

Electronic Supporting Information

Cu(I)-Catalyzed Stereoselective Synthesis of Trisubstituted *Z*-Enol Esters *via*

Interrupting 1,3-*O*-Transposition Reaction

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1. Condition optimization.

Table ESI 1. Optimization of reaction conditions.^a

Entry	cat. (5 mol %)	T (°C)	conv. (%)	yield (%) ^b	
				3a	4a
1		r.t.	0	--	--
2	Cu(OTf) ₂	r.t.	90	36	42
3	CuCl	r.t.	47	35	<5
4	CuCl	40	90	77	<5
5 ^c	CuCl	60	100	87	7
6^d	CuCl	60	100	86	8
7	CuBr	60	92	73	11
8	CuI	60	65	53	6
9	Cu(OTf) ₂	60	100	12	35
10	Cu(OAc) ₂	60	100	79	13
11 ^{d,e}	CuCl	60	100	82	7
12 ^{d,f}	CuCl	60	75	42	10
13 ^{d,g}	CuCl	60	60	35	9
14 ^{d,h}	CuCl	60	50	25	<5
15	CuCl (1 mol%)	60	42	36	<5

^aUnless otherwise noted, the reaction was performed with **1a** (0.2 mmol) and **2a** (0.4 mmol) in DCE (2 mL), 24 h, under N₂.

^bDetermined by ¹H NMR using CH₃NO₂ as internal standard.

^cThe reaction was carried out for 6 h.

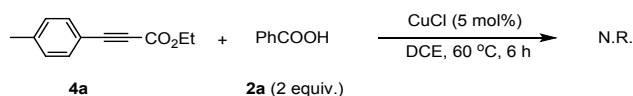
^dAir atmosphere, 6 h.

^ePhMe as solvent.

^fCH₃CN as solvent.

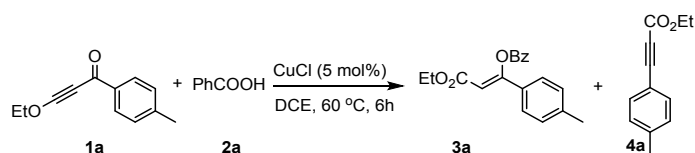
^gTHF as solvent.

^hDMSO as solvent.



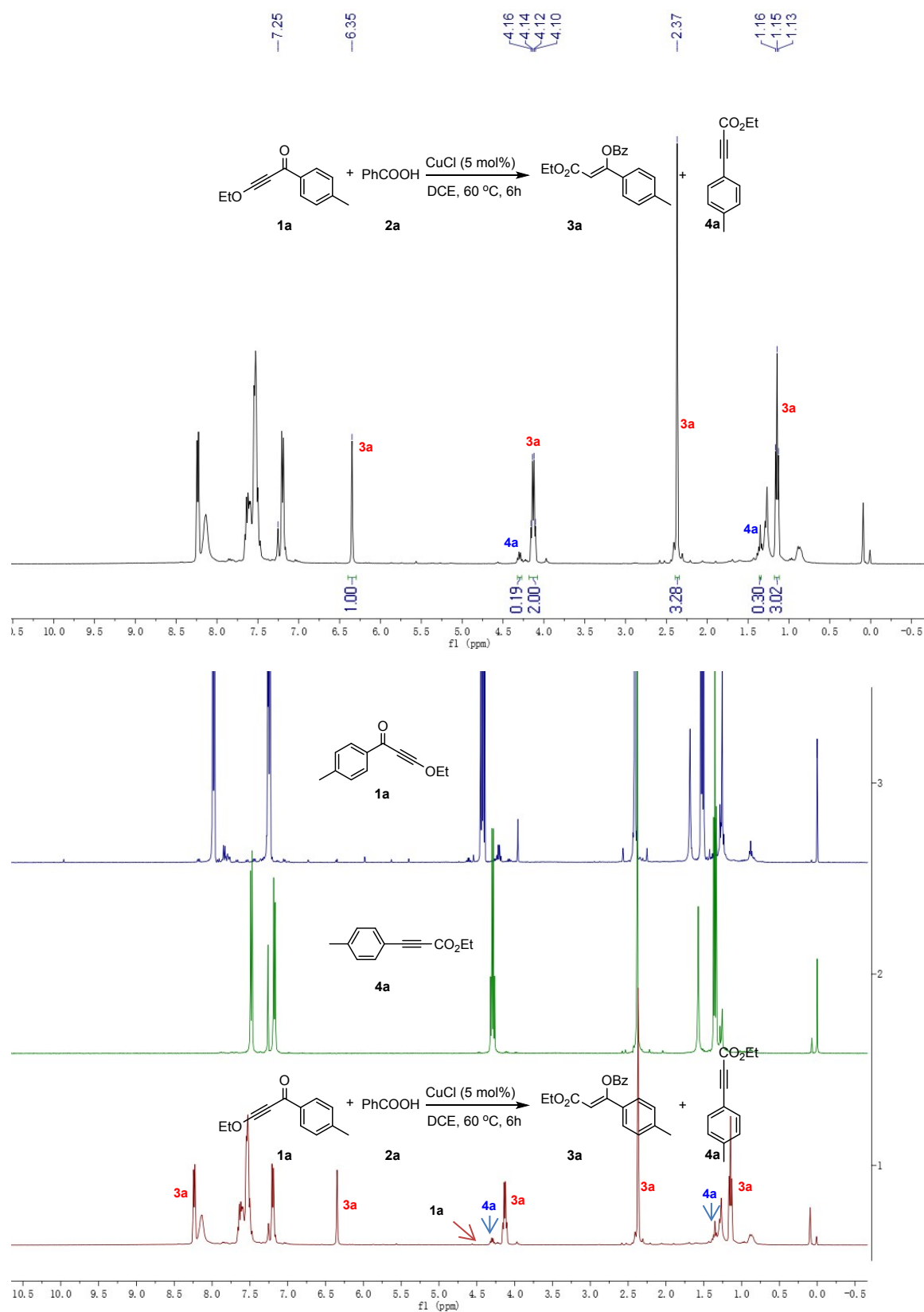
Scheme ESI 1. Control experiment

To a DCE (2 mL) solution of **4a** (0.2 mmol) in Schlenk tube with a magnetic bar was added carboxylic acid **2a** (0.4 mmol), CuCl (5 mol%) under air atmosphere. The reaction mixture was stirred at 60 °C for 6 h. The 1,3-*O*-transposition product propiolic ester **4a** remained unchanged, which rules out **4a** converted to *Z*-enol ester **3a**.



To a DCE (2 mL) solution of **1a** (0.2 mmol) in Schlenk tube with a magnetic bar was added carboxylic acid **2a** (0.4 mmol), CuCl (5 mol%) under air atmosphere. The reaction mixture was stirred at 60 °C for 6 h. Then the mixture was filtered over

celite and washed with dichloromethane, and the solvent was evaporated off. The raw material **1a** was completely consumed by ^1H NMR analysis of the crude reaction mixtures (**Scheme ESI 2**).



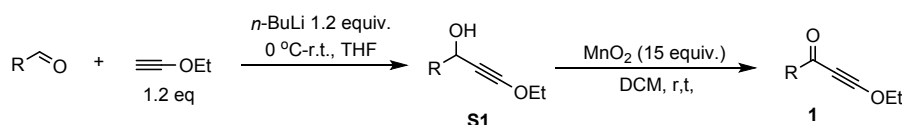
Scheme ESI 2. The ^1H NMR spectra of crude reaction mixtures

2. General information.

All reactions were carried out under an air atmosphere or dry N₂ in Schlenk tube. ¹H, ¹³C, ¹⁹F NMR spectra were recorded on a Bruker AVANCE 400 (400 MHz for ¹H; 100 MHz for ¹³C; 376 MHz for ¹⁹F). ¹H NMR and ¹³C NMR chemical shifts were determined relative to internal standard TMS at δ 0.0. Chemical shifts (δ) are reported in ppm, and coupling constants (J) are in Hertz (Hz). The following abbreviations were used to explain the multiplicities: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet. Infrared (IR) spectra were recorded on a Nicolet 210 spectrophotometer and were recorded in potassium bromide (KBr) pellet. Mass spectra were obtained using ESI or DART mass spectrometer. Melting points were determined using a hot stage apparatus. 1,2-Dichloroethane (DCE) was freshly distilled from CaH₂ and degassed by three Freeze-Pump-Thaw cycles prior to use. All reagents were used as received from commercial sources, unless specified otherwise, or prepared as described in the literature.

3. Experimental details

3.1 General Procedure for the Preparation of 1a-s



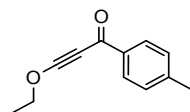
Step 1:

To a solution of ethoxyethyne (1.2 equiv.) in THF at 0 °C under N₂ atmosphere, *n*-BuLi (1.2 equiv., 2.5 M in hexane) was added dropwise. The mixture was stirred for 15 min at 0 °C. The corresponding aldehyde (1 equiv.) was then added and the reaction was stirred for additional 30 min at 0 °C and warmed up to room temperature for 30 min. Then, the mixture was quenched with saturated NH₄Cl (aq.) and extracted with diethyl ether. The organic layers were combined, washed with brine, dried over MgSO₄ and the solvent was evaporated under reduced pressure. The following distillation was purified through short column chromatography (silica gel, hexane/AcOEt = 4:1) and afforded product **S1** as a colorless liquid (85-99%).

Step 2:

The alkynol **S1** (1.0 equiv.) was dissolved in dichloromethane and treated with MnO₂ (15 equiv.). After stirring at room temperature for 6 h, the reaction was complete as determined by TLC. Excess MnO₂ was removed by filtration of the reaction mixture through a pad of celite. The filtrate was washed sequentially with water and brine, and then dried over MgSO₄. The solvent was removed under reduced pressure to afford a yellow residue that was purified by flash column chromatography (silica gel, hexane/AcOEt = 10:1). The desired ethoxy alkynones were obtained in 55-78% yield.

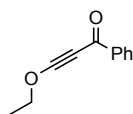
3-Ethoxy-1-(p-tolyl)prop-2-yn-1-one **1a**



Yellow liquid, R_f = 0.59, hexane /AcOEt = 10:1; ¹H NMR (400 MHz, CDCl₃) δ 7.98 (d, J = 8.1 Hz, 2H), 7.24 (d, J = 8.1 Hz, 2H), 4.42 (q, J = 7.1 Hz, 2H), 2.41 (s, 3H), 1.52 (t, J = 7.1 Hz, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 178.0, 144.3, 135.1, 129.3,

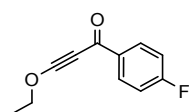
129.1, 103.9, 77.4, 43.3, 21.7, 14.5; IR (KBr) $\nu_{\max}$ 2919, 2852, 2220, 1744, 1607, 1360, 1248, 1190, 698 cm^{-1} ; HRMS (DART) calcd. for $\text{C}_{12}\text{H}_{13}\text{O}_2$ $[\text{M}+\text{H}]^+$: 189.0910, found 189.0909.

3-Ethoxy-1-phenylprop-2-yn-1-one 1b



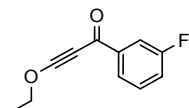
Yellow liquid, R_f = 0.59, hexane /AcOEt = 10:1; ^1H NMR (400 MHz, CDCl_3) δ 8.10 (d, J = 7.9 Hz, 1H), 7.58 (t, J = 7.3 Hz, 2H), 7.47 (t, J = 7.7 Hz, 2H), 4.45 (q, J = 7.1 Hz, 2H), 1.54 (t, J = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 178.3, 137.5, 133.3, 129.2, 128.4, 104.4, 77.5, 43.5, 14.5; IR (KBr) $\nu_{\max}$ 2923, 2358, 2226, 1637, 1195, 989, 943, 697 cm^{-1} ; HRMS (DART) calcd. for $\text{C}_{11}\text{H}_{11}\text{O}_2$ $[\text{M}+\text{H}]^+$: 175.0754, found 175.0753.

3-Ethoxy-1-(4-fluorophenyl)prop-2-yn-1-one 1d



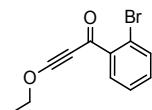
Yellow liquid, R_f = 0.58, hexane /AcOEt = 10:1; ^1H NMR (400 MHz, CDCl_3) δ 8.11 (dd, J = 8.7, 5.5 Hz, 2H), 7.12 (t, J = 8.6 Hz, 2H), 4.44 (q, J = 7.1 Hz, 2H), 1.53 (t, J = 7.1 Hz, 3H); ^{19}F NMR (376 MHz, CDCl_3) δ -105.0 (Trifluorotoluene δ -62.8 as reference compound); ^{13}C NMR (100 MHz, CDCl_3) δ 176.6, 166.0 (d, $J_{\text{C-F}}$ = 255.0 Hz), 133.9 (d, $J_{\text{C-F}}$ = 2.8 Hz), 131.7 (d, $J_{\text{C-F}}$ = 9.5 Hz), 115.5 (d, $J_{\text{C-F}}$ = 22.1 Hz), 104.5, 77.6, 43.2, 14.5; IR (KBr) $\nu_{\max}$ 2924, 2358, 2227, 1639, 1595, 1190, 945, 849 cm^{-1} ; HRMS (DART) calcd. for $\text{C}_{11}\text{H}_{10}\text{FO}_2$ $[\text{M}+\text{H}]^+$: 193.0659, found 193.0658.

3-Ethoxy-1-(3-fluorophenyl)prop-2-yn-1-one 1e



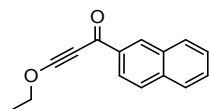
Yellow liquid, R_f = 0.58, hexane /AcOEt = 10:1; ^1H NMR (400 MHz, CDCl_3) δ 7.99 (td, J = 7.7, 1.4 Hz, 1H), 7.57 – 7.48 (m, 1H), 7.23 (t, J = 7.6 Hz, 1H), 7.13 (dd, J = 10.9, 8.5 Hz, 1H), 4.44 (q, J = 7.1 Hz, 2H), 1.53 (t, J = 7.1 Hz, 3H); ^{19}F NMR (376 MHz, CDCl_3) δ -112.4 (Trifluorotoluene δ -62.8 as reference compound); ^{13}C NMR (100 MHz, CDCl_3) δ 174.3, 161.8 (d, $J_{\text{C-F}}$ = 259.8 Hz), 134.7 (d, $J_{\text{C-F}}$ = 9.1 Hz), 131.4, 126.3 (d, $J_{\text{C-F}}$ = 8.0 Hz), 124.0 (d, $J_{\text{C-F}}$ = 3.9 Hz), 116.9 (d, $J_{\text{C-F}}$ = 22.2 Hz), 104.9, 77.6, 45.9, 14.5; IR (KBr) $\nu_{\max}$ 2989, 2226, 1690, 1610, 1482, 1334, 1283, 1043, 985, 753 cm^{-1} ; HRMS (ESI) calcd. for $\text{C}_{11}\text{H}_{10}\text{FO}_2$ $[\text{M}+\text{H}]^+$: 193.0659, found. 193.0663.

1-(2-Bromophenyl)-3-ethoxyprop-2-yn-1-one 1f



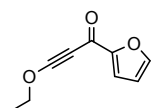
Yellow liquid, R_f = 0.57, hexane /AcOEt = 10:1; ^1H NMR (400 MHz, CDCl_3) δ 7.87 (dd, J = 7.6, 1.7 Hz, 1H), 7.65 (d, J = 7.9 Hz, 1H), 7.41 – 7.36 (m, 1H), 7.36 – 7.29 (m, 1H), 4.43 (q, J = 7.1 Hz, 2H), 1.52 (t, J = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 178.0, 138.8, 134.5, 132.5, 131.8, 127.2, 120.5, 106.0, 77.7, 45.4, 14.6; IR (KBr) $\nu_{\max}$ 2926, 2859, 2223, 1699, 1460, 1284, 1239, 986, 737 cm^{-1} ; HRMS (ESI) calcd. for $\text{C}_{11}\text{H}_{10}\text{BrO}_2$ $[\text{M}+\text{H}]^+$: 252.9859, found. 252.9860.

3-Ethoxy-1-(naphthalen-2-yl)prop-2-yn-1-one 1g



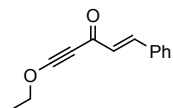
Yellow liquid, $R_f = 0.58$, hexane /AcOEt = 10:1; ^1H NMR (400 MHz, CDCl_3) δ 8.65 (s, 1H), 8.15 (dd, $J = 8.6, 1.6$ Hz, 1H), 8.00 (d, $J = 8.0$ Hz, 1H), 7.89 (d, $J = 8.5$ Hz, 2H), 7.65 – 7.53 (m, 2H), 4.50 (q, $J = 7.1$ Hz, 2H), 1.58 (t, $J = 7.1$ Hz, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 178.2, 135.9, 134.9, 132.5, 131.7, 129.7, 128.6, 128.2, 127.8, 126.8, 124.1, 104.3, 77.6, 43.6, 14.6; IR (KBr) ν_{max} 3058, 2925, 2225, 1697, 1584, 1463, 1242, 1160, 922, 760 cm^{-1} ; HRMS (ESI) calcd. for $\text{C}_{15}\text{H}_{13}\text{O}_2$ $[\text{M}+\text{H}]^+$: 225.0910, found. 225.0916

3-Ethoxy-1-(furan-2-yl)prop-2-yn-1-one 1h



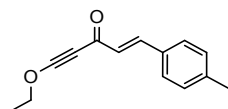
Yellow liquid, $R_f = 0.59$, hexane /AcOEt = 10:1; ^1H NMR (400 MHz, CDCl_3) δ 7.60 (s, 1H), 7.26 – 7.19 (m, 1H), 6.53 (d, $J = 1.7$ Hz, 1H), 4.42 (q, $J = 7.1$ Hz, 2H), 1.52 (t, $J = 7.1$ Hz, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 165.6, 153.4, 147.0, 118.9, 112.3, 103.0, 77.6, 42.5, 14.4; IR (KBr) ν_{max} 3132, 2983, 2230, 1735, 1577, 1468, 1388, 1231, 1023, 763 cm^{-1} ; HRMS (DART) calcd. for $\text{C}_9\text{H}_9\text{O}_3$ $[\text{M}+\text{H}]^+$: 165.0546, found 165.0546.

(E)-5-ethoxy-1-phenylpent-1-en-4-yn-3-one 1i



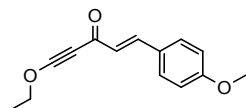
Yellow liquid, $R_f = 0.57$, hexane /AcOEt = 10:1; ^1H NMR (400 MHz, CDCl_3) δ 7.68 (d, $J = 16.1$ Hz, 1H), 7.56 – 7.51 (m, 2H), 7.42 – 7.37 (m, 3H), 6.73 (d, $J = 16.1$ Hz, 1H), 4.39 (q, $J = 7.1$ Hz, 2H), 1.51 (t, $J = 7.1$ Hz, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 178.5, 146.2, 134.4, 130.7, 129.0, 128.9, 128.4, 102.8, 77.3, 43.0, 14.5; IR (KBr) ν_{max} 2925, 2358, 1609, 1507, 1247, 977, 810, 686 cm^{-1} ; HRMS (DART) calcd. for $\text{C}_{13}\text{H}_{13}\text{O}_2$ $[\text{M}+\text{H}]^+$: 201.0910, found 201.0910.

(E)-5-ethoxy-1-(p-tolyl)pent-1-en-4-yn-3-one 1k



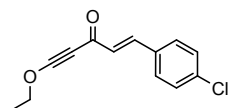
Yellow liquid, $R_f = 0.57$, hexane /AcOEt = 10:1; ^1H NMR (400 MHz, CDCl_3) δ 7.66 (d, $J = 16.0$ Hz, 1H), 7.44 (d, $J = 8.1$ Hz, 2H), 7.20 (d, $J = 8.0$ Hz, 2H), 6.70 (d, $J = 16.0$ Hz, 1H), 4.39 (q, $J = 7.1$ Hz, 2H), 2.38 (s, 3H), 1.51 (t, $J = 7.1$ Hz, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 178.6, 146.5, 141.3, 131.6, 129.7, 128.4, 128.0, 102.6, 77.3, 42.9, 21.5, 14.5; IR (KBr) ν_{max} 2924, 2359, 2228, 1621, 1334, 1111, 983, 816 cm^{-1} ; HRMS (DART) calcd. for $\text{C}_{14}\text{H}_{15}\text{O}_2$ $[\text{M}+\text{H}]^+$: 215.1067, found 215.1066.

(E)-5-ethoxy-1-(4-methoxyphenyl)pent-1-en-4-yn-3-one 1l



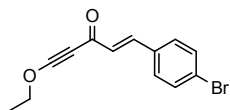
Yellow solid (m.p. 73-74 $^{\circ}\text{C}$), $R_f = 0.50$, hexane /AcOEt = 10:1; ^1H NMR (400 MHz, CDCl_3) δ 7.65 (d, $J = 16.0$ Hz, 1H), 7.50 (d, $J = 8.7$ Hz, 2H), 6.92 (d, $J = 8.7$ Hz, 2H), 6.63 (d, $J = 16.0$ Hz, 1H), 4.39 (q, $J = 7.1$ Hz, 2H), 3.84 (s, 3H), 1.51 (t, $J = 7.1$ Hz, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 178.6, 161.8, 146.3, 130.2, 127.1, 126.8, 114.5, 102.4, 77.2, 55.4, 42.8, 14.5; IR (KBr) ν_{max} 2920, 2358, 2231, 1593, 1255, 1103, 981, 819 cm^{-1} ; HRMS (DART) calcd. for $\text{C}_{14}\text{H}_{15}\text{O}_3$ $[\text{M}+\text{H}]^+$: 231.1016, found 231.1014.

(E)-1-(4-chlorophenyl)-5-ethoxypent-1-en-4-yn-3-one 1m



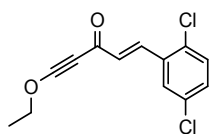
Yellow solid (m.p. 74-75 °C), R_f = 0.51, hexane /AcOEt = 10:1; ¹H NMR (400 MHz, CDCl₃) δ 7.62 (d, *J* = 16.1 Hz, 1H), 7.47 (d, *J* = 8.5 Hz, 2H), 7.37 (d, *J* = 8.5 Hz, 2H), 6.70 (d, *J* = 16.1 Hz, 1H), 4.40 (q, *J* = 7.1 Hz, 2H), 1.51 (t, *J* = 7.1 Hz, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 178.1, 144.6, 136.6, 132.9, 129.5, 129.3, 129.2, 103.0, 77.4, 43.0, 14.5; IR (KBr) ν_{max} 2923, 2385, 2235, 1619, 1341, 982, 810; HRMS (DART) calcd. for C₁₃H₁₂ClO₂ [M+H]⁺: 235.0520, found 235.0520.

(E)-1-(4-bromophenyl)-5-ethoxypent-1-en-4-yn-3-one 1n



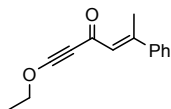
Yellow solid (m.p. 74-75 °C), R_f = 0.52, hexane /AcOEt = 10:1; ¹H NMR (400 MHz, CDCl₃) δ 7.60 (d, *J* = 16.1 Hz, 1H), 7.53 (d, *J* = 8.4 Hz, 2H), 7.40 (d, *J* = 8.4 Hz, 2H), 6.71 (d, *J* = 16.1 Hz, 1H), 4.40 (q, *J* = 7.1 Hz, 2H), 1.51 (t, *J* = 7.1 Hz, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 178.1, 144.6, 133.3, 132.2, 129.7, 129.3, 125.0, 103.1, 77.4, 43.0, 14.5; IR (KBr) ν_{max} 3025, 2924, 2235, 1619, 1398, 1142, 810, 725 cm⁻¹; HRMS (DART) calcd. for C₁₃H₁₂BrO₂ [M+H]⁺: 279.0015, found 279.0014.

(E)-1-(2,5-dichlorophenyl)-5-ethoxypent-1-en-4-yn-3-one 1o



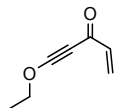
Thick oil, R_f = 0.56, hexane /AcOEt = 10:1; ¹H NMR (400 MHz, CDCl₃) δ 8.05 (d, *J* = 16.1 Hz, 1H), 7.56 (d, *J* = 8.5 Hz, 1H), 7.45 (d, *J* = 2.0 Hz, 1H), 7.32 – 7.24 (m, 1H), 6.68 (d, *J* = 16.1 Hz, 1H), 4.42 (q, *J* = 7.1 Hz, 2H), 1.53 (t, *J* = 7.1 Hz, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 178.0, 140.5, 136.7, 135.7, 131.3, 131.1, 130.1, 128.4, 127.7, 103.5, 77.5, 42.95, 14.5; IR (KBr) ν_{max} 2921, 2358, 2225, 1627, 1464, 1101, 816, 687 cm⁻¹; HRMS (DART) calcd. for C₁₃H₁₁Cl₂O₂ [M+H]⁺: 269.0131, found 269.0130.

(E)-1-ethoxy-5-phenylhex-4-en-1-yn-3-one 1p



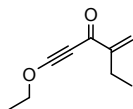
Thick oil, R_f = 0.57, hexane /AcOEt = 10:1; ¹H NMR (400 MHz, CDCl₃) δ 7.85 (s, 1H), 7.45 (t, *J* = 6.9 Hz, 2H), 7.41 (t, *J* = 7.5 Hz, 2H), 7.34 (t, *J* = 7.1 Hz, 1H), 4.38 (q, *J* = 7.1 Hz, 2H), 2.10 (s, 3H), 1.50 (t, *J* = 7.1 Hz, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 181.1, 143.3, 138.1, 135.9, 129.9, 128.8, 128.5, 103.0, 77.0, 42.3, 14.5, 12.5; IR (KBr) ν_{max} 2925, 2385, 2227, 1741, 1620, 1168, 1026, 695 cm⁻¹; HRMS (DART) calcd. for C₁₄H₁₅O₂ [M+H]⁺: 215.1067, found 215.1066.

5-Ethoxypent-1-en-4-yn-3-one 1q



Yellow oil, R_f = 0.57, hexane /AcOEt = 10:1; ¹H NMR (400 MHz, CDCl₃) δ 6.54 – 6.24 (m, 2H), 6.02 (dd, *J* = 8.9, 2.3 Hz, 1H), 4.37 (q, *J* = 7.1 Hz, 2H), 1.49 (t, *J* = 7.1 Hz, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 179.0, 138.3, 131.3, 103.3, 77.4, 42.4, 14.4; IR (KBr) ν_{max} 2924, 2227, 1645, 1605, 1403, 1160, 969, 810 cm⁻¹; HRMS (DART) calcd. for C₇H₉O₂ [M+H]⁺: 125.0597, found 125.0596.

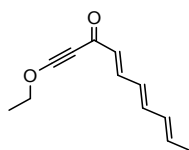
1-Ethoxy-4-methylenehex-1-yn-3-one 1r



Yellow oil, R_f = 0.58, hexane /AcOEt = 10:1; ¹H NMR (400 MHz, CDCl₃) δ 6.30 (s, 1H), 5.82 (s, 1H), 4.35 (q, *J* = 7.1 Hz, 2H), 2.33 (q, *J* = 7.4 Hz, 2H), 1.48 (t, *J* = 7.1 Hz, 3H), 1.06 (t, *J* = 7.4 Hz, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 180.2, 151.0, 126.9, 102.3, 77.0, 42.5, 22.8, 14.4, 12.5; IR (KBr) ν_{max} 2975, 2358, 2229, 1742, 1631, 1456, 1233, 994, 854 cm⁻¹; HRMS

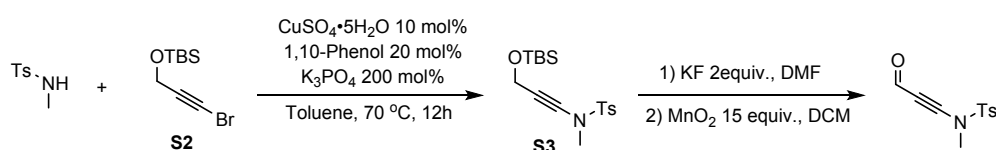
(DART) calcd. for C₉H₁₃O₂ [M+H]⁺: 153.0910, found 153.0909.

(4E,6E,8E)-1-ethoxydeca-4,6,8-trien-1-yn-3-one 1s



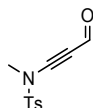
Thick oil, R_f = 0.58, hexane /AcOEt = 10:1; ¹H NMR (400 MHz, CDCl₃) δ 7.32 (dd, *J* = 15.3, 11.3 Hz, 1H), 6.61 (dd, *J* = 14.8, 10.8 Hz, 1H), 6.30 – 6.11 (m, 3H), 5.99 (dq, *J* = 14.0, 6.8 Hz, 1H), 4.37 (q, *J* = 7.1 Hz, 2H), 1.85 (d, *J* = 6.7 Hz, 3H), 1.49 (t, *J* = 7.1 Hz, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 178.5, 146.6, 142.4, 136.0, 131.4, 131.1, 127.8, 102.3, 77.1, 42.8, 18.6, 14.5; IR (KBr) ν_{max} 2986, 2926, 2227, 1613, 1381, 1207, 1162, 997, 818 cm⁻¹; HRMS (ESI) calcd. for C₁₂H₁₅O₂ [M+H]⁺: 191.1067, found. 191.1065,

3.2 General Procedure for the Preparation of 5a



Substrates **S2** were synthesized following slightly modified literature procedures.² To a 50 mL dry clean round-bottom flask was added dry K₃PO₄ (2.66 g, 10 mmol), CuSO₄·5H₂O (125 mg, 0.5 mmol) and 1,10-Phenanthroline monohydrate (180 mg, 1 mmol). Then amide (5.0 mmol) and toluene (15 mL) were added, and **S2** (5.5 mmol) was added dropwise via a syringe. The resulting black reaction mixture was stirred at 70 °C for 12 h. After that, the reaction mixture was filtered to remove the resulting salts and redundant K₃PO₄. The organic phase was concentrated under reduced pressure and the residue was purified by a silica gel flash column chromatography with petroleum ether-EtOAc (10:1) as an eluent to obtain pure Substrates **S3**. KF (3 equiv.) was added to the DMF solution of **S3**, and the mixture was stirred at room temperature for 4 h. The crude was filtered under a pad of celite and washed with dichloromethane. The filtrate was washed with ammonium chloride and brine, and then dried over MgSO₄. After evaporation of the solvent, the residue was purified by column chromatography on silica gel to afford the corresponding alkynol. The crude alkynol was dissolved in dichloromethane and treated with MnO₂ (15 equiv.). After stirring at room temperature for 6 h, the reaction was complete as determined by TLC. Excess MnO₂ was removed by filtration through a pad of celite. The filtrate was washed sequentially with water and brine, and then dried over MgSO₄. The solvent was removed under reduced pressure and purified by flash column chromatography, giving the desired alkynol.

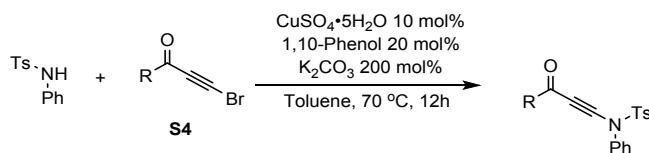
N,4-dimethyl-N-(3-oxoprop-1-yn-1-yl)benzenesulfonamide 5a



Yellow oil, R_f = 0.49, hexane /AcOEt = 7:3; ¹H NMR (400 MHz, DMSO) δ 9.24 (s, 1H), 7.87 (d, *J* = 8.4 Hz, 2H), 7.56 (d, *J* = 8.2 Hz, 2H), 3.32 (s, 3H), 3.24 (s, 3H); ¹³C NMR (100 MHz, DMSO) δ 176.8, 146.7, 132.8, 131.1, 128.1, 94.4, 76.5, 39.4, 21.7; IR (KBr) ν_{max} 3062, 2923, 1620, 1543, 1347, 1179, 690, 579 cm⁻¹; HRMS (DART) calcd. for C₁₁H₁₂NO₃S [M+H]⁺: 238.0532, found 238.0531.

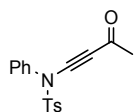
3.3 General Procedure for the Preparation of 5b-q

The compounds of ynamines **5** were prepared following slightly modified literature procedures.¹



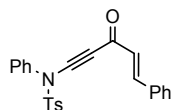
Substrates **S4** were synthesized following slightly modified literature procedures.¹ To a 50 mL dry clean round-bottom flask was added dry K₂CO₃ (1.38 g, 10 mmol), CuSO₄·5H₂O (125 mg, 0.5 mmol) and 1,10-Phenanthroline monohydrate (180 mg, 1 mmol). Then 5.0 mmol amide was added as the substrate and toluene (15 mL) was added as the solvent, **S4** (5.5 mmol) was added dropwise via a syringe. The resulting black reaction mixture was stirred at 70 °C for 12 h. After that, the reaction mixture was filtered to remove the resulting salts and redundant K₂CO₃. The organic phase was concentrated under reduced pressure and the residue was purified by a silica gel flash column chromatography with petroleum ether-EtOAc (10:1) as an eluent to afford **5** as pure product.

4-Methyl-N-(3-oxobut-1-yn-1-yl)-N-phenylbenzenesulfonamide **5b**^{1d}



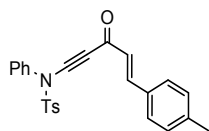
¹H NMR (400 MHz, CDCl₃) δ 7.65 (d, *J* = 8.1 Hz, 2H), 7.36 (dd, *J* = 14.7, 6.7 Hz, 5H), 7.26 – 7.19 (m, 2H), 2.48 (s, 3H), 2.36 (s, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 183.0, 145.9, 137.2, 132.9, 129.9, 129.4, 129.2, 128.2, 126.5, 88.4, 75.8, 31.9, 21.7.

(*E*)-4-methyl-N-(3-oxo-5-phenylpent-4-en-1-yn-1-yl)-N-phenylbenzenesulfonamide **5c**



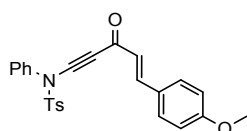
Yellow solid (m.p. 126-127 °C), R_f = 0.45, hexane /AcOEt = 7:3; ¹H NMR (400 MHz, CDCl₃) δ 8.02 (d, *J* = 16.3 Hz, 1H), 7.66 – 7.58 (m, 4H), 7.45 – 7.41 (m, 3H), 7.39 – 7.33 (m, 3H), 7.31 – 7.23 (m, 4H), 6.78 (d, *J* = 16.2 Hz, 1H), 2.43 (s, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 177.5, 148.3, 146.0, 137.2, 134.4, 132.9, 131.0, 130.0, 129.5, 129.2, 129.1, 128.7, 128.4, 128.1, 126.5, 88.8, 73.9, 21.7; IR (KBr) ν_{max} 3061, 2297, 2358, 2200, 1627, 1372, 1180, 692, 575 cm⁻¹; HRMS (DART) calcd. for C₂₄H₂₀NO₃S [M+H]⁺: 402.1158, found 402.1158.

(*E*)-4-methyl-N-(3-oxo-5-(*p*-tolyl)pent-4-en-1-yn-1-yl)-N-phenylbenzenesulfonamide **5e**



Yellow solid (m.p. 110-111 °C), R_f = 0.47, hexane /AcOEt = 7:3; ¹H NMR (400 MHz, CDCl₃) δ 7.99 (d, *J* = 16.2 Hz, 1H), 7.61 (d, *J* = 8.3 Hz, 2H), 7.52 (d, *J* = 8.1 Hz, 2H), 7.38 – 7.34 (m, 3H), 7.25 (dt, *J* = 11.6, 8.1 Hz, 6H), 6.74 (d, *J* = 16.2 Hz, 1H), 2.42 (s, 3H), 2.39 (s, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 177.6, 148.5, 145.9, 141.7, 137.2, 133.0, 131.7, 130.0, 129.8, 129.5, 129.2, 128.7, 128.1, 127.5, 126.5, 88.5, 73.8, 21.7, 21.6; IR (KBr) ν_{max} 3039, 2924, 2200, 1625, 1375, 1180, 806, 688, 578 cm⁻¹; HRMS (DART) calcd. for C₂₅H₂₂NO₃S [M+H]⁺: 416.1315, found 416.1315.

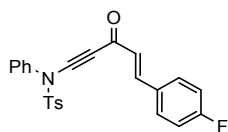
(*E*)-N-(5-(4-methoxyphenyl)-3-oxopent-4-en-1-yn-1-yl)-4-methyl-N-phenylbenzenesulfonamide **5f**



Yellow solid (m.p. 120-121 °C), R_f = 0.43, hexane /AcOEt = 7:3; ¹H NMR (400 MHz, CDCl₃) δ 7.98 (d, *J* = 16.2 Hz, 1H), 7.59 (dd, *J* = 11.6, 8.6 Hz, 4H), 7.40 – 7.34 (m, 3H), 7.31 – 7.23 (m, 4H), 6.94 (d, *J* = 8.7 Hz, 2H), 6.67 (d, *J* = 16.2 Hz, 1H), 3.85 (s, 3H), 2.42 (s, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 177.5, 162.1, 148.3, 145.9, 137.2, 133.0, 130.5, 130.0, 129.5, 129.1, 128.1, 127.1, 126.5, 126.3, 114.6, 88.2, 73.7, 55.5, 21.7; IR (KBr) ν_{max} 3199, 2928, 2358, 2201, 1598, 1374, 1176, 689 cm⁻¹;

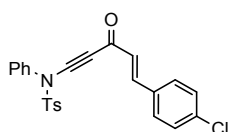
HRMS (DART) calcd. for $C_{25}H_{22}NO_4S$ $[M+H]^+$: 432.1264, found 432.1261.

(E)-N-(5-(4-fluorophenyl)-3-oxopent-4-en-1-yn-1-yl)-4-methyl-N-phenylbenzenesulfonamide 5g



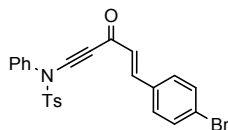
Yellow solid (m.p. 125-126 °C), R_f = 0.46, hexane /AcOEt = 7:3; 1H NMR (400 MHz, $CDCl_3$) δ 8.00 (d, J = 16.2 Hz, 1H), 7.64 – 7.58 (m, 4H), 7.39 – 7.34 (m, 3H), 7.31 – 7.23 (m, 4H), 7.12 (t, J = 8.6 Hz, 2H), 6.70 (d, J = 16.2 Hz, 1H), 2.43 (s, 3H); ^{19}F NMR (376 MHz, $CDCl_3$) δ -108.3 (Trifluorotoluene δ -62.8 as reference compound); ^{13}C NMR (100 MHz, $CDCl_3$) δ 177.3, 164.4 (d, J_{C-F} = 252.4 Hz), 147.0, 146.0, 137.1, 132.9, 130.6 (d, J_{C-F} = 8.6 Hz), 130.0, 129.5, 129.2, 128.1, 126.5, 116.3 (d, J_{C-F} = 22.0 Hz), 88.9, 73.8, 21.7; IR (KBr) ν_{max} 3064, 2358, 2200, 1630, 1501, 1451, 1174, 827 cm^{-1} ; HRMS (DART) calcd. for $C_{24}H_{19}FNO_3S$ $[M+H]^+$: 420.1064, found 420.1062.

(E)-N-(5-(4-chlorophenyl)-3-oxopent-4-en-1-yn-1-yl)-4-methyl-N-phenylbenzenesulfonamide 5h



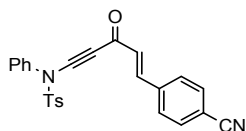
Yellow solid (m.p. 124-125 °C), R_f = 0.46, hexane /AcOEt = 7:3; 1H NMR (400 MHz, $CDCl_3$) δ 7.98 (d, J = 16.3 Hz, 1H), 7.60 (d, J = 8.3 Hz, 2H), 7.55 (d, J = 8.5 Hz, 2H), 7.40 (d, J = 8.5 Hz, 2H), 7.38 – 7.33 (m, 3H), 7.28 (d, J = 8.2 Hz, 2H), 7.26 – 7.22 (m, 2H), 6.74 (d, J = 16.2 Hz, 1H), 2.43 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 177.2, 146.7, 146.0, 137.1, 137.0, 132.9, 132.9, 130.0, 129.8, 129.5, 129.4, 129.3, 128.8, 128.1, 126.5, 89.1, 73.9, 21.7; IR (KBr) ν_{max} 3060, 2924, 2200, 1630, 1598, 1489, 1181, 1089, 814, 689 cm^{-1} ; HRMS (DART) calcd. for $C_{24}H_{19}ClNO_3S$ $[M+H]^+$: 436.0769, found 436.0767.

(E)-N-(5-(4-bromophenyl)-3-oxopent-4-en-1-yn-1-yl)-4-methyl-N-phenylbenzenesulfonamide 5i



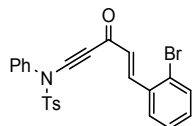
Yellow solid (m.p. 113-114 °C), R_f = 0.46, hexane /AcOEt = 7:3; 1H NMR (400 MHz, $CDCl_3$) δ 7.96 (d, J = 16.3 Hz, 1H), 7.60 (d, J = 8.3 Hz, 2H), 7.56 (d, J = 8.5 Hz, 2H), 7.48 (d, J = 8.5 Hz, 2H), 7.39 – 7.33 (m, 3H), 7.28 (d, J = 8.2 Hz, 2H), 7.26 – 7.22 (m, 2H), 6.75 (d, J = 16.2 Hz, 1H), 2.43 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 177.2, 146.7, 146.0, 137.1, 133.3, 132.9, 132.4, 130.1, 130.0, 129.5, 129.3, 128.8, 128.1, 126.5, 125.4, 89.1, 73.9, 21.8; IR (KBr) ν_{max} 3064, 2924, 2360, 2200, 1585, 1379, 1174, 688 cm^{-1} ; HRMS (DART) calcd. for $C_{24}H_{19}BrNO_3S$ $[M+H]^+$: 480.0264, found 480.0261.

(E)-N-(5-(4-cyanophenyl)-3-oxopent-4-en-1-yn-1-yl)-4-methyl-N-phenylbenzenesulfonamide 5j



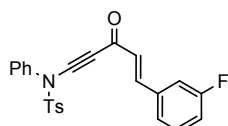
Yellow solid (m.p. 158-159 °C), R_f = 0.46, hexane /AcOEt = 7:3; 1H NMR (400 MHz, $CDCl_3$) δ 8.02 (d, J = 16.3 Hz, 1H), 7.71 (s, 4H), 7.59 (d, J = 8.0 Hz, 2H), 7.38 – 7.36 (m, 3H), 7.29 (d, J = 8.0 Hz, 2H), 7.25 (t, J = 6.6 Hz, 2H), 6.82 (d, J = 16.3 Hz, 1H), 2.43 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 176.6, 146.2, 145.2, 138.7, 136.9, 132.9, 132.8, 131.2, 130.1, 129.6, 129.4, 128.9, 128.1, 126.4, 118.3, 113.9, 89.9, 74.1, 21.7; IR (KBr) ν_{max} 3058, 2926, 2358, 21, 1630, 1368, 1176, 804, 576 cm^{-1} ; HRMS (DART) calcd. for $C_{25}H_{19}N_2O_3S$ $[M+H]^+$: 427.1111, found 427.1110.

(E)-N-(5-(2-bromophenyl)-3-oxopent-4-en-1-yn-1-yl)-4-methyl-N-phenylbenzenesulfonamide 5k



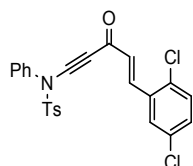
Yellow solid (m.p. 119-120 °C), Rf = 0.48, hexane /AcOEt = 7:3; ¹H NMR (400 MHz, CDCl₃) δ 8.15 (d, *J* = 16.2 Hz, 1H), 7.68 (d, *J* = 7.7 Hz, 2H), 7.61 (d, *J* = 7.9 Hz, 2H), 7.37 – 7.31 (m, 5H), 7.30 – 7.26 (m, 3H), 7.25 – 7.22 (m, 2H), 6.69 (d, *J* = 16.2 Hz, 1H), 2.43 (s, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 176.9, 145.9, 145.5, 137.4, 134.4, 133.6, 133.1, 131.7, 130.8, 130.0, 129.6, 129.2, 128.3, 128.0, 127.8, 126.7, 125.8, 89.2, 73.9, 21.7; IR (KBr) ν_{max} 2920, 2197, 1783, 1636, 1462, 1269, 1084, 752, 678 cm⁻¹; HRMS (DART) calcd. for C₂₄H₁₉BrNO₃S [M+H]⁺: 480.0264, found 480.0262.

(E)-N-(5-(3-fluorophenyl)-3-oxopent-4-en-1-yn-1-yl)-4-methyl-N-phenylbenzenesulfonamide 5l



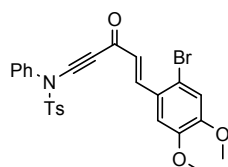
Yellow solid (m.p. 109-110 °C), Rf = 0.48, hexane /AcOEt = 7:3; ¹H NMR (400 MHz, CDCl₃) δ 7.99 (d, *J* = 16.2 Hz, 1H), 7.63 (d, *J* = 8.3 Hz, 2H), 7.43 – 7.37 (m, 5H), 7.32 – 7.30 (m, 3H), 7.28 – 7.26 (m, 2H), 7.17 – 7.12 (m, 1H), 6.77 (d, *J* = 16.2 Hz, 1H), 2.45 (s, 3H); ¹⁹F NMR (376 MHz, CDCl₃) δ -112.2 (Trifluorotoluene δ -62.8 as reference compound); ¹³C NMR (100 MHz, CDCl₃) δ 177.1, 163.1 (d, *J*_{C-F} = 247.3 Hz), 146.6, 146.0, 137.1, 136.6 (d, *J*_{C-F} = 7.7 Hz), 132.9, 130.6 (d, *J*_{C-F} = 8.3 Hz), 130.0, 129.5, 129.4, 129.3, 128.1, 126.5, 124.7, 117.8 (d, *J*_{C-F} = 21.4 Hz), 114.7 (d, *J*_{C-F} = 21.8 Hz), 89.3, 74.0, 21.7; IR (KBr) ν_{max} 3065, 2925, 2358, 2199, 1628, 1375, 1185, 692 cm⁻¹; HRMS (DART) calcd. For C₂₄H₁₉FNO₃S [M+H]⁺: 420.1064, found 420.1063.

(E)-N-(5-(2,5-dichlorophenyl)-3-oxopent-4-en-1-yn-1-yl)-4-methyl-N-phenylbenzenesulfonamide 5m



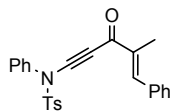
Yellow solid (m.p. 157-158 °C), Rf = 0.45, hexane /AcOEt = 7:3; ¹H NMR (400 MHz, CDCl₃) δ 8.16 (d, *J* = 16.2 Hz, 1H), 7.65 (d, *J* = 7.9 Hz, 2H), 7.58 (d, *J* = 8.5 Hz, 1H), 7.45 (s, 1H), 7.37 (d, *J* = 5.2 Hz, 3H), 7.32 – 7.22 (m, 5H), 6.72 (d, *J* = 16.2 Hz, 1H), 2.44 (s, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 176.7, 146.0, 141.7, 137.3, 137.0, 136.0, 133.0, 131.2, 130.9, 130.2, 130.0, 129.6, 129.3, 128.6, 128.2, 127.7, 126.6, 89.5, 73.9, 21.7; IR (KBr) ν_{max} 2924, 2385, 2198, 1628, 1378, 1180, 1111, 807, 686 cm⁻¹; HRMS (DART) calcd. For C₂₄H₁₈Cl₂NO₃S [M+H]⁺: 470.0379, found 470.0375.

(E)-N-(5-(2-bromo-4,5-dimethoxyphenyl)-3-oxopent-4-en-1-yn-1-yl)-4-methyl-N-phenylbenzenesulfonamide 5n



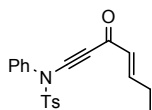
Yellow solid (m.p. 105-106 °C), Rf = 0.33, hexane /AcOEt = 7:3; ¹H NMR (400 MHz, CDCl₃) δ 8.08 (d, *J* = 16.1 Hz, 1H), 7.68 (d, *J* = 8.0 Hz, 2H), 7.39 – 7.35 (m, 3H), 7.34 – 7.25 (m, 4H), 7.07 (d, *J* = 16.2 Hz, 2H), 6.62 (d, *J* = 16.1 Hz, 1H), 3.90 (s, 3H), 3.89 (s, 3H), 2.44 (s, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 177.1, 151.9, 148.8, 145.9, 145.7, 137.5, 133.1, 130.0, 129.5, 129.2, 128.7, 128.3, 126.7, 126.2, 118.1, 115.8, 109.4, 88.8, 73.6, 56.3, 56.1, 21.7; IR (KBr) ν_{max} 3062, 2927, 2198, 1593, 1499, 1357, 1267, 1165, 1086, 686 cm⁻¹; HRMS (DART) calcd. For C₂₆H₂₃BrNO₅S [M+H]⁺: 540.0475, found 540.0478.

(E)-4-methyl-N-(4-methyl-3-oxo-5-phenylpent-4-en-1-yn-1-yl)-N-phenylbenzenesulfonamide 5o



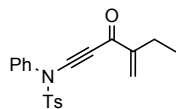
Yellow solid (m.p. 120-121 °C), $R_f = 0.47$, hexane /AcOEt = 7:3; ^1H NMR (400 MHz, CDCl_3) δ 8.13 (s, 1H), 7.62 (dd, $J = 8.5$, 2.1 Hz, 4H), 7.48 (t, $J = 7.5$ Hz, 2H), 7.43 – 7.37 (m, 4H), 7.30 – 7.28 (m, 4H), 2.44 (s, 3H), 2.20 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 179.9, 145.8, 144.9, 137.6, 137.2, 135.8, 133.0, 130.4, 130.0, 129.5, 129.2, 129.1, 128.7, 128.1, 126.5, 88.7, 73.9, 21.7, 12.3; IR (KBr) ν_{max} 3061, 2924, 2201, 1621, 1376, 1205, 1031, 888, 694, 579 cm^{-1} ; HRMS (DART) calcd. For $\text{C}_{25}\text{H}_{22}\text{NO}_3\text{S}$ $[\text{M}+\text{H}]^+$: 416.1315, found 416.1312.

(E)-4-methyl-N-(3-oxohept-4-en-1-yn-1-yl)-N-phenylbenzenesulfonamide 5p



Thick oil, $R_f = 0.50$, hexane /AcOEt = 7:3; ^1H NMR (400 MHz, CDCl_3) δ 7.59 (d, $J = 8.3$ Hz, 2H), 7.38 – 7.32 (m, 3H), 7.32 – 7.25 (m, 3H), 7.25 – 7.20 (m, 2H), 6.15 (d, $J = 15.9$ Hz, 1H), 2.44 (s, 3H), 2.40 – 2.30 (m, 2H), 1.14 (t, $J = 7.4$ Hz, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 177.7, 154.8, 145.9, 137.3, 132.9, 131.2, 129.9, 129.5, 129.1, 128.2, 126.5, 88.1, 73.6, 25.8, 21.7, 12.2; IR (KBr) ν_{max} 3061, 2970, 2358, 2201, 1645, 1376, 1176, 805, 578 cm^{-1} ; HRMS (DART) calcd. For $\text{C}_{20}\text{H}_{20}\text{NO}_3\text{S}$ $[\text{M}+\text{H}]^+$: 354.1158, found 354.1159.

4-Methyl-N-(4-methylene-3-oxohex-1-yn-1-yl)-N-phenylbenzenesulfonamide 5q

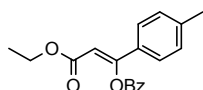


Thick oil, $R_f = 0.49$, hexane /AcOEt = 7:3; ^1H NMR (400 MHz, CDCl_3) δ 7.59 (d, $J = 8.3$ Hz, 2H), 7.37 – 7.33 (m, 3H), 7.29 (d, $J = 8.3$ Hz, 2H), 7.24 – 7.20 (m, 2H), 6.49 (s, 1H), 5.98 (s, 1H), 2.44 (s, 3H), 2.35 (q, $J = 7.4$ Hz, 2H), 1.08 (t, $J = 7.4$ Hz, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 178.9, 150.6, 145.9, 137.3, 133.0, 129.9, 129.5, 129.1, 128.3, 128.2, 126.5, 88.1, 73.9, 22.7, 21.7, 12.4; IR (KBr) ν_{max} 2971, 2358, 2198, 1630, 1375, 1174, 1082, 1003, 688 cm^{-1} ; HRMS (DART) calcd. For $\text{C}_{20}\text{H}_{20}\text{NO}_3\text{S}$ $[\text{M}+\text{H}]^+$: 354.1158, found 354.1157.

3.4 General Procedure for the synthesis of 3a-s

To a DCE (2 mL) solution of **1** (0.2 mmol) in Schlenk tube with a magnetic bar was added carboxylic acid **2** (0.4 mmol), CuCl (5 mol%) under air atmosphere. The reaction mixture was stirred at 60 °C, followed by TLC. After the **1** was completely consumed, the mixture was filtered over celite and washed with dichloromethane, then the solvent was evaporated off and the residue was purified by flash column chromatography (silica gel, mixture of hexane/ethyl acetate) to obtain pure product **3**.

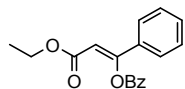
(Z)-3-ethoxy-3-oxo-1-(p-tolyl)prop-1-en-1-yl benzoate 3a



Yellow solid (m.p. 83-84 °C), $R_f = 0.58$, hexane /AcOEt = 10:1; ^1H NMR (400 MHz, CDCl_3) δ 8.23 (d, $J = 7.6$ Hz, 2H), 7.64 (t, $J = 7.4$ Hz, 1H), 7.57 – 7.48 (m, 4H), 7.19 (d, $J = 8.1$ Hz, 2H), 6.33 (s, 1H), 4.12 (q, $J = 7.1$ Hz, 2H), 2.37 (s, 3H), 1.14 (t, $J = 7.1$ Hz, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 164.3, 163.9, 158.1, 141.5, 133.7, 130.7, 130.4, 129.6, 129.3, 128.7, 126.0, 105.9, 60.3, 21.4, 14.1; IR (KBr) ν_{max} 2982, 2928, 1743, 1640, 1453, 1323, 1242, 1077, 703 cm^{-1} ; HRMS (DART) calcd. for

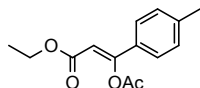
C₁₉H₁₉O₄ [M+H]⁺: 311.1278, found 311.1277.

(Z)-3-ethoxy-3-oxo-1-phenylprop-1-en-1-yl benzoate 3b^{3a}



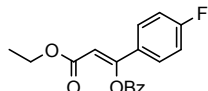
Yellow solid, R_f = 0.57, hexane /AcOEt = 10:1; ¹H NMR (400 MHz, CDCl₃) δ 8.26 (d, *J* = 7.8 Hz, 2H), 7.67 (t, *J* = 6.8 Hz, 3H), 7.55 (t, *J* = 7.7 Hz, 2H), 7.48 – 7.39 (m, 3H), 6.41 (s, 1H), 4.16 (q, *J* = 7.1 Hz, 2H), 1.18 (t, *J* = 7.1 Hz, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 164.1, 163.9, 157.9, 133.7, 133.5, 131.0, 130.4, 129.2, 128.9, 128.7, 126.0, 106.9, 60.4, 14.1.

Ethyl (Z)-3-acetoxy-3-(p-tolyl)acrylate 3c



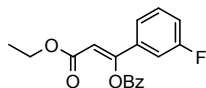
Thick oil, R_f = 0.59, hexane /AcOEt = 10:1; ¹H NMR (400 MHz, CDCl₃) δ 7.47 (d, *J* = 8.0 Hz, 2H), 7.20 (d, *J* = 8.0 Hz, 2H), 6.22 (s, 1H), 4.19 (q, *J* = 7.1 Hz, 2H), 2.38 (s, 3H), 2.37 (s, 3H), 1.29 (t, *J* = 7.1 Hz, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 168.1, 164.4, 158.2, 141.5, 130.6, 129.5, 125.9, 105.2, 60.2, 21.4, 20.9, 14.3; IR (KBr) ν_{max} 2985, 2926, 2354, 1773, 1712, 1640, 1166, 911, 735 cm⁻¹; HRMS (ESI) calcd. for C₁₄H₁₇O₄ [M+H]⁺: 249.1121, found 249.1123.

(Z)-3-ethoxy-1-(4-fluorophenyl)-3-oxoprop-1-en-1-yl benzoate 3d



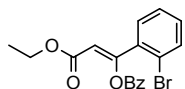
Yellow solid (m.p. 88-89 °C), R_f = 0.57, hexane /AcOEt = 10:1; ¹H NMR (400 MHz, CDCl₃) δ 8.24 (d, *J* = 7.7 Hz, 2H), 7.70 – 7.64 (m, 3H), 7.55 (t, *J* = 7.7 Hz, 2H), 7.11 (t, *J* = 8.6 Hz, 2H), 6.33 (s, 1H), 4.15 (q, *J* = 7.1 Hz, 2H), 1.17 (t, *J* = 7.1 Hz, 3H); ¹⁹F NMR (376 MHz, CDCl₃) δ -108.7 (Trifluorotoluene δ -62.8 as reference compound); ¹³C NMR (100 MHz, CDCl₃) δ 164.4 (d, *J*_{C-F} = 252.3 Hz), 164.0, 163.8, 156.9, 133.8, 130.4, 129.8 (d, *J*_{C-F} = 3.2 Hz), 129.0, 128.2 (d, *J*_{C-F} = 8.7 Hz), 128.1, 116.1 (d, *J*_{C-F} = 22.1 Hz), 106.7, 60.4, 14.1; IR (KBr) ν_{max} 2982, 2358, 1743, 1508, 1237, 1073, 699 cm⁻¹; HRMS (DART) calcd. for C₁₈H₁₆FO₄ [M+H]⁺: 315.1027, found 315.1026.

(Z)-3-ethoxy-1-(3-fluorophenyl)-3-oxoprop-1-en-1-yl benzoate 3e



Yellow solid (m.p. 62-63 °C), R_f = 0.58, hexane /AcOEt = 10:1; ¹H NMR (400 MHz, CDCl₃) δ 8.23 (d, *J* = 7.4 Hz, 2H), 7.66 (t, *J* = 7.4 Hz, 1H), 7.55 (dt, *J* = 15.4, 7.8 Hz, 3H), 7.42 (dd, *J* = 13.0, 6.2 Hz, 1H), 7.18 (dd, *J* = 16.3, 8.1 Hz, 2H), 6.52 (s, 1H), 4.16 (q, *J* = 7.1 Hz, 2H), 1.19 (t, *J* = 7.1 Hz, 3H); ¹⁹F NMR (376 MHz, CDCl₃) δ -111.8 (Trifluorotoluene δ -62.8 as reference compound); ¹³C NMR (100 MHz, CDCl₃) δ 164.0, 163.8, 161.7, 159.2, 152.5, 152.5, 133.8, 132.2, 132.1, 130.4, 129.1, 128.9, 128.7, 124.5, 124.5, 122.0, 121.9, 116.9, 116.6, 112.1, 112.0, 60.5, 14.1; IR (KBr) ν_{max} 2987, 2929, 1743, 1642, 1525, 1233, 1166, 1066, 757, 696 cm⁻¹; HRMS (ESI) calcd. for C₁₈H₁₆FO₄ [M+H]⁺: 315.1027, found 315.1028.

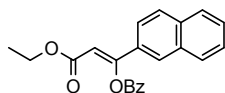
(Z)-1-(2-bromophenyl)-3-ethoxy-3-oxoprop-1-en-1-yl benzoate 3f



Thick oil, R_f = 0.58, hexane /AcOEt = 10:1; ¹H NMR (400 MHz, CDCl₃) δ 8.20 (d, *J* = 7.5 Hz, 2H), 7.67 – 7.57 (m, 3H), 7.50 (t, *J* = 7.7 Hz, 2H), 7.37 (t, *J* = 7.5 Hz, 1H), 7.30 – 7.25 (m, 1H), 6.11 (s, 1H), 4.18 (q, *J* = 7.1 Hz, 2H), 1.19 (t, *J* = 7.1 Hz, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 163.6, 163.5, 157.1, 135.8, 133.7, 133.6, 131.2, 131.2, 130.4, 129.0, 128.5, 127.4, 121.5, 112.8, 60.5, 14.0; IR (KBr) ν_{max} 3069, 2927, 1708, 1589, 1364, 1232, 1163, 1041, 848, 695 cm⁻¹; HRMS (DESI) calcd. for

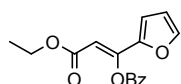
C₁₈H₁₆BrO₄ [M+H]⁺: 375.0226, found 375.0226.

(Z)-3-ethoxy-1-(naphthalen-2-yl)-3-oxoprop-1-en-1-yl benzoate 3g



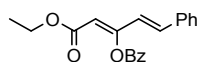
Yellow solid (m.p. 97-98 °C), R_f = 0.56, hexane /AcOEt = 10:1; ¹H NMR (400 MHz, CDCl₃) δ 8.33 (d, *J* = 7.5 Hz, 2H), 8.15 (s, 1H), 7.87 (t, *J* = 9.2 Hz, 3H), 7.78 – 7.66 (m, 2H), 7.61 – 7.50 (m, 4H), 6.55 (s, 1H), 4.19 (q, *J* = 7.1 Hz, 2H), 1.21 (t, *J* = 7.1 Hz, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 164.1, 163.9, 157.8, 134.4, 133.7, 132.9, 130.7, 130.5, 129.2, 128.9, 128.8, 128.7, 127.7, 127.6, 126.8, 126.5, 122.5, 107.1, 60.4, 14.1; IR (KBr) ν_{max} 3060, 2925, 1709, 1633, 1251, 1162, 1072, 848, 701 cm⁻¹; HRMS (ESI) calcd. for C₂₂H₁₉O₄ [M+H]⁺: 347.1278, found 347.1281.

(Z)-3-ethoxy-1-(furan-2-yl)-3-oxoprop-1-en-1-yl benzoate 3h



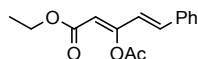
Yellow solid (m.p. 69-70 °C), R_f = 0.57, hexane /AcOEt = 10:1; ¹H NMR (400 MHz, CDCl₃) δ 8.22 (d, *J* = 7.9 Hz, 2H), 7.66 (t, *J* = 7.4 Hz, 1H), 7.58 – 7.51 (m, 3H), 6.71 (d, *J* = 3.4 Hz, 1H), 6.49 (d, *J* = 1.6 Hz, 1H), 6.34 (s, 1H), 4.13 (q, *J* = 7.1 Hz, 2H), 1.15 (t, *J* = 7.1 Hz, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 164.1, 163.6, 148.3, 148.1, 145.2, 133.8, 130.4, 128.9, 128.6, 112.8, 112.2, 104.3, 60.3, 14.0; IR (KBr) ν_{max} 3141, 2983, 1750, 1644, 1250, 1169, 1081, 754, 702; HRMS (DART) calcd. for C₁₆H₁₅O₅ [M+H]⁺: 287.0914, found 287.0913.

(1E,3Z)-5-ethoxy-5-oxo-1-phenylpenta-1,3-dien-3-yl benzoate 3i



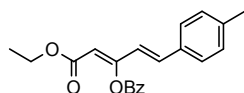
Yellow solid (m.p. 113-114 °C), R_f = 0.58, hexane /AcOEt = 10:1; ¹H NMR (400 MHz, CDCl₃) δ 8.24 (d, *J* = 7.8 Hz, 2H), 7.65 (t, *J* = 7.4 Hz, 1H), 7.53 (t, *J* = 7.6 Hz, 2H), 7.43 (d, *J* = 7.2 Hz, 2H), 7.36 – 7.28 (m, 3H), 7.02 (d, *J* = 15.8 Hz, 1H), 6.76 (d, *J* = 15.8 Hz, 1H), 5.90 (s, 1H), 4.09 (q, *J* = 7.1 Hz, 2H), 1.11 (t, *J* = 7.1 Hz, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 164.1, 163.6, 156.6, 136.0, 135.1, 133.7, 130.4, 129.4, 129.2, 128.8, 128.6, 127.5, 122.5, 109.8, 60.2, 14.0; IR (KBr) ν_{max} 3065, 2983, 2357, 1746, 1627, 1269, 1071, 698; HRMS (DART) calcd. for C₂₀H₁₉O₄ [M+H]⁺: 323.1278, found 323.1277.

Ethyl (2Z,4E)-3-acetoxy-5-phenylpenta-2,4-dienoate 3j



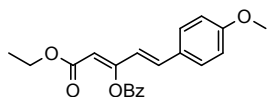
Yellow solid (m.p. 72-74 °C), R_f = 0.55, hexane /AcOEt = 10:1; ¹H NMR (400 MHz, CDCl₃) δ 7.45 (d, *J* = 7.1 Hz, 2H), 7.38 – 7.30 (m, 3H), 6.99 (d, *J* = 15.8 Hz, 1H), 6.65 (d, *J* = 15.8 Hz, 1H), 5.79 (s, 1H), 4.17 (q, *J* = 7.1 Hz, 2H), 2.39 (s, 3H), 1.28 (t, *J* = 7.1 Hz, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 167.8, 164.3, 156.7, 135.9, 135.1, 129.4, 128.8, 127.5, 122.5, 109.1, 60.2, 20.9, 14.2; IR (KBr) ν_{max} 2984, 1772, 1708, 1626, 1360, 1273, 1178, 1030, 960, 832; HRMS (ESI) calcd. for C₁₅H₁₇O₄ [M+H]⁺: 261.1121, found 261.1121.

(1E,3Z)-5-ethoxy-5-oxo-1-(p-tolyl)penta-1,3-dien-3-yl benzoate 3k



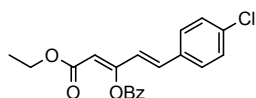
Yellow solid (m.p. 123-124 °C), R_f = 0.59, hexane /AcOEt = 10:1; ¹H NMR (400 MHz, CDCl₃) δ 8.30 – 8.21 (m, 2H), 7.64 (t, *J* = 7.4 Hz, 1H), 7.52 (t, *J* = 7.7 Hz, 2H), 7.33 (d, *J* = 8.1 Hz, 2H), 7.13 (d, *J* = 8.0 Hz, 2H), 7.00 (d, *J* = 15.8 Hz, 1H), 6.71 (d, *J* = 15.8 Hz, 1H), 5.87 (s, 1H), 4.08 (q, *J* = 7.1 Hz, 2H), 2.33 (s, 3H), 1.10 (t, *J* = 7.1 Hz, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 164.2, 163.6, 156.9, 139.7, 136.0, 133.6, 132.4, 130.4, 129.5, 129.2, 128.6, 127.5, 121.5, 109.2, 60.2, 21.3, 14.0; IR (KBr) ν_{max} 2981, 2926, 2358, 1745, 1624, 1265, 1144, 702; HRMS (DART) calcd. for C₂₁H₂₁O₄ [M+H]⁺: 337.1434, found 337.1432.

(1E,3Z)-5-ethoxy-1-(4-methoxyphenyl)-5-oxopenta-1,3-dien-3-yl benzoate 3l



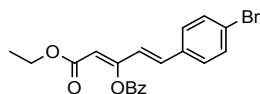
Yellow solid (m.p. 119-120 °C), Rf = 0.52, hexane /AcOEt = 10:1; ¹H NMR (400 MHz, CDCl₃) δ 8.24 (d, *J* = 7.6 Hz, 2H), 7.64 (t, *J* = 7.4 Hz, 1H), 7.52 (t, *J* = 7.7 Hz, 2H), 7.37 (d, *J* = 8.7 Hz, 2H), 6.97 (d, *J* = 15.8 Hz, 1H), 6.85 (d, *J* = 8.7 Hz, 2H), 6.63 (d, *J* = 15.8 Hz, 1H), 5.85 (s, 1H), 4.08 (q, *J* = 7.1 Hz, 2H), 3.80 (s, 3H), 1.10 (t, *J* = 7.1 Hz, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 164.3, 163.6, 160.7, 157.0, 135.6, 133.6, 130.4, 129.2, 129.1, 128.6, 127.9, 120.2, 114.3, 108.6, 60.1, 55.3, 14.0; IR (KBr) ν_{max} 2973, 2358, 1743, 1599, 1256, 1143, 836, 701; HRMS (DART) calcd. for C₂₁H₂₁O₅ [M+H]⁺: 353.1384, found 353.1384.

(1E,3Z)-1-(4-chlorophenyl)-5-ethoxy-5-oxopenta-1,3-dien-3-yl benzoate 3m



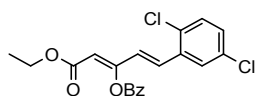
Yellow solid (m.p. 114-115 °C), Rf = 0.56, hexane /AcOEt = 10:1; ¹H NMR (400 MHz, CDCl₃) δ 8.33 – 8.21 (m, 2H), 7.68 (t, *J* = 7.4 Hz, 1H), 7.56 (t, *J* = 7.7 Hz, 2H), 7.39 (d, *J* = 8.6 Hz, 2H), 7.32 (d, *J* = 8.6 Hz, 2H), 6.99 (d, *J* = 15.8 Hz, 1H), 6.75 (d, *J* = 15.8 Hz, 1H), 5.93 (s, 1H), 4.11 (q, *J* = 7.1 Hz, 2H), 1.14 (t, *J* = 7.1 Hz, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 164.0, 163.5, 156.3, 135.2, 134.5, 133.7, 133.6, 130.4, 129.0, 128.7, 123.1, 110.3, 60.3, 14.0; IR (KBr) ν_{max} 3067, 2981, 2385, 1708, 1264, 1146, 1076, 703; HRMS (DART) calcd. for C₂₀H₁₈ClO₄ [M+H]⁺: 357.0888, found 357.0888.

(1E,3Z)-1-(4-bromophenyl)-5-ethoxy-5-oxopenta-1,3-dien-3-yl benzoate 3n



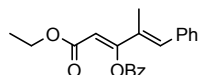
Yellow solid (m.p. 130-131 °C), Rf = 0.56, hexane /AcOEt = 10:1; ¹H NMR (400 MHz, CDCl₃) δ 8.30 – 8.22 (m, 2H), 7.68 (t, *J* = 7.4 Hz, 1H), 7.56 (t, *J* = 7.7 Hz, 2H), 7.49 (d, *J* = 8.5 Hz, 2H), 7.32 (d, *J* = 8.5 Hz, 2H), 6.97 (d, *J* = 15.8 Hz, 1H), 6.76 (d, *J* = 15.8 Hz, 1H), 5.94 (s, 1H), 4.11 (q, *J* = 7.1 Hz, 2H), 1.14 (t, *J* = 7.1 Hz, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 164.0, 163.5, 156.2, 134.5, 134.1, 133.7, 132.0, 130.4, 129.0, 128.9, 128.7, 123.5, 123.2, 110.3, 60.3, 14.0; IR (KBr) ν_{max} 3066, 2980, 2358, 1708, 1627, 1262, 1070, 702 cm⁻¹; HRMS (DART) calcd. for C₂₀H₁₈BrO₄ [M+H]⁺: 401.0383, found 401.0382.

(1E,3Z)-1-(2,5-dichlorophenyl)-5-ethoxy-5-oxopenta-1,3-dien-3-yl benzoate 3o



Yellow solid (m.p. 107-108 °C), Rf = 0.41, hexane /AcOEt = 10:1; ¹H NMR (400 MHz, CDCl₃) δ 8.23 (d, *J* = 7.7 Hz, 2H), 7.65 (t, *J* = 7.4 Hz, 1H), 7.58 – 7.49 (m, 3H), 7.37 (dd, *J* = 8.8, 7.0 Hz, 2H), 7.23 (dd, *J* = 8.5, 1.8 Hz, 1H), 6.72 (d, *J* = 15.8 Hz, 1H), 5.94 (s, 1H), 4.10 (q, *J* = 7.1 Hz, 2H), 1.11 (t, *J* = 7.1 Hz, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 163.9, 163.5, 155.9, 135.4, 134.8, 133.8, 131.9, 130.5, 130.3, 129.8, 128.9, 128.7, 127.8, 127.5, 125.4, 111.2, 60.4, 14.0; IR (KBr) ν_{max} 2980, 2358, 1710, 1628, 1268, 1066, 698 cm⁻¹; HRMS (DART) calcd. for C₂₀H₁₇Cl₂O₄ [M+H]⁺: 391.0498, found 391.0497.

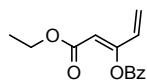
(1E,3Z)-5-ethoxy-2-methyl-5-oxo-1-phenylpenta-1,3-dien-3-yl benzoate 3p



Yellow solid (m.p. 65-66 °C), Rf = 0.41, hexane /AcOEt = 7:3; ¹H NMR (400 MHz, CDCl₃) δ 8.26 (d, *J* = 7.9 Hz, 2H), 7.66 (t, *J* = 7.4 Hz, 1H), 7.55 (t, *J* = 7.6 Hz, 2H), 7.40 – 7.34 (m, 2H), 7.34 – 7.27 (m, 3H), 6.08 (s, 1H), 4.13 (q, *J* = 7.1 Hz, 2H), 2.16 (s, 3H), 1.16 (t, *J* = 7.1 Hz, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 164.4, 163.8, 159.1, 136.3, 133.6, 133.2, 130.3, 130.3, 129.5, 129.3, 128.6, 128.2, 127.8, 107.1, 60.2, 14.4, 14.0; IR (KBr) ν_{max} 2982, 2358, 1743, 1621, 1275, 1165, 1087, 700 cm⁻¹; HRMS

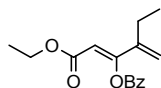
(DART) calcd. for C₂₁H₂₁O₄ [M+H]⁺: 337.1434, found 337.1433.

(Z)-5-ethoxy-5-oxopenta-1,3-dien-3-yl benzoate 3q



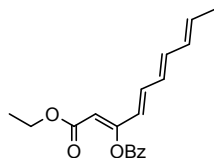
Thick oil, R_f = 0.59, hexane /AcOEt = 10:1; ¹H NMR (400 MHz, CDCl₃) δ 8.20 (d, *J* = 7.8 Hz, 2H), 7.65 (t, *J* = 7.3 Hz, 1H), 7.52 (t, *J* = 7.7 Hz, 2H), 6.42 (dd, *J* = 17.1, 10.7 Hz, 1H), 5.85 (s, 1H), 5.77 (d, *J* = 17.1 Hz, 1H), 5.52 (d, *J* = 10.7 Hz, 1H), 4.10 (q, *J* = 7.1 Hz, 2H), 1.12 (t, *J* = 7.1 Hz, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 163.9, 163.4, 156.0, 133.6, 131.4, 130.3, 129.0, 128.6, 121.6, 110.6, 60.3, 13.9; IR (KBr) ν_{max} 2981, 2358, 1737, 1651, 1455, 1262, 1070, 703 cm⁻¹; HRMS (DART) calcd. for C₁₄H₁₅O₄ [M+H]⁺: 247.0965, found 247.0964.

(Z)-1-ethoxy-4-methylene-1-oxohex-2-en-3-yl benzoate 3r



Thick oil, R_f = 0.59, hexane /AcOEt = 10:1; ¹H NMR (400 MHz, CDCl₃) δ 8.17 (d, *J* = 7.9 Hz, 2H), 7.61 (t, *J* = 7.4 Hz, 1H), 7.49 (t, *J* = 7.6 Hz, 2H), 5.97 (s, 1H), 5.62 (s, 1H), 5.33 (s, 1H), 4.08 (q, *J* = 7.1 Hz, 2H), 2.35 (q, *J* = 7.5 Hz, 2H), 1.19 (t, *J* = 7.4 Hz, 3H), 1.11 (t, *J* = 7.1 Hz, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 164.2, 163.8, 157.4, 142.9, 133.5, 130.2, 129.2, 128.5, 117.8, 107.0, 60.3, 24.9, 14.0, 12.5; IR (KBr) ν_{max} 2974, 2200, 1734, 1637, 1374, 1174, 856, 699 cm⁻¹; HRMS (DART) calcd. for C₁₆H₁₉O₄ [M+H]⁺: 275.1278, found 275.1277.

(2Z,4E,6E,8E)-1-ethoxy-1-oxodeca-2,4,6,8-tetraen-3-yl benzoate 3s

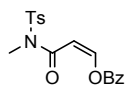


Yellow solid (m.p. 108-109 °C), R_f = 0.41, hexane /AcOEt = 7:3; ¹H NMR (400 MHz, CDCl₃) δ 8.22 (d, *J* = 7.3 Hz, 2H), 7.66 (t, *J* = 7.4 Hz, 1H), 7.54 (t, *J* = 7.7 Hz, 2H), 6.70 (dd, *J* = 15.0, 11.1 Hz, 1H), 6.37 (dd, *J* = 14.8, 10.7 Hz, 1H), 6.28 – 6.10 (m, 3H), 5.84 (dt, *J* = 22.9, 7.5 Hz, 1H), 5.78 (d, *J* = 8.1 Hz, 1H), 4.08 (q, *J* = 7.1 Hz, 2H), 1.82 (d, *J* = 6.8 Hz, 3H), 1.11 (t, *J* = 7.1 Hz, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 164.3, 163.5, 156.8, 139.0, 136.6, 133.9, 133.6, 131.5, 130.3, 129.2, 128.6, 128.5, 124.7, 108.6, 60.1, 18.5, 14.0; IR (KBr) ν_{max} 2984, 2924, 1707, 1604, 1449, 1216, 1137, 996, 700 cm⁻¹; HRMS (ESI) calcd. for C₁₉H₂₁O₄ [M+H]⁺: 313.1434, found 313.1435.

3.5 General Procedure for the synthesis of 6

To a DCE (2 mL) solution of **5** (0.2 mmol) in Schlenk tube with a magnetic bar was added carboxylic acid (0.4 mmol), CuCl (5 mol%) under air atmosphere. The reaction mixture was stirred at 80 °C, followed by TLC. After the substrate **5** was completely consumed, the mixture was filtered over celite and washed with dichloromethane, then the solvent was evaporated off and the residue was purified by flash column chromatography (silica gel, mixture of hexane/ethyl acetate) to obtain **6** as pure product.

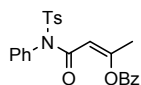
(Z)-3-((N,4-dimethylphenyl)sulfonamido)-3-oxoprop-1-en-1-yl benzoate 6a



Thick oil, R_f = 0.46, hexane /AcOEt = 7:3; ¹H NMR (400 MHz, CDCl₃) δ 8.18 – 8.08 (m, 2H), 7.76 (dd, *J* = 7.8, 2.8 Hz, 3H), 7.63 (t, *J* = 7.5 Hz, 1H), 7.48 (t, *J* = 7.8 Hz, 2H), 7.29 (d, *J* = 8.1 Hz, 2H), 6.32 (d, *J* = 7.3 Hz, 1H), 3.33 (s, 3H), 2.36 (s, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 163.5, 162.4, 144.9, 143.6, 136.1, 134.3, 130.6, 129.9, 128.7, 127.7, 127.3, 104.3, 32.7, 21.5;

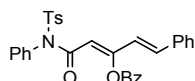
IR (KBr) $\nu_{\max}$ 2927, 1745, 1700, 1495, 1376, 1360, 1171, 1078, 699 cm^{-1} ; HRMS (DART) calcd. For $\text{C}_{18}\text{H}_{18}\text{NO}_5\text{S}$ $[\text{M}+\text{H}]^+$: 360.0900, found 360.0899.

(Z)-4-((4-methyl-N-phenylphenyl)sulfonamido)-4-oxobut-2-en-2-yl benzoate 6b



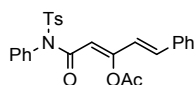
^1H NMR (400 MHz, CDCl_3) δ 7.96 (d, $J = 7.1$ Hz, 2H), 7.80 (d, $J = 8.3$ Hz, 2H), 7.67 – 7.60 (m, 1H), 7.52 – 7.45 (m, 5H), 7.37 – 7.33 (m, 2H), 7.19 (d, $J = 8.1$ Hz, 2H), 5.32 (d, $J = 0.9$ Hz, 1H), 2.43 (s, 3H), 1.92 (d, $J = 0.8$ Hz, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 163.4, 162.6, 159.4, 144.4, 136.1, 135.9, 133.4, 130.4, 130.2, 129.8, 129.6, 129.2, 129.2, 129.0, 128.3, 127.2, 121.7, 109.0, 21.7, 21.6; IR (KBr) $\nu_{\max}$ 2924, 2200, 1741, 1698, 1491, 1360, 1169, 1077, 695 cm^{-1} ; HRMS (DART) calcd. For $\text{C}_{24}\text{H}_{22}\text{NO}_5\text{S}$ $[\text{M}+\text{H}]^+$: 436.1213, found 436.1212.

(1E,3Z)-5-((4-methyl-N-phenylphenyl)sulfonamido)-5-oxo-1-phenylpenta-1,3-dien-3-yl benzoate 6c



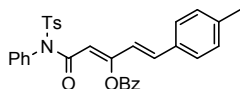
Yellow solid (m.p. 75-76 $^{\circ}\text{C}$), $R_f = 0.43$, hexane /AcOEt = 7:3; ^1H NMR (400 MHz, CDCl_3) δ 8.04 (d, $J = 7.7$ Hz, 2H), 7.77 (d, $J = 8.2$ Hz, 2H), 7.66 (t, $J = 7.4$ Hz, 1H), 7.54 – 7.45 (m, 5H), 7.34 (ddd, $J = 9.5, 5.6, 1.8$ Hz, 4H), 7.28 – 7.25 (m, 3H), 7.15 (d, $J = 8.2$ Hz, 2H), 6.94 (d, $J = 15.8$ Hz, 1H), 6.40 (d, $J = 15.8$ Hz, 1H), 5.48 (s, 1H), 2.42 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 163.4, 163.1, 156.3, 144.4, 136.2, 136.1, 135.8, 135.0, 133.6, 130.5, 130.4, 129.9, 129.7, 129.5, 129.3, 129.2, 129.0, 128.7, 128.4, 127.5, 122.5, 109.9, 21.7; IR (KBr) $\nu_{\max}$ 2919, 2852, 2200, 1743, 1607, 1360, 1248, 1141, 754 cm^{-1} ; HRMS (DART) calcd. For $\text{C}_{31}\text{H}_{26}\text{NO}_5\text{S}$ $[\text{M}+\text{H}]^+$: 524.1526, found 524.1525.

(1E,3Z)-5-((4-methyl-N-phenylphenyl)sulfonamido)-5-oxo-1-phenylpenta-1,3-dien-3-yl acetate 6d



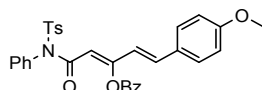
Yellow solid (m.p. 66-67 $^{\circ}\text{C}$), $R_f = 0.45$, hexane /AcOEt = 7:3; ^1H NMR (400 MHz, CDCl_3) δ 7.91 (d, $J = 8.3$ Hz, 2H), 7.55 – 7.48 (m, 3H), 7.40 – 7.35 (m, 3H), 7.33 – 7.30 (m, 6H), 6.94 (d, $J = 15.8$ Hz, 1H), 6.34 (d, $J = 15.8$ Hz, 1H), 5.41 (s, 1H), 2.48 (s, 3H), 2.30 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 167.7, 163.1, 157.0, 144.7, 136.5, 136.1, 136.0, 134.9, 130.4, 129.8, 129.7, 129.6, 129.3, 129.2, 128.8, 127.5, 122.5, 108.9, 21.6, 20.9; IR (KBr) $\nu_{\max}$ 3061, 2928, 1772, 1685, 1599, 1359, 1262, 1085, 692 cm^{-1} ; HRMS (DART) calcd. For $\text{C}_{26}\text{H}_{24}\text{NO}_5\text{S}$ $[\text{M}+\text{H}]^+$: 462.1370, found 462.1366.

(1E,3Z)-5-((4-methyl-N-phenylphenyl)sulfonamido)-5-oxo-1-(p-tolyl)penta-1,3-dien-3-yl benzoate 6e



Yellow solid (m.p. 81-82 $^{\circ}\text{C}$), $R_f = 0.45$, hexane /AcOEt = 7:3; ^1H NMR (400 MHz, CDCl_3) δ 8.04 (d, $J = 7.7$ Hz, 2H), 7.76 (d, $J = 8.2$ Hz, 2H), 7.66 (t, $J = 7.4$ Hz, 1H), 7.55 – 7.45 (m, 5H), 7.36 (dd, $J = 6.3, 2.6$ Hz, 2H), 7.21 (d, $J = 8.0$ Hz, 2H), 7.15 (d, $J = 8.1$ Hz, 2H), 7.07 (d, $J = 8.0$ Hz, 2H), 6.91 (d, $J = 15.7$ Hz, 1H), 6.35 (d, $J = 15.7$ Hz, 1H), 5.45 (s, 1H), 2.41 (s, 3H), 2.30 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 163.4, 163.1, 156.6, 144.3, 139.8, 136.2, 136.2, 135.8, 133.6, 132.2, 130.5, 130.4, 129.8, 129.6, 129.5, 129.2, 129.0, 128.3, 127.5, 121.4, 109.3, 21.6, 21.3; IR (KBr) $\nu_{\max}$ 3063, 2924, 2358, 2199, 1743, 1596, 1360, 1071, 694 cm^{-1} ; HRMS (DART) calcd. For $\text{C}_{32}\text{H}_{28}\text{NO}_5\text{S}$ $[\text{M}+\text{H}]^+$: 538.1683, found 538.1685.

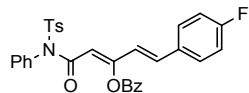
(1E,3Z)-1-(4-methoxyphenyl)-5-((4-methyl-N-phenylphenyl)sulfonamido)-5-oxopenta-1,3-dien-3-yl benzoate 6f



Yellow solid (m.p. 168-169 $^{\circ}\text{C}$), $R_f = 0.32$, hexane /AcOEt = 7:3; ^1H NMR (400 MHz, CDCl_3) δ 8.05 (d, $J = 7.6$ Hz, 2H), 7.76

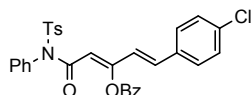
(d, $J = 8.2$ Hz, 2H), 7.66 (t, $J = 7.4$ Hz, 1H), 7.55 – 7.45 (m, 5H), 7.36 (dd, $J = 6.5, 2.6$ Hz, 2H), 7.28 (s, 2H), 7.15 (d, $J = 8.2$ Hz, 2H), 6.89 (d, $J = 15.7$ Hz, 1H), 6.79 (d, $J = 8.7$ Hz, 2H), 6.27 (d, $J = 15.7$ Hz, 1H), 5.42 (s, 1H), 3.77 (s, 3H), 2.41 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 163.4, 163.2, 160.8, 156.9, 144.3, 136.1, 135.9, 133.5, 130.5, 130.4, 129.8, 129.6, 129.3, 129.2, 129.1, 129.0, 128.3, 127.7, 120.2, 114.2, 108.6, 55.3, 21.6; IR (KBr) ν_{max} 3063, 2928, 1743, 1687, 1503, 1252, 1139, 1028, 695 cm^{-1} ; HRMS (DART) calcd. For $\text{C}_{32}\text{H}_{28}\text{NO}_6\text{S}$ $[\text{M}+\text{H}]^+$: 554.1632, found 554.1630.

(1E,3Z)-1-(4-fluorophenyl)-5-((4-methyl-N-phenylphenyl)sulfonamido)-5-oxopenta-1,3-dien-3-yl benzoate 6g



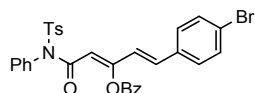
Yellow solid (m.p. 112-113 °C), $R_f = 0.44$, hexane /AcOEt = 7:3; ^1H NMR (400 MHz, CDCl_3) δ 8.07 (d, $J = 7.1$ Hz, 2H), 7.79 (d, $J = 8.3$ Hz, 2H), 7.70 (t, $J = 7.4$ Hz, 1H), 7.57 – 7.50 (m, 5H), 7.39 (dd, $J = 6.6, 2.9$ Hz, 2H), 7.33 (dd, $J = 8.7, 5.4$ Hz, 2H), 7.18 (d, $J = 8.2$ Hz, 2H), 6.99 (t, $J = 8.6$ Hz, 2H), 6.92 (d, $J = 15.8$ Hz, 1H), 6.35 (d, $J = 15.8$ Hz, 1H), 5.51 (s, 1H), 2.45 (s, 3H); ^{19}F NMR (376 MHz, CDCl_3) δ -110.7 (Trifluorotoluene δ -62.8 as reference compound); ^{13}C NMR (100 MHz, CDCl_3) δ 163.4, 163.3 (d, $J_{\text{C-F}} = 250.6$ Hz), 163.0, 156.2, 144.4, 136.1, 135.8, 134.7, 133.6, 131.2, 130.4 (d, $J_{\text{C-F}} = 8.8$ Hz), 129.8, 129.6, 129.3, 129.2, 129.1, 129.0, 128.4, 122.3, 115.8 (d, $J_{\text{C-F}} = 21.9$ Hz), 109.9, 21.6; IR (KBr) ν_{max} 3066, 2358, 1744, 1595, 1500, 1360, 1242, 1071, 696 cm^{-1} ; HRMS (DART) calcd. For $\text{C}_{31}\text{H}_{25}\text{FNO}_5\text{S}$ $[\text{M}+\text{H}]^+$: 542.1432, found 542.1429.

(1E,3Z)-1-(4-chlorophenyl)-5-((4-methyl-N-phenylphenyl)sulfonamido)-5-oxopenta-1,3-dien-3-yl benzoate 6h



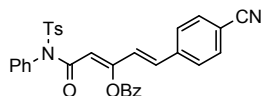
Yellow solid (m.p. 114-115 °C), $R_f = 0.44$, hexane /AcOEt = 7:3; ^1H NMR (400 MHz, CDCl_3) δ 8.03 (d, $J = 7.8$ Hz, 2H), 7.76 (d, $J = 8.2$ Hz, 2H), 7.67 (t, $J = 7.3$ Hz, 1H), 7.55 – 7.46 (m, 5H), 7.36 (dd, $J = 6.3, 2.7$ Hz, 2H), 7.27 – 7.24 (m, 4H), 7.15 (d, $J = 8.1$ Hz, 2H), 6.88 (d, $J = 15.8$ Hz, 1H), 6.36 (d, $J = 15.8$ Hz, 1H), 5.49 (s, 1H), 2.41 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 163.3, 163.0, 155.9, 144.4, 136.1, 135.7, 135.2, 134.6, 133.7, 133.5, 130.5, 130.4, 129.9, 129.7, 129.2, 129.0, 129.0, 128.6, 128.4, 123.1, 110.3, 21.7; IR (KBr) ν_{max} 3064, 2975, 2358, 1744, 1687, 1596, 1244, 1082, 695 cm^{-1} ; HRMS (DART) calcd. for $\text{C}_{31}\text{H}_{25}\text{ClNO}_5\text{S}$ $[\text{M}+\text{H}]^+$: 558.1136, found 558.1135.

(1E,3Z)-1-(4-bromophenyl)-5-((4-methyl-N-phenylphenyl)sulfonamido)-5-oxopenta-1,3-dien-3-yl benzoate 6i



Yellow solid (m.p. 135-136 °C), $R_f = 0.42$, hexane /AcOEt = 7:3; ^1H NMR (400 MHz, CDCl_3) δ 8.03 (d, $J = 7.2$ Hz, 2H), 7.76 (d, $J = 8.3$ Hz, 2H), 7.67 (t, $J = 7.4$ Hz, 1H), 7.55 – 7.48 (m, 5H), 7.43 – 7.34 (m, 4H), 7.18 (d, $J = 8.5$ Hz, 2H), 7.15 (d, $J = 8.2$ Hz, 2H), 6.86 (d, $J = 15.8$ Hz, 1H), 6.38 (d, $J = 15.8$ Hz, 1H), 5.50 (s, 1H), 2.41 (s, 3H); ^{13}C NMR (100MHz, CDCl_3) δ 163.3, 163.0, 155.9, 144.4, 136.1, 135.7, 134.6, 133.9, 133.7, 131.9, 130.5, 130.4, 129.9, 129.7, 129.2, 129.0, 128.9, 128.4, 123.5, 123.2, 110.4, 21.7; IR (KBr) ν_{max} 3063, 2358, 1743, 1687, 1610, 1360, 1243, 695 cm^{-1} ; HRMS (DART) calcd. for $\text{C}_{31}\text{H}_{25}\text{BrNO}_5\text{S}$ $[\text{M}+\text{H}]^+$: 602.0631, found 602.0634.

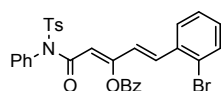
(1E,3Z)-1-(4-cyanophenyl)-5-((4-methyl-N-phenylphenyl)sulfonamido)-5-oxopenta-1,3-dien-3-yl benzoate 6j



Yellow solid (m.p. 130-131 °C), $R_f = 0.39$, hexane /AcOEt = 7:3; ^1H NMR (400 MHz, CDCl_3) δ 8.02 (d, $J = 7.9$ Hz, 2H), 7.76 (d, $J = 8.2$ Hz, 2H), 7.68 (t, $J = 7.5$ Hz, 1H), 7.57 – 7.48 (m, 7H), 7.41 (d, $J = 8.3$ Hz, 2H), 7.37 (dd, $J = 6.3, 2.6$ Hz, 2H), 7.15 (d, $J = 8.2$ Hz, 2H), 6.91 (d, $J = 15.8$ Hz, 1H), 6.48 (d, $J = 15.8$ Hz, 1H), 5.57 (s, 1H), 2.42 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 163.3, 162.8, 155.0, 144.5, 139.3, 135.9, 135.6, 133.8, 133.5, 132.4, 130.4, 130.4, 130.0, 129.7, 129.2, 129.1, 128.8, 128.4, 127.8, 126.0, 118.4, 112.4, 111.9, 21.7; IR (KBr) ν_{max} 3064, 2925, 2358, 2219, 1743, 1606, 1362, 1243, 1071, 695 cm^{-1} ;

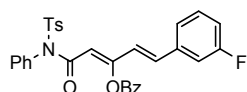
HRMS (DART) calcd. for $C_{32}H_{25}N_2O_5S$ $[M+H]^+$: 549.1479, found 549.1476.

(1E,3Z)-1-(2-bromophenyl)-5-((4-methyl-N-phenylphenyl)sulfonamido)-5-oxopenta-1,3-dien-3-yl benzoate 6k

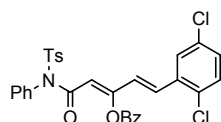


Yellow solid (m.p. 136-137 °C), R_f = 0.41, hexane /AcOEt = 7:3; 1H NMR (400 MHz, $CDCl_3$) δ 8.03 (d, J = 7.8 Hz, 2H), 7.78 (d, J = 8.2 Hz, 2H), 7.65 (t, J = 7.4 Hz, 1H), 7.50 (dd, J = 9.6, 5.3 Hz, 6H), 7.44 (d, J = 7.7 Hz, 1H), 7.41 – 7.33 (m, 3H), 7.20 (dd, J = 16.5, 7.9 Hz, 3H), 7.10 (t, J = 7.4 Hz, 1H), 6.33 (d, J = 15.7 Hz, 1H), 5.53 (s, 1H), 2.43 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 163.2, 162.9, 155.6, 144.4, 136.1, 135.8, 134.8, 134.5, 133.6, 133.3, 130.5, 130.4, 130.3, 129.9, 129.6, 129.2, 129.1, 128.4, 127.5, 127.1, 124.9, 110.9, 21.6; IR (KBr) ν_{max} 3063, 2923, 2358, 1744, 1688, 1609, 1360, 694, 561 cm^{-1} ; HRMS (DART) calcd. for $C_{31}H_{25}BrNO_5S$ $[M+H]^+$: 602.0631, found 602.0629.

(1E,3Z)-1-(3-fluorophenyl)-5-((4-methyl-N-phenylphenyl)sulfonamido)-5-oxopenta-1,3-dien-3-yl benzoate 6l

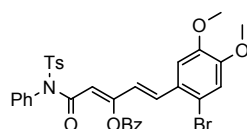


Yellow solid (m.p. 150-153 °C), R_f = 0.41, hexane /AcOEt = 7:3; 1H NMR (400 MHz, $CDCl_3$) δ 8.03 (d, J = 7.7 Hz, 2H), 7.76 (d, J = 7.8 Hz, 2H), 7.67 (t, J = 7.4 Hz, 1H), 7.51 (dd, J = 9.1, 4.8 Hz, 5H), 7.37 (d, J = 4.5 Hz, 2H), 7.24 – 7.19 (m, 1H), 7.15 (d, J = 7.9 Hz, 2H), 7.08 (d, J = 7.7 Hz, 1H), 7.02 (d, J = 9.8 Hz, 1H), 6.95 (t, J = 8.2 Hz, 1H), 6.88 (d, J = 15.7 Hz, 1H), 6.38 (d, J = 15.8 Hz, 1H), 5.51 (s, 1H), 2.41 (s, 3H); ^{19}F NMR (376 MHz, $CDCl_3$) δ -112.8 (Trifluorotoluene δ -62.8 as reference compound); ^{13}C NMR (101 MHz, $CDCl_3$) δ 163.3, 163.0 (d, J_{C-F} = 246.4 Hz), 162.9, 155.7, 144.4, 137.3 (d, J_{C-F} = 7.6 Hz), 136.1, 135.8, 134.6, 133.7, 130.4 (d, J_{C-F} = 8.2 Hz), 130.2 (d, J_{C-F} = 8.3 Hz), 129.9, 129.7, 129.2, 129.0, 128.4, 123.9, 123.5 (d, J_{C-F} = 2.8 Hz), 116.2 (d, J_{C-F} = 21.3 Hz), 113.7 (d, J_{C-F} = 22.0 Hz), 110.7, 21.6; IR (KBr) ν_{max} 3066, 2358, 1744, 1688, 1607, 1360, 1160, 694 cm^{-1} ; HRMS (DART) calcd. for $C_{31}H_{25}FNO_5S$ $[M+H]^+$: 542.1432, found 542.1429. **(1E,3Z)-1-(2,5-dichlorophenyl)-5-((4-methyl-N-phenylphenyl)sulfonamido)-5-oxopenta-1,3-dien-3-yl benzoate 6m**



Yellow solid (m.p. 167-168 °C), R_f = 0.44, hexane /AcOEt = 7:3; 1H NMR (400 MHz, $CDCl_3$) δ 8.01 (d, J = 8.0 Hz, 2H), 7.77 (d, J = 8.1 Hz, 2H), 7.66 (t, J = 7.5 Hz, 1H), 7.50 (dd, J = 9.3, 6.0 Hz, 5H), 7.41 – 7.35 (m, 3H), 7.33 – 7.30 (m, 1H), 7.25 (s, 1H), 7.16 (t, J = 8.0 Hz, 3H), 6.36 (d, J = 15.8 Hz, 1H), 5.54 (s, 1H), 2.43 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 163.3, 162.9, 155.4, 144.5, 136.0, 135.7, 135.4, 134.8, 133.7, 131.8, 130.5, 130.3, 129.9, 129.8, 129.7, 129.2, 129.1, 129.0, 128.4, 127.7, 127.4, 125.3, 111.3, 21.7; IR (KBr) ν_{max} 3066, 2925, 2358, 1745, 1608, 1361, 1233, 1062, 695, 557 cm^{-1} ; HRMS (DART) calcd. For $C_{31}H_{24}Cl_2NO_5S$ $[M+H]^+$: 592.0747, found 592.0747.

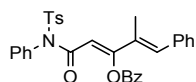
(1E,3Z)-1-(2-bromo-4,5-dimethoxyphenyl)-5-((4-methyl-N-phenylphenyl)sulfonamido)-5-oxopenta-1,3-dien-3-yl benzoate 6n



Yellow solid (m.p. 101-102 °C), R_f = 0.25, hexane /AcOEt = 7:3; 1H NMR (400 MHz, $CDCl_3$) δ 8.03 (d, J = 7.7 Hz, 2H), 7.77 (d, J = 7.6 Hz, 2H), 7.65 (t, J = 7.4 Hz, 1H), 7.50 (t, J = 6.8 Hz, 5H), 7.38 (d, J = 3.6 Hz, 2H), 7.30 (d, J = 15.6 Hz, 1H), 7.18 (d, J = 7.8 Hz, 2H), 6.92 (d, J = 19.0 Hz, 2H), 6.24 (d, J = 15.7 Hz, 1H), 5.54 (s, 1H), 3.83 (s, 6H), 2.43 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 163.3, 163.0, 156.2, 150.8, 148.6, 144.4, 136.2, 135.8, 134.6, 133.6, 130.5, 130.3, 129.7, 129.6, 129.2, 129.1, 129.0, 128.4, 126.8, 122.6, 116.7, 115.5, 109.9, 108.9, 56.1, 21.6; IR (KBr) ν_{max} 3065, 2936, 2847, 2358, 1744, 1687, 1500,

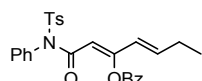
1358, 1076, 562 cm^{-1} ; HRMS (DART) calcd. For $\text{C}_{23}\text{H}_{29}\text{BrNO}_7\text{S}$ $[\text{M}+\text{H}]^+$: 662.0843, found 662.0840.

(1E,3Z)-2-methyl-5-((4-methyl-N-phenylphenyl)sulfonamido)-5-oxo-1-phenylpenta-1,3-dien-3-yl benzoate 6o



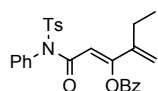
Yellow solid (m.p. 158-159 $^{\circ}\text{C}$), R_f = 0.42, hexane /AcOEt = 7:3; ^1H NMR (400 MHz, CDCl_3) δ 8.00 (d, J = 7.4 Hz, 2H), 7.78 (d, J = 8.3 Hz, 2H), 7.64 (t, J = 7.4 Hz, 1H), 7.48 (dd, J = 9.2, 6.3 Hz, 5H), 7.39 (dd, J = 6.6, 2.9 Hz, 2H), 7.28 (t, J = 7.3 Hz, 2H), 7.23 (d, J = 7.2 Hz, 1H), 7.17 (d, J = 7.4 Hz, 2H), 7.14 (d, J = 8.3 Hz, 2H), 7.01 (s, 1H), 5.60 (s, 1H), 2.41 (s, 3H), 1.69 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 163.7, 163.4, 158.2, 144.3, 136.3, 136.1, 135.8, 133.5, 133.3, 130.5, 130.3, 130.0, 129.8, 129.6, 129.5, 129.3, 129.2, 129.0, 128.3, 128.2, 127.9, 107.8, 21.7, 13.9; IR (KBr) ν_{max} 3062, 2924, 1743, 1605, 1361, 1161, 1087, 696, 573 cm^{-1} ; HRMS (DART) calcd. for $\text{C}_{32}\text{H}_{28}\text{NO}_5\text{S}$ $[\text{M}+\text{H}]^+$: 538.1683, found 538.1684.

(2Z,4E)-1-((4-methyl-N-phenylphenyl)sulfonamido)-1-oxohepta-2,4-dien-3-yl benzoate 6p



Yellow solid (m.p. 118-119 $^{\circ}\text{C}$), R_f = 0.47, hexane /AcOEt = 7:3; ^1H NMR (400 MHz, CDCl_3) δ 7.99 (d, J = 7.4 Hz, 2H), 7.75 (d, J = 8.2 Hz, 2H), 7.63 (t, J = 7.4 Hz, 1H), 7.54 – 7.43 (m, 5H), 7.34 (dd, J = 6.5, 2.8 Hz, 2H), 7.15 (d, J = 8.2 Hz, 2H), 6.24 (dt, J = 15.2, 6.5 Hz, 1H), 5.73 (d, J = 15.5 Hz, 1H), 5.30 (s, 1H), 2.41 (s, 3H), 2.09 (p, J = 6.6 Hz, 2H), 0.94 (t, J = 7.4 Hz, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 163.3, 163.2, 156.4, 144.3, 141.8, 136.2, 135.9, 133.5, 130.5, 130.3, 129.7, 129.6, 129.2, 129.2, 129.0, 128.3, 123.8, 108.1, 25.5, 21.6, 12.4; IR (KBr) ν_{max} 3063, 2970, 2385, 1744, 1603, 1361, 1169, 696 cm^{-1} ; HRMS (DART) calcd. For $\text{C}_{27}\text{H}_{26}\text{NO}_5\text{S}$ $[\text{M}+\text{H}]^+$: 476.1526, found 476.1523.

(Z)-1-((4-methyl-N-phenylphenyl)sulfonamido)-4-methylene-1-oxohex-2-en-3-yl benzoate 6q

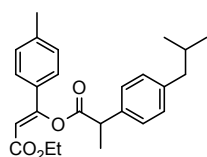


Yellow solid (m.p. 136-138 $^{\circ}\text{C}$), R_f = 0.44, hexane /AcOEt = 7:3; ^1H NMR (400 MHz, CDCl_3) δ 7.95 (d, J = 8.0 Hz, 2H), 7.77 (d, J = 8.1 Hz, 2H), 7.63 (t, J = 7.1 Hz, 1H), 7.47 (dd, J = 9.4, 6.1 Hz, 5H), 7.42 – 7.34 (m, 2H), 7.14 (d, J = 8.1 Hz, 2H), 5.53 (s, 1H), 5.47 (s, 1H), 5.18 (s, 1H), 2.40 (s, 3H), 1.89 (q, J = 7.4 Hz, 2H), 0.83 (t, J = 7.4 Hz, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 163.6, 163.3, 156.2, 144.3, 142.7, 136.2, 135.7, 133.5, 130.4, 130.2, 129.8, 129.6, 129.2, 129.0, 128.3, 117.9, 107.9, 24.8, 21.6, 12.4; IR (KBr) ν_{max} 2971, 2358, 1743, 1695, 1406, 1247, 1163, 695 cm^{-1} ; HRMS (DART) calcd. For $\text{C}_{27}\text{H}_{26}\text{NO}_5\text{S}$ $[\text{M}+\text{H}]^+$: 476.1526, found 476.1524.

3.6 General Procedure for the synthesis of 3t-x

To a DCE (2 mL) solution of **1** (0.2 mmol) in Schlenk tube with a magnetic bar was added carboxylic acid (0.4 mmol), CuCl (5 mol%), 4Å molecular sieve (100 mg) under air atmosphere. The reaction mixture was stirred at 60 $^{\circ}\text{C}$, followed by TLC. After the substrates were completely consumed, the mixture was filtered over celite and washed with dichloromethane, then the solvent was evaporated off and the residue was purified by flash column chromatography (silica gel, mixture of hexane/ethyl acetate).

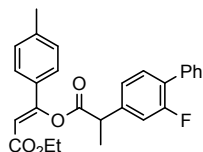
Ethyl (Z)-3-((2-(4-isobutylphenyl)propanoyl)oxy)-3-(p-tolyl)acrylate 3t



Thick oil, R_f = 0.66, hexane /AcOEt = 10:1; ^1H NMR (400 MHz, CDCl_3) δ 7.32 (d, J = 7.9 Hz, 2H), 7.15 (d, J = 7.8 Hz, 2H),

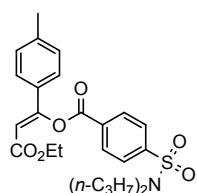
7.09 (d, $J = 8.1$ Hz, 2H), 6.99 (d, $J = 8.0$ Hz, 2H), 6.19 (s, 1H), 4.18 (q, $J = 7.1$ Hz, 2H), 4.07 (q, $J = 7.1$ Hz, 1H), 2.50 (d, $J = 7.1$ Hz, 2H), 2.29 (s, 3H), 1.89 (dp, $J = 13.3, 6.6$ Hz, 1H), 1.64 (d, $J = 7.1$ Hz, 3H), 1.29 (t, $J = 7.1$ Hz, 3H), 0.93 (d, $J = 6.6$ Hz, 6H); ^{13}C NMR (100 MHz, CDCl_3) δ 171.4, 164.3, 157.9, 141.2, 140.9, 137.1, 130.5, 129.4, 129.3, 127.6, 125.6, 105.3, 60.1, 45.2, 45.0, 30.2, 22.3, 22.3, 21.3, 17.8, 14.2; IR (KBr) ν_{max} 2918, 1915, 1761, 1628, 1453, 1162, 821, 579 cm^{-1} ; HRMS (ESI) calcd. For $\text{C}_{25}\text{H}_{31}\text{O}_4$ $[\text{M}+\text{H}]^+$: 395.2217, found 395.2220.

Ethyl (Z)-3-((2-(2-fluoro-[1,1'-biphenyl]-4-yl)propanoyl)oxy)-3-(p-tolyl)acrylate 3u



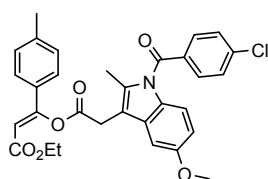
Thick oil, $R_f = 0.65$, hexane /AcOEt = 10:1; ^1H NMR (400 MHz, CDCl_3) δ 7.62 (d, $J = 7.8$ Hz, 2H), 7.50 (t, $J = 7.8$ Hz, 3H), 7.42 (t, $J = 7.3$ Hz, 1H), 7.34 – 7.27 (m, 2H), 7.25 (d, $J = 8.2$ Hz, 2H), 7.11 (d, $J = 8.1$ Hz, 2H), 6.26 (s, 1H), 4.21 (dq, $J = 18.3, 7.1$ Hz, 3H), 2.35 (s, 3H), 1.75 (d, $J = 7.2$ Hz, 3H), 1.33 (t, $J = 7.1$ Hz, 3H); ^{19}F NMR (376 MHz, CDCl_3) δ -117.5 (Trifluorotoluene δ -62.8 as reference compound); ^{13}C NMR (100 MHz, CDCl_3) δ 170.8, 164.2, 159.8 (d, $J_{\text{C-F}} = 248.7$ Hz), 157.9, 141.4, 141.2 (d, $J_{\text{C-F}} = 7.8$ Hz), 135.5, 130.9 (d, $J_{\text{C-F}} = 3.9$ Hz), 130.4, 129.4, 129.0 (d, $J_{\text{C-F}} = 2.9$ Hz), 128.5, 128.1 (d, $J_{\text{C-F}} = 13.5$ Hz), 127.7, 125.7, 124.0 (d, $J_{\text{C-F}} = 3.2$ Hz), 115.7 (d, $J_{\text{C-F}} = 23.6$ Hz), 105.4, 60.2, 45.1, 21.3, 18.0, 14.2; IR (KBr) ν_{max} 2957, 1766, 1715, 1639, 1457, 1275, 1167, 1122, 816 cm^{-1} ; HRMS (ESI) calcd. For $\text{C}_{27}\text{H}_{26}\text{FO}_4$ $[\text{M}+\text{H}]^+$: 433.1810, found 433.1808.

(Z)-3-ethoxy-3-oxo-1-(p-tolyl)prop-1-en-1-yl 4-(N,N-dipropylsulfamoyl)benzoate 3v



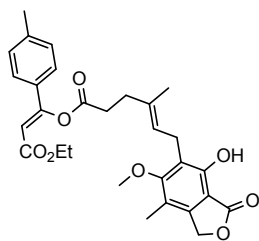
Thick oil, $R_f = 0.30$, hexane /AcOEt = 10:1; ^1H NMR (400 MHz, CDCl_3) δ 8.34 (d, $J = 8.3$ Hz, 2H), 7.95 (d, $J = 8.3$ Hz, 2H), 7.52 (d, $J = 8.2$ Hz, 2H), 7.21 (d, $J = 8.2$ Hz, 2H), 6.35 (s, 1H), 4.13 (q, $J = 7.1$ Hz, 2H), 3.18 – 3.07 (m, 4H), 2.38 (s, 3H), 1.64 – 1.54 (m, 4H), 1.18 (t, $J = 7.1$ Hz, 3H), 0.90 (t, $J = 7.4$ Hz, 6H); ^{13}C NMR (100 MHz, CDCl_3) δ 164.1, 162.6, 157.9, 144.8, 141.8, 132.5, 130.9, 130.2, 129.6, 127.2, 125.9, 105.8, 60.3, 50.2, 22.1, 21.4, 14.1, 11.1; IR (KBr) ν_{max} 2970, 1751, 1711, 1640, 1338, 1242, 1166, 1082, 812 cm^{-1} ; HRMS (ESI) calcd. For $\text{C}_{25}\text{H}_{32}\text{NO}_6\text{S}$ $[\text{M}+\text{H}]^+$: 474.1945, found 474.1946.

Ethyl (Z)-3-(2-(1-(4-chlorobenzoyl)-5-methoxy-2-methyl-1H-indol-3-yl)acetoxyl)-3-(p-tolyl)acrylate 3w



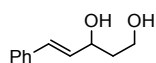
Yellow solid (m.p. 114-115 $^{\circ}\text{C}$), $R_f = 0.54$, hexane /AcOEt = 10:1; ^1H NMR (400 MHz, CDCl_3) δ 7.69 (d, $J = 8.4$ Hz, 2H), 7.48 (d, $J = 8.4$ Hz, 2H), 7.36 (d, $J = 8.2$ Hz, 2H), 7.14 (dd, $J = 9.6, 5.3$ Hz, 3H), 6.97 (d, $J = 9.0$ Hz, 1H), 6.73 (dd, $J = 9.0, 2.4$ Hz, 1H), 6.26 (s, 1H), 4.23 (q, $J = 7.1$ Hz, 2H), 4.07 (s, 2H), 3.85 (s, 3H), 2.47 (s, 3H), 2.36 (s, 3H), 1.33 (t, $J = 7.1$ Hz, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 168.3, 168.0, 164.2, 158.2, 156.1, 141.5, 139.2, 136.2, 133.9, 131.2, 130.8, 130.7, 130.4, 129.5, 129.1, 125.8, 114.9, 112.1, 112.1, 105.1, 101.2, 60.1, 55.6, 30.2, 21.4, 14.3, 13.4; IR (KBr) ν_{max} 2934, 1768, 1708, 1637, 1472, 1320, 1166, 1103, 916, 822 cm^{-1} ; HRMS (ESI) calcd. For $\text{C}_{31}\text{H}_{29}\text{ClNO}_6$ $[\text{M}+\text{H}]^+$: 546.1678, found 546.1679.

(Z)-3-ethoxy-3-oxo-1-(p-tolyl)prop-1-en-1-yl(E)-5-(4-hydroxy-6-methoxy-7-methyl-3-oxo-1,3-dihydroisobenzofuran-5-yl)-3-methylpent-3-enoate 3x



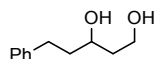
Thick oil, $R_f = 0.46$, hexane /AcOEt = 10:1; ^1H NMR (400 MHz, CDCl_3) δ 7.68 (s, 1H), 7.43 (d, $J = 8.2$ Hz, 2H), 7.17 (d, $J = 8.1$ Hz, 2H), 6.20 (s, 1H), 5.34 (t, $J = 6.6$ Hz, 1H), 5.19 (s, 2H), 4.16 (q, $J = 7.1$ Hz, 2H), 3.75 (s, 3H), 3.42 (d, $J = 6.9$ Hz, 2H), 2.83 – 2.72 (m, 2H), 2.53 – 2.43 (m, 2H), 2.36 (s, 3H), 2.14 (s, 3H), 1.87 (s, 3H), 1.27 (t, $J = 7.1$ Hz, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 172.9, 170.3, 164.2, 163.7, 158.2, 153.6, 144.0, 141.4, 134.0, 130.6, 129.5, 125.8, 122.8, 122.0, 116.7, 106.3, 105.1, 70.0, 61.0, 60.1, 34.0, 32.9, 22.6, 21.4, 16.3, 14.2, 11.5; IR (KBr) ν_{max} 2929, 1727, 1634, 1454, 1327, 1170, 1123, 1029, 819 cm^{-1} ; HRMS (ESI) calcd. For $\text{C}_{28}\text{H}_{31}\text{O}_8$ $[\text{M}+\text{H}]^+$: 495.2013, found 495.2012.

(E)-5-phenylpent-4-ene-1,3-diol 8^{4a}



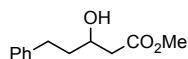
^1H NMR (400 MHz, CDCl_3) δ 7.38 (d, $J = 7.5$ Hz, 2H), 7.31 (t, $J = 7.5$ Hz, 2H), 7.26 – 7.18 (m, 1H), 6.61 (d, $J = 15.9$ Hz, 1H), 6.25 (dd, $J = 15.9, 6.4$ Hz, 1H), 4.56 (dd, $J = 12.2, 6.2$ Hz, 1H), 3.95 – 3.81 (m, 2H), 2.76 (s, 1H), 2.55 (s, 1H), 1.91 – 1.85 (m, 2H); ^{13}C NMR (100 MHz, CDCl_3) δ 136.6, 131.8, 130.2, 128.6, 127.7, 126.5, 72.5, 61.1, 38.6.

5-Phenylpentane-1,3-diol 9^{4b}



^1H NMR (400 MHz, CDCl_3) δ 7.22 – 7.17 (m, 2H), 7.15 – 7.07 (m, 3H), 3.82 (dt, $J = 9.6, 4.9$ Hz, 2H), 3.77 – 3.71 (m, 1H), 2.77 – 2.63 (m, 2H), 2.66 – 2.54 (m, 2H), 1.81 – 1.70 (m, 2H), 1.69 – 1.61 (m, 2H); ^{13}C NMR (100 MHz, CDCl_3) δ 141.9, 128.4, 128.4, 125.9, 71.5, 61.7, 39.3, 38.3, 31.9.

Methyl 3-hydroxy-5-phenylpentanoate 10^{4c}



^1H NMR (400 MHz, CDCl_3) δ 7.28 (t, $J = 7.6$ Hz, 2H), 7.22 – 7.16 (m, 3H), 4.04 – 4.00 (m, 1H), 3.70 (s, 3H), 3.00 (s, 1H), 2.87 – 2.77 (m, 1H), 2.74 – 2.66 (m, 1H), 2.55 – 2.42 (m, 2H), 1.89 – 1.72 (m, 2H); ^{13}C NMR (100 MHz, CDCl_3) δ 173.3, 141.7, 128.4, 128.4, 125.9, 67.2, 51.7, 41.1, 38.1, 31.7.

4. References

- [1](a) M. Zheng, F. Wu, K. Chen, Zhu, S. *Org. Lett.* **2016**, *18*, 3554-3557. (b) D. Rodriguez, M. F. Martinez-Esperon, L. Castedo, C. Saa, *Synlett* **2007**, *2007*, 1963-1965. (c) Z. F. Al-Rashid, W. L. Johnson, R. P. Hsung, Y. Wei, P. Y. Yao, R. Liu, K. Zhao, *J. Org. Chem.* **2008**, *73*, 8780-8784. (d) D. Li, Y. Wei, M. Shi. *Eur. J. Org. Chem.* **2015**, *2005*, 4108-4113.
- [2] T. Lam, Y. Wang, R. L. Danheiser, *J. Org. Chem.* **2013**, *78*, 9396-9414.
- [3] Y. Wang, Z. Wang, Y. Li, G. Wu, Z. Cao, L. Zhang, *Nat. Commun.* **2014**, *5*, 3470-3478.
- [4] (a) T. Cohen, I. Jeong, B. Mudryk, M. Bhupathy, M. A. Awad. *J. Org. Chem.* **1990**, *55*, 1528-1536. (b) H. Fujioka, Y. Ohba, H. Hirose, K. Murai, Y. Kita, *Org. Lett.* **2005**, *7*, 3303-3306. (c) H. Fujioka, H. Hirose, Y. Ohba, K. Murai, K. Nakahara, Y. Kita, *Tetrahedron*. **2007**, *63*, 625-637.

5. ORTEP Representation of the X-ray Structure of 6o.

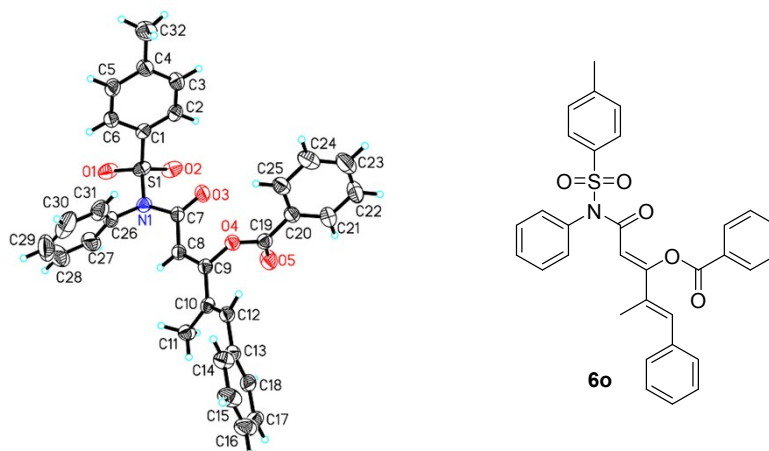
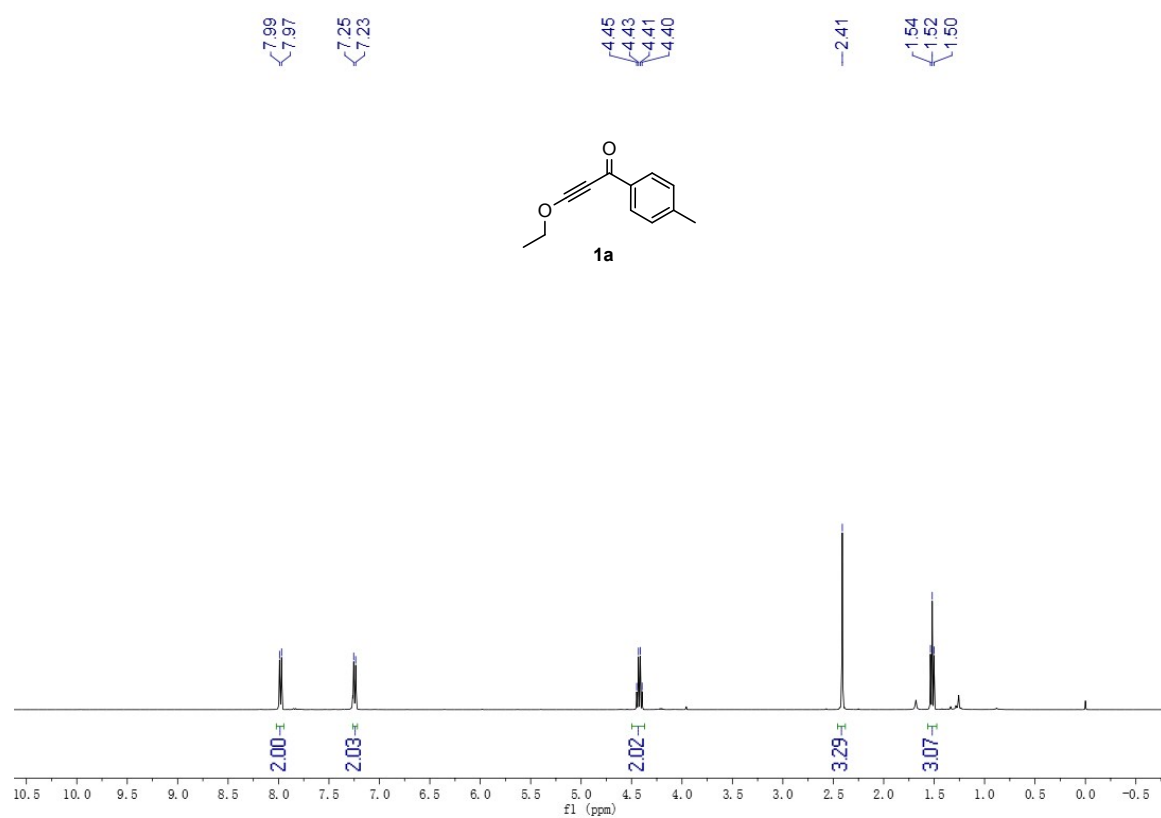


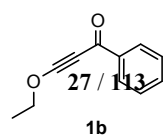
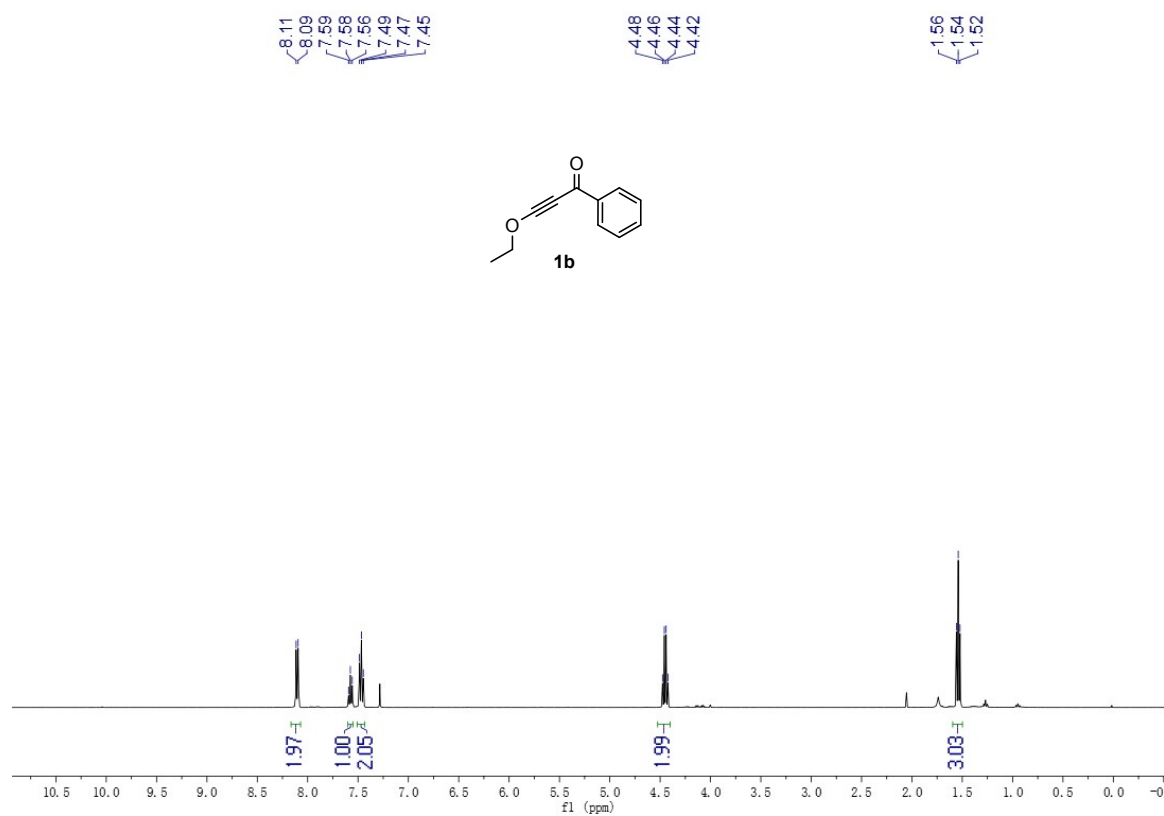
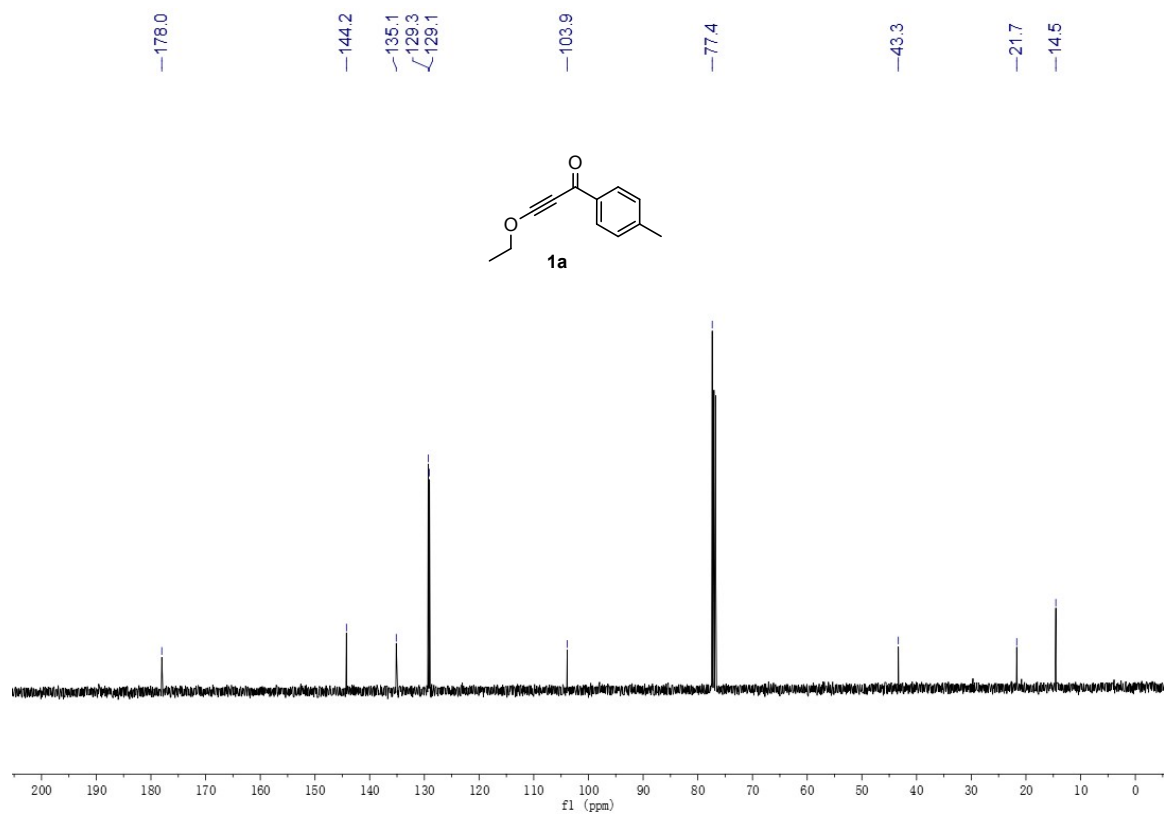
Table 1 Crystal data and structure refinement for 6o.

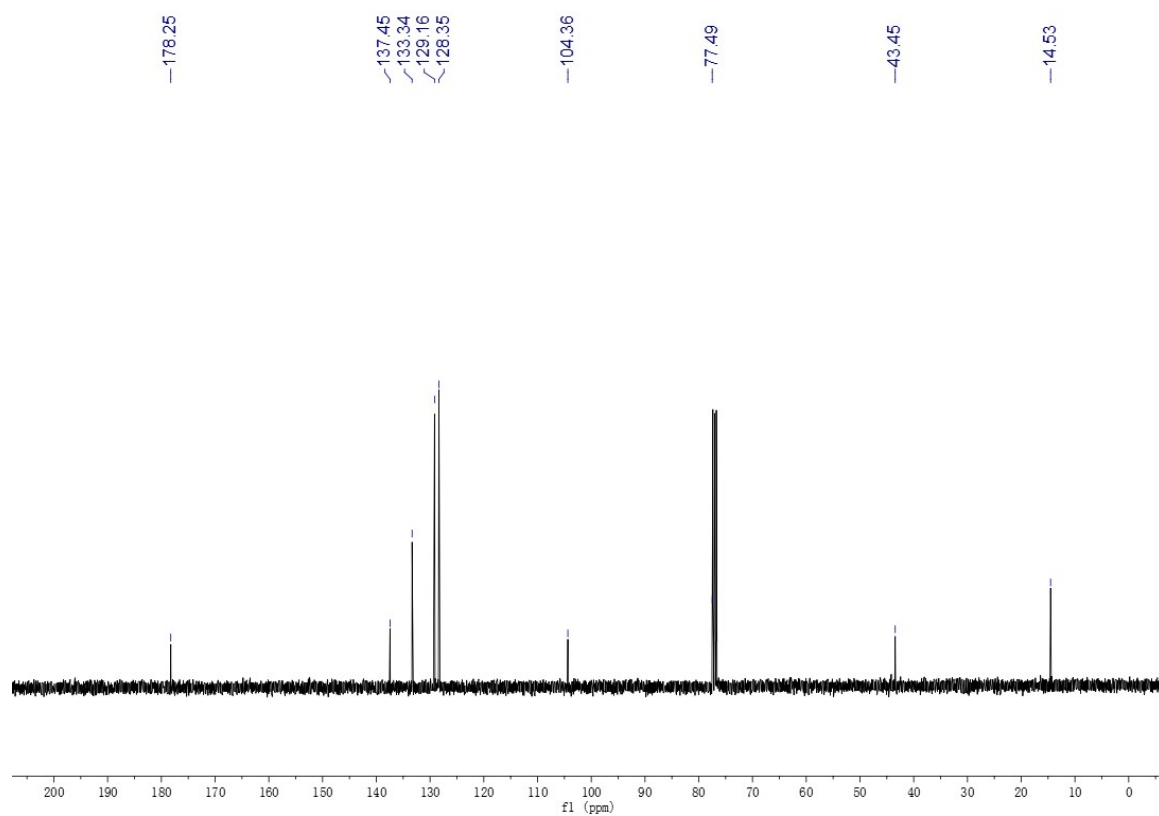
Identification code	6o
CCDC	1853356
Empirical formula	C ₃₂ H ₂₇ NO ₅ S
Formula weight	537.60
Temperature/K	268(40)
Crystal system	triclinic
Space group	P-1
a/Å	10.2760(12)
b/Å	12.5669(14)
c/Å	13.0463(13)
α /°	66.455(10)
β /°	73.203(9)
γ /°	66.317(11)
Volume/Å ³	1397.7(3)
Z	2
ρ _{calc} /cm ³	1.277
μ/mm ⁻¹	0.157
F(000)	564.0
Crystal size/mm ³	0.21 × 0.16 × 0.12
Radiation	MoK α (λ = 0.71073)
2θ range for data collection/°	6.624 to 59.022
Index ranges	-14 ≤ h ≤ 13, -16 ≤ k ≤ 17, -16 ≤ l ≤ 17
Reflections collected	12753
Independent reflections	6547 [R _{int} = 0.0428, R _{sigma} =

	0.0722]
Data/restraints/parameters	6547/1/355
Goodness-of-fit on F^2	1.064
Final R indexes [$I > 2\sigma$ (I)]	$R_1 = 0.0613$, $wR_2 = 0.1333$
Final R indexes [all data]	$R_1 = 0.1099$, $wR_2 = 0.1707$
Largest diff. peak/hole / $e \text{ \AA}^{-3}$	0.32/-0.34

6. Copies of ^1H , ^{13}C and ^{19}F NMR Spectra







8.12
8.11
8.10
8.09

7.14
7.12
7.10

4.47
4.45
4.43
4.42

1.55
1.53
1.51

