

Supporting Information

Synthesis of Multi-Substituted Furans via a Catalyst- and Additive-free Tandem Reaction of Enynones with Sulfinic Acids in Water

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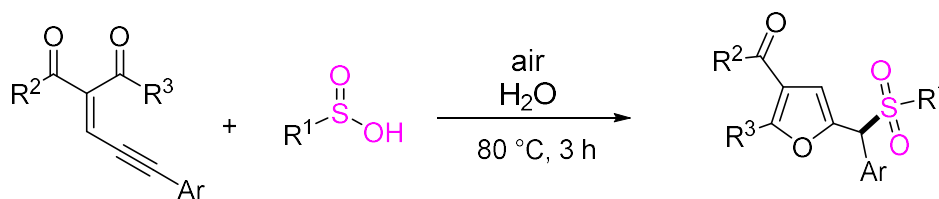
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1. General remarks

All reactions were conducted in clean glassware with magnetic stirring. Chromatographic purification was performed on silica gel and analytical thin layer chromatography (TLC) on silica gel 60-F₂₅₄ (Qindao), which was detected by fluorescence. ¹H NMR (400 MHz) and ¹³C NMR (100 MHz) spectra were measured with a Bruker AC 400 spectrometer with CDCl₃ as solvent and recorded in ppm relative to internal tetramethylsilane standard. NMR data are reported as follows: δ , chemical shift; coupling constants (*J* are given in Hertz, Hz) and integration. Abbreviations to denote the multiplicity of a particular signal were s (singlet), d (doublet), t (triplet), q (quartet), m (multiplet), and br (broad singlet). High resolution mass spectra were obtained with a Micromass GCT-TOF mass spectrometer. Melting points were determined on a digital melting point apparatus and temperatures were uncorrected. EPR spectra were recorded at room temperature using a Bruker A300 spectrometer.

2. General procedure for synthesis of substituted furans from enynones with sulfinic acids in water



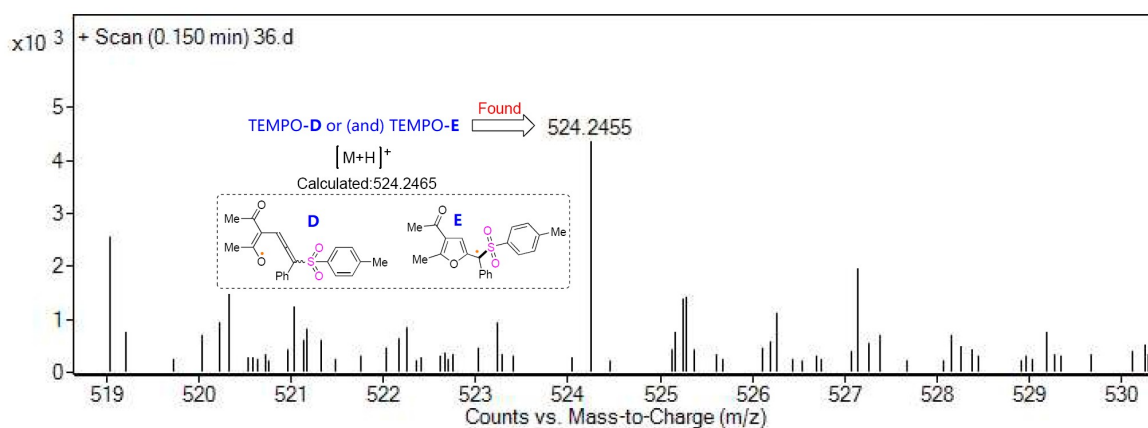
In 2.0 mL of an aqueous solution (tap water), enynone (0.25 mmol) and sulfinic acid (0.20 mmol) was added. The reaction mixture was heated in the air at 80 °C for 3 h. The residue was then purified by column chromatography on silica gel (petroleum ether/EtOAc = 10:1) to give the pure product.

The preparation of 1-(2-methyl-5-(phenyl(tosyl)methyl) furan-3-yl) ethanone (**3aa**) in 2.0 mmol and 5.0 mmol scale

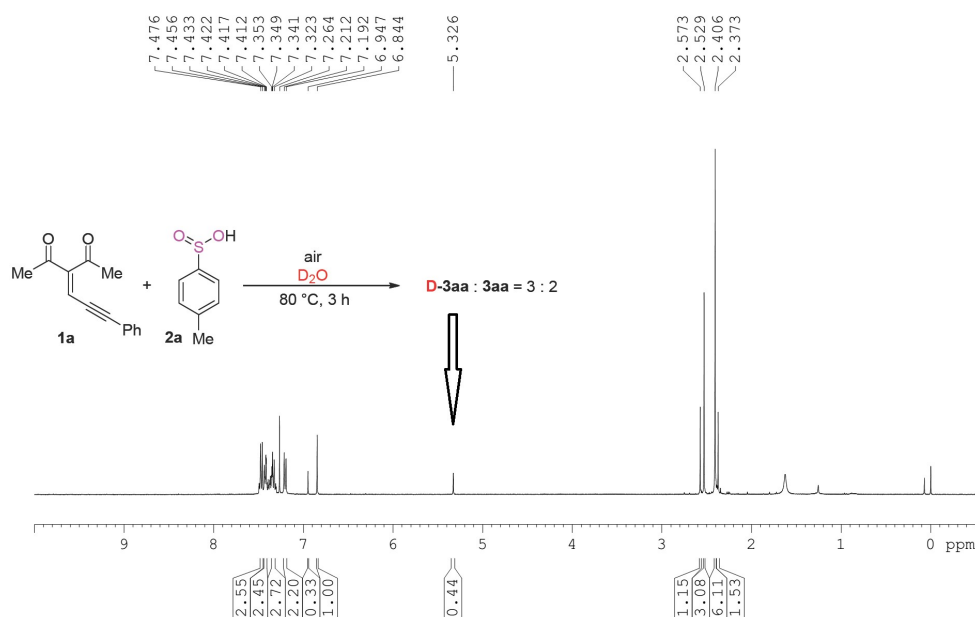
3-(3-Phenylprop-2-yn-1-ylidene)pentane-2,4-dione (580 mg, 2.5 mmol) and 4-methylbenzenesulfinic acid (312 mg, 2.0 mmol) were added in water (tap water, 25 mL), and the tandem reaction mixture was stirred at 80 °C for 12 h. The residue was then purified by silica gel column chromatography (petroleum ether/EtOAc = 10:1) to give pure product compound **3aa** (560 mg, 76% yield). If 5.0 mmol of 3-(3-phenylprop-2-yn-1-ylidene)pentane-2,4-dione (1.16 g) was added in the reaction, 72% yield of **3aa** was isolated.

3. HRMS spectra for detection of intermediate **D** or (and) **E**

HRMS (ESI) calcd for $C_{30}H_{38}NO_5S(M+H)^+$: 524.2465; Found: 524.2455

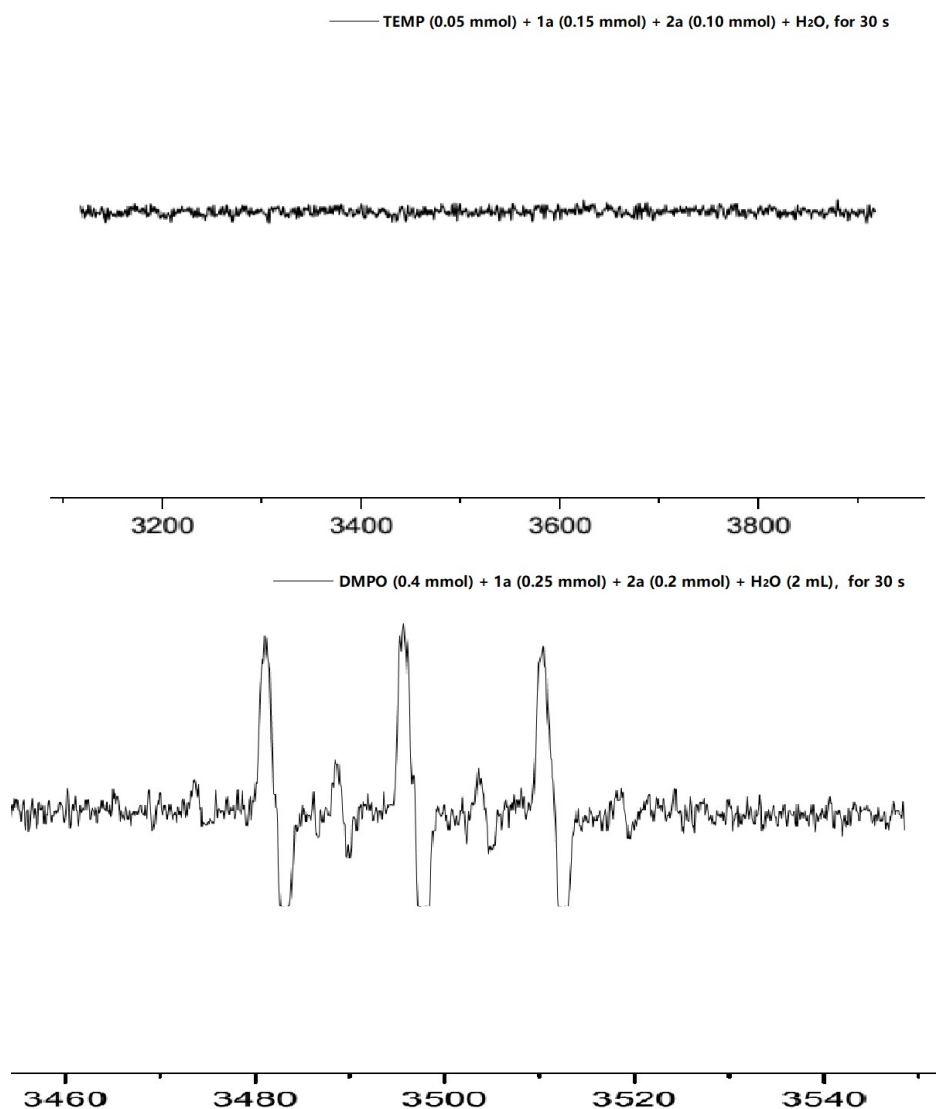


4. Deuterium experiment



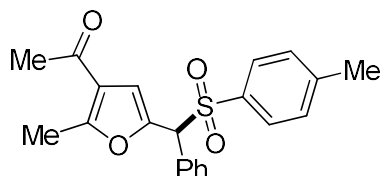
5. EPR experiments

When the 2,2,6,6-tetramethylpiperidine (TEMP) was employed as capture agents, no any signal was detected by electron paramagnetic resonance (EPR) experiments; furthermore, when 5,5-dimethyl-1-pyrroline-N-oxide (DMPO) was used as capture agents to trap some active intermediate, signals of hydroxyl radical ($\cdot\text{OH}$) was observed (the above test results as shown in the following spectra).



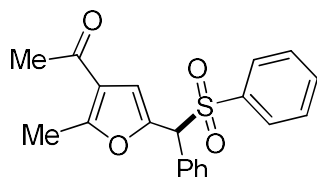
6. Characterization data for all products

1-(2-Methyl-5-(phenyl(tosyl)methyl)furan-3-yl)ethanone (3aa)



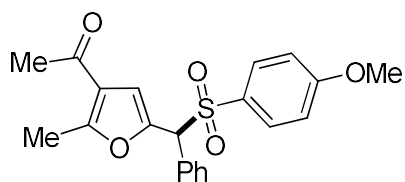
Yellow solid (69 mg, 94% yield). Mp: 115–116 °C. The compound was purified by flash chromatography on silica gel (eluent: petroleum ether/EtOAc = 10:1). ^1H NMR (400 MHz, CDCl_3): δ 7.47–7.41 (m, 4H), 7.35–7.29 (m, 3H), 7.20–7.18 (d, J = 8.0 Hz, 2H), 6.84 (s, 1H), 5.33 (s, 1H), 2.52 (s, 3H), 2.39 (s, 6H). ^{13}C NMR (100 MHz, CDCl_3): δ 193.7, 159.1, 144.9, 143.9, 134.4, 130.4, 130.2, 129.3, 129.2, 129.2, 128.6, 122.5, 112.2, 70.5, 29.1, 21.6, 14.3. MS (ESI) calcd for $\text{C}_{21}\text{H}_{21}\text{SO}_4$ ($\text{M}+\text{H}$) $^+$: 369.1155; Found: 369.1151.

1-(2-Methyl-5-(phenyl(phenylsulfonyl)methyl)furan-3-yl)ethanone (3ab)



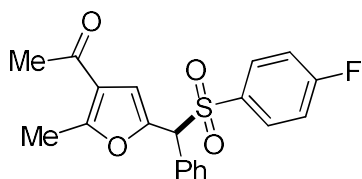
Yellow solid (55 mg, 78% yield). Mp: 135–136 °C. The compound was purified by flash chromatography on silica gel (eluent: petroleum ether/EtOAc = 10:1). ^1H NMR (400 MHz, CDCl_3): δ 7.60–7.55 (m, 3H), 7.44–7.37 (m, 4H), 7.35–7.28 (m, 3H), 6.84 (s, 1H), 5.37 (s, 1H), 2.51 (s, 3H), 2.38 (s, 3H). ^{13}C NMR (100 MHz, CDCl_3): δ 193.6, 159.1, 143.7, 137.4, 133.8, 130.3, 130.2, 129.2, 129.1, 128.7, 128.6, 122.5, 112.3, 70.5, 29.1, 14.3. MS (ESI) calcd for $\text{C}_{20}\text{H}_{19}\text{SO}_4$ ($\text{M}+\text{H}$) $^+$: 355.0999; Found: 355.0996.

1-(5-(((4-Methoxyphenyl)sulfonyl)(phenyl)methyl)-2-methylfuran-3-yl)ethanone (3ac)



Yellow solid (32 mg, 41% yield). Mp: 136–138 °C. The compound was purified by flash chromatography on silica gel (eluent: petroleum ether/EtOAc = 10:1). ¹H NMR (400 MHz, CDCl₃): δ 7.50 (d, *J* = 8.8 Hz, 2H), 7.42–7.40 (m, 2H), 7.36–7.30 (m, 3H), 6.86–6.84 (m, 3H), 5.31 (s, 1H), 3.84 (s, 3H), 2.53 (s, 3H), 2.40 (s, 3H). ¹³C NMR (100MHz, CDCl₃): δ 193.8, 163.9, 159.1, 144.0, 131.4, 130.6, 130.1, 129.1, 128.6, 122.5, 113.9, 112.1, 70.7, 55.6, 29.1, 14.4. MS (ESI) calcd for C₂₁H₂₁SO₄ (M+H)⁺: 385.1104; Found: 385.1108.

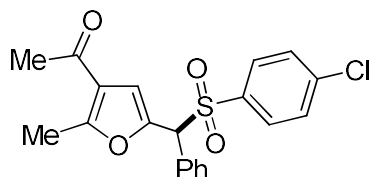
1-(5-(((4-Fluorophenyl)sulfonyl)(phenyl)methyl)-2-methylfuran-3-yl)ethanone (3ad)



Yellow solid (52 mg, 70% yield). Mp: 150–151 °C. The compound was purified by flash chromatography on silica gel (eluent: petroleum ether/EtOAc = 10:1). ¹H NMR (400 MHz, CDCl₃): δ 7.61–7.57 (m, 2H), 7.43–7.41 (m, 2H), 7.36–7.30 (m, 3H), 7.10 (t, *J* = 8.4 Hz, 2H), 6.86 (s, 1H), 5.36 (s, 1H), 2.53 (s, 3H), 2.40 (s, 3H). ¹³C NMR (100 MHz, CDCl₃): δ 193.5, 167.1 (d, *J* = 255.8 Hz), 159.2, 143.5, 133.3, 132.1 (d, *J* = 9.6 Hz), 130.2, 130.1, 129.4, 128.7,

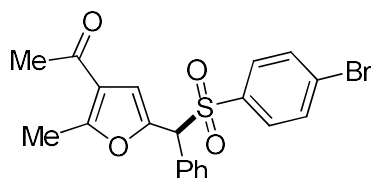
122.5, 116.1, (d, $J = 22.5$ Hz), 112.5, 70.6, 29.1, 14.3. MS (ESI) calcd for $C_{20}H_{18}FSO_4(M+H)^+$: 373.0904; Found: 373.0903.

1-(5-(((4-Chlorophenyl)sulfonyl)(phenyl)methyl)-2-methylfuran-3-yl)ethanone (3ae)



Yellow solid (67 mg, 86% yield). Mp: 165–166 °C. The compound was purified by flash chromatography on silica gel (eluent: petroleum ether/EtOAc = 10:1). 1H NMR (400 MHz, $CDCl_3$): δ 7.52 (d, $J = 8.8$ Hz, 2H), 7.43–7.41 (m, 2H), 7.38–7.31 (m, 5H), 6.86 (s, 1H), 5.36 (s, 1H), 2.53 (s, 3H), 2.40 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 193.6, 159.3, 143.3, 140.7, 135.8, 130.6, 130.2, 130.0, 129.4, 129.0, 128.8, 122.6, 112.6, 70.6, 29.1, 14.4. MS (ESI) calcd for $C_{20}H_{18}ClSO_4 (M+H)^+$: 389.0609; Found: 389.0606.

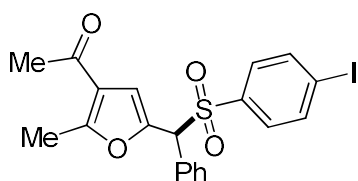
1-(5-(((4-Bromophenyl)sulfonyl)(phenyl)methyl)-2-methylfuran-3-yl)ethanone (3af)



Yellow solid (67 mg, 77% yield). Mp: 161–163 °C. The compound was purified by flash chromatography on silica gel (eluent: petroleum ether/EtOAc = 10:1). 1H NMR (400 MHz, $CDCl_3$): δ 7.56 (d, $J = 8.4$ Hz, 2H), 7.44–7.41

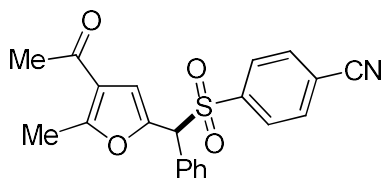
(m, 4H), 7.38–7.32 (m, 3H), 6.86 (s, 1H), 5.35 (s, 1H), 2.53 (s, 3H), 2.40 (s, 3H). ^{13}C NMR (100 MHz, CDCl_3): δ 193.5, 159.3, 143.3, 136.3, 132.0, 130.7, 130.2, 130.0, 129.4, 129.4, 128.8, 122.6, 112.5, 70.6, 29.1, 14.4. MS (ESI) calcd for $\text{C}_{20}\text{H}_{18}\text{BrSO}_4$ ($\text{M}+\text{H}$) $^+$: 433.0104; Found: 433.0109.

1-(5-(((4-Iodophenyl)sulfonyl)(phenyl)methyl)-2-methylfuran-3-yl)ethanone (3ag)



Yellow solid (70 mg, 73% yield). Mp: 143–145 °C. The compound was purified by flash chromatography on silica gel (eluent: petroleum ether/EtOAc = 10:1). ^1H NMR (400 MHz, CDCl_3): δ 7.77 (d, J = 8.4 Hz, 2H), 7.43–7.28 (m, 7H), 6.85 (s, 1H), 5.34 (s, 1H), 2.53 (s, 3H), 2.40 (s, 3H). ^{13}C NMR (100 MHz, CDCl_3): δ 193.6, 159.3, 143.3, 138.0, 137.0, 130.4, 130.2, 129.9, 129.4, 128.8, 122.5, 112.5, 102.1, 70.5, 29.1, 14.4. MS (ESI) calcd for $\text{C}_{20}\text{H}_{18}\text{ISO}_4$ ($\text{M}+\text{H}$) $^+$: 480.9965; Found: 480.9961.

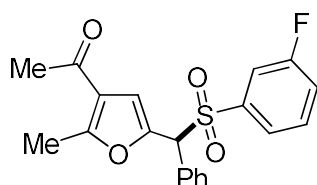
4-(((4-Acetyl-5-Methylfuran-2-yl)(phenyl)methyl)sulfonyl)benzonitrile (3ah)



Yellow solid (59 mg, 78% yield). Mp: 123–124 °C. The compound was purified by flash chromatography on silica gel (eluent: petroleum ether/EtOAc

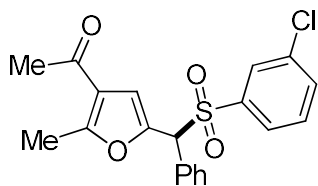
= 10:1). ^1H NMR (400 MHz, CDCl_3): δ 7.70 (s, 4H), 7.42–7.31 (m, 5H), 6.88 (s, 1H), 5.40 (s, 1H), 2.54 (s, 1H), 2.41 (s, 3H). ^{13}C NMR (100 MHz, CDCl_3): δ 193.4, 159.5, 142.7, 141.6, 132.4, 130.2, 129.9, 129.7, 129.5, 128.9, 122.7, 117.6, 117.0, 113.0, 70.6, 29.2, 14.4. MS (ESI) calcd for $\text{C}_{21}\text{H}_{18}\text{NSO}_4$ ($\text{M}+\text{H}$) $^+$: 380.0951; Found: 380.0956.

1-(5-(((3-Fluorophenyl)sulfonyl)(phenyl)methyl)-2-methylfuran-3-yl)ethanone (3ai)



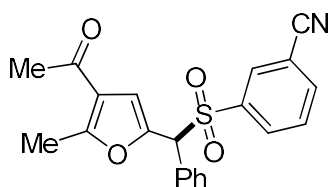
Yellow solid (54 mg, 72% yield). Mp: 130–132 °C. The compound was purified by flash chromatography on silica gel (eluent: petroleum ether/EtOAc = 10:1). ^1H NMR (400 MHz, CDCl_3): δ 7.45–7.27 (m, 9H), 6.86 (s, 1H), 5.38 (s, 1H), 2.53 (s, 3H), 2.40 (s, 3H). ^{13}C NMR (100 MHz, CDCl_3) : δ 193.5, 163.3 (d, J = 250.8 Hz), 160.2, 159.3, 143.2, 139.4 (d, J = 6.5 Hz), 130.5 (d, J = 7.4 Hz), 129.5, 128.8, 125.0, (d, J = 3.2 Hz), 122.6, 121.2 (d, J = 21.1 Hz), 116.6 (d, J = 24.2 Hz), 112.6, 70.5, 29.1, 14.3. MS (ESI) calcd for $\text{C}_{20}\text{H}_{18}\text{FSO}_4$ ($\text{M}+\text{H}$) $^+$: 373.0904; Found: 373.0907.

1-(5-(((3-Chlorophenyl)sulfonyl)(phenyl)methyl)-2-methylfuran-3-yl)ethanone (3aj)



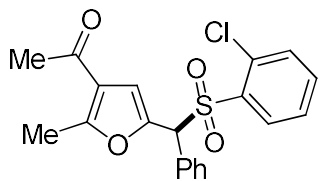
Yellow solid (66 mg, 85% yield). Mp: 121–122 °C. The compound was purified by flash chromatography on silica gel (eluent: petroleum ether/EtOAc = 10:1). ^1H NMR (400 MHz, CDCl_3): δ 7.57–7.53 (m, 2H), 7.47–7.43 (m, 3H), 7.38–7.32 (m, 4H), 6.85 (s, 1H), 5.38 (s, 1H), 2.54 (s, 3H), 2.40 (s, 3H). ^{13}C NMR (100 MHz, CDCl_3): δ 193.5, 159.3, 143.2, 139.0, 135.0, 134.0, 130.2, 129.9, 129.8, 129.5, 129.3, 128.8, 127.3, 122.6, 112.7, 70.6, 29.1, 14.3. MS (ESI) calcd for $\text{C}_{20}\text{H}_{18}\text{ClSO}_4$ ($\text{M}+\text{H}$) $^+$: 389.0609; Found: 389.0606.

3-(((4-Acetyl-5-methylfuran-2-yl)(phenyl)methyl)sulfonyl)benzonitrile (3ak)



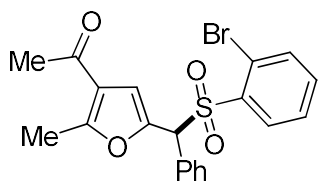
Yellow solid (61 mg, 80% yield). Mp: 123–124 °C. The compound was purified by flash chromatography on silica gel (eluent: petroleum ether/EtOAc = 10:1). ^1H NMR (400 MHz, CDCl_3): δ 7.86–7.85 (m, 2H), 7.80 (d, J = 8.0 Hz, 1H), 7.58 (t, J = 8.0 Hz, 1H), 7.43–7.33 (m, 5H), 6.88 (s, 1H), 5.41 (s, 1H), 2.55 (s, 3H), 2.41 (s, 3H). ^{13}C NMR (100 MHz, CDCl_3): δ 193.4, 159.5, 142.7, 139.0, 136.9, 133.1, 132.8, 130.2, 129.7, 129.7, 129.5, 128.9, 122.7, 116.7, 113.4, 113.0, 70.7, 29.1, 14.4. MS (ESI) calcd for $\text{C}_{21}\text{H}_{18}\text{NSO}_4$ ($\text{M}+\text{H}$) $^+$: 380.0951; Found: 380.0955.

**1-(5-(((2-Chlorophenyl)sulfonyl)(phenyl)methyl)-2-methylfuran-3-yl) ethanone
(3al)**



Yellow solid (70 mg, 90% yield). Mp: 119–120 °C. The compound was purified by flash chromatography on silica gel (eluent: petroleum ether/EtOAc = 10:1). ¹H NMR (400 MHz, CDCl₃): δ 7.76 (dd, *J* = 1.2, 7.6 Hz, 1H), 7.56–7.50 (m, 3H), 7.48 (td, *J* = 1.6, 7.2 Hz, 1H), 7.32–7.29 (m, 3H), 7.26 (td, *J* = 1.2, 7.2 Hz, 1H), 6.86 (s, 1H), 6.06 (s, 1H), 2.50 (s, 3H), 2.37 (s, 3H). ¹³C NMR (100 MHz, CDCl₃): δ 193.4, 159.5, 142.8, 140.8, 134.2, 133.6, 133.6, 131.3, 130.1, 129.6, 129.3, 128.8, 127.4, 122.6, 112.9, 68.1, 29.1, 14.3. MS (ESI) calcd for C₂₀H₁₈ClSO₄ (M+H)⁺: 389.0609; Found: 389.0604.

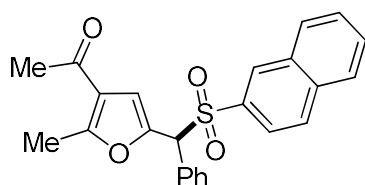
**1-(5-(((2-Bromophenyl)sulfonyl)(phenyl)methyl)-2-methylfuran-3-yl)ethanone
(3am)**



Yellow solid (73 mg, 84% yield). Mp: 134–135 °C. The compound was purified by flash chromatography on silica gel (eluent: petroleum ether/EtOAc = 10:1). ¹H NMR (400 MHz, CDCl₃): δ 7.77 (dd, *J* = 1.6, 8.0 Hz, 1H), 7.73 (dd, *J* = 0.80, 7.6 Hz, 1H), 7.56–7.54 (m, 2H), 7.38 (td, *J* = 1.6, 7.6 Hz, 1H), 7.32–7.25 (m, 4H), 6.86 (s, 1H), 6.18 (s, 1H), 2.50 (s, 3H), 2.37 (s, 3H). ¹³C

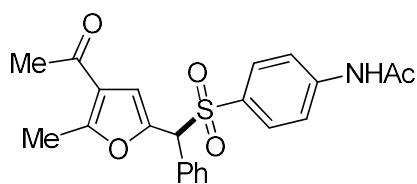
NMR (100 MHz, CDCl₃): δ 193.6, 159.4, 143.0, 137.1, 135.1, 134.7, 133.1, 130.2, 129.5, 129.4, 128.7, 127.6, 122.5, 120.9, 112.7, 67.2, 29.1, 14.3. MS (ESI) calcd for C₂₀H₁₈BrSO₄ (M+H)⁺: 435.0083; Found: 435.0083.

1-(2-Methyl-5-((naphthalen-2-ylsulfonyl)(phenyl)methyl)furan-3-yl)ethanone (3an)



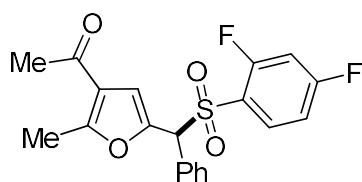
Yellow solid (64 mg, 79% yield). Mp: 138–140 °C. The compound was purified by flash chromatography on silica gel (eluent: petroleum ether/EtOAc = 10:1). ¹H NMR (400 MHz, CDCl₃): δ 8.17 (s, 1H), 7.89–7.82 (m, 3H), 7.67–7.63 (m, 1H), 7.60–7.57 (m, 1H), 7.54 (dd, *J* = 2.0, 8.8 Hz, 1H), 7.45–7.43 (m, 2H), 7.36–7.27 (m, 3H), 6.86 (s, 1H), 5.44 (s, 1H), 2.46 (s, 3H), 2.37 (s, 3H). ¹³C NMR (100 MHz, CDCl₃): δ 193.7, 159.2, 143.8, 135.2, 134.2, 131.8, 131.4, 130.3, 130.2, 129.4, 129.3, 129.3, 128.7, 128.7, 127.9, 127.6, 123.6, 122.5, 112.4, 70.7, 29.1, 14.3. MS (ESI) calcd for C₂₄H₂₁SO₄ (M+H)⁺: 405.1155; Found: 405.1148.

N-(3-(((4-Acetyl-5-methylfuran-2-yl)(phenyl)methyl)sulfonyl)phenyl)acetamide (3ao)



Yellow solid (67 mg, 82% yield). Mp: 100–101 °C. The compound was purified by flash chromatography on silica gel (eluent: petroleum ether/EtOAc = 10:1). ¹H NMR (400 MHz, CDCl₃): δ 8.17 (m, 1H), 7.59 (d, *J* = 8.8 Hz, 2H), 7.49 (d, *J* = 8.8 Hz, 2H), 7.43–7.41 (m, 2H), 7.37–7.29 (m, 3H), 6.83 (s, 1H), 5.35 (s, 1H), 2.52 (s, 3H), 2.39 (s, 3H), 2.15 (m, 3H). ¹³C NMR (100 MHz, CDCl₃): δ 193.9, 169.0, 159.3, 143.8, 143.4, 131.3, 130.4, 130.2, 130.2, 129.3, 128.7, 122.6, 118.7, 112.3, 70.6, 29.2, 24.6, 14.4. MS (ESI) calcd for C₂₂H₂₂NSO₅ (M+H)⁺: 412.1213; Found: 412.1216.

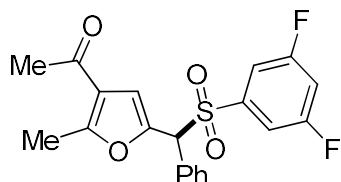
1-(5-(((2,4-Difluorophenyl)sulfonyl)(phenyl)methyl)-2-methylfuran-3-yl)ethanone (3ap)



Yellow solid (60 mg, 77% yield). Mp: 129–130 °C. The compound was purified by flash chromatography on silica gel (eluent: petroleum ether/EtOAc = 10:1). ¹H NMR (400 MHz, CDCl₃): δ 7.65–7.60 (m, 1H), 7.54–7.52 (m, 2H), 7.35–7.31 (m, 3H), 6.96–6.85 (m, 3H), 5.66 (s, 1H), 2.52 (s, 3H), 2.38 (s, 3H). ¹³C NMR (100 MHz, CDCl₃): δ 193.5, 167.9 (dd, *J* = 11.5, 258.1 Hz), 161.8 (dd, *J* = 13.0, 257.0 Hz), 159.5, 142.9, 133.5 (d, *J* = 9.8 Hz), 130.1, 129.6 (d, *J* = 17.5 Hz), 128.8, 122.5, 122.2 (dd, *J* = 3.6, 14.6 Hz), 122.2 (dd, *J* = 3.6, 14.6 Hz), 112.8, 112.3 (dd, *J* = 3.8, 21.9 Hz), 105.6 (t, *J* = 25.4 Hz), 69.8, 29.1, 14.3. MS (ESI) calcd for C₂₀H₁₇F₂SO₄ (M+H)⁺: 391.0810; Found:

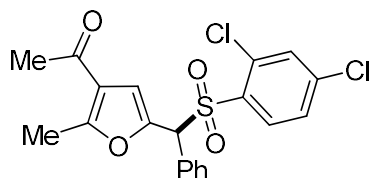
392.0812.

1-(5-(((3,5-Difluorophenyl)sulfonyl)(phenyl)methyl)-2-methylfuran-3-yl)ethanone (3aq)



Yellow solid (69 mg, 88% yield). Mp: 129–130 °C. The compound was purified by flash chromatography on silica gel (eluent: petroleum ether/EtOAc = 10:1). ¹H NMR (400 MHz, CDCl₃): δ 7.46–7.44 (m, 2H), 7.40–7.33 (m, 3H), 7.17–7.12 (m, 2H), 7.06–7.01 (m, 1H), 6.87 (s, 1H), 5.39 (s, 1H), 2.55 (s, 3H), 2.41 (s, 3H). ¹³C NMR (100 MHz, CDCl₃): δ 193.5, 163.7 (dd, *J* = 11.3, 254.2 Hz), 159.5, 142.8, 140.8 (t, *J* = 8.3 Hz), 131.2, 130.1, 129.7, 129.5, 128.9, 122.6, 112.9, 112.8 (d, *J* = 11.7 Hz), 112.6, 109.8 (t, *J* = 24.7 Hz), 70.6, 29.1, 14.3. MS (ESI) calcd for C₂₀H₁₇F₂SO₄ (M+H)⁺: 391.0810; Found: 391.0816.

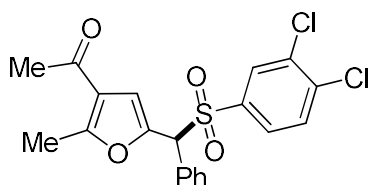
1-(5-(((2,4-Dichlorophenyl)sulfonyl)(phenyl)methyl)-2-methylfuran-3-yl)ethanone (3ar)



Yellow solid (75 mg, 89% yield). Mp: 151–153 °C. The compound was purified by flash chromatography on silica gel (eluent: petroleum ether/EtOAc = 10:1). ¹H NMR (400 MHz, CDCl₃): δ 7.68 (d, *J* = 8.8 Hz, 1H), 7.54–7.52

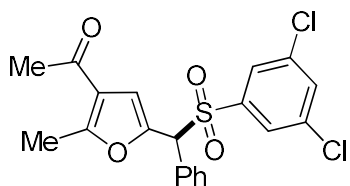
(m, 3H), 7.35–7.29 (m, 3H), 7.23 (dd, $J = 2.0, 8.0$ Hz, 1H), 6.87 (s, 1H), 6.00 (s, 1H), 2.52 (s, 3H), 2.38 (s, 3H). ^{13}C NMR (100 MHz, CDCl_3): δ 193.5, 159.6, 142.7, 140.8, 134.2, 133.6, 133.6, 131.3, 130.1, 129.6, 129.3, 128.8, 127.4, 122.5, 112.9, 68.0, 29.1, 14.4. MS (ESI) calcd for $\text{C}_{20}\text{H}_{17}\text{Cl}_2\text{SO}_4$ ($\text{M}+\text{H}$) $^+$: 423.0219; Found: 423.0224.

1-(5-(((3,4-Dichlorophenyl)sulfonyl)(phenyl)methyl)-2-methylfuran-3-yl)ethanone (3as)



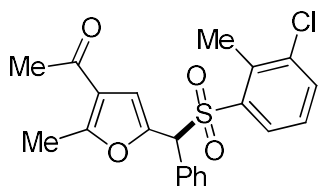
Yellow solid (68 mg, 80% yield). Mp: 161–163 °C. The compound was purified by flash chromatography on silica gel (eluent: petroleum ether/EtOAc = 10:1). ^1H NMR (400 MHz, CDCl_3): δ 7.65 (d, $J = 2.0$ Hz, 1H), 7.49–7.33 (m, 7H), 6.86 (s, 1H), 5.37 (s, 1H), 2.55 (s, 3H), 2.41 (s, 3H). ^{13}C NMR (100 MHz, CDCl_3): δ 193.4, 159.4, 143.0, 139.0, 137.0, 133.5, 131.2, 130.7, 130.2, 129.7, 129.6, 128.9, 128.2, 122.6, 112.8, 70.8, 29.1, 14.3. MS (ESI) calcd for $\text{C}_{20}\text{H}_{17}\text{Cl}_2\text{SO}_4$ ($\text{M}+\text{H}$) $^+$: 423.0219; Found: 423.0220.

1-(5-(((3,5-Dichlorophenyl)sulfonyl)(phenyl)methyl)-2-methylfuran-3-yl)ethanone (3at)



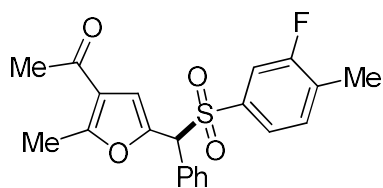
Yellow solid (42 mg, 50% yield). Mp: 148–149 °C. The compound was purified by flash chromatography on silica gel (eluent: petroleum ether/EtOAc = 10:1). ¹H NMR (400 MHz, CDCl₃): δ 7.56 (t, *J* = 1.6 Hz, 1H), 7.46–7.42 (m, 4H), 7.41–7.37 (m, 3H), 6.85 (s, 1H), 5.36 (s, 1H), 2.56 (s, 3H), 2.41 (s, 3H). ¹³C NMR (100 MHz, CDCl₃): δ 193.5, 159.5, 142.8, 140.1, 135.7, 133.7, 130.2, 129.8, 129.4, 128.9, 127.6, 122.6, 113.0, 70.9, 29.1, 14.3. MS (ESI) calcd for C₂₀H₁₇Cl₂SO₄ (M+H)⁺: 423.0219; Found: 423.0218.

1-(5-(((3-Chloro-2-methylphenyl)sulfonyl)(phenyl)methyl)-2-methylfuran-3-yl) ethanone (3au)



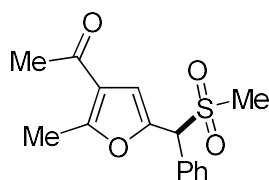
Yellow solid (57 mg, 71% yield). Mp: 140–141 °C. The compound was purified by flash chromatography on silica gel (eluent: petroleum ether/EtOAc = 10:1). ¹H NMR (400 MHz, CDCl₃): δ 7.63 (dd, *J* = 0.8, 8.0 Hz, 1H), 7.57 (d, *J* = 8.0 Hz, 1H), 7.45–7.43 (m, 2H), 7.37–7.29 (m, 3H), 7.15 (t, *J* = 8.0 Hz, 1H), 6.84 (s, 1H), 5.46 (s, 1H), 2.63 (s, 3H), 2.49 (s, 3H), 2.38 (s, 3H). ¹³C NMR (100 MHz, CDCl₃): δ 193.5, 159.2, 143.3, 137.8, 136.9, 136.8, 134.6, 130.2, 129.6, 129.5, 128.8, 126.6, 122.5, 112.6, 70.0, 29.1, 17.0, 14.3. MS (ESI) calcd for C₂₁H₂₀ClSO₄ (M+H)⁺: 403.0765; Found: 403.0767.

1-(5-(((3-Fluoro-4-methylphenyl)sulfonyl)(phenyl)methyl)-2-methylfuran-3-yl) ethanone (3av)



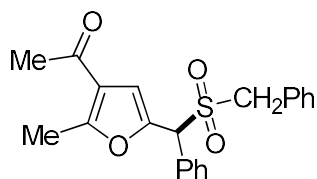
Yellow solid (63 mg, 82% yield). Mp: 133–134 °C. The compound was purified by flash chromatography on silica gel (eluent: petroleum ether/EtOAc = 10:1). ^1H NMR (400 MHz, CDCl_3): δ 7.44–7.42 (m, 2H), 7.37–7.31 (m, 3H), 7.28–7.22 (m, 3H), 6.86 (s, 1H), 5.37 (s, 1H), 2.53 (s, 3H), 2.39 (s, 3H), 2.31 (d, J = 1.6 Hz, 3H). ^{13}C NMR (100 MHz, CDCl_3): δ 193.6, 161.7 (d, J = 248.0 Hz), 159.2, 143.5, 136.4 (d, J = 6.4 Hz), 132.2 (d, J = 17.1 Hz), 131.7 (d, J = 4.6 Hz), 130.1, 130.1, 129.4, 128.7, 124.8 (d, J = 3.7 Hz), 122.5, 116.1 (d, J = 25.4 Hz), 112.5, 70.5, 29.1, 14.8, 14.3. MS (ESI) calcd for $\text{C}_{21}\text{H}_{20}\text{FSO}_4$ ($\text{M}+\text{H}$) $^+$: 387.1061; Found: 387.1060.

1-(2-Methyl-5-((methylsulfonyl)(phenyl)methyl)furan-3-yl)ethanone (3aw)



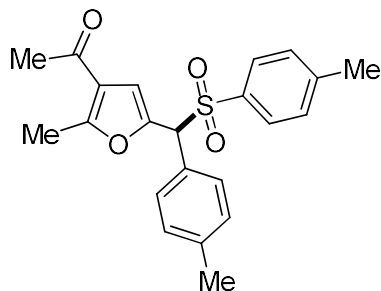
Yellow solid (49 mg, 84% yield). Mp: 110–112 °C. The compound was purified by flash chromatography on silica gel (eluent: petroleum ether/EtOAc = 10:1). ^1H NMR (400 MHz, CDCl_3): δ 7.64–7.61 (m, 2H), 7.46–7.43 (m, 3H), 6.89 (s, 1H), 5.39 (s, 1H), 2.85 (s, 3H), 2.62 (s, 3H), 2.41 (s, 3H). ^{13}C NMR (100 MHz, CDCl_3): δ 193.6, 159.4, 143.8, 130.2, 129.8, 129.6, 129.1, 122.6, 112.3, 68.8, 39.3, 29.1, 14.4. MS (ESI) calcd for $\text{C}_{15}\text{H}_{17}\text{SO}_4$ ($\text{M}+\text{H}$) $^+$: 293.0842; Found: 293.0840.

1-(5-((Benzylsulfonyl)(phenyl)methyl)-2-methylfuran-3-yl)ethanone (3ax)



Yellow solid (52 mg, 70% yield). Mp: 124–126 °C. The compound was purified by flash chromatography on silica gel (eluent: petroleum ether/EtOAc = 10:1). ^1H NMR (400 MHz, CDCl_3): δ 7.55–7.52 (m, 2H), 7.43–7.41 (m, 3H), 7.38–7.36 (m, 3H), 7.29–7.26 (m, 2H), 6.86 (s, 1H), 5.23 (s, 1H), 4.28–4.16 (m, 2H), 2.58 (s, 3H), 2.38 (s, 3H). ^{13}C NMR (100 MHz, CDCl_3): δ 193.6, 159.2, 143.9, 130.8, 130.1, 129.7, 129.5, 129.0, 129.0, 128.9, 127.2, 122.7, 112.4, 65.6, 58.1, 29.1, 14.4. MS (ESI) calcd for $\text{C}_{21}\text{H}_{21}\text{SO}_4$ ($\text{M}+\text{H}$) $^+$: 369.1155; Found: 369.1153.

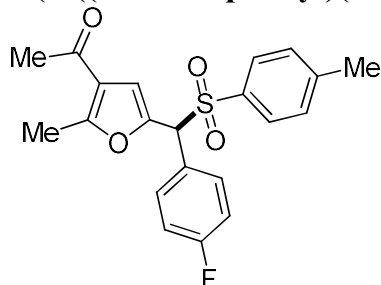
1-(2-Methyl-5-(*p*-tolyl(tosyl)methyl)furan-3-yl)ethanone (3ba)



Yellow solid (66 mg, 86% yield). Mp: 177–178 °C. The compound was purified by flash chromatography on silica gel (eluent: petroleum ether/EtOAc = 10:1). ^1H NMR (400 MHz, CDCl_3): δ 7.48 (d, J = 8.0 Hz, 2H), 7.32 (d, J = 8.0 Hz, 2H), 7.21 (d, J = 8.0 Hz, 2H), 7.14 (d, J = 8.0 Hz, 2H), 6.81 (s, 1H), 5.29 (s, 1H), 2.51 (s, 3H), 2.40–2.39 (m, 6H), 2.34 (s, 3H). ^{13}C NMR (100 MHz, CDCl_3): δ 193.8, 159.0, 144.8, 144.2, 139.2, 134.5, 130.0, 129.3, 129.3,

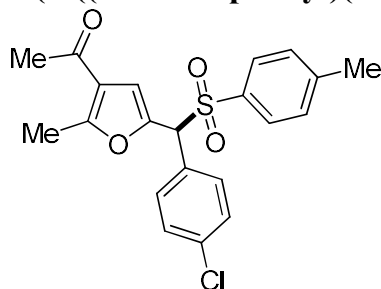
129.2, 127.3, 122.4, 112.0, 70.2, 29.1, 21.6, 21.2, 14.3. MS (ESI) calcd for $C_{22}H_{22}SNaO_4$ ($M+Na$)⁺: 405.1131; Found: 405.1139.

1-(5-((4-Fluorophenyl)(tosyl)methyl)-2-methylfuran-3-yl)ethanone (3ca)



Yellow solid (59 mg, 76% yield). Mp: 151–153 °C. The compound was purified by flash chromatography on silica gel (eluent: petroleum ether/EtOAc = 10:1). ¹H NMR (400 MHz, CDCl₃): δ 7.48 (d, *J* = 8.4 Hz, 2H), 7.43–7.39 (m, 2H), 7.23 (d, *J* = 8.0 Hz, 2H), 7.04 (t, *J* = 8.8 Hz, 2H), 6.81 (s, 1H), 5.31 (s, 1H), 2.53 (s, 3H), 2.41 (d, *J* = 4.8 Hz, 6H). ¹³C NMR (100 MHz, CDCl₃): δ 193.6, 164.4 (d, *J* = 247.9 Hz), 159.2, 145.1, 143.6, 134.1, 132.1 (d, *J* = 8.5 Hz), 129.4, 129.2, 126.3, 122.5, 115.8 (d, *J* = 21.6 Hz), 112.3, 69.6, 29.1, 21.6, 14.3. MS (ESI) calcd for $C_{21}H_{20}FSO_4$ ($M+H$)⁺: 387.1061; Found: 387.1065.

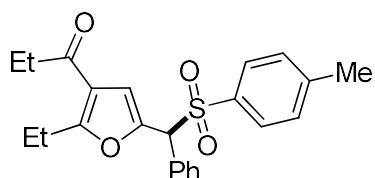
1-(5-((4-Chlorophenyl)(tosyl)methyl)-2-methylfuran-3-yl)ethanone (3da)



Yellow solid (73 mg, 90% yield). Mp: 160–162 °C. The compound was purified by flash chromatography on silica gel (eluent: petroleum ether/EtOAc

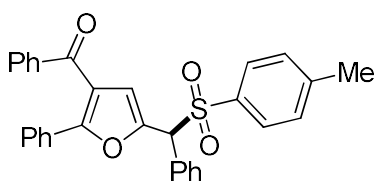
= 10:1). ^1H NMR (400 MHz, CDCl_3): δ 7.48 (d, J = 8.4 Hz, 2H), 7.39–7.36 (m, 2H), 7.30–7.27 (m, 2H), 7.23 (d, J = 8.4 Hz, 2H), 6.80 (s, 1H), 5.32 (s, 1H), 2.51 (s, 3H), 2.40 (s, 3H), 2.38 (s, 3H). ^{13}C NMR (100 MHz, CDCl_3): δ 193.5, 159.2, 145.2, 143.4, 135.4, 134.1, 131.5, 129.4, 129.1, 128.9, 128.8, 122.5, 112.3, 69.7, 29.1, 21.6, 14.3. MS (ESI) calcd for $\text{C}_{21}\text{H}_{19}\text{ClNaSO}_4$ ($\text{M}+\text{Na}$) $^+$: 425.0585; Found: 425.0587.

1-(2-Ethyl-5-(phenyl(tosyl)methyl)furan-3-yl)propan-1-one (3ea)



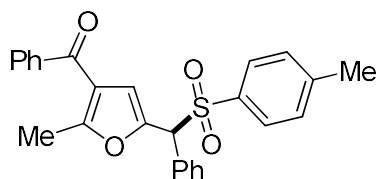
Yellow solid (64 mg, 81% yield). Mp: 117–119 °C. The compound was purified by flash chromatography on silica gel (eluent: petroleum ether/EtOAc = 10:1). ^1H NMR (400 MHz, CDCl_3): δ 7.48–7.45 (m, 4H), 7.37–7.31 (m, 3H), 7.20 (d, J = 8.0 Hz, 2H), 6.83 (s, 1H), 5.35 (s, 1H), 2.97–2.91 (m, 2H), 2.76–2.70 (m, 2H), 2.39 (s, 3H), 1.15–1.11 (m, 6H). ^{13}C NMR (100 MHz, CDCl_3): δ 196.6, 163.8, 144.9, 143.8, 134.4, 130.4, 130.2, 129.3, 129.2, 128.6, 121.0, 111.8, 70.6, 34.4, 21.5, 11.7, 7.7. MS (ESI) calcd for $\text{C}_{23}\text{H}_{25}\text{SO}_4$ ($\text{M}+\text{H}$) $^+$: 397.1468; Found: 397.1467.

Phenyl(2-phenyl-5-(phenyl(tosyl)methyl)furan-3-yl)methanone (3fa)



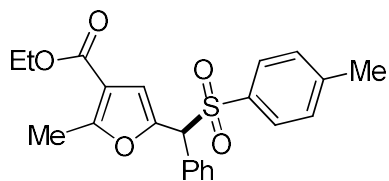
Yellow solid (32 mg, 32% yield). Mp: 156–158 °C. The compound was purified by flash chromatography on silica gel (eluent: petroleum ether/EtOAc = 10:1). ¹H NMR (400 MHz, CDCl₃): δ 7.78 (d, *J* = 7.6 Hz, 2H), 7.60–7.54 (m, 7H), 7.40–7.36 (m, 5H), 7.29–7.27 (m, 3H), 7.23 (d, *J* = 8.0 Hz, 2H), 6.80 (s, 1H), 5.47 (s, 1H), 2.38 (s, 3H). ¹³C NMR (100 MHz, CDCl₃): δ 191.1, 156.4, 145.0, 144.9, 137.7, 134.6, 133.0, 130.4, 130.1, 129.6, 129.5, 129.3, 129.3, 129.3, 129.1, 128.7, 128.4, 128.3, 127.5, 121.7, 115.5, 70.7, 21.6. MS (ESI) calcd for C₃₁H₂₅SO₄ (M+H)⁺: 493.1468; Found: 493.1465.

1-(2-Phenyl-5-(*p*-tolyl(tosyl)methyl)furan-3-yl)ethanone (3ga)



Yellow solid (40 mg, 46% yield). Mp: 143–144 °C. The compound was purified by flash chromatography on silica gel (eluent: petroleum ether/EtOAc = 10:1). ¹H NMR (400 MHz, CDCl₃): δ 7.74 (d, *J* = 7.6 Hz, 2H), 7.58–7.54 (m, 1H), 7.51–7.45 (m, 6H), 7.36–7.30 (m, 3H), 7.22 (d, *J* = 8.0 Hz, 2H), 6.73 (s, 1H), 5.36 (s, 1H), 2.49 (s, 3H), 2.40 (s, 3H). ¹³C NMR (100 MHz, CDCl₃): δ 190.7, 160.2, 144.9, 143.8, 138.7, 134.4, 132.3, 130.3, 130.3, 129.4, 129.2, 129.2, 128.9, 128.6, 128.4, 121.5, 113.6, 70.6, 21.6, 14.2. MS (ESI) calcd for C₂₆H₂₃SO₄ (M+H)⁺: 431.1312; Found: 431.1311.

Ethyl 2-methyl-5-(phenyl(tosyl)methyl)furan-3-carboxylate (3ha)



Yellow solid (45 mg, 57% yield). Mp: 121–123 °C. The compound was purified by flash chromatography on silica gel (eluent: petroleum ether/EtOAc = 10:1). ^1H NMR (400 MHz, CDCl_3): δ 7.48–7.41 (m, 4H), 7.34–7.31 (m, 3H), 7.20 (d, J = 8.0 Hz, 2H), 6.85 (s, 1H), 5.32 (s, 1H), 4.29 (q, J = 7.6 Hz, 2H), 2.50 (s, 3H), 2.39 (s, 3H), 1.35 (t, J = 7.2 Hz, 3H). ^{13}C NMR (100 MHz, CDCl_3): δ 163.5, 159.8, 144.8, 143.9, 134.5, 130.5, 130.2, 129.3, 129.2, 129.1, 128.5, 114.9, 112.6, 70.6, 60.2, 21.5, 14.3, 13.7. MS (ESI) calcd for $\text{C}_{22}\text{H}_{22}\text{SO}_5\text{Na}$ ($\text{M}+\text{Na}$) $^+$: 421.1080; Found: 421.1080.

7. ^1H and ^{13}C NMR spectra of the products

