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N-Heterocyclic Carbene-Catalyzed Synthesis of Ynones via C–H Alkynylation of Aldehydes with Alkynyliodonium Salts

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ABSTRACT

Alkynylation of aldehydes with alkynyl(aryl)iodonium salts catalyzed by an *N*-heterocyclic carbene (NHC) has been developed. The application of the organocatalyst and the hypervalent iodine group-transfer reagent allowed for metal-free C–H functionalization and C–C bond formation. The reaction proceeds under exceptionally mild conditions, at –40 °C and in the presence of an amine base, providing access to an array of heteroaryl-propargyl ketones containing various substituents in good to excellent yields. The mechanism of the reaction was investigated by means of both experiments and density functional theory calculations. ¹³C-labelling and computations determined that the key alkynyl transfer step occurs via an unusual direct S_N2 substitution of iodine-based leaving group by Breslow intermediate nucleophile at an acetylenic

carbon. Moreover, kinetic studies revealed that the turnover-limiting step of the catalytic cycle is the generation of the Breslow intermediate, whereas the subsequent C–C bond-formation is a fast process. These results were fully reproduced and rationalized by the computed full free energy profile of the reaction, showing that the largest energy span is located between protonated NHC and the transition state for the carbene attack on the aldehyde substrate.

INTRODUCTION

Over the last two decades, the organocatalysis with *N*-heterocyclic carbenes (NHCs) has established a strong position in synthetic organic chemistry. Its success stems primarily from enabling a smooth access to a group of versatile nucleophilic species, such as Breslow intermediate (acyl anion equivalent), homoenolate, acylazolium enolate, and other, via the umpolung of abundant carbonyl substrates. The coupling of these nucleophiles with a plethora of electrophiles has allowed for the development of numerous highly useful synthetic methods.¹ In the recent years, the applicability of NHC catalysis is being further expanded by employing novel unconventional electrophilic partners, which provide a direct entry to important structural motifs.² One class of such electrophilic reagents that has recently opened new opportunities in NHC organocatalysis are hypervalent iodine compounds. Due to the ability of iodine atom to undergo a very energetically favorable reduction from +III to +I oxidation state, accompanied by a simultaneous bond formation involving its ligands (resembling a reductive elimination at a metal center), the hypervalent iodine species are superior atom- and group-transfer reagents.³ At the same time, they lack the toxicity and high price of transition metal catalysts, making them a good alternative from the environmental and economical viewpoints.⁴ The group transfer reagents based on hypervalent iodine have been used in a number of organocatalyzed reactions,⁵ but there is so far only a handful examples of NHC-promoted processes utilizing these unique electrophilic coupling partners.⁶

Ynones, or propargyl ketones, are a prominent class of organic compounds. First, the ynone motif is present in several biologically active molecules.⁷ Even more importantly, the combined reactivities of the triple bond and the carbonyl group give rise to numerous reactions, wherein ynones serve as precursors for the preparation of a diverse array of molecular scaffolds.^{8,9} The high

synthetic utility of ynones is proven by their application as key intermediates in multiple total syntheses.¹⁰

Ynones have traditionally been synthesized by one of three methods: (1) the reaction of metal acetylides with acyl chlorides or other carboxylic derivatives; (2) the oxidation of propargylic position in alkynes or of propargylic alcohols; and (3) a carbonylative cross-coupling.^{8f,11} An interesting alternative to these standard approaches that has recently gained attention is the direct alkynylation of the C–H bond in aldehydes (Scheme 1).¹² Such strategy possesses the advantage of providing propargyl ketones in a single synthetic step from abundant and stable starting materials. The first example employing this concept was reported by Zhou and co-workers in 2015, who described a rhodium- and iridium-catalyzed alkynyl transfer from ethynylbenziodoxolone (EBX) to aromatic aldehydes (Scheme 1a).¹³ The reaction proceeds via the incipient directing group-assisted activation of the formyl C–H to form a metal carbonyl complex. The second existing approach to effect the alkynylation of aldehydes relies on the homolytic cleavage of the C–H bond. The groups of Wei, Yu, and Li described independently the synthesis of ynones in the presence of *tert*-butyl hydroperoxide as a radical initiator (Scheme 1b).¹⁴ Despite the robustness and simplicity of these methods, their considerable disadvantage is the high reaction temperature required, imposing constraints on the scope. To alleviate the above drawback, Glorius and co-workers employed photoredox catalysis to generate radicals from aldehydes (Scheme 1b).¹⁵ By the application of iridium complex, the alkynylation of a variety of aldehydes with EBX could be carried out at room temperature.

Scheme 1. Synthesis of Ynones via Direct C–H Alkynylation of Aldehydes.

Building on the seminal work by Gaunt on the NHC-catalyzed arylation of aldehydes,^{6a} as well as on our own studies on the vinylation of aldehydes,^{6b} we envisioned that the formation of a Breslow intermediate by the action of an NHC catalyst on aldehyde substrate may constitute an alternative mean to activate the formyl C–H bond allowing for the subsequent alkynyl group transfer. Herein, we present our work on the development of a novel NHC-catalyzed direct C–H alkynylation of aldehydes outlined in Scheme 1c. Importantly, the reaction makes use of alkynyl(aryl)iodonium salts as the alkynyl group donor, in contrast to all of the previously reported methods that employ EBX reagents (Schemes 1a and 1b). While alkynyl(aryl)iodonium salts have been widely applied for the direct alkynylation of heteroatom nucleophiles and enolates of 1,3-dicarbonyl compounds,^{16,17} their use for transferring alkynyl moiety to less trivial carbon nucleophiles have usually required transition metal catalysis.¹⁸ On the contrary, the application of NHC organocatalyst gives rise to an efficient metal-free C–C bond formation involving a noteworthy acyl anion equivalent. In addition to the synthetic studies, we perform a thorough

mechanistic investigations of this new transformation by the combination of experimental and computational approaches. In particular, we identify the turnover-limiting step of the catalytic cycle and elucidate that the transfer of alkynyl moiety from the iodonium salt to the Breslow intermediate follows an unusual pathway of a direct S_N2 substitution at an acetylenic carbon atom.

RESULTS AND DISCUSSION

Synthetic studies. First, we investigated the effect of a number of reaction parameters on a model coupling between 2-quinoxalinecarbaldehyde **1a** and phenylethynyl(aryl)iodonium salts containing different auxiliary aryl groups and counter-ions (Table 1). The established optimal conditions consist of *N*-pentafluorophenyl-triazolium carbene precursor **NHC-1**, tetramethylethylenediamine (TMEDA) as the base, and toluene at –40 °C, affording ynone **3a** in 86% yield (entry 1). The structure of the iodonium salt was found to be crucial for the selective and efficient alkynyl group transfer.¹⁹ Mesityl was identified as the superior auxiliary aryl group, securing the formation of product in high yield (entry 1). Less sterically hindered, including singly *ortho*-substituted, aryls lead to a loss of the selectivity of the transfer, and to the formation of a bisaryl ketone side-product (entries 2–4). The presence of two *ortho* substituents in *o*-xylyl suppresses the side aryl-transfer, but the desired ynone is furnished in a lower yield than for the mesityl-containing salt **2a** (entry 5 vs. 1). A significant effect of the counter-ion was also observed. The best result was obtained with a tosylate salt (entry 1), whereas iodonium trifluoromethanesulfonate and trifluoroacetate display only a moderate reactivity (entries 6–7), and a tetrafluoroborate salt is quite ineffective (entry 8). Finally, we tested EBX reagent **4**, but it provides only traces of product under these conditions (entry 9). Importantly, the optimal

alkynyl(mesityl)iodonium tosylates of type **2a** are stable and easy to handle, and they can be very conveniently prepared by the method reported by Stang.²⁰

Table 1. Effect of Reaction Parameters^a

entry	deviation from the standard conditions	yield (%) ^b
1	-	86
2	Ar = Ph (2b), instead of Ar = Mes	38 (16) ^c
3	Ar = <i>o</i> -anisyl (2c), instead of Ar = Mes	17 (11) ^c
4	Ar = <i>o</i> -tolyl (2d), instead of Ar = Mes	73 (20) ^c
5	Ar = <i>o</i> -xylyl (2e), instead Ar = Mes	67
6	X = OTf (2f), instead of X = OTs	64
7	X = CF ₃ COO (2g), instead of X = OTs	66
8	X = BF ₄ (2h), instead of X = OTs	24
9	Ph-EBX (4), instead of 2a	4
10	NHC-2, instead of NHC-1	50
11	NHC-3, instead of NHC-1	58
12	NHC-4, instead of NHC-1	11
13	NHC-5, instead of NHC-1	<1
14	NHC-6, instead of NHC-1	<1
15	NHC-7, instead of NHC-1	19
16	5 mol% of NHC-1	64
17	no NHC-1	<1

18	0 °C, instead of –40 °C	66
19	r.t., instead of –40 °C	47
20	DMAP, instead of TMEDA	32
21	DABCO, instead of TMEDA	80
22	K ₃ PO ₄ , instead of TMEDA	8
23	DCE, instead of toluene	62 ^d
24	CH ₂ Cl ₂ , instead of toluene	51
25	MeCN, instead of toluene	50

^aAll data are the average of two experiments. ^bDetermined through analysis by ¹H NMR spectroscopy. ^cThe formation of bisaryl ketone side-product was observed, its yield is given in parenthesis. ^dAt –35 °C. Mes = 2,4,6-trimethylphen-1-yl; OTs = *p*-tolenesulfonate; OTf = trifluoromethanesulfonate; TCIP = 2,4,6-trichlorophen-1-yl; DCE = 1,2-dichloroethane.

As far as the other reaction parameters are concerned, we found that the different types of NHCs commonly used in organocatalysis (entries 10–15) are inferior to the commercially available **NHC-1**, bearing an electron deficient pentafluorophenyl group. Lowering of the catalyst loading from 10 to 5 mol% decreases the yield to a moderate level (entry 16) and no product formation is observed in the absence of catalyst (entry 17). Elevated temperatures have an adverse effect on the reaction (entries 18–19). Application of other organic amine bases results in moderate to good yields (entries 20–21), while inorganic bases are ineffective in this transformation (*e.g.*, entry 22). Interestingly, more polar solvents that completely solubilize the reactants are not as efficient as toluene, which affords a heterogenous reaction mixture.

Having established the optimal conditions for the NHC-catalyzed alkynylation of aldehydes, we proceeded to evaluate the scope and limitations of this reaction. An array of heteroaromatic aldehydes could be efficiently alkynylated (Scheme 2). In particular, arylpropargyl ketones containing heterocyclic six-membered rings with nitrogen, such as quinoxaline (**3a**), quinoline (**3b**), and pyridine (**3g–3l**), as well as five-membered rings, *e.g.*, pyrazole (**3c–3d**) and thiazole (**3e–3f**), were synthesized in good to excellent yields. The ability to incorporate these moieties is highly advantageous, as they are prevalent in therapeutically important molecules.²¹ A number of functional groups is tolerated under the reaction conditions, including aryl bromide (**3i**), double (**3k**), and triple (**3l**) bonds, providing useful handles for further functionalization and built-up of the molecular complexity. The method is also compatible with fluorinated substituents (**3h** and **3j**), which adds to its value for the synthesis of pharmaceutically relevant compounds.²² On the downside, benzaldehydes are poor substrates and only the one containing a strongly electron-withdrawing nitro group afforded the desired product in an admissible yield (**3m**). Also, aliphatic aldehydes were found to be completely incompetent starting materials.

Scheme 2. Scope with Regard to the Aldehyde

Next, we examined the scope with regard to the alkynyliodonium salt. The method could be applied to transfer a range of arylethynyl groups, containing a multitude of substituents (Scheme 3). All the alkyl-substituted (**3n**, **3o**), aryl-substituted (**3p**), as well as extended (**3q**) aryl systems can be incorporated into the product. The reaction proceeds equally well for arylethynyl moieties bearing both electron-withdrawing and electron-donating groups. Thus, regardless of the substituent position, ynones containing halogens (**3r** and **3t**), trifluoromethyl (**3s**), cyano (**3u**), ketone (**3v**), ester (**3w**), and ether (**3x-3y**) functionalities were synthesized in good to excellent yields. Notably, we also prepared propargyl ketones with a phthalamide-masked amine (**3z**) and a sulfonamide (**3aa**), demonstrating a broad functional group tolerance of the developed methodology. Unfortunately, when iodonium salts containing alkylethynyl groups were tested, the desired product was not formed under these conditions.

Scheme 3. Scope with Regard to the Alkynyliodonium Salt

Qx = quinoxalin-2-yl

Finally, to validate the synthetic utility of the developed procedure, we have applied it to synthesize compound **3y** on a gram scale, which was obtained without any appreciable loss in the yield (80%, 1.64 g of product).

Experimental mechanistic studies. The hypervalent iodine compounds bearing an alkynyl group contain three distinct electrophilic centers: the iodine atom, the α -carbon of the triple bond, and

the β -carbon of the triple bond. Therefore, the reactions involving such reagents may in principle follow three general mechanistic pathways, outlined in Scheme 4 for the particular case of the NHC-catalyzed alkynylation of aldehydes with alkynyliodonium salts. In the first scenario the nucleophile, Breslow intermediate, is incorporated into the coordination sphere of iodine (Scheme 4a). After the expulsion of NHC catalyst, the key C–C bond-formation takes place via a reductive ligand coupling, affording the ynone product. This type of mechanism is common for related aryl transfer reactions with diaryliodonium salts, as revealed by several computational investigations.²³ The second possibility is a direct S_N2 substitution at the α -acetylenic carbon, *i.e.*, the displacement of iodine acting as a leaving group by the attacking nucleophile (Scheme 4b). Such a mechanistic route has so far been shown to operate only in a single instance of alkynyl transfer from hypervalent iodine species, namely for the alkynylation of thiols with EBX reagents.²⁴ In the final alternative, the nucleophile attacks at the β -carbon of the triple bond in a Michel-type conjugate addition (Scheme 4c). The resulting iodonium ylide, after a prior elimination of NHC, undergoes a fragmentation producing a vinylidene carbene intermediate. Subsequently, the vinylidene carbene rearranges to the final product by a 1,2-shift of the aryl substituent. This last mechanism is accepted to be implicated in the majority of alkynylations with hypervalent iodine reagents and there exists strong experimental evidence supporting such a pathway. In particular, first, in multiple cases the iodonium ylide could be trapped by protonation, yielding isolable vinyliodonium derivatives.²⁵ Secondly, in the absence of any substituents prone to migration, the emergence of products originating from the insertion of the vinylidene carbene into C–H bonds has been observed.^{17k,26} Finally, the acetylenic carbons have been shown to swap their positions during the reactions with ¹³C-labeled alkynyliodonium starting materials, in line with the 1,2-shift step.^{24b,26a,27}

Scheme 4. Outline of Possible General Mechanisms

The fact that alkylethynyliodonium salts are not effective in the NHC-catalyzed reaction (*vide supra*) suggested that it may follow the most common pathway starting with the nucleophilic attack on the β -carbon (Scheme 4c), since the alkyl substituents are not likely to undergo the 1,2-migration. On the other hand, we did not observe any products originating from the insertion of the vinylidene carbene into the C–H bonds of the alkyl chains, either. Therefore, in order to obtain a more direct proof distinguishing between the different possible mechanisms, we carried out the alkynylation of aldehyde **1a** using iodonium salt **2w** that was labeled with ^{13}C at the α -carbon (Scheme 5). The resulting product **3ab** was generated in an unchanged yield compared to its unlabeled counterpart (*cf.* **3a** in Scheme 2) and it contained the ^{13}C label exclusively incorporated at the acetylenic carbon adjacent to the carbonyl group. Such an outcome allows to unambiguously eliminate the attack of Breslow intermediate on the β -carbon of the alkynyliodonium salt (Scheme 4c) as the valid pathway of the investigated reaction.

Scheme 5. NHC-Catalyzed Alkynylation of Aldehyde **1a** with Alkynyliodonium Salt **2w** Labelled with ^{13}C at the α -Carbon.

Stimulated by the result of above experiment, demonstrating that the developed reaction does not follow the most prevalent mechanism for alkynylations with hypervalent iodine compounds, we decided to perform more thorough investigations of this interesting process. To obtain insight into its course, we carried out kinetics investigations. First, the progress of the reaction under the optimized conditions was monitored over time (Figure 1a). The analysis of the decay of the starting material shows that the reaction displays overall second order in the concentrations of the substrates, as the linear dependence of reciprocal substrate concentration vs. time was observed (Figure 1b).²⁸

Figure 1. (A) Time-course of the NHC-Catalyzed Alkynylation of Aldehyde **1a** with Alkynyliodonium salt **2a** in *ds*-Toluene at $-40\text{ }^{\circ}\text{C}$.^{a,b} (B) Corresponding Plot of Reciprocal Substrate Concentration vs. Time.

^aThe concentrations were determined by ^1H NMR spectroscopy relative to internal standard. ^bThe initial leap in the concentrations is due to a temporary heating of the sample during the addition of the initiating reagent (TMEDA).

In order to ascribe the orders to the concentrations of specific reagents, we conducted an initial rate study. Our first attempts to follow the initial rates under the optimized conditions were unsuccessful, as erratic and irreproducible time curves were being obtained. We were able to trace this problem to the heterogeneity of the reaction mixture, and, thus, upon switching the solvent from *d*₈-toluene to CDCl_3 , which solubilizes all the reactants at the reaction temperature of -40°C , better quality data could be acquired. However, due to the technical difficulties of measuring the reaction kinetics at so low temperature, the alignment of the data points is still not perfect (see the

Supporting Information for details). Anyhow, despite considerable error bars, we are confident that we were able to grasp the kinetic characteristics of the transformation.

Figure 2. Initial Rate Measurements for the NHC-Catalyzed Alkynylation of Aldehyde **1a** with Alkynyliodonium Salt **2a** in CDCl_3 at -40°C , with Varied Concentration of (a) **1a**, (b) **2a**, (c) TMEDA, and (d) **NHC-1**. The Insets Show the Corresponding LN-LN Plots.^a

^a Product concentration was determined by ^1H NMR spectroscopy relative to internal standard.

Figure 2 presents the initial rate plots measured with varied concentrations of the respective reagents and the catalyst precursor. The analysis of this data results in an experimental rate law, wherein the reaction is first order in the concentrations of **1a**, TMEDA, and **NHC-1**, whereas

zeroth order in the concentration of **2a** (eq 1). This is in agreement with the overall second order in the substrates (*i.e.*, **1a** and TMEDA), determined from the reaction monitored over a longer period (Figure 1; the concentration of **NHC-1** is constant with conversion, hence its influence on the rate does not appear in that experiment).

$$rate = k[\mathbf{1a}][\text{TMEDA}][\mathbf{NHC-1}] \quad (1)$$

The presence of the aldehyde and the NHC precatalyst concentrations in rate law (1) directly implies that the formation of Breslow intermediate is the turnover-limiting step of the catalytic cycle. In turn, since the concentration of the alkynyliodonium salt does not impact the rate, the subsequent key C–C bond formation must be a fast step, demonstrating a very high mutual affinity between the alkynyliodonium salt and the Breslow intermediate. Taking this into account, the appearance of the concentration of TMEDA in the rate law indicates its involvement also during the generation of the Breslow intermediate, in addition to the deprotonation needed to expel NHC toward the end of the mechanism (Scheme 4).

Computational studies. To gain insight into the details of the catalytic cycle and complement the mechanistic picture obtained in the previous section, we performed a computational density functional theory (DFT) investigation. The alkynylation of 2-pyridinecarboxaldehyde (**1g**) with (mesityl)(phenylethynyl)iodonium tosylate (**2a**) using precatalyst **NHC-1** was employed as a model reaction in the calculations. The computations were carried out at B3LYP-D3BJ/Def2-QZVP//B3LYP-D3BJ/Def2-SVPD level of theory with the modelling of toluene solvation using SMD method for both the geometry optimizations and the final energy calculations (see the

Supporting Information for the full computational details).²⁹ Figure 3 shows the free energy profile for the mechanism established by the calculations.

The initial formation of the Breslow intermediate was found to occur according to the standard mechanism implicated for the NHC-catalyzed processes.^{1c} Thus, the reaction begins by a facile deprotonation of catalyst precursor **NHC-1** with TMEDA via transition state **TS1**. The resulting free carbene **A** is higher in energy by 2.4 kcal/mol compared to its protonated form. In the following step, the NHC attacks aldehyde **1g**, generating alkoxide species **B**. The overall barrier for this transformation is calculated to be 16.7 kcal/mol relative to **NHC-1**. In the next step, **B** undergoes a barrierless protonation at oxygen by the salt of TMEDA, yielding the corresponding alcohol **C**. Finally, Breslow intermediate **D** is furnished upon the deprotonation of **C** at the carbon atom by TMEDA via a low-barrier **TS3**. Overall, the formation of the Breslow intermediate is exergonic by 2.1 kcal/mol relative to the catalyst precursor. The highest energy span along the way, amounting to 16.7 kcal/mol is located between **NHC-1** and **TS2**. Importantly, within this part of the energy diagram all three species, whose concentrations are present in the experimental rate-law (1), are involved, that is: the catalyst precursor, the aldehyde substrate, and TMEDA. The subsequent stepwise proton-shuttling (**B** → **D**) is facile and does not contribute to the reaction rate.

Figure 3. Free Energy Profile for the Alkynylation of Aldehyde **1g** with Alkynyliodonium Salt **2a** Using Precatalyst **NHC-1** in Toluene, Calculated at B3LYP-D3BJ/Def2-QZVP(SMD)//B3LYP-D3BJ/Def2-SVPD(SMD) Level of Theory.

Next, we examined the possible options for the reaction of Breslow intermediate **D** with alkynyliodonium salt **2a**. It was quickly established that the direct coordination of **D** to the iodine center is not feasible, as it does not result in a stable structure that constitutes a minimum on the energy surface. Therefore, the mechanism involving the inner-sphere reductive ligand coupling (Scheme 4a) can be discarded. On the other hand, we were capable of finding the plausible transition states, **TS4** and **TSβ**, for the other two alternative pathways, *i.e.*, the S_N2 substitution at the α -carbon (Scheme 4b) and the Michel-type addition to the β -carbon (Scheme 4c), respectively. The former one is calculated to be clearly energetically favorable over the latter (by 6.2 kcal/mol), thus, it constitutes the actual pathway of the C–C bond-formation. The transfer of the alkynyl group via **TS4** is found to be a very exergonic, thus, irreversible process (by 45.0 kcal/mol). This

is due to the accompanying reduction of iodine from +III to +I oxidation state and the loss of hypervalency. For completeness, we calculated the transition state for the transfer of the mesityl group in **2a** (TS-Mes), instead of the alkynyl group. Such course of the reaction would require crossing a very high barrier of 24.6 kcal/mol, explaining the excellent performance of the mesityl substituent as the auxiliary non-transferable aryl group in the alkynyl(aryl)iodonium salts.

Figure 4. Optimized Structures of (a) Alkynyliodonium Salt **2a**, (b) TS4, (c) TS β , and (d) TS-Mes (Distances Are Given in Å).

The optimized structures of transition states TS4, TS β , and TS-Mes, as well as of alkynyliodonium salt **2a**, are depicted in Figure 4. In all three transition states the ligand

participating in the new C–C bond formation occupies the hypervalent position. Hence, in the case of **TS4** and **TS β** (Figure 4b and 4c, respectively), the arrangement of ligands around the iodine center is the same as in the parent salt (Figure 4a), while in **TS-Mes** the phenylethynyl and mesityl groups are swapped (Figure 4d). Such opposite orientation of the ligands is probably the most significant contributor to the high barrier associated with **TS-Mes**, as the calculated energy of the isomer of **2a** having the mesityl group in the hypervalent position and the alkynyl group in the equatorial position is higher by as much as 10.0 kcal/mol compared to the energy of **2a**. As far as the energy difference between **TS4** and **TS β** is concerned, it most likely originates from distorting the conjugation between the forming double C–C bond and the phenyl substituent, which due to steric reasons must rotate nearly perpendicularly, in the latter transition state. On the other hand, in **TS4**, the phenyl ring can align itself in way allowing for a complete π -conjugation over the triple bond to both the breaking C–I bond and the newly forming C–C bond, providing stabilization. Importantly, in all the TSs, the hydroxyl group of Breslow intermediate is interacting with the iodine center. This is somewhat similar to the case of alkynylation of thiols with EBX, wherein the thiolate nucleophile has been shown to simultaneously interact with the alkynyl group and iodine in a three-center transition state structure.²⁴

The catalytic cycle is closed by **TS5**, releasing the final product **3g** and regenerating free NHC **A**. Importantly, as **A** is not the most stable form of the catalyst, it is converted to the more favorable off-cycle resting state **NHC-1**. Overall, the total thermodynamics of the reaction is calculated to – 59.9 kcal/mol.

The mechanistic picture emerging from the calculations is in a full agreement with the results of experimental studies described in the previous section. First, the lowest energy pathway established for the C–C bond formation, *i.e.*, the direct S_N2 substitution at α -acetylenic carbon via

TS4, explains the direct transfer of the ^{13}C -label between iodonium salt **2w** and product **3ab** without swapping (Scheme 5). Secondly, the computed free energy profile is in line with the experimental rate-law (1). It correctly predicts that only the NHC precatalyst, the aldehyde, and TMEDA are involved in the turnover-limiting step, constituted by the largest energy span between **NHC-1** and **TS2** (overall 16.7 kcal/mol).³⁰ The height of this turnover-limiting barrier is also quantitatively consistent with the experimental rate of the reaction at $-40\text{ }^{\circ}\text{C}$. Conversely, the iodonium salt enters the free energy profile within a lower barrier, later in the catalytic cycle (13.9 kcal/mol, **D** to **TS4**), thus, its concentration does not influence the overall rate.

CONCLUSIONS

In summary, we have developed an NHC-catalyzed direct C–H alkynylation of aldehydes using alkynyliodonium salts as alkynyl donors, expanding the scope of the NHC organocatalysis. The proper choice of the auxiliary aryl substituent secured the selective transfer of the alkynyl substituent from iodine, providing a facile entry to a variety of ynones in good to excellent yields. In particular, the method is well-suited for the synthesis of compounds bearing pharmaceutically relevant heterocyclic scaffolds. Due to the exceptionally mild reaction conditions, in terms of both the reaction temperature and the use of a weak amine base, a range of fragile functional groups is tolerated. Specifically, alkenes, alkynes, nitriles, ketones, esters, and amides can be incorporated into the products. Finally, the application of the organocatalyst in the combination with a hypervalent iodine reagent, allowed for a completely metal-free C–H functionalization, rendering the developed reaction a green alternative for the preparation of propargylic ketones from abundant aldehyde starting materials.

The mechanism of the reaction has been thoroughly studied by both experimental and computational methods. The ^{13}C -labeling and DFT calculations have shown that the alkynyl group transfer proceeds via a direct $\text{S}_{\text{N}}2$ substitution of iodine by the Breslow intermediate occurring at α -acetylenic carbon, and not by the prevalent pathway involving the initial attack of nucleophile at the β -position. This constitutes the second reported example of such a course of the alkynylation reaction with a hypervalent iodine reagent and, thus, the finding may implicate that analogous mechanisms can be more common than previously thought. Additionally, the kinetic studies, corroborated by the computed free energy profile, have identified the formation of Breslow intermediate to be the turnover-limiting step of the catalytic cycle. This demonstrates that the subsequent C–C bond-forming reaction between the Breslow intermediate and the alkynyliodonium salt is a very facile, low-barrier process. Above result opens opportunities for the application of alkynyliodonium salts as efficient alkynyl-transfer reagents for other non-trivial nucleophilic species, including catalytically generated ones, in the future.

ASSOCIATED CONTENT

Supporting Information:

Experimental procedures, compound characterization data, NMR spectra of compounds **2w** and **3a–3ab**, details of kinetic investigations, computational details, free-energy profile for the reaction in CHCl_3 , calculated energies and energy corrections, optimized structures and Cartesian coordinates of stationary points (PDF).

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Notes

The authors declare no conflict of interest.

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28. The data points did not show linear dependence in the coordinate systems corresponding to the 1st and 3rd overall orders. See the Supporting Information for details.
29. We have also calculated the full mechanism in CHCl₃, the solvent that was used in the initial rate studies. The overall mechanistic picture and conclusions are identical to these obtained for the calculations in toluene. See the Supporting Information for details.
30. The computed free energy profile predicts that the conjugated acid of TMEDA should inhibit the reaction, as it is expelled within the largest energy span. This should in turn result in the overall first order during the time-course experiment, instead of the observed second order (Figure 1). However, under the experimental conditions (toluene, -40 °C) the salts of TMEDA are insoluble, hence, their concentrations remain constant, lacking the impact on the kinetics of the reaction.

SYNOPSIS

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SUPPORTING INFORMATION

***N*-Heterocyclic Carbene-Catalyzed Synthesis of Ynones via C–H Alkynylation of Aldehydes with Alkynyliodonium Salts**

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1. General Information

Unless otherwise noted, all materials were purchased from commercial suppliers and used as received. Anhydrous CH_2Cl_2 , THF, and toluene were purified prior to use by passage through a column of neutral alumina under nitrogen. Triethylamine and water were degassed using freeze-pump-thaw method and kept in glovebox (triethylamine over molecular sieves $4\text{\AA}$). Catalysts precursors **NHC-1**,¹ **NHC-2**,² **NHC-3**,² **NHC-4**,³ **NHC-6**,⁴ **NHC-7**,⁵ and **NHC-9**⁵ were synthesized according to published procedures.

^1H , ^{13}C , and ^{19}F spectroscopic data were collected on Varian 400 MHz and Bruker 500 MHz spectrometers at ambient temperature. The chemical shifts are reported in ppm relative to solvent peaks. Assignment of the NMR signals of products **3a–3ab** was accomplished on the basis of 2D correlation experiments (atom-labeling scheme is arbitrary). Mass spectra were recorded on Thermo QExactive mass spectrometer. IR spectra were recorded on Shimadzu IRPrestige-21 FT-IR spectrometer with ATR attachment.

2. Safety/Hazards

During an attempted synthesis of (2-phenylethynyl)(2,4,6-trimethylphenyl)iodonium hexafluoroarsenate a sample of compound dried *in vacuo* violently decomposed upon touching it with a stainless-steel spatula. We recommend exercising special care during the preparation of this and similar alkynyliodonium salts containing very weakly-coordinating anions.

3. Preparation of Starting Materials

The yields in this section have not been optimized.

3.1. Synthesis of Aldehydes

Aldehydes **1j**, **1k**, and **1l** have been synthesized according to the following procedures.

Scheme S1.

¹ Vora, H. U.; Lathrop, S. P.; Reynolds, N. T.; Kerr, M. S.; Read de Alaniz, J.; Rovis, T. *Org. Synth.* **2010**, 87, 350.

² Davidson, R. W. M.; Fuchter, M. K. *Chem. Commun.* **2016**, 52, 11638-11641.

³ Kretschmer, M.; Dieckmann, M.; Li, P.; Rudolph, S.; Herkommer, D.; Troendlin, J.; Menche, D. *Chem. Eur. J.* **2013**, 19, 15993-16018.

⁴ Wilde, M. M.; Gravel, M. *Angew. Chem. Int. Ed.* **2013**, 52, 12651-12654.

⁵ Piel, I.; Pawelczyk, M. D.; Hirano, K.; Fröhlich, R.; Glorius, F. *Eur. J. Org. Chem.* **2011**, 5475-5484.

5-[2-(trifluoromethyl)phenyl]pyridine-2-carbaldehyde (1j).⁶ In a nitrogen-atmosphere glovebox, a pressure ampoule was charged with 5-bromo-2-pyridinecarboxaldehyde (949 mg, 5.0 mmol), Pd(PPh₃)₄ (472 mg, 0.4 mmol), and K₂CO₃ (2.28 g, 16.5 mmol). THF (anhydrous, 25 mL) and water (degassed, 10 mL) were added. Next, 2-(trifluoromethyl)phenylboronic acid (1.05 g, 5.5 mmol) was added in one portion and the ampoule was closed, removed from the glovebox, and stirred at 80 °C overnight. After cooling to room temperature, water (20 mL) was added and the resulting mixture was extracted with AcOEt (3 x 20 mL). Combined organic phases were washed with brine (30 mL), dried over anhydrous MgSO₄, filtered, and concentrated under reduced pressure. The product was purified by column chromatography (silica, petroleum ether:ethyl acetate/9:1 to 8:2) and it was obtained as a yellow solid (1.13 g, 90% yield). ¹H NMR (400 MHz, CDCl₃): δ 10.15 (d, *J* = 0.8 Hz, 1H), 8.75 (d, *J* = 2.1 Hz, 1H), 8.03 (dd, *J* = 8.0, 0.8 Hz, 1H), 7.86 (ddd, *J* = 8.0, 1.5, 0.7 Hz, 1H), 7.84 – 7.81 (m, 1H), 7.69 – 7.55 (m, 2H), 7.37 – 7.32 (m, 1H). ¹⁹F NMR (376 MHz, CDCl₃): δ -56.7 (s). The spectral data are in accordance with literature.⁶

Scheme S2.

[(1E)-4-phenylbut-1-en-1-yl]boronic acid.⁷ An oven-dried round bottom flask was capped with septum and evacuated/back-filled with nitrogen 3 times. Solution of borane-THF complex in THF (1 M, 2.0 mL, 2.0 mmol) was added via syringe, the flask was cooled down to 0 °C, and cyclohexene (413 μL, 4.0 mmol) was added. The resulting mixture was stirred at 0 °C for 45 min (within this time a precipitate of dicyclohexylborane appeared). Next, 4-phenyl-1-butyne (2.9 mL, 20 mmol) and solution of catecholborane in THF (1 M, 22 mL, 22 mmol) were added at 0 °C. The cooling bath was removed and the reaction mixture was stirred at room temperature for 2 h. The volatiles were removed under reduced pressure, water (20 mL) was added to the residue, and the mixture was heated to reflux for 1 h. After cooling to room temperature, the resulting mixture was kept for 1 h at 4 °C. The precipitated solid was filtrated, washed with water (3 x 20 mL), petroleum ether (2 x 20 mL), and dried under high vacuum. The product was obtained as a white solid (2.31 g, 67% yield).

¹H NMR (400 MHz, CDCl₃) δ 7.33 – 7.27 (m, 2H), 7.24 – 7.17 (m, 3H), 7.02 (dt, *J* = 17.7, 6.3 Hz, 1H), 5.60 (d, *J* = 17.7 Hz, 1H), 2.82 – 2.73 (m, 2H), 2.59 – 2.47 (m, 2H). The spectral data are in accordance with literature.⁸

⁶ Charoensutthivarakul, S.; David Hong, W.; Leung, S. C.; Gibbons, P. D.; Bedingfield, P. T. P.; Nixon, G. L.; Lawrenson, A. S.; Berry, N. G.; Ward, S. A.; Biagini, G. A.; O'Neill, P. M. *Med. Chem. Commun.* **2015**, 6, 1252-1259.

⁷ The procedure is a modified version of the procedure given in: Shirakawa, K.; Arase, A.; Hoshi, M. *Synthesis* **2004**, 1814-1820.

⁸ Molander, G. A.; Cavalcanti, L. N.; Canturk, B.; Pan, P.-S.; Kennedy, L. E. *J. Org. Chem.* **2009**, 74, 7364-7369.

5-[(1E)-4-phenylbut-1-en-1-yl]pyridine-2-carbaldehyde (1k).⁹ In a nitrogen-atmosphere glovebox, a pressure ampoule was charged with 5-bromo-2-pyridinecarboxaldehyde (949 mg, 5.0 mmol), Pd(PPh₃)₄ (295 mg, 0.25 mmol), [(1E)-4-phenylbut-1-en-1-yl]boronic acid (1.06 g, 6.0 mmol), and KOH (561 mg, 10.0 mmol). Next, 1,4-dioxane (anhydrous, 51 mL) and water (degassed, 8.5 mL) were added. The ampoule was closed, removed from the glovebox, and stirred at 90 °C for 24 h. After cooling to room temperature, water (40 mL) was added and the resulting mixture was extracted with AcOEt (3 x 50 mL). Combined organic phases were dried over anhydrous MgSO₄, filtered, and concentrated under reduced pressure. The product was purified by column chromatography (silica, petroleum ether:ethyl acetate/9:1 to 8:2) and it was obtained as a yellow solid (463 mg, 39% yield). ¹H NMR (400 MHz, CDCl₃) δ 10.04 (d, *J* = 0.8 Hz, 1H), 8.69 (d, *J* = 1.8 Hz, 1H), 7.90 (dd, *J* = 8.1, 0.6 Hz, 1H), 7.79 (dd, *J* = 8.1, 2.1 Hz, 1H), 7.34 – 7.28 (m, 2H), 7.24 – 7.19 (m, 3H), 6.56 – 6.42 (m, 2H), 2.87 – 2.80 (m, 2H), 2.62 (ddd, *J* = 9.5, 7.3, 6.1 Hz, 2H).

Scheme S3.

5-(hex-1-yn-1-yl)pyridine-2-carbaldehyde (1l).¹⁰ In a nitrogen-atmosphere glovebox, 20 mL oven-dried vial was charged with 5-bromo-2-pyridinecarboxaldehyde (569 mg, 3.0 mmol), Pd(PPh₃)₄ (88.4 mg, 0.075 mmol), and CuI (14.3 mg, 0.075 mmol). Next, Et₃N (degassed, 40 mL) was added, followed by the addition of 1-hexyne (531 μL, 4.5 mmol). The vial was capped, removed from the glovebox, and stirred at 80 °C overnight. After cooling to room temperature, the reaction mixture was transferred to a 100 mL round-bottom flask using CH₂Cl₂ and volatiles were removed under reduced pressure. Next, Et₂O (50 mL) was added, causing the formation of triethylammonium bromide precipitate, which was removed by passing the mixture through a short pad of silica using Et₂O. Collected filtrate was concentrated under reduced pressure and the product was purified by column chromatography (silica, petroleum ether:ethyl acetate/95:5 to 90:10). The product was obtained as a brownish oil, which solidified when kept at 4 °C (490 mg, 87% yield). ¹H NMR (400 MHz, CDCl₃) δ 10.05 (d, *J* = 0.8 Hz, 1H), 8.74 (dd, *J* = 1.9, 0.8 Hz, 1H), 7.88 (dd, *J* = 8.0, 0.9 Hz, 1H), 7.82 (ddd, *J* = 8.0, 2.0, 0.8 Hz, 1H), 2.47 (t, *J* = 7.1 Hz, 2H), 1.66 – 1.58 (m, 2H), 1.54 – 1.44 (m, 2H), 0.96 (t, *J* = 7.3 Hz, 3H).

3.2. Synthesis of Alkynyliodonium Salts

1-(Phenylethynyl)-1,2-benziodoxol-3(1*H*)-one **4** was synthesized according to the following sequence:

⁹ The procedure is a modified version of the procedure given in: Piali, A.; Mayi, D.; Handy, S. T. *Tetrahedron* **2011**, 67, 4147-4154.

¹⁰ The procedure is a modified version of the procedure given in: Musso, D. L.; Clarke, M. J.; Kelley, J. L.; Boswell, G. E.; Chena G. *Org. Biomol. Chem.* **2003**, 1, 498-506.

Scheme S4.

1-Hydroxy-1,2-benziodoxol-3-(1H)-one.¹¹ NaIO₄ (5.65 g, 26.4 mmol) and 2-iodobenzoic acid (6.24 g, 25.2 mmol) were suspended in aqueous AcOH (30% v:v, 48 mL). The mixture was vigorously stirred and refluxed for 4 h. The reaction mixture was then diluted with cold water (20 mL) and allowed to cool to room temperature, protecting it from light. After 1 h, the product was collected by filtration, washed with ice water (3 x 5 mL) and acetone (3 x 5 mL). After drying in air in the dark, the product was obtained as a colorless solid (6.28 g, 95% yield).

1-(Phenylethynyl)-1,2-benziodoxol-3(1H)-one (4).¹² Under nitrogen atmosphere, TMSOTf (2.0 mL, 11 mmol) was added via syringe to stirred suspension of 1-hydroxy-1,2-benziodoxol-3-(1H)-one (2.64 g, 10 mmol) in CH₂Cl₂ (anhydrous, 25 mL) at room temperature. The resulting yellow mixture was stirred for 1 h, followed by the addition of trimethyl(2-phenylethynyl)silane (1.92 g, 11 mmol). After stirring at room temperature overnight, saturated aqueous NaHCO₃ (50 mL) was added and the mixture was stirred vigorously for another 30 min. Organic phase was separated and washed once with saturated aqueous NaHCO₃ (50 mL), then dried over anhydrous MgSO₄, filtered, and concentrated under reduced pressure. The residue treated with Et₂O (25 mL) causing the precipitation of solid, which was filtered off and washed with a small amount of Et₂O (2 x 5 mL). After drying under high vacuum, the product was obtained as a colorless solid (2.35 g, 67% yield). ¹H NMR (400 MHz, CDCl₃) δ 8.46 – 8.40 (m, 1H), 8.29 – 8.22 (m, 1H), 7.81 – 7.74 (m, 2H), 7.63 – 7.59 (m, 2H), 7.53 – 7.41 (m, 3H). The spectral data are in accordance with literature.¹²

Alkynyliodonium salts were synthesized in a sequence of reactions shown in Scheme S5.

Scheme S5.^a

¹¹ Kraszkiewicz, L.; Skulski, L. *Arkivoc* **2003**, 6, 120-125.

¹² Huang, H.; Zhang, G.; Chen, Y. *Angew. Chem. Int. Ed.* **2015**, 54, 7872-7876.

^a Reagents and conditions: (a) NaBO₃·4H₂O, AcOH, 45 °C, 16 h; (b) I₂, *m*-CPBA, TsOH, CH₂Cl₂, r.t., overnight; (c) 3 M NaOH_(aq.), r.t., 1 h; (d) Pd(PPh₃)₄, CuI, Et₃N, 80 °C, overnight; (e) BF₃·Et₂O, CH₂Cl₂, 0 °C to r.t., overnight; followed by NaX, H₂O, rt, 30 min.

3.1.1. Synthesis of Iodine(III) Precursors

2-Methyl(diacetoxyiodo)benzene.¹³ NaBO₃·4H₂O (33.85 g, 220 mmol) was added portion-wise to the stirred solution of 2-iodotoluene (2.55 mL, 20 mmol) in acetic acid (170 mL) at 45 °C over 1 h period. After stirring for additional 16 h at 45 °C, the reaction mixture was cooled to room temperature and concentrated under reduced pressure. Water (170 mL) was added and the resulting mixture was extracted with CH₂Cl₂ (3 × 100 mL). The combined organic layers were dried over anhydrous Na₂SO₄, filtered, and concentrated under reduced pressure. Et₂O (100 mL) was added to the residue, and the precipitated product was filtered and washed with Et₂O. After drying under high vacuum, the product was obtained as a white solid (4.37 g, 65% yield). ¹H NMR (400 MHz, CDCl₃): δ 8.19 – 8.14 (m, 1H), 7.55 – 7.48 (m, 2H), 7.28 – 7.22 (m, 1H), 2.72 (s, 3H), 1.98 (s, 6H). The spectral data are in accordance with literature.¹⁴

2,6-Dimethyl(diacetoxyiodo)benzene. The title compound was prepared from 2-iodo-2,6-dimethylbenzene in 30 mmol scale, following the same procedure as for 2-methyl(diacetoxyiodo)benzene. The product was obtained as a white solid (3.54 g, 34% yield). ¹H NMR (400 MHz, CDCl₃) δ 7.38 (dd, *J* = 8.3, 6.6 Hz, 1H), 7.29 (d, *J* = 7.7 Hz, 2H), 2.75 (s, 6H), 1.97 (s, 6H). The spectral data are in accordance with literature.¹⁵

2-Methoxy(diacetoxyiodo)benzene. The title compound was prepared from 2-iodoanisole in 55 mmol scale, following the same procedure as for 2-methyl(diacetoxyiodo)benzene. The product was obtained as a white solid (10.8 g, 56% yield). ¹H NMR (400 MHz, CDCl₃): δ 8.14 (dd, *J* = 7.9, 1.6 Hz, 1H), 7.58 (ddd, *J* = 8.4, 7.4, 1.6 Hz, 1H), 7.15 (dd, *J* = 8.4, 1.3 Hz, 1H), 7.03 (ddd, *J* = 7.9, 7.4, 1.3 Hz, 1H), 3.98 (s, 3H), 1.97 (s, 6H). The spectral data are in accordance with literature.¹⁴

¹³ The procedure is a modified version of the procedure given in: Carroll, M. A.; Nairne, J.; Smith, G.; Widdowson, D. A. *J. Fluor. Chem.* **2007**, 128, 127-132.

¹⁴ Rajkiewicz, A. A.; Kalek, M. *Org. Lett.* **2018**, 20, 1906 – 1909.

¹⁵ Lucchetti, N.; Gilmour, R. *Chem. Eur. J.* **2018**, 24, 16266-16270.

2,4,6-Trimethyl(diacetoxyiodo)benzene. The title compound was prepared from 2-iodo-1,3,5-trimethylbenzene in 8 mmol scale, following the same procedure as for 2-methyl(diacetoxyiodo)benzene. The product was obtained as a white solid (1.93 g, 66% yield). ¹H NMR (400 MHz, CDCl₃): δ 7.10 (d, *J* = 0.5 Hz, 2H), 2.70 (s, 6H), 2.35 (s, 3H), 1.96 (s, 6H).

1-[Hydroxy(tosyloxy)iodo]-2,4,6-trimethylbenzene.¹⁶ 500 mL round-bottom flask was charged with fine-grinded iodine (9.01 g, 35.5 mmol), then CH₂Cl₂ (250 mL) was added. Resulting mixture was stirred for 15 min. at room temperature until iodine dissolved completely. Next, mesitylene (10.0 mL, 71 mmol), *m*-CPBA (70% of active oxidant, dried under high vacuum for 1 h; 26.3 g, 107 mmol), and *p*-toluenesulfonic acid monohydrate (13.5 g, 71 mmol) were sequentially added. The reaction mixture was stirred at room temperature overnight (after c.a. 15 minutes of stirring the color of the reaction mixture started to change from deep purple to bright yellow, also a precipitate appeared). The reaction mixture was concentrated under reduced pressure and Et₂O (250 mL) was added to the residue. The resulting mixture was stirred vigorously at room temperature for 1 h. Precipitated solid was filtered off, washed with Et₂O (3 x 100 mL) and dried under high vacuum providing the product as a white powder (30.0 g, 97% yield). ¹H NMR (400 MHz, CD₃CN) δ 7.30 – 7.26 (m, 2H), 7.12 – 7.07 (m, 2H), 2.32 (s, 6H), 2.31 (s, 6H). The spectral data are in accordance with literature.¹⁷

Iodosylbenzene.¹⁸ Round-bottom flask was charged with (diacetoxyiodo)benzene (1.61 g, 5 mmol) and aqueous NaOH (3 M, 7.5 mL) was added. The reaction mixture was stirred vigorously at room temperature for 1 h. Precipitated solid was filtered off, washed with water (3 x 10 mL) and CHCl₃ (5 mL). After drying in air, the product was obtained as a white powder (1.10 g, 99% yield).

2-Methyliodosylbenzene. The title compound was prepared from 2-methyl(diacetoxyiodo)benzene in 5.95 mmol scale, following the same procedure as for iodosylbenzene. The product was obtained as a white solid (1.17 g, 84% yield).

2,6-Dimethyliodosylbenzene. The title compound was prepared from 2,6-dimethyl(diacetoxyiodo)benzene in 5.7 mmol scale, following the same procedure as for iodosylbenzene. The product was obtained as a white solid (1.27 g, 90% yield).

¹⁶ McCamant, M. S.; Thompson, S.; Brooks, A. F.; Krska, S. W.; Scott, P. J. H.; Sanford, M. S. *Org. Lett.* **2017**, *19*, 3939-3942.

¹⁷ Merritt, E. A.; Carneiro, V. M. T.; Silva, L. F.; Olofsson, B. *J. Org. Chem.* **2010**, *75*, 7416-7419.

¹⁸ Saltzman, H.; Sharefkin J. G. *Org. Synth.* **1963**, *43*, 60.

2-Methoxyiodosylbenzene. The title compound was prepared from 2-methoxy(diacetoxyiodo)benzene in 3 mmol scale, following the same procedure as for iodosylbenzene. The product was obtained as a yellowish solid (415 mg, 55% yield).

2,4,6-Trimethyliodosylbenzene. The title compound was prepared from 1-[hydroxy(tosyloxy)iodo]-2,4,6-trimethylbenzene in 68.2 mmol scale, following the same procedure as for iodosylbenzene with the reaction time extended to 16 h. The product was obtained as a yellowish solid (15.8 g, 88% yield).

3.1.2. Synthesis of Trimethylsilylalkynes

Starting materials for synthesis of 2-{3-[2-(trimethylsilyl)ethynyl]phenyl}-2,3-dihydro-1*H*-isindole-1,3-dione and 4-{2-[2-(Trimethylsilyl)ethynyl]benzenesulfonyl}morpholine were prepared according to following procedures.

Scheme S6.

***N*-(3-bromophenyl)phthalimide.**¹⁹ Phthalic anhydride (1.5 g, 10 mmol) and 3-bromoaniline (1.09 mL, 10 mmol) were added to AcOH (60 mL) and refluxed overnight. After cooling to room temperature, water (50 mL) was added and the resulting suspension was stirred at room temperature for 15 minutes. Obtained solid was filtered off, washed with water (2 x 20 mL), and dried under high vacuum, providing the product as a white solid (2.79 g, 92% yield). ¹H NMR (400 MHz, CDCl₃) δ 7.96 (dd, *J* = 5.5, 3.1 Hz, 2H), 7.80 (dd, *J* = 5.5, 3.0 Hz, 2H), 7.65-7.61 (m, 2H), 7.37-7.34 (m, 2H). The spectral data are in accordance with literature.²⁰

Scheme S7.

¹⁹ The procedure is a modified version of the procedure given in: Yuan, Y.-C.; Kamaraj, R.; Bruneau, C.; Labasque, T.; Roisnel, T.; Gramage-Doria, R. *Org. Lett.* **2017**, *19*, 6404-6407.

²⁰ Shrestha, R.; Mukherjee, P.; Tan, Y.; Litman, Z. C.; Hartwig, J. F. *J. Am. Chem. Soc.* **2013**, *135*, 8480-8483.

4-(2-Bromobenzenesulfonyl)morpholine.²¹ A round-bottom flask was charged with 2-bromobenzenesulfonyl chloride (1.28 g, 5.0 mmol). Next, CH_2Cl_2 (25 mL) and Et_3N (anhydrous, 2.08 mL, 15 mmol) were added. The reaction mixture was cooled down to 0 °C and morpholine (484 μL , 5.5 mmol) was added dropwise. After the addition was completed, the cooling bath was removed and reaction mixture was stirred at room temperature for 12 h. The volatiles were removed under reduced pressure, and CH_2Cl_2 (25 mL) and water (25 mL) were added to the residue. The organic phase was separated and the aqueous phase was further extracted with CH_2Cl_2 (2 x 25 mL). The combined organic phases were dried over MgSO_4 , filtered, and evaporated under reduced pressure. The product was purified by column chromatography (silica, petroleum ether:ethyl acetate/4:1) and was obtained as a colorless solid (1.45 g, 95%). ^1H NMR (400 MHz, CDCl_3) δ 8.10 – 8.07 (m, 1H), 7.79 – 7.75 (m, 1H), 7.49 – 7.38 (m, 2H), 3.75 – 3.71 (m, 4H), 3.32 – 3.28 (m, 4H). The spectral data are in accordance with literature.²²

Trimethylsilylalkynes was prepared according to the following procedure.¹⁰

Scheme S8.

General Procedure 1

In a nitrogen-atmosphere glovebox, an oven-dried pressure ampoule (or an oven-dried 30 mL vial, depending on the reaction scale) was charged with aryl halide (1.0 equiv.), $\text{Pd(PPh}_3)_4$ (1.5 mol%), and CuI (3.3 mol%). Next, Et_3N (degassed, 2.5 mL/mmol of aryl halide) and trimethylsilylacetylene (1.5 equiv.) were added. The ampoule was capped, removed for the glovebox, and stirred at 80 °C for 16 h. After cooling to room temperature, the reaction mixture was transferred to round-bottom flask with CH_2Cl_2 . The volatiles were removed under reduced pressure and Et_2O (10 mL/mmol) was added to the residue, resulting in the formation of triethylammonium halide precipitate, which was removed by filtration through short pad of silica using Et_2O . The filtrate was concentrated under reduced pressure and the product was purified by column chromatography.

Trimethyl(2-phenylethynyl)silane. The title compound was prepared according to the General Procedure 1 in 15 mmol scale from iodobenzene (1.68 mL, 15 mmol), trimethylsilylacetylene (3.28 mL, 22.5 mmol), $\text{Pd(PPh}_3)_4$ (265 mg, 0.225 mmol), CuI (94.3 mg, 0.495 mmol), and Et_3N (37.5 mL). The product was purified by column chromatography (silica, petroleum ether) and it was obtained as a

²¹ The procedure is a modified version of the procedure given in: Bheeter, C. B.; Jin, R.; Bera, J. K.; Dixneuf, P. H.; Doucet, H. *Adv. Synth. Catal.* **2014**, 356, 119-124.

²² Yotphan, S.; Sumunnee, L.; Beukeaw, D.; Buathongjan, C.; Reutrakul, V. *Org. Biomol. Chem.* **2016**, 14, 590-597.

colorless liquid (2.56 g, 98% yield). ^1H NMR (400 MHz, CDCl_3) δ 7.50 – 7.43 (m, 2H), 7.34 – 7.26 (m, 3H), 0.26 (s, 9H). The spectral data are in accordance with literature.²³

[2-(2,6-Dimethylphenyl)ethynyl]trimethylsilane. The title compound was prepared according to the General Procedure 1 in 10 mmol scale from 2,6-dimethyliodobenzene (1.47 mL, 10 mmol), trimethylsilylacetylene (2.19 mL, 15 mmol), $\text{Pd}(\text{PPh}_3)_4$ (177 mg, 0.15 mmol), CuI (62.8 mg, 0.33 mmol), and Et_3N (25 mL). The product was purified by column chromatography (silica, petroleum ether:ethyl acetate/100:0 to 94:6) and it was obtained as a colorless liquid (1.93 g, 96% yield). ^1H NMR (400 MHz, CDCl_3) δ 7.10 (dd, J = 8.4, 6.6 Hz, 1H), 7.02 (d, J = 7.7 Hz, 2H), 2.43 (s, 6H), 0.27 (s, 9H). The spectral data are in accordance with literature.²⁴

[2-(4-*tert*-Butylphenyl)ethynyl]trimethylsilane. The title compound was prepared according to the General Procedure 1 in 4.75 mmol scale from 4-*tert*-butyliodobenzene (842 μL , 4.75 mmol), trimethylsilylacetylene (1.05 mL, 7.13 mmol), $\text{Pd}(\text{PPh}_3)_4$ (84 mg, 0.072 mmol), CuI (29.9 mg, 0.157 mmol), and Et_3N (12 mL). The product was purified by column chromatography (silica, petroleum ether) and it was obtained as a colorless solid (1.08 g, 99% yield). ^1H NMR (400 MHz, CDCl_3) δ 7.41 – 7.38 (m, 2H), 7.33 – 7.29 (m, 2H), 1.30 (s, 9H), 0.24 (s, 9H). The spectral data are in accordance with literature.²⁵

(2-{{1,1'-Biphenyl}}-3-yl)ethynyl)trimethylsilane. The title compound was prepared according to the General Procedure 1 in 8 mmol scale from 3-bromobiphenyl (1.36 mL, 8 mmol), trimethylsilylacetylene (1.76 mL, 12 mmol), $\text{Pd}(\text{PPh}_3)_4$ (142 mg, 0.12 mmol), CuI (50.3 mg, 0.264 mmol), and Et_3N (20 mL). The product was purified by column chromatography (silica, petroleum ether:ethyl acetate/20:0 to 19:1) and it was obtained as a yellowish liquid (1.80 g, 90% yield). ^1H NMR (400 MHz, CDCl_3) δ 7.73 – 7.71 (m, 1H), 7.61 – 7.57 (m, 2H), 7.55 (ddd, J = 7.7, 1.9, 1.3 Hz, 1H), 7.47 – 7.42 (m, 3H), 7.40 – 7.34 (m, 2H), 0.28 (s, 9H).

Trimethyl[2-(naphthalen-2-yl)ethynyl]silane. The title compound was prepared according to the General Procedure 1 in 10 mmol scale from 2-bromonaphthalene (2.07 g, 10 mmol),

²³ Truong, T.; Daugulis, O. *Org. Lett.* **2011**, *13*, 4172-4175.

²⁴ Panda, J.; Virkler, P. R.; Detty, M. R. *J. Org. Chem.* **2003**, *68*, 1804-1809.

²⁵ Xu, C.; Du, W.; Zeng, Y.; Dai, B.; Guo, H. *Org. Lett.* **2014**, *16*, 948-951.

trimethylsilylacetylene (2.19 mL, 15 mmol), Pd(PPh₃)₄ (177 mg, 0.15 mmol), CuI (62.8 mg, 0.33 mmol), and Et₃N (25 mL). The product was purified by column chromatography (silica, petroleum ether:ethyl acetate/100:0 to 94:6) and it was obtained as a yellowish solid (2.21 g, 98% yield). ¹H NMR (400 MHz, CDCl₃) δ 8.00 (d, *J* = 0.4 Hz, 1H), 7.83 – 7.74 (m, 3H), 7.54 – 7.45 (m, 3H), 0.29 (s, 9H). The spectral data are in accordance with literature.²⁶

[2-(3,5-Difluorophenyl)ethynyl]trimethylsilane. The title compound was prepared according to the General Procedure 1 in 6 mmol scale from 3,5-difluoroiodobenzene (719 μL, 6 mmol), trimethylsilylacetylene (1.32 mL, 9 mmol), Pd(PPh₃)₄ (106 mg, 0.09 mmol), CuI (37.7 mg, 0.198 mmol), and Et₃N (15 mL). The product was purified by column chromatography (silica, petroleum ether:ethyl acetate/20:0 to 19:1) and it was obtained as a colorless liquid (1.24 g, 98% yield). ¹H NMR (400 MHz, CDCl₃) δ 7.00 – 6.93 (m, 2H), 6.78 (tt, *J* = 9.0, 2.4 Hz, 1H), 0.25 (s, 9H). ¹⁹F NMR (376 MHz, CDCl₃) δ -109.8 – -109.9 (m). The spectral data are in accordance with literature.²⁷

Trimethyl({2-[2-(trifluoromethyl)phenyl]ethynyl})silane. The title compound was prepared according to the General Procedure 1 in 10 mmol scale from 2-(trifluoromethyl)iodobenzene (1.44 mL, 10 mmol), trimethylsilylacetylene (2.19 mL, 15 mmol), Pd(PPh₃)₄ (177 mg, 0.15 mmol), CuI (62.8 mg, 0.55 mmol), and Et₃N (25 mL). The product was purified by column chromatography (silica, petroleum ether:ethyl acetate/100:0 to 99:1) and it was obtained as a yellowish liquid (2.02 g, 83% yield). ¹H NMR (400 MHz, CDCl₃) δ 7.63 (dd, *J* = 7.8, 0.6 Hz, 1H), 7.60 (dd, *J* = 7.7, 0.6 Hz, 1H), 7.50 – 7.44 (m, 1H), 7.40 (ddd, *J* = 8.3, 1.3, 0.7 Hz, 1H), 0.26 (s, 5H). ¹⁹F NMR (376 MHz, CDCl₃) δ -62.5 (s).

[2-(3,4-Dichlorophenyl)ethynyl]trimethylsilane. The title compound was prepared according to the General Procedure 1 in 6 mmol scale from 3,4-dichlorobromobenzene (1.37 g, 6 mmol), trimethylsilylacetylene (1.32 mL, 9 mmol), Pd(PPh₃)₄ (106 mg, 0.09 mmol), CuI (37.7 mg, 0.196 mmol), and Et₃N (15 mL). The product was purified by column chromatography (silica, petroleum ether:ethyl acetate/20:0 to 19:1) and it was obtained as a colorless liquid (1.39 g, 95% yield). ¹H NMR (400 MHz, CDCl₃) δ 7.55 (d, *J* = 1.9 Hz, 1H), 7.37 (d, *J* = 8.3 Hz, 1H), 7.27 (dd, *J* = 8.2, 1.8 Hz, 2H), 0.25 (s, 9H). The spectral data are in accordance with literature.²⁸

²⁶ Hatial, I.; Mukherjee, R.; Senapati, K.; Basak, A. *Tetrahedron Lett.* **2015**, 56, 4275-4279.

²⁷ Lei, Y.; Hu, T.; Wu, X.; Wu, Y.; Xiang, H.; Sun, H.; You, Q.; Zhang, X. *Tetrahedron Lett.* **2016**, 57, 1100-1103.

²⁸ Onda, K.; Shiraki, R.; Yonetoku, Y.; Momose, K.; Katayama, N.; Orita, M.; Yamaguchi, T.; Ohta, M.; Tsukamoto, S.-i. *Bioorg. Med. Chem.* **2008**, 16, 8627-8634.

4-[2-(Trimethylsilyl)ethynyl]benzonitrile. The title compound was prepared according to the General Procedure 1 in 4.75 mmol scale from 4-iodobenzonitrile (1.09 g, 4.75 mmol), trimethylsilylacetylene (1.05 mL, 7.13 mmol), Pd(PPh₃)₄ (84 mg, 0.072 mmol), CuI (29.9 mg, 0.157 mmol), and Et₃N (12 mL). The product was purified by column chromatography (silica, petroleum ether:ethyl acetate/19:1 to 18:2) and it was obtained as a yellow solid (908 mg, 96% yield). ¹H NMR (400 MHz, CDCl₃) δ 7.61 – 7.57 (m, 2H), 7.55 – 7.51 (m, 2H), 0.26 (s, 9H). The spectral data are in accordance with literature.²⁹

1-{4-[2-(Trimethylsilyl)ethynyl]phenyl}ethan-1-one. The title compound was prepared according to the General Procedure 1 in 10 mmol scale from 4-iodoacetophenone (2.51 g, 10 mmol), trimethylsilylacetylene (2.19 mL, 15 mmol), Pd(PPh₃)₄ (177 mg, 0.15 mmol), CuI (62.8 mg, 0.55 mmol), and Et₃N (25 mL). The product was purified by column chromatography (silica, petroleum ether:ethyl acetate/19:1) and it was obtained as a yellow solid (2.04 g, 94% yield). ¹H NMR (400 MHz, CDCl₃) δ 7.91 – 7.86 (m, 2H), 7.56 – 7.52 (m, 2H), 2.59 (s, 3H), 0.26 (s, 9H). The spectral data are in accordance with literature.²⁴

Ethyl 3-[2-(trimethylsilyl)ethynyl]benzoate. The title compound was prepared according to the General Procedure 1 in 8 mmol scale from ethyl 3-iodobenzoate (137 μL, 8 mmol), trimethylsilylacetylene (1.76 mL, 12 mmol), Pd(PPh₃)₄ (142 mg, 0.12 mmol), CuI (50.3 mg, 0.264 mmol), and Et₃N (20 mL). The product was purified by column chromatography (silica, petroleum ether:ethyl acetate/19:1) and it was obtained as a yellowish liquid (1.94 g, 98% yield). ¹H NMR (400 MHz, CDCl₃) δ 8.13 (td, *J* = 1.7, 0.6 Hz, 1H), 7.98 (ddd, *J* = 7.9, 1.7, 1.3 Hz, 1H), 7.65 – 7.61 (m, 1H), 7.38 (td, *J* = 7.8, 0.5 Hz, 1H), 4.38 (q, *J* = 7.2 Hz, 2H), 1.40 (t, *J* = 7.1 Hz, 3H), 0.26 (s, 9H). The spectral data are in accordance with literature.³⁰

[2-(3-Methoxyphenyl)ethynyl]trimethylsilane. The title compound was prepared according to the General Procedure 1 in 5 mmol scale from 3-bromoanisole (636 μL, 5 mmol), trimethylsilylacetylene (1.1 mL, 7.5 mmol), Pd(PPh₃)₄ (88.4 mg, 0.075 mmol), CuI (31.4 mg, 0.165 mmol), and Et₃N (12.5 mL). The product was purified by column chromatography (silica, petroleum ether:ethyl acetate/19:1)

²⁹ Munoz, S. B.; Aloia, A. N.; Moore, A. K.; Papp, A.; Mathew, T.; Fustero, S.; Olah, G. A.; Surya Prakash, G. K. *Org. Biomol. Chem.* **2016**, *14*, 85-92.

³⁰ Iijima, T.; Endo, Y.; Tsuji, M.; Kawachi, E.; Kagechika, H.; Shudo, K. *Chem. Pharm. Bull.* **1999**, *47*, 398-404.

and it was obtained as a yellowish liquid (1.01 g, 99% yield). ^1H NMR (400 MHz, CDCl_3) δ 7.23 – 7.17 (dd, J = 8.3, 8.3 Hz, 1H), 7.06 (dt, J = 7.6, 1.2 Hz, 1H), 6.99 (dd, J = 2.6, 1.4 Hz, 1H), 6.87 (ddd, J = 8.3, 2.7, 1.0 Hz, 1H), 3.80 (s, 3H), 0.25 (s, 9H). The spectral data are in accordance with literature.³¹

Trimethyl({2-[4-(trifluoromethoxy)phenyl]ethynyl})silane. The title compound was prepared according to the General Procedure 1 in 25 mmol scale from 4-(trifluoromethoxy)iodobenzene (3.91 mL, 25 mmol), trimethylsilylacetylene (5.5 mL, 37.5 mmol), $\text{Pd}(\text{PPh}_3)_4$ (442 mg, 0.375 mmol), CuI (157 mg, 0.825 mmol), and Et_3N (62.5 mL). The product was purified by column chromatography (silica, petroleum ether:ethyl acetate/100:0 to 99:1) and it was obtained as a colorless liquid (6.10 g, 95% yield). ^1H NMR (400 MHz, CDCl_3) δ 7.51 – 7.46 (m, 2H), 7.17 – 7.11 (m, 2H), 0.25 (s, 9H). ^{19}F NMR (376 MHz, CDCl_3) δ -57.8 (s). The spectral data are in accordance with literature.²⁸

2-{3-[2-(Trimethylsilyl)ethynyl]phenyl}-2,3-dihydro-1H-isoindole-1,3-dione. The title compound was prepared according to the General Procedure 1 in 9.22 mmol scale from *N*-2-bromophenylphthalimide (2.79 g, 9.22 mmol), trimethylsilylacetylene (2.03 mL, 13.8 mmol), $\text{Pd}(\text{PPh}_3)_4$ (163 mg, 0.138 mmol), CuI (57.9 mg, 0.304 mmol), Et_3N (23 mL), and CH_2Cl_2 ³² (23 mL). The product was purified by column chromatography (silica, petroleum ether:ethyl acetate/9:1 to 8:2) and it was obtained as a colorless solid (2.33 g, 79% yield). ^1H NMR (400 MHz, CDCl_3) δ 7.99 – 7.93 (m, 2H), 7.83 – 7.78 (m, 2H), 7.59 – 7.56 (m, 1H), 7.51 – 7.47 (m, 1H), 7.46 – 7.39 (m, 2H), 0.25 (s, 9H).

4-{2-[2-(Trimethylsilyl)ethynyl]benzenesulfonyl}morpholine. The title compound was prepared according to the General Procedure 1 in 4.75 mmol scale from 4-(2-bromobenzenesulfonyl)morpholine (1.45 g, 4.75 mmol), trimethylsilylacetylene (1.05 mL, 7.13 mmol), $\text{Pd}(\text{PPh}_3)_4$ (84 mg, 0.072 mmol), CuI (29.9 mg, 0.157 mmol), and Et_3N (12 mL). The product was purified by column chromatography (silica, petroleum ether) and it was obtained as a yellow solid (1.34 g, 87% yield). ^1H NMR (400 MHz, CDCl_3) δ 7.94 – 7.90 (m, 1H), 7.69 – 7.65 (m, 1H), 7.51 (td, J = 7.6, 1.4 Hz, 1H), 7.47 – 7.41 (m, 1H), 3.74 – 3.69 (m, 4H), 3.26 – 3.22 (m, 4H), 0.26 (s, 9H).

3.1.3. Synthesis of Alkynyliodonium Salts

Iodonium salts **2f** and **2g** were prepared according to following procedures:

³¹ Ueda, H.; Yamaguchi, M.; Kameya, H.; Sugimoto, K.; Tokuyama, H. *Org. Lett.* **2014**, *16*, 4948-4951.

³² CH_2Cl_2 was used as a co-solvent due to the insolubility of substrate in Et_3N , the reaction was performed at 60 °C in a pressure ampoule.

Scheme S9.

(2-phenylethynyl)(2,4,6-trimethylphenyl)iodonium trifluoromethanesulfonate (2f).³³ To a solution of iodosylmesitylene (944 mg, 3.6 mmol) in CH_2Cl_2 (3.6 mL), Tf_2O (309 μL , 1.8 mmol) was slowly added dropwise via syringe at 0°C . The resulting mixture was stirred at 0°C , until it become a clear yellow solution (c.a. 10 min.). Next, trimethyl(2-phenylethynyl)silane (628 mg, 3.6 mmol) solution in CH_2Cl_2 (3.6 mL) was added via syringe and the reaction mixture was stirred at 0°C for 30 min. The volatiles were removed under reduced pressure and Et_2O (10 mL) was added to the residue. Precipitated solid was washed with Et_2O (2 x 5 mL) and dried under high vacuum, providing the product as colorless crystals (730 mg, 41% yield). ^1H NMR (400 MHz, CDCl_3) δ 7.49 – 7.43 (m, 3H), 7.41 – 7.34 (m, 2H), 7.15 (s, 2H), 2.78 (s, 6H), 2.38 (s, 3H). ^{19}F NMR (376 MHz, CDCl_3) δ -78.2 (s). The spectral data are in accordance with literature.³³

Scheme S10.

(2-phenylethynyl)(2,4,6-trimethylphenyl)iodonium trifluoroacetate (2g).³⁴ To a solution of 2,4,6-trimethyl-(diacetoxyiodo)benzene (839 mg, 2.27 mmol) in CH_2Cl_2 (13.6 mL), trifluoroacetic acid (355 μL , 4.54 mmol) was slowly added dropwise via syringe at -30°C . The reaction mixture was stirred at -30°C for 30 minutes and for further 1 h at room temperature. Next, phenylacetylene (249 μL , 2.27 mmol) was added via syringe and the reaction mixture was stirred at room temperature in darkness for 3.5 h. The volatiles were removed under reduced pressure, and Et_2O (10 mL) and petroleum ether (10 mL) were added to the residue, which initiated the crystallization of product. After being placed in a freezer (-28°C) overnight, the product was filtered off and dried under high vacuum, providing colorless crystals (434 mg, 42% yield). ^1H NMR (400 MHz, CDCl_3) δ 7.43 – 7.37 (m, 3H), 7.36 – 7.30 (m, 2H), 7.10 (s, 2H), 2.79 (s, 6H), 2.35 (s, 3H). ^{19}F NMR (376 MHz, CDCl_3) δ -75.3 (s). The spectral data are in accordance with literature.³⁴

Iodonium salts **2a-e** and **2h-v** were prepared according to following procedure:³⁵

³³ Bachi, M. D.; Bar-Ner, N.; Crittall, C. M.; Stang, P. J.; Williamson, B. L. *J. Org. Chem.* **1991**, 56, 3912-3915.

³⁴ Dixon, L. I.; Carroll, M. A.; Gregson, T. J.; Ellames, G. J.; Harrington, R. W.; Clegg, W. *Eur. J. Org. Chem.* **2013**, 2334-2345.

³⁵ Slightly modified version of the procedure given in Stang, P. J.; Kitamura, T. *Org. Synth.* **1992**, 70, 215.

Scheme S11.

General Procedure 2

A round bottom flask was charged with iodosylarene (1 equiv.) and solid (trimethylsilylethynyl)arene (1.1 equiv.). The flask was capped with a rubber septum and evacuated/back-filled with nitrogen. Next, CHCl₃ (2 mL/mmol substrate) was added via syringe, followed by liquid (trimethylsilylethynyl)arene. The resulting mixture was cooled down to 0 °C and BF₃·Et₂O (1.1 equiv.) was added dropwise via syringe. After the addition was complete, the cooling bath was removed, and the reaction mixture was stirred at room temperature for 16 h. Aqueous NaX (1 M, 4 equiv.) was added via syringe and the resulting mixture was stirred vigorously at room temperature for 30 minutes. Next, the biphasic mixture was transferred to separatory funnel and the organic phase was separated. The aqueous phase was extracted with CH₂Cl₂ (2 x 1 mL/mmol substrate) and the combined organic phases were dried over anhydrous MgSO₄, filtered, and concentrated under reduced pressure. Et₂O (2 mL/mmol substrate) was added to the residue, inducing the precipitation of iodonium salt.³⁶ The flask was kept at 4 °C or -30 °C for 1 h, the solid was filtered off, washed several times with Et₂O (0.5 mL/mmol of substrate for each washing), and dried under high vacuum.

(2-Phenylethynyl)(2,4,6-trimethylphenyl)iodonium *p*-toluenesulfonate (2a). The title compound was prepared according to the General Procedure 2 in 15 mmol scale from iodosylmesitylene (3.93 g, 15 mmol), trimethyl(2-phenylethynyl)silane (2.88 g, 16.5 mmol), and boron trifluoride etherate (2.06 mL, 16.5 mmol) in 30 mL of CHCl₃, using 60 mL of 1 M aqueous sodium *p*-toluenesulfonate (11.7 g, 60 mmol) in the second step. The product was precipitated from 30 mL of Et₂O and after drying under high vacuum it was obtained as a yellowish solid (4.15 g, 53% yield). ¹H NMR (400 MHz, CDCl₃) δ 7.53 – 7.49 (m, 2H), 7.43 – 7.38 (m, 3H), 7.36 – 7.31 (m, 2H), 7.08 – 7.04 (m, 2H), 7.03 (s, 2H), 2.73 (s, 6H), 2.33 (s, *J* = 1.3 Hz, 3H), 2.32 (s, 3H).

³⁶ Sometimes for the better quality of the precipitate, the crude residue was first dissolved in a minimal amount of CH₂Cl₂ (1-2 mL), and then Et₂O was added in one portion.

Phenyl(2-phenylethynyl)iodonium *p*-toluenesulfonate (2b). The title compound was prepared according to the General Procedure 2 in 4 mmol scale from iodosylbenzene (880 mg, 4 mmol), trimethyl(2-phenylethynyl)silane (767 mg, 4.4 mmol), and boron trifluoride etherate (549 μ L, 4.4 mmol) in 8 mL of CHCl_3 , using 16 mL of 1 M aqueous sodium *p*-toluenesulfonate (3.27 g, 16 mmol) in the second step. The product was precipitated from 8 mL of Et_2O and after drying under high vacuum it was obtained as an ivory solid (627 mg, 33% yield). ^1H NMR (400 MHz, CDCl_3) δ 8.18 – 8.14 (m, 2H), 7.69 – 7.64 (m, 2H), 7.61 – 7.56 (m, 1H), 7.50 – 7.42 (m, 5H), 7.40 – 7.34 (m, 2H), 7.12 (d, J = 8.0 Hz, 2H), 2.33 (s, 3H). The spectral data are in accordance with literature.³⁷

(2-Methoxyphenyl)(2-phenylethynyl)iodanium *p*-toluenesulfonate (2c). The title compound was prepared according to the General Procedure 2 in 2 mmol scale from 2-methoxy-iodosylbenzene (500 mg, 2 mmol), trimethyl(2-phenylethynyl)silane (384 mg, 2.2 mmol), and boron trifluoride etherate (274 μ L, 2.2 mmol) in 4 mL of CHCl_3 , using 8 mL of 1 M aqueous sodium *p*-toluenesulfonate (1.64 g, 8 mmol) in the second step. The product was precipitated from 4 mL of Et_2O and after drying under high vacuum it was obtained as an orange solid (380 mg, 38% yield). ^1H NMR (400 MHz, CDCl_3) δ 7.51 (d, J = 8.2 Hz, 2H), 7.23 (d, J = 8.0 Hz, 1H), 7.06 (d, J = 7.9 Hz, 2H), 7.03 (s, 2H), 7.01 – 6.98 (m, 1H), 6.95 (ddd, J = 8.4, 2.6, 0.9 Hz, 1H), 6.91 (dd, J = 2.4, 1.4 Hz, 1H), 3.78 (s, 3H), 2.73 (s, 6H), 2.33 (s, 3H), 2.32 (s, 3H). The spectral data are in accordance with literature.³⁸

(2-Methylphenyl)(2-phenylethynyl)iodonium *p*-toluenesulfonate (2d). The title compound was prepared according to the General Procedure 2 in 5 mmol scale from 2-methyl-iodosylbenzene (1.17 g,

³⁷ Bouma, M. J.; Olofsson, B. *Chem. Eur. J.* **2012**, *18*, 14242–14245.

³⁸ Hamnett, D. J.; Moran, W. J. *Org. Biomol. Chem.* **2014**, *12*, 4156–4162.

5 mmol), trimethyl(2-phenylethynyl)silane (959 mg, 5.5 mmol), and boron trifluoride etherate (686 μ L, 5.5 mmol) in 10 mL of CHCl_3 , using 20 mL of 1 M aqueous sodium *p*-toluenesulfonate (4.09 g, 20 mmol) in the second step. The product was precipitated from 10 mL of Et_2O and after drying under high vacuum it was obtained as an off-white solid (478 mg, 20% yield). ^1H NMR (400 MHz, CDCl_3) δ 8.16 (dd, $J = 8.2, 1.1$ Hz, 1H), 7.56 – 7.53 (m, 2H), 7.50 (dd, $J = 7.4, 1.0$ Hz, 1H), 7.45 (dd, $J = 7.6, 1.4$ Hz, 1H), 7.44 – 7.38 (m, 3H), 7.36 – 7.31 (m, 2H), 7.23 – 7.18 (m, 1H), 7.10 – 7.04 (m, 2H), 2.76 (s, 3H), 2.32 (s, 3H).

(2,6-Dimethylphenyl)(2-phenylethynyl)iodonium *p*-toluenesulfonate (2e). The title compound was prepared according to the General Procedure 2 in 5 mmol scale from 2,6-dimethyl-iodosylbenzene (1.24 g, 5 mmol), trimethyl(2-phenylethynyl)silane (959 mg, 5.5 mmol), and boron trifluoride etherate (686 μ L, 5.5 mmol) in 10 mL of CHCl_3 , using 20 mL of 1 M aqueous sodium *p*-toluenesulfonate (4.09 g, 20 mmol) in the second step. The product was precipitated from 10 mL of Et_2O and after drying under high vacuum it was obtained as an off-white solid (1.60 g, 63% yield). ^1H NMR (400 MHz, CDCl_3) δ 7.51 – 7.46 (m, 2H), 7.44 – 7.30 (m, 6H), 7.24 (d, $J = 7.4$ Hz, 2H), 7.08 – 7.02 (m, 2H), 2.78 (s, 3H), 2.32 (s, 3H).

(2-Phenylethynyl)(2,4,6-trimethylphenyl)iodonium tetrafluoroborate (2h). The title compound was prepared according to the General Procedure 2 in 1.3 mmol scale from iododimethylbenzene (341 mg, 1.3 mmol), trimethyl(2-phenylethynyl)silane (249 mg, 1.43 mmol), and boron trifluoride etherate (178 μ L, 1.43 mmol) in 3 mL of CHCl_3 , using 6 mL of 0.87 M aqueous sodium tetrafluoroborate (583 mg, 5.2 mmol) in the second step. The product was precipitated from 3 mL of Et_2O and after drying under high vacuum it was obtained as a brownish solid (169 mg, 30% yield). ^1H NMR (400 MHz, CDCl_3) δ 7.53 – 7.44 (m, 3H), 7.41 – 7.35 (m, 2H), 7.15 (s, 2H), 2.78 (s, 6H), 2.38 (s, 3H). ^{19}F NMR (376 MHz, CDCl_3) δ -146.7 (s).

[2-(2,6-dimethylphenyl)ethynyl](2,4,6-trimethylphenyl)iodonium *p*-toluenesulfonate (2i). The title compound was prepared according to the General Procedure 2 in 3.1 mmol scale from iodosylmesitylene (810 mg, 3.1 mmol), [2-(2,6-dimethylphenyl)ethynyl]trimethylsilane (688 mg, 3.41 mmol), and boron trifluoride etherate (424 μ L, 3.41 mmol) in 6.2 mL of CHCl_3 , using 12.4 mL of 1 M aqueous sodium *p*-toluenesulfonate (2.4 g, 12.4 mmol). The product was precipitated from 6 mL of Et_2O and after drying under high vacuum it was obtained as a yellowish solid (905 mg, 54% yield). ^1H NMR (400 MHz, CDCl_3) δ 7.55 – 7.50 (m, 2H), 7.19 – 7.13 (m, 1H), 7.06 (d, J = 8.0 Hz, 2H), 7.03 (s, 2H), 7.02 (d, J = 8.2 Hz, 2H), 2.75 (s, 6H), 2.33 (s, 6H), 2.30 (s, 6H).

[2-(4-*tert*-Butylphenyl)ethynyl](2,4,6-trimethylphenyl)iodonium *p*-toluenesulfonate (2j). The title compound was prepared according to the General Procedure 2 in 2 mmol scale from iodosylmesitylene (524 mg, 2 mmol), [2-(4-*tert*-butylphenyl)ethynyl]trimethylsilane (507 mg, 2.2 mmol), and boron trifluoride etherate (274 μ L, 2.2 mmol) in 4 mL of CHCl_3 , using 8 mL of 1 M aqueous sodium *p*-toluenesulfonate (1.64 g, 8 mmol) in the second step. The product was precipitated from 4 mL of Et_2O and after drying under high vacuum it was obtained as a white solid (556 mg, 48% yield). ^1H NMR (400 MHz, CDCl_3) δ 7.53 – 7.49 (m, 2H), 7.35 (s, 4H), 7.08 – 7.04 (m, 2H), 7.02 (s, 2H), 2.73 (s, 6H), 2.33 (s, 6H), 1.28 (s, 9H).

(2-([1,1'-Biphenyl]-3-yl)ethynyl)(2,4,6-trimethylphenyl)iodonium *p*-toluenesulfonate (2k). The title compound was prepared according to the General Procedure 2 in 4 mmol scale from iodosylmesitylene (1.05 g, 4 mmol), (2-([1,1'-biphenyl]-3-yl)ethynyl)trimethylsilane (1.10 g, 4.4 mmol), and boron trifluoride etherate (549 μ L, 4.4 mmol) in 8 mL of CHCl_3 , using 16 mL of 1 M aqueous sodium *p*-toluenesulfonate (3.11 g, 16 mmol) in the second step. The product was precipitated from 8 mL of Et_2O and after drying under high vacuum it was obtained as a brownish solid (1.20 g, 51% yield). ^1H NMR (400 MHz, CDCl_3) δ 7.63 – 7.59 (m, 2H), 7.54 – 7.49 (m, 4H), 7.46 – 7.35 (m, 5H), 7.04 (d, J = 8.8 Hz, 2H), 7.03 (s, 2H), 2.74 (s, 6H), 2.33 (s, 3H), 2.31 (s, 3H).

[2-(Naphthalen-2-yl)ethynyl](2,4,6-trimethylphenyl)iodonium *p*-toluenesulfonate (2l). The title compound was prepared according to the General Procedure 2 in 4 mmol scale from iodosylmesitylene (1.05 g, 4 mmol), trimethyl[2-(naphthalen-2-yl)ethynyl]silane (987 mg, 4.4 mmol), and boron trifluoride etherate (549 μ L, 4.4 mmol) in 8 mL of CHCl_3 , using 16 mL of 1 M aqueous sodium *p*-toluenesulfonate (3.11 g, 16 mmol) in the second step. The product was precipitated from 8 mL of Et_2O and after drying under high vacuum it was obtained as a brown solid (764 mg, 34% yield). ^1H NMR (400 MHz, CDCl_3) δ 7.96 (d, J = 0.9 Hz, 1H), 7.85 – 7.75 (m, 3H), 7.58 – 7.50 (m, 4H), 7.40 (dd, J = 8.5, 1.6 Hz, 1H), 7.06 (dd, J = 10.1, 0.5 Hz, 2H), 7.05 (s, 2H), 2.76 (s, 6H), 2.34 (s, 3H), 2.32 (s, 3H).

[2-(3,5-Difluorophenyl)ethynyl](2,4,6-trimethylphenyl)iodonium *p*-toluenesulfonate (2m). The title compound was prepared according to the General Procedure 2 in 4 mmol scale from iodosylmesitylene (1.05 g, 4 mmol), [2-(3,5-difluorophenyl)ethynyl]trimethylsilane (925 mg, 4.4 mmol), and boron trifluoride etherate (549 μ L, 4.4 mmol) in 8 mL of CHCl_3 , using 16 mL of 1 M aqueous sodium *p*-toluenesulfonate (3.11 g, 16 mmol) in the second step. The product was precipitated from 8 mL of Et_2O and after drying under high vacuum it was obtained as an off-white solid (1.49 g, 67% yield). ^1H NMR (400 MHz, CDCl_3) δ 7.52 – 7.47 (m, 2H), 7.04 (d, J = 8.0 Hz, 2H), 7.02 (s, 2H), 6.91 – 6.81 (m, 3H), 2.70 (s, 6H), 2.33 (s, 3H), 2.32 (s, 3H). ^{19}F NMR (376 MHz, CDCl_3) δ -108.1 – -108.2 (m).

{2-[2-(Trifluoromethyl)phenyl]ethynyl}(2,4,6-trimethylphenyl)iodonium *p*-toluenesulfonate (2n). The title compound was prepared according to the General Procedure 2 in 2 mmol scale from iodosylmesitylene (524 mg, 2 mmol), trimethyl[2-[2-(trifluoromethyl)phenyl]ethynyl]silane (533 mg,

2.2 mmol), and boron trifluoride etherate (274 μL , 2.2 mmol) in 4 mL of CHCl_3 , using 8 mL of 1 M aqueous sodium *p*-toluenesulfonate (1.64 g, 8 mmol) in the second step. The product was precipitated from 4 mL of Et_2O and after drying under high vacuum it was obtained as a yellowish solid (589 mg, 50% yield). ^1H NMR (400 MHz, CDCl_3) δ 7.66 – 7.63 (m, 1H), 7.59 – 7.50 (m, 3H), 7.48 (d, J = 8.2 Hz, 2H), 7.05 (d, J = 8.0 Hz, 2H), 7.03 (s, 2H), 2.72 (s, 6H), 2.33 (s, 3H), 2.32 (s, 3H). ^{19}F NMR (376 MHz, CDCl_3) δ -62.2 (s).

[2-(3,4-Dichlorophenyl)ethynyl](2,4,6-trimethylphenyl)iodonium *p*-toluenesulfonate (2o). The title compound was prepared according to the General Procedure 2 in 2 mmol scale from iodosylmesitylene (524 mg, 2 mmol), [2-(3,4-dichlorophenyl)ethynyl]trimethylsilane (535 mg, 2.2 mmol), and boron trifluoride etherate (274 μL , 2.2 mmol) in 4 mL of CHCl_3 , using 8 mL of 1 M aqueous sodium *p*-toluenesulfonate (1.64 g, 8 mmol) in the second step. The product was precipitated from 4 mL of Et_2O and after drying under high vacuum it was obtained as an off-white solid (605 mg, 52% yield). ^1H NMR (400 MHz, CDCl_3) δ 7.50 (d, J = 8.1 Hz, 2H), 7.47 (d, J = 1.9 Hz, 1H), 7.41 (d, J = 8.3 Hz, 1H), 7.23 (dd, J = 8.3, 1.9 Hz, 1H), 7.06 (d, J = 8.5 Hz, 2H), 7.04 (s, 2H), 2.71 (s, 6H), 2.34 (s, 3H), 2.33 (s, 3H).

[2-(4-Cyanophenyl)ethynyl](2,4,6-trimethylphenyl)iodonium *p*-toluenesulfonate (2p). The title compound was prepared according to the General Procedure 2 in 2 mmol scale from iodosylmesitylene (524 mg, 2 mmol), 4-[2-(trimethylsilyl)ethynyl]benzonitrile (439 mg, 2.2 mmol), and boron trifluoride etherate (274 μL , 2.2 mmol) in 4 mL of CHCl_3 , using 8 mL of 1 M aqueous sodium *p*-toluenesulfonate (1.64 g, 8 mmol) in the second step. The product was precipitated from 4 mL of Et_2O and after drying under high vacuum it was obtained as an off-white solid (414 mg, 38% yield). ^1H NMR (400 MHz, CDCl_3) δ 7.62 – 7.58 (m, 2H), 7.50 – 7.45 (m, 4H), 7.04 (d, J = 8.1 Hz, 2H), 7.03 (s, 2H), 2.70 (s, 6H), 2.33 (s, 3H), 2.32 (s, 3H).

[2-(4-Acetylphenyl)ethynyl](2,4,6-trimethylphenyl)iodonium *p*-toluenesulfonate (2q). The title compound was prepared according to the General Procedure 2 in 4 mmol scale from iodosylmesitylene (1.05 mg, 4 mmol), 1-{4-[2-(trimethylsilyl)ethynyl]phenyl}ethan-1-one (952 mg, 4.4 mmol), and boron trifluoride etherate (549 μ L, 4.4 mmol) in 8 mL of CHCl_3 , using 16 mL of 1 M aqueous sodium *p*-toluenesulfonate (3.27 g, 16 mmol) in the second step. The product was precipitated from 8 mL of Et_2O and after drying under high vacuum it was obtained as an orange solid (921 mg, 41% yield). ^1H NMR (400 MHz, CDCl_3) δ 7.93 – 7.88 (m, 2H), 7.53 – 7.46 (m, 4H), 7.05 (d, J = 10.5 Hz, 2H), 7.04 (s, 2H), 2.73 (s, 6H), 2.59 (s, 3H), 2.34 (s, 3H), 2.33 (s, 3H).

{2-[3-(Ethoxycarbonyl)phenyl]ethynyl}(2,4,6-trimethylphenyl)iodonium *p*-toluenesulfonate (2r). The title compound was prepared according to the General Procedure 2 in 4 mmol scale from iodosylmesitylene (1.05 g, 4 mmol), ethyl 3-[2-(trimethylsilyl)ethynyl]benzoate (1.08 g, 4.4 mmol), and boron trifluoride etherate (549 μ L, 4.4 mmol) in 8 mL of CHCl_3 , using 16 mL of 1 M aqueous sodium *p*-toluenesulfonate (3.27 g, 16 mmol) in the second step. The product was precipitated from 8 mL of Et_2O and after drying under high vacuum it was obtained as a yellowish solid (1.27 g, 54% yield). ^1H NMR (400 MHz, CDCl_3) δ 8.08 – 8.04 (m, 2H), 7.58 (dt, J = 7.7, 1.4 Hz, 1H), 7.53 – 7.49 (m, 2H), 7.45 – 7.40 (m, 1H), 7.06 (dd, J = 8.4, 0.5 Hz, 2H), 7.04 (s, 2H), 4.38 (q, J = 7.1 Hz, 2H), 2.73 (s, 6H), 2.34 (s, 3H), 2.33 (s, 3H), 1.39 (t, J = 7.1 Hz, 3H).

[2-(3-Methoxyphenyl)ethynyl](2,4,6-trimethylphenyl)iodonium *p*-toluenesulfonate (2s). The title compound was prepared according to the General Procedure 2 in 11.1 mmol scale from iodosylmesitylene (2.91 g, 11.1 mmol), [2-(3-methoxyphenyl)ethynyl]trimethylsilane (2.50 g, 12.2

mmol), and boron trifluoride etherate (1.52 mL, 12.2 mmol) in 22 mL of CHCl_3 , using 44 mL of 1 M aqueous sodium *p*-toluenesulfonate (8.62 g, 44.4 mmol) in the second step. The product was precipitated from 22 mL of Et_2O and after drying under high vacuum it was obtained as a reddish solid (1.85 g, 30% yield). ^1H NMR (400 MHz, CDCl_3) δ 7.53 – 7.48 (m, 1H), 7.26 – 7.21 (m, 1H), 7.05 (d, J = 8.0 Hz, 2H), 7.03 (s, 2H), 6.99 (dt, J = 7.6, 1.1 Hz, 1H), 6.95 (ddd, J = 8.4, 2.6, 0.9 Hz, 1H), 6.91 (dd, J = 2.5, 1.4 Hz, 1H), 3.78 (s, 3H), 2.73 (s, 6H), 2.33 (s, 3H), 2.32 (s, 3H).

{2-[4-(Trifluoromethoxy)phenyl]ethynyl}(2,4,6-trimethylphenyl)iodonium *p*-toluenesulfonate (2t). The title compound was prepared according to the General Procedure 2 in 24 mmol scale from iodosylmesitylene (6.29 g, 24 mmol), trimethyl({2-[4-(trifluoromethoxy)phenyl]ethynyl})silane (6.82 g, 26.4 mmol), and boron trifluoride etherate (3.29 mL, 26.4 mmol) in 48 mL of CHCl_3 , using 96 mL of 1 M aqueous sodium *p*-toluenesulfonate (18.6 g, 96 mmol) in the second step. The product was precipitated from 50 mL of Et_2O and after drying under high vacuum it was obtained as an off-white solid (6.19 g, 43% yield). ^1H NMR (400 MHz, CDCl_3) δ 7.52 – 7.47 (m, 2H), 7.45 – 7.40 (m, 2H), 7.18 – 7.14 (m, 2H), 7.06 – 7.02 (m, 2H), 7.02 (s, J = 5.6 Hz, 2H), 2.71 (s, 6H), 2.32 (s, 3H), 2.32 (s, 3H). ^{19}F NMR (376 MHz, CDCl_3) δ -57.8 (s).

{2-[3-(1,3-Dioxo-2,3-dihydro-1H-isoindol-2-yl)phenyl]ethynyl}(2,4,6-trimethylphenyl)iodonium *p*-toluenesulfonate (2u). The title compound was prepared according to the General Procedure 2 in 6 mmol scale from iodosylmesitylene (1.57 g, 6 mmol), 2-{3-[2-(trimethylsilyl)ethynyl]phenyl}-2,3-dihydro-1H-isoindole-1,3-dione (2.11 g, 6.6 mmol), and boron trifluoride etherate (823 μL , 6.6 mmol) in 12 mL of CHCl_3 , using 24 mL of 1 M aqueous sodium *p*-toluenesulfonate (4.66 g, 24 mmol) in the second step. The product was precipitated from 12 mL of Et_2O and after drying under high vacuum it was obtained as a brownish solid (1.35 g, 34% yield). ^1H NMR (400 MHz, CDCl_3) δ 7.99 – 7.93 (m, 2H), 7.84 – 7.78 (m, 2H), 7.55 – 7.41 (m, 6H), 7.06 (d, J = 7.9 Hz, 2H), 7.04 (s, 2H), 2.73 (s, 6H), 2.33 (s, 3H), 2.33 (s, 3H).

{2-[2-(Morpholine-4-sulfonyl)phenyl]ethynyl}(2,4,6-trimethylphenyl)iodonium *p*-toluenesulfonate (2v). The title compound was prepared according to the General Procedure 2 in 3.77 mmol scale from iodosylmesitylene (988 mg, 3.77 mmol), 4-{2-[2-(trimethylsilyl)ethynyl]benzenesulfonyl}morpholine (1.34 g, 4.15 mmol), and boron trifluoride etherate (517 μ L, 4.15 mmol) in 7.5 mL of CHCl_3 , using 15 mL of 1 M aqueous sodium *p*-toluenesulfonate (3.08 g, 15.1 mmol) in the second step. The product was precipitated from 12 mL of Et_2O and after drying under high vacuum it was obtained as an orange solid (1.37 g, 54% yield). ^1H NMR (400 MHz, CDCl_3) δ 7.85 – 7.82 (m, 1H), 7.67 – 7.63 (m, 1H), 7.57 – 7.51 (m, 2H), 7.50 – 7.46 (m, 2H), 7.04 (d, J = 8.0 Hz, 2H), 7.01 (s, 2H), 3.49 – 3.45 (m, 4H), 2.75 (dd, J = 5.6, 3.8 Hz, 4H), 2.72 (s, 6H), 2.32 (s, 6H).

3.1.4. Synthesis of [2-phenyl($1\text{-}^{13}\text{C}$)ethynyl](2,4,6-trimethylphenyl) iodonium *p*-toluenesulfonate (2w)

The title compound was prepared in a following sequence.

Scheme S12.

1-Phenyl(2- ^{13}C)ethan-1-one.³⁹ Under nitrogen atmosphere, [^{13}C]-iodomethane (99% ^{13}C ; 1.09 mL, 17.3 mmol,) was added via syringe to a stirred suspension of magnesium turnings (486 mg, 19.8 mmol) in Et_2O (anhydrous, 33 mL) at 0 °C. After the addition was complete, the cooling bath was removed and the reaction mixture was stirred at room temperature for 2 h, providing a solution of [^{13}C]-

³⁹ Zeng, M.; Li, L.; Herzon, S. B. *J. Am. Chem. Soc.* **2014**, *136*, 7058-7067.

methylmagnesium iodide (nominally 0.5 M). This solution was transferred to a dropping funnel via a cannula under nitrogen overpressure and it was slowly added to a solution of *N*-methoxy-*N*-methylbenzamide (2.73 g, 16.5 mmol) in THF (anhydrous, 23 mL) over a period of 20 minutes at 0 °C under nitrogen atmosphere. Upon the completion of the addition, the cooling bath was removed and the reaction mixture was stirred at room temperature for 13 h. Next, saturated aqueous NH₄Cl (30 mL) was added, the biphasic mixture was transferred to a separatory funnel, and the aqueous layer was discarded. The organic phase was washed sequentially with water (30 mL) and brine (30 mL), and it was dried over anhydrous Na₂SO₄, filtered, and concentrated under reduced pressure. The product was purified by column chromatography (silica, petroleum ether:diethyl ether/18:2 to 17:3) and it was obtained as a colorless liquid (1.47 g, 73% yield). ¹H NMR (400 MHz, CDCl₃) δ 7.98 – 7.94 (m, 2H), 7.59 – 7.54 (m, 1H), 7.50 – 7.43 (m, 2H), 2.61 (d, ¹J_{13C-H} = 127.5 Hz, 3H). ¹³C NMR (101 MHz, CDCl₃) δ 198.1, 137.3, 133.2, 128.7, 128.4, 26.8 (¹³C label). The spectral data are in accordance with literature.³⁹

[(2-¹³C)Ethyne]benzene.³⁹ An oven-dried round bottom flask was capped with septum and evacuated/back-filled with nitrogen 3 times, a freshly prepared solution of LDA in THF (1 M, 13.2 mL, 13.2 mmol) was added, and the flask was cooled down to –78 °C. Next, the solution of 1-phenyl(2-¹³C)ethan-1-one (1.47 g, 12 mmol) in THF (anhydrous, 7.2 mL) was added dropwise via syringe. Upon completion of the addition, the mixture was stirred at –78 °C for 1 h. Next, diethylchlorophosphate (1.97 mL, 13.2 mmol) was added dropwise via syringe and the resulting mixture was warmed to room temperature over 30 min. The reaction mixture was transferred via cannula under nitrogen overpressure to a freshly prepared solution of LDA in THF (1 M, 27.6 mL, 27.6 mmol) cooled to –78 °C. After the addition was complete, the reaction mixture was gradually warmed up to room temperature over 3 h. Water (40 mL) was added and the biphasic mixture was transferred to a separatory funnel. The organic layer was separated and the aqueous layer was extracted with petroleum ether (50 mL). The combined organic phases were washed sequentially with water (50 mL) and saturated aqueous NaHCO₃ (50 mL), dried with anhydrous Na₂SO₄, filtered, and concentrated under reduced pressure. The product was purified by column chromatography (silica, petroleum ether) and it was obtained as a colorless liquid (437 mg, 35% yield). ¹H NMR (400 MHz, CDCl₃) δ 7.53 – 7.48 (m, 2H), 7.38 – 7.30 (m, 3H), 3.08 (d, ¹J_{13C-H} = 251.2 Hz, 1H). ¹³C NMR (101 MHz, CDCl₃) δ 132.3 (d, *J* = 2.7 Hz), 128.9 (d, *J* = 0.9 Hz), 128.4, 122.2, 84.1 (d, *J* = 139.2 Hz), 77.3 (¹³C label). The spectral data are in accordance with literature.³⁹

Trimethyl[2-phenyl(1-¹³C)ethyne]silane.⁴⁰ Under nitrogen atmosphere, a solution of *n*-BuLi in hexanes (2.5 M, 1.87 mL, 4.66 mmol) was added dropwise via syringe to solution of [(2-¹³C)ethyne]benzene (437 mg, 4.24 mmol) in THF (anhydrous, 4.2 mL) at –78 °C. After stirring for 30 min at –78 °C, trimethylsilyl chloride (0.65 mL, 5.09 mmol) was added dropwise via syringe over a period of 10 min. The reaction mixture was stirred at –78 °C for 30 minutes and for further 1.5 hour at room temperature. Next, the reaction mixture was cooled down to 0 °C, and saturated aqueous NH₄Cl (10 mL) was added. The biphasic mixture was transferred to a separatory funnel and the organic layer was separated. The aqueous phase was extracted with Et₂O (2 x 10 mL) and the combined organic phases were washed with brine (10 mL), dried over anhydrous Na₂SO₄, filtered, and concentrated under reduced pressure. The residue was dissolved in petroleum ether (5 mL) and it was filtered through a short pad of silica using petroleum ether (20 mL). After concentration under reduced pressure, the product obtained as a colorless oil, that was used in the next step without further purification (595 mg, 90% yield). ¹H NMR (400 MHz, CDCl₃) δ 7.49 – 7.44 (m, 2H), 7.33 – 7.27 (m, 3H), 0.25 (d, ¹J_{13C-H} = 2.7 Hz, 9H). ¹³C NMR (101 MHz, CDCl₃) δ 132.1 (d, *J* = 2.3 Hz), 128.6 (d, *J* = 0.8 Hz), 128.3, 123.3, 105.3 (d, *J* = 135.9 Hz), 94.2 (¹³C label), 0.1 (d, *J* = 5.5 Hz).

⁴⁰ Boelke, A.; Caspers, L. D.; Nachtsheim, B. J. *Org. Lett.* **2017**, *19*, 5344-5347.

[2-Phenyl(1-¹³C)ethynyl](2,4,6-trimethylphenyl) iodonium *p*-toluenesulfonate (2w).³⁵ The title compound was prepared according to General Procedure 2 in 3.08 mmol scale from iodosylmesitylene (807 mg, 3.08 mmol), trimethyl[2-phenyl(1-¹³C)ethynyl]silane (595 mg, 3.39 mmol), and boron trifluoride etherate (442 μ L, 3.39 mmol) in 6 mL of CHCl₃, using 12 mL of 1 M aqueous sodium *p*-toluenesulfonate (2.39 g, 12.3 mmol) in the second step. The product was precipitated from 6 mL of Et₂O and after drying under high vacuum it was obtained as a yellowish solid (947 mg, 61% yield). ¹H NMR (400 MHz, CDCl₃) δ 7.53 – 7.48 (m, 2H), 7.43 – 7.37 (m, 3H), 7.36 – 7.30 (m, 2H), 7.05 (d, *J* = 8.0 Hz, 2H), 7.03 (s, 2H), 2.73 (s, 6H), 2.33 (s, 3H), 2.32 (s, 3H). ¹³C NMR (126 MHz, CDCl₃) δ 143.4, 141.5, 141.1, 139.9, 132.9 (d, *J* = 3.7 Hz), 130.6, 129.8, 128.5 (d, *J* = 9.0 Hz), 127.8, 126.0, 120.4, 120.4, 102.0 (d, *J* = 168.2 Hz), 37.2 (¹³C label), 27.1, 21.4, 21.1. ¹³C NMR spectra without NOE shows that the compound contains 99% ¹³C at the α -position. FT-IR-ATR: 3038, 2981, 2916, 2128, 1443, 1380, 1225, 1157, 1142, 1116, 1003, 758, 690, 679 cm⁻¹. HRMS (ESI): *m/z* 348.0323 ([M]⁺, C₁₆¹³CH₁₆I⁺ calcd. 348.0325).

4. NHC-Catalyzed Propargylation of Aldehydes with Alkynyliodonium Salts

General Procedure 3

An oven-dried 20 mL vial was charged with catalyst precursor **NHC-1** (18 mg, 0.05 mmol, 10 mol%), alkynyl(2,4,6-trimethylphenyl)iodonium *p*-toluenesulfonate **2** (0.60 mmol) and aldehyde **1** (0.50 mmol). The vial was capped and evacuated/back-filled with nitrogen three times. Toluene (anhydrous, 10 mL) was added via syringe, and the vial was cooled to -40 °C. Next, TMEDA (112 μ L, 0.75 mmol) was added via syringe, and the reaction mixture was stirred at -40 °C for 24 h. After warming to room temperature, the reaction mixture was concentrated under reduced pressure. The product was purified by column chromatography. The procedure could be scaled-up to 6.0 mmol of aldehyde without loss in yield (see compound **3y**).

3-Phenyl-1-(quinoxalin-2-yl)prop-2-yn-1-one (3a). The title compound was prepared according to the General Procedure 3 from quinoxaline-2-carbaldehyde (**1a**) and (2-phenylethynyl)(2,4,6-trimethylphenyl)iodonium *p*-toluenesulfonate (**2a**). After purification by column chromatography (silica, petroleum ether:ethyl acetate/9:1 to 8:2), the product was obtained as a yellow solid (103 mg, 80% yield). *R*_f = 0.46 (petroleum ether:ethyl acetate/8:2). ¹H NMR (400 MHz, CDCl₃) δ 9.60 (s, 1H, *H*³), 8.33 (dd, *J* = 8.2, 1.3 Hz, 1H, *H*⁸), 8.20 (dd, *J* = 8.3, 1.3 Hz, 1H, *H*⁵), 7.91 (dddd, *J* = 18.7, 8.3, 6.9, 1.5 Hz, 2H, *H*⁶, *H*⁷), 7.80 – 7.76 (m, 2H, *H*^o), 7.55 – 7.49 (m, 1H, *H*^p), 7.48 – 7.43 (m, 2H, *H*^m). ¹³C NMR (126 MHz, CDCl₃) δ 177.6 (*C*^{C=O}), 147.0 (*C*²), 144.1 (*C*^{8a}), 143.7 (d, *J* = 20.1 Hz, *C*³), 141.6 (*C*^{4a}), 133.8 (*C*^o), 132.8 (*C*⁶), 131.4 (*C*^p), 131.13 (*C*⁷), 131.10 (*C*⁸), 129.6 (*C*⁵), 128.9 (*C*^m), 120.1 (*C*ⁱ), 97.3 (*C*^β), 87.7 (*C*^α). FT-IR-ATR: 3053, 3036, 2195, 1638, 1326, 1202, 1130, 965, 766, 751, 687 cm⁻¹. HRMS (ESI): *m/z* 259.0865 ([M+H]⁺, C₁₇H₁₁N₂O⁺ calcd. 259.0866).

3-Phenyl-1-(quinolin-4-yl)prop-2-yn-1-one (3b). The title compound was prepared according to the General Procedure 3 from quinoline-4-carbaldehyde (**1b**) and (2-phenylethynyl)(2,4,6-trimethylphenyl)iodonium *p*-toluenesulfonate (**2a**). After purification by column chromatography (silica, petroleum ether:ethyl acetate/8:2 to 1:1), the product was obtained as a red solid (83 mg, 65% yield). $R_f = 0.16$ (petroleum ether:ethyl acetate/8:2). ^1H NMR (400 MHz, CDCl_3) δ 9.16 (d, $J = 4.4$ Hz, 1H, H^2), 8.98 (d, $J = 8.6$ Hz, 1H, H^5), 8.26 (d, $J = 4.4$ Hz, 1H, H^3), 8.23 (d, $J = 8.4$ Hz, 1H, H^8), 7.82 (ddd, $J = 8.3, 7.0, 1.3$ Hz, 1H, H^7), 7.72 (ddd, $J = 15.2, 7.7, 1.3$ Hz, 3H, H^o, H^6), 7.54 – 7.50 (m, 1H, H^p), 7.45 (t, $J = 7.5$ Hz, 2H, H^m). ^{13}C NMR (126 MHz, CDCl_3) δ 179.1 ($C^{C=O}$), 149.9 (C^2), 149.2 (C^{8a}), 134.0 (C^4), 133.4 (C^o), 131.5 (C^p), 130.3 (C^7), 130.0 (C^8), 129.3 (C^6), 129.0 (C^m), 125.7 (C^5), 124.2 (C^3), 119.7 (C^i), 94.0 (C^β), 88.2 (C^α). The spectral data are in accordance with literature.⁴¹

1-[1-(4-Methylbenzenesulfonyl)-1H-pyrazol-3-yl]-3-phenylprop-2-yn-1-one (3c). The title compound was prepared according to the General Procedure 3 from 1-(4-methylbenzenesulfonyl)-1H-pyrazole-3-carbaldehyde (**1c**) and (2-phenylethynyl)(2,4,6-trimethylphenyl)iodonium *p*-toluenesulfonate (**2a**). After purification by column chromatography (silica, petroleum ether:ethyl acetate/9:1 to 8:2), the product was obtained as a yellow solid (139 mg, 79% yield). $R_f = 0.42$ (petroleum ether:ethyl acetate/8:2). ^1H NMR (400 MHz, CDCl_3) δ 8.15 (d, $J = 2.8$ Hz, 1H, H^5), 8.02 – 7.97 (m, 2H, $H^{o'}$), 7.69 – 7.64 (m, 2H, $H^{o'}$), 7.53 – 7.48 (m, 1H, H^p), 7.46 – 7.41 (m, 2H, H^m), 7.39 – 7.34 (m, 2H, $H^{m'}$), 6.94 (d, $J = 2.8$ Hz, 1H, H^4), 2.43 (s, 3H, CH_3). ^{13}C NMR (126 MHz, CDCl_3) δ 171.5 ($C^{C=O}$), 155.3 (C^3), 146.9 ($C^{p'}$), 133.6 (C^o), 133.3 ($C^{i'}$), 132.3 (C^5), 131.2 (C^p), 130.4 ($C^{m'}$), 128.81, 128.80 ($C^{o'}, C^m$), 120.1 (C^i), 108.8 (C^4), 94.4 (C^β), 87.2 (C^α), 21.9 (CH_3). FT-IR-ATR: 3140, 3125, 2925, 2201, 1646, 1382, 1196, 1120, 1074, 1034, 959, 798, 756, 668 cm^{-1} . HRMS (ESI): m/z 351.0796 ($[\text{M}+\text{H}]^+$, $\text{C}_{19}\text{H}_{15}\text{N}_2\text{O}_3\text{S}^+$ calcd. 351.0798).

⁴¹ Boersch, C.; Merkul, E.; Müller, T. J. J. *Angew. Chem. Int. Ed.* **2011**, *50*, 10448-10452.

1-[1-(4-Methylbenzenesulfonyl)-1H-indazol-3-yl]-3-phenylprop-2-yn-1-one (3d). The title compound was prepared according to the General Procedure 3 from 1-(4-methylbenzenesulfonyl)-1H-indazole-3-carbaldehyde (**1d**) and (2-phenylethynyl)(2,4,6-trimethylphenyl)iodonium *p*-toluenesulfonate (**2a**). After purification by column chromatography (silica, petroleum ether:ethyl acetate/18:2 to 17:3), the product was obtained as a yellowish solid (169 mg, 84% yield). $R_f = 0.52$ (petroleum ether:ethyl acetate/8:2). ^1H NMR (400 MHz, CDCl_3) δ 8.34 (d, $J = 8.1$ Hz, 1H, H^d), 8.25 (d, $J = 8.6$ Hz, 1H, H^7), 7.99 (d, $J = 8.4$ Hz, 2H, H^o), 7.78 – 7.73 (m, 2H, H^o), 7.61 (ddd, $J = 8.4$, 7.1, 1.1 Hz, 1H, H^6), 7.55 – 7.50 (m, 1H, H^p), 7.49 – 7.42 (m, 3H, H^5 , H^m), 7.29 (d, $J = 8.2$ Hz, 2H, $H^{m'}$), 2.37 (s, 3H, CH_3). ^{13}C NMR (126 MHz, CDCl_3) δ 172.6 ($\text{C}^{\text{C=O}}$), 148.0, 141.6 (C^3 , C^{7a}), 146.3 ($\text{C}^{p'}$), 134.2 ($\text{C}^{i'}$), 133.6 (C^o), 131.2 (C^p), 130.2 ($\text{C}^{m'}$), 129.8 (C^6), 128.8 (C^m), 128.2 ($\text{C}^{o'}$), 126.0 (C^5), 123.4 (C^{3a}), 123.0 (C^4), 120.2 (C^i), 113.2 (C^7), 94.5 (C^β), 87.4 (C^α), 21.8 (CH_3). FT-IR-ATR: 3086, 3037, 2921, 2195, 1642, 1473, 1272, 1128, 1082, 950, 749 cm^{-1} . HRMS (ESI): m/z 401.0954 ($[\text{M}+\text{H}]^+$, $\text{C}_{23}\text{H}_{17}\text{N}_2\text{O}_3\text{S}^+$ *calcd.* 401.0954).

3-Phenyl-1-(1,3-thiazol-2-yl)prop-2-yn-1-one (3e). The title compound was prepared according to the General Procedure 3 from 1,3-thiazole-2-carbaldehyde (**1e**) and (2-phenylethynyl)(2,4,6-trimethylphenyl)iodonium *p*-toluenesulfonate (**2a**). After purification by column chromatography (silica, petroleum ether:ethyl acetate/18:2 to 17:3), the product was obtained as a yellow solid (90 mg, 84% yield). $R_f = 0.42$ (petroleum ether:ethyl acetate/8:2). ^1H NMR (400 MHz, CDCl_3) δ 8.13 (d, $J = 3.0$ Hz, 1H, H^d), 7.74 (d, $J = 3.0$ Hz, 1H, H^5), 7.73 – 7.70 (m, 2H, H^o), 7.51 – 7.46 (m, 1H, H^p), 7.43 – 7.38 (m, 2H, H^m). ^{13}C NMR (126 MHz, CDCl_3) δ 169.8 ($\text{C}^{\text{C=O}}$), 166.9 (C^2), 145.8 (C^5), 133.6 (C^o), 131.4 (C^p), 128.8 (C^m), 126.8 (C^4), 119.7 (C^i), 95.9 (C^β), 86.6 (C^α). FT-IR-ATR: 3103, 3085, 2186, 1630, 1384, 1325, 1310, 1216, 1062, 977, 750, 679 cm^{-1} . HRMS (ESI): m/z 214.0321 ($[\text{M}+\text{H}]^+$, $\text{C}_{12}\text{H}_8\text{NOS}^+$ *calcd.* 214.0321).

1-(4,5-Dimethyl-1,3-thiazol-2-yl)-3-phenylprop-2-yn-1-one (3f). The title compound was prepared according to the General Procedure 3 from 4,5-dimethyl-1,3-thiazole-2-carbaldehyde (**1f**) and (2-

phenylethynyl)(2,4,6-trimethylphenyl)iodonium *p*-toluenesulfonate (**2a**). After purification by column chromatography (silica, petroleum ether:ethyl acetate/18:2 to 17:3), the product was obtained as a yellow solid (108 mg, 90% yield). $R_f = 0.46$ (petroleum ether:ethyl acetate/8:2). ^1H NMR (400 MHz, CDCl_3) δ 7.73 – 7.70 (m, 2H, H^o), 7.51 – 7.46 (m, 1H, H^p), 7.44 – 7.39 (m, 2H, H^m), 2.49 (d, $J = 0.5$ Hz, 3H, H^7), 2.48 (d, $J = 0.6$ Hz, 3H, H^6). ^{13}C NMR (126 MHz, CDCl_3) δ 169.2 ($C^{C=O}$), 161.4 (C^2), 153.0 (C^4), 137.1 (C^5), 133.5 (C^o), 131.1 (C^p), 128.7 (C^m), 120.0 (C^i), 94.7 (C^β), 86.8 (C^α), 15.1 (C^6), 12.3 (C^7). FT-IR-ATR: 3067, 2923, 2855, 2195, 1616, 1419, 1308, 1285, 1175, 966, 763, 689 cm^{-1} . HRMS (ESI): m/z 242.0634 ($[\text{M}+\text{H}]^+$, $\text{C}_{14}\text{H}_{12}\text{NOS}^+$ *calcd.* 242.0634).

3-Phenyl-1-(pyridin-2-yl)prop-2-yn-1-one (3g). The title compound was prepared according to the General Procedure 3 from pyridine-2-carbaldehyde (**1g**) and (2-phenylethynyl)(2,4,6-trimethylphenyl)iodonium *p*-toluenesulfonate (**2a**). After purification by column chromatography (silica, petroleum ether:ethyl acetate/18:2 to 17:3), the product was obtained as a yellow liquid (96 mg, 93% yield) which turned to blue color upon standing. $R_f = 0.33$ (petroleum ether:ethyl acetate/8:2). ^1H NMR (400 MHz, CDCl_3) δ 8.84 (ddd, $J = 4.7, 1.7, 0.9$ Hz, 1H, H^6), 8.21 – 8.17 (m, 1H, H^3), 7.92 – 7.86 (m, 1H, H^4), 7.74 (ddd, $J = 6.9, 3.5, 1.7$ Hz, 2H, H^o), 7.53 (ddd, $J = 7.6, 4.7, 1.2$ Hz, 1H, H^5), 7.51 – 7.46 (m, 1H, H^p), 7.44 – 7.39 (m, 2H, H^m). ^{13}C NMR (126 MHz, CDCl_3) δ 178.3 ($C^{C=O}$), 153.3 (C^2), 150.0 (C^6), 137.1 (C^4), 133.5 (C^o), 131.0 (C^p), 128.7 (C^m), 127.6 (C^5), 123.5 (C^3), 120.3 (C^i), 95.6 (C^β), 88.0 (C^α). The spectral data are in accordance with literature.⁴²

1-(3-Fluoropyridin-2-yl)-3-phenylprop-2-yn-1-one (3h). The title compound was prepared according to the General Procedure 3 from 3-fluoropyridine-2-carbaldehyde (**1h**) and (2-phenylethynyl)(2,4,6-trimethylphenyl)iodonium *p*-toluenesulfonate (**2a**). After purification by column chromatography (silica, petroleum ether:ethyl acetate/16:4 to 12:8), the product was obtained as a brownish solid (90 mg, 80% yield). $R_f = 0.26$ (petroleum ether:ethyl acetate/8:2). ^1H NMR (400 MHz, CDCl_3) δ 8.65 – 8.62 (m, 1H, H^6), 7.72 – 7.68 (m, 2H, H^o), 7.62 – 7.54 (m, 2H, H^4 , H^5), 7.51 – 7.46 (m, 1H, H^p), 7.44 – 7.38 (m, 2H, H^m). ^{13}C NMR (126 MHz, CDCl_3) δ 175.1 (d, $J = 5.2$ Hz, $C^{C=O}$), 159.4 (d, $J = 274.5$ Hz, C^3), 145.5 (d, $J = 5.3$ Hz, C^6), 141.5 (d, $J = 5.8$ Hz, C^2), 133.5 (C^o), 131.1 (C^p), 129.1 (d, $J = 5.1$ Hz, C^5), 128.7 (C^m), 125.8 (d, $J = 19.3$ Hz, C^4), 120.1 (C^i), 95.1 (C^β), 88.6 (C^α). ^{19}F NMR (471 MHz, CDCl_3) δ -119.4 (dd, $J = 9.0, 4.9$ Hz). FT-IR-ATR: 3078, 2199, 1653, 1443, 1312, 1279, 1180, 1016, 994, 821, 767, 682 cm^{-1} . HRMS (ESI): m/z 226.0663 ($[\text{M}+\text{H}]^+$, $\text{C}_{14}\text{H}_9\text{FNO}^+$ *calcd.* 226.0663).

⁴² Friel, D. K.; Snapper, M. L.; Hoveyda, A. H. *J. Am. Chem. Soc.* **2008**, *130*, 9942-9951.

1-(5-Bromopyridin-2-yl)-3-phenylprop-2-yn-1-one (3i). The title compound was prepared according to the General Procedure 3 from 5-bromopyridine-2-carbaldehyde (**1i**) and (2-phenylethynyl)(2,4,6-trimethylphenyl)iodonium *p*-toluenesulfonate (**2a**). After purification by column chromatography (silica, petroleum ether:ethyl acetate/8:2), the product was obtained as a greenish solid (129 mg, 90% yield). $R_f = 0.71$ (petroleum ether:ethyl acetate/8:2). ^1H NMR (400 MHz, CDCl_3) δ 8.87 (dd, $J = 2.2$, 0.8 Hz, 1H, H^6), 8.06 (dd, $J = 8.4$, 0.8 Hz, 1H, H^3), 8.02 (dd, $J = 8.3$, 2.1 Hz, 1H, H^4), 7.74 – 7.70 (m, 2H, H^o), 7.52 – 7.47 (m, 1H, H^p), 7.45 – 7.39 (m, 2H, H^m). ^{13}C NMR (126 MHz, CDCl_3) δ 177.3 ($C^{C=O}$), 151.7 (C^2), 151.2 (C^6), 139.8 (C^4), 133.5 (C^o), 131.1 (C^p), 128.7 (C^m), 126.0 (C^5), 124.4 (C^3), 120.1 (C^i), 96.1 (C^β), 87.8 (C^α). FT-IR-ATR: 3036, 2199, 1653, 1600, 1366, 1306, 1212, 1197, 1084, 996, 869, 750, 678 cm^{-1} . HRMS (ESI): m/z 285.9862 ($[\text{M}+\text{H}]^+$, $\text{C}_{14}\text{H}_9\text{BrNO}^+$ *calcd.* 285.9862).

3-Phenyl-1-{5-[2-(trifluoromethyl)phenyl]pyridin-2-yl}prop-2-yn-1-one (3j). The title compound was prepared according to the General Procedure 3 from 5-[2-(trifluoromethyl)phenyl]pyridine-2-carbaldehyde (**1j**) and (2-phenylethynyl)(2,4,6-trimethylphenyl)iodonium *p*-toluenesulfonate (**2a**). After purification by column chromatography (silica, petroleum ether:ethyl acetate/18:2 to 17:3), the product was obtained as a reddish solid (169 mg, 96% yield). $R_f = 0.20$ (petroleum ether:ethyl acetate/9:1). ^1H NMR (400 MHz, CDCl_3) δ 8.79 (d, $J = 2.1$ Hz, 1H, H^6), 8.25 (dd, $J = 8.0$, 0.8 Hz, 1H, H^3), 7.89 – 7.85 (m, 1H, H^4), 7.85 – 7.81 (m, 1H, $H^{3'}$), 7.77 – 7.73 (m, 2H, H^o), 7.69 – 7.63 (m, 1H, $H^{5'}$), 7.62 – 7.56 (m, 1H, $H^{4'}$), 7.52 – 7.46 (m, 1H, H^p), 7.45 – 7.39 (m, 2H, H^m), 7.37 – 7.33 (m, 1H, $H^{6'}$). ^{13}C NMR (126 MHz, CDCl_3) δ 177.9 ($C^{C=O}$), 152.6 (C^2), 149.8 (C^6), 139.6, 136.6 ($C^{1'}$, C^5), 137.5 (C^4), 133.6 (C^o), 132.0, 131.9 ($C^{5'}$, $C^{6'}$), 131.0 (C^p), 129.0 (q, $J = 30.4$ Hz, $C^{2'}$), 129.0 ($C^{4'}$), 128.7 (C^m), 126.7 (q, $J = 5.2$ Hz, $C^{3'}$), 123.9 (q, $J = 273.9$ Hz, CF_3), 122.6 (C^3), 120.3 (C^i), 95.8 (C^β), 88.1 (C^α). ^{19}F NMR (471 MHz, CDCl_3) δ -56.7 (s). FT-IR-ATR: 3061, 2198, 1635, 1313, 1264, 1114, 1108, 1036, 997, 760, 693 cm^{-1} . HRMS (ESI): m/z 352.0943 ($[\text{M}+\text{H}]^+$, $\text{C}_{21}\text{H}_{13}\text{F}_3\text{NO}^+$ *calcd.* 352.0944).

3-Phenyl-1-{5-[(1E)-3-phenylprop-1-en-1-yl]pyridin-2-yl}prop-2-yn-1-one (3k). The title compound was prepared according to the General Procedure 3 from 5-[(1E)-4-phenylbut-1-en-1-yl]pyridine-2-carbaldehyde (**1k**) and (2-phenylethynyl)(2,4,6-trimethylphenyl)iodonium *p*-toluenesulfonate (**2a**). After purification by column chromatography (silica, petroleum ether:ethyl acetate/18:2 to 17:3), the product was obtained as a yellow solid (154 mg, 91% yield). $R_f = 0.20$

(petroleum ether:ethyl acetate/9:1). ^1H NMR (400 MHz, CDCl_3) δ 8.73 (d, $J = 1.7$ Hz, 1H, H^6), 8.12 (dd, $J = 8.2, 0.5$ Hz, 1H, H^3), 7.79 (dd, $J = 8.2, 2.2$ Hz, 1H, H^4), 7.74 – 7.71 (m, 2H, H^o), 7.50 – 7.45 (m, 1H, H^p), 7.44 – 7.39 (m, 2H, H^m), 7.34 – 7.29 (m, 2H, $H^{o'}$), 7.25 – 7.19 (m, 3H, $H^{p'}$, $H^{m'}$), 6.53 (dt, $J = 15.9, 5.8$ Hz, 1H, $H^{\beta'}$), 6.47 (d, $J = 16.1$ Hz, 1H, $H^{\alpha'}$), 2.87 – 2.82 (m, 2H, $H^{2'}$), 2.65 – 2.59 (m, 2H, $H^{1'}$). ^{13}C NMR (126 MHz, CDCl_3) δ 177.8 ($\text{C}^{\text{C=O}}$), 151.7 (C^2), 148.1 (C^6), 141.2 (C^i), 137.2 (C^5), 136.1 ($\text{C}^{\alpha'}$), 133.4 (C^o), 133.1 (C^4), 130.8 (C^m), 128.6 (C^p), 128.55, 128.51 ($\text{C}^{o'}$, $\text{C}^{m'}$), 126.5 ($\text{C}^{\beta'}$), 126.2 ($\text{C}^{p'}$), 123.6 (C^3), 120.4 (C^j), 95.1 (C^{β}), 88.1 (C^{α}), 35.4 ($\text{C}^{2'}$), 35.1 ($\text{C}^{1'}$). FT-IR-ATR: 3058, 2927, 2853, 2199, 1635, 1580, 1490, 1319, 1206, 1123, 1016, 963, 861, 765, 691 cm^{-1} . HRMS (ESI): m/z 338.1538 ($[\text{M}+\text{H}]^+$, $\text{C}_{24}\text{H}_{20}\text{NO}^+$ calcd. 338.1539).

1-[5-(Hex-1-yn-1-yl)pyridin-2-yl]-3-phenylprop-2-yn-1-one (3l). The title compound was prepared according to the General Procedure 3 from 5-(hex-1-yn-1-yl)pyridine-2-carbaldehyde (**1l**) and (2-phenylethynyl)(2,4,6-trimethylphenyl)iodonium *p*-toluenesulfonate (**2a**). After purification by column chromatography (silica, petroleum ether:ethyl acetate/18:2 to 17:3), the product was obtained as a reddish liquid (126 mg, 88% yield). $R_f = 0.75$ (petroleum ether:ethyl acetate/8:2). ^1H NMR (400 MHz, CDCl_3) δ 8.77 (dd, $J = 2.0, 0.8$ Hz, 1H, H^6), 8.10 (dd, $J = 8.1, 0.8$ Hz, 1H, H^3), 7.82 (dd, $J = 8.1, 2.0$ Hz, 1H, H^4), 7.74 – 7.70 (m, 2H, H^o), 7.51 – 7.45 (m, 1H, H^p), 7.44 – 7.38 (m, 2H, H^m), 2.48 (t, $J = 7.1$ Hz, 2H, $H^{1'}$), 1.68 – 1.58 (m, 2H, $H^{2'}$), 1.55 – 1.45 (m, 2H, $H^{3'}$), 0.97 (t, $J = 7.3$ Hz, 3H, CH_3). ^{13}C NMR (126 MHz, CDCl_3) δ 177.5 ($\text{C}^{\text{C=O}}$), 152.4 (C^6), 151.0 (C^2), 139.3 (C^4), 133.5 (C^o), 131.0 (C^p), 128.7 (C^m), 125.5 (C^5), 122.8 (C^3), 120.3 (C^i), 98.6 ($\text{C}^{\beta'}$), 95.6 (C^{β}), 88.0 (C^{α}), 77.5 ($\text{C}^{\alpha'}$), 30.5 ($\text{C}^{2'}$), 22.1 ($\text{C}^{3'}$), 19.4 ($\text{C}^{1'}$), 13.7 (CH_3). FT-IR-ATR: 3058, 2958, 2933, 2871, 2195, 2118, 1646, 1576, 1490, 1313, 1211, 1019, 997, 858, 756, 685 cm^{-1} . HRMS (ESI): m/z 288.1381 ($[\text{M}+\text{H}]^+$, $\text{C}_{20}\text{H}_{18}\text{NO}^+$ calcd. 288.1383).

1-(4-Nitrophenyl)-3-phenylprop-2-yn-1-one (3m). The title compound was prepared according to the General Procedure 3 from 4-nitrobenzaldehyde (**1m**) and (2-phenylethynyl)(2,4,6-trimethylphenyl)iodonium *p*-toluenesulfonate (**2a**). After purification by column chromatography (silica, petroleum ether:ethyl acetate/18:2 to 17:3), the product was obtained as a white solid (39 mg, 31% yield). $R_f = 0.69$ (petroleum ether:ethyl acetate/8:2). ^1H NMR (400 MHz, CDCl_3) δ 8.41 – 8.35 (m, 4H, $H^{o'}$, $H^{m'}$), 7.74 – 7.70 (m, 2H, H^o), 7.57 – 7.52 (m, 1H, H^p), 7.49 – 7.44 (m, 2H, H^m). ^{13}C NMR (126 MHz, CDCl_3) δ 176.0 ($\text{C}^{\text{C=O}}$), 151.0 (C^p), 141.2 ($\text{C}^{i'}$), 133.4 (C^o), 131.6 (C^p), 130.6 ($\text{C}^{o'}$), 129.0 (C^m), 124.0 ($\text{C}^{m'}$), 119.6 (C^i), 95.5 (C^{β}), 86.7 (C^{α}). The spectral data are in accordance with literature.⁴³

⁴³ Tang, T.; Fei, X.-D.; Ge, Z.-Y.; Chen, Z.; Zhu, Y.-M.; Ji, S.-J. *J. Org. Chem.* **2013**, 78, 3170-3175.

3-(2,6-Dimethylphenyl)-1-(quinoxalin-2-yl)prop-2-yn-1-one (3n). The title compound was prepared according to the General Procedure 3 from quinoxaline-2-carbaldehyde (**1a**) and [2-(2,6-dimethylphenyl)ethynyl](2,4,6-trimethylphenyl)iodonium *p*-toluenesulfonate (**2i**). After purification by column chromatography (silica, petroleum ether:ethyl acetate/17:3), the product was obtained as a yellow solid (130 mg, 83% yield). $R_f = 0.63$ (petroleum ether:ethyl acetate/8:2). ^1H NMR (400 MHz, CDCl_3) δ 9.62 (s, 1H, H^3), 8.26 – 8.20 (m, 2H, H^5 , H^8), 7.91 (dddd, $J = 18.0, 8.4, 6.9, 1.6$ Hz, 2H, H^6 , H^7), 7.32 – 7.27 (m, 1H, H^p), 7.15 (d, $J = 7.7$ Hz, 2H, H^m), 2.72 (s, 6H, CH_3). ^{13}C NMR (126 MHz, CDCl_3) δ 177.6 ($\text{C}^{\text{C=O}}$), 147.2 (C^2), 144.0 (C^{8a}), 143.8 (C^o), 143.5 (C^3), 141.6 (C^{4a}), 132.7 (C^6), 131.02 (C^p), 131.00 (C^7), 130.7 (C^8), 129.6 (C^5), 127.2 (C^m), 120.0 (C^i), 95.6, 95.5 (C^α , C^β), 21.3 (CH_3). FT-IR-ATR: 3061, 2921, 2855, 2176, 1640, 1507, 1457, 1313, 1244, 1198, 1023, 965, 763 cm^{-1} . HRMS (ESI): m/z 287.1177 ($[\text{M}+\text{H}]^+$, $\text{C}_{19}\text{H}_{15}\text{N}_2\text{O}^+$ *calcd.* 287.1179).

3-(4-*tert*-Butylphenyl)-1-(quinoxalin-2-yl)prop-2-yn-1-one (3o). The title compound was prepared according to the General Procedure 3 from quinoxaline-2-carbaldehyde (**1a**) and [2-(4-*tert*-butylphenyl)ethynyl](2,4,6-trimethylphenyl)iodonium *p*-toluenesulfonate (**2j**). After purification by column chromatography (silica, petroleum ether:ethyl acetate/17:3), the product was obtained as a yellow solid (132 mg, 92% yield). $R_f = 0.43$ (petroleum ether:ethyl acetate/8:2). ^1H NMR (400 MHz, CDCl_3) δ 9.62 (s, 1H, H^3), 8.35 – 8.32 (m, 1H, H^8), 8.23 – 8.20 (m, 1H, H^5), 7.96 – 7.88 (m, 2H, H^6 , H^7), 7.75 – 7.71 (m, 2H, H^o), 7.50 – 7.46 (m, 2H, H^m), 1.36 (s, $J = 2.1$ Hz, 9H, $\text{C}(\text{CH}_3)_3$). ^{13}C NMR (126 MHz, CDCl_3) δ 177.5 ($\text{C}^{\text{C=O}}$), 155.3 (C^p), 147.1 (C^2), 144.0 (C^{8a}), 143.8 (C^3), 141.6 (C^{4a}), 133.7 (C^o), 132.8 (C^6), 131.10, 131.07 (C^7 , C^8), 129.6 (C^5), 125.9 (C^m), 117.0 (C^i), 98.1 (C^β), 87.7 (C^α), 35.3 ($\text{C}(\text{CH}_3)_3$), 31.2 ($\text{C}(\text{CH}_3)_3$). FT-IR-ATR: 3065, 2962, 2924, 2869, 2195, 1641, 1570, 1496, 1322, 1201, 1108, 1025, 967, 836, 767 cm^{-1} . HRMS (ESI): m/z 315.1490 ($[\text{M}+\text{H}]^+$, $\text{C}_{21}\text{H}_{19}\text{N}_2\text{O}^+$ *calcd.* 315.1492).

3-([1,1'-Biphenyl]-3-yl)-1-(quinoxalin-2-yl)prop-2-yn-1-one (3p). The title compound was prepared according to the General Procedure 3 from quinoxaline-2-carbaldehyde (**1a**) and (2-([1,1'-biphenyl]-3-yl)ethynyl)(2,4,6-trimethylphenyl)iodonium *p*-toluenesulfonate (**2k**). After purification by column chromatography (silica, petroleum ether:ethyl acetate/17:3), the product was obtained as an orange solid (135 mg, 81% yield). $R_f = 0.49$ (petroleum ether:ethyl acetate/8:2). ^1H NMR (400 MHz, CDCl_3) δ 9.63 (s, 1H, H^3), 8.37 – 8.33 (m, 1H, H^8), 8.24 – 8.20 (m, 1H, H^5), 8.01 (dd, $J = 2.5, 1.0$ Hz, 1H, $H^{2'}$), 7.97 –

7.88 (m, 2H, H^6 , H^7), 7.79 – 7.73 (m, 2H, $H^{4'}$, $H^{6'}$), 7.62 (dq, $J = 2.9, 1.8$ Hz, 2H, H^o), 7.54 (t, $J = 7.6$ Hz, 1H, $H^{5'}$), 7.52 – 7.47 (m, 2H, H^m), 7.44 – 7.39 (m, 1H, H^p). ^{13}C NMR (126 MHz, CDCl_3) δ 177.6 ($\text{C}^{\text{C=O}}$), 146.9 (C^2), 144.1 (C^{8a}), 143.7 (C^3), 142.0 ($\text{C}^{3'}$), 141.6 (C^{4a}), 139.7 (C^i), 132.8 (C^6), 132.4 ($\text{C}^{6'}$), 132.3 ($\text{C}^{4'}$), 131.12, 131.10 (C^7 , C^8), 130.2 ($\text{C}^{4'}$), 129.6 (C^5), 129.3 ($\text{C}^{5'}$), 129.1 (C^m), 128.1 (C^p), 127.2 (C^o), 120.6 ($\text{C}^{1'}$), 97.2 (C^β), 87.7 (C^α). FT-IR-ATR: 3058, 3031, 2188, 1635, 1570, 1324, 1288, 1126, 1021, 965, 801, 752, 692 cm^{-1} . HRMS (ESI): m/z 335.1178 ($[\text{M}+\text{H}]^+$, $\text{C}_{23}\text{H}_{15}\text{N}_2\text{O}^+$ *calcd.* 335.1179).

3-(Naphthalen-2-yl)-1-(quinoxalin-2-yl)prop-2-yn-1-one (3q). The title compound was prepared according to the General Procedure 3 from quinoxaline-2-carbaldehyde (**1a**) and [2-(naphthalen-2-yl)ethynyl](2,4,6-trimethylphenyl)iodonium *p*-toluenesulfonate (**2l**). After purification by column chromatography (silica, petroleum ether:ethyl acetate/17:3), the product was obtained as a red solid (103 mg, 67% yield). $R_f = 0.48$ (petroleum ether:ethyl acetate/8:2). ^1H NMR (400 MHz, CDCl_3) δ 9.64 (s, 1H, H^3), 8.40 – 8.36 (m, 2H, H^8 , $\text{H}^{1'}$), 8.25 – 8.21 (m, 1H, H^5), 7.98 – 7.86 (m, 5H, H^6 , H^7 , $\text{H}^{4'}$, $\text{H}^{5'}$, $\text{H}^{8'}$), 7.77 (dd, $J = 8.5, 1.6$ Hz, 1H, $\text{H}^{3'}$), 7.63 – 7.55 (m, 2H, $\text{H}^{6'}$, $\text{H}^{7'}$). ^{13}C NMR (126 MHz, CDCl_3) δ 177.5 ($\text{CC}=\text{O}$), 147.0 (C^2), 144.0 (C^{8a}), 143.7 (C^3), 141.6 (C^{4a}), 135.3 ($\text{C}^{1'}$), 134.3 (s), 132.8 (C^6), 132.7 (s), 131.1 (C^7 , C^8), 129.6 (C^5), 128.8 ($\text{C}^{3'}$), 128.6, 128.5, 128.4, 128.0 ($\text{C}^{4'}$, $\text{C}^{5'}$, $\text{C}^{7'}$, $\text{C}^{8'}$), 127.2 ($\text{C}^{6'}$), 117.2 ($\text{C}^{1'}$), 97.8 (C^α), 88.0 (C^β). FT-IR-ATR: 3058, 2175, 1640, 1570, 1465, 1319, 1229, 1130, 1028, 970, 813, 759 cm^{-1} . HRMS (ESI): m/z 309.1021 ($[\text{M}+\text{H}]^+$, $\text{C}_{21}\text{H}_{13}\text{N}_2\text{O}^+$ *calcd.* 309.1022).

3-(3,5-Difluorophenyl)-1-(quinoxalin-2-yl)prop-2-yn-1-one (3r). The title compound was prepared according to the General Procedure 3 from quinoxaline-2-carbaldehyde (**1a**) and [2-(3,5-difluorophenyl)ethynyl](2,4,6-trimethylphenyl)iodonium *p*-toluenesulfonate (**2m**). After purification by column chromatography (silica, petroleum ether:ethyl acetate/17:3), the product was obtained as a yellowish solid (143 mg, 97% yield). $R_f = 0.47$ (petroleum ether:ethyl acetate/8:2). ^1H NMR (400 MHz, CDCl_3) δ 9.58 (s, 1H, H^3), 8.35 – 8.31 (m, 1H, H^8), 8.24 – 8.21 (m, 1H, $\text{H}^{5'}$), 7.99 – 7.89 (m, 2H, H^6 , H^7), 7.34 – 7.26 (m, 2H, H^o), 7.00 (tt, $J = 8.8, 2.4$ Hz, 1H, H^p). ^{13}C NMR (126 MHz, CDCl_3) δ 177.4 ($\text{C}^{\text{C=O}}$), 162.9 (dd, $J = 250.9, 12.9$ Hz, C^m), 146.6 (C^2), 144.3 (C^{8a}), 143.5 (C^3), 141.6 (C^{4a}), 133.1 (C^6), 131.3 (C^7), 131.1 (C^8), 129.7 (C^5), 122.8 (t, $J = 11.6$ Hz, C^i), 116.5 (dd, $J = 20.5, 6.9$ Hz, C^o), 107.5 (t, $J = 25.2$ Hz, C^p), 93.2 (t, $J = 4.0$ Hz, C^β), 88.1 (C^α). ^{19}F NMR (376 MHz, CDCl_3) δ -108.0 – -108.1 (m). FT-IR-ATR: 3078, 3050, 3035, 2204, 1653, 1592, 1430, 1301, 1290, 1122, 1050, 927, 863, 768, 671 cm^{-1} . HRMS (ESI): m/z 295.0677 ($[\text{M}+\text{H}]^+$, $\text{C}_{19}\text{H}_9\text{F}_2\text{N}_2\text{O}^+$ *calcd.* 295.0678).

1-(Quinoxalin-2-yl)-3-[2-(trifluoromethyl)phenyl]prop-2-yn-1-one (3s). The title compound was prepared according to the General Procedure 3 from quinoxaline-2-carbaldehyde (**1a**) and {2-[2-(trifluoromethyl)phenyl]ethynyl}(2,4,6-trimethylphenyl)iodonium *p*-toluenesulfonate (**2n**). After purification by column chromatography (silica, petroleum ether:ethyl acetate/17:3), the product was obtained as a yellow solid (120 mg, 74% yield). R_f = 0.37 (petroleum ether:ethyl acetate/8:2). ^1H NMR (400 MHz, CDCl_3) δ 9.60 (s, 1H, H^3), 8.35 – 8.31 (m, 1H, H^8), 8.23 – 8.20 (m, 1H, H^5), 7.98 – 7.88 (m, 3H, H^6 , H^7 , H^6), 7.83 – 7.78 (m, 1H, $H^{3'}$), 7.69 – 7.60 (m, 2H, $H^{4'}$, H^5). ^{13}C NMR (126 MHz, CDCl_3) δ 177.4 ($\text{C}^{\text{C=O}}$), 146.8 (C^2), 144.1 (C^{8a}), 143.5 (C^3), 141.7 (C^{4a}), 136.2 ($\text{C}^{6'}$), 133.2 (q, J = 31.3 Hz, $\text{C}^{2'}$), 133.0 (C^6), 131.9 ($\text{C}^{5'}$), 131.18 (C^7), 131.16 (C^8), 131.0 ($\text{C}^{4'}$), 129.5 (C^5), 126.5 (q, J = 5.0 Hz, $\text{C}^{3'}$), 123.3 (q, J = 273.8 Hz, CF_3), 118.3 (d, J = 2.1 Hz, $\text{C}^{1'}$), 91.5 (C^β), 91.3 (C^α). ^{19}F NMR (376 MHz, CDCl_3) δ -61.6 (s). FT-IR-ATR: 3058, 3011, 2196, 1648, 1570, 1448, 1312, 1121, 1060, 963, 769, 665 cm^{-1} . HRMS (ESI): m/z 327.0738 ($[\text{M}+\text{H}]^+$, $\text{C}_{18}\text{H}_{10}\text{F}_3\text{N}_2\text{O}^+$ *calcd.* 327.0740).

3-(3,4-Dichlorophenyl)-1-(quinoxalin-2-yl)prop-2-yn-1-one (3t). The title compound was prepared according to the General Procedure 3 from quinoxaline-2-carbaldehyde (**1a**) and [2-(3,4-dichlorophenyl)ethynyl](2,4,6-trimethylphenyl)iodonium *p*-toluenesulfonate (**2o**). After purification by column chromatography (silica, petroleum ether:ethyl acetate/18:2 to 14:6), the product was obtained as a yellow solid (130 mg, 80% yield). R_f = 0.55 (petroleum ether:ethyl acetate/8:2). ^1H NMR (400 MHz, CDCl_3) δ 9.59 (s, 1H, H^3), 8.36 – 8.31 (m, 1H, H^8), 8.24 – 8.20 (m, 1H, H^5), 7.99 – 7.89 (m, 2H, H^6 , H^7), 7.87 (d, J = 1.8 Hz, 1H, $H^{2'}$), 7.61 (dd, J = 8.3, 1.9 Hz, 1H, $H^{6'}$), 7.55 (d, J = 8.4 Hz, 1H, $H^{5'}$). ^{13}C NMR (126 MHz, CDCl_3) δ 177.3 ($\text{C}^{\text{C=O}}$), 146.6 (C^2), 144.1 (C^{8a}), 143.4 (d, J = 19.6 Hz, C^3), 141.4 (C^{4a}), 136.1 ($\text{C}^{3'}$), 134.9 ($\text{C}^{2'}$), 133.3 ($\text{C}^{4'}$), 132.9 (C^6), 132.4 ($\text{C}^{6'}$), 131.1 ($\text{C}^{5'}$), 130.94, 130.90 (C^7 , C^8), 129.6 (C^5), 112.0 ($\text{C}^{1'}$), 93.6 (C^β), 88.5 (C^α). FT-IR-ATR: 3061, 2199, 1646, 1465, 1327, 1128, 1029, 969, 853, 766 cm^{-1} . HRMS (ESI): m/z 327.0086 ($[\text{M}+\text{H}]^+$, $\text{C}_{17}\text{H}_9\text{Cl}_2\text{N}_2\text{O}^+$ *calcd.* 327.0086).

4-[3-Oxo-3-(quinoxalin-2-yl)prop-1-yn-1-yl]benzonitrile (3u). The title compound was prepared according to the General Procedure 3 from quinoxaline-2-carbaldehyde (**1a**) and [2-(4-cyanophenyl)ethynyl](2,4,6-trimethylphenyl)iodonium *p*-toluenesulfonate (**2p**). After purification by column chromatography (silica, petroleum ether:ethyl acetate/16:4 to 15:5), the product was obtained as a yellow solid (84 mg, 59% yield). R_f = 0.33 (petroleum ether:ethyl acetate/8:2). ^1H NMR (400 MHz, CDCl_3) δ 9.59 (s, 1H, H^3), 8.34 – 8.30 (m, 1H, H^8), 8.25 – 8.22 (m, 1H, H^5), 7.94 (dddd, J = 18.8, 8.4,

6.9, 1.6 Hz, 2H, H^6 , H^7), 7.89 – 7.85 (m, 2H, H^o), 7.78 – 7.74 (m, 2H, H^m). ^{13}C NMR (126 MHz, CDCl_3) δ 177.5 ($\text{C}^{\text{C=O}}$), 146.6 (C^2), 144.3 (C^{8a}), 143.5 (d, J = 13.6 Hz, C^3), 141.6 (C^{4a}), 133.8 (C^o), 133.2 (C^6), 132.4 (C^m), 131.3 (C^7), 131.0 (C^8), 129.7 (C^5), 125.0 (C^i), 118.0 (CN), 114.5 (C^p), 93.4 (C^β), 89.9 (C^α). FT-IR-ATR: 3064, 2202, 1653, 1507, 1457, 1319, 1204, 1128, 1026, 962, 842, 768 cm^{-1} . HRMS (ESI): m/z 284.0818 ($[\text{M}+\text{H}]^+$, $\text{C}_{18}\text{H}_{10}\text{N}_3\text{O}^+$ *calcd.* 284.0818).

3-(4-Acetylphenyl)-1-(quinoxalin-2-yl)prop-2-yn-1-one (3v). The title compound was prepared according to the General Procedure 3 from quinoxaline-2-carbaldehyde (**1a**) and [2-(4-acetylphenyl)ethynyl](2,4,6-trimethylphenyl)iodonium *p*-toluenesulfonate (**2q**). After purification by column chromatography (silica, petroleum ether:ethyl acetate/8:2), the product was obtained as a red solid (129 mg, 86% yield). R_f = 0.23 (petroleum ether:ethyl acetate/8:2). ^1H NMR (400 MHz, CDCl_3) δ 9.60 (s, 1H, H^3), 8.32 (dd, J = 8.4, 1.2 Hz, 1H, H^8), 8.21 (dd, J = 8.3, 1.1 Hz, 1H, H^5), 8.02 (d, J = 8.4 Hz, 2H, H^m), 7.92 (dddd, J = 20.4, 8.3, 6.9, 1.5 Hz, 2H, H^6 , H^7), 7.86 (d, J = 8.4 Hz, 2H, H^o), 2.66 (s, 3H, CH_3). ^{13}C NMR (126 MHz, CDCl_3) δ 197.2 ($\text{O}=\text{C}-\text{CH}_3$), 177.6 ($\text{C}^{\text{C=O}}$), 146.7 (C^2), 144.2 (C^{8a}), 143.6 (d, J = 15.3 Hz, C^3), 141.6 (C^{4a}), 138.5 (C^p), 133.7 (C^o), 133.0 (C^6), 131.2 (C^7), 131.1 (C^8), 129.7 (C^5), 128.5 (C^m), 124.7 (C^i), 95.1 (C^β), 89.3 (C^α), 26.9 (CH_3). FT-IR-ATR: 3061, 2195, 1690, 1636, 1507, 1465, 1319, 1262, 1126, 1030, 962, 825, 778 cm^{-1} . HRMS (ESI): m/z 301.0971 ($[\text{M}+\text{H}]^+$, $\text{C}_{19}\text{H}_{13}\text{N}_2\text{O}_2^+$ *calcd.* 301.0972).

Ethyl 3-[3-oxo-3-(quinoxalin-2-yl)prop-1-yn-1-yl]benzoate (3w). The title compound was prepared according to the General Procedure 3 from quinoxaline-2-carbaldehyde (**1a**) and {2-[3-(ethoxycarbonyl)phenyl]ethynyl}(2,4,6-trimethylphenyl)iodonium *p*-toluenesulfonate (**2r**). After purification by column chromatography (silica, petroleum ether:ethyl acetate/17:3), the product was obtained as a yellow solid (124 mg, 75% yield). R_f = 0.38 (petroleum ether:ethyl acetate/8:2). ^1H NMR (400 MHz, CDCl_3) δ 9.59 (s, 1H, H^3), 8.44 (t, J = 1.5 Hz, 1H, $H^{2'}$), 8.33 (dd, J = 7.9, 1.7 Hz, 1H, H^8), 8.20 – 8.16 (m, 2H, H^5 , $H^{4'}$), 7.96 – 7.90 (m, 2H, H^6 , H^7), 7.89 (ddd, J = 8.3, 6.9, 1.6 Hz, 1H, $H^{6'}$), 7.54 (t, J = 7.8 Hz, 1H, $H^{5'}$), 4.43 (q, J = 7.1 Hz, 2H, CH_2), 1.42 (t, J = 7.1 Hz, 3H, CH_3). ^{13}C NMR (126 MHz, CDCl_3) δ 177.6 ($\text{C}^{1'}$), 165.4 ($\text{C}^{7'}$), 146.8 (C^2), 144.2 (C^{8a}), 143.6 (C^3), 141.6 (C^{4a}), 137.4 ($\text{C}^{6'}$), 134.7 ($\text{C}^{2'}$), 132.9 (C^6), 132.2 ($\text{C}^{4'}$), 131.4 ($\text{C}^{3'}$), 131.2 (C^7), 131.1 (C^8), 129.6 (C^5), 129.0 ($\text{C}^{5'}$), 120.6 ($\text{C}^{1'}$), 95.6 (C^β), 87.9 (C^α), 61.6 (CH_2), 14.4 (CH_3). FT-IR-ATR: 3064, 2925, 2195, 1714, 1653, 1465, 1318, 1205, 1103, 1031, 971, 751, 680 cm^{-1} . HRMS (ESI): m/z 331.1076 ($[\text{M}+\text{H}]^+$, $\text{C}_{20}\text{H}_{15}\text{N}_2\text{O}_3^+$ *calcd.* 331.1077).

3-(3-Methoxyphenyl)-1-(quinoxalin-2-yl)prop-2-yn-1-one (3x). The title compound was prepared according to the General Procedure 3 from quinoxaline-2-carbaldehyde (**1a**) and [2-(3-methoxyphenyl)ethynyl](2,4,6-trimethylphenyl)iodonium *p*-toluenesulfonate (**2s**). After purification by column chromatography (silica, petroleum ether:ethyl acetate/17:3), the product was obtained as a red solid (99 mg, 69% yield). R_f = 0.34 (petroleum ether:ethyl acetate/8:2). ^1H NMR (400 MHz, CDCl_3) δ 9.59 (s, 1H, H^3), 8.31 (dd, J = 8.4, 1.2 Hz, 1H, H^8), 8.21 – 8.17 (m, 1H, H^5), 7.90 (dtd, J = 15.0, 7.0, 1.4 Hz, 2H, H^6 , H^7), 7.40 – 7.32 (m, 2H, $H^{5'}$, $H^{6'}$), 7.28 – 7.25 (m, 1H, $H^{2'}$), 7.06 (ddd, J = 7.9, 2.5, 1.3 Hz, 1H, $H^{4'}$), 3.85 (s, 3H, CH_3). ^{13}C NMR (126 MHz, CDCl_3) δ 177.5 ($\text{C}^{\text{C=O}}$), 159.5 ($\text{C}^{3'}$), 146.8 (C^2), 144.0 (C^{8a}), 143.6 (d, J = 15.0 Hz, C^3), 141.5 (C^{4a}), 132.7 (C^6), 131.01 (C^7), 130.98 (C^8), 129.8 ($\text{C}^{6'}$), 129.5 (C^5), 126.2 ($\text{C}^{5'}$), 120.9 ($\text{C}^{1'}$), 118.1 ($\text{C}^{4'}$), 118.0 ($\text{C}^{2'}$), 97.1 (C^β), 87.2 (C^α), 55.5 (CH_3). FT-IR-ATR: 3067, 2925, 2855, 2186, 1637, 1576, 1484, 1224, 1169, 1046, 970, 887, 769, 683 cm^{-1} . HRMS (ESI): m/z 289.0970 ($[\text{M}+\text{H}]^+$, $\text{C}_{18}\text{H}_{13}\text{N}_2\text{O}_2^+$ calcd. 289.0972).

1-(Quinoxalin-2-yl)-3-[4-(trifluoromethoxy)phenyl]prop-2-yn-1-one (3y). The title compound was prepared according to the General Procedure 3 from quinoxaline-2-carbaldehyde (**1a**) and {2-[4-(trifluoromethoxy)phenyl]ethynyl}(2,4,6-trimethylphenyl)iodonium *p*-toluenesulfonate (**2t**). After purification by column chromatography (silica, petroleum ether:ethyl acetate/18:2 to 17:3), the product was obtained as a yellow solid (139 mg, 81% yield). This product was also synthesized in a 6.0 mmol scale in 80% yield (1.64 g). R_f = 0.46 (petroleum ether:ethyl acetate/8:2). ^1H NMR (400 MHz, CDCl_3) δ 9.60 (s, 1H, H^3), 8.34 – 8.31 (m, 1H, H^8), 8.24 – 8.21 (m, 1H, H^5), 7.98 – 7.89 (m, 2H, H^6 , H^7), 7.85 – 7.81 (m, 2H, H^o), 7.34 – 7.28 (m, 2H, H^m). ^{13}C NMR (126 MHz, CDCl_3) δ 177.5 ($\text{C}^{\text{C=O}}$), 151.2 (d, J = 1.7 Hz, C^o), 146.8 (C^2), 144.1 (C^{8a}), 143.6 (d, J = 20.0 Hz, C^3), 141.6 (C^{4a}), 135.4 (C^o), 132.9 (C^6), 131.2 (C^7), 131.0 (C^8), 129.6 (C^5), 121.0 (C^m), 120.4 (q, J = 258.9 Hz, CF_3), 118.7 (C^i), 95.2 (C^α), 88.1 (C^β). ^{19}F NMR (376 MHz, CDCl_3) δ -57.7 (s). FT-IR-ATR: 3106, 3067, 2195, 1642, 1506, 1493, 1369, 1251, 1156, 1026, 966, 848, 769 cm^{-1} . HRMS (ESI): m/z 343.0689 ($[\text{M}+\text{H}]^+$, $\text{C}_{18}\text{H}_{10}\text{F}_3\text{N}_2\text{O}_2^+$ calcd. 343.0689).

2-{3-[3-Oxo-3-(quinoxalin-2-yl)prop-1-yn-1-yl]phenyl}-2,3-dihydro-1H-isoindole-1,3-dione (3z). The title compound was prepared according to the General Procedure 3 from quinoxaline-2-carbaldehyde (**1a**) and {2-[3-(1,3-dioxo-2,3-dihydro-1H-isoindol-2-yl)phenyl]ethynyl}(2,4,6-trimethylphenyl)iodonium *p*-toluenesulfonate (**2u**). After purification by column chromatography

(silica, dichloromethane:ethyl acetate/20:0 to 19:1), the product was obtained as an ivory solid (109 mg, 54% yield). $R_f = 0.40$ (petroleum ether:ethyl acetate/1:1). ^1H NMR (400 MHz, CDCl_3) δ 9.61 (s, 1H, H^3), 8.37 – 8.33 (m, 1H, H^8), 8.21 (dd, $J = 8.3, 1.4$ Hz, 1H, H^5), 8.03 – 7.98 (m, 2H, H^{12}), 7.97 – 7.87 (m, 3H, H^6 , H^7 , $H^{2'}$), 7.86 – 7.80 (m, 3H, H^{13} , $H^{6'}$), 7.68 – 7.64 (m, 1H, H^4), 7.61 (t, $J = 7.6$ Hz, 1H, $H^{5'}$). ^{13}C NMR (126 MHz, CDCl_3) δ 177.6 (C^9), 166.9 (C^{10}), 146.8 (C^2), 144.1 (C^{8a}), 143.6 (C^3), 141.6 (C^{4a}), 134.8 (C^{13}), 133.0 (C^6), 132.9 (C^6), 132.4 ($C^{3'}$), 131.7 (C^{11}), 131.20, 131.17, 131.14 (C^7 , C^8 , C^2), 129.7 ($C^{5'}$), 129.6 (C^5), 129.3 ($C^{4'}$), 124.1 (C^{13}), 121.3 ($C^{1'}$), 95.6 (C^β), 88.1 (C^α). FT-IR-ATR: 3036, 2199, 1714, 1653, 1378, 1324, 1105, 1037, 918, 870, 713, 676 cm^{-1} . HRMS (ESI): m/z 404.1029 ($[\text{M}+\text{H}]^+$, $\text{C}_{25}\text{H}_{14}\text{N}_3\text{O}_3^+$ calcd. 404.1030).

3-[2-(Morpholine-4-sulfonyl)phenyl]-1-(quinoxalin-2-yl)prop-2-yn-1-one (3aa). The title compound was prepared according to the General Procedure 3 from quinoxaline-2-carbaldehyde (**1a**) and {2-[2-(morpholine-4-sulfonyl)phenyl]ethynyl}(2,4,6-trimethylphenyl)iodonium *p*-toluenesulfonate (**2v**). After purification by column chromatography (silica, petroleum ether:ethyl acetate/3:1 to 2:2), the product was obtained as an orange solid (122 mg, 60% yield). $R_f = 0.26$ (petroleum ether:ethyl acetate/1:1). ^1H NMR (400 MHz, CDCl_3) δ 9.59 (s, 1H, H^3), 8.32 – 8.28 (m, 1H, H^8), 8.19 (d, $J = 8.2$ Hz, 1H, H^5), 8.04 (dd, $J = 7.5, 1.5$ Hz, 1H, $H^{3'}$), 7.99 (dd, $J = 7.3, 1.5$ Hz, 1H, $H^{6'}$), 7.96 – 7.86 (m, 2H, H^6 , H^7), 7.66 (pd, $J = 7.5, 1.5$ Hz, 2H, $H^{4'}$, $H^{5'}$), 3.72 – 3.69 (m, 4H, $H^{8'}$), 3.37 – 3.33 (m, 4H, $H^{7'}$). ^{13}C NMR (126 MHz, CDCl_3) δ 177.3 ($C^{C=O}$), 146.7 (C^2), 144.2 (C^{8a}), 143.6 (C^3), 141.6 (C^{4a}), 139.5 ($C^{2'}$), 137.2 ($C^{6'}$), 133.1 (C^6), 132.7 (C^{4a}), 131.3 (C^7), 131.1 ($C^{5'}$), 130.8 (C^8), 130.6 ($C^{3'}$), 129.7 (C^5), 119.1 ($C^{1'}$), 93.2 (C^β), 92.3 (C^α), 66.44 ($C^{8'}$), 46.14 ($C^{7'}$). FT-IR-ATR: 3065, 2924, 2847, 2198, 1653, 1569, 1473, 1357, 1272, 1176, 1023, 949, 802, 736, 611 cm^{-1} . HRMS (ESI): m/z 408.1012 ($[\text{M}+\text{H}]^+$, $\text{C}_{21}\text{H}_{18}\text{N}_3\text{O}_4\text{S}^+$ calcd. 408.1013).

3-Phenyl-1-(quinoxalin-2-yl)prop-2-yn-1-one (3ab). The title compound was prepared according to the General Procedure 3 from quinoxaline-2-carbaldehyde (**1a**) and [2-phenyl(1- ^{13}C)ethynyl](2,4,6-trimethylphenyl) iodonium *p*-toluenesulfonate (**2w**). After purification by column chromatography (silica, petroleum ether:ethyl acetate/9:1 to 8:2), the product was obtained as a yellow solid (102 mg, 79% yield). $R_f = 0.46$ (petroleum ether:ethyl acetate/8:2). ^1H NMR (500 MHz, CDCl_3) δ 9.52 (s, 1H, H^3), 8.26 – 8.22 (m, 1H, H^8), 8.14 – 8.09 (m, 1H, H^5), 7.87 – 7.78 (m, 2H, H^6 , H^7), 7.70 (dt, $J = 8.5, 1.8$ Hz, 2H, H^o), 7.47 – 7.41 (m, 1H, H^p), 7.40 – 7.33 (m, 2H, H^m). ^{13}C NMR (126 MHz, CDCl_3) δ 177.6 (d, $J = 97.2$ Hz, $C^{C=O}$), 146.9 (d, $J = 19.1$ Hz, C^2), 144.0 (C^{8a}), 143.7 (d, $J = 21.6$ Hz, C^3), 141.6 (C^{4a}), 133.7 (d, $J = 2.5$ Hz, C^o), 132.8 (C^6), 131.4 (C^p), 131.10 (C^7), 131.05 (C^8), 129.6 (C^5), 128.8 (C^m), 120.0 (d, $J = 11.7$ Hz, C^i), 97.3 (d, $J = 177.4$ Hz, C^β), 87.6 (C^α ; ^{13}C label). ^{13}C NMR spectra without NOE shows that the compound contains 99% ^{13}C at the α -position. FT-IR-ATR: 3053, 3036, 2195, 1638, 1490,

1326, 1202, 1033, 965, 766, 687 cm⁻¹. HRMS (ESI): *m/z* 260.0898 ([M+H]⁺, C₁₆¹³CH₁₁N₂O⁺*calcd.* 260.0899).

5. Kinetic Investigations

5.1. Time-Course Experiment (Figure 1)

In a nitrogen-atmosphere glovebox, an NMR tube was charged with aldehyde **1a** (5.5 mg, 0.035 mmol), alkynyliodonium salt **2a** (21.8 mg, 0.042 mmol), and catalyst precursor **NHC-1** (1.3 mg, 0.0035 mmol). Next, *d*₈-toluene (700 µL) was added, followed by 1-fluorododecane (internal standard; 8.1 µL, 0.035 mmol). The NMR tube was capped, removed from the glovebox, and inserted into NMR magnet with the probe temperature set to -40 °C. After 10 min, the time=0 spectra was taken. Then, the NMR tube was removed from the magnet and neat TMEDA (7.9 µL, 0.053 mmol) was quickly added via syringe to initiate the reaction. The NMR tube was shaken to ensure complete mixing of the solution and returned into the magnet. ¹H NMR spectra were taken in 5 minute intervals.

The data points for the decay of the starting material **1a** align linearly in the coordinate system corresponding to the overall second order in the substrates (Figure 1b), whereas deviations from linearity are present in the coordinate systems corresponding to the 1st and 3rd overall orders (Figures S1 and S2, respectively).

Table S1. Time-course experiment – data

time (min)	[1a] (mM)	[product] (mM)
0	38.298	0.000
2	30.875	5.606
7	30.284	6.372
12	29.366	6.900
17	28.133	7.192
22	27.348	7.966
27	26.568	8.034
32	26.336	8.213
37	25.366	8.745
42	24.850	9.016
47	24.233	9.124
52	23.951	9.303
57	23.560	9.629
62	23.131	10.182
67	22.453	10.160
72	22.111	10.636
77	21.698	10.704
82	21.444	10.972
87	21.280	11.143
92	20.835	11.297
97	20.472	11.710
102	20.045	11.755
107	20.018	11.989
112	19.749	11.934
117	19.206	12.236
122	18.938	12.443
127	18.466	12.713
132	18.398	12.760
137	18.030	12.877
142	17.742	13.119

147	17.568	13.168
152	17.114	13.329
157	16.912	13.416
162	16.609	13.337
167	16.492	13.658
172	16.220	13.842
177	16.173	13.704
182	15.927	13.839
187	15.477	13.972
192	15.442	14.010
197	14.971	14.195
202	14.815	14.251
207	14.728	14.308
212	14.472	14.561
217	14.105	14.460
222	14.006	14.750
227	13.763	14.645
232	13.591	14.704
237	13.270	14.829
242	13.110	15.173
247	12.843	15.321
252	12.779	15.195
257	12.736	15.213
262	12.567	15.133
267	12.239	15.143
272	12.092	15.409
277	11.983	15.483
282	11.551	15.301
287	11.570	15.525
292	11.186	15.888
297	11.294	15.585

Figure S1. Plot of $\text{LN}([\mathbf{1a}]/[\mathbf{1a}]_0)$ vs. time^a

^a $[\mathbf{1a}]_0$ was taken from the $t=2$ min spectra, due to the initial leap in the concentration, caused by the temporary heating of the sample during the addition of TMEDA.

Figure S2. Plot of $[1\mathbf{a}]^{-2}$ vs. time

5.2. Initial Rate Measurements (Figure 2)

In a nitrogen-atmosphere glovebox, appropriate amounts of stock solutions (see Tables below) of aldehyde **1a**, alkynyliodonium salt **2a**, catalyst precursor **NHC-1**, and CDCl_3 were mixed in an NMR tube. Next, 1-fluorododecane (internal standard) was added. The NMR tube was capped, removed from the glovebox, and inserted into NMR magnet with the probe temperature set to $-40\text{ }^\circ\text{C}$. After 10 min, the NMR tube was removed from the magnet and the appropriate amount of neat TMEDA was quickly added via syringe to initiate the reaction. The NMR tube was shaken to ensure complete mixing of the solution and returned into the magnet. After 3 min at $-40\text{ }^\circ\text{C}$, ^1H NMR spectra were taken in 2 minute intervals.

Due to the unavoidable heating of the sample during the time needed to add TMEDA, in the initial period, the reactions displayed noticeably higher and erratic rates. For this reason, the data from this initial period (first 3 minutes) was not taken into consideration in the initial rate analysis. Hence, the time was set to relative zero only when the first spectra was registered (*i.e.*, 3 min after the addition of TMEDA) and the concentration of product measured in this first spectra was also set to relative zero. This data is shown in Figure 3 in the article.

In the case of aldehyde **1a** and iodonium salt **2a**, whose concentrations could be directly determined from the NMR spectra, their 'initial concentrations' are these really measured in the first spectra of a given run. For **NHC-1** and TMEDA, the initial concentrations are based on the amounts used when preparing the samples.

Order in Aldehyde

Table S2. Order in aldehyde – sample preparation

run	1a solution 26 mM in CDCl_3 (μL)/final conc. (mM)	2a solution 30 mM in CDCl_3 (μL)/final conc. (mM)	NHC-1 solution 88 mM in CD_3CN (μL)/final conc. (mM)	CDCl_3 (μL)	TMEDA (μL) /final conc. (mM)	$\text{C}_{12}\text{H}_{25}\text{F}$ IS (μL) /final conc. (mM)
1	350/12.5	350/15.0	10/1.25	0	2.0/18.7	2.1/12.5

2	266/9.5	350/15.0	10/1.25	84	2.0/18.7	2.1/12.5
3	224/8.0	350/15.0	10/1.25	126	2.0/18.7	2.1/12.5
4	182/6.5	350/15.0	10/1.25	168	2.0/18.7	2.1/12.5

Table S3. Order in aldehyde – data

time (min)	measured [product] (mM)	relative [product] (mM)
run 1 - [1a] measured in the first spectra: 6.30 mM		
0	1.970	0.000
2	2.143	0.173
4	2.224	0.253
6	2.544	0.574
8	2.704	0.734
10	2.697	0.726
initial rate: 0.081 ± 0.010 mM/min		
run 2 - [1a] measured in the first spectra: 5.1 mM		
0	1.801	0.000
2	1.959	0.158
4	2.170	0.369
6	2.302	0.500
8	2.482	0.680
10	2.588	0.786
initial rate: 0.080 ± 0.003 mM/min		
run 3 - [1a] measured in the first spectra: 3.8 mM		
0	1.033	0.000
2	1.154	0.121
4	1.270	0.237
6	1.349	0.315
8	1.463	0.429
10	1.579	0.546
initial rate: 0.053 ± 0.001 mM/min		
run 4 - [1a] measured in the first spectra: 2.2 mM		
0	1.088	0.000
2	1.132	0.045
4	1.156	0.069
6	1.305	0.217
8	1.378	0.290
10	1.418	0.330
initial rate: 0.036 ± 0.004 mM/min		

Order in alkynyliodonium salt

Table S4. Order in alkynyliodonium salt – sample preparation

run	1a solution 90 mM in CDCl ₃ (μL)/final conc. (mM)	2a solution 42 mM in CDCl ₃ (μL)/final conc. (mM)	NHC-1 solution 175 mM in CD ₃ CN (μL) /final conc. (mM)	CDCl ₃ (μL)	TMEDA (μL) /final conc. (mM)	C ₁₂ H ₂₅ F IS (μL) /final conc. (mM)
1	200/25.0	500/30.0	10/2.5	0	7.9/37.4	4.2/25.0
2	200/25.0	450/27.0	10/2.5	50	7.9/37.4	4.2/25.0
3	200/25.0	400/24.0	10/2.5	100	7.9/37.4	4.2/25.0
4	200/25.0	350/21.0	10/2.5	150	7.9/37.4	4.2/25.0
5	200/25.0	300/17.0	10/2.5	200	7.9/37.4	4.2/25.0

Table S5. Order in alkynyliodonium salt – data

time (min)	measured [product] (mM)	relative [product] (mM)
run 1 - [2a] measured in the first spectra: 18.0 mM		
0	3.256	0.000
2	3.626	0.370
4	4.043	0.788
6	4.271	1.015
8	4.604	1.348
10	4.937	1.681
12	5.132	1.877
initial rate: 0.157 ± 0.006 mM/min		
run 2 - [2a] measured in the first spectra: 15.4 mM		
0	3.364	0.000
2	3.655	0.291
4	3.939	0.575
6	4.158	0.794
8	4.402	1.038
10	4.580	1.215
12	4.752	1.388
initial rate: 0.116 ± 0.005 mM/min		
run 3 - [2a] measured in the first spectra: 13.6 mM		
0	2.765	0.000
2	3.069	0.303
4	3.411	0.645
6	3.575	0.810
8	3.827	1.061
10	4.082	1.317
12	4.208	1.443
initial rate: 0.121 ± 0.006 mM/min		
run 4 - [2a] measured in the first spectra: 10.6 mM		
0	3.166	0.000
2	3.443	0.277
4	3.714	0.547
6	3.964	0.798
8	4.211	1.045
10	4.458	1.292
12	4.574	1.408
initial rate: 0.121 ± 0.005 mM/min		
run 5 - [2a] measured in the first spectra: 9.9 mM		
0	2.596	0.000
2	2.950	0.354
4	3.348	0.752
6	3.734	1.138
8	3.923	1.327
10	4.169	1.573
12	4.313	1.717
initial rate: 0.146 ± 0.011 mM/min		

Order in TMEDA**Table S6.** Order in TMEDA – sample preparation

run	1a solution	2a solution	NHC-1 solution	CDCl ₃ (μL)	TMEDA (μL)	C ₁₂ H ₂₅ F IS (μL)
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	26 mM in CDCl ₃ (μL)/final conc. (mM)	30 mM in CDCl ₃ (μL)/final conc. (mM)	88 mM in CD ₃ CN (μL) /final conc. (mM)		/final conc. (mM)	/final conc. (mM)
1	350/12.5	350/15.0	10/1.25	0	2.3/21.9	2.1/12.5
2	350/12.5	350/15.0	10/1.25	0	2.0/19.0	2.1/12.5
3	350/12.5	350/15.0	10/1.25	0	1.9/18.1	2.1/12.5
4	350/12.5	350/15.0	10/1.25	0	1.8/17.1	2.1/12.5
5	350/12.5	350/15.0	10/1.25	0	1.7/16.2	2.1/12.5

Table S7. Order in TMEDA – data

time (min)	measured [product] (mM)	relative [product] (mM)
run 1 - [TMEDA]=21.9 mM		
2.422	0.000	2.422
2.702	0.281	2.702
2.911	0.489	2.911
3.007	0.585	3.007
initial rate: 0.098 ± 0.015 mM/min		
run 2 - [TMEDA]=19.0 mM		
2.658	0.000	2.658
2.853	0.195	2.853
3.011	0.353	3.011
2.965	0.307	2.965
initial rate: 0.054 ± 0.020 mM/min		
run 3 - [TMEDA]=18.1 mM		
0	2.490	0.000
2	2.628	0.000
4	2.683	0.055
6	2.850	0.222
initial rate: 0.057 ± 0.007 mM/min		
run 4 - [TMEDA]=17.1 mM		
0	2.535	0.000
2	2.593	0.059
4	2.781	0.246
6	2.980	0.446
initial rate: 0.076 ± 0.012 mM/min		
run 5 - [TMEDA]=16.2 mM		
0	2.553	0.000
2	2.667	0.114
4	2.765	0.212
6	2.931	0.378
initial rate: 0.062 ± 0.005 mM/min		

Order in NHC precursor

Table S8. Order in NHC precursor – sample preparation

run	1a solution 26 mM in CDCl ₃ (μL)/final conc. (mM)	2a solution 30 mM in CDCl ₃ (μL)/final conc. (mM)	NHC-1 solution 88 mM in CD ₃ CN (μL) /final conc. (mM)	CDCl ₃ (μL)	TMEDA (μL) /final conc. (mM)	C ₁₂ H ₂₅ F IS (μL) /final conc. (mM)
1	350/12.5	350/15.0	20/2.50	0	2.0/18.7	2.1/12.5
2	350/12.5	350/15.0	18/2.25	0	2.0/18.7	2.1/12.5
3	350/12.5	350/15.0	16/2.00	0	2.0/18.7	2.1/12.5
4	350/12.5	350/15.0	14/1.75	0	2.0/18.7	2.1/12.5

5	350/12.5	350/15.0	12/1.50	0	2.0/18.7	2.1/12.5
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Table S9. Order in NHC precursor – data

time (min)	measured [product] (mM)	relative [product] (mM)
run 1 - [NHC-1]=2.50 mM		
0	3.776	0.000
2	4.279	0.503
4	4.781	1.005
6	4.780	1.004
8	5.027	1.251
10	6.004	2.228
12	5.335	1.559
initial rate: 0.150 ± 0.032 mM/min		
run 2 - [NHC-1]=2.25 mM		
0	3.364	0.000
2	3.644	0.281
4	3.983	0.620
6	4.374	1.010
8	4.643	1.279
10	4.761	1.397
12	5.032	1.669
initial rate: 0.141 ± 0.008 mM/min		
run 3 - [NHC-1]=2.00 mM		
0	4.054	0.000
2	4.372	0.318
4	4.659	0.605
6	4.739	0.684
8	5.102	1.048
10	5.137	1.083
12	5.312	1.258
initial rate: 0.103 ± 0.009 mM/min		
run 4 - [NHC-1]=1.75 mM		
0	2.725	0.000
2	2.929	0.204
4	3.502	0.776
6	3.876	1.150
8	3.820	1.094
10	4.231	1.505
12	4.136	1.410
initial rate: 0.128 ± 0.019 mM/min		
run 5 - [NHC-1]=1.50 mM		
0	2.326	0.000
2	2.621	0.295
4	2.688	0.361
6	2.885	0.559
8	3.030	0.704
10	3.088	0.762
12	3.427	1.101
initial rate: 0.082 ± 0.007 mM/min		

6. Computational Details

The calculations were carried out with Gaussian 16 software package⁴⁴ using B3LYP functional,⁴⁵ including the D3 dispersion correction with the BJ damping.⁴⁶ Geometries were optimized with SMD solvation model,⁴⁷ using Def2-SVPD basis set⁴⁸ that includes a pseudopotential for iodine.⁴⁹ For each stationary point a thorough conformational analysis was performed in order to locate the conformer with the lowest energy. This was done by identifying key rotatable bonds and movable entities (e.g. BF_4^- ion), and manually building possible starting geometries for optimizations.

The identified lowest energy stationary points were then characterized by frequency calculations to confirm their character as minima (no imaginary frequencies) or transition states (one single imaginary frequency). The final free energies were obtained from single-point calculations on the optimized geometries with a larger Def2-QZVP basis set^{48a,50} (with SMD solvation) and were corrected for the thermodynamic effects using the quasi-harmonic approximation⁵¹ as implemented in GoodVibes program.⁵²

⁴⁴ Gaussian 16, Revision A.03, M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, G. A. Petersson, H. Nakatsuji, X. Li, M. Caricato, A. V. Marenich, J. Bloino, B. G. Janesko, R. Gomperts, B. Mennucci, H. P. Hratchian, J. V. Ortiz, A. F. Izmaylov, J. L. Sonnenberg, D. Williams-Young, F. Ding, F. Lipparini, F. Egidi, J. Goings, B. Peng, A. Petrone, T. Henderson, D. Ranasinghe, V. G. Zakrzewski, J. Gao, N. Rega, G. Zheng, W. Liang, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, K. Throssell, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. J. Bearpark, J. J. Heyd, E. N. Brothers, K. N. Kudin, V. N. Staroverov, T. A. Keith, R. Kobayashi, J. Normand, K. Raghavachari, A. P. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, J. M. Millam, M. Klene, C. Adamo, R. Cammi, J. W. Ochterski, R. L. Martin, K. Morokuma, O. Farkas, J. B. Foresman, and D. J. Fox, Gaussian, Inc., Wallingford CT, 2016.

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⁵⁰ Weigend, F.; Furche, F.; Ahlrichs, R. *J. Chem. Phys.* **2003**, *119*, 12753-12762.

⁵¹ Grimme, S. *Chem. Eur. J.* **2012**, *18*, 9955-9964.

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7. Free Energy Profile for the Reaction in CHCl₃

Figure S3. Free energy profile for the alkynylation of 2-pyridinecarboxaldehyde (**1g**) with (mesityl)phenylacetyleneiodonium tosylate (**2a**) using precatalyst **NHC-1** in CHCl₃, calculated at B3LYP-D3BJ/Def2-QZVP(SMD)//B3LYP-D3BJ/Def2-SVPD(SMD) level of theory.

8. Energies and Energy Corrections of Stationary Points (in atomic units)

Table S10. Data for calculations in toluene

Stationary point	B3LYP-D3BJ/ Def2-SVPD (SMD toluene) optimization	B3LYP-D3BJ/ Def2-QZVP (SMD toluene) single-point	Thermal correction to Gibbs free energy (at 233.15 K)
1g	-361.658223	-361.804366	0.075548
2a	-1563.690802	-1850.665988	0.365256
3g	-668.917231	-669.181297	0.161041
A	-1086.239763	-1086.701756	0.133159
B	-1447.904831	-1448.509885	0.229864
C	-1873.049101	-1873.851283	0.253921
D	-1447.927274	-1448.534967	0.230342
E	-1755.157362	-1755.879604	0.314972
Mes-I	-361.056776	-647.605231	0.145528
NHC-1	-1511.368016	-1512.027553	0.157098
TMEDA	-347.813622	-347.950192	0.197720

TMEDAH ⁺ BF ₄ ⁻	-772.941928	-773.273989	0.223515
TMEDAH ⁺ TsO ⁻	-1243.301284	-1243.741586	0.336364
TS1	-1859.194148	-1859.984828	0.371678
TS2	-1447.897757	-1448.503254	0.228516
TS3	-2220.875742	-2221.809001	0.468107
TS4	-3011.626023	-3299.202145	0.619004
TS5	-1755.148092	-1755.870652	0.313341
TS β	-3011.617075	-3299.192656	0.619290
TS-Mes	-3011.607351	-3299.184117	0.617980

Table S11. Data for calculations in CHCl₃

Stationary point	B3LYP-D3BJ/ Def2-SVPD (SMD CHCl ₃) optimization	B3LYP-D3BJ/ Def2-QZVP (SMD CHCl ₃) single-point	Thermal correction to Gibbs free energy (at 233.15 K)
1g	-361.660059	-361.805902	0.075436
2a	-1563.699743	-1850.674148	0.364346
3g	-668.920149	-669.183817	0.160945
A	-1086.243036	-1086.704712	0.133009
B	-1447.915655	-1448.520072	0.230537
C	-1873.064797	-1873.866457	0.254010
D	-1447.931861	-1448.538932	0.230047
E	-1755.167157	-1755.888638	0.315522
Mes-I	-361.058298	-647.606570	0.145353
NHC-1	-1511.381319	-1512.040479	0.156313
TMEDA	-347.816190	-347.952533	0.197828
TMEDAH ⁺ BF ₄ ⁻	-772.953367	-773.285167	0.223612
TMEDAH ⁺ TsO ⁻	-1243.310781	-1243.750500	0.336521
TS1	-1859.208220	-1859.998731	0.371194
TS2	-1447.904218	-1448.509199	0.227861
TS3	-2220.892385	-2221.825560	0.468396
TS4	-3011.638901	-3299.214125	0.619415
TS5	-1755.158803	-1755.881007	0.313794
TS β	-3011.632857	-3299.207485	0.617465
TS-Mes	-3011.622360	-3299.197981	0.617433

9. NMR Spectra of Compounds 2w and 3a-3ab

^1H NMR, 500 MHz, CDCl_3

^{13}C NMR (without NOE), 126 MHz, CDCl_3

^1H NMR, 500 MHz, CDCl_3

^{13}C NMR, 126 MHz, CDCl_3

^1H NMR, 500 MHz, CDCl_3

^{13}C NMR, 126 MHz, CDCl_3

^1H NMR, 500 MHz, CDCl_3

^{13}C NMR, 126 MHz, CDCl_3

^1H NMR, 500 MHz, CDCl_3

^{13}C NMR, 126 MHz, CDCl_3

^1H NMR, 500 MHz, CDCl_3

^{13}C NMR, 126 MHz, CDCl_3

^1H NMR, 500 MHz, CDCl_3

^{13}C NMR, 126 MHz, CDCl_3

^1H NMR, 500 MHz, CDCl_3

^{13}C NMR, 126 MHz, CDCl_3

Chemical structure of 3h: c1ccc(cc1)C#CC(=O)c2cc(F)ccc2

¹H NMR spectrum (CDCl₃):

- Chemical shift range:** 0 to 8.64 ppm.
- Integration values (from left to right):** 1.00, 2.01, 2.02, 1.01, 2.00.
- Peak assignments:**
 - Aromatic and alkyne protons: 7.41–8.64 ppm.
 - Solvent (CDCl₃): 7.26 ppm.
 - Aliphatic protons (ethyl group): 1.0–1.5 ppm.

3h

Chemical structure of **3h** is shown above the spectrum.

Chemical shifts (ppm) labeled on the spectrum:

- 175.08
- 175.04
- 160.51
- 158.33
- 145.51
- 145.47
- 141.55
- 141.51
- 133.45
- 131.05
- 129.13
- 129.09
- 128.66
- 125.90
- 125.74
- 120.12
- 95.07
- 88.61
- 77.41
- 77.15
- 76.90

^{19}F NMR, 471 MHz, CDCl_3

^1H NMR, 500 MHz, CDCl_3

^{13}C NMR, 126 MHz, CDCl_3

^1H NMR, 500 MHz, CDCl_3

^{13}C NMR, 126 MHz, CDCl_3

^{19}F NMR, 471 MHz, CDCl_3

^1H NMR, 500 MHz, CDCl_3

^{13}C NMR, 126 MHz, CDCl_3

^1H NMR, 500 MHz, CDCl_3

^{13}C NMR, 126 MHz, CDCl_3

^1H NMR, 500 MHz, CDCl_3

^{13}C NMR, 126 MHz, CDCl_3

^1H NMR, 400 MHz, CDCl_3

^{13}C NMR, 126 MHz, CDCl_3

^1H NMR, 400 MHz, CDCl_3

^{13}C NMR, 126 MHz, CDCl_3

^1H NMR, 400 MHz, CDCl_3

^{13}C NMR, 126 MHz, CDCl_3

^1H NMR, 400 MHz, CDCl_3

^{13}C NMR, 126 MHz, CDCl_3

^1H NMR, 400 MHz, CDCl_3

^{13}C NMR, 126 MHz, CDCl_3

^{19}F NMR, 376 MHz, CDCl_3

^1H NMR, 400 MHz, CDCl_3

^{13}C NMR, 126 MHz, CDCl_3

^{19}F NMR, 376 MHz, CDCl_3

^1H NMR, 400 MHz, CDCl_3

^{13}C NMR, 126 MHz, CDCl_3

^1H NMR, 400 MHz, CDCl_3

^{13}C NMR, 126 MHz, CDCl_3

^1H NMR, 400 MHz, CDCl_3

^{13}C NMR, 126 MHz, CDCl_3

^1H NMR, 400 MHz, CDCl_3

^{13}C NMR, 126 MHz, CDCl_3

^1H NMR, 400 MHz, CDCl_3

^{13}C NMR, 126 MHz, CDCl_3

^1H NMR, 400 MHz, CDCl_3

^{13}C NMR, 126 MHz, CDCl_3

^{19}F NMR, 376 MHz, CDCl_3

^1H NMR, 400 MHz, CDCl_3

^{13}C NMR, 126 MHz, CDCl_3

^1H NMR, 400 MHz, CDCl_3

^{13}C NMR, 126 MHz, CDCl_3

^{13}C NMR (without NOE), 126 MHz, CDCl_3

10. Structures and Cartesian Coordinates of Stationary Points

1g (toluene)

C	-0.501807000	-0.195308000	-0.000052000
C	-0.009512000	1.114955000	0.000007000
C	1.371369000	1.300771000	0.000208000
C	2.197992000	0.175722000	0.000330000
C	1.609365000	-1.094207000	0.000236000
N	0.286844000	-1.285356000	0.000048000
H	1.795511000	2.300177000	0.000268000
H	-0.704064000	1.948023000	-0.000100000
H	3.278858000	0.272806000	0.000490000
H	2.226813000	-1.989145000	0.000331000
C	-1.962968000	-0.476539000	-0.000277000
O	-2.827360000	0.383531000	-0.000475000
H	-2.212789000	-1.554981000	-0.000236000

2a (toluene)

I	-0.87278700	-1.45676200	0.38251100
C	0.08063400	0.42724400	0.01612700
C	0.71896300	1.05120300	1.09709600
C	0.04468700	0.93233600	-1.28916400
C	1.35132800	2.26826800	0.81962600
C	0.69306600	2.15892000	-1.49062800
C	1.34786400	2.83546300	-0.45856000
H	1.87440100	2.77133300	1.62802100
H	0.69842700	2.57726900	-2.49349500
C	-2.74055400	-0.63634400	0.24664100
C	-3.88662100	-0.22649300	0.19037700
C	-5.22158800	0.27332400	0.12137900
C	-5.74232500	1.05392500	1.17256700
C	-6.02992300	-0.01053700	-0.99722400
C	-7.04588900	1.54092500	1.10012500
H	-5.11854800	1.27144800	2.03342300
C	-7.33310200	0.47913400	-1.05848600

H	-5.62773700	-0.61246400	-1.80558700
C	-7.84354700	1.25503900	-0.01270100
H	-7.44063400	2.14299800	1.91290100
H	-7.95093800	0.25546000	-1.92286200
H	-8.85934800	1.63524000	-0.06464200
O	1.37243100	-2.24690500	0.68908100
S	2.41067200	-2.24833400	-0.45298600
O	3.32238800	-3.40102000	-0.31548300
O	1.74214900	-2.07038300	-1.76559800
C	3.37587400	-0.76162600	-0.15656900
C	3.58371500	0.14705400	-1.18964000
C	3.93993300	-0.54738900	1.10510400
C	4.35734000	1.28664700	-0.95431000
H	3.13309900	-0.03213000	-2.15867100
C	4.70253100	0.59530200	1.32695300
H	3.77866800	-1.26512700	1.90247600
C	4.92429500	1.53072300	0.30104600
H	4.51208000	1.99992300	-1.75930200
H	5.13668100	0.76571100	2.30917400
C	5.75050600	2.76595600	0.55935900
H	6.77822500	2.50291200	0.83684800
H	5.79697700	3.40777600	-0.32497300
H	5.33660400	3.35568000	1.38610500
C	-0.60646200	0.22288900	-2.44504800
H	-0.15268200	-0.76326000	-2.58803200
H	-1.68178000	0.09038400	-2.28267900
H	-0.47408700	0.79831600	-3.36409800
C	0.77306300	0.47226000	2.48509300
H	-0.23027500	0.36096000	2.91195400
H	1.24582800	-0.51423900	2.47659300
H	1.35011900	1.12484200	3.14379200
C	2.04335300	4.14765700	-0.71271800
H	2.98407300	4.20979500	-0.15722500
H	2.26173600	4.28410300	-1.77567000
H	1.41750800	4.98996300	-0.39202400

3g (toluene)

C	-2.48469000	0.34103900	-0.00004800
C	-3.82304100	0.75007900	0.00001000
C	-4.81416300	-0.22957300	-0.00005300
C	-4.43059900	-1.57132200	-0.00011900
C	-3.06533200	-1.87793000	-0.00014100
N	-2.10645400	-0.94758700	-0.00010600
H	-5.86387100	0.04761700	-0.00002300
H	-4.05841100	1.80807600	0.00012200
H	-5.16765200	-2.36799100	-0.00014000
H	-2.73201900	-2.91303600	-0.00014200

C	-1.39604600	1.37553400	0.00012700
O	-1.65665100	2.57914200	0.00039400
C	-0.03907000	0.89977200	0.00003300
C	1.13215200	0.56762400	-0.00014600
C	2.48964100	0.14541600	-0.00005800
C	3.53322400	1.09390200	-0.00034900
C	2.80019600	-1.23054700	0.00025900
C	4.85982500	0.66920700	-0.00027400
H	3.28934300	2.15119600	-0.00062000
C	4.13014100	-1.64372800	0.00031300
H	1.99223500	-1.95475200	0.00048900
C	5.16070700	-0.69719400	0.00007100
H	5.66009900	1.40298300	-0.00047400
H	4.36466100	-2.70386700	0.00054700
H	6.19633800	-1.02392900	0.00007700

A (toluene)

N	-1.630678000	-0.004792000	1.103863000
N	-0.938698000	-0.052774000	-0.124031000
C	-1.705312000	-0.105918000	-1.247407000
N	-2.936717000	-0.087483000	-0.673246000
C	-4.314942000	-0.156009000	-1.168407000
H	-4.541289000	-1.184116000	-1.468082000
H	-4.446894000	0.501521000	-2.028476000
C	-5.124948000	0.287736000	0.076604000
H	-6.097383000	-0.205706000	0.125002000
H	-5.294437000	1.367648000	0.031887000
C	-4.232001000	-0.042157000	1.309657000
H	-4.340629000	0.679868000	2.121508000
H	-4.452591000	-1.036875000	1.714078000
C	-2.866257000	-0.032834000	0.701614000
C	0.472929000	-0.022470000	-0.083955000
F	0.482747000	2.345915000	-0.093159000
C	1.161330000	1.191890000	-0.061237000
F	3.199915000	2.403411000	0.010393000
C	2.550809000	1.229977000	-0.006332000
F	4.607160000	0.066807000	0.082735000
C	3.270146000	0.038147000	0.031428000
F	3.299975000	-2.327824000	0.058043000
C	2.601921000	-1.183485000	0.016903000
F	0.583797000	-2.388432000	-0.039845000
C	1.211915000	-1.205857000	-0.036455000

B (toluene)

C	1.45506200	1.86026300	0.50076500
H	1.88320500	2.09682000	1.50864800
C	-0.06037100	2.02610800	0.68233400
C	-0.77661700	2.82003800	-0.21436800
C	-1.94958600	1.55183600	1.90369800
C	-2.15056400	2.96700900	-0.02338500
H	-0.23390000	3.28341300	-1.03039200
C	-2.75405500	2.31883900	1.05686400
H	-2.38262300	1.03182600	2.75600800
H	-2.74226100	3.57146100	-0.70519900
H	-3.81994600	2.40300600	1.24443400
O	2.00847000	2.50022100	-0.53312900
C	1.82678200	0.37508900	0.28561000
N	1.14840800	-0.69725600	-0.18876200
N	3.10755100	-0.02853800	0.24428200
N	1.98787200	-1.75980500	-0.54715600
C	-0.25012200	-0.88146300	-0.29002600
C	4.41297500	0.59843800	0.47370100
C	3.17385500	-1.29733200	-0.26514700
C	-0.97338800	-0.35124600	-1.35798600
C	-0.92556600	-1.60633200	0.69315800
H	4.60616900	0.64480500	1.54899000
H	4.39148100	1.60600200	0.05590800
C	5.35734600	-0.38399800	-0.26994000
C	4.59660700	-1.74238600	-0.36945800
F	-0.34874700	0.32928800	-2.32122100
C	-2.35433900	-0.50779900	-1.42340300
C	-2.30140500	-1.78311900	0.62761000
F	-0.24950300	-2.11277100	1.72926400
H	6.31493600	-0.48761700	0.24261100
H	5.54862500	-0.00277600	-1.27655000
H	4.79818600	-2.27950300	-1.29785300
H	4.83965200	-2.40818500	0.46633000
F	-3.04933300	0.02812900	-2.43523200
C	-3.01468200	-1.22697700	-0.43158700
F	-2.94800000	-2.46041100	1.58668400
F	-4.34242600	-1.37326700	-0.48833700
N	-0.62965900	1.40252300	1.72607000

C (toluene)

C	0.63017100	0.79162600	-0.89390900
H	0.93858200	-0.05951200	-1.51393500
C	1.71645400	1.86869700	-0.91806000
C	3.02130100	1.61553900	-1.33868600
C	2.13548600	4.11042200	-0.61213200
C	3.91308100	2.69136200	-1.38204500
H	3.32941600	0.61308600	-1.61778400
C	3.46702300	3.96010900	-1.01098700
H	1.74293600	5.08323000	-0.32625200
H	4.93649300	2.53598200	-1.71038600
H	4.12797400	4.82065100	-1.03748900
O	-0.58023600	1.31398600	-1.40118100
C	0.38852900	0.22792500	0.50363000
N	-0.79985600	-0.16453700	1.01482000
N	1.27995400	-0.05936600	1.45930100
N	-0.67217800	-0.68712600	2.29014900
C	-2.09975500	-0.16165800	0.43151000
C	2.73903400	0.06499900	1.70481900
C	0.60700000	-0.60628400	2.52584600
C	-2.53888300	-1.24836300	-0.32597800
C	-2.98218300	0.88812300	0.68988000
H	2.96124900	1.11596500	1.90788200
H	3.29936300	-0.28340000	0.83924000
C	2.92180300	-0.84767800	2.94389400
C	1.53618100	-0.93375600	3.64676400
F	-1.71721900	-2.27211900	-0.56759300
C	-3.83255900	-1.27513600	-0.84040300
C	-4.27557700	0.87095600	0.18242900
F	-2.57494900	1.93768400	1.41587300
H	3.69504700	-0.45704000	3.60760500
H	3.22412900	-1.84076800	2.60528300
H	1.33298100	-1.91818600	4.07316500
H	1.42711000	-0.19062100	4.44536000
F	-4.24914800	-2.31686100	-1.56814300
C	-4.69922700	-0.21527000	-0.58258400
F	-5.11306000	1.88730500	0.42483500
F	-5.94274500	-0.23951200	-1.06805100
N	1.27518600	3.08551700	-0.56657000
H	-0.57285400	2.26473800	-1.17766400
B	3.10446100	-2.44011400	-1.08975400
F	3.65389500	-3.58310700	-1.67059700
F	4.11842100	-1.46368600	-0.86394300
F	2.50213300	-2.75068700	0.15523000
F	2.12357700	-1.86863200	-1.94257200

D (toluene)

C	-1.39919100	1.59151500	0.05389600
C	-0.17981900	2.26890800	-0.34153800
C	0.76172700	1.79014800	-1.28079300
C	1.02999400	4.23689500	-0.08196400
C	1.87157800	2.56747700	-1.57565000
H	0.59283900	0.85817900	-1.80307300
C	2.03191500	3.81380700	-0.95270300
H	1.08513500	5.21228200	0.39639700
H	2.59971700	2.21627300	-2.30121900
H	2.88978300	4.44519900	-1.15669300
O	-2.33241800	2.37985200	0.70811200
C	-1.72401300	0.27393500	-0.10452800
N	-0.91901400	-0.82316300	-0.48160100
N	-2.96852200	-0.30432100	0.08882500
N	-1.71332700	-2.00969400	-0.63909800
C	0.40855700	-1.02145200	-0.07483800
C	-4.34057700	0.18800300	0.21959200
C	-2.90043100	-1.61805100	-0.30358400
C	0.88033800	-0.68838200	1.20185400
C	1.32996500	-1.56871600	-0.97742300
H	-4.63307200	0.72223300	-0.69285500
H	-4.43094900	0.86673700	1.06624100
C	-5.11536900	-1.13999700	0.40118900
C	-4.27158200	-2.22083500	-0.33101500
F	0.04178200	-0.20690400	2.13103900
C	2.21863400	-0.84795900	1.54609000
C	2.66252300	-1.76204200	-0.63524500
F	0.93462500	-1.87847100	-2.22139000
H	-6.13282400	-1.07251400	0.01153000
H	-5.17415500	-1.38014900	1.46686500
H	-4.31134800	-3.20118000	0.14832600
H	-4.58875800	-2.34465900	-1.37264500
F	2.64407200	-0.51180700	2.77369400
C	3.11222900	-1.39294300	0.62945800
F	3.52365600	-2.27616100	-1.52745600
F	4.39875900	-1.56455800	0.96283900
N	-0.04433200	3.49813100	0.21830600
H	-1.86557600	3.23136500	0.84189400

E (toluene)

C	0.75488400	0.01254500	1.18734300
C	-0.23584600	-1.17206900	1.04476700
C	-0.85858200	-1.66166700	2.19164400
C	-1.28807400	-2.70811100	-0.29768400
C	-1.73981800	-2.73520400	2.05886300
H	-0.64219000	-1.18079700	3.13827000
C	-1.96153700	-3.27223500	0.78899900
H	-1.43793500	-3.09453800	-1.30374300
H	-2.24815800	-3.14293000	2.92794300
H	-2.63992300	-4.10602700	0.63784300
O	0.82557700	0.55141600	2.40397100
C	0.30676000	1.20550400	0.28697600
N	-0.90229000	1.59341700	-0.18458300
N	1.07106500	2.29929600	0.12548000
N	-0.91240000	2.92345100	-0.62178000
C	-2.08457800	0.83373200	-0.34305600
C	2.43968900	2.70152200	0.47635000
C	0.31484300	3.30780500	-0.40983000
C	-2.93458600	0.58480700	0.73376000
C	-2.41657900	0.32911100	-1.60124400
H	3.13472800	2.26905700	-0.24679700
H	2.67337900	2.33011800	1.47400000
C	2.33622300	4.24633500	0.37915300
C	1.13033200	4.55035600	-0.56052900
F	-2.65187900	1.07623200	1.94178300
C	-4.07815700	-0.19021500	0.56663200
C	-3.56577200	-0.42908500	-1.78210600
F	-1.60606900	0.54790200	-2.64115400
H	3.26422500	4.68715600	0.01179800
H	2.13305700	4.65591800	1.37232600
H	0.57843300	5.44790100	-0.27623400
H	1.44480700	4.66208500	-1.60441400
F	-4.87727500	-0.45069000	1.60951000
C	-4.39284200	-0.69228800	-0.69258100
F	-3.86741400	-0.93233900	-2.98741000
F	-5.48660000	-1.44397100	-0.85505200
N	-0.44150300	-1.67651800	-0.17942600
C	2.07234300	-0.45365700	0.63567200
C	3.18536800	-0.79326800	0.28609700
C	4.49846200	-1.17646900	-0.12686700
C	5.59108600	-1.03923300	0.75286500
C	4.72204600	-1.69041900	-1.41992800
C	6.87288900	-1.40626600	0.34499800

H	5.41992900	-0.64947700	1.75131900
C	6.00738800	-2.05369800	-1.81991000
H	3.88093200	-1.80220400	-2.09674800
C	7.08638000	-1.91310800	-0.94102300
H	7.70639700	-1.29857200	1.03308400
H	6.16681300	-2.45014400	-2.81850900
H	8.08599700	-2.19895300	-1.25502100

Mes-I (toluene)

C	-2.24649200	-1.19649900	-0.00591500
C	-0.84593800	-1.23062000	-0.00243100
C	-0.16549600	0.00146000	-0.00003700
C	-0.84206700	1.23278300	-0.00234200
C	-2.24527600	1.20142500	-0.00578700
C	-2.96466000	0.00423500	-0.00616000
H	-2.78630200	-2.14065100	-0.00936300
H	-2.78260700	2.14654600	-0.00907400
C	-0.13130200	2.56117900	-0.00310800
H	0.51145500	2.67133100	0.87746700
H	0.51297400	2.66974500	-0.88278700
H	-0.85301300	3.38228100	-0.00444500
C	-0.13600200	-2.55948900	-0.00306200
H	0.50829100	-2.66849300	-0.88264400
H	0.50656100	-2.66995900	0.87759100
H	-0.85835700	-3.38003100	-0.00442600
C	-4.47341200	-0.00166200	0.01031500
H	-4.85517000	-0.32026700	0.98835700
H	-4.87838600	0.99331000	-0.19607700
H	-4.87748000	-0.69452900	-0.73600300
I	1.96520600	-0.00124800	0.00174700

NHC-1 (toluene)

N	2.025514000	-1.698297000	-0.133982000
N	1.170787000	-0.648040000	0.150823000

C	1.830433000	0.489958000	0.400039000
H	1.352971000	1.436031000	0.636405000
N	3.119564000	0.180341000	0.278864000
C	4.430526000	0.841893000	0.413646000
H	4.647558000	0.967060000	1.477609000
H	4.413673000	1.816426000	-0.073873000
C	5.359177000	-0.189037000	-0.278087000
H	6.345018000	-0.207720000	0.187977000
H	5.482934000	0.085702000	-1.328718000
C	4.638120000	-1.567171000	-0.184107000
H	4.807114000	-2.197770000	-1.058534000
H	4.944657000	-2.130892000	0.704032000
C	3.209736000	-1.154351000	-0.047751000
C	-0.236486000	-0.824581000	0.115139000
F	-0.177668000	-1.007177000	-2.240427000
C	-0.884950000	-0.998735000	-1.107914000
F	-2.887696000	-1.314869000	-2.326535000
C	-2.263989000	-1.151772000	-1.154797000
F	-4.325991000	-1.266048000	-0.015107000
C	-3.000435000	-1.122902000	0.027780000
F	-3.078688000	-0.922009000	2.383640000
C	-2.364045000	-0.944528000	1.253117000
F	-0.368754000	-0.632818000	2.470318000
C	-0.983205000	-0.798034000	1.291964000
B	-0.925360000	2.606555000	-0.242174000
F	-0.152524000	1.951760000	-1.240714000
F	-2.174297000	1.978415000	-0.127748000
F	-1.059849000	3.960876000	-0.545265000
F	-0.217585000	2.460306000	0.999824000

TMEDA (toluene)

C	-0.704811000	0.299158000	0.954348000
H	-0.647331000	1.385005000	1.089499000
H	-1.219252000	-0.099416000	1.854186000
C	0.704964000	-0.299381000	0.954330000
H	1.219431000	0.099202000	1.854157000
H	0.647542000	-1.385228000	1.089467000
N	1.482099000	-0.049306000	-0.255596000
N	-1.482067000	0.049237000	-0.255577000
C	-1.609597000	-1.367234000	-0.566806000
H	-2.097834000	-1.942716000	0.246133000
H	-2.212605000	-1.485964000	-1.472492000
H	-0.625352000	-1.799093000	-0.761276000
C	-2.784409000	0.693654000	-0.171152000
H	-3.325519000	0.563375000	-1.113971000
H	-3.415070000	0.286777000	0.645501000
H	-2.658337000	1.767578000	0.003567000
C	1.609257000	1.367225000	-0.566729000
H	2.097360000	1.942764000	0.246253000
H	2.212232000	1.486187000	-1.472407000
H	0.624902000	1.798858000	-0.761154000

C	2.784588000	-0.693425000	-0.171295000
H	3.325579000	-0.563051000	-1.114174000
H	3.415268000	-0.286402000	0.645278000
H	2.658805000	-1.767375000	0.003463000

TMEDAH⁺BF₄⁻ (toluene)

C	-2.44536500	0.10668100	0.71079900
H	-3.21968500	0.64312800	0.15371500
H	-2.92112600	-0.24736100	1.64506100
C	-1.33639300	1.07836300	1.10821500
H	-1.76234300	1.98583900	1.54493800
H	-0.64422100	0.63613200	1.82538800
N	-0.48772600	1.49643600	-0.06285400
N	-1.95239300	-0.98238800	-0.12207700
C	-1.17596400	-1.96695300	0.63243100
H	-1.79757000	-2.49858100	1.37735200
H	-0.75530200	-2.70139900	-0.05880200
H	-0.33941900	-1.49371000	1.14785600
C	-3.03102800	-1.62699300	-0.86352900
H	-2.60951700	-2.38251200	-1.53264800
H	-3.76686700	-2.12447400	-0.20369600
H	-3.56282900	-0.88954500	-1.47404600
C	-1.27236700	2.00607200	-1.22411900
H	-1.90014800	2.83723100	-0.89717700
H	-0.56985000	2.34387400	-1.98641400
H	-1.87574400	1.19381100	-1.62372900
C	0.54577000	2.48891800	0.36341700
H	1.22897200	2.65872300	-0.46854900
H	0.04440700	3.41795900	0.64078800
H	1.09800300	2.07861900	1.20666500
H	0.02008200	0.65336500	-0.39747200
F	1.69197300	-0.27266300	1.16708300
B	2.29232400	-0.55796100	-0.09047700
F	1.28281300	-0.31835200	-1.09526100
F	3.35889700	0.32057600	-0.31312300
F	2.69347700	-1.88913300	-0.14932300

TMEDAH⁺TsO⁻ (toluene)

C	-3.08997900	1.87732000	0.10095800
H	-3.06865900	2.24111700	1.13280200
H	-3.85286000	2.48229900	-0.42761200
C	-3.58804400	0.43488500	0.08329000
H	-4.51617500	0.36841900	0.65944800
H	-3.79736200	0.09339600	-0.93295500
N	-2.61969000	-0.55321500	0.66123700
N	-1.75864200	2.04994000	-0.46649900
C	-1.71993500	1.81099700	-1.90807700
H	-2.37832500	2.50644000	-2.46224000
H	-0.69632700	1.94247200	-2.26716300
H	-2.00452200	0.78408900	-2.14041600
C	-1.22120300	3.36750700	-0.14200800
H	-0.20472900	3.45395400	-0.53628800
H	-1.82305900	4.19215100	-0.56851600
H	-1.18030500	3.49933000	0.94427600
C	-2.05494800	-0.15028100	1.97882000
H	-2.86832300	-0.00578900	2.69427800
H	-1.38385000	-0.94419300	2.30400400
H	-1.48540000	0.76823800	1.85155000
C	-3.23712700	-1.90873000	0.73914200
H	-2.46064100	-2.61364500	1.03519800
H	-4.05268400	-1.89390000	1.46581100
H	-3.61632900	-2.17795100	-0.24771500
H	-1.80459700	-0.66428400	-0.02599900
O	-0.72897600	-1.12466400	-1.08888900
S	0.38260100	-1.93383000	-0.44239500
O	-0.03799800	-2.39547700	0.91694300
O	0.92519000	-2.98918900	-1.32519700
C	1.70535500	-0.74191300	-0.17424800
C	3.02794000	-1.18640300	-0.10886200
C	1.39849300	0.60328400	0.03117100
C	4.04577300	-0.27361200	0.16329200
H	3.25330700	-2.23335500	-0.28202100
C	2.42969700	1.50593400	0.30419800
H	0.36895000	0.94183600	-0.03917300
C	3.76477800	1.08573100	0.37646200
H	5.07551400	-0.61994800	0.20785000
H	2.19338500	2.55580300	0.45950000
C	4.87871600	2.06167200	0.66429100
H	4.49249900	3.07229900	0.82635800

H	5.44196700	1.76805300	1.55797400
H	5.59241700	2.10366300	-0.16721500

TS1 (toluene)

H	1.44403400	0.51207200	1.16196000
N	1.48295000	1.66025500	1.78372100
C	1.30203100	2.81156500	0.85442700
C	2.78598000	1.67865700	2.47325200
C	0.37755700	1.62377700	2.76801900
C	2.37794000	2.92810200	-0.22017200
H	1.29749000	3.73953700	1.44230900
H	0.31318400	2.70327900	0.41129100
H	2.90940500	2.60228300	3.05140200
H	2.83863100	0.82652900	3.15625600
H	3.59373000	1.59823600	1.74542600
H	0.46734300	0.71921900	3.37423100
H	0.41888100	2.50093600	3.42456600
H	-0.57286000	1.61408500	2.23507400
H	3.33961500	3.18976800	0.23372700
H	2.09030800	3.78336800	-0.86051000
N	2.57096300	1.70849400	-1.00611900
C	1.39046700	1.38106300	-1.81103700
C	3.74611500	1.83401200	-1.86230000
H	1.14401900	2.17757700	-2.53434500
H	1.57415600	0.45811500	-2.36854900
H	0.51593900	1.22665800	-1.18117300
H	3.90770500	0.89782100	-2.40667800
H	3.64647300	2.64394700	-2.60910900
H	4.63590800	2.04215200	-1.25755000
C	1.54602800	-0.75827300	0.59449200
N	0.63448900	-1.63652500	0.11955200
N	2.70650500	-1.35739100	0.26887000
N	1.18806800	-2.76230700	-0.49437200
C	-0.77353800	-1.49770700	0.13793000
C	4.13328900	-1.05009900	0.41011600
C	2.46654100	-2.54579100	-0.37845500
C	-1.48682200	-1.41142300	-1.05898700
C	-1.47253800	-1.43892400	1.34235700
H	4.44218100	-1.23365800	1.44323800
H	4.30761500	-0.00635400	0.15254600
C	4.77001200	-2.05186600	-0.58827900
C	3.74859100	-3.21801700	-0.74808800
F	-0.83575100	-1.44848600	-2.22675800
C	-2.86960000	-1.27488800	-1.05535800
C	-2.85146700	-1.28029500	1.35859200

F	-0.81163700	-1.53568700	2.51003800
H	5.74390100	-2.40109600	-0.24179900
H	4.91024000	-1.55809800	-1.55367600
H	3.72865200	-3.63355300	-1.75715400
H	3.95513300	-4.03764900	-0.05064100
F	-3.54564400	-1.20413000	-2.20503700
C	-3.55004400	-1.20010900	0.15707200
F	-3.51018500	-1.21438600	2.52500400
F	-4.87705200	-1.05830500	0.16932900
F	-1.56978400	1.43345500	0.26536800
B	-2.26654100	2.14011600	-0.76536300
F	-1.98577900	1.51635400	-1.99761000
F	-3.64271200	2.09120800	-0.49571600
F	-1.80401600	3.47196200	-0.78096000

TS2 (toluene)

C	-1.53581300	1.97340700	-1.08306300
H	-1.61719400	1.76736400	-2.16692100
C	-0.07353400	2.15860200	-0.70260000
C	0.27165900	2.83489500	0.47094100
C	2.13338400	1.85947600	-1.27256000
C	1.62178900	3.00740100	0.77032000
H	-0.51969200	3.20956100	1.11057600
C	2.57749000	2.51186700	-0.12001600
H	2.84690000	1.46386800	-1.99259100
H	1.92583600	3.51978300	1.67855800
H	3.64017900	2.62679100	0.06909600
O	-2.42963400	2.64076600	-0.48887900
C	-1.79943900	0.11602700	-0.52979800
N	-1.08950000	-0.85074700	0.09758700
N	-3.06404200	-0.24698300	-0.25002000
N	-1.87179800	-1.80656800	0.76397000
C	0.31802700	-0.96582200	0.15253600
C	-4.40415600	0.28133800	-0.54131600
C	-3.08041400	-1.38793400	0.51566100
C	1.02029200	-0.50968700	1.26833600
C	1.02757700	-1.53580200	-0.90427800
H	-4.66428300	0.03453000	-1.57493600
H	-4.39493100	1.36410900	-0.41782000
C	-5.26744700	-0.48677400	0.49093900
C	-4.48460000	-1.79168600	0.83010800
F	0.36041100	0.03762500	2.29526400
C	2.40637100	-0.59785700	1.32208100
C	2.41379700	-1.63176300	-0.86060200
F	0.37714500	-1.98873400	-1.98120900
H	-6.26761100	-0.69448900	0.10687100
H	-5.36944500	0.11883100	1.39598800
H	-4.60811000	-2.10925600	1.86717500
H	-4.78472500	-2.62508800	0.18444900

F	3.07716000	-0.13017600	2.38366600
C	3.10049900	-1.16101100	0.25501400
F	3.09211700	-2.16252200	-1.88774600
F	4.43630600	-1.22772600	0.29240000
N	0.83805300	1.67481300	-1.56025200

TS3 (toluene)

C	0.06310300	0.76484000	-0.66785300
H	0.70910100	0.97792700	0.62531000
C	-1.14246100	1.66812100	-0.62051100
C	-1.40028600	2.56732900	-1.67205500
C	-2.93190000	2.49839800	0.58428700
C	-2.47460200	3.44659600	-1.56353500
H	-0.76155700	2.55843100	-2.54740200
C	-3.26157200	3.42148900	-0.40820400
H	-3.51323400	2.44818000	1.50363100
H	-2.69720500	4.14066500	-2.36953700
H	-4.10140700	4.09638600	-0.27630800
O	1.01224900	1.17306100	-1.63576500
C	-0.11436100	-0.67116900	-0.76707500
N	-1.13642600	-1.50393200	-0.37470200
N	0.84264800	-1.53949200	-1.19541800
N	-0.80603200	-2.85963500	-0.51602900
C	-2.48213900	-1.22677800	-0.03694400
C	2.20870500	-1.49507000	-1.77264200
C	0.39523500	-2.82363500	-1.00709000
C	-3.43235200	-0.97830100	-1.03005200
C	-2.91105400	-1.30721500	1.28951000
H	2.92813500	-1.25977200	-0.98681600
H	2.25928300	-0.74077100	-2.55294900
C	2.37533300	-2.94622800	-2.28634100
C	1.42881000	-3.82133800	-1.41878000
F	-3.05873300	-0.92484800	-2.31538900
C	-4.77094400	-0.77635000	-0.70907000
C	-4.24599000	-1.11436700	1.62469500
F	-2.02684400	-1.55740000	2.26307400
H	3.41505500	-3.26814000	-2.21161100
H	2.06951200	-3.00299300	-3.33588700
H	1.00075900	-4.67033300	-1.95564100
H	1.94293100	-4.20366500	-0.52952400
F	-5.67061300	-0.52593700	-1.67047300
C	-5.17605700	-0.84715300	0.62155500
F	-4.64205200	-1.17583100	2.90402000

F	-6.46095600	-0.65484800	0.93823700
N	-1.90200100	1.64322700	0.49276600
H	1.65452600	1.81397500	-1.20724300
N	2.78600000	2.97233700	-0.58306500
C	3.19080900	2.75126200	0.81872400
C	2.18349400	4.29870100	-0.77992100
C	3.94685400	2.81146600	-1.47721900
C	2.04656700	2.50947300	1.80553400
H	3.74495200	3.62983700	1.19265800
H	3.89263200	1.91491000	0.84129700
H	2.89447900	5.10844900	-0.54257300
H	1.87359900	4.40547100	-1.82344600
H	1.29634800	4.42287800	-0.15406300
H	3.62548900	2.93752900	-2.51545700
H	4.73354100	3.55452400	-1.26507400
H	4.37163100	1.81210900	-1.35885900
H	1.26645700	3.26869700	1.69993900
H	2.46240700	2.61205700	2.81694300
N	1.36006000	1.17952200	1.74555400
C	2.30653600	0.04220400	1.86615500
C	0.35796000	1.11465400	2.83932800
H	2.91039800	0.13877700	2.77508900
H	1.73632600	-0.88670200	1.92322600
H	2.96960600	0.00095100	1.00513900
H	-0.20755800	0.18575500	2.75855300
H	0.86361800	1.14535100	3.81186300
H	-0.33401700	1.95262900	2.75404400
B	5.39743900	-1.45869100	0.67750400
F	4.98431200	-0.34156600	-0.11031700
F	6.49223900	-2.08471700	0.06445800
F	4.30745100	-2.36574000	0.76314200
F	5.73532300	-1.00799000	1.96820300

TS4 (toluene)

C	1.79470800	-1.75918000	1.04569300
C	3.10332700	-1.39186100	1.64845400
C	3.89738300	-0.29655400	1.28046500
C	4.50987100	-1.88903200	3.42426200
C	5.05556100	-0.03866600	2.00904600
H	3.59153100	0.37383500	0.49381900
C	5.38569100	-0.85489300	3.09243500
H	4.69721500	-2.53081800	4.28118500

H	5.67919500	0.81024600	1.74598100
H	6.27943300	-0.68116800	3.68176800
O	1.06675200	-2.61657700	1.86064700
C	1.51866900	-2.04233100	-0.33131500
N	1.92319900	-1.42348500	-1.49628900
N	0.51061500	-2.86396000	-0.75274400
N	1.17139400	-1.83684500	-2.60646600
C	3.04366100	-0.61430100	-1.74541700
C	-0.35914600	-3.92594200	-0.19403600
C	0.33210100	-2.69189200	-2.10332600
C	4.34323300	-1.10370500	-1.58860800
C	2.87407100	0.69651100	-2.20332400
H	-1.17077500	-3.46636500	0.36849900
H	0.22102900	-4.58582400	0.44633000
C	-0.89168900	-4.60599300	-1.47706900
C	-0.78872600	-3.54008900	-2.60073000
F	4.53681500	-2.36582700	-1.18485300
C	5.44676300	-0.29034100	-1.81785600
C	3.97051200	1.51375700	-2.45244400
F	1.64444900	1.17814000	-2.40471300
H	-1.91995500	-4.93741700	-1.33341100
H	-0.26828600	-5.46997400	-1.72732500
H	-0.59627200	-3.95729300	-3.59038200
H	-1.70228000	-2.93743900	-2.63561600
F	6.68651100	-0.75871200	-1.62179500
C	5.25864900	1.01995700	-2.24987000
F	3.79751500	2.76808800	-2.88506900
F	6.31621700	1.80771700	-2.46918500
N	3.39900500	-2.14536800	2.72641800
H	1.67558400	-2.80786900	2.61462800
I	-1.19806400	-0.77684000	1.64791100
C	-2.10158900	0.99856100	0.92639100
C	0.77648800	0.05436100	1.29595200
O	-3.78155400	-1.69539900	1.58693300
C	-2.66851300	1.88332300	1.85500200
C	-2.07450300	1.23321600	-0.45748000
C	1.22496900	1.21035500	1.27869000
S	-4.26219000	-2.13802600	0.22343800
C	-3.23058900	3.05911300	1.34201700
C	-2.70527100	1.61703400	3.33760000
C	-2.65017800	2.42782900	-0.90376400
C	-1.46368400	0.27358600	-1.44127800
C	1.86161900	2.47062500	1.22692700
O	-3.12557300	-2.51656200	-0.67441300
O	-5.34223200	-3.15169400	0.29567000
C	-4.97943200	-0.65781300	-0.51234800
C	-3.22764400	3.34905400	-0.02581300
H	-3.68534200	3.76082900	2.03645300
H	-3.26346300	0.70268100	3.56609200
H	-1.69617700	1.49981600	3.74749100
H	-3.18681000	2.44680000	3.86065600
H	-2.65709500	2.62965900	-1.97124500
H	-0.39934100	0.13334500	-1.23514400
H	-1.95763600	-0.70121500	-1.38705200
H	-1.55826500	0.65686000	-2.45981600
C	1.78354600	3.28063900	0.06852900
C	2.61140000	2.94748900	2.33049700
C	-5.57797100	0.30206300	0.30576100
C	-4.97105000	-0.49579700	-1.89725500
C	-3.82038000	4.63445700	-0.54375400
C	2.44299300	4.50701500	0.01705000
H	1.19610600	2.94056300	-0.77636100
C	3.26150700	4.17639500	2.26555300

H	2.67908700	2.33648900	3.22502200
C	-6.16831600	1.42472100	-0.27007000
H	-5.56180600	0.17378000	1.38198000
C	-5.56299400	0.63564100	-2.46226500
H	-4.49271500	-1.24124800	-2.52325100
H	-4.64173400	4.98050300	0.09128400
H	-3.06413300	5.42971900	-0.56372600
H	-4.19784600	4.51530800	-1.56341000
C	3.18866800	4.96388500	1.10911900
H	2.37306100	5.10950800	-0.88432900
H	3.83218900	4.52284800	3.12297100
C	-6.17475300	1.60898600	-1.66095300
H	-6.62105500	2.17716100	0.37073500
H	-5.54784000	0.76365300	-3.54178700
H	3.70169900	5.91959100	1.06280100
C	-6.83553300	2.82069200	-2.26973000
H	-6.54224200	2.95411100	-3.31537900
H	-7.92854100	2.72657800	-2.24225500
H	-6.57680800	3.73324600	-1.72249000

TS5 (toluene)

C	0.84665600	0.96250500	1.65832500
C	-0.31189500	0.14292100	2.26232200
C	-1.02189800	0.68796200	3.33783300
C	-1.51065400	-1.81532300	2.36552300
C	-2.02559400	-0.07592200	3.93204700
H	-0.75760200	1.67846600	3.69002300
C	-2.27438000	-1.36066300	3.44265500
H	-1.66815600	-2.81317100	1.95966500
H	-2.59470000	0.31728600	4.77011600
H	-3.03405000	-1.99870400	3.88401200
O	1.21192300	2.00093200	2.30110800
C	0.14950400	1.58095000	0.00822100
N	-0.80605900	1.30326300	-0.91306600
N	0.66656600	2.73579900	-0.45268900
N	-0.89746100	2.25192100	-1.93983600
C	-1.69715500	0.20133500	-0.96652500
C	1.75350600	3.66273000	-0.07544200
C	0.03020600	3.10514300	-1.61267800
C	-3.00115000	0.32243400	-0.48207200
C	-1.31514900	-0.99648000	-1.57438800
H	2.70933200	3.19809200	-0.33419100
H	1.72891000	3.83899200	0.99752600
C	1.42733200	4.89683300	-0.95379100
C	0.60650700	4.36821500	-2.16763300
F	-3.39890800	1.46532400	0.09119600
C	-3.90187800	-0.73300200	-0.58041500

C	-2.20609500	-2.06000800	-1.67656500
F	-0.08299800	-1.13278300	-2.07421700
H	2.33481400	5.41789800	-1.26517900
H	0.81549900	5.59910700	-0.37944700
H	-0.16141500	5.06679000	-2.50670300
H	1.24886800	4.13500200	-3.02500000
F	-5.14886900	-0.60973500	-0.10427600
C	-3.50063000	-1.92478600	-1.17998500
F	-1.82883800	-3.20901300	-2.25447300
F	-4.36085900	-2.94460100	-1.27553000
N	-0.55574900	-1.08112500	1.77542300
C	1.92760300	0.10140900	1.10759500
C	2.90134300	-0.50797600	0.70730800
C	4.03115000	-1.24765900	0.23520900
C	5.34230100	-0.79271900	0.48752100
C	3.85228900	-2.44482800	-0.48913100
C	6.44120900	-1.51727800	0.02578700
H	5.48577100	0.12504700	1.04975100
C	4.95691700	-3.16251300	-0.94772100
H	2.84504400	-2.80051800	-0.68269800
C	6.25375100	-2.70287700	-0.69316800
H	7.44588800	-1.15683300	0.22927200
H	4.80498300	-4.08372500	-1.50352900
H	7.11182500	-3.26533900	-1.05059200

TS β (toluene)

C	-1.87658600	-0.02852800	-0.58371800
C	-2.87350000	0.82128200	-1.28344000
C	-3.92347100	1.52892600	-0.67592800
C	-3.40936600	1.69939600	-3.36378500
C	-4.73922800	2.32432700	-1.47341300
H	-4.08359600	1.47958400	0.39132700
C	-4.49009100	2.41197300	-2.84659100
H	-3.15945800	1.74424900	-4.42042500
H	-5.55386800	2.88289800	-1.02248700
H	-5.10600000	3.02401200	-3.49630300
O	-0.89185300	-0.49161100	-1.45089300
C	-2.23339500	-1.04932400	0.36547600
N	-3.43760700	-1.38752900	0.92875500
N	-1.35164000	-1.87169200	0.98716000
N	-3.30183800	-2.36614700	1.92388400
C	-4.73271000	-1.14084600	0.42883700
C	0.10955100	-2.07852300	1.02054600
C	-2.02534100	-2.62110800	1.91895800
C	-5.06547500	-1.46227300	-0.89031000
C	-5.71924300	-0.58940300	1.25114000
H	0.56743600	-1.22232600	1.52014000
H	0.52314500	-2.17196700	0.02118200
C	0.21492700	-3.38709100	1.83763000

C	-1.07887800	-3.47567300	2.69749300
F	-4.14835400	-2.01087100	-1.69551200
C	-6.33261600	-1.19728300	-1.39562700
C	-6.99522600	-0.33686000	0.76026300
F	-5.43960600	-0.26979100	2.51872200
H	1.11963100	-3.39749800	2.44552800
H	0.26401000	-4.23488200	1.15017400
H	-1.44723000	-4.49549100	2.82385300
H	-0.93862000	-3.04333300	3.69479800
F	-6.62781700	-1.48656200	-2.66815500
C	-7.29944700	-0.63479200	-0.56619400
F	-7.92823000	0.20525000	1.55325100
F	-8.52075700	-0.37816500	-1.04289300
N	-2.62552200	0.92621500	-2.60420500
H	-1.17599000	-0.13424200	-2.33153300
I	1.66961900	0.48556300	-0.99570900
C	3.45156200	1.41825400	-0.28832700
C	0.43283900	1.53333600	0.29397300
O	3.55309600	-1.16503300	-2.18859000
C	3.88746200	1.12179600	1.01286800
C	4.16007000	2.25589900	-1.16292200
C	-0.80877100	1.34743500	0.57460600
S	3.95213300	-2.29481100	-1.27030300
C	5.07163000	1.73365700	1.44245500
C	3.15139500	0.18412800	1.93405000
C	5.33898000	2.83447200	-0.67638200
C	3.72465300	2.52508100	-2.58131300
C	-1.75643300	1.99904600	1.47537800
O	2.92758100	-2.55186000	-0.20961800
O	4.39082200	-3.50857500	-2.00284100
C	5.39622000	-1.67051400	-0.38716900
C	5.80720500	2.58868000	0.61809400
H	5.43221100	1.51543800	2.44400400
H	2.17566600	0.59790900	2.21310300
H	2.99048900	-0.78597800	1.45240900
H	3.72824400	0.02222900	2.84794900
H	5.90744800	3.48720600	-1.33449600
H	3.72065700	1.60246400	-3.17240000
H	2.71494100	2.94777200	-2.62240600
H	4.40658600	3.23107000	-3.06193600
C	-2.12598500	3.33643800	1.24357400
C	-2.34081400	1.31442400	2.55421400
C	6.26572200	-0.78103200	-1.01731400
C	5.66168100	-2.11220600	0.91034500
C	7.10775000	3.18652500	1.08999600
C	-3.06016000	3.96707800	2.06499200
H	-1.67497400	3.86542400	0.41062500
C	-3.27785900	1.94558000	3.37291800
H	-2.05150700	0.29071100	2.76453000
C	7.40078600	-0.33122500	-0.34220100
H	6.04393600	-0.43498000	-2.02039700
C	6.79758400	-1.65334000	1.57632000
H	4.97593900	-2.80106500	1.39163000
H	7.94971400	2.53748800	0.81987100
H	7.28801100	4.16450100	0.63279300
H	7.12251700	3.30789400	2.17744600
C	-3.64677000	3.27161800	3.12705300
H	-3.33481400	5.00013100	1.87200100
H	-3.71980700	1.40135700	4.20178800
C	7.68428500	-0.75523900	0.96283600
H	8.07127800	0.36764300	-0.83542300
H	6.99955000	-1.99639600	2.58845800
H	-4.37951600	3.75989900	3.76264400

C	8.88908000	-0.23548300	1.70758200
H	8.60504700	0.55532200	2.41380700
H	9.37229100	-1.02873000	2.28803500
H	9.63257800	0.18411000	1.02304700

TS-Mes (toluene)

C	-1.85405500	0.89554200	1.34075000
C	-2.82891000	-0.00100100	1.98050300
C	-3.44372600	-1.11694100	1.39254000
C	-3.82029700	-0.46715300	4.02862800
C	-4.30859000	-1.88671000	2.16481300
H	-3.20491600	-1.40965900	0.38054200
C	-4.52154200	-1.55410200	3.50452300
H	-3.91457800	-0.19035700	5.07546600
H	-4.79037500	-2.75708700	1.72948600
H	-5.18637400	-2.13456300	4.13460600
O	-1.08976600	1.59841100	2.25808300
C	-1.98464300	1.60814600	0.12537500
N	-2.63512100	1.30554500	-1.05574300
N	-1.32346400	2.76530900	-0.16844200
N	-2.35938900	2.24583500	-2.06229200
C	-3.73808800	0.45842400	-1.26660900
C	-0.53826000	3.79564600	0.55219800
C	-1.56222200	3.09282000	-1.47892800
C	-4.92258500	0.62454300	-0.54270600
C	-3.69178500	-0.54340200	-2.24116800
H	0.47062100	3.43232400	0.73975400
H	-1.03254100	4.04094100	1.49028600
C	-0.54440900	4.96469100	-0.46423600
C	-0.84907900	4.34469800	-1.85607700
F	-5.01340700	1.59858100	0.37196600
C	-6.00545000	-0.22653700	-0.72747900
C	-4.77412100	-1.39262800	-2.44389000
F	-2.59944900	-0.70622700	-2.99087500
H	0.41690300	5.47875100	-0.45826000
H	-1.32655700	5.68231000	-0.19781500
H	-1.44850200	4.98725100	-2.50335900
H	0.08402400	4.07654500	-2.36025900
F	-7.11536400	-0.08147900	0.00790500
C	-5.92918500	-1.23851600	-1.68002800
F	-4.70933600	-2.36060400	-3.36722200
F	-6.96343400	-2.06642800	-1.85978100

N	-2.99597400	0.28225600	3.29248000
H	-1.52126000	1.40437600	3.12745500
I	1.40696300	0.55735300	1.74093100
C	-0.31934700	-0.97389800	0.64065000
C	2.70904700	-0.79286900	1.09505900
O	2.71876100	3.65102000	0.86130800
C	-0.56882100	-2.07703100	1.45830400
C	-0.16695800	-1.02359400	-0.73995600
C	3.36770000	-1.72160000	0.66833100
S	2.98749600	3.41315000	-0.59268800
C	-0.81067900	-3.29126400	0.80014300
C	-0.52782800	-2.04706800	2.96443000
C	-0.43643800	-2.27077100	-1.33706100
C	0.32283000	0.10720700	-1.60511700
C	4.13800200	-2.79848600	0.14430600
O	1.77847600	2.90503600	-1.31996800
O	3.65026300	4.55627200	-1.27784500
C	4.16414900	2.04428600	-0.64556700
C	-0.76625700	-3.40599500	-0.59428200
H	-1.03169200	-4.16677600	1.40761100
H	0.48269600	-2.29612700	3.31154900
H	-0.78097000	-1.07109900	3.37421900
H	-1.21568000	-2.78523600	3.38551500
H	-0.36467900	-2.33754600	-2.42039100
H	0.49964500	1.03166900	-1.06118800
H	1.28586500	-0.16968700	-2.04715700
H	-0.36611400	0.30780900	-2.42934600
C	3.94276300	-3.21603900	-1.18697100
C	5.09559100	-3.45322900	0.94176700
C	5.05853700	1.84631700	0.40587000
C	4.21120800	1.21663100	-1.77047100
C	-1.00690200	-4.73470000	-1.26899800
C	4.69353400	-4.26888000	-1.70505600
H	3.20644200	-2.70634900	-1.79877300
C	5.84386600	-4.50371200	0.41313100
H	5.24858100	-3.12575600	1.96488300
C	6.00239800	0.81955300	0.32675900
H	5.00396300	2.48600300	1.28040400
C	5.15802500	0.19653400	-1.83855800
H	3.50219300	1.37225700	-2.57664500
H	-1.82119300	-5.28733400	-0.78833200
H	-1.26087900	-4.60456800	-2.32519400
H	-0.11166000	-5.36734000	-1.21975200
C	5.64615000	-4.91455400	-0.90877500
H	4.53885900	-4.58418000	-2.73266200
H	6.58516700	-4.99987100	1.03233400
C	6.07459700	-0.01424600	-0.79634900
H	6.69294800	0.66379300	1.15205700
H	5.18778000	-0.44978400	-2.71253700
H	6.23250700	-5.73187800	-1.31775000
C	7.11511800	-1.10078300	-0.89973400
H	7.92539200	-0.80072500	-1.57677300
H	7.56264400	-1.31966300	0.07387100
H	6.68737400	-2.02765200	-1.29313200

1g (CHCl₃)

C	-0.50237500	-0.19491100	-0.00020700
C	-0.00972300	1.11509200	-0.00007100
C	1.37153100	1.30104000	0.00024300
C	2.19781900	0.17590000	0.00040200
C	1.60970200	-1.09443700	0.00023300
N	0.28656200	-1.28618300	-0.00005800
H	1.79552600	2.30043300	0.00036200
H	-0.70175900	1.95040000	-0.00021500
H	3.27871400	0.27261600	0.00065100
H	2.22841300	-1.98832000	0.00035500
C	-1.96135000	-0.47697400	-0.00057500
O	-2.82829000	0.38347900	-0.00011400
H	-2.21412900	-1.55393200	0.00001700

2a (CHCl₃)

I	0.89376900	-1.46952700	-0.36932000
C	-0.06669500	0.40782400	0.01746200
C	-0.67580600	1.05713700	-1.06612800
C	-0.06240800	0.88604300	1.33405500
C	-1.31150800	2.27057800	-0.77946800
C	-0.71272200	2.11030300	1.54485800
C	-1.33887500	2.81090000	0.51056400
H	-1.81159800	2.79274700	-1.59035600
H	-0.74232700	2.50766000	2.55577700
C	2.76023800	-0.67066400	-0.24717900
C	3.90082300	-0.24615200	-0.19234600
C	5.23054000	0.26804000	-0.12677900
C	5.74173600	1.04839100	-1.18327500
C	6.04107100	-0.00028600	0.99446300
C	7.03987700	1.55085800	-1.11312200
H	5.11599500	1.25402600	-2.04575100
C	7.33882400	0.50476000	1.05280000
H	5.64568300	-0.60163800	1.80673100
C	7.84041400	1.28048900	0.00204300
H	7.42790700	2.15292300	-1.92921500

H	7.95901500	0.29345900	1.91867400
H	8.85182800	1.67270500	0.05199700
O	-1.40694600	-2.26841900	-0.68444900
S	-2.47409400	-2.24872800	0.41728800
O	-3.41762100	-3.37845000	0.24029200
O	-1.85616700	-2.12196300	1.76208400
C	-3.39795800	-0.73787100	0.12084500
C	-3.63432200	0.14900200	1.16723500
C	-3.90697200	-0.48539700	-1.15758200
C	-4.38204600	1.30539900	0.92867600
H	-3.22687100	-0.05713100	2.15004100
C	-4.64482100	0.67317600	-1.38142200
H	-3.72191700	-1.18348200	-1.96727100
C	-4.89457400	1.58739300	-0.34248200
H	-4.55735800	2.00282000	1.74314200
H	-5.03458700	0.87436400	-2.37625500
C	-5.68728800	2.84307000	-0.60497700
H	-6.69766700	2.60468400	-0.95797400
H	-5.78062500	3.45181200	0.29865400
H	-5.21263200	3.45501300	-1.38139200
C	0.56162000	0.15619600	2.49275500
H	0.11608900	-0.83786800	2.60117100
H	1.64225100	0.03592800	2.35797200
H	0.39720400	0.71065600	3.41939400
C	-0.69564100	0.50887300	-2.46752200
H	0.31866200	0.39478900	-2.86636900
H	-1.17884700	-0.47246100	-2.49509600
H	-1.24668500	1.18219600	-3.12766100
C	-2.03668200	4.11969700	0.77484900
H	-2.97083000	4.18924200	0.20929800
H	-2.26550900	4.24110300	1.83735500
H	-1.40651800	4.96511200	0.47113300

3g (CHCl₃)

C	2.48666200	0.34080100	0.00002700
C	3.82293400	0.75548500	0.00006900
C	4.81886000	-0.21993400	0.00000400
C	4.44121600	-1.56319300	-0.00008900
C	3.07729200	-1.87676500	-0.00011600
N	2.11358400	-0.95054300	-0.00005500
H	5.86715700	0.06225500	0.00003000
H	4.05664800	1.81388700	0.00014500
H	5.18152000	-2.35681500	-0.00013800
H	2.75002200	-2.91362200	-0.00018500
C	1.39387600	1.36779900	0.00010200
O	1.64665800	2.57539500	0.00018200
C	0.03877600	0.88943400	0.00003500
C	-1.13343800	0.55849700	-0.00001600
C	-2.49216700	0.14081400	-0.00001600
C	-3.53176200	1.09437400	0.00005100
C	-2.80718800	-1.23454500	-0.00009600
C	-4.86003400	0.67447000	0.00004700

H	-3.28442700	2.15096400	0.00011000
C	-4.13893800	-1.64239500	-0.00010300
H	-2.00278000	-1.96286300	-0.00015200
C	-5.16582100	-0.69128400	-0.00002900
H	-5.65769200	1.41114800	0.00010100
H	-4.37765700	-2.70161500	-0.00016300
H	-6.20274100	-1.01403700	-0.00003300

A (CHCl₃)

N	-1.63223400	0.00075100	1.10430500
N	-0.93790800	-0.05176900	-0.12190700
C	-1.70584900	-0.10954900	-1.24413100
N	-2.93800300	-0.08941800	-0.67277100
C	-4.31811400	-0.16123300	-1.16765800
H	-4.54221500	-1.19138200	-1.46089600
H	-4.45040500	0.49289200	-2.03014200
C	-5.12680000	0.28757700	0.07568400
H	-6.09788500	-0.20791400	0.12654100
H	-5.29609500	1.36722800	0.02670200
C	-4.23342100	-0.03748700	1.30935400
H	-4.34132600	0.68725400	2.11884800
H	-4.45109600	-1.03220100	1.71530900
C	-2.86883000	-0.02936900	0.70098100
C	0.47392300	-0.02191600	-0.08342600
F	0.48459500	2.34664600	-0.09769000
C	1.16337700	1.19161200	-0.06278800
F	3.20187400	2.40310900	0.00853700
C	2.55232500	1.22914900	-0.00699400
F	4.60852600	0.06538100	0.08379300
C	3.27100400	0.03740900	0.03193500
F	3.29957000	-2.32895500	0.05991300
C	2.60218400	-1.18347700	0.01786000
F	0.58331000	-2.38821700	-0.04029300
C	1.21272700	-1.20513400	-0.03616500

B (CHCl₃)

C	-1.27575500	1.45021900	1.21807200
H	-1.94210400	2.33511700	1.08005300
C	0.11789500	1.93462600	0.78662900
C	1.22725800	1.69059300	1.59788900

C	1.40582300	3.00464100	-0.79156300
C	2.48015300	2.12355500	1.16399600
H	1.07654100	1.15908800	2.53084500
C	2.57590000	2.79198900	-0.05903100
H	1.43959800	3.52445400	-1.74652400
H	3.36699400	1.94039800	1.76451300
H	3.52980000	3.14293300	-0.43961300
O	-1.35992200	0.83748900	2.41158400
C	-1.80786100	0.42240500	0.21028300
N	-1.17348500	-0.63528500	-0.34645300
N	-3.10092600	0.19195800	-0.06086400
N	-2.04974500	-1.53951800	-0.94968000
C	0.21628300	-0.89316800	-0.32964700
C	-4.38725700	0.85113700	0.20466200
C	-3.21573800	-0.98914700	-0.75185600
C	0.79512400	-1.60714100	0.72093700
C	1.03273900	-0.41116100	-1.35461200
H	-4.49244400	1.70719100	-0.46668000
H	-4.42702600	1.18884700	1.24041500
C	-5.38483300	-0.29367600	-0.11199200
C	-4.64585500	-1.27109900	-1.07474400
F	0.03307700	-2.10994800	1.69432200
C	2.17201100	-1.79207400	0.77354500
C	2.40990200	-0.58547300	-1.30641400
F	0.49198000	0.23846100	-2.39029700
H	-6.30748300	0.09192100	-0.54775200
H	-5.63400200	-0.81788300	0.81431000
H	-4.91273400	-2.31654200	-0.91075300
H	-4.83834500	-1.03119400	-2.12654500
F	2.72935000	-2.45946600	1.79356100
C	2.97669100	-1.27278200	-0.23664800
F	3.19281800	-0.09715700	-2.27853400
F	4.30274500	-1.43627000	-0.18061000
N	0.19786500	2.58777400	-0.38414300

H	5.30788100	3.43223000	-1.45050500
O	-0.44631200	2.21671400	-0.74411200
C	0.46150000	0.37978400	0.48021200
N	-0.67138000	-0.12722100	1.00570000
N	1.42059900	0.02556400	1.33892600
N	-0.44874100	-0.79634600	2.19510500
C	-1.98471900	-0.03728900	0.47910500
C	2.88597100	0.16806500	1.49328000
C	0.84044400	-0.68639600	2.36457000
C	-2.47638900	-1.02930800	-0.37000200
C	-2.80808100	1.03313600	0.83027200
H	3.09793800	1.19389900	1.80048800
H	3.38049700	-0.05625700	0.55145900
C	3.18642200	-0.87935200	2.59350100
C	1.85584300	-1.12184900	3.36271700
F	-1.71064300	-2.06986000	-0.70020000
C	-3.76908200	-0.94380800	-0.87825100
C	-4.09900000	1.12597400	0.32765300
F	-2.35374100	1.98292100	1.65412100
H	3.98199100	-0.53241900	3.25419000
H	3.50609900	-1.80838500	2.11930200
H	1.71695500	-2.16471700	3.65270900
H	1.77840800	-0.50127500	4.26228600
F	-4.24039200	-1.89482600	-1.69396700
C	-4.57615100	0.13511000	-0.52825900
F	-4.88528600	2.15868100	0.65912100
F	-5.81840200	0.22018000	-1.01178800
N	2.17013900	2.86758500	-0.35348700
H	-0.01341200	2.97390300	-0.30663700
B	2.05214500	-2.60712100	-0.85942400
F	2.08400300	-3.80869800	-1.58479300
F	3.36817100	-2.11525500	-0.68159100
F	1.45741600	-2.81677000	0.40563400
F	1.29495300	-1.63783400	-1.56818200

C (CHCl₃)

C	0.52388000	1.18404800	-0.80562500
H	0.24469100	0.50759300	-1.61563200
C	1.91120700	1.75201100	-1.05074100
C	2.81871400	1.16474400	-1.92906100
C	3.36795700	3.44619800	-0.50945400
C	4.06760700	1.77108900	-2.08143600
H	2.55973500	0.25459500	-2.45671300
C	4.35046900	2.93021500	-1.35853500
H	3.54640300	4.35168200	0.06469600
H	4.80400200	1.34289700	-2.75420400

D (CHCl₃)

C	-1.38829200	1.59658700	0.05152500
C	-0.16449400	2.26202400	-0.34878000
C	0.76052100	1.77355700	-1.29971700
C	1.08011800	4.20954100	-0.09181000
C	1.88020000	2.53384500	-1.60165500
H	0.57246100	0.84658300	-1.82445100
C	2.06631500	3.77485000	-0.97432300
H	1.15671200	5.18172600	0.39016400

H	2.59577900	2.17401600	-2.33548500
H	2.93203000	4.39384200	-1.18360400
O	-2.31356000	2.39158600	0.71605500
C	-1.72533500	0.28115800	-0.10465100
N	-0.92659200	-0.81987900	-0.48100600
N	-2.97252800	-0.28817800	0.09127600
N	-1.72876200	-2.00301500	-0.63367300
C	0.40017300	-1.02126100	-0.07215400
C	-4.34392100	0.21319200	0.21718200
C	-2.91429200	-1.60253700	-0.29823000
C	0.87284500	-0.68050600	1.20206400
C	1.32084300	-1.57852100	-0.96890800
H	-4.62808900	0.74660900	-0.69787500
H	-4.43342300	0.89208600	1.06368100
C	-5.12719000	-1.10906900	0.39903500
C	-4.28798100	-2.19679700	-0.32754600
F	0.03553200	-0.18893200	2.12849300
C	2.21009100	-0.84086200	1.54795100
C	2.65244300	-1.77245300	-0.62491100
F	0.92497200	-1.90132600	-2.21057100
H	-6.14187000	-1.03522400	0.00377400
H	-5.19117700	-1.34635400	1.46497600
H	-4.33460400	-3.17541300	0.15471700
H	-4.60138000	-2.31972100	-1.37042600
F	2.63585100	-0.49590600	2.77393000
C	3.10279500	-1.39440600	0.63631300
F	3.51238300	-2.29729600	-1.51301100
F	4.38936700	-1.56653100	0.97171000
N	-0.00416700	3.48632500	0.21677100
H	-1.84559300	3.24225700	0.84925700

E (CHCl₃)

C	-0.75575000	0.00051500	-1.17982600
C	0.20947900	-1.19771900	-0.98164400
C	0.85290500	-1.73463000	-2.09493700
C	1.20404900	-2.70562900	0.43665600
C	1.71539100	-2.81538400	-1.90495600
H	0.67065500	-1.28760100	-3.06482900
C	1.89836400	-3.31261300	-0.61320200
H	1.32366300	-3.06114100	1.45784900
H	2.23877000	-3.25823600	-2.74750000
H	2.56212900	-4.14866900	-0.41687500
O	-0.79932100	0.49630100	-2.42228400

C	-0.30222100	1.20535600	-0.30374400
N	0.91543800	1.58328800	0.15276400
N	-1.06017400	2.29995500	-0.12709200
N	0.93452900	2.90732300	0.60376800
C	2.09934700	0.82143400	0.29631500
C	-2.44362700	2.70961300	-0.41853500
C	-0.29380200	3.30009000	0.41173700
C	2.94245200	0.57396600	-0.78602700
C	2.45119000	0.32933900	1.55437900
H	-3.10639500	2.26871000	0.32909100
H	-2.72615500	2.35791100	-1.40992600
C	-2.33446200	4.25167600	-0.30407900
C	-1.10188000	4.54004700	0.60336100
F	2.64493400	1.05274800	-1.99674700
C	4.09761700	-0.18414200	-0.62385000
C	3.61136100	-0.41229800	1.73007600
F	1.64910200	0.54705300	2.60220300
H	-3.25070000	4.68582100	0.09847000
H	-2.16013800	4.67435600	-1.29710700
H	-0.55663500	5.44075000	0.31628500
H	-1.38447800	4.63340300	1.65806900
F	4.88937000	-0.44217300	-1.67379900
C	4.43164300	-0.67245100	0.63528400
F	3.93005700	-0.90233900	2.93683200
F	5.53723300	-1.40819300	0.79281100
N	0.37394400	-1.66785600	0.26285400
C	-2.08939800	-0.43384400	-0.64429500
C	-3.20712600	-0.77021400	-0.30620500
C	-4.52485700	-1.14755500	0.09914700
C	-5.61708000	-0.97558200	-0.77518000
C	-4.75078800	-1.69147400	1.37976300
C	-6.90224200	-1.33943900	-0.37385700
H	-5.44493500	-0.56098200	-1.76350500
C	-6.03954300	-2.05112500	1.77305300
H	-3.91046300	-1.82862300	2.05306600
C	-7.11853500	-1.87691300	0.89960100
H	-7.73590000	-1.20476400	-1.05701700
H	-6.20151100	-2.47042900	2.76189400
H	-8.12066900	-2.15988100	1.20833400

Mes-I (CHCl₃)

C	-2.24720700	-1.19705200	-0.00594300
C	-0.84620500	-1.23101500	-0.00240100
C	-0.16535700	0.00145400	-0.00000600
C	-0.84234000	1.23314800	-0.00231800
C	-2.24601600	1.20190400	-0.00578900
C	-2.96547300	0.00418800	-0.00614400
H	-2.78690300	-2.14132200	-0.00944400

H	-2.78336500	2.14709200	-0.00915300
C	-0.13255900	2.56208500	-0.00308200
H	0.51000600	2.67220300	0.87776900
H	0.51157900	2.67058800	-0.88300100
H	-0.85536900	3.38223300	-0.00445700
C	-0.13722200	-2.56040100	-0.00295800
H	0.50695000	-2.66936100	-0.88276700
H	0.50512700	-2.67077500	0.87799300
H	-0.86066200	-3.38000000	-0.00433700
C	-4.47414800	-0.00153000	0.01021200
H	-4.85524700	-0.32091600	0.98831600
H	-4.87820800	0.99402500	-0.19555300
H	-4.87767600	-0.69485600	-0.73603900
I	1.96609300	-0.00123800	0.00172200

NHC-1 (CHCl_3)

N	2.03097700	-1.68839500	-0.26176700
N	1.17838400	-0.65435200	0.08515300
C	1.84283900	0.46294200	0.40735300
H	1.37997000	1.39933800	0.69983800
N	3.13013800	0.15644200	0.27272700
C	4.44516000	0.80097300	0.45784600
H	4.65296200	0.85455600	1.52927000
H	4.43497000	1.80403800	0.03244100
C	5.37197000	-0.18974000	-0.29122100
H	6.35313700	-0.24481900	0.18138000
H	5.50369400	0.14947600	-1.32182000
C	4.64317600	-1.56660100	-0.28869600
H	4.81326400	-2.14289100	-1.19959800
H	4.93785700	-2.18475200	0.56665000
C	3.21755800	-1.15514200	-0.13505100
C	-0.22764400	-0.83385900	0.04757800
F	-0.20399600	-0.73587100	-2.31383300
C	-0.89290000	-0.87522200	-1.17787500
F	-2.90826000	-1.08986800	-2.40043400
C	-2.26884800	-1.05459800	-1.22520900
F	-4.30926800	-1.36238000	-0.08101800
C	-2.98564000	-1.19277300	-0.03885700
F	-3.03011800	-1.28935000	2.32478500
C	-2.33283300	-1.15303300	1.19006700
F	-0.32605500	-0.95037200	2.41010200
C	-0.95512200	-0.97904700	1.22794300
B	-0.95698700	2.71407800	-0.04865000
F	-0.29406600	2.11344200	-1.14700700
F	-2.14436600	2.01502800	0.22940900
F	-1.22727500	4.06100200	-0.32754400
F	-0.09145100	2.62896800	1.08765400

TMEDA (CHCl_3)

C	-0.69763600	0.31429800	0.91350100
H	-0.61583800	1.40134100	1.01897900
H	-1.20729500	-0.04973000	1.82994400
C	0.69767800	-0.31437600	0.91344000
H	1.20738000	0.04957000	1.82989200
H	0.61588200	-1.40142800	1.01882500
N	1.50539100	-0.04721800	-0.27561500
N	-1.50540400	0.04724300	-0.27553900
C	-1.71289400	-1.37770200	-0.50320200
H	-2.21002400	-1.87716000	0.35276300
H	-2.34268900	-1.51614900	-1.38747500
H	-0.75965500	-1.87753100	-0.68989500
C	-2.77940600	0.75087900	-0.18962100
H	-3.35184900	0.59774600	-1.11018400
H	-3.40117800	0.40864100	0.66204100
H	-2.60461800	1.82532500	-0.07020400
C	1.71287300	1.37774600	-0.50316500
H	2.21003600	1.87713100	0.35282500
H	2.34263800	1.51626600	-1.38744800
H	0.75962900	1.87759200	-0.68978200
C	2.77939600	-0.75086400	-0.18981600
H	3.35179300	-0.59765700	-1.11039500
H	3.40120900	-0.40869800	0.66184300
H	2.60461000	-1.82531900	-0.07047900

TMEDA H^+BF_4^- (CHCl_3)

C	2.54794500	0.02469100	-0.54285100
H	3.25647600	0.45805000	0.16902400
H	3.13949300	-0.29921500	-1.41972200
C	1.58053300	1.10098800	-1.02444400
H	2.12500500	1.99524700	-1.33773800

H	0.97068000	0.75419300	-1.85978500
N	0.60984500	1.51882100	0.04745900
N	1.85852800	-1.08220300	0.11100200
C	1.13757500	-1.93341700	-0.83574600
H	1.82188600	-2.43159700	-1.54806400
H	0.58892700	-2.70206400	-0.28536500
H	0.40574100	-1.35493600	-1.40194500
C	2.77336100	-1.87541900	0.92703500
H	2.21009200	-2.65011100	1.45539500
H	3.55933000	-2.37062300	0.32619200
H	3.26075200	-1.23877900	1.67221800
C	1.27506500	2.01036200	1.29101700
H	1.95041700	2.82720000	1.03101700
H	0.50110400	2.36310800	1.97305200
H	1.81883900	1.18940900	1.75365500
C	-0.35447600	2.53274200	-0.47772600
H	-1.10925600	2.72142200	0.28527000
H	0.19340800	3.44872800	-0.70488100
H	-0.82823000	2.13431900	-1.37281800
H	0.06383800	0.68253100	0.31878600
F	-1.77352000	-0.16041200	-1.17017800
B	-2.33555700	-0.49243300	0.08715300
F	-1.36162900	-0.18203000	1.09290700
F	-3.48520800	0.28177600	0.31322400
F	-2.63401500	-1.85941400	0.13927000

TMEDAH⁺TsO⁻ (CHCl₃)

C	3.04825900	1.87627400	-0.20728400
H	2.87488400	2.26614900	-1.21457100
H	3.86205000	2.48654800	0.23022700
C	3.57366100	0.44756200	-0.29552100
H	4.41113500	0.41040900	-0.99752600
H	3.92569000	0.08581200	0.67229600
N	2.55071100	-0.54633600	-0.76328300
N	1.80377900	1.99642400	0.54401500
C	1.97145300	1.71470200	1.96813500
H	2.67253600	2.42030500	2.45251600
H	1.00207600	1.79126700	2.46753200
H	2.33334200	0.69652500	2.12248400
C	1.19957200	3.31000500	0.34128900

H	0.24806800	3.36148000	0.87832100
H	1.84145300	4.13442900	0.70493100
H	1.00421900	3.47186100	-0.72385200
C	1.86165900	-0.14902900	-2.02424100
H	2.60716800	-0.00872100	-2.80992100
H	1.16650800	-0.94548800	-2.28688800
H	1.30727200	0.77122100	-1.85150900
C	3.16178200	-1.90193900	-0.89579400
H	2.36406900	-2.61077000	-1.11559000
H	3.90101200	-1.88426400	-1.69910300
H	3.63813400	-2.16402500	0.04989600
H	1.80921900	-0.64769300	-0.01553500
O	0.72544500	-1.19879200	1.11094200
S	-0.43264100	-1.96695600	0.51310800
O	-0.06996300	-2.52950600	-0.82550600
O	-1.01965700	-2.95507500	1.45331300
C	-1.69861000	-0.72620100	0.20230200
C	-3.02479600	-1.13092900	0.02360700
C	-1.34334400	0.61699200	0.08002100
C	-3.99704000	-0.17914700	-0.27789800
H	-3.29269700	-2.17733300	0.12780900
C	-2.33038700	1.55949600	-0.22470000
H	-0.31174400	0.92271000	0.22866500
C	-3.66704300	1.18078100	-0.40832200
H	-5.02910100	-0.49412200	-0.41142200
H	-2.05577100	2.60732100	-0.31629600
C	-4.73364600	2.19922500	-0.72482100
H	-4.30516700	3.19654700	-0.85988900
H	-5.27515100	1.93397900	-1.64030900
H	-5.47409000	2.25675600	0.08225900

TS1 (CHCl₃)

H	1.47838600	0.48190100	1.15741100
N	1.45752400	1.61875300	1.80785200
C	1.19262300	2.75794500	0.88767400
C	2.76045800	1.70623700	2.49290900
C	0.35814100	1.48735900	2.78785800
C	2.30103900	3.01444000	-0.12800400
H	1.05144900	3.67032000	1.48260200
H	0.24344900	2.54584900	0.39349500
H	2.84298900	2.63971600	3.06255600
H	2.85176500	0.86280700	3.18243000
H	3.56817400	1.65184300	1.76244900
H	0.50517200	0.57474000	3.37045100

H	0.34136800	2.34802400	3.46705100
H	-0.59176800	1.43284900	2.25540900
H	3.19970900	3.36992000	0.38558700
H	1.95787900	3.84574700	-0.77229600
N	2.67182300	1.83905600	-0.91797900
C	1.60716200	1.43590200	-1.83717600
C	3.90886900	2.08581500	-1.65334200
H	1.37569900	2.22319700	-2.57744000
H	1.91369900	0.53700900	-2.38027300
H	0.68744900	1.21022800	-1.29796500
H	4.19403100	1.18627300	-2.20854800
H	3.81429200	2.91455500	-2.38021300
H	4.71806100	2.33574200	-0.95873600
C	1.60904100	-0.75022700	0.55077300
N	0.70818500	-1.61964700	0.04351800
N	2.77630600	-1.32538800	0.21661200
N	1.27724100	-2.72238800	-0.60076300
C	-0.70061500	-1.49965000	0.07525000
C	4.20012000	-1.00954300	0.38294700
C	2.55394300	-2.49636300	-0.46728600
C	-1.42218100	-1.34787100	-1.11011800
C	-1.39883700	-1.56201800	1.28120100
H	4.49696800	-1.22464600	1.41314000
H	4.36609600	0.04364900	0.16193400
C	4.85347900	-1.97361700	-0.64060000
C	3.84520000	-3.14464500	-0.84399800
F	-0.77608100	-1.27766300	-2.27986700
C	-2.80910300	-1.26806000	-1.09533800
C	-2.78358700	-1.46292700	1.30932400
F	-0.73292400	-1.73138000	2.43569600
H	5.82703000	-2.32484700	-0.29564400
H	4.99538700	-1.44984000	-1.58978800
H	3.83828800	-3.53145500	-1.86450900
H	4.05111700	-3.98021100	-0.16550200
F	-3.48928300	-1.12717000	-2.23803400
C	-3.48878600	-1.32127100	0.11808100
F	-3.44126000	-1.51422900	2.47736000
F	-4.82145600	-1.23508800	0.14179900
F	-2.06401800	1.57882600	0.54332300
B	-2.54602500	2.15504000	-0.66245400
F	-1.76782200	1.67556700	-1.74038000
F	-3.89265200	1.78517400	-0.84542000
F	-2.43182900	3.55926200	-0.58302300

TS2 (CHCl₃)

C	-1.52128500	2.01437300	-1.10847900
H	-1.57813000	1.76846400	-2.18387000
C	-0.07433100	2.18652000	-0.67998300
C	0.24261100	2.81147600	0.52960800

C	2.14712000	1.90467100	-1.20512300
C	1.58497600	2.96757100	0.87032300
H	-0.55980800	3.16019600	1.17040100
C	2.56215800	2.50593400	-0.01496100
H	2.87863000	1.53637200	-1.92111700
H	1.86611600	3.43953900	1.80735500
H	3.61984600	2.60658100	0.20707400
O	-2.43184700	2.69338700	-0.55785700
C	-1.80250300	0.12274600	-0.51274200
N	-1.08802000	-0.85257100	0.09543000
N	-3.06520800	-0.24462900	-0.22970300
N	-1.86576600	-1.82120100	0.74974600
C	0.31995300	-0.96626000	0.13806300
C	-4.41189000	0.27003400	-0.52284500
C	-3.07689600	-1.39986000	0.51542400
C	1.02945000	-0.54767000	1.26375100
C	1.02469400	-1.50137400	-0.93994500
H	-4.66157000	0.03057400	-1.56045400
H	-4.42560500	1.35054800	-0.38698600
C	-5.27146600	-0.51939200	0.49546100
C	-4.47693300	-1.81983500	0.82140000
F	0.37574600	-0.03226400	2.31220900
C	2.41518100	-0.64016200	1.30796600
C	2.41061200	-1.60036700	-0.90694000
F	0.36828100	-1.91804800	-2.02937700
H	-6.26639900	-0.73317300	0.10165600
H	-5.38401800	0.07332100	1.40769900
H	-4.60008500	-2.15070100	1.85435200
H	-4.76508900	-2.64756900	0.16323900
F	3.09176500	-0.20716300	2.38141200
C	3.10349100	-1.16882100	0.22014500
F	3.08267000	-2.09710900	-1.95587800
F	4.43982900	-1.23893600	0.24895600
N	0.85850800	1.73882000	-1.53535000

TS3 (CHCl₃)

C	0.10592800	0.40739600	-0.63735100
H	0.68293400	0.69225600	0.60907800
C	-1.11345100	1.28663900	-0.67832900
C	-1.52354000	1.89041600	-1.87623900
C	-2.81987600	2.31311600	0.48810700
C	-2.63838200	2.72417200	-1.86418500
H	-0.97218800	1.69273900	-2.78825800
C	-3.30699000	2.94439100	-0.65638200
H	-3.30692700	2.46155100	1.44975400

H	-2.98563200	3.19048400	-2.78162400
H	-4.17886700	3.58794900	-0.60004900
O	1.08432300	0.74972800	-1.59808400
C	-0.07014000	-1.01834500	-0.59596100
N	-1.13694300	-1.77241500	-0.17835100
N	0.88741200	-1.94582100	-0.84921000
N	-0.83806700	-3.14281300	-0.12683400
C	-2.46500900	-1.35452000	0.04091300
C	2.29524700	-1.97498700	-1.29606100
C	0.39555400	-3.19044000	-0.53725100
C	-3.28902100	-1.00453700	-1.03054300
C	-2.97497800	-1.26007900	1.33597500
H	2.93974400	-1.64216000	-0.48241000
H	2.43235600	-1.31738100	-2.15010900
C	2.48007500	-3.47750800	-1.61545400
C	1.43994500	-4.23748300	-0.74381900
F	-2.83284000	-1.10447100	-2.28601900
C	-4.57662400	-0.52767100	-0.81587400
C	-4.26746300	-0.80532000	1.56333900
F	-2.20278700	-1.57884900	2.38181200
H	3.50211700	-3.79847900	-1.41055200
H	2.26746900	-3.65474200	-2.67363500
H	1.04432700	-5.13537900	-1.22191800
H	1.86129600	-4.52520000	0.22618800
F	-5.35040700	-0.16799900	-1.84929000
C	-5.06454800	-0.43248100	0.48441100
F	-4.74016900	-0.69523900	2.81354800
F	-6.30179400	0.02822900	0.69871400
N	-1.74738900	1.50817400	0.48932500
H	1.57427000	1.53885400	-1.21005700
N	2.22061400	2.97357200	-0.55148600
C	2.68534200	2.93851400	0.84557300
C	1.18754800	3.99743200	-0.75476500
C	3.35900800	3.21263600	-1.45213800
C	1.67561600	2.40790200	1.85892800
H	2.95887900	3.95551800	1.17524200
H	3.60035000	2.34417900	0.88134500
H	1.56659600	5.00571100	-0.51825700
H	0.86259100	3.98180200	-1.79789800
H	0.31585800	3.79478800	-0.12947500
H	3.00745800	3.21267900	-2.48795100
H	3.84580200	4.18047900	-1.24806000
H	4.09475900	2.41375900	-1.33247600
H	0.73500700	2.96138600	1.80924800
H	2.10068000	2.57091000	2.85871900
N	1.33389600	0.96537400	1.73841000
C	2.52464800	0.09096900	1.72149200
C	0.41958000	0.57422600	2.83068500
H	3.15363800	0.27219800	2.59997200
H	2.19420100	-0.94871500	1.73151700
H	3.10531900	0.26594800	0.81935000
H	0.11484400	-0.46366400	2.68684000
H	0.92354400	0.66922700	3.80028700
H	-0.46705300	1.20717000	2.80195200
B	5.74876300	-0.63354700	0.31677500
F	4.99708400	0.01608900	-0.69381800
F	6.98167300	-1.06243900	-0.21170100
F	5.01778800	-1.75321200	0.78856900
F	5.96709200	0.26532600	1.38492200

TS4 (CHCl₃)

C	1.79382000	-1.83736200	1.00783000
C	3.08837500	-1.49325600	1.64209400
C	3.91496000	-0.41768700	1.28649800
C	4.44343500	-2.00553800	3.45467100
C	5.06273900	-0.18002700	2.03750200
H	3.63949300	0.25390800	0.49043800
C	5.35013400	-0.99457200	3.13492200
H	4.59715200	-2.64262100	4.32182900
H	5.71173500	0.65184500	1.78122700
H	6.23390400	-0.83647700	3.74350400
O	1.02086300	-2.67608900	1.79796200
C	1.51553200	-2.06918400	-0.37401400
N	1.93720400	-1.43825900	-1.52728900
N	0.49877000	-2.87175200	-0.81824400
N	1.18933000	-1.82623400	-2.64956300
C	3.04786600	-0.60969000	-1.76081900
C	-0.39658000	-3.92642900	-0.28368700
C	0.33525100	-2.67788600	-2.16624300
C	4.35285200	-1.09711200	-1.65493100
C	2.85890600	0.71671000	-2.16256700
H	-1.20694700	-3.45891800	0.27519100
H	0.16288100	-4.60422700	0.35623500
C	-0.91615400	-4.58442600	-1.58280400
C	-0.78938000	-3.50435100	-2.68997500
F	4.56247300	-2.37421800	-1.30948600
C	5.44533000	-0.26795500	-1.87810200
C	3.94411000	1.55041500	-2.40533800
F	1.62115300	1.19468400	-2.32160900
H	-1.94631900	-4.91821400	-1.45880300
H	-0.29130800	-5.44588900	-1.83722100
H	-0.58825400	-3.91115800	-3.68227600
H	-1.69298600	-2.88703300	-2.73681800
F	6.69353400	-0.73519400	-1.73407800
C	5.23847200	1.05710800	-2.25095200
F	3.75493800	2.82000000	-2.78631300
F	6.28710700	1.85968100	-2.46397500
N	3.34292200	-2.24566700	2.73315800
H	1.59066100	-2.87499400	2.57937900
I	-1.18548800	-0.76338000	1.64700800
C	-2.06777400	1.01954100	0.91176000
C	0.79141600	0.04155700	1.28872100
O	-3.84476200	-1.65456200	1.66118300
C	-2.53005900	1.96647300	1.84022100

C	-2.11935600	1.20526700	-0.47884000
C	1.26818800	1.18454400	1.28671300
S	-4.37907600	-2.11730000	0.32860500
C	-3.06789200	3.14939300	1.32009000
C	-2.47313300	1.76123100	3.33211700
C	-2.66474400	2.41326000	-0.93289400
C	-1.61486000	0.19192300	-1.47030500
C	1.91396900	2.44257400	1.25233000
O	-3.29627100	-2.60433600	-0.58028500
O	-5.51616800	-3.06876800	0.47059000
C	-5.03726000	-0.63455100	-0.45360200
C	-3.14265800	3.39043000	-0.05661100
H	-3.43693100	3.89965000	2.01488400
H	-3.04933700	0.88008600	3.63496700
H	-1.44336700	1.61550400	3.67640400
H	-2.88415300	2.63117100	3.84997300
H	-2.72174800	2.58289800	-2.00437000
H	-0.54006500	0.03416500	-1.35006800
H	-2.11634200	-0.77081900	-1.33768100
H	-1.79052300	0.53877400	-2.49123400
C	1.76038700	3.30670200	0.14202600
C	2.73676300	2.86410500	2.32537500
C	-5.54987400	0.39756400	0.33132200
C	-5.06761200	-0.54362400	-1.84727300
C	-3.75684300	4.66486100	-0.57575900
C	2.41807400	4.53489300	0.10616900
H	1.11921500	3.00585500	-0.67852200
C	3.38326800	4.09653400	2.27818200
H	2.86386000	2.20942600	3.18170600
C	-6.09111300	1.52683500	-0.28512000
H	-5.50941200	0.32447200	1.41228700
C	-5.60804400	0.59086300	-2.45070700
H	-4.65999200	-1.34843200	-2.44958700
H	-4.84409500	4.65669500	-0.43334000
H	-3.36668100	5.53880200	-0.04292300
H	-3.55978900	4.79686100	-1.64320500
C	3.23475400	4.93901900	1.16846900
H	2.29051000	5.18070300	-0.75823800
H	4.01095700	4.40138500	3.11125200
C	-6.12781200	1.64388000	-1.68097400
H	-6.48072100	2.33356800	0.32980600
H	-5.62470100	0.66229300	-3.53564700
H	3.74557100	5.89660700	1.13468100
C	-6.68001900	2.87932400	-2.34677400
H	-5.87406300	3.48505200	-2.77929700
H	-7.36207900	2.61900500	-3.16371300
H	-7.22436700	3.50672300	-1.63510700

TS5 (CHCl₃)

C	0.62729400	1.05579400	1.80205500
C	-0.64817700	0.27423400	2.13015600
C	-1.72054000	0.94852500	2.72306600
C	-1.79387000	-1.71850100	2.14530400
C	-2.87914900	0.23316600	3.01573600
H	-1.62749400	2.00620800	2.94165000
C	-2.91966000	-1.13336800	2.72492800
H	-1.78253200	-2.78019700	1.90894100
H	-3.73462800	0.72881500	3.46521800
H	-3.79927000	-1.73180900	2.93953800
O	0.89578400	2.08396000	2.49404400
C	0.11968200	1.69614600	0.00793200
N	-0.67562300	1.30462500	-1.00976800
N	0.57318600	2.88474300	-0.41848400
N	-0.73499700	2.21638500	-2.07396900
C	-1.42968900	0.11114200	-1.06434000
C	1.50175000	3.91744200	0.07189700
C	0.05500200	3.16846900	-1.66147900
C	-2.78230400	0.11425100	-0.72395100
C	-0.82811700	-1.09262100	-1.43020100
H	2.52467100	3.55236600	-0.05283400
H	1.31961900	4.11095700	1.12687800
C	1.16601400	5.10072900	-0.86896800
C	0.57439900	4.47383800	-2.16700800
F	-3.37622400	1.25770100	-0.35934700
C	-3.52197300	-1.06171200	-0.73536000
C	-1.55821000	-2.27514800	-1.44635100
F	0.46707400	-1.12113900	-1.76173100
H	2.04605300	5.71262100	-1.07294500
H	0.41019800	5.73446400	-0.39624400
H	-0.20396700	5.08741900	-2.62448300
H	1.34991600	4.29249700	-2.91984800
F	-4.81526300	-1.05654500	-0.38190900
C	-2.90534000	-2.25629300	-1.09755100
F	-0.97148700	-3.43184600	-1.78624100
F	-3.60829000	-3.39499100	-1.09176100
N	-0.68114600	-1.03312700	1.84036200
C	1.74773000	0.21420300	1.33954300
C	2.72701800	-0.39828400	0.96245900
C	3.84404900	-1.15549000	0.49623700
C	5.16145500	-0.70271900	0.71038100
C	3.63766400	-2.37008100	-0.18967800
C	6.24422500	-1.44967100	0.24726200

H	5.32248400	0.23015400	1.24153400
C	4.72648900	-3.10959200	-0.64942100
H	2.62333000	-2.71979400	-0.35250300
C	6.03155100	-2.65328600	-0.43358300
H	7.25561600	-1.09261500	0.41882400
H	4.55641900	-4.04414800	-1.17624000
H	6.87731600	-3.23265300	-0.79231200

TS β (CHCl₃)

C	-1.88980200	-0.11701400	-0.54912300
C	-2.83439200	0.70441100	-1.33655300
C	-3.89605500	1.46001700	-0.81168700
C	-3.27361600	1.47279100	-3.48175100
C	-4.67024300	2.21701800	-1.68386400
H	-4.09590500	1.47228700	0.24998200
C	-4.36523700	2.22419100	-3.04898900
H	-2.98202300	1.45796400	-4.52858900
H	-5.49559300	2.80819600	-1.29875100
H	-4.94681400	2.80460300	-3.75688600
O	-0.87380600	-0.65349800	-1.33160800
C	-2.28439700	-1.02919500	0.48394500
N	-3.51165300	-1.30094300	1.03530900
N	-1.43412400	-1.79683000	1.21218000
N	-3.41991100	-2.17864900	2.12659900
C	-4.78415000	-1.09221300	0.46619500
C	0.02271500	-1.99402000	1.33044400
C	-2.14694300	-2.44312000	2.19076100
C	-5.07286300	-1.52413000	-0.83114400
C	-5.79099600	-0.45522000	1.19601900
H	0.45802300	-1.09189600	1.76793900
H	0.47400200	-2.17898100	0.35917100
C	0.08801500	-3.21833300	2.27339100
C	-1.23677200	-3.21431600	3.08853600
F	-4.13679900	-2.15521900	-1.55096600
C	-6.31481500	-1.28471100	-1.40579600
C	-7.04311500	-0.22876300	0.63769900
F	-5.54686600	-0.02452000	2.43870000
H	0.96889100	-3.17453600	2.91473500
H	0.14904800	-4.12965400	1.67331900
H	-1.61455300	-4.21507500	3.30585800
H	-1.13034600	-2.67835800	4.03847700
F	-6.56808200	-1.68083700	-2.65974000
C	-7.30171400	-0.63703600	-0.66827100
F	-7.99567000	0.39477800	1.34429600
F	-8.50038700	-0.40767100	-1.21370100
N	-2.52990300	0.73235100	-2.65083500

H	-1.10270600	-0.35191200	-2.24820700
I	1.67127100	0.37408200	-0.95663100
C	3.44035600	1.37212400	-0.30663900
C	0.44114400	1.50308200	0.26517400
O	3.56760600	-1.32941700	-2.15885400
C	3.91046000	1.10902300	0.98956400
C	4.09161700	2.23938500	-1.19861900
C	-0.80043100	1.37541500	0.55495200
S	4.05009500	-2.40038200	-1.21423300
C	5.07489200	1.77632900	1.39308200
C	3.22786700	0.15760100	1.93782100
C	5.25269500	2.87277700	-0.73879100
C	3.60609200	2.49469800	-2.60335100
C	-1.76901900	2.06368700	1.39667800
O	3.06615100	-2.69304600	-0.12704900
O	4.53550200	-3.61413000	-1.92989800
C	5.48212400	-1.67947400	-0.39145900
C	5.75682200	2.65580300	0.54880400
H	5.46132100	1.58502600	2.39043500
H	2.24318900	0.53836000	2.23235000
H	3.08771500	-0.82457500	1.47569200
H	3.82769400	0.03134200	2.84240100
H	5.77680800	3.54825800	-1.41072300
H	3.60510300	1.57263300	-3.19514500
H	2.58419700	2.88935200	-2.61037300
H	4.25414700	3.21813100	-3.10429500
C	-2.21490700	3.35013400	1.04175500
C	-2.29592400	1.45584300	2.54949000
C	6.28032700	-0.75720400	-1.06816700
C	5.81177800	-2.07908900	0.90548400
C	7.03345800	3.32313900	0.99271000
C	-3.17051900	4.00633800	1.81825500
H	-1.80927400	3.81970400	0.15166500
C	-3.25435300	2.11235500	3.32124800
H	-1.94030900	0.47582600	2.84919000
C	7.40896600	-0.23064700	-0.43879600
H	6.00998900	-0.44273600	-2.06986200
C	6.94065000	-1.54340100	1.52465400
H	5.18207200	-2.79275300	1.42587200
H	7.90416100	2.82428200	0.54992500
H	7.06499600	4.37168000	0.67827000
H	7.14648400	3.28636900	2.08000300
C	-3.70063500	3.38654500	2.95441200
H	-3.50666200	4.99868400	1.53150800
H	-3.65320200	1.62911700	4.20805300
C	7.75598700	-0.61038000	0.86491100
H	8.02219300	0.49536100	-0.96582400
H	7.19163100	-1.85107100	2.53704900
H	-4.45122700	3.89372200	3.55348700
C	8.95043200	-0.00745800	1.56099500
H	8.63735600	0.75544200	2.28499100
H	9.51392200	-0.76654500	2.11422300
H	9.62953400	0.47007700	0.84858000

TS-Mes (CHCl₃)

C	1.86291600	-0.88729400	1.34990000
C	2.81797400	0.03537200	1.97961900
C	3.42688800	1.14091900	1.36747600
C	3.78119200	0.56900000	4.02397600
C	4.27415600	1.94284300	2.12667600
H	3.19790600	1.40065500	0.34451300
C	4.47383800	1.65079200	3.47795100
H	3.86865500	0.32319400	5.07916800
H	4.75151400	2.80541100	1.67145000
H	5.12288000	2.25741900	4.09996600
O	1.08792400	-1.57663800	2.26819400
C	2.00215700	-1.61236400	0.14594800
N	2.68270400	-1.33866000	-1.02537400
N	1.33501000	-2.76886500	-0.14333900
N	2.41882500	-2.29412600	-2.02175800
C	3.79187500	-0.49800600	-1.23008300
C	0.49722300	-3.76477600	0.56551400
C	1.59908600	-3.12132900	-1.44138200
C	4.96322600	-0.65461100	-0.48397900
C	3.76135200	0.49113400	-2.21754200
H	-0.51178000	-3.37489700	0.69103800
H	0.93658400	-3.99396700	1.53384300
C	0.53327100	-4.95870300	-0.41904900
C	0.87585600	-4.36882900	-1.81439400
F	5.03643000	-1.61434900	0.44810500
C	6.05045900	0.19078400	-0.66593000
C	4.84860200	1.33364100	-2.41793100
F	2.67537600	0.64889300	-2.97984900
H	-0.42469000	-5.47890600	-0.42624000
H	1.31284600	-5.66332000	-0.11406400
H	1.47998100	-5.03130600	-2.43658700
H	-0.04058700	-4.09925200	-2.34783100
F	7.15007400	0.05362700	0.08764400
C	5.99164900	1.18697800	-1.63559500
F	4.79964400	2.28936100	-3.35605500
F	7.03251400	2.00776000	-1.81431200
N	2.97541800	-0.21346200	3.30010100
H	1.49089000	-1.35614000	3.14450900
I	-1.39248700	-0.53110800	1.77827600
C	0.29926800	0.97084700	0.58891500
C	-2.70378700	0.80908200	1.11976400
O	-2.82183300	-3.73547000	0.82681900
C	0.54741200	2.10625100	1.35951200
C	0.13316500	0.96299400	-0.79161700

C	-3.34127900	1.74925800	0.68437000
S	-3.11170000	-3.46243200	-0.61606400
C	0.76996900	3.29646000	0.64880600
C	0.52014600	2.14483000	2.86571500
C	0.37864900	2.18749600	-1.44115900
C	-0.33207000	-0.21116600	-1.61161900
C	-4.08493800	2.83789100	0.14491200
O	-1.90048600	-3.02558000	-1.37888400
O	-3.85811600	-4.56946200	-1.28719100
C	-4.22445400	-2.04268100	-0.63525200
C	0.70454200	3.35564000	-0.74734100
H	0.99029000	4.19678200	1.21882400
H	-0.48871600	2.40658300	3.20859700
H	0.77987700	1.18931600	3.31691800
H	1.20842600	2.90487300	3.24485600
H	0.29404000	2.20992000	-2.52560800
H	-0.54789000	-1.09544800	-1.01773300
H	-1.26277500	0.05239300	-2.12454600
H	0.39773500	-0.47271300	-2.38259000
C	-3.88589800	3.22362600	-1.19578800
C	-5.01727500	3.53570300	0.93617800
C	-5.10793100	-1.83027100	0.42340200
C	-4.24847300	-1.19954700	-1.74948300
C	0.91636100	4.65786600	-1.48069100
C	-4.60995300	4.28746900	-1.72983600
H	-3.16828100	2.68178900	-1.80244100
C	-5.73885200	4.59697100	0.39132500
H	-5.17238900	3.23403000	1.96703200
C	-6.02021900	-0.77449200	0.36031800
H	-5.07345400	-2.48074100	1.29100400
C	-5.16529300	-0.15074300	-1.80160800
H	-3.54831800	-1.36382300	-2.56172200
H	1.57116200	5.33064100	-0.91813900
H	1.35975800	4.49223600	-2.46773100
H	-0.03705400	5.17969600	-1.63335300
C	-5.53859000	4.97557800	-0.94017700
H	-4.45286500	4.57836400	-2.76432000
H	-6.46079100	5.12691300	1.00553500
C	-6.07258300	0.07355200	-0.75414300
H	-6.70153400	-0.60702900	1.19083700
H	-5.17677000	0.50750000	-2.66674400
H	-6.10396100	5.80145700	-1.36159300
C	-7.08461800	1.18770600	-0.84075900
H	-7.92915000	0.89512900	-1.47819400
H	-7.48617800	1.43935300	0.14478100
H	-6.64641800	2.09165800	-1.27324700

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