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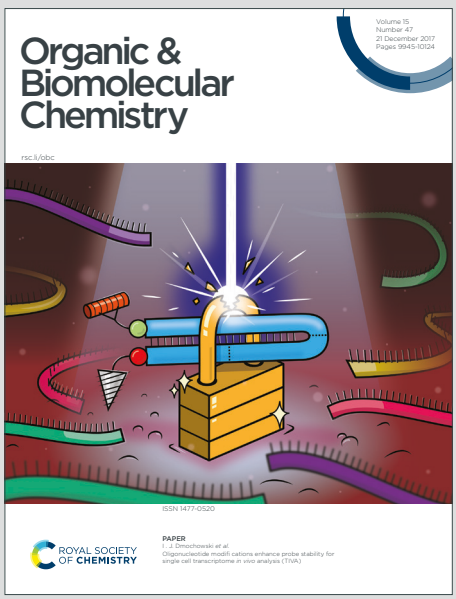

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PAPER

Rhodium(I)-Catalyzed Vinylation/[2+1] Carbocyclization of 1,6-Enynes with α-Diazocarbonyl Compounds†

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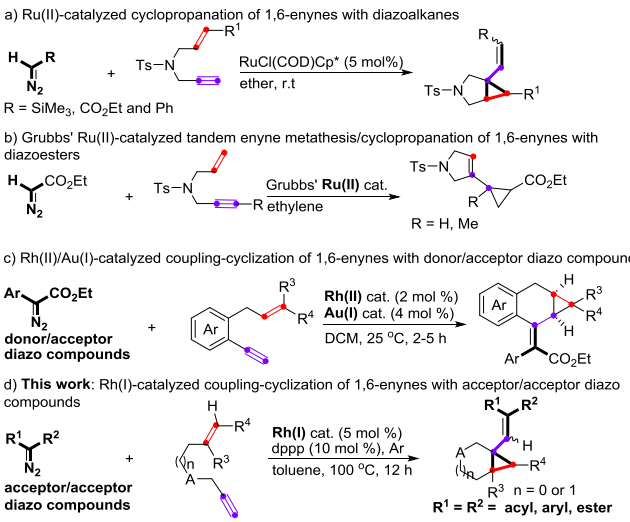
A sequential Rh(I)-catalyzed vinylation/[2+1]carbocyclization of between enynes and diazo compounds has been developed. This transformation features a wide range of enynes and acceptor/acceptor diazo compounds, providing easy access to versatile vinyl-substituted azabicyclo[3.1.0]hexanes with a broad tolerance of functional groups.

Introduction

Cycloaddition reactions of unsaturated hydrocarbons provides a powerful platform for assembling complex molecules.[1] Among them, 1,n-enynes (n = 5-7) have emerged as important synthons to access diverse fused ring systems through redox metal-catalysis that are inaccessible using traditional organic reactions.[2] In this regards, much progress about enyne-based [m+n+o] cycloadditions with various coupling partners such as alkynes,[3] alkenes,[4] arenes,[5] aldehydes,[6] silanes,[7] azirines,[8] *N*-hydroxyanilines,[9] silylboranes,[10] carbon monoxide [11] and others, [12] have been achieved for rapidly furnishing polycyclic compounds. Nevertheless, in the light of the fact that structurally diverse polycyclic systems are commonly encountered in many natural products and pharmaceutical molecules,[13] developing novel cycloaddition of enynes with diverse coupling partners for constructing versatile fused polycycles is always desirable.

It is well-known that the cross-coupling reactions involved diazo compounds provide a powerful tool to form C-X bonds (X = C, N, etc). To date, the couplings of diazo compounds with alkanes,[14] arenes,[15] alcohols,[16] amines,[17] amides,[18] alkynes,[19] and alkenes,[20] etc. have been widely explored to make particular molecules. Unfortunately, the coupling-cyclization between enynes and diazo compounds are rarely reported possibly due to that metal carbenes could independently undergo [2+1] cycloaddition with alkynyl and alkenyl moiety of enynes to form three-member cycles.[21] Up to now, this transformation has been pioneeringly developed by Dixneuf to assemble alkenylbicyclo[3.1.0]hexanes by employing Ru(II) catalysts, in which the scope of diazo compounds was very limited (**Scheme 1a**).[22] Subsequently, Snapper found Grubbs's Ru(II)-catalyzed coupling-cyclization enynes with diazoacetate led to the formation of cyclopropyl-substituted cycloolefines through tandem enyne metathesis/cyclopropanation process (**Scheme 1b**).[23] More recently, Liu reported that Au(I)/Rh(II)-catalyzed cycloaddition reaction of enynes with diazo compounds could efficiently furnish complex tetrahydro-1H-cyclopropa[b]naphthalenes (**Scheme 1c**).[24] Thus it can be seen that the coupling reaction between enynes and diazo compounds would afford structurally diverse polycyclic molecules employing different catalytical systems.

As the continuation of our interest in exploring diazo compound-based cross-coupling reactions,[25] we herein disclose a Rh(I)-catalyzed coupling–cyclization of enynes with diazo compounds for rapidly assembling diverse functionalized vinyl-substituted bicyclo[3.1.0]hexanes, in which diazo compounds could be extend to acceptor/acceptor or donor/acceptor diazo compounds (**Scheme 1d**).



Scheme 1. Cycloadditions of enynes with diazo compounds under different catalytical systems

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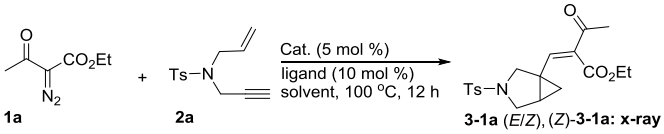
†Electronic supplementary information (ESI) available: ^{1}H and ^{13}C NMR spectra, mass of the compounds and crystallographic data of compound *(Z)*-**3-1a** in CIF. CCDC 1887226. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/x0xx00000x

Results and discussion

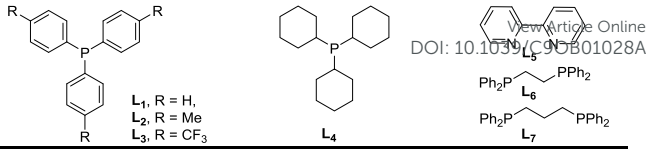
Our initial efforts focused on screening various metal catalysts (5 mol %), which could possibly enable the coupling-cyclization of α-diazo-β-ketoester (**1a**) with *N*-allyl-*N*-propargyl-4-methylbenzenesulfonamide (**2a**) in the presence of PPh_3 (10 mol %) in 1,2-dichloroethane (DCE) at 100 °C under Ar atmosphere for 12 h (Table 1, entries 1-6). Gratifyingly, we soon found that $[Rh(COD)Cl]_2$ could produce the vinylation/[2+1]carbocyclization product **3-1a** in 35% yield (*E*/*Z* = 14 : 21) (entry 6), and the other catalysts including $Pd(PPh_3)_4$, $Ni(COD)_2$, $Ru_3(CO)_{12}$, $[Rh(C_2H_4)_2Cl]_2$ and $[Rh(COD)(OH)]_2$ did not efficiently enhance the coupling reaction at all (compare entries 1-5 with 6). Moreover, the structures of (*Z*)-**3-1a** was already unambiguously confirmed by its single crystal X-ray analysis.[26] Subsequently, the solvent screening was further performed employing $[Rh(COD)Cl]_2$ as catalysts, and toluene proved to be the most suitable solvent (entries 6-9 vs 10). Finally, different types of ligands (**L_1**-**L_7**) were evualated in order to improve the reaction conversion. It was found that the electron-deficient monodentate ligands (**L_3** and **L_4** vs **L_1** and **L_2**) did not enable this reaction to occur at all (entries 10 and 11 vs 12 and 13). To our satisfaction, switching 1,2-bis(diphenylphosphino)ethane (DPPE) to 1,3-bis(diphenylphosphino)propane (DPPP), which has a slightly larger bite-angle and better flexibility range,[27] significantly increased the yield of **3-1a** to 84% (entries 10-15 vs 16). It should be noted that the transformation could not occur in the absence of ligands (entry 17).

Table 1. Optimization of the reaction parameters [a]



1a 2a 3-1a (*E*/*Z*), (*Z*)-3-1a: x-ray

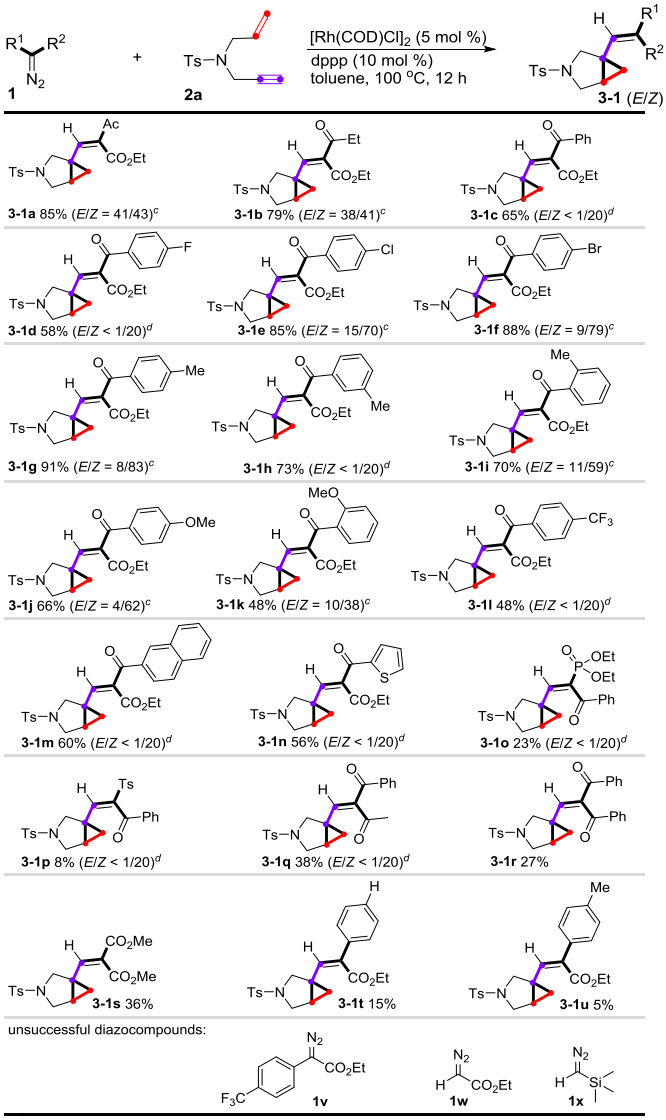
entry	catalyst	ligand	solvent	yield (%) [b] (*E*/*Z*) [c]
1	$Pd(PPh_3)_4$	L_1	DCE	0
2	$Ni(COD)_2$	L_1	DCE	0
3	$Ru_3(CO)_{12}$	L_1	DCE	0
4	$[Rh(C_2H_4)_2Cl]_2$	L_1	DCE	0
5	$[Rh(COD)(OH)]_2$	L_1	DCE	trace
6	$[Rh(COD)Cl]_2$	L_1	DCE	35(14/21)
7	$[Rh(COD)Cl]_2$	L_1	CH_3CN	trace
8	$[Rh(COD)Cl]_2$	L_1	dioxane	trace
9	$[Rh(COD)Cl]_2$	L_1	$PhCF_3$	24(11/13)
10	$[Rh(COD)Cl]_2$	L_1	toluene	38(16/22)
11	$[Rh(COD)Cl]_2$	L_2	toluene	22(8/14)
12	$[Rh(COD)Cl]_2$	L_3	toluene	0
13	$[Rh(COD)Cl]_2$	L_4	toluene	0
14	$[Rh(COD)Cl]_2$	L_5	toluene	0
15	$[Rh(COD)Cl]_2$	L_6	toluene	0
16	$[Rh(COD)Cl]_2$	L_7	toluene	84(41/43)
17	$[Rh(COD)Cl]_2$	--	toluene	0



[a]All the reactions were performed using diazo compound **1a** (0.4 mmol) and enyne **2a** (0.4 mmol) in the presence of catalysts (5 mol %) with ligand (10 mol %) in solvent (2.0 mL) at 100 °C for 12 h under Ar in a sealed reaction tube. Followed by flash chromatography on SiO_2; [b]Isolated yield. [c]The *E*/*Z* ratios were calculated based on the isolated yields.

With the optimized reaction conditions known, various diazo compounds were first employed to react with enyne **2a**. As shown in **Table 2**, α-diazo-β-alkylketoesters could smoothly couple with **2a** to produce 1-fatty acyl-1-ethoxycarbonyl-vinyl-substiuted azabicyclo[3.1.0]hexanes **3-1a** and **3-2b** in 85% and 79% yields, respectively. Meanwhile, α-diazo-β-arylketoesters also tolerated this reaction system, and afforded versatile 1-arylacyl-1-ethoxycarbonylvinyl-substituted azabicyclo[3.1.0] hexanes **3-1c** – **3-1l** in 48-91% yields. Among them, α-diazo-β-(4-chlorophenyl)ketoester, α-diazo-β-(4-bromophenyl) ketoester, α-diazo-β-(4- methylphenyl)ketoester and α-diazo-β-(4-methoxyphenyl)ketoester could be efficiently converted into the corresponding polycycles (**3-1e** – **3-1g** and **3-1j**) in good to excellent yields (66-91%). In comparison, the electron-deficient α-diazo-β-(4-flurophenyl)ketoester and α-diazo-β-(4-trifluromethylphenyl)ketoester led to inferior transformations, affording 58% and 48% yied of **3-1d** and **3-1l**, respectively. Moreover, the steric hindrance of the *ortho*-substituent on the β-phenyl ring of diazo compounds inhibited the reaction conversion to some degree, and produced 70% and 48% yields of **3-1i** and **3-1k** (**3-1g** *vs* **3-1i**, **3-1j** *vs* **3-1k**), respectively. To our satisfactory, α-diazo-β-(2-naphthyl)ketoester, α-diazo-β-(2-thiophyl)ketoester, α-diazo phosphonate, α-diazo diketones, and even α-diazo diester could also react with **2a** to assemble the desired products **3-1m** – **3-1s** in acceptable yields (8-60% yields). On the contrary, donor/acceptor diazo compounds made the transformation very sluggish. For examples, the electron-rich ethyl 2-diazo-2-phenylacetate and 2-diazo-2-(4-methyl)phenylacetate only gave 15% yield of **3-1t** and 5% yield of **3-1u**, respectively, and electron-deficient ethyl 2-diazo-2-(4-(trifluoromethyl)phenyl)acetate (**1v**) did not afford the desired product at all. Meanwhile, the simple diazo compounds such as acceptor diazo compound ethyl α-diazoacetate (**1w**) and donor diazo compound diazomethyltrimethylsilane (**1x**) could not undergo the coupling-cyclization with enyne **2a** to afford the corresponding products, and **2a** was almost recovered completely.

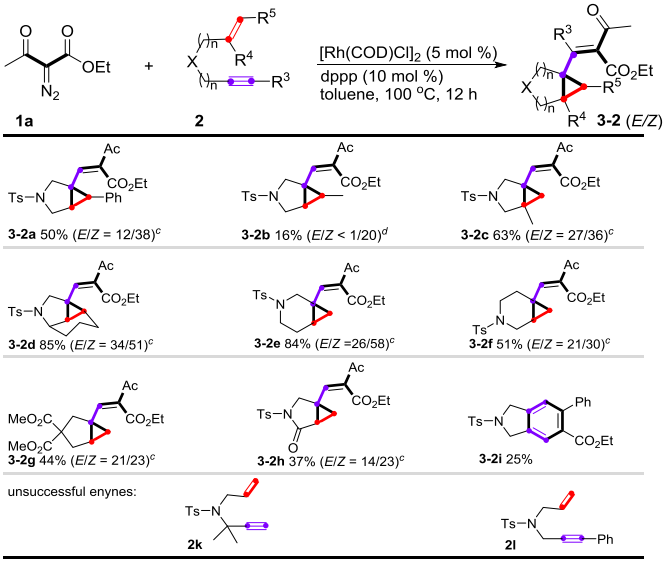
Table 2. Scope of diazo compounds [a, b]



[a]All the reactions were performed using diazo compounds **1** (0.4 mmol) and 1,6-enyne **2a** (0.40 mmol) with $[Rh(COD)Cl]_2$ (5 mol %) and dppp (10 mol %) in toluene (2.0 mL) at 100 °C for 12 h under Ar in a sealed reaction tube. Followed by flash chromatography on SiO_2; [b]Isolated yield. [c]The *E*/Z ratios were calculated based on the isolated yields. [d]The *E*/*Z* ratios were calculated based on the ^1H NMR spectrum.

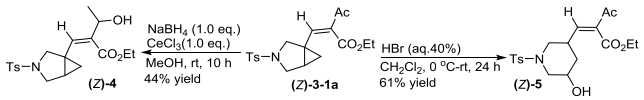
To further investigate the scope of enynes, the coupling-cyclization of diazo compound **1a** with different types of enynes was further systemically evaluated. As shown in **Table 3**, besides the terminal alkene-substituted 1,6-enynes, internal olefin-containing 1,6-enynes such as 1-phenyl-, 1-methyl-, or 2-methyl-substituted 1,6-enynes and even cyclohexene-containing 1,6-enyne all tolerated this reaction system, assembling the vinyl-functionalized azabicyclo[3.1.0]hexanes **3-2a** – **3-2d** in 16-85% yields. Moreover, *N*-homoallyl-substituted proparglyamide and *N*-homopropargyl-substituted allylamide could also smoothly couple with **1a** to produce azabicyclo[4.1.0]heptanes **3-2e** (84%) and **3-2f** (51%), respectively. It is gratifying that the coupling-cyclization could still be extended to diethyl 2-allyl-2-(prop-2-yn-1-yl)malonate and electron-deficient 1,6-enyne [*N*-(prop-2-yn-1-yl)-*N*-tosylacrylamide], affording 44% yield of **3-2g** and 37% yield of **3-2h**, respectively. However, when *N*-Ts-*N*,*N*-dipropynylamine (1,6-diyne) coupled with 2-diazo-3-oxo-3-phenyl-propionic acid ethyl ester under the reaction system, the unexpected [2+2+2] product *N*-tosylisoindoline **3-2i** could be obtained in 25% yield. Unfortunately, the 1,6-enynes containing the steric linker (**2k**) or internal alkyne (**2l**) could not react with diazo compound **1a** to produce the desired products possibly due to the steric factors.

Table 3. Scope of enynes[a, b]



[a]All the reactions were performed using diazo compound **1a** (0.4 mmol) and enynes **2** (0.40 mmol) with $[Rh(COD)Cl]_2$ (5 mol %) and dppp (10 mol %) in toluene (2.0 mL) at 100 °C for 12 h under Ar in a sealed reaction tube. Followed by flash chromatography on SiO_2; [b]Isolated yield. [c]The E/Z ratios were calculated based on the isolated yields. [d]The E/Z ratios were calculated based on the ^1H NMR spectrum.

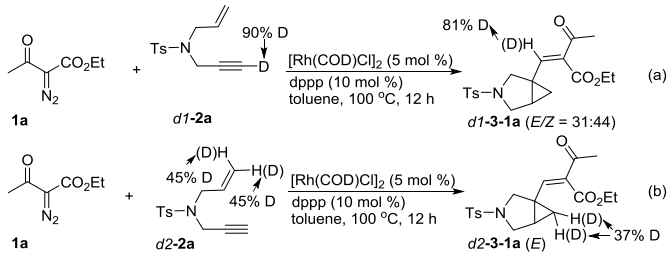
The synthetic applications of this transformation (**Scheme 2**) indicated that the ketone moiety of the vinyl-functionalized *beta*-ketoacetate (***Z***)-**3-1a** could be selectively reduced by $NaBH_4$ to furnish *beta*-hydroxy-*alpha*-methylene-acetate (*Z*)-**4** (44%). Moreover, the bridgehead Csp^3-Csp^3 bond of azabicyclo[3.1.0]hexane moiety could also be easily cleavaged by aqueous HBr to give piperidin-3-ol derivative (*Z*)-**5** (61%).



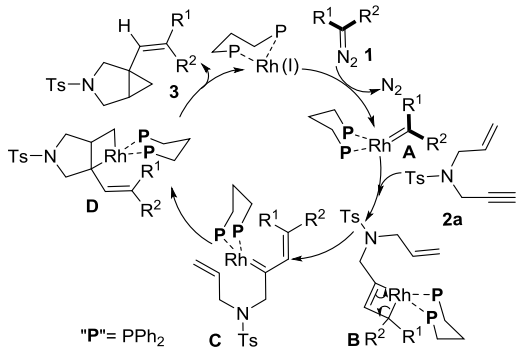
Scheme 2. Synthetic applications

To elucidate the possible reaction mechanism, the terminal deuterated alkyne *d*1-**2a** (90% D) was first treated with α-diazoacetate **1a**, and 81 atom % D was incorporated into β-position of α, β-unsaturated ester *d*1-**3-1a**, demonstrating that the terminal carbon of alkynes was involved in the cross-coupling with rhodium carbenes (**Scheme 3a**). Meanwhile, when the terminal deuterated alkene *d*2-**2a** (45% D) was employed to cyclize with **1a**, 37 atom % D was detected at the 6-position of azabicyclo[3.1.0]hexane (*d*2-**3-1a**), which indicated that the olefinic double bond was involved in the [2+1] carbocyclization (**Scheme 3b**).

Scheme 3. Preliminary mechanistic studies



On the basis of the above-mentioned experiments, we have proposed a plausible mechanism in **Scheme 4**. The initial reaction of α-diazo acetate (**1**) with Rh(I) catalysts affords rhodium carbene complex **A** with the extrusion of a N_2 molecule. Subsequently, the coupling reaction between Rh(I)-carbene **A** and alkyne led to the formation of rhodiumcyclobutene **B**,[22] which could further undergoes a ring-opening reaction to generate intermediate **C**. Finally, the intramolecular cascade cycloaddition/reductive elimination of rhodium carbene **C** with alkene produced the desired 1-vinyl-azabicyclo[3.1.0]hexanes **3**.



Scheme 4. The possible reaction mechanism

Conclusions

In conclusion, we have successfully developed a highly step and atom economical Rh(I)-catalyzed coupling cyclization of enynes with diazo compounds, affording 1-vinyl-substituted azabicyclo[3.1.0]hexanes with tolerance of various enynes and acceptor/acceptor diazo compounds. Moreover, the utility of this method demonstrated that these azabicycloalkanes could be further converted into versatile nitrogen heterocycles.

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Experimental Section

General Information

General Methods. All reactions were carried out in flame-dried sealed tubes with magnetic stirring. Unless otherwise noted, all experiments were performed under argon atmosphere. Solvents were treated with 4 Å molecular sieves or sodium and distilled prior to use. Purifications of reaction products were carried out by flash chromatography using silica gel (400 – 630 mesh). Infrared Spectra (IR) are reported as wavelength number (cm-1). Infrared spectra were recorded by preparing a KBr pellet containing the title compounds. ^{1}H NMR and ^{13}C NMR spectra were recorded with tetramethylsilane (TMS) as internal standard at ambient temperature (400 MHz for ^{1}H NMR and 101 MHz for ^{13}C NMR). Chemical shifts are reported in parts per million (ppm) and coupling constants are reported as Hertz (Hz). Splitting patterns are designated as singlet (s), broad singlet (bs), doublet (d), triplet (t). Splitting patterns that could not be interpreted or easily visualized are designated as multiple (m). High resolution mass spectra (HRMS) were recorded on an IF-TOF spectrometer (Micromass). Gas chromatograph mass spectra were obtained with a SHIMADZU model GCMS-QP5000 spectrometer. All the α-diazo-β-ketoesters (**1a-1v**, see SI for the details)[28] and 1,6-enynes (**2a-2k**, see SI for the details)[29, 30] were prepared according to the previous literature.

General Procedure for the Synthesis of Azabicyclo[3.1.0]hexanes Derivatives (3-1a~3-1u) and (3-2a~3-2i)

To an oven-dried sealed tube charged with $[Rh(COD)Cl]_2$ (5 mol %), dppp (10 mol %), *alpha*-diazo compounds (0.4 mmol) and 1,6-enynes (0.4 mmol), toluene (2.0 mL) were added under argon atmosphere. The reaction mixture was allowed to stir at 100 °C for 12 h, the corresponding solution was diluted by ethyl acetate (5.0 mL), filtrated and concentrated to get the crude products. The desired compounds were purified by column chromatography using petroleum ether / ethyl acetate as eluent.

Ethyl (*E*)-3-oxo-2-((3-tosyl-3-azabicyclo[3.1.0]hexan-1-yl)methylene)butanoate (3-1a). The title compound was prepared from *ethyl 2-diazo-3-oxobutanoate* (**1a)** (62.4 mg, 0.4 mmol) and *N-allyl-4-methyl-N-(prop-2-yn-1-yl)benzenesulfonamide* **(2a)** (99.6 mg, 0.4 mmol), and purified by column chromatography to give white solid (62.0 mg, 41%). R_f (petroleum ether/ethyl acetate = 5:1) 0.34; m.p. 126.0-128.0 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.66 (d, *J* = 7.9 Hz, 2H), 7.34 (d, *J* = 7.9 Hz, 2H), 6.47 (s, 1H), 4.21 (q, *J* = 7.1 Hz, 2H), 3.54 (q, *J* = 14.2, 9.4 Hz, 2H), 3.08 (q, *J* = 9.4, 3.6 Hz, 1H), 2.86 (d, *J* = 9.4 Hz, 1H), 2.44 (s, 3H), 2.37 (s, 3H), 1.74 – 1.67 (m, 1H), 1.26 (t, *J* = 7.1 Hz, 3H), 1.21 (t, *J* = 5.3 Hz, 1H), 1.10 – 1.05 (m, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 201.5, 164.2, 146.1, 143.9, 135.0, 132.9, 129.8, 127.6, 61.4, 51.1, 48.9, 31.4, 28.9, 28.0, 21.5, 17.6, 14.1; HR-MS (ESI) calcd for $[M + H]^+$: $C_{19}H_{23}NO_5S$: 378.1370,

found: 378.1364; IR (KBr): 3029, 2955, 1716, 1597, 1478, 1162, 820 cm^{-1}.

Ethyl (*Z*)-3-oxo-2-((3-tosyl-3-azabicyclo[3.1.0]hexan-1-yl)methylene)butanoate (3-1a). The title compound was prepared from *ethyl 2-diazo-3-oxobutanoate* (**1a)** (62.4 mg, 0.4 mmol) and *N-allyl-4-methyl-N-(prop-2-yn-1-yl)benzenesulfonamide* (**2a)** (99.6 mg, 0.4 mmol), and purified by column chromatography to give white solid (65.0 mg, 43%). R_f (petroleum ether/ethyl acetate = 5:1) 0.33; m.p. 126.0-128.0 ^oC, ^1H NMR (400 MHz, $CDCl_3$) δ 7.66 (d, *J* = 7.9 Hz, 2H), 7.34 (d, *J* = 7.9 Hz, 2H), 6.47 (s, 1H), 4.21 (q, *J* = 7.1 Hz, 2H), 3.54 (q, *J* = 14.2, 9.4 Hz, 2H), 3.08 (q, *J* = 9.4, 3.6 Hz, 1H), 2.86 (d, *J* = 9.4 Hz, 1H), 2.44 (s, 3H), 2.37 (s, 3H), 1.74 – 1.67 (m, 1H), 1.26 (t, *J* = 7.1 Hz, 3H), 1.21 (t, *J* = 5.3 Hz, 1H), 1.10 – 1.05 (m, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 201.5, 164.2, 146.1, 143.9, 135.0, 132.9, 129.8, 127.6, 61.4, 51.1, 48.9, 31.4, 28.8, 28.0, 21.5, 17.6, 14.1; HR-MS (ESI) calcd for $[M + H]^+$: $C_{19}H_{23}NO_5S$: 378.1370, found: 378.1364; IR (KBr): 3029, 2955, 1716, 1597, 1478, 1162, 820 cm^{-1}.

Ethyl (*E*)-3-oxo-2-((3-tosyl-3-azabicyclo[3.1.0]hexan-1-yl)methylene)pentanoate (3-1b). The title compound was prepared from *ethyl 2-diazo-3-oxopentanoate* **(1b)** (68.0 mg, 0.4 mmol) and *N-allyl-4-methyl-N-(prop-2-yn-1-yl)benzenesulfonamide* (**2a)** (99.6 mg, 0.4 mmol), and purified by column chromatography to give yellow oily liquid (59.0 mg, 38%). R_f (petroleum ether/ethyl acetate = 5:1) 0.34; ^1H NMR (400 MHz, $CDCl_3$) δ 7.58 (d, *J* = 8.2 Hz, 2H), 7.27 (d, *J* = 8.0 Hz, 2H), 6.39 (d, *J* = 7.4 Hz, 1H), 4.17 (m, 2H), 3.59 – 3.34 (m, 2H), 3.10 – 2.82 (m, 1H), 2.73 (d, *J* = 9.4 Hz, 1H), 2.66 – 2.42 (m, 2H), 2.37 (s, 3H), 1.72 – 1.59 (m, 1H), 1.29 (t, *J* = 7.2 Hz, 1H), 1.18 (t, *J* = 7.1 Hz, 3H), 1.05 (t, *J* = 7.3 Hz, 3H), 0.98 (t, *J* = 7.2 Hz, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 205.0, 164.3, 145.7, 143.9, 134.7, 132.6, 129.8, 127.6, 61.4, 50.9, 48.9, 37.3, 28.7, 27.8, 21.6, 17.5, 14.1, 7.86; HR-MS (ESI) calcd for $[M + H]^+$: $C_{20}H_{26}NO_5S$: 392.1526, found: 392.1514; IR (KBr): 3026, 2982, 1725, 1698, 1633, 1456, 1165, 816 cm^{-1}.

Ethyl (*Z*)-3-oxo-2-((3-tosyl-3-azabicyclo[3.1.0]hexan-1-yl)methylene)pentanoate (3-1b). The title compound was prepared from *ethyl 2-diazo-3-oxopentanoate* **(1b)** (68.0 mg, 0.4 mmol) and *N-allyl-4-methyl-N-(prop-2-yn-1-yl)benzenesulfonamide* **(2a)** (99.6 mg, 0.4 mmol), and purified by column chromatography to give yellow oily liquid (65.3 mg, 41%). R_f (petroleum ether/ethyl acetate = 5:1) 0.33; ^1H NMR (400 MHz, $CDCl_3$) δ 7.57 (d, *J* = 8.0 Hz, 2H), 7.26 (d, *J* = 8.0 Hz, 2H), 6.38 (s, 1H), 4.35 – 4.02 (m, 2H), 3.53 (q, *J* = 17.0, 9.3 Hz, 2H), 2.99 (q, *J* = 9.3, 3.7 Hz, 2H), 2.92 (d, *J* = 9.2 Hz, 2H), 2.47 (q, *J* = 17.9, 7.2 Hz, 2H), 2.36 (s, 3H), 1.76 – 1.64 (m, 1H), 1.64 – 1.54 (m, 1H), 1.29 (t, *J* = 7.1 Hz, 4H), 1.18 (t, *J* = 5.1 Hz, 1H), 1.06 – 1.01 (m, 1H), 0.98 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 196.4, 167.5, 144.7, 143.9, 135.1, 132.9, 129.8, 127.5, 618, 50.21, 48.9, 32.1, 28.9, 27.7, 21.6, 17.6, 14.1, 7.85; HR-MS (ESI) calcd for $[M + H]^+$: $C_{20}H_{26}NO_5S$: 392.1526, found: 392.1514; IR (KBr): 3026, 2982, 1725, 1698, 1633, 1456, 1165, 816, cm^{-1}.

Ethyl (*Z*)-2-benzoyl-3-(3-tosyl-3-azabicyclo[3.1.0]hexan-1-yl)acrylate (3-1c). The title compound was prepared from *ethyl 2-diazo-3-oxo-3-phenylpropanoate* **(1c)** (87.0 mg, 0.4 mmol) and *N-allyl-4-methyl-N-(prop-2-yn-1-yl)benzenesulfonamide* **(2a)** (99.6 mg, 0.4 mmol), and purified by column chromatography to give white solid (114.2 mg, 65%). R_f (petroleum ether/ethyl acetate = 5:1) 0.33; m.p. 134.0-137.0 ^oC; ^1H NMR (400 MHz, $CDCl_3$) δ 7.71 (d, *J* = 4.8 Hz, 1H), 7.46 (d, *J* = 3.7 Hz, 1H), 7.42 (s, 2H), 7.18 (d, *J* = 8.0 Hz, 2H), 7.09 – 7.05 (m, 1H), 6.64 (s, 1H), 4.07 (m, 2H), 3.43 (d, *J* = 9.3 Hz, 1H), 3.26 (d, *J* = 9.3 Hz, 1H), 2.85 – 2.74 (m, 2H), 2.34 (s, 3H), 1.74 – 1.61 (m, 1H), 1.15 (t, *J* = 5.3 Hz, 1H), 1.06 (q, *J* = 7.4 Hz, 4H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 186.4, 164.3, 147.2, 144.5, 143.7, 135.5, 134.4, 132.1, 131.8, 129.7, 128.5, 127.5, 61.5, 50.5, 48.8, 29.1, 28.0, 21.6, 17.9, 14.0; HR-MS (ESI) calcd for $[M + H]^+$: $C_{24}H_{26}NO_5S$: 440.1526, found: 440.1515; IR (KBr): 3032, 2982, 1719, 1669, 1597, 1475, 1164, 813 cm^{-1}.

Ethyl (*Z*)-2-(4-fluorobenzoyl)-3-(3-tosyl-3-azabicyclo[3.1.0]hexan-1-yl)acrylate (3-1d). The title compound was prepared from *ethyl 2-diazo-3-(4-fluorophenyl)-3-oxopropanoate* **(1d)** (94.2 mg, 0.4 mmol) and *N-allyl-4-methyl-N-(prop-2-yn-1-yl)benzenesulfonamide* **(2a)** (99.6 mg, 0.4 mmol), and purified by column chromatography to give yellow oil liquid (106.3 mg, 58%). R_f (petroleum ether/ethyl acetate = 5:1) 0.33; ^1H NMR (400 MHz, $CDCl_3$) δ 7.81 (dd, *J* = 8.4, 5.5 Hz, 2H), 7.34 (d, *J* = 8.0 Hz, 2H), 7.09 (d, *J* = 9.6 Hz, 4H), 6.66 (s, 1H), 4.11 – 3.96 (m, 2H), 3.43 (d, *J* = 9.3 Hz, 1H), 3.24 (d, *J* = 9.3 Hz, 1H), 2.83 (q, *J* = 9.3, 3.7 Hz, 1H), 2.59 (d, *J* = 9.3 Hz, 1H), 2.33 (s, 3H), 1.72 – 1.60 (m, 1H), 1.21 – 1.09 (m, 1H), 1.01 (t, *J* = 7.1 Hz, 4H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 192.7, 166.1(d, *J* = 255.0 Hz, $^1J_{CF}$), 164.3, 147.5, 143.7, 133.5(d, J = 2 Hz, $^3J_{CF}$), 132.0, 131.9, 131.8, 129.6, 127.4, 116.1(d, *J* = 22.0 Hz, $^2J_{CF}$), 61.5, 50.8, 48.8, 29.1, 27.9, 21.5, 17.9, 13.9; HR-MS (ESI) calcd for $[M + H]^+$: $C_{24}H_{25}FNO_5S$: 458.1432, found: 458.1417; IR (KBr): 3064, 2981, 1716, 1597, 1505, 1167, 817 cm^{-1}.

Ethyl (*E*)-2-(4-chlorobenzoyl)-3-(3-tosyl-3-azabicyclo[3.1.0]hexan-1-yl)acrylate (3-1e). The title compound was prepared from *ethyl 3-(4-chlorophenyl)-2-diazo-3-oxopropanoate* **(1e)** (111.0 mg, 0.4 mmol) and *N-allyl-4-methyl-N-(prop-2-yn-1-yl)benzenesulfonamide* **(2a)** (99.6 mg, 0.4 mmol), and purified by column chromatography to give yellow oil liquid (28.1 mg, 15%). R_f (petroleum ether/ethyl acetate = 4:1) 0.34; ^1H NMR (400 MHz, $CDCl_3$) δ 7.72 (d, *J* = 8.4 Hz, 2H), 7.38 (d, *J* = 8.4 Hz, 2H), 7.31 (d, *J* = 8.1 Hz, 2H), 7.07 (d, *J* = 8.0 Hz, 2H), 6.65 (s, 1H), 4.03 (m, 2H), 3.41 (s, 1H), 3.25 (d, *J* = 9.3 Hz, 1H), 2.82 (q, *J* = 9.3, 3.8 Hz, 1H), 2.54 (d, *J* = 9.3 Hz, 1H), 2.33 (s, 3H), 1.71 – 1.62 (m, 1H), 1.18 (t, *J* = 5.4 Hz, 1H), 1.02 (m, 4H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 193.1, 164.2, 148.0, 143.7, 140.3, 135.4, 131.9, 131.6, 130.5, 129.6, 129.2, 127.4, 61.5, 50.9, 48.8, 29.18, 28.0, 21.5, 18.0, 13.9; HR-MS (ESI) calcd for $[M + H]^+$: $C_{24}H_{25}ClNO_5S$: 474.1136, found: 474.1121; IR (KBr): 3061, 2995, 1770, 1636, 1587, 1460, 1165, 817 cm^{-1}.

Ethyl (*Z*)-2-(4-chlorobenzoyl)-3-(3-tosyl-3-azabicyclo[3.1.0]hexan-1-yl)acrylate (3-1e). The title compound was prepared from *ethyl 3-(4-chlorophenyl)-2-diazo-3-oxopropanoate* **(1e)** (111.2 mg, 0.4 mmol) and *N-allyl-4-methyl-N-(prop-2-yn-1-yl)benzenesulfonamide* **(2a)** (99.6 mg, 0.4 mmol), and purified by column chromatography to give yellow oil liquid (131.7 mg, 70%). R_f (petroleum ether/ethyl acetate = 4:1) 0.33; ^1H NMR (400 MHz, $CDCl_3$) δ 7.72 (d, J = 8.4 Hz, 2H), 7.39 (d, *J* = 8.4 Hz, 2H), 7.32 (d, *J* = 8.1 Hz, 2H), 7.08 (d, *J* = 8.1 Hz, 2H), 6.65 (s, 1H), 4.03 (m, 2H), 3.43 (d, *J* = 9.3 Hz, 1H), 3.25 (d, *J* = 9.3 Hz, 1H), 2.82

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(q, *J* = 9.3, 3.8 Hz, 1H), 2.55 (d, *J* = 9.3 Hz, 1H), 2.34 (s, 3H), 1.71 – 1.63 (m, 1H), 1.18 (t, *J* = 5.3 Hz, 1H), 1.03 (m, 4H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 193.1, 164.2, 148.0, 143.7, 140.4, 135.4, 131.8, 131.6, 130.5, 129.6, 129.2, 127.4, 61.5, 50.8, 48.8, 29.18, 28.0, 21.5, 18.0, 13.9; HR-MS (ESI) calcd for $[M + H]^+$: $C_{24}H_{25}ClNO_5S$: 474.1136, found: 474.1121; IR (KBr): 3061, 2995, 1770, 1636, 1587, 1460, 1165, 817 cm^{-1}.

Ethyl (*E*)-2-(4-bromobenzoyl)-3-(3-tosyl-3-azabicyclo[3.1.0]hexan-1-yl)acrylate (3-1f). The title compound was prepared from *ethyl 3-(4-bromophenyl)-2-diazo-3-oxopropanoate* **(1f)** (130.2 mg, 0.4 mmol) and *N-allyl-4-methyl-N-(prop-2-yn-1-yl)benzenesulfonamide* **(2a)** (99.6 mg, 0.4 mmol), and purified by column chromatography to give yellow oil liquid (19.3 mg, 9%). R_f (petroleum ether/ethyl acetate = 4:1) 0.34; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.64 (d, *J* = 8.4 Hz, 2H), 7.56 (d, *J* = 8.3 Hz, 2H), 7.30 (d, *J* = 8.0 Hz, 2H), 7.08 (d, *J* = 7.9 Hz, 2H), 6.65 (s, 1H), 4.13 – 3.91 (m, 2H), 3.43 (d, *J* = 9.3 Hz, 1H), 3.25 (d, *J* = 9.2 Hz, 1H), 2.82 (q, *J* = 9.3, 3.7 Hz, 1H), 2.54 (d, *J* = 9.2 Hz, 1H), 2.34 (s, 3H), 1.70 – 1.59 (m, 1H), 1.19 (t, *J* = 5.1 Hz, 1H), 1.08 – 0.98 (m, 4H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 193.3, 164.2, 148.1, 143.8, 135.8, 132.2, 131.8, 131.6, 130.6, 130.5, 129.6, 129.2, 127.4, 61.5, 50.9, 48.8, 29.2, 28.0, 21.6, 18.0, 14.0; HR-MS (ESI) calcd for $[M + H]^+$: $C_{24}H_{25}BrNO_5S$: 518.0631, found: 518.0597; IR (KBr): 3009, 2926, 1719, 1698, 1635, 1399, 1165, 818 cm^{-1}.

Ethyl (*Z*)-2-(4-bromobenzoyl)-3-(3-tosyl-3-azabicyclo[3.1.0]hexan-1-yl)acrylate (3-1f). The title compound was prepared from *ethyl 3-(4-bromophenyl)-2-diazo-3-oxopropanoate* **(1f)** (130.2 mg, 0.4 mmol) and *N-allyl-4-methyl-N-(prop-2-yn-1-yl)benzenesulfonamide* **(2a)** (99.6 mg, 0.4 mmol), and purified by column chromatography to give yellow oil liquid (163.2 mg, 79%). R_f (petroleum ether/ethyl acetate = 4:1) 0.33; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.64 (d, *J* = 8.4 Hz, 2H), 7.56 (d, *J* = 8.3 Hz, 2H), 7.30 (d, *J* = 8.0 Hz, 2H), 7.08 (d, *J* = 7.9 Hz, 2H), 6.65 (s, 1H), 4.13 – 3.91 (m, 2H), 3.43 (d, *J* = 9.3 Hz, 1H), 3.25 (d, *J* = 9.2 Hz, 1H), 2.82 (q, *J* = 9.3, 3.7 Hz, 1H), 2.54 (d, *J* = 9.2 Hz, 1H), 2.34 (s, 3H), 1.70 – 1.59 (m, 1H), 1.19 (t, *J* = 5.1 Hz, 1H), 1.08 – 0.98 (m, 4H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 193.3, 164.2, 148.05, 143.8, 135.8, 132.2, 131.8, 131.6, 130.6, 130.5, 129.6, 129.2, 127.4, 61.5, 50.9, 48.8, 29.2, 28.0, 21.6, 18.0, 14.0; HR-MS (ESI) calcd for $[M + H]^+$: $C_{24}H_{25}BrNO_5S$: 518.0631, found: 518.0597; IR (KBr): 3009, 2926, 1719, 1698, 1635, 1399, 1165, 818 cm^{-1}.

Ethyl (*E*)-2-(4-methylbenzoyl)-3-(3-tosyl-3-azabicyclo[3.1.0]hexan-1-yl)acrylate (3-1g). The title compound was prepared from *ethyl 2-diazo-3-oxo-3-(p-tolyl)propanoate* **(1g)** (93.2 mg, 0.4 mmol) and *N-allyl-4-methyl-N-(prop-2-yn-1-yl)benzenesulfonamide* **(2a)** (99.6 mg, 0.4 mmol), and purified by column chromatography to give yellow oil liquid (15.4 mg, 8%). R_f (petroleum ether/ethyl acetate = 4:1) 0.34; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.68 (d, *J* = 8.2 Hz, 2H), 7.36 (d, *J* = 8.2 Hz, 2H), 7.21 (d, *J* = 8.0 Hz, 2H), 7.10 (d, *J* = 8.0 Hz, 2H), 6.65 (s, 1H), 4.03 (m, 2H), 3.40 (d, *J* = 9.3 Hz, 1H), 3.23 (d, *J* = 9.3 Hz, 1H), 2.81 (q, *J* = 9.3, 3.8 Hz, 1H), 2.68 (d, *J* = 9.3 Hz, 1H), 2.41 (s, 3H), 2.33 (s, 3H), 1.67 – 1.60 (m, 1H), 1.17 (t, 1H), 1.10 (t, *J* = 5.2 Hz, 1H), 1.00 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 194.0, 164.6, 146.8, 144.9, 143.5, 134.5, 132.4, 132.1, 129.6, 129.3, 127.5, 61.3, 50.9, 48.9, 29.0, 27.7, 21.9, 21.5, 17.7, 14.0.HR-MS (ESI) calcd for $[M + H]^+$: $C_{25}H_{27}NO_5S$: 454.1683, found: 454.1658; IR (KBr): 3018, 2923, 1722, 1696, 1635, 1399, 1166, 1050, 817 cm^{-1}.

Ethyl (*Z*)-2-(4-methylbenzoyl)-3-(3-tosyl-3-azabicyclo[3.1.0]hexan-1-yl)acrylate (3-1g). The title compound was prepared from *ethyl 2-diazo-3-oxo-3-(p-tolyl)propanoate* **(1g)** (93.2 mg, 0.4 mmol) and *N-allyl-4-methyl-N-(prop-2-yn-1-yl)benzenesulfonamide* **(2a)** (99.6 mg, 0.4 mmol), and purified by column chromatography to give yellow oil liquid (150.4 mg, 83%). R_f (petroleum ether/ethyl acetate = 4:1) 0.33; ^{1}H NMR (400 MHz, CDCl3) δ 7.76 (d, *J* = 8.1 Hz, 2H), 7.43 (d, *J* = 8.0 Hz, 2H), 10.21 – 5.69 (m, 5H), 7.38 – 7.25 (m, 2H), 7.17 (d, *J* = 8.1 Hz, 2H), 6.73 (s, 1H), 4.11 (m, 2H), 3.48 (d, *J* = 9.3 Hz, 1H), 3.32 (d, *J* = 9.3 Hz, 1H), 2.89 (q, *J* = 9.3, 3.8 Hz, 1H), 2.75 (d, *J* = 9.3 Hz, 1H), 2.49 (s, 3H), 2.41 (s, 3H), 1.78 – 1.63 (m, 1H), 1.26 (t, *J* = 7.1 Hz, 1H), 1.19 (q, *J* = 6.5, 3.9 Hz, 1H), 1.09 (t, *J* = 7.1 Hz, 4H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 194.0, 164.6, 146.8, 144.9, 143.5, 134.5, 132.4, 132.1, 129.6, 129.3, 127.5, 61.3, 50.9, 48.9, 29.0, 27.7, 21.9, 21.5, 17.7, 14.0; HR-MS (ESI) calcd for $[M + H]^+$: $C_{25}H_{27}NO_5S$: 454.1683, found: 454.1658; IR (KBr): 3018, 2923, 1722, 1696, 1635, 1399, 1166, 1050, 817 cm^{-1}.

Ethyl (*Z*)-2-(3-methylbenzoyl)-3-(3-tosyl-3-azabicyclo[3.1.0]hexan-1-yl)acrylate (3-1h). The title compound was prepared from *ethyl 2-diazo-3-oxo-3-(m-tolyl)propanoate* **(1h)** (93.0 mg, 0.4 mmol) and *N-allyl-4-methyl-N-(prop-2-yn-1-yl)benzenesulfonamide* **(2a)** (99.6 mg, 0.4 mmol), and purified by column chromatography to give yellow oil liquid (132.4 mg, 73%). R_f (petroleum ether/ethyl acetate = 4:1) 0.33; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.72 – 7.57 (m, 2H), 7.48 – 7.34 (m, 4H), 7.18 (d, *J* = 8.1 Hz, 2H), 6.75 (s, 1H), 4.28 – 3.94 (m, 2H), 3.53 (t, *J* = 22.4 Hz, 1H), 3.33 (d, *J* = 9.3 Hz, 1H), 2.92 (q, *J* = 9.3, 3.8 Hz, 1H), 2.74 (t, *J* = 10.1 Hz, 1H), 2.44 (s, 3H), 2.41 (s, 3H), 1.77 – 1.71 (m, 1H), 1.20 (q, *J* = 5.4 Hz, 1H), 1.13 – 1.04 (m, 4H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 194.5, 164.6, 147.0, 143.5, 138.7, 136.9, 134.7, 132.4, 132.1, 129.6, 129.4, 128.7, 127.5, 126.6, 61.4, 50.9, 48.9, 29.1, 27.8, 21.5, 21.4, 17.7, 13.9; HR-MS (ESI) calcd for $[M + H]^+$: $C_{25}H_{27}NO_5S$: 454.1683, found: 454.1672; IR (KBr): 3018, 2923, 1722, 1696, 1635, 1399, 1166, 1050, 817 cm^{-1}.

Ethyl (*E*)-2-(2-methylbenzoyl)-3-(3-tosyl-3-azabicyclo[3.1.0]hexan-1-yl)acrylate (3-1i). The title compound was prepared from *ethyl 2-diazo-3-oxo-3-(o-tolyl)propanoate* **(1i)** (93.2 mg, 0.4 mmol) and *N-allyl-4-methyl-N-(prop-2-yn-1-yl)benzenesulfonamide* **(2a)** (99.6 mg, 0.4 mmol), and purified by column chromatography to give white solid (20.1 mg, 11%). R_f (petroleum ether/ethyl acetate = 4:1) 0.34; m.p. 109.0-110 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.58 (d, *J* = 8.2 Hz, 2H), 7.26 (d, *J* = 8.2 Hz, 3H), 7.13 (m, *J* = 21.0, 11.1, 7.0 Hz, 3H), 6.11 (s, 1H), 4.11 (q, *J* = 7.1 Hz, 2H), 3.61 (d, *J* = 9.4 Hz, 1H), 3.51 (d, *J* = 9.4 Hz, 1H), 3.03 (q, *J* = 9.4, 3.8 Hz, 1H), 2.97 (d, *J* = 9.4 Hz, 1H), 2.36 (s, 3H), 2.25 (s, 3H), 1.69 – 1.61 (m, 1H), 1.24 – 1.16 (m, 1H), 1.13 (t, *J* = 7.1 Hz, 3H), 1.01 (q, *J* = 8.0, 5.6 Hz, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 194.5, 166.5, 149.0, 143.9, 137.5, 136.8, 136.6, 133.2, 131.2, 130.6, 129.8, 127.6, 127.5, 125.3, 61.7, 50.3, 48.8, 29.3, 28.2, 21.6, 19.7, 18.0, 13.9; HR-MS (ESI) calcd for $[M + H]^+$: $C_{25}H_{27}NO_5S$: 454.1683, found: 454.1670; IR (KBr): 3018, 2923, 1722, 1696, 1635, 1399, 1166, 1050, 817 cm^{-1}.

Ethyl (*Z*)-2-(2-methylbenzoyl)-3-(3-tosyl-3-azabicyclo[3.1.0]hexan-1-yl)acrylate (3-1i). The title compound was prepared from *ethyl 2-diazo-3-oxo-3-(o-tolyl)propanoate* **(1i)** (93.0 mg, 0.4 mmol) and *N-allyl-4-methyl-N-(prop-2-yn-1-yl)benzenesulfonamide* **(2a)** (99.6 mg, 0.4 mmol), and purified by column chromatography to give white solid (107.3 mg, 59%). R_f (petroleum ether/ethyl acetate = 4:1) 0.33; m.p. 109.0-110 ^oC; ^1H NMR (400 MHz, $CDCl_3$) δ 7.53 – 7.42 (m, 4H), 7.35 (d, *J* = 7.5 Hz, 1H), 7.20 (t, *J* = 6.7 Hz, 3H), 6.69 (s, 1H), 4.08 (m, 2H), 3.53 (d, *J* = 9.4 Hz, 1H), 3.38 (d, *J* = 9.4 Hz, 1H), 2.97 (q, *J* = 9.3, 3.8 Hz, 1H), 2.84 (d, *J* = 9.4 Hz, 1H), 2.67 (s, 3H), 2.42 (s, 3H), 1.82 – 1.68 (m, 1H), 1.22 (t, *J* = 5.3 Hz, 1H), 1.12 (q, *J* = 7.9, 5.6 Hz, 1H), 1.11 – 1.01 (m, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 196.0, 164.7, 146.5, 143.6, 140.1, 136.2, 134.0, 132.5, 132.4, 132.3, 131.4, 129.6, 127.5, 125.7, 61.3, 50.9, 48.9, 29.1, 27.8, 21.7, 21.5, 17.7, 13.8; HR-MS (ESI) calcd for $[M + H]^+$: $C_{25}H_{27}NO_5S$: 454.1683, found: 454.1670; IR (KBr): 3018, 2923, 1722, 1696, 1635, 1399, 1166, 1050, 817 cm^{-1}.

Ethyl (*E*)-2-(4-methoxybenzoyl)-3-(3-tosyl-3-azabicyclo[3.1.0]hexan-1-yl)acrylate (3-1j). The title compound was prepared from *ethyl 2-diazo-3-(4-methoxyphenyl)-3-oxopropanoate* **(1j)** (99.2 mg, 0.4 mmol) and *N-allyl-4-methyl-N-(prop-2-yn-1-yl)benzenesulfonamide* **(2a)** (99.6 mg, 0.4 mmol), and purified by column chromatography to give yellow oil liquid (7.5 mg, 4%). R_f (petroleum ether/ethyl acetate = 4:1) 0.34; ^1H NMR (400 MHz, $CDCl_3$) δ 7.76 (d, *J* = 8.8 Hz, 2H), 7.36 (d, *J* = 8.2 Hz, 2H), 7.10 (d, *J* = 10.9 Hz, 2H), 6.88 (d, *J* = 7.6 Hz, 2H), 6.63 (s, 1H), 4.09 – 4.00 (m, 2H), 3.86 (s, 3H), 3.41 (d, *J* = 9.3 Hz, 1H), 3.24 (d, *J* = 9.3 Hz, 1H), 2.82 (q, *J* = 9.3, 3.8 Hz, 1H), 2.70 (d, *J* = 9.3 Hz, 1H), 2.33 (s, 3H), 1.66 – 1.61 (m, 1H), 1.16 (t, *J* = 7.0 Hz, 1H), 1.11 (t, *J* = 4.2 Hz, 1H), 1.03 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 192.8, 164.6, 164.2, 146.5, 143.6, 132.4, 132.1, 131.6, 130.1, 129.6, 127.5, 114.1, 61.3, 55.6, 50.8, 48.9, 29.0, 27.7, 21.5, 17.7, 14.0; HR-MS (ESI) calcd for $[M + H]^+$: $C_{25}H_{28}NO_6S$: 470.1632, found: 470.1611; 3050, 2980, 1716, 1660, 1598, 1510, 1206, 1166, 815 cm^{-1}.

Ethyl (*Z*)-2-(4-methoxybenzoyl)-3-(3-tosyl-3-azabicyclo[3.1.0]hexan-1-yl)acrylate (3-1j). The title compound was prepared from *ethyl 2-diazo-3-(4-methoxyphenyl)-3-oxopropanoate* **(1j)** (99 mg, 0.4 mmol) and *N-allyl-4-methyl-N-(prop-2-yn-1-yl)benzenesulfonamide* **(2a)** (99.6 mg, 0.4 mmol), and purified by column chromatography to give yellow oil liquid (116 mg, 62%). R_f (petroleum ether/ethyl acetate = 4:1) 0.33; ^1H NMR (400 MHz, $CDCl_3$) δ 7.55 – 7.43 (m, 4H), 7.35 (d, *J* = 7.5 Hz, 1H), 7.20 (t, *J* = 6.7 Hz, 3H), 6.69 (s, 1H), 4.13 – 4.03 (m, 2H), 3.53 (d, *J* = 9.4 Hz, 1H), 3.38 (d, *J* = 9.4 Hz, 1H), 2.97 (q, *J* = 9.3, 3.8 Hz, 1H), 2.84 (d, *J* = 9.4 Hz, 1H), 2.67 (s, 3H), 2.42 (s, 3H), 1.81 – 1.70 (m, 1H), 1.22 (t, *J* = 5.3 Hz, 1H), 1.14 – 1.09 (m, 1H), 1.06 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 192.8, 164.6, 164.2, 146.5, 143.6, 132.4, 132.1, 131.6, 130.1, 129.6, 127.5, 114.1, 61.3, 55.6, 50.8, 48.9, 29.0, 27.7, 21.5, 17.7, 14.0; HR-MS (ESI) calcd for $[M + H]^+$: $C_{25}H_{28}NO_6S$: 470.1632, found: 470.1611; IR (KBr): 3050, 2980, 1716, 1660, 1598, 1510, 1206, 1166, 815 cm^{-1}.

Ethyl (*E*)-2-(2-methoxybenzoyl)-3-(3-tosyl-3-azabicyclo[3.1.0]hexan-1-yl)acrylate (3-1k). The title compound was prepared from *ethyl 2-diazo-3-(2-methoxyphenyl)-3-oxopropanoate* **(1k)** (99.0 mg, 0.4 mmol) and *N-allyl-4-methyl-N-(prop-2-yn-1-yl)benzenesulfonamide* **(2a)** (99.6 mg, 0.4 mmol), and purified by column chromatography to give yellow oil liquid (19.3 mg, 10%). R_f (petroleum ether/ethyl acetate = 4:1) 0.34; ^1H NMR (400 MHz, $CDCl_3$) δ 7.66 (d, *J* = 8.0 Hz, 2H), 7.42 (t, *J* = 7.2 Hz, 2H), 7.32 (d, *J* = 8.0 Hz, 2H), 6.97 (t, *J* = 7.5 Hz, 1H), 6.88 (d, *J* = 8.7 Hz, 1H), 6.36 (s, 1H), 4.10 (q, *J* = 13.0, 6.2 Hz, 2H), 3.80 – 3.69 (m, 4H), 3.58 (d, *J* = 9.3 Hz, 1H), 3.13 (q, *J* = 9.3, 3.8 Hz, 1H), 3.03 (d, *J* = 9.4 Hz, 1H), 2.43 (s, 3H), 1.72 (m, 1H), 1.26 (s, 2H), 1.13 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 191.6, 165.8, 157.4, 148.3, 143.8, 136.9, 133.2, 132.8, 129.9, 129.7, 127.8, 127.6, 120.6, 111.1, 61.1, 55.4, 50.9, 49.0, 29.7, 29.2, 28.2, 21.5, 17.8, 13.9; HR-MS (ESI) calcd for $[M + H]^+$: $C_{25}H_{28}NO_6S$: 470.1632, found: 470.1627; IR (KBr): 3050, 2980, 1716, 1660, 1598, 1510, 1206, 1166, 815 cm^{-1}.

Ethyl (*Z*)-2-(2-methoxybenzoyl)-3-(3-tosyl-3-azabicyclo[3.1.0]hexan-1-yl)acrylate (3-1k). The title compound was prepared from *ethyl 2-diazo-3-(2-methoxyphenyl)-3-oxopropanoate* **(1k)** (99.0 mg, 0.4 mmol) and *N-allyl-4-methyl-N-(prop-2-yn-1-yl)benzenesulfonamide* **(2a)** (99.6 mg, 0.4 mmol), and purified by column chromatography to give yellow oil liquid (71.2 mg, 38%). R_f (petroleum ether/ethyl acetate = 4:1) 0.33; ^1H NMR (400 MHz, $CDCl_3$) δ 7.93 (d, *J* = 7.7 Hz, 1H), 7.57 (t, *J* = 7.7 Hz, 1H), 7.09 (t, *J* = 7.5 Hz, 1H), 6.92 (d, *J* = 8.4 Hz, 1H), 6.48 (s, 1H), 4.08 (q, *J* = 12.6, 7.0 Hz, 2H), 3.70 (s, 3H), 3.49 (d, *J* = 9.3 Hz, 1H), 3.42 (d, *J* = 9.3 Hz, 1H), 2.40 (s, 3H), 1.68 – 1.61 (m, 1H), 1.10 (t, *J* = 5.1 Hz, 1H), 1.05 (t, *J* = 7.1 Hz, 4H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 192.1, 164.8, 159.4, 143.4, 143.1, 136.9, 135.1, 132.5, 131.1, 129.6, 127.5, 126.7, 121.0, 111.9, 60.9, 55.4, 51.7, 49.1, 28.7, 27.4, 21.5, 17.4, 13.9; HR-MS (ESI) calcd for $[M + H]^+$: $C_{25}H_{28}NO_6S$: 470.1632, found: 470.1627; IR (KBr): 3058, 2980, 1721, 1651, 1597, 1484, 1214, 1166, 816 cm^{-1}.

Ethyl (*Z*)-3-(3-tosyl-3-azabicyclo[3.1.0]hexan-1-yl)-2-(4-(trifluoromethyl)benzoyl)acrylate (3-1l). The title compound was prepared from *ethyl 2-diazo-3-oxo-3-(4-(trifluoromethyl)phenyl)propanoate* **(1l)** (114.3 mg, 0.4 mmol) and *N-allyl-4-methyl-N-(prop-2-yn-1-yl)benzenesulfonamide* **(2a)** (99.6 mg, 0.4 mmol), and purified by column chromatography to give yellow oil liquid (97.0 mg, 48%). R_f (petroleum ether/ethyl acetate = 4:1) 0.30; ^1H NMR (400 MHz, $CDCl_3$) δ 7.98 (d, *J* = 8.0 Hz, 2H), 7.78 (d, *J* = 8.0 Hz, 2H), 7.39 (d, *J* = 7.8 Hz, 2H), 7.11 (d, *J* = 7.8 Hz, 2H), 6.78 (s, 1H), 4.11 (q, *J* = 12.7, 5.9 Hz, 2H), 3.52 (d, *J* = 9.3 Hz, 1H), 3.36 (d, *J* = 9.2 Hz, 1H), 2.92 (q, *J* = 9.2, 3.3 Hz, 1H), 2.62 (d, *J* = 9.2 Hz, 1H), 2.38 (s, 3H), 1.87 – 1.70 (m, 1H), 1.30 (t, *J* = 5.1 Hz, 1H), 1.18 – 1.12 (m, 1H), 1.07 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (101 MHz, CDCl3) δ 193.24, 164.10, 148.80, 143.79, 139.55, 135.08, 131.96, 131.40, 129.5, 129.4, 127.4, 125.9 (q, *J* = 10 Hz, $^2J_{CF}$), 61.6, 51.0, 48.8, 29.3, 28.2, 21.5, 18.1, 13.9; HR-MS (ESI) calcd for $[M + H]^+$: $C_{25}H_{25}F_3NO_5S$: 508.1400, found: 508.1385; IR (KBr): 3058, 2980, 1721, 1651, 1597, 1484, 1214, 1166, 816 cm^{-1}.

Ethyl (*Z*)-2-(2-naphthoyl)-3-(3-tosyl-3-azabicyclo[3.1.0]hexan-1-yl)acrylate (3-1m). The title compound was prepared from *ethyl 2-diazo-3-(naphthalen-2-yl)-3-oxopropanoate* **(1m)** (107.2 mg, 0.4 mmol) and *N-allyl-4-methyl-N-(prop-2-yn-1-yl)benzenesulfonamide* **(2a)** (99.6 mg, 0.4 mmol), and purified by column chromatography to give yellow oil liquid (117.4 mg, 60%). R_f (petroleum ether/ethyl acetate = 4:1) 0.33; ^1H NMR (400 MHz, $CDCl_3$) δ 8.18 (s, 1H), 7.96

(dd, *J* = 8.6, 1.4 Hz, 1H), 7.93 – 7.87 (m, 2H), 7.84 (d, *J* = 8.2 Hz, 1H), 7.62 (t, *J* = 7.5 Hz, 1H), 7.52 (t, *J* = 7.5 Hz, 1H), 7.11 (d, *J* = 8.1 Hz, 2H), 6.69 (s, 1H), 6.59 (d, *J* = 7.9 Hz, 2H), 4.02 (m, 2H), 3.39 (d, *J* = 9.3 Hz, 1H), 3.29 (d, *J* = 9.3 Hz, 1H), 2.76 (q, *J* = 9.3, 3.8 Hz, 1H), 2.57 (d, *J* = 9.3 Hz, 1H), 2.02 (s, 3H), 1.73 – 1.63 (m, 1H), 1.19 – 1.16 (m, 1H), 1.07 (q, *J* = 7.8, 5.6 Hz, 1H), 0.97 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 194.2, 164.6, 147.8, 143.4, 136.0, 134.5, 132.6, 132.2, 131.8, 131.4, 129.8, 129.3, 129.1, 128.9, 128.0, 127.3, 127.1, 124.0, 61.4, 51.0, 48.9, 29.4, 28.0, 21.2, 18.0, 14.0; HR-MS (ESI) calcd for $[M + H]^+$: $C_{28}H_{28}NO_5S$: 490.1683, found: 490.1670; IR (KBr): 3061, 2986, 1719, 1664, 1600, 1466, 1167, 817 cm$^{-1.}$

Ethyl (*Z*)-2-(thiophene-2-carbonyl)-3-(3-tosyl-3-azabicyclo[3.1.0]hexan-1-yl)acrylate (3-1n). The title compound was prepared from *ethyl 2-diazo-3-oxo-3-(thiophen-2-yl)propanoate* **(1n)** (90.2 mg, 0.4 mmol) and **N-allyl-4-methyl-N-(prop-2-yn-1-yl)benzenesulfonamide (2a)** (99.6 mg, 0.4 mmol), and purified by column chromatography to give yellow oil liquid (100.2 mg, 56%). R_f (petroleum ether/ethyl acetate = 4:1) 0.33; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.71 (d, *J* = 4.8 Hz, 1H), 7.46 (d, *J* = 3.7 Hz, 1H), 7.43 (d, *J* = 8.1 Hz, 2H), 7.18 (d, *J* = 8.0 Hz, 2H), 7.09 – 7.04 (m, 1H), 6.64 (s, 1H), 4.07 (m, 2H), 3.43 (d, *J* = 9.3 Hz, 1H), 3.26 (d, *J* = 9.3 Hz, 1H), 2.87 – 2.73 (m, 2H), 2.34 (s, 3H), 1.72 – 1.61 (m, 1H), 1.15 (t, *J* = 5.3 Hz, 1H), 1.06 (q, *J* = 7.4 Hz, 4H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 186.4, 164.3, 147.2, 144.5, 143.7, 135.5, 134.4, 132.1, 131.8, 129.7, 128.5, 127.5, 61.5, 50.5, 48.8, 29.1, 28.0, 21.6, 17.9, 14.0; HR-MS (ESI) calcd for $[M + H]^+$: $C_{28}H_{28}NO_5S$: 446.1090, found: 446.1098; IR (KBr): 3058, 2986, 1717, 1640, 1595, 1515, 1166, 815 cm^{-1}.

Diethyl (*Z*)-(3-oxo-3-phenyl-1-(3-tosyl-3-azabicyclo[3.1.0]

hexan-1-yl)prop-1-en-2-yl)phosphonate (3-1o). The title compound was prepared from *diethyl (1-diazo-2-oxo-2-phenylethyl)phosphonate* **(1o)** (113.2 mg, 0.4 mmol) and *N-allyl-4-methyl-N-(prop-2-yn-1-yl)benzenesulfonamide* **(2a)** (99.6 mg, 0.4 mmol), and purified by column chromatography to give yellow oil liquid (46.3 mg, 23%). R_f (petroleum ether/ethyl acetate = 4:1) 0.33; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.85 (d, 2H), 7.57 (t, *J* = 7.4 Hz, 1H), 7.41 (t, *J* = 7.7 Hz, 2H), 7.34 (d, *J* = 8.2 Hz, 2H), 7.14 (d, *J* = 8.0 Hz, 2H), 6.50 (d, *J* = 25.3 Hz, 1H), 3.96 (m, 4H), 3.38 (d, *J* = 9.4 Hz, 1H), 3.06 (d, *J* = 9.3 Hz, 1H), 2.79 (q, *J* = 9.3, 3.8 Hz, 1H), 2.70 (d, *J* = 9.3 Hz, 1H), 2.36 (s, 3H), 1.64 – 1.55 (m, 1H), 1.18 (s, 1H), 1.12 (m, *J* = 7.1, 1.5 Hz, 6H), 0.97 (d, *J* = 3.6 Hz, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 194.6, 194.5, 149.9, 143.6, 136.6, 134.1, 132.3, 129.7, 129.7, 128.7, 127.4, 62.7, 58.4, 50.7, 48.7, 30.1, 29.8, 27.3, 21.5, 18.4, 17.2, 16.1, 16.0; HR-MS (ESI) calcd for $[M + H]^+$: $C_{25}H_{30}NO_6PS$: 504.1554, found: 504.1602; IR (KBr): 3066, 2986, 1658, 1632, 1595, 1500, 1166, 818 cm^{-1}.

(*Z*)-1-Phenyl-2-tosyl-3-(3-tosyl-3-azabicyclo[3.1.0]hexan-1-yl)prop-2-en-1-one (3-1p). The title compound was prepared from *2-diazo-1-phenyl-2-tosylethan-1-one* **(1p)** (120.2 mg, 0.4 mmol) and *N-allyl-4-methyl-N-(prop-2-yn-1-yl)benzenesulfonamide* **(2a)** (99.6 mg, 0.4 mmol), and purified by column chromatography to give yellow oil (17.2 mg, 8%). R_f (petroleum ether/ethyl acetate = 4:1) 0.33; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.88 (d, *J* = 7.8 Hz, 2H), 7.68 (t, *J* = 7.4 Hz, 1H), 7.62 (d, *J* = 8.0 Hz, 2H), 7.49 (t, *J* = 7.6 Hz, 2H), 7.40 (d, *J* = 7.9 Hz, 2H), 7.29 (d, *J* = 7.8 Hz, 2H), 7.23 (d, *J* = 7.9 Hz, 2H), 6.83 (s, 1H), 3.48 (d, *J* = 9.4 Hz, 1H), 3.04 (d, *J* = 9.2 Hz, 1H), 2.87 (q, *J* = 9.4, 3.5 Hz, 1H), 2.71 (d, *J* = 9.2 Hz, 1H), 2.43 (s, 6H), 1.80 – 1.73 (m, 1H), 1.29 (d, *J* = 5.9 Hz, 1H), 1.16 – 1.06 (m, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 191.2, 145.0, 144.6, 143.7, 140.8, 136.6, 136.3, 134.7, 132.4, 130.0, 129.8, 129.8, 129.0, 128.6, 127.4, 50.2, 48.6, 28.7, 28.0, 21.7, 21.5, 17.7; HR-MS (ESI) calcd for $[M + H]^+$: $C_{28}H_{27}NO_5S_2$: 522.1403, found: 522.1402; IR (KBr): 3066, 2983, 1595, 1494, 1166, 818 cm^{-1}.

(*Z*)-1-Phenyl-2-((3-tosyl-3-azabicyclo[3.1.0]hexan-1-yl)methylene)butane-1,3-dione (3-1q). The title compound was prepared from *2-diazo-1-phenylbutane-1,3-dione* **(1q)** (75.1 mg, 0.4 mmol) and *N-allyl-4-methyl-N-(prop-2-yn-1-yl)benzenesulfonamide* **(2a)** (99.6 mg, 0.4 mmol), and purified by column chromatography to give yellow oil (62.3 mg, 38%). R_f (petroleum ether/ethyl acetate = 4:1) 0.33; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.85 (d, *J* = 7.6 Hz, 2H), 7.66 (t, *J* = 7.3 Hz, 1H), 7.50 (t, *J* = 7.6 Hz, 2H), 7.41 (d, *J* = 8.1 Hz, 2H), 7.19 (d, *J* = 7.9 Hz, 2H), 6.60 (s, 1H), 3.48 (d, *J* = 9.3 Hz, 1H), 3.25 (d, *J* = 9.3 Hz, 1H), 2.88 (q, *J* = 9.3, 3.6 Hz, 1H), 2.73 (d, *J* = 9.3 Hz, 1H), 2.41 (s, 3H), 2.19 (s, 3H), 1.76 – 1.70 (m, 1H), 1.19 (t, *J* = 5.2 Hz, 1H), 1.12 – 1.06 (m, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 196.8, 195.0, 145.8, 143.7, 140.8, 136.8, 134.2, 132.1, 129.7, 129.2, 129.1, 127.4, 50.8, 48.8, 29.0, 28.1, 27.0, 21.5, 17.9; HR-MS (ESI) calcd for $[M + H]^+$: $C_{23}H_{23}NO_4S$: 410.1421, found: 410.1411; IR (KBr): 3067, 2925, 1655, 1623, 1597, 1449, 1166, 816 cm^{-1}.

1,3-Diphenyl-2-((3-tosyl-3-azabicyclo[3.1.0]hexan-1-yl)methylene)propane-1,3-dione (3-1r). The title compound was prepared from *2-diazo-1,3-diphenylpropane-1,3-dione* **(1r)** (99.6 mg, 0.4 mmol) and *N-allyl-4-methyl-N-(prop-2-yn-1-yl)benzenesulfonamide* **(2a)** (99.6 mg, 0.4 mmol), and purified by column chromatography to give white solid (51.0 mg, 27%). R_f (petroleum ether/ethyl acetate = 4:1) 0.33; m.p. 167.0-168.0 ^{0}C ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.85 (d, *J* = 7.7 Hz, 2H), 7.69 (d, *J* = 7.6 Hz, 2H), 7.59 (t, *J* = 7.4 Hz, 1H), 7.52 – 7.36 (m, 8H), 7.16 (d, *J* = 8.0 Hz, 2H), 6.38 (s, 1H), 3.50 (d, *J* = 9.4 Hz, 1H), 3.40 (d, *J* = 9.4 Hz, 1H), 2.96 (q, *J* = 9.4, 3.7 Hz, 1H), 2.78 (d, *J* = 9.4 Hz, 1H), 2.39 (s, 3H), 1.76 – 1.65 (m, 1H), 1.19 (t, *J* = 5.3 Hz, 1H), 1.09 – 1.02 (m, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 195.4, 193.6, 148.6, 143.6, 140.9, 137.2, 137.0, 133.9, 132.6, 132.4, 129.6, 129.3, 129.3, 128.9, 128.2, 127.5, 51.3, 48.9, 29.4, 28.2, 21.5, 18.0; HR-MS (ESI) calcd for $[M + H]^+$: $C_{28}H_{26}NO_4S$: 473.1577, found: 473.1571; IR (KBr): 3072, 2919, 1632, 1491, 1165 cm^{-1}.

Dimethyl 2-((3-tosyl-3-azabicyclo[3.1.0]hexan-1-yl)methylene)malonate (3-1s). The title compound was prepared from *dimethyl 2-diazomalonate* **(1s)** (63.2 mg, 0.4 mmol) and *N-allyl-4-methyl-N-(prop-2-yn-1-yl)benzenesulfonamide* **(2a)** (99.6 mg, 0.4 mmol), and purified by column chromatography to give yellow oil (66.9 mg, 44%). R_f (petroleum ether/ethyl acetate = 4:1) 0.33; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.58 (d, *J* = 8.2 Hz, 2H), 7.27 (d, *J* = 8.0 Hz, 2H), 6.54 (s, 1H), 3.75 (s, 3H), 3.67 (s, 3H), 3.51 (t, *J* = 9.8 Hz, 2H), 2.97 (q, *J* = 9.3, 3.8 Hz, 1H), 2.91 (d, *J* = 9.1 Hz, 1H), 2.37 (s, 3H), 1.68 (q, *J* = 8.0, 4.2 Hz, 1H), 1.19 (t, *J* = 5.2 Hz, 1H), 1.04 (q, *J* = 8.0, 5.6 Hz, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 166.4, 164.0, 147.3, 144.0, 132.8, 129.8, 127.6, 126.5, 53.4, 52.6, 50.0, 48.8, 28.9, 27.8, 21.6, 17.6; HR-MS (ESI) calcd for $[M + H]^+$: $C_{18}H_{22}NO_6S$:

380.1162, found: 380.1151; IR (KBr): 3003, 2954, 2924, 1727, 1638, 1270, 814, cm^{-1}.

Ethyl (*Z*)-2-phenyl-3-(3-tosyl-3-azabicyclo[3.1.0]hexan-1-yl)acrylate (3-1t). The title compound was prepared from *ethyl 2-diazo-2-phenylacetate* **(1t)** (76.4 mg, 0.4 mmol) and *N-allyl-4-methyl-N-(prop-2-yn-1-yl)benzenesulfonamide* **(2a)** (99.6 mg, 0.4 mmol), and purified by column chromatography to give yellow oil (25.2 mg, 15%). R_f (petroleum ether/ethyl acetate = 5:1) 0.33; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.72 (d, *J* = 8.1 Hz, 2H), 7.41 – 7.02 (m, 7H), 5.98 (s, 1H), 4.38 – 4.10 (m, 2H), 3.72 (d, *J* = 9.2 Hz, 1H), 3.60 (d, *J* = 9.3 Hz, 1H), 3.18 (q, *J* = 9.2, 3.7 Hz, 1H), 3.10 (d, *J* = 9.2 Hz, 1H), 2.46 (s, 3H), 1.66 – 1.52 (m, 1H), 1.32 (t, *J* = 7.1 Hz, 3H), 1.01 – 0.88 (m, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 168.6, 143.6, 138.1, 136.4, 133.5, 132.1, 129.7, 128.5, 128.2, 127.6, 126.3, 61.3, 52.2, 49.7, 28.3, 25.0, 21.5, 15.5, 14.2; HR-MS (ESI) calcd for $[M + H]^+$: $C_{23}H_{25}NO_4S$: 412.1577, found: 412.1555; IR (KBr): 3003, 2926, 1729, 1552, 1494, 1165, 818 cm^{-1}.

Ethyl (*Z*)-2-(*p*-tolyl)-3-(3-tosyl-3-azabicyclo[3.1.0]hexan-1-yl)acrylate (3-1u)

The title compound was prepared from *ethyl 2-diazo-2-(p-tolyl)acetate* **(1u)** (81.6 mg, 0.4 mmol) and *N-allyl-4-methyl-N-(prop-2-yn-1-yl)benzenesulfonamide* **(2a)** (99.6 mg, 0.4 mmol), and purified by column chromatography to give white oil (9.1 mg, 5%). R_f (petroleum ether/ethyl acetate = 4:1) 0.45; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.42 (d, *J* = 7.9 Hz, 2H), 7.28 (d, *J* = 8.0 Hz, 2H), 7.15 (d, *J* = 7.7 Hz, 2H), 7.01 (d, *J* = 7.7 Hz, 2H), 6.62 (s, 1H), 4.21 – 4.08 (m, 2H), 3.44 (d, *J* = 9.2 Hz, 1H), 3.03 (d, *J* = 9.6 Hz, 1H), 2.88 (dd, *J* = 9.2, 3.7 Hz, 1H), 2.47 – 2.40 (m, 7H), 1.55 – 1.49 (m, 1H), 1.20 (t, 3H), 1.05 (t, *J* = 5.1 Hz, 1H), 0.88 (t, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 167.3, 143.6, 143.0, 137.7, 133.9, 132.5, 132.2, 129.9, 129.5, 128.6, 127.6, 61.0, 51.5, 49.0, 29.7, 29.4, 28.6, 27.1, 17.2, 14.2; HR-MS (ESI) calcd for $[M + H]^+$: $C_{24}H_{28}NO_4S$: 426.1734, found: 426.1734; IR (KBr): 3416, 2920, 1701, 1631, 1400, 1166, 750 cm^{-1}.

Ethyl (*E*)-3-oxo-2-((6-phenyl-3-tosyl-3-azabicyclo[3.1.0]hexan-1-yl)methylene)butanoate (3-2a). The title compound was prepared from *ethyl 2-diazo-3-oxobutanoate* **(1a)** (62.4 mg, 0.4 mmol) and *N-cinnamyl-4-methyl-N-(prop-2-yn-1-yl)benzenesulfonamide* **(2b)** (130.1 mg, 0.4 mmol), and purified by column chromatography to give yellow oil (22.4 mg, 12%). R_f (petroleum ether/ethyl acetate = 5:1) 0.34; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.71 (d, *J* = 7.8 Hz, 2H), 7.37 (d, *J* = 7.8 Hz, 2H), 7.26 (t, *J* = 5.1 Hz, 2H), 7.21 – 7.17 (m, 1H), 7.02 (d, *J* = 7.5 Hz, 2H), 6.44 (s, 1H), 4.11 (dd, *J* = 11.8, 6.1 Hz, 2H), 3.76 (q, *J* = 12.7, 9.9 Hz, 2H), 3.28 (q, *J* = 9.4, 3.6 Hz, 1H), 3.01 (d, *J* = 9.6 Hz, 1H), 2.56 (d, *J* = 4.6 Hz, 1H), 2.45 (s, 3H), 2.15 (t, *J* = 4.0 Hz, 1H), 2.05 (s, 3H), 1.26 (s, 1H), 1.18 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 200.5, 163.9, 143.9, 143.2, 138.1, 135.5, 133.1, 129.8, 128.5, 128.33, 127.6, 126.9, 61.3, 53.0, 49.8, 35.2, 33.2, 32.6, 30.5, 21.6, 14.0; HR-MS (ESI) calcd for $[M + H]^+$: $C_{25}H_{28}NO_4S$: 454.1642, found:454.1678; IR (KBr): 3036, 2928, 1722, 1630, 1553, 1496, 1164, 819 cm^{-1}.

Ethyl (*Z*)-3-oxo-2-((6-phenyl-3-tosyl-3-azabicyclo[3.1.0]hexan-1-yl)methylene)butanoate (3-2a). The title compound was prepared from *ethyl 2-diazo-3-oxobutanoate* **(1a)** (62.4 mg, 0.4 mmol) and *N-cinnamyl-4-methyl-N-(prop-2-yn-1-yl)benzenesulfonamide* **(2b)** (130.2 mg, 0.4 mmol), and purified by column chromatography to give yellow oil (69.3 mg, 38%). R_f (petroleum ether/ethyl acetate = 5:1) 0.33; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.61 (d, *J* = 7.8 Hz, 2H), 7.28 (d, *J* = 7.8 Hz, 2H), 7.18 (t, *J* = 7.1 Hz, 2H), 7.16 – 7.09 (m, 1H), 7.01 (d, *J* = 7.5 Hz, 2H), 6.11 (s, 1H), 4.23 – 4.02 (m, 2H), 3.76 – 3.66 (m, 2H), 3.15 (q, *J* = 9.3, 3.6 Hz, 1H), 3.06 (d, *J* = 9.3 Hz, 1H), 2.65 (d, *J* = 4.8 Hz, 1H), 2.36 (s, 3H), 2.22 (t, *J* = 4.0 Hz, 1H), 1.91 (s, 3H), 1.23 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 194.0, 166.7, 144.0, 143.2, 138.4, 135.1, 133.1, 129.9, 128.6, 128.4, 127.6, 127.1, 61.7, 51.5, 49.5, 35.1, 33.4, 32.0, 26.2, 21.6 14.1; HR-MS (ESI) calcd for $[M + H]^+$: $C_{25}H_{28}NO_4S$: 454.1642, found: 454.1678; IR (KBr): 3036, 2928, 1722, 1630, 1553, 1496, 1164, 819 cm^{-1}.

Ethyl (*Z*)-2-((6-methyl-3-tosyl-3-azabicyclo[3.1.0]hexan-1-yl)methylene)-3-oxobutanoate (3-2b). The title compound was prepared from *ethyl 2-diazo-3-oxobutanoate* **(1a)** (62.4 mg, 0.4 mmol) and *N-(but-2-en-1-yl)-4-methyl-N-(prop-2-yn-1-yl)benzenesulfonamide* (**2c)** (105.0 mg, 0.4 mmol), and purified by column chromatography to give yellow oil (25.2 mg, 16%). R_f (petroleum ether/ethyl acetate = 5:1) 0.33; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.64 (d, *J* = 8.0 Hz, 2H), 7.33 (d, *J* = 8.0 Hz, 2H), 6.65 (s, 1H), 4.37 – 4.12 (m, 2H), 3.60 (q, *J* = 9.1, 4.1 Hz, 2H), 3.04 (q, *J* = 9.2, 2.8 Hz, 1H), 2.98 (d, *J* = 9.1 Hz, 1H), 2.43 (s, 4H), 2.25 (s, 3H), 1.51 (s, 1H), 1.32 (t, *J* = 7.1 Hz, 3H), 1.13 (d, *J* = 5.8 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 193.7, 167.1, 144.0, 143.8, 138.2, 133.1, 129.7, 127.6, 61.7, 51.17, 49.3, 34.6, 32.7, 26.8, 24.3, 21.5, 14.6, 13.2; HR-MS (ESI) calcd for $[M + H]^+$: $C_{20}H_{26}NO_4S$: 392.1526, found:392.1511; IR (KBr): 3009, 2923, 1727, 1692, 1465, 1400, 1165, 817 cm^{-1}.

Ethyl (*E*)-2-((5-methyl-3-tosyl-3-azabicyclo[3.1.0]hexan-1-yl)methylene)-3-oxobutanoate (3-2c). The title compound was prepared from *ethyl 2-diazo-3-oxobutanoate* **(1a)** (62.4 mg, 0.4 mmol) and *4-methyl-N-(2-methylallyl)-N-(prop-2-yn-1-yl)benzenesulfonamide* (**2d)** (105.2 mg, 0.4 mmol), and purified by column chromatography to give yellow oil (42.1 mg, 27%). R_f (petroleum ether/ethyl acetate = 5:1) 0.35; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.59 (d, *J* = 7.5 Hz, 2H), 7.27 (d, *J* = 7.7 Hz, 2H), 6.45 (s, 1H), 4.14 (q, *J* = 7.1 Hz, 2H), 3.48 (q, *J* = 18.8, 9.3 Hz, 2H), 2.80 – 2.69 (m, 2H), 2.35 (s, 3H), 2.30 (s, 3H), 1.24 – 1.15 (m, 4H), 1.11 (s, 3H), 0.78 (d, J = 5.2 Hz, 1H); ^{13}C NMR (101 MHz, CDCl3) δ 193.6, δ 167.3, 143.9, 143.5, 137.3, 132.9, 129.8, 127.6, 61.8, 54.1, 51.2, 33.6, 31.8, 26.7, 23.5, 21.6, 15.3, 14.1; HR-MS (ESI) calcd for $[M + H]^+$: $C_{20}H_{26}NO_4S$: 392.1526, found: 392.1517; IR (KBr): 3009, 2927, 1727, 1666, 1599, 1444, 1165, 814 cm^{-1}.

Ethyl (*Z*)-2-((5-methyl-3-tosyl-3-azabicyclo[3.1.0]hexan-1-yl)methylene)-3-oxobutanoate (3-2c). The title compound was prepared from *ethyl 2-diazo-3-oxobutanoate* **(1a)** (62.4 mg, 0.4 mmol) and *4-methyl-N-(2-methylallyl)-N-(prop-2-yn-1-yl)benzenesulfonamide* **(2d)** (105.2 mg, 0.4 mmol), and purified by column chromatography to give yellow oil (56 mg, 36%). R_f (petroleum ether/ethyl acetate = 5:1) 0.33; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.58 (d, *J* = 8.1 Hz, 2H), 7.27 (d, *J* = 8.0 Hz, 2H), 6.42 (s, 1H), 4.22 (q, *J* = 7.2 Hz, 2H), 3.54 (t, *J* = 9.3 Hz, 2H), 2.94 (d, *J* = 9.2 Hz, 1H), 2.76 (d, *J* = 9.3 Hz, 1H), 2.37 (s, 3H), 2.17 (s, 3H), 1.29 (t, *J* = 7.1 Hz, 3H), 1.19 (t, *J* = 4.8 Hz, 1H), 1.13 (s, 3H), 0.84 (d, *J* = 5.4 Hz, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 193.5, 167.3, 143.9, 143.5, 137.3, 133.1, 129.8, 127.6, 61.8, 54.1, 51.2, 33.6, 31.8, 26.7, 23.4, 21.5, 15.3, 14.1; HR-MS (ESI) calcd for $[M + H]^+$:

$C_{20}H_{26}NO_4S$: 392.1526, found: 392.1517; IR (KBr): 3009, 2927, 1727, 1666, 1599, 1444, 1165, 814 cm^{-1}.

Ethyl (*E*)-3-oxo-1-tosyloctahydro-2aH-cyclopropa[cd]indol-2a-yl)meth- ylene) butanoate (3-2d). The title compound was prepared from *ethyl 2-diazo-3-oxobutanoate* **(1a)** (62.4 mg, 0.4 mmol) and *N-(cyclohex-2-en-1-yl)-4-methyl-N-(prop-2-yn-1-yl)benzenesulfonamide* **(2e)** (116.3 mg, 0.4 mmol), and purified by column chromatography to give yellow oil (57.4 mg, 34%). R_f (petroleum ether/ethyl acetate = 5:1) 0.34; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.70 (d, *J* = 8.2 Hz, 2H), 7.32 (d, *J* = 8.1 Hz, 2H), 6.34 (s, 1H), 4.32 (q, *J* = 6.3, 2.9 Hz, 1H), 4.22 (q, *J* = 7.1 Hz, 2H), 3.50 (d, *J* = 11.5 Hz, 1H), 3.42 (d, *J* = 11.5 Hz, 1H), 2.44 (s, 3H), 2.37 (s, 3H), 2.04 – 1.84 (m, 4H), 1.41 – 1.34 (m, 4H), 1.29 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 201.3, 164.4, 149.5, 143.5, 135.7, 134.6, 129.7, 127.2, 61.3, 55.9, 51.5, 34.4, 32.9, 31.3, 26.9, 25.5, 21.5, 16.7, 15.5, 14.1; HR-MS (ESI) calcd for $[M + H]^+$: $C_{22}H_{27}NO_5S$: 418.1683, found: 418.1670; IR (KBr): 3009, 2925, 1724, 1655, 1631, 1400, 1159, 818 cm^{-1}.

Ethyl (*Z*)-3-oxo-1-tosyloctahydro-2aH-cyclopropa[cd]indol-2a-yl)meth- ylene) butanoate (3-2d). The title compound was prepared from *ethyl 2-diazo-3-oxobutanoate* **(1a)** (62.4 mg, 0.4 mmol) and *N-(cyclohex-2-en-1-yl)-4-methyl-N-(prop-2-yn-1-yl)benzenesulfonamide* **(2e)** (116.3 mg, 0.4 mmol), and purified by column chromatography to give yellow oil (85.4 mg, 51%). R_f (petroleum ether/ethyl acetate = 5:1) 0.33; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.68 (d, *J* = 8.2 Hz, 2H), 7.30 (d, *J* = 8.1 Hz, 2H), 6.21 (s, 1H), 4.37 – 4.29 (m, 2H), 4.26 (q, *J* = 6.2, 2.9 Hz, 1H), 3.60 (q, *J* = 28.2, 11.8 Hz, 2H), 2.43 (s, 3H), 2.21 (s, 3H), 2.06 – 1.91 (m, 4H), 1.47 – 1.34 (m, 7H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 193.9, 167.1, 149.0, 143.6, 135.4, 135.2, 129.8, 127.3, 61.8, 55.7, 50.8, 34.9, 33.3, 27.1, 26.9, 25.9, 21.5, 16.9, 15.6, 14.1; HR-MS (ESI) calcd for $[M + H]^+$: $C_{22}H_{27}NO_5S$: 418.1683, found: 418.1670; IR (KBr): 3009, 2925, 1724, 1655, 1631, 1400, 1159, 818 cm^{-1}.

Ethyl (*E*)-3-oxo-2-((3-tosyl-3-azabicyclo[4.1.0]heptan-5-yl)methylene)butanoate (3-2e). The title compound was prepared from *ethyl 2-diazo-3-oxobutanoate* **(1a)** (62.4 mg, 0.4 mmol) and *N-(but-3-en-1-yl)-4-methyl-N-(prop-2-yn-1-yl)benzenesulfonamide* **(2f)** (105.2 mg, 0.4 mmol), and purified by column chromatography to give yellow oil (41.1 mg, 26%). R_f (petroleum ether/ethyl acetate = 5:1) 0.34; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.53 (d, *J* = 8.2 Hz, 2H), 7.26 (d, *J* = 8.0 Hz, 2H), 6.53 (s, 1H), 4.14 (q, *J* = 7.1 Hz, 2H), 3.61 (d, *J* = 11.4 Hz, 1H), 3.25 (m, *J* = 10.4, 6.7, 3.3 Hz, 1H), 2.67 (d, *J* = 11.4 Hz, 1H), 2.36 (s, 4H), 2.29 (s, 2H), 2.28 – 2.27 (m, 1H), 1.95 (m, 1H), 1.87 – 1.79 (m, 1H), 1.21 (t, *J* = 7.1 Hz, 3H), 1.14 – 1.09 (m, 1H), 0.99 (q, *J* = 9.3, 4.2 Hz, 1H), 0.90 – 0.86 (m, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 201.7, 164.4, 149.0, 143.7, 135.5, 133.4, 129.7, 127.5, 61.4, 47.8, 42.7, 31.5, 22.9, 21.5, 21.5, 20.0, 18.9, 14.1; HR-MS (ESI) calcd for $[M + H]^+$: $C_{20}H_{26}NO_5S$: 392.1526, found: 392.1519; IR (KBr): 3009, 2925, 1724, 1655, 1631, 1400, 1166, 818 cm^{-1}.

Ethyl (*Z*)-3-oxo-2-((3-tosyl-3-azabicyclo[4.1.0]heptan-5-yl)methylene)butanoate (3-2e). The title compound was prepared according to general procedure A from *ethyl 2-diazo-3-oxobutanoate* **(1a)** (62.4 mg, 0.4 mmol) and *N-(but-3-en-1-yl)-4-methyl-N-(prop-2-yn-1-yl)benzenesulfonamide* **(2f)** (105.2 mg, 0.4 mmol), and purified by column chromatography to give yellow oil (91.2 mg, 58%). R_f (petroleum ether/ethyl acetate = 5:1) 0.33; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.61 (d, *J* = 8.0 Hz, 2H), 7.33 (d, *J* = 8.0 Hz, 2H), 6.53 (s, 1H), 4.33 – 4.19 (m, 2H), 3.75 (q, *J* = 52.4, 11.3 Hz, 1H), 3.40 (q, *J* = 24.3, 16.0 Hz, 1H), 2.76 (q, *J* = 29.8, 11.3 Hz, 1H), 2.44 (s, 3H), 2.36 – 2.21 (m, 4H), 2.10 – 1.88 (m, 2H), 1.31 (m, 4H), 1.14 – 1.00 (m, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 194.4, 167.1, 148.4, 143.7, 136.7, 133.7, 129.8, 127.5, 61.7, 46.7, 42.8, 26.5, 22.9, 21.8, 21.5, 19.4, 18.8, 14.0; HR-MS (ESI) calcd for $[M + H]^+$: $C_{20}H_{26}NO_5S$: 392.1526, found: 392.1519; IR (KBr): 3009, 2925, 1724, 1655, 1631, 1400, 1166, 818 cm^{-1}.

Ethyl (*E*)-3-oxo-2-((3-tosyl-3-azabicyclo[4.1.0]heptan-6-yl)methylene)butanoate (3-2f). The title compound was prepared from *ethyl 2-diazo-3-oxobutanoate* **(1a)** (62.4 mg, 0.4 mmol) and enyne **2g** (105.2 mg, 0.4 mmol), and purified by column chromatography to give yellow oil (33.3 mg, 21%). R_f (petroleum ether/ethyl acetate = 5:1) 0.34; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.61 (d, J = 8.3 Hz, 2H), 7.32 (d, J = 8.0 Hz, 2H), 6.58 (s, 1H), 4.21 (q, *J* = 7.1 Hz, 2H), 3.54 (d, *J* = 11.7 Hz, 1H), 3.12 (m, 2H), 2.61 (m, 1H), 2.43 (s, 3H), 2.37 (s, 3H), 1.99 (m, 1H), 1.89 (m, 1H), 1.30 – 1.24 (m, 4H), 0.98 – 0.93 (m, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 201.9, 164.6, 152.0, 143.6, 134.5, 133.7, 129.8, 127.5, 61.3, 44.0, 42.3, 31.6, 27.9, 21.8, 21.5, 19.3, 18.7, 14.1; HR-MS (ESI) calcd for $[M + H]^+$: $C_{20}H_{26}NO_5S$: 392.1526, found: 392.1509; IR (KBr): 3009, 2924, 1727, 1655, 1631, 1400, 1164, 818 cm^{-1}.

Ethyl (*Z*)-3-oxo-2-((3-tosyl-3-azabicyclo[4.1.0]heptan-6-yl)methylene)butanoate (3-2f). The title compound was prepared from *ethyl 2-diazo-3-oxobutanoate* **(1a)** (62.4 mg, 0.4 mmol) and *N-allyl-N-(but-3-yn-1-yl)-4-methylbenzenesulfonamide* **(2g)** (105.2 mg, 0.4 mmol), and purified by column chromatography to give yellow oil (47.1 mg, 30%). R_f (petroleum ether/ethyl acetate = 5:1) 0.33; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.61 (d, *J* = 8.3 Hz, 2H), 7.32 (d, J = 8.0 Hz, 2H), 6.58 (s, 1H), 4.21 (q, *J* = 7.1 Hz, 2H), 3.54 (d, *J* = 11.7 Hz, 1H), 3.12 (m, 2H), 2.61 (m, 1H), 2.43 (s, 3H), 2.37 (s, 3H), 1.99 (m, 1H), 1.89 (m, 1H), 1.30 – 1.24 (m, 4H), 0.98 – 0.93 (m, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 194.5, 167.3, 151.1, 143.7, 135.8, 133.6, 129.7, 127.6, 61.6, 44.1, 42.4, 27.3, 26.5, 21.5, 21.5, 19.2, 19.0, 14.0; HR-MS (ESI) calcd for $[M + H]^+$: $C_{20}H_{26}NO_5S$: 392.1526, found: 392.1509; IR (KBr): 3009, 2924, 1727, 1655, 1631, 1400, 1164, 818 cm^{-1}.

Dimethyl (*E*)-1-(2-(ethoxycarbonyl)-3-oxobut-1-en-1-yl)bicyclo[3.1.0]hexane-3,3-dicarboxylate (3-2g). The title compound was prepared from *ethyl 2-diazo-3-oxobutanoate* **(1a)** (62.4 mg, 0.4 mmol) and *diethyl 2-allyl-2-(prop-2-yn-1-yl)malonate* **(2h)** (84.3 mg, 0.4 mmol), and purified by column chromatography to give yellow oil (28.1 mg, 21%). R_f (petroleum ether/ethyl acetate = 5:1) 0.34; ^{1}H NMR (400 MHz, CDCl3) δ 6.53 (d, *J* = 18.5 Hz, 1H), 4.42 – 4.19 (m, 2H), 3.73 (d, *J* = 2.8 Hz, 3H), 3.70 (s, 3H), 2.76 – 2.26 (m, 7H), 1.72 (dd, *J* = 8.5, 4.9 Hz, 1H), 1.41 – 1.28 (m, 3H), 1.05 – 0.96 (m, 1H), 0.87 – 0.78 (m, 1H); ^{13}C NMR (101 MHz, CDCl3) δ 194.1, 172.7, 171.4, 167.8, 149.6, 134.9, 61.6, 59.5, 53.1, 36.9, 35.0, 30.7, 30.1, 26.4, 20.0, 14.0; HR-MS (ESI) calcd for $[M + H]^+$: $C_{17}H_{23}O_7$: 339.1366, found: 339.1367; IR (KBr): 3009, 2924, 1727, 1655, 1630, 1400, 1164, 818 cm^{-1}.

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Dimethyl (*Z*)-1-(2-(ethoxycarbonyl)-3-oxobut-1-en-1-yl)bicyclo[3.1.0]hexane-3,3-dicarboxylate (3-2g). The title compound was prepared from *ethyl 2-diazo-3-oxobutanoate* **(1a)** (62.4 mg, 0.4 mmol) and *diethyl 2-allyl-2-(prop-2-yn-1-yl)malonate* **(2h)** (84.2 mg, 0.4 mmol), and purified by column chromatography to give yellow oil (31.1 mg, 23%). R_f (petroleum ether/ethyl acetate = 5:1) 0.33; ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.51 (s, 1H), 4.43 – 4.28 (m, 2H), 3.73 (s, 3H), 3.69 (s, 3H), 2.63 (m, *J* = 18.0, 14.7, 7.3 Hz, 3H), 2.54 – 2.45 (m, 1H), 2.26 (s, 3H), 1.78 – 1.71 (m, 1H), 1.38 (t, *J* = 7.2 Hz, 3H), 1.03 (t, 1H), 0.86 (t, *J* = 5.7 Hz, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 194.1, 172.7, 171.4, 167.8, 149.6, 134.9, 61.6, 59.4, 53.6, 53.1, 36.8, 35.0, 30.7, 30.1, 26.4, 20.0, 14.0; HR-MS (ESI) calcd for $[M + H]^+$: $C_{17}H_{23}O_7$ 339.1438, found: 339.1434; IR (KBr): 3009, 2924, 1727, 1655, 1630, 1400, 1164, 818 cm^{-1}.

Ethyl (*E*)-3-oxo-2-((4-oxo-3-tosyl-3-azabicyclo[3.1.0]hexan-1-yl)methylene)butanoate (3-2h)

The title compound was prepared from *ethyl 2-diazo-3-oxobutanoate* **(1a)** (62.4 mg, 0.4 mmol) and *N-(prop-2-yn-1-yl)-N-tosylacrylamide* **(2i)** (105.2 mg, 0.4 mmol), and purified by column chromatography to give white solid (21.9 mg, 14%) m.p. 133.0-140 °C. R_f (petroleum ether/ethyl acetate = 5:1) 0.33; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.89 (d, *J* = 7.9 Hz, 2H), 7.35 (d, *J* = 7.8 Hz, 2H), 6.57 (s, 1H), 4.25 (q, *J* = 7.1 Hz, 2H), 4.03 (d, *J* = 10.5 Hz, 1H), 3.66 (d, *J* = 10.5 Hz, 1H), 2.45 (s, 3H), 2.42 (s, 3H), 2.10 (d, *J* = 6.2 Hz, 1H), 1.53 – 1.45 (m, 1H), 1.30 (t, *J* = 7.2 Hz, 4H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 200.4, 170.5, 163.8, 145.5, 143.02, 137.9, 134.7, 129.8, 128.1, 61.9, 51.1, 31.1, 30.5, 24.3, 21.7, 19.9, 14.1; HR-MS (ESI) calcd for $[M + H]^+$: $C_{19}H_{22}NO_6S$: 392.1162, found: 392.1169; IR (KBr): 2976, 1726, 1595, 1450, 1366, 1152, 818, 740 cm^{-1}.

Ethyl (*Z*)-3-oxo-2-((4-oxo-3-tosyl-3-azabicyclo[3.1.0]hexan-1-yl)methylene)butanoate (3-2h) The title compound was prepared from *ethyl 2-diazo-3-oxobutanoate* **(1a)** (62.4 mg, 0.4 mmol) and *N-(prop-2-yn-1-yl)-N-tosylacrylamide* **(2i)** (105.2 mg, 0.4 mmol), and purified by column chromatography to give white solid (36.1 mg, 23%) m.p. 133.0-140 °C. R_f (petroleum ether/ethyl acetate = 5:1) 0.30; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.90 (d, *J* = 8.1 Hz, 2H), 7.36 (d, *J* = 7.8 Hz, 2H), 6.55 (s, 1H), 4.33 – 4.25 (m, 2H), 4.09 (d, *J* = 10.2 Hz, 1H), 3.81 (d, *J* = 10.2 Hz, 1H), 2.46 (s, 3H), 2.30 (s, 3H), 2.15 (d, *J* = 8.6 Hz, 1H), 1.61 – 1.56 (m, 1H), 1.35 (t, *J* = 7.0 Hz, 4H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 193.7, 170.4, 166.2, 145.5, 141.7, 138.3, 134.6, 129.8, 128.1, 62.2, 50.5, 30.2, 27.1, 24.4, 21.7, 19.9, 14.1; HR-MS (ESI) calcd for $[M + H]^+$: $C_{19}H_{22}NO_6S$: 392.1162, found: 392.1169; IR (KBr): 2976, 1726, 1595, 1450, 1366, 1152, 818, 740 cm^{-1}.

Ethyl 6-phenyl-2-tosylisoindoline-5-carboxylate (3-2i). The title compound was prepared from *ethyl 2-diazo-3-oxobutanoate* **(1a)** (62.4 mg, 0.4 mmol) and *4-methyl-N,N-di(prop-2-yn-1-yl)benzenesulfonamide* **(2j)** (99.1 mg, 0.4 mmol), and purified by column chromatography to give yellow solid (42.0 mg, 25%) m.p. 136.0-142 °C. R_f (petroleum ether/ethyl acetate = 5:1) 0.33; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.71 (d, *J* = 8.2 Hz, 2H), 7.55 (s, 1H), 7.31 – 7.23 (m, 5H), 7.15 (dd, *J* = 7.4, 1.9 Hz, 2H), 7.09 (s, 1H), 4.60 (s, 4H), 3.96 (q, *J* = 7.1 Hz, 2H), 2.34 (s, 3H), 0.87 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 168.3, 143.9, 142.6, 141.0, 139.4, 135.3, 133.6, 131.3, 129.9, 128.3, 128.1, 127.6, 127.4, 124.8, 124.0, 61.1, 53.7, 53.4, 21.5, 13.6; HR-MS (ESI) calcd for $[M + H]^+$: $C_{24}H_{24}NO_4S$: 422.1421, found: 422.1406; IR (KBr): 2919, 1727, 1633, 1549, 1400, 1169, 818, 750 cm^{-1}.

Mechanism studies of this transformation

Coupling-cyclization of 1a with *d*1-2a

*d*1-**2a** was produced according to previous literature.[31] *d*1-**2a** : ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.73 (d, *J* = 8.3 Hz, 2H), 7.29 (d, *J* = 8.1 Hz, 2H), 5.73 (m, 1H), 4.09 (s, 2H), 3.83 (d, *J* = 6.5 Hz, 2H), 2.42 (s, 3H).

A Schlenk tube (20 mL) with a stirring bar was loaded with the **1a** (62.4 mg, 0.4 mmol), *d1*-**2a** (100.4 mg, 0.4 mmol), $[Rh(COD)Cl]_2$ (9.9 mg, 5 mol %), dppp (16.5 mg, 10 mol %) and dry toluene (2.0 mL) under an Ar atmosphere (1 atm). The reaction mixture was then allowed to stir at 100 ℃ for 12 h. After cooling to room temperature, the compound was purified by column chromatography using petroleum ether/AcOEt (10:1) as eluent to give the product *d*1-**3-1a** (*E*/*Z* = 31/44, 75 % overall yield).

Coupling-cyclization of 1a with *d*2-2a

*d*2-**2a** was produced according to previous literature.[32] *d*2-**2a**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.76 (d, *J* = 8.2 Hz, 2H), 7.32 (d, *J* = 8.1 Hz, 2H), 5.75 (m, 1H), 5.35 – 5.22 (m, 1H), 4.11 (d, *J* = 2.3 Hz, 2H), 3.85 (d, *J* = 6.4 Hz, 2H), 2.45 (s, 3H), 2.03 (t, *J* = 2.3 Hz, 1H).

A Schlenk tube (20 mL) with a stirring bar was loaded with the **1a** (62.4 mg, 0.4 mmol), *d*2-**2a** (100.4 mg, 0.4 mmol), $[Rh(COD)Cl]_2$ (9.9 mg, 5 mol %), dppp (16.5 mg, 10 mol %) and dry toluene (2.0 mL) under an Ar atmosphere (1 atm). The reaction mixture was then allowed to stir at 100 ℃ for 12 h. After cooling to room temperature, the compound was purified by column chromatography using petroleum ether/AcOEt (10:1) as eluent to give the product *d*2-**3a** (*E*/*Z* = 29/51, overall yield: 80 %).

Synthetic applications

A Schlenk tube (20 mL) with a stirring bar was loaded with the (*Z*)-**3-1a** (151.1 mg, 0.4 mmol), $CeCl_3$•$7H_2O$ (149.0 mg, 0.4 mmol), and MeOH (2ml). Then $NaBH_4$ (15.1 mg, 0.4 mmol) was added during 30 min and the reaction mixture was allowed to stir at room temperature for 12 h. After cooling to room temperature, the mixture is extracted with AcOEt (3×10 ml) and the organic layers are dried with Na_2SO_4 and evaporated under reduced pressure. The residue was purified by column chromatography using petroleum ether /AcOEt = 2:1 (R_f = 0.3) as eluent to give the product (*Z*)-**4** (67.4 mg, 44%).

Ethyl(*Z*)-3-hydroxy-2-((3-tosyl-3-azabicyclo[3.1.0] hexan-1-yl)methylene)butanoate (*Z*)-4. Yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.59 (d, *J* = 7.6 Hz, 2H), 7.26 (d, *J* = 7.6 Hz, 2H), 5.78 (s, 1H), 4.46 – 4.23 (m, 1H), 4.22 – 3.96 (m, 2H), 3.58 (d, *J* = 9.2 Hz, 1H), 3.46 (d, *J* = 9.2 Hz, 1H), 3.06 (d, *J* = 8.7 Hz, 1H), 2.90 (d, *J* = 9.2 Hz, 1H), 2.36 (s, 3H), 1.37 (s, 1H), 1.21 (t, *J* = 6.5 Hz, 6H), 0.85 (s, 1H), 0.74 (s, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 167.8, 143.6, 139.6, 133.8, 133.7, 133.6, 133.5, 129.7, 127.5, 69.4, 69.2, 61.0, 52.3, 49.6, 27.5, 27.5, 25.2, 22.3, 21.5, 15.7, 15.7, 14.2; HR-MS (ESI) calcd for $[M + H]^+$: $C_{19}H_{25}NO_5S$: 380.1526, found: 380.1530; IR (KBr): 3026, 2982, 1725, 1698, 1633, 1456, 1165, 818 cm^{-1}.

A Schlenk tube (20 mL) with a stirring bar was loaded with the (*Z*)-**3-1a** (151.1 mg, 0.4 mmol), HBr aqueous (w_t% = 40 %, 81.0 mg, 0.4mmol) and MeOH (2.0 mL). Then the reaction mixture was allowed to stir at room temperature for 24 h. After cooling to room temperature, the mixture is extracted with CH_2Cl_2 (3×10 ml) and the

organic layers are dried with Na_2SO_4 and evaporated under reduced pressure. The residue was purified by column chromatography using cyclohexane/acetone (5:1) as eluent to give the product **(*Z*)-5** (96.1 mg, 61%).

Ethyl (*Z*)-2-((5-hydroxy-1-tosylpiperidin-3-yl)methylene)-3-oxobutanoate (*Z*)-**5**: Yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 13.00 (s, 1H), 7.66 (d, *J* = 8.1 Hz, 2H), 7.35 (d, *J* = 7.9 Hz, 2H), 5.88 (s, 1H), 4.22 (dd, *J* = 7.1, 3.7 Hz, 2H), 4.12 (dd, *J* = 9.1, 4.8 Hz, 1H), 3.89 (t, *J* = 10.4 Hz, 2H), 3.01 (d, *J* = 12.7 Hz, 1H), 2.90 (dd, *J* = 18.0, 8.5 Hz, 2H), 2.63 – 2.40 (m, 5H), 2.01 (s, 3H), 1.29 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 174.5, 171.9, 144.0, 133.0, 132.1, 129.8, 127.7, 121.7, 97.3, 60.8, 53.3, 47.0, 44.7, 44.0, 21.6, 19.9, 14.3; HR-MS (ESI) calcd for $[M + H]^+$: $C_{19}H_{25}NO_5S$: 396.1480, found: 396.0096; IR (KBr): 3336, 3022, 2980, 1725, 1698, 1633, 1456, 1165, 816 cm^{-1}.

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Table of Content

A Rh(I)-catalyzed coupling-cyclization of enynes with diazo compounds has been developed to assemble versatile vinyl-substituted azabicyclo[3.1.0]hexanes.