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Triflic acid promoted solvent free synthesis of densely functionalized furans

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Contents

Representative Experimental Procedure for the Synthesis of Furan Derivatives by Using Triflic Acid:

To mixture of 1,4-dienone (**1a)** (1.0 mmol) and 1,3-dimethoxybenzene **(2a)** (1.5 mmol), TfOH (1.0 mmol) was added and the resulting reaction mixture was stirred at 90 ^{o}C for 2 h. After completion of reaction as shown by TLC, the reaction mixture was diluted with 10 mL of DCM. The organic layer was washed with saturated $NaHCO_3$ solution (10 mL), followed by water (2x10 mL). The organic layer was separated, dried over Na_2SO_4 and the solvent was evaporated under reduced pressure. Thus obtained crude reaction mixture was purified by silica gel column chromatography to afford the product **3a (**Ethyl 4-(2,4-dimethoxyphenyl)-2,5-diphenylfuran-3-carboxylate) in 94% yield.

Spectral Data

Ethyl 4-(2,4-dimethoxyphenyl)-2,5-diphenylfuran-3-carboxylate (3a) (Table 2, entry 1):

Pale yellow Liquid, ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.95-7.92 (m, 2H), 7.53-7.35 (m, 5H), 7.28-7.12 (m, 4H), 6.56 (d, *J* = 2.2 Hz, 1H), 6.51 (dd, *J* = 2.2, 8.3 Hz, 1H), 4.08 (q, *J* = 7.2 Hz, 2H), 3.85 (s, 3H), 3.71 (s, 3H), 0.99 (t, *J* = 7.07 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 164.3, 160.7, 158.4, 154.1, 148.3, 131.6, 130.4, 129.9, 128.8, 128.2, 128.0, 127.8, 127.4, 125.5, 119.7, 117.2, 114.7, 104.4, 98.6, 60.2, 55.4, 55.3, 13.6. FT-IR (neat): 3063, 2975, 2838, 1720, 1506, 1210, 1117, 1035, 958, 767, 690 cm^{-1}. Mass ESI (*m/z*) 429 $(M+H)^{+}$. ESI-HRMS calcd. for $[C_{27}H_{25}O_5]$ requires 429.1704, found: 429.1697.

Ethyl 5-(4-chlorophenyl)-4-(2,4-dimethoxyphenyl)-2-phenylfuran-3-carboxylate (3b) (Table 2, entry 2):

Yellow Solid, m.p:132-134 ˚C, ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.89-7.95 (m, 2H), 7.38-7.48 (m, 5H), 7.22 (d, *J* = 8.4 Hz, 2H), 7.12 (d, *J* = 8.4 Hz, 1H), 6.59 (d, *J* = 2.0 Hz, 1H), 6.52 (dd, *J* = 2.4, 8.4 Hz, 1H), 4.08 (q, *J* = 7.2 Hz, 2H), 3.87 (s, 3H), 3.72 (s, 3H), 1.00 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 164.2, 161.0, 158.4, 154.4, 147.3, 133.2, 131.6, 129.8, 129.0, 129.0, 128.5, 127.8, 126.7, 120.2, 117.4, 114.3, 104.5, 98.7, 60.3, 55.4, 55.3, 13.7.

FT-IR (KBr): 3008, 2964, 2893, 1715, 1550, 1298, 1112, 832, 778 cm^{-1}. Mass ESI (*m/z*) 463.5 $(M+H)^+$. ESI-HRMS calcd. for $[C_{27}H_{24}ClO_5]$ requires 463.1314, found: 463.1305.

Ethyl 4-(2,4-dimethoxyphenyl)-5-(naphthalen-2-yl)-2-phenylfuran-3-carboxylate (3c) (Table 2, entry 3):

Yellow Liquid, ^1H NMR (400 MHz, $CDCl_3$): δ 8.03 (s, 1H), 7.96-8.0 (m, 2H), 7.74 (q, *J* = 5.6 Hz, 2H), 7.68 (d, *J* = 8.8 Hz, 1H), 7.52 (dd, *J* = 1.6, 8.4 Hz, 1H), 7.38-7.50 (m, 5H), 7.18 (d, *J* = 8.0 Hz, 1H), 6.59 (d, *J* = 2.4 Hz, 1H), 6.52 (dd, *J* = 2.8, 8.4 Hz, 1H), 4.11 (q, *J* = 7.2 Hz, 2H), 3.88 (s, 3H), 3.73 (s, 3H), 1.02 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 164.4, 160.9, 158.5, 154.3, 148.4, 133.2, 132.5, 131.8, 130.0, 128.9, 128.3, 128.2, 127.9, 127.9, 127.8, 127.5, 126.2, 126.1, 124.5, 123.5, 120.2, 117.5, 114.7, 104.5, 98.75, 60.31, 55.4, 55.3,13.7. FT-IR (NEAT):3057, 2980, 2832, 1726, 1578, 1304, 1210, 1112, 734 cm^{-1}. Mass ESI (*m/z*) 479 $(M+H)^+$. ESI-HRMS calcd. for $[C_{31}H_{27}O_5]$ requires 479.1860, found: 479.1861.

Ethyl 4-(4-hydroxy-3,5-diisopropylphenyl)-2,5-diphenylfuran-3-carboxylate (3d) (Table 2, entry 4):

Yellow Solid, m.p:110-112°C, ^1H NMR (400 MHz, $CDCl_3$): δ 7.89-7.95 (m, 2H), 7.37-7.53 (m, 5H), 7.18-7.28 (m, 3H), 7.05 (s, 2H), 4.09 (q, *J* = 7.2 Hz, 2H), 3.18 (q, *J* = 6.8 Hz, 2H), 1.23 (d, *J* = 6.8 Hz, 12H), 0.96 (t, *J* = 7.2 Hz, 3H) . ^{13}C NMR (100 MHz, $CDCl_3$): δ 164.9, 153.3, 149.4, 147.9, 133.8, 130.4, 129.9, 128.9, 128.3, 128.2, 127.5, 124.9, 127.4, 125.6, 125.0, 124.3, 117.4, 60.7, 27.1, 22.8, 13.7. FT-IR (KBr): 3474, 2964, 2832, 1699, 1496, 1194, 1117, 772, 696 cm^{-1}. Mass ESI (*m/z*) 469 $(M+H)^+$. ESI-HRMS calcd. for $[C_{31}H_{33}O_4]$ requires 469.2381, found: 469.2372.

Ethyl 5-(4-chlorophenyl)-4-(4-hydroxy-3,5-diisopropylphenyl)-2-phenylfuran-3-carboxylate (3e) (Table 2, entry 5):

Yellow Solid, m.p:175-177 °C, ^1H NMR (400 MHz, $CDCl_3$): δ 7.88-7.93 (m, 2H),7.39-7.49 (m, 5H),7.21 (d, *J* = 8.8 Hz, 2 H), 7.03 (s, 2H), 4.08 (q, *J* = 6.8 Hz, 2H), 3.18 (q, *J* = 6.8 Hz, 2H), 1.24 (d, *J* = 6.8 Hz, 12 H), 0.96 (t, *J* = 7.2 Hz, 3H).^{13}C NMR (100 MHz, $CDCl_3$): δ 164.7, 153.6, 149.6, 146.9, 134.0, 133.3, 129.8, 129.1, 128.9, 128.5, 128.4, 127.4, 126.7, 124.9, 124.8, 124.6, 117.5, 60.7, 27.2, 22.8,13.7.FT-IR (KBr): 3468, 3068, 2958, 2860,

1709, 1490, 1139, 816, 684 cm^{-1}. Mass ESI (*m/z*) 503.5 $(M+H)^+$. ESI-HRMS calcd. for $[C_{31}H_{32}ClO_4]$ requires 503.1980, found: 503.1982.

Ethyl 4-(4-hydroxy-3,5-diisopropylphenyl)-5-(naphthalen-2-yl)-2-phenylfuran-3-carboxylate (3f) (Table 2, entry 6):

Brown Solid, m.p:118-120°C, ^1H NMR (400 MHz, $CDCl_3$): δ 8.03 (d, *J* = 1.2 Hz. 1H), 7.95-7.99 (m, 2H), 7.65-7.77 (m, 3H), 7.55 (dd, *J* = 1.6, 8.4 Hz, 1H), 7.40-7.51 (m, 5H), 7.11 (s, 2H), 4.10 (q, *J* = 6.8 Hz, 2H), 3.20 (q, *J* = 6.8 Hz, 2H), 1.24 (d, *J* = 6.8 Hz, 12H), 0.98 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 164.9, 153.6, 149.5, 148.1, 133.9, 133.2, 132.6, 130.0, 129.0, 128.4, 128.3,127.9, 127.7, 127.6, 126.3, 126.1, 125.2, 125.0, 124.8, 124.5, 123.5, 117.6,27.2, 60.7, 22.9,13.7. FT-IR (KBr): 3484, 3046, 2958, 2860, 1704, 1457, 1243, 1063, 745, 684 cm^{-1}. Mass ESI (*m/z*) 519 $(M+H)^+$. ESI-HRMS calcd. for $[C_{35}H_{35}O_4]$ requires 519.2537, found: 519.2534.

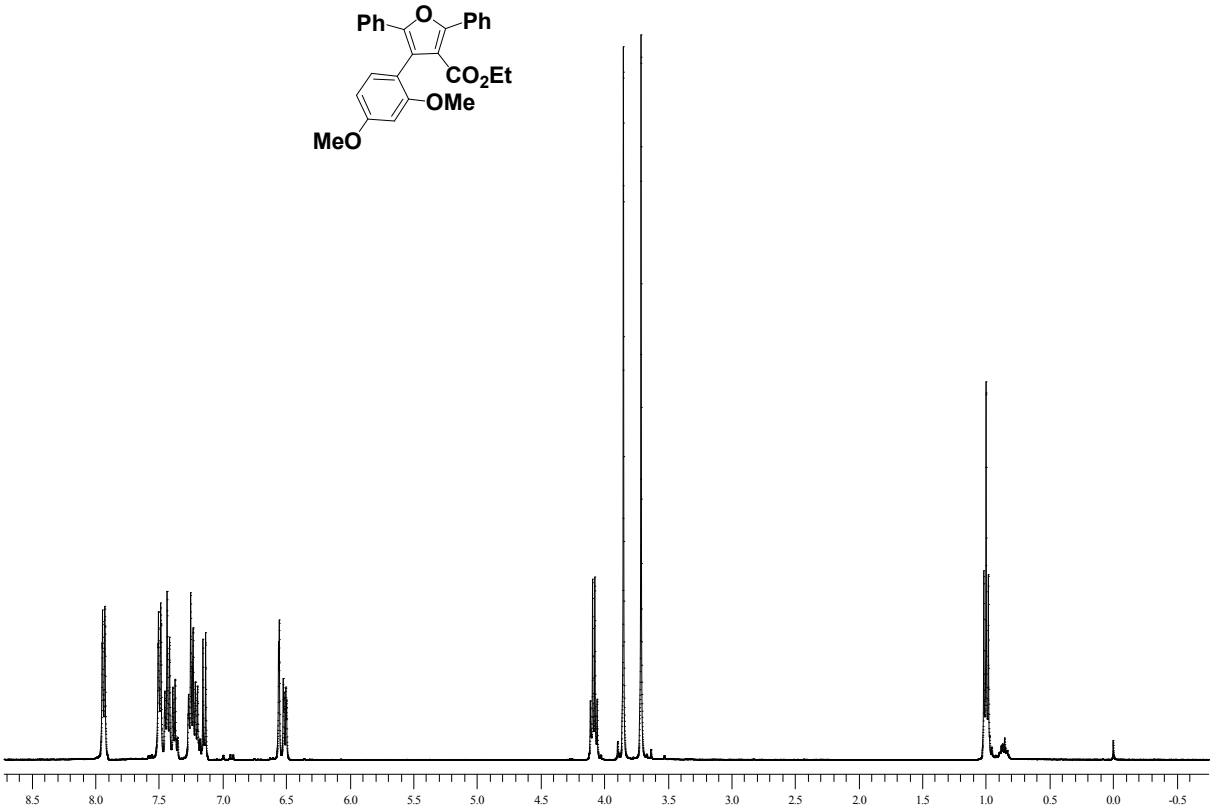
Ethyl 4-(4-hydroxyphenyl)-2,5-diphenylfuran-3-carboxylate (3g) (Table 2, entry 7):

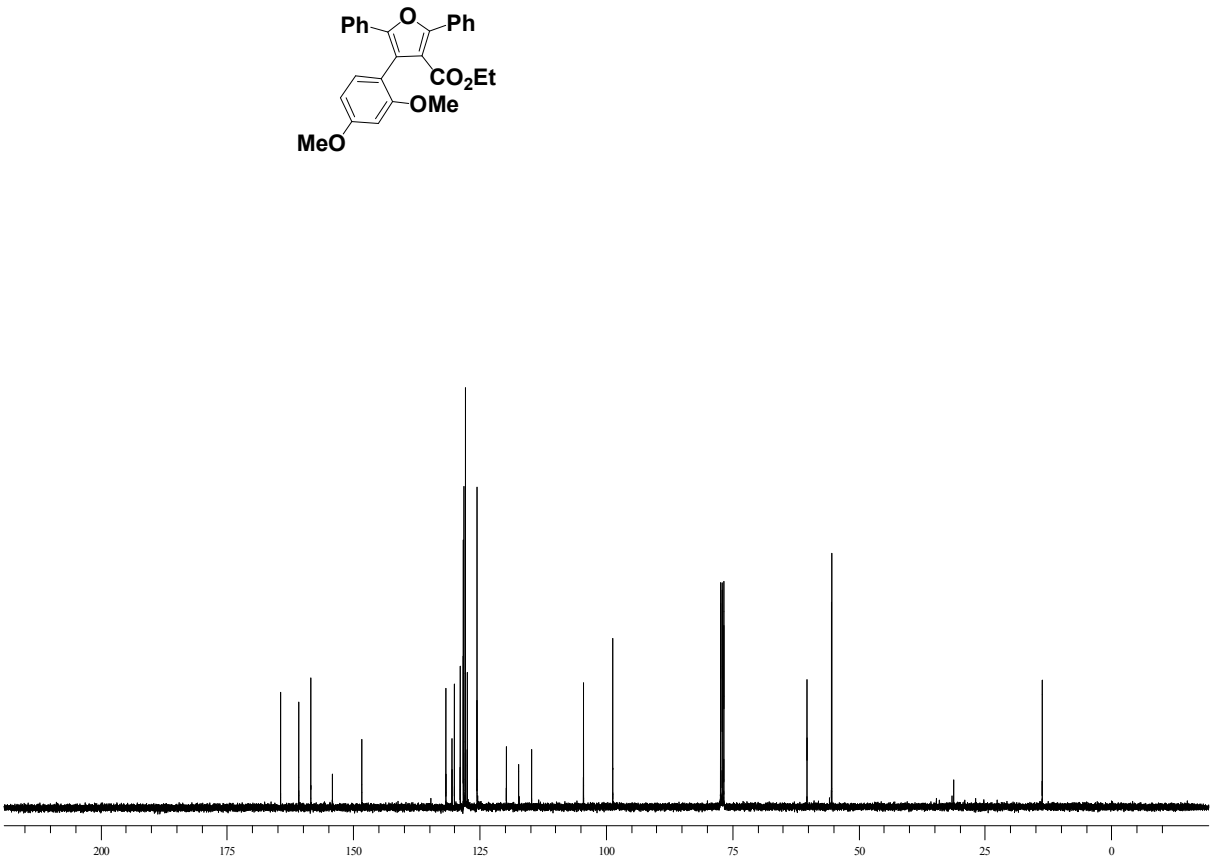
Pale yellow Solid, m.p:115-117°C, ^1H NMR (400 MHz, $CDCl_3$): δ 7.87-7.90 (m, 2H), 7.38-7.50 (m, 5H), 7.21-7.29 (m, 5H), 6.82-6.85 (m, 2H), 4.14 (q, *J* = 7.2 Hz, 2H), 1.03 (t, *J* = 7.5 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 164.9, 155.5, 154.3, 148.4, 131.3, 130.2, 129.9, 129.1, 128.3, 127.8, 127.7, 125.8, 124.9, 123.4, 116.9, 115.6, 60.9, 28.4, 13.7. FT-IR (KBr): 3347, 3063, 2980, 2920, 2832, 1699, 1336, 1134, 695 cm^{-1}. Mass ESI (*m/z*) 385 $(M+H)^+$. ESI-HRMS calcd. for $[C_{25}H_{21}O_4]$ requires 385.1442, found: 385.1434.

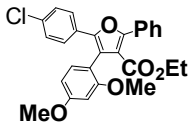
5-(4-chlorophenyl)-4-(4-hydroxyphenyl)-2-phenylfuran-3-carboxylate (3h) (Table 2, entry 8):

Yellow Solid, m.p:69-71°C, ^1H NMR (400 MHz, $CDCl_3$): δ7.86-7.91 (m, 2H), 7.41-7.48 (m, 3H), 7.22 (d, *J* = 8.8 Hz, 4H), 7.37 (d, *J* = 8.8 Hz, 2H), 6.87 (d, *J* = 8.4 Hz, 2H), 4.11 (q, *J* = 6.8 Hz, 2H), 1.02 (t, *J* = 7.2 Hz, 3H).^{13}C NMR (100 MHz, $CDCl_3$): δ 164.8, 155.7, 154.6, 147.4, 133.5, 131.1, 129.7, 129.3, 128.6, 128.3, 127.8, 126.9, 124.5, 123.8, 122.0, 116.9, 115.7 ,61.0, 13.7. FT-IR (KBr): 3319, 2958, 2846, 1704, 1572, 1484, 1331, 1008, 832, 767, 684 cm^{-1}. Mass ESI (*m/z*) 419.5 $(M+H)^+$. ESI-HRMS calcd. for $[C_{25}H_{20}ClO_4]$ requires 419.1052, found: 419.1045.

Copies of ^{1}H NMR and ^{13}C NMR of Compounds



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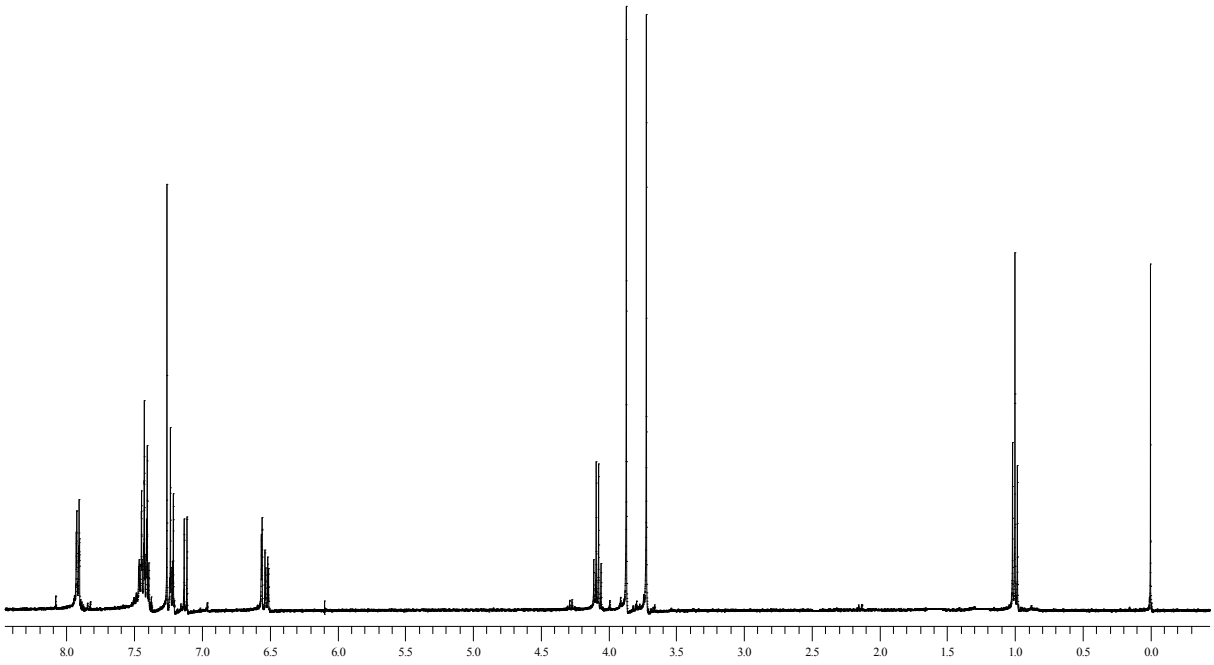
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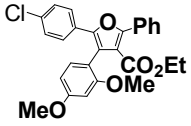
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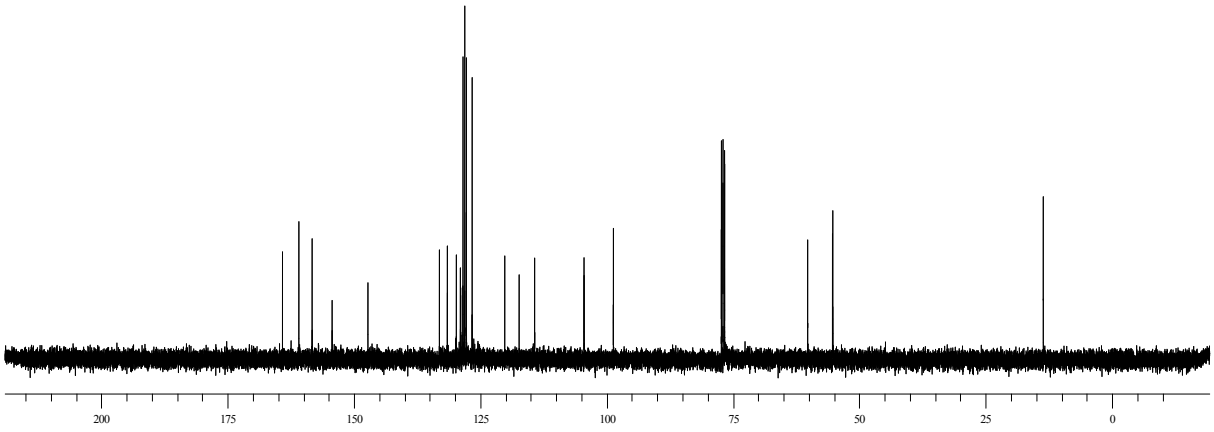
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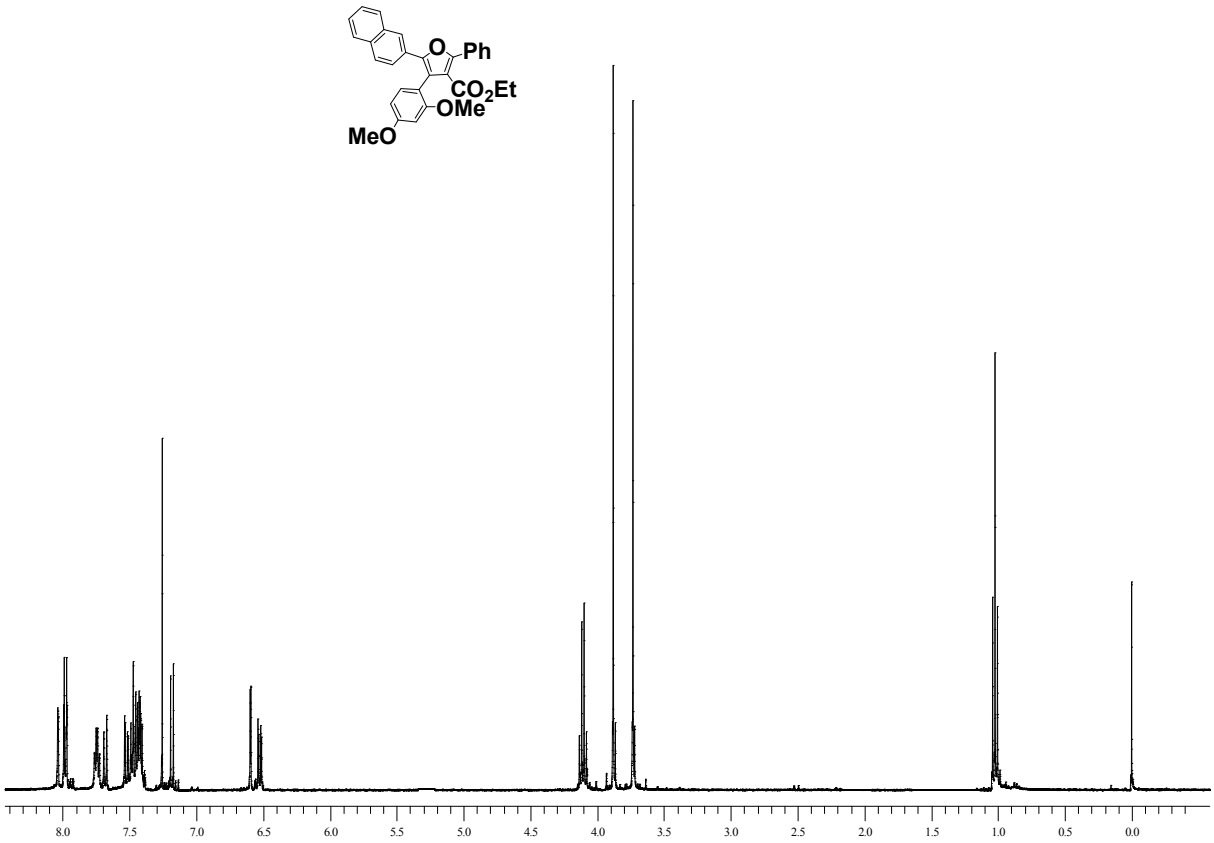
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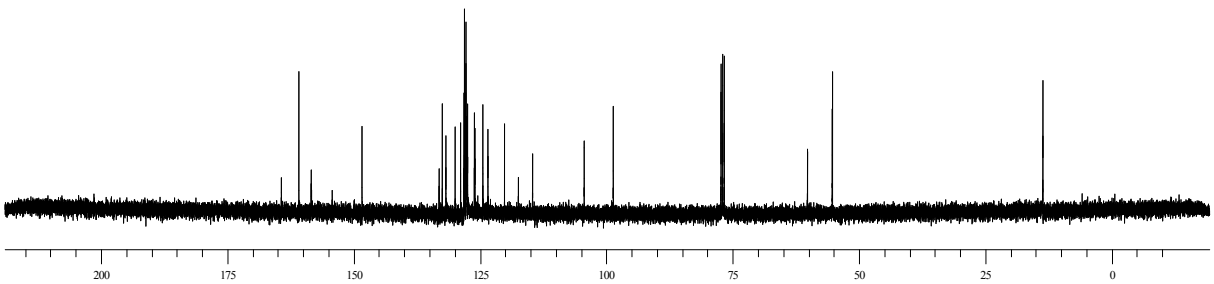
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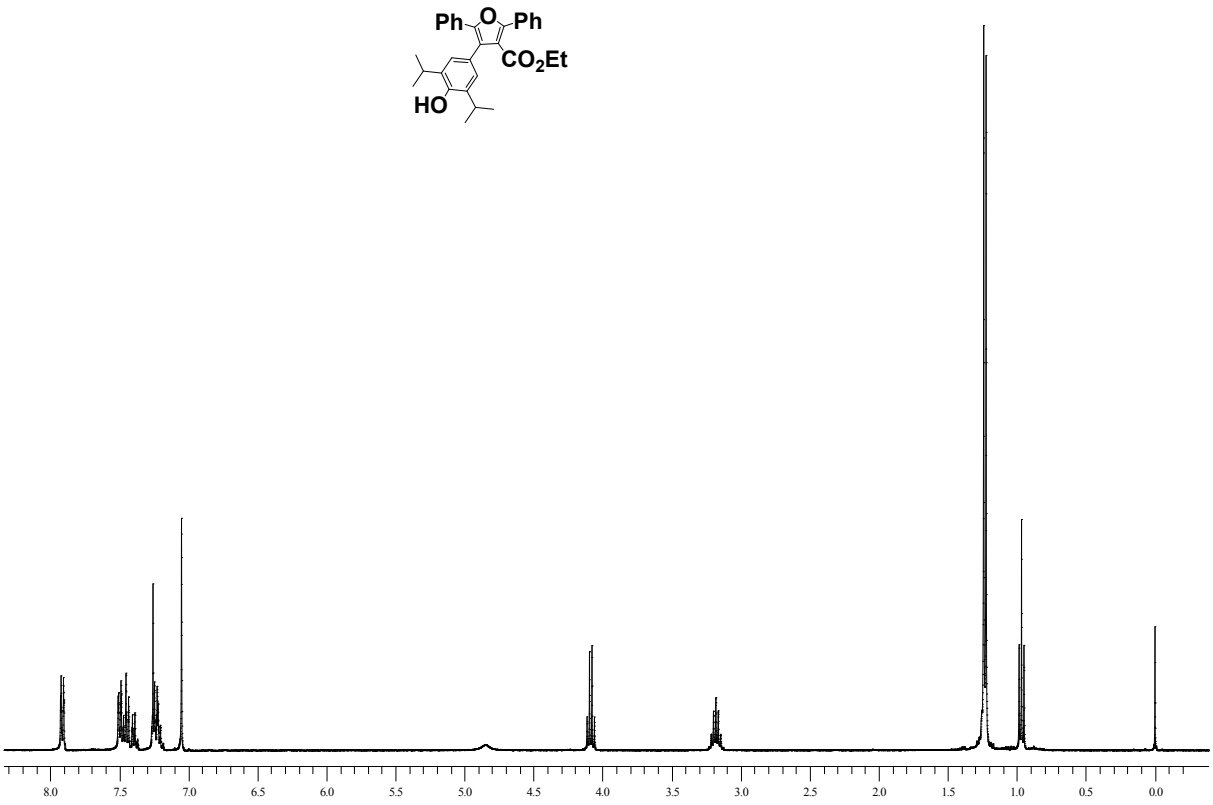
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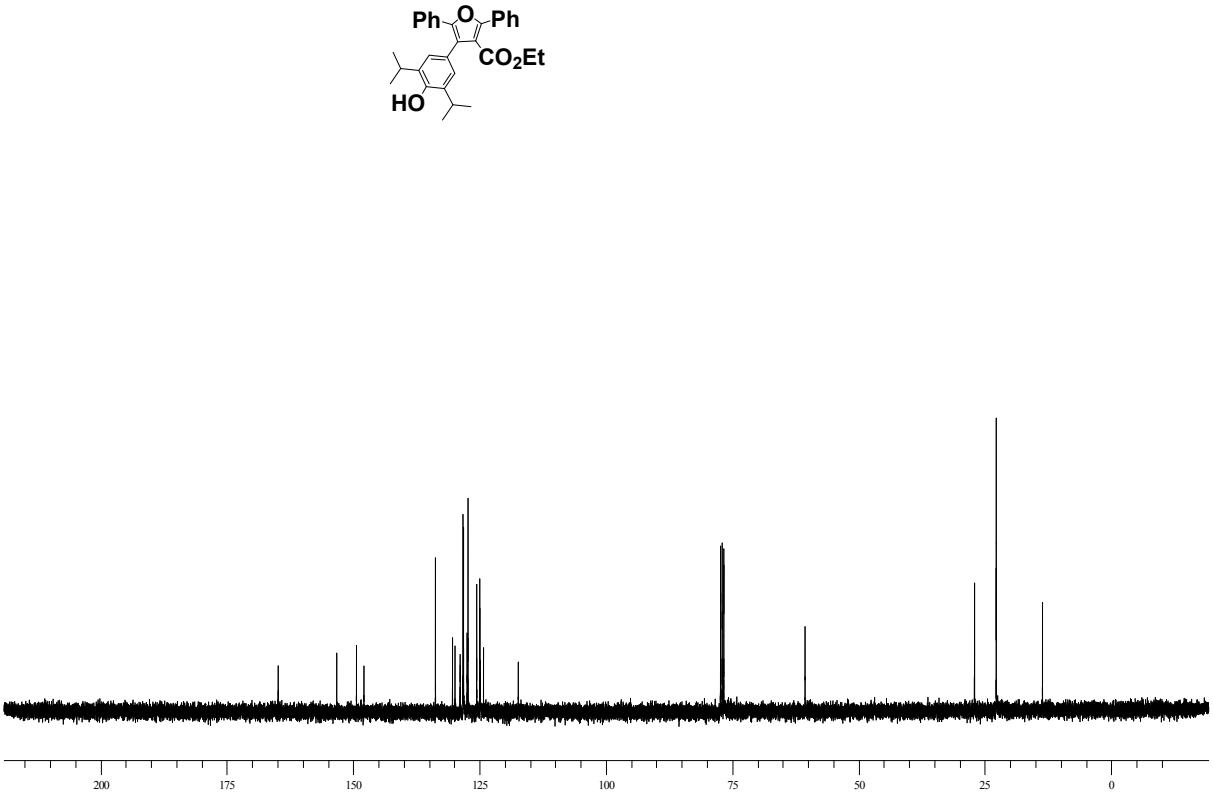
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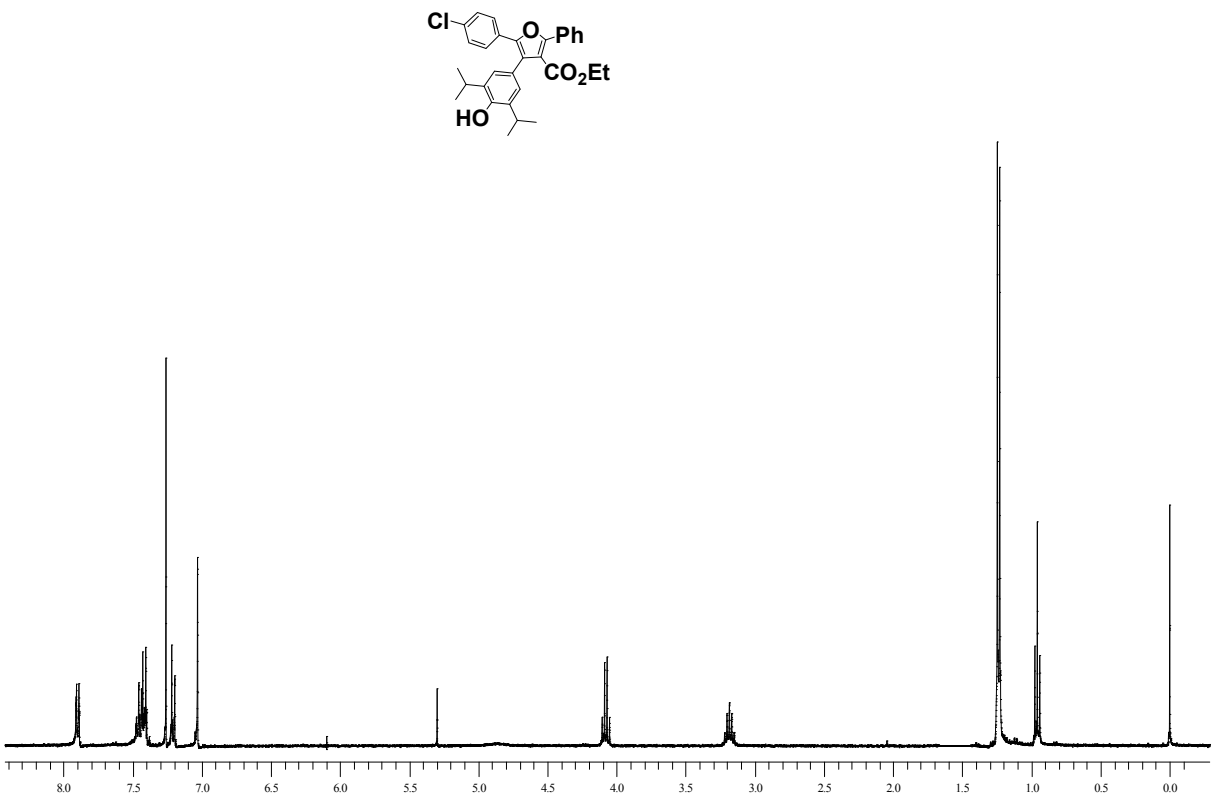
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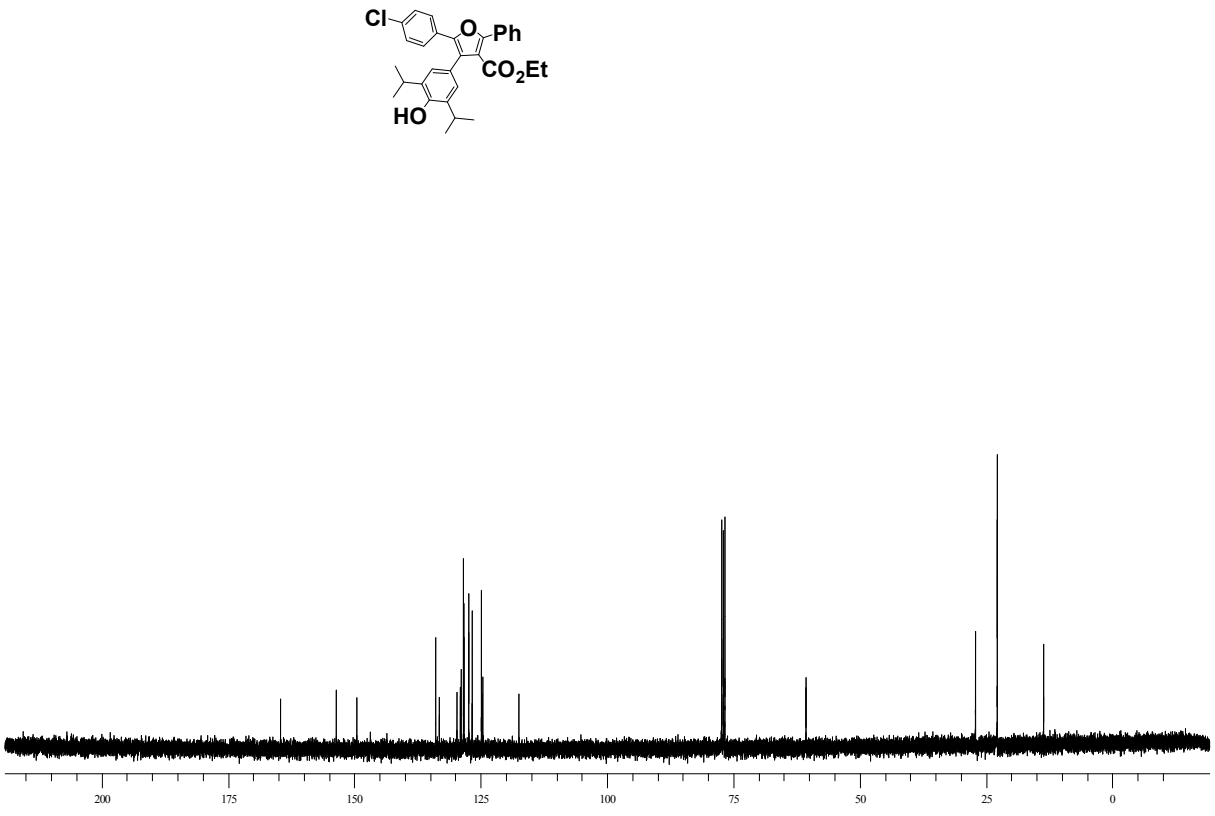
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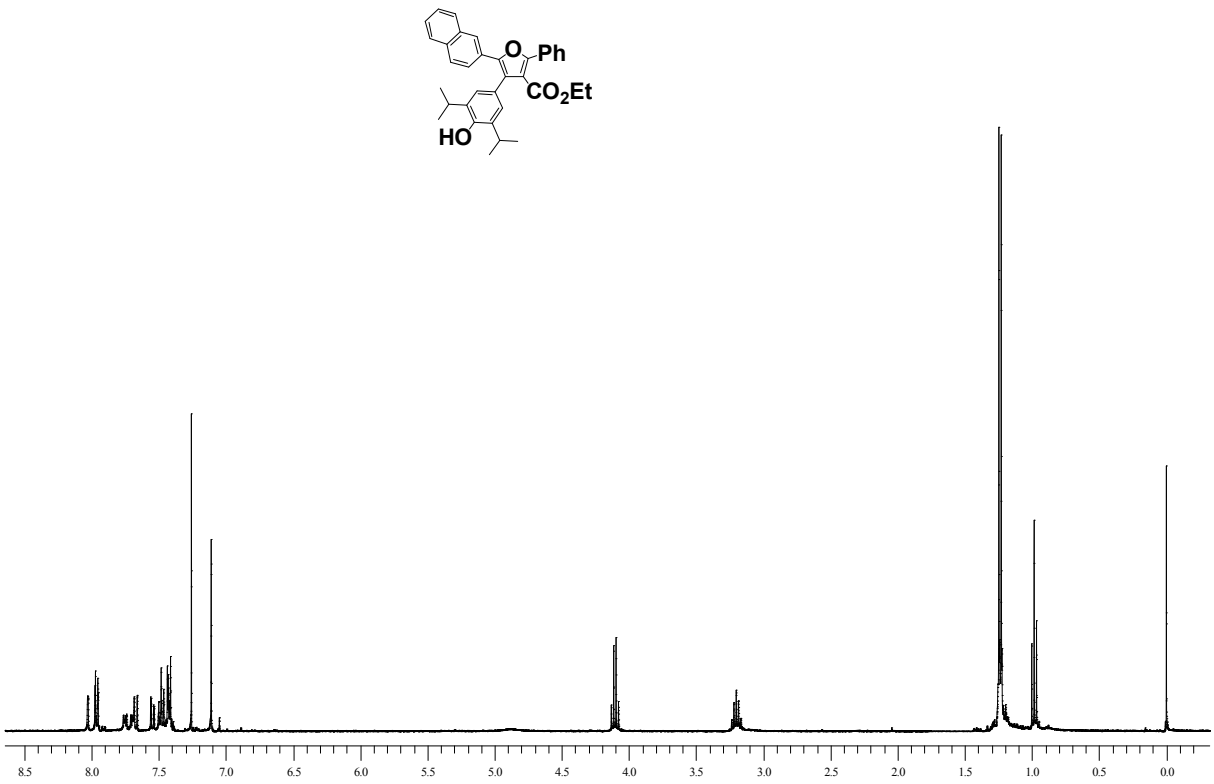
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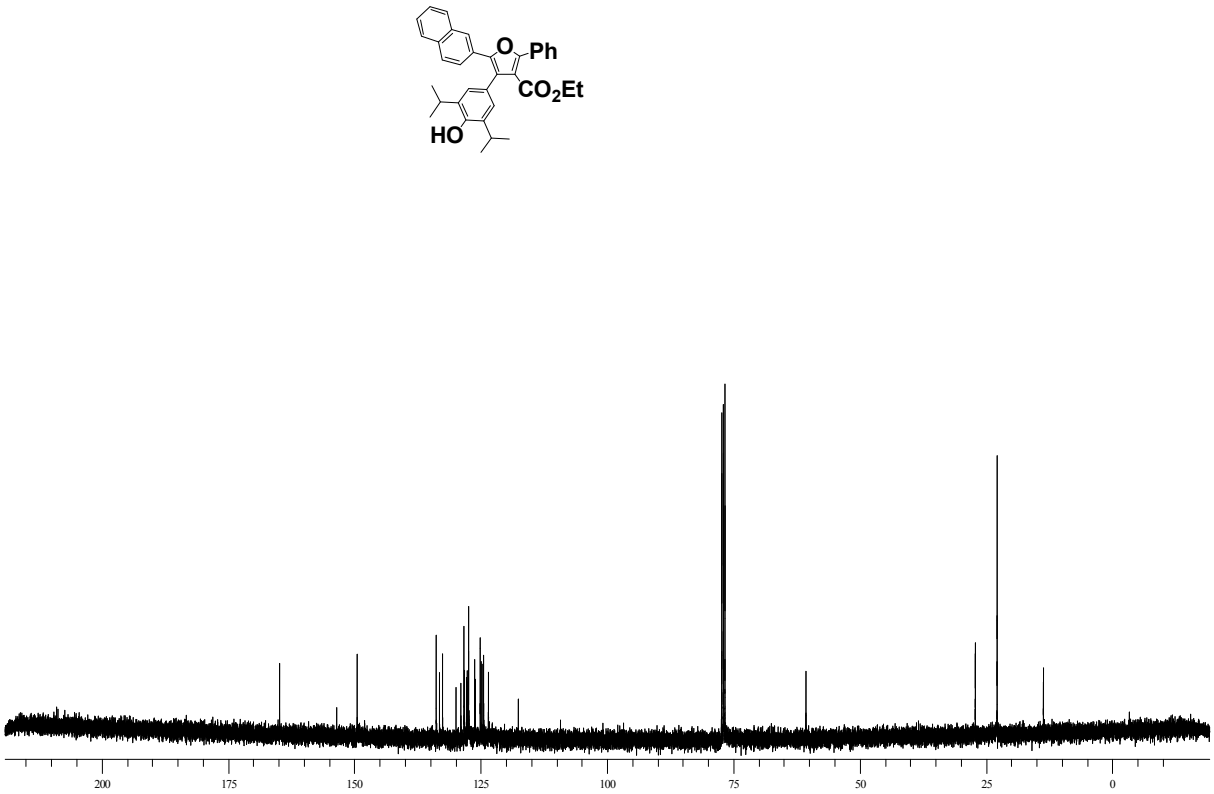
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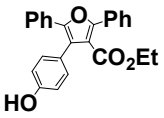
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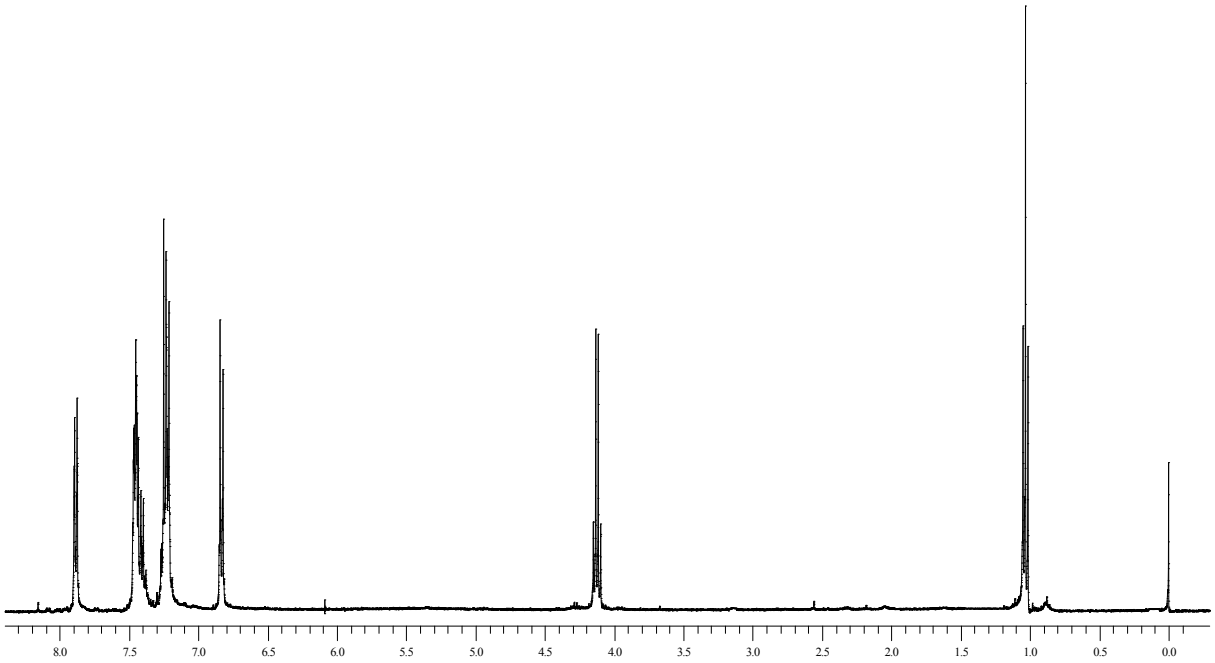
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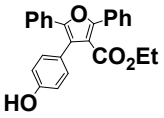
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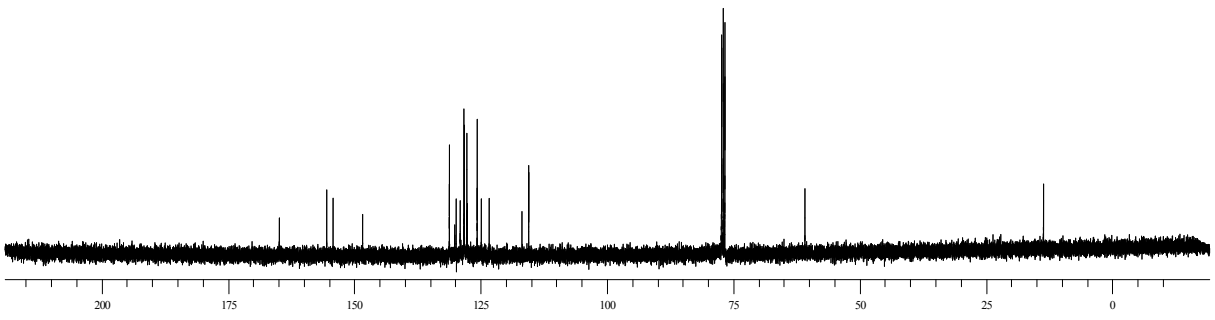
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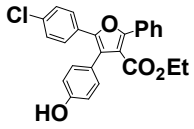
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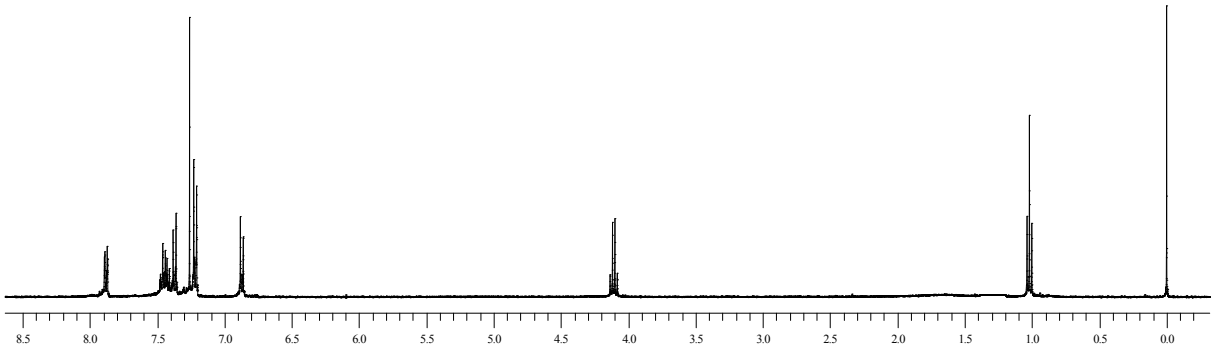
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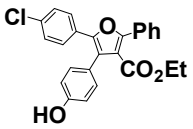
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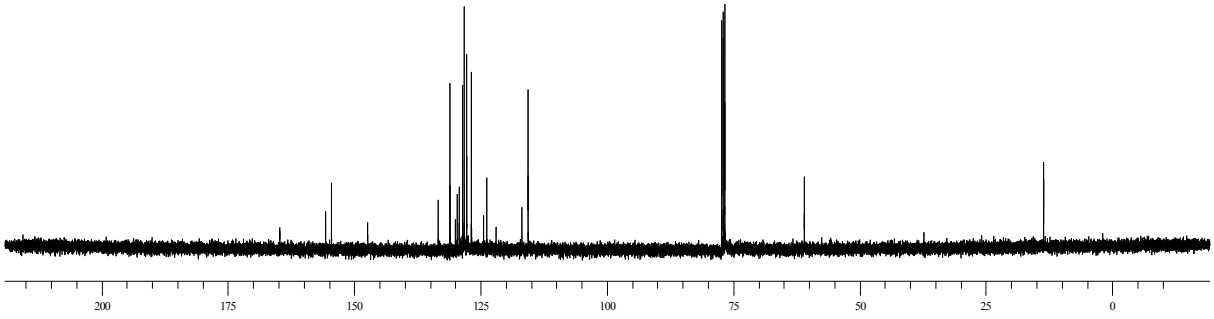
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