Desaturation via Redox-Neutral Hydrogen Transfer Process: Synthesis of 2-Allyl Anilines, Mechanism and Applications

HIGHLIGHTS

- Highly site and regioselective synthesis enabled by ancillary group
- Desaturation via redox-neutral inert hydrogen transfer process
- Missing link in the synthesis of 2-allyl anilines with broad substrate scope
- Methodology development and diversity synthesis based on 2-allyl anilines

Enhanced scope

Versatile transformations

Bioactive compound synthesis

inhibitor of myeloid cell leukemia-1

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Desaturation via Redox-Neutral Hydrogen Transfer Process: Synthesis of 2-Allyl Anilines, Mechanism and Applications

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SUMMARY
An unprecedented desaturation method via redox-neutral hydrogen transfer process has been disclosed under mild conditions for the selective formation of terminal alkene with alkyl diazo compounds and aza-o-QMs. The control experiments and DFT calculations suggest that the visible light was introduced as a key parameter to enhance the reactivity via a radical process in the formation of closed-shell cyclopropane intermediate, followed by a ring opening and redox-neutral hydrogen transfer process to give the desaturated product. The high regioselectivity in this transformation is enabled by the internal amino species as an ancillary group (AG) in the final olefin formation step. This method provides a missing link in the expeditious preparation of synthetically useful 2-allyl anilines with broad substrate generality. Further applications of these generated products in N-heterocycle construction, including 5- and 6-membered rings with structural diversity, have been tactfully explored, which highlight the potential in methodology development and drug discovery.

INTRODUCTION
Alkene is one of the common and key chemical stocks, which is prevalent in natural (Moosophon et al., 2009; Rukachaisirikul et al., 2012) and synthetic molecules (Kolb et al., 1994; Singh et al., 2012; Poplata et al., 2016) with a wide spectrum of applications. Its practical and selective synthesis has drawn broad attentions in synthetic chemistry (Negishi et al., 2008). In this context, carbonyl olefination, alkene metathesis, and coupling reactions constitute the most general and widely used methods for the selective construction of C=C bonds (Blakemore, 2002; Seechurn et al., 2012). Mechanistically, in the formation of alkynes via reactive intermediates, such as metal carbenes (Doyle et al., 1998; Zheng et al., 2015), organometal species (Bras and Muzart, 2011; Barluengoa et al., 2007; Barluengoa and Valdés, 2011; Xia et al., 2017), and cationic and radical intermediates (Mohring, 2013), the β-H elimination step is regarded as the key process for the selectivity control (Figure 1A) (Seechurn et al., 2012). However, selective β-H elimination for the generation of terminal alkenes is still a great challenge in this content. Arguably, the formation of internal alkenes is usually favored via these conventional intermediates (see Note S1 for extended bibliography).

Recently, methods for the site-controlled desaturation via activating the inert C(sp3)-H bonds with the assistance of the embedded directing group (DG) or the tethered radical initiator (RI) have achieved great breakthrough (Figure 1B) (Cekovic et al., 1979; Bigi et al., 2011; Voica et al., 2012; Chen and Baran, 2009; Chuentragool et al., 2018; Parasram et al., 2017; Chen and Dong, 2019; Cheng et al., 2018a, 2018b). Representative advances have been reported by Cekovic (Cekovic et al., 1979), White (Bigi et al., 2011), Baran (Voica et al., 2012; Chen and Baran, 2009), Gevorgyan (Chuentragool et al., 2018; Parasram et al., 2017), and others (Chen and Dong, 2019; Cheng et al., 2018a, 2018b). Nevertheless, the selectivity control in the following β-H elimination step is still a big challenge in some cases, although the initial radical intermediate formation step has been enabled selectively. Inspired by these advances, we reasoned that, if the intermediate could be temporarily stabilized before the H-elimination, thus, by avoiding the general β-H-elimination process, an alternative pathway, a delayed and selective β’-H elimination, might be enabled to form the terminal alkenes with the assistance of a neighboring functional group (or named as ancillary group, AG) (Figure 1C).
As a continuation of our interest in the transformations of diazo compounds (Kang et al., 2019; Zeng et al., 2019; Zhang et al., 2019a), we envisioned that intermediate A (Figure 1D in dashed box), which is formed via the electrophilic addition of diazo compound to aza-o-QM (Lee et al., 2014; Yang et al., 2012; Wang et al., 2016; Yang and Gao, 2018), is relatively stable and herein could act as a proper candidate for delaying the followed H-elimination based on previous observations (Ma et al., 2016; Dong et al., 2016; Zheng et al., 2017). In this protocol, the amino group was designed as the AG for the selective desaturation (Figure 1D in black box). At the stage, challenges are initially evaluated (Figure 1D in black box): (1) side reactions could take place from the in situ generated alkyl diazocompounds and the aza-o-QMs individually or in combination, which would disturb the formation of the intermediate A; (2) the formation of energetically favorable internal alkene; (3) the AG acts as the nucleophile, thus leading to the 5-membered N-hetero-cycle via intramolecular addition.

**RESULTS AND DISCUSSION**

We began our investigation by using hydrazone 2a and N-(ortho-chloromethyl)arylamide 3a as the model substrates. After the reaction mixture was stirred under natural light at 0°C to room temperature (rt) in 1,2-dichloromethane (DCE) for 10 h, all 2a and 3a were consumed. To our delight, the desired product 4a was isolated in 43% yield together with the annulation product 13 in 15% yield (Table 1, entry 1). To indentify the internal alkene 4a, the crude reaction mixture was submitted to the proton NMR analysis and only trace of the internal alkene was observed (terminal:internal >20:1, see Figure S110). Besides, other observed side products may come from the decomposition of diazocompound 1a and the dimerization of 3a via N-alkylation reaction (Zhan et al., 2015). Then the reaction was conducted in the dark to decrease the decomposition of 1a. However, the 2-allyl aniline 4a was only yielded in 35% (entry 2), which indicates that the light might have a positive effect on this reaction, and the annulation product 13 was isolated in 18% yield. To verify the assumption, compact fluorescent light (CFL) was introduced, and the yield of 4a was improved to 59%. Meanwhile, the yield of annulation product 13 was 13%, which is not significantly different under natural light or in the dark (entries 1 to 3). After that, we tried to reduce the reaction’s temperature (from −20°C or −40°C to rt) to avoid the side reactions of 3a (entries 4 to 5). Much to our delight, the by-product 13 was inhibited obviously (i.e., 8% yield in entry 4, and <5% yield in entries 5–8), and the best results have been obtained in terms of yield when the reaction was conducted under CFL at −40°C to rt (entry 5, 80% yield, see also Method A in SI). Investigation of different inorganic bases could not enhance the yields (entries 6 and 7). To simplify the operation, we also conducted a one-pot method, using iodosobenzene as the oxidant instead of manganese dioxide, and the desired product 4a could be isolated in 66% yield (entry 8, see also Method B in SI).

**Figure 1. Strategies for the Desaturation**

(A) General approaches to alkenes via β-H elimination/shift.
(B) Site-controlled desaturation.
(C) Our proposal: ancillary group (AG)-assisted desaturation via novel and relative stable intermediate.
(D) This work: formation of terminal alkenes via selective hydrogen transfer with the assistance of AG.
With the optimized reaction conditions in hand (see also Method A in SI), we turned our attention to exploration of the scope of applicable hydrazones, and the results have been listed in Scheme 1. Hydrazones containing both electron-donating and electron-withdrawing groups on the aryl ring gave the desired products in high yields (4a-4i). Notably, the iodide substituent is tolerated well, which usually would not survive in the transition-metal-catalyzed transformations, generating the desired product 4g in 76% yield.

Moreover, both the alkynyl and alkenyl hydrazones are tolerated under current reaction conditions and produced the terminal-alkene products in >80% yield (4j and 4k). The 2-naphthyl and 2-thienyl hydrazones worked well, leading to the corresponding products 4l and 4m in 76% and 78% yields, respectively. The desaturated products 4n and 4o were generated smoothly in 83% and 78% yields from ethyl and cyclic hydrazones, and two isomers were detected in the case with 4n (see Figures S11 and 112). Furthermore, the representative examples of L-menthol, 1,2,3,4-diacetone galactose, and cholesterol derivatives (4p-4r) smoothly delivered the corresponding products in good yield, which highlighted the applicability of this method for the late-stage modification of complex molecules. In addition, the reaction performed well on a gram scale (5.0 mmol) with synthetic useful yields (note c, 60% yield). We also demonstrated the results with the fungible one-pot method in a few examples. Generally, the reactions went smoothly albeit in slightly lower yields compared with the optimal method (note b, see also Method B in SI). The structure of product 4f was confirmed by X-ray analysis (see Table S1).
Subsequently, a series of \(N\)-(ortho-chloromethyl) aryl amides were explored. Arylamides with substituent at the benzylic position, including methyl and phenyl groups, underwent the transformation smoothly to give the corresponding products in high yields (\(5a\) and \(5b\)). Good tolerance for both electron-donating and electron-withdrawing groups on the different position of phenyl ring of \(3\) was observed, and the desired products were afforded in 76%–84% yields (\(5c\)–\(5i\)). Substituents on the sulfonyl part had little impact on the reaction, and corresponding products were isolated in high yields (\(5j\) and \(5k\)). In addition, substrate with \(N\)-CO\(_2\)Bn group instead of \(N\)-Ts was examined, and the reaction proceeded smoothly to give \(5l\) in 65% yield. Moreover, the azadiene was also tolerated well in the transformation in the absence of base.

Scheme 1. Reaction Scope

\(^*\)Reaction conditions: \(2\) (0.45 mmol), MnO\(_2\) (8.0 equiv. based on \(2\)), MgSO\(_4\) (60.0 mg), and DCE (3.0 mL) was pre-stirred for 45 min, then the reaction mixture was filtered and the filtrate was injected to the oven-dried tube containing a magnetic stirring bar, \(3\) (0.15 mmol), and Cs\(_2\)CO\(_3\) (2.0 equiv.) at \(-40^\circ\)C under argon atmosphere. Then the reaction mixture was stirred under these conditions with the irradiation of visible light (8 W CFL) for 10 h, and the reaction temperature warmed up to rt slowly in this period of time. Yields are given in isolated yields.

\(^b\)Reaction conditions: conditions in Table 1, entry 8 was used. \(2\) (0.30 mmol), PhIO (0.30 mmol), \(3\) (0.15 mmol), Na\(_2\)CO\(_3\) (0.30 mmol), and 4A˚ MS (50 mg) in DCE (2.0 mL). Yields are given in isolated yields.

\(^c\)The reaction was conducted on a 5.0 mmol scale.

\(^d\)The reaction was conducted in the absence of base.
of the base, affording the product 5m in 67% yield. Notably, the by-products (internal alkenes or annulation product) were not detected in all above cases.

Encouraged by the above results, we further explored this formal coupling reaction with carbonyl diazo compounds 6, which are readily available and stable, as the starting materials in the absence of oxidant (Scheme 2, see also Method C in SI). Herein, minor optimization with Na2CO3 as the base rather than Cs2CO3 was applied in the absence of visible light (8 W CFL), and no obvious difference was observed when the reactions were conducted under the visible light or dark. A variety of diazoamides were first investigated, and both electron-donating and electron-withdrawing groups on the aryl ring of 6 generally gave the desired 2-allyl aniline products 7a–7d in good yields (76%–84%). The sterically hindered ortho-methyl-substituted substrate 6e afforded the product 7e in moderate yield. The N-benzyl-protected diazoamide (6f) performed well and gave 7f in 69% yield.

In addition, the α-methyl diazoacetates and diazophosphonate were also tolerated under these conditions, and the corresponding alkenes were isolated in moderate to high yields (7g–7j).

Next, we turned our attention to other types of diazo compounds that do not have the α-methyl group, and the cyclized products 9 were obtained (Figure 2, see also Method D in SI). The α-phenyl diazoacetate 8a generated the formal [4 + 1] product 9a in 55% yield, and the residual of unreacted diazoacetate 8a was recovered in 40% (Figure 2A). We also examined the ethyl diazoacetate 8b (EDA) and diazoacetamide 8c, and both delivered the isomerized products 9b (see Figure S113) and 9c in 62% and 70% yields, respectively (Figure 2B). Besides, when diphenyl diazo compound 8d was subjected to the optimized conditions, the annulation product 9d was isolated in 45% yield contaminated with the internal olefin 9d' in 50% yield (Figure 2C). Both the structures of 9a and 9d' were confirmed by X-ray (Figure 2D, see also Table S2).

Control experiments were subsequently conducted to verify the proposed reaction mechanism (see also Methods for mechanistic studies in SI). First, the intramolecular isotope labeling experiments show that the reaction undergoes a hydrogen transfer process (see Figures S114 and S115). The intermolecular kinetic isotope effect (KIE) experiment (kH/kD = 1.4:1) shows that the hydrogen transfer process is not the rate-limiting step (Figure 3A, see also Figure S114). Then 2a was exposed under the 8-W CFL, and the hydrazine product was generated in 80% yield, which suggested the possibility of the existence of free carbene (Figure 3B) (Sha and Wei, 2013). The parallel reactions were conducted, and the results are shown in Figure 3C. Variable from optimized conditions in Table 1, we carried out the template reaction in the dark, and thebishomoallylic amine 4f was given in 55% yield (Figure 3C, condition A), whereas 4f was obtained in 80% yield under optimal conditions in the presence of visible light (Figure 3C, condition B). Then preliminary radical-inhibition test was conducted. Partial inhibition was observed when TEMPO was added, and the yield of 4f dropped to 40% yield (Figure 3C, condition C), which might be contributed via the non-radical pathway. Meanwhile, 70% yield of acetophenone (yield based on 1a) was observed after the reaction, due to the oxidization of the free carbene by TEMPO. In addition, electron paramagnetic
resonance (EPR) experiments were carried out (Figure 3D, see also Figure S116). No obvious signal of the diradical spin adduct was observed when diazo compound (1a) was treated with 3a in the presence of 5,5-dimethyl-1-pyrroline N-oxide (DMPO) at room temperature in dark. On the other hand, the EPR signal of the carbon-diradical spin adduct emerged after the reaction mixture was irradiated by 8-W CFL lamps for 5 min, which obviously strengthened in the following 20 min (Figure 3D, blue line). These experiments indicated that the visible light facilitates the reaction pathway via the radical process. On basis of the literature reports (Boratyński et al., 2010; Gallagher et al., 2019; Hommelsheim et al., 2019; Jurberg and Davies, 2018; Snyder and Dougherty, 1989; Zhang et al., 2019b) and the EPR signal, we deduced that the radical process may be involved under the visible light conditions.

Computational studies were carried out to gain a mechanistic insight on this selective formation of the 2-allyl aniline 4f (see also Computational Methods in SI). The diazo substrate 2f could undergo intermolecular electrophilic attack to the terminal alkenyl carbon of the in situ generated intermediate 3a' to form an adduct \( \text{INT1} \) (Figure 4, the red line, path a). The predicted energy barrier is 11.5 kcal/mol relative to separated 2f and 3a'. The formed \( \text{INT1} \) is very ready to release \( \text{N}_2 \) via \( \text{TS1} \) to yield the corresponding cyclopropane derivative \( \text{INT2} \). Computational study results indicate that it is very facile for \( \text{INT1} \) to convert to \( \text{INT2} \) via \( \text{TS1} \) along with the extrusion of \( \text{N}_2 \) in a concerted manner. The direct \( \text{N}_2 \) dissociation from 2f (via \( \text{TS3} \)) to afford a free carbene intermediate (path a'), however, has a much higher energy barrier, which is unlikely to occur compared with the competitive intermolecular electrophilic addition process. Alternatively, a possible reaction route leading to \( \text{INT2} \) in the presence of visible light was also considered (Figure 4, the blue line, path b). Irradiated by visible light, the diazo compound 2f might be excited to triplet state \( \text{3}_2f \). Subsequently, the dissociation of \( \text{N}_2 \) via \( \text{3TS1b} \) could follow to yield the triplet carbene intermediate \( \text{3INT1b} \). Afterward, the formed \( \text{3INT1b} \) could attach to the terminal alkenyl carbon of the in situ-generated intermediate 3a' to form the intermediate \( \text{INT2} \) via \( \text{3TS2b} \). The predicted energy barrier of this step is only 7.3 kcal/mol. Thus, it is also feasible for the formation of \( \text{INT2} \) in the presence of light.

It should be noted that the formed \( \text{INT2} \) might not be stable under the driving force of the aromatization and the ring strain release of the three-membered ring. Next, we evaluated two competitive processes, desaturation versus ring expansion, which were observed above. The hydrogen transfer from the methyl group attached to the three-membered ring to the N atom of the imine moiety can generate the unsaturated amine product 4f (path a, Figure 5) and the [1,3] C-migration can lead to the cyclized product 9 (path b, Figure 5). The located \( \text{TS} \) for path a is shown as \( \text{TS4} \), in which the C\( ^{-} \)... H bond distance is lengthened to 1.22 Å, whereas the H... N distance is shortened to 1.52 Å. Meanwhile, the C\( ^{-} \)... C\( ^{2} \) distance is lengthened to 2.29 Å (Figure 5A). The calculated \( \Delta G^\ddagger \) of the hydrogen transfer step is 8.0 kcal/mol relative to \( \text{INT2} \), and the formed product 4f is exothermic by 19.2 kcal/mol. The optimized \( \text{TS} \) of the [1,3] C-migration to form product 9 is shown as \( \text{TS5} \), in which the C\( ^{-} \)... C\( ^{2} \) distance is lengthened to 2.44 Å, whereas the C\( ^{2} \)... N distance is shortened to 2.80 Å (Figure 5B). The predicted energy barrier of path b is 11.4 kcal/mol, which is 3.4 kcal/mol higher in energy than that of path a. Therefore, computational results suggest that it is more feasible for \( \text{INT2} \) to form product 4f via the redox-neutral hydrogen transfer pathway (it is consistent with Figure 2. Cyclization Transformations of 3a with Other Types of Diazo Compounds without the \( \alpha \)-Methyl Group (A) With \( \alpha \)-phenyl diazacetate. (B) With ethyl diazacetate (EDA) and diazacetamide. (C) With diphenyl diazocompound. (D) X-ray diffraction of compounds 9a and 9d\( ^{0} \).
In the cases of substrates without the adjacent C-H bond, the annulation product could be formed via the [1,3] C-migration pathway. The carbocation intermediate is very unlikely to form as a key intermediate (Suneja and Schneider, 2018; Pandit et al., 2019), which cannot be located as a local minimum computationally, owing to the presence of highly nucleophilic negatively charged C and N atoms. Thus, this alternative mechanistic pathway is discarded. However, other possibility could not be totally ruled out so far.

Recently, elegant cycloannulation reactions of o-QMs and diazo ketones/esters were reported by Schneider (Suneja and Schneider, 2018) and Ryu (Pandit et al., 2019), independently. And corresponding cyclopropane derivatives are the key intermediates in these transformations. However, the manner of ring opening is different from ours. Besides, redox-neutral hydrogen transfer processes instead of intramolecular rearrangement (Li et al., 2019; Gandamana et al., 2018; Mavroskoufis et al., 2020; Mori et al., 2018; Kaiser et al., 2019; Tian et al., 2019; Haibach and Seidel, 2014) thereafter took place in our protocol to form the desaturation products (see Note S2 for extended discussion). Moreover, the desaturation product of 2-allyl anilines are prized building blocks for the divergent synthesis of heterocycles through various transformations (Lu et al., 2018; Lin et al., 2017; Wdowik and Chemler, 2017; Jiang et al., 2017; Chemler, 2013; Du et al., 2015; Miyazaki et al., 2014; Pan et al., 2014; Yu et al., 2017). Yet the current methods for the synthesis of these motifs usually took a long synthetic route and with limited substrate scope (Du et al., 2015; Miyazaki et al., 2014; Pan et al., 2014; Yu et al., 2017) (see Note S3 for extended discussion). This method provides a missing link in the synthesis of 2-allyl anilines with high control of the terminal selectivity and broad substrate generality under mild conditions.

To show the synthetic utility of this method, a variety of 5- and 6-membered N-heterocycles have been expeditiously synthesized with these obtained 2-allyl aniline products (Figure 6, see also Methods for further transformations in SI). Catalytic 5-exo-cyclization, which selectively promoted the formation of new C-N bonds in conjunction with vicinal C-CN (Pan et al., 2014), C-Br (Yu et al., 2017), C-O, C-H, or C-S bonds, delivered the corresponding functionalized indolines 10–14 in high yields. In addition, the 6-endo-cyclization products 15 and 16 were smoothly obtained in 70% and 82% yields under catalytic vicinal chlorination and reductive conditions, respectively. Owing to the limitation of diazo compounds, the di-alkyl-substituted alkenes were not directly delivered currently. However, they can be realized by the late-state modifications, i.e., the corresponding 2-allyl aniline 17 could be readily generated from 7a with lithium aluminum hydride (LAH) in 70% yield, which further demonstrate the utility of our methodology. Comparing with the results of 16 and 17, we reasoned that the product 16 may come from the annulation under the alkaline condition then reduction. To verify this assumption, the reaction of 7f was conducted only under the basic condition, and the corresponding annulation product was observed. After screening the bases, we found that DBU is the best one for this annulation. This discovery was applied in the efficient synthesis of 18 (from the generated 2-allyl aniline 7j), which could be further used for the synthesis of a leukemia inhibitor in three steps with high yields (Figure 7) (Chen et al., 2016).
Conclusion

In summary, we have developed a novel visible-light-enhanced desaturation method for highly site-/regio-controlled synthesis of 2-allylic anilines. Mechanically, two reaction pathways, including a direct electronic addition of diazo compound and light-enhancing induced radical processes, may simultaneously contribute to the formation of closed-shell cyclopropane intermediate, followed by a ring opening and redox-neutral hydrogen transfer process to give the desaturated product. This desaturated approach provides a facile access to a wide range of 2-allyl aniline derivatives under mild conditions with good tolerance of functional groups. Notably, further applications in N-heterocycle construction, including 5- and 6-membered-ring with a variety of functional groups, have been explored as well, which show potential in diversity synthesis and drug discovery. Novel desaturation method could be envisioned with this AG-assisted hydrogen transfer strategy.

Limitations of the Study

Owing to the limitation of diazo compounds, the di-alkyl substituted alkenes were not directly delivered currently.

Resource Availability

Lead Contact

Further information and requests for resources and reagents should be directed to and will be fulfilled by the Lead Contact, Xinfang Xu (xinfangxu@suda.edu.cn).

Materials Availability

All unique/stable reagents generated in this study are available from the Lead Contact with a completed Materials Transfer Agreement.
Figure 6. Versatile Transformations with Obtained 2-Allyl Anilines
(A) BrCN, Et3N, Et2O, 0°C, 3 h, then B(C6F5)3 (20 mol%), PhMe, 100°C, 48 h.
(B) 10 mol% BINAP(S), NBS, toluene/CH2Cl2, -78°C, 50 h.
(C) m-CPBA, CH2Cl2, rt, 36 h.
(D) NbCl5 (2.5 mol %), AgNTf2 (5 mol %), DCE, 80°C, 6 h.
(E) CuCl (20 mol%), B2Pin2 (20 mol%), NFSI, CH3CN, 45°C, 15 h.
(F) CaCl2 (0.50 mmol), Pd(OAc)2 (0.01 mmol) and H2O2 (30% aq. wt.), HOAc, rt, 30 h.
(G) LiAIH4, THF, 0°C to rt, 3 h.
(H) LiAIH4, THF, 0°C to rt, 3 h.

Data and Code Availability
The crystallography data have been deposited at the Cambridge Crystallographic Data Center (CCDC) under accession number CCDC: 1579217 (4f); 1579222 (9a); 1579218 (9d) and can be obtained free of charge from www.ccdc.cam.ac.uk/getstructures. Original/source data for Schemes 1 and 2 together with Figures 2, 3, 6, and 7 in the paper is available at https://doi.org/10.17632/k23x374cz3.1.

METHODS
All methods can be found in the accompanying Transparent Methods supplemental file.

SUPPLEMENTAL INFORMATION
Supplemental Information can be found online at https://doi.org/10.1016/j.isci.2020.101168.
Figure 7. Formal Synthesis of a Leukemia Inhibitor

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AUTHOR CONTRIBUTIONS

X.X. supervised the project. Y.Z., K.H., and S.D. conducted the experimental works. L.Q. performed X-ray analysis. P.D., D.G., L.K., and X.B. performed the computational studies. Y.Z., J.H., W.H., X.B., and X.X. co-wrote the manuscript.

DECLARATION OF INTERESTS

The authors declare no competing interests.

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Supplemental Information

Desaturation via Redox-Neutral Hydrogen Transfer Process: Synthesis of 2-Allyl Anilines, Mechanism and Applications

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Figure S1. $^1$H NMR spectra (400 MHz) of 4a in CDCl$_3$, related to Table 1 and Scheme 1.

Figure S2. $^{13}$C NMR spectra (400 MHz) of 4a in CDCl$_3$, related to Table 1 and Scheme 1.
Figure S3. $^1$H NMR spectra (400 MHz) of 4b in CDCl$_3$, related to Scheme 1.

Figure S4. $^{13}$C NMR spectra (400 MHz) of 4b in CDCl$_3$, related to Scheme 1.
Figure S5. $^1$H NMR spectra (400 MHz) of 4c in CDCl$_3$, related to Scheme 1.

Figure S6. $^{13}$C NMR spectra (400 MHz) of 4c in CDCl$_3$, related to Scheme 1.
Figure S7. $^1$H NMR spectra (400 MHz) of 4d in CDCl$_3$, related to Scheme 1.

Figure S8. $^{13}$C NMR spectra (400 MHz) of 4d in CDCl$_3$, related to Scheme 1.
Figure S9. $^1$H NMR spectra (400 MHz) of 4e in CDCl$_3$, related to Scheme 1.

Figure S10. $^{13}$C NMR spectra (400 MHz) of 4e in CDCl$_3$, related to Scheme 1.
Figure S11. $^1$H NMR spectra (400 MHz) of 4f in CDCl$_3$, related to Scheme 1.

Figure S12. $^{13}$C NMR spectra (400 MHz) of 4f in CDCl$_3$, related to Scheme 1.
Figure S13. $^1$H NMR spectra (400 MHz) of 4g in CDCl$_3$, related to Scheme 1.

Figure S14. $^{13}$C NMR spectra (400 MHz) of 4g in CDCl$_3$, related to Scheme 1.
Figure S15. $^1$H NMR spectra (400 MHz) of 4h in CDCl$_3$, related to Scheme 1.

Figure S16. $^{13}$C NMR spectra (400 MHz) of 4h in CDCl$_3$, related to Scheme 1.
Figure S17. $^1$H NMR spectra (400 MHz) of 4i in CDCl$_3$, related to Scheme 1.

Figure S18. $^{13}$C NMR spectra (400 MHz) of 4i in CDCl$_3$, related to Scheme 1.
Figure S19. $^1$H NMR spectra (400 MHz) of 4j in CDCl$_3$, related to Scheme 1.

Figure S20. $^{13}$C NMR spectra (400 MHz) of 4j in CDCl$_3$, related to Scheme 1.
Figure S21. $^1$H NMR spectra (400 MHz) of 4k in CDCl$_3$, related to Scheme 1.

Figure S22. $^{13}$C NMR spectra (400 MHz) of 4k in CDCl$_3$, related to Scheme 1.
Figure S23. $^1$H NMR spectra (400 MHz) of 4l in CDCl$_3$, related to Scheme 1.

Figure S24. $^{13}$C NMR spectra (400 MHz) of 4l in CDCl$_3$, related to Scheme 1.
Figure S25. $^1$H NMR spectra (400 MHz) of 4m in CDCl$_3$, related to Scheme 1.

Figure S26. $^{13}$C NMR spectra (400 MHz) of 4m in CDCl$_3$, related to Scheme 1.
Figure S27. $^1$H NMR spectra (400 MHz) of (E)-4n in CDCl$_3$, related to Scheme 1.

Figure S28. $^{13}$C NMR spectra (400 MHz) of (E)-4n in CDCl$_3$, related to Scheme 1.
Figure S29. $^1$H NMR spectra (400 MHz) of (Z)-4n in CDCl$_3$, related to Scheme 1.

Figure S30. $^{13}$C NMR spectra (400 MHz) of (Z)-4n in CDCl$_3$, related to Scheme 1.
Figure S31. $^1$H NMR spectra (400 MHz) of 4o in CDCl$_3$, related to Scheme 1.

Figure S32. $^{13}$C NMR spectra (400 MHz) of 4o in CDCl$_3$, related to Scheme 1.
Figure S33. $^1$H NMR spectra (400 MHz) of $4p$ in CDCl$_3$, related to Scheme 1.

Figure S34. $^{13}$C NMR spectra (400 MHz) of $4p$ in CDCl$_3$, related to Scheme 1.
Figure S35. $^1$H NMR spectra (400 MHz) of 4q in CDCl$_3$, related to Scheme 1.

Figure S36. $^{13}$C NMR spectra (400 MHz) of 4q in CDCl$_3$, related to Scheme 1.
Figure S37. $^1$H NMR spectra (400 MHz) of $4r$ in CDCl$_3$, related to Scheme 1.

Figure S38. $^{13}$C NMR spectra (400 MHz) of $4r$ in CDCl$_3$, related to Scheme 1.
Figure S39. $^1$H NMR spectra (400 MHz) of 5a in CDCl$_3$, related to Scheme 1.

Figure S40. $^{13}$C NMR spectra (400 MHz) of 5a in CDCl$_3$, related to Scheme 1.
Figure S41. $^1$H NMR spectra (400 MHz) of 5b in CDCl$_3$, related to Scheme 1.

Figure S42. $^{13}$C NMR spectra (400 MHz) of 5b in CDCl$_3$, related to Scheme 1.
Figure S43. $^1$H NMR spectra (400 MHz) of $5c$ in CDCl$_3$, related to Scheme 1.

Figure S44. $^{13}$C NMR spectra (400 MHz) of $5c$ in CDCl$_3$, related to Scheme 1.
Figure S45. $^1$H NMR spectra (400 MHz) of 5d in CDCl$_3$, related to Scheme 1.

Figure S46. $^{13}$C NMR spectra (400 MHz) of 5d in CDCl$_3$, related to Scheme 1.
Figure S47. $^1$H NMR spectra (400 MHz) of 5e in CDCl$_3$, related to Scheme 1.

Figure S48. $^{13}$C NMR spectra (400 MHz) of 5e in CDCl$_3$, related to Scheme 1.
Figure S49. $^1$H NMR spectra (400 MHz) of 5f in CDCl$_3$, related to Scheme 1.

Figure S50. $^{13}$C NMR spectra (400 MHz) of 5f in CDCl$_3$, related to Scheme 1.
Figure S51. $^1$H NMR spectra (400 MHz) of 5g in CDCl$_3$, related to Scheme 1.

Figure S52. $^{13}$C NMR spectra (400 MHz) of 5g in CDCl$_3$, related to Scheme 1.
Figure S53. $^1$H NMR spectra (400 MHz) of 5h in CDCl$_3$, related to Scheme 1.

Figure S54. $^{13}$C NMR spectra (400 MHz) of 5h in CDCl$_3$, related to Scheme 1.
Figure S55. $^1$H NMR spectra (400 MHz) of 5i in CDCl$_3$, related to Scheme 1.

Figure S56. $^{13}$C NMR spectra (400 MHz) of 5i in CDCl$_3$, related to Scheme 1.
Figure S57. $^1$H NMR spectra (400 MHz) of 5j in CDCl$_3$, related to Scheme 1.

Figure S58. $^{13}$C NMR spectra (400 MHz) of 5j in CDCl$_3$, related to Scheme 1.
Figure S59. $^1$H NMR spectra (400 MHz) of 5k in CDCl$_3$, related to Scheme 1.

Figure S60. $^{13}$C NMR spectra (400 MHz) of 5k in CDCl$_3$, related to Scheme 1.
Figure S61. $^1$H NMR spectra (400 MHz) of 5l in CDCl$_3$, related to Scheme 1.

Figure S62. $^{13}$C NMR spectra (400 MHz) of 5l in CDCl$_3$, related to Scheme 1.
Figure S63. $^1$H NMR spectra (400 MHz) of 5m in CDCl$_3$, related to Scheme 1.

Figure S64. $^{13}$C NMR spectra (400 MHz) of 5m in CDCl$_3$, related to Scheme 1.
Figure S65. $^1$H NMR spectra (400 MHz) of $7a$ in CDCl$_3$, related to Scheme 2.

Figure S66. $^{13}$C NMR spectra (400 MHz) of $7a$ in CDCl$_3$, related to Scheme 2.
Figure S67. \textsuperscript{1}H NMR spectra (400 MHz) of 7b in CDCl\textsubscript{3}, related to Scheme 2.

Figure S68. \textsuperscript{13}C NMR spectra (400 MHz) of 7b in CDCl\textsubscript{3}, related to Scheme 2.
Figure S69. $^1$H NMR spectra (400 MHz) of 7c in CDCl$_3$, related to Scheme 2.

Figure S70. $^{13}$C NMR spectra (400 MHz) of 7c in CDCl$_3$, related to Scheme 2.
Figure S71. $^1$H NMR spectra (400 MHz) of 7d in CDCl$_3$, related to Scheme 2.

Figure S72. $^{13}$C NMR spectra (400 MHz) of 7d in CDCl$_3$, related to Scheme 2.
Figure S73. $^1$H NMR spectra (400 MHz) of 7e in CDCl$_3$, related to Scheme 2.

Figure S74. $^{13}$C NMR spectra (400 MHz) of 7e in CDCl$_3$, related to Scheme 2.
Figure S75. $^1$H NMR spectra (400 MHz) of 7f in CDCl$_3$, related to Scheme 2.

Figure S76. $^{13}$C NMR spectra (400 MHz) of 7f in CDCl$_3$, related to Scheme 2.
Figure S77. $^1$H NMR spectra (400 MHz) of 7g in CDCl$_3$, related to Scheme 2.

Figure S78. $^{13}$C NMR spectra (400 MHz) of 7g in CDCl$_3$, related to Scheme 2.
Figure S79. $^1$H NMR spectra (400 MHz) of 7h in CDCl$_3$, related to Scheme 2.

Figure S80. $^{13}$C NMR spectra (400 MHz) of 7h in CDCl$_3$, related to Scheme 2.
Figure S81. $^1$H NMR spectra (400 MHz) of 7i in CDCl$_3$, related to Scheme 2.

Figure S82. $^{13}$C NMR spectra (400 MHz) of 7i in CDCl$_3$, related to Scheme 2.
Figure S83. $^{13}$P NMR spectra (400 MHz) of 7i in CDCl$_3$, related to Scheme 2.

Figure S84. $^1$H NMR spectra (400 MHz) of 7j in CDCl$_3$, related to Scheme 2.
Figure S85. \(^{13}\)C NMR spectra (400 MHz) of 7j in CDCl\(_3\), related to Scheme 2.

Figure S86. \(^1\)H NMR spectra (400 MHz) of 9a in CDCl\(_3\), related to Figure 2A.
Figure S87. $^{13}$C NMR spectra (400 MHz) of 9a in CDCl$_3$, related to Figure 2A.

Figure S88. $^1$H NMR spectra (400 MHz) of 9b in CDCl$_3$, related to Figure 2B.
Figure S89. $^{13}$C NMR spectra (400 MHz) of 9b in CDCl$_3$, related to Figure 2B.

Figure S90. $^1$H NMR spectra (400 MHz) of 9c in CDCl$_3$, related to Figure 2B.
Figure S91. $^{13}$C NMR spectra (400 MHz) of 9c in CDCl$_3$, related to Figure 2B.

Figure S92. $^1$H NMR spectra (400 MHz) of 9d in CDCl$_3$, related to Figure 2C.
Figure S93. $^{13}$C NMR spectra (400 MHz) of 9d in CDCl$_3$, related to Figure 2C.

Figure S94. $^1$H NMR spectra (400 MHz) of 9d$'$ in CDCl$_3$, related to Figure 2C.
Figure S95. $^{13}$C NMR spectra (400 MHz) of $9d'$ in CDCl$_3$, related to Figure 2C.

Figure S96. $^1$H NMR spectra (400 MHz) of $12$ in CDCl$_3$, related to Figure 6C.
Figure S97. $^{13}$C NMR spectra (400 MHz) of 12 in CDCl$_3$, related to Figure 6C.

Figure S98. $^1$H NMR spectra (400 MHz) of 13 in CDCl$_3$, related to Figure 6D.
Figure S99. $^{13}$C NMR spectra (400 MHz) of 13 in CDCl$_3$, related to Figure 6D.

Figure S100. $^1$H NMR spectra (400 MHz) of 14 in CDCl$_3$, related to Figure 6E.
Figure S101. $^{13}$C NMR spectra (400 MHz) of 14 in CDCl$_3$, related to Figure 6E.

Figure S102. $^1$H NMR spectra (400 MHz) of 15 in CDCl$_3$, related to Figure 6F.
Figure S103. $^{13}$C NMR spectra (400 MHz) of 15 in CDCl$_3$, related to Figure 6F.

Figure S104. $^1$H NMR spectra (400 MHz) of 16 in CDCl$_3$, related to Figure 6G.
Figure S105. $^{13}$C NMR spectra (400 MHz) of 16 in CDCl$_3$, related to Figure 6G.

Figure S106. $^1$H NMR spectra (400 MHz) of 17 in CDCl$_3$, related to Figure 6H.
Figure S107. $^{13}$C NMR spectra (400 MHz) of 17 in CDCl$_3$, related to Figure 6H.

Figure S108. $^1$H NMR spectra (400 MHz) of 18 in CDCl$_3$, related to Figure 7.
Figure S109. $^{13}$C NMR spectra (400 MHz) of 18 in CDCl$_3$, related to Figure 7.
Figure S110. Crude NMR Spectra for the reaction of 2f and 3a under the conditions of Table 1, entry 1, related to Table 1. (Note: E/Z 4f' is known product, see ref.: (2014). Org. Lett. 16, 3720-3723)

Figure S111. 1D-NOE NMR Spectra for E-4n, related to Scheme 1.
Figure S112. 1D-NOE NMR Spectra for Z4n, related to Scheme 1.

Figure S113. 1D-NOE NMR Spectra for 9b, related to Figure 2B.
Figure S114. Intermolecular Kinetic Isotope Effect (KIE) Experiment, related to Figure 3A.

Figure S115. Intramolecular Isotope Labeling Experiment, related to Figure 3A.
Figure S116. EPR Analysis, related to Figure 3D.
Supplemental Tables

Table S1. X-ray crystal structures of 4f, related to Scheme 1.

| Supplemental Tables |
|---------------------|
| **Table S1. X-ray crystal structures of 4f, related to Scheme 1.** |

![Diagram of X-ray crystal structures](image)

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The missing CIF items (i.e., `_computing_data_collection; `_computing_publication_material) were added as fellow:

*ata_xcalibur*

* _audit_creation_date;  
  'Mon Dec 12 10:27:52 2016';  
  _audit_creation_method;  
  CrysAlisPro, Agilent Technologies,  
  Version 1.171.36.32

(release 02-08-2013 CrysAlis171 .NET)

(compiled Aug 2 2013,16:46:58);  
  _computing_data_collection;  
  CrysAlisPro, Agilent Technologies,  
  Version 1.171.36.32

(release 02-08-2013 CrysAlis171 .NET)

(compiled Aug 2 2013,16:46:58);  
  _computing_cell_refinement;  
  CrysAlisPro, Agilent Technologies,  
  Version 1.171.36.32
Table S2. X-ray crystal structures of 9a and 9d, related to Figure 2D.
**Transparent Methods**

**General Information**

All reactions were carried out in oven-dried (110 °C) glassware under an atmosphere of dry argon. Solvents were dried and degassed by the standard methods. Flash column chromatography was performed using silica gel (300-400 mesh). Analytical thin-layer chromatography was performed using glass plates pre-coated with 200-300 mesh silica gel impregnated with a fluorescent indicator (254 nm). $^1$H NMR and $^{13}$C NMR spectra were recorded in CDCl$_3$ on a 400 MHz spectrometer; chemical shifts are reported in ppm with the solvent signals as reference, and coupling constants ($J$) are given in Hertz. The peak information is described as: br = broad, s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, comp = composite. High-resolution mass spectra (HRMS) were recorded on a commercial apparatus (ESI or CI Source).
Note S1. Expanded discussion on the formation of linear/branched alkenes via organometal intermediates

Organometal species, as the very common intermediate, have broadly existed in organic synthesis. Basically, functionalization or β-H elimination are the major reactions based on organometal intermediate. In terms of the β-H elimination, linear alkenes are usually formed as the major products (comparing to branched alkenes) because of the energetically favorable process. For example, the Pd-catalyzed cross coupling reactions of N-tosylhydrazones with halides that take place with carbene migratory insertion and β-H elimination to form linear alkenes were well developed by Barluenga ((2007). Angew. Chem. Int. Ed. 46, 5587-5590.), Valdés ((2011). Angew. Chem. Int. Ed. 50, 7486–7500.) and Wang ((2017). Chem. Rev. 117, 13810–13889.). Whilst, the only analogous version for the selective branched alkene formation was disclosed by Barluenga and Valdés through a regioselective β-H elimination via a steric less hindered transition state ((2010). Angew. Chem. Int. Ed. 49, 6856–6859.), demonstrating that highly regioselective access to branched alkenes are much more challenging ((2017). J. Am. Chem. Soc. 139, 6086–6089.).

To overcome the problem of selectivity for the branched alkenes, the strategy through the catalytic formation of terminal alkyl-metal species in Heck alkenylation was developed last decade. Representative works were reported by Jamison ((2011). J. Am. Chem. Soc. 133, 19020–19023; (2013). J. Am. Chem. Soc. 135, 1585–1592; (2014). Angew. Chem. Int. Ed. 53, 1858–1861.), Zhou ((2012). Angew. Chem. Int. Ed. 51, 5915–5919.), Stahl ((2012). J. Am. Chem. Soc. 134, 16496–16499; (2015). Chem. Commun. 51, 12771–12774.), Goossen ((2016). Angew. Chem. Int. Ed. 55, 11296–11299.), and Bower ((2018). Angew. Chem. Int. Ed. 57, 14198–14202.), independently. Despite of these advances, the development of alternative methods for the effective synthesis of branched alkenes are still highly demand.
Note S2. Expanded discussion on the reactions of o-QMs/aza-o-QMs with diazo-compounds

When we prepared this work, elegant cycloannulation reactions of o-QMs and diazo-ketones/esters were recently reported by Schneider and Ryu, independently. However, the chemistries are quite different: (1) the substrates (o-QMs versus aza-o-QMs). In addition, the more reactive alkyl diazo compounds were also investigated in our protocol; (2) the pathways to the INT (besides the traditional way of electrophilic addition, we also found a visible light promoted path, which include free carbene and radical species; (3) the manner of ring opening (C2–C4 bond cleavage versus C2–C3 bond cleavage); (4) the reactions (cycloannulation versus desaturation).

Highlights (1) and (4) can be observed in the manuscript and the reported papers. Highlights (2) is supported by control experiments and DFT calculations. Highlight (3) can also be verified by our cycloannulation products (Figure 2).

Note S3. Expanded discussion on the strategies for the synthesis of 2-allyl anilines

Based on the reported literature ((2015). J. Am. Chem. Soc. 137, 1130–1135; (2014). J. Am. Chem. Soc. 136, 3732–3735; (2014). Angew. Chem. Int. Ed. 53, 5170–5174; (2017). Adv. Synth. Catal. 359, 2499–2508.), we found that the strategies they used are usually coupling with C2 and C3. In this context, alkylation of the ortho-halo-anilines or -nitrobenzene following by reduction are usually employed. However, the main problem needs to overcome is the compatibility of aniline. Many steps were taken to protect and de-protect the amine group. Moreover, the substrates (branched alkenes) are not easy to obtained, which largely limited the scopes.
In this new developed strategy, C₃ catch C₄ by the electrophilic addition without transition metal catalyst, which perfectly overcome the compatibility of aniline. Besides, the precursors of the two partners are commercially available and not expensive. With this method, a wide spectrum of 2-allyl anilines can be provided.

In terms of C₃-C₄ bond formation strategy, the alkenylation of the benzylic halides was also evaluated. However, to the best of knowledge ((2011). J. Am. Chem. Soc. 133, 19020−19023; (2013). J. Am. Chem. Soc. 135, 1585−1592), the substrates of ortho-amine benzylic halides were not involved in the scopes.

**Experimental procedure**

**General procedure for the preparation of 2-allyl anilines 4 and 5 (Method A, related to Table 1 and Scheme 1).**

![Experimental procedure diagram](image)

To a 10 mL oven-dried flask containing a magnetic stirring bar, hydrazone 2 (0.45 mmol), anhydrous MgSO₄ (60 mg), MnO₂ (312.0 mg, 8.0 equiv), and 1,2-dichloroethane (3.0 mL) were added in sequence under argon atmosphere. Then the flask was wrapped in foil and the reaction mixture was allowed to stir for 45 min at 0 °C. After that, removing the solid by filtering through a pad of Celite with Teflon filter (0.22 μm) at the bottom, we could obtain the pink solution as the diazo compound 1.

To a 10 mL oven-dried vial, which contains a magnetic stirring bar, N(2-chloromethylaryl) amide 3 (0.15 mmol), Cs₂CO₃ (97.7 mg, 2.0 equiv) under argon atmosphere at -40 °C, the above-mentioned pink solution was added via syringe. The reaction was carried out by irradiation of visible light (8 W CFL) and warm to room temperature slowly. When the reaction was completed (monitored by TLC), the reaction mixture was quenched by saturated NH₄Cl (aq), extracted with ethyl acetate (15 X 3 mL), and washed with brine (50 mL). The organic phase was dried with Na₂SO₄ and evaporated in vacuo. The resulting residue was purified by
column chromatography on silica gel with hexanes/ethyl acetate (20:1 to 10:1) as the eluent to give the desired pure products 4 or 5 in moderate to good or high yields.

**General procedure for the preparation of 2-allyl anilines 4 and 5 (Method B, related to Table 1 and Scheme 1).**

To a 10 mL oven-dried vial, which contains a magnetic stirring bar, hydrazone 2 (0.30 mmol), \(N\)-(2-chloromethylaryl) amide 3 (0.15 mmol), \(\text{Cs}_2\text{CO}_3\) (97.7 mg, 2.0 equiv) and \(\text{PhIO}\) (66.0 mg, 0.30 mmol) in DCE (2 mL) under argon atmosphere at \(-40^\circ\text{C}\). The reaction was carried out by irradiation of visible light (8 W CFL) and warm to room temperature slowly. When the reaction was completed (monitored by TLC), the reaction mixture was quenched by saturated \(\text{NH}_4\text{Cl}\) (aq), extracted with ethyl acetate (15 X 3 mL), and washed with brine (50 mL). The organic phase was dried with \(\text{Na}_2\text{SO}_4\) and evaporated in vacuo. The organic layer was dried over \(\text{Na}_2\text{SO}_4\), filtered, and concentrated. The resulting residue was purified by column chromatography on silica gel with hexane/ethyl acetate (20:1 to 10:1) as the eluent to give the desired pure products 4 or 5 in moderate to good or high yields.

\(N\)-(2-[2-(4-Bromophenyl)allyl]phenyl)-4-methylbenzenesulfonamide (4a).

Following the general procedure A, 53.7 mg, 81% yield. Yellow solid, mp: 150-151 \(^\circ\text{C}\). \(^1\)H NMR (400 MHz, CDCl\(_3\)) (\(\delta\), ppm) 7.58 (d, \(J = 8.2\) Hz, 2H), 7.40 (d, \(J = 8.4\) Hz, 2H), 7.35 (d, \(J = \ldots\)
7.9 Hz, 1H), 7.23-7.19 (m, 3H), 7.17-7.06 (comp, 4H), 6.48 (s, 1H), 5.44 (s, 1H), 4.80 (s, 1H), 3.43 (s, 2H), 2.41 (s, 3H); 13C NMR (100 MHz, CDCl₃) (δ, ppm) 144.6, 144.0, 138.9, 136.9, 134.9, 132.5, 131.6, 130.9, 129.8, 127.9, 127.7, 127.2, 126.7, 125.3, 122.0, 115.3, 37.4, 21.7. HRMS (TOF MS ESI⁺) calculated for C₂₂H₂₁BrNO₂S [M+H]+: 442.0471, found 442.0468.

4-Methyl-N-(2-(p-tolyl)allyl]phenyl]benzenesulfonamide (4b).

Following the general procedure A, 46.4 mg, 82% yield. Yellow solid, mp: 141-142 °C. ¹H NMR (400 MHz, CDCl₃) (δ, ppm) 7.58 (d, J = 8.3 Hz, 2H), 7.43 (d, J = 8.0 Hz, 1H), 7.22-7.19 (comp, 5H), 7.12-7.09 (comp, 4H), 6.52(s, 1H), 5.41 (s, 1H), 4.69 (s, 1H), 3.38 (s, 2H), 2.41 (s, 3H), 2.34 (s, 3H); 13C NMR (100 MHz, CDCl₃) (δ, ppm) 145.4, 143.9, 138.0, 137.1, 137.0, 135.1, 132.4, 131.2, 129.8, 129.2, 127.8, 127.2, 126.5, 125.9, 124.9, 113.8, 37.7, 21.7, 21.2. HRMS (TOF MS ESI⁺) calculated for C₂₃H₂₄NO₂S [M+H]+: 378.1522, found 378.1527.

N-(2-(2-(4-Methoxyphenyl)allyl]phenyl)-4-methylbenzenesulfonamide (4c).

Following the general procedure A, 49.6 mg, 84% yield. Yellow solid, mp: 143-145 °C. ¹H NMR (400 MHz, CDCl₃) (δ, ppm) 7.58 (d, J = 11.2 Hz, 2H), 7.41 (d, J = 10.4 Hz, 1H), 7.25-7.20 (comp, 5H), 7.11-7.09 (m, 2H), 6.84-6.81 (m, 2H), 6.50 (br, 1H), 5.36 (s, 1H), 4.65 (s, 1H), 3.81 (s, 3H), 3.37 (s, 2H), 2.41 (s, 3H); 13C NMR (100 MHz, CDCl₃) (δ, ppm) 144.9, 143.9, 137.1, 135.2, 132.4, 132.3, 131.2, 129.8, 127.9, 127.3, 127.2, 126.5, 124.9, 113.9, 113.0, 55.4, 37.8,
21.7. HRMS (TOF MS ESI⁺) calculated for C_{23}H_{24}NO_{3}S [M+H]⁺ 394.1471, found 394.1467.

**N'-(2-[(4-Fluorophenyl)allyl]phenyl)-4-methylbenzenesulfonamide (4d).**

Following the general procedure A, 45.7 mg, 80% yield. Yellow solid, mp: 95-96 °C. ¹H NMR (400 MHz, CDCl₃) (δ, ppm) 7.58 (d, J = 8.3 Hz, 2H), 7.36 (d, J = 7.7 Hz, 1H), 7.28-7.27 (m, 1H), 7.25-7.17 (comp, 4H), 7.13-7.06 (comp, 2H), 7.00-6.94 (comp, 2H), 6.48 (s, 1H), 5.39 (s, 1H), 4.75 (s, 1H), 3.42 (s, 2H), 2.41 (s, 3H); ¹³C NMR (150 MHz, CDCl₃) (δ, ppm) 162.6 (d, J = 246.2 Hz), 144.7, 144.0, 137.0, 136.1 (d, J = 3.1 Hz), 135.1, 132.4, 131.1, 129.8, 127.9, 127.7 (d, J = 8.0 Hz), 127.3, 126.6, 125.2, 115.4 (d, J = 21.3 Hz), 114.7, 37.8, 21.7. HRMS (TOF MS ESI⁺) calculated for C_{22}H_{21}FNO_{2}S [M+H]⁺: 382.1272, found 382.1282.

**N'-(2-[(4-Chlorophenyl)allyl]phenyl)-4-methylbenzenesulfonamide (4e).**

Following the general procedure A, 45.9 mg, 77% yield. Yellow solid, mp: 155-156 °C. ¹H NMR (400 MHz, CDCl₃) (δ, ppm) 7.58 (d, J = 8.3 Hz, 2H), 7.35 (d, J = 7.6 Hz, 1H), 7.25-7.17 (comp, 7H), 7.13-7.06 (comp, 2H), 6.50 (s, 1H), 5.43 (s, 1H), 4.79 (s, 1H), 3.43 (s, 2H), 2.41 (s, 3H); ¹³C NMR (100 MHz, CDCl₃) (δ, ppm) 144.6, 144.0, 138.4, 136.9, 134.9, 133.9, 132.4, 131.0, 129.8, 128.7, 127.9, 127.3, 127.2, 126.7, 125.3, 115.2, 37.6, 21.7. HRMS (TOF MS ESI⁺) calculated for C_{22}H_{21}ClNO_{2}S [M+H]⁺: 398.0976, found 398.0979.
4-Methyl-\(N\)\{-2\-(2-phenylallyl)phenyl\}benzenesulfonamide (4f).

Following the general procedure A, 46.9 mg, 86% yield; Following the general procedure B, 39.8 mg, 73% yield. Yellow solid, mp: 140-141 °C. \(^1\)H NMR (400 MHz, CDCl\(_3\)) (\(\delta\), ppm) 7.59 (d, \(J = 8.2\) Hz, 2H), 7.41 (d, \(J = 7.9\) Hz, 1H), 7.30-7.28 (comp, 5H), 7.22-7.18 (comp, 3H), 7.11-7.10 (comp, 2H), 6.59 (s, 1H), 5.44 (s, 1H), 4.75 (s, 1H), 3.43 (s, 2H), 2.40 (s, 3H); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) (\(\delta\), ppm) 145.6, 143.9, 140.0, 136.9, 135.0, 132.5, 131.1, 129.7, 128.5, 128.1, 127.8, 127.2, 126.5, 125.9, 125.1, 114.6, 37.6, 21.7. HRMS (TOF MS ESI\(^{+}\)) calculated for C\(_{22}\)H\(_{22}\)NO\(_2\)S [M+H]\(^{+}\): 364.1366, found 364.1378.

\(N\)\{-2\-(2\-(4-Iodophenyl)allyl)phenyl\}-4-methylbenzenesulfonamide (4g).

Following the general procedure A, 55.8 mg, 76% yield. Yellow solid, mp: 150-151 °C. \(^1\)H NMR (400 MHz, CDCl\(_3\)) (\(\delta\), ppm) 7.61-7.57 (comp, 4H), 7.35 (d, \(J = 7.9\) Hz, 1H), 7.23-7.17 (m, 3H), 7.12-7.06 (comp, 2H), 7.02-7.00 (comp, 2H), 6.47 (s, 1H), 5.44 (s, 1H), 4.79 (s, 1H), 3.42 (s, 2H), 2.41 (s, 3H); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) (\(\delta\), ppm) 144.7, 144.0, 139.5, 137.6, 136.9, 134.9, 132.4, 131.0, 129.8, 127.9, 127.8, 127.3, 126.7, 125.3, 115.4, 93.7, 37.4, 21.7. HRMS (TOF MS ESI\(^{+}\)) calculated for C\(_{22}\)H\(_{21}\)INO\(_2\)S [M+H]\(^{+}\): 490.0332, found 490.0319.

\(N\)\{-2\-(2\-(3-Bromophenyl)allyl)phenyl\}-4-methylbenzenesulfonamide (4h).
Following the general procedure A, 53.0 mg, 80% yield; Following the general procedure B, 43.1 mg, 65% yield. Yellow solid, mp: 135-136 °C. ¹H NMR (400 MHz, CDCl₃) (δ, ppm) 7.57 (d, J = 8.3 Hz, 2H), 7.42-7.38 (comp, 3H), 7.24-7.22 (m, 4H), 7.20-7.07 (comp, 3H), 6.40 (s, 1H), 5.43 (s, 1H), 4.75 (s, 1H), 3.35 (s, 2H), 2.42 (s, 3H); ¹³C NMR (150 MHz, CDCl₃) (δ, ppm) 144.4, 144.1, 142.2, 136.9, 134.9, 132.4, 131.2, 131.0, 130.1, 129.9, 129.1, 128.0, 127.2, 126.8, 125.7, 124.7, 122.8, 115.7, 37.3, 21.7. HRMS (TOF MS ESI⁺) calculated for C₂₂H₂₁BrNO₂S [M+H]⁺: 442.0471, found 442.0472.

**N-[2-{2-(2-Fluorophenyl)allyl]phenyl}-4-methylbenzenesulfonamide (4i).**

Following the general procedure A, 48.1 mg, 84% yield. Yellow solid, mp: 70-71 °C. ¹H NMR (400 MHz, CDCl₃) (δ, ppm) 7.59 (d, J = 8.2 Hz, 2H), 7.50 (d, J = 8.1 Hz, 2H), 7.25-7.16 (comp, 4H), 7.14-7.04 (comp, 5H), 6.61 (s, 1H), 5.22 (s, 1H), 4.85 (s, 1H), 3.33 (s, 2H), 2.37 (s, 3H); ¹³C NMR (100 MHz, CDCl₃) (δ, ppm) 160.9, 158.5, 143.8, 142.8, 136.8, 135.2, 131.2, 131.19 (d, J = 3.2 Hz), 129.9 (d, J = 4.2 Hz), 129.6, 129.5 (d, J = 8.5 Hz), 129.2 (d, J = 14.3 Hz), 128.0, 127.2, 126.1, 124.4, 124.3, 118.0 (d, J = 3.2 Hz), 115.9 (d, J = 22.7 Hz), 38.7, 21.7. HRMS (TOF MS ESI⁺) calculated for C₂₂H₂₁FNO₂S [M+H]⁺: 382.1272, found 382.1273.

**4-Methyl-**N-[2-{2-(4-(phenylethynyl)phenyl)allyl]phenyl]benzenesulfonamide (4j).
Following the general procedure A, 55.6 mg, 80% yield. Yellow solid, mp: 180-181 °C. \( ^1\)H NMR (400 MHz, CDCl\(_3\)) (\(\delta\), ppm) 7.56 (d, \(J = 8.2\) Hz, 2H), 7.52-7.50 (m, 2H), 7.43 (d, \(J = 8.3\) Hz, 2H), 7.39-7.32 (comp, 5H), 7.24-7.19 (comp, 4H), 7.11-7.05 (m, 2H), 6.47 (s, 1H), 5.47 (s, 1H), 4.77 (s, 1H), 3.41 (s, 2H), 2.39 (s, 3H); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) (\(\delta\), ppm) 144.9, 143.9, 139.7, 137.0, 135.0, 132.5, 131.73, 131.68, 131.1, 129.8, 128.49, 128.48, 127.9, 127.2, 126.6, 125.9, 125.3, 123.3, 122.9, 115.3, 90.4, 89.2, 37.4, 21.7. HRMS (TOF MS ESI\(^+\)) calculated for C\(_{30}\)H\(_{26}\)NO\(_2\)S [M+H]\(^+\): 464.1679, found 464.1674.

4-Methyl-\(N\)-(2-[2-(4-styrylphenyl)allyl]phenyl)benzenesulfonamide (4k).

Following the general procedure A, 57.9 mg, 83% yield. Yellow solid, mp: 127-128 °C. \( ^1\)H NMR (400 MHz, CDCl\(_3\)) (\(\delta\), ppm) 7.60-7.58 (m, 2H), 7.53-7.51 (m, 2H), 7.46-7.44 (m, 2H), 7.42-7.39 (m, 2H), 7.37-7.35 (m, 2H), 7.31-7.28 (comp, 4H), 7.32-7.21 (m, 2H), 7.12-7.10 (comp, 3H), 6.48 (br, 1H), 5.49 (s, 1H), 4.75 (s, 1H), 3.42 (s, 2H), 2.41 (s, 3H); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) (\(\delta\), ppm) 145.1, 144.0, 139.1, 137.3, 137.2, 137.0, 135.1, 131.1, 129.8, 129.2, 128.89, 128.86, 128.1, 127.92, 129.91, 127.3, 126.68, 126.65, 126.57, 126.3, 125.1, 114.5, 37.6, 21.8. HRMS (TOF MS ESI\(^+\)) calculated for C\(_{30}\)H\(_{28}\)NO\(_2\)S [M+H]\(^+\): 466.1835, found 466.1831.
4-Methyl-N-[2-[2-(naphthalen-2-yl)allyl]phenyl]benzenesulfonamide (4l).

Following the general procedure A, 47.1 mg, 76% yield; Following the general procedure B, 36.6 mg, 59% yield. Yellow solid, mp: 122-123 °C. ¹H NMR (400 MHz, CDCl₃) (δ, ppm) 7.85-7.77 (comp, 3H), 7.70 (d, J = 1.2 Hz, 1H), 7.58 (d, J = 8.3 Hz, 2H), 7.53-7.52 (m, 1H), 7.50-7.47 (comp, 2H), 7.42 (d, J = 7.4 Hz, 1H), 7.23-7.10 (comp, 5H), 6.57 (s, 1H), 5.59 (s, 1H), 4.85 (s, 1H), 3.54 (s, 2H), 2.39 (s, 3H); ¹³C NMR (100 MHz, CDCl₃) (δ, ppm) 145.5, 143.9, 137.2, 137.1, 135.1, 133.3, 133.1, 132.5, 131.2, 129.8, 128.3, 128.2, 127.9, 127.7, 127.2, 126.6, 126.5, 126.3, 125.3, 124.9, 124.2, 115.1, 37.7, 21.7. HRMS (TOF MS ESI⁺) calculated for C₂₆H₂₄NO₂S [M+H]⁺: 414.1522, found 414.1526.

4-Methyl-N-[2-[2-(thiophen-2-yl)allyl]phenyl]benzenesulfonamide (4m).

Following the general procedure A, 43.2 mg, 78% yield. Yellow solid, mp: 112-113 °C. ¹H NMR (400 MHz, CDCl₃) (δ, ppm) 7.58 (d, J = 8.2 Hz, 2H), 7.44 (d, J = 8.1 Hz, 1H), 7.23-7.21 (m, 3H), 7.19 (d, J = 5.1 Hz, 1H), 7.13 (d, J = 4.2 Hz, 2H), 6.95-6.93 (m, 1H), 6.86-6.85 (m, 1H), 6.45 (s, 1H), 5.47 (s, 1H), 4.55 (s, 1H), 3.40 (s, 2H), 2.41 (s, 3H); ¹³C NMR (100 MHz, CDCl₃) (δ, ppm) 144.0, 143.9, 138.9, 136.9, 135.1, 131.9, 131.2, 129.8, 128.1, 127.5, 127.3, 126.6, 125.2, 124.9, 124.1, 112.9, 37.4, 21.7. HRMS (TOF MS ESI⁺) calculated for C₂₀H₂₀NO₂S₂ [M+H]⁺: 370.0930, found 370.0939.

4-Methyl-N-[2-(2-phenylbut-2-1-yl)phenyl]benzenesulfonamide (4n).
Following the general procedure A, 46.9 mg, 83% overall yield. ($E$: $Z = 1.2 : 1$).

$E$: $^1$H NMR (400 MHz, CDCl$_3$) ($\delta$, ppm) 7.59 (d, $J = 8.2$ Hz, 2H), 7.32 (d, $J = 7.9$ Hz, 1H), 7.22-7.15 (comp, 5H), 7.13-7.00 (comp, 5H), 6.43 (s, 1H), 6.05 (q, $J = 6.9$ Hz, 1H), 3.51 (s, 2H), 2.38 (s, 3H), 1.71 (d, $J = 6.9$ Hz, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$) ($\delta$, ppm) 143.9, 142.3, 137.1, 137.0, 134.7, 132.6, 129.8, 129.6, 128.4, 127.3, 127.2, 126.9, 126.4, 126.3, 126.1, 124.5, 15.2, 14.5. HRMS (TOF MS ESI$^+$) calculated for C$_{23}$H$_{24}$NO$_2$S [M+H]$^+$: 378.1522, found 378.1528.

$Z$: $^1$H NMR (400 MHz, CDCl$_3$) ($\delta$, ppm) 7.56 (d, $J = 8.3$ Hz, 2H), 7.42 (d, $J = 8.0$ Hz, 1H), 7.31-7.27 (m, 2H), 7.25-7.23 (m, 2H), 7.20-7.16 (comp, 3H), 7.06-7.02 (m, 1H), 6.98-6.96 (m, 2H), 6.53 (s, 1H), 5.38 (q, $J = 7.0$ Hz, 1H), 3.19 (s, 2H), 2.37 (s, 3H), 1.54 (s, 3H); $^{13}$C NMR (150 MHz, CDCl$_3$) ($\delta$, ppm) 143.9, 139.9, 139.5, 137.1, 135.3, 131.9, 131.3, 129.7, 128.5, 128.2, 127.8, 127.2, 127.1, 126.1, 124.4, 123.9, 41.8, 21.7, 14.9. HRMS (TOF MS ESI$^+$) calculated for C$_{23}$H$_{24}$NO$_2$S [M+H]$^+$: 378.1522, found 378.1526.

**N-(2-[(3,4-Dihyronaphthalen-1-yl)methyl]phenyl)-4-methylbenzenesulfonamide (4o).**

Following the general procedure A, 45.6 mg, 78% yield; Following the general procedure B, 37.4 mg, 64% yield. Yellow solid, mp: 120-121 °C. $^1$H NMR (400 MHz, CDCl$_3$) ($\delta$, ppm) 7.57 (d, $J = 8.2$ Hz, 2H), 7.49 (d, $J = 8.0$ Hz, 1H), 7.23-7.09 (comp, 8H), 6.91 (d, $J = 7.4$ Hz, 1H), 6.55 (s, 1H), 5.46 (t, $J = 4.4$ Hz, 1H), 3.34 (s, 2H), 2.77 (t, $J = 8.0$ Hz, 2H), 2.41 (s, 3H), 2.23-2.20 (m, 2H); $^{13}$C NMR (100 MHz, CDCl$_3$) ($\delta$, ppm) 144.0, 136.9, 136.7, 135.3, 134.2, 133.6, 131.8, 131.1, 129.80, 129.76, 127.9, 127.7, 127.4, 127.3, 126.5, 126.2, 124.3, 122.7, 35.0, 28.2, 23.3, 21.7. HRMS (TOF MS ESI$^+$) calculated for C$_{26}$H$_{26}$NO$_2$S [M+H]$^+$: 390.1522, found 390.1517.
(1S,2R,5S)-2-Isopropyl-5-methylcyclohexyl 4-{3-[2-(4-methylphenylsulfonamido)phenyl]prop-1-en-2-yl}benzoate (4p).

Following the general procedure A, 58.5 mg, 71% yield; Following the general procedure B, 47.8 mg, 58% yield. Yellow oil. \(^1\)H NMR (400 MHz, CDCl\(_3\)) (\(\delta\), ppm) 7.94 (d, \(J = 8.0\) Hz, 2H), 7.59 (d, \(J = 8.0\) Hz, 2H), 7.37-7.31 (comp, 3H), 7.23-7.17 (comp, 3H), 7.10-7.18 (m, 2H), 6.49 (br, 1H), 5.53 (s, 1H), 4.96-4.89 (m, 1H), 4.88 (s, 1H), 3.48 (s, 2H), 2.40 (s, 3H), 2.15-2.10 (m, 1H), 1.97-1.91 (m, 1H), 1.75-1.71 (m, 2H), 1.60-1.51 (m, 2H), 1.32-1.27 (m, 1H), 1.16-1.06 (m, 1H), 0.94-0.91 (comp, 6H), 0.79 (d, \(J = 8.0\) Hz, 3H); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) (\(\delta\), ppm) 165.9, 144.9, 144.2, 144.0, 136.9, 134.9, 132.4, 130.9, 130.3, 129.8, 127.9, 127.3, 126.7, 125.9, 125.4, 116.6, 75.1, 47.4, 41.1, 37.4, 34.5, 31.6, 26.7, 23.8, 22.2, 21.7, 20.9, 16.7. HRMS (TOF MS ESI\(^+\)) calculated for C\(_{33}\)H\(_{40}\)NO\(_4\)S [M+H]\(^+\): 546.2678, found 546.2687.

\(((3aR,5R,5aS,8aS,8bR)-2,2,7,7-tetramethyltetrahydro-3aH-bis[1,3]dioxolo[4,5-b:4',5'-d]pyran-5-yl)methyl 4-{3-[2-(4-methylphenylsulfonamido)phenyl]prop-1-en-2-yl}benzoate (4q).

Following the general procedure A, 60.4 mg, 62% yield; Following the general procedure B, 52.6 mg, 54% yield. Yellow oil. \(^1\)H NMR (400 MHz, CDCl\(_3\)) (\(\delta\), ppm) 7.97 (d, \(J = 8.0\) Hz, 2H),
7.58 (d, J = 8.0 Hz, 2H), 7.38-7.31 (comp, 3H), 7.24-7.18 (comp, 3H), 7.13-7.06 (m, 2H), 6.38 (br, 1H), 5.57 (d, J = 5.6 Hz, 1H), 5.53 (s, 1H), 4.86 (s, 1H), 4.67-4.64 (m, 1H), 4.55-4.51 (m, 1H), 4.45-4.40 (m, 1H), 4.36-4.31 (m, 2H), 4.20-4.16 (m, 1H), 3.45 (s, 2H), 2.41 (s, 3H), 1.58 (m, 2H), 1.52 (s, 3H), 1.48 (s, 3H), 1.36 (s, 3H), 1.34 (s, 3H); 13C NMR (100 MHz, CDCl$_3$) (δ, ppm) 166.2, 145.0, 144.6, 144.1, 137.1, 135.0, 132.4, 131.1, 130.0, 129.8, 129.6, 128.2, 128.0, 127.9, 127.7, 127.3, 126.8, 126.0, 125.5, 116.6, 109.9, 109.0, 96.5, 71.3, 70.9, 70.7, 66.3, 64.1, 37.5, 26.2, 26.2, 25.1, 24.7, 21.7. HRMS (TOF MS ESI$^+$) calculated for C$_{35}$H$_{40}$NO$_9$S [M+H]$^+$: 650.2424, found 650.2430.

(3S,8R,9S,10S,13R,14S,17R)-10,13-dimethyl-17-[(3R)-6-methylheptan-2-yl]hexadecahydro-1$H$-cyclopenta[a]phenanthren-3-yl 4-{(3-[2-(4-methylphenylsulfonamido)phenyl]prop-1-en-2-yl)benzoate (4r).

Following the general procedure A, 70.0 mg, 60% yield; Following the general procedure B, 57.2 mg, 49% yield. Yellow oil. $^1$H NMR (400 MHz, CDCl$_3$) (δ, ppm) 7.94 (d, J = 8.0 Hz, 2H), 7.58 (d, J = 8.0 Hz, 2H), 7.36 (d, J = 7.4 Hz, 1H), 7.31 (d, J = 7.3 Hz, 2H), 7.22 (d, J = 7.3 Hz, 2H), 7.19-7.17 (m, 1H), 7.12-7.05 (m, 2H), 6.47 (br, 1H), 5.53 (s, 1H), 4.89-4.81 (comp, 2H), 3.47 (s, 2H), 2.46 (d, J = 2.5 Hz, 2H), 2.41 (s, 3H), 2.04-1.99 (comp, 3H), 1.86-1.82 (m, 1H), 1.75-1.68 (m, 1H), 1.61-1.48 (comp, 7H), 1.36-1.33 (comp, 4H), 1.27-1.22 (comp, 3H), 1.16-1.09 (comp, 5H), 1.07 (s, 3H), 1.05-1.00 (comp, 3H), 0.92-0.90 (comp, 3H), 0.88-0.85 (comp, 6H), 0.69 (s, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$) (δ, ppm) 165.8, 144.9, 144.2, 144.0, 139.7, 137.0, 134.9, 132.4, 131.0, 130.3, 129.8, 128.0, 127.3, 126.7, 125.9, 125.4, 123.0, 121.8, 116.6, 74.8, 71.9, 56.8, 56.3, 50.2, 42.5, 39.9, 39.7, 38.4, 37.4, 37.2, 36.8, 36.3, 35.9, 32.1, 28.4, 28.2, 28.0, 24.4, 24.0, 23.0, 22.7, 21.7, 21.2, 19.4, 18.8, 12.0. HRMS (TOF MS ESI$^+$) calculated for C$_{50}$H$_{68}$NO$_9$S [M+H]$^+$: 778.4869, found 778.4888.

$^N$-[2-[3-(4-Bromophenyl)but-3-en-2-yl]phenyl]-4-methylbenzenesulfonamide (5a).
Following the general procedure A, 54.7 mg, 80% yield. Yellow solid, mp: 104-105 °C. $^1$H NMR (400 MHz, CDCl$_3$) ($\delta$, ppm) 7.63 (d, $J = 8.3$ Hz, 2H), 7.36 (d, $J = 8.5$ Hz, 2H), 7.25-7.23 (m, 2H), 7.21-7.11 (comp, 4H), 7.06 (d, $J = 8.5$ Hz, 2H), 6.41 (s, 1H), 5.28 (s, 1H), 4.92 (s, 1H), 3.90 (t, $J = 6.9$ Hz, 1H), 2.41 (s, 3H), 1.24 (d, $J = 7.0$ Hz, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$) ($\delta$, ppm) 145.8, 143.9, 139.5, 138.4, 138.1, 137.9, 133.0, 131.5, 130.0, 129.8, 128.8, 128.2, 127.7, 127.2, 121.8, 114.6, 37.8, 21.7, 19.1. HRMS (TOF MS ESI$^+$) calculated for C$_{23}$H$_{23}$BrNO$_2$S [M+H]$^+$: 456.0627, found 456.0638.

$N\{2\{-2\{-4\text{-Bromophenyl}\}\{-1\text{-phenylallyl}\}\}-4\text{-chlorophenyl}\}-4\text{-methylbenzenesulfonamide (5b).}$

Following the general procedure A, 68.0 mg, 82% yield. Yellow solid, mp: 154-155 °C. $^1$H NMR (400 MHz, CDCl$_3$) ($\delta$, ppm) 7.58 (d, $J = 8.2$ Hz, 2H), 7.38-7.26 (comp, 8H), 7.20-7.17 (m, 1H), 7.05 (d, $J = 8.5$ Hz, 2H), 6.86 (d, $J = 6.2$ Hz, 2H), 6.76 (d, $J = 2.3$ Hz, 1H), 6.17 (s, 1H), 5.70 (s, 1H), 4.87 (s, 1H), 4.65 (s, 1H), 2.46 (s, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$) ($\delta$, ppm) 147.3, 144.4, 139.2, 138.99, 138.91, 137.1, 132.8, 132.6, 131.8, 130.1, 130.0, 129.4, 129.2, 128.1, 127.8, 127.7, 127.3, 122.2, 118.8, 50.9, 21.8. HRMS (TOF MS ESI$^+$) calculated for C$_{28}$H$_{23}$BrClNO$_2$SNa [M+Na]$^+$: 574.0214, found 574.0199.

$N\{2\{-2\{-4\text{-Bromophenyl}\}\{-allyl\}\}[-5\text{-fluorophenyl}\}-4\text{-methylbenzenesulfonamide (5c).}$
Following the general procedure A, 57.9 mg, 84% yield. Yellow solid, mp: 135-136 °C. \(^1\)H NMR (400 MHz, CDCl\(_3\)) (\(\delta\), ppm) 7.62 (d, \(J = 8.3\) Hz, 2H), 7.42-7.39 (m, 2H), 7.24 (d, \(J = 8.1\) Hz, 2H), 7.20-7.16 (m, 1H), 7.14-7.11 (m, 2H), 7.03-6.99 (m, 1H), 6.81-6.76 (m, 1H), 6.59 (s, 1H), 5.43 (s, 1H), 4.80 (s, 1H), 3.41 (s, 2H), 2.42 (s, 3H); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) (\(\delta\), ppm) 161.9 (d, \(J = 244.5\) Hz), 144.4, 144.3, 138.6, 136.6, 136.4 (d, \(J = 10.6\) Hz), 132.1 (d, \(J = 9.0\) Hz), 131.7, 129.9, 128.3, 127.6, 127.3, 126.6 (d, \(J = 3.4\) Hz), 122.2, 115.5, 113.0 (d, \(J = 21.1\) Hz), 111.3 (d, \(J = 25.2\) Hz), 36.9, 21.7. HRMS (TOF MS ESI\(^+\)) calculated for C\(_{22}\)H\(_{20}\)BrFNO\(_2\)S [M+H]: 460.0377, found 460.0368.

\(N\)-\{2-\{2-\{4-Bromophenyl\}\}allyl\}-5-chlorophenyl\}-4-methylbenzenesulfonamide (5d).

Following the general procedure A, 57.8 mg, 81% yield. Yellow solid, mp: 132-134 °C. \(^1\)H NMR (400 MHz, CDCl\(_3\)) (\(\delta\), ppm) 7.61 (d, \(J = 8.2\) Hz, 2H), 7.42-7.39 (comp, 3H), 7.26-7.24 (m, 2H), 7.13-7.05 (comp, 3H), 7.00-6.98 (m, 1H), 6.49 (s, 1H), 5.44 (s, 1H), 4.81 (s, 1H), 3.40 (s, 2H), 2.42 (s, 3H); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) (\(\delta\), ppm) 144.4, 144.2, 138.6, 136.6, 136.2, 133.4, 131.9, 131.7, 130.1, 129.9, 127.6, 127.3, 126.5, 124.6, 122.3, 115.6, 37.1, 21.8. HRMS (TOF MS ESI\(^+\)) calculated for C\(_{22}\)H\(_{20}\)BrClNO\(_2\)S [M+H]: 476.0081, found 476.0080.

\(N\)-\{5-Bromo-2-\{2-\{4-bromophenyl\}\}allyl\}phenyl\}-4-methylbenzenesulfonamide (5e).
Following the general procedure A, 61.7 mg, 79% yield. Yellow solid, mp: 137-138 °C. \( ^1H \) NMR (400 MHz, CDCl\(_3\)) (\( \delta \), ppm) 7.57 (d, \( J = 8.4 \) Hz, 2H), 7.53-7.50 (m, 1H), 7.37 (d, \( J = 8.4 \) Hz, 2H), 7.22-7.17 (comp, 4H), 7.08 (d, \( J = 8.5 \) Hz, 2H), 6.90 (d, \( J = 8.2 \) Hz, 1H), 6.43 (s, 1H), 5.41 (s, 1H), 4.77 (s, 1H), 3.35 (s, 2H), 2.39 (s, 3H); \( ^{13}C \) NMR (100 MHz, CDCl\(_3\)) (\( \delta \), ppm) 144.4, 144.1, 138.5, 136.6, 136.4, 132.3, 131.7, 130.8, 129.9, 129.5, 127.63, 127.61, 127.3, 122.3, 121.1, 115.6, 37.2, 21.8. HRMS (TOF MS ESI\(^+\)) calculated for C\(_{22}\)H\(_{19}\)Br\(_2\)NO\(_2\)SNa [M+Na\(^+\)]: 543.9375, found 543.9363.

\( N \)-{2-[2-(4-Bromophenyl)allyl]-3-methylphenyl}-4-methylbenzenesulfonamide (5f).

Following the general procedure A, 56.7 mg, 83% yield. Yellow solid, mp: 114-115 °C. \( ^1H \) NMR (400 MHz, CDCl\(_3\)) (\( \delta \), ppm) 7.60 (d, \( J = 8.2 \) Hz, 2H), 7.48 (d, \( J = 8.2 \) Hz, 2H), 7.26-7.21 (comp, 5H), 7.13 (t, \( J = 7.8 \) Hz, 1H), 7.05 (d, \( J = 7.4 \) Hz, 1H), 6.32 (s, 1H), 5.28 (s, 1H), 4.40 (s, 1H), 3.39 (s, 1H), 2.41 (s, 3H), 2.19 (s, 3H); \( ^{13}C \) NMR (100 MHz, CDCl\(_3\)) (\( \delta \), ppm) 143.9, 143.6, 139.6, 138.4, 137.1, 135.2, 131.6, 131.3, 129.7, 128.7, 127.5, 127.4, 127.3, 123.2, 122.1, 113.5, 32.8, 21.7, 20.0. HRMS (TOF MS ESI\(^+\)) calculated for C\(_{23}\)H\(_{23}\)BrNO\(_2\)S [M+H\(^+\)]: 456.0627, found 456.0615.

\( N \)-{2-[2-(4-Bromophenyl)allyl]-6-methylphenyl}-4-methylbenzenesulfonamide (5g).
Following the general procedure A, 56.0 mg, 82% yield. Yellow solid, mp: 157-158 °C. $^1$H NMR (400 MHz, CDCl$_3$) (δ, ppm) 7.58 (d, $J$ = 8.2 Hz, 2H), 7.39 (d, $J$ = 8.5 Hz, 2H), 7.21 (d, $J$ = 8.2 Hz, 2H), 7.13 (d, $J$ = 8.5 Hz, 2H), 7.11-7.06 (m, 2H), 7.01-6.99 (m, 1H), 5.96 (s, 1H), 5.38 (s, 1H), 4.72 (s, 1H), 3.51 (s, 2H), 2.42 (s, 3H), 2.10 (s, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$) (δ, ppm) 145.8, 143.9, 139.5, 138.4, 138.1, 137.9, 133.0, 131.5, 130.0, 129.8, 128.8, 128.2, 127.7, 127.2, 121.8, 114.6, 37.8, 21.7, 19.1. HRMS (TOF MS ESI$^+$) calculated for C$_{23}$H$_{23}$BrNO$_2$S [M+H]$^+$: 456.0627, found 456.0612.

$^N$-{2-[2-(4-Bromophenyl)allyl]-4-methylphenyl}-4-methylbenzenesulfonamide (5h).

Following the general procedure A, 53.4 mg, 78% yield. Yellow solid, mp: 149-150 °C. $^1$H NMR (400 MHz, CDCl$_3$) (δ, ppm) 7.57 (d, $J$ = 8.2 Hz, 2H), 7.40 (d, $J$ = 8.5 Hz, 2H), 7.22-7.14 (comp, 5H), 6.98 (d, $J$ = 8.1 Hz, 1H), 6.88 (s, 1H), 6.39 (s, 1H), 5.42 (s, 1H), 4.77 (s, 1H), 3.88 (s, 2H), 2.41 (s, 3H), 2.25 (s, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$) (δ, ppm) 144.8, 143.9, 139.1, 137.1, 136.8, 133.06, 133.04, 132.1, 131.6, 129.7, 128.5, 127.6, 127.3, 126.0, 121.9, 115.1, 37.3, 21.7, 21.1. HRMS (TOF MS ESI$^+$) calculated for C$_{23}$H$_{23}$BrNO$_2$S [M+H]$^+$: 456.0627, found
**N'-{2-[2-(4-Bromophenyl)allyl]-4-methoxyphenyl}-4-methylbenzenesulfonamide (5i).**

![Diagram of 5i]

Following the general procedure A, 53.8 mg, 76% yield. Yellow solid, mp: 129-130 °C. \(^1\)H NMR (400 MHz, CDCl\(_3\)) (δ, ppm) 7.55 (d, J = 8.2 Hz, 2H), 7.39 (d, J = 8.5 Hz, 2H), 7.22 (d, J = 8.2 Hz, 2H), 7.15-7.10 (comp, 3H), 6.70-6.67 (m, 1H), 6.62 (d, J = 2.8 Hz, 1H), 6.24 (s, 1H), 5.43 (s, 1H), 4.81 (s, 1H), 3.72 (s, 3H), 3.40 (s, 2H), 2.42 (s, 3H); \(^13\)C NMR (100 MHz, CDCl\(_3\)) (δ, ppm) 158.6, 144.7, 143.8, 139.0, 136.9, 136.6, 131.6, 129.7, 128.8, 127.7, 127.3, 127.2, 121.9, 116.2, 115.3, 112.5, 55.4, 37.4, 21.7. HRMS (TOF MS ESI\(^+\)) calculated for C\(_{23}\)H\(_{23}\)BrNO\(_3\)S [M+H]\(^+\): 472.0577, found 472.0565.

**N'-{2-[2-(4-Bromophenyl)allyl]phenyl}-4-chlorobenzenesulfonamide (5j).**

![Diagram of 5j]

Following the general procedure A, 52.7 mg, 76% yield. Yellow solid, mp: 134-135 °C. \(^1\)H NMR (400 MHz, CDCl\(_3\)) (δ, ppm) 7.62 (d, J = 8.6 Hz, 2H), 7.43-7.38 (comp, 4H), 7.32 (d, J = 7.8 Hz, 1H), 7.23-7.09 (comp, 5H), 6.52 (s, 1H), 5.44 (s, 1H), 4.79 (s, 1H), 3.45 (s, 2H); \(^13\)C NMR (100 MHz, CDCl\(_3\)) (δ, ppm) 144.6, 139.7, 138.8, 138.4, 134.5, 132.7, 131.7, 131.3, 129.5, 128.7, 128.1, 127.6, 127.1, 125.5, 122.2, 115.3, 37.6. HRMS (TOF MS ESI\(^+\)) calculated for C\(_{21}\)H\(_{18}\)BrClNO\(_2\)S [M+H]\(^+\): 461.9925, found 461.9918.

**N'-{2-[2-(4-Bromophenyl)allyl]phenyl}-4-nitrobenzenesulfonamide (5k).**
Following the general procedure A, 56.0 mg, 79% yield. Yellow solid, mp: 140-141 °C. ¹H NMR (400 MHz, CDCl₃) (δ, ppm) 8.27 (d, J = 8.8 Hz, 2H), 7.87 (d, J = 8.8 Hz, 2H), 7.43 (d, J = 8.4 Hz, 2H), 7.29-7.25 (m, 2H), 7.23-7.13 (comp, 4H), 6.59 (s, 1H), 5.44 (s, 1H), 4.79 (s, 1H), 3.47 (s, 2H); ¹³C NMR (100 MHz, CDCl₃) (δ, ppm) 145.56, 144.74, 138.71, 134.0, 133.0, 131.8, 131.6, 128.5, 128.3, 127.7, 127.6, 125.6, 124.4, 122.4, 115.5, 115.4, 37.8. HRMS (TOF MS ESI⁺) calculated for C₂₁H₁₇BrN₂O₄SNa [M+Na]⁺: 494.9985, found 494.9975.

**Benzyl (2-[2-(4-bromophenyl)allyl]phenyl)carbamate (5l).**

Following the general procedure A, 41.2 mg, 65% yield. Yellow solid, mp: 90-91 °C. ¹H NMR (400 MHz, CDCl₃) (δ, ppm) 7.76 (br, 1H), 7.44-7.34 (comp, 7H), 7.29-7.24 (comp, 3H), 7.17-7.15 (m, 1H), 7.09-7.06 (m, 1H), 6.54 (s, 1H), 5.48 (s, 1H), 5.18 (s, 2H), 4.90 (s, 1H), 3.73 (s, 2H); ¹³C NMR (100 MHz, CDCl₃) (δ, ppm) 154.0, 144.9, 144.8, 139.4, 136.3, 136.1, 131.7, 130.8, 128.7, 128.47, 128.45, 127.9, 127.8, 124.9, 122.0, 119.8, 115.2, 67.2, 37.8. HRMS (TOF MS ESI⁺) calculated for C₂₃H₂₀BrNO₂Na [M+Na]⁺: 444.0570, found 444.0563.

**N'-(2-{2-(4-Bromophenyl)-1-phenylallyl}benzofuran-3-yl)-4-methylbenzenesulfonamide (5m).**
Following the general procedure B in the absence of Cs₂CO₃, 56.1 mg, 67% yield. Yellow oil.

1H NMR (400 MHz, CDCl₃) (δ, ppm) 7.60 (d, J = 7.60 Hz, 2H), 7.36-7.31 (comp, 3H), 7.26-7.14 (comp, 10H), 7.04-7.69 (m, 2H), 5.99 (s, 1H), 5.51 (comp, 2H), 4.93 (s, 1H), 2.34 (s, 3H); 13C NMR (100 MHz, CDCl₃) (δ, ppm) 155.1, 153.4, 146.7, 144.2, 139.5, 138.2, 136.5, 131.5, 129.8, 129.2, 128.7, 128.3, 127.7, 127.3, 125.8, 124.5, 123.2, 121.8, 119.0, 117.2, 113.6, 111.7, 47.0, 21.7. HRMS (TOF MS ESI⁺) calculated for C₃₀H₂₅BrNO₃S [M+H]⁺: 558.0739, found: 558.0730.

**General Procedure for the Preparation of Terminal Alkenes 7 (Method C, related to Scheme 2).**

To a 10 mL oven-dried flask containing a magnetic stirring bar, sulfonaminobenzyl chloride 3a (59.2 mg, 0.2 mmol), α-methyl diazo compounds 6 (0.15 mmol), Na₂CO₃ (25.4 mg, 0.24 mmol) and DCE (2.0 mL) were added in sequence at 0 °C under argon atmosphere. The reaction mixture was stirred under these conditions for 8 h and the temperature was warmed to room temperature slowly. Then the reaction mixture was quenched with H₂O and extracted with DCM (15 × 3 mL). The organic phase was dried with anhydrous Na₂SO₄ and the solvent was evaporated under vacuum after filtration. The resulting residues was purified by column chromatography on silica gel with hexanes/ethyl acetate (10:1 to 5:1) as the eluent to give the desired pure products 7 in moderate to good or high yields.
$N$-Methyl-2-[[4-(methylphenyl)sulfonamido]benzyl]-$N$-phenylacrylamide (7a).

50.4 mg, 80% yield. Yellow solid, mp: 131-132 °C. $^1$H NMR (400 MHz, CDCl$_3$) ($\delta$, ppm) 8.68 (s, 1H), 7.71 (d, $J$ = 8.0 Hz, 2H), 7.58 (d, $J$ = 8.0 Hz, 1H), 7.34-7.24 (comp, 6H), 7.12 (t, $J$ = 7.4 Hz, 1H), 7.02 (d, $J$ = 7.3 Hz, 1H), 6.83 (d, $J$ = 7.2 Hz, 2H), 4.98 (s, 1H), 4.81 (s, 1H), 4.71 (s, 1H), 3.38 (s, 3H), 3.16 (s, 2H), 2.42 (s, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$) ($\delta$, ppm) 171.8, 144.5, 143.3, 141.8, 137.7, 135.4, 131.3, 131.1, 129.54, 129.50, 128.1, 127.4, 127.2, 126.5, 125.5, 124.9, 121.6, 38.3, 35.6, 21.7. HRMS (TOF MS ESI$^+$) calculated for C$_{24}$H$_{25}$N$_2$O$_3$S [M+H]$^+$: 421.1580, found 421.1596.

$N$-[4-Methoxyphenyl]-$N$-methyl-2-[[4-(methylphenyl)sulfonamido]benzyl]acrylamide (7b).

56.7 mg, 84% yield. Yellow solid, mp: 123-124 °C. $^1$H NMR (400 MHz, CDCl$_3$) ($\delta$, ppm) 8.57 (s, 1H), 7.65 (d, $J$ = 8.2 Hz, 2H), 7.52 (d, $J$ = 8.0 Hz, 1H), 7.23-7.18 (comp, 3H), 7.06 (t, $J$ = 7.4 Hz, 1H), 6.96 (d, $J$ = 7.4 Hz, 1H), 6.78 (d, $J$ = 8.8 Hz, 2H), 6.68 (d, $J$ = 8.2 Hz, 2H), 4.91 (s, 1H), 4.76 (s, 1H), 3.79 (s, 3H), 3.28 (s, 3H), 3.09 (s, 2H), 2.37 (s, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$) ($\delta$, ppm) 171.8, 158.6, 143.3, 141.9, 137.7, 137.4, 135.4, 131.3, 131.2, 129.6, 128.1, 127.6, 127.2, 125.5, 124.9, 121.3, 114.6, 55.6, 38.4, 35.7, 21.7. HRMS (TOF MS ESI$^+$) calculated for C$_{25}$H$_{26}$N$_2$O$_3$S [M+H]$^+$: 451.1686, found 451.1691.

$N$-[4-Chlorophenyl]-$N$-methyl-2-[[4-(methylphenyl)sulfonamido]benzyl]acrylamide
51.9 mg, 76% yield. Yellow solid, mp: 131-132 °C. $^1$H NMR (400 MHz, CDCl$_3$) ($\delta$, ppm) 8.53 (s, 1H), 7.65 (d, $J$ = 8.0 Hz, 2H), 7.51 (d, $J$ = 8.1 Hz, 1H), 7.26-7.19 (comp, 5H), 7.09 (t, $J$ = 7.4 Hz, 1H), 6.97 (d, $J$ = 7.1 Hz, 1H), 6.67 (d, $J$ = 8.5 Hz, 1H), 5.01 (s, 1H), 4.76 (s, 1H), 3.29 (s, 3H), 3.12 (s, 2H), 2.37 (s, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$) ($\delta$, ppm) 171.7, 143.4, 143.1, 141.6, 137.6, 135.3, 133.1, 131.3, 131.1, 129.7, 129.6, 128.2, 127.8, 127.2, 125.6, 125.2, 121.9, 38.3, 35.6, 21.7. HRMS (TOF MS ESI$^+$) calculated for C$_{24}$H$_{24}$ClN$_2$O$_3$S [M+H]$^+$: 455.1191, found 455.1195.

$N$-Methyl-2-[2-(4-methylphenylsulfonamido)benzyl]-$N$-(m-tolyl)acrylamide (7d).

50.2 mg, 77% yield. Yellow solid, mp: 108-109 °C. $^1$H NMR (400 MHz, CDCl$_3$) ($\delta$, ppm) 8.65 (s, 1H), 7.66 (d, $J$ = 8.0 Hz, 2H), 7.56-7.53 (m, 1H), 7.25-7.13 (comp, 4H), 7.10-7.02 (comp, 2H), 6.98-6.95 (m, 1H), 6.62-6.61 (m, 1H), 6.46 (s, 1H), 4.97 (s, 1H), 4.78 (s, 1H), 3.30 (s, 3H), 3.11 (s, 2H), 2.37 (s, 3H), 2.25 (s, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$) ($\delta$, ppm) 171.1, 144.5, 143.3, 141.8, 139.5, 137.7, 135.4, 131.4, 131.1, 129.6, 129.3, 128.2, 128.0, 127.2, 127.18, 125.6, 125.2, 123.5, 38.4, 35.7, 21.7, 21.4. HRMS (TOF MS Cl$^+$) calculated for C$_{25}$H$_{27}$N$_2$O$_3$S [M+H]$^+$: 435.1737, found 435.1740.

$N$-Methyl-2-[2-(4-methylphenylsulfonamido)benzyl]-$N$-(o-tolyl)acrylamide (7e).
32.6 mg, 50% yield. Yellow oil. $^1$H NMR (400 MHz, CDCl$_3$) (δ, ppm) 8.92 (s, 1H), 7.67 (d, $J$ = 8.0 Hz, 2H), 7.54-7.52 (m, 1H), 7.22-7.16 (comp, 5H), 7.10-7.01 (comp, 2H), 6.93-6.89 (m, 1H), 6.57-6.55 (m, 1H), 4.87 (s, 1H), 4.71 (s, 1H), 3.23 (s, 3H), 3.15 (d, $J$ = 15.2 Hz, 1H), 3.01 (d, $J$ = 15.2 Hz, 1H), 2.37 (s, 3H), 2.13 (s, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$) (δ, ppm) 171.9, 143.3, 143.2, 141.7, 137.7, 135.5, 134.5, 131.5, 131.0, 129.5, 128.2, 128.0, 127.9, 127.0, 127.3, 127.2, 125.3, 124.6, 120.9, 37.4, 35.6, 21.7, 17.5. HRMS (TOF MS Cl$^+$) calculated for C$_{25}$H$_{27}$N$_2$O$_3$S [M+H]$^+$: 435.1737, found 435.1740.

$^N$-Benzyl-2-{2-[[4-methylphenyl)sulfonamido]benzyl}$^N$-phenylacrylamide (7f).

51.4 mg, 69% yield. Yellow solid, mp: 101-102 °C. $^1$H NMR (400 MHz, CDCl$_3$) (δ, ppm) 8.55 (s, 1H), 7.64 (d, $J$ = 8.4 Hz, 2H), 7.54 (d, $J$ = 8.0 Hz, 1H), 7.23-7.14 (comp, 9H), 7.10-7.05 (comp, 3H), 6.94 (d, $J$ = 7.4 Hz, 1H), 6.56-6.54 (m, 2H), 4.95 (s, 1H), 4.93 (s, 2H), 4.77 (s, 1H), 3.09 (s, 2H), 2.37 (s, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$) (δ, ppm) 171.5, 143.3, 142.8, 141.8, 137.7, 136.7, 135.4, 131.5, 131.3, 129.6, 129.3, 128.6, 128.5, 128.2, 127.6, 127.5, 127.2, 125.7, 125.6, 121.2, 53.8, 35.8, 21.7. HRMS (TOF MS ESI$^+$) calculated for C$_{30}$H$_{29}$N$_2$O$_3$S [M+H]$^+$: 497.1893, found 497.1897.

Methyl 2-{2-[[4-methylphenyl)sulfonamido]benzyl}acrylate (7g).
30.0 mg, 58% yield. White solid, mp: 161-162 °C. \(^1\)H NMR (400 MHz, CDCl\(_3\)) (\(\delta\), ppm) 8.10 (s, 1H), 7.61 (d, \(J = 8.3\) Hz, 2H), 7.45-7.47 (m, 1H), 7.21-7.16 (comp, 3H), 7.12-7.05 (m, 2H), 6.12 (s, 1H), 5.60 (s, 1H), 3.73 (s, 3H), 3.13 (s, 2H), 2.37 (s, 3H); \(^13\)C NMR (100 MHz, CDCl\(_3\)) (\(\delta\), ppm) 168.1, 143.5, 138.8, 134.7, 132.4, 129.6, 127.9, 127.4, 127.1, 126.3, 125.6, 52.6, 33.4, 21.6. HRMS (TOF MS ESI\(^+\)) calculated for C\(_{18}\)H\(_{20}\)NO\(_4\)S [M+H]\(^+\): 346.1108, found 346.1112.

4-Bromobenzyl-2-{2-[4-(methylphenyl)sulfonamido]benzyl}acrylate (7h).

41.2 mg, 55% yield. Yellow solid, mp: 135-138 °C. \(^1\)H NMR (400 MHz, CDCl\(_3\)) (\(\delta\), ppm) 7.85 (s, 1H), 7.59 (d, \(J = 8.3\) Hz, 2H), 7.49-7.46 (m, 2H), 7.42-7.40 (m, 1H), 7.22-7.17 (comp, 5H), 7.13-7.05 (m, 2H), 6.17 (s, 1H), 5.62 (s, 1H), 5.11 (s, 2H), 3.16 (s, 2H), 2.38 (s, 3H); \(^13\)C NMR (100 MHz, CDCl\(_3\)) (\(\delta\), ppm) 167.3, 143.6, 138.8, 137.3, 134.8, 134.5, 132.4, 131.9, 130.6, 130.1, 129.7, 128.0, 127.8, 127.2, 126.5, 125.8, 122.7, 66.6, 33.5, 21.7. HRMS (TOF MS ESI\(^+\)) calculated for C\(_{24}\)H\(_{23}\)BrNO\(_4\)S [M+H]\(^+\): 500.0526, found 500.0531.

Diethyl {3-[2-(4-methylphenylsulfonamido)phenyl]prop-1-en-2-yl}phosphonate (7i).

30.5 mg, 48% yield. Yellow solid, mp: 104-105 °C. \(^1\)H NMR (400 MHz, CDCl\(_3\)) (\(\delta\), ppm) 8.14 (s,
1H), 7.60 (d, J = 8.0 Hz, 2H), 7.42-7.39 (m, 1H), 7.18-7.15 (comp, 3H), 7.11-7.05 (m, 2H), 5.88-5.83 (m, 1H), 5.63-5.51 (m, 1H), 4.09-3.91 (m, 4H), 3.17-3.13 (m, 2H), 2.36 (s, 3H), 1.23 (t, J = 7.2 Hz, 6H); 13C NMR (100 MHz, CDCl3) (δ, ppm) 143.4, 138.6, 137.5, 136.9, 134.9, 132.1 (d, J = 5.4 Hz), 130.9, 130.4 (d, J = 46.1 Hz), 129.5, 128.0, 127.1, 126.2, 125.8, 62.5 (d, J = 5.9 Hz), 34.1 (d, J = 12.7 Hz), 21.6, 16.2 (d, J = 6.2 Hz); 31P{1H} NMR (162 MHz): δ 19.1. HRMS (TOF MS ESI+) calculated for C20H27NO5PS [M+H]+: 424.1342, found 424.1350.

Methyl 2-(2-(4-fluorophenylsulfonamido)benzyl)acrylate (7j).

![Methyl 2-(2-(4-fluorophenylsulfonamido)benzyl)acrylate (7j).](image)

32.0 mg, 61% yield. Yellow oil. 1H NMR (400 MHz, CDCl3) (δ, ppm) 8.25 (br, 1H), 7.76-7.73 (m, 2H), 7.44 (d, J = 7.4 Hz, 1H), 7.24-7.19 (m, 1H), 7.15-7.08 (comp, 4H), 6.14 (s, 1H), 5.76 (s, 1H), 3.75 (s, 3H), 3.11 (s, 2H); 13C NMR (100 MHz, CDCl3) (δ, ppm) 168.1, 166.2, 163.7, 138.1, 136.1, 136.1, 134.2, 132.7, 130.5, 129.7, 129.6, 127.8, 127.5, 126.6, 125.7, 116.2, 116.0, 52.4, 33.2. HRMS (TOF MS ESI+) calculated for C17H17FNO4S [M+H]+: 350.0862, found 350.0880.

General procedure for the preparation of cyclization products 9 (Method D, related to Figure 2).
To a 10 mL oven-dried flask containing a magnetic stirring bar, sulfonaminobenzyl chloride 3a (59.2 mg, 0.20 mmol), diazo compound 8 (0.15 mmol), Na$_2$CO$_3$ (25.4 mg, 0.24 mmol) and DCE (2.0 mL) were added in sequence at 0 °C under argon atmosphere. The reaction mixture was stirred under these conditions for 8 h and the temperature was warmed to room temperature slowly. Then the reaction mixture was quenched with H$_2$O and extracted with DCM (15 X 3 mL). The organic phase was dried with anhydrous Na$_2$SO$_4$ and the solvent was evaporated under vacuum after filtration. The resulting residues was purified by column chromatography on silica gel with hexanes/ethyl acetate (10:1 to 5:1) as the eluent to give the desired pure products 9a-9c.

Methyl 2-phenyl-1-tosylindoline-2-carboxylate (9a).

33.6 mg, 55% yield. White solid, mp: 225-226 °C. $^1$H NMR (400 MHz, CDCl$_3$) (δ, ppm) 7.56-7.53 (m, 2H), 7.39-7.37 (m, 1H), 7.34-7.37 (comp, 5H), 7.20-7.16 (m, 1H), 7.11-7.07 (comp, 3H), 6.98-6.94 (m, 1H), 3.91 (d, $J$ = 16.4 Hz, 1H), 3.90 (s, 3H), 3.70 (d, $J$ = 16.4 Hz, 1H), 2.33 (s, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$) (δ, ppm) 172.3, 143.7, 141.5, 139.8, 137.2, 129.3, 128.34,
Ethoxy (1-tosylindolin-2-ylidene)methanol (9b).

32.0 mg, 62% yield. Yellow oil. $^1$H NMR (400 MHz, CDCl$_3$) ($\delta$, ppm) 8.67 (br, 1H), 7.63 (d, $J$ = 8.0 Hz, 2H), 7.49-7.47 (m, 1H), 7.24-7.20 (comp, 3H), 7.13-7.09 (m, 1H), 7.03-7.01 (m, 1H), 4.27 (q, $J$ = 7.0 Hz, 2H), 3.14 (s, 2H), 2.38 (s, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$) ($\delta$, ppm) 143.6, 137.4, 135.1, 131.5, 130.2, 130.0, 129.7, 128.7, 127.2, 126.3, 125.6, 62.0, 25.9, 21.7, 14.6. HRMS (TOF MS CI$^+$) calculated for C$_{18}$H$_{20}$NO$_3$S [M+H]$^+$: 346.1108, found 346.1119.

Methyl (phenyl)amino(1-tosylindolin-2-ylidene)methanol (9c).

42.7 mg, 70% yield. Yellow oil. $^1$H NMR (400 MHz, CDCl$_3$) ($\delta$, ppm) 9.94 (s, 1H), 7.70 (d, $J$ = 8.4 Hz, 2H), 7.60-7.58 (m, 1H), 7.39-7.35 (m, 2H), 7.33-7.29 (m, 1H), 7.25-7.20 (comp, 3H), 7.16-7.13 (m, 2H), 7.02-6.98 (m, 1H), 6.80-6.78 (m, 1H), 3.37 (s, 3H), 3.14 (s, 2H), 2.37 (s, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$) ($\delta$, ppm) 166.7, 143.2, 143.1, 137.8, 135.9, 130.4, 130.1, 129.6, 128.6, 128.2, 127.1, 126.8, 125.3, 124.7, 39.3, 28.1, 21.7. HRMS (TOF MS CI$^+$) calculated for C$_{23}$H$_{23}$N$_2$O$_3$S [M+H]$^+$: 407.1424, found 407.1435.

2,2-Diphenyl-1-tosylindoline (9d).
28.7 mg, 45% yield. White solid, mp: 227-228 °C. $^1$H NMR (400 MHz, CDCl$_3$) (δ, ppm) 7.90 (d, $J$ = 8.0 Hz, 1H), 7.55-7.51 (comp, 4H), 7.35-7.30 (comp, 7H) 7.13-7.11 (m, 1H), 7.07-7.03 (m, 1H), 6.99-6.93 (comp, 4H), 3.93 (s, 2H), 2.35 (s, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$) (δ, ppm) 143.8, 143.1, 142.2, 137.8, 132.5, 130.2, 129.2, 128.9, 128.4, 128.2, 127.8, 127.4, 126.9, 124.6, 123.2, 114.1, 78.9, 52.4, 21.5. HRMS (TOF MS Cl$^+$) calculated for C$_{27}$H$_{24}$NO$_2$S [M+H]$^+$: 426.1522, found 426.1536.

$N$-[2-(2,2-diphenylvinyl)phenyl]-4-methylbenzenesulfonamide (9d').

31.8 mg, 50% yield. Yellow solid, mp: 127-128 °C. $^1$H NMR (400 MHz, CDCl$_3$) (δ, ppm) 7.58 (d, $J$ = 8.4 Hz, 2H), 7.45-7.43 (m, 1H), 7.35-7.32 (comp, 3H), 7.25-7.09 (comp, 8H), 6.94-6.88 (comp, 3H), 6.83-6.80 (m, 1H), 6.54 (s, 1H), 6.36 (s, 1H), 2.45 (s, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$) (δ, ppm) 146.4, 143.9, 142.5, 139.0, 137.1, 134.2, 131.4, 130.7, 130.4, 129.8, 128.6, 128.5, 128.31, 128.28, 128.1, 128.0, 127.3, 125.5, 124.1, 122, 21.7. HRMS (TOF MS Cl$^+$) calculated for C$_{27}$H$_{24}$NO$_2$S [M+H]$^+$: 426.1522, found 426.1534.

Methods for further transformations (related to Figure 6 and Figure 7)

Procedure for the preparation of 12 (Liu et al., 2015).

To a 10 mL oven-dried vial containing a magnetic stirring bar, alkenylamine 4f (36.4 mg,
0.1 mmol), m-CPBA (20.7 mg, 0.12 mmol) and DCM (3.0 mL) were added in sequence, and the reaction mixture was stirred at room temperature for 36 h. After the reaction completed, DCM (10 mL) was then added and the mixture was washed with aqueous Na₂S₂O₃ (20 mL) and aqueous NaHCO₃ (20 mL) in sequence, and the organic phase was dried over MgSO₄, and the solvent was evaporated under vacuum after filtration. The resulting residues was purified by column chromatography on silica gel with hexanes/ethyl acetate (10:1 to 5:1) as the eluent to give the desired product 12 in 80% yield, 30.4 mg. Yellow oil. ¹H NMR (400 MHz, CDCl₃) (δ, ppm) 7.63 (d, J = 8.2 Hz, 1H), 7.32-7.30 (m, 2H), 7.23-7.19 (comp, 4H), 7.16-7.12 (comp, 3H), 7.03-6.98 (m, 3H), 4.83 (d, J = 11.8 Hz, 2H), 4.30 (d, J = 11.8 Hz, 1H), 3.79 (d, J = 16.4 Hz, 1H), 3.29 (d, J = 16.4 Hz, 1H), 2.32 (s, 3H), 1.68 (s, 1H), ¹³C NMR (100 MHz, CDCl₃) (δ, ppm) 143.6, 142.9, 141.6, 137.4, 129.4, 128.7, 128.5, 127.9, 126.9, 126.3, 124.9, 123.3, 113.7, 76.4, 66.5, 44.2, 21.6. HRMS (TOF MS Cl⁺) calculated for C₂₂H₂₂NO₃S [M+H⁺]: 380.1315, found 380.1326.

Procedure for the preparation of 13 (Ferrand et al., 2017).

To an oven-dried schlenk flask containing a magnetic stirring bar, NbCl₅ (2.5 mol %, 0.0025 mmol, 0.7 mg) and AgNTf₂ (5 mol %, 0.005 mmol, 2.0 mg), and fresh distilled DCE (1.5 mL) were added under argon atmosphere. The reaction mixture was allowed to stir at 80 °C for 10 min. Then a solution of alkenylamine 4a (1.0 equiv., 44.2 mg, 0.1 mmol) in DCE (1.5 mL) was added via syringe. The reaction mixture was allowed to stir at 80 °C for 6 h, then filtered through a pad of silica, washed with Et₂O, and the solvent was evaporated under vacuum. The resulting residues was purified by flash chromatography on silica gel with hexanes/ethyl acetate (20:1 to 10:1) as the eluent to afforded desired product 13 in 66% yield, 29.2 mg. Yellow solid, 131-132 °C. ¹H NMR (400 MHz, CDCl₃) (δ, ppm) 7.67 (d, J = 8.4
Hz, 1H), 7.49 (d, J = 8.0 Hz, 2H), 7.33 (d, J = 8.8 Hz, 2H), 7.28-7.23 (comp, 3H), 7.16-7.11 (comp, 3H), 7.04-7.00 (m, 1H), 3.35 (q, J = 16.4 Hz, 2H), 2.39 (s, 3H), 2.13 (s, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$) ($\delta$, ppm) 144.4, 143.5, 142.4, 138.4, 131.3, 129.4, 128.2, 127.71, 127.69, 126.8, 125.1, 123.1, 121.5, 113.8, 72.1, 49.2, 27.1, 21.6. HRMS (TOF MS CI$^+$) calculated for C$_{22}$H$_{21}$BrNO$_2$S [M+H]$^+$: 442.0471, found 442.0477.

**Procedure for the preparation of 14 (Li et al., 2017).**

![Reaction Scheme](image)

To an oven-dried schlenk flask containing a magnetic stirring bar, alkenylamine $4a$ (1 equiv., 44.2 mg, 0.1 mmol) and thiols (18.6 mg, 0.15 mmol), NFSI (47.3 mg, 0.15 mmol), CuCl (2.0 mg, 20 mol%), B$_2$Pin$_2$ (5.1 mg, 20 mol%), and CH$_3$CN (1.5 mL) were added under argon atmosphere. Then the mixture was heated to 45 °C for 15 h. After the reaction was completed (monitored by TLC), it was cooled to room temperature and concentrated under reduced pressure. The residues was purified by flash chromatography on silica gel with hexanes/ethyl acetate (20:1 to 10:1) as the eluent to give the desired product $14$ in 75% yield, 42.3 mg. $^1$H NMR (400 MHz, CDCl$_3$) ($\delta$, ppm); 7.73 (d, J = 8.4 Hz, 1H), 7.34-7.32 (m, 2H), 7.30-7.27 (m, 1H), 7.21-7.18 (comp, 4H), 7.15-7.07 (comp, 5H), 7.06-7.01 (comp, 3H), 4.29 (d, J = 12.4 Hz, 1H), 4.13 (d, J = 12.4 Hz, 1H), 3.90 (d, J = 16.8 Hz, 1H), 3.49 (d, J = 16.8 Hz, 1H), 2.37 (s, 3H), 2.36 (s, 3H). $^{13}$C NMR (100 MHz, CDCl$_3$) ($\delta$, ppm) 143.5, 142.6, 140.6, 137.8, 136.9, 132.9, 131.1, 130.9, 130.0, 129.2, 128.9, 128.3, 127.9, 126.6, 124.9, 123.3, 122.3, 113.8, 74.1, 45.9, 44.9, 21.6, 21.2. HRMS (TOF MS CI$^+$) calculated for C$_{29}$H$_{27}$BrNO$_2$S$_2$ [M+H]$^+$: 564.0661, found 564.0665.

**Procedure for the Preparation of 15 (Yin et al., 2014).**
To a 5 mL oven-dried vial containing a magnetic stirring bar, alkenylamine 4f (1.0 equiv., 44.2 mg, 0.10 mmol), CaCl₂ (55.6 mg, 0.50 mmol), and dry acetic acid (0.8 mL) were added at room temperature. After stirring for 5 minutes at room temperature, Pd(OAc)₂ (1.2 mg, 0.01 mmol) and H₂O₂ (30% aq wt., 23 μL, 0.20 mmol) were added, and the reaction mixture was stirred at room temperature for about 30 h. Until 4f was consumed (monitored by thin layer chromatography). Diethyl ether (15 mL) was added and the mixture was filtered through a pad of Celite to remove the solid. Then the mixture was concentrated in vacuum and the resulting residues was purified by silica gel column chromatography with hexanes/ethyl acetate (20:1 to 10:1) as the eluent to give the corresponding product 15 in 70% yield, 41.7 mg. 

1H NMR (400 MHz, CDCl₃) (δ, ppm) 7.54 (d, J = 8.7 Hz, 1H), 7.27-7.13 (comp, 8H), 7.08 (d, J = 8.4 Hz, 2H), 6.97 (d, J = 8.1 Hz, 2H), 4.65 (dd, J = 40.8, 11.4 Hz, 2H), 3.87 (d, J = 17.2 Hz, 1H), 3.47 (d, J = 17.3 Hz, 1H), 2.31 (s, 3H); 13C NMR (100 MHz, CDCl₃) (δ, ppm) 143.7, 141.2, 139.9, 137.0, 129.8, 129.2, 128.4, 128.3, 128.2, 128.1, 127.1, 126.9, 124.9, 114.3, 74.8, 49.9, 45.1, 21.6. HRMS (TOF MS CI⁺) calculated for C₂₂H₂₁ClNO₂S [M+H]⁺: 398.0976, found 398.0983.

Procedure for the preparation of 16.

To a 10 mL oven-dried vial containing a magnetic stirring bar, 7h (51.8 mg, 0.15 mmol) in dry THF (5.0 mL), was added Lithium aluminium hydride (28.5 mg, 0.75 mmol) at 0 °C. The reaction mixture was stirred under this condition for 3 h and the temperature was warmed to room temperature slowly. Then reaction was quenched with Na₂SO₄·10H₂O, filtered through
a pad of Celite and washed with EtOAc (15 mL). The filtrate was concentrated under reduced
pressure to give crude product. The obtained residues was purified by flash column
chromatography on silica gel (Hexanes : EtOAc = 20:1 to 10:1) to give the pure product 16
in 82% yield, 39.0 mg, yellow oil. ¹H NMR (400 MHz, CDCl₃) (δ, ppm) 7.68 (d, J = 8.4 Hz, 1H),
7.57 (d, J = 8.0 Hz, 2H), 7.23 (d, J = 8.4 Hz, 2H), 7.19-7.14 (m, 1H), 7.08-7.02 (m, 2H), 4.13-
4.08 (m, 1H), 3.54 (d, J = 6.4 Hz, 2H), 3.48-3.43 (m, 1H), 2.64-2.59 (m, 1H), 2.39 (s, 3H), 2.29-
2.23 (m, 1H), 2.00-1.95 (m, 1H), 1.74 (br, 1H); ¹³C NMR (100 MHz, CDCl₃) (δ, ppm) 143.8, 137.2,
136.9, 129.8, 129.5, 129.3, 127.1, 126.7, 124.9, 123.9, 64.4, 48.4, 35.3, 29.5, 21.7. HRMS (TOF
MS Cl⁺) calculated for C₁₇H₂₀NO₃S [M+H]⁺: 318.1158, found 318.1156.

Procedure for the preparation of 17.

To a 10 mL oven-dried vial containing a magnetic stirring bar, 7a (63.0 mg, 0.15 mmol)
in dry THF (5 mL), was added Lithium aluminium hydride (28.5 mg, 0.75 mmol) at 0 °C. The
reaction mixture was stirred under this condition for 3 h and the temperature was warmed to
room temperature slowly. Then reaction was quenched with Na₂SO₄·10H₂O, filtered through
a pad of Celite and washed with EtOAc (15 mL). The filtrate was concentrated under reduced
pressure to give crude product. The obtained residues was purified by flash column
chromatography on silica gel (Hexanes : EtOAc = 20:1 to 10:1) to give the pure product 17
in 70% yield, 42.6 mg, yellow oil. ¹H NMR (400 MHz, CDCl₃) (δ, ppm) 7.56 (br, 1H), 7.45-7.39
(comp, 3H), 7.29-7.25 (m, 2H), 7.23-7.19 (m, 1H), 7.13-7.07 (comp, 4H), 6.88-6.82 (comp, 3H),
5.02 (s, 1H), 4.79 (s, 1H), 3.61 (s, 2H), 2.94 (s, 2H), 2.89 (s, 3H), 2.33 (s, 3H); ¹³C NMR (100 MHz,
CDCl₃) (δ, ppm) 143.6, 137.2, 135.4, 131.9, 130.9, 129.6, 129.4, 127.9, 127.1, 126.2, 124.8,
118.94, 118.91, 114.9, 114.35, 114.34, 58.3, 39.7, 36.2, 21.7. HRMS (TOF MS Cl⁺) calculated
for C₂₅H₂₇N₂O₃S [M+H]⁺: 407.1788, found 407.1790.
Procedure for the preparation of 18.

To a 10 mL oven-dried vial containing a magnetic stirring bar, 7j (52.4 mg, 0.15 mmol) in dry THF (2 mL) was added DBU (27.4 mg, 1.2 equiv.). The reaction mixture was stirred under this condition for 8 h. When the reaction was completed (monitored by TLC), the reaction mixture was quenched by saturated NH₄Cl (aq), extracted with ethyl acetate (15 X 3 mL), and washed with brine (50 mL). The organic phase was dried with Na₂SO₄ and evaporated in vacuo. The resulting residue was purified by the flash column to afford the product 18 in 93% yield. After that, according to the literature, inhibitor Mcl-1 can be easily obtained within two steps. ¹H NMR (400 MHz, CDCl₃) (δ, ppm) 7.76 (d, J = 7.8 Hz, 1H), 7.65-7.62 (m, 2H), 7.24-7.20 (m, 1H), 7.14-7.05 (comp, 4H), 4.45-4.40 (m, 1H), 3.70 (s, 3H), 3.54-3.48 (m, 1H), 2.77-2.64 (m, 2H), 2.60-2.52 (m, 1H); ¹³C NMR (100 MHz, CDCl₃) (δ, ppm) 172.7, 166.7, 164.1, 136.0, 135.5, 135.5, 130.0, 129.9, 129.4, 128.8, 127.2, 125.9, 125.0, 116.7, 116.5, 52.4, 47.5, 38.1, 29.3.

Methods for mechanistic studies

To a 10 mL oven-dried vial containing a magnetic stirring bar, hydrazone 2f-d (41.2 mg, 0.30 mmol), N-(2-chloromethylaryl) amide 3a (44.4 mg, 0.15 mmol), Na₂CO₃ (31.8 mg, 2.0 equiv.), PhIO (66.0 mg, 0.30 mmol), and DCE (2.0 mL) were added in sequence under argon atmosphere at -40 °C under the irradiation of visible light (8 W CFL). The reaction was stirred for 10 h under these conditions and the reaction temperature warmed to room temperature.
slowly in this period of time. When the reaction was completed (monitored by TLC), the solid was removed by filtering through a pad of Celite with Teflon filter (0.22 \( \mu m \)) at the bottom. And the filtrate was evaporated \textit{in vacuo}. The resulting residue was directly subjected to proton NMR analysis with CDCl\(_3\) as the solvent without any further purification (see fig. S115). According to this spectrum, 94\% proton was transferred from methyl group to the \textit{N}.

![Chemical Reaction](image)

To a 10 mL oven-dried flask containing a magnetic stirring bar, hydrazone \(2a\) and \(2a-d\) (each on a 0.3 mmol scale in separated vial), anhydrous MgSO\(_4\) (50 mg), MnO\(_2\) (208.1 mg, 8.0 equiv), and 1,2-dichloroethane (3.0 mL) were added in sequence under argon atmosphere. Then the flask was wrapped in foil and the reaction mixture was allowed to stir for 45 min at 0 °C. After that, removing the solid by filtering through a pad of Celite with Teflon filter (0.22 \( \mu m \)) at the bottom, we could obtain the two pink solutions. Then two obtained pink solutions were mixed.

To a 10 mL oven-dried vial, which contains a magnetic stirring bar, \(N(2\text{-chloromethylaryl})\) amide \(3a\) (44.4 mg, 0.15 mmol), Cs\(_2\)CO\(_3\) (97.7 mg, 2.0 equiv) under argon atmosphere, the above-mentioned mixed pink solution was added via syringe at -40 °C. The reaction was carried out by irradiation of visible light (8 W CFL) and warm to room temperature slowly. When the reaction was completed (monitored by TLC), the reaction mixture was quenched by saturated NH\(_4\)Cl (aq), extracted with ethyl acetate (15 X 3 mL), and washed with brine (50 mL). The organic phase was dried with Na\(_2\)SO\(_4\) and evaporated \textit{in vacuo}. The resulting residue was directly subjected to proton NMR analysis with CDCl\(_3\) as the solvent without any further purification (see fig. S114). According to this spectrum, \(4a/4a-d = 1.4:1\).
To a 10 mL oven-dried flask containing a magnetic stirring bar, hydrazone 2a (63.9 mg, 0.3 mmol), anhydrous MgSO₄ (50 mg), MnO₂ (208.1 mg, 8.0 equiv), and 1,2-dichloroethane (3.0 mL) were added in sequence under argon atmosphere. Then the flask was wrapped in foil and the reaction mixture was allowed to stir for 45 min at 0 °C. After that, removing the solid by filtering through a pad of Celite with Teflon filter (0.22 μm) at the bottom, we could obtain the pink solution as the diazo compound 1a.

Then to a 10 mL oven-dried vial, which contains a magnetic stirring bar, was added the obtained pink solutions at -40 °C under argon atmosphere. The reaction was carried out by irradiation of visible light (8 W CFL) and warm to room temperature slowly. When the reaction was completed (monitored by TLC), the reaction mixture was quenched by saturated NH₄Cl (aq), extracted with ethyl acetate (15 X 3 mL), and washed with brine (50 mL). The organic phase was dried with Na₂SO₄ and evaporated in vacuo. The resulting residue was purified by the flash column to afford the hydrazines product in 80% yield, and the data of NMR is consistence with the literature. ¹H NMR (400 MHz, CDCl₃) (δ, ppm) 7.78 (d, J = 7.8 Hz, 4H), 7.55 (d, J = 7.8 Hz, 4H), 2.29 (s, 6H); ¹³C NMR (100 MHz, CDCl₃) (δ, ppm) 157.5, 137.3, 131.7, 128.3, 124.3, 15.0.
To a 10 mL oven-dried flask containing a magnetic stirring bar, hydrazone 2a (95.9 mg, 0.45 mmol), anhydrous MgSO$_4$ (60 mg), MnO$_2$ (312.0 mg, 8.0 equiv), and 1,2-dichloroethane (3.0 mL) were added in sequence under argon atmosphere. Then the flask was wrapped in foil and the reaction mixture was allowed to stir for 45 min at 0 °C. After that, removing the solid by filtering through a pad of Celite with Teflon filter (0.22 μm) at the bottom, we could obtain the pink solution.

To a 10 mL oven-dried vial, which contains a magnetic stirring bar, N-(2-chloromethylaryl) amide 3a (44.4 mg, 0.15 mmol), Cs$_2$CO$_3$ (97.7 mg, 2.0 equiv) under argon atmosphere, the above-mentioned mixed pink solution was added via syringe at -40 °C. For the condition A: The reaction was carried out under the dark and warm to room temperature slowly. When the reaction was completed, when the reaction was completed (monitored by TLC), the reaction mixture was quenched by saturated NH$_4$Cl (aq), extracted with ethyl acetate (15 X 3 mL), and washed with brine (50 mL). The organic phase was dried with Na$_2$SO$_4$ and evaporated in vacuo. The resulting residue was purified by the flash column to afford 4f in 55% yield. For the condition B: The reaction was the same to condition A except by irradiation of visible light (8 W CFL) rather than under the dark. And the isolated yield is 80%. For the condition C: The reaction was the same to condition B except adding 2.0 equiv. TEMPO, and the isolated yield is 40%.

To a 10 mL oven-dried flask containing a magnetic stirring bar, hydrazone 2a (95.9 mg, 0.45 mmol), anhydrous MgSO$_4$ (60 mg), MnO$_2$ (312.0 mg, 8.0 equiv), and 1,2-dichloroethane (3.0 mL) were added in sequence under argon atmosphere. Then the flask was wrapped in foil and the reaction mixture was allowed to stir for 45 min at 0 °C. After that, removing the solid by filtering through a pad of Celite with Teflon filter (0.22 μm) at the bottom, we could obtain the pink solution.

To a 10 mL oven-dried vial, which contains a magnetic stirring bar, N-(2-chloromethylaryl)
amide 3a (44.4 mg, 0.15 mmol), Cs₂CO₃ (97.7 mg, 2.0 equiv) under argon atmosphere, the above-mentioned mixed pink solution was added via syringe at -40 °C. The reaction was carried out under the dark or by irradiation of visible light (8 W CFL) and warm to room temperature slowly. After 40 min, the solution of DMPO in 1,2-dichoroethane was added via syringe rapidly. Then after 5 min or 20 min, the reaction mixture was directly subjected to electron paramagnetic resonance (EPR) analysis (see fig. S5).

**Computational Methods (related to Figure 4 and Figure 5)**

All structures were optimized with the M06 (Zhao et al., 2008) density functional theory method combined with the 6-31G(d) (Hariharan et al., 1973) basis set for C, H, O, N, S atoms. Vibrational frequency analyses at the same level of theory were performed on all optimized structures to characterize stationary points as local minima or transition states. Further, intrinsic reaction coordinate (IRC) computations were carried out to confirm that transition states connect appropriate reactants and products. The gas-phase Gibbs free energies for all species were obtained at 298.15 K and 1 atm at their respective optimized structures. To consider solvation effects, single-point energy computations using the SMD model (Marenich et al., 2009) with dichloroethane as solvent were performed based on the optimized gas-phase geometries of all species. The basis sets, 6-311++G(d,p) for C, H, O, N, S atoms, were utilized for single-point energy calculations on stationary points. The solution-phase Gibbs free energy was determined by adding the solvation single-point energy and the gas-phase thermal correction to the Gibbs free energy obtained from the vibrational frequencies. Unless otherwise specified, the solution-phase Gibbs free energy was used in the present discussions. The Gaussian 09 suite of programs (Frisch et al., 2010) was used throughout.

**Cartesian Coordinates and Energies**

| Center Number | Atomic Number | Atomic Type | Coordinates (Angstroms) | X    | Y    | Z    |
|---------------|---------------|-------------|-------------------------|------|------|------|
| 1             | 6             | 0           | 2.320160                | 1.009128 | -0.000090 |
| 2             | 6             | 0           | 0.946468                | 1.218348 | -0.000023 |
| 3             | 6             | 0           | 0.059470                | 0.133078 | 0.000087 |
| 4             | 6             | 0           | 0.594998                | -1.164141 | 0.000101 |
| 5             | 6             | 0           | 1.966115                | -1.364303 | 0.000053 |
| 6             | 6             | 0           | 2.840264                | -0.279705 | 0.000049 |
| 7             | 1             | 0           | 2.989005                | 1.868486 | -0.000211 |
| 8             | 1             | 0           | 0.560263                | 2.236423 | 0.000033 |
| 9             | 1             | 0           | -0.071887               | -2.026293 | 0.000178 |
| 10            | 1             | 0           | 2.357401                | -2.380381 | 0.000103 |
| 11            | 1             | 0           | 3.916659                | -0.439206 | -0.000082 |
Zero-point correction=                           0.142956 (Hartree/Particle)
Thermal correction to Energy=                    0.151745
Thermal correction to Enthalpy=                  0.152690
Thermal correction to Gibbs Free Energy=         0.108903
Sum of electronic and zero-point Energies=       -418.664951
Sum of electronic and thermal Energies=          -418.656161
Sum of electronic and thermal Enthalpies=        -418.655217
Sum of electronic and thermal Free Energies=     -418.699004
M06/6-311++G(d,p)/SMD//M06/6-31G(d) energy =    -418.91751654

3a'

| Center | Atomic Number | Atomic Number | Atomic Type | Coordinates (Angstroms) |
|--------|----------------|----------------|-------------|-------------------------|
| 1      | 6              | 0              |             | 2.292961 -0.124163 -1.241462 |
| 2      | 6              | 0              |             | 1.952463 0.079209 0.155070 |
| 3      | 6              | 0              |             | 2.814149 -0.623172 1.153224 |
| 4      | 6              | 0              |             | 3.863011 -1.506991 0.682718 |
| 5      | 6              | 0              |             | 4.100836 -1.673347 -0.632977 |
| 6      | 6              | 0              |             | 3.298733 -0.957952 -1.593805 |
| 7      | 1              | 0              |             | 1.717260 0.404480 -1.993247 |
| 8      | 1              | 0              |             | 4.457514 -2.023003 1.436114 |
| 9      | 1              | 0              |             | 4.892380 -2.332314 -0.982091 |
| 10     | 1              | 0              |             | 3.513520 -1.102675 -2.652453 |
| 11     | 6              | 0              |             | 2.637209 -0.424938 2.473692 |
| 12     | 1              | 0              |             | 1.871903 0.253845 2.840995 |
| 13     | 1              | 0              |             | 3.639387 -0.937664 3.201189 |
| 14     | 7              | 0              |             | 0.973804 0.780072 0.653051 |
| 15     | 16             | 0              |             | -0.141445 1.664619 -0.232149 |
| 16     | 8              | 0              |             | -0.423925 2.840997 0.573003 |
| 17     | 8              | 0              |             | 0.197983 1.828828 -1.645702 |
| 18     | 6              | 0              |             | -1.528083 0.561801 -0.131800 |
| 19     | 6              | 0              |             | -2.360723 0.620949 0.980104 |
| 20     | 6              | 0              |             | -1.743199 -0.363022 -1.147336 |
| 21     | 6              | 0              |             | -3.428657 -0.260855 1.066795 |
| 22     | 1              | 0              |             | -2.168638 1.362653 1.753048 |
| 23     | 6              | 0              |             | -2.814492 -1.239275 -1.042748 |
| 24     | 1              | 0              |             | -1.083095 -0.378308 -2.013061 |
| 25     | 6              | 0              |             | -3.671939 -1.199029 0.059933 |
| 26     | 1              | 0              |             | -4.091886 -0.223163 1.931233 |
| 27     | 1              | 0              |             | -2.996464 -1.967285 -1.833588 |
| 28     | 6              | 0              |             | -4.848672 -2.123159 0.145391 |
| 29     | 1              | 0              |             | -5.740088 -1.670129 -0.310833 |
| 30     | 1              | 0              |             | -4.660855 -3.066955 -0.380626 |
| 31     | 1              | 0              |             | -5.103093 -2.358006 1.186053 |

Zero-point correction=                           0.239970 (Hartree/Particle)
Thermal correction to Energy=                    0.256243
Thermal correction to Enthalpy = 0.257187
Thermal correction to Gibbs Free Energy = 0.192787
Sum of electronic and zero-point Energies = -1143.808911
Sum of electronic and thermal Energies = -1143.792638
Sum of electronic and thermal Enthalpies = -1143.791694
Sum of electronic and thermal Free Energies = -1143.856094

M06/6-311++G(d,p)/SMD//M06/6-31G(d) energy = -1144.27268306

N2

| Center | Atomic Number | Atomic Type | Coordinates (Angstroms) |
|--------|----------------|-------------|-------------------------|
|        |                |             | X       | Y       | Z         |
| 1      | 7              | 0           | 0.000000 | 0.000000 | 0.552597 |
| 2      | 7              | 0           | 0.000000 | 0.000000 | -0.552597|

Zero-point correction = 0.005622 (Hartree/Particle)
Thermal correction to Energy = 0.007983
Thermal correction to Enthalpy = 0.008927
Thermal correction to Gibbs Free Energy = -0.012827
Sum of electronic and zero-point Energies = -109.453327
Sum of electronic and thermal Energies = -109.450967
Sum of electronic and thermal Enthalpies = -109.450023
Sum of electronic and thermal Free Energies = -109.471777
M06/6-311++G(d,p)/SMD//M06/6-31G(d) energy = -109.48474327

'TS1'

| Center | Atomic Number | Atomic Type | Coordinates (Angstroms) |
|--------|----------------|-------------|-------------------------|
|        |                |             | X       | Y       | Z         |
| 1      | 6              | 0           | -0.181548 | 3.571807 | 0.086311 |
| 2      | 6              | 0           | -0.253712 | 2.199724 | 0.489423 |
| 3      | 6              | 0           | -1.547221 | 1.716131 | 0.937601 |
| 4      | 6              | 0           | -2.694752 | 2.553470 | 0.847378 |
| 5      | 6              | 0           | -2.586765 | 3.847920 | 0.426449 |
| 6      | 6              | 0           | -1.308536 | 4.346387 | 0.056664 |
| 7      | 1              | 0           | 0.779828  | 3.985233 | -0.208928|
| 8      | 1              | 0           | -3.656520 | 2.139940 | 1.155684 |
| 9      | 1              | 0           | -3.457399 | 4.498207 | 0.384838 |
| 10     | 1              | 0           | -1.223823 | 5.382558 | -0.269486|
| 11     | 6              | 0           | -1.650998 | 0.386152 | 1.343702 |
| 12     | 7              | 0           | 0.714174  | 1.285878 | 0.432221 |
| 13     | 16             | 0           | 2.118976  | 1.646191 | -0.339455|
| 14     | 8              | 0           | 1.862784  | 1.821618 | -1.775079|
| 15     | 8              | 0           | 2.906589  | 2.664511 | 0.356750 |
| 16     | 6              | 0           | 2.945415  | 0.082183 | -0.140197|
| 17     | 6              | 0           | 2.962142  | -0.820480| -1.195334|
| 18     | 6              | 0           | 3.546161  | -0.226871| 1.075373 |
| 19     | 6              | 0           | 3.590061  | -2.049979| -1.027610|
| 20     | 1              | 0           | 2.496240  | -0.543656| -2.139935|
| 21     | 6              | 0           | 4.163604  | -1.459391| 1.229637 |
| 22     | 1              | 0           | 3.528163  | 0.501234 | 1.884742 |
| 23     | 6              | 0           | 4.197499  | -2.386079| 0.182369 |
| 24     | 1              | 0           | 3.614102  | -2.762776| -1.852445|
| 25     | 1              | 0           | 4.637332  | -1.712338| 2.178791 |
| 26     | 6              | 0           | 4.900463  | -3.699503| 0.350620 |
Zero-point correction = 0.385056 (Hartree/Particle)
Thermal correction to Energy = 0.410107
Thermal correction to Enthalpy = 0.411051
Thermal correction to Gibbs Free Energy = 0.329926
Sum of electronic and zero-point Energies = -1562.480026
Sum of electronic and thermal Energies = -1562.454975
Sum of electronic and thermal Enthalpies = -1562.454030
Sum of electronic and thermal Free Energies = -1562.535156

M06/6-311++G(d,p)/SMD//M06/6-31G(d)  energy = -1563.20003768

| Center Number | Atomic Number | Atomic Type | Coordinates (Angstroms) |
|---------------|---------------|-------------|-------------------------|
|               |               |             | X    | Y    | Z    |
| 1             | 6             | 0           | 0.437529 | 3.701445 | -0.217475 |
| 2             | 6             | 0           | 0.627988 | 2.322856 | -0.443910 |
| 3             | 6             | 0           | 1.929574 | 1.884488 | -0.770258 |
| 4             | 6             | 0           | 2.975457 | 2.795249 | -0.884899 |
| 5             | 6             | 0           | 2.771026 | 4.153919 | -0.686269 |
| 6             | 6             | 0           | 1.493602 | 4.590360 | -0.346646 |
| 7             | 1             | 0           | -0.552800 | 4.071184 | 0.030802 |
| 8             | 1             | 0           | 3.971000 | 2.421593 | -1.32260 |
| 9             | 1             | 0           | 3.593558 | 4.858942 | -0.786049 |
| 10            | 1             | 0           | 1.308500 | 5.650531 | -0.178337 |
| 11            | 6             | 0           | 2.190677 | 0.422976 | -0.926726 |
| 12            | 7             | 0           | -0.360714 | 1.340951 | -0.397843 |
| 13            | 16            | 0           | -1.694993 | 1.661232 | 0.513724 |
| 14            | 8             | 0           | -1.380346 | 1.620386 | 1.948546 |
| 15            | 8             | 0           | -2.431154 | 2.824028 | 0.009728 |
| 16            | 6             | 0           | -2.674675 | 0.225111 | 0.146641 |
| 17            | 6             | 0           | -3.228053 | -0.494382 | 1.197740 |
| 18            | 6             | 0           | -2.915967 | -0.137988 | -1.175927 |
|   |   |   | X       | Y       | Z       |
|---|---|---|---------|---------|---------|
| 19| 6 | 0  | -4.017281 | -1.603964 | 0.918988 |
| 20| 1 | 0  | -3.014590 | -0.189900 | 2.220431 |
| 21| 6 | 0  | -3.696860 | -1.253400 | -1.437239 |
| 22| 1 | 0  | -2.470409 | 0.441921  | 1.982159  |
| 23| 6 | 0  | -4.259913 | -2.000330 | -0.396253 |
| 24| 1 | 0  | -4.449502 | -2.179857 | 1.737600  |
| 25| 1 | 0  | -3.881206 | -1.556550 | -2.468770 |
| 26| 6 | 0  | -5.123863 | -3.188214 | -0.695188 |
| 27| 1 | 0  | -2.470409 | 0.441921  | 1.982159  |
| 28| 6 | 0  | -4.449502 | -2.179857 | 1.737600  |
| 29| 1 | 0  | -3.881206 | -1.556550 | -2.468770 |
| 30| 6 | 0  | -5.123863 | -3.188214 | -0.695188 |
| 31| 6 | 0  | -3.409348 | -2.281600 | 1.102816  |
| 32| 6 | 0  | -2.488322 | -1.820359 | 0.162632  |
| 33| 6 | 0  | -2.19773  | -2.619916 | -0.948408 |
| 34| 6 | 0  | -2.814680 | -3.852445 | -1.116262 |
| 35| 6 | 0  | 3.763024  | -4.303634 | -0.170442 |
| 36| 1 | 0  | 4.751565  | -3.857460 | 1.674011  |
| 37| 1 | 0  | 3.660117  | -1.680576 | 1.973471  |
| 38| 1 | 0  | 1.475975  | -2.283801 | -1.691362 |
| 39| 1 | 0  | 2.571468  | -4.464240 | -1.977990 |
| 40| 1 | 0  | 4.218071  | -5.270931 | -0.297723 |
| 41| 6 | 0  | 1.858157  | -0.449438 | 0.294369  |
| 42| 6 | 0  | 2.067452  | 0.249302  | 1.621867  |
| 43| 1 | 0  | 3.098966  | 0.622022  | 1.660625  |
| 44| 1 | 0  | 1.394072  | 1.105775  | 1.718499  |
| 45| 1 | 0  | 1.889448  | -0.427922 | 2.463910  |
| 46| 1 | 0  | 3.261171  | 0.251412  | -1.112749 |
| 47| 1 | 0  | 1.659345  | 0.005935  | -1.796526 |
| 48| 7 | 0  | 0.324082  | -0.705080 | 0.253908  |
| 49| 7 | 0  | -0.461361 | -1.507705 | 0.342939  |

Zero-point correction= 0.387158 (Hartree/Particle)
Thermal correction to Energy= 0.412163
Thermal correction to Enthalpy= 0.413107
Thermal correction to Gibbs Free Energy= 0.331037
Sum of electronic and zero-point Energies= -1562.503468
Sum of electronic and thermal Energies= -1562.478464
Sum of electronic and thermal Enthalpies= -1562.477519
Sum of electronic and thermal Free Energies= -1562.559589

**TS2**

|   |   |   | X       | Y       | Z       |
|---|---|---|---------|---------|---------|
| 1 | 6 | 0  | 0.796750 | 3.370188 | 0.203587 |
| 2 | 6 | 0  | 0.622948 | 2.100471 | -0.380000 |
| 3 | 6 | 0  | 1.732046 | 1.505727 | -1.031599 |
| 4 | 6 | 0  | 2.942720 | 2.184543 | -1.122237 |
| 5 | 6 | 0  | 3.094572 | 3.447353 | -0.561094 |
| 6 | 6 | 0  | 2.013352 | 4.026163 | 0.102606 |
| 7 | 1 | 0  | -0.034960 | 3.840003 | 0.724371 |
| 8 | 1 | 0  | 3.773984 | 1.716420 | -1.654418 |
| 9 | 1 | 0  | 4.039753 | 3.978788 | -0.650256 |
| 10| 1 | 0  | 2.120611 | 5.013087 | 0.550795 |
11  6  0  1.521608  0.159420 -1.670644
12  7  0  -0.516973  1.325371 -0.375293
13  16  0  -1.786879  1.760509  1.982597
14  1  0  -3.330361  0.985178 -1.725675
15  8  0  -2.478593  2.940159  0.020124
16  8  0  -1.437997  1.760509  1.982597
17  6  0  -3.432379  0.196078 -0.982169
18  6  0  -2.930544 -0.641618  1.231032
19  6  0  -4.168164 -0.949798 -1.242892
20  1  0  -3.330361  0.985178 -1.725675
21  6  0  -2.806859  0.335867  0.254281
22  6  0  -3.432379  0.196078 -0.982169
23  6  0  -4.301396 -1.783608 -0.982169
24  1  0  -4.658936 -1.071063 -2.209613
25  1  0  -3.786777 -2.555233  1.720118
26  6  0  -5.123081 -3.175922 -0.569562
27  1  0  -4.972978 -3.955350  0.186895
28  1  0  -4.877676 -3.603083 -1.550776
29  1  0  -6.195487 -2.937267  0.586552
30  6  0  -3.569621 -3.826953  0.318097
31  6  0  -3.435327 -1.756974 -0.224483
32  6  0  -3.567051 -1.046539  0.208903
33  6  0  -4.787888 -1.719791  0.687643
34  6  0  -4.685471 -3.112280  0.738724
35  6  0  -3.569030 -4.914192  0.356596
36  1  0  -1.584595 -3.731412 -0.476787
37  1  0  -3.553793  0.042615  0.189846
38  1  0  -5.545128 -1.155669  1.025641
39  1  0  -5.560913 -3.639390  1.113060
40  1  0  -1.263329 -1.036258 -0.757818
41  1  0  -0.669434  0.229961 -2.360616
42  1  0  -2.409042 -0.110729 -2.263122
43  7  0  -0.583627 -0.314127  0.820261
44  7  0  -0.562159 -0.391405  1.934309
45  6  0  -0.038576 -1.809816 -1.133739
46  1  0  -0.235139 -2.582904 -0.408491
47  1  0  -0.229995 -2.284425 -2.108009
48  1  0  -0.799772 -1.113262 -1.254550
49  1  0  -0.799772 -1.113262 -1.254550

Zero-point correction=                           0.385962 (Hartree/Particle)
Thermal correction to Energy=                    0.410700
Thermal correction to Enthalpy=                  0.411644
Thermal correction to Gibbs Free Energy=         0.331499
Sum of electronic and zero-point Energies=        -1562.505146
Sum of electronic and thermal Energies=           -1562.480408
Sum of electronic and thermal Enthalpies=         -1562.479463
Sum of electronic and thermal Free Energies=      -1562.559609

M06/6-311++G(d,p)/SMD//M06/6-31G(d)  energy=  -1563.23075077

*TS3*

| Center Number | Atomic Number | Atomic Type | Coordinates (Angstroms) X | Y | Z |
|---------------|---------------|-------------|---------------------------|---|---|
| 1             | 6             | 0           | 2.371372                  | 0.869472 | -0.348909 |
| 2             | 6             | 0           | 1.033392                  | 1.194983 | -0.166024 |
Zero-point correction=                           0.138264 (Hartree/Particle)
Thermal correction to Energy=                    0.147596
Thermal correction to Enthalpy=                  0.148540
Thermal correction to Gibbs Free Energy=         0.103043
Sum of electronic and zero-point Energies=       -418.610151
Sum of electronic and thermal Energies=          -418.600819
Sum of electronic and thermal Enthalpies=         -418.599875
Sum of electronic and thermal Free Energies=      -418.645372
M06/6-311++G(d,p)/SMD//M06/6-31G(d)  energy= -418.86170347

INT2

| Center Number | Atomic Number | Atomic Type | Coordinates (Angstroms) |
|---------------|---------------|-------------|-------------------------|
|               |               |             | X           | Y           | Z           |
| 1             | 6             | 0           | 0.685390    | 2.721698    | 0.276505    |
| 2             | 6             | 0           | 0.432037    | 1.395758    | -0.246735   |
| 3             | 6             | 0           | 1.608606    | 0.660518    | -0.775900   |
| 4             | 6             | 0           | 2.820101    | 1.431698    | -1.046279   |
| 5             | 6             | 0           | 2.953257    | 2.709530    | -0.643155   |
| 6             | 6             | 0           | 1.874740    | 3.337183    | 0.069033    |
| 7             | 1             | 0           | -0.114525   | 3.238204    | 0.799559    |
| 8             | 1             | 0           | 3.634838    | 0.921295    | -1.558632   |
| 9             | 1             | 0           | 3.866343    | 3.266037    | -0.840158   |
| 10            | 1             | 0           | 2.014033    | 4.351165    | 0.442426    |
| 11            | 6             | 0           | 1.381158    | -0.596370   | -1.61108    |
| 12            | 7             | 0           | -0.725414   | 0.793934    | -0.300969   |
| 13            | 16            | 0           | -2.081471   | 1.530253    | 0.342828    |
| 14            | 8             | 0           | -1.899281   | 1.776258    | 1.773175    |
| 15            | 8             | 0           | -2.512633   | 2.622348    | -0.525845   |
| 16            | 6             | 0           | -3.235316   | 0.194658    | 0.166702    |
| 17            | 6             | 0           | -3.327084   | -0.759928   | 1.172418    |
| 18            | 6             | 0           | -4.027753   | 0.122337    | -0.972176   |
| 19            | 6             | 0           | -4.226456   | -1.807361   | 1.025810    |
| 20            | 1             | 0           | -2.704848   | -0.667358   | 2.060937    |
| 21            | 6             | 0           | -4.922906   | -0.930817   | -1.101783   |
| 22            | 1             | 0           | -3.939286   | 0.893163    | -1.735407   |
| 23            | 6             | 0           | -5.036457   | -1.906477   | -0.108089   |
| 24            | 1             | 0           | -4.310667   | -2.562385   | 1.807774    |
| 25            | 1             | 0           | -5.552336   | -0.998332   | -1.989527   |
|   |   |   |    X      |    Y      |    Z     |
|---|---|---|----------|----------|----------|
| 1 | 6 | 0 | 0.982948 | 2.840123 | 0.457321 |
| 2 | 6 | 0 | 0.661644 | 1.693421 | -0.314397|
| 3 | 6 | 0 | 1.691552 | 1.111352 | -1.111108|
| 4 | 6 | 0 | 2.974223 | 1.680839 | -1.104844|
| 5 | 6 | 0 | 3.251584 | 2.817640 | -0.377125|
| 6 | 6 | 0 | 2.240331 | 3.394082 | 0.406724 |
| 7 | 1 | 0 | 0.219147 | 3.282756 | 1.091788 |
| 8 | 1 | 0 | 3.752893 | 1.223050 | -1.715795|
| 9 | 1 | 0 | 4.240671 | 3.269092 | -0.418556|
| 10| 1| 0 | 2.453563 | 4.287362 | 0.991677 |
| 11| 6| 0 | 1.450093 | -0.157229 | -1.897009|
| 12| 7| 0 | -0.558992 | 1.074341 | -0.344245|
| 13| 16| 0| -1.816040 | 1.642150 | 0.576859 |
| 14| 8 | 0 | -1.503883 | 1.630493 | 2.007935 |
| 15| 8 | 0 | -2.355328 | 2.863933 | -0.015100|
| 16| 6 | 0 | -2.945245 | 0.303470 | 0.264146 |
| 17| 6 | 0 | -3.182812 | -0.638609 | 1.255034 |
| 18| 6 | 0 | -3.541438 | 0.196142 | -0.989309|
| 19| 6 | 0 | -4.027452 | -1.709275 | 0.980115 |

Zero-point correction=                           0.377442 (Hartree/Particle)
Thermal correction to Energy=                    0.400618
Thermal correction to Enthalpy=                  0.401563
Thermal correction to Gibbs Free Energy=         0.323335
Sum of electronic and zero-point Energies=       -1453.110862
Sum of electronic and thermal Energies=          -1453.087686
Sum of electronic and thermal Enthalpies=        -1453.086741
Sum of electronic and thermal Free Energies=     -1453.164969
M06/6-311++G(d,p)/SMD/M06/6-31G(d) energy=     -1453.79032560
|   |   |   | X           | Y           | Z           |
|---|---|---|-------------|-------------|-------------|
| 20| 1 | 0 | -2.707116   | -0.521706   | 2.226986    |
| 21| 6 | 0 | -4.378114   | -0.878470   | -1.248386   |
| 22| 1 | 0 | -3.344029   | 0.954710    | -1.744980   |
| 23| 6 | 0 | -4.633615   | -1.844989   | -0.268650   |
| 24| 1 | 0 | -4.222316   | -2.455614   | 1.750680    |
| 25| 1 | 0 | -4.849153   | -0.975505   | -2.227255   |
| 26| 6 | 0 | -5.560897   | -2.987527   | -0.554592   |
| 27| 1 | 0 | -5.454002   | -3.193835   | 1.187925    |
| 28| 6 | 0 | -5.560897   | -3.193835   | 1.187925    |
| 29| 1 | 0 | -4.222316   | -2.455614   | 1.750680    |
| 30| 6 | 0 | 3.987078    | -2.351577   | 1.751272    |
| 31| 6 | 0 | 2.799650    | -1.913835   | 1.187925    |
| 32| 6 | 0 | 2.732181    | -1.562367   | -0.170753   |
| 33| 6 | 0 | 3.900376    | -1.672849   | -0.942387   |
| 34| 6 | 0 | 5.082763    | -2.132653   | -0.381530   |
| 35| 6 | 0 | 5.132340    | -2.468757   | 0.967772    |
| 36| 1 | 0 | 4.021314    | -2.600531   | 2.809970    |
| 37| 1 | 0 | 1.917596    | -1.806221   | 1.816011    |
| 38| 1 | 0 | 3.875280    | -1.428603   | -2.002740   |
| 39| 1 | 0 | 5.972030    | -2.226841   | -1.001601   |
| 40| 1 | 0 | 6.062984    | -2.820868   | 1.408620    |
| 41| 6 | 0 | 1.427073    | -1.139747   | -0.771865   |
| 42| 6 | 0 | 0.211086    | -1.474701   | -0.219186   |
| 43| 1 | 0 | 0.185020    | -2.166426   | 0.623351    |
| 44| 1 | 0 | -0.254190   | -0.369377   | 0.028494    |
| 45| 1 | 0 | -0.556030   | -1.699100   | -0.974279   |
| 46| 1 | 0 | 2.240012    | -0.304834   | -2.641642   |
| 47| 1 | 0 | 0.476526    | -0.151652   | -2.401281   |

Zero-point correction= 0.373250 (Hartree/Particle)
Thermal correction to Energy= 0.395790
Thermal correction to Enthalpy= 0.396734
Thermal correction to Gibbs Free Energy= 0.318832
Sum of electronic and zero-point Energies= -1453.090258
Sum of electronic and thermal Energies= -1453.067718
Sum of electronic and thermal Enthalpies= -1453.066773
Sum of electronic and thermal Free Energies= -1453.144676

M06/6-311++G(d,p)/SMD//M06/6-31G(d) energy= -1453.77308595

TSS5

| Center Number | Atomic Number | Atomic Type | X     | Y     | Z     |
|---------------|---------------|-------------|-------|-------|-------|
| 1             | 6             | 0           | -1.401630 | -2.874825 | 0.608901 |
| 2             | 6             | 0           | -1.010425 | -1.704842 | -0.108476 |
| 3             | 6             | 0           | -1.959138 | -1.166502 | -1.030092 |
| 4             | 6             | 0           | -3.237375 | -1.713484 | -1.135902 |
| 5             | 6             | 0           | -3.600731 | -2.829224 | -0.401403 |
| 6             | 6             | 0           | -2.663497 | -3.402651 | 0.472187 |
| 7             | 1             | 0           | -0.699779 | -3.306968 | 1.319166 |
| 8             | 1             | 0           | -3.940005 | -1.291597 | -1.857667 |
| 9             | 1             | 0           | -4.584190 | -3.276755 | -0.528940 |
| 10            | 1             | 0           | -2.938565 | -4.279350 | 1.057086 |
| 11            | 6             | 0           | -1.528523 | -0.024873 | -1.926396 |
| 12            | 7             | 0           | 0.160452  | -1.047976 | 0.026401 |
| 13            | 16            | 0           | 1.445800  | -1.799238 | 0.694510 |
14 8 0 1.823004 -3.016282 -0.029844
15 8 0 1.333485 -1.878300 2.156780
16 6 0 2.667042 -0.554971 0.327714
17 6 0 3.297603 -0.561781 -0.911328
18 6 0 2.930102 0.443828 1.256780
19 6 0 4.186894 0.457408 -1.225158
20 1 0 3.083943 1.366255 1.613153
21 6 0 3.824039 1.457592 0.929579
22 1 0 2.434818 0.408226 2.225821
23 6 0 4.460978 1.480855 -0.312957
24 1 0 4.038443 2.245485 1.652742
25 6 0 5.446831 2.559851 -0.648419
26 1 0 5.440903 2.795255 -1.720043
27 1 0 6.471484 2.255685 -0.392307
28 1 0 5.237389 3.484295 -0.096291
29 6 0 -4.491323 2.335127 0.218176
30 6 0 -3.554648 1.618861 -0.498749
31 6 0 -2.169069 1.826885 -0.300228
32 6 0 -1.780907 2.776311 0.672698
33 6 0 -2.723710 3.479247 1.401660
34 6 0 -4.080883 3.265586 1.174811
35 6 0 -5.551243 2.166823 0.409294
36 6 0 -3.893256 0.888945 1.228224
37 6 0 -0.725436 2.942500 0.872280
38 6 0 -2.400771 4.194508 2.154834
39 6 0 -4.822626 3.819947 1.746457
40 6 0 -1.177638 1.147323 -1.086162
41 6 0 -2.354309 0.219269 -2.611653
42 6 0 -0.661266 -0.314176 -2.532612
43 6 0 0.216682 1.640325 -1.059622
44 6 0 0.841419 1.126719 -1.795440
45 6 0 0.679708 1.442879 0.87549
46 6 0 0.244760 2.726480 -1.229126
47 6 0 0.216682 1.640325 -1.059622
48 6 0 0.841419 1.126719 -1.795440
49 6 0 0.679708 1.442879 0.87549
50 6 0 0.244760 2.726480 -1.229126

Zero-point correction= 0.376684 (Hartree/Particle)
Thermal correction to Energy= 0.399062
Thermal correction to Enthalpy= 0.400006
Thermal correction to Gibbs Free Energy= 0.323959
Sum of electronic and zero-point Energies= -1453.077930
Sum of electronic and thermal Energies= -1453.055552
Sum of electronic and thermal Enthalpies= -1453.054608
Sum of electronic and thermal Free Energies= -1453.130655
M06/6-311++G(d,p)/SMD/M06/6-31G(d) energy= -1453.77275630

4f
| Center Number | Atomic Number | Atomic Type | Coordinates (Angstroms) |
|---------------|---------------|-------------|------------------------|
|               |               |             | X          | Y           | Z          |
| 1             | 6             | 0           | -3.168939 | -1.554166 | 0.622981  |

Zero-point correction= 0.379313 (Hartree/Particle)
Thermal correction to Energy= 0.402134
Thermal correction to Enthalpy= 0.403078
Thermal correction to Gibbs Free Energy= 0.326109
Sum of electronic and zero-point Energies= -1453.137785
Sum of electronic and thermal Energies= -1453.114964
Sum of electronic and thermal Enthalpies= -1453.114020
Sum of electronic and thermal Free Energies= -1453.190989

M06/6-311++G(d,p)/SMD//M06/6-31G(d) energy= -1453.82364954
|   |   |   |                           |                           |                           |                           |
|---|---|---|--------------------------|--------------------------|--------------------------|--------------------------|
| 2 | 6 | 0 | -2.393209                | -0.743709                | -0.200845                |
| 3 | 6 | 0 | -2.984307                | 0.177940                 | -1.063374                |
| 4 | 6 | 0 | -4.361223                | 0.308784                 | -1.16316                 |
| 5 | 6 | 0 | -5.153392                | -0.487952                | -0.291039                |
| 6 | 6 | 0 | -4.553471                | -1.406143                | 0.564355                 |
| 7 | 1 | 0 | -2.716913                | -2.281605                | 1.290623                 |
| 8 | 1 | 0 | -4.814839                | 1.031290                 | -1.794587                |
| 9 | 1 | 0 | -6.236874                | -0.390664                | -0.315910                |
|10 | 1 | 0 | -5.173244                | -2.028426                | 1.207788                 |
|11 | 6 | 0 | -1.928720                | 0.177940                 | -1.063374                |
|12 | 7 | 0 | -0.977063                | -0.693237                | -0.326102                |
|13 | 16| 0 |                           |                          |                          |
|14 | 8 | 0 | -0.415681                | -2.745455                | 1.019272                 |
|15 | 8 | 0 | -0.294452                | -0.522849                | 2.184986                 |
|16 | 6 | 0 | 1.591630                 | -1.157024                | 0.474689                 |
|17 | 6 | 0 | 2.146973                 | -2.143966                | -0.336337                |
|18 | 6 | 0 | 2.340077                 | -0.075169                | 0.921707                 |
|19 | 6 | 0 | 3.467889                 | -2.015345                | -0.735082                |
|20 | 1 | 0 | 1.538700                 | -2.993394                | -0.642652                |
|21 | 6 | 0 | 3.660207                 | 0.039947                 | 0.504745                 |
|22 | 1 | 0 | 1.888330                 | 0.662530                 | 1.582325                 |
|23 | 6 | 0 | 4.239427                 | -0.920389                | -0.326967                |
|24 | 1 | 0 | 3.917079                 | -2.776005                | -1.373682                |
|25 | 1 | 0 | 4.253752                 | 0.893391                 | 0.832719                 |
|26 | 6 | 0 | 5.672689                 | -0.807671                | -0.748374                |
|27 | 1 | 0 | 5.816443                 | -1.144336                | -1.782497                |
|28 | 1 | 0 | 6.317583                 | -1.432782                | -0.115158                |
|29 | 1 | 0 | 6.038590                 | 0.222570                 | -0.669534                |
|30 | 6 | 0 | -0.351748                | 3.166508                 | 1.531684                 |
|31 | 6 | 0 | -0.773446                | 2.073111                 | 0.787282                 |
|32 | 6 | 0 | -0.077195                | 1.673869                 | -0.358677                |
|33 | 6 | 0 | 1.033410                 | 2.423111                 | -0.750915                |
|34 | 6 | 0 | 1.455587                 | 3.522338                 | -0.008158                |
|35 | 6 | 0 | 0.767668                 | 3.895307                 | 1.139430                 |
|36 | 1 | 0 | -0.900954                | 3.446548                 | 2.428701                 |
|37 | 1 | 0 | -1.638247                | 1.504368                 | 1.123126                 |
|38 | 1 | 0 | 1.600700                 | 2.145572                 | -1.637119                |
|39 | 1 | 0 | 2.329782                 | 4.085775                 | -0.331198                |
|40 | 1 | 0 | 1.098268                 | 4.751080                 | 1.725641                 |
|41 | 6 | 0 | -0.576213                | 0.492533                 | -1.181901                |
|42 | 1 | 0 | -2.049929                | 1.957147                 | -1.90615                 |
|43 | 1 | 0 | -1.931074                | 0.499954                 | -2.902273                |
|44 | 6 | 0 | 0.401356                 | 0.047681                 | -2.263142                |
|45 | 1 | 0 | 0.033822                 | -0.882845                | -2.712090                |
|46 | 1 | 0 | 1.415881                 | -0.125592                | -1.889750                |
|47 | 1 | 0 | 0.454719                 | 0.808602                 | -3.053392                |

Zero-point correction=                           0.380433 (Hartree/Particle)
Thermal correction to Energy=                    0.402575
Thermal correction to Enthalpy=                  0.403519
Thermal correction to Gibbs Free Energy=         0.329139
Sum of electronic and zero-point Energies=        -1453.158094
Sum of electronic and thermal Energies=          -1453.135952
Sum of electronic and thermal Enthalpies=         -1453.135008
Sum of electronic and thermal Free Energies=      -1453.209388

M06/6-311++G(d,p)/SMD//M06/6-31G(d) energy= -1453.83772402
### \(^32f\)

| Center Number | Atomic Number | Atomic Type | Coordinates (Angstroms) |
|---------------|---------------|-------------|------------------------|
|               | 1             | 6           | 0                      |
|               | 2             | 6           | 0                      |
|               | 3             | 6           | 0                      |
|               | 4             | 6           | 0                      |
|               | 5             | 6           | 0                      |
|               | 6             | 6           | 0                      |
|               | 7             | 1           | 0                      |
|               | 8             | 1           | 0                      |
|               | 9             | 1           | 0                      |
|               | 10            | 1           | 0                      |
|               | 11            | 1           | 0                      |
|               | 12            | 6           | 0                      |
|               | 13            | 6           | 0                      |
|               | 14            | 1           | 0                      |
|               | 15            | 1           | 0                      |
|               | 16            | 1           | 0                      |
|               | 17            | 7           | 0                      |
|               | 18            | 7           | 0                      |

Zero-point correction= 0.140472 (Hartree/Particle)
Thermal correction to Energy= 0.149412
Thermal correction to Enthalpy= 0.150357
Thermal correction to Gibbs Free Energy= 0.105255
Sum of electronic and zero-point Energies= -418.627442
Sum of electronic and thermal Energies= -418.618502
Sum of electronic and thermal Enthalpies= -418.617558
Sum of electronic and thermal Free Energies= -418.662515
M06/6-311++G(d,p)//SMD//M06/6-31G(d) energy= -418.87644952

### \(^3TS1b\)

| Center Number | Atomic Number | Atomic Type | Coordinates (Angstroms) |
|---------------|---------------|-------------|------------------------|
|               | 1             | 6           | 0                      |
|               | 2             | 6           | 0                      |
|               | 3             | 6           | 0                      |
|               | 4             | 6           | 0                      |
|               | 5             | 6           | 0                      |
|               | 6             | 6           | 0                      |
|               | 7             | 1           | 0                      |
|               | 8             | 1           | 0                      |
|               | 9             | 1           | 0                      |
|               | 10            | 1           | 0                      |
|               | 11            | 1           | 0                      |
|               | 12            | 6           | 0                      |
|               | 13            | 6           | 0                      |
|               | 14            | 1           | 0                      |
|               | 15            | 1           | 0                      |
|               | 16            | 1           | 0                      |
|               | 17            | 7           | 0                      |
|               | 18            | 7           | 0                      |

M06/6-311++G(d,p)//SMD//M06/6-31G(d) energy= -418.87644952
Zero-point correction=                           0.137614 (Hartree/Particle)
Thermal correction to Energy=                    0.147105
Thermal correction to Enthalpy=                  0.148049
Thermal correction to Gibbs Free Energy=         0.101499
Sum of electronic and zero-point Energies=        -418.61392
Sum of electronic and thermal Energies=          -418.603901
Sum of electronic and thermal Enthalpies=         -418.602957
Sum of electronic and thermal Free Energies=      -418.649507

M06/6-311++G(d,p)/SMD//M06/6-31G(d)  energy= -418.85963934

| Center Number | Atomic Number | Atomic Type | Coordinates (Angstroms) |
|---------------|---------------|-------------|-------------------------|
| 1             | 6             | 0           | -1.329097     1.349123     -0.000004 |
| 2             | 6             | 0           | 0.023181       1.057450     -0.000023 |
| 3             | 6             | 0           | 0.476992      -0.291159     -0.000024 |
| 4             | 6             | 0           | -0.506717     -1.315898     -0.000001 |
| 5             | 6             | 0           | -1.853439     -1.007154     0.000028 |
| 6             | 6             | 0           | -2.277724     0.324460      0.000018 |
| 7             | 1             | 0           | -1.653571     2.389006      -0.000013 |
| 8             | 1             | 0           | 0.758109      1.862524     -0.000033 |
| 9             | 1             | 0           | -0.175419     -2.353431     0.000008 |
| 10            | 1             | 0           | -2.589316      1.089975     0.000066 |
| 11            | 1             | 0           | -3.339849     0.561941      0.000009 |
| 12            | 6             | 0           | 1.838109       0.562516     -0.000113 |
| 13            | 6             | 0           | 3.081079      0.175387      0.000060 |
| 14            | 1             | 0           | 3.160907      0.825115     0.888460 |
| 15            | 1             | 0           | 3.964121      -0.477189     -0.000292 |
| 16            | 1             | 0           | 3.160718      0.825815     -0.887848 |

Zero-point correction=                           0.130151 (Hartree/Particle)
Thermal correction to Energy=                    0.137487
Thermal correction to Enthalpy=                  0.138431
Thermal correction to Gibbs Free Energy=         0.097479
Sum of electronic and zero-point Energies=        -309.174191
Sum of electronic and thermal Energies=          -309.166856
Sum of electronic and thermal Enthalpies=         -309.165911
Sum of electronic and thermal Free Energies=      -309.206863

M06/6-311++G(d,p)/SMD//M06/6-31G(d)  energy= -309.38935151

| Center Number | Atomic Number | Atomic Type | Coordinates (Angstroms) |
|---------------|---------------|-------------|-------------------------|
| 1             | 6             | 0           | 1.424410     2.237839     0.172727 |
| 2             | 6             | 0           | 0.815814     1.168088     -0.579742 |
| 3             | 6             | 0           | 1.600292     0.605328     -1.700012 |
| 4             | 6             | 0           | 2.932470     1.096843     -1.935138 |
| 5             | 6             | 0           | 3.457729     2.094362     -1.184597 |
| 6             | 6             | 0           | 2.676709     2.670598     -0.130405 |
| 7             | 1             | 0           | 0.856861     2.697614     0.976477 |
| 8             | 1             | 0           | 3.503488     0.635799     -2.741028 |
| 9             | 1             | 0           | 4.465062     2.461100     -1.367677 |
| Center | Atomic Number | Atomic Type | Coordinates (Angstroms) |
|--------|---------------|-------------|------------------------|
| X      | Y             | Z           |
| 1      | 6             | 0           | -1.549979              | 0.890501  | -1.489936  |
| 2      | 6             | 0           | -0.727353              | 1.210677  | -0.345283  |
| 3      | 6             | 0           | -1.382332              | 1.956386  | 0.760553   |
|   |   |   |    |    |    |    |
|---|---|---|----|----|----|----|
|4  |6  |0  |-2.724945|2.467821|0.540529|
|5  |6  |0  |-3.416513|2.184101|-0.584623|
|6  |6  |0  |-2.815289|1.366875|-1.597910|
|7  |1  |0  |-1.118365|0.300574|-2.294303|
|8  |1  |0  |-3.153494|3.090671|1.326053|
|9  |1  |0  |-4.422876|2.569845|-0.733475|
|10 |1  |0  |-3.939471|1.128318|-2.491207|
|11 |6  |0  |-0.585184|2.590583|1.726535|
|12 |7  |0  |0.539318 |0.904717|-0.176122|
|13 |16 |0  |1.240871 |-0.205407|-1.195822|
|14 |8  |0  |0.615662 |-1.512409|-0.967388|
|15 |8  |0  |1.349598 |0.298498|-2.564068|
|16 |6  |0  |2.873623 |-0.256327|-0.505232|
|17 |6  |0  |3.147621 |-1.129674|0.542304|
|18 |6  |0  |3.855136 |0.575513|-1.025657|
|19 |6  |0  |4.426276 |-1.156345|1.077995|
|20 |1  |0  |2.364704 |-1.788762|0.913379|
|21 |6  |0  |5.131586 |0.536319|-0.476727|
|22 |1  |0  |3.613585 |1.231584|-1.859558|
|23 |6  |0  |5.433992 |-0.324388|0.578577|
|24 |1  |0  |4.656962 |-1.839353|1.893613|
|25 |1  |0  |5.912216 |1.182544|-0.878034|
|26 |6  |0  |6.812002 |-0.376083|1.166274|
|27 |1  |0  |7.478597 |0.358943|0.700754|
|28 |1  |0  |6.793998 |-0.176452|2.245984|
|29 |1  |0  |7.264970 |-1.368002|1.033885|
|30 |6  |0  |-3.450462|2.652084|-0.401921|
|31 |6  |0  |-2.499096|1.894943|0.259365|
|32 |6  |0  |-2.878171|0.731621|0.968096|
|33 |6  |0  |-4.240027|0.373735|0.991180|
|34 |6  |0  |-5.186558|-1.144341|0.330115|
|35 |6  |0  |-4.795581|2.280594|-0.372261|
|36 |1  |0  |-3.142097|3.536347|-0.957012|
|37 |1  |0  |-1.442800|2.150979|0.193286|
|38 |1  |0  |-4.542337|0.506853|1.554400|
|39 |1  |0  |-6.236967|0.859991|0.367458|
|40 |1  |0  |-5.538543|2.880222|-0.895431|
|41 |6  |0  |-1.887172|0.052917|1.631082|
|42 |6  |0  |-0.680320|0.385609|2.340184|
|43 |1  |0  |-0.717086|1.468955|2.523659|
|44 |1  |0  |0.234808 |0.169309|1.759830|
|45 |1  |0  |0.576644 |0.121149|3.311362|
|46 |1  |0  |-1.040195|3.243973|2.468362|
|47 |1  |0  |0.486742 |2.421111|1.762314|

Zero-point correction= 0.370846 (Hartree/Particle)
Thermal correction to Energy= 0.394748
Thermal correction to Enthalpy= 0.395692
Thermal correction to Gibbs Free Energy= 0.315549
Sum of electronic and zero-point Energies= -1452.988857
Sum of electronic and thermal Energies= -1452.964955
Sum of electronic and thermal Enthalpies= -1452.964011
Sum of electronic and thermal Free Energies= -1453.044154

M06/6-311++G(d,p)/SMD//M06/6-31G(d) energy= -1453.66178869

INT2b
| Center Number | Atomic Number | Atomic Type | X (Angstroms) | Y (Angstroms) | Z (Angstroms) |
|---------------|---------------|-------------|---------------|---------------|---------------|
| 1             | 6             | 0           | 0.141840      | -3.198753     | 0.036720      |
| 2             | 6             | 0           | -0.004380     | -1.781528     | -0.141421     |
| 3             | 6             | 0           | -1.329198     | -1.253052     | -0.361913     |
| 4             | 6             | 0           | -2.408788     | -2.120619     | -0.365237     |
| 5             | 6             | 0           | -2.238002     | -3.492789     | -0.184701     |
| 6             | 6             | 0           | -0.954303     | -4.024292     | 0.013423      |
| 7             | 1             | 0           | 1.134103      | -3.615281     | 0.188016      |
| 8             | 1             | 0           | -3.409047     | -1.709441     | -0.507094     |
| 9             | 1             | 0           | -3.104184     | -4.151958     | -0.195245     |
| 10            | 1             | 0           | -0.825729     | 0.036720      | 0.013423      |
| 11            | 6             | 0           | 1.555694      | -2.225554     | -0.570080     |
| 12            | 7             | 0           | 0.988850      | -0.886818     | -0.105262     |
| 13            | 16            | 0           | 2.134103      | -1.415281     | 0.200517      |
| 14            | 8             | 0           | 2.639061      | -1.829535     | 1.594179      |
| 15            | 8             | 0           | 3.009797      | -2.239075     | -0.863773     |
| 16            | 6             | 0           | 3.414501      | 0.139035      | 0.032104      |
| 17            | 6             | 0           | 4.090030      | 0.415796      | -1.150555     |
| 18            | 6             | 0           | 3.410946      | 1.039430      | 1.091154      |
| 19            | 6             | 0           | 4.765738      | 1.622065      | -1.270742     |
| 20            | 1             | 0           | 4.089946      | 2.241964      | -0.951685     |
| 21            | 6             | 0           | 2.892351      | 0.789585      | 2.041985      |
| 22            | 6             | 0           | 4.771799      | 2.551401      | -0.227525     |
| 23            | 6             | 0           | 5.306644      | 1.849308      | -2.189689     |
| 24            | 1             | 0           | 4.100282      | 2.934925      | 1.775976      |
| 25            | 6             | 0           | 5.487420      | 3.859399      | -0.380492     |
| 26            | 6             | 0           | 5.249235      | 4.466588      | 0.588101      |
| 27            | 1             | 0           | 6.464459      | 3.729470      | -0.862687     |
| 28            | 1             | 0           | 4.910711      | 4.554701      | -1.006151     |
| 29            | 6             | 0           | 5.999953      | 2.131855      | 0.790054      |
| 30            | 6             | 0           | 4.714945      | 1.719778      | 1.090594      |
| 31            | 6             | 0           | 3.845024      | 1.203840      | 0.091285      |
| 32            | 6             | 0           | 4.371579      | 1.129978      | -1.126692     |
| 33            | 6             | 0           | 5.658574      | 1.543957      | -1.169272     |
| 34            | 6             | 0           | 6.487684      | 2.050590      | -0.514937     |
| 35            | 6             | 0           | 6.635678      | 2.522344      | 1.583569      |
| 36            | 1             | 0           | 4.363079      | 1.794020      | 2.117591      |
| 37            | 1             | 0           | 3.757311      | 0.736008      | -2.034525     |
| 38            | 1             | 0           | 6.025144      | 1.470800      | -2.539892     |
| 39            | 1             | 0           | 7.499901      | 2.375260      | -0.747810     |
| 40            | 6             | 0           | 2.527264      | 0.785113      | 0.425942      |
| 41            | 6             | 0           | 2.037817      | 0.830610      | 1.839333      |
| 42            | 1             | 0           | 0.992639      | 0.503421      | 1.903490      |
| 43            | 1             | 0           | 2.091979      | 1.844147      | 2.265416      |
| 44            | 1             | 0           | 2.625985      | 0.796684      | 2.505766      |
| 45            | 1             | 0           | 1.889810      | 0.855867      | -1.603822     |
| 46            | 1             | 0           | 0.590119      | 0.740625      | -0.475482     |
| 47            | 1             | 0           | 0.590119      | 0.740625      | -0.475482     |

Zero-point correction= 0.375322 (Hartree/Particle)
Thermal correction to Energy= 0.399081
Thermal correction to Enthalpy= 0.400025
Thermal correction to Gibbs Free Energy= 0.317882
Sum of electronic and zero-point Energies= -1453.085736
Sum of electronic and thermal Energies= -1453.061977
Sum of electronic and thermal Enthalpies = -1453.061033
Sum of electronic and thermal Free Energies = -1453.143176
M06/6-311++G(d,p)/SMD//M06/6-31G(d) energy = -1453.76144776

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