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Photoinduced Deaminative Coupling of Alkylpyridium Salts with Terminal Arylalkynes

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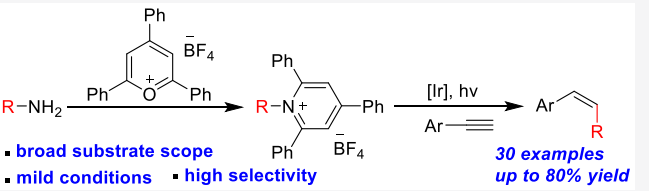
ABSTRACT: A novel and simple *Z*-alkene synthesis by the photocatalyzed coupling reactions of alkylpyridium salts, which were prepared from primary amines, with terminal aryl alkynes at room temperature is reported here. A wide range of primary amines, which contain different functional groups, were tolerated under these conditions. The mild reaction conditions, broad substrate scope, functional group tolerance, and operational simplicity make this deaminative coupling reaction a valuable method in organic syntheses.



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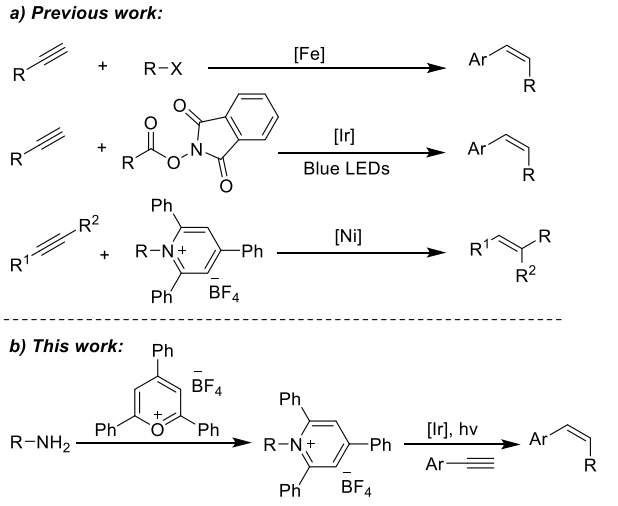
Primary amines are widely available in drugs, natural products, and synthetic chemicals.[1] However, cross-coupling of primary amines is limited in employing the only electronically activated or strain-activated amine derivatives until recently.[2] The inactivated alkyl amines are less applied in synthetic field owing to the inert C(sp^3)–N bonds.[3] Bench-stable alkylpyridium salts (Katritzky salts), which were prepared by condensation of alkyl amines with commercially available triphenyl pyrylium salts,[4] emerged as convenient radical precursors by single electron reduction (SER) and have attracted broad attention. In 2017, Watson published the first example of an unactivated amine derivative in a deaminative cross-coupling reaction.[2a] Afterward, many elegant studies have been carried out in this area.[5] For example, Watson[6] and Glorius[7] reported that alkyl radicals were generated from Katritzky salts via SER in the presence of nickel or a photocatalyst. In addition, Aggarwal employed Katritzky salts as alkylation regents by irradiation of electron–donor–acceptor (EDA) complexes between the salts and Hantzsch esters.[8]

Alkenes have been applied as fundamental building blocks in synthetic chemistry, material and life science.[9] Recently, many strategies had been developed for syntheses of alkenes by coupling readily available alkynes with alkyl electrophiles (Scheme 1).[10] In 2015, Hu reported the iron-catalyzed reductive coupling of terminal alkynes with alkyl halides for the selective synthesis of *Z*-olefins.[10a] In 2019, a nickel-catalyzed deaminative hydroalkylation of internal alkynes was described by Liu.[11] Watson published a nickel-catalyzed deaminative alkyl-vinyl coupling of alkyl pyridium salts to form *E*-olefins.[6c] Inspired by these advances and based on our previous work,[12] we expected that alkyl radicals derived from Katritzky salts could add to terminal alkynes through visible-light photoredox catalysis. Herein, we report that the photoinduced deaminative coupling reaction of Katritzky salts with terminal arylalkynes, which leads to the unique physiologically active *Z*-olefins.[13]

Scheme 1. Hydroalkylation of Alkynes with Alkyl Electrophiles



Our studies commenced with the model reaction of *N*-cyclohexyl Katritzky pyridinium salt **1a** and 1-chloro-ethynylbenzene **2a** (Table 1). The previous results reported that DIPEA and catalyst fac-Ir(ppy)$_3$ play an important role in (E)- to (Z)- isomerization,[14] which was also confirmed by our

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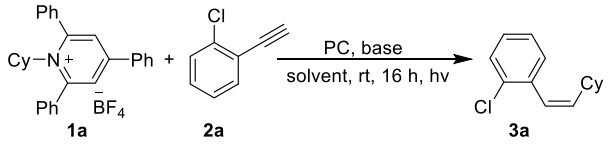
Table 1. Optimization of Reaction Conditions[a]



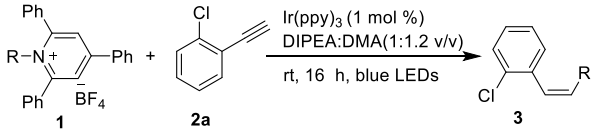
Entry	Solvent	Base	PC	Yield % (*Z*/*E*)
1	DMA	DIPEA	$Ir(ppy)_3$	37 (84:16)
2	THF	DIPEA	$Ir(ppy)_3$	37 (78:22)
3	DMF	DIPEA	$Ir(ppy)_3$	35 (83:17)
4	DMSO	DIPEA	$Ir(ppy)_3$	30 (83:17)
5	DCE	DIPEA	$Ir(ppy)_3$	34 (82:18)
6	CH_3CN	DIPEA	$Ir(ppy)_3$	27 (85:15)
7	DMA	Et_3N	$Ir(ppy)_3$	30 (78:22)
8	DMA	DABCO	$Ir(ppy)_3$	16 (83:17)
9	DMA	DBU	$Ir(ppy)_3$	30 (84:16)
10	DMA	TMEDA	$Ir(ppy)_3$	21 (83:17)
11	DMA	K_2CO_3	$Ir(ppy)_3$	0
12	DMA	None	$Ir(ppy)_3$	0
13	DMA	DIPEA	$Ir(dtppy)(ppy)_2PF_6$	29 (81:19)
14	DMA	DIPEA	$Ru(bpy)_3Cl_2{\cdot}6H_2O$	25 (78:22)
15	DMA	DIPEA	none	21 (72:28)
16[b]	DMA	DIPEA	$Ir(ppy)_3$	0
17[c]	DMA	DIPEA	$Ir(ppy)_3$	51 (95:5)
18[c,d]	DMA	DIPEA	none	38 (72:28)
19[c,d]	**DMA**	**DIPEA**	**$Ir(ppy)_3$**	**68** (95:5)
20[c,d,e]	DMA	DIPEA	$Ir(ppy)_3$	38 (86:14)
21[c,d,f]	DMA	DIPEA	$Ir(ppy)_3$	59 (87:13)

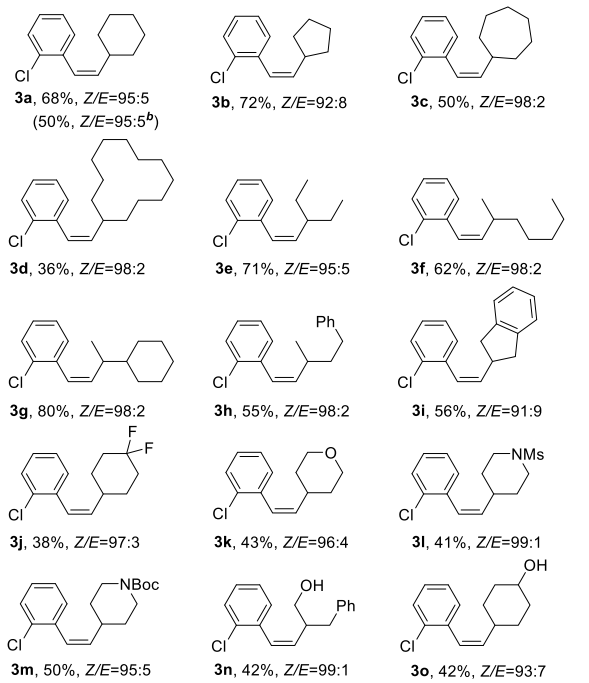
[a]Conditions: **1a** (0.2 mmol), **2a** (0.1 mmol), DIPEA (7 equiv), and $Ir(ppy)_3$ (1 mol %) in DMA (1 mL) were irradiated by blue LEDs for 16 h under Ar. Isolated yields. The *Z*/*E* ratio was determined by ^{1}H NMR. [b]No light. [c]DIPEA (50 equiv). [d]**1a** (3 equiv). [e]6 h. [f]11 h.

earlier research.[12] Inspired by those results, we discovered that simple mixing of **1a** (0.2 mmol), **2a** (0.1 mmol), DIPEA (7 equiv) and $Ir(ppy)_3$ (1 mol %) in DMA irradiated by blue LEDs for 16 h under argon afforded 37% (*Z*/*E* = 84:16) coupling product **3a** (entry 1). The initial results prompted us to further improve both yield and *Z*/*E* selectivity. Different solvents were screened under current conditions. Hydrophilic solvents, such as DMF, DMA, and THF, resulted in better yields than hydrophobic solvent (entries 2−6). When DIPEA was replaced by Et_3N, DABCO, and DBU, both yields and *Z*/*E* ratios diminished (entries 7−9). No product was formed when an inorganic base (K_2CO_3) was employed. Further photocatalysts screening proved fac-$Ir(ppy)_3$ as the best catalyst. Control experiments confirmed that light and a base were necessary for this coupling reaction. Increasing the amount of DIPEA to 50 equiv increased the yield (51%) and *Z*/*E* ratio (95:5). Finally, increasing the amount of **1a** to 3 equiv produced the coupling product **3a** with a 68% yield and *Z*/*E* selectivity of 95:5 (entry 19). It is surprising to observe a 38% yield without an iridium photocatalyst, which implied that the EDA mechanism played some role in this transformation. During our preliminary kinetic studies with reaction times of 6 and 11 h, the fac-$Ir(ppy)_3$ dramatically improved both the yield and selectivity (entries 20−21). Overall, the optimal combination of base, solvent, and catalyst was the key for this transformation.

With the optimized reaction conditions in hand, the alkylpyridium salt substrate scope was evaluated. As demonstrated in Scheme 2, a range of cyclic and acyclic alkylpyridium

Scheme 2. Substrate Scope with Respect to the Alkylpyridium Salts[a]





[a]Conditions: **1** (0.3 mmol), **2a** (0.1 mmol), and $Ir(ppy)_3$ (1 mol %) in a mixture of DIPEA/DMA (0.85 mL/1 mL) were irradiated by blue LEDs for 16 h under Ar. Isolated yields of *Z*/*E* mixtures and the *Z*/*E* ratio were determined by ^{1}H NMR. [b]Gram-scale reaction (1 mmol).

salts, which were prepared from alkyl primary amines, were subjected to the standard conditions and afforded the desired products with good yields and excellent selectivities. When the cyclic alkyl group is smaller, the yield improved (**3a**−**3d**). Various aryl and heterocyclic groups were also well tolerated, including pyran and piperidine (**3i**−**3m**). To our delight, alkyl Katritzky salts with an unprotected alcohol also work well in this coupling with moderate yields and high *Z*/*E* ratios (**3n** and **3o**). Finally, primary, tertiary alkyl amines, and *α*-amino acid derivatives pyridium salts were also tested and no products were obtained. To demonstrate the robustness and scale-up potential of our method, a gram-scale reaction of substrate **3a** (1 mmol) was checked and comparable results were observed (50% vs 68%).

Subsequently, we sought to explore the scope of aryl alkynes (Scheme 3). A wide range of alkynyl arenes with electron-withdrawing or -donating functional groups including halogen, trifluoromethyl, methoxy, and nitrile groups were all tolerated under the standard conditions. Alkynyl arenes with *ortho*-substitution generally have better selectivities and similar yields with the *meta*- and *para*-substituted ones. Alkynyl heteroarene, such as pyridine, could also form the product with a moderate yield and a high *Z*/*E* ratio (**4o**). Alkyl alkyne (**4p**) and internal aryl alkyne failed to afford the desired product under our photocatalyzed conditions. A nickel-catalyzed deaminative

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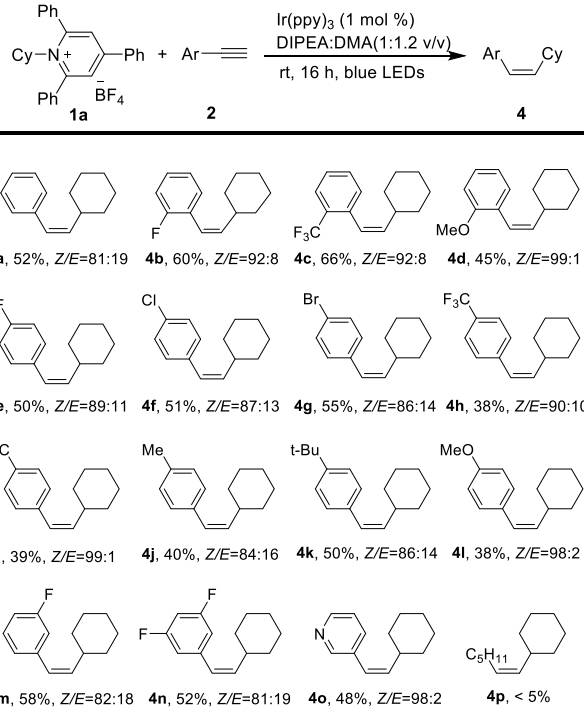
Scheme 3. Substrate Scope with Respect to Terminal (Hetero) Arylalkynes[a]

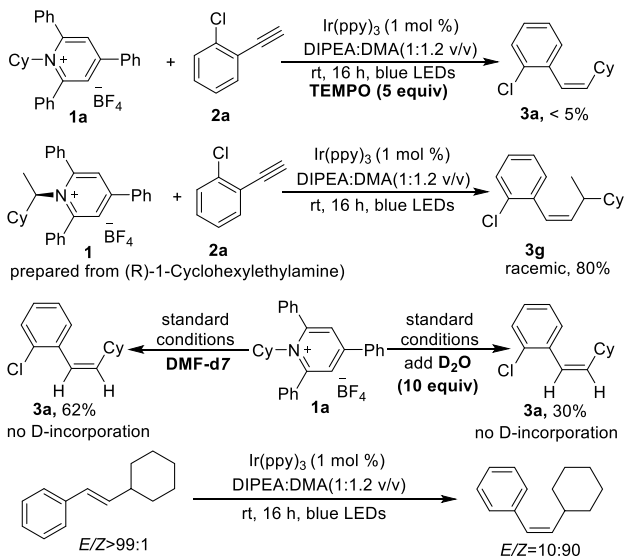


[a]Conditions: **1a** (0.3 mmol), and **2** (0.1 mmol), $Ir(ppy)_3$ (1 mol %) in a mixture of DIPEA/DMA (0.85 mL/1 mL) were irradiated by blue LEDs for 16 h under Ar. Isolated yields of Z/E mixtures and the Z/E ratio were determined by ^1H NMR.

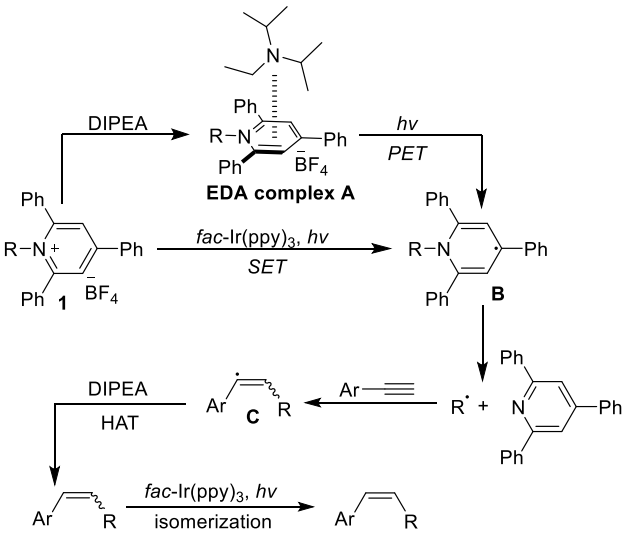
hydroalkylation of alkylpyridinium salts with internal alkynes was previously reported by Liu's group.[11]

To understand the reaction mechanism, several control experiments were conducted (Scheme 4). No desired product was observed when radical scavenger 2,2,6,6-tetramethyl-1-piperidinyloxy (TEMPO) was added into the reaction system. Moreover, the reaction with a chiral Katritzky salt prepared from (*R*)-cyclohexylethylamine resulted in the racemic product **3g** under the standard conditions. These results proved that an alkyl radical intermediate was involved in this transformation. Isotopic labeling experiments were performed with the addition of D_2O in DMA or deuterated DMF as solvent. No deuterated product was detected in either condition, which implied that the hydrogen atom source could not be the trace amount of water in solvent or solvent. In addition, the *Z*/*E* isomerization of olefin product under the standard conditions was explored. This result further confirmed Weaver's[14] and Uchiyama's[15] reports that fac-$Ir(ppy)_3$ promoted the isomerization to the *Z*-isomer under visible light irradiation.

Scheme 4. Control Experiments



Scheme 5. Proposed Mechanism



Based on the mechanic studies and the previous reports,[16] a plausible mechanism is proposed in Scheme 5. There are two possible routes to form alkyl radical from alkyl pyridium salt **1**. Based on our UV/vis adsorption spectroscopy study between alkyl pyridium salt **1** and DIPEA,[5b] there is a characteristic bathchromic shift which indicates formation of EDA complex **A** (see Supporting Information for UV/vis adsorption spectrum). Photoinduced electron transfer (PET) and fragmentation provided alkyl radical **B**. An alternative route involves dihydropyridine radical **B** being formed from **1** via single-electron transfer by photoexcited Ir(Ir*), which then undergoes fragmentation to generate a reactive alkyl radical. The alkyl radical was intercepted by aryl alkynes, generating another radical intermediate, **C**. A hydrogen atom transfer (HAT) from DIPEA to radical intermediate **C** delivers the olefin product. Other hydrogen atom sources such as Hantzsch's ester, thiol, and silane were also tested, and none of them produced the olefin product (see Supporting Information for additive tests).[6c,8,11] Finally, the *Z*-olefin is formed from the isomerization effect of $Ir(ppy)_3$ under the standard conditions.

In conclusion, we have developed a convenient protocol for the synthesis of *Z*-selective alkenes with readily available primary amines and terminal aryl alkynes as starting materials. The reaction occurs under mild conditions with high selectivity and broad substrate scope. As it is complementary to the current synthesis approach of *Z*-alkenes, it also expands the utility of prevalent primary amines. Further efforts toward the other photoinduced deaminative of Katritzky salts coupling reaction are underway.

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EXPERIMENTAL SECTION

General Information. All reactions were carried out in a liquid scintillation vial under argon atmosphere. The vial was placed in 1 of the 16 wells of the SynLED Parallel Photoreactor purchased from Sigma-Aldrich (Z742680, 12W, 465−470 nm, 130−140 LM); the distance between light source and bottom of the reaction vial is 1.5 cm. Reagents **2** used in this study are commercially available from Energy Chemical and used without purification. Substrates **1** were prepared as the reported procedures in the literatures.[2a,4] All of the reactions were monitored by thin layer chromatography (TLC). Flash chromatography was performed using Dynamic Adsorbents Silica Gel 40−63 μm particle size. NMR spectra were recorded on a Bruker Avance 400 (400 MHz for ^{1}H, 100 MHz for ^{13}C) with $CDCl_3$ as solvent. High-resolution mass spectra were obtained on the MAT 95XP (Thermo) mass spectrometer at Sun Yat-sen University Mass Spectrometry Facilities and the GCT mass spectrometer at Institute of Chemistry, Chinese Academy of Sciences.

General Procedure for the Synthesis of Pyridinium Salts 1. Primary amine (1.2 equiv) was added to a suspension of 2,4,6-triphenylpyrylium tetrafluoroborate (1.0 equiv) and EtOH (0.1 M) in a round-bottomed flask equipped with a magnetic stirrer bar. The reaction mixture was heated to 85−90 °C for 4 h and cooled to ambient temperature. If precipitation occurred during this step, the solid was collected by filtration and washed with EtOH and Et_2O. In case no precipitation occurred, Et_2O was added to the reaction mixture and the resulting suspension was stirred at room temperature for at least 1 h to complete the precipitation process. If no precipitation occurred at this point, the flask containing the reaction mixture and Et_2O was sealed and stored at −20 °C for 1−3 days (or until precipitation occurred). The solid was collected by filtration and washed with Et_2O. If the salt still did not precipitate, it was subjected to silica gel chromatography with acetone/DCM.

General Procedure for the Synthesis of *Z*-Alkenes. To a 3 mL vial, equipped with a magnetic stir bar, pyridium salt (0.3 mmol, 3 equiv), terminal (hetero) arylalkyne (0.1 mmol, 1 equiv), and $Ir(ppy)_3$ (1 mmol %) were added. DIPEA (50 equiv, 0.85 mL) and DMA (1 mL) were added. The reaction mixture was degassed by argon and placed in a SynLED Parallel Photoreactor. The vial was stirred at room temperature under visible light irradiation for 16 h. Upon completion, the mixture was quenched with water and extracted three times with ethyl acetate. The combined organic extracts were dried with Na_2SO_4 and concentrated in vacuo. The product was further purified by flash chromatography to obtain the desired product.

*(Z)-1-Chloro-2-(2-cyclohexylvinyl)benzene (**3a**).* Colorless oil, 15.0 mg, 68% yield, *Z*/*E* = 95:5. Gram Scale: **1a** (3 mmol, 1.43 g),**2a** (1 mmol, 0.12 mL), 110.3 mg, 50% yield, *Z*/*E* = 95:5. R_f 0.8 (petroleum ether). This compound is known, and the data reported here are consistent with the literature.[12] ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38 (d, *J* = 7.6 Hz, 1H), 7.28−7.16 (m, 3H), 6.38 (d, *J* = 11.6 Hz, 1H), 5.61 (t, *J* = 10.9 Hz, 1H), 2.39−2.34 (m, 1H), 1.70−1.64 (m, 5H), 1.26−1.12 (m, 5H). ^{13}C{H} NMR (100 MHz, $CDCl_3$) δ 140.0, 136.2, 133.5, 130.3, 129.3, 127.9, 126.3, 124.1, 37.0, 33.1, 25.9, 25.6. HRMS (EI) Calcd for $C_{14}H_{17}Cl^+$ $[M]^+$: 220.1019, found: 220.1023.

*1-Chloro-2-(2-cyclopentylvinyl)benzene (**3b**).* Colorless oil, 14.8 mg, 72% yield, *Z*/*E* = 92:8. R_f 0.8 (petroleum ether). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.52 (d, *J* = 7.6 Hz, 0.09H), 7.38−7.29 (m, 2H), 7.24−7.10 (m, 2H), 6.75 (d, *J* = 15.7 Hz, 0.09H), 6.42 (d, *J* = 11.4 Hz, 1H), 6.19 (dd, J = 15.8 Hz, *J* = 7.8 Hz, 0.09H), 5.70 (t, *J* = 10.8 Hz, 1H), 2.80−2.63 (m, 1H), 1.83−1.79 (m, 2H), 1.73−1.65 (m, 2H), 1.62−1.55 (m, 2H), 1.46−1.26 (m, 2H). ^{13}C{H} NMR (100 MHz, $CDCl_3$) δ 139.5, 138.6, 136.2, 135.9, 133.6, 132.5, 130.5, 129.6, 129.3, 127.9, 127.7, 126.7, 126.5, 126.2, 124.5, 124.1, 44.0, 38.9, 34.1, 33.2, 25.6, 25.3. HRMS (EI) Calcd for $C_{13}H_{15}Cl^+$ $[M]^+$: 206.0857, found: 206.0854.

*(Z)-1-Chloro-2-(2-cycloheptylvinyl)benzene (**3c**).* Colorless oil, 11.7 mg, 50% yield, *Z*/*E* = 98:2. R_f 0.8 (petroleum ether). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38 (d, *J* = 7.9 Hz, 1H), 7.28−7.16 (m, 3H), 6.33 (d, *J* = 11.5 Hz, 1H), 5.74 (t, *J* = 11.0 Hz, 1H), 2.53−2.50 (m, 1H), 1.73−1.66 (m, 6H), 1.42−1.26 (m, 6H). ^{13}C{H} NMR (100 MHz, $CDCl_3$) δ 140.7, 136.2, 133.6, 130.4, 129.3, 127.9, 126.3, 122.6, 38.2, 34.9, 28.5, 26.3. HRMS (EI) Calcd for $C_{15}H_{19}Cl^+$ $[M]^+$: 234.1170, found: 234.1171.

*(Z)-1-Chloro-2-(2-cyclododecylvinyl)benzene (**3d**).* Colorless oil, 10.9 mg, 36% yield, *Z*/*E* = 98:2. R_f 0.8 (petroleum ether). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38−7.36 (m, 1H), 7.28−7.26 (m, 1H), 7.23−7.16 (m, 2H), 6.44 (d, *J* = 11.3 Hz, 1H), 5.59 (t, *J* = 10.9 Hz, 1H), 2.62−2.51 (m, 1H), 1.55−1.47 (m, 2H), 1.35−1.13 (m, 18H), 1.11−1.11 (m, 2H). ^{13}C{H} NMR (100 MHz, $CDCl_3$) δ 140.0, 136.6, 133.6, 130.6, 129.1, 127.9, 126.1, 125.5, 32.2, 30.4, 23.9, 23.7, 23.3, 22.8, 22.3. HRMS (EI) Calcd for $C_{20}H_{29}Cl^+$ $[M]^+$: 304.1952, found: 304.1951.

*(Z)-1-Chloro-2-(3-ethylpent-1-en-1-yl)benzene (**3e**).* Colorless oil, 14.7 mg, 71% yield, *Z*/*E* = 95:5. R_f 0.8 (petroleum ether). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40−7.18 (m, 4H), 6.56 (d, *J* = 11.6 Hz, 1H), 5.51 (t, *J* = 11.2 Hz, 1H), 2.31−2.23 (m, 1H), 1.50−1.41 (m, 2H), 1.32−1.23 (m, 2H), 0.95−0.85 (m, 6H). ^{13}C{H} NMR (100 MHz, $CDCl_3$) δ 138.9, 136.5, 133.7, 130.5, 129.2, 127.8, 126.8, 126.1, 40.7, 28.0, 11.7. HRMS (EI-TOF) Calcd for $C_{13}H_{17}Cl^+$ $[M]^+$: 208.1019, found: 208.1022.

*(Z)-1-Chloro-2-(3-methyloct-1-en-1-yl)benzene (**3f**).* Colorless oil, 14.5 mg, 62% yield, *Z*/*E* = 98:2. R_f 0.8 (petroleum ether). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37 (d, *J* = 7.4 Hz, 1H), 7.26−7.12 (m, 3H), 6.42 (d, *J* = 11.5 Hz, 1H), 5.56 (t, *J* = 11.0 Hz, 1H), 2.51−2.47 (m, 1H), 1.26−1.08 (m, 8H), 1.01 (d, *J* = 6.6 Hz, 3H), 0.83 (t, *J* = 7.2 Hz, 3H). ^{13}C{H} NMR (100 MHz, $CDCl_3$) δ 140.5, 136.4, 133.6, 130.5, 129.3, 127.9, 126.2, 124.9, 37.3, 32.2, 31.9, 26.9, 22.6, 21.1, 14.1. HRMS (EI) Calcd for $C_{15}H_{21}Cl^+$ $[M]^+$: 236.1326, found: 236.1328.

*(Z)-1-Chloro-2-(3-cyclohexylbut-1-en-1-yl)benzene (**3g**).* Colorless oil, 19.8 mg, 80% yield, *Z*/*E* = 98:2. R_f 0.8 (petroleum ether). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38 (d, *J* = 11.6 Hz, 1H), 7.29−7.17 (m, 3H), 6.46 (d, *J* = 11.6 Hz, 1H), 5.65 (t, *J* = 11.2 Hz, 1H), 2.34−2.28 (m, 1H), 1.79−1.62 (m, 5H), 1.29−1.10 (m, 4H), 1.02 (d, *J* = 6.7 Hz, 3H), 0.94−0.81 (m, 2H). ^{13}C{H} NMR (100 MHz, $CDCl_3$) δ 139.3, 136.5, 133.6, 130.5, 129.2, 127.8, 126.2, 125.2, 43.4, 37.6, 30.6, 30.4, 26.6 (2C), 18.1. HRMS (EI-TOF) Calcd for $C_{16}H_{21}Cl^+$ $[M]^+$: 248.1332, found: 248.1328.

*(Z)-1-Chloro-2-(3-methyl-5-penylpent-1-en-1-yl)benzene (**3h**).* Colorless oil, 14.8 mg, 55% yield, *Z*/*E* = 98:2. R_f 0.8 (petroleum ether). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40 (d, *J* = 7.5 Hz, 1H), 7.22−7.11 (m, 6H), 7.06 (d, *J* = 7.3 Hz, 2H), 6.51 (d, *J* = 11.5 Hz, 1H), 5.61 (t, *J* = 11.0 Hz, 1H), 2.66−2.53 (m, 2H), 2.50−2.42 (m, 1H), 1.70−1.57 (m, 2H), 1.08 (d, *J* = 6.6 Hz, 3H). ^{13}C{H} NMR (100 MHz, $CDCl_3$) δ 142.5, 139.9, 136.2, 133.6, 130.4, 129.3, 128.4, 128.2, 128.0, 126.3, 125.6, 125.5, 39.3, 33.6, 31.8, 21.1. HRMS (EI) Calcd for $C_{18}H_{19}Cl^+$ $[M]^+$: 270.1170, found: 270.1171.

*2-(2-chlorostyryl)-2,3-dihydro-1H-indene (**3i**).* White solid, 14.3 mg, 56% yield, *Z*/*E* = 91:9, mp 71−73 °C. R_f 0.7 (petroleum ether). ^{1}H NMR (400 MHz, $CDCl_3$) δ7.47−7.39 (m, 2H), 7.32−7.20 (m, 6H), 6.96 (d, *J* = 15.7 Hz, 0.09H), 6.61 (d, *J* = 11.4 Hz, 0.91H), 6.44 (dd, *J* = 15.8 Hz, *J* = 8.0 Hz, 0.09H), 6.01 (t, *J* = 10.8 Hz, 0.91H), 3.57−3.40 (m, 1H), 3.23−3.14 (m, 2H), 3.00−2.89 (m, 2H). ^{13}C{H} NMR (100 MHz, $CDCl_3$) δ 142.9, 137.8, 135.9, 133.7, 130.4, 129.4, 128.2, 126.3, 125.9, 124.4, 40.2, 39.0. HRMS (EI) Calcd for $C_{17}H_{15}Cl^+$ $[M]^+$: 254.0857, found: 254.0854.

*(Z)-1-Chloro-2-(2-(4,4-difluorocyclohexyl)vinyl)benzene (**3j**).* Colorless oil, 9.7 mg, 38% yield, *Z*/*E* = 97:3. R_f 0.8 (petroleum ether). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.43−7.37 (m, 1H), 7.23 (br s, 3H), 6.47 (d, *J* = 11.5 Hz, 1H), 5.62 (t, *J* = 10.8 Hz, 1H), 2.44−2.36 (m, 1H), 2.17−2.00 (m, 2H), 1.78−1.48 (m, 6H). ^{13}C{H} NMR (100 MHz, $CDCl_3$) δ 137.2 (d, *J* = 2.6 Hz), 135.9, 133.6, 130.1, 129.5, 128.3, 126.5, 126.2, 121.9 (d, *J* = 239.6 Hz), 35.0, 33.3, 33.0 (d, *J* = 2.6), 32.8, 29.2 (d, *J* = 9.5 Hz). HRMS (EI) Calcd for $C_{14}H_{15}ClF_2^+$ $[M]^+$: 256.0825, found: 256.0822.

*(Z)-4-(2-Cyclorostyryl)-tetrahydropyran (**3k**).* Colorless oil, 9.5 mg, 43% yield, *Z*/*E* = 96:4. R_f 0.8 (petroleum ether: ethyl acetate = 6:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39 (d, *J* = 6.6 Hz, 1H), 7.25−7.18 (m, 3H), 6.45 (d, *J* = 11.5 Hz, 1H), 5.61 (t, *J* = 10.8 Hz, 1H), 3.95−3.91 (m, 2H), 3.39−3.32 (m, 2H), 2.60−2.54 (m, 1H), 1.58−

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1.49 (m, 4H). $^{13}C\{H\}$ NMR (100 MHz, $CDCl_3$) δ 138.0, 135.9, 133.6, 130.2, 129.5, 128.3, 126.4, 125.6, 67.3, 34.3, 32.6. HRMS (EI) Calcd for $C_{13}H_{15}ClO^+$ $[M]^+$: 222.0806, found: 222.0804.

*(Z)-4-(2-Cyclorostyryl)-1-(methylsulfonyl)piperidine (**3l**).* Colorless oil, 12.2 mg, 41% yield, Z/E = 99:1. R_f 0.8 (petroleum ether: ethyl acetate = 2:1); ^1H NMR (400 MHz, $CDCl_3$) δ 7.41−7.37 (m, 1H), 7.25−7.17 (m, 3H), 6.49 (d, J = 11.5 Hz, 1H), 5.65−5.55 (m, 1H), 3.76 (d, J = 11.9 Hz, 2H), 2.74 (s, 3H), 2.64−2.57 (m, 2H), 2.46−2.36 (m, 1H), 1.79−1.75 (m, 2H), 1.61−1.51 (m, 2H). $^{13}C\{H\}$ NMR (100 MHz, $CDCl_3$) δ 136.8, 135.8, 133.6, 130.0, 129.6, 128.4, 126.6, 126.5, 45.6, 34.6, 34.5, 31.5. HRMS (EI-TOF) Calcd for $C_{14}H_{18}ClNO_2S^+$ $[M]^+$: 299.0747, found: 299.0750.

*(Z)-Tert-butyl-4-(2-cyclorostyryl)piperidine-1-carboxylate (**3m**).* Colorless oil, 16.0 mg, 50% yield, Z/E = 95:5. R_f 0.7 (petroleum ether: ethyl acetate = 6:1). ^1H NMR (400 MHz, $CDCl_3$) δ 7.39 (d, J = 6.7 Hz, 1H), 7.24−7.18 (m, 3H), 6.45 (d, J = 11.5 Hz, 1H), 5.62−5.54 (m, 1H), 4.05 (br s, 2H), 2.66 (t, J = 12.2 Hz, 2H), 2.53−2.41 (m, 1H), 1.61 (s, 2H), 1.45 (s, 9H), 1.40−1.28 (m, 2H). $^{13}C\{H\}$ NMR (100 MHz, $CDCl_3$) δ 154.8, 137.8, 135.9, 133.6, 130.1, 129.5, 128.3, 126.4, 125.7, 79.4, 35.3, 31.9, 28.5. HRMS (EI) Calcd for $C_{18}H_{24}ClNO_2^+$ $[M]^+$: 321.1490, found: 321.1492.

*(Z)-2-Benzyl-4-(2-chlorophenyl)but-3-en-1-ol (**3n**).* Colorless oil, 11.4 mg, 42% yield, Z/E = 99:1. R_f 0.8 (petroleum ether: ethyl acetate = 6:1). ^1H NMR (400 MHz, $CDCl_3$) δ 7.37−7.03 (m, 9H), 6.75 (d, J = 7.2 Hz, 1H), 6.63 (d, J = 11.5 Hz, 1H), 5.62 (t, J = 11.0 Hz, 1H), 3.60 (dd, J = 10.6 Hz, J = 5.3 Hz, 1H), 3.51 (dd, J = 10.6 Hz, J = 7.7 Hz, 1H), 2.93−2.87 (m, 1H), 2.77 (dd, J = 13.4 Hz, J = 5.9 Hz, 1H), 2.62 (dd, J = 13.5 Hz, J = 8.2 Hz, 1H). $^{13}C\{H\}$ NMR (100 MHz, $CDCl_3$) δ 139.4, 135.5, 134.2, 133.5, 130.3, 130.1, 129.2, 129.1, 128.4, 128.3, 126.3, 126.2, 65.8, 42.9, 37.9. HRMS (EI-TOF) Calcd for $C_{17}H_{17}ClO^+$ $[M]^+$: 272.0968, found: 272.0963.

*(Z)-4-(2-Cyclorostyryl)cyclohexan-1-ol (**3o**).* Colorless oil, 9.9 mg, 42% yield, Z/E = 93:7. R_f 0.6 (petroleum ether: ethyl acetate = 2:1). ^1H NMR (400 MHz, $CDCl_3$) δ 7.38 (dd, J = 7.5 Hz, J = 1.3 Hz, 1H, 7.26−7.15 (m, 3H), 6.42 (d, J = 11.6 Hz, 1H), 5.73 (t, J = 10.9 Hz, 1H), 3.97 (s, 1H), 2.43 (dd, J = 11.4 Hz, J = 7.9 Hz, 1H), 1.81−1.70 (m, 2H), 1.69−1.60 (m, 2H), 1.56−1.48 (m, 2H), 1.35−1.23 (m, 2H). $^{13}C\{H\}$ NMR (100 MHz, $CDCl_3$) δ 138.8, 136.2, 133.6, 130.3, 129.4, 128.0, 126.3, 124.8, 66.3, 35.6, 31.7, 27.0. HRMS (EI-TOF) Calcd for $C_{14}H_{17}ClO^+$ $[M]^+$: 236.0968, found: 236.0972.

*(2-Cyclohexylvinyl)benzene (**4a**).* Colorless oil, 9.7 mg, 52% yield, Z/E = 81:19. R_f 0.8 (petroleum ether). This compound is known, and the data reported here are consistent with the literature.[12] ^1H NMR (400 MHz, $CDCl_3$) δ 7.38−7.16 (m, 5H), 6.36−6.29 (m, 1H), 6.18 (dd, J = 15.7 Hz, J = 6.8 Hz, 0.19H), 5.53−5.44 (m, 0.81H), 2.62−2.54 (m, 0.081H), 2.14−2.10 (m, 0.19H), 1.82−1.65 (m, 5H), 1.33−1.12 (m, 5H). $^{13}C\{H\}$ NMR (100 MHz, $CDCl_3$) δ 139.0, 138.0, 137.9, 136.8, 128.6, 128.4, 128.2, 127.2, 126.8, 126.7, 126.4, 125.9, 41.2, 36.9, 33.3, 32.9, 26.2, 26.0, 25.7.

*1-(2-Cyclohexylvinyl)-2-fluorobenzene (**4b**).* Colorless oil, 11.2 mg, 60% yield, Z/E = 92:8. R_f 0.8 (petroleum ether). ^1H NMR (400 MHz, $CDCl_3$) δ 7.46−7.41 (m, 0.09H), 7.28−7.19 (m, 2H), 7.11−7.02 (m, 2H), 6.51 (d, J = 16.1 Hz, 0.09H), 6.31 (d, J = 11.6 Hz, 1H), 6.24 (dd, J = 16.1 Hz, J = 7.0 Hz, 0.09H), 5.61 (t, J = 10.9 Hz, 1H), 2.45−2.37 (m, 1H), 2.21−2.11 (m, 0.09H), 1.83−1.64 (m, 5H), 1.30−1.11 (m, 5H). $^{13}C\{H\}$ NMR (100 MHz, $CDCl_3$) δ 160.2 (d, J = 246.5 Hz), 140.9, 130.4 (d, J = 3.6 Hz), 128.2 (d, J = 8.2 Hz), 125.6 (d, J = 14.7 Hz), 123.6 (d, J = 3.6 Hz), 119.3 (d, J = 3.5 Hz), 115.3 (d, J = 22.3 Hz). 37.4, 33.1, 26.0, 25.6. HRMS (EI) Calcd for $C_{14}H_{17}F^+$ $[M]^+$: 204.1309, found: 204.1310.

*1-(2-Cyclohexylvinyl)-2-(triflloromethyl)benzene (**4c**).* Colorless oil, 16.8 mg, 66% yield, Z/E = 92:8. R_f 0.8 (petroleum ether). ^1H NMR (400 MHz, $CDCl_3$) δ 7.66−7.58 (m, 1H), 7.51−7.47 (m, 1H), 7.36−7.28 (m, 2H), 6.71 (d, J = 14.2 Hz, 0.08H), 6.51 (d, J = 11.3 Hz, 1H), 6.14 (dd, J = 15.4 Hz, J = 7.1 Hz, 0.08H), 5.61 (t, J = 11.0 Hz, 1H), 2.22−2.20 (m, 1H), 1.84−1.62 (m, 5H), 1.25−1.15 (m, 5H). $^{13}C\{H\}$ NMR (100 MHz, $CDCl_3$) δ 141.0, 140.4, 136.9, 131.7, 131.3, 130.9, 128.5 (q, J = 29.5 Hz), 128.3, 127.1, 126.6, 126.4, 125.7 (q, J = 5.5 Hz), 125.6, 123.8, 123.5, 122.9, 120.2, 41.3, 37.0, 32.9, 32.7, 26.1, 25.9, 25.5. HRMS (EI) Calcd for $C_{15}H_{17}F_3^+$ $[M]^+$: 254.1277, found: 254.1276.

*(Z)-1-(2-cyclohexylvinyl)-2-methoxybenzene (**4d**).* Colorless oil, 9.7 mg, 45% yield, Z/E = 99:1. R_f 0.8 (petroleum ether). ^1H NMR (400 MHz, $CDCl_3$) δ 7.26−7.21 (m, 2H), 6.93 (t, J = 7.4 Hz, 1H), 6.88 (d, J = 8.1 Hz, 1H), 6.40 (d, J = 11.7 Hz, 1H), 5.54 (dd, J = 11.3 Hz, J = 10.6 Hz, 1H), 3.83 (s, 3H), 2.48−2.45 (m, 1H), 1.72−1.63 (m, 5H), 1.26−1.15 (m, 5H). $^{13}C\{H\}$ NMR (100 MHz, $CDCl_3$) δ 157.0, 138.9, 129.8, 127.9, 126.9, 122.1, 120.1, 110.4, 55.4, 37.1, 33.3, 26.1, 25.7. HRMS (EI) Calcd for $C_{15}H_{20}O^+$ $[M]^+$: 216.1509, found: 216.1508.

*1-(2-cyclohexylvinyl)-4-fluorobenzene (**4e**).* Colorless oil, 10.2 mg, 50% yield, Z/E = 89:11. R_f 0.8 (petroleum ether). This compound is known, and the data reported here are consistent with the literature.[10a] ^1H NMR (400 MHz, $CDCl_3$) δ7.30−7.19 (m, 2H), 7.03−6.95 (m, 2H), 6.32−6.25 (m, 1H), 6.09 (dd, J = 16.0 Hz, J = 7.0 Hz, 0.11H), 5.46 (t, J = 10.9 Hz, 0.89H), 2.55−2.47 (m, 0.89H), 2.14−2.08 (m, 0.11H), 1.81−1.66 (m, 5H), 1.33−1.12 (m, 5H). $^{13}C\{H\}$ NMR (100 MHz, $CDCl_3$) δ 161.5 (d, J = 245.5 Hz), 138.9 (d, J = 1.0 Hz), 133.9 (d, J = 3.4 Hz), 130.1 (d, J = 7.8 Hz), 125.8, 115.0 (d, J = 21.3 Hz), 36.8, 33.2, 26.0, 25.7. HRMS (EI) Calcd for $C_{14}H_{17}F^+$ $[M]^+$: 204.1314, found: 204.1312.

*1-Chloro-4-(2-cyclohexylvinyl)benzene (**4f**).* Colorless oil, 11.2 mg, 51% yield, Z/E = 87:13. R_f 0.8 (petroleum ether). This compound is known, and the data reported here are consistent with the literature.[10a] ^1H NMR (400 MHz, $CDCl_3$) δ 7.29 (d, J = 8.4 Hz, 1.7H), 7.26−7.24 (m, 0.6H), 7.18 (d, J = 8.4 Hz, 1.7H), 6.31−6.24 (m, 1H), 6.15 (dd, J = 16.0 Hz, J = 6.8 Hz, 0.13H), 5.51 (dd, J = 11.3 Hz, J = 10.6 Hz, 0.87H), 2.54−2.47 (m, 0.87H), 2.13−2.09 (m, 0.13H), 1.73−1.69 (m, 5H), 1.29−1.15 (m, 5H). $^{13}C\{H\}$ NMR (100 MHz, $CDCl_3$) δ 139.6, 137.6, 136.6, 136.4, 132.2, 132.1, 129.9, 128.6, 128.3, 127.2, 126.1, 125.7, 41.2, 36.9, 33.2, 32.9, 26.2, 26.0, 25.9, 25.7. HRMS (EI) Calcd for $C_{14}H_{17}Cl^+$ $[M]^+$: 220.1019, found: 220.1015.

*1-Bromo-4-(2-cyclohexylvinyl)benzene (**4g**).* Colorless oil, 14.5 mg, 55% yield, Z/E = 86:14. R_f 0.8 (petroleum ether). This compound is known, and the data reported here are consistent with the literature.[10a] ^1H NMR (400 MHz, $CDCl_3$) δ 7.44 (d, J = 8.3 Hz, 1.68H), 7.40 (d, J = 8.3 Hz, 0.32H), 7.20 (d, J = 8.3 Hz, 0.32H), 7.11 (d, J = 8.3 Hz, 1.68H), 6.29−6.22 (m, 1H), 6.16 (dd, J = 15.9 Hz, J = 6.8 Hz, 0.14H), 5.55−5.48 (m, 0.86H), 2.54−2.46 (m, 0.86H), 2.12−2.11 (m, 0.14H), 1.81−1.65 (m, 5H), 1.32−1.11 (m, 5H). $^{13}C\{H\}$ NMR (100 MHz, $CDCl_3$) δ 139.7, 137.7, 137.0, 136.8, 131.5, 131.3, 130.2, 127.5, 126.2, 125.7, 120.3, 120.2, 41.2, 36.9, 33.1, 32.8, 26.1, 26.0, 25.9, 25.6. HRMS (EI) Calcd for $C_{14}H_{17}Br^+$ $[M]^+$: 264.0514, 266.0493, found: 264.0518, 266.0491.

*1-(2-cyclohexylvinyl)-4-(trifluoromethyl)benzene (**4h**).* Colorless oil, 9.7 mg, 38% yield, Z/E = 90:10. R_f 0.8 (petroleum ether). This compound is known, and the data reported here are consistent with the literature.[12] ^1H NMR (400 MHz, $CDCl_3$) δ 7.58 (d, J = 8.1 Hz, 1.80H), 7.53 (d, J = 8.2 Hz, 0.2H), 7.42 (d, J = 8.2 Hz, 0.2H), 7.34 (d, J = 8.1 Hz, 1.8H), 6.39−6.29 (m, 1H), 5.64−5.56 (m, 1H), 2.56−2.48 (m, 0.9H), 2.18−2.14 (m, 0.1H), 1.80−1.66 (m, 5H), 1.32−1.17 (m, 5H). $^{13}C\{H\}$ NMR (100 MHz, $CDCl_3$) δ 141.6, 141.5, 141.0, 139.6, 128.8, 128.6, 128.2, 126.1, 126.0, 125.7, 125.4 (q, J = 7.2 Hz), 125.1 (q, J = 6.8 Hz), 123.0, 41.2, 37.0, 33.1, 32.8, 26.1, 26.0, 25.9, 25.6. HRMS (EI) Calcd for $C_{15}H_{17}F_3^+$ $[M]^+$: 254.1282, found: 254.1285.

*(Z)-1-(2-cyclohexylvinyl)-4-cyanobenzene (**4i**).* Colorless oil, 8.2 mg, 39% yield, Z/E = 99:1. R_f 0.8 (petroleum ether: ethyl acetate = 9:1). This compound is known, and the data reported here are consistent with the literature.[10a] ^1H NMR (400 MHz, $CDCl_3$) δ7.61 (d, J = 8.2 Hz, 2H), 7.33 (d, J = 8.1 Hz, 2H), 6.30 (d, J = 11.8 Hz, 1H), 5.64 (t, J = 11.0 Hz, 1H), 2.52−2.47 (m, 1H), 1.75−1.69 (m, 5H), 1.29−1.17 (m, 5H). $^{13}C\{H\}$ NMR (100 MHz, $CDCl_3$) δ 142.7, 142.0, 132.0, 129.1, 125.5, 119.0, 109.9, 37.1, 33.0, 25.9, 25.5. HRMS (EI) Calcd for $C_{15}H_{17}N^+$ $[M]^+$: 211.1361, found: 211.1362.

*1-(2-cyclohexylvinyl)-4-methylbenzene (**4j**).* Colorless oil, 8.0 mg, 40% yield, Z/E = 84:16. R_f 0.8 (petroleum ether). This compound is known, and the data reported here are consistent with the literature.[10c] ^1H NMR (400 MHz, $CDCl_3$) δ 7.25−7.08 (m, 4H),

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6.33−6.25 (m, 1H), 6.12 (dd, J = 15.9 Hz, J = 6.9 Hz, 0.16H), 5.48−5.40 (m, 0.84H), 2.62−2.50 (m, 0.84H), 2.35 (s, 3H), 2.12−2.08 (m, 0.16H), 1.82−1.65 (m, 5H), 1.33−1.11 (m, 5H). ^{13}C{H} NMR (100 MHz, $CDCl_3$) δ 138.4, 136.4, 136.1, 135.9, 135.3, 135.1, 129.2, 128.9, 128.5, 127.0, 126.7, 125.8, 41.2, 36.9, 33.3, 33.0, 26.2, 26.1(2C), 25.7, 21.2, 21.1. HRMS (EI) Calcd for $C_{15}H_{20}^+$ $[M]^+$: 200.1565, found: 200.1566.

*1-(tert-Butyl)-4-(2-cyclohexylvinyl)benzene (**4k**).* Colorless oil, 12.9 mg, 50% yield, Z/E = 86:14. R_f 0.8 (petroleum ether). This compound is known, and the data reported here are consistent with the literature.[10a] ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.36 (d, J = 8.3 Hz, 1.7H), 7.32−7.29 (m, 0.6H), 7.21 (d, J = 8.3 Hz, 1.7H), 6.34−6.25 (m, 1H), 6.13 (dd, J = 16.0 Hz, J = 6.9 Hz, 0.14H), 5.49−5.40 (m, 0.86H), 2.63−2.61 (m, 1H), 1.75−1.71 (m, 5H), 1.33 (s, 9H), 1.30−1.12 (m, 5H). ^{13}C{H} NMR (100 MHz, $CDCl_3$) δ 149.8, 149.3, 138.4, 136.1, 135.3, 135.1, 128.4, 126.9, 126.6, 125.6, 125.4, 125.1, 41.2, 36.9, 34.5, 33.3, 33.1, 31.3, 26.2, 26.1, 26.0, 25.7. HRMS (EI) Calcd for $C_{18}H_{26}^+$ $[M]^+$: 242.2035, found: 242.2034.

*(Z)-1-(2-cyclohexylvinyl)-4-methoxybenzene (**4l**).* Colorless oil, 8.2 mg, 38% yield, Z/E = 98:2. R_f 0.8 (petroleum ether). This compound is known, and the data reported here are consistent with the literature.[10a] ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.20 (d, J = 8.6 Hz, 2H), 6.87 (d, J = 8.7 Hz, 2H), 6.24 (d, J = 11.7 Hz, 1H), 5.40 (dd, J = 11.4 Hz, J = 10.2 Hz, 1H), 3.82 (s, 3H), 2.61−2.53 (m, 1H), 1.74−1.65 (m, 5H), 1.31−1.15 (m, 5H). ^{13}C{H} NMR (100 MHz, $CDCl_3$) δ 158.2, 137.6, 130.6, 129.8, 126.3, 113.6, 55.3, 36.9, 33.3, 26.1, 25.8. HRMS (EI) Calcd for $C_{15}H_{20}O^+$ $[M]^+$: 216.1514, found: 216.1517.

*1-(2-Cyclohexylvinyl)-3-fluorobenzene (**4m**).* Colorless oil, 11.8 mg, 58% yield, Z/E = 82:18. R_f 0.8 (petroleum ether). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.30−7.21 (m, 1H), 7.10−6.85 (m, 3H), 6.33−6.25 (m, 1H), 6.18 (dd, J = 16.0 Hz, J = 6.8 Hz, 0.18H), 5.52 (dd, J = 11.3 Hz, J = 10.6 Hz, 0.82H), 2.58−2.50 (m, 0.82H), 2.14−2.12 (m, 0.18H), 1.82−1.65 (m, 5H), 1.34−1.13 (m, 5H). ^{13}C{H} NMR (100 MHz, $CDCl_3$) δ 163.2 (d, J = 244.7 Hz), 162.8 (d, J = 244.9 Hz), 140.5 (d, J = 7.7 Hz), 140.2 (d, J = 7.7 Hz), 140.1, 138.3, 129.8 (d, J = 8.5 Hz), 129.6 (d, J = 8.4 Hz), 126.3 (d, J = 2.5 Hz), 125.8 (d, J = 2.2 Hz), 124.3 (d, J = 2.7 Hz), 121.8 (d, J = 2.6 Hz), 115.3 (d, J = 21.3 Hz), 113.6, 113.3 (d, J = 21.1 Hz), 112.3 (d, J = 21.6 Hz), 41.1, 36.9, 33.1, 32.8, 26.1, 26.0, 25.6. HRMS (EI) Calcd for $C_{14}H_{17}F^+$ $[M]^+$: 204.1309, found: 204.1307.

*1-(2-Cyclohexylvinyl)-3,5-difluorobenzene (**4n**).* Colorless oil, 11.5 mg, 52% yield, Z/E = 81:19. R_f 0.8 (petroleum ether). ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.84−6.74 (m, 2H), 6.70−6.64 (m, 1H), 6.24−6.19 (m, 1H), 6.18−6.16 (m, 0.2H), 5.56 (t, J = 11.0 Hz, 0.8H), 2.54−2.46 (m, 0.8H), 2.14−2.12 (m, 0.2H), 1.78−1.69 (m, 5H), 1.34−1.12 (m, 5H). ^{13}C{H} NMR (100 MHz, $CDCl_3$) δ 163.3 (d, J = 247.1 Hz), 163.2 (d, J = 247.0 Hz), 162.9 (d, J = 247.2 Hz), 162.8 (d, J = 247.3 Hz), 141.6, 141.1, 139.6, 125.6 (t, J = 2.7 Hz), 125.1 (t, J = 2.4 Hz), 111.3 (d, J = 25.0 Hz), 111.3 (d, J = 11.7 Hz), 108.5 (d, J = 11.8 Hz), 108.5 (d, J = 25.2 Hz), 101.8 (t, J = 25.8 Hz), 101.8 (t, J = 25.5 Hz), 100.0, 41.0, 37.0, 33.0, 32.7, 26.1, 25.9, 25.5. HRMS (EI) Calcd for $C_{14}H_{16}F_2^+$ $[M]^+$: 222.1215, found: 222.1213.

*(Z)-3-(2-cyclohexylvinyl)pyridine (**4o**).* Colorless oil, 9.0 mg, 48% yield, Z/E = 98:2. R_f 0.8 (petroleum ether: ethyl acetate = 6:1). This compound is known, and the data reported here are consistent with the literature.[12] ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.53 (s, 1H), 8.47 (d, J = 4.4 Hz, 1H), 7.61 (d, J = 7.8 Hz, 1H), 7.33−7.30 (m, 1H), 6.25 (d, J = 11.7 Hz, 1H), 5.66 (t, J = 11.0 Hz, 1H), 2.51−2.43 (m, 1H), 1.73−1.65 (m, 5H), 1.33−1.15 (m, 5H). ^{13}C{H} NMR (100 MHz, $CDCl_3$) δ 149.5, 147.3, 141.4, 135.8, 133.7, 123.2, 123.1, 37.1, 33.1, 25.9, 25.6. HRMS (EI) Calcd for $C_{13}H_{17}N^+$ $[M]^+$: 187.1361, found: 187.1362.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.joc.0c01928.

^{1}H and ^{13}C NMR spectra for all products (PDF)

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Notes

The authors declare no competing financial interest.

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