

Supporting Information

Palladium-Catalyzed Four-Component Domino Sulfonation and Carbonylation of 1,3-Enynes at Room Temperature

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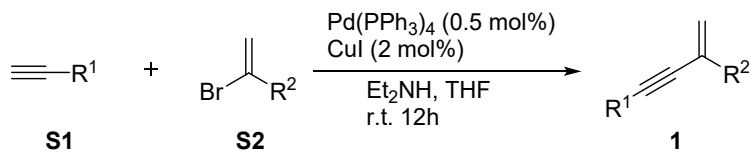
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1. General experimental information

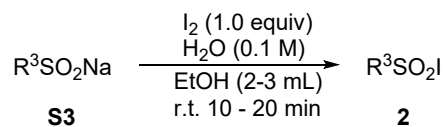
Unless otherwise noted, all reactions were carried out under nitrogen atmosphere. All commercially available reagents were used without further purification. All of the solvents were treated according to known methods. Column chromatography was performed on silica gel (200-400 mesh). ¹H NMR (400 MHz) chemical shifts were reported in ppm (δ) relative to tetramethylsilane (TMS) with the solvent resonance employed as the internal standard. ¹³C NMR (100 MHz) chemical shifts were reported in ppm (δ) from tetramethylsilane (TMS) with the solvent resonance as the internal standard. Data were reported as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, dd = doublet of doublets, td = triplet of doublets, qd = quartet of doublets, m = multiplet), coupling constants (Hz) and integration. HRMS measurements were obtained on a TOF analyzer.

2. General procedure for the synthesis of 1,3-enynes¹



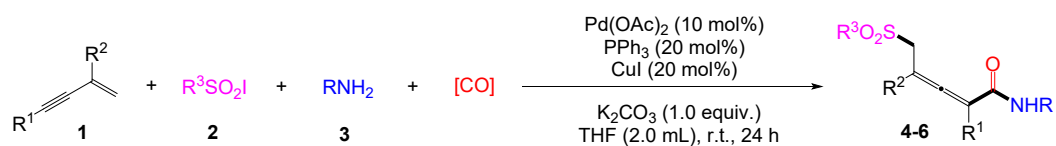
Copper (I) iodide (2 mol%) and tetrakis(triphenylphosphine)palladium (0.5 mol%) were dissolved in diethylamine (0.50 mL/1.0 mmol alkyne) under nitrogen which was then cooled to 0 °C. Phenylacetylene **S1** (1.0 equiv) and vinyl bromide **S2** (1.3 equiv, 1.0 M in THF) were added and the resulting mixture was stirred and warmed up to room temperature until complete conversion. The reaction mixture was washed with water followed by extraction with petroleum ether. The combined organic layers were washed with 1 M HCl and dried over magnesium sulfate. The crude product was afforded after evaporation of the solvent in vacuo and ready to be purified by column chromatography (petroleum ether) to afford 1,3-enynes **1**.

3. General procedures for the synthesis of sulfonyl iodide²



To a round-bottom flask (50 mL) was added sodium sulfite **S3** (0.56 mmol, 1.0 equiv) in distilled water at room temperature. A saturated solution of iodine (0.56 mmol, 1.0 equiv) in ethanol (2-3 mL) was prepared and added gradually to the sodium sulfite solution. During this addition period, yellow precipitates were formed gradually. The precipitates were filtered, washed with cold water, and dried carefully at room temperature to give sulfonyl iodide as a yellow solid. The synthesized sulfonyl iodide immediately used for next step because of spontaneous decomposition of sulfonyl iodides **2**.

4. General procedure for the synthesis of sulfone- and carbonyl-containing allene derivatives (**4a - 4u**, **5a - 5m**, **6a - 6i**)

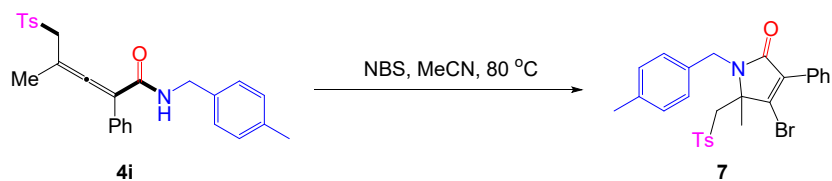


1,3-enyne **1** (0.2 mmol, 1.0 equiv), sulfonyl iodide **2** (0.26 mmol, 1.3 equiv), $Pd(OAc)_2$ (2.3 mg, 5 mol%), PPh_3 (5.4 mg, 10 mol%) were added to an oven-dried tube (15.0 mL) which was then placed under vacuum and refilled with nitrogen three times. THF (2.0 mL) was added into the tube via syringe and the tube was sealed and stirred at room temperature for 1 h. Then, $Pd(OAc)_2$ (2.3 mg, 5 mol%), PPh_3 (5.4 mg, 10 mol%), sulfonyl iodide **2** (0.2 mmol, 1.0 equiv), CuI (7.6 mg, 20 mol%), amine **3** and K_2CO_3 (27.6 mg, 0.2 mmol, 1.0 equiv) were added into the tube which was then placed under vacuum and refilled with nitrogen three times. Then a mixture of formic acid (1.4 mmol) and acetic anhydride (1.4 mmol), which was stirred for 1.5 h at room temperature, was added to the small inner tube with 10 drops of Et_3N . The tube was sealed and stirred at room temperature for 23 h. Upon the reaction was completed, the resulting mixture was purified by silica gel column using chromatography (petroleum ether / ethyl acetate = 3:1) to obtain products (**4a-4u**, **5a-5m**, **6a-6i**).

1 mmol scale: 1,3-enyne **1a** (1.0 mmol, 1.0 equiv), sulfonyl iodide **2a** (1.3 mmol, 1.3 equiv), $Pd(OAc)_2$ (11.5 mg, 5 mol%), PPh_3 (27.0 mg, 10 mol%) were added to an oven-dried tube (100.0 mL) which was then placed under vacuum and refilled with nitrogen three times. THF (10.0 mL) was added into the tube via syringe and the tube was sealed and stirred at room temperature for 1 h. Then, $Pd(OAc)_2$ (11.5 mg, 5 mol%), PPh_3 (27.0 mg, 10 mol%), sulfonyl iodide **2a** (1 mmol, 1.0 equiv), CuI (38 mg, 20 mol%), amine **3i** and K_2CO_3 (138 mg, 1.0 mmol, 1.0 equiv) were added into the tube which was then placed under vacuum and refilled with nitrogen three times. Then a mixture of formic acid (1.0 mmol) and acetic anhydride (1.0 mmol), which was stirred for 1.5 h at room temperature, was added to the small inner tube with 10 drops of Et_3N . The tube was sealed and stirred at room temperature for 23 h. Upon the reaction was completed, the resulting mixture was purified by silica gel column using chromatography (petroleum ether / ethyl acetate = 3:1) to obtain product **4i** in 72% yield (320.5 mg).

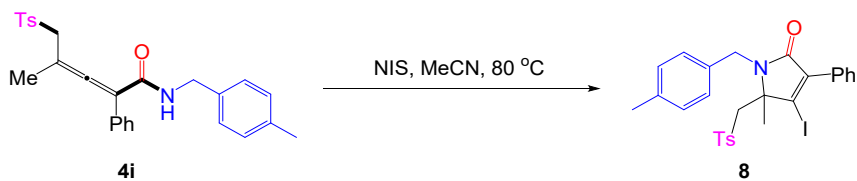
5. Transformations of product into compounds (7, 8)

1)



In an oven-dried tube was charged with allene **4i** (0.1 mmol), NBS (0.13 mmol) and MeCN (1 mL). The resulting suspension was stirred at 80 °C (oil bath) for 24 h. Upon completion of the reaction as monitored by TLC, the solvent was concentrated under vacuum. The crude residue was purified by silica gel column using chromatography (petroleum ether / ethyl acetate = 5:1) to obtain product **7** as a yellow oil in 78% yield (40.9 mg).

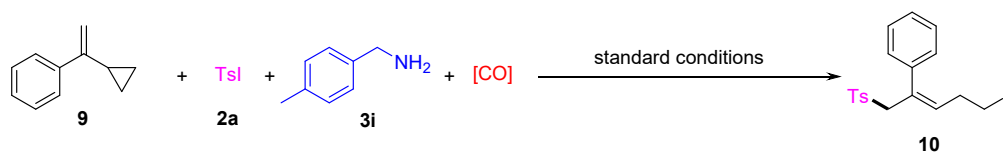
2)



In an oven-dried tube was charged with allene **4i** (0.1 mmol), NIS (0.13 mmol) and MeCN (1 mL). The resulting suspension was stirred at 80 °C (oil bath) for 24 h. Upon completion of the reaction as monitored by TLC, the solvent was concentrated under vacuum. The crude residue was purified by silica gel column using chromatography (petroleum ether / ethyl acetate = 5:1) to obtain product **8** as a yellow oil in 63% yield (36.0 mg).

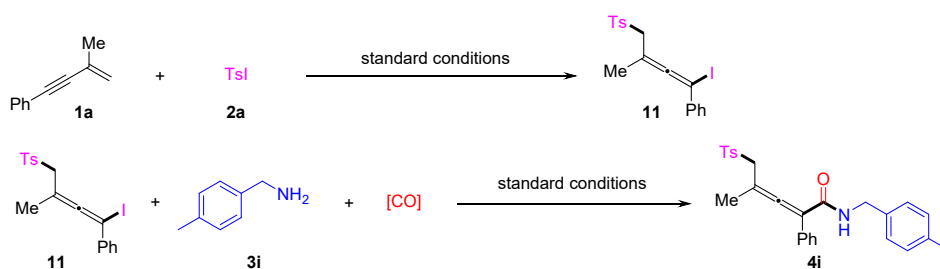
6. Preliminary mechanistic studies

Radical clock experiment



Compound **9** (0.2 mmol, 1.0 equiv), sulfonamide **2a** (0.26 mmol, 1.3 equiv), Pd(OAc)₂ (2.3 mg, 5 mol%), PPh₃ (5.4 mg, 10 mol%) were added to an oven-dried tube (15.0 mL) which was then placed under vacuum and refilled with nitrogen three times. THF (2.0 mL) was added into the tube via syringe and the tube was sealed and stirred at room temperature for 1 h. Then, Pd(OAc)₂ (2.3 mg, 5 mol%), PPh₃ (5.4 mg, 10 mol%), sulfonamide **2a** (0.2 mmol, 1.0 equiv), CuI (7.6 mg, 20 mol%), amine **3i** and K₂CO₃ (27.6 mg, 0.2 mmol, 1.0 equiv) were added into the tube which was then placed under vacuum and refilled with nitrogen three times. Then a mixture of formic acid (1.4 mmol) and acetic anhydride (1.4 mmol), which was stirred for 1.5 h at room temperature, was added to the small inner tube with 10 drops of Et₃N. The tube was sealed and stirred at room temperature for 23 h. Upon the reaction was completed, the resulting mixture was purified by silica gel column using chromatography (petroleum ether / ethyl acetate = 5:1) to obtain product **10** (72.5 mg, 85% yield).

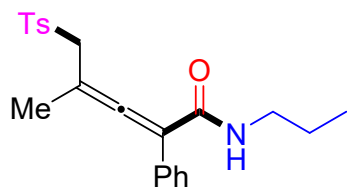
Control experiments



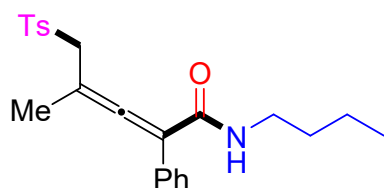
1,3-enyne **1a** (0.2 mmol, 1.0 equiv), sulfonamide **2a** (0.26 mmol, 1.3 equiv), Pd(OAc)₂ (2.3 mg, 5 mol%), PPh₃ (5.4 mg, 10 mol%) were added to an oven-dried tube (15.0 mL) which was then placed under vacuum and refilled with nitrogen three times. THF (2.0 mL) was added into the tube via syringe and the tube was sealed and stirred at room temperature for 1 h. Upon the reaction was completed, the resulting mixture was purified by silica gel column using chromatography (petroleum ether / ethyl acetate = 5:1) to obtain product **11** (81.7 mg, 93% yield).

Compound **11** (0.18 mmol, 1.0 equiv), Pd(OAc)₂ (2.1 mg, 5 mol%), PPh₃ (4.9 mg, 10 mol%), sulfonyl iodide **2a** (0.18 mmol, 1.0 equiv), CuI (6.8 mg, 20 mol%), amine **3i** and K₂CO₃ (25.0 mg, 0.2 mmol, 1.0 equiv) were added into the tube which was then placed under vacuum and refilled with nitrogen three times. Then a mixture of formic acid (1.4 mmol) and acetic anhydride (1.4 mmol), which was stirred for 1.5 h at room temperature, was added to the small inner tube with 10 drops of Et₃N. The tube was sealed and stirred at room temperature for 23 h. Upon the reaction was completed, the resulting mixture was purified by silica gel column using chromatography (petroleum ether / ethyl acetate = 3:1) to obtain product **4i** (66.5 mg, 83% yield).

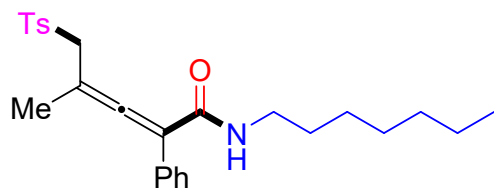
7. Characterization data of products (4a - 4u, 5a - 5m, 6a - 6i, 7, 8, 10)



4-methyl-2-phenyl-N-propyl-5-tosylpenta-2,3-dienamide (4a). The product was purified by column chromatography (petroleum ether / ethyl acetate = 3:1); Pale yellow oil, 46.0 mg, 60% yield; ^1H NMR (400 MHz, CDCl_3) δ 7.79 (d, $J = 8.3$ Hz, 2H), 7.66 (t, $J = 4.7$ Hz, 1H), 7.41 (t, $J = 1.8$ Hz, 2H), 7.35 (d, $J = 8.1$ Hz, 2H), 7.33 – 7.29 (m, 2H), 7.27 – 7.25 (m, 1H), 3.80 (dd, $J = 95.3, 13.5$ Hz, 2H), 3.46 – 3.31 (m, 2H), 2.45 (s, 3H), 1.91 (s, 3H), 1.73 – 1.62 (m, 2H), 0.99 (t, $J = 7.4$ Hz, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 208.2, 165.3, 145.6, 136.0, 132.7, 130.3, 128.7, 128.4, 128.2, 128.0, 106.9, 94.4, 60.9, 41.9, 22.8, 21.8, 19.8, 11.6; HRMS (ESI-TOF) m/z : $[\text{M}+\text{Na}]^+$ Calcd. for $\text{C}_{22}\text{H}_{25}\text{NNaO}_3\text{S}^+$: 406.1447; found: 406.1457.

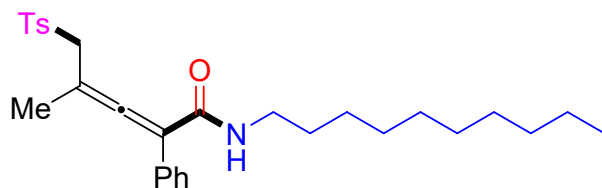


N-butyl-4-methyl-2-phenyl-5-tosylpenta-2,3-dienamide (4b). The product was purified by column chromatography (petroleum ether / ethyl acetate = 3:1); Pale yellow oil, 51.6 mg, 65% yield; ^1H NMR (400 MHz, CDCl_3) δ 7.83 (d, $J = 8.3$ Hz, 2H), 7.64 (t, $J = 5.7$ Hz, 1H), 7.45 – 7.43 (m, 2H), 7.38 (d, $J = 8.1$ Hz, 2H), 7.34 (t, $J = 7.3$ Hz, 2H), 7.31 – 7.28 (m, 1H), 3.83 (dd, $J = 91.3, 13.5$ Hz, 2H), 3.54 - 3.37 (m, 2H), 2.49 (s, 3H), 1.94 (s, 3H), 1.71 – 1.64 (m, 2H), 1.52 – 1.42 (m, 2H), 1.00 (t, $J = 7.3$ Hz, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 208.2, 165.3, 145.6, 136.0, 132.6, 130.3, 128.7, 128.4, 128.2, 127.9, 106.8, 94.4, 60.9, 39.9, 31.5, 21.8, 20.3, 19.8, 13.9; HRMS (ESI-TOF) m/z : $[\text{M}+\text{Na}]^+$ Calcd. for $\text{C}_{23}\text{H}_{27}\text{NNaO}_3\text{S}^+$: 420.1604; found: 420.1613.

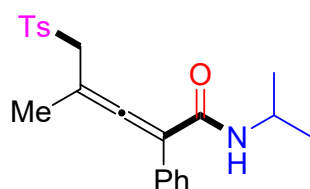


N-heptyl-4-methyl-2-phenyl-5-tosylpenta-2,3-dienamide (4c). The product was purified by column chromatography (petroleum ether / ethyl acetate = 3:1); Pale yellow oil, 56.2 mg, 64% yield; ^1H NMR

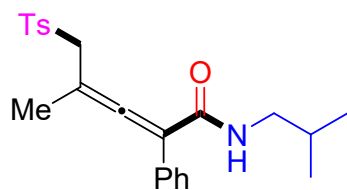
(400 MHz, CDCl₃) δ 7.79 (d, J = 8.2 Hz, 2H), 7.64 (t, J = 5.1 Hz, 1H), 7.40 – 7.29 (m, 6H), 7.27 – 7.25 (m, 1H), 3.79 (dd, J = 92.2, 13.5 Hz, 2H), 3.40 (dp, J = 19.1, 6.0 Hz, 2H), 2.45 (s, 3H), 1.90 (s, 3H), 1.68 – 1.61 (m, 2H), 1.42 – 1.25 (m, 8H), 0.86 (t, J = 6.9 Hz, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 208.2, 165.2, 145.5, 136.2, 132.7, 130.2, 128.7, 128.4, 128.2, 127.9, 106.9, 94.4, 60.9, 40.3, 31.9, 29.5, 29.1, 27.1, 22.7, 21.8, 19.7, 14.2; HRMS (ESI-TOF) m/z : [M+Na]⁺ Calcd. for C₂₆H₃₃NNaO₃S⁺ : 462.2073; found: 462.2077.



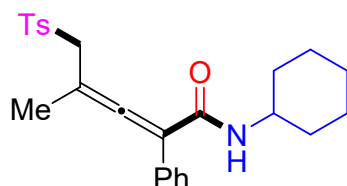
***N*-decyl-4-methyl-2-phenyl-5-tosylpenta-2,3-dienamide (4d).** The product was purified by column chromatography (petroleum ether / ethyl acetate = 3:1); Pale yellow oil, 64.5 mg, 67% yield; ¹H NMR (400 MHz, CDCl₃) δ 7.79 (d, J = 8.3 Hz, 2H), 7.64 (t, J = 5.3 Hz, 1H), 7.41 – 7.25 (m, 7H), 3.79 (dd, J = 93.2, 13.5 Hz, 2H), 3.48 – 3.33 (m, 2H), 2.45 (s, 3H), 1.90 (s, 3H), 1.68 (d, J = 7.0 Hz, 2H), 1.41 – 1.25 (m, 14H), 0.86 (t, J = 6.8 Hz, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 208.2, 165.2, 145.5, 136.2, 132.7, 130.3, 128.7, 128.4, 128.2, 128.0, 106.9, 94.4, 60.9, 40.3, 32.0, 29.74, 29.69, 29.5, 29.4, 27.2, 22.8, 21.8, 19.8, 14.2; HRMS (ESI-TOF) m/z : [M+H]⁺ Calcd. for C₂₉H₄₀NO₃S⁺ : 482.2723; found: 482.2741.



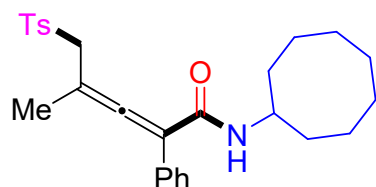
***N*-isopropyl-4-methyl-2-phenyl-5-tosylpenta-2,3-dienamide (4e).** The product was purified by column chromatography (petroleum ether / ethyl acetate = 3:1); Pale yellow oil, 39.9 mg, 52% yield; ¹H NMR (400 MHz, CDCl₃) δ 7.81 (d, J = 8.3 Hz, 2H), 7.56 (d, J = 7.6 Hz, 1H), 7.41 – 7.35 (m, 4H), 7.33 – 7.29 (m, 2H), 7.27 – 7.25 (m, 1H), 4.27 – 4.18 (m, 1H), 3.79 (dd, J = 103.7, 13.5 Hz, 2H), 2.46 (s, 3H), 1.86 (s, 3H), 1.29 (d, J = 6.6 Hz, 6H); ¹³C NMR (100 MHz, CDCl₃) δ 208.2, 164.4, 145.6, 136.2, 132.8, 130.3, 128.7, 128.4, 128.3, 127.9, 107.0, 94.3, 60.9, 42.2, 22.8, 22.7, 21.8, 19.8; HRMS (ESI-TOF) m/z : [M+Na]⁺ Calcd. for C₂₂H₂₅NNaO₃S⁺ : 406.1447; found: 406.1457.



***N*-isobutyl-4-methyl-2-phenyl-5-tosylpenta-2,3-dienamide (4f).** The product was purified by column chromatography (petroleum ether / ethyl acetate = 3:1); Pale yellow oil, 50.9 mg, 64% yield; ^1H NMR (400 MHz, CDCl_3) δ 7.78 (d, $J = 8.3$ Hz, 2H), 7.68 (t, $J = 5.5$ Hz, 1H), 7.41 – 7.39 (m, 2H), 7.35 – 7.29 (m, 4H), 7.27 – 7.25 (m, 1H), 3.80 (dd, $J = 93.1, 13.5$ Hz, 2H), 3.32 – 3.18 (m, 2H), 2.44 (s, 3H), 1.99 – 1.92 (m, 4H), 0.99 (d, $J = 6.7$ Hz, 6H); ^{13}C NMR (100 MHz, CDCl_3) δ 208.1, 165.4, 145.5, 136.1, 132.7, 130.3, 128.7, 128.4, 128.2, 127.9, 106.9, 94.4, 60.8, 47.6, 28.6, 21.8, 20.4, 20.3, 19.8; HRMS (ESI-TOF) m/z : $[\text{M}+\text{Na}]^+$ Calcd. for $\text{C}_{23}\text{H}_{27}\text{NNaO}_3\text{S}^+$: 420.1604; found: 420.1611.

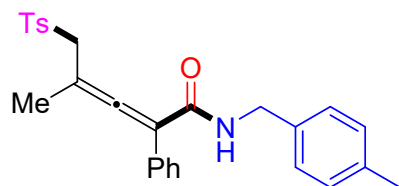


***N*-cyclohexyl-4-methyl-2-phenyl-5-tosylpenta-2,3-dienamide (4g).** The product was purified by column chromatography (petroleum ether / ethyl acetate = 3:1); Pale yellow oil, 44.9 mg, 53% yield; ^1H NMR (400 MHz, CDCl_3) δ 7.81 (d, $J = 8.3$ Hz, 2H), 7.54 (d, $J = 8.0$ Hz, 1H), 7.41 – 7.34 (m, 4H), 7.33 – 7.28 (m, 2H), 7.27 – 7.25 (m, 1H), 3.93 – 3.87 (m, 2H), 3.65 (d, $J = 13.5$ Hz, 1H), 2.45 (s, 3H), 2.05 – 2.02 (m, 2H), 1.86 (s, 3H), 1.78 – 1.75 (m, 2H), 1.67 – 1.61 (m, 2H), 1.41 – 1.33 (m, 4H); ^{13}C NMR (100 MHz, CDCl_3) δ 208.0, 164.4, 145.5, 136.1, 132.8, 131.7, 130.2, 128.7, 128.4, 128.32, 128.27, 127.9, 107.0, 94.3, 60.9, 49.3, 33.2, 33.0, 25.6, 25.3, 21.8, 19.8; HRMS (ESI-TOF) m/z : $[\text{M}+\text{Na}]^+$ Calcd. for $\text{C}_{25}\text{H}_{29}\text{NNaO}_3\text{S}^+$: 446.1760; found: 446.1769.

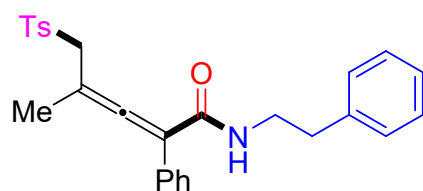


***N*-cyclooctyl-4-methyl-2-phenyl-5-tosylpenta-2,3-dienamide (4h).** The product was purified by column chromatography (petroleum ether / ethyl acetate = 4:1); Pale yellow oil, 51.4 mg, 57% yield; ^1H NMR (400 MHz, CDCl_3) δ 7.81 (d, $J = 8.2$ Hz, 2H), 7.57 – 7.55 (m, 1H), 7.40 – 7.27 (m, 7H), 4.18 – 4.09 (m, 1H), 3.79 (dd, $J = 103.3, 13.5$ Hz, 2H), 2.45 (s, 3H), 1.96 – 1.88 (m, 2H), 1.88 (s, 3H), 1.78 – 1.71 (m, 4H), 1.62 – 1.50 (m, 8H); ^{13}C NMR (100 MHz, CDCl_3) δ 208.0, 164.1, 145.5, 136.2, 132.9,

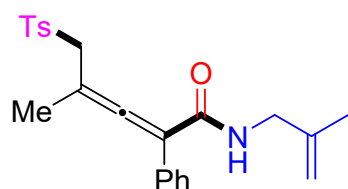
130.3, 128.7, 128.4, 128.3, 127.9, 107.0, 94.3, 60.9, 50.4, 32.4, 32.2, 27.4, 27.3, 25.8, 24.2, 24.0, 21.8, 19.8; HRMS (ESI-TOF) m/z : $[M+Na]^+$ Calcd. for $C_{27}H_{33}NNaO_3S^+$: 474.2073; found: 474.2073.



4-methyl-N-(4-methylbenzyl)-2-phenyl-5-tosylpenta-2,3-dienamide (4i). The product was purified by column chromatography (petroleum ether / ethyl acetate = 3:1); Pale yellow oil, 71.2 mg, 80% yield; 1H NMR (400 MHz, $CDCl_3$) δ 8.03 (t, $J = 5.9$ Hz, 1H), 7.60 (d, $J = 8.3$ Hz, 2H), 7.42 (d, $J = 1.5$ Hz, 2H), 7.33 – 7.23 (m, 5H), 7.24 (d, $J = 8.1$ Hz, 2H), 7.16 (d, $J = 7.8$ Hz, 2H), 4.58 (ddd, $J = 51.5, 14.6, 6.1$ Hz, 2H), 3.79 (dd, $J = 89.9, 13.6$ Hz, 2H), 2.43 (s, 3H), 2.35 (s, 3H), 1.77 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 208.4, 165.2, 145.4, 136.8, 135.94, 135.86, 132.5, 130.2, 129.3, 128.7, 128.4, 128.24, 128.19, 128.0, 106.8, 94.8, 60.9, 43.6, 21.8, 21.2, 19.5; HRMS (ESI-TOF) m/z : $[M+Na]^+$ Calcd. for $C_{27}H_{27}NNaO_3S^+$: 468.1604; found: 468.1613.

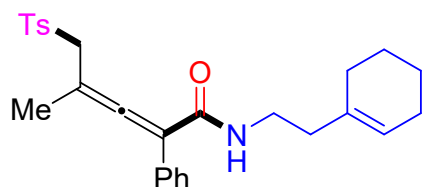


4-methyl-N-phenethyl-2-phenyl-5-tosylpenta-2,3-dienamide (4j). The product was purified by column chromatography (petroleum ether / ethyl acetate = 3:1); Pale yellow oil, 62.3 mg, 70% yield; 1H NMR (400 MHz, $CDCl_3$) δ 7.74 (d, $J = 8.3$ Hz, 2H), 7.65 (s, 1H), 7.36 – 7.27 (m, 11H), 7.26 – 7.20 (m, 1H), 3.87 (d, $J = 13.5$ Hz, 1H), 3.72 – 3.65 (m, 3H), 2.98 (t, $J = 7.4$ Hz, 2H), 2.44 (s, 3H), 1.91 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 208.2, 165.2, 145.5, 139.3, 135.9, 132.5, 130.2, 129.0, 128.7, 128.5, 128.4, 128.1, 128.0, 126.3, 106.7, 94.6, 60.8, 41.3, 35.7, 21.8, 19.7; HRMS (ESI-TOF) m/z : $[M+Na]^+$ Calcd. for $C_{27}H_{27}NNaO_3S^+$: 468.1604; found: 468.1612.

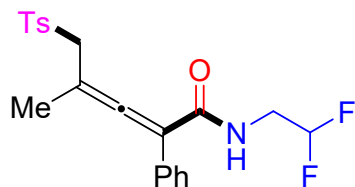


4-methyl-N-(2-methylallyl)-2-phenyl-5-tosylpenta-2,3-dienamide (4k). The product was purified by column chromatography (petroleum ether / ethyl acetate = 3:1); Pale yellow oil, 47.4 mg, 60% yield; 1H NMR (400 MHz, $CDCl_3$) δ 7.78 – 7.76 (m, 3H), 7.41 – 7.39 (m, 2H), 7.34 – 7.25 (m, 5H), 4.97 (s,

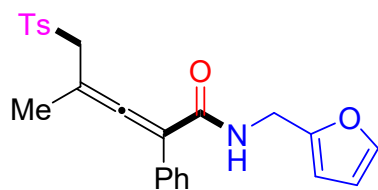
1H), 4.89 (s, 1H), 3.98 (d, $J = 6.0$ Hz, 2H), 3.81 (dd, $J = 90.4, 13.6$ Hz, 2H), 2.44 (s, 3H), 1.89 (s, 3H), 1.82 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 208.2, 165.3, 145.5, 142.1, 135.9, 132.5, 130.2, 128.7, 128.4, 128.2, 128.0, 110.9, 106.7, 94.7, 60.7, 45.5, 21.8, 20.6, 19.7; HRMS (ESI-TOF) m/z : $[\text{M}+\text{Na}]^+$ Calcd. for $\text{C}_{23}\text{H}_{25}\text{NNaO}_3\text{S}^+$: 418.1447; found: 418.1456.



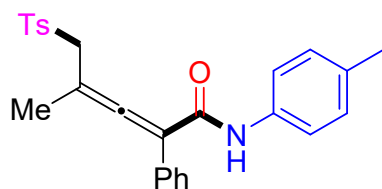
***N*-(2-(cyclohex-1-en-1-yl)ethyl)-4-methyl-2-phenyl-5-tosylpenta-2,3-dienamide (4l)**. The product was purified by column chromatography (petroleum ether / ethyl acetate = 3:1); Pale yellow oil, 63.8 mg, 71% yield; ^1H NMR (400 MHz, CDCl_3) δ 7.77 (d, $J = 8.2$ Hz, 2H), 7.46 (t, $J = 5.1$ Hz, 1H), 7.37 – 7.25 (m, 7H), 5.51 (s, 1H), 3.79 (dd, $J = 77.3, 13.6$ Hz, 2H), 3.49 (dt, $J = 15.2, 7.2$ Hz, 2H), 2.43 (s, 3H), 2.26 (t, $J = 7.0$ Hz, 2H), 2.00 – 1.97 (m, 4H), 1.93 (s, 3H), 1.63 – 1.54 (m, 4H); ^{13}C NMR (100 MHz, CDCl_3) δ 208.1, 165.1, 145.4, 136.0, 134.9, 132.6, 130.2, 128.7, 128.4, 128.1, 127.9, 123.2, 106.8, 94.5, 60.8, 38.3, 37.8, 28.1, 25.4, 23.0, 22.5, 21.8, 19.7; HRMS (ESI-TOF) m/z : $[\text{M}+\text{Na}]^+$ Calcd. for $\text{C}_{27}\text{H}_{31}\text{NNaO}_3\text{S}^+$: 472.1917; found: 472.1923.



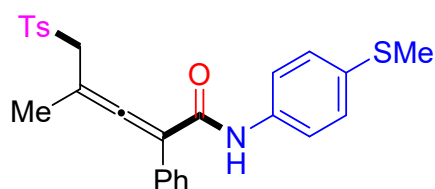
***N*-(2,2-difluoroethyl)-4-methyl-2-phenyl-5-tosylpenta-2,3-dienamide (4m)**. The product was purified by column chromatography (petroleum ether / ethyl acetate = 3:1); Pale yellow oil, 51.9 mg, 64% yield; ^1H NMR (400 MHz, CDCl_3) δ 8.05 (t, $J = 5.7$ Hz, 1H), 7.81 (d, $J = 8.3$ Hz, 2H), 7.41 – 7.35 (m, 4H), 7.33 – 7.27 (m, 3H), 6.01 (tt, $J = 56.2, 4.3$ Hz, 1H), 3.92 (d, $J = 13.4$ Hz, 1H), 3.83 – 3.74 (m, 2H), 3.71 (d, $J = 13.5$ Hz, 1H), 2.46 (s, 3H), 1.90 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 208.9, 166.2, 145.8, 135.9, 132.1, 130.4, 128.7, 128.5, 128.2, 113.9 (t, $J = 241.6$ Hz, 1C), 106.1, 95.3, 60.9, 42.5 (t, $J = 27.4$ Hz, 1C), 21.8, 19.6; HRMS (ESI-TOF) m/z : $[\text{M}+\text{Na}]^+$ Calcd. for $\text{C}_{21}\text{H}_{21}\text{F}_2\text{NNaO}_3\text{S}^+$: 428.1102; found: 428.1112.



***N*-(furan-2-ylmethyl)-4-methyl-2-phenyl-5-tosylpenta-2,3-dienamide (4n).** The product was purified by column chromatography (petroleum ether / ethyl acetate = 3:1); Pale yellow oil, 69.1 mg, 82% yield; ¹H NMR (400 MHz, CDCl₃) δ 7.99 (t, *J* = 5.2 Hz, 1H), 7.72 (s, 2H), 7.38 (s, 3H), 7.33 – 7.28 (m, 5H), 6.34 (s, 2H), 4.68 – 4.54 (m, 2H), 3.80 (dd, *J* = 91.7, 13.6 Hz, 2H), 2.44 (s, 3H), 1.78 (s, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 208.5, 165.3, 151.8, 145.5, 142.1, 135.7, 132.4, 130.2, 128.7, 128.4, 128.3, 128.1, 128.0, 110.5, 107.6, 106.5, 94.9, 60.8, 36.9, 21.8, 19.5; HRMS (ESI-TOF) *m/z*: [M+Na]⁺ Calcd. for C₂₄H₂₃NNaO₄S⁺ : 444.1240; found: 444.1250.

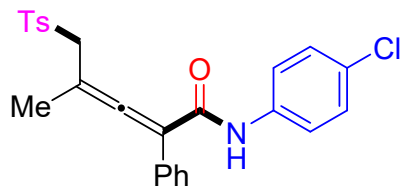


4-methyl-2-phenyl-*N*-(*p*-tolyl)-5-tosylpenta-2,3-dienamide (4o). The product was purified by column chromatography (petroleum ether / ethyl acetate = 3:1); Pale yellow oil, 62.1 mg, 72% yield; ¹H NMR (400 MHz, CDCl₃) δ 9.55 (s, 1H), 7.86 (d, *J* = 8.3 Hz, 2H), 7.79 (d, *J* = 8.4 Hz, 2H), 7.50 – 7.47 (m, 2H), 7.38 (dd, *J* = 7.7, 4.9 Hz, 4H), 7.35 – 7.32 (m, 1H), 7.18 (d, *J* = 8.3 Hz, 2H), 3.89 (dd, *J* = 117.5, 13.5 Hz, 2H), 2.48 (s, 3H), 2.36 (s, 3H), 1.95 (s, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 208.3, 163.2, 145.8, 136.5, 135.9, 133.6, 132.6, 130.4, 129.5, 128.9, 128.5, 128.3, 128.2, 119.9, 107.6, 95.2, 60.8, 21.8, 21.0, 20.0; HRMS (ESI-TOF) *m/z*: [M+Na]⁺ Calcd. for C₂₆H₂₅NNaO₃S⁺ : 454.1447; found: 454.1457.

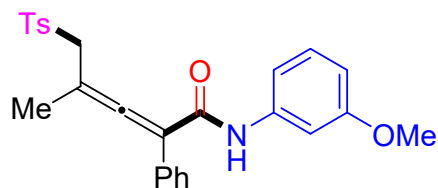


4-methyl-*N*-(4-(methylthio)phenyl)-2-phenyl-5-tosylpenta-2,3-dienamide (4p). The product was purified by column chromatography (petroleum ether / ethyl acetate = 3:1); Pale yellow oil, 69.5 mg, 75% yield; ¹H NMR (400 MHz, CDCl₃) δ 9.61 (s, 1H), 7.83 (dd, *J* = 8.6, 2.5 Hz, 4H), 7.46 – 7.43 (m, 2H), 7.37 – 7.27 (m, 7H), 7.25 (s, 1H), 2.47 (s, 3H), 2.45 (s, 3H), 1.94 (s, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 208.5, 163.3, 145.8, 136.8, 135.8, 133.0, 132.4, 130.4, 128.9, 128.5, 128.3, 128.2, 120.5,

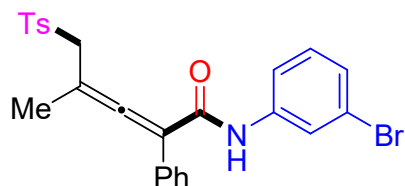
107.5, 95.3, 60.8, 21.8, 20.0, 17.0; HRMS (ESI-TOF) m/z : $[M+Na]^+$ Calcd. for $C_{26}H_{25}NNaO_3S_2^+$: 486.1168; found: 486.1177.



***N*-(4-chlorophenyl)-4-methyl-2-phenyl-5-tosylpenta-2,3-dienamide (4q).** The product was purified by column chromatography (petroleum ether / ethyl acetate = 3:1); Yellow oil, 63.2 mg, 70% yield; 1H NMR (400 MHz, $CDCl_3$) δ 9.68 (s, 1H), 7.85 – 7.81 (m, 4H), 7.46 – 7.43 (m, 2H), 7.38 – 7.36 (m, 3H), 7.34 – 7.28 (m, 4H), 3.85 (dd, J = 114.6, 13.4 Hz, 2H), 2.46 (s, 3H), 1.97 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 208.6, 163.4, 145.9, 137.7, 135.8, 132.3, 130.5, 129.0, 128.93, 128.89, 128.6, 128.3, 128.2, 121.2, 107.4, 95.4, 60.8, 21.8, 20.0; HRMS (ESI-TOF) m/z : $[M+Na]^+$ Calcd. for $C_{25}H_{22}ClNNaO_3S^+$: 474.0901; found: 474.0909.

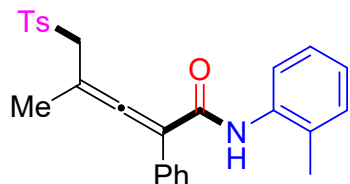


***N*-(3-methoxyphenyl)-4-methyl-2-phenyl-5-tosylpenta-2,3-dienamide (4r).** The product was purified by column chromatography (petroleum ether / ethyl acetate = 3:1); Pale yellow oil, 73.4 mg, 82% yield; 1H NMR (400 MHz, $CDCl_3$) δ 9.67 (s, 1H), 7.88 (d, J = 8.2 Hz, 2H), 7.73 (t, J = 2.3 Hz, 1H), 7.50 (d, J = 7.2 Hz, 2H), 7.46 – 7.28 (m, 7H), 6.73 (dd, J = 8.2, 2.2 Hz, 1H), 4.04 (d, J = 13.4 Hz, 1H), 3.85 (s, 3H), 3.76 (d, J = 13.5 Hz, 1H), 2.49 (s, 3H), 1.99 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 208.3, 163.4, 160.1, 145.8, 140.2, 135.7, 132.4, 130.3, 129.6, 128.9, 128.5, 128.2, 112.2, 110.4, 107.5, 105.1, 95.3, 60.6, 55.3, 21.8, 19.9; HRMS (ESI-TOF) m/z : $[M+Na]^+$ Calcd. for $C_{26}H_{25}NNaO_4S^+$: 470.1397; found: 470.1407.

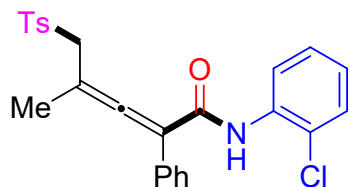


***N*-(3-bromophenyl)-4-methyl-2-phenyl-5-tosylpenta-2,3-dienamide (4s).** The product was purified by column chromatography (petroleum ether / ethyl acetate = 3:1); Pale yellow oil, 64.4 mg, 65% yield; 1H NMR (400 MHz, $CDCl_3$) δ 9.69 (s, 1H), 8.22 (s, 1H), 7.83 (d, J = 8.2 Hz, 2H), 7.71 (d, J = 8.0 Hz,

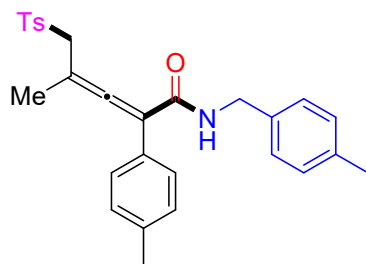
1H), 7.44 (d, $J = 7.3$ Hz, 2H), 7.38 – 7.30 (m, 5H), 7.24 – 7.16 (m, 2H), 3.85 (dd, $J = 110.3, 13.4$ Hz, 2H), 2.45 (s, 3H), 1.97 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 208.5, 163.6, 145.9, 140.3, 135.7, 132.2, 130.4, 130.2, 128.9, 128.6, 128.3, 128.2, 127.0, 122.8, 122.7, 118.5, 107.3, 95.6, 60.7, 21.8, 20.0; HRMS (ESI-TOF) m/z : $[\text{M}+\text{Na}]^+$ Calcd. for $\text{C}_{25}\text{H}_{22}\text{BrNNaO}_3\text{S}^+$: 518.0396; found: 518.0405.



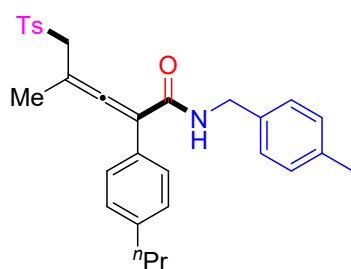
4-methyl-2-phenyl-*N*-(*o*-tolyl)-5-tosylpenta-2,3-dienamide (4t). The product was purified by column chromatography (petroleum ether / ethyl acetate = 3:1); Pale yellow oil, 55.2 mg, 64% yield; ^1H NMR (400 MHz, CDCl_3) δ 8.87 (s, 1H), 7.75 (d, $J = 8.3$ Hz, 3H), 7.45 (d, $J = 7.2$ Hz, 2H), 7.36 – 7.31 (m, 3H), 7.29 – 7.28 (m, 2H), 7.23 (d, $J = 7.2$ Hz, 2H), 7.12 (t, $J = 7.6$ Hz, 1H), 3.88 (dd, $J = 87.9, 13.6$ Hz, 2H), 2.39 (s, 3H), 2.37 (s, 3H), 2.02 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 208.1, 163.7, 145.5, 135.8, 135.6, 132.3, 131.6, 130.7, 130.2, 128.8, 128.5, 128.2, 128.1, 126.5, 125.8, 124.8, 107.1, 95.5, 60.5, 21.8, 19.8, 18.2; HRMS (ESI-TOF) m/z : $[\text{M}+\text{Na}]^+$ Calcd. for $\text{C}_{26}\text{H}_{25}\text{NNaO}_3\text{S}^+$: 454.1447; found: 454.1457.



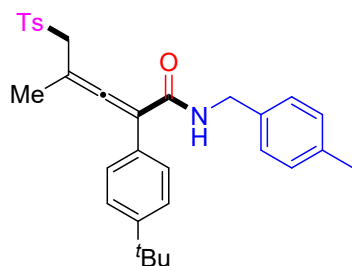
***N*-(2-chlorophenyl)-4-methyl-2-phenyl-5-tosylpenta-2,3-dienamide (4u).** The product was purified by column chromatography (petroleum ether / ethyl acetate = 3:1); Pale yellow oil, 64.1 mg, 71% yield; ^1H NMR (400 MHz, CDCl_3) δ 8.54 (s, 1H), 8.27 (d, $J = 8.2$ Hz, 1H), 7.72 (d, $J = 8.1$ Hz, 2H), 7.40 (d, $J = 8.0$ Hz, 1H), 7.34 – 7.27 (m, 6H), 7.14 – 7.07 (m, 3H), 4.00 – 3.91 (m, 2H), 2.29 (s, 3H), 2.14 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 208.1, 163.0, 145.2, 135.2, 134.6, 131.7, 130.0, 129.3, 128.9, 128.5, 128.3, 128.1, 127.8, 125.3, 124.0, 122.5, 106.8, 97.3, 60.4, 21.7, 19.3; HRMS (ESI-TOF) m/z : $[\text{M}+\text{Na}]^+$ Calcd. for $\text{C}_{25}\text{H}_{22}\text{ClNNaO}_3\text{S}^+$: 474.0901; found: 474.0909.



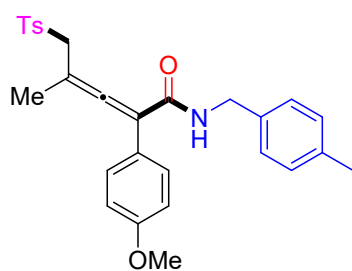
4-methyl-N-(4-methylbenzyl)-2-(*p*-tolyl)-5-tosylpenta-2,3-dienamide (5a). The product was purified by column chromatography (petroleum ether / ethyl acetate = 3:1); Pale yellow oil, 69.8 mg, 76% yield; ^1H NMR (400 MHz, CDCl_3) δ 8.00 (t, $J = 5.9$ Hz, 1H), 7.60 (d, $J = 8.3$ Hz, 2H), 7.31 (dd, $J = 11.1, 8.1$ Hz, 4H), 7.24 (d, $J = 8.1$ Hz, 2H), 7.14 (dd, $J = 12.6, 7.9$ Hz, 4H), 4.58 (ddd, $J = 54.3, 14.7, 6.1$ Hz, 2H), 3.78 (dd, $J = 87.6, 13.6$ Hz, 2H), 2.43 (s, 3H), 2.34 (d, $J = 4.2$ Hz, 6H), 1.75 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 208.3, 165.3, 145.4, 137.9, 136.8, 135.9, 135.8, 130.1, 129.4, 129.3, 129.1, 128.6, 128.22, 128.18, 106.7, 94.5, 60.9, 43.5, 21.8, 21.3, 21.2, 19.5; HRMS (ESI-TOF) m/z : $[\text{M}+\text{Na}]^+$ Calcd. for $\text{C}_{28}\text{H}_{29}\text{NNaO}_3\text{S}^+$: 482.1760; found: 482.1770.



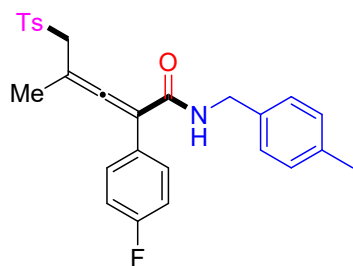
4-methyl-N-(4-methylbenzyl)-2-(4-propylphenyl)-5-tosylpenta-2,3-dienamide (5b). The product was purified by column chromatography (petroleum ether / ethyl acetate = 3:1); Pale yellow oil, 72.1 mg, 74% yield; ^1H NMR (400 MHz, CDCl_3) δ 8.05 (t, $J = 5.9$ Hz, 1H), 7.64 (d, $J = 8.2$ Hz, 2H), 7.35 (dd, $J = 8.1, 2.3$ Hz, 4H), 7.28 (d, $J = 8.0$ Hz, 2H), 7.20 – 7.16 (m, 4H), 4.62 (ddd, $J = 52.3, 14.7, 6.1$ Hz, 2H), 3.82 (dd, $J = 93.0, 13.6$ Hz, 2H), 2.63 – 2.58 (m, 2H), 2.47 (s, 3H), 2.38 (s, 3H), 1.75 (s, 3H), 1.66 (h, $J = 7.3$ Hz, 2H), 0.97 (t, $J = 7.3$ Hz, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 208.3, 165.4, 145.4, 142.7, 136.8, 136.0, 135.8, 130.2, 129.7, 129.3, 128.60, 128.57, 128.3, 128.2, 106.8, 94.5, 61.0, 43.5, 37.9, 24.6, 21.8, 21.2, 19.6, 13.9; HRMS (ESI-TOF) m/z : $[\text{M}+\text{Na}]^+$ Calcd. for $\text{C}_{30}\text{H}_{33}\text{NNaO}_3\text{S}^+$: 510.2073; found: 510.2074.



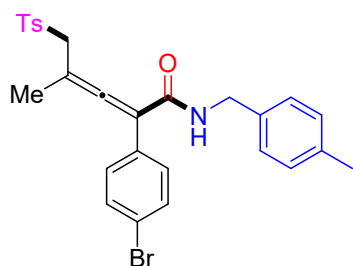
2-(4-(*tert*-butyl)phenyl)-4-methyl-*N*-(4-methylbenzyl)-5-tosylpenta-2,3-dienamide (4c). The product was purified by column chromatography (petroleum ether / ethyl acetate = 3:1); Yellow oil, 64.2 mg, 64% yield; ^1H NMR (400 MHz, CDCl_3) δ 8.01 (t, $J = 6.1$ Hz, 1H), 7.60 (d, $J = 8.3$ Hz, 2H), 7.35 – 7.31 (m, 6H), 7.25 (d, $J = 8.5$ Hz, 2H), 7.16 (d, $J = 7.8$ Hz, 2H), 4.58 (ddd, $J = 49.5, 14.6, 6.1$ Hz, 2H), 3.78 (dd, $J = 90.8, 13.6$ Hz, 2H), 2.44 (s, 3H), 2.35 (s, 3H), 1.75 (s, 3H), 1.31 (s, 9H); ^{13}C NMR (100 MHz, CDCl_3) δ 208.4, 165.4, 151.1, 145.4, 136.8, 136.0, 135.8, 130.2, 129.5, 129.3, 128.4, 128.3, 128.2, 125.4, 106.6, 94.5, 61.0, 43.5, 34.7, 31.4, 21.8, 21.2, 19.6; HRMS (ESI-TOF) m/z : $[\text{M}+\text{Na}]^+$ Calcd. for $\text{C}_{31}\text{H}_{35}\text{NNaO}_3\text{S}^+$: 524.2230; found: 524.2236.



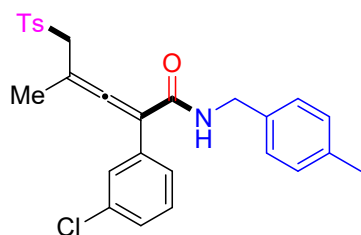
2-(4-methoxyphenyl)-4-methyl-*N*-(4-methylbenzyl)-5-tosylpenta-2,3-dienamide (5d). The product was purified by column chromatography (petroleum ether / ethyl acetate = 3:1); Pale yellow oil, 59.9 mg, 63% yield; ^1H NMR (400 MHz, CDCl_3) δ 7.99 – 7.95 (m, 1H), 7.60 (d, $J = 8.2$ Hz, 2H), 7.35 – 7.30 (m, 4H), 7.24 (d, $J = 8.2$ Hz, 2H), 7.15 (d, $J = 7.9$ Hz, 2H), 6.85 (d, $J = 8.8$ Hz, 2H), 4.63 (dd, $J = 14.9, 6.3$ Hz, 1H), 4.50 (dd, $J = 14.7, 5.8$ Hz, 1H), 3.89 (d, $J = 13.6$ Hz, 1H), 3.80 (s, 3H), 3.68 (d, $J = 13.6$ Hz, 1H), 2.43 (s, 3H), 2.34 (s, 3H), 1.76 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 208.2, 165.5, 159.5, 145.4, 136.8, 136.0, 135.8, 130.2, 130.0, 129.3, 128.24, 128.19, 124.6, 113.9, 106.4, 94.6, 61.0, 55.4, 43.5, 21.8, 21.2, 19.6; HRMS (ESI-TOF) m/z : $[\text{M}+\text{Na}]^+$ Calcd. for $\text{C}_{28}\text{H}_{29}\text{NNaO}_4\text{S}^+$: 498.1710; found: 498.1718.



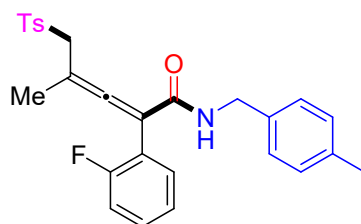
2-(4-fluorophenyl)-4-methyl-N-(4-methylbenzyl)-5-tosylpenta-2,3-dienamide (5e). The product was purified by column chromatography (petroleum ether / ethyl acetate = 3:1); Pale yellow oil, 59.3 mg, 64% yield; ^1H NMR (400 MHz, CDCl_3) δ 8.03 (t, $J = 5.7$ Hz, 1H), 7.61 (d, $J = 8.2$ Hz, 2H), 7.39 (dd, $J = 8.7, 5.5$ Hz, 2H), 7.31 (d, $J = 7.9$ Hz, 2H), 7.25 (d, $J = 7.5$ Hz, 2H), 7.15 (d, $J = 7.8$ Hz, 2H), 6.99 (t, $J = 8.7$ Hz, 2H), 4.65 – 4.48 (m, 2H), 3.79 (dd, $J = 85.3, 13.6$ Hz, 2H), 2.43 (s, 3H), 2.34 (s, 3H), 1.78 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 208.3, 165.1, 162.5 (d, $J = 247.6$ Hz, 1C), 145.5, 136.9, 135.8, 130.5 (d, $J = 8.2$ Hz, 2C), 130.2, 129.3, 128.4 (d, $J = 3.4$ Hz, 1C), 128.2, 115.4 (d, $J = 21.6$ Hz, 2C), 105.9, 95.1, 60.8, 43.6, 21.8, 21.2, 19.5; HRMS (ESI-TOF) m/z : $[\text{M}+\text{Na}]^+$ Calcd. for $\text{C}_{27}\text{H}_{26}\text{FNNaO}_3\text{S}^+$: 486.1510; found: 486.1520.



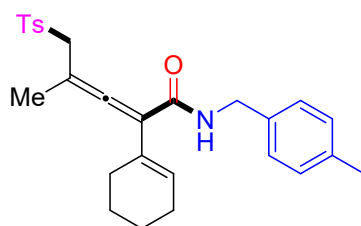
2-(4-bromophenyl)-4-methyl-N-(4-methylbenzyl)-5-tosylpenta-2,3-dienamide (5f). The product was purified by column chromatography (petroleum ether / ethyl acetate = 3:1); Pale yellow oil, 52.3 mg, 50% yield; ^1H NMR (400 MHz, CDCl_3) δ 8.07 (t, $J = 5.7$ Hz, 1H), 7.60 (d, $J = 8.2$ Hz, 2H), 7.37 (s, 1H), 7.35 – 7.30 (m, 3H), 7.25 – 7.23 (m, 4H), 7.16 (d, $J = 7.8$ Hz, 2H), 4.63 (dd, $J = 14.6, 6.3$ Hz, 1H), 4.50 (dd, $J = 14.6, 5.8$ Hz, 1H), 3.80 (dd, $J = 89.1, 13.6$ Hz, 2H), 2.43 (s, 3H), 2.34 (s, 3H), 1.79 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 208.3, 164.7, 145.6, 136.9, 135.8, 135.7, 134.4, 134.2, 130.2, 129.6, 129.4, 128.7, 128.2, 128.1, 126.9, 105.8, 95.5, 60.7, 43.6, 21.8, 21.3, 19.5; HRMS (ESI-TOF) m/z : $[\text{M}+\text{Na}]^+$ Calcd. for $\text{C}_{27}\text{H}_{26}\text{BrNNaO}_3\text{S}^+$: 546.0709; found: 546.0714.



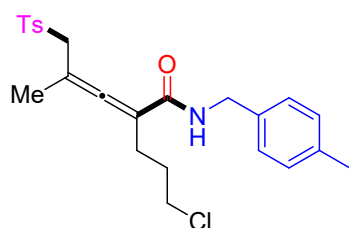
2-(3-chlorophenyl)-4-methyl-N-(4-methylbenzyl)-5-tosylpenta-2,3-dienamide (5g). The product was purified by column chromatography (petroleum ether / ethyl acetate = 3:1); Pale yellow oil, 52.7 mg, 55% yield; ^1H NMR (400 MHz, CDCl_3) δ 8.04 (t, $J = 5.9$ Hz, 1H), 7.60 (d, $J = 8.3$ Hz, 2H), 7.42 (d, $J = 8.6$ Hz, 2H), 7.32 – 7.24 (m, 6H), 7.15 (d, $J = 7.8$ Hz, 2H), 4.56 (ddd, $J = 49.7, 14.6, 6.1$ Hz, 2H), 3.79 (dd, $J = 85.2, 13.6$ Hz, 2H), 2.44 (s, 3H), 2.34 (s, 3H), 1.78 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 208.2, 164.8, 145.6, 136.9, 135.8, 135.7, 131.53, 131.49, 130.4, 130.2, 129.4, 128.2, 122.1, 105.9, 95.4, 60.7, 43.6, 21.8, 21.3, 19.5; HRMS (ESI-TOF) m/z : $[\text{M}+\text{Na}]^+$ Calcd. for $\text{C}_{27}\text{H}_{26}\text{ClNNaO}_3\text{S}^+$: 502.1214; found: 502.1217.



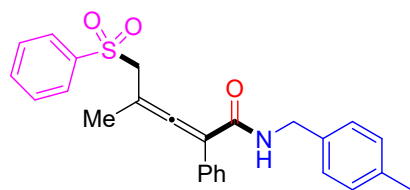
2-(2-fluorophenyl)-4-methyl-N-(4-methylbenzyl)-5-tosylpenta-2,3-dienamide (5h). The product was purified by column chromatography (petroleum ether / ethyl acetate = 3:1); Pale yellow oil, 47.3 mg, 51% yield; ^1H NMR (400 MHz, CDCl_3) δ 8.00 (t, $J = 5.7$ Hz, 1H), 7.61 (d, $J = 8.2$ Hz, 2H), 7.44 – 7.38 (m, 1H), 7.32 (d, $J = 7.9$ Hz, 2H), 7.25 (d, $J = 10.2$ Hz, 2H), 7.17 – 7.03 (m, 5H), 4.56 (ddd, $J = 54.4, 14.7, 6.1$ Hz, 2H), 3.77 (dd, $J = 98.0, 13.5$ Hz, 2H), 2.43 (s, 3H), 2.35 (s, 3H), 1.76 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 209.1, 164.8, 160.2 (d, $J = 249.2$ Hz, 1C), 145.5, 136.8, 135.9 (d, $J = 10.0$ Hz, 1C), 131.65, 131.62, 130.2, 129.8 (d, $J = 7.9$ Hz, 1C), 129.5, 129.3, 128.6, 128.3, 127.8, 124.0 (d, $J = 3.7$ Hz, 1C), 115.8 (d, $J = 22.0$ Hz, 2C), 100.4, 94.0, 60.9, 43.7, 21.8, 21.3, 19.3; HRMS (ESI-TOF) m/z : $[\text{M}+\text{Na}]^+$ Calcd. for $\text{C}_{27}\text{H}_{26}\text{FNNaO}_3\text{S}^+$: 486.1510; found: 486.1529.



2-(cyclohex-1-en-1-yl)-4-methyl-N-(4-methylbenzyl)-5-tosylpenta-2,3-dienamide (5i). The product was purified by column chromatography (petroleum ether / ethyl acetate = 3:1); Pale yellow oil, 49.4 mg, 55% yield; $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.84 – 7.81 (m, 1H), 7.58 (d, $J = 8.2$ Hz, 2H), 7.27 (t, 4H), 7.13 (d, $J = 7.9$ Hz, 2H), 6.23 (t, $J = 4.0$ Hz, 1H), 4.50 (ddd, 2H), 3.73 (dd, $J = 101.8, 13.7$ Hz, 2H), 2.45 – 2.40 (m, 5H), 2.33 (s, 3H), 2.18 – 2.10 (m, 2H), 1.89 (s, 2H), 1.65 – 1.60 (m, 2H), 1.58 (s, 3H); $^{13}\text{C NMR}$ (100 MHz, CDCl_3) δ 206.6, 165.4, 145.3, 136.7, 136.0, 135.8, 130.1, 129.6, 129.34, 129.29, 128.6, 128.4, 128.3, 128.1, 109.1, 94.0, 61.2, 43.3, 27.2, 26.0, 22.7, 22.0, 21.8, 21.2, 20.0; HRMS (ESI-TOF) m/z : $[\text{M}+\text{Na}]^+$ Calcd. for $\text{C}_{27}\text{H}_{31}\text{NNaO}_3\text{S}^+$: 472.1917; found: 472.1927.

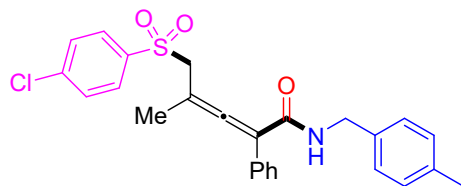


2-(3-chloropropyl)-4-methyl-N-(4-methylbenzyl)-5-tosylpenta-2,3-dienamide (5j). The product was purified by column chromatography (petroleum ether / ethyl acetate = 3:1); Pale yellow solid, 52.0 mg, 58% yield, mp: 111.0 - 112.0 °C; $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.86 – 7.77 (m, 1H), 7.61 (dd, $J = 8.3, 3.3$ Hz, 2H), 7.40 – 7.23 (m, 4H), 7.14 (d, $J = 5.0$ Hz, 2H), 4.59 – 4.36 (m, 2H), 3.84 – 3.63 (m, 2H), 3.56 – 3.51 (m, 2H), 2.46 (s, 5H), 2.34 (d, $J = 3.0$ Hz, 3H), 1.93 – 1.86 (m, 2H), 1.69 (d, $J = 3.5$ Hz, 3H); $^{13}\text{C NMR}$ (100 MHz, CDCl_3) δ 207.1, 165.8, 145.5, 136.8, 136.1, 135.9, 130.2, 129.9, 129.3, 128.21, 128.17, 102.7, 94.0, 61.4, 44.4, 43.5, 30.8, 26.1, 21.8, 21.2, 19.5; HRMS (ESI-TOF) m/z : $[\text{M}+\text{Na}]^+$ Calcd. for $\text{C}_{24}\text{H}_{28}\text{ClNNaO}_3\text{S}^+$: 468.1371; found: 468.1378.

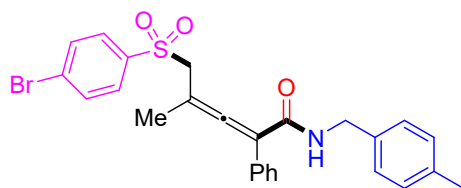


4-methyl-N-(4-methylbenzyl)-2-phenyl-5-(phenylsulfonyl)penta-2,3-dienamide (5k). The product was purified by column chromatography (petroleum ether / ethyl acetate = 3:1); Pale yellow oil, 64.7 mg, 75% yield; $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.99 (t, $J = 6.3$ Hz, 1H), 7.73 (d, $J = 7.6$ Hz, 2H), 7.64 (t, $J = 7.5$ Hz, 1H), 7.47 (t, $J = 7.8$ Hz, 2H), 7.40 (d, $J = 7.3$ Hz, 2H), 7.36 – 7.26 (m, 5H), 7.16 (d, $J = 7.8$ Hz, 2H), 4.58 (ddd, $J = 48.9, 14.6, 6.1$ Hz, 2H), 3.81 (dd, $J = 90.4, 13.6$ Hz, 2H), 2.34 (s, 3H), 1.77 (s, 3H); $^{13}\text{C NMR}$ (100 MHz, CDCl_3) δ 208.5, 165.2, 138.7, 136.9, 135.9, 134.3, 132.5, 129.6, 129.4,

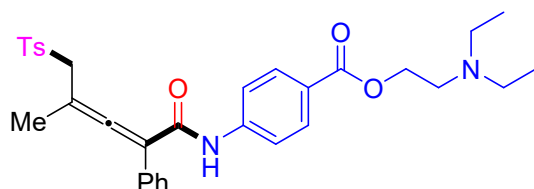
128.8, 128.5, 128.3, 128.1, 106.9, 94.6, 60.9, 43.6, 21.3, 19.5; HRMS (ESI-TOF) m/z : $[M+Na]^+$ Calcd. for $C_{26}H_{25}NNaO_3S^+$: 454.1447; found: 454.1456.



5-((4-chlorophenyl)sulfonyl)-4-methyl-N-(4-methylbenzyl)-2-phenylpenta-2,3-dienamide (5l). The product was purified by column chromatography (petroleum ether / ethyl acetate = 3:1); Pale yellow oil, 74.4 mg, 80% yield; 1H NMR (400 MHz, $CDCl_3$) δ 7.81 (t, J = 5.7 Hz, 1H), 7.62 (d, J = 8.6 Hz, 2H), 7.39 – 7.36 (m, 4H), 7.32 – 7.28 (m, 5H), 7.16 (d, J = 7.8 Hz, 2H), 4.54 (ddd, 2H), 3.81 (dd, J = 84.4, 13.7 Hz, 2H), 2.35 (s, 3H), 1.81 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 208.4, 165.0, 141.1, 137.0, 135.8, 132.3, 129.8, 129.7, 129.4, 128.7, 128.5, 128.21, 128.17, 107.0, 94.3, 60.8, 43.6, 21.2, 19.6; HRMS (ESI-TOF) m/z : $[M+Na]^+$ Calcd. for $C_{26}H_{24}ClNNaO_3S^+$: 488.1058; found: 488.1066.

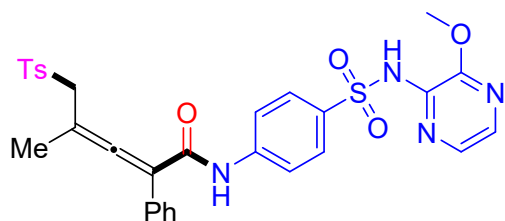


5-((4-bromophenyl)sulfonyl)-4-methyl-N-(4-methylbenzyl)-2-phenylpenta-2,3-dienamide (5m). The product was purified by column chromatography (petroleum ether / ethyl acetate = 3:1); Pale yellow oil, 77.4 mg, 76% yield; 1H NMR (400 MHz, $CDCl_3$) δ 7.80 (t, J = 5.8 Hz, 1H), 7.54 (s, 4H), 7.38 – 7.34 (m, 2H), 7.33 – 7.28 (m, 5H), 7.16 (d, J = 7.8 Hz, 2H), 4.56 (ddd, J = 72.1, 14.7, 6.1 Hz, 2H), 3.81 (dd, J = 80.8, 13.7 Hz, 2H), 2.35 (s, 3H), 1.82 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 208.4, 165.0, 137.5, 137.0, 135.8, 132.9, 132.3, 129.7, 129.4, 128.7, 128.5, 128.23, 128.21, 107.1, 94.4, 60.8, 43.6, 21.2, 19.6; HRMS (ESI-TOF) m/z : $[M+Na]^+$ Calcd. for $C_{26}H_{24}BrNNaO_3S^+$: 532.0552; found: 532.0558.



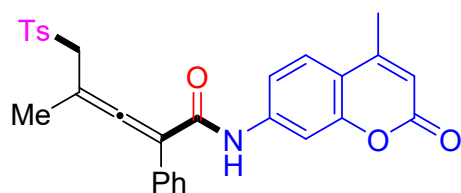
2-(diethylamino)ethyl 4-(4-methyl-2-phenyl-5-tosylpenta-2,3-dienamido)benzoate (6a). The product was purified by column chromatography (ethyl acetate / methanol = 10:1, R_f = 0.3); Pale yellow oil, 59.4 mg, 53% yield; 1H NMR (400 MHz, $CDCl_3$) δ 9.82 (s, 1H), 8.03 – 7.94 (m, 4H), 7.83

(d, $J = 8.2$ Hz, 2H), 7.46 – 7.43 (m, 2H), 7.37 (d, $J = 8.4$ Hz, 4H), 7.35 – 7.30 (m, 1H), 4.37 (t, $J = 6.2$ Hz, 2H), 3.86 (dd, $J = 115.2, 13.4$ Hz, 2H), 2.85 (t, $J = 6.2$ Hz, 2H), 2.63 (q, $J = 7.1$ Hz, 4H), 2.46 (s, 3H), 1.98 (s, 3H), 1.07 (t, $J = 7.1$ Hz, 6H); ^{13}C NMR (100 MHz, CDCl_3) δ 208.7, 166.5, 163.7, 146.0, 143.2, 135.8, 132.3, 130.9, 130.5, 129.0, 128.6, 128.4, 128.3, 125.5, 119.3, 107.5, 95.6, 63.4, 60.7, 51.1, 48.0, 21.9, 20.1, 12.2; HRMS (ESI-TOF) m/z : $[\text{M}+\text{H}]^+$ Calcd. for $\text{C}_{32}\text{H}_{37}\text{N}_2\text{O}_5\text{S}^+$: 561.2418; found: 561.2426.



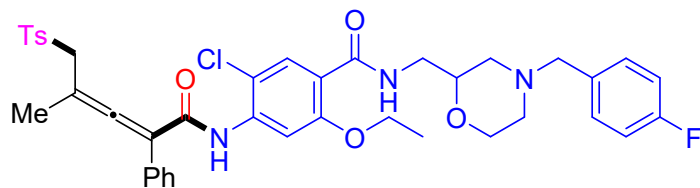
***N*-(4-(*N*-(3-methoxypyrazin-2-yl)sulfamoyl)phenyl)-4-methyl-2-phenyl-5-tosylpenta-2,3-**

dienamide (6b). The product was purified by column chromatography (petroleum ether / ethyl acetate = 1:1, $R_f = 0.3$); Pale yellow oil, 70.1 mg, 58% yield; ^1H NMR (400 MHz, CDCl_3) δ 9.91 (s, 1H), 8.10 (d, $J = 8.9$ Hz, 2H), 8.02 (d, $J = 8.9$ Hz, 2H), 7.82 (d, $J = 8.3$ Hz, 2H), 7.73 (d, $J = 2.8$ Hz, 1H), 7.65 (d, $J = 2.8$ Hz, 1H), 7.63 (s, 1H), 7.44 – 7.30 (m, 7H), 4.01 – 3.69 (m, 5H), 2.47 (s, 3H), 2.01 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 208.8, 163.9, 148.7, 146.1, 143.7, 137.8, 135.7, 134.0, 133.8, 133.6, 132.0, 130.5, 129.9, 128.9, 128.6, 128.5, 128.2, 119.4, 107.3, 95.8, 60.7, 54.1, 21.9, 20.1; HRMS (ESI-TOF) m/z : $[\text{M}+\text{Na}]^+$ Calcd. for $\text{C}_{30}\text{H}_{28}\text{N}_4\text{NaO}_6\text{S}_2^+$: 627.1342; found: 627.1350.

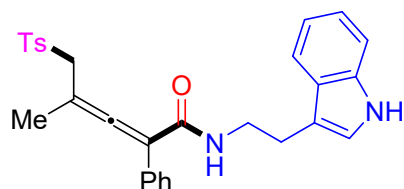


4-methyl-*N*-(4-methyl-2-oxo-2*H*-chromen-7-yl)-2-phenyl-5-tosylpenta-2,3-dienamide (6c). The product was purified by column chromatography (dichloromethane / ethyl acetate = 20:1, $R_f = 0.5$); Pale yellow oil, 59.9 mg, 60% yield; ^1H NMR (400 MHz, CDCl_3) δ 9.94 (s, 1H), 7.99 – 7.98 (m, 1H), 7.83 (d, $J = 4.2$ Hz, 3H), 7.52 (dd, $J = 8.7, 3.7$ Hz, 1H), 7.44 (d, $J = 5.6$ Hz, 2H), 7.39 – 7.29 (m, 5H), 6.16 (s, 1H), 3.86 (ddd, $J = 111.1, 13.2, 3.6$ Hz, 2H), 2.45 (d, $J = 3.2$ Hz, 3H), 2.39 (d, $J = 2.7$ Hz, 3H), 2.01 (d, $J = 3.7$ Hz, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 208.8, 163.8, 161.4, 154.4, 152.3, 146.0, 142.4, 135.7, 132.1, 130.4, 128.9, 128.6, 128.4, 128.2, 125.1, 116.1, 116.0, 113.3, 107.6, 107.3, 95.8,

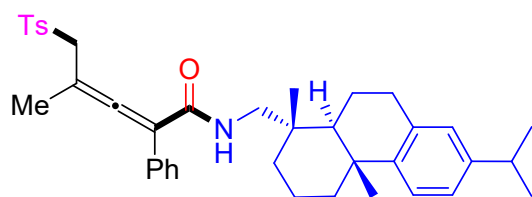
60.7, 21.8, 20.1, 18.7; HRMS (ESI-TOF) m/z : $[M+Na]^+$ Calcd. for $C_{29}H_{25}NNaO_5S^+$: 522.1346; found: 522.1355.



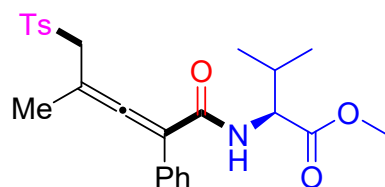
5-chloro-2-ethoxy-*N*-((4-(4-fluorobenzyl)morpholin-2-yl)methyl)-4-(4-methyl-2-phenyl-5-tosylpenta-2,3-dienamido)benzamide (6d). The product was purified by column chromatography (dichloromethane / ethyl acetate = 3:1, R_f = 0.3); Pale yellow oil, 93.9 mg, 63% yield; 1H NMR (400 MHz, $CDCl_3$) δ 8.58 (s, 1H), 8.37 (s, 1H), 8.23 (s, 2H), 7.70 (d, J = 8.1 Hz, 2H), 7.57 – 7.43 (m, 1H), 7.35 – 7.30 (m, 5H), 7.28 – 7.24 (m, 1H), 7.12 (d, J = 8.1 Hz, 2H), 6.99 (t, J = 8.6 Hz, 2H), 4.19 (q, J = 7.0 Hz, 2H), 4.01 – 3.92 (m, 2H), 3.87 (d, J = 11.2 Hz, 1H), 3.72 – 3.66 (m, 3H), 3.46 (s, 2H), 3.34 (ddd, J = 11.9, 8.0, 3.8 Hz, 1H), 2.70 (dd, J = 44.3, 11.1 Hz, 2H), 2.29 (s, 3H), 2.17 – 2.13 (m, 4H), 1.98 (t, J = 10.5 Hz, 1H), 1.49 (t, J = 6.9 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 208.4, 163.8, 163.3, 162.17 (d, J = 245.1 Hz, 1C), 156.5, 145.1, 137.9, 135.3, 133.3, 132.2, 132.1, 132.0 (d, J = 2.5 Hz, 1C), 131.4, 130.7 (d, J = 8.0 Hz, 2C), 130.0, 129.1, 128.7, 128.6, 128.54, 128.49, 128.1, 117.7, 115.2 (d, J = 21.3 Hz, 2C), 114.6, 106.9, 104.8, 98.0, 74.5, 66.7, 65.5, 62.5, 60.2, 56.0, 52.9, 42.4, 21.7, 19.3, 14.7; HRMS (ESI-TOF) m/z : $[M+Na]^+$ Calcd. for $C_{40}H_{41}ClFN_3NaO_6S^+$: 768.2281; found: 768.2288.



***N*-(2-(1*H*-indol-3-yl)ethyl)-4-methyl-2-phenyl-5-tosylpenta-2,3-dienamide (6e).** The product was purified by column chromatography (petroleum ether / ethyl acetate = 2:1, R_f = 0.3); Pale yellow oil, 53.3 mg, 55% yield; 1H NMR (400 MHz, $CDCl_3$) δ 8.12 (s, 1H), 7.68 (d, J = 8.1 Hz, 3H), 7.60 (t, J = 5.5 Hz, 1H), 7.34 (q, J = 7.0, 6.1 Hz, 4H), 7.28 (d, J = 8.0 Hz, 2H), 7.25 – 7.22 (m, 2H), 7.18 (t, J = 7.5 Hz, 1H), 7.12 – 7.08 (m, 2H), 3.84 – 3.75 (m, 3H), 3.62 (d, J = 13.6 Hz, 1H), 3.13 (t, J = 7.2 Hz, 2H), 2.41 (s, 3H), 1.83 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 208.2, 165.4, 145.5, 136.4, 135.9, 132.6, 130.2, 128.8, 128.4, 128.2, 128.0, 127.8, 122.2, 122.0, 119.4, 119.1, 113.4, 111.2, 106.8, 94.7, 60.8, 40.5, 25.3, 21.8, 19.5; HRMS (ESI-TOF) m/z : $[M+Na]^+$ Calcd. for $C_{29}H_{28}N_2NaO_3S^+$: 507.1713; found: 507.1721.

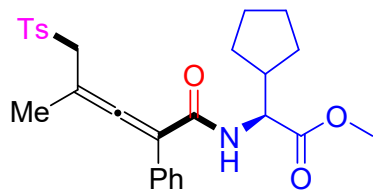


N-(((1S,4aR,10aS)-7-isopropyl-1,4a-dimethyl-1,2,3,4,4a,9,10,10a-octahydrophenanthren-1-yl)methyl)-4-methyl-2-phenyl-5-tosylpenta-2,3-dienamide (6f). The product was purified by column chromatography (petroleum ether / ethyl acetate = 5:1, $R_f = 0.3$); Pale yellow oil, 63.4 mg, 52% yield; $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.70 (d, $J = 8.2$ Hz, 2H), 7.54 (t, $J = 6.6$ Hz, 1H), 7.34 – 7.30 (m, 4H), 7.17 (dd, $J = 13.3, 8.2$ Hz, 2H), 6.97 (d, $J = 8.1$ Hz, 2H), 6.88 – 6.84 (m, 2H), 3.80 (d, $J = 13.7$ Hz, 1H), 3.58 (d, $J = 13.8$ Hz, 1H), 3.44 (dd, $J = 13.6, 6.9$ Hz, 1H), 3.26 (dd, $J = 13.6, 6.3$ Hz, 1H), 3.04 (dd, $J = 9.5, 6.5$ Hz, 2H), 2.87 (d, $J = 6.5$ Hz, 3H), 2.83 – 2.80 (m, 2H), 2.43 (s, 3H), 2.31 – 2.23 (m, 2H), 1.74 (s, 3H), 1.53 – 1.51 (m, 2H), 1.42 (d, $J = 2.1$ Hz, 1H), 1.23 (s, 3H), 1.01 (s, 3H), 0.88 (s, 6H); $^{13}\text{C NMR}$ (100 MHz, CDCl_3) δ 207.3, 165.7, 158.6, 147.6, 147.5, 145.6, 145.5, 145.4, 135.9, 135.2, 135.0, 132.5, 130.2, 128.6, 128.5, 128.4, 128.1, 127.9, 126.9, 124.3, 124.2, 123.8, 123.7, 107.2, 94.5, 60.4, 50.8, 50.2, 45.0, 44.9, 38.6, 38.5, 38.3, 37.62, 37.56, 37.53, 37.47, 36.3, 36.2, 33.5, 30.2, 30.1, 25.4, 25.3, 24.1, 21.8, 19.5, 19.13, 19.06, 18.9, 18.8, 18.7; HRMS (ESI-TOF) m/z : $[\text{M}+\text{Na}]^+$ Calcd. for $\text{C}_{39}\text{H}_{47}\text{NNaO}_3\text{S}^+$: 632.3169; found: 632.3175.

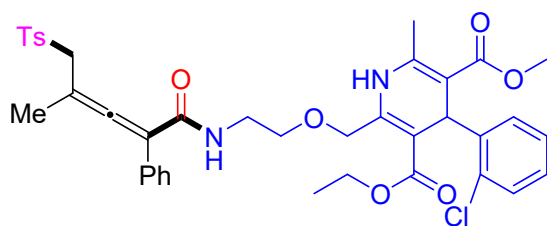


methyl (4-methyl-2-phenyl-5-tosylpenta-2,3-dienoyl)valinate (6g). The product was purified by column chromatography (petroleum ether / ethyl acetate = 5:1, $R_f = 0.3$), $dr = 2:3$; Pale yellow oil, 45.3 mg, 50% yield; $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.89 (d, $J = 8.3$ Hz, 1.66H), 7.79 (d, $J = 8.2$ Hz, 2.66H), 7.70 (d, $J = 8.2$ Hz, 0.66H), 7.36 – 7.33 (m, 5H), 7.29 (s, 1.66H), 7.28 – 7.23 (m, 5H), 4.61 – 4.53 (m, 1.66H), 3.95 (d, $J = 13.8$ Hz, 1H), 3.90 (d, $J = 13.5$ Hz, 0.66H), 3.76 (s, 3H), 3.73 – 3.72 (m, 3H), 3.70 – 3.68 (m, 0.66H), 2.43 (s, 3H), 2.40 (s, 2H), 2.30 – 2.25 (m, 1.66H), 2.06 (s, 3H), 1.77 (s, 2H), 1.02 (d, $J = 6.9$ Hz, 6H), 0.91 (d, $J = 6.8$ Hz, 2H), 0.85 (d, $J = 6.9$ Hz, 2H); $^{13}\text{C NMR}$ (100 MHz, CDCl_3) δ 208.3, 208.2, 174.0, 172.6, 172.5, 165.65, 165.56, 157.5, 145.4, 145.3, 136.0, 135.8, 132.5, 132.4, 130.2, 130.1, 128.64, 128.59, 128.41, 128.36, 106.3, 106.2, 95.4, 95.0, 60.6, 60.4, 58.6, 58.5, 58.1,

52.12, 52.08, 52.0, 31.5, 30.9, 30.8, 21.8, 19.7, 19.5, 19.3, 19.2, 19.1, 18.6, 18.5, 17.8; HRMS (ESI-TOF) m/z: [M+Na]⁺ Calcd. for C₂₅H₂₉NNaO₅S⁺ : 478.1659; found: 478.1669.

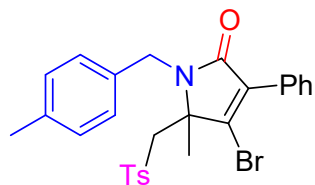


methyl 2-cyclopentyl-2-(4-methyl-2-phenyl-5-tosylpenta-2,3-dienamido)acetate (6h). The product was purified by column chromatography (petroleum ether / ethyl acetate = 5:1, R_f = 0.3), dr = 1:1; Yellow oil, 51.0 mg, 53% yield; ¹H NMR (400 MHz, CDCl₃) δ 7.93 (d, *J* = 8.2 Hz, 2H), 7.84 – 7.80 (m, 4H), 7.38 – 7.35 (m, 6H), 7.32 (s, 2H), 7.30 – 7.29 (m, 4H), 7.26 – 7.24 (m, 2H), 4.52 (q, *J* = 7.9 Hz, 2H), 3.97 (d, *J* = 13.7 Hz, 1H), 3.91 (d, *J* = 13.4 Hz, 1H), 3.77 (s, 3H), 3.71 (d, *J* = 4.5 Hz, 4H), 3.68 (d, *J* = 8.2 Hz, 1H), 2.45 (s, 3H), 2.42 (s, 3H), 2.07 (s, 3H), 1.96 – 1.92 (m, 1H), 1.91 – 1.84 (m, 1H), 1.72 (s, 3H), 1.68 – 1.62 (m, 8H), 1.57 – 1.53 (m, 4H), 1.48 – 1.44 (m, 4H); ¹³C NMR (100 MHz, CDCl₃) δ 208.5, 208.3, 174.2, 173.1, 173.0, 165.53, 165.47, 157.4, 145.5, 145.4, 136.1, 135.7, 132.4, 130.3, 130.2, 128.8, 128.7, 128.6, 128.43, 128.36, 128.2, 128.01, 127.97, 106.4, 106.2, 95.3, 94.9, 60.8, 60.5, 57.3, 57.0, 56.3, 52.1, 52.0, 42.8, 42.0, 41.9, 29.8, 29.5, 29.4, 29.3, 29.2, 29.0, 28.5, 25.53, 25.49, 25.34, 25.14, 25.10, 25.07, 21.78, 21.76, 19.7, 19.5; HRMS (ESI-TOF) m/z: [M+Na]⁺ Calcd. for C₂₇H₃₁NNaO₅S⁺ : 504.1815; found: 504.1824.



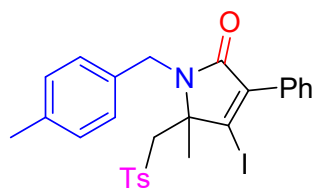
3-ethyl 5-methyl 4-(2-chlorophenyl)-6-methyl-2-((2-(4-methyl-2-phenyl-5-tosylpenta-2,3-dienamido)ethoxy)methyl)-1,4-dihydropyridine-3,5-dicarboxylate (6i). The product was purified by column chromatography (petroleum ether / ethyl acetate = 2:1, R_f = 0.3); Pale yellow oil, 80.5 mg, 55% yield; ¹H NMR (400 MHz, CDCl₃) δ 8.11 – 8.08 (m, 1H), 7.79 (d, *J* = 8.1 Hz, 2H), 7.61 (dd, *J* = 8.2, 2.9 Hz, 1H), 7.55 (s, 1H), 7.42 (d, *J* = 7.1 Hz, 2H), 7.34 (d, *J* = 7.9 Hz, 4H), 7.20 (d, *J* = 6.6 Hz, 1H), 7.08 – 7.00 (m, 3H), 5.36 (s, 1H), 4.86 – 4.66 (m, 4H), 4.04 (dd, *J* = 7.1, 2.6 Hz, 2H), 3.80 – 3.75 (m, 2H), 3.67 (d, *J* = 13.3 Hz, 2H), 3.58 (s, 3H), 2.45 (s, 3H), 2.20 (s, 3H), 1.95 (s, 3H), 1.18 (t, *J* = 5.2 Hz, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 208.5, 168.1, 167.3, 166.1, 146.2, 145.8, 145.5, 145.0, 135.8,

132.4, 132.2, 131.5, 130.3, 129.7, 129.1, 128.70, 128.67, 128.4, 128.14, 128.08, 127.3, 126.9, 126.0, 106.7, 103.5, 101.2, 94.5, 70.9, 68.2, 60.9, 59.8, 50.7, 39.9, 37.0, 21.8, 19.9, 19.3, 14.4; HRMS (ESI-TOF) m/z : $[M+Na]^+$ Calcd. for $C_{39}H_{41}ClN_2NaO_8S^+$: 755.2164; found: 755.2172.



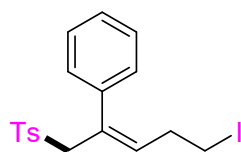
4-bromo-5-methyl-1-(4-methylbenzyl)-3-phenyl-5-(tosylmethyl)-1,5-dihydro-2H-pyrrol-2-one (7).

The product was purified by column chromatography (petroleum ether / ethyl acetate = 5:1); Yellow oil, 40.9 mg, 78% yield; 1H NMR (400 MHz, $CDCl_3$) δ 7.77 – 7.70 (m, 4H), 7.44 – 7.39 (m, 3H), 7.25 (d, J = 8.5 Hz, 2H), 7.14 – 7.09 (m, 4H), 4.13 (d, J = 16.1 Hz, 1H), 3.88 – 3.79 (m, 2H), 3.68 (d, J = 15.2 Hz, 1H), 2.32 (d, J = 7.9 Hz, 6H), 1.70 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 157.7, 145.0, 137.5, 137.3, 136.1, 135.9, 133.2, 130.1, 129.6, 129.3, 129.0, 128.3, 128.2, 127.3, 86.6, 61.8, 50.3, 29.5, 25.3, 21.7, 21.2; HRMS (ESI-TOF) m/z : $[M+H]^+$ Calcd. for $C_{27}H_{27}BrNO_3S^+$: 524.1890; found: 524.0899.



4-iodo-5-methyl-1-(4-methylbenzyl)-3-phenyl-5-(tosylmethyl)-1,5-dihydro-2H-pyrrol-2-one (8).

The product was purified by column chromatography (petroleum ether / ethyl acetate = 5:1); Yellow oil, 36.0 mg, 63% yield; 1H NMR (400 MHz, $CDCl_3$) δ 7.76 (d, J = 8.3 Hz, 2H), 7.62 (dd, J = 7.8, 1.7 Hz, 2H), 7.44 – 7.39 (m, 3H), 7.25 (d, J = 6.2 Hz, 2H), 7.10 (s, 4H), 4.09 (d, J = 16.1 Hz, 1H), 3.84 – 3.79 (m, 2H), 3.67 (d, J = 15.1 Hz, 1H), 2.32 (d, J = 3.5 Hz, 6H), 1.69 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 158.4, 145.0, 140.1, 137.5, 135.9, 131.1, 130.1, 129.6, 129.3, 129.0, 128.3, 128.2, 127.3, 114.4, 88.1, 62.5, 50.3, 29.5, 25.9, 21.7, 21.2; HRMS (ESI-TOF) m/z : $[M+H]^+$ Calcd. for $C_{27}H_{27}INO_3S^+$: 572.0751; found: 572.0759.



(E)-1-((5-iodo-2-phenylpent-2-en-1-yl)sulfonyl)-4-methylbenzene (10).³ The product was purified by column chromatography (petroleum ether / ethyl acetate = 5:1); Yellow oil, 72.5 mg, 85% yield; 1H

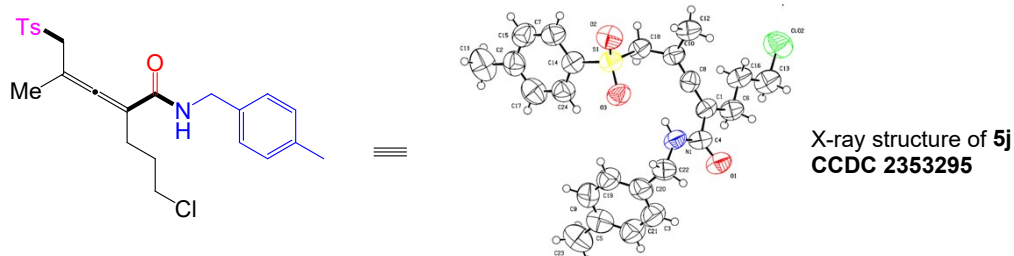
NMR (400 MHz, CDCl₃) δ 7.62 (d, J = 8.2 Hz, 2H), 7.20 – 7.16 (m, 7H), 5.94 (t, J = 7.3 Hz, 1H), 4.33 (s, 2H), 3.15 (t, J = 6.9 Hz, 2H), 2.72 (q, J = 7.0 Hz, 2H), 2.37 (s, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 144.8, 140.7, 136.3, 130.3, 129.7, 128.5, 128.4, 127.5, 126.6, 125.2, 58.2, 33.2, 21.7, 4.3.

8. References

1. Zhang, Y.; Yu, B.; Gao, B. Zhang, T. Huang, H. Triple-Bond Insertion Triggers Highly Regioselective 1,4-Aminomethylation of 1,3-Enynes with Aminals Enabled by Pd-Catalyzed C-N Bond Activation. *Org. Lett.* **2019**, *21*, 535-539.
2. Mutra, M.; Chen, Y.-T.; Wang, J.-J. Photoinduced Radical Cyclization of 1,6-Diynes: Rapid Access to Highly Substituted Carbocyclic and Heterocyclic Compounds. *Adv. Synth. Catal.* **2023**, *365*, 1012-1019.
3. Kadari, L.; Palakodety, R. K.; Yallapragada, L. P. Iodine-Catalyzed Facile Approach to Sulfones Employing TosMIC as a Sulfonylating Agent. *Org. Lett.* **2017**, *19*, 2580-2583.

9. X-ray crystal data for product 5j (CCDC: 2353295)

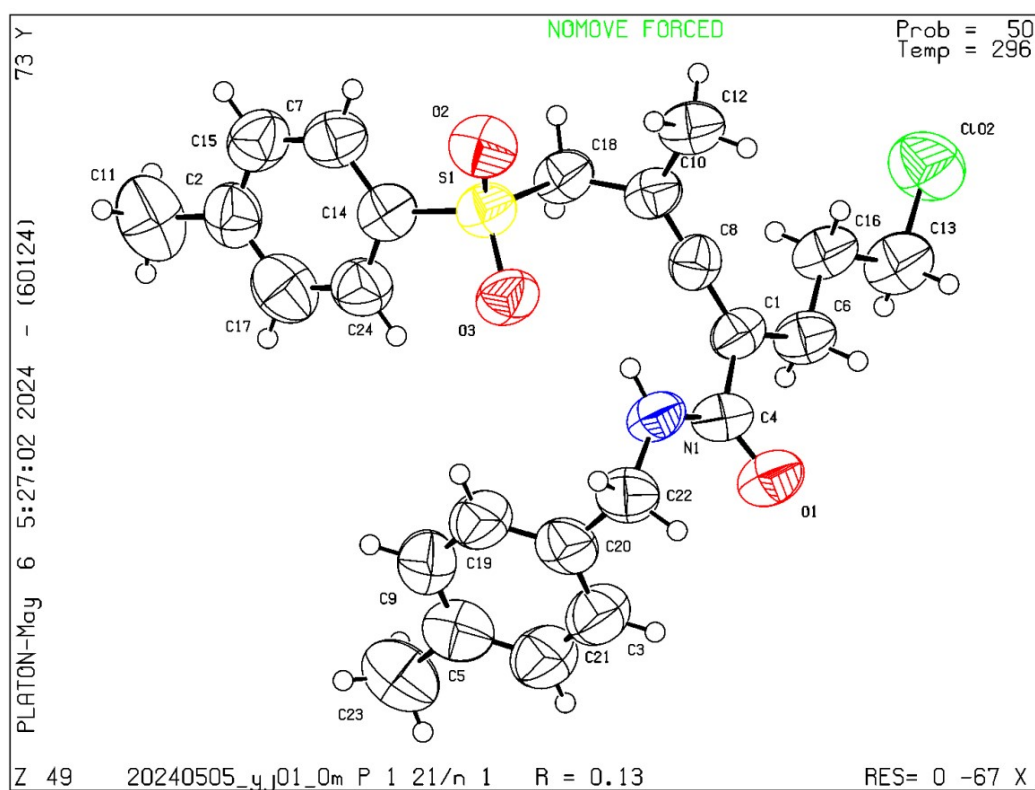
Bruker Apex2 CCD was used for the crystal measurement and the ellipsoid contour is shown at 30% probability levels. Single crystals of compound **5j** were obtained by slow evaporation of its petroleum ether / dichloromethane solution.



Compound	3aa
Empirical formula	C ₂₄ H ₂₈ ClNO ₃ S
Formula weight	445.98
Temperature/K	296.09
Crystal system	monoclinic
Space group	P2 ₁ /c
a/Å	4.9709 (6)
b/Å	15.9820 (19)
c/Å	29.501 (4)
α/°	90
β/°	91.962 (7)
γ/°	90
Volume/Å ³	2342.3 (5)
Z	4
ρ _{calc} /cm ³	1.265
μ/mm ⁻¹	2.471
F(000)	944.0
Crystal size/mm ³	0.26 × 0.14 × 0.02
Radiation	CuKα (λ = 1.54178)
2θ range for data collection/°	6.29 to 127.31
Index ranges	-5 ≤ h ≤ 5, -18 ≤ k ≤ 18, -34 ≤ l ≤ 34
	S29

Reflections collected	27566
Independent reflections	3793 [$R_{\text{int}} = 0.2152$, $R_{\text{sigma}} = 0.0936$]
Data/restraints/parameters	3793/0/251
Goodness-of-fit on F^2	1.453
Final R indexes [$I \geq 2\sigma(I)$]	$R_1 = 0.1247$, $wR_2 = 0.3248$
Final R indexes [all data]	$R_1 = 0.2308$, $wR_2 = 0.4522$
Largest diff. peak/hole / $e \text{ \AA}^{-3}$	0.70/-0.82

Datablock 20240505_yj01_0m - ellipsoid plot



10. ^1H , ^{13}C spectra of products (4a - 4u, 5a - 5m, 6a - 6i, 7, 8, 10)

