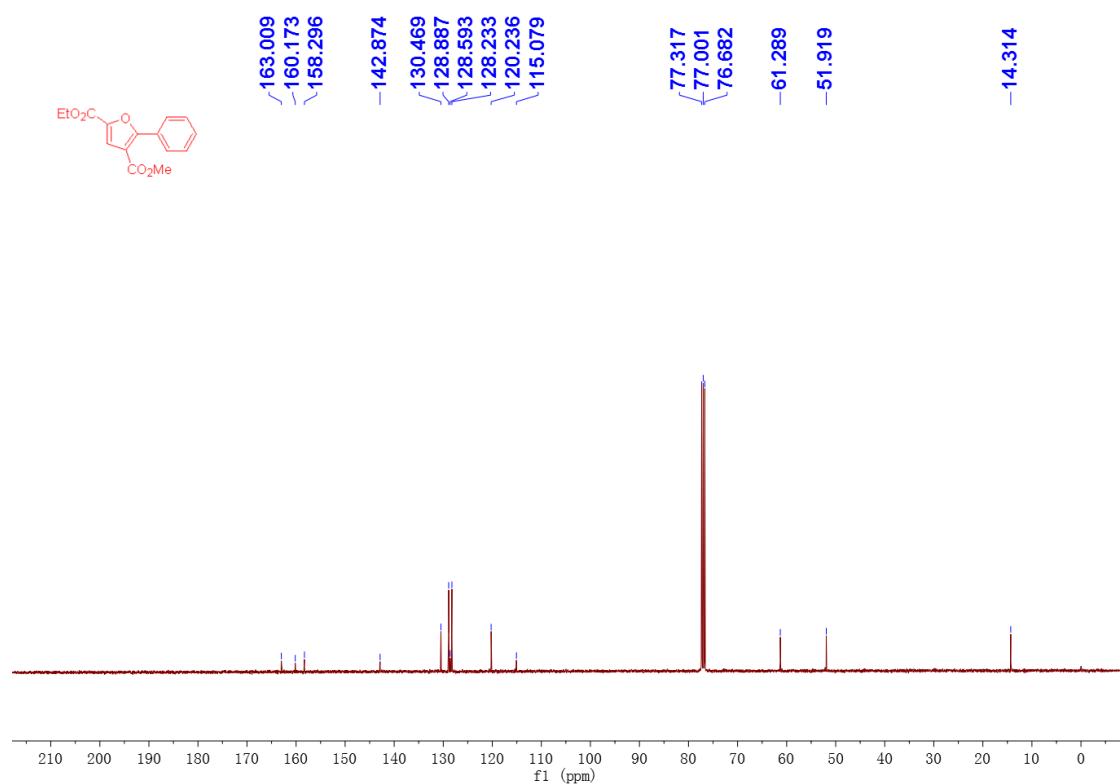
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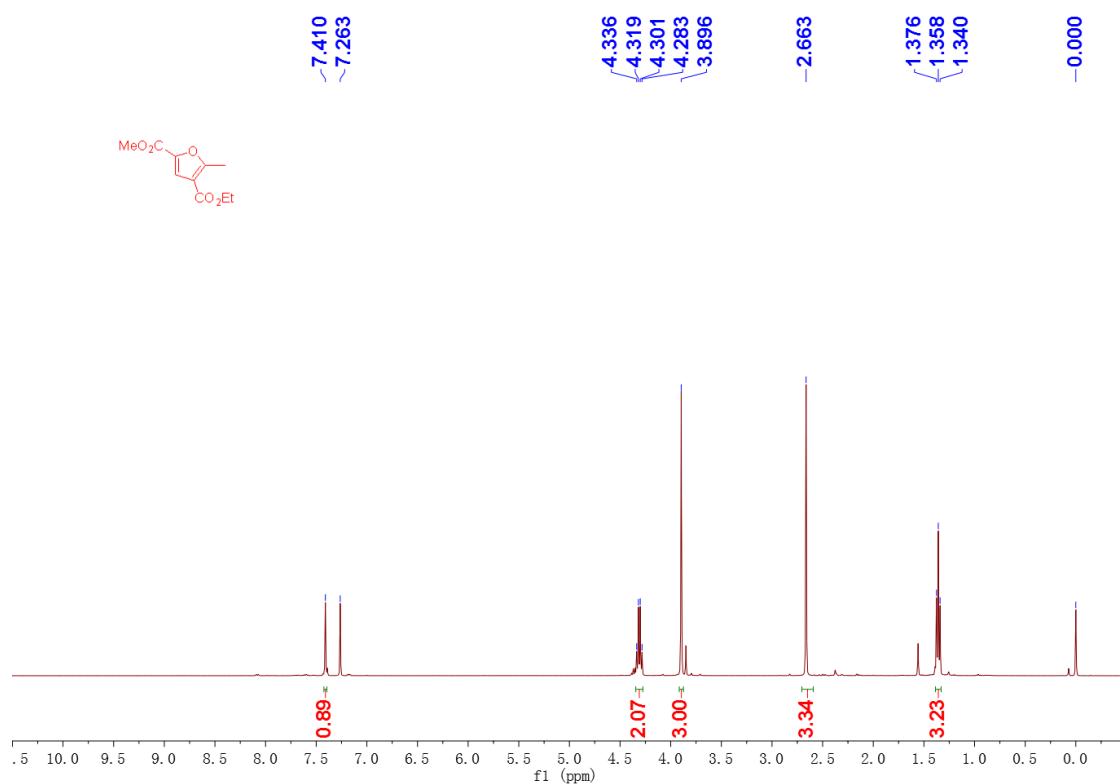
¹H NMR (400 MHz, CDCl₃) of compound 3dm



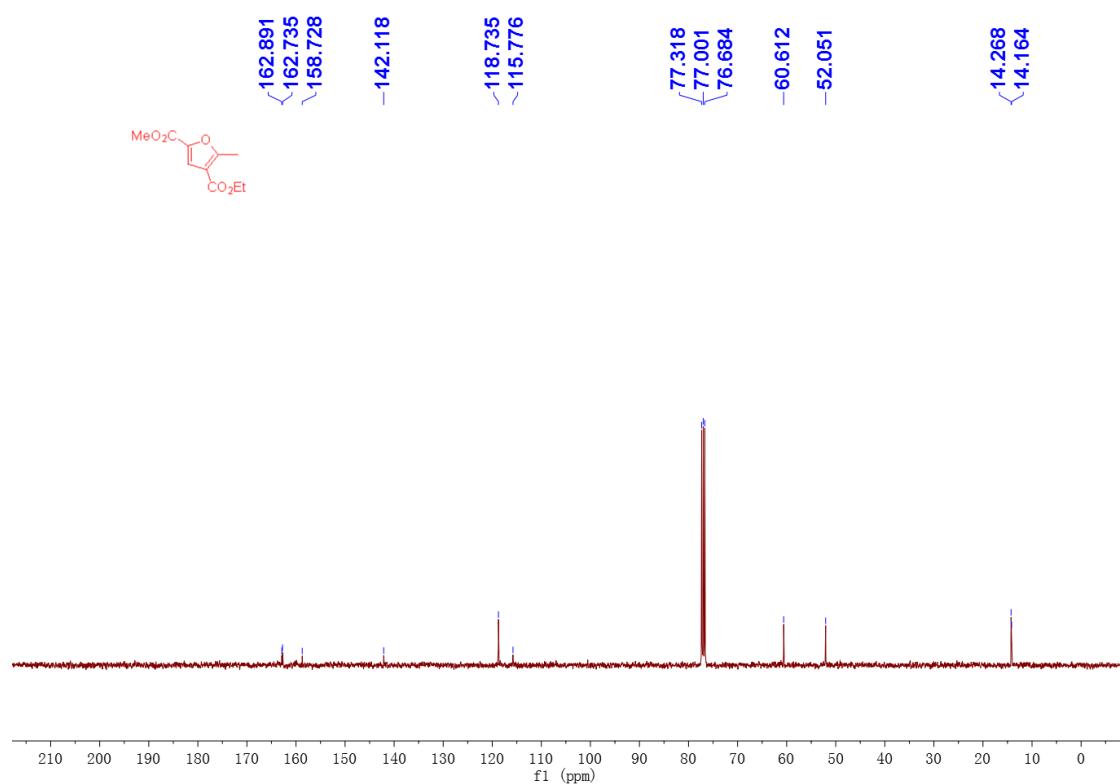
¹³C NMR (101 MHz, CDCl₃)



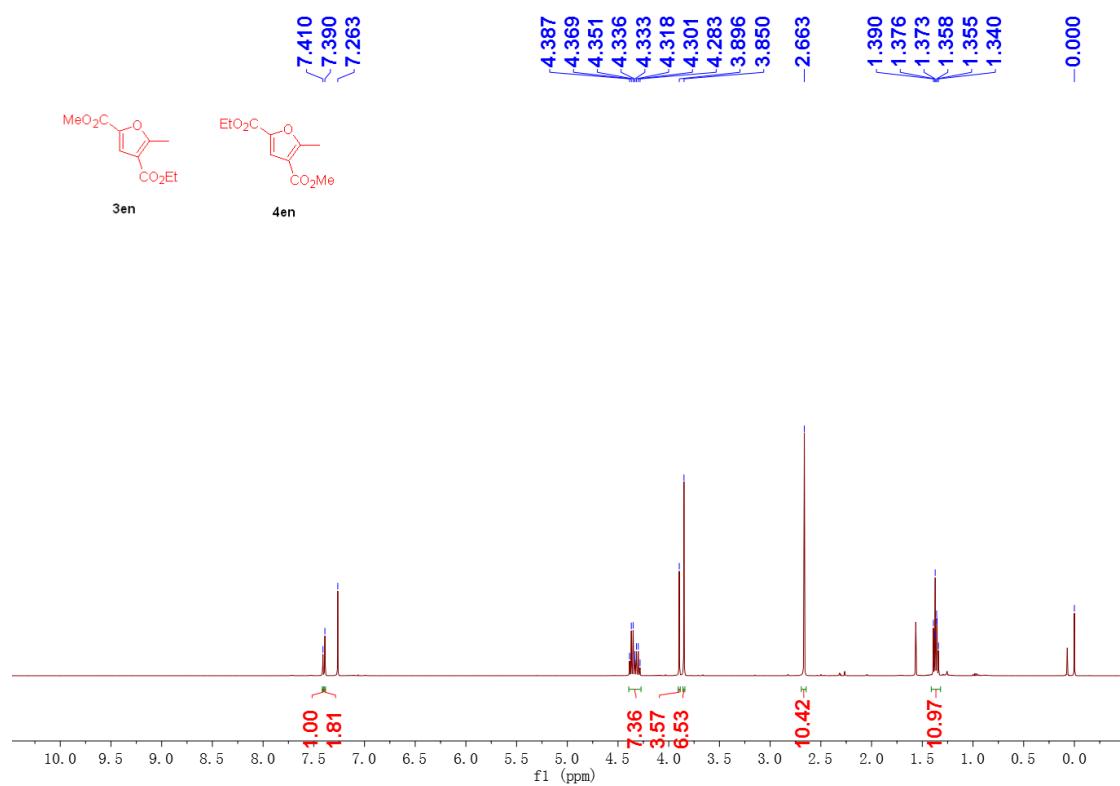
¹H NMR (400 MHz, CDCl₃) of compound 3en



¹³C NMR (101 MHz, CDCl₃)



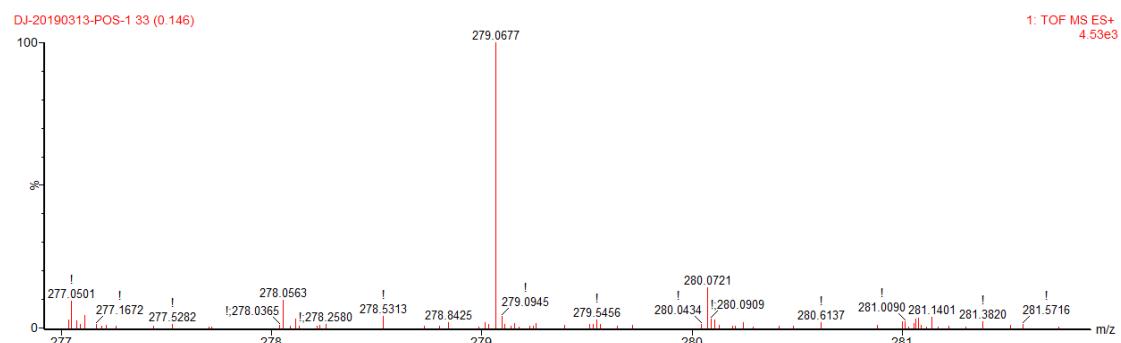
¹H NMR (400 MHz, CDCl₃) of compound 3en and 4en



Copies of HR-MS spectra of unknown furan products 3

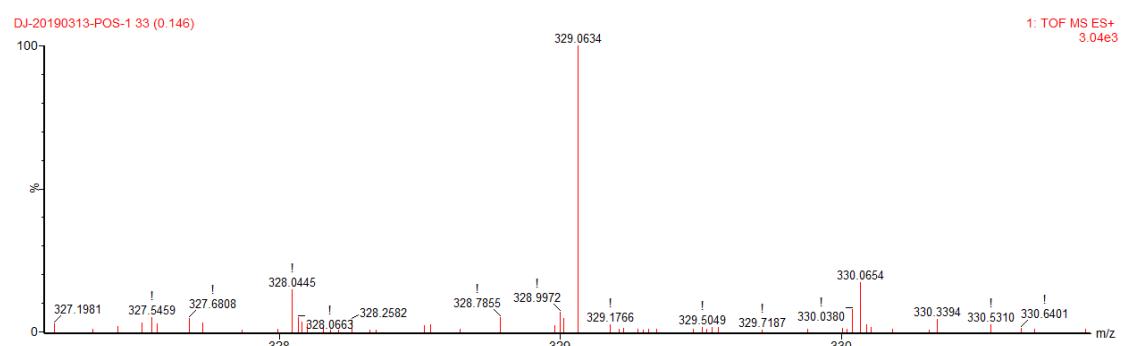
Copy of HR-MS spectra of **3ad**

HR-MS (ESI) m/z [M+H]⁺ calcd for C₁₄H₁₂FO₅⁺: 279.0663, found: 279.0667.



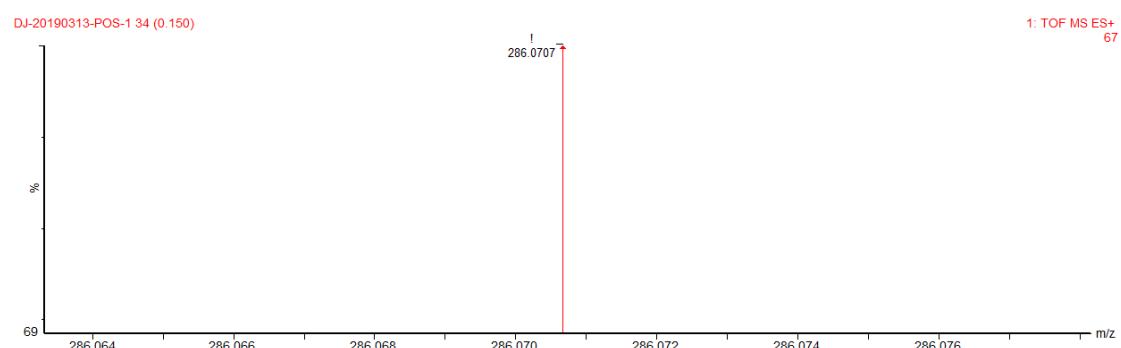
Copy of HR-MS spectra of **3ag**

HR-MS (ESI) m/z [M+H]⁺ calcd for C₁₅H₁₂F₃O₅⁺: 329.0631, found: 329.0634.



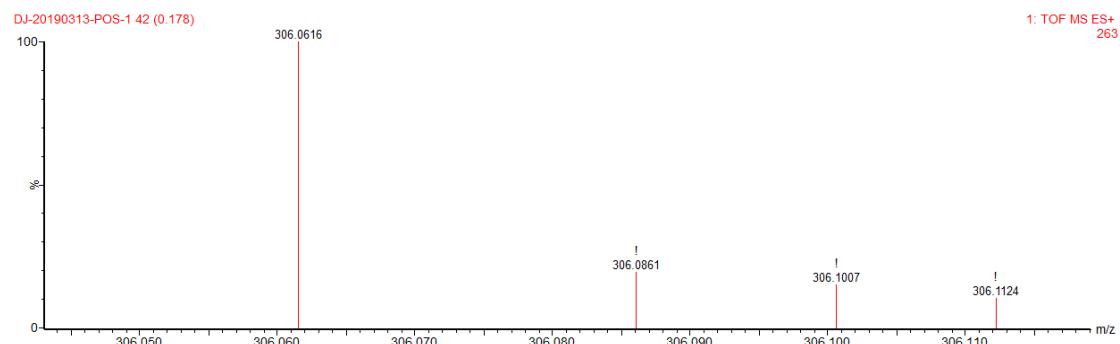
Copy of HR-MS spectra of **3ah**

HR-MS (ESI) m/z [M+H]⁺ calcd for C₁₅H₁₂NO₅⁺: 286.0710, found: 286.0707.



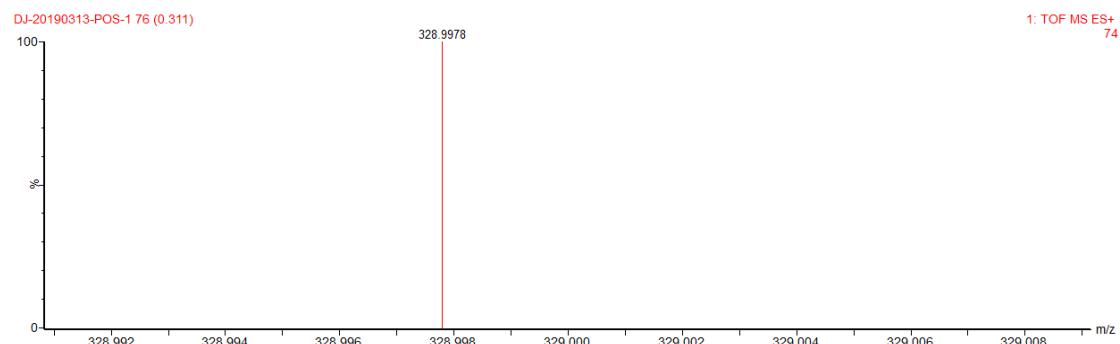
Copy of HR-MS spectra of **3ai**

HR-MS (ESI) m/z [M+H] $^+$ calcd for C₁₄H₁₂NO₇ $^+$: 306.0608, found: 306.0616.



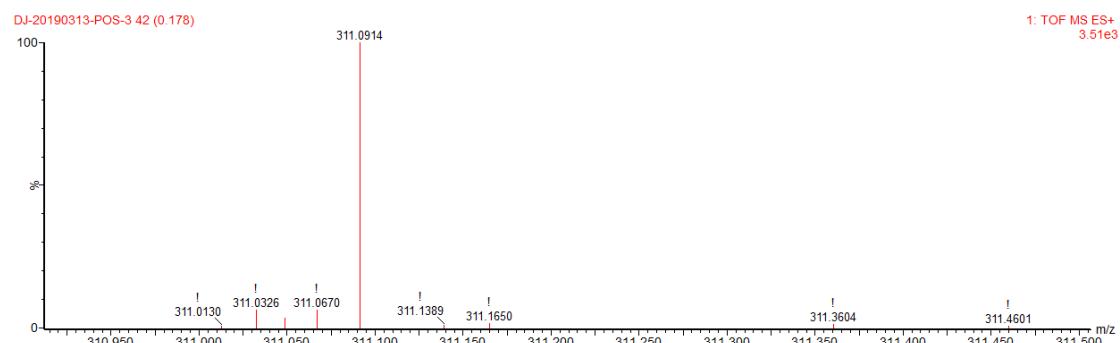
Copy of HR-MS spectra of **3aj**

HR-MS (ESI) m/z [M+H] $^+$ calcd for C₁₄H₁₁Cl₂O₅ $^+$: 328.9978, found: 328.9978.



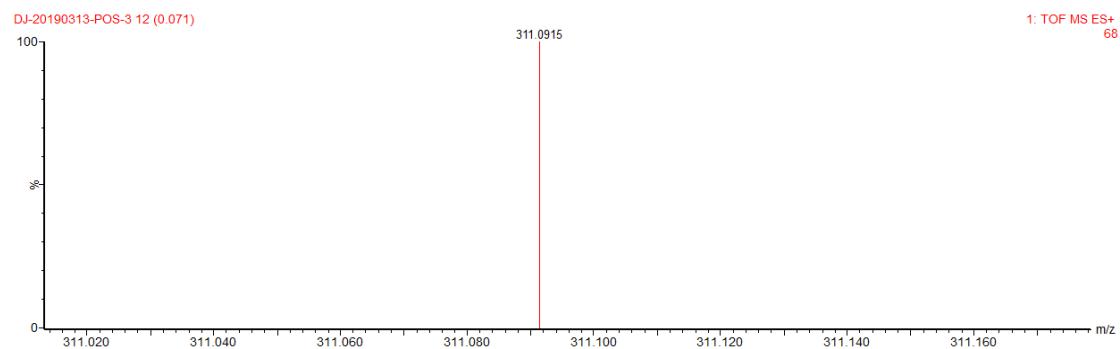
Copy of HR-MS spectra of **3ak**

HR-MS (ESI) m/z [M+H] $^+$ calcd for C₁₈H₁₅O₅ $^+$: 311.0914, found: 311.0914.



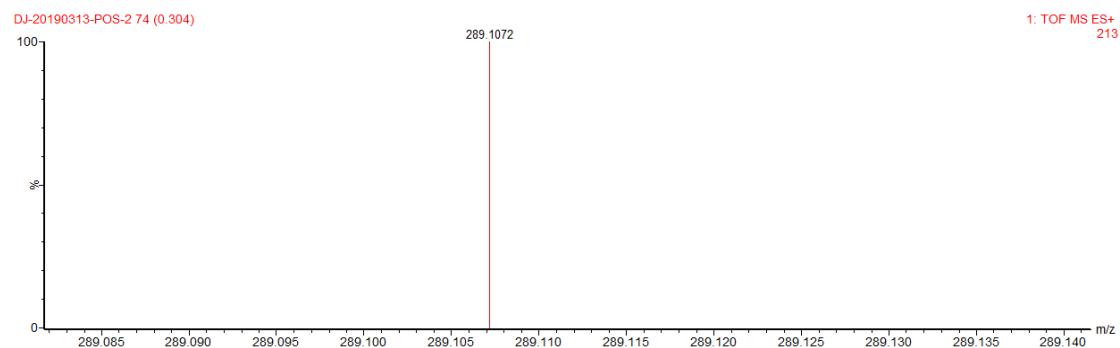
Copy of HR-MS spectra of **3al**

HR-MS (ESI) m/z [M+H] $^+$ calcd for C₁₈H₁₅O₅ $^+$: 311.0914, found: 311.0915.



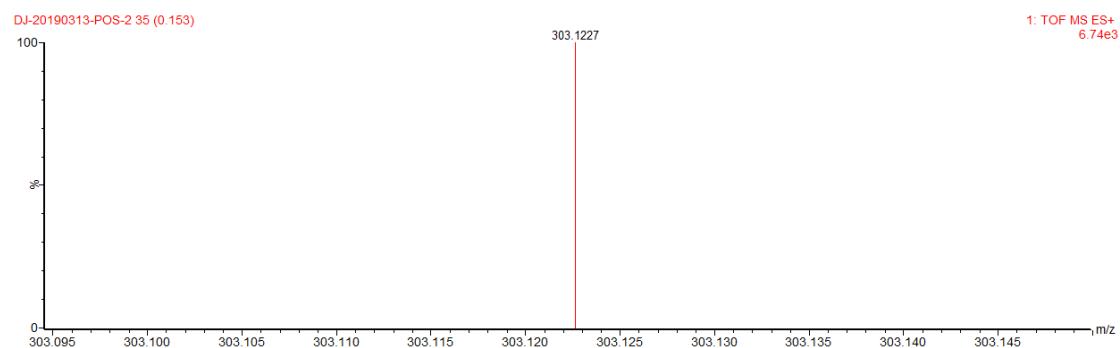
Copy of HR-MS spectra of **3ba**

HR-MS (ESI) m/z [M+H] $^+$ calcd for C₁₆H₁₇O₅ $^+$: 289.1071, found: 289.1072.



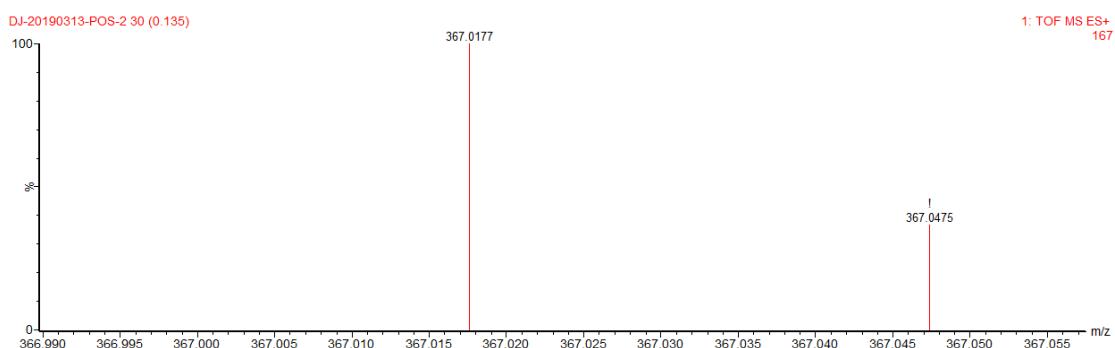
Copy of HR-MS spectra of **3bb**

HR-MS (ESI) m/z [M+H] $^+$ calcd for C₁₇H₁₉O₅ $^+$: 303.1227, found: 303.1227.



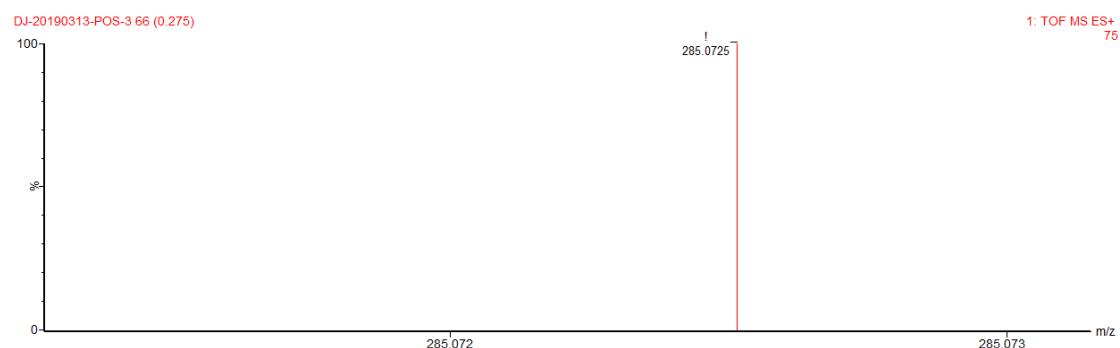
Copy of HR-MS spectra of **3bf**

HR-MS (ESI) m/z [M+H]⁺ calcd for C₁₆H₁₆BrO₅⁺: 367.0176, found: 367.0177.



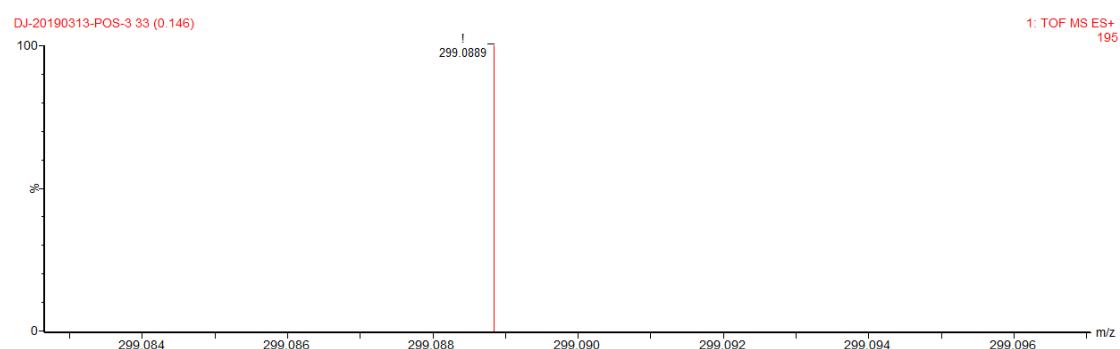
Copy of HR-MS spectra of **3ca**

HR-MS (ESI) m/z [M+H]⁺ calcd for C₁₄H₁₂F₃O₃⁺: 285.0733, found: 285.0725.



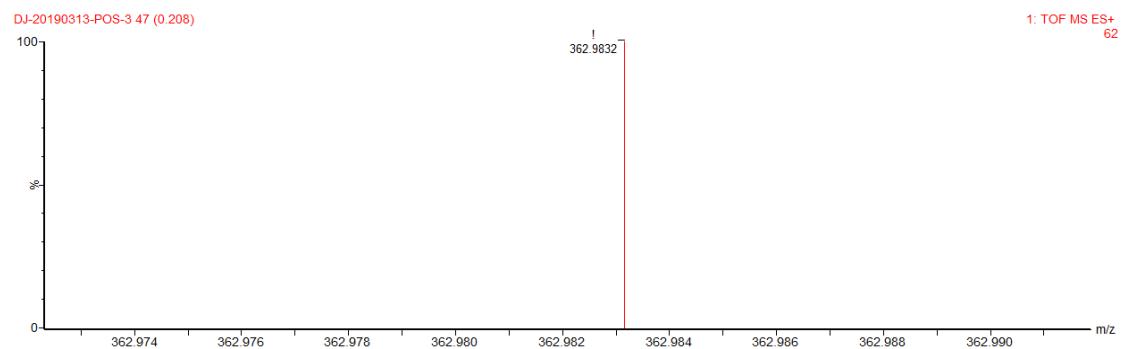
Copy of HR-MS spectra of **3cb**

HR-MS (ESI) m/z [M+H]⁺ calcd for C₁₅H₁₄F₃O₃⁺: 299.0890, found: 299.0889.



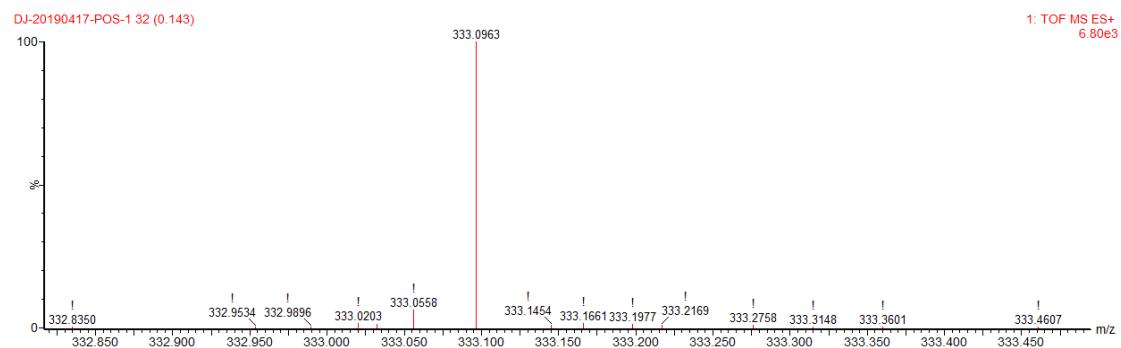
Copy of HR-MS spectra of **3cf**

HR-MS (ESI) m/z [M+H]⁺ calcd for C₁₄H₁₁BrF₃O₃⁺: 362.9838, found: 362.9832.



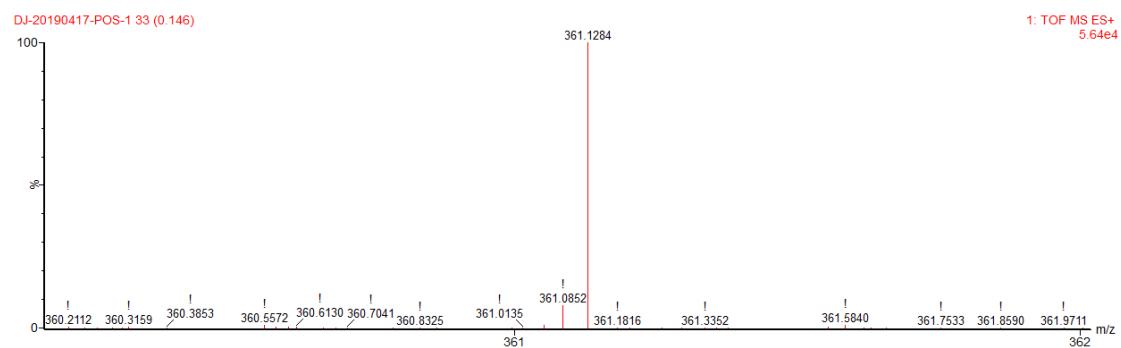
Copy of HR-MS spectra of **3am**

HR-MS (ESI) m/z [M+H]⁺ calcd for C₁₇H₁₇O₇⁺: 333.0969, found: 333.0963.



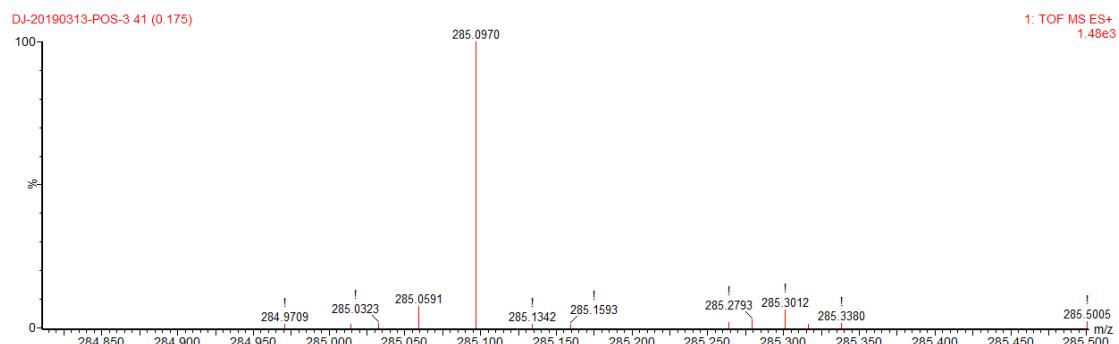
Copy of HR-MS spectra of **3bm**

HR-MS (ESI) m/z [M+H]⁺ calcd for C₁₉H₂₁O₇⁺: 361.1282, found: 361.1284.



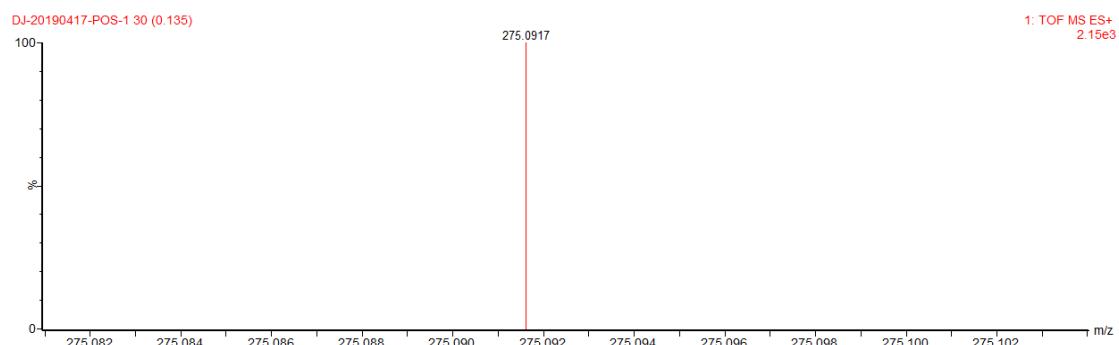
Copy of HR-MS spectra of **3bn**

HR-MS (ESI) m/z [M+H]⁺ calcd for C₁₃H₁₇O₇⁺: 285.0969, found: 285.0970.



Copy of HR-MS spectra of 3dm

HR-MS (ESI) m/z [M+H]⁺ calcd for C₁₅H₁₅O₅⁺: 275.0914, found: 275.0917.



Copy of HR-MS spectra of **3en**

HR-MS (ESI) m/z [M+H]⁺ calcd for C₁₀H₁₃O₅⁺: 213.0757, found: 213.0756.

